Supporting Information

Copper-Catalyzed Chemo- and Enantioselective Radical 1,2-Carbosulfenylation of Diverse Alkenes with Broad Radical and Sulfur Compatibility

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Table of contents

1. Supplementary tables for experiments.....3

2. Supplementary figures for experiments.....10

3. General information 20

4. General procedure for synthesis of substrates.....21

5. Synthesis of the optimal chiral ligand. 41

6. Copper-catalyzed chemo- and enantioselective radical 1, 2-carbosulfuration of acrylamide 46

7. Copper-catalyzed chemo- and enantioselective 1,2-carbosulfidation of phenyl-substituted acrylamides.....64

8. Copper-catalyzed chemo- and enantioselective radical 1,2-carbosulfuration of styrene-type alkenes.....79

9. Synthetic utility 88

10. Radical trap experiments 96

11. References 109

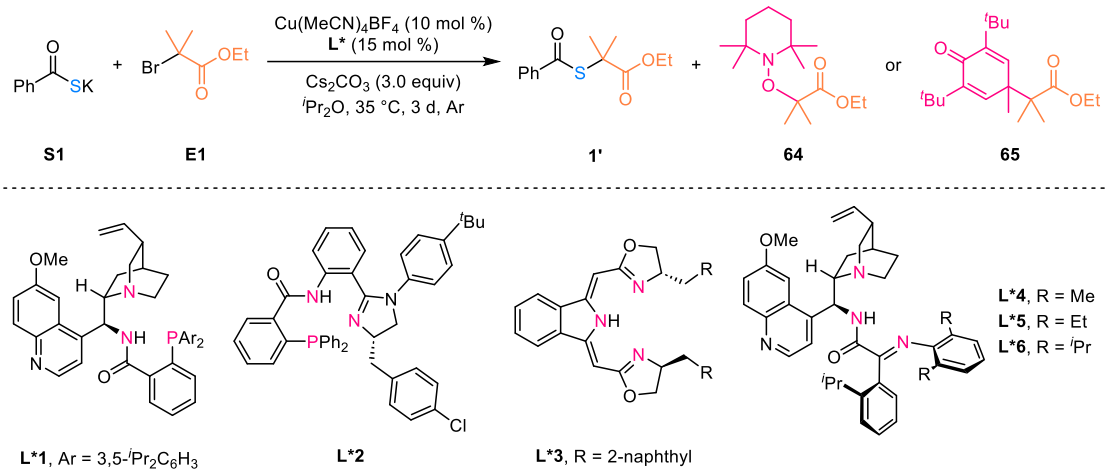
12. NMR spectrum 110

13. HPLC spectra 184

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1. Supplementary tables for experiments

Table S1. The ligand effects on byproduct formation and radical trapping experiments[a]



Entry	L*	yield of **1'** (%)	yield of **64** (%)	yield of **65** (%)
1	**L*1**	59		
2	**L*2**	62		
3	**L*3**	90		
4	**L*4**	21		
5	**L*5**	10		
6	**L*6**	5		
7[b]	**L*6**	trace	12	
8[c]	**L*6**	trace		70

[a]Reaction conditions: **S1** (0.05 mmol), **E1** (0.05 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L*** (15 mol %), and Cs_2CO_3 (3.0 equiv) in $^iPr_2O$ (1.0 mL) at 35 °C for 3 days under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard;

[b]The reaction was conducted in the presence of TEMPO (2.0 equiv);

[c]The reaction was conducted in the presence of BHT (2.0 equiv).

In the absence of alkene substrate **A1**, ligands **L*1**–**L*3** (Entries 1–3) predominantly afford the byproduct **1'** derived from the direct reaction between tertiary alkyl radical and sulfur nucleophile **S1**. By contrast, iminocarboxamide N,N,N-ligand **L*4** (Entry 4) reduce the formation of such byproducts. Furthermore, increasing the steric hindrance of the substituents on iminocarboxamide ligands (**L*5**, **L*6**) leads to a gradual decrease

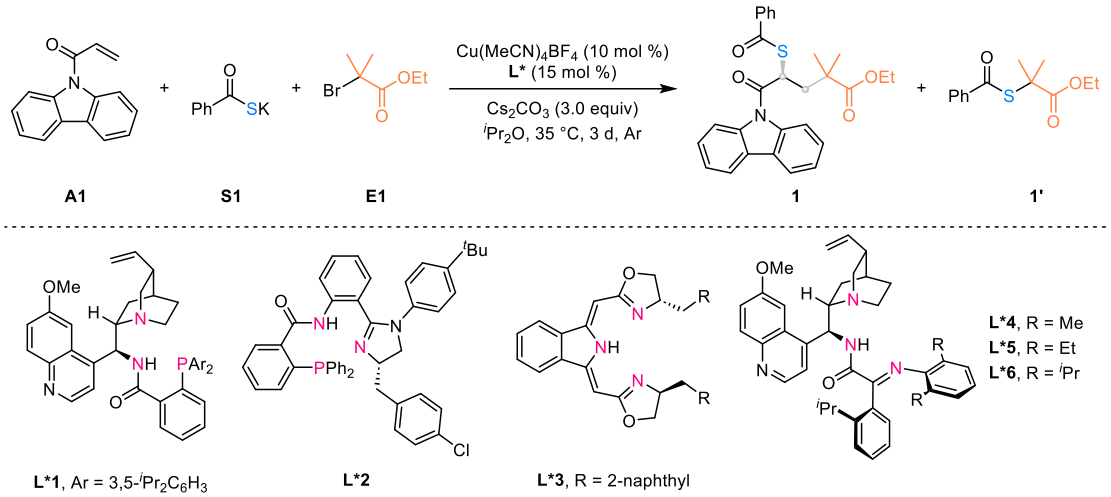
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in byproduct **1'** formation. Notably, the ligand **L*6** (Entry 6) can almost completely suppress the generation of the byproduct **1'**.

In addition, when the radical scavengers TEMPO (Entry 7) and BHT (Entry 8) were added to the reaction system, the corresponding trapped products **64** and **65** derived from tertiary alkyl radicals were detected, respectively.

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Table S2. Screening of reaction conditions[a]



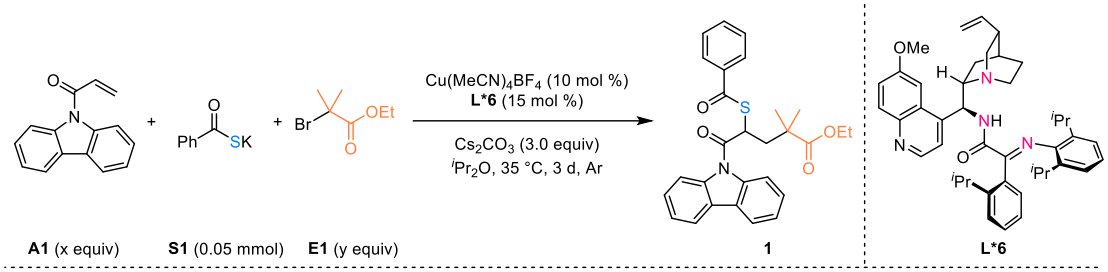
entry	[Cu]	L*	Solvent	yield of **1** (%)[b]	yield of **1'** (%)	Ee of **1** (%)
1	$Cu(MeCN)_4BF_4$	**L*1**	$^iPr_2O$	35 (39)	55	8
2	$Cu(MeCN)_4BF_4$	**L*2**	$^iPr_2O$	43 (57)	32	3
3	$Cu(MeCN)_4BF_4$	**L*3**	$^iPr_2O$	32 (44)	41	7
4	$Cu(MeCN)_4BF_4$	**L*4**	$^iPr_2O$	77 (93)	65	40
5	$Cu(MeCN)_4BF_4$	**L*5**	$^iPr_2O$	69 (93)	5	70
6	$Cu(MeCN)_4BF_4$	**L*6**	$^iPr_2O$	61 (97)	2	90
7	$Cu(MeCN)_4BF_4$	**L*6**	MTBE	23(85)	4	72
8	$Cu(MeCN)_4BF_4$	**L*6**	DCM	38(95)	2	62
9	$Cu(MeCN)_4BF_4$	**L*6**	Et_2O	26(90)	3	63
10	$Cu(MeCN)_4BF_4$	**L*6**	Toluene	31(89)	4	61
11	CuI	**L*6**	$^iPr_2O$	8(89)	1	90
12	CuTc	**L*6**	$^iPr_2O$	35(97)	1	91
13	$Cu(MeCN)_4PF_6$	**L*6**	$^iPr_2O$	31(97)	1	84
14	$Cu(OTf)_2$	**L*6**	$^iPr_2O$	18(95)	1	90
15	$Cu(OAc)_2$	**L*6**	$^iPr_2O$	19(95)	1	92

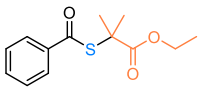
[a]Reaction conditions: **A1** (0.05 mmol), **S1** (0.05 mmol), **E1** (0.05 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L*6** (15 mol %), and Cs_2CO_3 (3.0 equiv) in $^iPr_2O$ (1.0 mL) at 35 °C for 3 days under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard; ee values were determined by HPLC analysis.

[b]The percentage of **1** among the two products is shown in parentheses.

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Table S3. Screening of substrate ratios[a]





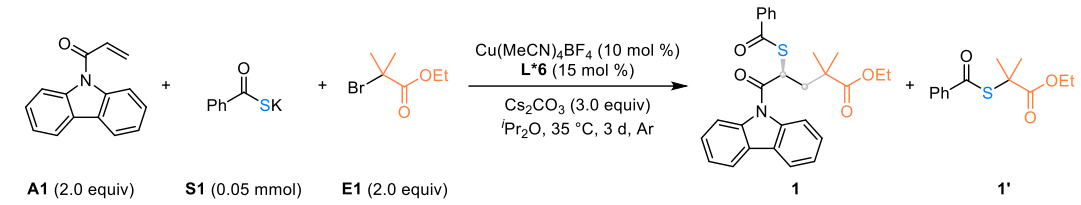
1'

entry	x	y	yield of **1** (%)	yield of **1'** (%)	Ee of **1** (%)
1	1	1	61	<5	90
2	2	1	34	<5	93
3	0.5	0.5	30	trace	81
4	1	2	45	trace	87
5	0.5	1	52	<5	90
6	1	0.5	14	<5	93
7	2	2	81	1	91

[a]Reaction conditions: **A1** (x equiv), **S1** (0.05 mmol), **E1** (y equiv), $Cu(MeCN)_4BF_4$ (10 mol %), **L*6** (15 mol %), and Cs_2CO_3 (3.0 equiv) in $^iPr_2O$ (1.0 mL) at 35 °C for 3 days under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard; ee values were determined by HPLC analysis.

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Table S4. Control experiments[a]



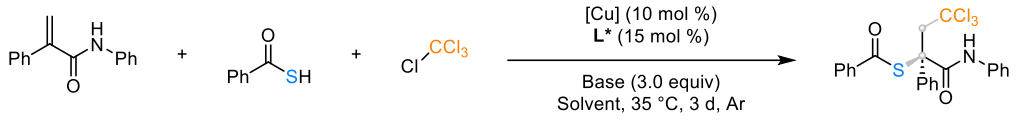
Entry	$Cu(MeCN)_4BF_4$	**L*6**	Cs_2CO_3	yield of **1** (%)	yield of **1'** (%)	Ee (%)
1	×	✓	✓	trace	trace	N.D.[b]
2	✓	×	✓	trace	trace	N.D.[b]
3	✓	✓	×	trace	trace	N.D.[b]
4	×	×	✓	trace	trace	N.D.[b]

[a]Reaction conditions: **A1** (0.05 mmol), **S1** (0.05 mmol), **E1** (0.05 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L*6** (15 mol %), and Cs_2CO_3 (3.0 equiv) in $^iPr_2O$ (1.0 mL) at 35 °C for 3 days under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard.

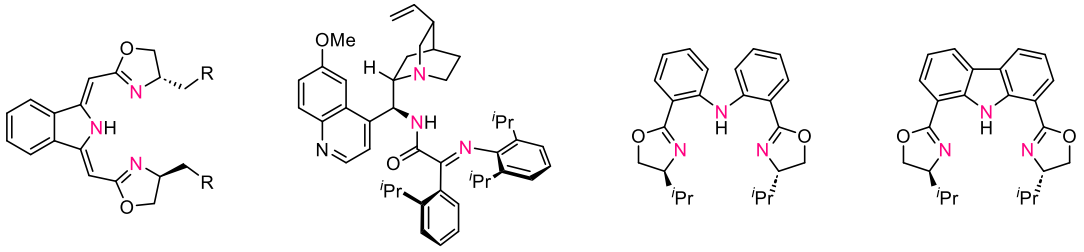
[b]Not determined.

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Table S5. Screening reaction conditions for phenyl-substituted acrylamide[a]



A6 S10 E10 24



L*3, R = 2-naphthyl L*6 L*7 L*8

entry	[Cu]	L*	Solvent	Base	yield of **24**(%)	Ee of **24**(%)
1	$Cu(PPh_3)_3CF_3$	**L*3**	Toluene	Cs_2CO_3	16	49
2	$Cu(PPh_3)_3CF_3$	**L*6**	Toluene	Cs_2CO_3	trace	N.D.[b]
3	$Cu(PPh_3)_3CF_3$	**L*7**	Toluene	Cs_2CO_3	18	63
4	$Cu(PPh_3)_3CF_3$	**L*8**	Toluene	Cs_2CO_3	30	82
5	$Cu(MeCN)_4BF_4$	**L*8**	Toluene	Cs_2CO_3	48	64
6	CuI	**L*8**	Toluene	Cs_2CO_3	43	43
7	$Cu(PPh_3)_2BH_4$	**L*8**	Toluene	Cs_2CO_3	47	85
8	$Cu(PPh_3)_2BH_4$	**L*8**	Et_2O	Cs_2CO_3	49	80
9	$Cu(PPh_3)_2BH_4$	**L*8**	$PhCF_3$	Cs_2CO_3	27	79
10	$Cu(PPh_3)_2BH_4$	**L*8**	$^iPr_2O$	Cs_2CO_3	50	84
11	$Cu(PPh_3)_2BH_4$	**L*8**	Toluene	Rb_2CO_3	69	89
12	$Cu(PPh_3)_2BH_4$	**L*8**	Toluene	Rb_2CO_3	80	90[c]
13	$Cu(PPh_3)_2BH_4$	**L*8**	Toluene	Rb_2CO_3	90	91[cd]

[a]Reaction conditions: **A6** (0.05 mmol), **S10** (0.075 mmol), **E10** (0.25 mmol), $Cu(PPh_3)_2BH_4$ (10 mol %), **L*8** (15 mol %), and Rb_2CO_3 (3.0 equiv) in Toluene (1.0 mL) at 35 °C for 3 days under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard; ee values were determined by HPLC analysis;

[b]Not determined;

[c]H_2O (1.0 equiv) in toluene at 35 °C for 3 days;

[d]**A6** (0.20 mmol), **S10** (0.30 mmol), **E10** (1.0 mmol). The yield is the isolated yield.

Screening of different copper precursors revealed that the PPh_3-containing Cu(I)

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complexes $Cu(PPh_3)_3CF_3$ (entry 4) and $Cu(PPh_3)_2BH_4$ (entry 7) afforded substantially higher enantioselectivities than Cu(I) precursors lacking PPh_3, such as $Cu(MeCN)_4BF_4$ (entry 5) and CuI (entry 6). This observation suggests that PPh_3 may serve as an ancillary ligand that helps shape the chiral environment around the copper center and thereby contributes to stereochemical discrimination during the C–S bond-forming step. Notably, $Cu(PPh_3)_2BH_4$ provided a higher yield than $Cu(PPh_3)_3CF_3$ under otherwise identical conditions. Although the origin of this difference is not fully established, we speculate that the relatively labile nature of the BH_4^- ligand may facilitate hydrolysis and/or ligand exchange under the reaction conditions, potentially leading to greater availability of soluble Cu species and more efficient formation of the catalytically relevant Cu–S intermediates.

Replacing Cs_2CO_3 (entry 7) with Rb_2CO_3 (entry 11) increased the yield from 47% to 69%. This difference may arise from cation-dependent solvation and ion-pairing effects, which can influence the availability of the ionic sulfur nucleophile and/or the speciation of the copper catalyst. On the basis of Rb_2CO_3 the addition of 1.0 equiv of H_2O further increased the yield to 80% (entry 12). We therefore reason that the addition of a small amount of a highly polar solvent may facilitate dissolution of catalyst-derived intermediates, thereby enhancing the overall reaction efficiency.

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2. Supplementary figures for experiments

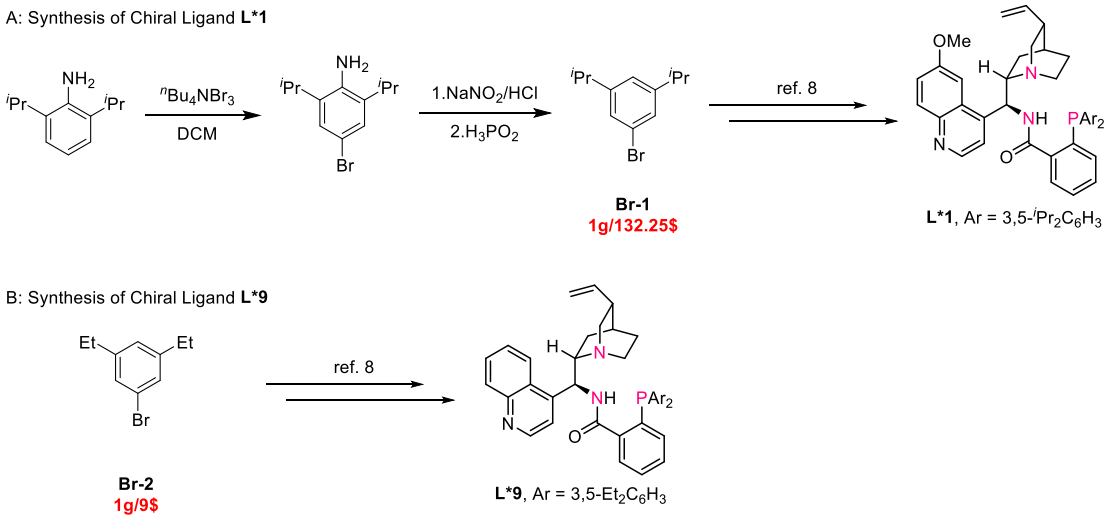
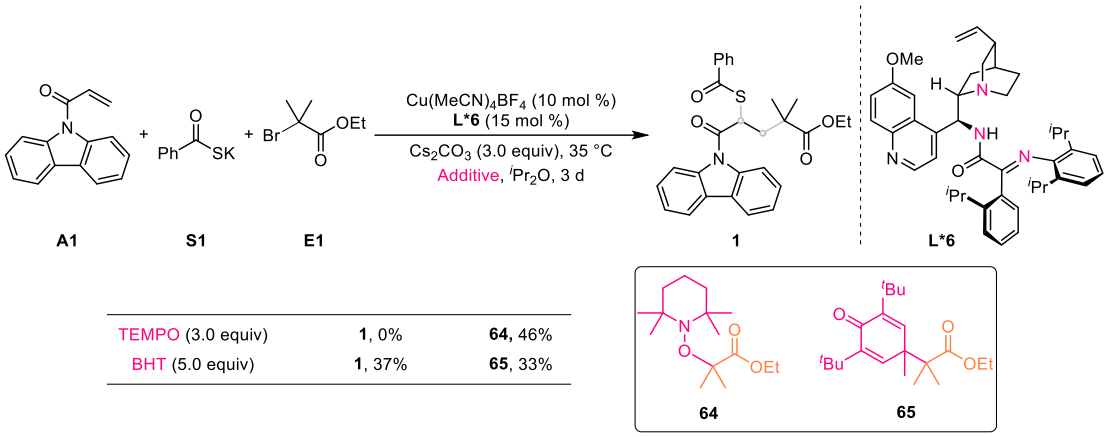


Figure S1. Due to the relatively high cost of **Br-1**(Sigma-Aldrich 1g/132.25$), it was synthesized in two steps according to a literature procedure[7]. Whereas **Br-2** (Sigma-Aldrich 1g/9$) was commercially available and used directly.

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TEMPO (3.0 equiv)	**1**, 0%	**64**, 46%
BHT (5.0 equiv)	**1**, 37%	**65**, 33%

Figure S2. The results showed that TEMPO completely suppressed the reaction, and the TEMPO-trapped adduct **64** was isolated in 46% yield. In contrast, BHT partially inhibited the reaction, and the BHT-trapped product **65** was obtained in 33% yield.

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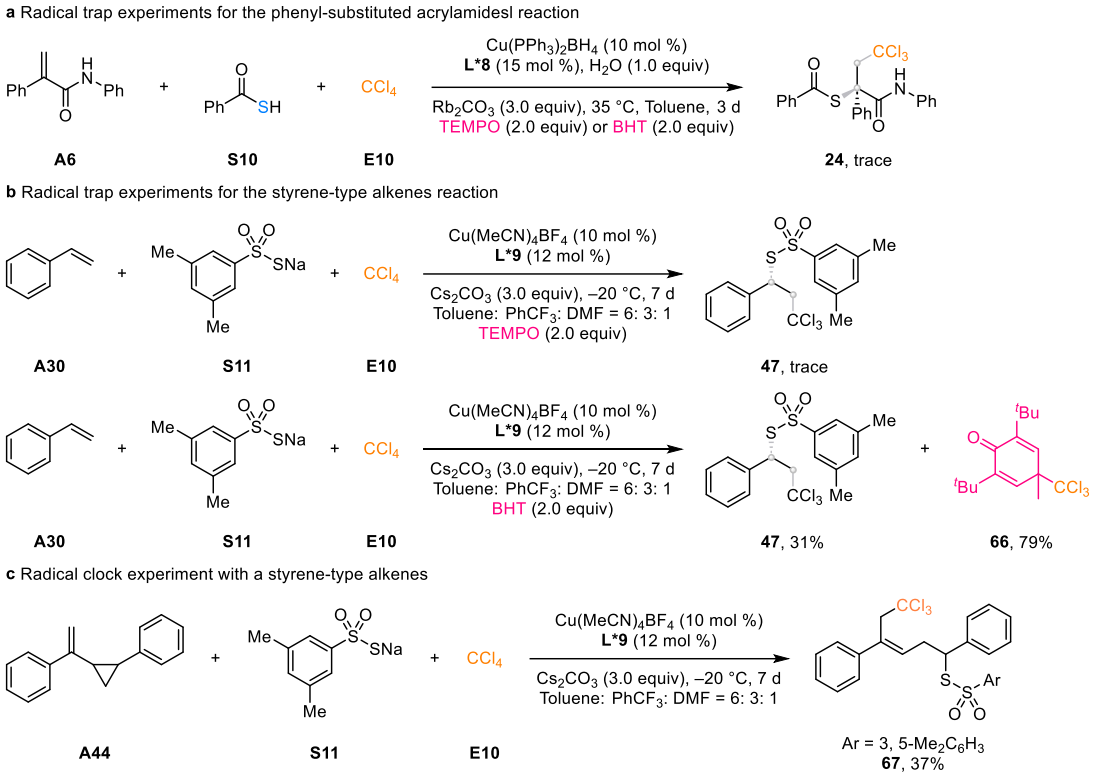


Figure S3. Mechanistic Studies: a) The phenyl-substituted acrylamide couplings were inhibited by TEMPO and BHT. b) The styrene-type alkene couplings were inhibited by TEMPO and BHT, and the BHT-trapped adduct **66** was isolated. c) The radical clock experiment using the styrene-type alkene substrate afforded the target product **67**.

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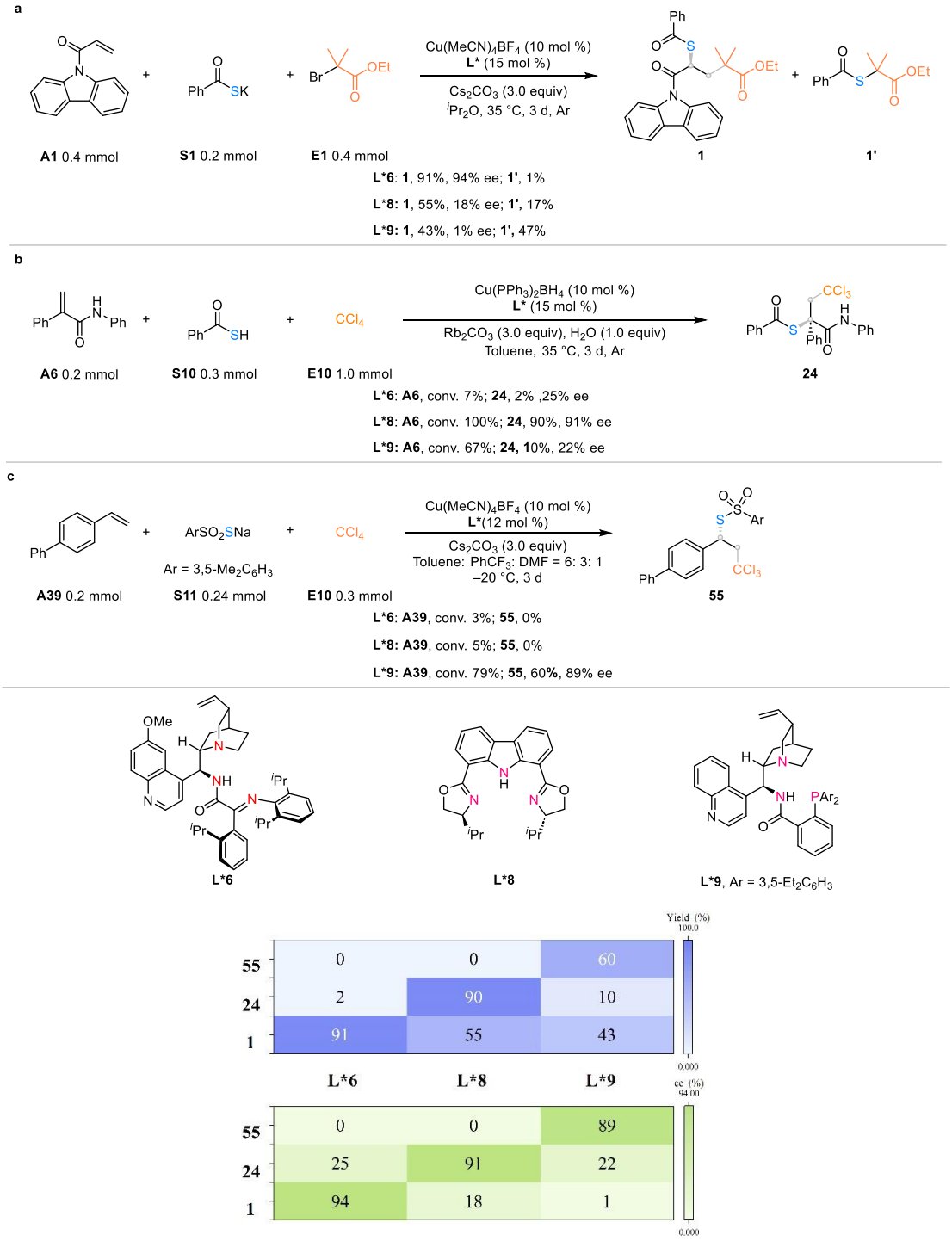


Figure S4. Investigation of ligand effect across different alkene classes. ee values were determined by HPLC analysis; Yield was based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard.

These ligand crossover experiments indicate that the optimal ligand scaffold is governed by the distinct steric and electronic requirements associated with each substrate class. For acrylamides, a highly confined chiral pocket (**L*6**) is important for

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suppressing competing reactivity; for 1,1-disubstituted acrylamides, a less hindered chiral environment facilitates C–S bond formation from the sterically demanding tertiary radical intermediate; and for styrenes, an electronically more reducing N,N,P ligand (**L*9**) environment is important for efficient radical generation at the low reaction temperature. We have incorporated this mechanistic rationale into the revised manuscript and supporting information.

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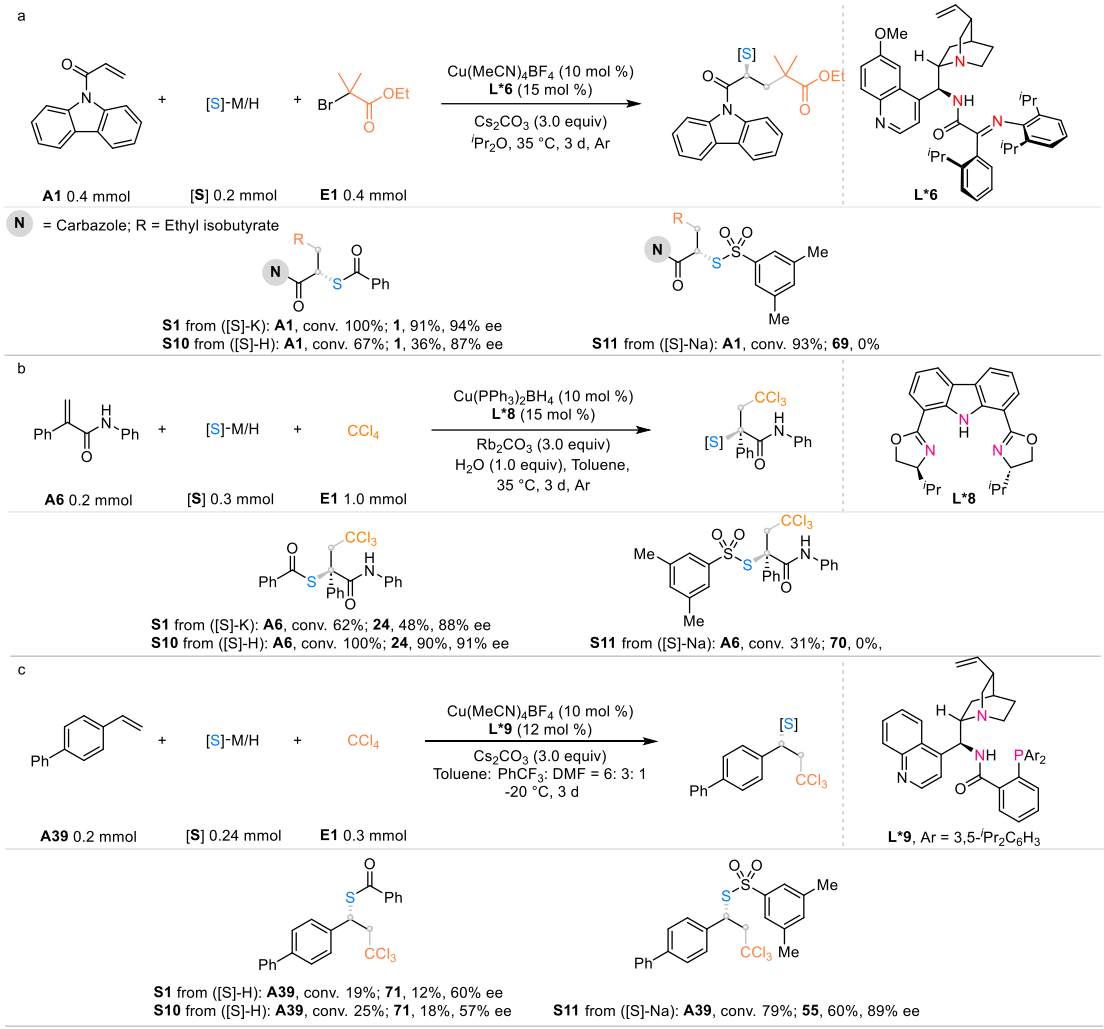


Figure S5. Investigation of sulfur nucleophile compatibility across different alkene classes. ee values were determined by HPLC analysis; Yield was based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethylbenzene as an internal standard.

These crossover experiments demonstrate that the sulfur nucleophiles are not strictly restricted to a single alkene class and can exhibit substantial cross-compatibility. Nevertheless, their performance is dependent on several factors, including sulfur-nucleophile solubility, counterion effects, steric properties, product stability, and the ability of the sulfur nucleophile to coordinate to copper. These results also highlight that the optimal sulfur nucleophile for each alkene class is determined by the balance between nucleophile reactivity and compatibility with the corresponding copper/ligand environment.

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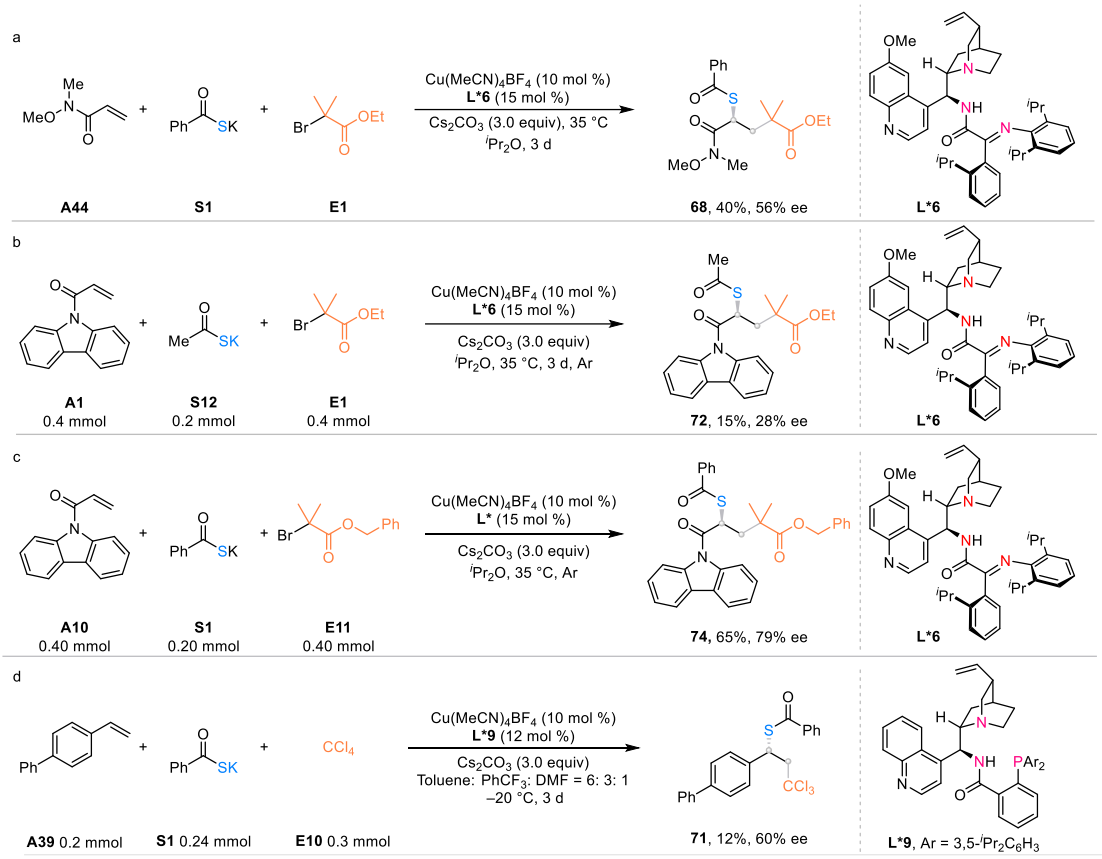
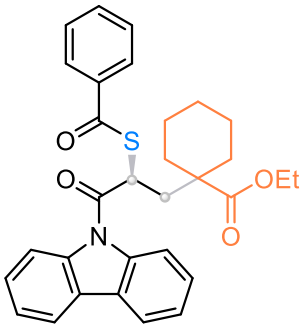


Figure S6. Preliminary Studies on Additional Substrates.

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8

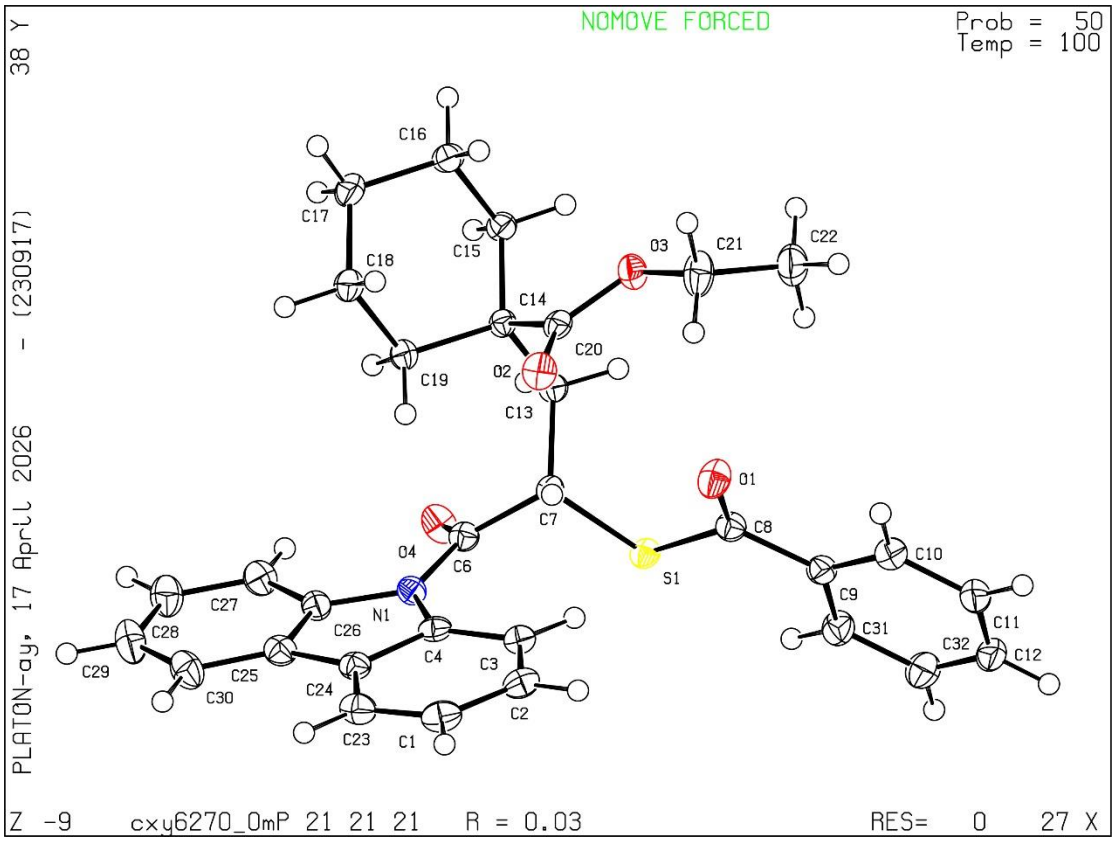
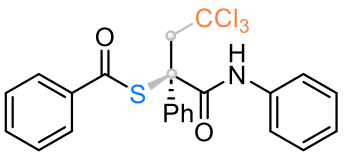


Figure S7. The X-ray structure of compound **8** displays sulfur, oxygen, and nitrogen atoms in yellow, red, blue, respectively, with all other atoms depicted in gray (CCDC 2535305, 50% probability ellipsoids).

