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A general copper-catalysed enantioconvergent C(sp^3)–S cross-coupling via biomimetic radical homolytic substitution

In the format provided by the authors and unedited

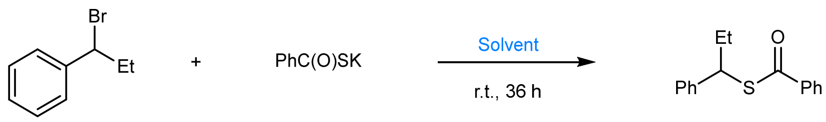
Table of Contents

General information

Reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. $Cu(MeCN)_4BF_4$ was purchased from TCI. CuI was purchased from Sigma-Aldrich. $Cu(PPh_3)_3CF_3$ was purchased from Bide Pharmatech Ltd. Anhydrous toluene and diethyl ether (Et_2O) distilled from sodium (Na) and stored under argon. Cs_2CO_3 and Rb_2CO_3 were purchased from Bide Pharmatech Ltd, which were dry at 200 °C for 3 h in vacuum. Chloroform ($CHCl_3$) was distilled from anhydrous calcium hydride (CaH_2) and stored under argon. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As the eluent, the petroleum ether (PE) and EtOAc were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 spectrometers at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$, CD_3OD or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (e.e.) was determined using SHIMADZU LC-20AD with SPD-20AV detector (at appropriate wavelength). Column conditions were reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.

1. Supplementary tables for experiments

Supplementary Table 1 | Investigation of the nucleophilic substitution reaction with benzyl electrophile.[a]



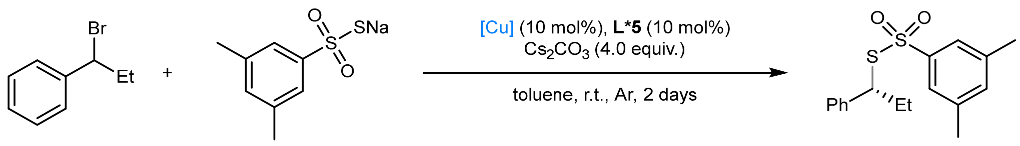
E1 **S1** **1a**

Entry	Solvent	Yield (%)[b]
1	DMF	97
2	MeOH	81
3	MeCN	100
4	THF	98
5	Et_2O	7
6	DCM	4
7	Toluene	3

[a]Reaction conditions: **E1** (0.05 mmol) and **S1** (1.2 equiv.) in solvent (1.0 mL) at room temperature (r.t.) for 36 h;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard.

Supplementary Table 2 | Reaction condition optimization with benzyl electrophile: screening of different copper salts.[a]



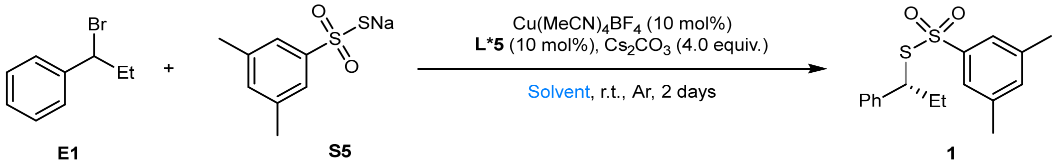
Entry	[Cu]	Yield (%)[b]	E.e. (%)[c]
1	CuI	80	79
2	CuTc	64	78
3	$Cu(MeCN)_4PF_6$	88	80
4	$Cu(MeCN)_4BF_4$	90	80
5	$Cu(PPh_3)_2BH_4$	51	77
6	$Cu(OTf)_2$	41	76

[a]Reaction conditions: **E1** (0.05 mmol), **S5** (1.2 equiv.), [Cu] (10 mol%), **L*1** (10 mol%), and Cs_2CO_3 (4.0 equiv.) in toluene (0.5 mL) at r.t. for 2 days under argon;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard;

[c]E.e. values were based on chiral HPLC analysis.

Supplementary Table 3 | Reaction condition optimization with benzyl electrophile: screening of different solvents and temperature.[a]



Entry	Solvent	Yield (%)[b]	E.e. (%)[c]
1	Toluene	90	80
2	Et_2O	23	68
3	DCM	88	79
4	MeCN	14	62
5	Toluene/DMF (10/1)	80	82
6[d]	Toluene/DMF (10/1)	79	88
7[e]	Toluene/DMF (10/1)	81	92
8[f]	Toluene/DMF (10/1)	76	92
9[g]	Toluene/DMF (10/1)	54	92

[a]Reaction conditions: **E1** (0.05 mmol), **S5** (1.2 equiv.), $Cu(MeCN)_4BF_4$ (10 mol%), **L*5** (10 mol%), and Cs_2CO_3 (4.0 equiv.) in solvent (0.5 mL) at r.t. for 2 days under argon;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard;

[c]E.e. values were based on chiral HPLC analysis;

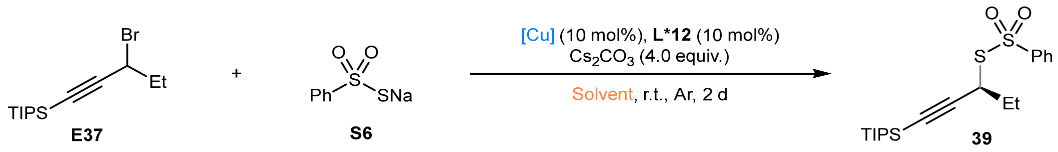
[d]Run at 0 °C, 3 days;

[e]Run at –15 °C, 3 days;

[f]H_2O (1.0 equiv.) in toluene/DMF (vol/vol = 10/1) at –15 °C for 3 days;

[g]$Cu(MeCN)_4BF_4$ (2.5 mol%), **L*5** (2.5 mol%) was used.

Supplementary Table 4 | Reaction condition optimization with propargyl electrophile: screening of different copper salts and solvents.[a]



Entry	[Cu]	Solvent	Yield (%)[b]	E.e. (%)[c]
1	$Cu(MeCN)_4BF_4$	Toluene	31	63
2	CuI	Toluene	38	63
3	CuTc	Toluene	13	62
4	$Cu(OTf)_2$	Toluene	4	60
5	$Cu(PPh_3)_3CF_3$	Toluene	14	62
6	CuI	Et_2O	trace	--[d]
7	CuI	CH_2Cl_2	13	78
8	CuI	$CHCl_3$	trace	--[d]
9	CuI	MeCN	trace	--[d]

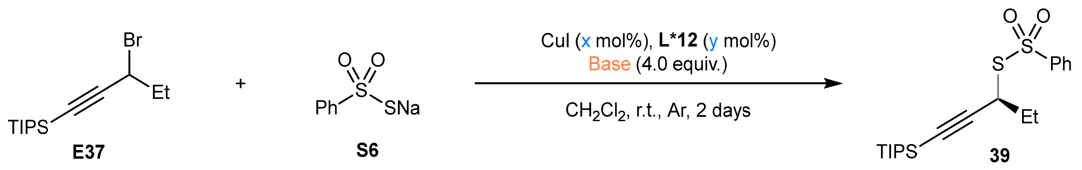
[a]Reaction conditions: **E37** (0.05 mmol), **S6** (1.2 equiv.), [Cu] (10 mol%), **L*12** (10 mol%), and Cs_2CO_3 (4.0 equiv.) in solvent (0.5 mL) at r.t. for 2 days under argon;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard;

[c]E.e. values were based on chiral HPLC analysis;

[d]Not determined.

Supplementary Table 5 | Reaction condition optimization with propargyl electrophile: screening of different catalyst ratios and bases.[a]



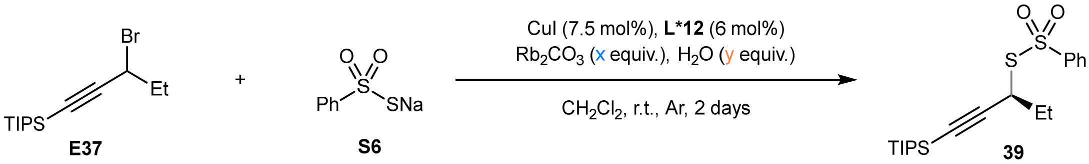
Entry	CuI	**L*12**	Base	Yield (%)[b]	E.e. (%)[c]
1	10 mol%	10 mol%	Cs_2CO_3	13	78
2	10 mol%	8 mol%	Cs_2CO_3	14	78
3	7.5 mol%	6 mol%	Cs_2CO_3	13	78
4	7.5 mol%	6 mol%	Rb_2CO_3	60	78
5	7.5 mol%	6 mol%	K_2CO_3	29	67
6	7.5 mol%	6 mol%	K_3PO_4	59	78

[a]Reaction conditions: **E37** (0.05 mmol), **S6** (1.2 equiv.), CuI (x mol%), **L*12** (y mol%), and Base (4.0 equiv.) in CH_2Cl_2 (0.5 mL) at r.t. for 2 days under argon;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard;

[c]E.e. values were based on chiral HPLC analysis.

Supplementary Table 6 | Reaction condition optimization with propargyl electrophile: screening of equivalent of base, H_2O, and temperature.[a]



Entry	Rb_2CO_3	H_2O	Yield (%)[b]	E.e. (%)[c]
1	4.0 equiv.	none	60	78
2	2.0 equiv.	none	58	78
3[d]	2.0 equiv.	none	32	83
4[d]	2.0 equiv.	2.0 equiv.	83	83
5[e]	2.0 equiv.	2.0 equiv.	91	88
6[f]	2.0 equiv.	2.0 equiv.	93	90

[a]Reaction conditions: **E37** (0.05 mmol), **S6** (1.2 equiv.), CuI (7.5 mol%), **L*12** (6 mol%), Rb_2CO_3 (x equiv.) and H_2O (y equiv.) in CH_2Cl_2 (0.5 mL) at r.t. for 2 days under argon;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard;

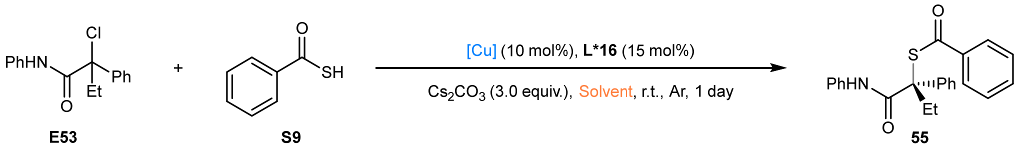
[c]E.e. values were based on chiral HPLC analysis;

[d]E.e. run at 0 °C, 2 days;

[e]E.e. run at –20 °C, 3 days;

[f]E.e. run at –20 °C in $CHCl_3$, 3 days.

Supplementary Table 7 | Reaction condition optimization with tertiary electrophile: screening of different solvents and copper salts.[a]



Entry	[Cu]	Solvent	Yield (%)[b]	E.e. (%)[c]
1	CuI	EtOAc	85	76
2	CuI	$CHCl_3$	10	44
3	CuI	THF	74	66
4	CuI	Toluene	86	78
5	CuI	1,4-Dioxane	55	60
6	CuI	Et_2O	81	79
7	CuCN	Et_2O	78	67
8	CuTc	Et_2O	77	57
9	$Cu(MeCN)_4PF_6$	Et_2O	82	80
10	$Cu(PPh_3)_3CF_3$	Et_2O	84	83
11[d]	$Cu(PPh_3)_3CF_3$	Et_2O	90	87
12[e]	$Cu(PPh_3)_3CF_3$	Et_2O	93	90
13[f]	$Cu(PPh_3)_3CF_3$	Et_2O	93	90

[a]Reaction conditions: **E53** (0.05 mmol), **S9** (1.5 equiv.), CuI (10 mol%), **L*16** (15 mol%) and Cs_2CO_3 (3.0 equiv.) in EtOAc (1.0 mL) at r.t. for 1 day under argon;

[b]Yield was based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethylbenzene as an internal standard;

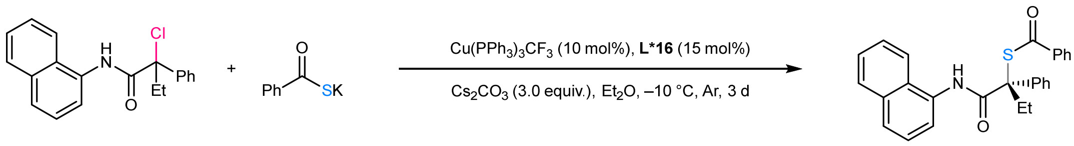
[c]E.e. values were based on chiral HPLC analysis;

[d]run at 0 °C, 2 days;

[e]run at –10 °C, 3 days;

[f] **S1** was used, run at –10 °C, 3 days.

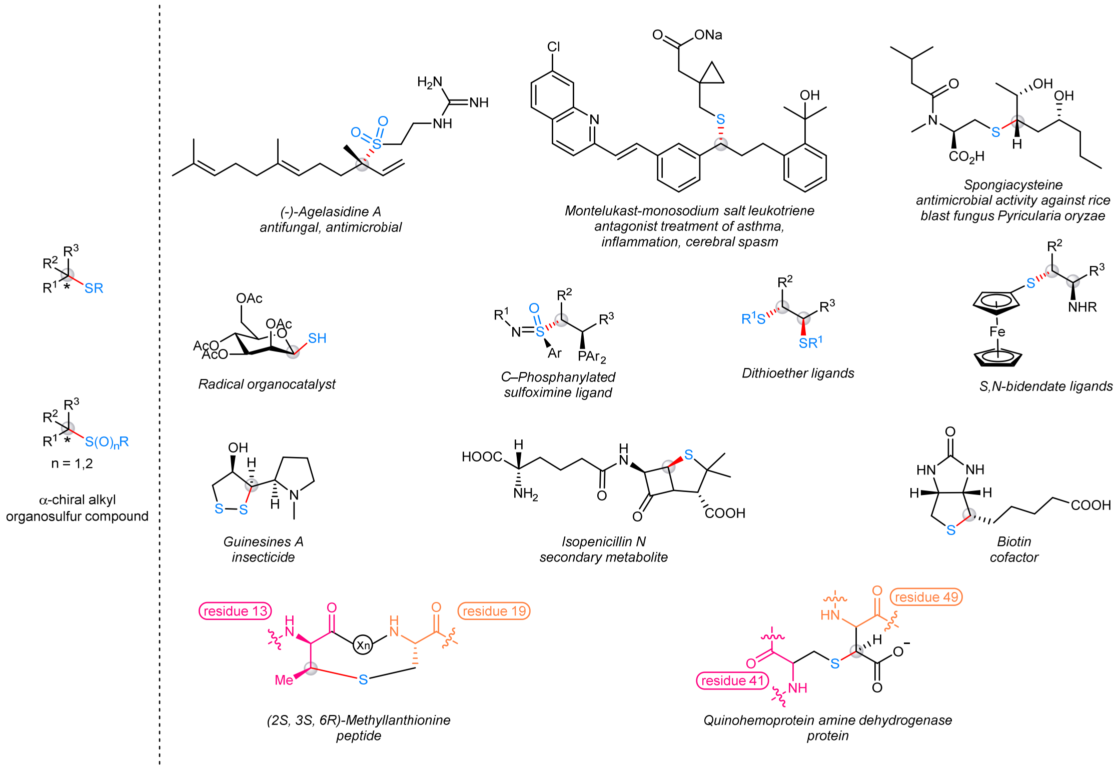
Supplementary Table 8 | Investigation of the background reactions.



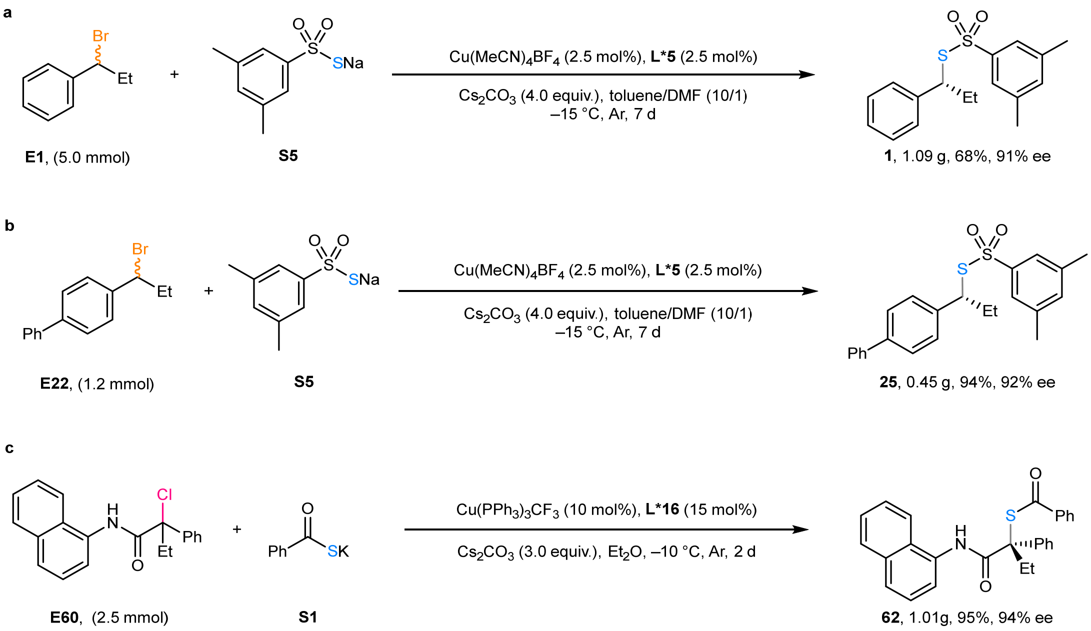
Entry	[Cu]	**L*16**	Cs_2CO_3	Yield	E.e.
1	×	✓	✓	52%	1%
2	✓	×	✓	45%	--
3	×	×	✓	36%	--
4	✓	✓	✓	95%	95%

Reaction conditions: **E60** (0.05 mmol, 1.0 equiv.), **S1** (1.5 equiv.), $Cu(PPh_3)_3CF_3$ (10 mol%), **L*16** (15 mol%), and Cs_2CO_3 (3.0 equiv.) in Et_2O (1.0 mL) at –10 °C for 3 days under argon. Yield is based on ^{1}H-NMR analysis of the crude products using 1,3,5-trimethylbenzene as an internal standard; E.e. is based on chiral HPLC analysis.

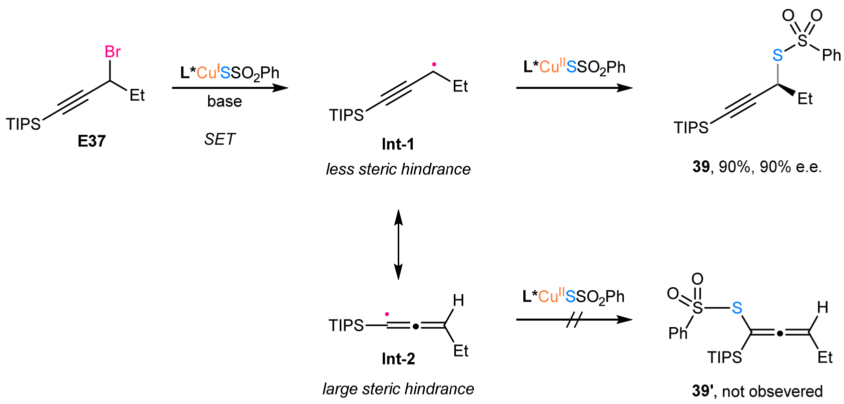
2. Supplementary figures for experiments



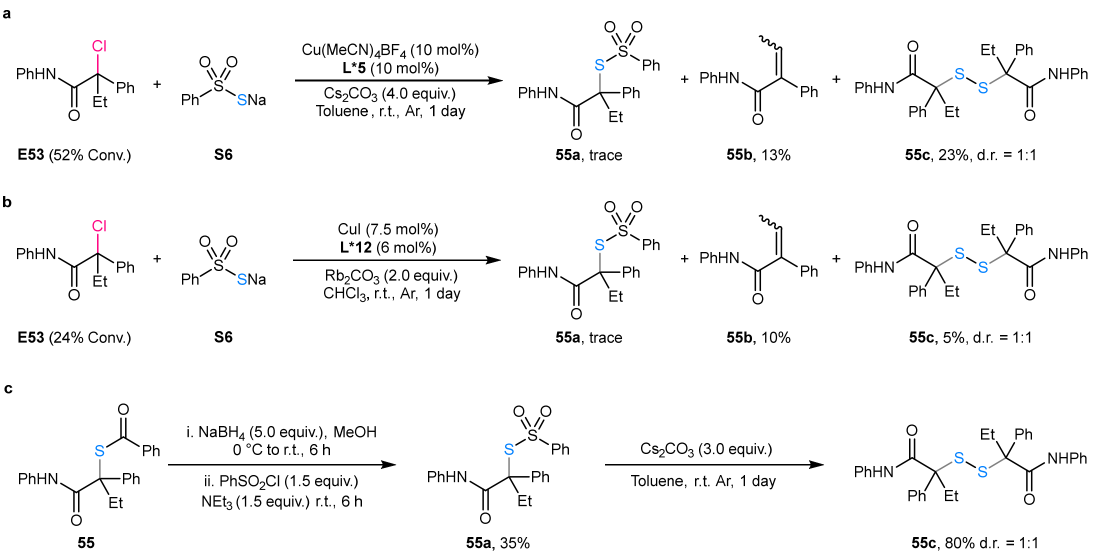
Supplementary Fig. 1 | α-Chiral alkyl organosulfur compounds in drugs, natural products, catalysts, ligands, metabolites, biomacromolecules and cofactors.



Supplementary Fig. 2 | Large-scale experiments. **a**, Reaction conditions: **E1** (5.0 mmol), **S5** (1.2 equiv.), Cu(MeCN)$_4$BF$_4$ (2.5 mol%), **L*5** (2.5 mol%) and Cs_2CO_3 (4.0 equiv.) in toluene/DMF (vol/vol = 10/1, 55 mL) at –15 °C for 7 days under argon; **b**, Reaction conditions: **E22** (1.2 mmol), **S5** (1.2 equiv.), Cu(MeCN) $_4$BF$_4$ (2.5 mol%), **L*5** (2.5 mol%) and Cs_2CO_3 (4.0 equiv.) in toluene/DMF (vol/vol = 10/1, 13.2 mL) at –15 °C for 7 days under argon. **c**, **E60** (2.5 mmol, 1.0 equiv.), **S1** (1.5 equiv.), Cu(PPh$_3$)$_3$CF$_3$ (10 mol%), **L*16** (15 mol%), and Cs_2CO_3 (3.0 equiv.) in Et_2O (50 mL) at –10 °C for 2 days under argon. Isolated yields are shown; E.e. is based on chiral HPLC analysis.

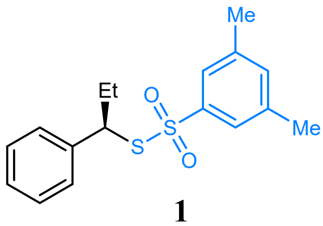


Supplementary Fig. 3 | Explanation for the observed regioselectivity. The complex **L***Cu^{I}SSO2Ph reduced **E37** to generate a propargylic radical (**Int-1**) and its resonance structure allenyl radical (**Int-2**). Subsequently, the propargylic radical (**Int-1**) coupled with the complex **L***Cu^{II}SSO2Ph, giving rise to the propargylic cross-coupling product **39** in high yield. It was difficult for the allenyl radical (**Int-2**) to react with the complex **L***Cu^{II}SSO2Ph due to the steric hindrance of the TIPS group. Therefore, we reasoned that the exclusive regioselectivity might be attributed to the less steric **int-I** than **int-II**.[1–3]

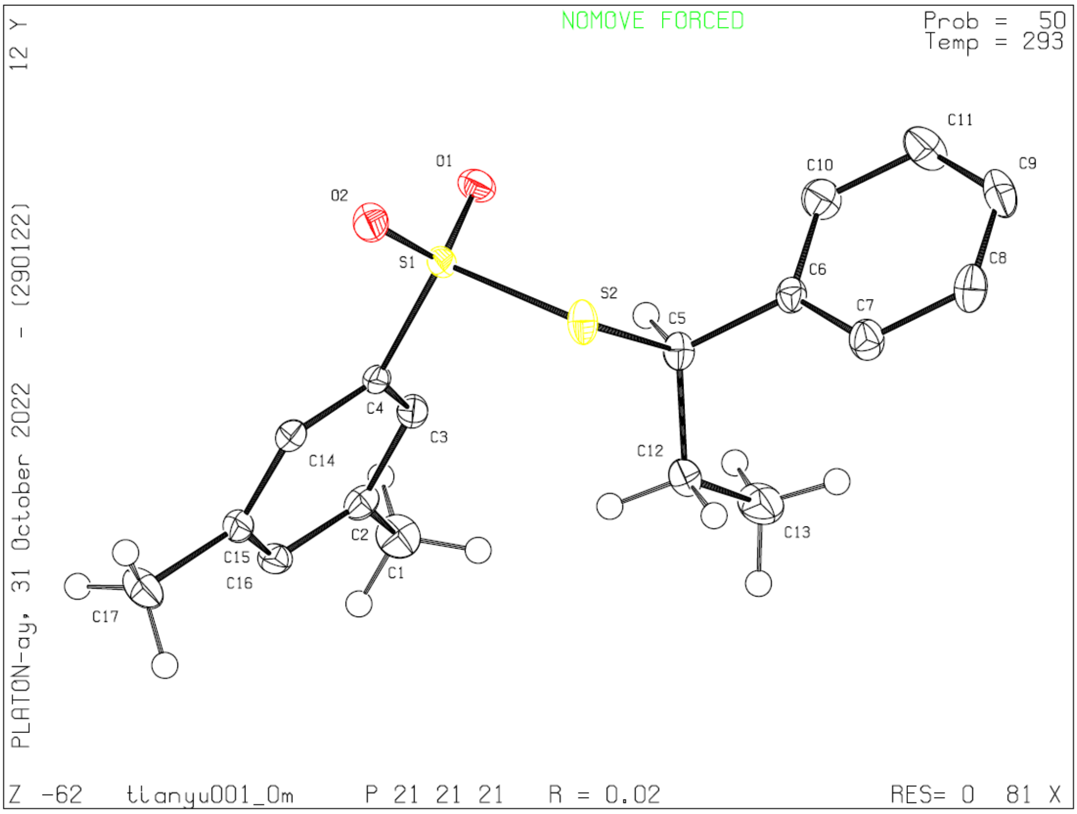


Supplementary Fig. 4 | Investigation of the reaction with tertiary electrophiles and S6. a, Reaction conditions: **E53** (0.2 mmol), **S6** (0.24 mmol, 1.2 equiv.), $Cu(MeCN)_4BF_4$ (10 mol%), **L*5** (10 mol%) and Cs_2CO_3 (4.0 equiv.) in toluene (2.0 mL) at r.t. for 1 day under argon; **b**, Reaction conditions: **E53** (0.2 mmol), **S6** (0.24 mmol, 1.2 equiv.), CuI (7.5 mol%), **L*12** (6 mol%) and Rb_2CO_3 (2.0 equiv.) in CH_3Cl (2.0 mL) at r.t. for 1 day under argon. The major side product was elimination by-product **55b** and dimerization by-product **55c**, of which the latter was possibly derived from **55a**.

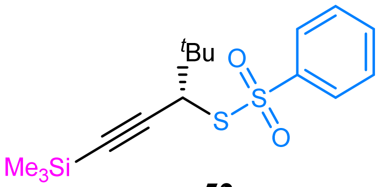
We have carefully analyzed the NMR spectrum of the crude product for the reaction of **E53** and **S6** in the presence of **L*5**. We have found that the conversion of **E53** was ca. 52% and the elimination by-product **55b** (13% yield) together with the disulfide by-product **55c** (23% yield) was formed. The reaction with **L*12** gave a similar result. We theorized that **55c** was probably derived from the desired product **55a** under basic conditions. To verify our hypothesis, we synthesized compound **55a** and found that it could be easily converted to **55c** upon exposure to simply basic conditions.



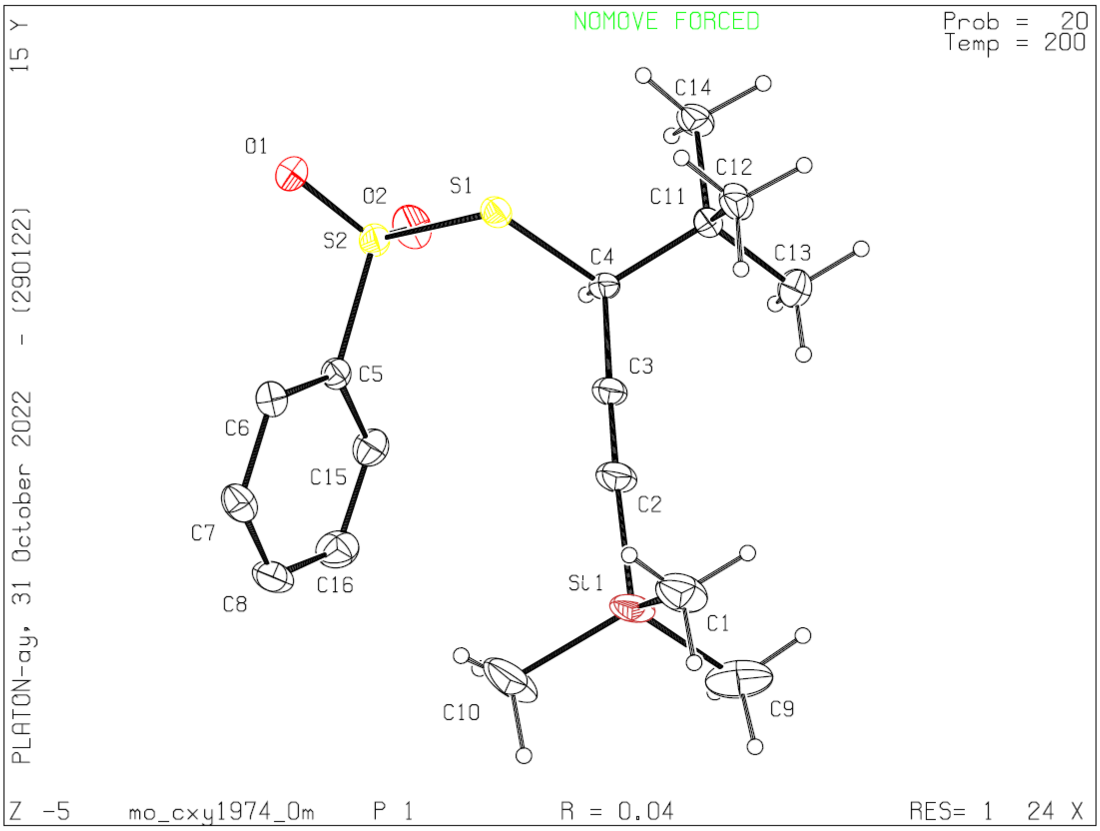
1



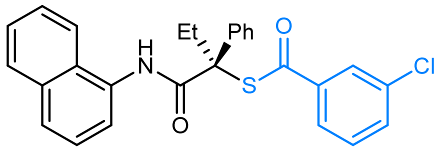
Supplementary Fig. 5 | The X-ray structure of 1 (CCDC 2212974, 50% probability ellipsoids).



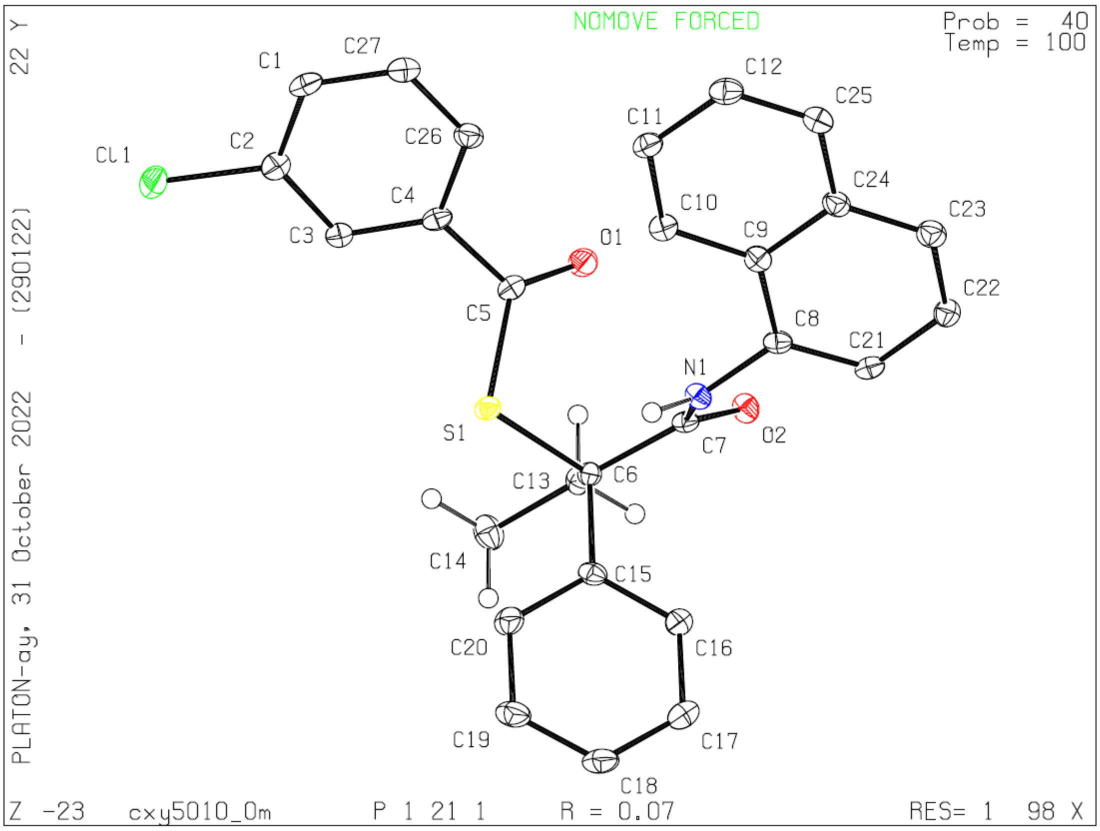
52



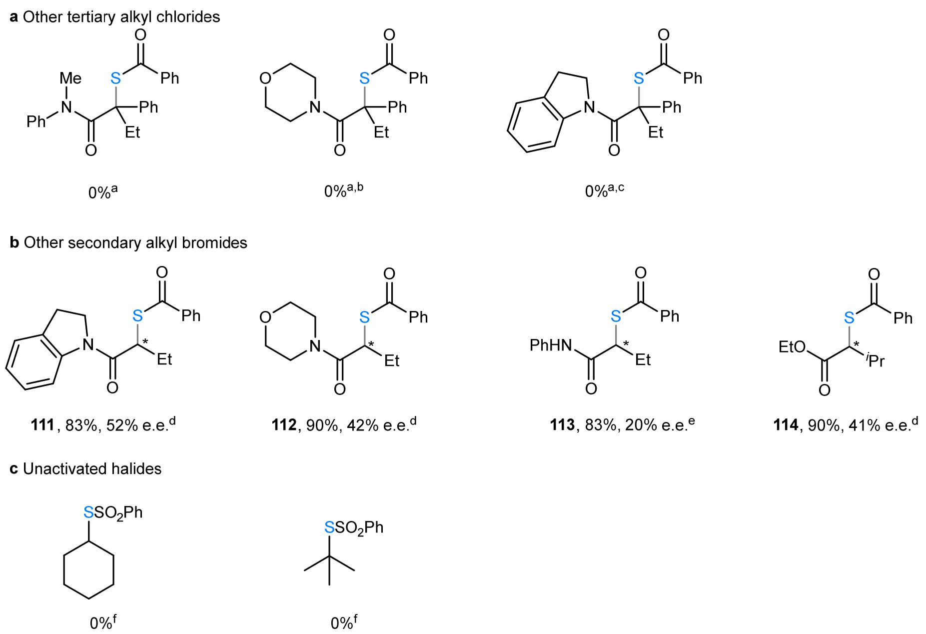
Supplementary Fig. 6 | The X-ray structure of 52 (CCDC 2213037, 50% probability ellipsoids).



83



Supplementary Fig. 7 | The X-ray structure of 83 (CCDC 2213038, 50% probability ellipsoids).



Supplementary Fig. 8 | Unsuccessful examples. [a]$Cu(PPh_3)_3CF_3$ (10 mol%), **L*16** (15 mol%), Cs_2CO_3 (3.0 equiv.), Et_2O, Ar, –10 °C, 3 d. low conversion was observed at –10 °C, with the radical cyclization by-product (**107**) detected.

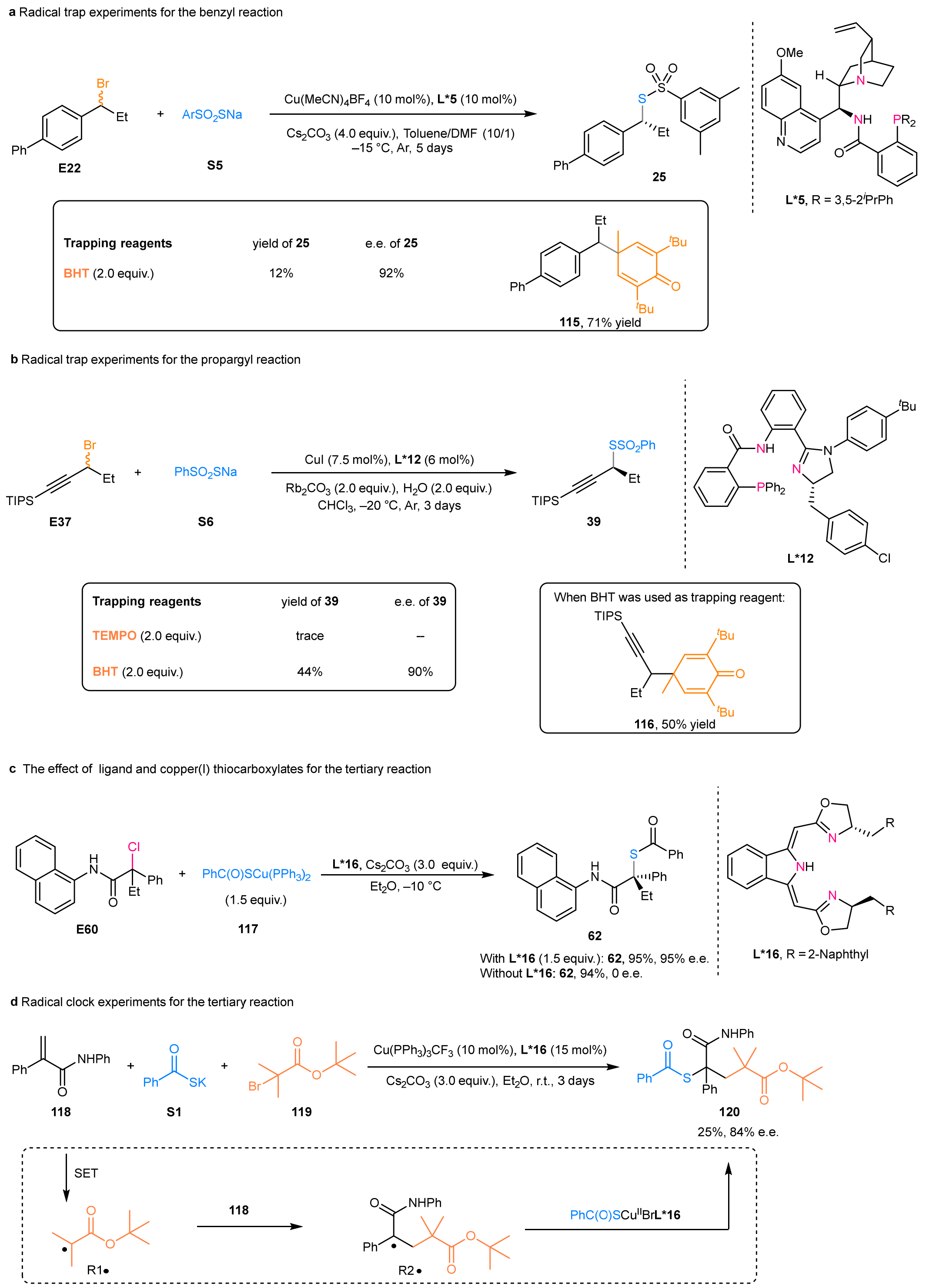
[b]No conversion was observed at –10 °C, low conversion was observed with the major elimination by-product (**108**) detected at 40 °C.

[c]No conversion was observed at –10 °C, low conversion was observed with the elimination and hydrogen abstraction by-products (**109** and **110**) detected at 40 °C.

[d]$Cu(MeCN)_4BF_4$ (10 mol%), **L*5** (10 mol%), Cs_2CO_3 (4.0 equiv.), toluene, –10 °C, Ar, 3 d.

[e]$Cu(PPh_3)_3CF_3$ (10 mol%), **L*16** (15 mol%), Cs_2CO_3 (3.0 equiv.), Et_2O, r.t., Ar, 1 d.

[f]$Cu(MeCN)_4BF_4$ (10 mol%), **L*5** (10 mol%), Cs_2CO_3 (4.0 equiv.), toluene, r.t., 2 d. Both alkyl bromide and iodide was used and low conversion of alkyl bromide/iodide was observed.



Supplementary Fig. 9 | Mechanistic discussion. a, The benzyl coupling was inhibited by BHT and the BHT-trapped product **115** was isolated. **b**, The propargyl coupling were inhibited by TEMPO and BHT and the BHT-trapped product **116** was isolated. **c**, The effects of the lignad and copper(I) thiocarboxylates for the tertiary reaction. **d**, Radical clock experiment for the tertiary reaction. Ar, 3,5-dimethyl phenyl; TEMPO, 2,2,6,6-tetramethyl-1-piperidinyloxy; BHT, 2,6-di-*tert*-butyl-4-methylphenol.

The radical trap experiment and isolated BHT-trapped product **115** indicateded the formation of benzyl radical species from benzyl halides via a single-electron-transfer process.

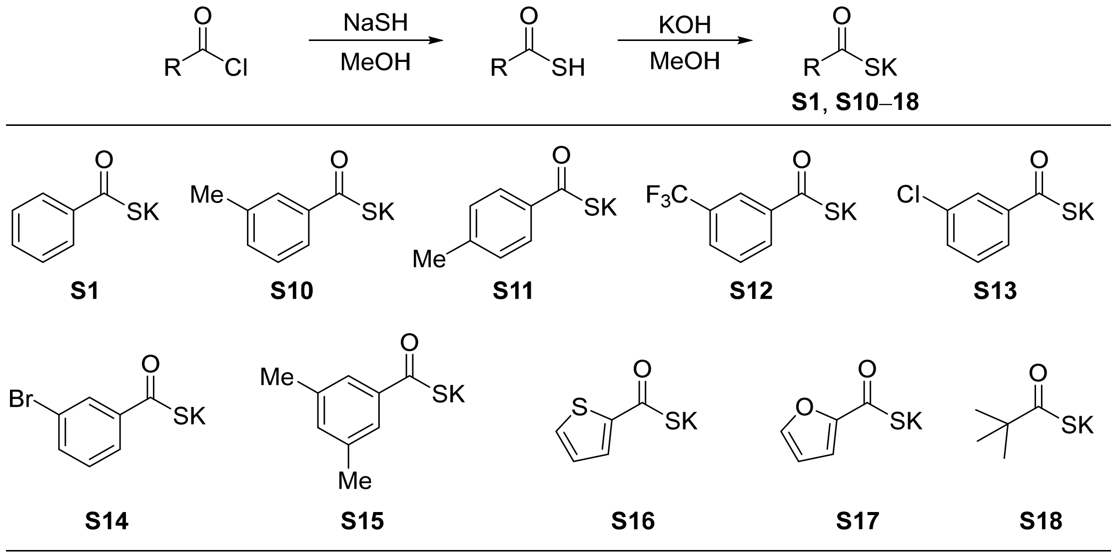
The radical trap experiment and isolated BHT-trapped product **116** indicateded the formation of propargyl radical species from propargyl halides via a single-electron-transfer process.

There was a strong background reaction without chiral ligand **L*16** in the tertiary reaction. The combination of **L*16** and copper(I) thiocarboxylates effectively tuned reactivity and enantioselectivity of this reaction.
The PhC(O)SCu^{I}**L*16** reduced the radical precursor **119**, leading to the PhC(O)SCu^{II}Br**L*16** and a R1 radical. The R1 radical underwent a facile addition to alkene **118** and provided the prochiral tertiary alkyl R2 radical. Next, R2 radical interacted with PhC(O)SCu^{II}Br**L*16** to deliver the desired product **120** and regenerated the copper(I) species.

3. General procedure for synthesis of substrates

Note: The sodium benzenesulfinate **S2**, sodium benzenethiolate **S3**, sodium hydrosulfide **S4** and thiobenzoic acid **S9** were known compounds and commercially available.

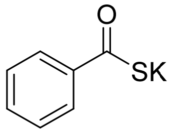
The structures and synthesis of potassium arylthioates or alkylthioate:



General procedure 1:
NaSH (purity: 70%, 2.4 g, 30 mmol, 3.0 equiv.) was suspended in MeOH (20.0 mL) and cooled to 0 °C. Acyl chloride (10.0 mmol, 1.0 equiv.) was added slowly. After stirring at this temperature for 2 hours, the mixture was quenched with HCl (1.0 M) and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated to get the thiocarboxylic acid. Then the thiocarboxylic acid was dissolved in MeOH (10.0 mL). A solution of KOH (8.0 mmol) in MeOH (5.0 mL) was added to the thiocarboxylic acid solution. After shaking, the solvent was removed using rotary evaporator. The resulting solid was washed with CH_2Cl_2 (20.0 mL) and collected by filtration. The solid was then recrystallized from MeOH/toluene for further purification.

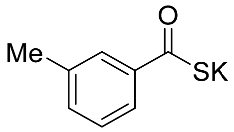
Note: The substrates **S1**, **S16** and **S17** were known compounds and synthesized according to reported literature[4].

Potassium benzothioate (S1)


S1

^{1}H NMR (400 MHz, CD_3OD) δ 8.23 – 8.14 (m, 2H), 7.47 – 7.40 (m, 1H), 7.40 – 7.31 (m, 2H).
^{13}C NMR (100 MHz, CD_3OD) δ 214.6, 145.6, 131.4, 129.1, 128.3.

Potassium 3-methylbenzothioate (S10)

 **S10**

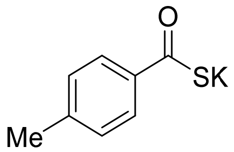
According to **General procedure 1** with 3-methylbenzoyl chloride (1.55 g, 10 mmol, 1.0 equiv.), yield the product **S10** as a white solid (1.35 g, 71% yield).

^{1}H NMR (400 MHz, CD_3OD) δ 7.98 – 7.94 (m, 1H), 7.93 – 7.88 (m, 1H), 7.24 – 7.18 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 214.9, 145.8, 137.9, 132.0, 129.8, 128.2, 126.3, 21.4.

HRMS (ESI) *m/z* calcd for $C_8H_7K_2OS$ $[M + K]^+$ 228.9486, found: 228.9485.

Potassium 4-methylbenzothioate (S11)

 **S11**

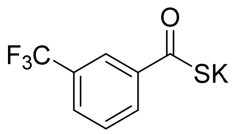
According to **General procedure 1** with 4-methylbenzoyl chloride (1.55 g, 10 mmol, 1.0 equiv.), yield the product **S11** as a white solid (1.52 g, 80% yield).

^{1}H NMR (400 MHz, CD_3OD) δ 8.02 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 214.4, 143.1, 141.8, 129.4, 128.9, 21.3.

HRMS (ESI) *m/z* calcd for $C_8H_7K_2OS$ $[M + K]^+$ 228.9486, found: 228.9485.

Potassium 3-(trifluoromethyl)benzothioate (S12)

 **S12**

According to **General procedure 1** with 3-(trifluoromethyl)benzoyl chloride (2.09 g, 10 mmol, 1.0 equiv.), yield the product **S12** as a light yellow solid (2.07 g, 85% yield).

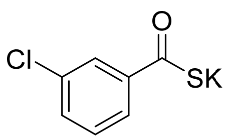
^{1}H NMR (400 MHz, CD_3OD) δ 8.56 (s, 1H), 8.45 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H).

^{13}C NMR (100 MHz, CD_3OD) δ 212.2, 146.1, 132.5 (d, J = 1.4 Hz), 130.6 (q, J = 32.1 Hz), 129.2, 127.5 (q, J = 3.8 Hz), 126.0 (q, J = 3.9 Hz), 125.7 (d, J = 271.4 Hz).

^{19}F NMR (376 MHz, CD_3OD) δ –63.86.

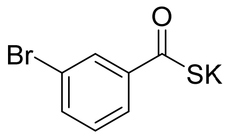
HRMS (ESI) *m/z* calcd for $C_8H_4F_3OS$ $[M - K]^-$ 204.9940, found: 204.9934.

Potassium 3-chlorobenzothioate (S13)

 **S13**

According to **General procedure 1** with 3-chlorobenzoyl chloride (1.75 g, 10 mmol, 1.0 equiv.), yield the product **S13** as a white solid (1.64 g, 78% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 8.15 (t, *J* = 1.9 Hz, 1H), 8.06 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.40 (ddd, *J* = 7.9, 2.2, 1.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ 212.4, 147.4, 134.3, 130.9, 129.8, 129.2, 127.4.
HRMS (ESI) *m/z* calcd for $C_7H_4ClK_2OS$ $[M + K]^+$ 248.8940, found: 248.8937.

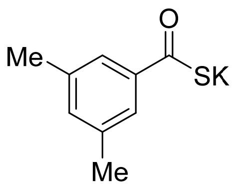
Potassium 3-bromobenzothioate (S14)



S14

According to **General procedure 1** with 3-bromobenzoyl chloride (2.19 g, 10 mmol, 1.0 equiv.), yield the product **S14** as a white solid (2.04 g, 80% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 8.28 (t, *J* = 1.8 Hz, 1H), 8.10 – 8.04 (m, 1H), 7.56 – 7.50 (m, 1H), 7.24 (t, *J* = 7.8 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ 212.3, 147.7, 133.9, 132.2, 130.1, 127.8, 122.4.
HRMS (ESI) *m/z* calcd for C_7H_4BrOS $[M - K]^-$ 214.9172, found: 214.9167.

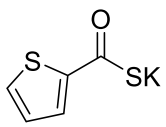
Potassium 3,5-dimethylbenzothioate (S15)



S15

According to **General procedure 1** with 3,5-dimethylbenzoyl chloride (1.69 g, 10 mmol, 1.0 equiv.), yield the product **S15** as a yellow solid (1.68 g, 82% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.79 – 7.73 (m, 2H), 7.09 – 7.03 (m, 1H), 2.33 (d, *J* = 0.8 Hz, 6H).
^{13}C NMR (100 MHz, CD_3OD) δ 215.1, 145.8, 137.8, 132.8, 127.0, 21.3.
HRMS (ESI) *m/z* calcd for $C_9H_9K_2OS$ $[M + K]^+$ 242.9643, found: 242.9641.

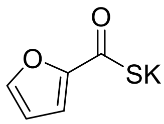
Potassium thiophene-2-carbothioate (S16)



S16

^{1}H NMR (400 MHz, CD_3OD) δ 7.68 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.46 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.02 (dd, *J* = 5.0, 3.7 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ 205.0, 153.2, 131.3, 130.0, 128.1.

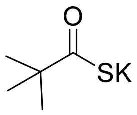
Potassium furan-2-carbothioate (S17)



S17

^{1}H NMR (400 MHz, CD_3OD) δ 7.66 – 7.60 (m, 1H), 7.24 (dd, J = 3.5, 0.9 Hz, 1H), 6.53 (dd, J = 3.4, 1.8 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ 201.0, 157.9, 145.1, 116.0, 112.5.

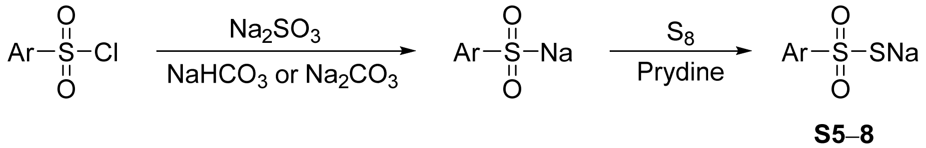
Potassium 2,2-dimethylpropanethioate (S18)

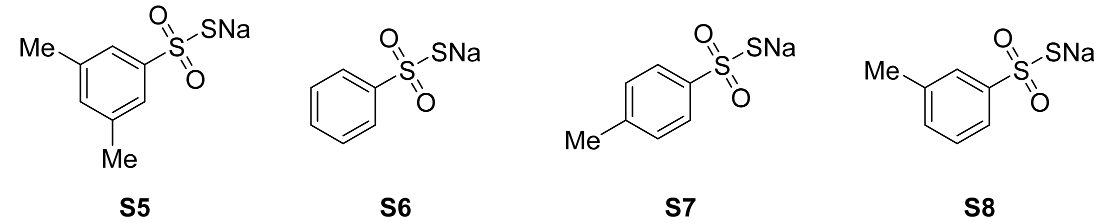


S18

According to **General procedure 1** with pivaloyl chloride (1.21 g, 10 mmol, 1.0 equiv.), yield the product **S18** as a yellow solid (1.17 g, 75% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 1.36 (s, 9H).
^{13}C NMR (100 MHz, CD_3OD) δ 230.2, 30.0, 28.5.
HRMS (ESI) *m/z* calcd for $C_5H_9K_2OS$ $[M + K]^+$194.9643, found: 194.9642.

The structures and synthesis of sodium arylsulfonothioates:

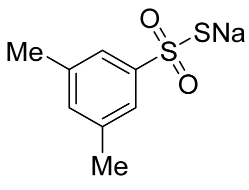




General procedure 2:
Sodium sulfite (20.0 mmol, 2.0 equiv.), sodium bicarbonate or sodium carbonate (20.0 mmol, 2.0 equiv.) and the corresponding aryl sulfonyl chloride (10.0 mmol, 1.0 equiv.) were dissolved in distilled water (10.0 mL). The reaction mixture was stirred for 4 hours at 80 °C. After cooling down to room temperature, water was removed in vacuo. 50 mL of ethanol was then added to this white residue and the resulting heterogeneous solution was filtered. The filtrate was concentrated under reduced pressure and the desired sodium aryl sulfinates were obtained as white powders.
sodium aryl sulfinates (10.0 mmol, 1.0 equiv.) and S_8 (10.0 mmol, 1.0 equiv.) were dissolved in pyridine (8.0 mL) to give a yellow solution under argon. After the reaction was stirred 6 hours, 30.0 mL anhydrous diethyl ether was added, giving a white suspension, the reaction was filtered and washed with anhydrous diethyl ether. The residue was recrystallized from anhydrous ethanol to afford the desired compound as a white solid

Note: The sodium benzenesulfinate for the synthesis of substrate **S6** was commercially available, and the substrate **S6** was known compound and synthesized according to reported literature[5].

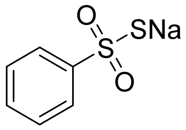
Sodium 3,5-dimethylbenzenesulfonothioate (S5)



S5

According to **General procedure 2** with 3,5-dimethylbenzenesulfonyl chloride (2.05 g, 10 mmol, 1.0 equiv.), yield the product **S5** as a white solid (2.02 g, 90% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.63 (s, 2H), 7.13 (s, 1H), 2.40 (s, 6H).
^{13}C NMR (100 MHz, CD_3OD) δ 154.4, 139.1, 132.6, 123.1, 21.3.
HRMS (ESI) *m/z* calcd for $C_8H_9O_2S_2$ $[M - Na]^-$ 201.0049, found: 201.0042

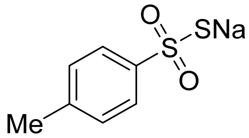
Sodium benzenesulfonothioate (S6)



S6

^{1}H NMR (400 MHz, CD_3OD) δ 8.04 – 7.95 (m, 2H), 7.51 – 7.41 (m, 3H).

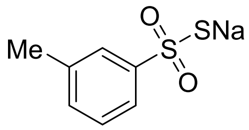
Sodium 4-methylbenzenesulfonothioate (S7)



S7

According to **General procedure 2** with 4-methylbenzenesulfonyl chloride (1.91 g, 10 mmol, 1.0 equiv.), yield the product **S7** as a white solid (1.85 g, 88% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.93 – 7.85 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 152.1, 141.7, 129.6, 125.6, 21.3.
HRMS (ESI) *m/z* calcd for $C_7H_7O_2S_2$ $[M - Na]^-$ 186.9893, found: 186.9885.

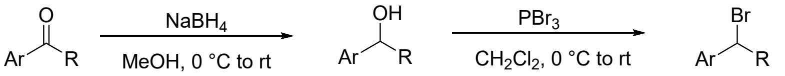
Sodium 3-methylbenzenesulfonothioate (S8)



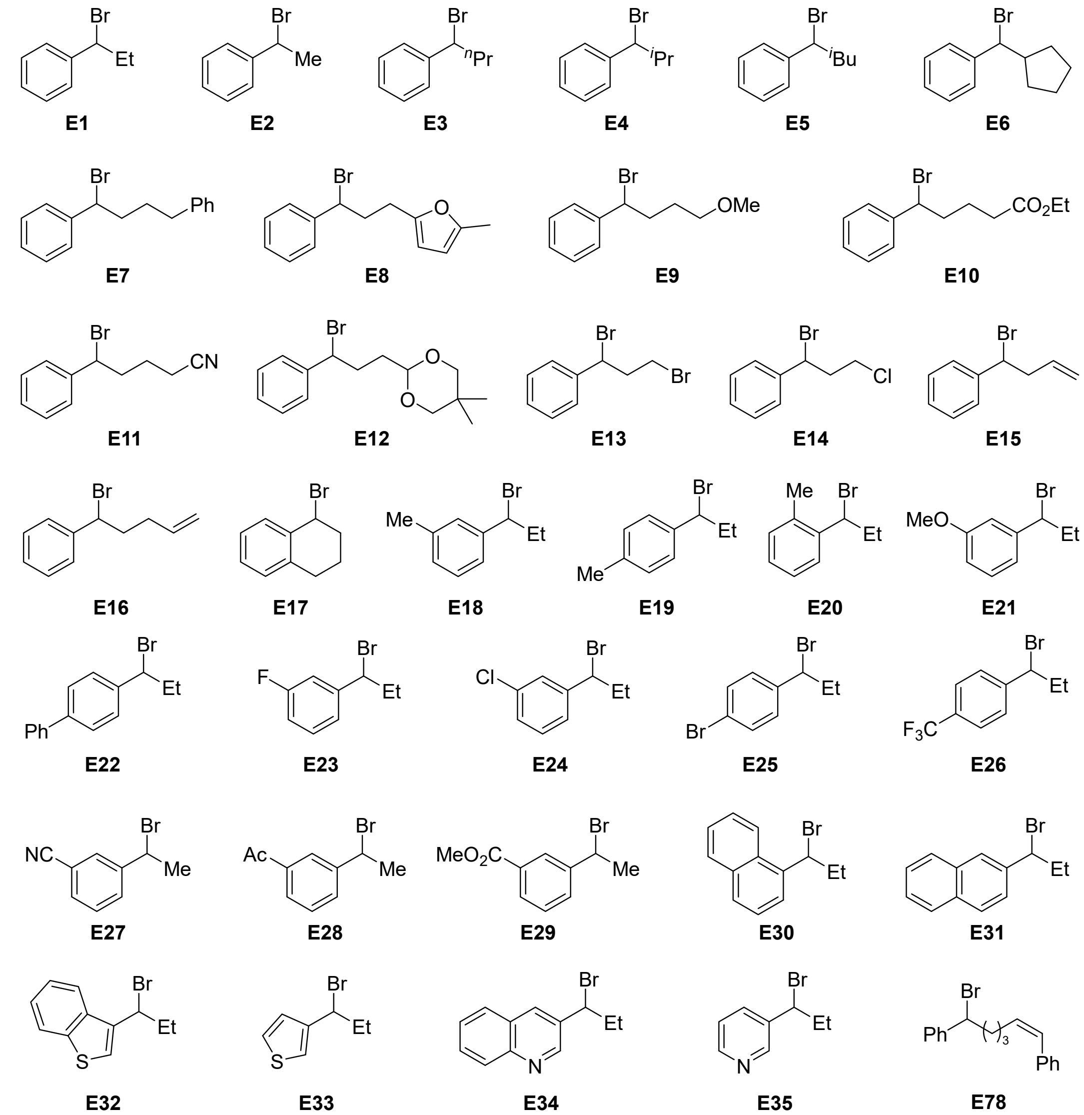
S8

According to **General procedure 2** with 3-methylbenzenesulfonyl chloride (1.91 g, 10 mmol, 1.0 equiv.), yield the product **S8** as a white solid (1.93 g, 92% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.83 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 154.3, 139.2, 131.9, 129.0, 125.9, 122.6, 21.4.
HRMS (ESI) *m/z* calcd for $C_7H_7O_2S_2$ $[M - Na]^-$ 186.9893, found: 186.9885.

The structures and synthesis of benzyl electrophiles:



E1–35

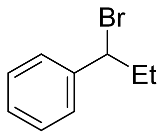


To a solution of ketone (3.0 mmol) in MeOH (9.0 mL) was added $NaBH_4$ (136.2 mg, 3.6 mmol) at ice bath and the reaction mixture was stirred at room temperature for 0.5–2 hours. After completion of reaction (monitored by TLC), the reaction was quenched by water, and the mixture was extracted with CH_2Cl_2 three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the corresponding alcohol. The crude product was purified by flash chromatography on silica gel to provide the desired product.

To a solution of the residue obtained above in CH_2Cl_2 (9.0 mL) was added PBr_3 (0.20 mL, 2.1 mmol) under an argon atmosphere at ice water bath and the resulting reaction mixture was stirred at room temperature. After completion of reaction (monitored by TLC), the mixture was quenched by water at ice water bath, and the mixture was extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the corresponding crude benzyl bromides, which was directly used in the next step without further purification or stored in a refridgerator.

Note: Benzyl bromide **E2** was purchased from Bide Pharmatech. The benzyl bromide **E1**, **E3–35**, **E78** were known compounds and synthesized according to reported literature[6,7]. The purities of crude benzyl bromides were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethylbenzene or 1,1,1,2,2-pentachloroethane as an internal standard.

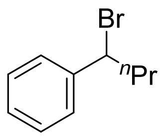
(1-Bromopropyl)benzene (E1)



E1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 4.91 (dd, J = 8.1, 6.8 Hz, 1H), 2.41 – 2.27 (m, 1H), 2.26 – 2.13 (m, 1H), 1.04 (t, J = 7.3 Hz, 3H).

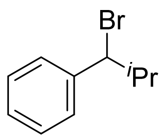
(1-Bromobutyl)benzene (E3)



E3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 4.97 (dd, J = 8.2, 6.9 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.17 – 2.04 (m, 1H), 1.56 – 1.42 (m, 1H), 1.41 – 1.26 (m, 1H), 0.94 (t, J = 7.4 Hz, 3H).

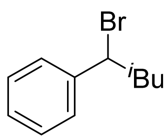
(1-Bromo-2-methylpropyl)benzene (E4)



E4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 4.71 (d, J = 8.5 Hz, 1H), 2.37 – 2.29 (m, 1H), 1.18 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.7 Hz, 3H).

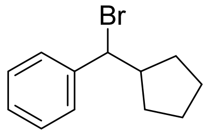
(1-Bromo-3-methylbutyl)benzene (E5)



E5

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 5.04 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.25 – 2.15 (m, 1H), 2.04 – 1.92 (m, 1H), 1.77 – 1.63 (m, 1H), 0.93 (t, *J* = 6.6 Hz, 6H).

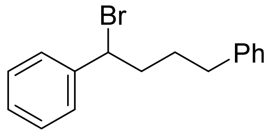
(Bromo(cyclopentyl)methyl)benzene (E6)



E6

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 4.77 (d, *J* = 10.2 Hz, 1H), 2.81 – 2.65 (m, 1H), 2.17 – 2.08 (m, 1H), 1.74 – 1.44 (m, 6H), 1.11 – 0.99 (m, 1H).

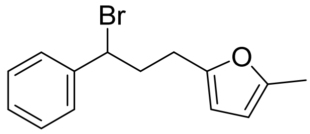
(1-Bromobutane-1,4-diyl)dibenzene (E7)



E7

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 6H), 7.25 – 7.21 (m, 1H), 7.20 – 7.11 (m, 3H), 4.95 (dd, *J* = 8.1, 6.9 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.37 – 2.31 (m, 1H), 2.21 – 2.11 (m, 1H), 1.90 – 1.77 (m, 2H), 1.70 – 1.56 (m, 1H).

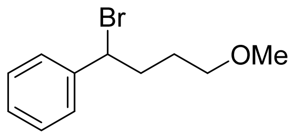
2-(3-Bromo-3-phenylpropyl)-5-methylfuran (E8)



E8

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 5.90 – 5.78 (m, 2H), 4.94 (dd, *J* = 8.3, 6.4 Hz, 1H), 2.74 – 2.66 (m, 2H), 2.61 – 2.52 (m, 1H), 2.50 – 2.37 (m, 1H), 2.24 (s, 3H).

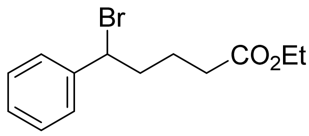
(1-Bromo-4-methoxybutyl)benzene (E9)



E9

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.42 – 7.29 (m, 3H), 5.02 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.50 – 3.39 (m, 2H), 3.35 (s, 3H), 2.45 – 2.35 (m, 1H), 2.31 – 2.22 (m, 1H), 1.88 – 1.76 (m, 1H), 1.70 – 1.61 (m, 1H).

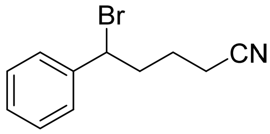
Ethyl 5-bromo-5-phenylpentanoate (E10)



E10

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 5H), 4.95 (dd, *J* = 8.2, 6.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 7.3 Hz, 3H), 2.24 – 2.11 (m, 1H), 1.91 – 1.77 (m, 1H), 1.71 – 1.57 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

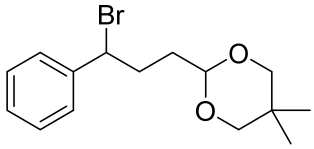
5-Bromo-5-phenylpentanenitrile (E11)



E11

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 4.93 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.46 – 2.34 (m, 3H), 2.32 – 2.28 (m, 1H), 1.99 – 1.85 (m, 1H), 1.76 – 1.62 (m, 1H).

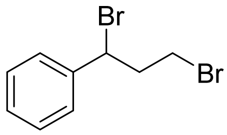
2-(3-Bromo-3-phenylpropyl)-5,5-dimethyl-1,3-dioxane (E12)



E12

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.29 – 7.25 (m, 1H), 4.99 (dd, *J* = 8.4, 6.7 Hz, 1H), 4.45 (t, *J* = 4.7 Hz, 1H), 3.62 – 3.53 (m, 2H), 3.39 (d, *J* = 11.1 Hz, 2H), 2.47 – 2.36 (m, 1H), 2.36 – 2.29 (m, 1H), 1.91 – 1.78 (m, 1H), 1.72 – 1.61 (m, 1H), 1.17 (s, 3H), 0.71 (s, 3H).

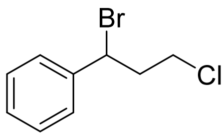
(1,3-Dibromopropyl)benzene (E13)



E13

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.38 – 7.27 (m, 3H), 5.24 – 5.13 (m, 1H), 3.61 – 3.48 (m, 1H), 3.46 – 3.34 (m, 1H), 2.84 – 2.68 (m, 1H), 2.63 – 2.48 (m, 1H).

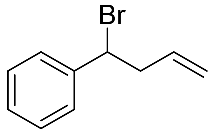
(1-Bromo-3-chloropropyl)benzene (E14)



E14

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 3H), 5.20 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.74 – 3.66 (m, 1H), 3.59 – 3.52 (m, 1H), 2.76 – 2.62 (m, 1H), 2.52 – 2.40 (m, 1H).

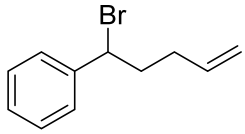
(1-Bromobut-3-en-1-yl)benzene (E15)



E15

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 5.82 – 5.65 (m, 1H), 5.17 – 5.05 (m, 2H), 4.95 (t, *J* = 7.5 Hz, 1H), 3.11 – 2.85 (m, 2H).

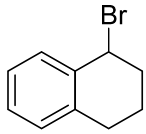
(1-Bromopent-4-en-1-yl)benzene (E16)



E16

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.36 – 7.24 (m, 3H), 5.84 – 5.70 (m, 1H), 5.09 – 4.99 (m, 2H), 4.95 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.46 – 2.33 (m, 1H), 2.24 – 2.03 (m, 3H).

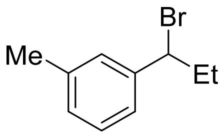
1-Bromo-1,2,3,4-tetrahydronaphthalene (E17)



E17

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.21 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 5.60 (t, *J* = 3.6 Hz, 1H), 2.94 (ddd, 1H), 2.85 (ddd, *J* = 17.1, 11.1, 5.8 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.34 – 2.20 (m, 1H), 2.20 – 2.09 (m, 1H), 1.96 – 1.85 (m, 1H).

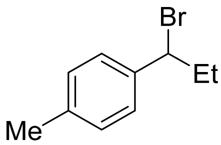
1-(1-Bromopropyl)-3-methylbenzene (E18)



E18

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 3H), 7.11 – 7.04 (m, 1H), 4.84 (dd, *J* = 8.1, 6.8 Hz, 1H), 2.36 – 2.33 (m, 4H), 2.19 – 2.11 (m, 1H), 0.99 (t, *J* = 7.3 Hz, 3H).

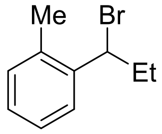
1-(1-Bromopropyl)-4-methylbenzene (E19)



E19

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.15 – 7.12 (m, 2H), 4.87 (t, *J* = 7.4 Hz, 1H), 2.33 (s, 3H), 2.20 – 2.08 (m, 1H), 1.88 – 1.83 (m, 1H), 0.99 (t, *J* = 7.3 Hz, 3H).

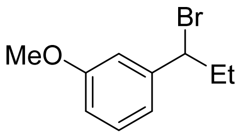
1-(1-Bromopropyl)-2-methylbenzene (E20)



E20

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 3H), 7.11 – 7.06 (m, 1H), 4.85 (dd, *J* = 8.2, 6.7 Hz, 1H), 2.35 (s, 3H), 2.33 – 2.29 (m, 1H), 2.18 – 2.13 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

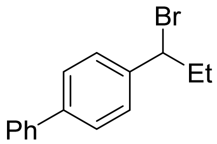
1-(1-Bromopropyl)-3-methoxybenzene (E21)



E21

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 6.99 – 6.95 (m, 1H), 6.93 (t, 1H), 6.84 – 6.80 (m, 1H), 4.84 (dd, *J* = 8.0, 6.7 Hz, 1H), 3.81 (s, 3H), 2.27 – 2.21 (m, 1H), 2.21 – 2.09 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

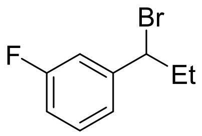
4-(1-Bromopropyl)-1,1'-biphenyl (E22)



E22

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 4H), 7.46 – 7.41 (m, 4H), 7.37 – 7.31 (m, 1H), 4.93 (dd, *J* = 8.1, 6.7 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.25 – 2.14 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

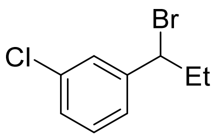
1-(1-Bromopropyl)-3-fluorobenzene (E23)



E23

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 1H), 7.19 – 7.07 (m, 2H), 7.00 – 6.93 (m, 1H), 4.88 – 4.76 (m, 1H), 2.33 – 2.20 (m, 1H), 2.20 – 2.08 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

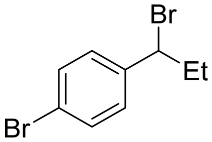
1-(1-Bromopropyl)-3-chlorobenzene (E24)



E24

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 1H), 7.27 – 7.25 (m, 3H), 4.80 (dd, *J* = 8.1, 6.8 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.19 – 2.07 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

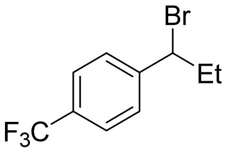
1-Bromo-4-(1-bromopropyl)benzene (E25)



E25

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.29 – 7.26 (m, 2H), 4.85 – 4.79 (m, 1H), 2.32 – 2.20 (m, 1H), 2.20 – 2.07 (m, 1H), 0.99 (t, *J* = 7.2 Hz, 3H).

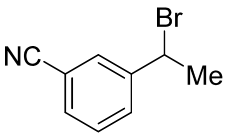
1-(1-Bromopropyl)-4-(trifluoromethyl)benzene (E26)



E26

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 4.86 (dd, *J* = 8.1, 6.7 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.21 – 2.08 (m, 1H), 1.01 (t, *J* = 7.3 Hz, 3H).

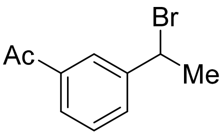
1-(1-Bromoethyl)-3-isocyanobenzene (E27)



E27

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 1.8 Hz, 1H), 7.67 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.57 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 5.15 (q, *J* = 6.9 Hz, 1H), 2.03 (d, *J* = 6.9 Hz, 3H).

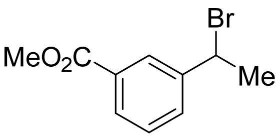
1-(3-(1-Bromoethyl)phenyl)ethan-1-one (E28)



E28

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.9 Hz, 1H), 7.87 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.65 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 5.23 (q, *J* = 7.0 Hz, 1H), 2.61 (s, 3H), 2.06 (d, *J* = 7.0 Hz, 3H).

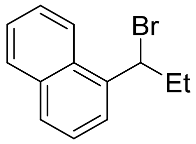
Methyl 3-(1-bromoethyl)benzoate (E29)



E29

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.9 Hz, 1H), 7.96 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.63 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 5.22 (q, *J* = 6.9 Hz, 1H), 3.93 (s, 3H), 2.06 (d, *J* = 6.9 Hz, 3H).

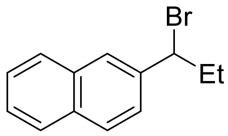
1-(1-Bromopropyl)naphthalene (E30)



E30

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.59 – 7.48 (m, 2H), 5.75 (t, *J* = 7.3 Hz, 1H), 2.67 – 2.54 (m, 1H), 2.52 – 2.40 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).

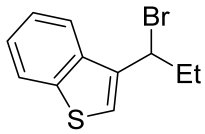
2-(1-Bromopropyl)naphthalene (E31)



E31

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.61 – 7.57 (m, 1H), 7.54 – 7.51 (m, 2H), 5.10 (t, *J* = 7.4 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.37 – 2.33 (m, 1H), 1.07 (t, *J* = 7.3 Hz, 3H).

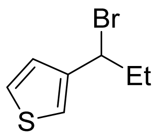
3-(1-Bromopropyl)benzo[b]thiophene (E32)



E32

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 1H), 7.87 – 7.83 (m, 1H), 7.47 (s, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.35 (m, 1H), 5.31 – 5.24 (m, 1H), 2.49 – 2.37 (m, 2H), 1.13 (t, *J* = 7.3 Hz, 3H).

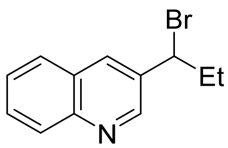
3-(1-Bromopropyl)thiophene (E33)



E33

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 1H), 7.25 – 7.20 (m, 1H), 7.14 (d, *J* = 5.1 Hz, 1H), 5.02 (t, *J* = 7.3 Hz, 1H), 2.25 – 2.14 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H).

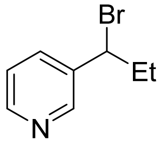
3-(1-Bromopropyl)quinoline (E34)



E34

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.20 – 8.11 (m, 2H), 7.85 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.80 – 7.71 (m, 1H), 7.64 – 7.56 (m, 1H), 5.09 (dd, *J* = 8.2, 6.7 Hz, 1H), 2.53 – 2.40 (m, 1H), 2.40 – 2.23 (m, 1H), 1.10 (t, *J* = 7.2 Hz, 3H).

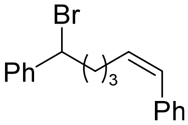
3-(1-Bromopropyl)pyridine (E35)



E35

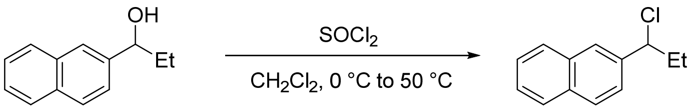
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 2.4 Hz, 1H), 8.57 – 8.46 (m, 1H), 7.75 (dt, J = 8.0, 2.0 Hz, 1H), 7.30 (dd, J = 8.0, 4.8 Hz, 1H), 4.87 (t, J = 7.4 Hz, 1H), 2.40 – 2.24 (m, 1H), 2.16 (dp, J = 14.2, 7.1 Hz, 1H), 1.09 – 0.97 (m, 3H).

(*Z*)-(6-Bromohex-1-ene-1,6-diyl)dibenzene (E78)



E78

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 7H), 7.28 – 7.25 (m, 2H), 7.23 – 7.21 (m, 2H), 6.43 (d, *J* = 11.5 Hz, 1H), 5.65 – 5.55 (m, 1H), 4.90 (t, *J* = 7.5 Hz, 1H), 2.38 – 2.33 (m, 2H), 1.98 – 1.87 (m, 1H), 1.82 – 1.71 (m, 1H), 1.70 – 1.56 (m, 2H), 1.50 – 1.40 (m, 1H).

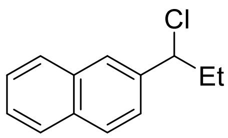


E36

In a vacuum dried 50 mL round bottomed flask, 1-(naphthalen-2-yl)propan-1-ol (0.93 g, 5.0 mmol) was dissolved in dry CH_2Cl_2 (12.0 mL). Then, thionyl chloride (1.81 mL, 25.0 mmol) was added at 0 °C under argon atmosphere. Then, the reaction mixture was warmed to 50 °C. After stirred for 3 hours, the solvent and the unreacted thionyl chloride were removed by evaporation. The residue was quenched by saturated aqueous $NaHCO_3$ (1.0 mL) and H_2O (20.0 mL), and then extracted with EtOAc three times (20.0 mL × 3). The combined organic layer was then dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporator to obtain the corresponding chloride product **E36** (1.05 g, 90% yield) as a pale yellow oil.

Note: The substrate **E36** was known compound and synthesized according to reported literature[8].

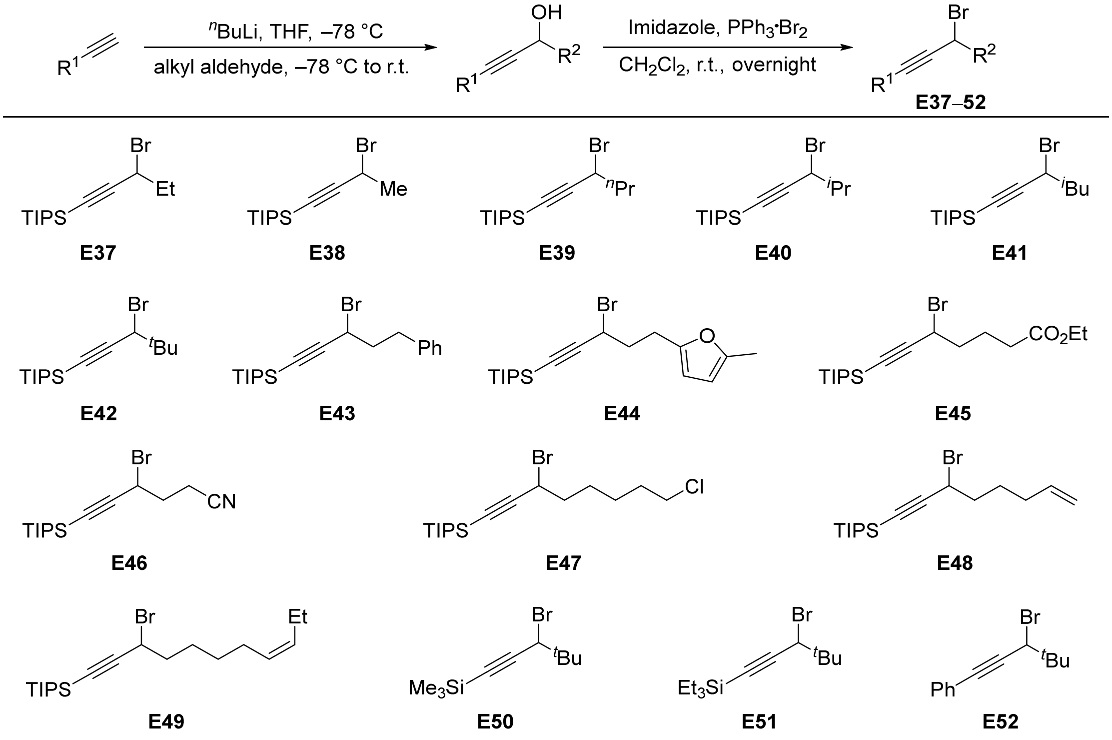
2-(1-Chloropropyl)naphthalene (E36)



E36

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.53 – 7.42 (m, 3H), 4.93 (t, *J* = 7.0 Hz, 1H), 2.31 – 2.05 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

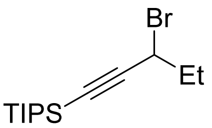
The structures and synthesis of propargyl electrophiles:



^{n}BuLi (2.4 M in hexane, 1.3 equiv.) was added dropwise into a solution of alkynes (1.3 equiv.) in anhydrous THF (1.0 M) at −78 °C. The mixture was stirred at room temperature for 30 min and cooled to −78 °C. Aldehyde (1.0 equiv.) was added dropwise. Then the mixture was warmed up to room temperature and stirred for overnight. The mixture was quenched by a saturated NH_4Cl aqueous solution, extracted with EtOAc, and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure and then subjected to flash chromatography to afford the desired product.
Under an argon atmosphere, to a solution of imidazole (1.2 equiv.) in dry CH_2Cl_2(1.0 M) was added propargyl alcohol (1.0 equiv.). The solution was stirred for 15 min, followed by the addition of dibromotriphenylphosphorane (1.2 equiv.). The reaction mixture was stirred at room temperature overnight. Then the reaction was quenched by the addition of silica gel. The solvent was removed under reduced pressure, and then the plug of silica gel was subjected to flash chromatography to afford the desired product.

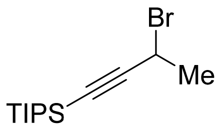
Note: The substrates **E37–44**, **E46**, **E48**, **E49** were known compounds and synthesized according to reported literature[9]. The substrate **E52** was known compound and synthesized according to reported literature[10].

(3-Bromopent-1-yn-1-yl)triisopropylsilane (E37)

 **E37**

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (t, *J* = 6.3 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H), 1.09 – 1.05 (m, 21H).

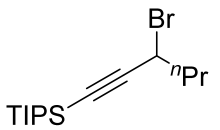
(3-Bromobut-1-yn-1-yl)triisopropylsilane (E38)



E38

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (q, *J* = 6.9 Hz, 1H), 1.91 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 21H).

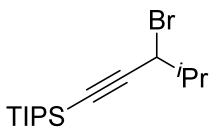
(3-Bromohex-1-yn-1-yl)triisopropylsilane (E39)



E39

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (t, *J* = 6.8 Hz, 1H), 2.07 – 1.95 (m, 2H), 1.66 – 1.58 (m, 2H), 1.10 (d, *J* = 1.2 Hz, 21H), 0.98 (t, *J* = 7.4 Hz, 3H).

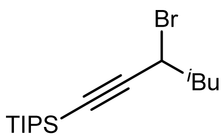
(3-Bromo-4-methylpent-1-yn-1-yl)triisopropylsilane (E40)



E40

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (d, *J* = 4.4 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.15 (d, *J* = 6.7 Hz, 6H), 1.10 (s, 21H).

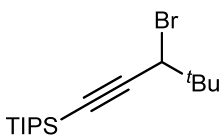
(3-Bromo-5-methylhex-1-yn-1-yl)triisopropylsilane (E41)



E41

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (t, *J* = 7.4 Hz, 1H), 1.97 – 1.86 (m, 3H), 1.08 – 1.00 (m, 21H), 0.94 (d, *J* = 6.3 Hz, 6H).

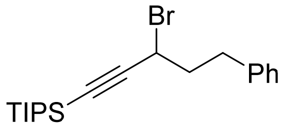
(3-Bromohept-1-yn-1-yl)triisopropylsilane (E42)



E42

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (s, 1H), 1.15 (s, 9H), 1.08 (s, 21H).

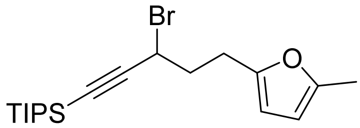
(3-Bromo-5-phenylpent-1-yn-1-yl)triisopropylsilane (E43)



E43

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 4.49 (t, *J* = 6.8 Hz, 1H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.36 – 2.27 (m, 2H), 1.09 (s, 21H).

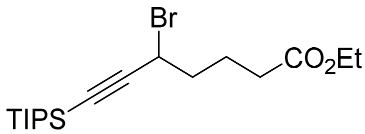
(3-Bromo-5-(5-methylfuran-2-yl)pent-1-yn-1-yl)triisopropylsilane (E44)



E44

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 – 5.79 (m, 2H), 4.53 (t, *J* = 6.8 Hz, 1H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.35 – 2.27 (m, 2H), 2.25 (d, *J* = 1.0 Hz, 3H), 1.08 (s, 21H).

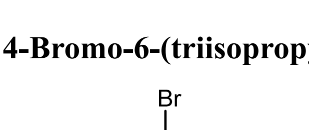
Ethyl 5-bromo-7-(triisopropylsilyl)hept-6-ynoate (**E45**)



E45

According to **General procedure 3**, ethyl 5-oxopentanoate (2.70 g, 18.7 mmol, 1.0 equiv.) with ethynyltriisopropylsilane (4.43 g, 24.3 mmol, 1.3 equiv.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 75/1) to yield the product as a colorless oil (2.62 g, 36% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (t, *J* = 6.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.10 – 2.01 (m, 2H), 1.96 – 1.84 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.13 – 0.99 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 105.5, 89.3, 60.5, 39.0, 36.8, 33.4, 22.9, 18.7, 14.3, 11.2.
HRMS (ESI) *m/z* calcd. For $C_{18}H_{34}BrO_2Si$ $[M + H]^+$ 389.1506, found 389.1506.

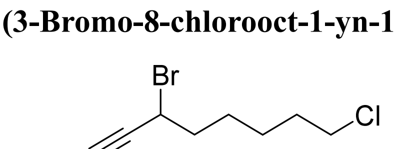
4-Bromo-6-(triisopropylsilyl)hex-5-ynenitrile (E46)



E46

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (t, *J* = 6.1 Hz, 1H), 2.67 (td, *J* = 7.4, 2.0 Hz, 2H), 2.39 – 2.32 (m, 2H), 1.09 – 1.06 (m, 21H).

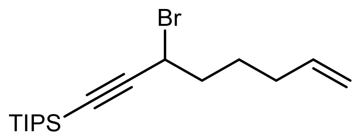
(3-Bromo-8-chlorooct-1-yn-1-yl)triisopropylsilane (**E47**)



E47

According to **General procedure 3**, 6-chlorohexanal (0.67 g, 5 mmol, 1.0 equiv.) with ethynyltriisopropylsilane (1.19 g, 6.5 mmol, 1.3 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product as a colorless oil (0.21 g, 11% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (t, *J* = 6.6 Hz, 1H), 3.54 (t, 2H), 2.07 – 1.98 (m, 2H), 1.85 – 1.75 (m, 2H), 1.64 – 1.45 (m, 4H), 1.07 (s, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 105.8, 89.0, 44.9, 39.7, 37.3, 32.5, 26.7, 26.1, 18.7, 11.3.
HRMS (ESI) *m/z* calcd. For $C_{17}H_{33}BrClSi$ $[M + H]^+$ 379.1218, found 379.1206.

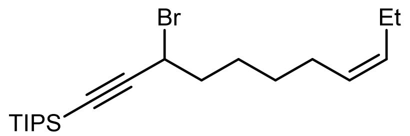
(3-Bromooct-7-en-1-yn-1-yl)triisopropylsilane (E48)



E48

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.74 (m, 1H), 5.06 – 4.96 (m, 2H), 4.56 (t, *J* = 6.7 Hz, 1H), 2.14 – 2.07 (m, 2H), 2.05 – 1.99 (m, 2H), 1.71 – 1.63 (m, 2H), 1.07 (s, 21H).

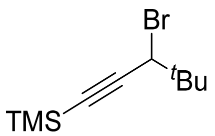
(*Z*)-(3-bromoundec-8-en-1-yn-1-yl)triisopropylsilane (E49)



E49

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.27 (m, 2H), 4.54 (t, *J* = 6.7 Hz, 1H), 2.08 – 1.98 (m, 6H), 1.60 – 1.54 (m, 2H), 1.43 – 1.35 (m, 2H), 1.07 (s, 21H), 0.96 (t, *J* = 7.5 Hz, 3H).

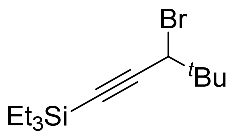
(3-Bromo-4,4-dimethylpent-1-yn-1-yl)trimethylsilane (E50)



E50

According to **General procedure 3**, pivalaldehyde (1.66 g, 19.3 mmol, 1.0 equiv.) with ethynyltrimethylsilane (2.46 g, 25.1 mmol, 1.3 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product as a colorless oil (0.86 g, 18% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (s, 1H), 1.13 (s, 9H), 0.18 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 103.1, 92.8, 51.4, 36.6, 26.9, –0.1.
HRMS (ESI) *m/z* calcd. For $C_{10}H_{19}BrNaSi$ $[M + Na]^+$ 269.0332, found 269.0331.

(3-Bromo-4,4-dimethylpent-1-yn-1-yl)triethylsilane (E51)



E51

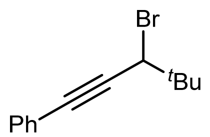
According to **General procedure 3**, pivalaldehyde (0.89 g, 10.3 mmol, 1.0 equiv.) with triethyl(ethynyl)silane (1.88 g, 13.4 mmol, 1.3 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product as a colorless oil (0.83g, 28% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (s, 1H), 1.14 (s, 9H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 104.4, 90.5, 51.6, 36.6, 27.0, 7.6, 4.5.

HRMS (ESI) *m/z* calcd. For $C_{13}H_{26}BrSi$ $[M + H]^+$ 289.0982, found 289.0981.

(3-Bromo-4,4-dimethylpent-1-yn-1-yl)benzene (E52)



E52

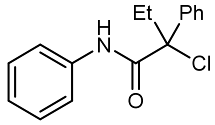
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.37 – 7.32 (m, 3H), 4.65 (s, 1H), 1.24 (s, 9H).

The structures and synthesis of tertiary α-chloroamides:

The *α*-chloro acid chloride in anhydrous CH_2Cl_2 (5.0 mL) was added dropwise to a solution of the corresponding amine (10.0 mmol) and triethylamine (4.2 mL, 30.0 mmol) in CH_2Cl_2 (30.0 mL) at 0 °C. The reaction was stirred at 0 °C for 15 min and then warmed up to room temperature. After completion (monitored by TLC), the reaction was quenched by the addition of 1.0 M HCl, the organic layer was washed by brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude material, which was purified by flash chromatography to yield the tertiary α-chloroamide.

Note: The substrates **E53–77** were known compounds and synthesized according to reported literature[11,12]

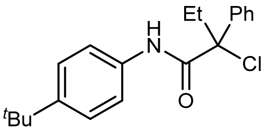
2-Chloro-*N*,2-diphenylbutanamide (E53)



E53

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.64 – 7.57 (m, 2H), 7.57 – 7.48 (m, 2H), 7.42 – 7.27 (m, 5H), 7.18 – 7.10 (m, 1H), 2.66 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.42 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.07 (t, *J* = 7.2 Hz, 3H).

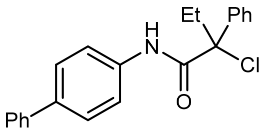
***N*-(4-(*Tert*-butyl)phenyl)-2-chloro-2-phenylbutanamide (E54)**



E54

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.66 – 7.55 (m, 2H), 7.49 – 7.44 (m, 2H), 7.39 – 7.29 (m, 5H), 2.67 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.30 (s, 9H), 1.07 (t, *J* = 7.2 Hz, 3H).

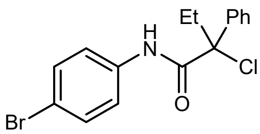
***N*-([1,1'-Biphenyl]-4-yl)-2-chloro-2-phenylbutanamide (E55)**



E55

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.66 – 7.59 (m, 4H), 7.59 – 7.54 (m, 4H), 7.45 – 7.31 (m, 6H), 2.68 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.44 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H).

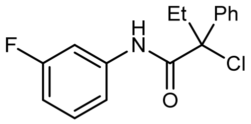
***N*-(4-Bromophenyl)-2-chloro-2-phenylbutanamide (E56)**



E56

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.63 – 7.54 (m, 2H), 7.44 (s, 4H), 7.41 – 7.30 (m, 3H), 2.64 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).

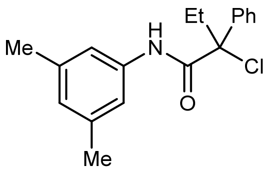
2-Chloro-*N*-(3-fluorophenyl)-2-phenylbutanamide (E57)



E57

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.61 – 7.57 (m, 2H), 7.53 (dt, *J* = 10.8, 2.2 Hz, 1H), 7.42 – 7.30 (m, 3H), 7.28 – 7.24 (m, 1H), 7.16 – 7.12 (m, 1H), 6.86 – 6.80 (m, 1H), 2.64 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).

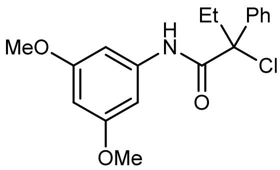
2-Chloro-*N*-(3,5-dimethylphenyl)-2-phenylbutanamide **(E58)**



E58

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.64 – 7.55 (m, 2H), 7.43 – 7.28 (m, 3H), 7.19 (s, 2H), 6.83 – 6.75 (m, 1H), 2.66 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.29 (s, 6H), 1.07 (t, *J* = 7.2 Hz, 3H).

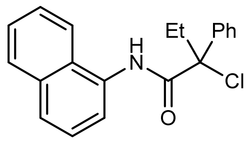
2-Chloro-*N*-(3,5-dimethoxyphenyl)-2-phenylbutanamide (E59)



E59

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.64 – 7.55 (m, 2H), 7.40 – 7.30 (m, 3H), 6.78 (d, *J* = 2.3 Hz, 2H), 6.26 (t, *J* = 2.2 Hz, 1H), 3.78 (s, 6H), 2.65 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.07 (t, *J* = 7.2 Hz, 3H).

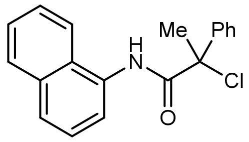
2-Chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide (E60)



E60

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.80 (m, 1H), 7.70 (d, *J* = 7.9 Hz, 4H), 7.54 – 7.32 (m, 6H), 2.73 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.49 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H).

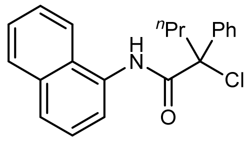
2-Chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide (E61)



E61

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.34 – 8.17 (m, 1H), 7.83 – 7.74 (m, 3H), 7.69 – 7.60 (m, 2H), 7.49 – 7.31 (m, 6H), 2.25 (s, 3H).

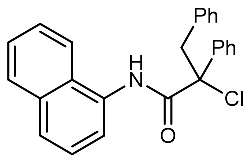
2-Chloro-*N*-(naphthalen-1-yl)-2-phenylpentanamide (E62)



E62

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.74 – 7.65 (m, 4H), 7.52 – 7.29 (m, 6H), 2.72 – 2.61 (m, 1H), 2.47 – 2.36 (m, 1H), 1.64 – 1.54 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

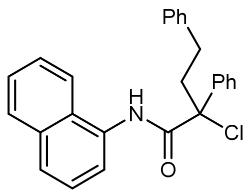
2-Chloro-*N*-(naphthalen-1-yl)-2,3-diphenylpropanamide (E63)



E63

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.89 – 7.78 (m, 2H), 7.75 – 7.65 (m, 3H), 7.52 – 7.34 (m, 7H), 7.29 – 7.15 (m, 5H), 4.08 (d, *J* = 13.9 Hz, 1H), 3.66 (d, *J* = 13.9 Hz, 1H).

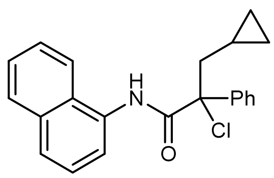
2-Chloro-*N*-(naphthalen-1-yl)-2,4-diphenylbutanamide (E64)



E64

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.03 – 7.95 (m, 1H), 7.88 – 7.82 (m, 1H), 7.76 – 7.67 (m, 4H), 7.54 – 7.45 (m, 3H), 7.45 – 7.38 (m, 2H), 7.38 – 7.32 (m, 1H), 7.30 – 7.20 (m, 4H), 7.20 – 7.13 (m, 1H), 3.07 – 2.95 (m, 1H), 2.93 – 2.84 (m, 2H), 2.77 – 2.65 (m, 1H).

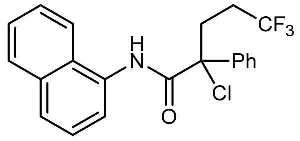
2-Chloro-3-cyclopropyl-*N*-(naphthalen-1-yl)-2-phenylpropanamide (E65)



E65

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.80 – 7.75 (m, 1H), 7.73 – 7.66 (m, 3H), 7.54 – 7.44 (m, 3H), 7.43 – 7.31 (m, 3H), 2.54 (d, *J* = 6.6 Hz, 2H), 1.08 – 0.94 (m, 1H), 0.52 – 0.42 (m, 2H), 0.33 – 0.25 (m, 1H), 0.18 – 0.10 (m, 1H).

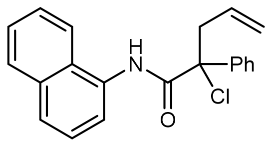
2-Chloro-3-cyclopropyl-*N*-(naphthalen-1-yl)-2-phenylpropanamide (E66)



E66

¹H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.74 – 7.67 (m, 3H), 7.61 – 7.56 (m, 1H), 7.51 – 7.37 (m, 6H), 2.96 – 2.86 (m, 1H), 2.73 – 2.64 (m, 1H), 2.51 – 2.19 (m, 2H).

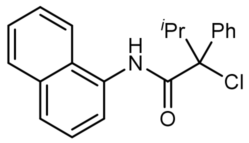
2-Chloro-*N*-(naphthalen-1-yl)-2-phenylpent-4-enamide (E67)



E67

¹H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.99 – 7.93 (m, 1H), 7.90 – 7.83 (m, 1H), 7.74 – 7.67 (m, 4H), 7.53 – 7.46 (m, 3H), 7.46 – 7.40 (m, 2H), 7.39 – 7.34 (m, 1H), 5.97 – 5.82 (m, 1H), 5.31 – 5.14 (m, 2H), 3.50 – 3.41 (m, 1H), 3.26 – 3.16 (m, 1H).

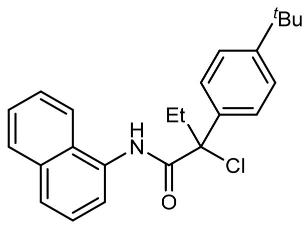
2-Chloro-3-methyl-*N*-(naphthalen-1-yl)-2-phenylbutanamide (E68)



E68

¹H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.87 – 7.80 (m, 3H), 7.73 – 7.67 (m, 2H), 7.51 – 7.32 (m, 6H), 3.33 – 3.14 (m, 1H), 1.24 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H).

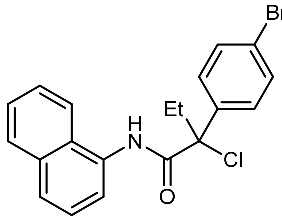
2-(4-(*Tert*-butyl)phenyl)-2-chloro-*N*-(naphthalen-1-yl)butanamide (E69)



E69

¹H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.73 – 7.68 (m, 2H), 7.65 – 7.57 (m, 2H), 7.52 – 7.41 (m, 5H), 2.75 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.49 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.33 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H).

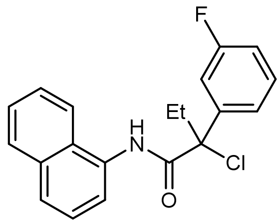
2-(4-Bromophenyl)-2-chloro-*N*-(naphthalen-1-yl)butanamide (E70)



E70

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.78 – 7.69 (m, 2H), 7.62 – 7.44 (m, 7H), 2.71 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.45 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H).

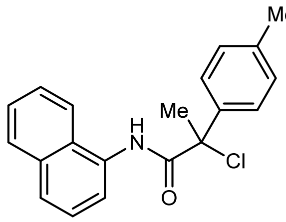
2-Chloro-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)butanamide (E71)



E71

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.77 – 7.71 (m, 2H), 7.56 – 7.44 (m, 5H), 7.42 – 7.34 (m, 1H), 7.11 – 6.99 (m, 1H), 2.72 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.47 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H).

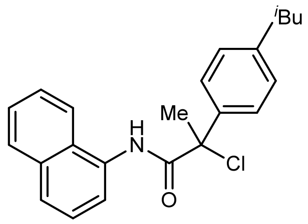
2-Chloro-*N*-(naphthalen-1-yl)-2-(*p*-tolyl)propanamide (E72)



E72

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.02 – 7.94 (m, 1H), 7.83 – 7.77 (m, 1H), 7.72 – 7.62 (m, 2H), 7.60 – 7.51 (m, 2H), 7.48 – 7.40 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H), 2.25 (s, 3H).

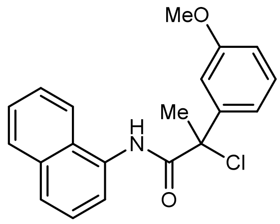
2-Chloro-2-(4-isobutylphenyl)-*N*-(naphthalen-1-yl)propanamide (E73)



E73

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.72 – 7.58 (m, 4H), 7.51 – 7.45 (m, 3H), 7.20 (d, *J* = 8.3 Hz, 2H), 2.50 (d, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.94 – 1.83 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 6H).

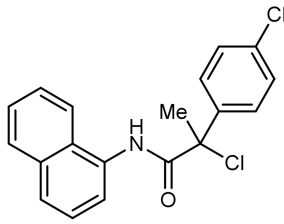
2-Chloro-2-(3-methoxyphenyl)-*N*-(naphthalen-1-yl)propanamide (E74)



E74

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.75 – 7.67 (m, 2H), 7.54 – 7.45 (m, 3H), 7.39 – 7.26 (m, 3H), 6.94 – 6.88 (m, 1H), 3.83 (s, 3H), 2.28 (s, 3H).

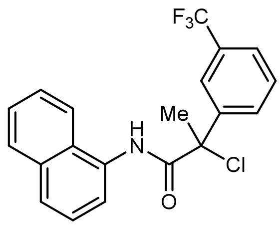
2-Chloro-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)propanamide (E75)



E75

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.76 – 7.71 (m, 2H), 7.67 – 7.60 (m, 2H), 7.56 – 7.46 (m, 3H), 7.42 – 7.35 (m, 2H), 2.28 (s, 3H).

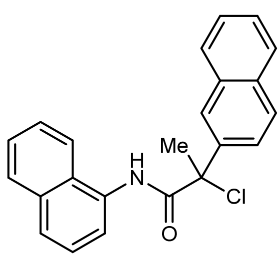
2-Chloro-*N*-(naphthalen-1-yl)-2-(3-(trifluoromethyl)phenyl)propanamide (E76)



E76

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.00 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.76 – 7.71 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.46 (m, 4H), 2.32 (s, 3H).

2-Chloro-*N*-(naphthalen-1-yl)-2-(naphthalen-2-yl)propanamide (E77)



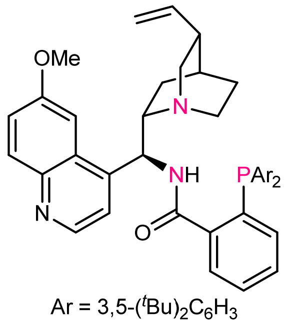
E77

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.19 – 8.13 (m, 1H), 8.03 – 7.97 (m, 1H), 7.92 – 7.80 (m, 4H), 7.77 – 7.67 (m, 3H), 7.55 – 7.42 (m, 5H), 2.38 (s, 3H).

4. Characterization data of ligands

Note: **L*6** and **L*8** were purchased from Daicel Corp. **L*1**, **L*2**, **L*4**, **L*5**, **L*9**, **L*13–15** were known compounds.

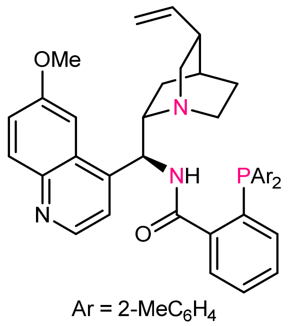
2-(Bis(3,5-di-*tert*-butylphenyl)phosphanyl)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5R)-5-vinylquinuclidin-2-yl)methyl)benzamide (L*1)



L*1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.6 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.59 (s, 1H), 7.41 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 7.15 (s, 1H), 7.10 – 7.04 (m, 2H), 7.00 – 6.93 (m, 2H), 6.90 – 6.83 (m, 1H), 5.72 – 5.59 (m, 1H), 5.40 (s, 1H), 4.99 – 4.84 (m, 2H), 3.98 (s, 3H), 3.12 – 2.98 (m, 2H), 2.83 (s, 1H), 2.55 (s, 1H), 2.49 – 2.37 (m, 1H), 2.20 (s, 1H), 1.63 – 1.46 (m, 3H), 1.39 – 1.30 (m, 1H), 1.23 (s, 18H), 1.19 (s, 18H), 0.97 – 0.87 (m, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ –8.74.

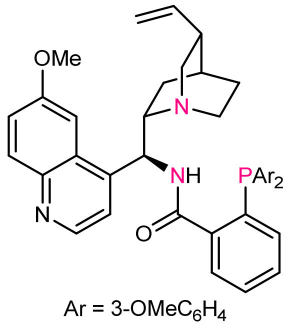
2-(Di-*o*-tolylphosphanyl)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide (L*2)



L*2

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.6 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.42 – 7.32 (m, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 2H), 7.17 – 7.09 (m, 3H), 7.08 – 6.98 (m, 2H), 6.88 – 6.81 (m, 1H), 6.74 – 6.68 (m, 1H), 6.68 – 6.63 (m, 1H), 5.77 – 5.63 (m, 1H), 5.49 (s, 1H), 5.01 – 4.96 (m, 1H), 4.95 – 4.92 (m, 1H), 3.95 (s, 3H), 3.24 – 3.03 (m, 2H), 2.89 (s, 1H), 2.67 – 2.45 (m, 2H), 2.27 – 2.22 (m, 1H), 2.17 (d, *J* = 9.5 Hz, 6H), 1.66 – 1.49 (m, 3H), 1.45 – 1.35 (m, 1H), 0.90 – 0.78 (m, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ –26.32.

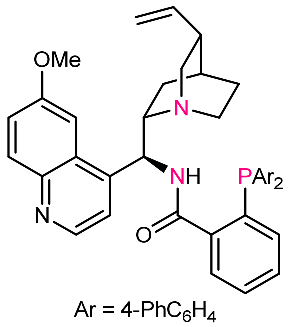
2-(Bis(3-methoxyphenyl)phosphanyl)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide (L*3)



L*3

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.6 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.39 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 7.20 – 7.11 (m, 2H), 6.95 – 6.87 (m, 1H), 6.85 – 6.77 (m, 2H), 6.77 – 6.65 (m, 4H), 5.77 – 5.62 (m, 1H), 5.57 – 5.32 (m, 1H), 5.01 – 4.90 (m, 2H), 3.96 (s, 3H), 3.68 (s, 6H), 3.23 – 3.07 (m, 2H), 3.01 (s, 1H), 2.71 – 2.58 (m, 1H), 2.58 – 2.48 (m, 1H), 2.25 (s, 1H), 1.67 – 1.52 (m, 3H), 1.43 – 1.35 (m, 1H), 0.90 – 0.84 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 159.7, 159.6(1), 159.5(8), 159.5(3), 157.9, 147.6, 144.8, 141.3, 138.6, 138.4, 134.4, 131.6, 130.4, 129.7, 129.6, 129.5, 129.0, 128.5, 126.2, 126.0, 121.7, 119.2(4), 119.1(7), 119.0, 118.9, 114.7, 114.4(2), 114.3(5), 102.3, 55.9, 55.8, 55.2(4), 55.2(2), 41.1, 39.5, 27.9, 27.5, 27.0, 26.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ –9.11.
HRMS (ESI) *m/z* calcd. for $C_{41}H_{43}N_3O_4P$ $[M + H]^+$ 672.2986, found: 672.2979.

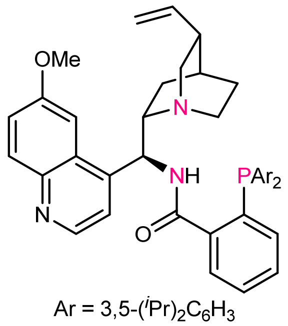
2-(Di([1,1'-biphenyl]-4-yl)phosphanyl)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide (L*4)



L*4

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.5 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 2.7 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.61 – 7.55 (m, 4H), 7.55 – 7.48 (m, 4H), 7.47 – 7.39 (m, 5H), 7.38 – 7.36 (m, 1H), 7.36 – 7.28 (m, 4H), 7.28 – 7.25 (m, 2H), 7.25 – 7.18 (m, 3H), 7.07 – 7.00 (m, 1H), 5.78 – 5.62 (m, 1H), 5.46 (s, 1H), 4.99 – 4.93 (m, 1H), 4.93 – 4.89 (m, 1H), 3.96 (s, 3H), 3.23 – 3.07 (m, 2H), 3.02 (s, 1H), 2.68 – 2.50 (m, 2H), 2.28 – 2.18 (m, 1H), 1.66 – 1.59 (m, 1H), 1.59 – 1.48 (m, 2H), 1.47 – 1.35 (m, 1H), 0.94 – 0.84 (m, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ –12.32.

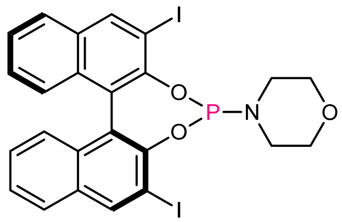
2-(Bis(3,5-diisopropylphenyl)phosphanyl)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide (L*5)



L*5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.56 (m, 1H), 8.04 – 7.98 (m, 1H), 7.75 – 7.67 (m, 2H), 7.54 (s, 1H), 7.41 – 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 7.21 (s, 1H), 7.10 – 7.03 (m, 2H), 6.97 – 6.91 (m, 3H), 6.87 – 6.81 (m, 2H), 5.76 – 5.62 (m, 1H), 5.45 (s, 1H), 5.01 – 4.89 (m, 2H), 4.00 (s, 3H), 3.20 – 3.01 (m, 2H), 2.87 – 2.76 (m, 4H), 2.65 – 2.53 (m, 1H), 2.52 – 2.44 (m, 1H), 2.28 – 2.18 (m, 1H), 1.65 – 1.60 (m, 1H), 1.60 – 1.51 (m, 2H), 1.21 – 1.17 (m, 12H), 1.14 (d, J = 6.9 Hz, 12H), 0.98 – 0.89 (m, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ –10.06.

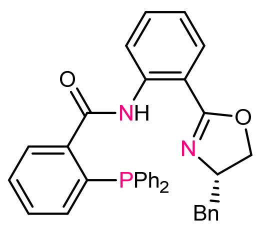
1-((11b*S*)-2,6-diiododinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)piperidine (L*7)



L*7

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.47 – 7.36 (m, 2H), 7.27 – 7.24 (m, 3H), 7.20 – 7.15 (m, 1H), 3.68 – 3.57 (m, 2H), 3.57 – 3.49 (m, 2H), 3.20 – 3.08 (m, 2H), 3.08 – 2.94 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.0, 134.0, 139.9, 132.7, 132.6, 132.4, 132.0, 127.4(3), 127.4(2), 126.9, 125.8, 125.7, 124.5(1), 124.4(5), 122.9, 91.5, 91.3, 68.0, 67.9, 44.6, 44.4.
^{31}P NMR (162 MHz, $CDCl_3$) δ 143.74.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{19}I_2NO_3P$ $[M + H]^+$ 653.9186, found: 653.9178.

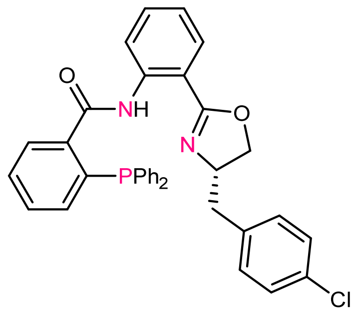
(*S*)-*N*-(2-(4-benzyl-4,5-dihydrooxazol-2-yl)phenyl)-2-(diphenylphosphanyl)-benzamide (L*9)



L*9

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.68 (s, 1H), 8.79 – 8.72 (m, 1H), 7.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.45 – 7.39 (m, 1H), 7.36 – 7.25 (m, 12H), 7.23 – 7.11 (m, 5H), 7.09 – 7.03 (m, 2H), 4.67 – 4.57 (m, 1H), 4.36 (t, *J* = 8.9 Hz, 1H), 4.12 – 4.05 (m, 1H), 3.06 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.79 (dd, *J* = 13.9, 7.4 Hz, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ –8.06.

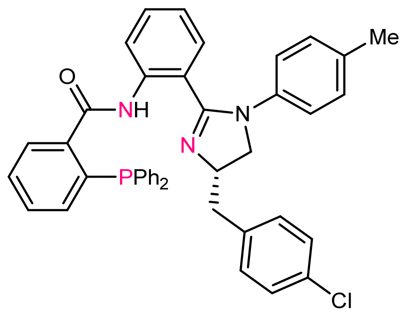
(*S*)-*N*-(2-(4-(4-chlorobenzyl)-4,5-dihydrooxazol-2-yl)phenyl)-2-(diphenylphosphanyl)benzamide (L*10)



L*10

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1H), 8.75 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.70 – 7.63 (m, 1H), 7.45 – 7.39 (m, 1H), 7.39 – 7.33 (m, 1H), 7.33 – 7.25 (m, 10H), 7.24 – 7.19 (m, 1H), 7.12 – 7.01 (m, 6H), 4.61 – 4.50 (m, 1H), 4.38 (t, *J* = 8.9 Hz, 1H), 4.07 – 3.99 (m, 1H), 2.90 (dd, *J* = 13.9, 7.7 Hz, 1H), 2.79 (dd, *J* = 14.0, 6.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 164.3, 141.5, 141.3, 140.2, 138.8, 138.6(2), 138.5(8), 138.4(9), 138.4(6), 138.3, 136.2, 135.0, 134.1, 134.0, 133.9, 133.8, 132.9, 132.5, 130.6, 130.4, 129.2, 128.7, 128.6, 128.5(2), 128.4(8), 128.4(5), 128.4(1), 128.3(8), 127.4, 127.3, 122.5, 120.3, 113.3, 70.8, 67.7, 41.6.
^{31}P NMR (162 MHz, $CDCl_3$) δ –8.25.
HRMS (ESI) *m/z* calcd. for $C_{35}H_{29}ClN_2O_2P$ $[M + H]^+$ 575.1650, found: 575.1646.

(*S*)-*N*-(2-(4-(4-chlorobenzyl)-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-2-(diphenylphosphanyl)benzamide (L*11)

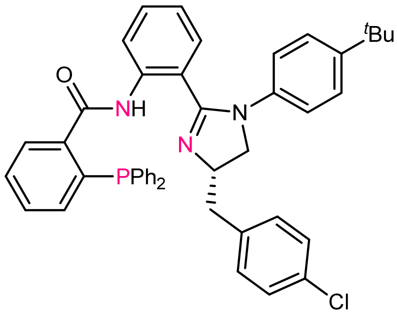


L*11

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.72 (m, 1H), 7.37 – 7.22 (m, 13H), 7.16 (d, 2H), 7.09 – 6.99 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 4.57 – 4.42 (m, 1H), 3.96 (t, *J* = 9.9 Hz, 1H), 3.54 (t, *J* = 8.7 Hz, 1H), 2.98 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.74 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.7, 141.3, 141.2, 141.1, 139.0, 138.8, 138.6, 138.5(2), 138.4(8), 138.4(0), 136.7, 134.9, 134.3, 134.1(2), 134.0(9), 133.9(2), 133.8(9), 132.4, 131.0, 130.6(5), 130.5(9), 130.1, 129.6, 128.6, 128.5(4), 128.5(1), 128.5, 128.4(4), 128.4(2), 127.4(1), 127.3(7), 123.7, 122.3, 121.5, 117.1, 65.5, 58.3, 42.0, 20.9.
^{31}P NMR (162 MHz, $CDCl_3$) δ –8.22.
HRMS (ESI) *m/z* calcd. for $C_{42}H_{36}ClN_3OP$ $[M + H]^+$ 664.2279, found: 664.2278.

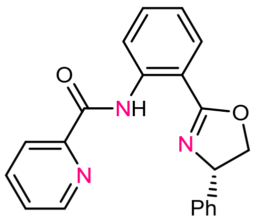
(*S*)-*N*-(2-(1-(4-(*tert*-butyl)phenyl)-4-(4-chlorobenzyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-2-(diphenylphosphanyl)benzamide (L*12)



L*12

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.73 (m, 1H), 7.38 – 7.24 (m, 13H), 7.18 – 7.11 (m, 4H), 7.09 – 7.01 (m, 4H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.66 – 6.56 (m, 2H), 4.58 – 4.41 (m, 1H), 3.99 (t, *J* = 9.9 Hz, 1H), 3.61 – 3.50 (m, 1H), 3.03 – 2.91 (m, 1H), 2.74 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.26 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.6, 147.3, 141.4, 141.1, 141.0, 138.9, 138.8, 138.6, 138.5, 138.4, 136.6, 134.9, 134.1(2), 134.0(9), 133.9(2), 133.8(9), 132.4, 131.0, 130.6(4), 130.5(9), 130.2, 128.6(1), 128.5(5), 128.5(1), 128.4(9), 128.4(4), 128.4(2), 127.4(1), 127.3(8), 125.8, 123.0, 122.4, 121.5, 117.2, 65.5, 58.2, 42.0, 34.4, 31.4.
^{31}P NMR (162 MHz, $CDCl_3$) δ –8.20.
HRMS (ESI) *m/z* calcd. for $C_{45}H_{42}ClN_3OP$ $[M + H]^+$ 706.2749, found: 706.2745.

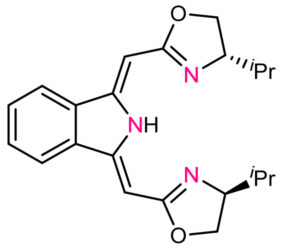
(*S*)-*N*-(2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (L*13)



L*13

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.86 (s, 1H), 9.11 – 9.03 (m, 1H), 8.29 – 8.22 (m, 2H), 7.97 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.60 – 7.50 (m, 3H), 7.40 – 7.28 (m, 4H), 7.20 – 7.13 (m, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 4.86 (dd, *J* = 10.1, 8.2 Hz, 1H), 4.35 – 4.18 (m, 1H).

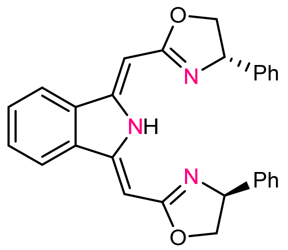
(1*Z*,3*Z*)-1,3-bis(((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)methylene)isoindoline (L*14)



L*14

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.71 – 7.59 (m, 2H), 7.54 – 7.38 (m, 2H), 5.63 (s, 2H), 4.39 – 4.28 (m, 2H), 4.08 – 3.94 (m, 4H), 1.83 – 1.72 (m, 2H), 1.09 (d, *J* = 6.7 Hz, 6H), 0.96 (d, *J* = 6.7 Hz, 6H).

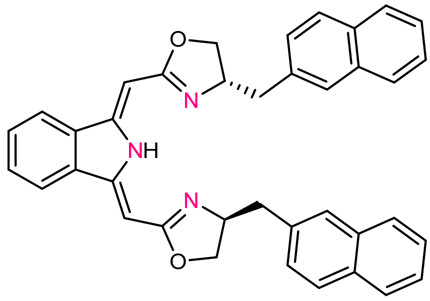
(1*Z*,3*Z*)-1,3-bis(((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)methylene)isoindoline (L*15)



L*15

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 7.76 – 7.65 (m, 2H), 7.55 – 7.45 (m, 2H), 7.35 – 7.16 (m, 10H), 5.71 (s, 2H), 5.29 (t, *J* = 9.3 Hz, 2H), 4.64 (t, *J* = 9.1 Hz, 2H), 4.05 (t, *J* = 8.4 Hz, 2H).

(1*Z*,3*Z*)-1,3-bis(((*S*)-4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazol-2-yl)methylene)isoindoline (L*16)

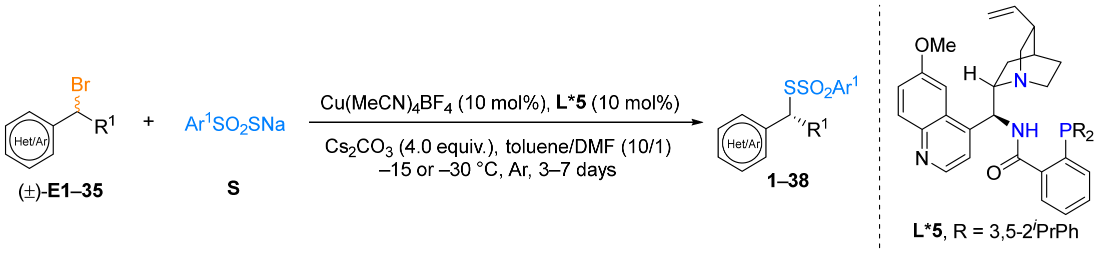


L*16

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 7.78 – 7.71 (m, 6H), 7.68 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.66 – 7.64 (m, 2H), 7.48 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.36 (dd, *J* = 8.4, 1.7 Hz, 2H), 5.64 (s, 2H), 4.61 – 4.50 (m, 2H), 4.23 – 4.16 (m, 2H), 3.95 (t, *J* = 7.9 Hz, 2H), 3.29 (dd, *J* = 13.8, 5.4 Hz, 2H), 2.90 (dd, *J* = 13.8, 8.3 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 147.7, 135.8, 134.9, 133.7, 132.3, 129.9, 128.2, 127.9, 127.8, 127.7(2), 127.6(7), 126.1, 125.6, 121.1, 83.2, 71.4, 67.4, 42.5.
HRMS (ESI) *m/z* calcd. for $C_{38}H_{32}N_3O_2$ $[M + H]^+$ 562.2489, found: 562.2485.

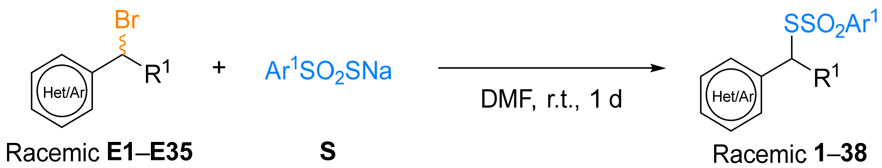
5. Enantioconvergent cross-coupling of benzyl electrophiles with sodium arylthiosulfonate

General procedure A: Substrate scope of (hetero)benzyl halides and sodium arylthiosulfonate (Table 2, 1–38)



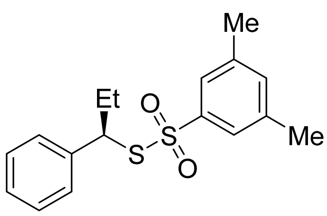
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium arylthiosulfonate (0.24 mmol, 1.2 equiv.), $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol%), **L*5** (15.6 mg, 0.02 mmol, 10 mol%) and Cs_2CO_3 (260 mg, 0.80 mmol, 4.0 equiv.), Then, (hetero)benzyl halide (0.20 mmol, 1.0 equiv.) and toluene/DMF (v/v = 10/1, 2.2 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 or –30 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic products (±)-**1**–**38**:



The mixture of sodium arylthiosulfonate (0.12 mmol, 1.2 eq.) and (hetero)benzyl halide (0.10 mmol, 1.0 eq.) in DMF (0.5 mL) was stirring for 1 day. Brine was added to the above reaction solution to quench the reaction. Then, the mixture was extracted with EtOAc (3x) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography to afford the desired racemates.

(*R*)-*S*-(1-Phenylpropyl) 3,5-dimethylbenzenesulfonothioate (1)



1

According to **General procedure A**, (1-bromopropyl)benzene **E1** (28.0 μL, 0.2 mmol, 1.0 eq.) with sodium 3,5-dimethylbenzenesulfonothioate **S5** (54.0 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **1** as a white solid (47.4 mg, 74% yield, 92% e.e.).

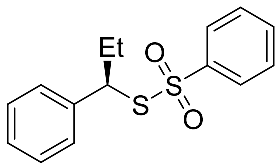
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 17.53 min, t_R (major) = 19.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 5H), 7.13 – 7.08 (m, 2H), 7.05 (s, 1H), 4.41 (dd, *J* = 8.9, 6.5 Hz, 1H), 2.24 (s, 6H), 2.07 – 1.95 (m, 1H), 1.95 – 1.82 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.5, 138.9, 134.8, 128.4, 127.9, 127.7, 124.3, 57.7, 29.9, 21.2, 12.0.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}NaO_2S_2$ $[M + Na]^+$ 343.0797, found: 343.0794.

(*R*)-*S*-(1-Phenylpropyl) benzenesulfonothioate (2)



2

According to **General procedure A**, (1-bromopropyl)benzene **E1** (28 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.1 mg, 0.24 mmol, 1.2 eq.) run at –30 °C for 5 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **2** as a white solid (45.8 mg, 78% yield, 90% e.e.).

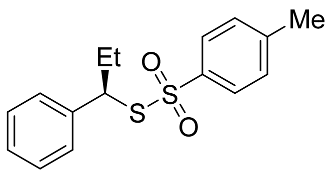
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 23.27 min, t_R (major) = 28.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.48 – 7.42 (m, 1H), 7.34 – 7.27 (m, 2H), 7.16 – 7.11 (m, 3H), 7.10 – 7.04 (m, 2H), 4.39 (dd, *J* = 8.9, 6.5 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.95 – 1.82 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 139.1, 133.1, 128.9, 128.6, 127.8 (two carbon overlapped), 126.7, 57.8, 29.8, 12.0.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}NaO_2S_2$ $[M + Na]^+$ 315.0484, found 315.0483.

(*R*)-*S*-(1-Phenylpropyl) 4-methylbenzenesulfonothioate (3)



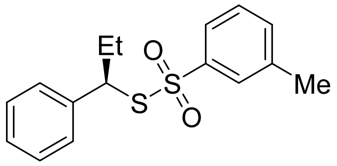
3

According to **General procedure A**, (1-bromopropyl)benzene **E1** (28 μL, 0.2 mmol, 1.0 eq.) with sodium 4-methylbenzenesulfonothioate **S7** (50.5 mg, 0.24 mmol, 1.2 eq.) run at –30 °C for 5 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **3** as a white solid (55.2 mg, 90% yield, 90% e.e.).

HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 30.41 min, t_R (major) = 35.59 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.17 – 7.13 (m, 3H), 7.13 – 7.10 (m, 1H), 7.10 – 7.05 (m, 3H), 4.36 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.36 (s, 3H), 2.07 – 1.95 (m, 1H), 1.95 – 1.83 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.5, 139.3, 129.5, 128.6, 127.8, 127.6, 126.8, 57.6, 29.8, 21.6, 12.0.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NaO_2S_2$ $[M + Na]^+$ 329.0640, found 329.0640.

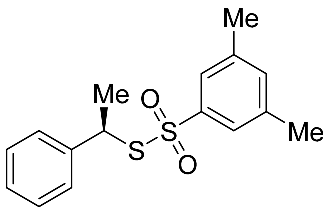
(*R*)-*S*-(1-Phenylpropyl) 3-methylbenzenesulfonothioate (4)



4

According to **General procedure A**, (1-bromopropyl)benzene **E1** (28 μL, 0.2 mmol, 1.0 eq.) with sodium 3-methylbenzenesulfonothioate **S8** (50.5 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **4** as a white solid (55.9 mg, 91% yield, 90% e.e.).
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 22.73 min, t_R (major) = 27.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.17 – 7.12 (m, 3H), 7.11 – 7.05 (m, 3H), 7.01 – 6.94 (m, 1H), 4.39 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.75 (s, 3H), 2.07 – 1.96 (m, 1H), 1.96 – 1.83 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.3, 139.2, 129.9, 128.5, 127.7 (two carbon overlapped), 119.8, 119.0, 111.1, 57.8, 55.7, 29.9, 12.0.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NaO_2S_2$ $[M + Na]^+$ 329.0640, found 329.0641.

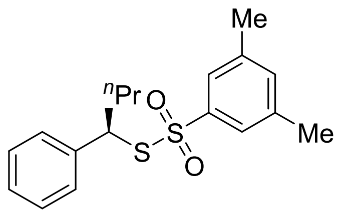
(*R*)-*S*-(1-Phenylethyl) 3,5-dimethylbenzenesulfonothioate (5)



5

According to **General procedure B**, (1-bromoethyl)benzene **E2** (24 μL, 0.2 mmol, 1.0 eq.) with **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –30 °C for 5 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **5** as a colorless oil (54.8 mg, 89% yield, 91% e.e.).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 29.35 min, t_R (major)= 33.72 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 2H), 7.21 – 7.13 (m, 5H), 7.10 (s, 1H), 4.65 (q, *J* = 7.2 Hz, 1H), 2.27 (s, 6H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.6, 139.0, 135.0, 128.6, 127.9, 127.3, 124.3, 50.9, 22.8, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NaO_2S_2$ $[M + Na]^+$ 329.0640, found 329.0639.

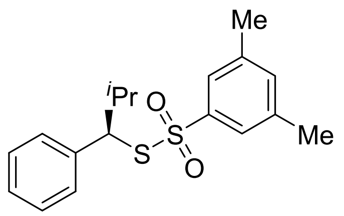
(*R*)-*S*-(1-Phenylbutyl) 3,5-dimethylbenzenesulfonothioate (6)



6

According to the **general procedure A** with (1-bromobutyl)benzene **E3** (30 μL, 0.20 mmol, 1.0 eq.) and **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **6** as a white solid (49.9 mg, 75% yield, 91% e.e.).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 22.64 min, t_R (major) = 24.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 5H), 7.12 – 7.08 (m, 2H), 7.04 (s, 1H), 4.49 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.23 (s, 6H), 1.97 – 1.77 (m, 2H), 1.36 – 1.18 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.7, 138.8, 134.8, 128.4, 127.8, 127.7, 124.3, 55.8, 38.5, 21.2, 20.5, 13.6.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{23}O_2S_2$ $[M + H]^+$ 335.1134, found 335.1127.

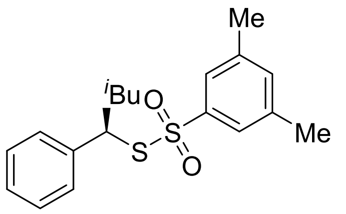
(*R*)-*S*-(2-Methyl-1-phenylpropyl) 3,5-dimethylbenzenesulfonothioate (7)



7

According to the **general procedure A** with (1-bromo-2-methylpropyl)benzene **E4** (31.6 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 7 days, **t**he reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **7** as a light yellow solid (38.6 mg, 58% yield, 93% e.e.).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 16.30 min, t_R (major) = 19.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.08 (m, 3H), 7.08 – 7.03 (m, 4H), 6.98 (s, 1H), 4.36 (d, *J* = 7.3 Hz, 1H), 2.19 (s, 6H), 2.17 – 2.07 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 138.9, 138.7, 134.6, 128.5, 127.9, 127.4, 124.3, 63.5, 34.4, 21.1, 20.8, 20.6.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NaO_2S_2$ $[M + Na]^+$ 357.0953, found: 357.0952.

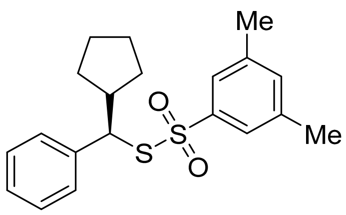
(*R*)-*S*-(3-Methyl-1-phenylbutyl) 3,5-dimethylbenzenesulfonothioate (8)



8

According to the **general procedure A** with (1-bromo-3-methylbutyl)benzene **E5** (35.1 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **8** as a yellow oil (54.2 mg, 78% yield, 90% e.e.).
HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 12.47 min, t_R (major) = 13.71 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 5H), 7.14 – 7.10 (m, 2H), 7.06 (s, 1H), 4.56 (t, *J* = 8.1 Hz, 1H), 2.25 (s, 6H), 1.80 – 1.73 (m, 2H), 1.52 – 1.42 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.7, 138.8, 134.8, 128.4, 127.8, 127.7, 124.3, 54.3, 45.2, 25.7, 22.7, 21.7, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{25}O_2S_2$ $[M + H]^+$ 349.1290, found: 349.1285.

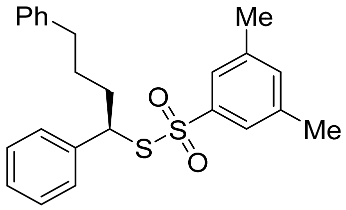
(*R*)-*S*-(Cyclopentyl(phenyl)methyl) 3,5-dimethylbenzenesulfonothioate (9)



9

According to the **general procedure A** with (bromo(cyclopentyl)methyl)benzene **E6** (45.6 μL,, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 7 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **9** as a yellow solid (38.2 mg, 53% yield, 89% e.e.).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 15.07 min, t_R (major) = 19.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.06 (m, 5H), 7.03 (s, 2H), 6.98 (s, 1H), 4.36 (d, *J* = 10.0 Hz, 1H), 2.28 – 2.21 (m, 1H), 2.19 (s, 6H), 1.97 – 1.88 (m, 1H), 1.71 – 1.53 (m, 3H), 1.49 – 1.33 (m, 3H), 1.22 – 1.10 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 140.2, 138.6, 134.5, 128.1, 128.0, 127.3, 124.2, 62.0, 45.9, 31.6(4), 31.6(1), 25.3, 25.1, 21.1.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{25}O_2S_2$ $[M + H]^+$ 361.1290, found: 361.1286.

(*R*)-*S*-(1,4-Diphenylbutyl) 3,5-dimethylbenzenesulfonothioate (10)



10

According to the **general procedure A** with (1-bromobutane-1,4-diyl)dibenzene **E7** (44.0 µL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~10/1) to yield the product 10 as a colorless oil (57.2 mg, 70% yield, 86% e.e.).

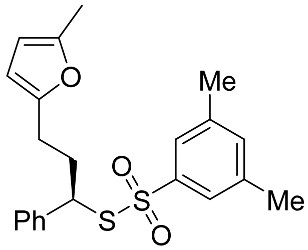
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 23.29 min, t_R (major) = 28.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.18 – 7.11 (m, 6H), 7.10 – 7.04 (m, 4H), 7.04 – 7.01 (m, 1H), 4.49 (dd, *J* = 8.9, 6.7 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.22 (s, 6H), 2.04 – 1.93 (m, 1H), 1.92 – 1.82 (m, 1H), 1.69 – 1.57 (m, 1H), 1.56 – 1.44 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 141.5, 139.6, 138.9, 134.8, 128.4(4), 128.4(3), 128.4(0), 127.8 (two carbon overlapped), 126.0, 124.3, 55.9, 35.9, 35.2, 29.0, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NaO_2S_2$ $[M + Na]^+$ 433.1266, found: 433.1256.

(*R*)-*S*-(3-(5-Methylfuran-2-yl)-1-phenylpropyl) 3,5-dimethylbenzenesulfonothioate (11)



11

According to the **general procedure A** with 2-(3-bromo-3-phenylpropyl)-5-methylfuran **E8** (56.0 µL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3.5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~5/1) to yield the product **11** as a brown oil (63.0 mg, 79% yield, 85% e.e.).

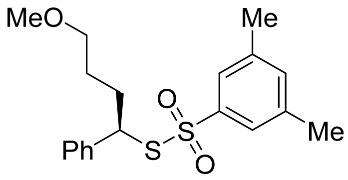
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor)= 15.12 min, t_R (major) = 19.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 5H), 7.13 – 7.08 (m, 2H), 7.07 – 7.04 (m, 1H), 5.85 – 5.79 (m, 2H), 4.49 (dd, *J* = 9.3, 6.3 Hz, 1H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.36 – 2.26 (m, 1H), 2.24 (s, 6H), 2.23 (s, 3H), 2.21 – 2.11 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.8, 145.1, 139.1, 138.9, 134.9, 128.5, 127.9(1), 127.8(8), 124.3, 106.4, 106.0, 55.1, 34.8, 25.8, 21.2, 13.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}NaO_3S_2$ $[M + Na]^+$ 423.1059, found: 423.1057.

(*R*)-*S*-(4-Methoxy-1-phenylbutyl) 3,5-dimethylbenzenesulfonothioate (12)



12

According to the **general procedure A** with (1-bromo-4-methoxybutyl)benzene **E9** (42.6 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.83 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1~5/1) to yield the product **12** as a white solid (65.6 mg, 90% yield, 87% e.e.).

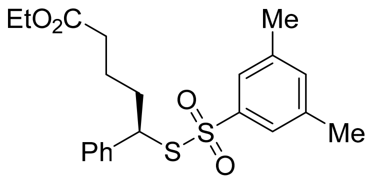
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 75/25, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 18.97 min, t_R (major) = 21.93 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.16 – 7.12 (m, 3H), 7.12 – 7.08 (m, 2H), 7.05 (s, 1H), 4.50 (dd, *J* = 9.0, 6.7 Hz, 1H), 3.30 (t, *J* = 6.2 Hz, 2H), 3.26 (s, 3H), 2.24 (s, 6H), 2.10 – 1.99 (m, 1H), 1.99 – 1.89 (m, 1H), 1.65 – 1.52 (m, 1H), 1.52 – 1.39 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.5, 138.9, 134.8, 128.4, 127.8, 127.7, 124.3, 71.8, 58.6, 55.9, 33.3, 27.4, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}NaO_3S_2$ $[M + Na]^+$ 387.1059, found: 387.1058.

Ethyl (*R*)-5-(((3,5-dimethylphenyl)sulfonyl)thio)-5-phenylpentanoate (13)



13

According to the **general procedure A** with ethyl 5-bromo-5-phenylpentanoate **E10** (59.8 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5.5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~10/1) to yield the product **13** as a yellow oil (60.4 mg, 74% yield, 84% e.e.).

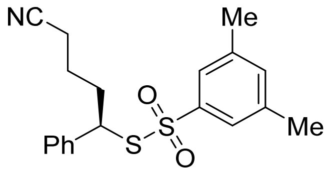
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 21.36 min, t_R (major) = 27.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 5H), 7.13 – 7.09 (m, 2H), 7.06 (s, 1H), 4.47 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.28 – 2.22 (m, 8H), 2.06 – 1.97 (m, 1H), 1.96 – 1.86 (m, 1H), 1.68 – 1.60 (m, 1H), 1.59 – 1.46 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 145.0, 139.2, 139.0, 134.9, 128.5, 127.9, 127.8, 124.3, 60.5, 55.7, 35.8, 33.6, 22.7, 21.2, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}O_4S_2$ $[M+ H]^+$ 407.1345, found: 407.1334.

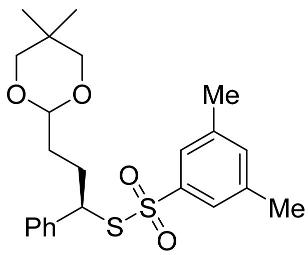
(*R*)-*S*-(4-Cyano-1-phenylbutyl) 3,5-dimethylbenzenesulfonothioate (14)



14

According to the **general procedure A** with 5-bromo-5-phenylpentanenitrile **E11** (35.2 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~5/1) to yield the product **14** as a colorless oil (55.9 mg, 78% yield, 86% e.e.).
HPLC analysis: Chiralcel IC (n-hexane/*i*-PrOH = 50/50, flow rate 1.5 mL/min, λ = 230 nm), t_R (minor) = 31.63 min, t_R (major) = 43.25 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 5H), 7.14 – 7.07 (m, 3H), 4.46 (dd, *J* = 8.6, 7.0 Hz, 1H), 2.31 (t, *J* = 7.1 Hz, 2H), 2.26 (s, 6H), 2.19 – 2.08 (m, 1H), 2.08 – 1.98 (m, 1H), 1.79 – 1.66 (m, 1H), 1.64 – 1.53 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 139.1, 138.8, 135.2, 128.8, 128.2, 127.6, 124.3, 119.0, 55.0, 35.4, 23.3, 21.2, 16.8.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}NNaO_2S_2$ $[M + Na]^+$ 382.0906, found: 382.0903.

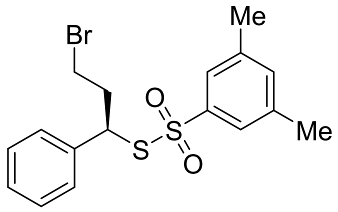
(*R*)-*S*-(3-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-phenylpropyl) 3,5-dimethylbenzenesulfonothioate (15)



15

According to the **general procedure A** with 2-(3-bromo-3-phenylpropyl)-5,5-dimethyl-1,3-dioxane **E12** (62.0 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~10/1) to yield the product **15** as a white solid (68.7 mg, 79% yield, 84% e.e.).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 12.98 min, t_R (major) = 15.83 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.15 – 7.09 (m, 5H), 7.05 (s, 1H), 4.50 (dd, *J* = 9.2, 6.6 Hz, 1H), 4.35 (t, *J* = 4.8 Hz, 1H), 3.54 (d, *J* = 11.1 Hz, 2H), 3.35 (d, *J* = 11.0 Hz, 2H), 2.24 (s, 6H), 2.17 – 2.06 (m, 1H), 2.04 – 1.92 (m, 1H), 1.69 – 1.60 (m, 1H), 1.56 – 1.45 (m, 1H), 1.13 (s, 3H), 0.69 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.4, 138.9, 134.8, 128.4, 127.9, 127.8, 124.3, 101.1, 56.0, 32.5, 30.7, 30.2, 23.1, 21.9, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{30}NaO_4S_2$ $[M + Na]^+$ 457.1478, found: 457.1476.

(*R*)-*S*-(3-Bromo-1-phenylpropyl) 3,5-dimethylbenzenesulfonothioate (16)



16

According to the **general procedure A** with (1,3-dibromopropyl)benzene **E13** (29.6 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **16** as a colorless oil (66.4 mg, 83% yield, 91% e.e.).

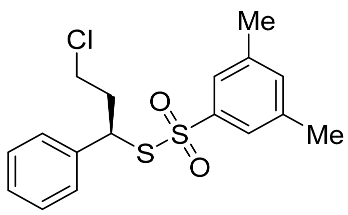
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 37.23 min, t_R (major) = 40.22 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 2H), 7.23 – 7.19 (m, 3H), 7.16 – 7.11 (m, 3H), 4.66 (dd, *J* = 9.4, 6.1 Hz, 1H), 3.40 – 3.29 (m, 1H), 3.15 – 3.05 (m, 1H), 2.59 – 2.47 (m, 1H), 2.47 – 2.35 (m, 1H), 2.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 139.2, 137.9, 135.2, 128.9, 128.3, 127.8, 124.5, 53.6, 38.7, 29.9, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}BrNaO_2S_2$ $[M + Na]^+$ 420.9902, found: 420.9899.

(*R*)-*S*-(3-Chloro-1-phenylpropyl) 3,5-dimethylbenzenesulfonothioate (17)



17

According to the **general procedure A** with (1-bromo-3-chloropropyl)benzene **E14** (45.0 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **17** as a white solid (52.4 mg, 74% yield, 91% e.e.).

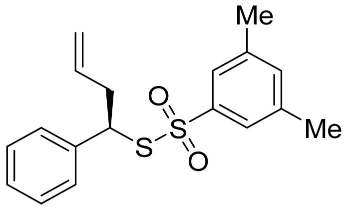
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 37.59 min, t_R (major) = 40.53 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 7.23 – 7.18 (m, 3H), 7.16 – 7.09 (m, 3H), 4.69 (dd, *J* = 9.4, 6.2 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.32 – 3.20 (m, 1H), 2.51 – 2.40 (m, 1H), 2.36 – 2.30 (m, 1H), 2.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 139.2, 138.1, 135.2, 128.8, 128.3, 127.8, 124.5, 52.6, 41.7, 38.7, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}ClO_2S_2$ $[M + H]^+$ 355.0588, found: 355.0581.

(*R*)-*S*-(1-Phenylbut-3-en-1-yl) 3,5-dimethylbenzenesulfonothioate (18)



18

According to the **general procedure A** with (1-bromobut-3-en-1-yl)benzene **E15** (32.0 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **18** as a light yellow solid (53.2 mg, 80% yield, 90% e.e.).

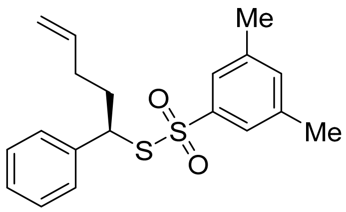
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 35.60 min, t_R (major) = 38.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 5H), 7.13 – 7.09 (m, 2H), 7.06 (s, 1H), 5.65 – 5.51 (m, 1H), 5.06 – 5.01 (m, 1H), 5.01 – 4.96 (m, 1H), 4.55 (dd, *J* = 8.3, 6.9 Hz, 1H), 2.72 – 2.61 (m, 2H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 139.0, 138.9, 134.9, 133.5, 128.4, 127.9, 127.8, 124.3, 118.6, 55.5, 40.8, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}O_2S_2$ $[M + H]^+$ 333.0977, found: 333.0970.

(*R*)-*S*-(1-Phenylpent-4-en-1-yl) 3,5-dimethylbenzenesulfonothioate (19)



19

According to the **general procedure B** with (1-bromopent-4-en-1-yl)benzene **E16** (42.6 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1~20/1) to yield the product **19** as a light yellow solid (60.0 mg, 87% yield, 90% e.e.).

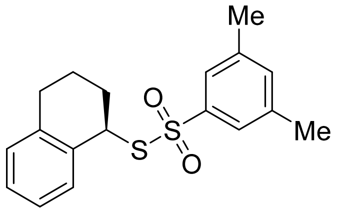
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 39.92 min, t_R (major) = 42.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 5H), 7.12 – 7.08 (m, 2H), 7.06 (s, 1H), 5.78 – 5.64 (m, 1H), 5.02 – 4.91 (m, 2H), 4.49 (t, *J* = 7.3 Hz, 1H), 2.25 (s, 6H), 2.09 – 1.92 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.3, 138.9, 136.7, 134.9, 128.5, 127.8 (two carbon overlapped), 124.3, 116.1, 55.2, 35.5, 31.2, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}O_2S_2$ $[M + H]^+$ 347.1134, found: 347.1132.

(*R*)-*S*-(1,2,3,4-Tetrahydronaphthalen-1-yl) 3,5-dimethylbenzenesulfonothioate (20)



20

According to the **general procedure A** with 1-bromo-1,2,3,4-tetrahydronaphthalene **E17** (32.0 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **20** as a yellow solid (50.9 mg, 77% yield, 77% e.e.).

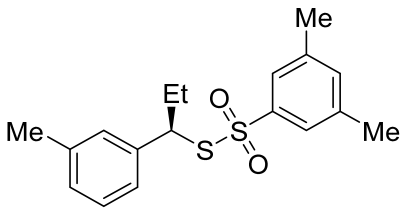
HPLC analysis: Chiralcel IE (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 230 nm), t_R (major) = 18.18 min, t_R (minor) = 19.40 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.27 (s, 1H), 7.15 – 7.09 (m, 1H), 7.08 – 6.97 (m, 3H), 4.72 (t, J = 3.7 Hz, 1H), 2.84 – 2.63 (m, 2H), 2.42 (s, 6H), 2.33 – 2.23 (m, 1H), 2.14 – 2.02 (m, 1H), 1.98 – 1.87 (m, 1H), 1.87 – 1.75 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 139.5, 138.1, 135.4, 132.7, 130.7, 129.5, 127.9, 126.3, 124.6, 51.3, 30.1, 28.7, 21.4, 19.0.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_2S_2$ $[M + Na]^+$ 355.0797, found: 355.0797.

(*R*)-*S*-(1-(*m*-Tolyl)propyl) 3,5-dimethylbenzenesulfonothioate (21)



21

According to the **general procedure A** with 1-(1-bromopropyl)-3-methylbenzene **E18** (42.4 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 7 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **21** as a colorless oil (48.1 mg, 72% yield, 90% e.e.).

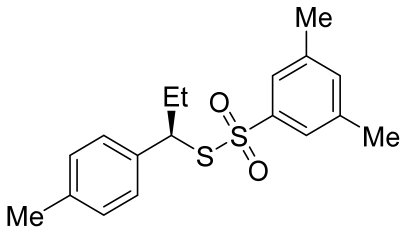
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 18.87 min, t_R (major) = 21.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.08 – 7.02 (m, 2H), 6.94 (d, J = 7.7 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.86 (s, 1H), 4.37 (dd, J = 8.8, 6.5 Hz, 1H), 2.25 (s, 6H), 2.20 (s, 3H), 2.05 – 1.94 (m, 1H), 1.93 – 1.81 (m, 1H), 0.88 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.3, 138.8, 138.1, 134.7, 128.5, 128.4, 128.2, 125.0, 124.3, 57.7, 29.9, 21.4, 21.2, 12.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NaO_2S_2$ $[M + Na]^+$ 357.0953, found: 357.0951.

(*R*)-*S*-(1-(*p*-Tolyl)propyl) 3,5-dimethylbenzenesulfonothioate (22)



22

According to the **general procedure A** with 1-(1-bromopropyl)-4-methylbenzene **E19** (63.2 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 7 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **22** as a colorless oil (54.8 mg, 82% yield, 90% e.e.).

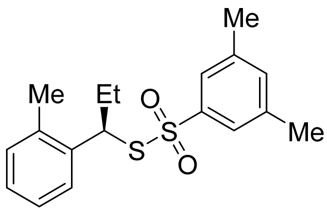
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 20.35 min, t_R (major) = 22.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.06 (s, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.38 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 6H), 2.06 – 1.94 (m, 1H), 1.93 – 1.81 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.8, 137.4, 136.4, 134.6, 129.1, 127.8, 124.4, 57.6, 29.9, 21.2 (two carbon overlaped), 12.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NaO_2S_2$ $[M + Na]^+$ 357.0953, found: 357.0951.

(*R*)-*S*-(1-(*o*-Tolyl)propyl) 3,5-dimethylbenzenesulfonothioate (23)



23

According to the **general procedure A** with 1-(1-bromopropyl)-2-methylbenzene **E20** (43.6 μL, 0.20 mmol, 1.0 equiv) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 equiv) run at –15 °C for 7 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **23** as a colorless oil (50.3 mg, 75% yield, 91% e.e.).

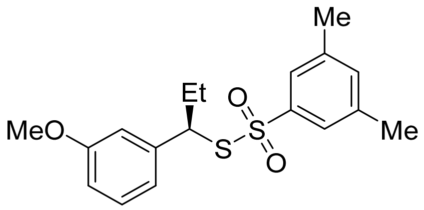
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 18.99 min, t_R (major) = 21.15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 2H), 7.10 – 7.02 (m, 4H), 7.00 – 6.94 (m, 1H), 4.69 (dd, *J* = 9.2, 6.1 Hz, 1H), 2.31 – 2.25 (m, 9H), 2.12 – 2.02 (m, 1H), 2.02 – 1.89 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.0, 137.1, 136.1, 134.9, 130.4, 127.6, 127.4, 126.4, 124.3, 53.3, 29.8, 21.3, 19.5, 12.0.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NaO_2S_2$ $[M + Na]^+$ 357.0953, found: 357.0952.

(*R*)-*S*-(1-(3-Methoxyphenyl)propyl) 3,5-dimethylbenzenesulfonothioate (24)



24

According to the **general procedure A** with 1-(1-bromopropyl)-3-methoxybenzene **E21** (49.2 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **24** as a white solid (50.8 mg, 72% yield, 92% e.e.).

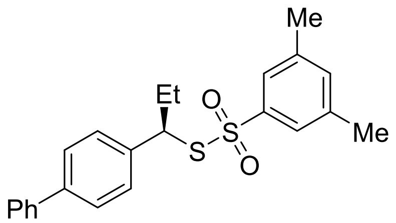
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 20.14 min, t_R (major) = 22.10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 7.11 – 7.03 (m, 2H), 6.73 – 6.63 (m, 2H), 6.60 (t, *J* = 2.1 Hz, 1H), 4.37 (dd, *J* = 8.8, 6.5 Hz, 1H), 3.68 (s, 3H), 2.25 (s, 6H), 2.05 – 1.93 (m, 1H), 1.93 – 1.80 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 145.2, 140.9, 138.8, 134.8, 129.3, 124.3, 120.4, 113.3, 113.2, 57.7, 55.1, 29.8, 21.2, 12.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NaO_3S_2$ $[M + Na]^+$ 373.0903, found: 373.0901.

(*R*)-*S*-(1-([1,1'-Biphenyl]-4-yl)propyl) 3,5-dimethylbenzenesulfonothioate (25)



25

According to the **general procedure A** with 4-(1-bromopropyl)-1,1'-biphenyl **E22** (55.0 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **25** as a colorless oil (69.8 mg, 88% yield, 92% e.e.).

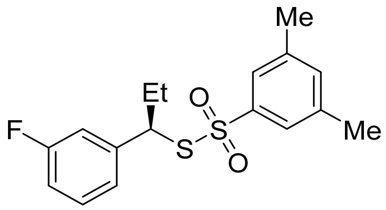
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 23.00 min, t_R (major) = 25.91 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.21 – 7.12 (m, 4H), 7.01 (s, 1H), 4.47 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.18 (s, 6H), 2.10 – 1.98 (m, 1H), 1.98 – 1.85 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 145.1, 140.4(3), 140.4(2), 138.9, 138.5, 134.7, 129.0, 128.3, 127.6, 126.9(5), 126.9(4), 124.4, 57.5, 29.9, 21.2, 12.1.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}NaO_2S_2$ $[M + Na]^+$ 419.1110, found: 419.1111.

(*R*)-*S*-(1-(3-Fluorophenyl)propyl) 3,5-dimethylbenzenesulfonothioate (26)



26

According to the **general procedure A** with 1-(1-bromopropyl)-3-fluorobenzene **E23** (35.2 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **26** as a colorless oil (47.9 mg, 71% yield, 93% e.e.).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 16.32 min, t_R (major) = 18.80 min.

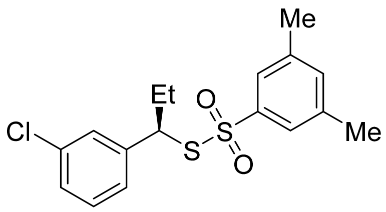
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 7.15 – 7.09 (m, 1H), 7.06 (s, 1H), 6.93 – 6.88 (m, 1H), 6.85 – 6.79 (m, 1H), 6.79 – 6.74 (m, 1H), 4.38 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.25 (s, 6H), 2.04 – 1.92 (m, 1H), 1.90 – 1.78 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 246.6 Hz), 145.0, 142.1 (d, *J* = 7.0 Hz), 139.0, 135.0, 129.8 (d, *J* = 8.3 Hz), 124.3, 123.7 (d, *J* = 2.9 Hz), 114.8 (d, *J* = 13.4 Hz), 114.5 (d, *J* = 12.4 Hz), 57.0 (d, *J* = 1.9 Hz), 29.7, 21.2, 12.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –112.85.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}FNaO_2S_2$ $[M + Na]^+$ 361.0703, found: 361.0701.

(*R*)-*S*-(1-(3-Chlorophenyl)propyl) 3,5-dimethylbenzenesulfonothioate (27)



27

According to the **general procedure A** with 1-(1-bromopropyl)-3-chlorobenzene **E24** (37.0 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3.5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **27** as a colorless oil (48.0 mg, 68% yield, 92% e.e.).

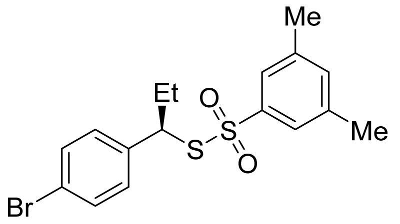
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 15.23 min, t_R (major) = 17.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 2H), 7.10 – 7.04 (m, 3H), 7.03 – 6.96 (m, 2H), 4.36 (dd, J = 8.5, 6.8 Hz, 1H), 2.26 (s, 6H), 2.02 – 1.90 (m, 1H), 1.89 – 1.77 (m, 1H), 0.90 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.5, 139.0, 135.1, 134.3, 129.4, 127.9, 127.7, 126.2, 124.2, 56.9, 29.7, 21.2, 12.0.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}ClNaO_2S_2$ $[M + Na]^+$ 377.0407, found: 377.0405.

(*R*)-*S*-(1-(4-Bromophenyl)propyl) 3,5-dimethylbenzenesulfonothioate (28)



28

According to the **general procedure A** with 1-bromo-4-(1-bromopropyl)benzene **E25** (55.6 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **28** as a white solid (70.0 mg, 88% yield, 92% e.e.).

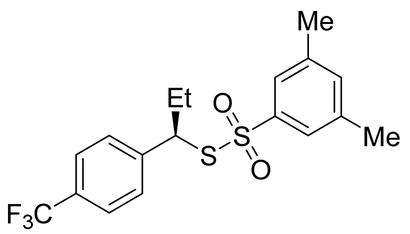
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 13.67 min, t_R (major) = 16.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 2H), 7.11 – 7.05 (m, 3H), 6.99 – 6.93 (m, 2H), 4.39 (dd, *J* = 8.8, 6.6 Hz, 1H), 2.26 (s, 6H), 2.02 – 1.90 (m, 1H), 1.86 – 1.74 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 138.9, 138.6, 134.7, 131.3, 129.6, 124.2, 121.5, 57.0, 29.6, 21.2, 12.0.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}BrNaO_2S_2$ $[M + Na]^+$ 420.9902, found: 420.9899.

(*R*)-*S*-(1-(4-(Trifluoromethyl)phenyl)propyl) 3,5-dimethylbenzenesulfonothioate (29)



29

According to the **general procedure A** with 1-(1-bromopropyl)-4-(trifluoromethyl)benzene **E26** (45.8 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 3.5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **29** as a white solid (58.4 mg, 75% yield, 92% e.e.).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 20.28 min, t_R (major) = 23.05 min.

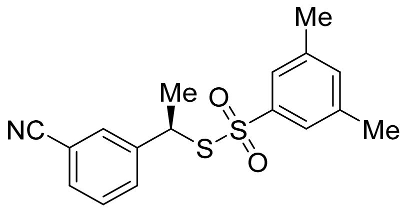
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.12 (s, 2H), 7.02 (s, 1H), 4.46 (dd, *J* = 8.5, 6.8 Hz, 1H), 2.22 (s, 6H), 2.05 – 1.94 (m, 1H), 1.92 – 1.80 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.8, 139.0, 135.0, 129.8 (q, *J* = 32.4 Hz), 128.3, 125.2 (q, *J* = 3.7 Hz), 124.3, 124.0 (q, *J* = 272.1 Hz), 56.9, 29.7, 21.0, 12.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.67.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}F_3NaO_2S_2$ $[M + Na]^+$ 411.0671, found: 411.0661.

(*R*)-*S*-(1-(3-Cyanophenyl)ethyl) 3,5-dimethylbenzenesulfonothioate (30)



30

According to the **general procedure A** with 1-(1-bromoethyl)-3-isocyanobenzene **E27** (35.4 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –30 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1 ~ 5/1) to yield the product **30** as a colorless oil (59.2 mg, 89% yield, 88% e.e.).

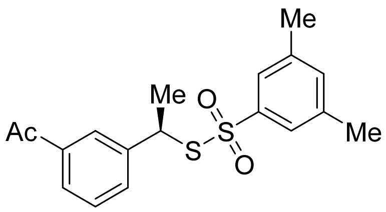
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 230 nm), t_R (major) = 29.46 min, t_R (minor) = 33.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.36 – 7.26 (m, 2H), 7.18 (s, 2H), 7.13 (s, 1H), 4.66 (q, *J* = 7.3 Hz, 1H), 2.29 (s, 6H), 1.64 (d, *J* = 7.4, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.4, 139.3, 135.4, 131.9, 131.2, 130.8, 129.3, 124.3, 118.2, 112.6, 49.7, 22.5, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}NO_2S_2$ $[M + H]^+$ 332.0773, found: 332.0770.

(*R*)-*S*-(1-(3-Acetylphenyl)ethyl) 3,5-dimethylbenzenesulfonothioate (31)



31

According to the **general procedure A** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one **E28** (42.1 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –30 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1 ~ 3/1) to yield the product **31** as a colorless oil (54.6 mg, 78% yield, 89% e.e.).

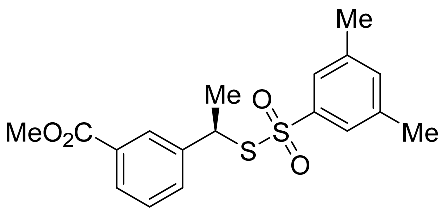
HPLC analysis: Chiralcel IE (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 55.27 min, t_R (minor) = 61.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.68 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.19 (s, 2H), 7.05 (s, 1H), 4.71 (q, *J* = 7.3 Hz, 1H), 2.50 (s, 3H), 2.25 (s, 6H), 1.67 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 144.8, 141.3, 139.1, 137.3, 135.0, 132.1, 128.8, 127.7, 127.0, 124.3, 50.4, 26.7, 22.7, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_3S_2$ $[M + Na]^+$ 371.0746, found: 371.0744.

Methyl (*R*)-3-(1-(((3,5-dimethylphenyl)sulfonyl)thio)ethyl)benzoate (32)



32

According to the **general procedure A** with methyl 3-(1-bromoethyl)benzoate **E29** (41.2 µL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –30 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1 ~ 10/1) to yield the product **32** as a colorless oil (63.6 mg, 87% yield, 87% e.e.).

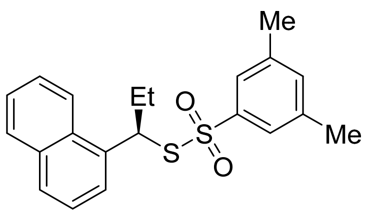
HPLC analysis: Chiralcel IE (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 24.46 min, t_R (minor) = 26.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.76 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.18 (s, 2H), 7.03 (s, 1H), 4.70 (q, *J* = 7.3 Hz, 1H), 3.90 (s, 3H), 2.24 (s, 6H), 1.66 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 144.8, 141.1, 139.0, 134.9, 132.0, 130.4, 129.0, 128.5, 128.3, 124.3, 52.3, 50.4, 22.7, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}O_4S_2$ $[M + H]^+$ 365.0876, found: 365.0870.

(*R*)-*S*-(1-(Naphthalen-1-yl)propyl) 3,5-dimethylbenzenesulfonothioate (33)



33

According to the **general procedure A** with 1-(1-bromopropyl)naphthalene **E30** (49.8 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **33** as a white solid (63.5 mg, 86% yield, 93% e.e.).

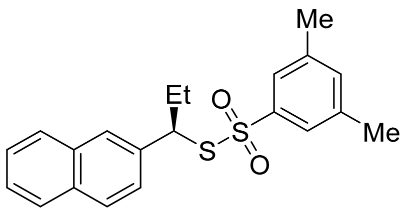
HPLC analysis: Chiralcel IE (*n*-hexane/*i*-PrOH = 92/8, flow rate 0.0 mL/min, λ = 214 nm), t_R (minor) = 23.82 min, t_R (major) = 25.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 1H), 7.83 – 7.75 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.11 (s, 2H), 6.94 (s, 1H), 5.20 (s, 1H), 2.29 – 2.16 (m, 2H), 2.10 (s, 6H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.8, 134.8, 134.5, 133.9, 131.0, 129.0, 128.5, 126.5, 125.9, 125.1, 124.4 (two carbon overlapped), 122.8, 30.0, 29.8, 21.1, 12.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NaO_2S_2$ $[M + Na]^+$ 393.0953, found: 393.0953.

(*R*)-*S*-(1-(Naphthalen-2-yl)propyl) 3,5-dimethylbenzenesulfonothioate (34)



34

According to the **general procedure A** with 2-(1-bromopropyl)naphthalene **E31** (49.8 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **34** as a white solid (64.6 mg, 87% yield, 93% e.e.).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 21.78 min, t_R (major) = 24.07 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.53 (s, 1H), 7.48 – 7.41 (m, 2H), 7.16 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.99 (s, 2H), 6.71 (s, 1H), 4.60 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.12 – 2.01 (m, 1H), 2.00 – 1.92 (m, 1H), 1.91 (s, 6H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.6, 136.4, 134.4, 132.9, 132.8, 128.2, 127.9, 127.6, 127.3, 126.3(2), 126.3(0), 125.1, 124.1, 58.0, 29.4, 20.7, 12.1.

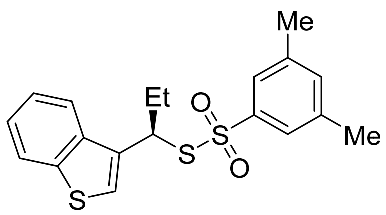
HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NaO_2S_2$ $[M + Na]^+$ 393.0953, found: 393.0953.

34 was prepared from 2-(1-chloropropyl)naphthalene **E36**:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.), $Cu(MeCN)_4BF_4$ (12.6 mg, 0.04 mmol, 20 mol%), **L*5** (31.2 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (260 mg, 0.80 mmol, 4.0 eq.), Then, 2-(1-chloropropyl)naphthalene **E36** (40.9 mg, 0.20 mmol, 1.0 eq.) and toluene/DMF (v/v = 10/1, 2.2 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 °C for 7 days, **t**he reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **34** as a white solid (29.7 mg, 40% yield, 91% e.e.).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 20.94 min, t_R (major) = 23.21 min.

(*R*)-*S*-(1-(Benzo[*b*]thiophen-3-yl)propyl) 3,5-dimethylbenzenesulfonothioate (35)

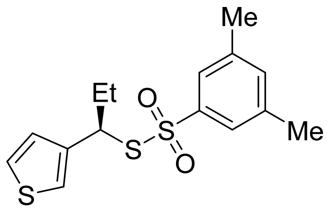


35

According to the **general procedure A** with 3-(1-bromopropyl)benzo[*b*]thiophene **E32**

(51.2 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **35** as a colorless oil (56.9 mg, 76% yield, 92% e.e.).
HPLC analysis: Chiralcel IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 13.61 min, t_R (minor) = 16.24 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H), 7.65 – 7.59 (m, 1H), 7.31 – 7.26 (m, 2H), 7.18 (s, 1H), 7.15 (s, 2H), 6.94 (s, 1H), 4.78 (dd, *J* = 8.4, 6.7 Hz, 1H), 2.20 – 2.11 (m, 8H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 140.5, 138.8, 136.9, 134.8, 133.0, 125.3, 124.6, 124.3, 124.1, 122.8, 121.9, 51.5, 28.7, 21.1, 12.3.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}NaO_2S_3$ $[M + Na]^+$ 399.0518, found: 399.0515.

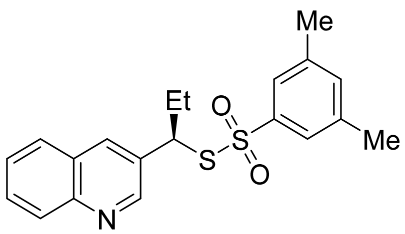
(*R*)-*S*-(1-(Thiophen-3-yl)propyl) 3,5-dimethylbenzenesulfonothioate (36)



36

According to the **general procedure A** with 3-(1-bromopropyl)thiophene **E33** (34.4 µL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **36** as a colorless oil (44.5 mg, 68% yield, 88% e.e.).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 19.47 min, t_R (major) = 22.40 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.13 – 7.08 (m, 2H), 7.01 – 6.99 (m, 1H), 6.80 (dd, *J* = 5.0, 1.3 Hz, 1H), 4.54 (dd, *J* = 8.6, 6.5 Hz, 1H), 2.32 – 2.29 (m, 6H), 2.06 – 1.95 (m, 1H), 1.95 – 1.84 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 140.2, 139.0, 134.9, 126.6, 126.1, 124.3, 122.9, 52.9, 29.5, 21.3, 12.0.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{18}NaO_2S_3$ $[M + Na]^+$ 349.0361, found: 349.0359.

(*R*)-*S*-(1-(Quinolin-3-yl)propyl) 3,5-dimethylbenzenesulfonothioate (37)

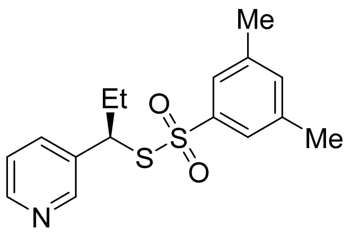


37

According to the **general procedure A** with 3-(1-bromopropyl)quinoline **E34** (50 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 10/1 ~ 5/1) to yield the product **37** as a light yellow solid (69.1 mg, 93% yield, 94% e.e.).
HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 10.60 min, t_R (minor) = 15.75 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.3 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 2.3 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.66 – 7.60 (m, 1H), 7.54 – 7.48 (m, 1H), 7.01 (s, 2H), 6.65 (s, 1H), 4.62 (dd, *J* = 8.6, 6.7 Hz, 1H), 2.15 – 2.06 (m, 1H), 2.03 – 1.93 (m, 7H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.3, 144.6, 138.8, 134.6, 134.6, 132.0, 129.7, 129.2, 127.6, 127.3, 126.9, 124.0, 55.1, 29.4, 20.8, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}NO_2S_2$ $[M + H]^+$ 372.1086, found: 372.1079.

(R)-*S*-(1-(Pyridin-3-yl)propyl) 3,5-dimethylbenzenesulfonothioate (38)

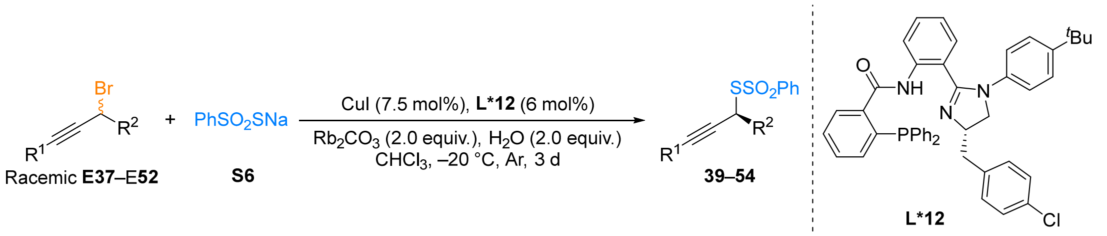


38

According to the **general procedure A** with 3-(1-bromopropyl)pyridine **E35** (40 μL, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (53.8 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **38** as a light yellow solid (33.0 mg, 51% yield, 88% e.e.).
HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 28.83 min, t_R (minor) = 32.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.32 (m, 2H), 7.45 – 7.38 (m, 1H), 7.15 (s, 2H), 7.10 – 7.01 (m, 2H), 4.41 (t, *J* = 7.7 Hz, 1H), 2.26 (s, 6H), 2.05 – 1.98 (m, 1H), 1.93 – 1.81 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 148.9, 144.8, 139.1, 135.5, 135.1, 135.0, 124.2, 123.3, 54.8, 29.6, 21.2, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{20}NO_2S_2$ $[M + H]^+$ 322.0930, found: 322.0923.

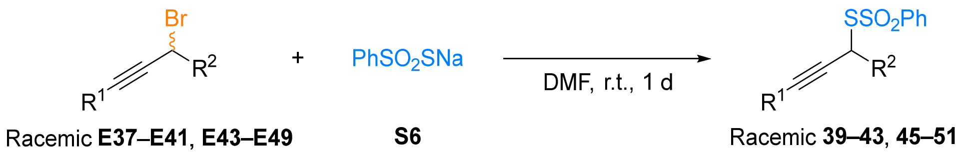
6. Enantioconvergent cross-coupling of propargyl electrophiles with sodium benzenethiosulfonate

General procedure B: Substrate scope of propargyl halides and sodium benzenethiosulfonate (Table 3, 39–54)



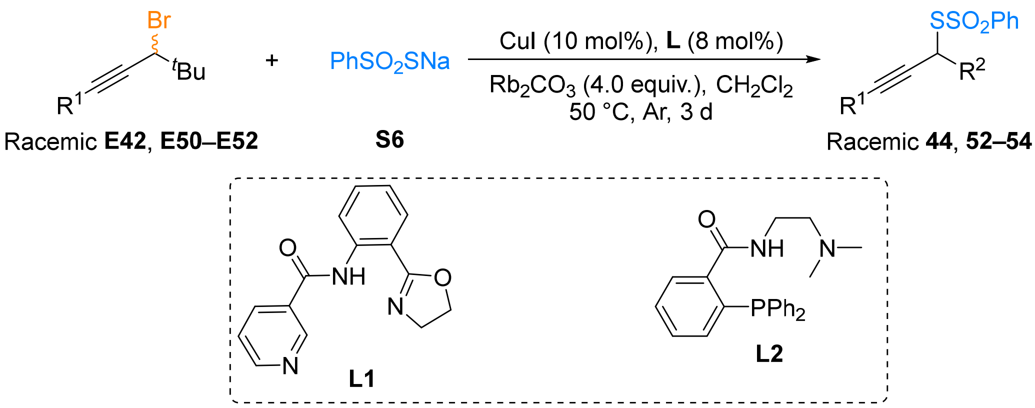
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium benzenethiosulfonate **S6** (47.2mg, 0.24 mmol, 1.2 equiv.), CuI (2.86 mg, 0.015 mmol, 7.5 mol%), **L*12** (8.47 mg, 0.012 mmol, 6 mol%) and Rb_2CO_3 (92.8 mg, 0.40 mmol, 2.0 equiv.), Then, propargyl halide (0.20 mmol, 1.0 equiv.), H_2O (7.2 μL, 0.40 mmol, 2.0 equiv.) and $CHCl_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at –20 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic products **39–43**, **45–51**:



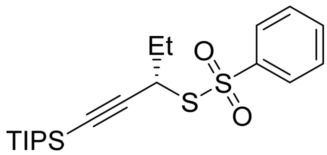
The mixture of sodium benzenethiosulfonate **S6** (23.6 mg, 0.12 mmol, 1.2 equiv.) and propargyl halide (0.10 mmol, 1.0 equiv.) in DMF (0.5 mL) was stirring for 1 d. Brine was added to the above reaction solution to quench the reaction. Then, the mixture was extracted with EtOAc (3x) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography to afford the desired racemates.

The preparation of racemic products (±)-**44**, **52–54**:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium benzenethiosulfonate **S6** (47.2mg, 0.24 mmol, 1.2 equiv.), CuI (3.81 mg, 0.02 mmol, 10 mol%), **L1** (4.28 mg, 0.016 mmol, 8 mol%, for synthesis of (±)-**44**, **53**) or **L2** (6.02 mg, 0.016 mmol, 8 mol%, for synthesis of (±)-**52**, **54**), Rb_2CO_3 (185.6 mg, 0.80 mmol, 4.0 equiv.), Then, propargyl halide (0.20 mmol, 1.0 equiv.) and CH_2Cl_2 (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 50 °C for 3days, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*S*)-*S*-(1-(Triisopropylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (39)



39

According to **General procedure B**, (3-bromopent-1-yn-1-yl)triisopropylsilane **E37** (59.2 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **39** as a colorless oil (71.4 mg, 90% yield, 90% e.e.).

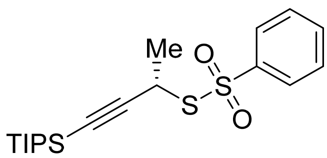
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 11.27 min, t_R (major) = 13.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.64 – 7.59 (m, 1H), 7.56 – 7.51 (m, 2H), 4.17 (dd, *J* = 7.6, 5.2 Hz, 1H), 1.98 – 1.78 (m, 2H), 1.05 (d, *J* = 7.3 Hz, 3H), 1.01 – 0.95 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.7, 129.4, 127.0, 103.6, 87.9, 44.2, 29.6, 18.6, 11.1(5), 11.1(3).

HRMS (ESI) *m/z* calcd. for $C_{20}H_{33}O_2S_2Si$ $[M + H]^+$ 397.1686, found: 397.1682.

(*S*)-*S*-(4-(Triisopropylsilyl)but-3-yn-2-yl) benzenesulfonothioate (40)



40

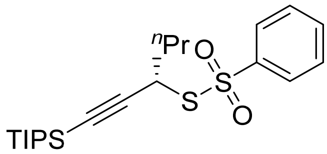
According to **General procedure B**, (3-bromobut-1-yn-1-yl)triisopropylsilane **E38** (56.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **40** as a light yellow oil (69.1 mg, 90% yield, 91% e.e.).

HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 11.20 min, t_R (major) = 12.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.66 – 7.59 (m, 1H), 7.58 – 7.51 (m, 2H), 4.24 (q, *J* = 7.0 Hz, 1H), 1.62 (d, *J* = 7.0 Hz, 3H), 1.02 – 0.95 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 133.8, 129.4, 127.0, 104.8, 87.2, 37.5, 23.4, 18.6, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{30}NaO_2S_2Si$ $[M + Na]^+$ 405.1349, found: 405.1347.

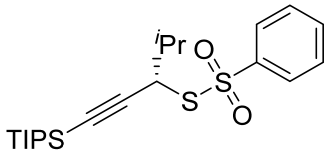
(*S*)-*S*-(1-(Triisopropylsilyl)hex-1-yn-3-yl) benzenesulfonothioate (41)



41

According to **General procedure B**, (3-bromohex-1-yn-1-yl)triisopropylsilane **E39** (63.0 µL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **41** as a colorless oil (69.7 mg, 85% yield, 90% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 10.08 min, t_R (major) = 11.91 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 4.19 (dd, *J* = 7.9, 5.7 Hz, 1H), 1.86 – 1.73 (m, 2H), 1.58 – 1.46 (m, 2H), 1.01 – 0.93 (m, 21H), 0.90 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.7, 129.4, 127.0, 104.0, 87.6, 42.5, 38.2, 20.1, 18.6, 13.5, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{35}O_2S_2Si$ $[M + H]^+$ 411.1842, found: 411.1839.

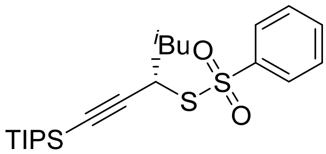
(*S*)-*S*-(4-Methyl-1-(triisopropylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (42)



42

According to **General procedure B**, (3-bromo-4-methylpent-1-yn-1-yl)triisopropylsilane **E40** (100 µL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.) run at 5 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **42** as a colorless oil (50.1 mg, 61% yield, 90% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 10.07 min, t_R (major) = 12.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.51 (m, 2H), 4.13 (d, *J* = 4.3 Hz, 1H), 2.19 – 2.09 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 1.00 – 0.95 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 133.7, 129.4, 127.0, 102.3, 88.5, 49.8, 33.8, 20.7, 18.7, 18.3, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{35}O_2S_2Si$ $[M + H]^+$ 411.1842, found: 411.1839.

(*S*)-*S*-(5-Methyl-1-(triisopropylsilyl)hex-1-yn-3-yl) benzenesulfonothioate (43)



43

According to **General procedure B**, (3-bromo-5-methylhex-1-yn-1-yl)triisopropylsilane **E41** (63.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **43** as a colorless oil (80.7 mg, 95% yield, 90% e.e.).

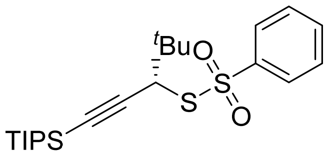
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 8.70 min, t_R (major) = 11.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.65 – 7.59 (m, 1H), 7.57 – 7.51 (m, 2H), 4.17 (dd, *J* = 9.5, 6.1 Hz, 1H), 1.95 – 1.83 (m, 1H), 1.78 – 1.69 (m, 1H), 1.68 – 1.59 (m, 1H), 1.02 – 0.94 (m, 21H), 0.91 (dd, *J* = 6.6, 4.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.7, 129.4, 127.1, 104.2, 87.5, 45.1, 41.1, 26.4, 22.8, 21.5, 18.6, 11.1.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{37}O_2S_2Si$ $[M + H]^+$ 425.1992, found: 425.1999.

(*S*)-*S*-(4,4-Dimethyl-1-(triisopropylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (44)



44

According to **General procedure B**, (3-bromo-4,4-dimethylpent-1-yn-1-yl)triisopropylsilane **E42** (65.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.) run at 7 days. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **44** as a colorless oil (51.8 mg, 61% yield, 96% e.e.).

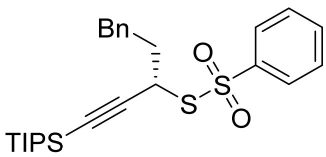
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 9.05 min, t_R (major) = 12.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.63 – 7.56 (m, 1H), 7.56 – 7.48 (m, 2H), 3.91 (s, 1H), 1.09 (s, 9H), 0.98 – 0.93 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 133.6, 129.3, 127.0, 104.1, 87.5, 55.2, 36.5, 27.5, 18.7, 11.2.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{36}NaO_2S_2Si$ $[M + Na]^+$ 447.1818, found: 447.1816.

(*S*)-*S*-(5-Phenyl-1-(triisopropylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (45)

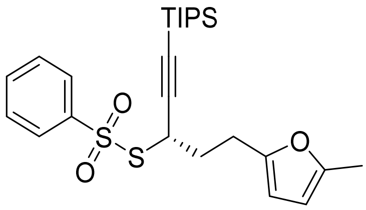


45

According to **General procedure B**, (3-bromo-5-phenylpent-1-yn-1-yl)triisopropylsilane **E43** (70.4 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2

mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **45** as a colorless oil (75.8 mg, 80% yield, 87% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (major) = 28.24 min, t_R (minor) = 29.95 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.16 – 7.08 (m, 2H), 4.11 (dd, *J* = 8.5, 5.0 Hz, 1H), 2.89 – 2.73 (m, 2H), 2.25 – 2.04 (m, 2H), 1.04 – 0.96 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 140.2, 133.8, 129.4, 128.7 (two carbon overlapped), 127.0, 126.4, 103.3, 88.6, 41.8, 38.0, 33.0, 18.7, 11.2.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{36}NaO_2S_2Si$ $[M + Na]^+$ 495.1818, found: 495.1814.

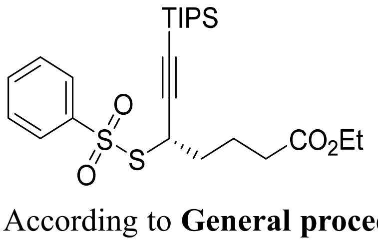
(*S*)-*S*-(5-(5-Methylfuran-2-yl)-1-(triisopropylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (46)



46

According to **General procedure B**, (3-bromo-5-(5-methylfuran-2-yl)pent-1-yn-1-yl)triisopropylsilane **E44** (71.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **46** as a brown oil (76.3 mg, 80% yield, 87% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 11.63 min, t_R (major) = 13.50 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.65 – 7.55 (m, 1H), 7.56 – 7.48 (m, 2H), 5.89 – 5.82 (m, 2H), 4.18 (dd, *J* = 8.4, 5.3 Hz, 1H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.25 (s, 3H), 2.25 – 2.13 (m, 1H), 2.15 – 2.01 (m, 1H), 1.05 – 0.93 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 150.9, 145.3, 133.8, 129.4, 127.0, 106.7, 106.1, 103.2, 88.4, 41.7, 34.8, 25.4, 18.6, 13.6, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{37}O_3S_2Si$ $[M + H]^+$ 477.1948, found: 477.1946.

Ethyl (*S*)-5-((phenylsulfonyl)thio)-7-(triisopropylsilyl)hept-6-ynoate (47)

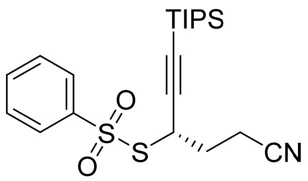


47

According to **General procedure B**, ethyl 5-bromo-7-(triisopropylsilyl)hept-6-ynoate **E45** (62.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **47** as a colorless oil

(82.6 mg, 86% yield, 87% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 45.86 min, t_R (major) = 53.00 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.66 – 7.60 (m, 1H), 7.58 – 7.50 (m, 2H), 4.22 – 4.16 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.33 – 2.26 (m, 2H), 2.00 – 1.89 (m, 1H), 1.89 – 1.79 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.02 – 0.94 (m, 21H).
^{13}C NMR (100 MHz, CDCl3) δ 172.9, 145.4, 133.8, 129.4, 127.0, 103.3, 88.3, 60.5, 42.2, 35.4, 33.5, 22.2, 18.6, 14.3, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{39}O_4S_2Si$ $[M + H]^+$ 483.2054, found: 483.2052.

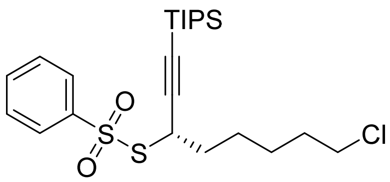
(*S*)-*S*-(5-Cyano-1-(triisopropylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (48)



48

According to **General procedure B**, 4-bromo-6-(triisopropylsilyl)hex-5-ynenitrile **E46** (56.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **48** as a brown oil (68.3 mg, 81% yield, 85% e.e.).
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 214 nm), t_R (major) = 18.86 min, t_R (minor) = 24.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.70 – 7.64 (m, 1H), 7.62 – 7.56 (m, 2H), 4.24 (dd, *J* = 7.9, 5.3 Hz, 1H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.36 – 2.26 (m, 1H), 2.24 – 2.14 (m, 1H), 1.01 – 0.96 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 134.3, 129.7, 127.1, 118.3, 100.7, 90.7, 40.8, 31.9, 18.6, 14.7, 11.0.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{31}NNaO_2S_2Si$ $[M + Na]^+$ 444.1458, found: 444.1456.

(*S*)-*S*-(8-Chloro-1-(triisopropylsilyl)oct-1-yn-3-yl) benzenesulfonothioate (49)

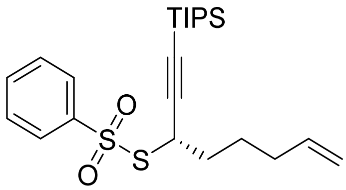


49

According to **General procedure B**, (3-bromo-8-chlorooct-1-yn-1-yl)triisopropyl-silane **E47** (72.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **49** as a light yellow oil (81.5 mg, 86% yield, 84% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 16.36 min, t_R (major) = 17.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.65 – 7.59 (m, 1H), 7.58 – 7.50 (m, 2H), 4.19 (dd, *J* = 7.9, 5.5 Hz, 1H), 3.50 (t, *J* = 6.6 Hz, 2H), 1.94 – 1.77 (m, 2H), 1.77 – 1.68 (m, 2H), 1.57 – 1.48 (m, 2H), 1.47 – 1.37 (m, 2H), 1.03 – 0.90 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 133.8, 129.4, 127.0, 103.6, 88.0, 44.8, 42.5, 35.9, 32.3, 26.1, 25.9, 18.6, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}ClNaO_2S_2Si$ $[M + Na]^+$ 495.1585, found: 495.1582.

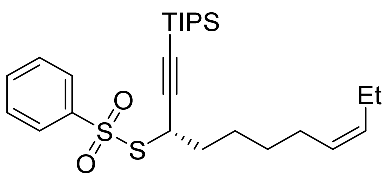
(*S*)-*S*-(1-(Triisopropylsilyl)oct-7-en-1-yn-3-yl) benzenesulfonothioate (50)



50

According to **General procedure B**, (3-bromooct-7-en-1-yn-1-yl)triisopropylsilane **E48** (68.5 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **50** as a colorless oil (69.9 mg, 80% yield, 86% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (major) = 20.46 min, t_R (minor) = 22.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.65 – 7.59 (m, 1H), 7.57 – 7.50 (m, 2H), 5.78 – 5.66 (m, 1H), 5.02 – 4.92 (m, 2H), 4.20 (dd, *J* = 8.1, 5.3 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.93 – 1.74 (m, 2H), 1.64 – 1.56 (m, 2H), 1.02 – 0.93 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.8, 133.8, 129.4, 127.0, 115.3, 103.7, 87.9, 42.6, 35.5, 32.9, 25.9, 18.6, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}O_2S_2Si$ $[M + H]^+$ 437.1999, found: 437.1997.

(*S,Z*)-*S*-(1-(Triisopropylsilyl)undec-8-en-1-yn-3-yl) benzenesulfonothioate (51)

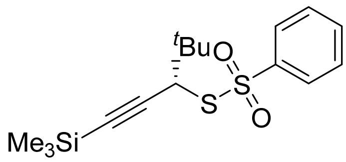


51

According to **General procedure B**, (3-bromooct-7-en-1-yn-1-yl)triisopropylsilane **E49** (78.0 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **51** as a colorless oil (78.0 mg, 81% yield, 85% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 13.67 min, t_R (major) = 15.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.49 (m, 2H), 5.40 – 5.32 (m, 1H), 5.31 – 5.22 (m, 1H), 4.19 (dd, *J* = 8.1, 5.4 Hz, 1H), 2.07 – 1.94 (m, 4H), 1.89 – 1.74 (m, 2H), 1.57 – 1.45 (m, 2H), 1.38 – 1.24 (m, 2H), 1.02 – 0.92 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.7, 132.2, 129.3, 128.6, 127.0, 103.8, 87.8, 42.6, 36.0, 29.0, 26.9, 26.4, 20.6, 18.6, 14.5, 11.1.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{42}NaO_2S_2Si$ $[M + Na]^+$ 501.2288, found: 501.2286.

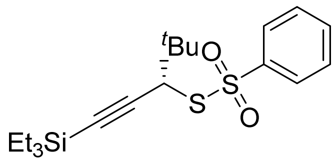
(*S*)-*S*-(4,4-Dimethyl-1-(trimethylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (52)



52

According to **General procedure B**, (3-bromo-4,4-dimethylpent-1-yn-1-yl)trimethylsilane **E50** (46.6 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **52** as a white solid (54.5 mg, 80% yield, 95% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 12.05 min, t_R (major) = 15.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 3.92 (s, 1H), 1.06 (s, 9H), 0.01 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 133.6, 129.2, 127.3, 102.2, 91.1, 54.9, 36.3, 27.6, –0.1.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}O_2S_2Si$ $[M + H]^+$ 341.1056, found: 341.1060.

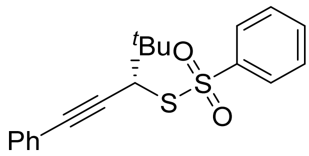
(*S*)-*S*-(4,4-Dimethyl-1-(triethylsilyl)pent-1-yn-3-yl) benzenesulfonothioate (53)



53

According to **General procedure B**, (3-bromo-4,4-dimethylpent-1-yn-1-yl)triethylsilane **E51** (55.5 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **53** as a colorless oil (57.4 mg, 75% yield, 97% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 10.65 min, t_R (major) = 13.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.49 (m, 2H), 3.92 (s, 1H), 1.08 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.46 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 133.6, 129.2, 127.1, 103.5, 88.6, 55.1, 36.4, 27.5, 7.6, 4.4.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{31}O_2S_2Si$ $[M + H]^+$ 383.1523, found: 383.1529.

(*S*)-*S*-(4,4-Dimethyl-1-phenylpent-1-yn-3-yl) benzenesulfonothioate (54)



54

According to **General procedure B**, (3-bromo-4,4-dimethylpent-1-yn-1-yl)benzene **E52** (42.5 μL, 0.2 mmol, 1.0 eq.) with sodium benzenesulfonothioate **S6** (47.2 mg, 0.24 mmol, 1.2 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to yield the product **54** as a white solid (63.4 mg, 92% yield, 95% e.e.).

HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 25.71 min, t_R (major) = 34.43 min.

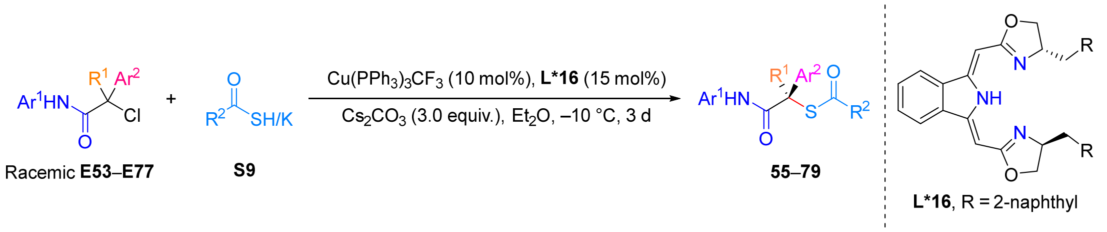
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.52 – 7.39 (m, 3H), 7.33 – 7.19 (m, 3H), 7.16 – 7.08 (m, 2H), 4.18 (s, 1H), 1.13 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 133.5, 131.6, 129.1, 128.5, 128.2, 127.3, 122.5, 86.5, 86.1, 55.0, 36.7, 27.7.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}O_2S_2Si$ $[M + H]^+$ 345.0972, found: 345.0978.

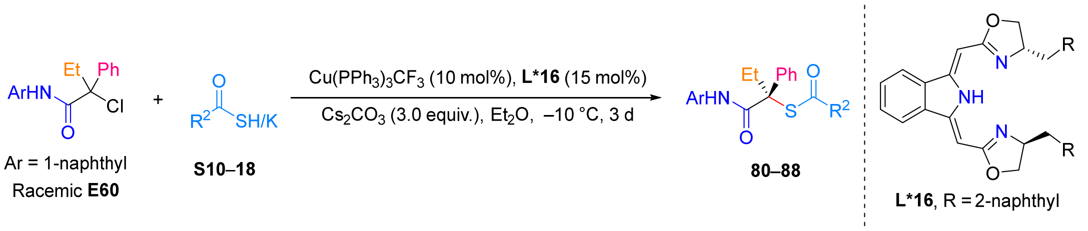
7. Enantioconvergent cross-coupling of tertiary alkyl electrophiles with thiobenzoic acid or potassium thiocarboxylates.

General procedure C: Substrate scope of tertiary alkyl electrophiles and thiobenzoic acid (Table, 55–79)



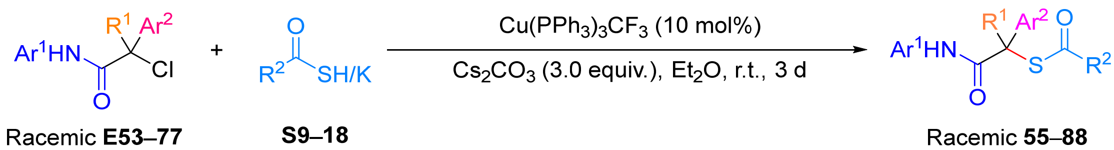
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with tertiary alkyl electrophiles (0.10 mmol, 1.0 equiv.), $Cu(PPh_3)_3CF_3$ (9.24 mg, 0.010 mmol, 10 mol%), **L*16** (8.44 mg, 0.015 mmol, 15 mol%) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). Then, thiobenzoic acid **S9** (17.6 μL, 0.15 mmol, 1.5 equiv.) and Et_2O (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at –10 °C for 3 days. The precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure D: Substrate scope of (±)-E60 and potassium thiocarboxylates. (Table, 80–88)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with tertiary alkyl electrophiles **E60** (32.4 mg, 0.10 mmol, 1.0 equiv.), $Cu(PPh_3)_3CF_3$ (9.24 mg, 0.010 mmol, 10 mol%), **L*16** (8.44 mg, 0.015 mmol, 15 mol%), potassium thiocarboxylates (0.15 mmol, 1.5 equiv.) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). Then, Et_2O (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at –10 °C for 3 days. The precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

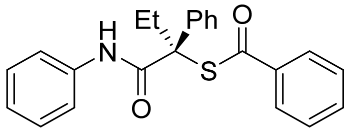
The preparation of racemic products **55–88**:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with tertiary alkyl electrophiles (0.10 mmol, 1.0 equiv.),

$Cu(PPh_3)_3CF_3$ (9.24 mg, 0.010 mmol, 10 mol%), Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). Then, thiobenzoic acid or potassium thiocarboxylates (0.15 mmol, 1.5 equiv.) and Et_2O (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at r.t. for 3 days. The precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

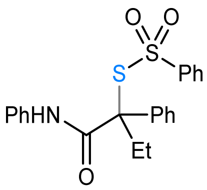
(*R*)-*S*-(1-Oxo-2-phenyl-1-(phenylamino)butan-2-yl) benzothioate (55)



55

According to **General procedure C**, 2-chloro-*N*,2-diphenylbutanamide **E53** (27.4 mg, 0.1 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **55** as a white solid (34.9 mg, 93% yield, 90% e.e.).
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 16.11 min, t_R (major) = 20.49 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.03 – 7.94 (m, 2H), 7.64 – 7.56 (m, 1H), 7.54 – 7.48 (m, 4H), 7.48 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 7.10 – 7.04 (m, 1H), 2.54 – 2.43 (m, 1H), 2.37 – 2.26 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 169.9, 138.4, 138.1, 136.9, 134.2, 129.0, 128.9, 128.6, 128.0, 127.7, 127.4, 124.2, 120.0, 66.0, 32.5, 9.4.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1366, found: 376.1362.

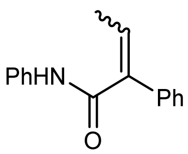
***S*-(1-Oxo-2-phenyl-1-(phenylamino)butan-2-yl) benzenesulfonothioate (55a)**



55a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.34 – 7.18 (m, 8H), 7.18 – 7.06 (m, 4H), 2.92 – 2.78 (m, 1H), 2.55 – 2.40 (m, 1H), 1.08 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 145.0, 137.1, 136.9, 133.0, 129.0, 128.9, 128.7, 128.7, 128.1, 126.7, 125.0, 120.1, 72.5, 30.8, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NO_3S_2$ $[M + H]^+$ 412.1036, found: 412.1039.

***N*,2-Diphenylbut-2-enamide (55b)**

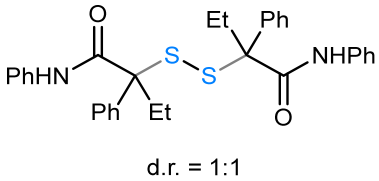


55b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.24 (m, 5H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.15 (q, *J* = 7.2 Hz, 1H), 2.00 (d, *J*

= 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 139.0, 137.9, 137.3, 130.0, 129.0, 128.8, 127.9, 126.7, 124.5, 112.0, 15.8.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226, found: 238.1222

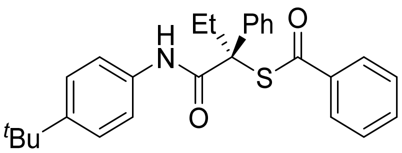
2,2'-Disulfanediylbis(*N*,2-diphenylbutanamide) (55c)



55c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.66 (s, 1H), 7.53 – 7.46 (m, 4H), 7.43 – 7.26 (m, 14H), 7.11 (q, J = 7.1 Hz, 2H), 2.38 – 2.25 (m, 2H), 2.22 – 2.08 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H), 0.78 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 139.0, 138.9, 137.7(5), 137.7(3), 129.1(0), 129.0(5), 128.8, 128.7, 128.4, 128.30, 128.2(5), 128.1(6), 124.6(3), 124.5(7), 120.0(3), 119.9(8), 68.5, 68.1, 31.1, 30.9, 9.9, 9.8.
HRMS (ESI) *m/z* calcd. for $C_{32}H_{33}N_2O_2S_2$ $[M + H]^+$ 541.1978, found: 541.1992.

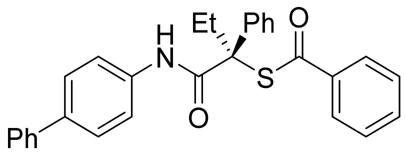
(*R*)-*S*-(1-((4-(*Tert*-butyl)phenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (56)



56

According to **General procedure C**, *N*-(4-(tert-butyl)phenyl)-2-chloro-2-phenylbutanamide **E54** (33.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **56** as a white solid (41.0 mg, 95% yield, 87% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.3 mL/min, λ = 254 nm), t_R (major) = 24.83 min, t_R (minor) = 29.95 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.02 – 7.93 (m, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.48 (m, 2H), 7.47 – 7.41 (m, 4H), 7.38 – 7.27 (m, 5H), 2.54 – 2.44 (m, 1H), 2.37 – 2.26 (m, 1H), 1.28 (s, 9H), 0.88 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ192.2, 169.8, 147.2, 138.2, 136.9, 135.8, 134.1, 128.9, 128.6, 127.9, 127.6, 127.5, 125.8, 119.6, 66.0, 34.5, 32.5, 31.5, 9.4.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{30}NO_2S$ $[M + H]^+$ 432.1992, found: 432.1989.

(*R*)-*S*-(1-([1,1'-Biphenyl]-4-ylamino)-1-oxo-2-phenylbutan-2-yl) benzothioate (57)



57

According to **General procedure C**, *N*-([1,1'-biphenyl]-4-yl)-2-chloro-2-phenylbutanamide **E55** (35.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **57** as a colorless oil (42.5 mg, 94% yield, 89% e.e.).

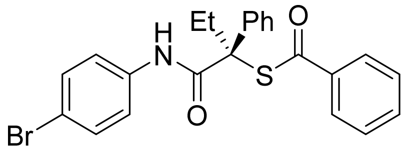
HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 90/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 17.66 min, t_R (major) = 20.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.06 – 7.96 (m, 2H), 7.64 – 7.57 (m, 3H), 7.56 – 7.49 (m, 6H), 7.49 – 7.43 (m, 2H), 7.43 – 7.35 (m, 4H), 7.35 – 7.27 (m, 2H), 2.55 – 2.44 (m, 1H), 2.38 – 2.27 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 170.0, 140.8, 138.1, 137.7, 137.1, 136.9, 134.2, 128.9(2), 128.8(7), 128.6, 128.0, 127.7 (two carbon overlapped), 127.4, 127.1, 127.0, 120.2, 66.1, 32.6, 9.4.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO_2S$ $[M + H]^+$ 452.1679, found: 452.1674.

(*R*)-*S*-(1-((4-Bromophenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (58)



58

According to **General procedure C**, *N*-(4-bromophenyl)-2-chloro-2-phenylbutanamide **E56** (35.3 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **58** as a light yellow solid (41.8 mg, 92% yield, 84% e.e.).

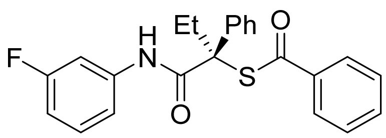
HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 19.06 min, t_R (major) = 27.43 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.04 – 7.93 (m, 2H), 7.64 – 7.56 (m, 1H), 7.49 – 7.43 (m, 4H), 7.43 – 7.37 (m, 4H), 7.37 – 7.29 (m, 3H), 2.51 – 2.38 (m, 1H), 2.35 – 2.23 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 170.0, 137.8, 137.5, 136.7, 134.3, 132.0, 128.9, 128.6, 128.0, 127.7, 127.3, 121.5, 116.7, 65.9, 32.6, 9.4.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}BrNO_2S$ $[M + H]^+$ 454.0471, found: 454.0466.

(*R*)-*S*-(1-((3-Fluorophenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (59)



59

According to **General procedure C**, 2-chloro-*N*-(3-fluorophenyl)-2-

phenylbutanamide **E57** (29.2 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **59** as a light yellow solid (38.2 mg, 97% yield, 87% e.e.).

HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 15.77 min, t_R (major) = 18.69 min.

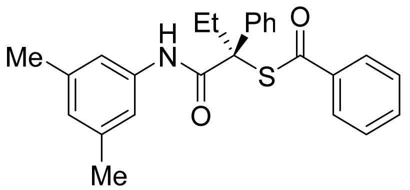
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.50 – 7.43 (m, 4H), 7.40 – 7.29 (m, 3H), 7.24 – 7.16 (m, 1H), 7.14 – 7.07 (m, 1H), 6.79 – 6.72 (m, 1H), 2.52 – 2.39 (m, 1H), 2.36 – 2.22 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 170.1, 163.1 (d, *J* = 244.6 Hz), 139.9 (d, *J* = 10.9 Hz), 137.7, 136.7, 134.3, 130.0 (d, *J* = 9.4 Hz), 128.9, 128.7, 128.0, 127.7, 127.3, 115.2 (d, *J* = 3.0 Hz), 110.9 (d, *J* = 21.3 Hz), 107.4 (d, *J* = 26.3 Hz), 65.9, 32.6, 9.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ –111.58.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}FNO_2S$ $[M + H]^+$ 394.1272, found: 394.1267.

(*R*)-*S*-(1-((3,5-Dimethylphenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (60)



60

According to **General procedure C**, 2-chloro-*N*-(3,5-dimethylphenyl)-2-phenylbutanamide **E58** (30.2 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **60** as a colorless oil (36.3 mg, 90% yield, 86% e.e.).

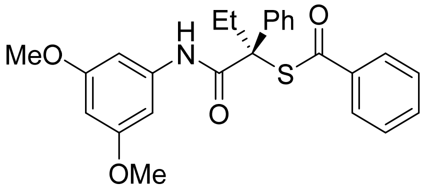
HPLC analysis: Chiralcel AS-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 12.85 min, t_R (major) = 15.71 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.03 – 7.94 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.42 (m, 4H), 7.39 – 7.28 (m, 3H), 7.16 (s, 2H), 6.72 (s, 1H), 2.54 – 2.44 (m, 1H), 2.37 – 2.28 (m, 1H), 2.26 (s, 6H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 169.9, 138.8, 138.2(2), 138.1(9), 136.9, 134.1, 128.9, 128.6, 127.9, 127.7, 127.4, 125.9, 117.6, 66.0, 32.5, 21.5, 9.5.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NO_2S$ $[M + H]^+$ 404.1679, found: 404.1673.

(*R*)-*S*-(1-((3,5-Dimethoxyphenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (61)



61

According to **General procedure C**, 2-chloro-*N*-(3,5-dimethoxyphenyl)-2-phenylbutanamide **E59** (33.4 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **61** as a yellow oil (41.4 mg, 95% yield, 90% e.e.).

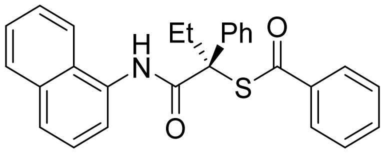
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 28.53 min, t_R (minor) = 32.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.02 – 7.94 (m, 2H), 7.65 – 7.56 (m, 1H), 7.51 – 7.40 (m, 4H), 7.40 – 7.28 (m, 3H), 6.78 (d, *J* = 2.3 Hz, 2H), 6.21 (t, *J* = 2.3 Hz, 1H), 3.76 (s, 6H), 2.53 – 2.41 (m, 1H), 2.36 – 2.23 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 170.0, 161.1, 140.1, 137.9, 136.8, 134.2, 128.9, 128.6, 128.0, 127.7, 127.4, 97.9, 97.0, 66.1, 55.5, 32.5, 9.4.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NO_4S$ $[M + H]^+$ 436.1577, found: 436.1572.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) benzothioate (62)



62

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **62** as a light yellow oil (40.5 mg, 95% yield, 95% e.e.).

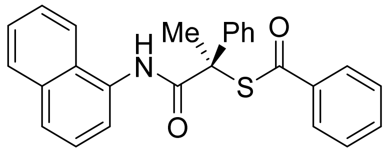
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 28.39 min, t_R (major) = 32.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.29 (s, 1H), 8.03 – 7.96 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.47 – 7.39 (m, 4H), 7.39 – 7.28 (m, 4H), 2.58 – 2.46 (m, 1H), 2.41 – 2.29 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 170.2, 138.1, 136.8, 135.8, 134.2, 134.0, 130.6, 128.9, 128.7, 128.6, 128.0, 127.8, 127.7, 127.6, 127.4, 126.5, 125.0, 120.0, 116.5, 66.0, 32.6, 9.5.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{24}NO_2S$ $[M + H]^+$ 426.1522, found: 426.1518.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylpropan-2-yl) benzothioate (63)



63

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide **E61** (31.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **63** as a light yellow solid (38.7 mg, 94% yield, 92% e.e.).

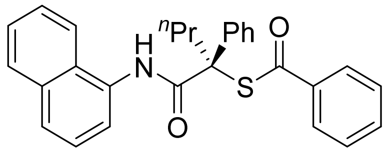
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 18.76 min, t_R (major) = 23.65 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.16 – 8.06 (m, 1H), 8.06 – 7.95 (m, 2H), 7.88 – 7.76 (m, 1H), 7.73 – 7.62 (m, 4H), 7.62 – 7.55 (m, 1H), 7.52 – 7.32 (m, 8H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 170.5, 140.9, 136.6, 134.3, 134.2, 132.8, 129.1, 128.9, 128.7, 128.2, 127.7, 127.2, 126.6, 126.4, 126.0, 125.9, 125.6, 120.8, 120.2, 61.3, 27.9.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}NO_2S$ $[M + H]^+$ 412.1366, found: 412.1361.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylpentan-2-yl) benzothioate (64)



64

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpentanamide **E62** (33.8 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **64** as a light yellow solid (40.9 mg, 93% yield, 92% e.e.).

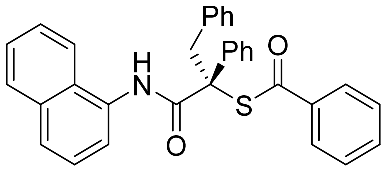
HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 13.41 min, t_R (major) = 18.51 min.

^{1}H NMR (400 MHz, CDCl3) δ 9.17 (s, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.61 (m, 4H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.32 (m, 8H), 2.58 – 2.48 (m, 1H), 2.40 – 2.29 (m, 1H), 1.45 – 1.28 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 170.6, 139.0, 136.8, 134.2, 134.1, 132.9, 128.9, 128.7(1), 128.6(6), 128.0, 127. 7, 127.4, 127.2, 126.3, 125.9, 125.8, 125.4, 120.9, 120.1, 65.6, 41.6, 18.5, 14.4.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{26}NO_2S$ $[M + H]^+$ 440.1679, found: 440.1675.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2,3-diphenylpropan-2-yl) benzothioate (65)



65

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2,3-diphenylpropanamide **E63** (38.6 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **65** as a white solid (46.4 mg, 95% yield, 95% e.e.).

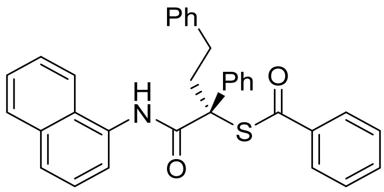
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 21.68 min, t_R (minor) = 24.15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.07 – 8.03 (m, 1H), 8.02 – 7.96 (m, 2H), 7.83 – 7.76 (m, 1H), 7.67 – 7.63 (m, 1H), 7.61 – 7.56 (m, 1H), 7.56 – 7.53 (m, 1H), 7.51 – 7.44 (m, 3H), 7.43 – 7.39 (m, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.28 (m, 4H), 7.19 – 7.13 (m, 1H), 7.12 – 7.06 (m, 2H), 6.80 – 6.74 (m, 2H), 3.83 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 170.6, 138.0, 136.8, 135.8, 134.3, 134.1, 132.7, 131.6, 129.0, 128.6, 128.5, 128.3, 127.7(6), 127.7(0), 127.5, 127.4, 126.9, 126.3, 125.9, 125.8, 125.7, 120.9, 120.5, 66.0, 44.5.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{26}NO_2S$ $[M + H]^+$ 488.1679, found: 488.1675.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2,4-diphenylbutan-2-yl) benzothioate (66)



66

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2,4-diphenylbutanamide **E64** (39.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **66** as a light yellow solid (44.1 mg, 88% yield, 93% e.e.).

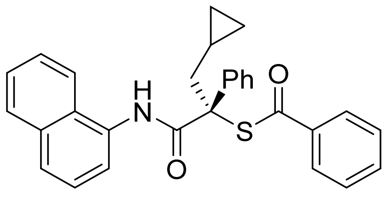
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 27.03 min, t_R (minor) = 37.59 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.12 – 8.07 (m, 1H), 8.04 – 7.98 (m, 2H), 7.85 – 7.80 (m, 1H), 7.73 – 7.64 (m, 4H), 7.63 – 7.58 (m, 1H), 7.52 – 7.42 (m, 6H), 7.41 – 7.35 (m, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.12 (m, 3H), 2.95 – 2.84 (m, 1H), 2.77 – 2.57 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 170.3, 141.7, 138.8, 136.8, 134.3, 134.2, 132.8, 128.9(6), 128.9(5), 128.7, 128.6, 128.5, 128.3, 127.7, 127.4, 127.3, 126.4, 126.1, 126.0, 125.9, 125.6, 121.0, 120.3, 65.3, 41.6, 31.7.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{28}NO_2S$ $[M + H]^+$ 502.1835, found: 502.1830.

(*R*)-*S*-(3-Cyclopropyl-1-(naphthalen-1-ylamino)-1-oxo-2-phenylpropan-2-yl) benzothioate (67)



67

According to **General procedure C**, 2-chloro-3-cyclopropyl-*N*-(naphthalen-1-yl)-2-phenylpropanamide **E65** (35.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **67** as a light yellow solid (40.7 mg, 90% yield, 93% e.e.).

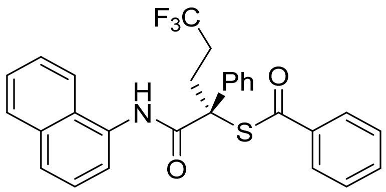
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 9.87 min, t_R (major) = 13.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.17 – 8.08 (m, 1H), 8.07 – 7.98 (m, 2H), 7.87 – 7.79 (m, 1H), 7.73 – 7.56 (m, 5H), 7.53 – 7.46 (m, 3H), 7.46 – 7.38 (m, 4H), 7.38 – 7.34 (m, 1H), 2.53 (dd, *J* = 14.6, 6.4 Hz, 1H), 2.39 (dd, *J* = 14.6, 6.9 Hz, 1H), 0.95 – 0.77 (m, 1H), 0.48 – 0.39 (m, 1H), 0.39 – 0.31 (m, 1H), 0.08 – 0.00 (m, 1H), 0.00 – -0.09 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 170.7, 139.1, 136.9, 134.1(5), 134.1(3), 132.8, 128.9, 128.7, 128.6, 128.0, 127.7, 127.5, 127.2, 126.3, 125.9, 125.8, 125.4, 120.9, 120.1, 66.3, 44.3, 7.1, 5.4, 5.1.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO_2S$ $[M + H]^+$ 452.1679, found:452.1675

(*R*)-*S*-(5,5,5-Trifluoro-1-(naphthalen-1-ylamino)-1-oxo-2-phenylpentan-2-yl) benzothioate (68)



68

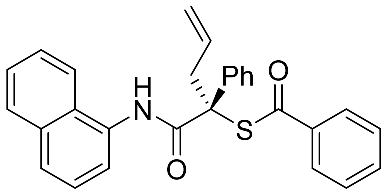
According to **General procedure C**, 2-chloro-5,5,5-trifluoro-*N*-(naphthalen-1-yl)-2-phenylpentanamide **E66** (39.2 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **68** as a yellow solid (42.0 mg, 85% yield, 92% e.e.).

HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 12.82 min, t_R (major) = 15.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.05 – 7.96 (m, 3H), 7.86 – 7.79 (m, 1H), 7.70 – 7.56 (m, 5H), 7.52 – 7.39 (m, 7H), 7.39 – 7.32 (m, 1H), 3.02 – 2.88 (m, 1H), 2.63 – 2.52 (m, 1H), 2.39 – 2.20 (m, 1H), 2.20 – 2.00 (m, 1H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 190.7, 169.8, 137.6, 136.4, 134.6, 134.2, 132.4, 129.3, 129.1, 128.8(2), 128.7(7), 127.8, 127.3, 127.1(0) (q, *J* = 276.4 Hz), 127.0(6), 126.5, 126.0, 125.9, 125.8, 120.8, 120.5, 63.6, 32.2 (q, *J* = 3.0 Hz), 30.4 (q, *J* = 28.6 Hz).
^{19}**F NMR** (376 MHz, $CDCl_3$) δ –66.23.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}F_3NO_2S$ $[M + H]^+$ 494.1396, found: 494.1393.

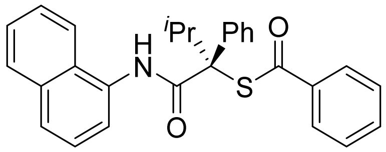
(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylpent-4-en-2-yl) benzothioate (69)



69

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpent-4-enamide **E67** (33.6 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **69** as a light yellow solid (41.1 mg, 94% yield, 90% e.e.).
HPLC analysis: Chiralcel OZ-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 30.88 min, t_R (minor) = 46.89 min.
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.10 – 8.03 (m, 1H), 8.03 – 7.97 (m, 2H), 7.84 – 7.78 (m, 1H), 7.68 – 7.56 (m, 5H), 7.51 – 7.43 (m, 3H), 7.43 – 7.38 (m, 3H), 7.38 – 7.32 (m, 2H), 5.89 – 5.66 (m, 1H), 5.15 – 4.98 (m, 2H), 3.36 – 3.18 (m, 2H).
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 191.7, 170.3, 138.6, 136.8, 134.3, 134.2, 133.0, 132.7, 128.9, 128.8, 128.7, 128.2, 127.7, 127.3 (two carbons overlap), 126.3, 125.9, 125.8, 125.6, 120.9, 120.4, 119.7, 64.8, 43.9.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{24}NO_2S$ $[M + H]^+$ 438.1522, found: 438.1518.

(*R*)-*S*-(3-Methyl-1-(naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) benzothioate (70)

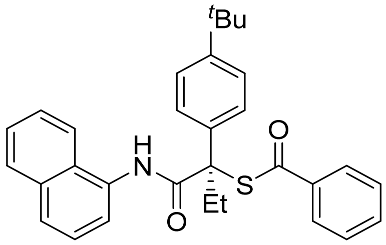


70

According to **General procedure C**, 2-chloro-3-methyl-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E68** (33.8 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **70** as a brown oil (33.0 mg, 75% yield, 89% e.e.).
HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 15.26 min, t_R (major) = 16.09 min.
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.66 – 7.55 (m, 4H), 7.52 – 7.42

(m, 4H), 7.42 – 7.36 (m, 4H), 3.01 – 2.88 (m, 1H), 1.13 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 170.1, 137.0, 136.1, 134.2 (two carbon overlapped), 133.1, 128.9, 128.8, 128.6, 127.9(9), 127.9(6), 127.7, 127.2, 126.3, 125.9, 125.8, 125.3, 121.2, 119.9, 70.0, 36.2, 19.2, 18.9.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{26}NO_2S$ $[M + H]^+$ 440.1679, found: 440.1674.

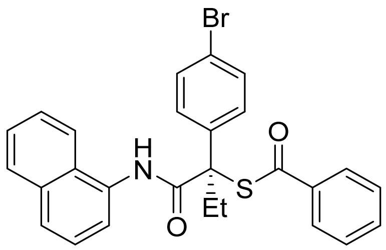
(*R*)-*S*-(2-(4-(*Tert*-butyl)phenyl)-1-(naphthalen-1-ylamino)-1-oxobutan-2-yl) benzothioate (71)



71

According to **General procedure C**, 2-chloro-2-(4-isobutylphenyl)-*N*-(naphthalen-1-yl)butanamide **E69** (48.2 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **71** as a light yellow oil (45.3 mg, 94% yield, 88% e.e.).
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.3 mL/min, λ = 254 nm), t_R (major) = 65.30 min, t_R (minor) = 76.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.11 – 8.01 (m, 3H), 7.82 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.63 – 7.54 (m, 4H), 7.52 – 7.41 (m, 6H), 7.35 (t, J = 7.8 Hz, 1H), 2.77 – 2.64 (m, 1H), 2.60 – 2.49 (m, 1H), 1.37 (s, 9H), 1.01 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 170.8, 151.0, 137.0, 135.4, 134.1, 134.0, 132.7, 128.8, 128.6, 127.6, 127.3, 127.1, 126.2, 125.9, 125.8, 125.6, 125.4, 120.9, 120.3, 66.1, 34.6, 31.7, 31.4, 9.7.
HRMS (ESI) *m/z* calcd. for $C_{31}H_{32}NO_2S$ $[M + H]^+$ 482.2148, found: 482.2142.

(*R*)-*S*-(2-(4-Bromophenyl)-1-(naphthalen-1-ylamino)-1-oxobutan-2-yl) benzothioate (72)

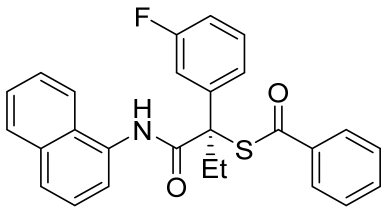


72

According to **General procedure C**, 2-(4-bromophenyl)-2-chloro-*N*-(naphthalen-1-yl)butanamide **E70** (40.3 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **72** as a brown

solid (46.9 mg, 93% yield, 89% e.e.).
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 23.44 min, t_R (major) = 28.73min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.09 – 8.04 (m, 1H), 8.03 – 7.96 (m, 2H), 7.85 – 7.79 (m, 1H), 7.69 – 7.63 (m, 2H), 7.63 – 7.58 (m, 1H), 7.56 – 7.36 (m, 9H), 2.63 – 2.49 (m, 1H), 2.47 – 2.34 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 170.0, 137.9, 136.7, 134.4, 134.2, 132.7, 131.8, 129.3, 129.0, 128.7, 127.7, 127.2, 126.5, 126.0, 125.8, 125.6, 122.1, 120.8, 120.2, 65.6, 32.5, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}BrNO_2S$ $[M + H]^+$ 504.0627, found: 504.0622.

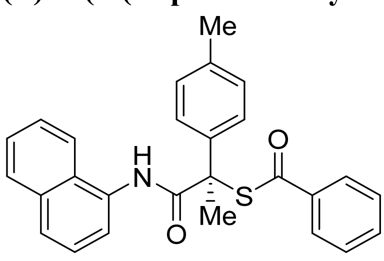
(*R*)-*S*-(2-(3-Fluorophenyl)-1-(naphthalen-1-ylamino)-1-oxobutan-2-yl) benzothioate (73)



73

According to **General procedure C**, 2-chloro-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)butanamide **E71** (34.2 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **73** as a yellow solid (39.9 mg, 90% yield, 90% e.e.).
HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 16.56 min, t_R (major) = 19.17 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.09 – 8.03 (m, 1H), 8.03 – 7.96 (m, 2H), 7.84 – 7.78 (m, 1H), 7.68 – 7.63 (m, 2H), 7.63 – 7.57 (m, 1H), 7.51 – 7.42 (m, 4H), 7.42 – 7.33 (m, 4H), 7.09 – 7.03 (m, 1H), 2.66 – 2.54 (m, 1H), 2.48 – 2.37 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 169.9, 162.9 (d, *J* = 246.6 Hz), 141.4 (d, *J* = 7.1 Hz), 136.7, 134.4, 134.2, 132.7, 130.2 (d, *J* = 8.3 Hz), 129.0, 128.7, 127.7, 127.3, 126.4, 126.0, 125.8, 125.7, 123.2 (d, *J* = 2.8 Hz), 120.8, 120.3, 115.1 (d, *J* = 21.0 Hz), 114.8 (d, *J* = 23.5 Hz), 65.6 (d, *J* = 1.8 Hz), 32.5, 9.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ –111.88.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}FNO_2S$ $[M + H]^+$ 444.1428, found: 444.1421.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-(*p*-tolyl)propan-2-yl) benzothioate (74)



74

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-(p-tolyl)propanamide **E72** (32.4 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **74** as a yellow solid (39.2 mg, 92% yield, 91% e.e.).

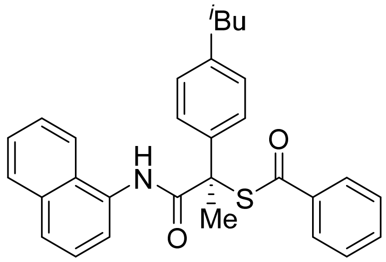
HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 19.06 min, t_R (minor) = 25.50 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.13 – 8.09 (m, 1H), 8.02 – 7.97 (m, 2H), 7.84 – 7.80 (m, 1H), 7.71 – 7.64 (m, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.52 (m, 2H), 7.51 – 7.42 (m, 4H), 7.42 – 7.36 (m, 1H), 7.24 – 7.20 (m, 2H), 2.37 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 170.7, 138.1, 137.9, 136.7, 134.2(1), 134.1(7), 132.8, 129.8, 128.9, 128.7, 127.7, 127.2, 126.5, 126.4, 126.0, 125.9, 125.5, 120.9, 120.2, 61.2, 27.8, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{24}NO_2S$ $[M + H]^+$ 426.1522, found: 426.1516.

(*R*)-*S*-(2-(4-Isobutylphenyl)-1-(naphthalen-1-ylamino)-1-oxopropan-2-yl) benzothioate (75)



75

According to **General procedure C**, 2-chloro-2-(4-isobutylphenyl)-*N*-(naphthalen-1-yl)propanamide **E73** (36.6 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **75** as a brown solid (42.1 mg, 90% yield, 93% e.e.).

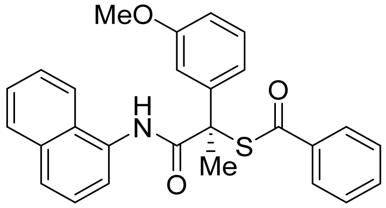
HPLC analysis: Chiralcel IA (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 11.79 min, t_R (minor) = 14.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.12 – 8.05 (m, 1H), 8.02 – 7.95 (m, 2H), 7.84 – 7.78 (m, 1H), 7.69 – 7.63 (m, 1H), 7.63 – 7.53 (m, 4H), 7.52 – 7.39 (m, 4H), 7.38 – 7.31 (m, 1H), 7.22 – 7.16 (m, 2H), 2.50 (d, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 1.96 – 1.80 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 170.7, 141.9, 138.0, 136.8, 134.1(6), 134.1(3), 132.7, 129.8, 128.9, 128.7, 127.6, 127.2, 126.5, 126.3, 125.9(4), 125.9(1), 125.5, 120.8, 120.2, 61.3, 45.1, 30.2, 27.5, 22.6, 22.5.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{29}NO_2S$ $[M + H]^+$ 468.1992, found: 468.1987.

(*R*)-*S*-(2-(3-Methoxyphenyl)-1-(naphthalen-1-ylamino)-1-oxopropan-2-yl) benzothioate (76)



76

According to **General procedure C**, 2-chloro-2-(3-methoxyphenyl)-*N*-(naphthalen-1-yl)propanamide **E74** (34.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **76** as a light yellow solid (40.2 mg, 91% yield, 92% e.e.).

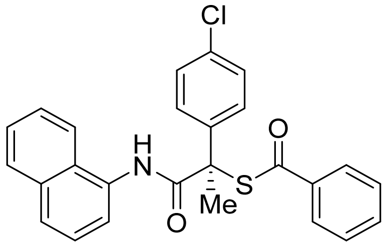
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 41.58 min, t_R (minor) = 47.27 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.11 – 8.06 (m, 1H), 8.02 – 7.96 (m, 2H), 7.84 – 7.79 (m, 1H), 7.72 – 7.64 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.41 (m, 4H), 7.41 – 7.36 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.22 (t, *J* = 2.2 Hz, 1H), 6.92 – 6.87 (m, 1H), 3.77 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 170.4, 160.0, 142.5, 136.7, 134.2(4), 134.1(6), 132.7, 130.1, 128.9, 128.7, 127.7, 127.3, 126.4, 126.0, 125.9, 125.6, 120.9, 120.3, 118.9, 113.4, 112.8, 61.2, 55.4, 27.8.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{24}NO_2S$ $[M + H]^+$ 442.1471, found: 442.1465.

(*R*)-*S*-(2-(4-Chlorophenyl)-1-(naphthalen-1-ylamino)-1-oxopropan-2-yl) benzothioate (77)



77

According to **General procedure C**, 2-chloro-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)propanamide **E75** (34.4 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **77** as a brown solid (40.6 mg, 91% yield, 95% e.e.).

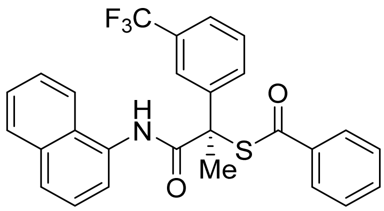
HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 47.99 min, t_R (major) = 52.05min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.12 – 8.04 (m, 1H), 8.02 – 7.94 (m, 2H), 7.86 – 7.79 (m, 1H), 7.72 – 7.65 (m, 2H), 7.63 – 7.55 (m, 3H), 7.51 – 7.40 (m, 5H), 7.40 – 7.34 (m, 2H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 170.1, 139.6, 136.4, 134.5, 134.1(7), 134.1(2), 132.6, 129.2, 129.0, 128.8, 128.1, 127.7, 127.2, 126.5, 126.0, 125.9, 125.7, 120.7, 120.3, 60.6, 28.0.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}ClNO_2S$ $[M + H]^+$ 446.0976, found: 446.0971.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-(3-(trifluoromethyl)phenyl)propan-2-yl) benzothioate (78)



78

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-(3-(trifluoromethyl)phenyl)propanamide **E76** (37.8 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **78** as a light yellow oil (45.6 mg, 95% yield, 84% e.e.).

HPLC analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 22.00 min, t_R (major) = 27.05 min.

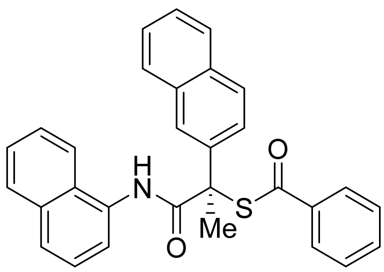
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.05 – 7.92 (m, 4H), 7.88 – 7.80 (m, 2H), 7.71 – 7.66 (m, 2H), 7.65 – 7.57 (m, 2H), 7.56 – 7.51 (m, 1H), 7.51 – 7.37 (m, 5H), 2.19 – 2.08 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 169.9, 142.2, 136.3, 134.6, 134.2, 132.4, 131.4 (q, *J* = 32.2 Hz), 130.1, 129.6, 129.0, 128.7, 127.7, 127.5, 126.5, 126.1, 126.0, 125.8, 125.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.7 Hz), 123.6 (q, *J* = 4.0, 3.5 Hz), 120.8(2), 120.7(9), 60.6, 27.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.52.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{21}F_3NO_2S$ $[M + H]^+$ 480.1240, found: 480.1232.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-2-(naphthalen-2-yl)-1-oxopropan-2-yl) benzothioate (79)



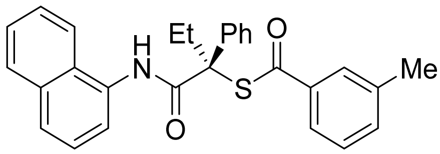
79

According to **General procedure C**, 2-chloro-*N*-(naphthalen-1-yl)-2-(naphthalen-2-yl)propanamide **E77** (36.0 mg, 0.10 mmol, 1.0 eq.) with thiobenzoic acid **S9** (17.7 μL, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **79** as a white solid (40.2 mg, 87% yield, 88% e.e.).

HPLC analysis: Chiralcel AD-3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 22.63 min, t_R (minor) = 29.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.16 – 8.07 (m, 2H), 8.05 – 7.97 (m, 2H), 7.92 – 7.87 (m, 1H), 7.87 – 7.76 (m, 4H), 7.71 – 7.65 (m, 2H), 7.63 – 7.57 (m, 1H), 7.55 – 7.48 (m, 3H), 7.48 – 7.38 (m, 3H), 7.34 – 7.28 (m, 1H), 2.21 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 170.6, 138.3, 136.7, 134.3, 134.2, 133.3, 132.9, 132.8, 129.0(3), 128.9(7), 128.7, 128.4, 127.7(4), 127.7(2), 127.4, 126.8 (two carbon overlapped), 126.4, 126.0, 125.9(0), 125.8(5), 125.7, 124.3, 120.9, 120.5, 61.5, 27.9.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{24}NO_2S$ $[M + H]^+$ 462.1522, found: 462.1519.

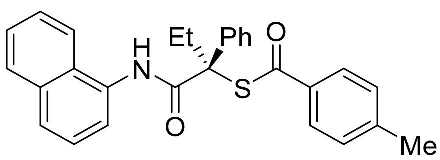
(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 3-methylbenzothioate (80)



80

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 3-methylbenzothioate **S10** (28.5 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **80** as a colorless oil (41.8 mg, 95% yield, 95% e.e.).
HPLC analysis: Chiralcel AD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 20.23 min, t_R (major) = 23.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.11 – 8.04 (m, 1H), 7.84 – 7.76 (m, 3H), 7.67 – 7.59 (m, 4H), 7.49 – 7.44 (m, 1H), 7.44 – 7.30 (m, 7H), 2.67 – 2.55 (m, 1H), 2.50 – 2.40 (m, 1H), 2.38 (s, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 170.6, 138.8, 138.6, 136.9, 135.0, 134.1, 132.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.5, 127.2, 126.3, 125.9, 125.8, 125.4, 124.9, 120.9, 120.1, 66.1, 32.4, 21.4, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{26}NO_2S$ $[M + H]^+$ 440.1679, found: 440.1675.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 4-methylbenzothioate (81)

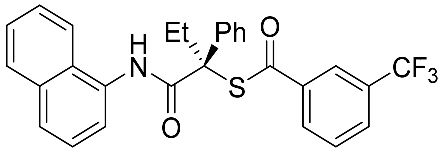


81

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 4-methylbenzothioate **S11** (28.5 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **81** as a brown oil (41.8 mg, 95% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 24.88 min, t_R (major) = 27.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.12 – 8.05 (m, 1H), 7.95 – 7.87 (m, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.68 – 7.58 (m, 4H), 7.50 – 7.45 (m, 1H), 7.45 – 7.32 (m, 5H), 7.28 – 7.22 (m, 2H), 2.66 – 2.53 (m, 1H), 2.48 – 2.36 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 170.7, 145.3, 138.7, 134.4, 134.2, 132.9, 129.6, 128.6(7), 128.6(4), 128.0, 127.8, 127.5, 127.3, 126.3, 125.9(1), 125.8(6), 125.4, 121.0, 120.1, 65.9, 32.5, 21.9, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{26}NO_2S$ $[M + H]^+$ 440.1670, found: 440.1679.

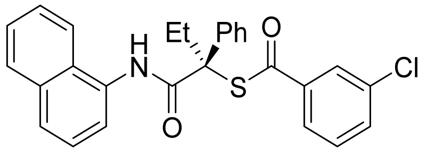
(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 3-(trifluoromethyl)-benzothioate (82)



82

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 3-(trifluoromethyl)benzothioate **S12** (36.6 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **82** as a brown solid (45.4 mg, 92% yield, 96% e.e.).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 16.17 min, t_R (major) = 17.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.28 – 8.22 (m, 1H), 8.21 – 8.15 (m, 1H), 8.10 – 8.02 (m, 1H), 7.88 – 7.77 (m, 2H), 7.69 – 7.62 (m, 3H), 7.62 – 7.56 (m, 1H), 7.56 – 7.52 (m, 1H), 7.50 – 7.46 (m, 1H), 7.46 – 7.33 (m, 5H), 2.76 – 2.62 (m, 1H), 2.56 – 2.42 (m, 1H), 0.98 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 170.1, 138.3, 137.5, 134.1, 132.6, 131.5 (q, J = 33.3 Hz), 130.8, 130.4 (q, J = 3.5 Hz), 129.6, 128.9, 128.8, 128.3, 127.5, 127.2, 126.4, 126.0, 125.8, 125.6, 124.4 (q, J = 3.8 Hz), 123.5 (q, J = 272.6 Hz), 120.6, 120.2, 66.9, 32.0, 9.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.79.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}F_3NO_2S$ $[M + H]^+$ 494.1387, found: 494.1396.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 3-chlorobenzo-thioate (83)

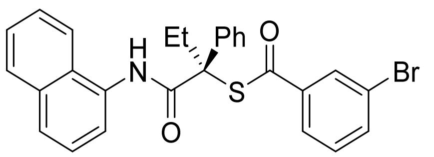


83

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 3-chlorobenzothioate **S13** (31.6 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **83** as a yellow solid (45.5 mg, 99% yield, 95% e.e.).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 214

nm), t_R (minor) = 18.98 min, t_R (major) = 21.44 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.08 – 8.03 (m, 1H), 7.99 – 7.94 (m, 1H), 7.91 – 7.85 (m, 1H), 7.83 – 7.77 (m, 1H), 7.68 – 7.59 (m, 3H), 7.59 – 7.51 (m, 2H), 7.50 – 7.45 (m, 1H), 7.45 – 7.33 (m, 6H), 2.72 – 2.57 (m, 1H), 2.53 – 2.37 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 170.2, 138.3, 135.2, 134.1, 134.0(two carbons overlap), 132.6, 130.2, 128.8, 128.7, 128.2, 127.6, 127.5, 127.2, 126.4, 126.0, 125.8, 125.7, 125.6, 120.7, 120.2, 66.7, 32.1, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}ClNO_2S$ $[M + H]^+$ 460.1133, found: 460.1120.

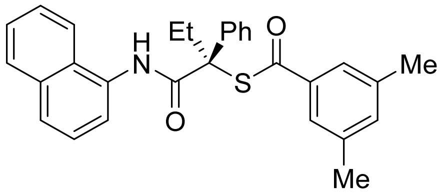
(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 3-bromobenzo-thioate (84)



84

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 3-bromobenzothioate **S14** (38.3 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **84** as a yellow solid (50.0 mg, 99% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 19.92 min, t_R (major) = 22.64 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.14 – 8.08 (m, 1H), 8.08 – 8.02 (m, 1H), 7.96 – 7.88 (m, 1H), 7.84 – 7.77 (m, 1H), 7.72 – 7.67 (m, 1H), 7.67 – 7.59 (m, 3H), 7.58 – 7.53 (m, 1H), 7.49 – 7.34 (m, 6H), 7.34 – 7.27 (m, 1H), 2.76 – 2.53 (m, 1H), 2.53 – 2.33 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 170.2, 138.5, 138.3, 136.9, 134.1, 132.6, 130.5, 130.4, 128.8, 128.7, 128.2, 127.5, 127.2, 126.4, 126.2, 126.0, 125.8, 125.6, 123.1, 120.7, 120.2, 66.7, 32.1, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}BrNO_2S$ $[M + H]^+$ 504.0627, found: 504.0616.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 3,5-dimethylbenzo-thioate (85)

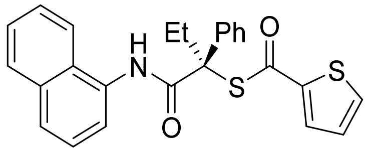


85

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 3,5-dimethylbenzothioate **S15** (30.6 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **85** as a yellow oil (42.2 mg, 93% yield, 95% e.e.).

HPLC analysis: Chiralcel AD-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 17.19 min, t_R (major) = 22.22 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.57 (m, 6H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.32 (m, 5H), 7.21 (s, 1H), 2.65 – 2.55 (m, 1H), 2.49 – 2.38 (m, 1H), 2.34 (s, 6H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 170.7, 138.6(8), 138.6(5), 136.9, 135.8, 134.1, 132.9, 128.6, 128.6, 128.0, 127.5, 127.2, 126.3, 125.8(8), 125.8(3), 125.4(two carbons overlap), 121.0, 120.1, 66.0, 32.4, 21.3, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{28}NO_2S$ $[M + H]^+$ 454.1835, found: 454.1834.

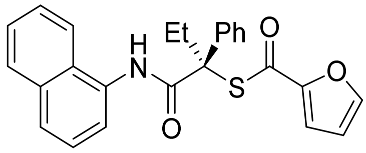
(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) thiophene-2-carbothioate (86)



86

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium thiophene-2-carbothioate **S16** (27.3 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **86** as a brown solid (42.8 mg, 99% yield, 96% e.e.).
HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 95/15, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 25.66 min, t_R (major) = 28.32 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.11 – 8.02 (m, 1H), 7.93 – 7.87 (m, 1H), 7.83 – 7.77 (m, 1H), 7.68 – 7.57 (m, 5H), 7.50 – 7.44 (m, 1H), 7.44 – 7.30 (m, 5H), 7.13 – 7.08 (m, 1H), 2.65 – 2.54 (m, 1H), 2.47 – 2.36 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 170.4, 141.5, 138.5, 134.1 (two carbon overlapped), 132.8, 132.3, 128.7, 128.6, 128.3, 128.1, 127.4, 127.3, 126.3, 125.9, 125.8, 125.5, 121.0, 120.2, 66.7, 32.5, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}NO_2S$ $[M + H]^+$ 432.1086, found: 432.1081.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) furan-2-carbothioate (87)

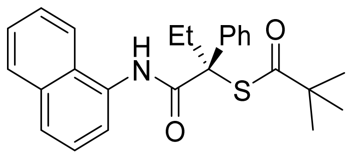


87

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium furan-2-carbothioate **S17** (25.0 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **87** as a brown oil (41.2 mg, 99% yield, 92% e.e.).
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 16.58 min, t_R (major) = 19.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.10 – 8.04 (m, 1H), 7.83 – 7.77 (m, 1H), 7.68 – 7.56 (m, 5H), 7.50 – 7.44 (m, 1H), 7.44 – 7.32 (m, 5H), 7.25 – 7.22 (m, 1H), 6.56 – 6.50 (m, 1H), 2.67 – 2.52 (m, 1H), 2.50 – 2.35 (m, 1H), 0.95 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 170.4, 150.4, 147.1, 138.5, 134.1, 132.8, 128.7, 128.6, 128.1, 127.4, 127.2, 126.3, 125.9, 125.8, 125.5, 120.9, 120.1, 117.2, 112.7, 66.1, 32.5, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}NO_3S$ $[M + H]^+$ 416.1315, found: 416.1303.

(*R*)-*S*-(1-(Naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) 2,2-dimethyl-propanethioate (88)

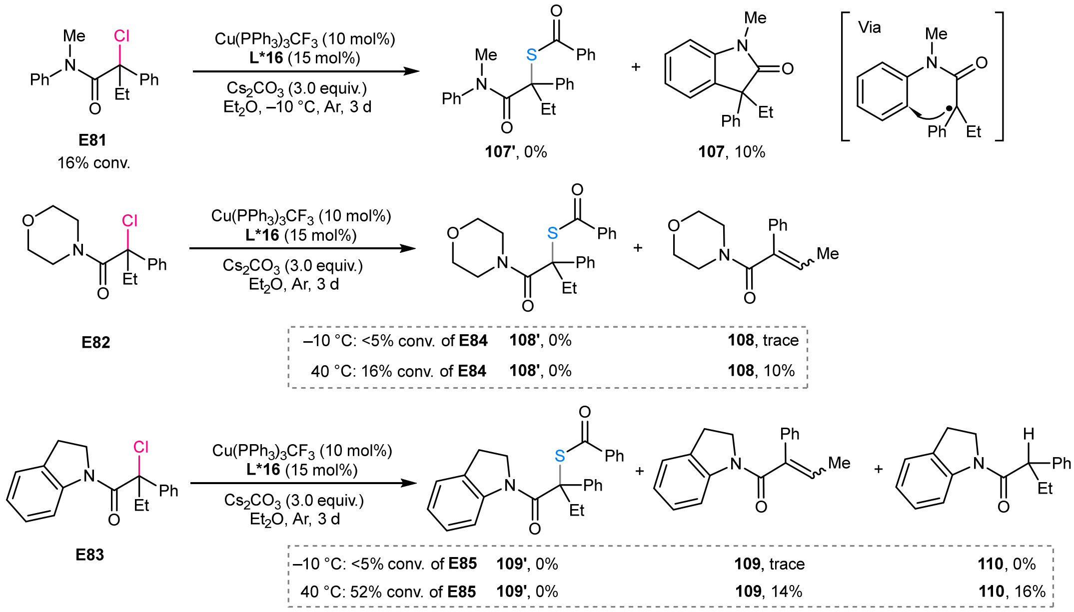


88

According to **General procedure D**, 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide **E60** (32.4 mg, 0.10 mmol, 1.0 eq.) with potassium 2,2-dimethylpropanethioate **S18** (23.4 mg, 0.15 mmol, 1.5 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 10/1) to yield the product **88** as a yellow oil (40.2 mg, 99% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 9.29 min, t_R (minor) = 12.95 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.09 – 8.02 (m, 1H), 7.85 – 7.77 (m, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.56 – 7.51 (m, 2H), 7.51 – 7.42 (m, 2H), 7.41 – 7.30 (m, 4H), 2.56 – 2.44 (m, 1H), 2.37 – 2.25 (m, 1H), 1.28 (s, 9H), 0.88 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 170.8, 138.8, 134.2, 133.0, 128.7, 128.6, 127.9, 127.3(3), 127.2(6), 126.2, 125.9(4), 125.9(1), 125.4, 121.0, 120.1, 65.2, 47.7, 32.3, 27.5, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{28}NO_2S$ $[M + H]^+$ 406.1835, found: 406.1824.

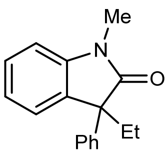
8. Investigation of other electrophiles

Investigation of tertiary alkyl chlorides containing no N–H bond



We examined the reaction of tertiary α-carbonyl alkyl chlorides containing no N–H bond. Under the standard conditions, **E81** gave rise to the corresponding radical cyclization product **107** rather than C–S coupling product **107'**. Under the standard conditions, almost no conversion of **E82** was observed. Only 16% conversion of **E82** was observed at an elevated temperature (40 °C), and the reaction afforded no desired product **108'** but elimination by-product **108** (10% yield). Under the standard conditions, no conversion of **E83** was observed as well. At 40 °C, the reaction of **E83** afforded no desired product **109'**, but furnished the elimination by-product **109** and hydrogen atom abstraction by-product **110**. These results revealed that the N–H bond on tertiary α-carbonyl alkyl chlorides is crucial in tuning reactivity and chemoselectivity.

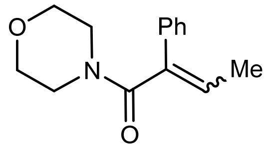
3-Ethyl-1-methyl-3-phenylindolin-2-one (107)



107

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 5H), 7.25 – 7.18 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 3.22 (s, 3H), 2.48 – 2.38 (m, 1H), 2.29 – 2.17 (m, 1H), 0.68 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 144.2, 140.4, 132.2, 128.6, 128.2, 127.3, 127.1, 124.9, 122.7, 108.3, 57.5, 31.0, 26.4, 9.2.
Note: **107** is a known compound[12].

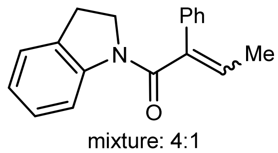
1-Morpholino-2-phenylbut-2-en-1-one (108)



108

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 6.19 (q, *J* = 7.1 Hz, 1H), 3.85 – 3.76 (m, 2H), 3.76 – 3.70 (m, 2H), 3.55 – 3.45 (m, 2H), 3.41 – 3.33 (m, 2H), 1.87 (d, *J* = 7.1 Hz, 3H).
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 168.7, 137.5, 136.0, 128.9, 127.9, 125.3, 124.8, 67.0, 66.9, 46.8, 41.6, 15.6.
HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1332, found: 232.1327.

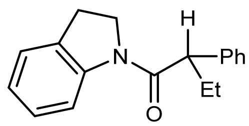
1-(Indolin-1-yl)-2-phenylbut-2-en-1-one (109)



109

^{1}**H NMR** (400 MHz, $CDCl_3$) (major) δ 8.40 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.18 (q, *J* = 7.1 Hz, 1H), 3.80 (t, *J* = 8.4 Hz, 2H), 3.06 (t, *J* = 8.4 Hz, 2H), 1.91 (d, *J* = 7.0 Hz, 3H).
^{13}**C NMR** (100 MHz, $CDCl_3$) (major) δ 168.0, 142.6, 139.7, 135.8, 131.9, 128.9, 127.9, 127.7, 125.5, 124.8, 124.7, 124.3, 117.4, 48.5, 28.1, 15.6.
HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO$ $[M + H]^+$ 264.1383, found: 264.1386.

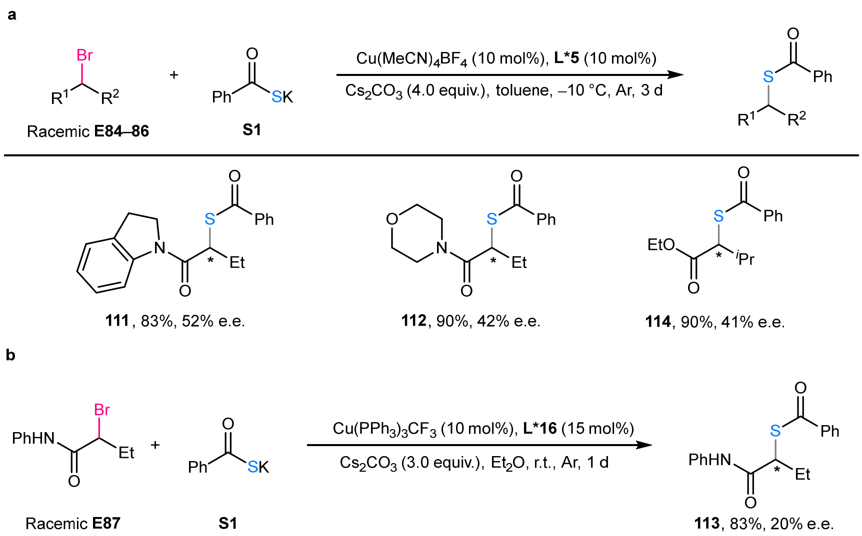
1-(indolin-1-yl)-2-phenylbutan-1-one (110)



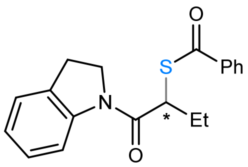
110

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.26 – 7.14 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.88 – 3.77 (m, 1H), 3.57 (t, *J* = 7.3 Hz, 1H), 3.18 – 3.05 (m, 1H), 3.05 – 2.91 (m, 1H), 2.28 – 2.15 (m, 1H), 1.89 – 1.72 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 171.6, 143.4, 139.5, 131.2, 128.9, 128.2, 127.5, 127.1, 124.5, 123.7, 117.3, 54.0, 47.8, 28.1, 28.1, 12.6.
HRMS (ESI) *m/z* calcd for $C_{18}H_{19}NNaO$ $[M + Na]^+$ 288.1359, found: 288.1361.