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24

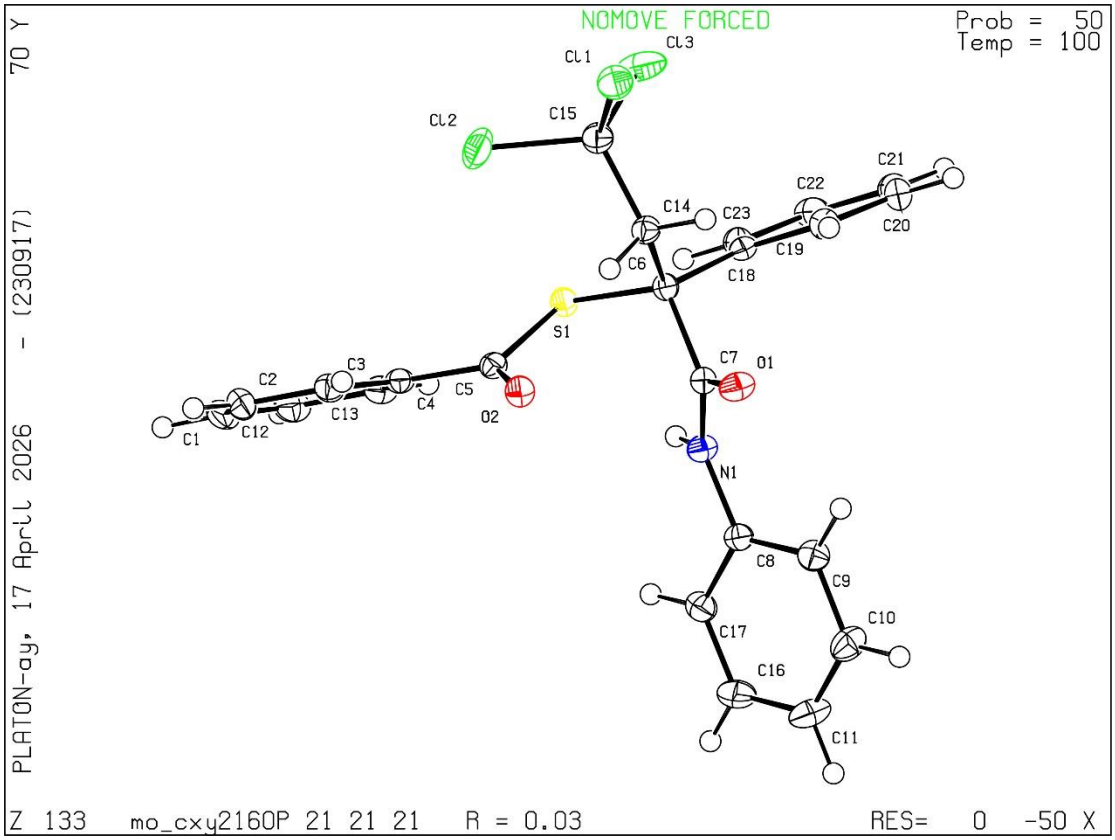
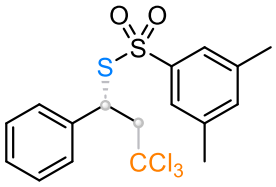


Figure S8. The X-ray structure of compound **24** displays sulfur, oxygen, nitrogen, and chlorine atoms in yellow, red, blue, green, respectively, with all other atoms depicted in gray (CCDC 2535306, 50% probability ellipsoids).

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47

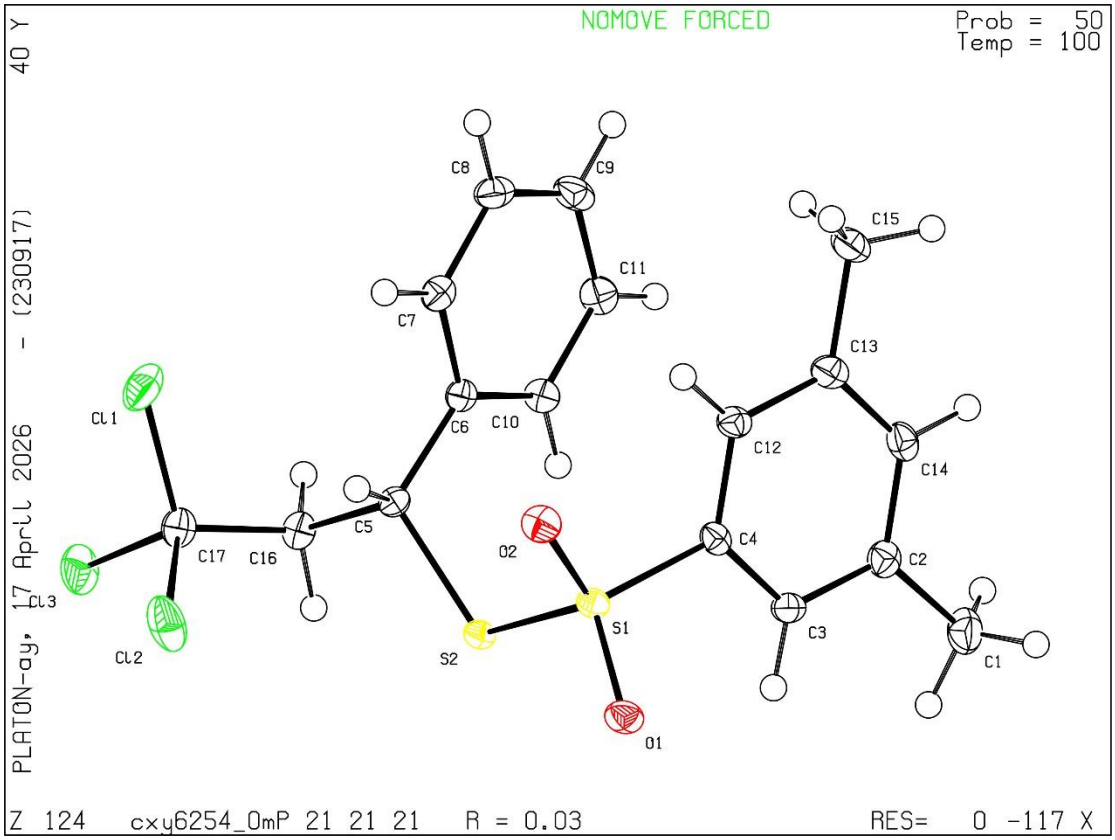


Figure S9. The X-ray structure of compound **47** displays sulfur, oxygen, and chlorine atoms in yellow, red, green, respectively, with all other atoms depicted in gray. (CCDC 2535304, 50% probability ellipsoids).

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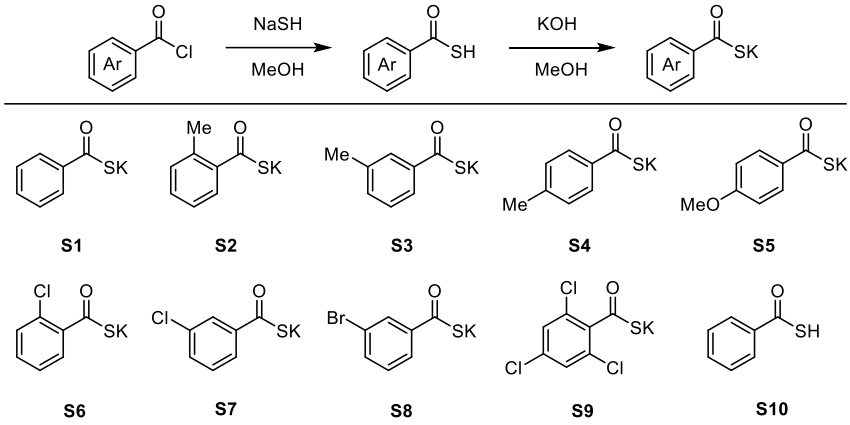
3. General information

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. $Cu(PPh_3)_2BH_4$ was purchased from Bide Pharmatech Ltd. Anhydrous toluene 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. 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 hexane, ethyl acetate (EA), Dichloromethane (DCM) and methanol 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 or 600 spectrometers at 400 or 600 MHz for ^1H NMR, 100 or 150 MHz for ^{13}C NMR and 376 or 565 MHz for ^{19}F NMR, respectively, in $CDCl_3$ or CD_3OD 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 (ee) 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.

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4. General procedure for synthesis of substrates

According to the literature reported procedure[1-2], potassium arylthioates substrates were synthesized.

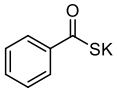


General procedure 1:

Sodium hydrosulfide (NaSH, 70% purity, 2.4 g, 30.0 mmol, 3.0 equiv) was suspended in methanol (MeOH, 20.0 mL) and cooled to 0 °C. To this suspension, the acyl chloride (10.0 mmol, 1.0 equiv) was added slowly. The reaction mixture was stirred at 0 °C for 2 h, then quenched HCl (1.0 M) and extracted with DCM. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude thiocarboxylic acid.

This crude product was dissolved in MeOH (10.0 mL). A solution of KOH (8.0 mmol) in MeOH (5.0 mL) was added. After stirring, the solvent was removed using a rotary evaporator. The resulting solid was triturated with DCM (20.0 mL) and collected by filtration. Final purification was achieved by recrystallization from a mixture of MeOH and toluene which afforded the purified thiocarboxylic acid.

Potassium benzothioate (S1)

 **S1**

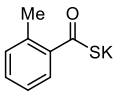
According to **General procedure 1** with benzothioic S-acid (6.9 g, 50 mmol, 1.0 equiv), which afforded the product **S1** as a white solid (6.6 g, 75% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 8.17 – 8.01 (m, 2H), 7.41 – 7.35 (m, 1H), 7.31 (m, 2H).

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^{13}C NMR (100 MHz, CD_3OD): δ 214.4, 145.4, 131.2, 129.0, 128.1.

Potassium 2-methylbenzothioate (S2)



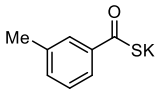
S2

According to **General procedure 1** with 2-methylbenzoyl chloride (1.54 g, 10 mmol, 1.0 equiv), which afforded the product **S2** as a white solid (0.969 g, 51% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 7.44 – 7.38 (m, 1H), 7.17 – 7.07 (m, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 178.9, 142.3, 135.7, 131.1, 128.9, 128.0, 126.2, 20.5.

Potassium 3-methylbenzothioate (S3)



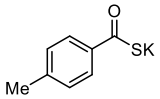
S3

According to **General procedure 1** with 3-methylbenzoyl chloride (1.54 g, 10 mmol, 1.0 equiv), which afforded the product **S3** as a white solid (1.42 g, 71% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 7.95 (s, 1H), 7.92 – 7.86 (m, 1H), 7.24 – 7.14 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 214.7, 145.6, 137.7, 131.8, 129.6, 128.0, 126.2, 21.2.

Potassium 4-methylbenzothioate (S4)



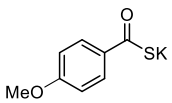
S4

According to **General procedure 1** with 4-methylbenzoyl chloride (1.54 g, 10 mmol, 1.0 equiv), which afforded the product **S4** as a white solid (1.69 g, 85% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 8.04 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 214.1, 142.8, 141.6, 129.2, 128.7, 21.2.

Potassium 4-methoxybenzothioate (S5)



S5

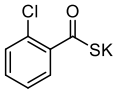
According to **General procedure 1** with 4-methoxybenzoyl chloride (1.70 g, 10 mmol, 1.0 equiv), which afforded the product **S5** as a white solid (1.43 g, 69% yield).

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^{1}H NMR (400 MHz, CD_3OD): δ 8.17 – 8.09 (m, 2H), 6.87 – 6.80 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 213.1, 163.1, 138.3, 131.2, 113.1, 55.6.

Potassium 2-chlorobenzothioate (S6)



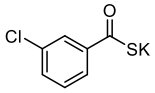
S6

According to **General procedure 1** with 2-chlorobenzoyl chloride (1.74 g, 10 mmol, 1.0 equiv), which afforded the product **S6** as a white solid (1.45 g, 69% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 7.52 – 7.46 (m, 1H), 7.31 – 7.25 (m, 1H), 7.24 – 7.15 (m, 2H).

^{13}C NMR (100 MHz, CD_3OD): δ 215.7, 145.0, 130.2, 129.1, 128.7, 128.2, 127.1.

Potassium 3-chlorobenzothioate (S7)



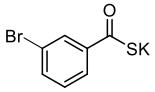
S7

According to **General procedure 1** with 3-chlorobenzoyl chloride (1.74 g, 10 mmol, 1.0 equiv), which afforded the product **S7** as a white solid (1.50 g, 72% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 8.13 – 8.09 (m, 1H), 8.04 – 7.99 (m, 1H), 7.40 – 7.34 (m, 1H), 7.33 – 7.25 (m, 1H).

^{13}C NMR (100 MHz, CD_3OD): δ 212.2, 147.2, 134.1, 130.7, 129.6, 129.0, 127.2.

Potassium 3-chlorobenzothioate (S8)



S8

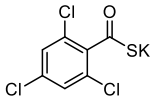
According to **General procedure 1** with 3-bromobenzoyl chloride (2.18 g, 10 mmol, 1.0 equiv), which afforded the product **S8** as a white solid (2.0 g, 80% yield).

^{1}H NMR (400 MHz, CD_3OD): δ 8.30 – 8.24 (m, 1H), 8.08 – 8.03 (m, 1H), 7.54 – 7.49 (m, 1H), 7.26 – 7.18 (m, 1H).

^{13}C NMR (100 MHz, CD_3OD): δ 212.0, 147.4, 133.7, 132.0, 129.9, 127.6, 122.2.

Potassium 2,4,6-trichlorobenzothioate (S9)

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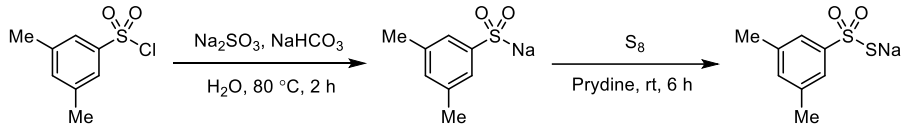
S9

According to **General procedure 1** with 2,4,6-trichlorobenzoyl chloride (2.42 g, 10 mmol, 1.0 equiv), which afforded the product **S9** as a white solid (2.1 g, 76 % yield).

^{1}H NMR (400 MHz, CD_3OD): δ 7.34 (s, 2H).

^{13}C NMR (100 MHz, CD_3OD): δ 210.7, 145.8, 132.6, 130.8, 128.5.

According to the literature reported procedure[1], sodium arylsulfonothioates synthesized.



S11

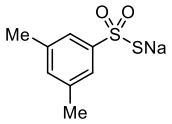
General procedure 2:

Sodium sulfite (6.15 g, 48.8 mmol, 2.0 equiv), sodium bicarbonate (4.1 g, 48.8 mmol, 2.0 equiv) and the 3,5-dimethylbenzenesulfonyl chloride (5 g, 24.4 mmol, 1.0 equiv) were dissolved in distilled water (30.0 mL). The reaction mixture was stirred for 2 hours at 80 °C. After cooling down to room temperature, water was removed in vacuo. 100 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 3,5-dimethylbenzenesulfinate (4.68 g, 24.4 mmol, 1.0 equiv) and S_8 (0.78 g, 24.4 mmol, 1.0 equiv) were dissolved in pyridine (30 mL) to give a yellow solution under argon. After the reaction was stirred 6 hours, 100.0 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

Sodium 3,5-dimethylbenzenesulfonothioate (S11)

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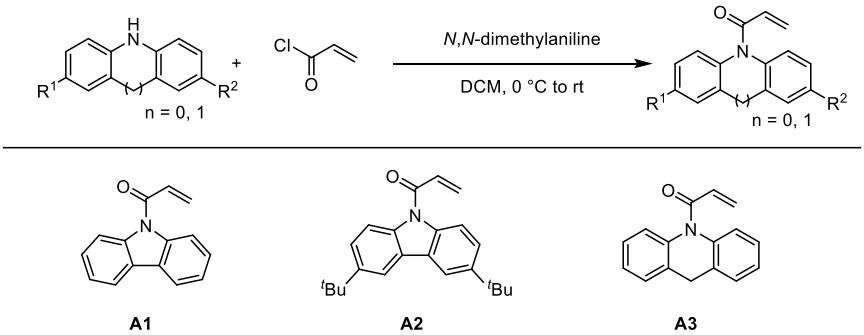
S11

According to **General procedure 1** with 3,5-dimethylbenzenesulfonyl chloride (5.0 g, 24.4 mmol, 1.0 equiv), which afforded the product **S11** as a white solid (4.57 g, 91 % yield).

^{1}H NMR (400 MHz, CD_3OD): δ 7.57 (s, 2H), 7.08 (s, 1H), 2.34 (s, 6H).

^{13}C NMR (100 MHz, CD_3OD): δ 154.2, 138.9, 132.4, 123.0, 21.1.

Synthesis of Carbazole-Derived Alkenes

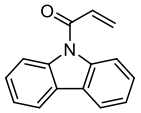


General procedure 3:

In a vacuum dried 50 mL round bottomed flask, 9,10-Dihydroacridine or carbazole and its derivatives (2.0 mmol, 1.0 equiv), *N*,*N*-dimethylaniline (6.0 mmol, 3.0 equiv) was dissolved in dry DCM (10.0 mL). Then, Acryloyl chloride (10.0 mmol, 5.0 equiv) was added at 0 °C under argon atmosphere. The reaction mixture was then warmed to reflux, and its progress was monitored by TLC.

Upon completion, the mixture was quenched with saturated aqueous $NaHCO_3$ solution (10.0 mL) and the mixture was extracted with DCM three times. The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (PE/EA = 100/0 ~ 100/5) on silica gel.

1-(9*H*-Carbazol-9-yl)prop-2-en-1-one (A1)



A1

According to **General procedure 3** with 9*H*-carbazole (8.35 g, 50 mmol, 1.0 equiv), which afforded the product **A1** as a white solid (8.73 g, 79% yield).

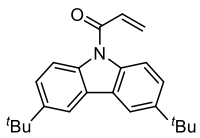
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^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 8.2, 0.9 Hz, 2H), 8.01 (dt, J = 7.6, 1.0 Hz, 2H), 7.50 (ddd, J = 8.4, 7.3, 1.4 Hz, 2H), 7.41 (td, J = 7.5, 1.0 Hz, 2H), 7.15 (dd, J = 17.0, 10.5 Hz, 1H), 6.72 (dd, J = 17.0, 1.5 Hz, 1H), 6.10 (dd, J = 10.4, 1.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 138.5, 131.8, 130.9, 127.2, 126.3, 123.8, 120.1, 115.9.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{12}NO$ $[M + H]^+$ 222.0913, found 222.0912.

1-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)prop-2-en-1-one (A2)



A2

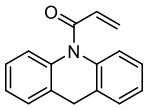
According to **General procedure 3** with 3,6-di-*tert*-butyl-9*H*-carbazole (1.40 g, 5 mmol, 1.0 equiv), which afforded the product **A2** as a white solid (1.09 g, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.06 (m, 4H), 7.57 (dd, J = 8.8, 2.0 Hz, 2H), 7.21 (dd, J = 17.0, 10.5 Hz, 1H), 6.73 (dd, J = 17.0, 1.5 Hz, 1H), 6.09 (dd, J = 10.5, 1.5 Hz, 1H), 1.53 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 146.9, 136.8, 131.8, 130.3, 126.4, 124.7, 116.2, 115.5, 34.9, 31.8.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{28}NO$ $[M + H]^+$ 334.2165, found 334.2164.

1-(Acridin-10(9*H*)-yl)prop-2-en-1-one (A3)



A3

According to **General procedure 4** with 9,10-dihydroacridine (362 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A3** as a white solid (366 mg, 78% yield).

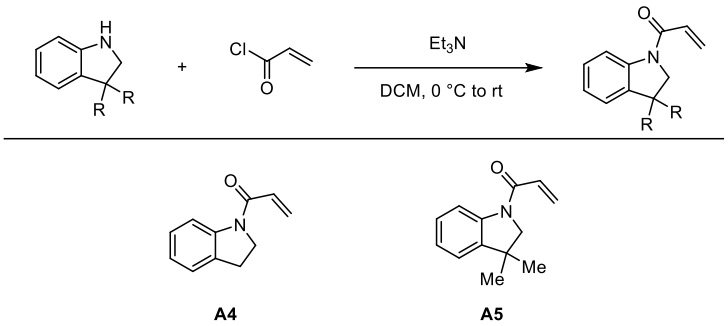
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.66 (m, 2H), 7.34 – 7.28 (m, 4H), 7.22 (td, J = 7.4, 1.3 Hz, 2H), 6.75 – 6.56 (m, 2H), 5.78 (dd, J = 9.9, 2.3 Hz, 1H), 3.84 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 138.8, 133.7, 129.5, 129.0, 127.3, 126.3, 126.0, 125.1, 34.0.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{14}NO$ $[M + H]^+$ 236.1070, found 236.1072.

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According to the literature reported procedure[3]. Synthesis of Indoline-Derived Alkenes

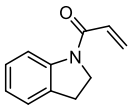


General procedure 4:

In a vacuum dried 50 mL round bottomed flask, Indoline and its derivatives (2.0 mmol, equiv), Triethylamine (Et_3N) (2.4 mmol, 1.2 equiv) was dissolved in dry DCM (10.0 mL). Then, Acryloyl chloride (4.0 mmol, 2.0 equiv) was added at 0 °C under argon atmosphere. The reaction mixture was then warmed to reflux, and its progress was monitored by TLC.

Upon completion, the mixture was quenched with saturated aqueous $NaHCO_3$ solution (10.0 mL) and the mixture was extracted with DCM three times. The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (PE/EA = 90/10 ~ 80/20) on silica gel.

1-(Indolin-1-yl)prop-2-en-1-one (A4)



A4

According to **General procedure 5** with indoline (238 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A4** as a white solid (315 mg, 91% yield).

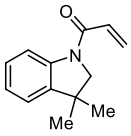
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 8.2 Hz, 1H), 7.19 (q, J = 7.2, 6.6 Hz, 2H), 7.02 (t, J = 7.5 Hz, 1H), 6.53 (qd, J = 16.8, 6.2 Hz, 2H), 5.78 (dd, J = 9.3, 2.9 Hz, 1H), 4.14 (t, J = 8.4 Hz, 2H), 3.19 (t, J = 8.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 142.9, 131.6, 129.2, 128.9, 127.6, 124.6, 124.1, 117.6, 48.1, 28.1.

HRMS (ESI) m/z calcd. for $C_{11}H_{11}NO$ Na $[M + Na]^+$ 196.0733, found 196.0735.

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1-(3,3-Dimethylindolin-1-yl)prop-2-en-1-one (A5)



A5

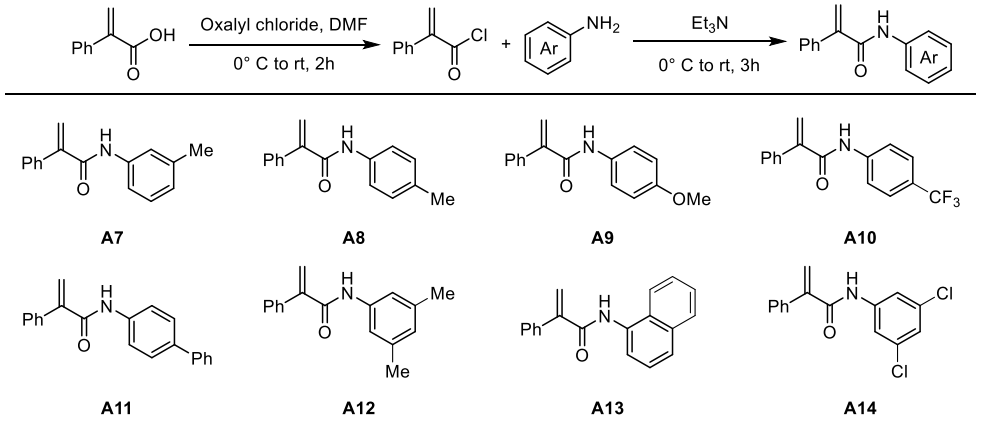
According to **General procedure 4** with 3,3-dimethylindoline (294 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A5** as a white solid (361 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.1 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.15 (d, J = 7.6, 1.9 Hz, 1H), 7.07 (t, J = 7.4, 1.2 Hz, 1H), 6.54 (t, J = 6.2 Hz, 2H), 5.79 (dd, J = 8.6, 3.7 Hz, 1H), 3.89 (d, J = 2.6 Hz, 2H), 1.36 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 141.3, 129.2, 129.0, 127.8, 124.4, 122.0, 117.1, 62.9, 40.4, 28.7.

HRMS (ESI) m/z calcd. for $C_{13}H_{15}NO$ Na $[M + Na]^+$ 224.1046, found 224.1044.

According to the literature reported procedure[4-6], tertiary α,β-unsaturated alkenes synthesized (I).



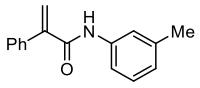
General procedure 5:

In a vacuum dried 100 mL round bottomed flask, to a solution of 2-phenylacrylic acid (1.48 g, 10.0 mmol, 1.0 equiv) in DCM (20 mL) was added oxalyl chloride (1.2 mL, 15.0 mmol, 1.5 equiv) and a drop of DMF at 0 °C. The reaction mixture was stirred at room temperature for 2 h. Then, the solvent was removed under reduced pressure to give the acyl chloride, which was used directly in the next step without further purification.

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To a solution of amine (10.0 mmol, 1.0 equiv) and Et_3N (1.67 mL, 12.0 mmol, 1.2 equiv) in DCM (20 mL) was added the above acyl chloride in DCM (5 mL) dropwise at 0 °C. Then the reaction mixture was warmed up to room temperature and stirred for 3 h. Upon completion, the reaction was quenched with 1M HCl(aq.) (25 mL) and extracted with DCM Three times. The combined organic phase was washed with saturated aqueous brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (PE/DCM = 90/10 ~ 20/10) on silica gel to give the desired product.

2-Phenyl-*N*-(*m*-tolyl)acrylamide (A7)



A7

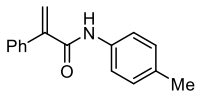
According to **General procedure 5** with *m*-toluidine (214 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A7** as a white solid (383.9 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 5H), 7.36 (d, J = 2.0 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.96 – 6.88 (m, 1H), 6.28 (d, J = 1.2 Hz, 1H), 5.72 (d, J = 1.2 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 145.3, 139.1, 137.6, 136.8, 129.1, 128.96, 128.95, 128.4, 125.5, 123.4, 120.6, 117.1, 21.6.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226, found 238.1225.

2-Phenyl-*N*-(*p*-tolyl)acrylamide (A8)



A8

According to **General procedure 5** with *p*-toluidine (224 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A8** as a white solid (403 mg, 85% yield).

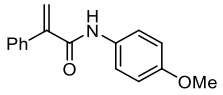
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.32 (m, 8H), 7.11 (d, J = 8.3 Hz, 2H), 6.27 (d, J = 1.2 Hz, 1H), 5.71 (d, J = 1.2 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 145.2, 136.9, 135.2, 134.4, 129.6, 129.1, 128.9, 128.4, 123.4, 120.1, 21.0.

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HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226, found238.1225.

N-(4-Methoxyphenyl)-2-phenylacrylamide (A9)



A9

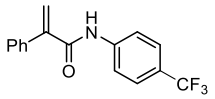
According to **General procedure 5** with 4-methoxyaniline (246 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A9** as a white solid (380 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.33 (m, 8H), 6.89 – 6.80 (m, 2H), 6.25 (d, J = 1.3 Hz, 1H), 5.70 (d, J = 1.3 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 156.7, 145.2, 136.9, 130.9, 129.0, 128.9, 128.4, 123.2, 121.8, 114.2, 55.6.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NO_2$ $[M + H]^+$ 254.1176, found 254.1175.

2-Phenyl-*N*-(4-(trifluoromethyl)phenyl)acrylamide (A10)



A10

According to **General procedure 5** with 4-(trifluoromethyl)aniline (322 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A10** as a white solid (454 mg, 79% yield).

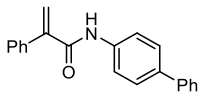
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.6 Hz, 2H), 7.61 (s, 1H), 7.56 (d, J = 8.7 Hz, 2H), 7.44 (s, 5H), 6.30 (s, 1H), 5.77 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 144.8, 140.8, 136.4, 129.2, 128.4, 126.8 (q, J = 3.8 Hz), 126.4 (q, J = 3.7 Hz), 126.4 (q, J = 122.8 Hz), 124.2, 119.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.1.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{13}F_3NO$ $[M + H]^+$ 292.0944, found 292.0924.

N-([1,1'-Biphenyl]-4-yl)-2-phenylacrylamide (A11)



A11

According to **General procedure 5** with [1,1'-biphenyl]-4-amine (338 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A11** as a white solid (490 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.52 (m, 6H), 7.50 – 7.38 (m, 8H), 7.33 (t, J =

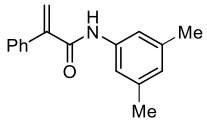
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7.3 Hz, 1H), 6.32 (s, 1H), 5.75 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 145.1, 140.5, 137.6, 137.0, 136.8, 129.2, 129.0, 128.9, 128.5, 127.8, 127.3, 127.0, 123.8, 120.3.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{13}F_3NO$ $[M + H]^+$ 300.1383, found 300.1383.

N-(3,5-Dimethylphenyl)-2-phenylacrylamide (A12)



A12

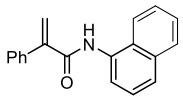
According to **General procedure 5** with 3,5-dimethylaniline (242 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A12** as a white solid (432 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.38 (m, 5H), 7.34 (s, 1H), 7.15 (s, 2H), 6.76 (s, 1H), 6.26 (d, J = 1.3 Hz, 1H), 5.70 (d, J = 1.2 Hz, 1H), 2.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 145.3, 138.8, 137.6, 136.8, 129.0, 128.9, 128.5, 126.5, 123.3, 117.7, 21.4.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383, found 252.1382.

N-(Naphthalen-1-yl)-2-phenylacrylamide (A13)



A13

According to **General procedure 5** with naphthalen-1-amine (286 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A13** as a white solid (388 mg, 71% yield).

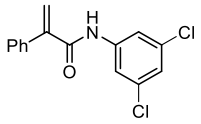
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.6 Hz, 1H), 7.84 (t, J = 6.8 Hz, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 7.1 Hz, 2H), 7.54 – 7.41 (m, 7H), 6.46 (s, 1H), 5.79 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 145.0, 137.1, 134.2, 132.2, 129.2(3), 129.1(6), 129.0, 128.7, 126.8, 126.5, 126.1, 126.0, 125.9, 124.4, 120.1.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{16}NO$ $[M + H]^+$ 274.1226, found 274.1225.

N-(3,5-Dichlorophenyl)-2-phenylacrylamide (A14)

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A14

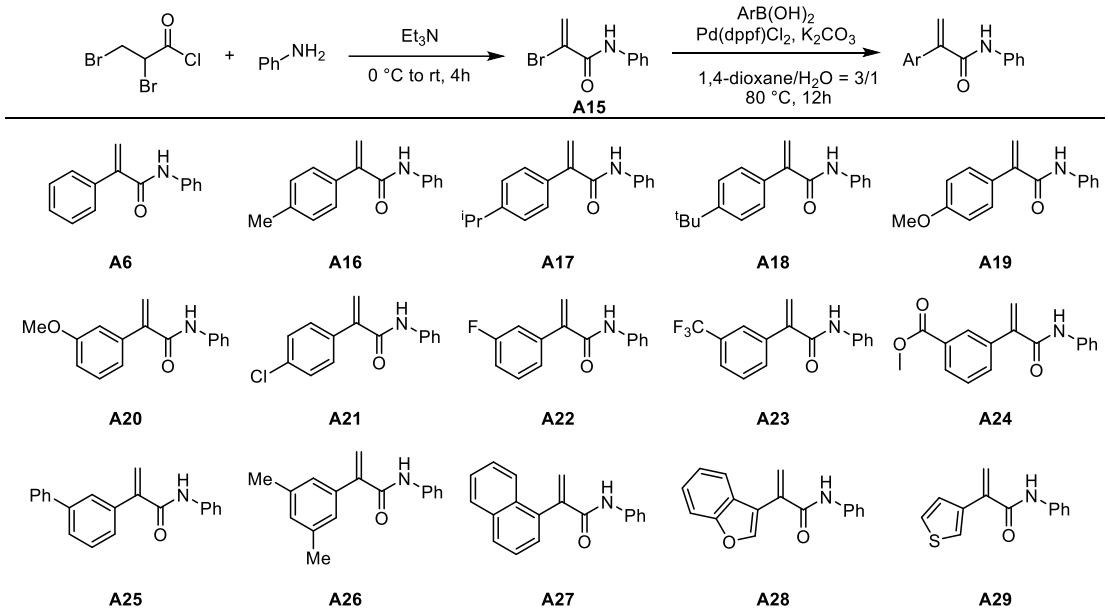
According to **General procedure 5** with 3,5-dichloroaniline (382 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A14** as a white solid (258 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.47 (d, J = 1.8 Hz, 2H), 7.45 – 7.35 (m, 5H), 7.08 (q, J = 1.6 Hz, 1H), 6.25 (s, 1H), 5.74 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 144.6, 144.6, 139.5, 136.2, 135.3, 129.2(2), 129.2(0), 128.2(8), 128.2(6), 124.6, 124.3, 118.3(0), 118.2(8).

HRMS (ESI) m/z calcd. for $C_{15}H_{12}Cl_2NO$ $[M + H]^+$ 292.0290, found 292.0288.

According to the literature reported procedure[4-6], tertiary α,β-unsaturated alkenes synthesized (II).



General procedure 6:

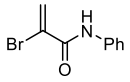
In a vacuum dried 500 mL round bottomed flask, To a solution of Aniline (4.56 mL, 50 mmol, 1.0 equiv) and Et_3N (10.4 mL, 75 mmol, 1.5 equiv) in MeCN (150 mL) was added 2,3-dibromopropionyl chloride (5.75 mL, 50 mmol, 1.0 equiv) dropwise at 0 °C. After being stirred at 0 °C for 1.0 h, the reaction mixture was warmed up to room temperature and stirred for another 3 h. After completion, the reaction was quenched with saturated NH_4Cl solution, and the MeCN was removed by evaporation. The aqueous layer was extracted with EA three times, and the combined organic layers were

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washed with saturated aqueous brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (PE/DCM = 90/10 ~ 20/10) to give the desired 2-bromo-*N*-phenylacrylamide.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 2-bromo-*N*-phenylacrylamide (450 mg, 2.0 mmol, 1.0 equiv), aryl boronic acid (2.4 mmol, 1.2 equiv), Pd(dppf)Cl_2 (29.2 mg, 2 mol %), K_2CO_3 (331.7 mg, 2.4 mmol, 1.2 equiv), 1,4-dioxane/water = 3:1 (8 mL). The reaction mixture was stirred at 80 °C for 12 h. Upon completion, the precipitate was filtered off and washed with saturated aqueous brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (PE/EA = 95/5 ~ 90/10) on silica gel to give the desired coupling product.

2-Bromo-*N*-phenylacrylamide (A15)



A15

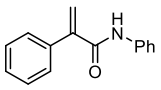
According to **General procedure 6** with aniline (4.56 mL, 50 mmol, 1.0 equiv), which afforded the product **A15** as a white solid (10.24 g, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7 8.36 (s, 1H), 7.64 – 7.55 (m, 2H), 7.42 – 7.32 (m, 2H), 7.21 – 7.15 (m, 1H), 7.13 (d, J = 1.7 Hz, 1H), 6.14 (d, J = 1.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 137.1, 129.3, 128.8, 125.4, 122.8, 120.3.