Investigation of other secondary alkyl bromides



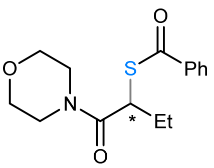
S-(1-(Indolin-1-yl)-1-oxobutan-2-yl) benzothioate (111)



111

HPLC analysis: Chiralcel AD-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 14.81 min, t_R (major) = 19.04 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.03 – 7.84 (m, 2H), 7.64 – 7.52 (m, 1H), 7.52 – 7.37 (m, 2H), 7.24 – 7.14 (m, 2H), 7.07 – 7.00 (m, 1H), 4.62 (t, *J* = 7.4 Hz, 1H), 4.43 – 4.30 (m, 1H), 4.28 – 4.14 (m, 1H), 3.22 (t, *J* = 8.5 Hz, 2H), 2.30 – 2.14 (m, 1H), 2.01 – 1.85 (m, 1H), 1.09 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 169.1, 143.0, 136.4, 134.0, 131.8, 128.9, 127.7, 127.6, 124.7, 124.3, 117.6, 48.3, 47.4, 28.2, 26.4, 12.0.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}NO_2S$ $[M + H]^+$326.1209, found: 326.1208.

S-(1-Morpholino-1-oxobutan-2-yl) benzothioate (112)

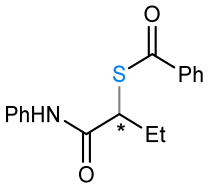


112

HPLC analysis: Chiralcel AD-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 10.21 min, t_R (major) = 11.33 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.81 (m, 2H), 7.66 – 7.54 (m, 1H), 7.51 – 7.38 (m, 2H), 4.64 (t, *J* = 7.3 Hz, 1H), 3.77 – 3.55 (m, 8H), 2.19 – 2.03 (m, 1H), 1.94 – 1.80 (m, 1H), 1.03 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 169.8, 136.3, 134.0, 128.9, 127.5, 67.0, 66.9, 46.7, 43.8, 42.9, 26.4, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}NO_3S$ $[M + H]^+$ 294.1158, found: 294.1156.

S-(1-Oxo-1-(phenylamino)butan-2-yl) benzothioate (113)



113

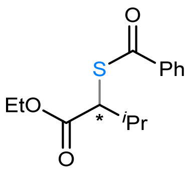
HPLC analysis: Chiralcel AD-H (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 12.83 min, t_R (major) = 15.56 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.01 – 7.93 (m, 2H), 7.65 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.51 – 7.43 (m, 2H), 7.34 – 7.27 (m, 2H), 7.12 – 7.06 (m, 1H), 4.20 (t, J = 7.6 Hz, 1H), 2.34 – 2.16 (m, 1H), 1.96 – 1.83 (m, 1H), 1.12 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 169.1, 138.0, 136.3, 134.3, 129.1, 129.0, 127.6, 124.5, 119.9, 48.5, 23.4, 12.3.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}NO_2S$ $[M + H]^+$300.1053, found: 300.1054.

Ethyl 2-(benzoylthio)-3-methylbutanoate (114)



114

HPLC analysis: Chiralcel AD-H (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 11.09 min, t_R (major) = 14.57 min.

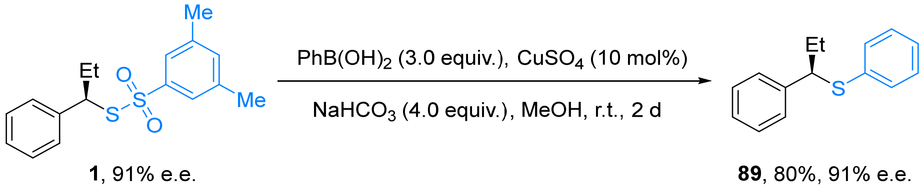
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.61 – 7.54 (m, 1H), 7.50 – 7.41 (m, 2H), 4.34 (d, J = 6.6 Hz, 1H), 4.27 – 4.18 (m, 2H), 2.42 – 2.28 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.07 (dd, J = 6.8, 5.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 171.5, 136.7, 133.8, 128.8, 127.6, 61.6, 53.4, 30.9, 20.5, 19.9, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}O_3S$ $[M + H]^+$ 267.1049, found: 267.1050.

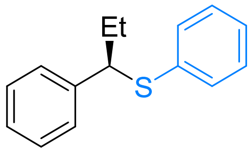
9. Procedure for synthetic applications (89–102)

The synthesis of 89



To a mixture of copper(II) sulfate (16.0 mg, 0.1 mmol, 10 mol%) and sodium bicarbonate (336.0 mg, 4.0 mmol, 4.0 equiv.) was added a solution of corresponding thiosulfonates **1** (320.5 mg, 1.0 mmol, 1.0 equiv.) and phenylboronic acid (366.0 mg, 3.0 mmol, 3.0 equiv.) dissolved in methanol (5.0 mL) at room temperature. After stirring for 48 hours at the same temperature, the mixture was passed through a short pad of silica gel with EtOAc and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 100/1 ~ 20/1) to give product **89** (183.3 mg, 80%, 91% e.e.) as a white solid.

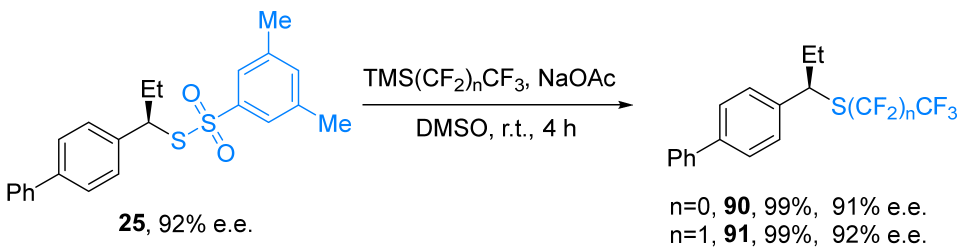
(*R*)-Phenyl(1-phenylpropyl)sulfane (89)



89

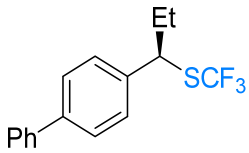
HPLC analysis: Chiralcel OJ-H (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.68 min, t_R (major) = 13.98 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 6H), 7.22 – 7.15 (m, 4H), 4.05 (dd, *J* = 8.8, 6.0 Hz, 1H), 2.07 – 1.86 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 135.3, 132.4, 128.7, 128.4, 128.0, 127.2, 127.0, 55.4, 29.5, 12.4.
HRMS (ESI) *m/z* calcd for $C_{15}H_{17}S$ $[M + H]^+$ 229.1045, found: 229.1042.

The synthesis of 90 or 91



An oven-dried Schlenk tube was sequentially charged with the corresponding thiosulfonates **25** (79.3 mg, 0.2 mmol, 1.0 equiv) and NaOAc (49.2 mg, 0.6 mmol, 3.0 equiv). Anhydrous DMSO (1.0 mL) was then added followed by dropwise addition of $TMS(CF_2)_nCF_3$ (n = 0 or 1) (3.0 equiv) with stirring. Then the reaction was stirred at room temperature for 4 hours. After the reaction was completed, it was diluted with DCM. The organic layer was washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding perfluoroalkyl sulfides **90** or **91**.

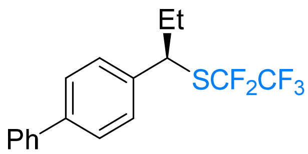
(*R*)-(1-([1,1'-Biphenyl]-4-yl)propyl)(trifluoromethyl)sulfane (90)



90

25 with Me_3SiCF_3 (88.8 μL, 0.6 mmol, 3.0 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **90** as a light yellow solid (58.7 mg, 99% yield, 91% e.e.).
HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.55 min, t_R (minor) = 17.61 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.30 (m, 3H), 4.24 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.14 – 1.91 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.6, 139.6, 130.8 (q, *J* = 307.2 Hz), 128.9, 128.0, 127.6, 127.5, 127.2, 51.2 (d, *J* = 1.7 Hz), 30.0, 12.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ –39.66.
HRMS (ESI) *m/z* calcd for $C_{16}H_{16}F_3S$ $[M + H]^+$ 297.0919, found: 297.0933.

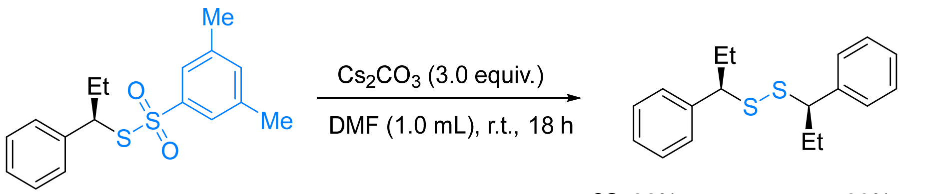
(*R*)-(1-([1,1'-Biphenyl]-4-yl)propyl)(perfluoroethyl)sulfane (91)



91

25 with $Me_3SiCF_2CF_3$ (105.2 μL, 0.6 mmol, 3.0 eq.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **91** as a white solid (68.6 mg, 99% yield, 92% e.e.).
HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.60 min, t_R (minor) = 15.65 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.30 (m, 3H), 4.34 (dd, *J* = 8.8, 6.5 Hz, 1H), 2.17 – 1.96 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.6, 139.8, 128.9, 128.0(4), 127.5(9), 127.5(8), 127.2, 122.0 (tq, *J* = 40.6 Hz), 118.7 (qt, *J* = 36.4 Hz), 50.1 (t, *J* = 2.6 Hz), 30.7, 12.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ –83.41 (t, *J* = 3.9 Hz, 3F), –90.31 (q, *J* = 3.8 Hz, 1F), –90.45 (q, *J* = 4.0 Hz, 1F).
HRMS (ESI) *m/z* calcd for $C_{17}H_{16}F_5S$ $[M + H]^+$ 347.0887, found: 347.0882.

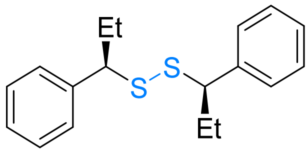
The synthesis of 92



1, 91% e.e.   **92**, 86%, d.r. = 10 : 1, >99% e.e.

An oven-dried Schlenk tube was sequentially charged with the corresponding thiosulfonates **1** (64.1 mg, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (195.6 mg, 0.6 mmol, 3.0 equiv). Anhydrous DMF (1.0 mL) was then added, then the reaction was stirred at room temperature for 18 hours. After the reaction was completed, it was diluted with DCM. The organic layer was washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether) to afford the product **92** (52.0 mg, 86%, d.r. = 10:1, >99% e.e.) as a light yellow solid. The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

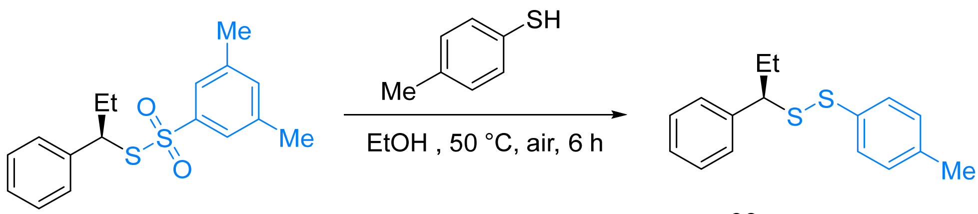
1,2-Bis((*R*)-1-phenylpropyl)disulfane (92)



92

HPLC analysis: Chiralcel OJ-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 6.64 min, t_R (major) = 8.82 min, t_R (meso) = 10.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 6H + 6H × 0.1), 7.19 – 7.12 (m, 4H + 4H × 0.1), 3.23 (dd, *J* = 9.1, 6.1 Hz, 2H × 0.1) 3.16 (dd, *J* = 9.6, 5.6 Hz, 2H), 2.09 – 1.98 (m, 2H), 1.97 – 1.91 (m, 2H × 0.1), 1.78 (m, 2H + 2H × 0.1), 0.81 – 0.71 (m, 6H + 6H × 0.1).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 128.5 (two carbon overlapped), 127.5, 57.0, 27.8, 12.3.
HRMS (ESI) *m/z* calcd for $C_{18}H_{23}S_2$ $[M + H]^+$ 303.1236, found: 303.1227.

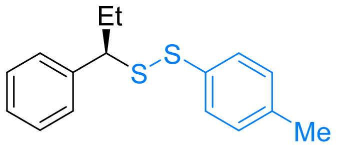
The synthesis of 93



1, 91% e.e.   **93**, 98%, 91% e.e.

A mixture of corresponding thiosulfonates **1** (64.1 mg, 0.2 mmol, 1.0 equiv.) and 4-methylphenylthiol (24.8 mg, 0.2 mmol, 1.0 equiv.) in EtOH (1.0 mL) was stirred at 50 °C for 6 hours in air. After the residue was dissolved in Et_2O, the solution was washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether) to afford the product **93** (53.8 mg, 98%, 91% e.e.) as white solid.

(*R*)-1-(1-Phenylpropyl)-2-(*p*-tolyl)disulfane (93)



93

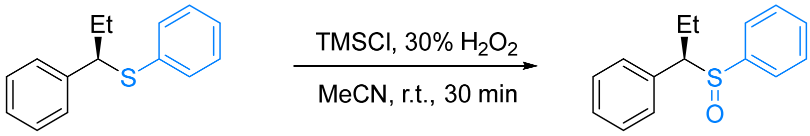
HPLC analysis: Chiralcel OJ (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 15.54 min, t_R (major) = 19.50 min .

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 4H), 7.25 – 7.20 (m, 3H), 7.05 (d, *J* = 8.1 Hz, 2H), 3.79 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.31 (s, 3H), 2.20 – 2.09 (m, 1H), 1.98 – 1.85 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.9, 134.3, 129.7, 128.6, 128.4, 128.3, 127.6, 57.7, 28.0, 21.1, 12.4.

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}S_2$ $[M + H]^+$ 275.0923, found: 275.0918.

The synthesis of 94

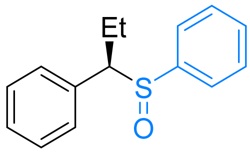


89, 91% e.e.

94, 99%, d.r. = 2.8:1
91% e.e. (major), 91% e.e. (minor)

In a round bottomed flask (10 mL) equipped with a stir bar, a solution of **89** (45.7 mg, 0.20 mmol, 1.0 equiv.) in CH_3CN (1.0 mL) was prepared, the solution was cooled to 0 °C. Aqueous 30% H_2O_2 (40.0 μL, 0.4 mmol, 2.0 equiv.) and Me_3SiCl (17.6 μL, 0.20 mmol, 1.0 equiv.) were added and the mixture was stirred at room temperature for 30 min. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (10 mL), extracted with EtOAc (3 × 5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 20/1 ~ 3/1) to afford the product **94** (48.4 mg, 99%, d.r. = 2.8:1, 91% e.e. (major), 91% e.e. (minor)) as a white solid. The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

(((*R*)-1-Phenylpropyl)sulfinyl)benzene (94)

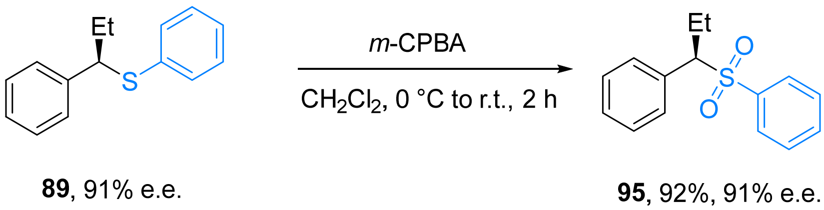


94

HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ =

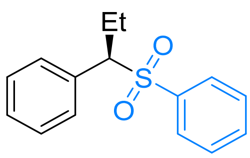
214 nm), t_R (minor1) = 17.38 min, t_R (major2) = 18.84 min, t_R (minor2) = 20.04 min, t_R (major1) = 26.49 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 1H + 1H × 0.36), 7.32 – 7.13 (m, 7H + 5H × 0.36), 7.11 – 7.07 (m, 2H × 0.36), 6.94 – 6.88 (m, 2H), 6.88 – 6.84 (m, 2H × 0.36), 3.57 (m, 1H + 1H × 0.36), 2.50 – 2.39 (m, 1H), 2.39 – 2.29 (m, 1H × 0.36), 2.12 – 2.00 (m, 1H), 2.00 – 1.92 (m, 1H × 0.36), 1.03 (t, J = 7.4 Hz, 3H× 0.36), 0.90 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$), (major), δ 142.3, 133.6, 131.0, 129.3, 128.5(3), 128.4(6), 128.0, 125.0, 75.0, 22.4, 11.6.
^{13}C NMR (100 MHz, $CDCl_3$), (minor), δ 141.3, 132.2, 130.7, 129.4, 128.4, 128.3, 128.1, 124.8, 72.2, 21.4, 12.1.
HRMS (ESI) *m/z* calcd for $C_{15}H_{17}OS$ $[M + H]^+$ 245.0995, found: 245.0989.

The synthesis of 95



In a round-bottomed flask (10 mL) equipped with a stir bar, a solution of **89** (45.7 mg, 0.20 mmol, 1.0 equiv.) in CH_2Cl_2 (0.8 mL) was prepared. The solution was cooled to 0 °C. A solution of *m*-CPBA (purity: 85%, 162.4 mg, 0.8 mmol, 4.0 equiv.) in CH_2Cl_2 (4.0 mL) was added dropwise and the mixture was stirred at room temperature for 2 hours. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (10 mL), extracted with EtOAc (3 × 5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 20/1 ~ 3/1) to afford the product **95** (47.9 mg, 92%, 91% e.e.) as a white solid.

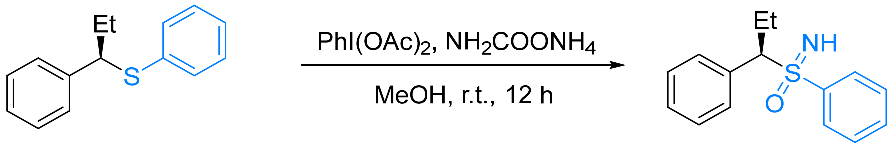
(*R*)-((1-Phenylpropyl)sulfonyl)benzene (95)



95

HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 7.96 min, t_R (major) = 9.88 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 3H), 7.36 (t, J = 7.7 Hz, 2H), 7.30 – 7.19 (m, 3H), 7.09 (d, J = 7.4 Hz, 2H), 3.96 (dd, J = 11.5, 3.7 Hz, 1H), 2.56 – 2.41 (m, 1H), 2.24 – 2.08 (m, 1H), 0.87 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.5, 132.2, 130.0, 129.1, 128.8, 128.7, 128.5, 73.2, 21.0, 11.6.
HRMS (ESI) *m/z* calcd for $C_{15}H_{17}O_2S$ $[M + H]^+$ 261.0944, found: 261.0938.

The synthesis of 96

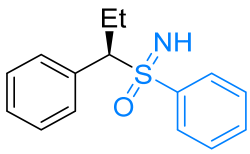


89, 91% e.e.

96, 72%, d.r. = 2.5:1
92% e.e. (major), 90% e.e. (minor)

The sulfide **89** (45.7 mg, 0.20 mmol, 1.0 equiv.), (diacetoxyiodo)benzene (193.2 mg, 0.60 mmol, 3.0 equiv.) and ammonium carbamate (46.8 mg, 0.60 mmol, 3.0 equiv.) were added to a flask containing a stirrer bar. MeOH (1.0 mL) was added and the reaction was stirred at room temperature for 12 h. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (10 mL), extracted with EtOAc (3 × 5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 20/1 ~ 3/1) to afford the product **96** (37.3 mg, 72%, d.r. = 2.5:1, 92% e.e. (major), 90% e.e. (minor)) as a light yellow solid. The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

Imino(phenyl)((*R*)-1-phenylpropyl)-λ^6-sulfanone (96)



96

HPLC analysis: Chiralcel OJ (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor1) = 13.43 min, t_R (minor2) = 15.97 min, t_R (major2) = 18.22 min, t_R (major1) = 37.84 min.

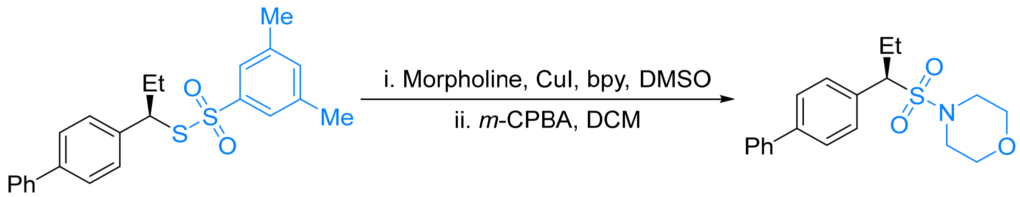
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.68 – 7.63 (m, 2H × 0.4), 7.59 – 7.54 (m, 1H), 7.52 – 7.48 (m, 1H × 0.4), 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 1H), 7.34 – 7.28 (m, 2H + 3H × 0.4), 7.26 – 7.20 (m, 2H + 2H × 0.4), 7.14 – 7.07 (m, 2H × 0.4), 4.04 (dd, *J* = 11.9, 3.6 Hz, 1H × 0.4), 3.92 (dd, *J* = 11.0, 4.3 Hz, 1H), 2.69 (s, 1H + 1H × 0.4), 2.51 – 2.39 (m, 1H × 0.4), 2.25 – 2.10 (m, 2H + 1H × 0.4), 0.82 (t, *J* = 7.4 Hz, 3H × 0.4), 0.78 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) (major), δ 139.3, 133.0, 132.0, 130.3, 129.4, 128.9, 128.6(0), 128.5(8), 75.2, 22.4, 11.6(5).

^{13}C NMR (100 MHz, $CDCl_3$) (minor),δ 139.9, 132.8, 132.4, 130.2, 129.3, 129.0, 128.7, 128.4, 74.4, 21.2, 11.5(9).

HRMS (ESI) *m/z* calcd for $C_{15}H_{18}ONS$ $[M + H]^+$ 260.1104, found: 260.1096.

The synthesis of 97

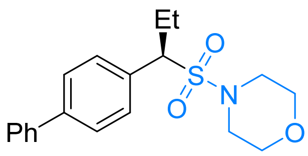


25, 92% e.e. **97**, 56%, 92% e.e.

A mixture of corresponding thiosulfonates **25** (79.3 mg, 0.2 mmol, 1.0 equiv.), morpholine (35.0 µL, 0.4 mmol, 2.0 equiv.), CuI (5.73 mg, 0.03 mmol, 10 mol%) and 2,2'-bipyridine (bpy, 4.68 mg, 0.03 mmol, 10 mol%) in DMSO (1.0 mL) was stirred at 60 °C for 19 hours in air. After the residue was dissolved in Et_2O, the solution was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the corresponding sulfenamides, which was directly used in the next step without further purification.

In a round-bottomed flask (10 mL) equipped with a stir bar, a solution of the crude sulfenamides obtained above in CH_2Cl_2 (0.6 mL) was prepared. The solution was cooled to 0 °C. A solution of *m*-CPBA (purity: 85%, 121.8 mg, 0.6 mmol, 3.0 equiv.) in CH_2Cl_2 (3.0 mL) was added dropwise and the mixture was stirred at room temperature for 3 hours. After disappearance of the sulfenamides, the reaction mixture was quenched by adding H_2O (10 mL), extracted with EtOAc (3 × 5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 20/1 ~ 3/1) to afford the product **97** (38.7 mg, 56% for 2 steps, 92% e.e.) as a white solid.

(*R*)-4-((1-([1,1'-Biphenyl]-4-yl)propyl)sulfonyl)morpholine (97)



97

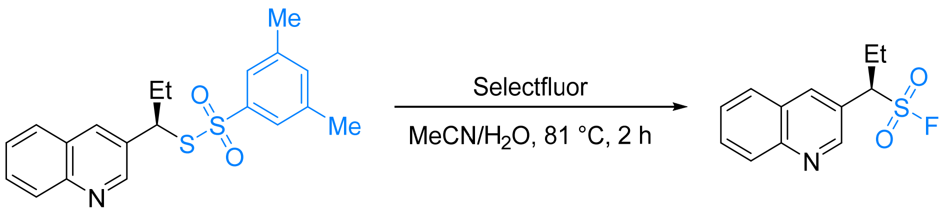
HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 10.04 min, t_R (major) = 11.55 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 4H), 7.51 – 7.43 (m, 4H), 7.40 – 7.35 (m, 1H), 4.00 (dd, *J* = 11.2, 3.9 Hz, 1H), 3.60 – 3.52 (m, 2H), 3.52 – 3.45 (m, 2H), 3.14 – 3.05 (m, 2H), 2.89 – 2.78 (m, 2H), 2.50 – 2.38 (m, 1H), 2.25 – 2.11 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.1, 132.1, 130.1, 129.0, 127.9, 127.5, 127.1, 69.7, 66.9, 46.3, 23.5, 11.5.

HRMS (ESI) calcd for $C_{19}H_{23}NNaO_3S$ $[M + Na]^+$ 368.1291, found: 368.1280.

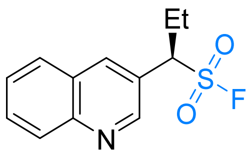
The synthesis of 98



37, 94% e.e. **98**, 96%, 93% e.e.

To a stirred solution of thiosulfonate **37** (37.2 mg, 0.1 mmol, 1.0 equiv.) in acetonitrile (1.0 mL) and water (0.1 mL), Selectfluor (159.5 mg, 0.45 mmol, 4.5 equiv.) was added and the resulting mixture was heated at 81 °C for 2 hours. The reaction was monitored via TLC. After the thiosulfonate disappeared from the TLC, water (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 5 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 10/1 ~ 4/1) to afford the product **98** (24.2 mg, 96%, 93% e.e.) as a yellow oil.

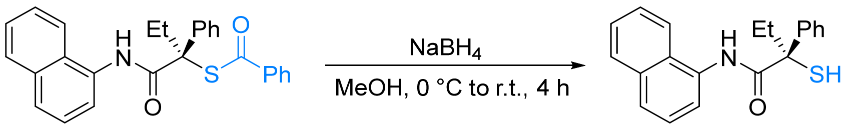
(*R*)-1-(Quinolin-3-yl)propane-1-sulfonyl fluoride (98)



98

HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 34.80 min, t_R (minor) =37.90 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 2.4 Hz, 1H), 8.28 (d, *J* = 2.3 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.85 – 7.75 (m, 1H), 7.67 – 7.58 (m, 1H), 4.60 (dd, *J* = 10.7, 4.6 Hz, 1H), 2.71 – 2.56 (m, 1H), 2.50 – 2.34 (m, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.7, 137.0, 131.0, 129.5, 128.2, 127.8, 127.6, 123.4, 67.4 (d, *J* = 13.3 Hz), 23.6, 11.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ 46.44.
HRMS (ESI) calcd for $C_{12}H_{13}O_2NFS$ $[M + H]^+$ 254.0646, found: 254.0639.

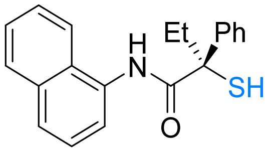
The synthesis of 99



62, 95% e.e. **99**, 92%, 95% e.e.

In a round-bottomed flask (10 mL) equipped with a stir bar, a solution of the **62** (42.6 mg, 0.1 mmol, 1.0 equiv.) in MeOH (2.0 mL) was prepared. The solution was cooled to 0 °C. $NaBH_4$ (18.9 mg, 0.5 mmol, 5.0 equiv.) was added and the mixture was stirred at room temperature for 4 hours. the reaction mixture was quenched by adding 3N HCl (aq.) and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /CH_2Cl_2 = 5/1 ~ 1/1) to afford the product **99** (29.6 mg, 92%, 95% e.e.) as a white solid.

(*R*)-2-Mercapto-*N*-(naphthalen-1-yl)-2-phenylbutanamide (99)



99

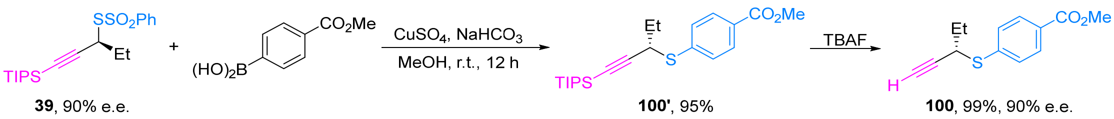
HPLC analysis: Chiralcel AS-H (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 12.60 min, t_R (minor) = 15.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.92 – 7.78 (m, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 3H), 7.53 – 7.45 (m, 3H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 2.65 (s, 1H), 2.62 – 2.52 (m, 1H), 2.52 – 2.42 (m, 1H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 141.7, 134.2, 132.3, 129.1, 129.0, 128.2, 126.9, 126.8, 126.5, 126.1, 125.9, 125.7, 120.3, 119.6, 61.6, 34.8, 9.9.

HRMS (ESI) *m/z* calcd for $C_{20}H_{20}ONS$ $[M + H]^+$ 322.1260, found: 322.1253.

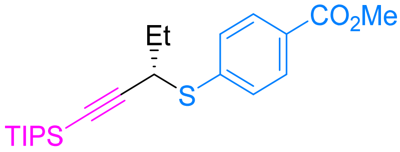
The synthesis of 100' and 100



To a mixture of copper(II) sulfate (3.2 mg, 0.02 mmol, 10 mol%) and sodium bicarbonate (33.6 mg, 0.4 mmol, 2.0 equiv.) was added a solution of corresponding thiosulfonates **39** (79.3 mg, 0.2 mmol, 1.0 equiv.) and (4-(methoxycarbonyl)phenyl)boronic acid (54.0 mg, 0.3 mmol, 1.5 equiv.) dissolved in methanol (1.0 mL) at room temperature. After stirring for 16 hours at the same temperature, the mixture was passed through a short pad of silica gel with EtOAc and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 100/1 ~ 60/1) to give product **100'** (74.2 mg, 95%) as a colorless oil.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **100'** (46.9 mg, 0.12 mmol, 1.0 equiv.) dissolved in anhydrous THF (1.2 mL) cooled to –78 °C, Then, tetrabutylammonium fluoride (0.13 mL, 1.0 M in THF, 0.13 mmol, 1.1 equiv.) diluted in anhydrous THF (1.2 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 °C for 10 min. Upon completion (monitored by TLC), water (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 5 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 60/1 ~ 20/1) to afford the product **100** (27.8 mg, 99%, 90% e.e.) as a colorless oil.

Methyl (*S*)-4-((1-(triisopropylsilyl)pent-1-yn-3-yl)thio)benzoate (100')



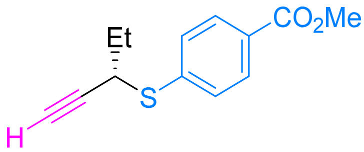
100'

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.53 – 7.46 (m, 2H), 3.96 (dd, J = 7.9, 5.6 Hz, 1H), 3.90 (s, 3H), 1.95 – 1.77 (m, 2H), 1.16 (t, J = 7.3 Hz, 3H), 1.04 – 0.97 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 142.1, 129.9, 129.5, 128.0, 106.5, 85.7, 52.2, 39.7, 28.5, 18.7, 11.8, 11.3.

HRMS (ESI) *m/z* calcd for $C_{22}H_{34}NaO_2SSi$ $[M + Na]^+$ 413.1941, found: 413.1949.

Methyl (*S*)-4-(pent-1-yn-3-ylthio)benzoate (100)



100

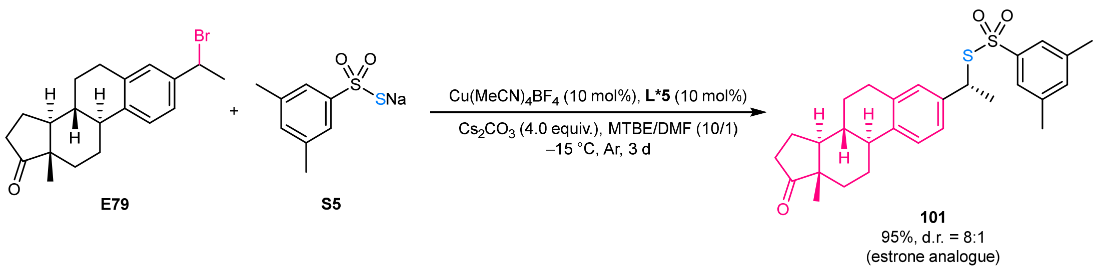
HPLC analysis: Chiralcel OD-H (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 12.12 min, t_R (major) = 14.16 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 3.89 – 3.86 (m, 1H), 2.37 (d, J = 2.4 Hz, 1H), 1.93 – 1.81 (m, 2H), 1.15 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.5, 130.0, 129.5, 128.2, 83.0, 72.7, 52.3, 38.6, 28.2, 11.7.

HRMS (ESI) *m/z* calcd for $C_{13}H_{15}O_2S$ $[M + H]^+$ 235.0787, found: 235.0787.

The synthesis of 101

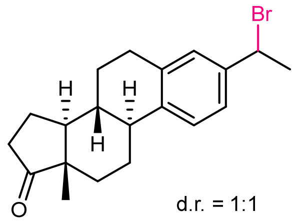


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S5** (54.0 mg, 0.24 mmol, 1.2 equiv.), $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol%), **L*5** (15.6 mg, 0.02 mmol, 10 mol%) and Cs_2CO_3 (260 mg, 0.80 mmol, 4.0 equiv.), Then, **E79** (72.2 mg, 0.20 mmol, 1.0 equiv.) and MTBE/DMF (v/v = 10/1, 2.2 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 or –30 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by CH_2Cl_2 and EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1 ~ 5/1) to afford the desired product **101** as a white solid

(86.6 mg, 95% yield, d.r. = 8:1). The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

Note: The substrates **E79** were known compounds and synthesized according to reported literature[6], the diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

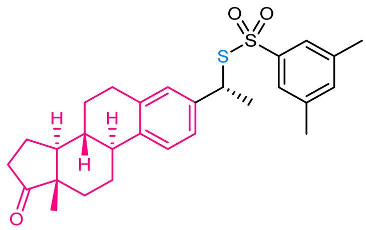
(8*R*,9*S*,13*S*,14*S*)-3-(1-bromoethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16 decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (E79)



E79

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 2H), 7.17 (s, 1H), 5.28 – 5.09 (m, 1H), 2.98 – 2.87 (m, 2H), 2.56 – 2.46 (m, 1H), 2.45 – 2.38 (m, 1H), 2.33 – 2.24 (m, 1H), 2.22 – 2.09 (m, 2H), 2.07 – 2.01 (m, 4H), 1.99 – 1.93 (m, 1H), 1.69 – 1.60 (m, 2H), 1.56 – 1.38 (m, 4H), 0.90 (s, 3H).

***S*-((*R*)-1-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)ethyl) 3,5-dimethylbenzenesulfonothioate (101)**



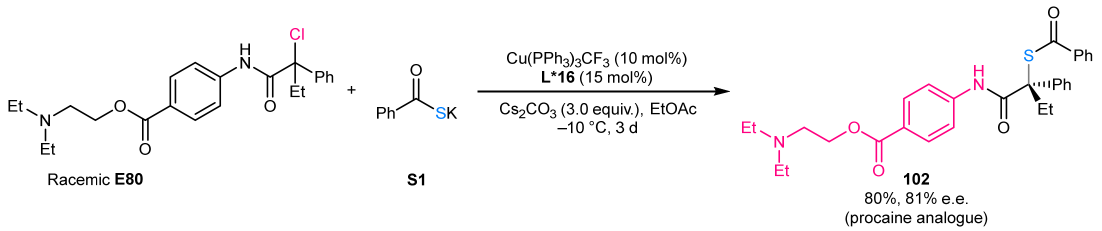
101

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.16 – 7.10 (m, 2H), 6.97 – 6.91 (m, 1H), 6.88 – 6.82 (m, 1H), 4.63 – 4.54 (m, 1H), 2.85 – 2.74 (m, 2H), 2.55 – 2.46 (m, 1H), 2.41 – 2.34 (m, 1H), 2.31 (s, 6H), 2.25 – 1.93 (m, 6H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.60 – 1.41 (m, 5H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.7, 145.0 139.4, 139.0, 137.8, 136.8, 134.9, 127.8, 125.6, 124.5, 124.4, 124.4, 50.6, 50.5, 48.0, 44.4, 38.1, 35.9, 31.6, 29.3, 26.5, 25.6, 22.8, 21.6, 21.3, 13.9.

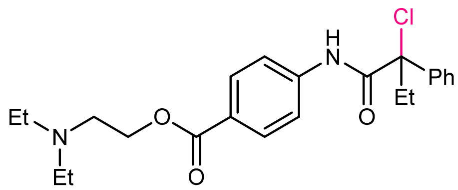
HRMS (ESI) *m/z* calcd. for $C_{28}H_{34}NaO_3S_2$ $[M + Na]^+$ 505.1842, found: 505.1837.

The synthesis of 102



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with tertiary alkyl electrophiles **E80** (41.7 mg, 0.1 mmol, 1.0 equiv.), $Cu(PPh_3)_3CF_3$ (9.24 mg, 0.010 mmol, 10 mol%), **L*16** (8.44 mg, 0.015 mmol, 15 mol%), **S1** (0.15 mmol, 1.5 equiv.) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). Then, EtOAc (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at –10 °C for 3 days. The precipitate was filtered off and washed by CH_2Cl_2 and EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 200/1 ~ 30/1) to afford the desired product **102** as a light yellow oli (41.7 mg, 80% yield, 81% e.e.).

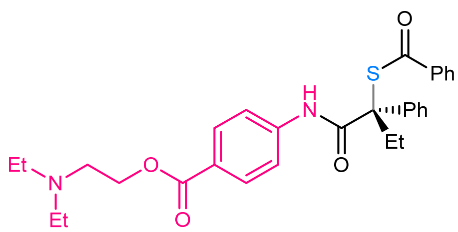
2-(Diethylamino)ethyl 4-(2-chloro-2-phenylbutanamido)benzoate (E80)



E80

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.04 – 7.92 (m, 2H), 7.72 – 7.62 (m, 2H), 7.62 – 7.54 (m, 2H), 7.43 – 7.29 (m, 3H), 4.73 (t, J = 5.4 Hz, 2H), 3.38 (t, J = 5.4 Hz, 2H), 3.15 (q, J = 7.3 Hz, 4H), 2.70 – 2.55 (m, 1H), 2.49 – 2.35 (m, 1H), 1.35 (t, J = 7.3 Hz, 6H), 1.04 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 165.2, 141.8, 139.6, 130.8, 128.6, 128.5, 126.2, 124.9, 119.3, 79.0, 59.5, 49.9, 47.4, 34.8, 9.3, 9.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{30}ClN_2O_3$ $[M + H]^+$ 417.1939, found: 417.1944.

2-(Diethylamino)ethyl (*R*)-4-(2-(benzoylthio)-2-phenylbutanamido)benzoate (102)



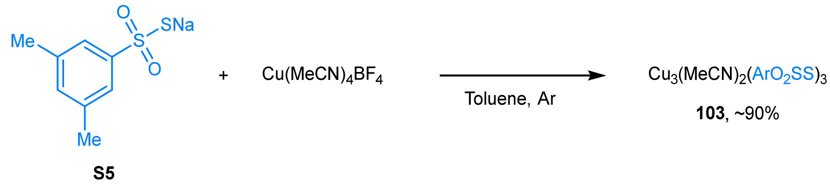
102

HPLC analysis: Chiralcel ADH (*n*-Hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 17.06 min, t_R (major) = 23.40 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.05 – 7.91 (m, 4H), 7.66 – 7.56 (m, 3H), 7.51 – 7.42 (m, 4H), 7.40 – 7.31 (m, 3H), 4.39 (t, J = 6.2 Hz, 2H), 2.88 (t, J = 6.2 Hz, 2H), 2.66 (q, J = 7.1 Hz, 4H), 2.50 – 2.40 (m, 1H), 2.34 – 2.25 (m, 1H), 1.08 (t, J = 7.1 Hz, 6H), 0.87 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 170.3, 166.2, 142.6, 137.6, 136.7, 134.4, 130.9, 129.0, 128.7, 128.1, 127.7, 127.3, 125.6, 119.1, 66.0, 63.1, 51.0, 47.9, 32.7, 12.0, 9.3.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{35}N_2O_4S$ $[M + H]^+$ 519.2312, found: 519.2296.

10. Mechanistic studies

The synthesis of copper(I) 3,5-dimethylbenzenesulfonothioate 103



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate **S5** (67.8 mg, 0.3 mmol, 1.0 eq.), $Cu(MeCN)_4BF_4$ (0.3 mmol, 1.0 eq.). Then, toluene (1.5 mL) were sequentially added into the mixture and the reaction mixture was stirred at r.t. for 5 hours, the toluene was evaporated under vacuum to afford analytically pure **103** (~90% yield) as a light yellow solid.

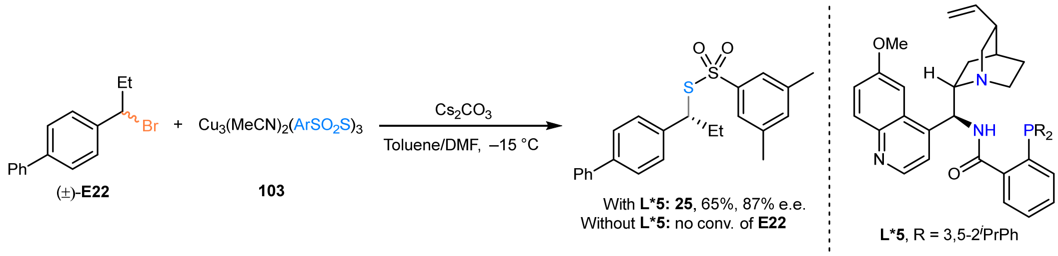
Bis(acetonitrile)tri(copper) tri(3,5-dimethylbenzenesulfonothioate) (103)

$Cu_3(MeCN)_2(ArSSO_2)_3$

(Ar = 3,5-Me_2Ph)

^{1}H NMR (400 MHz, DMSO-*d*6) δ 7.48 (s, 6H), 7.14 (s, 3H), 2.31 (s, 18H), 2.07 (s, 6H).
^{13}C NMR (100 MHz, DMSO-*d*6) δ 150.8, 137.6, 132.1, 122.4, 117.9, 20.6, 0.9.
HRMS (ESI) *m/z* calcd for $C_{24}H_{27}Cu_3NaO_6S_6$ [M – 2MeCN + Na]$^+$ 816.7894, found: 816.7871.

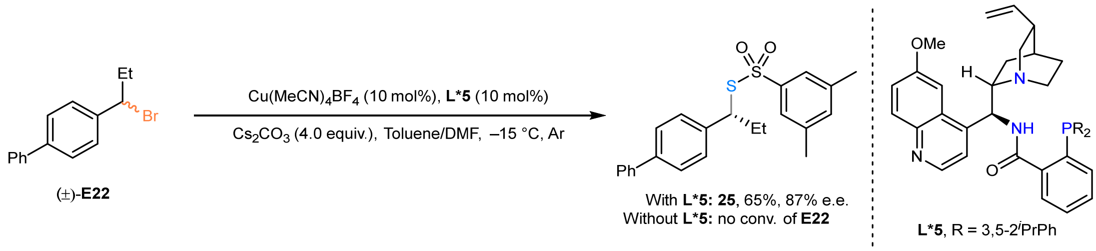
The effects of the ligand and copper 3,5-dimethylbenzenesulfonothioate 103 on the reaction initiation and product formation



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **103** (17.5 mg, 0.02 mmol, 0.4 eq.), **L*5** (46.8 mg, 0.06 mmol, 1.2 eq.), Cs_2CO_3 (65.0 mg, 0.20 mmol, 4.0 eq.), Then, 4-(1-bromopropyl)-1,1'-biphenyl **E22** (13.8 mg, 0.05 mmol, 1.0 eq.) and toluene/DMF (v/v = 10/1, 0.55 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 °C for 3.5 days. Upon completion, the reaction was quenched with H_2O and extracted with EtOAc. The combined organic layer was concentrated to afford crude product. The residue was analyzed by ^{1}H NMR spectroscopy using 1,3,5-trimethybenzene as an internal standard. The product was then separated by preparative TLC. The e.e. values of **25** was determined by HPLC analysis.

The procedure for the reaction without **L*5** was the same with that described above except that **L*5** was not added. There was no conversion of **E22**.

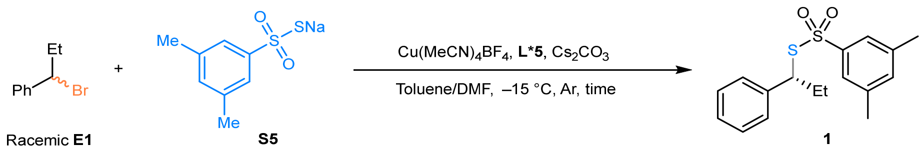
The effects of sodium 3,5-dimethylbenzenesulfonothioate S5 on the reaction initiation and product formation



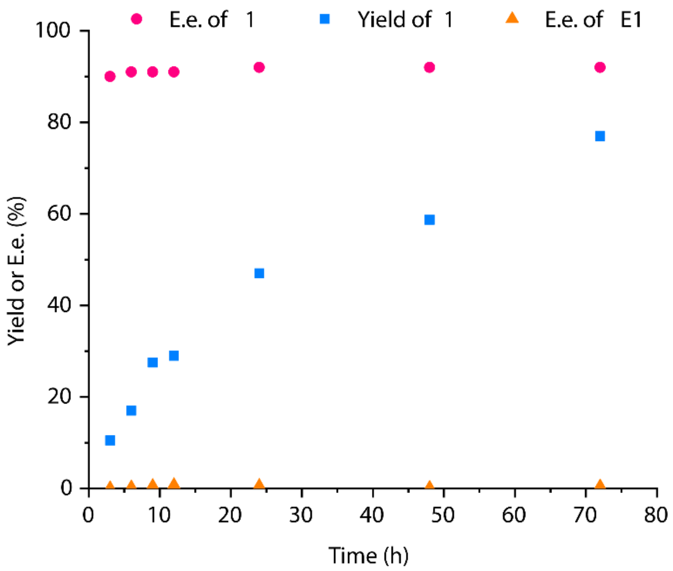
According to the **general procedure A** with 4-(1-bromopropyl)-1,1'-biphenyl **E22** (55.0 mg, 0.20 mmol, 1.0 eq.) and sodium 3,5-dimethylbenzenesulfonothioate **S5** (54.0 mg, 0.24 mmol, 1.2 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1 ~ 20/1) to yield the product **25** as a colorless oil (69.8 mg, 88% yield, 92% e.e.).

The procedure for the reaction without **S5** was the same with that described above except that **L*5** was not added. There was no conversion of **E22**.

The stereochemistry of benzyl halide and product during the reaction

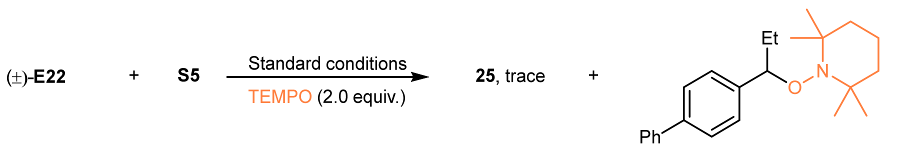


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S5** (0.0.6 mmol, 1.2 eq.), $Cu(MeCN)_4BF_4$ (1.57 mg, 0.005 mmol, 10 mol%), **L*5** (3.9 mg, 0.005 mmol, 10 mol%) and Cs_2CO_3 (65 mg, 0.20 mmol, 4.0 eq.), Then, **E1** (0.05 mmol, 1.0 eq.) and toluene/DMF (v/v = 10/1, 0.55 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 °C for appropriate time. Upon completion, the reaction was quenched with H_2O and extracted with EtOAc. The combined organic layer was concentrated to afford crude product. The residue was analyzed by ^{1}H NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard. The product was then separated by preparative TLC. The e.e. values of **1** and recovered **E1** were determined by HPLC analysis.



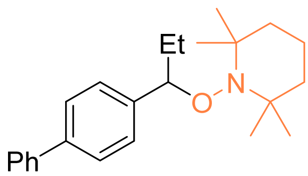
No apparent enantioenrichment of the recovered alkyl bromide **E1** was observed under typical conditions, disfavoring a possible kinetic resolution of **E1**, and therefore ruling out the typical S_N2-type substitution pathway. Moreover, the observed e.e. values of the product **1** remained nearly constant at different time intervals, favoring the involvement of a uniform mechanism throughout the reaction course.

Radical trap experiments



According to the **general procedure A** with 4-(1-bromopropyl)-1,1'-biphenyl **E22** (55.0 mg, 0.20 mmol, 1.0 eq.), sodium 3,5-dimethylbenzenesulfonothioate **S5** (54.0 mg, 0.24 mmol, 1.2 eq.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 62.5 mg, 0.40 mmol, 2.0 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1) to yield the TEMPO-trapped products **104** as a white solid (30.5 mg, 43% yield).

1-(1-([1,1'-Biphenyl]-4-yl)propoxy)-2,2,6,6-tetramethylpiperidine (104)

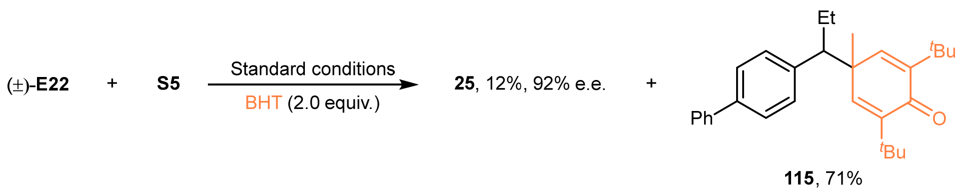


104

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.36 – 7.28 (m, 3H), 4.59 (dd, J = 9.5, 3.8 Hz, 1H), 2.19 – 2.07 (m, 1H), 1.91 – 1.77 (m, 1H), 1.49 (s, 3H), 1.41 – 1.14 (m, 10H), 1.03 (s, 3H), 0.71 (t, J = 7.4 Hz, 3H), 0.65 (s, 2H).

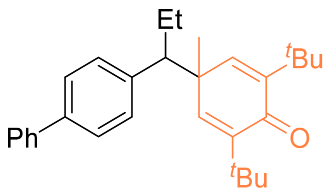
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 142.8, 141.2, 139.6, 128.8, 128.3, 127.2, 127.1, 126.6, 88.5, 60.0 – 59.7 (m, 1C), 40.6, 34.5 – 34.3 (m, 1C), 28.9, 20.7 – 20.5 (m, 1C), 17.4, 9.9.

Note: **104** is a known compound[9].



According to the **general procedure A** with 4-(1-bromopropyl)-1,1'-biphenyl **E22** (55.0 mg, 0.20 mmol, 1.0 eq.), sodium 3,5-dimethylbenzenesulfonothioate **S5** (54.0 mg, 0.24 mmol, 1.2 eq.) and 2,6-di-*tert*-butyl-4-methylphenol (BHT, 88.1 mg, 0.40 mmol, 2.0 eq.) run at –15 °C for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1) to yield the BHT-trapped products **115** as a colorless oil (58.7 mg, 71% yield).

4-(1-([1,1'-Biphenyl]-4-yl)propyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one (115)



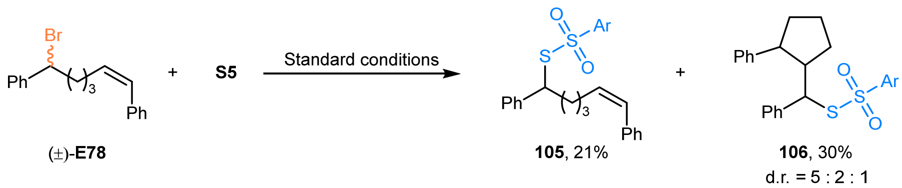
115

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 6.59 (s, 1H), 6.44 (s, 1H), 2.67 – 2.60 (m, 1H), 1.83 – 1.72 (m, 1H), 1.64 – 1.52 (m, 1H), 1.28 (s, 9H), 1.15 (s, 3H), 1.12 (s, 9H), 0.72 (t, J = 7.2 Hz, 3H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 186.5, 147.1, 146.1, 145.8, 145.4, 141.0, 139.7, 139.4, 129.7, 128.8, 127.2, 127.1, 126.6, 57.8, 43.1, 35.0, 34.8, 29.6, 29.5, 25.5, 22.9, 13.1.

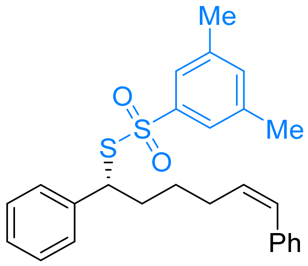
HRMS (ESI) *m/z* calcd for $C_{30}H_{39}O$ $[M + H]^+$ 415.2995, found: 415.2992.

Radical clock experiments



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate **S5** (54.0 mg, 0.24 mmol, 1.2 eq.), $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol%), **L*5** (15.6 mg, 0.02 mmol, 10 mol%) and Cs_2CO_3 (260 mg, 0.80 mmol, 4.0 eq.), Then, (*Z*)-(6-bromohex-1-ene-1,6-diyl)dibenzene **E78** and toluene/DMF (v/v = 10/1, 2.2 mL) were sequentially added into the mixture and the reaction mixture was stirred at –15 °C for 5 days. The precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography (petroleum ether/EtOAc = 60/1 ~ 20/1) on silica gel to afford the desired product **105** as a colorless oil (18.2 mg, 21% yield) and the radical clock product **106** was then separated by preparative TLC (*n*-Hexane/EtOAc = 20/1) as a colorless oil (26.0 mg, 30% yield, d.r. = 5:2:1). The diastereomeric ratio was determined by crude ^1H NMR spectroscopy.

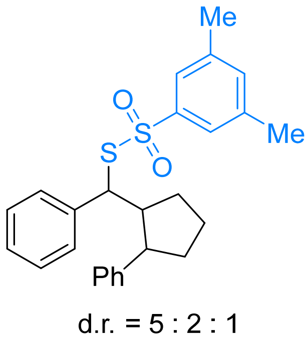
(*R*,*Z*)-*S*-1,6-Diphenylhex-5-en-1-yl) 3,5-dimethylbenzenesulfonothioate (105)



105

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.16 – 7.12 (m, 5H), 7.09 – 7.05 (m, 2H), 7.03 (s, 1H), 6.39 (d, *J* = 11.6 Hz, 1H), 5.50 (dt, *J* = 11.7, 7.2 Hz, 1H), 4.46 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.35 – 2.24 (m, 2H), 2.22 (s, 6H), 2.01 – 1.81 (m, 2H), 1.51 – 1.40 (m, 1H), 1.39 – 1.28 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.5, 138.9, 137.5, 134.8, 131.8, 129.6, 128.8, 128.4, 128.3, 127.8 (two carbon overlapped), 126.7, 124.3, 55.9, 36.0, 28.0, 27.6, 21.2.
HRMS (ESI) *m/z* calcd for $C_{26}H_{28}NaO_2S_2$ $[M + Na]^+$ 459.1423, found: 459.1422.

***S*-(Phenyl(2-phenylcyclopentyl)methyl) 3,5-dimethylbenzenesulfonothioate (106)**

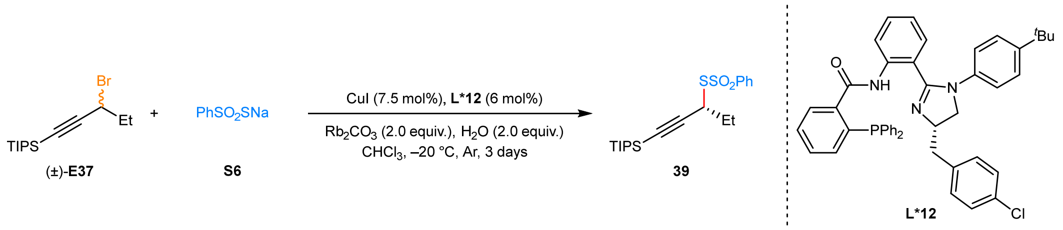


106

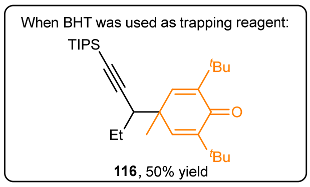
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.10 (m, 6.4H), 7.04 – 6.91 (m, 12.4H), 6.77 – 6.69 (m, 1H), 6.64 – 6.54 (m, 1H), 4.50 (d, *J* = 5.9 Hz, 1H), 4.47 – 4.44 (m, 0.2H), 4.04 (d, *J* = 11.8 Hz, 0.4H), 2.92 (q, *J* = 8.9 Hz, 1H), 2.87 – 2.82 (m, 0.2H), 2.79 – 2.65 (m, 0.4H), 2.53 (t, *J* = 7.7 Hz, 0.4H), 2.46 – 2.35 (m, 1.2H), 2.23 (s, 1.2H), 2.21 (s, 2.4H), 2.15 (s, 6H), 2.11 – 2.03 (m, 1.4H), 2.01 – 1.91 (m, 1.8H), 1.82 – 1.55 (m, 6.4H).
^{13}C NMR (100 MHz, $CDCl_3$) (major 1) δ 145.1, 144.6, 139.9, 138.6(8), 134.6, 128.5, 128.2, 127.9, 127.5, 127.2, 126.2, 124.3, 59.8, 54.5, 49.8, 35.6, 30.3, 24.7, 21.1.
^{13}C NMR (100 MHz, $CDCl_3$) (major 2) δ 145.1, 143.2, 139.6(6), 138.7(4), 134.8, 129.2, 128.2, 128.1, 127.8, 127.4, 126.3, 124.4, 58.6, 49.6, 47.9, 34.8, 31.1, 29.8, 23.9, 21.2.

^{13}C NMR (100 MHz, $CDCl_3$) (minor) δ 145.2, 142.5, 139.6(7), 138.9, 129.0, 128.8, 128.4(2), 128.3(8), 127.7, 125.8, 124.3, 124.2, 56.1, 36.4, 35.8, 31.2, 29.5, 28.7, 27.2. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{28}NaO_2S_2$ $[M + Na]^+$ 459.1423, found: 459.1422.

Radical trap experiments for the propargyl reaction



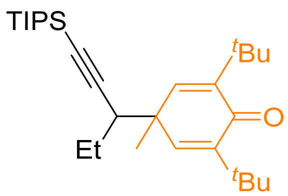
Trapping reagents	yield of 39	e.e. of 39
TEMPO (2.0 equiv.)	trace	–
BHT (2.0 equiv.)	44%	90%



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium benzenethiosulfonate **S6** (47.2mg, 0.24 mmol, 1.2 equiv.), CuI (2.86 mg, 0.015 mmol, 7.5 mol%), **L*12** (8.47 mg, 0.012 mmol, 6 mol%), Rb_2CO_3 (92.8 mg, 0.40 mmol, 2.0 equiv.) and the corresponding trapping reagents (2.0 equiv.), Then, propargyl halide (0.20 mmol, 1.0 equiv.), H_2O (7.2 μL, 0.40 mmol, 2.0 equiv.) and $CHCl_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at –20 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 ~ 50/1) to afford the desired product **39**.

Note: When TEMPO was used as trapping reagent, the coupling was completely inhibited. When BHT was used as trapping reagent, the residue was purified by preparative TLC (*n*-Hexane/Et_2O = 60/1) to afford the BHT-trapped products **116** as colorless oil (44.3 mg, 50% yield).

2,6-Di-*tert*-butyl-4-methyl-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)cyclohexa-2,5-dien-1-one (116)

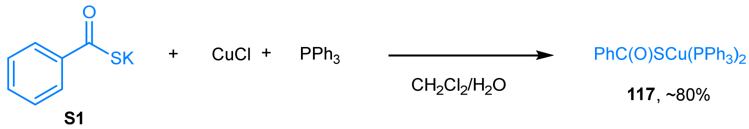


116

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 2.9 Hz, 1H), 6.36 (d, J = 2.9 Hz, 1H), 2.41 (dd, J = 11.0, 3.8 Hz, 1H), 1.35 (s, 3H), 1.25 – 1.20 (m, 19H), 1.13 – 1.07 (m, 22H), 0.98 (t, J = 7.1 Hz, 3H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 186.6, 147.3(4), 147.3(1), 145.9, 144.3, 108.1, 85.1, 45.3, 42.5, 35.0, 34.9, 29.7, 26.2, 24.1, 18.8, 12.8, 11.4.
HRMS (ESI) *m/z* calcd for $C_{29}H_{51}OSi$ $[M + H]^+$ 443.3704, found: 443.3699.

The synthesis of copper(I) thiocarboxylate 117



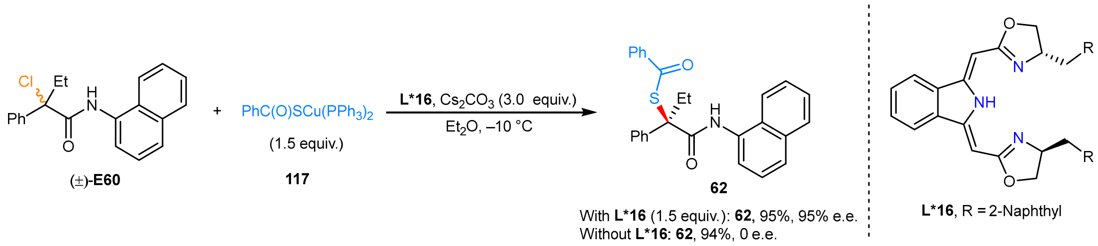
Potassium benzothioate **S1** (123.4 mg, 0.7 mmol, 1.0 eq.) in 1.0 mL of water was added a suspension of CuCl (69.3 mg, 0.7 mmol, 1.0 eq.) in 2.0 mL of CH_2Cl_2 containing triphenylphosphine (367.2 mg, 1.4 mmol, 2.0 eq.). The reddish CH_2Cl_2 layer was separated and layered with Et_2O. Greenish yellow solid were filtered off, washed with Et_2O, and dried under vacuum to afford the product **117** as greenish yellow solid (~80% yield).
Note: The **117** is a known compound and synthesized according to reported literature[13].

Bis(triphenylphosphine)copper(I) thiocarboxylate (117)

$PhC(O)SCu(PPh_3)_2$

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.40 – 7.30 (m, 14H), 7.29 – 7.25 (m, 5H), 7.21 – 7.13 (m, 14H).
^{31}**P NMR** (162 MHz, $CDCl_3$) δ –1.83.
Note: **117** is a known compound and NMR spectra match with the literature report[13].

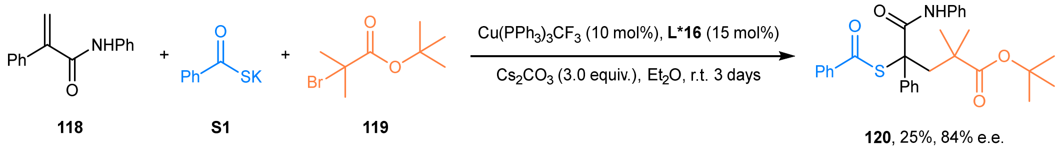
The effect of ligand and copper(I) thiocarboxylates 117 for the tertiary reaction



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with tertiary alkyl electrophiles **E60** (16.2 mg, 0.05 mmol, 1.0 equiv.), $PhC(O)SCu(PPh_3)_2$ (54.4 mg, 0.075 mmol, 1.5 equiv.), **L*16** (42.2 mg, 0.075 mmol, 1.5 equiv) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). Then, Et_2O (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at –10 °C for 3 days. Upon completion, the reaction was quenched with H_2O and extracted with EtOAc. The combined organic layer was concentrated to afford crude product. The residue was analyzed by ^{1}H NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard. The product was then separated by preparative TLC. The e.e. values of **62** was determined by HPLC analysis.

The procedure for the reaction without **L*16** was the same with that described above except that **L*16** was not added. The racemic product **62** was obtained in high yield, which indicated that there was a strong background reaction without chiral ligand **L*16**. While combination **L*16** and copper(I) thiocarboxylates effectively tuned reactivity and enantioselectivity of this reaction.

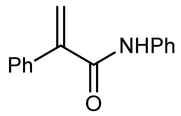
Radical clock experiments for the tertiary reaction



Note: The substrate **118** was a known compound and synthesized according to reported literature[14], and **119** was commercially available.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with *N*,2-diphenylacrylamide **118** (0.1 mmol, 1.0 equiv.), potassium benzothioate **S1** (0.15 mmol, 1.5 equiv.), $Cu(PPh_3)_3CF_3$ (9.24 mg, 0.010 mmol, 10 mol%), **L*16** (8.44 mg, 0.015 mmol, 15 mol%) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). Then, *tert*-butyl 2-bromo-2-methylpropanoate **119** (22.4 μL, 0.12 mmol, 1.2 equiv.) and Et_2O (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at r.t. for 3 days. The precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1 ~ 10/1) to afford the desired product **120** as cloroless oil (12.6 mg, 25% yield, 84% e.e.).

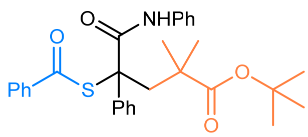
N,2-Diphenylacrylamide (118)



118

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.37 (m, 6H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.26 (s, 1H), 5.71 (s, 1H).

Tert-butyl 4-(benzoylthio)-2,2-dimethyl-5-oxo-4-phenyl-5-(phenylamino)pentanoate (120)

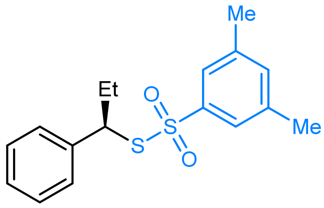


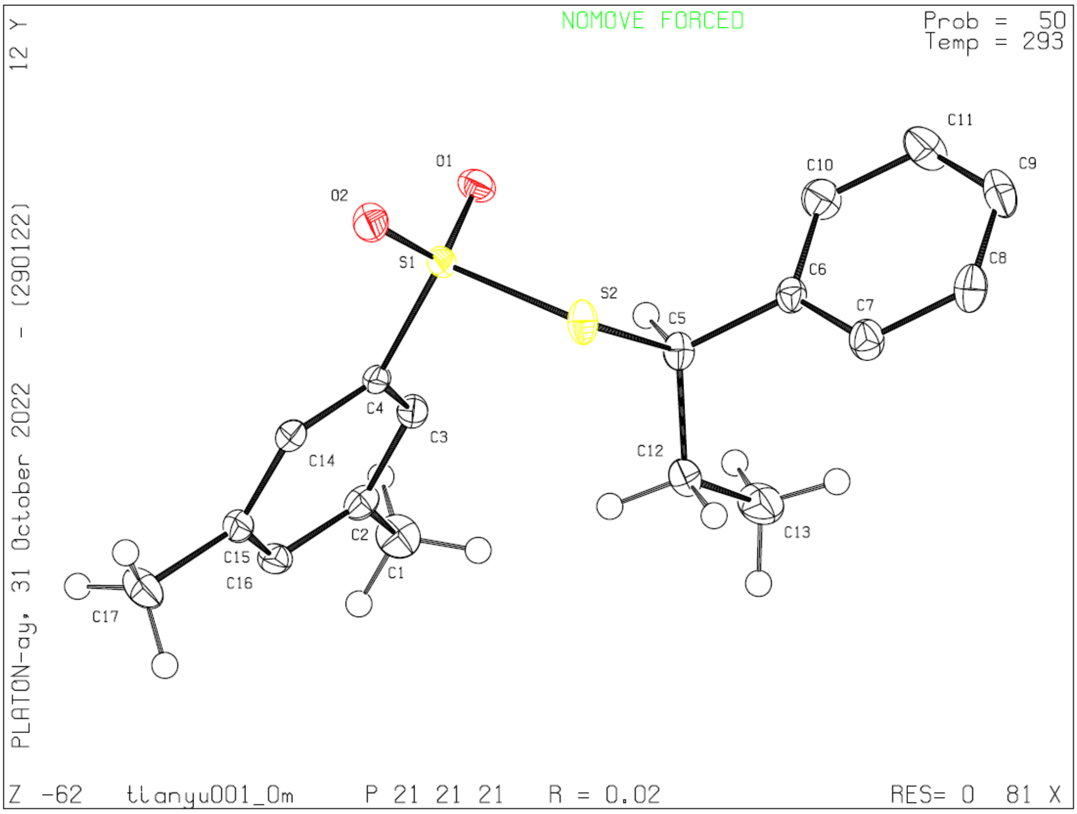
120

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.54 min, t_R (minor) = 17.50 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.63 – 7.55 (m, 3H), 7.49 – 7.41 (m, 4H), 7.35 – 7.25 (m, 5H), 7.06 (t, *J* = 7.4 Hz, 1H), 3.07 (d, *J* = 15.2 Hz, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 1.36 (s, 9H), 1.21 (s, 3H), 1.00 (s, 3H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 191.2, 176.9, 169.8, 139.9, 138.3, 136.9, 134.2, 129.0, 128.8, 128.7, 128.0, 127.8, 127.5, 124.3, 120.2, 80.2, 64.7, 46.9, 43.0, 28.0, 27.7, 26.7.
HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_4S$ $[M + H]^+$ 504.2203, found: 504.2198.

11. X-ray crystallography

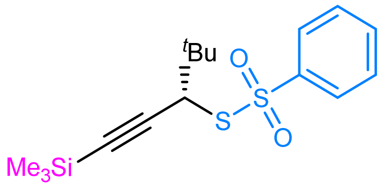


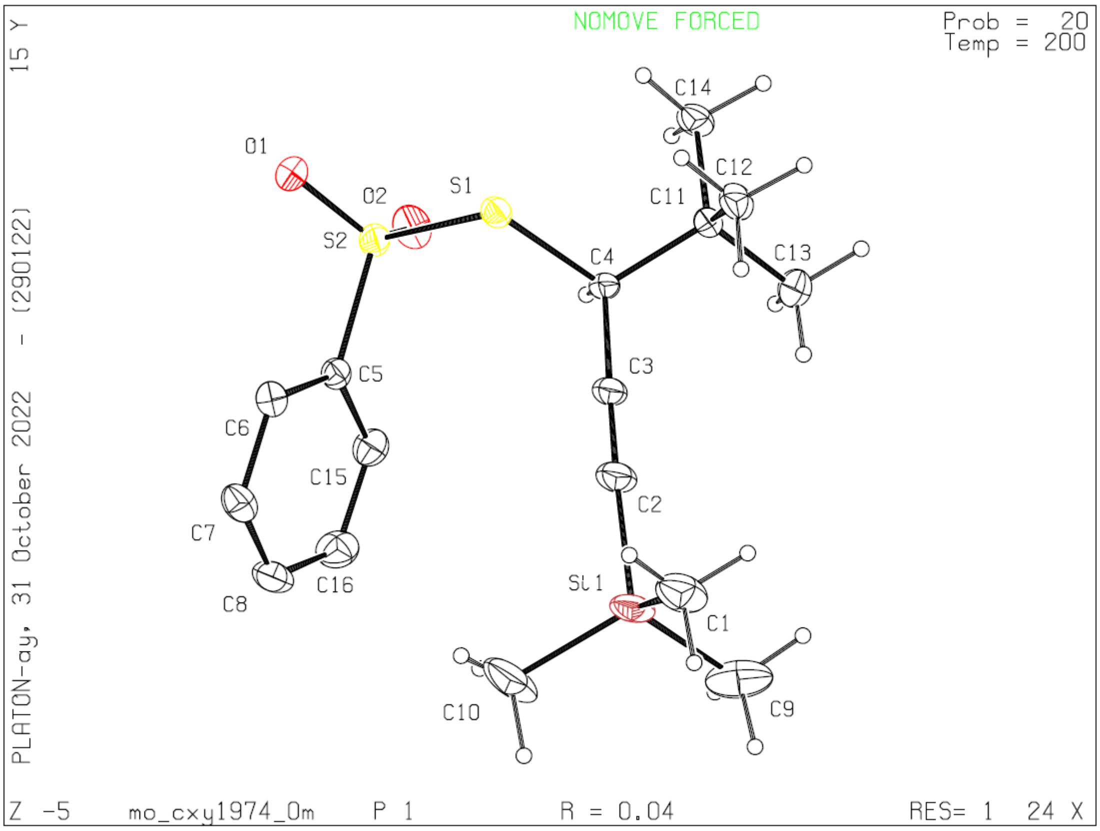


Supplementary Fig. 5′ | The X-ray structure of 1 (CCDC 2212974, 50% probability ellipsoids).

Supplementary Table 9 | Crystal data and structure refinement for Compound 1.

Empirical formula	$C_{17}H_{20}O_2S_2$
Formula weight	320.45
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.676(4)
b/Å	10.434(6)
c/Å	17.758(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1607.6(13)
Z	4
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	3.008
F(000)	680.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	13.272 to 136.93
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 12$, $-14 \le l \le 21$
Reflections collected	10708
Independent reflections	2911 [R_{int} = 0.0326, R_{sigma} = 0.0315]
Data/restraints/parameters	2911/0/193
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1= 0.0232, wR_2= 0.0589
Final R indexes [all data]	R_1 = 0.0236, wR_2 = 0.0590
Largest diff. peak/hole / e Å^{-3}	0.34/–0.27
Flack parameter	0.034(6)

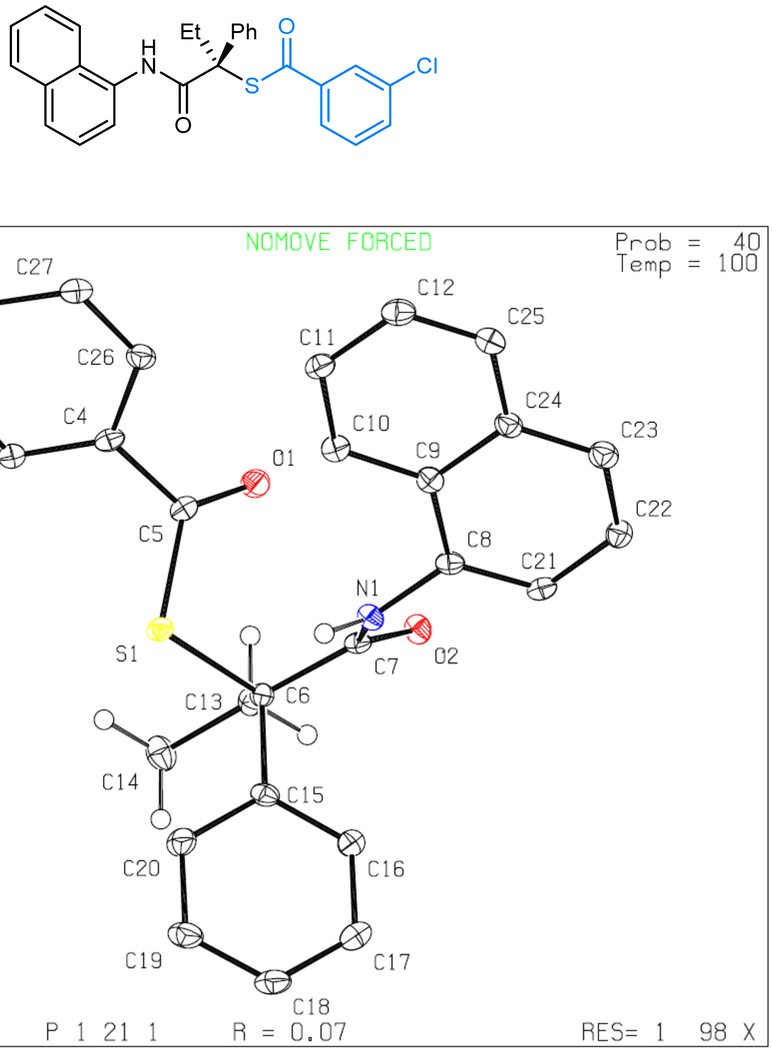




Supplementary Fig. 6′ | The X-ray structure of 52 (CCDC 2213037, 50% probability ellipsoids).

Supplementary Table 10 | Crystal data and structure refinement for Compound 52.

Empirical formula	$C_{16}H_{24}O_2S_2Si$
Formula weight	340.56
Temperature/K	200.0(2)
Crystal system	triclinic
Space group	P_1
a/Å	9.4425(3)
b/Å	10.3552(4)
c/Å	10.7218(4)
α/°	91.4010(10)
β/°	92.7930(10)
γ/°	111.4310(10)
Volume/Å^3	973.71(6)
Z	2
ρ_{calc}g/cm^3	1.162
μ/mm^{-1}	0.336
F(000)	364.0
Crystal size/mm^3	0.34 × 0.29 × 0.28
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.644 to 56.706
Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	38244
Independent reflections	9568 [R_{int} = 0.0487, R_{sigma} = 0.0353]
Data/restraints/parameters	9568/3/391
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1= 0.0449, wR_2= 0.1225
Final R indexes [all data]	R_1 = 0.0517, wR_2 = 0.1264
Largest diff. peak/hole / e Å^{-3}	0.44/–0.35
Flack parameter	–0.01(3)



Supplementary Fig. 7′ | The X-ray structure of 83 (CCDC 2213038, 50% probability ellipsoids).

Supplementary Table 11 | Crystal data and structure refinement for Compound 83.

Empirical formula	$C_{27}H_{22}ClNO_2S$
Formula weight	459.96
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.6349(7)
b/Å	9.8818(6)
c/Å	19.6807(11)
α/°	90
β/°	92.263(3)
γ/°	90
Volume/$Å^3$	2261.0(2)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	1.682
F(000)	960.0
Crystal size/mm^3	0.28 × 0.03 × 0.03
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	3.908 to 114.118
Index ranges	$-14 \le h \le 14$, $-12 \le k \le 12$, $-24 \le l \le 24$
Reflections collected	49135
Independent reflections	9250 [R_{int} = 0.0759, R_{sigma} = 0.0501]
Data/restraints/parameters	9250/3/585
Goodness-of-fit on F^2	1.141
Final R indexes [I>=2σ (I)]	R_1= 0.0697, wR_2= 0.1826
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.1859
Largest diff. peak/hole / e $Å^{-3}$	0.32/–0.72
Flack parameter	–0.02(2)

12. Computational studies

12.1. Computational Details

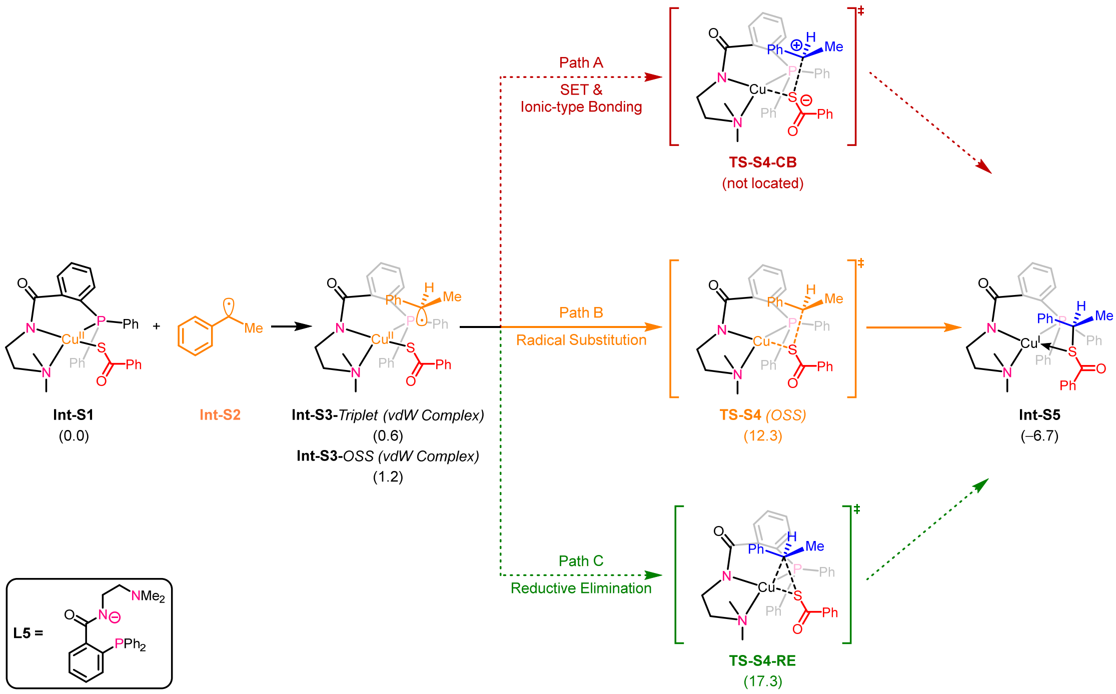
All density functional theory (DFT) calculation results are obtained with Gaussian 16 program[15]. Default SCF convergence criteria, optimization convergence criteria and integral grid parameters for Gaussian 16 are applied unless otherwise stated. (5d,7f) keyword in Gaussian 16 was used. Geometry optimizations are conducted with B3LYP functional[16,17], employing the D3 version of Grimme's dispersion corrections[18] with Becke-Johnson damping[19]. LANL2DZ basis set[20-23] is used for copper and 6-31G(d) basis set is used for all other light atoms. Single-point energies and solvent effects at toluene and diethyl ether are also evaluated with B3LYP functional with Grimme's dispersion corrections and Becke-Johnson damping. SDD basis set[20,24-27] is used for copper and 6-311+G(d,p) basis set is used for all other light atoms. The solvation energies are calculated with a self-consistent reaction field (SCRF) using the SMD implicit solvent model[28]. Frequency analysis is also performed at the same level of theory as geometry optimization using harmonic oscillator model to confirm whether optimized stationary points are either local minimum or transition state, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K. Mulliken spin distribution is obtained at the same level of theory as geometry optimization.

In addition, geometry optimization, frequency analysis and single point energy of open-shell transition states and local minimums are calculated with unrestricted DFT methods, while same computations for closed-shell structures are performed with restricted DFT methods. Wavefunction stability test at the same level of theory as geometry optimizations is employed to ensure that the SCF converged wavefunction is stable.

To correct the Gibbs free energies under 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_s/c_g)$ is added to energies of all species. c_s stands for the standard molar concentration in solution (1 mol/L), c_g stands for the standard molar concentration in gas phase (about 0.040876 mol/L), and R is the gas constant. For calculated intermediates at the standard state of 1 mol/L at 298.15 K, the correction value equaling to 1.89 kcal/mol is used.

The 3D diagrams of optimized structures shown in this supplementary information for computations are generated with CYLview software[29]. Cartesian coordinates of computed species are included in the Computational Archives.

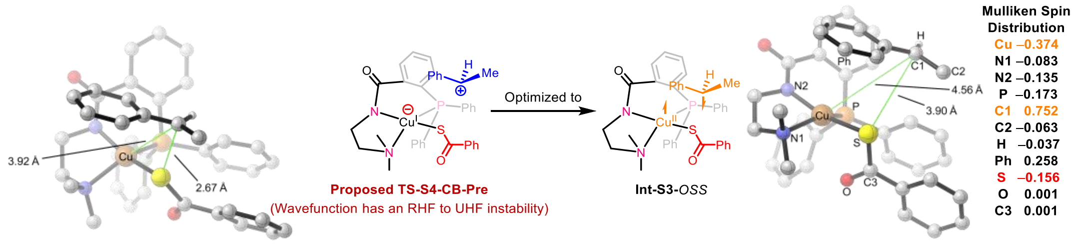
12.2. Discussion on Cu-Mediated C–S Bonding Mechanism of Secondary Benzyl Radical and Benzothioate



Supplementary Fig. 10 | DFT exploration of C–S bond formation pathways with L5Cu(II)(benzoylthiolate) species Int-S1 and secondary benzyl radical Int-S2. Free energies in kcal/mol are shown in parentheses, which are compared to **Int-S1** and **Int-S2**.

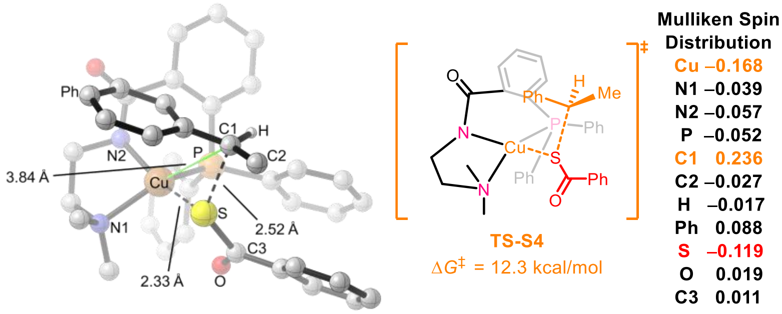
DFT calculations in model systems are performed to study Cu-mediated C–S bond formation pathway for secondary benzyl radical and benzothioate. Simplified achiral *N,N,P*-ligand based on **L*5** is used for calculations in this section.

The proposed C–S bond formation pathways between **L5**Cu(II)(benzoylthiolate) species **Int-S1** and secondary benzyl radical **Int-S2** include three major possibilities: sequential SET and ion-type C–S bonding (path A in **Supplementary Fig. 10**), outer-sphere radical-substitution-type C–S bond formation via **TS-S4** (path B in **Supplementary Fig. 10**), and reductive elimination via **TS-S4-RE** (path C in **Supplementary Fig. 10**).



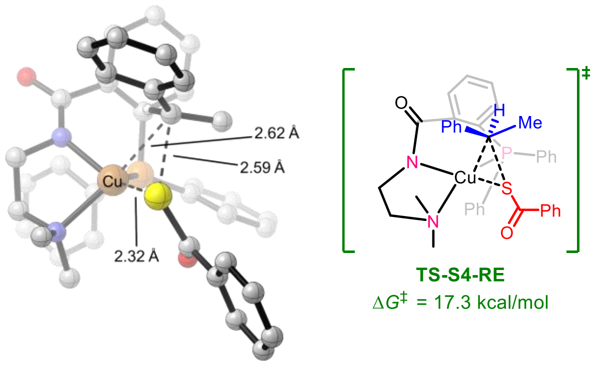
Supplementary Fig. 11 | Proposed closed-shell structure of pre-intermediate ion-type C–S bond formation and further geometry optimization results. Trivial hydrogen atoms are omitted for clarity.

Regarding path A, the ion-type C–S bonding, the transition state cannot be located after extensive efforts. The structure of the pre-intermediate prior to the proposed ion-type C–S bonding transition state, **Proposed TS-S4-CB-Pre**, has an RHF to UHF 'wavefunction' instability, indicating that such closed-shell singlet, zwitterionic intermediate does not exist at computed potential energy surface. Further open-shell singlet optimization with unrestricted Hartree-Fock (UHF) calculation of **Proposed TS-S4-CB-Pre** leads to the open-shell singlet intermediate **Int-S3**-*OSS*, which is a VdW (van der Waals) complex of **L5**Cu(II)(benzoylthiolate) species **Int-S1** and secondary benzyl radical **Int-S2**, and also the pre-intermediate for the radical substitution C–S bond formation. Also, the Mulliken spin distribution indicates the open-shell singlet diradical nature of **Int-S3**-*OSS*. Based on these results, the ion-type C–S bonding pathway is not operative. (**Supplementary Fig. 11**)



Supplementary Fig. 12 | Located radical-substitution-type C–S bond formation transition state. Trivial hydrogen atoms are omitted for clarity.

Regarding path B, the radical-substitution-type C–S bonding, the transition state is located as **TS-S4**. The free energy barrier of C–S bond formation via **TS-S4** is 12.3 kcal/mol. The Mulliken spin distribution indicates the open-shell singlet nature of **TS-S4**. (**Supplementary Fig. 12**)

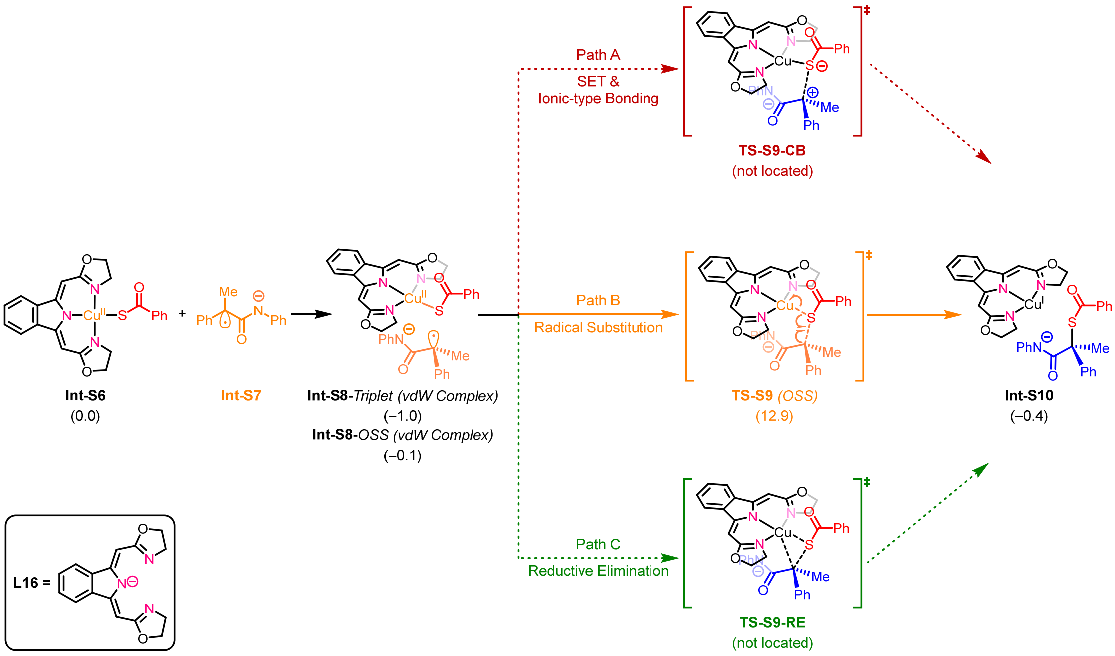


Supplementary Fig. 13 | Located C–S reductive elimination transition state. Trivial hydrogen atoms are omitted for clarity.

Regarding path C, C–S reductive elimination, the transition state is located as **TS-S4-RE**. This **TS-S4-RE** already has a stable wavefunction using RHF (restricted Hartree-Fock) calculation. This result illustrates that open-shell form of **TS-S4-RE** doesn't exist. The free energy barrier of C–S bond formation via **TS-S4-RE** is 17.3 kcal/mol, which is 5.0 kcal/mol unfavorable compared to radical-substitution-type C–S bond formation via **TS-S4.** (**Supplementary Fig. 13, Supplementary Table. 12**)

Based on the above calculations and discussions, Cu-mediated C–S bond formation for secondary benzyl radical and benzothioate via open-shell singlet radical substitution transition state **TS-S4** is the most favorable.

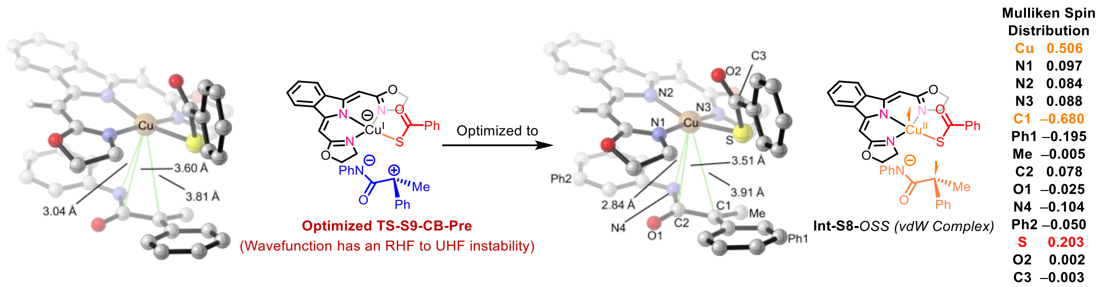
12.3. Discussion on Cu-Mediated C–S Bonding Mechanism of Tertiary Benzyl Radical and Benzothioate



Supplementary Fig. 14 | DFT exploration of C–S bond formation pathways with L16Cu(II)(benzoylthiolate) species Int-S6 and tertiary benzyl radical Int-S7. Free energies in kcal/mol are shown in parentheses, which are compared to **Int-S6** and **Int-S7**.

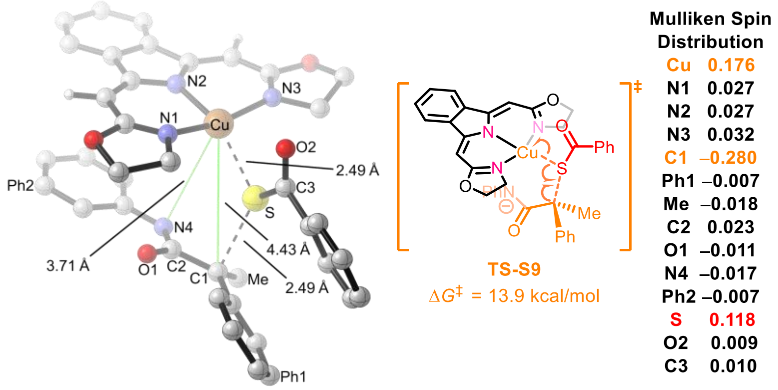
DFT calculations in model systems are performed to study Cu-mediated C–S bond formation pathway for tertiary benzyl radical and benzothioate. Simplified achiral *N,N,N*-ligand based on **L*16** is used for calculations in this section.

The proposed C–S bond formation pathways between **L16**Cu(II)(benzoylthiolate) species **Int-S6** and tertiary benzyl radical **Int-S7** include three major possibilities: sequential SET and ion-type C–S bonding (path A in **Supplementary Fig. 14**), outer-sphere radical-substitution-type C–S bond formation via **TS-S9** (path B in **Supplementary Fig. 14**), and reductive elimination (path C in **Supplementary Fig. 14**).



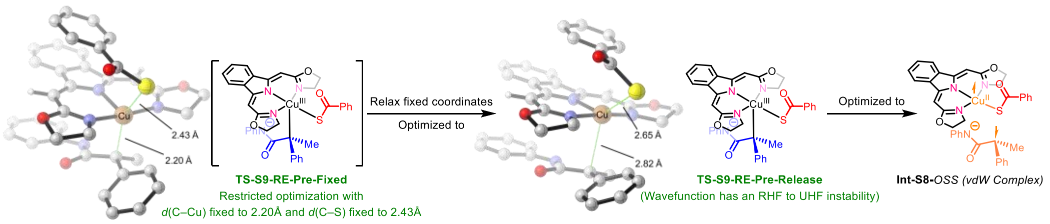
Supplementary Fig. 15 | Optimized closed-shell structure of pre-intermediate ion-type C–S bond formation and further geometry optimization results. Trivial hydrogen atoms are omitted for clarity.

Regarding path A, the ion-type C–S bonding, the transition state cannot be located after extensive efforts. The structure of the pre-intermediate prior to the proposed ion-type C–S bonding transition state can be located using restricted Hartree-Fock (RHF) calculation as **Optimized TS-S9-CB-Pre**. The sequential wavefunction test indicates that this **Optimized TS-S9-CB-Pre** has an RHF to UHF 'wavefunction' instability. Such closed-shell singlet, zwitterionic intermediate does not exist at computed potential energy surface. Further open-shell singlet optimization with unrestricted Hartree-Fock (UHF) calculation of **Optimized TS-S9-CB-Pre** leads to the open-shell singlet intermediate **Int-S8**-*OSS*, which is a VdW (van der Waals) complex of **L16**Cu(II)(benzoylthio) species **Int-S6** and tertiary benzyl radical **Int-S7**, and also the pre-intermediate for the radical substitution C–S bond formation. Mulliken spin distribution indicates the open-shell singlet diradical nature of **Int-S8**-*OSS*. Based on these results, the ion-type C–S bonding pathway is not operative. (**Supplementary Fig. 15**)



Supplementary Fig. 16 | Located radical-substitution-type C–S bond formation transition state. Trivial hydrogen atoms are omitted for clarity.

Regarding path B, the radical-substitution-type C–S bonding, the transition state is located as **TS-S9**. The free energy barrier of C–S bond formation via **TS-S4** is 13.9 kcal/mol compared to the favored VdW complex **Int-S8**-*Triplet*. The Mulliken spin distribution indicates the open-shell singlet nature of **TS-S9**. (**Supplementary Fig. 16**)



Supplementary Fig. 17 | Results on sequential geometry optimizations for closed-shell structure of pre-intermediate C–S reductive elimination. Trivial hydrogen atoms are omitted for clarity.

Regarding path C, C–S reductive elimination, the reductive elimination transition state cannot be located after extensive efforts. The pre-intermediate of reductive elimination, **TS-S9-RE-Pre-Fixed**, is firstly optimized with *d*(C–Cu) fixed to 2.20Å and *d*(C–S) fixed to 2.43Å in order to maintain the characteristics of the proposed Cu(III) structure during optimization. Sequential geometry optimization with full degrees of freedom leads to **TS-S9-RE-Pre-Release** with C–Cu bond length of 2.82Å. Wavefunction test indicates that this **TS-S9-RE-Pre-Release** has an RHF to UHF 'wavefunction' instability. Further open-shell singlet optimization with unrestricted Hartree-Fock (UHF) calculation of **TS-S9-RE-Pre-Release** leads to **Int-S8**-*OSS*. Based on these results, the C–S reductive elimination pathway is not operative. (**Supplementary Fig. 17**)

Based on the above calculations and discussions, Cu-mediated C–S bond formation between tertiary benzyl radical and benzothioate via open-shell singlet radical substitution transition state **TS-S9** is the most favorable.

12.4. Table of Energies

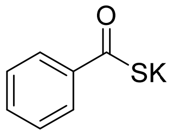
Supplementary Table 12 | Energies in **Supplementary Figs. 10, 12** and **14**. Zero-point correction (***ZPE***), thermal correction to enthalpy (***TCH***), thermal correction to Gibbs free energy (***TCG***), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-311+G(d,p)-SDD-SMD(Toluene)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
Int-S1	0.527361	0.562973	0.458709	−2358.237425	−2357.674452	−2357.778716	
Int-S2	0.143393	0.151750	0.110895	−310.353457	−310.201707	−310.242562	
Int-S3-*OSS*	0.672446	0.717195	0.592468	−2668.608790	−2667.891595	−2668.016322	
Int-S3- *Triplet*	0.672460	0.717199	0.591489	−2668.608809	−2667.891610	−2668.017320	
TS-S4	0.672600	0.716539	0.593891	−2668.592583	−2667.876044	−2667.998692	235.9*i*
TS-S4-RE	0.673177	0.717210	0.592332	−2668.583021	−2667.865811	−2667.990689	104.6*i*
Int-S5	0.675801	0.719455	0.598784	−2668.627689	−2667.908234	−2668.028905	

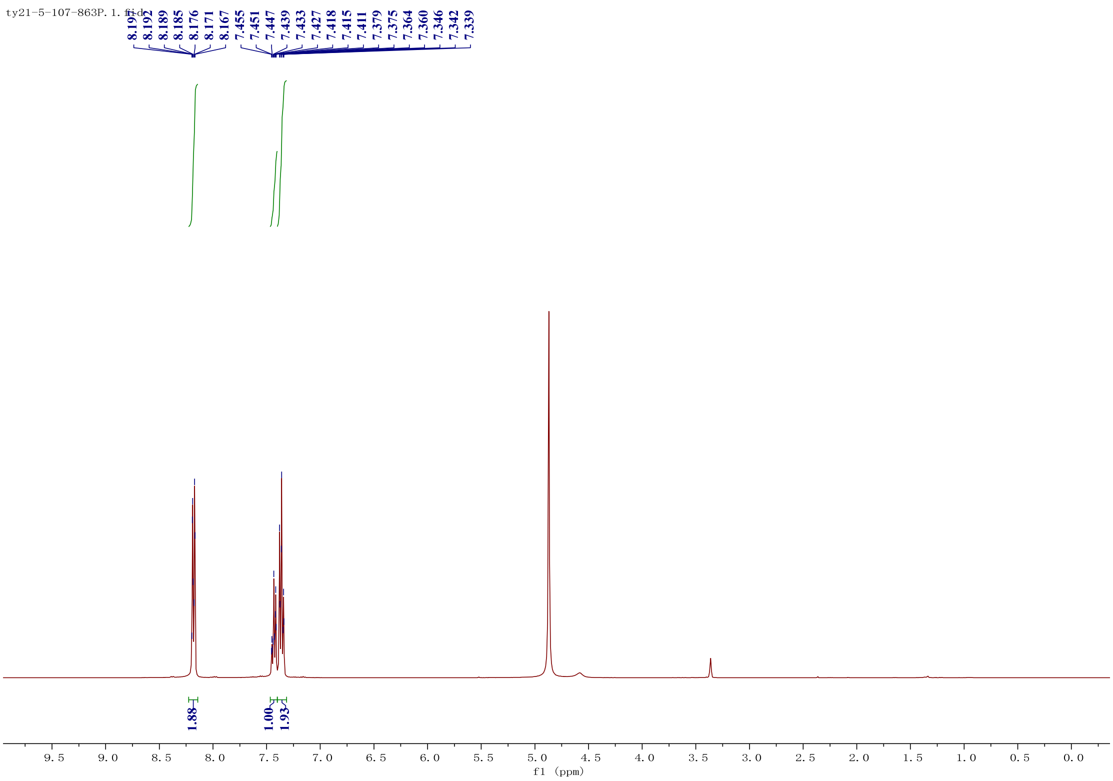
Supplementary Table 13 | Energies in **Supplementary Figs. 14** and **16** Zero-point correction (***ZPE***), thermal correction to enthalpy (***TCH***), thermal correction to Gibbs free energy (***TCG***), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-311+G(d,p)-SDD-SMD(Diethyl Ether)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

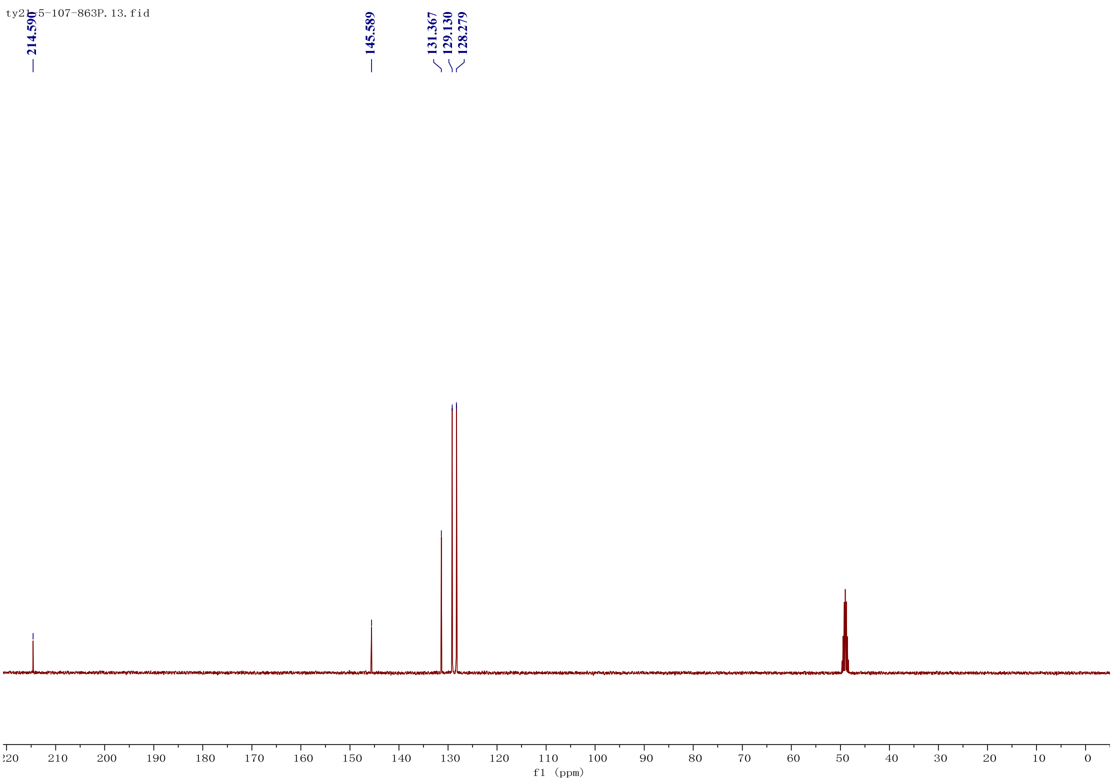
Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
Int-S6	0.383519	0.411261	0.322601	−1873.966007	−1873.554746	−1873.643406	
Int-S7	0.23856	0.253748	0.194709	−709.748212	−709.494464	−709.553503	
Int-S8- *OSS*	0.624067	0.667389	0.546065	−2583.740099	−2583.072710	−2583.194034	
Int-S8- *Triplet*	0.624005	0.667356	0.544790	−2583.740237	−2583.072881	−2583.195447	
TS-S9	0.622438	0.665361	0.545773	−2583.719100	−2583.053739	−2583.173327	201.8*i*
Int-S10	0.624152	0.667367	0.545544	−2583.740048	−2583.072681	−2583.194504	

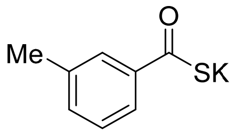
13. NMR spectra



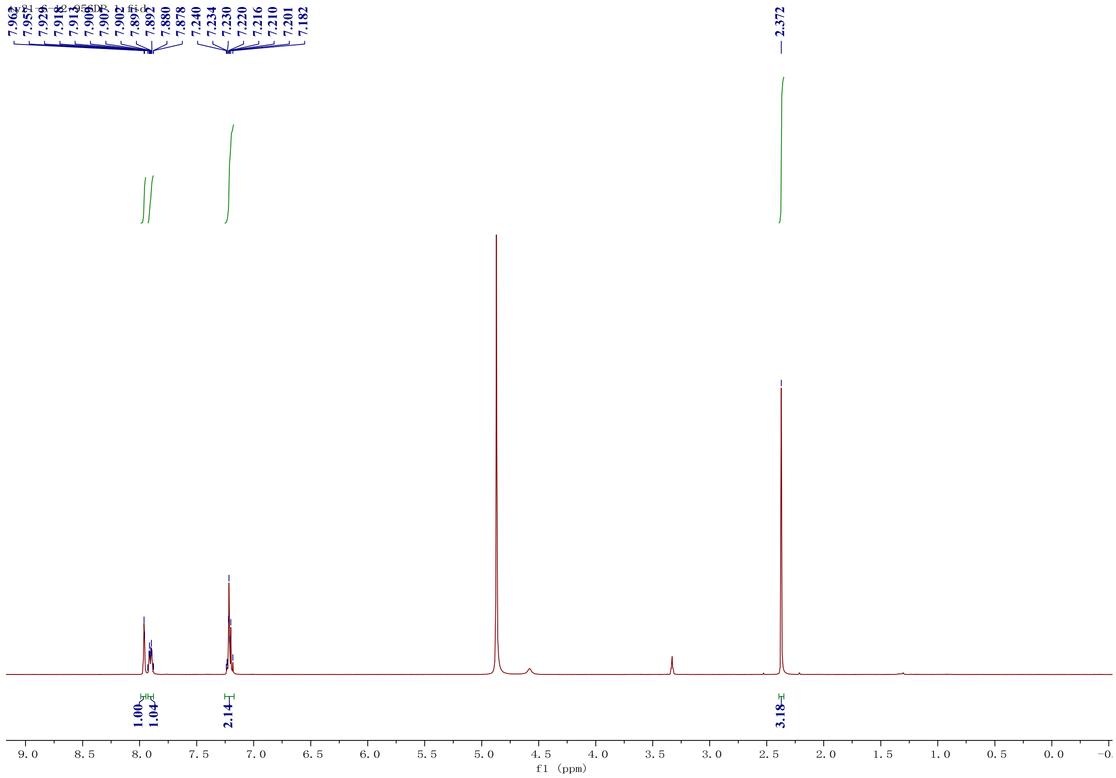
S1

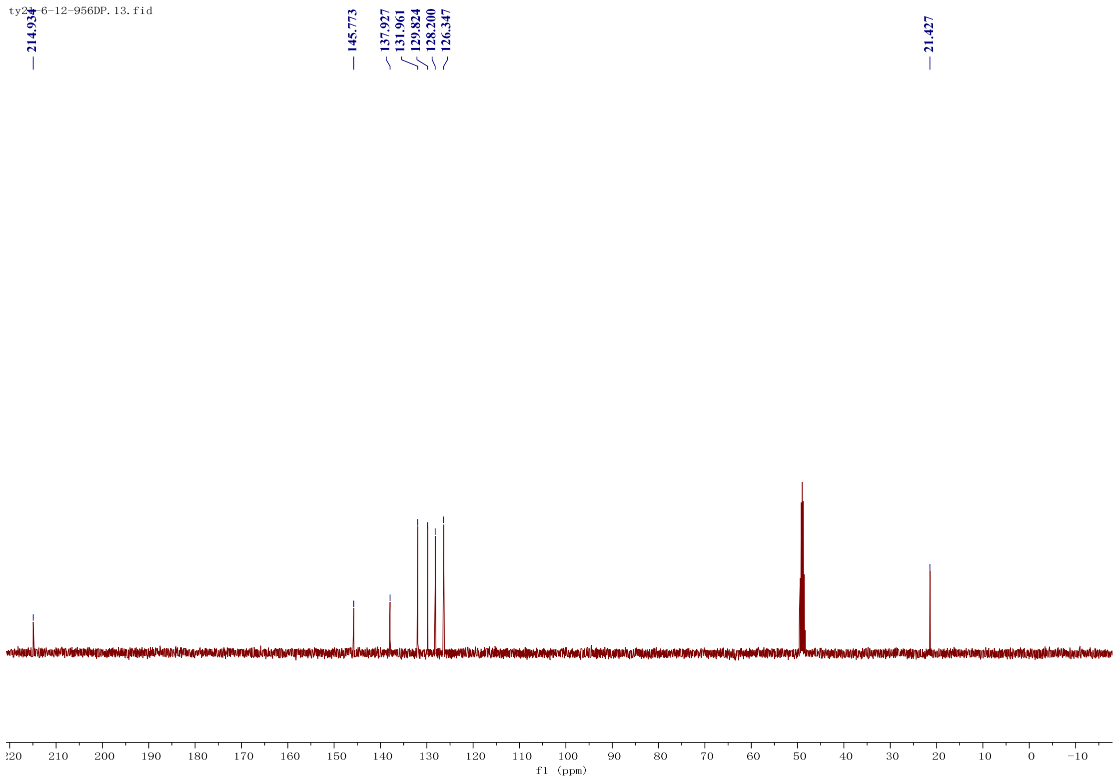


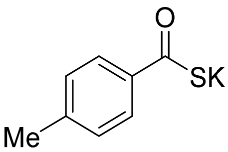




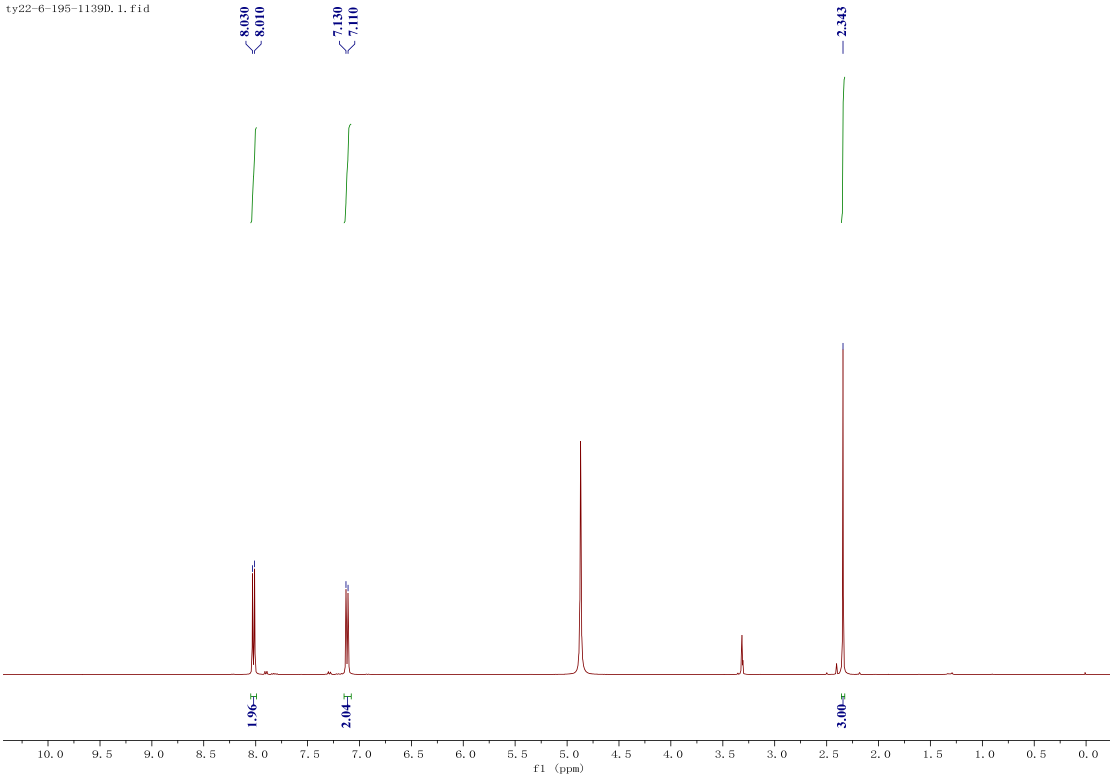
S10



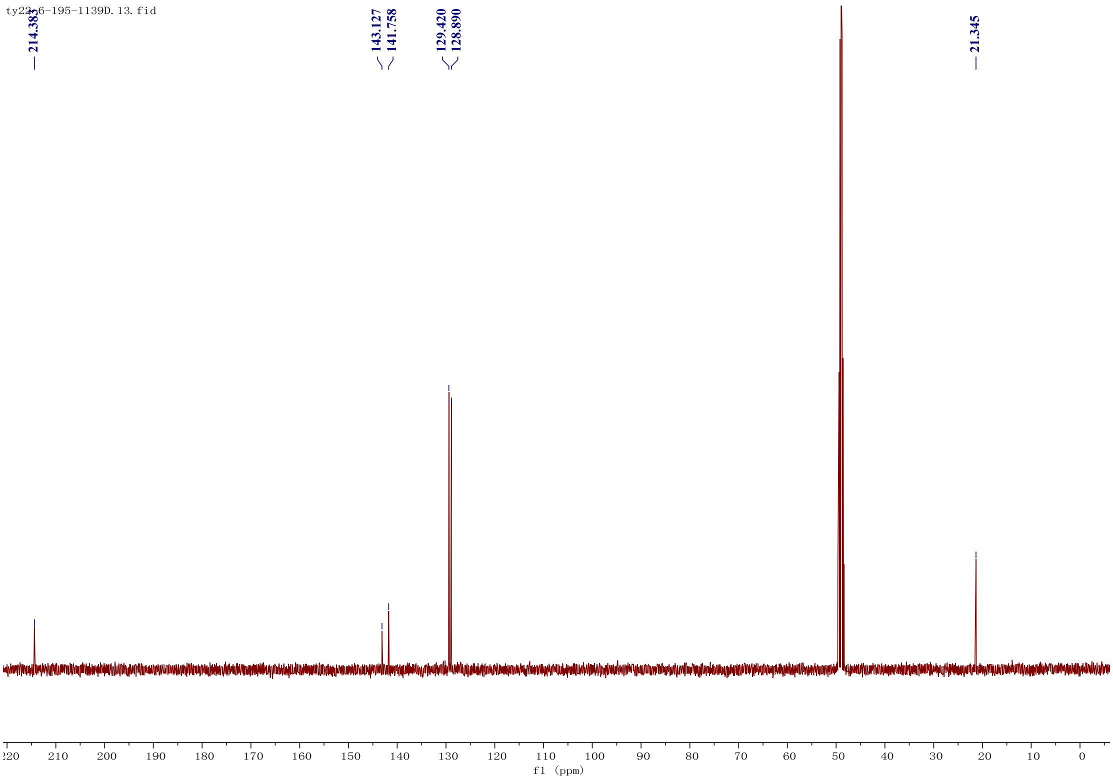




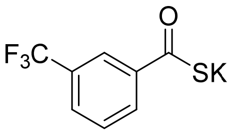
S11



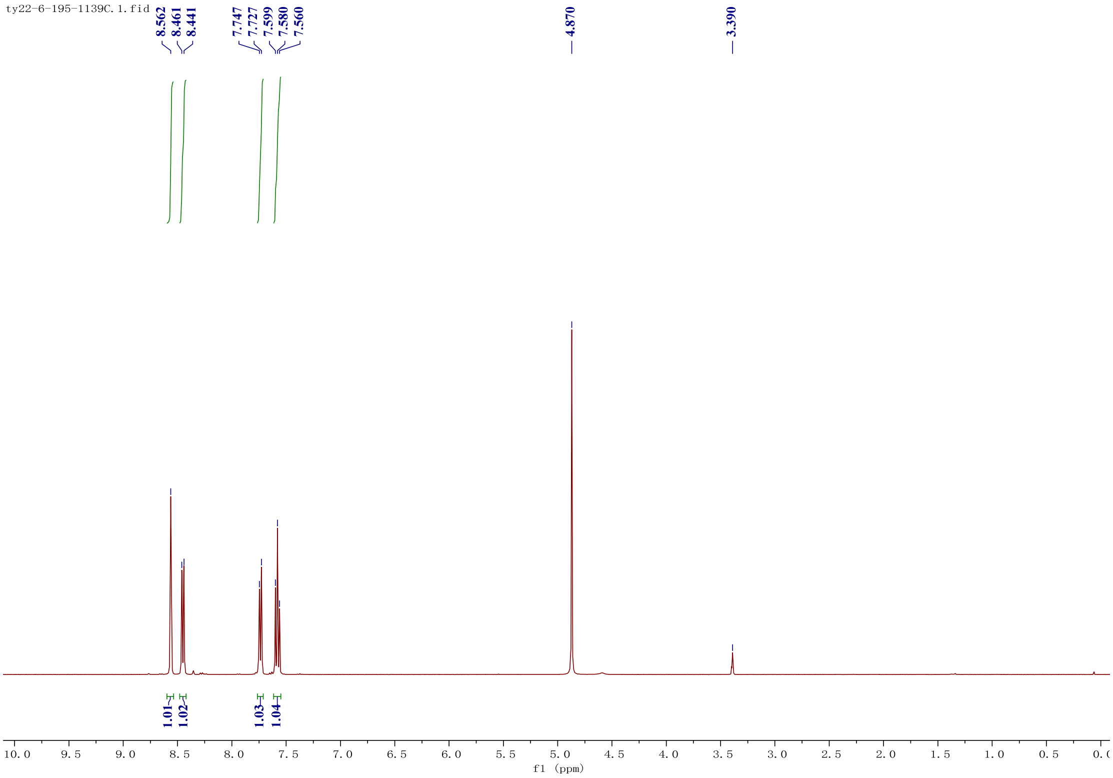
ty22-6-195-1139D.1.fid
8.030
8.010
7.130
7.110
2.343
1.96
2.04
3.00
f1 (ppm)

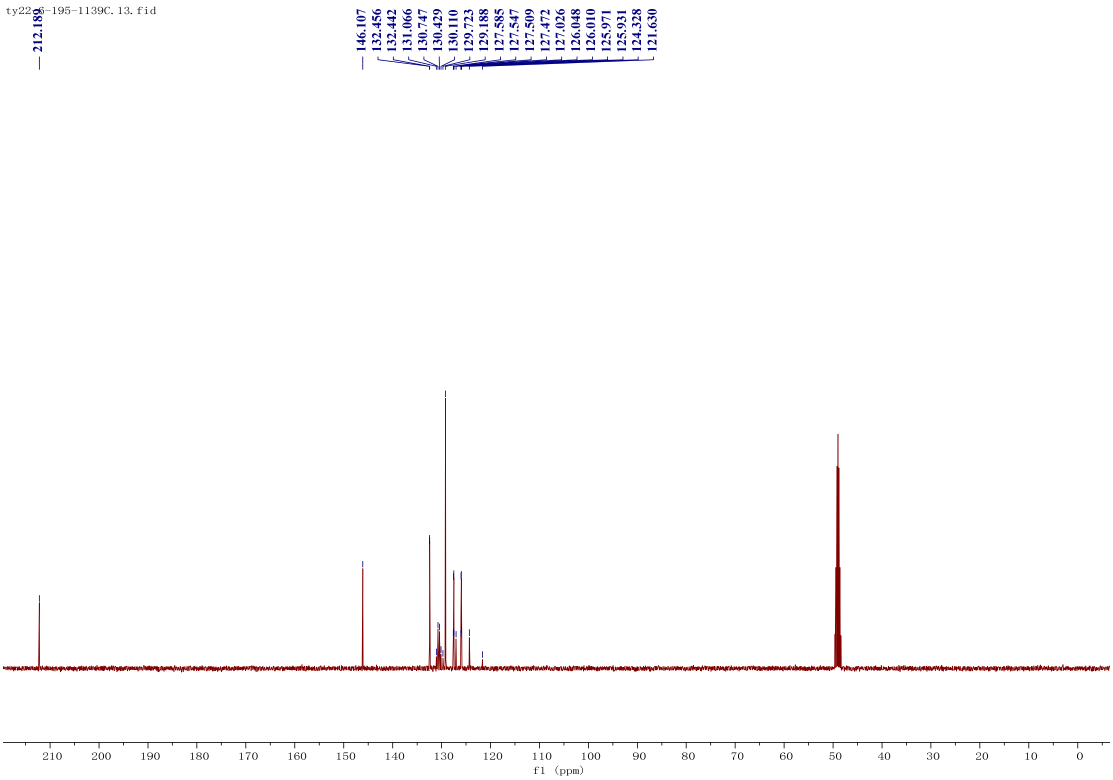


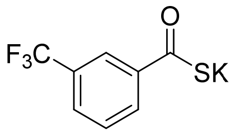
ty22-6-195-1139D.13.fid
214.383
143.127
141.758
129.420
128.890
21.345
f1 (ppm)


F3C
O
SK

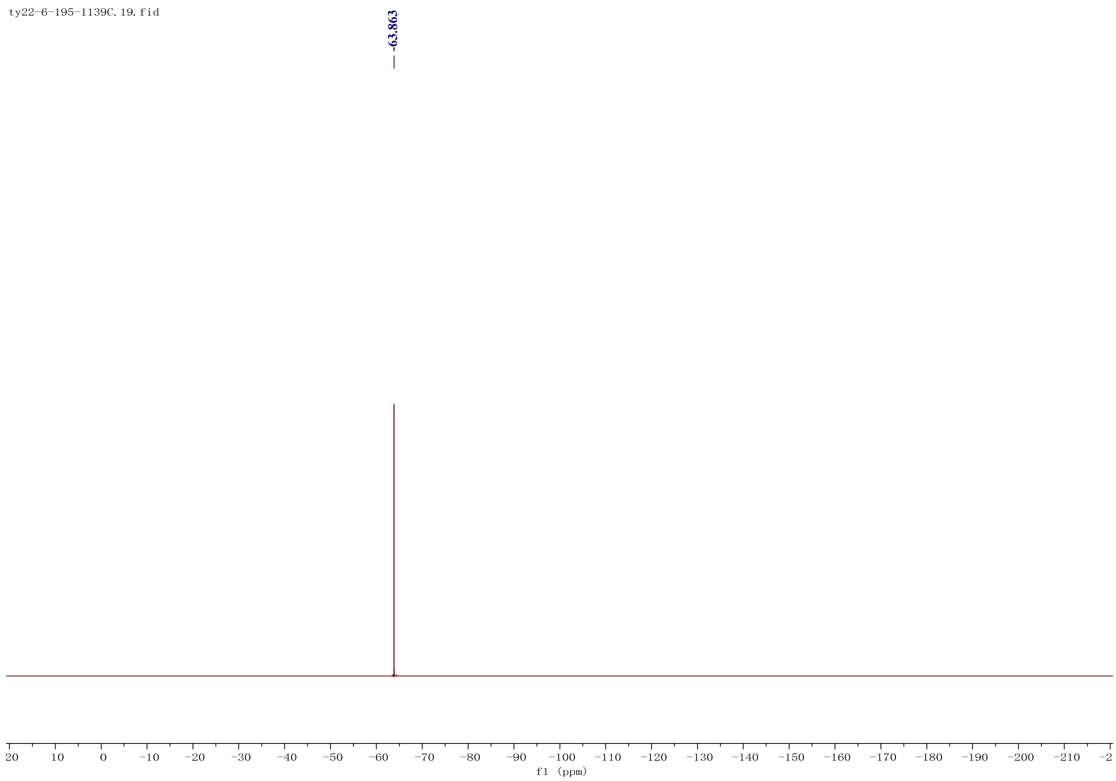
S12


ty22-6-195-1139C.1.fid
8.562
8.461
8.441
7.747
7.727
7.599
7.580
7.560
4.870
3.390
1.01
1.02
1.03
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

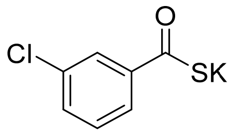

ty22-6-195-1139C.13.fid
212.189
146.107
132.456
132.442
131.066
130.747
130.429
130.110
129.723
129.188
127.585
127.547
127.509
127.472
127.026
126.048
126.010
125.971
125.931
124.328
121.630
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



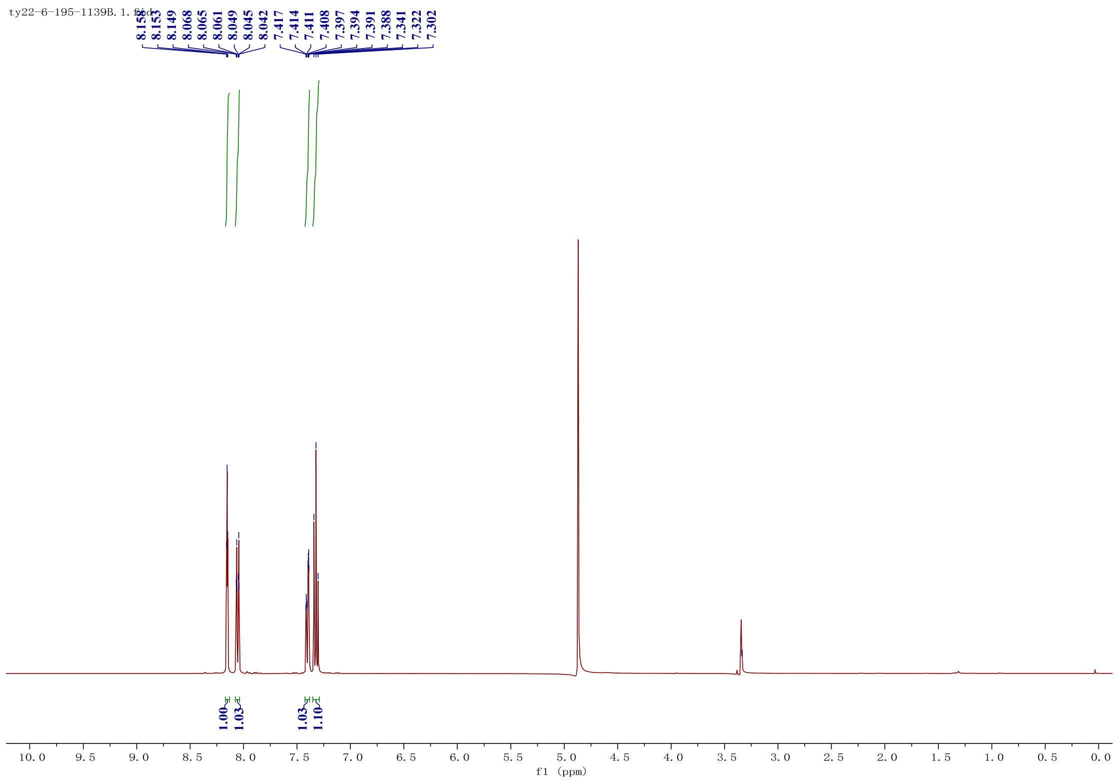
S12

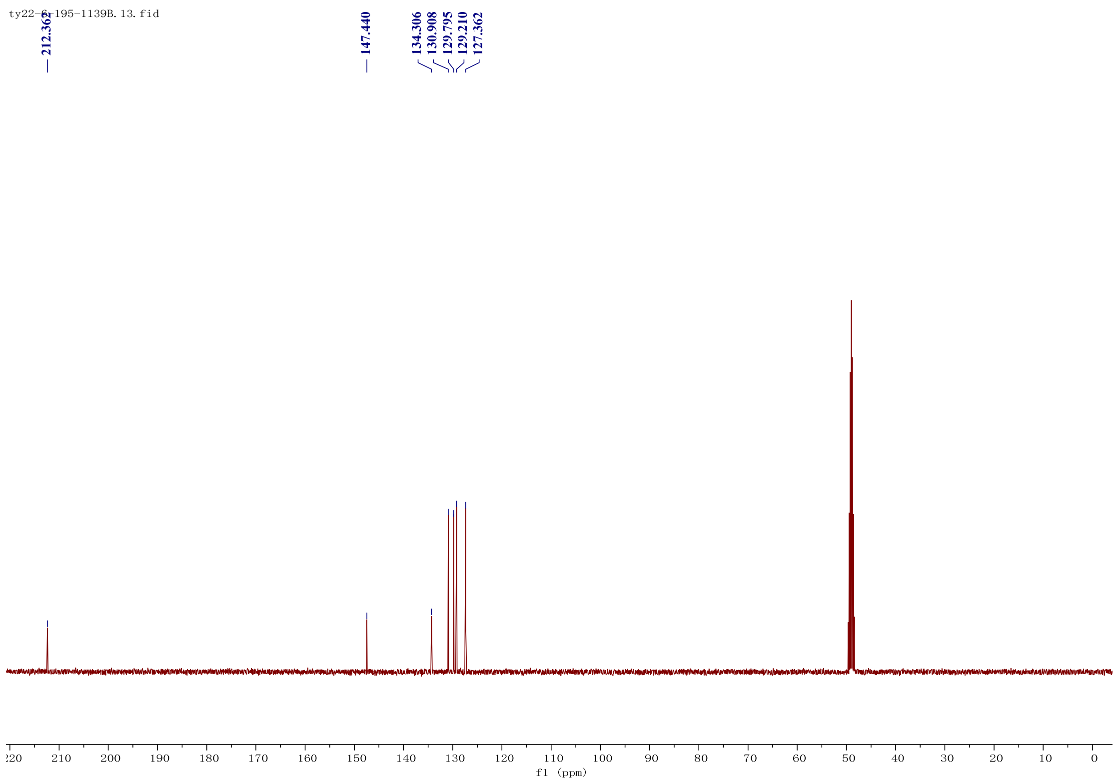


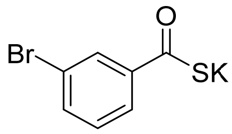
ty22-6-195-1139C.19.fid
-63.863
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)



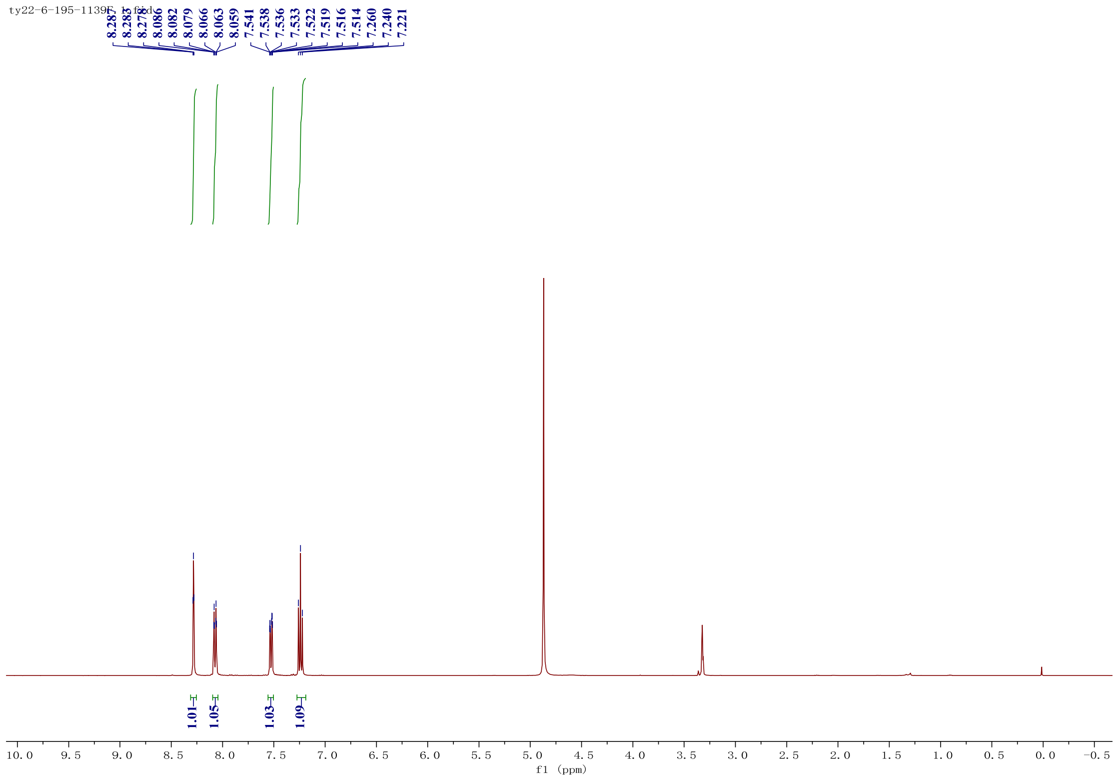
S13

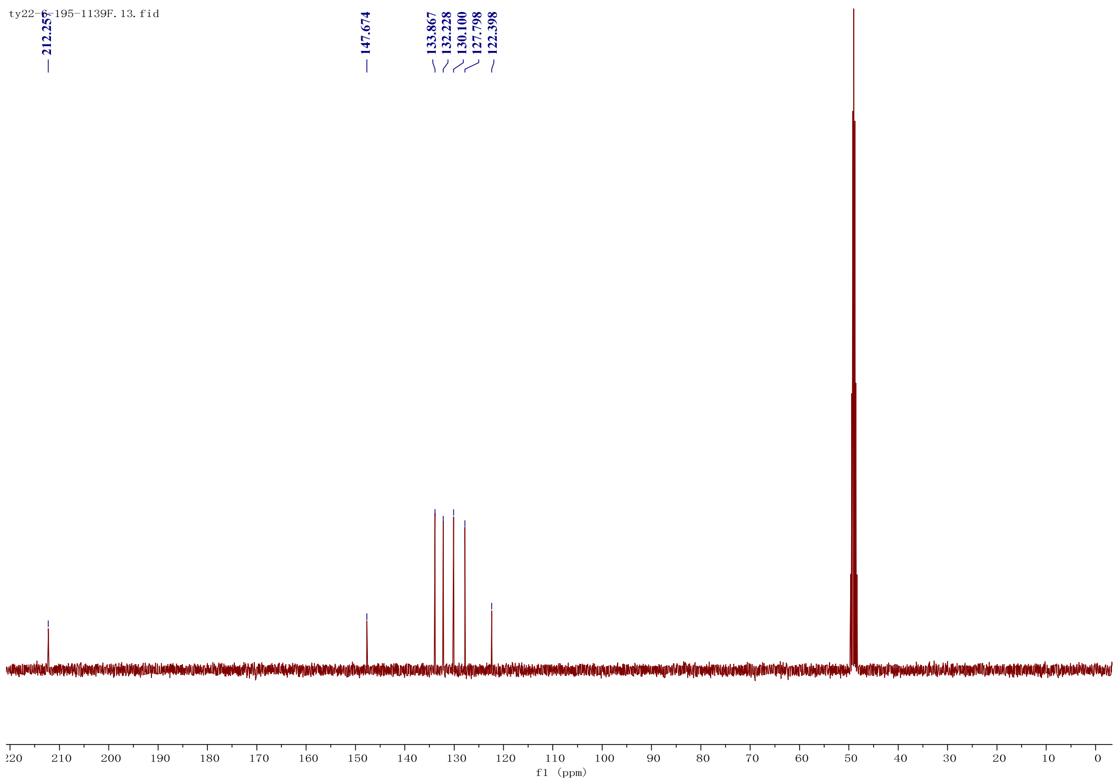

ty22-6-195-1139B.1.fid
8.158
8.153
8.149
8.068
8.065
8.061
8.049
8.045
8.042
7.417
7.414
7.411
7.408
7.397
7.394
7.391
7.388
7.341
7.322
7.302
1.00
1.03
1.03
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

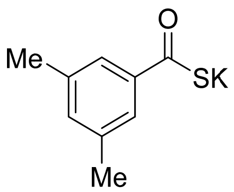

ty22-6-195-1139B.13.fid
212.362
147.440
134.306
130.908
129.795
129.210
127.362
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



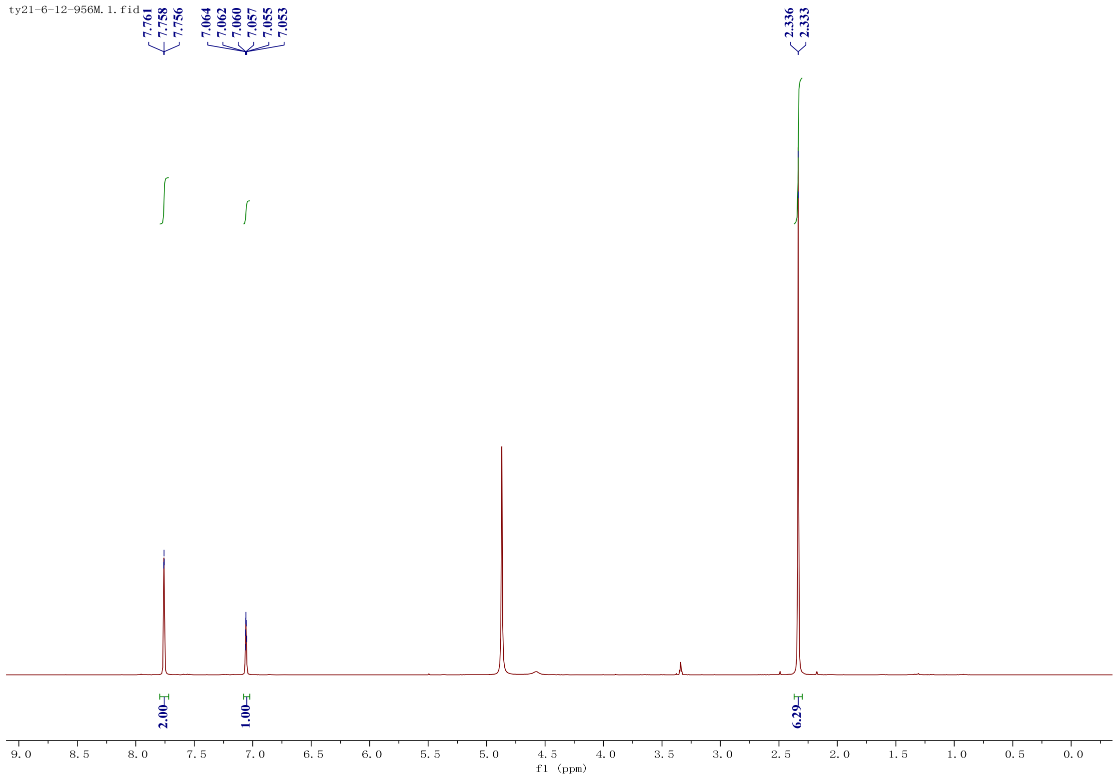
S14

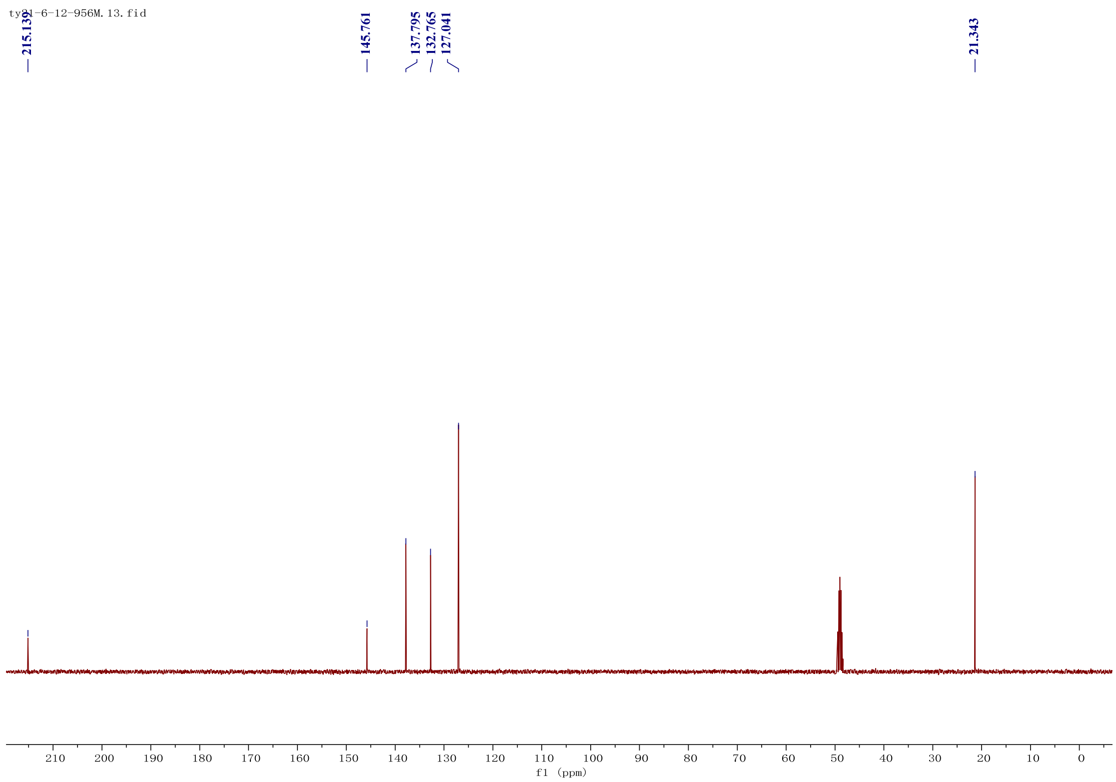


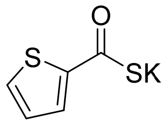




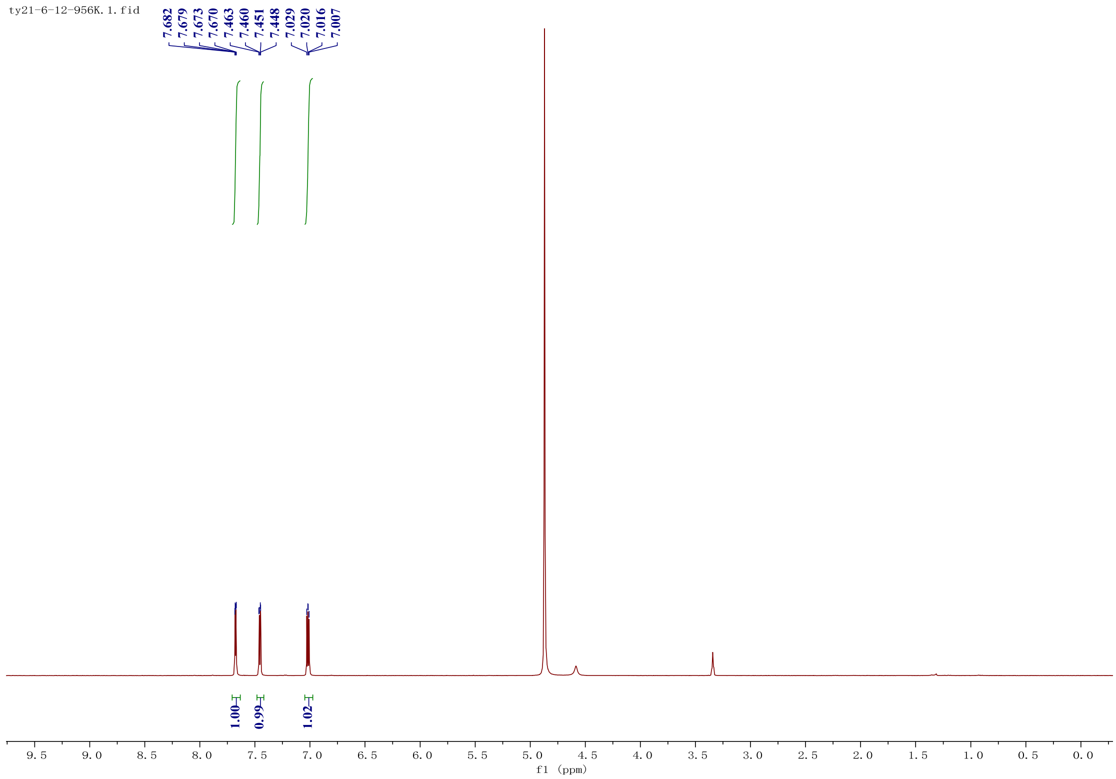
S15

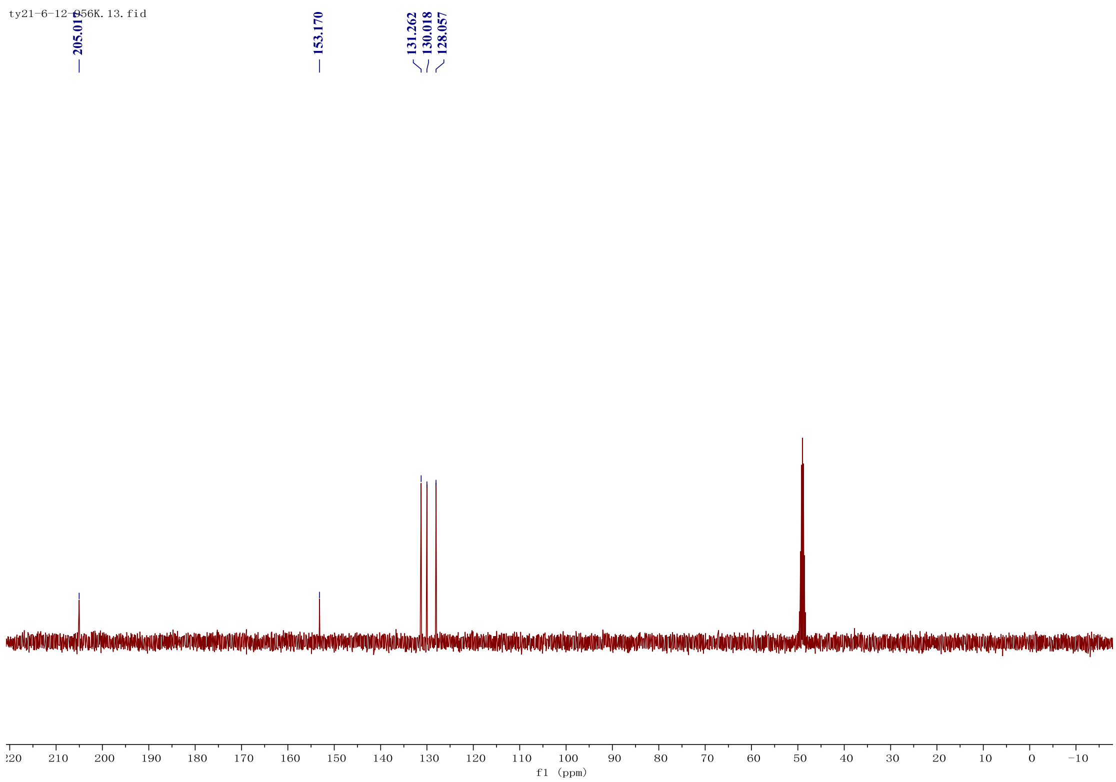

ty21-6-12-956M.1.fid
7.761
7.758
7.756
7.064
7.062
7.060
7.057
7.055
7.053
2.336
2.333
2.00
1.00
6.29
f1 (ppm)

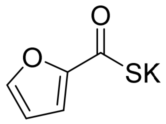

ty21-6-12-956M.13.fid
215.139
145.761
137.795
132.765
127.041
21.343
f1 (ppm)


O
S
SK

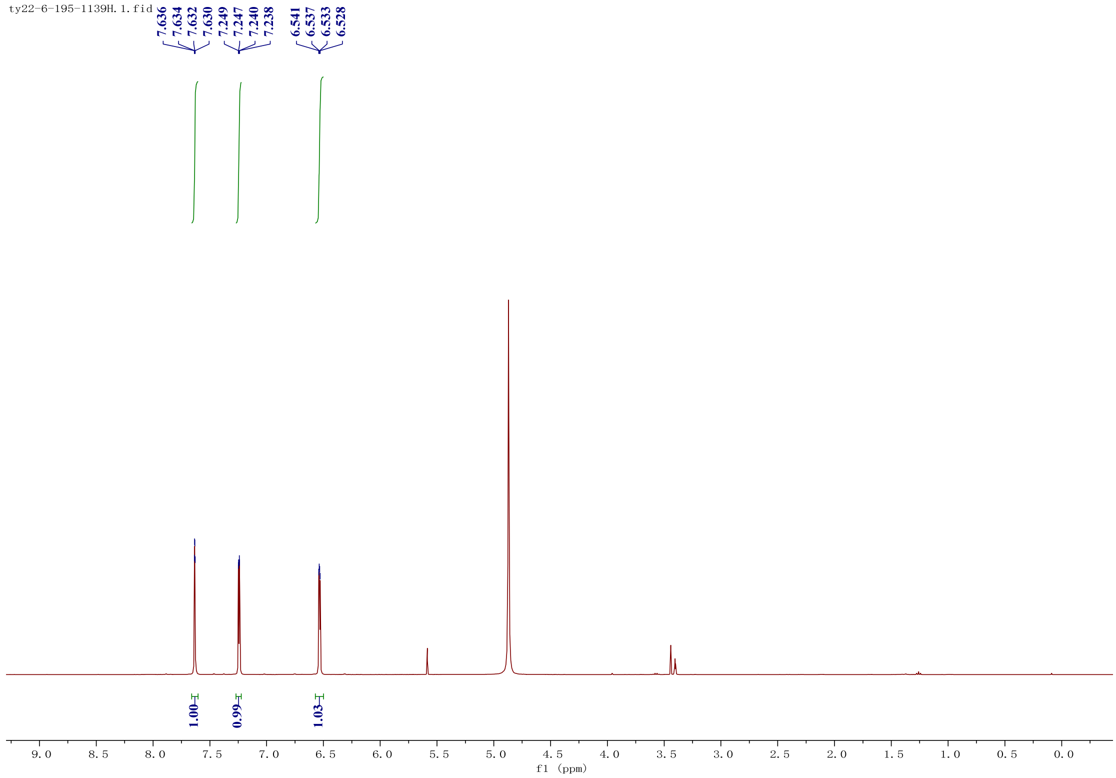
S16

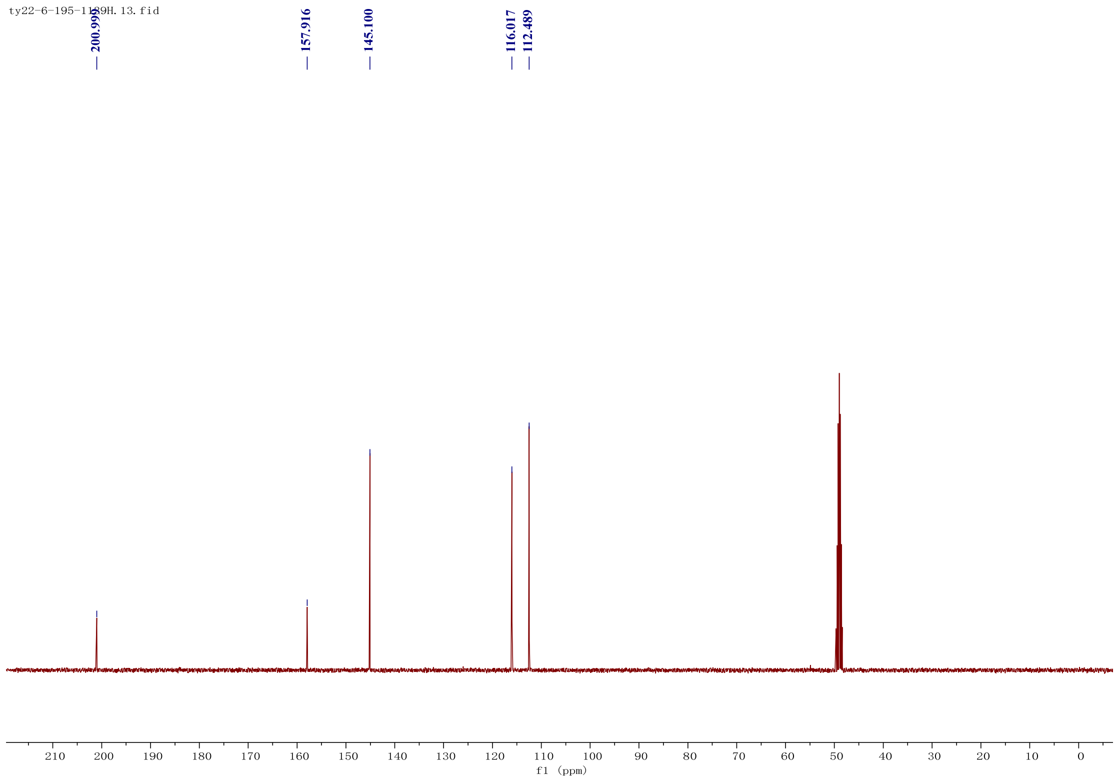

ty21-6-12-956K.1.fid
7.682
7.679
7.673
7.670
7.463
7.460
7.451
7.448
7.029
7.020
7.016
7.007
1.00
0.99
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

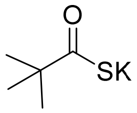

ty21-6-12-956K.13.fid
205.015
153.170
131.262
130.018
128.057
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



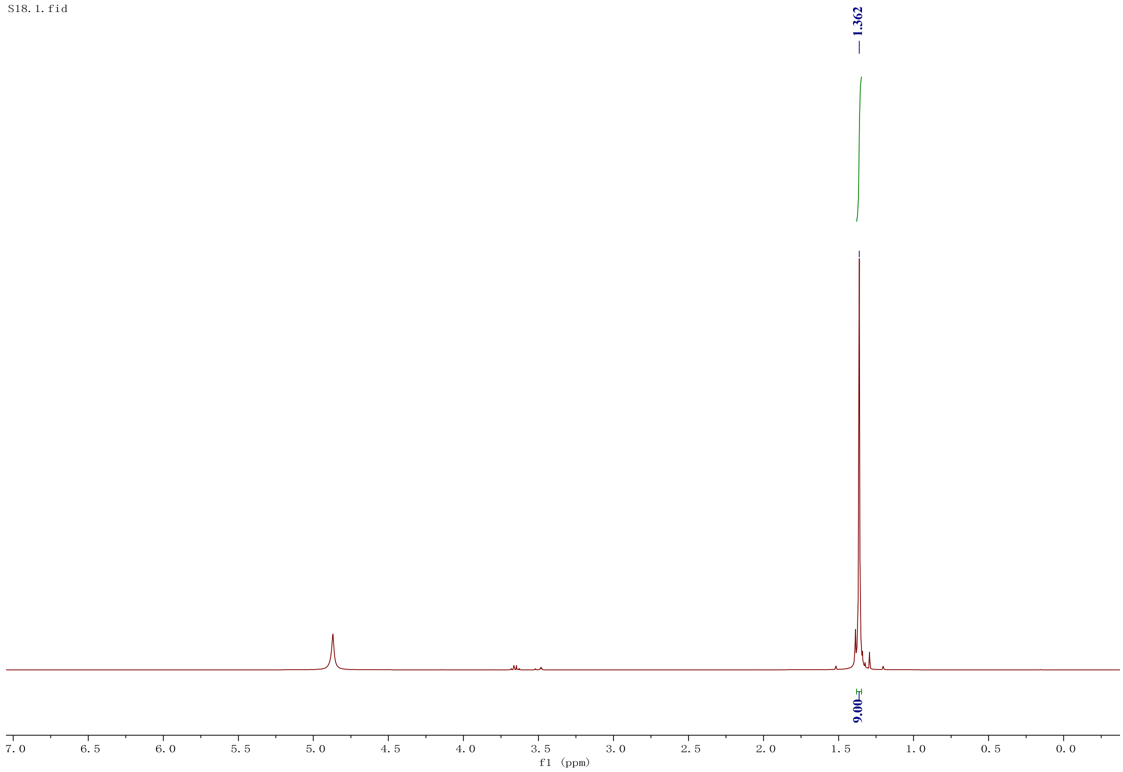
S17

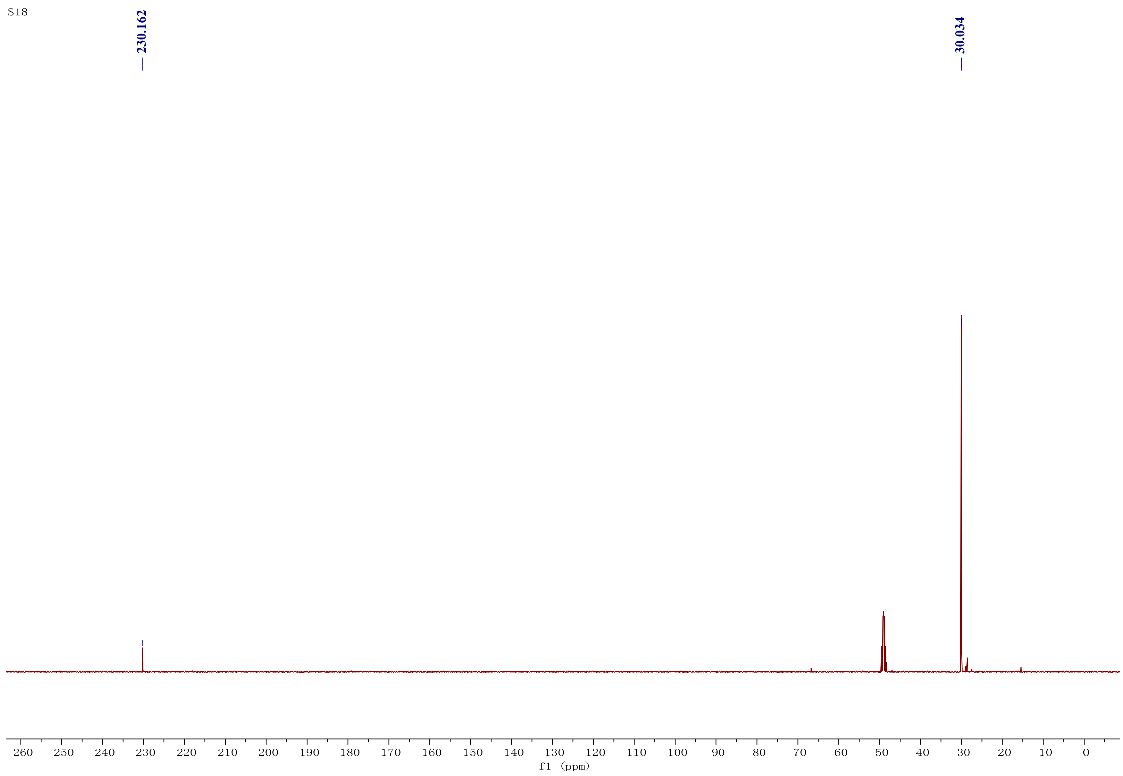

ty22-6-195-1139H.1.fid
7.636
7.634
7.632
7.630
7.249
7.247
7.240
7.238
6.541
6.537
6.533
6.528
1.00
0.99
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

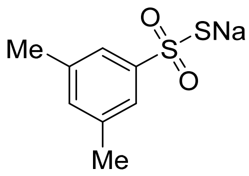

ty22-6-195-1139H.13.fid
200.995
157.916
145.100
116.017
112.489
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
SK

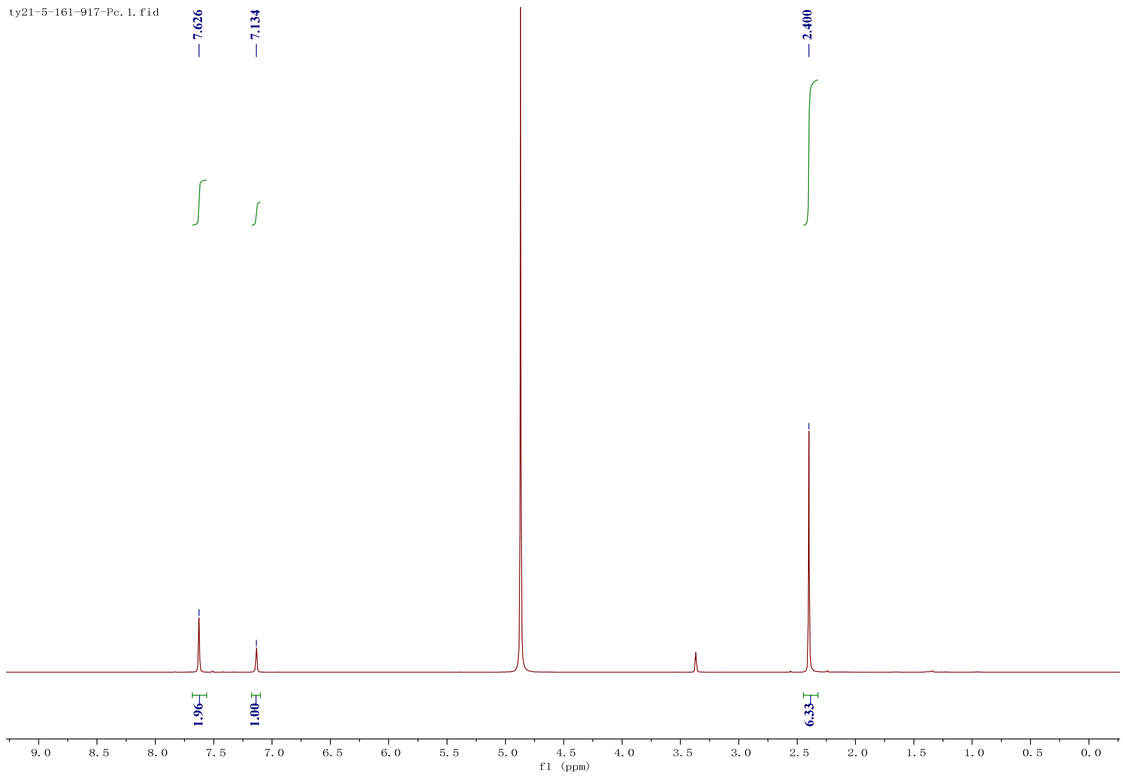
S18

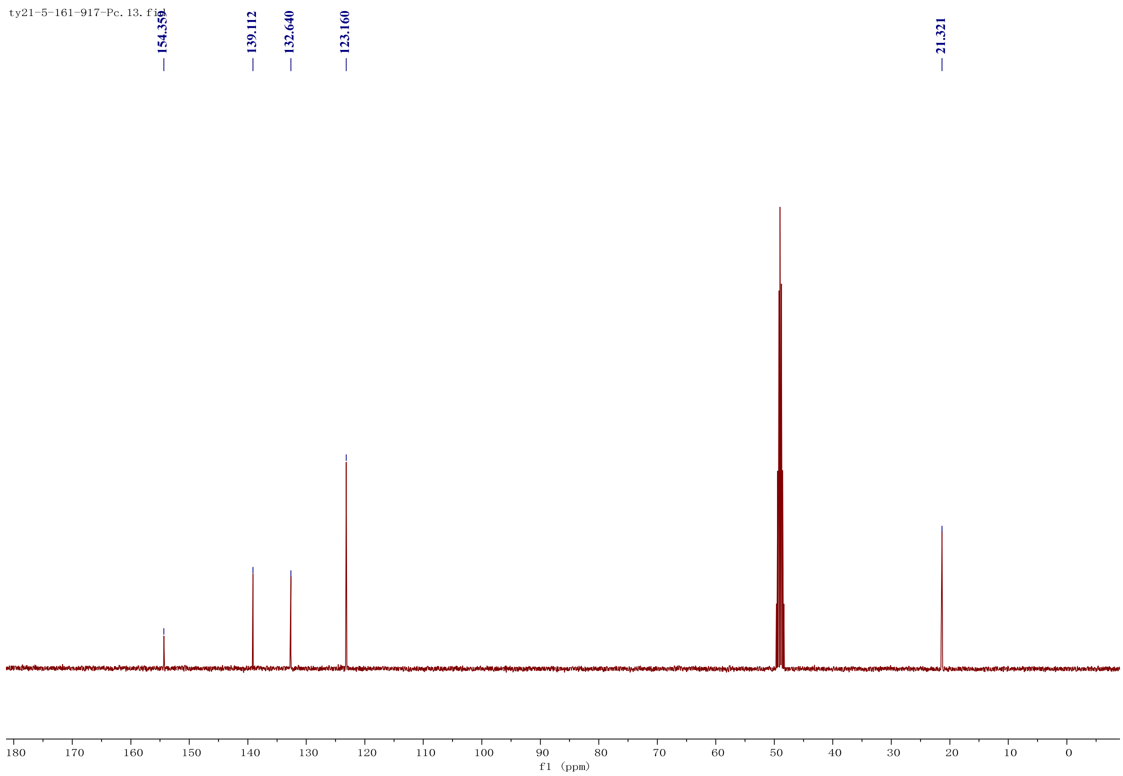

S18.1.fid
1.362
9.00
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

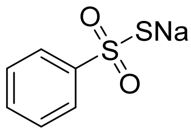

S18
230.162
30.034
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



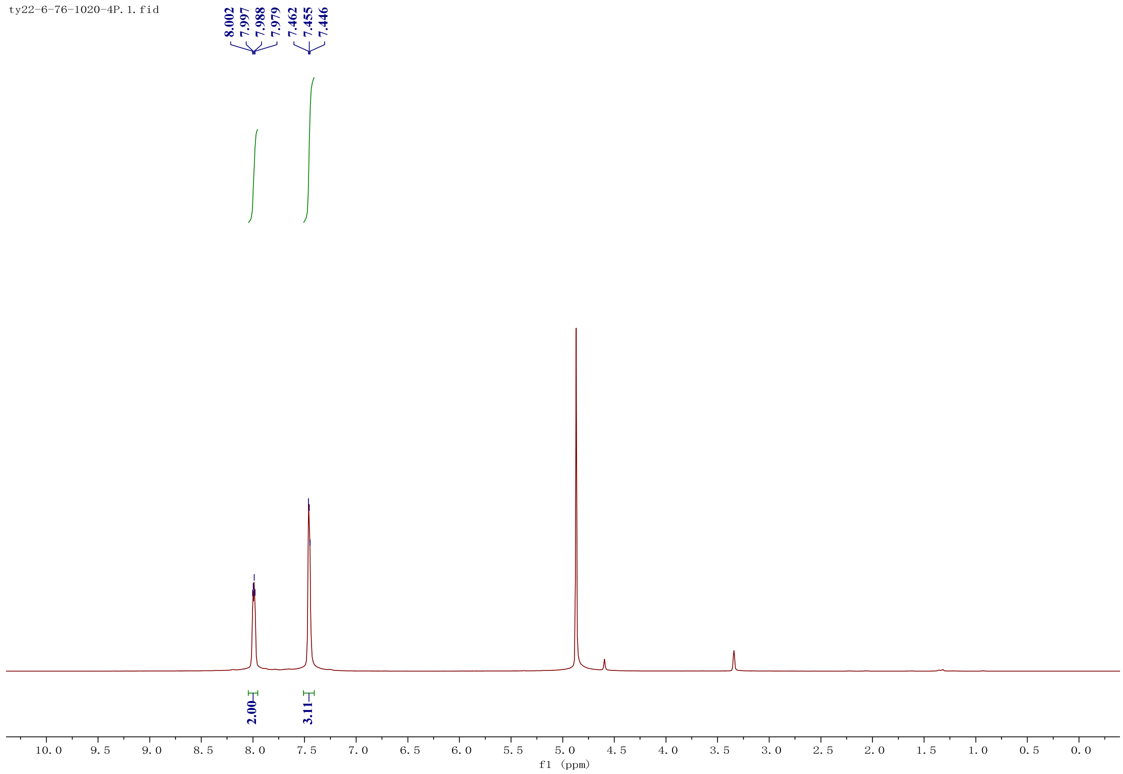
S5

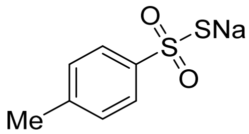

ty21-5-161-917-Pc.1.fid
7.626
7.134
2.400
1.96
1.00
6.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ty21-5-161-917-Pc.13.fid
154.359
139.112
132.640
123.160
21.321
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

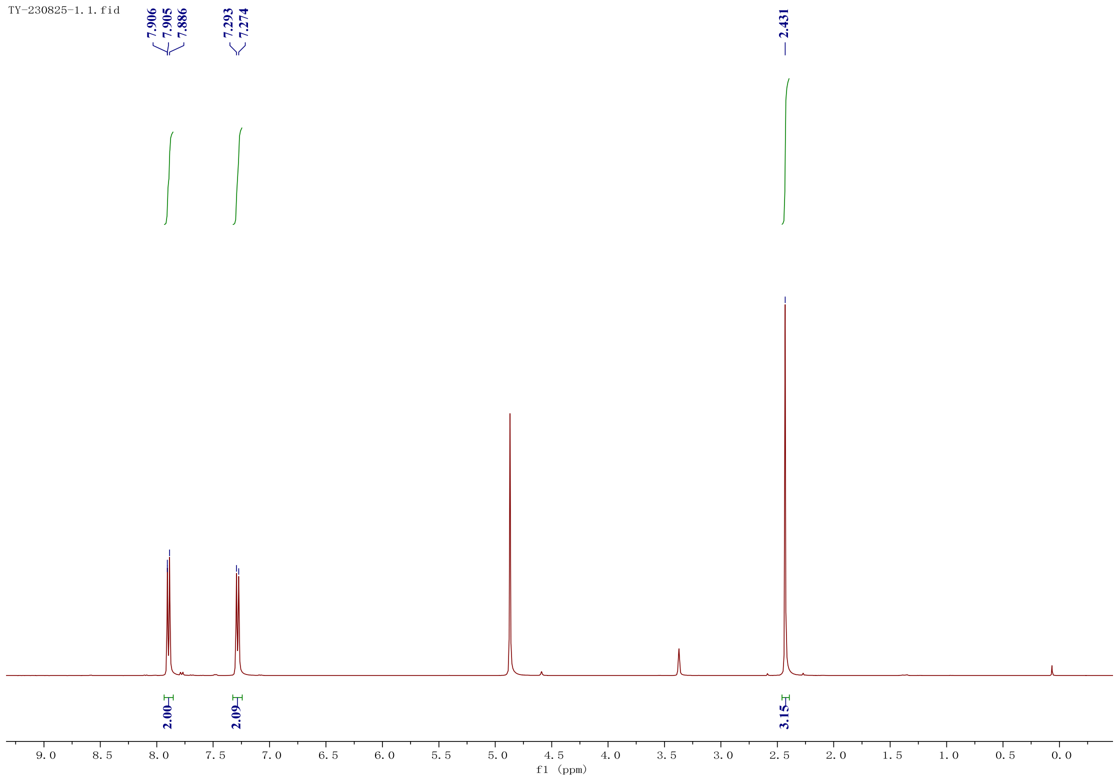


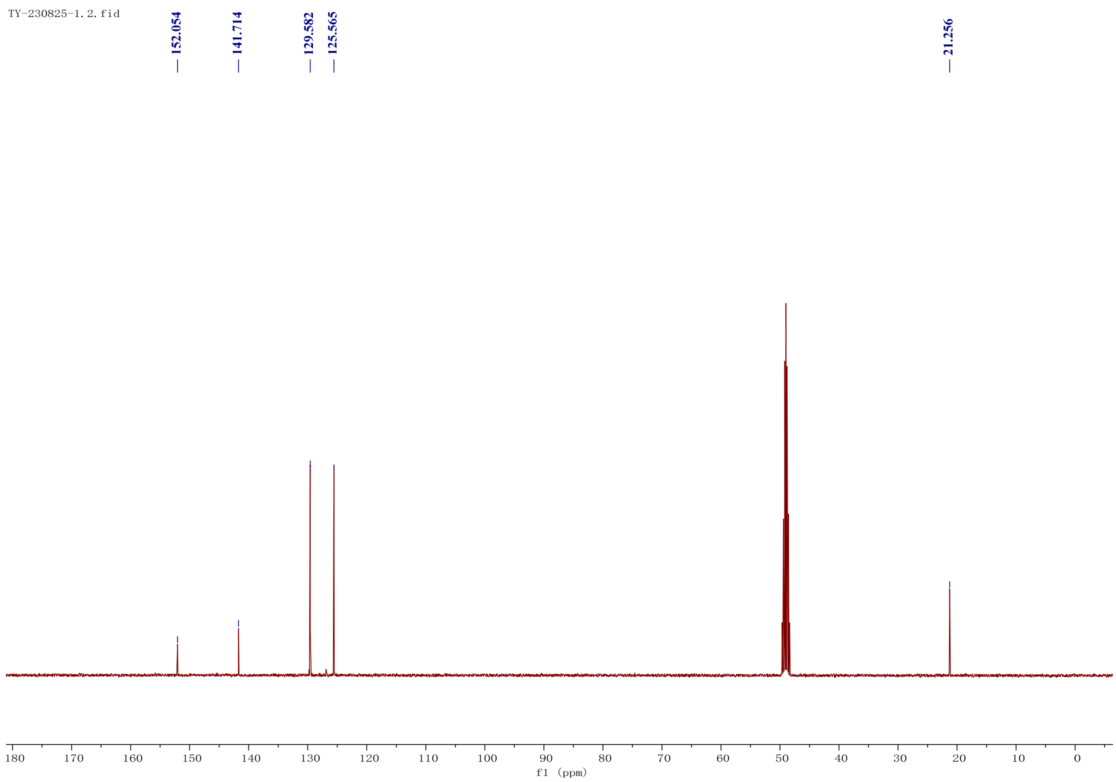
S6

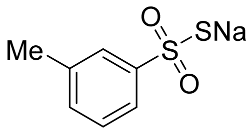

ty22-6-76-1020-4P.1.fid
8.002
7.997
7.988
7.979
7.462
7.455
7.446
2.00
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


SNa
Me

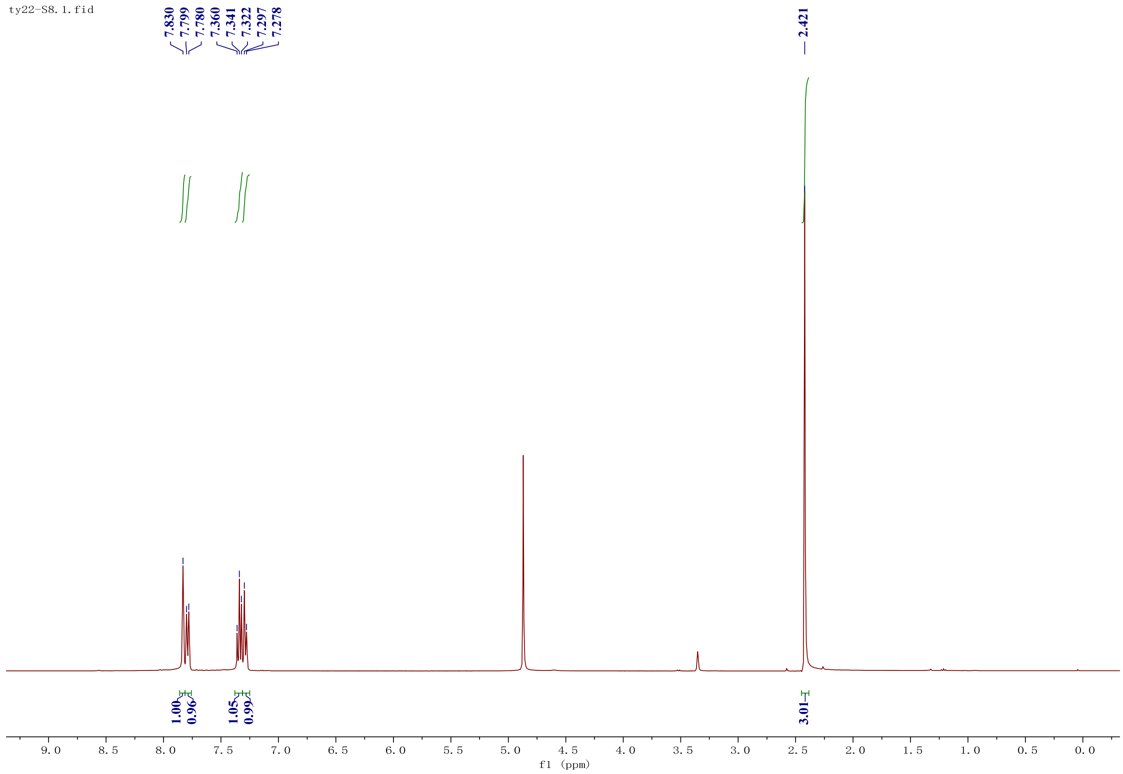
S7

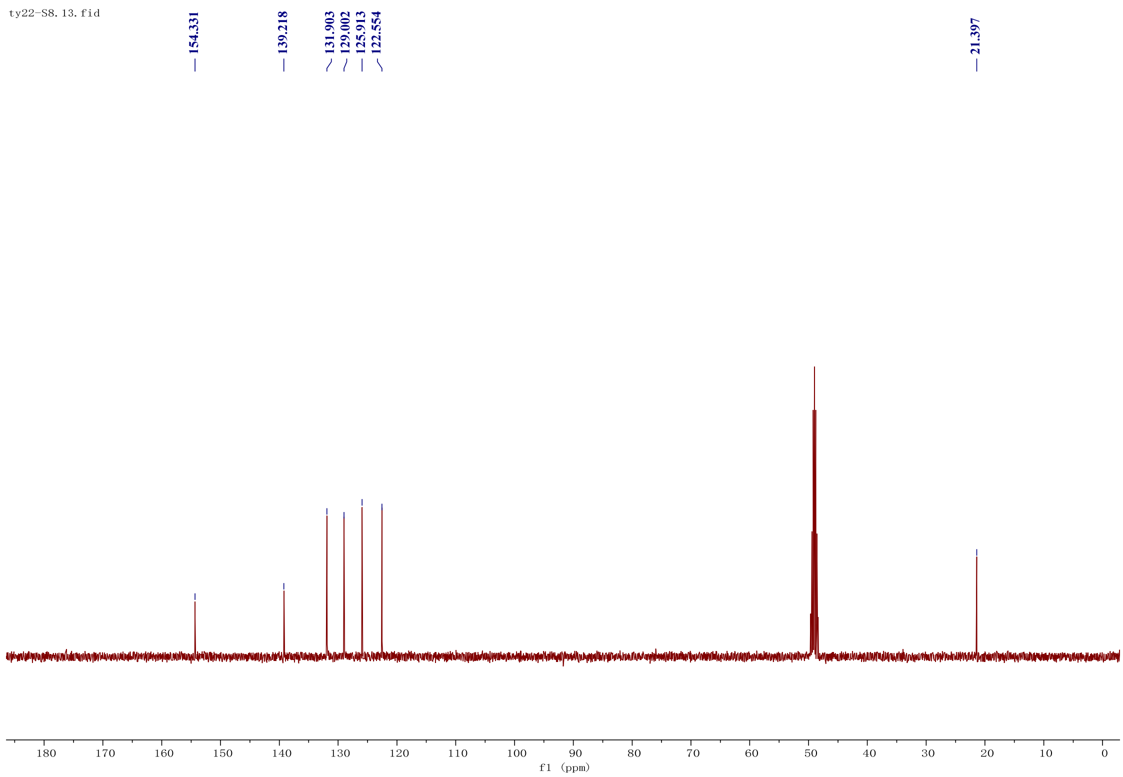

TY-230825-1.1.fid
7.906
7.905
7.886
7.293
7.274
2.431
2.00
2.09
3.15
f1 (ppm)

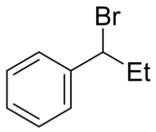

TY-230825-1.2.fid
152.054
141.714
129.582
125.565
21.256
f1 (ppm)


Me
O
SNa
S
O

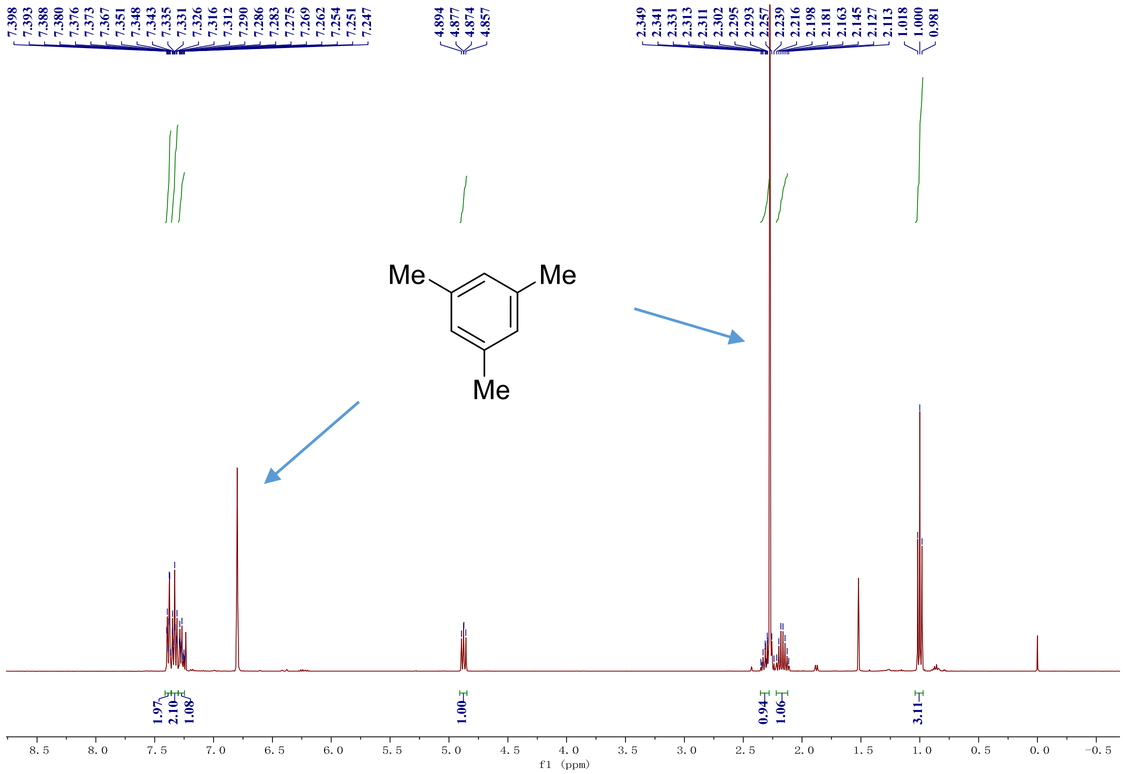
S8

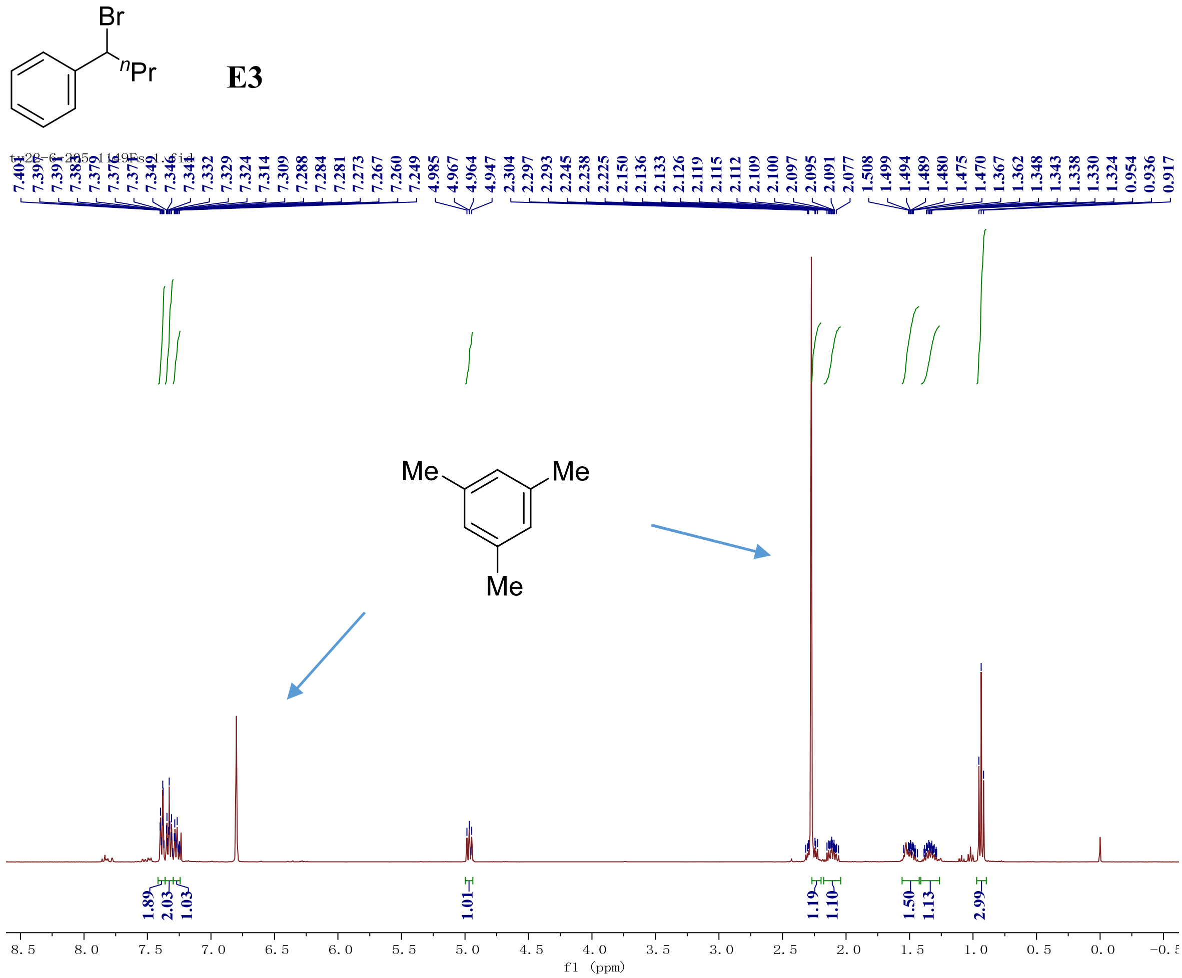

ty22-S8.1.fid
7.830
7.799
7.780
7.360
7.341
7.322
7.297
7.278
2.421
1.00
0.96
1.05
0.99
3.01
f1 (ppm)


ty22-S8.13.fid
154.331
139.218
131.903
129.002
125.913
122.554
21.397
f1 (ppm)

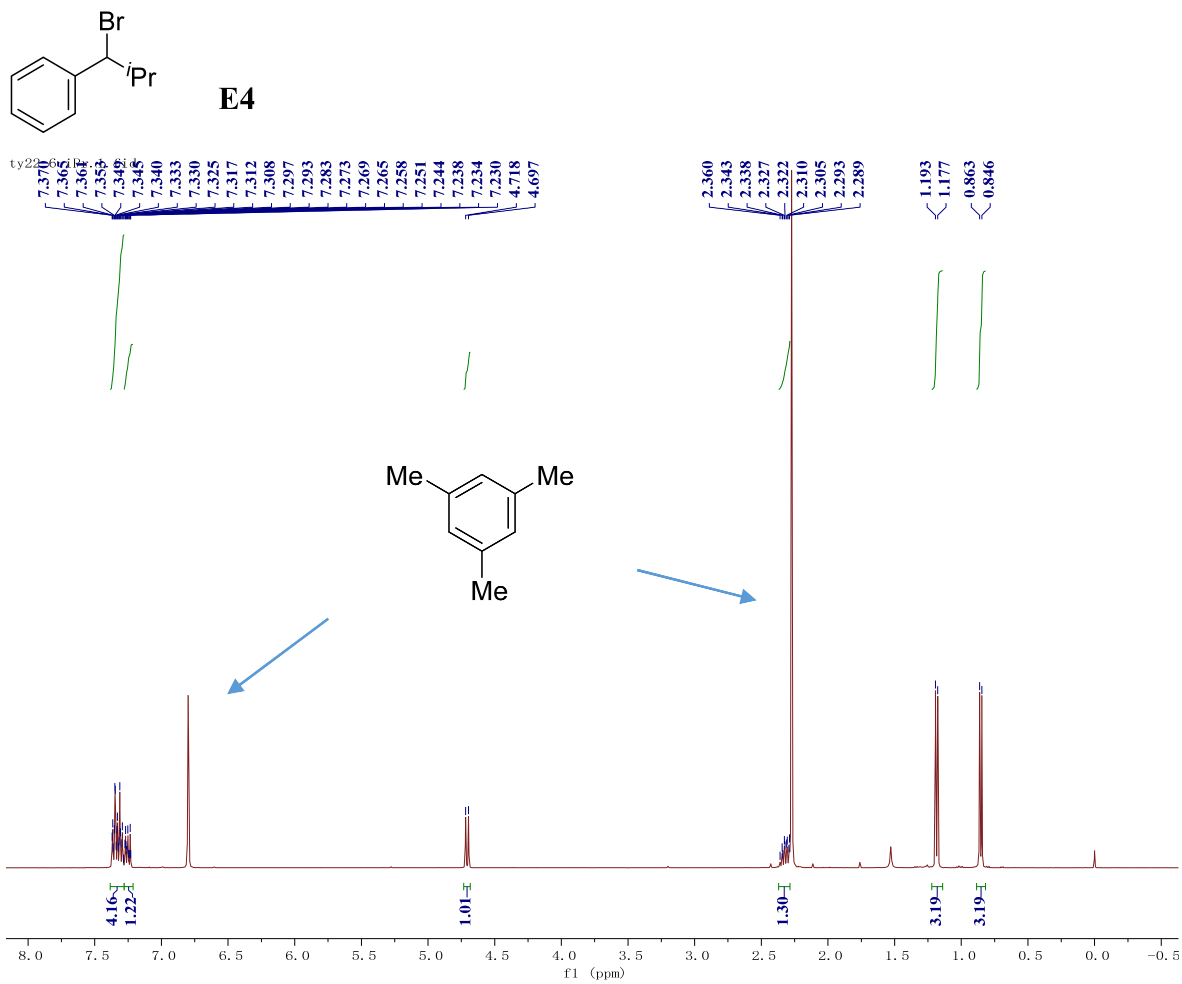


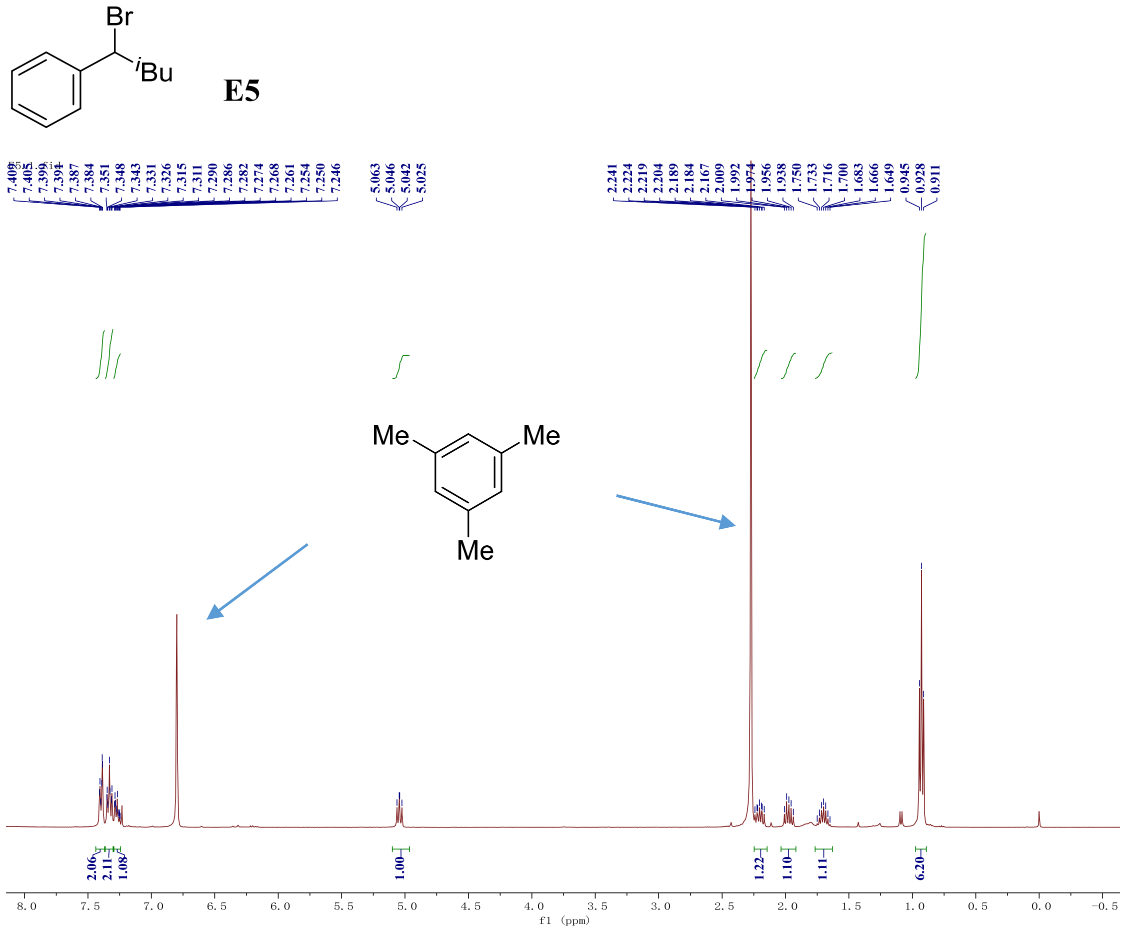
E1

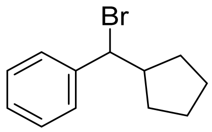




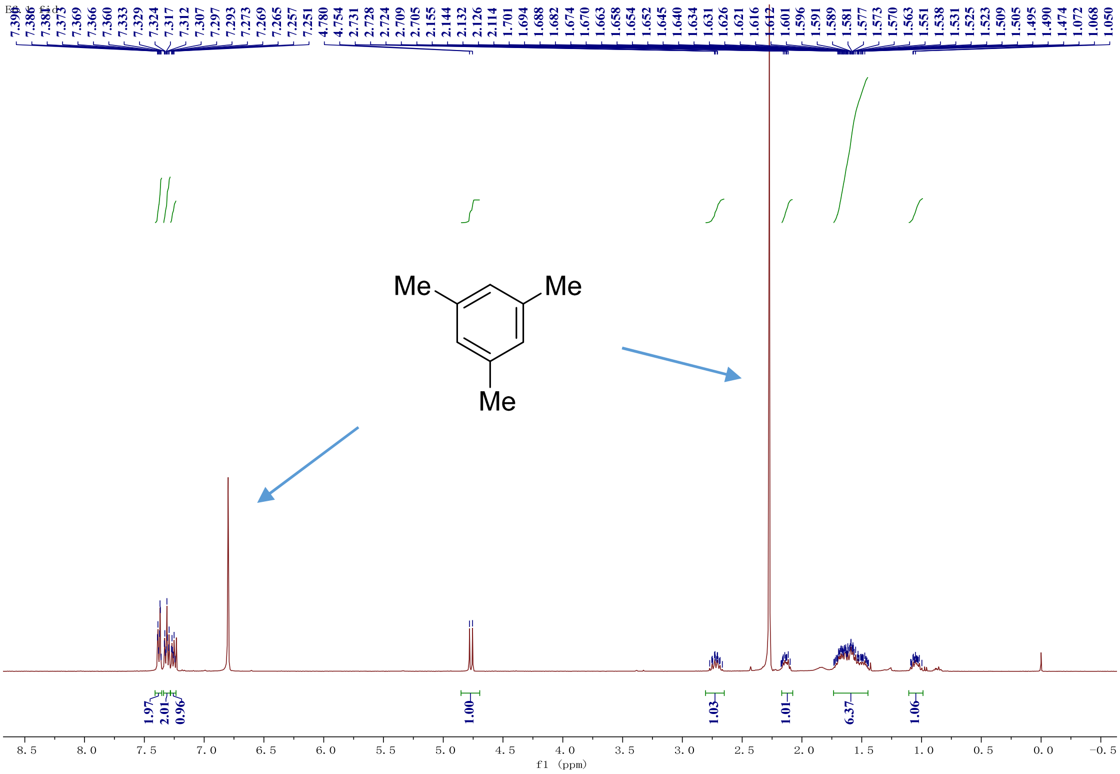
E3


Br
ⁱPr
E4
Me
Me
Me
4.16
1.22
1.01
1.30
3.19
3.19
f1 (ppm)

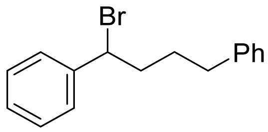




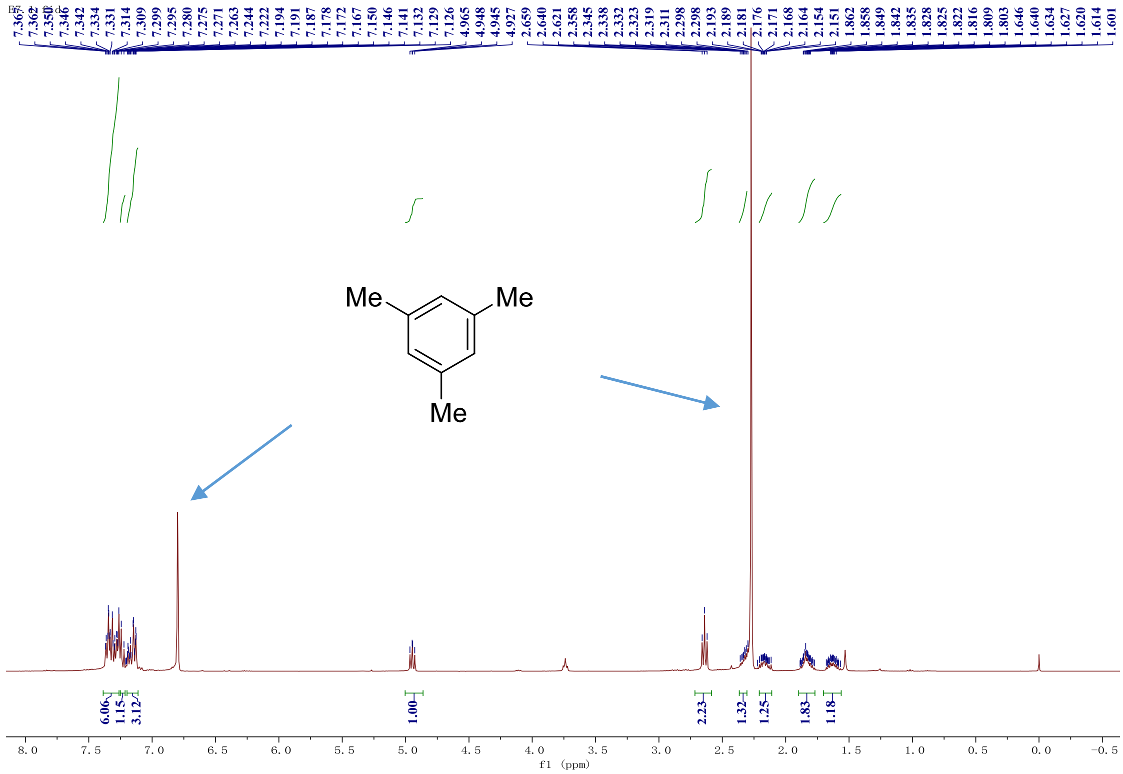
E6

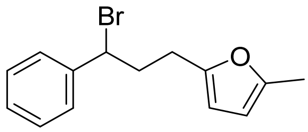


Me
Me
Me
1.97
2.01
0.96
1.00
1.03
1.01
6.37
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

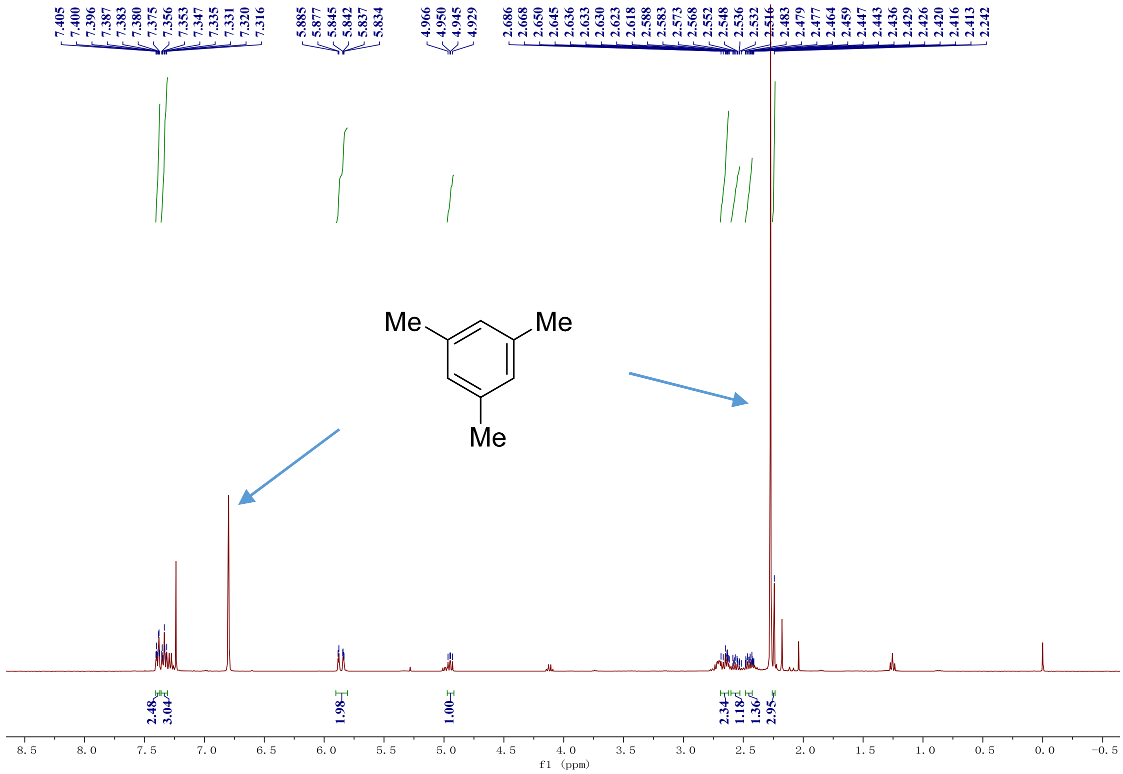


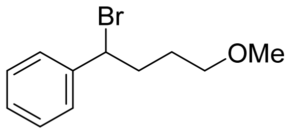
E7



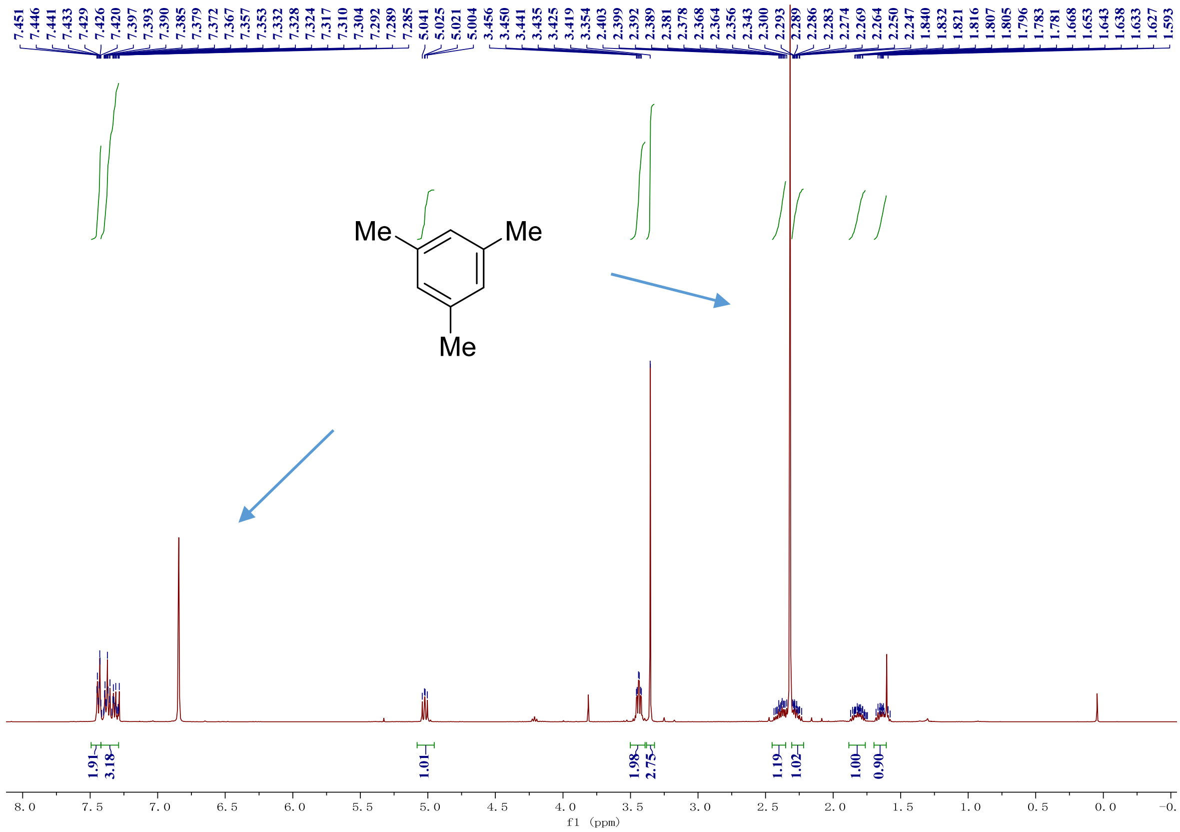


E8

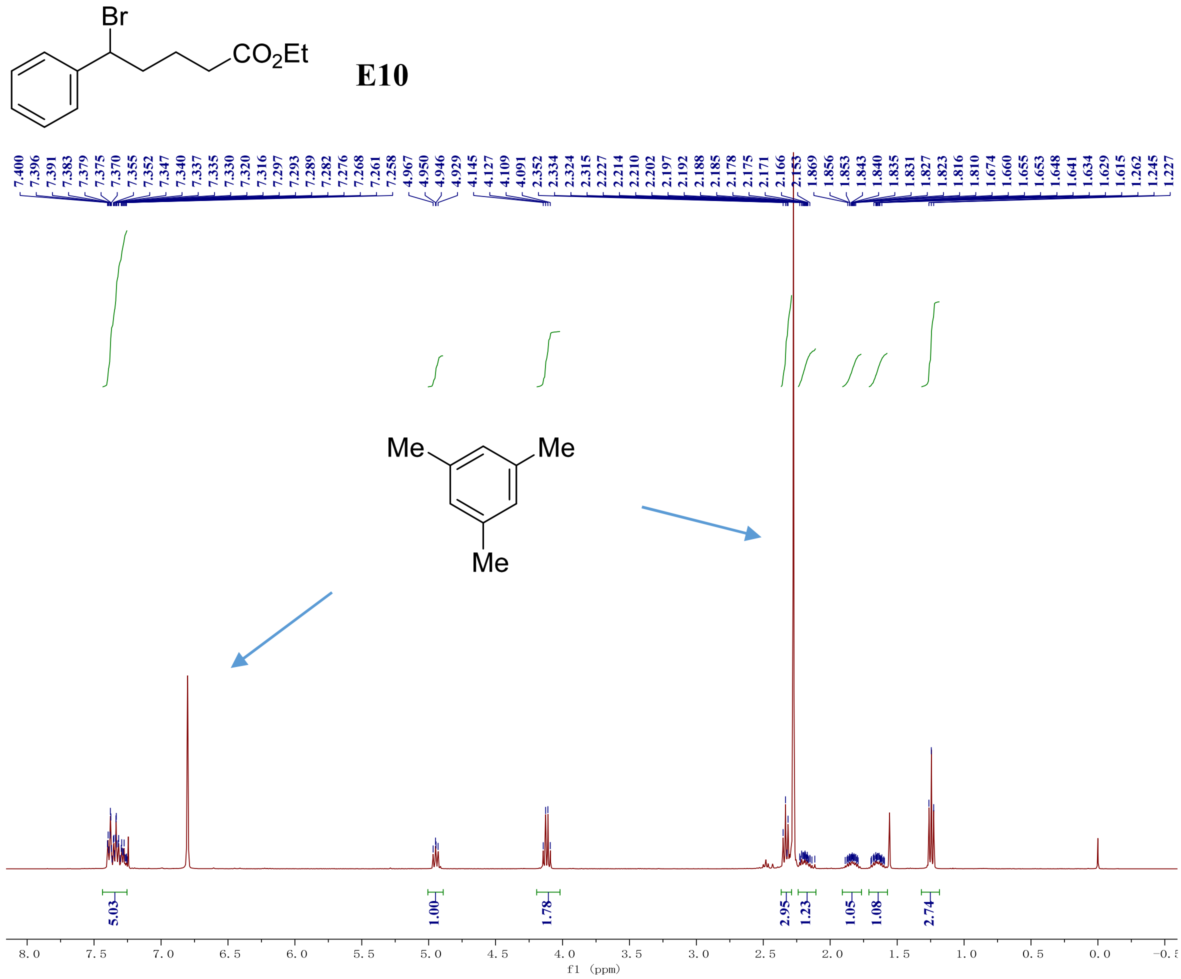


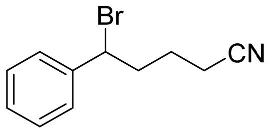

Br
OMe

E9

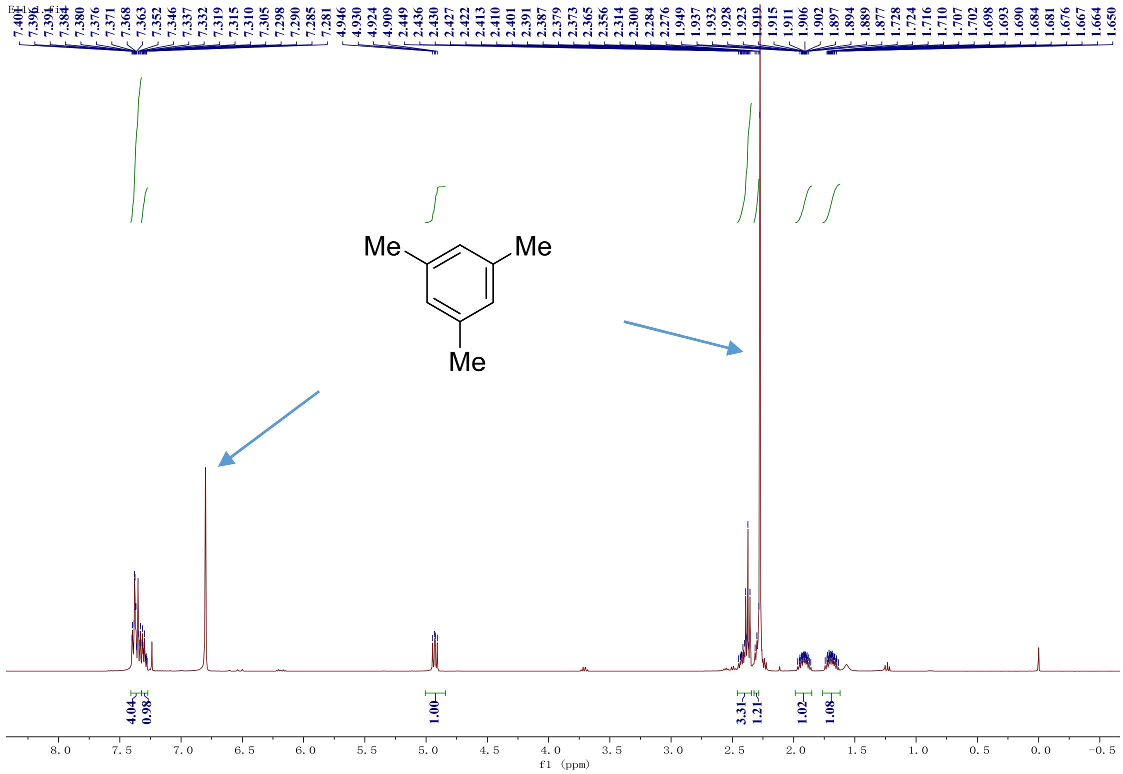

7.451
7.446
7.441
7.433
7.429
7.426
7.420
7.397
7.393
7.390
7.385
7.379
7.372
7.367
7.357
7.353
7.332
7.328
7.324
7.317
7.310
7.304
7.292
7.289
7.285
5.041
5.025
5.021
5.004
3.456
3.450
3.441
3.435
3.425
3.419
3.354
2.403
2.399
2.392
2.389
2.381
2.378
2.368
2.364
2.356
2.343
2.300
2.293
2.289
2.286
2.283
2.274
2.269
2.264
2.250
2.247
1.840
1.832
1.821
1.816
1.807
1.805
1.796
1.783
1.781
1.668
1.653
1.643
1.638
1.633
1.627
1.593
Me
Me
Me
1.91
3.18
1.01
1.98
2.75
1.19
1.02
1.00
0.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

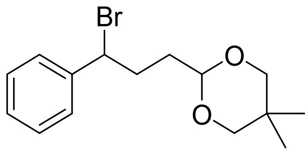
E10



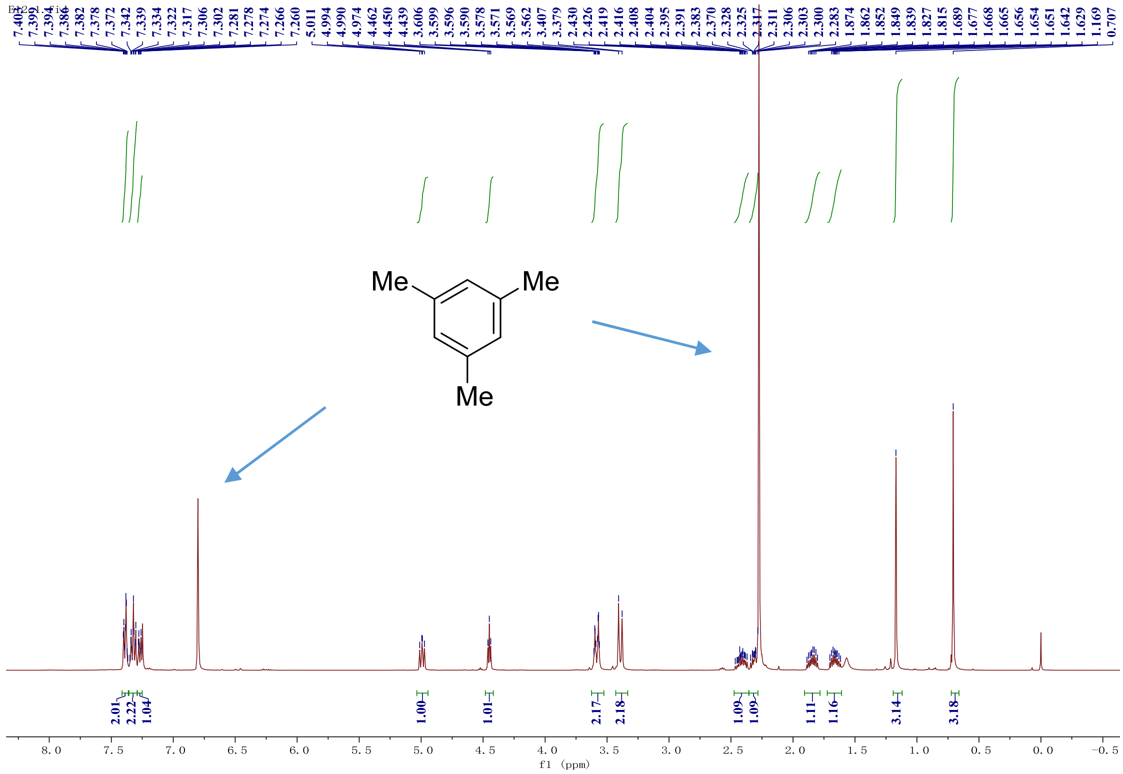


E11

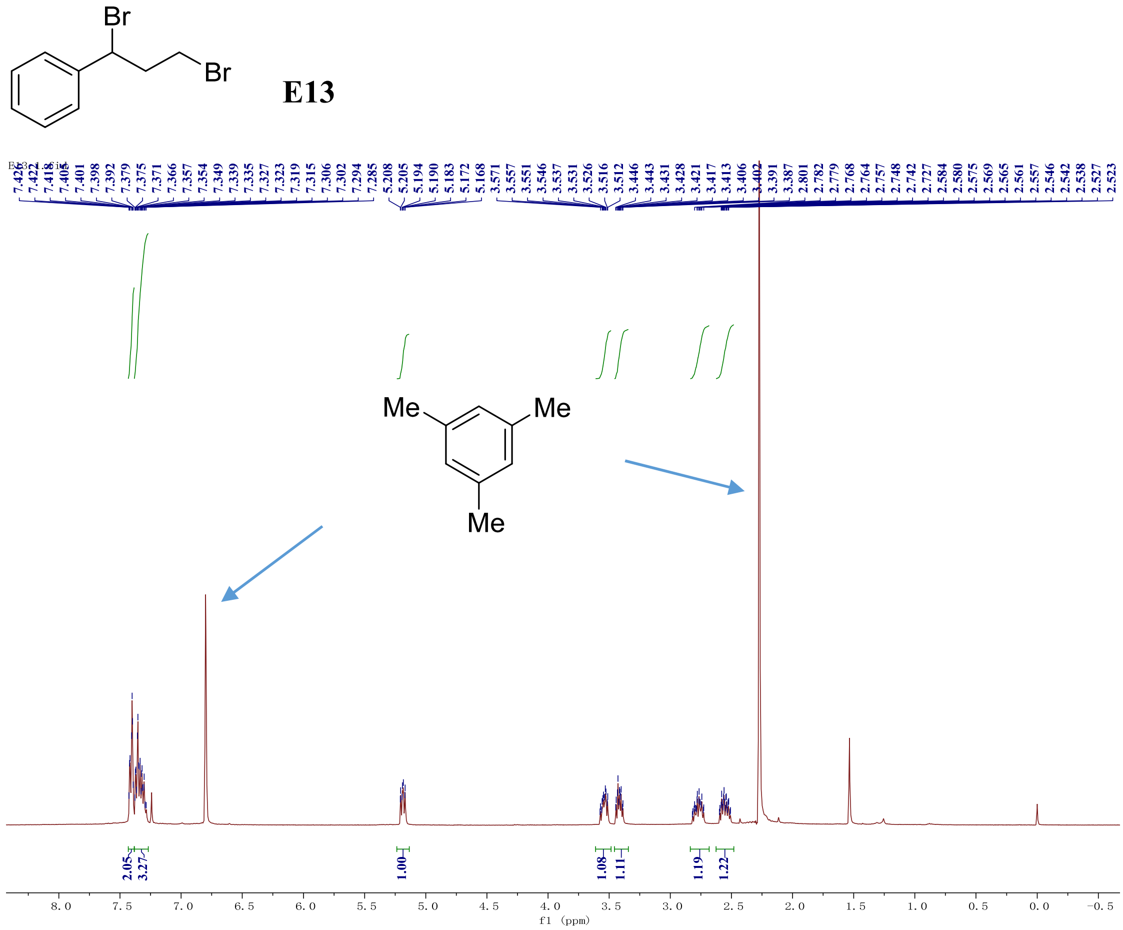


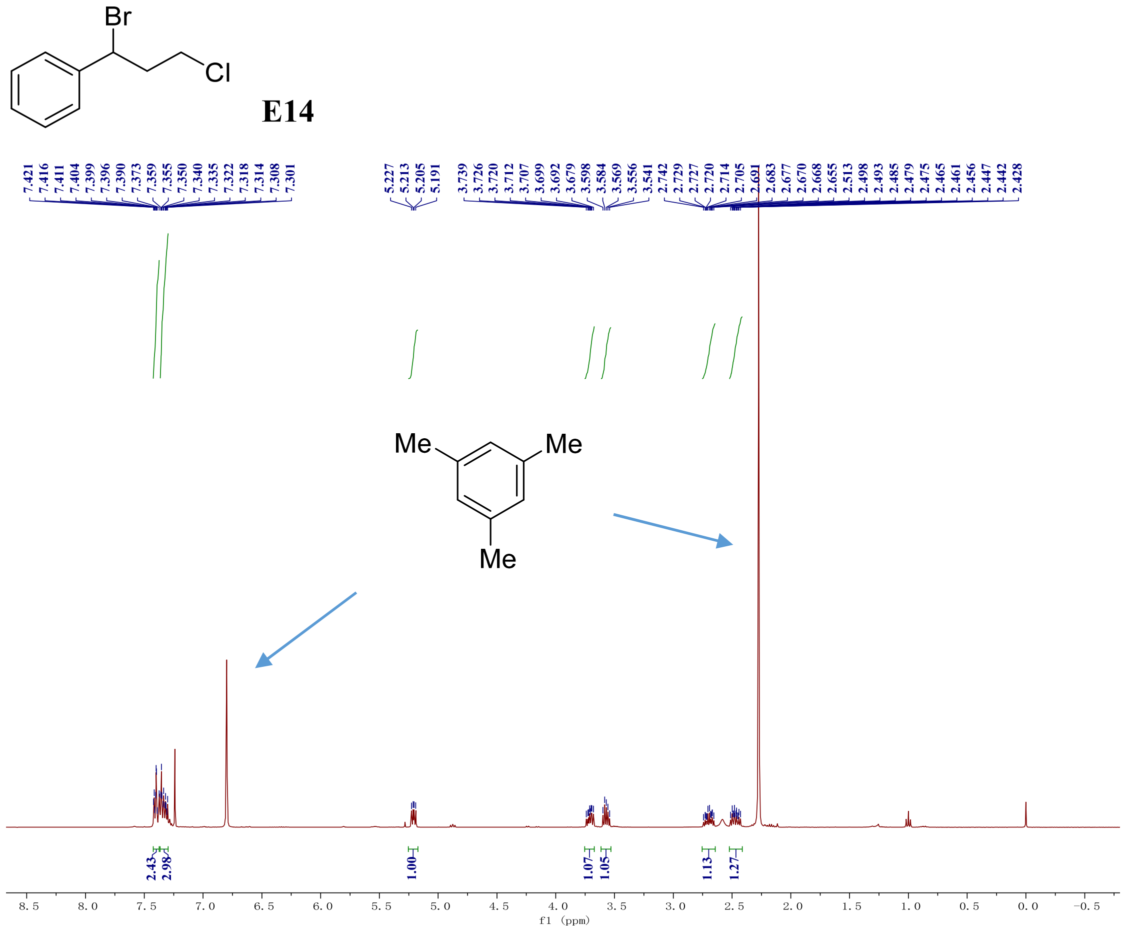


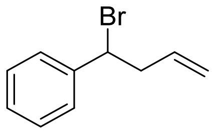
E12



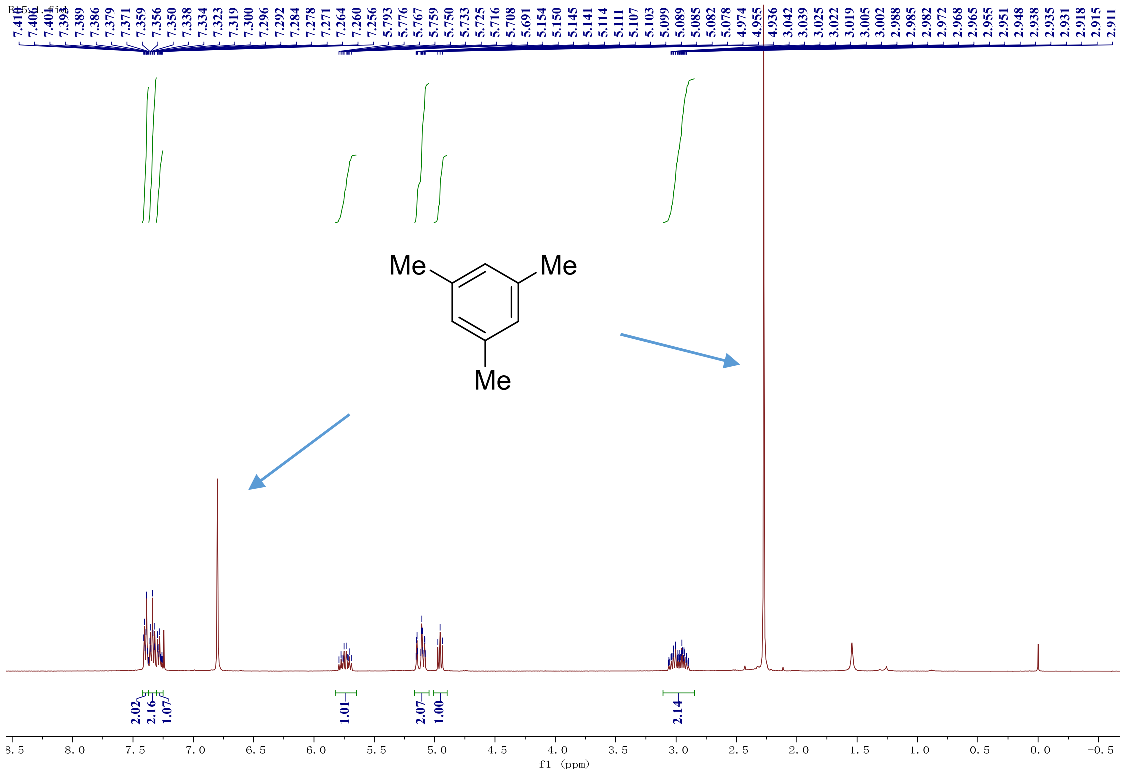
E13

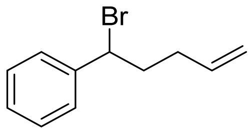



Br
Cl
E14
Me
Me
Me
f1 (ppm)

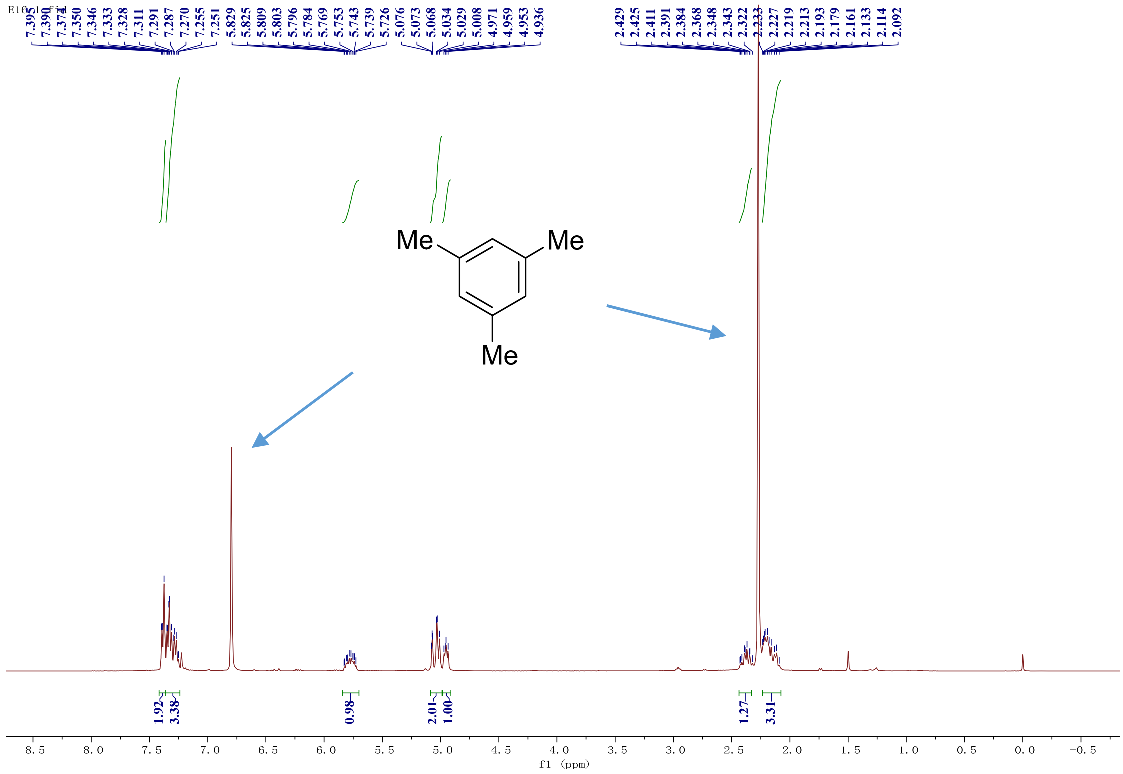


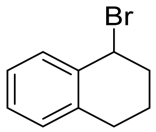
E15



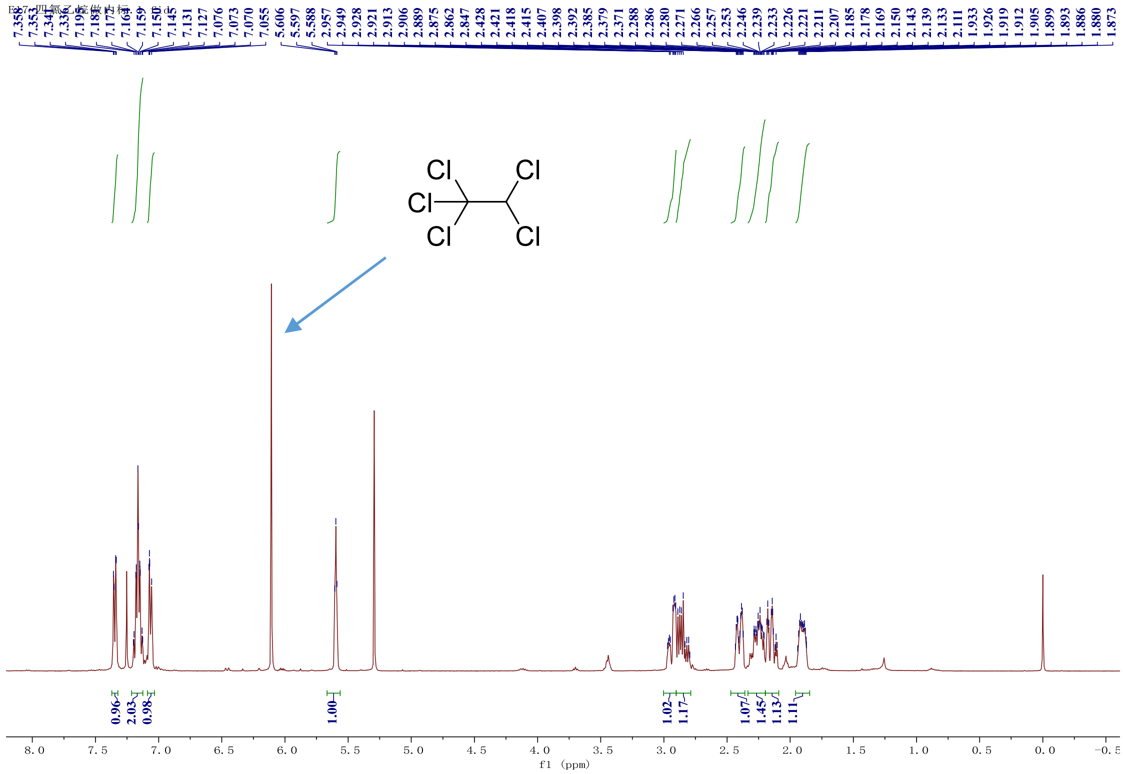


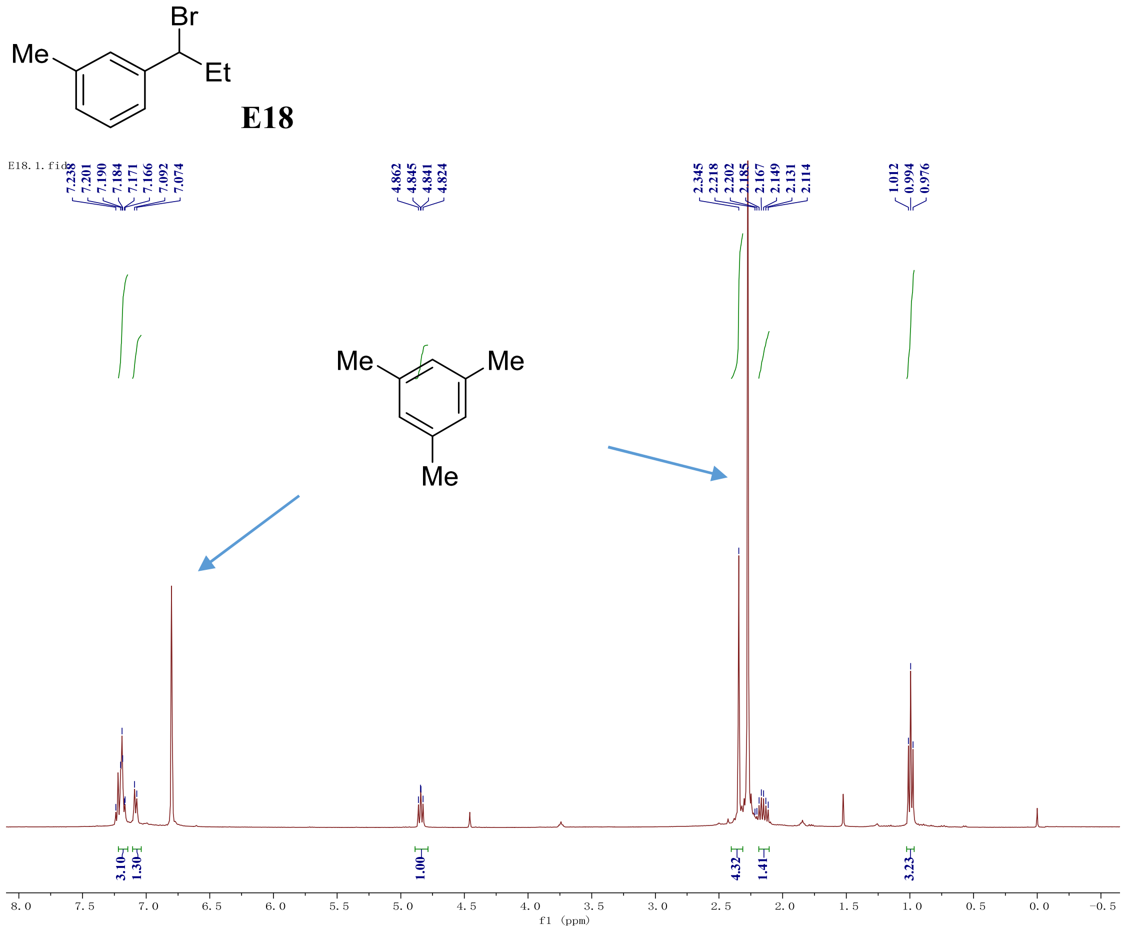
E16



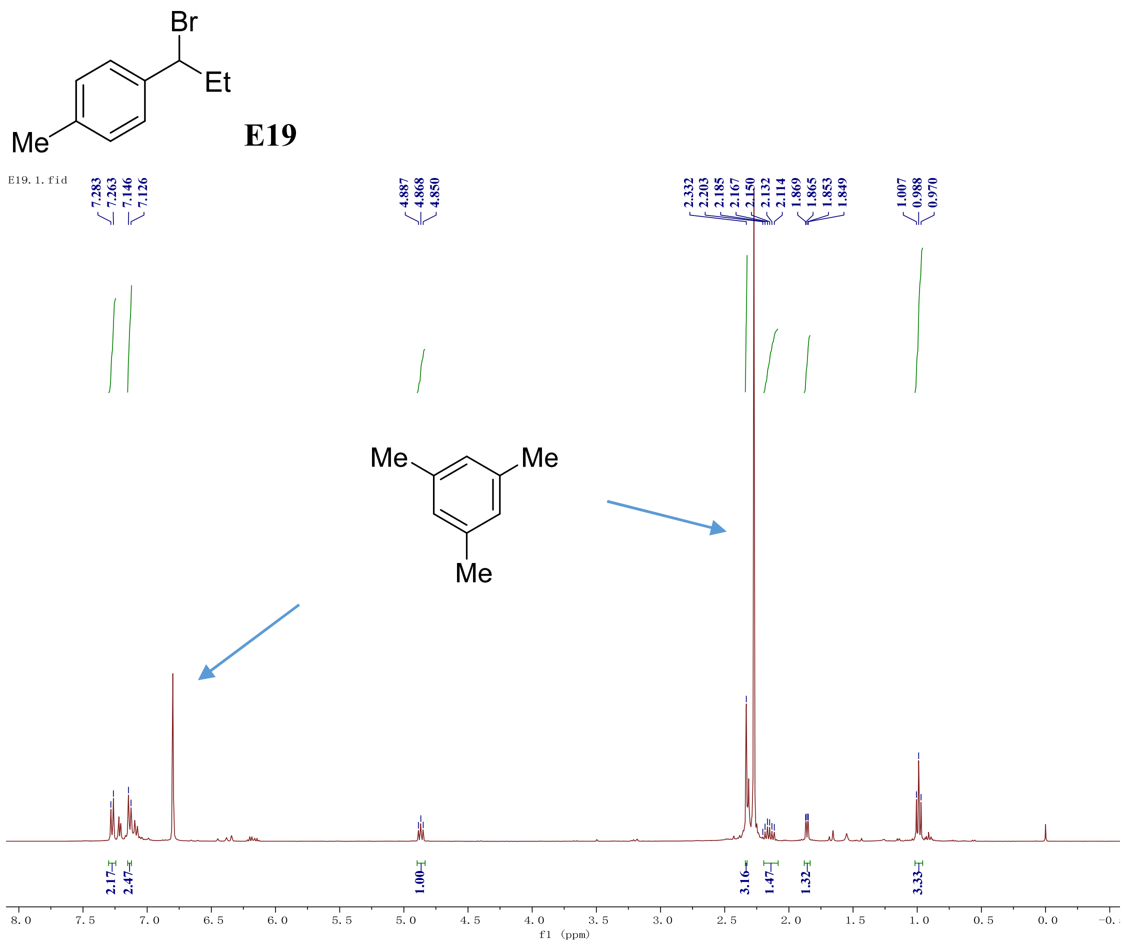


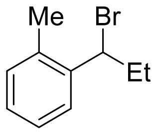
E17



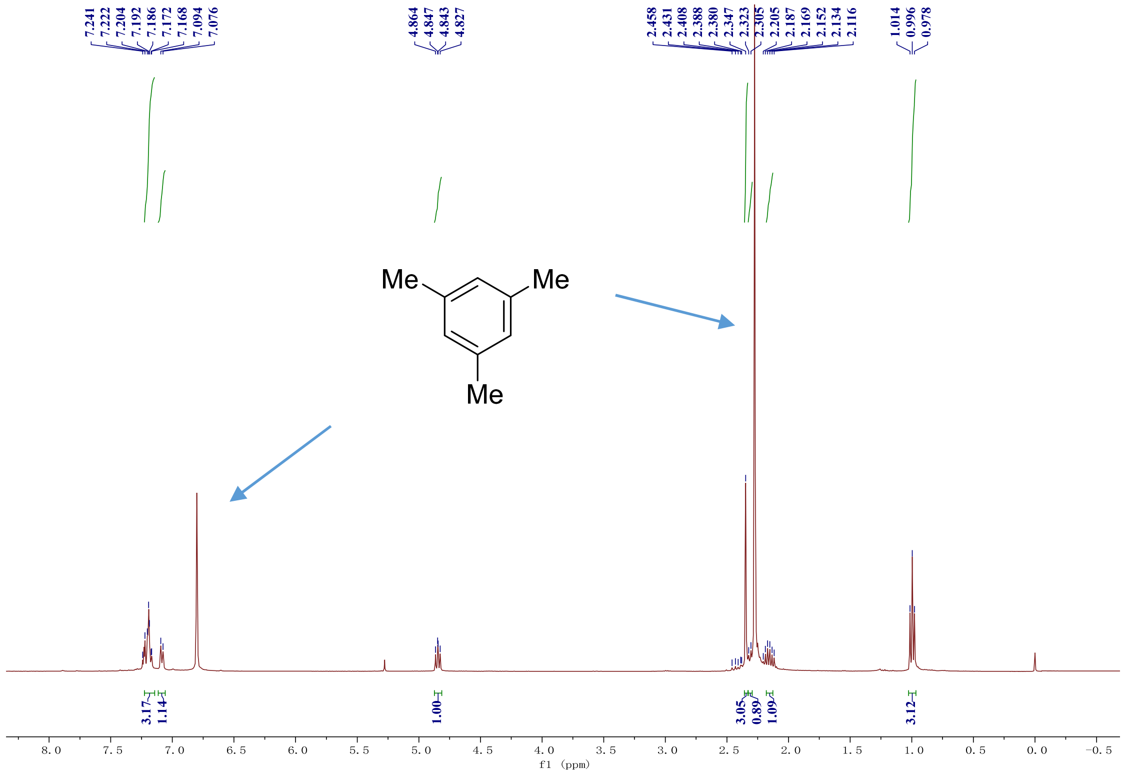

Me
Br
Et
Me
Me
Me
E18.1.fid
7.238
7.201
7.190
7.184
7.171
7.166
7.092
7.074
4.862
4.845
4.841
4.824
2.345
2.218
2.202
2.185
2.167
2.149
2.131
2.114
1.012
0.994
0.976
3.10
1.30
1.00
4.32
1.41
3.23
f1 (ppm)

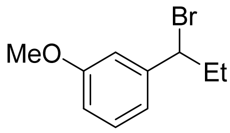
E18


Br
Et
Me
E19
E19.1.fid
7.283
7.263
7.146
7.126
4.887
4.868
4.850
2.332
2.203
2.185
2.167
2.150
2.132
2.114
1.869
1.865
1.853
1.849
1.007
0.988
0.970
Me
Me
Me
2.17
2.47
1.00
3.16
1.47
1.32
3.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

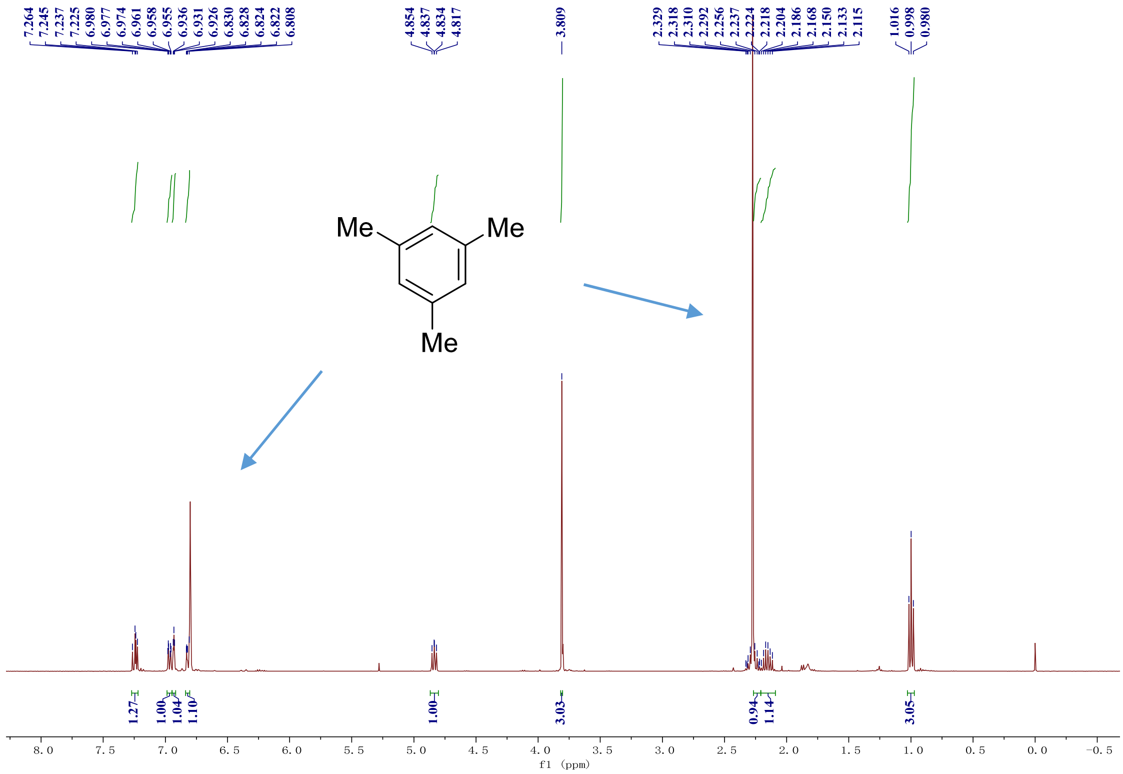


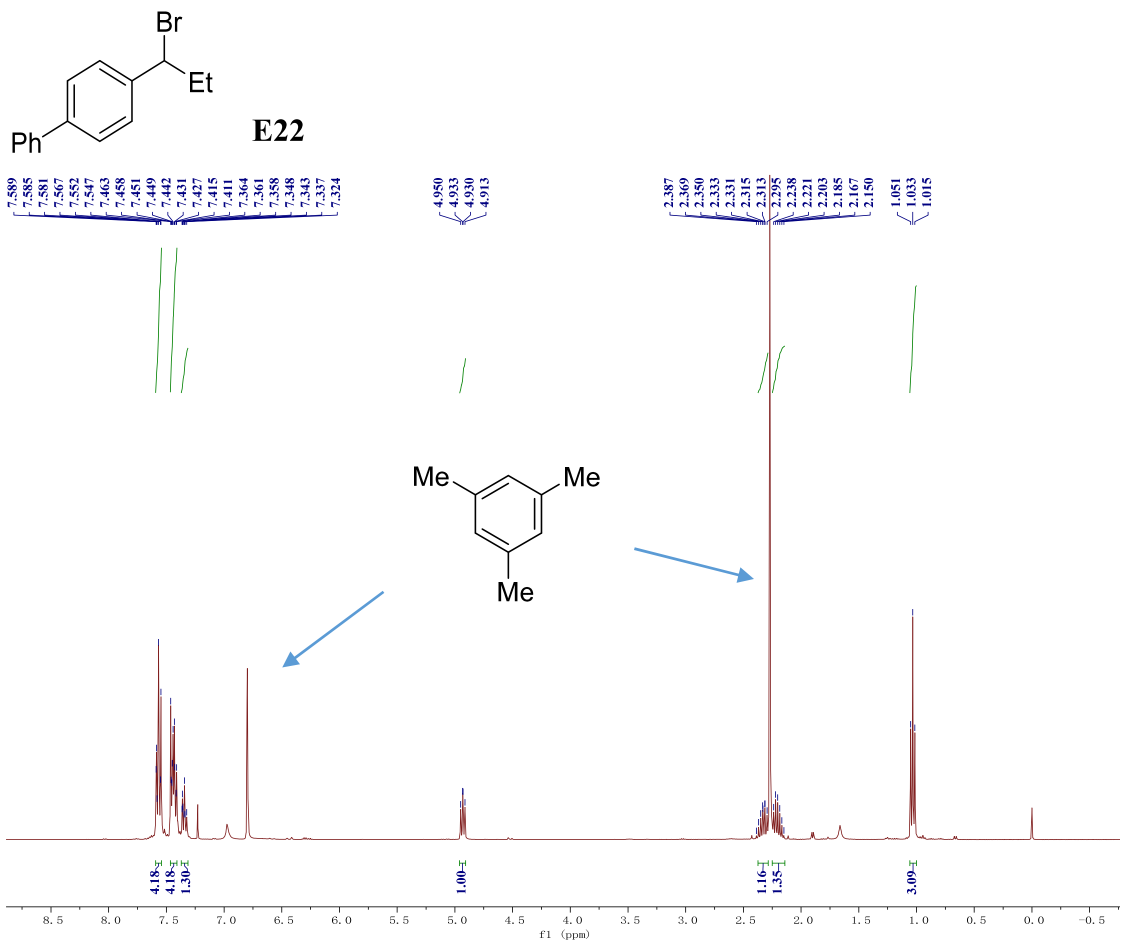
E20


Me
Me
Me
7.241
7.222
7.204
7.192
7.186
7.172
7.168
7.094
7.076
4.864
4.847
4.843
4.827
2.458
2.431
2.408
2.388
2.380
2.347
2.323
2.305
2.205
2.187
2.169
2.152
2.134
2.116
1.014
0.996
0.978
3.17
1.14
1.00
3.05
0.89
1.09
3.12
f1 (ppm)