HRMS (ESI) *m*/*z* calcd. for C_9H_9BrNO $[M + H]^+$ 225.9862, found 225.9860.

***N*,2-Diphenylacrylamide (A6)**



A6

According to **General procedure 6** with phenylboronic acid (244 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A6** as a white solid (329 mg, 88% yield).

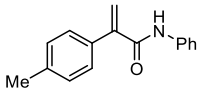
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 2H), 7.43 (tt, J = 5.2, 2.4 Hz, 6H), 7.34 – 7.28 (m, 2H), 7.14 – 7.08 (m, 1H), 6.27 (s, 1H), 5.72 (d, J = 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.35, 145.19, 137.75, 136.74, 129.11, 129.07, 128.97, 128.37, 124.72, 123.40, 120.04.

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HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{14}NO$ $[M + H]^+$ 224.1070, found 224.1069.

N-Phenyl-2-(*p*-tolyl)acrylamide (A16)



A16

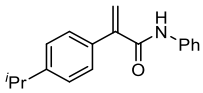
According to **General procedure 6** with *p*-tolylboronic acid (272 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A16** as a white solid (431.3 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.9 Hz, 2H), 7.45 (s, 1H), 7.40 – 7.31 (m, 4H), 7.27 (t, J = 6.2 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 6.28 (s, 1H), 5.72 (d, J = 1.2 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 145.0, 139.0, 137.8, 133.8, 129.8, 129.1, 128.3, 124.7, 123.0, 120.0, 21.4.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226, found 238.1225.

2-(4-Isopropylphenyl)-*N*-phenylacrylamide (A17)



A17

According to **General procedure 6** with (4-isopropylphenyl)boronic acid (328.2 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A17** as a white solid (440 mg, 83% yield).

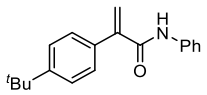
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.48 (m, 2H), 7.41 (s, 1H), 7.39 – 7.35 (m, 2H), 7.35 – 7.27 (m, 4H), 7.15 – 7.08 (m, 1H), 6.26 (d, J = 1.3 Hz, 1H), 5.70 (d, J = 1.3 Hz, 1H), 2.96 (hept, J = 6.9 Hz, 1H), 1.30 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 149.9, 145.1, 137.8, 134.2, 129.1, 128.4, 127.2, 124.7, 123.1, 120.1, 34.1, 24.0.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{20}NO$ $[M + H]^+$ 266.1539, found 266.1537.

2-(4-(*tert*-Butyl)phenyl)-*N*-phenylacrylamide (A18)

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A18

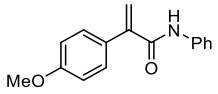
According to **General procedure 6** with (4-(*tert*-butyl)phenyl)boronic acid (356.2 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A18** as a white solid (474 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.53 (m, 2H), 7.53 – 7.45 (m, 3H), 7.44 – 7.39 (m, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.18 – 7.12 (m, 1H), 6.28 (s, 1H), 5.74 (s, 1H), 1.39 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 152.2, 145.0, 137.8, 133.8, 129.1, 128.1, 126.0, 124.7, 123.0, 120.1, 34.8, 31.4.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{22}NO$ $[M + H]^+$ 280.1696, found 280.1695.

2-(4-Methoxyphenyl)-*N*-phenylacrylamide (A19)



A19

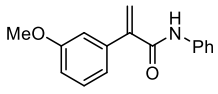
According to **General procedure 6** with (4-methoxyphenyl)boronic acid (304.1 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A19** as a white solid (380 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.0 Hz, 2H), 7.40 (dd, J = 8.0, 1.8 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.06 (dt, J = 19.2, 7.4 Hz, 2H), 6.96 (d, J = 8.3 Hz, 1H), 6.37 (d, J = 1.6 Hz, 1H), 5.63 (d, J = 1.6 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 157.0, 143.0, 138.1, 131.3, 130.7, 129.1, 126.4, 124.9, 124.4, 121.4, 120.1, 111.3, 55.9.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NO_2$ $[M + H]^+$ 254.1176, found 254.1175.

2-(3-Methoxyphenyl)-*N*-phenylacrylamide (A20)



A20

According to **General procedure 6** with (3-methoxyphenyl)boronic acid (304.1 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A20** as a white solid (390 mg, 76% yield).

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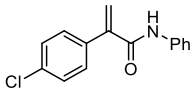
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.4 Hz, 3H), 7.37 – 7.27 (m, 3H), 7.15 – 7.07 (m, 1H), 7.01 (dt, J = 7.7, 1.1 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.29 (d, J = 1.2 Hz, 1H), 5.72 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 156.0, 144.9, 138.1, 137.7, 130.2, 129.1, 124.8, 123.8, 120.7, 120.1, 114.5, 114.0, 55.4.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NO_2$ $[M + H]^+$ 254.1176, found 254.1176.

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2-(4-Chlorophenyl)-*N*-phenylacrylamide (A21)



A21

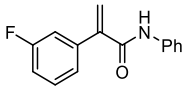
According to **General procedure 6** with (4-chlorophenyl)boronic acid (312 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A21** as a white solid (396 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.48 – 7.33 (m, 7H), 7.16 (t, J = 7.4 Hz, 1H), 6.24 (s, 1H), 5.77 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 144.4, 137.6, 135.1, 135.0, 129.6, 129.3, 129.2, 124.9, 123.1, 120.1.

HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{13}ClNO$ $[M + H]^+$ 258.0680, found 258.0678.

2-(3-Fluorophenyl)-*N*-phenylacrylamide (A22)



A22

According to **General procedure 6** with (3-fluorophenyl)boronic acid (280 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A22** as a white solid (385 mg, 80% yield).

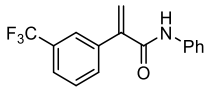
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.9 Hz, 2H), 7.40 (td, J = 7.8, 5.6 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.23 (s, 1H), 7.21 – 7.07 (m, 3H), 6.25 (s, 1H), 5.77 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 163.0 (d, J = 247.5 Hz), 144.4 (d, J = 1.8 Hz), 138.8 (d, J = 7.7 Hz), 137.6, 130.6 (d, J = 8.4 Hz), 129.2, 124.9, 124.0 (d, J = 3.1 Hz), 123.6, 120.1, 116.0 (d, J = 21.1 Hz), 115.4 (d, J = 22.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –111.8

HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{13}FNO$ $[M + H]^+$ 242.0976, found 242.0975.

_N_-Phenyl-2-(3-(trifluoromethyl)phenyl)acrylamide (A23)



A23

According to **General procedure 6** with (3-(trifluoromethyl)phenyl)boronic acid (380 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A23** as a white solid (378 mg, 65% yield).

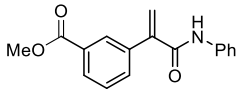
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.67 (dd, J = 7.5, 1.7 Hz, 2H), 7.55 (t, J = 8.2 Hz, 3H), 7.40 (s, 1H), 7.34 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 6.24 (s, 1H), 5.83 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 144.5, 137.5, 137.4, 131.5 (q, J = 15.6 Hz)., 129.5, 129.2, 125.7 (q, J = 3.6 Hz), 125.0 (q, J = 3.6 Hz), 123.5 (q, J = 270.8 Hz). 123.4, 120.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.3.

HRMS (ESI) m/z calcd. for $C_{16}H_{13}F_3NO$ $[M + H]^+$ 292.0944, found 292.0945.

Methyl 3-(3-oxo-3-(phenylamino)prop-1-en-2-yl)benzoate (A24)



A24

According to **General procedure 6** with (3-(methoxycarbonyl)phenyl)boronic acid (360 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A24** as a white solid (378 mg, 65% yield).

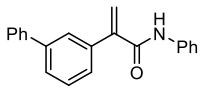
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.12 (m, 1H), 8.08 (dt, J = 7.9, 1.4 Hz, 1H), 7.66 (ddd, J = 7.7, 1.8, 1.2 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.39 (s, 1H), 7.37 – 7.29 (m, 2H), 7.18 – 7.11 (m, 1H), 6.26 (s, 1H), 5.81 (d, J = 0.8 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 165.2, 144.7, 137.6, 137.0, 132.7, 131.0, 130.1, 129.3, 129.2(0), 129.1(6), 124.9, 123.4, 120.2, 52.5.

HRMS (ESI) m/z calcd. for $C_{17}H_{16}NO_3$ $[M + H]^+$ 282.1125 found 282.1126.

2-([1,1'-Biphenyl]-3-yl)-_N_-phenylacrylamide (A25)

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 **A25**

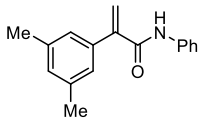
According to **General procedure 6** with [1,1'-biphenyl]-3-ylboronic acid (396.2 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A25** as a white solid (478 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.57 (m, 4H), 7.57 – 7.49 (m, 3H), 7.45 (q, J = 7.6 Hz, 4H), 7.38 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.34 (s, 1H), 5.80 (d, J = 1.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 145.2, 142.2, 140.5, 137.7, 137.3, 129.5, 129.2, 129.1, 127.9, 127.8, 127.3, 127.2, 124.8, 123.8, 120.1.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{18}NO$ $[M + H]^+$ 300.1383, found 300.1382.

2-(3,5-Dimethylphenyl)-*N*-phenylacrylamide (A26)

 **A26**

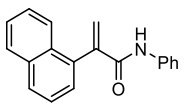
According to **General procedure 6** with (3,5-dimethylphenyl)boronic acid (300.2 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A26** as a white solid (392 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 2H), 7.43 (s, 1H), 7.32 (t, J = 8.0 Hz, 2H), 7.15 – 7.08 (m, 1H), 7.05 (s, 3H), 6.27 (d, J = 1.4 Hz, 1H), 5.68 (d, J = 1.3 Hz, 1H), 2.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 145.3, 138.8, 137.8, 136.8, 130.6, 129.1, 126.2, 124.7, 123.4, 120.0, 21.4.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383, found 252.1382.

2-(Naphthalen-1-yl)-*N*-phenylacrylamide (A27)

 **A27**

According to **General procedure 6** with naphthalen-1-ylboronic acid (344 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A27** as a white solid (382 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J = 10.6, 8.3 Hz, 3H), 7.57 – 7.44 (m, 4H),

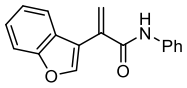
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7.29 (d, J = 8.1 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 1.8 Hz, 1H), 5.75 (d, J = 1.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 142.9, 137.5, 134.4, 133.8, 131.7, 129.6, 129.3, 128.9, 128.6, 128.0, 127.8, 127.1, 126.7, 125.6, 125.3, 124.6, 120.1.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{16}NO$ $[M + H]^+$ 274.1226, found 274.1225.

2-(Benzofuran-3-yl)-*N*-phenylacrylamide (A28)



A28

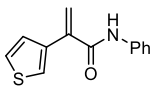
According to **General procedure 6** with benzofuran-3-ylboronic acid (324 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A28** as a white solid (316 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.74 – 7.60 (m, 2H), 7.57 (dt, J = 8.3, 0.9 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.39 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H), 7.32 (tdd, J = 7.4, 4.2, 1.6 Hz, 3H), 7.16 – 7.10 (m, 1H), 6.40 (s, 1H), 5.98 (d, J = 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 155.6, 144.3, 137.6, 135.5, 129.2, 126.1, 125.4, 124.9, 123.7(1), 123.6(6), 120.5, 120.3, 117.3, 112.2.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{14}NO_2$ $[M + H]^+$ 264.1019, found 264.1017.

N-Phenyl-2-(thiophen-3-yl)acrylamide (A29)



A29

According to **General procedure 6** with thiophen-3-ylboronic acid (256 mg, 2.0 mmol, 1.0 equiv), which afforded the product **A29** as a white solid (334 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.1 Hz, 3H), 7.49 (d, J = 3.0 Hz, 1H), 7.39 (dd, J = 5.0, 3.0 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.13 (t, J = 7.4 Hz, 1H), 6.11 (s, 1H), 5.78 (s, 1H).

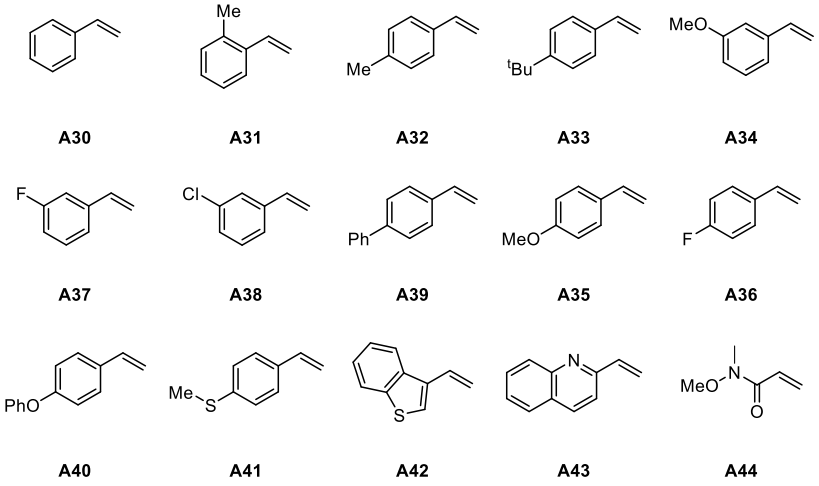
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 140.2, 137.7, 137.2, 129.2, 127.0, 126.8, 124.8, 124.5, 121.2, 120.1.

HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{12}NOS$ $[M + H]^+$ 230.0634, found 230.0635.

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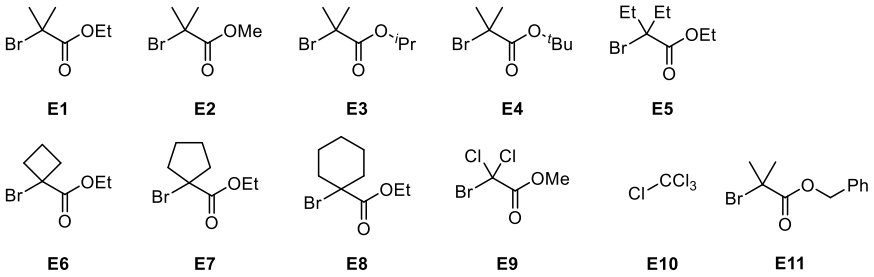
Synthesis of alkene

Note: All alkene, are known compounds and are commercially available.



Synthesis of Radical Precursors

Note: All radical precursors, are known compounds and are commercially available.

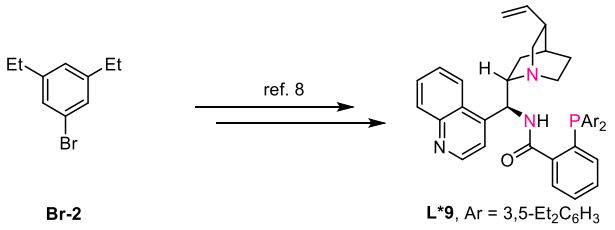


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5. Synthesis of the optimal chiral ligand.

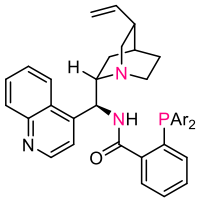
Synthesis of chiral ligand L*9

Note: The chiral ligand **L*9** were synthesized according to the procedure described in the literature[7-8].



Br-2 **L*9**, Ar = 3,5-$Et_2C_6H_3$

2-(Bis(3,5-diethylphenyl)phosphaneyl)-*N*-((*S*)-quinolin-4-yl((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide (L*9)



L*9, Ar = 3,5-$Et_2C_6H_3$

L*9

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, J = 4.6 Hz, 1H), 8.43 (dd, J = 8.7, 1.3 Hz, 1H), 8.10 (dd, J = 8.4, 1.4 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.61 – 7.54 (m, 1H), 7.44 – 7.17 (m, 4H), 7.02 (s, 1H), 7.00 – 6.91 (m, 4H), 6.84 (dd, J = 7.9, 1.7 Hz, 2H), 5.63 (ddd, J = 17.5, 10.4, 7.4 Hz, 1H), 5.56 – 5.29 (m, 1H), 4.98 – 4.85 (m, 2H), 3.11 – 2.97 (m, 2H), 2.95 – 2.75 (m, 1H), 2.71 – 2.62 (m, 1H), 2.62 – 2.51 (m, 8H), 2.49 – 2.40 (m, 1H), 2.25 – 2.15 (m, 1H), 1.65 – 1.43 (m, 3H), 1.27 – 1.22 (m, 2H), 1.17 (t, J = 7.6 Hz, 6H), 1.11 (t, J = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 150.2, 148.4, 144.5(3), 144.4(6), 144.4, 144.3, 141.5, 137.2, 137.1, 136.8, 136.7, 135.7, 135.4, 134.5, 130.8, 130.6(1), 130.5(8), 130.4, 130.3, 130.2, 128.9, 128.8, 128.2, 128.0, 127.6, 127.5, 126.6, 123.6, 114.4, 60.4, 55.8, 40.8, 39.7, 28.8(3), 28.8(2), 27.9, 27.4, 25.7, 21.1, 15.6.

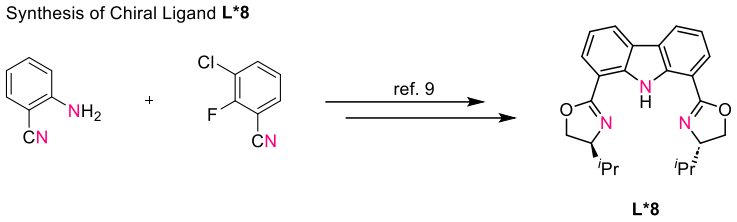
^{31}P NMR (162 MHz, $CDCl_3$): δ –10.43.

HRMS (ESI) *m/z* calcd. for $C_{46}H_{53}N_3OP$ $[M + H]^+$ 694.3921, found: 694.3918.

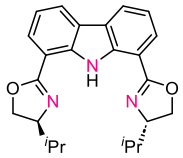
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Synthesis of chiral ligand L*8

Note: The chiral ligand **L*8** were synthesized according to the procedure described in the literature.[9]



1,8-Bis((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)-9*H*-carbazole (L*8)



L*8

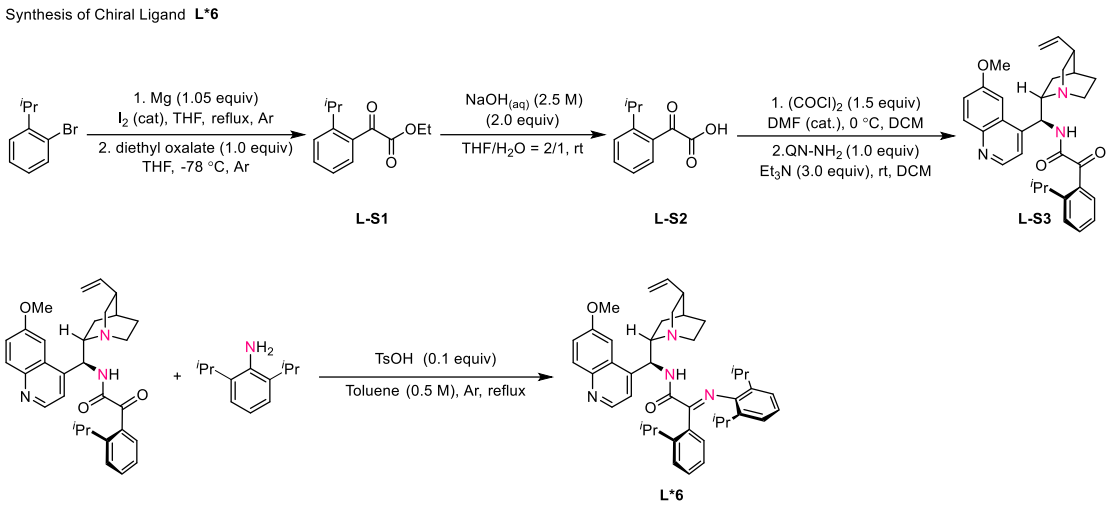
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.06 (s, 1H), 8.19 (dt, J = 7.8, 0.9 Hz, 2H), 7.92 (dd, J = 7.6, 1.1 Hz, 2H), 7.26 (t, J = 7.7 Hz, 2H), 4.53 – 4.42 (m, 2H), 4.28 – 4.16 (m, 4H), 1.89 (h, J = 6.7 Hz, 2H), 1.65 (s, 1H), 1.15 (d, J = 6.7 Hz, 6H), 1.02 (d, J = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 139.1, 125.8, 123.5(4), 123.4(7), 118.8, 110.6, 73.0, 70.0, 33.5, 19.3, 18.7.

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Synthesis of chiral ligand L*6

Note: The synthesis of chiral ligand precursor **L-S2** was performed according to the literature procedure.[10]



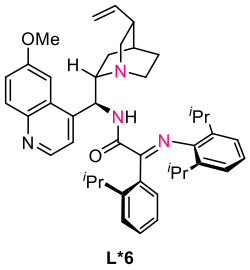
Synthesis of L–S3: Under an argon atmosphere, a round-bottom flask equipped with a magnetic stir bar was charged with 2-(2-isopropylphenyl)-2-oxoacetic acid (2.3 g, 12.0 mmol, 1.2 equiv) and dry DCM (50 mL). The flask was placed in an ice bath, and the mixture was cooled to 0 °C. Oxalyl chloride (1.27 mL, 15.0 mmol, 1.5 equiv) and a catalytic amount of DMF were added dropwise. After the mixture had been stirred at 0 °C for 0.5 h, the ice bath was removed, and the mixture was allowed to warm to room temperature and stirred for an additional 1 h. Upon completion, the solvent and excess oxalyl chloride were removed under reduced pressure to afford 2-(2-isopropylphenyl)-2-oxoacetyl chloride. Under an argon atmosphere, the flask containing the above acyl chloride was charged with dry DCM (40 mL) and cooled in an ice bath. Quinine amine (3.23 g, 10.0 mmol, 1.0 equiv) dissolved in dry DCM (10 mL) was added slowly, followed by the dropwise addition of Et_3N (4.2 mL, 10.0 mmol, 3.0 equiv). The reaction mixture was stirred for 12 h. The reaction was monitored by TLC. After completion, the mixture was quenched with saturated aqueous NH_4Cl (30 mL). The aqueous phase was extracted with DCM (3 × 30 mL), and the combined organic layers were washed with brine (3 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash

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column chromatography on silica gel (PE/EA = 10/1) to afford the ligand precursor **L–S3** as a pale yellow solid (3.58 g, 72% yield).

Synthesis of Ligand L*6: Under an argon atmosphere, a dry two-necked flask equipped with a magnetic stir bar was charged with ligand precursor **L–S3** (2.49 g, 5 mmol), TsOH (86.1 mg, 0.5 mmol, 0.1 equiv), and dry toluene (20 mL). The mixture was stirred until homogeneous. A Dean-Stark trap and a reflux condenser were attached, and the reaction mixture was heated at reflux in an oil bath for 72 h. The reaction was monitored by TLC. After completion, the mixture was washed with saturated aqueous NH_4Cl (25 mL) and extracted with a small amount of EA. The aqueous layer was further extracted with EA (2 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/1) to afford the desired product **L*6** as a yellow solid (1.64 g, 50% yield).

(*E*)-2-((2,6-Diisopropylphenyl)imino)-2-(2-isopropylphenyl)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)acetamide (L*6)



L*6

L*6

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 4.5 Hz, 1H), 8.52 (d, J = 4.6 Hz, 1H × 0.2), 8.08 (d, J = 9.2 Hz, 1H), 7.97 (d, J = 9.2 Hz, 1H × 0.2), 7.75 (s, 1H), 7.50 (d, J = 4.5 Hz, 1H), 7.48 – 7.28 (m, 2H + 2H × 0.2), 7.25 – 7.19 (m, 3H × 0.2), 7.18 – 7.07 (m, 3H), 7.06 – 6.99 (m, 1H + 2H × 0.2), 6.98 – 6.90 (m, 1H + 1H × 0.2), 6.84 (d, J = 7.3 Hz, 1H), 6.77 (d, J = 4.1 Hz, 1H × 0.2), 6.68 (d, J = 7.8 Hz, 1H), 6.29 (d, J = 4.6 Hz, 1H × 0.2), 5.86 – 5.55 (m, 1H + 1H × 0.2), 5.30 – 5.19 (m, 1H × 0.2), 5.05 – 4.89 (m, 2H + 2H × 0.2), 3.94 (s, 3H), 3.88 (s, 3H × 0.2), 3.51 – 3.09 (m, 3H + 2H × 0.2), 3.00 (m, 1H + 3H × 0.2), 2.77 (m, 2H + 1H × 0.2), 2.70 – 2.55 (m, 3H × 0.2), 2.56 – 2.13

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(m, 3H + 5H × 0.2), 1.79 – 1.49 (m, 4H + 4H × 0.2), 1.40 – 1.32 (m, 1H), 1.31 – 0.95 (m, 13H + 13H × 0.2), 0.89 (m, 1H + 1H × 0.2), 0.81 – 0.73 (m, 1H + 1H × 0.2), 0.69 – 0.51 (m, 4H).

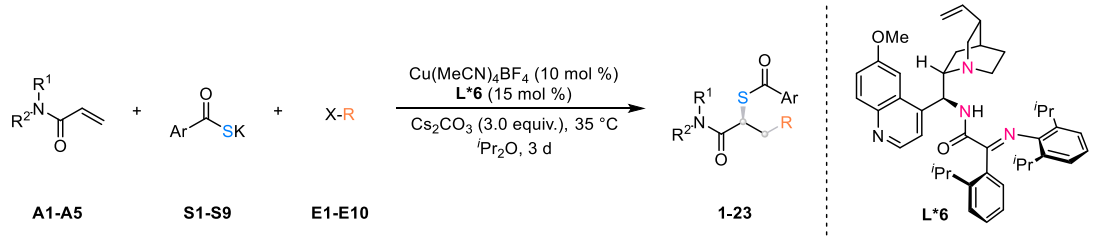
^{13}C NMR (100 MHz, $CDCl_3$) (minor) δ 165.2, 161.9, 147.5, 147.4, 143.1, 141.5, 137.5, 132.2 – 131.8 (two carbons overlapped), 130.9, 129.7, 129.3, 128.8 – 128.3 (two carbons overlapped), 126.0, 125.8, 125.0, 124.8, 123.3, 122.7, 114.6, 102.1, 56.3, 55.4, 40.9, 39.8, 31.5, 29.0, 28.1, 28.0, 27.5, 23.9, 23.8 – 23.5 (two carbons overlapped), 21.8.

^{13}C NMR (100 MHz, $CDCl_3$) (major) δ 163.9, 163.3, 157.9, 147.8, 147.3, 145.4, 144.5, 144.3, 141.3, 136.0, 135.6, 135.5, 131.6, 129.9, 129.3, 124.2, 123.9, 123.0, 121.5, 118.5, 101.4, 60.6, 56.0, 55.5, 50.0, 39.6, 30.4, 28.8, 27.2, 25.6, 24.3, 24.2, 22.4, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{43}H_{53}N_4O_2$ $[M + H]^+$ 657.4163, found: 657.4159

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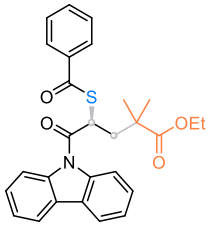
6. Copper-catalyzed chemo- and enantioselective radical 1, 2-carbosulfuration of acrylamide



General procedure A

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium thiocarboxylates (0.20 mmol, 1.0 equiv), alkene (0.40 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), **L*6** (19.75 mg, 0.03 mmol, 15 mol %) and Cs_2CO_3 (195.50 mg, 0.60 mmol, 3.0 equiv), Then, diisopropyl ether (4.0 mL) was added by syringe under argon atmosphere. Finally, radical precursor (0.40 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Ethyl *(S)*-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate (1)



1

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **1** as a colorless oil (86.4 mg, 91% yield, 93% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ =

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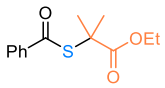
254 nm), t_R (minor) = 16.77 min, t_R (major) = 22.21 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 – 8.05 (m, 2H), 7.98 (dd, J = 12.5, 7.6 Hz, 4H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (dt, J = 15.0, 7.6 Hz, 4H), 7.40 (t, J = 7.5 Hz, 2H), 5.65 (dd, J = 9.4, 3.5 Hz, 1H), 4.05 – 3.88 (m, 2H), 2.94 (dd, J = 14.2, 9.5 Hz, 1H), 2.19 (dd, J = 14.2, 3.5 Hz, 1H), 1.27 (s, 3H), 1.19 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 176.7, 170.8, 138.6, 136.0, 134.2, 128.9, 127.7, 127.6, 126.8, 124.2, 120.0, 116.4, 61.0, 44.7, 42.3, 25.9, 25.1, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{25}NO_4SNa$ $[M + Na]^+$ 496.1553, found 496.1557

Ethyl 2-(benzoylthio)-2-methylpropanoate (1′)



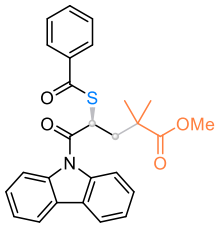
1′

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.87 (m, 2H), 7.59 – 7.53 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.69 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 174.0, 136.7, 133.6, 128.7, 127.2, 61.8, 51.2, 26.2, 14.1.

HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{17}O_3S$ $[M + H]^+$ 253.0893, found 253.0892

Methyl *(S)*-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate (2)



2

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with methyl 2-bromo-2-methylpropanoate (51.7 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **2** as a colorless oil (75 mg, 82% yield, 92% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 20.55 min, t_R (major) = 25.32 min.

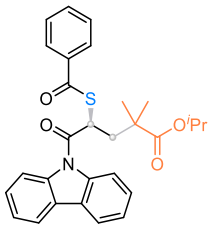
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^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 – 8.04 (m, 2H), 8.02 – 7.94 (m, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.40 (t, J = 7.4 Hz, 2H), 5.65 (dd, J = 9.5, 3.4 Hz, 1H), 3.45 (s, 3H), 2.95 (dd, J = 14.2, 9.5 Hz, 1H), 2.14 (dd, J = 14.2, 3.4 Hz, 1H), 1.29 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 177.0, 170.7, 138.6, 136.0, 134.3, 129.0, 127.8, 127.6, 126.8, 124.2, 120.0, 116.5, 52.1, 44.8, 44.6, 42.3, 25.7, 25.3.

HRMS (ESI) m/z calcd. for $C_{27}H_{25}NO_4SNa$ $[M + Na]^+$ 482.1397, found 482.1392

Isopropyl *(S)*-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate (3)



3

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with isopropyl 2-bromo-2-methylpropanoate (59.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **3** as a colorless oil (67.2 mg, 69% yield, 94% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.81 min, t_R (major) = 13.77 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 – 8.05 (m, 2H), 7.98 (dd, J = 14.3, 7.8 Hz, 4H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (dt, J = 14.6, 7.7 Hz, 4H), 7.39 (t, J = 7.5 Hz, 2H), 5.65 (dd, J = 9.3, 3.7 Hz, 1H), 4.94 – 4.82 (m, 1H), 2.89 (dd, J = 14.2, 9.3 Hz, 1H), 2.23 (dd, J = 14.2, 3.7 Hz, 1H), 1.22 (s, 3H), 1.16 (d, J = 5.3 Hz, 6H), 1.12 (d, J = 6.3 Hz, 3H).

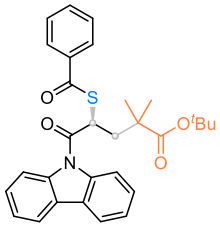
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 176.3, 171.0, 138.7, 136.1, 134.2, 128.9, 127.7, 127.6, 126.8, 124.2, 120.0, 116.5, 68.4, 44.8, 44.3, 42.3, 26.2, 24.8, 21.7(3), 21.6(6).

HRMS (ESI) m/z calcd. for $C_{29}H_{29}NO_4SNa$ $[M + Na]^+$ 510.1710, found 510.1705.

***tert*-Butyl *(S)*-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate**

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(4)



4

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with tert-butyl 2-bromo-2-methylpropanoate (68.8 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **4** as a colorless oil (60.1 mg, 60% yield, 92% ee).

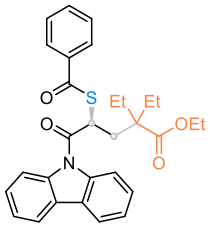
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.18 min, t_R (major) = 16.96 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 – 8.06 (m, 2H), 7.98 (dd, J = 14.0, 7.5 Hz, 4H), 7.59 (t, J = 7.4 Hz, 1H), 7.51 -7.42 (m, 4H), 7.39 (t, J = 7.4 Hz, 2H), 5.63 (dd, J = 9.3, 4.0 Hz, 1H), 2.82 (dd, J = 14.2, 9.3 Hz, 1H), 2.25 (dd, J = 14.2, 4.0 Hz, 1H), 1.36 (s, 9H), 1.18 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 176.1, 171.3, 138.7, 136.1, 134.1, 128.9, 127.7(0), 127.6(6), 126.8, 124.2, 120.0, 116.5, 80.8, 44.9, 44.1, 43.0, 27.9, 26.7, 24.7.

HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{31}NO_4SNa$ $[M + Na]^+$ 524.1866, found 524.1865

Ethyl *(S)*-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-diethyl-5-oxopentanoate (5)



5

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-ethylbutanoate (77.8 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA =

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10/1), which afforded the product **5** as a colorless oil (70.1 mg, 70% yield, 92% ee).

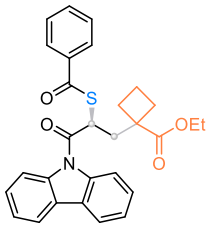
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.38 min, t_R (minor) = 14.45 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 – 8.06 (m, 2H), 8.02 – 7.94 (m, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.39 (t, J = 7.5 Hz, 2H), 5.63 (dd, J = 9.4, 3.6 Hz, 1H), 4.03 – 3.86 (m, 2H), 2.91 (dd, J = 14.5, 9.4 Hz, 1H), 2.15 (dd, J = 14.5, 3.6 Hz, 1H), 1.73 -1.45 (m, 4H), 1.05 (t, J = 7.1 Hz, 3H), 0.80 (t, J = 7.4 Hz, 3H), 0.75 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 175.8, 170.8, 138.7, 136.0, 134.1, 128.8, 127.6(1), 127.5(6), 126.7, 124.2, 119.8, 116.4, 60.6, 49.5, 44.2, 39.6, 26.8, 26.2, 13.9, 8.2(3), 8.1(9).

HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{31}NO_4SNa$ $[M + Na]^+$ 524.1866, found 524.1861

Ethyl *(S)*-1-(2-(benzoylthio)-3-(9*H*-carbazol-9-yl)-3-oxopropyl)cyclobutane-1-carboxylate (6)



6

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 1-bromocyclobutane-1-carboxylate (64, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1) which afforded the product **6** as a colorless oil (70 mg, 67% yield, 92% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 23.51 min, t_R (major) = 25.69 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 – 8.06 (m, 2H), 8.02 – 7.91 (m, 4H), 7.62 – 7.55 (m, 1H), 7.51 – 7.42 (m, 4H), 7.39 (t, J = 7.4 Hz, 2H), 5.63 (dd, J = 8.8, 4.9 Hz, 1H), 3.89 (qt, J = 7.2, 3.7 Hz, 2H), 3.02 (dd, J = 14.1, 8.9 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.35 – 2.23 (m, 2H), 2.05 – 1.79 (m, 3H), 1.01 (t, J = 7.1 Hz, 3H).

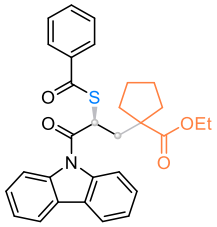
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 176.2, 171.0, 138.7, 136.1, 134.2, 128.9, 127.6(two carbons overlapped), 126.8, 124.2, 119.9, 116.5, 61.0, 47.4, 45.0, 41.9, 31.3,

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30.9, 16.1, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{27}NO_4SNa$ $[M + Na]^+$ 508.1553, found 508.1551

Ethyl *(S)*-1-(2-(benzoylthio)-3-(9*H*-carbazol-9-yl)-3-oxopropyl)cyclopentane-1-carboxylate (7)



7

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 1-bromocyclopentane-1-carboxylate (63 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **7** as a colorless oil (32 mg, 32% yield, 92% ee).

HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.85 min, t_R (minor) = 15.80 min.

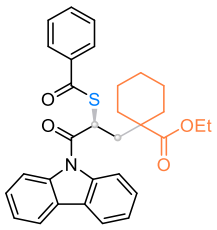
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 – 8.04 (m, 2H), 7.99 (ddd, J = 7.6, 1.4, 0.7 Hz, 2H), 7.97 – 7.92 (m, 2H), 7.59 (ddt, J = 8.7, 7.2, 1.3 Hz, 1H), 7.51 – 7.43 (m, 4H), 7.39 (td, J = 7.5, 0.9 Hz, 2H), 5.64 (dd, J = 9.3, 3.9 Hz, 1H), 3.93 – 3.82 (m, 2H), 2.97 (dd, J = 14.2, 9.3 Hz, 1H), 2.28 – 2.19 (m, 2H), 2.11 – 2.04 (m, 1H), 1.75 (ddd, J = 13.0, 8.7, 7.4 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.56 – 1.42 (m, 3H), 0.99 (t, J = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 190.0, 176.5, 170.7, 138.8, 136.1, 134.2, 129.0, 127.7(0), 127.6(7), 126.8, 124.2, 120.0, 116.6, 61.0, 54.3, 45.5, 43.0, 36.6, 36.0, 24.5, 24.3, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{29}NO_4SNa$ $[M + Na]^+$ 522.1710, found 522.1706

Ethyl (*S*)-1-(2-(benzoylthio)-3-(9*H*-carbazol-9-yl)-3-oxopropyl)cyclohexane-1-carboxylate (8)

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8

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 1-bromocyclohexane-1-carboxylate (68 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **8** as a colorless solid (67.8 mg, 66% yield, 90% ee).

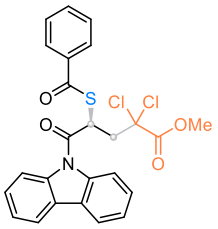
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.99 min, t_R (minor) = 12.23 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 – 8.01 (m, 2H), 8.01 – 7.92 (m, 4H), 7.63 – 7.56 (m, 1H), 7.49- 7.42 (m, 4H), 7.39 (t, J = 7.5 Hz, 2H), 5.60 (dd, J = 10.1, 2.6 Hz, 1H), 4.07 – 3.85 (m, 2H), 2.97 (dd, J = 14.1, 10.1 Hz, 1H), 2.32 (d, J = 12.6 Hz, 1H), 2.08 – 1.95 (m, 2H), 1.67 – 1.59 (m, 1H), 1.51 (d, J = 8.3 Hz, 2H), 1.41 – 1.31 (m, 1H), 1.20 (d, J = 8.9 Hz, 4H), 1.02 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 175.4, 170.3, 138.5, 136.1, 134.2, 129.0, 127.8, 127.6, 126.8, 124.2, 119.9, 116.7, 60.8, 47.1, 45.2, 43.8, 34.8, 34.3, 25.7, 23.5, 23.4, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{31}H_{31}NO_4SNa$ $[M + Na]^+$ 536.1866, found 536.1864

Methyl (*S*)-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-dichloro-5-oxopentanoate (9)



9

According to **General procedure A**, potassium benzothioate (42.2 mg, 0.24 mmol, 1.2 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (44.2 mg, 0.2 mmol, 1.0 equiv) with ethyl 2-bromo-2,2-dichloroacetate (35.4 μL, 0.3 mmol, 1.5 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **9** as a colorless oil (18 mg, 20% yield, 89% ee).

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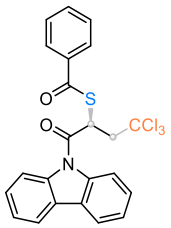
HPLC analysis: Chiralcel IH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.42 min, t_R (major) = 11.64 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 – 8.02 (m, 2H), 8.02 – 7.92 (m, 4H), 7.65 – 7.58 (m, 1H), 7.53 – 7.37 (m, 6H), 5.97 (dd, J = 9.7, 2.5 Hz, 1H), 3.97 (dd, J = 14.8, 9.7 Hz, 1H), 3.81 (s, 3H), 3.05 (dd, J = 14.9, 2.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 169.3, 165.9, 135.5, 134.5, 129.0, 127.7, 127.6, 126.8, 124.3, 119.9, 82.0, 54.8, 48.9, 43.9.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{19}Cl_2NO_4SNa$ $[M + Na]^+$ 522.0304, found 522.0302

(S)-S-(1-(9*H*-Carbazol-9-yl)-4,4,4-trichloro-1-oxobutan-2-yl) benzothioate (10)



10

According to **General procedure A**, potassium benzothioate (42.2 mg, 0.24 mmol, 1.2 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (44.2 mg, 0.2 mmol, 1.0 equiv) with carbon tetrachloride (29 μL, 0.3 mmol, 1.5 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **10** as a colorless oil (63.6 mg, 63% yield, 91% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.70 min, t_R (minor) = 13.66 min.

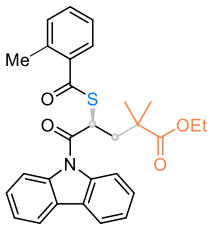
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (s, 2H), 8.00 – 7.92 (m, 4H), 7.62 (t, J = 7.5 Hz, 1H), 7.48 (q, J = 7.2 Hz, 4H), 7.40 (t, J = 7.5 Hz, 2H), 6.01 (dd, J = 10.1, 1.9 Hz, 1H), 4.30 (dd, J = 14.8, 10.1 Hz, 1H), 3.27 (dd, J = 14.8, 1.9 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 188.9, 169.0, 138.7, 135.6, 134.7, 129.1, 127.9, 127.8, 126.9, 124.5, 120.1, 116.2, 96.5, 58.3, 44.5.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{16}Cl_3NO_2SNa$ $[M + Na]^+$ 497.9860, found 497.9858

Ethyl (*S*)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-((2-methylbenzoyl)thio)-5-oxopentanoate (11)

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11

According to **General procedure A**, potassium 2-methylbenzothioate (38.0 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **11** as a colorless oil (72.3 mg, 74% yield, 83% ee).

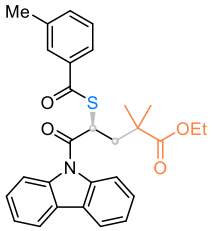
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.99 min, t_R (major) = 23.08 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 2H), 8.03 – 7.95 (m, 2H), 7.71 (dd, J = 7.8, 1.4 Hz, 1H), 7.48 (ddd, J = 8.6, 7.3, 1.4 Hz, 2H), 7.39 (tt, J = 7.5, 1.3 Hz, 3H), 7.25 – 7.19 (m, 2H), 5.57 (dd, J = 9.6, 3.4 Hz, 1H), 3.98 (ddq, J = 37.4, 10.8, 7.1 Hz, 2H), 2.98 (dd, J = 14.2, 9.6 Hz, 1H), 2.49 (s, 3H), 2.15 (dd, J = 14.2, 3.4 Hz, 1H), 1.28 (s, 3H), 1.20 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 176.8, 170.7, 138.8, 137.3, 136.4, 132.4, 131.9, 128.7, 127.7, 126.8, 126.1, 124.2, 120.0, 116.5, 61.0, 45.3, 44.7, 42.3, 25.9, 25.2, 20.7, 14.0.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{29}NO_4SNa$ $[M + Na]^+$ 510.1708, found 510.1710.

Ethyl *(S)*-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-((3-methylbenzoyl)thio)-5-oxopentanoate (12)



12

According to **General procedure A**, potassium 3-methylbenzothioate (38.0 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel

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(PE/EA = 10/1), which afforded the product **12** as a colorless oil (72.3 mg, 74% yield, 89% ee).

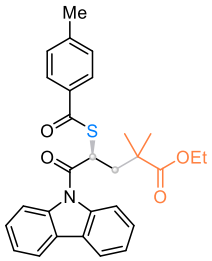
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 15.38 min, t_R (major) = 18.81 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 – 8.04 (m, 2H), 7.99 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.5 Hz, 3H), 7.33 (t, J = 7.5 Hz, 1H), 5.63 (dd, J = 9.5, 3.5 Hz, 1H), 4.03 – 3.86 (m, 2H), 2.93 (dd, J = 14.2, 9.5 Hz, 1H), 2.38 (s, 3H), 2.16 (dd, J = 14.2, 3.5 Hz, 1H), 1.26 (s, 3H), 1.18 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 176.7, 170.8, 138.9, 136.1, 135.0, 128.8, 128.1, 127.7, 126.8, 124.9, 124.2, 120.0, 116.5, 61.0, 44.7, 44.6, 42.3, 25.9, 25.1, 21.4, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{29}NO_4SNa$ $[M + Na]^+$ 510.1710, found 510.1710.

Ethyl *(S)*-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-((4-methylbenzoyl)thio)-5-oxopentanoate (13)



13

According to **General procedure A**, potassium 4-methylbenzothioate (38.0 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **13** as a colorless oil (68.2 mg, 70% yield, 93% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.58 min, t_R (major) = 22.09 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.25 – 7.21 (m, 2H), 5.62 (dd, J = 9.5, 3.5 Hz, 1H), 4.03 – 3.86 (m, 2H), 2.92 (dd, J = 14.2, 9.5 Hz, 1H), 2.39 (s, 3H), 2.16 (dd, J = 14.2, 3.5 Hz, 1H), 1.26 (s, 3H), 1.18 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H).

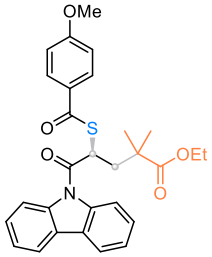
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 176.7, 170.9, 145.3, 138.6, 133.5, 129.6,

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127.7(two carbons overlapped), 126.8, 124.2, 119.9, 116.5, 61.0, 44.7, 44.5, 42.3, 25.8, 25.1, 21.8, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{29}NO_4SNa$ $[M + Na]^+$ 510.1710, found 510.1710.

Ethyl *(S)*-5-(9*H*-carbazol-9-yl)-4-((4-methoxybenzoyl)thio)-2,2-dimethyl-5-oxopentanoate (14)



14

According to **General procedure A**, potassium 4-methoxybenzothioate (41.2 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **14** as a colorless oil (40.2 mg, 40% yield, 91% ee).

HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 21.35 min, t_R (minor) = 29.00 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 – 8.03 (m, 2H), 7.99 (d, J = 7.5 Hz, 2H), 7.96 – 7.90 (m, 2H), 7.51 – 7.44 (m, 2H), 7.39 (t, J = 7.5 Hz, 2H), 6.96 – 6.89 (m, 2H), 5.60 (dd, J = 9.5, 3.5 Hz, 1H), 4.03 – 3.87 (m, 2H), 3.85 (s, 3H), 2.91 (dd, J = 14.2, 9.5 Hz, 1H), 2.16 (dd, J = 14.2, 3.5 Hz, 1H), 1.25 (s, 3H), 1.17 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H).

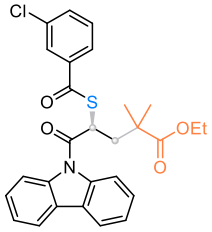
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.2, 176.8, 171.0, 164.4, 138.7, 129.9, 128.9, 127.8, 126.8, 124.2, 119.9, 116.6, 114.1, 61.0, 55.7, 44.8, 44.5, 42.3, 25.8, 25.1, 13.9.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{29}NO_5SNa$ $[M + Na]^+$ 526.1659, found 526.1656.

Ethyl *(S)*-5-(9*H*-carbazol-9-yl)-4-((3-chlorobenzoyl)thio)-2,2-dimethyl-5-

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oxopentanoate (15)



15

According to **General procedure A**, potassium 3-chlorobenzothioate (42.0 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **15** as a colorless oil (45.6 mg, 45% yield, 88% ee).

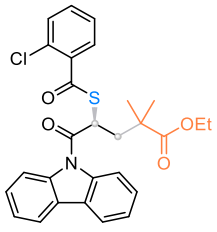
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 22.13 min, t_R (major) = 27.73 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 – 8.05 (m, 2H), 8.02 – 7.97 (m, 2H), 7.93 (t, J = 1.8 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.55 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.48 (td, J = 8.5, 8.0, 1.4 Hz, 2H), 7.42 – 7.36 (m, 3H), 5.66 (dd, J = 9.3, 3.7 Hz, 1H), 4.03 – 3.88 (m, 2H), 2.90 (dd, J = 14.2, 9.3 Hz, 1H), 2.17 (dd, J = 14.2, 3.7 Hz, 1H), 1.26 (s, 3H), 1.17 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 176.6, 170.6, 138.6, 137.5, 135.3, 134.1, 130.2, 127.8, 127.6, 126.8, 125.8, 124.3, 120.0, 116.4, 61.0, 44.9, 44.5, 42.3, 26.0, 25.0, 14.0.

HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{26}ClNO_4SNa$ $[M + Na]^+$ 530.1162, found 530.1163.

Ethyl *(S)*-5-(9*H*-carbazol-9-yl)-4-((2-chlorobenzoyl)thio)-2,2-dimethyl-5-oxopentanoate (16)



16

According to **General procedure A**, potassium 2-chlorobenzothioate (42.0 mg, 0.2 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel

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(PE/EA = 101), which afforded the product **16** as a colorless oil (66.0 mg, 65% yield, 87% ee).

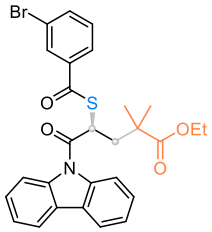
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.57 min, t_R (minor) = 11.39 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 – 8.03 (m, 2H), 8.02 – 7.97 (m, 2H), 7.61 (dd, J = 7.7, 1.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.37 (m, 4H), 7.29 (td, J = 7.4, 1.6 Hz, 1H), 5.61 (dd, J = 9.7, 3.3 Hz, 1H), 3.97 (ddq, J = 40.8, 10.7, 7.1 Hz, 2H), 3.00 (dd, J = 14.1, 9.7 Hz, 1H), 2.17 (dd, J = 14.2, 3.3 Hz, 1H), 1.28 (s, 3H), 1.20 (s, 3H), 1.06 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 176.7, 170.2, 138.7, 136.3, 133.0, 131.1(3), 131.1(1), 129.4, 127.8, 127.0, 126.8, 124.3, 120.0, 116.5, 61.0, 45.7, 44.6, 42.3, 25.8, 25.2, 13.9.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{26}ClNO_4SNa$ $[M + Na]^+$ 530.1163, found 530.1163.

Ethyl *(S)*-4-((3-bromobenzoyl)thio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate (17)



17

According to **General procedure A**, potassium 3-bromobenzothioate (47.7 mg, 0.2 mmol, 1.0 equiv), 1-(9H-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **17** as a colorless oil (49.6 mg, 45% yield, 98% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 23.29 min, t_R (major) = 28.55 min.

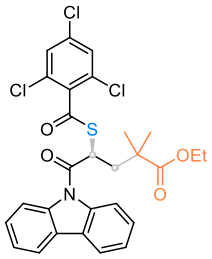
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 – 8.10 (m, 2H), 8.08 (t, J = 1.7 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.9 Hz, 1H), 5.66 (dd, J = 9.3, 3.7 Hz, 1H), 4.03 – 3.88 (m, 2H), 2.90 (dd, J = 14.2, 9.3 Hz, 1H), 2.17 (dd, J = 14.3, 3.7 Hz, 1H), 1.26 (s, 3H), 1.17 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H).

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^{13}C NMR (100 MHz, $CDCl_3$): δ 188.7, 176.6, 170.5, 138.6, 137.6, 137.0, 130.4(8), 130.4(6), 127.8, 126.8, 126.2, 124.3, 123.2, 120.0, 116.4, 61.0, 44.9, 44.5, 42.3, 26.0, 25.0, 14.0.

HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{26}BrNO_4SNa$ $[M + Na]^+$ 574.0658, found 574.0658.

Ethyl *(S)*-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxo-4-((2,4,6-trichlorobenzoyl)thio)pentanoate (18)



18

According to **General procedure A**, potassium 2,4,6-trichlorobenzothioate (55.6 mg, 0.2 mmol, 1.0 equiv), 1-(9H-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **18** as a colorless oil (73.6 mg, 64% yield, 85% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 20.15 min, t_R (major) = 27.14 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 - 7.55 (m, 4H), 7.53 – 7.44 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (s, 2H), 5.67 (dd, J = 10.0, 2.8 Hz, 1H), 4.08 – 3.89 (m, 2H), 3.06 (dd, J = 14.2, 10.0 Hz, 1H), 2.21 (dd, J = 14.2, 2.8 Hz, 1H), 1.29 (s, 3H), 1.18 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H).

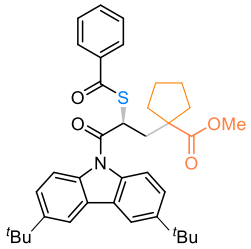
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.7, 176.6, 169.6, 137.2, 135.0, 132.6(two carbons overlappeded), 128.6(two carbons overlapped), 127.7, 126.8, 124.4, 120.0, 61.1, 45.5, 44.2, 42.4, 25.8, 25.1, 14.0.

HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{24}Cl_3NO_4SNa$ $[M + Na]^+$ 598.0384, found 598.0381.

Methyl (*S*)-4-((3-bromobenzoyl)thio)-5-(3,6-di-tert-butyl-9*H*-carbazol-9-yl)-2,2-

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dimethyl-5-oxopentanoate (19)



19

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(3,3-dimethylindolin-1-yl)prop-2-en-1-one (80.4 mg, 0.4 mmol, 2.0 equiv) with methyl 1-bromocyclopentane-1-carboxylate (59.0 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **19** as a colorless oil (65.1 mg, 70% yield, 89% ee).

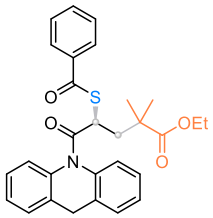
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 4.24 min, t_R (minor) = 4.64 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J = 8.2, 1.7 Hz, 5H), 7.62 – 7.56 (m, 1H), 7.54 – 7.38 (m, 5H), 5.61 (dd, J = 9.6, 3.5 Hz, 1H), 3.39 (s, 3H), 3.02 (dd, J = 14.0, 9.5 Hz, 1H), 2.30 – 2.15 (m, 2H), 2.15 – 2.07 (m, 1H), 1.85-1.76 (m, 1H), 1.72 – 1.53 (m, 5H), 1.43 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 176.9, 170.1, 147.2, 138.2, 136.2, 134.2, 128.9, 127.7, 125.2, 123.6, 116.3, 110.1, 54.3, 52.1, 45.2, 43.0, 36.3, 36.0, 34.9, 32.2, 31.8, 24.4, 24.3.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}BrNO_4SNa$ $[M + Na]^+$ 586.0658, found 586.0655

Ethyl *(S)*-5-(acridin-10(9*H*)-yl)-4-(benzoylthio)-2,2-dimethyl-5-oxopentanoate (20)



20

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(acridin-10(9H)-yl)prop-2-en-1-one (94.0 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 101), which afforded the product **20** as a colorless oil (48.7 mg, 50% yield,

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86% ee).

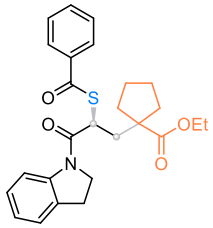
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.45 min, t_R (major) = 9.36 min.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 – 7.51 (m, 5H), 7.44 (t, J = 7.3 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.13 (m, 3H), 5.18 (dd, J = 9.4, 4.6 Hz, 1H), 4.21 – 3.59 (m, 4H), 2.78 – 2.41 (m, 1H), 2.01 (dd, J = 14.2, 4.6 Hz, 1H), 1.28 – 1.08 (m, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.1, 177.0, 169.7, 138.9, 136.4, 135.1, 133.8, 128.8, 127.4(two carbons overlapped), 126.5, 125.3, 60.9, 44.1, 42.2, 34.1, 29.8, 26.2, 14.1.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{29}NO_4SNa$ $[M + Na]^+$ 510.1710, found 510.1712.

Ethyl *(S)*-1-(2-(benzoylthio)-3-(indolin-1-yl)-3-oxopropyl)cyclopentane-1-carboxylate (21)



21

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(indolin-1-yl)prop-2-en-1-one (69.2 mg, 0.4 mmol, 2.0 equiv) with ethyl 1-bromocyclopentane-1-carboxylate (62.2 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **21** as a colorless oil (64.0 mg, 71% yield, 88% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.97 min, t_R (major) = 9.25 min.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.24 (d, J = 8.0 Hz, 1H), 7.94 (dd, J = 8.2, 1.4 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.19 (t, J = 8.5 Hz, 2H), 7.03 (td, J = 7.4, 1.0 Hz, 1H), 4.73 (dd, J = 9.7, 3.7 Hz, 1H), 4.31 (td, J = 10.3, 6.9 Hz, 1H), 4.22 (td, J = 10.3, 6.3 Hz, 1H), 4.11 (qd, J = 7.2, 2.1 Hz, 2H), 3.30 – 3.13 (m, 2H), 2.84 (dd, J = 14.0, 9.7 Hz, 1H), 2.30 – 2.24 (m, 1H), 2.15 (ddd, J = 21.0, 13.2, 5.5 Hz, 2H), 1.73 – 1.59 (m, 5H), 1.50 (dt, J = 12.8, 7.4 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H).

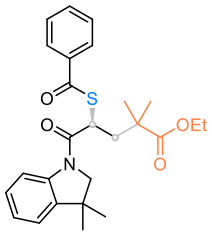
^{13}C NMR (150 MHz, $CDCl_3$): δ 190.3, 177.1, 168.7, 143.0, 136.3, 134.0, 132.1, 128.9, 127.6(3), 127.5(6), 124.8, 124.3, 117.5, 61.1, 54.5, 48.1, 43.2, 42.6, 36.8, 35.6, 28.1,

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24.7, 24.4, 14.2.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{27}NO_4SNa$ $[M + Na]^+$ 460.1553, found 460.1552.

Ethyl *(S)*-4-(benzoylthio)-5-(3,3-dimethylindolin-1-yl)-2,2-dimethyl-5-oxopentanoate (22)



22

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(3,3-dimethylindolin-1-yl)prop-2-en-1-one (80.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (55.6 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **22** as a colorless oil (74.3 mg, 82% yield, 92% ee).

HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.84 min, t_R (minor) = 16.65 min.

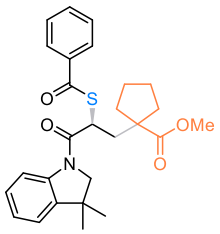
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.18 (m, 1H), 7.98 – 7.91 (m, 2H), 7.63 – 7.56 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.21 (ddd, J = 8.3, 7.2, 1.5 Hz, 1H), 7.14 (dd, J = 7.5, 1.5 Hz, 1H), 7.07 (td, J = 7.4, 1.1 Hz, 1H), 4.76 (dd, J = 9.7, 3.5 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 4.04 – 3.91 (m, 2H), 2.79 (dd, J = 14.1, 9.7 Hz, 1H), 2.02 (dd, J = 14.1, 3.5 Hz, 1H), 1.41 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.26 (d, J = 7.1 Hz, 3H), 1.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 177.0, 168.6, 141.6, 141.4, 136.2, 134.0, 128.9, 127.8, 127.5, 124.6, 120.0, 117.5, 62.6, 61.0, 44.1, 42.4, 42.3, 40.4, 28.6, 28.5, 26.1, 24.9, 14.2.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{29}NO_4SNa$ $[M + Na]^+$ 476.1866, found 476.1863.

Methyl *(S)*-1-(2-(benzoylthio)-3-(3,3-dimethylindolin-1-yl)-3-oxopropyl)cyclopentane-1-carboxylate (23)

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23

According to **General procedure A**, potassium benzothioate (35.2 mg, 0.2 mmol, 1.0 equiv), 1-(3,3-dimethylindolin-1-yl)prop-2-en-1-one (80.4 mg, 0.4 mmol, 2.0 equiv) with ethyl 2-bromo-2-methylpropanoate (59.0 μL, 0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **23** as a colorless oil (65.1 mg, 70% yield, 90% ee).

HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.65 min, t_R (minor) = 17.27 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.1 Hz, 1H), 7.98 – 7.89 (m, 2H), 7.64 – 7.56 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.21 (ddd, J = 8.2, 7.3, 1.5 Hz, 1H), 7.14 (dd, J = 7.5, 1.4 Hz, 1H), 7.07 (td, J = 7.4, 1.1 Hz, 1H), 4.70 (dd, J = 9.9, 3.4 Hz, 1H), 4.01 (d, J = 10.0 Hz, 1H), 3.91 (d, J = 10.0 Hz, 1H), 3.66 (s, 3H), 2.87 (dd, J = 14.0, 9.9 Hz, 1H), 2.36 – 2.23 (m, 1H), 2.18 (dt, J = 11.7, 5.9 Hz, 1H), 2.07 (dd, J = 14.0, 3.4 Hz, 1H), 1.78 – 1.61 (m, 4H), 1.58 – 1.45 (m, 2H), 1.42 (s, 3H), 1.30 (s, 3H).

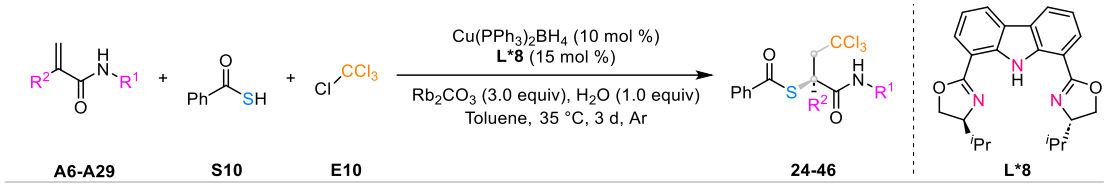
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 177.4, 168.5, 141.7, 141.5, 136.3, 134.1, 128.9, 127.8, 127.6, 124.6, 122.0, 117.5, 62.6, 54.5, 52.3, 43.1, 42.6, 40.4, 36.5, 35.6, 28.7, 28.6, 24.6, 24.4.

HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{31}NO_4SNa$ $[M + Na]^+$ 488.1886, found 488.1885.

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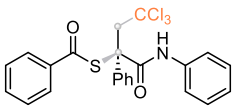
7. Copper-catalyzed chemo- and enantioselective 1,2-carbosulfidation of phenyl-substituted acrylamides

General procedure B



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene (0.20 mmol, 1.0 equiv), benzothioic S-acid (0.30 mmol, 1.5 equiv), $Cu(PPh_3)_2BH_4$ (12.0 mg, 0.02 mmol, 10 mol %), **L*8** (11.67 mg, 0.03 mmol, 15 mol %) and Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), Then, H_2O (3.6 μL, 0.20 mmol, 1.0 equiv) and Toluene (4.0 mL) was added by syringe under argon atmosphere. Finally, perchloromethane (1.0 mmol, 5.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(R)-S-(4,4,4-Trichloro-1-oxo-2-phenyl-1-(phenylamino)butan-2-yl) benzothioate (24)



24

According to **General procedure B**, *N*,2-diphenylacrylamide (44.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **24** as a colorless solid (85.9 mg, 90% yield, 91% ee).

HPLC analysis: Chiralcel ADH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 27.60 min, t_R (major) = 33.09 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.68 – 7.61 (m, 3H), 7.49 (t, J = 7.7 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.28 (d, J = 7.7 Hz, 2H), 7.07 (t, J =

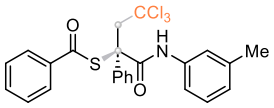
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7.4 Hz, 1H), 4.32 (d, J = 16.3 Hz, 1H), 4.19 (d, J = 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 168.8, 137.7, 136.4, 136.0, 134.5, 129.1, 129.0, 128.9, 127.8, 127.7, 124.7, 120.3, 96.8, 62.8, 57.1.

HRMS (ESI) m/z calcd. for $C_{23}H_{18}Cl_3NO_2SNa$ $[M + Na]^+$ 500.0016, found 500.0013.

***(R)-S*-(4,4,4-Trichloro-1-oxo-2-phenyl-1-(*m*-tolylamino)butan-2-yl) benzothioate (25)**



25

According to **General procedure B**, 2-phenyl-*N*-(*m*-tolyl)acrylamide (47.4 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **25** as a colorless oil (58.9 mg, 60% yield, 86% ee).

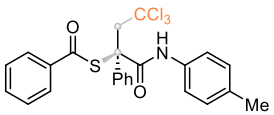
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.91 min, t_R (major) = 8.89 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.08 – 8.01 (m, 2H), 7.67 (dd, J = 11.3, 7.4 Hz, 3H), 7.52 (t, J = 7.8 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.31 (s, 1H), 7.18 (d, J = 5.7 Hz, 2H), 6.97 – 6.88 (m, 1H), 4.35 (d, J = 16.3 Hz, 1H), 4.22 (d, J = 16.3 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 168.8, 139.1, 137.6, 136.4, 134.5, 129.1, 129.1(0), 129.0(6), 128.9, 127.8, 127.7, 125.5, 120.8, 117.2, 96.8, 62.8, 57.1, 21.6.

HRMS (ESI) m/z calcd. for $C_{24}H_{20}Cl_3NO_2SNa$ $[M + Na]^+$ 514.0173, found 514.0174.

***(R)-S*-(4,4,4-Trichloro-1-oxo-2-phenyl-1-(*p*-tolylamino)butan-2-yl) benzothioate (26)**



26

According to **General procedure B**, 2-phenyl-*N*-(*p*-tolyl)acrylamide (47.4 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1),

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which afforded the product **26** as a colorless oil (78.6 mg, 80% yield, 87% ee).

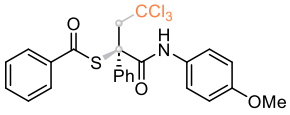
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.78 min, t_R (major) = 12.49 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.05 – 7.98 (m, 2H), 7.70 – 7.60 (m, 3H), 7.49 (t, J = 7.8 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.27 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 4.38 – 4.16 (m, 2H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 168.8, 136.4, 136.2, 135.1, 134.4(9), 134.4(7), 129.6, 129.1, 129.0, 128.9, 127.8, 127.7, 120.5, 96.8, 62.7, 57.2, 21.0.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{20}Cl_3NO_2SNa$ $[M + Na]^+$ 514.0173, found 514.0172.

(R)-S-(4,4,4-Trichloro-1-((4-methoxyphenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (27)



27

According to **General procedure B**, *N*-(4-methoxyphenyl)-2-phenylacrylamide (50.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **27** as a colorless oil (59.8 mg, 59% yield, 89% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.16 min, t_R (major) = 14.60 min.

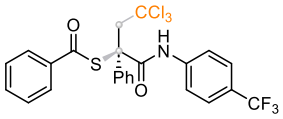
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 8.09 – 8.00 (m, 2H), 7.72 – 7.63 (m, 3H), 7.52 (t, J = 7.8 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.30 (d, J = 9.1 Hz, 2H), 6.86 – 6.80 (m, 2H), 4.35 (d, J = 16.3 Hz, 1H), 4.22 (d, J = 16.3 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 168.8, 156.9, 136.5, 136.2, 134.5, 130.7, 129.1, 129.0, 128.9, 127.8, 127.7, 122.3, 114.2, 96.9, 62.6, 57.1, 55.6.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{20}Cl_3NO_3SNa$ $[M + Na]^+$ 530.0122, found 530.0118.

(R)-S-(4,4,4-Trichloro-1-oxo-2-phenyl-1-((4-(trifluoromethyl)phenyl)amino)butan-2-yl) benzothioate (28)

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28

According to **General procedure B**, 2-phenyl-*N*-(4-(trifluoromethyl)phenyl)acrylamide (50.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **28** as a yellow oil (60.0 mg, 55% yield, 84% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.32 min, t_R (major) = 18.89 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.06 – 7.98 (m, 2H), 7.69 – 7.61 (m, 3H), 7.59 – 7.46 (m, 6H), 7.44 – 7.33 (m, 3H), 4.29 (d, J = 16.3 Hz, 1H), 4.14 (d, J = 16.3 Hz, 1H).

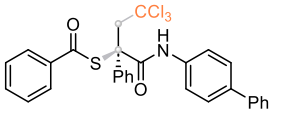
^{13}C NMR (150 MHz, $CDCl_3$): δ 189.7, 169.2, 140.8, 136.2, 135.4, 134.8, 129.1(9), 129.1(7), 129.1(5), 128.4(q, J = 79.7 Hz), 127.9, 127.8, 126.7, 126.4 (q, J = 3.9 Hz), 124.1(q, J = 271.6 Hz), 119.8, 96.6, 62.9, 57.2.

126.37 (q, J = 3.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ –62.20.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{17}Cl_3F_3NO_2SNa$ $[M + Na]^+$ 567.9890, found 567.9889.

***(R)-S*-(1-([1,1'-Biphenyl]-4-ylamino)-4,4,4-trichloro-1-oxo-2-phenylbutan-2-yl) benzothioate (29)**



29

According to **General procedure B**, *N*-([1,1'-biphenyl]-4-yl)-2-phenylacrylamide (59.8 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **29** as a colorless oil (55.3 mg, 50% yield, 87% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.81 min, t_R (major) = 26.78 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.06 (d, J = 7.8 Hz, 2H), 7.74 – 7.64 (m,

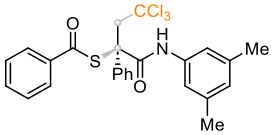
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3H), 7.53 (q, J = 7.4 Hz, 8H), 7.46 – 7.37 (m, 5H), 7.34 (t, J = 7.3 Hz, 1H), 4.37 (d, J = 16.3 Hz, 1H), 4.23 (d, J = 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 168.9, 140.6, 137.7, 137.0, 136.4, 136.0, 134.6, 129.1(2), 129.0(6), 129.0, 128.9, 127.8, 127.7(8), 127.7(6), 127.3, 127.0, 120.5, 96.8, 62.8, 57.1.

HRMS (ESI) m/z calcd. for $C_{29}H_{22}Cl_3NO_2SNa$ $[M + Na]^+$ 576.0329, found 576.0327.

(R)-S-(4,4,4-Trichloro-1-((3,5-dimethylphenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (30)



30

According to **General procedure B**, *N*-(3,5-dimethylphenyl)-2-phenylacrylamide (50.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **30** as a colorless oil (62.6 mg, 50% yield, 88% ee).

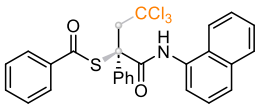
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.83 min, t_R (major) = 10.47 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.02 (d, J = 7.7 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.41 – 7.33 (m, 3H), 7.05 (s, 2H), 6.72 (s, 1H), 4.32 (d, J = 16.3 Hz, 1H), 4.20 (d, J = 16.3 Hz, 1H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 168.7, 138.9, 137.6, 134.5, 132.4, 131.7, 129.1, 129.0, 127.8, 127.7, 126.4, 117.8, 96.8, 62.7, 57.0, 21.4.

HRMS (ESI) m/z calcd. for $C_{25}H_{22}Cl_3NO_2SNa$ $[M + Na]^+$ 528.0329, found 528.0328.

(R)-S-(4,4,4-Trichloro-1-(naphthalen-1-ylamino)-1-oxo-2-phenylbutan-2-yl) benzothioate (31)



31

According to **General procedure B**, 2-(3,5-di-tert-butylphenyl)-*N*-phenylacrylamide (67.0 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The

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reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **31** as a colorless oil (50.6 mg, 48% yield, 85% ee).

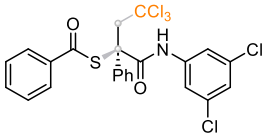
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 4.61 min, t_R (minor) = 5.04 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.11 – 8.04 (m, 2H), 7.82 – 7.74 (m, 4H), 7.66 (t, J = 7.5 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.38 (m, 5H), 7.33 – 7.23 (m, 2H), 4.43 – 4.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 169.6, 136.8, 136.5, 134.6, 134.1, 132.1, 129.1(9), 129.1(6), 129.0, 128.7, 127.8(7), 127.8(4), 127.5, 126.4, 126.2, 126.0, 125.8, 121.3, 120.7, 97.0, 62.7, 56.8.

HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{20}Cl_3NO_2SNa$ $[M + Na]^+$ 635.9764, found 635.9764.

***(R)-S*-(4,4,4-Trichloro-1-((3,5-dichlorophenyl)amino)-1-oxo-2-phenylbutan-2-yl) benzothioate (32)**



32

According to **General procedure B**, *N*-(3,5-dichlorophenyl)-2-phenylacrylamide (58.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **32** as a yellow oil (55.6 mg, 51% yield, 85% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.68 min, t_R (major) = 8.44 min.

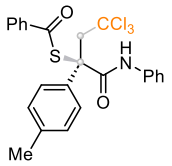
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.06 – 8.00 (m, 2H), 7.66 (ddt, J = 7.9, 7.2, 1.3 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.53 – 7.49 (m, 2H), 7.42 – 7.34 (m, 5H), 7.06 (t, J = 1.8 Hz, 1H), 4.26 (d, J = 16.3 Hz, 1H), 4.12 (d, J = 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ189.5, 169.0, 139.4, 136.0 135.2, 135.1, 134.7, 129.0(three carbons overlap), 127.8, 127.6, 124.4, 118.1, 96.3, 62.6, 57.0.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{16}Cl_5NO_2SNa$ $[M + Na]^+$ 567.9237, found 567.9236.

***(R)-S*-(4,4,4-Trichloro-1-oxo-1-(phenylamino)-2-(p-tolyl)butan-2-yl) benzothioate (33)**

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33

According to **General procedure B**, *N*-phenyl-2-(p-tolyl)acrylamide (44.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **33** as a colorless oil (60.9 mg, 62% yield, 81% ee).

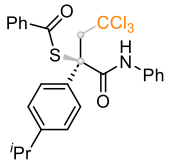
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.73 min, t_R (major) = 9.02 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.01 (dd, J = 8.4, 1.3 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.55 – 7.45 (m, 4H), 7.42 – 7.36 (m, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 7.09 – 7.04 (m, 1H), 4.30 (d, J = 16.3 Hz, 1H), 4.18 (d, J = 16.3 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 169.0, 138.9, 137.8, 136.4, 134.5, 133.0, 129.7, 129.1(two carbons overlapped), 127.8. 127.6, 124.6, 120.2, 96.9, 62.6, 57.0, 21.2.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{20}Cl_3NO_2SNa$ $[M + Na]^+$ 514.0173, found 514.0172.