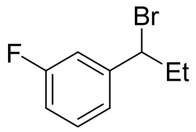


E21



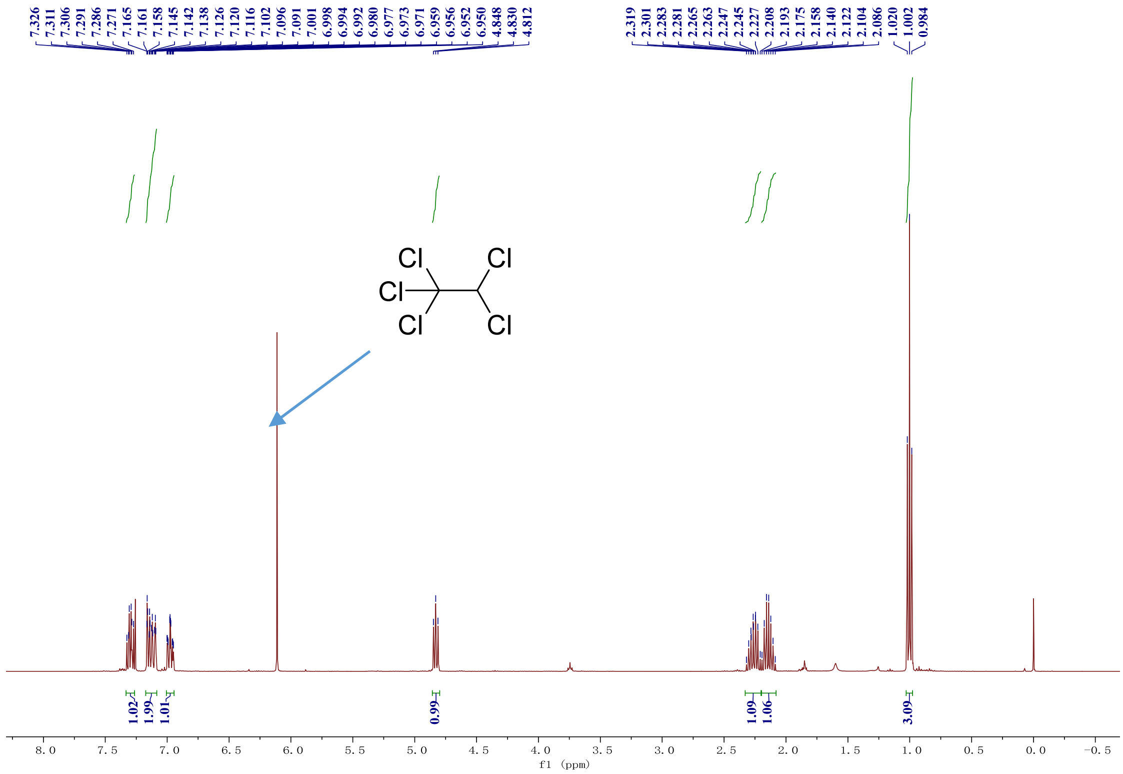


E22

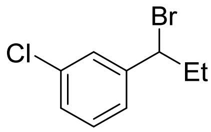


F
Br
Et

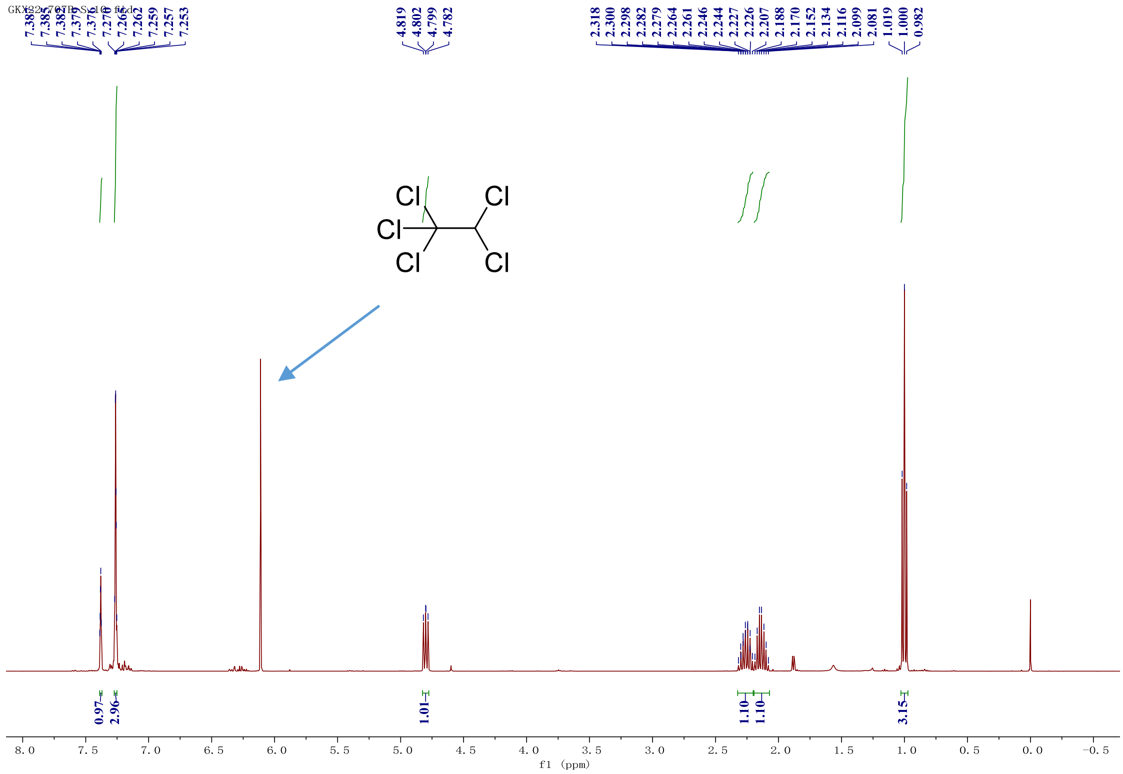
E23

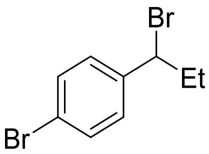


7.326 7.311 7.306 7.291 7.286 7.271 7.165 7.161 7.158 7.145 7.142 7.138 7.126 7.120 7.116 7.102 7.096 7.091 7.001 6.998 6.994 6.992 6.980 6.977 6.973 6.971 6.959 6.956 6.952 6.950 4.848 4.830 4.812
2.319 2.301 2.283 2.281 2.265 2.263 2.247 2.245 2.227 2.208 2.193 2.175 2.158 2.140 2.122 2.104 2.086 1.020 1.002 0.984
Cl
Cl
Cl
Cl
Cl
1.02
1.99
1.01
0.99
1.09
1.06
3.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

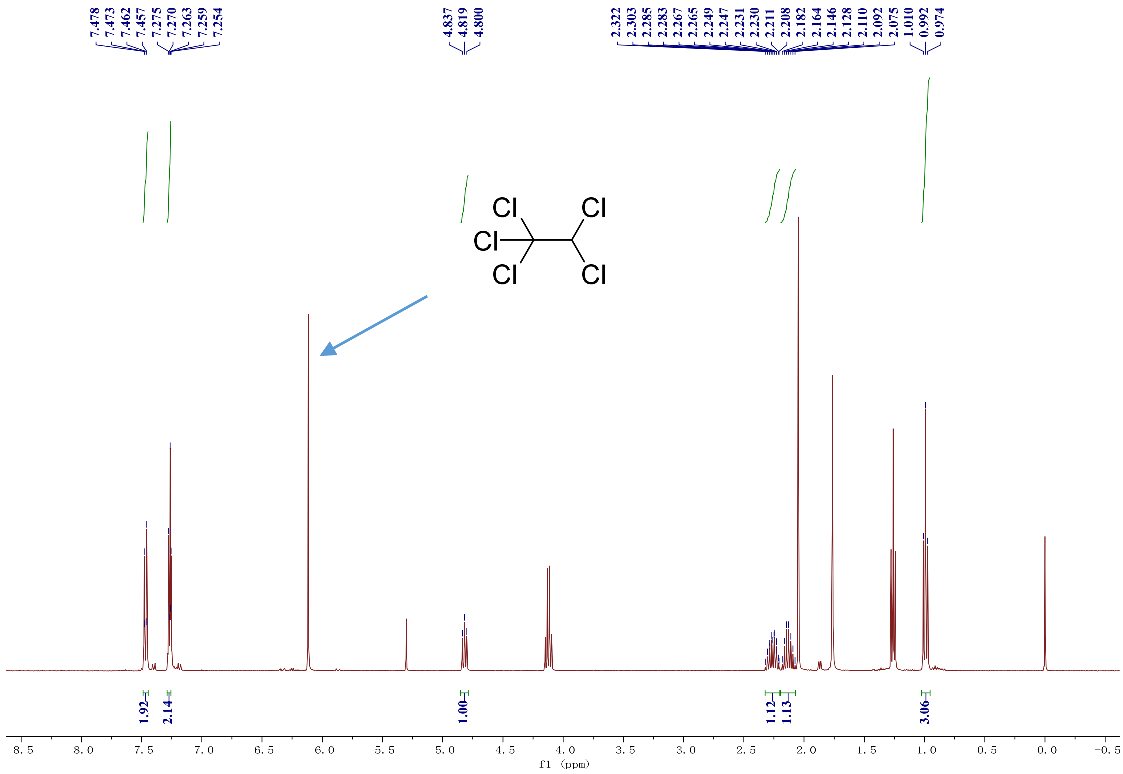


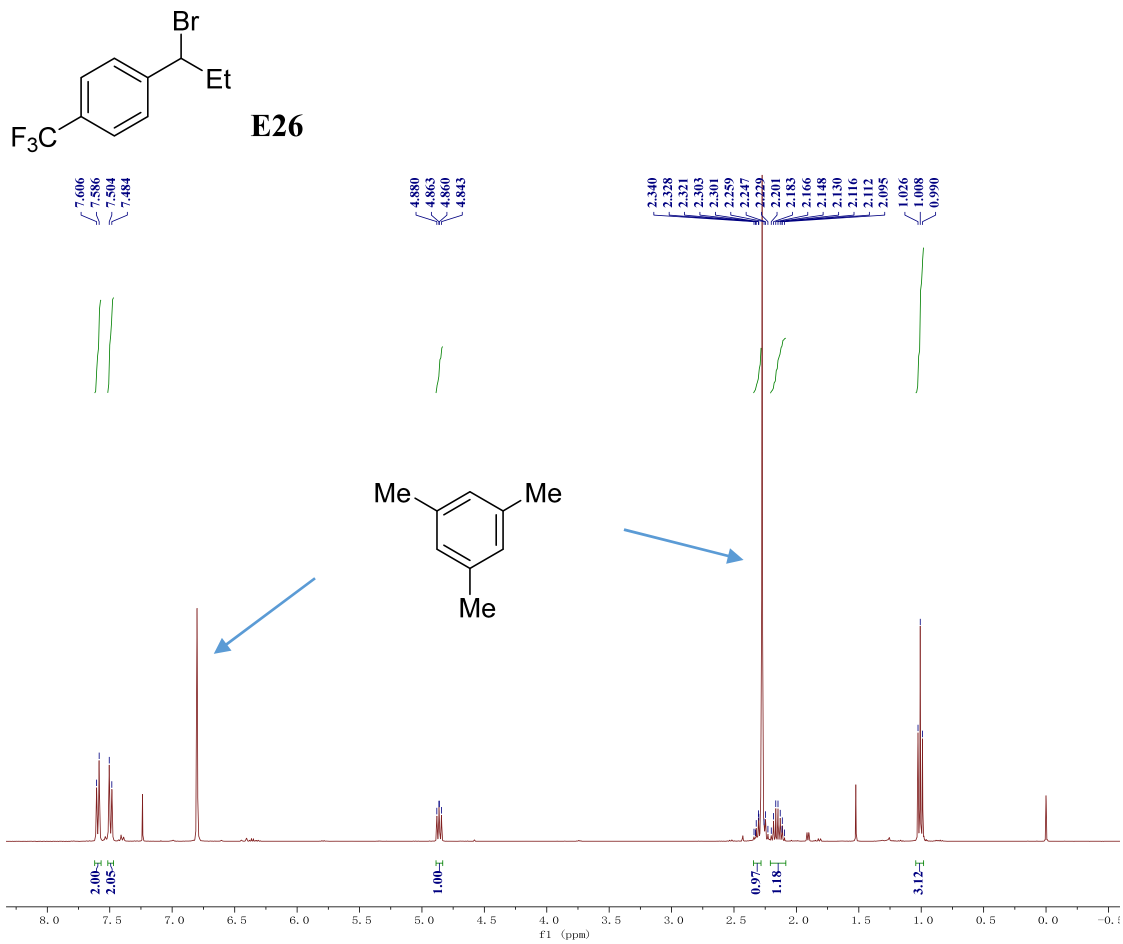
E24



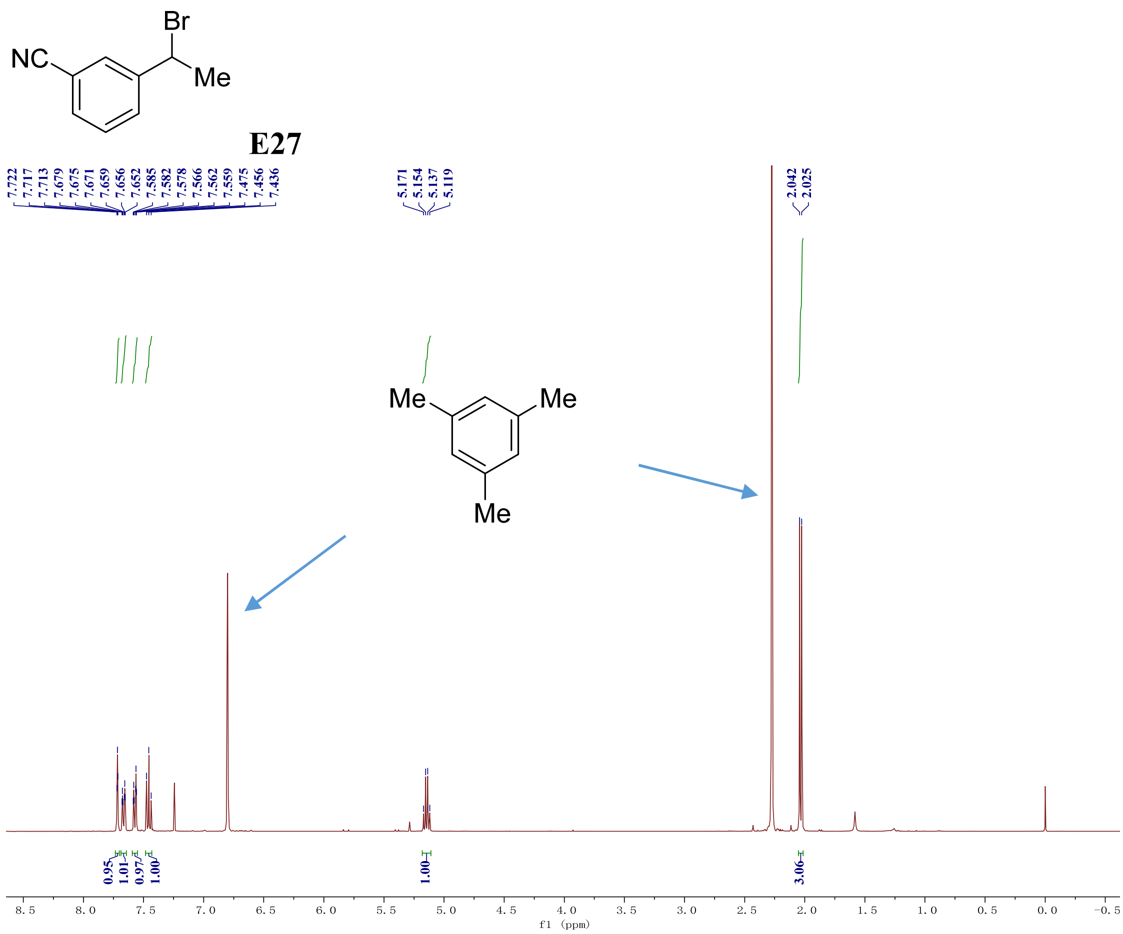


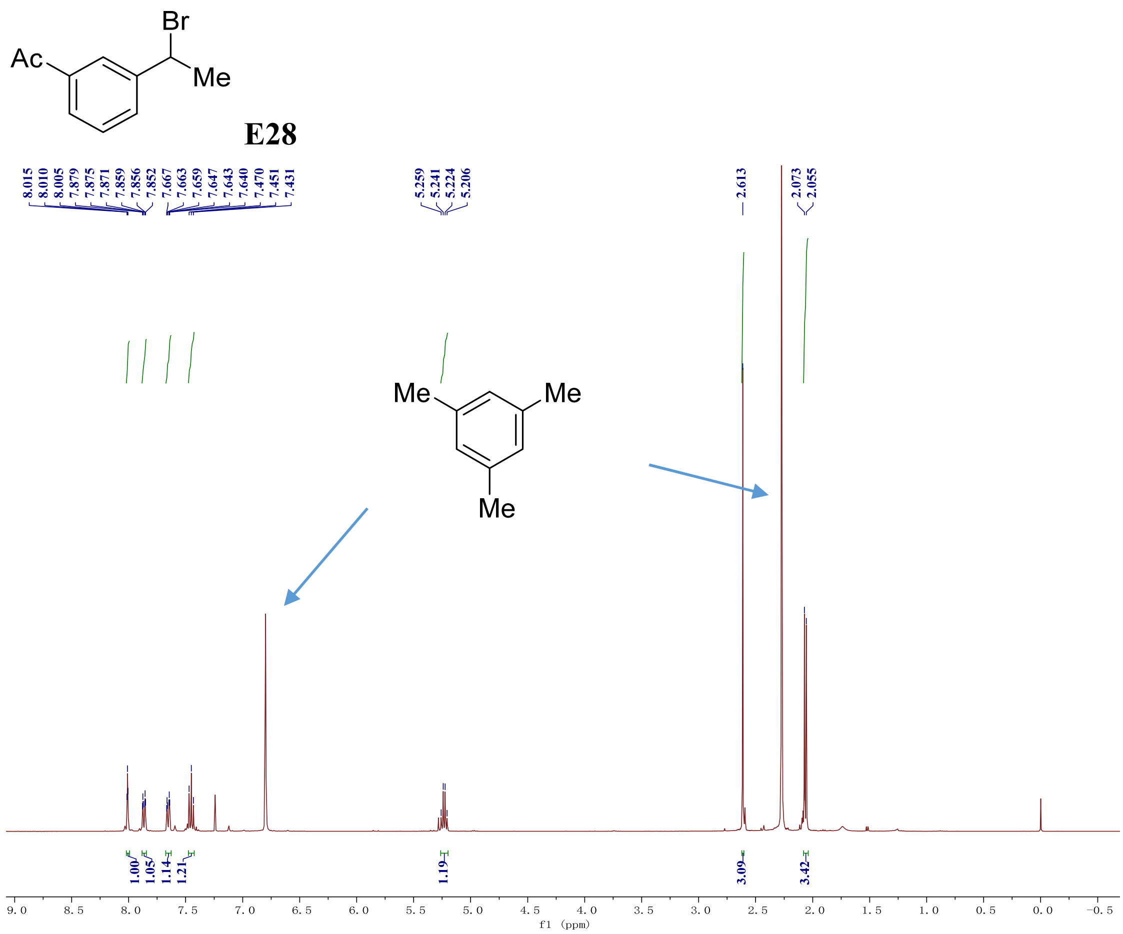
E25

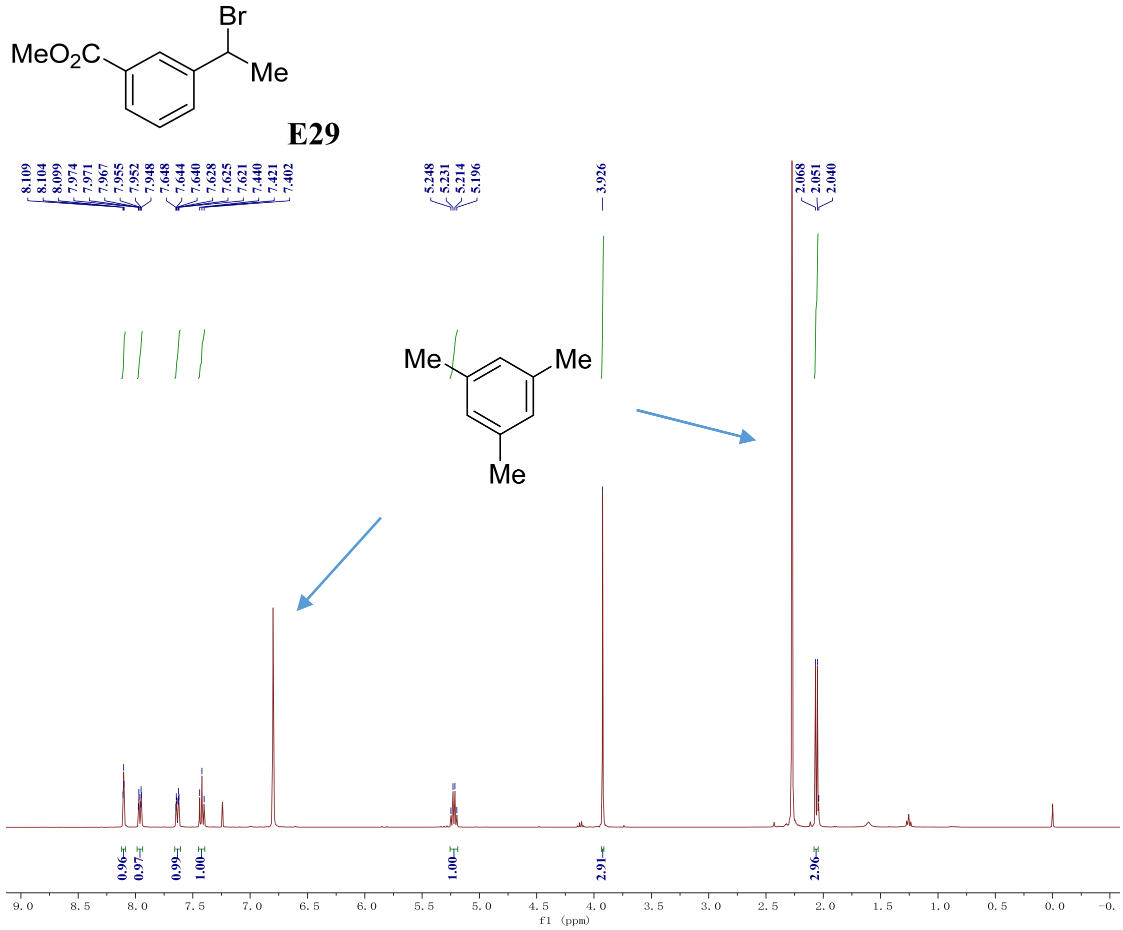



Br
Et
F3C
Me
Me
Me
7.606
7.586
7.504
7.484
4.880
4.863
4.860
4.843
2.340
2.328
2.321
2.303
2.301
2.259
2.247
2.229
2.201
2.183
2.166
2.148
2.130
2.116
2.112
2.095
1.026
1.008
0.990
2.00
2.05
1.00
0.97
1.18
3.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

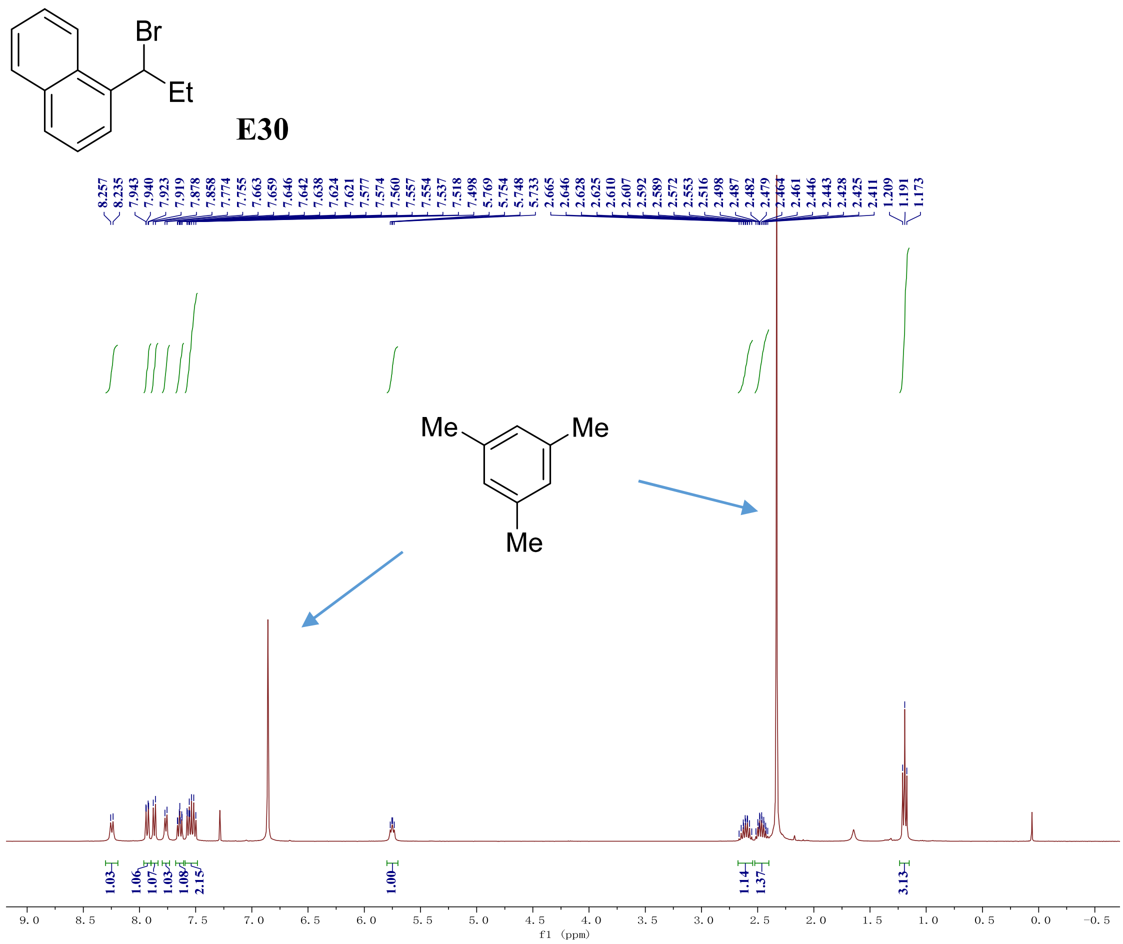
E26

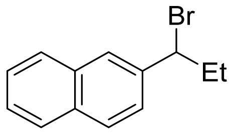

NC
Br
Me
E27
Me
Me
Me
7.722
7.717
7.713
7.679
7.675
7.671
7.659
7.656
7.652
7.585
7.582
7.578
7.566
7.562
7.559
7.475
7.456
7.436
5.171
5.154
5.137
5.119
2.042
2.025
0.95
1.01
0.97
1.00
1.00
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Ac
Br
Me
E28
Me
Me
Me
f1 (ppm)

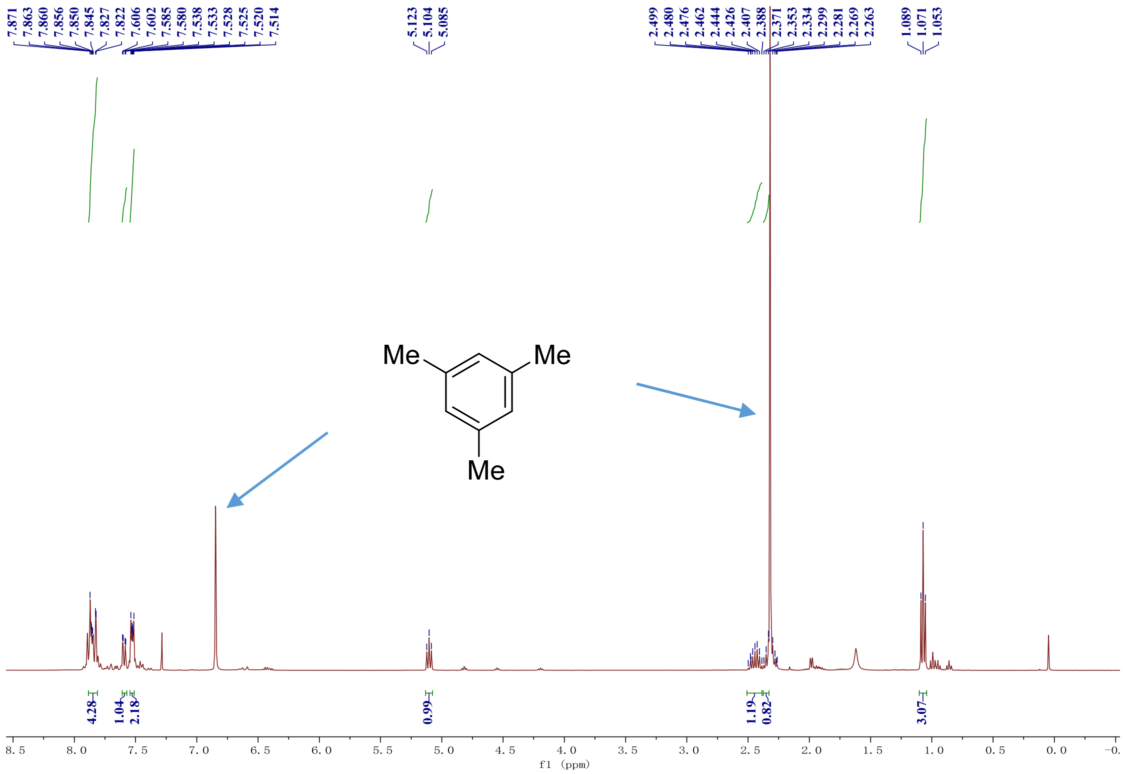


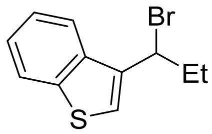
Br
MeO2C
Me
E29
Me
Me
Me
f1 (ppm)


Br
Et
E30
Me
Me
Me
f1 (ppm)

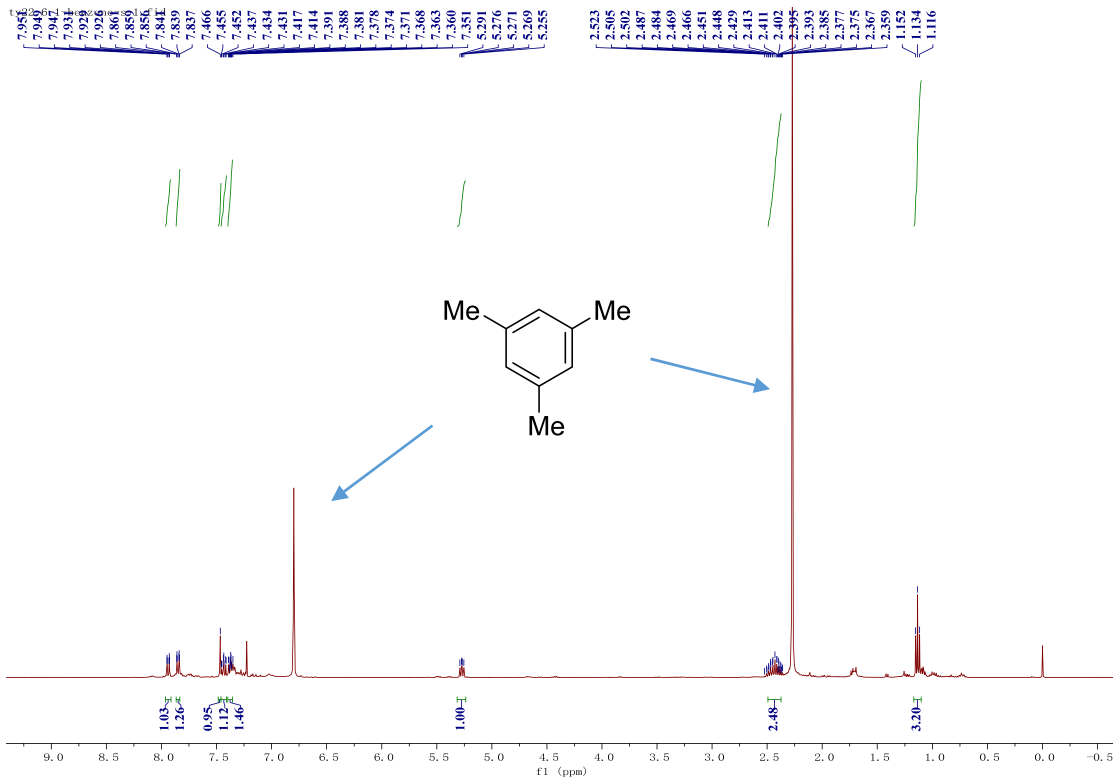

Br
Et

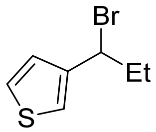
E31


7.871
7.863
7.860
7.856
7.850
7.845
7.827
7.822
7.606
7.602
7.585
7.580
7.538
7.533
7.528
7.525
7.520
7.514
5.123
5.104
5.085
2.499
2.480
2.476
2.462
2.444
2.426
2.407
2.388
2.371
2.353
2.334
2.299
2.281
2.269
2.263
1.089
1.071
1.053
Me
Me
Me
4.28
1.04
2.18
0.99
1.19
0.82
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

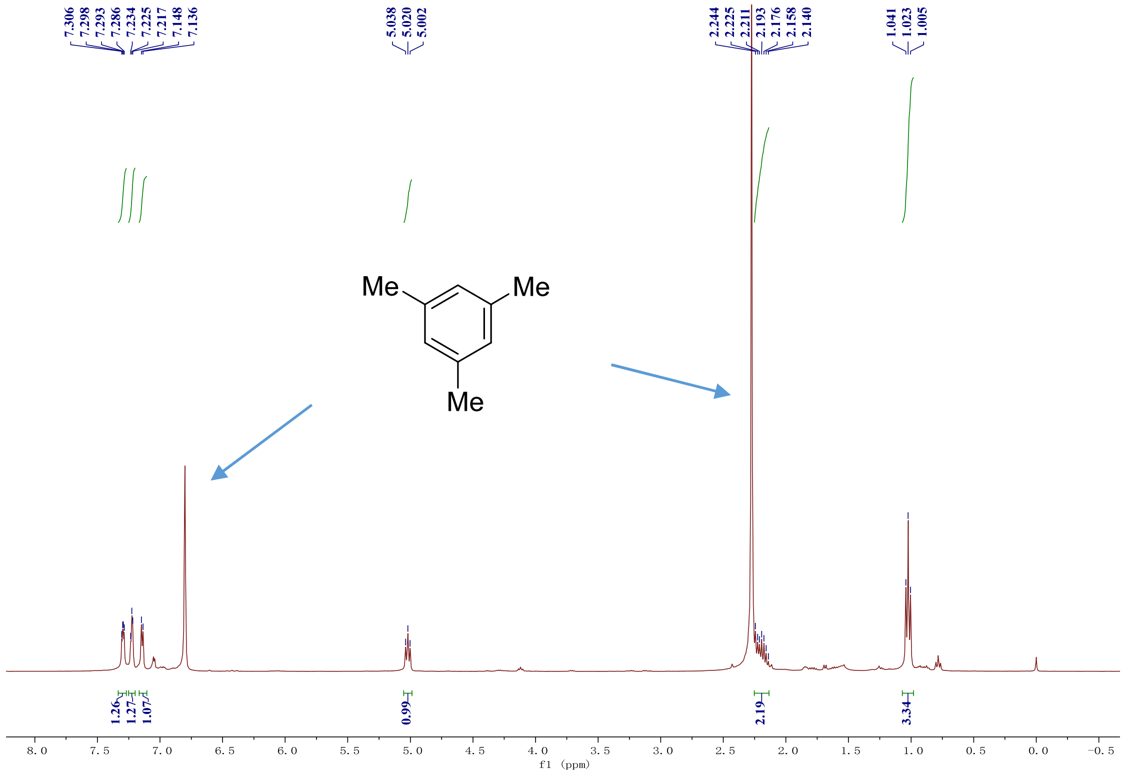


E32

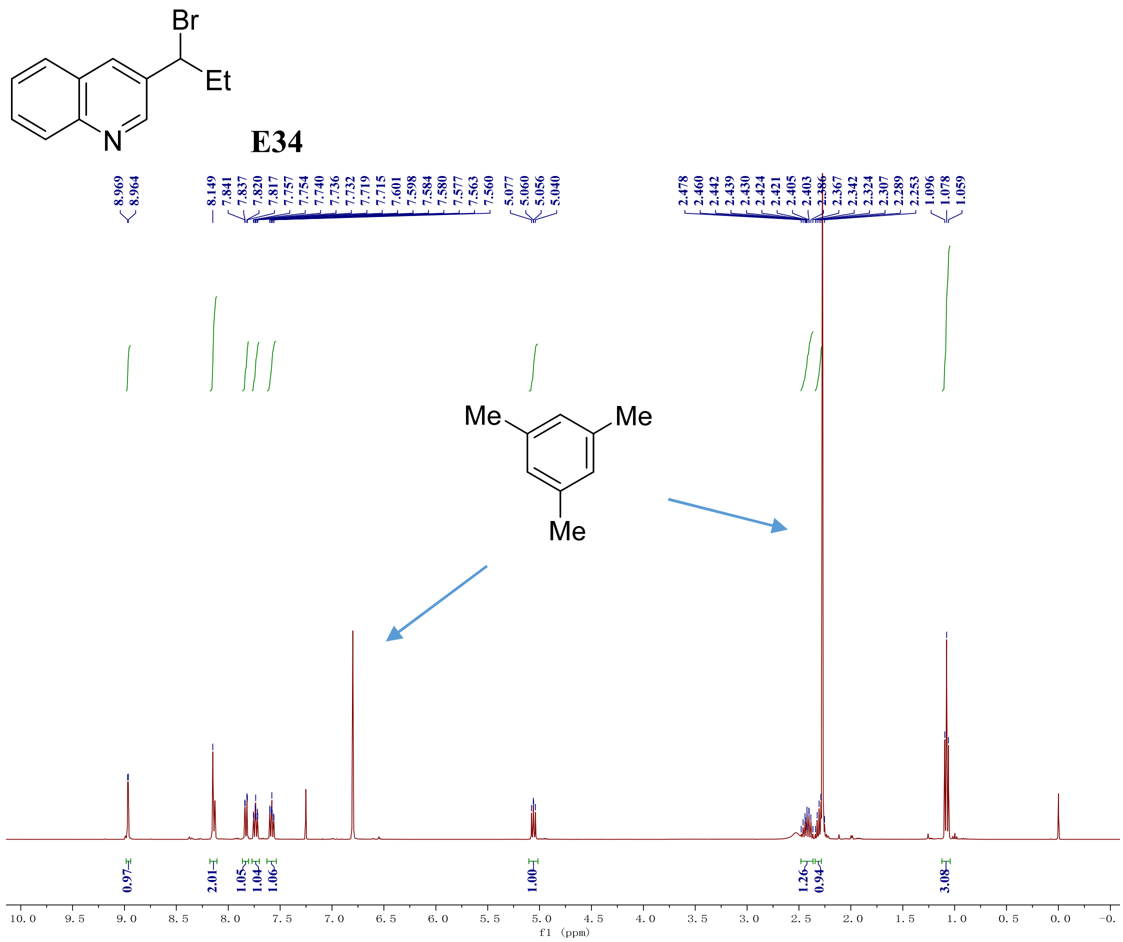




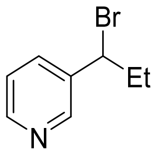
E33



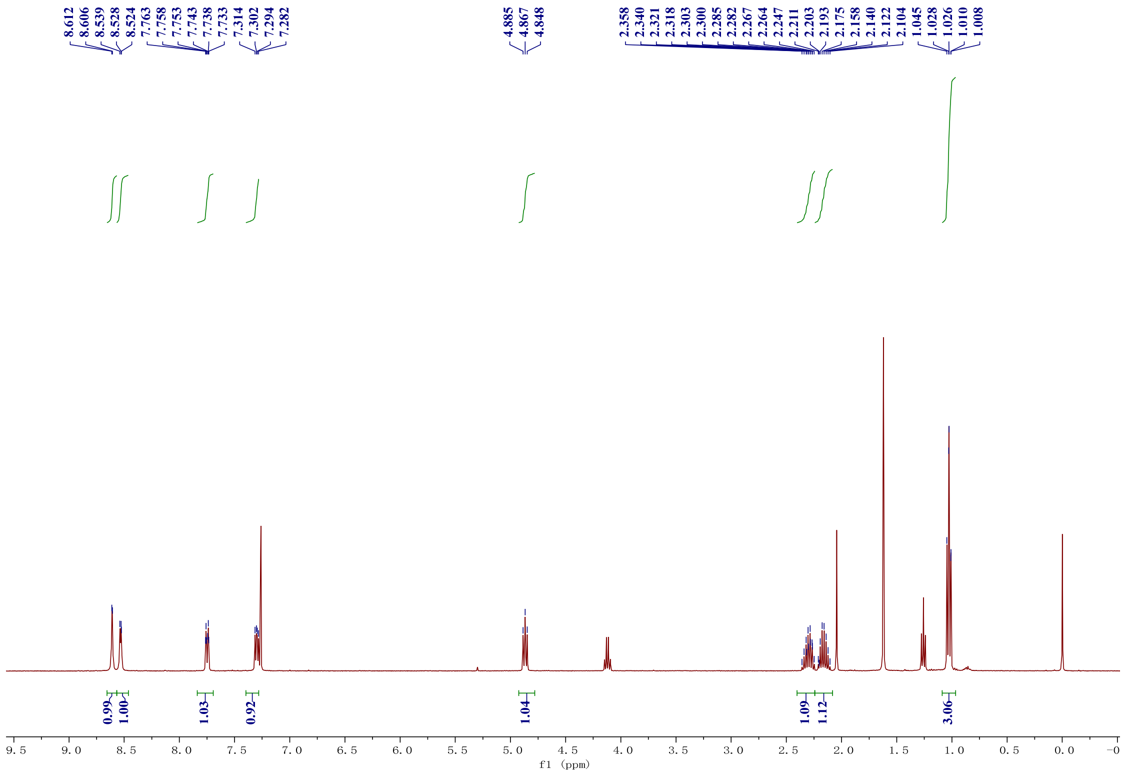
7.306
7.298
7.293
7.286
7.234
7.225
7.217
7.148
7.136
5.038
5.020
5.002
2.244
2.225
2.211
2.193
2.176
2.158
2.140
1.041
1.023
1.005
Me
Me
Me
1.26
1.27
1.07
0.99
2.19
3.34
f1 (ppm)



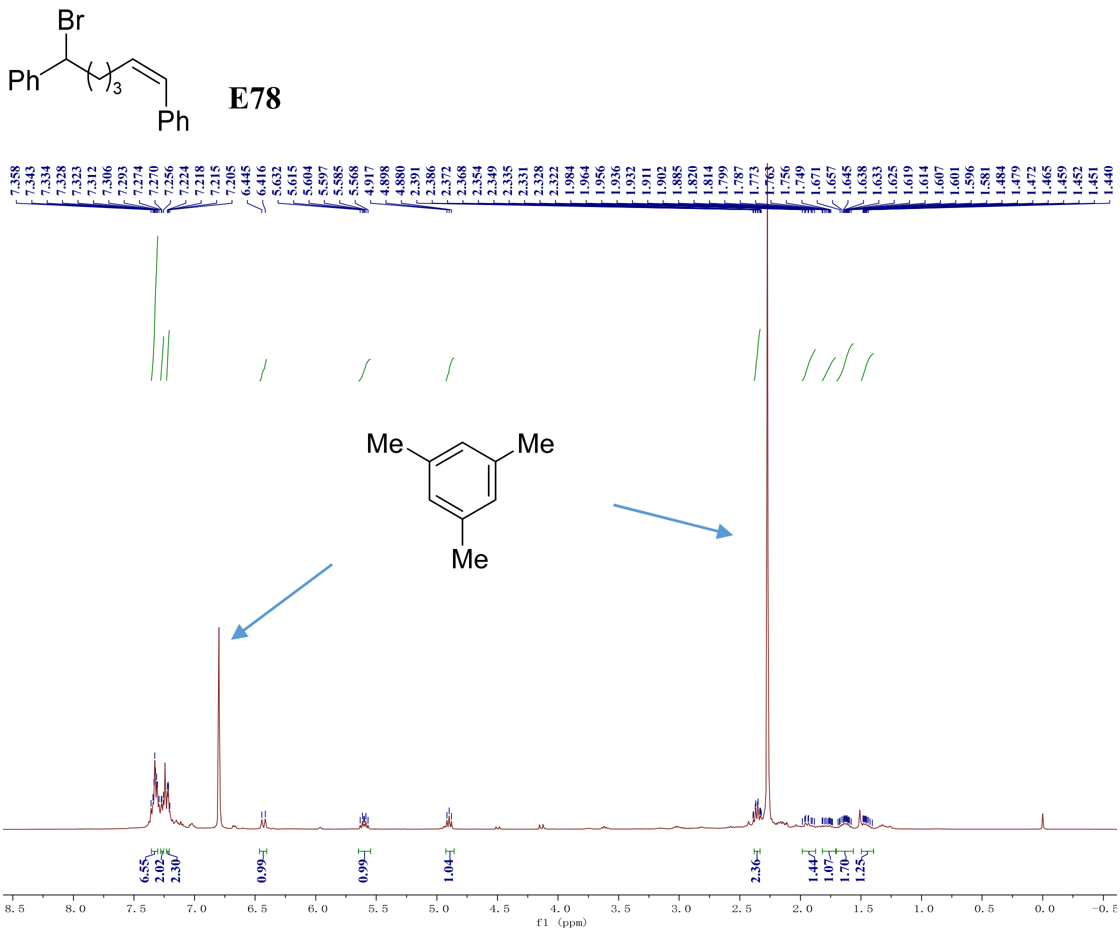
E34
Br
Et
N
Me
Me
Me
f1 (ppm)



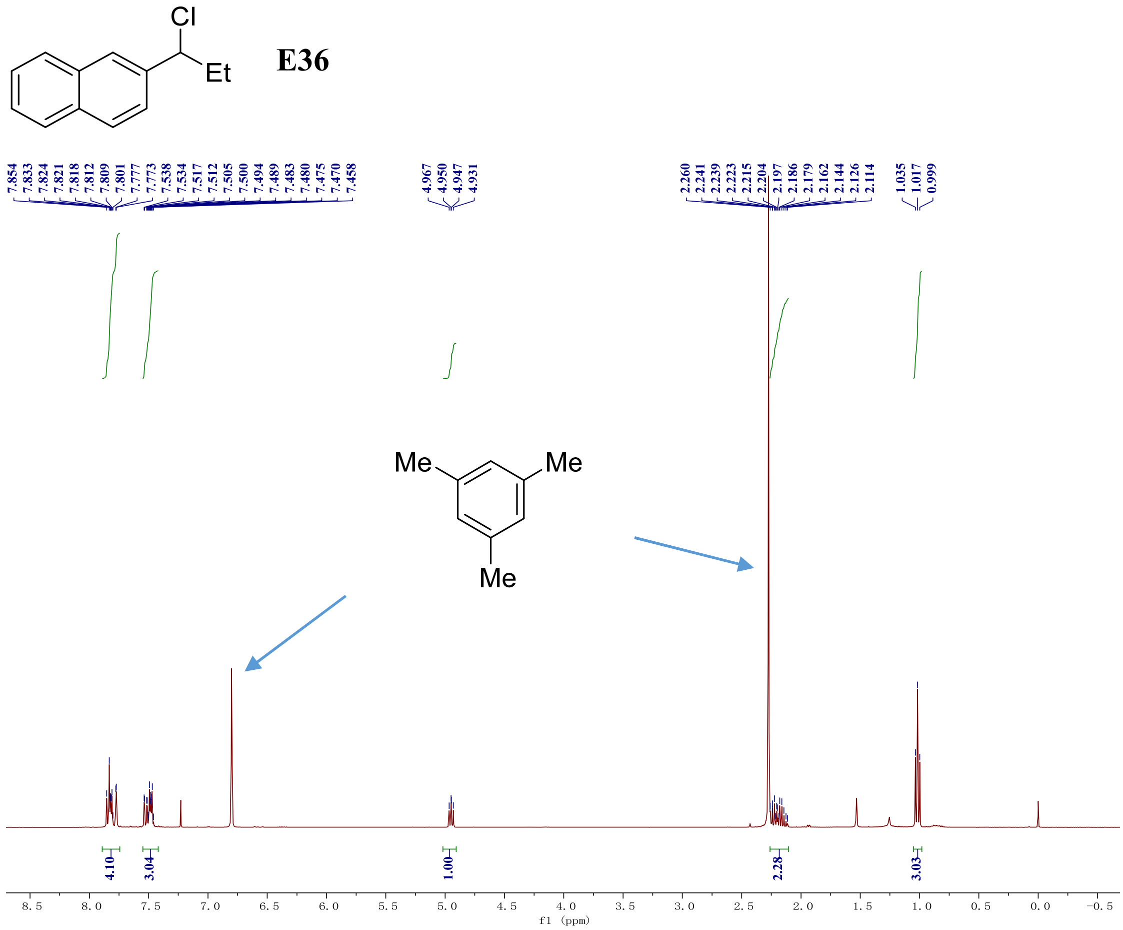
E35

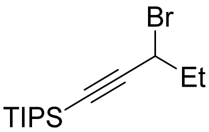

8.612
8.606
8.539
8.528
8.524
7.763
7.758
7.753
7.743
7.738
7.733
7.314
7.302
7.294
7.282
4.885
4.867
4.848
2.358
2.340
2.321
2.318
2.303
2.300
2.285
2.282
2.267
2.264
2.247
2.211
2.203
2.193
2.175
2.158
2.140
2.122
2.104
1.045
1.028
1.026
1.010
1.008
0.99
1.00
1.03
0.92
1.04
1.09
1.12
3.06
f1 (ppm)

E78



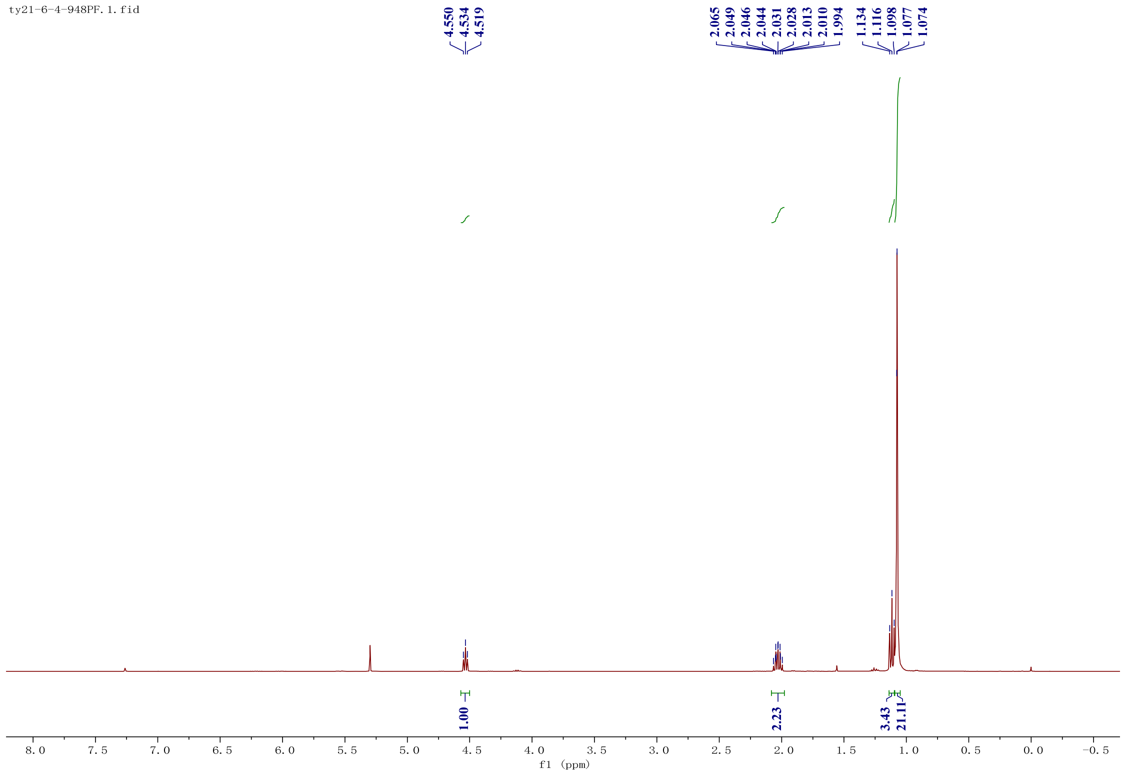
E36



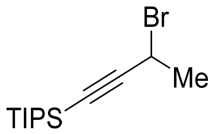


Br
Et
TIPS

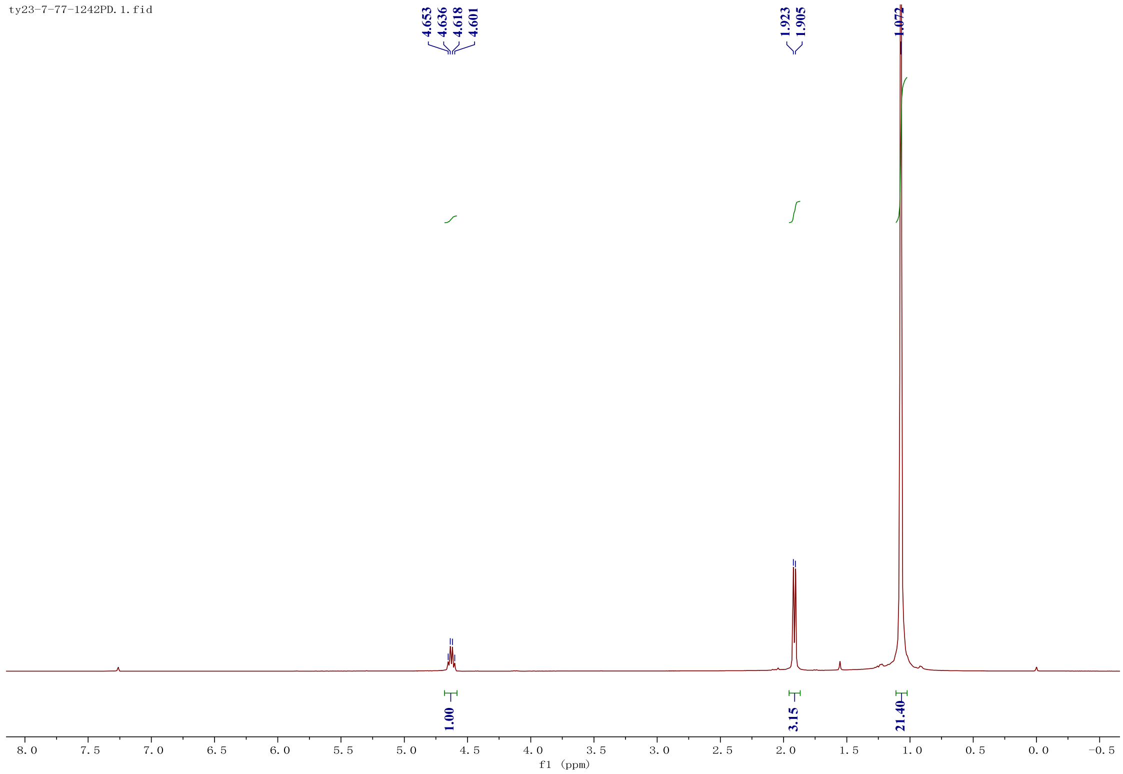
E37

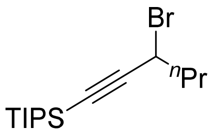


ty21-6-4-948PF.1.fid
4.550
4.534
4.519
2.065
2.049
2.046
2.044
2.031
2.028
2.013
2.010
1.994
1.134
1.116
1.098
1.077
1.074
1.00
2.23
3.43
21.11
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

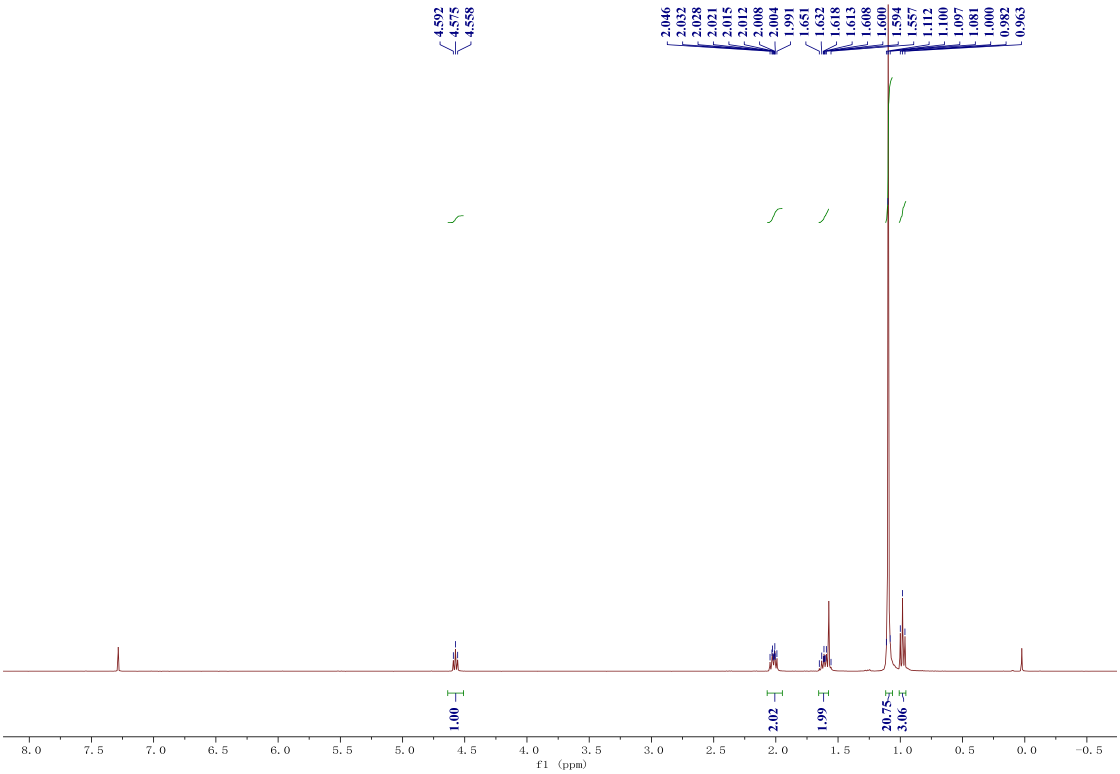


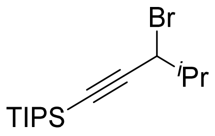
E38


ty23-7-77-1242PD.1.fid
4.653
4.636
4.618
4.601
1.923
1.905
1.072
1.00
3.15
21.40
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

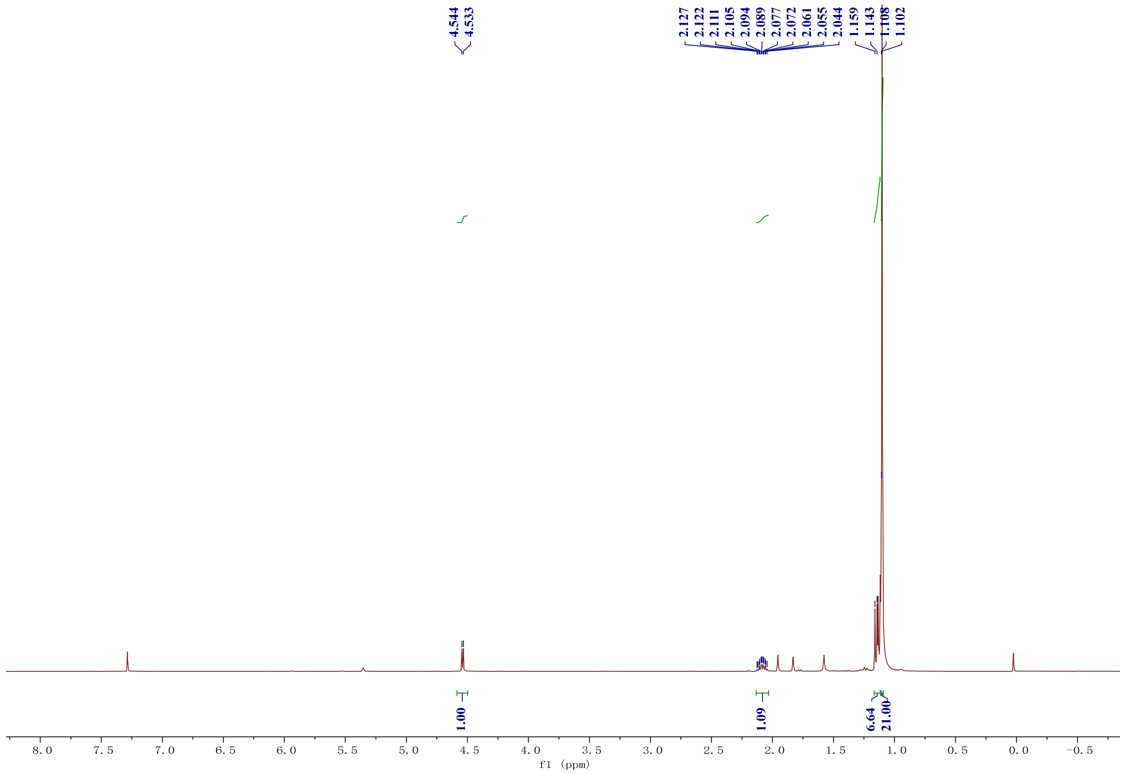

Br
nPr
TIPS

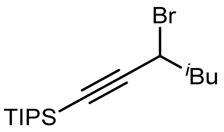
E39


4.592
4.575
4.558
2.046
2.032
2.028
2.021
2.015
2.012
2.008
2.004
1.991
1.651
1.632
1.618
1.613
1.608
1.600
1.594
1.557
1.112
1.100
1.097
1.081
1.000
0.982
0.963
1.00
2.02
1.99
20.75
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

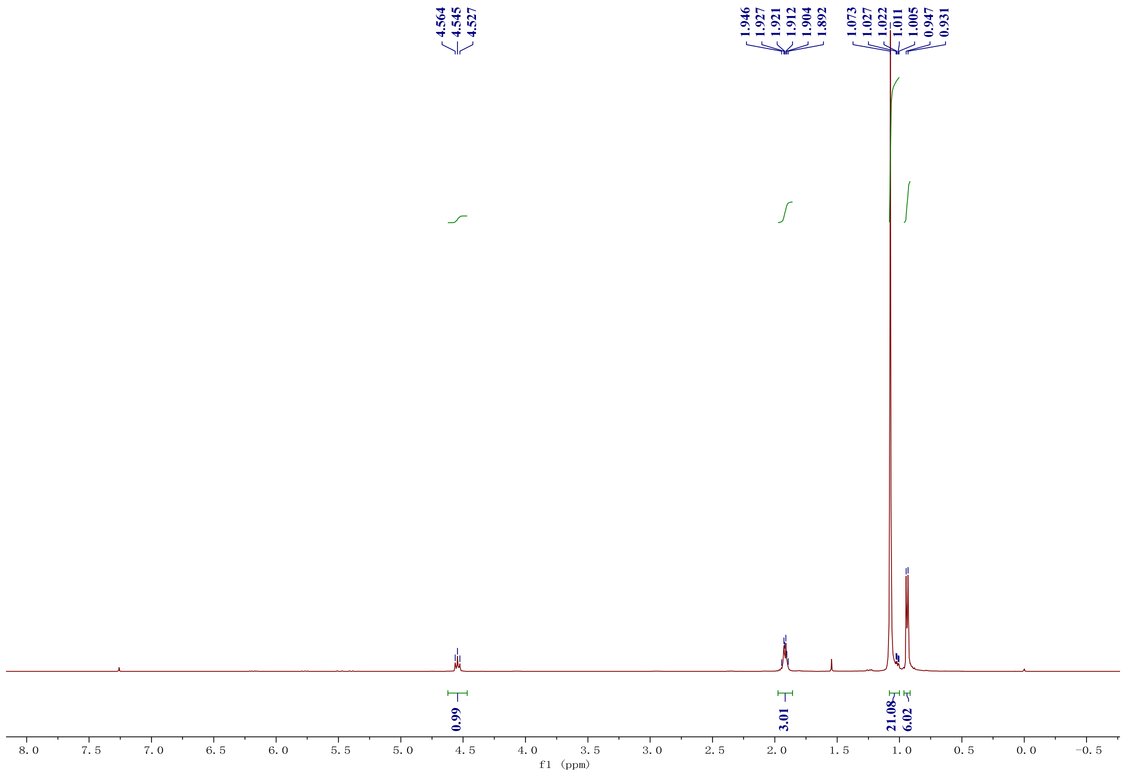


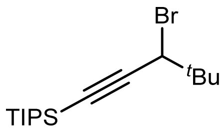
E40



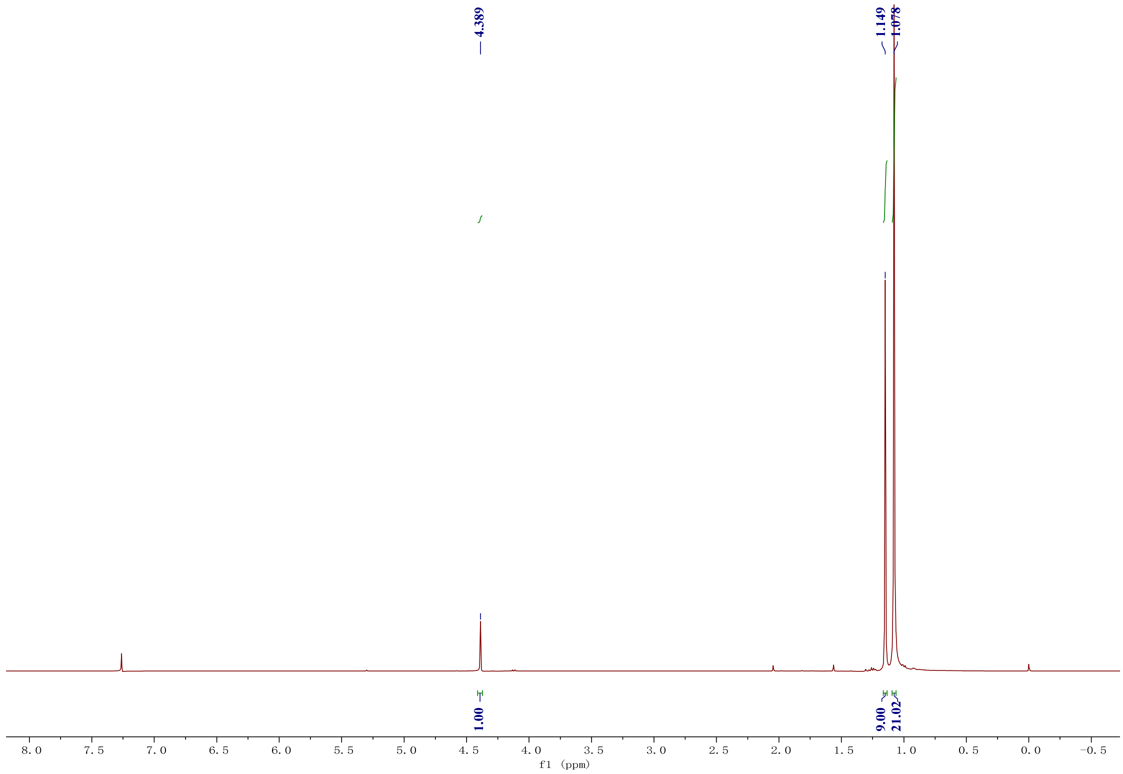


E41

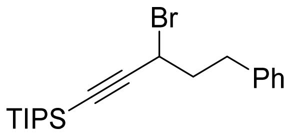

4.564
4.545
4.527
1.946
1.927
1.921
1.912
1.904
1.892
1.073
1.027
1.022
1.011
1.005
0.947
0.931
0.99
3.01
21.08
6.02
f1 (ppm)



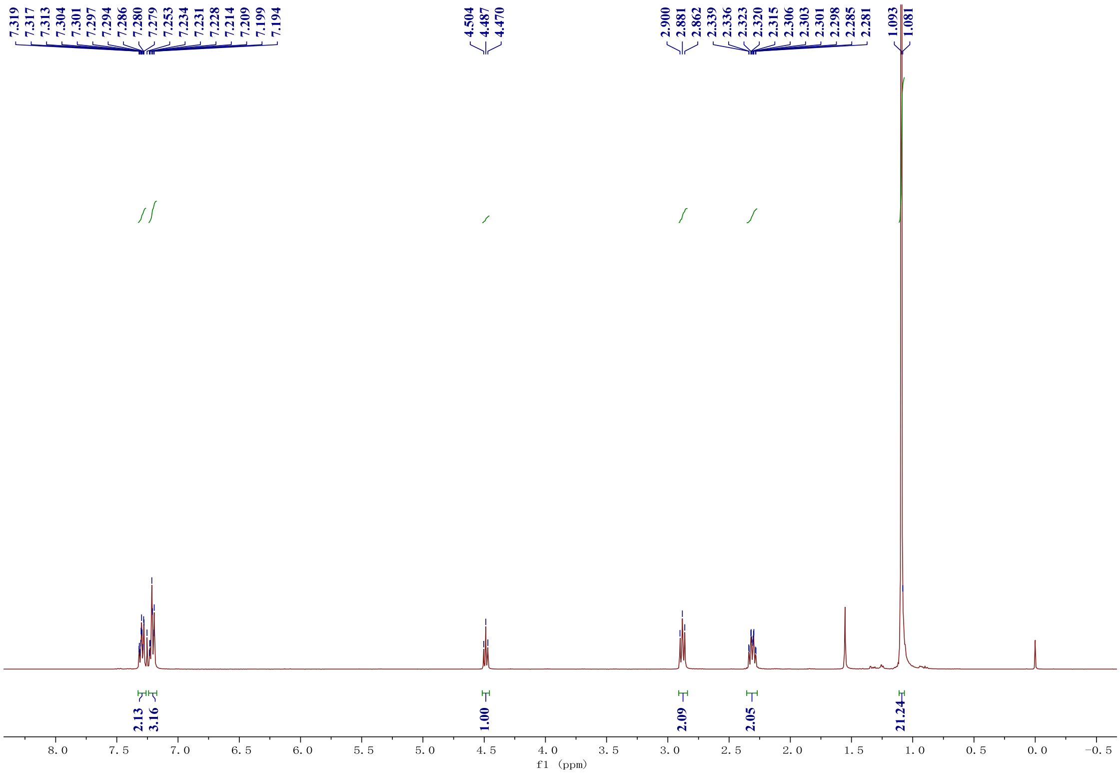
E42

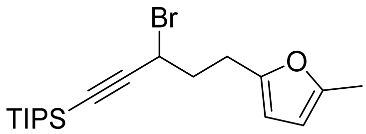


4.389
1.149
1.078
1.00
9.00
21.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

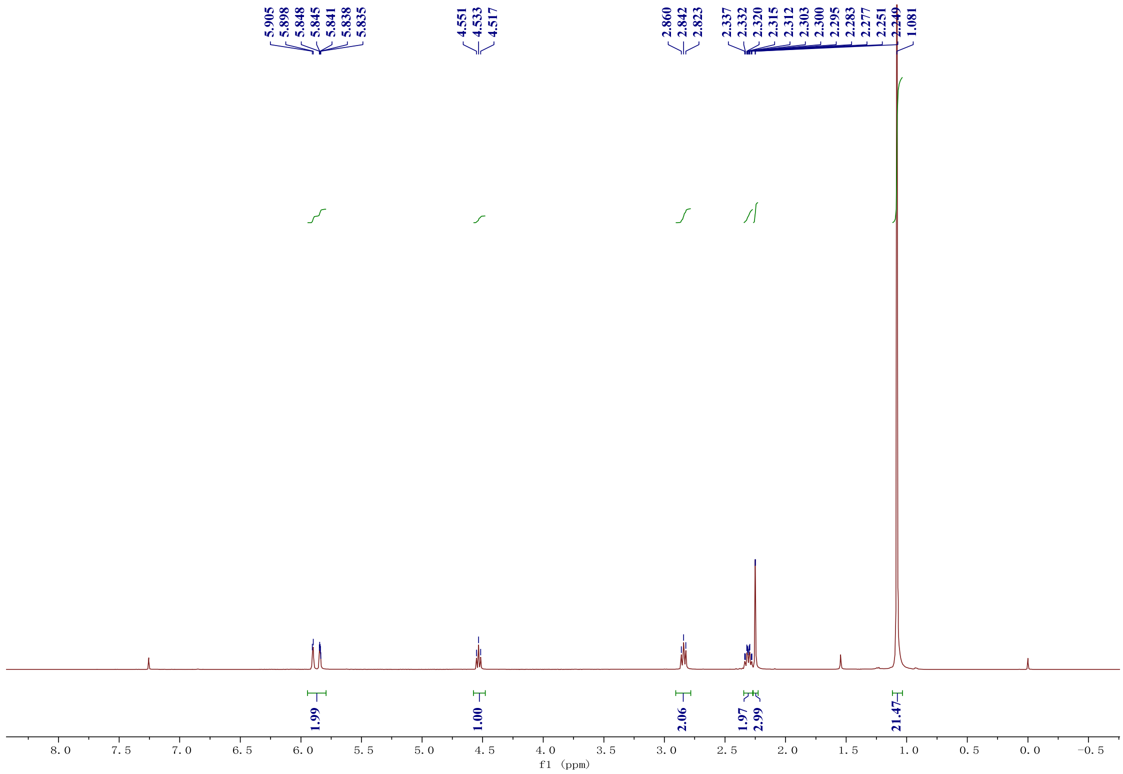

Br
Ph
TIPS

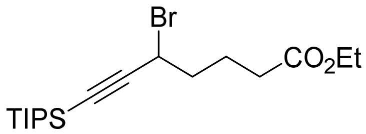
E43


7.319
7.317
7.313
7.304
7.301
7.297
7.294
7.286
7.280
7.279
7.253
7.234
7.231
7.228
7.214
7.209
7.199
7.194
4.504
4.487
4.470
2.900
2.881
2.862
2.339
2.336
2.323
2.320
2.315
2.306
2.303
2.301
2.298
2.285
2.281
1.093
1.081
2.13
3.16
1.00
2.09
2.05
21.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

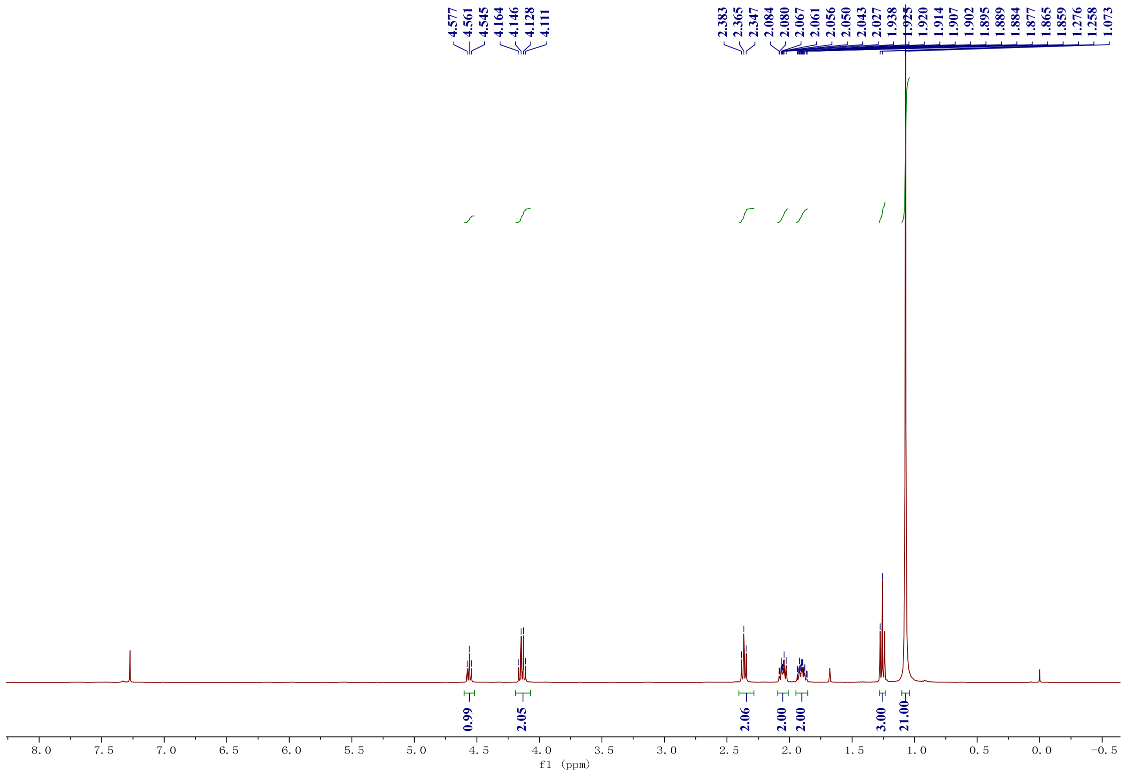


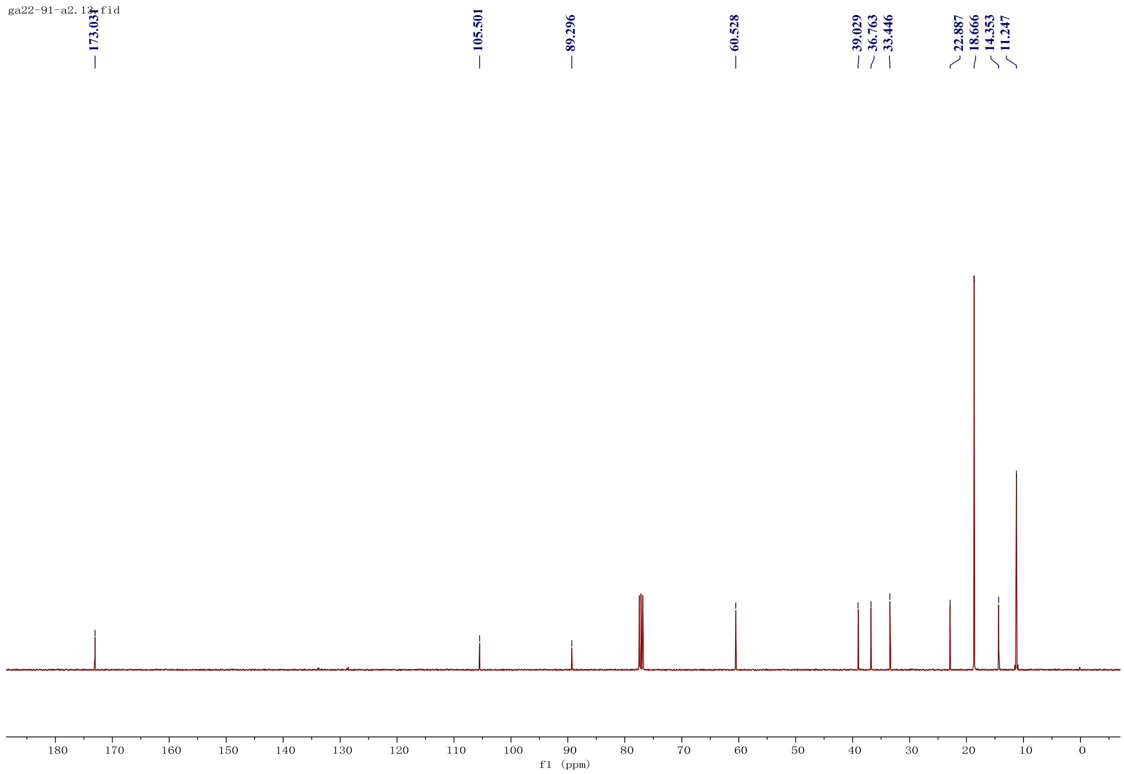
E44

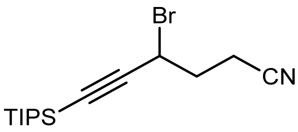

5.905
5.898
5.848
5.845
5.841
5.838
5.835
4.551
4.533
4.517
2.860
2.842
2.823
2.337
2.332
2.320
2.315
2.312
2.303
2.300
2.295
2.283
2.277
2.251
2.249
1.081
1.99
1.00
2.06
1.97
2.99
21.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Br
CO2Et
TIPS

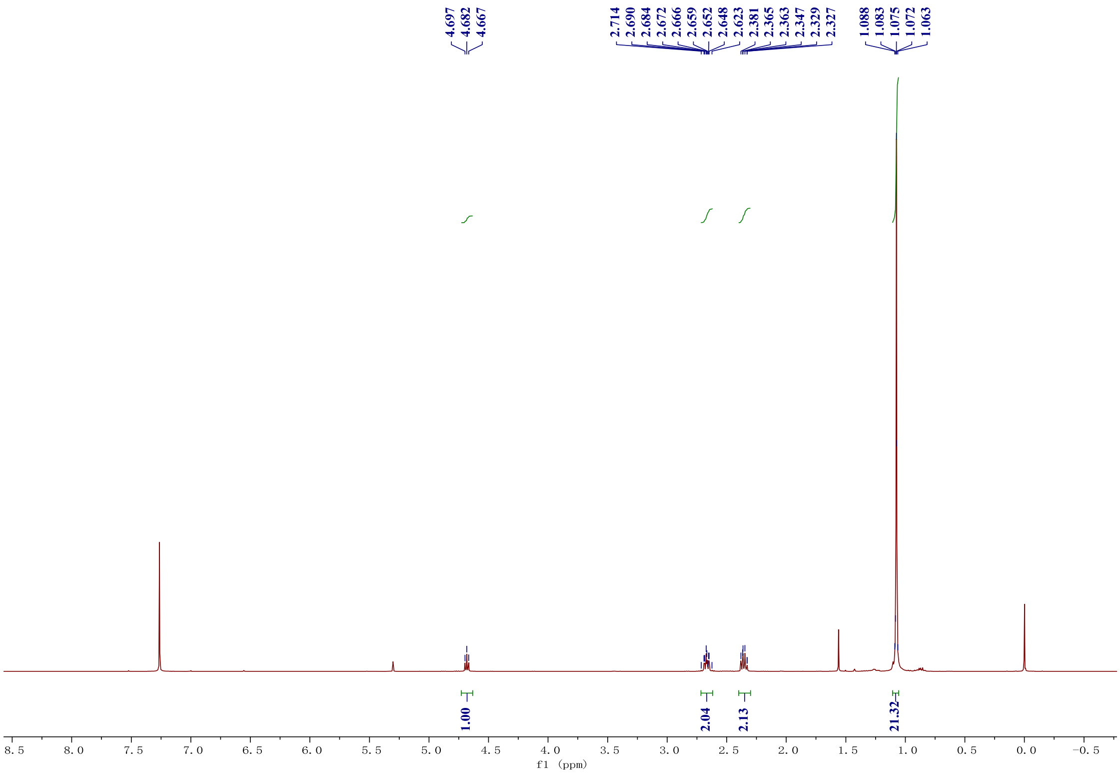
E45

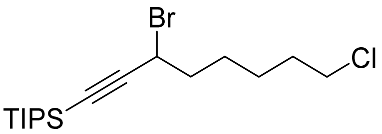

4.577
4.561
4.545
4.164
4.146
4.128
4.111
2.383
2.365
2.347
2.084
2.080
2.067
2.061
2.056
2.050
2.043
2.027
1.938
1.925
1.920
1.914
1.907
1.902
1.895
1.889
1.884
1.877
1.865
1.859
1.276
1.258
1.073
0.99
2.05
2.06
2.00
2.00
3.00
21.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


ga22-91-a2.13.fid
173.031
105.501
89.296
60.528
39.029
36.763
33.446
22.887
18.666
14.353
11.247
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

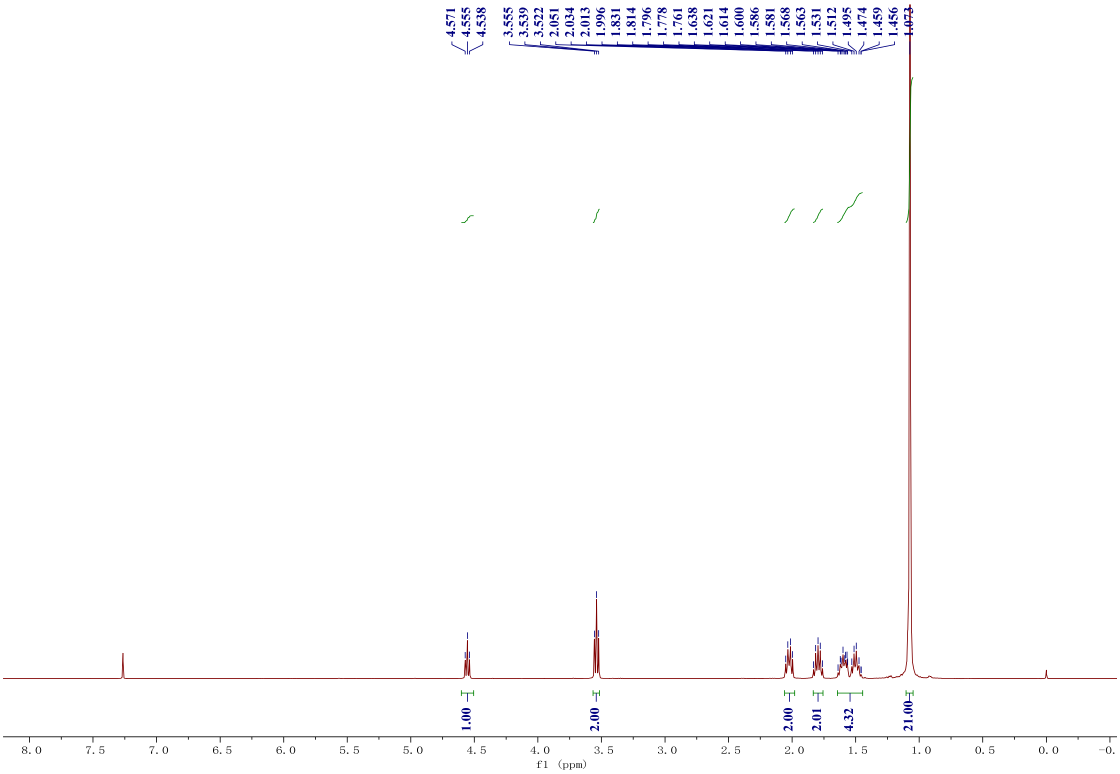


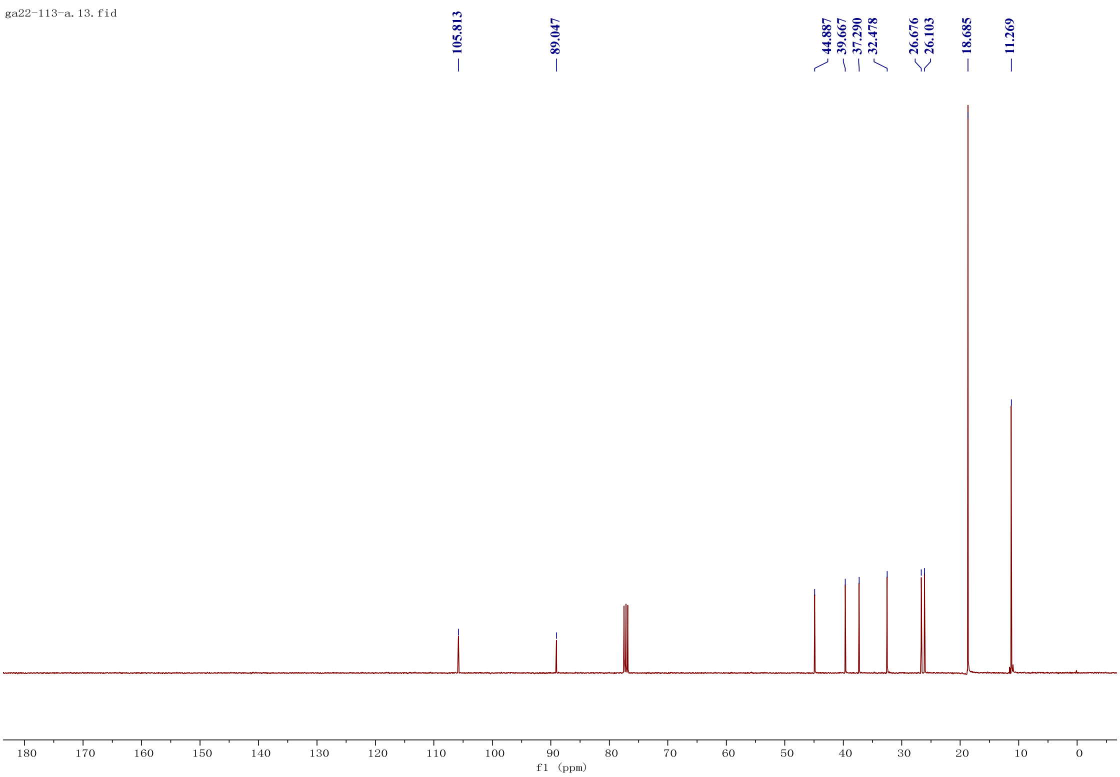
E46

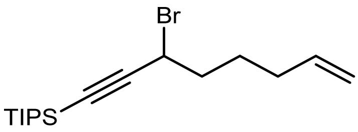

4.697
4.682
4.667
2.714
2.690
2.684
2.672
2.666
2.659
2.652
2.648
2.623
2.381
2.365
2.363
2.347
2.329
2.327
1.088
1.083
1.075
1.072
1.063
1.00
2.04
2.13
21.32
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



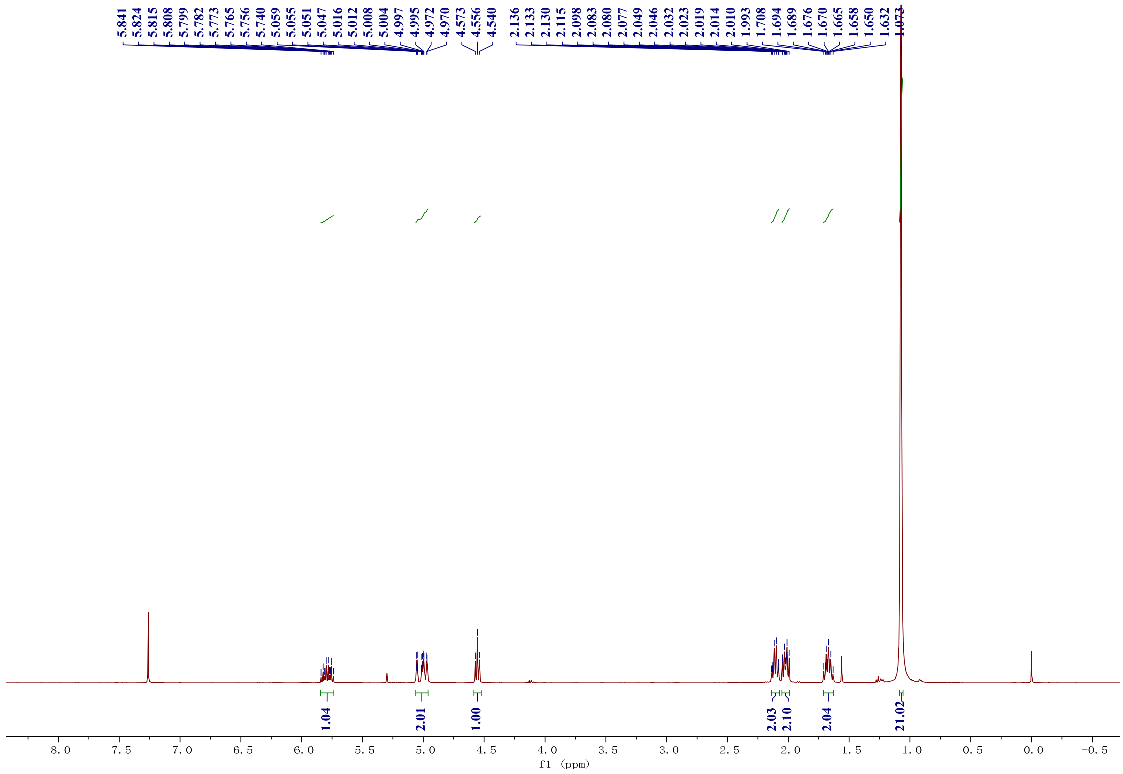
E47

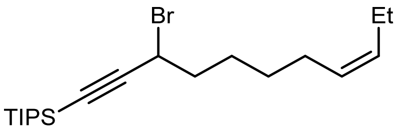




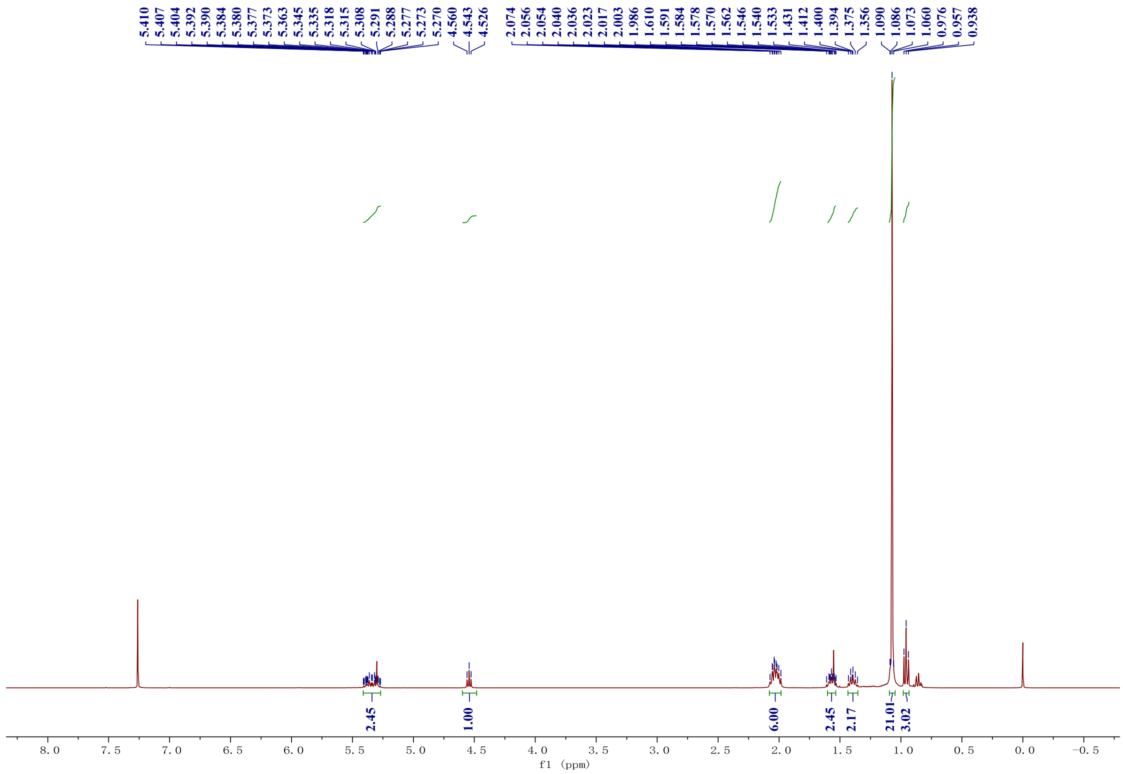


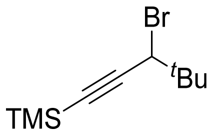
E48



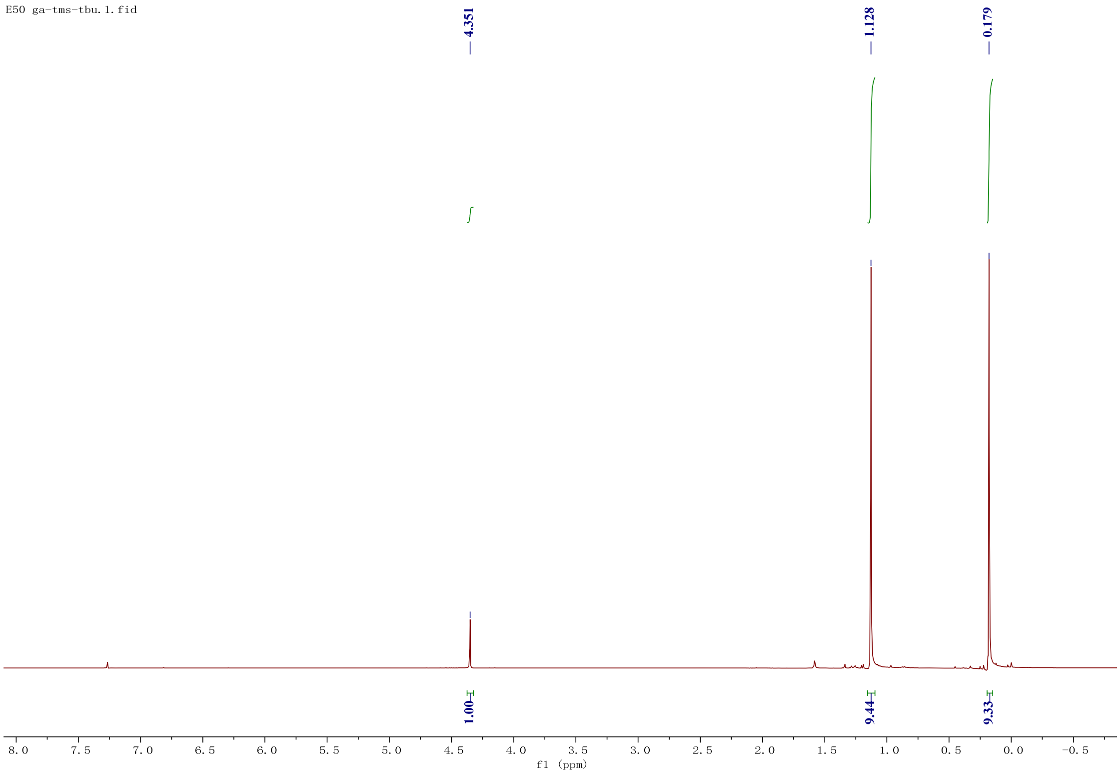


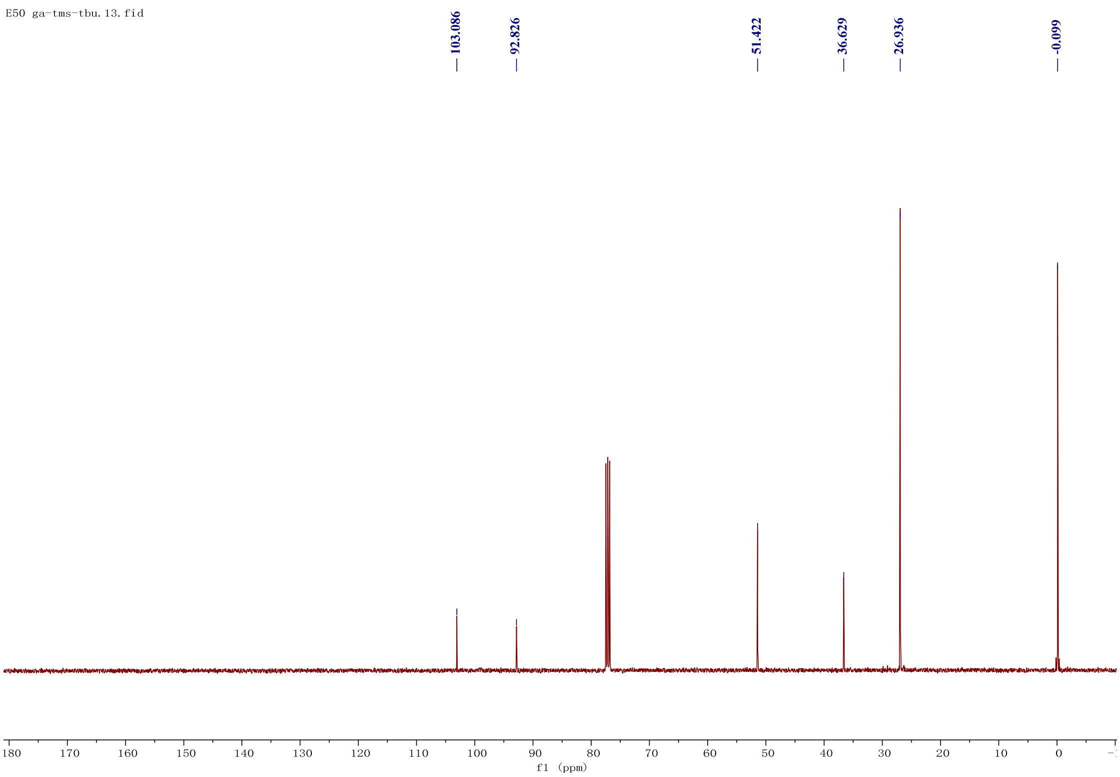
E49

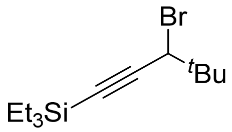




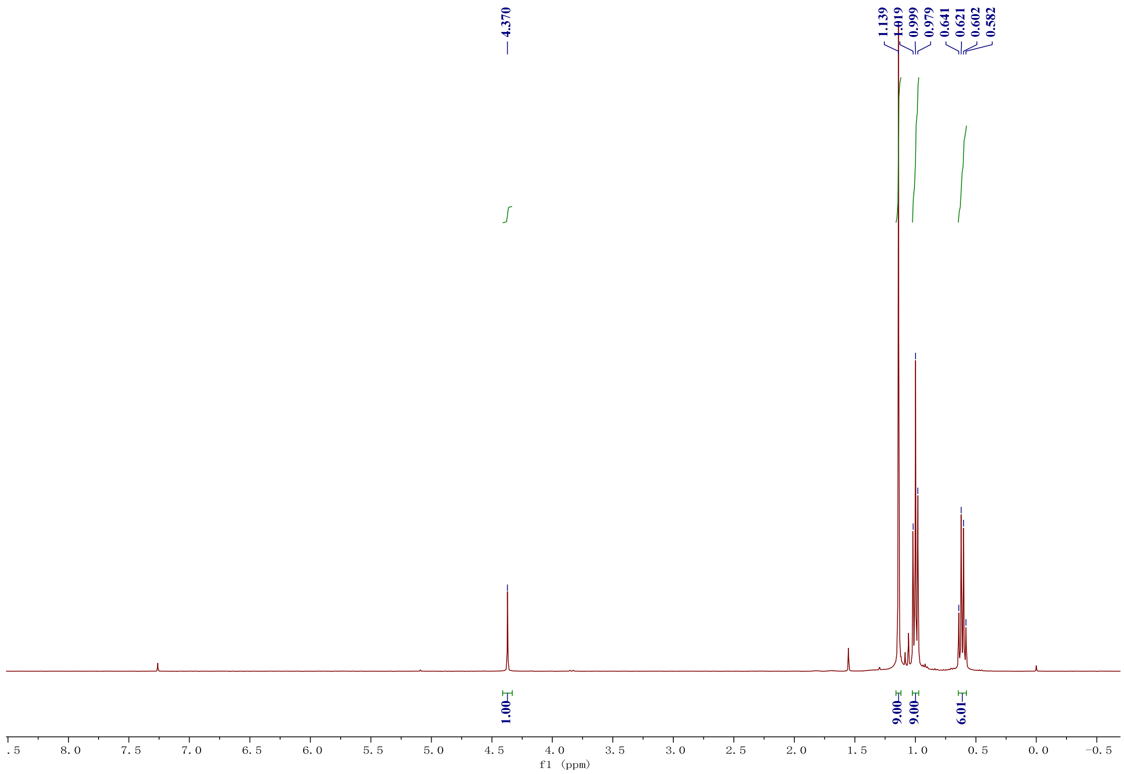
E50

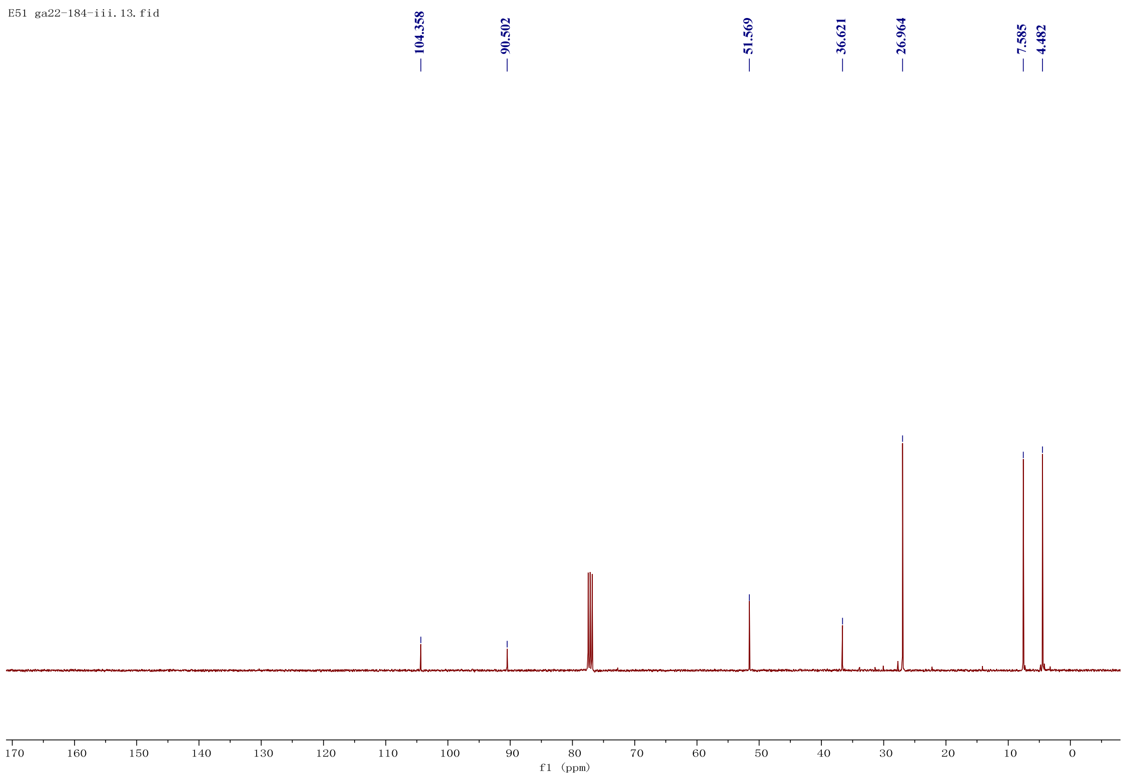

E50 ga-tms-tbu.1.fid
4.351
1.128
0.179
1.00
9.44
9.33
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

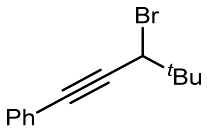

E50 ga-tms-tbu.13.fid
103.086
92.826
51.422
36.629
26.936
-0.099
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
tBu
Et3Si

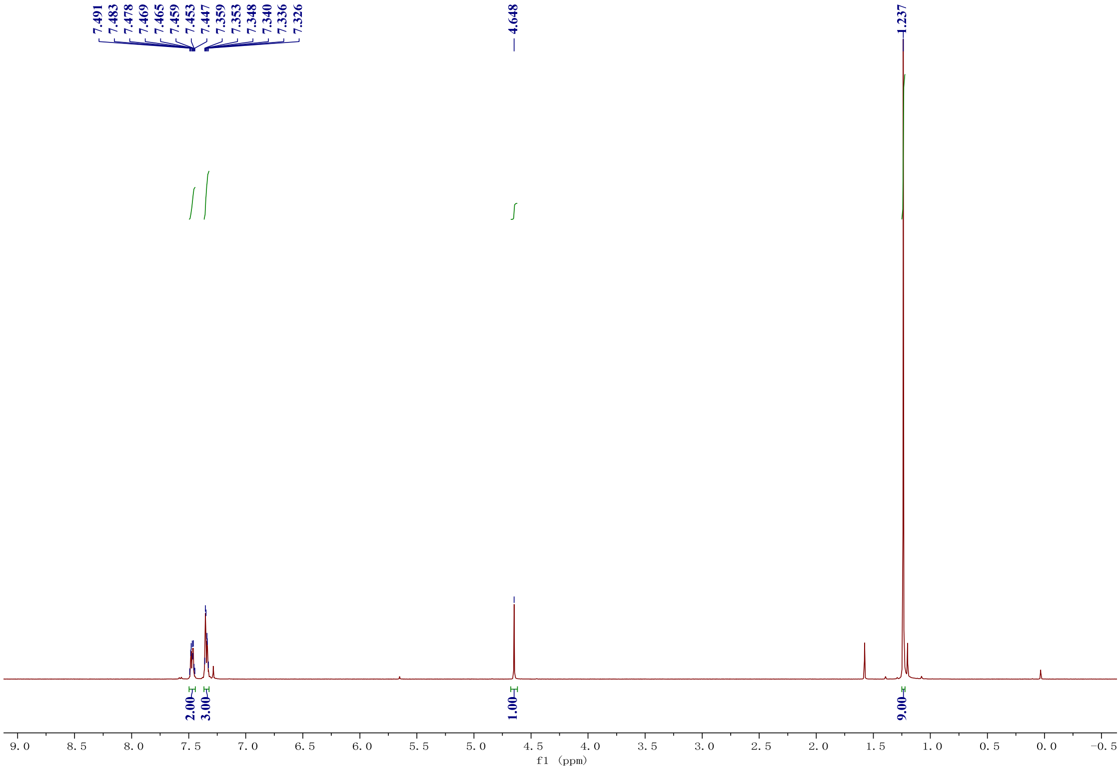
E51

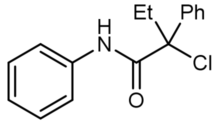

4.370
1.139
1.019
0.999
0.979
0.641
0.621
0.602
0.582
1.00
9.00
9.00
6.01
f1 (ppm)


E51 ga22-184-iii.13.fid
104.358
90.502
51.569
36.621
26.964
7.585
4.482
f1 (ppm)



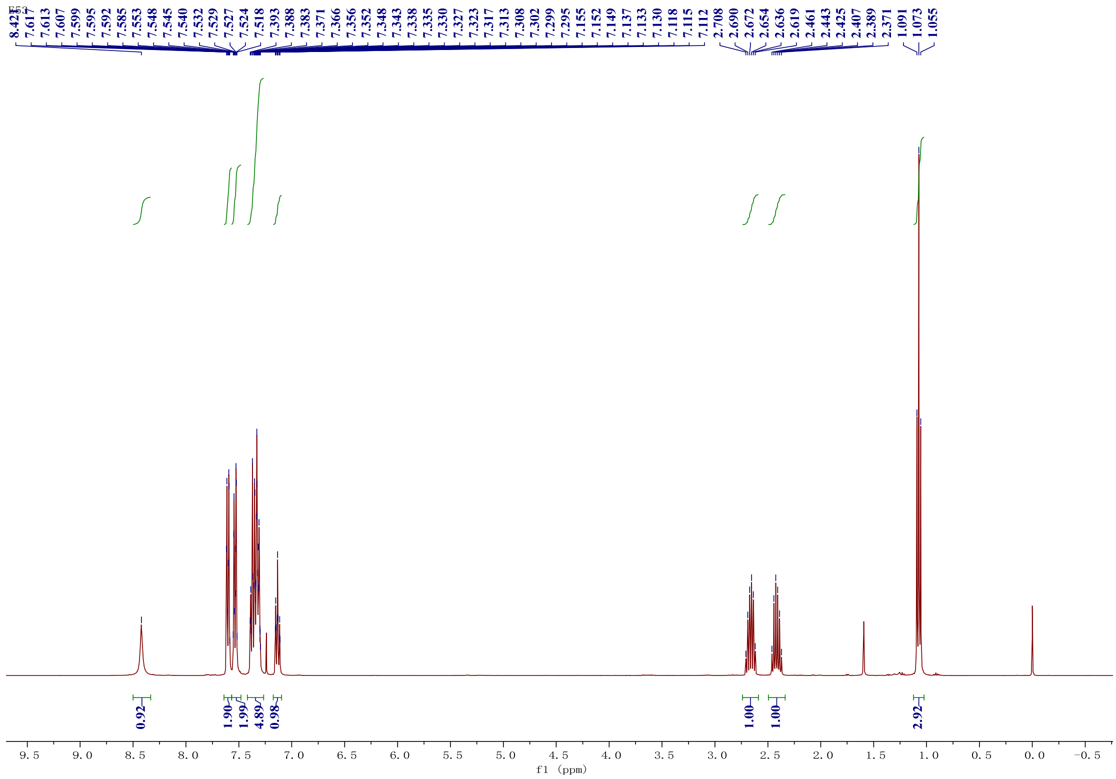
E52


7.491
7.483
7.478
7.469
7.465
7.459
7.453
7.447
7.359
7.353
7.348
7.340
7.336
7.326
4.648
1.237
2.00
3.00
1.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

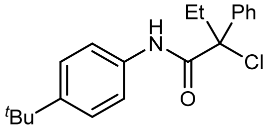


Et
Ph
H
N
Cl
O

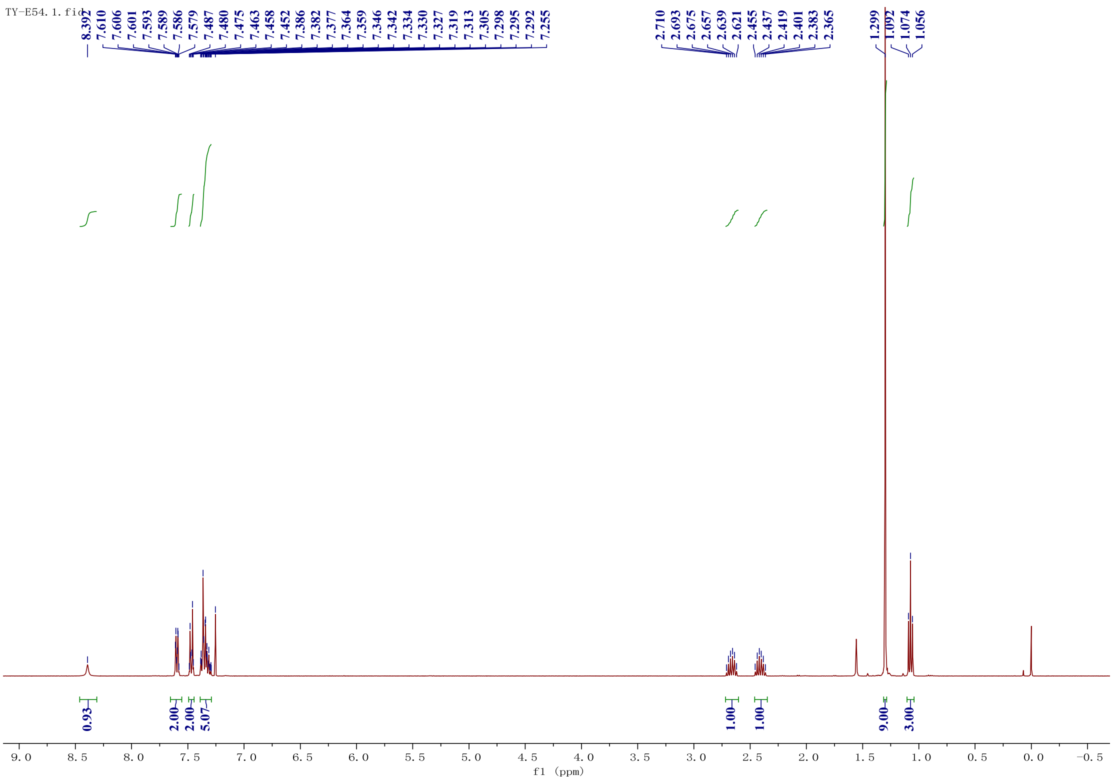
E53

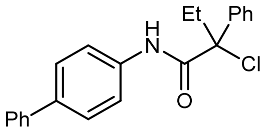


8.425
7.617
7.613
7.607
7.599
7.595
7.592
7.585
7.553
7.548
7.545
7.540
7.532
7.529
7.527
7.524
7.518
7.393
7.388
7.383
7.371
7.366
7.356
7.352
7.348
7.343
7.338
7.335
7.330
7.327
7.323
7.317
7.313
7.308
7.302
7.299
7.295
7.155
7.152
7.149
7.137
7.133
7.130
7.118
7.115
7.112
2.708
2.690
2.672
2.654
2.636
2.619
2.461
2.443
2.425
2.407
2.389
2.371
1.091
1.073
1.055
0.92
1.90
1.99
4.89
0.98
1.00
1.00
2.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

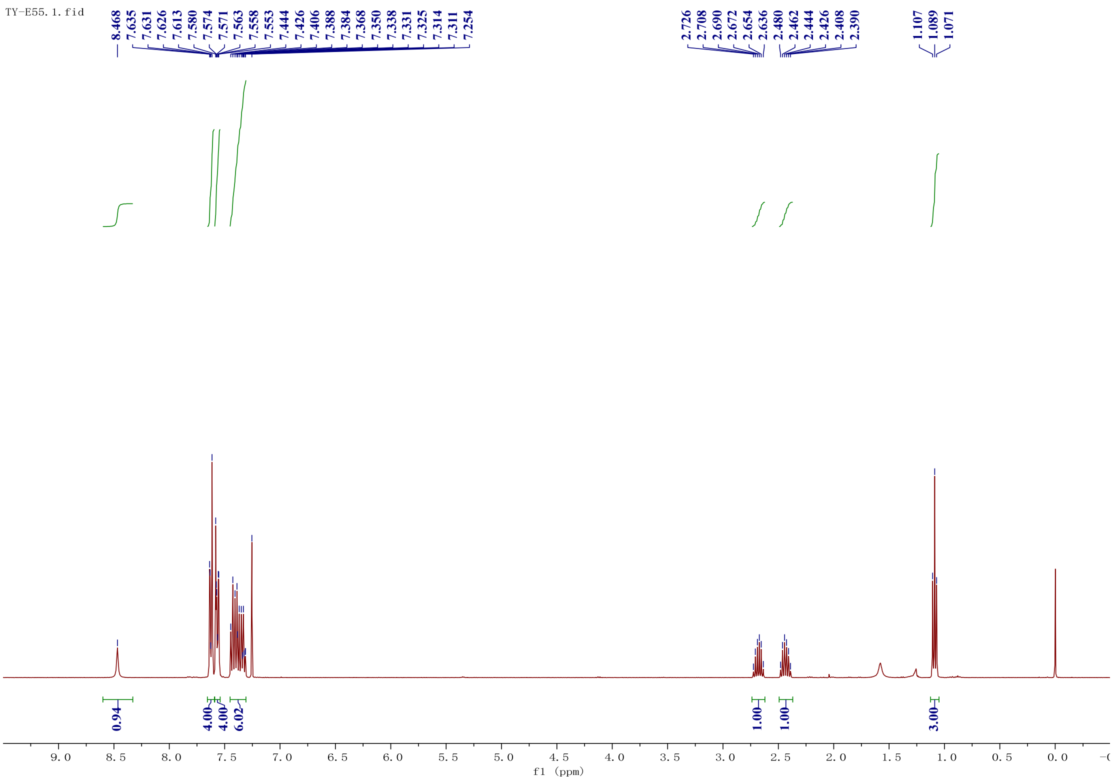


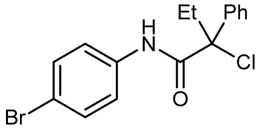
E54



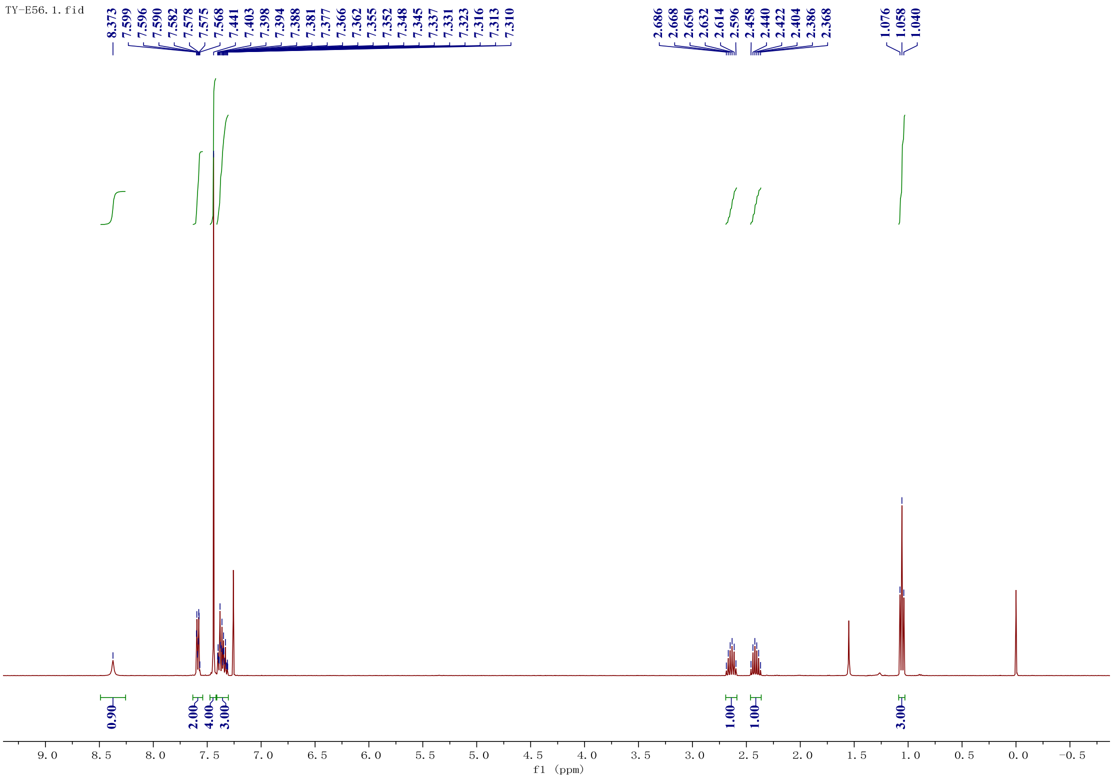


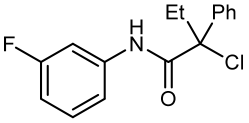
E55



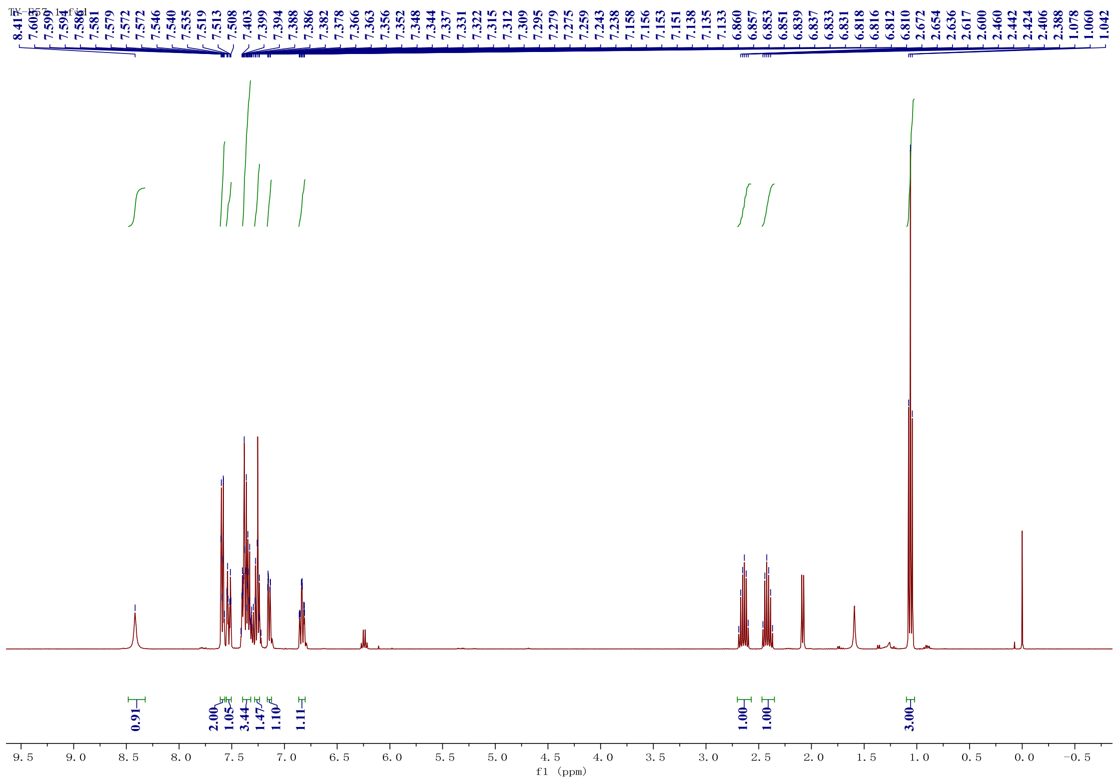


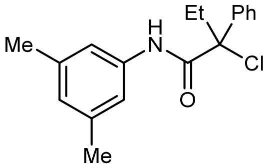
E56


TY-E56.1.fid
8.373
7.599
7.596
7.590
7.582
7.578
7.575
7.568
7.441
7.403
7.398
7.394
7.388
7.381
7.377
7.366
7.362
7.355
7.352
7.348
7.345
7.337
7.331
7.323
7.316
7.313
7.310
2.686
2.668
2.650
2.632
2.614
2.596
2.458
2.440
2.422
2.404
2.386
2.368
1.076
1.058
1.040
0.90
2.00
4.00
3.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

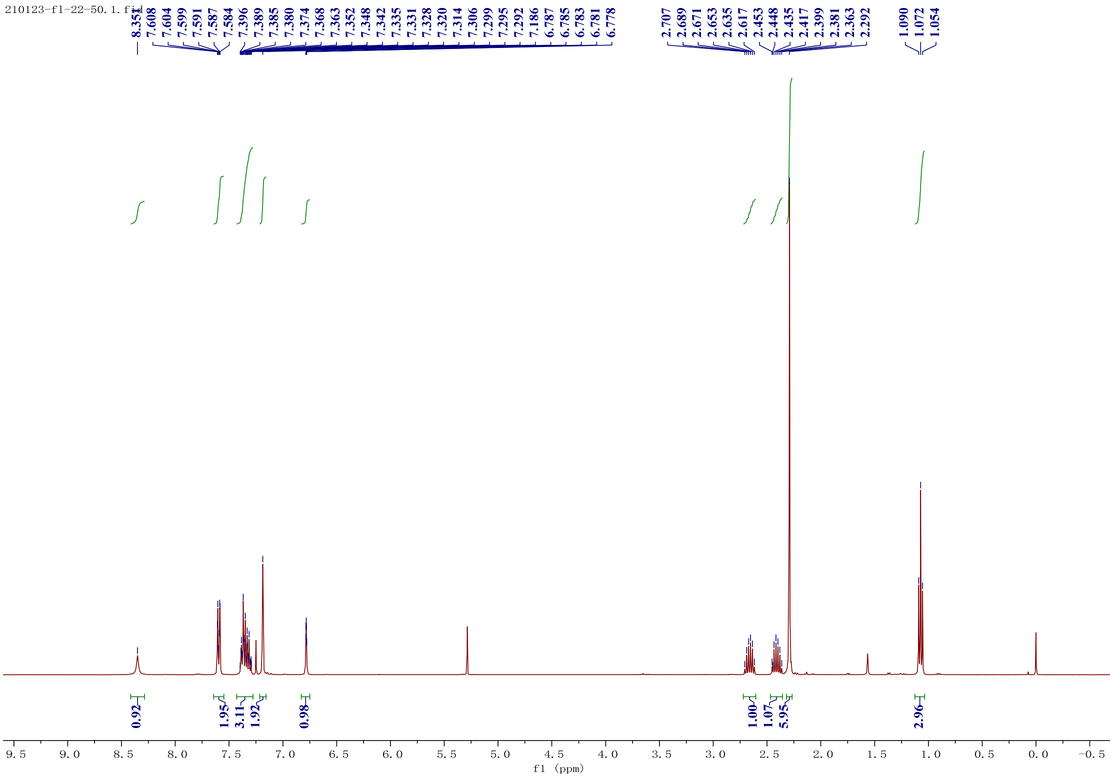


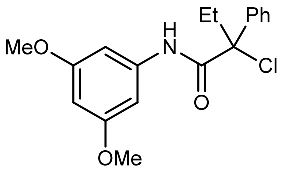
E57



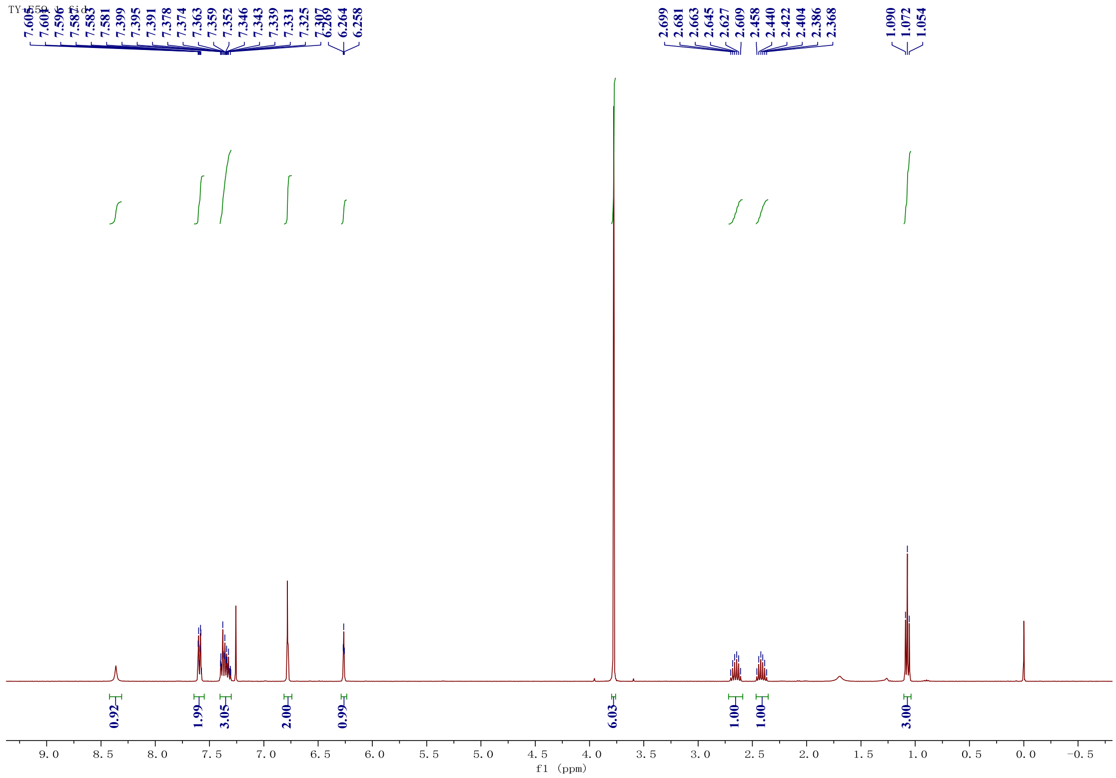


E58

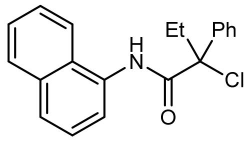




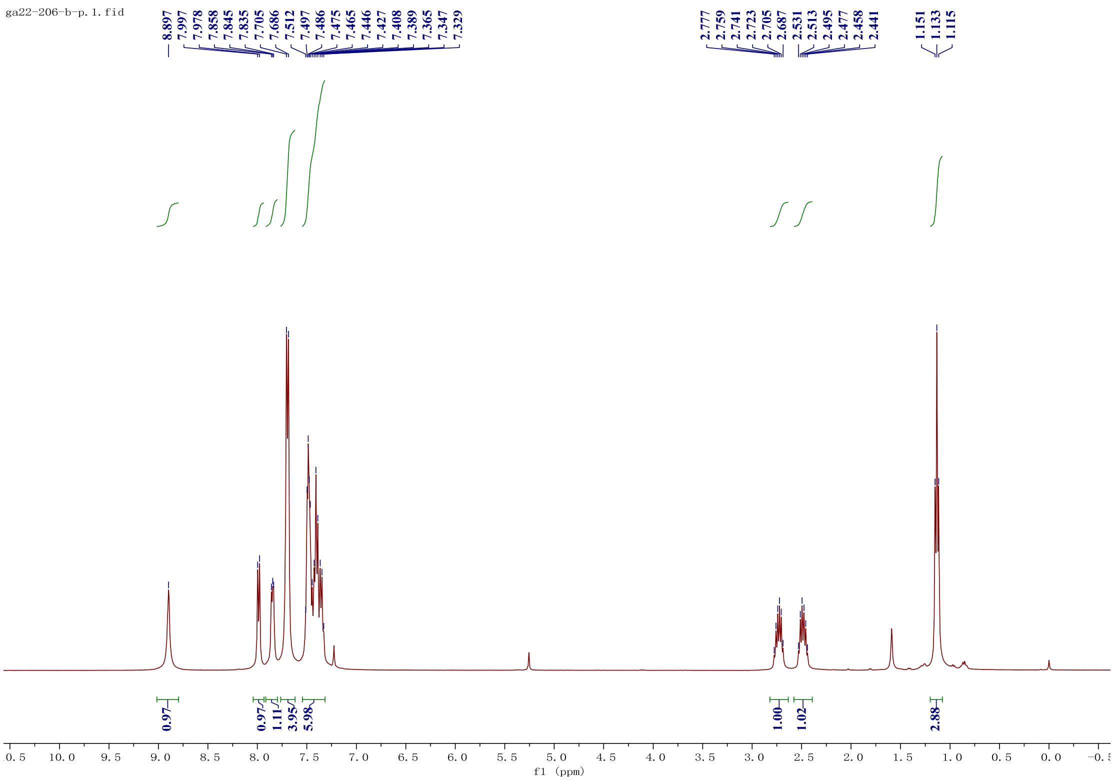
E59

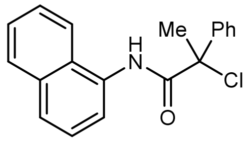


TY-E59
7.605
7.601
7.596
7.587
7.583
7.581
7.399
7.395
7.391
7.378
7.374
7.363
7.359
7.352
7.346
7.343
7.339
7.331
7.325
7.307
6.269
6.264
6.258
2.699
2.681
2.663
2.645
2.627
2.609
2.458
2.440
2.422
2.404
2.386
2.368
1.090
1.072
1.054
0.92
1.99
3.05
2.00
0.99
6.03
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

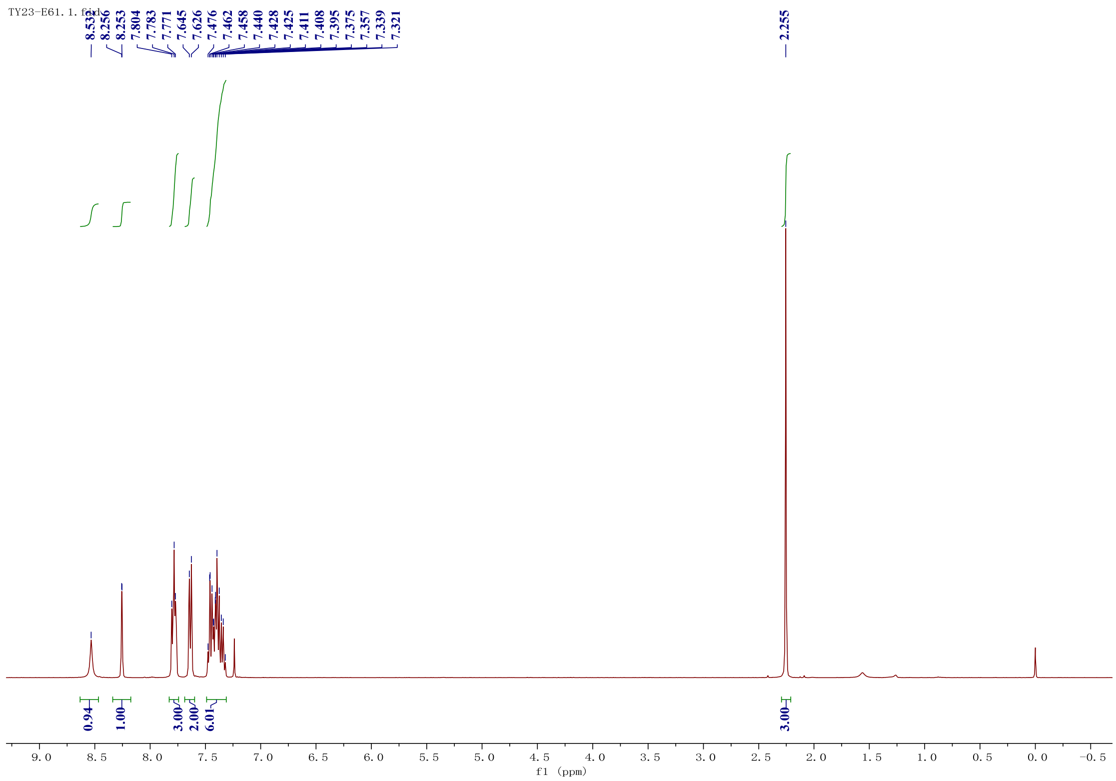


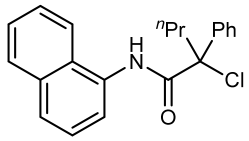
E60


ga22-206-b-p.1.fid
8.897
7.997
7.978
7.858
7.845
7.835
7.705
7.686
7.512
7.497
7.486
7.475
7.465
7.446
7.427
7.408
7.389
7.365
7.347
7.329
2.777
2.759
2.741
2.723
2.705
2.687
2.531
2.513
2.495
2.477
2.458
2.441
1.151
1.133
1.115
0.97
0.97
1.11
3.95
5.98
1.00
1.02
2.88
f1 (ppm)

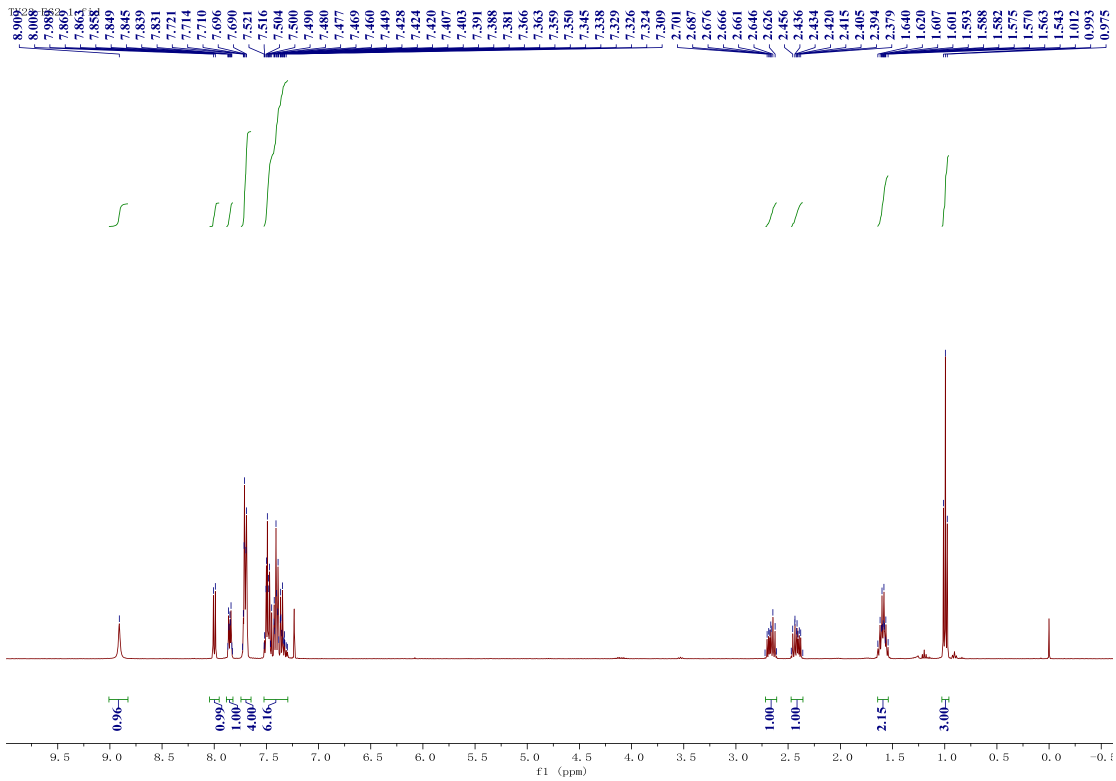


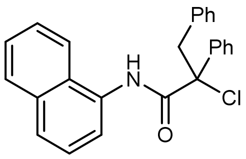
E61


TY23-E61.1.fid
8.532
8.256
8.253
7.804
7.783
7.771
7.645
7.626
7.476
7.462
7.458
7.440
7.428
7.425
7.411
7.408
7.395
7.375
7.357
7.339
7.321
2.255
0.94
1.00
3.00
2.00
6.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

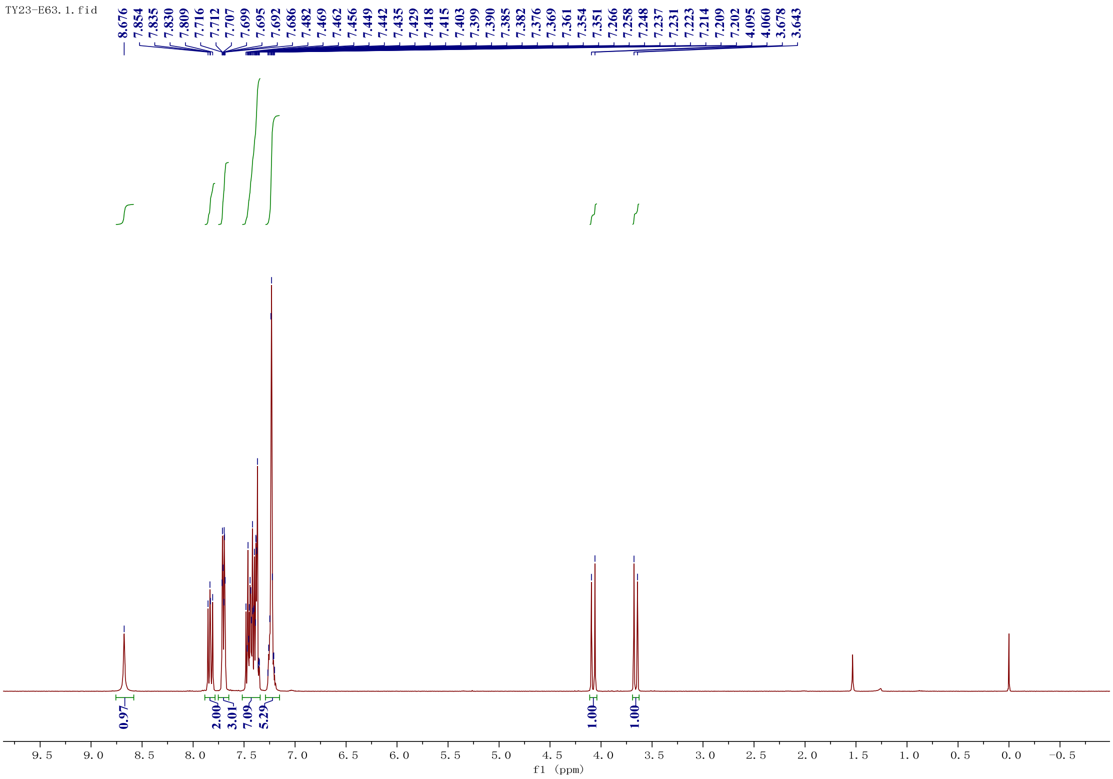


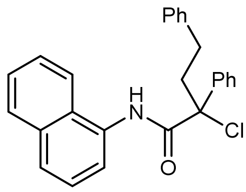
E62



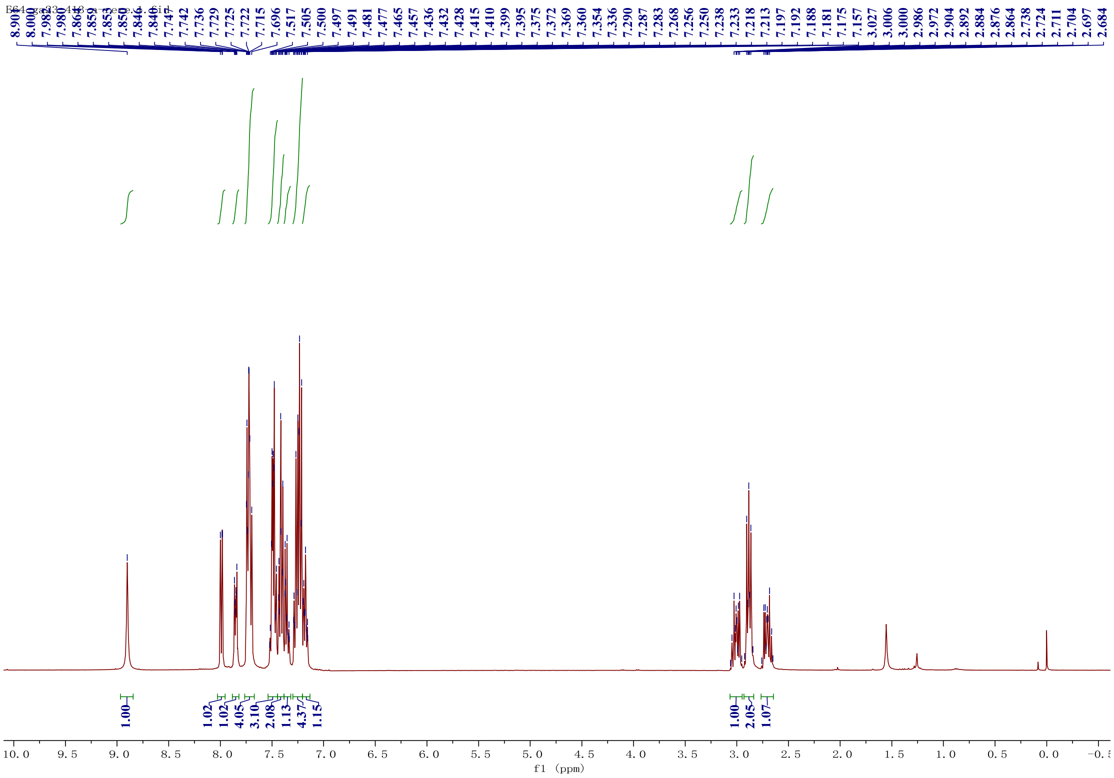

Ph
Ph
H
N
Cl
O

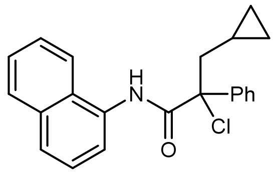
E63


TY23-E63.1.fid
8.676
7.854
7.835
7.830
7.809
7.716
7.712
7.707
7.699
7.695
7.692
7.686
7.482
7.469
7.462
7.456
7.449
7.442
7.435
7.429
7.418
7.415
7.403
7.399
7.390
7.385
7.382
7.376
7.369
7.361
7.354
7.351
7.266
7.258
7.248
7.237
7.231
7.223
7.214
7.209
7.202
4.095
4.060
3.678
3.643
0.97
2.00
3.01
7.09
5.29
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

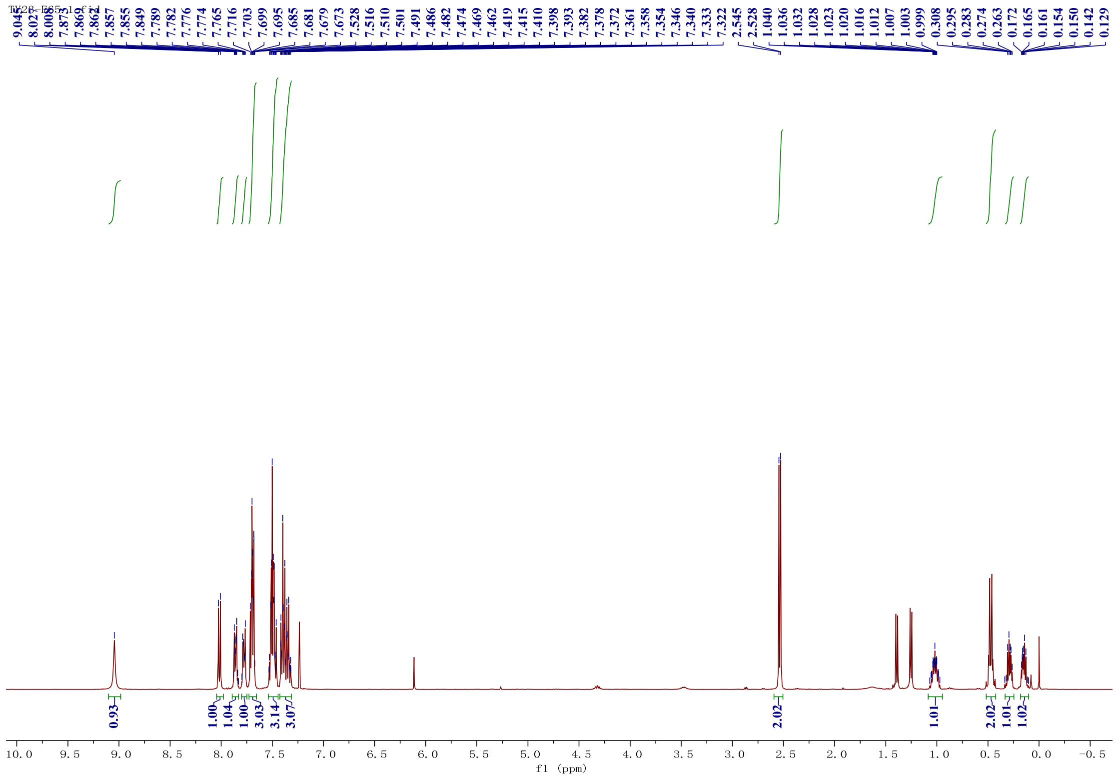


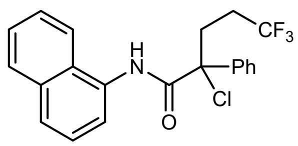
E64



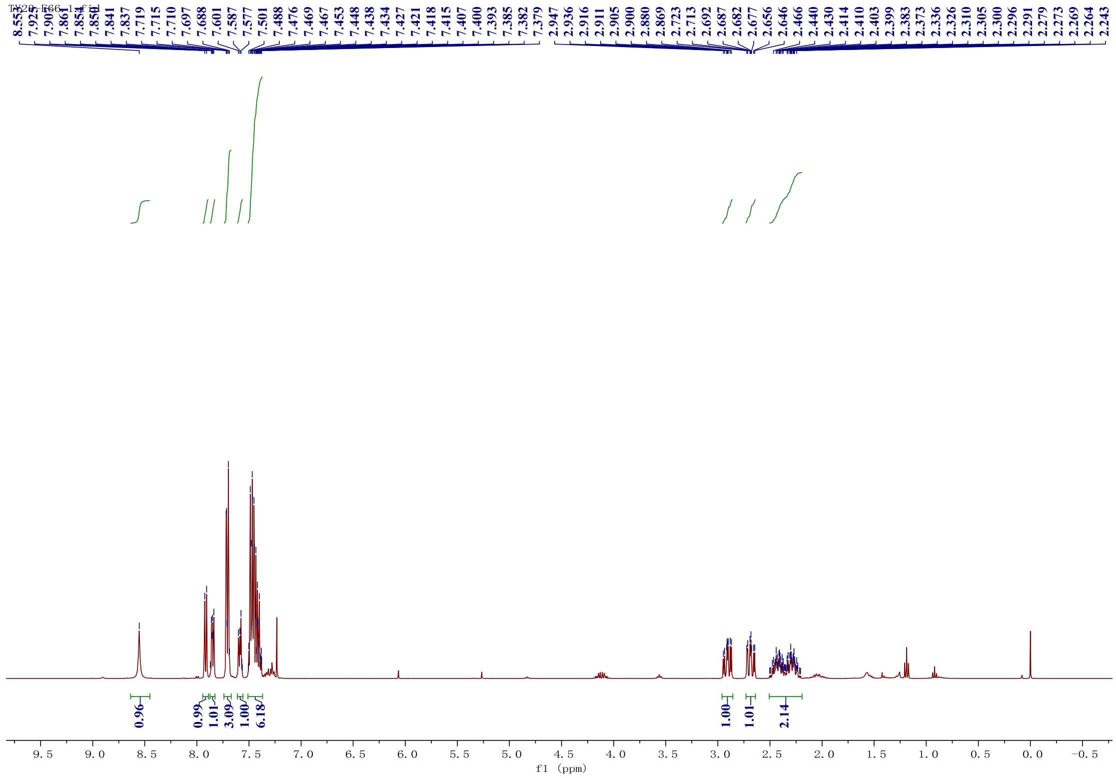


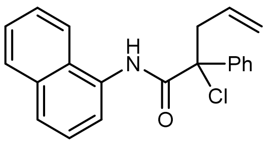
E65



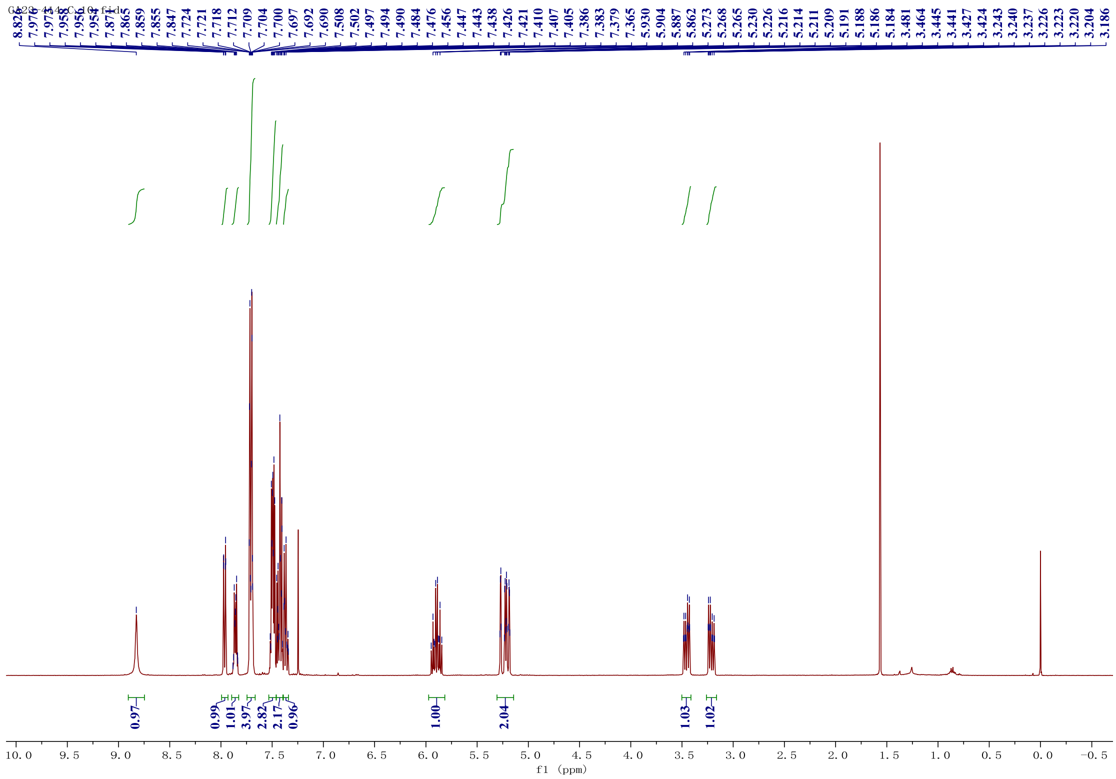


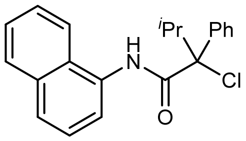
E66



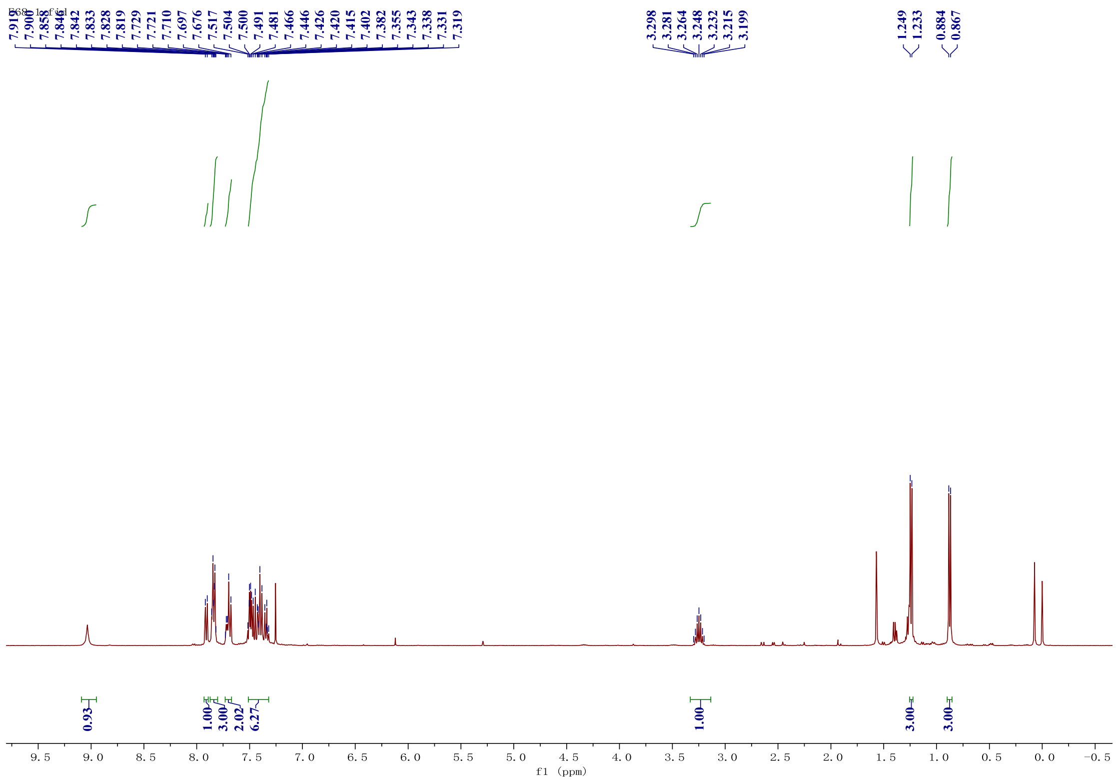


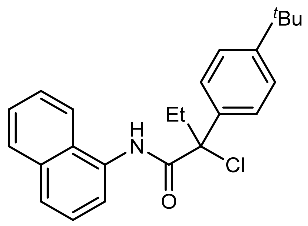
E67



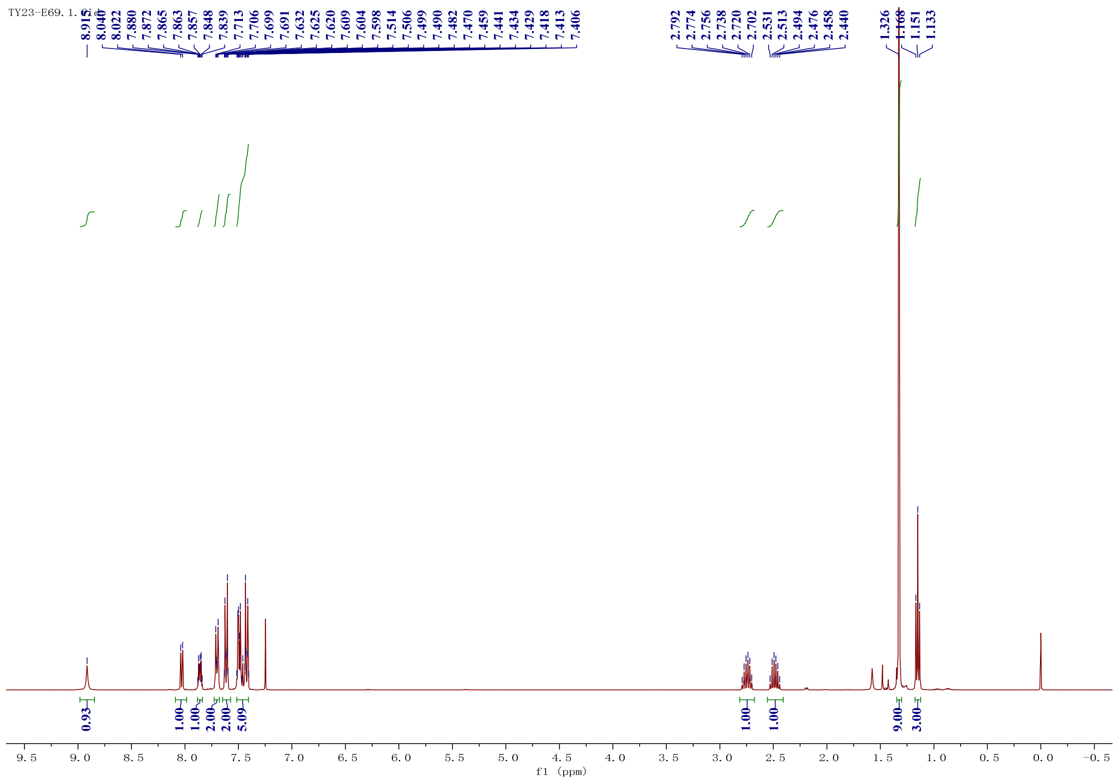


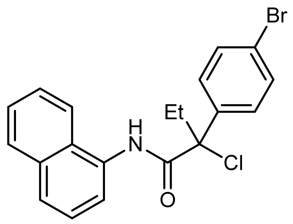
E68



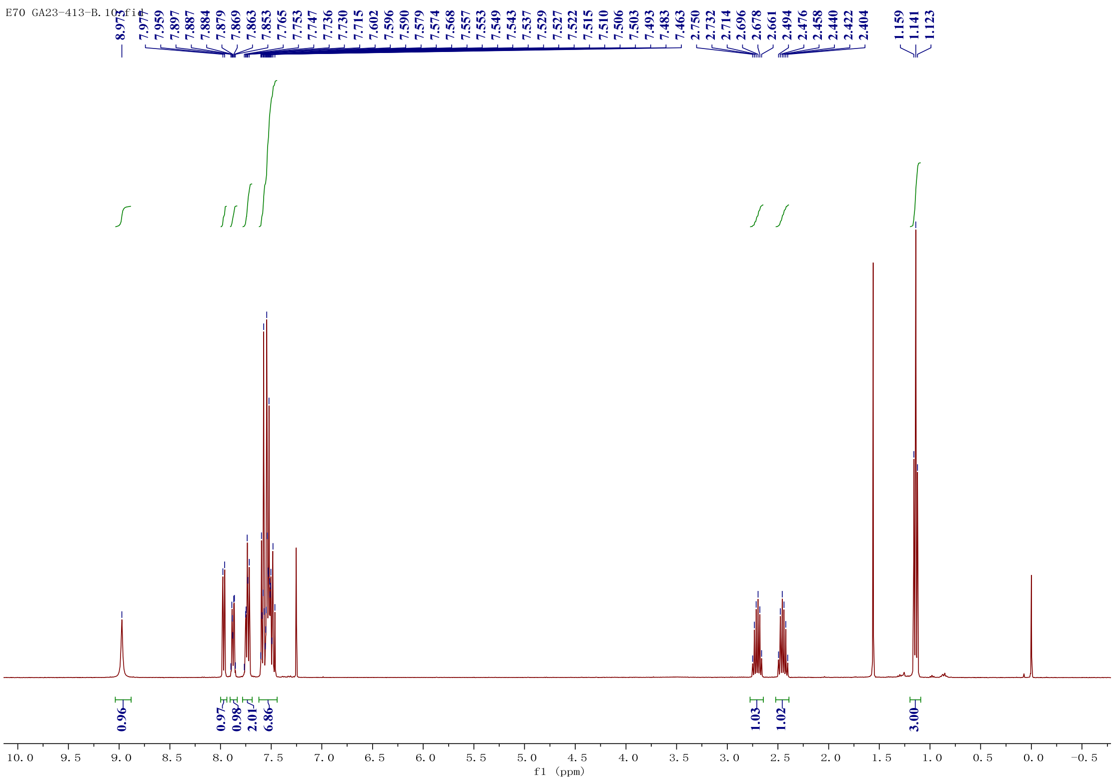


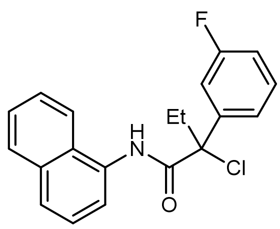
E69



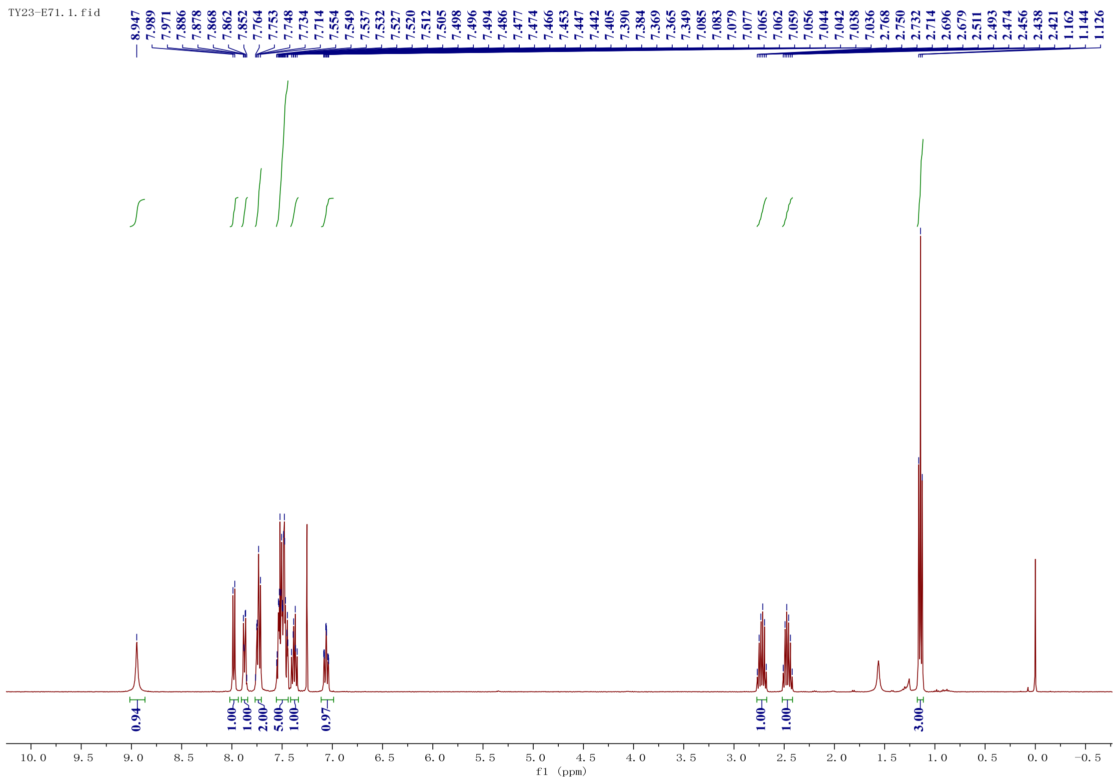

Br
Et
H
N
Cl
O

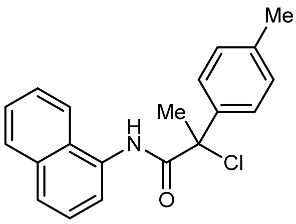
E70


E70 GA23-413-B.10.fid
8.973
7.977
7.959
7.897
7.887
7.884
7.879
7.869
7.863
7.853
7.765
7.753
7.747
7.736
7.730
7.715
7.602
7.596
7.590
7.579
7.574
7.568
7.557
7.553
7.549
7.543
7.537
7.529
7.527
7.522
7.515
7.510
7.506
7.503
7.493
7.483
7.463
2.750
2.732
2.714
2.696
2.678
2.661
2.494
2.476
2.458
2.440
2.422
2.404
1.159
1.141
1.123
0.96
0.97
0.98
2.01
6.86
1.03
1.02
3.00
f1 (ppm)

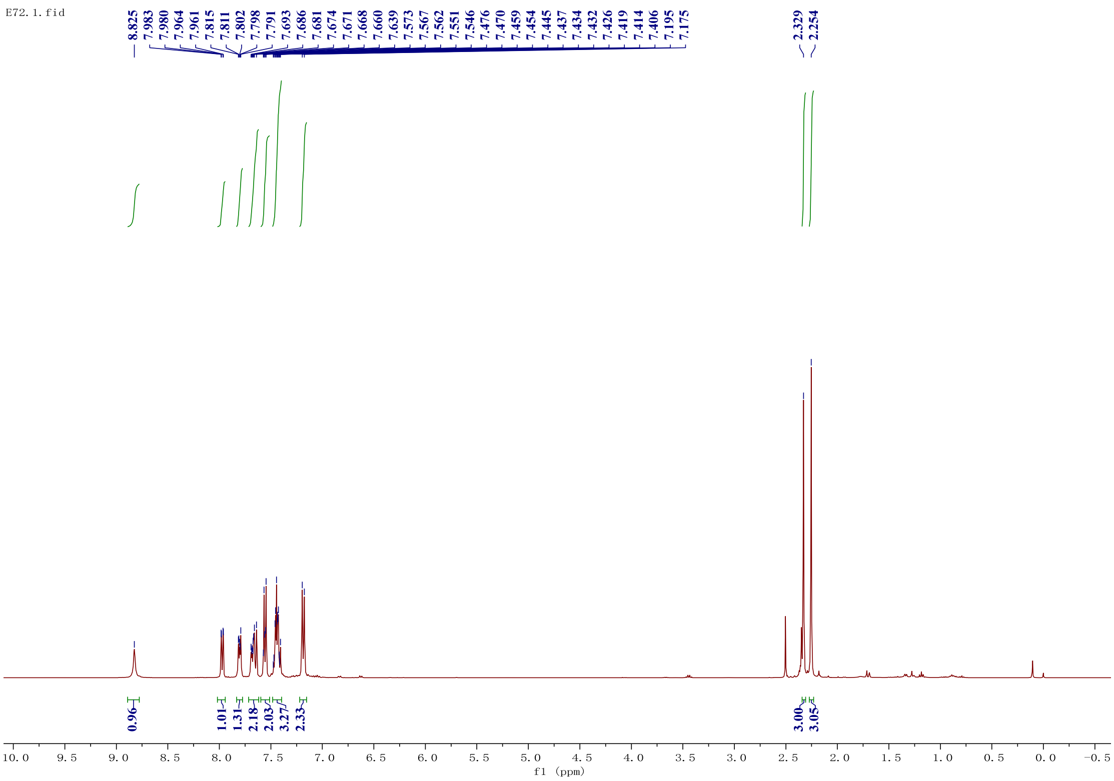


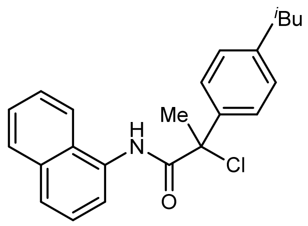
E71





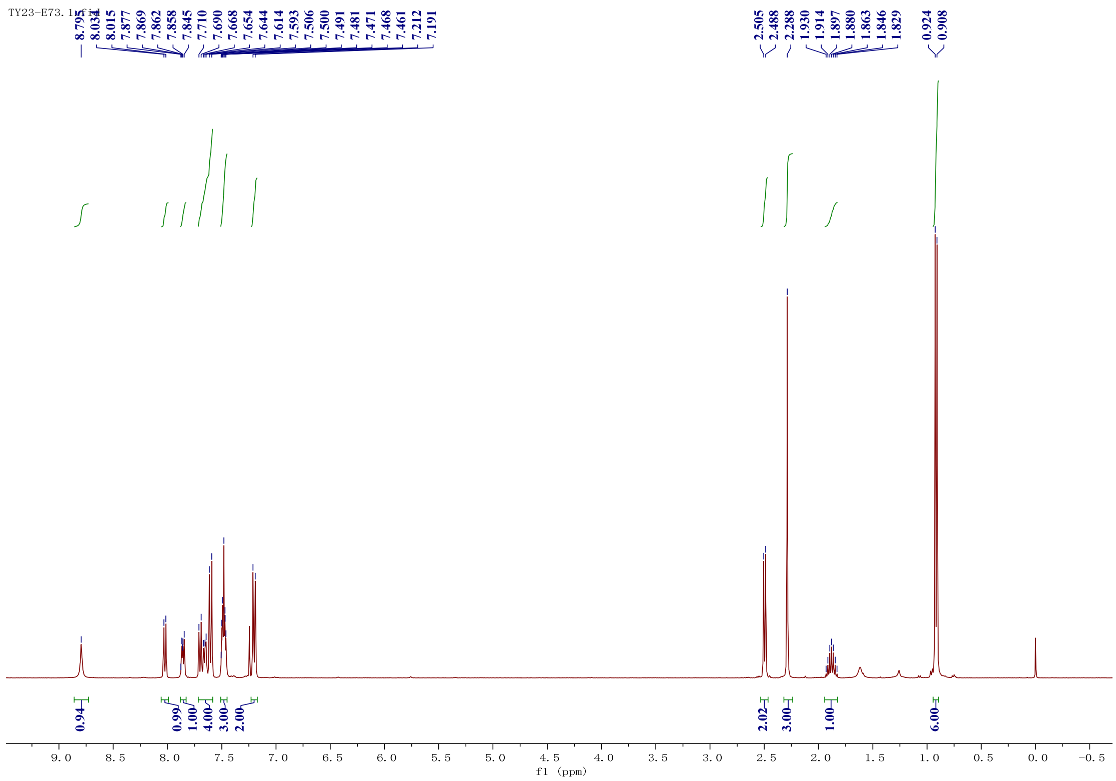
E72


E72.1.fid
8.825
7.983
7.980
7.964
7.961
7.815
7.811
7.802
7.798
7.791
7.693
7.686
7.681
7.674
7.671
7.668
7.660
7.639
7.573
7.567
7.562
7.551
7.546
7.476
7.470
7.459
7.454
7.445
7.437
7.434
7.432
7.426
7.419
7.414
7.406
7.195
7.175
2.329
2.254
0.96
1.01
1.31
2.18
2.03
3.27
2.33
3.00
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

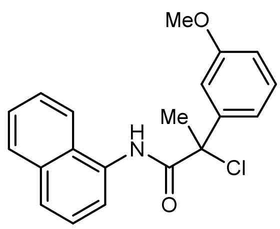


iBu
Me
H
N
O
Cl

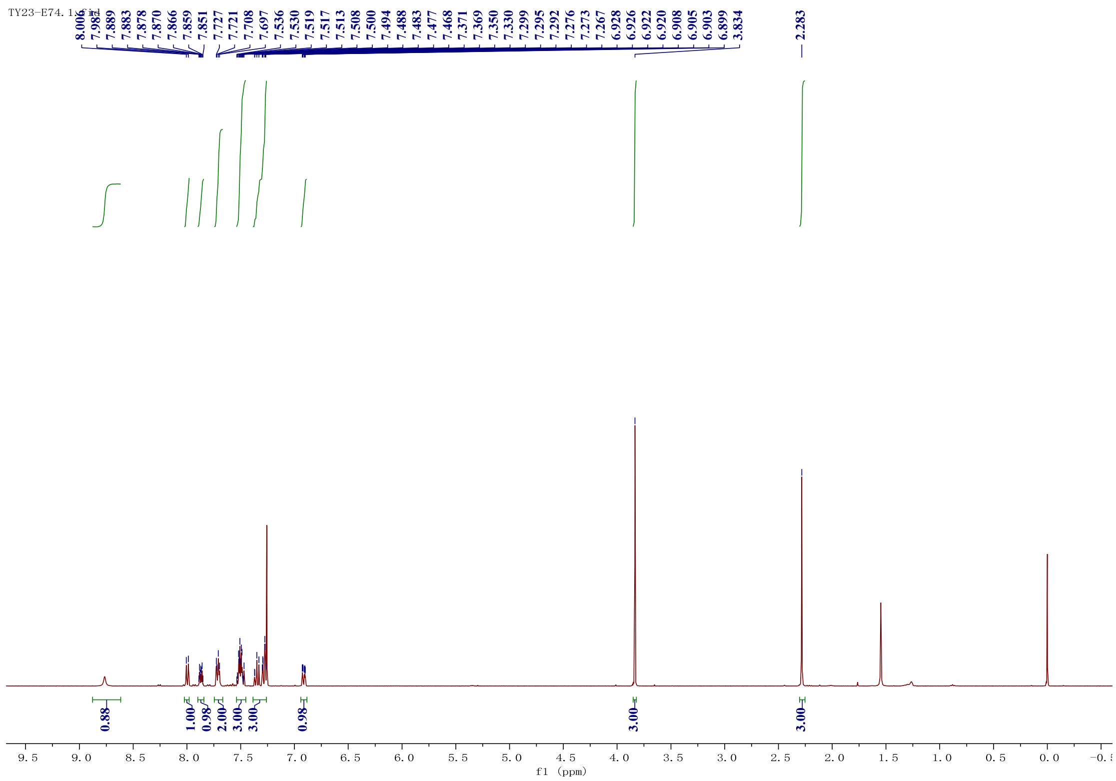
E73

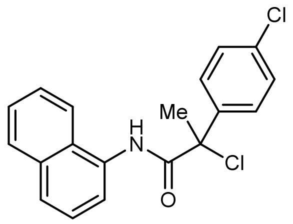


TY23-E73.1
8.795
8.034
8.015
7.877
7.869
7.862
7.858
7.845
7.710
7.690
7.668
7.654
7.644
7.614
7.593
7.506
7.500
7.491
7.481
7.471
7.468
7.461
7.212
7.191
2.505
2.488
2.288
1.930
1.914
1.897
1.880
1.863
1.846
1.829
0.924
0.908
0.94
0.99
1.00
4.00
3.00
2.00
2.02
3.00
1.00
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

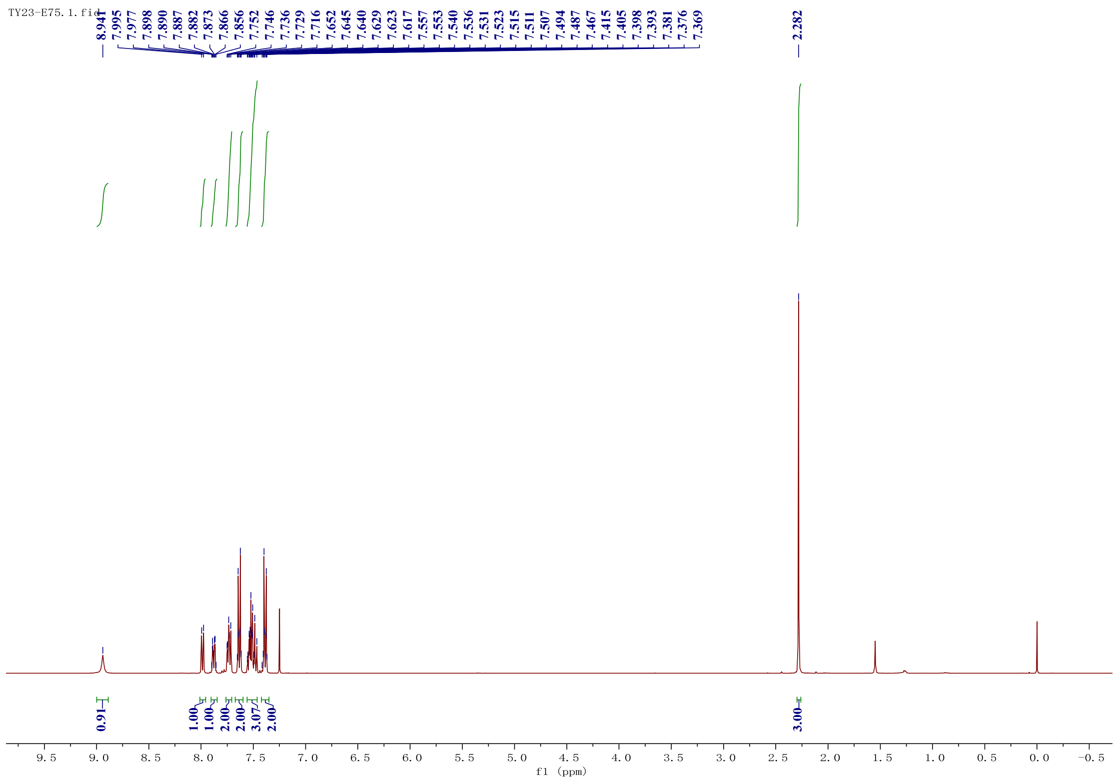


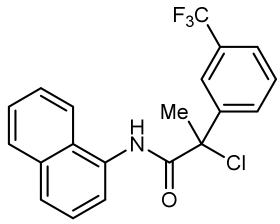
E74



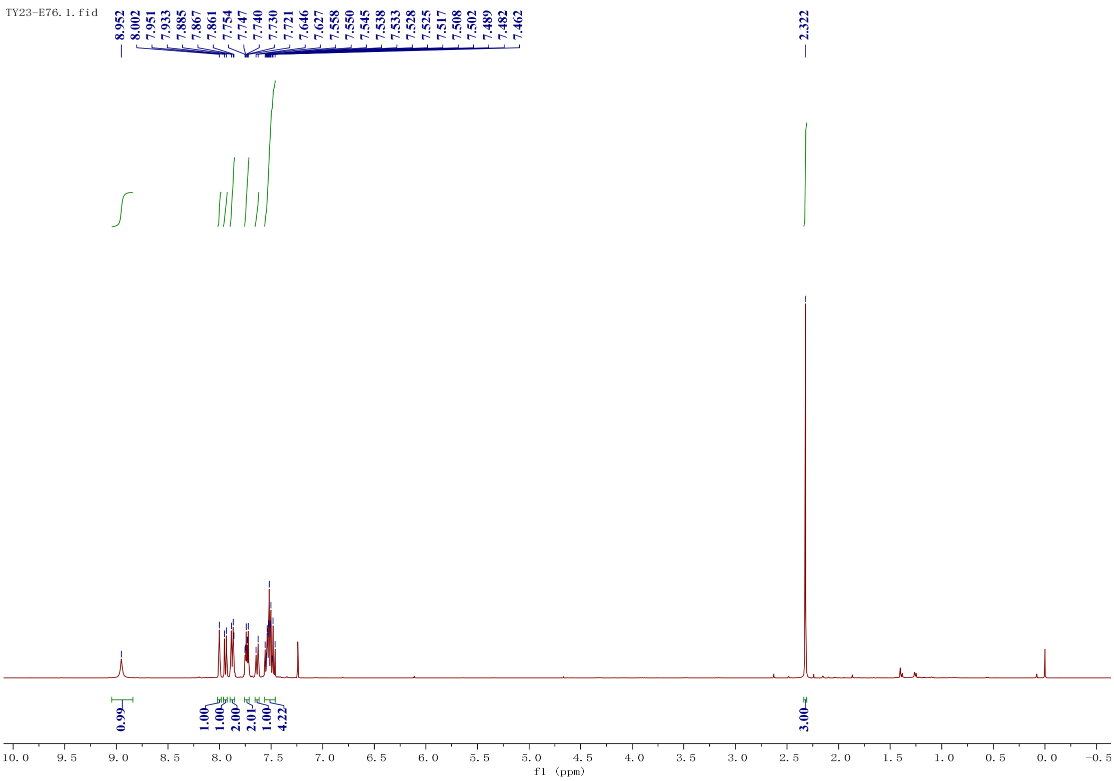

Cl
Me
H
N
Cl
O

E75

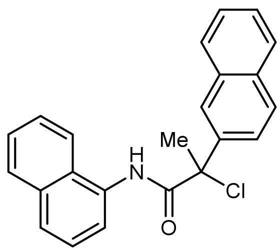

TY23-E75.1.fid
8.941
7.995
7.977
7.898
7.890
7.887
7.882
7.873
7.866
7.856
7.752
7.746
7.736
7.729
7.716
7.652
7.645
7.640
7.629
7.623
7.617
7.557
7.553
7.540
7.536
7.531
7.523
7.515
7.511
7.507
7.494
7.487
7.467
7.415
7.405
7.398
7.393
7.381
7.376
7.369
2.282
0.91
1.00
1.00
2.00
2.00
3.07
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



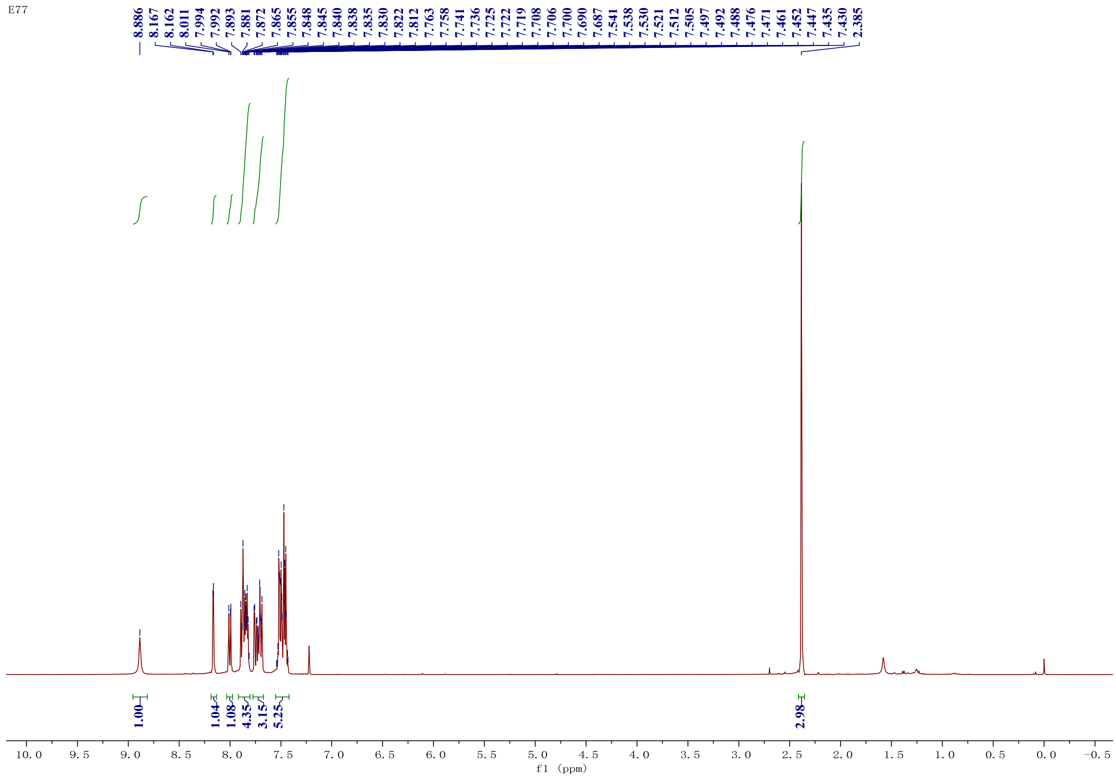
E76

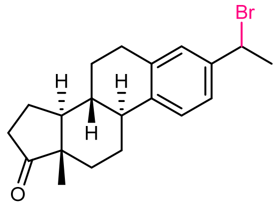


TY23-E76.1.fid
8.952
8.002
7.951
7.933
7.885
7.867
7.861
7.754
7.747
7.740
7.730
7.721
7.646
7.627
7.558
7.550
7.545
7.538
7.533
7.528
7.525
7.517
7.508
7.502
7.489
7.482
7.462
2.322
0.99
1.00
1.00
2.00
2.01
1.00
4.22
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

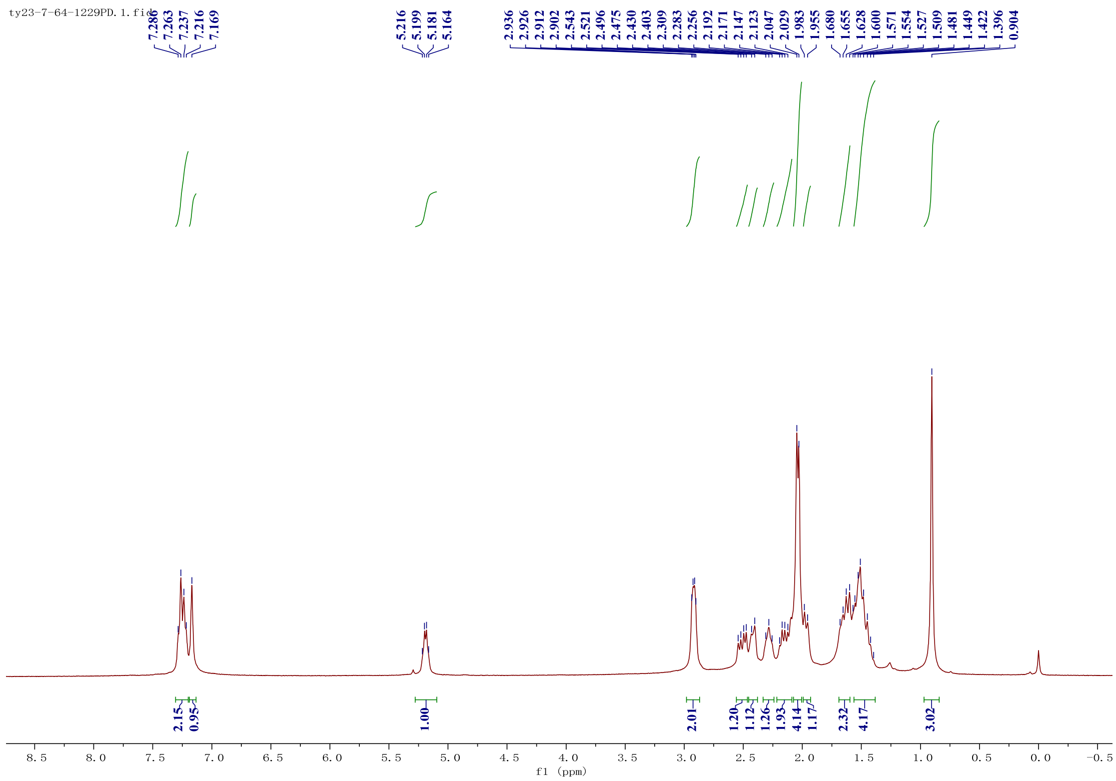

Me
H
N
Cl
O

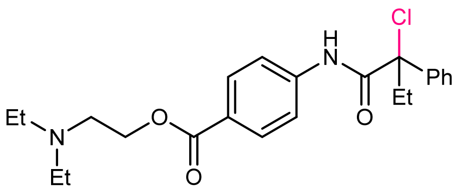
E77


E77
8.886
8.167
8.162
8.011
7.994
7.992
7.893
7.881
7.872
7.865
7.855
7.848
7.845
7.840
7.838
7.835
7.830
7.822
7.812
7.763
7.758
7.741
7.736
7.725
7.722
7.719
7.708
7.706
7.700
7.690
7.687
7.541
7.538
7.530
7.521
7.512
7.505
7.497
7.492
7.488
7.476
7.471
7.461
7.452
7.447
7.435
7.430
2.385
1.00
1.04
1.08
4.35
3.15
5.25
2.98
f1 (ppm)

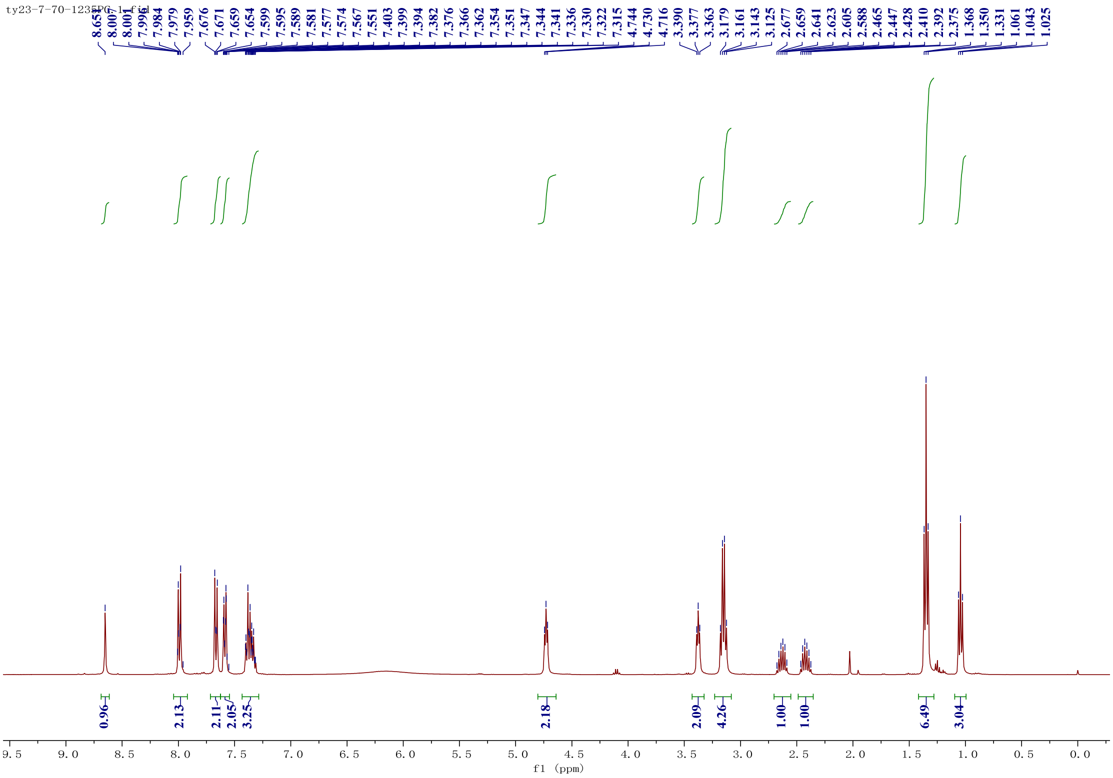


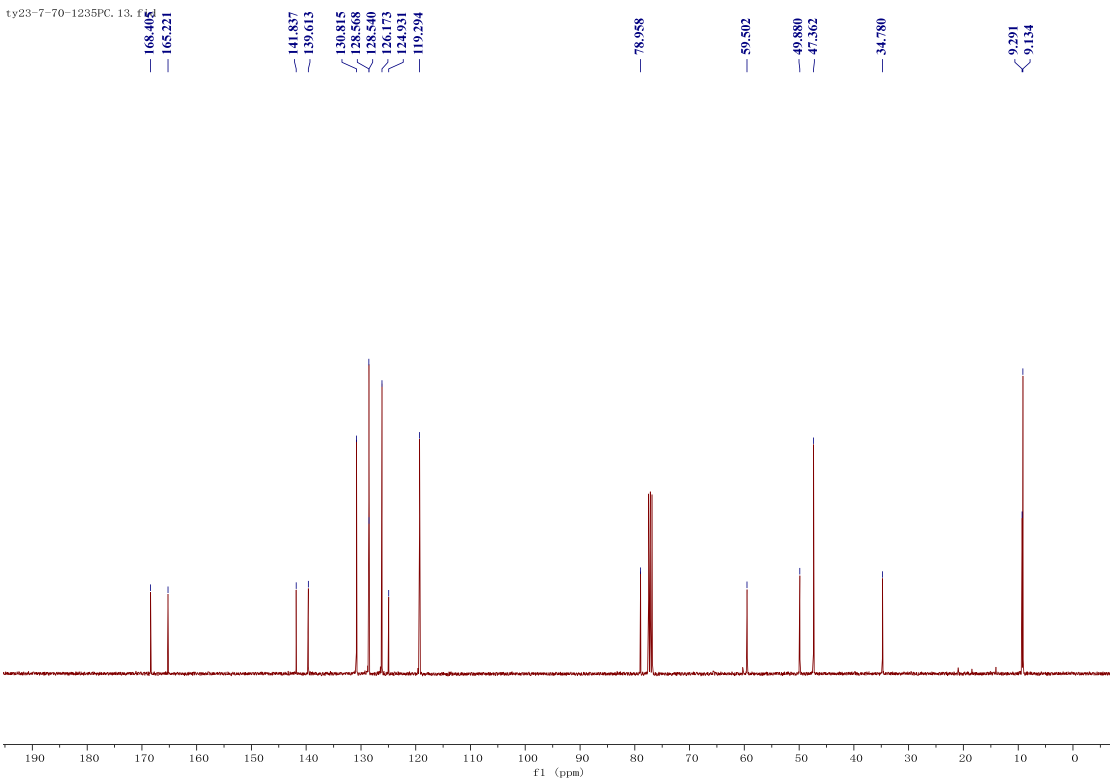
E79

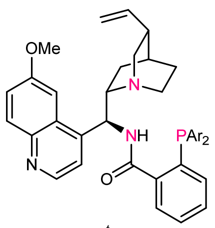




E80

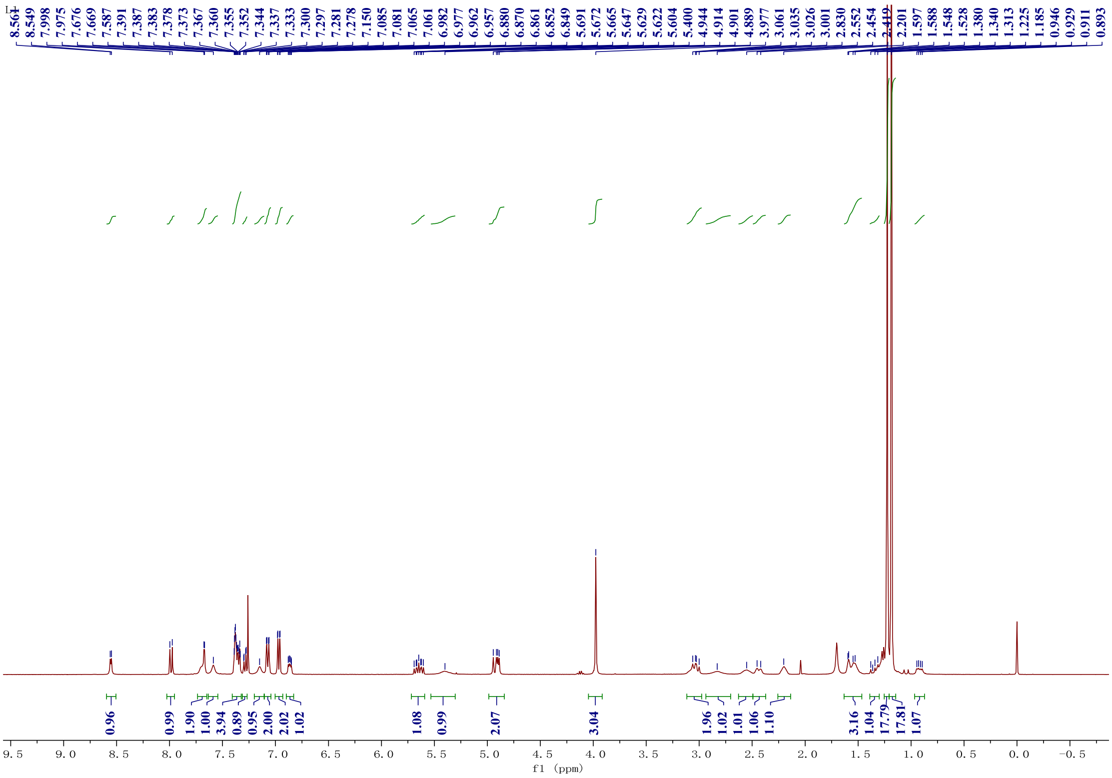




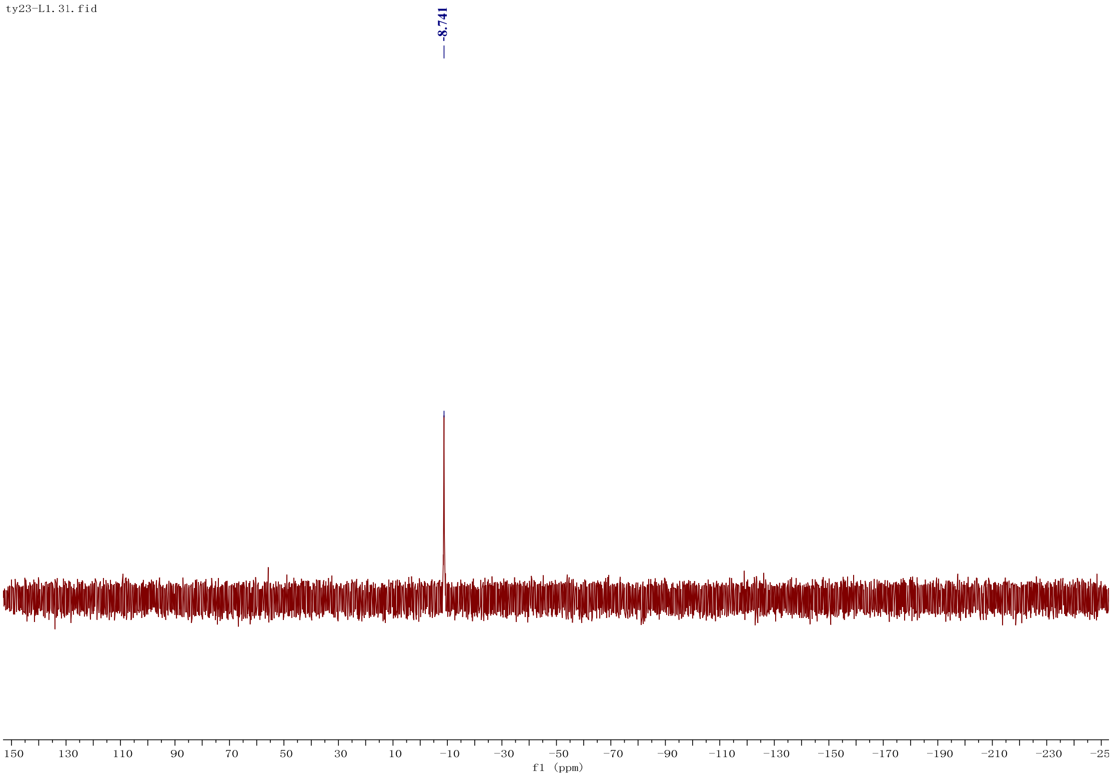


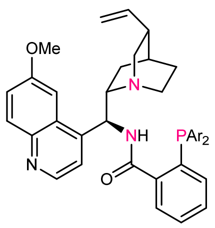
L*1

Ar = 3,5-(^{t}Bu)$_2$C$_6$H$_3$



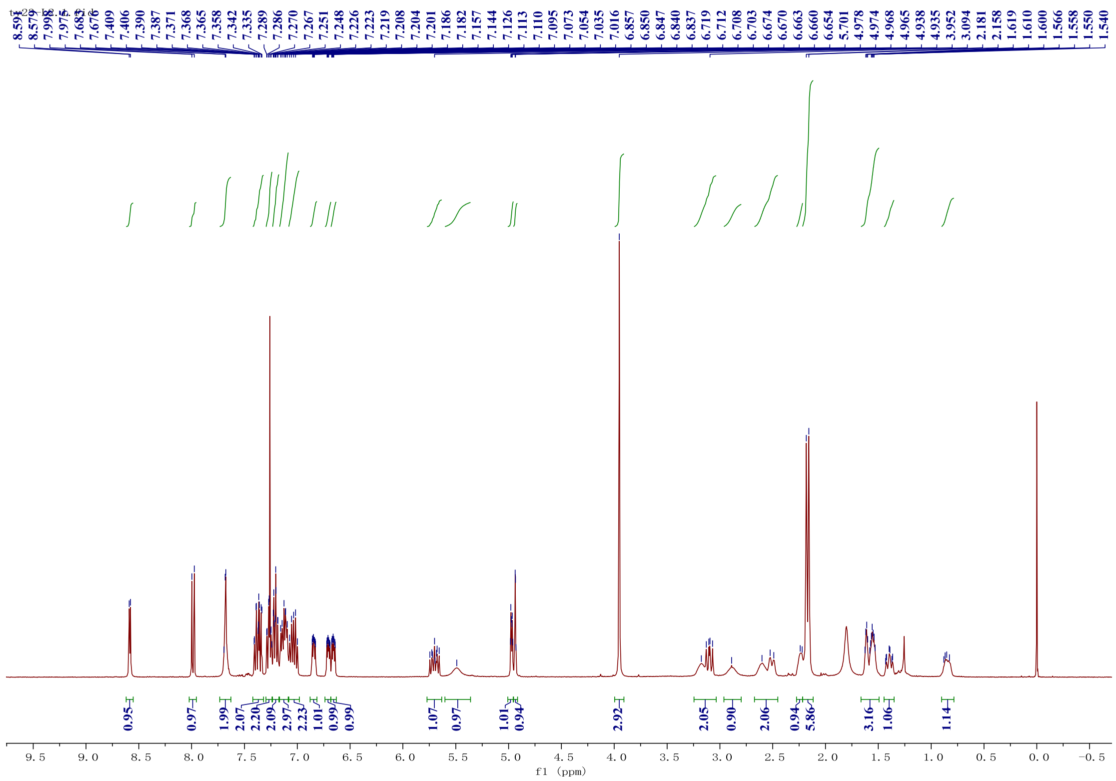
ty23-L1.31.fid

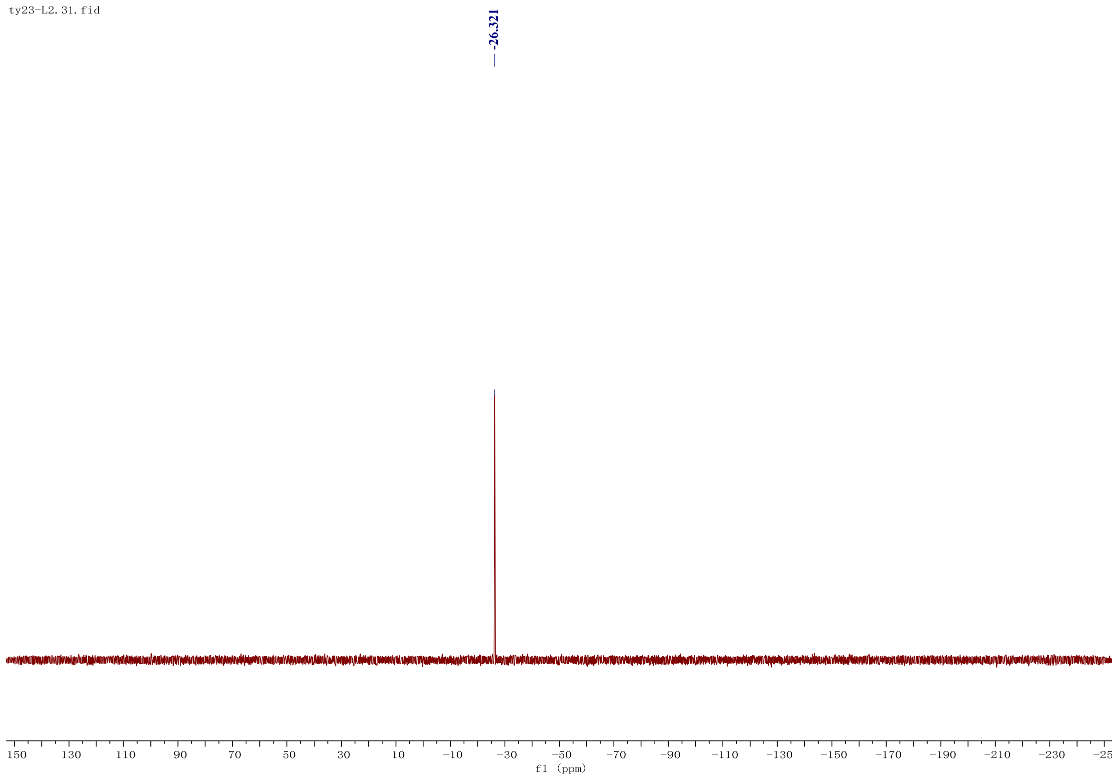


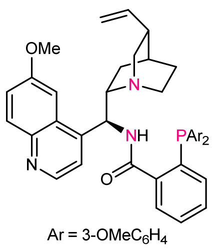


L*2

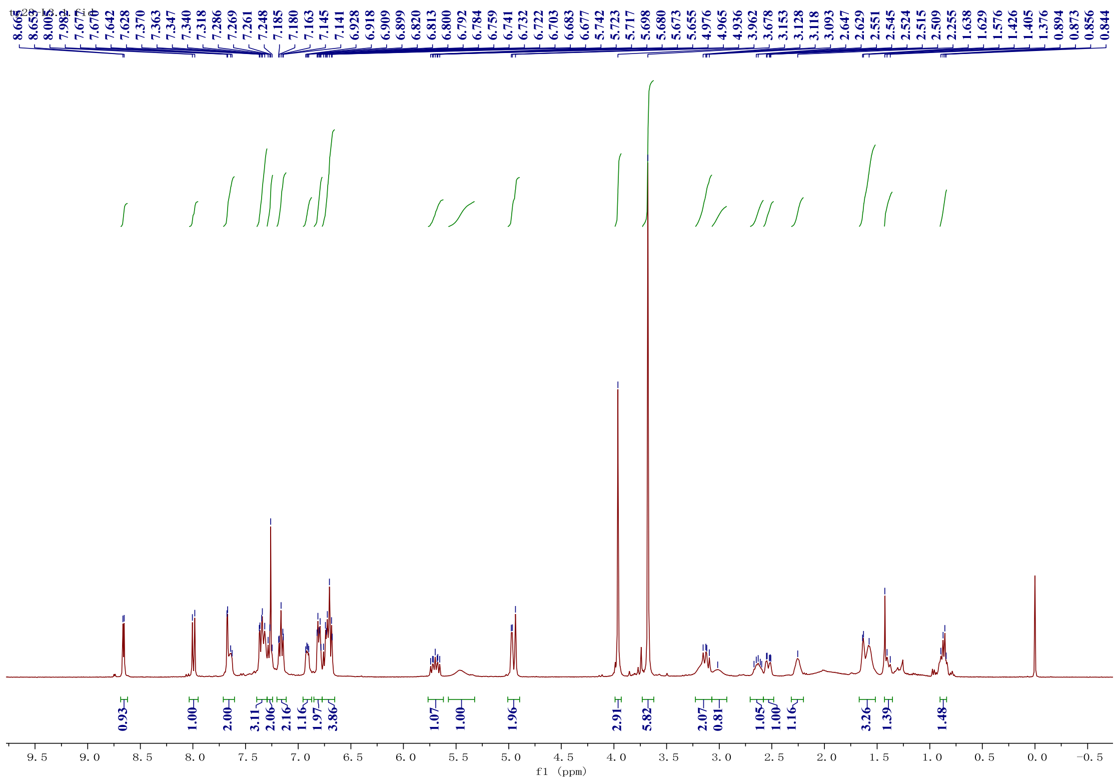
Ar = 2-MeC$_6$H$_4$

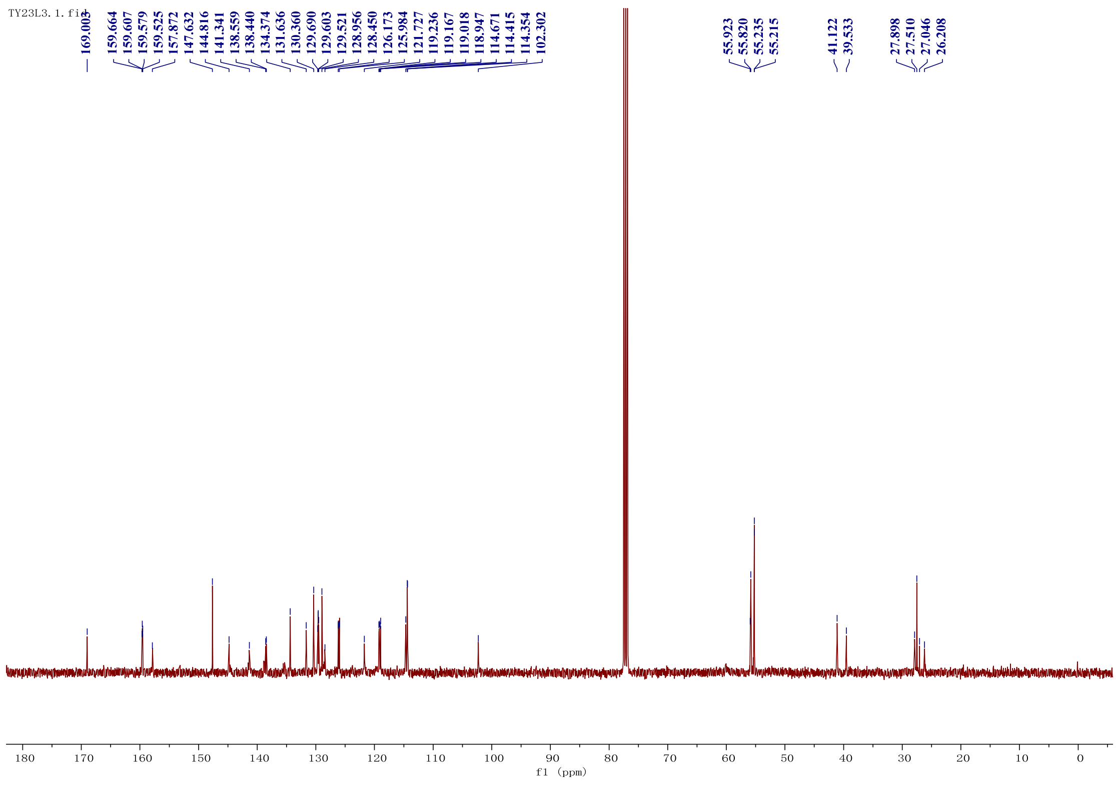


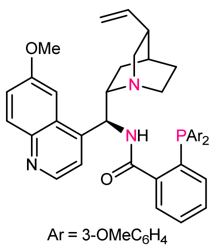



OMe
N
NH
PAr2
O
N
Ar = 3-OMeC6H4

L*3

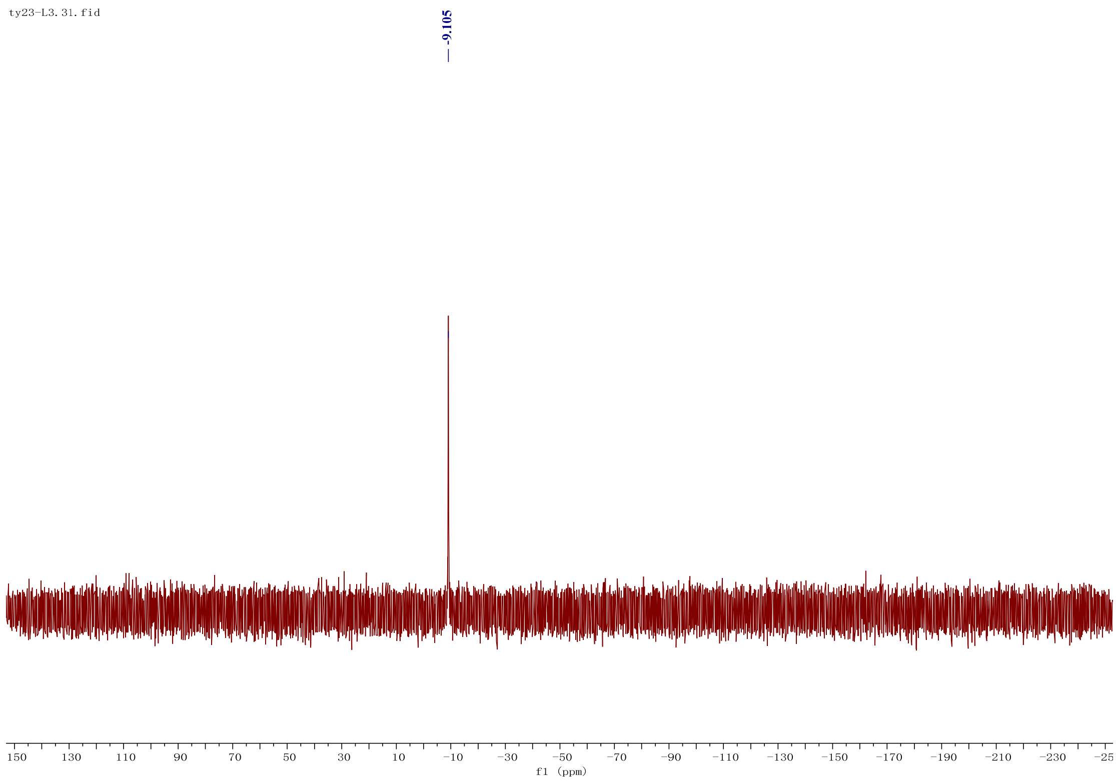

8.665
8.653
8.005
7.982
7.672
7.670
7.642
7.628
7.370
7.363
7.347
7.340
7.318
7.286
7.269
7.261
7.248
7.185
7.180
7.163
7.145
7.141
6.928
6.918
6.909
6.899
6.820
6.813
6.800
6.792
6.784
6.759
6.741
6.732
6.722
6.703
6.683
6.677
5.742
5.723
5.717
5.698
5.680
5.673
5.655
4.976
4.965
4.936
3.962
3.678
3.153
3.128
3.118
3.093
2.647
2.629
2.551
2.545
2.524
2.515
2.509
2.255
1.638
1.629
1.576
1.426
1.405
1.376
0.894
0.873
0.856
0.844
0.93
1.00
2.00
3.11
2.06
2.16
1.16
1.97
3.86
1.07
1.00
1.96
2.91
5.82
2.07
0.81
1.05
1.00
1.16
3.26
1.39
1.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


TY23L3.1.fid
169.003
159.664
159.607
159.579
159.525
157.872
147.632
144.816
141.341
138.559
138.440
134.374
131.636
130.360
129.690
129.603
129.521
128.956
128.450
126.173
125.984
121.727
119.236
119.167
119.018
118.947
114.671
114.415
114.354
102.302
55.923
55.820
55.235
55.215
41.122
39.533
27.898
27.510
27.046
26.208
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

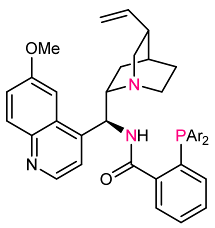


OMe
N
N
NH
PAr2
O
Ar = 3-OMeC6H4

L*3

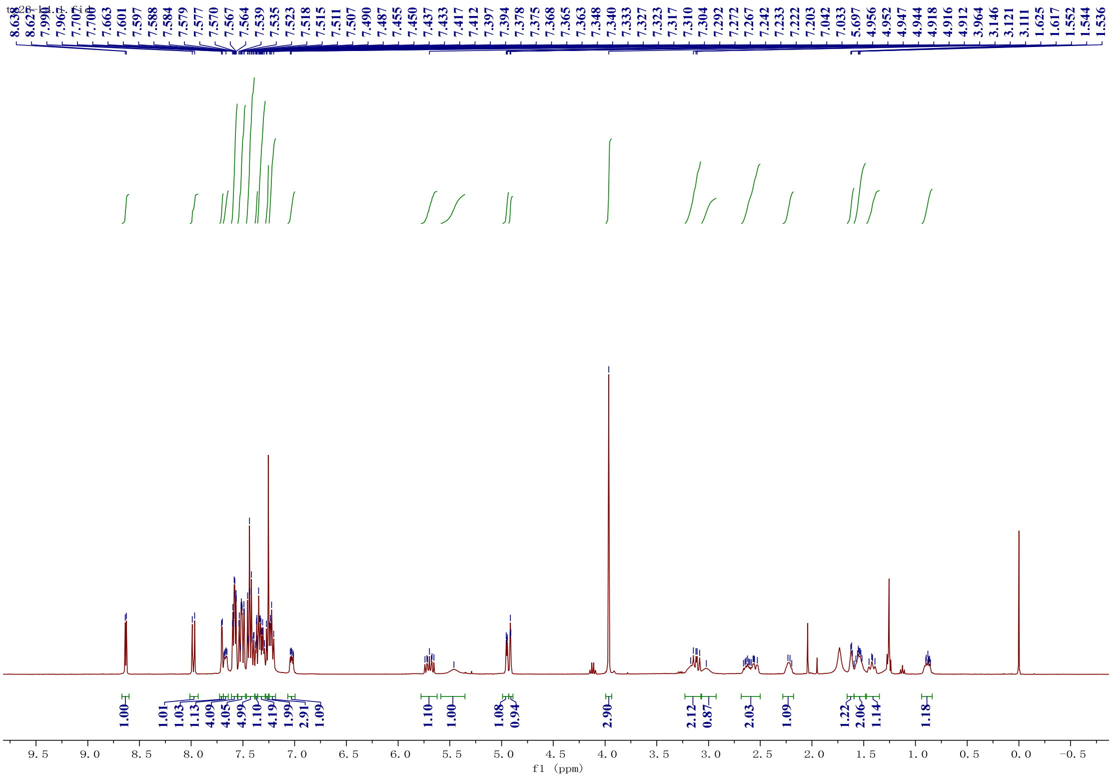


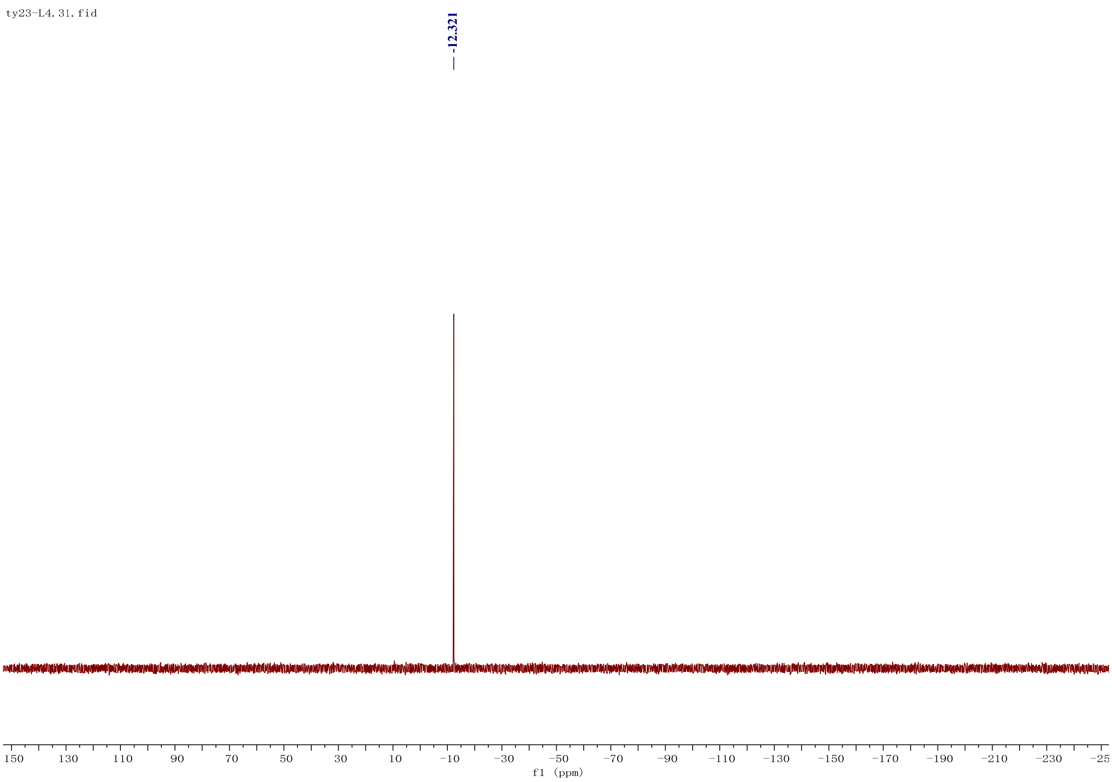
ty23-L3.31.fid
-9.105
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

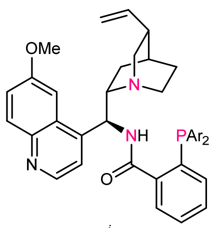


Ar = 4-PhC$_6$H$_4$

L*4

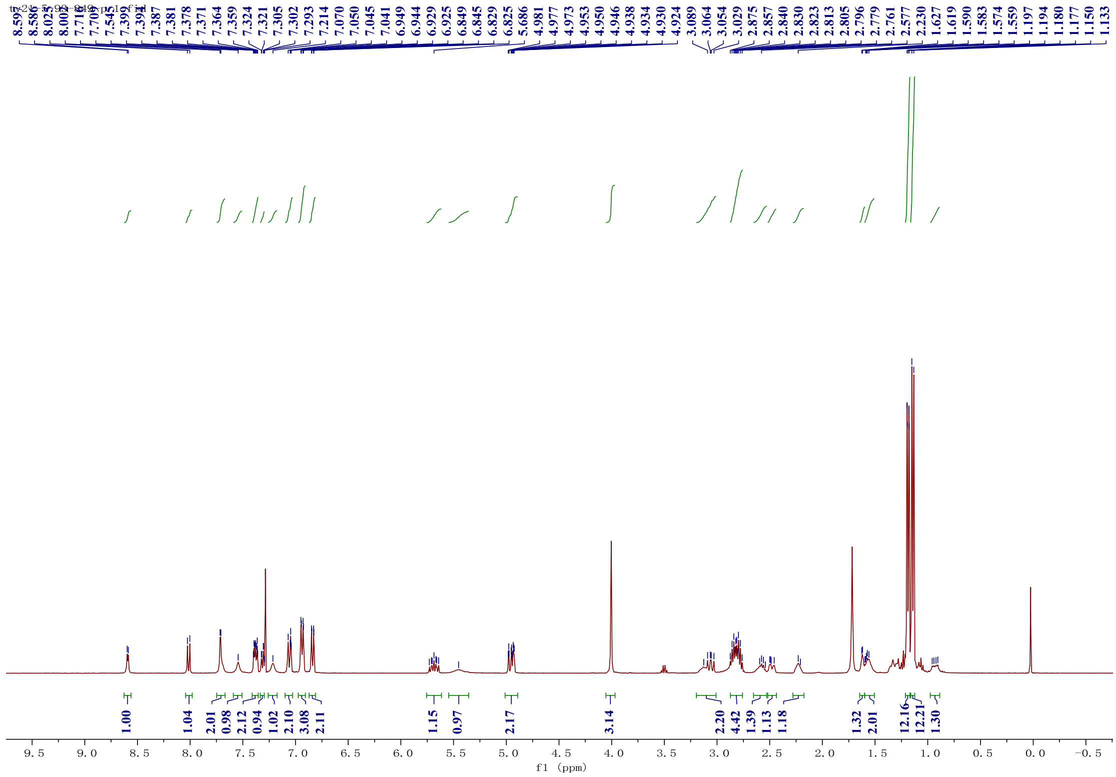




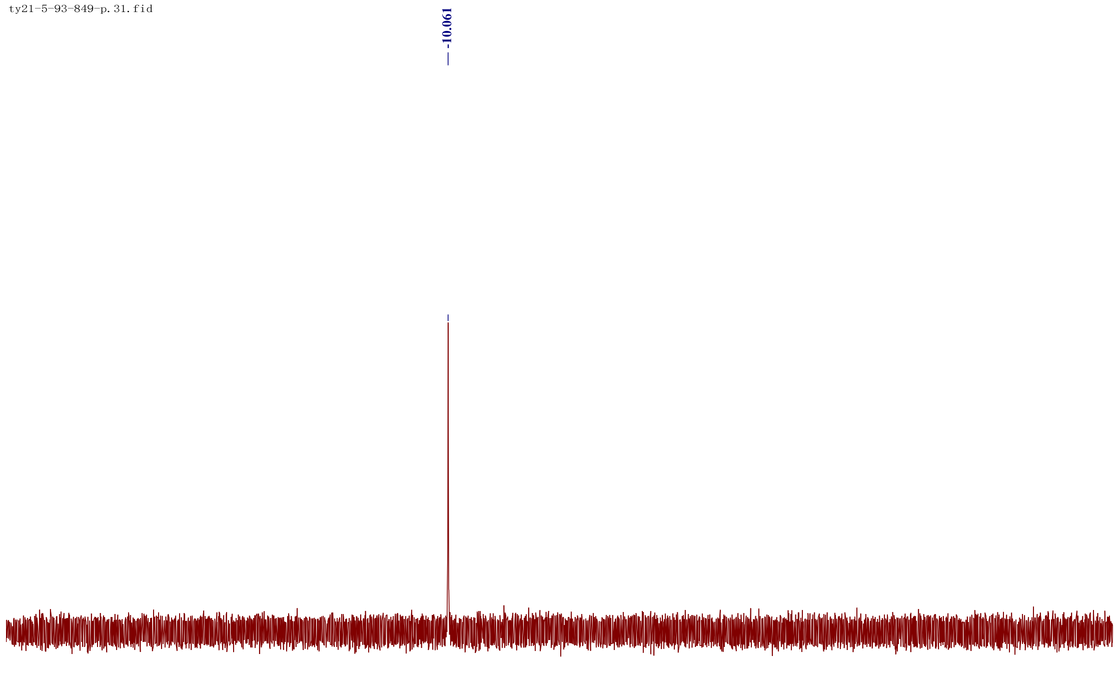


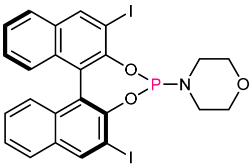
L*5

Ar = 3,5-(^{i}Pr)$_2$C$_6$H$_3$

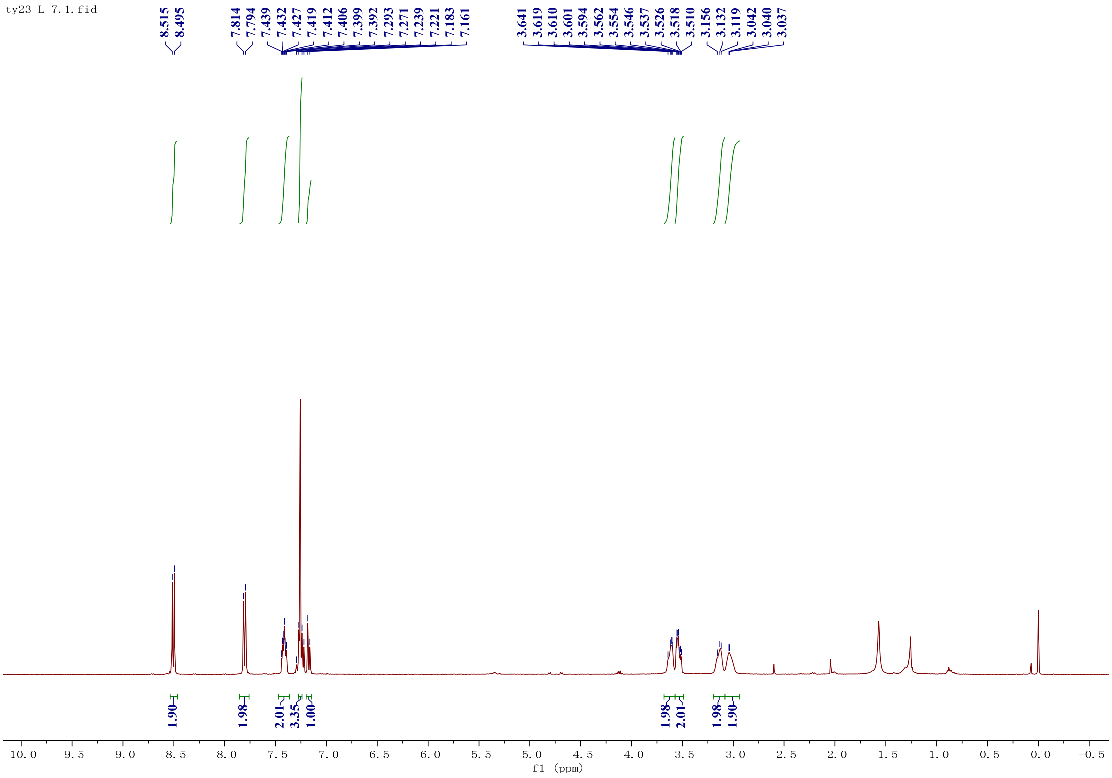


ty21-5-93-849-p.31.fid

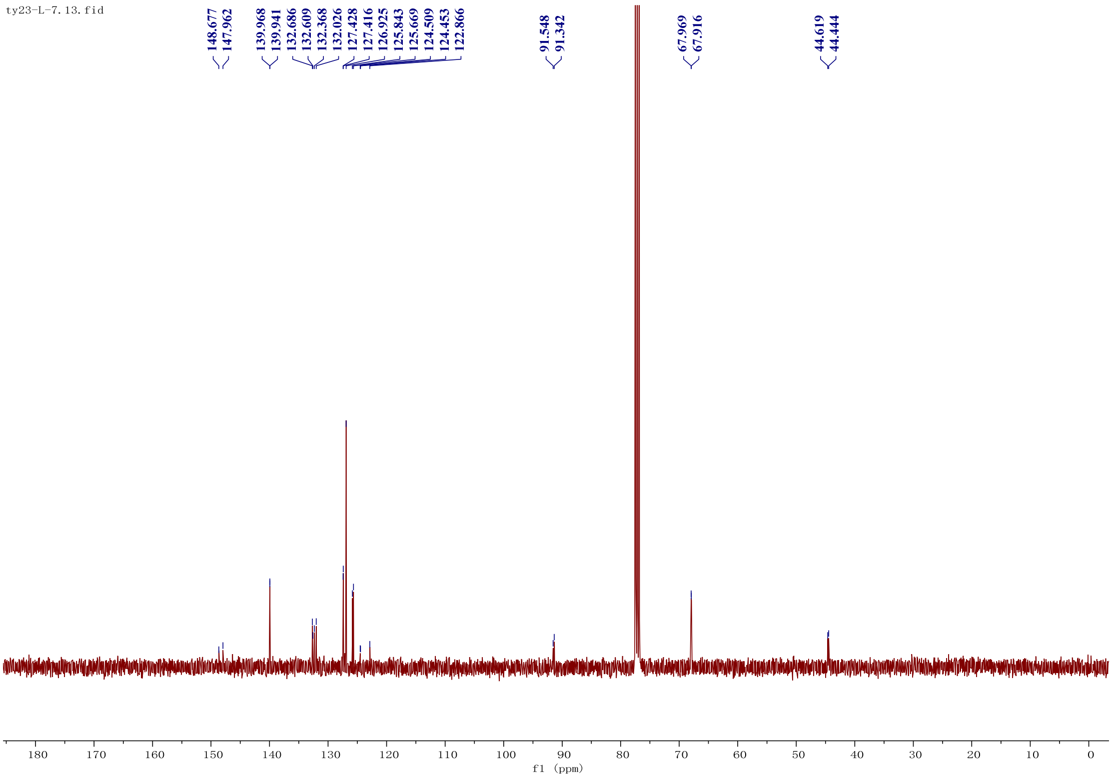




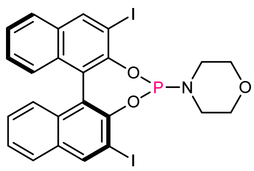
L*7



ty23-L-7.1.fid
8.515
8.495
7.814
7.794
7.439
7.432
7.427
7.419
7.412
7.406
7.399
7.392
7.293
7.271
7.239
7.221
7.183
7.161
3.641
3.619
3.610
3.601
3.594
3.562
3.554
3.546
3.537
3.526
3.518
3.510
3.156
3.132
3.119
3.042
3.040
3.037
1.90
1.98
2.01
3.35
1.00
1.98
2.01
1.98
1.90
f1 (ppm)

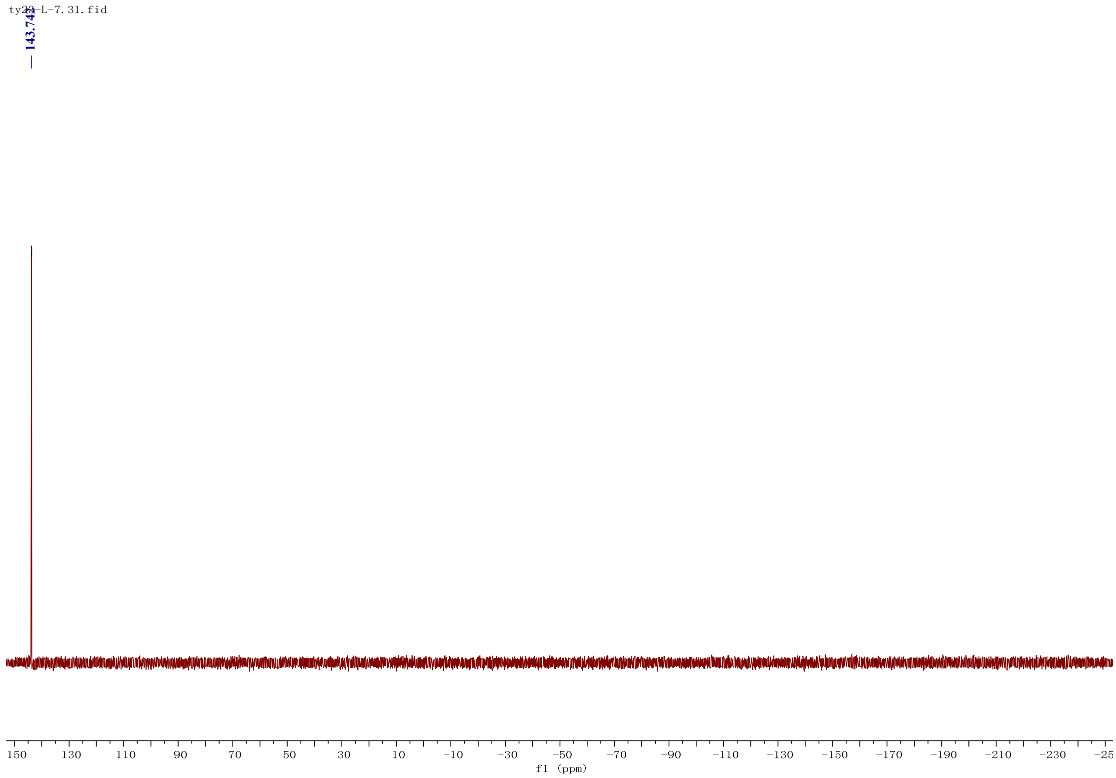


ty23-L-7.13.fid
148.677
147.962
139.968
139.941
132.686
132.609
132.368
132.026
127.428
127.416
126.925
125.843
125.669
124.509
124.453
122.866
91.548
91.342
67.969
67.916
44.619
44.444
f1 (ppm)

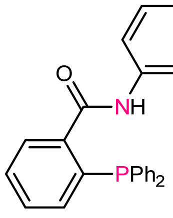


O
P
N
O
I

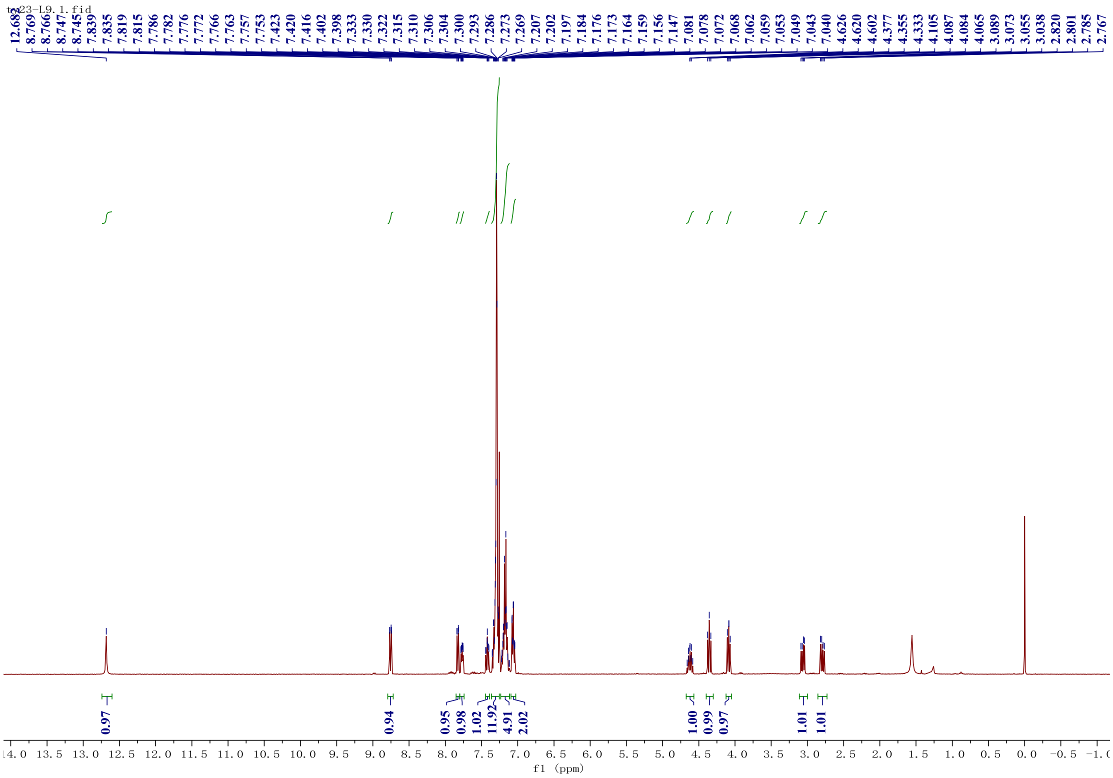
L*7

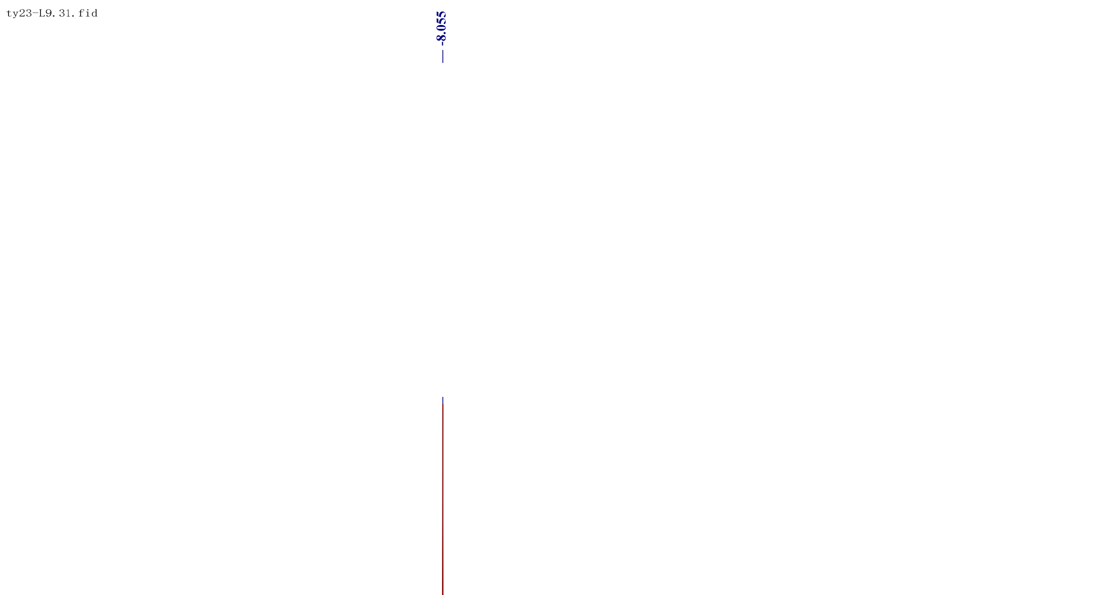


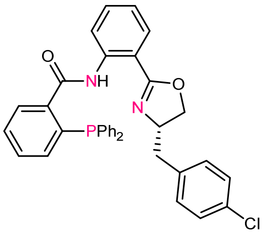
ty23-L-7.31.fid
143.742
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-25
f1 (ppm)


O
NH
N
O
PPh2
Bn

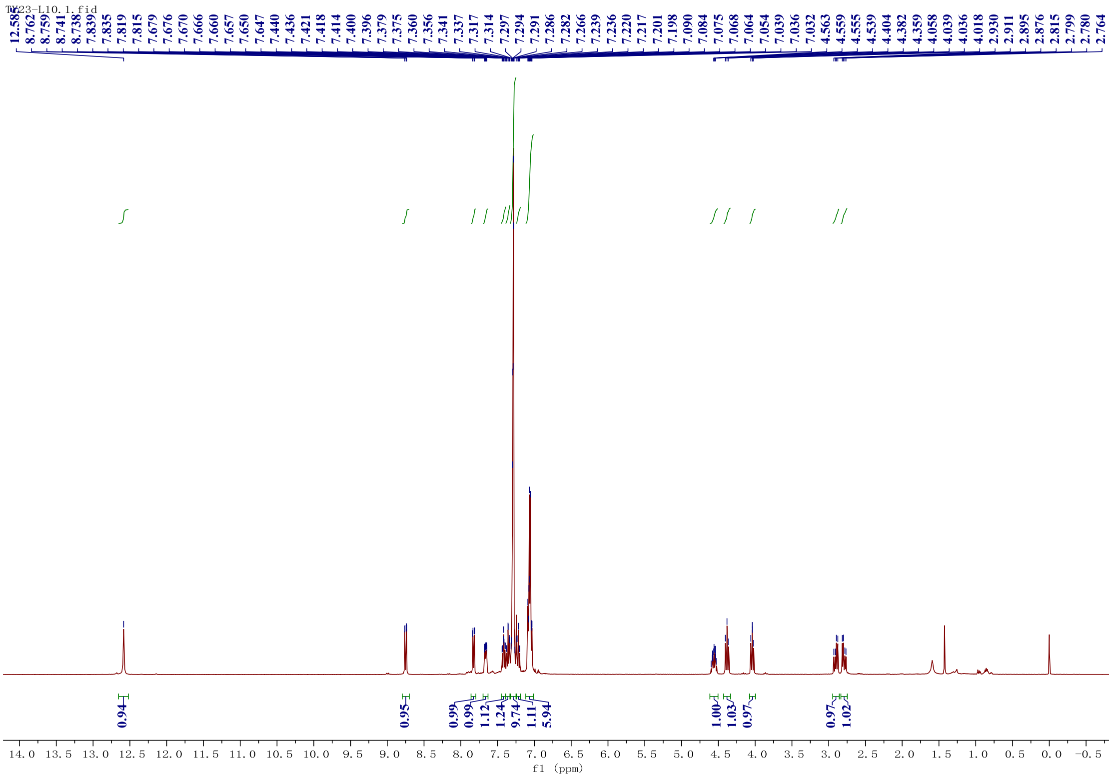
L*9

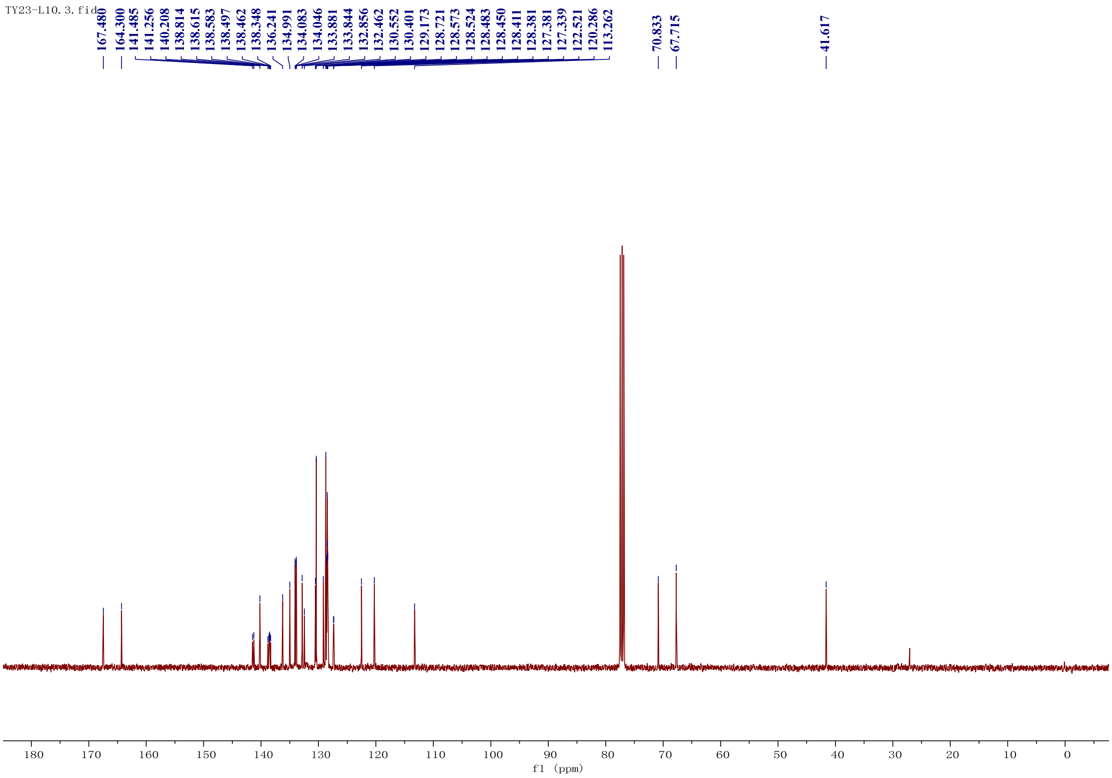

ty23-L9.1.fid
12.689
8.769
8.766
8.747
8.745
7.839
7.835
7.819
7.815
7.786
7.782
7.776
7.772
7.766
7.763
7.757
7.753
7.423
7.420
7.416
7.402
7.398
7.333
7.330
7.322
7.315
7.310
7.306
7.304
7.300
7.293
7.286
7.273
7.269
7.207
7.202
7.197
7.184
7.176
7.173
7.164
7.159
7.156
7.147
7.081
7.078
7.072
7.068
7.062
7.059
7.053
7.049
7.043
7.040
4.626
4.620
4.602
4.377
4.355
4.333
4.105
4.087
4.084
4.065
3.089
3.073
3.055
3.038
2.820
2.801
2.785
2.767
0.97
0.94
0.95
0.98
1.02
11.92
4.91
2.02
1.00
0.99
0.97
1.01
1.01
f1 (ppm)

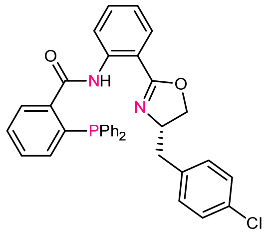

ty23-L9.31.fid
-8.055
f1 (ppm)