***(R)-S*-(4,4,4-Trichloro-2-(4-isopropylphenyl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (34)**



34

According to **General procedure B**, 2-(4-isopropylphenyl)-*N*-phenylacrylamide (53.0 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **34** as a colorless oil (95.5 mg, 94% yield, 88% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.09 min, t_R (minor) = 19.18 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 7.99 (m, 2H), 7.67 – 7.60 (m, 1H), 7.59 – 7.52 (m, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.30 – 7.20 (m, 5H), 7.11 – 7.02

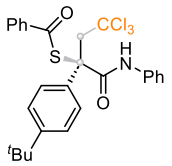
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(m, 1H), 4.34 – 4.16 (m, 2H), 2.90 (hept, J = 6.9 Hz, 1H), 1.23 (d, J = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 169.0, 149.8, 137.8, 136.4, 134.4, 133.2, 129.0(7), 129.0(6), 127.8, 127.5, 127.1, 124.6, 120.2, 97.0, 62.6, 56.9, 33.7, 23.9.

HRMS (ESI) m/z calcd. for $C_{26}H_{24}Cl_3NO_2SNa$ $[M + Na]^+$ 542.0486, found 542.0484.

(R)-*S*-(2-(4-(Tert-butyl)phenyl)-4,4,4-trichloro-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (35)



35

According to **General procedure B**, 2-(4-(tert-butyl)phenyl)-*N*-phenylacrylamide (55.8 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **35** as a colorless oil (64 mg, 60% yield, 85% ee).

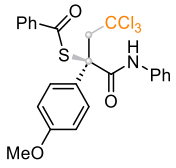
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.11 min, t_R (minor) = 15.20 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.05 (dd, J = 8.3, 1.4 Hz, 2H), 7.70 – 7.64 (m, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.42 (dd, J = 14.8, 8.2 Hz, 4H), 7.30 (t, J = 7.9 Hz, 2H), 7.14 – 7.07 (m, 1H), 4.37 – 4.21 (m, 2H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 169.0, 152.1, 137.8, 136.4, 134.4, 132.8, 132.4, 132.3, 131.6(9), 131.6(6), 129.1, 129.0, 128.7, 128.6, 127.7, 127.2, 125.9, 124.6, 120.2, 97.0, 62.5, 56.8, 34.7, 31.3.

HRMS (ESI) m/z calcd. for $C_{27}H_{26}Cl_3NO_2SNa$ $[M + Na]^+$ 556.0642, found 556.0642.

(R)-*S*-(4,4,4-Trichloro-2-(4-methoxyphenyl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (36)



36

According to **General procedure B**, 2-(4-methoxyphenyl)-*N*-phenylacrylamide (50.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with

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perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **36** as a colorless oil (89.2 mg, 88% yield, 92% ee).

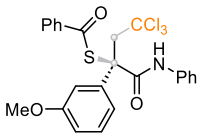
HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 23.06 min, t_R (minor) = 31.78 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.06 – 8.00 (m, 2H), 7.75 (dd, J = 7.8, 1.6 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.52 – 7.42 (m, 5H), 7.33 – 7.27 (m, 2H), 7.11 – 7.02 (m, 2H), 6.97 – 6.91 (m, 1H), 4.43 (d, J = 16.8 Hz, 1H), 3.82 (s, 3H), 3.76 (d, J = 16.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 169.0, 158.3, 138.3, 137.0, 134.2, 132.1, 131.0, 129.0, 128.9, 127.6, 124.0, 120.5, 120.0(1), 119.9(7), 111.6, 96.6, 62.8, 55.8, 55.3.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{20}Cl_3NO_3SNa$ $[M + Na]^+$ 530.0122, found 530.0120.

***(R)-S*-(4,4,4-Trichloro-2-(3-methoxyphenyl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (37)**



37

According to **General procedure B**, 2-(3-methoxyphenyl)-*N*-phenylacrylamide (50.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **37** as a colorless oil (71.0 mg, 70% yield, 93% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 27.64 min, t_R (minor) = 34.40 min.

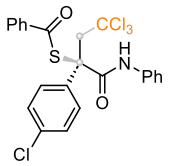
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.04 – 7.98 (m, 2H), 7.66 – 7.60 (m, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.33 – 7.25 (m, 3H), 7.25 – 7.20 (m, 2H), 7.09 – 7.04 (m, 1H), 6.87 (ddd, J = 8.0, 2.4, 1.1 Hz, 1H), 4.32 (d, J = 16.3 Hz, 1H), 4.20 (d, J = 16.3 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 168.7, 160.0, 137.7, 137.6, 136.4, 134.5, 130.0, 129.0(9), 129.0(7), 127.8, 124.7, 120.2, 120.0, 114.1, 113.8, 96.8, 62.5, 56.8, 55.5.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{20}Cl_3NO_3SNa$ $[M + Na]^+$ 530.0122, found 530.0121.

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***(R)*-*S*-(4,4,4-Trichloro-2-(4-chlorophenyl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (38)**



38

According to **General procedure B**, 2-(4-chlorophenyl)-*N*-phenylacrylamide (51.4 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **38** as a yellow oil (61.3 mg, 60% yield, 88% ee).

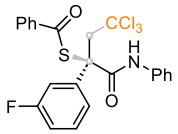
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.57 min, t_R (major) = 26.24 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.01 (dd, J = 8.3, 1.4 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.62 – 7.58 (m, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.28 (t, J = 8.0 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 4.29 (d, J = 16.3 Hz, 1H), 4.14 (d, J = 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 168.4, 137.5, 136.2, 135.0, 134.7, 134.6, 129.3, 129.2(three carbons overlap), 127.8, 124.9, 120.3, 96.5, 62.3, 57.1.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{17}Cl_4NO_2SNa$ $[M + Na]^+$ 533.9626, found 533.9626.

***(R)*-*S*-(4,4,4-Trichloro-2-(3-fluorophenyl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (39)**



39

According to **General procedure B**, 2-(3-fluorophenyl)-*N*-phenylacrylamide (48.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **39** as a yellow oil (71.3 mg, 72% yield, 88% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.13 min, t_R (major) = 29.06 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.07 – 7.95 (m, 2H), 7.69 – 7.61 (m, 1H),

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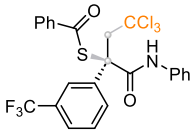
7.53 – 7.33 (m, 7H), 7.32 – 7.26 (m, 2H), 7.13 – 7.01 (m, 2H), 4.30 (d, J = 16.3 Hz, 1H), 4.18 (d, J = 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 168.2, 163.0 (d, J = 245.7 Hz), 138.7 (d, J = 7.3 Hz), 137.5, 136.2, 134.7, 130.6 (d, J = 8.4 Hz), 129.1(7), 129.1(5), 127.8, 124.9, 123.5 (d, J = 3.0 Hz), 120.3, 116.0 (d, J = 20.8 Hz), 115.3 (d, J = 24.0 Hz), 96.5, 62.2 (d, J = 1.8 Hz), 57.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –111.73.

HRMS (ESI) m/z calcd. for $C_{23}H_{17}Cl_3FNO_2SNa$ $[M + Na]^+$ 517.9922, found 517.9920.

(R)-*S*-(4,4,4-Trichloro-1-oxo-1-(phenylamino)-2-(3-(trifluoromethyl)phenyl)butan-2-yl) benzothioate (40)



40

According to **General procedure B**, *N*-phenyl-2-(3-(trifluoromethyl)phenyl)acrylamide (58.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **40** as a yellow oil (103.5 mg, 95% yield, 90% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.66 min, t_R (major) = 18.43 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.05 – 7.99 (m, 2H), 7.94 (d, J = 1.8 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.69 – 7.60 (m, 2H), 7.52 (q, J = 7.9 Hz, 3H), 7.42 – 7.37 (m, 2H), 7.28 (t, J = 7.9 Hz, 2H), 7.13 – 7.06 (m, 1H), 4.34 (d, J = 16.4 Hz, 1H), 4.18 (d, J = 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 168.1, 137.4, 137.2, 136.1, 134.8, 131.4 (q, J = 32.5Hz), 131.2, 129.6, 129.2(0), 129.1(7), 129.0, 127.8, 125.8 (q, J = 3.7 Hz), 125.1, 124.9 (q, J = 3.7 Hz), 123.7 (q, J = 236.5 Hz), 120.4, 96.4, 62.3, 57.1.

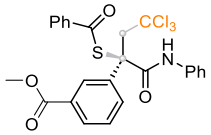
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.54.

HRMS (ESI) m/z calcd. for $C_{24}H_{17}Cl_3F_3NO_2SNa$ $[M + Na]^+$ 567.9890, found 567.9886.

Methyl *(R)*-3-(2-(benzoylthio)-4,4,4-trichloro-1-oxo-1-(phenylamino)butan-2-

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yl)benzoate (41)



41

According to **General procedure B**, methyl 3-(3-oxo-3-(phenylamino)prop-1-en-2-yl)benzoate (56.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 8/1), which afforded the product **41** as a colorless oil (40.7 mg, 38% yield, 99% ee).

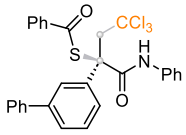
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.36 min, t_R (major) = 8.68 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (t, J = 1.9 Hz, 1H), 8.25 (s, 1H), 8.08 – 8.00 (m, 3H), 7.87 (ddd, J = 8.1, 2.3, 1.1 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.55 – 7.45 (m, 3H), 7.42 – 7.35 (m, 2H), 7.28 (t, J = 8.36 Hz, 2H), 7.12 – 7.05 (m, 1H), 4.40 – 4.19 (m, 2H), 3.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 168.4, 166.5, 137.5, 136.9, 136.2, 134.7, 132.0, 131.0, 130.1, 129.2(2), 129.1(5), 129.1, 128.9, 127.8, 124.9, 120.4, 96.6, 62.4, 56.8, 52.6.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{18}Cl_3NO_2SNa$ $[M + Na]^+$ 500.0016, found 500.0013.

***(R)-S*-(2-([1,1'-Biphenyl]-3-yl)-4,4,4-trichloro-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (42)**



42

According to **General procedure B**, 2-([1,1'-biphenyl]-3-yl)-*N*-phenylacrylamide (59.8 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **42** as a colorless oil (105 mg, 95% yield, 89% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.96 min, t_R (major) = 18.78 min.

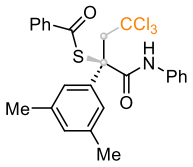
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^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.06 – 8.00 (m, 2H), 7.88 (t, J = 1.9 Hz, 1H), 7.63 (ddt, J = 7.0, 4.5, 2.0 Hz, 2H), 7.56 (dd, J = 7.3, 1.8 Hz, 3H), 7.51 – 7.34 (m, 8H), 7.26 (t, J = 7.9 Hz, 2H), 7.10 – 7.03 (m, 1H), 4.44 – 4.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 168.8, 142.0, 140.6, 137.7, 136.4, 136.3, 134.6, 129.4, 129.1(1), 129.0(9), 129.0, 127.9, 127.8(4), 127.8(0), 127.4, 126.7, 126.5, 124.8, 120.3, 96.9, 62.8, 57.0.

HRMS (ESI) m/z calcd. for $C_{29}H_{22}Cl_3NO_2SNa$ $[M + Na]^+$ 576.0329, found 576.0327.

(R)-S-(4,4,4-Trichloro-2-(3,5-dimethylphenyl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (43)



43

According to **General procedure B**, 2-(3,5-dimethylphenyl)-*N*-phenylacrylamide (50.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **43** as a colorless oil (97 mg, 96% yield, 88% ee).

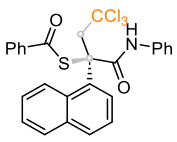
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.66 min, t_R (major) = 11.38 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.06 – 8.01 (m, 2H), 7.67 – 7.58 (m, 1H), 7.49 (t, J = 7.9 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.27 (dd, J = 7.0, 1.6 Hz, 2H), 7.24 (d, J = 1.4 Hz, 2H), 7.10 – 7.03 (m, 1H), 6.96 (s, 1H), 4.33 – 4.19 (m, 2H), 2.32 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 169.1, 138.6, 137.8, 136.4, 136.1, 134.4, 130.6, 129.0(two carbons overlapped), 127.8, 125.1, 124.6, 120.2, 97.0, 62.4, 56.7, 21.6.

HRMS (ESI) m/z calcd. for $C_{25}H_{22}Cl_3NO_2SNa$ $[M + Na]^+$ 528.0329, found 528.0326.

(R)-S-(4,4,4-Trichloro-2-(naphthalen-1-yl)-1-oxo-1-(phenylamino)butan-2-yl) benzothioate (44)



44

According to **General procedure B**, 2-(naphthalen-1-yl)-*N*-phenylacrylamide (50.2

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mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **44** as a colorless oil (50.6 mg, 48% yield, 91% ee).

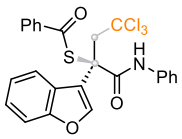
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.42 min, t_R (major) = 12.25 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.17 – 8.04 (m, 2H), 8.02 – 7.96 (m, 2H), 7.95 – 7.86 (m, 2H), 7.65 – 7.58 (m, 1H), 7.47 (dddd, J = 12.6, 7.8, 6.6, 1.2 Hz, 5H), 7.36 – 7.29 (m, 2H), 7.22 (t, J = 8.0 Hz, 2H), 7.07 – 6.99 (m, 1H), 4.53 (d, J = 16.8 Hz, 1H), 4.10 (d, J = 16.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 169.3, 137.6, 137.0, 134.5, 134.4(two carbons overlapped), 131.1, 129.8, 129.0(2), 128.9(9)(two carbons overlapped), 127.7(two carbons overlapped), 127.2, 125.8, 124.8, 124.7, 123.9, 120.5, 96.2, 65.8, 57.0.

HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{20}Cl_3NO_2SNa$ $[M + Na]^+$ 550.0173, found 550.0171.

(R)-S-(2-(Benzofuran-3-yl)-4,4,4-trichloro-1-oxo-1-(phenylamino)butan-2-yl) *benzothioate* (45)



45

According to **General procedure B**, 2-(benzofuran-3-yl)-*N*-phenylacrylamide (50.2 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **45** as a colorless oil (51.7 mg, 50% yield, 86% ee).

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.58 min, t_R (minor) = 25.48 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.00 (d, J = 7.3 Hz, 2H), 7.95 (s, 1H), 7.88 (dd, J = 7.8, 1.3 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.51 (td, J = 8.0, 2.7 Hz, 3H), 7.42 (d, J = 7.6 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.29 (s, 1H), 7.26 (d, J = 7.4 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 4.51 (d, J = 16.2 Hz, 1H), 4.22 (d, J = 16.2 Hz, 1H).

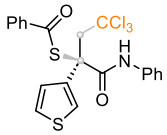
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 167.1, 155.5, 144.6, 137.4, 136.2, 134.6, 129.1(two carbons overlapped), 127.7, 125.5, 125.3, 124.9, 123.6, 121.3, 120.4, 116.8,

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112.1, 96.5, 56.7, 54.4.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{18}Cl_3NO_3SNa$ $[M + Na]^+$ 539.9965, found 539.9962.

(R)-S-(4,4,4-Trichloro-1-oxo-1-(phenylamino)-2-(thiophen-3-yl)butan-2-yl) benzothioate (46)



46

According to **General procedure B**, *N*-phenyl-2-(thiophen-3-yl)acrylamide (45.8 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), with perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **46** as a colorless oil (48.3 mg, 50% yield, 84% ee).

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.78 min, t_R (major) = 22.97 min.

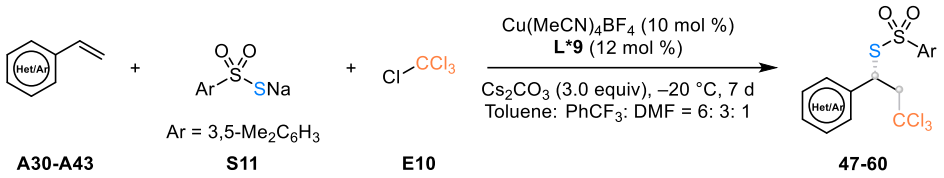
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.03 – 7.96 (m, 2H), 7.68 – 7.61 (m, 1H), 7.52 – 7.46 (m, 3H), 7.41 (d, J = 7.9 Hz, 2H), 7.34 (dd, J = 5.2, 2.9 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.13 – 7.05 (m, 1H), 4.34 (d, J = 16.2 Hz, 1H), 4.09 (d, J = 16.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 168.2, 137.6, 136.5, 136.2, 134.6, 129.1(two carbons overlapped), 127.8, 127.1, 126.8, 124.8, 124.4, 120.3, 96.8, 59.6, 56.2.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{16}Cl_3NO_2S_2Na$ $[M + Na]^+$ 505.9580, found 505.9579.

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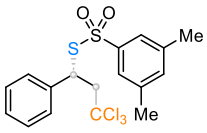
8. Copper-catalyzed chemo- and enantioselective radical 1,2-carbosulfuration of styrene-type alkenes



General procedure C

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), alkene (0.2 mmol, 1.0 equiv) $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), **L*9** (16.6 mg, 0.024 mmol, 12 mol %) and Cs_2CO_3 (195.50 mg, 0.60 mmol, 3.0 equiv), Then, Toluene/$PhCF_3$/DMF (2.0 mL, (v/v/v = 6:3:1)) was added by syringe under argon atmosphere. Finally, tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) 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 DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(R)-S-(3,3,3-Trichloro-1-phenylpropyl) 3,5-dimethylbenzenesulfonothioate (47)



47

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), styrene (23 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **47** as a colorless solid (72.6 mg, 86% yield, 91% ee).

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 22.14 min, t_R (minor) = 26.42 min.

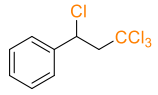
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.36 (m, 2H), 7.23 (qd, J = 4.0, 1.4 Hz, 3H), 7.20 – 7.16 (m, 3H), 4.91 (dd, J = 8.2, 4.9 Hz, 1H), 3.48 – 3.40 (m, 2H), 2.33 (s, 6H).

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^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 139.4, 137.6, 135.6, 130.0., 128.7, 128.3, 124.7, 96.6, 59.0, 52.6, 21.3.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{17}Cl_3O_2S_2Na$ $[M + Na]^+$ 444.9628, found 444.9627.

(1,3,3,3-Tetrachloropropyl)benzene[11] **(47′)**

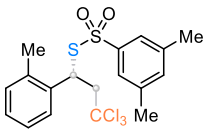


47′

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.45 (m, 2H), 7.44 – 7.34 (m, 3H), 5.33 (dd, J = 6.5, 5.4 Hz, 1H), 3.72 – 3.49 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 129.0, 127.5, 96.3, 62.8, 58.4.

***(R)-S*-(3,3,3-Trichloro-1-(o-tolyl)propyl) 3,5-dimethylbenzenesulfonothioate (48).**



48

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-methyl-2-vinylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **48** a colorless oil (70.6 mg, 81% yield, 86% ee).

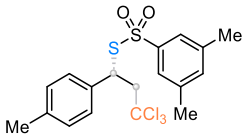
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 22.71 min, t_R (major) = 23.45 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 2H), 7.25 (s, 1H), 7.12 (tq, J = 14.9, 5.1, 4.1 Hz, 4H), 5.07 (t, J = 6.7 Hz, 1H), 3.62 (d, J = 7.4 Hz, 2H), 2.38 (s, 6H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 139.7, 136.0, 135.7, 135.2, 131.2, 128.6, 127.0, 126.8, 125.0, 96.9, 58.8, 47.4, 21.3, 19.2.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{16}Cl_3FO_2S_2Na$ $[M + Na]^+$ 462.9534, found 462.9535.

***(R)-S*-(3,3,3-Trichloro-1-(p-tolyl)propyl) 3,5-dimethylbenzenesulfonothioate (49)**



49

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8

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mg, 0.24 mmol, 1.2 equiv), 1-methyl-4-vinylbenzene (26.3 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **49** as a colorless oil (55 mg, 63% yield, 88% ee)

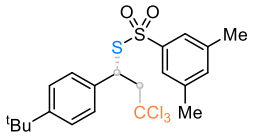
HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 19.88 min, t_R (minor) = 23.25 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 2H), 7.19 (s, 1H), 7.08 – 7.01 (m, 4H), 4.88 (dd, J = 8.4, 4.7 Hz, 1H), 3.49 – 3.37 (m, 2H), 2.33 (s, 6H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 139.3, 138.5, 135.3, 134.4, 129.6, 128.0, 124.6, 95.6, 58.8, 52.3, 21.2.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{19}Cl_3O_2S_2Na$ $[M + Na]^+$ 458.9784, found 458.9783.

***(R)-S*-(1-(4-(Tert-butyl)phenyl)-3,3,3-trichloropropyl) 3,5-dimethylbenzenesulfonothioate (50)**



50

According to **General procedure B**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-(tert-butyl)-4-vinylbenzene (36.6 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **50** as a colorless oil (48.8 mg, 51% yield, 87% ee).

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 15.16 min, t_R (minor) = 18.60 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 2H), 7.26 – 7.23 (m, 2H), 7.19 (s, 1H), 7.11 – 7.06 (m, 2H), 4.86 (dd, J = 8.6, 4.5 Hz, 1H), 3.51 – 3.43 (m, 2H), 2.35 (s, 6H), 1.26 (s, 9H).

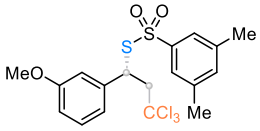
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 144.2, 139.4, 135.5, 134.2, 127.6, 125.8, 124.7, 96.6, 58.9, 52.2, 34.6, 31.2, 21.3.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{25}Cl_3O_2S_2Na$ $[M + Na]^+$ 501.0254, found 501.0252.

***(R)-S*-(3,3,3-Trichloro-1-(3-methoxyphenyl)propyl) 3,5-**

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dimethylbenzenesulfonothioate (51)



51

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-methoxy-3-vinylbenzene (27.8 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **51** as a colorless oil (43.4 mg, 48% yield, 89% ee)

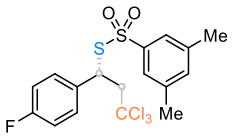
HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 25.36 min, t_R (minor) = 28.22 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 2H), 7.20 – 7.12 (m, 2H), 6.80 – 6.72 (m, 2H), 6.68 – 6.66 (m, 1H), 4.86 (dd, J = 7.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.44 – 3.38 (m, 2H), 2.33 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 144.3, 139.3, 138.8, 135.4, 129.9, 124.6, 120.4, 113.8(5), 113.7(7), 96.5, 58.9, 55.2, 52.4, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}Cl_3O_3S_2Na$ $[M + Na]^+$ 474.9733, found 474.9732.

***(R)*-*S*-(3,3,3-Trichloro-1-(4-fluorophenyl)propyl) 3,5-dimethylbenzenesulfonothioate (52)**



52

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-fluoro-4-vinylbenzene (23.9 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **52** as a colorless oil (47.5 mg, 54% yield, 87% ee).

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 214 nm), t_R (major) = 23.95 min, t_R (minor) = 25.43 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 2H), 7.22 – 7.13 (m, 3H), 6.91 (t, J = 8.6 Hz, 2H), 4.94 (dd, J = 8.9, 4.2 Hz, 1H), 3.44 – 3.31 (m, 2H), 2.33 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, J = 248.5 Hz), 144.4, 139.4, 135.5, 133.4 (d,

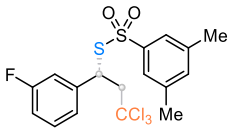
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J = 3.3 Hz), 130.1 (d, J = 8.3 Hz), 124.5, 115.8 (d, J = 21.9 Hz), 96.3, 58.8, 51.7, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ –112.59.

HRMS (ESI) m/z calcd. for $C_{17}H_{16}Cl_3FO_2S_2Na$ $[M + Na]^+$ 462.9534, found 462.9535.

(R)-S-(3,3,3-Trichloro-1-(3-fluorophenyl)propyl) 3,5-dimethylbenzenesulfonothioate (53)



53

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-fluoro-3-vinylbenzene (23.8 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **53** as a colorless oil (23 mg, 26% yield, 87% ee).

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 20.99 min, t_R (minor) = 23.31 min.

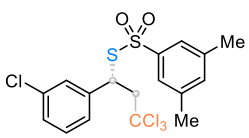
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 2H), 7.24 – 7.17 (m, 2H), 7.01 – 6.97 (m, 1H), 6.94 – 6.84 (m, 2H), 4.89 (dd, J = 8.5, 4.5 Hz, 1H), 3.42 (dd, J = 15.2, 4.6 Hz, 1H), 3.36 (dd, J = 15.2, 8.6 Hz, 1H), 2.34 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, J = 247.7 Hz), 144.2, 140.0 (d, J = 7.2 Hz), 139.4, 135.6, 130.4 (d, J = 8.4 Hz), 124.6, 124.0 (d, J = 3.0 Hz), 115.5 (d, J = 21.0 Hz), 115.2 (d, J = 22.4 Hz), 96.3, 58.8, 51.8 (d, J = 8.0 Hz), 51.7, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ –111.70.

HRMS (ESI) m/z calcd. for $C_{17}H_{16}Cl_3FO_2S_2Na$ $[M + Na]^+$ 462.9534, found 462.9532.

(R)-S-(3,3,3-Trichloro-1-(3-chlorophenyl)propyl) 3,5-dimethylbenzenesulfonothioate (54)



54

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-chloro-3-vinylbenzene (24.0 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The

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reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **54** as a colorless oil (45.6 mg, 50% yield, 87% ee).

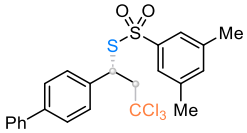
HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 21.32 min, t_R (minor) = 24.99 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 2H), 7.22 – 7.09 (m, 5H), 4.91 (dd, J = 8.3, 4.5 Hz, 1H), 3.45 – 3.32 (m, 2H), 2.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.8, 139.5, 135.7, 134.8, 130.0, 128.7, 128.4, 126.6, 125.0, 96.3, 58.9, 51.8, 21.3.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{16}Cl_4O_2S_2Na$ $[M + Na]^+$ 478.9238, found 478.9240.

***(R)*-*S*-(1-([1,1'-Biphenyl]-4-yl)-3,3,3-trichloropropyl) 3,5-dimethylbenzenesulfonothioate (55)**



55

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 4-vinyl-1,1'-biphenyl (36.0 mg, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **55** as a colorless oil (69.7 mg, 70% yield, 87% ee).

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 28.77 min, t_R (minor) = 37.28 min.

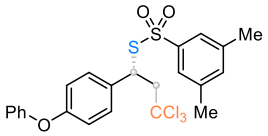
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.50 (m, 2H), 7.47 – 7.37 (m, 6H), 7.37 – 7.32 (m, 1H), 7.26 – 7.22 (m, 2H), 7.15 (s, 1H), 4.97 (dd, J = 7.8, 5.2 Hz, 1H), 3.50 – 3.41 (m, 2H), 2.28 (s, 6H).

^{13}C NMR (100 MHz, CDCl3): δ 144.4, 141.3, 140.0, 139.3, 136.5, 135.4, 128.9, 128.6, 127.7, 127.4, 126.9, 124.6, 96.6, 58.9, 52.2, 21.2.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{21}Cl_3O_2S_2Na$ $[M + Na]^+$ 520.9941, found 520.9942.

***(R)*-*S*-(3,3,3-Trichloro-1-(4-phenoxyphenyl)propyl) 3,5-dimethylbenzenesulfonothioate (56)**

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56

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 1-phenoxy-4-vinylbenzene (37 μL, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **56** as a colorless oil (61 mg, 59% yield, 86% ee)

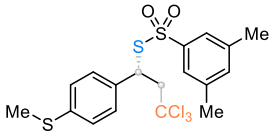
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.51 min, t_R (major) = 19.38 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 2H), 7.34 (m, 2H), 7.22 (s, 1H), 7.16 – 7.10 (m, 3H), 7.00 – 6.94 (m, 2H), 6.88 – 6.82 (m, 2H), 4.91 (dd, J = 8.9, 4.3 Hz, 1H), 3.48 – 3.43 (m, 1H), 3.39 (dd, J = 15.1, 8.9 Hz, 1H), 2.36 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 156.3, 144.4, 139.4, 135.5, 131.7, 129.9, 129.6, 124.6, 123.9, 119.4, 118.5, 96.5, 58.9, 52.0, 21.2.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{21}Cl_3O_3S_2Na$ $[M + Na]^+$ 536.9890, found 536.9888.

(R)-S-(3,3,3-Trichloro-1-(4-(methylthio)phenyl)propyl) 3,5-dimethylbenzenesulfonothioate (57)



57

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), methyl(4-vinylphenyl)sulfane (30 mg, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **57** as a colorless oil (64.6 mg, 69% yield, 90% ee)

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 29.64 min, t_R (minor) = 36.25 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 2H), 7.18 (s, 1H), 7.11 – 7.04 (m, 4H), 4.90 (dd, J = 8.7, 4.4 Hz, 1H), 3.46 – 3.40 (m, 1H), 3.40 – 3.34 (m, 1H), 2.44 (s, 3H), 2.34 (s, 6H).

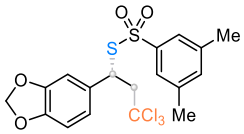
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 139.5, 139.4, 135.5, 133.9, 128.7, 126.2, 124.7,

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96.6, 58.8, 52.2, 21.3, 15.4.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{19}Cl_3O_2S_3Na$ $[M + Na]^+$ 490.9503, found 490.9502.

(R)-S-(1-(Benzo[d][1,3]dioxol-5-yl)-3,3,3-trichloropropyl) 3,5-dimethylbenzenesulfonothioate (58)



According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 5-vinylbenzo[d][1,3]dioxole (29.6 mg, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **58** as a colorless oil (28 mg, 30% yield, 83% ee).

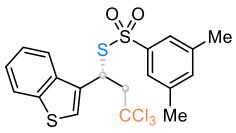
HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 16.40 min, t_R (minor) = 20.19 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.41 – 7.35 (m, 2H), 7.22 – 7.18 (m, 1H), 6.71 – 6.62 (m, 2H), 6.60 (d, *J* = 1.7 Hz, 1H), 5.92 (dd, *J* = 7.4, 1.4 Hz, 2H), 4.85 (dd, *J* = 8.9, 4.2 Hz, 1H), 3.45 – 3.28 (m, 2H), 2.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.1, 147.9, 144.6, 139.4, 135.4, 131.0, 124.7, 122.3, 108.4, 108.3, 101.5, 96.6, 77.5, 77.2, 76.8, 59.0, 52.5, 21.3.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{17}Cl_3O_4S_2Na$ $[M + Na]^+$ 488.9526, found 488.9525.

(R)-S-(1-(Benzo[b]thiophen-3-yl)-3,3,3-trichloropropyl) 3,5-dimethylbenzenesulfonothioate (59)



59

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 3-vinylbenzo[b]thiophene (32 mg, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **59** as a colorless oil (63.1 mg, 65% yield, 94% ee)

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ =

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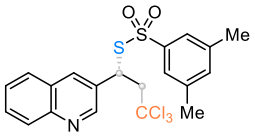
254 nm), t_R (major) = 9.90 min, t_R (minor) = 11.27 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.34 – 7.27 (m, 4H), 7.10 (s, 1H), 5.29 (dd, J = 8.5, 4.2 Hz, 1H), 3.70 – 3.57 (m, 2H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 140.4, 139.2, 136.2, 135.3, 131.0, 126.6, 124.9, 124.6, 124.4, 122.9, 121.4, 96.6, 58.0, 45.8, 21.2.

HRMS (ESI) m/z calcd. for $C_{19}H_{17}Cl_3O_2S_3Na$ $[M + Na]^+$ 500.9348, found 500.9350.

***(R)-S*-(3,3,3-Trichloro-1-(quinolin-3-yl)propyl) 3,5-dimethylbenzenesulfonothioate (60)**



60

According to **General procedure C**, sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), 3-vinylquinoline (31 mg, 0.2 mmol, 1.0 equiv) with tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 20/1), which afforded the product **60** as a colorless oil (47 mg, 50% yield, 86% ee)

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 28.69 min, t_R (major) = 36.33 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 2.4 Hz, 1H), 8.03 (dd, J = 8.4, 1.1 Hz, 1H), 7.94 (d, J = 2.3 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.55 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.88 (tt, J = 1.6, 0.8 Hz, 1H), 5.17 (dd, J = 8.0, 4.9 Hz, 1H), 3.57 – 3.46 (m, 2H), 2.13 – 2.08 (m, 6H).

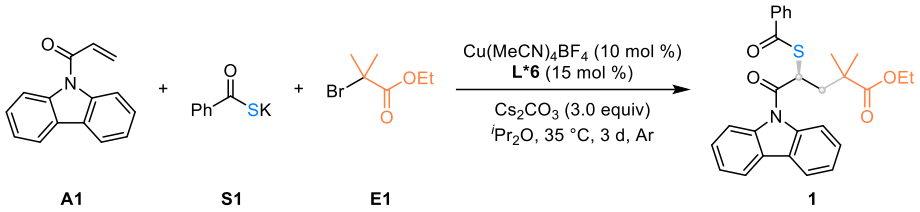
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 147.6, 144.2, 139.4, 135.4(two carbons overlapped), 130.7, 130.3, 129.4, 127.9, 127.4, 127.3, 124.4, 96.3, 58.6, 50.1, 21.0.

HRMS (ESI) m/z calcd. for $C_{20}H_{18}Cl_3NO_2S_2Na$ $[M + Na]^+$ 459.9737, found 459.9735

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9. Synthetic utility

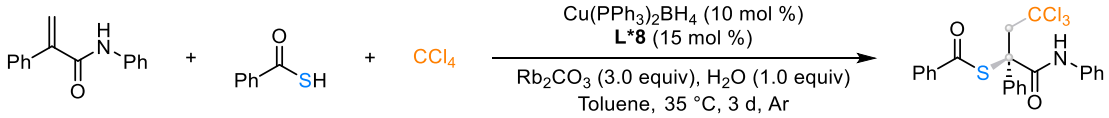
Large-scale reaction



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium thiocarboxylates (2.0 mmol, 1.0 equiv), alkene (4.0 mmol, 2.0 equiv) $Cu(MeCN)_4BF_4$ (0.2 mmol, 10 mol %), **L*6** (0.3 mmol, 15 mol %) and Cs_2CO_3 (6.0 mmol, 3.0 equiv), Then, diisopropyl ether (16.0 mL) was added by syringe under argon atmosphere. Finally, radical precursor (4.0 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by DCM. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **1** as a colorless oil (747.0 mg, 79% yield, 93% ee).

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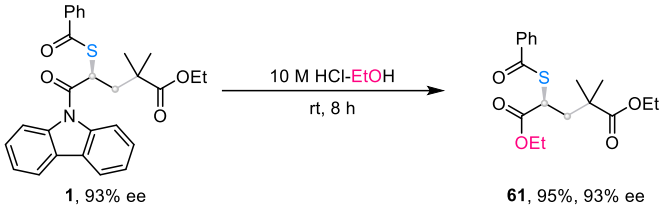
Large-scale reaction



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene (2.0 mmol, 1.0 equiv), benzothioic S-acid (3.0 mmol, 1.5 equiv), $Cu(PPh_3)_2BH_4$ (0.2 mmol, 10 mol %), **L*8** (0.3 mmol, 15 mol %) and Rb_2CO_3 (6.0 mmol, 3.0 equiv), Then, Toluene (16.0 mL) was added by syringe under argon atmosphere. Finally, perchloromethane (10.0 mmol, 5.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Upon completion (monitored by TLC), the precipitate was filtered off and washed by DCM. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product **24** as a colorless oil (716 mg, 75% yield, 94% ee).

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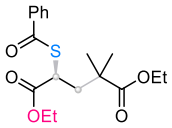
Synthesis of 61



1, 93% ee **61**, 95%, 93% ee

Compound **1** (94.6 mg, 0.20 mmol, 93% ee) was dissolved in HCl-EtOH (10.0 M, 2.0 mL), and the resulting mixture was stirred at room temperature for 8 h. Upon completion, the reaction mixture was diluted with EA (10 mL) and washed with H_2O (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 20/1) to afford **61** as a colorless oil (66.9 mg, 95% yield, 93% ee).

Diethyl *(S)*-4-(benzoylthio)-2,2-dimethylpentanedioate (61)



61

HPLC analysis: Chiralcel ADH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.99 min, t_R (major) = 16.31 min.

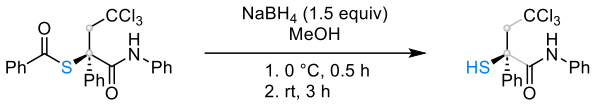
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.88 (m, 2H), 7.63 – 7.52 (m, 1H), 7.45 (dd, J = 8.4, 7.2 Hz, 2H), 4.44 (dd, J = 8.3, 5.6 Hz, 1H), 4.19 (qd, J = 7.1, 1.5 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.46 (dd, J = 14.4, 8.4 Hz, 1H), 2.11 (dd, J = 14.4, 5.7 Hz, 1H), 1.28 (q, J = 4.0 Hz, 6H), 1.24 (q, J = 4.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.6, 176.9, 171.9, 136.4, 133.9, 128.9, 127.5, 61.9, 60.9, 42.7, 42.2, 42.1, 25.8, 24.9, 14.2, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{24}O_5SNa$ $[M + Na]^+$ 375.1237, found 375.1235

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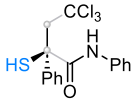
Synthesis of 62



24, 95% ee **62**, 80%,95% ee

In a round-bottomed flask (10 mL) equipped with a stir bar, a solution of the 24 (47.7 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 (PE/DCM = 5/1) to afford the product **62** (29.8 mg, 80%, 95% ee) as a colorless solid.

(R)-4,4,4-Trichloro-2-mercapto-*N*,2-diphenylbutanamide (62)



62

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 24.58 min, t_R (major) = 30.85 min.

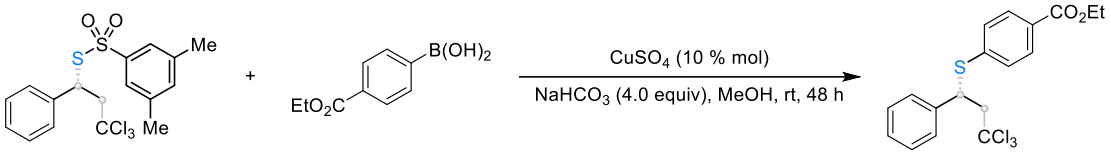
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 7.61 – 7.54 (m, 4H), 7.37 (q, J = 6.9 Hz, 5H), 7.17 (t, J = 7.4 Hz, 1H), 4.54 (d, J = 15.4 Hz, 1H), 3.64 (d, J = 15.5 Hz, 1H), 3.11 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 138.7, 129.6, 129.2, 128.3, 128.0, 124.8, 120.0, 98.7, 57.3, 52.1.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{14}Cl_3NOSNa$ $[M + Na]^+$ 395.9754, found 395.9755

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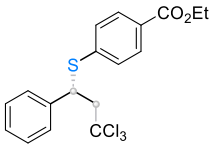
Synthesis of 63



47, 90% ee

63, 78%, 89% ee

To a mixture of copper(II) sulfate (3.2 mg, 0.02 mmol, 10 mol%) and sodium bicarbonate (67.2 mg, 0.80 mmol, 4.0 equiv.) was added a solution of corresponding thiosulfonates **47** (84.4 mg, 0.20 mmol, 1.0 equiv, 90% ee) and (4-(ethoxycarbonyl)phenyl)boronic acid (116.4 mg, 0.6 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 EA and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE /EA = 100/1 ~ 20/1) to give product **63** (62.7 mg, 78%, 89% ee) as a white solid.



63

Ethyl (*R*)-4-((3,3,3-trichloro-1-phenylpropyl)thio)benzoate (63)

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 13.39 min, t_R (major) = 15.31 min.

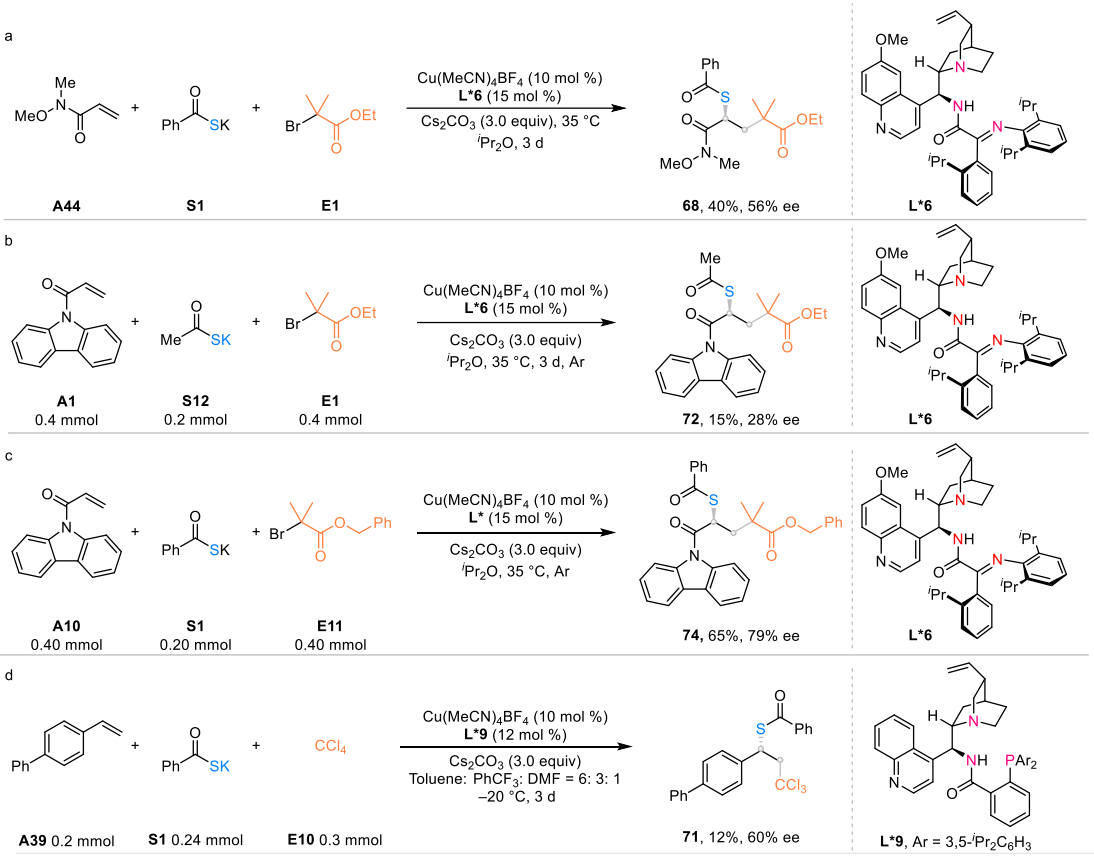
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.89 (m, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.28 (m, 2H), 7.27 –7.22 (m, 1H), 4.77 (dd, J = 8.6, 3.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.49 (dd, J = 15.1, 8.6 Hz, 1H), 3.30 (dd, J = 15.1, 3.3 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 140.4, 139.6, 130.8, 130.2, 129.3, 128.9, 128.4, 128.2, 97.5, 61.2, 59.5, 49.7, 14.4.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}Cl_3O_2SNa$ $[M + Na]^+$ 424.9907, found 424.9905

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Additional Substrate Scope

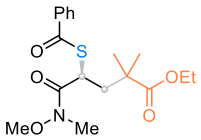


Compounds **68, 72**, and **74** were synthesized according to **General Procedure A**: sulfur source substrates (0.2 mmol, 1.0 equiv), acrylamide substrates (0.4 mmol, 2.0 equiv) with radical precursor (0.4 mmol, 2.0 equiv) stirred at 35 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 10/1), which afforded the product.

Compounds **71** were synthesized according to **General Procedure C**: sulfur source substrates (0.24 mmol, 1.2 equiv), styrene (0.2 mmol, 1.0 equiv) with tetrachloromethane (0.3 mmol, 1.5 equiv) stirred at –20 °C for 7 days. The reaction mixture was purified by column chromatography on silica gel (PE/EA = 40/1), which afforded the product **47.**

Ethyl (*S*)-4-(benzoylthio)-5-(methoxy(methyl)amino)-2,2-dimethyl-5-oxopentanoate (68).

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68

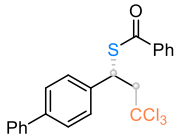
HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 18.05 min, t_R (minor) = 20.40 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.88 (m, 2H), 7.62 – 7.53 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H), 5.21 – 4.90 (m, 1H), 4.14 (qd, J = 7.1, 3.0 Hz, 2H), 3.80 (s, 3H), 3.21 (s, 3H), 2.52 (dd, J = 14.2, 8.8 Hz, 1H), 2.06 (dd, J = 14.2, 4.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 177.1, 136.5, 133.8, 128.8, 127.5, 60.9, 43.2, 42.3, 26.1, 24.6, 14.2.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{25}NO_5SNa$ $[M + Na]^+$ 390.1346, found 390.1344

(*R*)-*S*-(1-([1,1'-Biphenyl]-4-yl)-3,3,3-trichloropropyl) benzothioate (71).



71

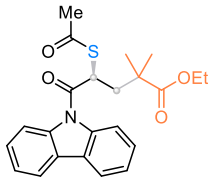
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 25.90 min, t_R (minor) = 30.13 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.91 (m, 2H), 7.61 – 7.55 (m, 5H), 7.51 (d, J = 8.4 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.36 – 7.32 (m, 1H), 5.37 (dd, J = 8.2, 4.6 Hz, 1H), 3.62 – 3.49 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 141.0, 140.6, 138.9, 136.5, 133.9, 128.9, 128.9, 128.8, 127.6, 127.6, 127.5, 127.2, 97.4, 59.6, 45.4.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{17}Cl_3OSNa$ $[M + Na]^+$ 456.9958, found 456.9957.

Ethyl (*S*)-4-(acetylthio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate (72).



72

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 23.56 min, t_R (minor) = 32.32 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.05 (m, 2H), 8.04 – 7.94 (m, 2H), 7.48 (ddd, *J*

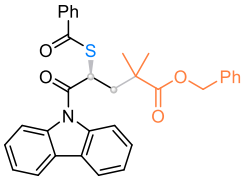
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= 8.5, 7.3, 1.4 Hz, 2H), 7.40 (td, *J* = 7.4, 1.0 Hz, 2H), 5.45 (dd, *J* = 9.3, 3.8 Hz, 1H), 4.03 – 3.85 (m, 2H), 2.81 (dd, *J* = 14.3, 9.3 Hz, 1H), 2.37 (s, 3H), 2.09 (dd, *J* = 14.2, 3.9 Hz, 1H), 1.22 (s, 3H), 1.14 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9, 176.7, 170.8, 127.7, 126.8, 124.2, 120.0, 61.0, 44.9, 44.5, 42.2, 30.4, 26.1, 25.0, 14.0.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{25}NO_4SNa$ $[M + Na]^+$ 434.1397, found 434.1398.

Benzyl (*S*)-4-(benzoylthio)-5-(9*H*-carbazol-9-yl)-2,2-dimethyl-5-oxopentanoate (74).



74

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.14 min, t_R (major) = 20.87 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.06 (m, 2H), 7.94 (td, *J* = 8.5, 8.1, 1.4 Hz, 4H), 7.61 – 7.56 (m, 1H), 7.47 – 7.42 (m, 4H), 7.37 (td, *J* = 7.5, 1.0 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.13 (dt, *J* = 4.8, 3.7 Hz, 2H), 5.65 (dd, *J* = 9.4, 3.5 Hz, 1H), 4.99 – 4.86 (m, 2H), 2.98 (dd, *J* = 14.2, 9.4 Hz, 1H), 2.19 (dd, *J* = 14.2, 3.5 Hz, 1H), 1.30 (s, 3H), 1.22 (s, 3H).

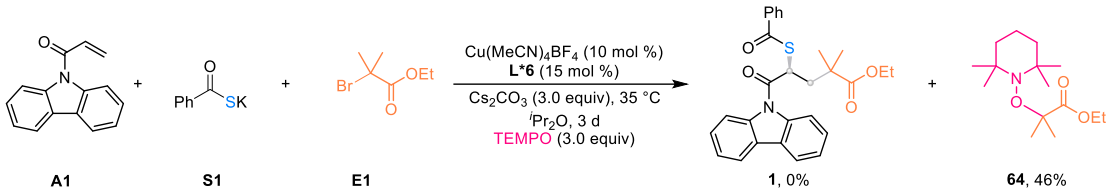
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 176.5, 170.7, 136.1, 136.0, 134.2, 129.0, 128.4, 128.0, 127.8, 127.8, 127.7, 126.8, 125.9, 124.2, 120.4, 120.0, 116.5, 66.6, 44.7, 44.7, 42.5, 25.7, 25.2.

HRMS (ESI) *m*/*z* calcd. for $C_{33}H_{29}NO_4SNa$ $[M + Na]^+$ 558.1718, found 558.1711

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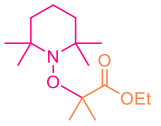
10. Radical trap experiments

Control experiment with TEMPO



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium benzothioate (35.2 mg, 0.20 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.40 mmol, 2.0 equiv) $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), **L*6** (19.75 mg, 0.03 mmol, 15 mol %), TEMPO (93.8 mg, 0.60 mmol, 3.0 equiv) and Cs_2CO_3 (195.6 mg, 0.60 mmol, 3.0 equiv), Then, diisopropyl ether (4.0 mL) was added by syringe under argon atmosphere. Finally, ethyl 2-bromo-2-methylpropanoate (55.7 µl, 0.40 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Upon completion, the reaction was filtered through a pad of celite and rinsed with DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afforded **64** (49.8 mg, 54% yield). No product **1** was observed.

Ethyl 2-methyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (64), these data are consistent with the literature.[12]



64

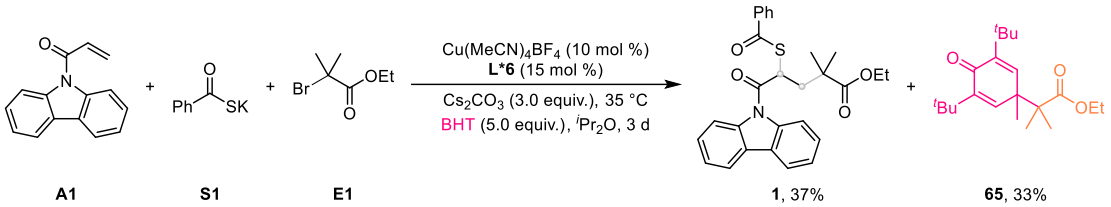
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (q, J = 7.1 Hz, 2H), 1.51 - 1.43(m, 12H), 1.31 (t, J = 7.1 Hz, 3H), 1.15 (s, 6H), 1.00 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 80.4, 60.0, 58.9, 40.0, 32.8, 23.7, 19.8, 16.4, 13.6.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{29}NO_3$ $[M + H]^+$ 272.2215, found 272.2219

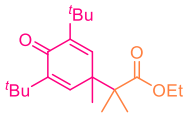
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Control experiment with BHT



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium benzothioate (35.2 mg, 0.20 mmol, 1.0 equiv), 1-(9H-carbazol-9-yl)prop-2-en-1-one (88.4 mg, 0.40 mmol, 2.0 equiv) $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), **L*6** (19.75 mg, 0.03 mmol, 15 mol %), BHT (220.4 mg, 1.0 mmol, 5.0 equiv) and Cs_2CO_3 (195.50 mg, 0.60 mmol, 3.0 equiv), Then, diisopropyl ether (4.0 mL) was added by syringe under argon atmosphere. Finally, ethyl 2-bromo-2-methylpropanoate (55.7 µl, 0.40 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Upon completion, the reaction was filtered through a pad of celite and rinsed with DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afforded **65** (44.0 mg, 33% yield) and product **1** (35.0 mg, 37% yield)

Ethyl 2-(3,5-di-*tert*-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (65), these data are consistent with the literature[13].



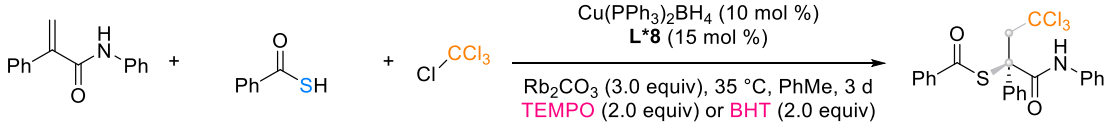
65

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.31 – 1.28 (m, 3H), 1.24 (s, 18H), 1.21 (s, 3H), 1.15 (s, 6H).

HRMS (ESI) *m/z* calcd. for $C_{21}H_{34}O_3Na$ $[M + Na]^+$ 357.2400, found 357.2399

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Control experiment with TEMPO and BHT

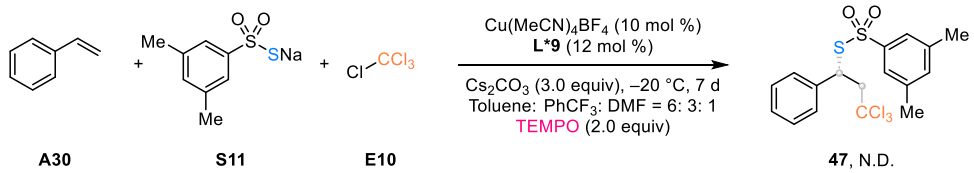


A6 **S10** **E10** **24**, N.D.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with N,2-diphenylacrylamide (44.6 mg, 0.20 mmol, 1.0 equiv), benzothioic S-acid (35.3 μL, 0.30 mmol, 1.5 equiv), $Cu(PPh_3)_2BH_4$ (12.0 mg, 0.02 mmol, 10 mol %), TEMPO (93.8 mg, 0.60 mmol, 3.0 equiv) or BHT (220.4 mg, 1.0 mmol, 5.0 equiv) **L*8** (11.67 mg, 0.03 mmol, 15 mol %) and Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), Then, Toluene (4.0 mL) was added by syringe under argon atmosphere. Finally, perchloromethane (96.7 μL, 1.0 mmol, 5.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. No product **24** was observed.

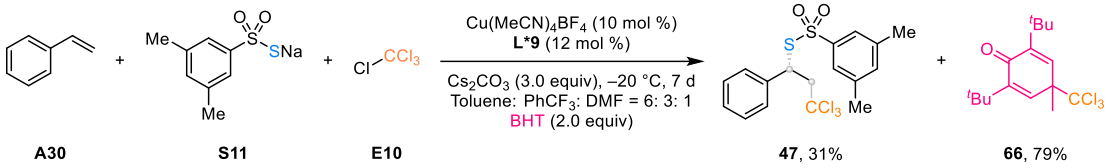
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Control experiment with TEMPO



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), styrene (23 μL, 0.2 mmol, 1.0 equiv) $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), TEMPO (93.8 mg, 0.60 mmol, 3.0 equiv), **L*9** (16.6 mg, 0.024 mmol, 12 mol %) and Cs_2CO_3 (195.50 mg, 0.60 mmol, 3.0 equiv), Then, Toluene/$PhCF_3$/DMF (2.0 mL, (v/v/v = 6:3:1)) was added by syringe under argon atmosphere. Finally, tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –20 °C. No product **47** was observed.

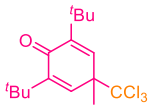
Control experiment with BHT



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), styrene (23 μL, 0.2 mmol, 1.0 equiv) $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), BHT (220.4 mg, 1.0 mmol, 5.0 equiv), **L*9** (16.6 mg, 0.024 mmol, 12 mol %) and Cs_2CO_3 (195.50 mg, 0.60 mmol, 3.0 equiv), Then, Toluene/$PhCF_3$/DMF (2.0 mL, (v/v/v = 6:3:1)) was added by syringe under argon atmosphere. Finally, tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –20 °C. Upon completion, the reaction was filtered through a pad of celite and rinsed with DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **66** (53.1 mg, 79% yield) and product **47** (26.1 mg, 31% yield).

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2,6-Di-*tert*-butyl-4-methyl-4-(trichloromethyl)cyclohexa-2,5-dien-1-one (66), these data are consistent with the literature[14].



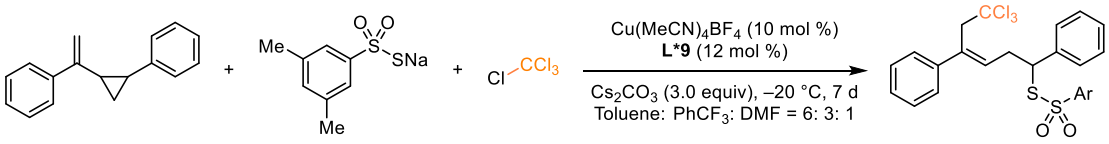
66

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 2H), 2.27 (s, 3H), 1.43 (s, 18H).

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{23}Cl_3ONa$ $[M + Na]^+$ 359.0707, found 359.0705

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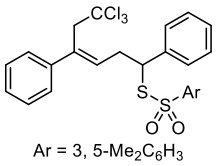
Radical clock experiment



A44 **S11** **E10**

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sodium 3,5-dimethylbenzenesulfonothioate (53.8 mg, 0.24 mmol, 1.2 equiv), (1-(2-phenylcyclopropyl)vinyl)benzene (44.0 mg, 0.2 mmol, 1.0 equiv), $Cu(MeCN)_4BF_4$ (6.28 mg, 0.02 mmol, 10 mol %), **L*9** (16.6 mg, 0.024 mmol, 12 mol %) and Cs_2CO_3 (195.50 mg, 0.60 mmol, 3.0 equiv), Then, Toluene/$PhCF_3$/DMF (2.0 mL, (v/v/v = 6/3/1)) was added by syringe under argon atmosphere. Finally, tetrachloromethane (29 μL, 0.3 mmol, 1.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –20 °C. Upon completion, the reaction was filtered through a pad of celite and rinsed with DCM. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **67** (35.0 mg, 37% yield).

(*E*)-*S*-(6,6,6-trichloro-1,4-diphenylhex-3-en-1-yl) 3,5-dimethylbenzenesulfonothioate (67).



67

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.23 (m, 4H), 7.23 – 7.11 (m, 10H), 7.05 (d, J = 5.5 Hz, 1H), 7.00 (ddd, J = 9.9, 7.6, 1.6 Hz, 1H), 5.75 (t, J = 7.3 Hz, 1H), 4.64 (dd, J = 8.2, 6.7 Hz, 1H), 3.77 (d, J = 2.2 Hz, 2H), 3.08 – 2.86 (m, 2H), 2.25 (s, 6H), 2.23 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 142.5, 139.1, 138.8, 137.0, 135.1, 132.4, 128.6, 128.4, 128.2, 127.9, 127.5, 127.1, 124.3, 124.3, 98.4, 55.4, 53.8, 36.9, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}Cl_3O_2S_2Na$ $[M + Na]^+$ 561.0254, found 561.0254

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Control Experiments for Kinetic Studies.

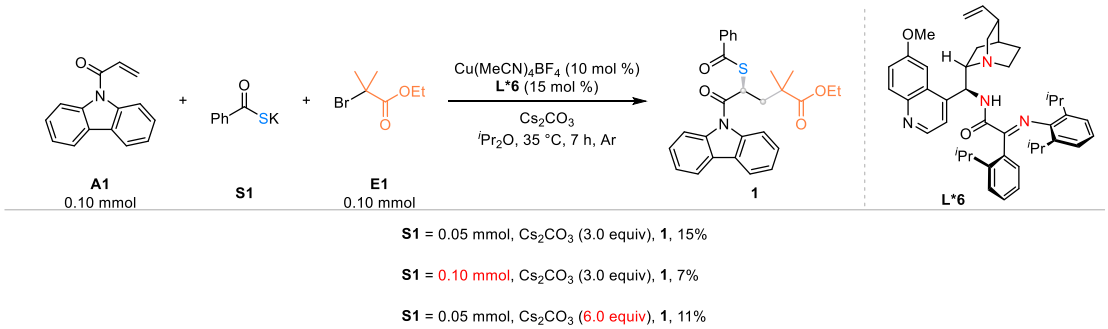
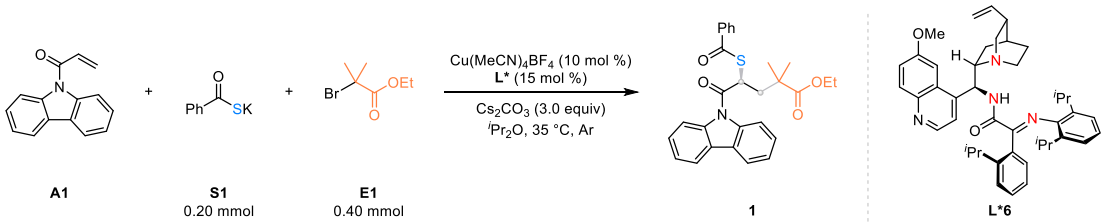


Figure S10. Control Experiments with Varying Equivalents of Sulfur Salt and Base.

Because the sulfur nucleophile **S1** and the base are introduced as ionic salts, their solubility and the resulting heterogeneity of the reaction mixture make rigorous determination of their kinetic orders by variable time normalization analysis (VTNA) challenging. We therefore first performed comparative experiments to assess their effects on the reaction. Increasing the loading of **S1** led to a gradual decrease in the reaction rate, indicating an inhibitory effect of the sulfur nucleophile. In contrast, increasing the amount of base resulted in only a slight improvement in the product yield, suggesting that the base loading has a relatively minor effect on the overall reaction efficiency under the conditions examined.

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Kinetic experiments were conducted to determine the dependence of the reaction rate on the concentration of acrylamide A1[15].



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium thiocarboxylates (0.20 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (0.05–0.1 mmol, 0.25–0.50 equiv), $Cu(MeCN)_4BF_4$ (0.02 mmol, 10 mol %), **L*6** (0.03 mmol, 15 mol %) ,1,3,5-Trimethoxybenzene (0.20 mmol, 1.0 equiv) and Cs_2CO_3 (0.60 mmol, 3.0 equiv), Then, diisopropyl ether (4.0 mL) was added by syringe under argon atmosphere. Finally, ethyl 2-bromo-2-methylpropanoate (0.40 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Aliquots (~100 μL) were taken from reaction mixture at various reaction times, the product was filtered off and washed by $CHCl_3$ for three times. The combined organic layers was concentrated to afford crude product. The yield of **A1** and **1** were analyzed by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S6. Concentrations of Starting Material **A1** and Product **1** at Different Time Points ($\times 10^{-3}$ M). [**A1**] = 0.05 mmol.

Time (h)	**A1** [M]	**1** [M]
2	7	1.75
4	5.625	2.75
6	5.125	4
8	4.25	4.625
10	3.875	5.25

Table S7. Concentrations of Starting Material **A1** and Product **1** at Different Time Points ($\times 10^{-3}$ M). [**A1**] = 0.10 mmol.

Time (h)	**A1** [M]	**1** [M]
2	15	3.875
4	12.25	5.625
6	10.375	7.375
8	8.375	8.5
10	8	9.75

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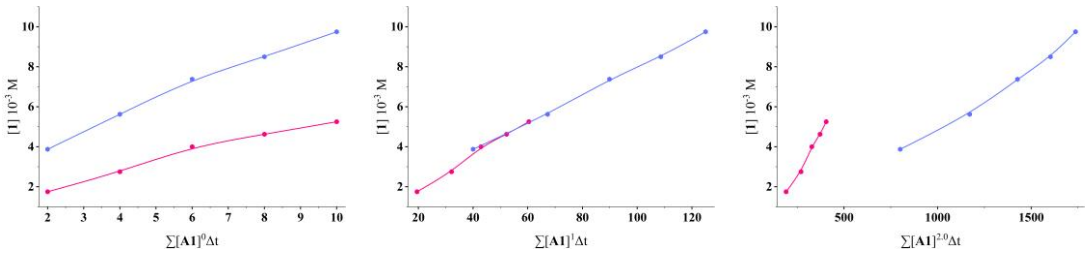
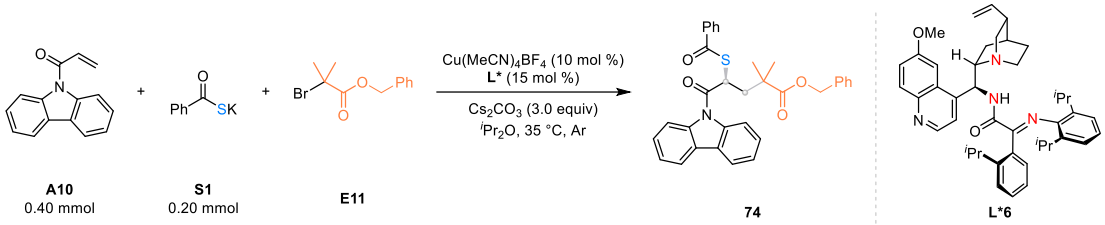


Figure S11. Variable time normalization analysis (VTNA) enables the determination of the reaction order with respect to substrate **A1**.

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Kinetic experiments were conducted to determine the dependence of the reaction rate on the concentration of E11[15].



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium thiocarboxylates (0.20 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (0.40 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (0.02 mmol, 10 mol %), **L*6** (0.03 mmol, 15 mol %) ,1,3,5-Trimethoxybenzene (0.20 mmol, 1.0 equiv) and Cs_2CO_3 (0.60 mmol, 3.0 equiv), Then, diisopropyl ether (4.0 mL) was added by syringe under argon atmosphere. Finally, benzyl 2-bromo-2-methylpropanoate (0.05–0.1 mmol, 0.25–0.50 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Aliquots (~100 μL) were taken from reaction mixture at various reaction times, the product was filtered off and washed by $CHCl_3$ for three times. The combined organic layers were concentrated to afford crude product. The yield of **E11** and **74** were analyzed by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S8. Concentrations of Starting Material **E11** and Product **75** at Different Time Points ($\times10^{-3}$ M). [**E11**] = 0.05 mmol.

Time (h)	**E11** [M]	**74** [M]
2	6.5625	0.25
4	4.4375	1
6	2.125	1.75
8	1.5	2.0625
10	1.25	2.1875

Table S9. Concentrations of Starting Material **E11** and Product **75** at Different Time Points ($\times10^{-3}$ M). [**E11**] = 0.10 mmol

Time (h)	**E11** [M]	**74** [M]
2	17.0625	0
4	14.9375	1
6	13.0625	1.75
8	11.0625	2.5
10	10.3125	3.25

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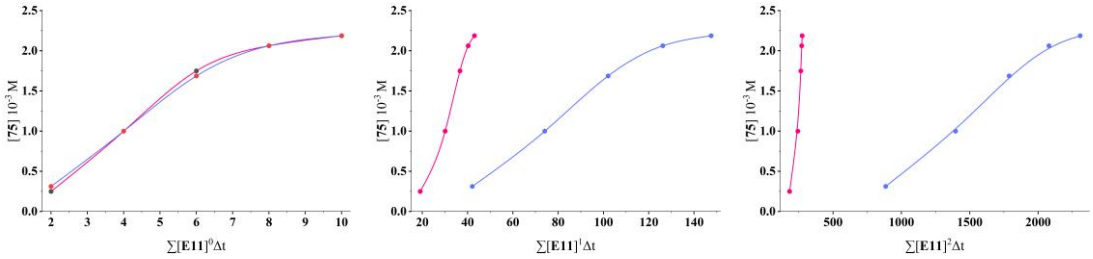
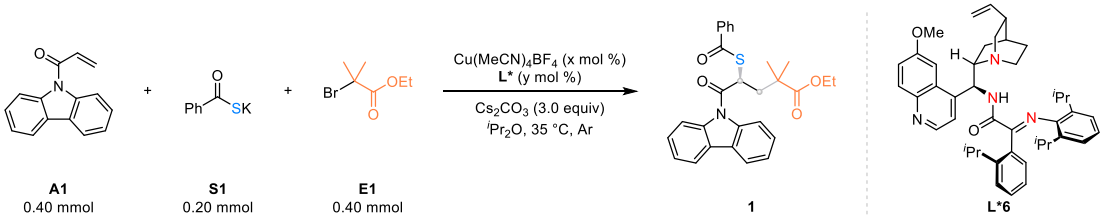


Figure S12. Variable time normalization analysis (VTNA) enables the determination of the reaction order with respect to substrate **E11**.

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Kinetic experiments were conducted to determine the dependence of the reaction rate on the concentration of catalyst([Cu/L*])[15].



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with potassium thiocarboxylates (0.20 mmol, 1.0 equiv), 1-(9*H*-carbazol-9-yl)prop-2-en-1-one (0.20 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (5–10 mol %), **L*6** (7.5–15 mol %) ,1,3,5-Trimethoxybenzene (0.20 mmol, 1.0 equiv) and Cs_2CO_3 (0.60 mmol, 3.0 equiv), Then, diisopropyl ether (4.0 mL) was added by syringe under argon atmosphere. Finally, ethyl 2-bromo-2-methylpropanoate (0.40 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at 35 °C. Aliquots (~100 μL) were taken from reaction mixture at various reaction times, the product was filtered off and washed by $CHCl_3$ for three times. The combined organic layers were concentrated to afford crude product. The yield of **A1** and **1** were analyzed by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S10. Concentrations of Starting Material **A1** and Product **1** at Different Time Points ($\times 10^{-3}$ M). [Cu/**L***] = 10% mol

Time (h)	**A1** [M]	**1** [M]
2	35.125	0.625
4	28	2
8	23.75	3.125
12	20.875	4.125
24	17	5.375

Table S11. Concentrations of Starting Material **A1** and Product **1** at Different Time Points ($\times 10^{-3}$ M). [Cu/**L***] = 5% mol

Time (h)	**A1** [M]	**1** [M]
2	50.5	0
4	49.125	1
8	39.75	1.75
12	36.125	2.5
24	30.875	3.25

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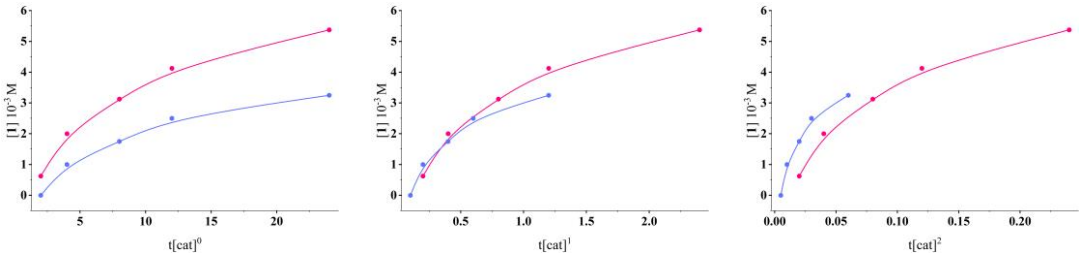


Figure S13. Variable time normalization analysis (VTNA) enables the determination of the reaction order with respect to [Cu/**L***].