O
NH
N
O
PPh2
Cl

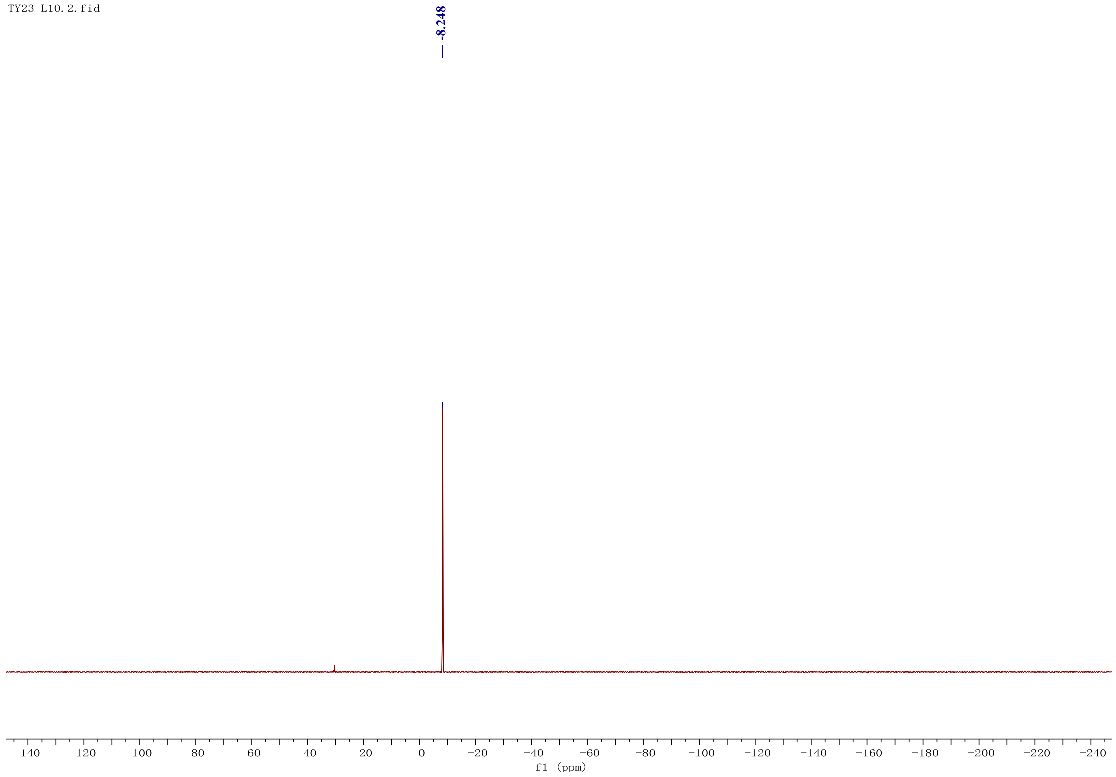
L*10

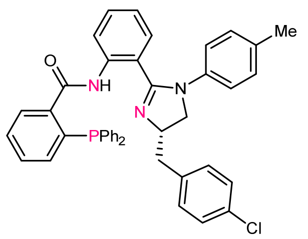

TY23-L10.1.fid
12.583 8.762 8.759 8.741 8.738 7.839 7.835 7.819 7.815 7.679 7.676 7.670 7.666 7.660 7.657 7.650 7.647 7.440 7.436 7.421 7.418 7.414 7.400 7.396 7.379 7.375 7.360 7.356 7.341 7.337 7.317 7.314 7.297 7.294 7.291 7.286 7.282 7.266 7.239 7.236 7.220 7.217 7.201 7.198 7.090 7.084 7.075 7.068 7.064 7.054 7.039 7.036 7.032 4.563 4.559 4.555 4.539 4.404 4.382 4.359 4.058 4.039 4.036 4.018 2.930 2.911 2.895 2.876 2.815 2.799 2.780 2.764
0.94 0.95 0.99 0.99 1.12 1.24 9.74 1.11 5.94 1.00 1.03 0.97 0.97 1.02
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


TY23-L10.3.fid
167.480 164.300 141.485 141.256 140.208 138.814 138.615 138.583 138.497 138.462 138.348 136.241 134.991 134.083 134.046 133.881 133.844 132.856 132.462 130.552 130.401 129.173 128.721 128.573 128.524 128.483 128.450 128.411 128.381 127.381 127.339 122.521 120.286 113.262 70.833 67.715 41.617
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

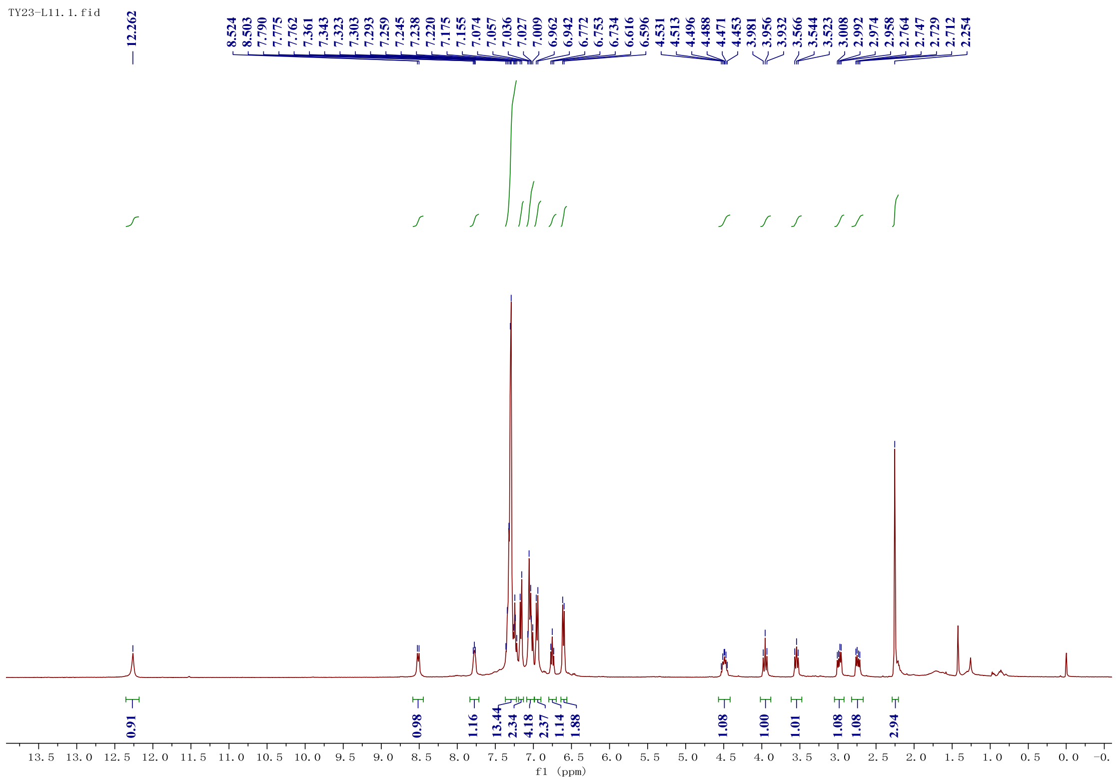

O
NH
N
O
PPh2
Cl

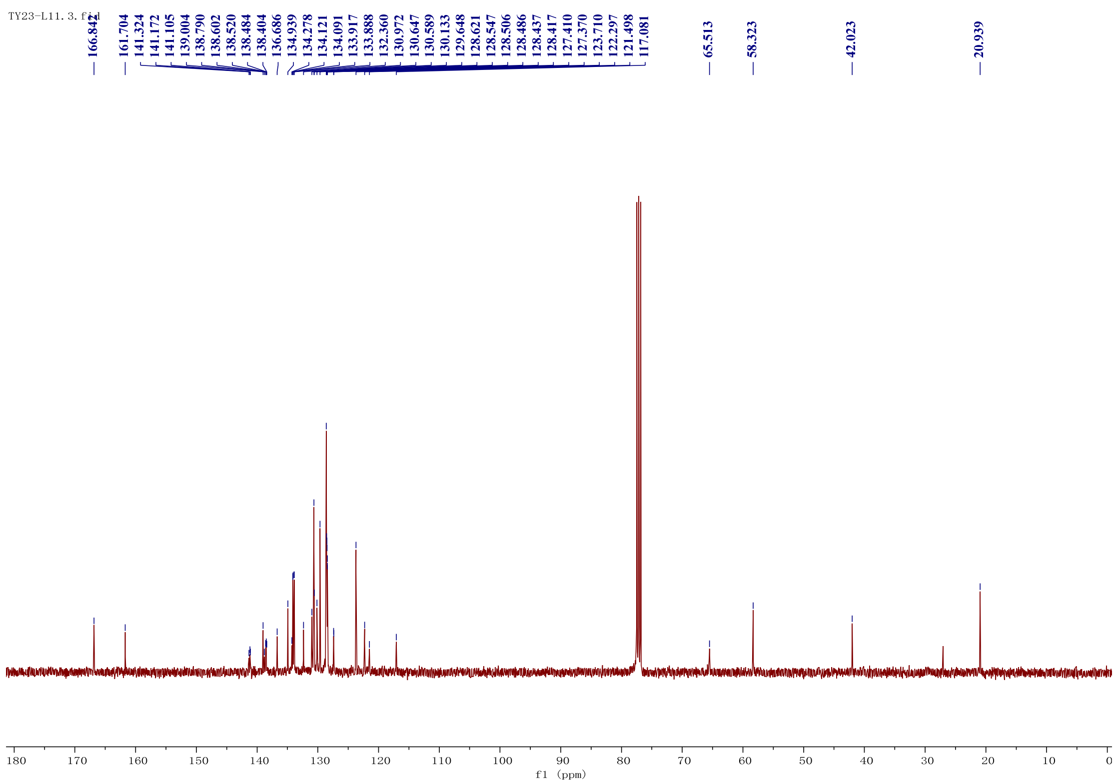
L*10

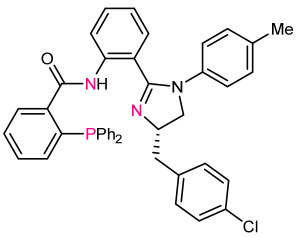

TY23-L10.2.fid
-8.248
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)



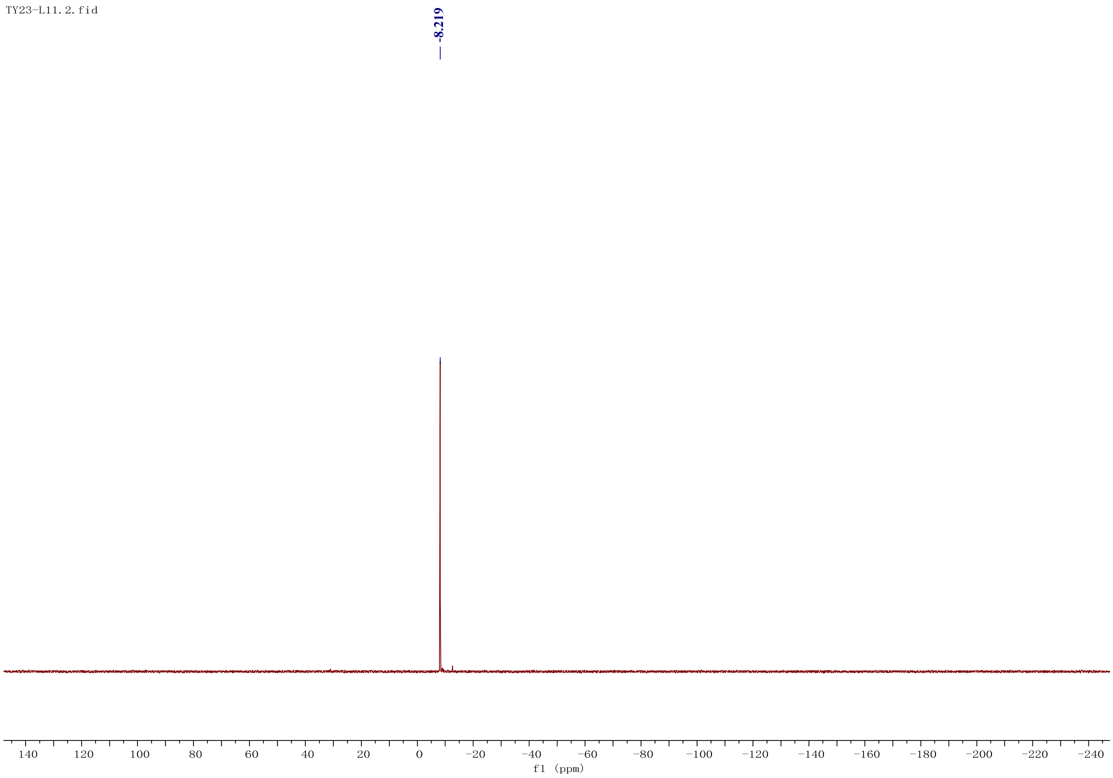
L*11

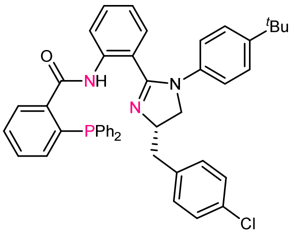




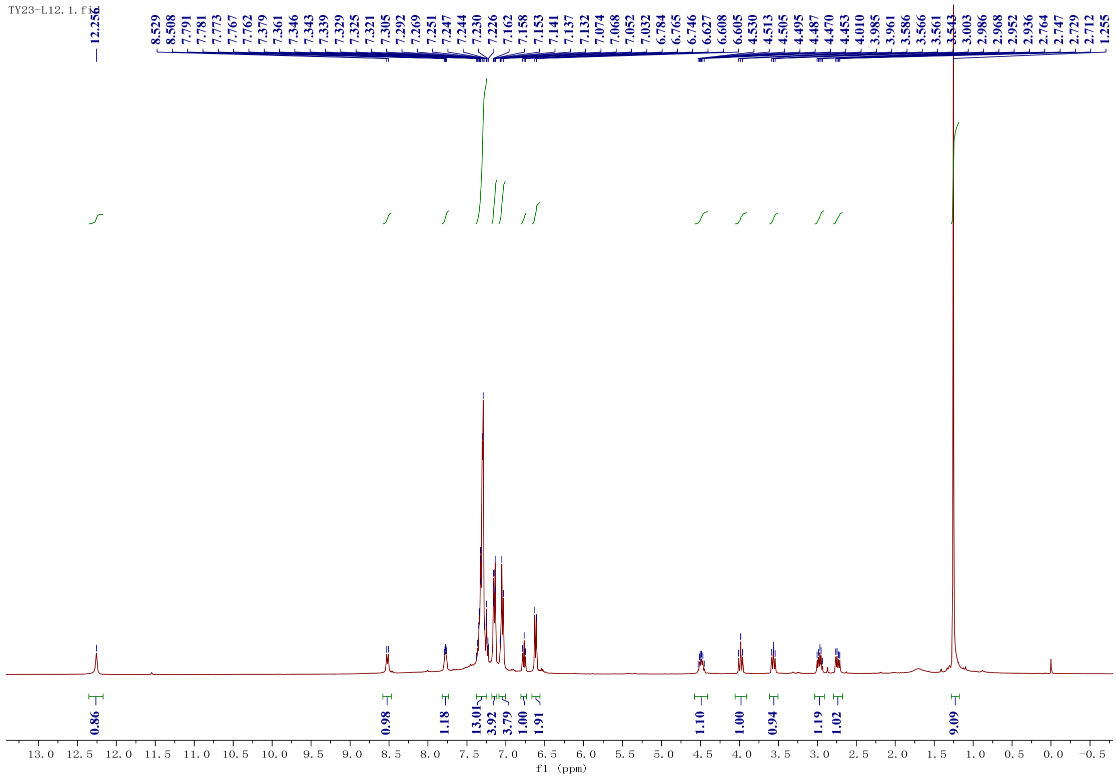

O
NH
N
N
Me
PPh2
Cl

L*11


TY23-L11.2.fid
-8.219
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)


O
NH
N
N
tBu
PPh2
Cl

L*12


TY23-L12.1.fid
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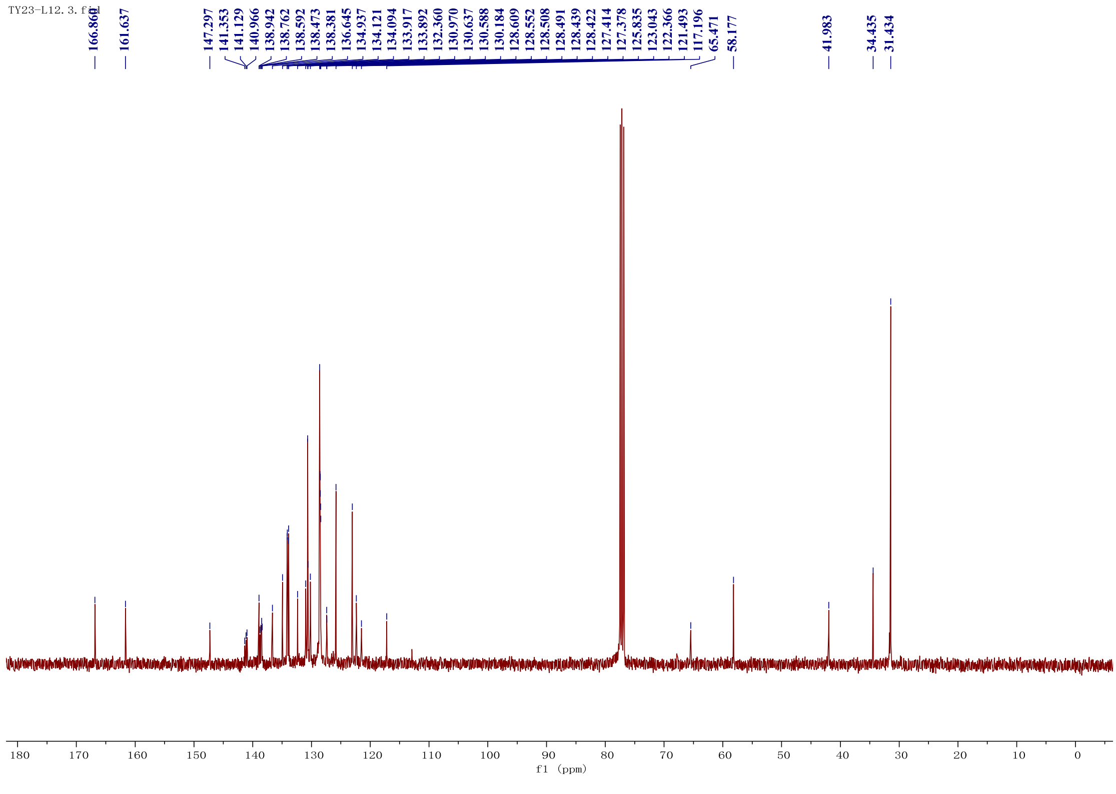
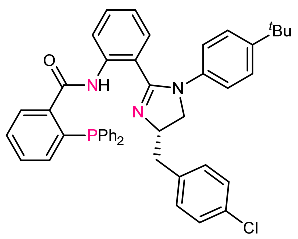
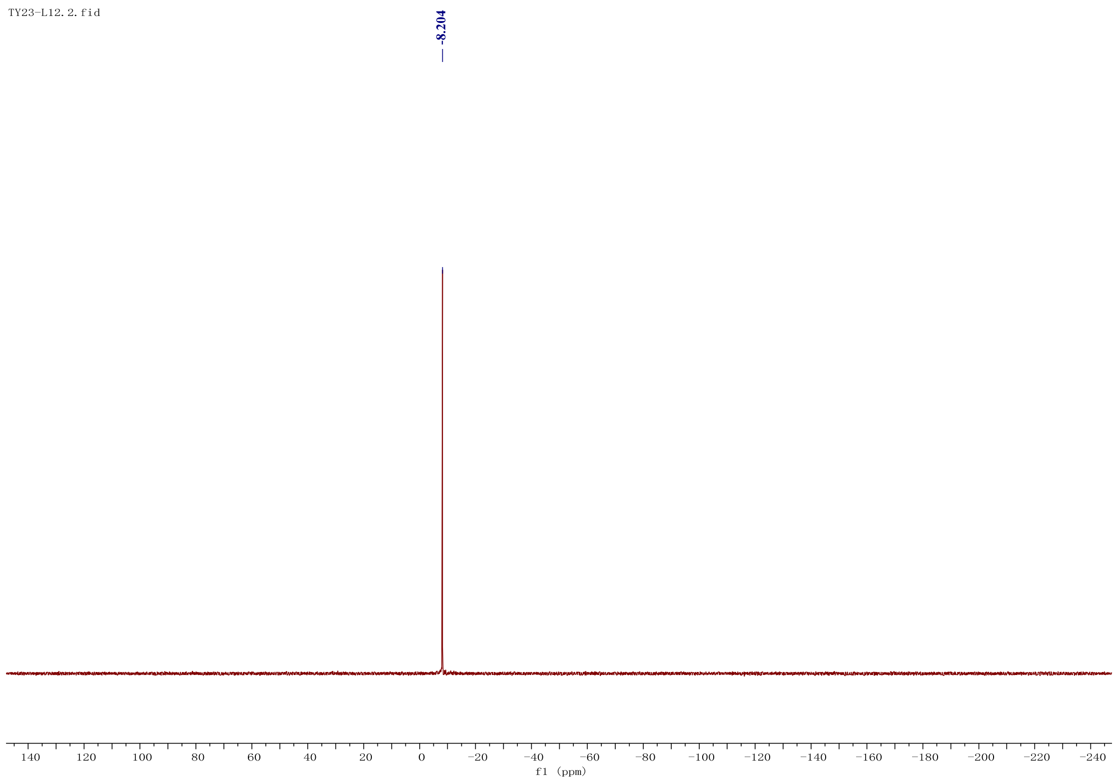
8.529
8.508
7.791
7.781
7.773
7.767
7.762
7.379
7.361
7.346
7.343
7.339
7.329
7.325
7.321
7.305
7.292
7.269
7.251
7.247
7.244
7.230
7.226
7.162
7.158
7.153
7.141
7.137
7.132
7.074
7.068
7.052
7.032
6.784
6.765
6.746
6.627
6.608
6.605
4.530
4.513
4.505
4.495
4.487
4.470
4.453
4.010
3.985
3.961
3.586
3.566
3.561
3.543
3.003
2.986
2.968
2.952
2.936
2.764
2.747
2.729
2.712
1.255
0.86
0.98
1.18
13.01
3.92
3.79
1.00
1.91
1.10
1.00
0.94
1.19
1.02
9.09
f1 (ppm)


TY23-L12.3.fid
166.860
161.637
147.297
141.353
141.129
140.966
138.942
138.762
138.592
138.473
138.381
136.645
134.937
134.121
134.094
133.917
133.892
132.360
130.970
130.637
130.588
130.184
128.609
128.552
128.508
128.491
128.439
128.422
127.414
127.378
125.835
123.043
122.366
121.493
117.196
65.471
58.177
41.983
34.435
31.434
f1 (ppm)

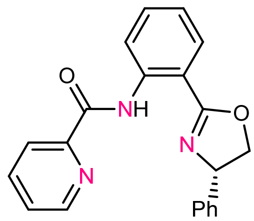


O
NH
N
N
tBu
PPh2
Cl

L*12

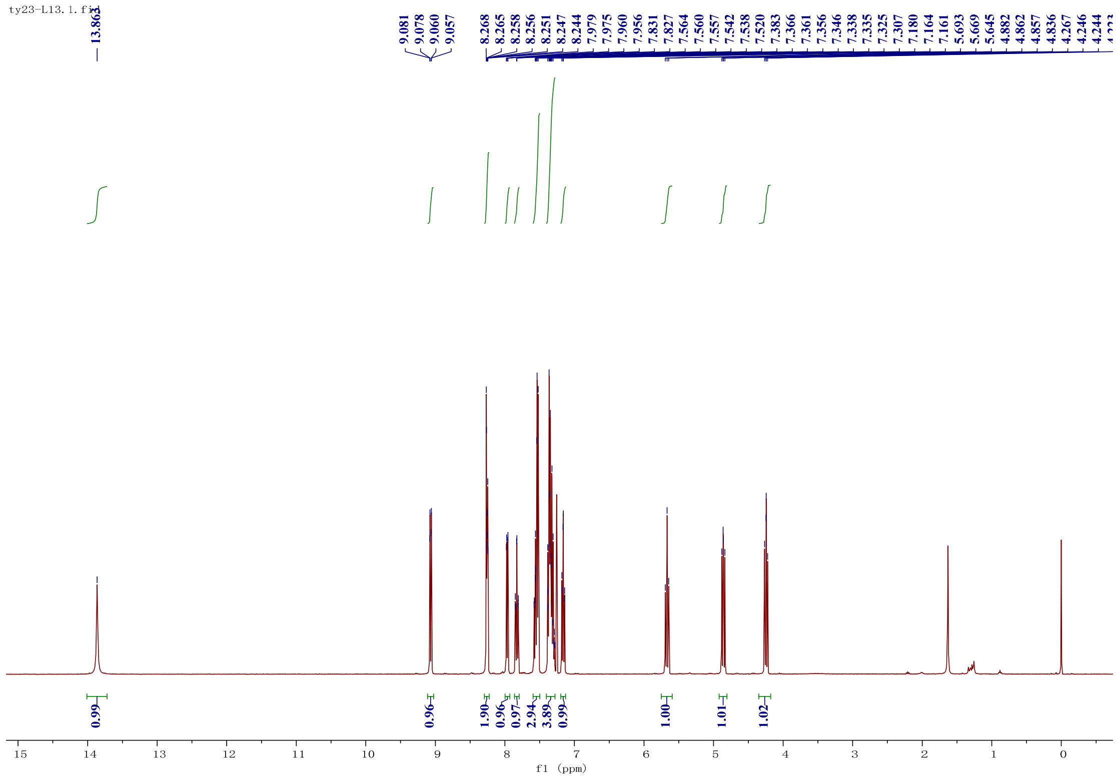


TY23-L12.2.fid
-8.204
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

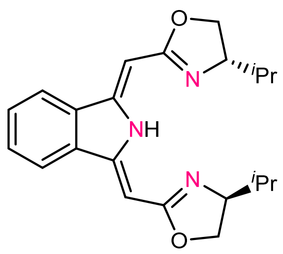


O
NH
O
N
N
Ph

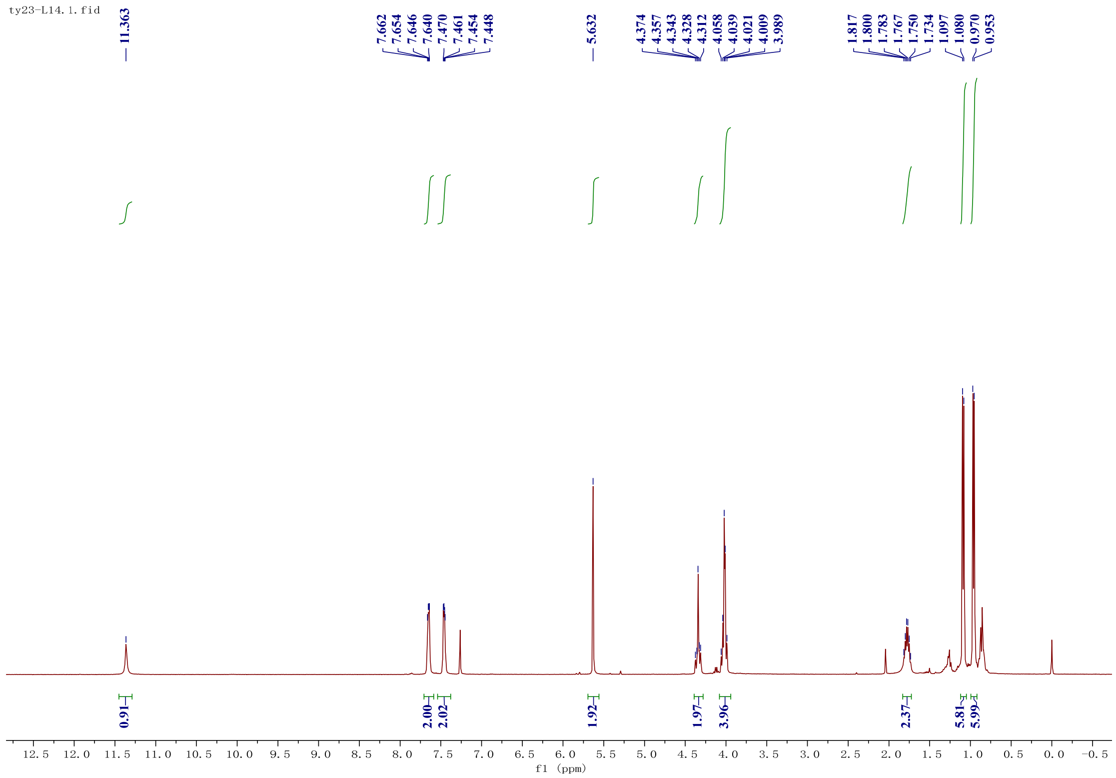
L*13

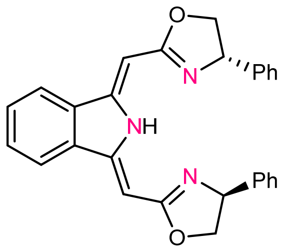


ty23-L13.1.fid
13.863
9.081
9.078
9.060
9.057
8.268
8.265
8.258
8.256
8.251
8.247
8.244
7.979
7.975
7.960
7.956
7.831
7.827
7.564
7.560
7.557
7.542
7.538
7.520
7.383
7.366
7.361
7.356
7.346
7.338
7.335
7.325
7.307
7.180
7.164
7.161
5.693
5.669
5.645
4.882
4.862
4.857
4.836
4.267
4.246
4.244
0.99
0.96
1.90
0.96
0.97
2.94
3.89
0.99
1.00
1.01
1.02
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

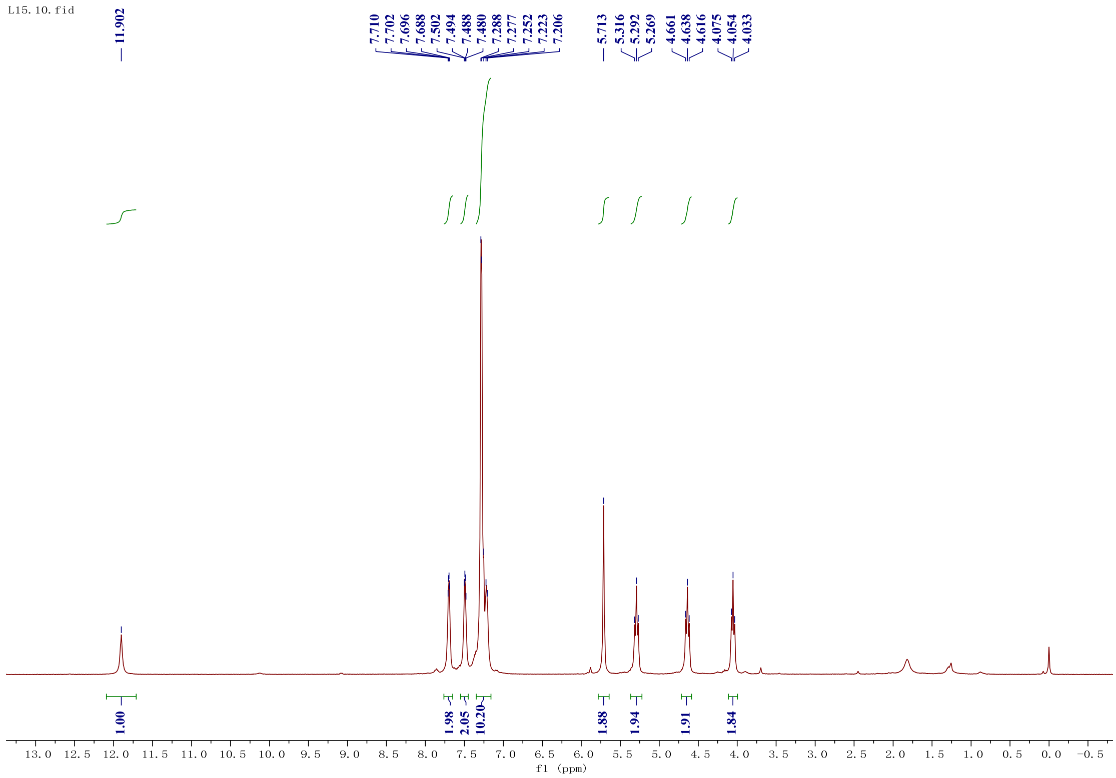


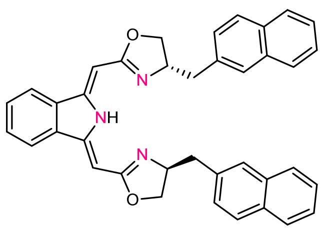
L*14


ty23-L14.1.fid
11.363
7.662
7.654
7.646
7.640
7.470
7.461
7.454
7.448
5.632
4.374
4.357
4.343
4.328
4.312
4.058
4.039
4.021
4.009
3.989
1.817
1.800
1.783
1.767
1.750
1.734
1.097
1.080
0.970
0.953
0.91
2.00
2.02
1.92
1.97
3.96
2.37
5.81
5.99
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

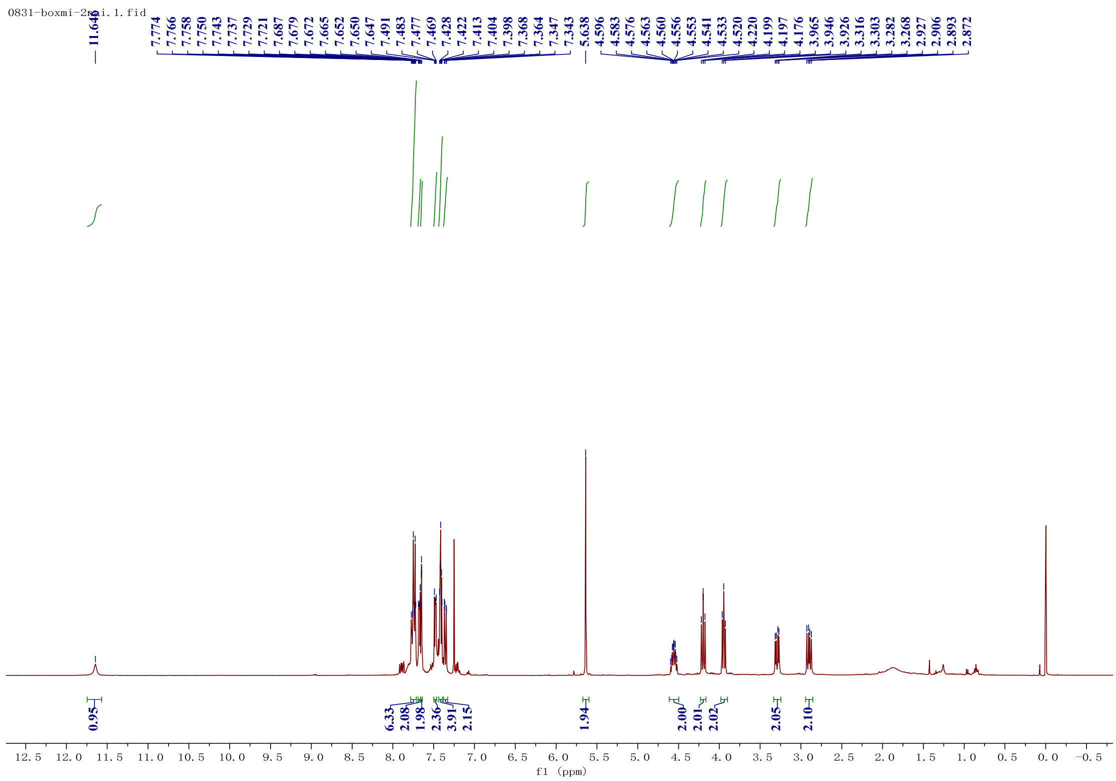


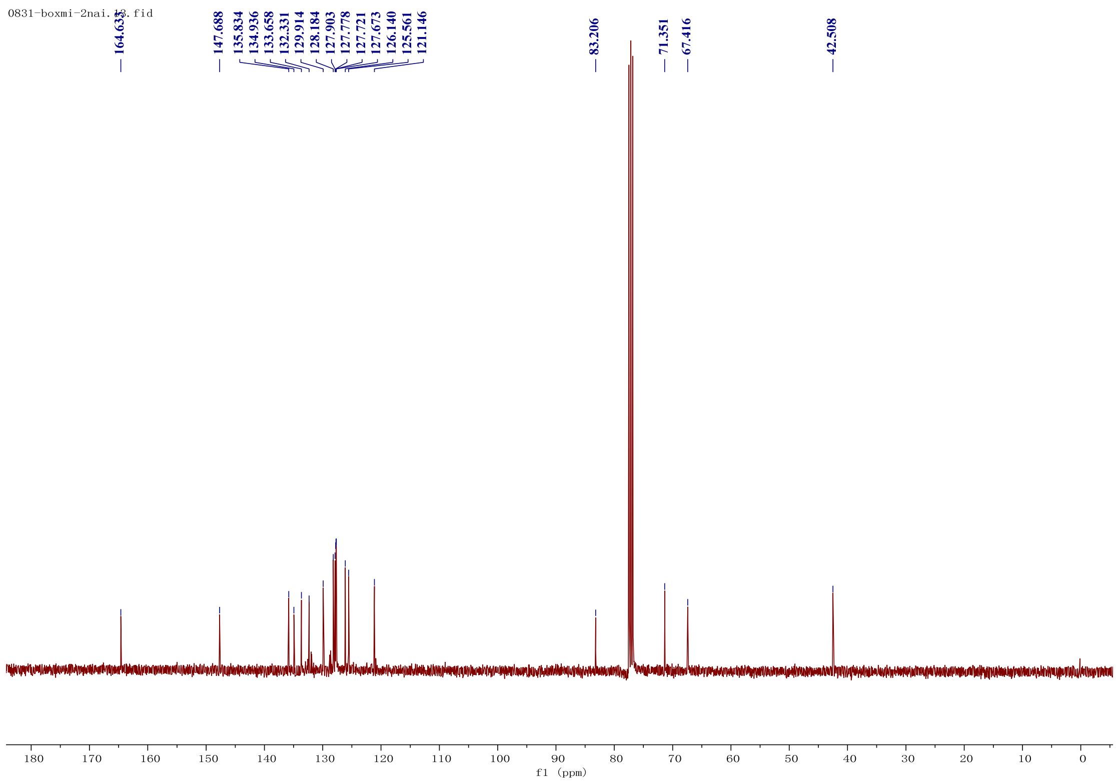
L*15

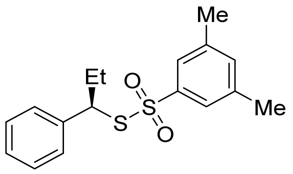

L15.10.fid
11.902
7.710
7.702
7.696
7.688
7.502
7.494
7.488
7.480
7.288
7.277
7.252
7.223
7.206
5.713
5.316
5.292
5.269
4.661
4.638
4.616
4.075
4.054
4.033
1.00
1.98
2.05
10.20
1.88
1.94
1.91
1.84
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



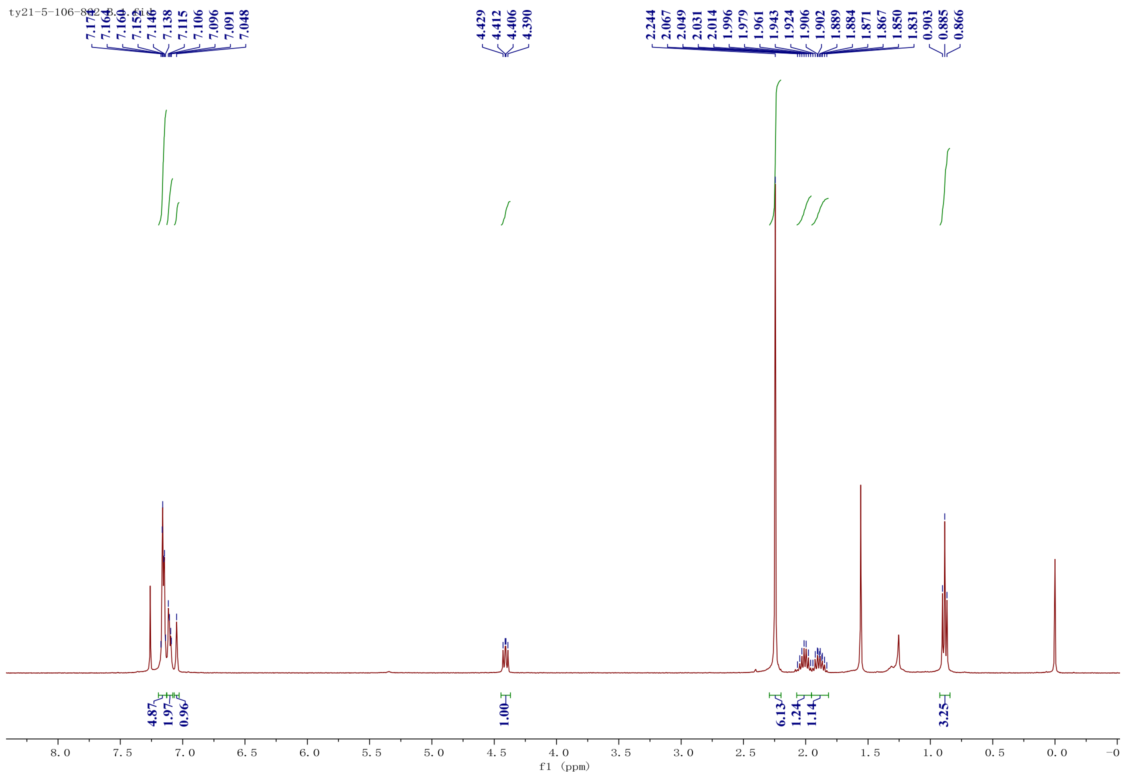
L*16

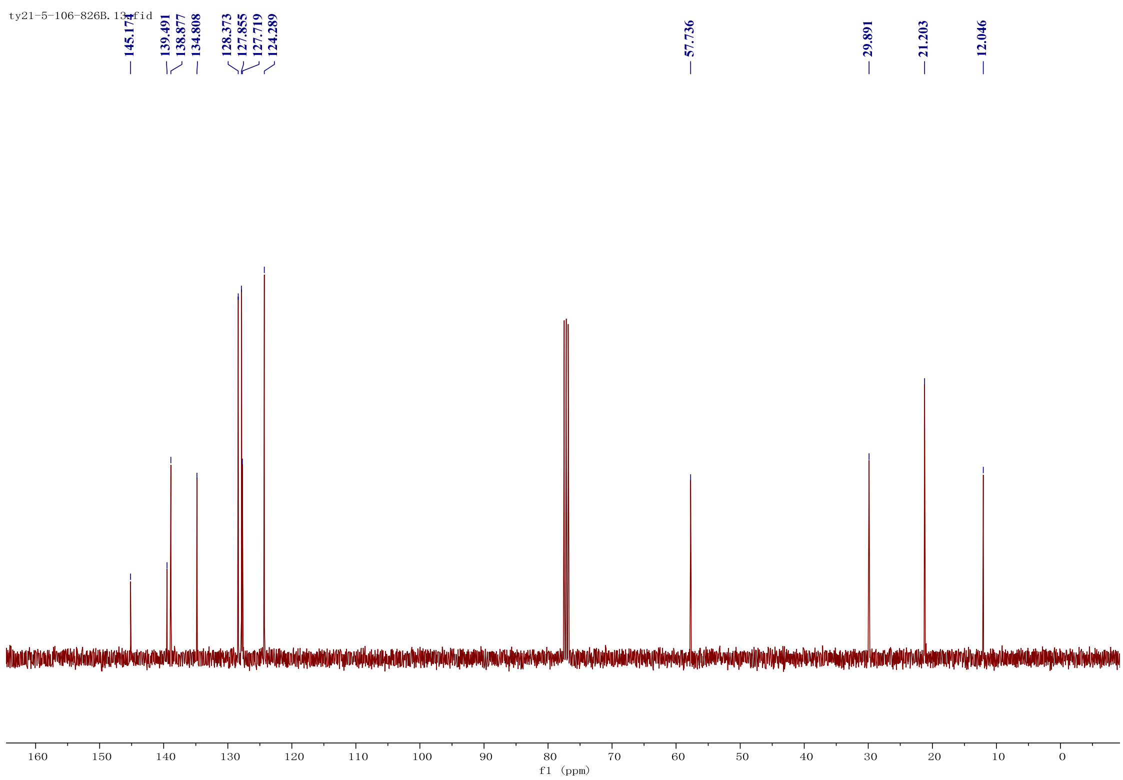

0831-boxmi-2nai.1.fid
11.646
7.774 7.766 7.758 7.750 7.743 7.737 7.729 7.721 7.687 7.679 7.672 7.665 7.652 7.650 7.647 7.491 7.483 7.477 7.469 7.428 7.422 7.413 7.404 7.398 7.368 7.364 7.347 7.343
5.638
4.596 4.583 4.576 4.563 4.560 4.556 4.553 4.541 4.533 4.520 4.220 4.199 4.197 4.176 3.965 3.946 3.926 3.316 3.303 3.282 3.268 2.927 2.906 2.893 2.872
0.95 6.33 2.08 1.98 2.36 3.91 2.15 1.94 2.00 2.01 2.02 2.05 2.10
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

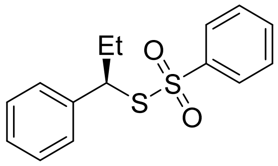

0831-boxmi-2nai.13.fid
164.633
147.688
135.834 134.936 133.658 132.331 129.914 128.184 127.903 127.778 127.721 127.673 126.140 125.561 121.146
83.206
71.351
67.416
42.508
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



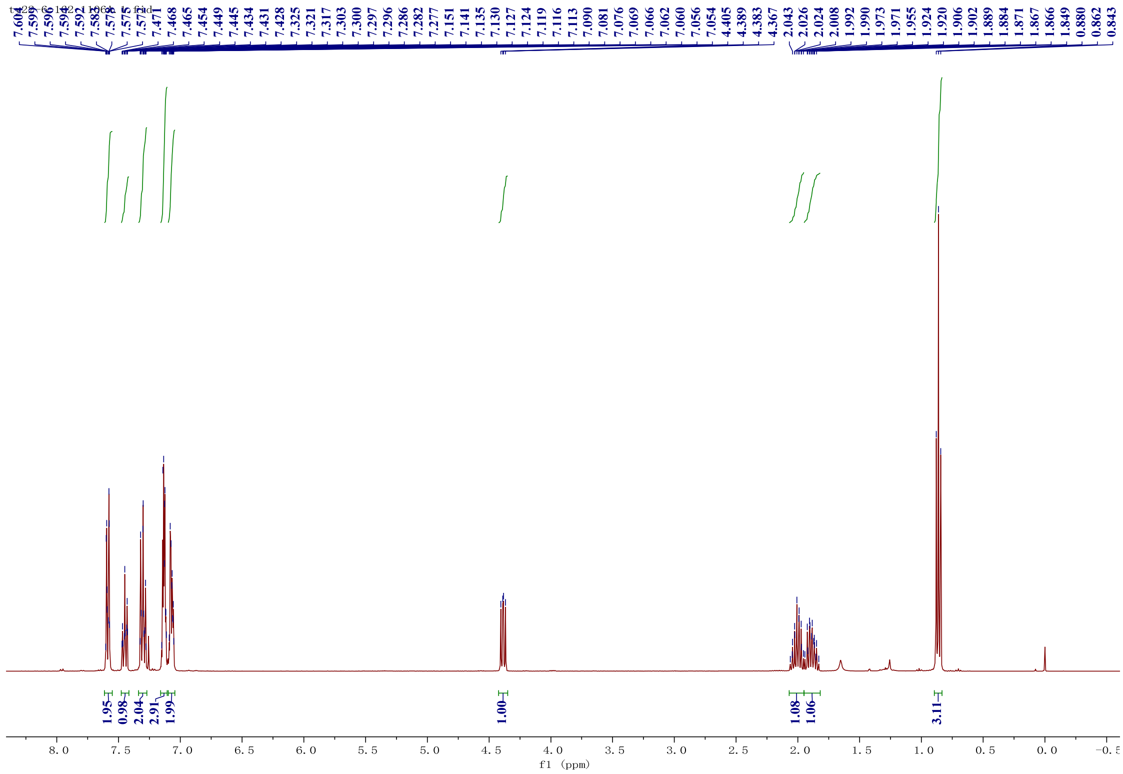
1

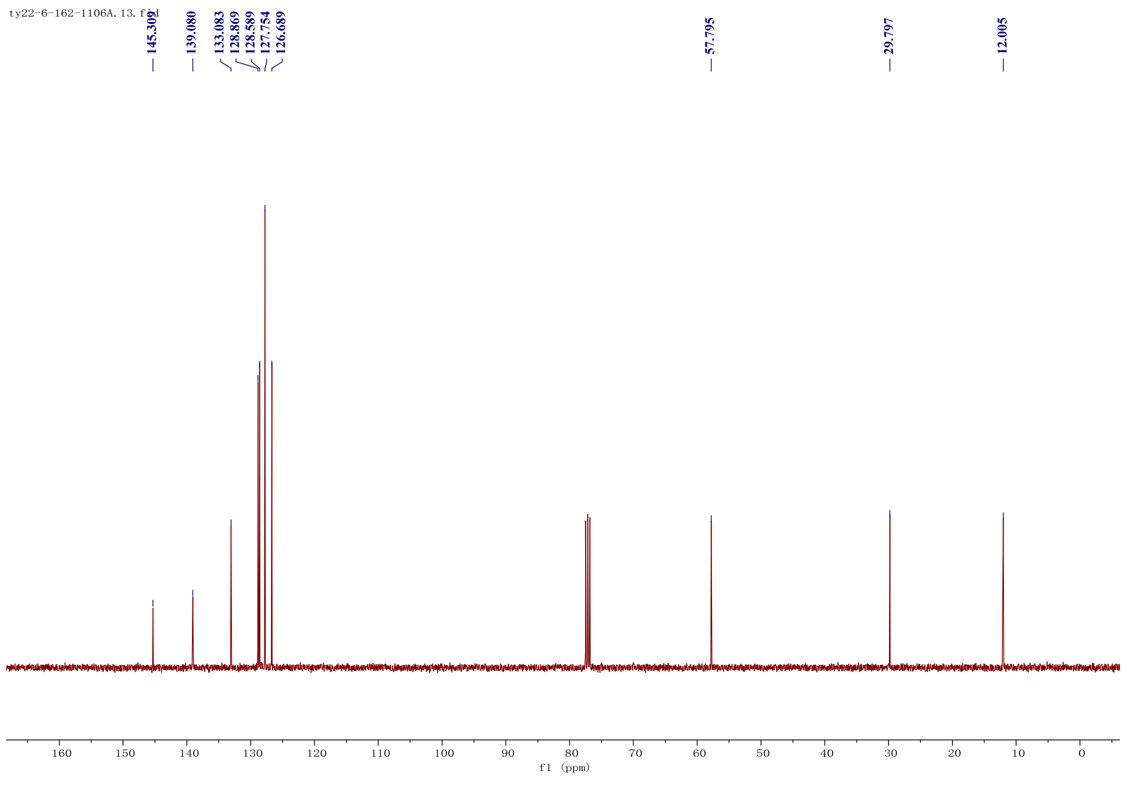


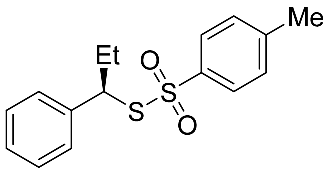




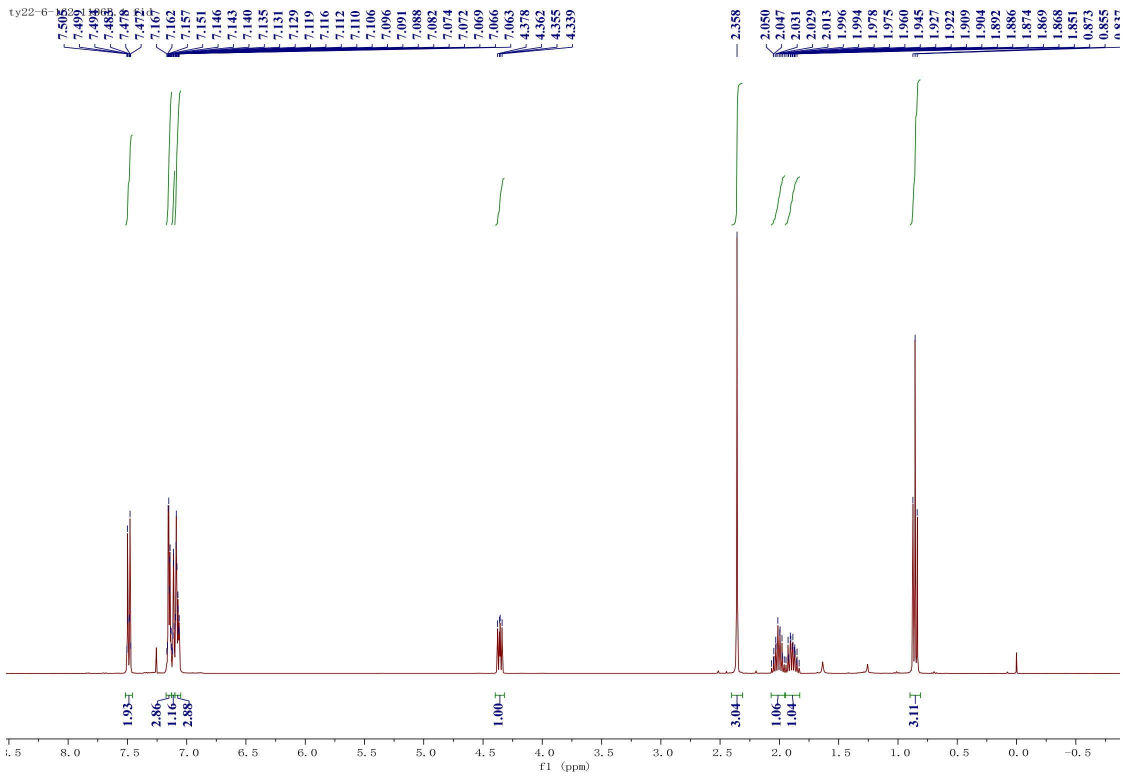
2

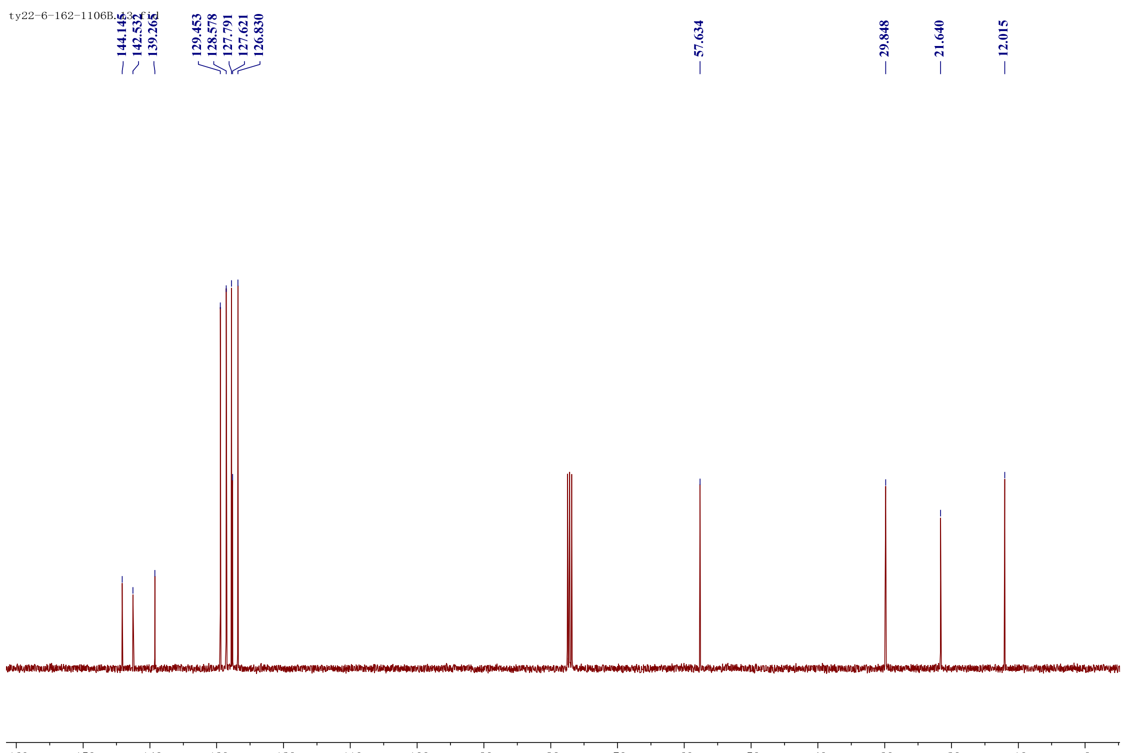


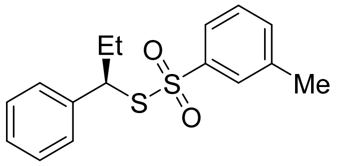




3

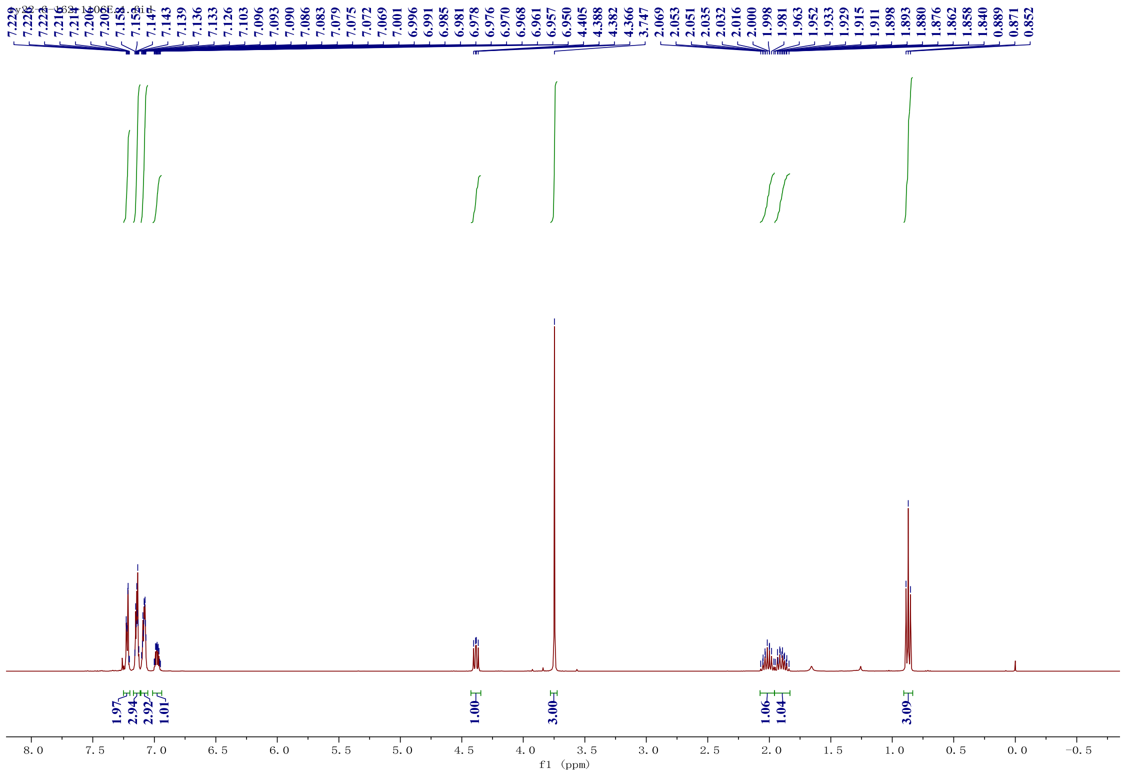




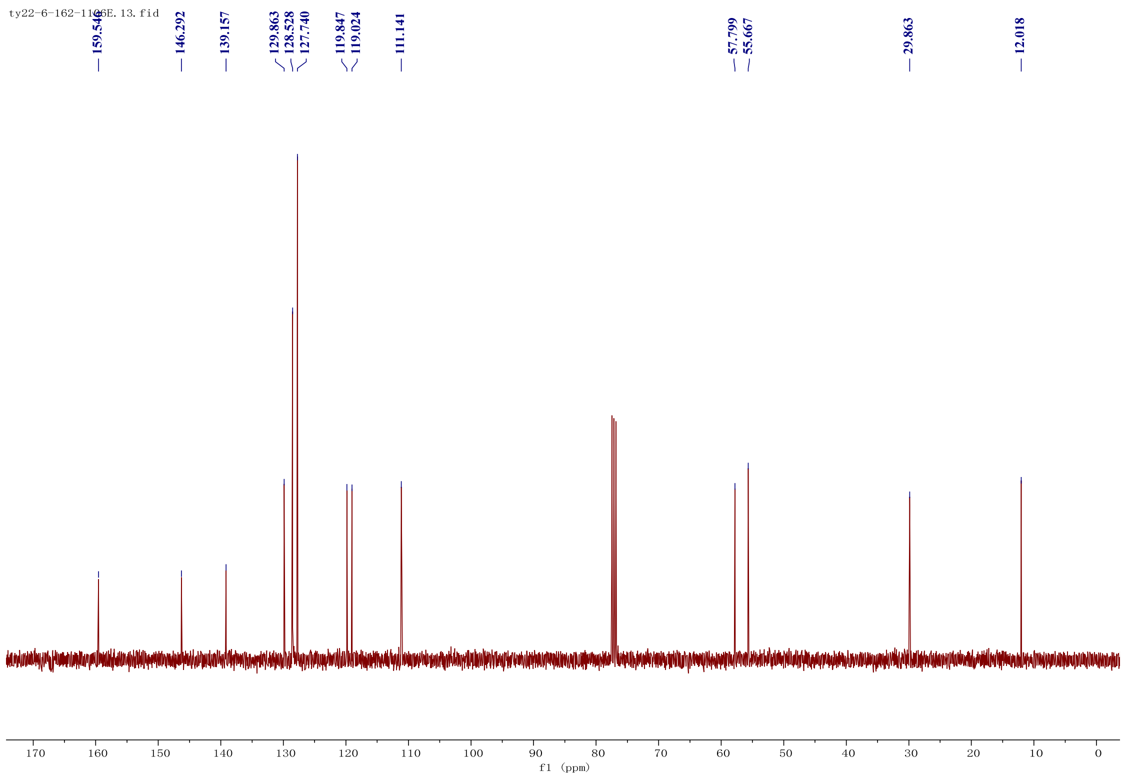


Et
O
S
S
O
Me

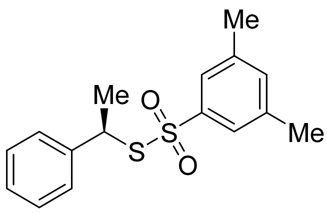
4



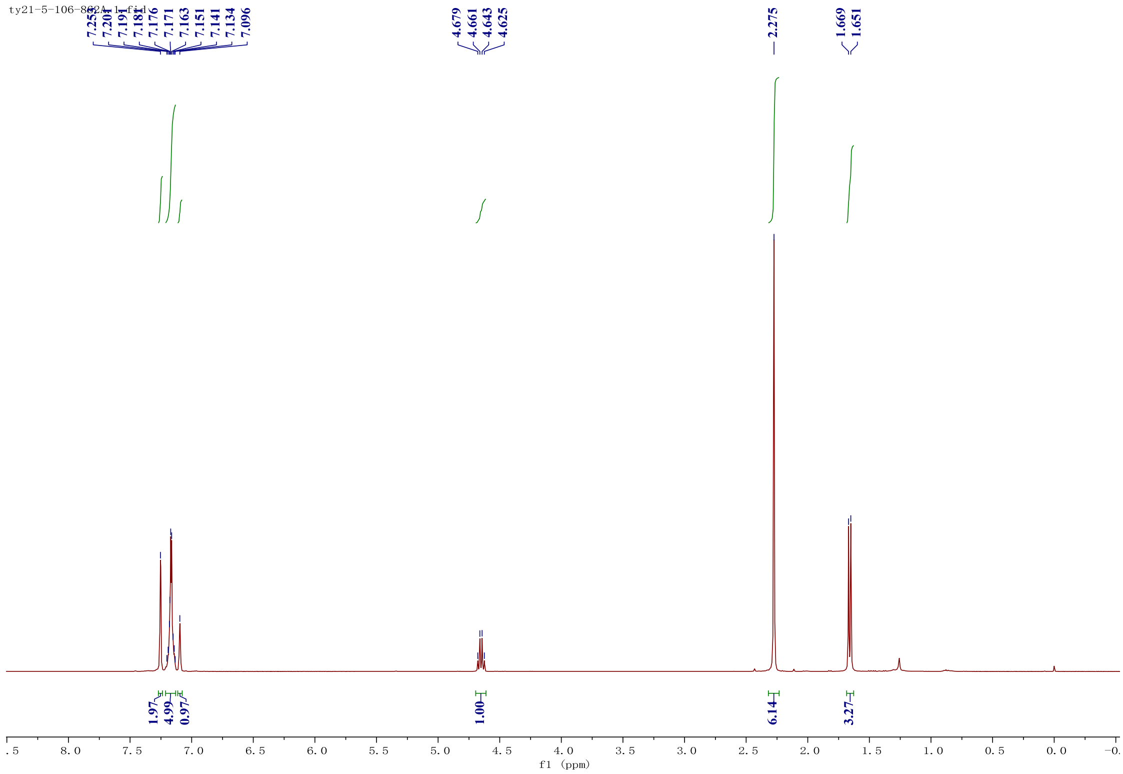
f1 (ppm)



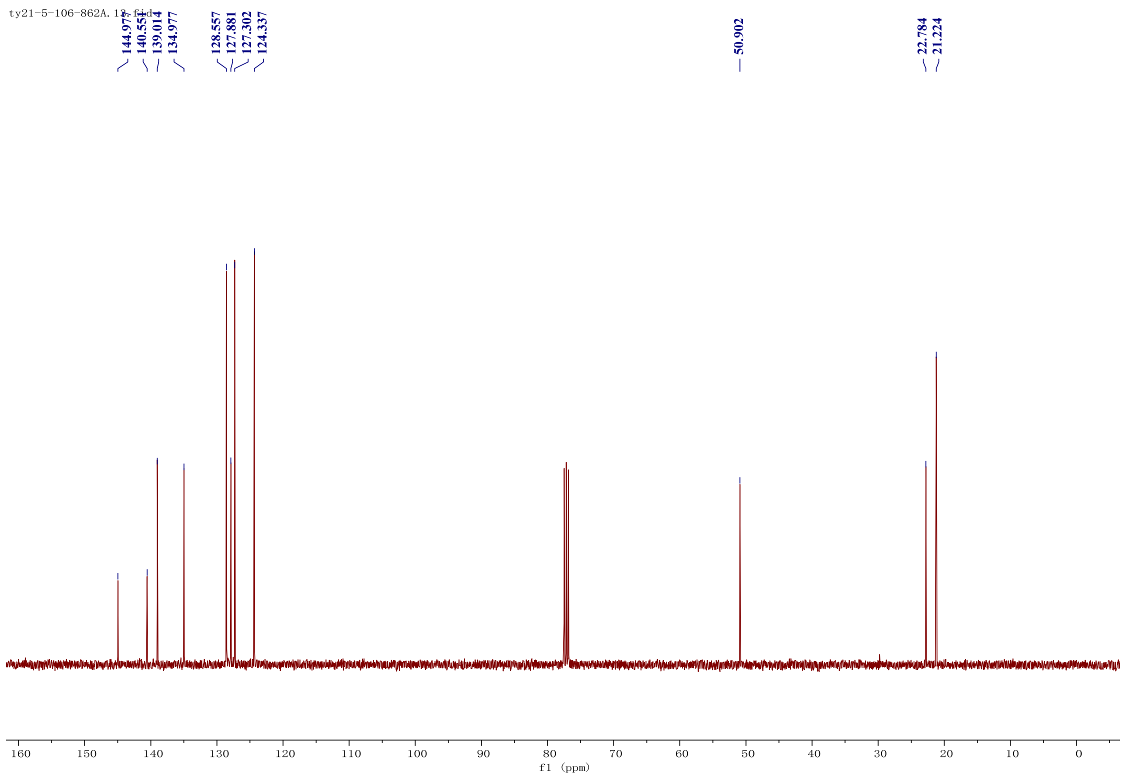
ty22-6-162-1106E.13.fid
159.546
146.292
139.157
129.863
128.528
127.740
119.847
119.024
111.141
57.799
55.667
29.863
12.018
f1 (ppm)



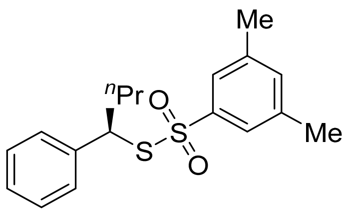
5



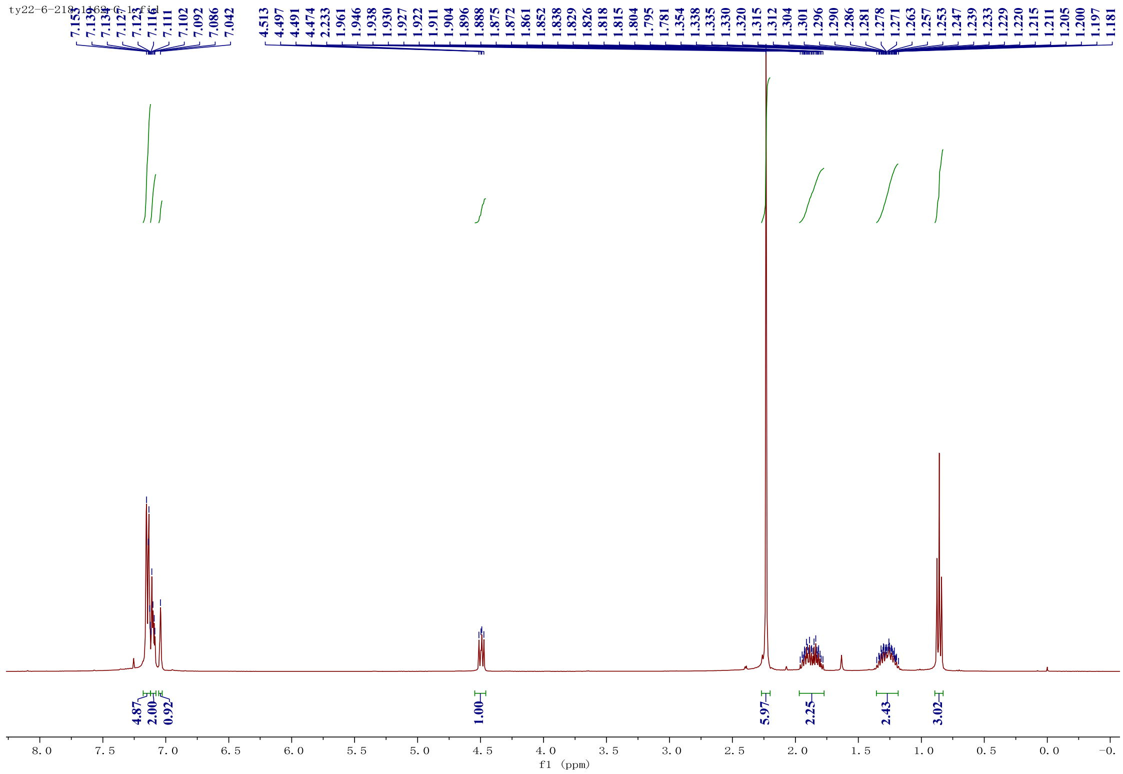
ty21-5-106-862A.1.fid
7.253
7.201
7.191
7.181
7.176
7.171
7.163
7.151
7.141
7.134
7.096
4.679
4.661
4.643
4.625
2.275
1.669
1.651
1.97
4.99
0.97
1.00
6.14
3.27
f1 (ppm)

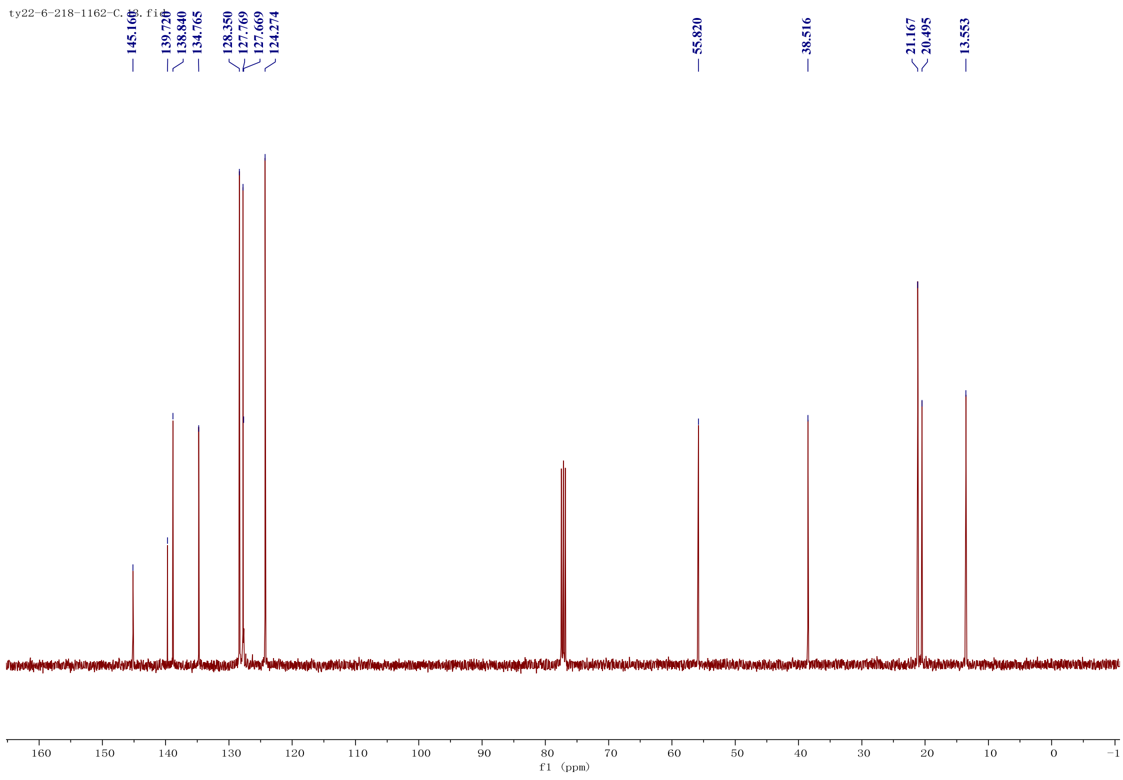


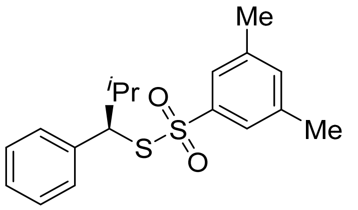
ty21-5-106-862A.13.fid
144.975
140.551
139.014
134.977
128.557
127.881
127.302
124.337
50.902
22.784
21.224
f1 (ppm)



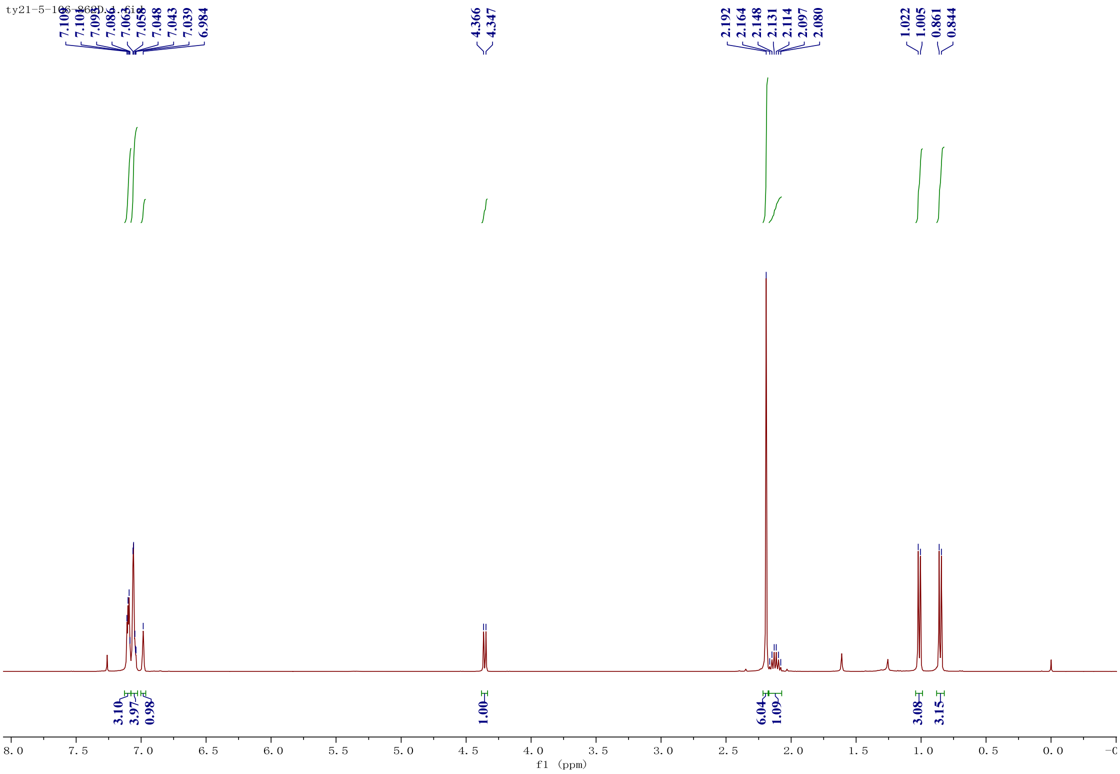
6

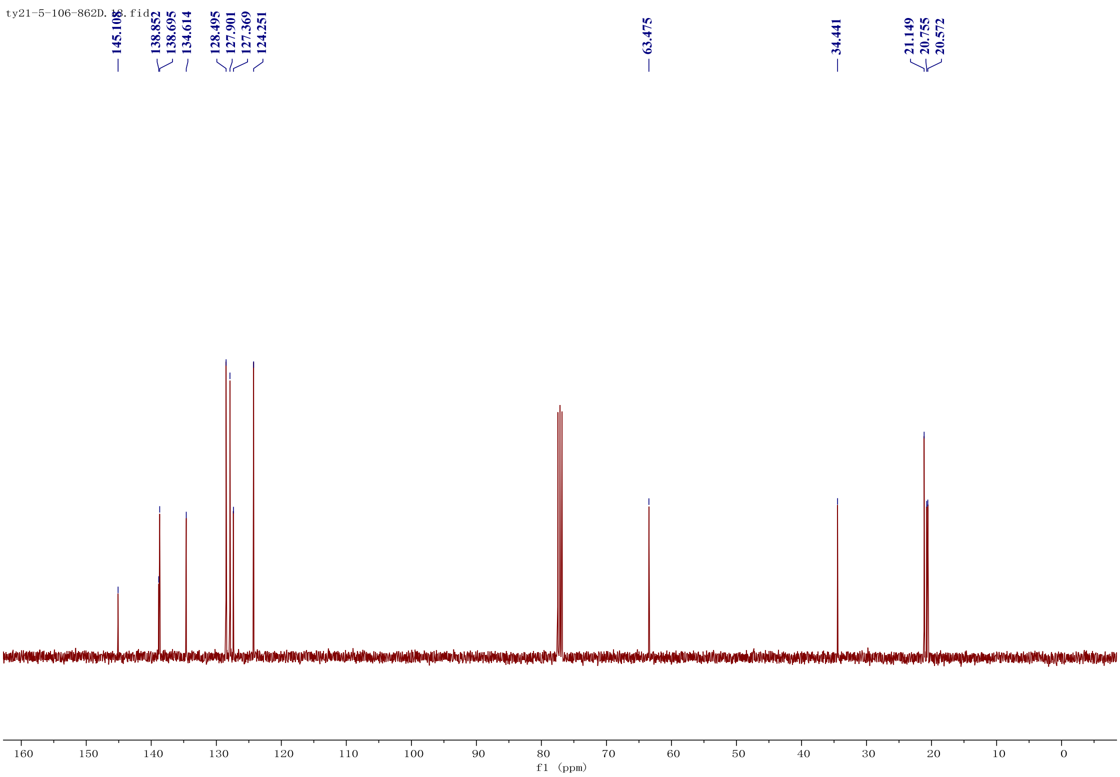

ty22-6-218-1162-6-1.fid
7.153
7.136
7.134
7.127
7.123
7.116
7.111
7.102
7.092
7.086
7.042
4.513
4.497
4.491
4.474
2.233
1.961
1.946
1.938
1.930
1.927
1.922
1.911
1.904
1.896
1.888
1.875
1.872
1.861
1.852
1.838
1.829
1.826
1.818
1.815
1.804
1.795
1.781
1.354
1.338
1.335
1.330
1.320
1.315
1.312
1.304
1.301
1.296
1.290
1.286
1.281
1.278
1.271
1.263
1.257
1.253
1.247
1.239
1.233
1.229
1.220
1.215
1.211
1.205
1.200
1.197
1.181
4.87
2.00
0.92
1.00
5.97
2.25
2.43
3.02
f1 (ppm)

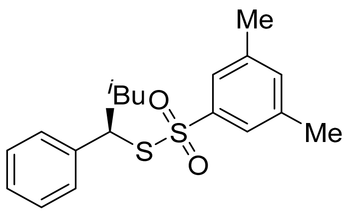

ty22-6-218-1162-C.13.fid
145.160
139.720
138.840
134.765
128.350
127.769
127.669
124.274
55.820
38.516
21.167
20.495
13.553
f1 (ppm)


Me
iPr
O
S
S
O
Me

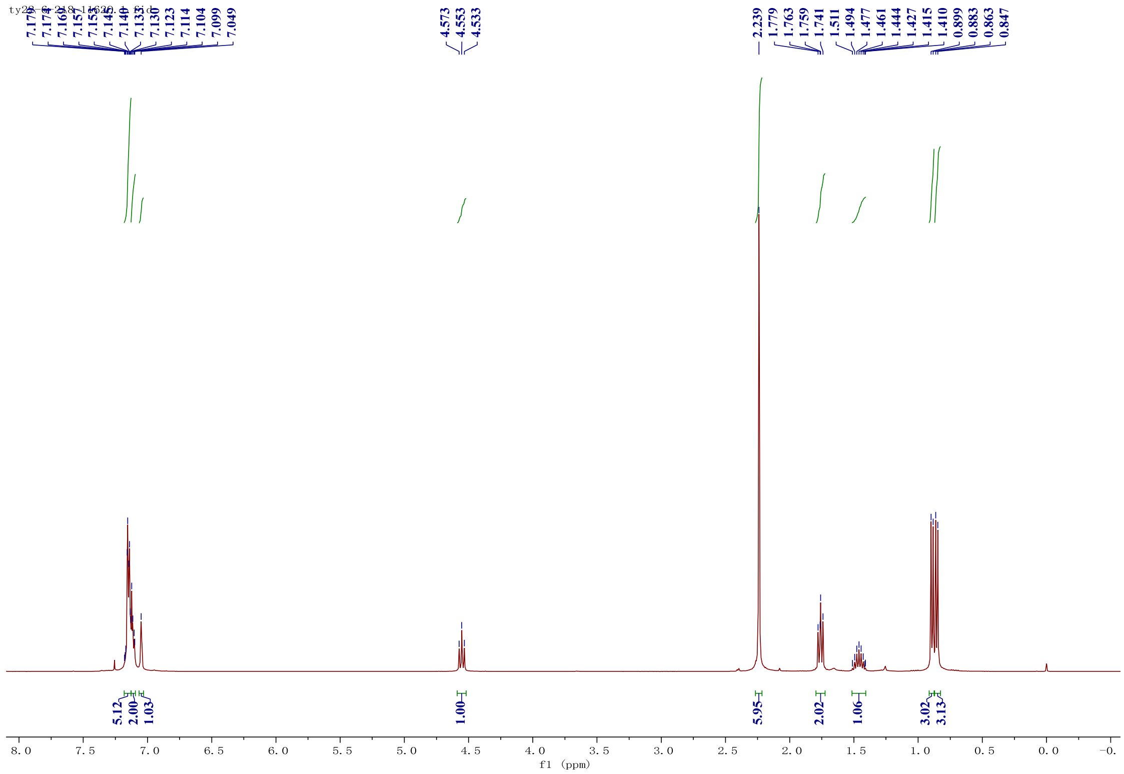
7

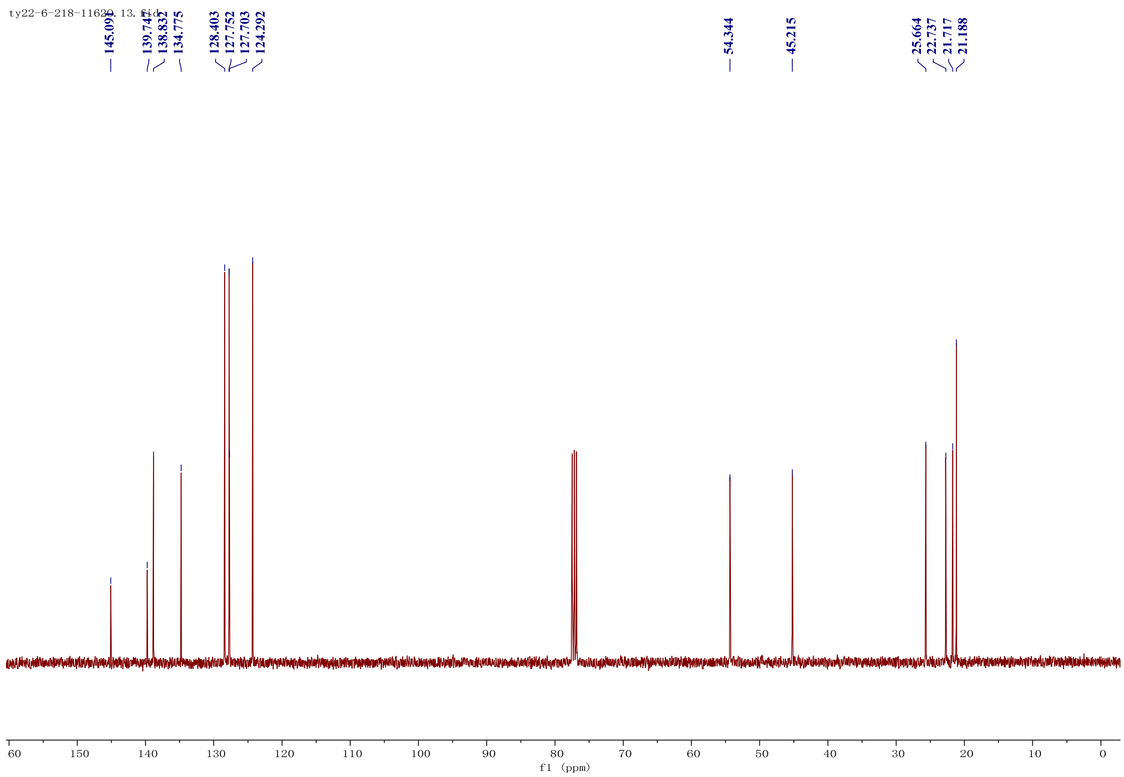

7.106
7.101
7.093
7.086
7.063
7.058
7.048
7.043
7.039
6.984
4.366
4.347
2.192
2.164
2.148
2.131
2.114
2.097
2.080
1.022
1.005
0.861
0.844
3.10
3.97
0.98
1.00
6.04
1.09
3.08
3.15
f1 (ppm)


ty21-5-106-862D.13.fid
145.108
138.852
138.695
134.614
128.495
127.901
127.369
124.251
63.475
34.441
21.149
20.755
20.572
f1 (ppm)


Me
iBu
O
S
S
O
Me

8


7.179
7.174
7.169
7.157
7.153
7.145
7.140
7.133
7.130
7.123
7.114
7.104
7.099
7.049
4.573
4.553
4.533
2.239
1.779
1.763
1.759
1.741
1.511
1.494
1.477
1.461
1.444
1.427
1.415
1.410
0.899
0.883
0.863
0.847
5.12
2.00
1.03
1.00
5.95
2.02
1.06
3.02
3.13
f1 (ppm)


ty22-6-218-11620
145.099
139.742
138.832
134.775
128.403
127.752
127.703
124.292
54.344
45.215
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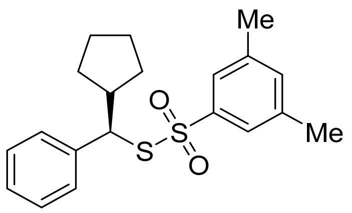
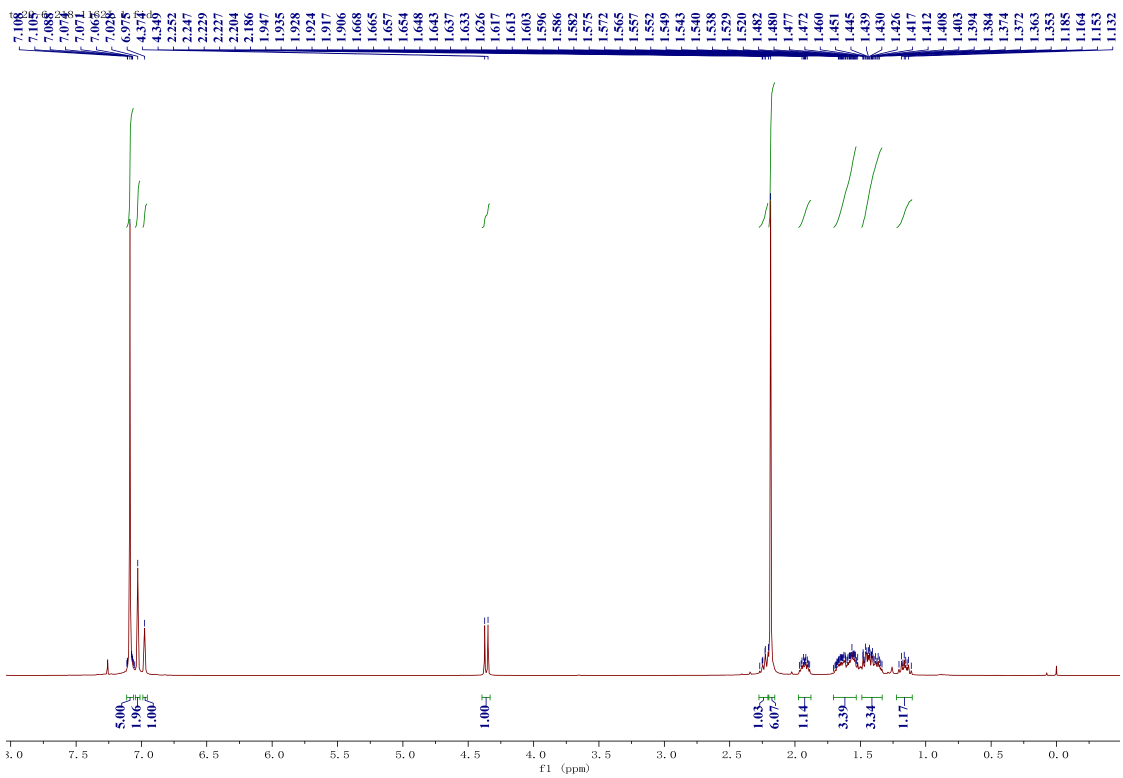
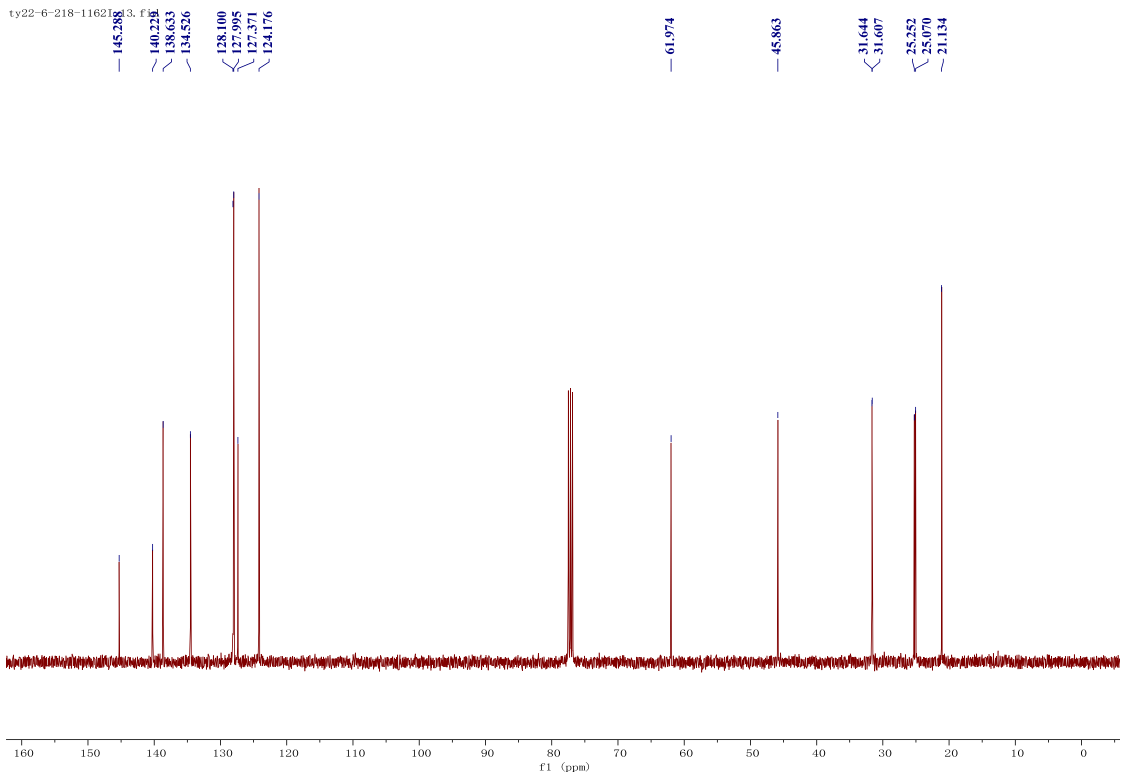
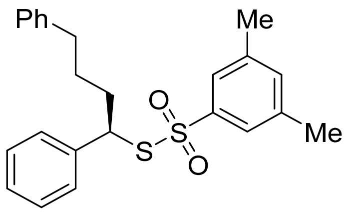
22.737
21.717
21.188
f1 (ppm)



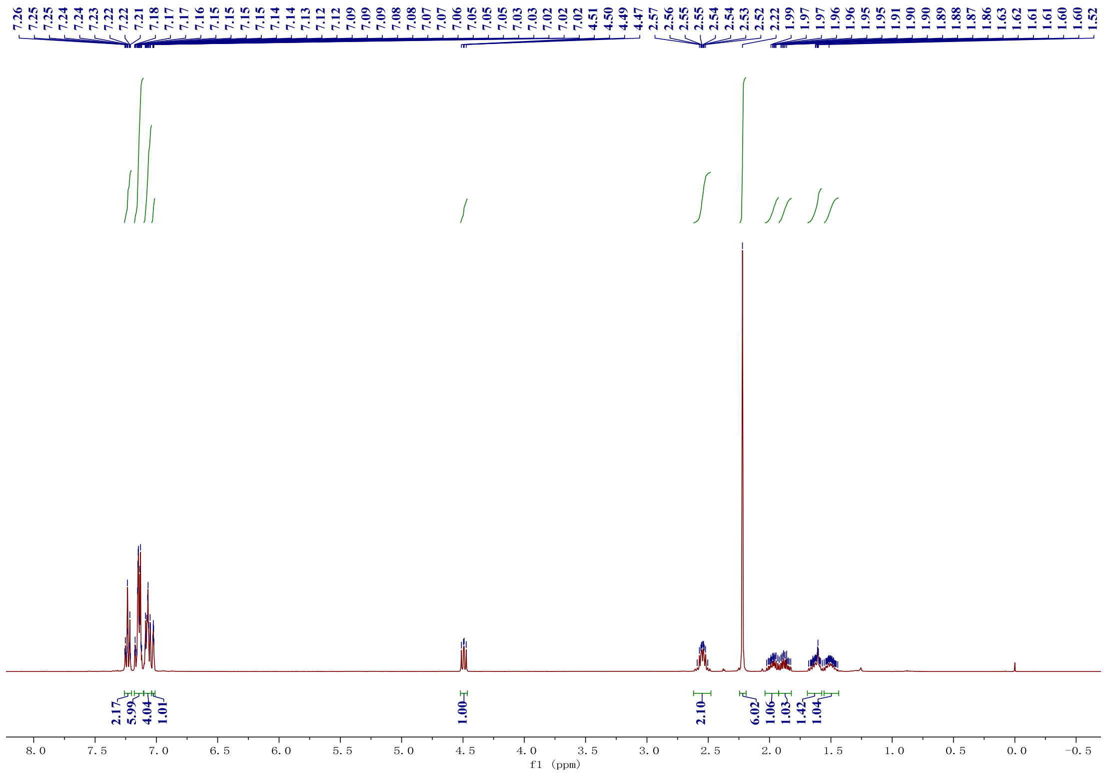
9

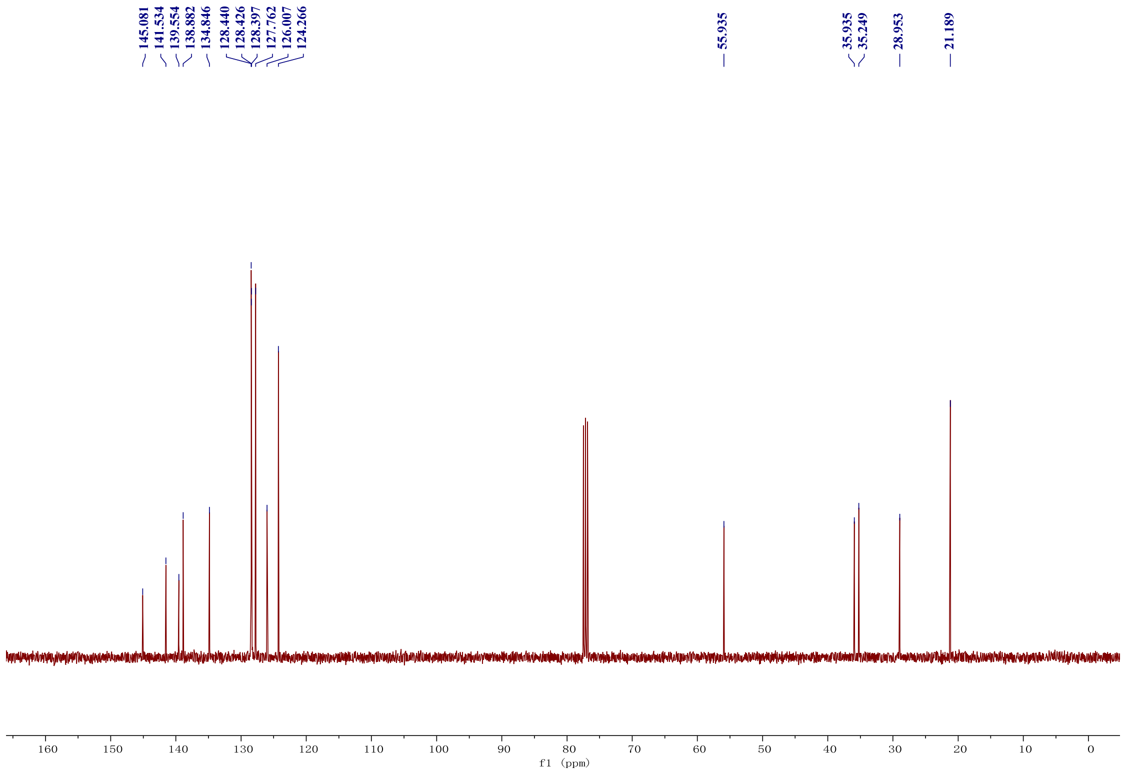


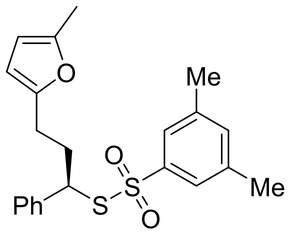




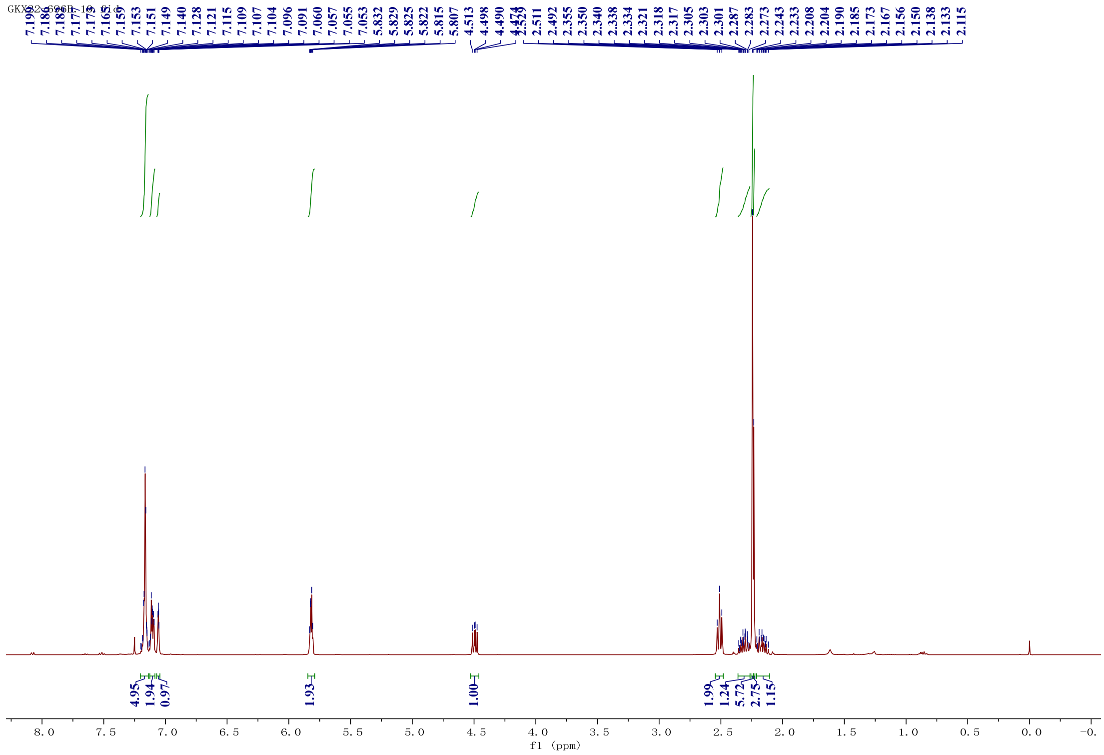
10

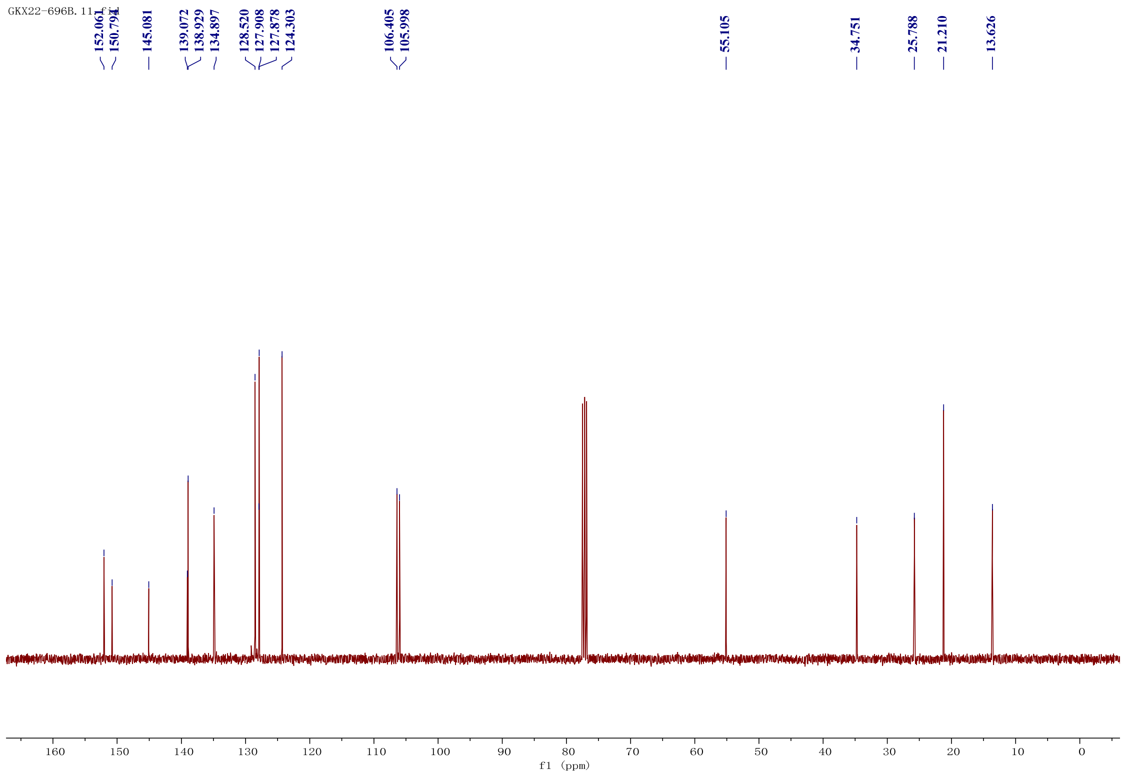


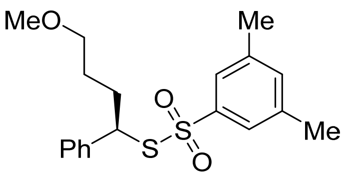




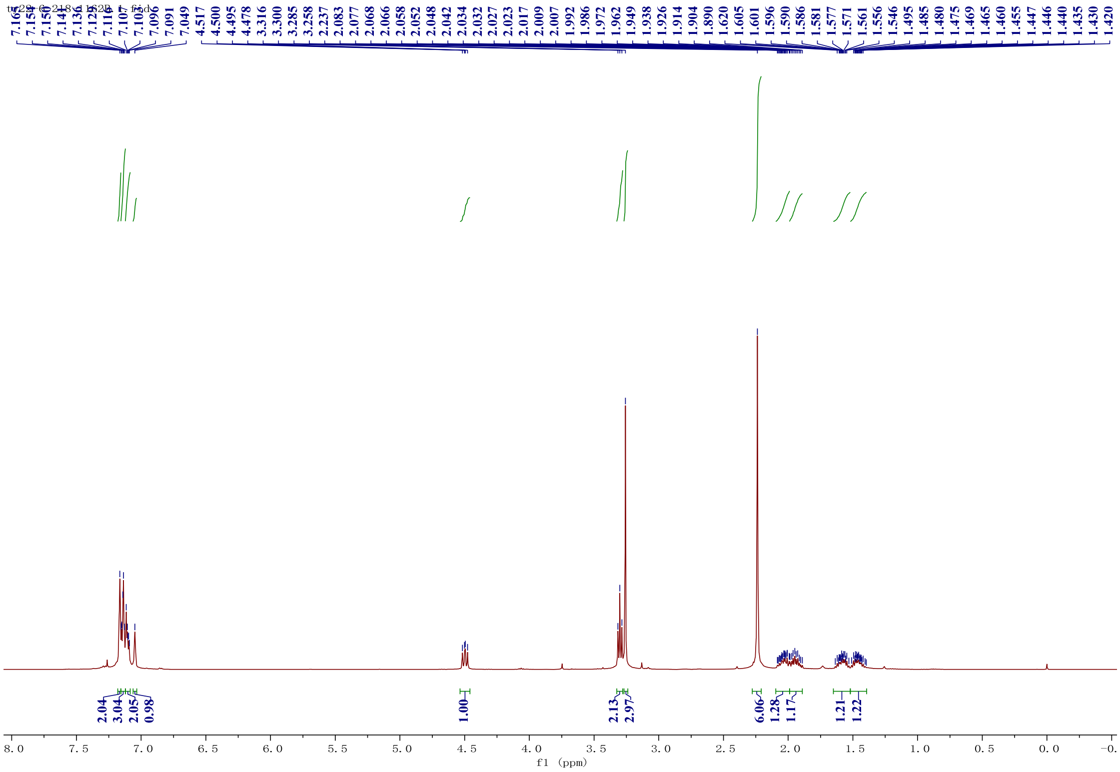
11

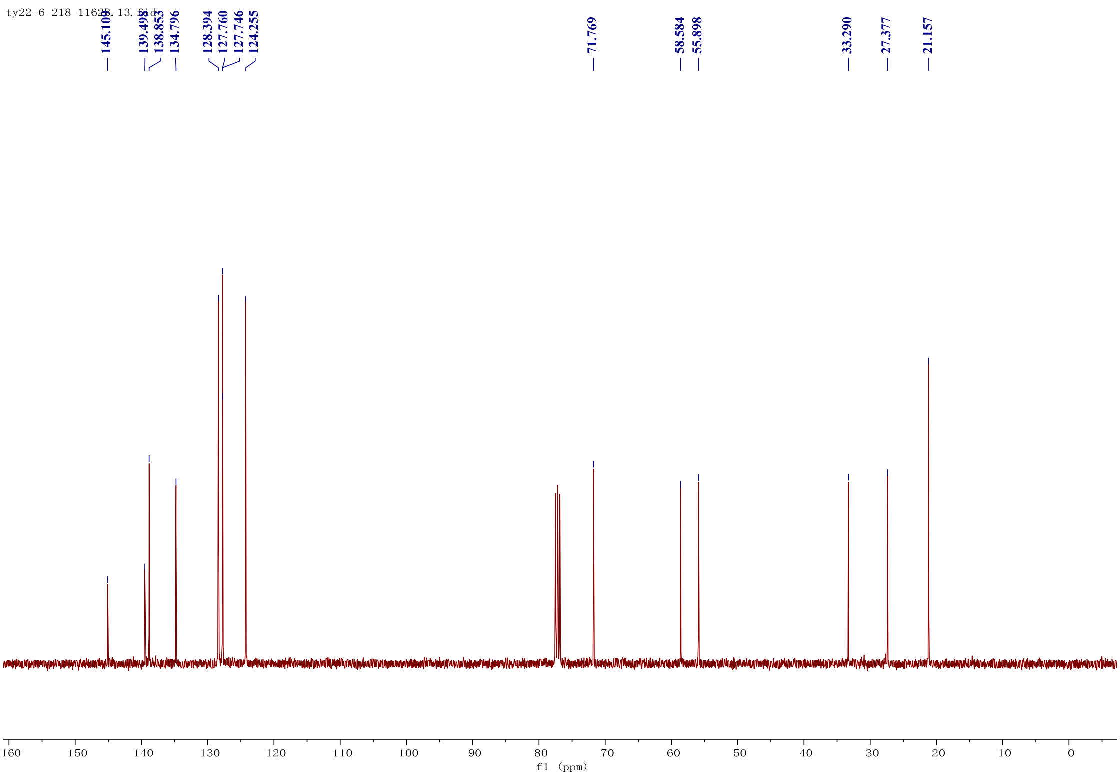


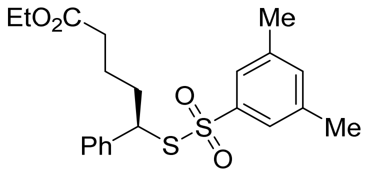



MeO
Me
Me
Ph
S
S
O
O

12

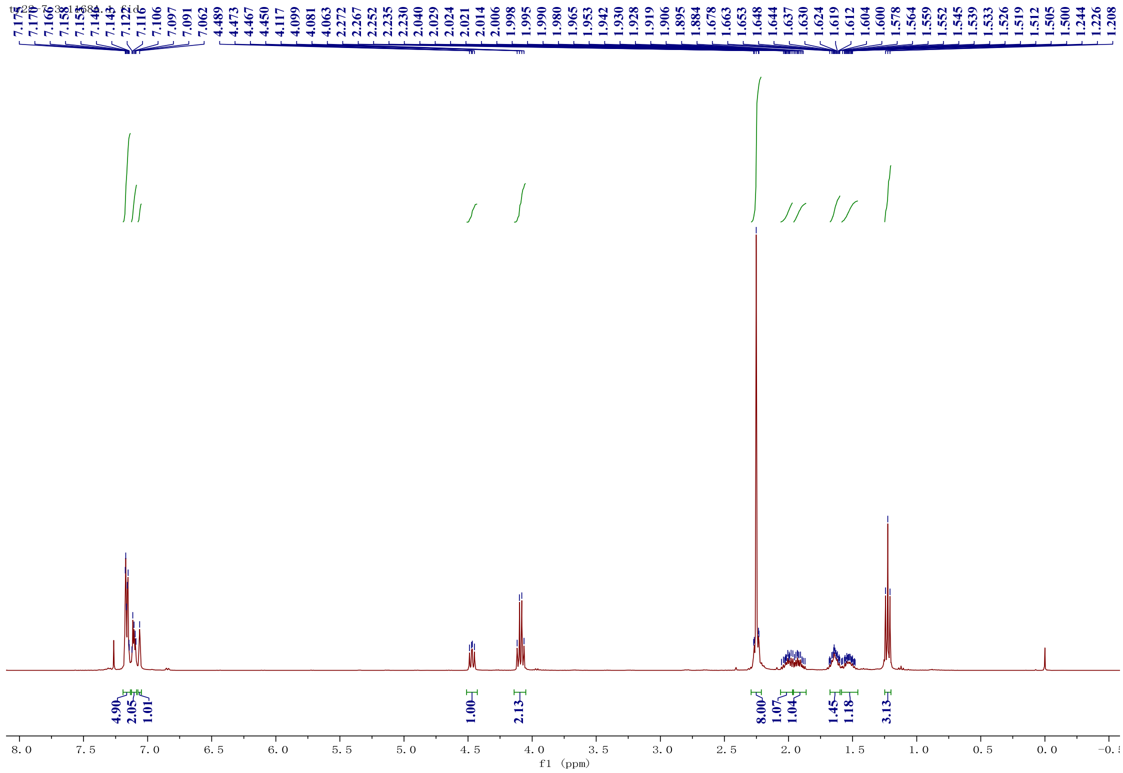

f1 (ppm)


145.108
139.498
138.853
134.796
128.394
127.760
127.746
124.255
71.769
58.584
55.898
33.290
27.377
21.157
f1 (ppm)

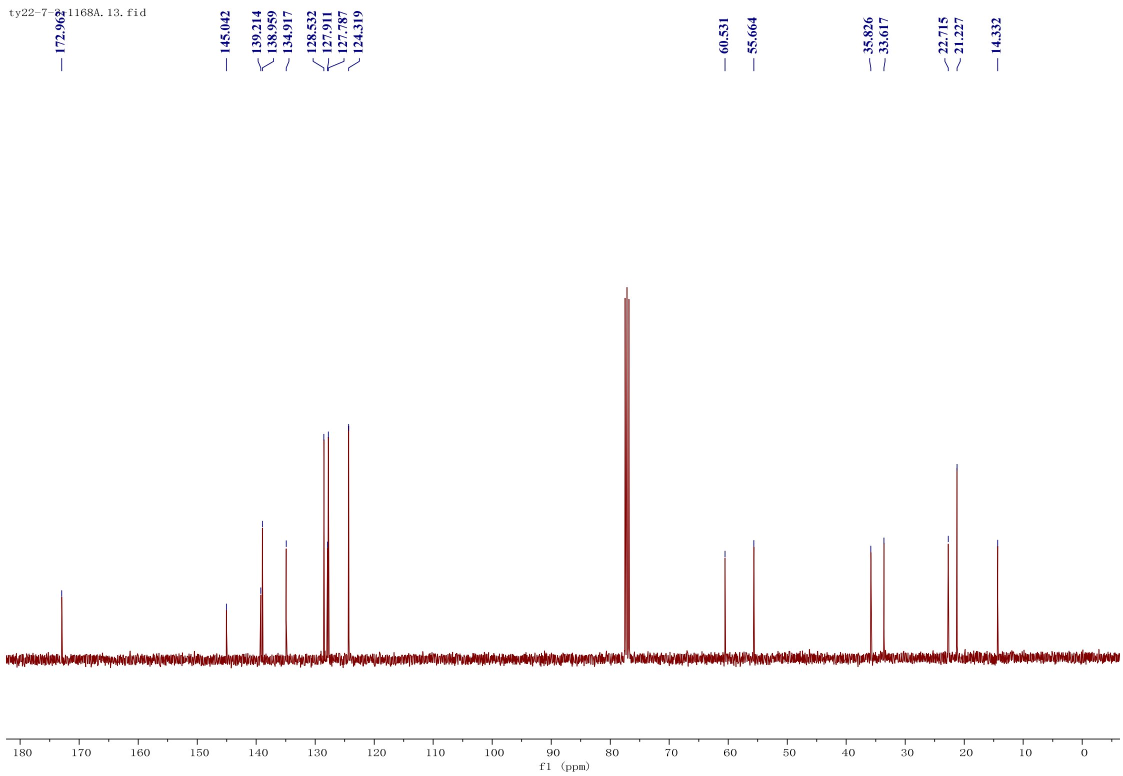


EtO2C
Me
Me
O
S
O
Ph
S

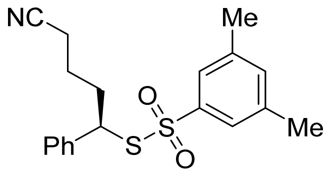
13



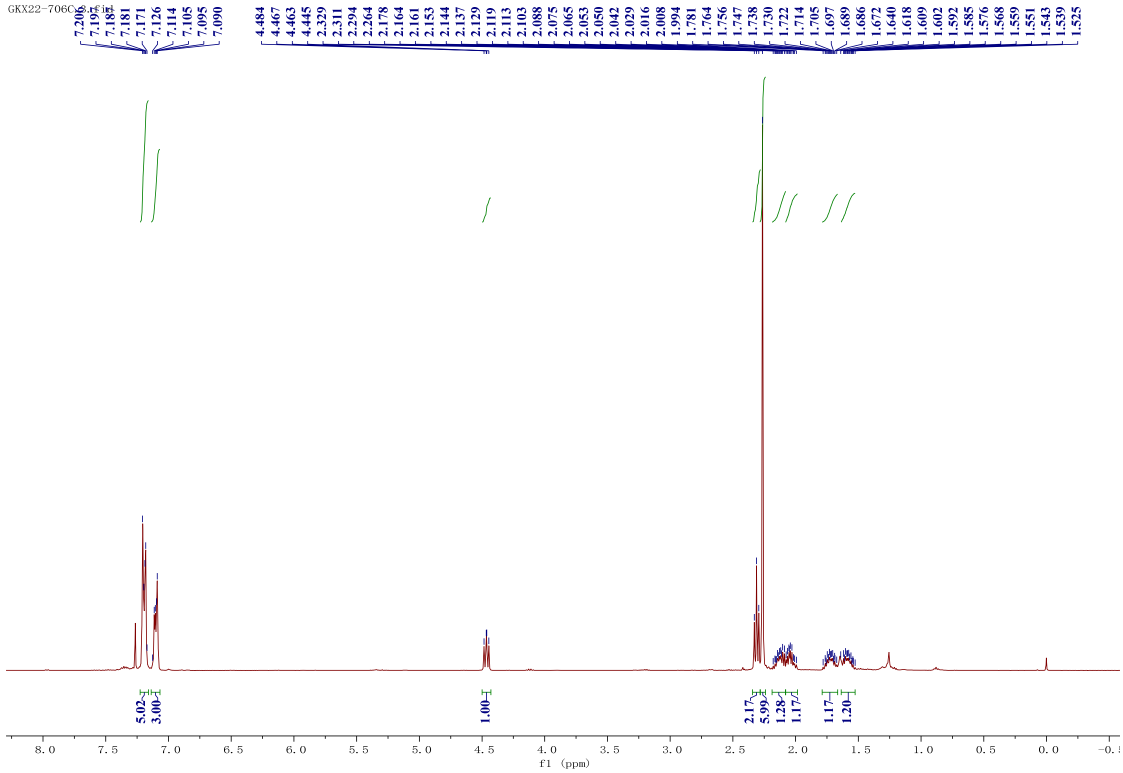
7.175
7.170
7.167
7.158
7.153
7.146
7.143
7.122
7.116
7.106
7.097
7.091
7.062
4.489
4.473
4.467
4.450
4.117
4.099
4.081
4.063
2.272
2.267
2.252
2.235
2.230
2.040
2.029
2.024
2.021
2.014
2.006
1.998
1.995
1.990
1.980
1.965
1.953
1.942
1.930
1.928
1.919
1.906
1.895
1.884
1.678
1.663
1.653
1.648
1.644
1.637
1.630
1.624
1.619
1.612
1.604
1.600
1.578
1.564
1.559
1.552
1.545
1.539
1.533
1.526
1.519
1.512
1.505
1.500
1.244
1.226
1.208
4.90
2.05
1.01
1.00
2.13
8.00
1.07
1.04
1.45
1.18
3.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

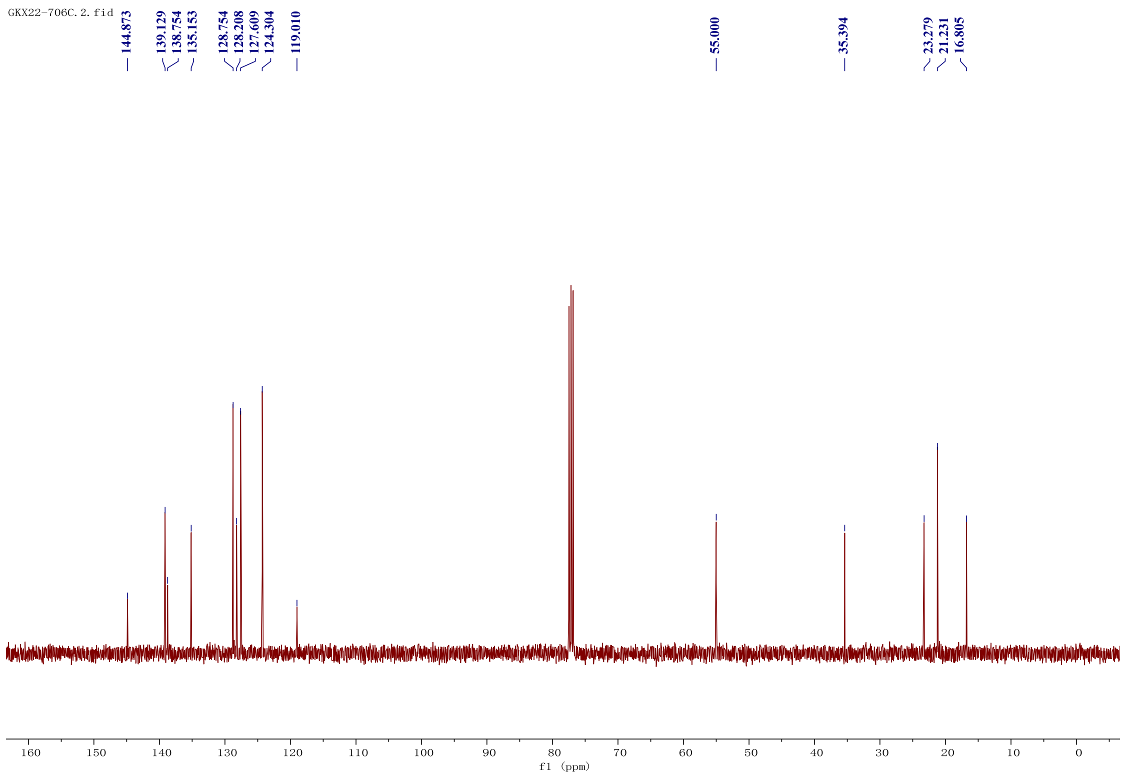


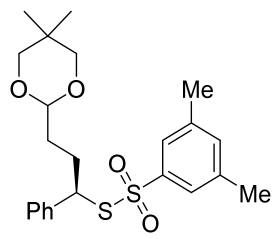
ty22-7-3-1168A.13.fid
172.962
145.042
139.214
138.959
134.917
128.532
127.911
127.787
124.319
60.531
55.664
35.826
33.617
22.715
21.227
14.332
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NC
Me
O
S
O
Ph
S
Me

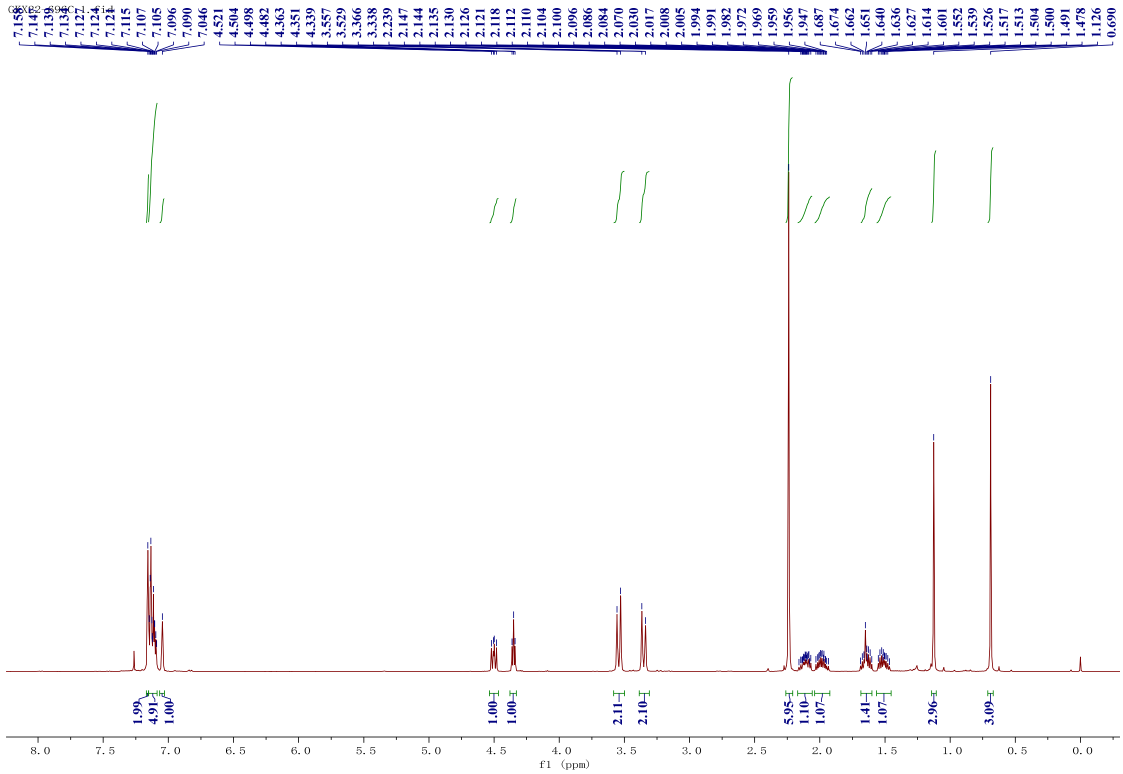
14

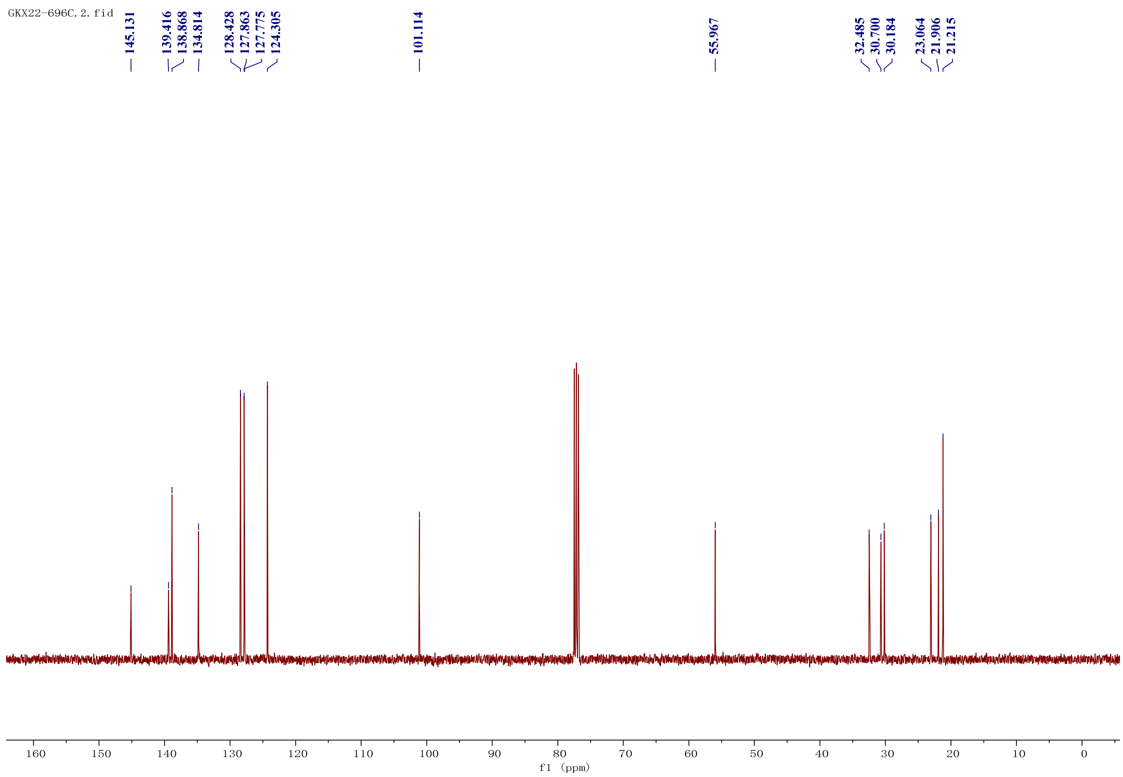

7.206
7.197
7.184
7.181
7.171
7.126
7.114
7.105
7.095
7.090
4.484
4.467
4.463
4.445
2.329
2.311
2.294
2.264
2.178
2.164
2.161
2.153
2.144
2.137
2.129
2.119
2.113
2.103
2.088
2.075
2.065
2.053
2.050
2.042
2.029
2.016
2.008
1.994
1.781
1.764
1.756
1.747
1.738
1.730
1.722
1.714
1.705
1.697
1.689
1.686
1.672
1.640
1.618
1.609
1.602
1.592
1.585
1.576
1.568
1.559
1.551
1.543
1.539
1.525
5.02
3.00
1.00
2.17
5.99
1.28
1.17
1.17
1.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

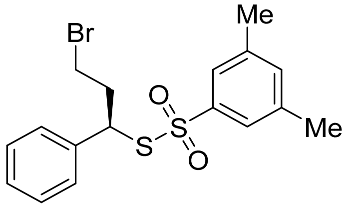

GKX22-706C.2.fid
144.873
139.129
138.754
135.153
128.754
128.208
127.609
124.304
119.010
55.000
35.394
23.279
21.231
16.805
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



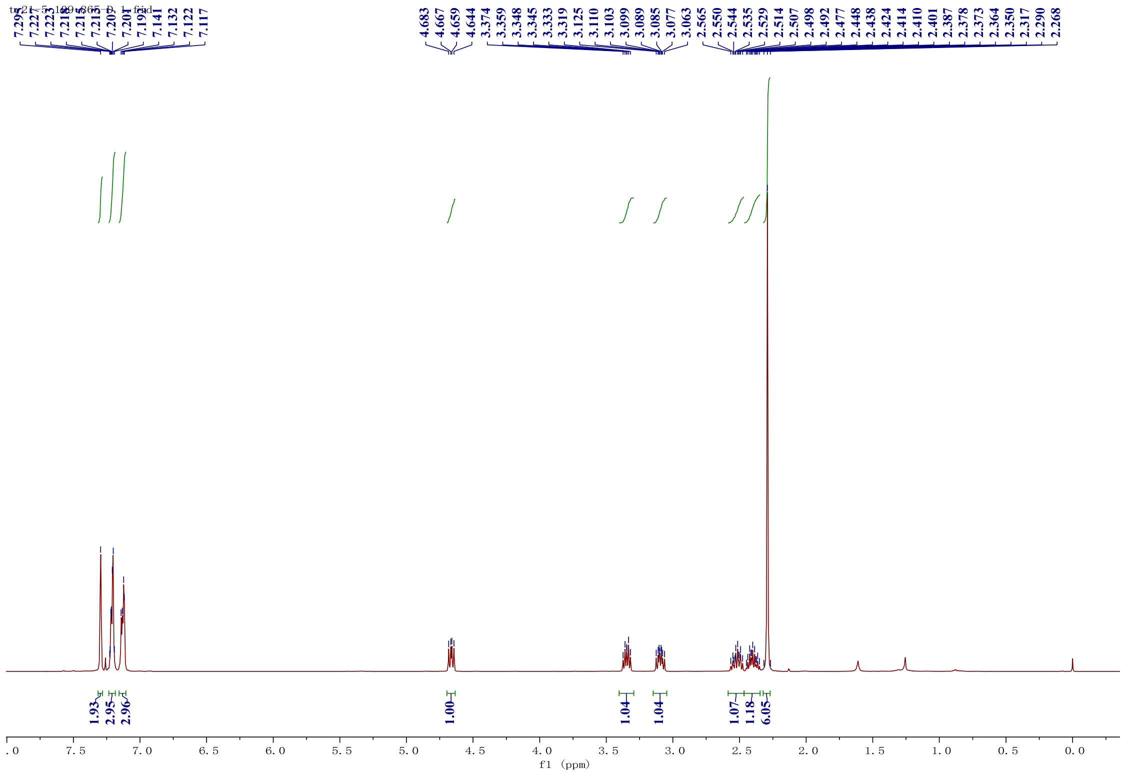
15

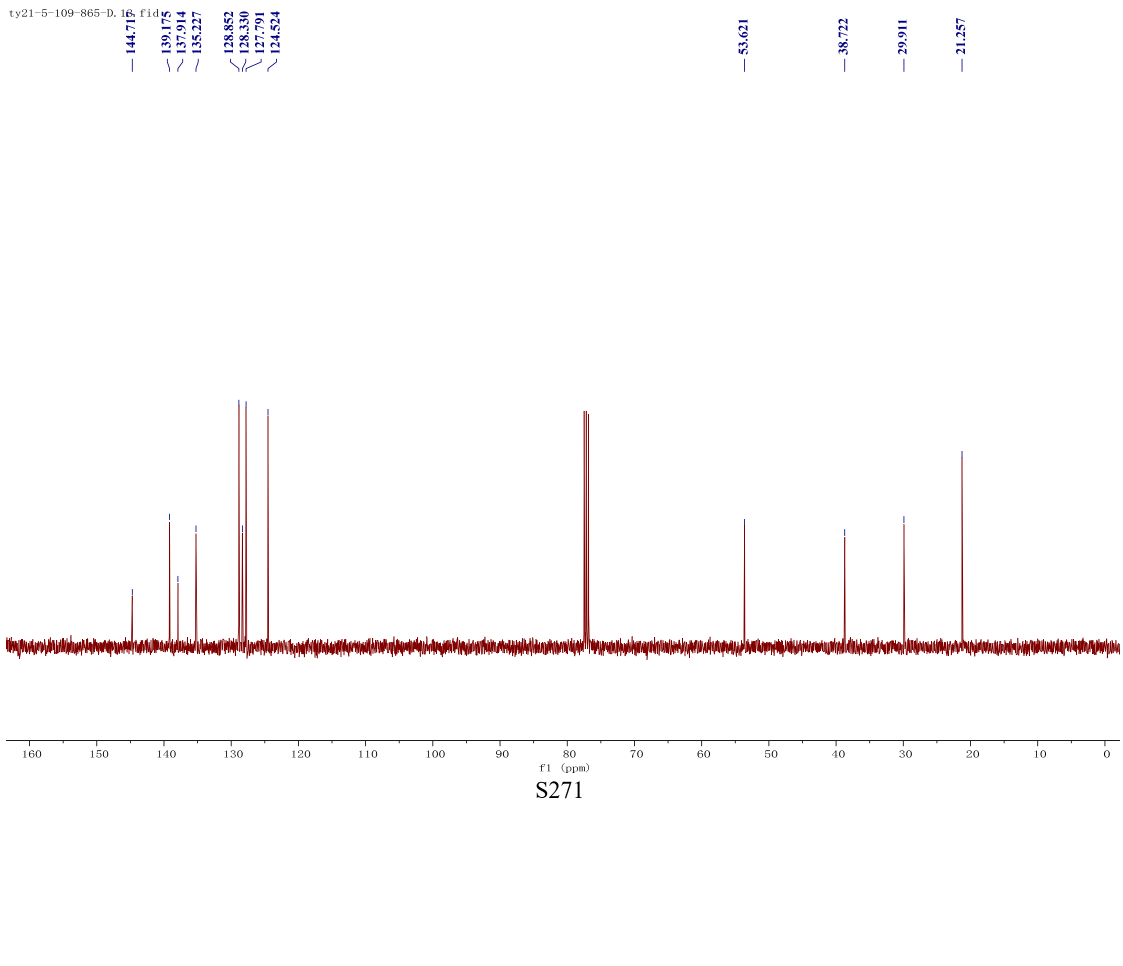


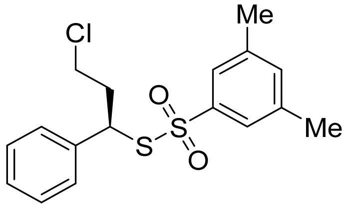



Br
O
S
S
O
Me
Me

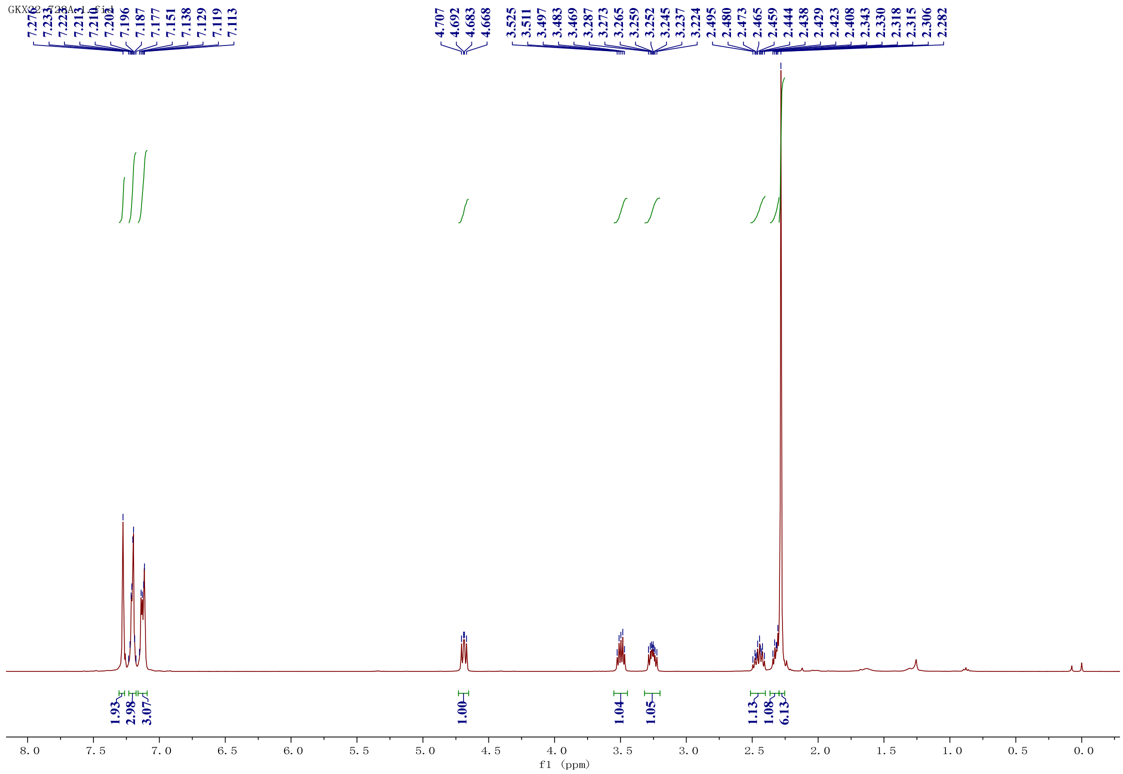
16

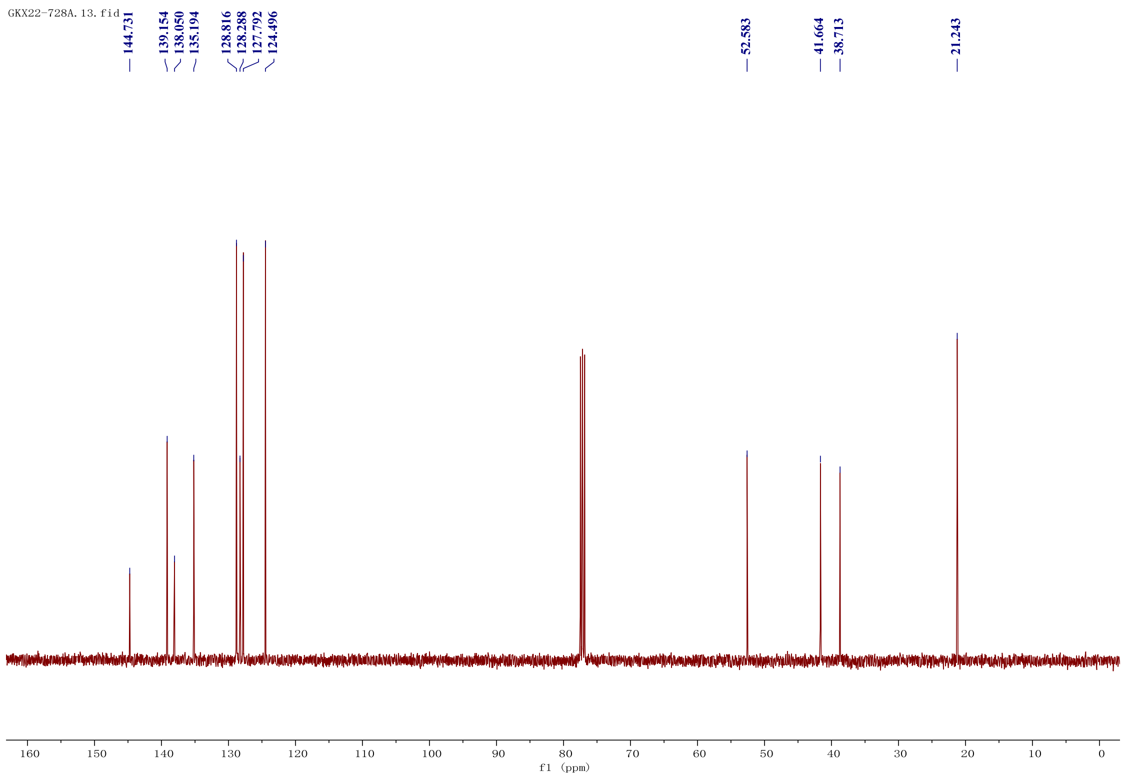

7.297
7.227
7.223
7.218
7.215
7.213
7.202
7.201
7.193
7.141
7.132
7.122
7.117
4.683
4.667
4.659
4.644
3.374
3.359
3.348
3.345
3.333
3.319
3.125
3.110
3.103
3.099
3.089
3.085
3.077
3.063
2.565
2.550
2.544
2.535
2.529
2.514
2.507
2.498
2.492
2.477
2.448
2.438
2.424
2.414
2.410
2.401
2.387
2.378
2.373
2.364
2.350
2.317
2.290
2.268
1.93
2.95
2.96
1.00
1.04
1.04
1.07
1.18
6.05
f1 (ppm)

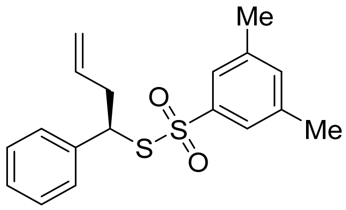

ty21-5-109-865-D.10.fid
144.715
139.175
137.914
135.227
128.852
128.330
127.791
124.524
53.621
38.722
29.911
21.257
f1 (ppm)



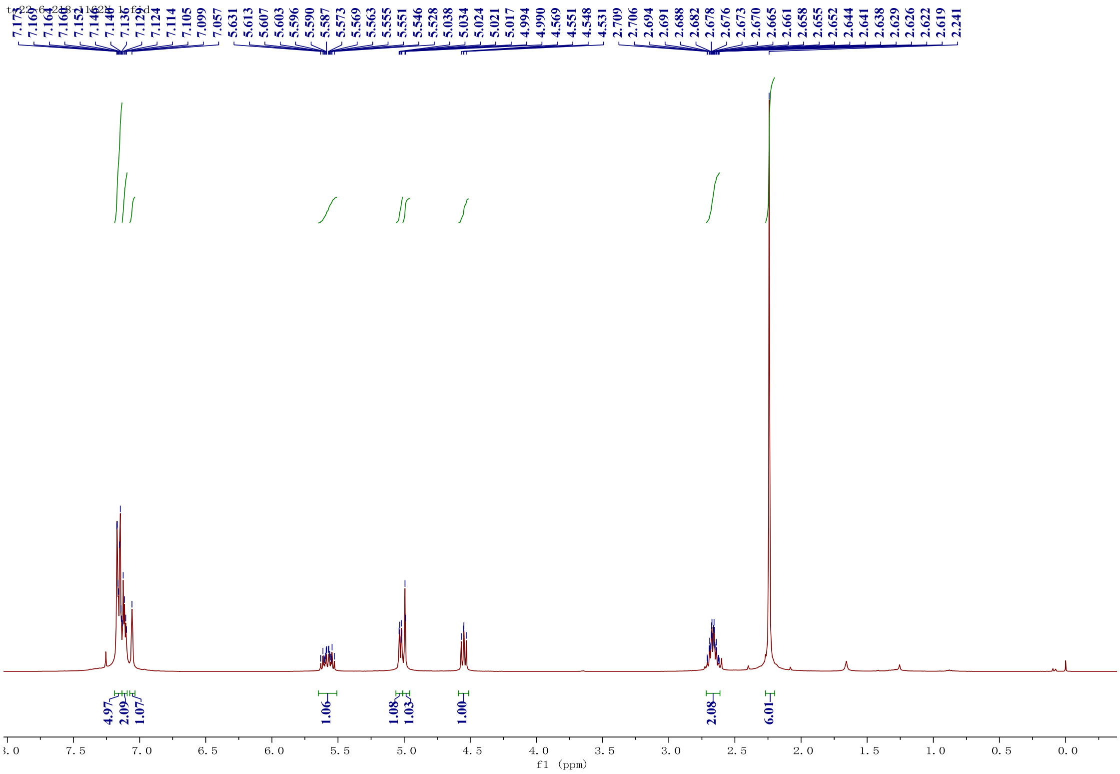
17

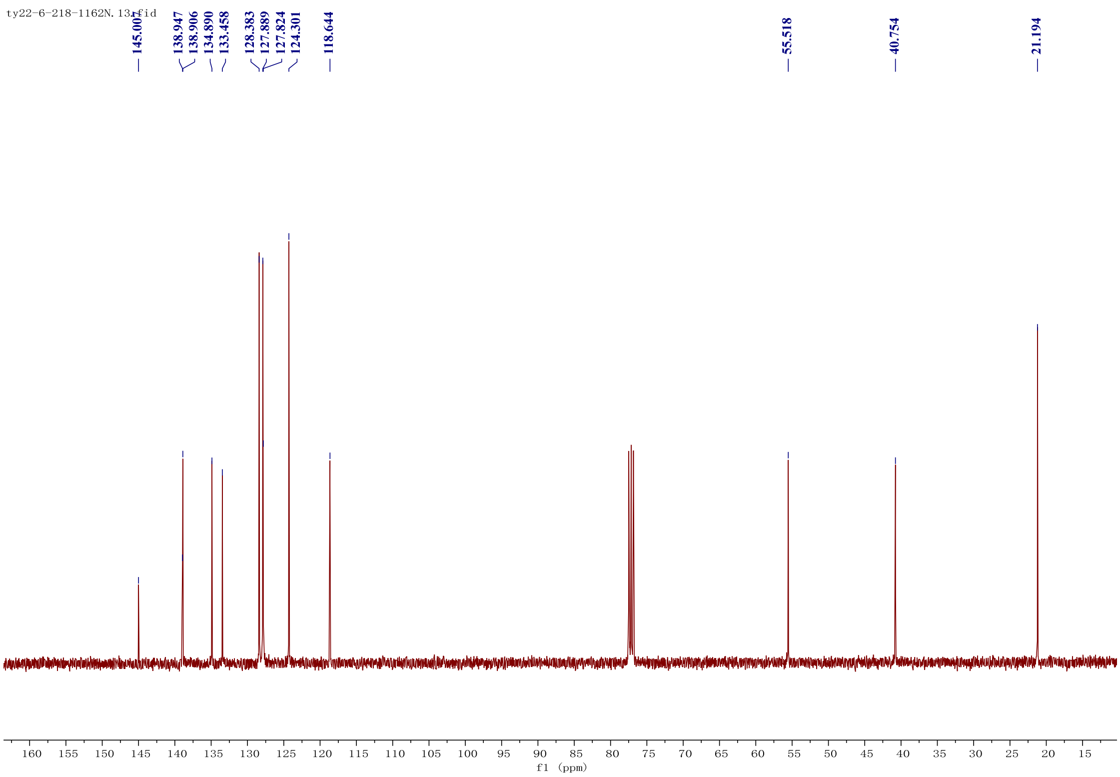


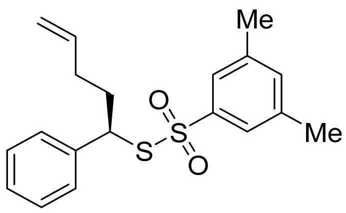



Me
O
S
S
O
Me

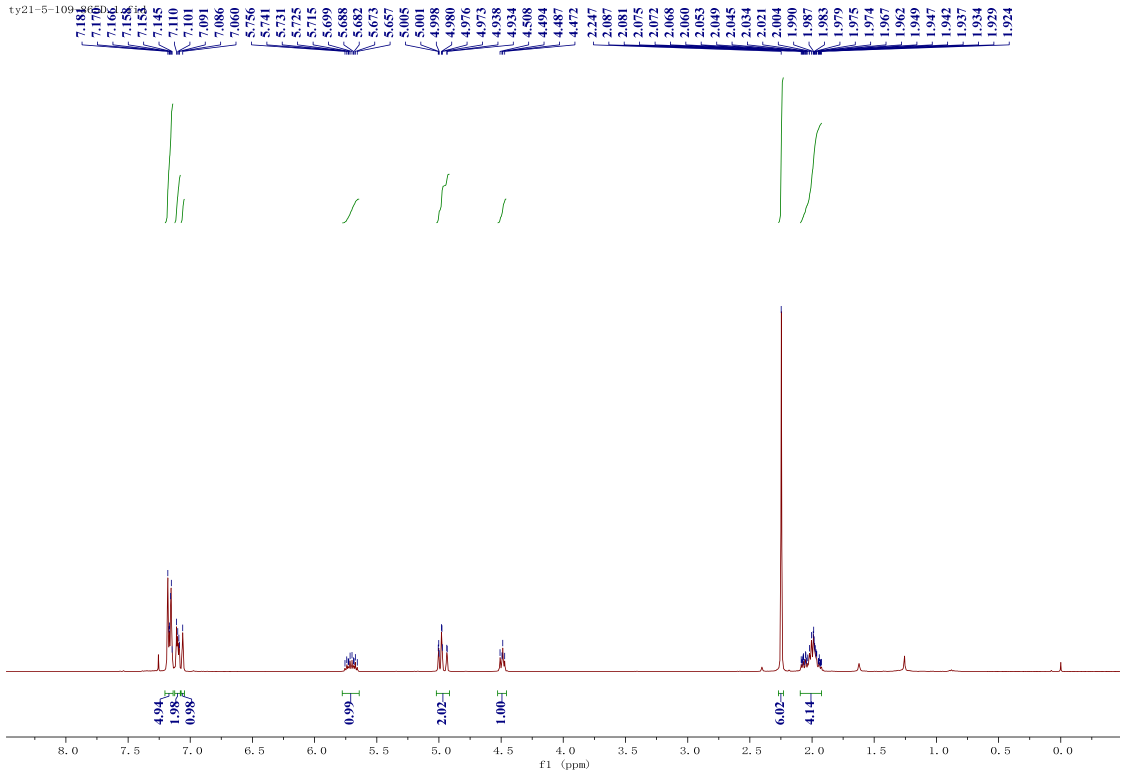
18

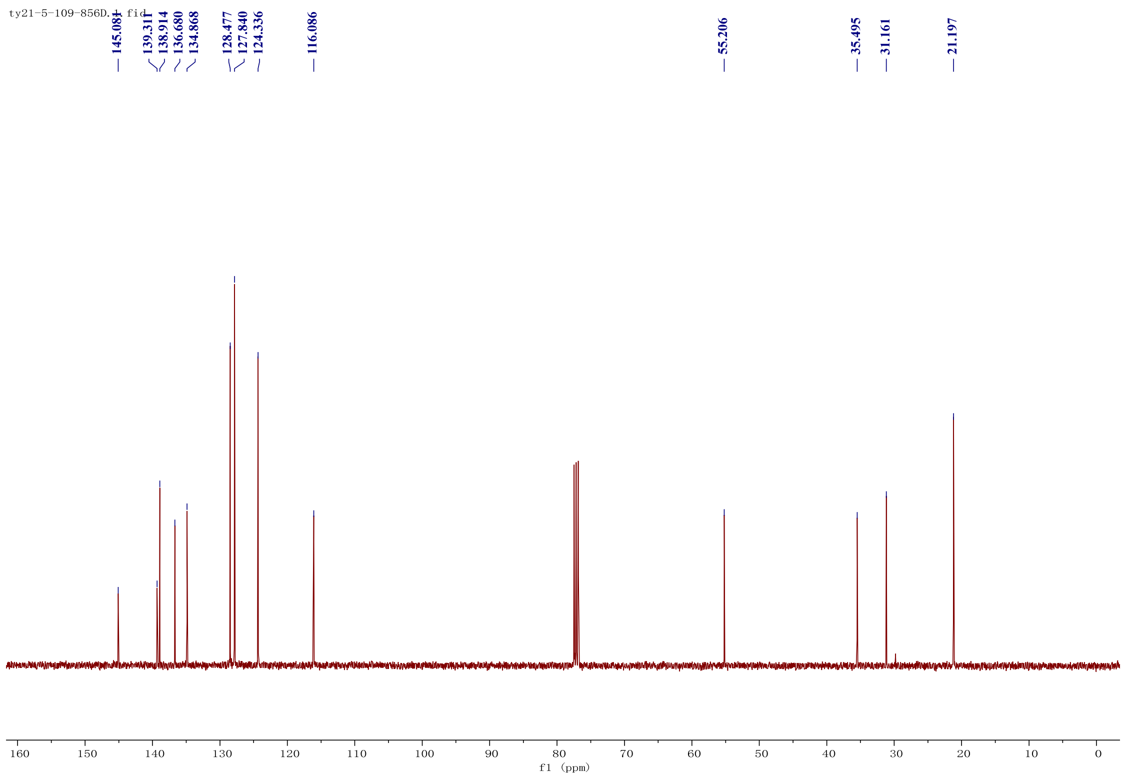

ty22-6-218-1162N.1.fid
7.173 7.167 7.164 7.160 7.152 7.148 7.140 7.136 7.129 7.124 7.114 7.105 7.099 7.057 5.631 5.613 5.607 5.603 5.596 5.590 5.587 5.573 5.569 5.563 5.555 5.551 5.546 5.528 5.038 5.034 5.024 5.021 5.017 4.994 4.990 4.569 4.551 4.548 4.531 2.709 2.706 2.694 2.691 2.688 2.682 2.678 2.676 2.673 2.670 2.665 2.661 2.658 2.655 2.652 2.644 2.641 2.638 2.629 2.626 2.622 2.619 2.241
4.97
2.09
1.07
1.06
1.08
1.03
1.00
2.08
6.01
f1 (ppm)

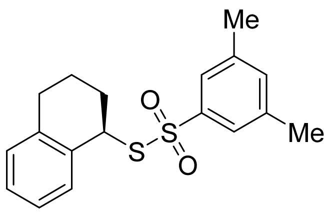

ty22-6-218-1162N.13.fid
145.001
138.947
138.906
134.890
133.458
128.383
127.889
127.824
124.301
118.644
55.518
40.754
21.194
f1 (ppm)



19

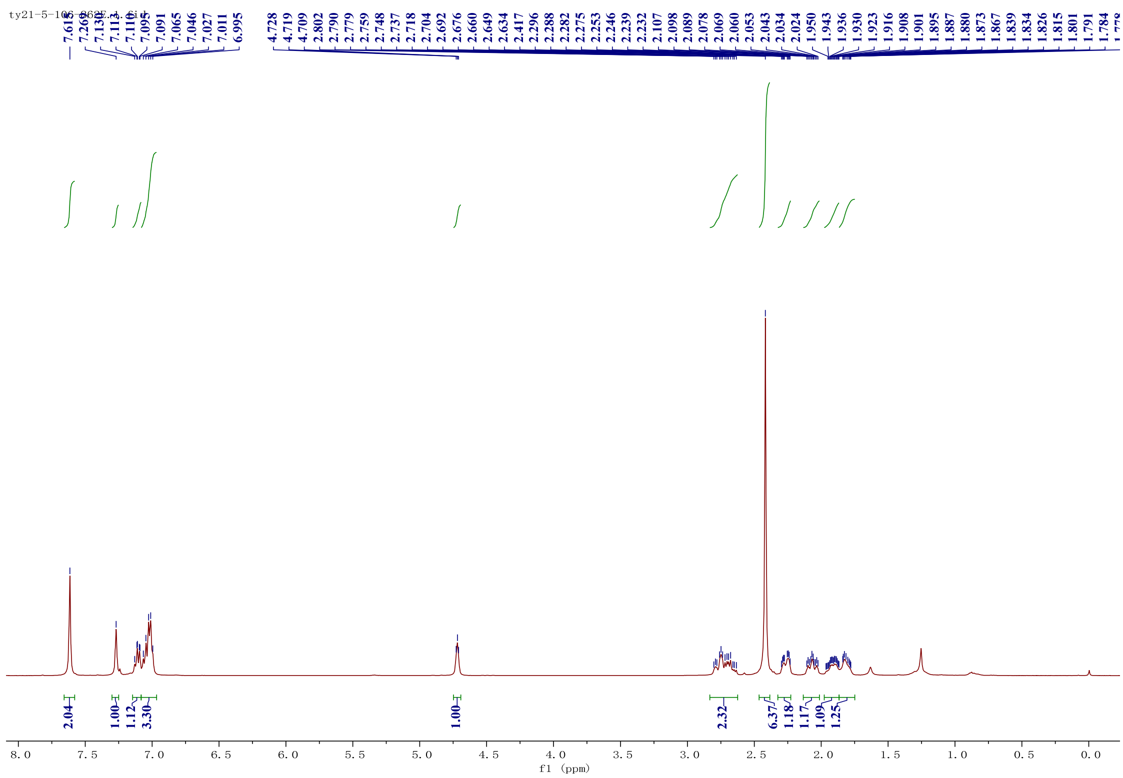




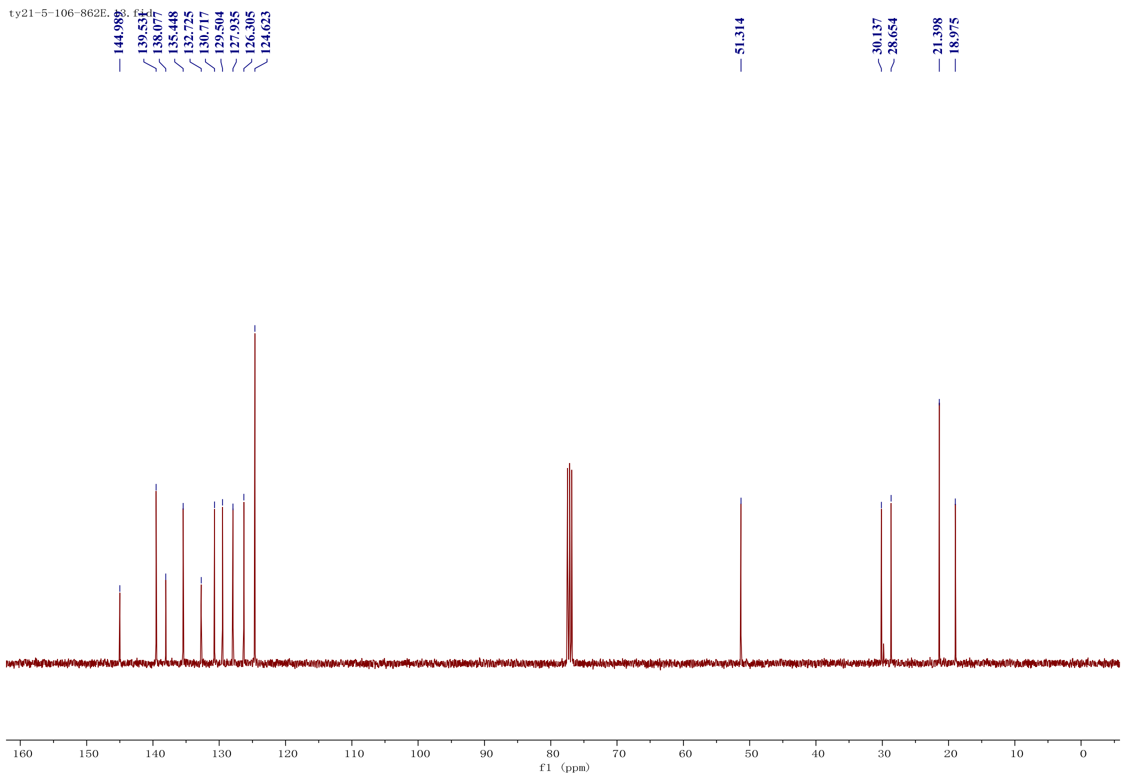


Me
O
S
S
O
Me

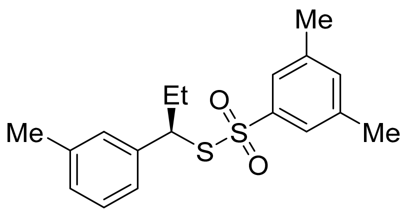
20



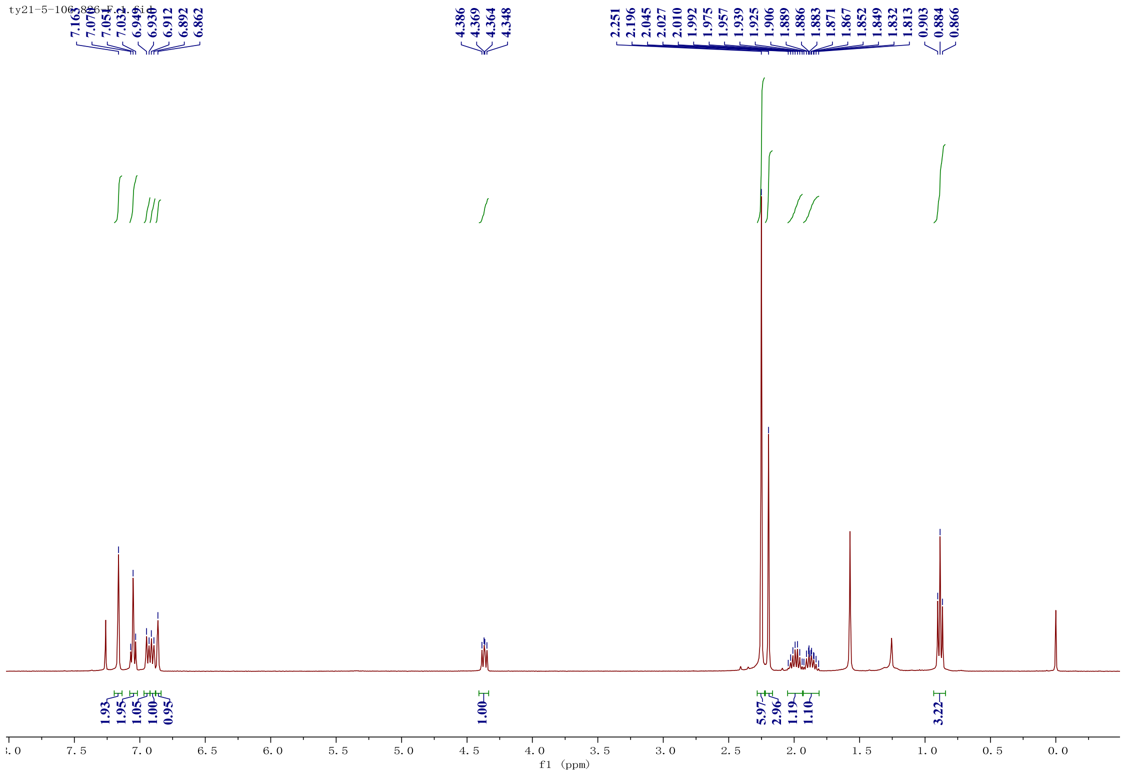
7.615
7.268
7.130
7.113
7.110
7.095
7.091
7.065
7.046
7.027
7.011
6.995
4.728
4.719
4.709
2.802
2.790
2.779
2.759
2.748
2.737
2.718
2.704
2.692
2.676
2.660
2.649
2.634
2.417
2.296
2.288
2.282
2.275
2.253
2.246
2.239
2.232
2.107
2.098
2.089
2.078
2.069
2.060
2.053
2.043
2.034
2.024
1.950
1.943
1.936
1.930
1.923
1.916
1.908
1.901
1.895
1.887
1.880
1.873
1.867
1.839
1.834
1.826
1.815
1.801
1.791
1.784
2.04
1.00
1.12
3.30
1.00
2.32
6.37
1.18
1.17
1.09
1.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

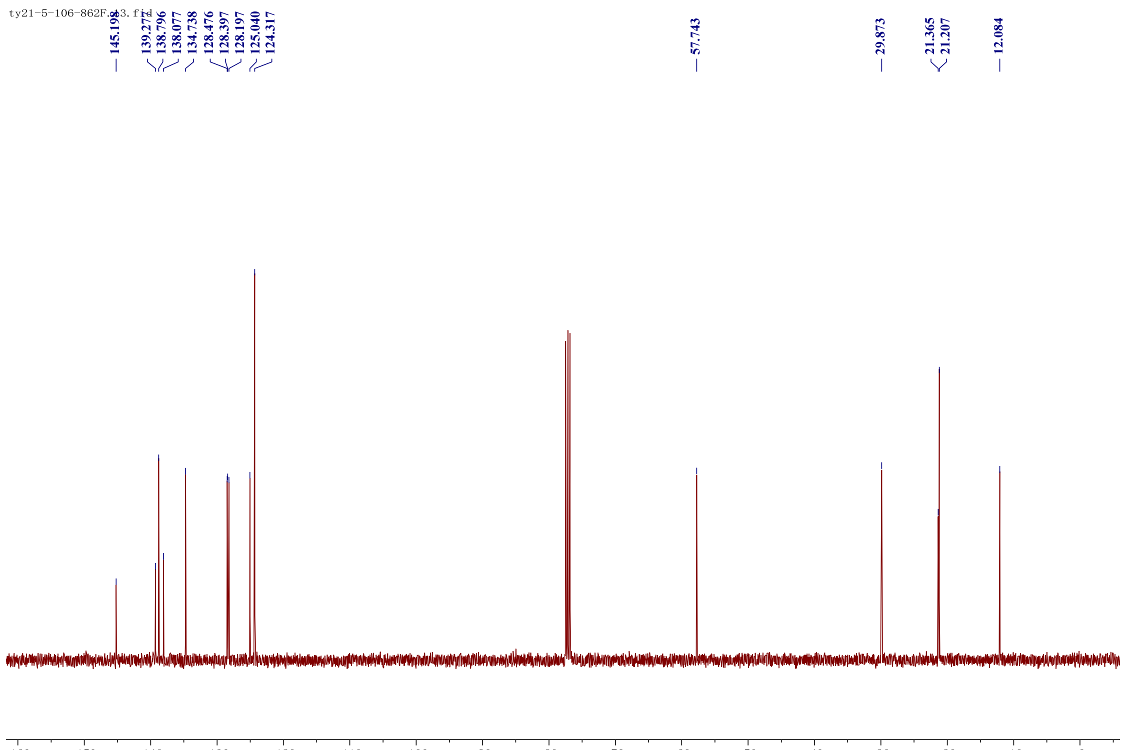


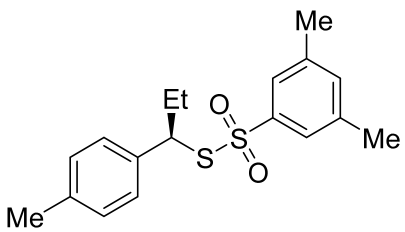
ty21-5-106-862E.13.fid
144.989
139.534
138.077
135.448
132.725
130.717
129.504
127.935
126.305
124.623
51.314
30.137
28.654
21.398
18.975
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



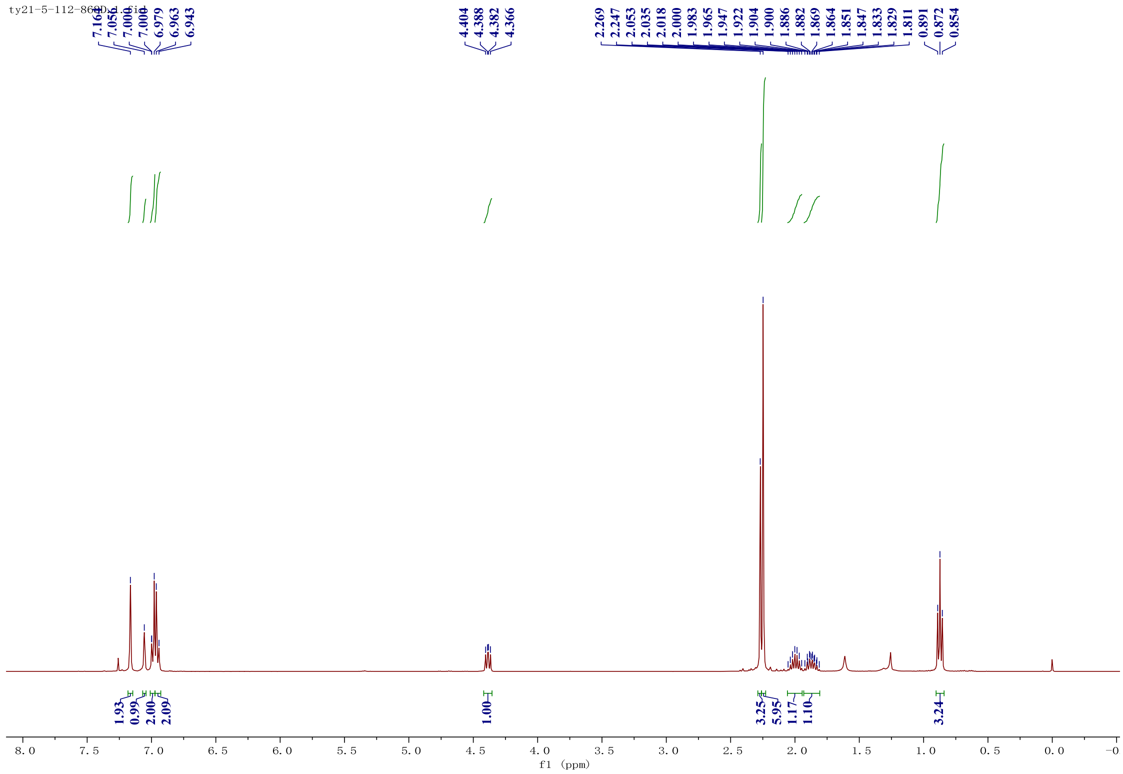
21

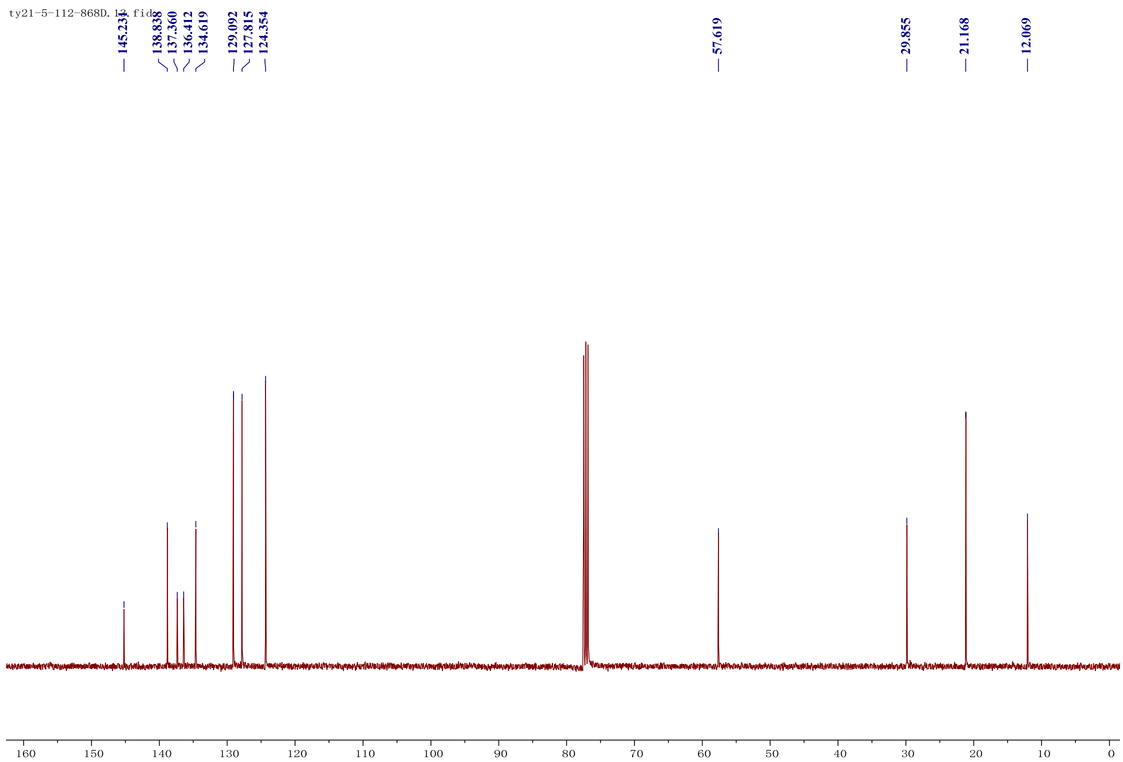


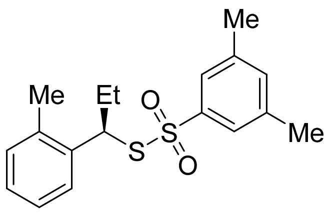




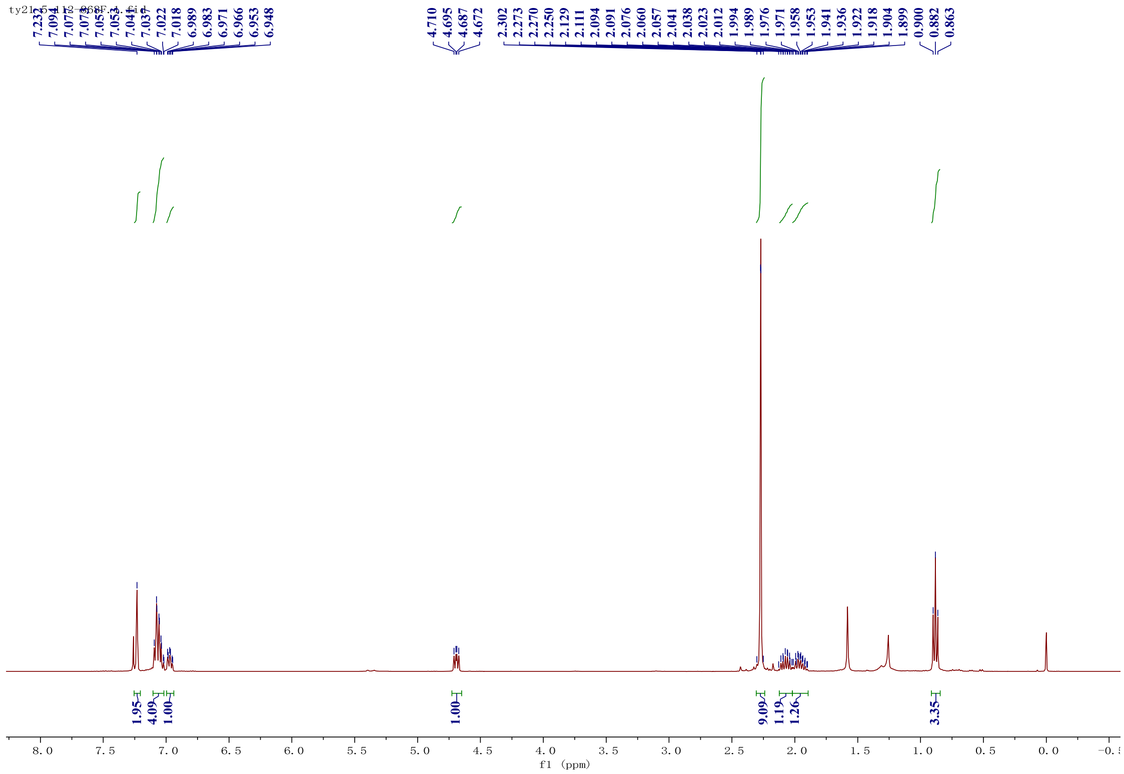
22

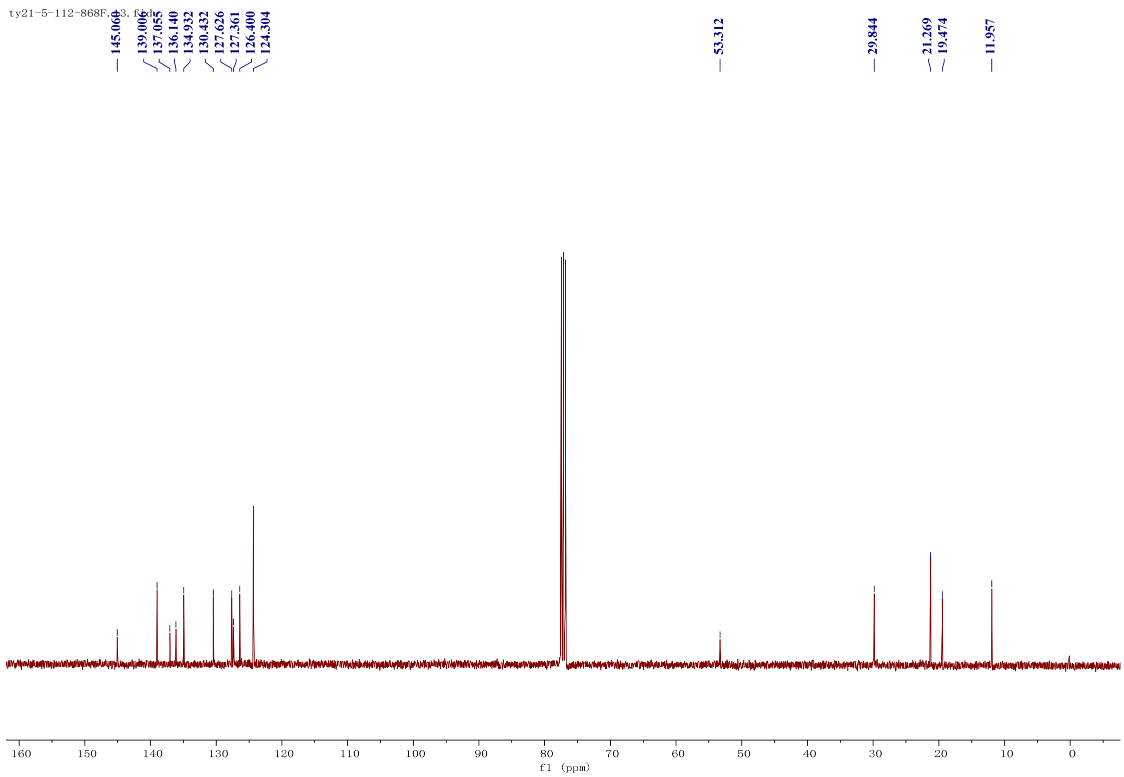


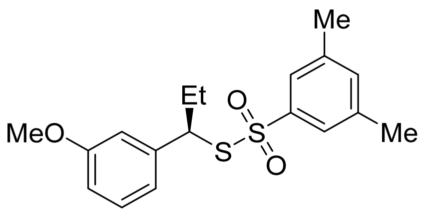




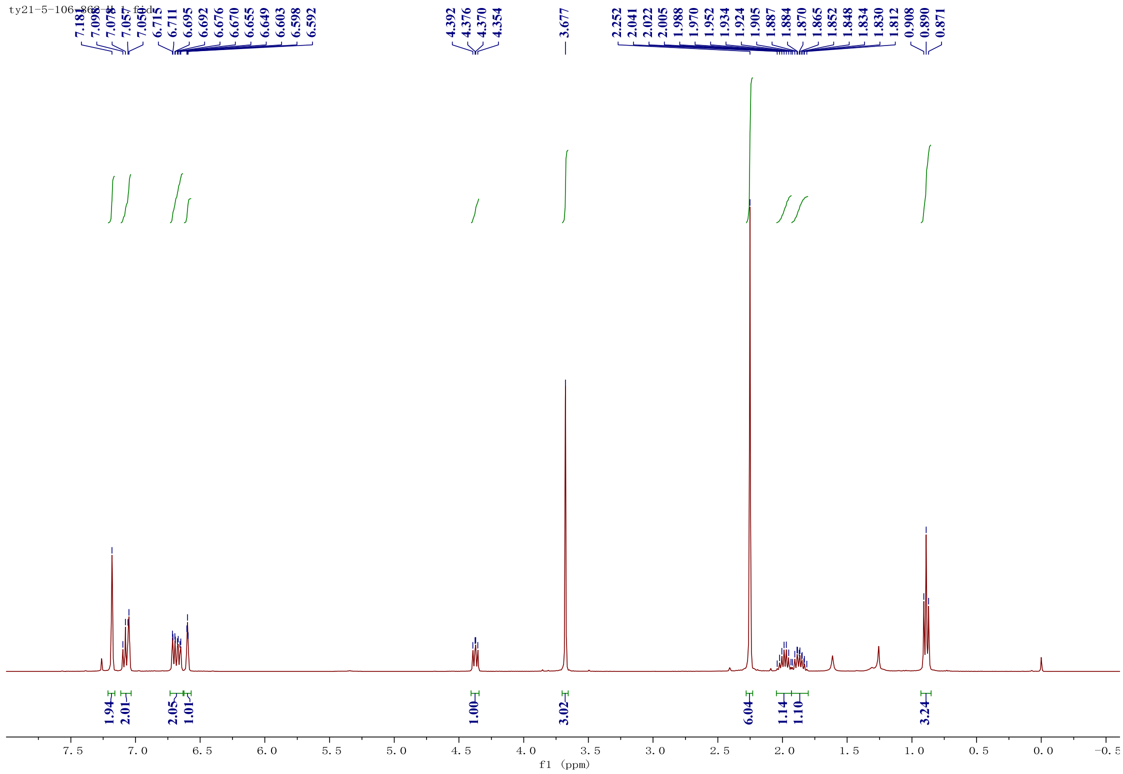
23

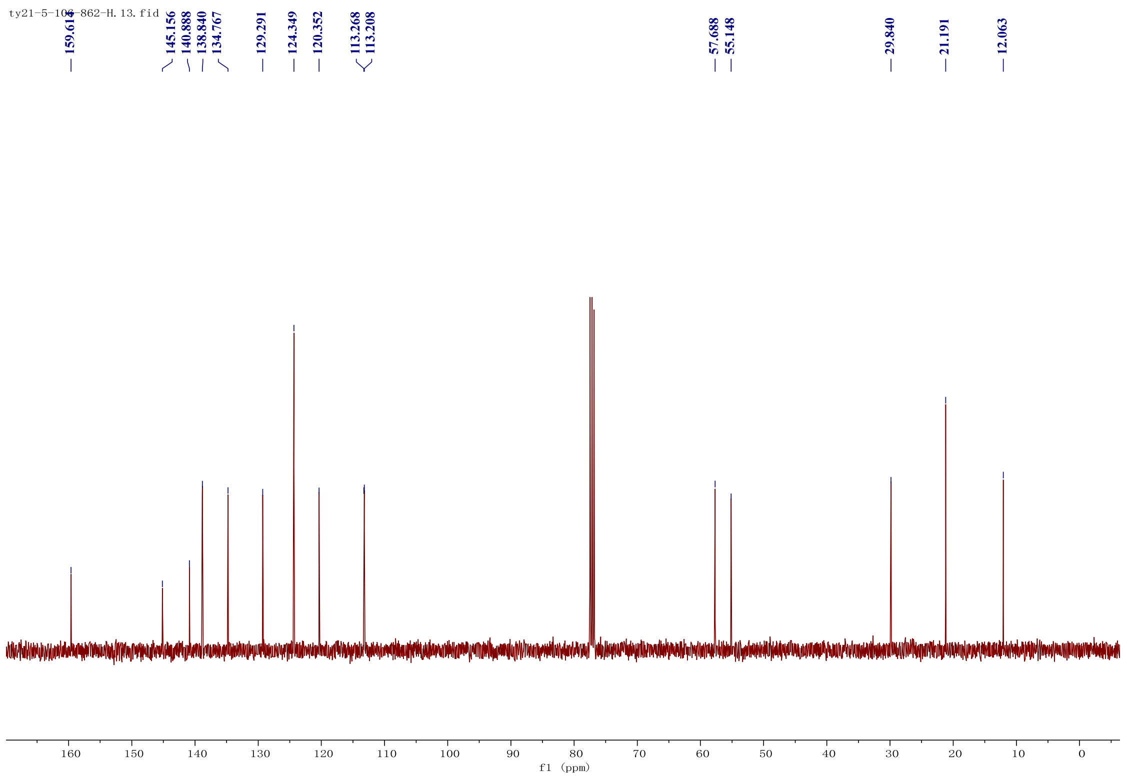

ty21-5-112-868F.1.fid
7.231 7.094 7.075 7.071 7.058 7.053 7.041 7.037 7.022 7.018 6.989 6.983 6.971 6.966 6.953 6.948
4.710 4.695 4.687 4.672
2.302 2.273 2.270 2.250 2.129 2.111 2.094 2.091 2.076 2.060 2.057 2.041 2.038 2.023 2.012 1.994 1.989 1.976 1.971 1.958 1.953 1.941 1.936 1.922 1.918 1.904 1.899
0.900 0.882 0.863
1.95 4.09 1.00 1.00 9.09 1.19 1.26 3.35
f1 (ppm)

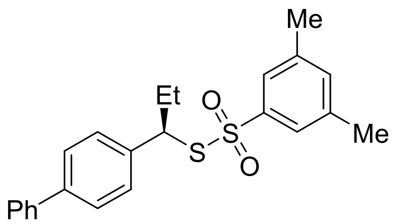

ty21-5-112-868F.13.fid
145.060 139.006 137.055 136.140 134.932 130.432 127.626 127.361 126.400 124.304
53.312
29.844
21.269 19.474
11.957
f1 (ppm)



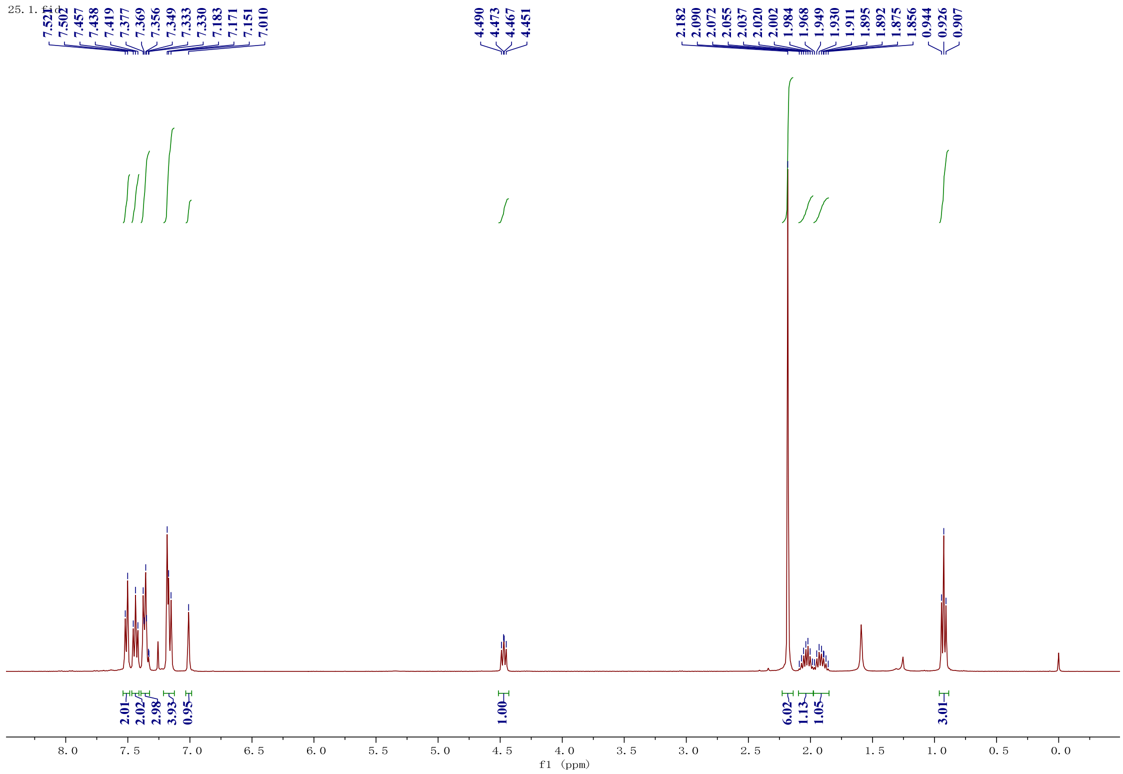
24

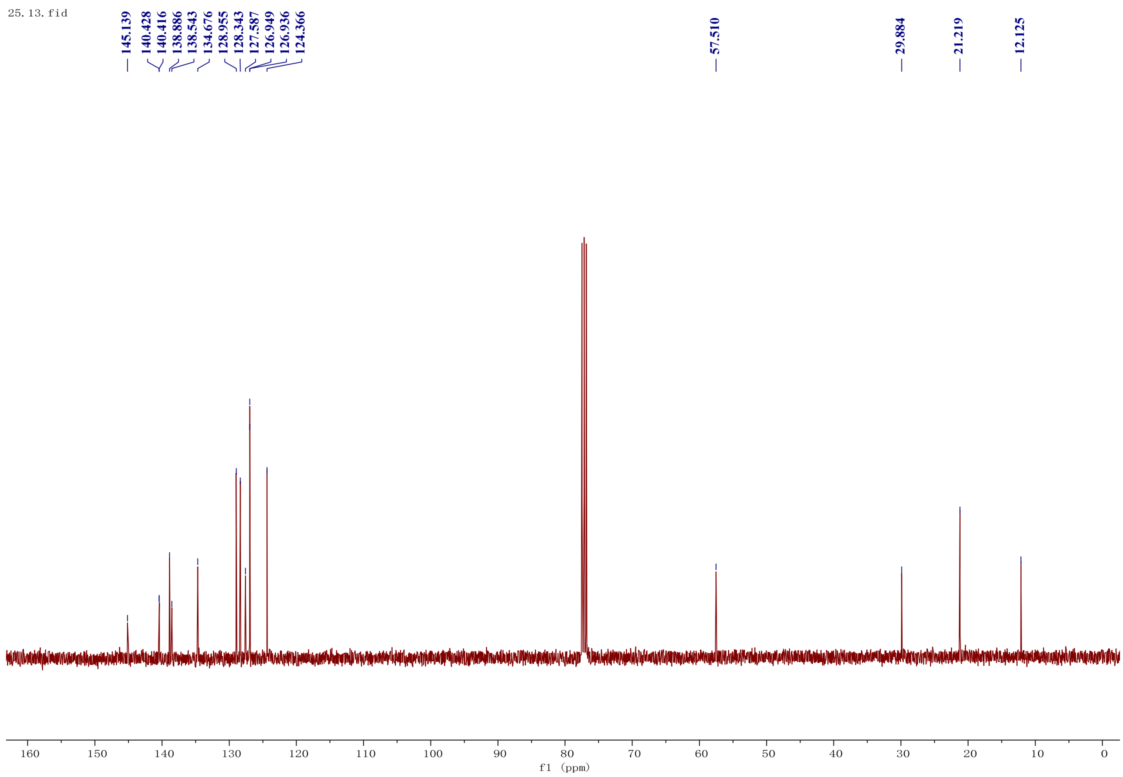


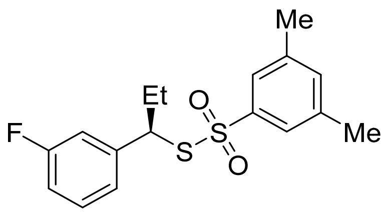



Me
Et
O
S
S
O
Me
Ph

25

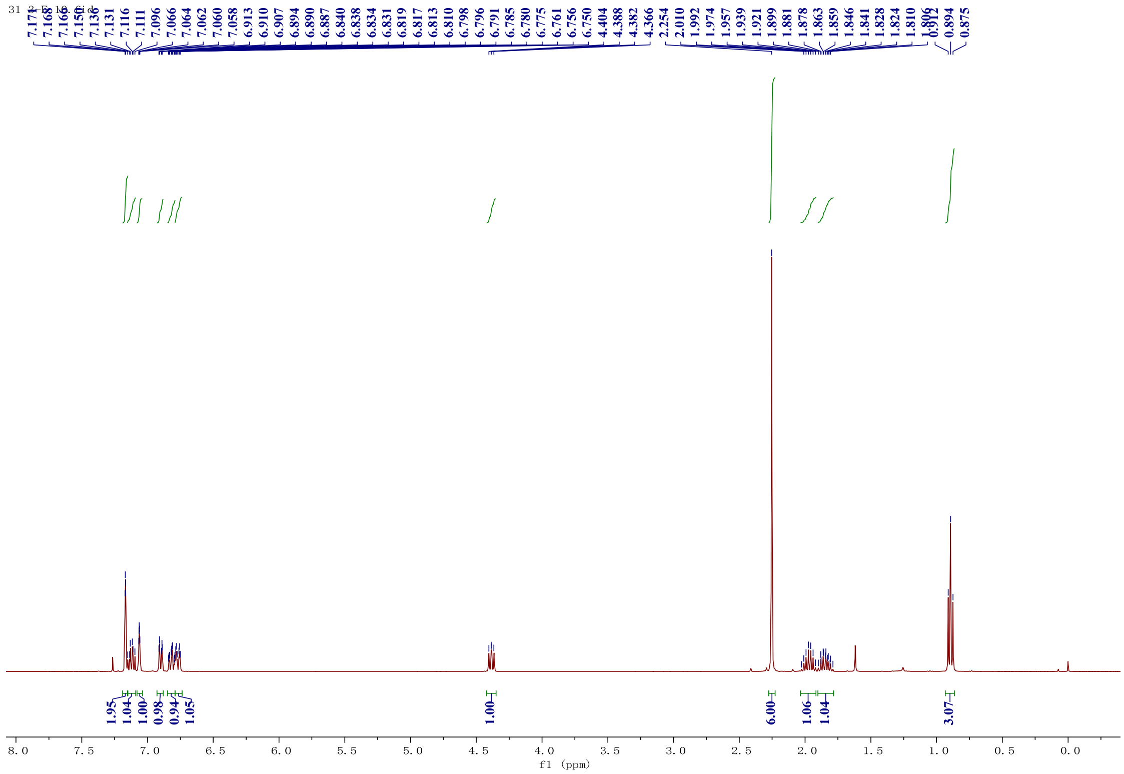

25.1.fid
7.521 7.502 7.457 7.438 7.419 7.377 7.369 7.356 7.349 7.333 7.330 7.183 7.171 7.151 7.010
4.490 4.473 4.467 4.451
2.182 2.090 2.072 2.055 2.037 2.020 2.002 1.984 1.968 1.949 1.930 1.911 1.895 1.892 1.875 1.856 0.944 0.926 0.907
2.01 2.02 2.98 3.93 0.95
1.00
6.02 1.13 1.05
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


25.13.fid
145.139 140.428 140.416 138.886 138.543 134.676 128.955 128.343 127.587 126.949 126.936 124.366
57.510
29.884
21.219
12.125
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

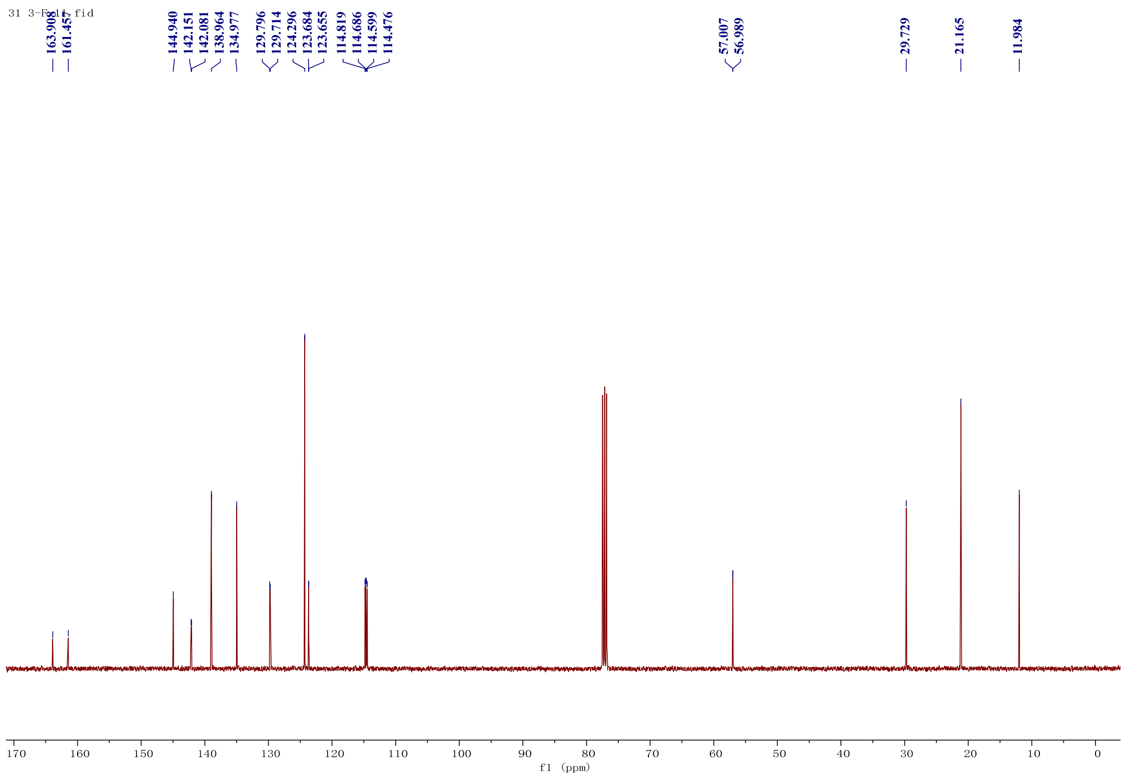


F
Et
O
S
S
O
Me
Me

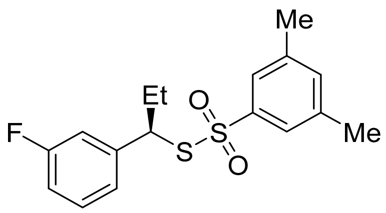
26



7.171 7.168 7.160 7.150 7.136 7.131 7.116 7.111 7.096 7.066 7.064 7.062 7.060 7.058 6.913 6.910 6.907 6.894 6.890 6.887 6.840 6.838 6.834 6.831 6.819 6.817 6.813 6.810 6.798 6.796 6.791 6.785 6.780 6.775 6.761 6.756 6.750 4.404 4.388 4.382 4.366 2.254 2.010 1.992 1.974 1.957 1.939 1.921 1.899 1.881 1.878 1.863 1.859 1.846 1.841 1.828 1.824 1.810 1.806 0.912 0.894 0.875
1.95 1.04 1.00 0.98 0.94 1.05 1.00 6.00 1.06 1.04 3.07
f1 (ppm)

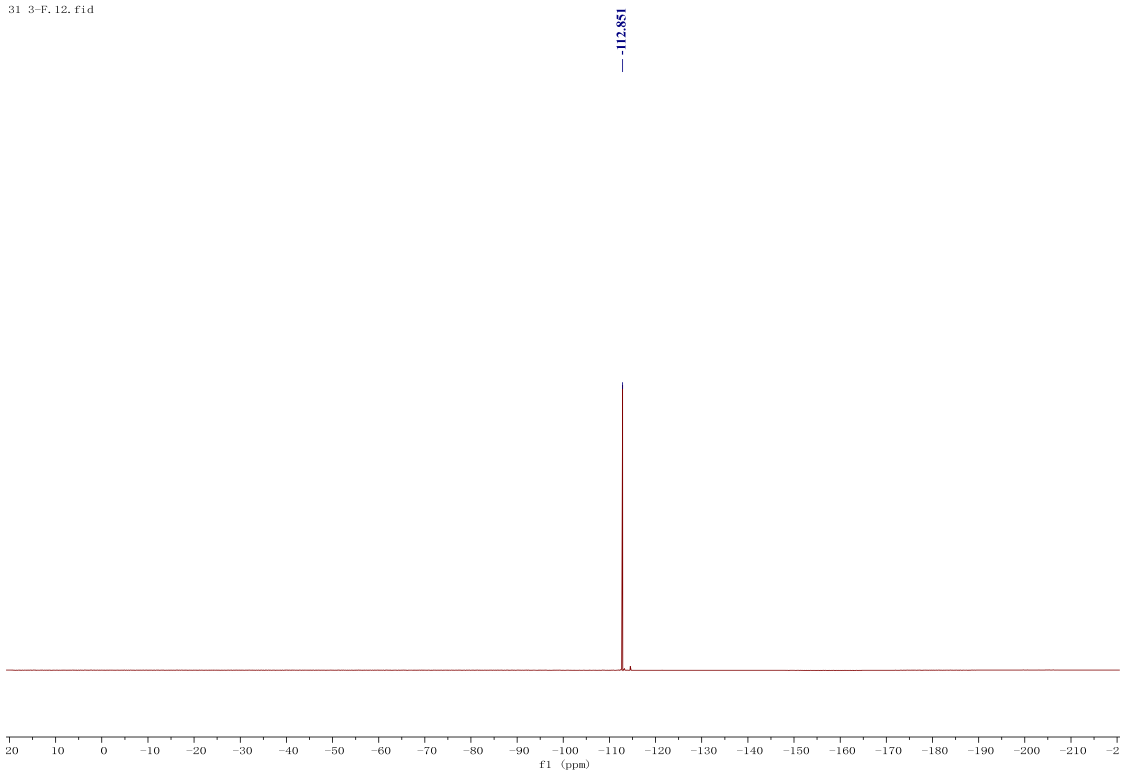


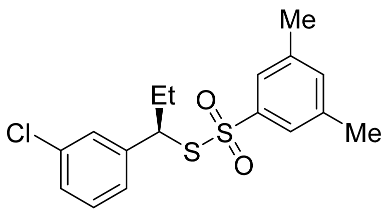
163.908 161.457 144.940 142.151 142.081 138.964 134.977 129.796 129.714 124.296 123.684 123.655 114.819 114.686 114.599 114.476 57.007 56.989 29.729 21.165 11.984
f1 (ppm)



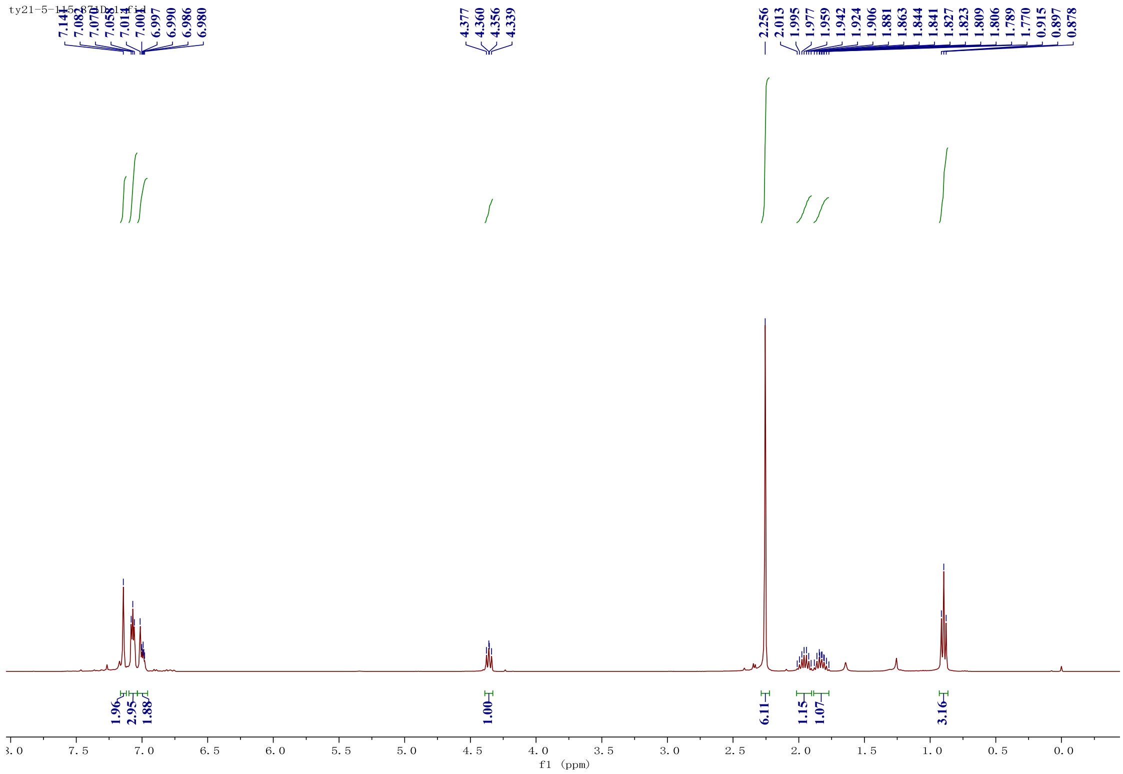
26

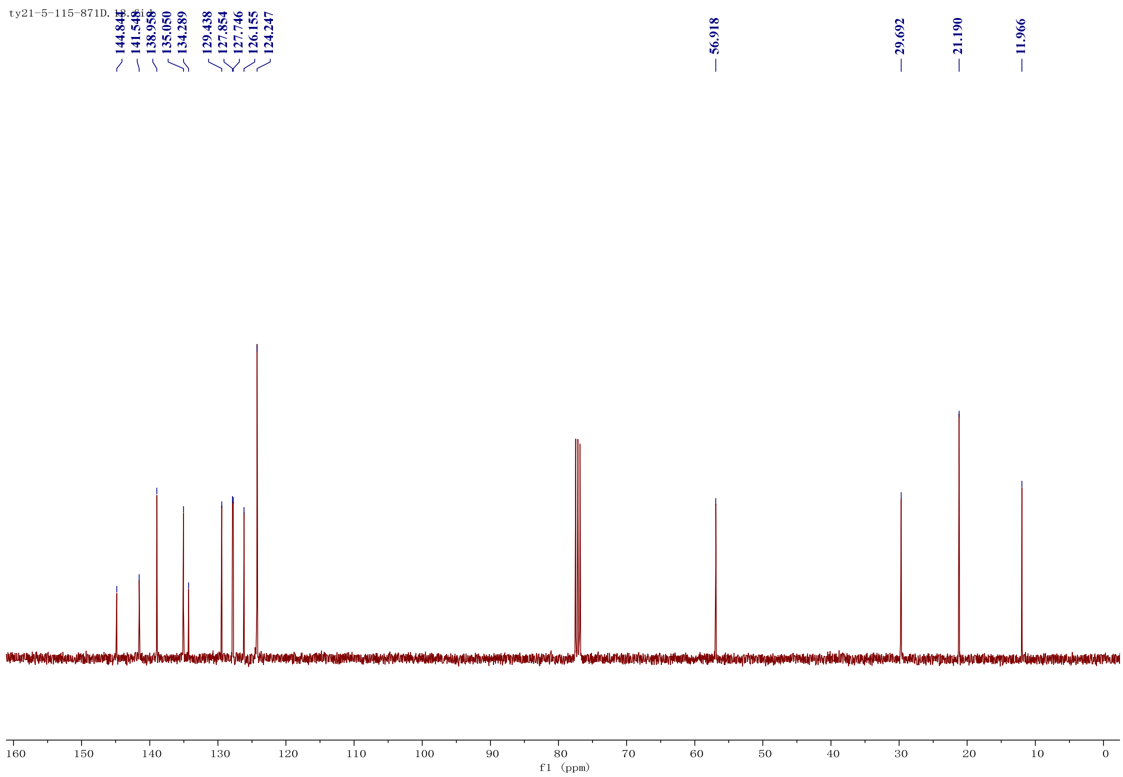
31 3-F.12.fid

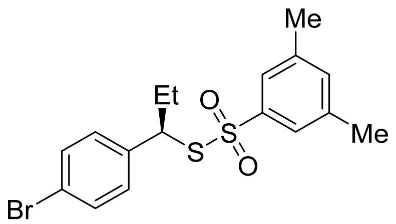



Me
Et
O
Cl
S
S
O
Me

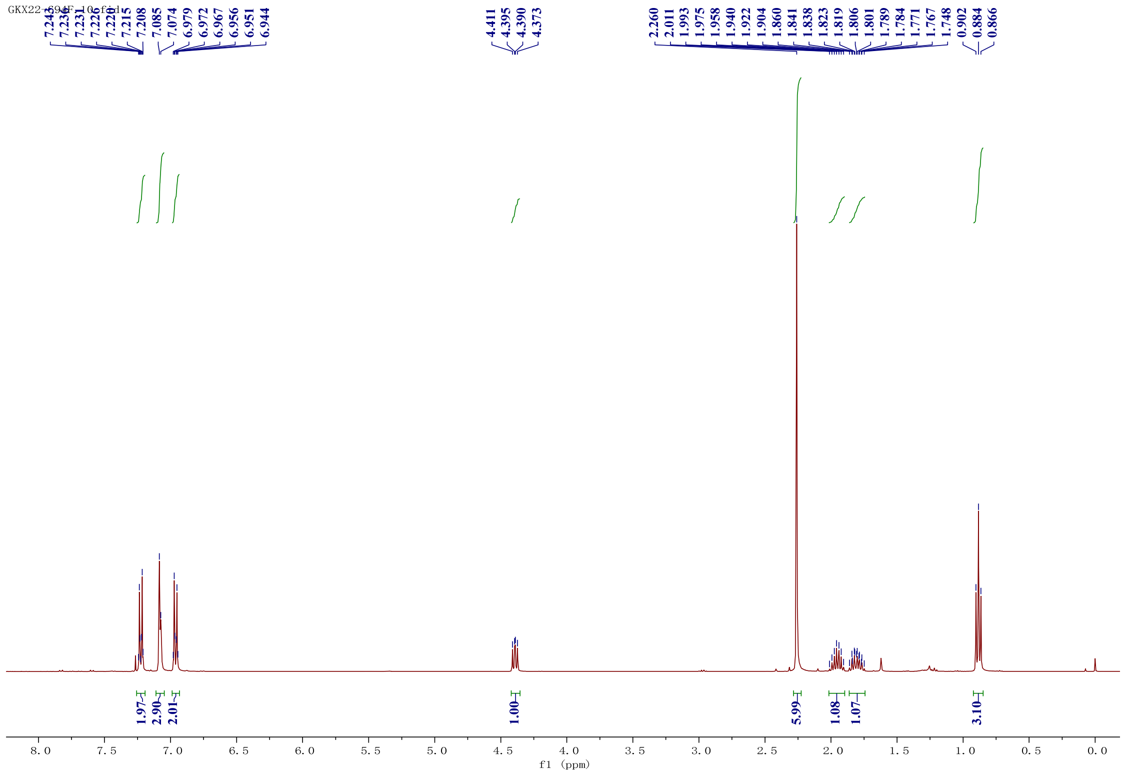
27

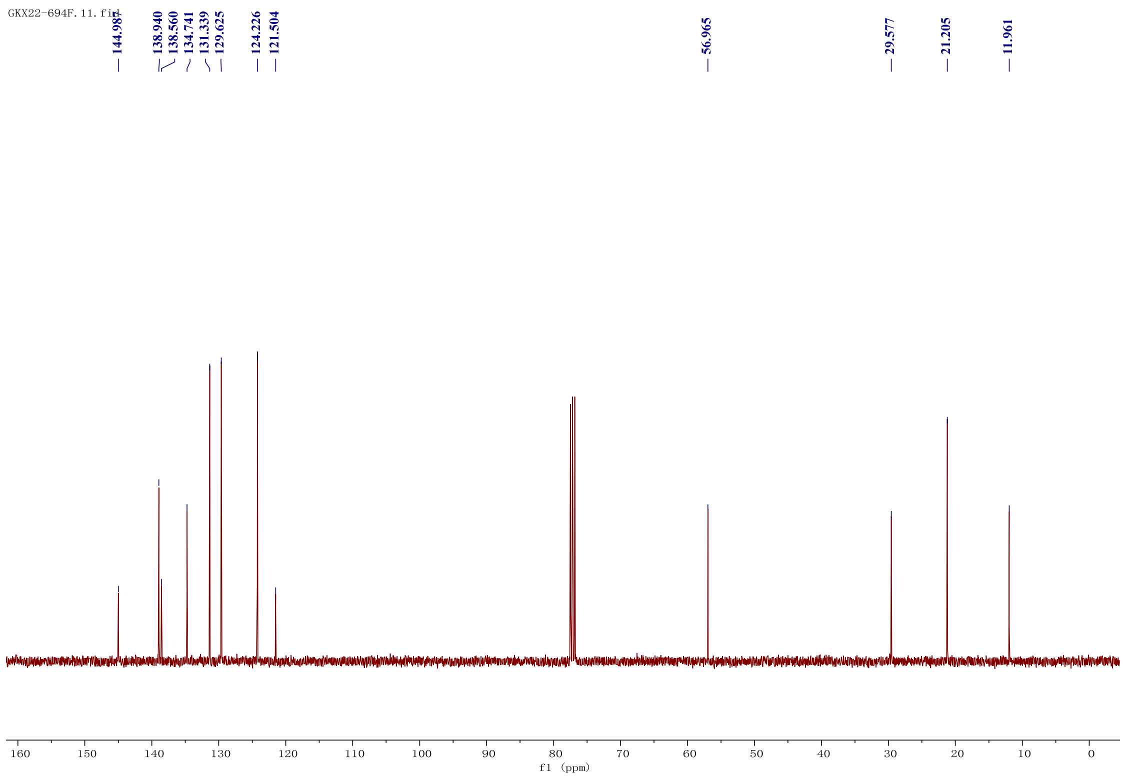

ty21-5-115-871D.1.fid
7.141
7.082
7.070
7.058
7.014
7.001
6.997
6.990
6.986
6.980
4.377
4.360
4.356
4.339
2.256
2.013
1.995
1.977
1.959
1.942
1.924
1.906
1.881
1.863
1.844
1.841
1.827
1.823
1.809
1.806
1.789
1.770
0.915
0.897
0.878
1.96
2.95
1.88
1.00
6.11
1.15
1.07
3.16
f1 (ppm)

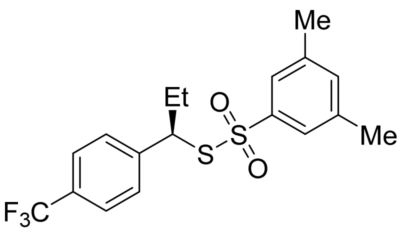

ty21-5-115-871D.13.fid
144.844
141.549
138.958
135.050
134.289
129.438
127.854
127.746
126.155
124.247
56.918
29.692
21.190
11.966
f1 (ppm)


Me
Et
O
S
S
O
Me
Br

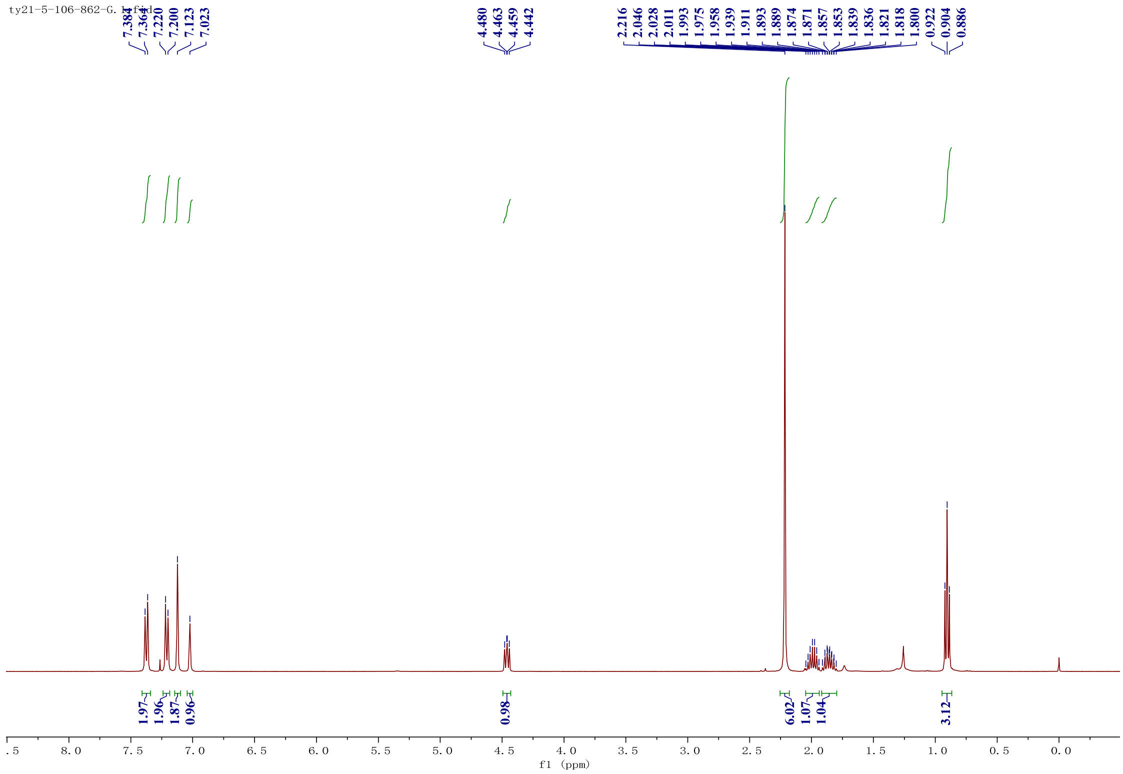
28

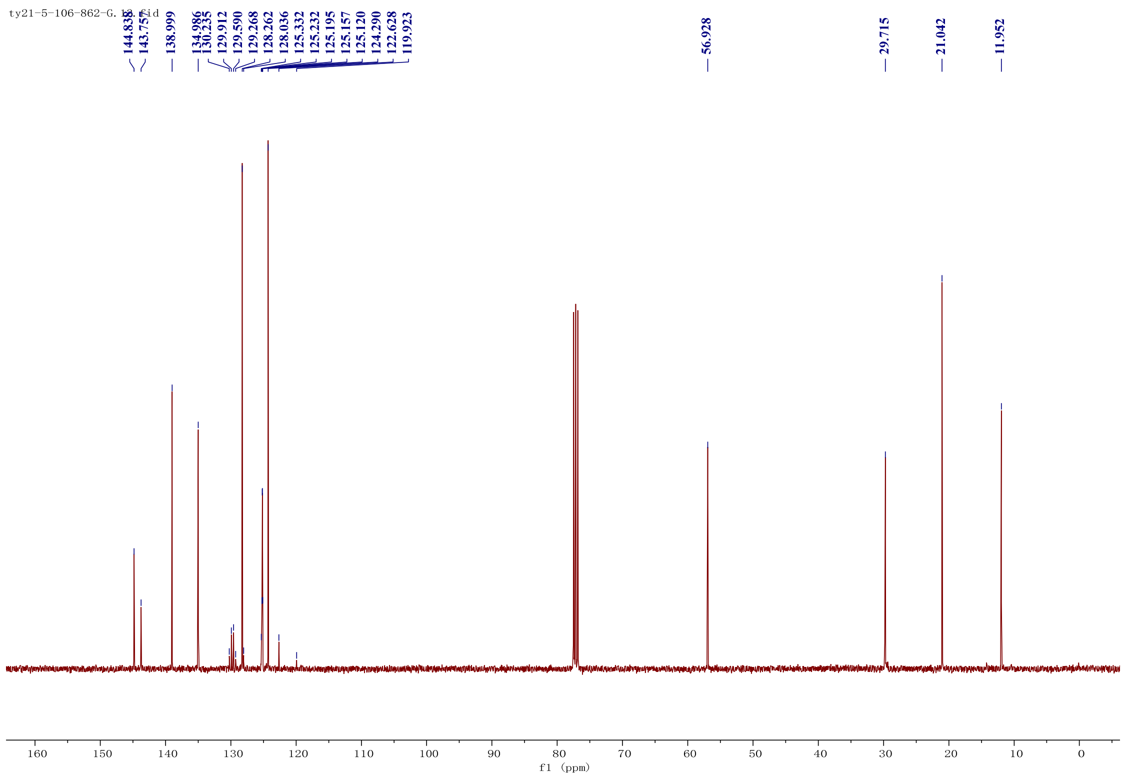

GKX22-694F.10.fid
7.243
7.236
7.231
7.226
7.220
7.215
7.208
7.085
7.074
6.979
6.972
6.967
6.956
6.951
6.944
4.411
4.395
4.390
4.373
2.260
2.011
1.993
1.975
1.958
1.940
1.922
1.904
1.860
1.841
1.838
1.823
1.819
1.806
1.801
1.789
1.784
1.771
1.767
1.748
0.902
0.884
0.866
1.97
2.90
2.01
1.00
5.99
1.08
1.07
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

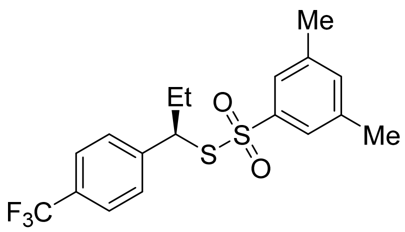

GKX22-694F.11.fid
144.987
138.940
138.560
134.741
131.339
129.625
124.226
121.504
56.965
29.577
21.205
11.961
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



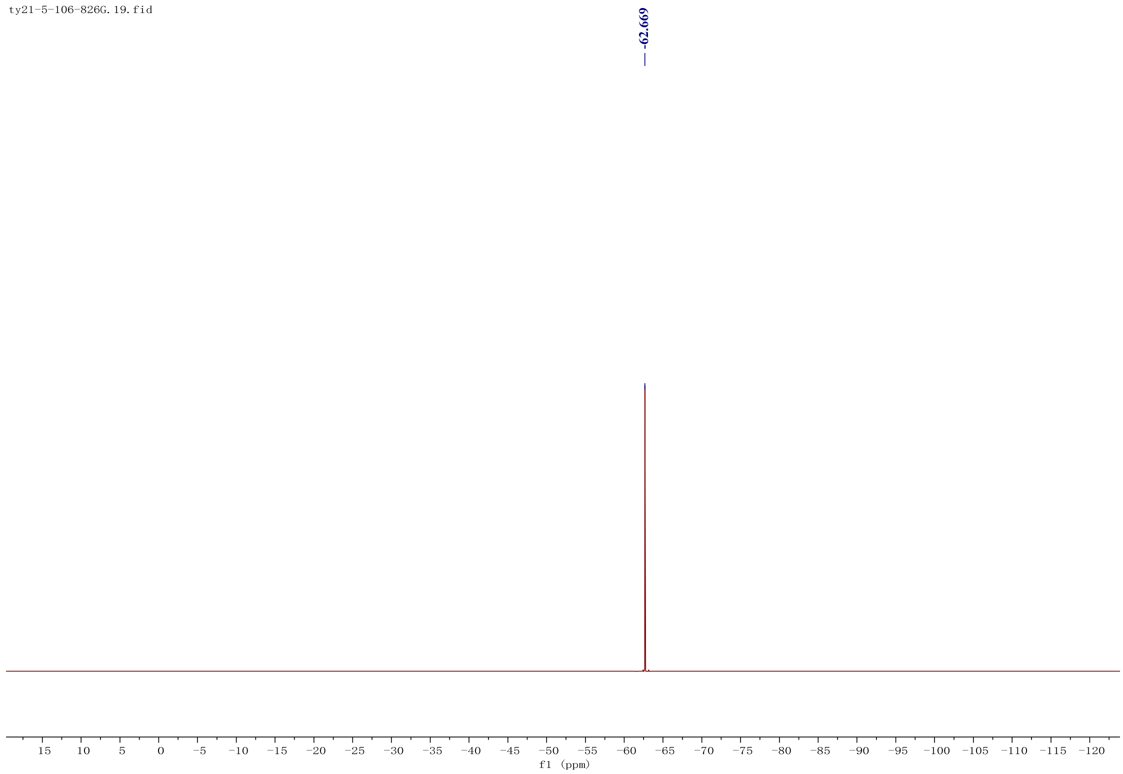
29

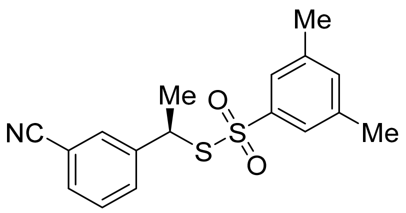

ty21-5-106-862-G.1.fid
7.384
7.364
7.220
7.200
7.123
7.023
4.480
4.463
4.459
4.442
2.216
2.046
2.028
2.011
1.993
1.975
1.958
1.939
1.911
1.893
1.889
1.874
1.871
1.857
1.853
1.839
1.836
1.821
1.818
1.800
0.922
0.904
0.886
1.97
1.96
1.87
0.96
0.98
6.02
1.07
1.04
3.12
f1 (ppm)


144.838
143.757
138.999
134.986
130.235
129.912
129.590
129.268
128.262
128.036
125.332
125.232
125.195
125.157
125.120
124.290
122.628
119.923
56.928
29.715
21.042
11.952
f1 (ppm)

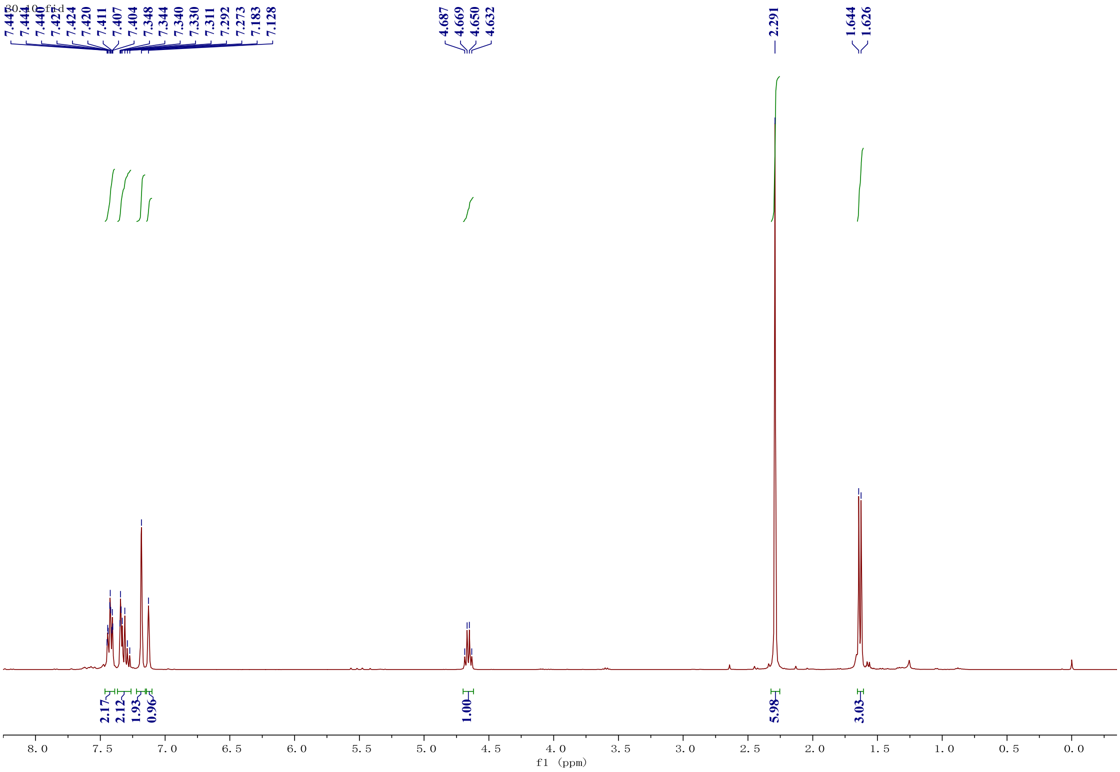

Me
Et
O
S
S
O
Me
F3C

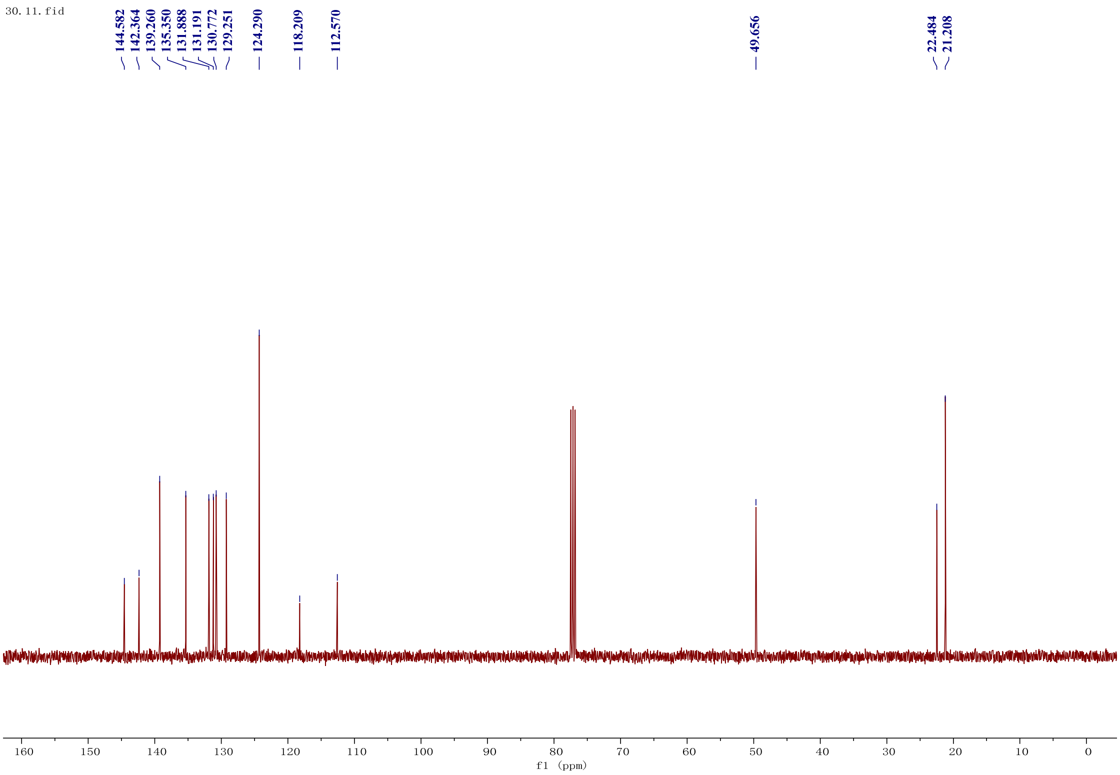
29

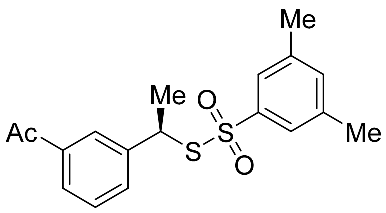

ty21-5-106-826G.19.fid
-62.669
15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)


Me
O
NC
S
S
O
Me
Me

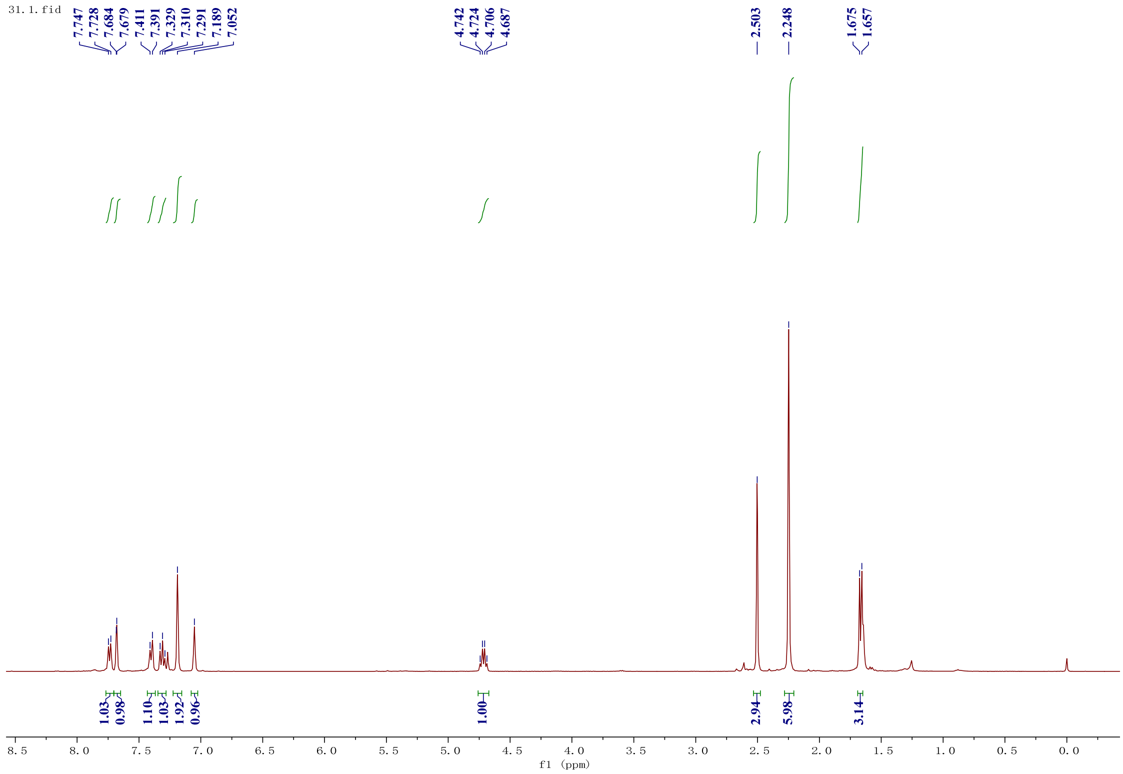
30

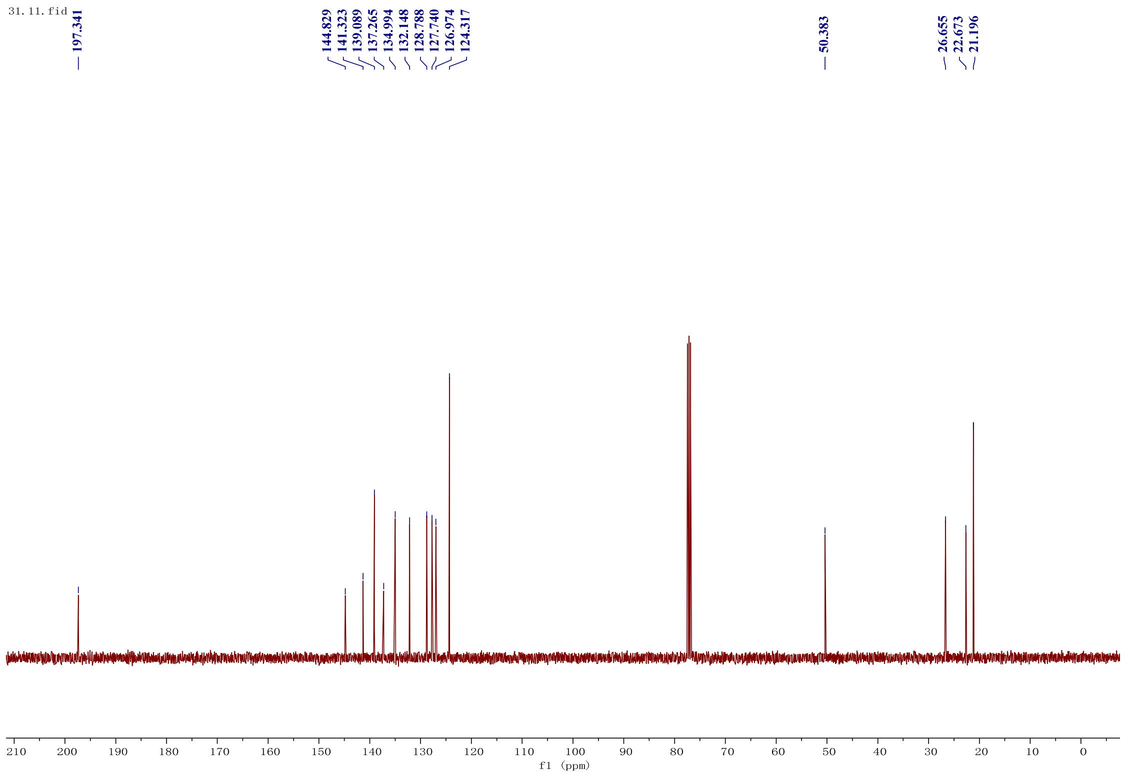

30.10.fid
7.444 7.441 7.440 7.427 7.424 7.420 7.411 7.407 7.404 7.348 7.344 7.340 7.330 7.311 7.292 7.273 7.183 7.128
4.687 4.669 4.650 4.632
2.291
1.644 1.626
2.17 2.12 1.93 0.96
1.00
5.98
3.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

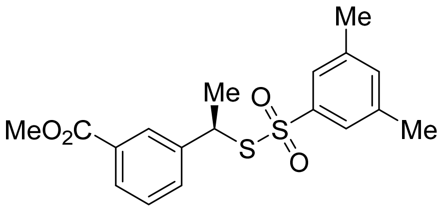

30.11.fid
144.582 142.364 139.260 135.350 131.888 131.191 130.772 129.251
124.290
118.209
112.570
49.656
22.484 21.208
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
O
O
S
S
Ac
Me

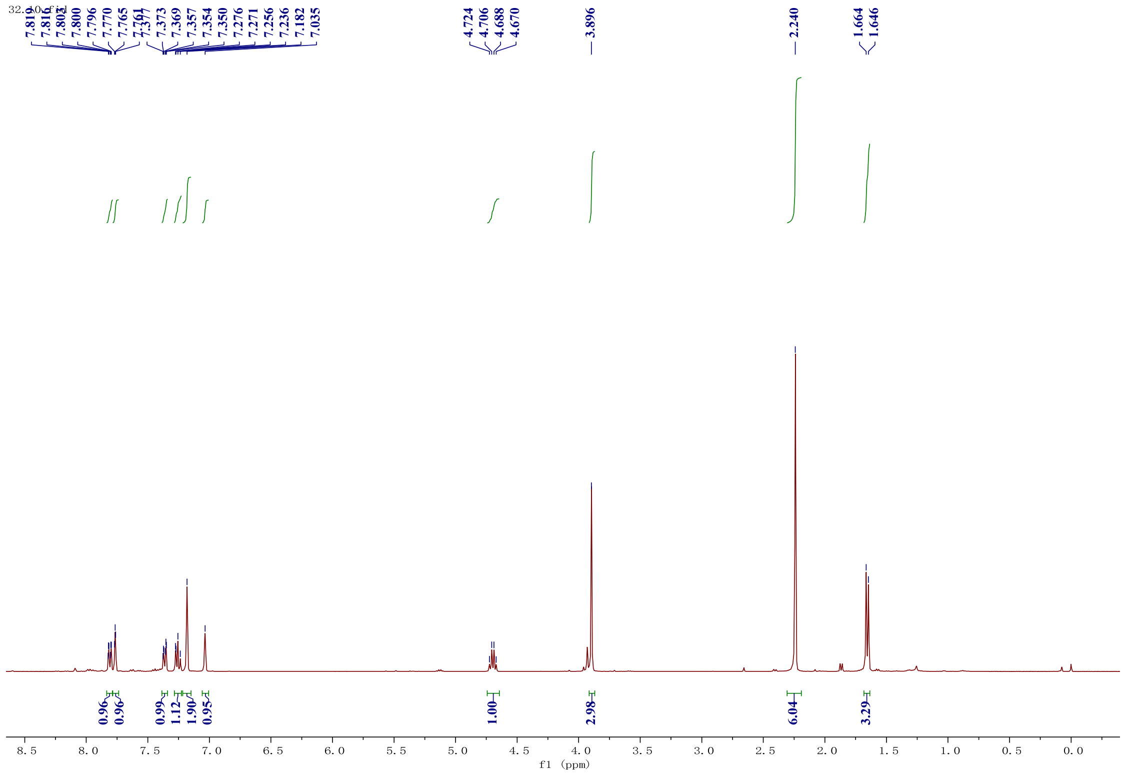
31

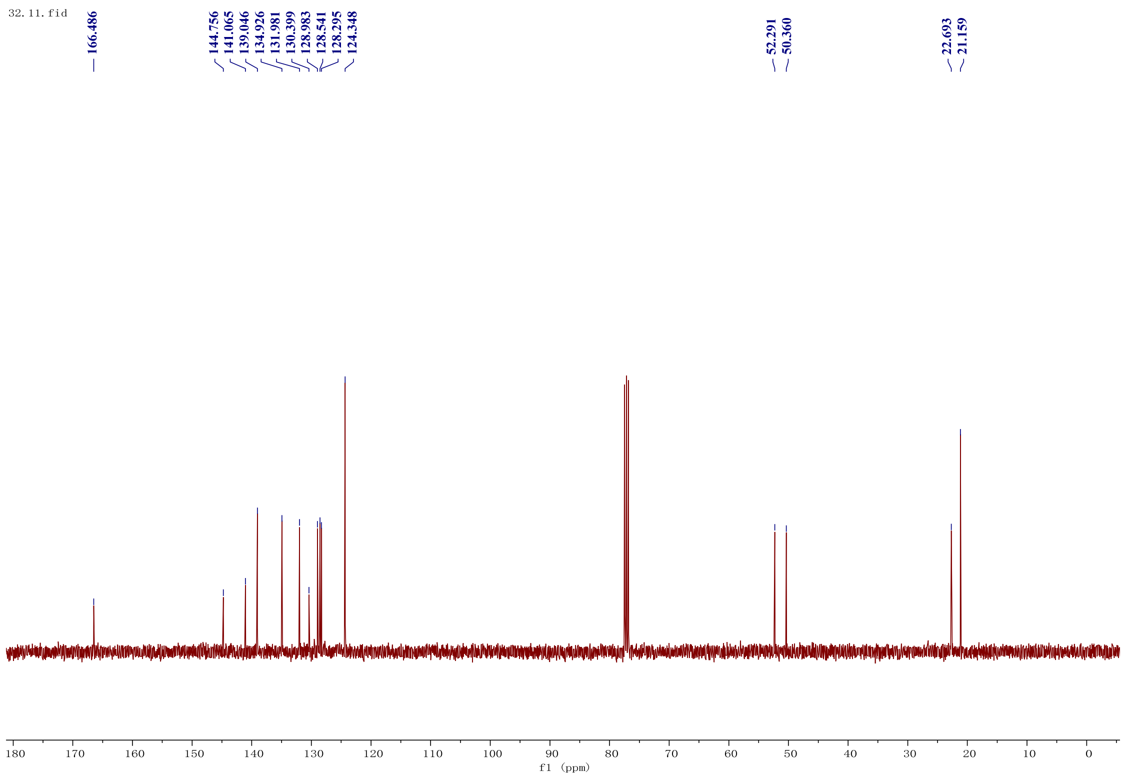

31.1.fid
7.747
7.728
7.684
7.679
7.411
7.391
7.329
7.310
7.291
7.189
7.052
4.742
4.724
4.706
4.687
2.503
2.248
1.675
1.657
1.03
0.98
1.10
1.03
1.92
0.96
1.00
2.94
5.98
3.14
f1 (ppm)

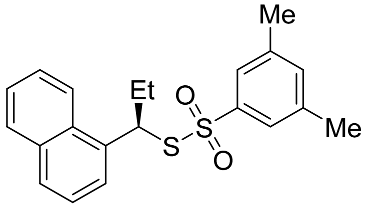

31.11.fid
197.341
144.829
141.323
139.089
137.265
134.994
132.148
128.788
127.740
126.974
124.317
50.383
26.655
22.673
21.196
f1 (ppm)


Me
Me
O
MeO2C
S
S
O
Me

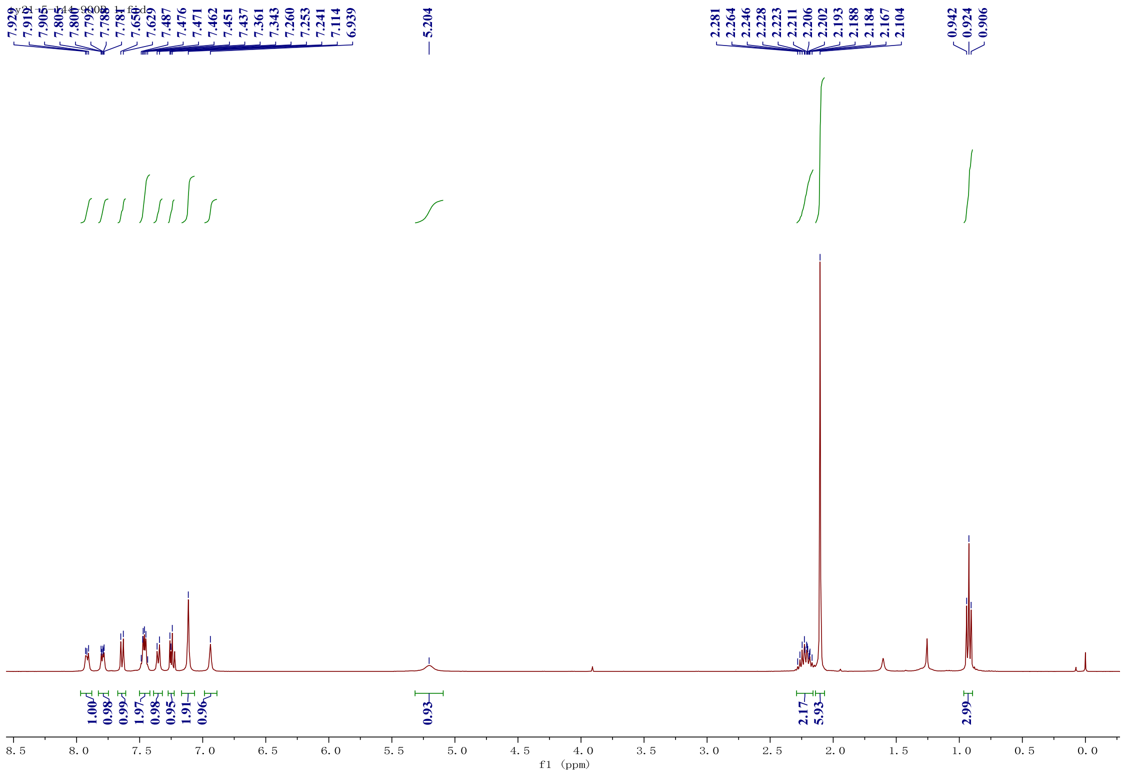
32

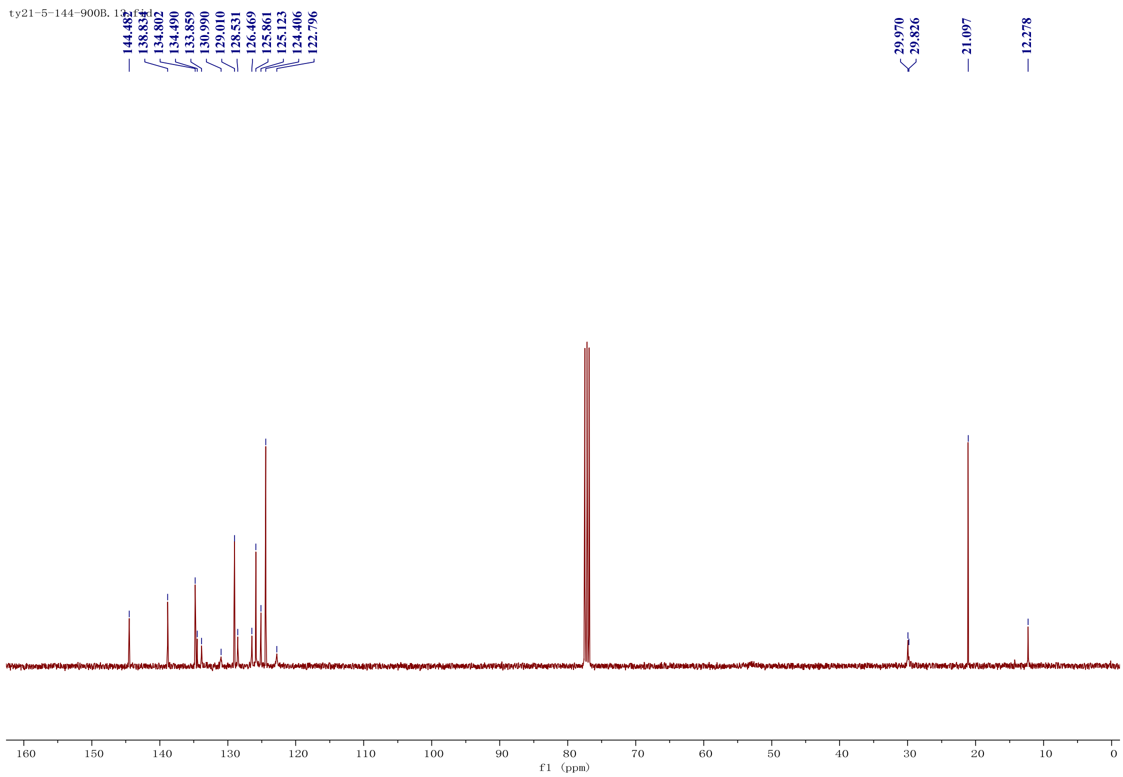

32.10.fid
7.819
7.816
7.803
7.800
7.796
7.770
7.765
7.761
7.373
7.369
7.357
7.354
7.350
7.276
7.271
7.256
7.236
7.182
7.035
4.724
4.706
4.688
4.670
3.896
2.240
1.664
1.646
0.96
0.96
0.99
1.12
1.90
0.95
1.00
2.98
6.04
3.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