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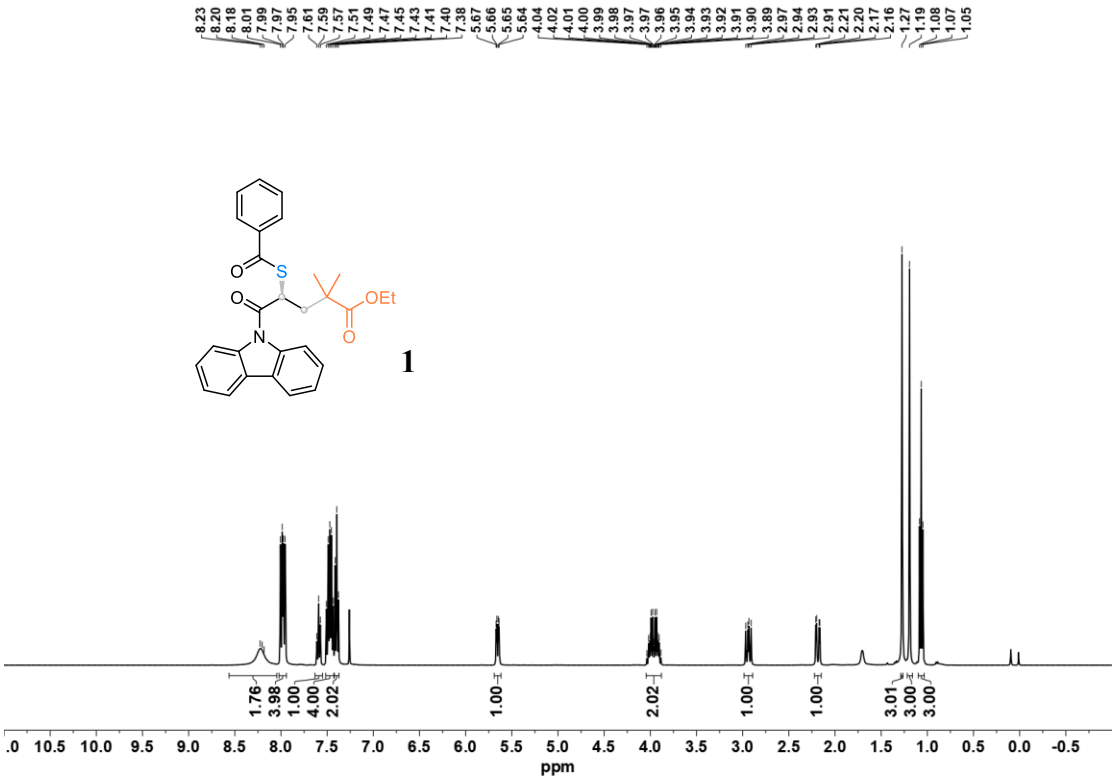
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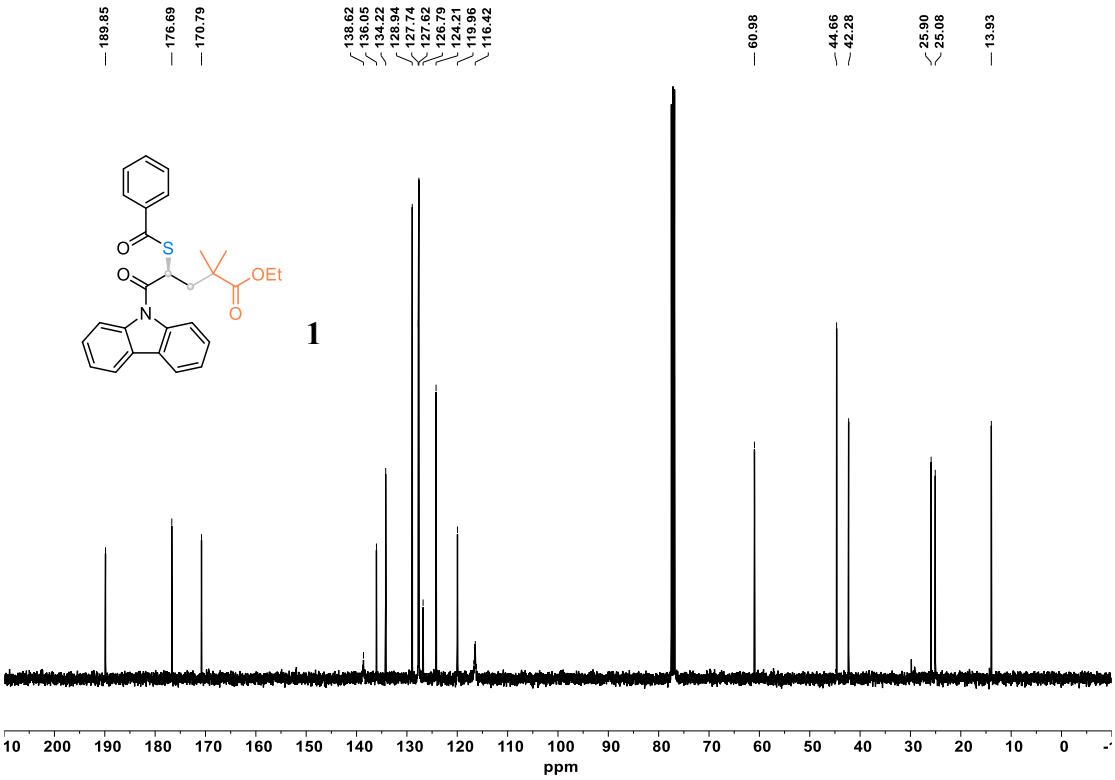
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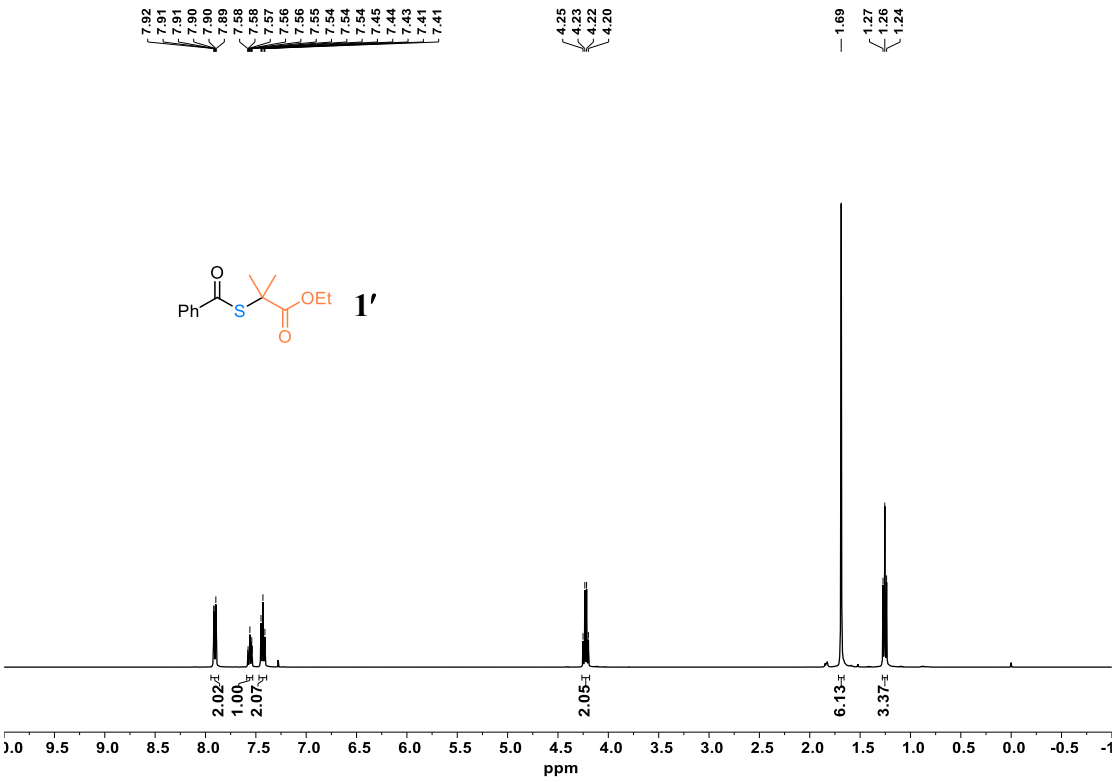
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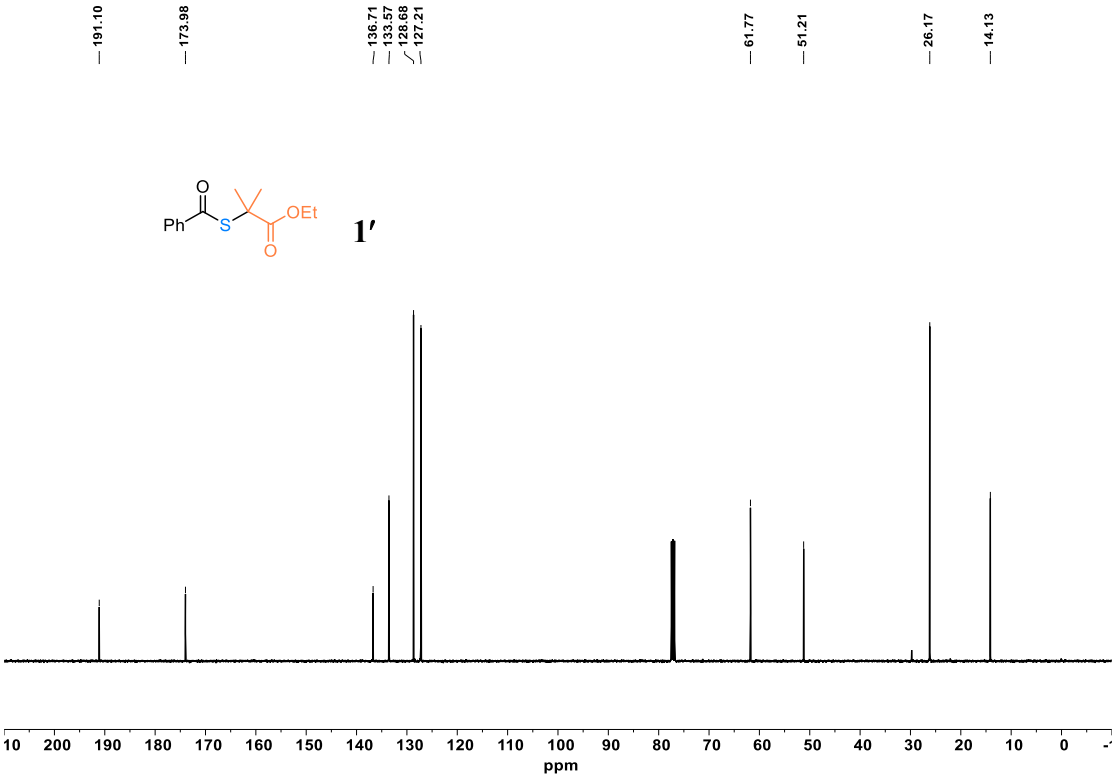
12. NMR spectrum



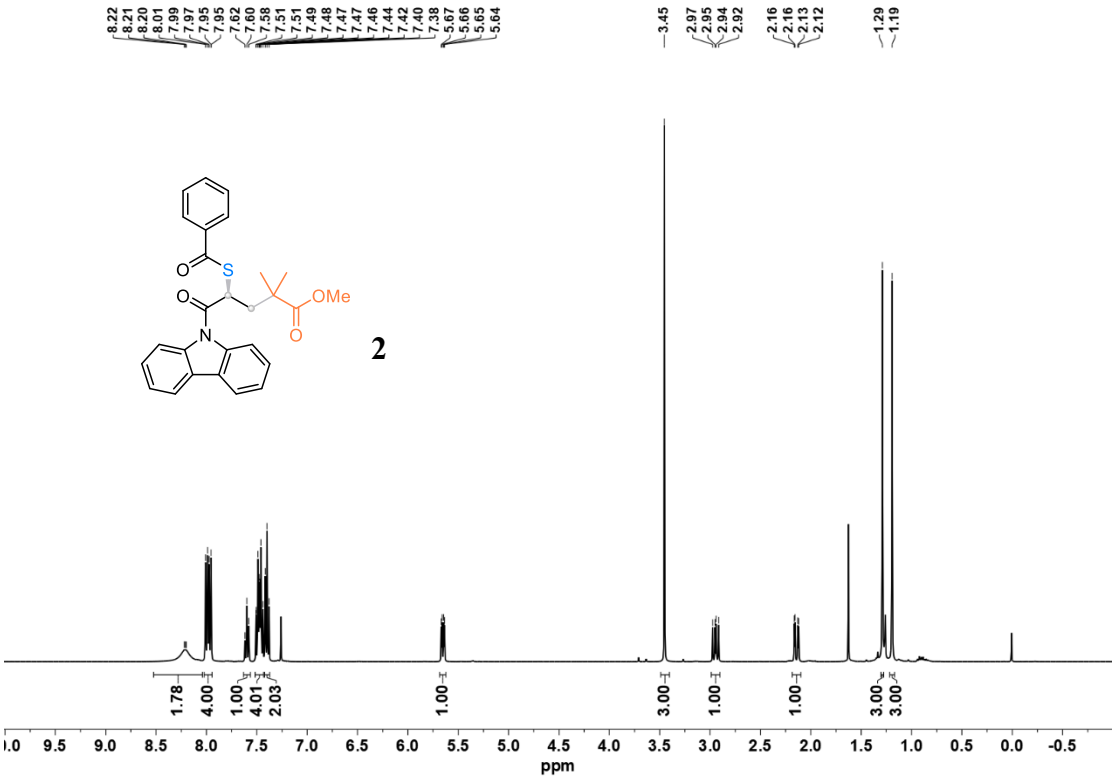


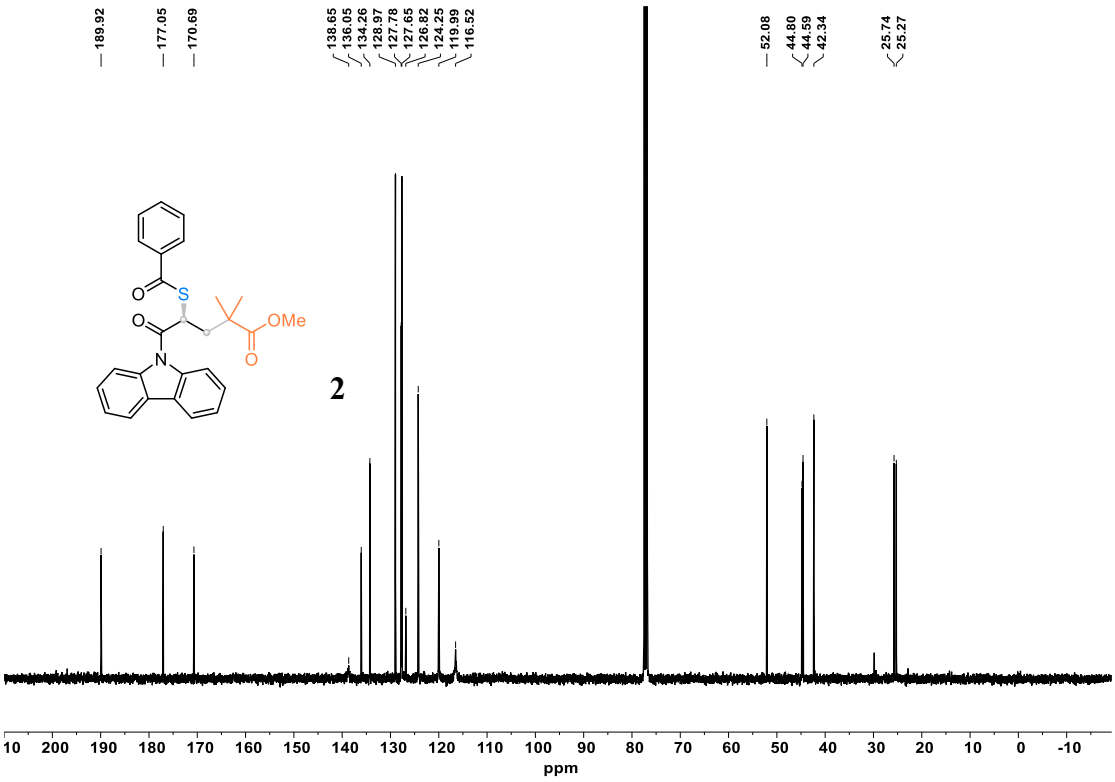
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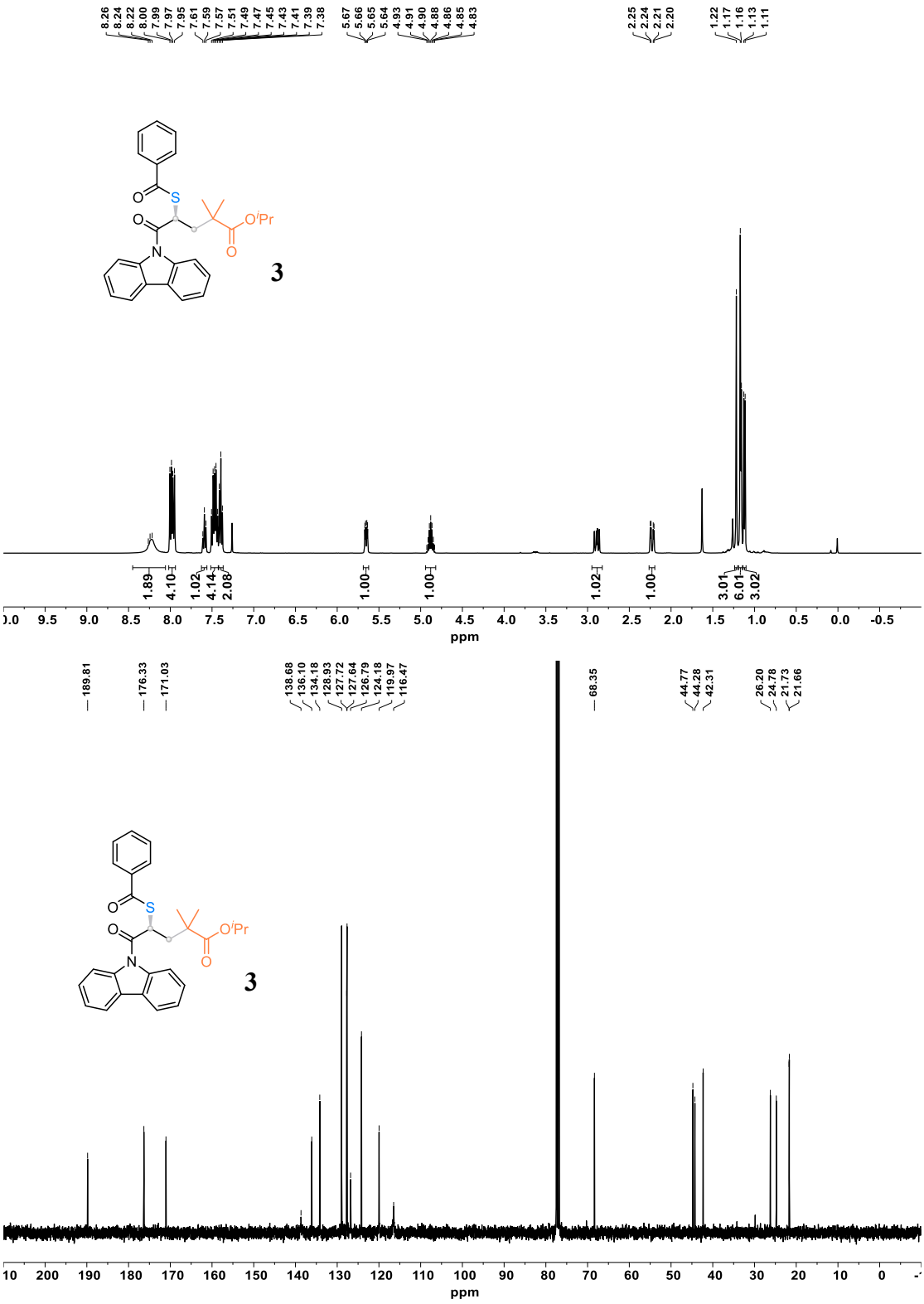


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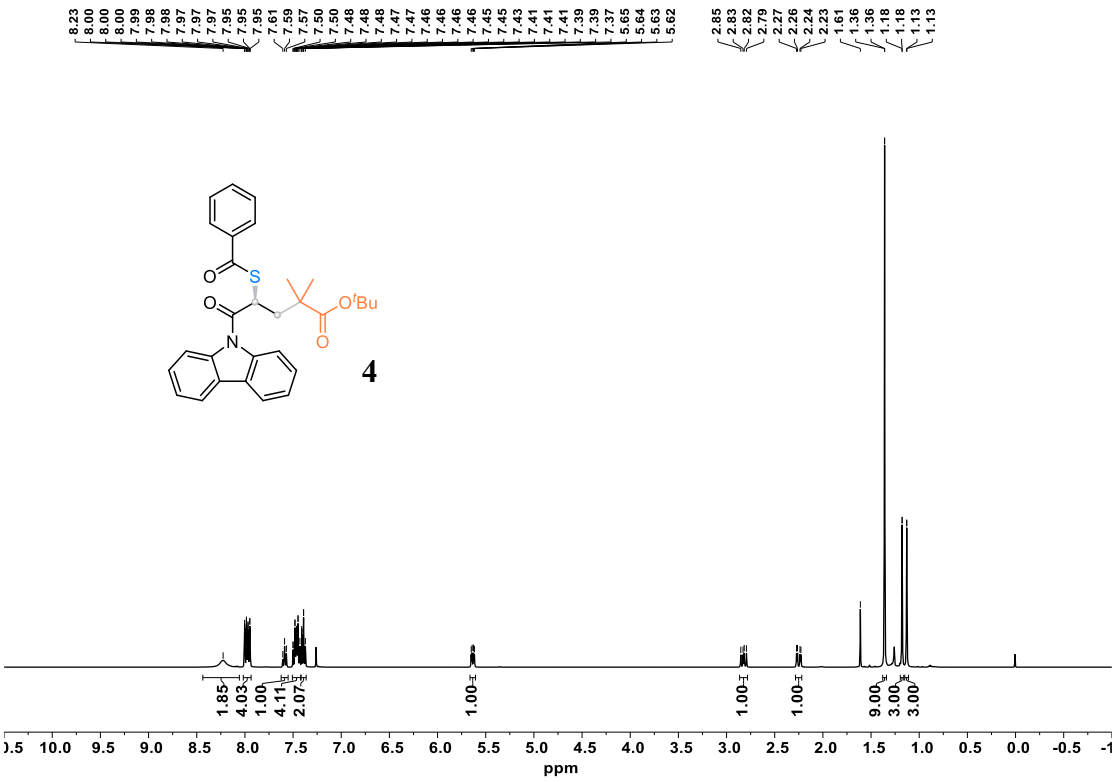


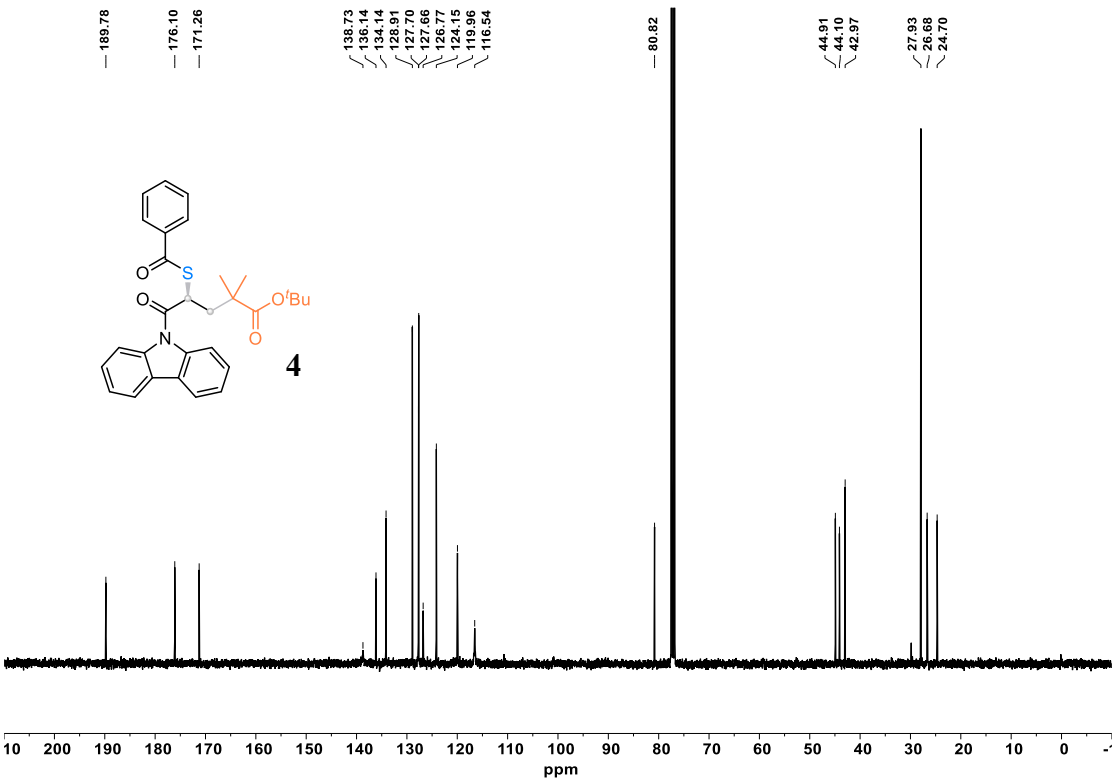


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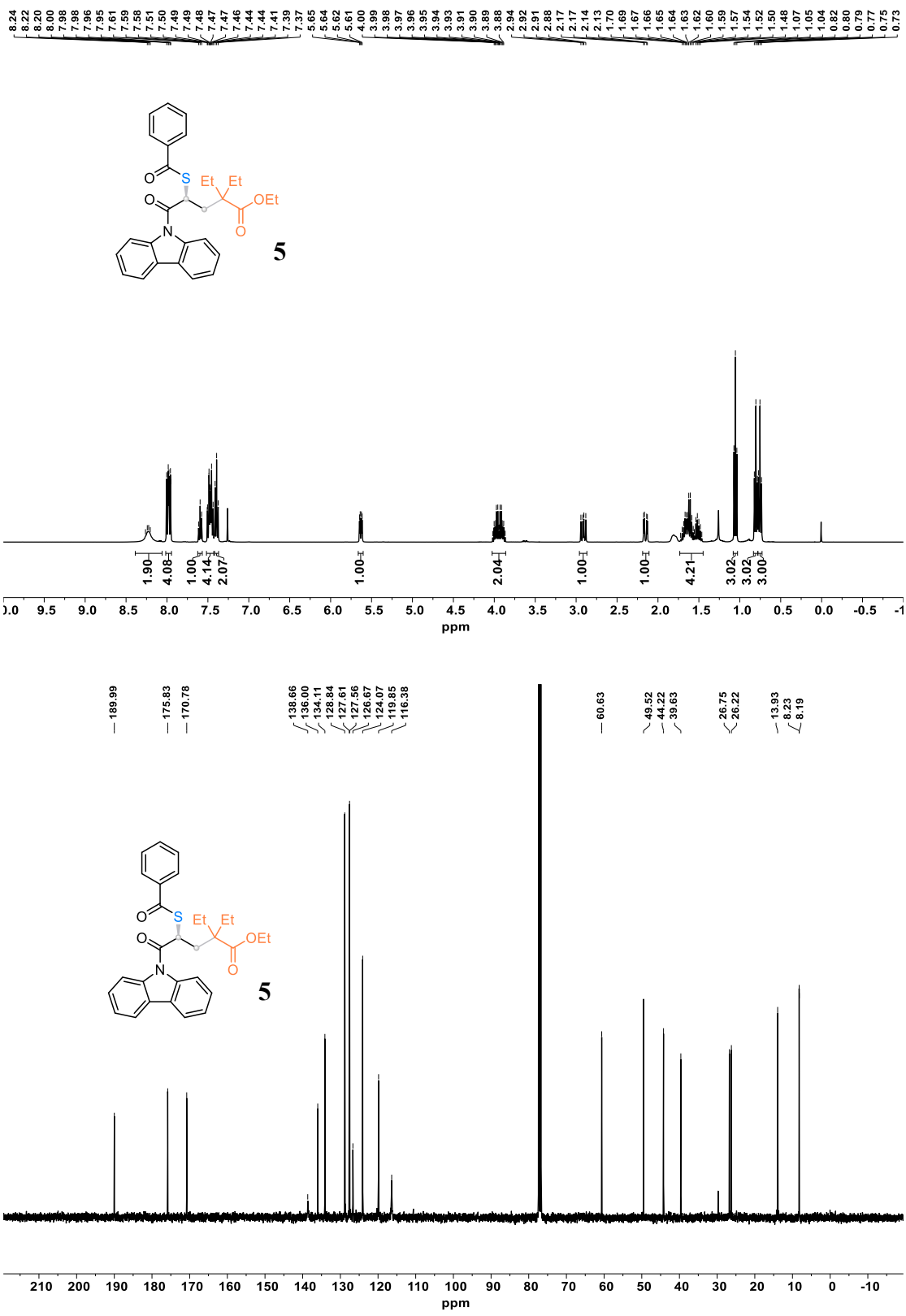


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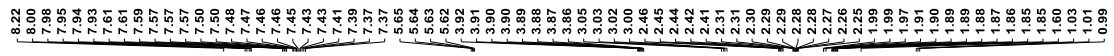


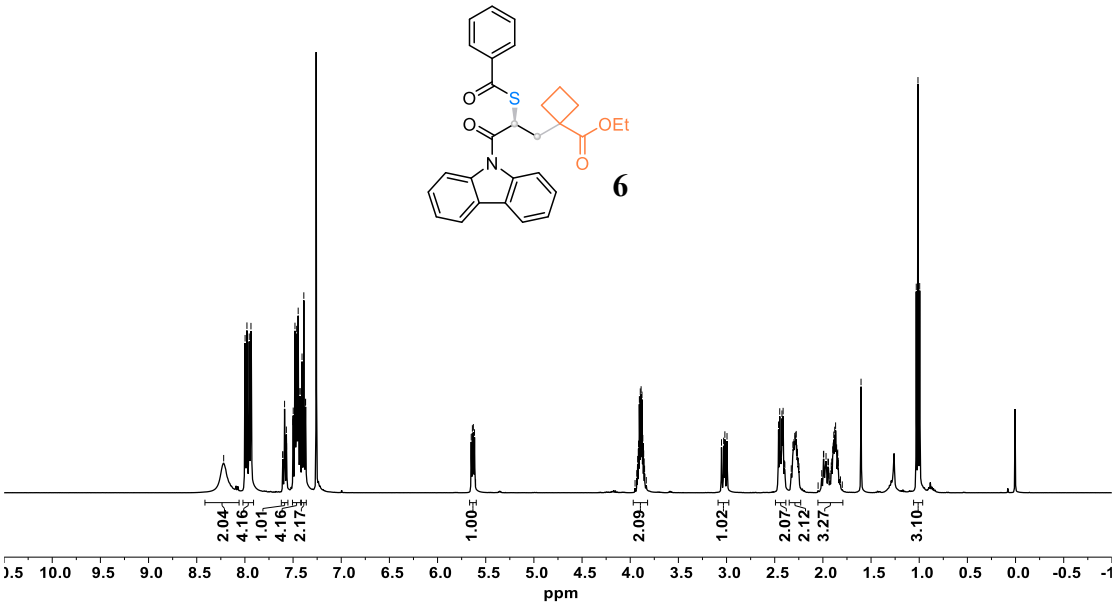


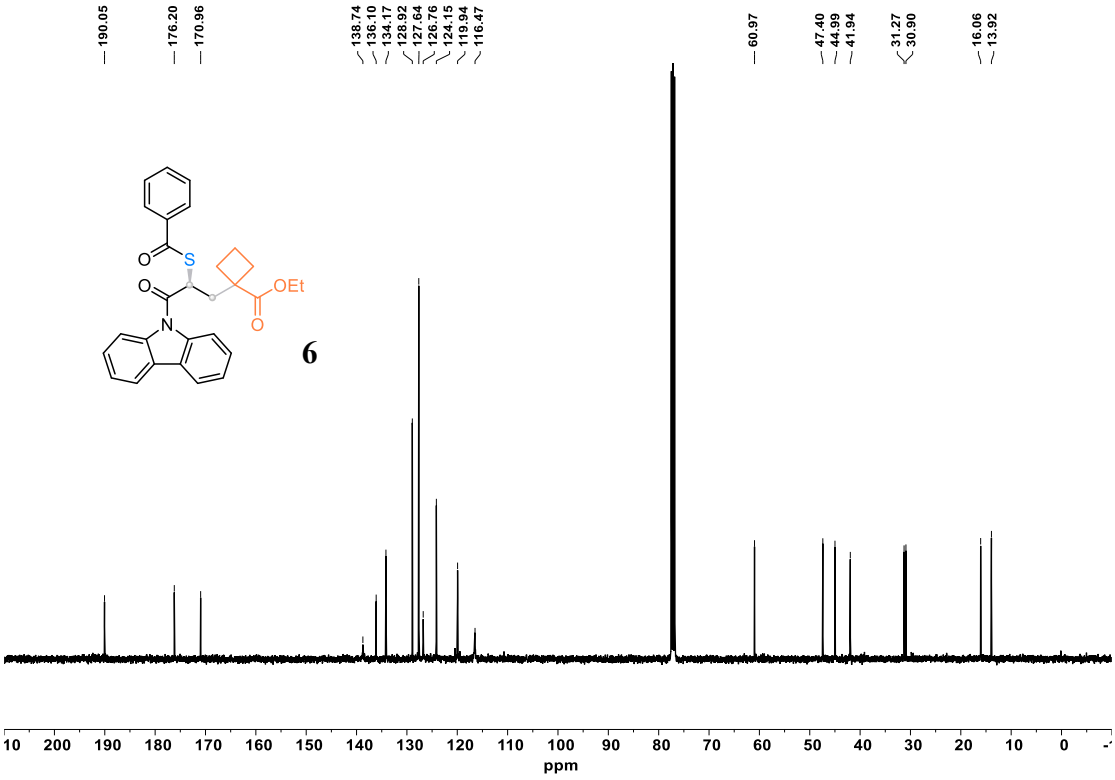
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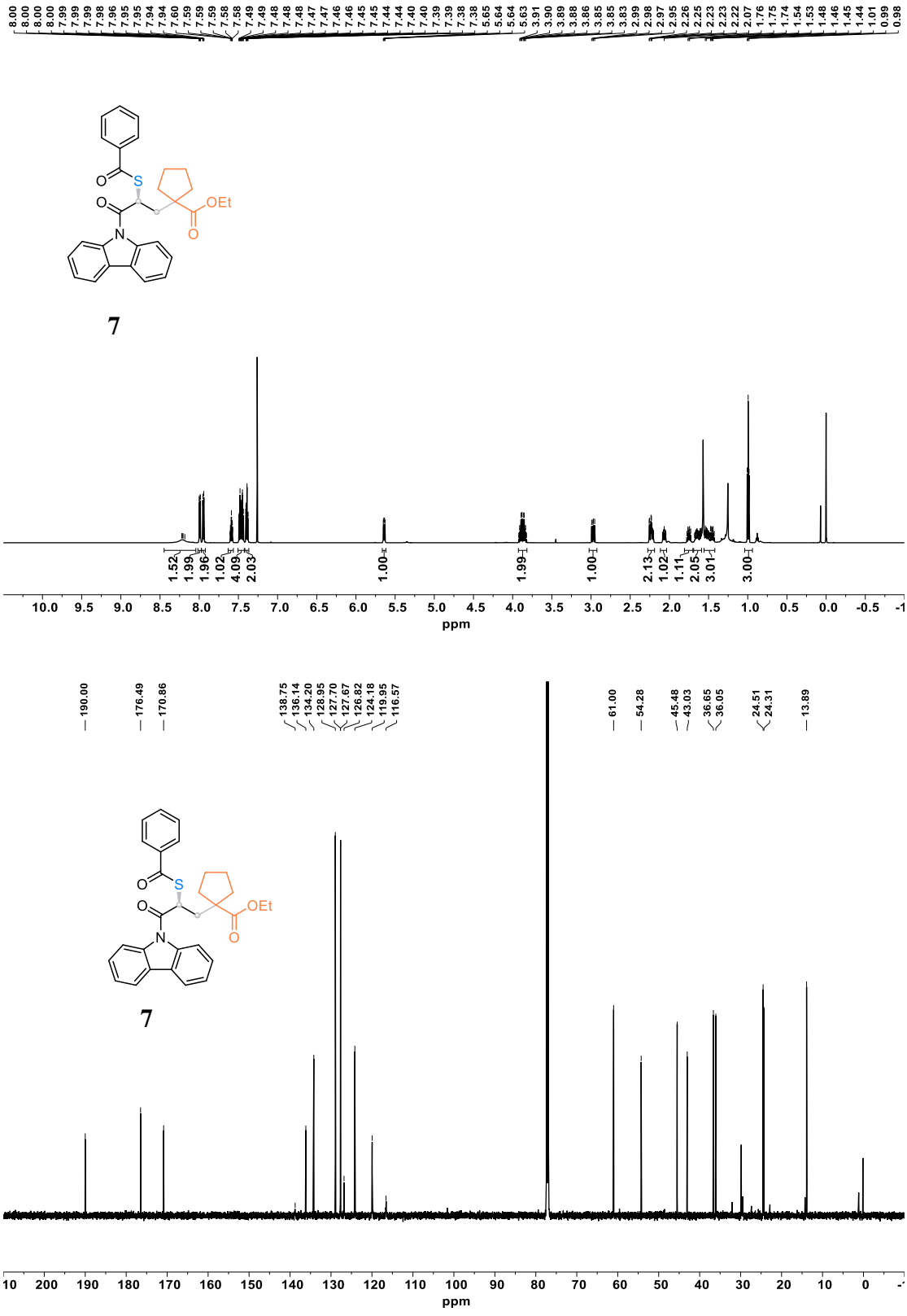
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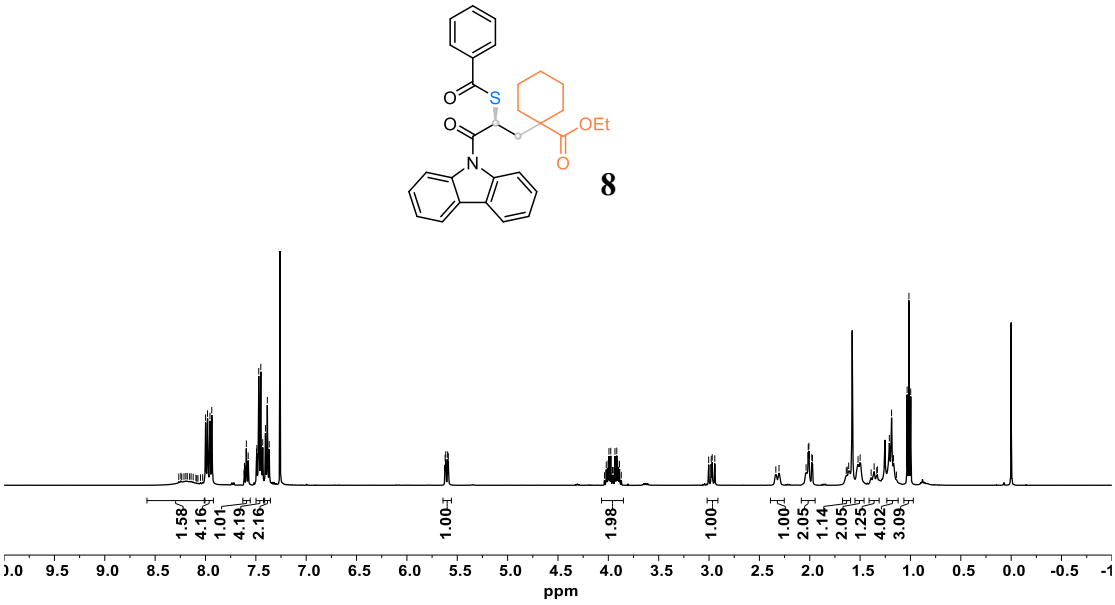