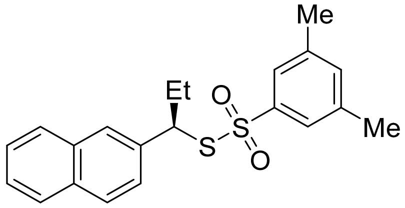

32.11.fid
166.486
144.756
141.065
139.046
134.926
131.981
130.399
128.983
128.541
128.295
124.348
52.291
50.360
22.693
21.159
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



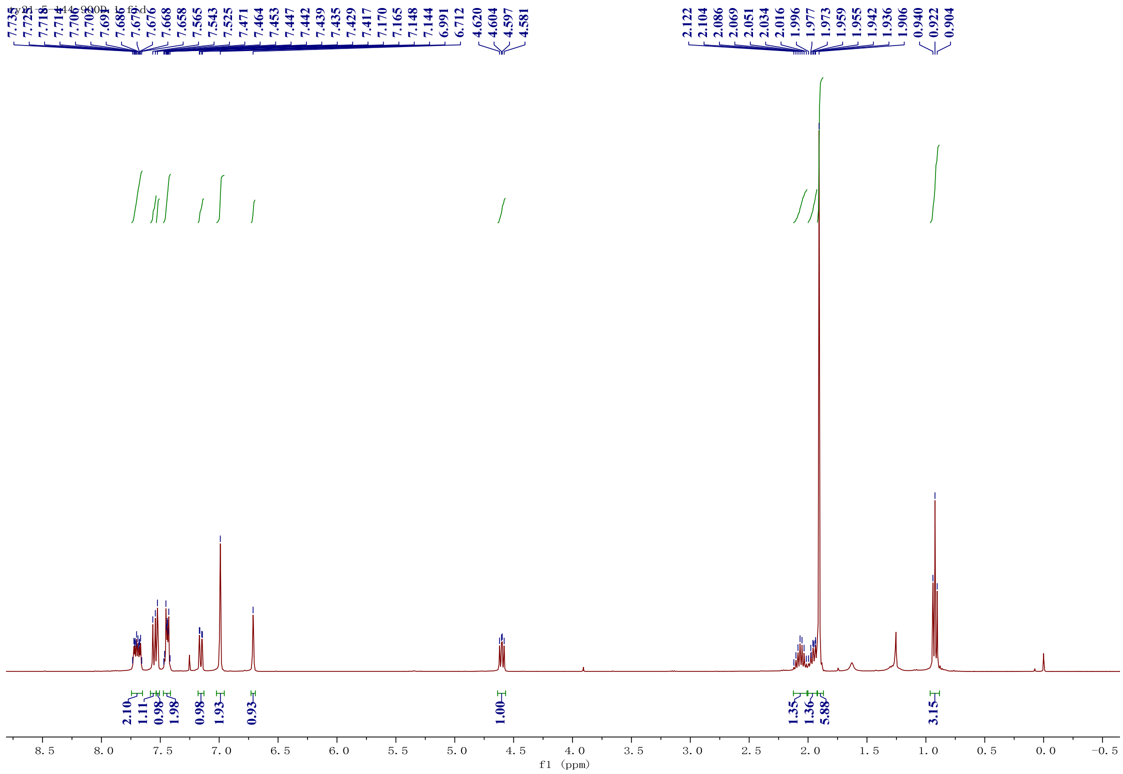
33

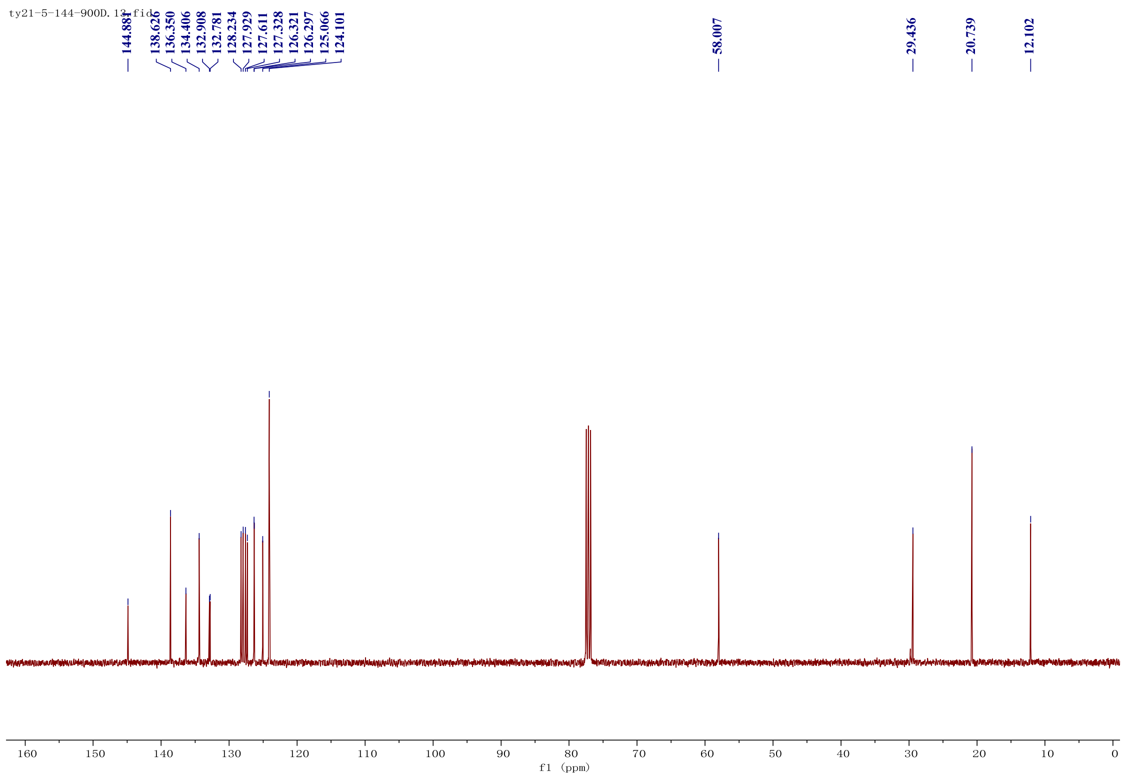


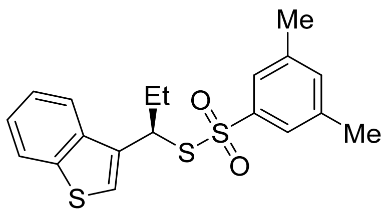




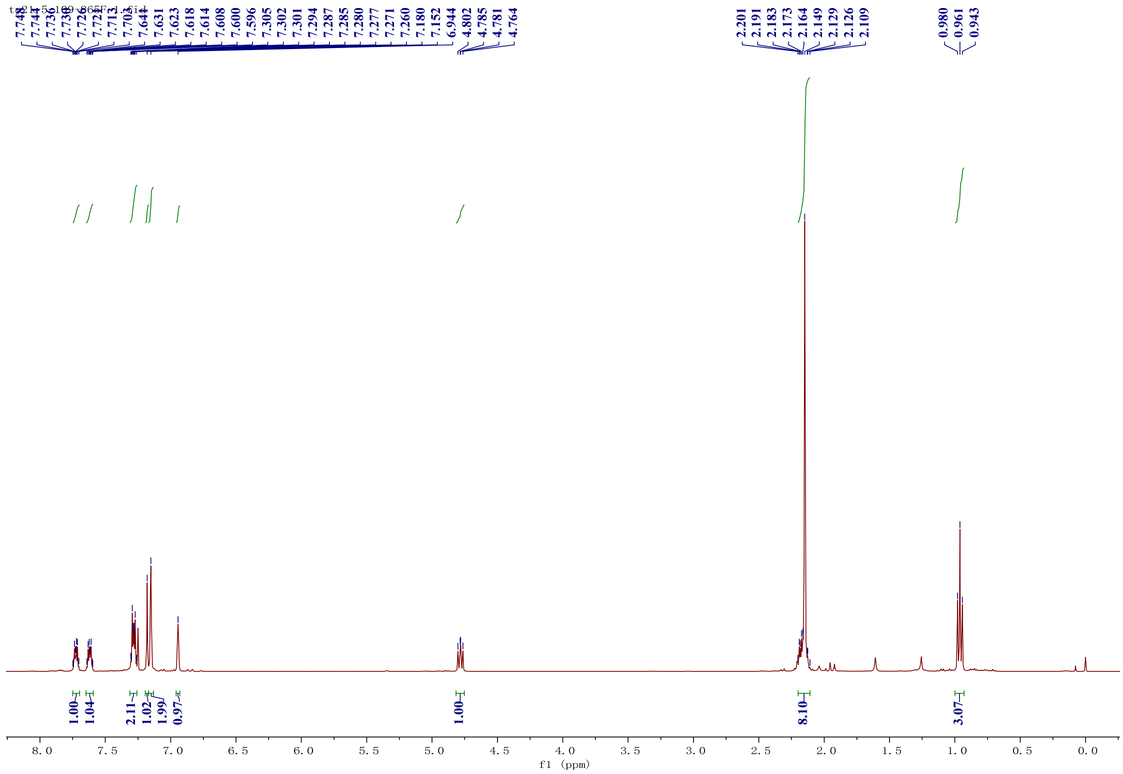
34

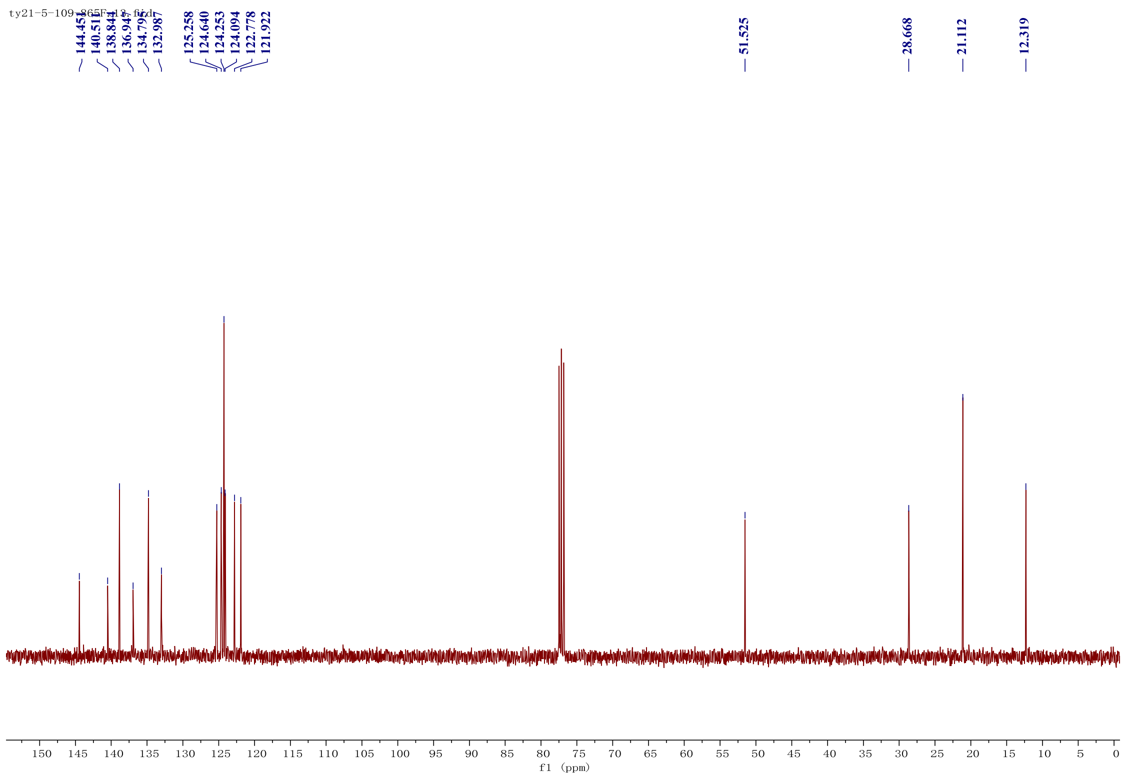


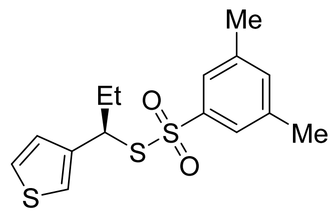



Me
Et
O
S
S
O
Me
S

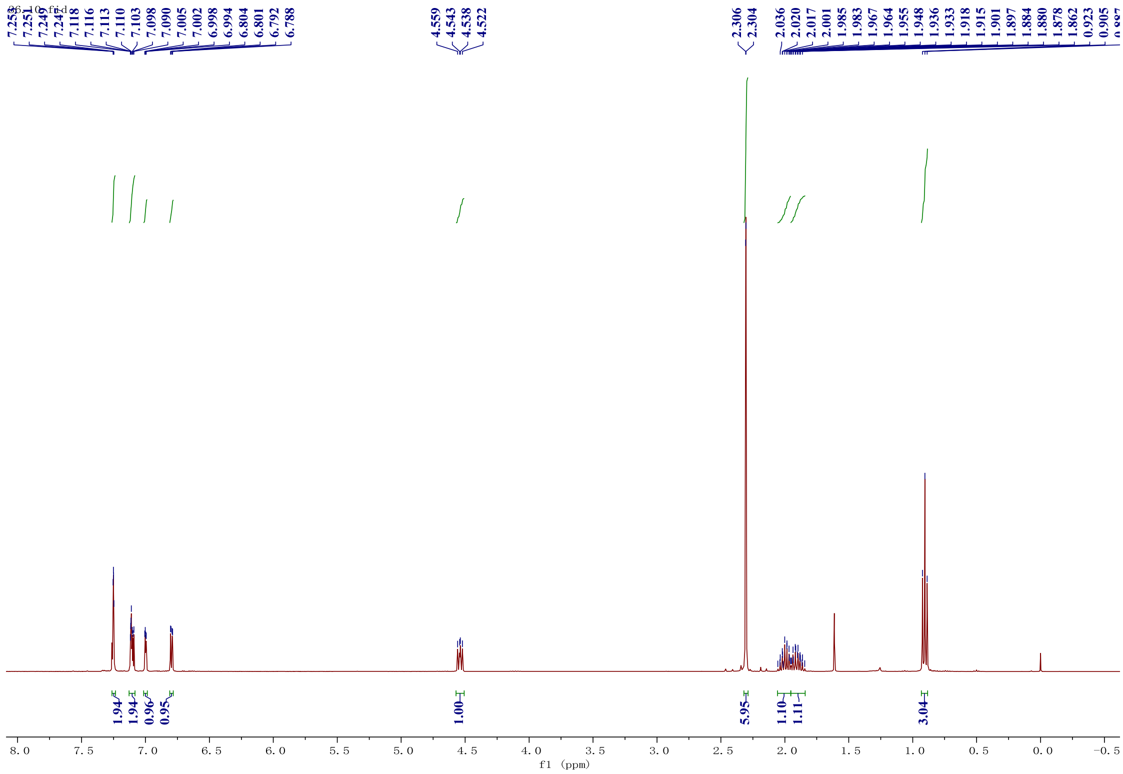
35

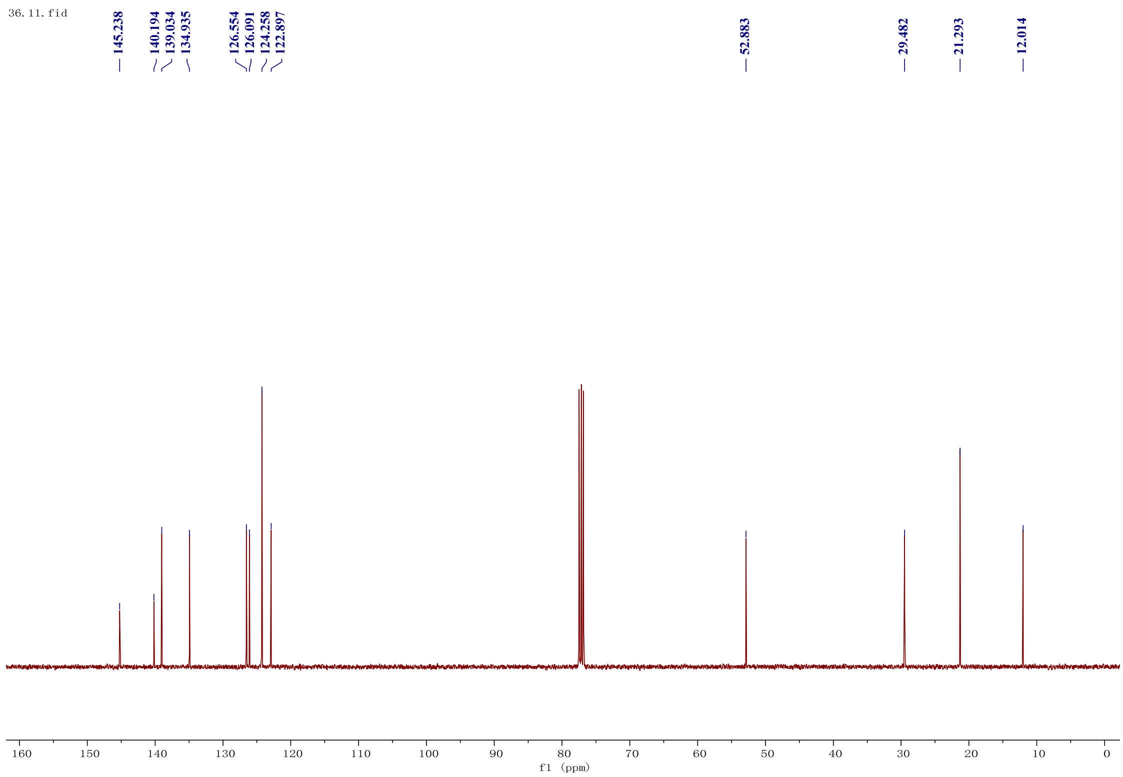

7.748
7.744
7.736
7.730
7.726
7.721
7.713
7.703
7.644
7.631
7.623
7.618
7.614
7.608
7.600
7.596
7.305
7.302
7.301
7.294
7.287
7.285
7.280
7.277
7.271
7.260
7.180
7.152
6.944
4.802
4.785
4.781
4.764
2.201
2.191
2.183
2.173
2.164
2.149
2.129
2.126
2.109
0.980
0.961
0.943
1.00
1.04
2.11
1.02
1.99
0.97
1.00
8.10
3.07
f1 (ppm)

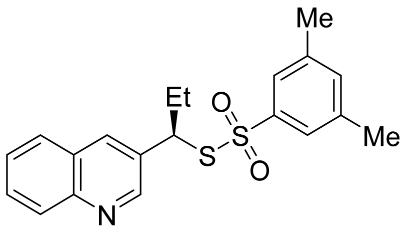

144.451
140.511
138.841
136.947
134.795
132.987
125.258
124.640
124.253
124.094
122.778
121.922
51.525
28.668
21.112
12.319
f1 (ppm)



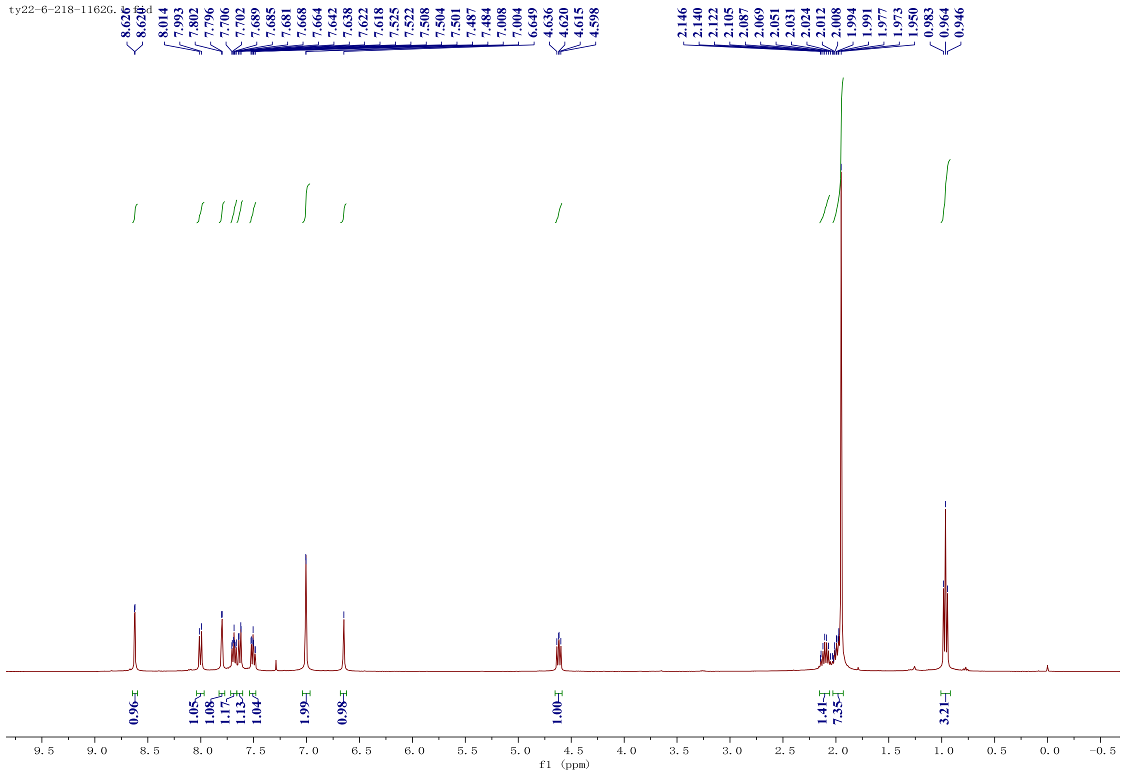
36

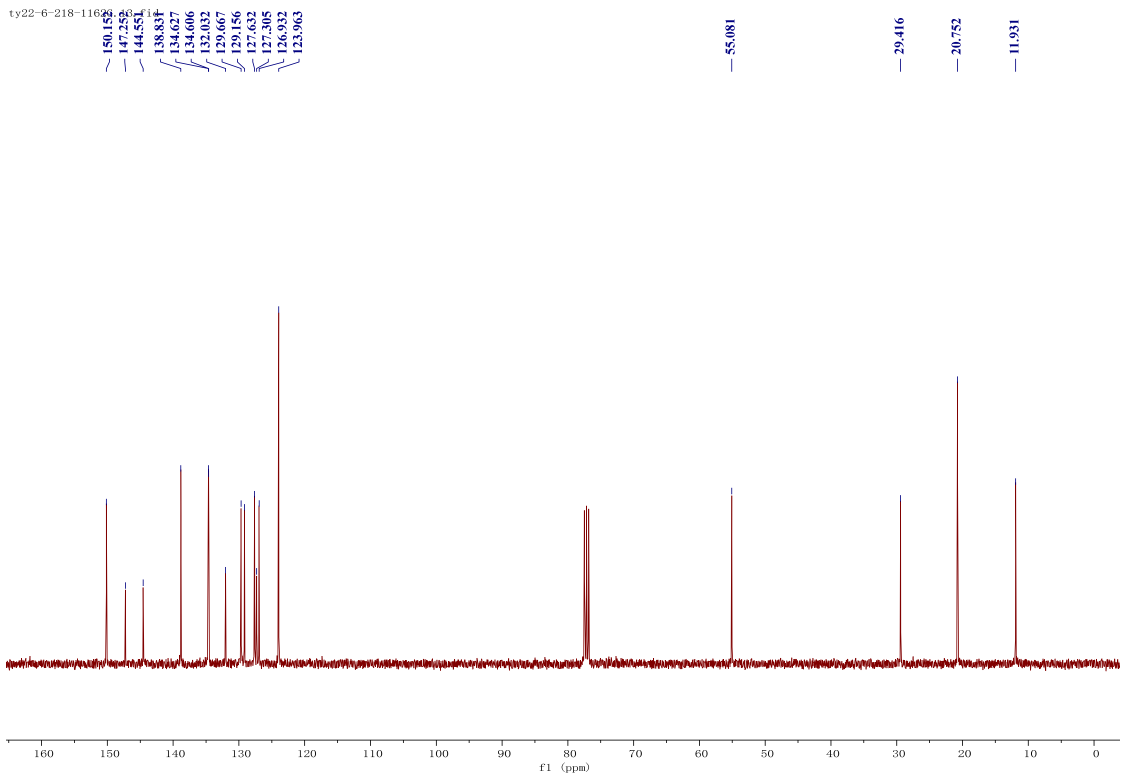

36.10.fid
7.253
7.251
7.249
7.247
7.118
7.116
7.113
7.110
7.103
7.098
7.090
7.005
7.002
6.998
6.994
6.804
6.801
6.792
6.788
4.559
4.543
4.538
4.522
2.306
2.304
2.036
2.020
2.017
2.001
1.985
1.983
1.967
1.964
1.955
1.948
1.936
1.933
1.918
1.915
1.901
1.897
1.884
1.880
1.878
1.862
0.923
0.905
1.94
1.94
0.96
0.95
1.00
5.95
1.10
1.11
3.04
f1 (ppm)

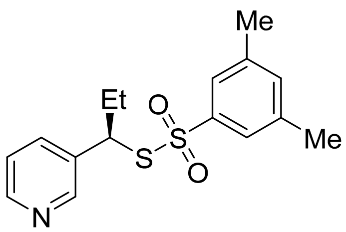

36.11.fid
145.238
140.194
139.034
134.935
126.554
126.091
124.258
122.897
52.883
29.482
21.293
12.014
f1 (ppm)



37

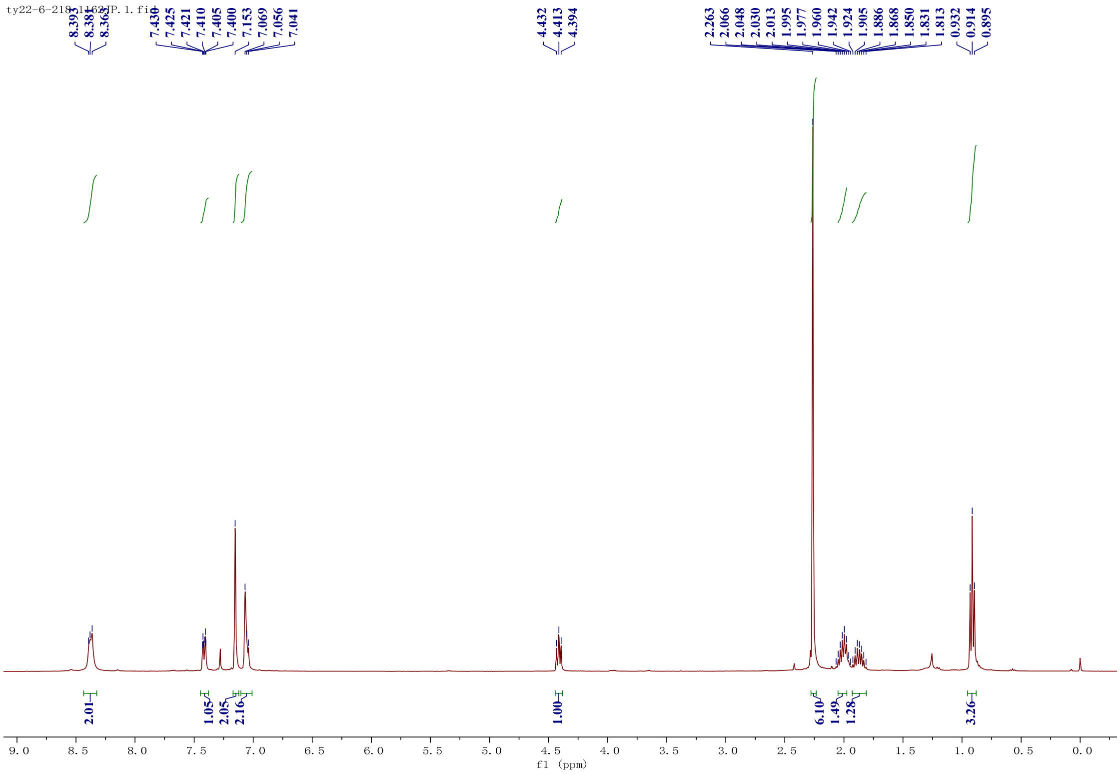




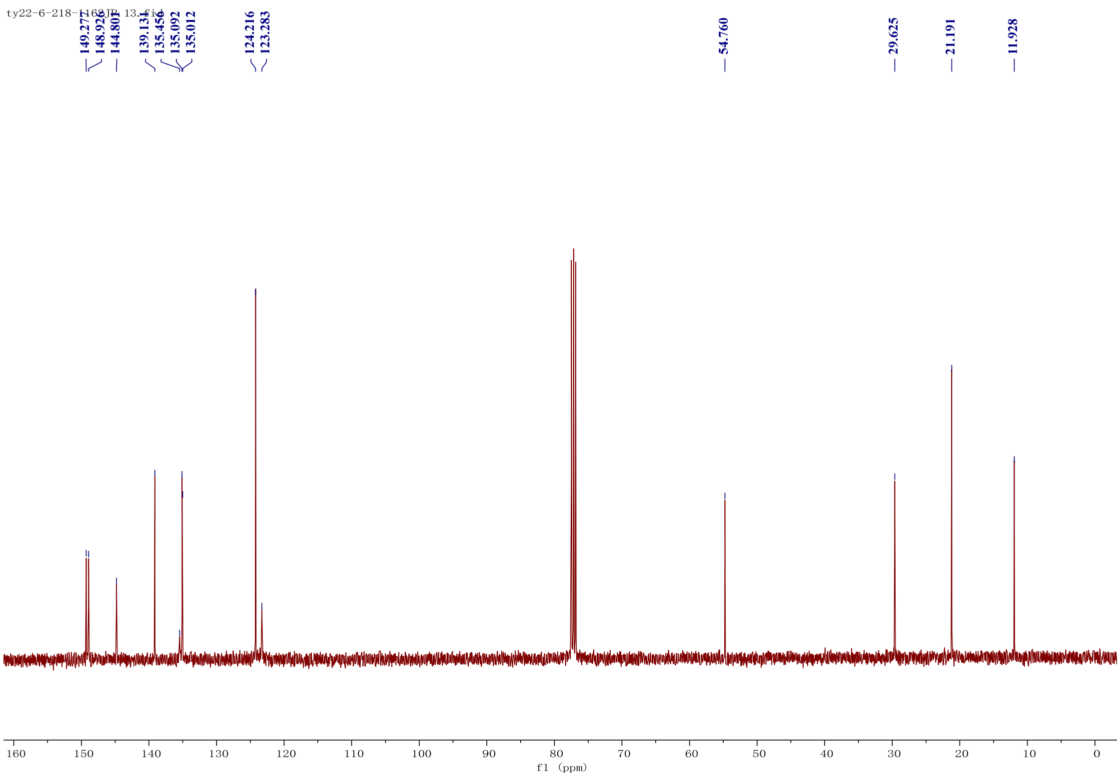


Me
Et
O
S
S
O
Me
N

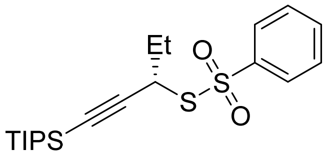
38



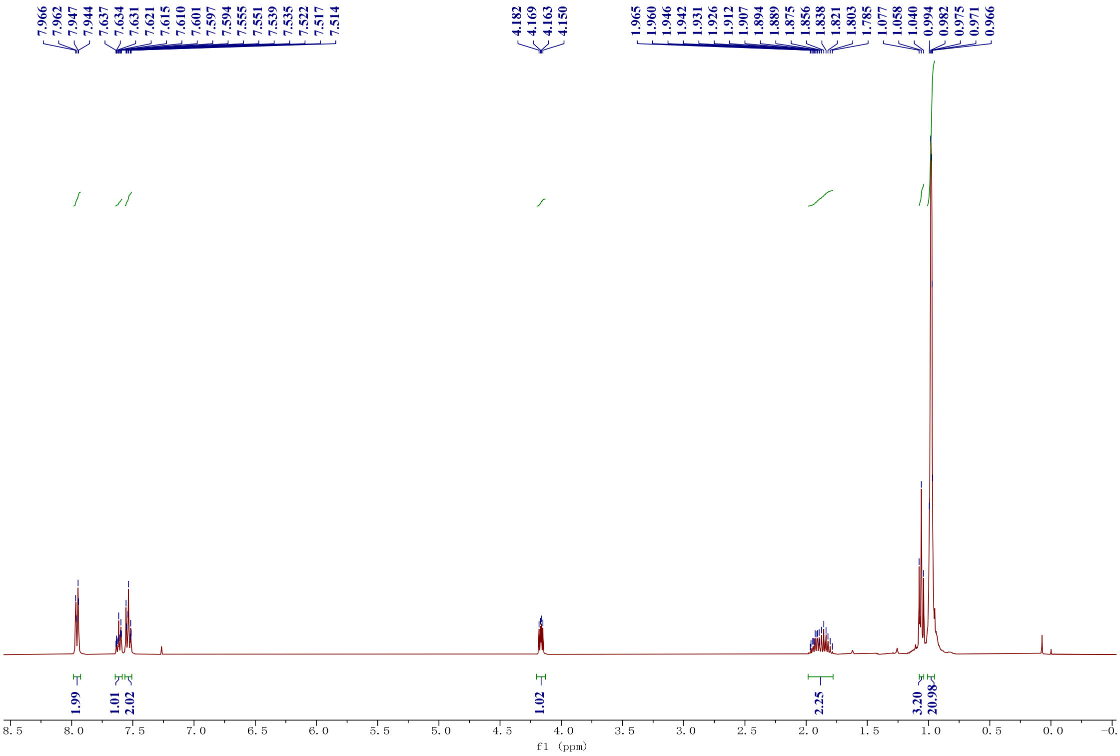
8.393
8.381
8.363
7.430
7.425
7.421
7.410
7.405
7.400
7.153
7.069
7.056
7.041
4.432
4.413
4.394
2.263
2.066
2.048
2.030
2.013
1.995
1.977
1.960
1.942
1.924
1.905
1.886
1.868
1.850
1.831
1.813
0.932
0.914
0.895
2.01
1.05
2.05
2.16
1.00
6.10
1.49
1.28
3.26
f1 (ppm)

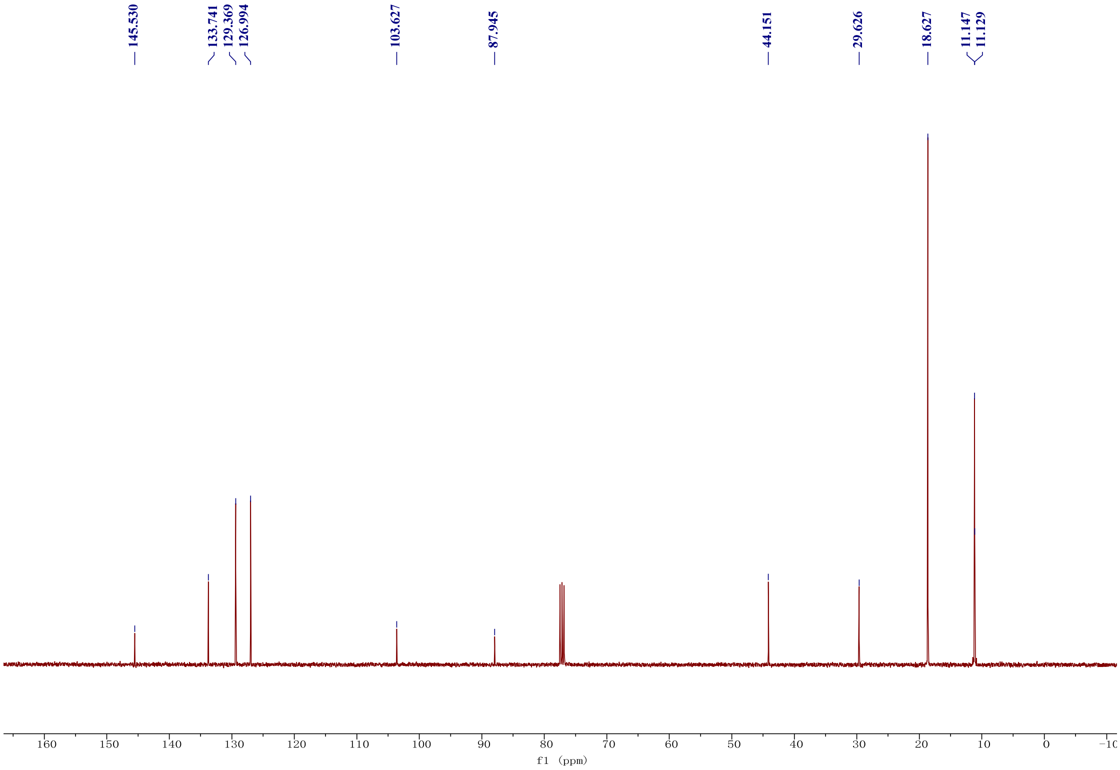


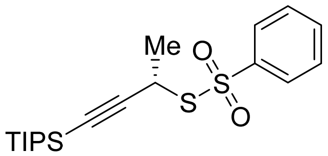
149.271
148.926
144.801
139.131
135.456
135.092
135.012
124.216
123.283
54.760
29.625
21.191
11.928
f1 (ppm)


Et
O
S
S
O
TIPS

39

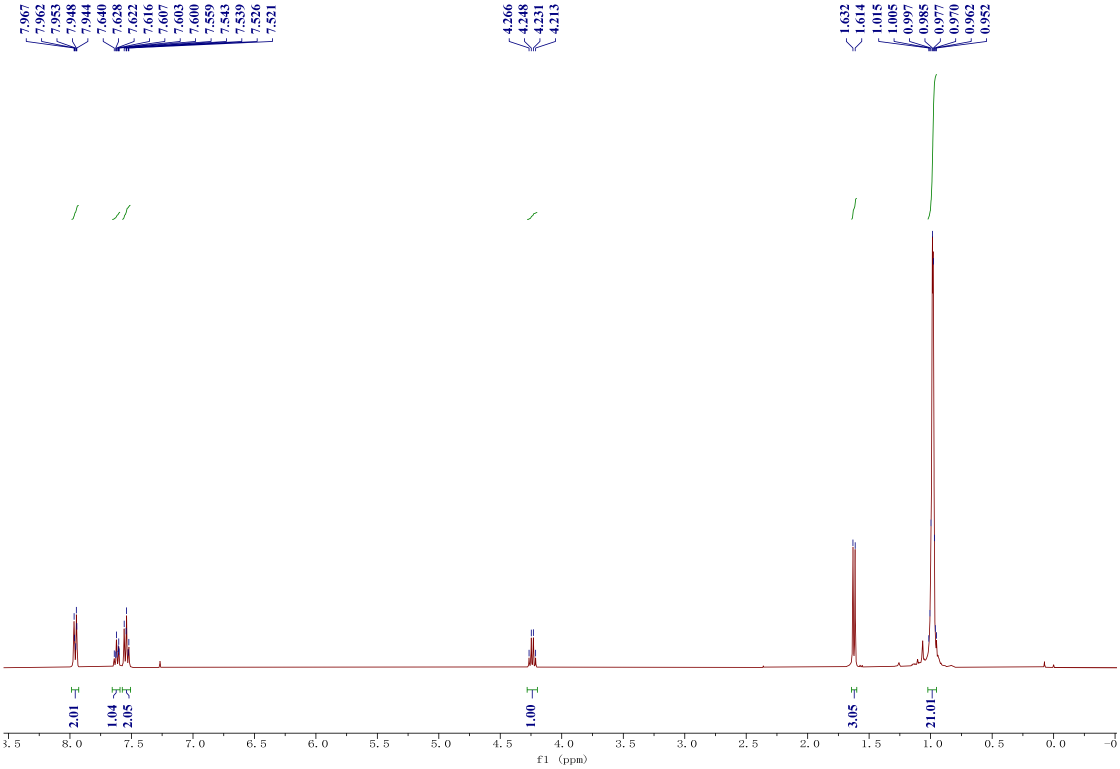

7.966
7.962
7.947
7.944
7.637
7.634
7.631
7.621
7.615
7.610
7.601
7.597
7.594
7.555
7.551
7.539
7.535
7.522
7.517
7.514
4.182
4.169
4.163
4.150
1.965
1.960
1.946
1.942
1.931
1.926
1.912
1.907
1.894
1.889
1.875
1.856
1.838
1.821
1.803
1.785
1.077
1.058
1.040
0.994
0.982
0.975
0.971
0.966
1.99
1.01
2.02
1.02
2.25
3.20
20.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.530
133.741
129.369
126.994
103.627
87.945
44.151
29.626
18.627
11.147
11.129
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

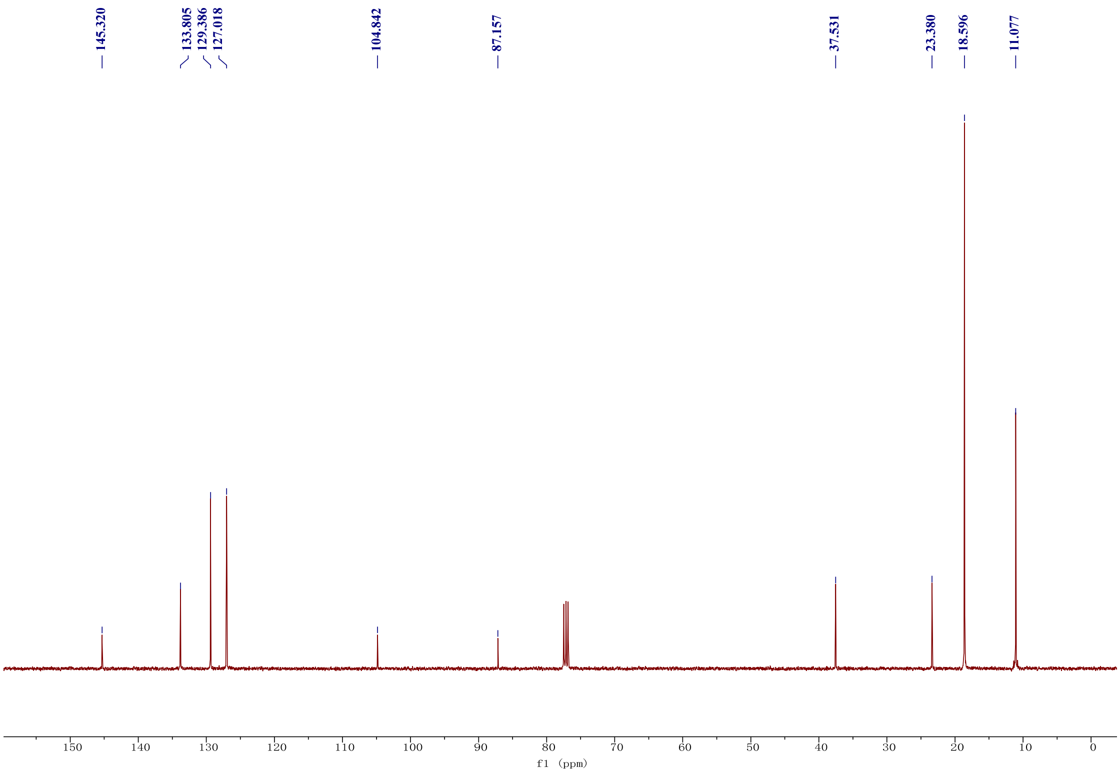


Me
O
S
S
O
TIPS

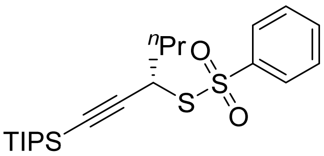
40



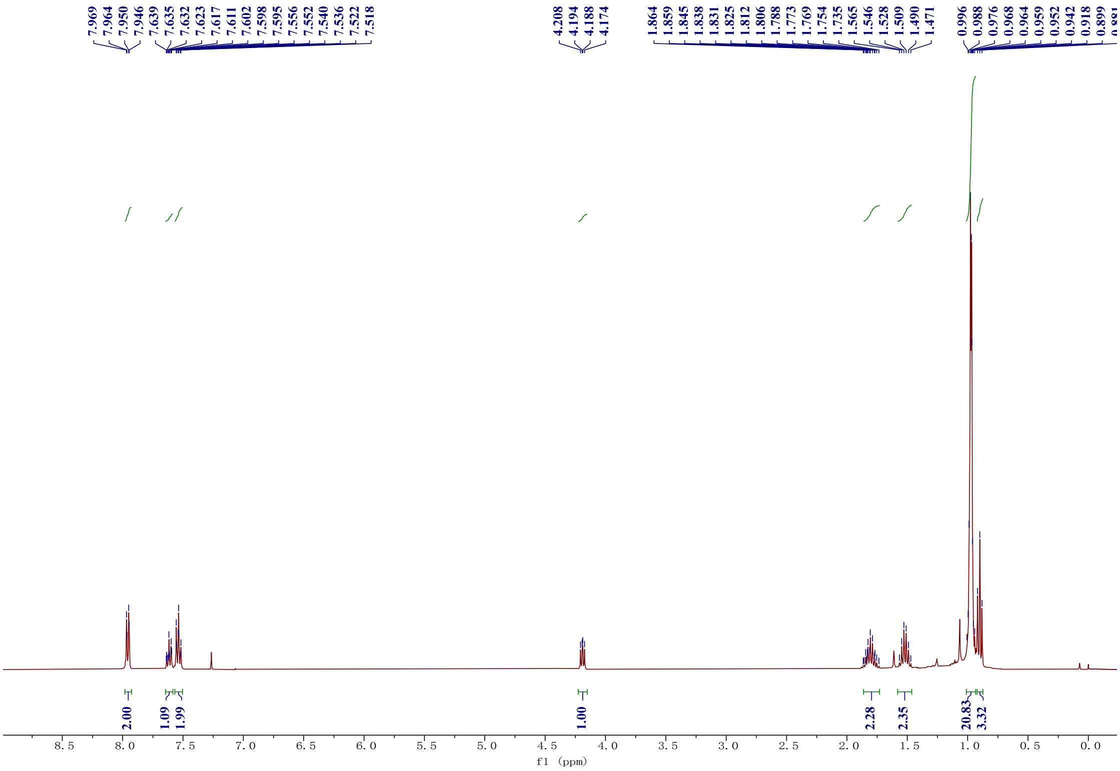
7.967 7.962 7.953 7.948 7.944 7.640 7.628 7.622 7.616 7.607 7.603 7.600 7.559 7.543 7.539 7.526 7.521
4.266 4.248 4.231 4.213
1.632 1.614 1.015 1.005 0.997 0.985 0.977 0.970 0.962 0.952
2.01 1.04 2.05 1.00 3.05 21.01
f1 (ppm)

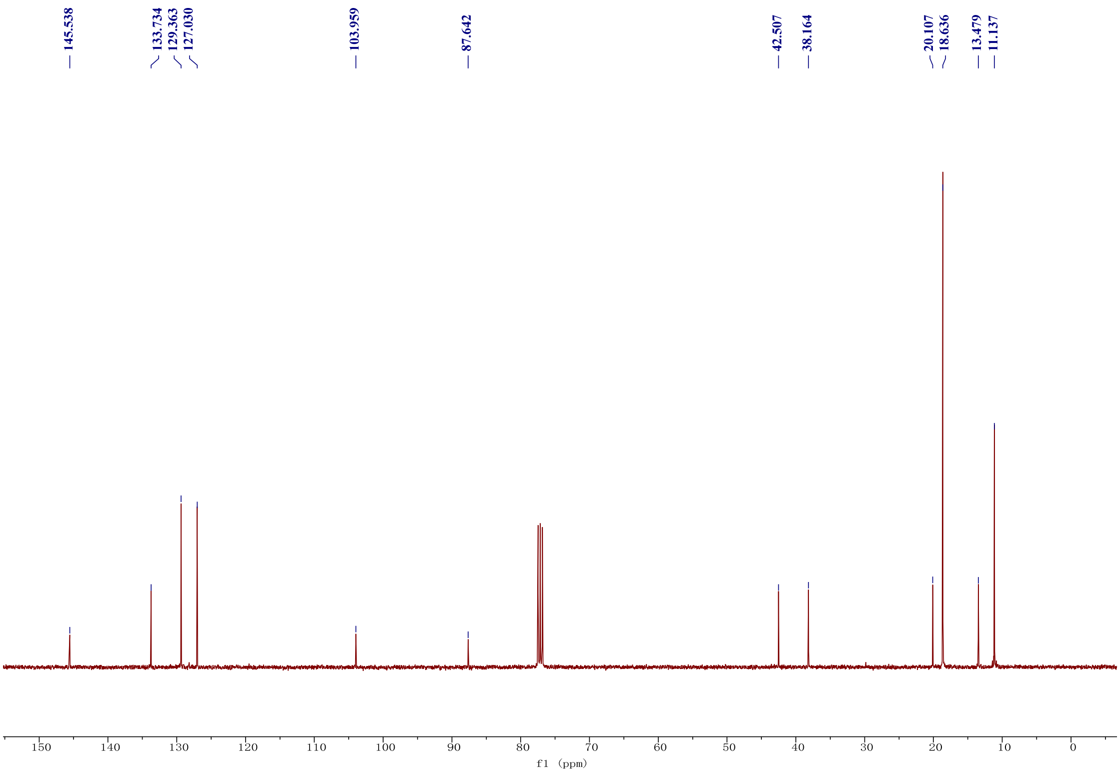


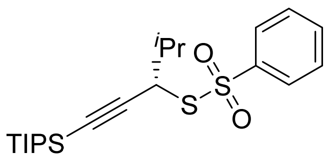
145.320
133.805 129.386 127.018
104.842
87.157
37.531
23.380
18.596
11.077
f1 (ppm)


nPr
O
S
S
O
TIPS

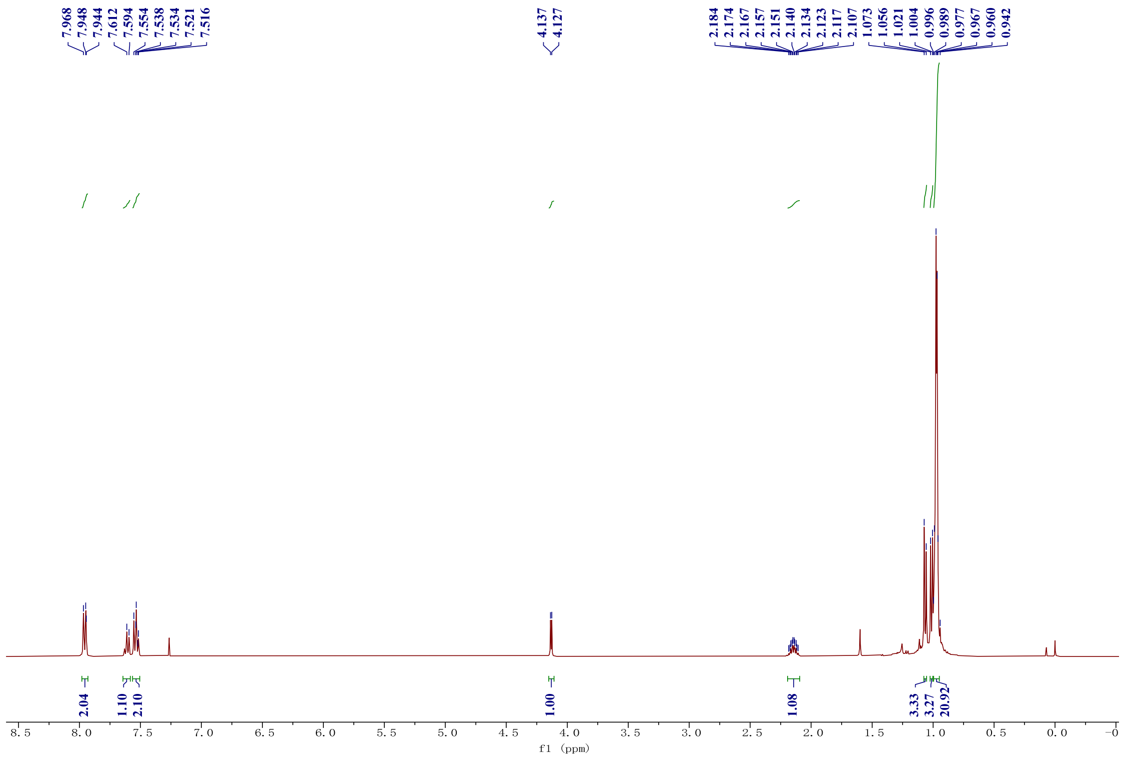
41

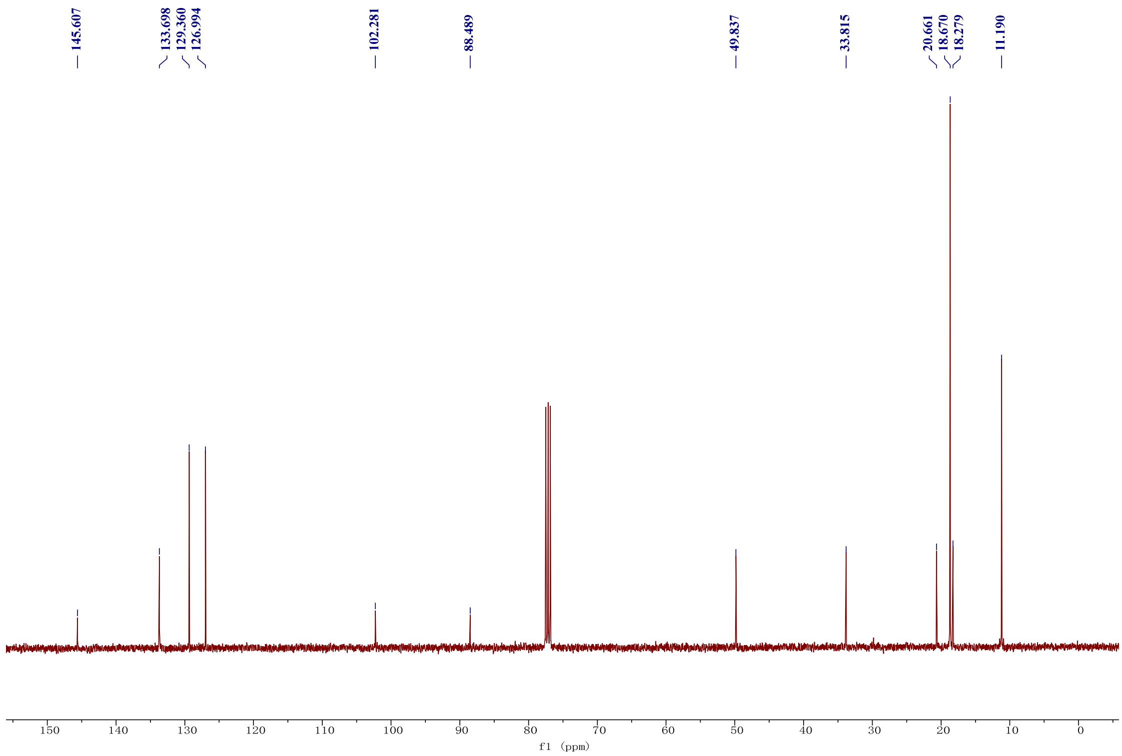

7.969
7.964
7.950
7.946
7.639
7.635
7.632
7.623
7.617
7.611
7.602
7.598
7.595
7.556
7.552
7.540
7.536
7.522
7.518
4.208
4.194
4.188
4.174
1.864
1.859
1.845
1.838
1.831
1.825
1.812
1.806
1.788
1.773
1.769
1.754
1.735
1.565
1.546
1.528
1.509
1.490
1.471
0.996
0.988
0.976
0.968
0.964
0.959
0.952
0.942
0.918
0.899
2.00
1.09
1.99
1.00
2.28
2.35
20.83
3.32
f1 (ppm)

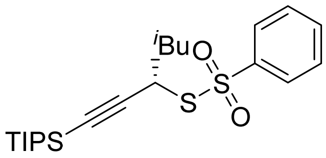

145.538
133.734
129.363
127.030
103.959
87.642
42.507
38.164
20.107
18.636
13.479
11.137
f1 (ppm)



42







iBu
O
S
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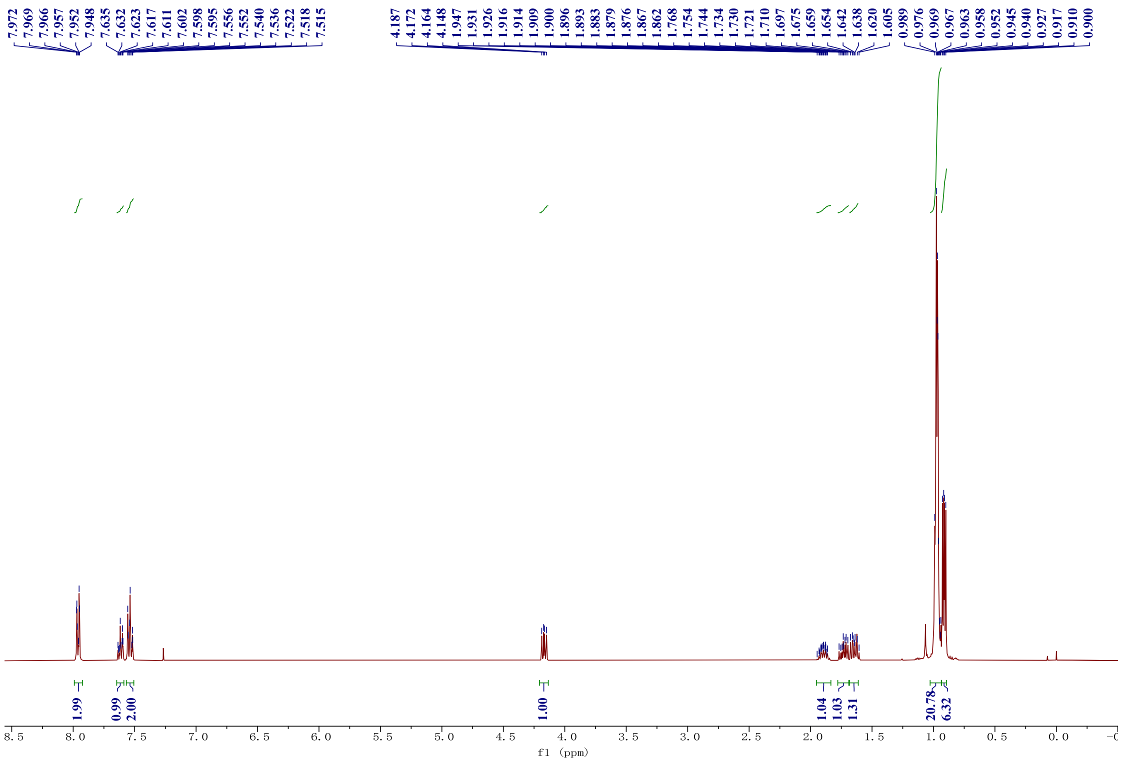
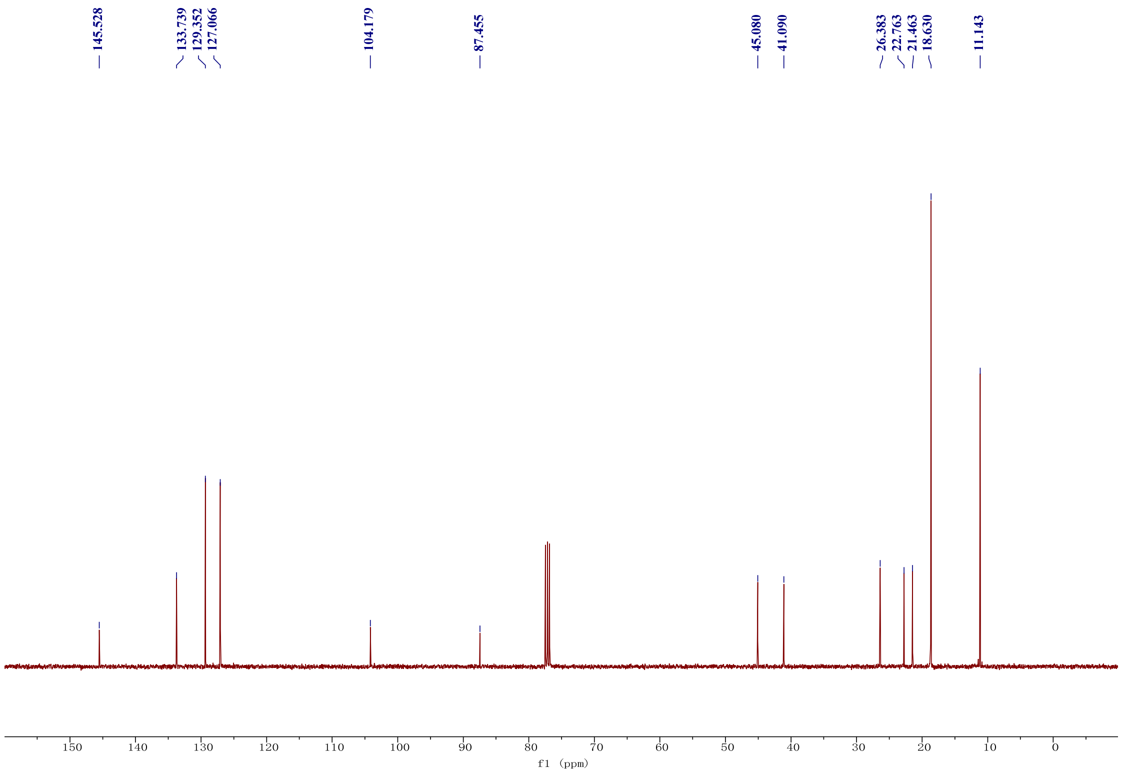
TIPS

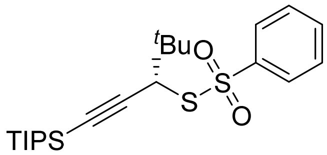
43



7.972 7.969 7.966 7.957 7.952 7.948 7.635 7.632 7.623 7.617 7.611 7.602 7.598 7.595 7.556 7.552 7.540 7.536 7.522 7.518 7.515
4.187 4.172 4.164 4.148 1.947 1.931 1.926 1.916 1.914 1.909 1.900 1.896 1.893 1.883 1.879 1.876 1.867 1.862 1.768 1.754 1.744 1.734 1.730 1.721 1.710 1.697 1.675 1.659 1.654 1.642 1.638 1.620 1.605
0.989 0.976 0.969 0.967 0.963 0.958 0.952 0.945 0.940 0.927 0.917 0.910 0.900
1.99
0.99
2.00
1.00
1.04
1.03
1.31
20.78
6.32
f1 (ppm)



145.528
133.739 129.352 127.066
104.179
87.455
45.080
41.090
26.383 22.763 21.463 18.630
11.143
f1 (ppm)



tBu
O
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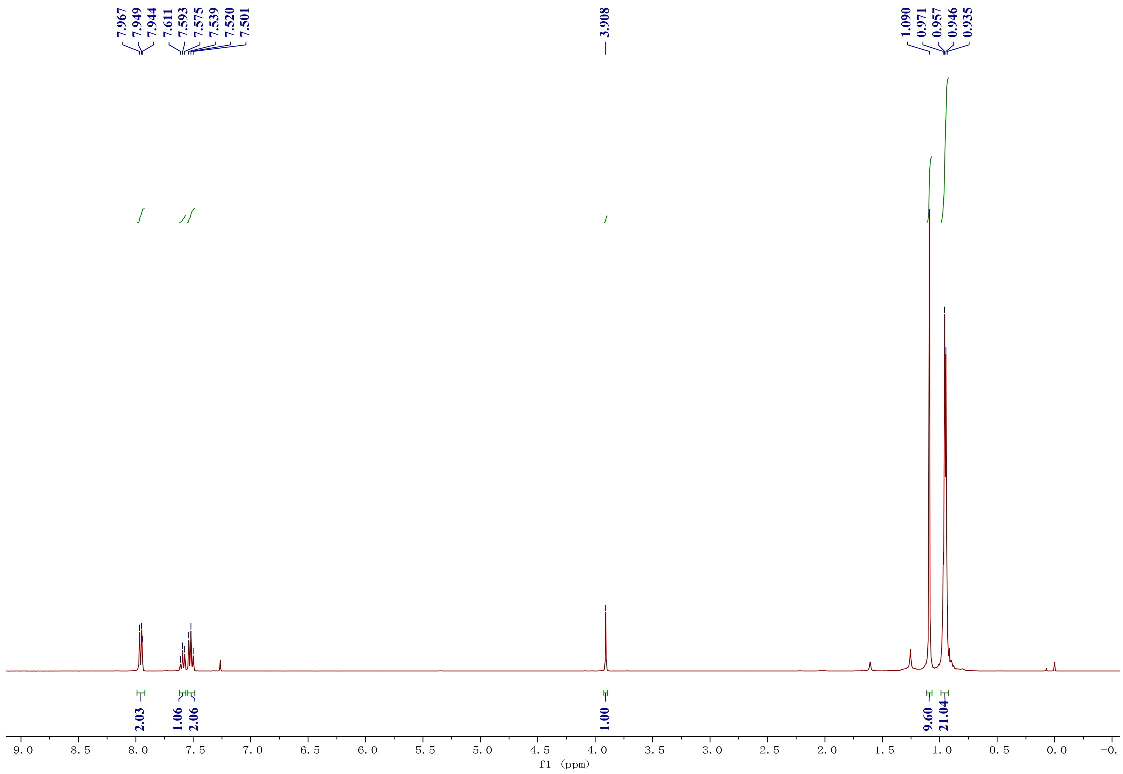
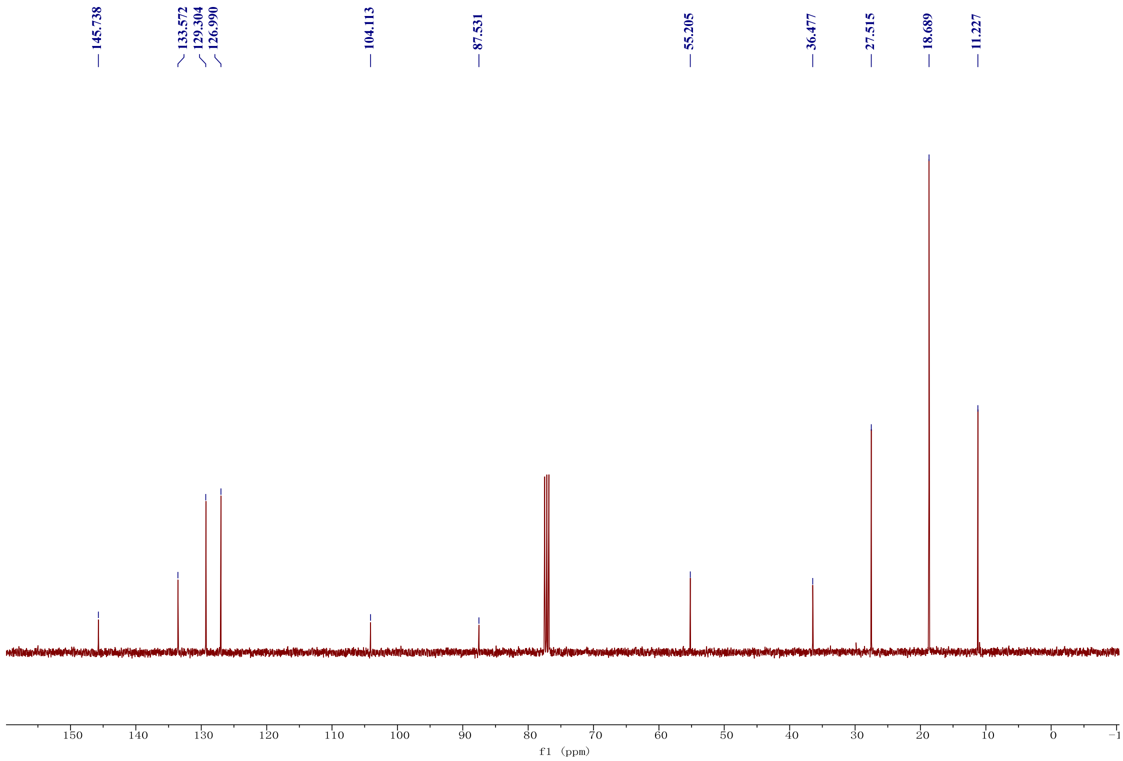
S
O
TIPS

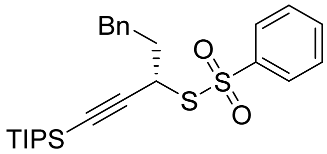
44



7.967
7.949
7.944
7.611
7.593
7.575
7.539
7.520
7.501
3.908
1.090
0.971
0.957
0.946
0.935
2.03
1.06
2.06
1.00
9.60
21.04
f1 (ppm)

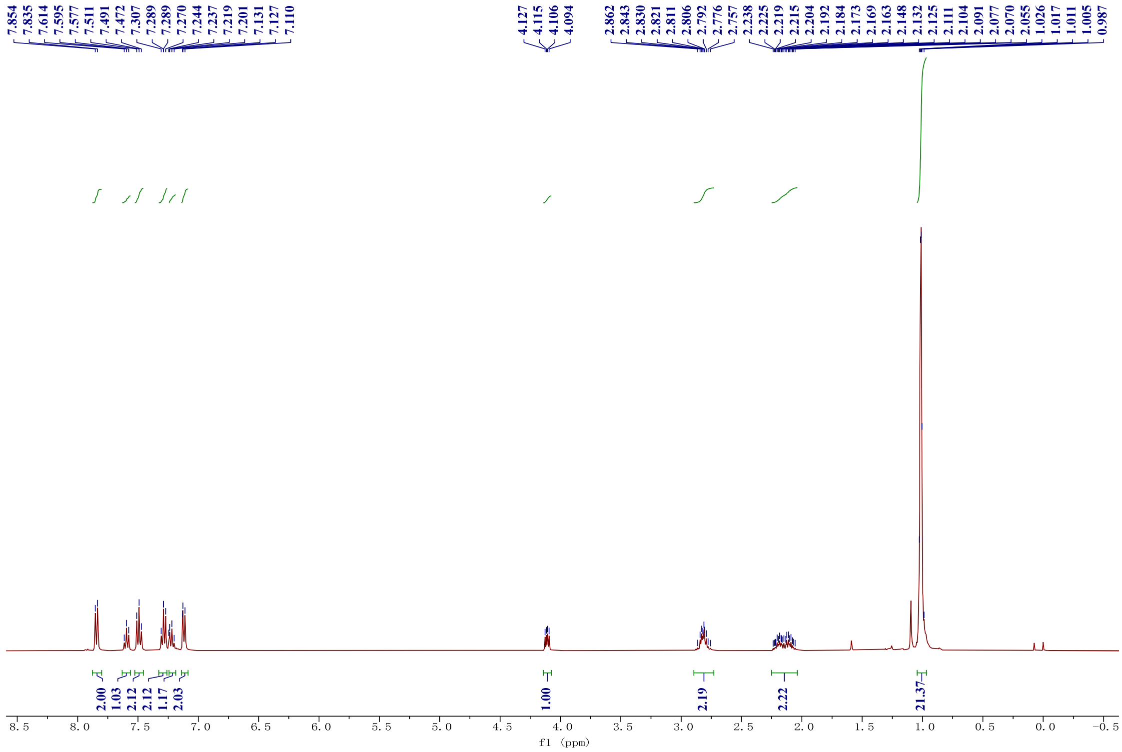


145.738
133.572
129.304
126.990
104.113
87.531
55.205
36.477
27.515
18.689
11.227
f1 (ppm)

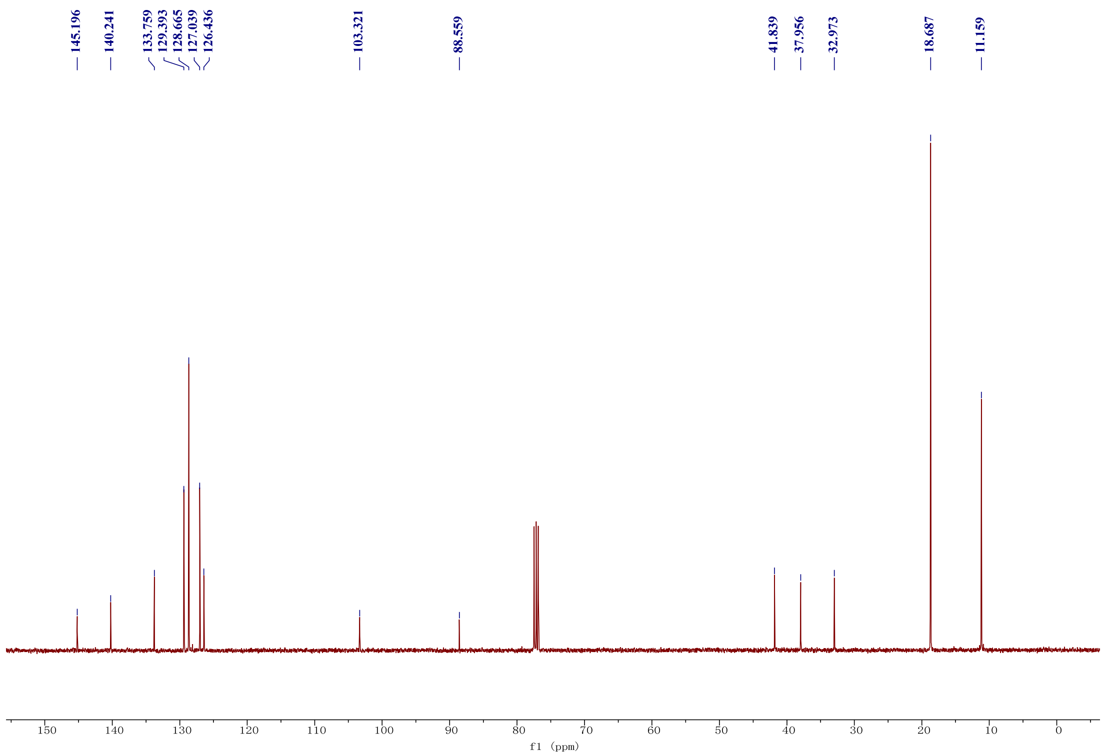


Bn
O
S
S
O
TIPS

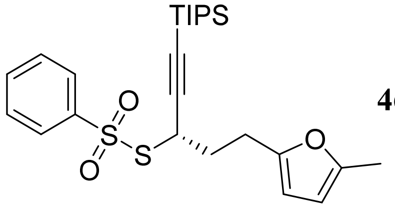
45



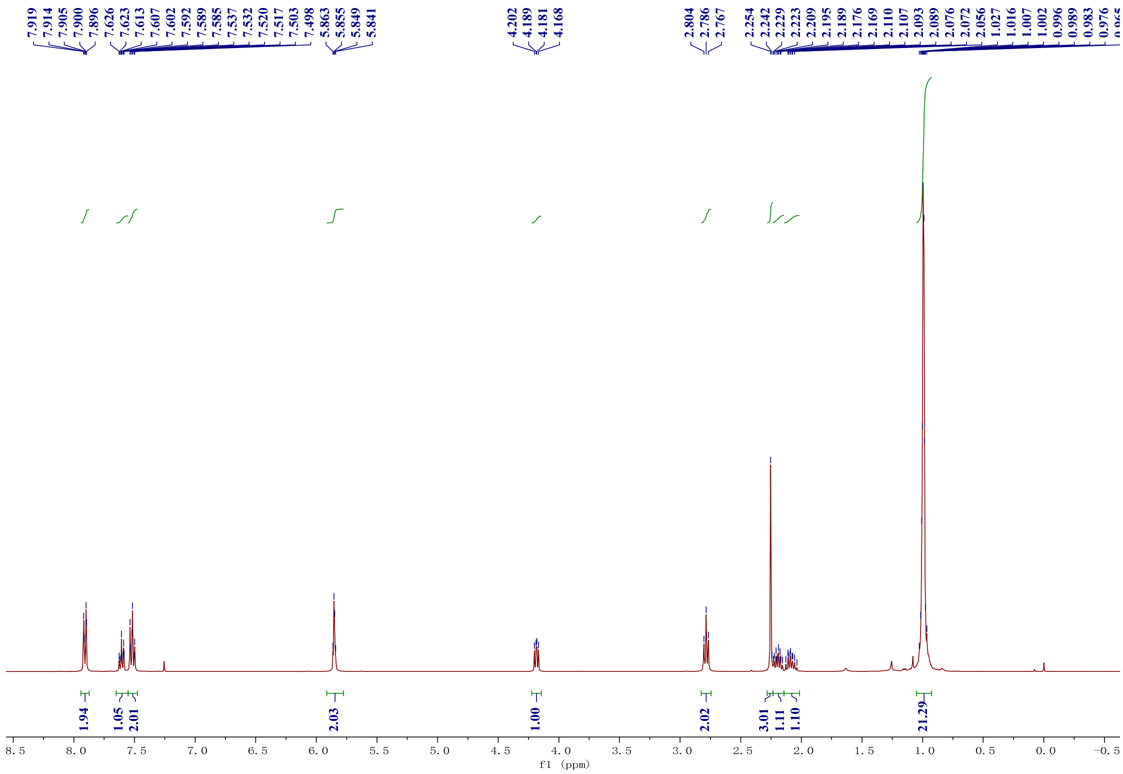
7.854 7.835 7.614 7.595 7.577 7.511 7.491 7.472 7.307 7.289 7.289 7.270 7.244 7.237 7.219 7.201 7.131 7.127 7.110
4.127 4.115 4.106 4.094
2.862 2.843 2.830 2.821 2.811 2.806 2.792 2.776 2.757 2.238 2.225 2.219 2.215 2.204 2.192 2.184 2.173 2.169 2.163 2.148 2.132 2.125 2.111 2.104 2.091 2.077 2.070 2.055 1.026 1.017 1.011 1.005 0.987
2.00 1.03 2.12 2.12 1.17 2.03 1.00 2.19 2.22 21.37
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



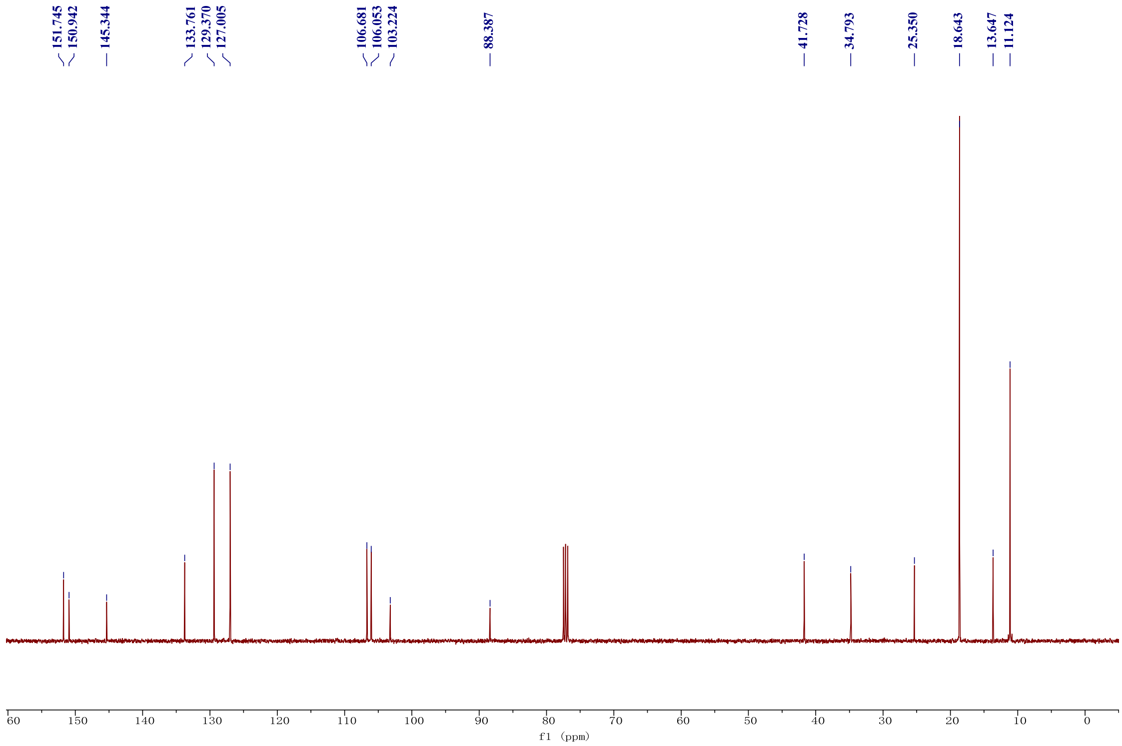
145.196 140.241 133.759 129.393 128.665 127.039 126.436 103.321 88.559 41.839 37.956 32.973 18.687 11.159
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



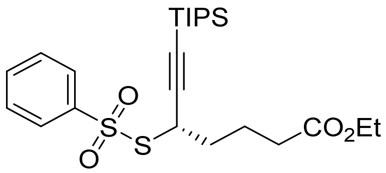
46



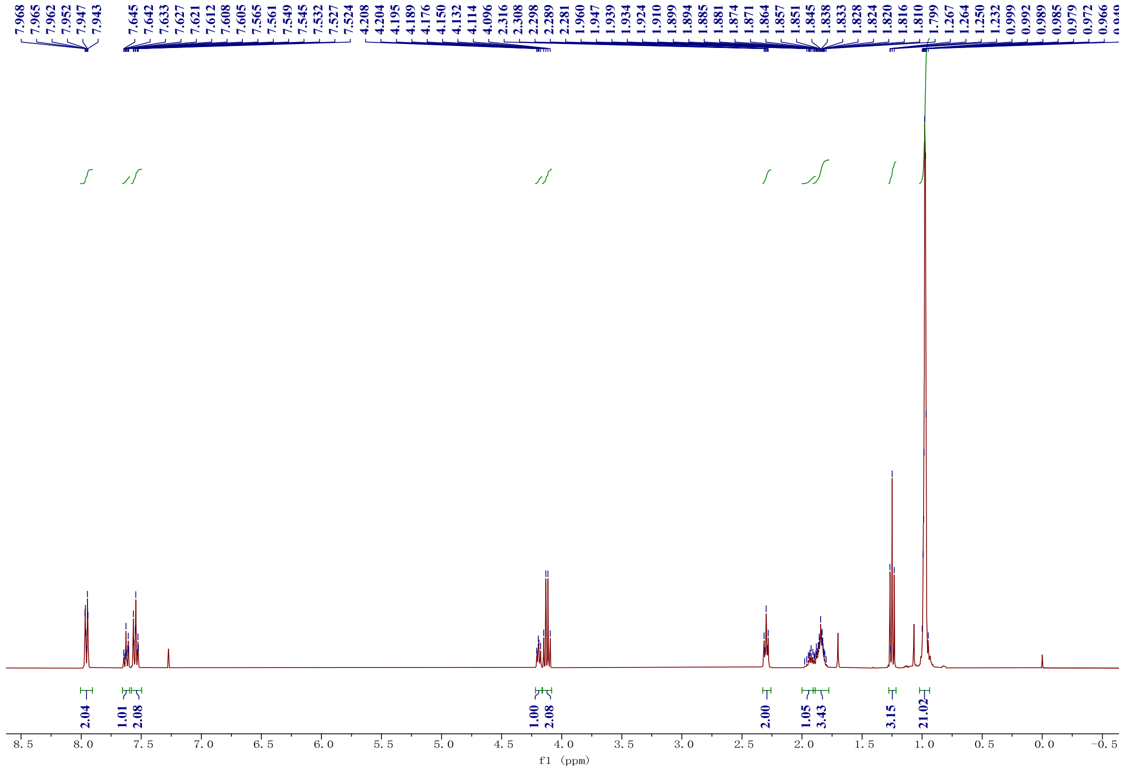
7.919
7.914
7.905
7.900
7.896
7.626
7.623
7.613
7.607
7.602
7.592
7.589
7.585
7.537
7.532
7.520
7.517
7.503
7.498
5.863
5.855
5.849
5.841
4.202
4.189
4.181
4.168
2.804
2.786
2.767
2.254
2.242
2.229
2.223
2.209
2.195
2.189
2.176
2.169
2.110
2.107
2.093
2.089
2.076
2.072
2.056
1.027
1.016
1.007
1.002
0.996
0.989
0.983
0.976
1.94
1.05
2.01
2.03
1.00
2.02
3.01
1.11
1.10
21.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

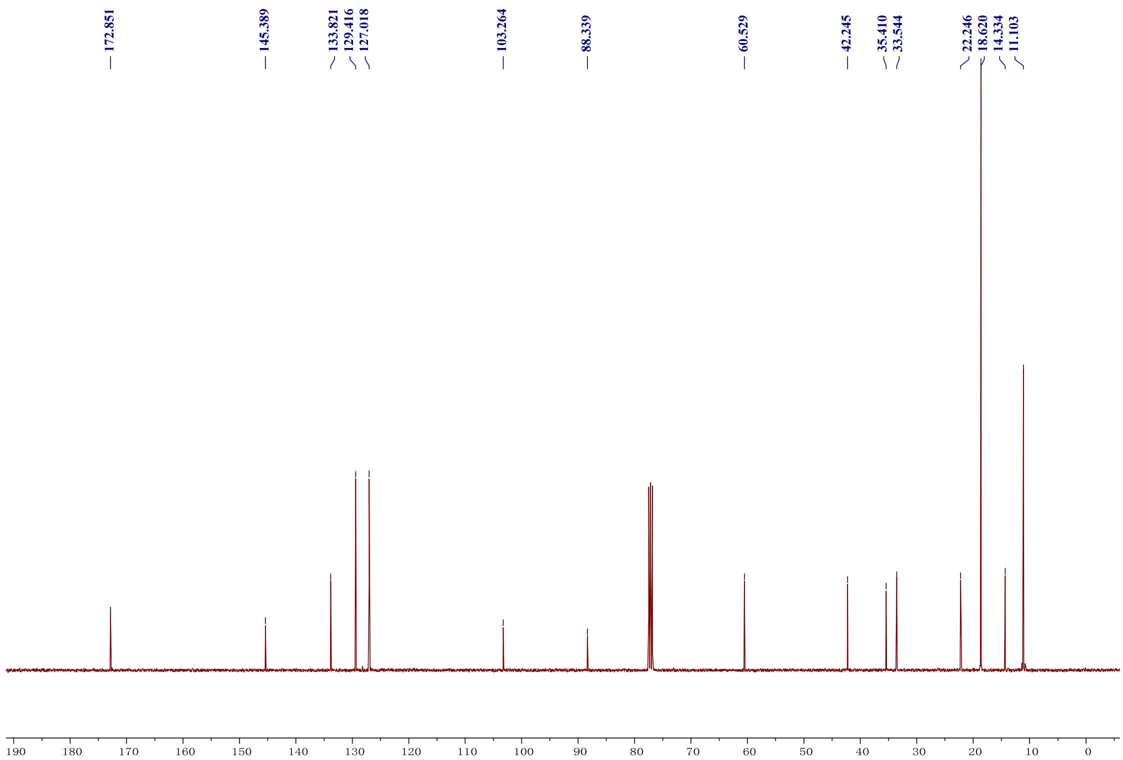


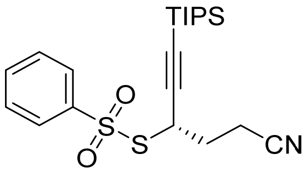
151.745
150.942
145.344
133.761
129.370
127.005
106.681
106.053
103.224
88.387
41.728
34.793
25.350
18.643
13.647
11.124
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TIPS
S
S
O
O
CO2Et

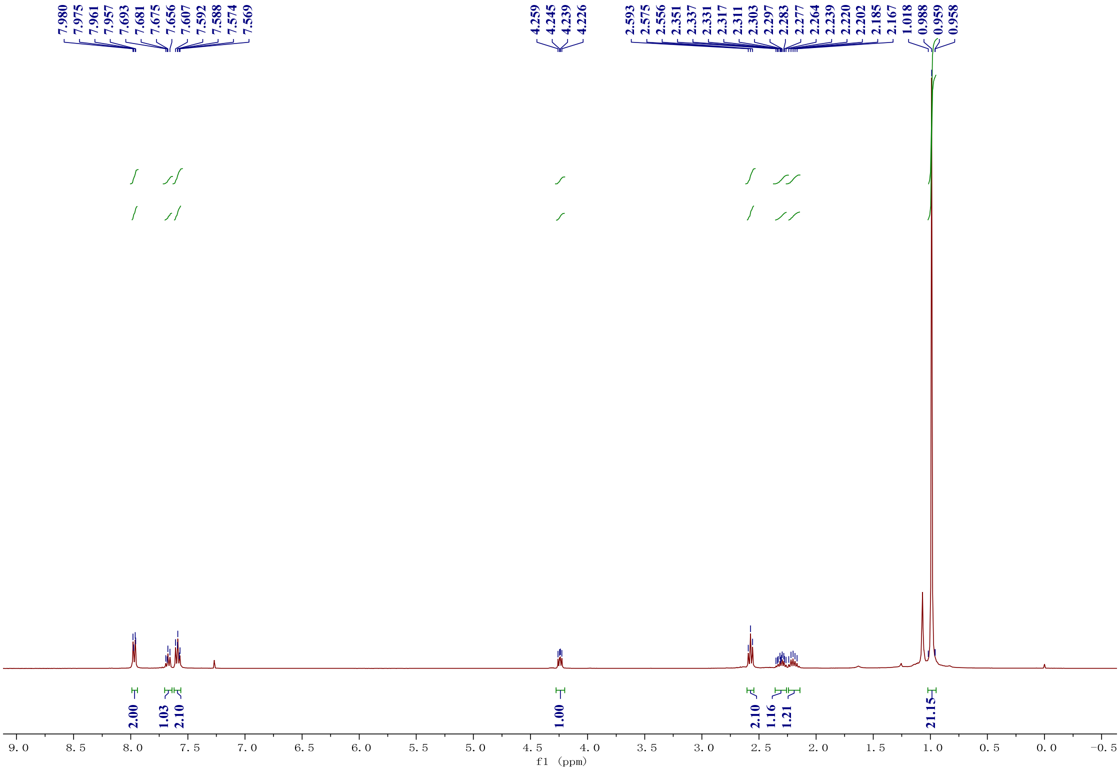
47

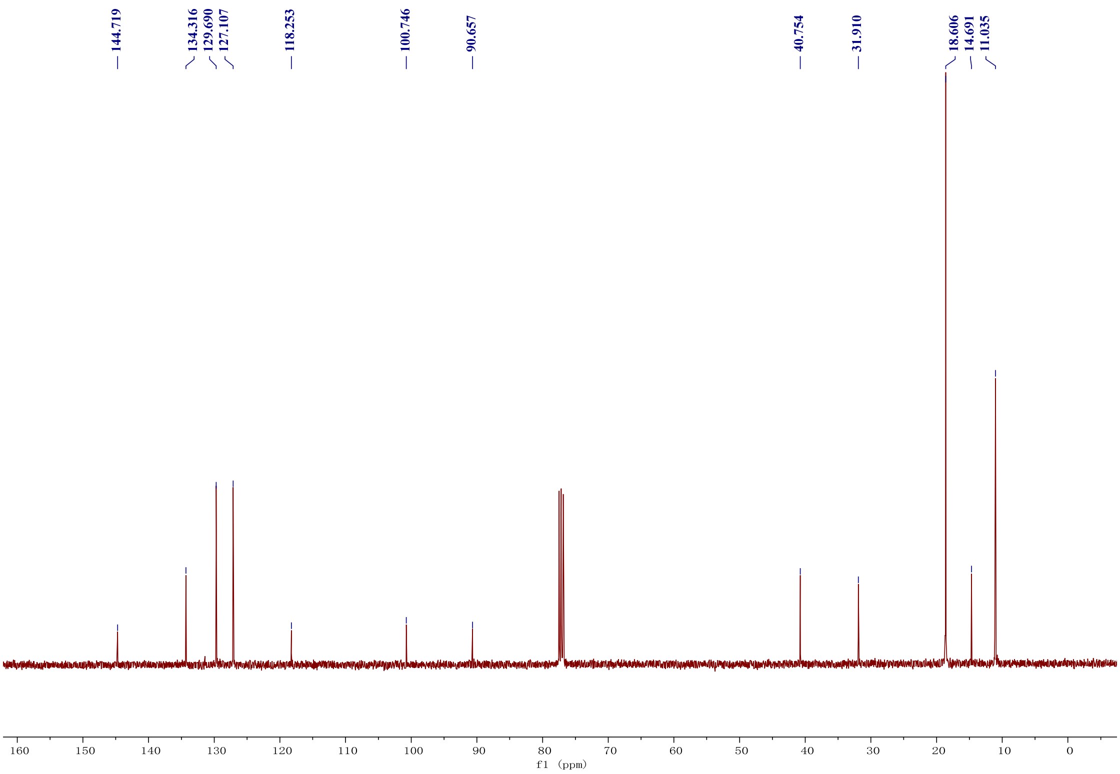

7.968 7.965 7.962 7.952 7.947 7.943 7.645 7.642 7.633 7.627 7.621 7.612 7.608 7.605 7.565 7.561 7.549 7.545 7.532 7.527 7.524 4.208 4.204 4.195 4.189 4.176 4.150 4.132 4.114 4.096 2.316 2.308 2.298 2.289 2.281 1.960 1.947 1.939 1.934 1.924 1.910 1.899 1.894 1.885 1.881 1.874 1.871 1.864 1.857 1.851 1.845 1.838 1.833 1.828 1.824 1.820 1.816 1.810 1.799 1.267 1.264 1.250 1.232 0.999 0.992 0.989 0.985 0.979 0.972 0.966
2.04
1.01
2.08
1.00
2.08
2.00
1.05
3.43
3.15
21.02
f1 (ppm)

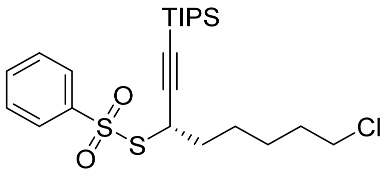

172.851
145.389
133.821
129.416
127.018
103.264
88.339
60.529
42.245
35.410
33.544
22.246
18.620
14.334
11.103
f1 (ppm)


TIPS
O
S
S
O
CN

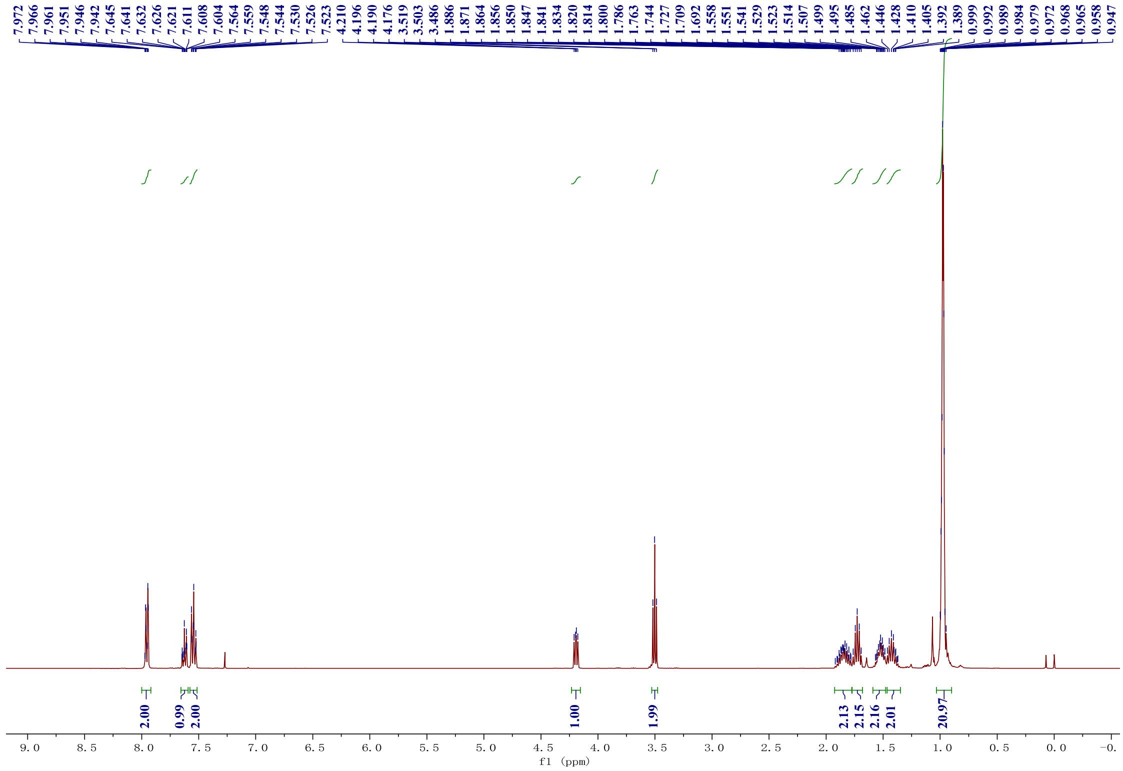
48

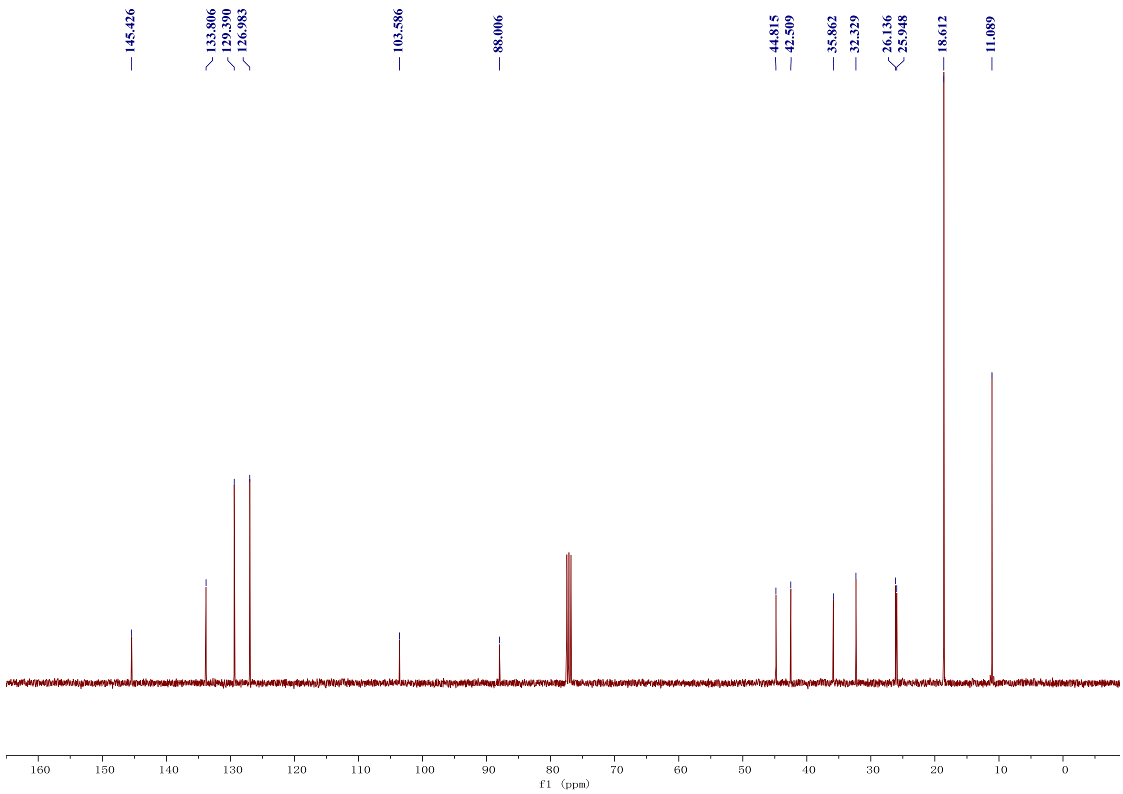

7.980 7.975 7.961 7.957 7.693 7.681 7.675 7.656 7.607 7.592 7.588 7.574 7.569
4.259 4.245 4.239 4.226
2.593 2.575 2.556 2.351 2.337 2.331 2.317 2.311 2.303 2.297 2.283 2.277 2.264 2.239 2.220 2.202 2.185 2.167
1.018 0.988 0.959 0.958
2.00
1.03
2.10
1.00
2.10
1.16
1.21
21.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

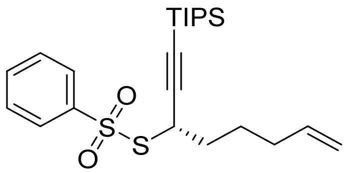

144.719
134.316
129.690
127.107
118.253
100.746
90.657
40.754
31.910
18.606
14.691
11.035
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



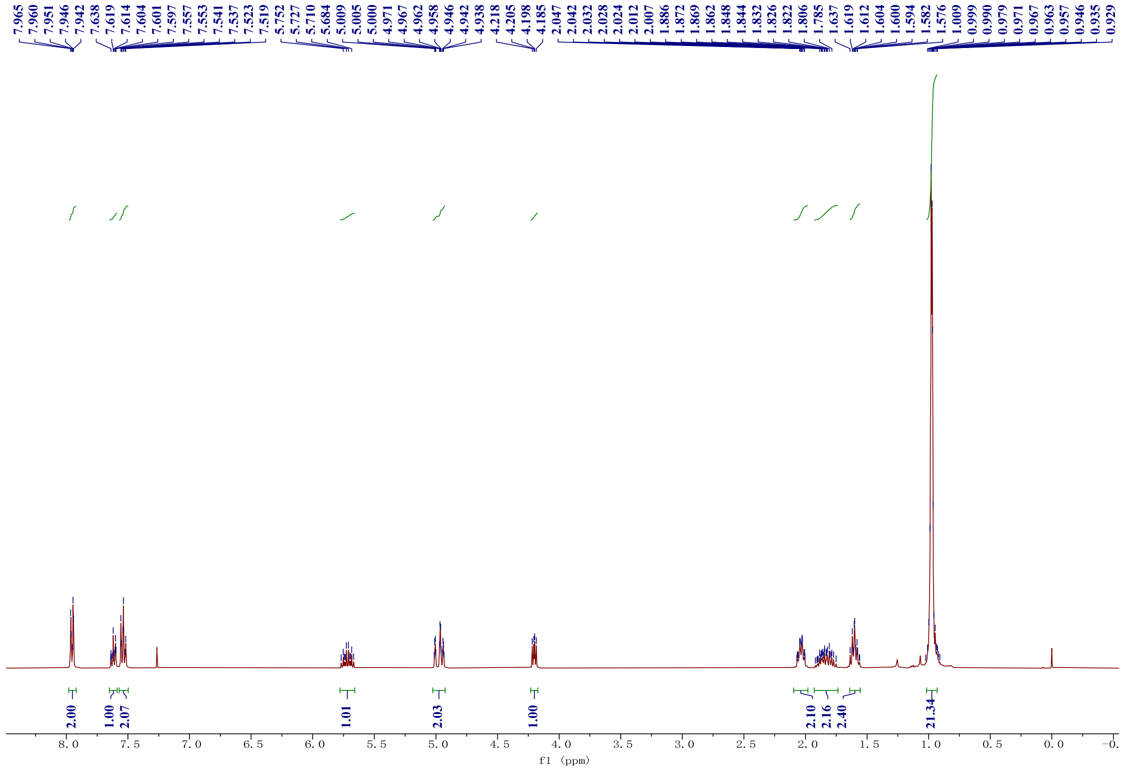
49

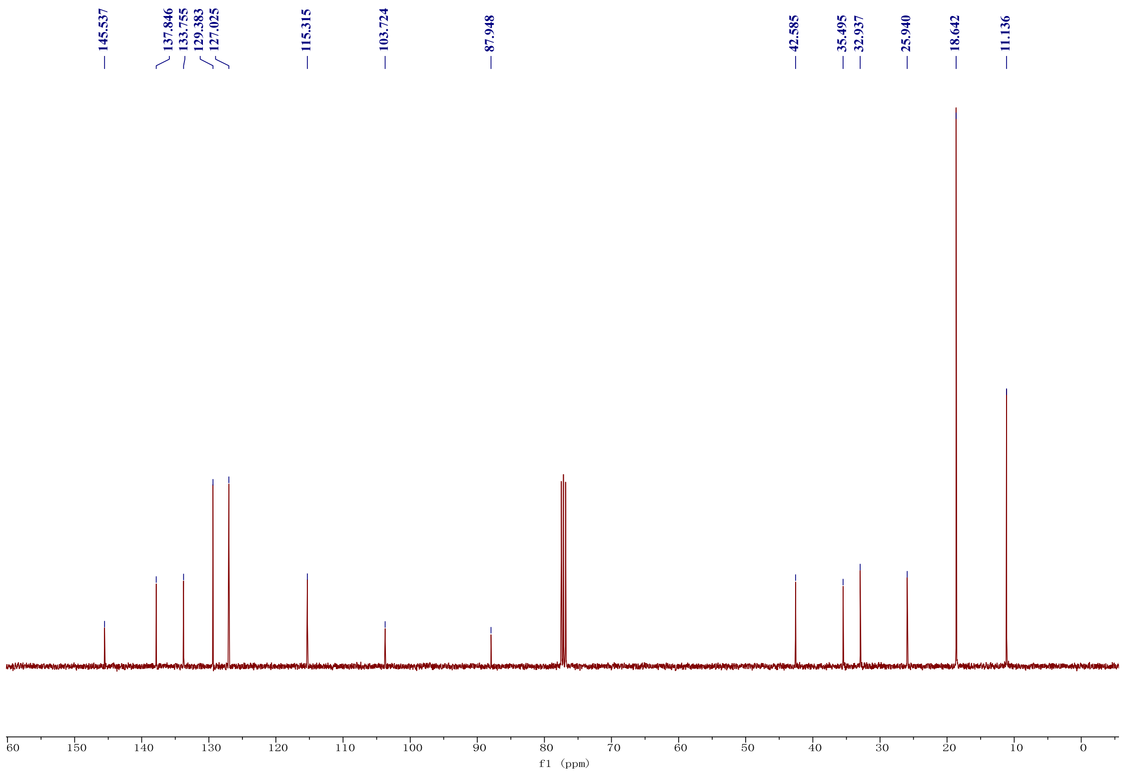


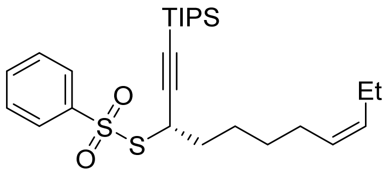



TIPS
O
S
O
S

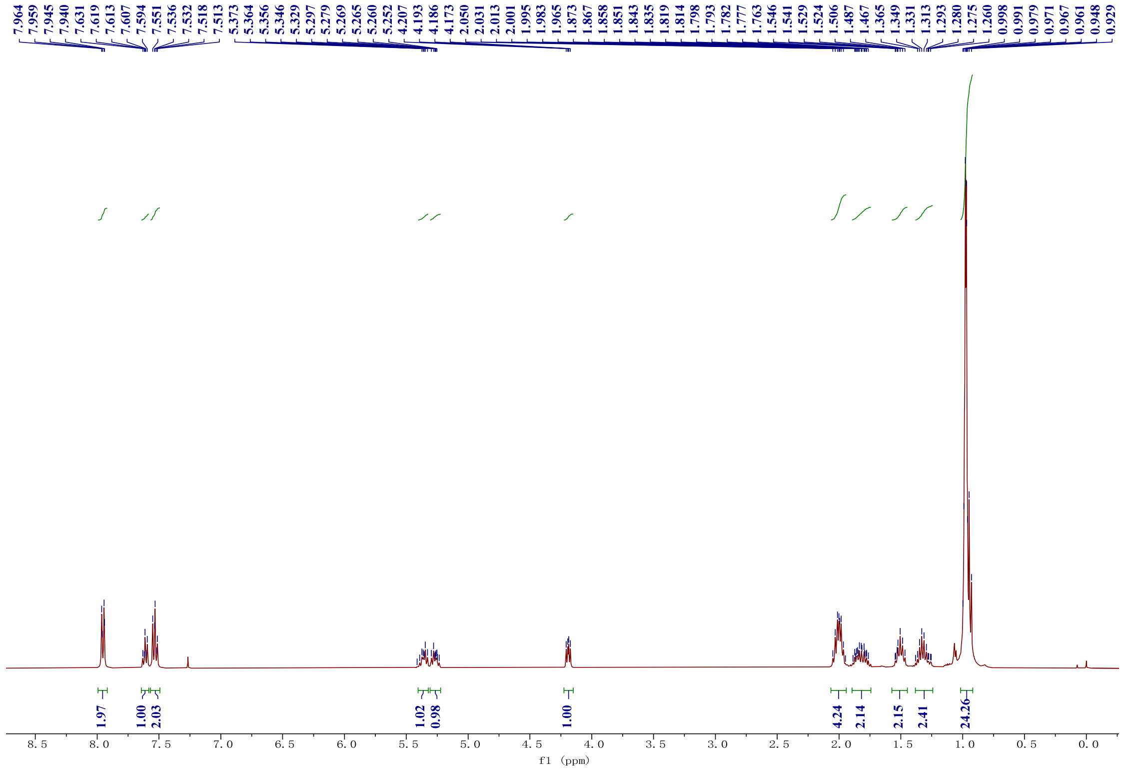
50

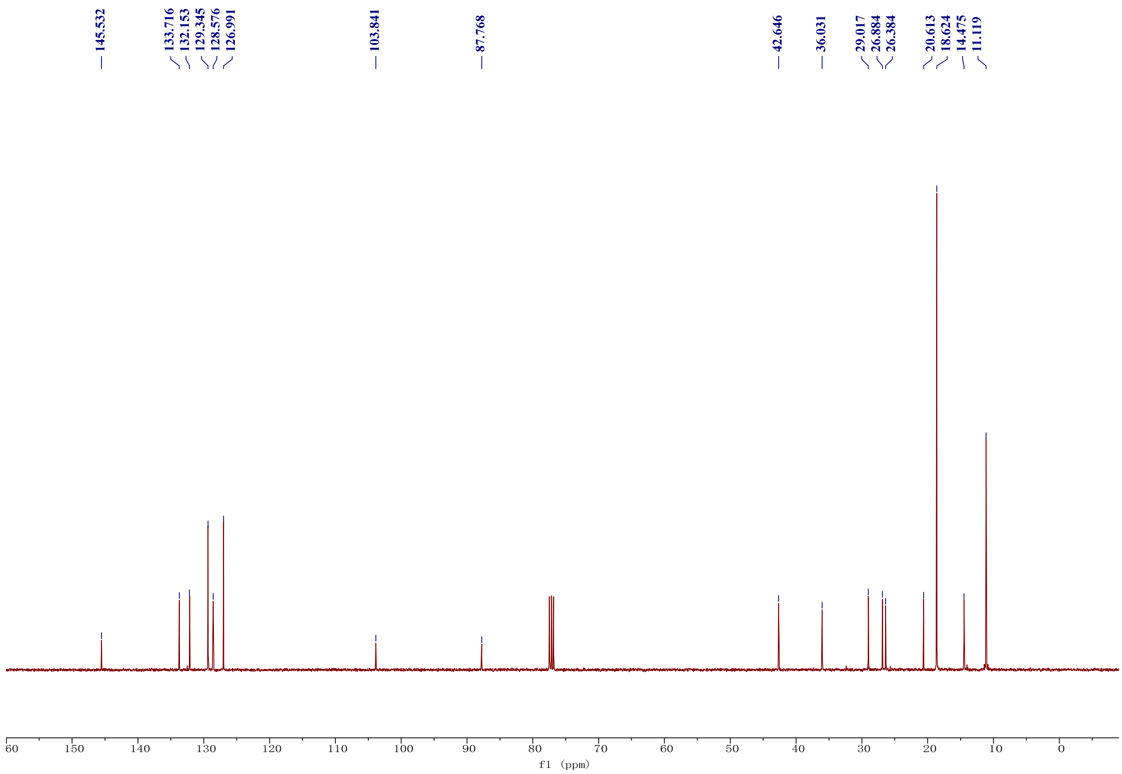

7.965
7.960
7.951
7.946
7.942
7.638
7.619
7.614
7.604
7.601
7.597
7.557
7.553
7.541
7.537
7.523
7.519
5.752
5.727
5.710
5.684
5.009
5.005
5.000
4.971
4.967
4.962
4.958
4.946
4.942
4.938
4.218
4.205
4.198
4.185
2.047
2.042
2.032
2.028
2.024
2.012
2.007
1.886
1.872
1.869
1.862
1.848
1.844
1.832
1.826
1.822
1.806
1.785
1.637
1.619
1.612
1.604
1.600
1.594
1.582
1.576
1.009
0.999
0.990
0.979
0.971
0.967
0.963
0.957
0.946
0.935
0.929
2.00
1.00
2.07
1.01
2.03
1.00
2.10
2.16
2.40
21.34
f1 (ppm)

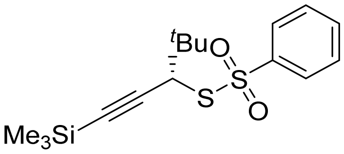

145.537
137.846
133.755
129.383
127.025
115.315
103.724
87.948
42.585
35.495
32.937
25.940
18.642
11.136
f1 (ppm)



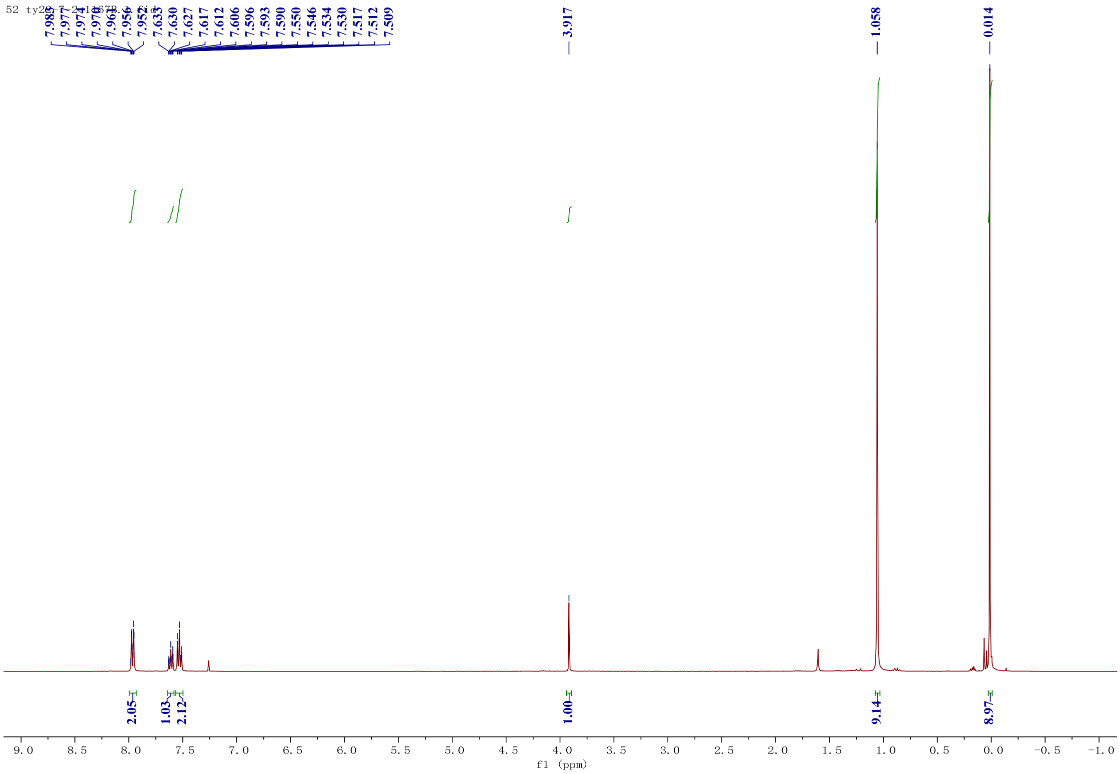
51

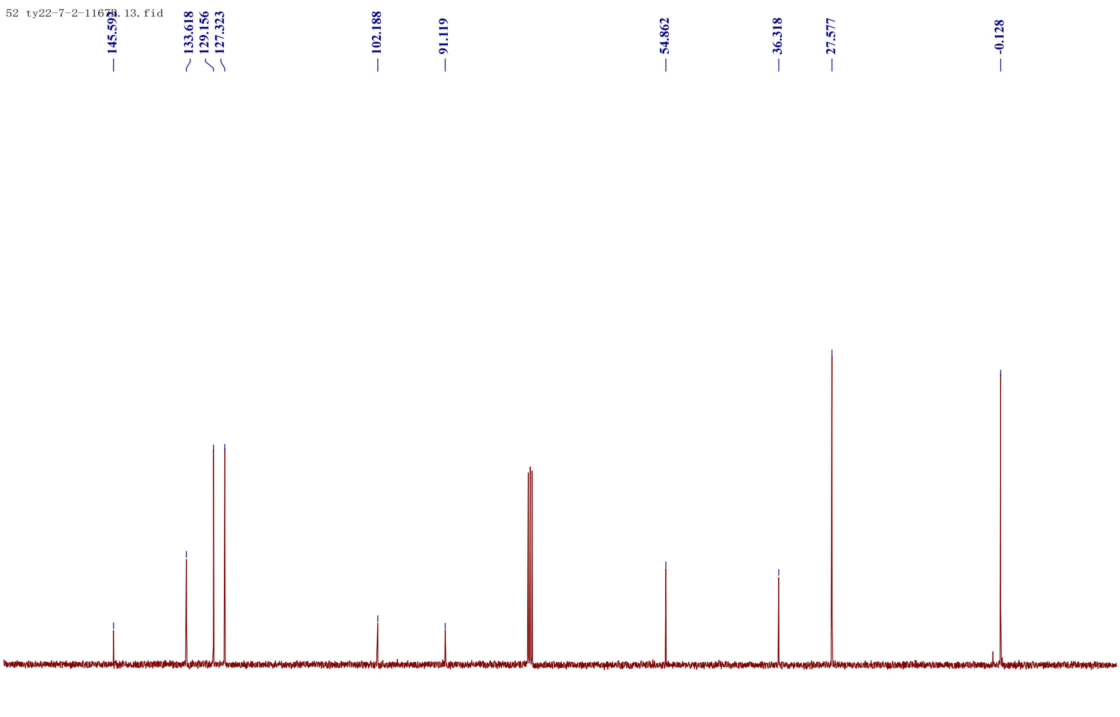


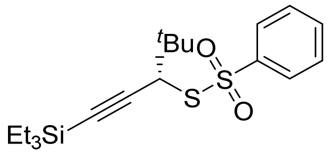



tBu
O
S
S
O
Me3Si

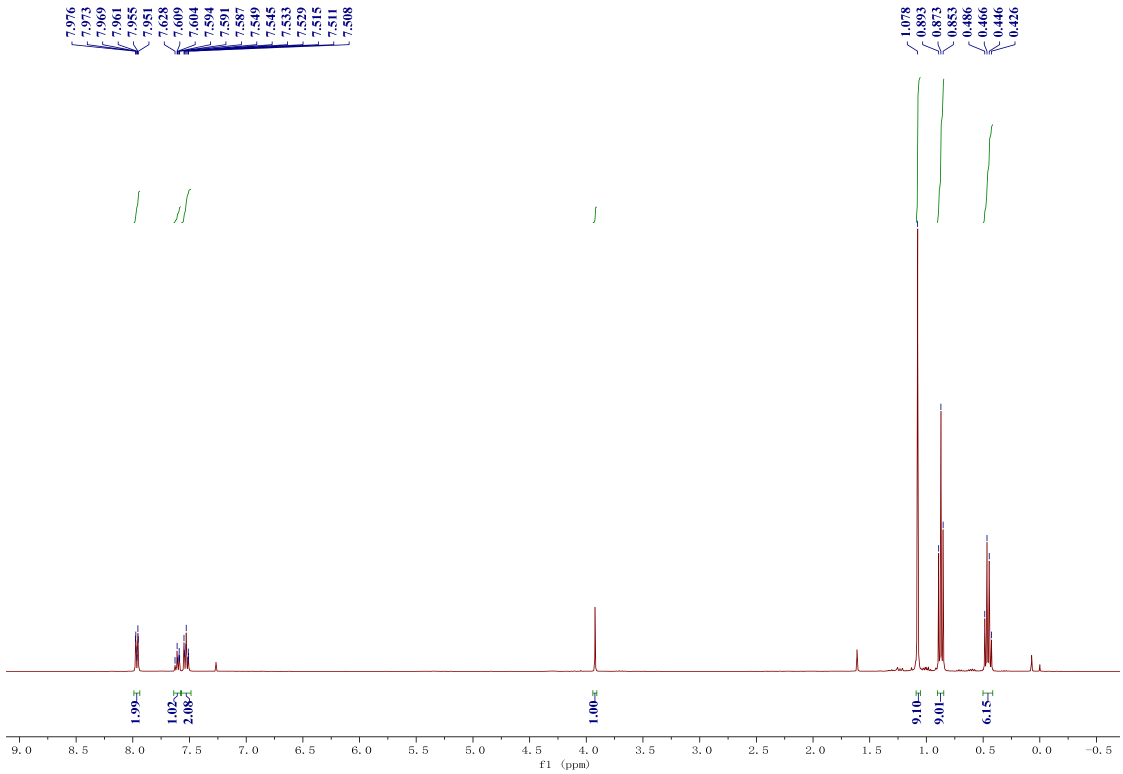
52

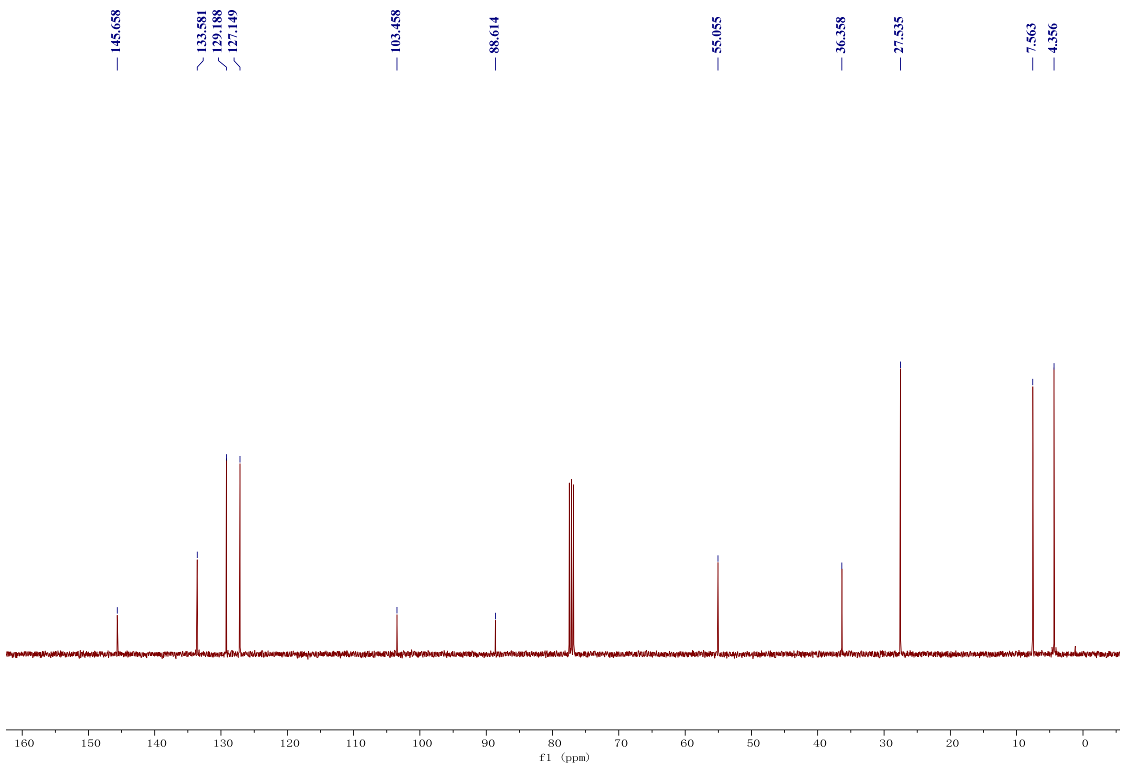

7.983
7.977
7.974
7.970
7.961
7.956
7.952
7.633
7.630
7.627
7.617
7.612
7.606
7.596
7.593
7.590
7.550
7.546
7.534
7.530
7.517
7.512
7.509
3.917
1.058
0.014
2.05
1.03
2.12
1.00
9.14
8.97
f1 (ppm)

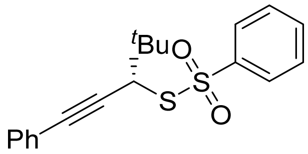

52 ty22-7-2-11678.13.fid
145.591
133.618
129.156
127.323
102.188
91.119
54.862
36.318
27.577
-0.128
f1 (ppm)



53

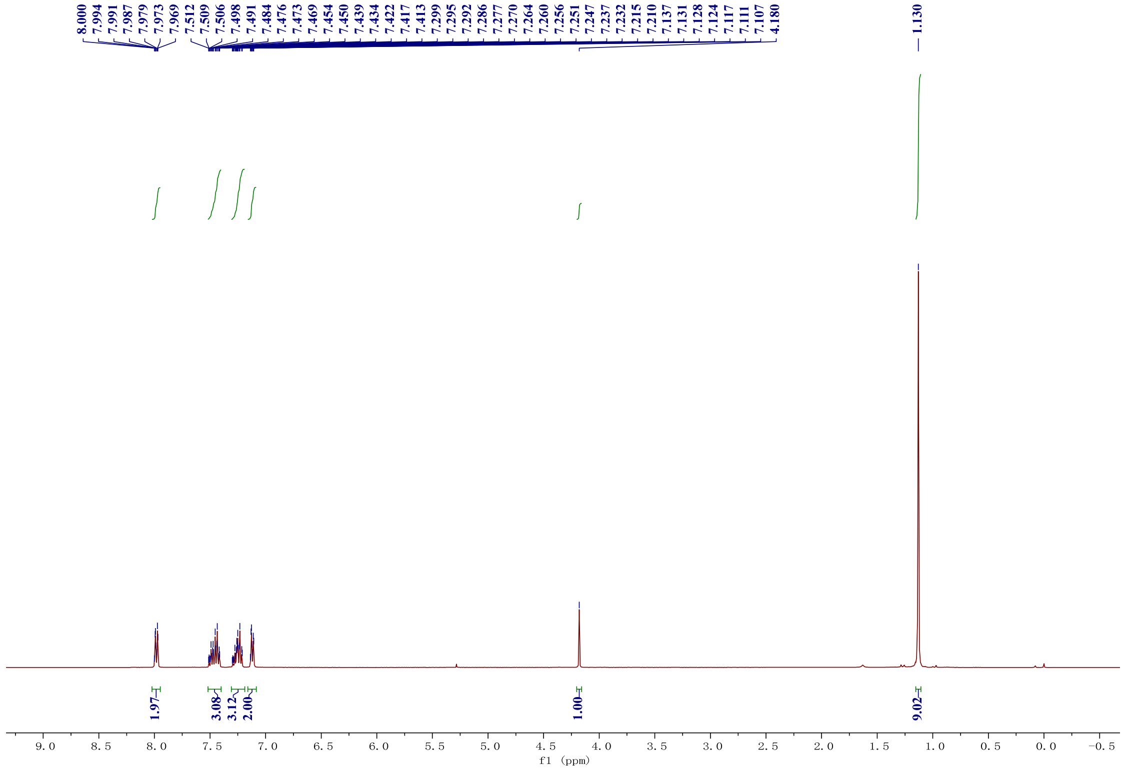

7.976
7.973
7.969
7.961
7.955
7.951
7.628
7.609
7.604
7.594
7.591
7.587
7.549
7.545
7.533
7.529
7.515
7.511
7.508
1.078
0.893
0.873
0.853
0.486
0.466
0.446
0.426
1.99
1.02
2.08
1.00
9.10
9.01
6.15
f1 (ppm)


145.658
133.581
129.188
127.149
103.458
88.614
55.055
36.358
27.535
7.563
4.356
f1 (ppm)

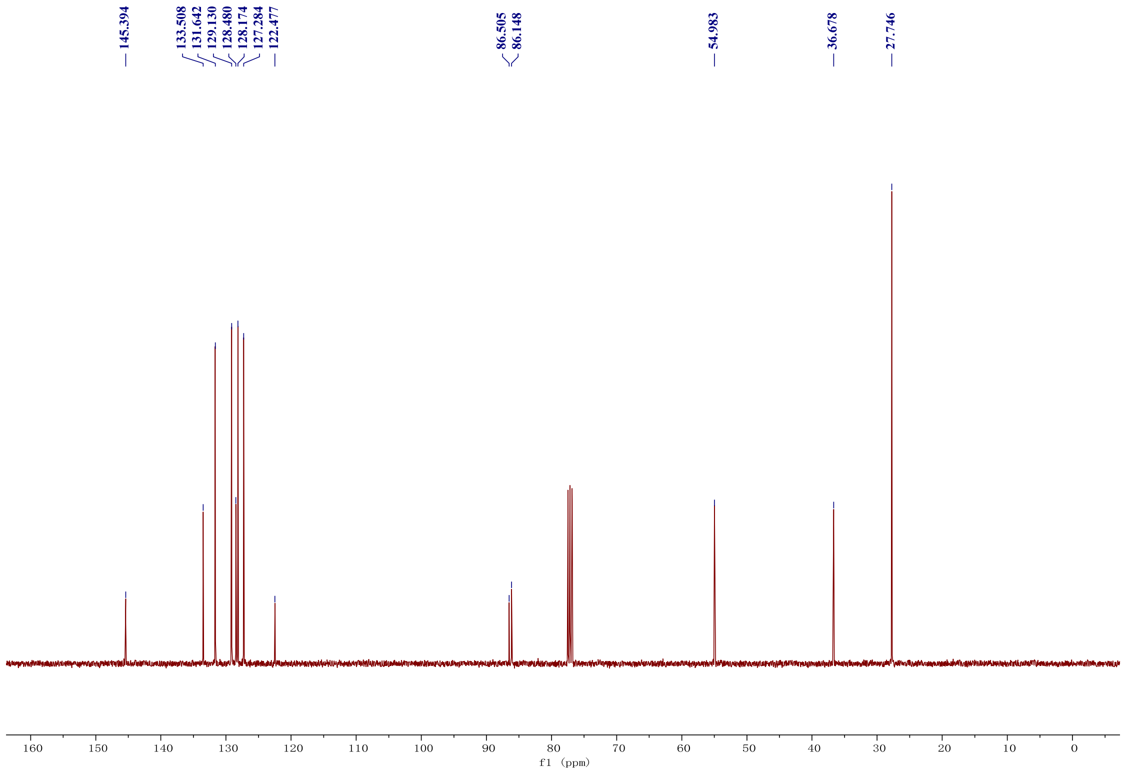


tBu
O
S
S
O
Ph

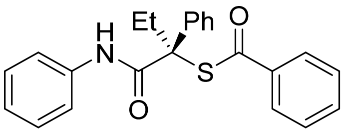
54



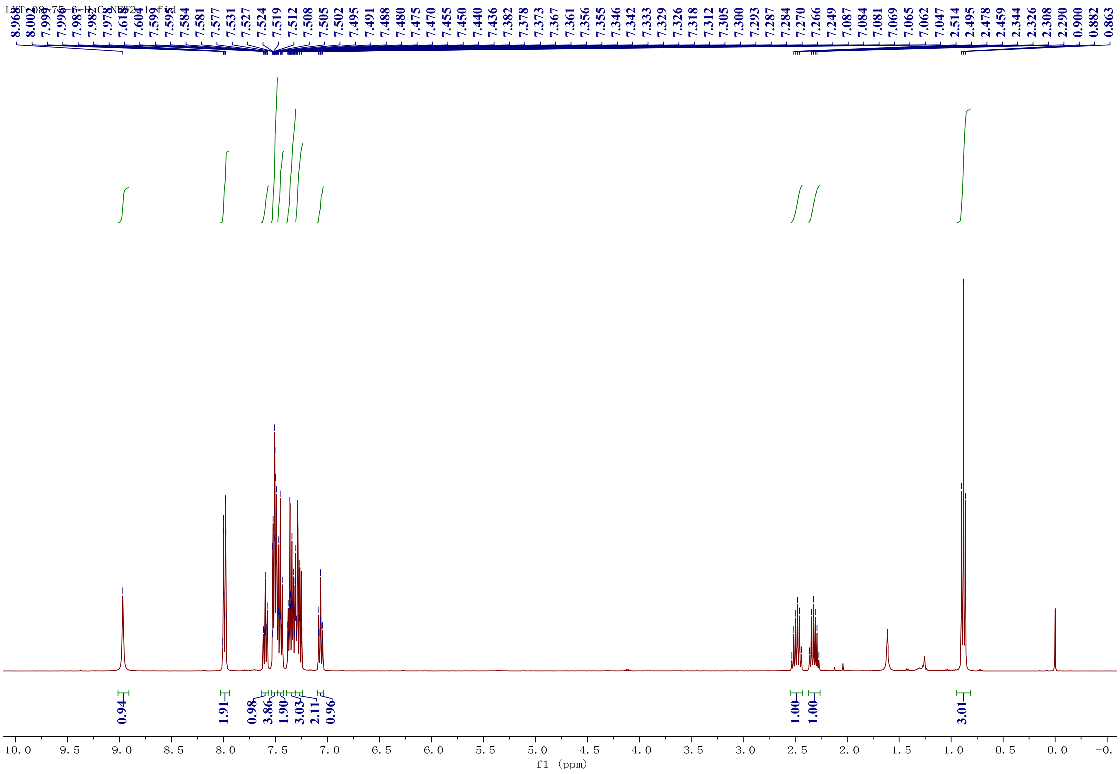
8.000
7.994
7.991
7.987
7.979
7.973
7.969
7.512
7.509
7.506
7.498
7.491
7.484
7.476
7.473
7.469
7.454
7.450
7.439
7.434
7.422
7.417
7.413
7.299
7.295
7.292
7.286
7.277
7.270
7.264
7.260
7.256
7.251
7.247
7.237
7.232
7.215
7.210
7.137
7.131
7.128
7.124
7.117
7.111
7.107
4.180
1.130
1.97
3.08
3.12
2.00
1.00
9.02
f1 (ppm)

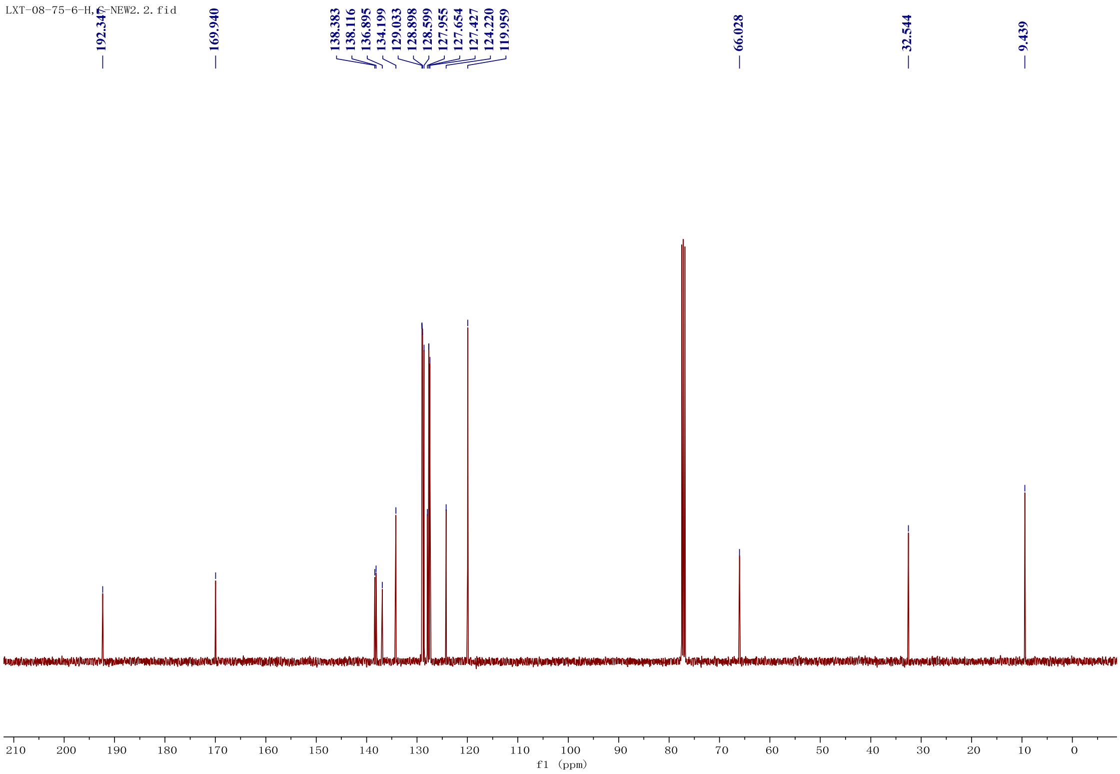


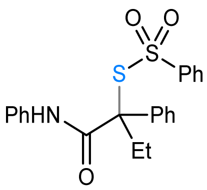
145.394
133.508
131.642
129.130
128.480
128.174
127.284
122.477
86.505
86.148
54.983
36.678
27.746
f1 (ppm)


H
N
O
Et
Ph
S
O

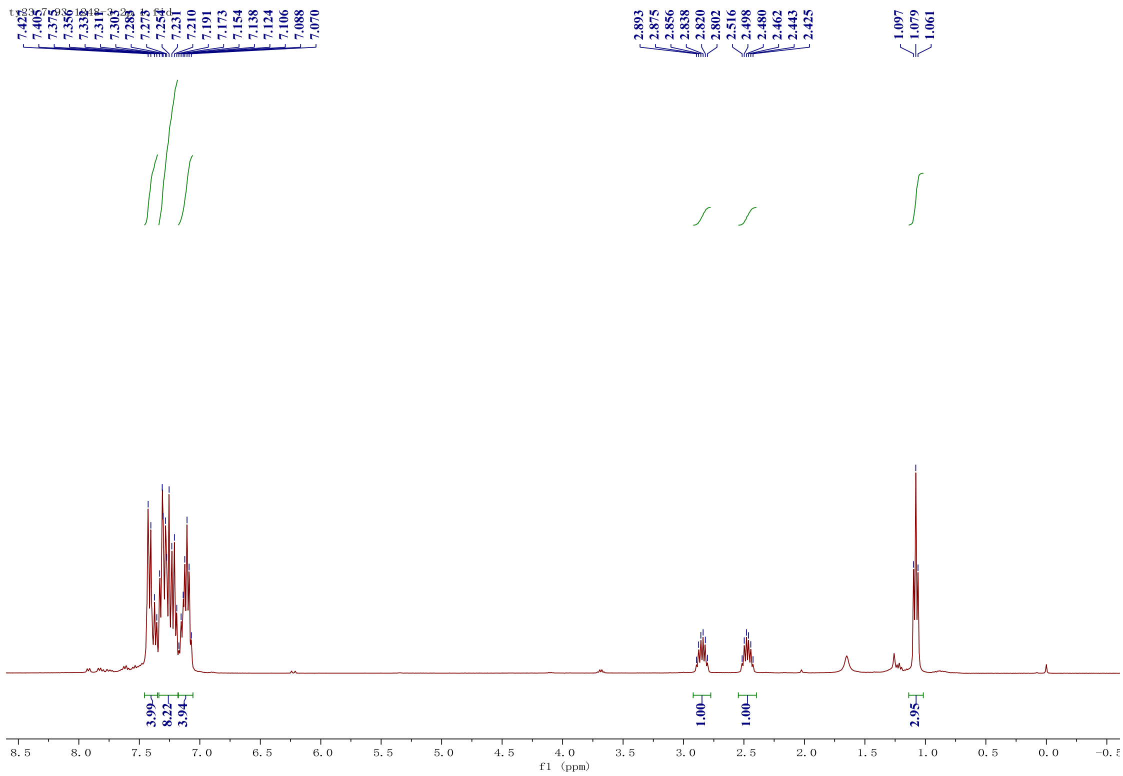
55

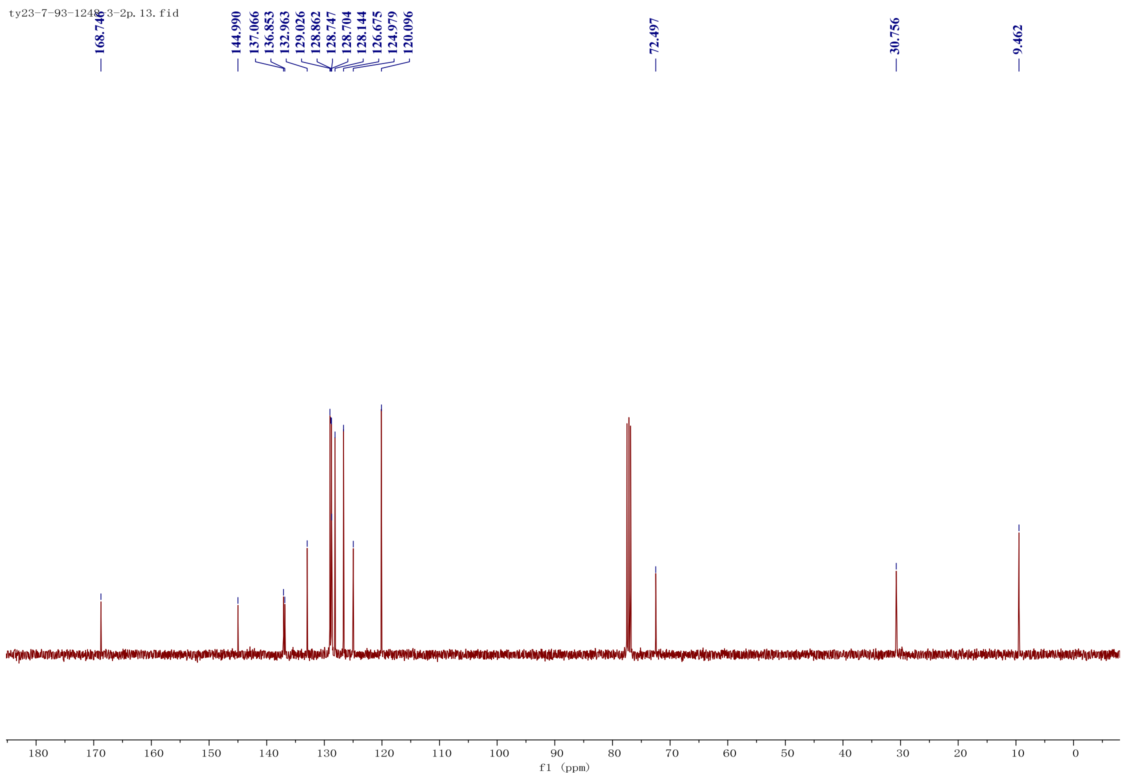

8.968
8.002
7.996
7.987
7.982
7.978
7.618
7.604
7.599
7.595
7.584
7.581
7.577
7.531
7.527
7.524
7.519
7.512
7.508
7.505
7.502
7.495
7.491
7.488
7.480
7.475
7.470
7.455
7.450
7.440
7.436
7.382
7.378
7.373
7.367
7.361
7.356
7.355
7.346
7.342
7.333
7.329
7.326
7.318
7.312
7.305
7.300
7.293
7.287
7.284
7.270
7.266
7.249
7.087
7.084
7.081
7.069
7.065
7.062
7.047
2.514
2.495
2.478
2.459
2.344
2.326
2.308
2.290
0.900
0.882
0.863
0.94
1.91
0.98
3.86
1.90
3.03
2.11
0.96
1.00
1.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

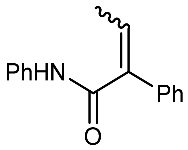

LXT-08-75-6-H,C-NEW2.2.fid
192.347
169.940
138.383
138.116
136.895
134.199
129.033
128.898
128.599
127.955
127.654
127.427
124.220
119.959
66.028
32.544
9.439
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



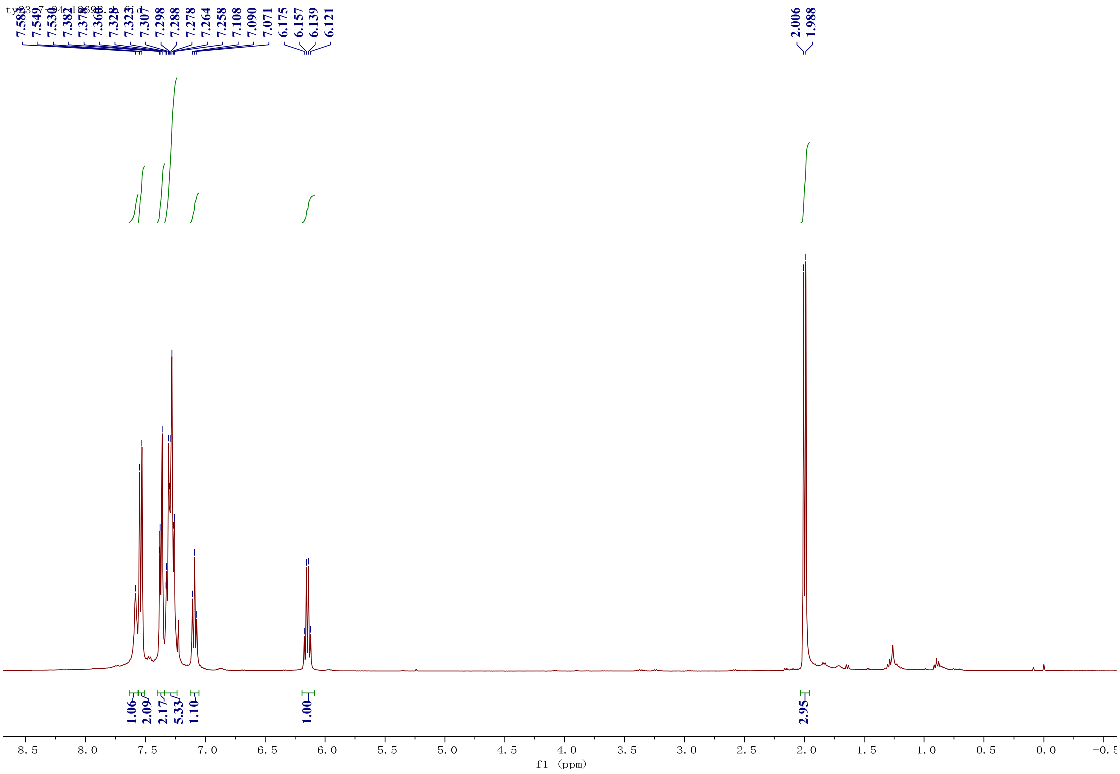
55a

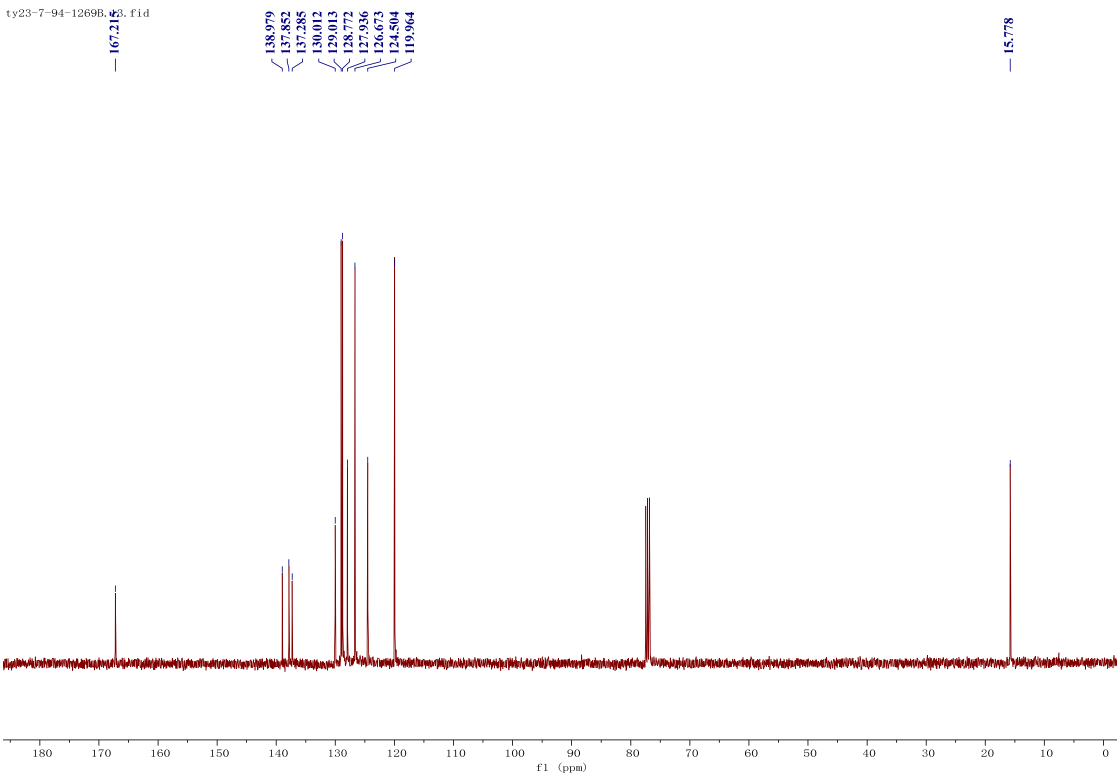


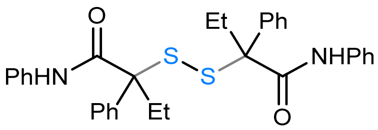




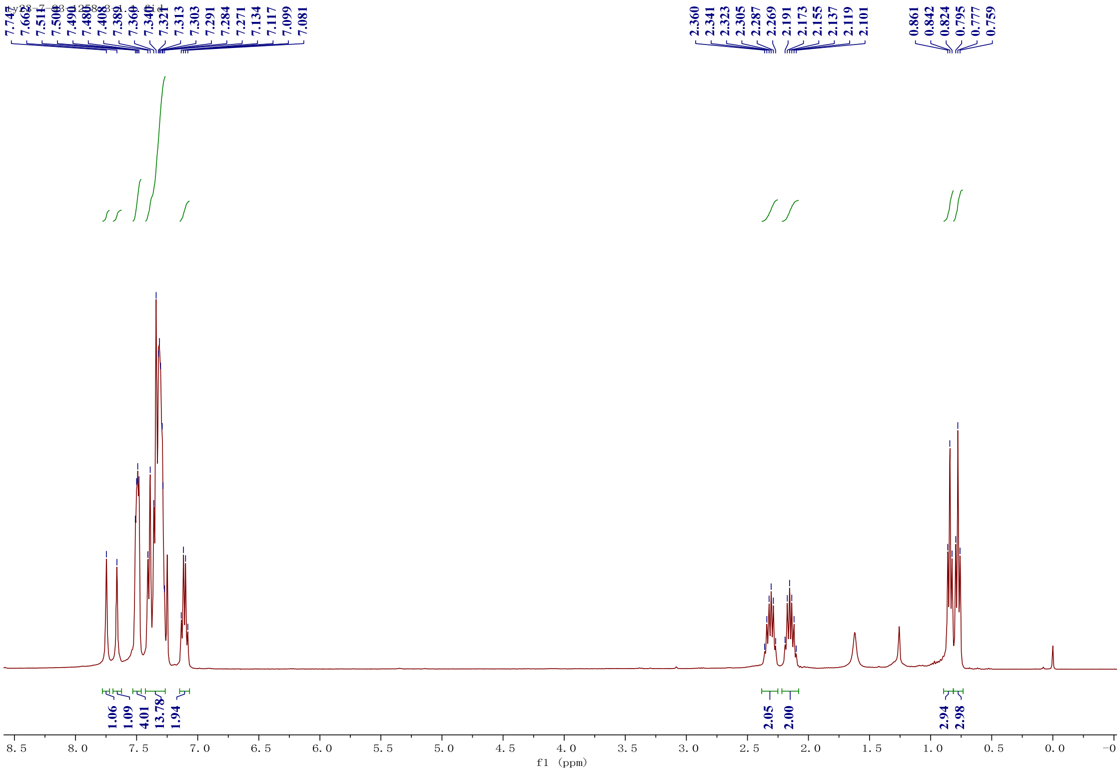
55b

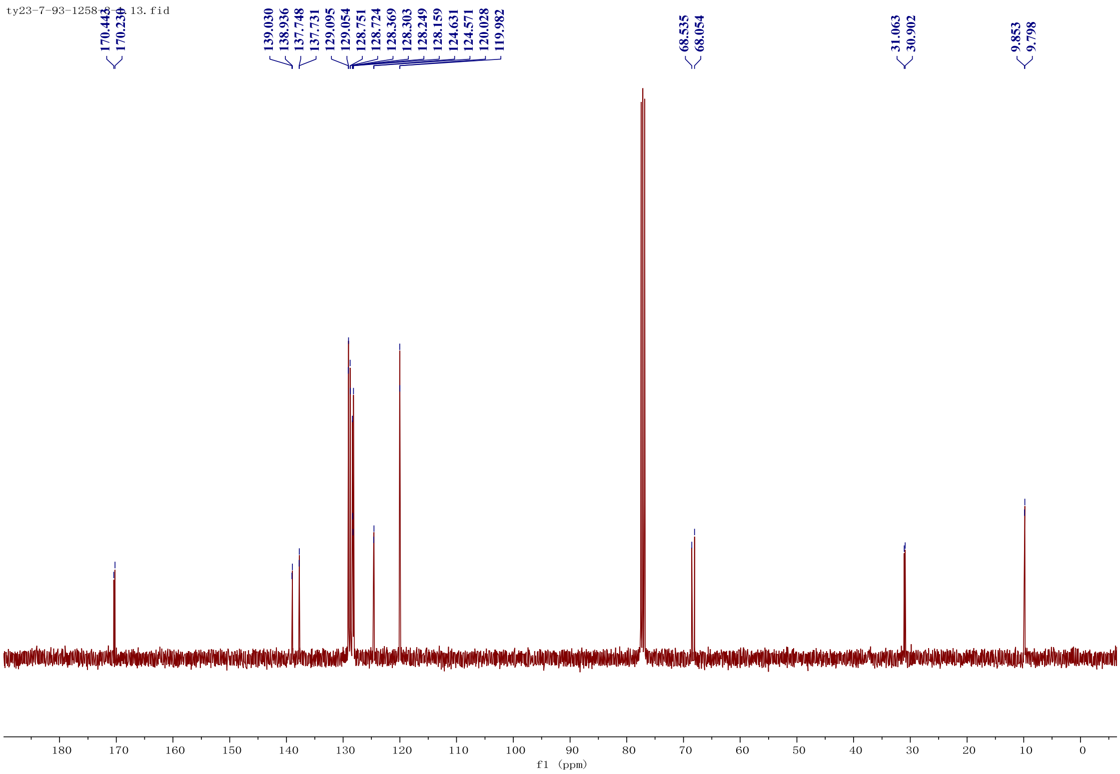


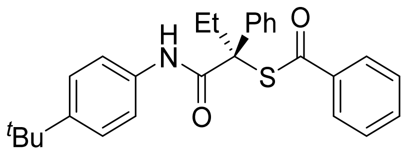



PhHN
O
S
S
Et
Ph
NHPh
Ph
Et
O

55c

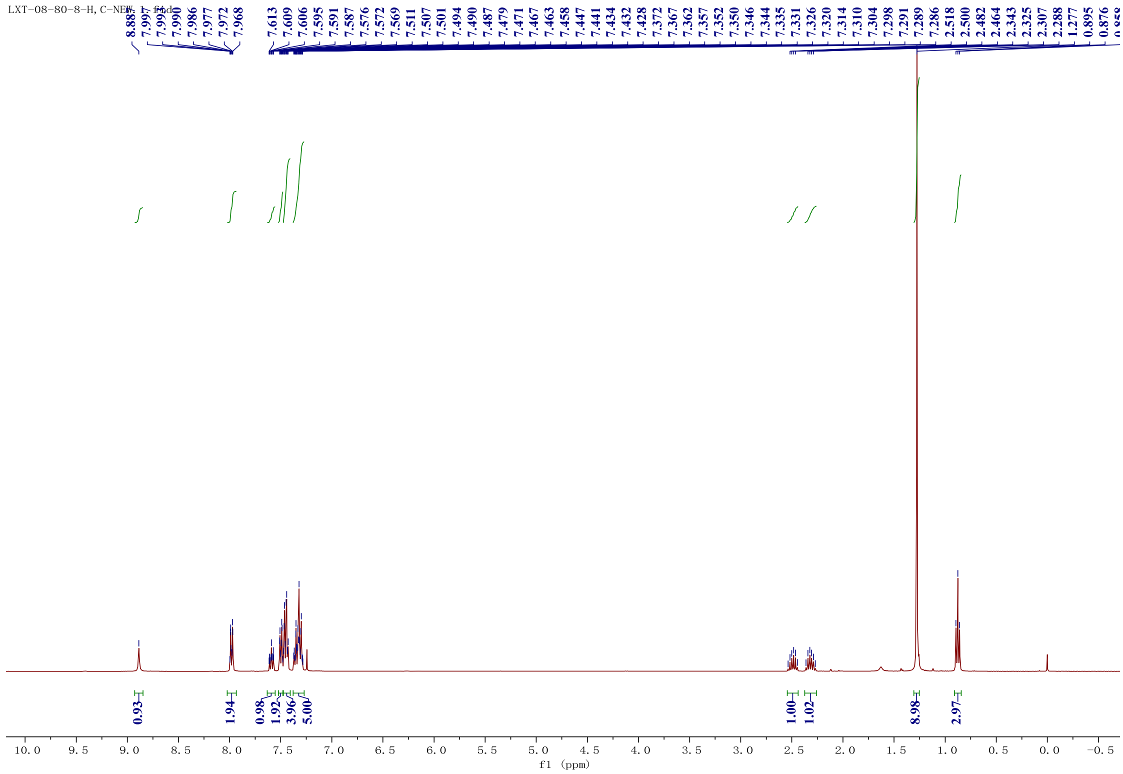

7.313
7.303
7.291
7.284
7.271
7.134
7.117
7.099
7.081
2.360
2.341
2.323
2.305
2.287
2.269
2.191
2.173
2.155
2.137
2.119
2.101
0.861
0.842
0.824
0.795
0.777
0.759
1.06
1.09
4.01
13.78
1.94
2.05
2.00
2.94
2.98
f1 (ppm)


139.030
138.936
137.748
137.731
129.095
129.054
128.751
128.724
128.369
128.303
128.249
128.159
124.631
124.571
120.028
119.982
68.535
68.054
31.063
30.902
9.853
9.798
f1 (ppm)

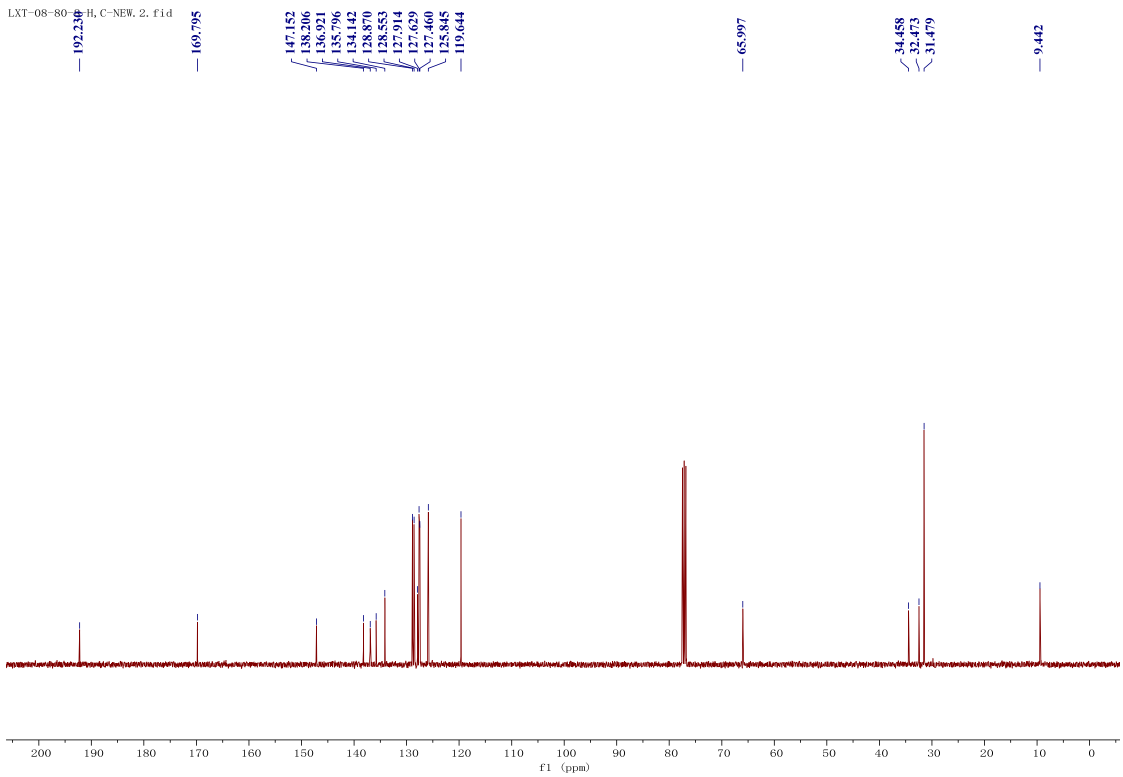


H
N
Et
Ph
O
S
O
tBu

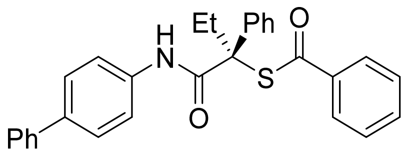
56



LXT-08-80-8-H, C-NEW. 1. fid
8.883
7.997
7.993
7.990
7.986
7.977
7.972
7.968
7.613
7.609
7.606
7.595
7.591
7.587
7.576
7.572
7.569
7.511
7.507
7.501
7.494
7.490
7.487
7.479
7.471
7.467
7.463
7.458
7.447
7.441
7.434
7.432
7.428
7.372
7.367
7.362
7.357
7.352
7.350
7.346
7.344
7.335
7.331
7.326
7.320
7.314
7.310
7.304
7.298
7.291
7.289
7.286
2.518
2.500
2.482
2.464
2.343
2.325
2.307
2.288
1.277
0.895
0.876
0.93
1.94
0.98
1.92
3.96
5.00
1.00
1.02
8.98
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

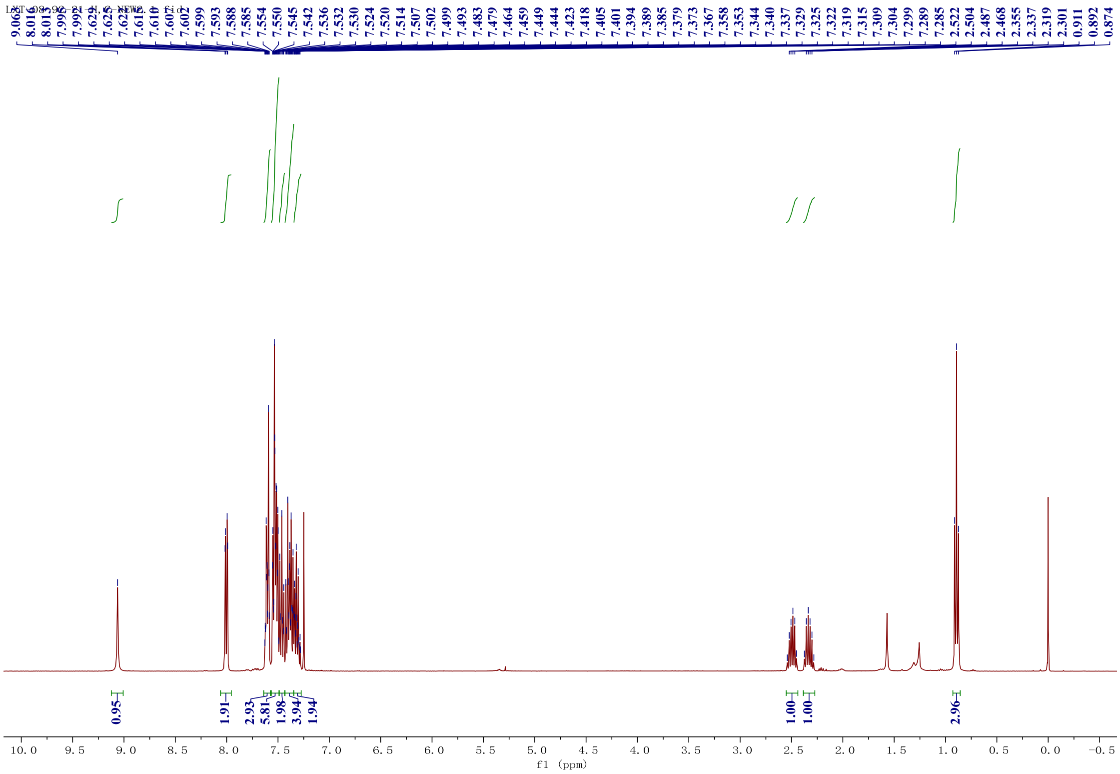


LXT-08-80-8-H, C-NEW. 2. fid
192.230
169.795
147.152
138.206
136.921
135.796
134.142
128.870
128.553
127.914
127.629
127.460
125.845
119.644
65.997
34.458
32.473
31.479
9.442
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

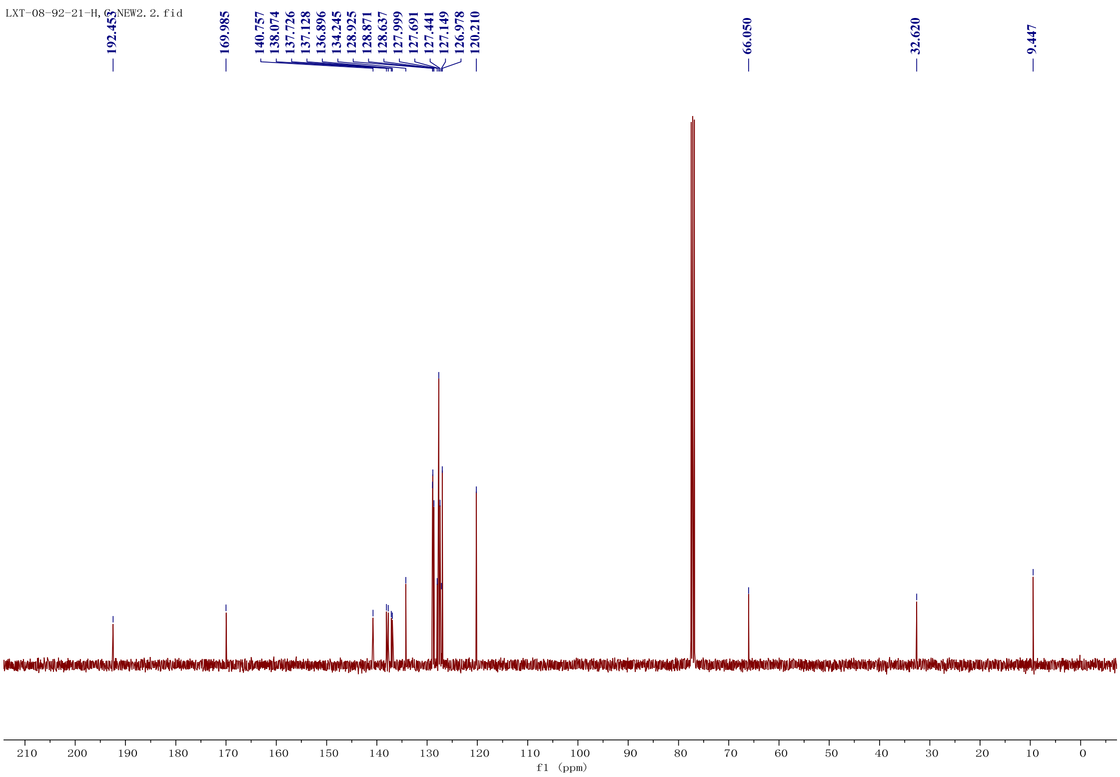


H
N
Et
Ph
O
S
O
Ph

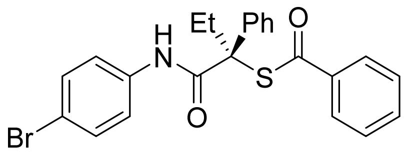
57



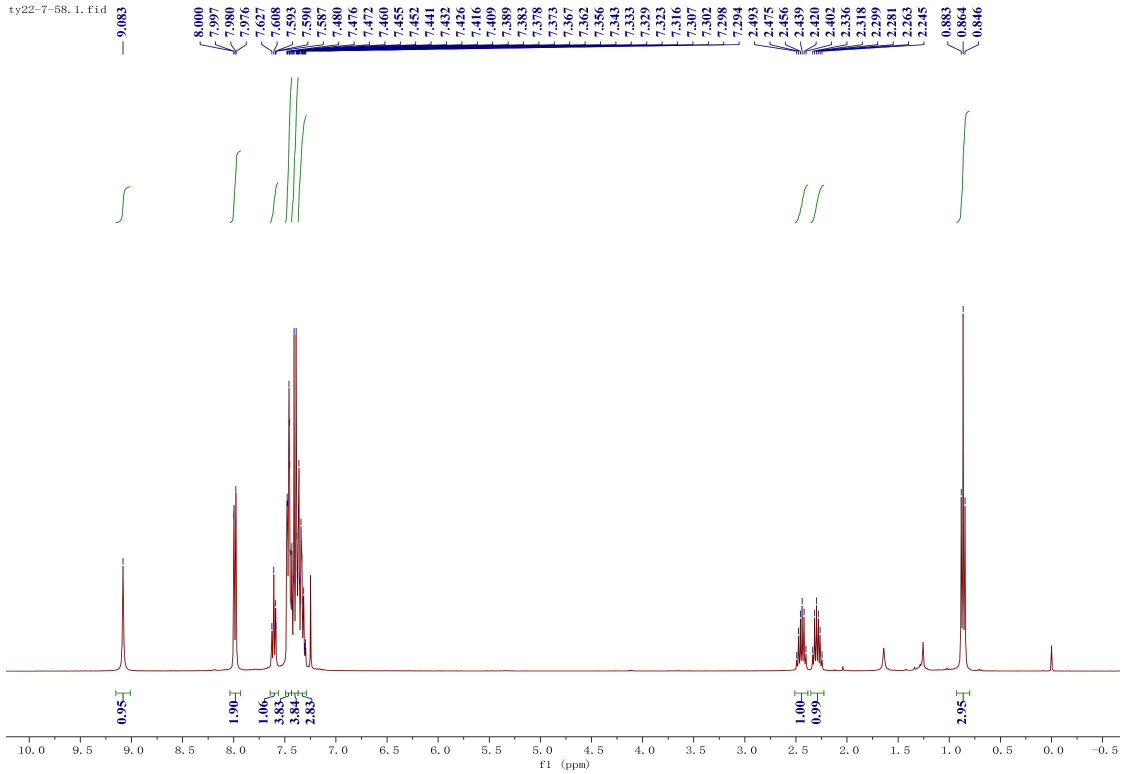
9.063
8.016
8.013
7.995
7.992
7.629
7.625
7.615
7.610
7.602
7.602
7.599
7.593
7.588
7.585
7.554
7.550
7.545
7.542
7.536
7.532
7.530
7.524
7.520
7.514
7.507
7.502
7.499
7.493
7.483
7.479
7.464
7.459
7.449
7.444
7.423
7.418
7.405
7.401
7.394
7.389
7.385
7.379
7.373
7.367
7.358
7.353
7.344
7.340
7.337
7.329
7.325
7.322
7.319
7.315
7.309
7.304
7.299
7.289
7.285
2.522
2.504
2.487
2.468
2.355
2.337
2.319
2.301
0.911
0.892
0.874
0.95
1.91
2.93
5.81
1.98
3.94
1.94
1.00
1.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

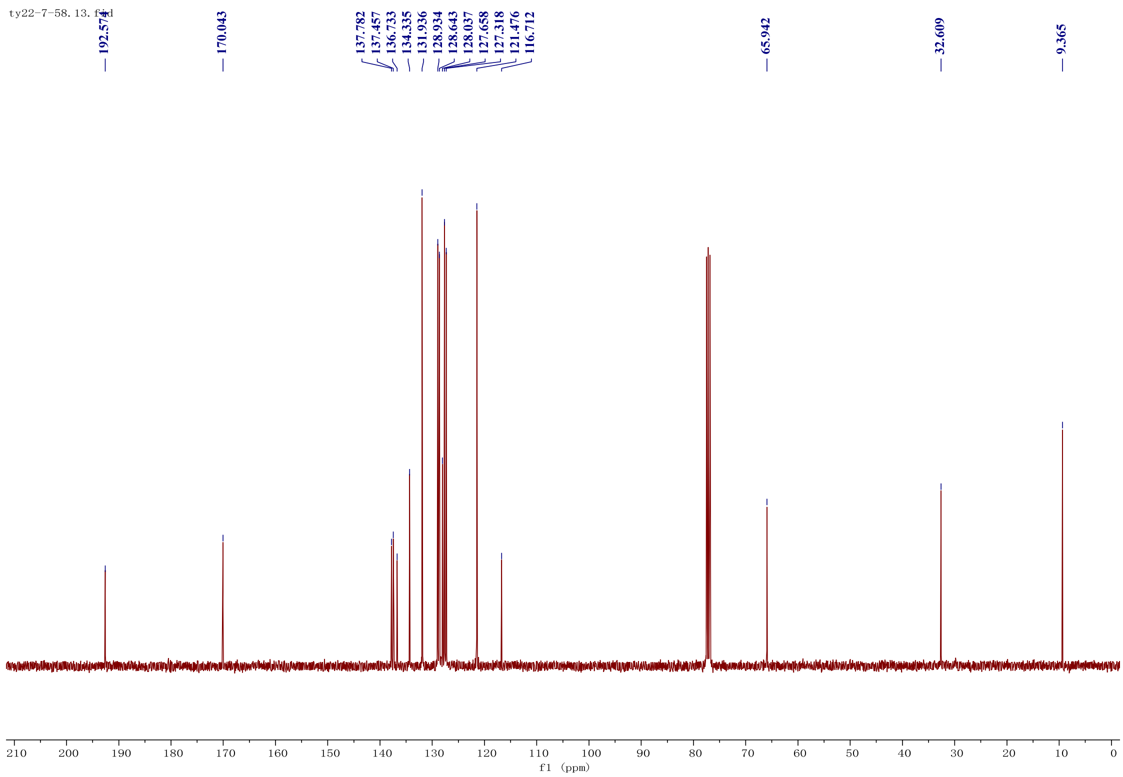


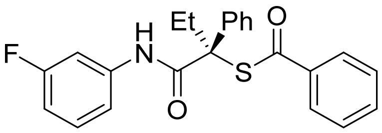
LXT-08-92-21-H,C-NEW2.2.fid
192.453
169.985
140.757
138.074
137.726
137.128
136.896
134.245
128.925
128.871
128.637
127.999
127.691
127.441
127.149
126.978
120.210
66.050
32.620
9.447
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



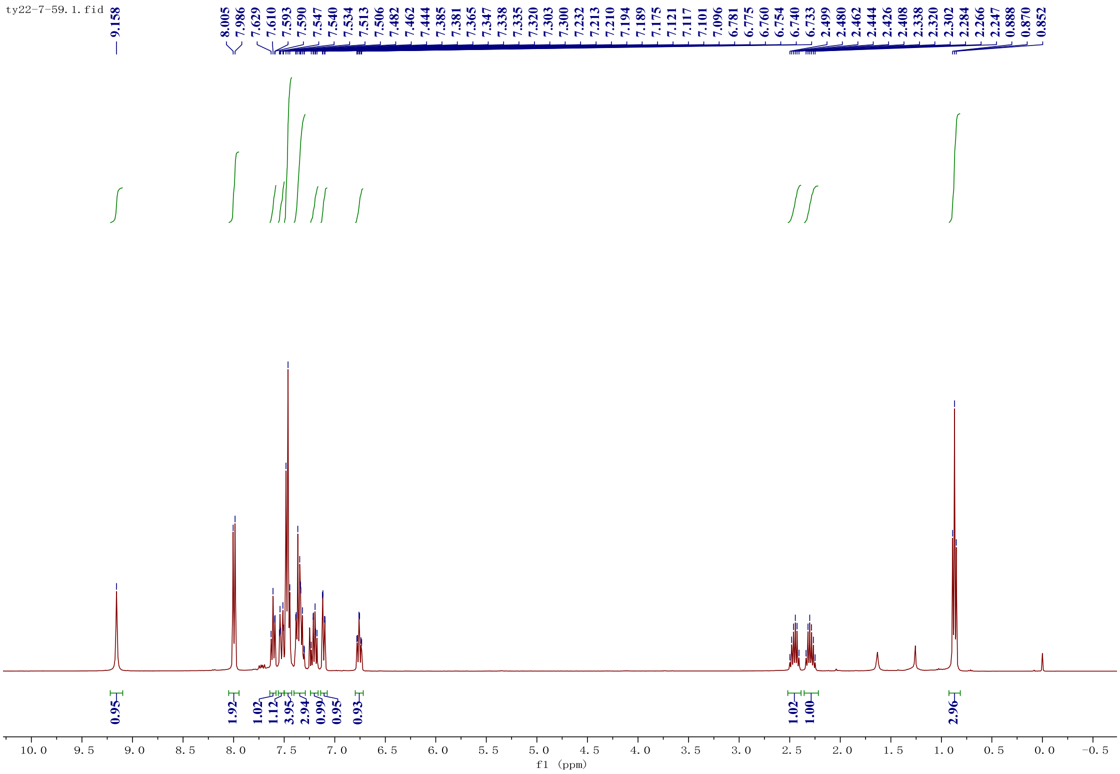
58

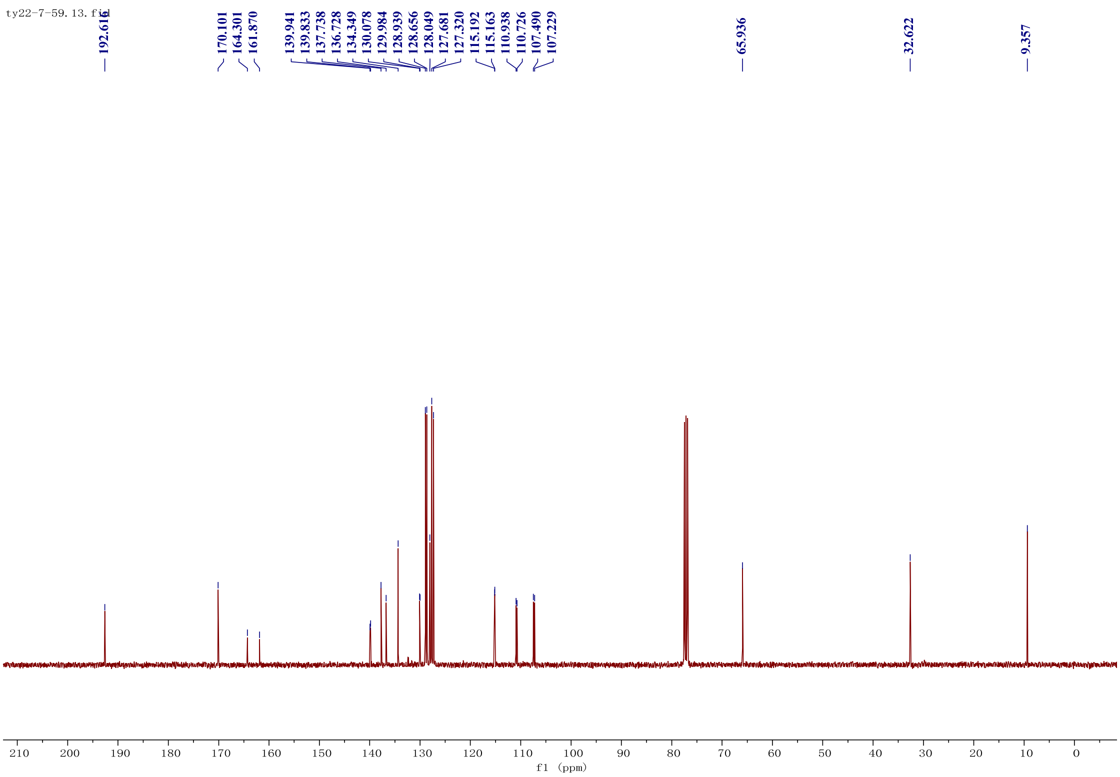


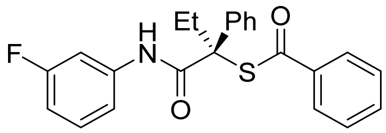



F
H
N
O
Et
Ph
S
O

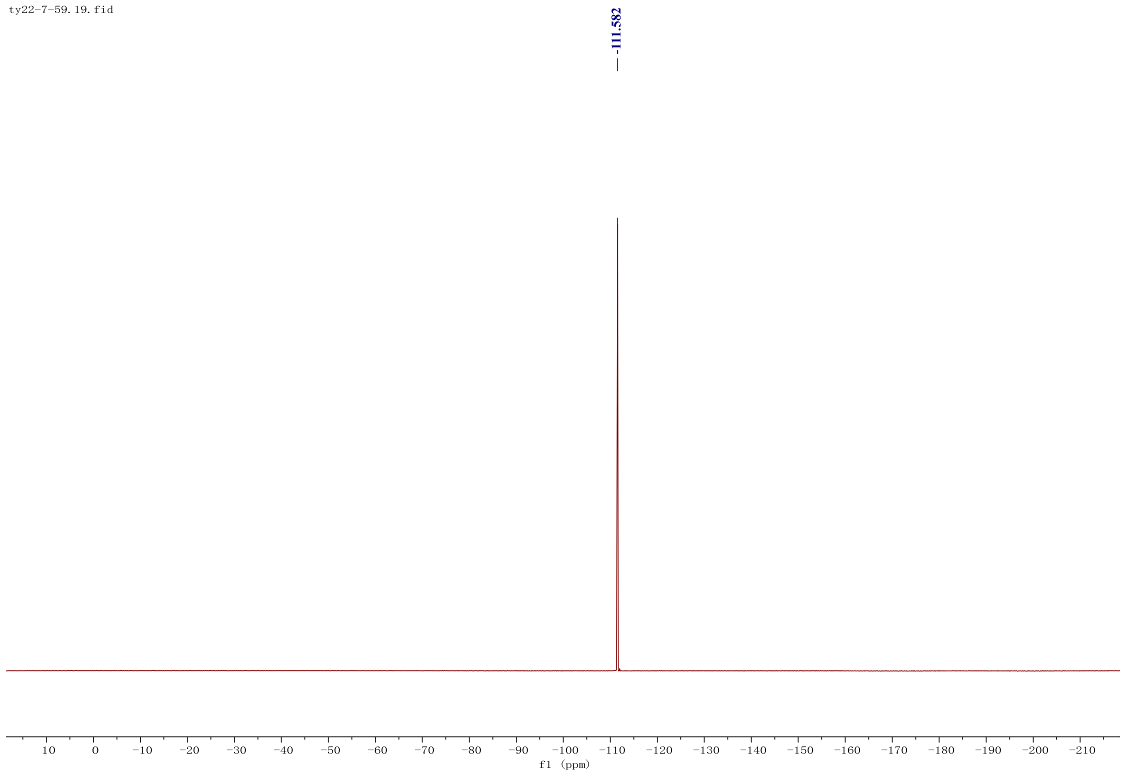
59

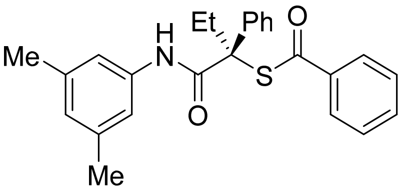

ty22-7-59.1.fid
9.158
8.005
7.986
7.629
7.610
7.593
7.590
7.547
7.540
7.534
7.513
7.506
7.482
7.462
7.444
7.385
7.381
7.365
7.347
7.338
7.335
7.320
7.303
7.300
7.232
7.213
7.210
7.194
7.189
7.175
7.121
7.117
7.101
7.096
6.781
6.775
6.760
6.754
6.740
6.733
2.499
2.480
2.462
2.444
2.426
2.408
2.338
2.320
2.302
2.284
2.266
2.247
0.888
0.870
0.852
0.95
1.92
1.02
1.12
3.95
2.94
0.99
0.95
0.93
1.02
1.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


ty22-7-59.13.fid
192.616
170.101
164.301
161.870
139.941
139.833
137.738
136.728
134.349
130.078
129.984
128.939
128.656
128.049
127.681
127.320
115.192
115.163
110.938
110.726
107.490
107.229
65.936
32.622
9.357
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

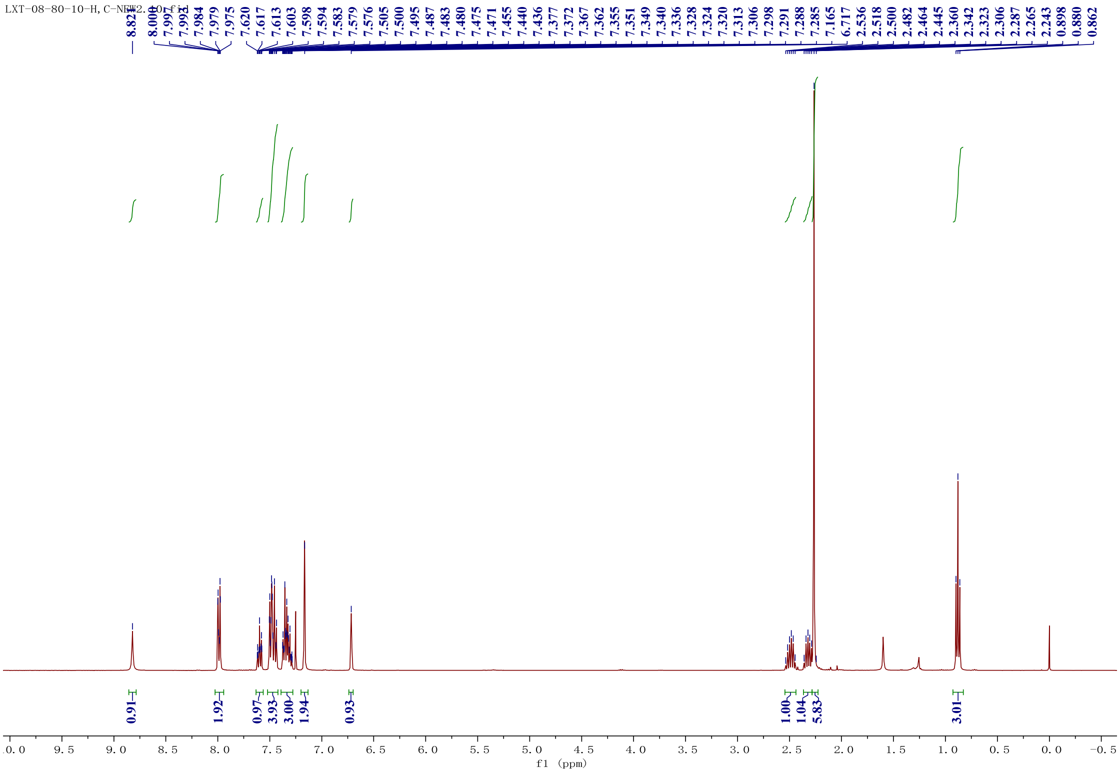


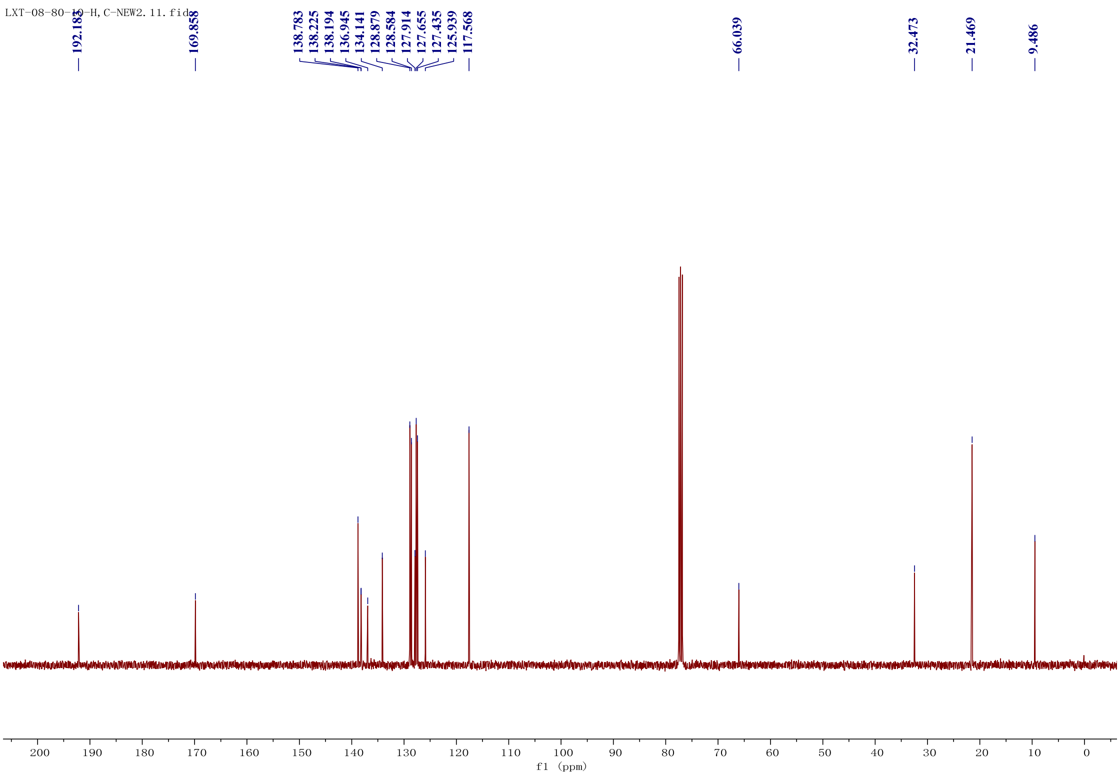
59

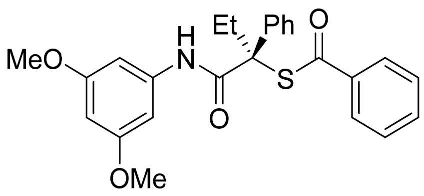

ty22-7-59.19.fid
-111.582
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



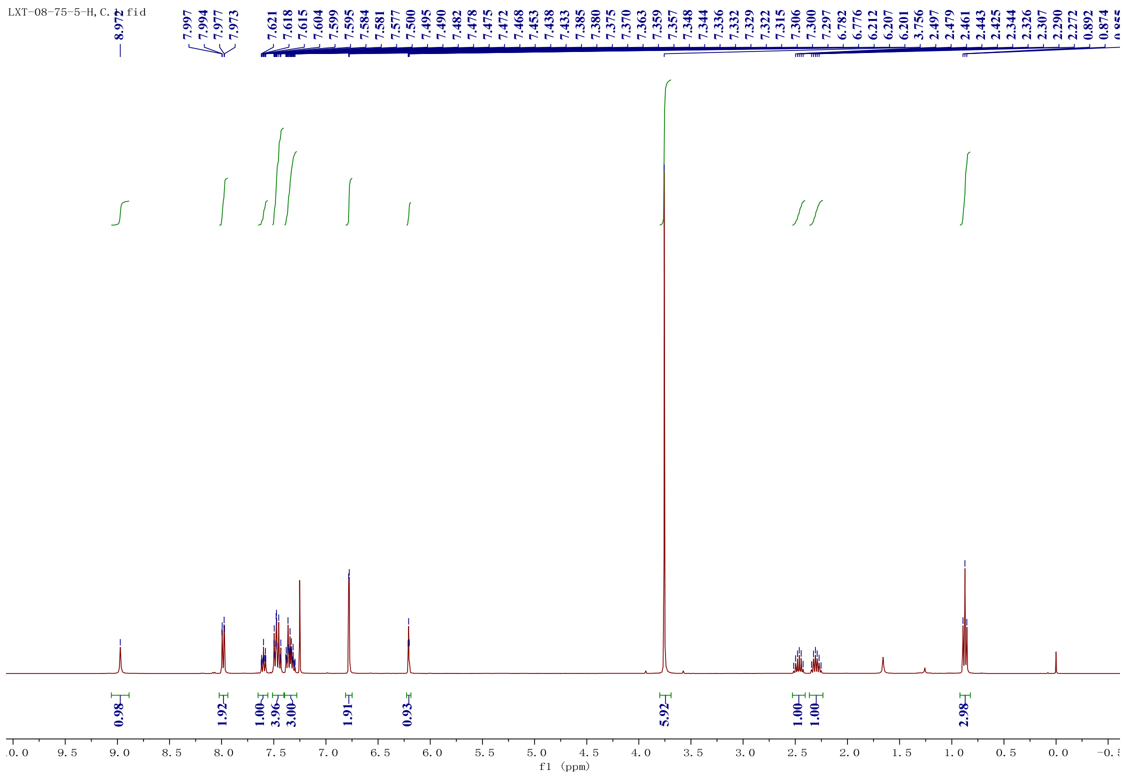
60



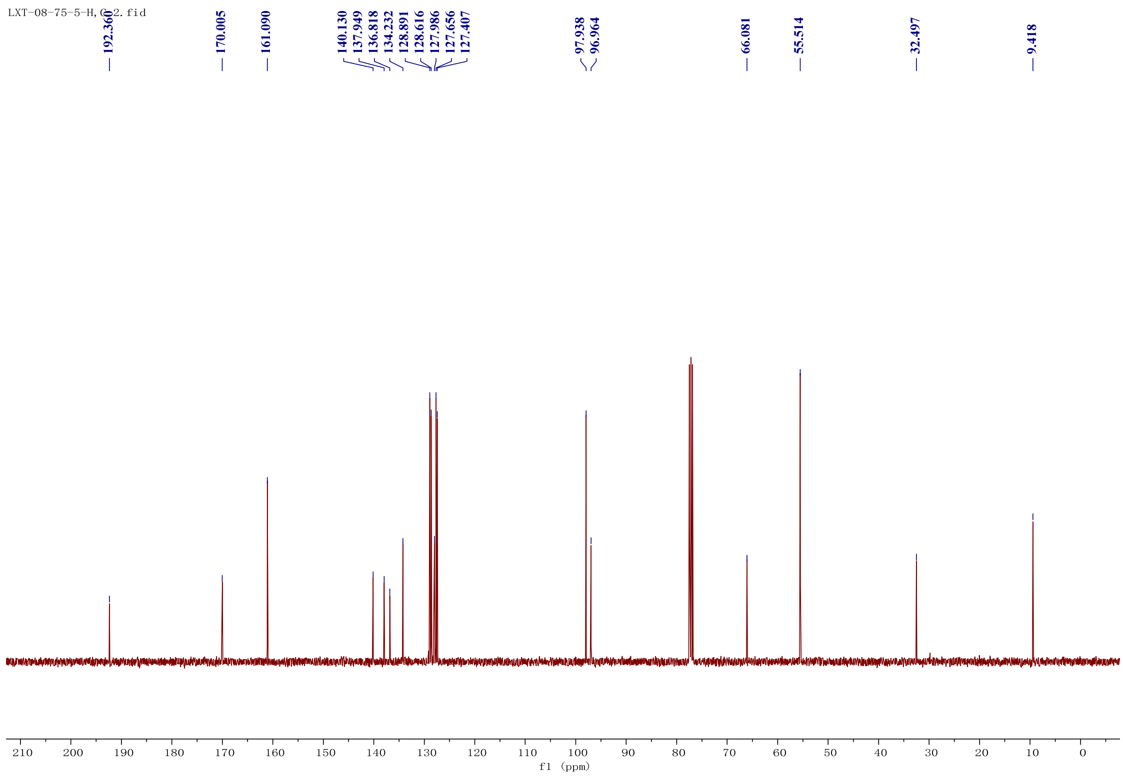




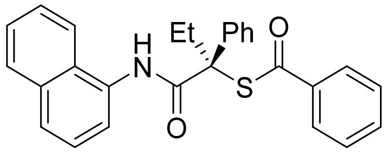
61



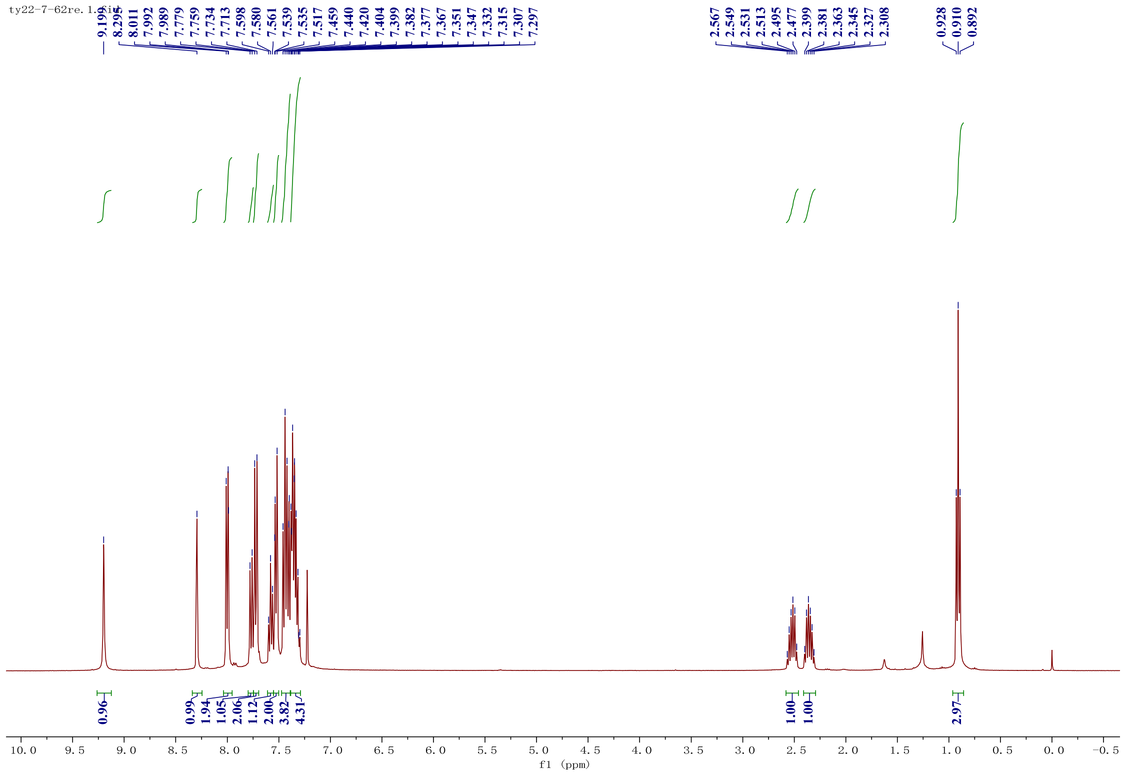
LXT-08-75-5-H,C.1.fid
f1 (ppm)

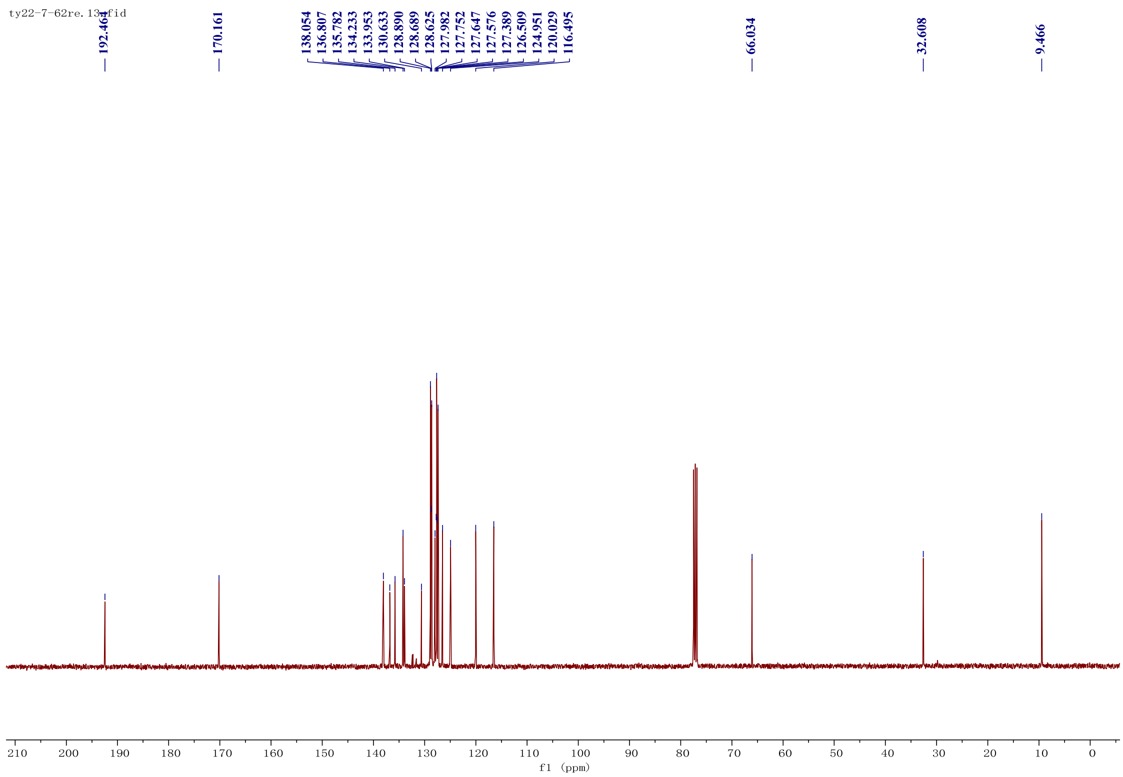


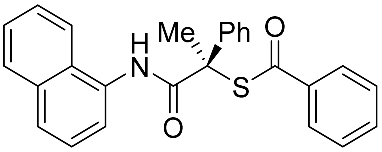
LXT-08-75-5-H,C.2.fid
192.360
170.005
161.090
140.130
137.949
136.818
134.232
128.891
128.616
127.986
127.656
127.407
97.938
96.964
66.081
55.514
32.497
9.418
f1 (ppm)



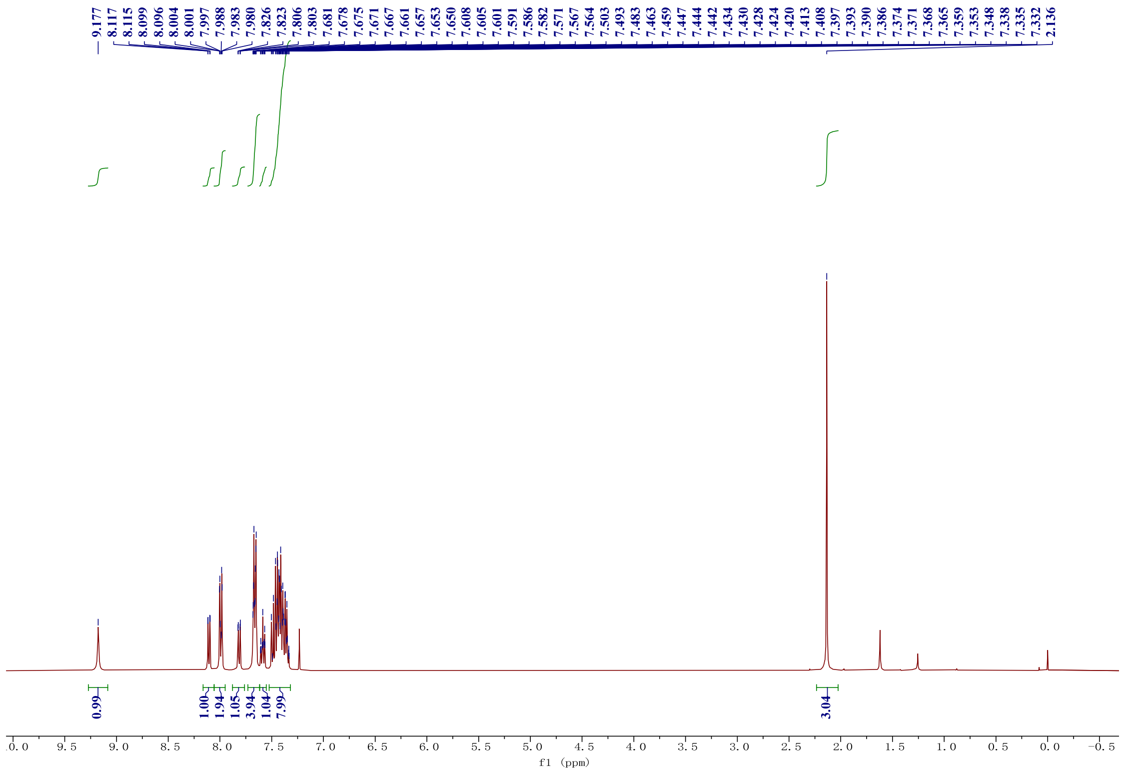
62

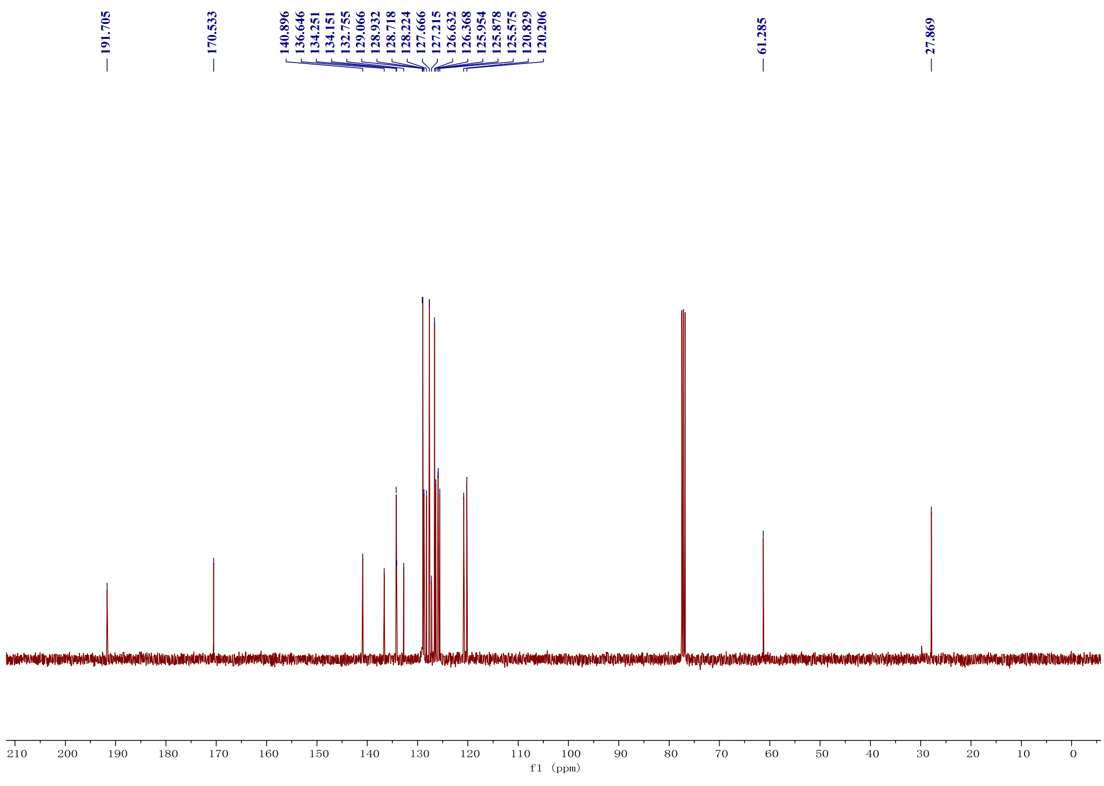


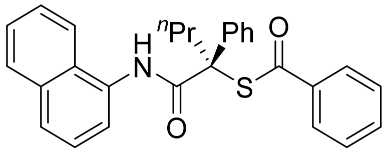




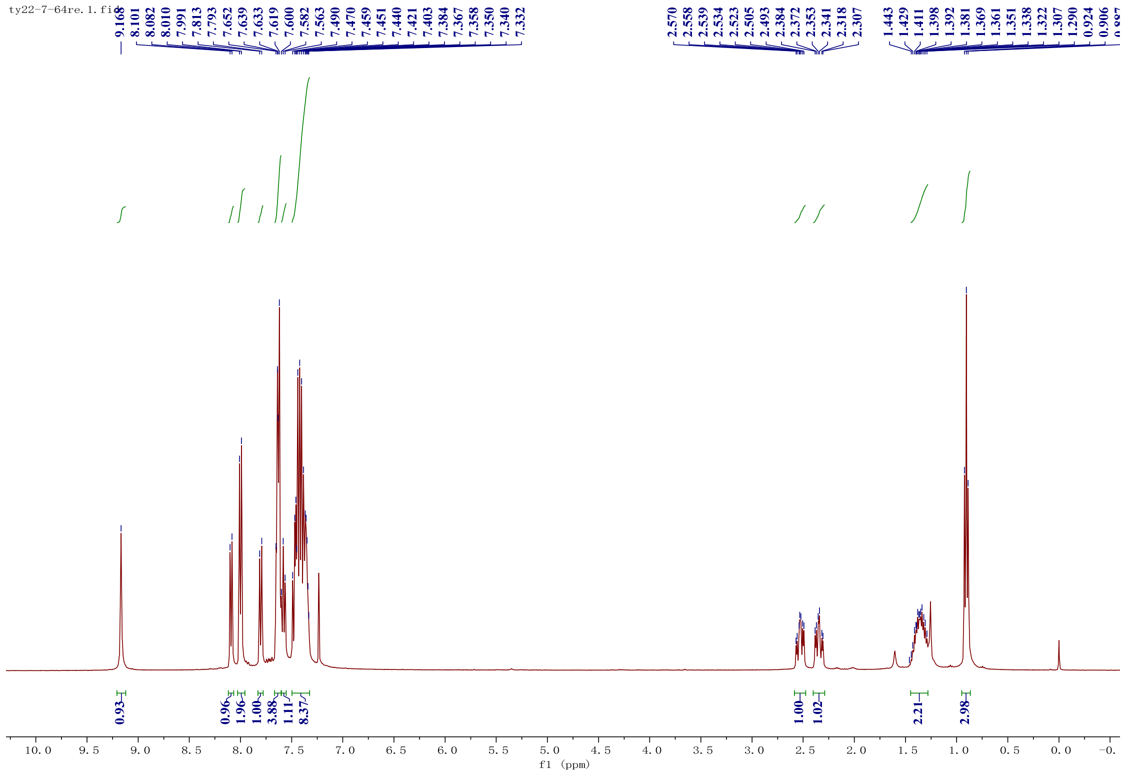
63

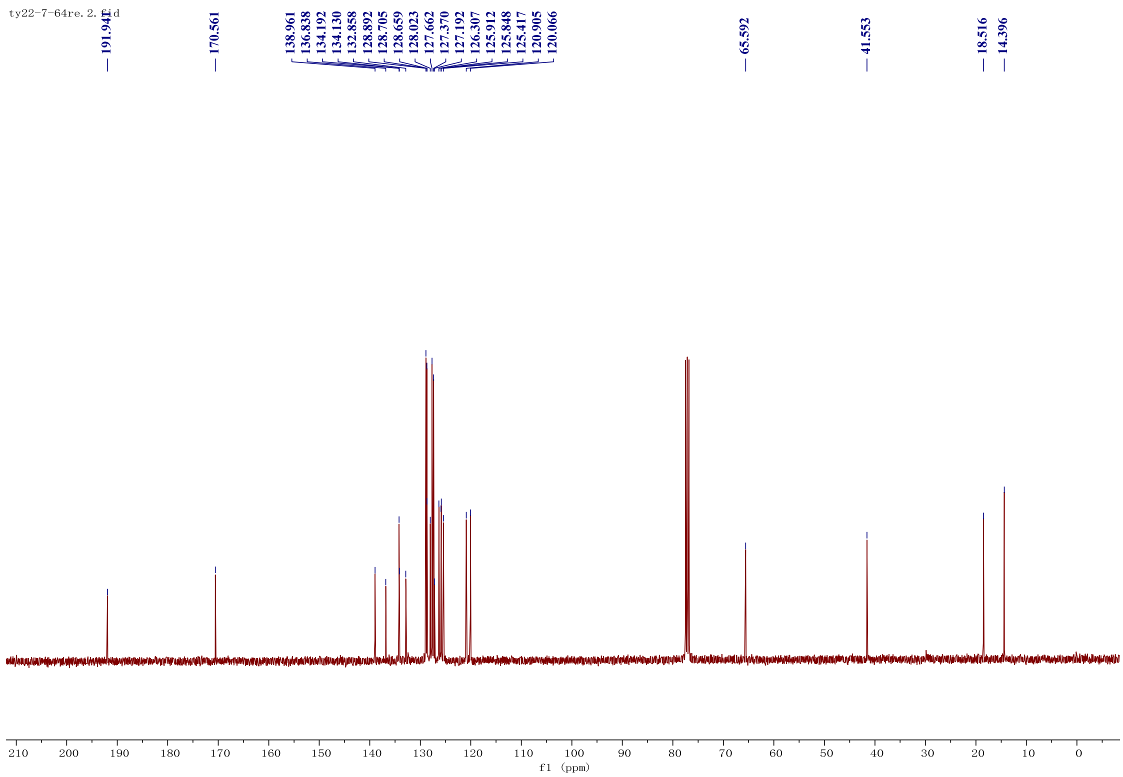


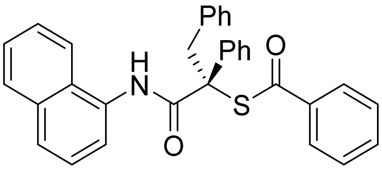



H
N
nPr
Ph
O
S
O

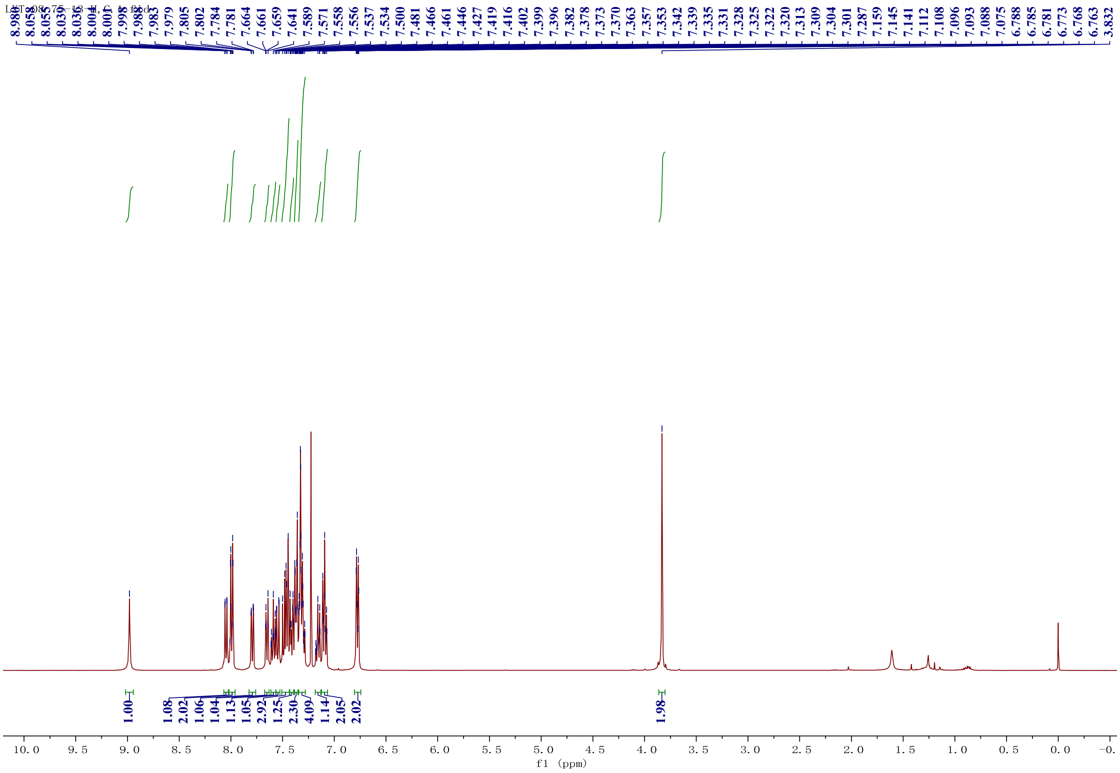
64

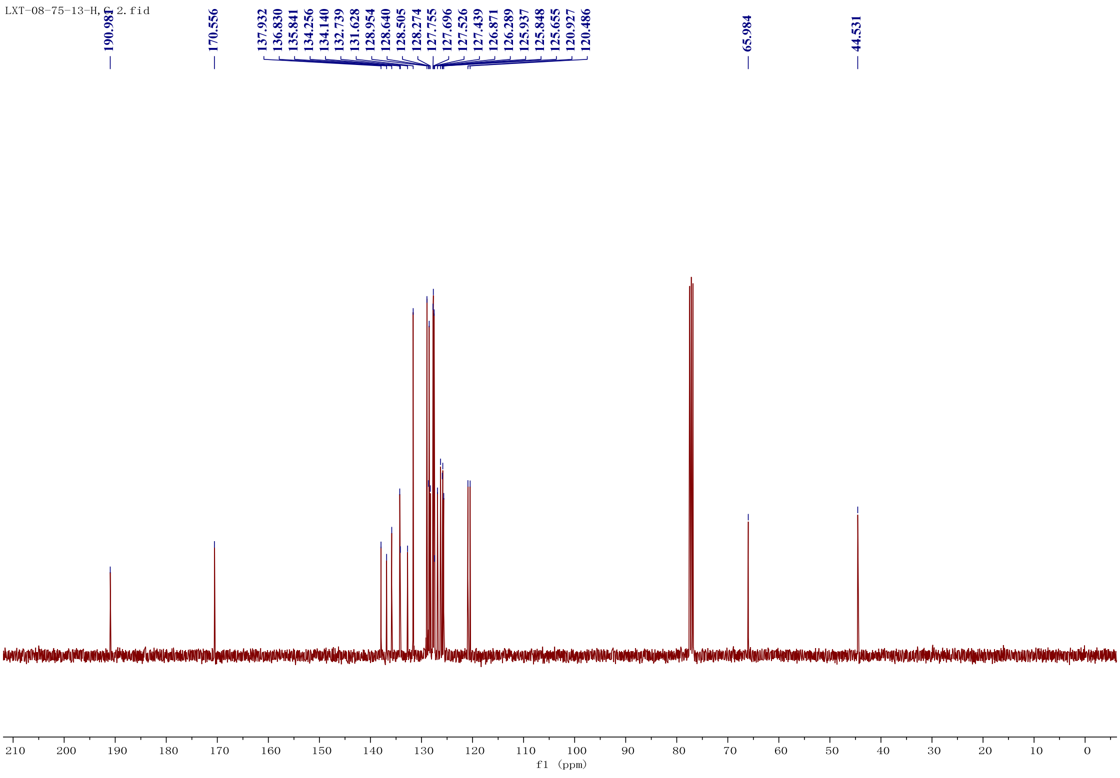

ty22-7-64re.1.fid
9.168
8.101
8.082
8.010
7.991
7.813
7.793
7.652
7.639
7.633
7.619
7.600
7.582
7.563
7.490
7.470
7.459
7.451
7.440
7.421
7.403
7.384
7.367
7.358
7.350
7.340
7.332
2.570
2.558
2.539
2.534
2.523
2.505
2.493
2.384
2.372
2.353
2.341
2.318
2.307
1.443
1.429
1.411
1.398
1.392
1.381
1.369
1.361
1.351
1.338
1.322
1.307
1.290
0.924
0.906
0.93
0.96
1.96
1.00
3.88
1.11
8.37
1.00
1.02
2.21
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

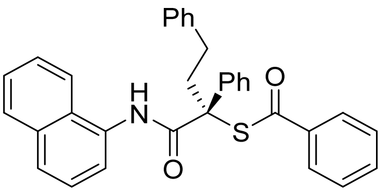

ty22-7-64re.2.fid
191.941
170.561
138.961
136.838
134.192
134.130
132.858
128.892
128.705
128.659
128.023
127.662
127.370
127.192
126.307
125.912
125.848
125.417
120.905
120.066
65.592
41.553
18.516
14.396
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



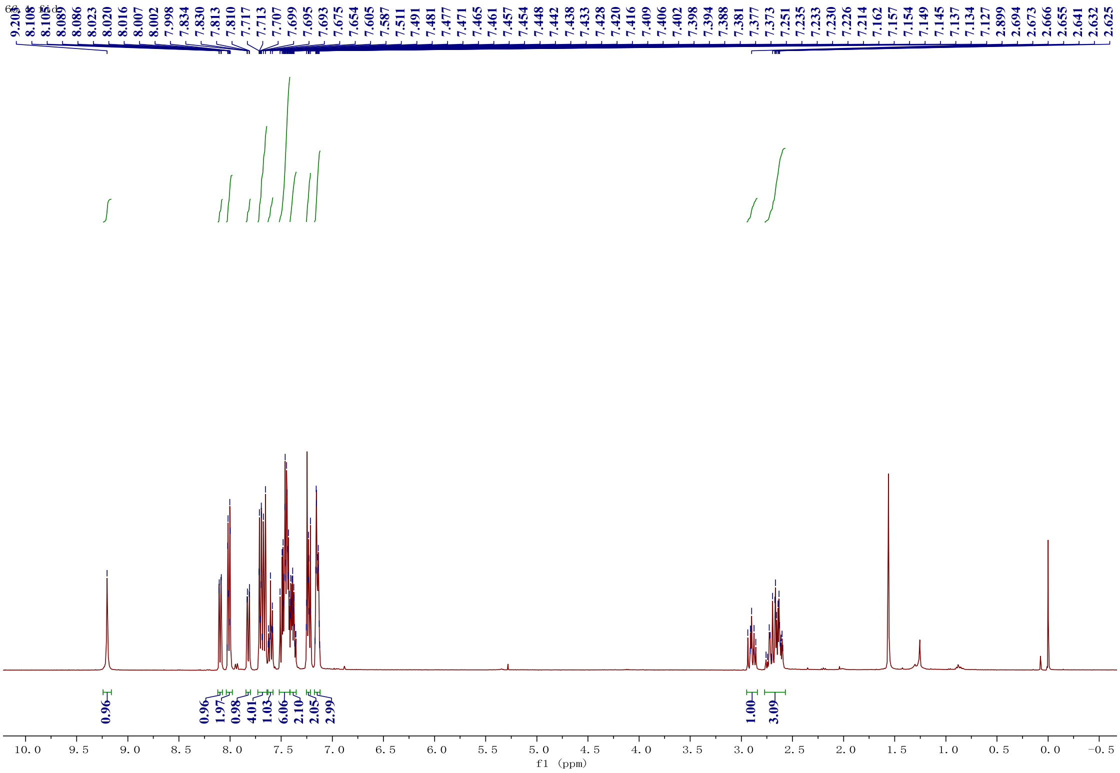
65

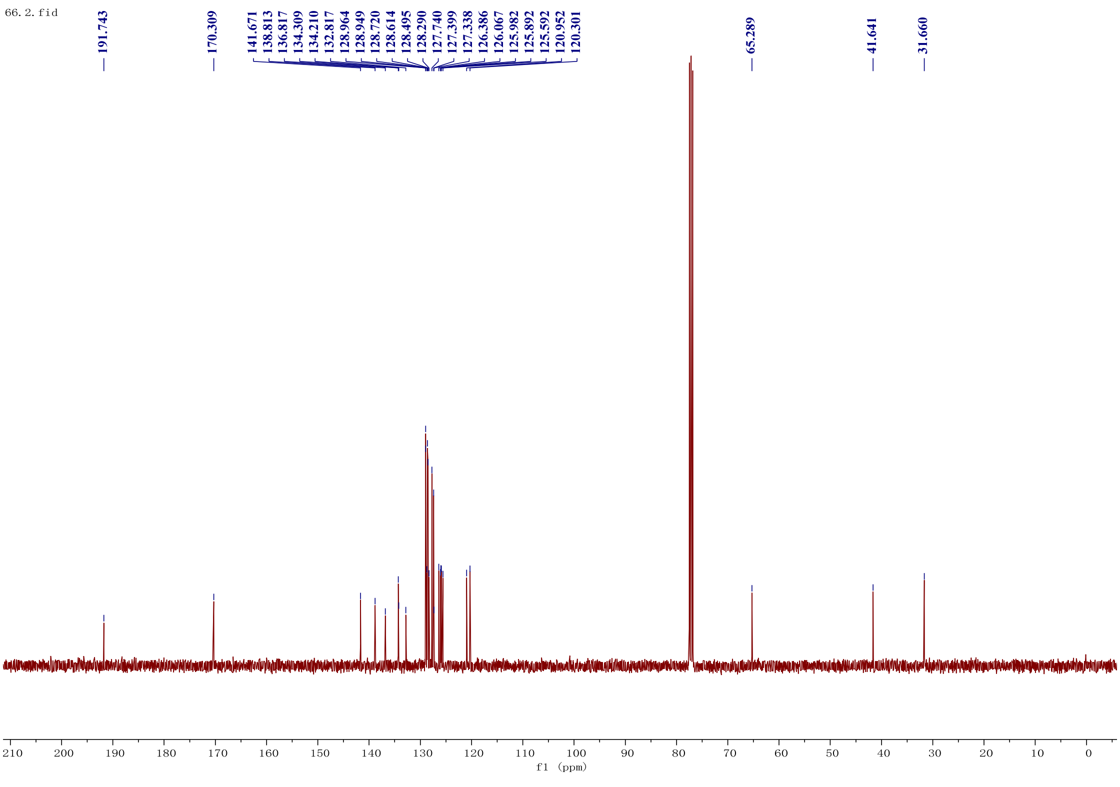


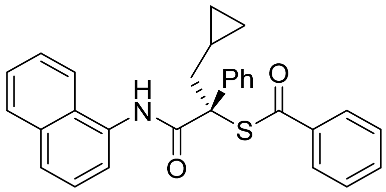




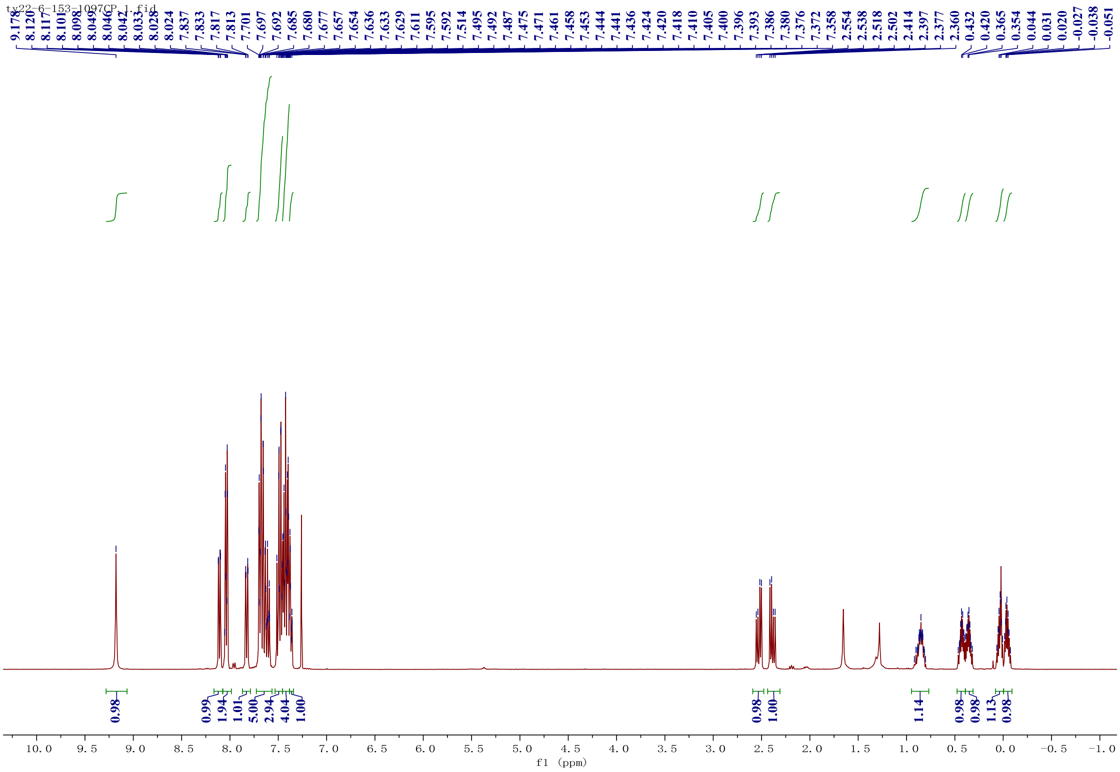
66

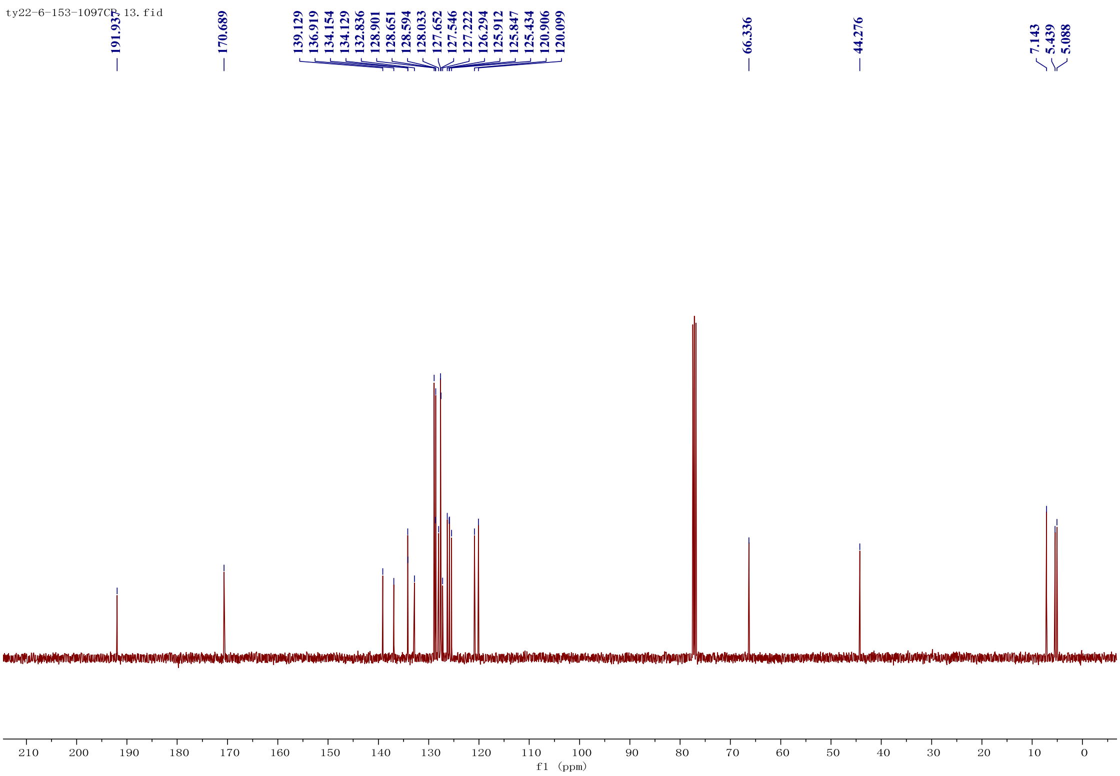


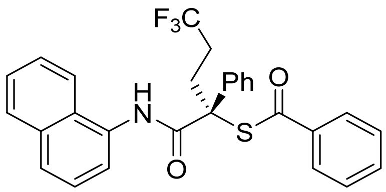



H
N
O
Ph
S
O

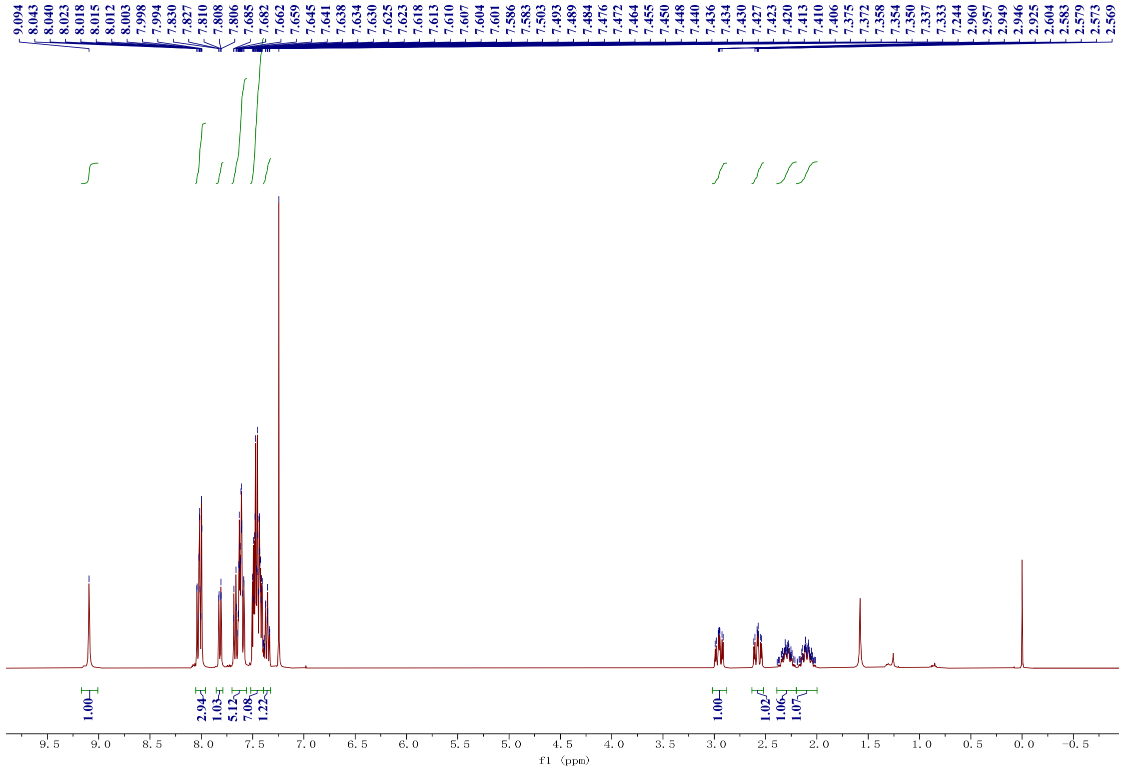
67

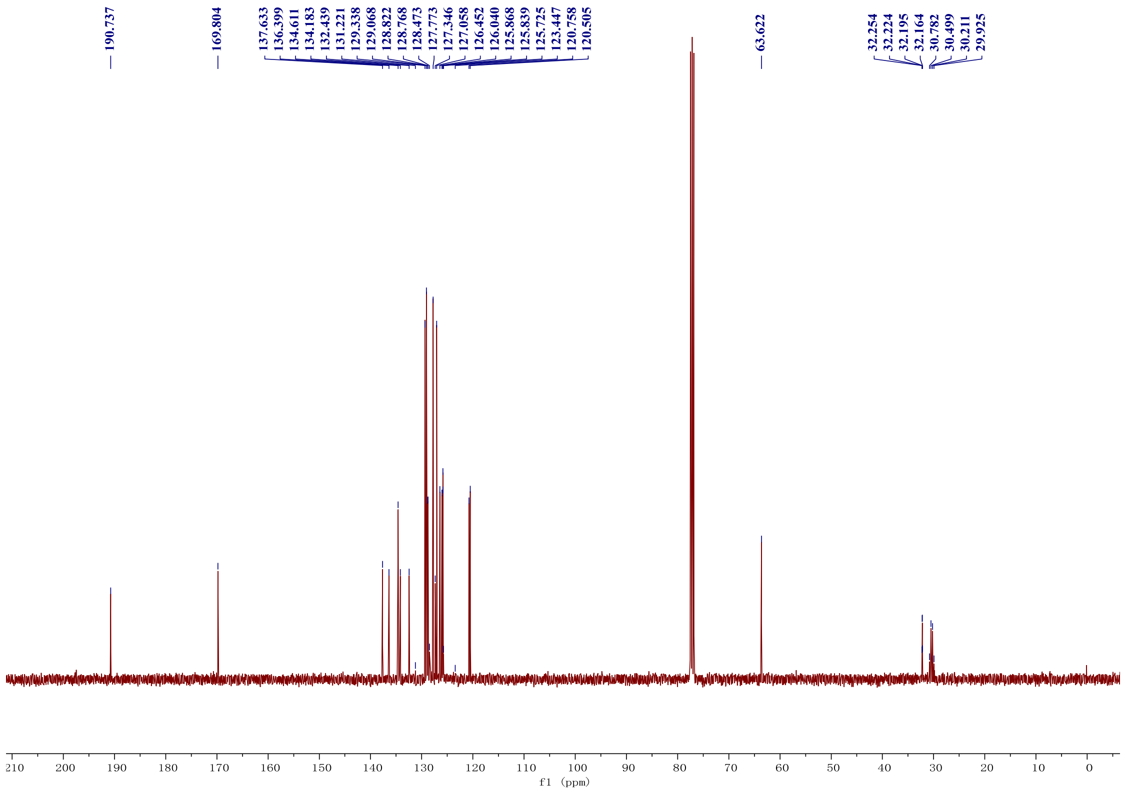

ty22-6-153-1097CP_1.fid
9.178
8.120
8.117
8.101
8.098
8.049
8.046
8.042
8.033
8.028
8.024
7.837
7.833
7.817
7.813
7.701
7.697
7.692
7.685
7.680
7.677
7.657
7.654
7.636
7.633
7.629
7.611
7.595
7.592
7.514
7.495
7.492
7.487
7.475
7.471
7.461
7.458
7.453
7.444
7.441
7.436
7.424
7.420
7.418
7.410
7.405
7.400
7.396
7.393
7.386
7.380
7.376
7.372
7.358
2.554
2.538
2.518
2.502
2.414
2.397
2.377
2.360
0.432
0.420
0.365
0.354
0.044
0.031
0.020
-0.027
-0.038
-0.051
0.98
0.99
1.94
1.01
5.00
2.94
4.04
1.00
0.98
1.00
1.14
0.98
0.98
1.13
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

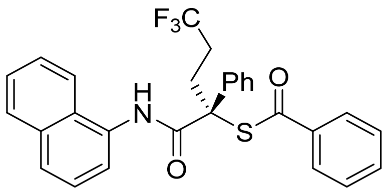

ty22-6-153-1097CP_13.fid
191.937
170.689
139.129
136.919
134.154
134.129
132.836
128.901
128.651
128.594
128.033
127.652
127.546
127.222
126.294
125.912
125.847
125.434
120.906
120.099
66.336
44.276
7.143
5.439
5.088
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



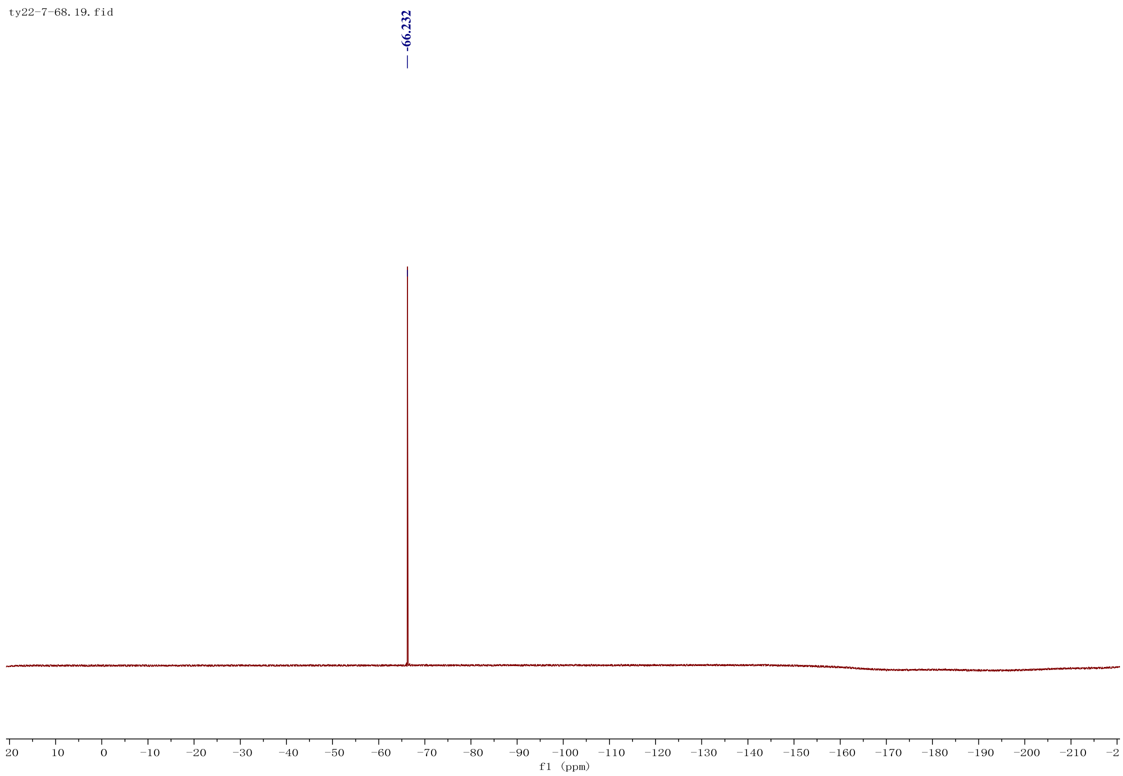
68

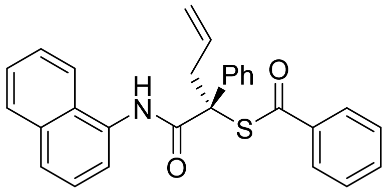




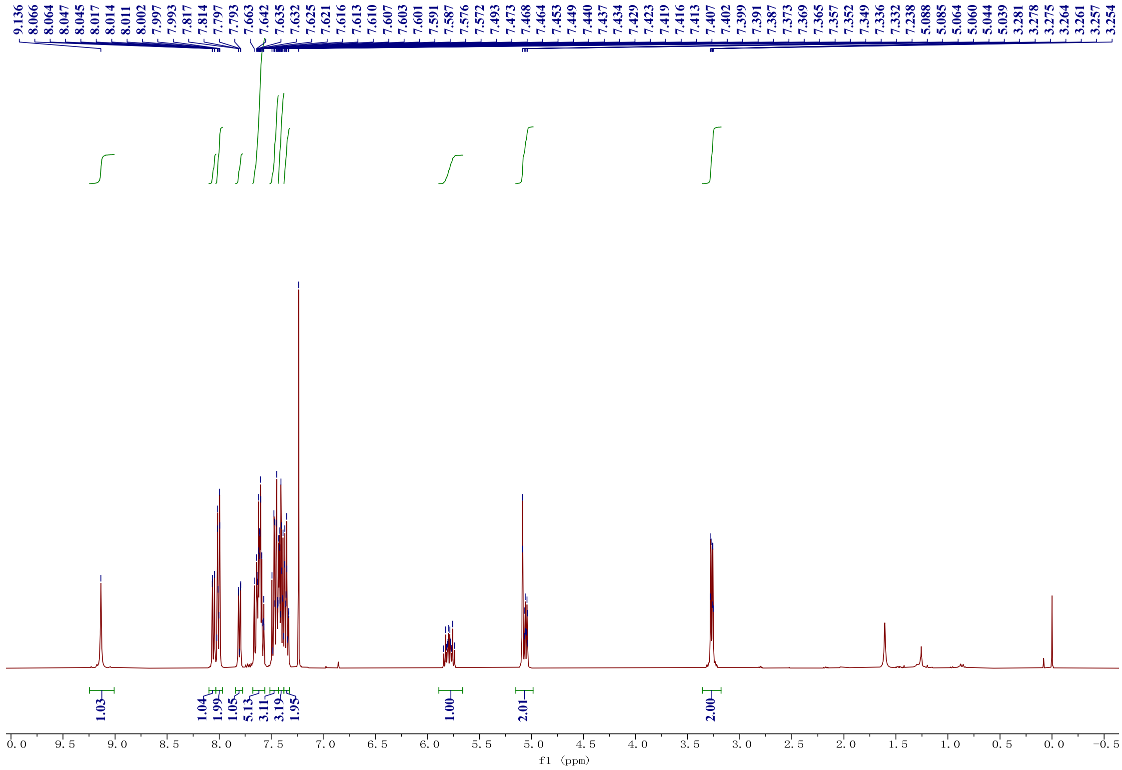

F3C
Ph
H
N
O
S
O

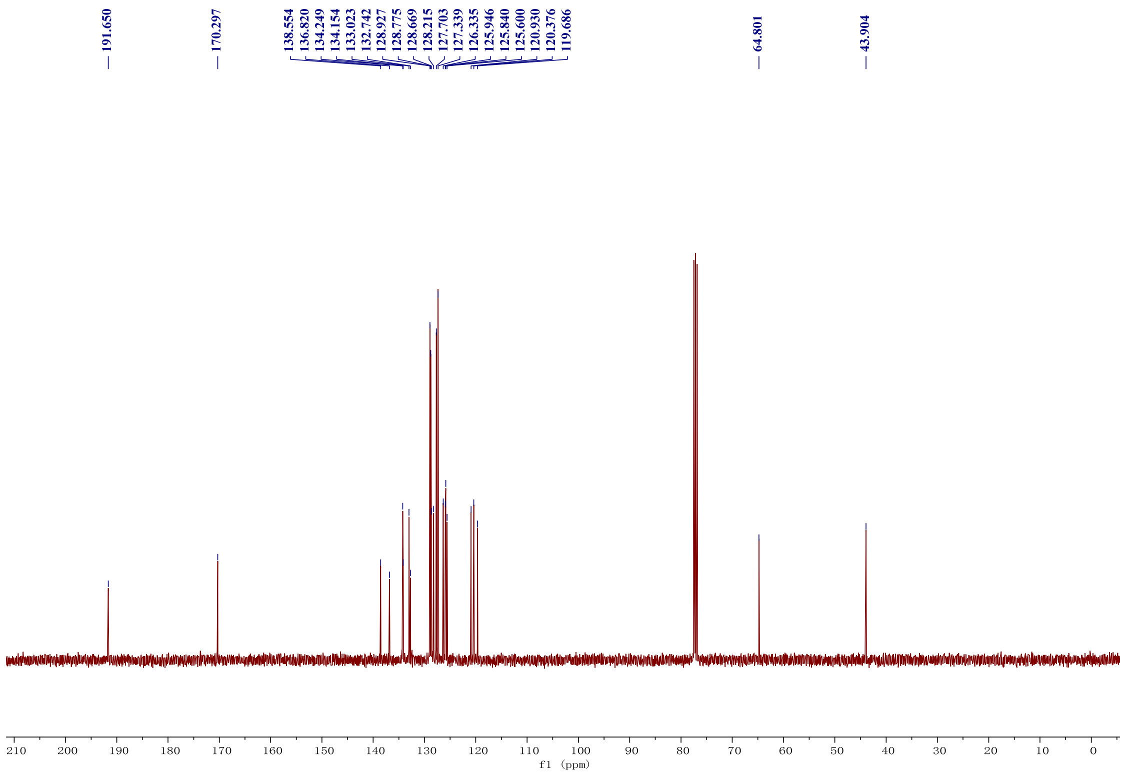
68

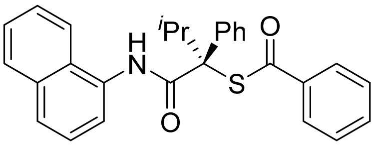

ty22-7-68.19.fid
-66.232
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


H
N
O
Ph
S
O

69

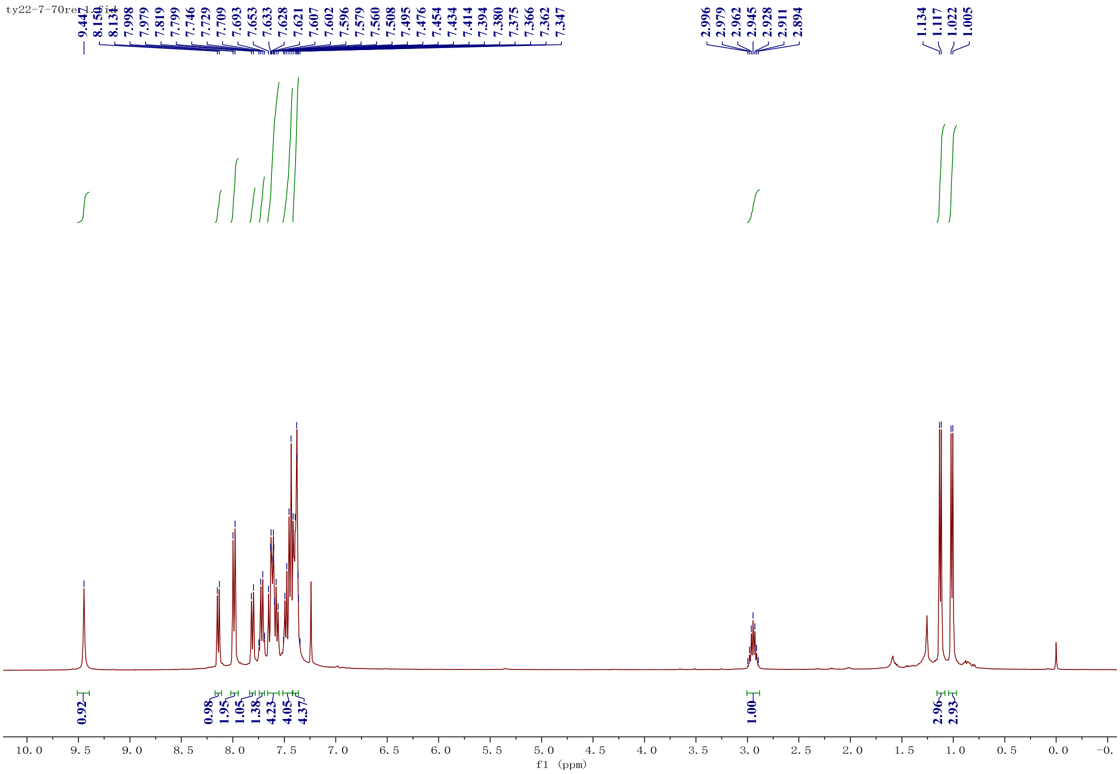

9.136
8.066
8.064
8.047
8.045
8.017
8.014
8.011
8.002
7.997
7.993
7.817
7.814
7.797
7.793
7.663
7.642
7.635
7.632
7.625
7.621
7.616
7.613
7.610
7.607
7.603
7.601
7.591
7.587
7.576
7.572
7.493
7.473
7.468
7.464
7.453
7.449
7.440
7.437
7.434
7.429
7.423
7.419
7.416
7.413
7.407
7.402
7.399
7.391
7.387
7.373
7.369
7.365
7.357
7.352
7.349
7.336
7.332
7.238
5.088
5.085
5.064
5.060
5.044
5.039
3.281
3.278
3.275
3.264
3.261
3.257
3.254
1.03
1.04
1.99
1.05
5.13
3.11
3.19
1.95
1.00
2.01
2.00
f1 (ppm)


191.650
170.297
138.554
136.820
134.249
134.154
133.023
132.742
128.927
128.775
128.669
128.215
127.703
127.339
126.335
125.946
125.840
125.600
120.930
120.376
119.686
64.801
43.904
f1 (ppm)

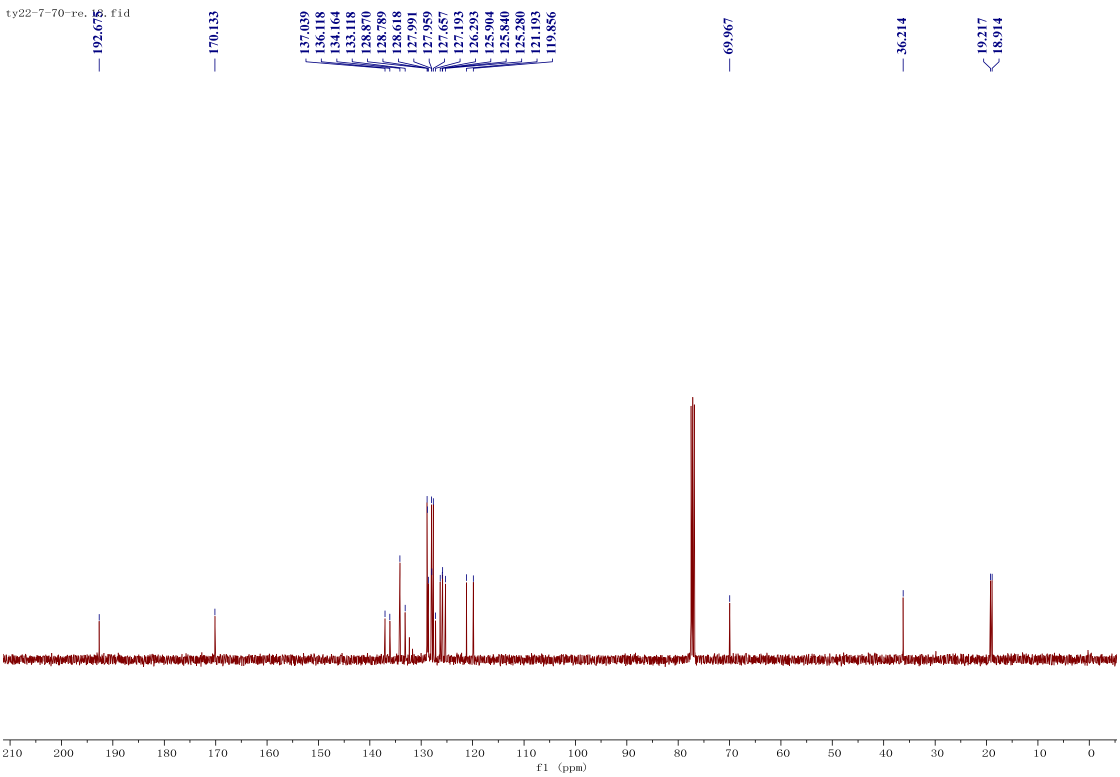


H
N
iPr
Ph
O
S
O

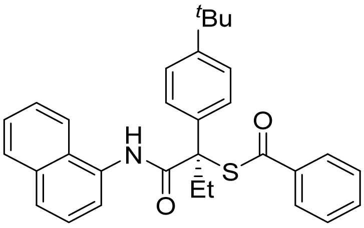
70



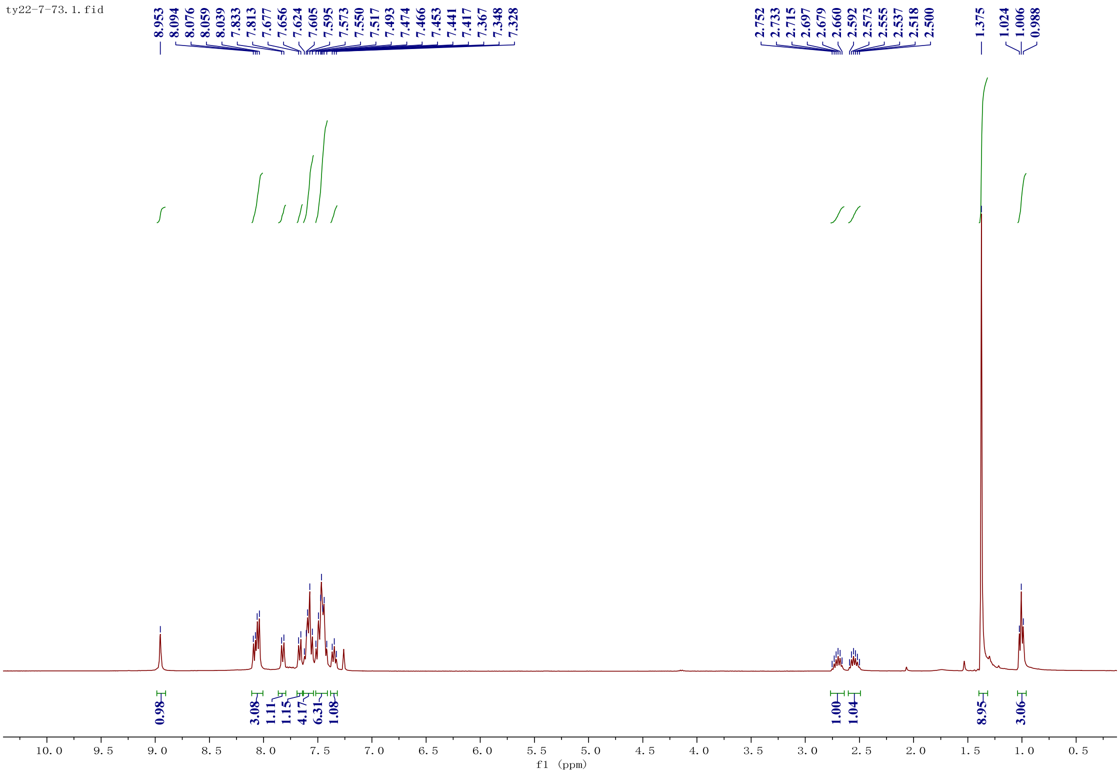
ty22-7-70re.1.fid
9.447
8.150
8.134
7.998
7.979
7.819
7.799
7.746
7.729
7.709
7.693
7.653
7.633
7.628
7.621
7.607
7.602
7.596
7.579
7.560
7.508
7.495
7.476
7.454
7.434
7.414
7.394
7.380
7.375
7.366
7.362
7.347
2.996
2.979
2.962
2.945
2.928
2.911
2.894
1.134
1.117
1.022
1.005
0.92
0.98
1.95
1.05
1.38
4.23
4.05
4.37
1.00
2.96
2.93
f1 (ppm)

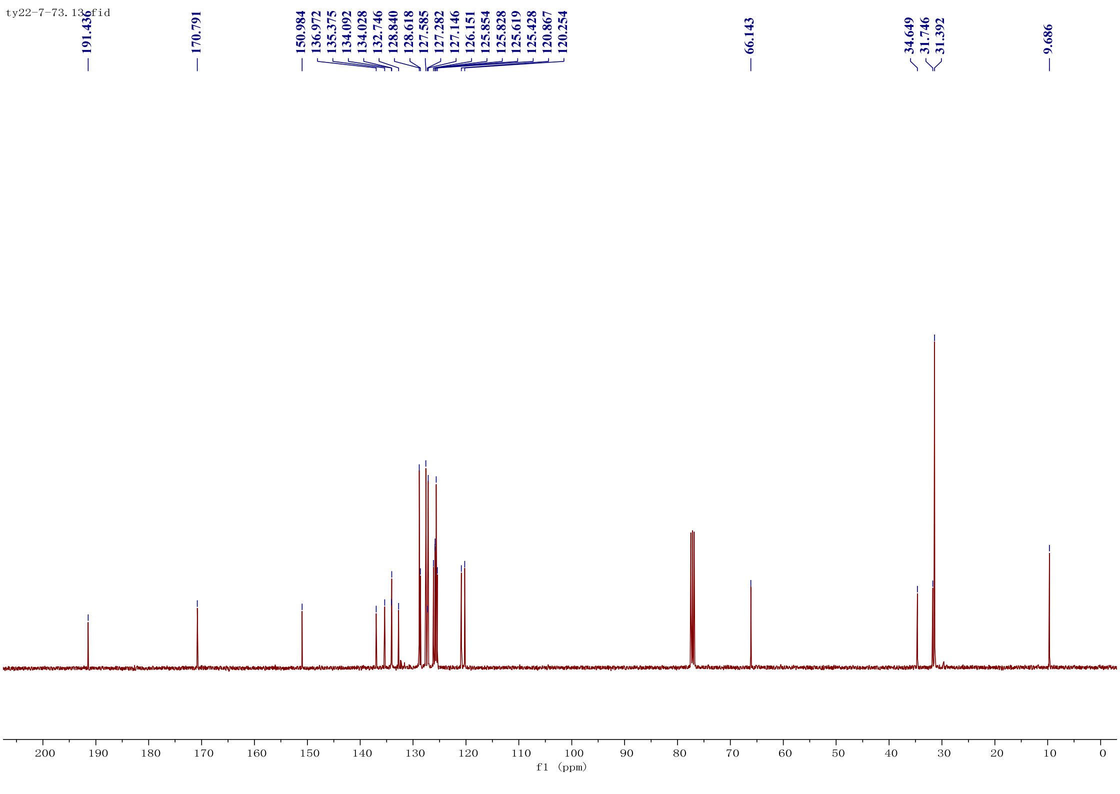


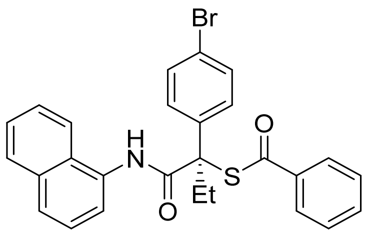
ty22-7-70-re.10.fid
192.675
170.133
137.039
136.118
134.164
133.118
128.870
128.789
128.618
127.991
127.959
127.657
127.193
126.293
125.904
125.840
125.280
121.193
119.856
69.967
36.214
19.217
18.914
f1 (ppm)


tBu
H
N
O
O
S
Et

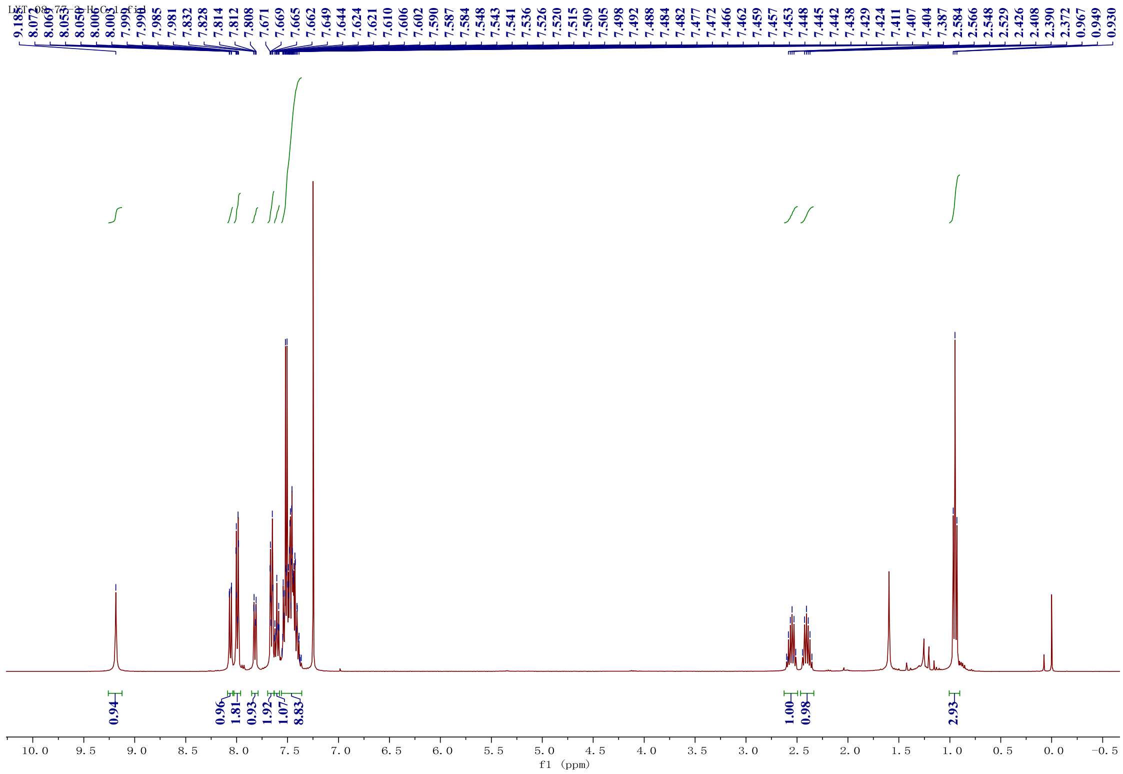
71

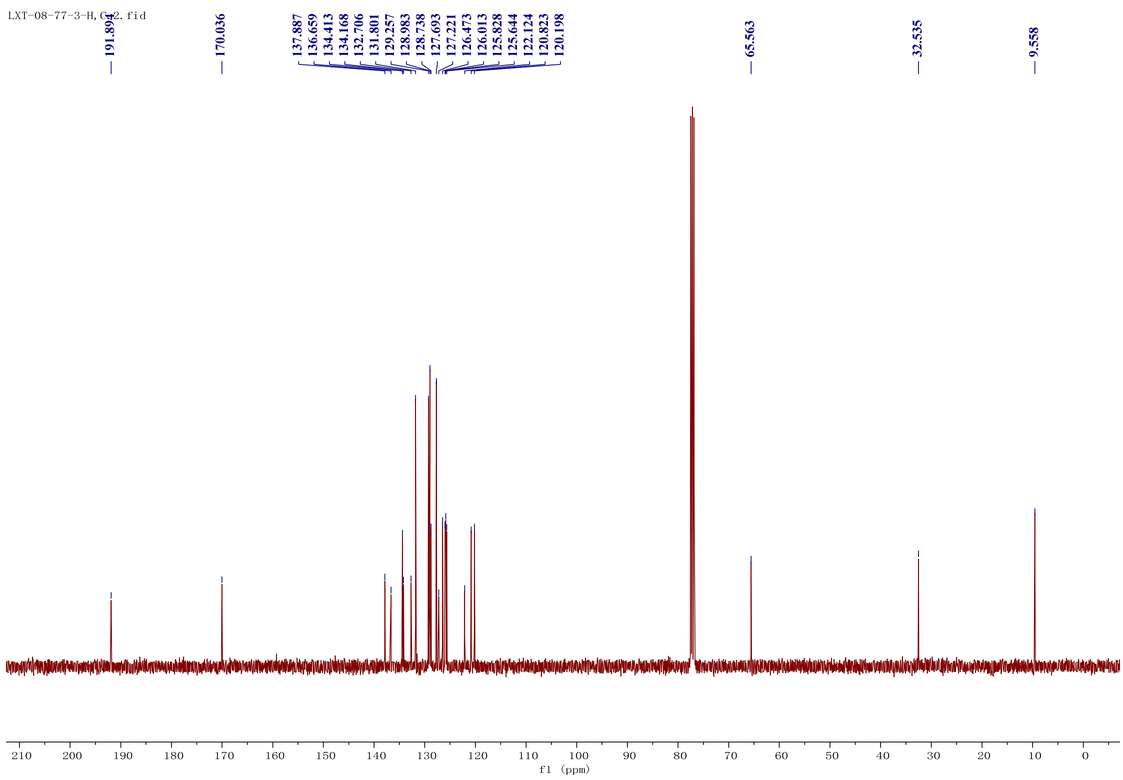

ty22-7-73.1.fid
8.953
8.094
8.076
8.059
8.039
7.833
7.813
7.677
7.656
7.624
7.605
7.595
7.573
7.550
7.517
7.493
7.474
7.466
7.453
7.441
7.417
7.367
7.348
7.328
2.752
2.733
2.715
2.697
2.679
2.660
2.592
2.573
2.555
2.537
2.518
2.500
1.375
1.024
1.006
0.988
0.98
3.08
1.11
1.15
4.17
6.31
1.08
1.00
1.04
8.95
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

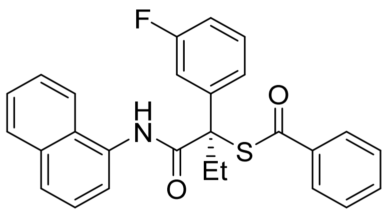

ty22-7-73.13C.fid
191.436
170.791
150.984
136.972
135.375
134.092
134.028
132.746
128.840
128.618
127.585
127.282
127.146
126.151
125.854
125.828
125.619
125.428
120.867
120.254
66.143
34.649
31.746
31.392
9.686
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



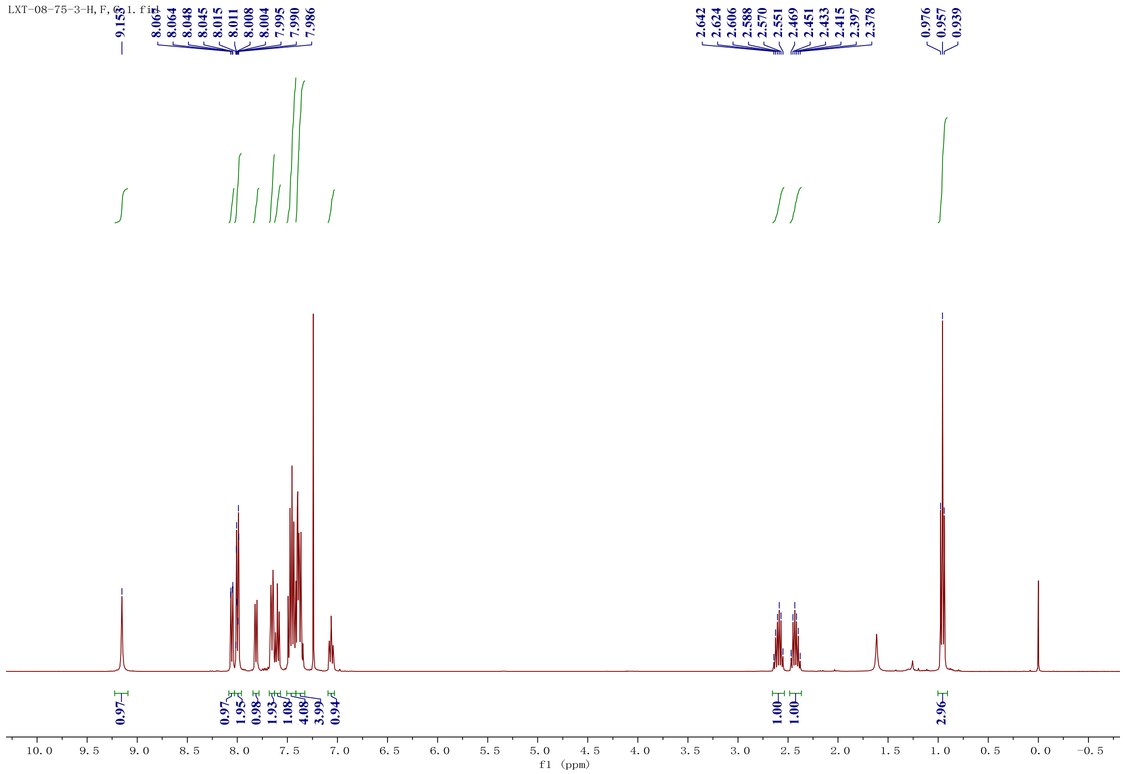
72

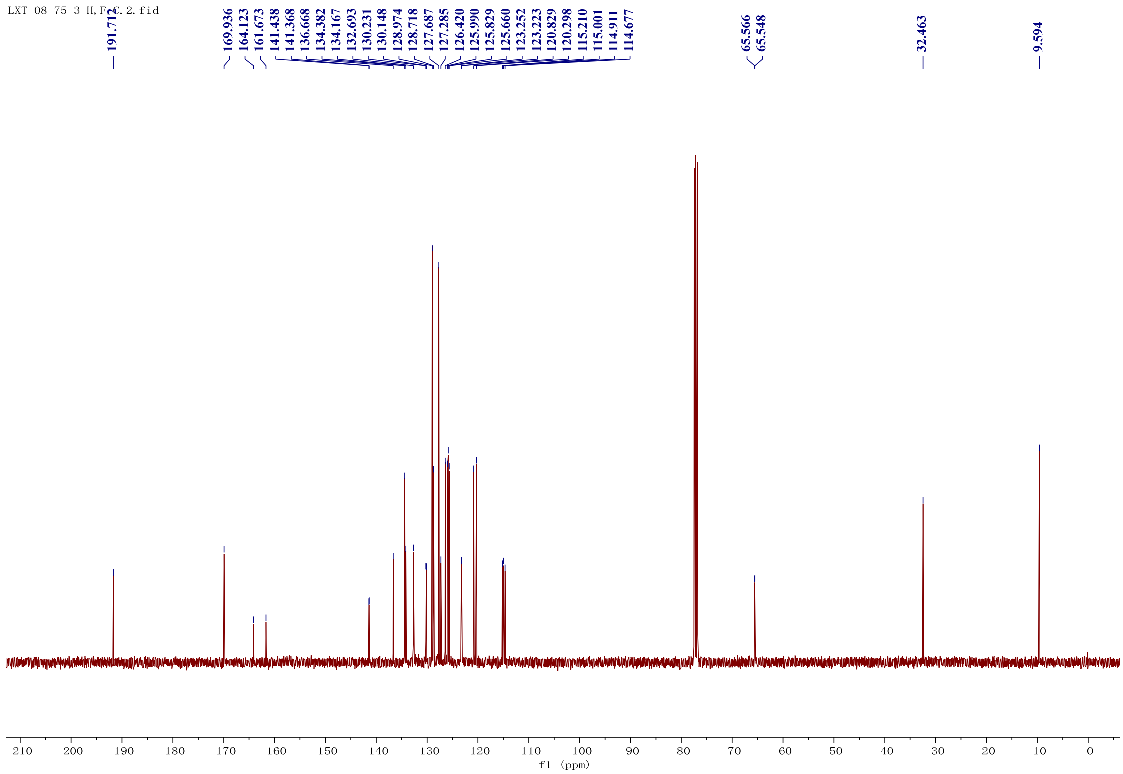


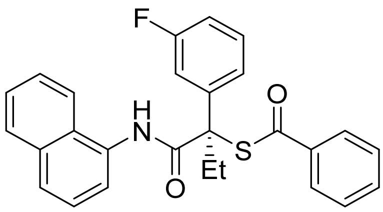



F
H
N
O
S
Et
O

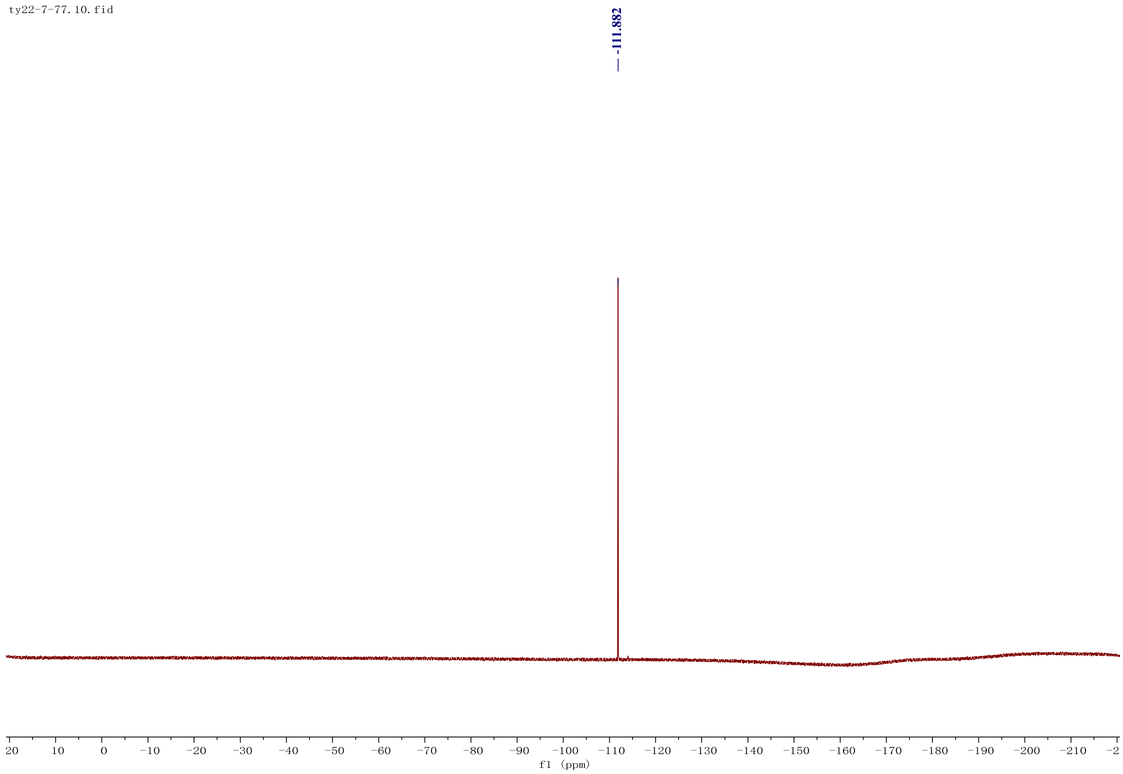
73

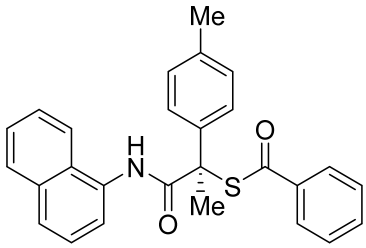

LXT-08-75-3-H,F,C.1.fid
9.153
8.061
8.064
8.048
8.045
8.015
8.011
8.008
8.004
7.995
7.990
7.986
2.642
2.624
2.606
2.588
2.570
2.551
2.469
2.451
2.433
2.415
2.397
2.378
0.976
0.957
0.939
0.97
0.97
1.95
0.98
1.93
1.08
4.08
3.99
0.94
1.00
1.00
2.96
f1 (ppm)


LXT-08-75-3-H,F,C.2.fid
191.712
169.936
164.123
161.673
141.438
141.368
136.668
134.382
134.167
132.693
130.231
130.148
128.974
128.718
127.687
127.285
126.420
125.990
125.829
125.660
123.252
123.223
120.829
120.298
115.210
115.001
114.911
114.677
65.566
65.548
32.463
9.594
f1 (ppm)

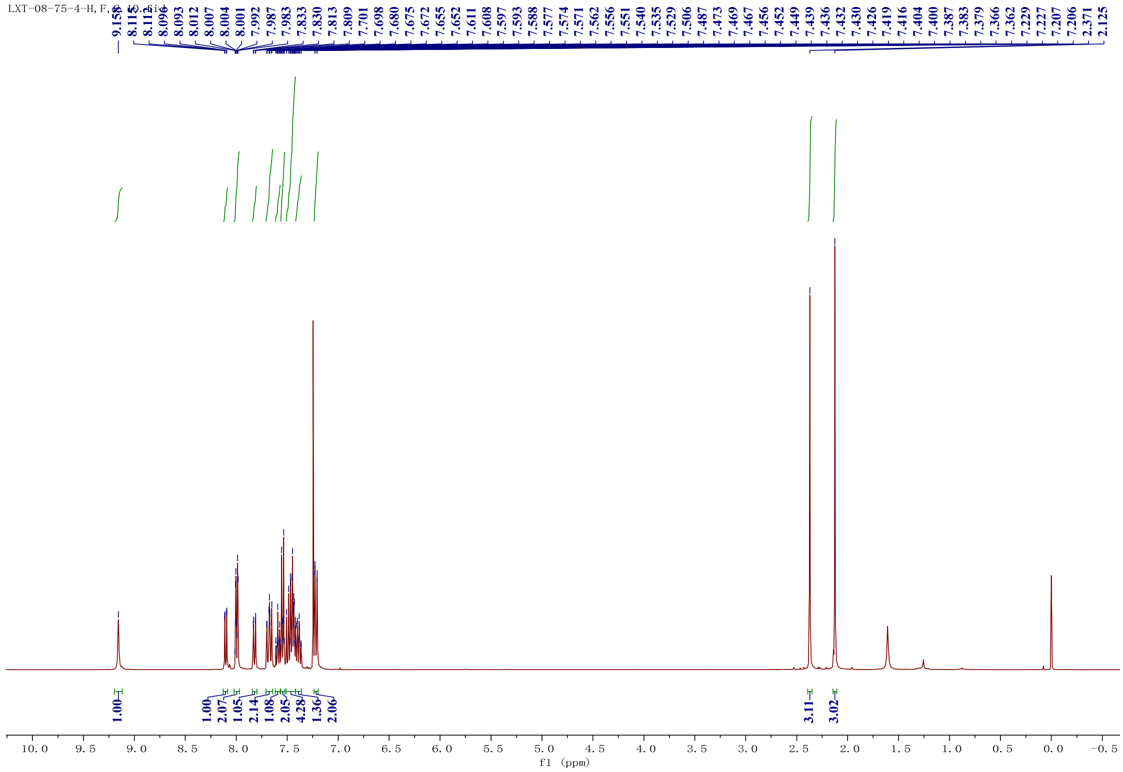


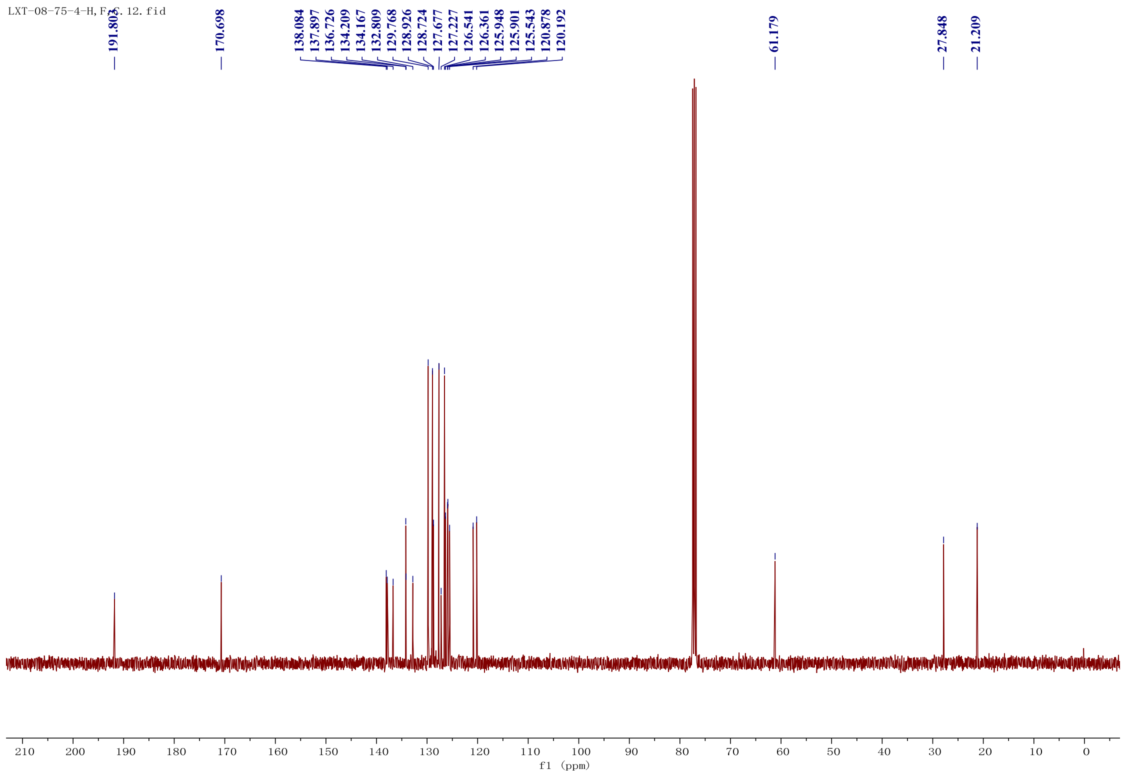
73

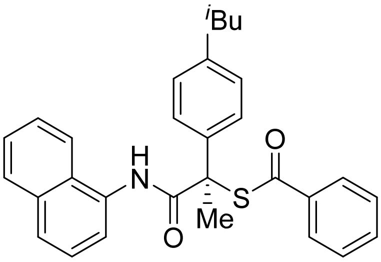

ty22-7-77.10.fid
-111.882
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2
f1 (ppm)



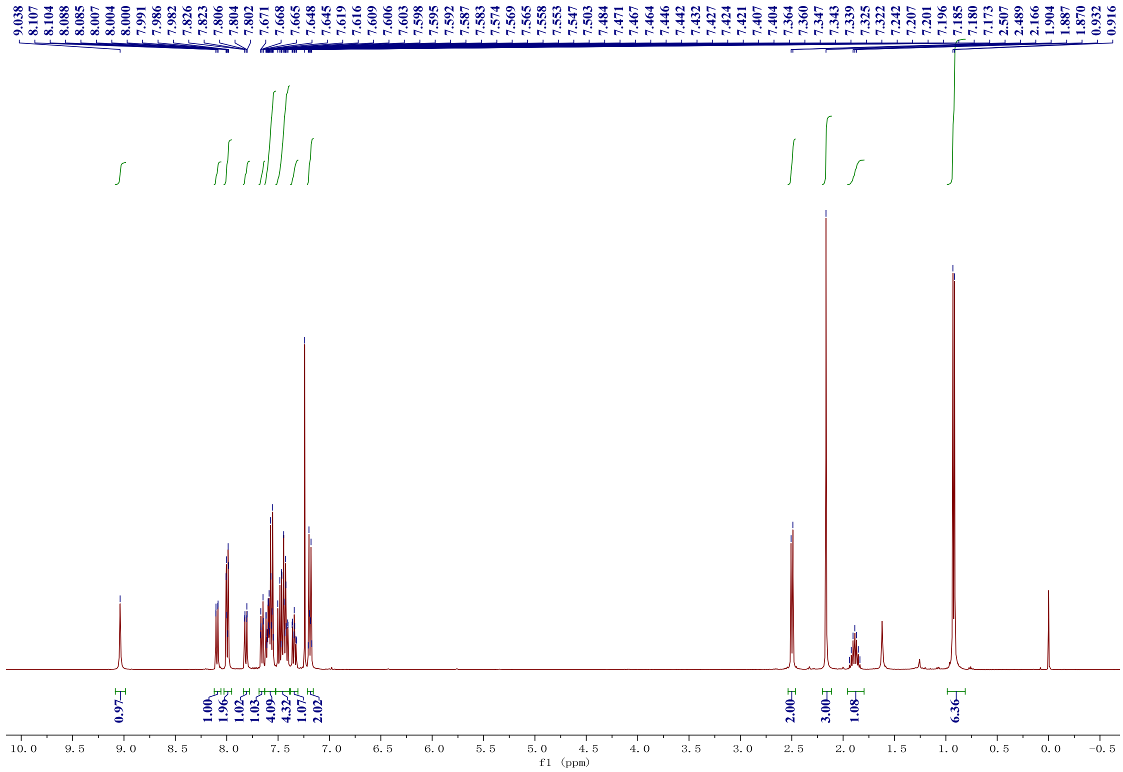
74

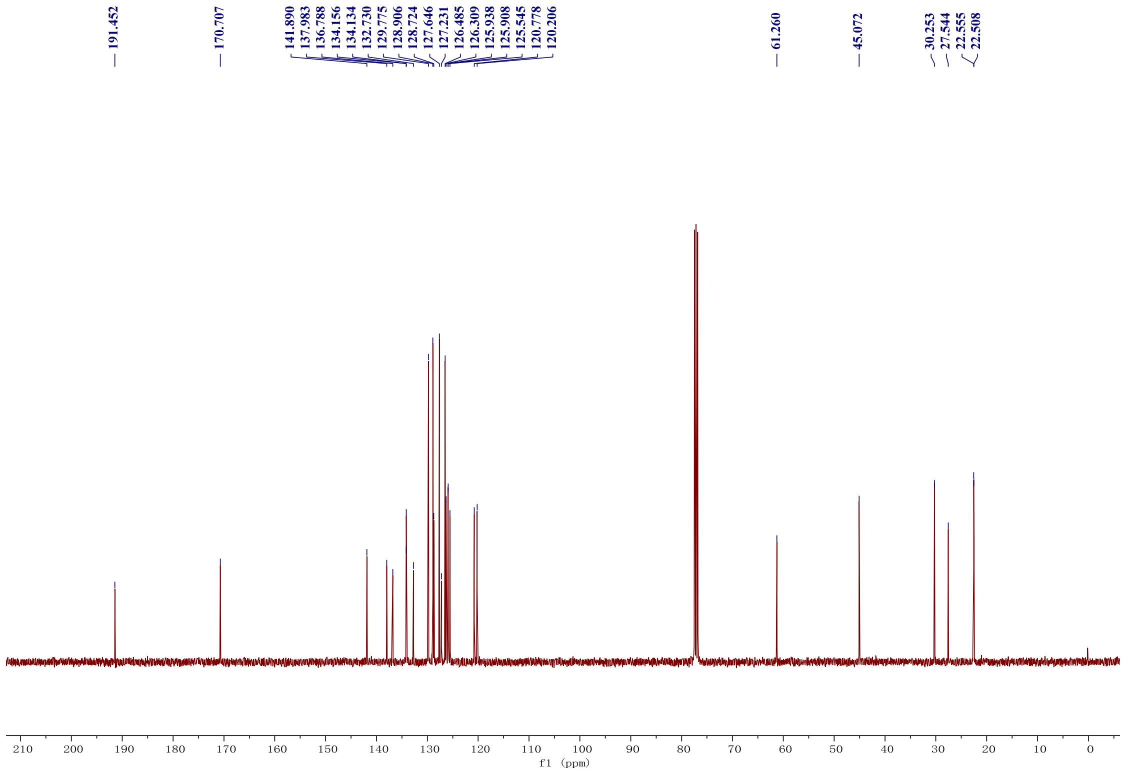


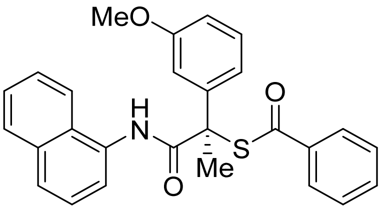




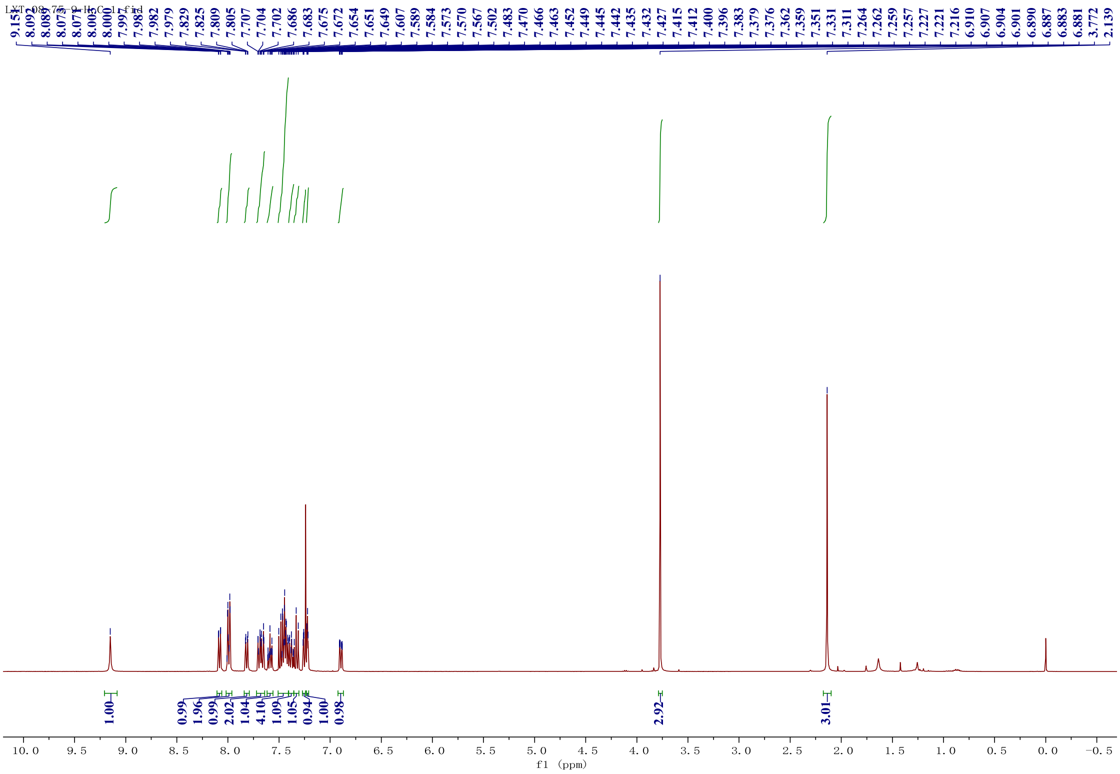
75

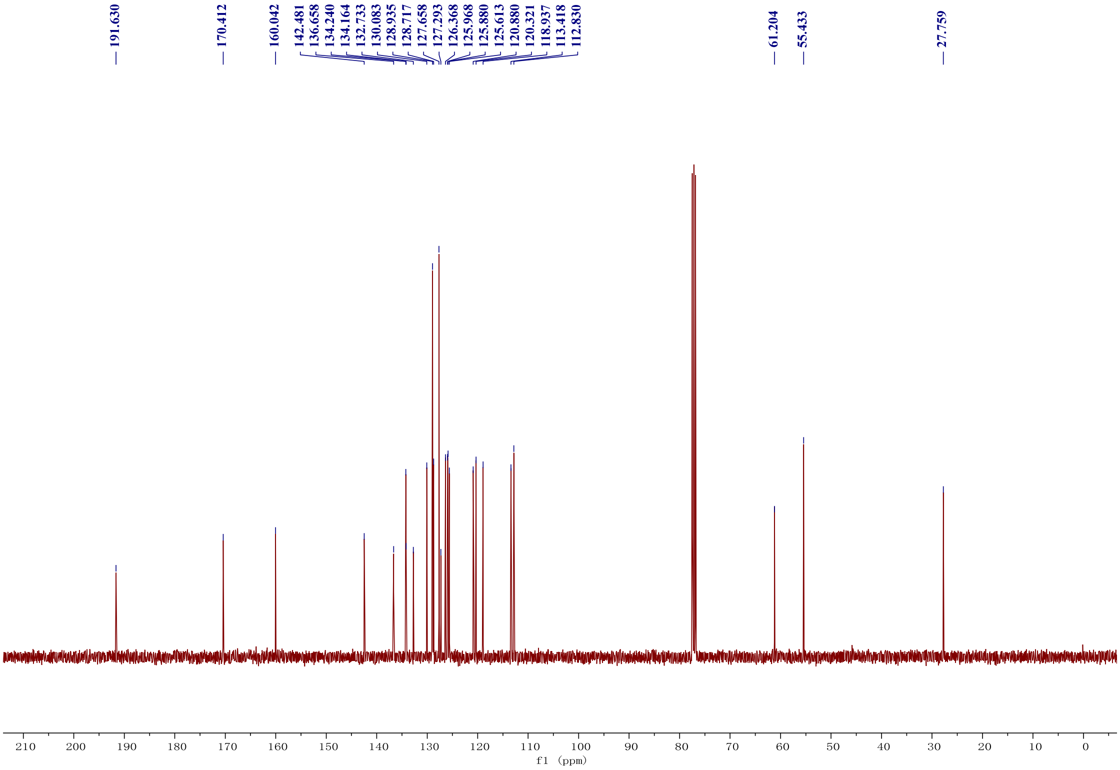


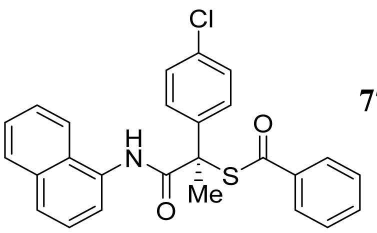



MeO
H
N
O
Me
S
O

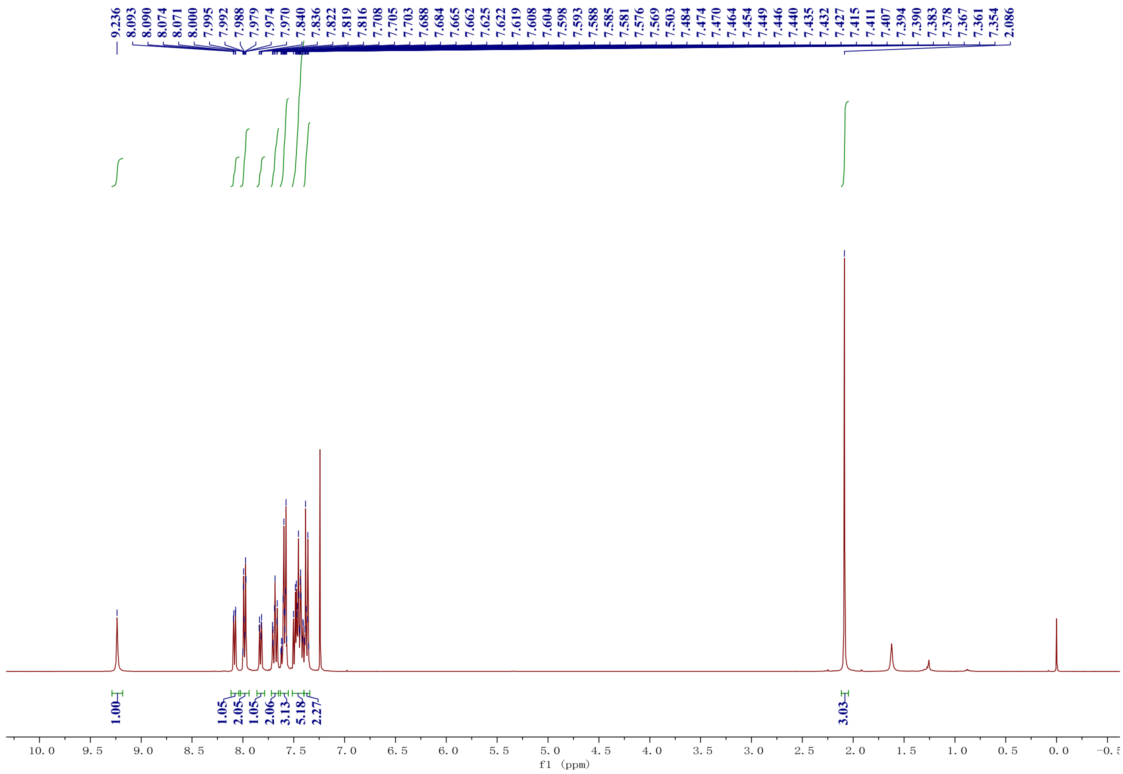
76

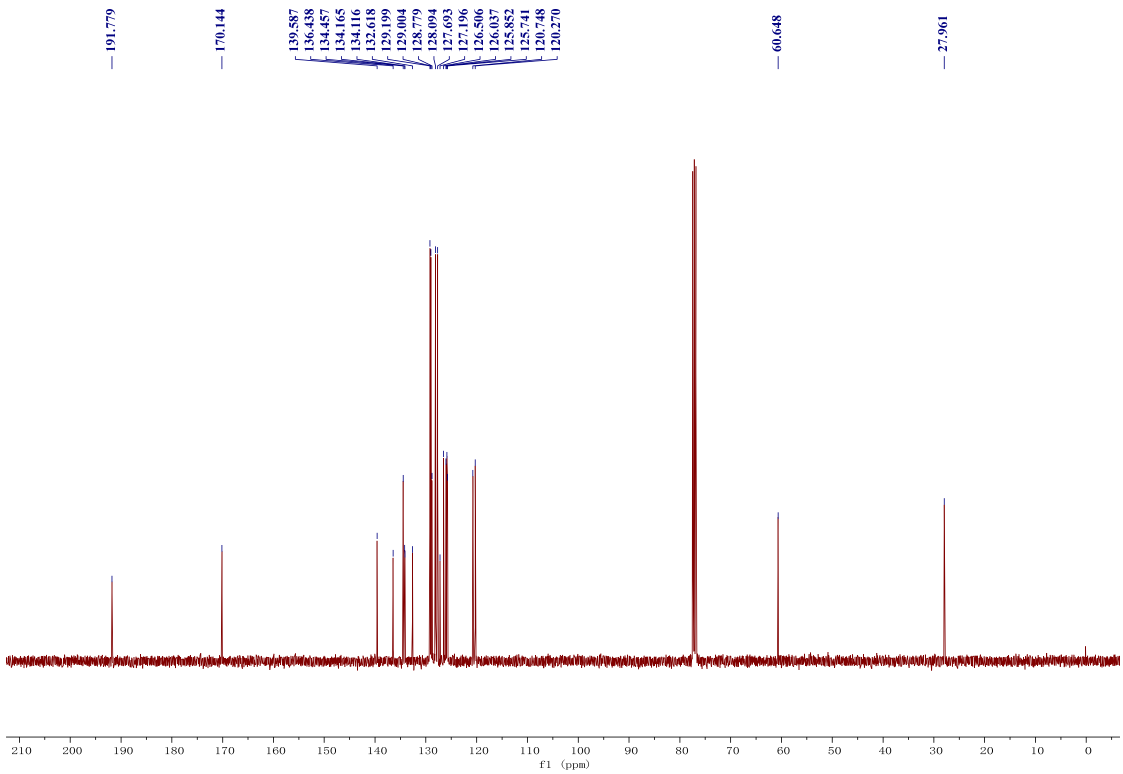

f1 (ppm)


191.630
170.412
160.042
142.481
136.658
134.240
134.164
132.733
130.083
128.935
128.717
127.658
127.293
126.368
125.968
125.880
125.613
120.880
120.321
118.937
113.418
112.830
61.204
55.433
27.759
f1 (ppm)


Cl
H
N
O
Me
S
O

77


9.236
8.093
8.090
8.074
8.071
8.000
7.995
7.992
7.988
7.979
7.974
7.970
7.840
7.836
7.822
7.819
7.816
7.708
7.705
7.703
7.688
7.684
7.665
7.662
7.625
7.622
7.619
7.608
7.604
7.598
7.593
7.588
7.585
7.581
7.576
7.569
7.503
7.484
7.474
7.470
7.464
7.454
7.449
7.446
7.440
7.435
7.432
7.427
7.415
7.411
7.407
7.394
7.390
7.383
7.378
7.367
7.361
7.354
2.086
1.00
1.05
2.05
1.05
2.06
3.13
5.18
2.27
3.03
f1 (ppm)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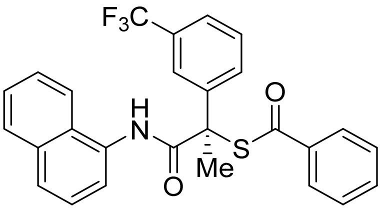
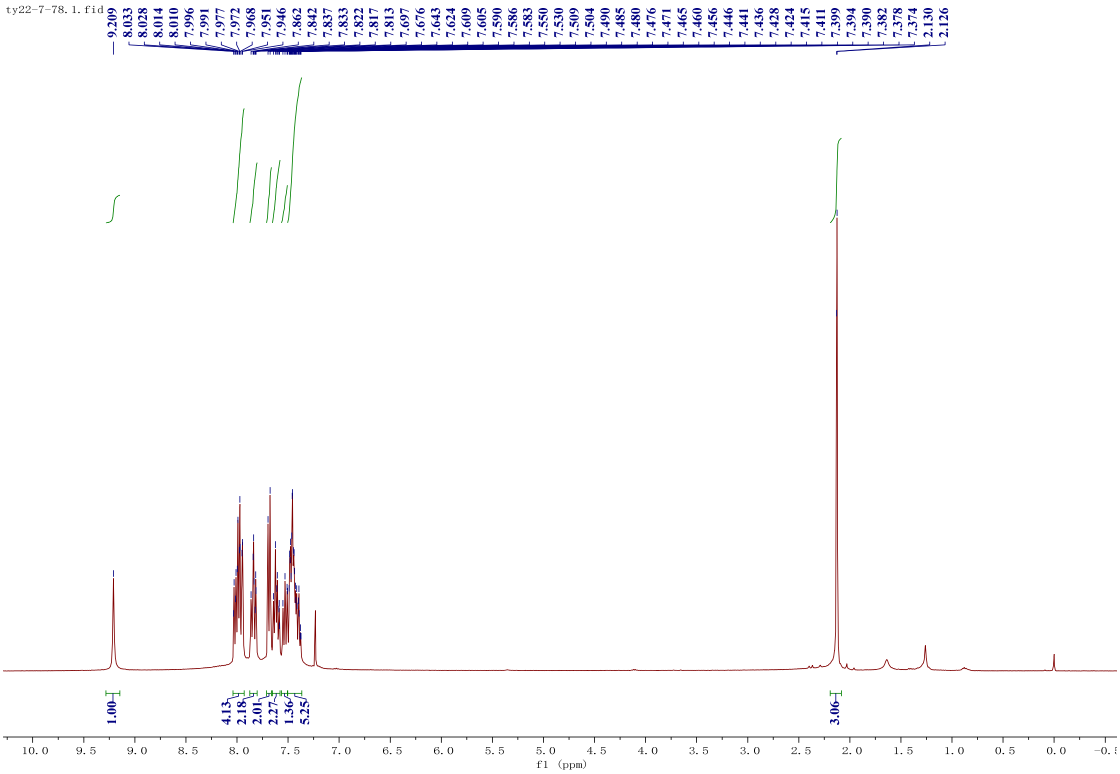
139.587
136.438
134.457
134.165
134.116
132.618
129.199
129.004
128.779
128.094
127.693
127.196
126.506
126.037
125.852
125.741
120.748
120.270
60.648
27.961
f1 (ppm)


F3C
H
N
O
S
O
Me

78


ty22-7-78.1.fid
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8.014
8.010
7.996
7.991
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7.972
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7.951
7.946
7.862
7.842
7.837
7.833
7.822
7.817
7.813
7.697
7.676
7.643
7.624
7.609
7.605
7.590
7.586
7.583
7.550
7.530
7.509
7.504
7.490
7.485
7.480
7.476
7.471
7.465
7.460
7.456
7.446
7.441
7.436
7.428
7.424
7.415
7.411
7.399
7.394
7.390
7.382
7.378
7.374
2.130
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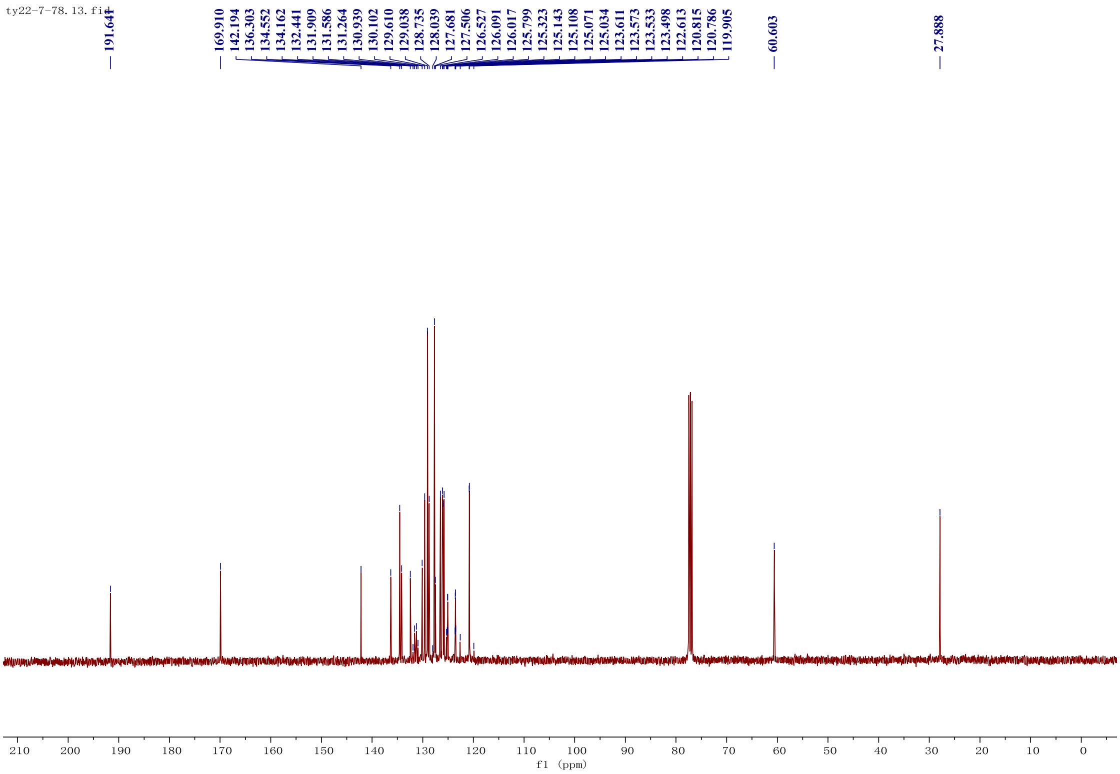
1.00
4.13
2.18
2.01
2.27
1.36
5.25
3.06
f1 (ppm)


ty22-7-78.13.fid
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142.194
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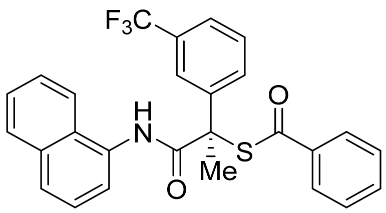
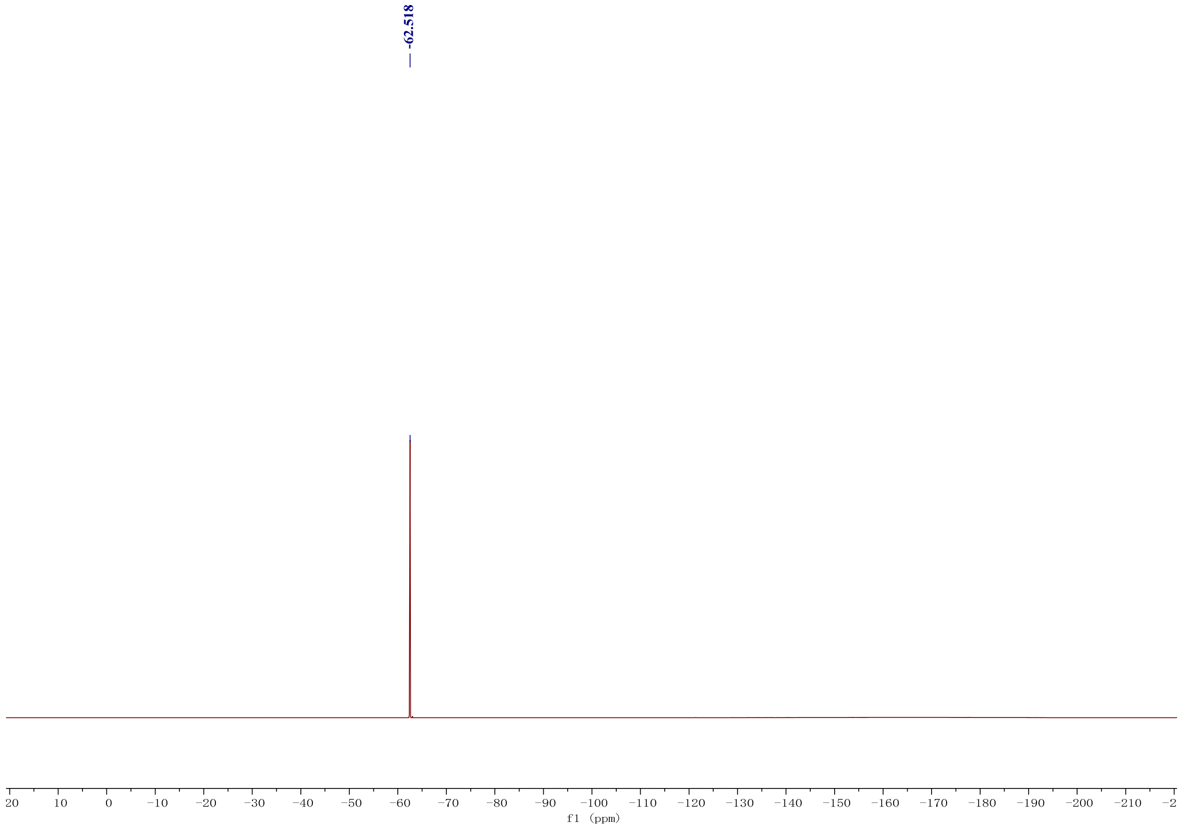
134.552
134.162
132.441
131.909
131.586
131.264
130.939
130.102
129.610
129.038
128.735
128.039
127.681
127.506
126.527
126.091
126.017
125.799
125.323
125.143
125.108
125.071
125.034
123.611
123.573
123.533
123.498
122.613
120.815
120.786
119.905
60.603
27.888
f1 (ppm)



78



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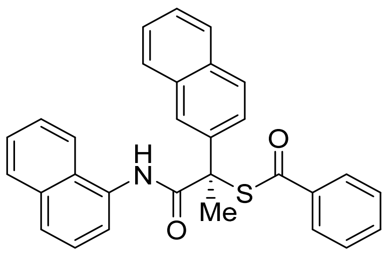
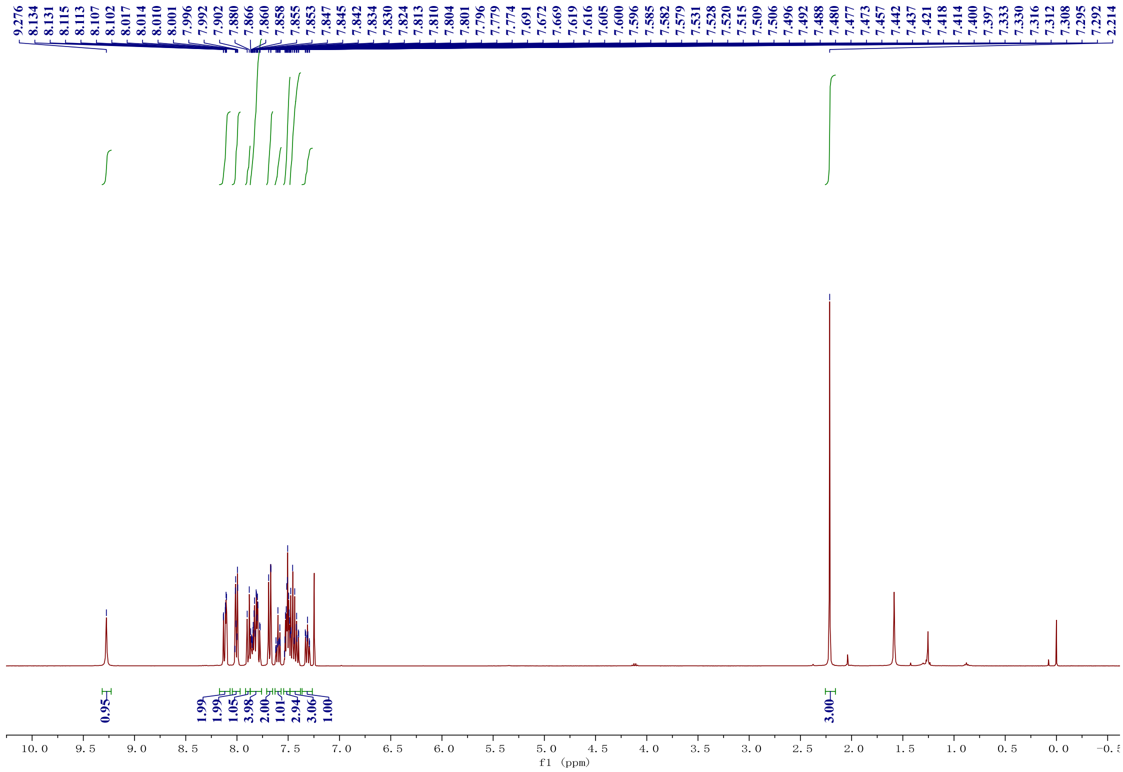
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2
f1 (ppm)


H
N
O
Me
S
O

79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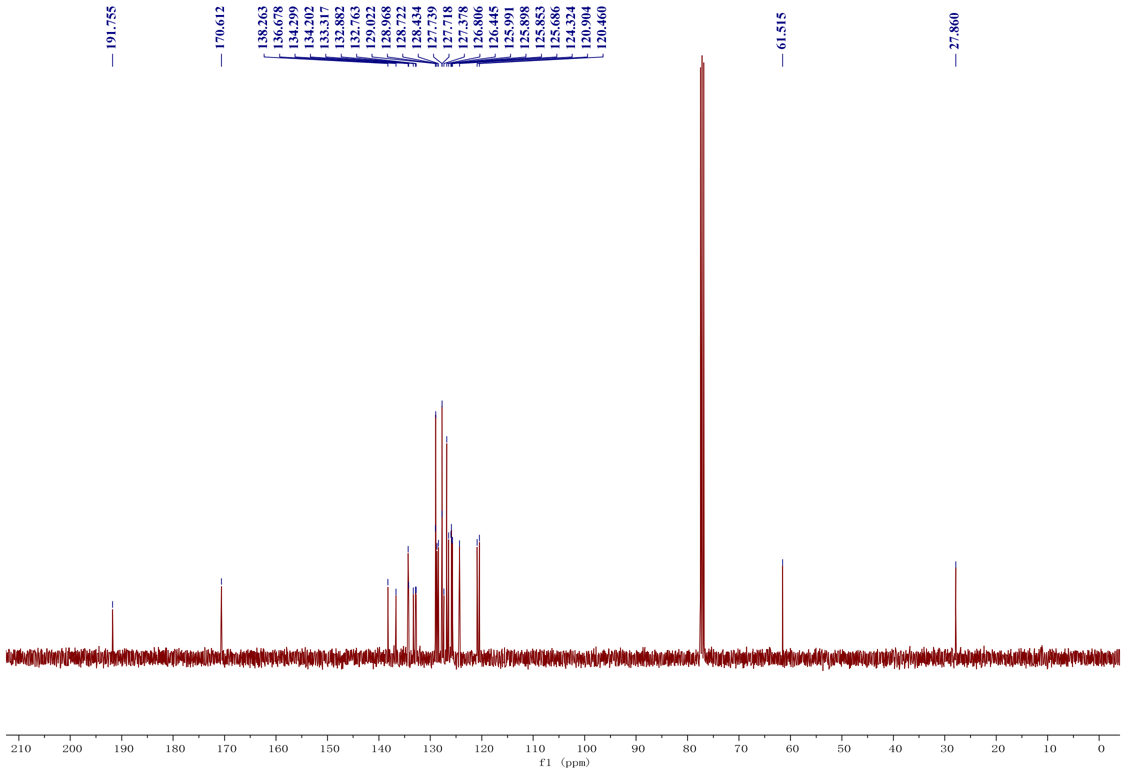
8.134
8.131
8.115
8.113
8.107
8.102
8.017
8.014
8.010
8.001
7.996
7.992
7.902
7.880
7.866
7.860
7.858
7.855
7.853
7.847
7.845
7.842
7.834
7.830
7.824
7.813
7.810
7.804
7.801
7.796
7.779
7.774
7.691
7.672
7.669
7.619
7.616
7.605
7.600
7.596
7.585
7.582
7.579
7.531
7.528
7.520
7.515
7.509
7.506
7.496
7.492
7.488
7.480
7.477
7.473
7.457
7.442
7.437
7.421
7.418
7.414
7.400
7.397
7.333
7.330
7.316
7.312
7.308
7.295
7.292
2.214
0.95
1.99
1.99
1.05
3.98
2.00
1.01
2.94
3.06
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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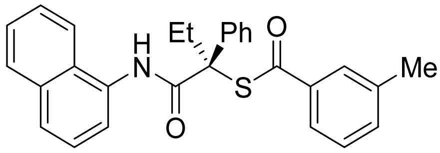
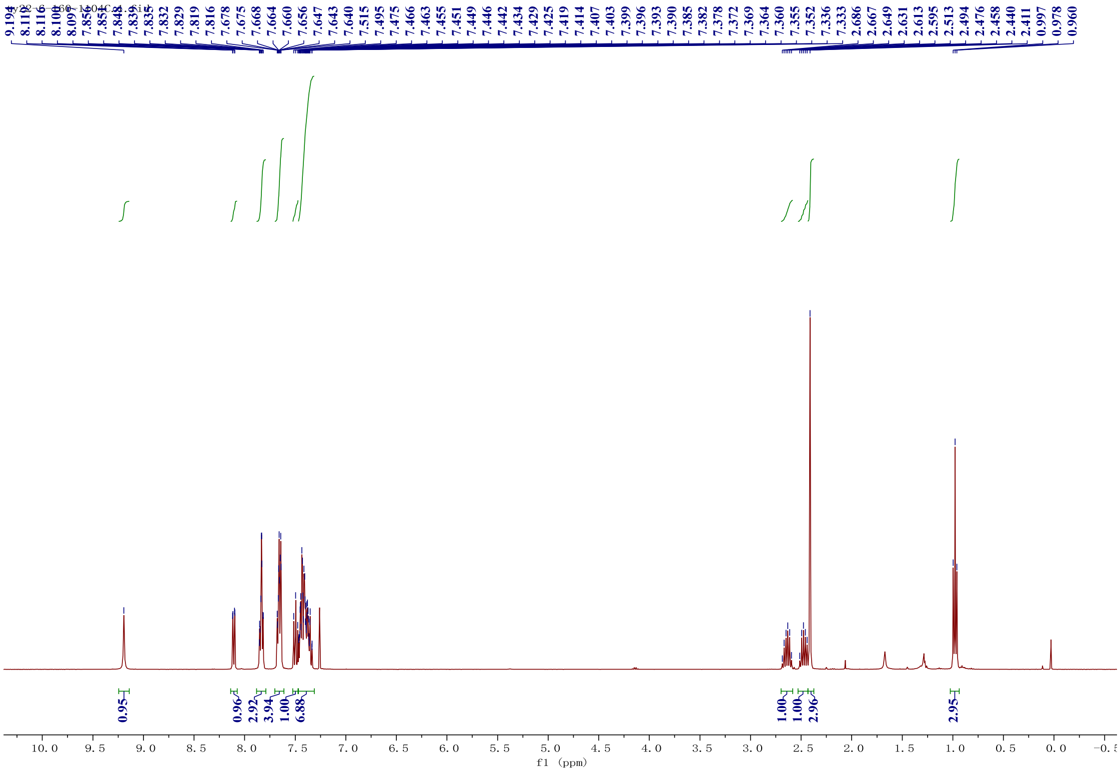
138.263
136.678
134.299
134.202
133.317
132.882
132.763
129.022
128.968
128.722
128.434
127.739
127.718
127.378
126.806
126.445
125.991
125.898
125.853
125.686
124.324
120.904
120.460
61.515
27.860
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Et
Ph
O
H
N
S
Me
O

80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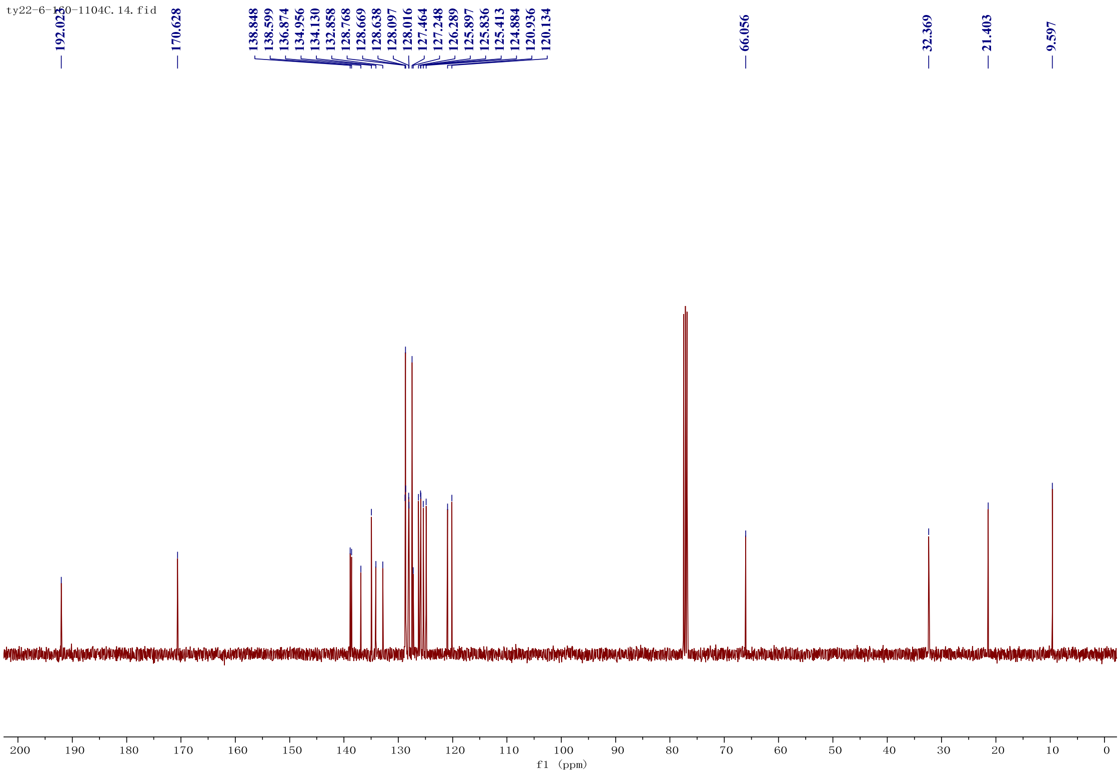
8.116
8.097
7.856
7.851
7.848
7.839
7.835
7.832
7.829
7.819
7.816
7.678
7.675
7.668
7.664
7.660
7.656
7.647
7.643
7.640
7.515
7.495
7.475
7.466
7.463
7.455
7.451
7.449
7.446
7.442
7.434
7.429
7.425
7.419
7.414
7.407
7.403
7.399
7.396
7.393
7.390
7.385
7.382
7.378
7.372
7.369
7.364
7.360
7.355
7.352
7.336
7.333
2.686
2.667
2.649
2.631
2.613
2.595
2.513
2.494
2.476
2.458
2.440
2.411
0.997
0.978
0.960
0.95
0.96
2.92
3.94
1.00
6.88
1.00
1.00
2.96
2.95
f1 (ppm)


ty22-6-160-1104C.14.fid
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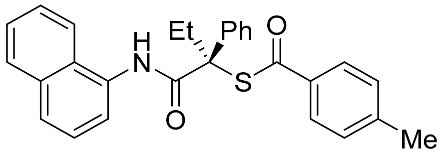
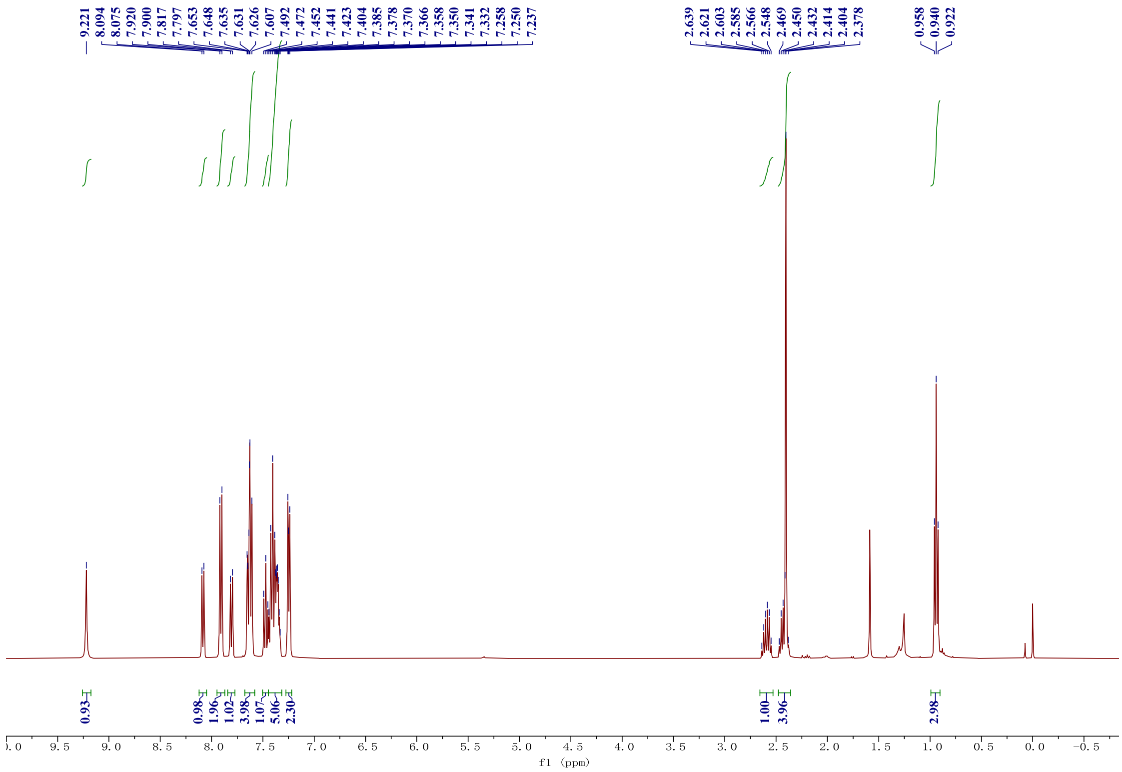
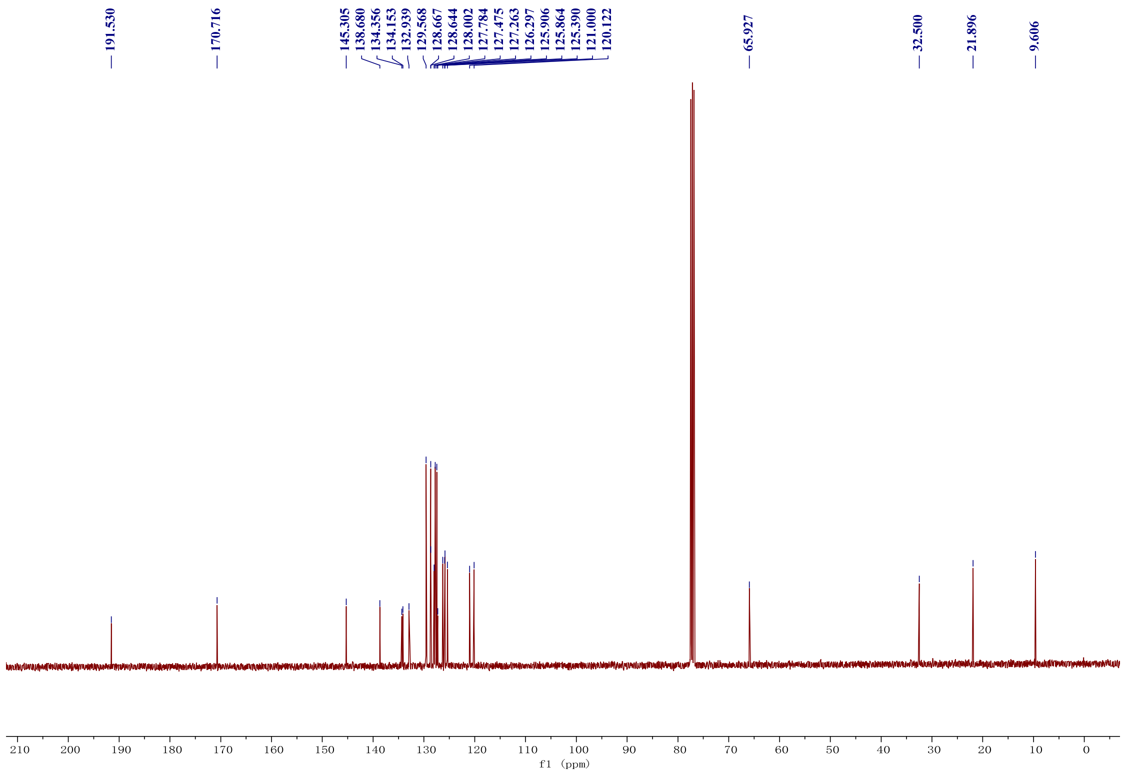
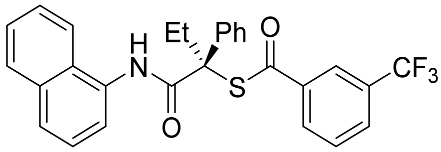
170.628
138.848
138.599
136.874
134.956
134.130
132.858
128.768
128.669
128.638
128.097
128.016
127.464
127.248
126.289
125.897
125.836
125.413
124.884
120.936
120.134
66.056
32.369
21.403
9.597
f1 (ppm)



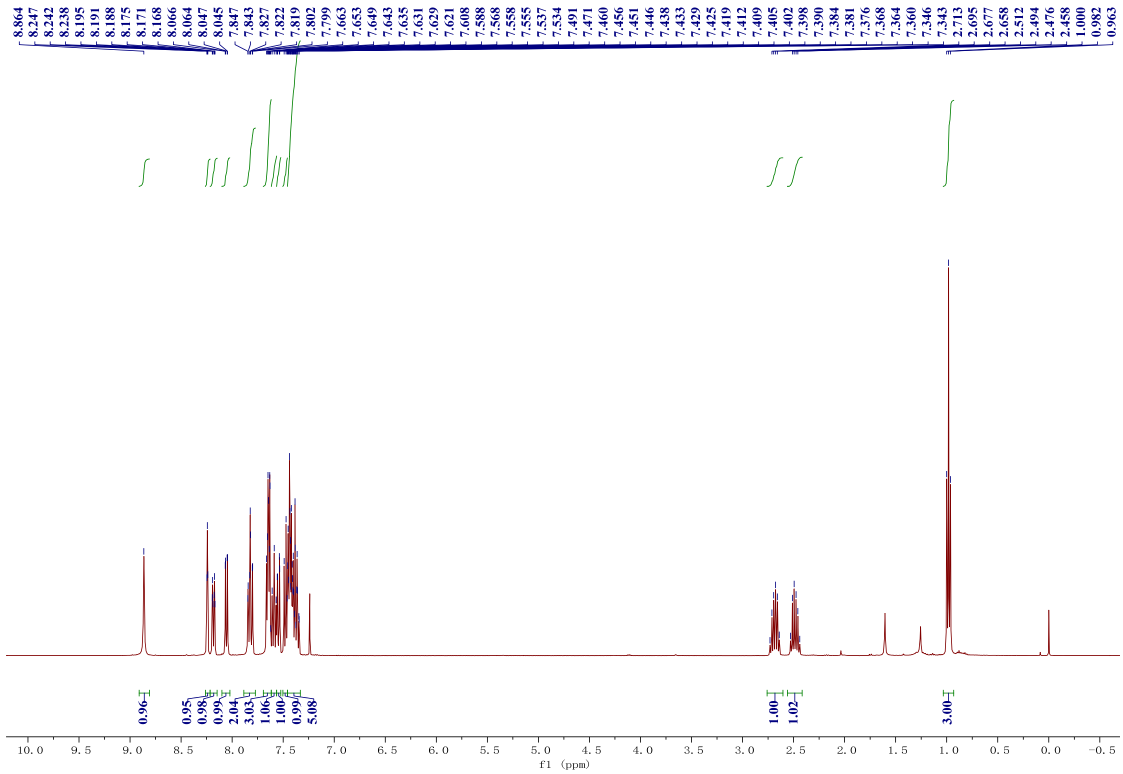
81

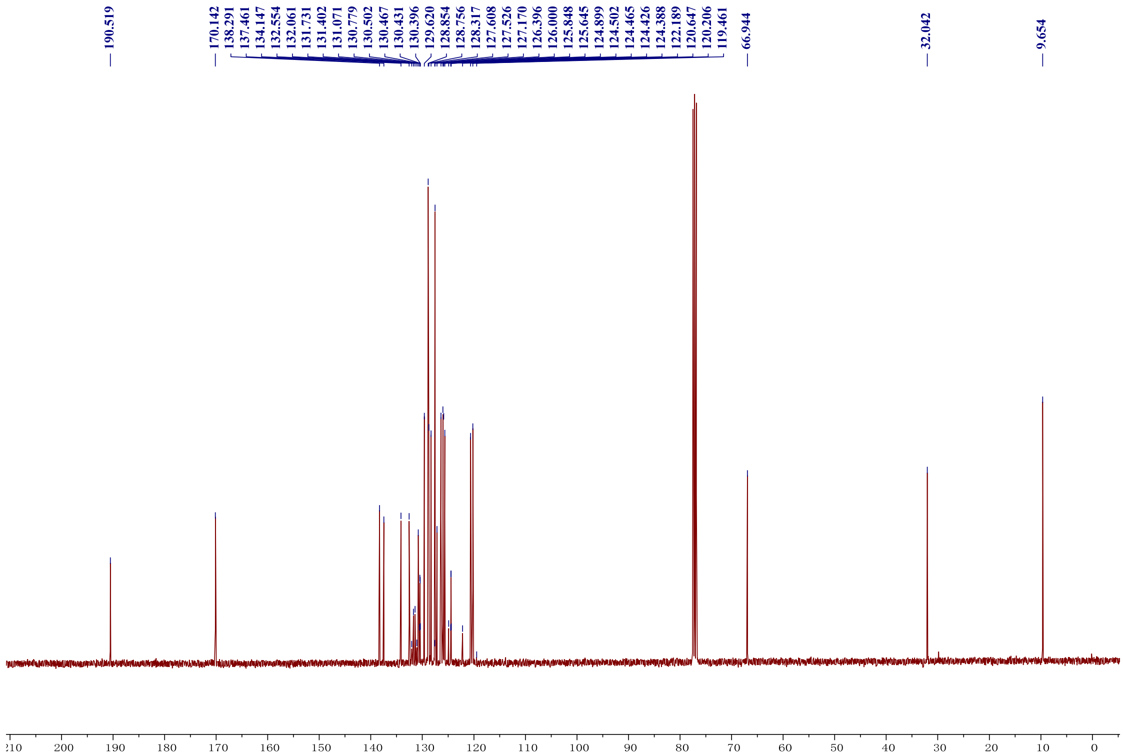


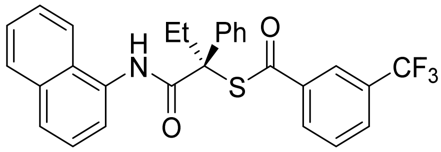




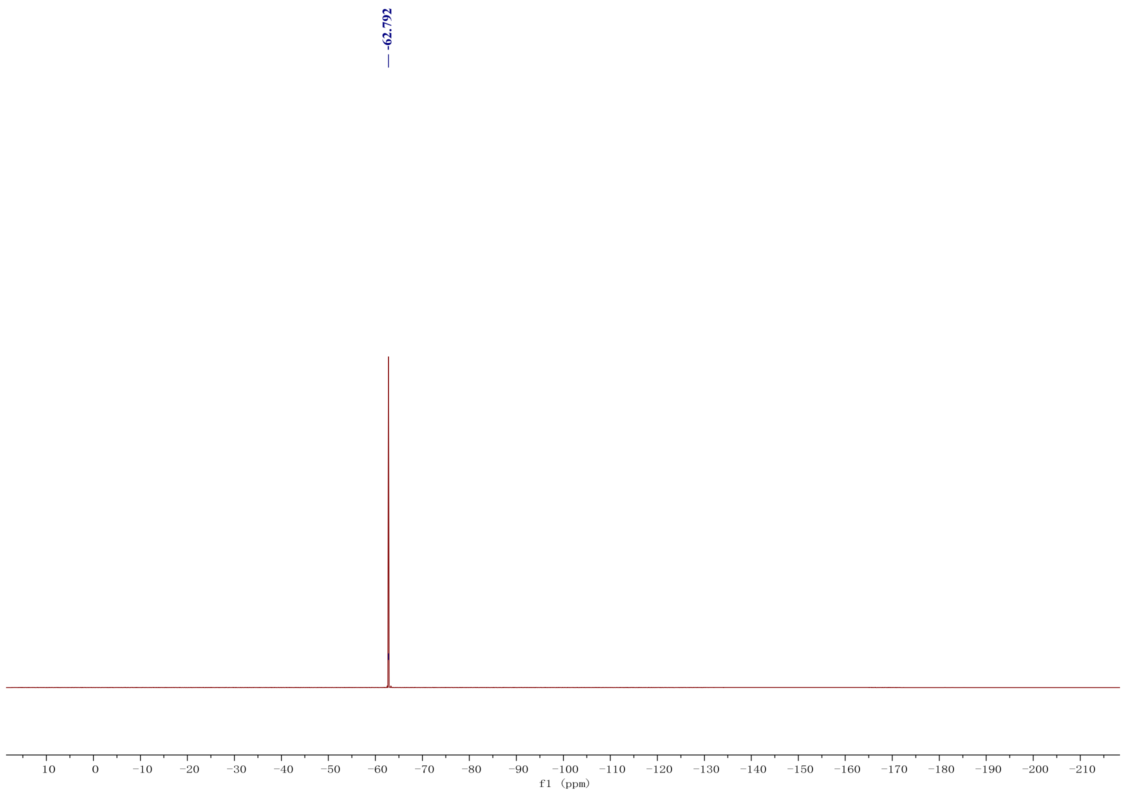
82

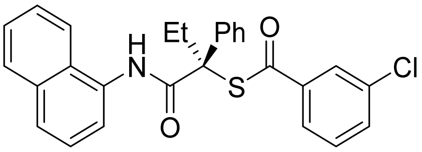




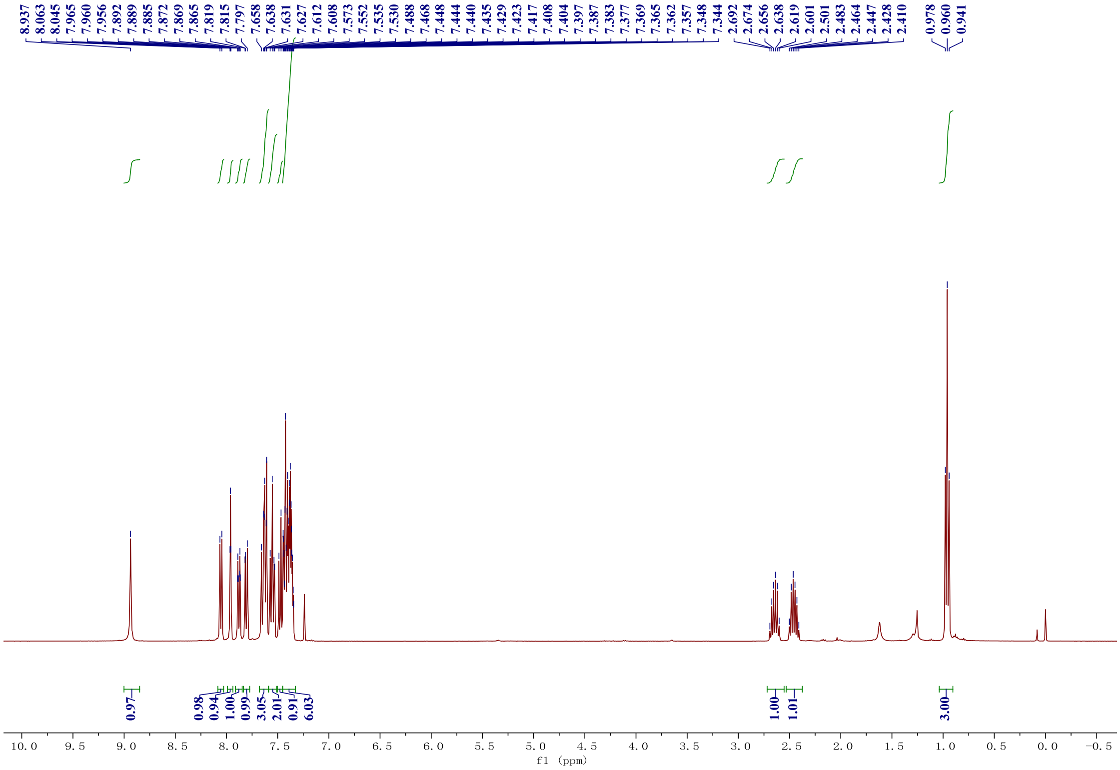

H
N
Et
Ph
O
O
S
CF3

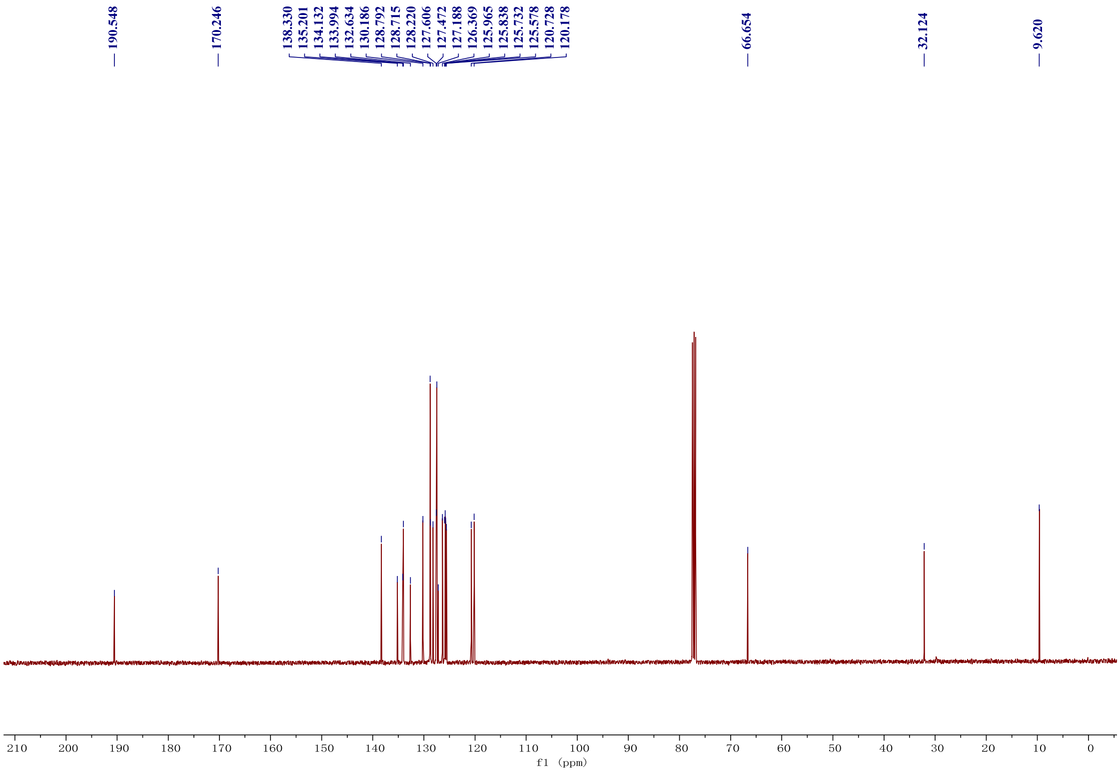
82

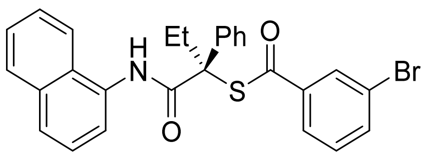

-62.792
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)



83

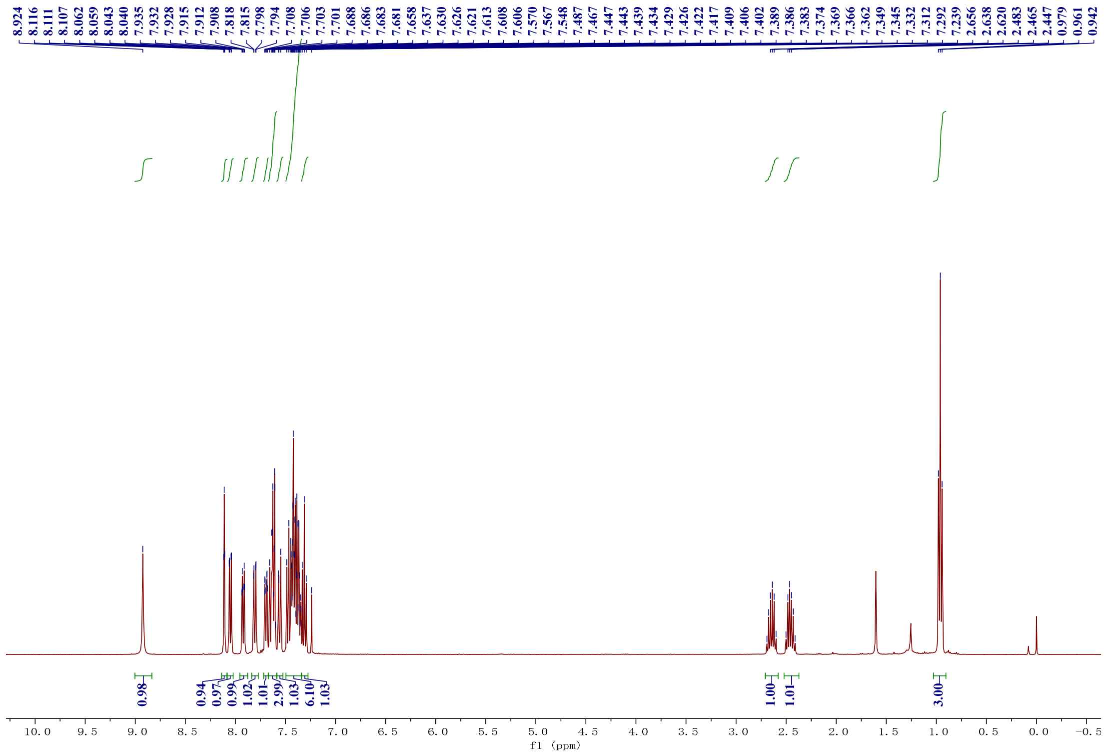




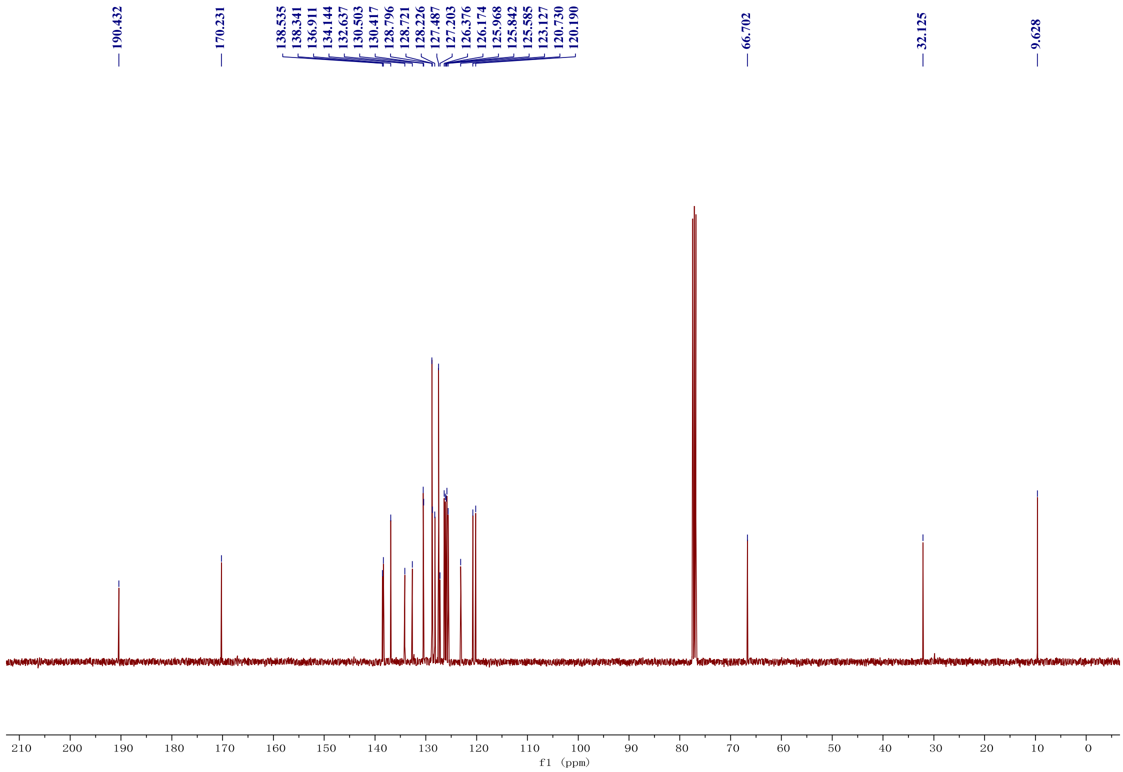


H
N
Et
Ph
O
S
Br
O

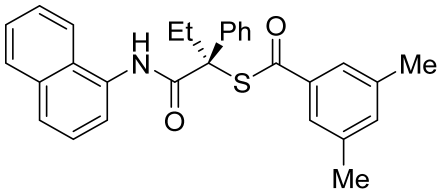
84



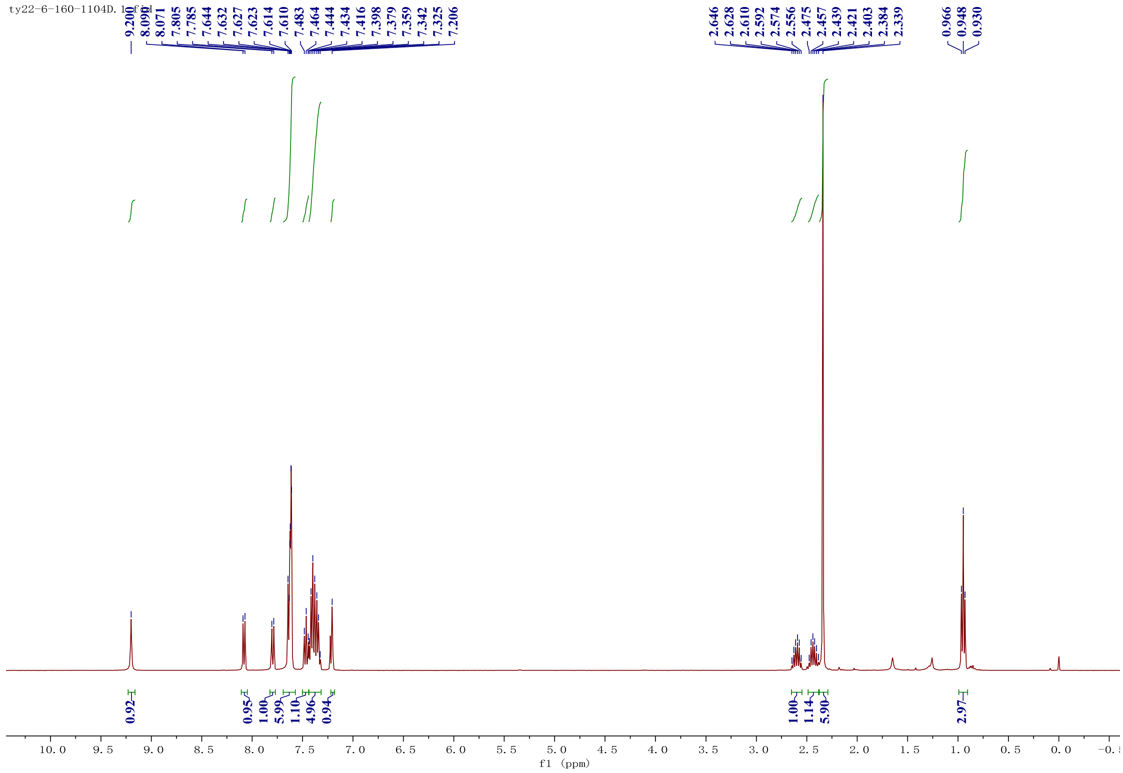
8.924 8.116 8.111 8.107 8.062 8.059 8.043 8.040 7.935 7.932 7.928 7.915 7.912 7.908 7.818 7.815 7.798 7.794 7.708 7.706 7.703 7.701 7.688 7.686 7.683 7.681 7.658 7.637 7.630 7.626 7.621 7.613 7.608 7.606 7.570 7.567 7.548 7.487 7.467 7.447 7.443 7.439 7.434 7.429 7.426 7.422 7.417 7.409 7.406 7.402 7.389 7.386 7.383 7.374 7.369 7.366 7.362 7.349 7.345 7.332 7.312 7.292 7.239 2.656 2.638 2.620 2.483 2.465 2.447 0.979 0.961 0.942
0.98
0.94 0.97 0.99 1.02 1.01 2.99 1.03 6.10 1.03
1.00 1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



190.432
170.231
138.535 138.341 136.911 134.144 132.637 130.503 130.417 128.796 128.721 128.226 127.487 127.203 126.376 126.174 125.968 125.842 125.585 123.127 120.730 120.190
66.702
32.125
9.628
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H
N
Et
Ph
O
S
Me
O
Me

85


ty22-6-160-1104D.1.fid
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8.071
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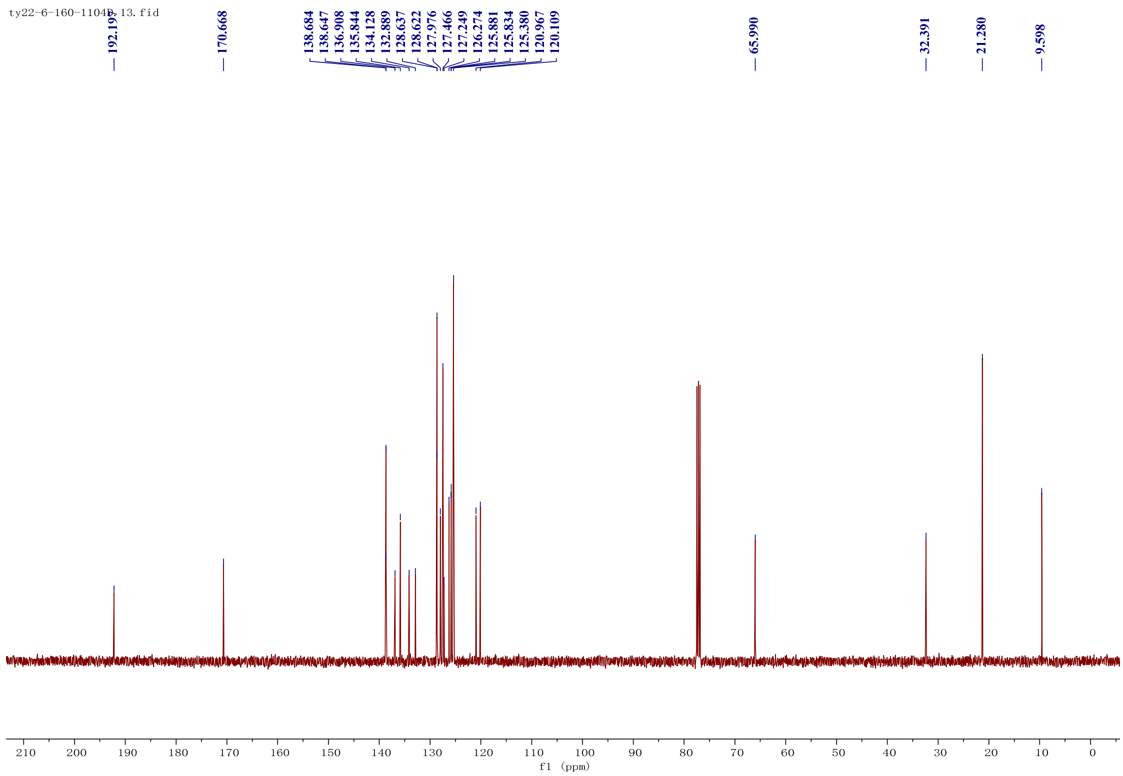
7.785
7.644
7.632
7.627
7.623
7.614
7.610
7.483
7.464
7.444
7.434
7.416
7.398
7.379
7.359
7.342
7.325
7.206
2.646
2.628
2.610
2.592
2.574
2.556
2.475
2.457
2.439
2.421
2.403
2.384
2.339
0.966
0.948
0.930
0.92
0.95
1.00
5.99
1.10
4.96
0.94
1.00
1.14
5.90
2.97
f1 (ppm)


ty22-6-160-1104D.13.fid
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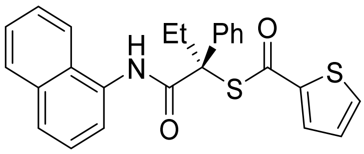
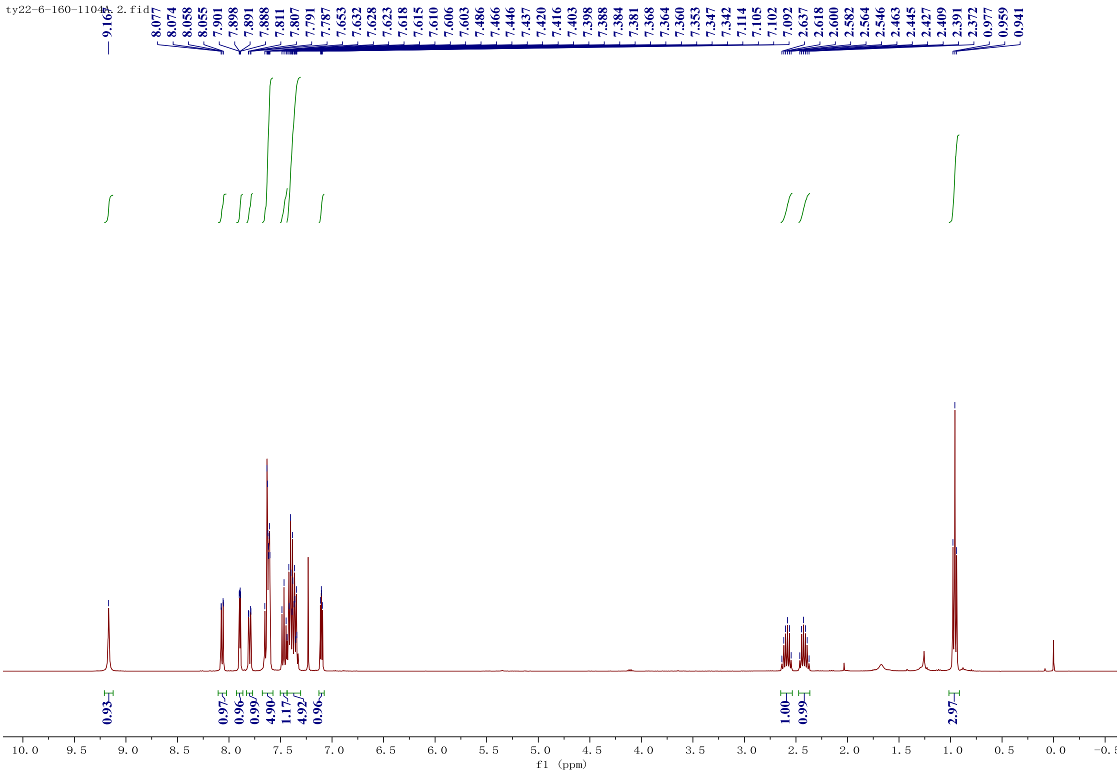
170.668
138.684
138.647
136.908
135.844
134.128
132.889
128.637
128.622
127.976
127.466
127.249
126.274
125.881
125.834
125.380
120.967
120.109
65.990
32.391
21.280
9.598
f1 (ppm)



86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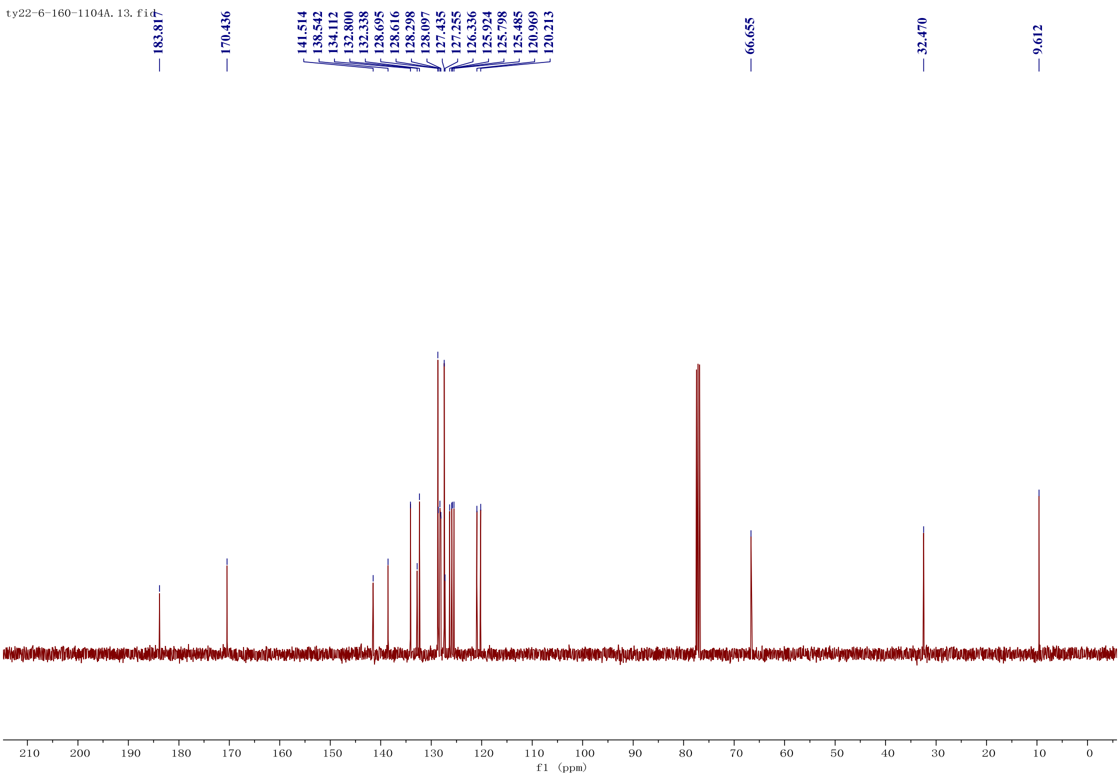
8.074
8.058
8.055
7.901
7.898
7.891
7.888
7.811
7.807
7.791
7.787
7.653
7.632
7.628
7.623
7.618
7.615
7.610
7.606
7.603
7.486
7.466
7.446
7.437
7.420
7.416
7.403
7.398
7.388
7.384
7.381
7.368
7.364
7.360
7.353
7.347
7.342
7.114
7.105
7.102
7.092
2.637
2.618
2.600
2.582
2.564
2.546
2.463
2.445
2.427
2.409
2.391
2.372
0.977
0.959
0.941
0.93
0.97
0.96
0.99
4.90
1.17
4.92
0.96
1.00
0.99
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ty22-6-160-1104A.13.fid
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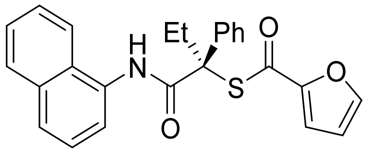
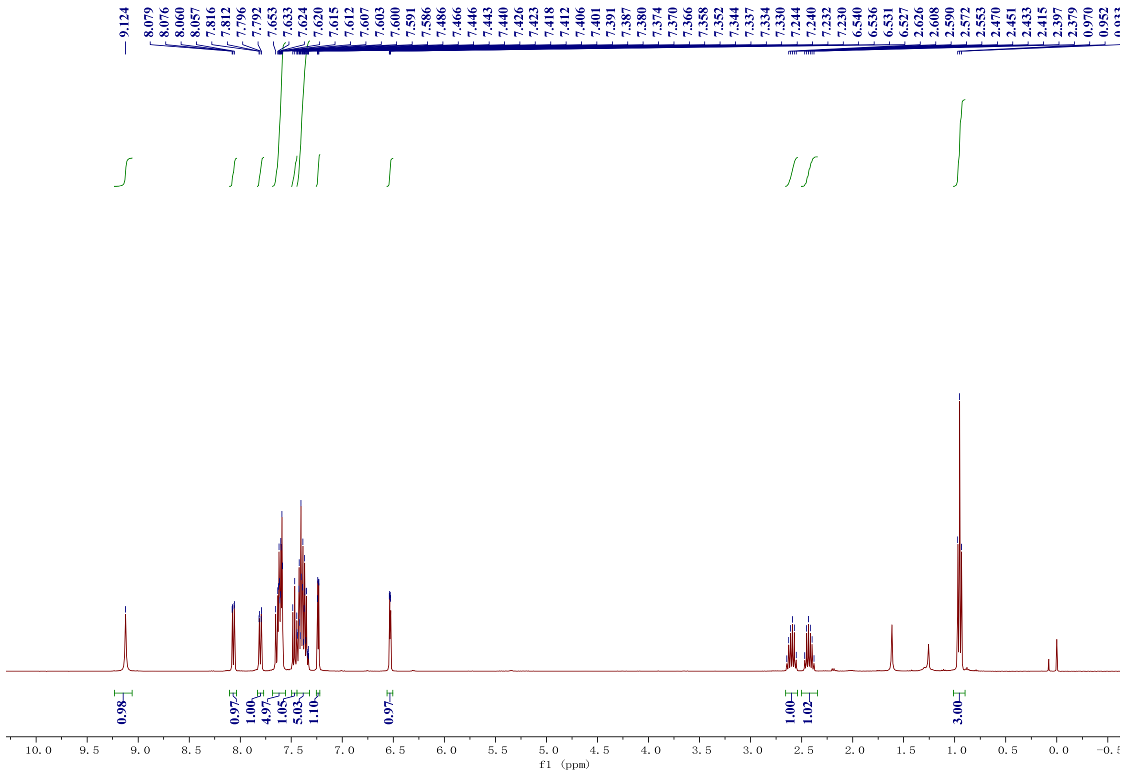
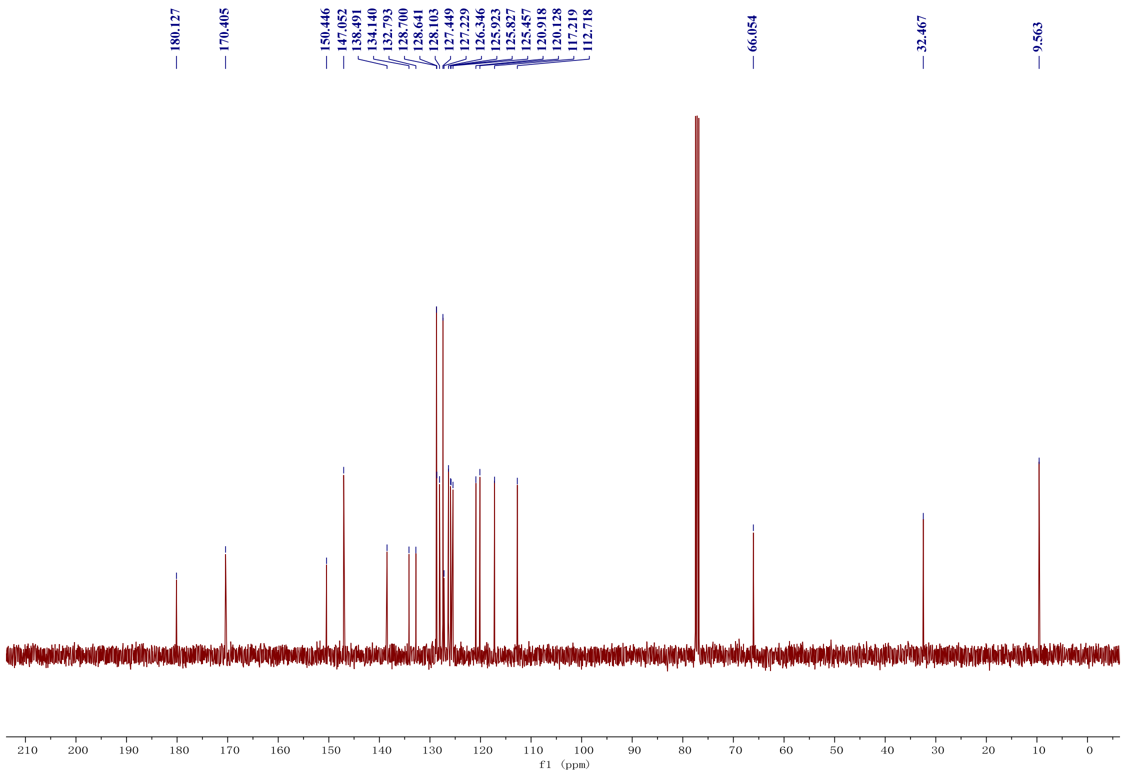
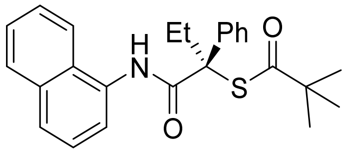
170.436
141.514
138.542
134.112
132.800
132.338
128.695
128.616
128.298
128.097
127.435
127.255
126.336
125.924
125.798
125.485
120.969
120.213
66.655
32.470
9.612
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



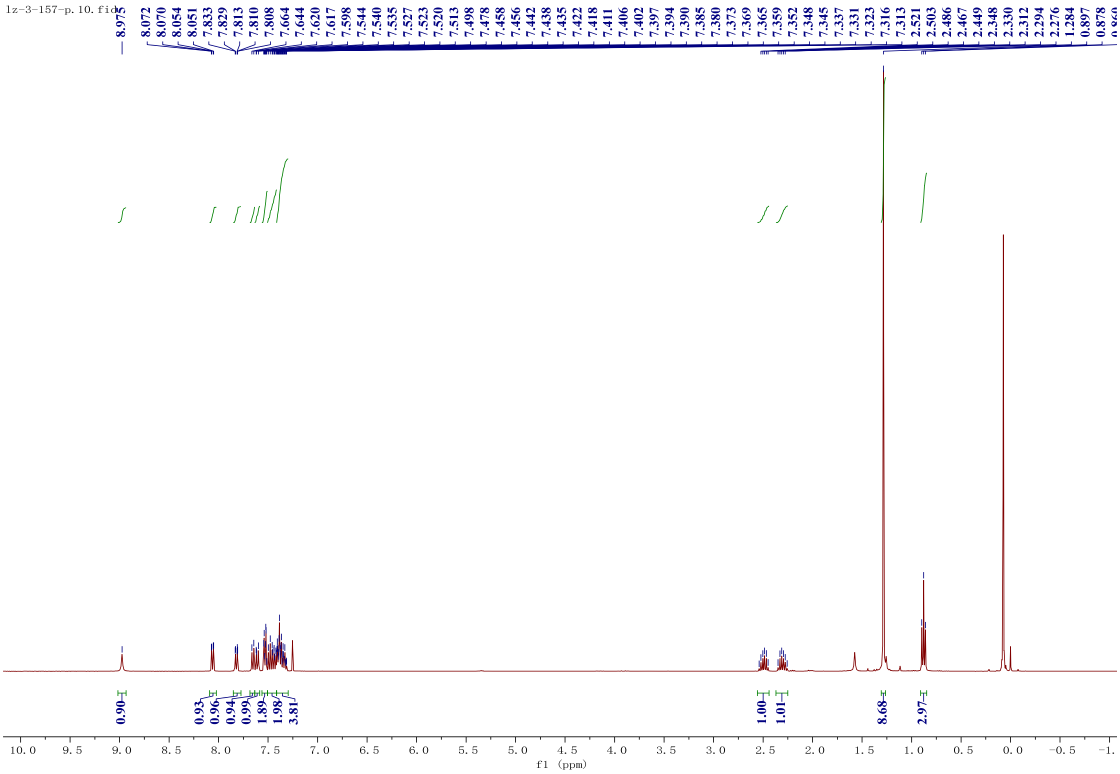
87

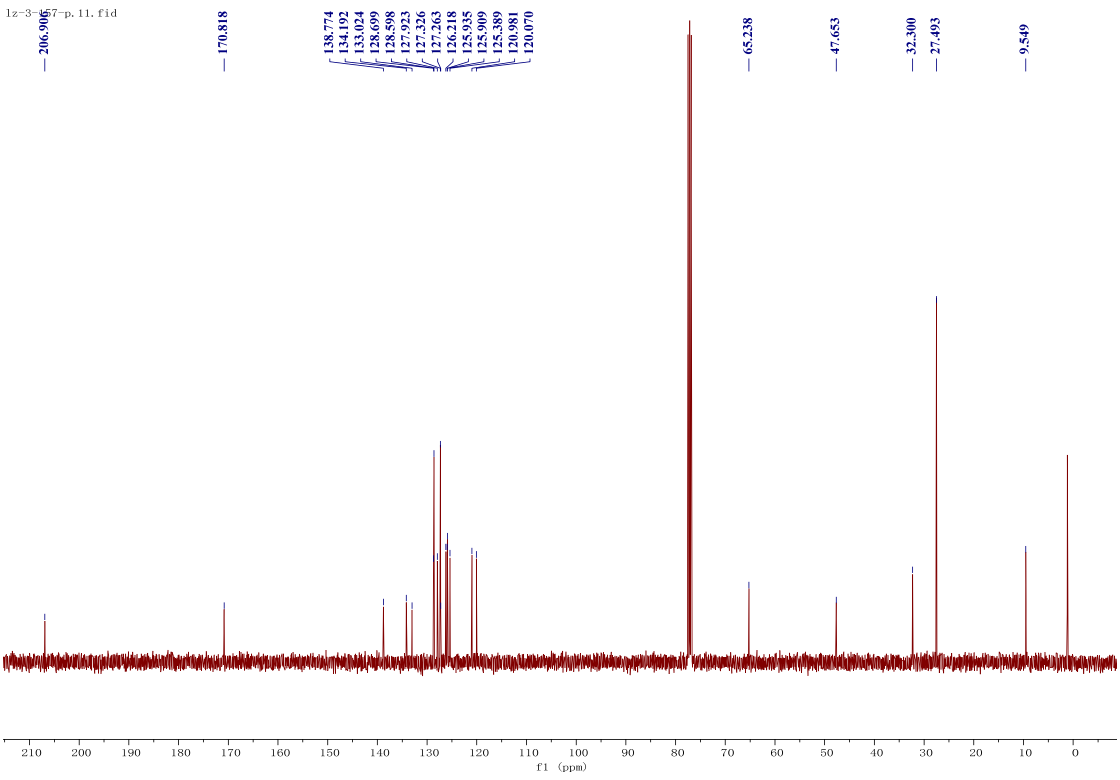


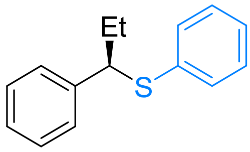




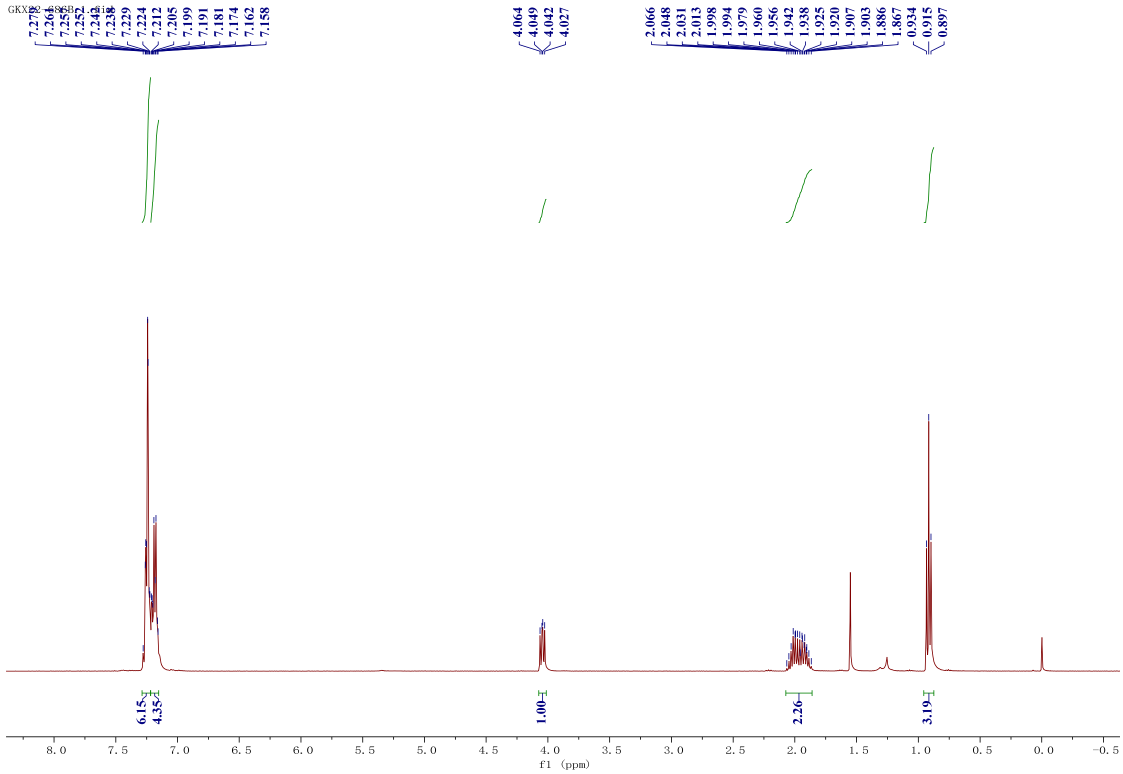
88







89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7.256
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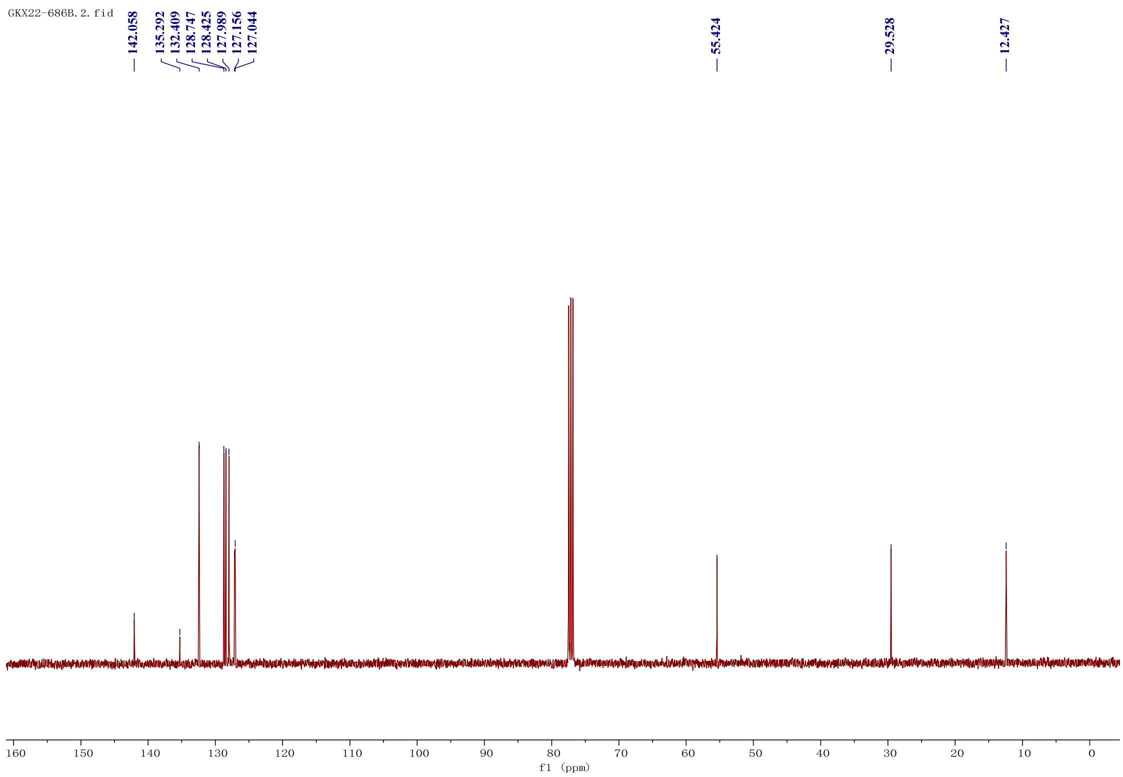
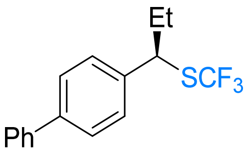
7.243
7.238
7.229
7.224
7.212
7.205
7.199
7.191
7.181
7.174
7.162
7.158
4.064
4.049
4.042
4.027
2.066
2.048
2.031
2.013
1.998
1.994
1.979
1.960
1.956
1.942
1.938
1.925
1.920
1.907
1.903
1.886
1.867
0.934
0.915
0.897
6.15
4.35
1.00
2.26
3.19
f1 (ppm)


GKX22-686B.2.fid
142.058
135.292
132.409
128.747
128.425
127.989
127.156
127.044
55.424
29.528
12.427
f1 (ppm)



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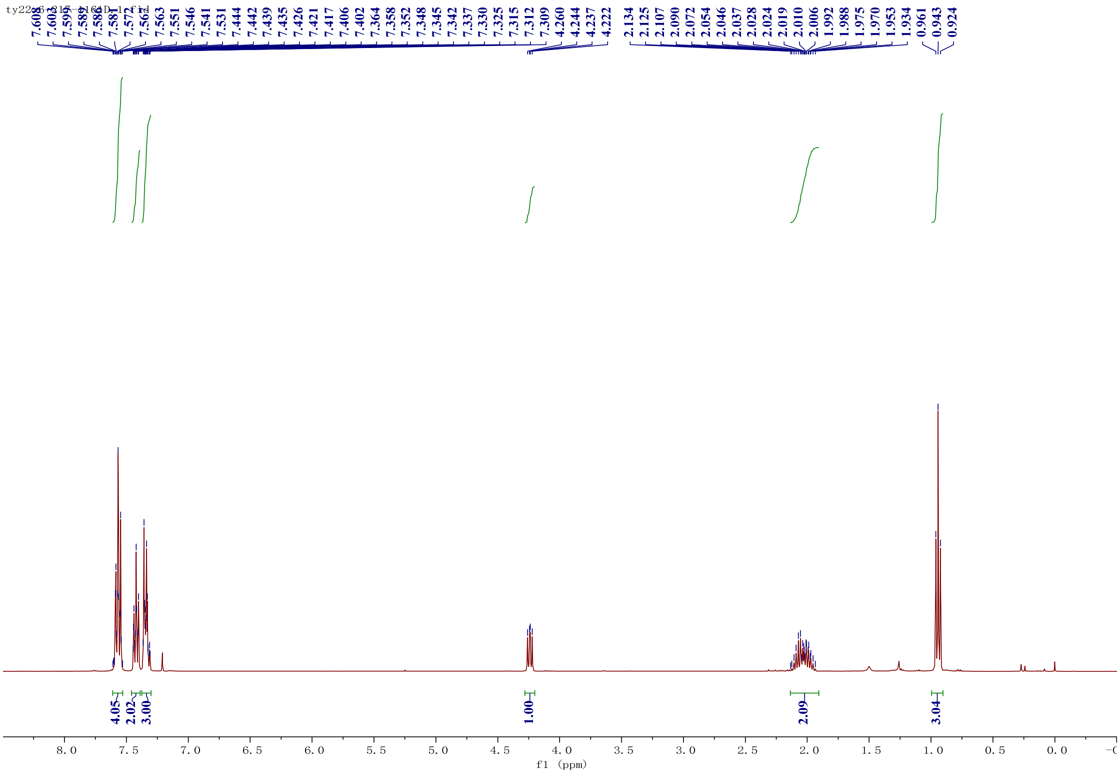
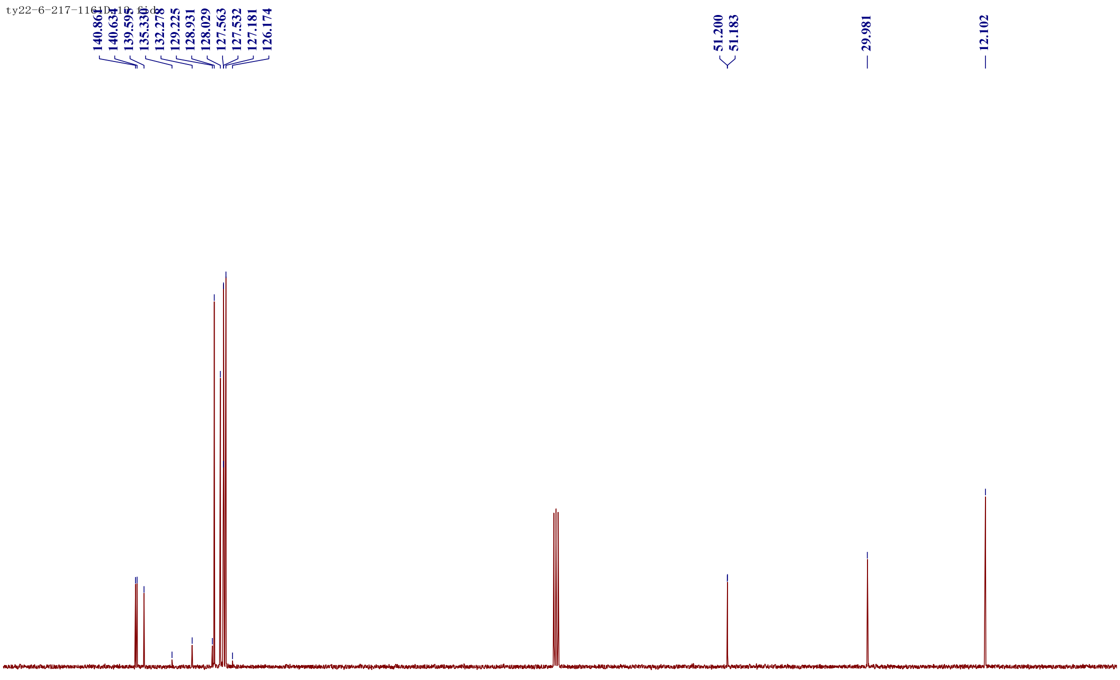
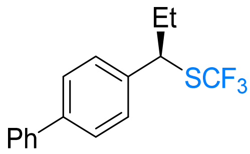
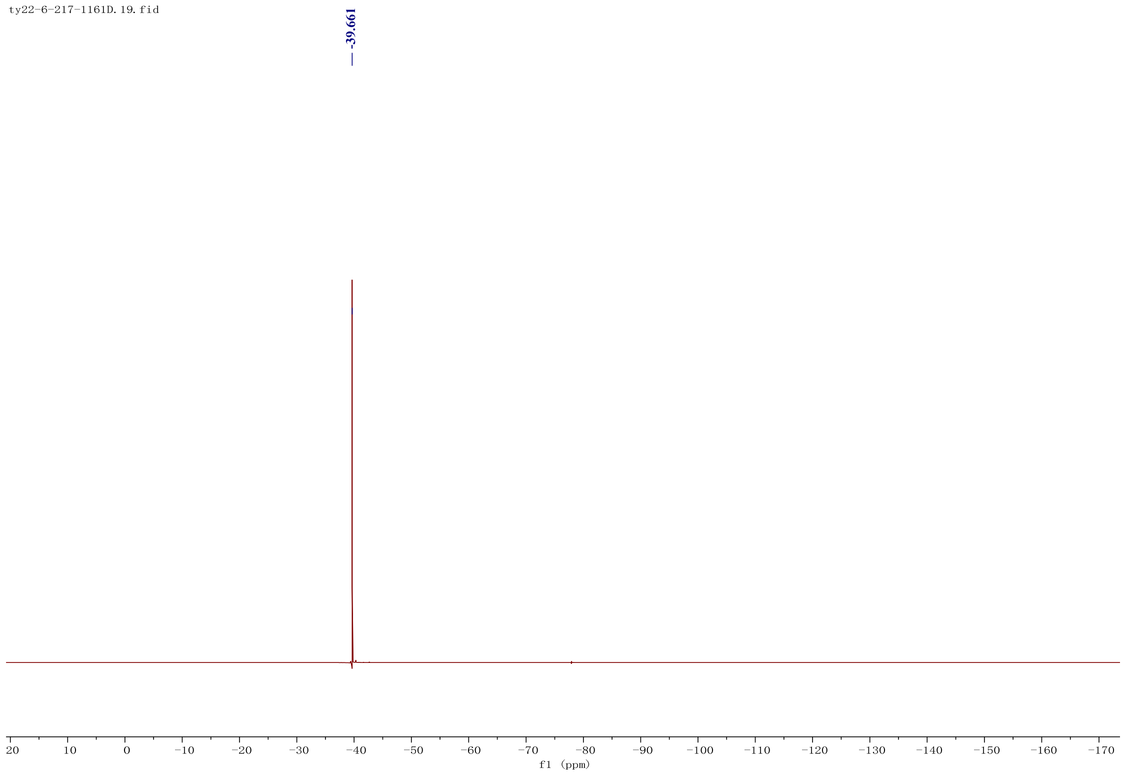
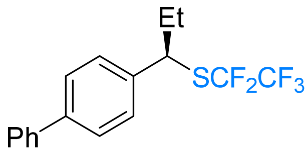




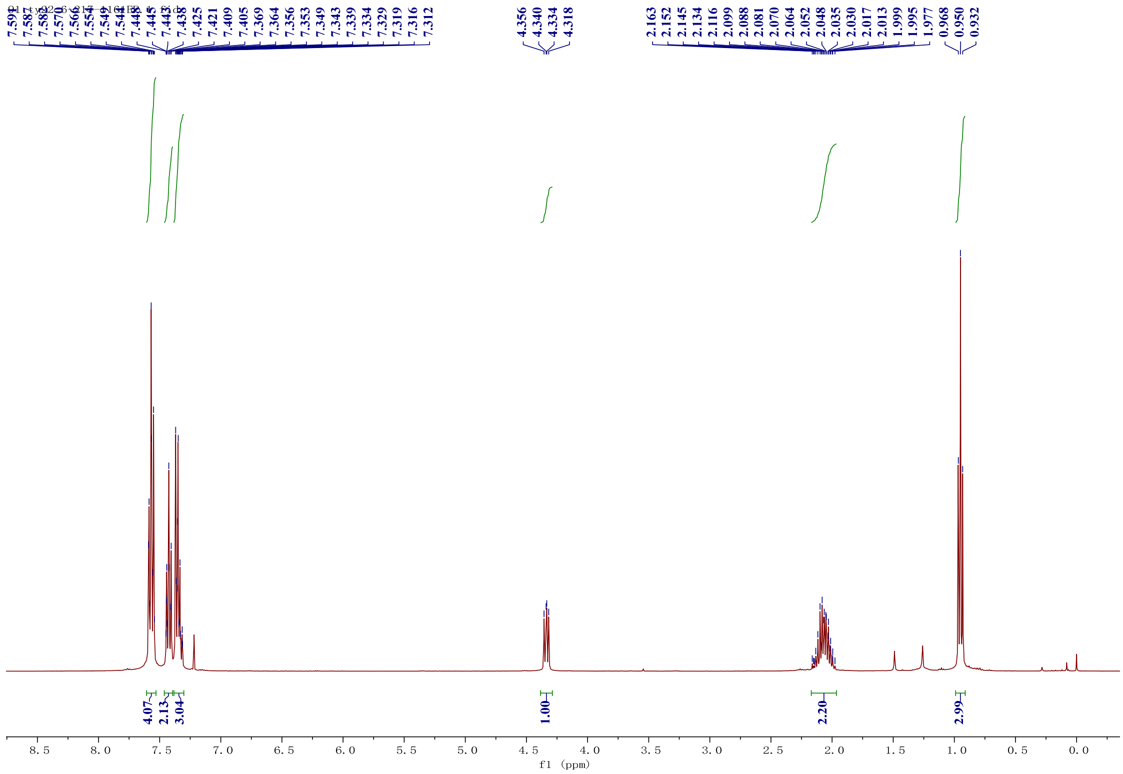

Et
SCF3
Ph

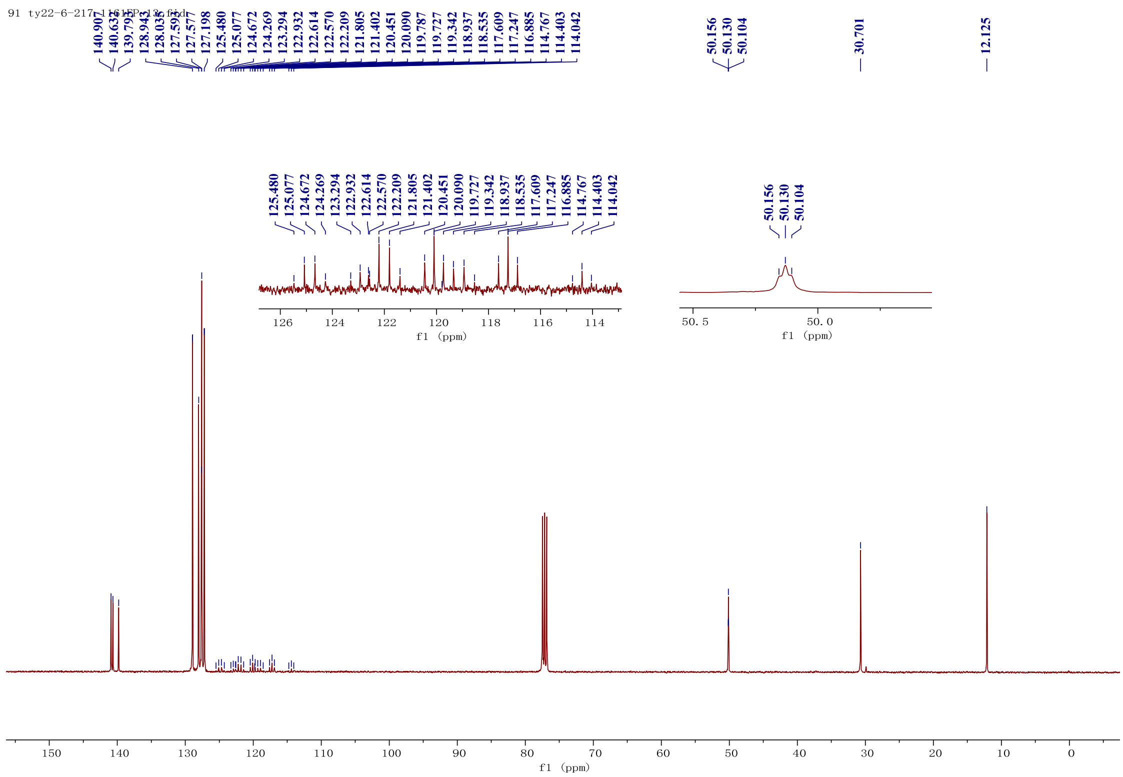
90

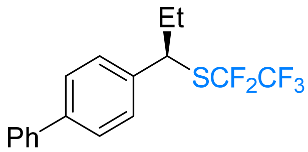

ty22-6-217-1161D.19.fid
-39.661
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170
f1 (ppm)



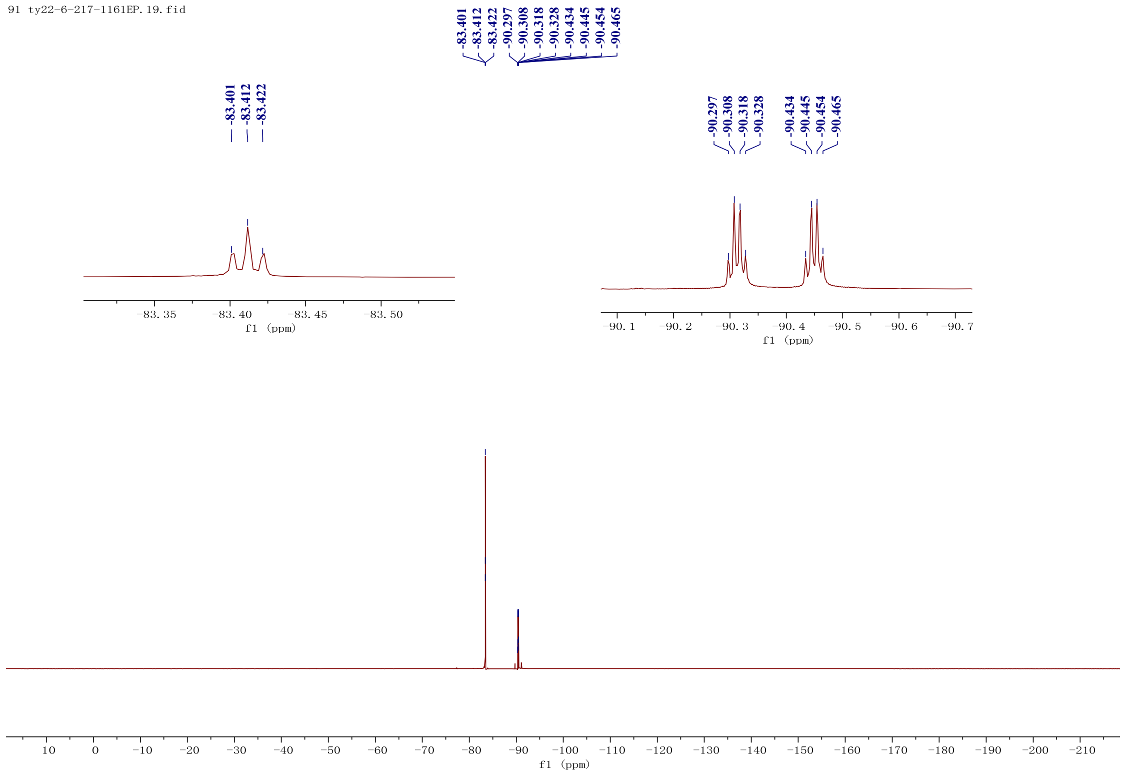
91



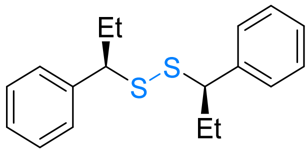




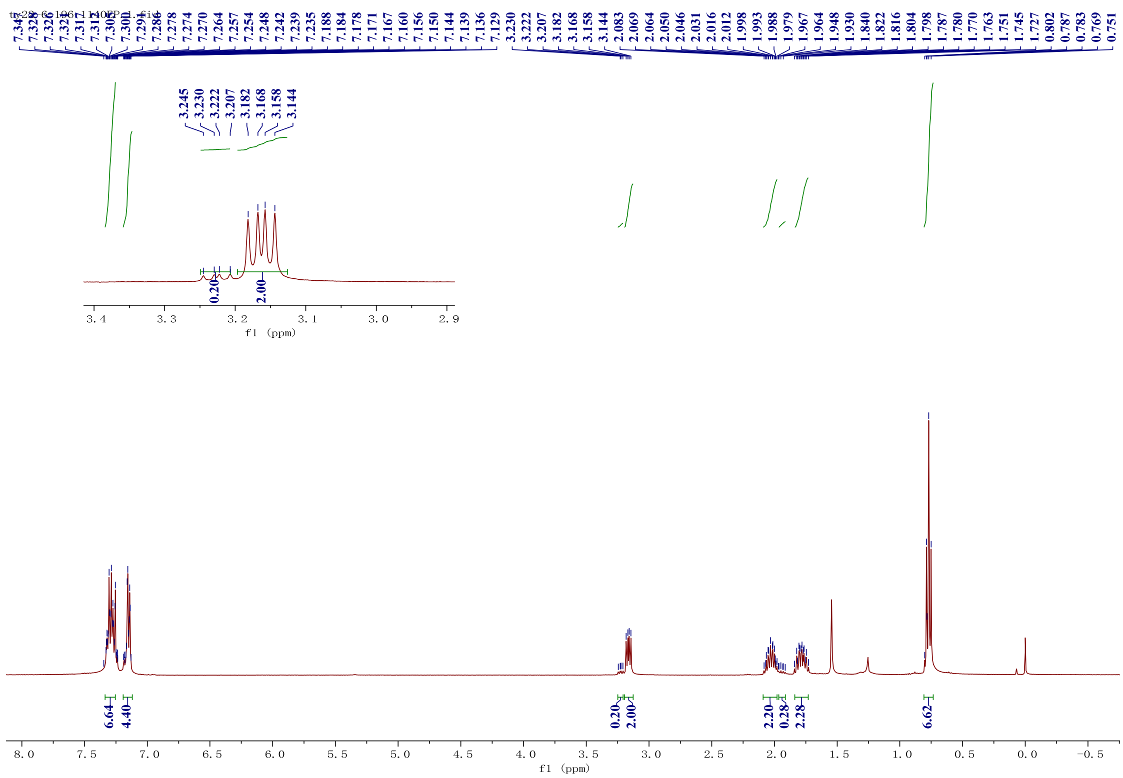
91

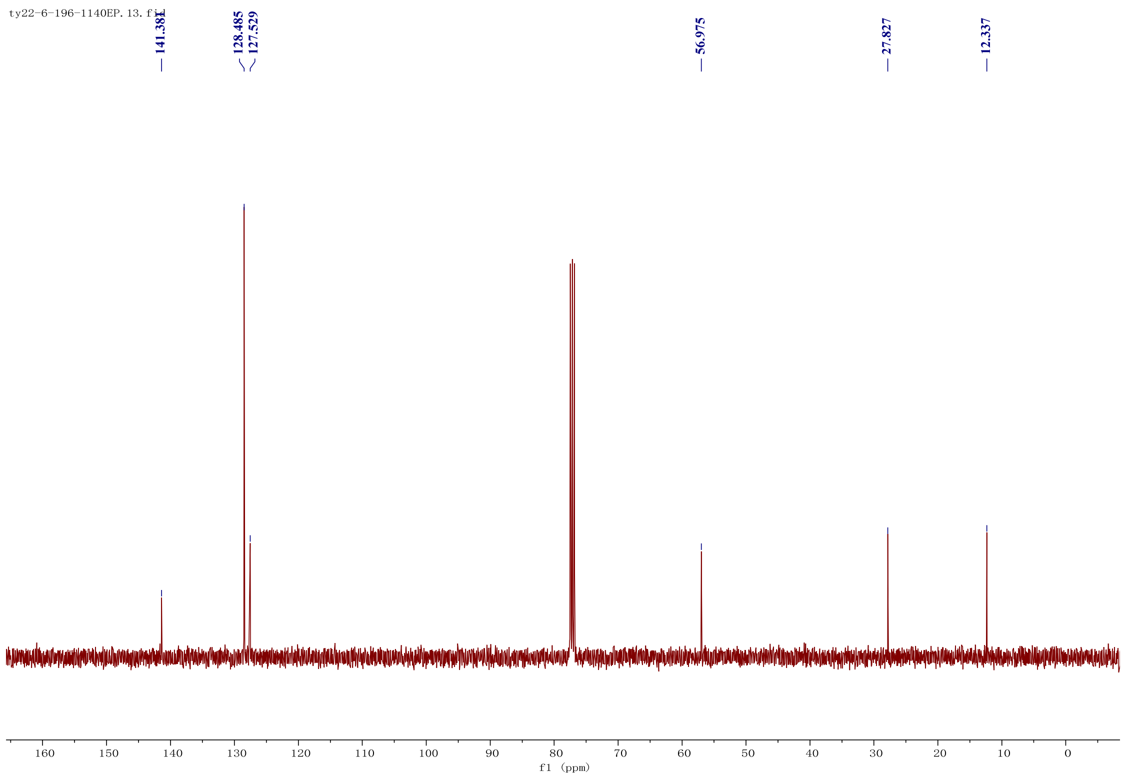


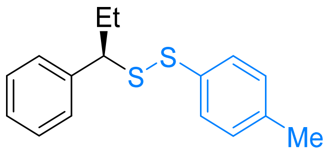
91 ty22-6-217-1161EP.19.fid
-83.401
-83.412
-83.422
-90.297
-90.308
-90.318
-90.328
-90.434
-90.445
-90.454
-90.465
f1 (ppm)



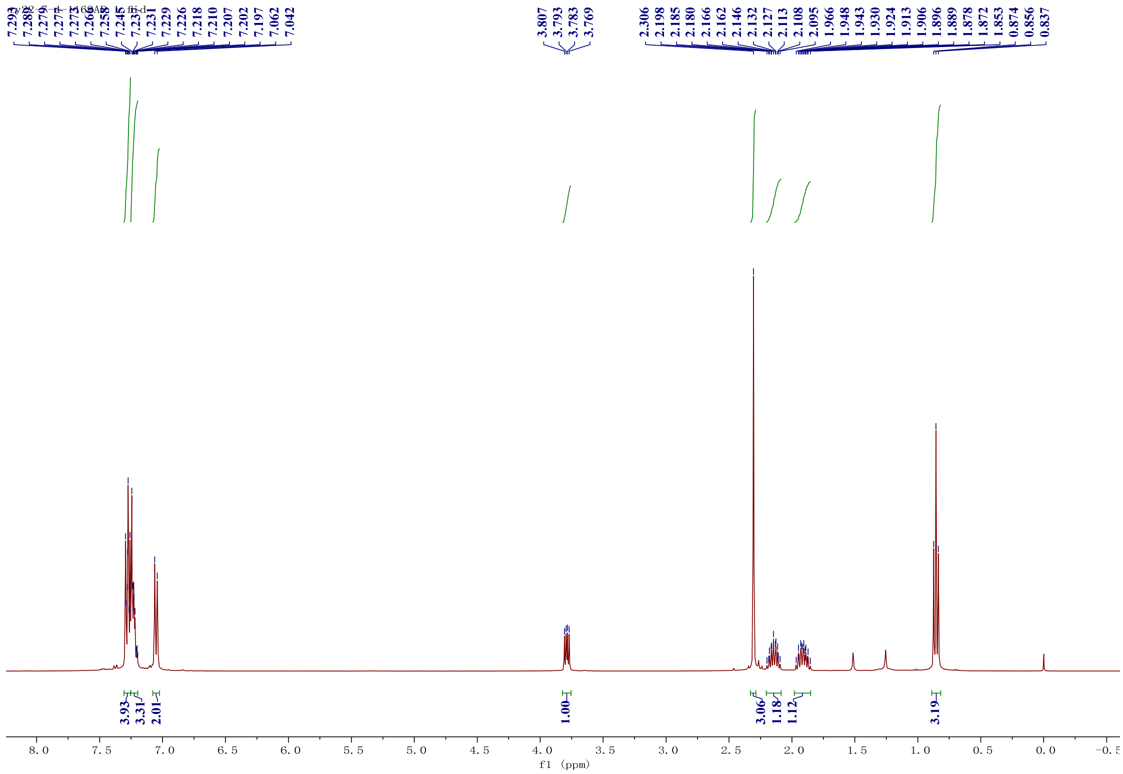
92

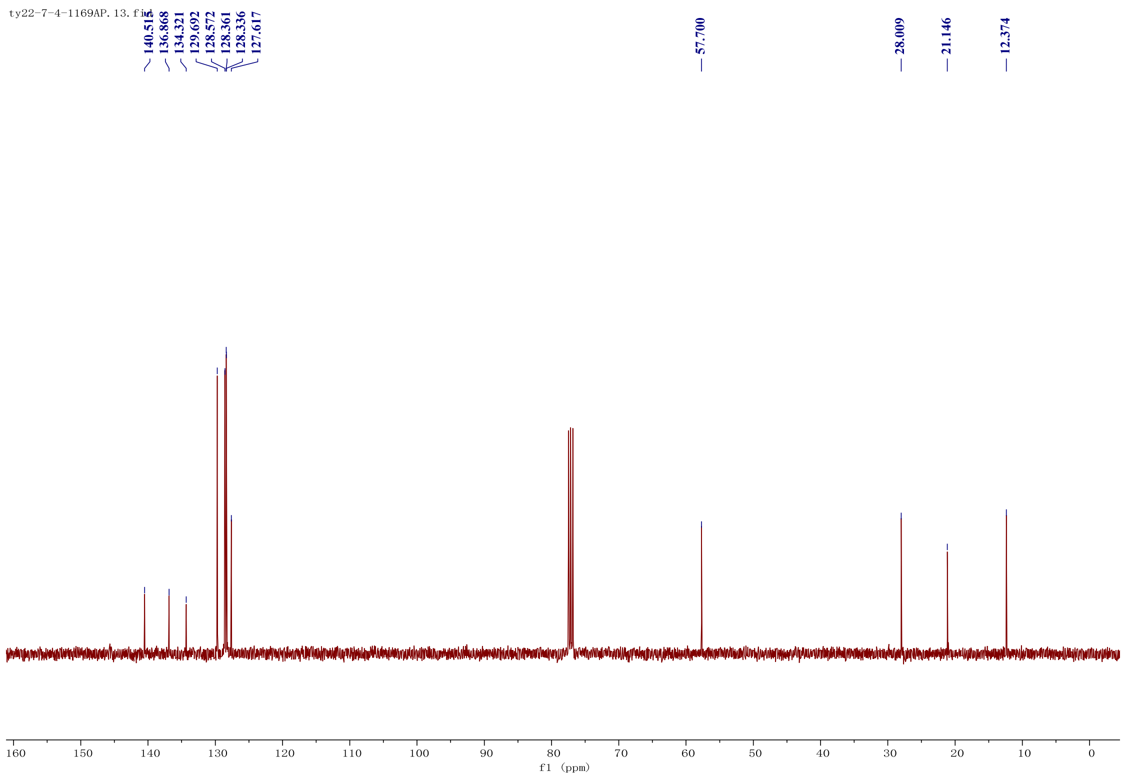


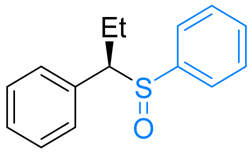



Et
S
S
Me

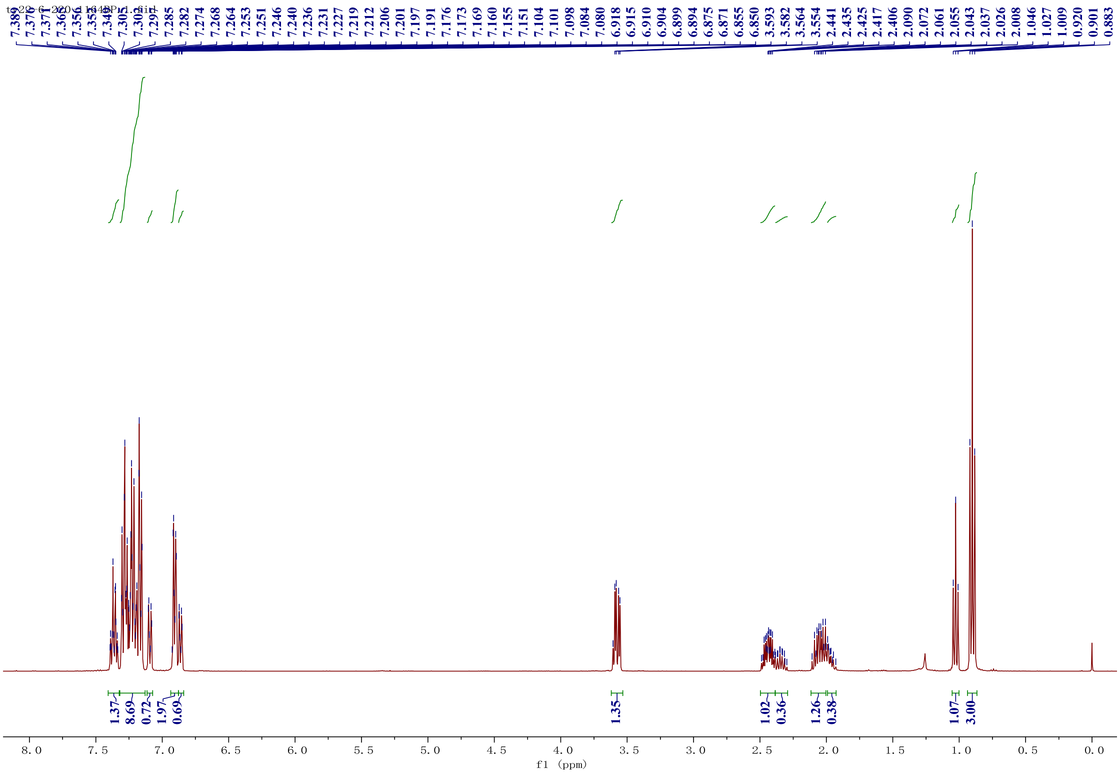
93

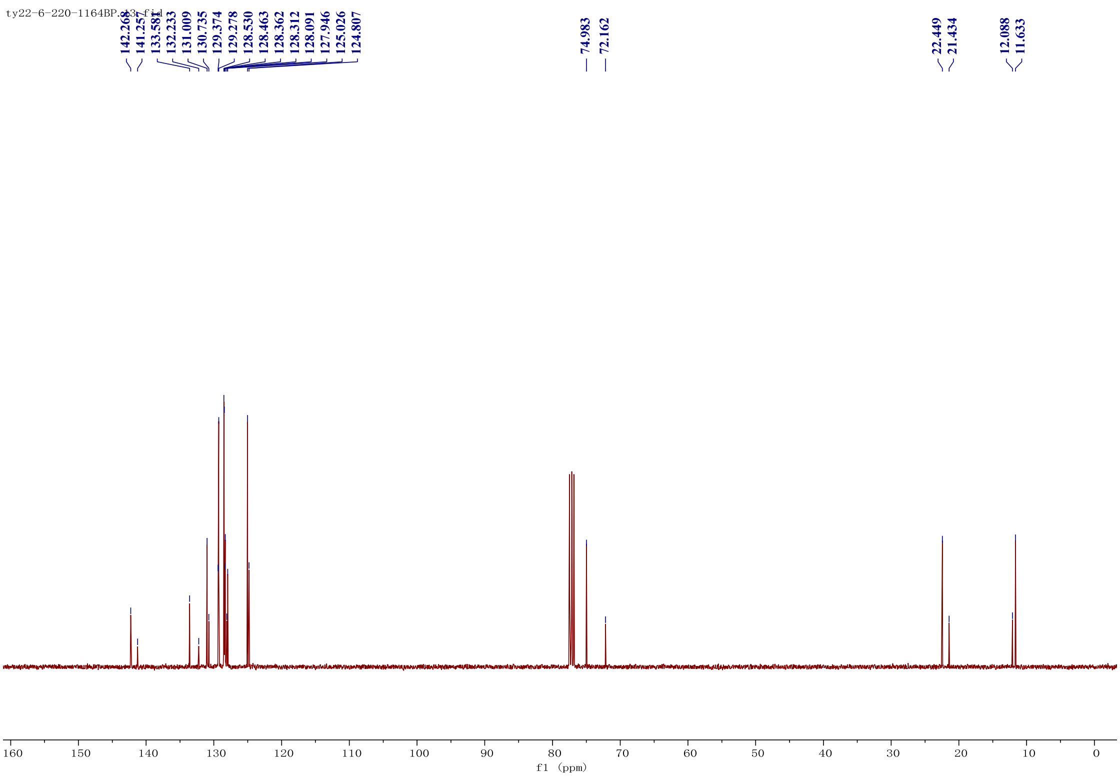

7.293
7.282
7.279
7.277
7.273
7.266
7.258
7.245
7.237
7.231
7.229
7.226
7.218
7.210
7.207
7.202
7.197
7.062
7.042
3.807
3.793
3.783
3.769
2.306
2.198
2.185
2.180
2.166
2.162
2.146
2.132
2.127
2.113
2.108
2.095
1.966
1.948
1.943
1.930
1.924
1.913
1.906
1.896
1.889
1.878
1.872
1.853
0.874
0.856
0.837
3.93
3.31
2.01
1.00
3.06
1.18
1.12
3.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

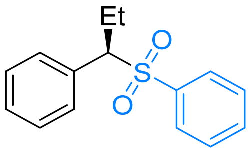

ty22-7-4-1169AP.13.fid
140.515
136.868
134.321
129.692
128.572
128.361
128.336
127.617
57.700
28.009
21.146
12.374
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Et
S
O

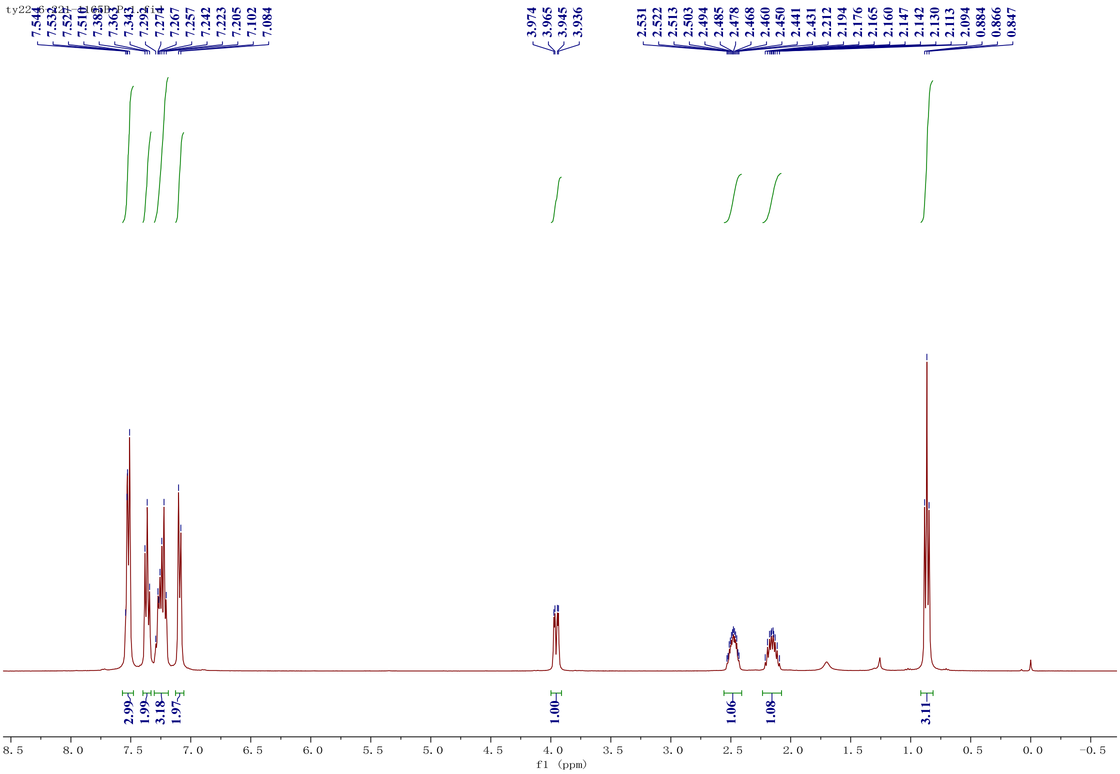
94

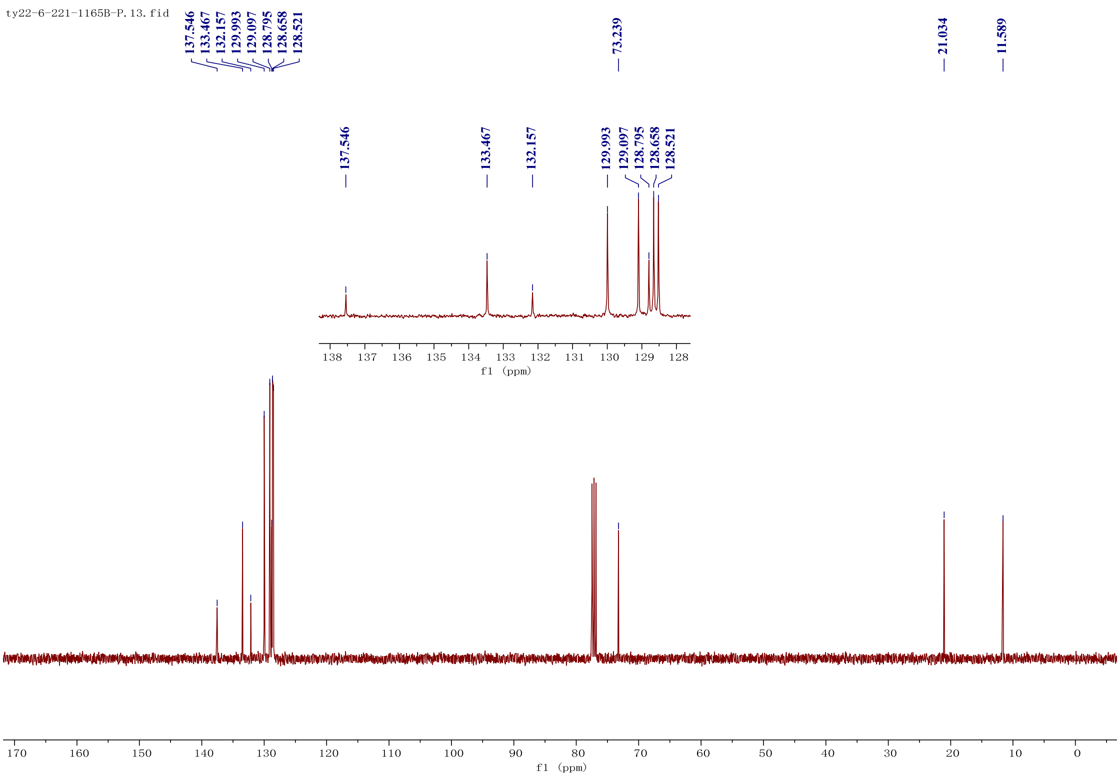

7.389 7.376 7.371 7.362 7.356 7.355 7.349 7.305 7.302 7.297 7.285 7.282 7.274 7.268 7.264 7.253 7.251 7.246 7.240 7.236 7.231 7.227 7.219 7.212 7.206 7.201 7.197 7.191 7.176 7.173 7.169 7.160 7.155 7.151 7.104 7.101 7.098 7.084 7.080 6.918 6.915 6.910 6.904 6.899 6.894 6.875 6.871 6.855 6.850 3.593 3.582 3.564 3.554 2.441 2.435 2.425 2.417 2.406 2.090 2.072 2.061 2.055 2.043 2.037 2.026 2.008 1.046 1.027 1.009 0.920 0.901 0.883
1.37 8.69 0.72 1.97 0.69 1.35 1.02 0.36 1.26 0.38 1.07 3.00
f1 (ppm)

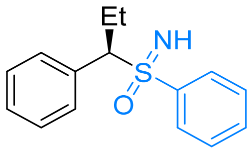

142.268 141.257 133.581 132.233 131.009 130.735 129.374 129.278 128.530 128.463 128.362 128.312 128.091 127.946 125.026 124.807
74.983 72.162
22.449 21.434
12.088 11.633
f1 (ppm)


Et
O
S
O

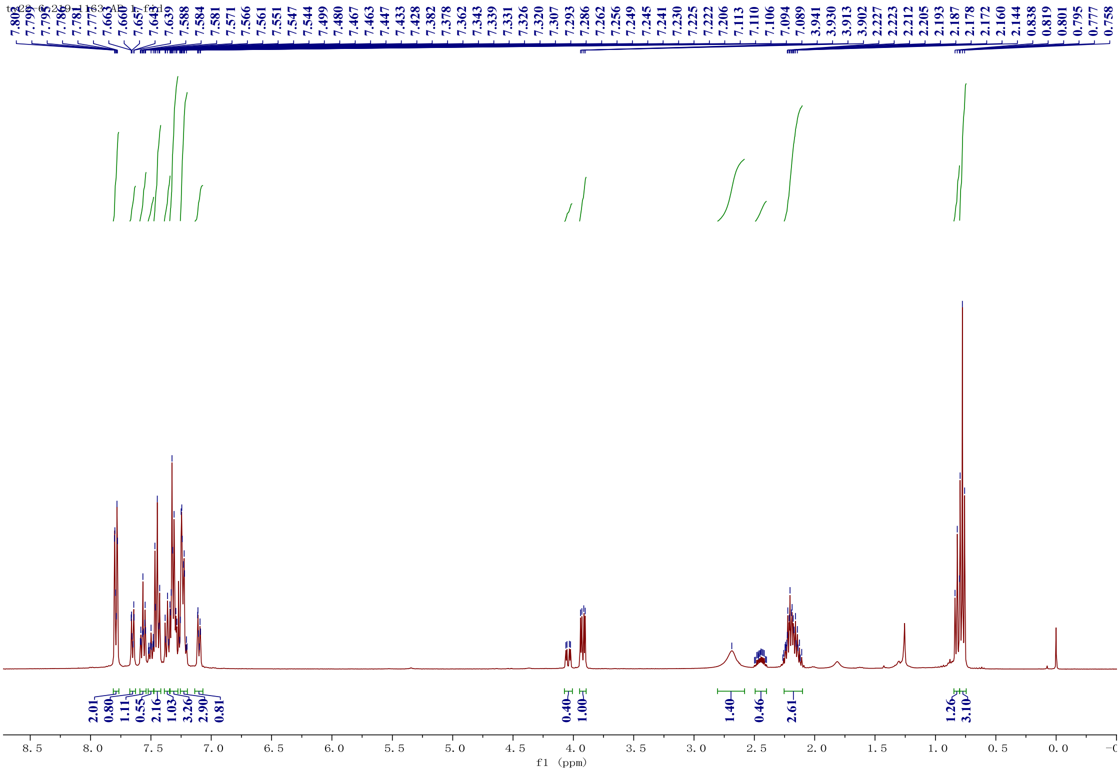
95

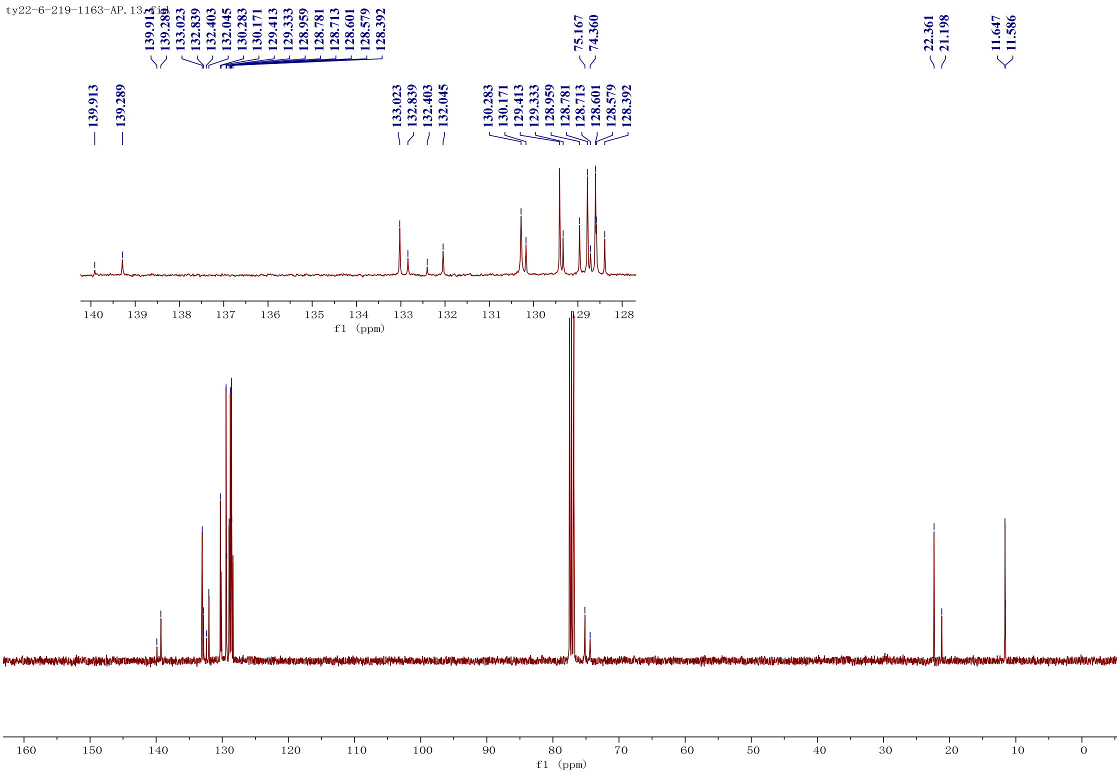

7.544 7.532 7.527 7.512 7.385 7.363 7.343 7.292 7.274 7.267 7.257 7.242 7.223 7.205 7.102 7.084
3.974 3.965 3.945 3.936
2.531 2.522 2.513 2.503 2.494 2.485 2.478 2.468 2.460 2.450 2.441 2.431 2.212 2.194 2.176 2.165 2.160 2.147 2.142 2.130 2.113 2.094 0.884 0.866 0.847
2.99 1.99 3.18 1.97 1.00 1.06 1.08 3.11
f1 (ppm)

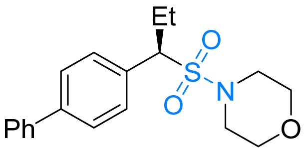

ty22-6-221-1165B-P.13.fid
137.546 133.467 132.157 129.993 129.097 128.795 128.658 128.521
73.239
21.034
11.589
f1 (ppm)


Et
NH
S
O

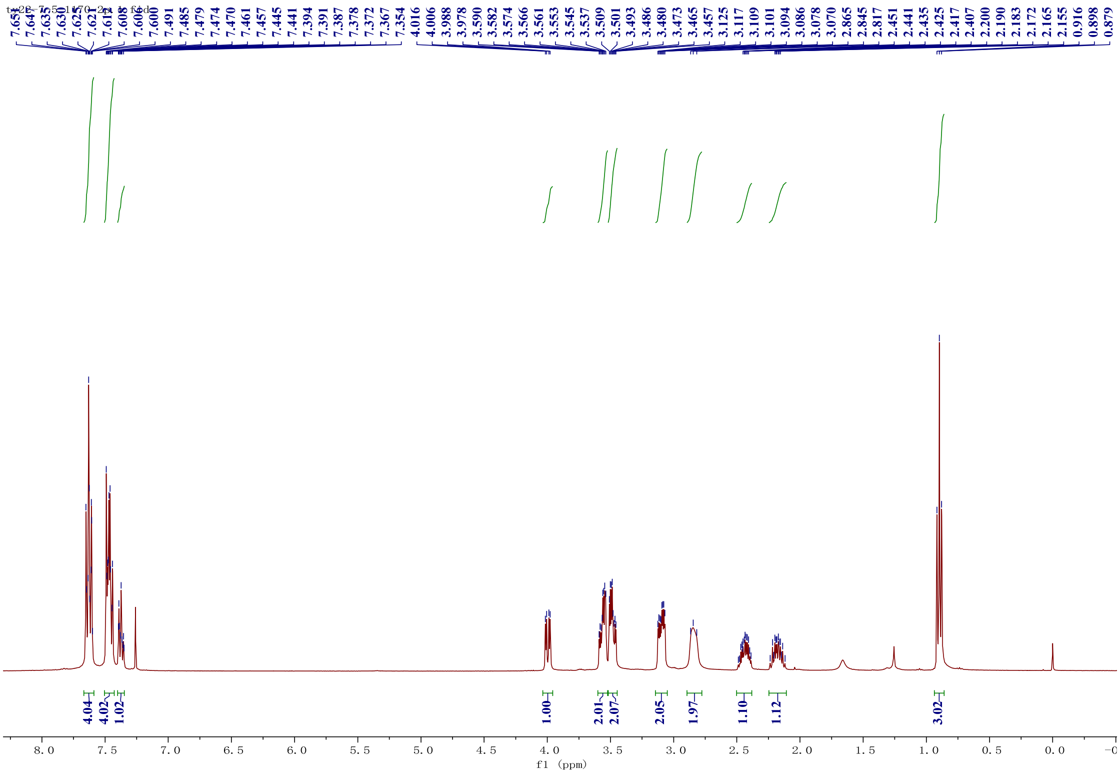
96

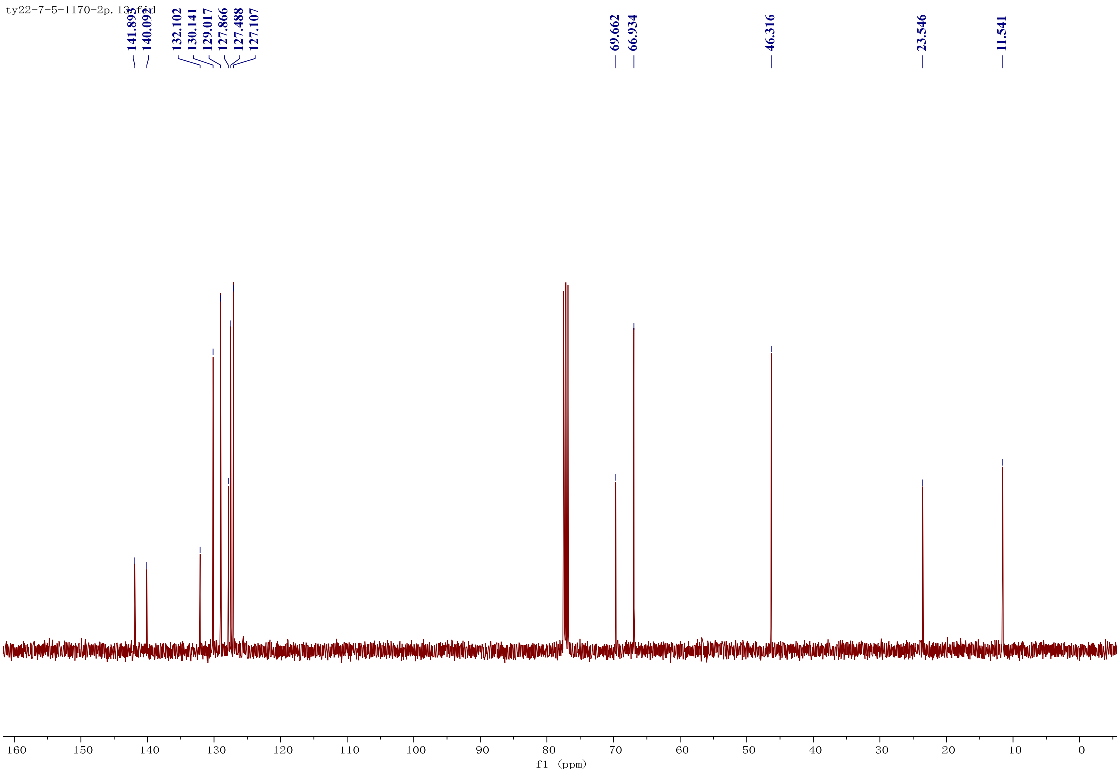

7.803
7.799
7.795
7.786
7.781
7.777
7.663
7.660
7.657
7.643
7.639
7.588
7.584
7.581
7.571
7.566
7.561
7.551
7.547
7.544
7.499
7.480
7.467
7.463
7.447
7.433
7.428
7.382
7.378
7.362
7.343
7.339
7.331
7.326
7.320
7.307
7.293
7.286
7.262
7.256
7.249
7.245
7.241
7.230
7.225
7.222
7.206
7.113
7.110
7.106
7.094
7.089
3.941
3.930
3.913
3.902
2.227
2.223
2.212
2.205
2.193
2.187
2.178
2.172
2.160
2.144
0.838
0.819
0.801
0.795
0.777
0.758
2.01
0.80
1.11
0.55
2.16
1.03
3.26
2.90
0.81
0.40
1.00
1.40
0.46
2.61
1.26
3.10
f1 (ppm)

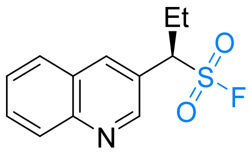

ty22-6-219-1163-AP.13.fid
139.913
139.289
133.023
132.839
132.403
132.045
130.283
130.171
129.413
129.333
128.959
128.781
128.713
128.601
128.579
128.392
75.167
74.360
22.361
21.198
11.647
11.586
f1 (ppm)



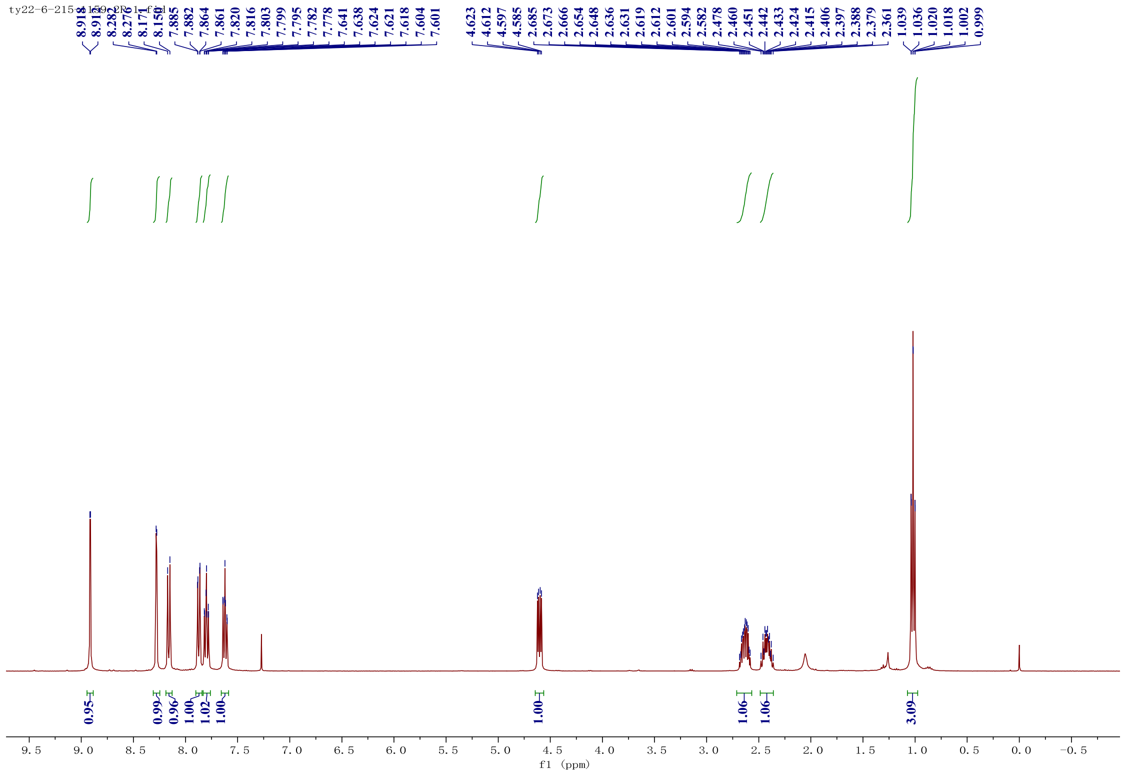
97

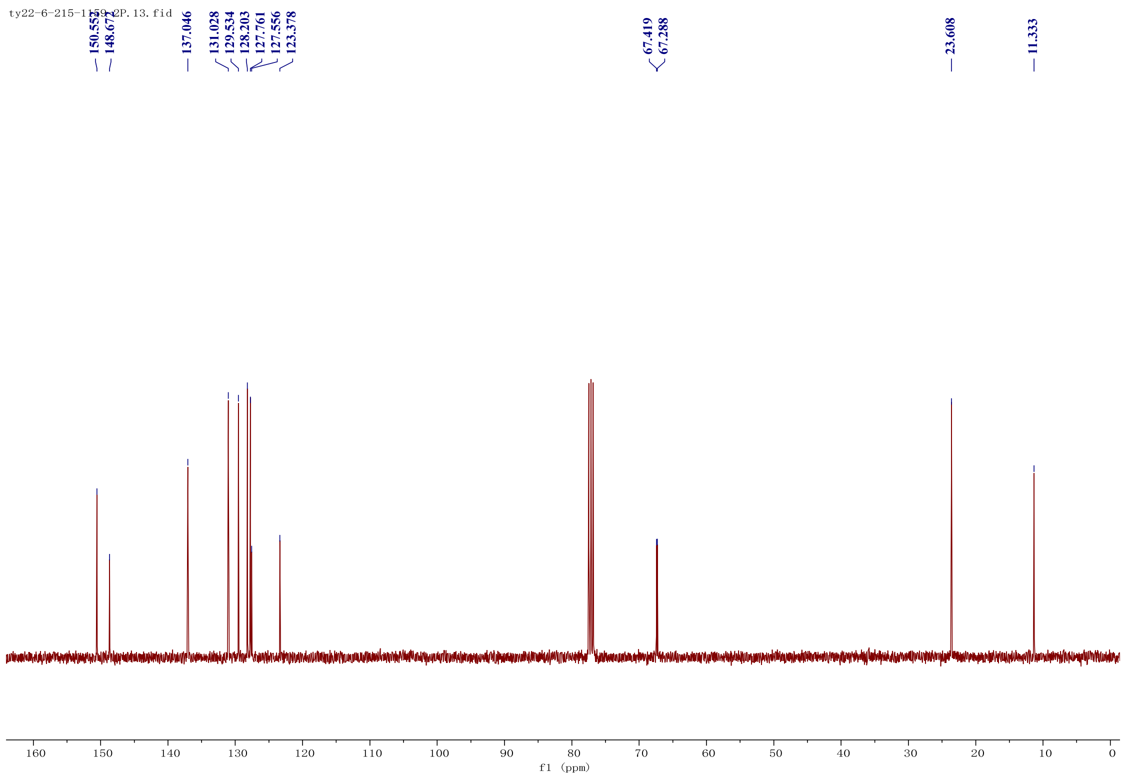


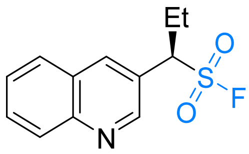




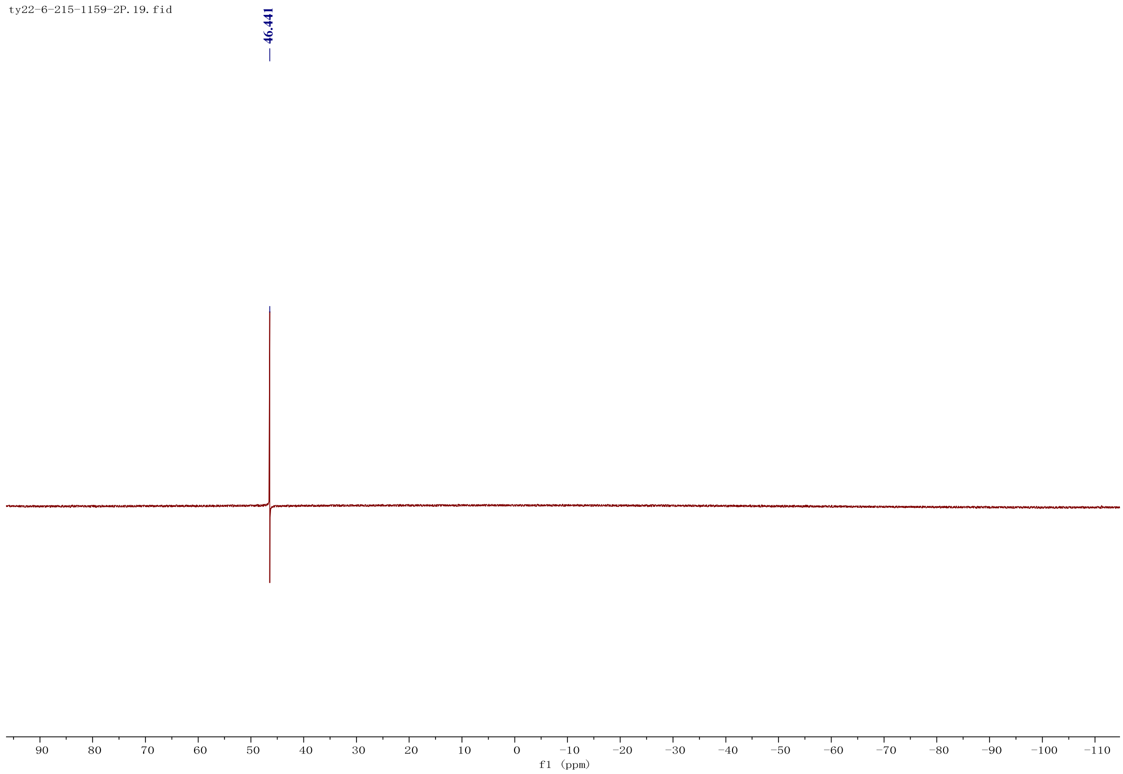
98

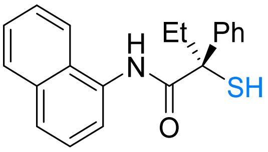






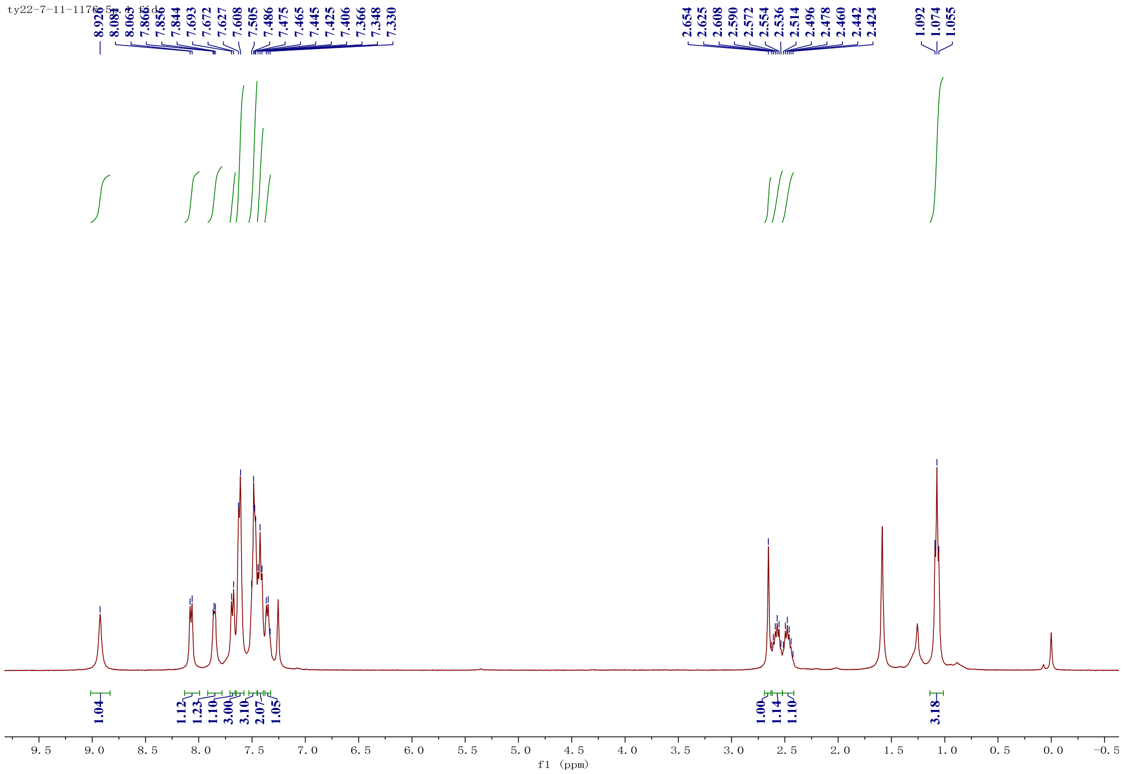
98


ty22-6-215-1159-2P.19.fid
46.441
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110
f1 (ppm)

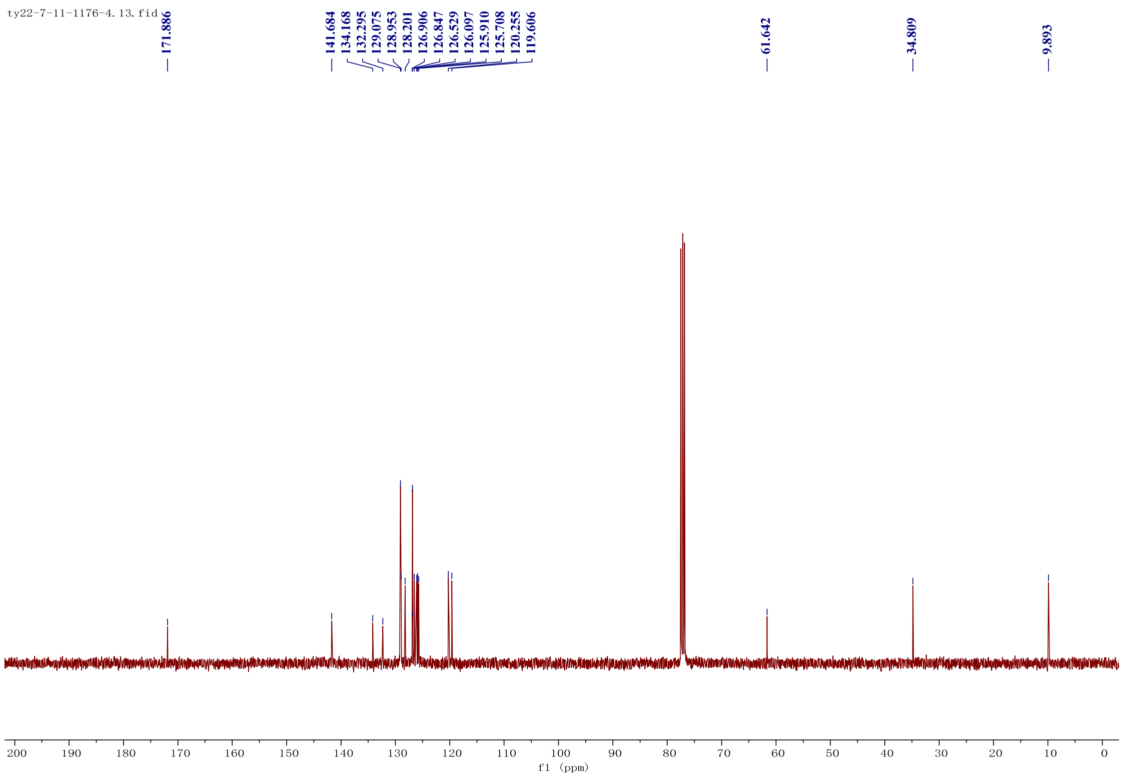


H
N
Et
Ph
SH
O

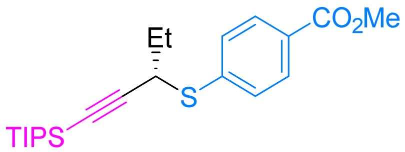
99



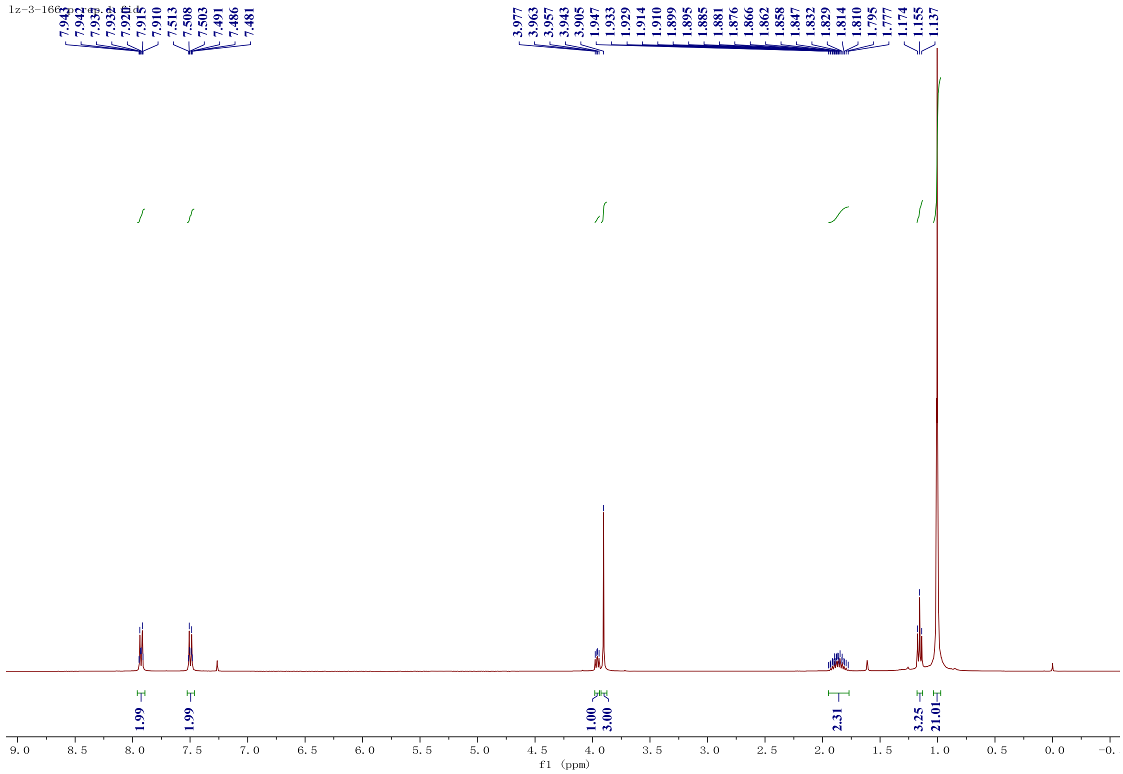
ty22-7-11-1176
8.926
8.084
8.063
7.866
7.856
7.844
7.693
7.672
7.627
7.608
7.505
7.486
7.475
7.465
7.445
7.425
7.406
7.366
7.348
7.330
2.654
2.625
2.608
2.590
2.572
2.554
2.536
2.514
2.496
2.478
2.460
2.442
2.424
1.092
1.074
1.055
1.04
1.12
1.23
1.10
3.00
3.10
2.07
1.05
1.00
1.14
1.10
3.18
f1 (ppm)

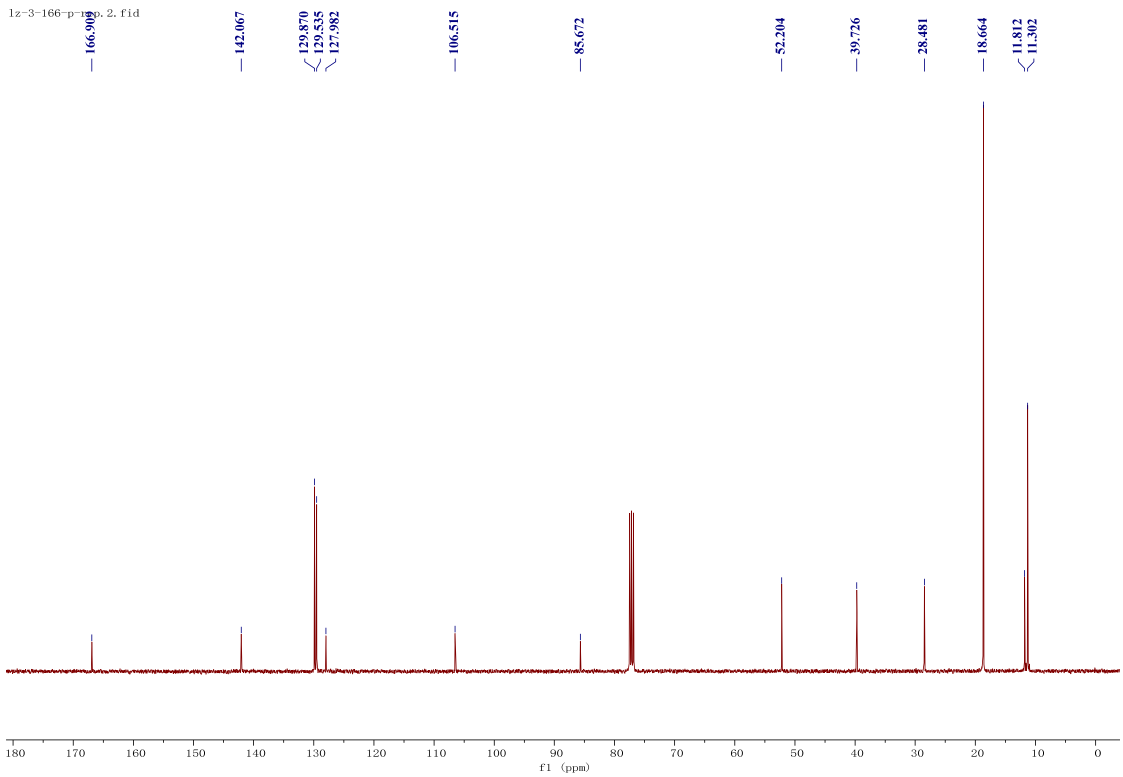


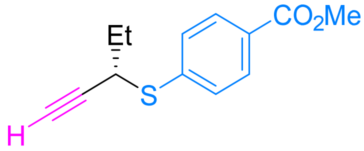
ty22-7-11-1176-4.13.fid
171.886
141.684
134.168
132.295
129.075
128.953
128.201
126.906
126.847
126.529
126.097
125.910
125.708
120.255
119.606
61.642
34.809
9.893
f1 (ppm)



100’

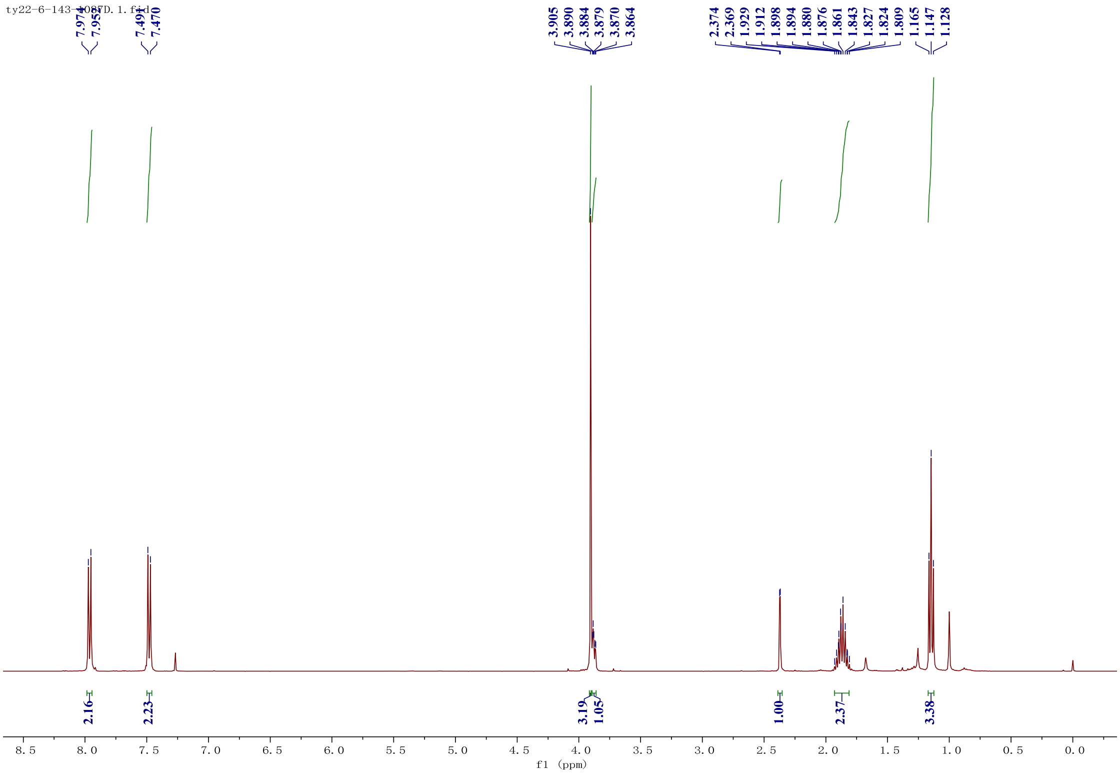




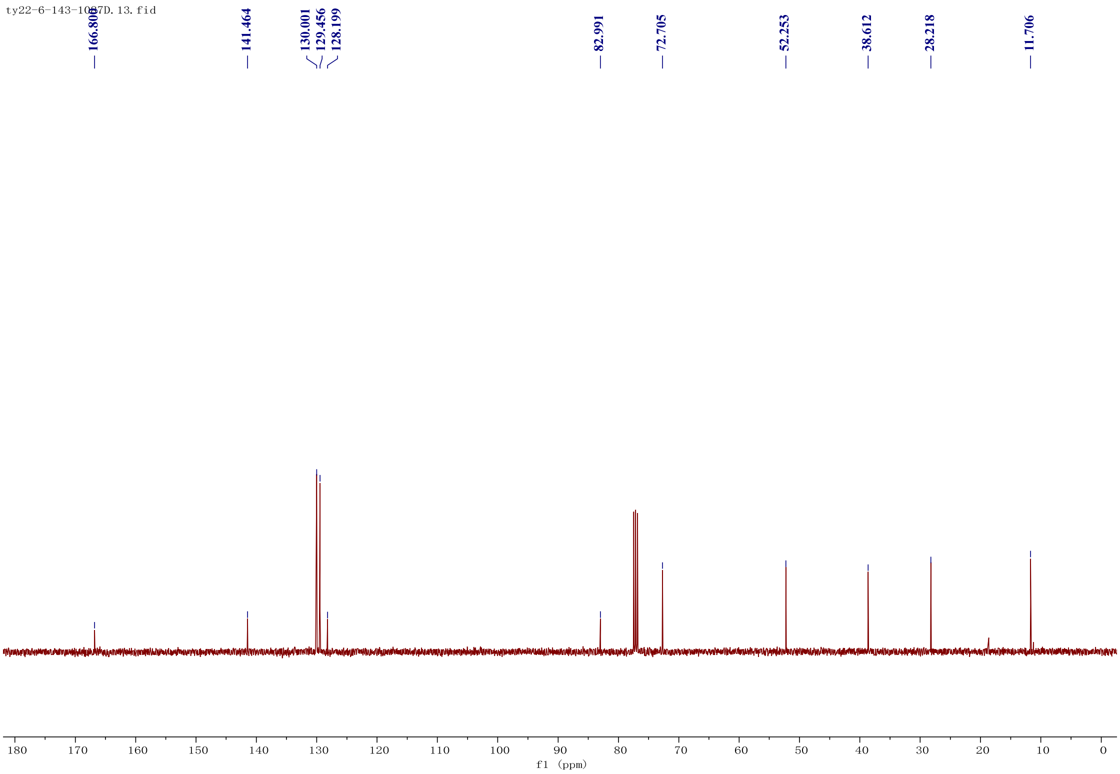


Et
S
CO2Me
H

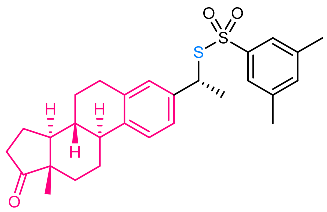
100



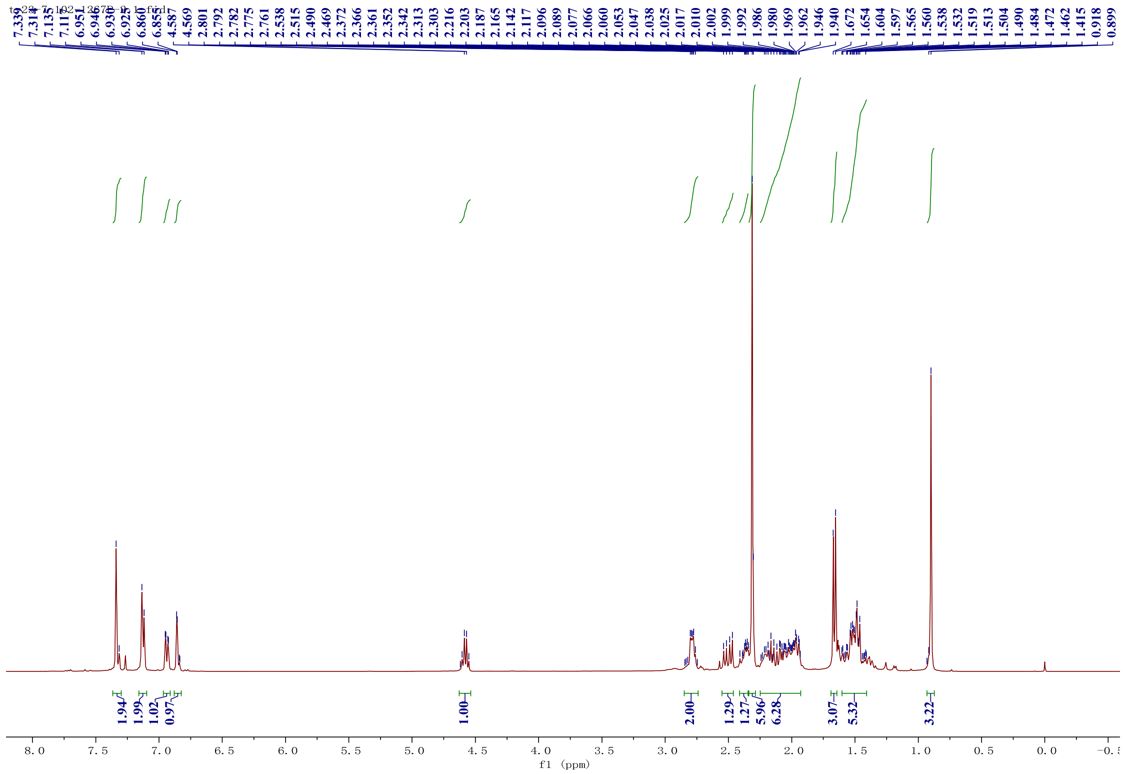
ty22-6-143-108?D.1.fid
7.974
7.955
7.491
7.470
3.905
3.890
3.884
3.879
3.870
3.864
2.374
2.369
1.929
1.912
1.898
1.894
1.880
1.876
1.861
1.843
1.827
1.824
1.809
1.165
1.147
1.128
2.16
2.23
3.19
1.05
1.00
2.37
3.38
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



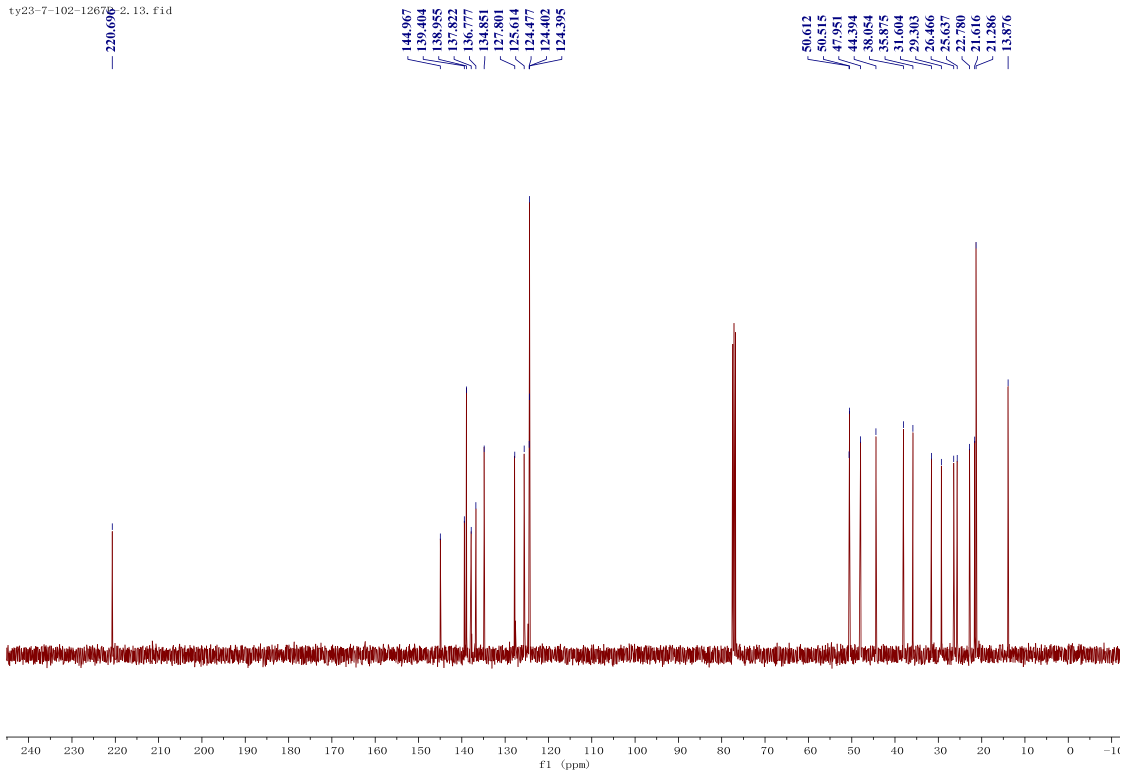
ty22-6-143-108?D.13.fid
166.80?
141.464
130.001
129.456
128.199
82.991
72.705
52.253
38.612
28.218
11.706
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



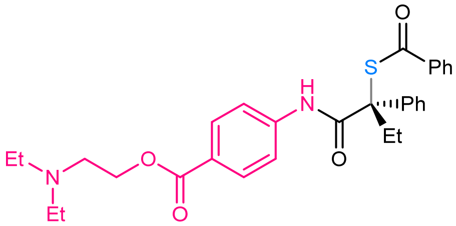
101



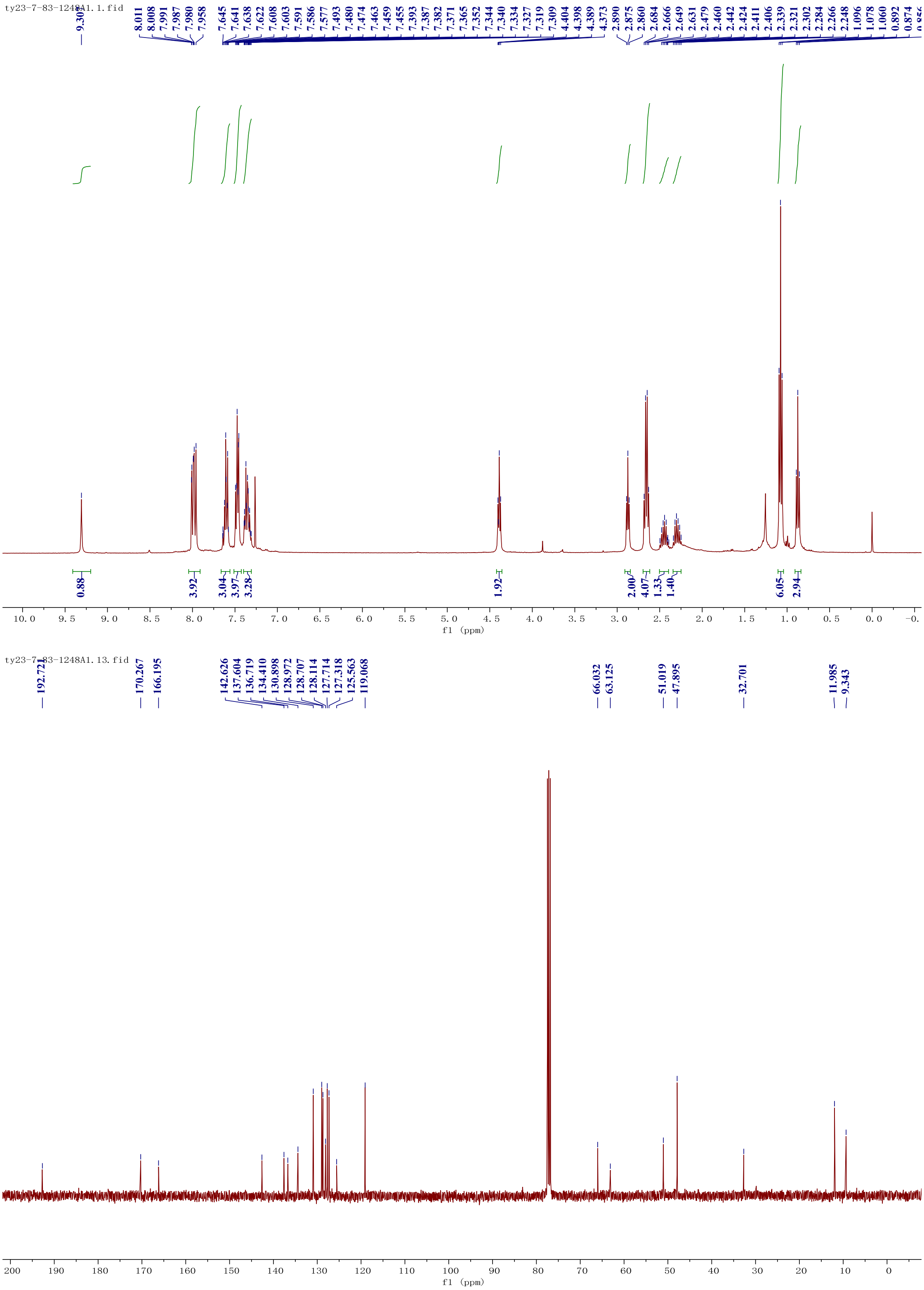
7.339
7.314
7.135
7.111
6.951
6.946
6.930
6.925
6.860
6.855
4.587
4.569
2.801
2.792
2.782
2.775
2.761
1.94
1.99
1.02
0.97
1.00
2.00
1.29
1.27
5.96
6.28
3.07
5.32
3.22
f1 (ppm)



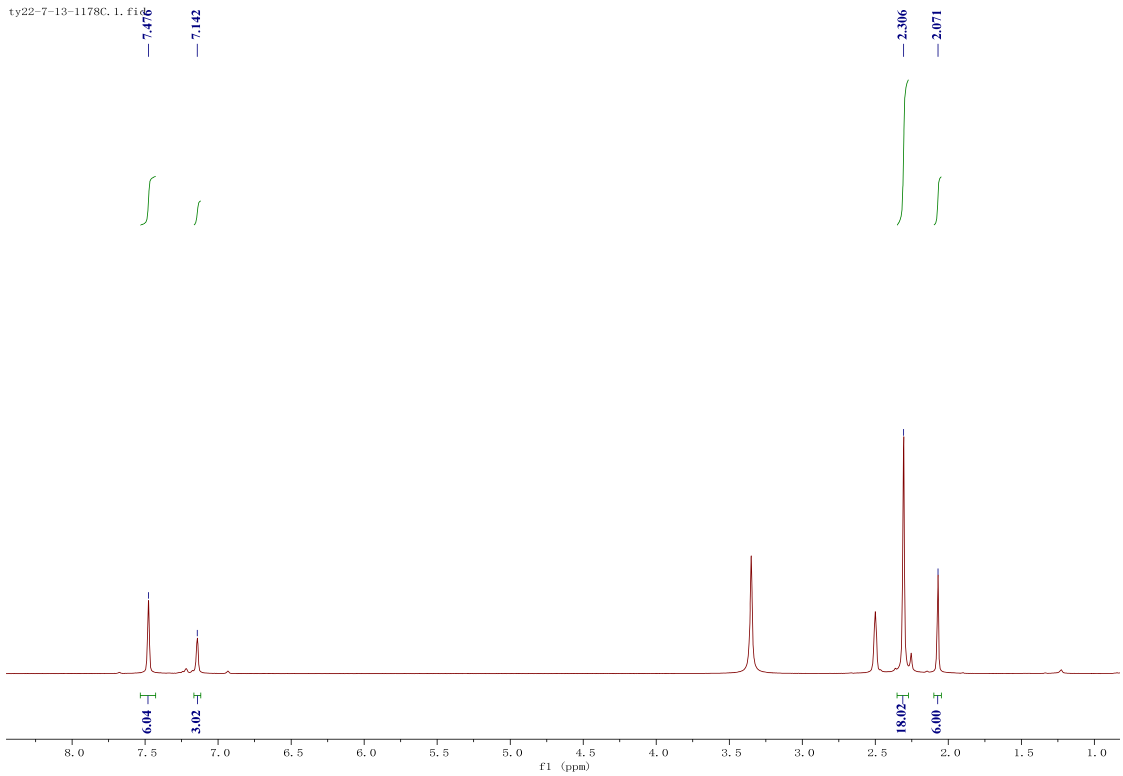
ty23-7-102-12670-2.13.fid
220.696
144.967
139.404
138.955
137.822
136.777
134.851
127.801
125.614
124.477
124.402
124.395
50.612
50.515
47.951
44.394
38.054
35.875
31.604
29.303
26.466
25.637
22.780
21.616
21.286
13.876
f1 (ppm)

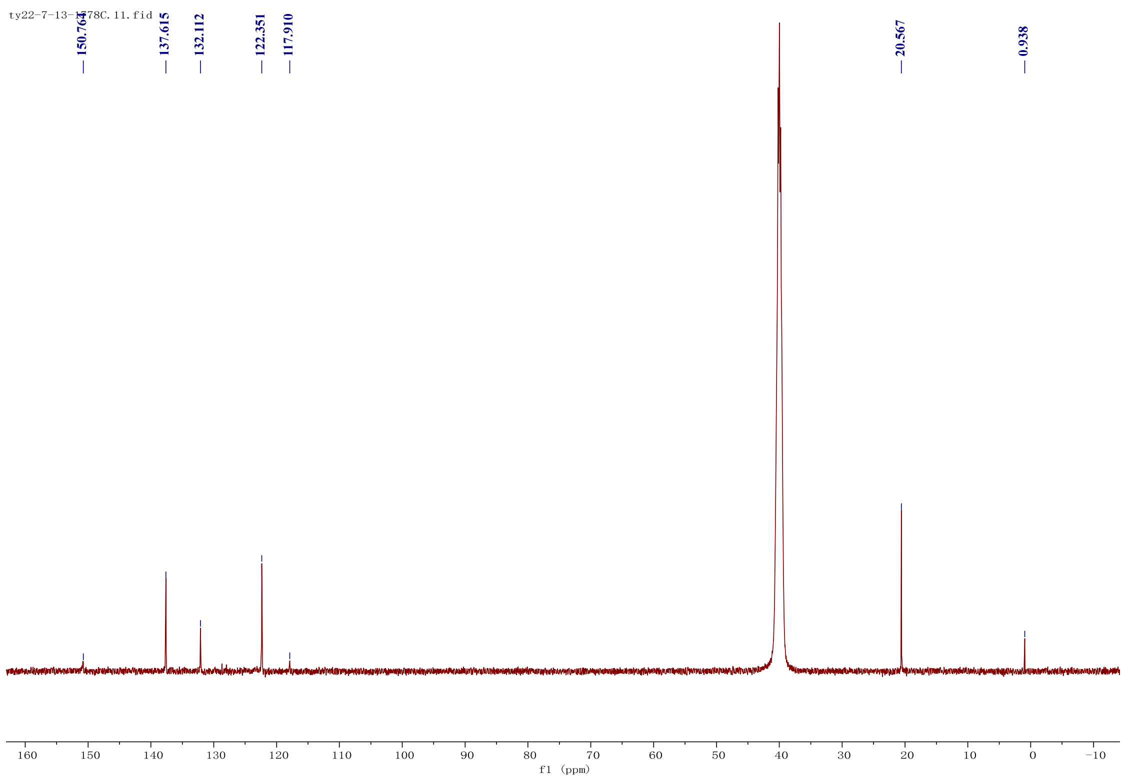


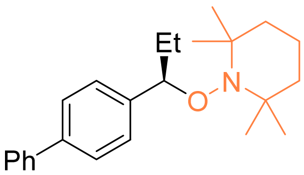
102



$Cu_3(MeCN)_2(ArSSO_2)_3$ **103**
($Ar = 3,5\text{-}Me_2C_6H_3$)

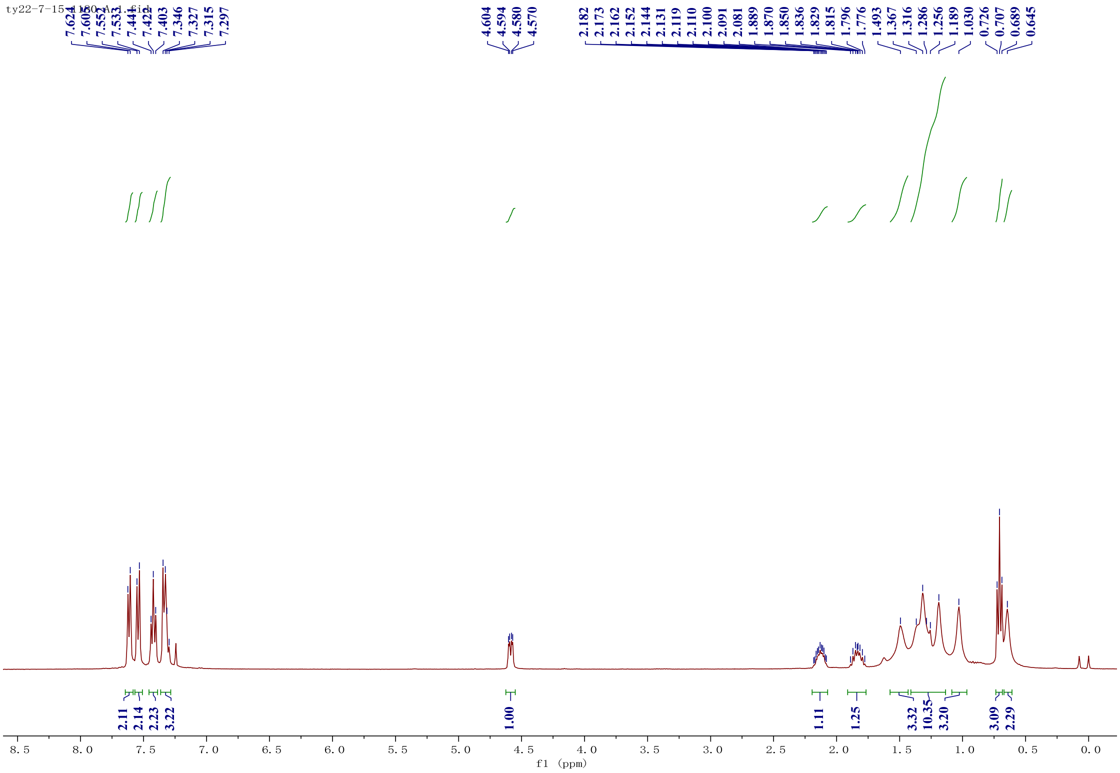




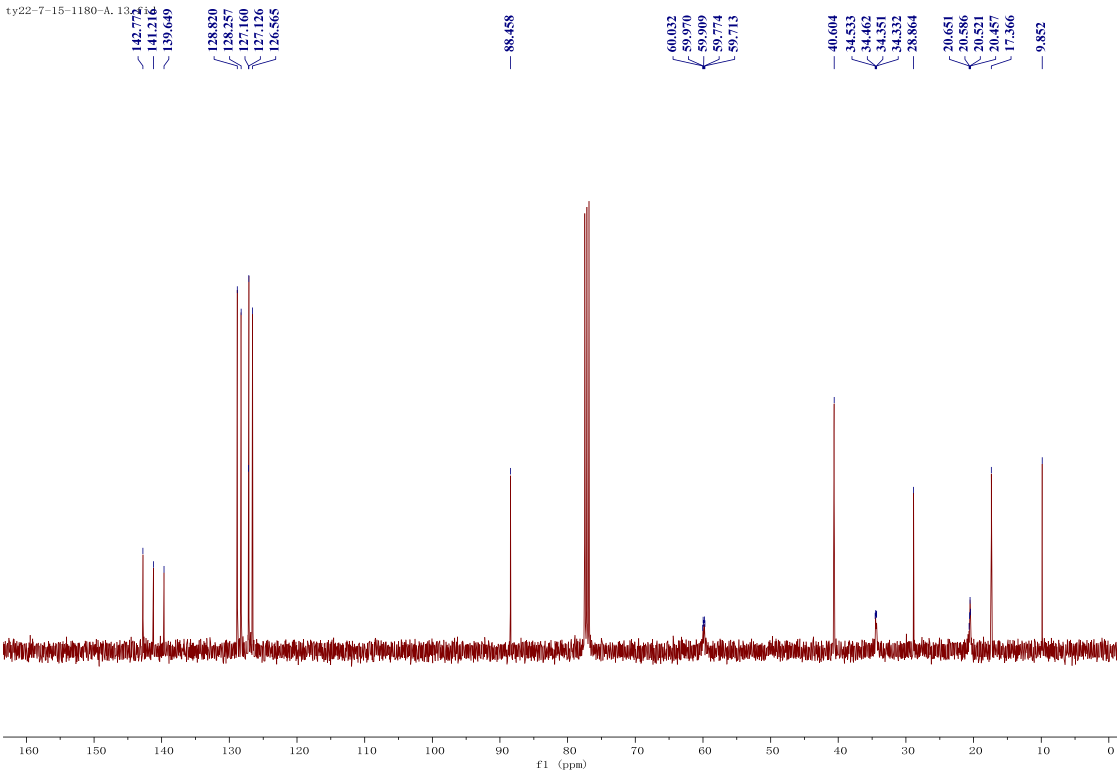


Et
O
N
Ph

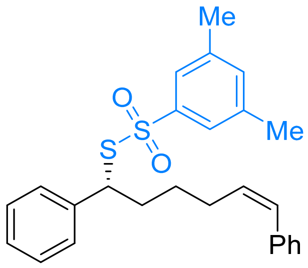
104



7.624
7.605
7.552
7.533
7.441
7.422
7.403
7.346
7.327
7.315
7.297
4.604
4.594
4.580
4.570
2.182
2.173
2.162
2.152
2.144
2.131
2.119
2.110
2.100
2.091
2.081
1.889
1.870
1.850
1.836
1.829
1.815
1.796
1.776
1.493
1.367
1.316
1.286
1.256
1.189
1.030
0.726
0.707
0.689
0.645
2.11
2.14
2.23
3.22
1.00
1.11
1.25
3.32
10.35
3.20
3.09
2.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

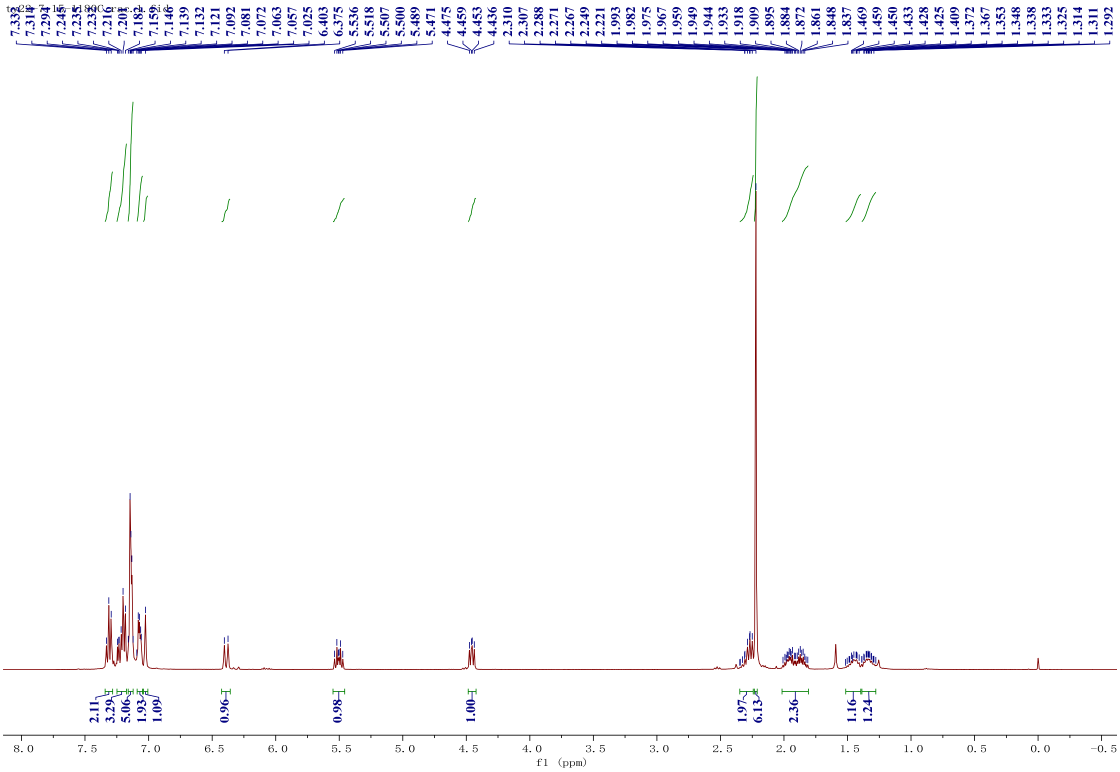


142.772
141.216
139.649
128.820
128.257
127.160
127.126
126.565
88.458
60.032
59.970
59.909
59.774
59.713
40.604
34.533
34.462
34.351
34.332
28.864
20.651
20.586
20.521
20.457
17.366
9.852
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

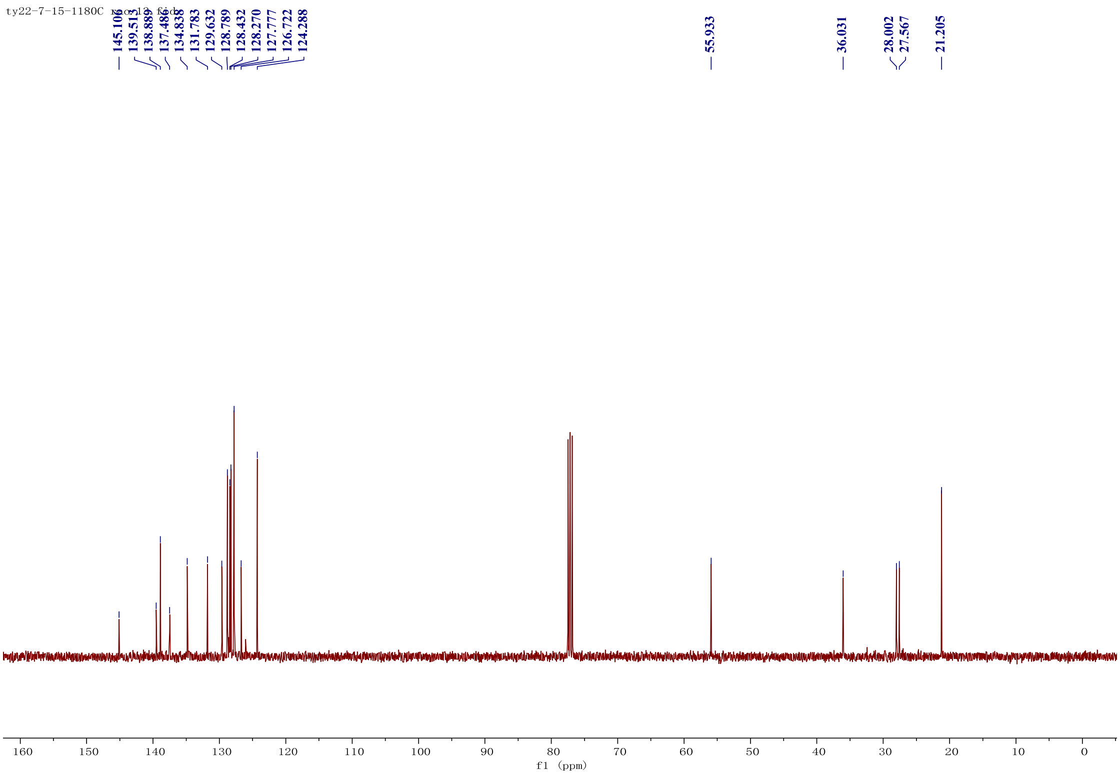


Me
Me
O
S
O
S
Ph

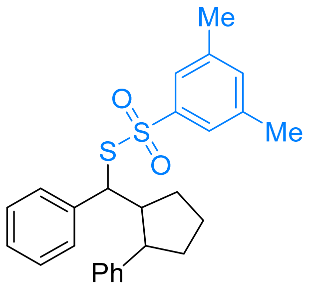
105



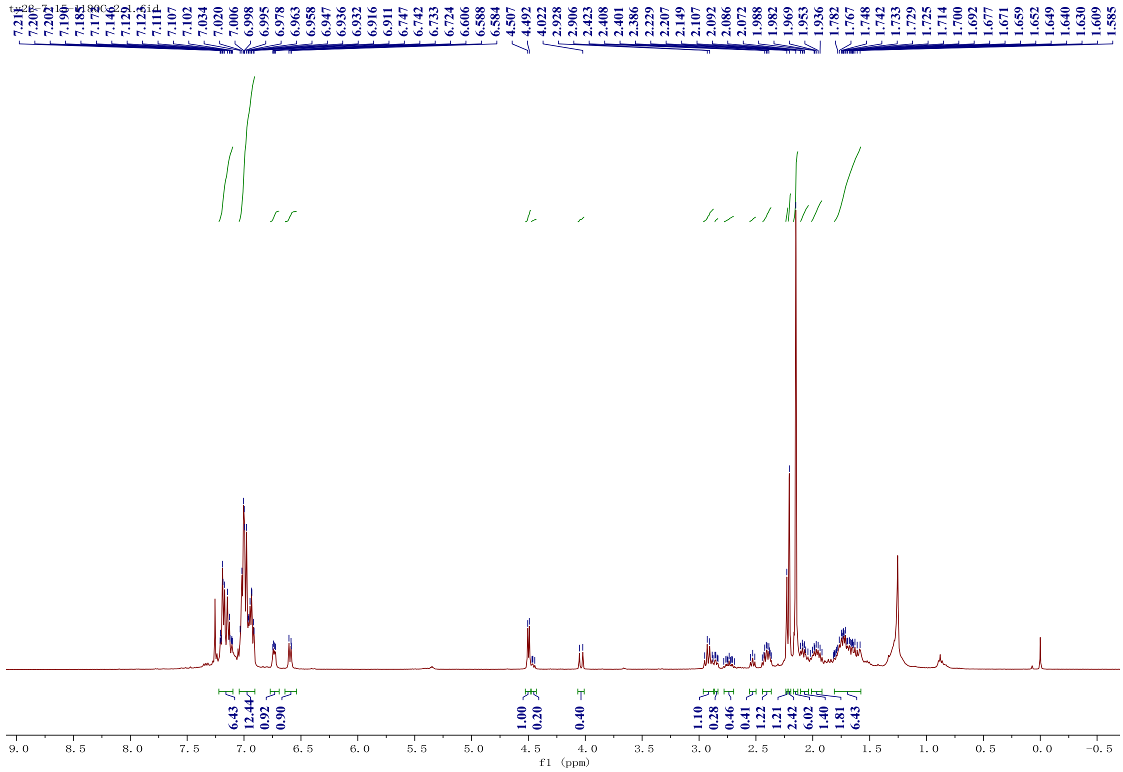
7.333
7.311
7.294
7.245
7.235
7.232
7.213
7.201
7.182
7.159
7.146
7.139
7.132
7.121
7.092
7.081
7.072
7.063
7.057
7.025
6.403
6.375
5.536
5.518
5.507
5.500
5.489
5.471
4.475
4.459
4.453
4.436
2.310
2.307
2.288
2.271
2.267
2.249
2.221
1.993
1.982
1.975
1.967
1.959
1.949
1.944
1.933
1.918
1.909
1.895
1.884
1.872
1.861
1.848
1.837
1.469
1.459
1.450
1.433
1.428
1.425
1.409
1.372
1.367
1.353
1.348
1.338
1.333
1.325
1.314
1.311
1.292
2.11
3.29
5.06
1.93
1.09
0.96
0.98
1.00
1.97
6.13
2.36
1.16
1.24
f1 (ppm)

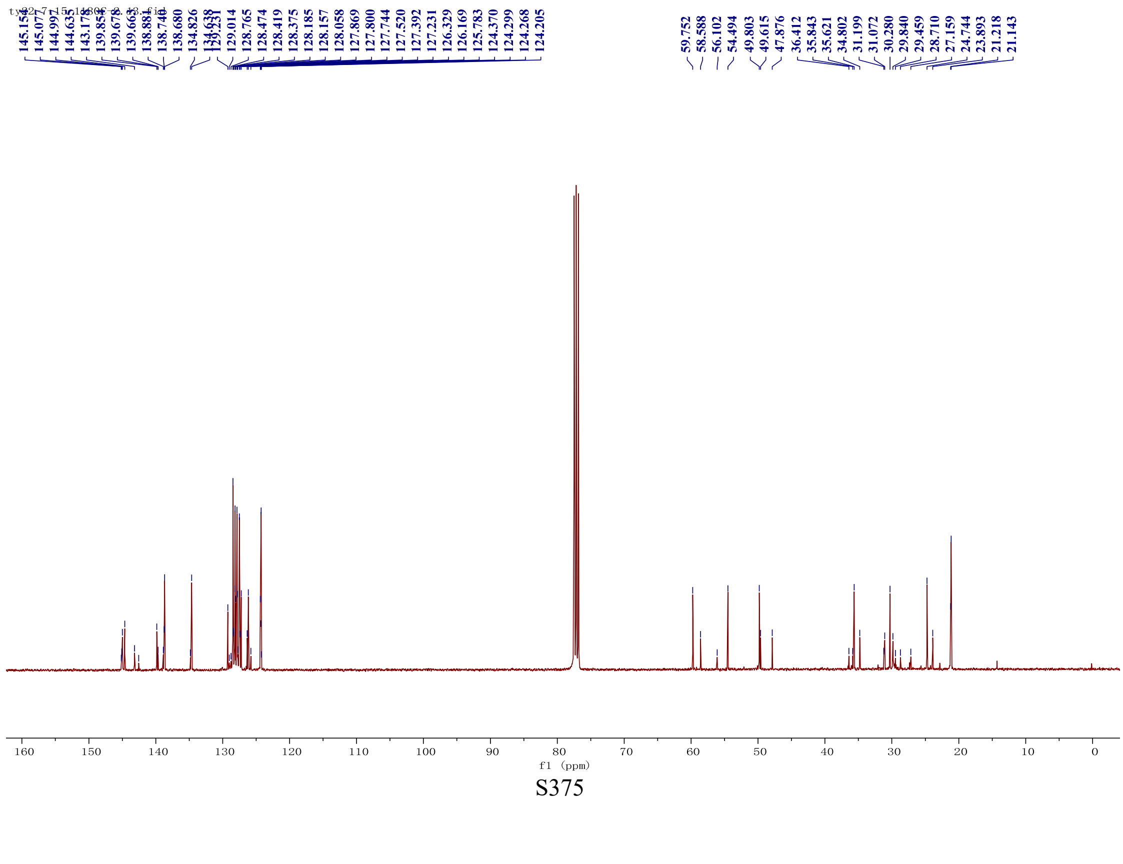


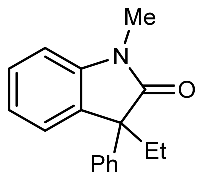
ty22-7-15-1180C
145.106
139.513
138.889
137.486
134.838
131.783
129.632
128.789
128.432
128.270
127.777
126.722
124.288
55.933
36.031
28.002
27.567
21.205
f1 (ppm)



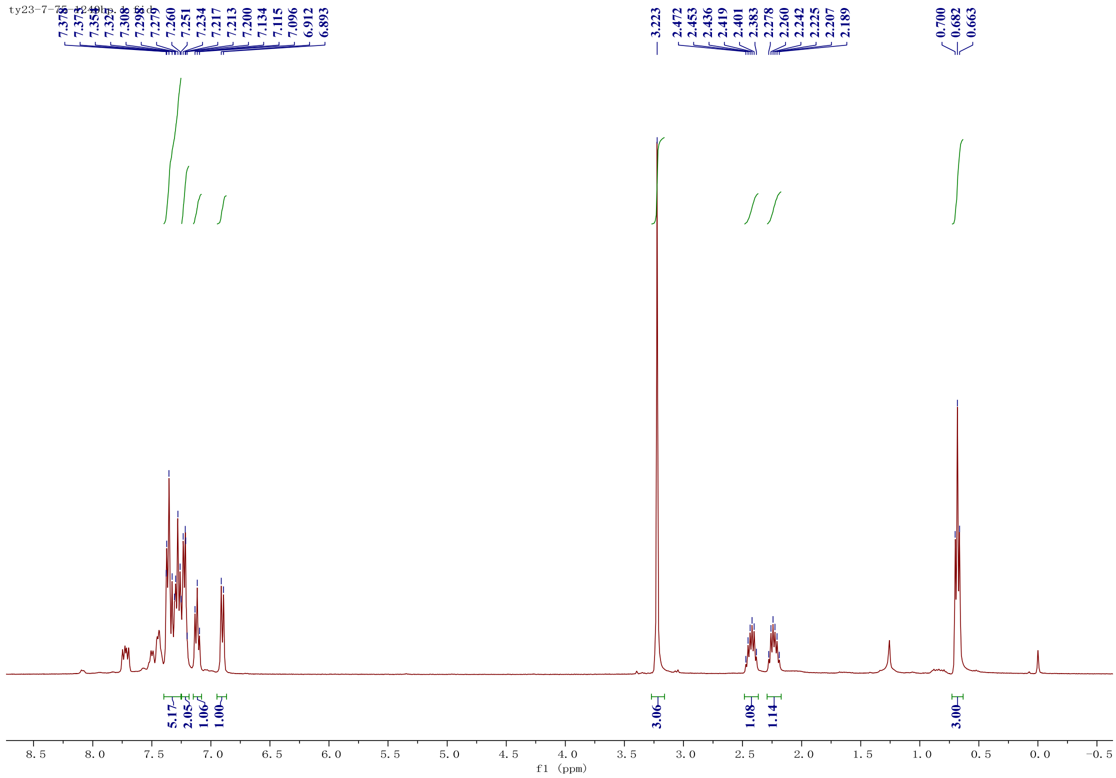
106

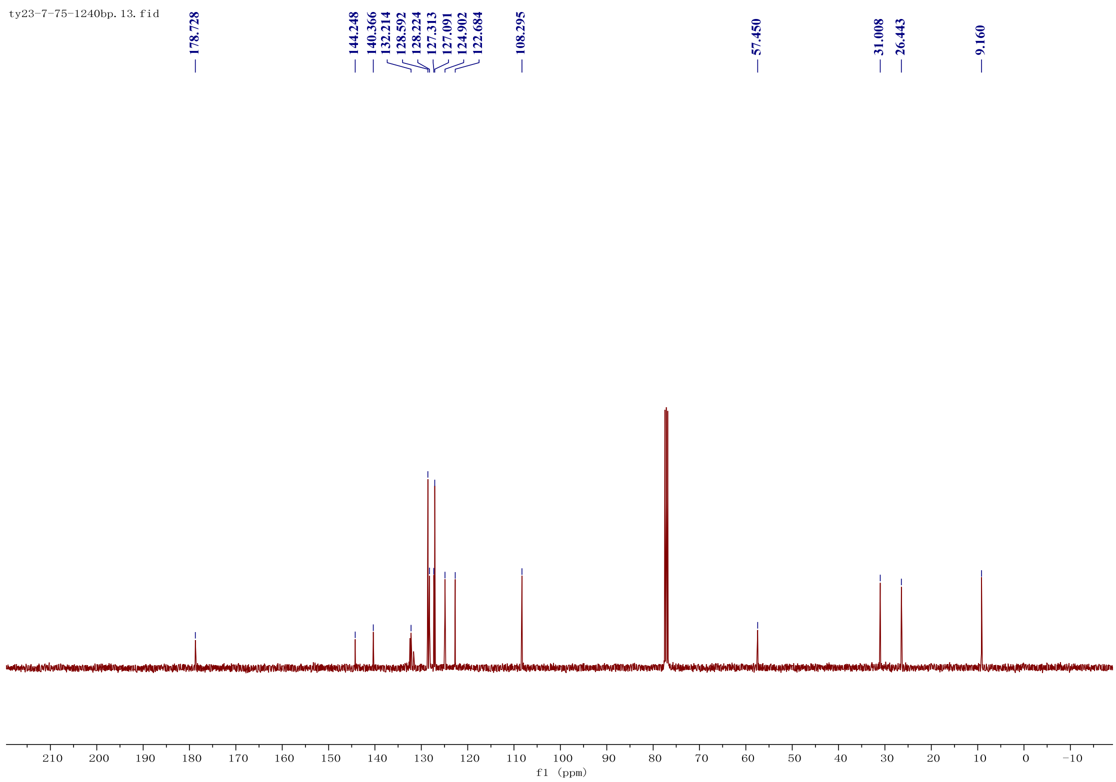


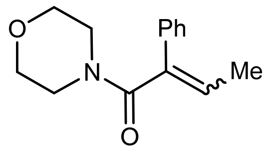



Me
N
O
Ph
Et

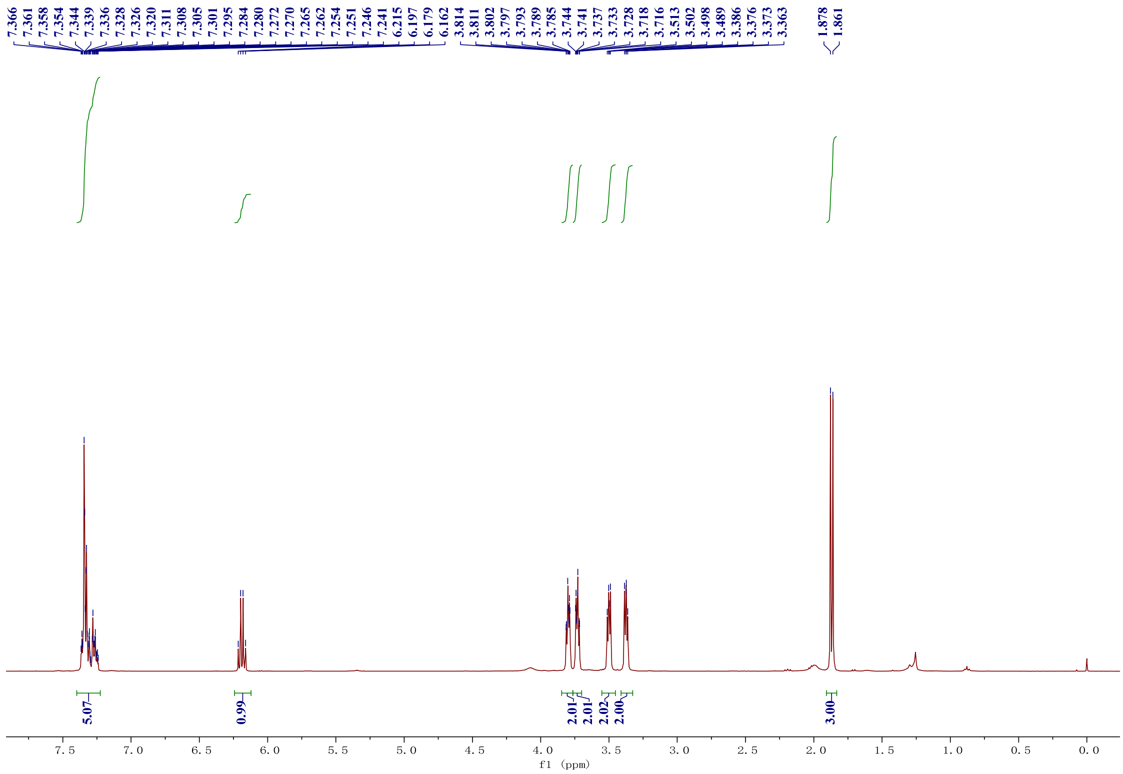
107

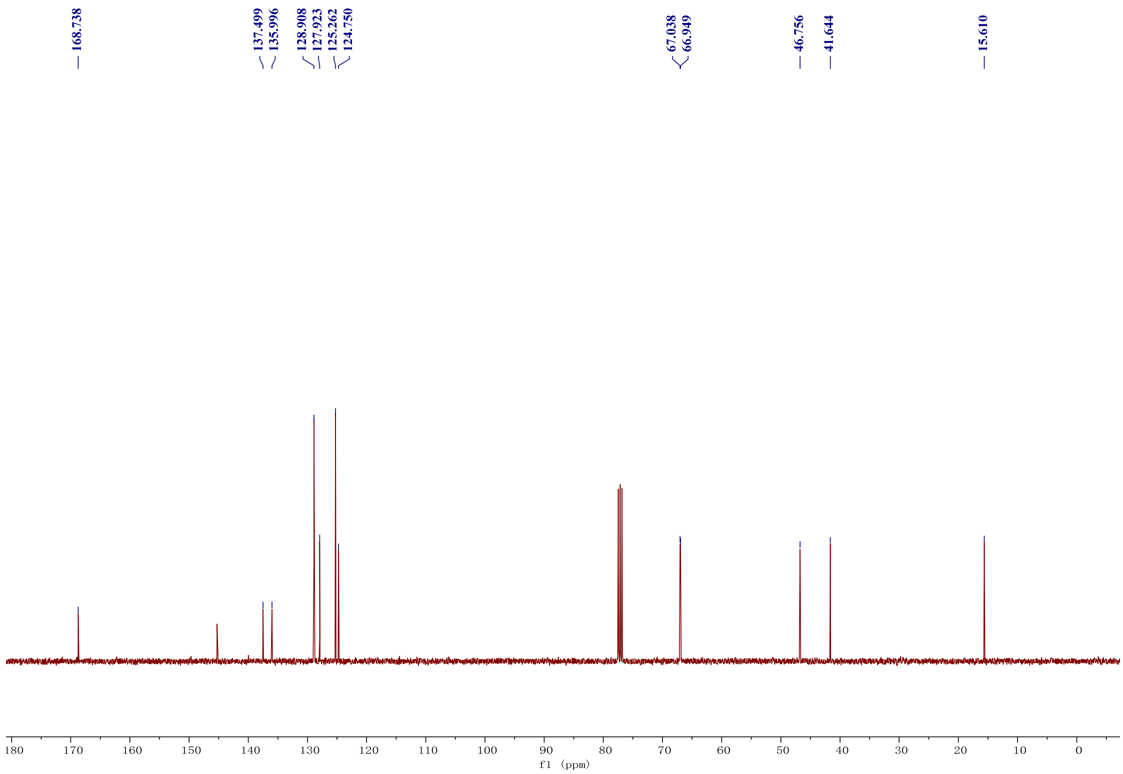

7.378
7.373
7.358
7.327
7.308
7.298
7.279
7.260
7.251
7.234
7.217
7.213
7.200
7.134
7.115
7.096
6.912
6.893
3.223
2.472
2.453
2.436
2.419
2.401
2.383
2.278
2.260
2.242
2.225
2.207
2.189
0.700
0.682
0.663
5.17
2.05
1.06
1.00
3.06
1.08
1.14
3.00
f1 (ppm)

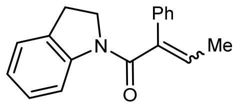

ty23-7-75-1240bp.13.fid
178.728
144.248
140.366
132.214
128.592
128.224
127.313
127.091
124.902
122.684
108.295
57.450
31.008
26.443
9.160
f1 (ppm)


O
N
O
Ph
Me

108

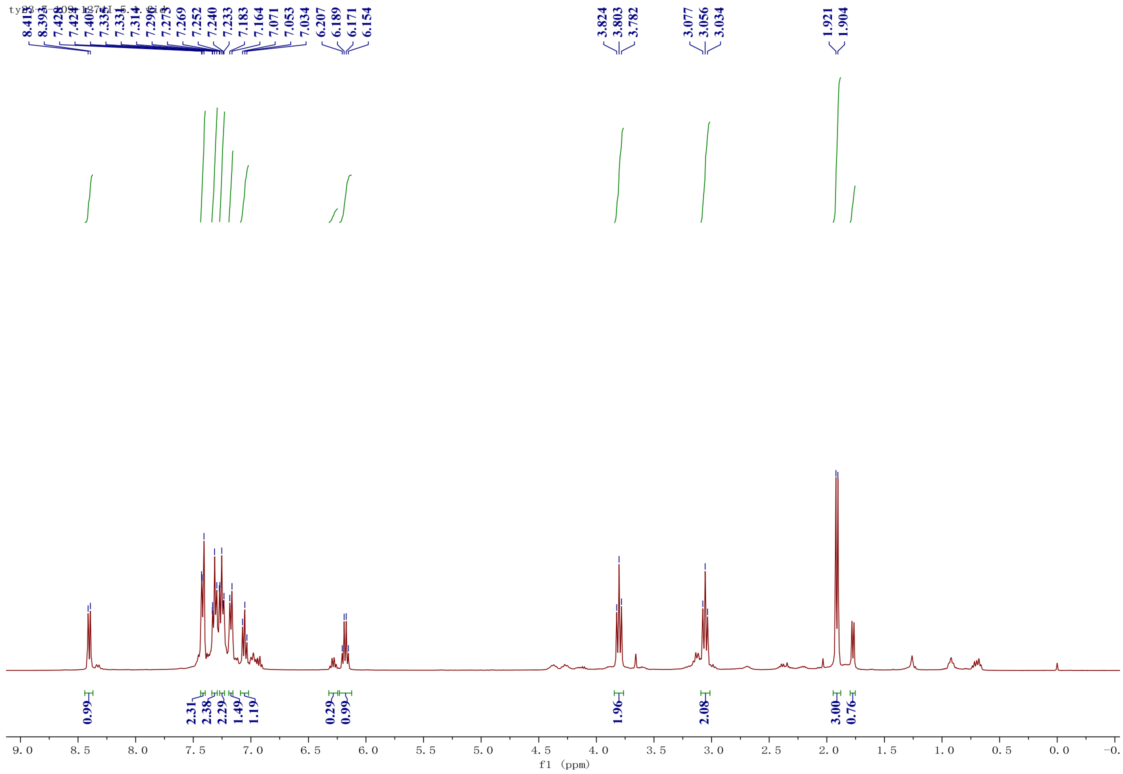

7.366
7.361
7.358
7.354
7.344
7.339
7.336
7.328
7.326
7.320
7.311
7.308
7.305
7.301
7.295
7.284
7.280
7.272
7.270
7.265
7.262
7.254
7.251
7.246
7.241
6.215
6.197
6.179
6.162
3.814
3.811
3.802
3.797
3.793
3.789
3.785
3.744
3.741
3.737
3.733
3.728
3.718
3.716
3.513
3.502
3.498
3.489
3.386
3.376
3.373
3.363
1.878
1.861
5.07
0.99
2.01
2.01
2.02
2.00
3.00
f1 (ppm)

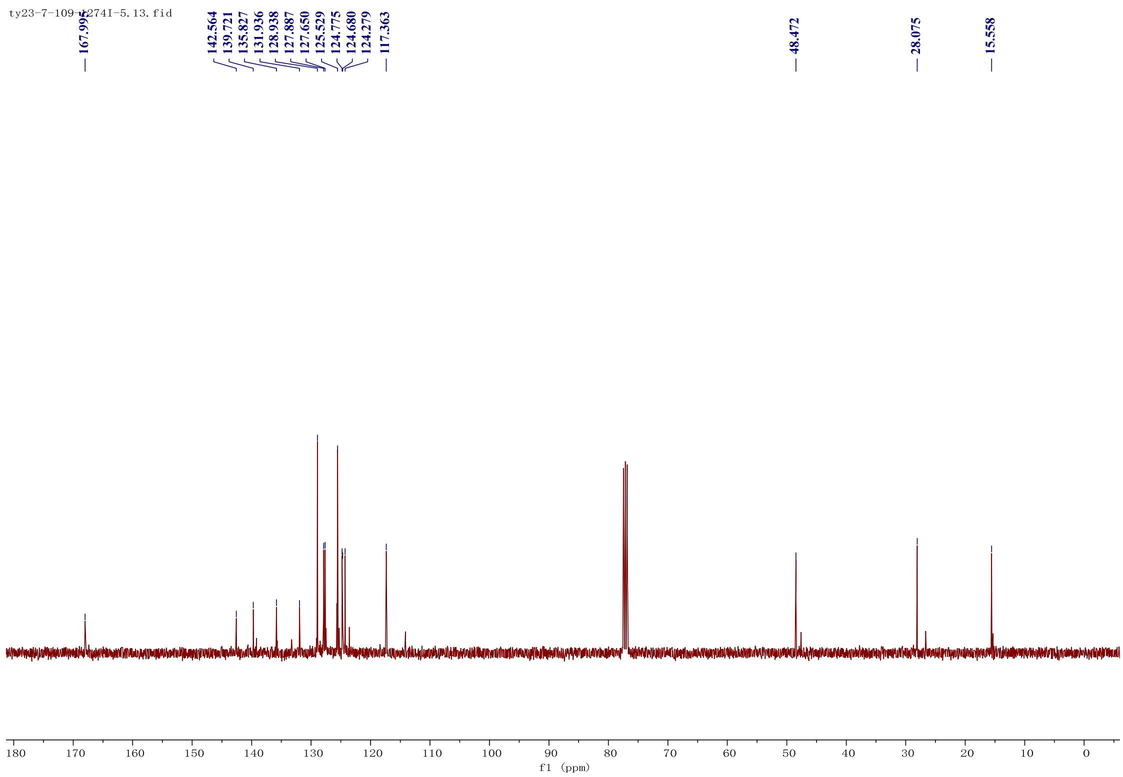

168.738
137.499
135.996
128.908
127.923
125.262
124.750
67.038
66.949
46.756
41.644
15.610
f1 (ppm)

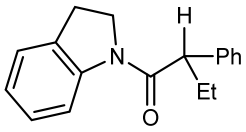


109

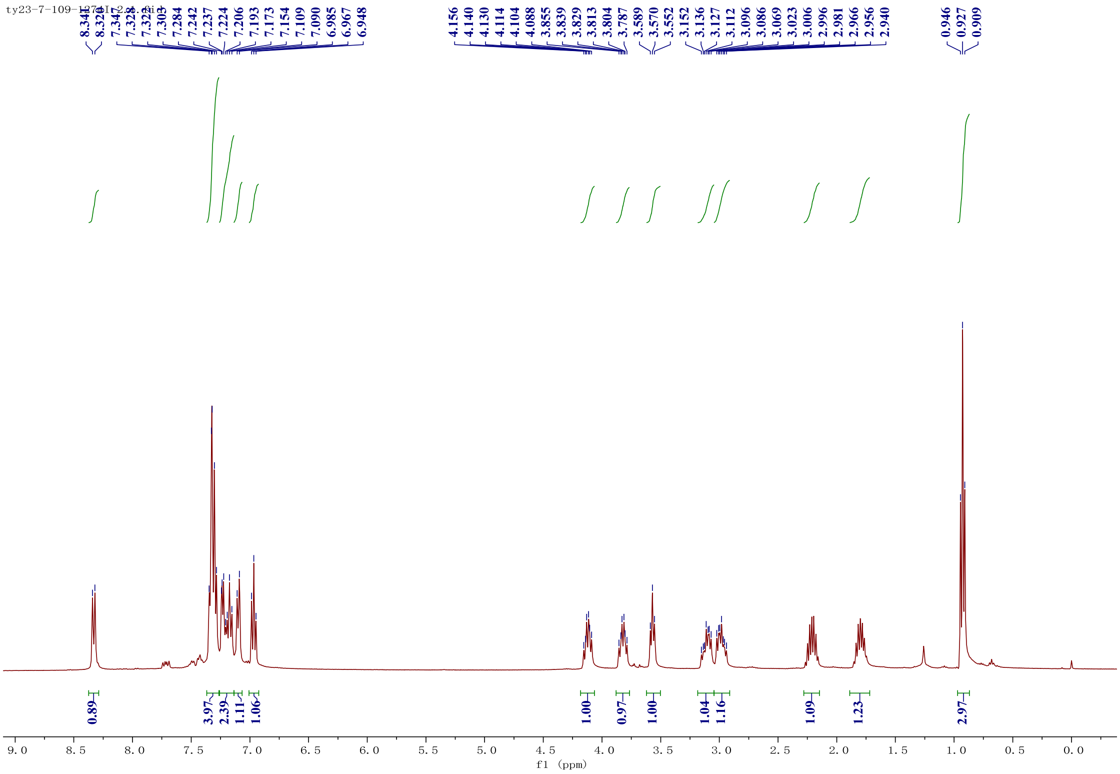
mixture: 4:1

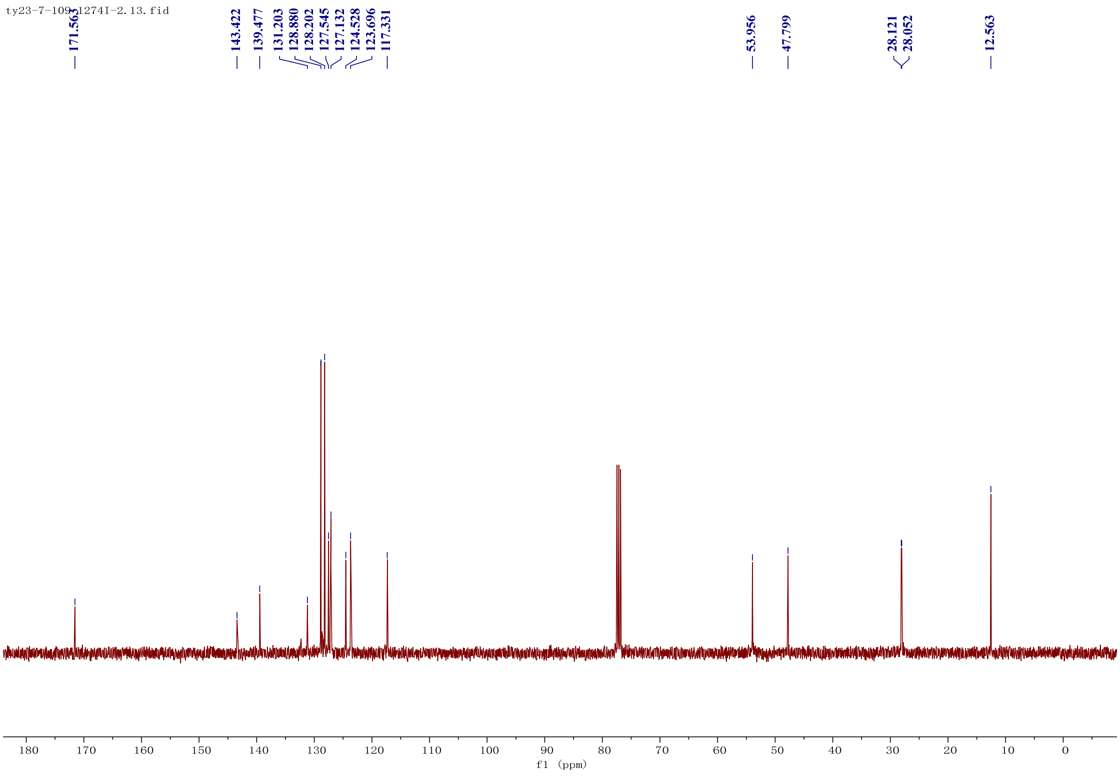


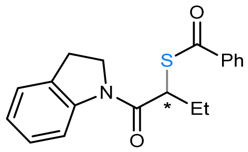




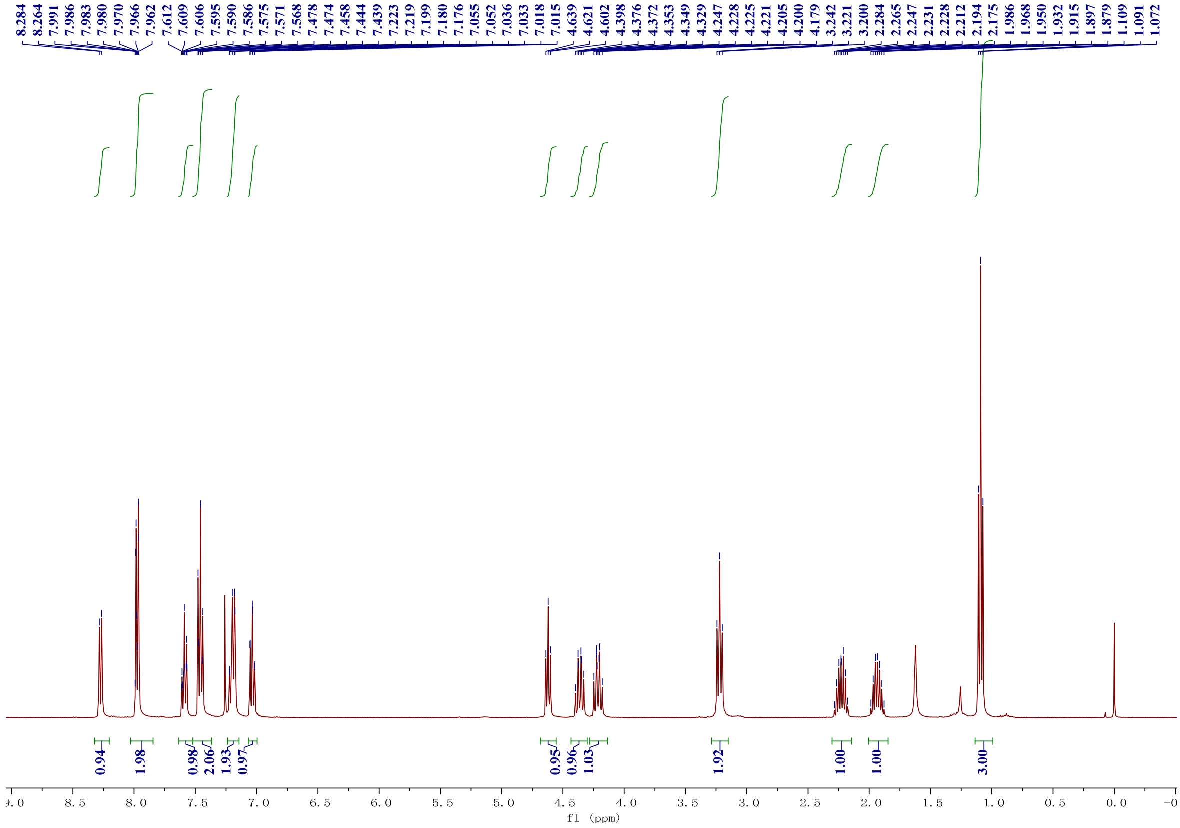
110

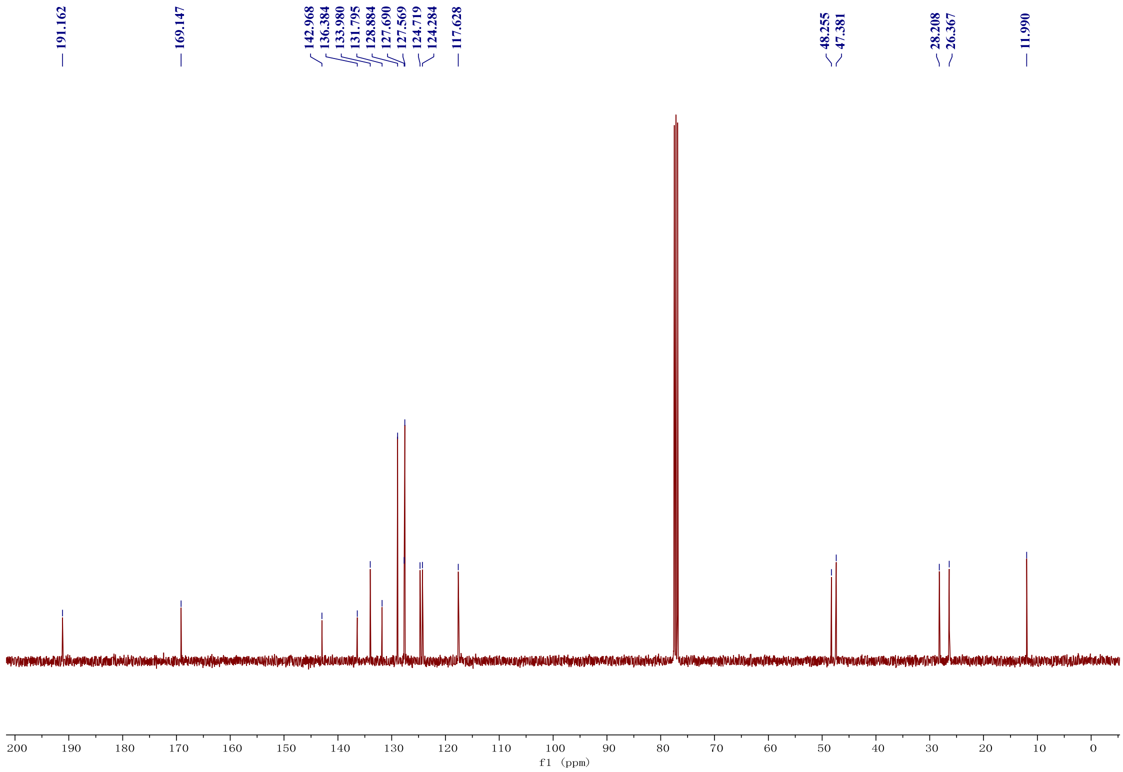


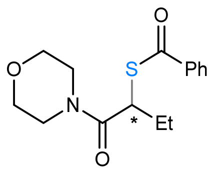




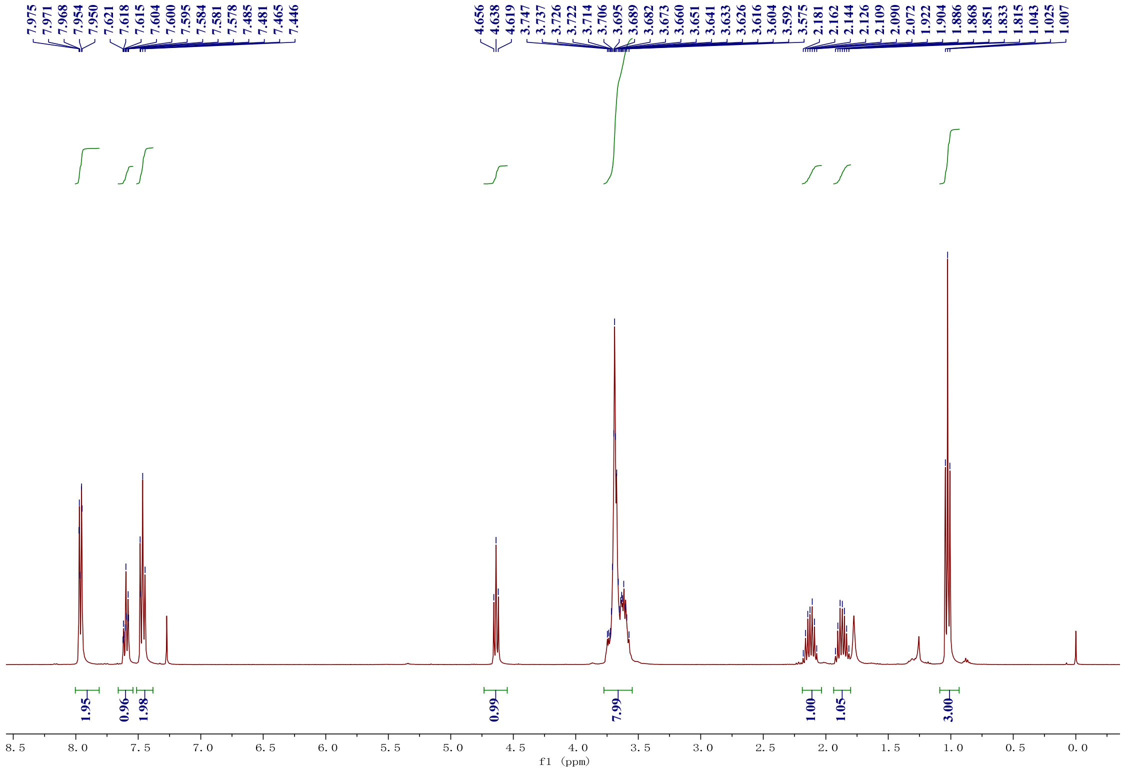
111

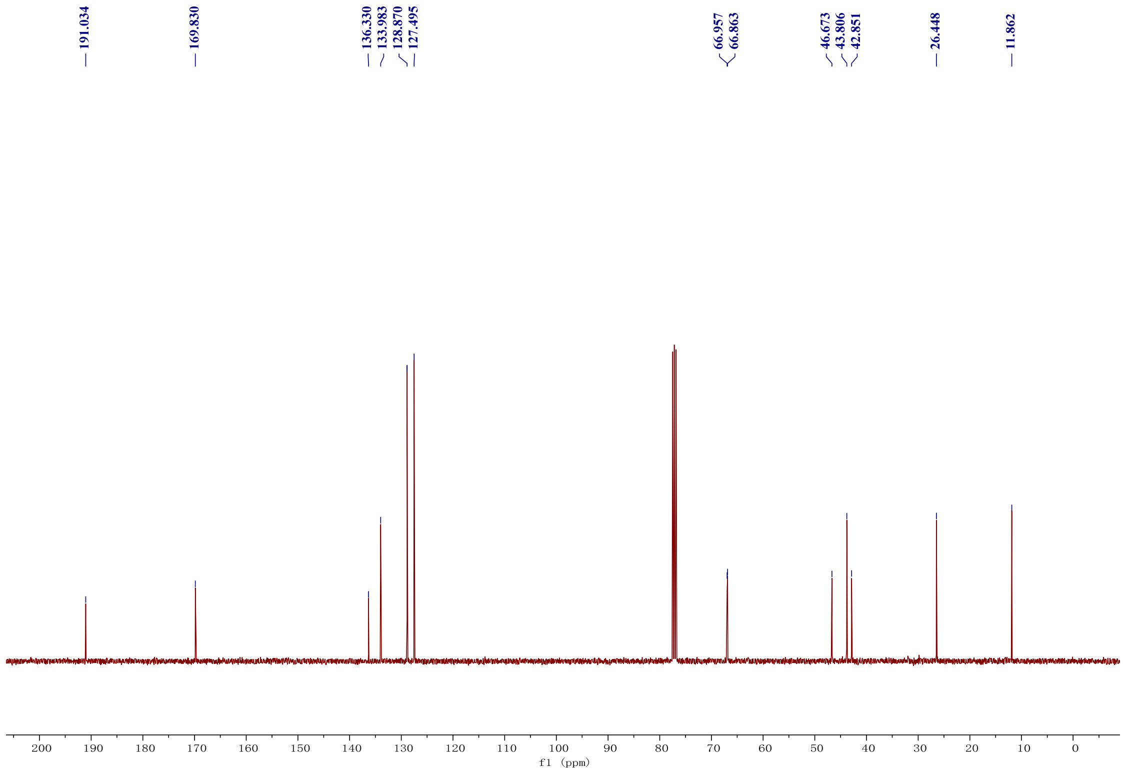


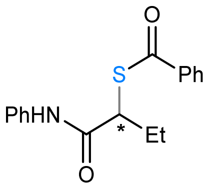




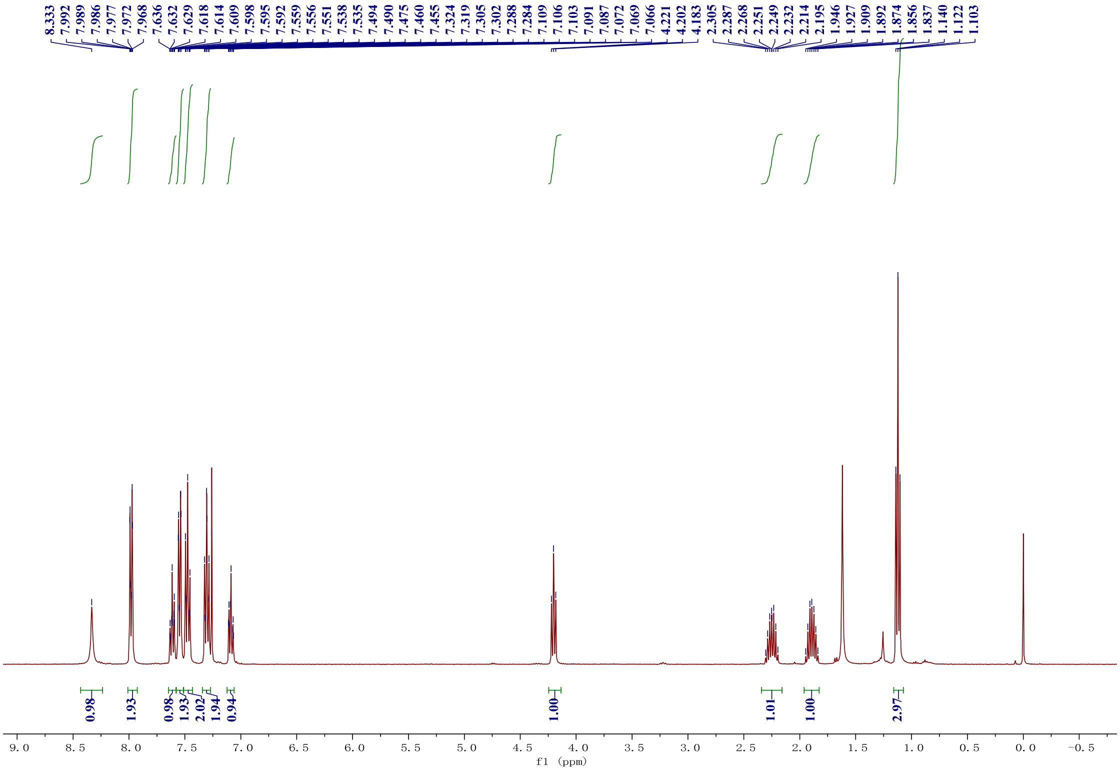
112

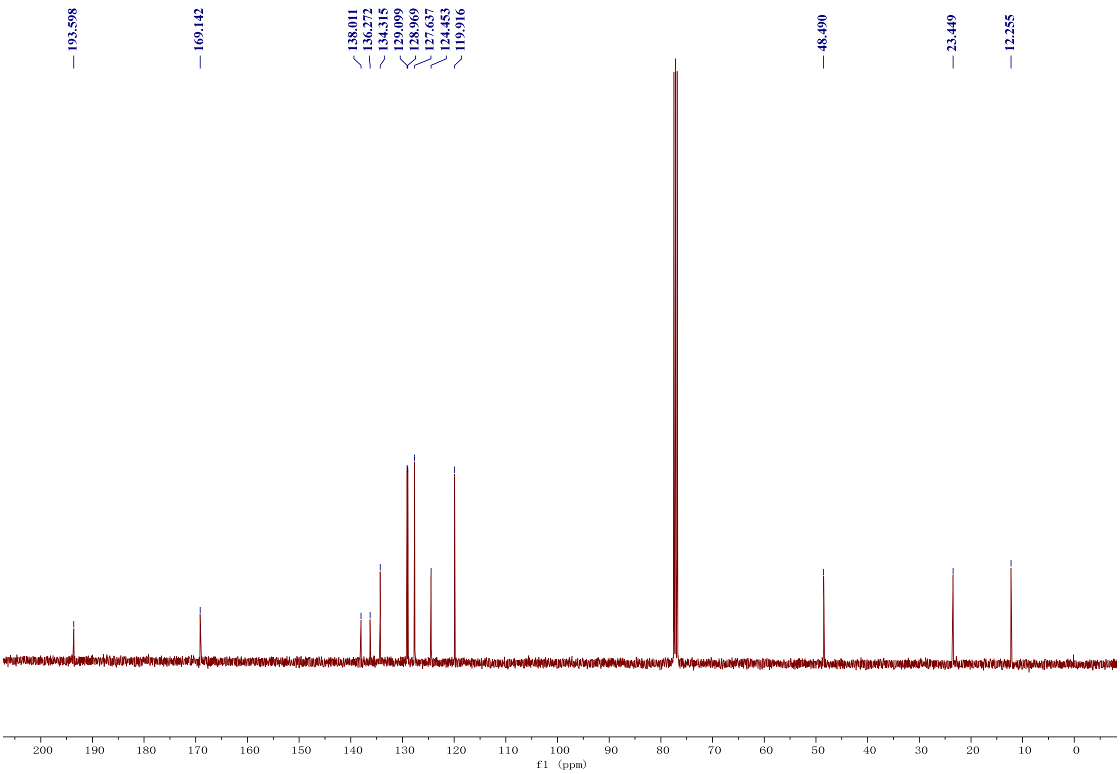


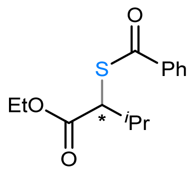




113

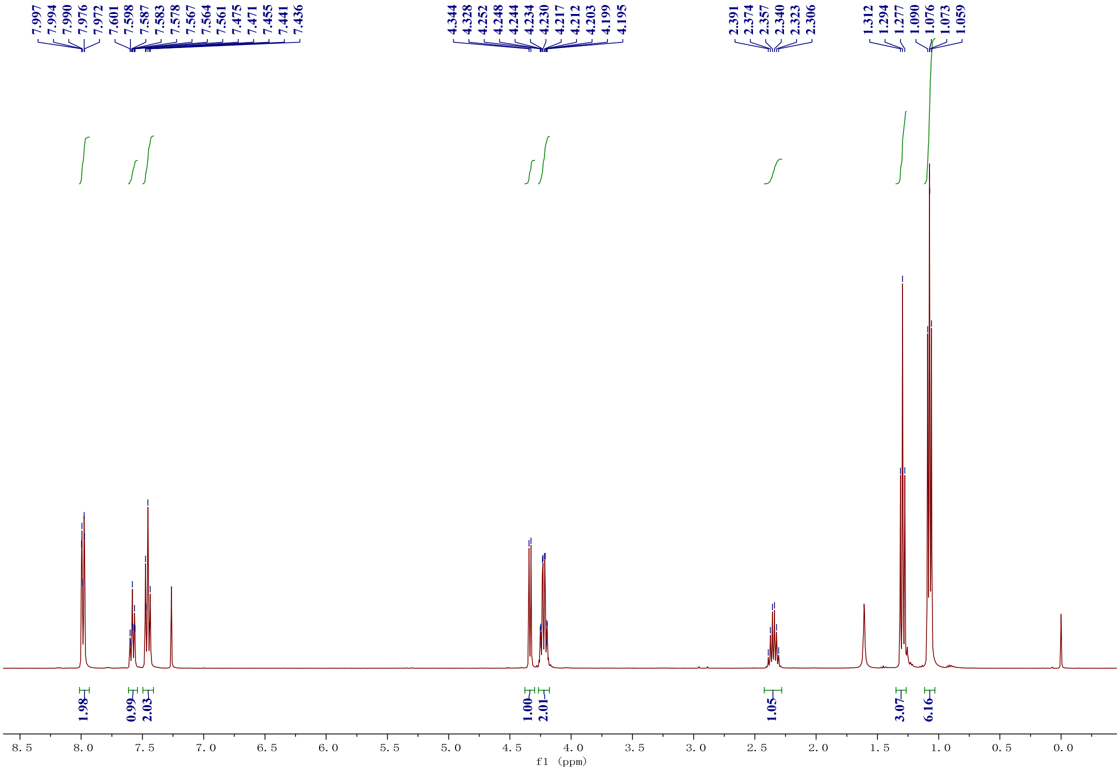




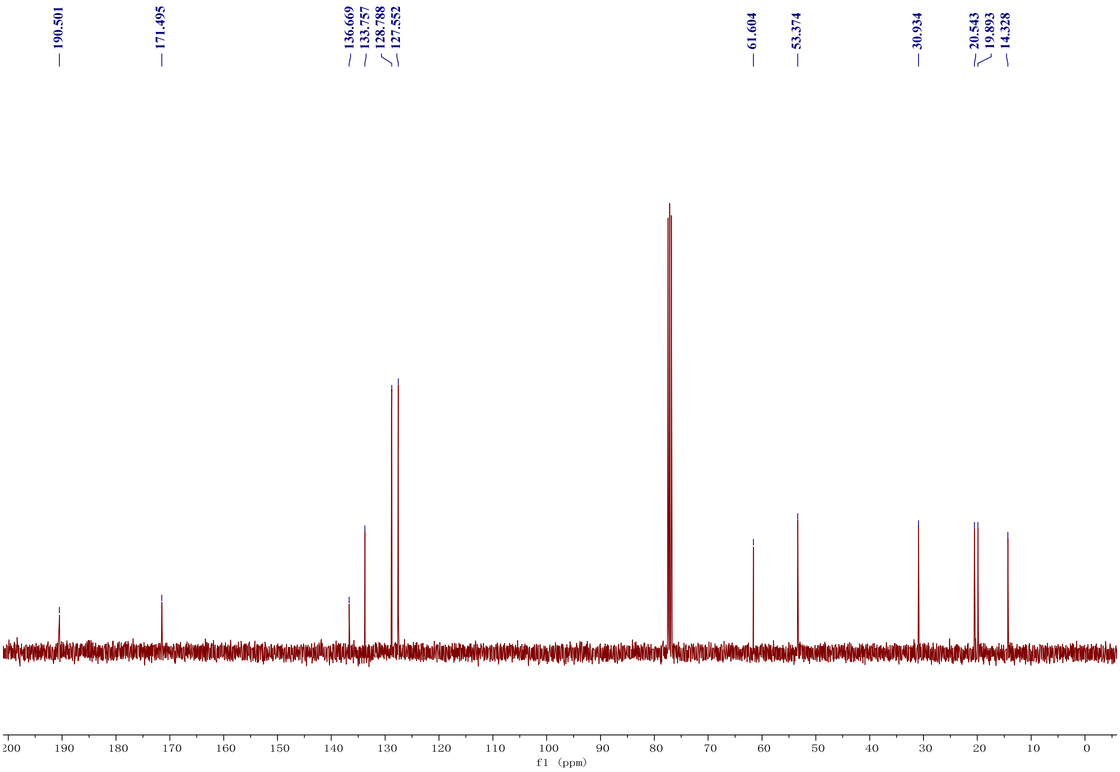


O
S
Ph
EtO
*
iPr
O

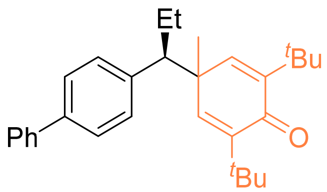
114



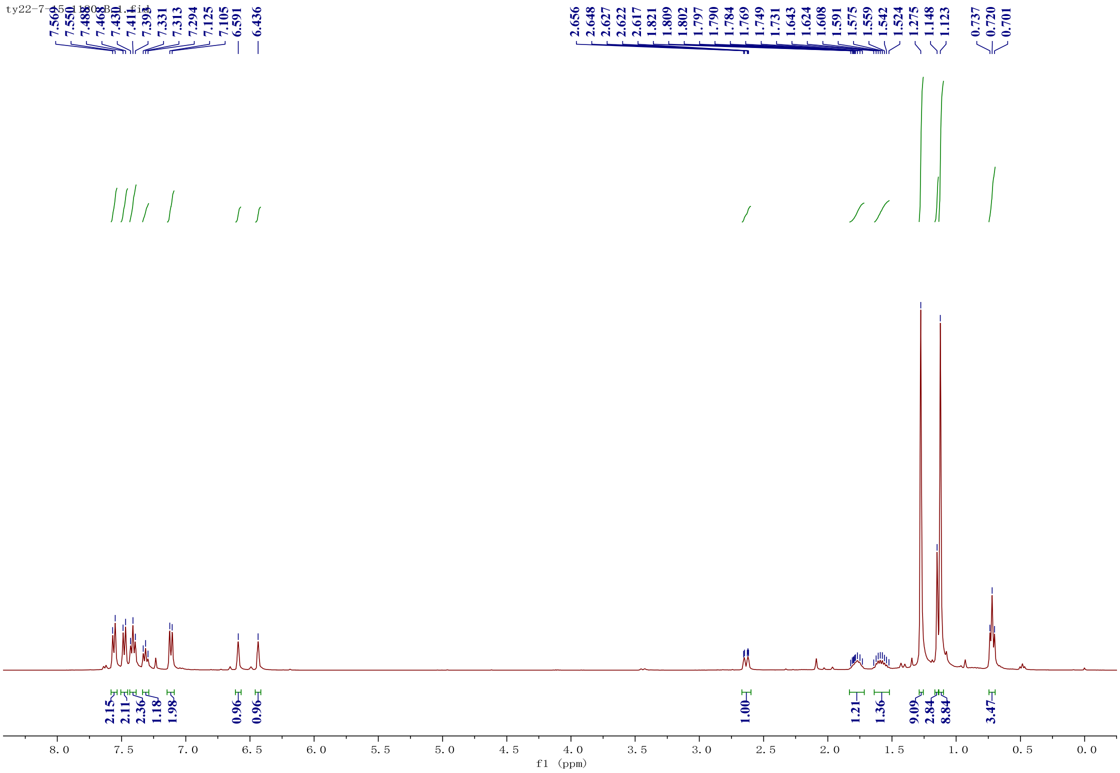
7.997 7.994 7.990 7.976 7.972 7.601 7.598 7.587 7.583 7.578 7.567 7.564 7.561 7.475 7.471 7.455 7.441 7.436
4.344 4.328 4.252 4.248 4.244 4.234 4.230 4.217 4.212 4.203 4.199 4.195
2.391 2.374 2.357 2.340 2.323 2.306
1.312 1.294 1.277 1.090 1.076 1.073 1.059
1.98
0.99
2.03
1.00
2.01
1.05
3.07
6.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

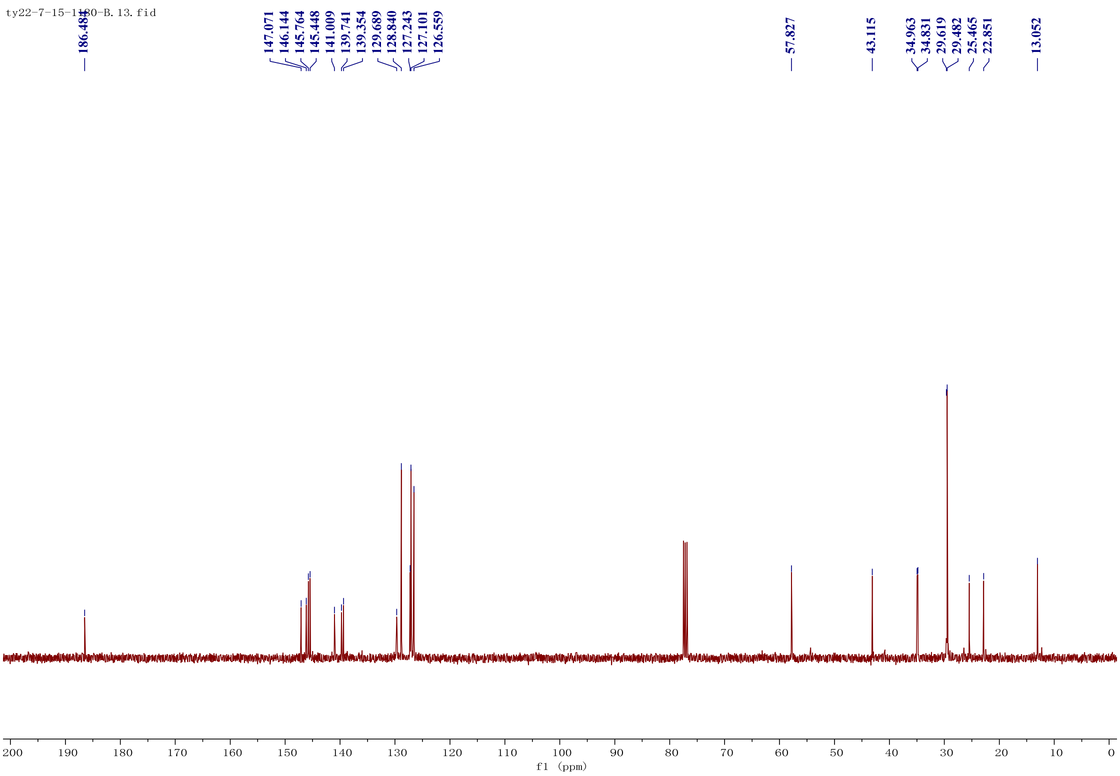


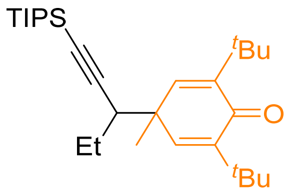
190.501
171.495
136.669 133.757 128.788 127.552
61.604
53.374
30.934
20.543 19.893 14.328
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



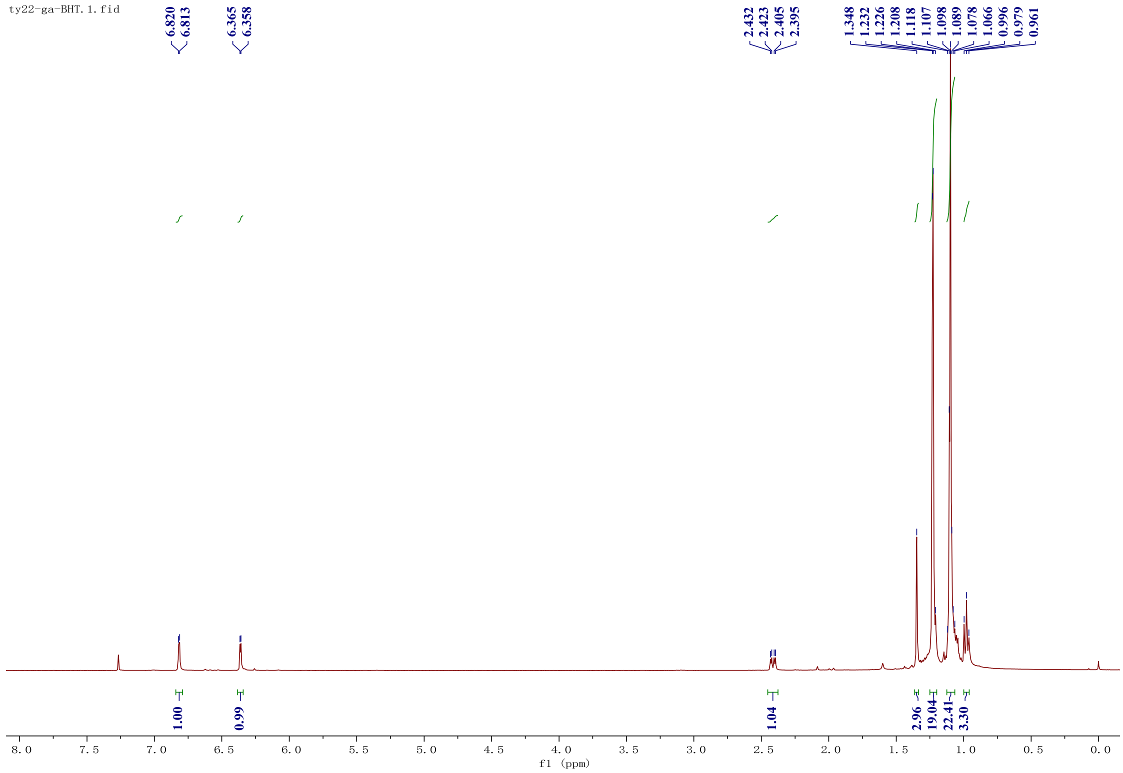
115

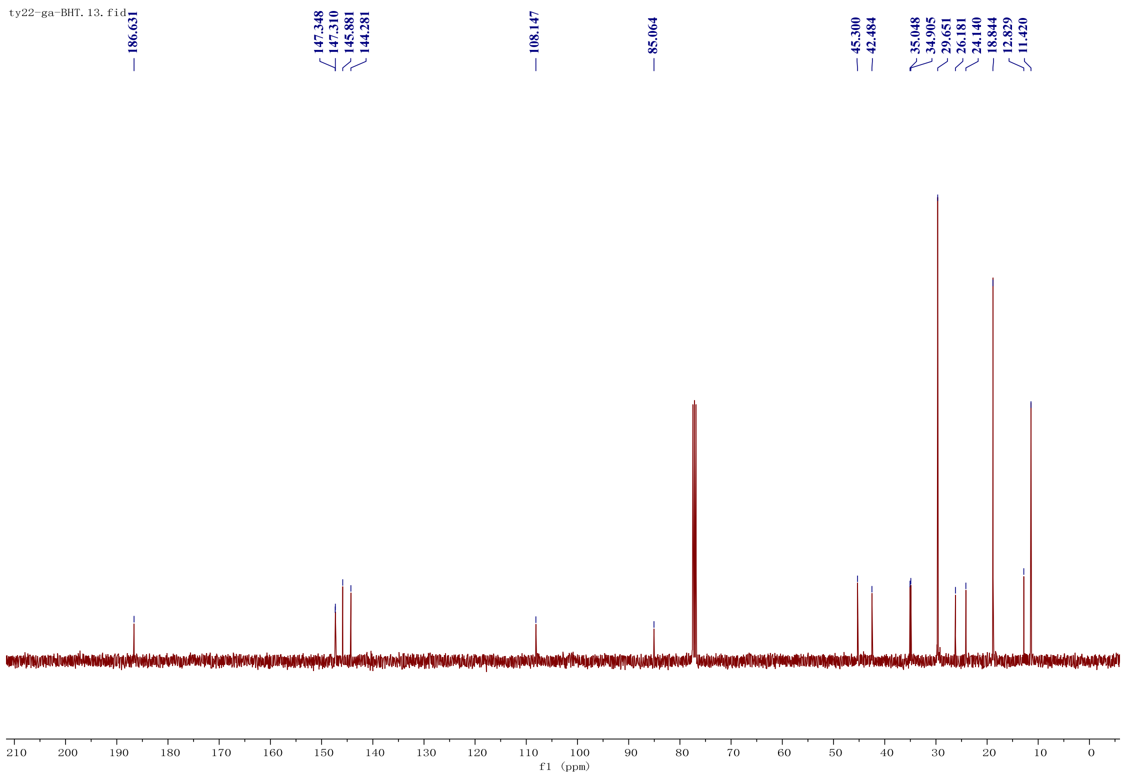




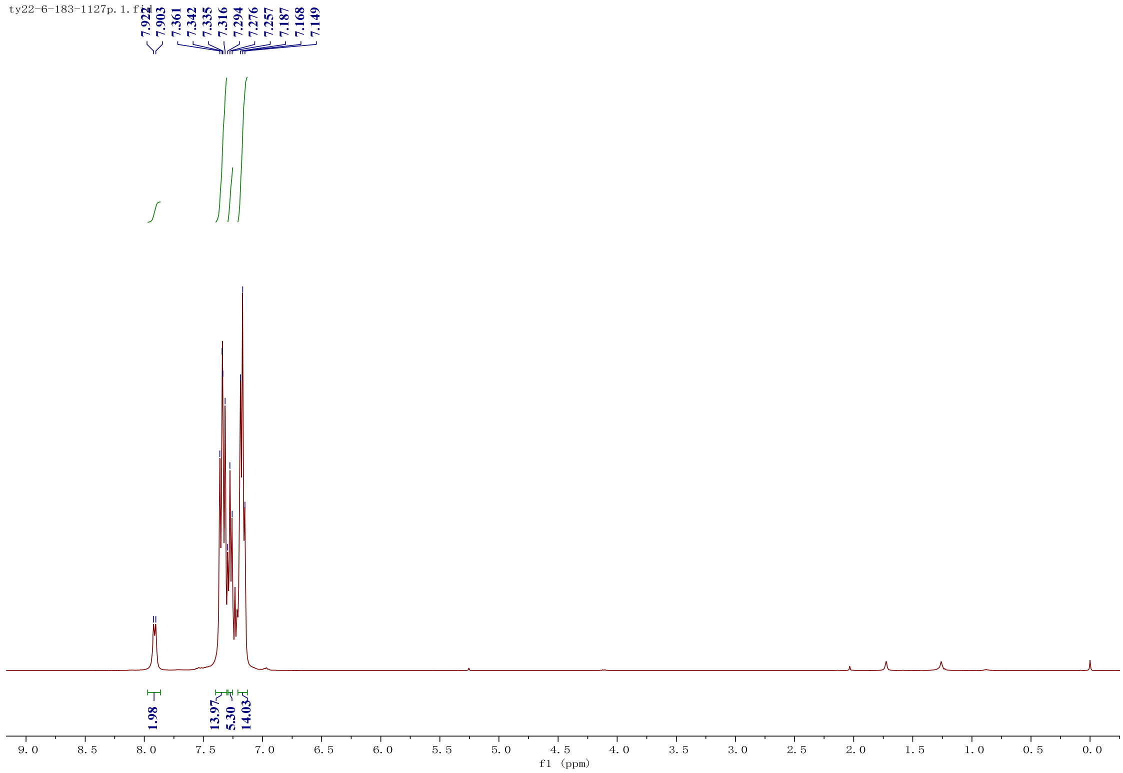

TIPS
tBu
O
Et
tBu

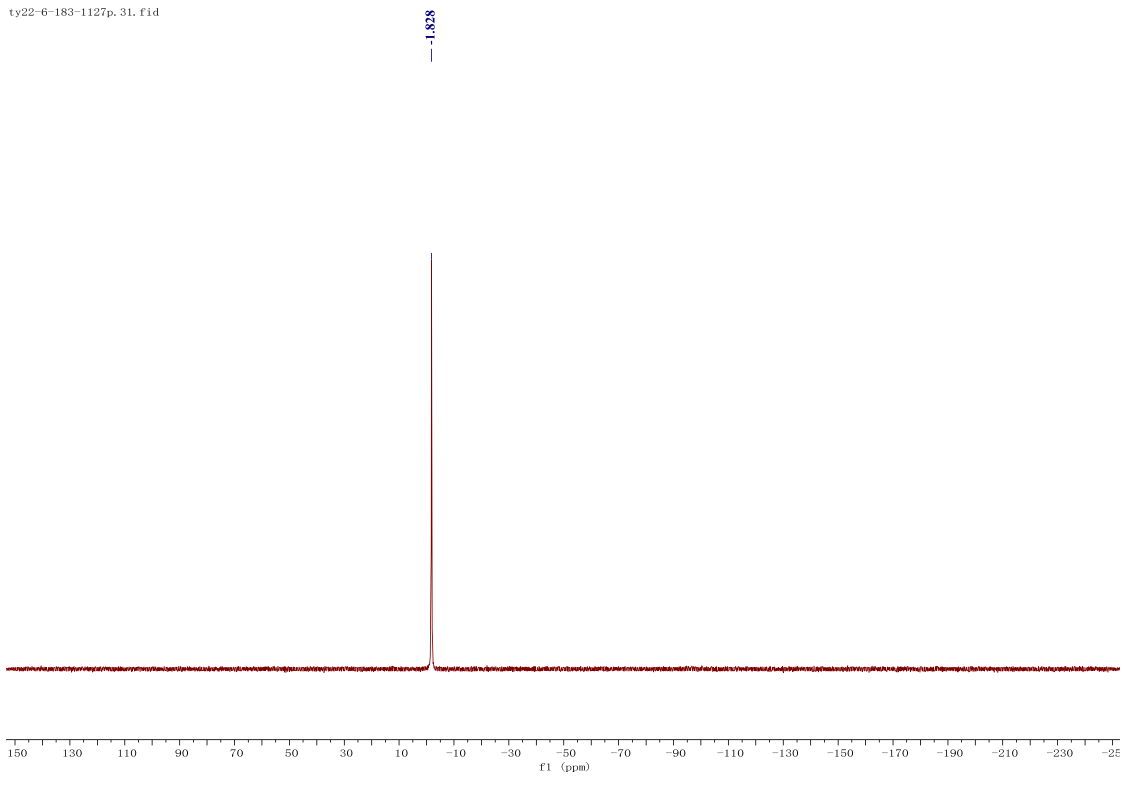
116

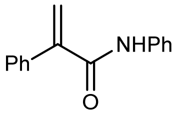

ty22-ga-BHT.1.fid
6.820
6.813
6.365
6.358
2.432
2.423
2.405
2.395
1.348
1.232
1.226
1.208
1.118
1.107
1.098
1.089
1.078
1.066
0.996
0.979
0.961
1.00
0.99
1.04
2.96
19.04
22.41
3.30
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


ty22-ga-BHT.13.fid
186.631
147.348
147.310
145.881
144.281
108.147
85.064
45.300
42.484
35.048
34.905
29.651
26.181
24.140
18.844
12.829
11.420
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

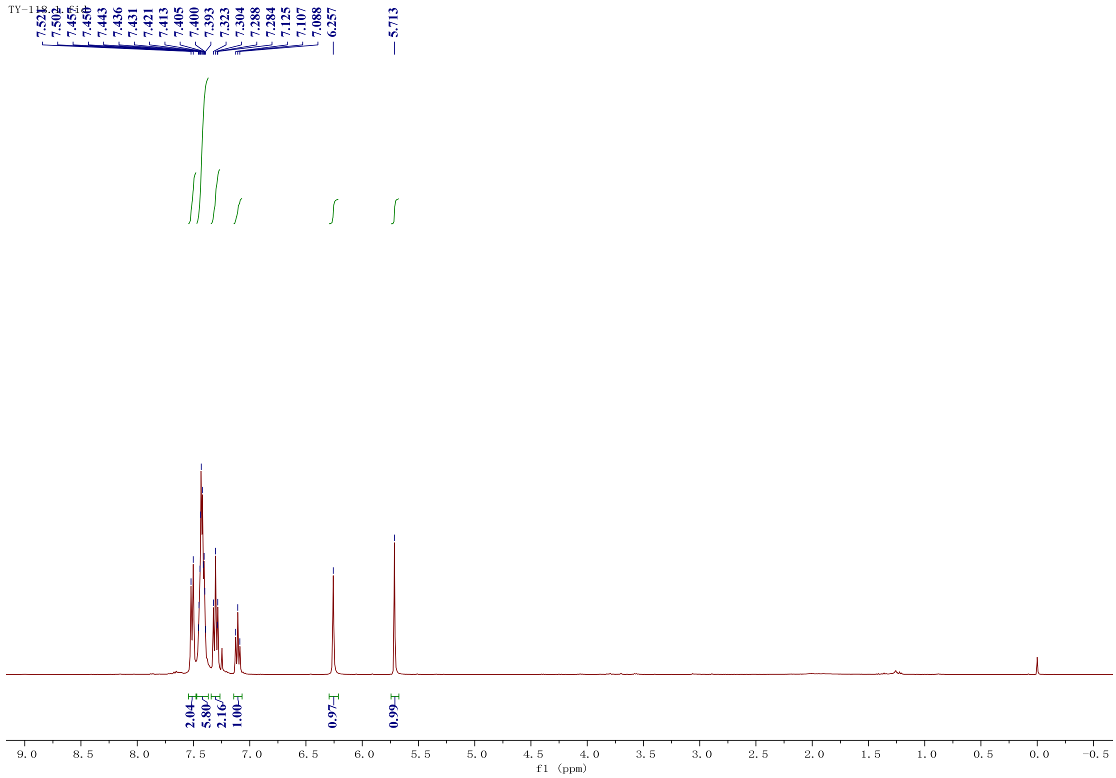
PhC(O)SCu(PPh$_3$)$_2$ **117**

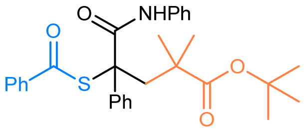




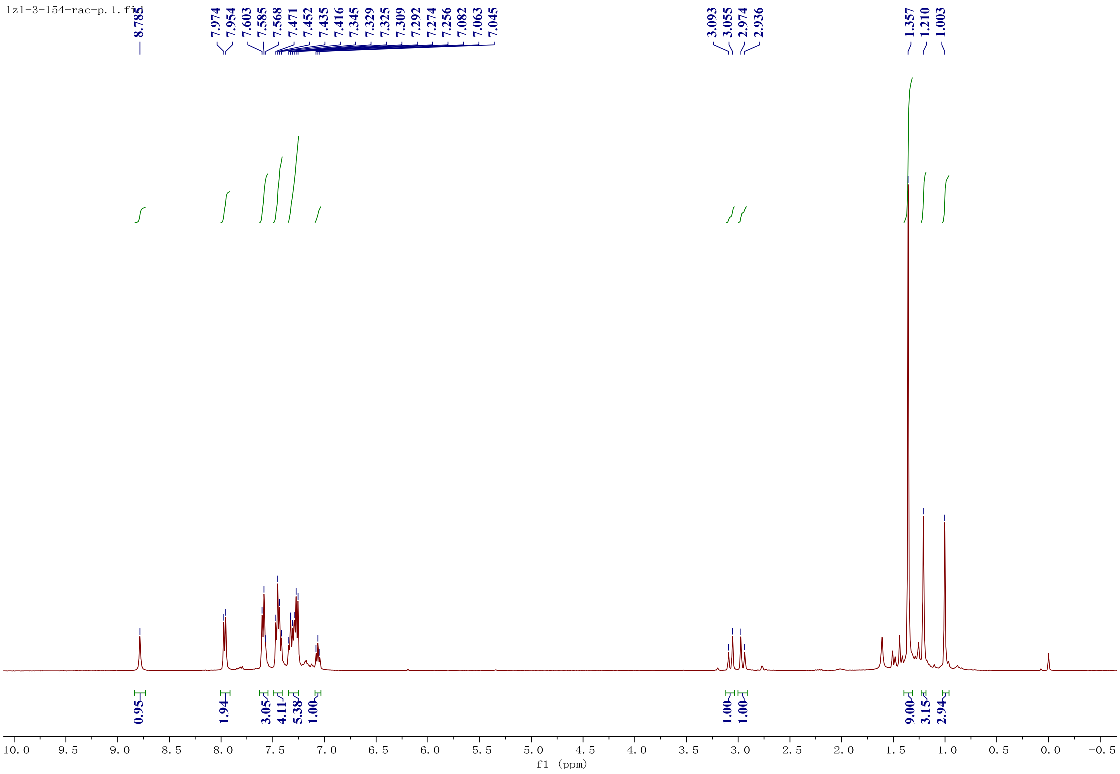


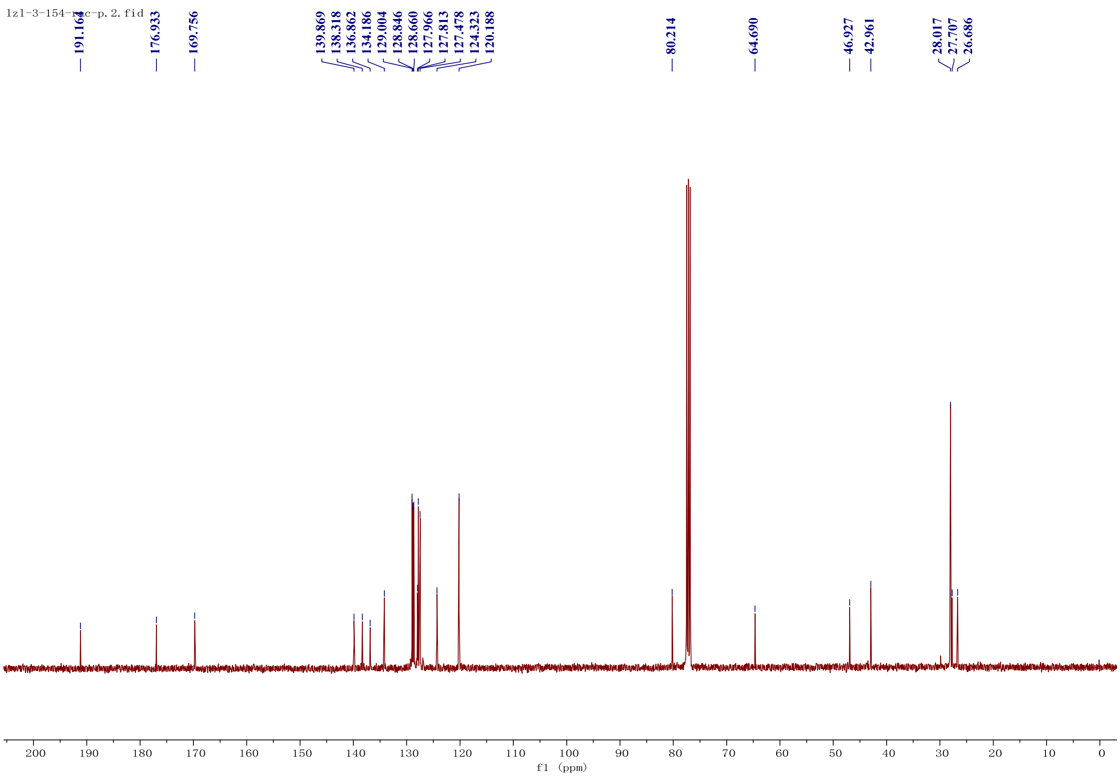
118


TY-118
7.521
7.502
7.457
7.450
7.443
7.436
7.431
7.421
7.413
7.405
7.400
7.393
7.323
7.304
7.288
7.284
7.125
7.107
7.088
6.257
5.713
2.04
5.80
2.16
1.00
0.97
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

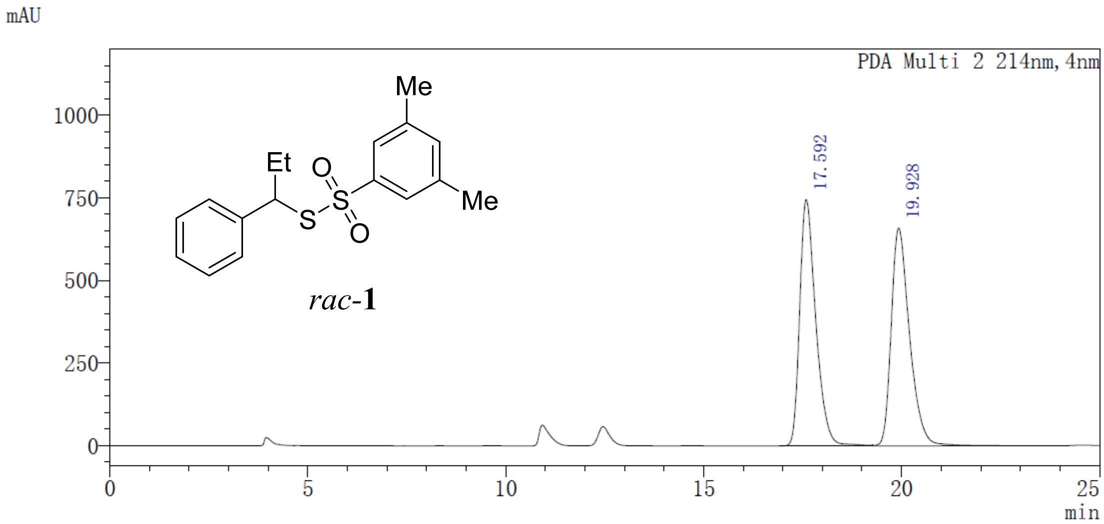


120



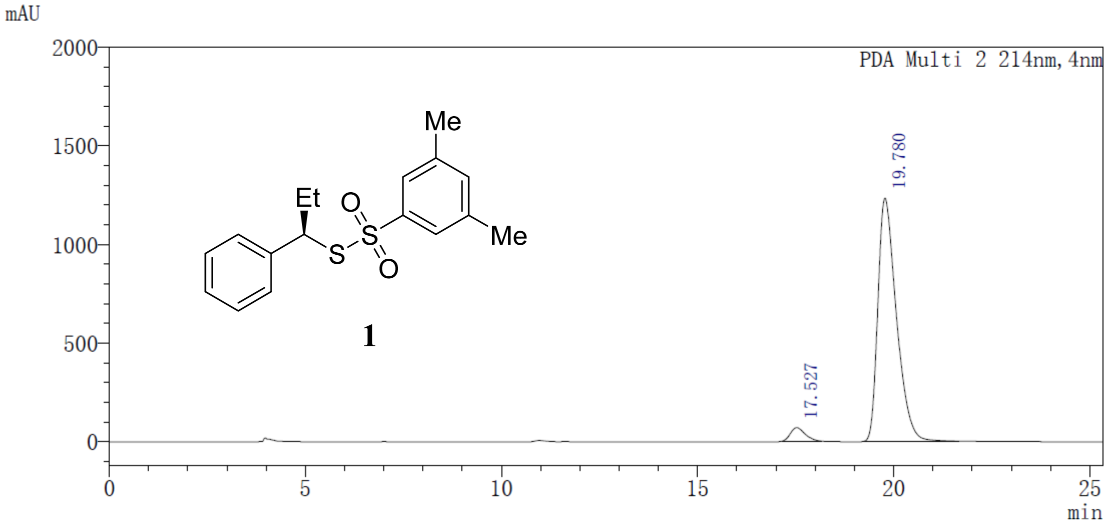


14. HPLC spectra



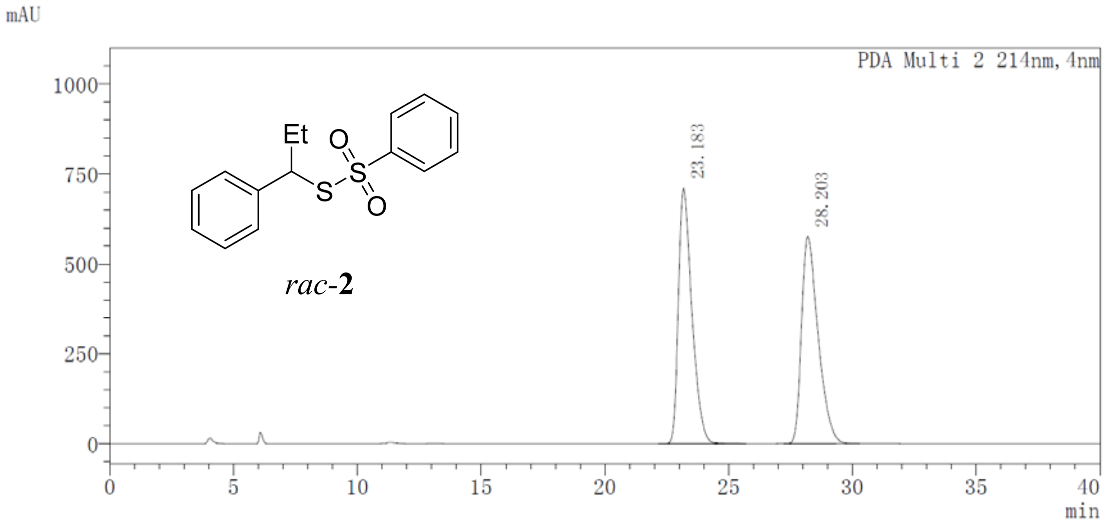
PDA Ch2 214nm

T	Hight	Area	Area%
17.592	745141	21013181	49.792
19.928	658842	21188391	50.208



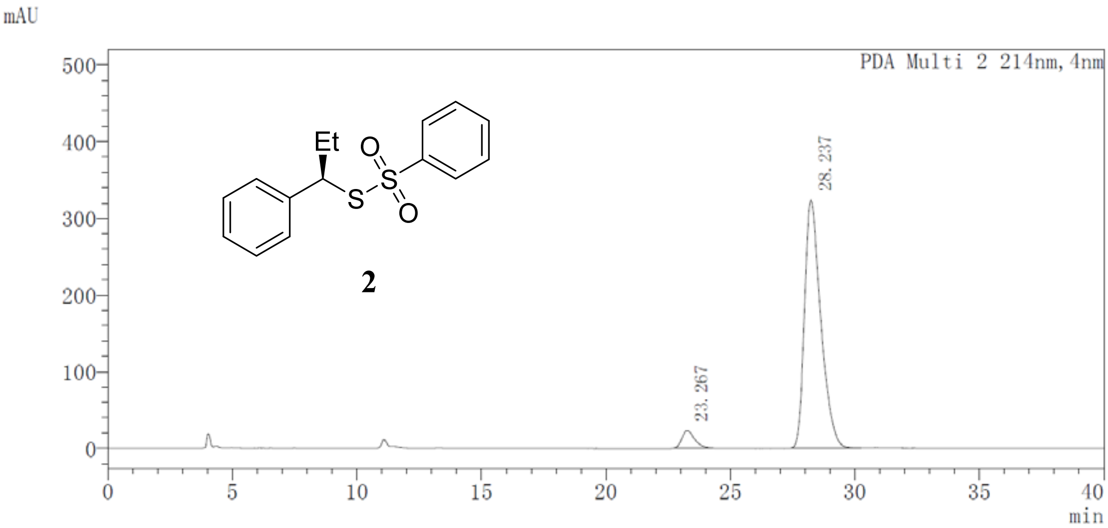
PDA Ch2 214nm

T	Hight	Area	Area%
17.527	68664	1776427	4.205
19.780	1231847	40467078	95.795



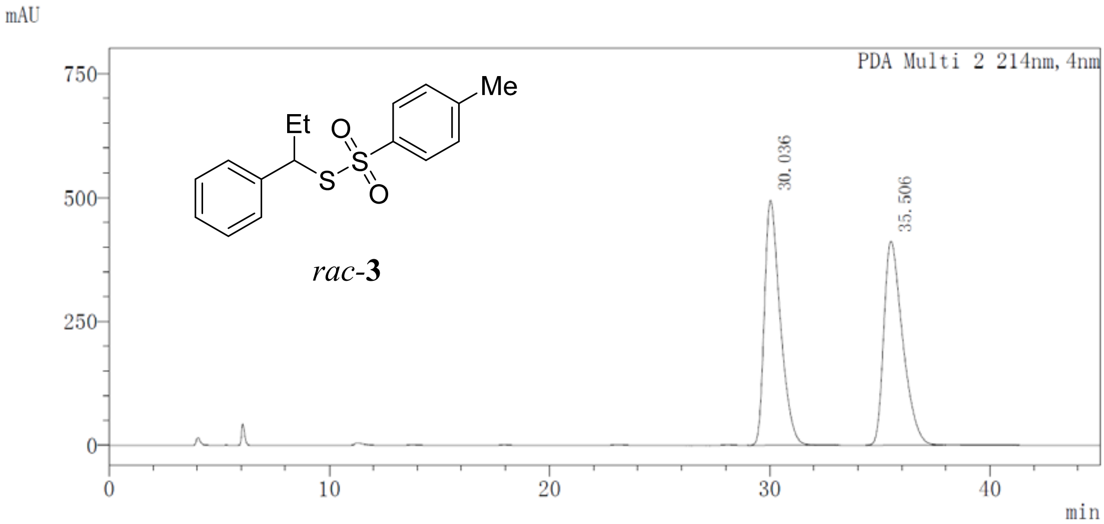
PDA Ch2 214nm

T	Hight	Area	Area%
23.183	709940	26913022	50.057
28.203	575249	26851529	49.943



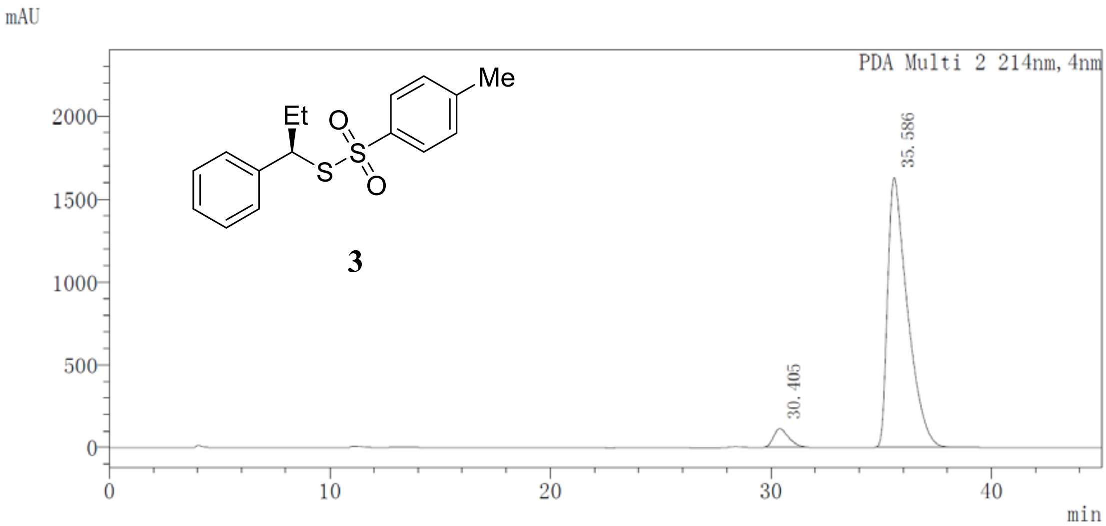
PDA Ch2 214nm

T	Hight	Area	Area%
23.267	22903	808353	5.209
28.237	323184	14711073	94.791



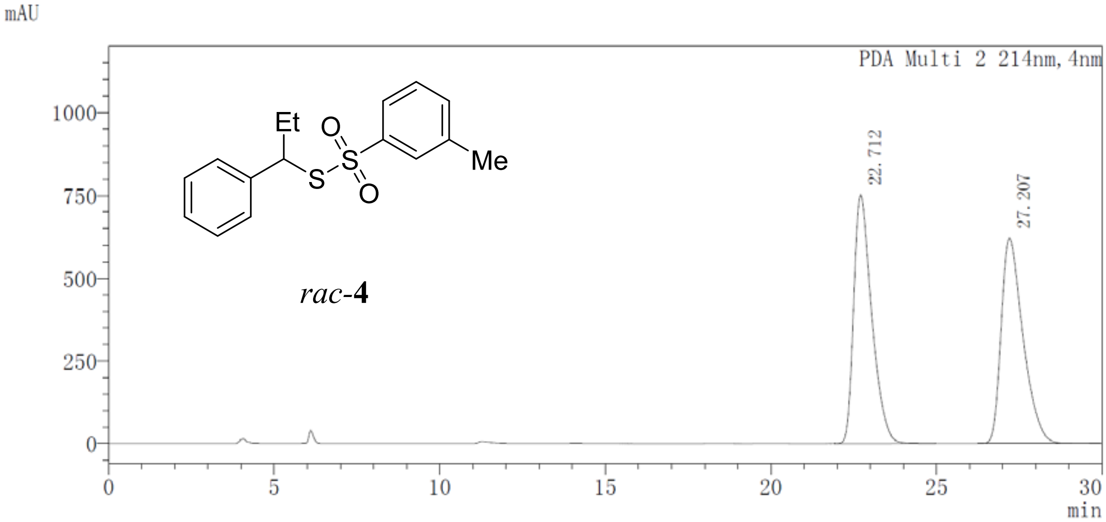
PDA Ch2 214nm

T	Hight	Area	Area%
30.036	493878	24538554	50.058
35.506	411578	24481263	49.942



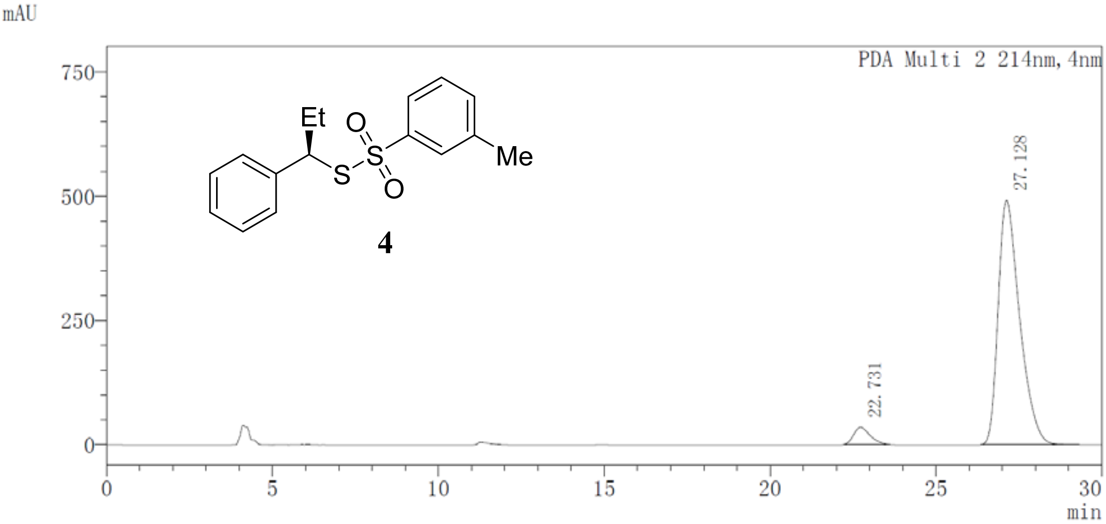
PDA Ch2 214nm

T	Hight	Area	Area%
30.405	113602	5439496	5.065
35.586	1630018	101958464	94.935



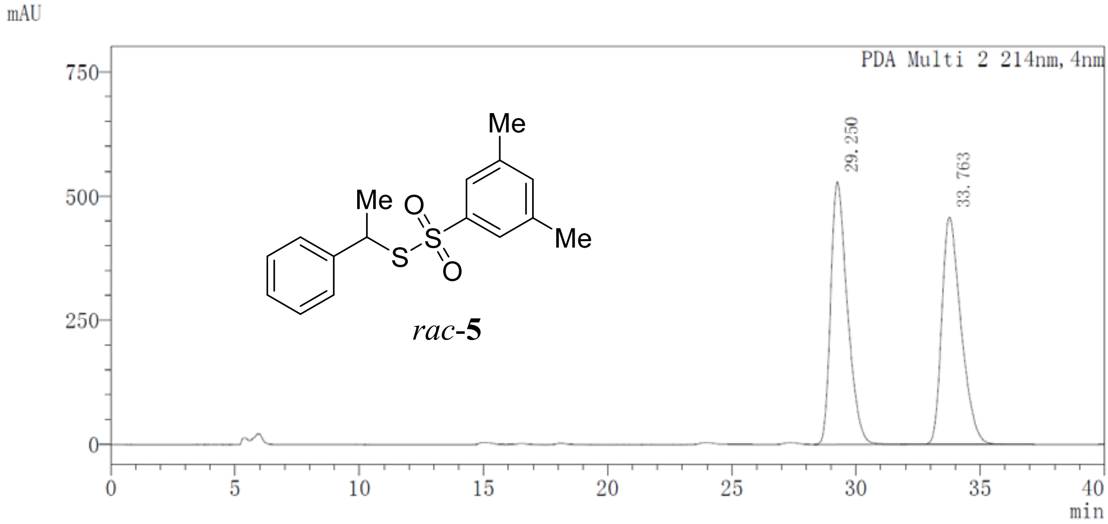
PDA Ch2 214nm

T	Hight	Area	Area%
22.712	751476	28532489	49.952
27.207	621007	28587612	50.048



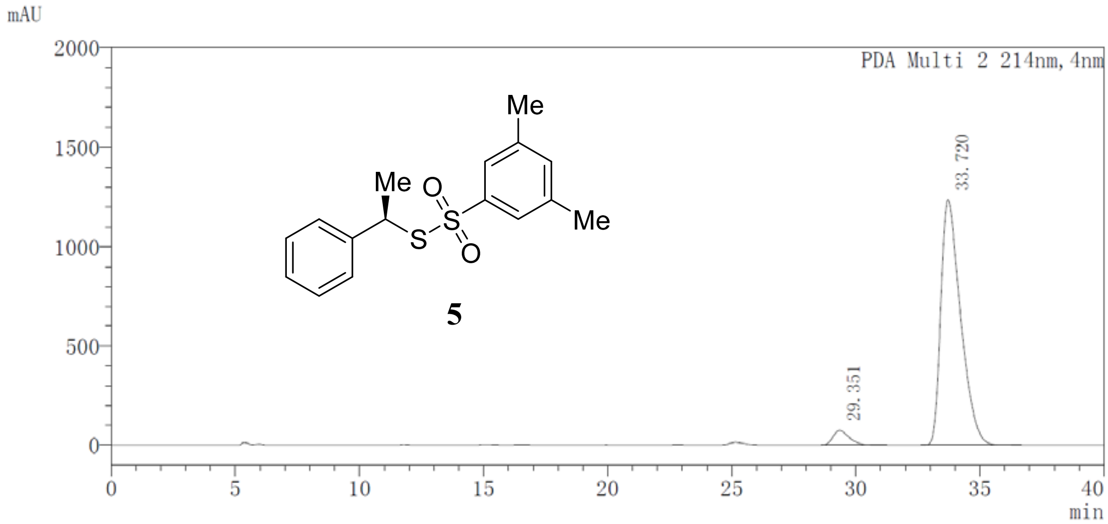
PDA Ch2 214nm

T	Hight	Area	Area%
22.731	35009	1221261	5.227
27.128	491035	22142498	94.773



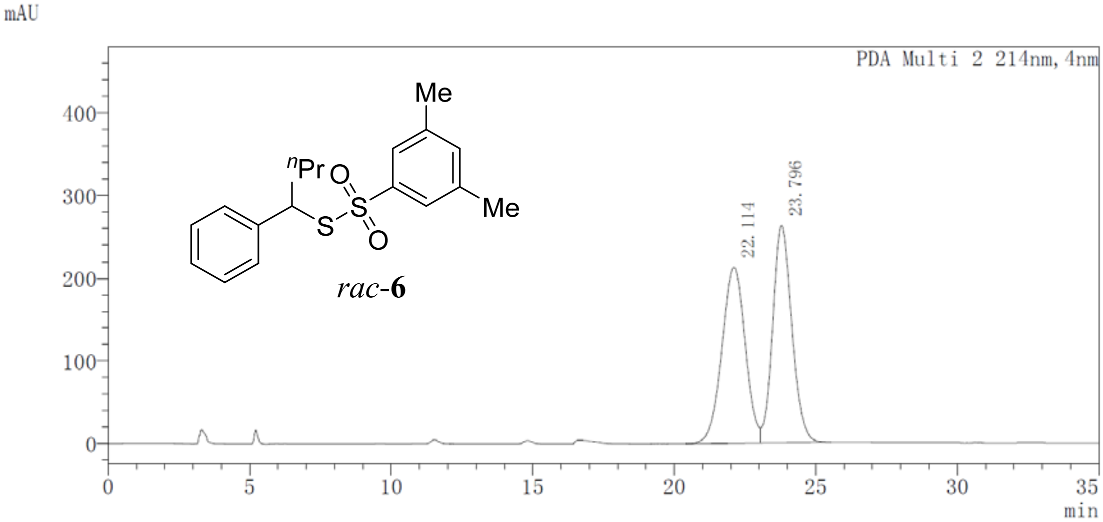
PDA Ch2 214nm

T	Hight	Area	Area%
29.250	527823	24644777	50.094
33.763	456584	24552104	49.906



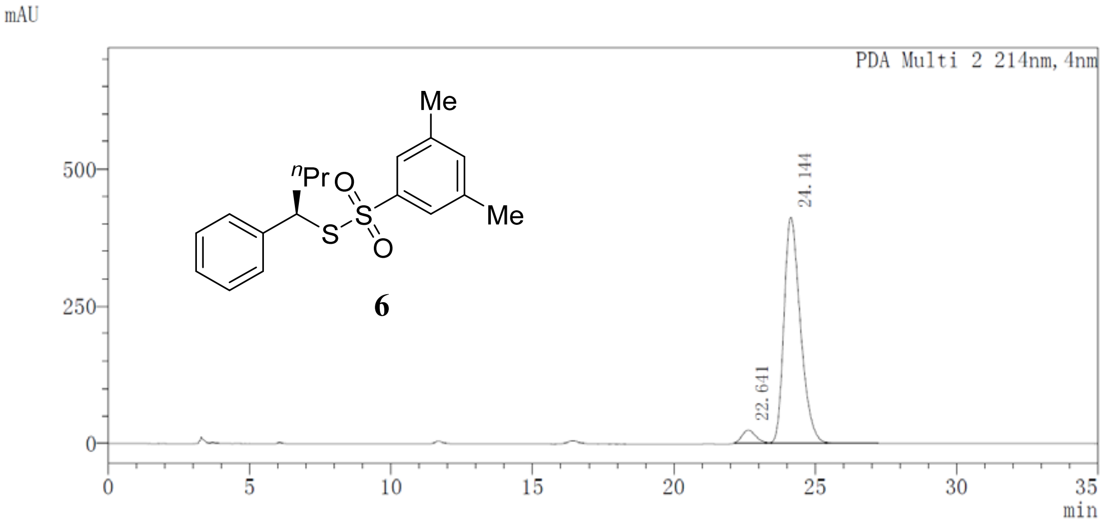
PDA Ch2 214nm

T	Hight	Area	Area%
29.351	74255	3363908	4.684
33.720	1236422	68456512	95.316



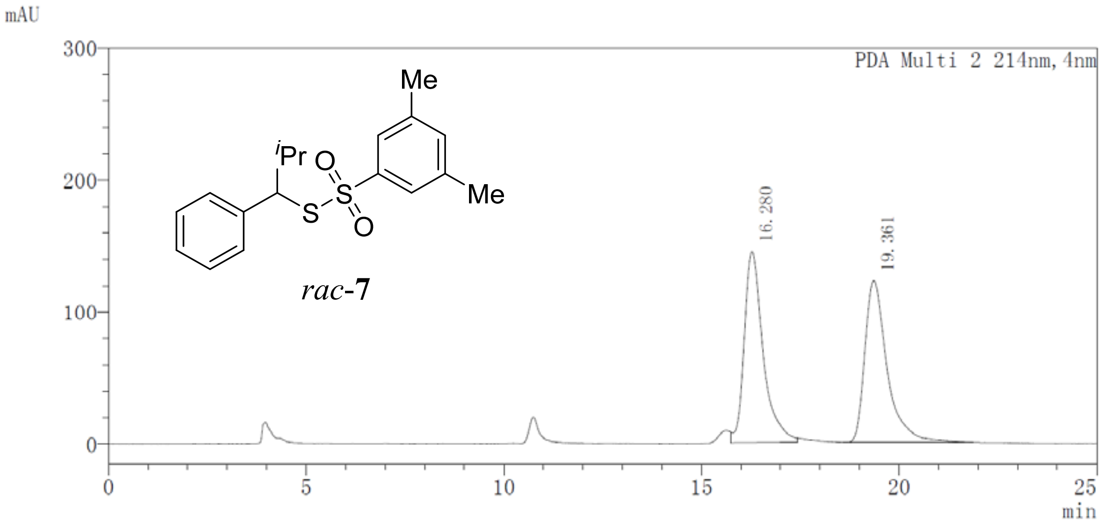
PDA Ch2 214nm

T	Hight	Area	Area%
22.114	213390	12233929	49.713
23.796	263059	12375388	50.287



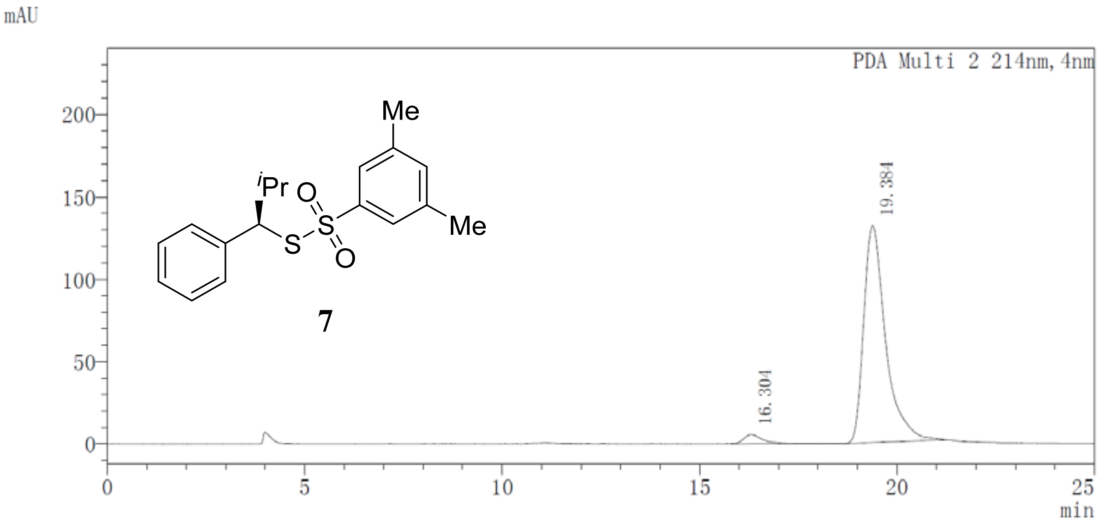
PDA Ch2 214nm

T	Hight	Area	Area%
22.641	23471	783763	4.506
24.144	411116	16610480	95.494



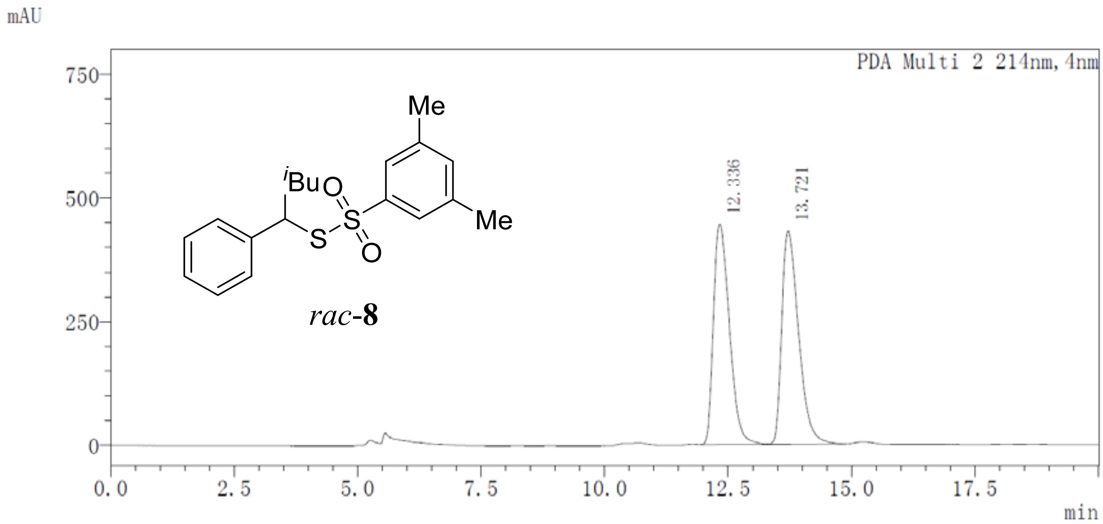
PDA Ch2 214nm

T	Hight	Area	Area%
16.280	144840	4824361	49.915
19.361	122760	4840714	50.085



PDA Ch2 214nm

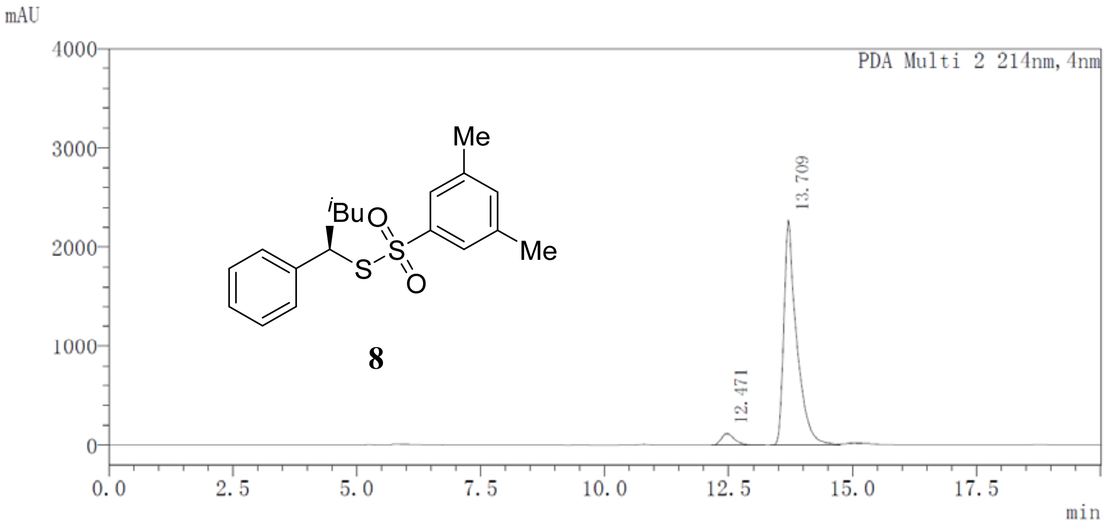
T	Hight	Area	Area%
16.304	5755	186925	3.536
19.384	131771	5099858	96.464



Peak Table

PDA Ch2 214nm

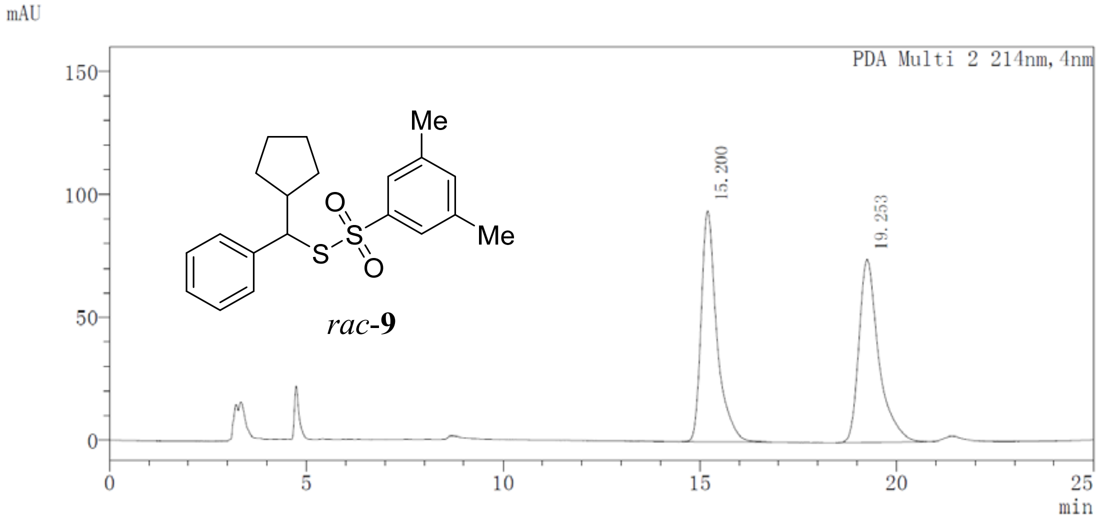
Peak#	Ret. Time	Area	Area%
1	12.336	10018606	49.541
2	13.721	10204272	50.459



Peak Table

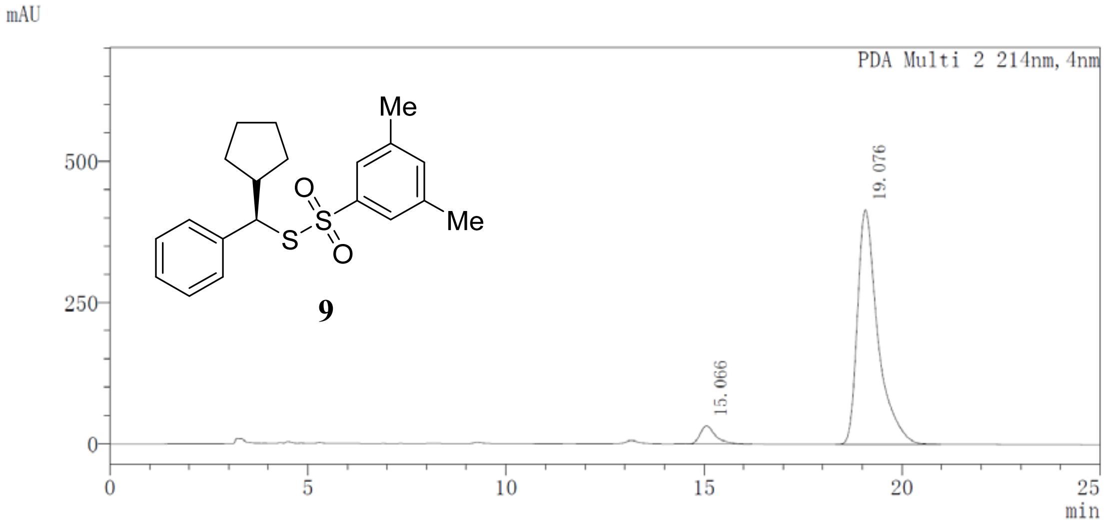
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	12.471	2189204	5.086
2	13.709	40852376	94.914



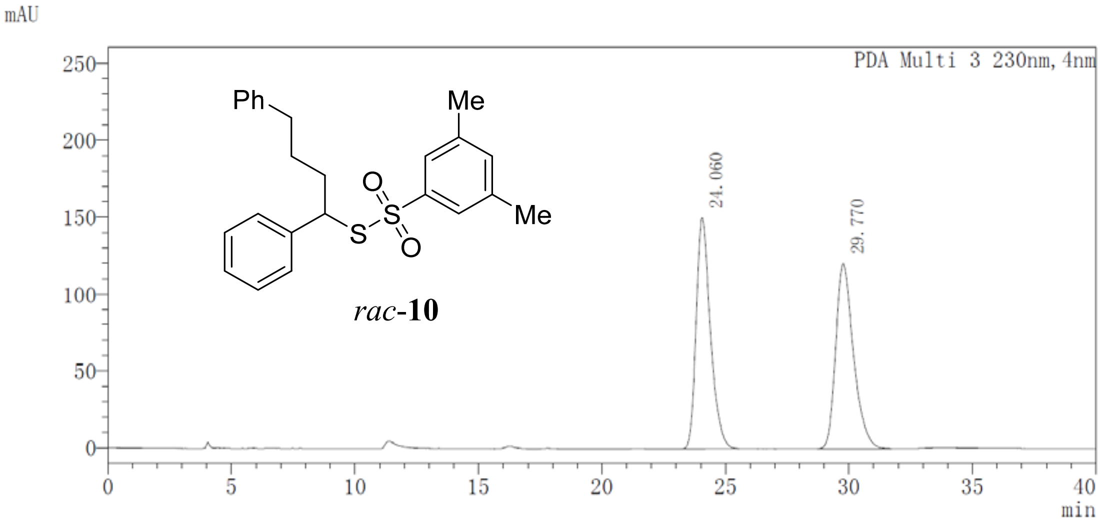
PDA Ch2 214nm

T	Hight	Area	Area%
15.200	94054	2608311	50.073
19.253	74428	2600659	49.927



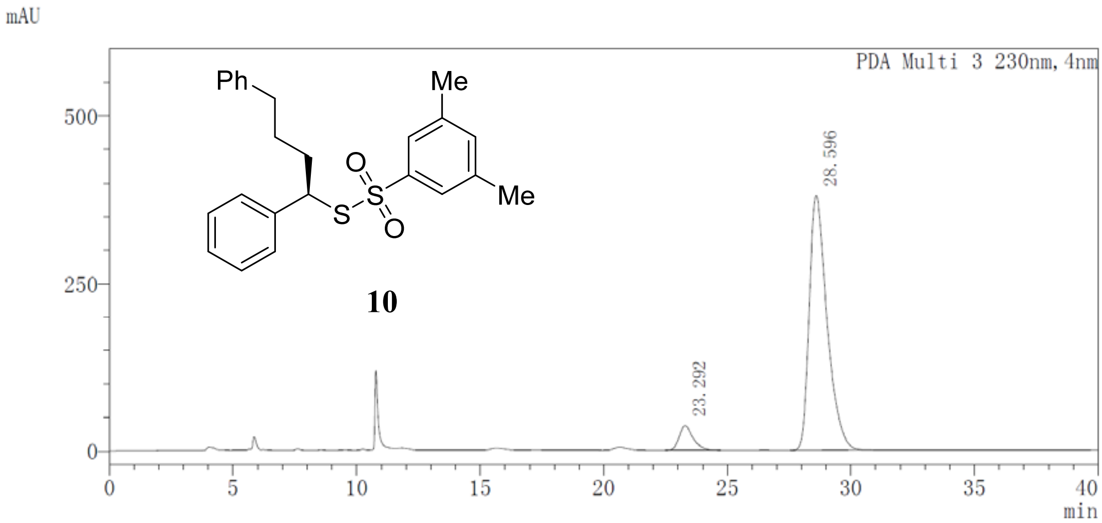
PDA Ch2 214nm

T	Hight	Area	Area%
15.066	32201	875199	5.556
19.076	414111	14876319	94.444



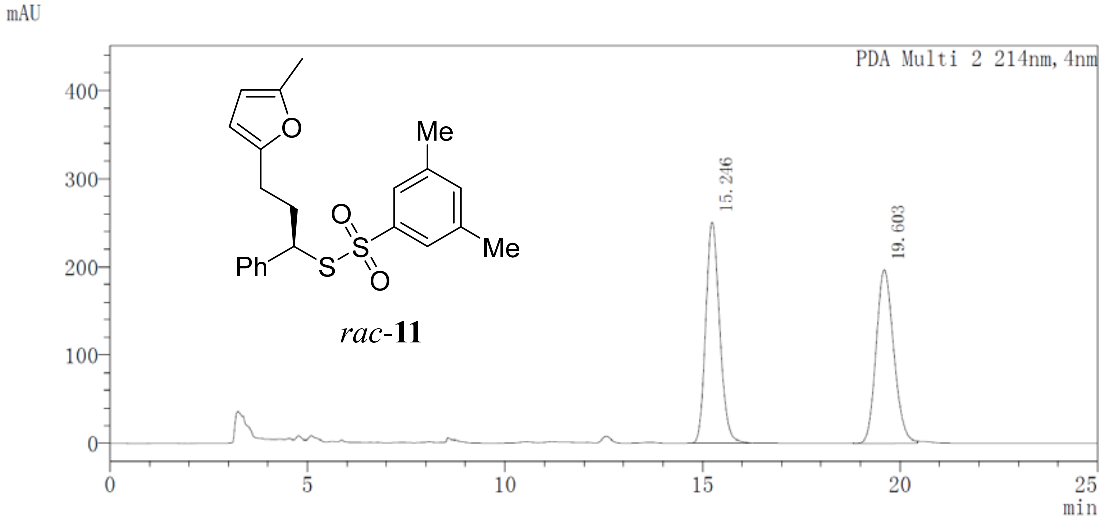
PDA Ch3 230nm

T	Hight	Area	Area%
24.060	150292	6000378	49.968
29.770	120251	6008024	50.032



PDA Ch3 230nm

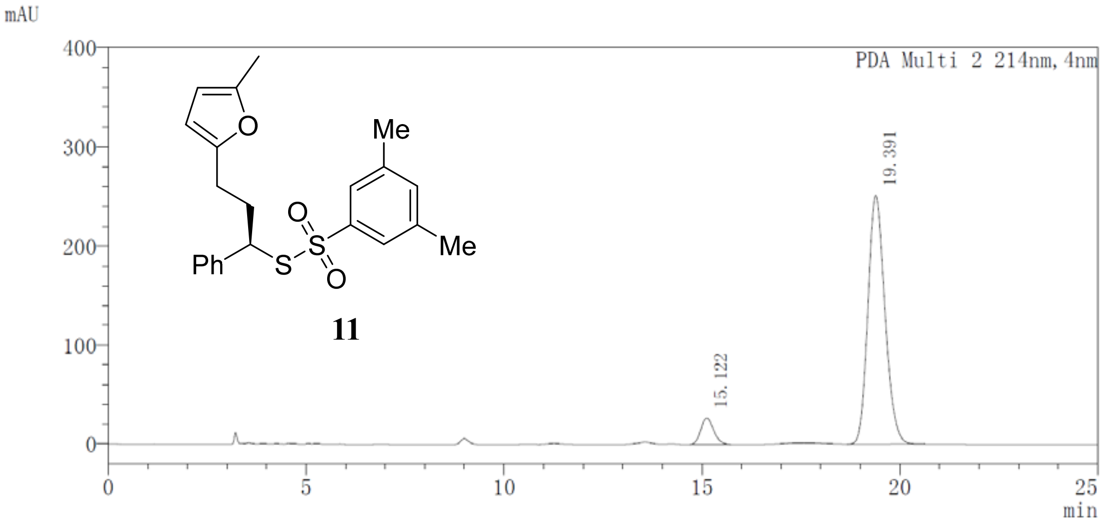
T	Hight	Area	Area%
23.292	36526	1433258	7.009
28.596	380290	19016121	92.991



rac-**11**

PDA Ch2 214nm

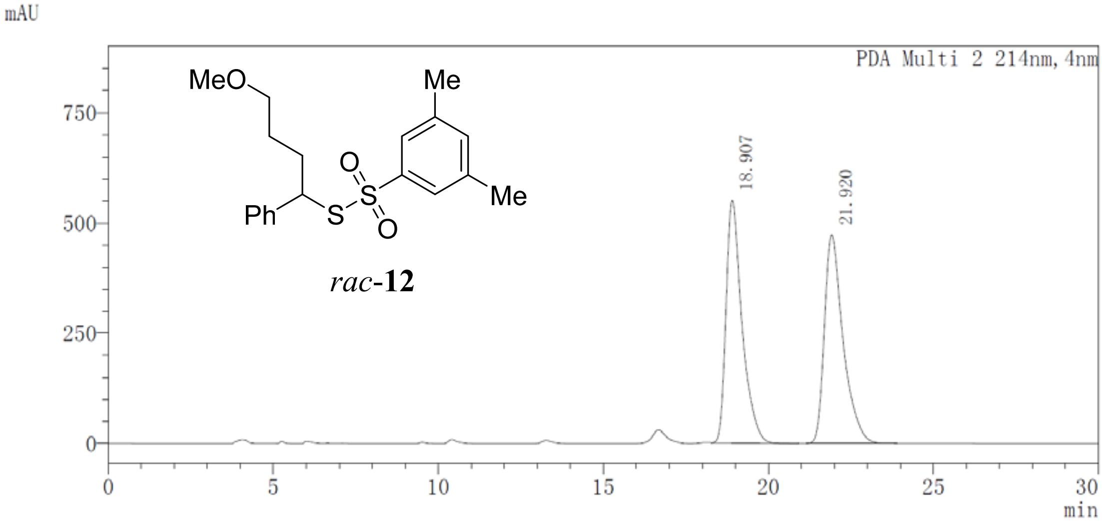
T	Hight	Area	Area%
15.246	251020	6138647	50.024
19.603	197101	6132793	49.976



11

PDA Ch2 214nm

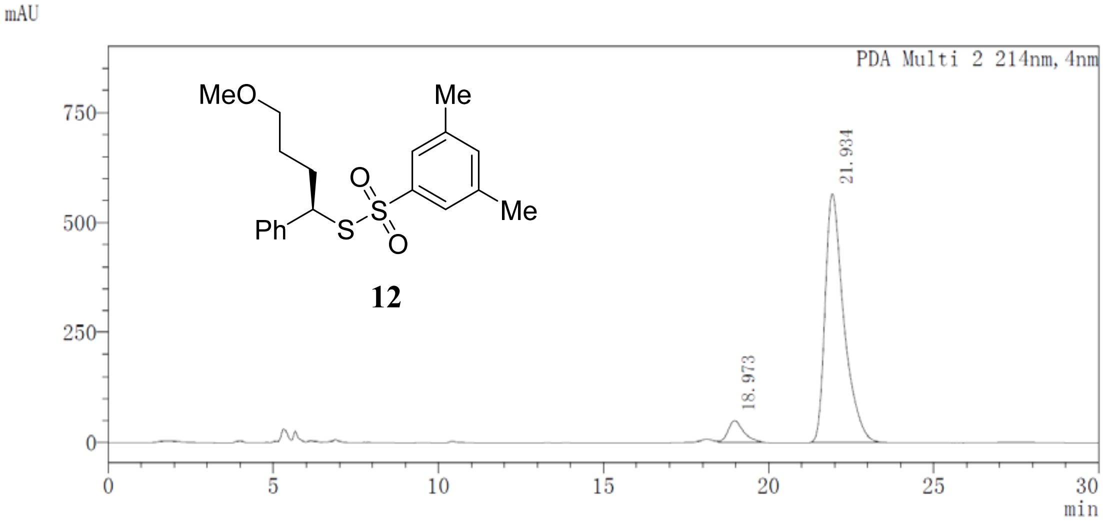
T	Hight	Area	Area%
15.122	26853	603477	7.433
19.391	251242	7515036	92.567



rac-**12**

PDA Ch2 214nm

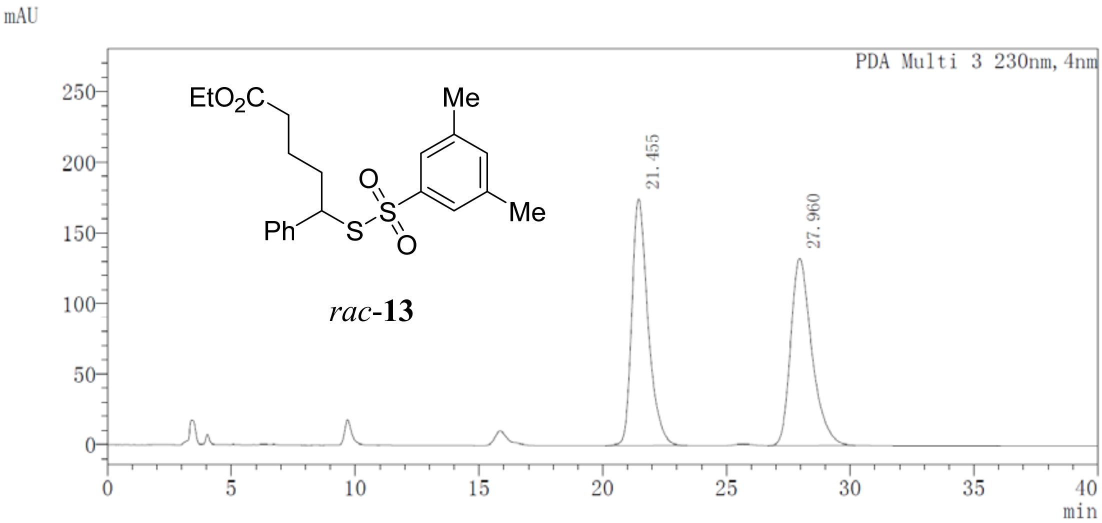
T	Hight	Area	Area%
18.907	550440	18484914	49.772
21.920	473180	18654472	50.228



12

PDA Ch2 214nm

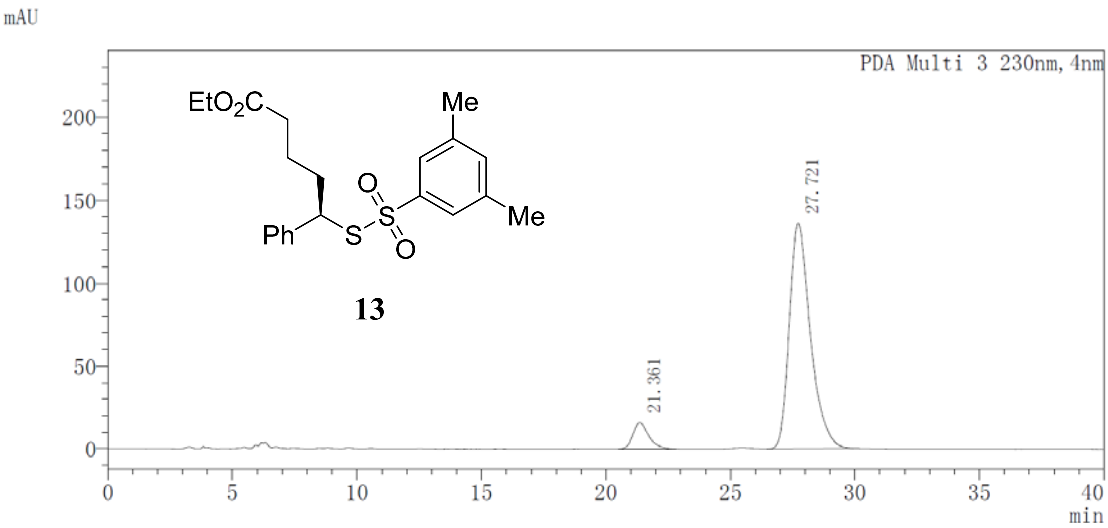
T	Hight	Area	Area%
18.973	48944	1548221	6.499
21.934	565047	22275284	93.501



rac-**13**

PDA Ch3 230nm

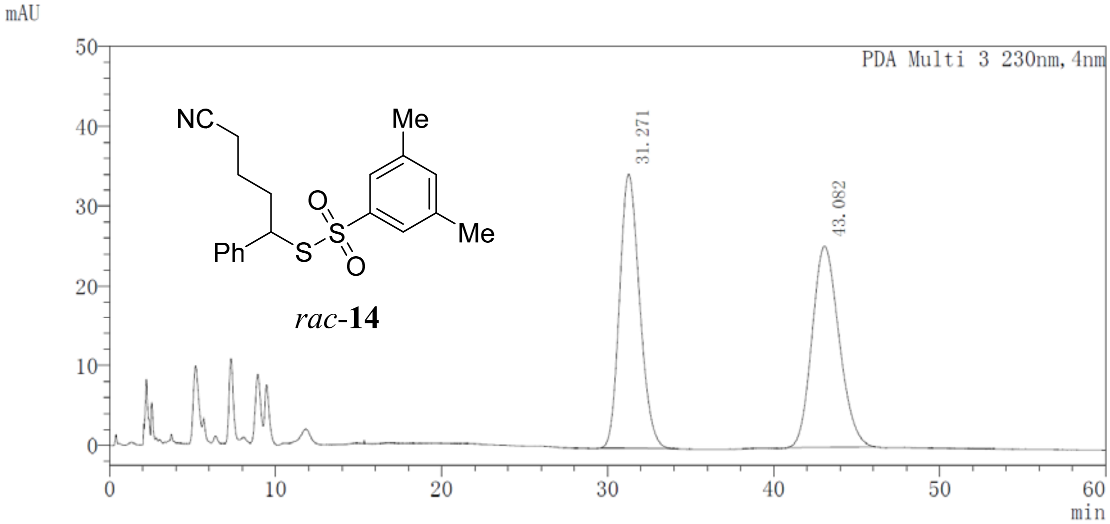
T	Hight	Area	Area%
21.455	174492	7940563	50.251
27.960	132268	7861218	49.749



13

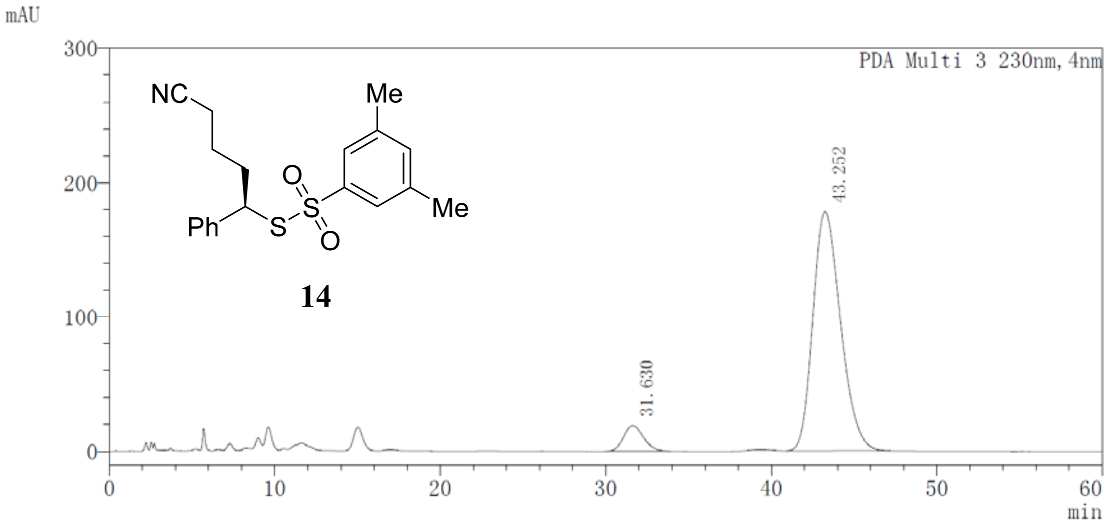
PDA Ch3 230nm

T	Hight	Area	Area%
21.361	16002	706336	8.064
27.721	136112	8053247	91.936



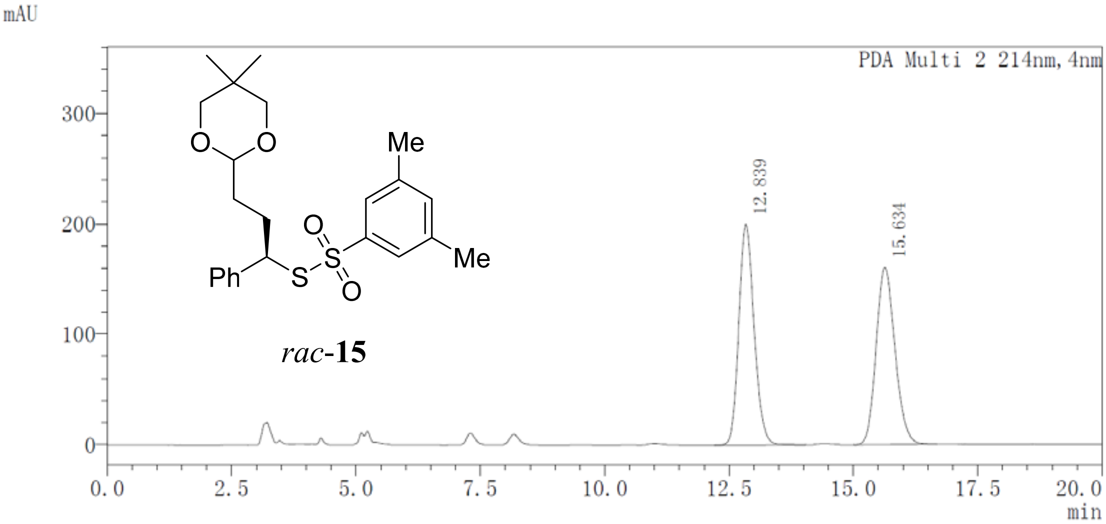
PDA Ch3 230nm

T	Hight	Area	Area%
31.271	34308	2874512	50.160
43.082	25204	2856223	49.840



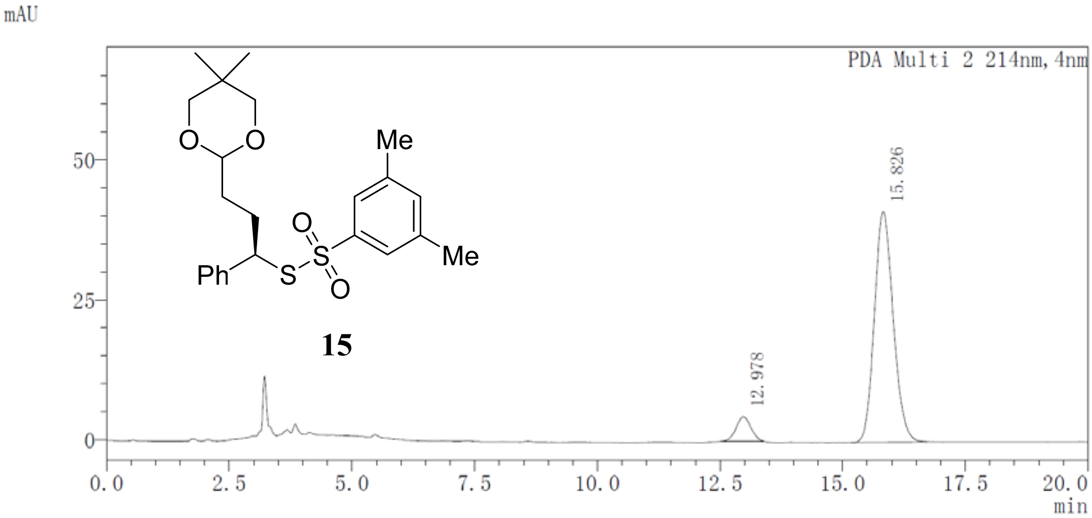
PDA Ch3 230nm

T	Hight	Area	Area%
31.630	19107	1598334	7.175
43.252	177909	20677589	92.825



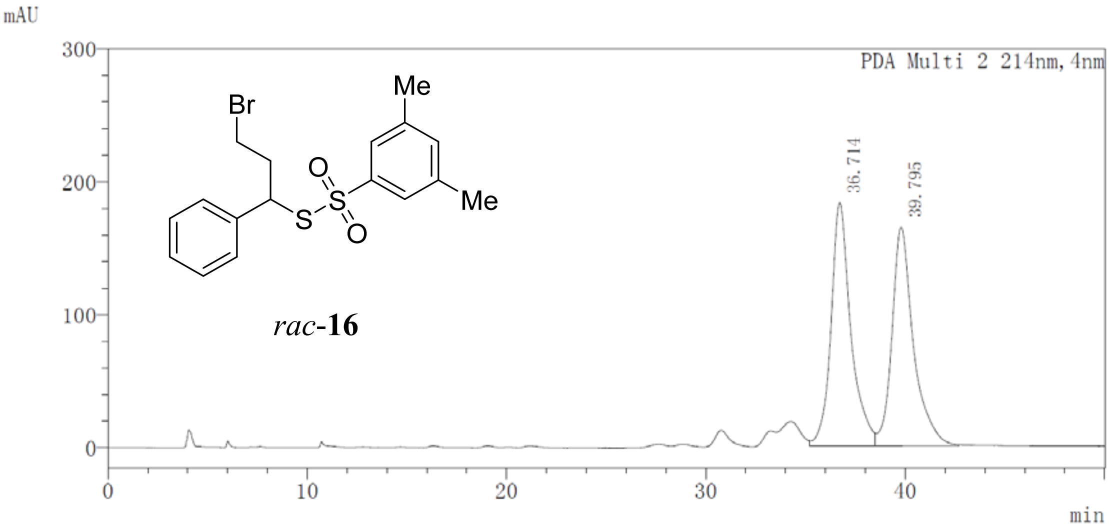
PDA Ch2 214nm

T	Hight	Area	Area%
12.839	199750	4265698	50.249
15.634	160334	4223485	49.751



PDA Ch2 214nm

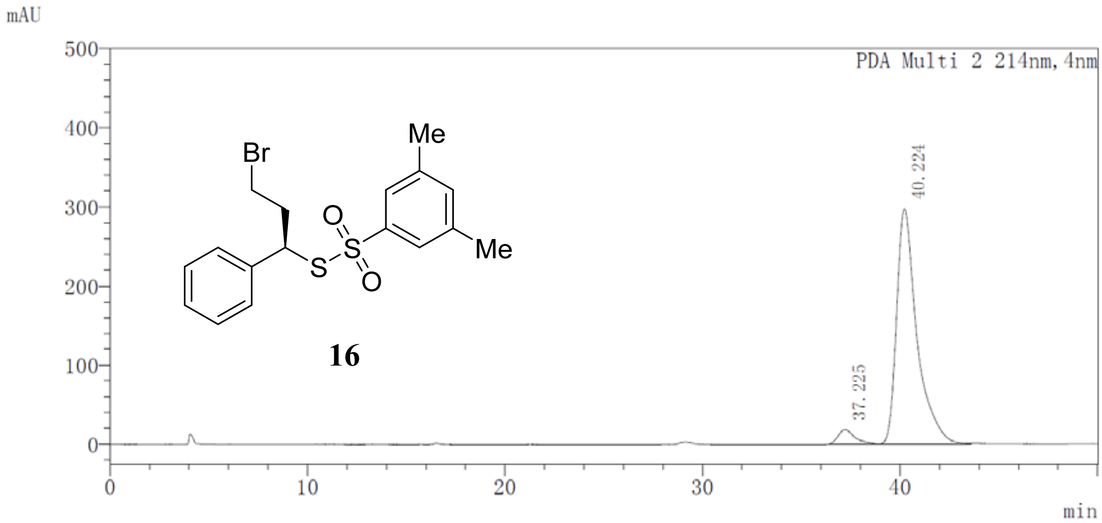
T	Hight	Area	Area%
12.978	4393	93666	7.873
15.826	41076	1096097	92.127



Peak Table

PDA Ch2 214nm

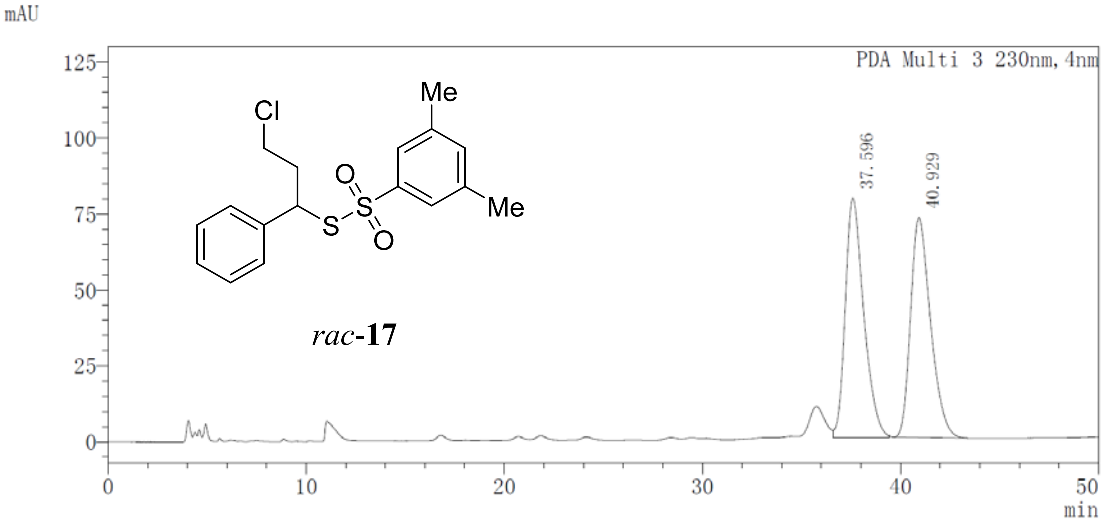
Peak#	Ret. Time	Area	Area%
1	36.714	12669850	50.640
2	39.795	12349512	49.360



Peak Table

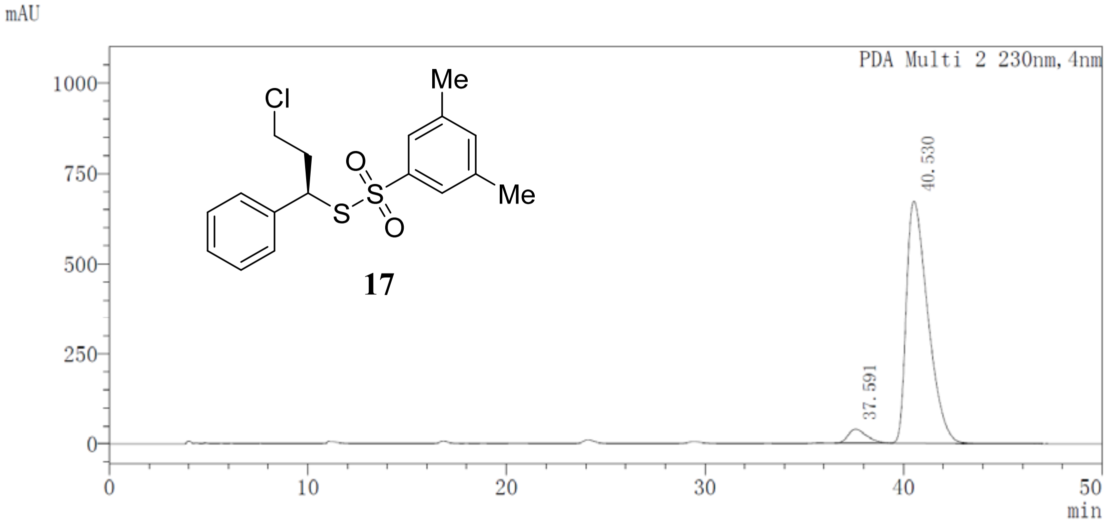
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	37.225	1045553	4.701
2	40.224	21197831	95.299



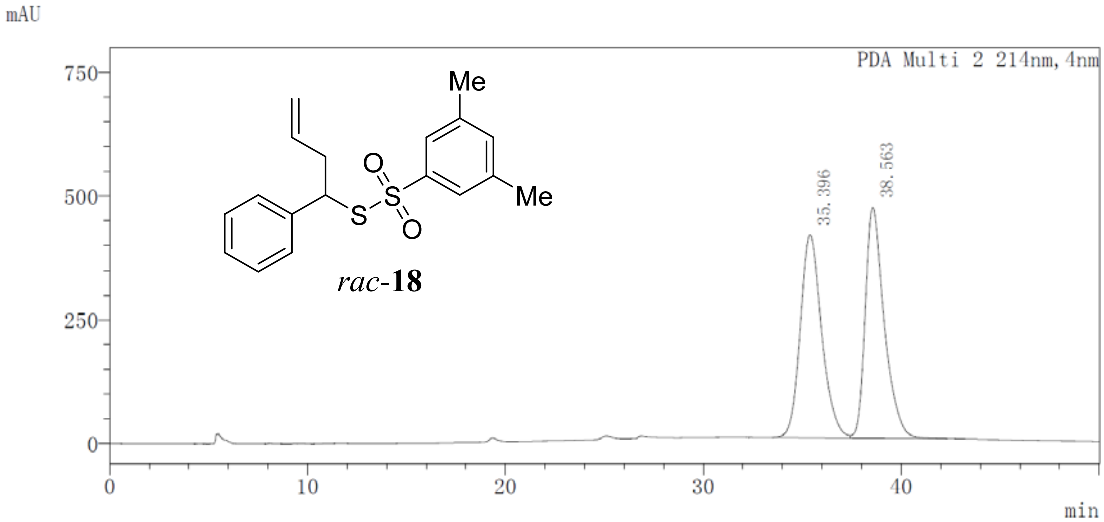
PDA Ch3 230nm

T	Hight	Area	Area%
37.596	78800	5099901	50.139
40.929	72383	5071606	49.861



PDA Ch2 230nm

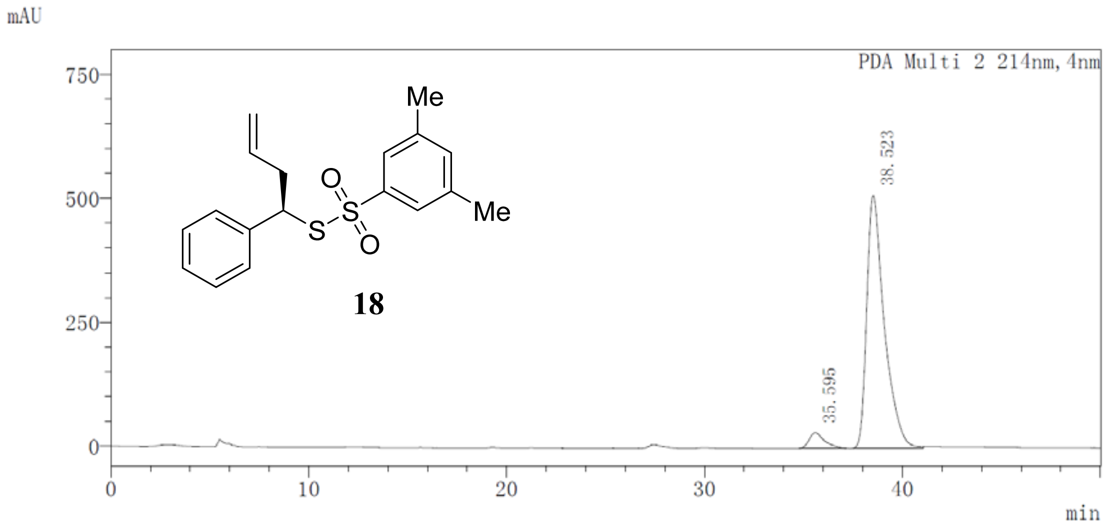
T	Hight	Area	Area%
37.591	39098	2486549	4.684
40.530	670939	50599447	95.316



Peak Table

PDA Ch2 214nm

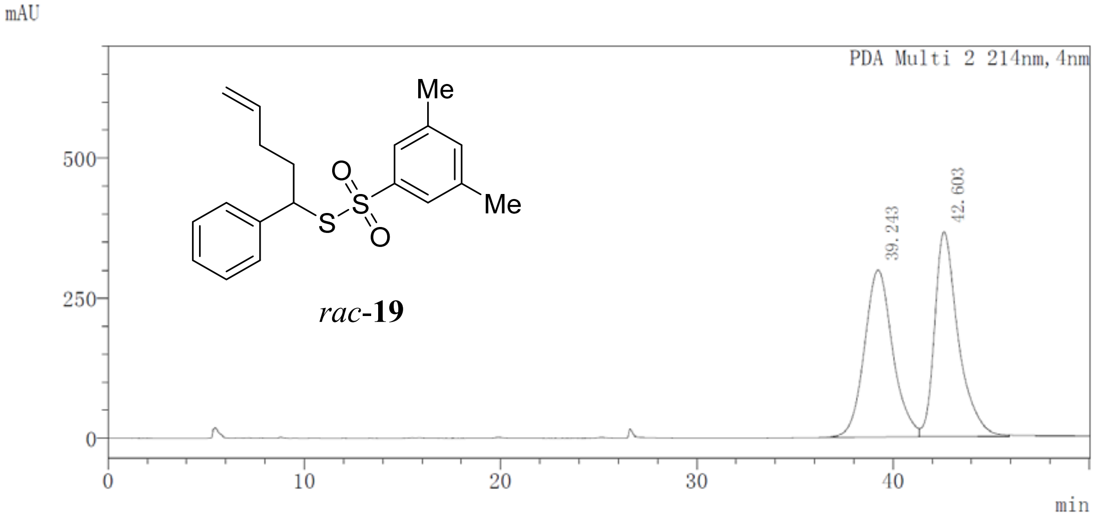
Peak#	Ret. Time	Area	Area%
1	35.396	30898732	49.785
2	38.563	31165803	50.215



Peak Table

PDA Ch2 214nm

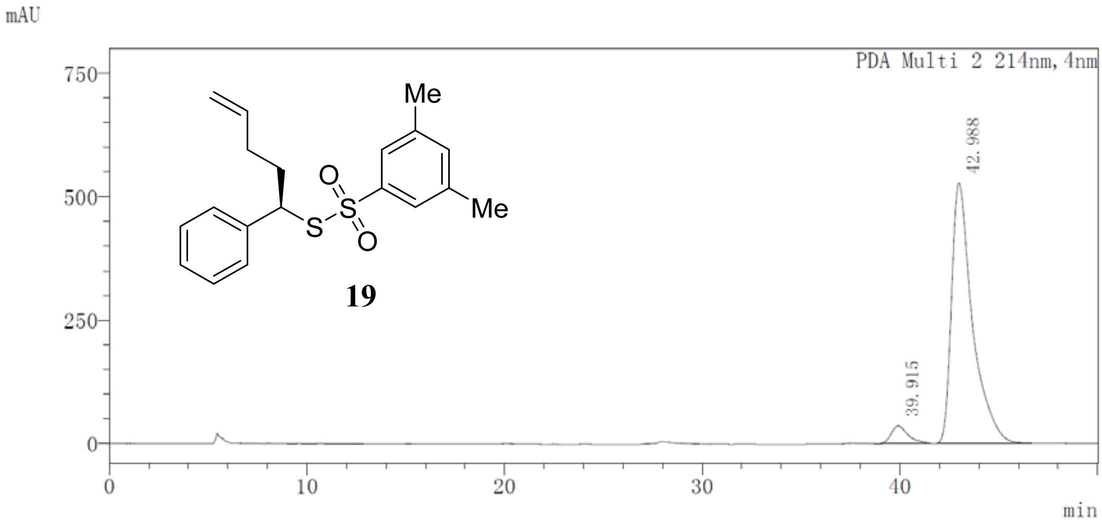
Peak#	Ret. Time	Area	Area%
1	35.595	1679186	5.060
2	38.523	31506008	94.940



Peak Table

PDA Ch2 214nm

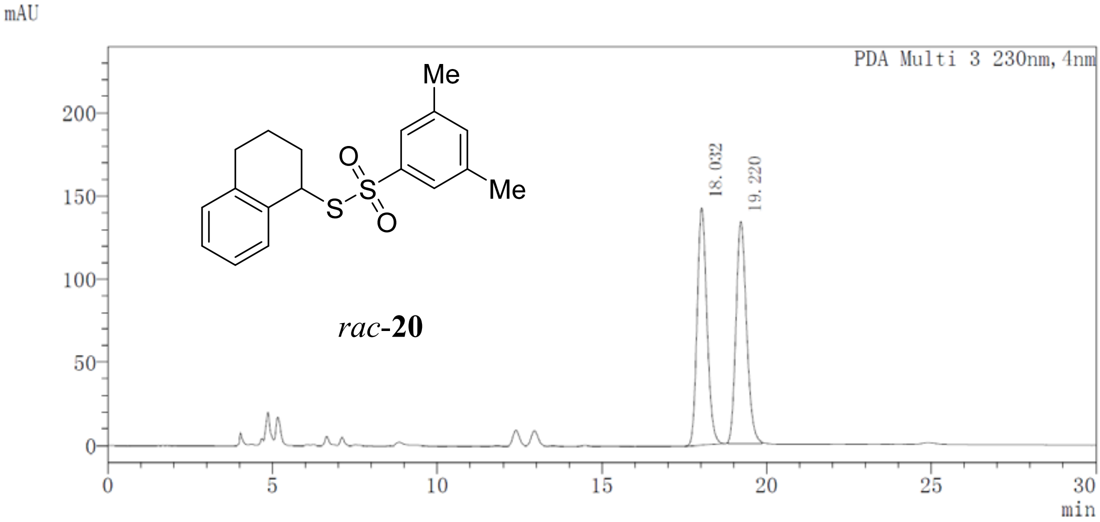
Peak#	Ret. Time	Area	Area%
1	39.243	29907225	49.241
2	42.603	30829769	50.759



Peak Table

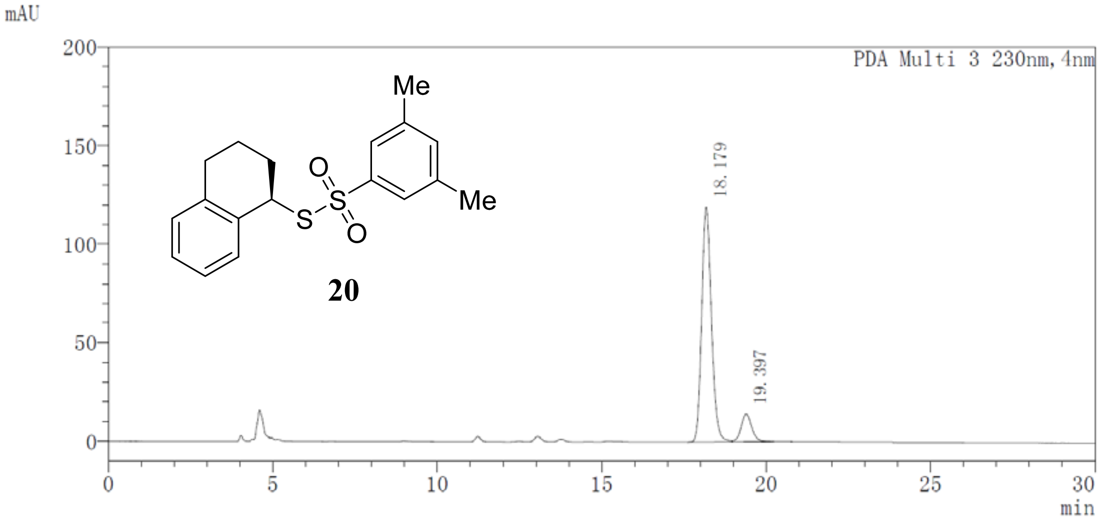
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	39.915	2092683	5.108
2	42.988	38878166	94.892



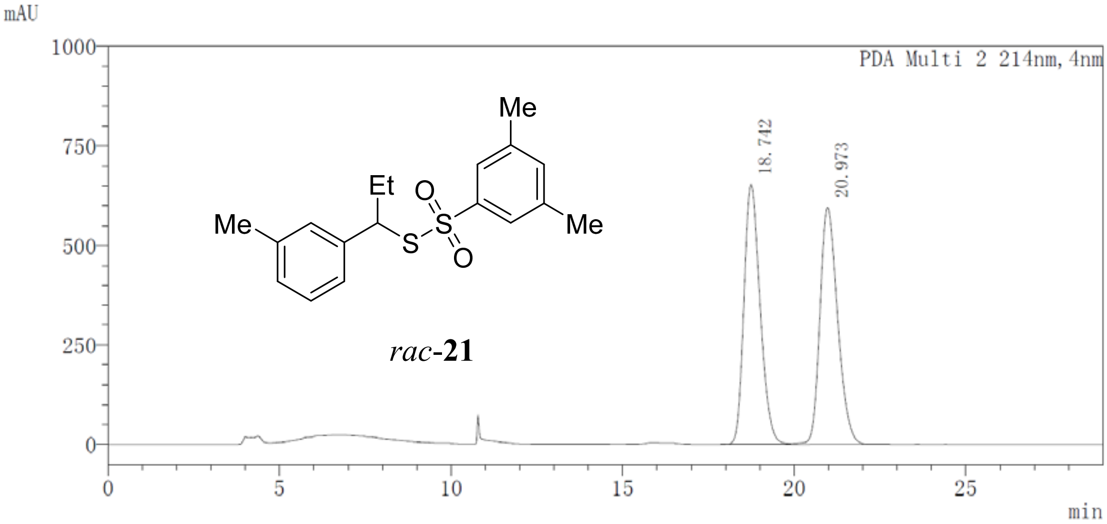
PDA Ch3 230nm

T	Hight	Area	Area%
18.032	142887	2954148	49.937
19.220	133485	2961615	50.063



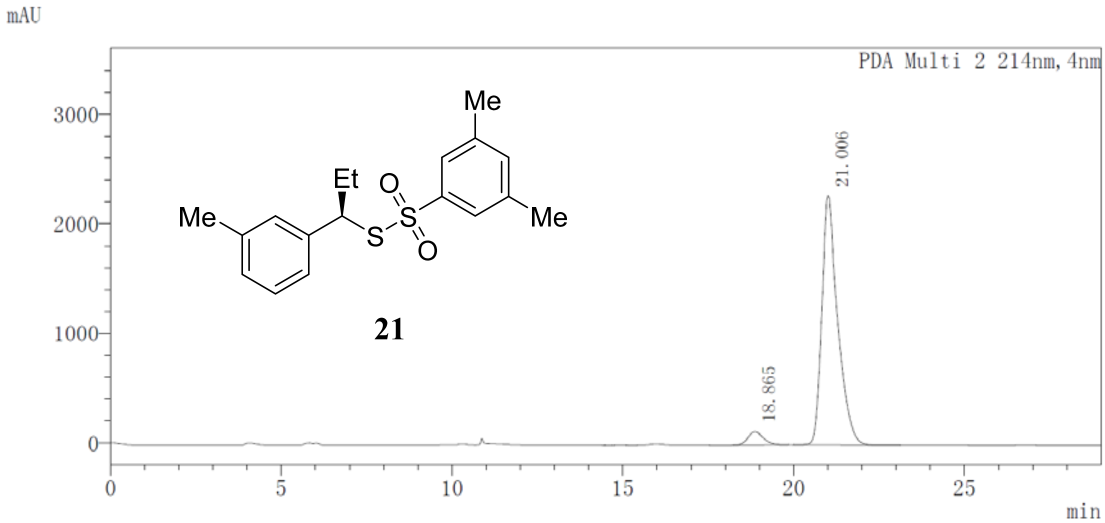
PDA Ch3 230nm

T	Hight	Area	Area%
18.179	119246	2453140	88.593
19.397	14074	315845	11.407



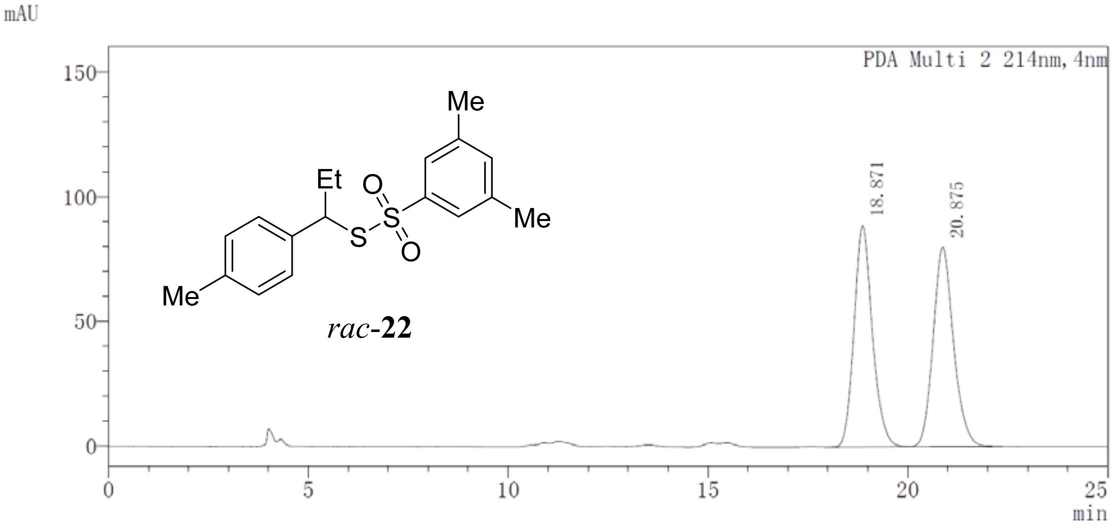
PDA Ch2 214nm

T	Hight	Area	Area%
18.742	653023	21351237	50.020
20.973	594982	21333921	49.980



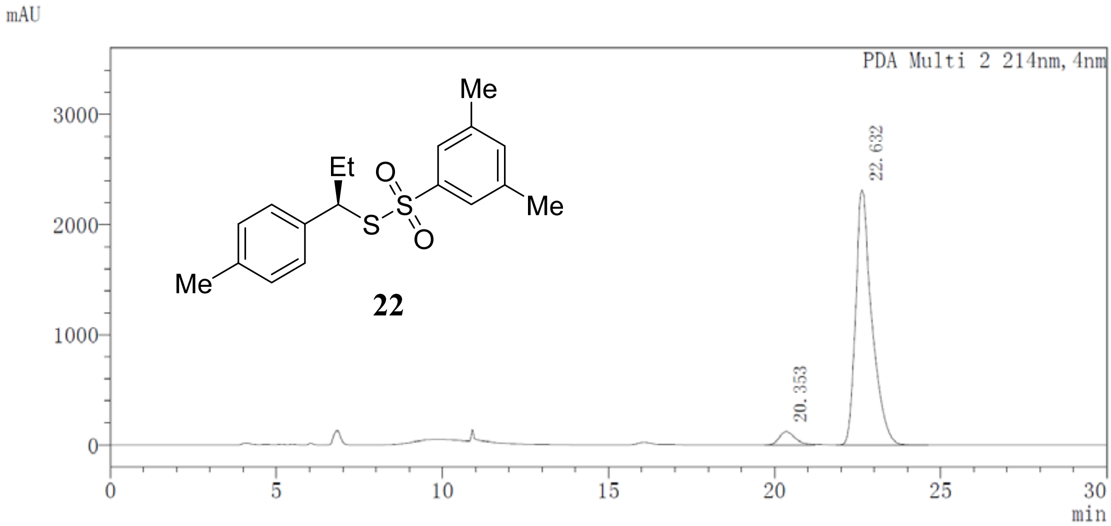
PDA Ch2 214nm

T	Hight	Area	Area%
18.865	123704	3862936	4.996
21.006	2273772	73457719	95.004



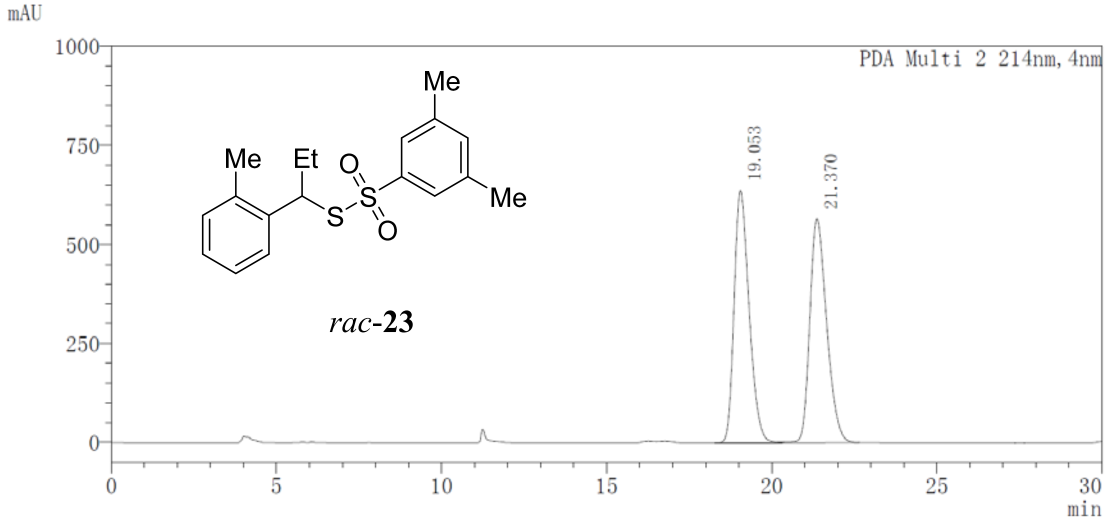
PDA Ch2 214nm

T	Hight	Area	Area%
18.871	88502	2828989	49.913
20.875	79903	2838873	50.087



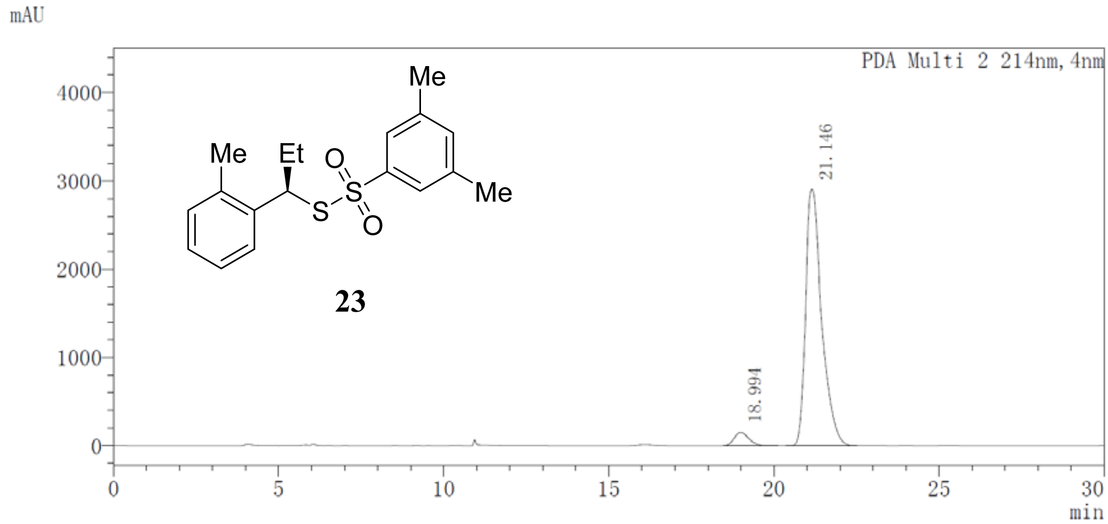
PDA Ch2 214nm

T	Hight	Area	Area%
20.353	122278	4163974	5.030
22.632	2311520	78614100	94.970



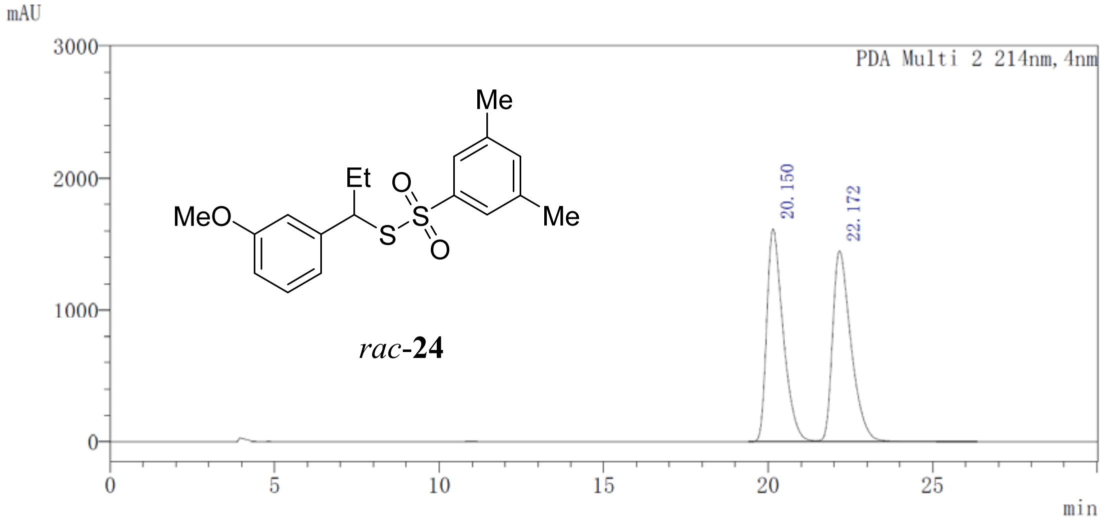
PDA Ch2 214nm

T	Hight	Area	Area%
19.053	636304	20093260	50.061
21.370	564731	20044651	49.939



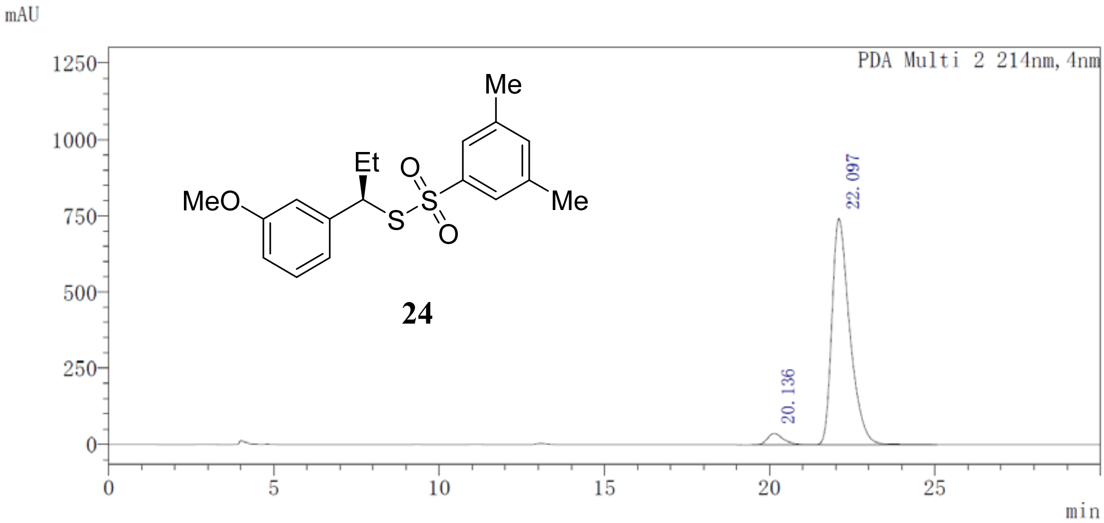
PDA Ch2 214nm

T	Hight	Area	Area%
18.994	153593	4777801	4.642
21.146	2907391	98146756	95.358



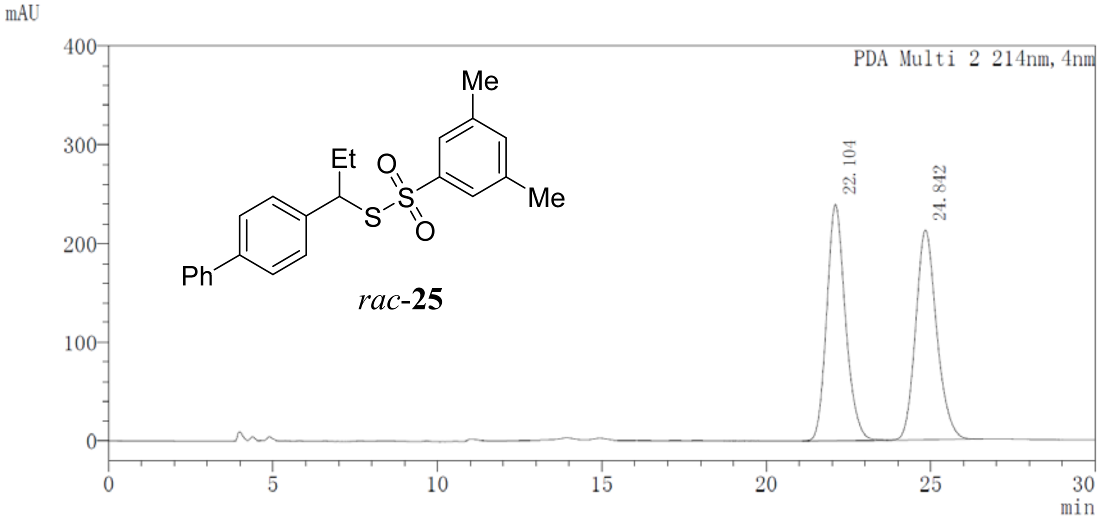
PDA Ch2 214nm

T	Hight	Area	Area%
20.150	1617825	56057133	49.749
22.172	1450152	56622997	50.251



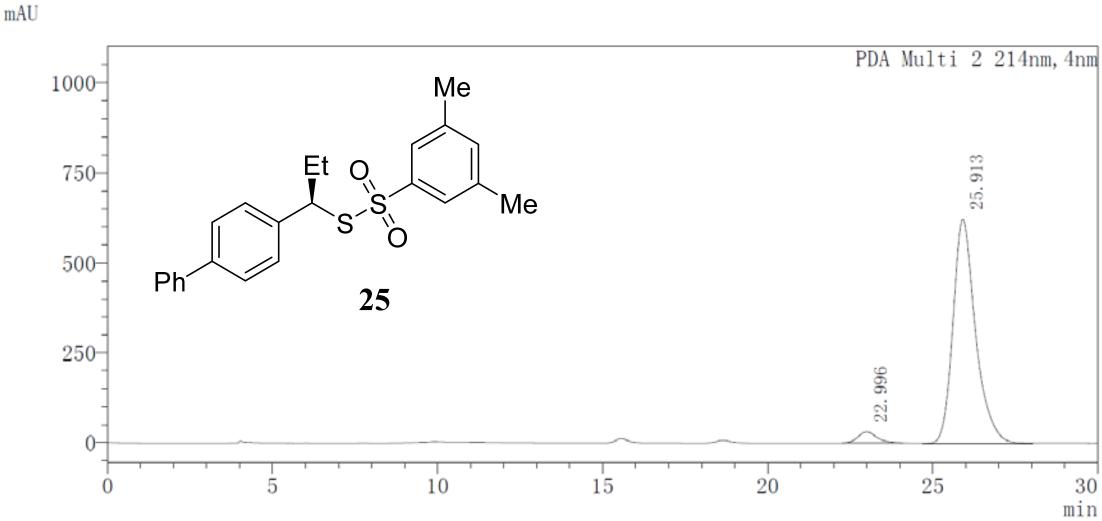
PDA Ch2 214nm

T	Hight	Area	Area%
20.136	37268	1228563	4.232
22.097	740827	27804243	95.768



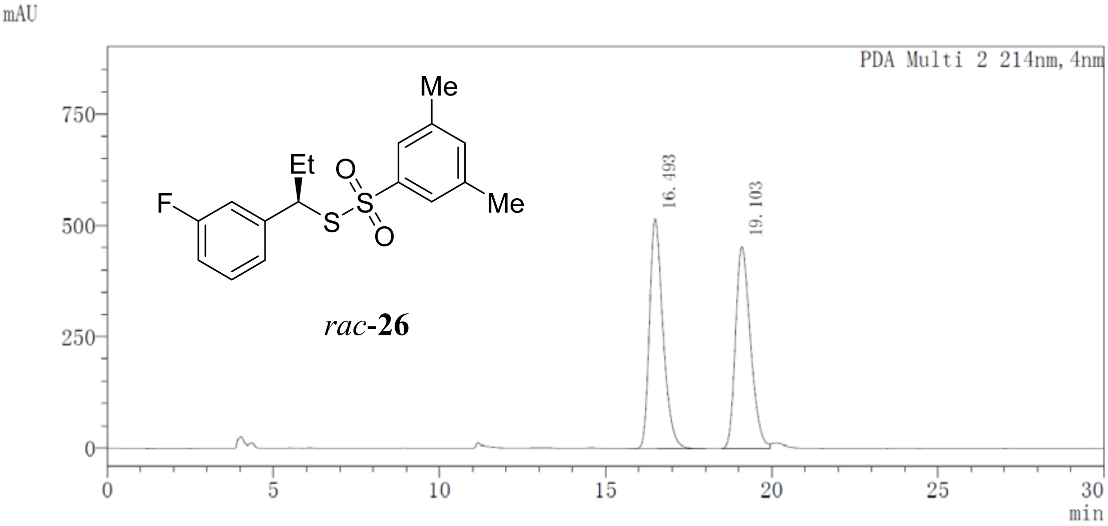
PDA Ch2 214nm

T	Hight	Area	Area%
22.104	239452	9480182	49.999
24.842	212830	9480530	50.001



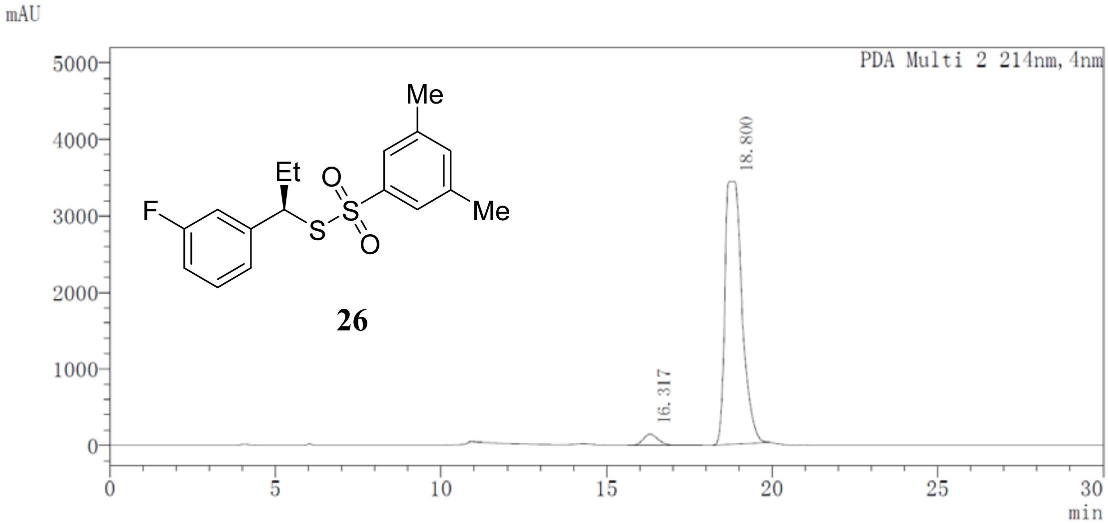
PDA Ch2 214nm

T	Hight	Area	Area%
22.996	32580	1305689	4.223
25.913	623333	29609744	95.777



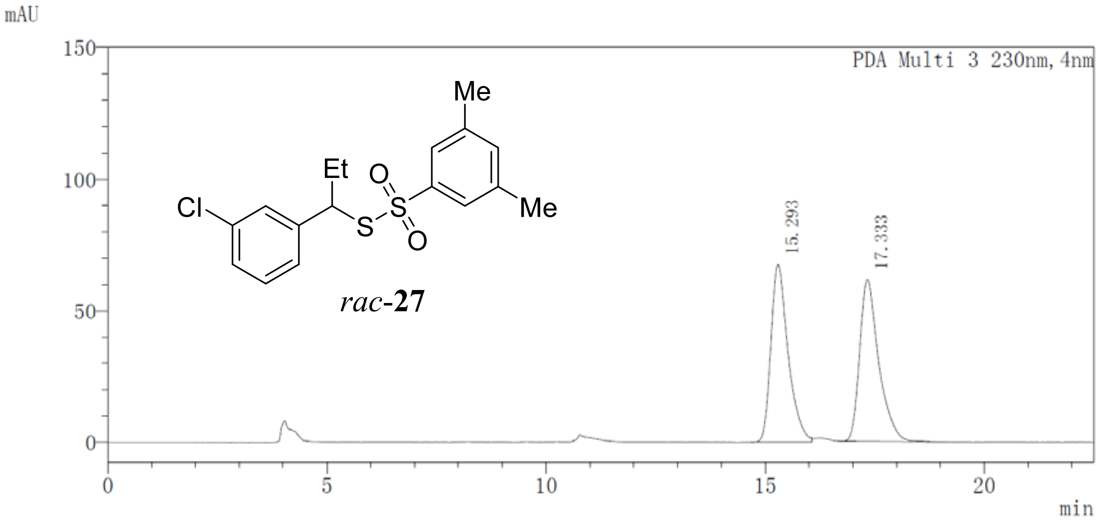
PDA Ch2 214nm

T	Hight	Area	Area%
16.493	514707	14562075	50.555
19.103	453383	14242460	49.445



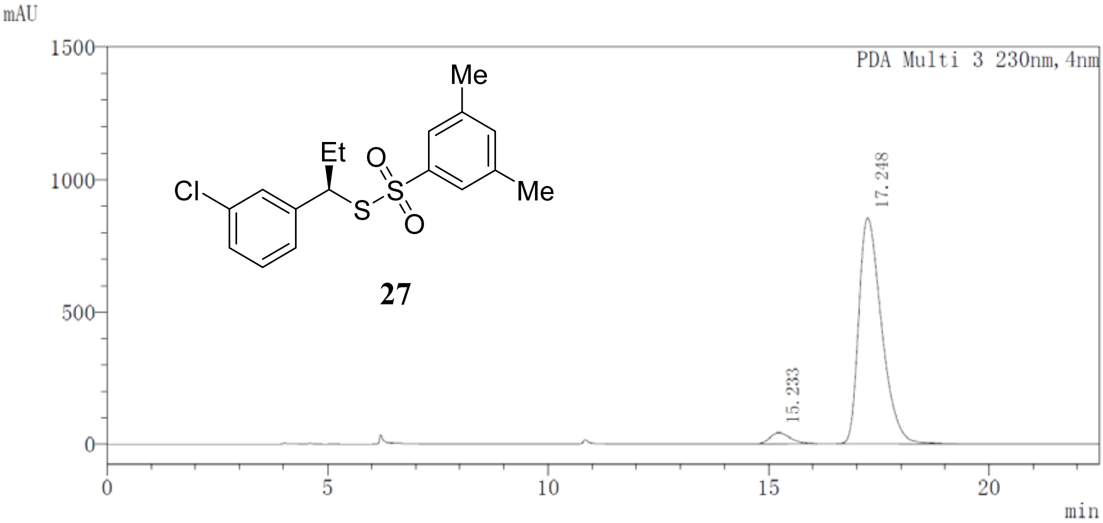
PDA Ch2 214nm

T	Hight	Area	Area%
16.317	144950	4587210	3.593
18.800	3433945	123074142	96.407



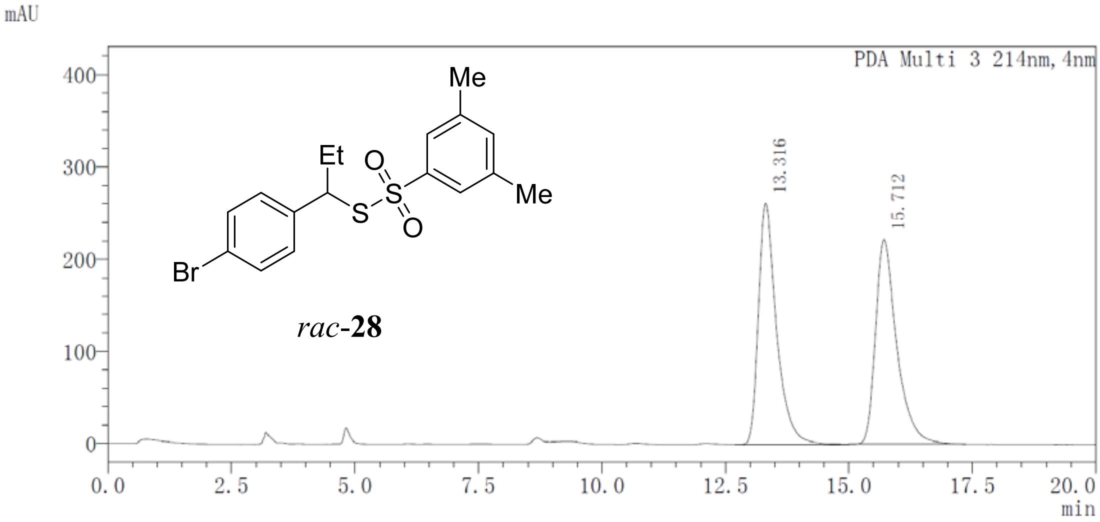
PDA Ch3 230nm

T	Hight	Area	Area%
15.293	67656	1846037	49.684
17.333	61575	1869483	50.316



PDA Ch3 230nm

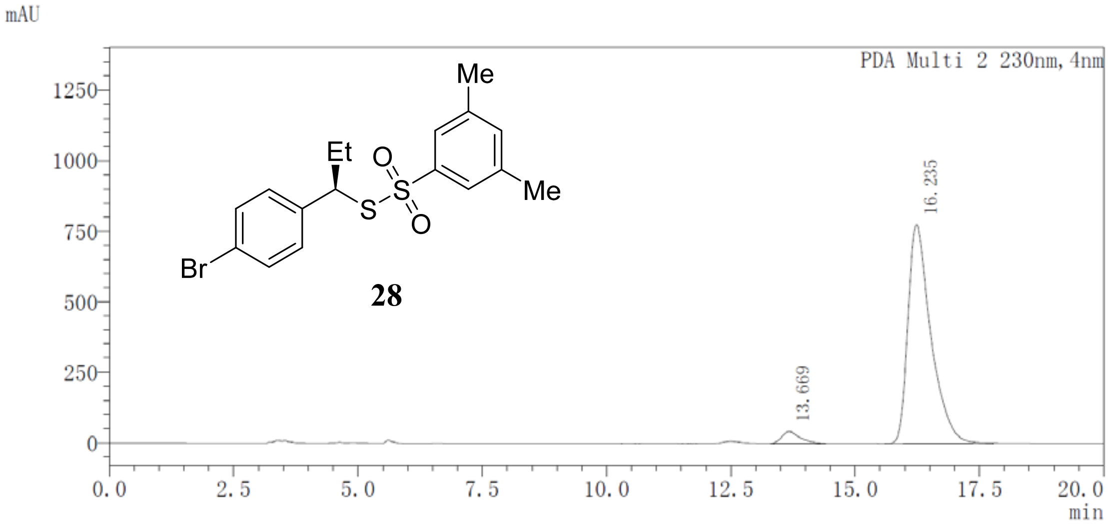
T	Hight	Area	Area%
15.233	41544	1296315	4.047
17.248	854397	30736560	95.953



rac-**28**

PDA Ch3 214nm

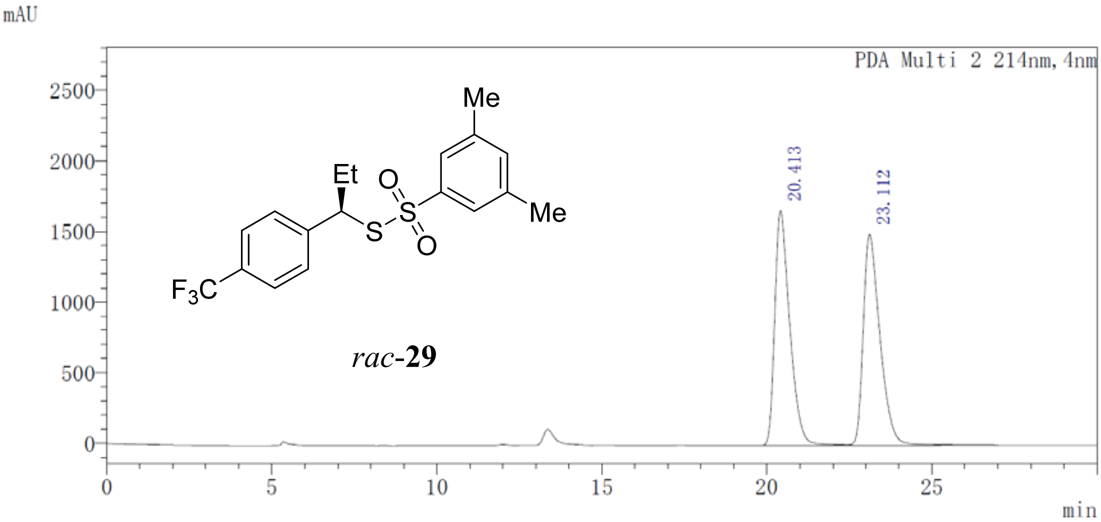
T	Hight	Area	Area%
13.316	260416	6662816	50.089
15.712	221452	6639180	49.911



28

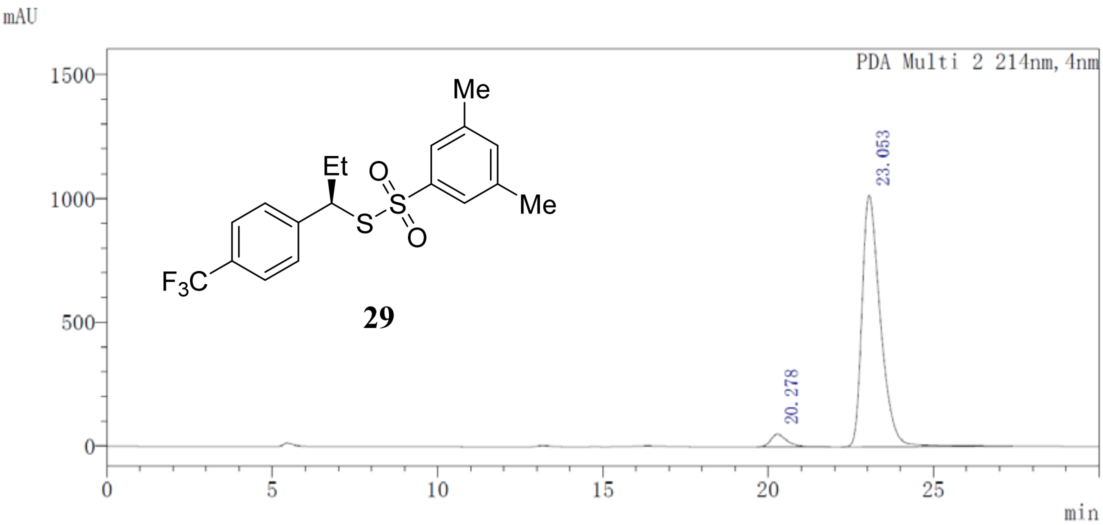
PDA Ch2 230nm

T	Hight	Area	Area%
13.669	42538	1066671	4.100
16.235	776407	24947828	95.900



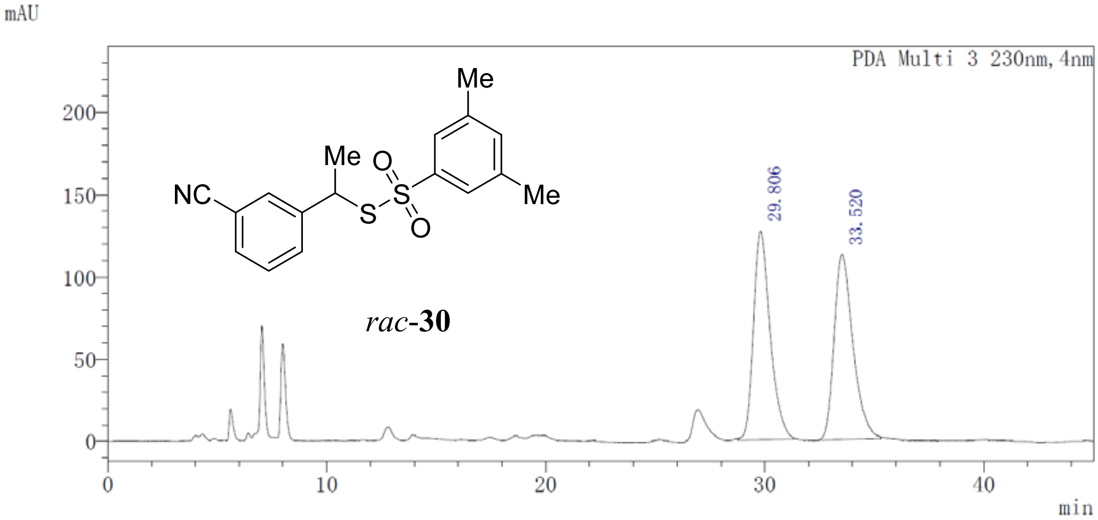
PDA Ch2 214nm

T	Hight	Area	Area%
20.413	1660533	52219775	49.851
23.112	1491375	52532813	50.149



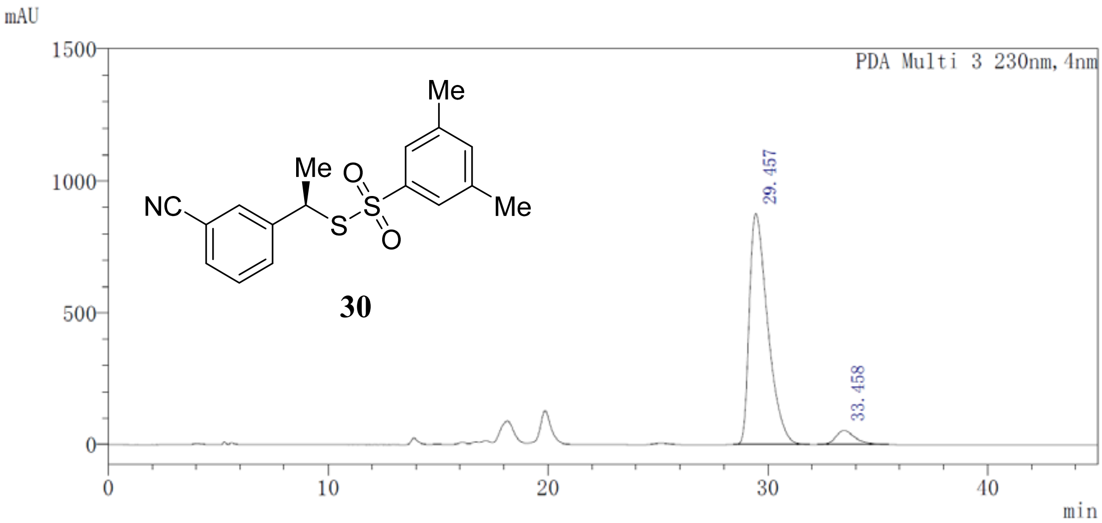
PDA Ch2 214nm

T	Hight	Area	Area%
20.278	50444	1673396	4.117
23.053	1014288	38972494	95.883



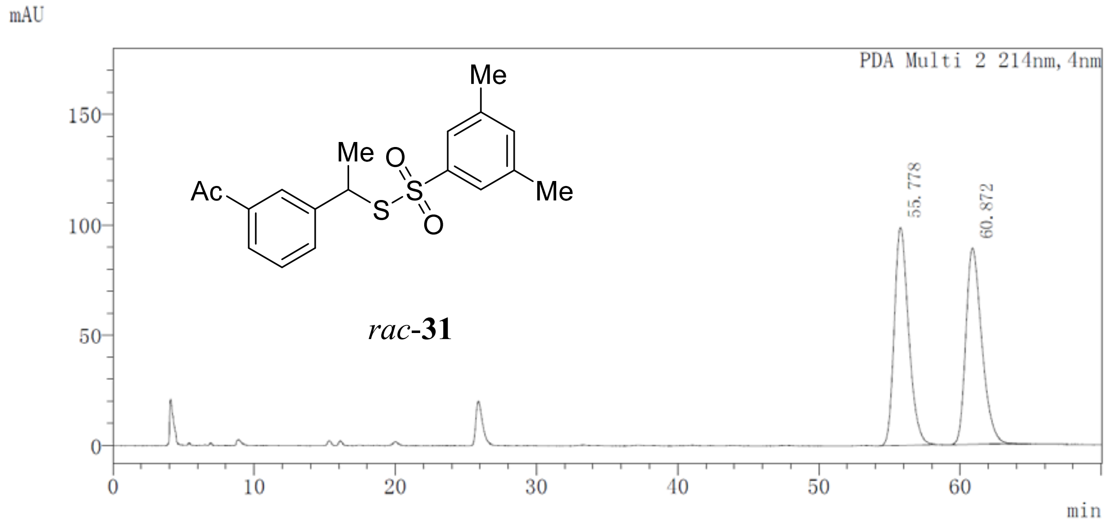
PDA Ch3 230nm

T	Hight	Area	Area%
29.806	126952	6709551	49.948
33.520	112676	6723391	50.052



PDA Ch3 230nm

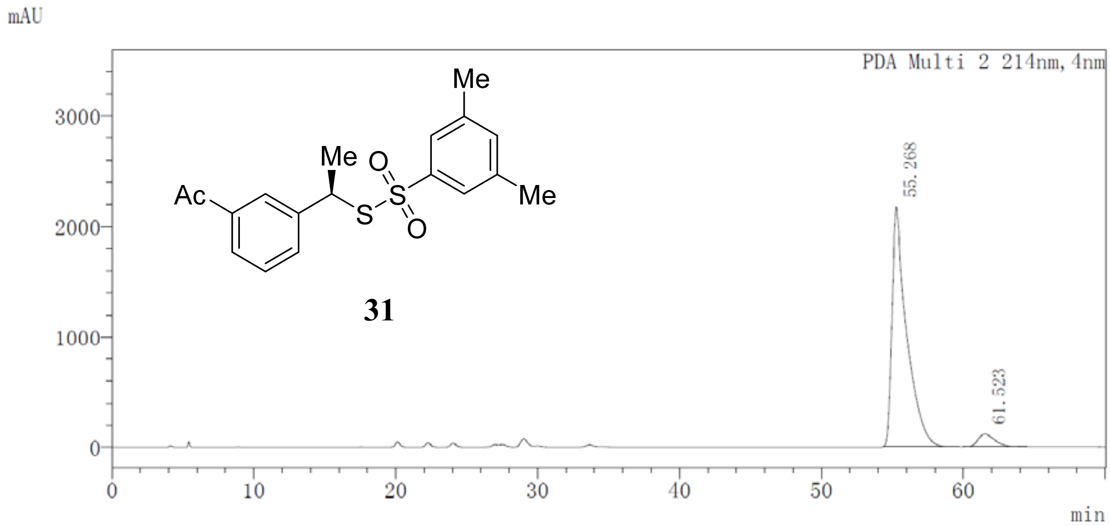
T	Hight	Area	Area%
29.457	876044	50972839	94.003
33.458	53484	3251874	5.997



Peak Table

PDA Ch2 214nm

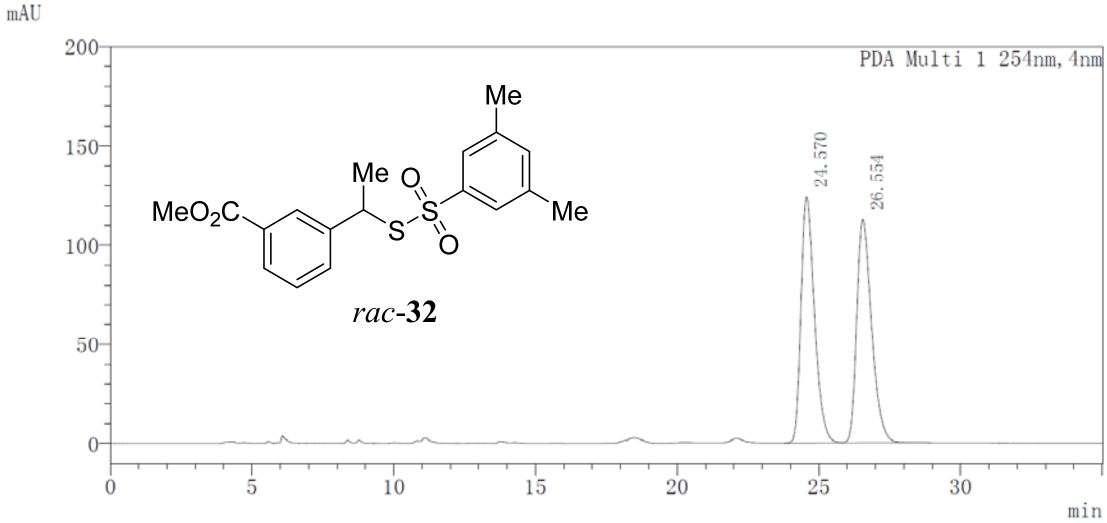
Peak#	Ret. Time	Area	Area%
1	55.778	6982046	49.928
2	60.872	7002321	50.072



Peak Table

PDA Ch2 214nm

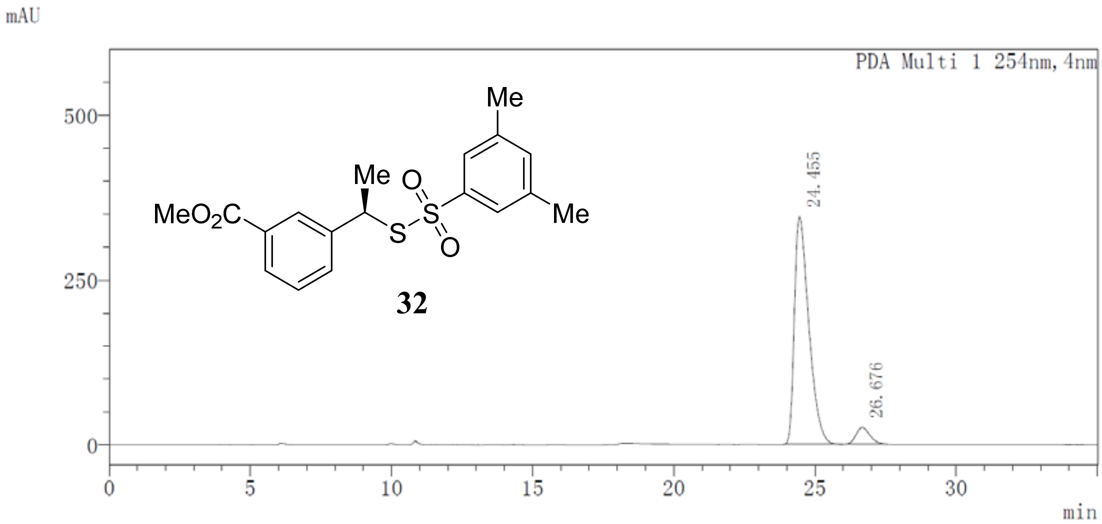
Peak#	Ret. Time	Area	Area%
1	55.268	155313083	94.276
2	61.523	9429281	5.724



Peak Table

PDA Ch1 254nm

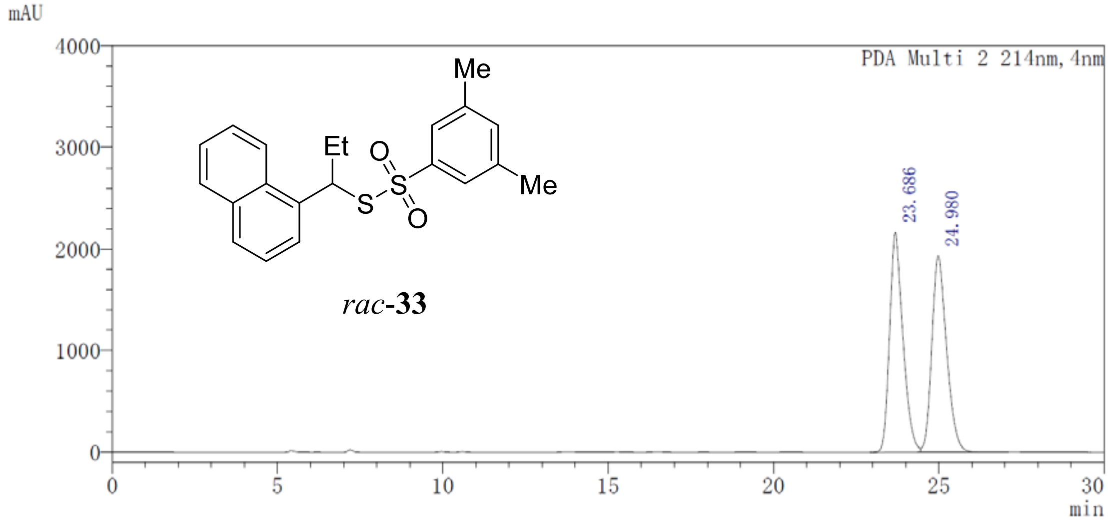
Peak#	Ret. Time	Area	Area%
1	24.570	4108846	50.003
2	26.554	4108398	49.997



Peak Table

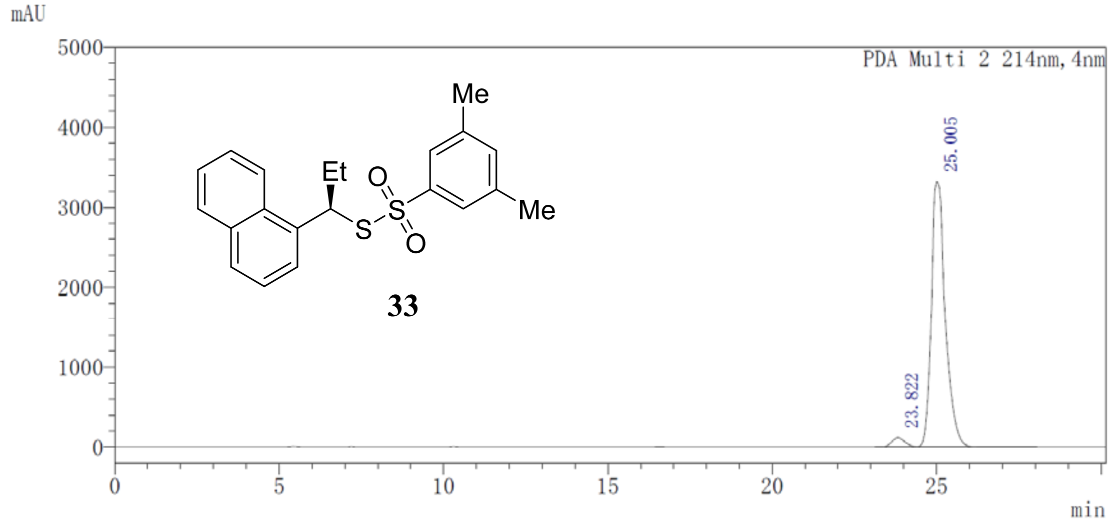
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.455	12278353	93.324
2	26.676	878330	6.676



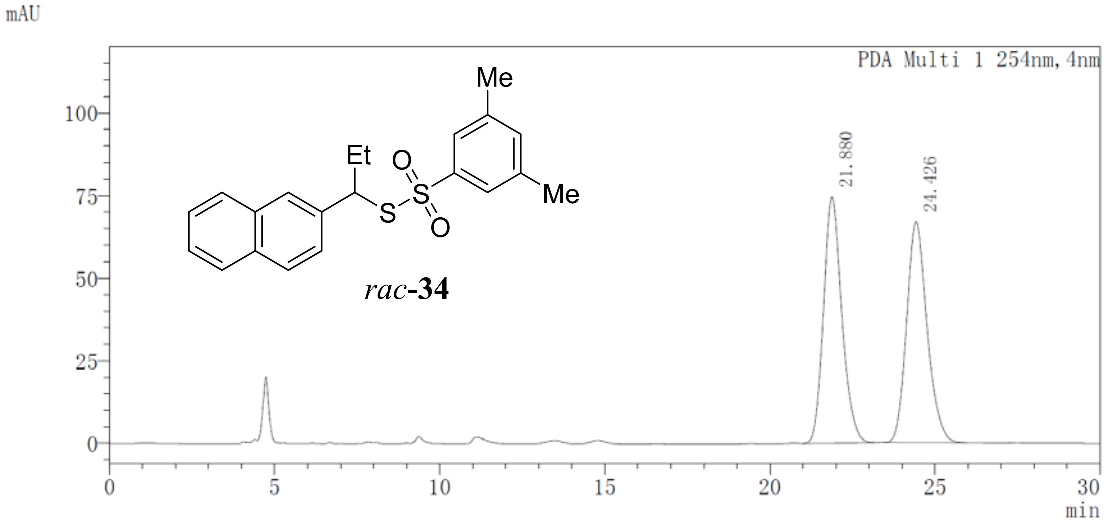
PDA Ch2 214nm

T	Hight	Area	Area%
23.686	2169874	60540714	50.228
24.980	1935396	59991702	49.772



PDA Ch2 214nm

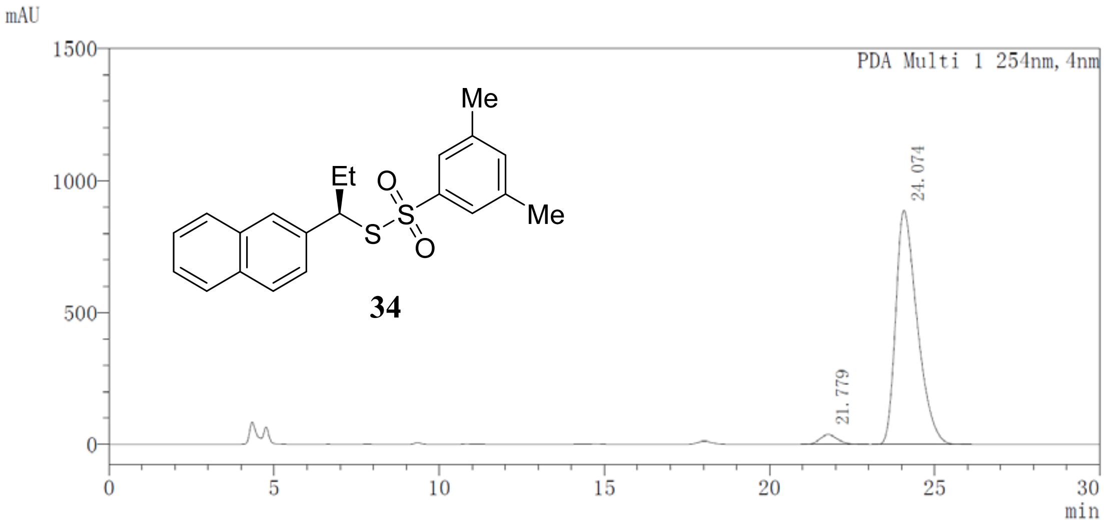
T	Hight	Area	Area%
23.822	116624	3327716	3.278
25.005	3323083	98196349	96.722



PDA Ch1 254nm

T	Hight	Area	Area%
21.880	74501	2871647	49.886
24.426	66915	2884728	50.114

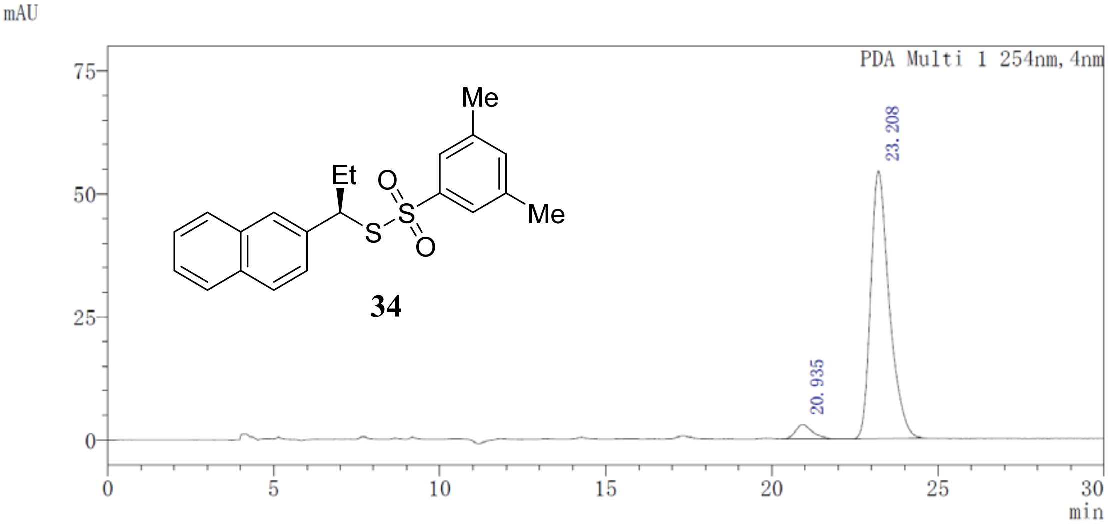
34 was prepared from 2-(1-bromopropyl)naphthalene **E31**:



PDA Ch1 254nm

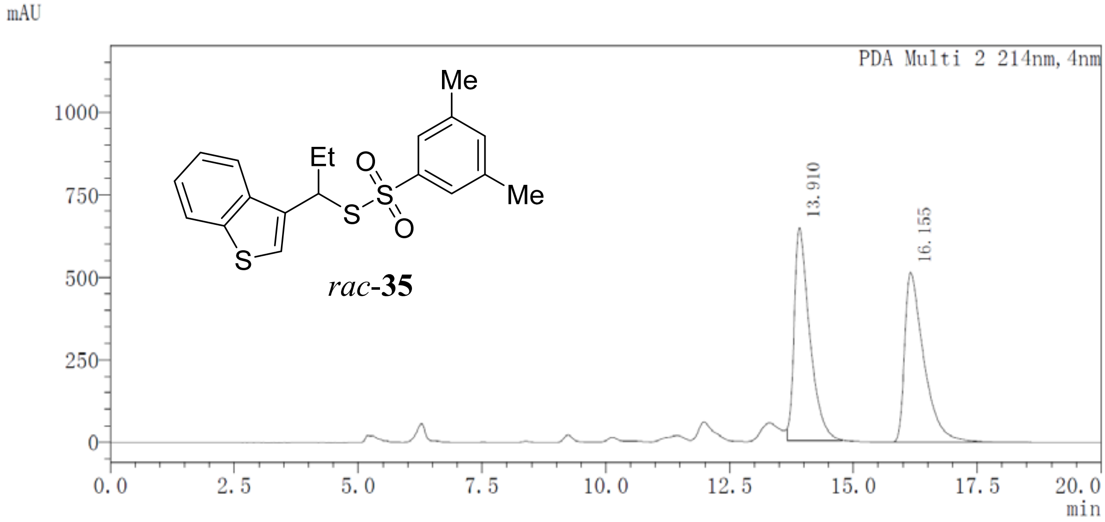
T	Hight	Area	Area%
21.779	37634	1424263	3.424
24.074	886600	40166670	96.576

34 was prepared from 2-(1-chloropropyl)naphthalene **E36**:



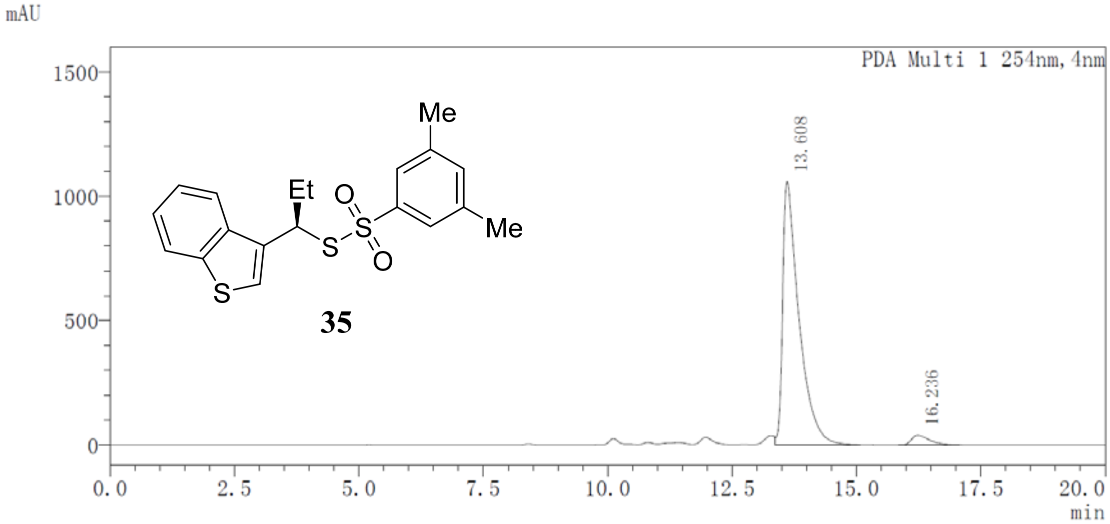
PDA Ch1 254nm

T	Hight	Area	Area%
20.935	2880	99940	4.526
23.208	54349	2108424	95.474



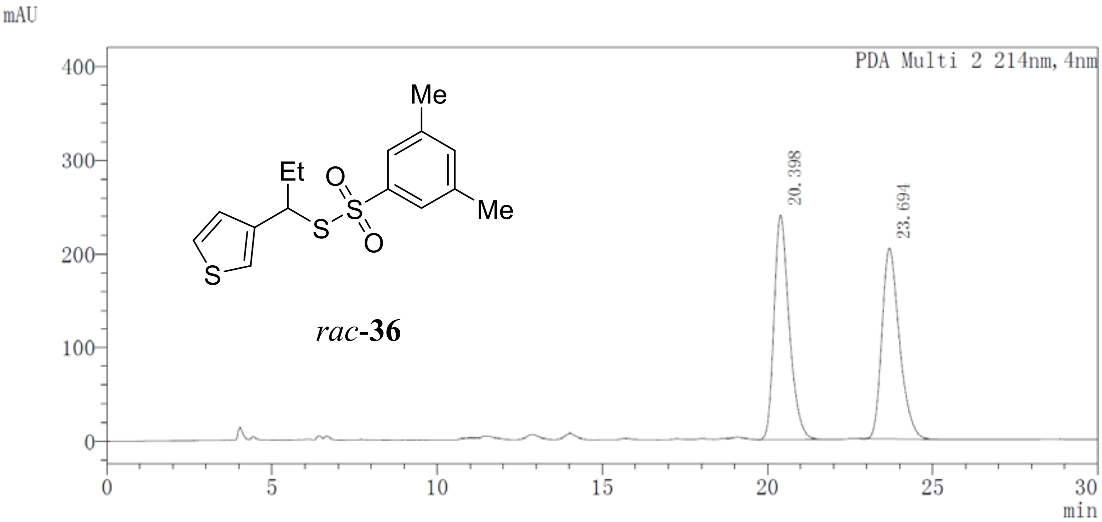
PDA Ch2 214nm

T	Hight	Area	Area%
13.910	644298	13988049	50.290
16.155	513572	13826774	49.710



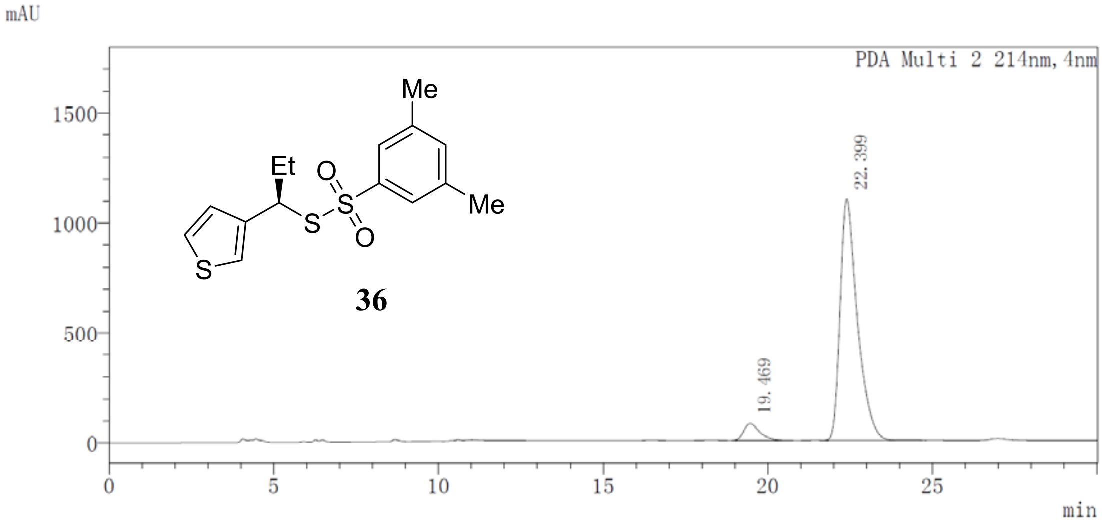
PDA Ch1 254nm

T	Hight	Area	Area%
13.608	1059304	24112620	96.053
16.236	39716	990840	3.947



PDA Ch2 214nm

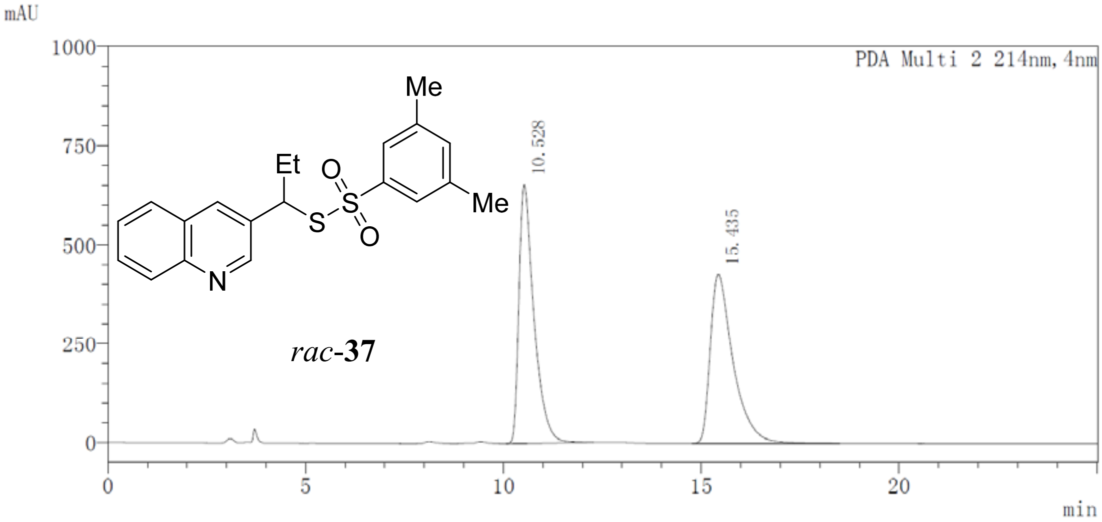
T	Hight	Area	Area%
20.398	237844	7572426	50.309
23.694	202687	7479463	49.691



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	19.469	2622476	6.140
2	22.399	40090585	93.860

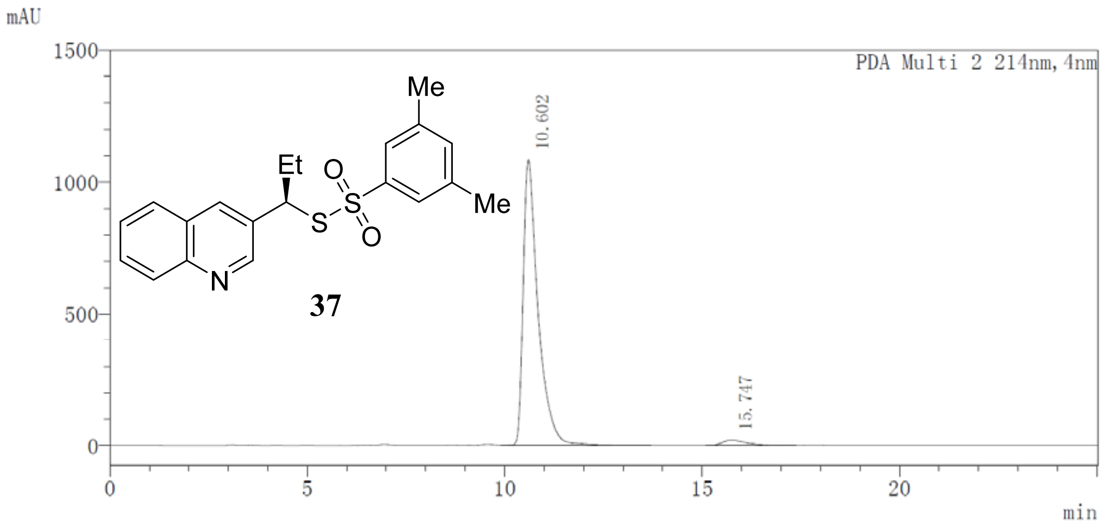


rac-**37**

Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	10.528	17233364	50.095
2	15.435	17168042	49.905

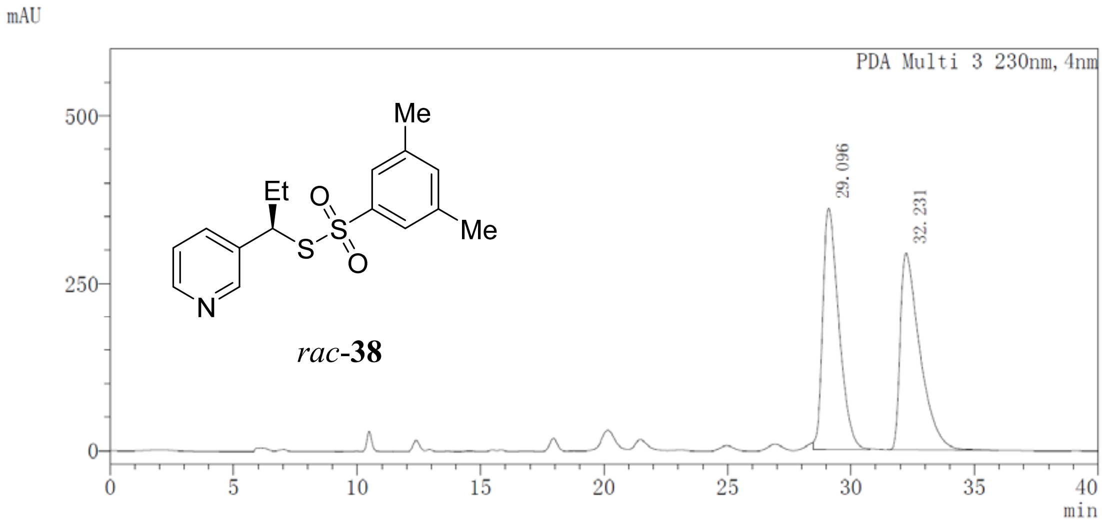


37

Peak Table

PDA Ch2 214nm

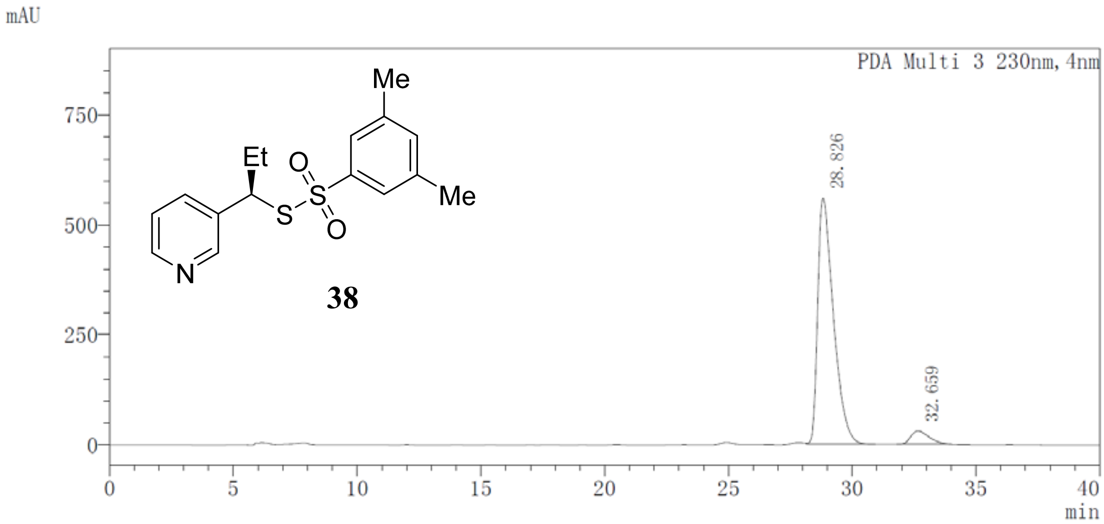
Peak#	Ret. Time	Area	Area%
1	10.602	28366142	97.183
2	15.747	822199	2.817



rac-**38**

PDA Ch3 230nm

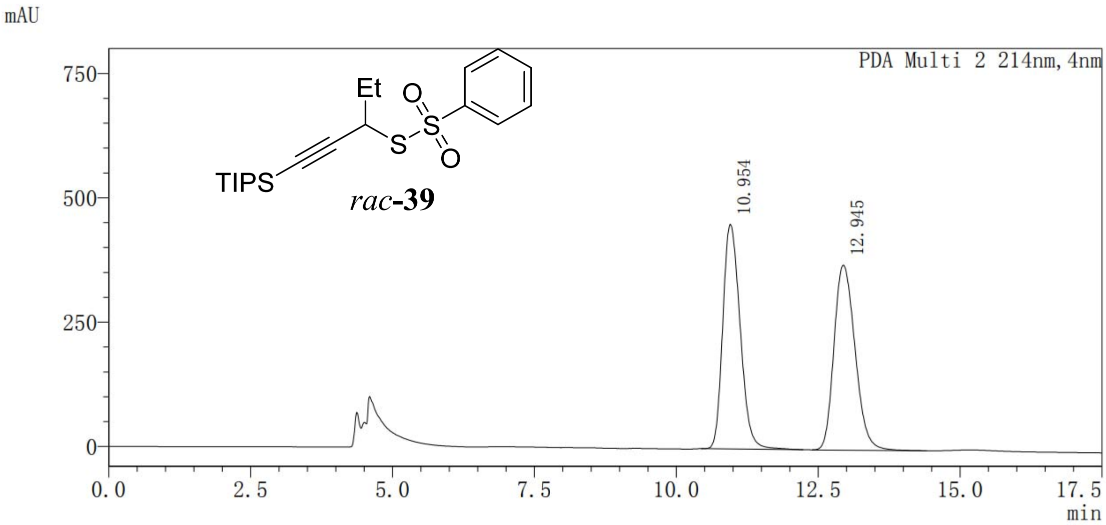
T	Hight	Area	Area%
29.096	360919	16416962	50.079
32.231	294449	16365268	49.921



38

PDA Ch3 230nm

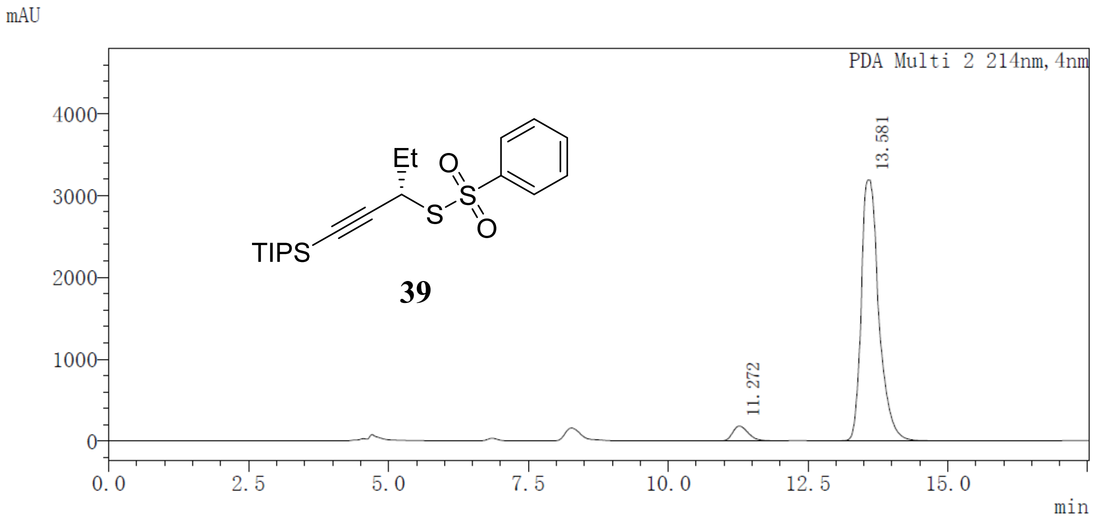
T	Hight	Area	Area%
28.826	559048	24716240	94.004
32.659	30352	1576603	5.996



Peak Table

PDA Ch2 214nm

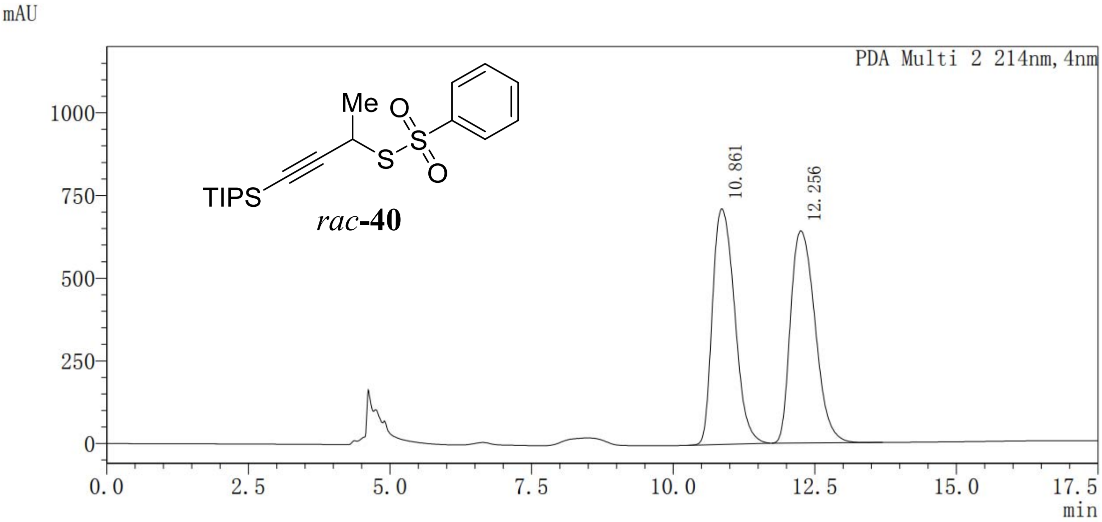
Peak#	Ret. Time	Area	Area%
1	10.954	9626412	50.015
2	12.945	9620560	49.985



Peak Table

PDA Ch2 214nm

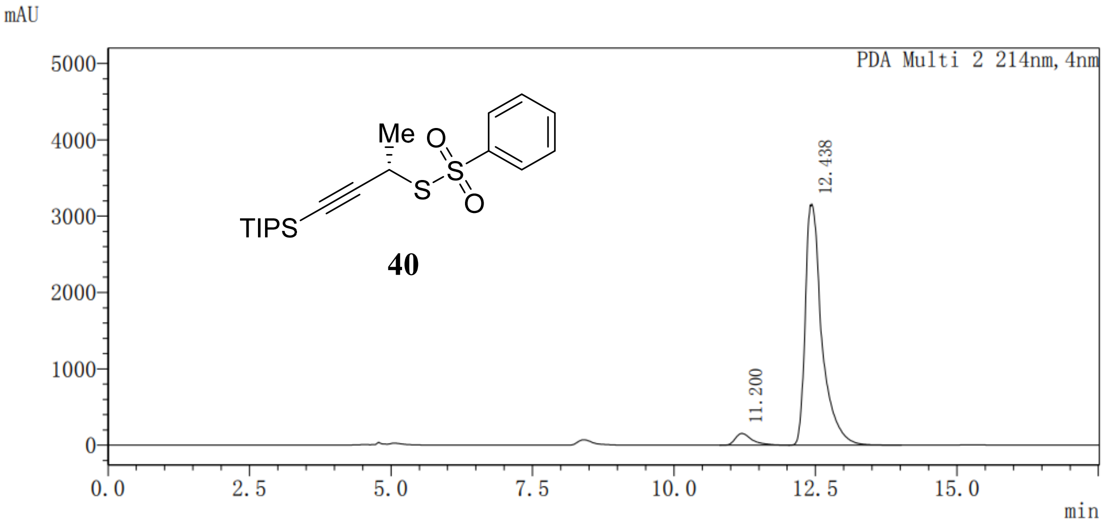
Peak#	Ret. Time	Area	Area%
1	11.272	3495492	4.786
2	13.581	69535203	95.214



Peak Table

PDA Ch2 214nm

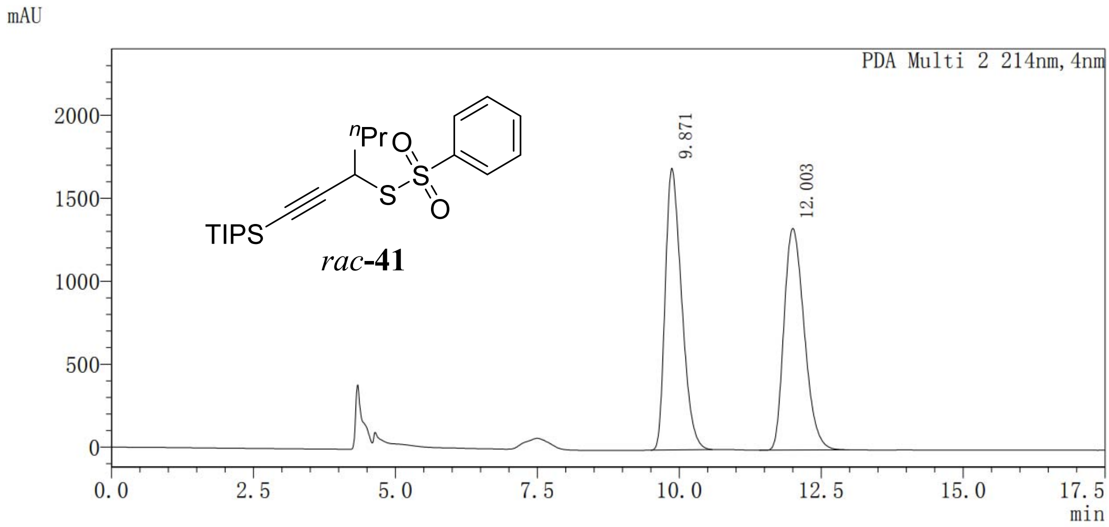
Peak#	Ret. Time	Area	Area%
1	10.861	19373455	50.003
2	12.256	19371001	49.997



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	11.200	3172138	4.701
2	12.438	64300973	95.299

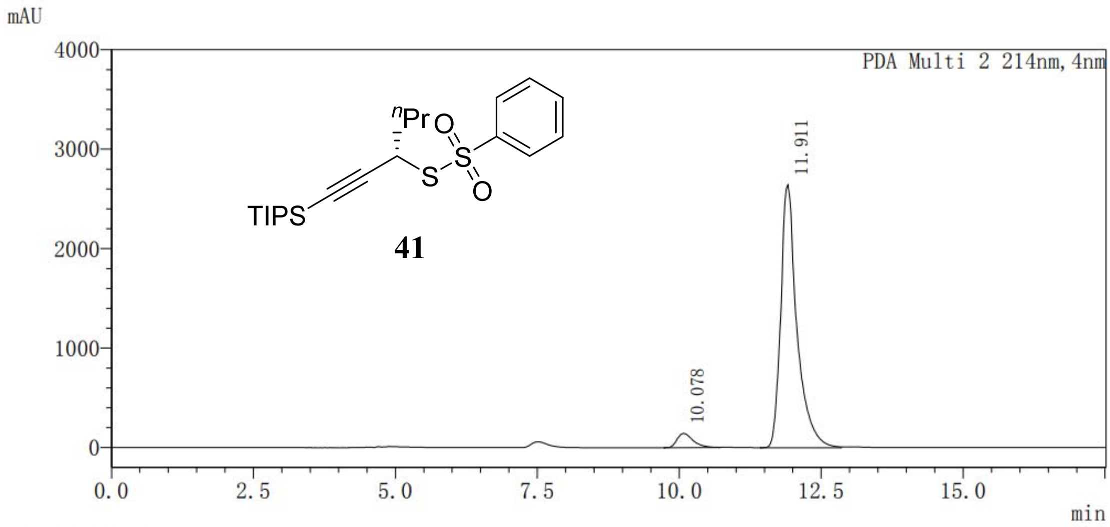


rac-**41**

Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	9.871	33951911	50.567
2	12.003	33190654	49.433

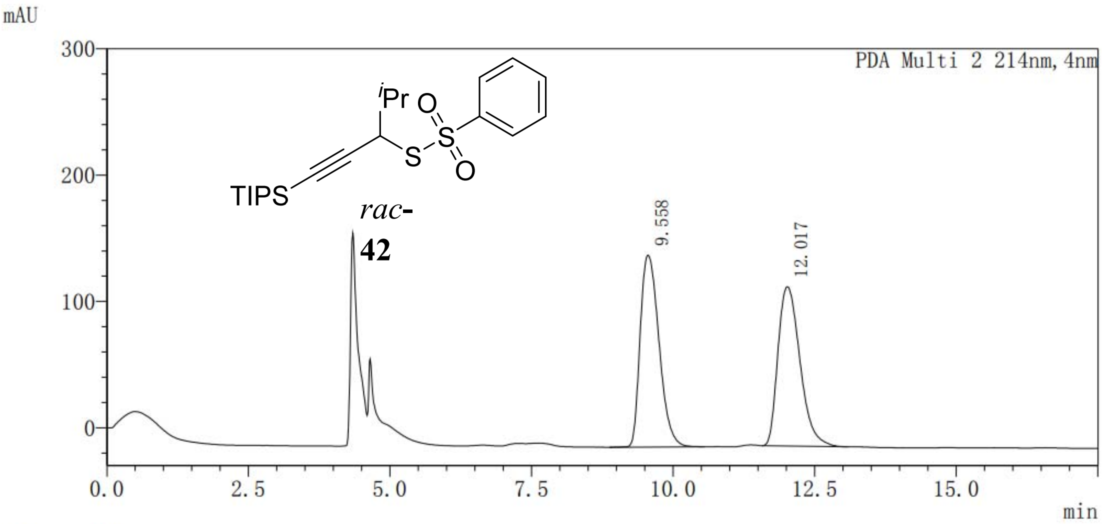


41

Peak Table

PDA Ch2 214nm

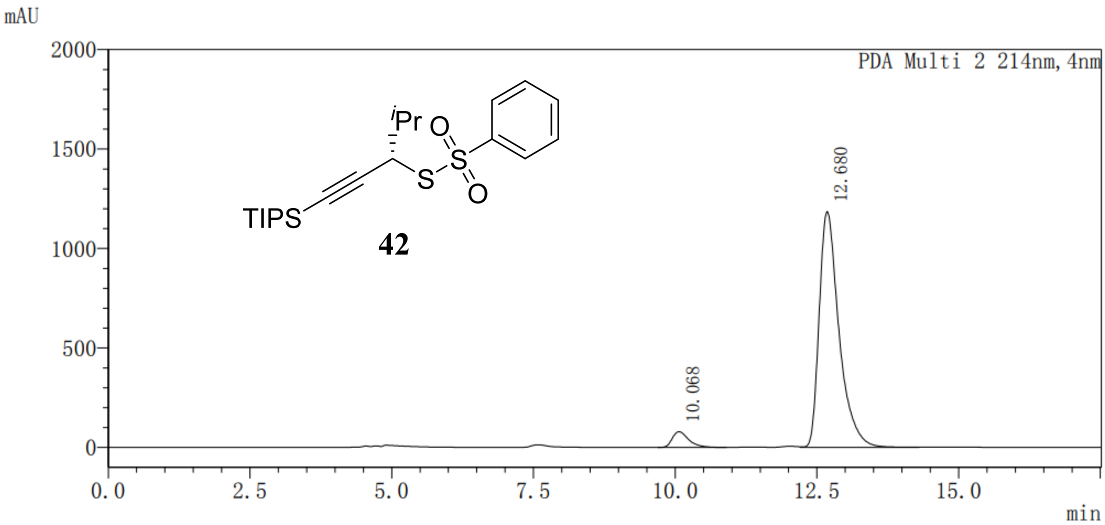
Peak#	Ret. Time	Area	Area%
1	10.078	2753426	5.002
2	11.911	52288905	94.998



Peak Table

PDA Ch2 214nm

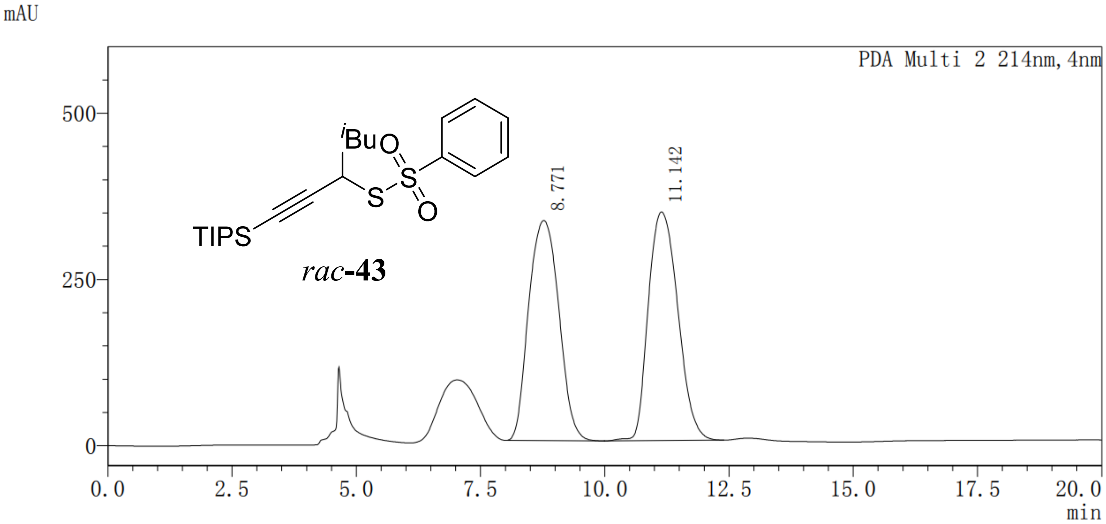
Peak#	Ret. Time	Area	Area%
1	9.558	3512670	50.646
2	12.017	3423118	49.354



Peak Table

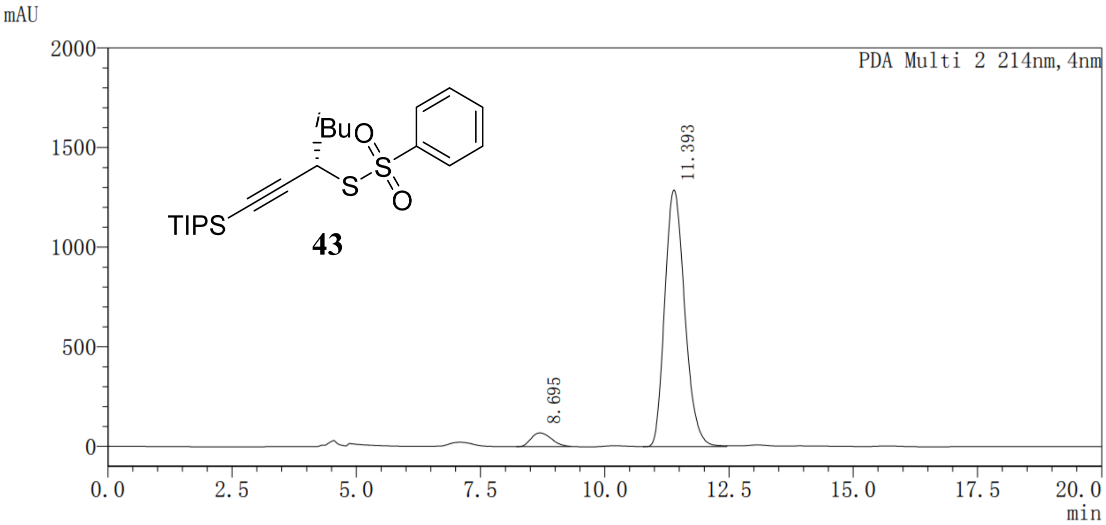
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	10.068	1585805	5.197
2	12.680	28928937	94.803



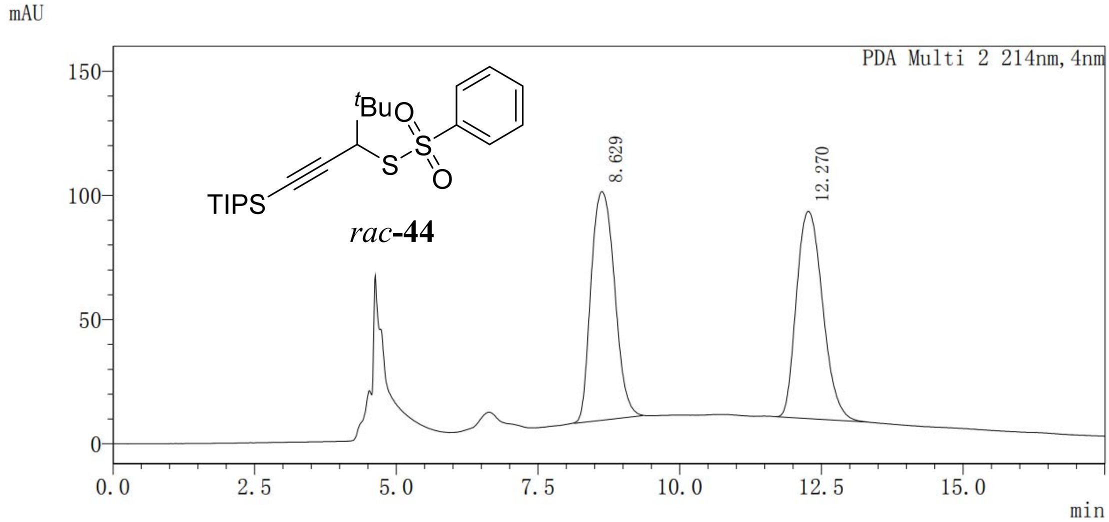
PDA Ch2 214nm

T	Hight	Area	Area%
8.771	331172	14016254	49.583
11.142	343906	14252136	50.417



PDA Ch2 214nm

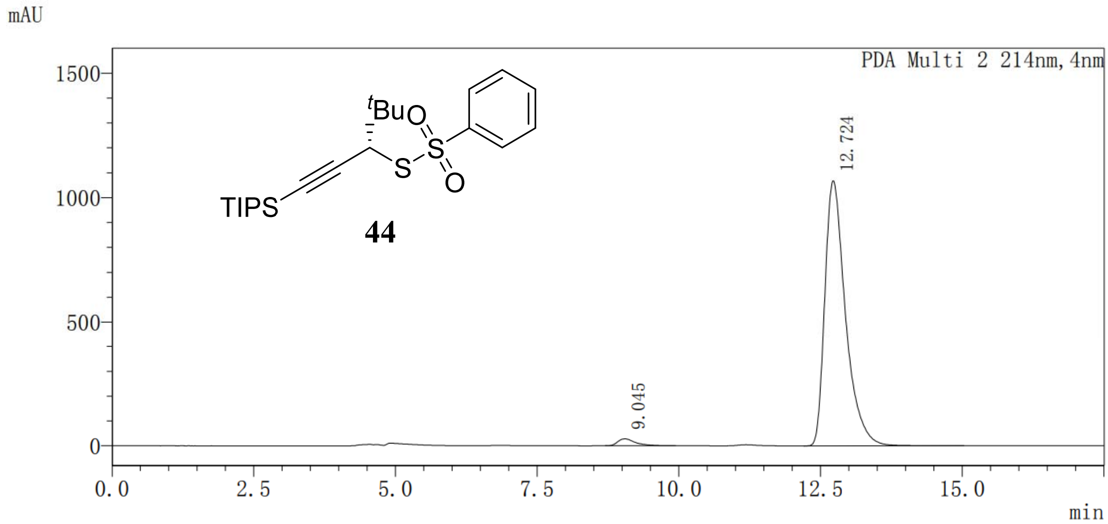
T	Hight	Area	Area%
8.695	68697	1949392	5.126
11.393	1288459	36081745	94.874



Peak Table

PDA Ch2 214nm

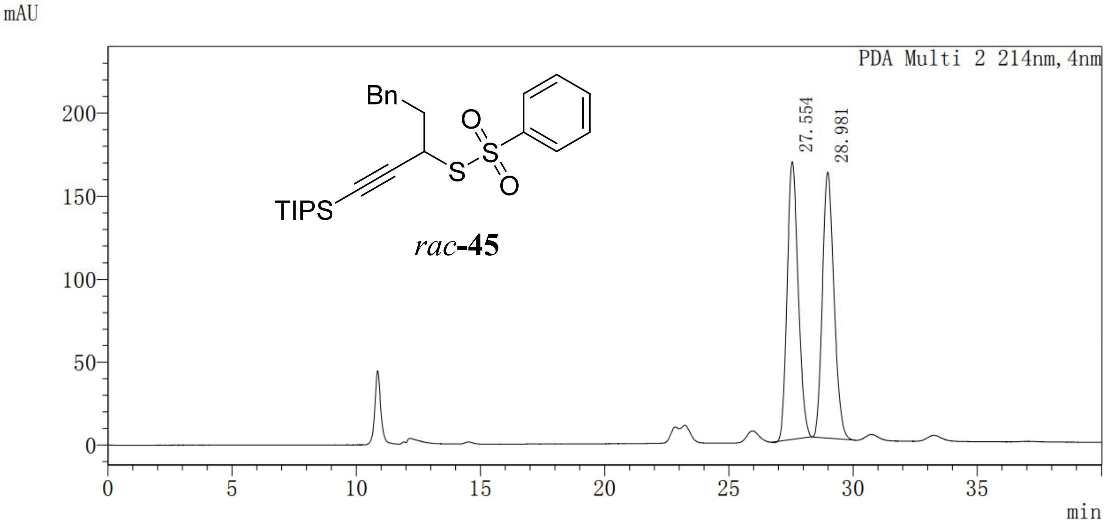
Peak#	Ret. Time	Area	Area%
1	8.629	2666770	49.781
2	12.270	2690278	50.219



Peak Table

PDA Ch2 214nm

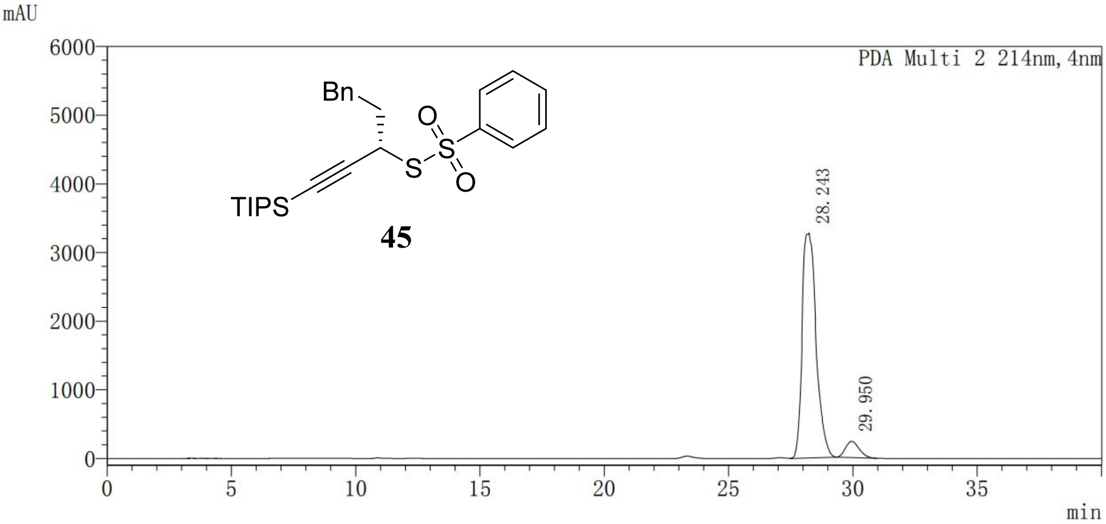
Peak#	Ret. Time	Area	Area%
1	9.045	612506	2.208
2	12.724	27133258	97.792



Peak Table

PDA Ch2 214nm

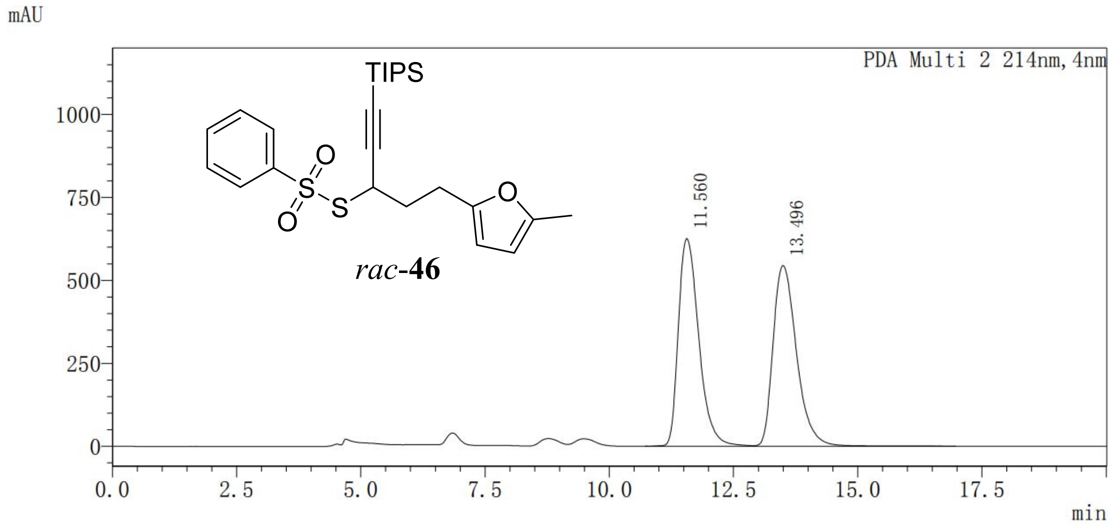
Peak#	Ret. Time	Area	Area%
1	27.554	5176525	49.878
2	28.981	5201761	50.122



Peak Table

PDA Ch2 214nm

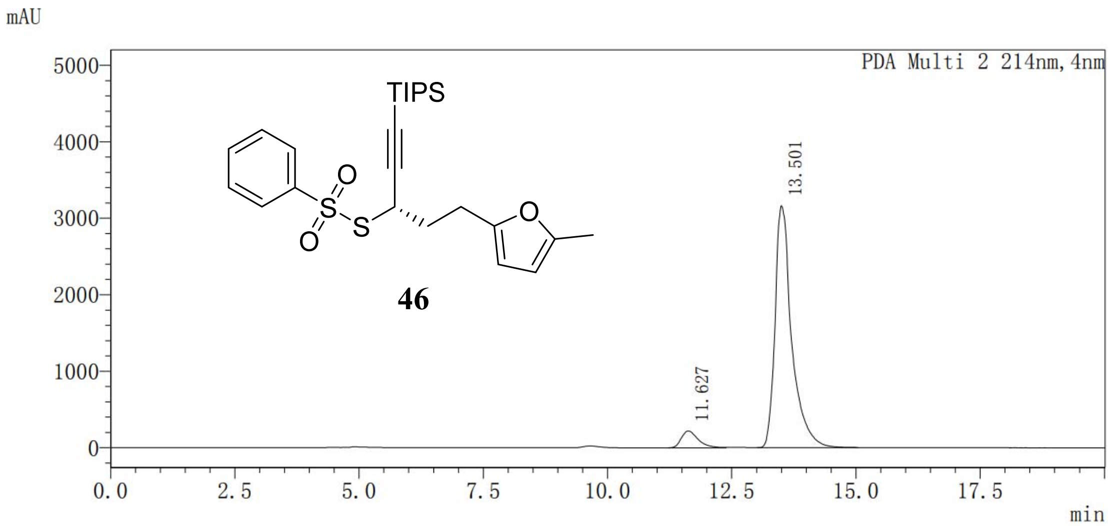
Peak#	Ret. Time	Area	Area%
1	28.243	127945881	93.363
2	29.950	9095280	6.637



Peak Table

PDA Ch2 214nm

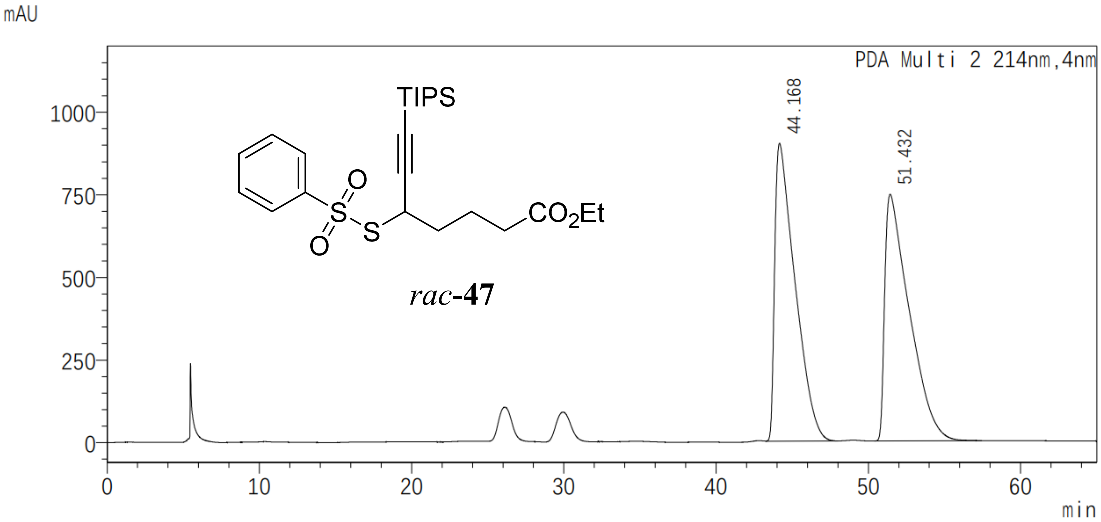
Peak#	Ret. Time	Area	Area%
1	11.560	17924527	50.023
2	13.496	17908287	49.977



Peak Table

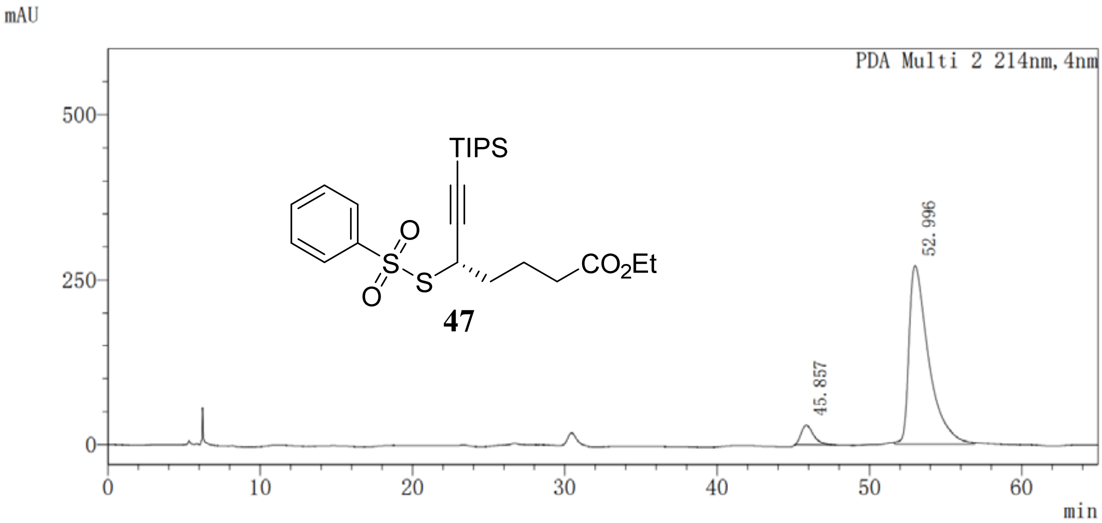
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	11.627	5177961	6.546
2	13.501	73928096	93.454



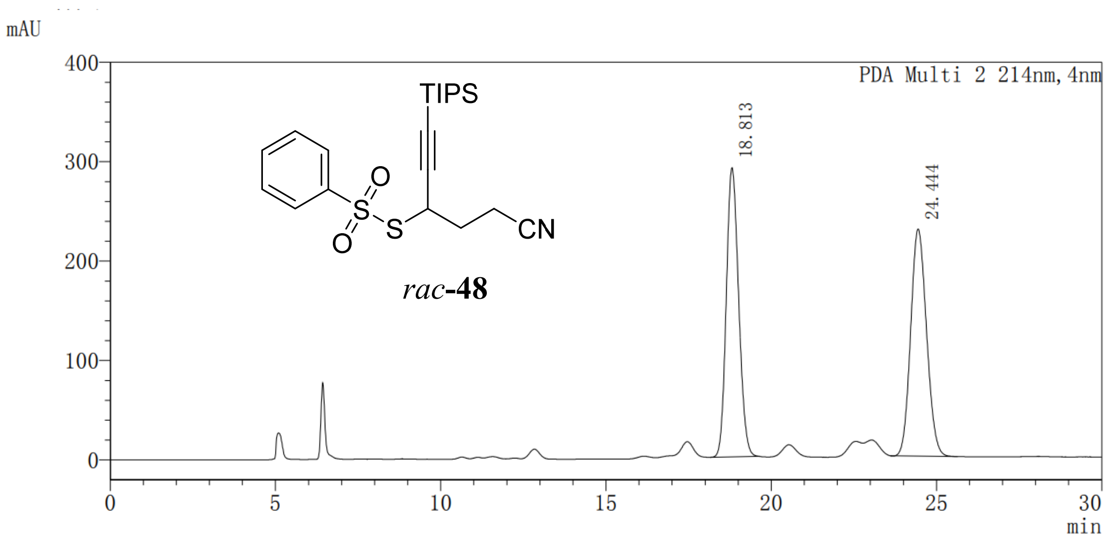
PDA Ch2 214nm

T	Hight	Area	Area%
44.168	901243	83368531	49.898
51.432	746750	83710518	50.102



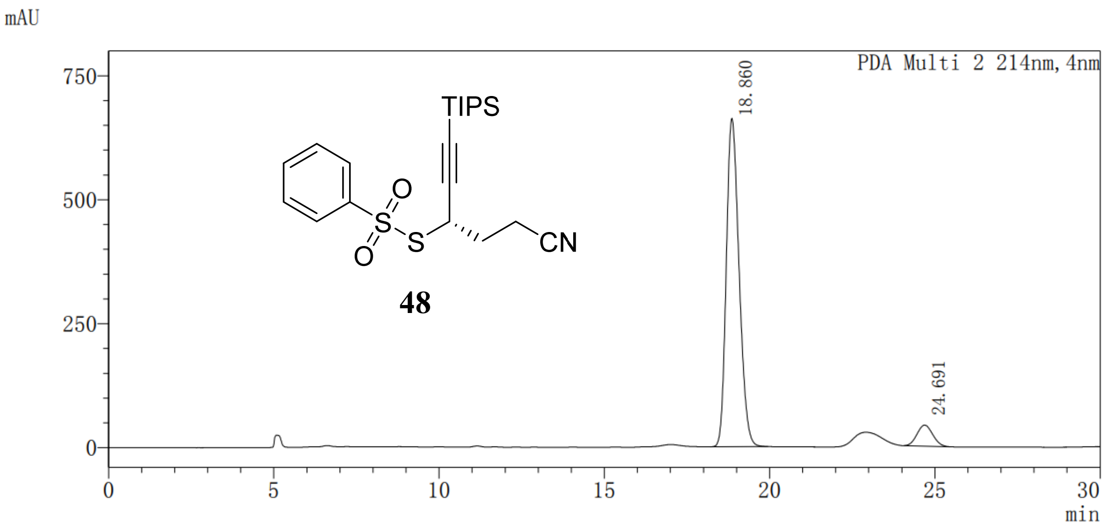
PDA Ch2 214nm

T	Hight	Area	Area%
45.857	29614	1663674	6.433
52.996	270900	24198370	93.567



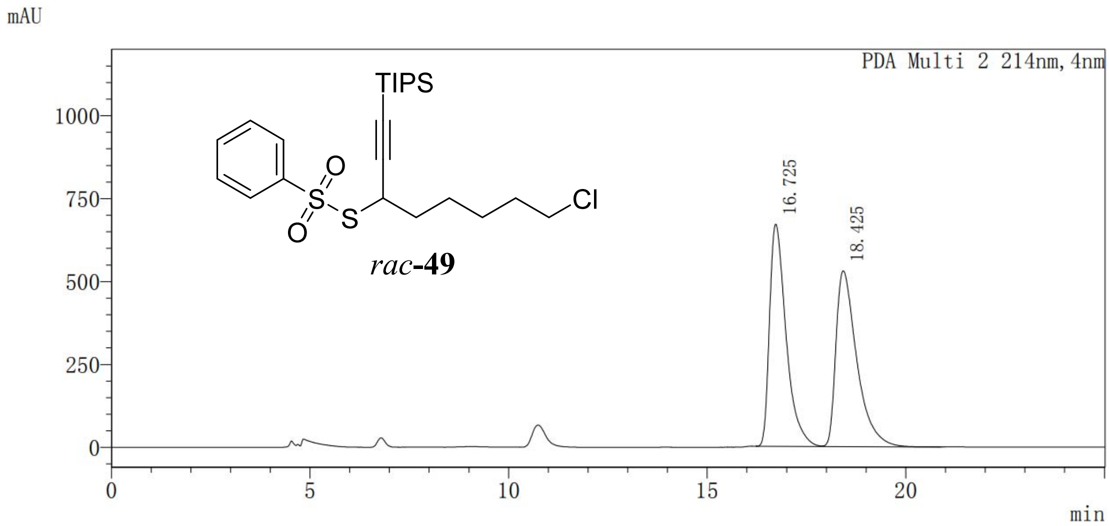
PDA Ch2 214nm

T	Hight	Area	Area%
18.813	290955	7555798	49.737
24.444	228412	7635770	50.263



PDA Ch2 214nm

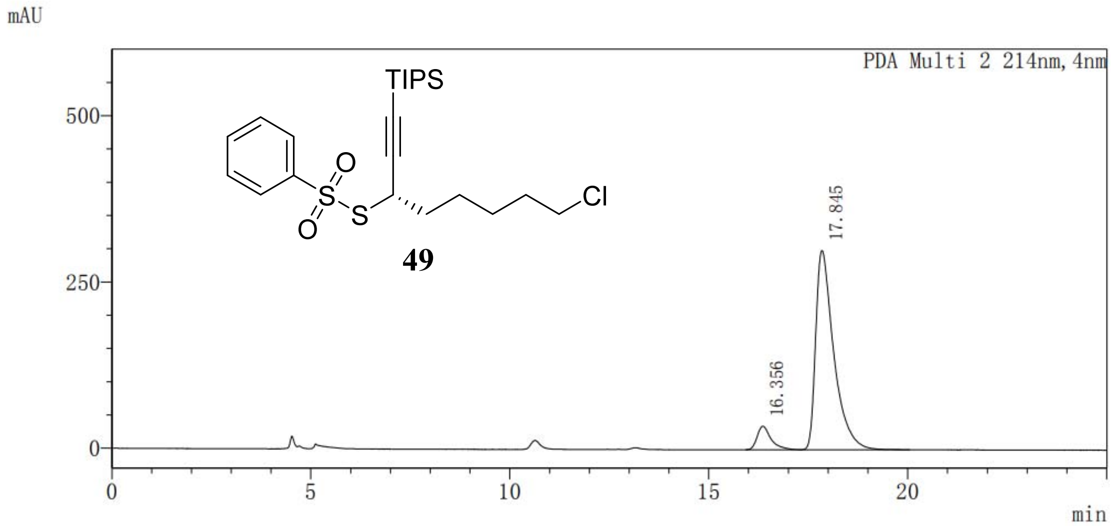
T	Hight	Area	Area%
18.860	661823	17748479	92.701
24.691	42449	1397547	7.299



Peak Table

PDA Ch2 214nm

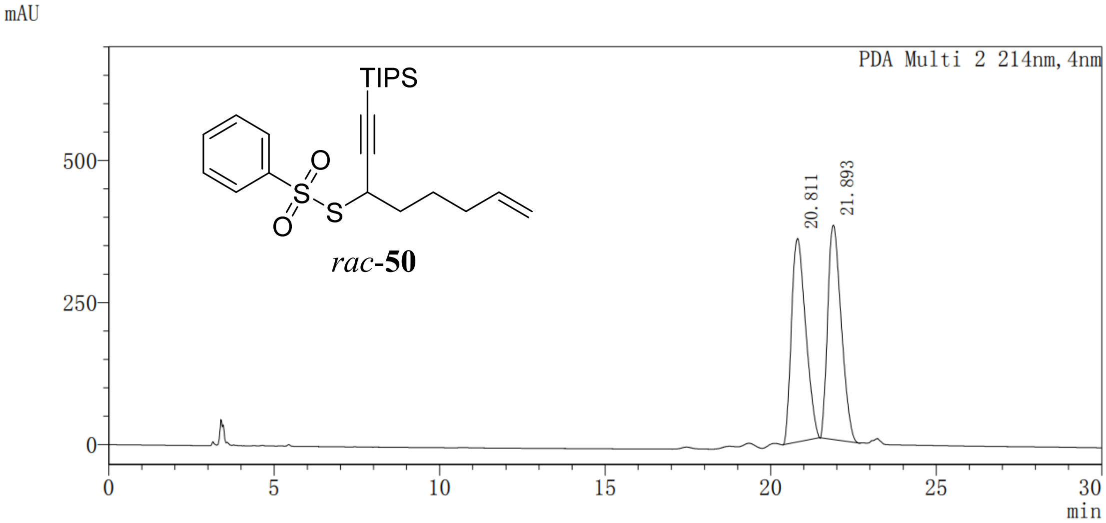
Peak#	Ret. Time	Area	Area%
1	16.725	19402061	50.019
2	18.425	19387302	49.981



Peak Table

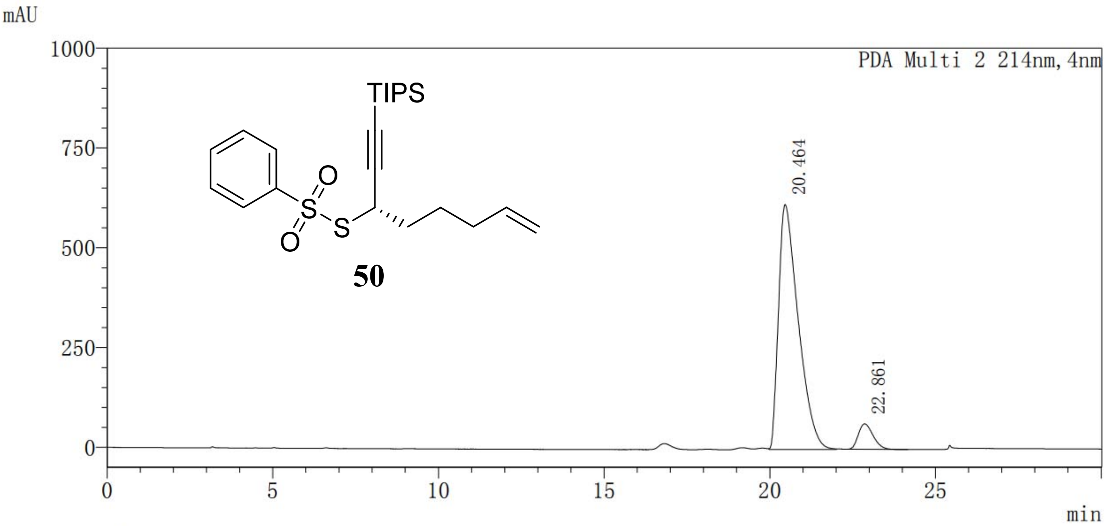
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	16.356	850585	8.239
2	17.845	9472794	91.761



PDA Ch2 214nm

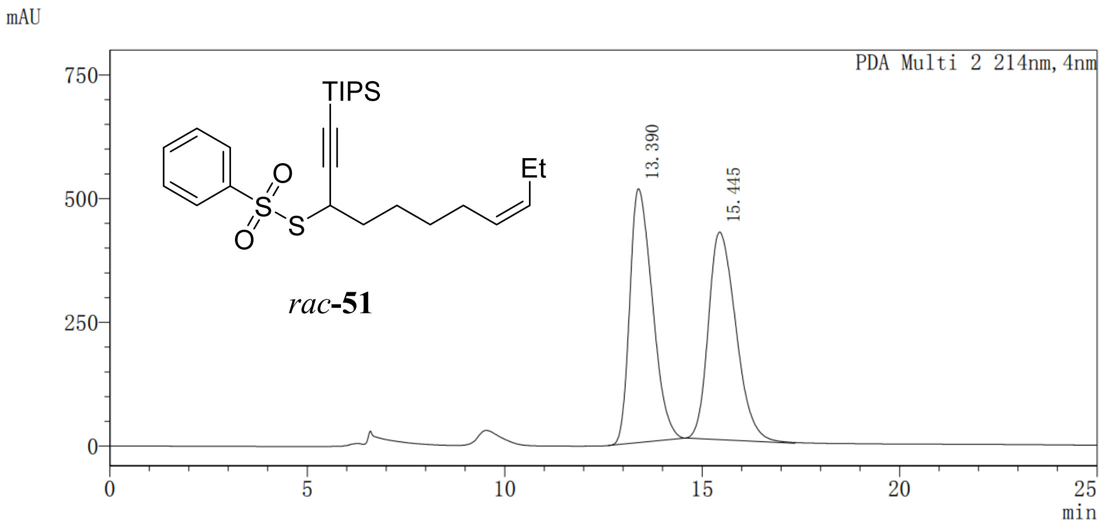
T	Hight	Area	Area%
20.811	357940	10691955	49.859
21.893	376878	10752490	50.141



Peak Table

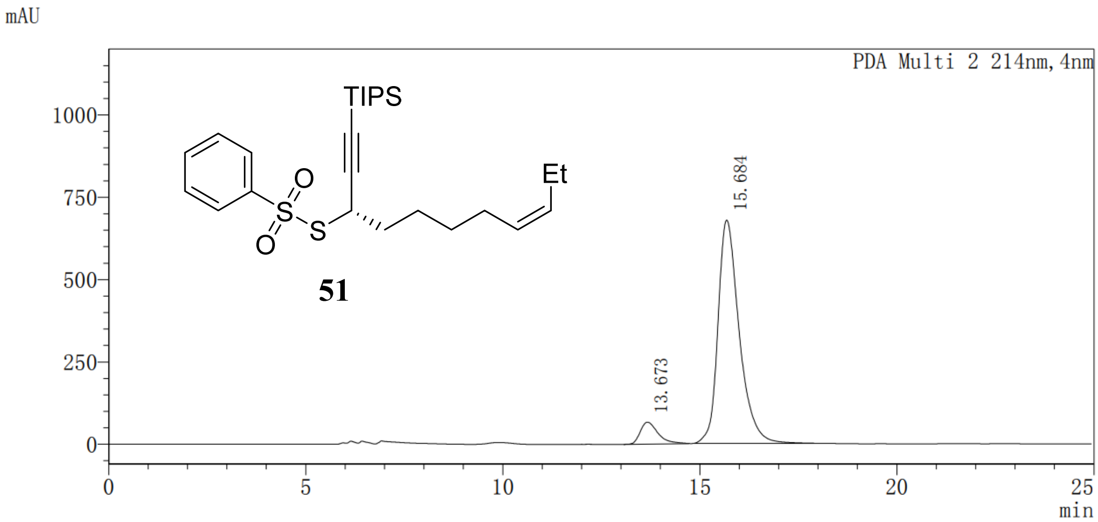
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	20.464	25422970	92.798
2	22.861	1972921	7.202



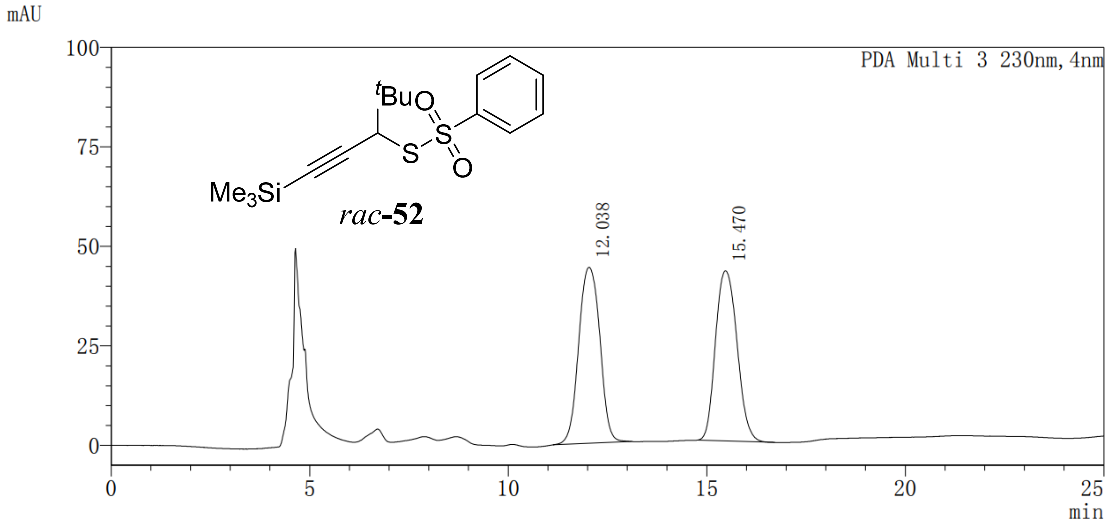
PDA Ch2 214nm

T	Hight	Area	Area%
13.390	513017	20440421	50.072
15.445	419559	20381397	49.928



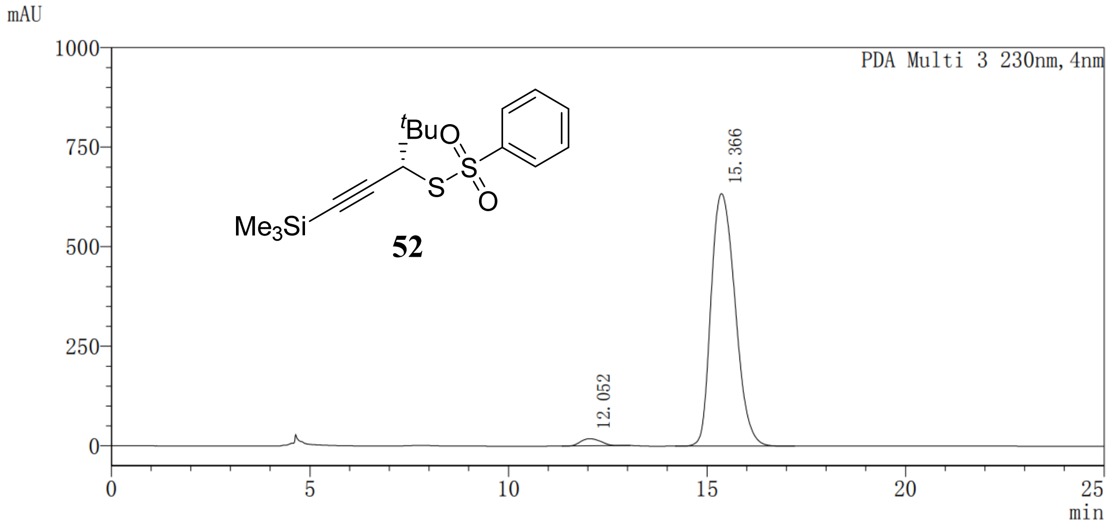
PDA Ch2 214nm

T	Hight	Area	Area%
13.673	66592	2100045	7.614
15.684	678286	25482564	92.386



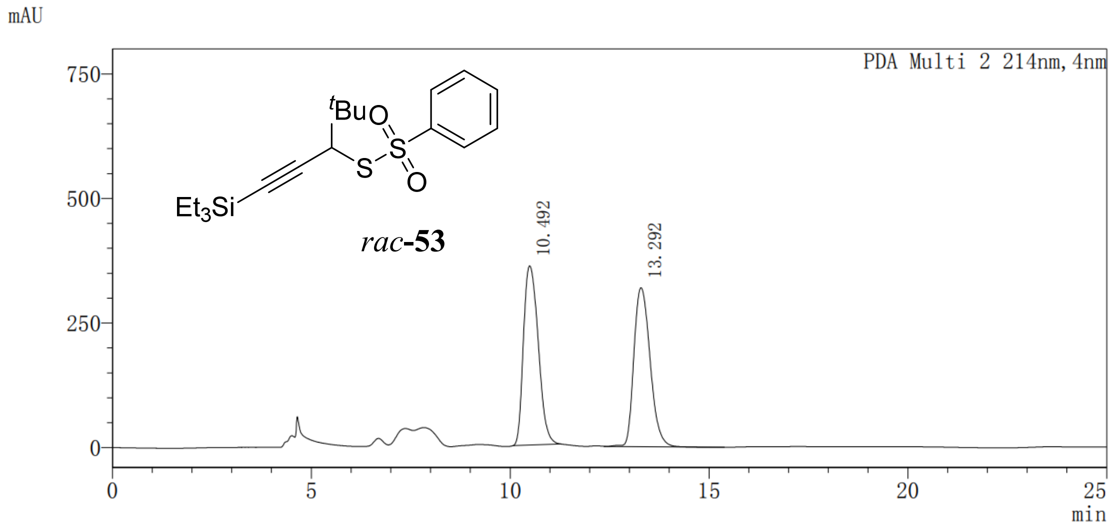
PDA Ch3 230nm

T	Hight	Area	Area%
12.038	44204	1640057	50.342
15.470	42768	1617794	49.658



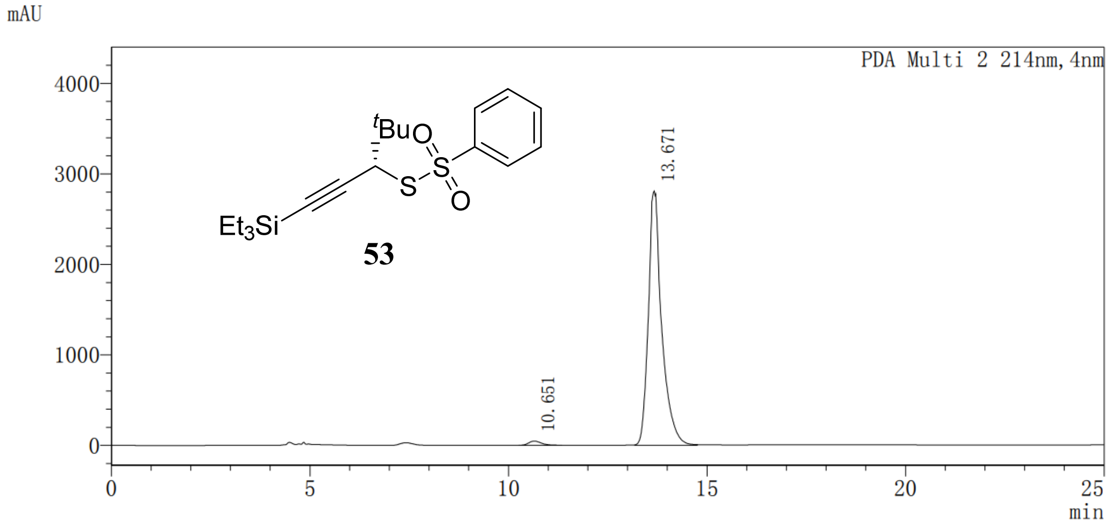
PDA Ch3 230nm

T	Hight	Area	Area%
12.052	17915	637380	2.327
15.366	634269	26750181	97.673



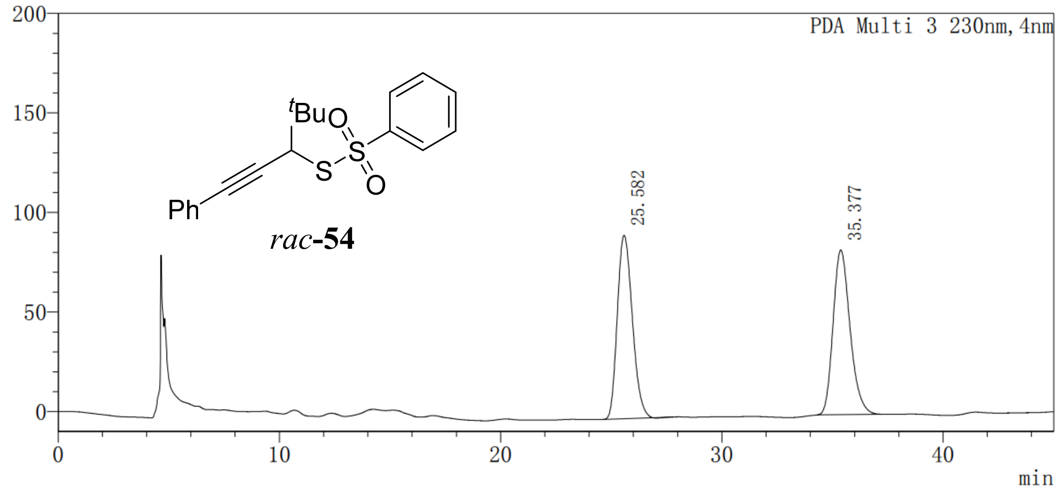
PDA Ch2 214nm

T	Hight	Area	Area%
10.492	359414	9298040	50.642
13.292	318856	9062274	49.358



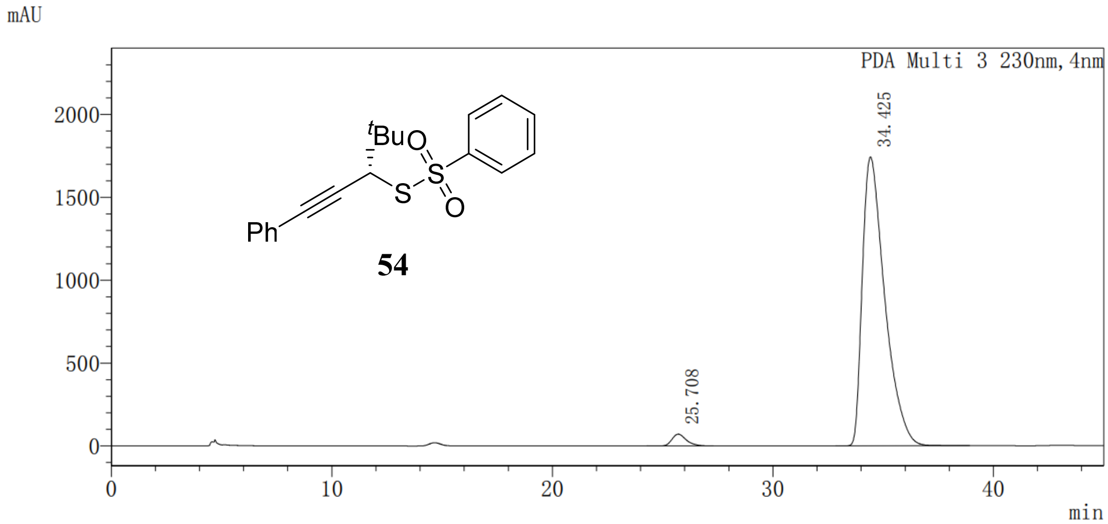
PDA Ch2 214nm

T	Hight	Area	Area%
10.651	46725	1041140	1.554
13.671	2808470	65961398	98.446



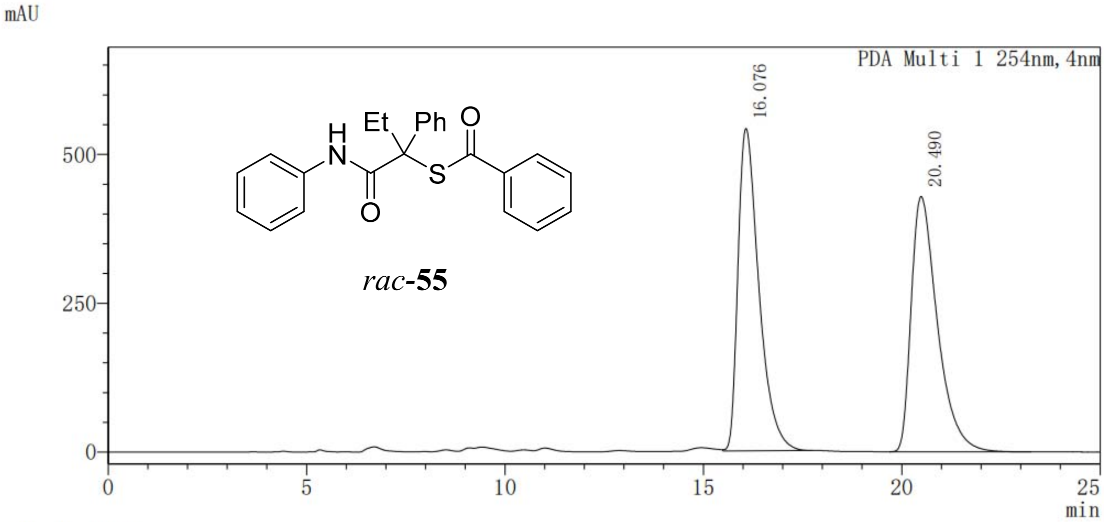
PDA Ch3 230nm

T	Hight	Area	Area%
25.582	92158	4341491	49.614
35.377	82723	4409126	50.386



PDA Ch3 230nm

T	Hight	Area	Area%
25.708	71352	3233865	2.557
34.425	1743639	123239984	97.443

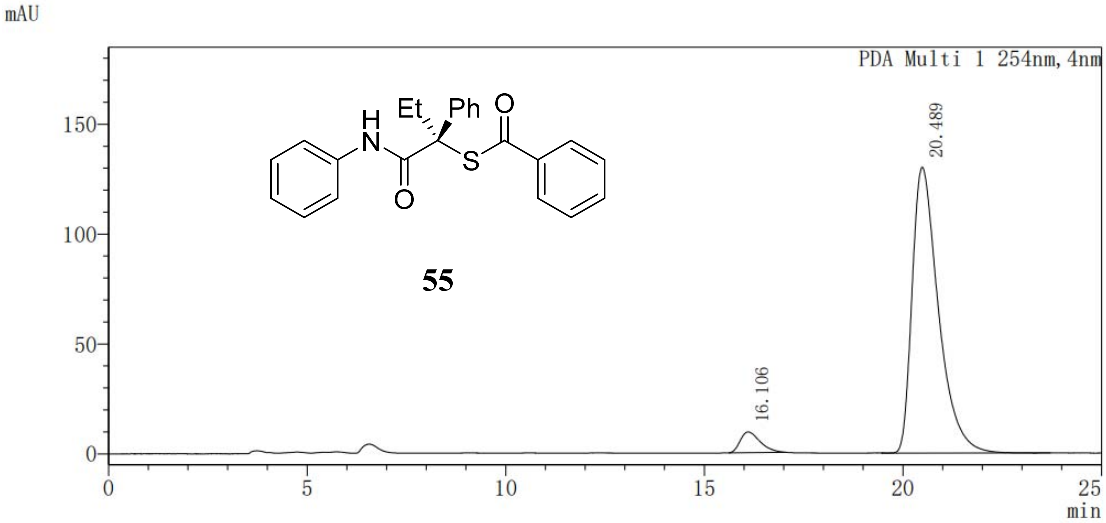


rac-**55**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.076	19840907	50.170
2	20.490	19706629	49.830

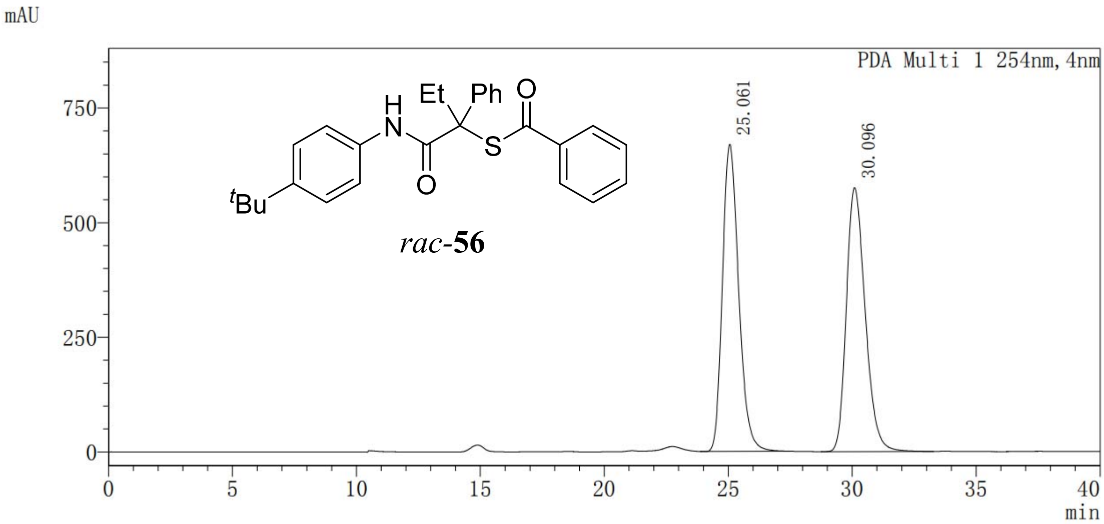


55

Peak Table

PDA Ch1 254nm

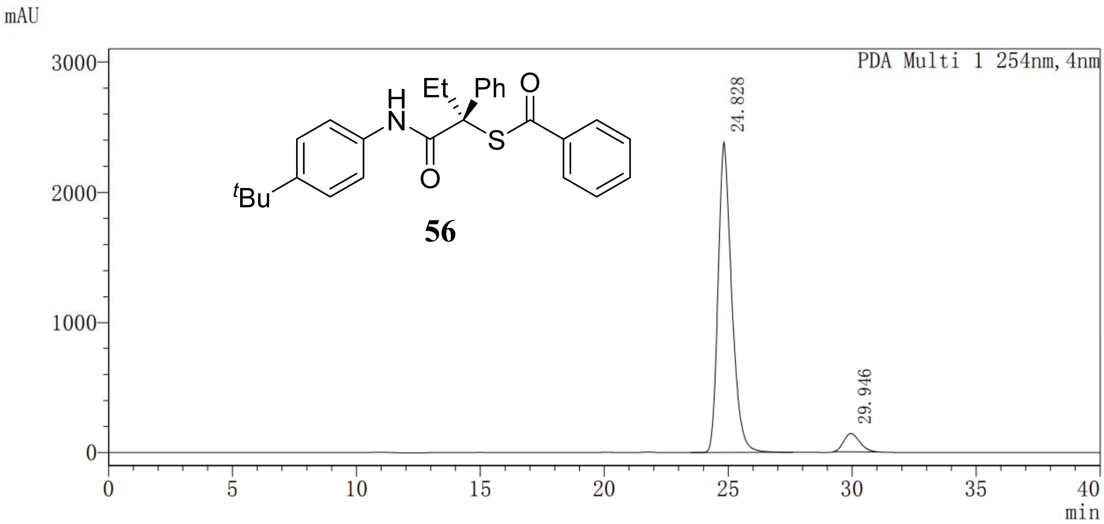
Peak#	Ret. Time	Area	Area%
1	16.106	325087	5.148
2	20.489	5989633	94.852



Peak Table

PDA Ch1 254nm

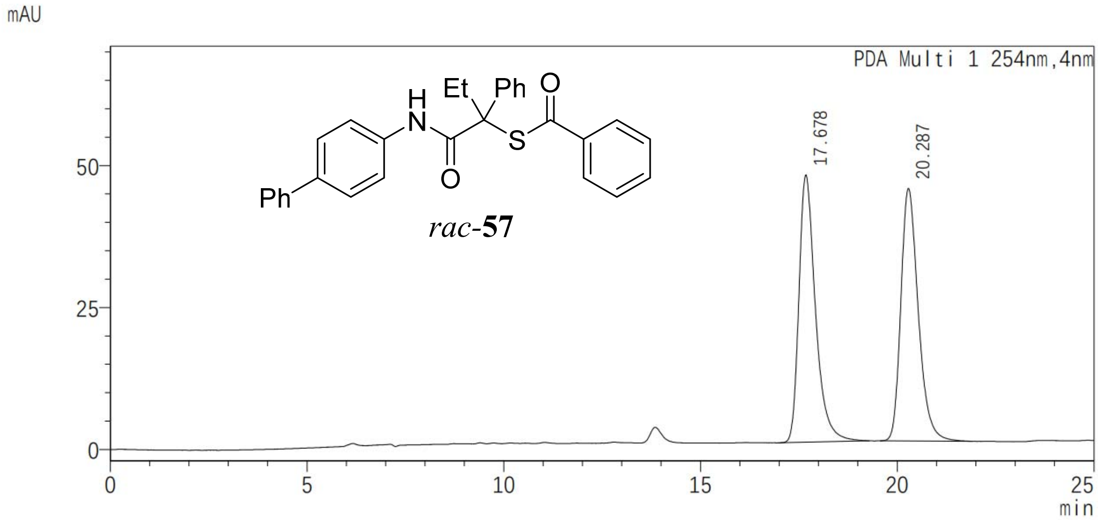
Peak#	Ret. Time	Area	Area%
1	25.061	30562400	50.145
2	30.096	30386015	49.855



Peak Table

PDA Ch1 254nm

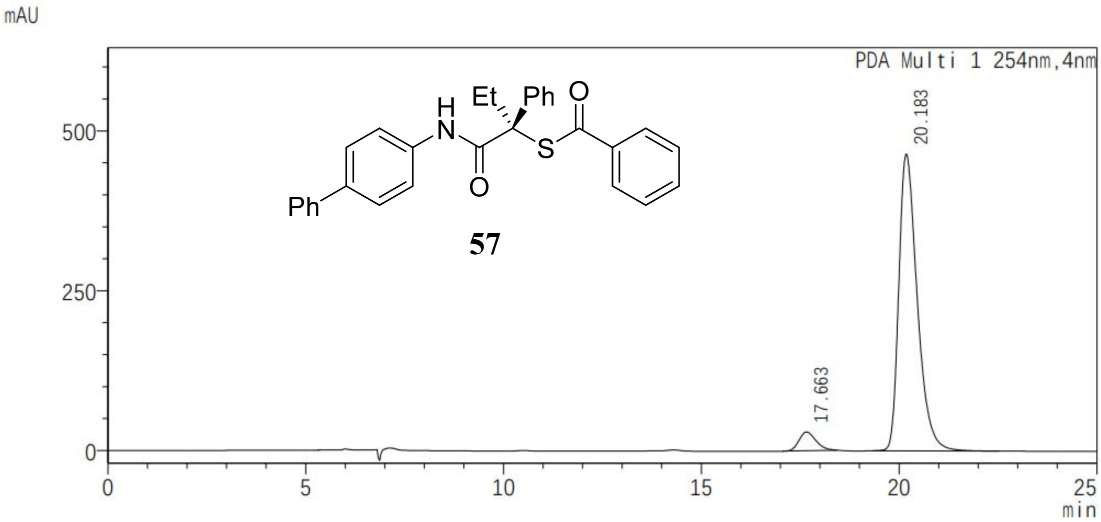
Peak#	Ret. Time	Area	Area%
1	24.828	90639272	93.417
2	29.946	6386883	6.583



Peak Table

PDA Ch1 254nm

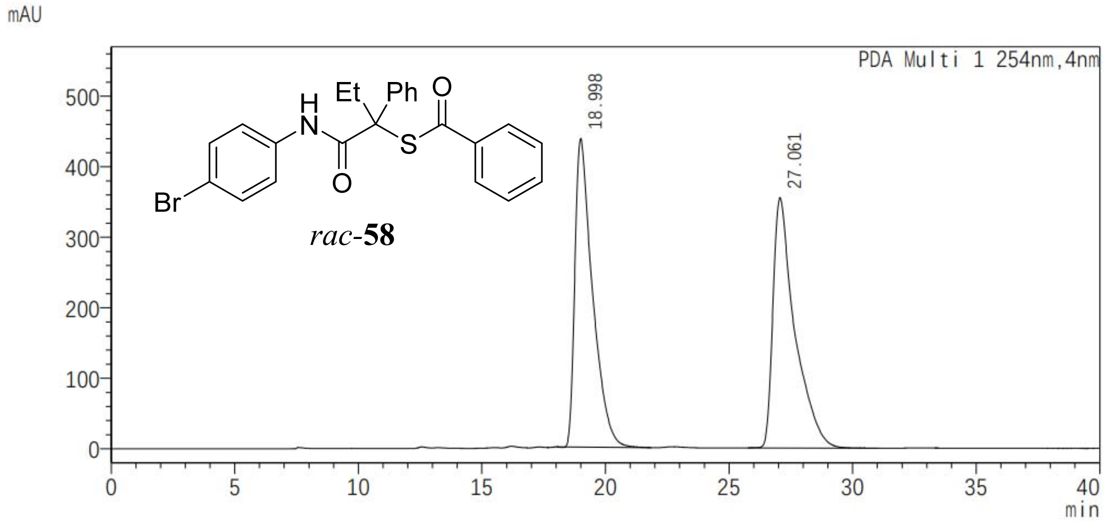
Peak#	Ret. Time	Area	Area%
1	17.678	1378141	50.196
2	20.287	1367374	49.804



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.663	870371	5.471
2	20.183	15039201	94.529

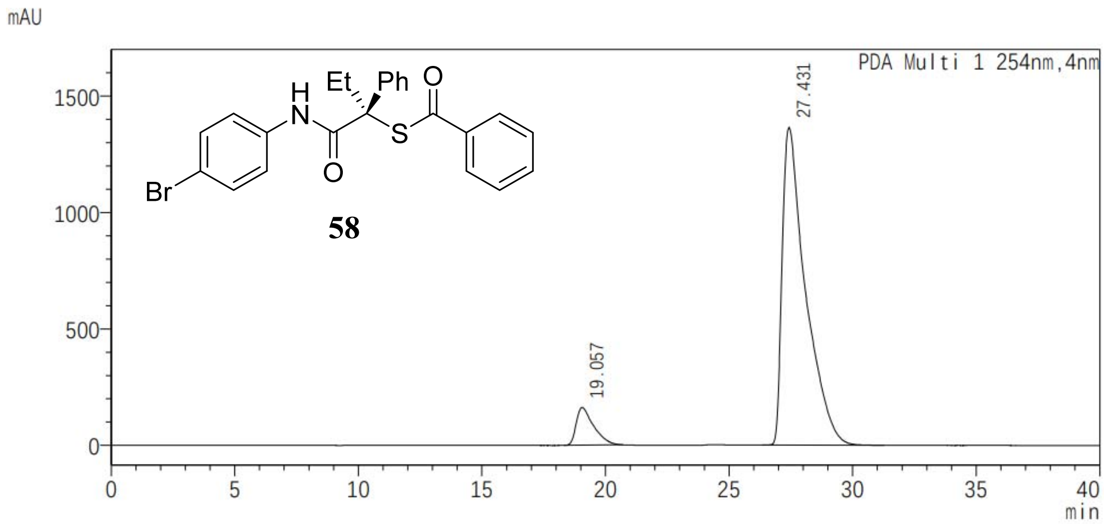


rac-**58**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.998	21698332	49.919
2	27.061	21769020	50.081

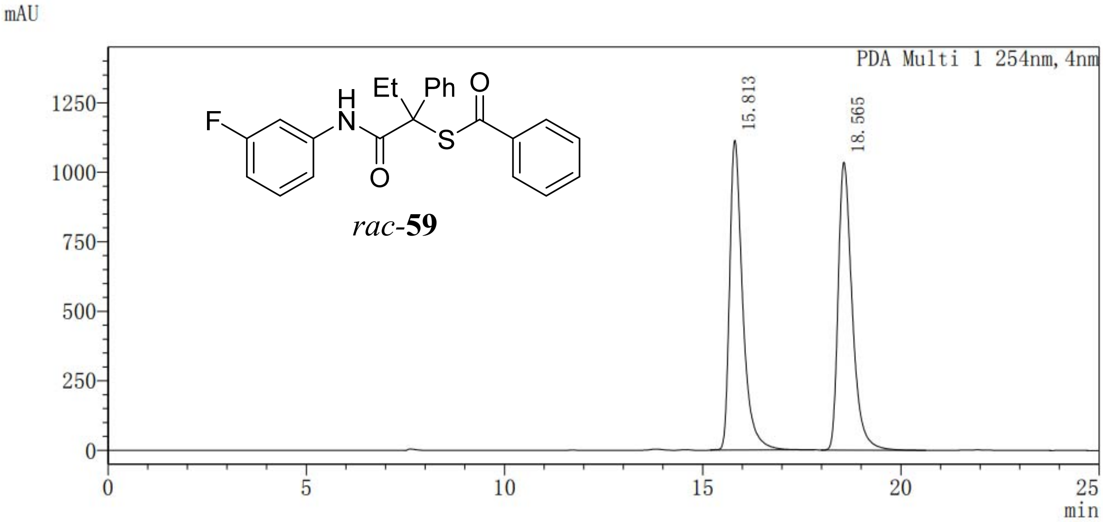


58

Peak Table

PDA Ch1 254nm

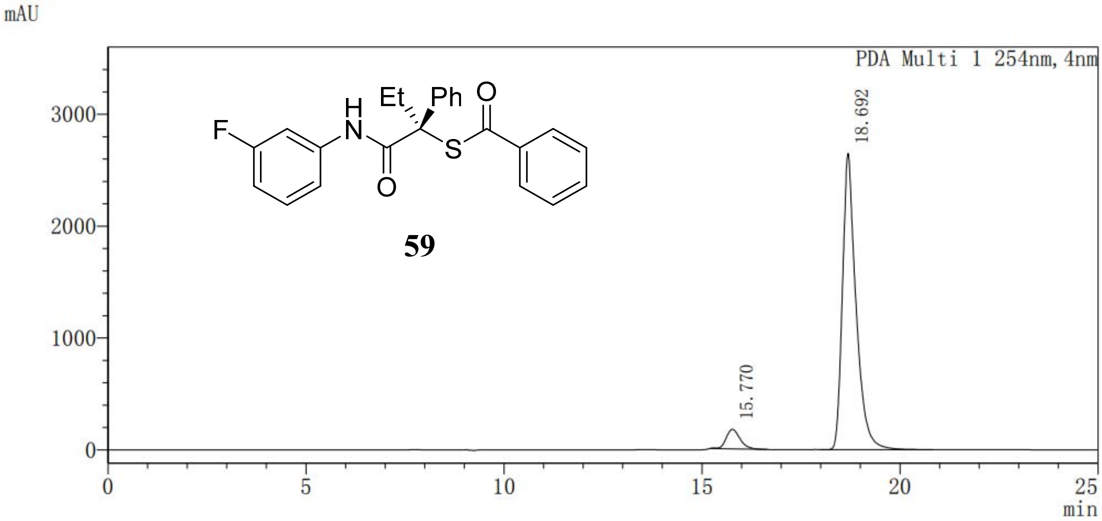
Peak#	Ret. Time	Area	Area%
1	19.057	7914961	8.135
2	27.431	89385045	91.865



Peak Table

PDA Ch1 254nm

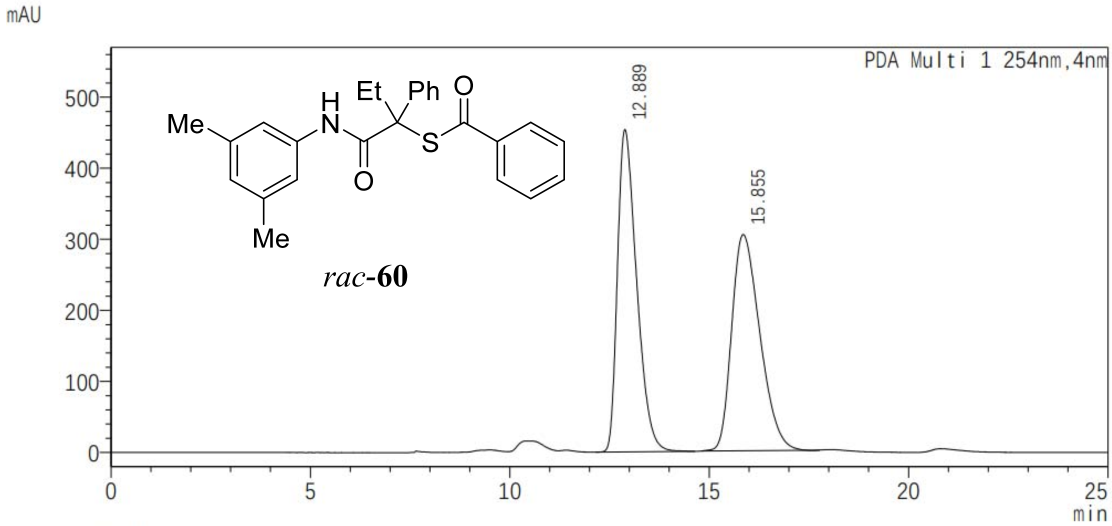
Peak#	Ret. Time	Area	Area%
1	15.813	25409763	49.961
2	18.565	25449458	50.039



Peak Table

PDA Ch1 254nm

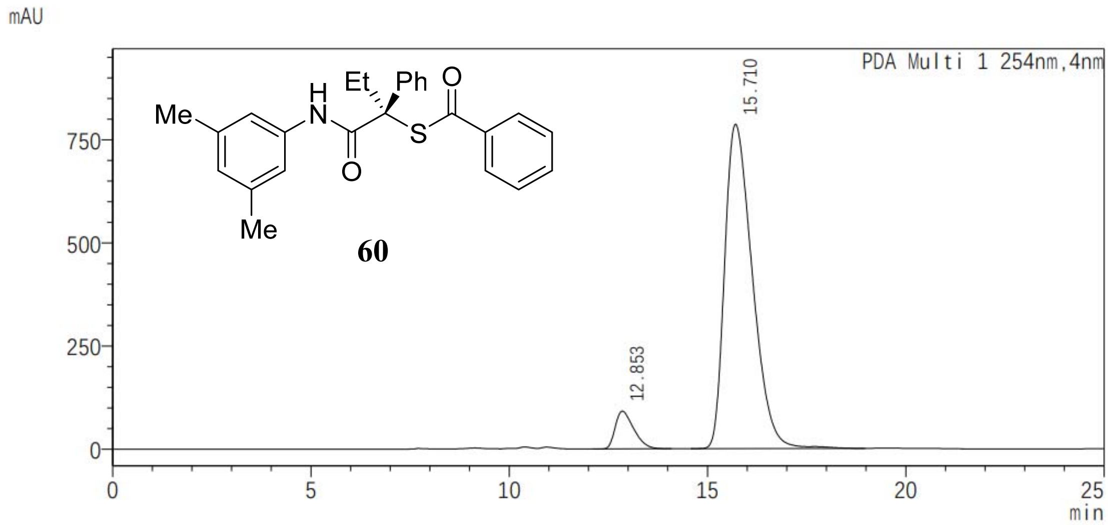
Peak#	Ret. Time	Area	Area%
1	15.770	4276206	6.369
2	18.692	62869264	93.631



Peak Table

PDA Ch1 254nm

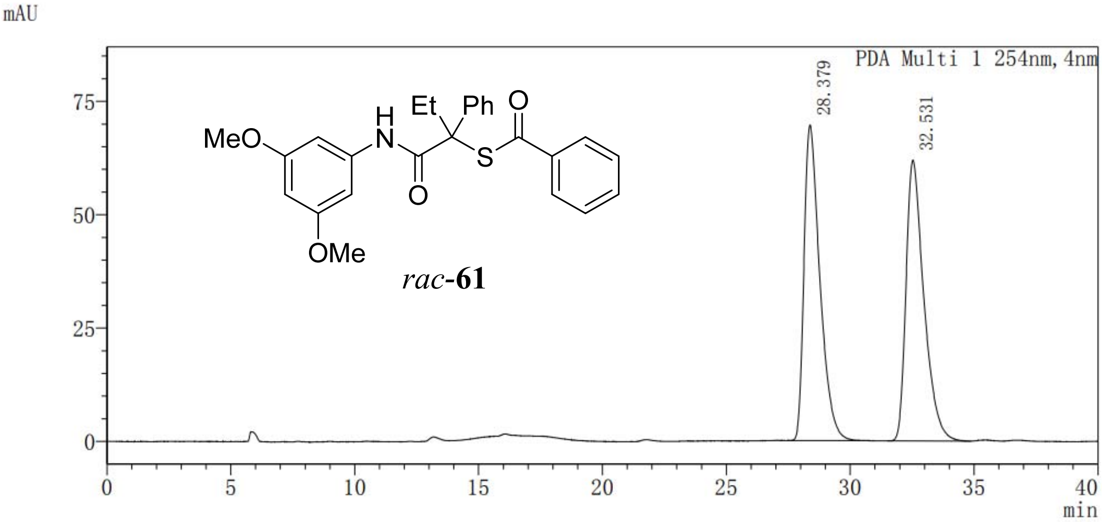
Peak#	Ret. Time	Area	Area%
1	12.889	15208794	50.445
2	15.855	14940249	49.555



Peak Table

PDA Ch1 254nm

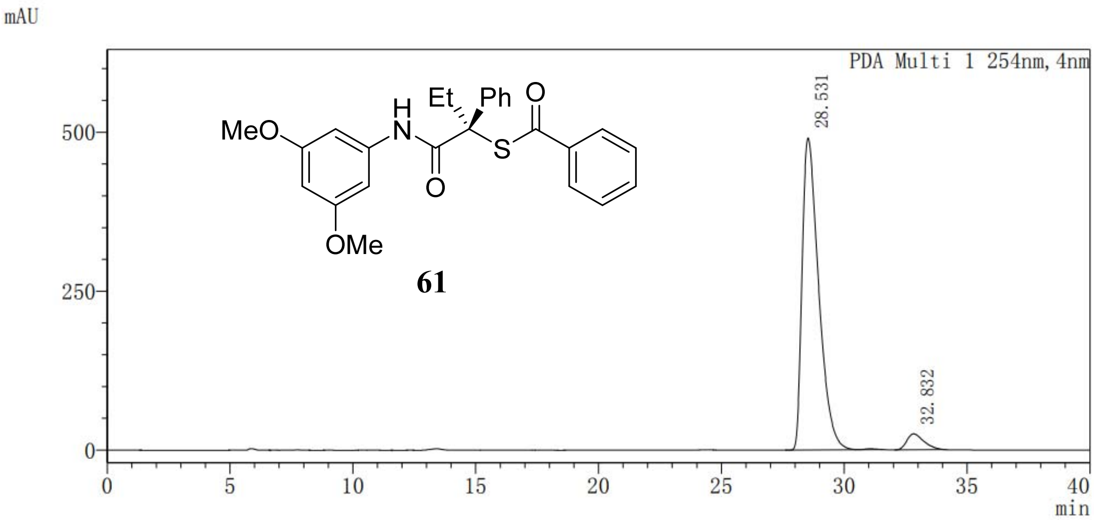
Peak#	Ret. Time	Area	Area%
1	12.853	2975448	7.226
2	15.710	38199272	92.774



Peak Table

PDA Ch1 254nm

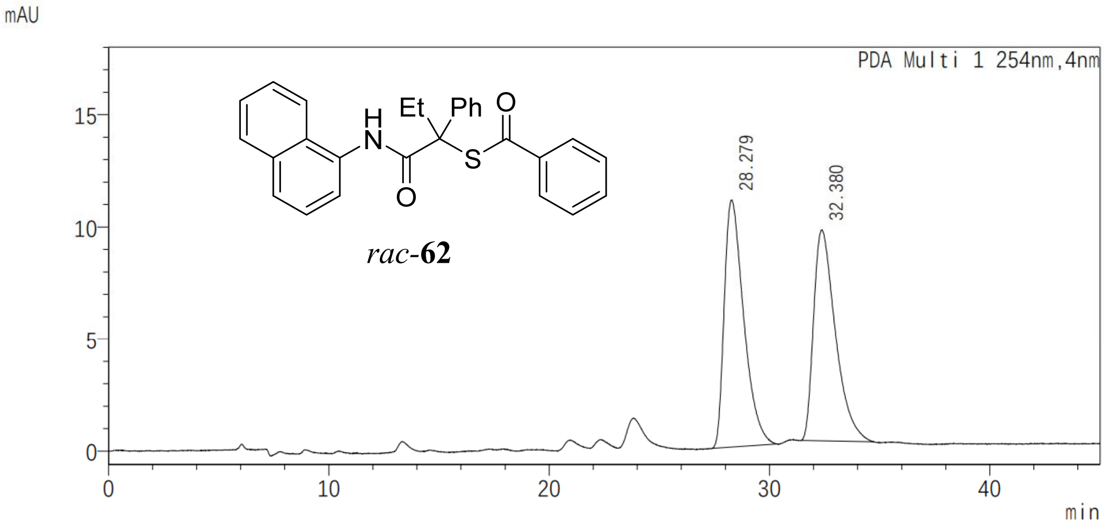
Peak#	Ret. Time	Area	Area%
1	28.379	3097972	49.947
2	32.531	3104562	50.053



Peak Table

PDA Ch1 254nm

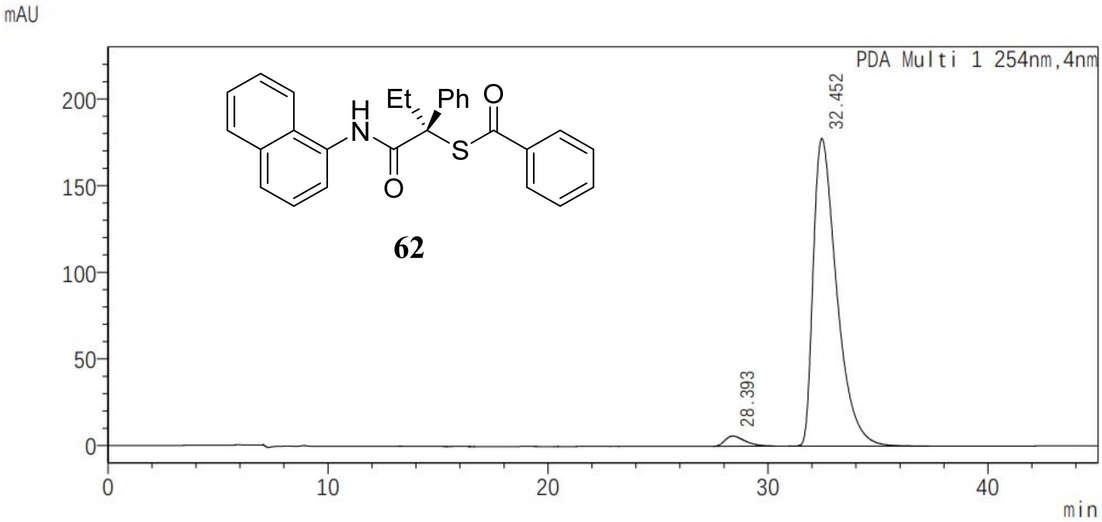
Peak#	Ret. Time	Area	Area%
1	28.531	22985131	94.946
2	32.832	1223383	5.054



Peak Table

PDA Ch1 254nm

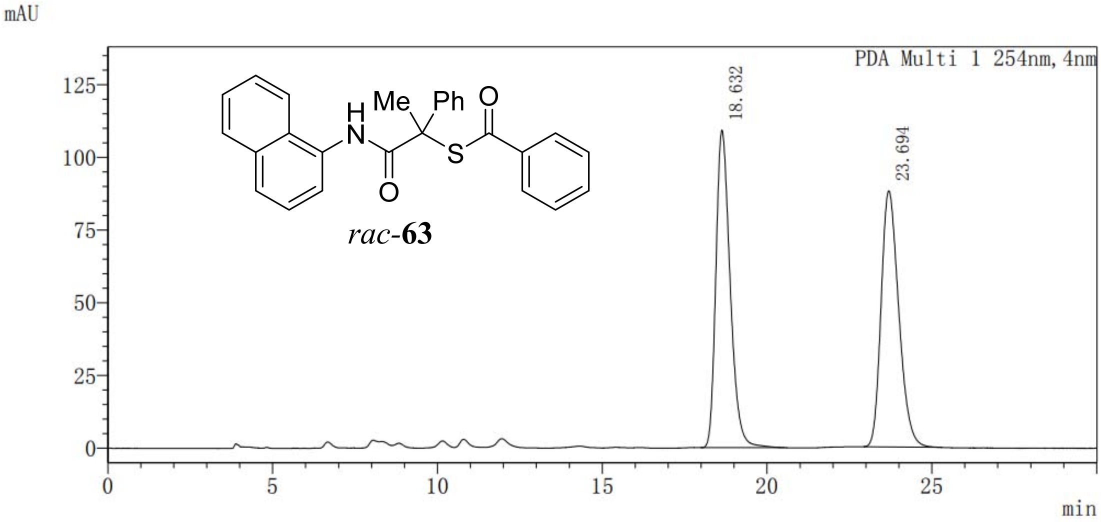
Peak#	Ret. Time	Area	Area%
1	28.279	678941	51.095
2	32.380	649836	48.905



Peak Table

PDA Ch1 254nm

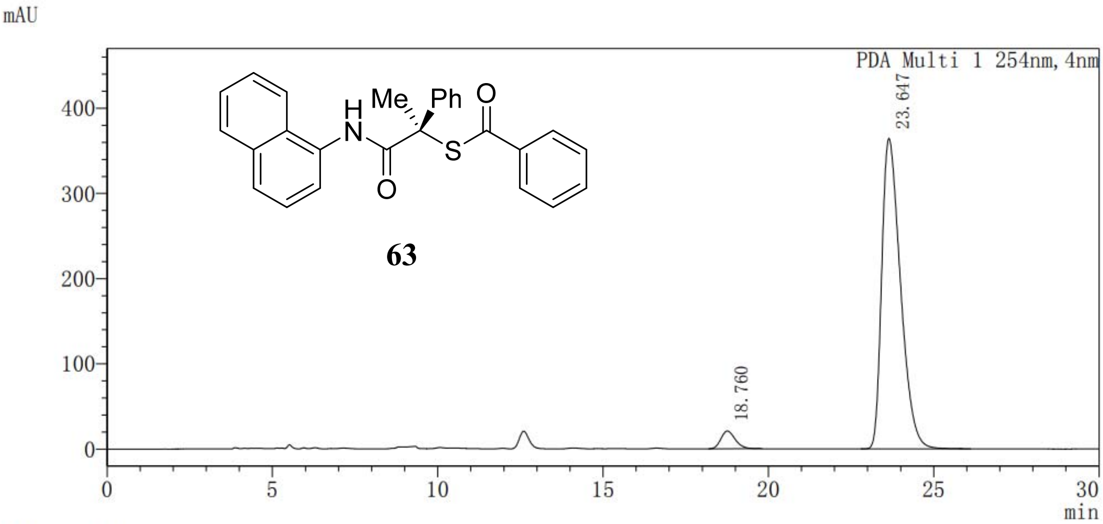
Peak#	Ret. Time	Area	Area%
1	28.393	367108	2.713
2	32.452	13163809	97.287



Peak Table

PDA Ch1 254nm

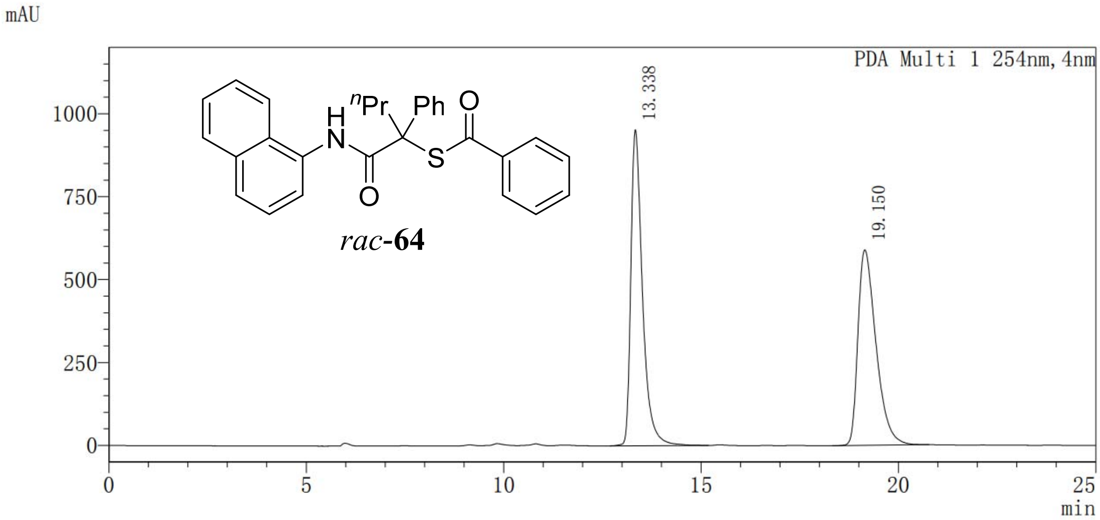
Peak#	Ret. Time	Area	Area%
1	18.632	3282819	50.024
2	23.694	3279631	49.976



Peak Table

PDA Ch1 254nm

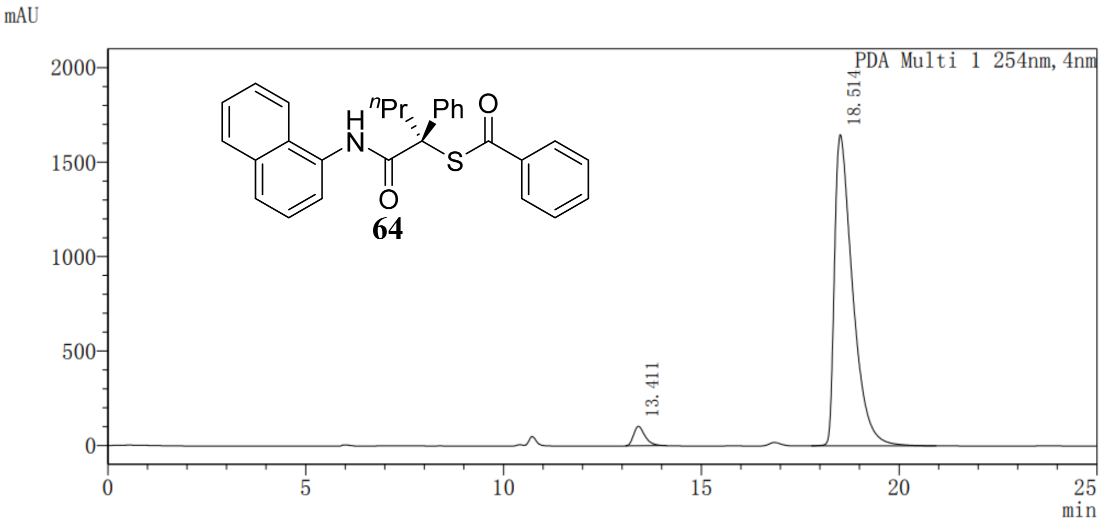
Peak#	Ret. Time	Area	Area%
1	18.760	631139	4.206
2	23.647	14373000	95.794



Peak Table

PDA Ch1 254nm

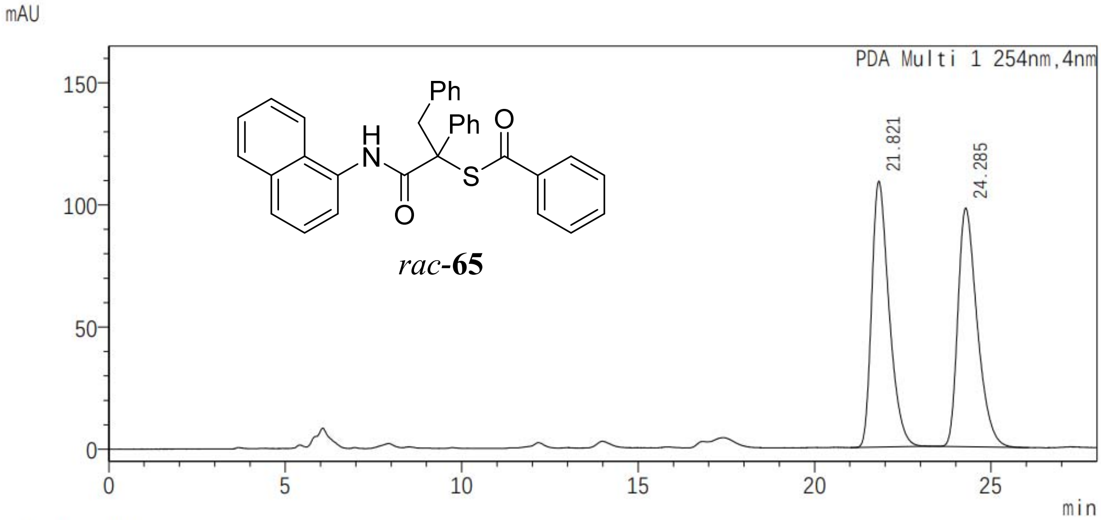
Peak#	Ret. Time	Area	Area%
1	13.338	19519969	50.988
2	19.150	18763310	49.012



Peak Table

PDA Ch1 254nm

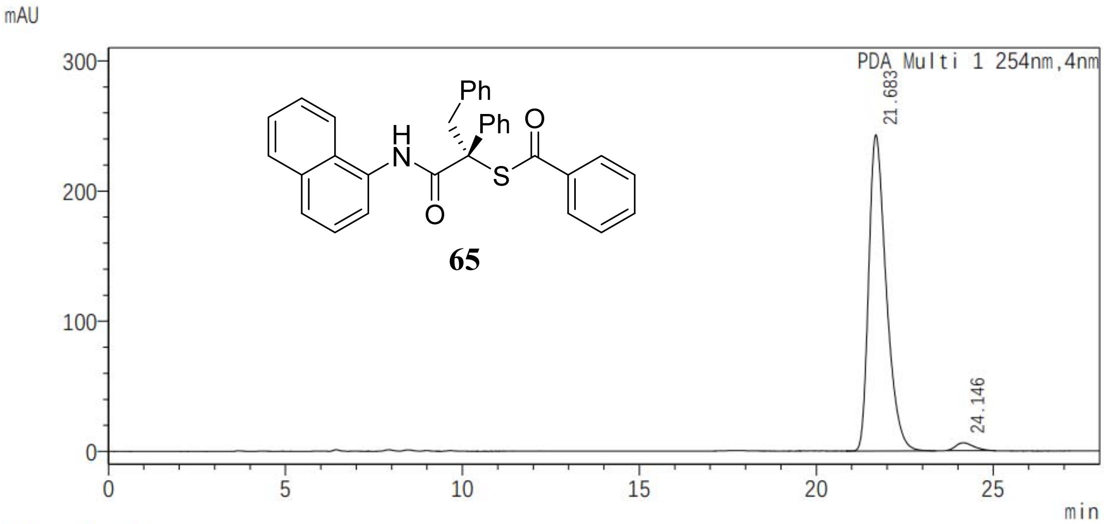
Peak#	Ret. Time	Area	Area%
1	13.411	2060449	3.775
2	18.514	52527294	96.225



Peak Table

PDA Ch1 254nm

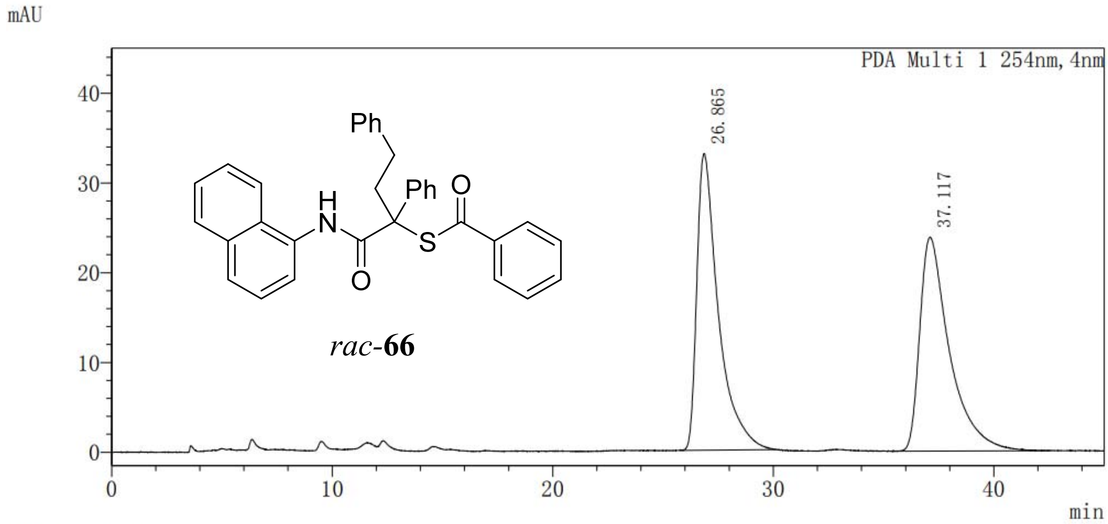
Peak#	Ret. Time	Area	Area%
1	21.821	3723162	50.016
2	24.285	3720791	49.984



Peak Table

PDA Ch1 254nm

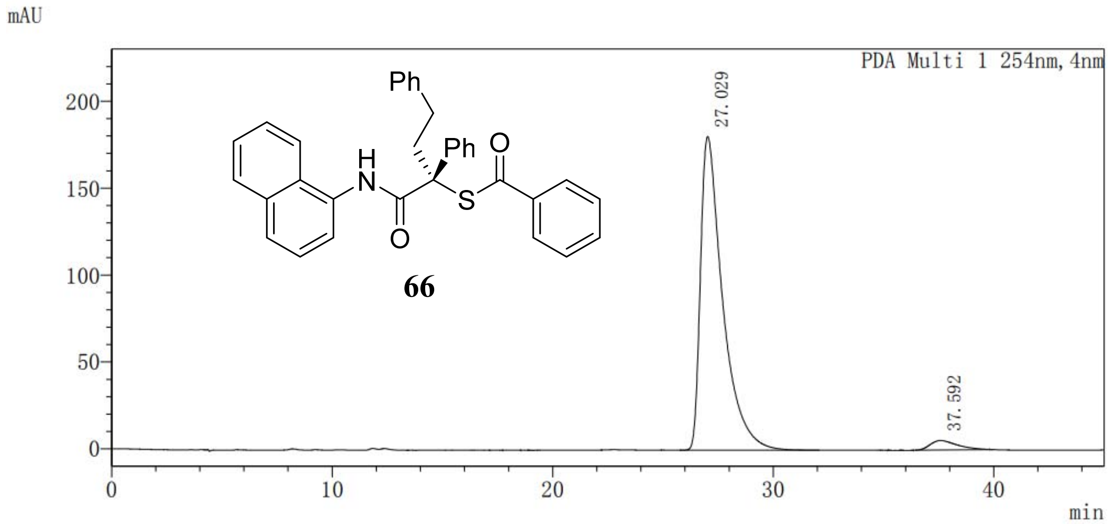
Peak#	Ret. Time	Area	Area%
1	21.683	8347986	97.592
2	24.146	205975	2.408



Peak Table

PDA Ch1 254nm

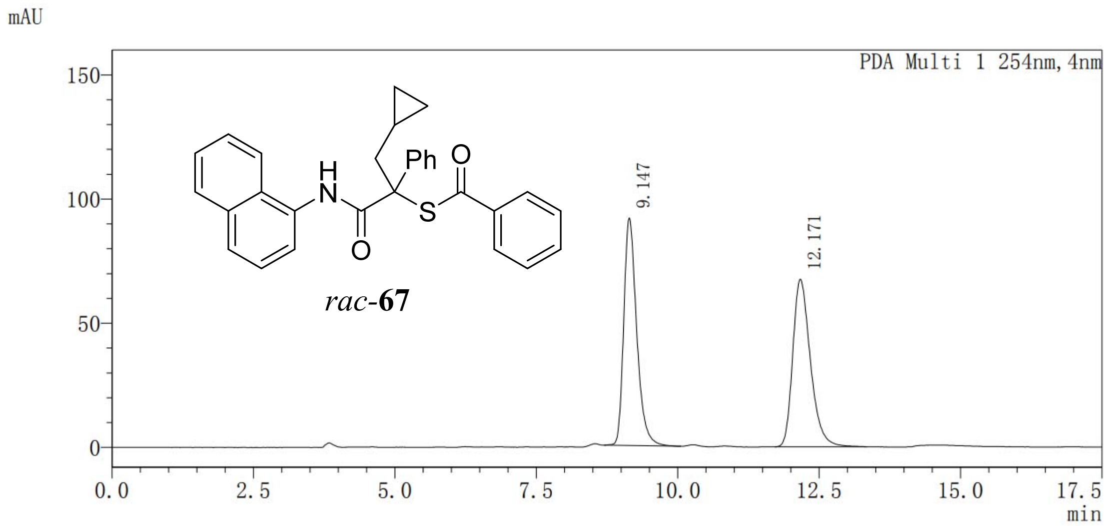
Peak#	Ret. Time	Area	Area%
1	26.865	2239294	50.141
2	37.117	2226728	49.859



Peak Table

PDA Ch1 254nm

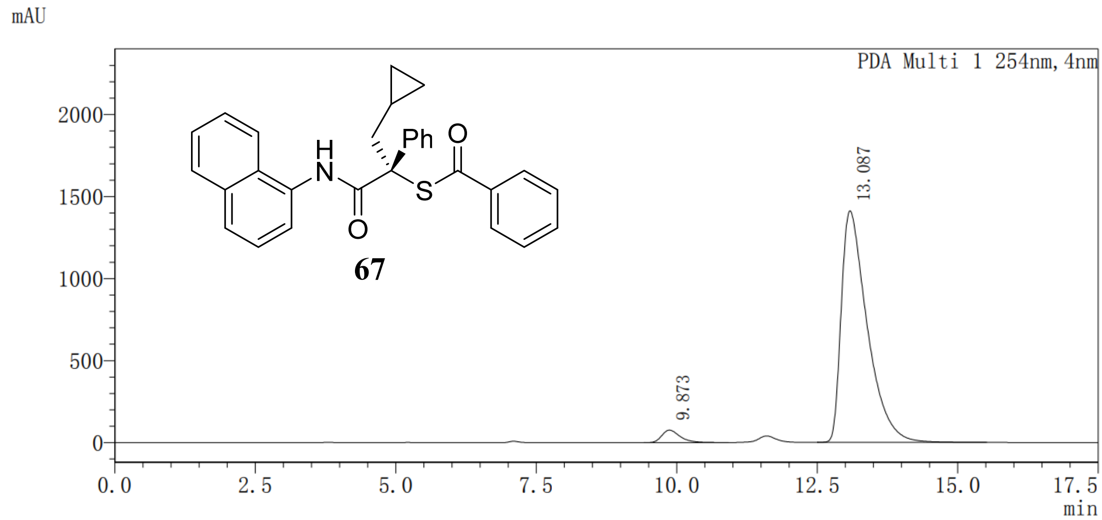
Peak#	Ret. Time	Area	Area%
1	27.029	12610516	96.386
2	37.592	472828	3.614



Peak Table

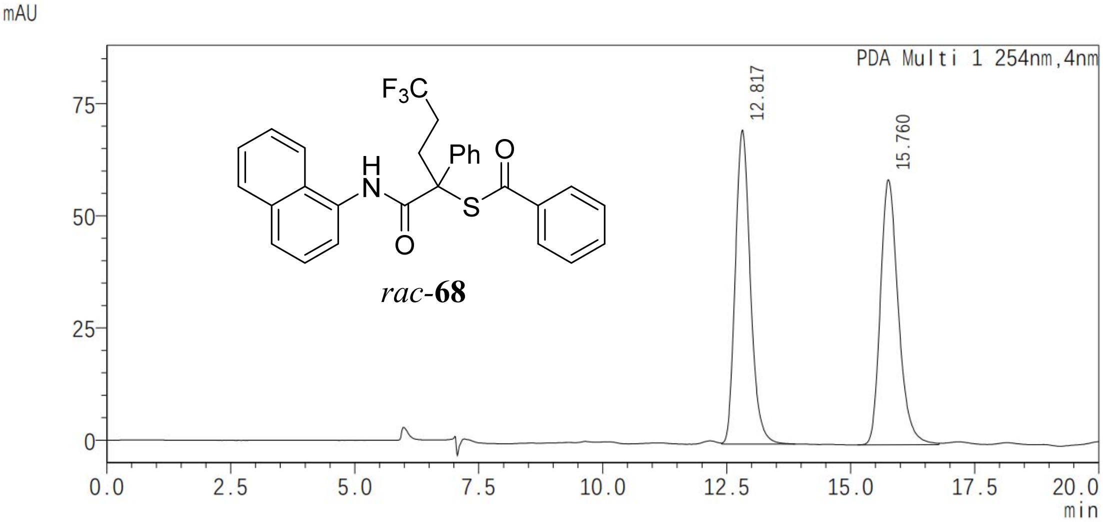
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.147	1456202	49.824
2	12.171	1466488	50.176



PDA Ch1 254nm

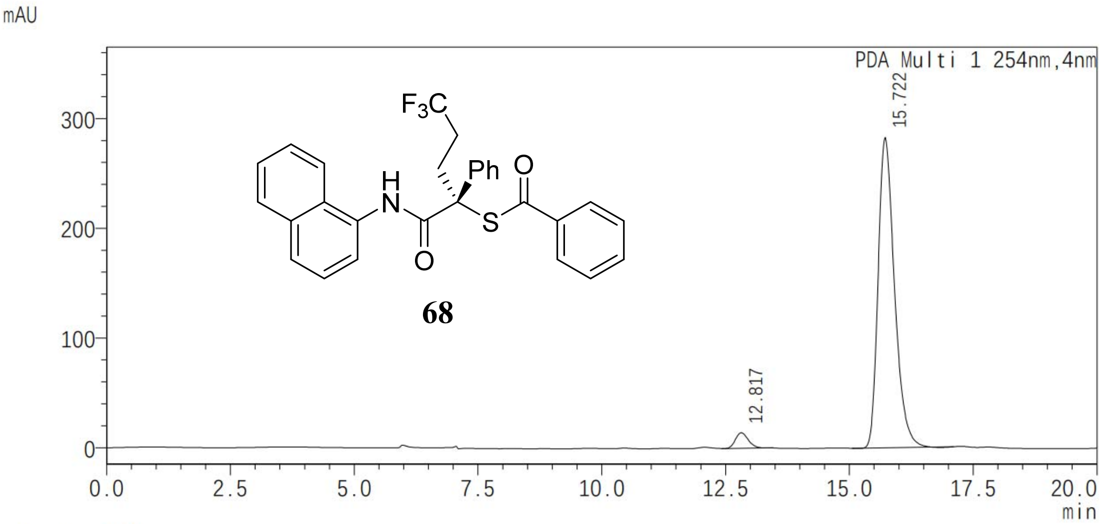
T	Hight	Area	Area%
9.873	76037	1722928	3.659
13.087	1411410	45365374	96.341



Peak Table

PDA Ch1 254nm

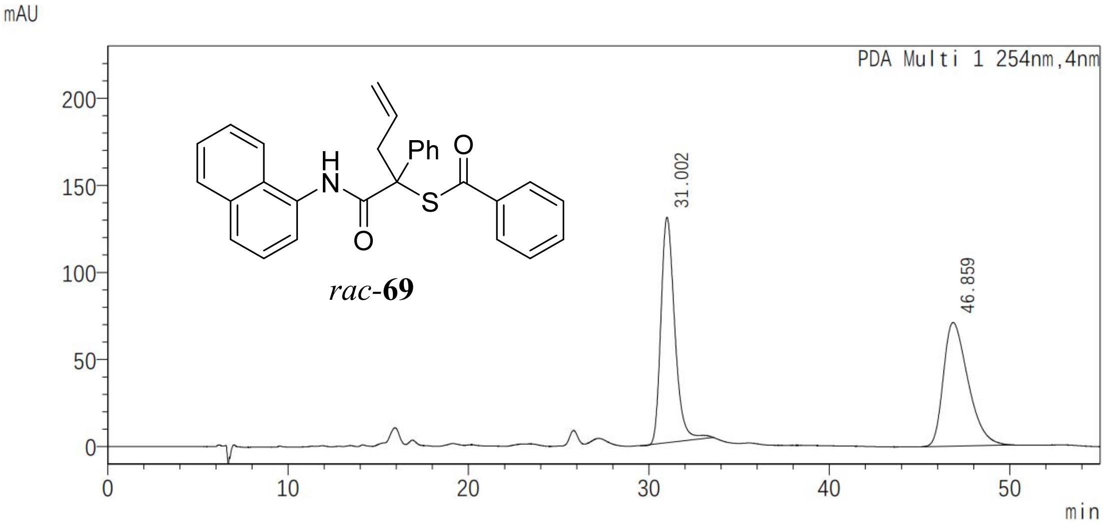
Peak#	Ret. Time	Area	Area%
1	12.817	1481149	49.925
2	15.760	1485611	50.075



Peak Table

PDA Ch1 254nm

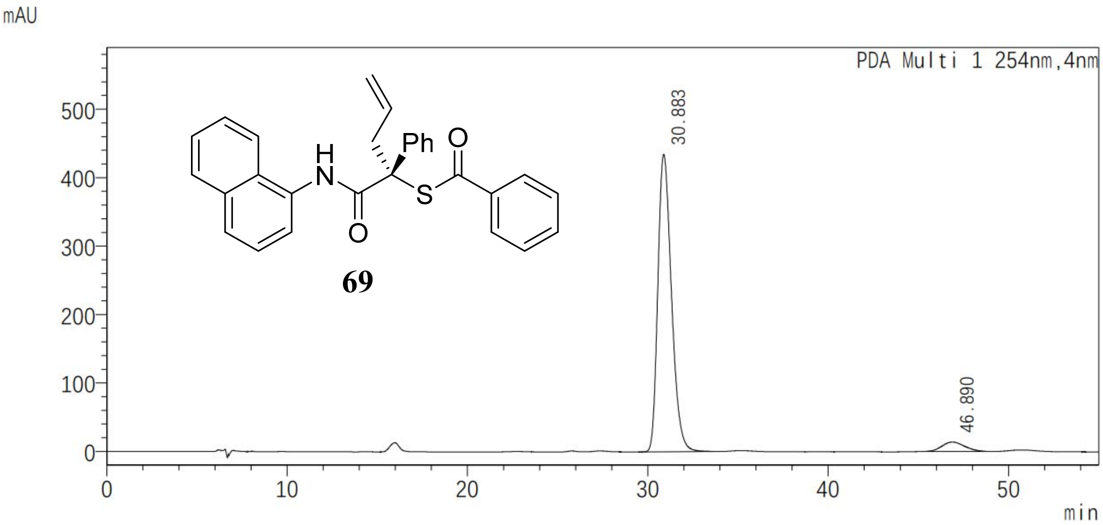
Peak#	Ret. Time	Area	Area%
1	12.817	257100	3.809
2	15.722	6493207	96.191



Peak Table

PDA Ch1 254nm

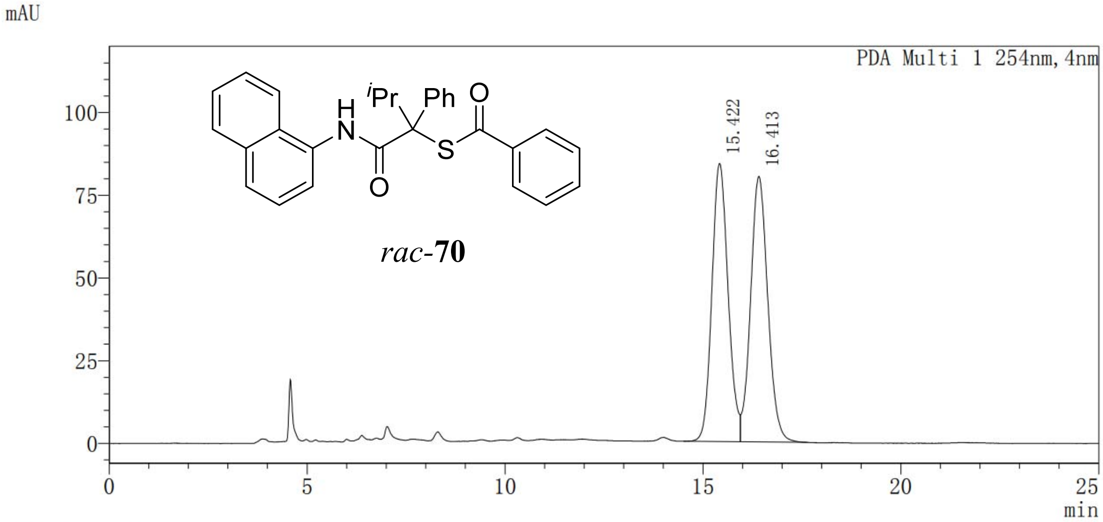
Peak#	Ret. Time	Area	Area%
1	31.002	6885086	50.463
2	46.859	6758690	49.537



Peak Table

PDA Ch1 254nm

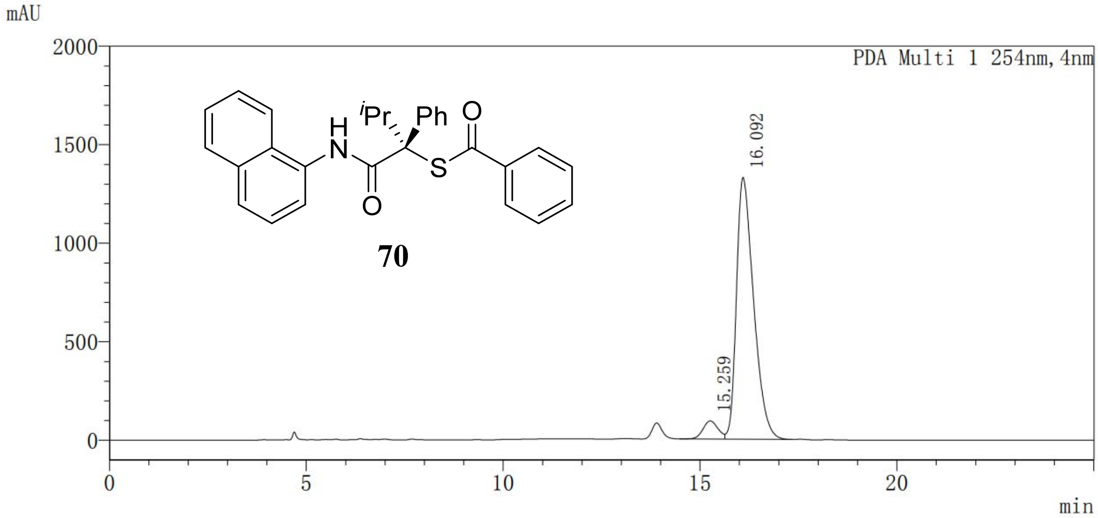
Peak#	Ret. Time	Area	Area%
1	30.883	22619031	95.013
2	46.890	1187174	4.987



Peak Table

PDA Ch1 254nm

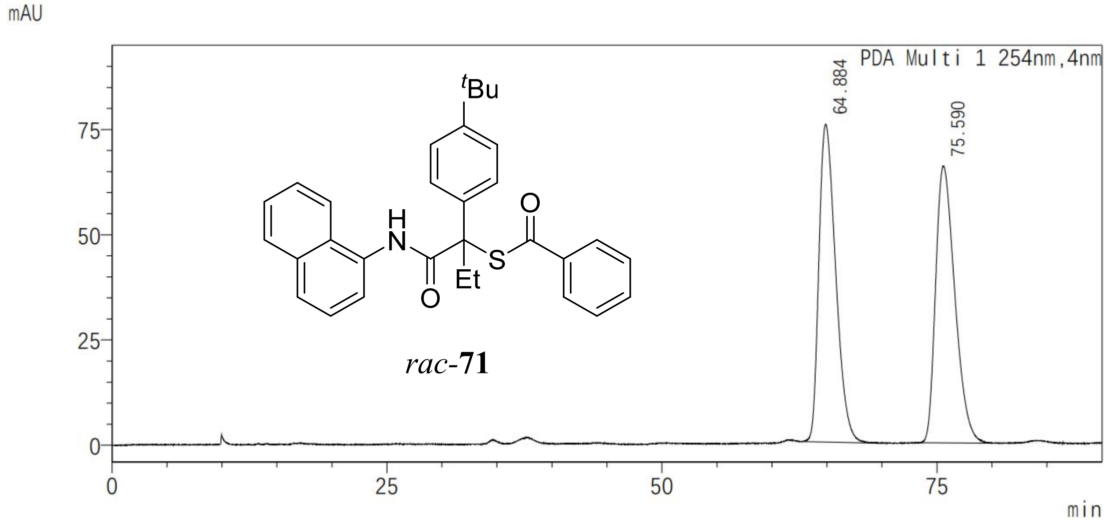
Peak#	Ret. Time	Area	Area%
1	15.422	2391264	49.681
2	16.413	2421961	50.319



Peak Table

PDA Ch1 254nm

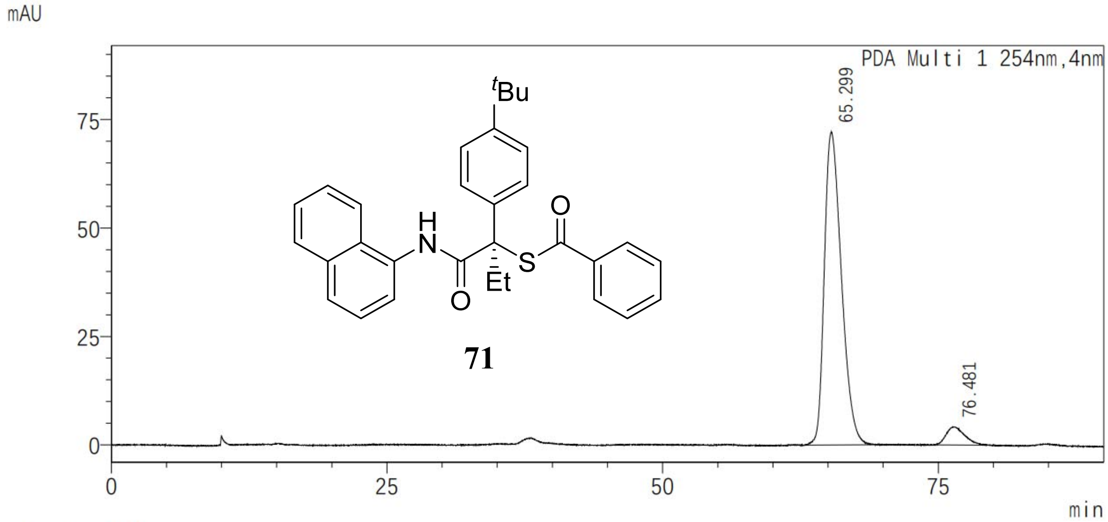
Peak#	Ret. Time	Area	Area%
1	15.259	2448160	5.736
2	16.092	40230220	94.264



Peak Table

PDA Ch1 254nm

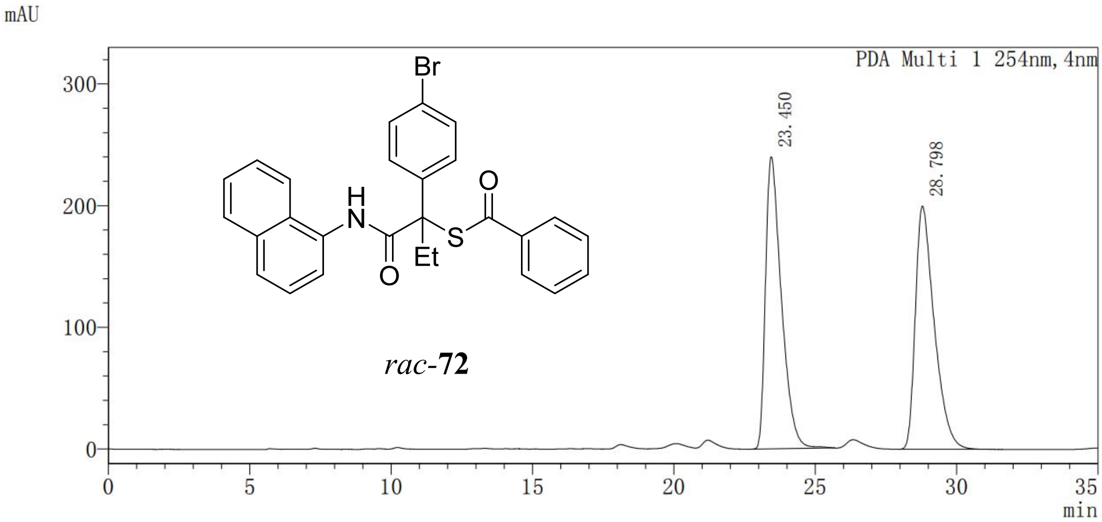
Peak#	Ret. Time	Area	Area%
1	64.884	8023396	50.070
2	75.590	8001112	49.930



Peak Table

PDA Ch1 254nm

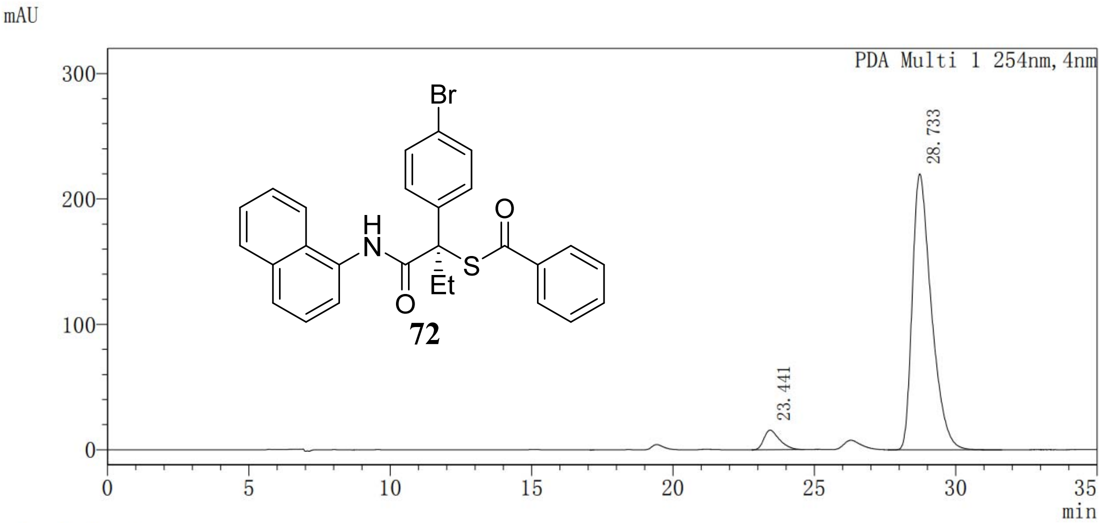
Peak#	Ret. Time	Area	Area%
1	65.299	7788616	94.148
2	76.481	484108	5.852



Peak Table

PDA Ch1 254nm

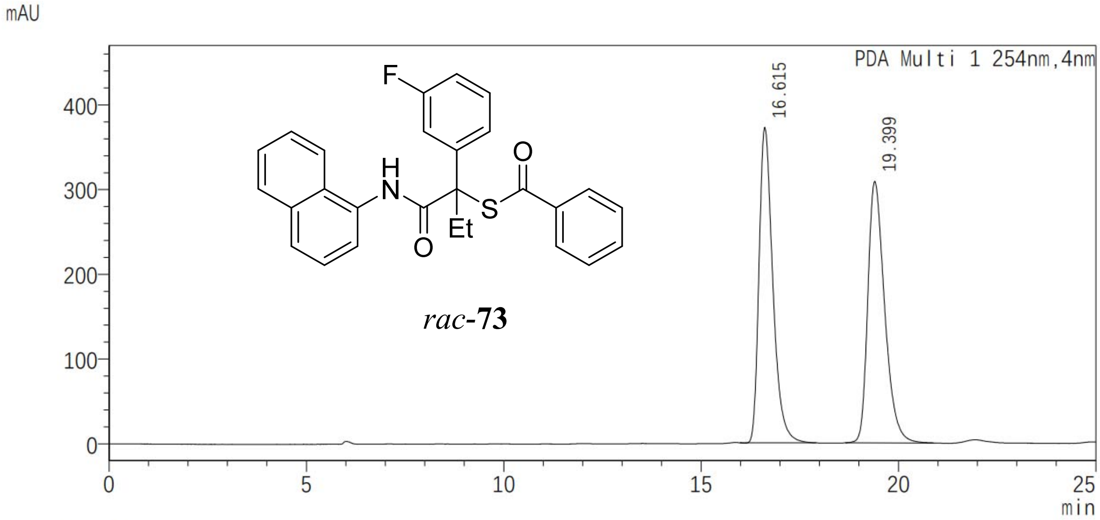
Peak#	Ret. Time	Area	Area%
1	23.450	9356145	50.164
2	28.798	9294871	49.836



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.441	598561	5.477
2	28.733	10329282	94.523

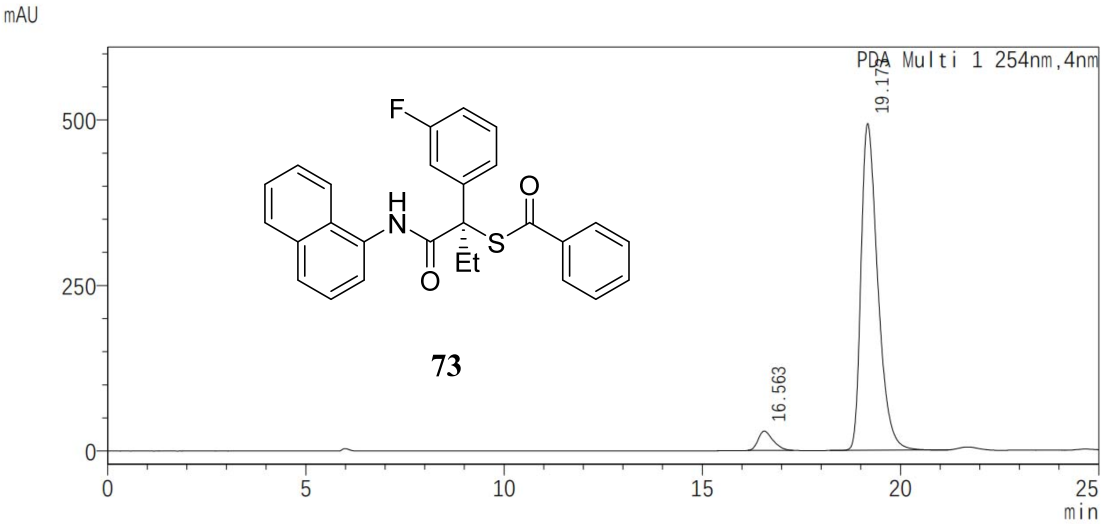


rac-**73**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.615	9035215	49.652
2	19.399	9161901	50.348

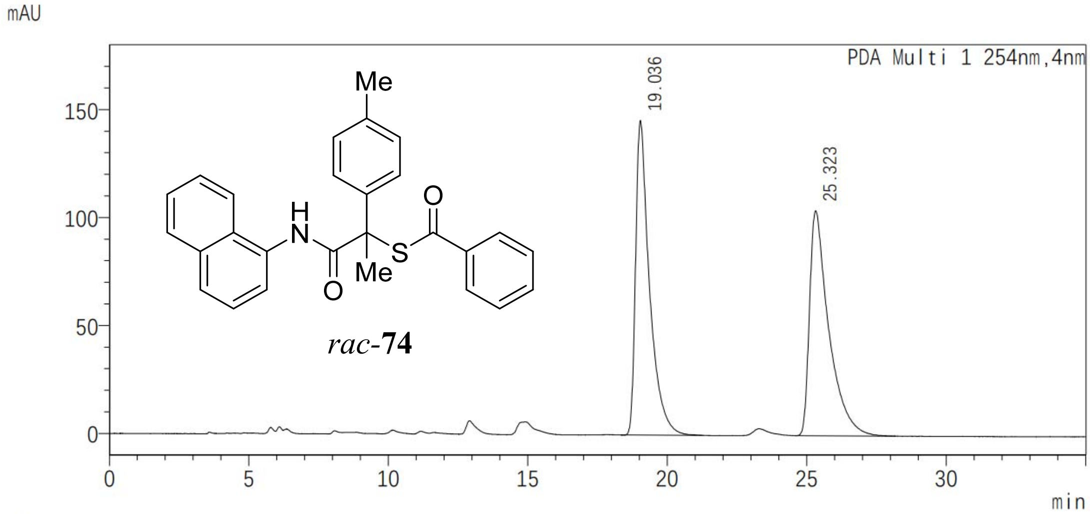


73

Peak Table

PDA Ch1 254nm

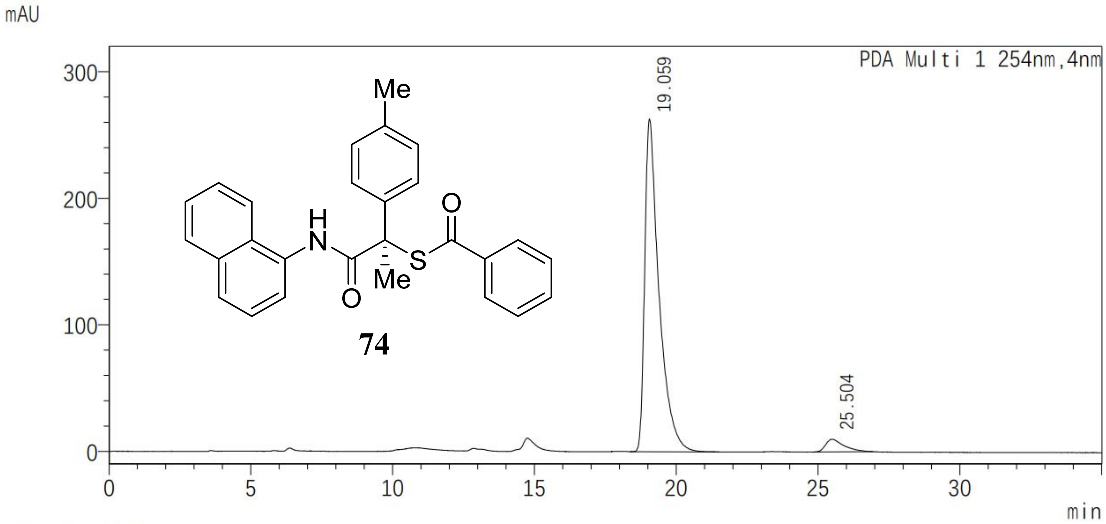
Peak#	Ret. Time	Area	Area%
1	16.563	758940	4.983
2	19.173	14471460	95.017



Peak Table

PDA Ch1 254nm

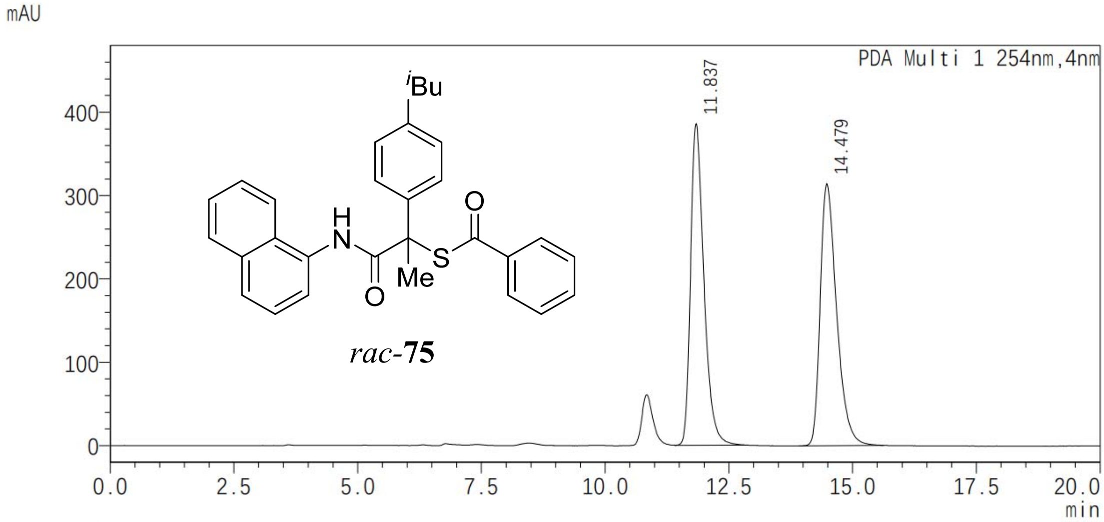
Peak#	Ret. Time	Area	Area%
1	19.036	5047698	50.198
2	25.323	5007806	49.802



Peak Table

PDA Ch1 254nm

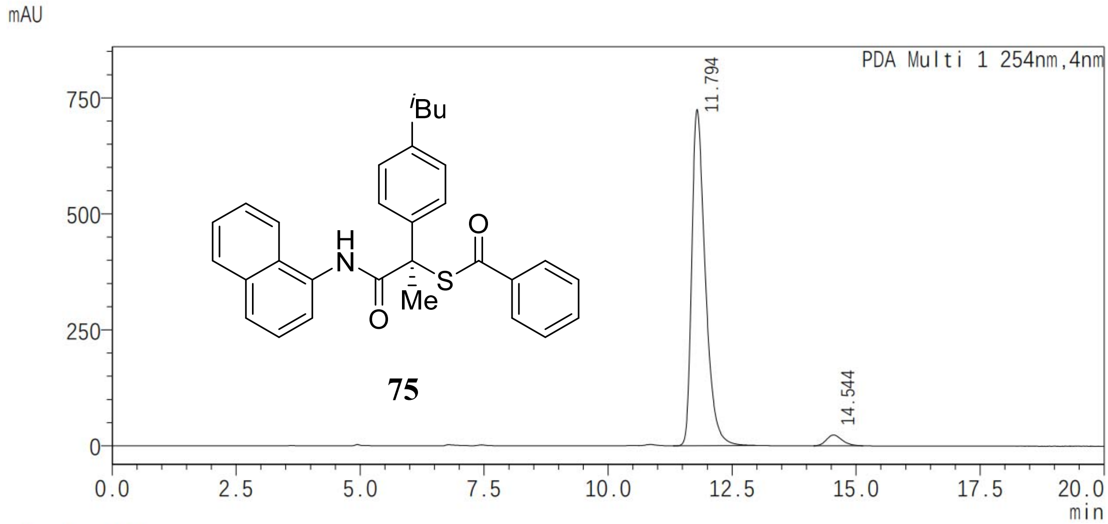
Peak#	Ret. Time	Area	Area%
1	19.059	9202620	95.334
2	25.504	450450	4.666



Peak Table

PDA Ch1 254nm

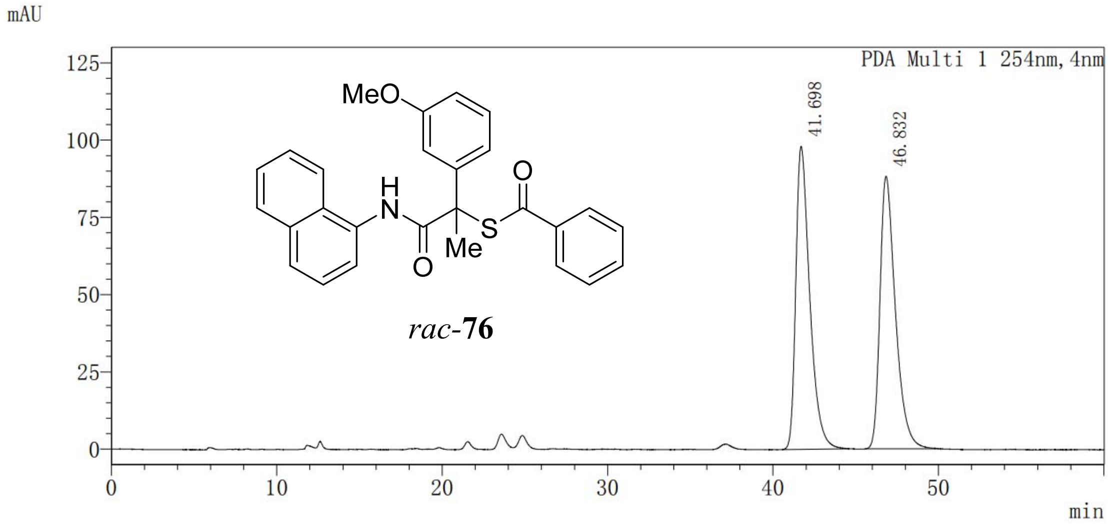
Peak#	Ret. Time	Area	Area%
1	11.837	7229705	49.977
2	14.479	7236311	50.023



Peak Table

PDA Ch1 254nm

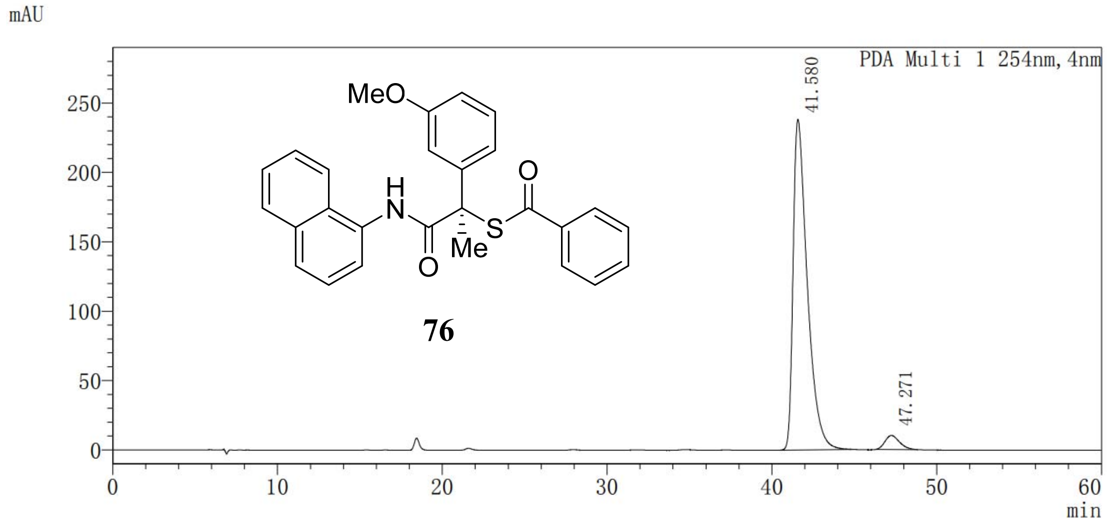
Peak#	Ret. Time	Area	Area%
1	11.794	13774900	96.444
2	14.544	507968	3.556



Peak Table

PDA Ch1 254nm

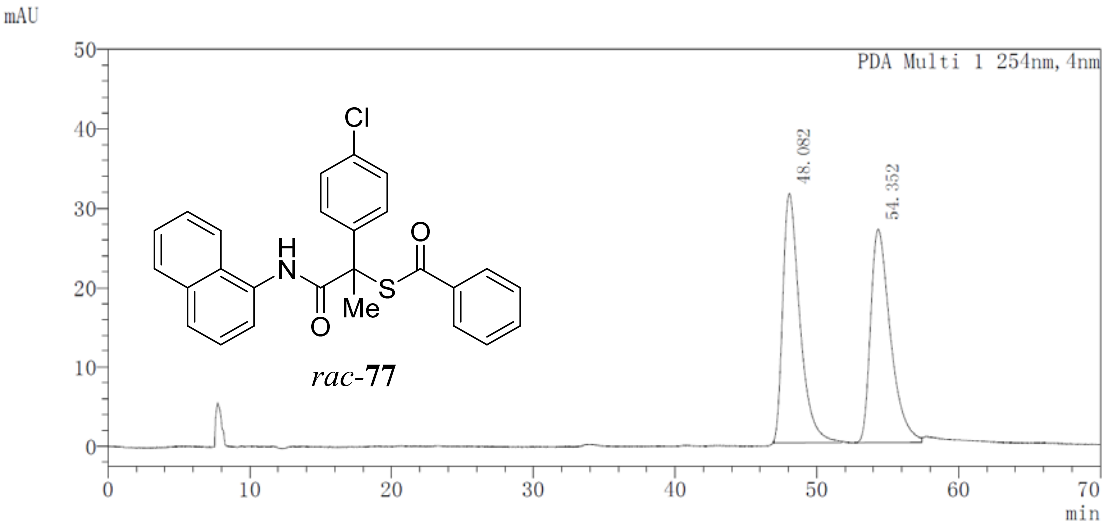
Peak#	Ret. Time	Area	Area%
1	41.698	5733158	50.002
2	46.832	5732780	49.998



Peak Table

PDA Ch1 254nm

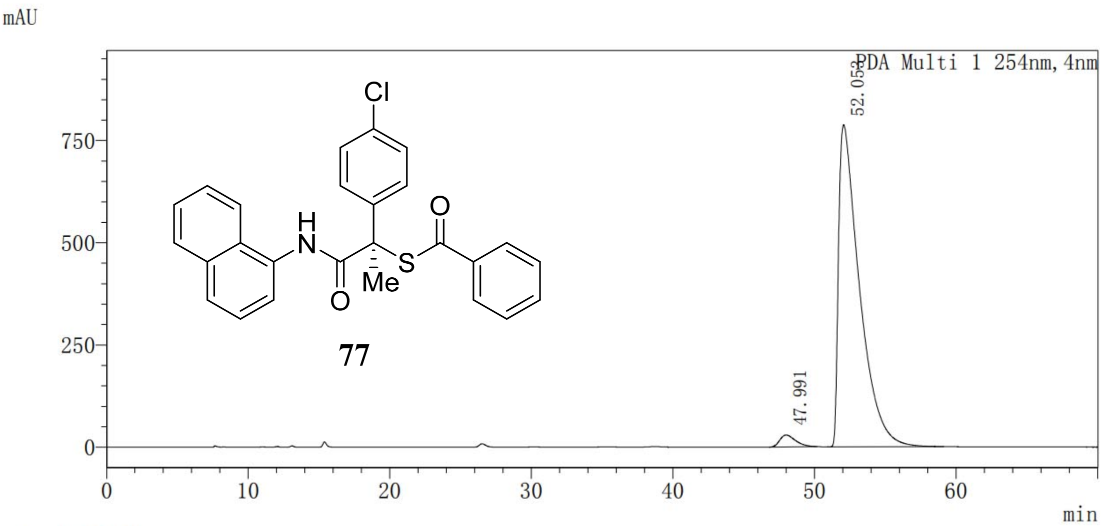
Peak#	Ret. Time	Area	Area%
1	41.580	14254970	95.822
2	47.271	621487	4.178



Peak Table

PDA Ch1 254nm

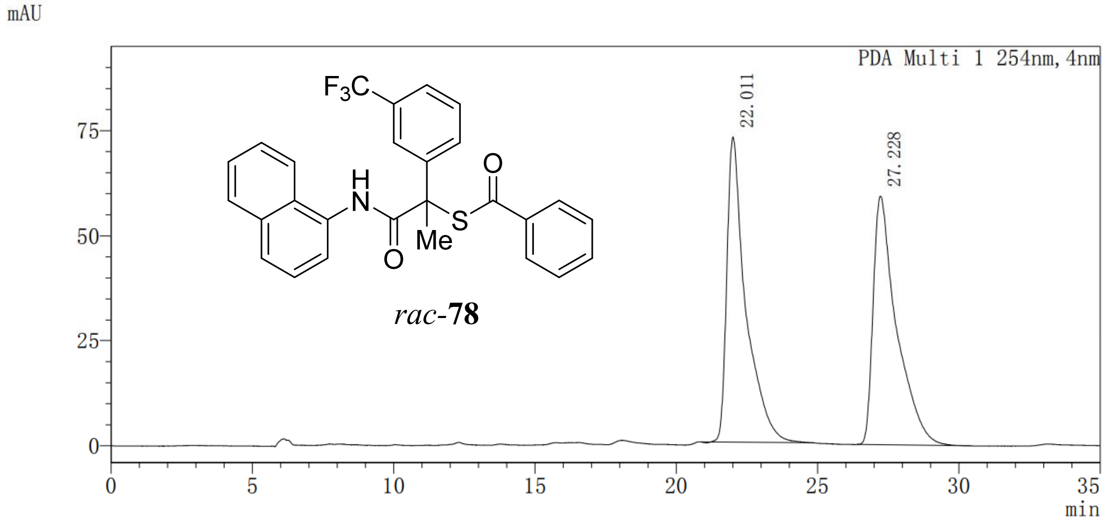
Peak#	Ret. Time	Area	Area%
1	48.082	2633414	50.142
2	54.352	2618461	49.858



Peak Table

PDA Ch1 254nm

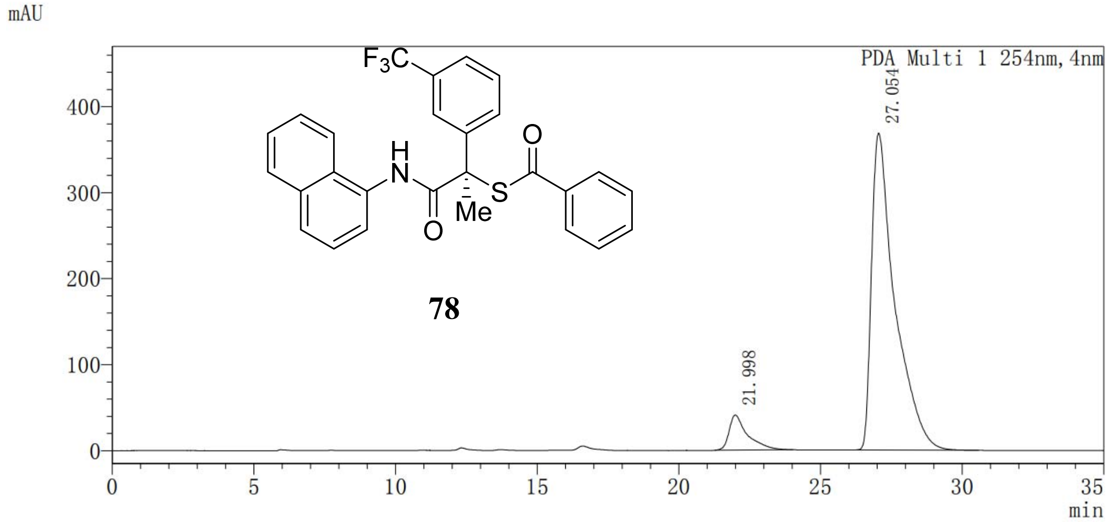
Peak#	Ret. Time	Area	Area%
1	47.991	2261933	2.725
2	52.053	80750287	97.275



Peak Table

PDA Ch1 254nm

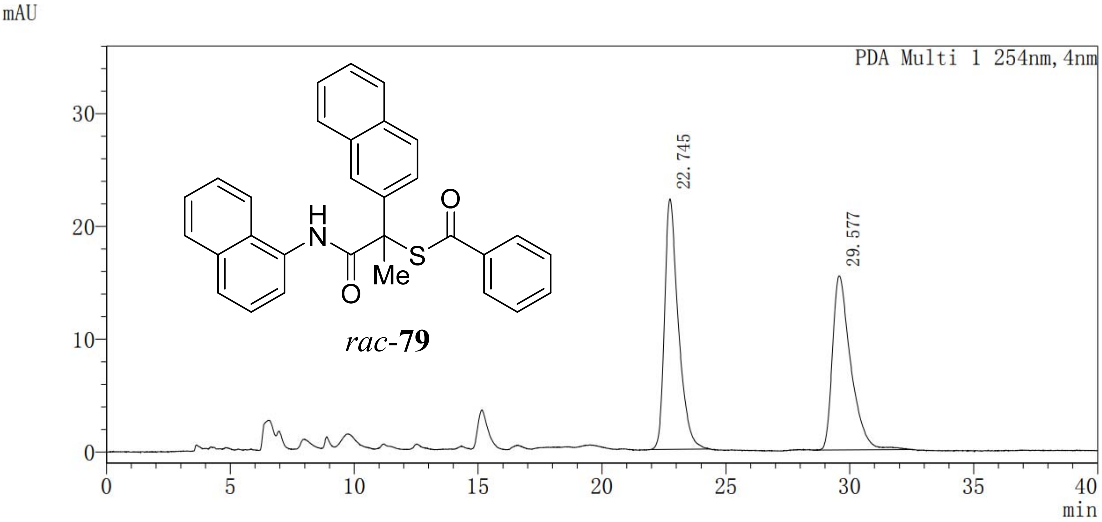
Peak#	Ret. Time	Area	Area%
1	22.011	3393305	49.833
2	27.228	3416000	50.167



Peak Table

PDA Ch1 254nm

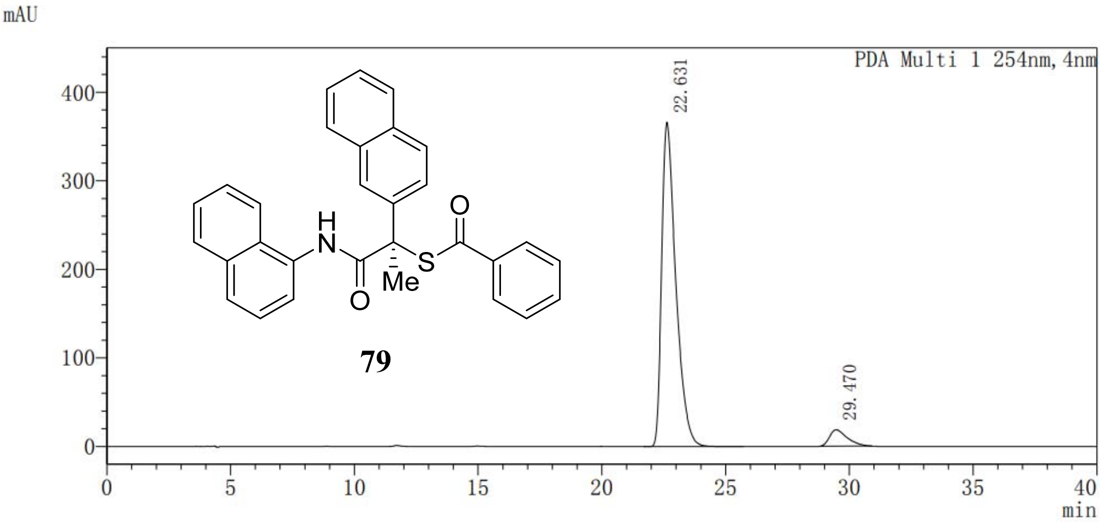
Peak#	Ret. Time	Area	Area%
1	21.998	1845198	8.038
2	27.054	21110567	91.962



Peak Table

PDA Ch1 254nm

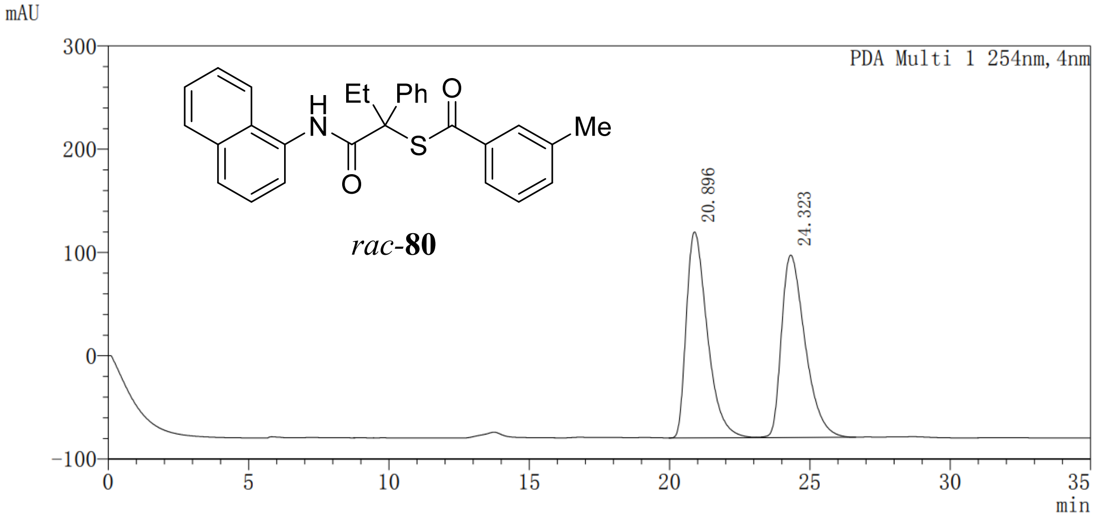
Peak#	Ret. Time	Area	Area%
1	22.745	858869	51.953
2	29.577	794292	48.047



Peak Table

PDA Ch1 254nm

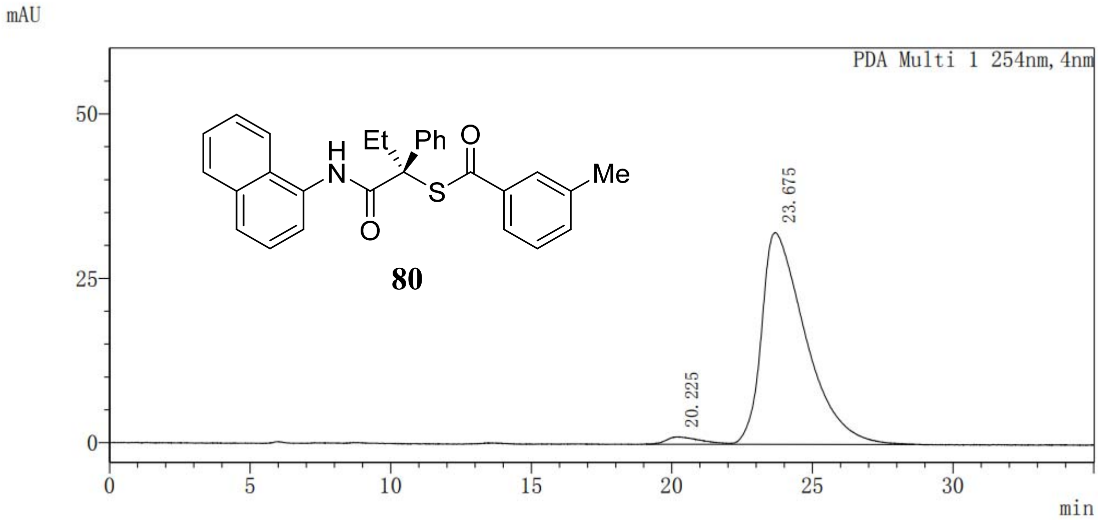
Peak#	Ret. Time	Area	Area%
1	22.631	14512109	94.074
2	29.470	914167	5.926



rac-**80**

PDA Ch1 254nm

T	Hight	Area	Area%
20.896	199388	10394972	50.094
24.323	176623	10356150	49.906

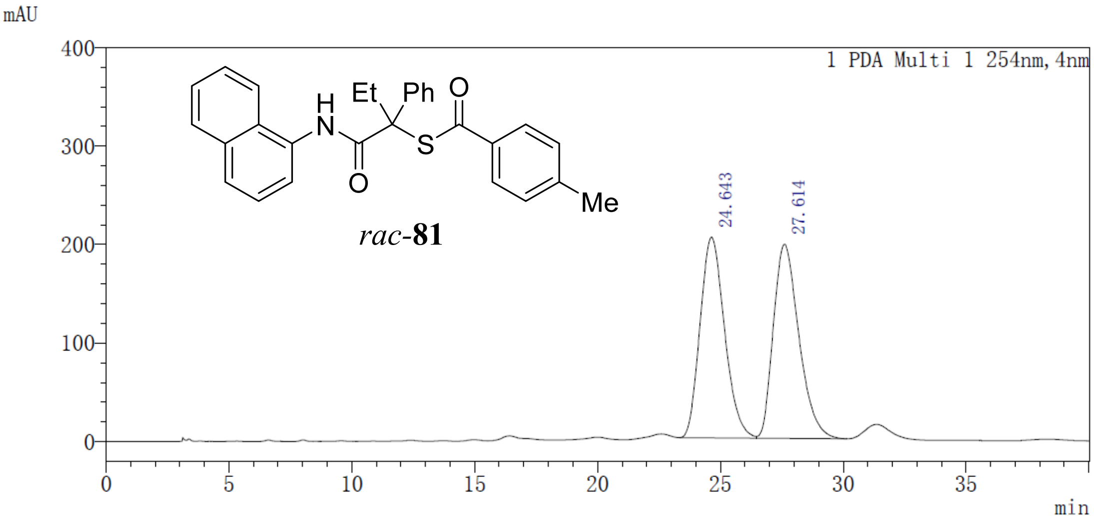


80

Peak Table

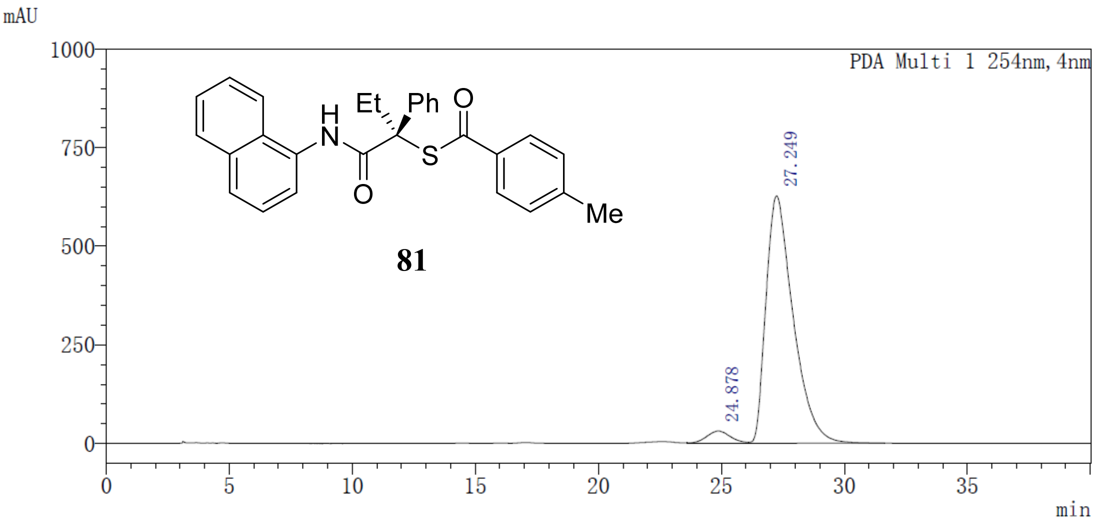
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.225	97047	2.685
2	23.675	3516725	97.315



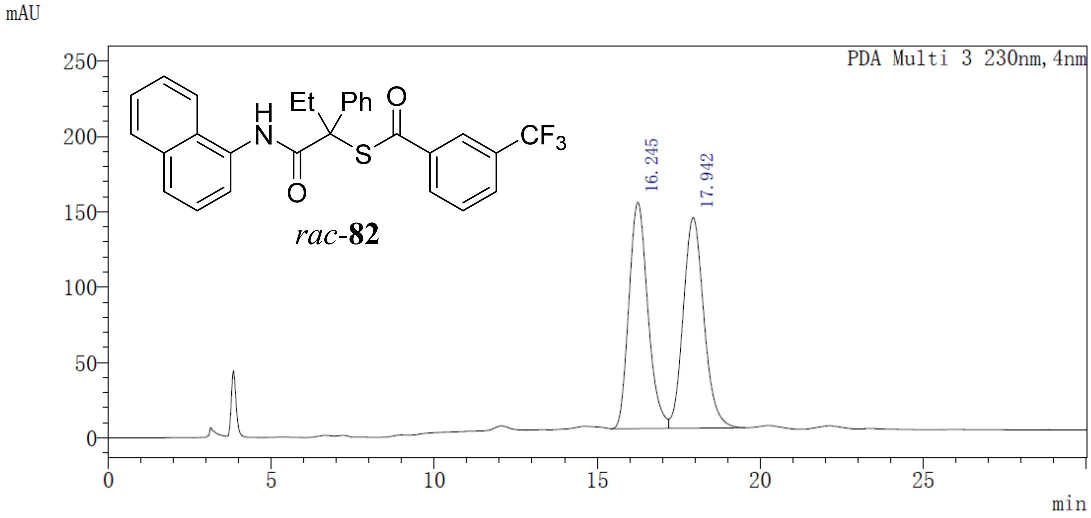
PDA Ch1 254nm

T	Hight	Area	Area%
24.643	203841	14153464	49.798
27.614	197139	14268054	50.202



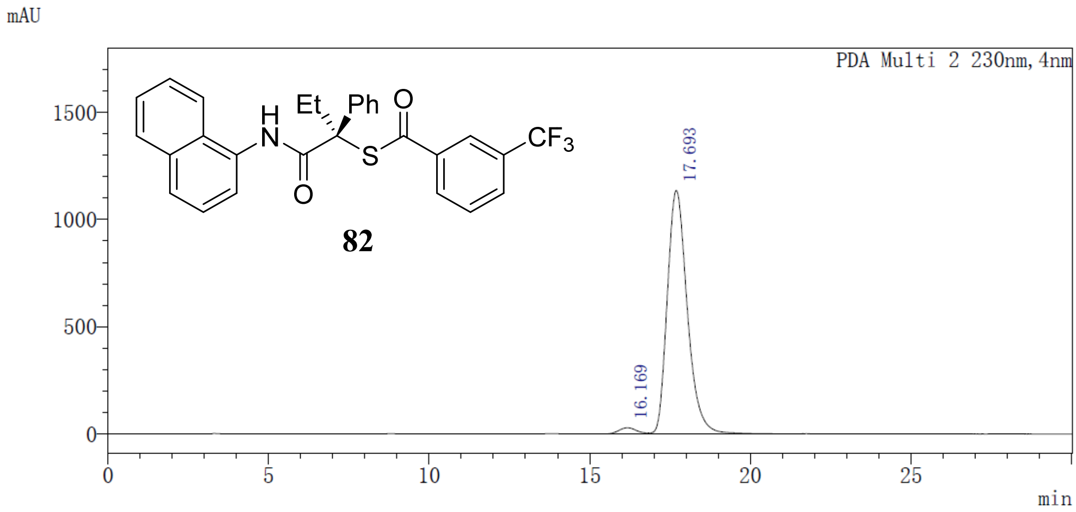
PDA Ch1 254nm

T	Hight	Area	Area%
24.878	30921	2084672	4.146
27.249	627362	48199881	95.854



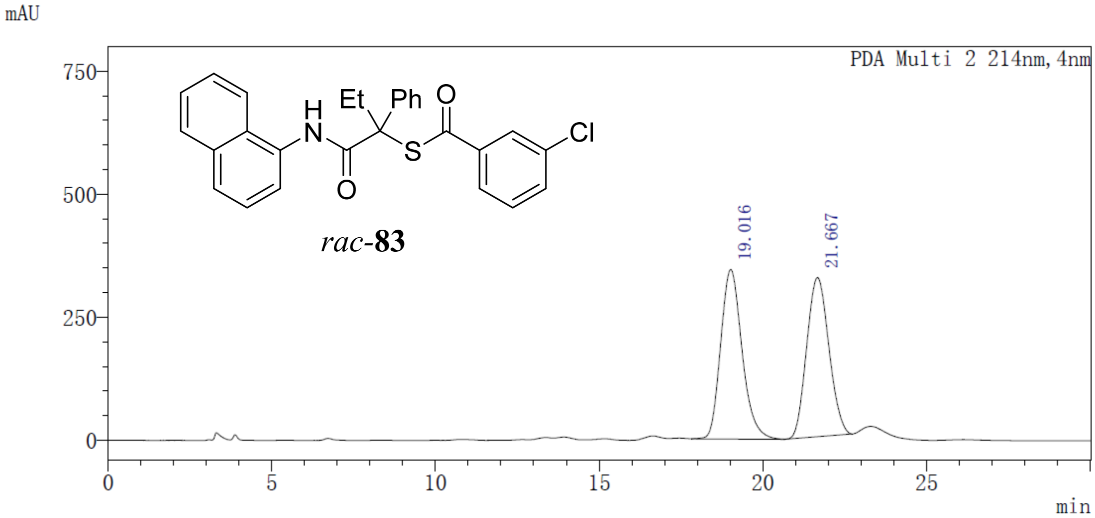
PDA Ch3 230nm

T	Hight	Area	Area%
16.245	150129	6069049	49.573
17.942	139732	6173721	50.427



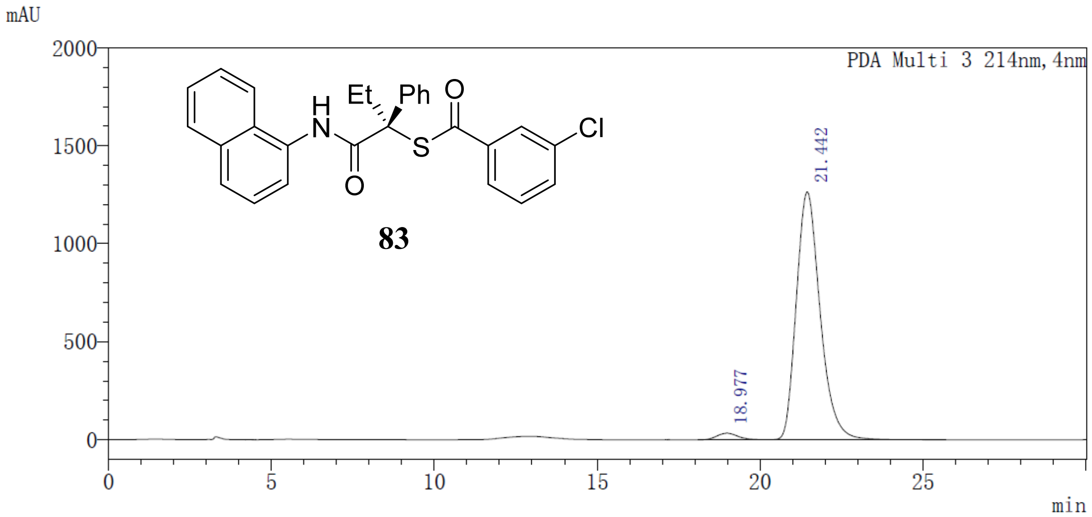
PDA Ch2 230nm

T	Hight	Area	Area%
16.169	28944	1095505	2.179
17.693	1136385	49190891	97.821



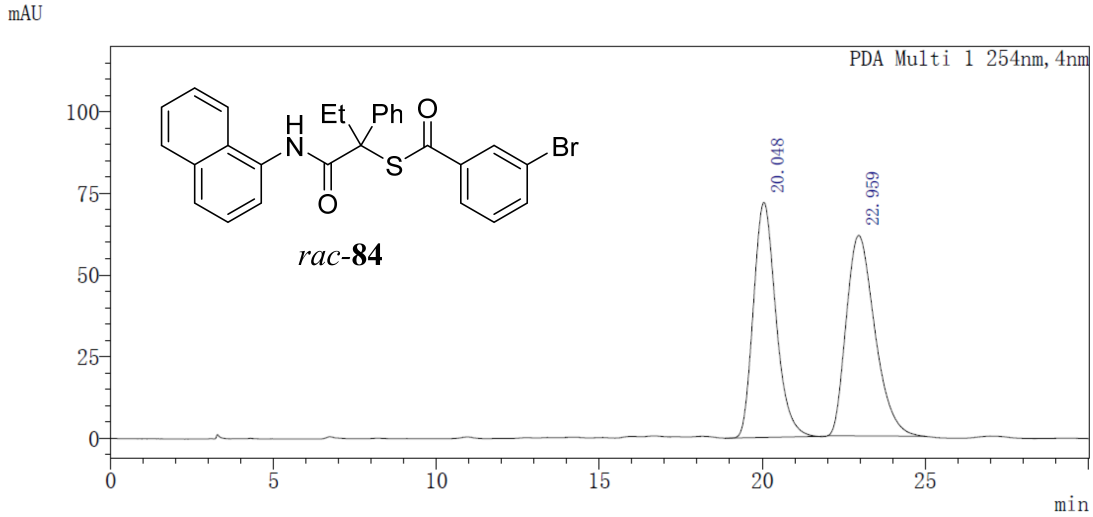
PDA Ch2 214nm

T	Hight	Area	Area%
19.016	344495	15655560	50.624
21.667	323551	15269473	49.376



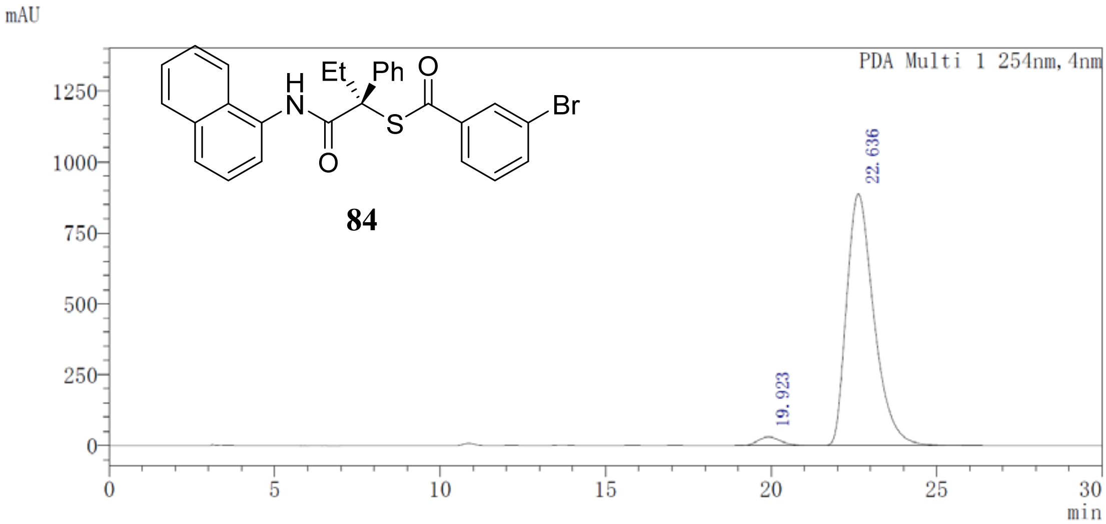
PDA Ch3 214nm

T	Hight	Area	Area%
18.977	34049	1562057	2.365
21.442	1266399	64481374	97.635



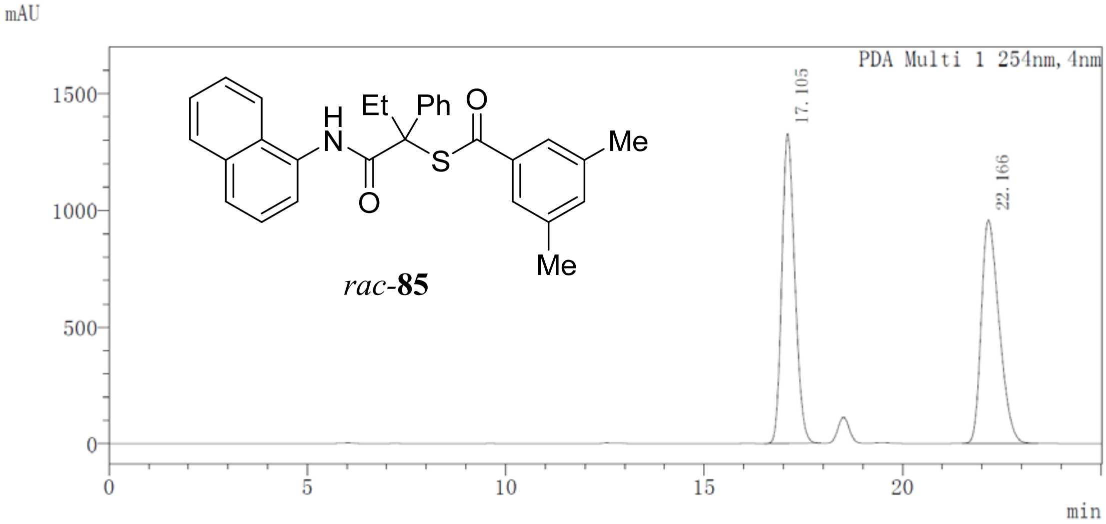
PDA Ch1 254nm

T	Hight	Area	Area%
20.048	71930	3445433	47.831
22.959	61383	3757847	52.169



PDA Ch1 254nm

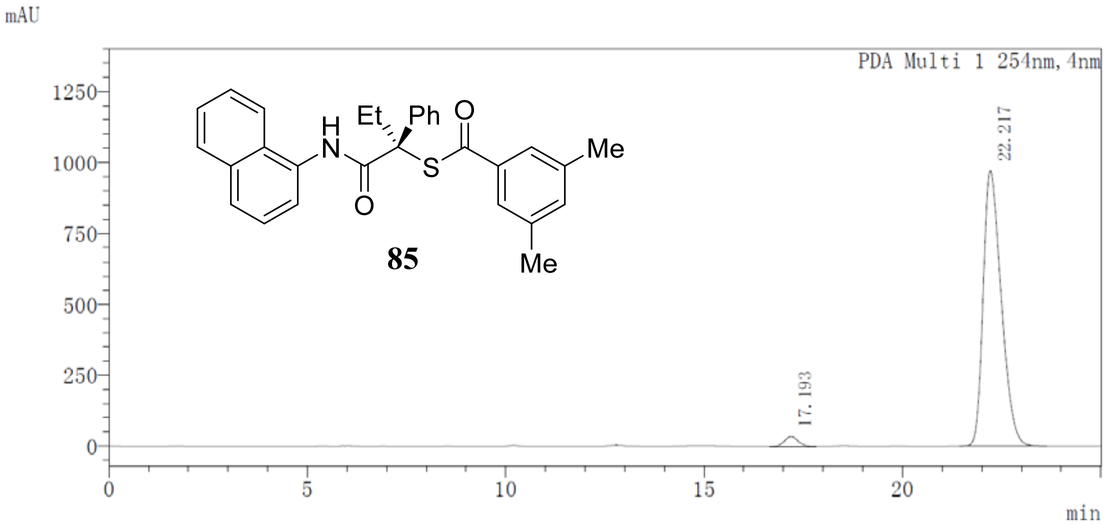
T	Hight	Area	Area%
19.923	30835	1541098	2.929
22.636	887479	51077690	97.071



Peak Table

PDA Ch1 254nm

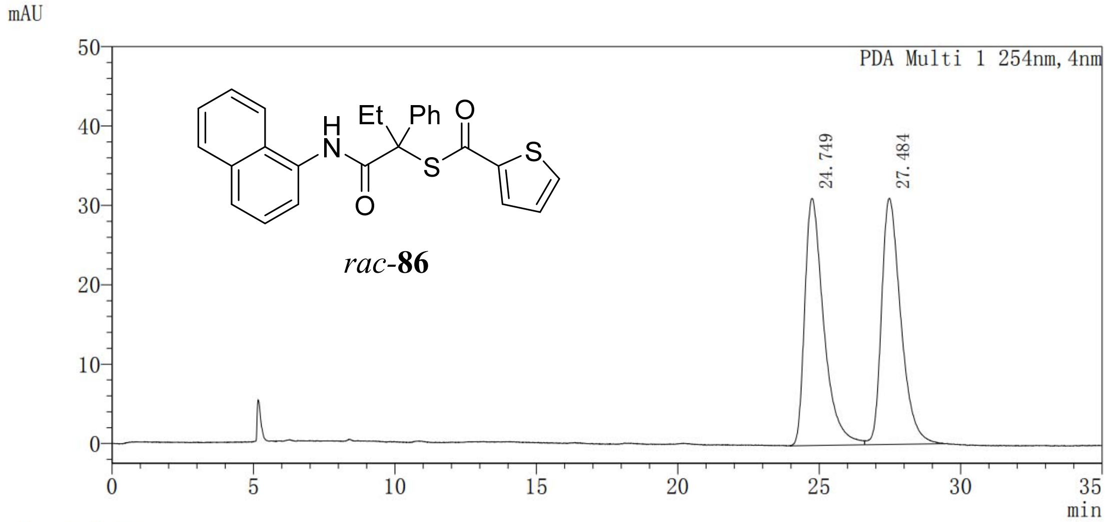
Peak#	Ret. Time	Area	Area%
1	17.105	30284686	50.187
2	22.166	30058489	49.813



Peak Table

PDA Ch1 254nm

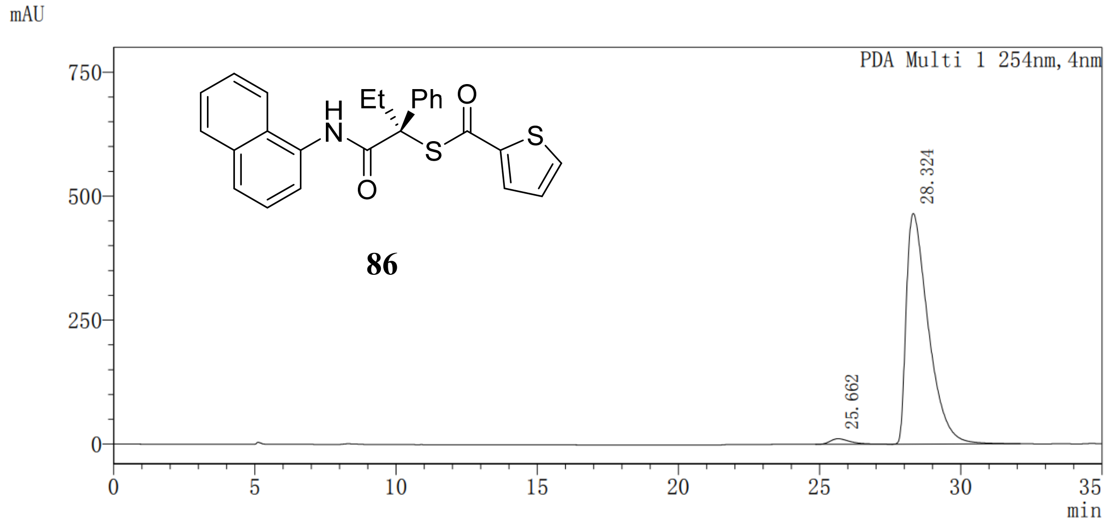
Peak#	Ret. Time	Area	Area%
1	17.193	769141	2.445
2	22.217	30689465	97.555



Peak Table

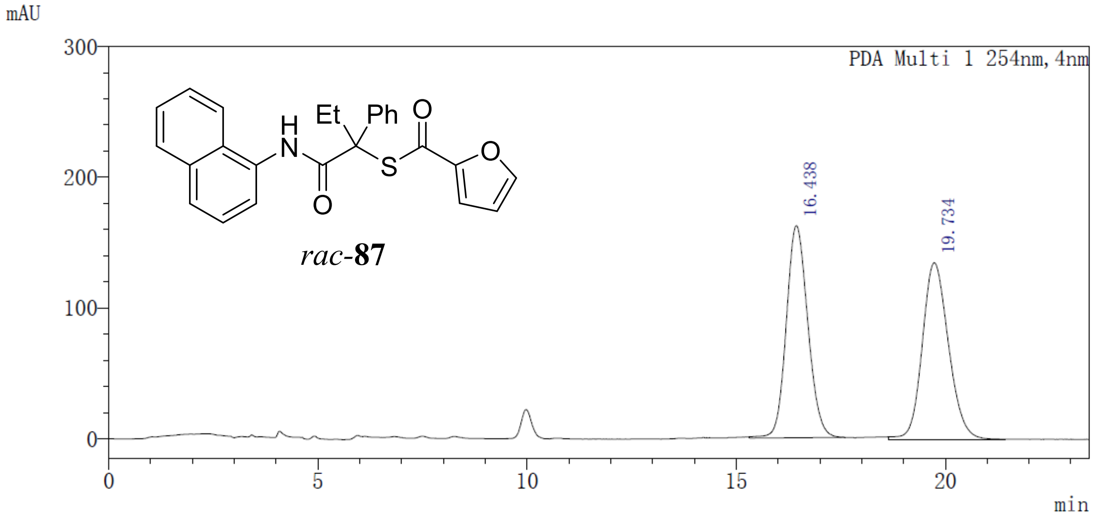
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.749	1457793	49.808
2	27.484	1469038	50.192



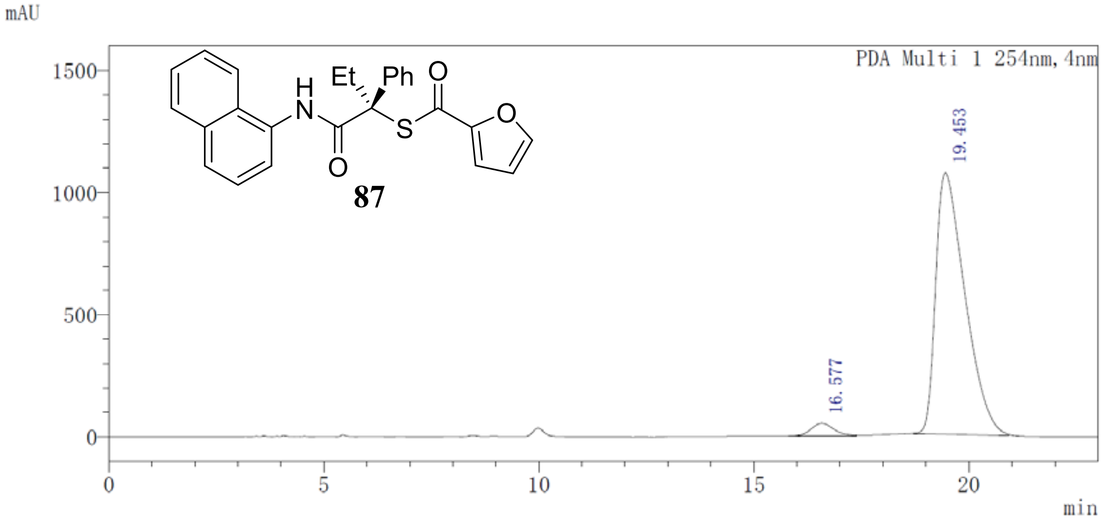
PDA Ch1 254nm

T	Hight	Area	Area%
25.662	11130	545562	2.112
28.324	464999	25285422	97.888



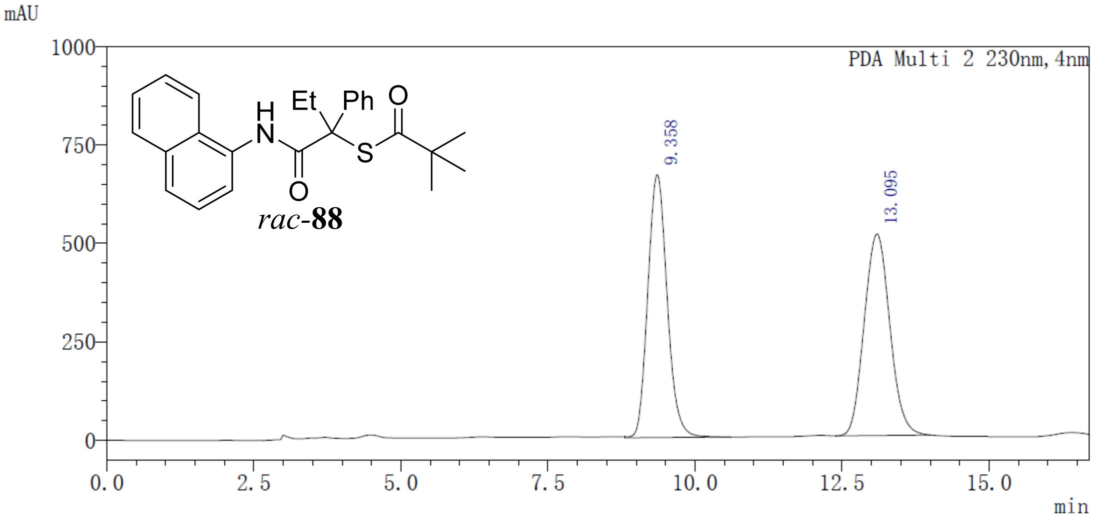
PDA Ch1 254nm

T	Hight	Area	Area%
16.438	162145	5802024	49.666
19.734	135039	5880076	50.334



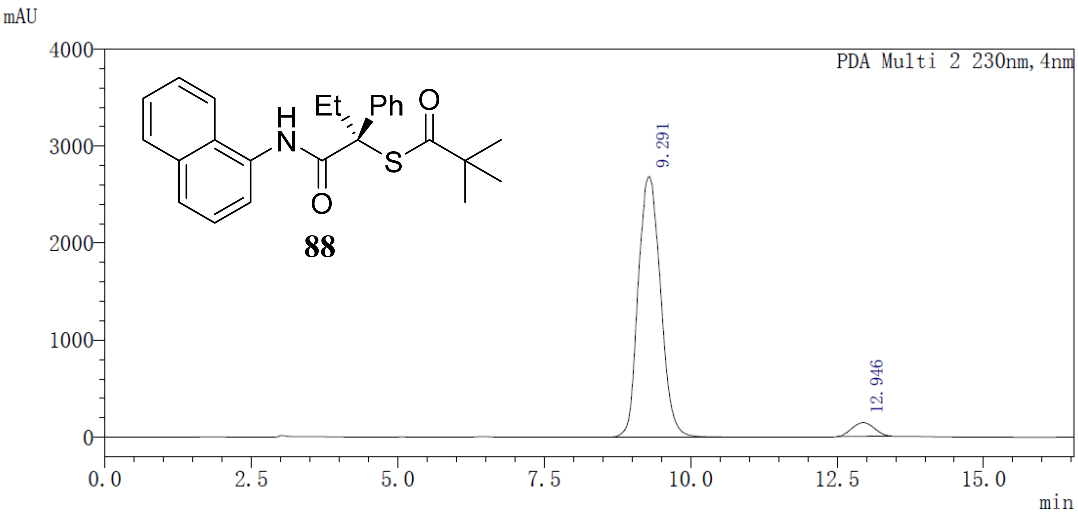
PDA Ch1 254nm

T	Hight	Area	Area%
16.577	53274	1990102	3.775
19.453	1070660	50725012	96.225



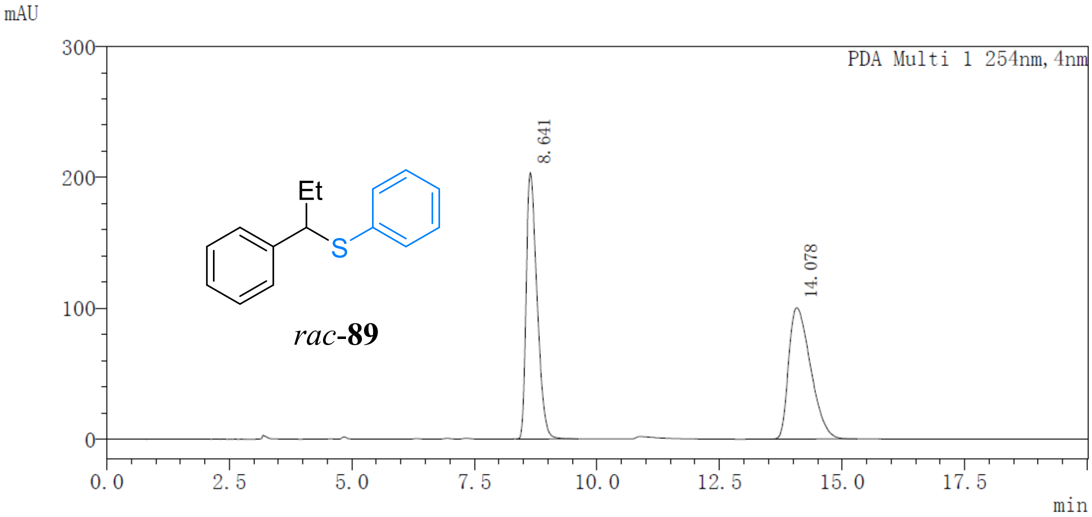
PDA Ch2 230nm

T	Hight	Area	Area%
9.358	668131	15303737	49.646
13.095	511963	15522271	50.354



PDA Ch2 230nm

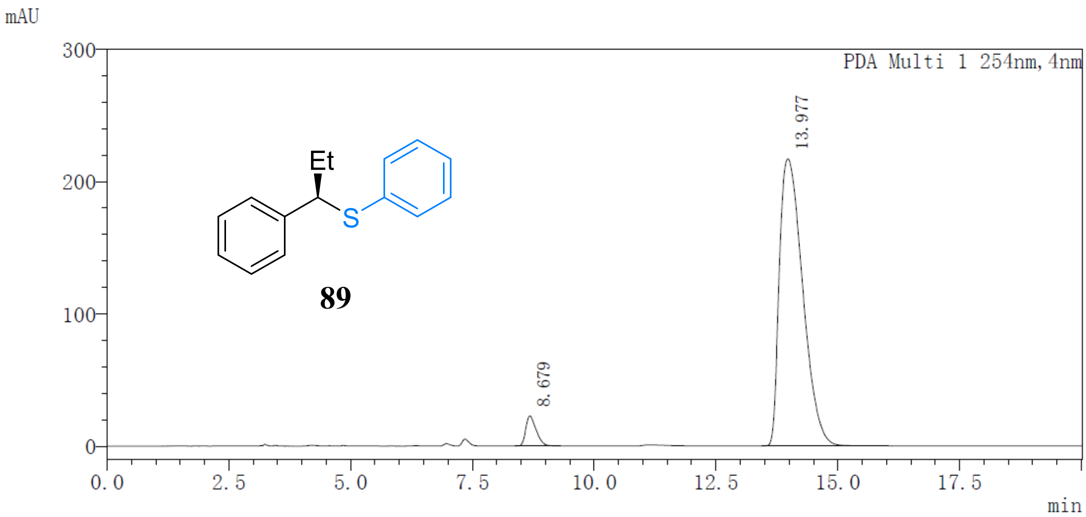
T	Hight	Area	Area%
9.291	2684726	71280710	95.012
12.946	141491	3742143	4.988



Peak Table

PDA Ch1 254nm

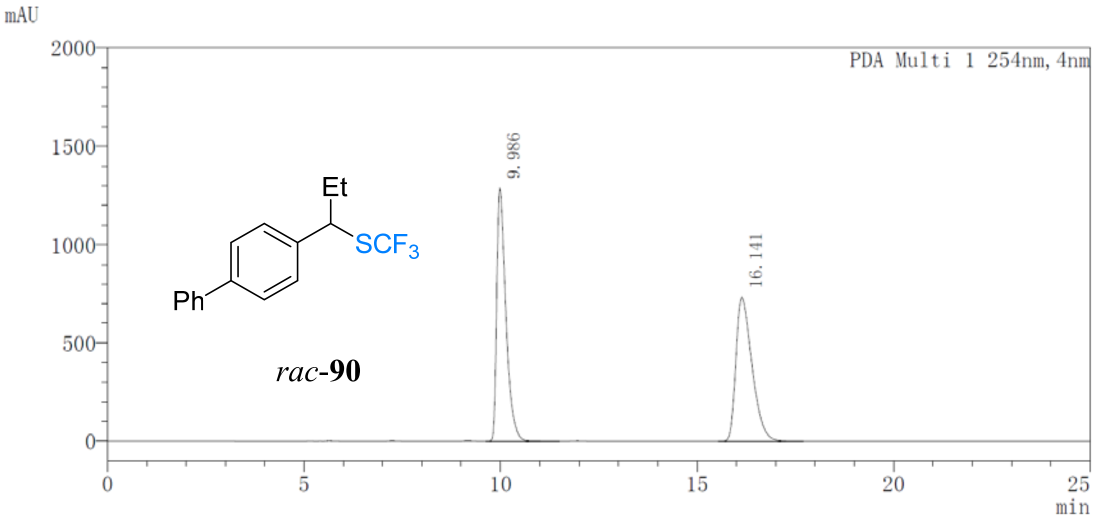
Peak#	Ret. Time	Area	Area%
1	8.641	3131699	50.051
2	14.078	3125336	49.949



Peak Table

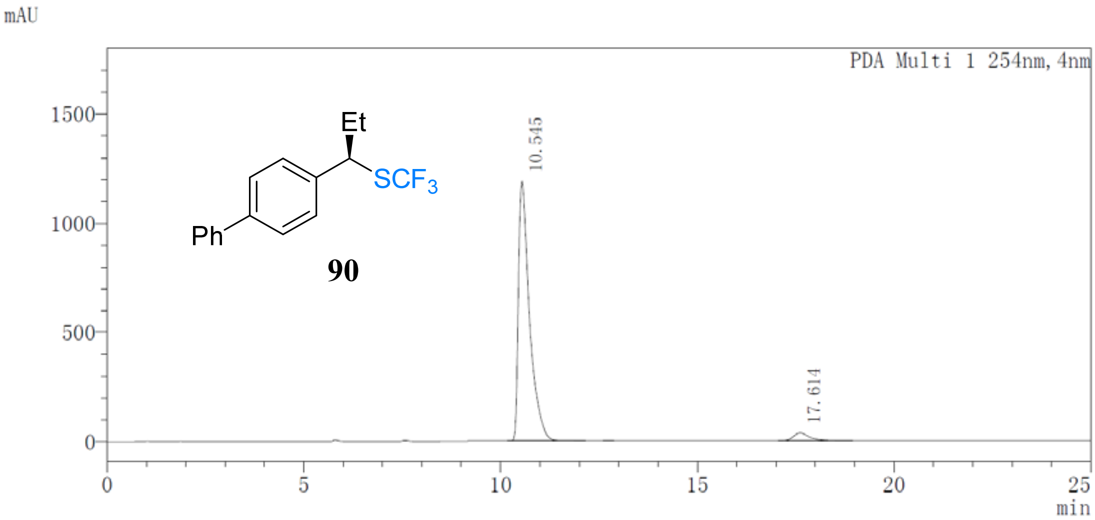
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.679	340295	4.488
2	13.977	7242389	95.512



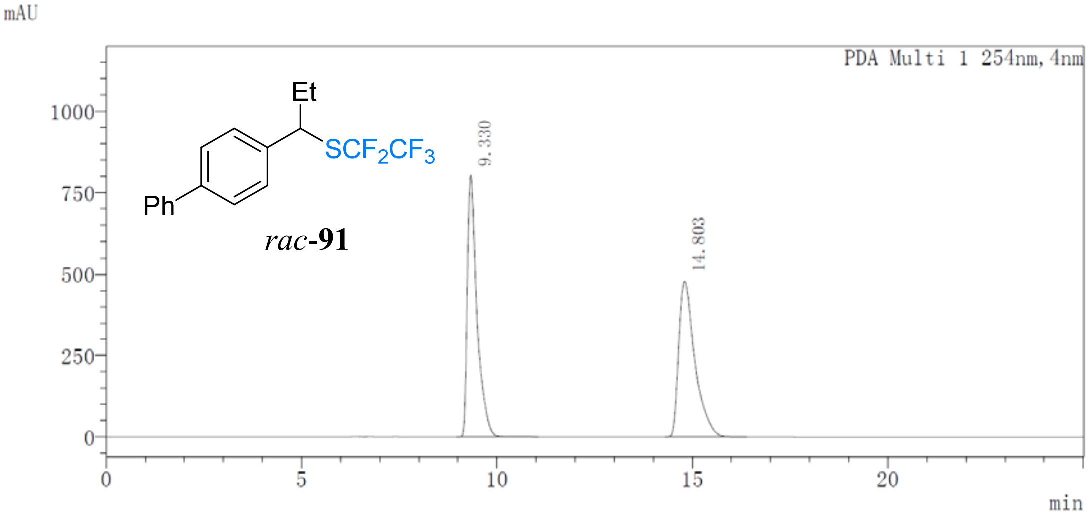
PDA Ch1 254nm

T	Hight	Area	Area%
9.986	1288359	20927958	50.052
16.141	733994	20884215	49.948



PDA Ch1 254nm

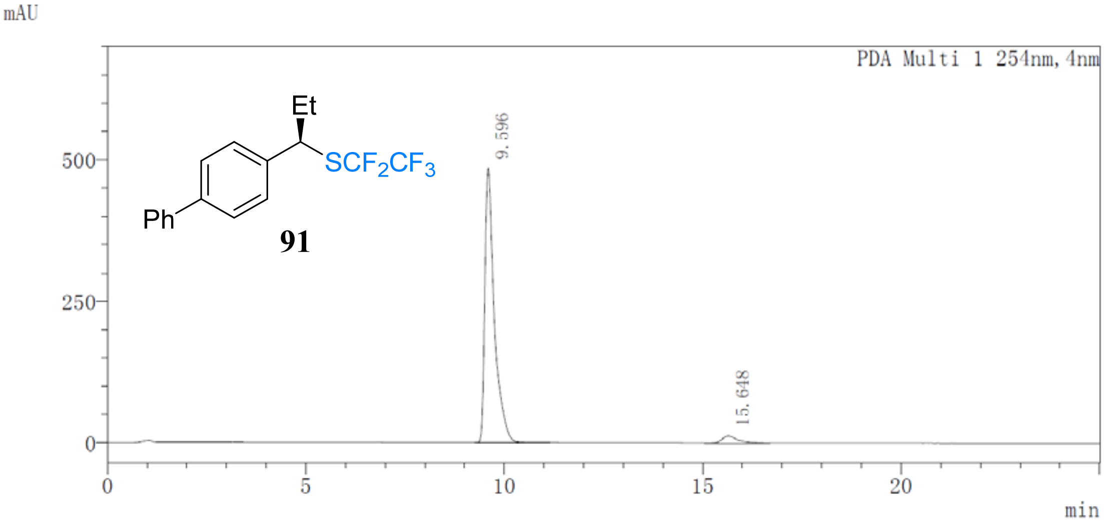
T	Hight	Area	Area%
10.545	1186227	23220545	95.653
17.614	37177	1055360	4.347



Peak Table

PDA Ch1 254nm

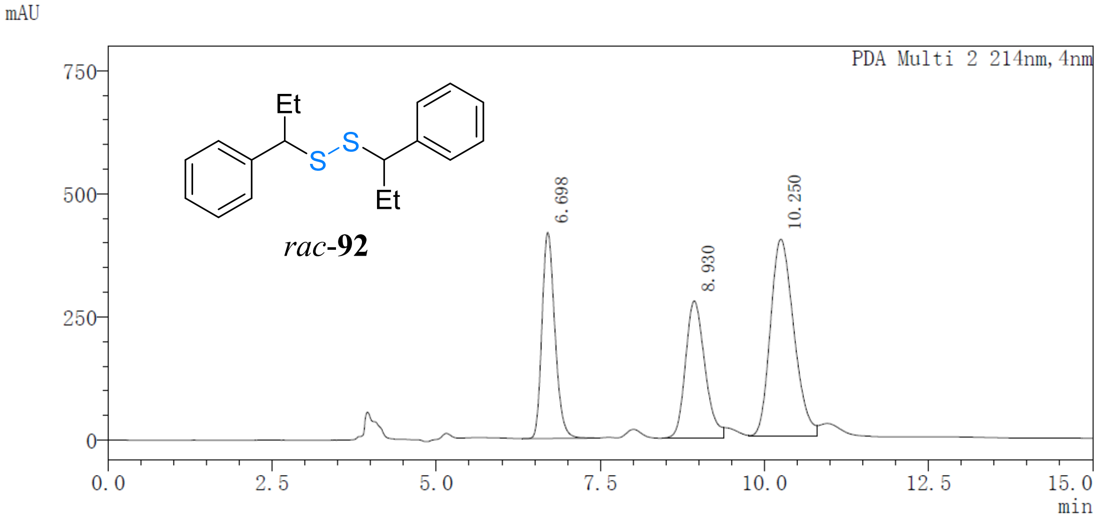
Peak#	Ret. Time	Area	Area%
1	9.330	13766033	50.028
2	14.803	13750745	49.972



Peak Table

PDA Ch1 254nm

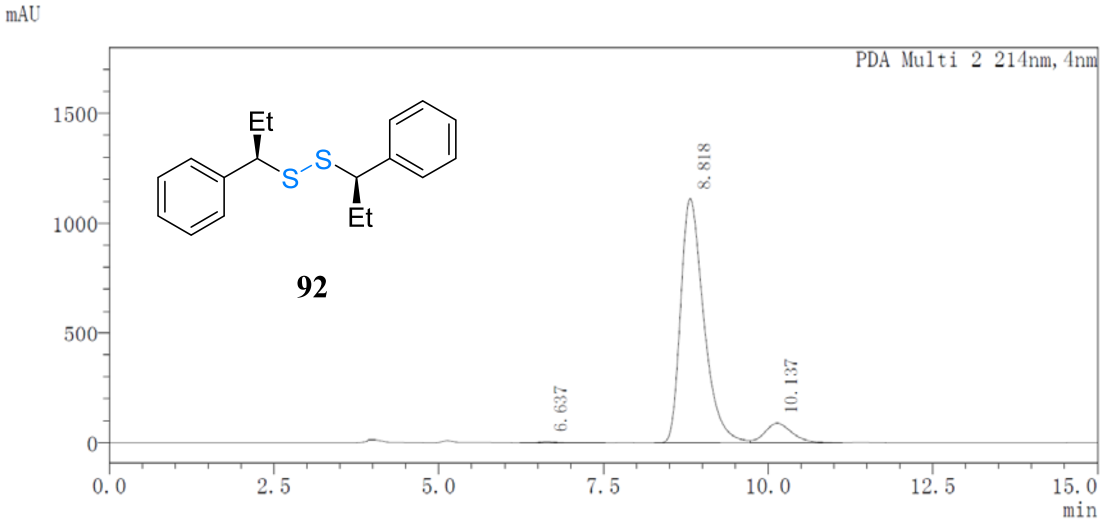
Peak#	Ret. Time	Area	Area%
1	9.596	8033868	95.870
2	15.648	346105	4.130



rac-**92**

PDA Ch2 214nm

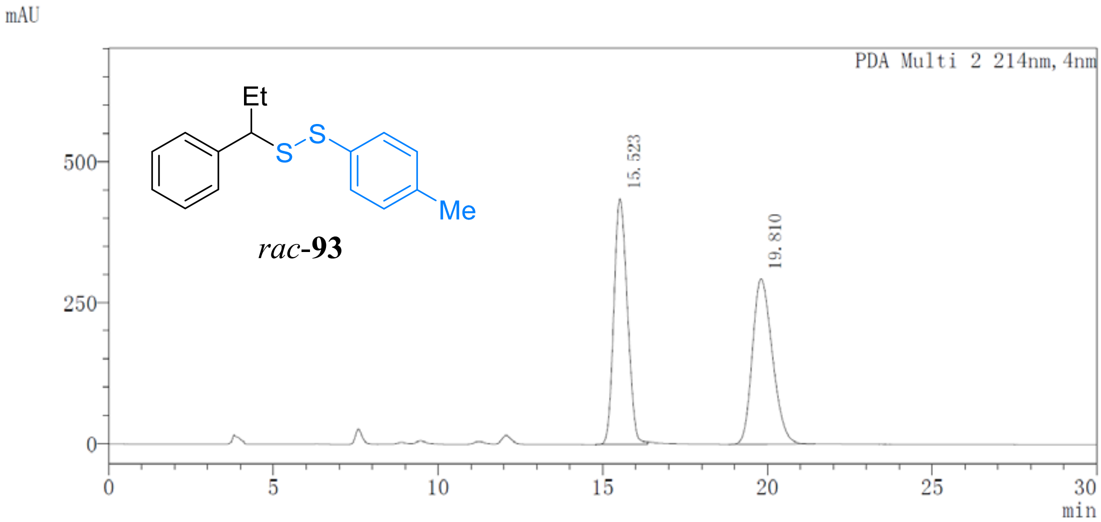
T	Hight	Area	Area%
6.698	418806	5732286	26.778
8.930	279018	5757785	26.898
10.250	399431	9916295	46.324



92

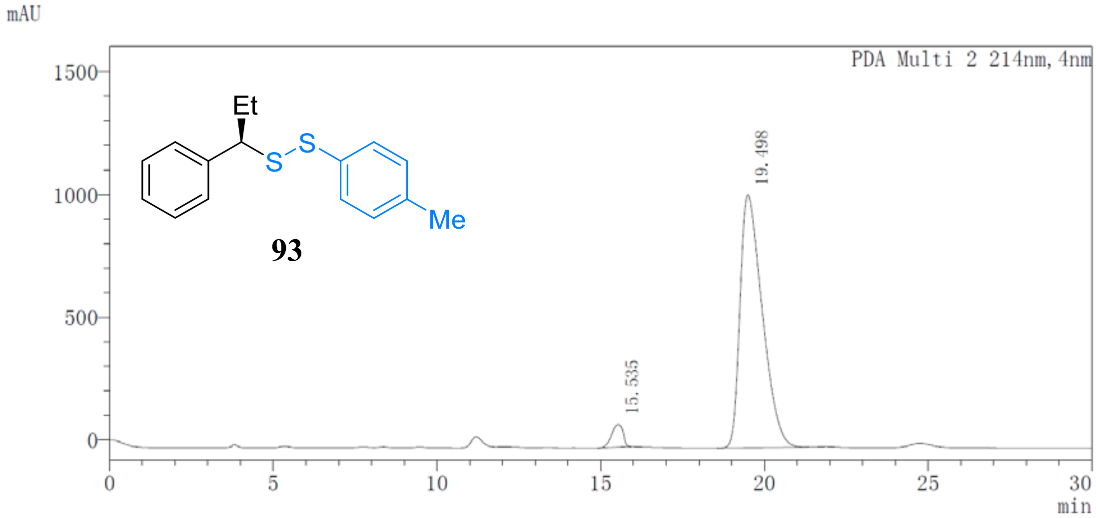
PDA Ch2 214nm

T	Hight	Area	Area%
6.637	5899	118100	0.396
8.818	1112107	27186171	91.189
10.137	87769	2508836	8.415



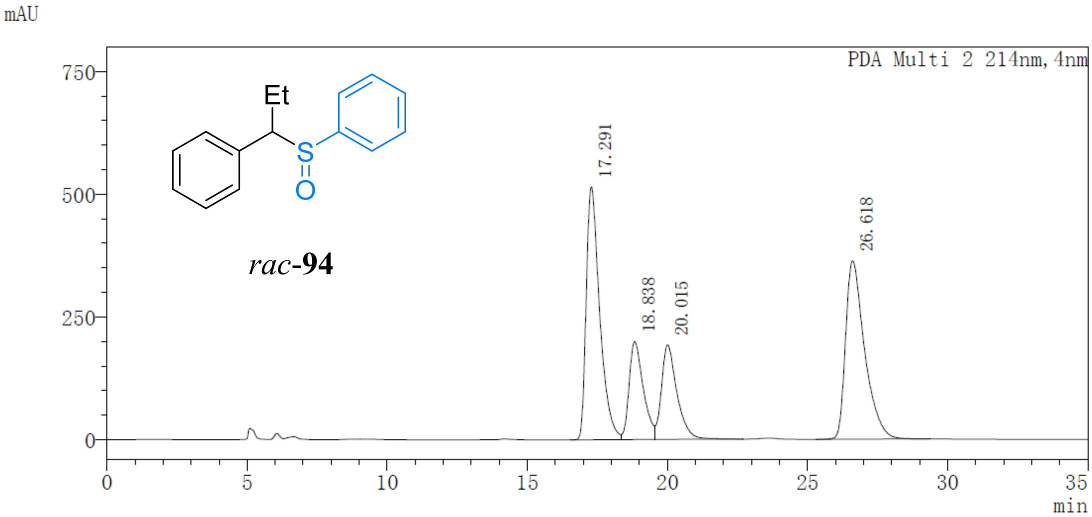
PDA Ch2 214nm

T	Hight	Area	Area%
15.523	434274	12397993	50.053
19.810	292959	12371532	49.947



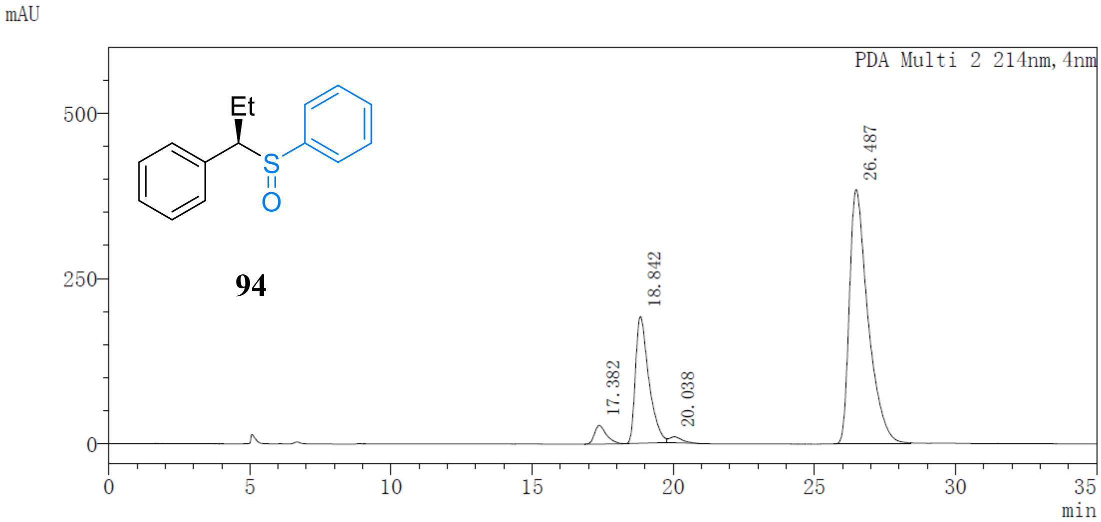
PDA Ch2 214nm

T	Hight	Area	Area%
15.535	93013	2260320	4.438
19.498	1029215	48668117	95.562



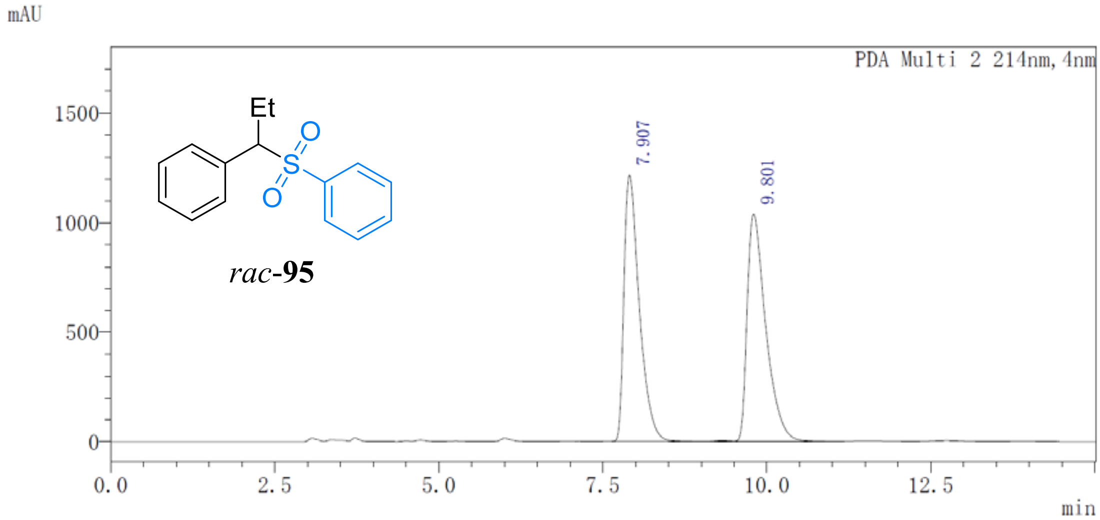
PDA Ch2 214nm

T	Hight	Area	Area%
17.291	514859	17218035	35.244
18.838	199311	7040740	14.412
20.015	192429	7422621	15.194
26.618	363244	17172036	35.150



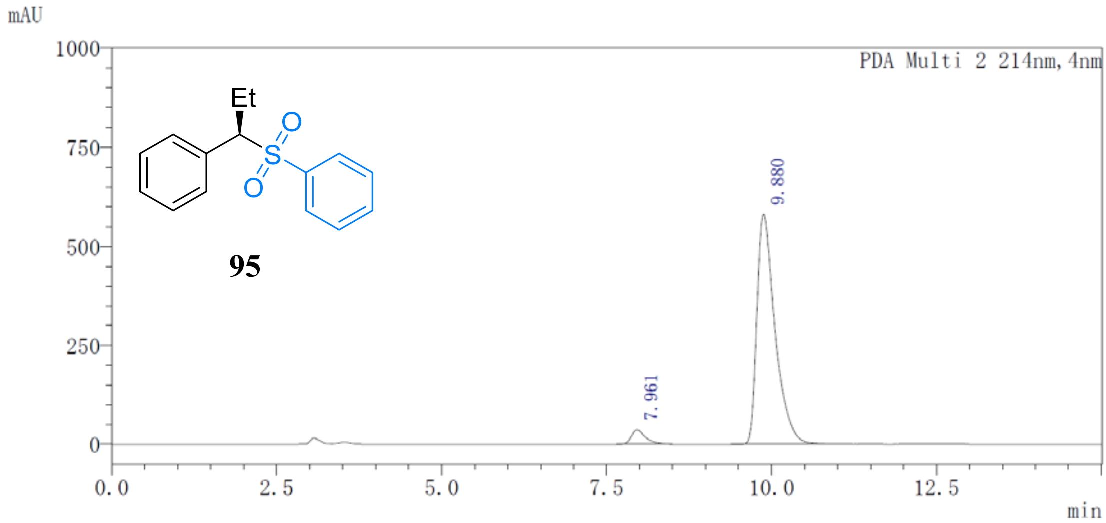
PDA Ch2 214nm

T	Hight	Area	Area%
17.382	28281	839026	3.336
18.842	191820	6298604	25.046
20.038	8882	287179	1.142
26.487	384871	17722909	70.475



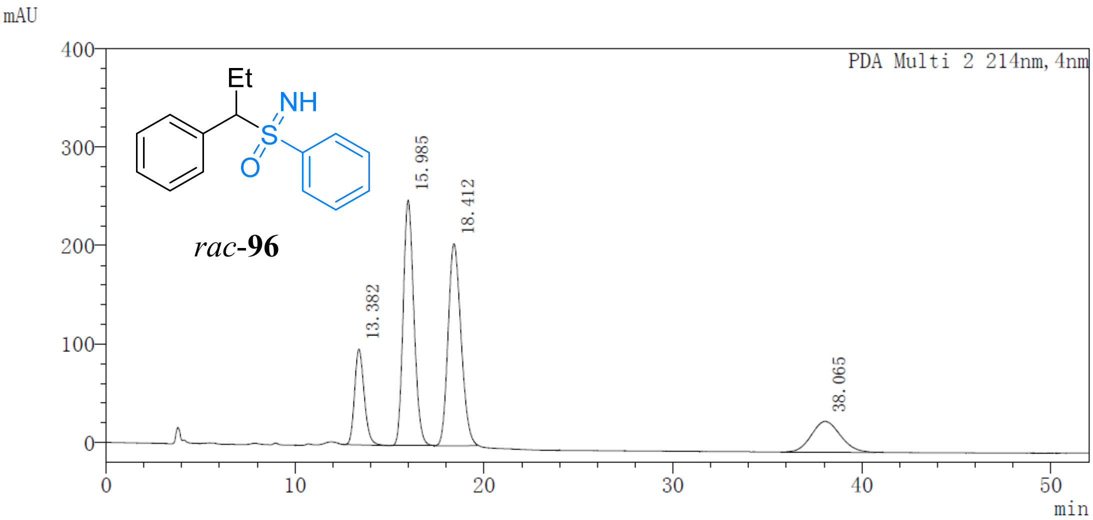
PDA Ch2 214nm

T	Hight	Area	Area%
7.907	1214541	19789818	49.164
9.801	1037398	20462937	50.836



PDA Ch2 214nm

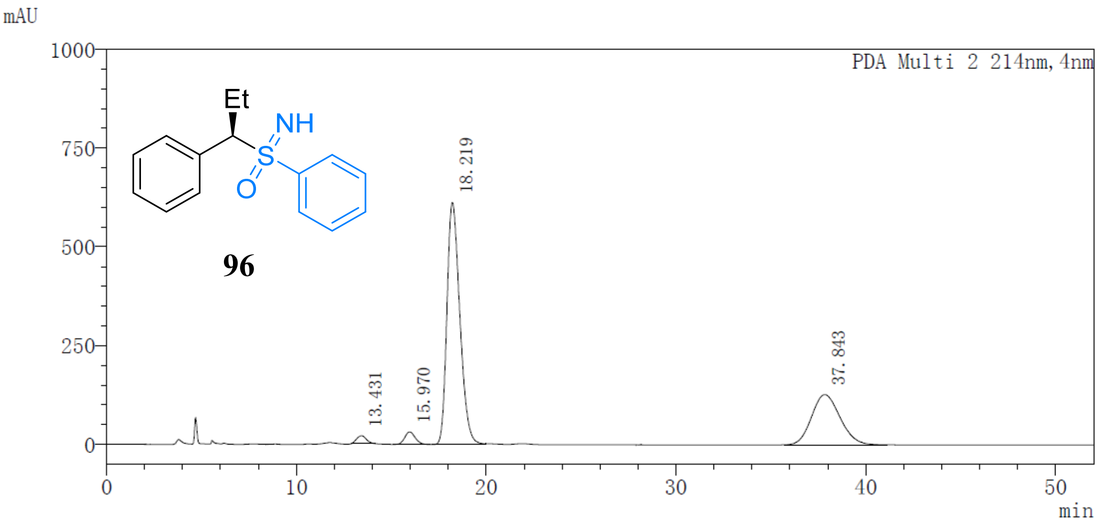
T	Hight	Area	Area%
7.961	37051	553977	4.731
9.880	581981	11156404	95.269



Peak Table

PDA Ch2 214nm

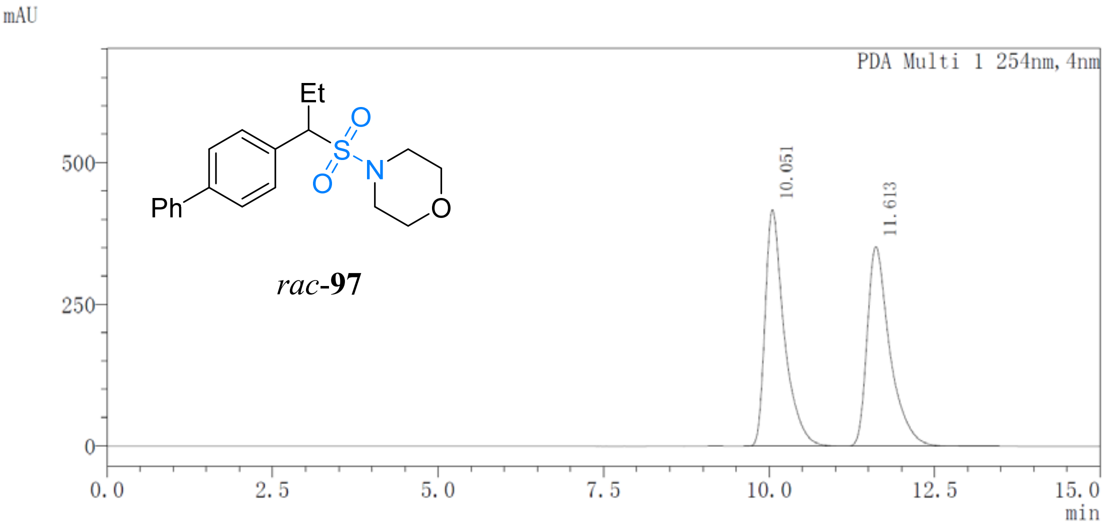
Peak#	Ret. Time	Area	Area%
1	13.382	3455734	13.048
2	15.985	9841333	37.158
3	18.412	9795203	36.984
4	38.065	3392652	12.810



Peak Table

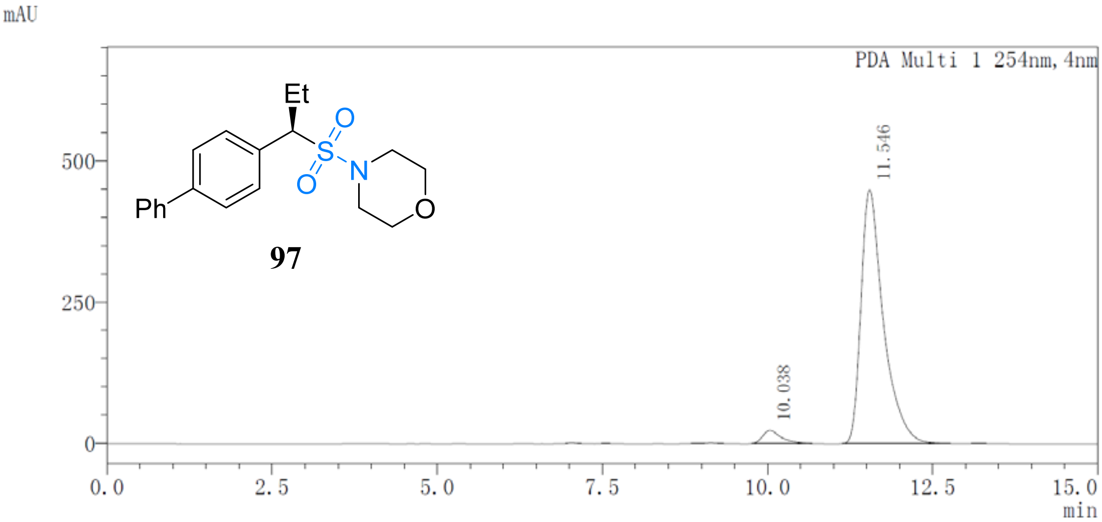
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	13.431	715117	1.619
2	15.970	1256124	2.843
3	18.219	28903736	65.425
4	37.843	13303643	30.113



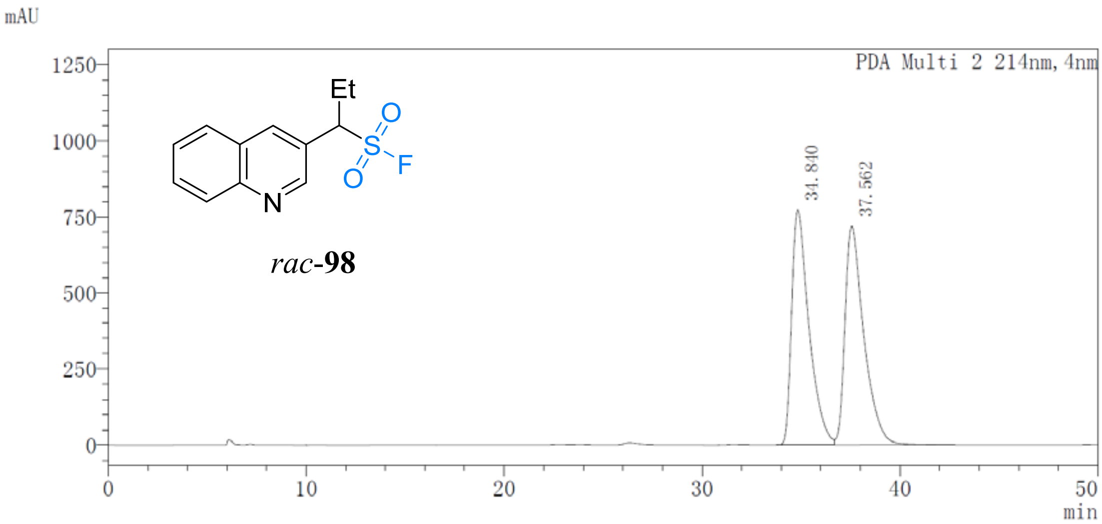
PDA Ch1 254nm

T	Hight	Area	Area%
10.051	416900	8398131	49.952
11.613	352296	8414379	50.048



PDA Ch1 254nm

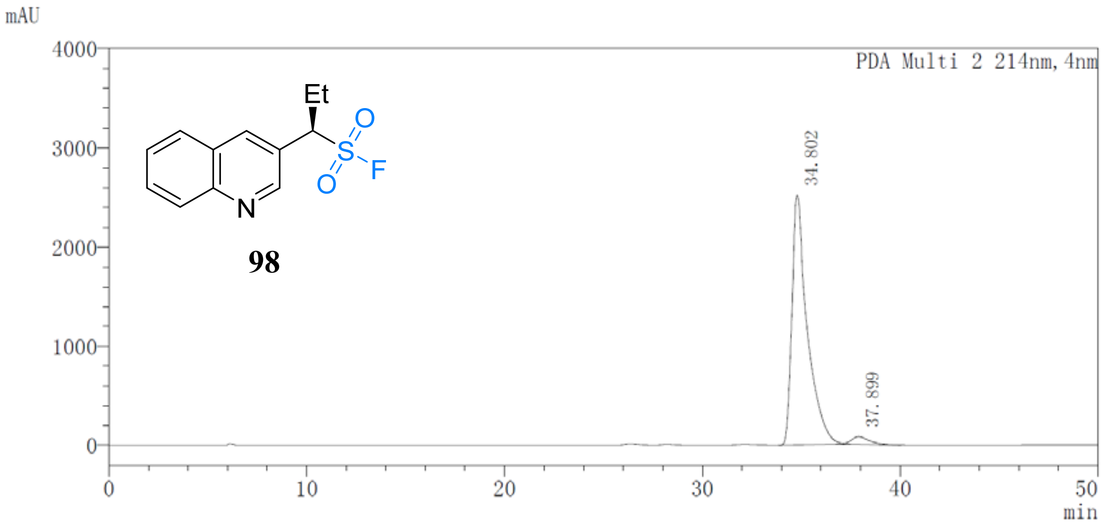
T	Hight	Area	Area%
10.038	23291	461349	4.183
11.546	448010	10566669	95.817



rac-**98**

PDA Ch2 214nm

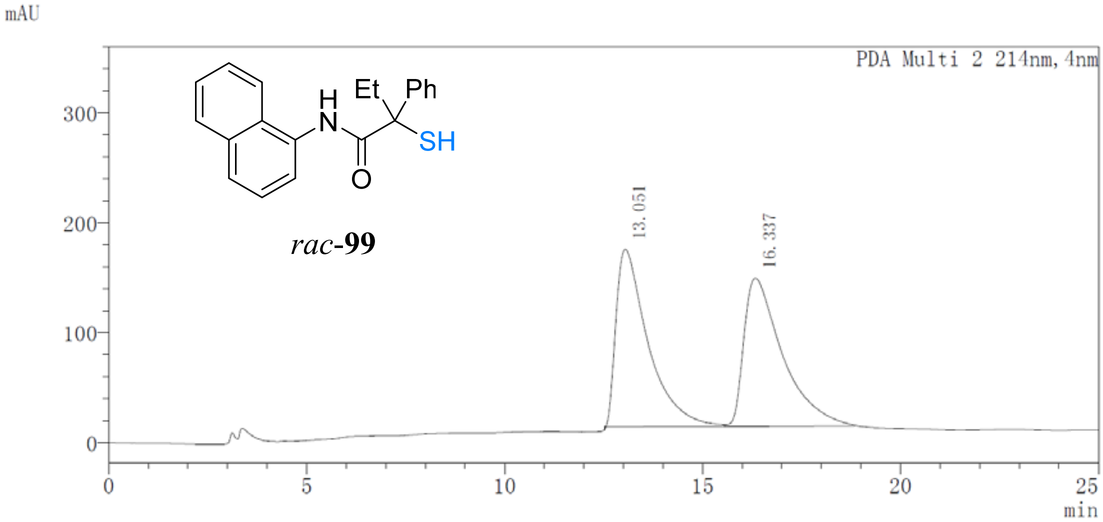
T	Hight	Area	Area%
34.840	771929	46942234	49.514
37.562	719003	47863740	50.486



98

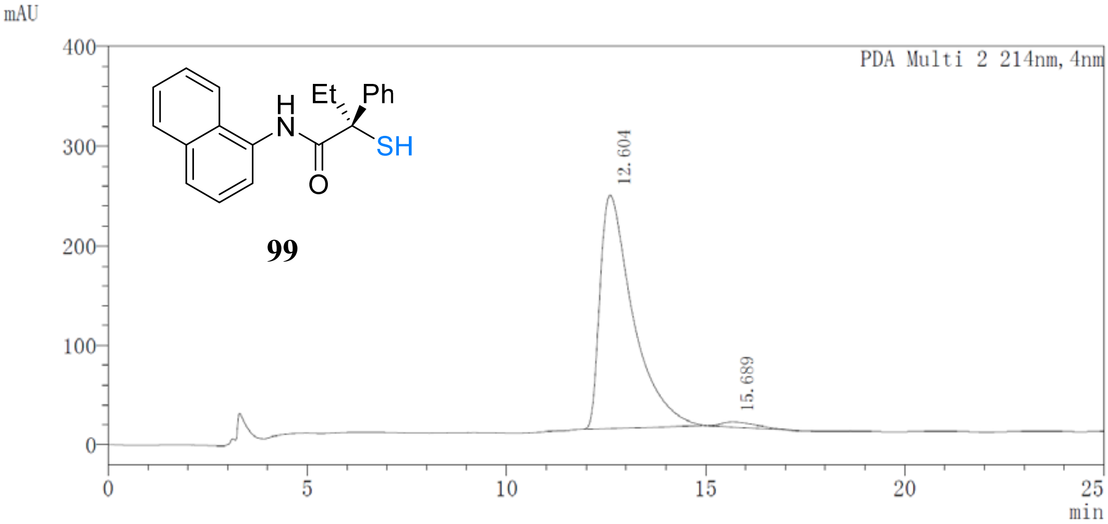
PDA Ch2 214nm

T	Hight	Area	Area%
34.802	2519072	135790328	96.479
37.899	79130	4955636	3.521



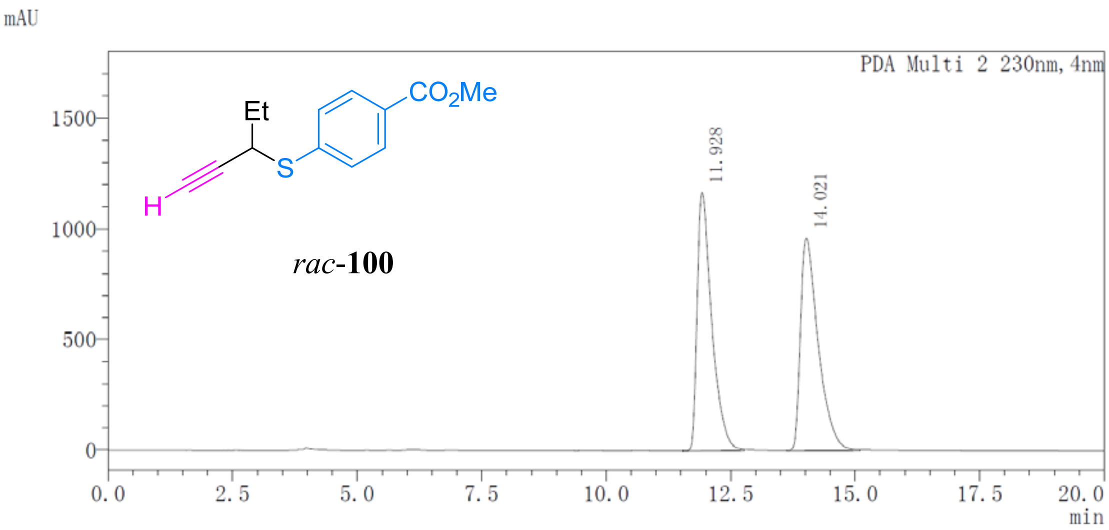
PDA Ch2 214nm

T	Hight	Area	Area%
13.051	161229	9036873	49.799
16.337	134858	9109928	50.201



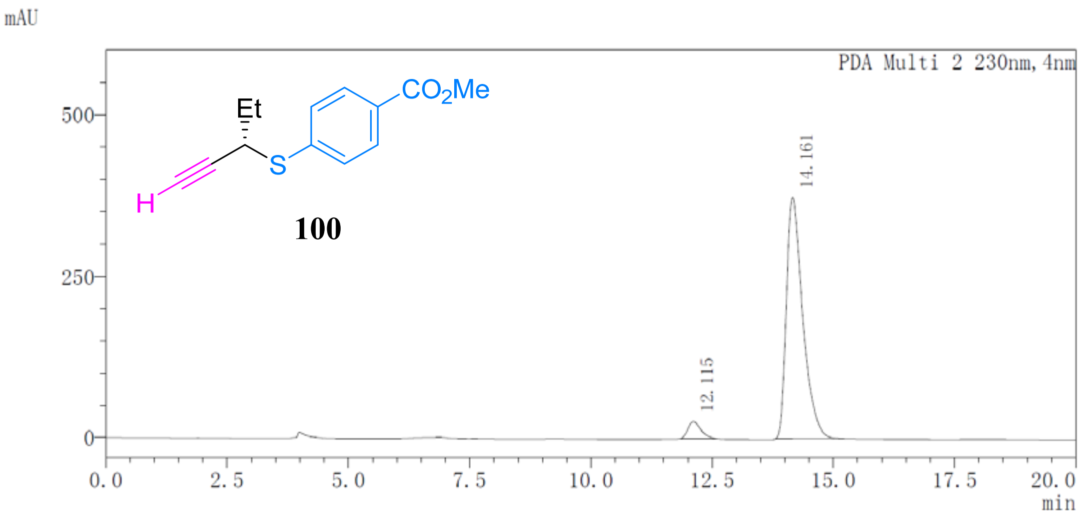
PDA Ch2 214nm

T	Hight	Area	Area%
12.604	234601	13552525	97.571
15.689	5472	337332	2.429



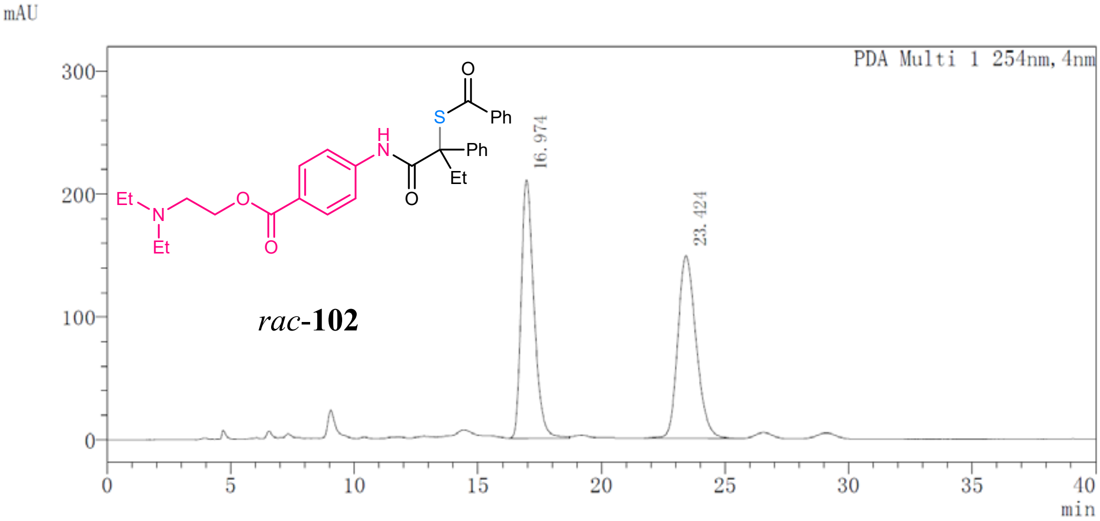
PDA Ch2 230nm

T	Hight	Area	Area%
11.928	1166215	23767531	49.956
14.021	960646	23808924	50.044



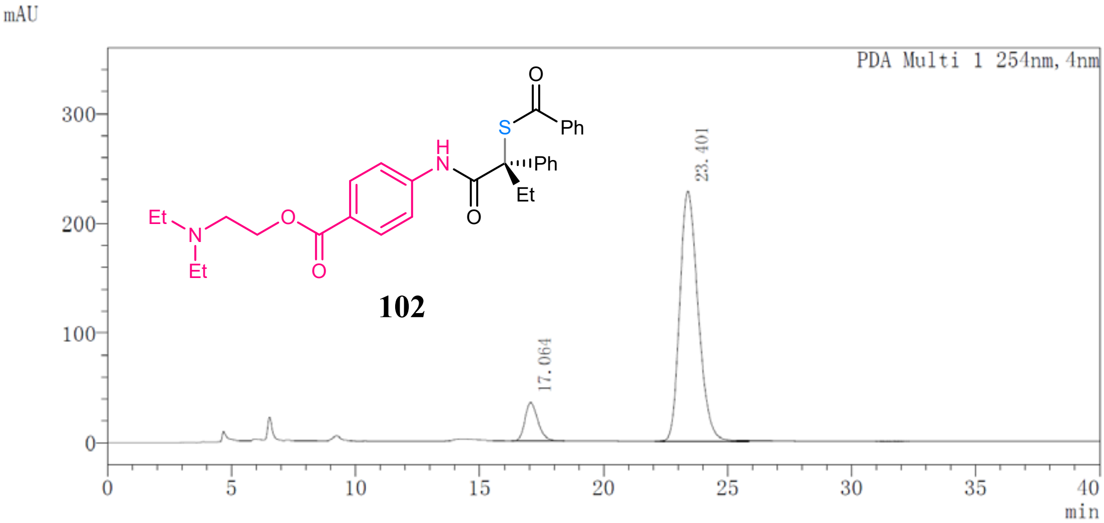
PDA Ch2 230nm

T	Hight	Area	Area%
12.115	26419	478091	5.178
14.161	373536	8754947	94.822



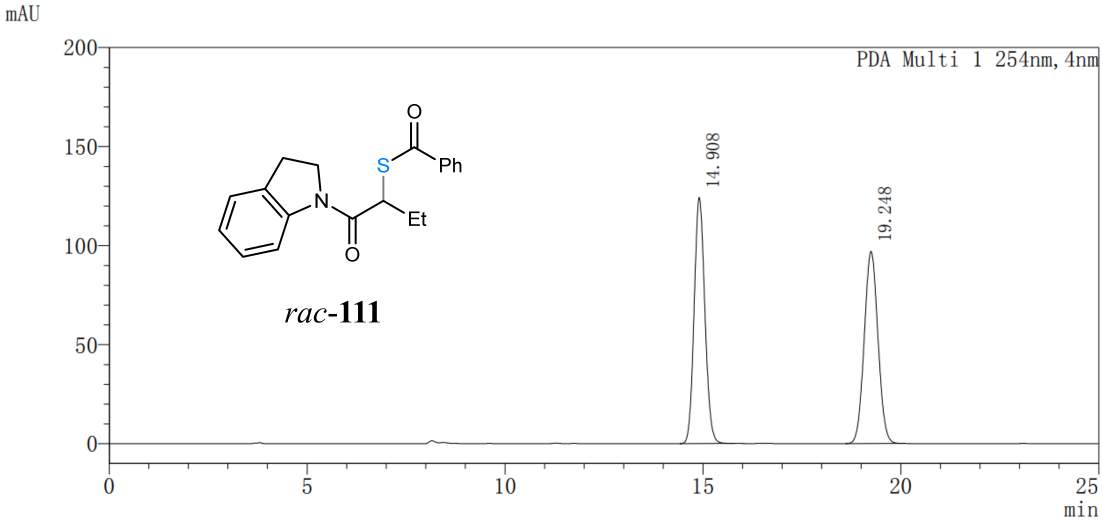
PDA Ch1 254nm

T	Hight	Area	Area%
16.974	210172	7549285	49.717
23.424	148599	7635268	50.283



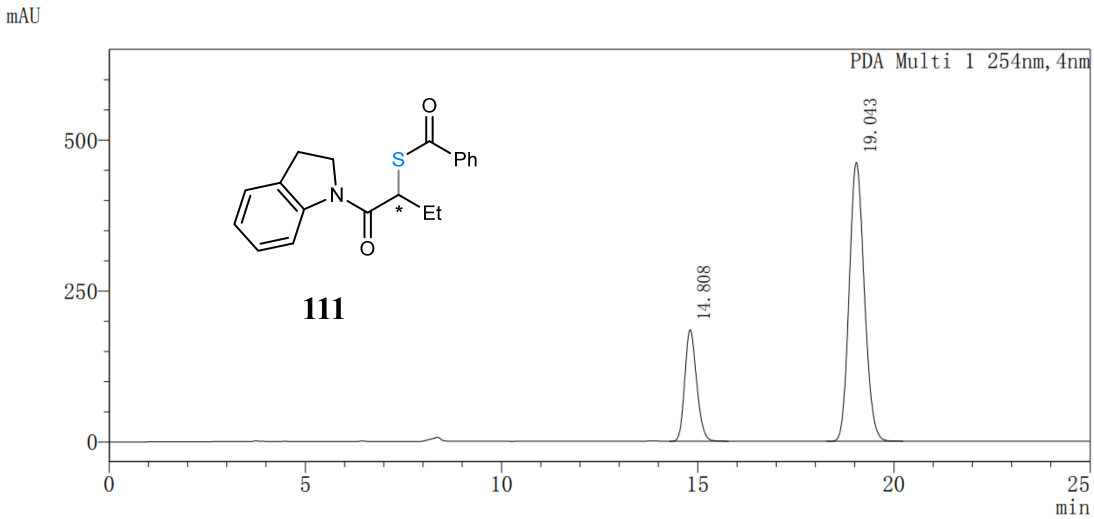
PDA Ch1 254nm

T	Hight	Area	Area%
17.064	34919	1263566	9.743
23.401	228113	11705287	90.257



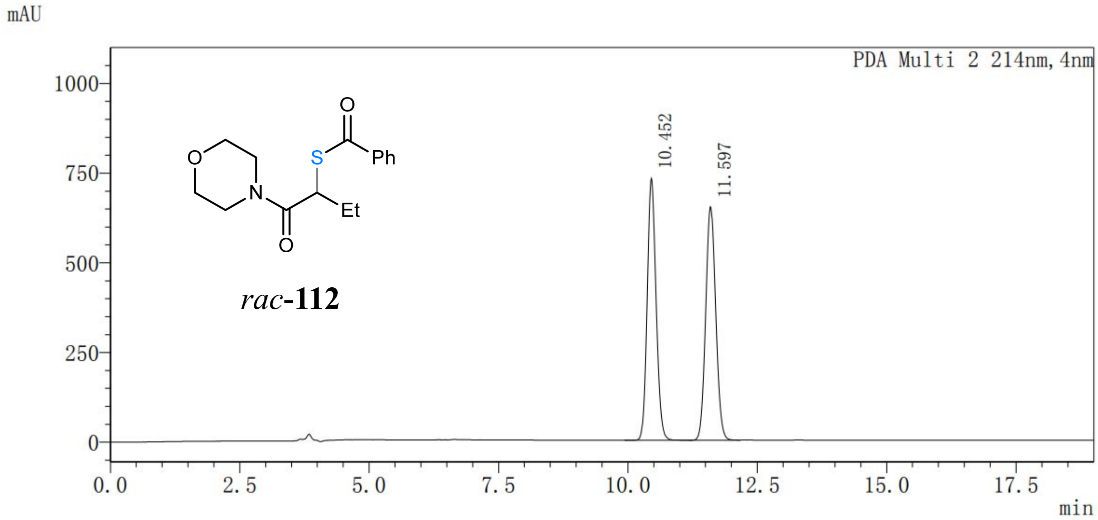
PDA Ch1 254nm

T	Hight	Area	Area%
14.908	124268	2349324	50.044
19.248	96985	2345233	49.956



PDA Ch1 254nm

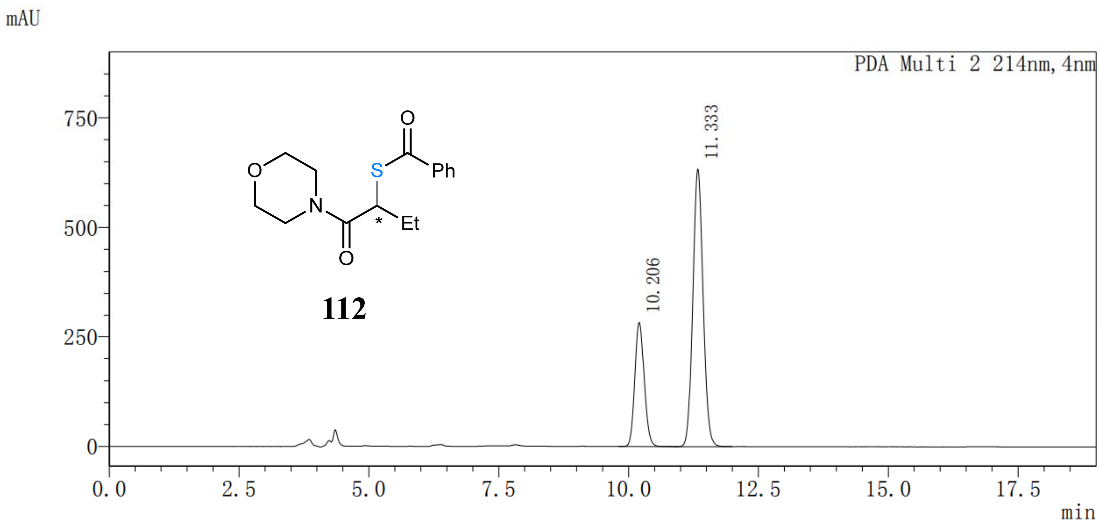
T	Hight	Area	Area%
14.808	184442	3874071	23.878
19.043	461333	12350262	76.122



Peak Table

PDA Ch2 214nm

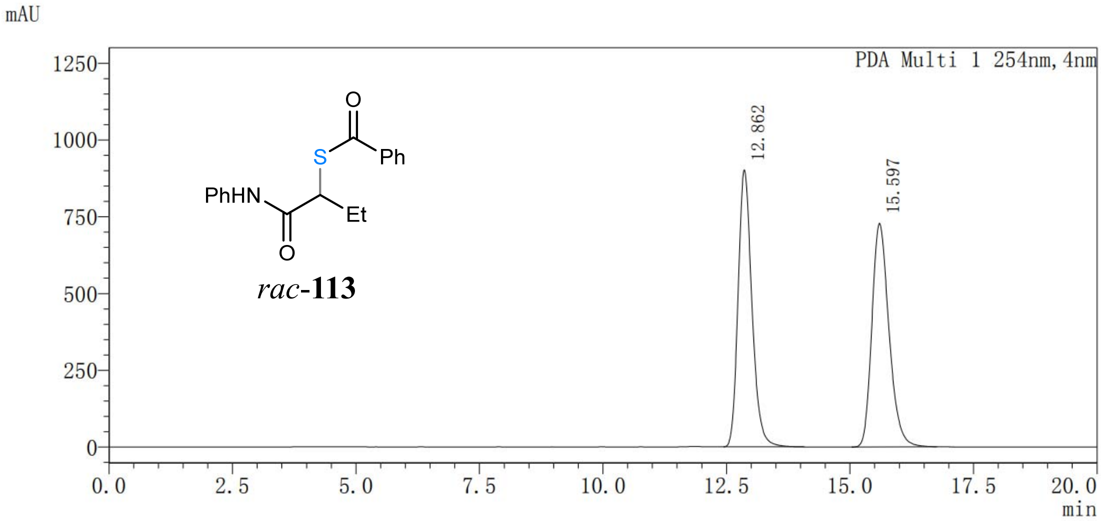
Peak#	Ret. Time	Area	Area%
1	10.452	8806726	50.179
2	11.597	8743977	49.821



Peak Table

PDA Ch2 214nm

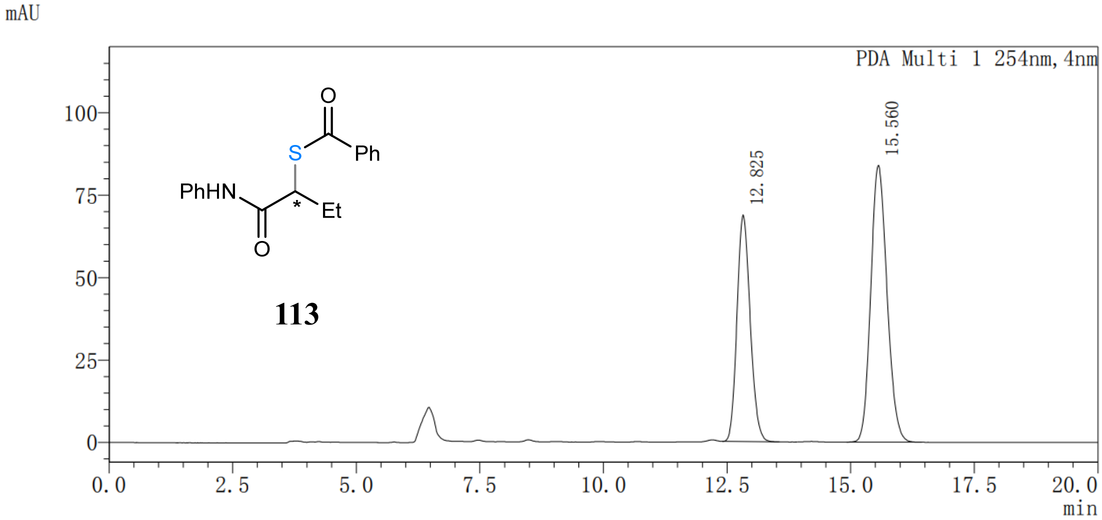
Peak#	Ret. Time	Area	Area%
1	10.206	3558194	28.903
2	11.333	8752604	71.097



Peak Table

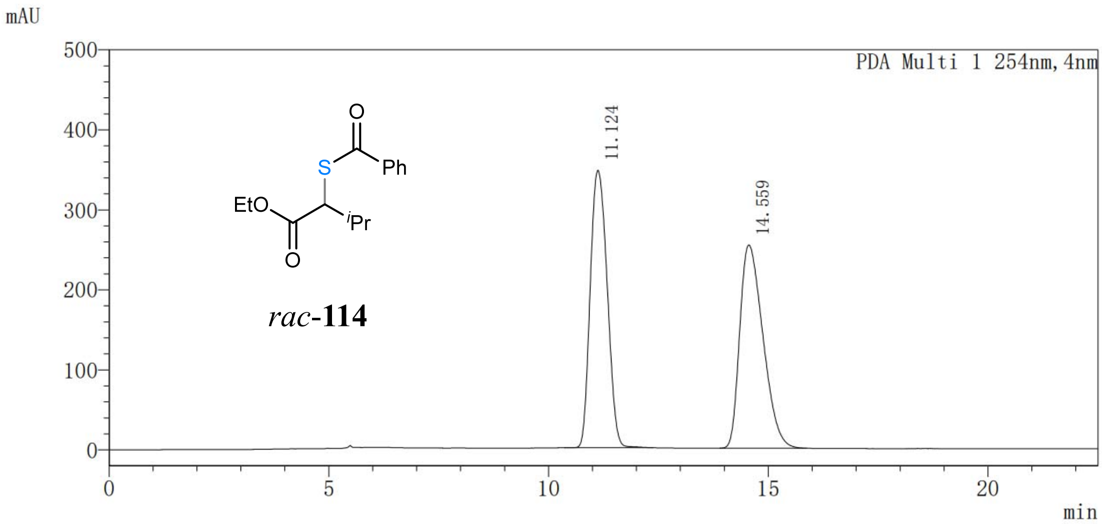
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.862	17535425	49.955
2	15.597	17567353	50.045



PDA Ch1 254nm

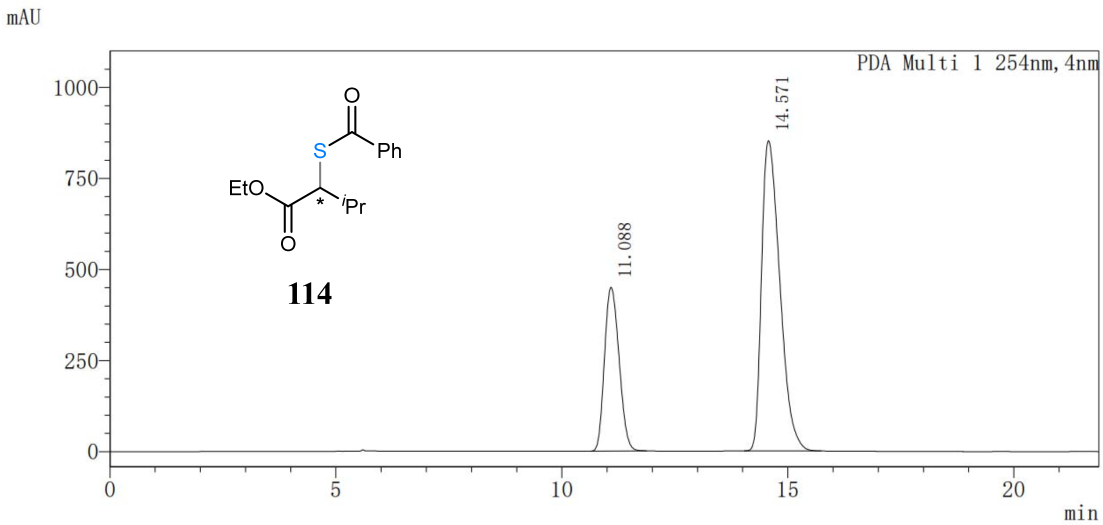
T	Hight	Area	Area%
12.825	68691	1275356	39.857
15.560	83935	1924455	60.143



Peak Table

PDA Ch1 254nm

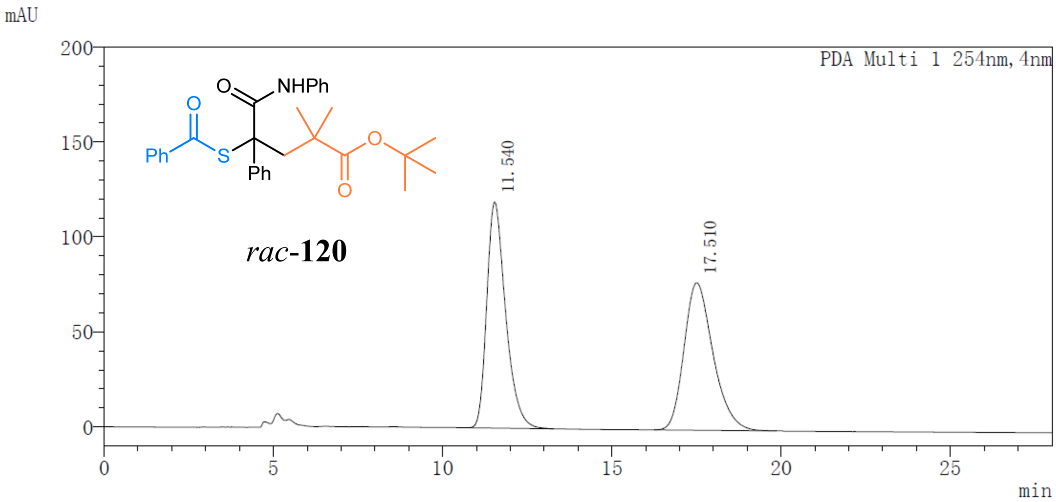
Peak#	Ret. Time	Area	Area%
1	11.124	9307251	49.918
2	14.559	9337882	50.082



Peak Table

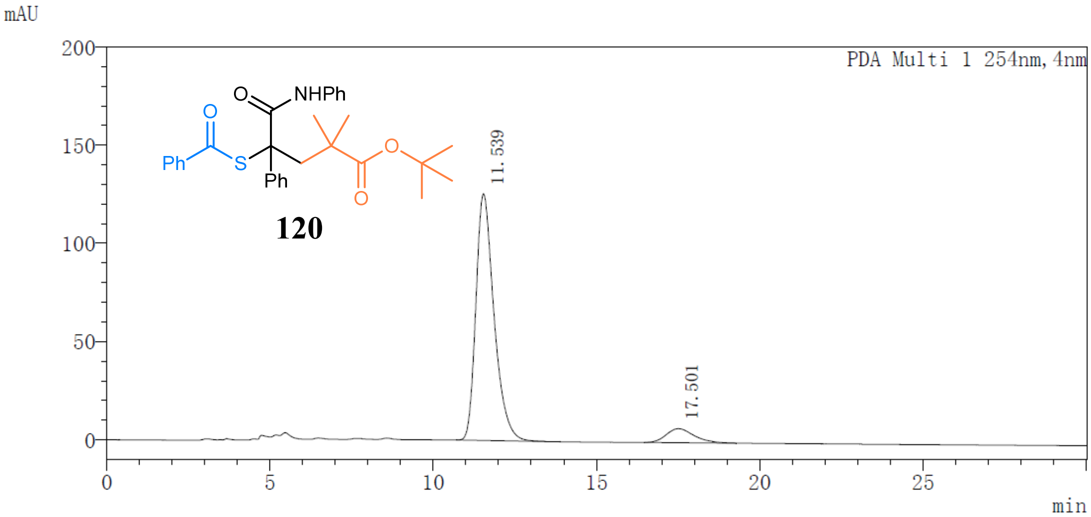
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.088	10092800	29.652
2	14.571	23944208	70.348



PDA Ch1 254nm

T	Hight	Area	Area%
11.540	119037	4614070	49.901
17.510	77640	4632398	50.099



PDA Ch1 254nm

T	Hight	Area	Area%
11.539	125584	4850095	91.967
17.501	7146	423657	8.033

15. Reference

1. Song, Y., Fu, C. & Ma, S. Copper-catalyzed syntheses of multiple functionalizatized allenes via three-component reaction of enynes. *ACS Catal.* **11**, 10007–10013 (2021).
2. Lu, R. et al. Enantioselective copper-catalyzed radical cyanation of propargylic C−H bonds: easy access to chiral allenyl nitriles. *J. Am. Chem. Soc*. **143**, 14451−14451 (2021).
3. Guo, X., Shi, Z., Zhang, F.-H. & Wang, Z. Cr-catalyzed regio-, diastereo-, and enantioselective reductive couplings of ketones and propargyl halides. *ACS Catal*. **13**, 3170−3178 (2023).
4. Zhang, X. et al. An enantioconvergent halogenophilic nucleophilic substitution (S_N2X) reaction. *Science* **363**, 400–404 (2019).
5. Xiao, X., Feng, M. & Jiang, X. New design of a disulfurating reagent: facile and straightforward pathway to unsymmetrical disulfanes by copper-catalyzed oxidative cross-coupling. *Angew. Chem. Int. Ed.* **55**, 14121–14125 (2016).
6. Dong, X.-Y. et al. A general asymmetric copper-catalysed Sonogashira C(sp^3)–C(*sp*) coupling. *Nat. Chem.* **11**, 1158–1166 (2019).
7. Li, C. et al. Transition-metal-free stereospecific cross-coupling with alkenylboronic acids as nucleophiles. *J. Am. Chem. Soc.* **138**, 10774–10777 (2016).
8. Iwamoto, H. et al. Copper(I)-catalyzed enantioconvergent borylation of racemic benzyl chlorides enabled by quadrant-by-quadrant structure modification of chiral bisphosphine ligands. *Angew. Chem. Int. Ed.* **58**, 11112–11117 (2019).
9. Wang, P.-F. et al. Design of hemilabile N,N,N-Ligands in copper-catalyzed enantioconvergent radical cross-coupling of benzyl/propargyl halides with alkenylboronate esters. *J. Am. Chem. Soc.* **144**, 6442–6452 (2022).
10. Soler-Yanes, R., Arribas-Álvarez, I., Guisán-Ceinos, M., Buñuel, E. & Cárdenas, D. J. Ni^I catalyzes the regioselective cross-coupling of alkylzinc halides and propargyl bromides to allenes. *Chem. Eur. J.* **23**, 15840–11590 (2017).
11. Kainz, Q. M. et al. Asymmetric copper-catalyzed C–N cross-couplings induced by visible light. *Science* **351**, 681–684 (2016).
12. Wang, F.-L. et al. Mechanism-based ligand design for copper-catalysed enantioconvergent C(sp^3)–C(*sp*) cross-coupling of tertiary electrophiles with alkynes. *Nat. Chem.* **14**, 949–957 (2022).

13. Deivaraj, T. C., Lai, G. X. & Vittal, J. J. Chemistry of thiocarboxylates: synthesis and structures of neutral copper(I) thiocarboxylates with triphenylphosphine. *Inorg. Chem.* **39**, 1028–1034 (2000).

14. Wu, H. et al. High-valent palladium-promoted formal Wagner–Meerwein rearrangement. *Org. Lett.* **18**, 5804–5807 (2016).

15. Gaussian 16, Revision A.03, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B. & Fox, D. J., Gaussian, Inc., Wallingford CT, 2016.

16. Lee, C., Yang, W. & Parr, R. G. Development of the colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **37**, 785–789 (1988).

17. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).

18. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).

19. Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comp. Chem.* **32**, 1456–1465 (2011).

20. Dunning Jr., T. H. & Hay, P. J. *Modern Theoretical Chemistry*, Ed. Schaefer III, H. F. Vol. 3 (Plenum, New York, 1977) 1–28.

21. Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. 82, 270–283 (1985).

22. Wadt, W. R. & Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. 82, 284–298 (1985).
23. Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. 82, 299–310 (1985).
24. Stoll, H., Fuentealba, P., Schwerdtfeger, P., Flad, J., Szentpály, L. V. & Preuss, H. Cu and Ag as one-valence-electron Atoms: CI results and quadrupole corrections for Cu2, Ag2, CuH, and AgH. *J. Chem. Phys.* **81**, 2732–2736 (1984).
25. Dolg, M., Wedig, U., Stoll, H. & Preuss, H. Energy-adjusted ab initio pseudopotentials for the first row transition elements. *J. Chem. Phys.* **86**, 866–872 (1987).
26. Häussermann, U. et al. Accuracy of energy-adjusted quasirelativistic ab initio pseudopotentials. *Mole. Phys.* **78**, 1211–1224 (1993).
27. Bergner, A., Dolg, M., Küchle, W., Stoll, H. & Preuß, H. Ab initio energy-adjusted pseudopotentials for elements of groups 13–17. *Mole. Phys.* **80**, 1431–1441 (2006).
28. Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).
29. Legault, C. Y. *CYLView, 1.0b*; Universitéde Sherbrooke: Québec, Montreal, Canada, 2009; (http://www.cylview.org).