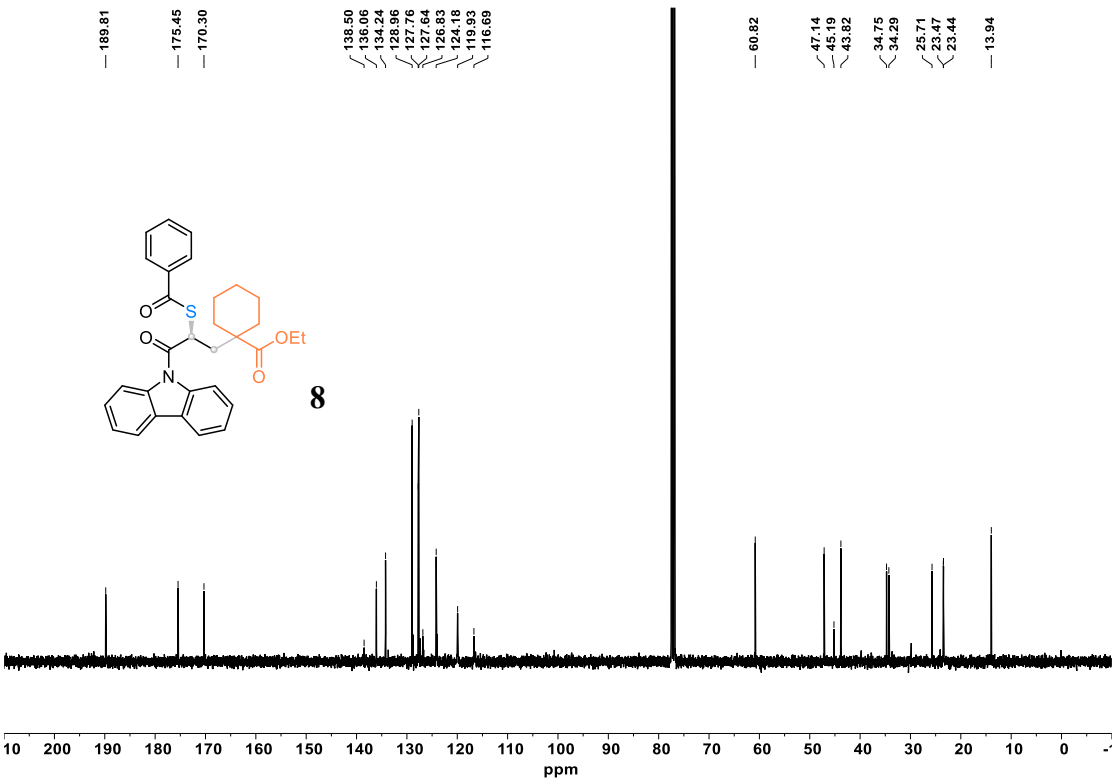
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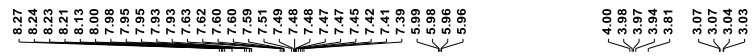
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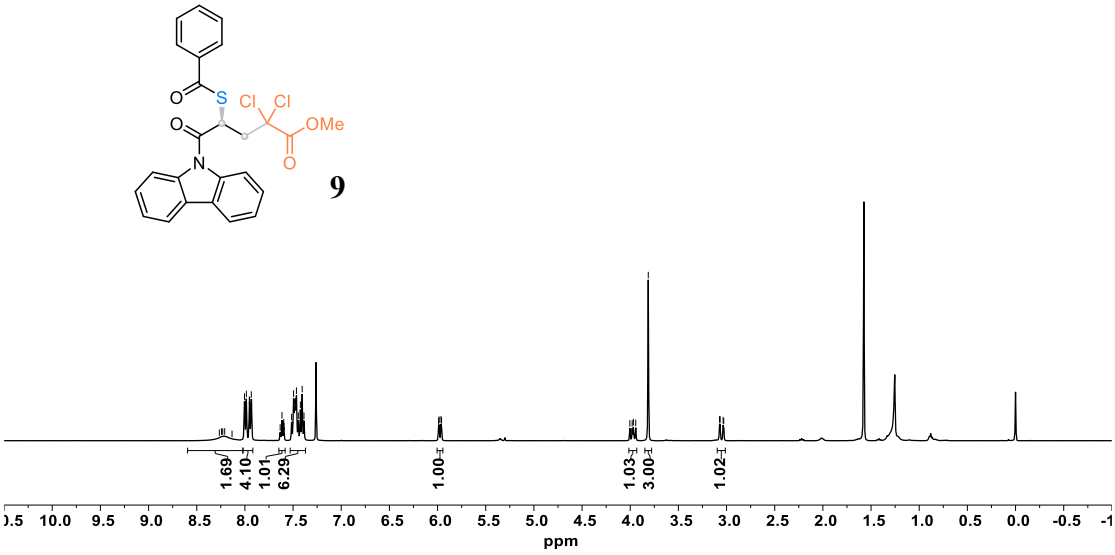


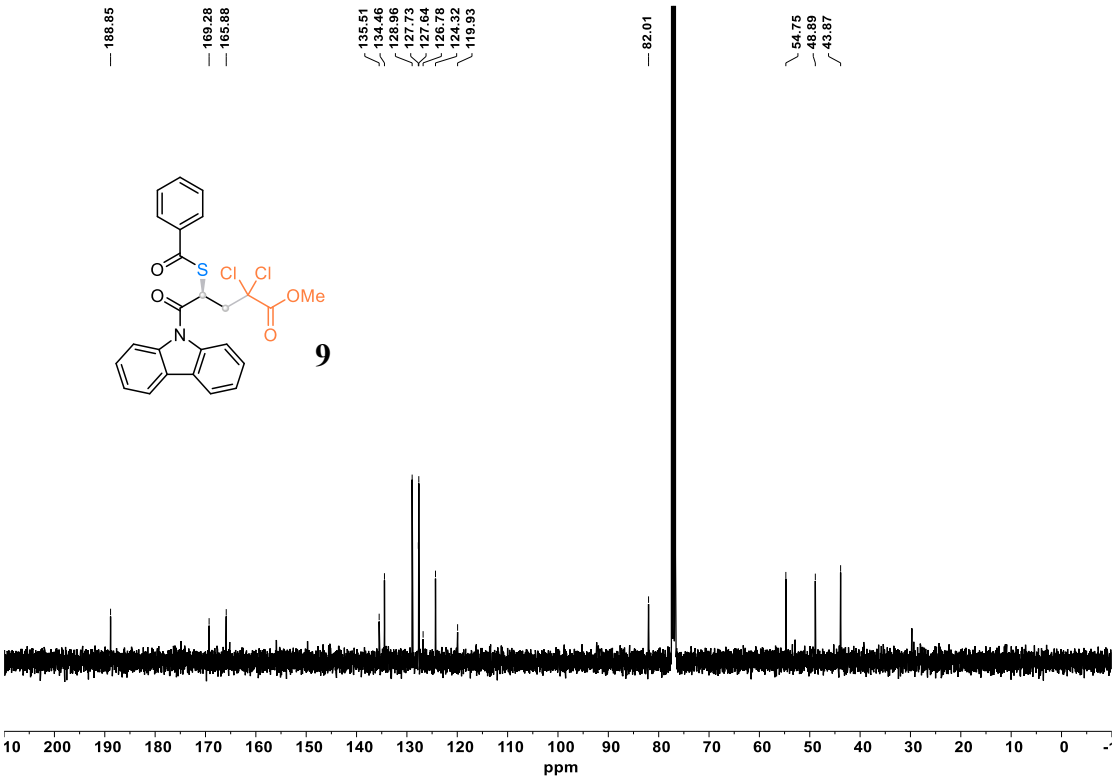




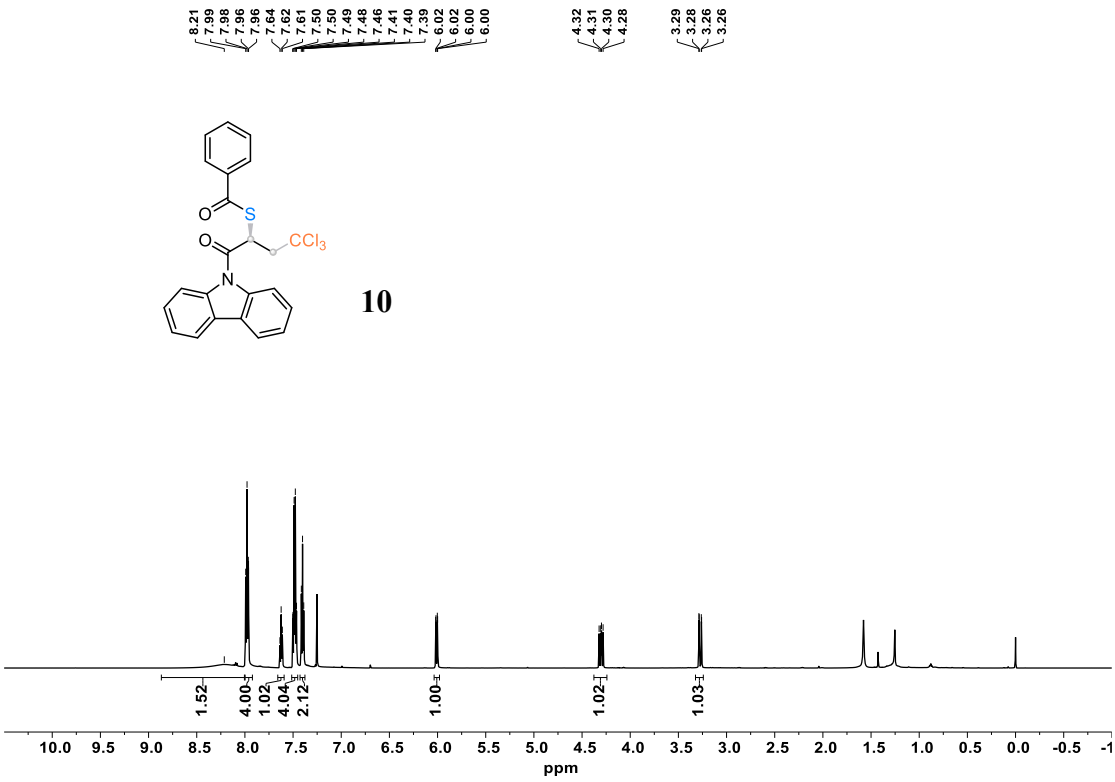
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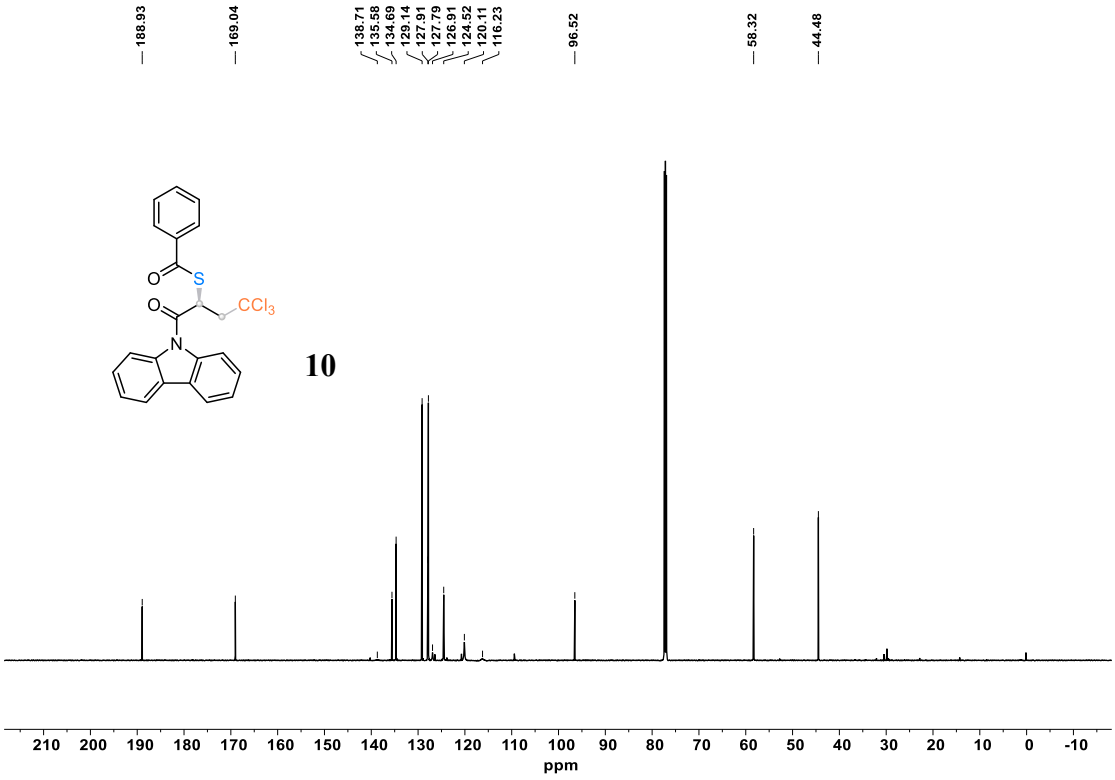




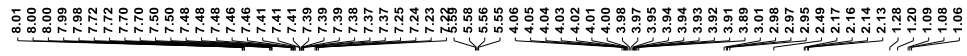


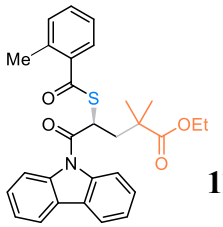
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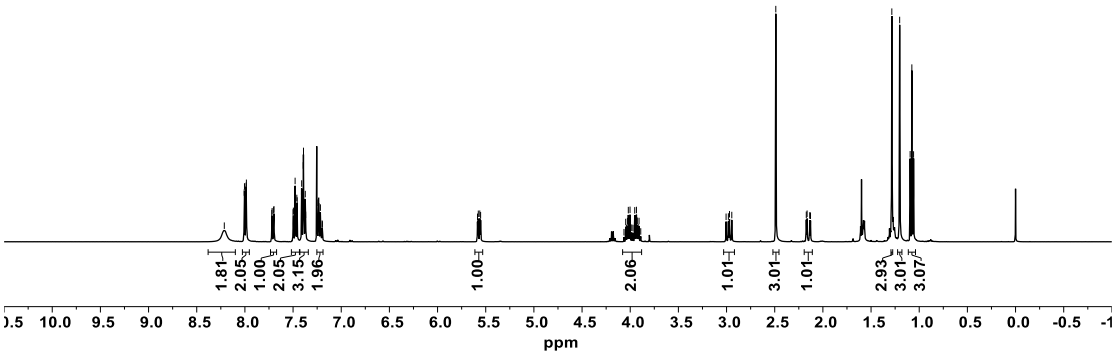


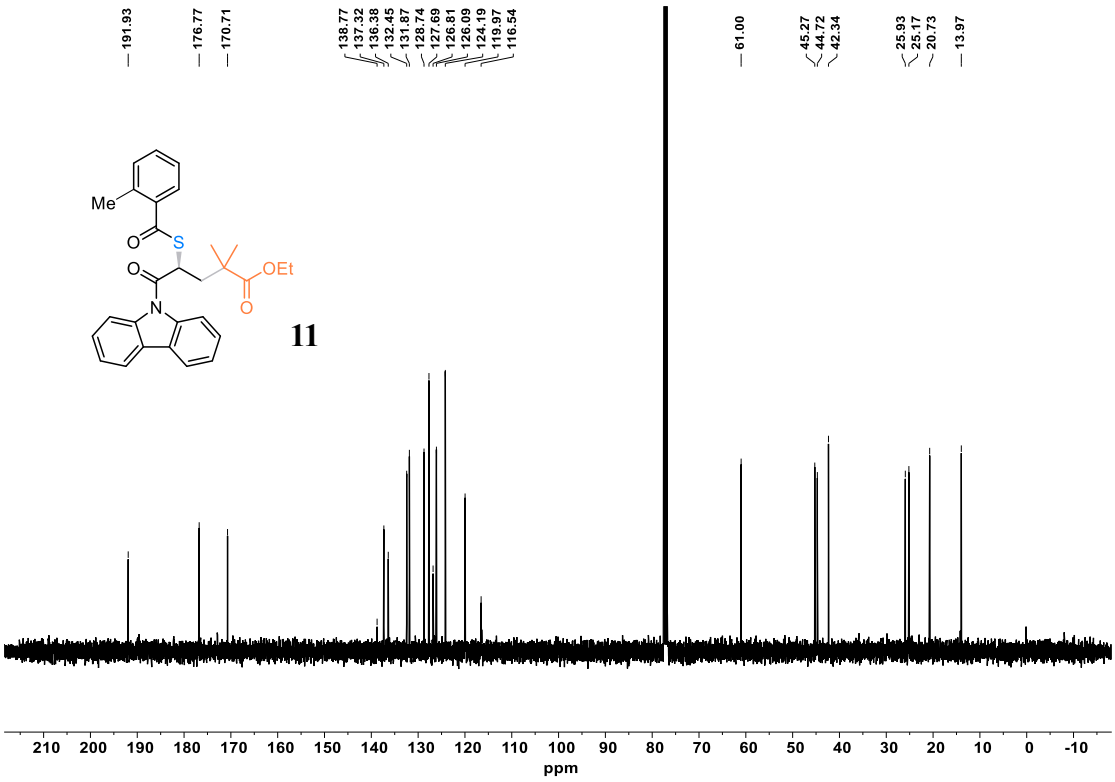
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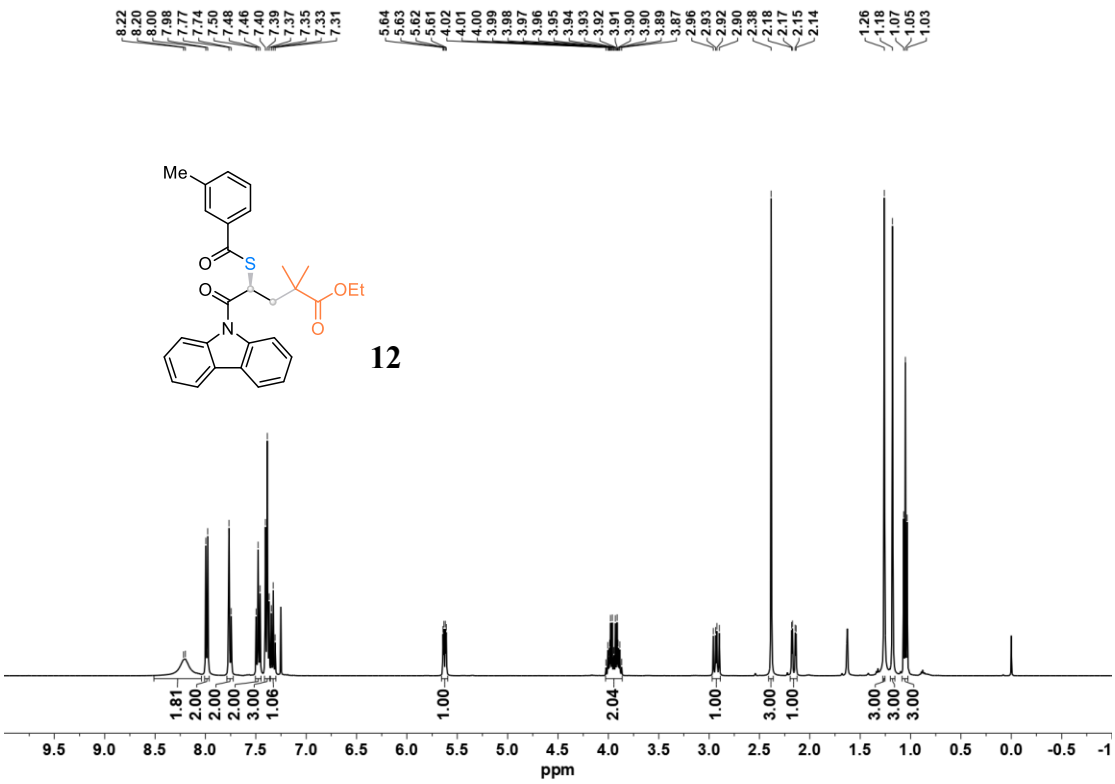
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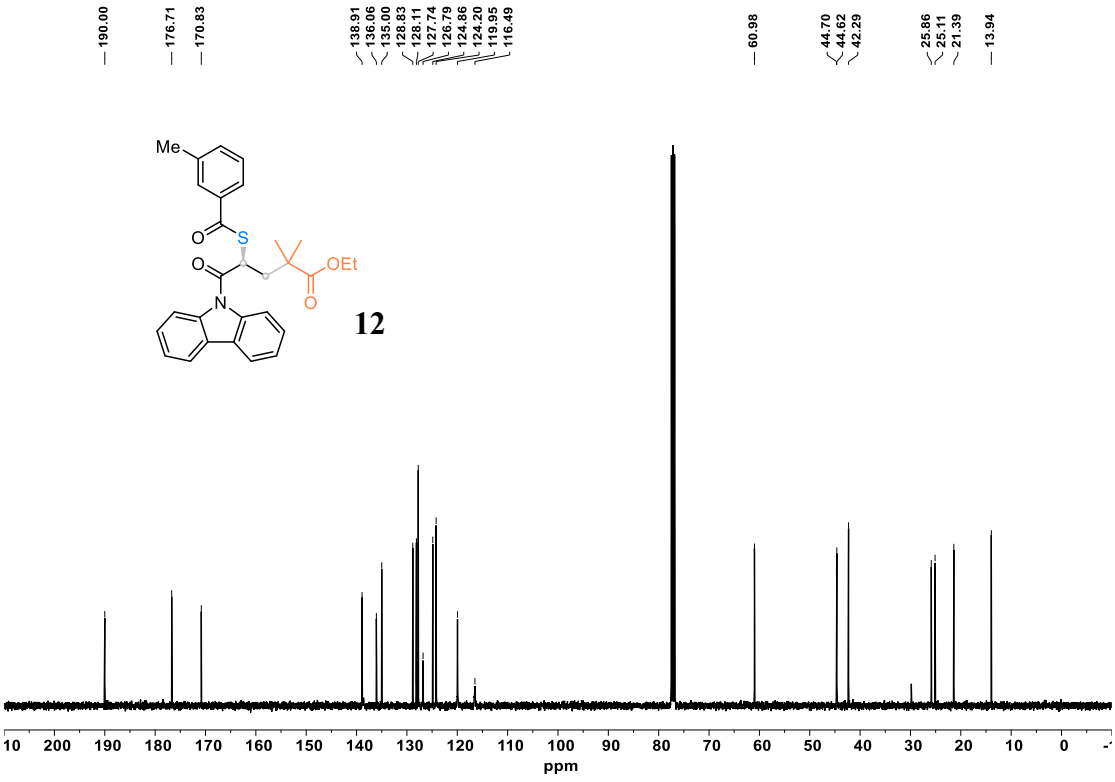




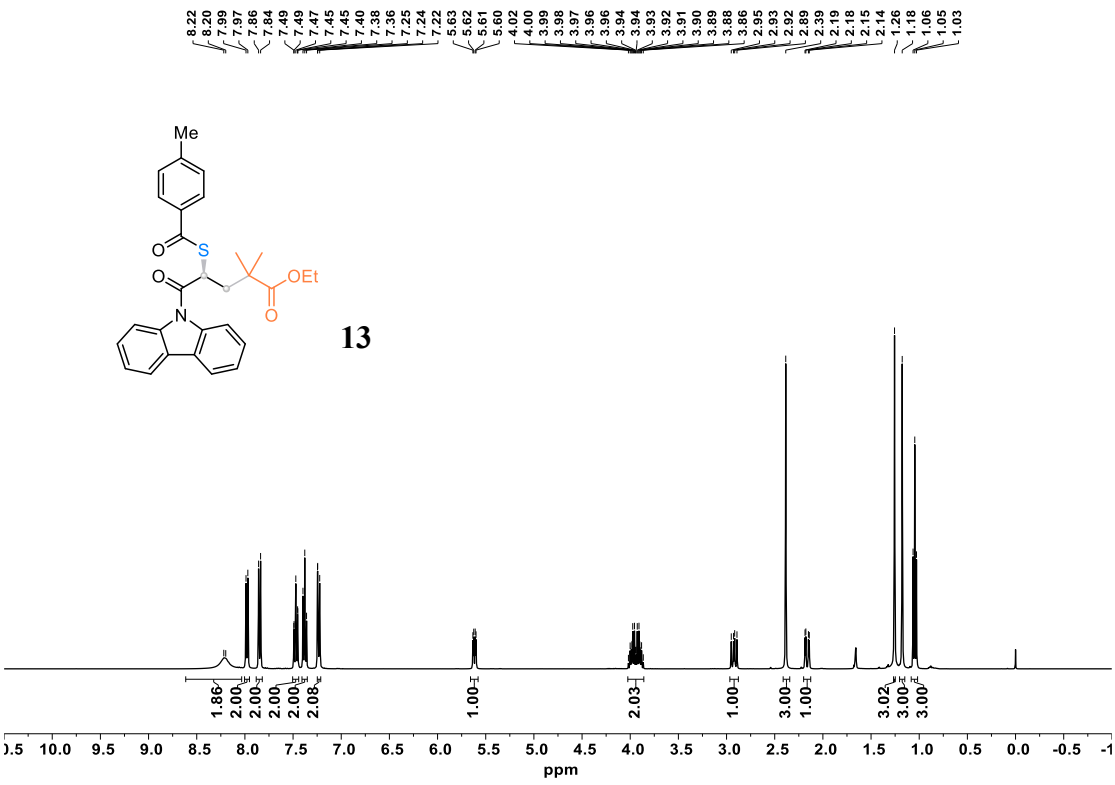
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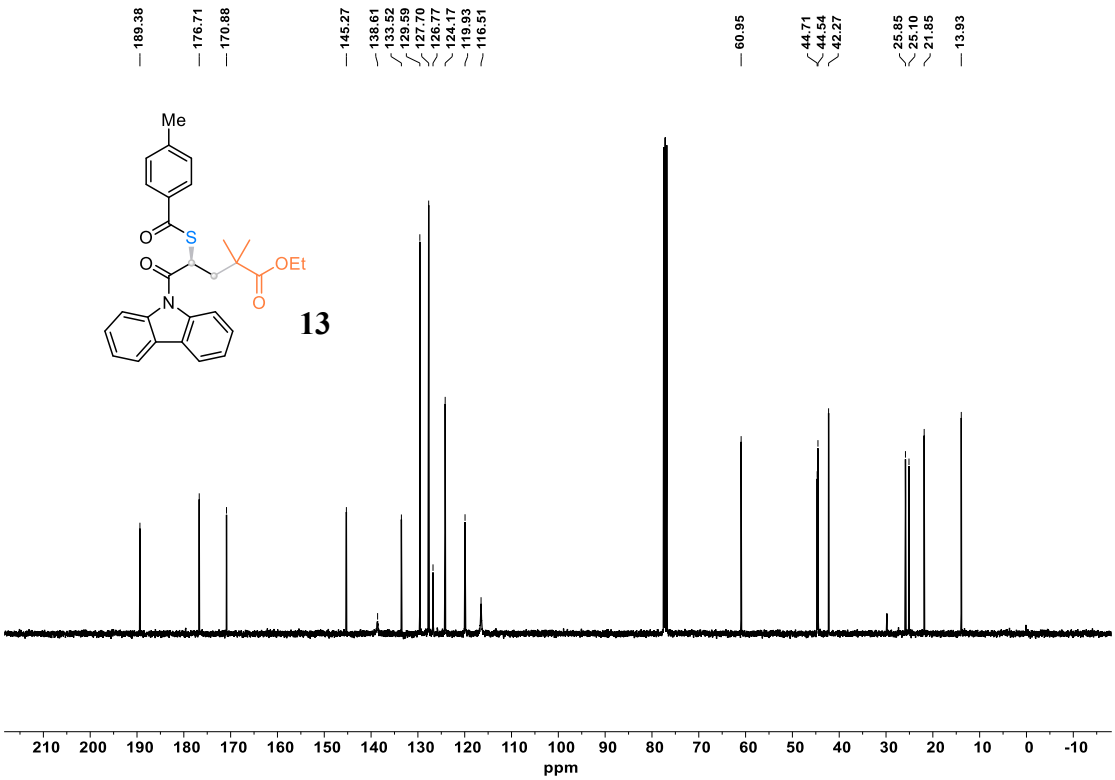
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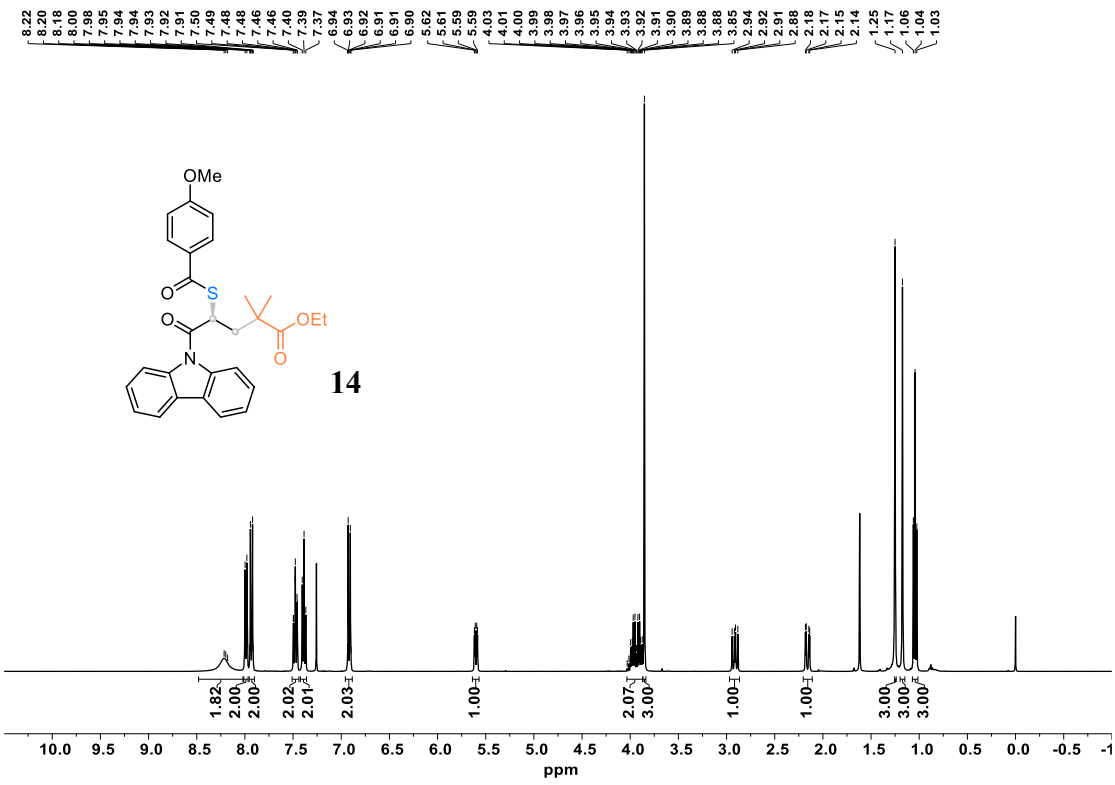


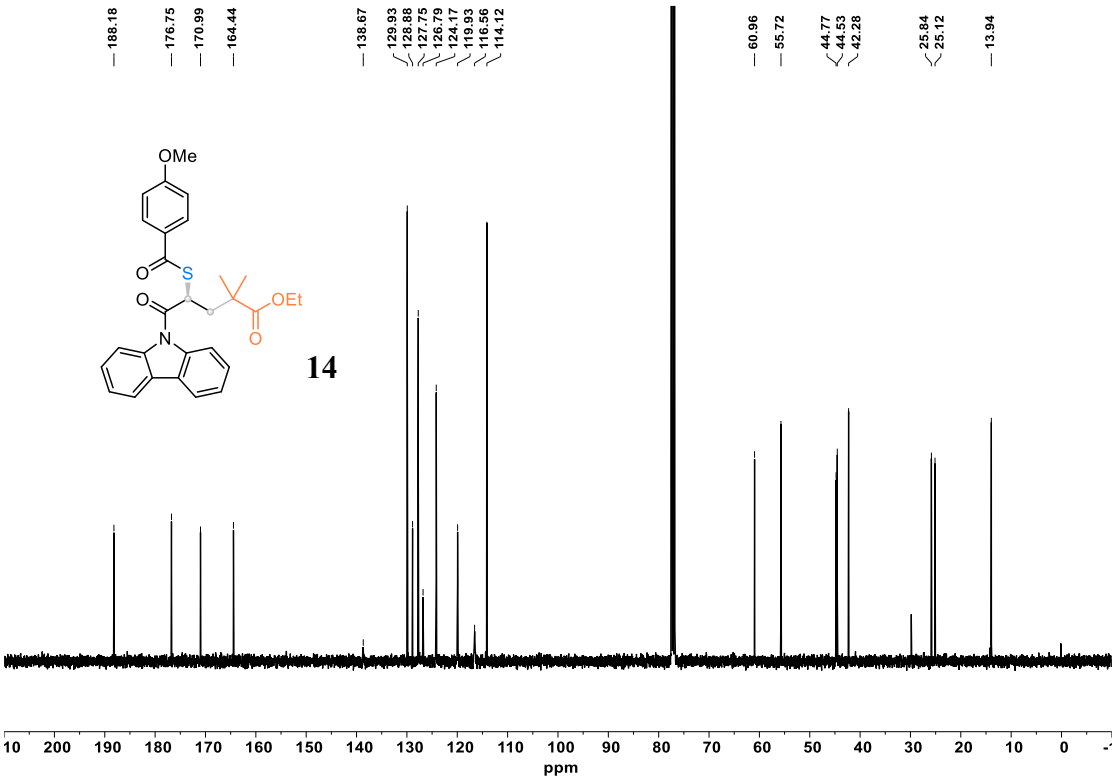
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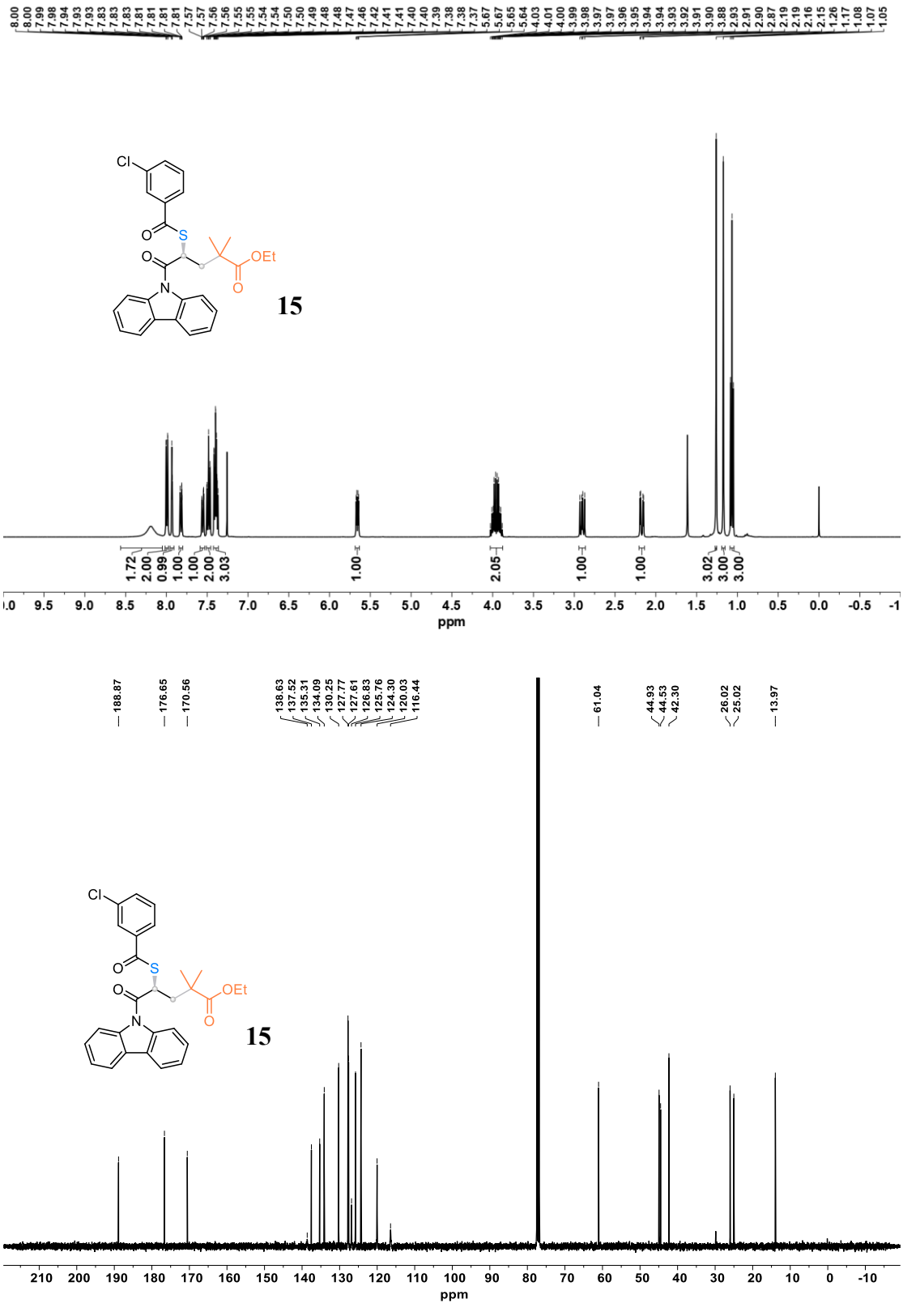


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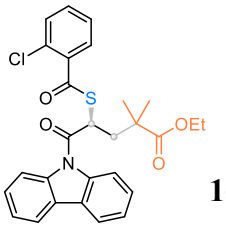


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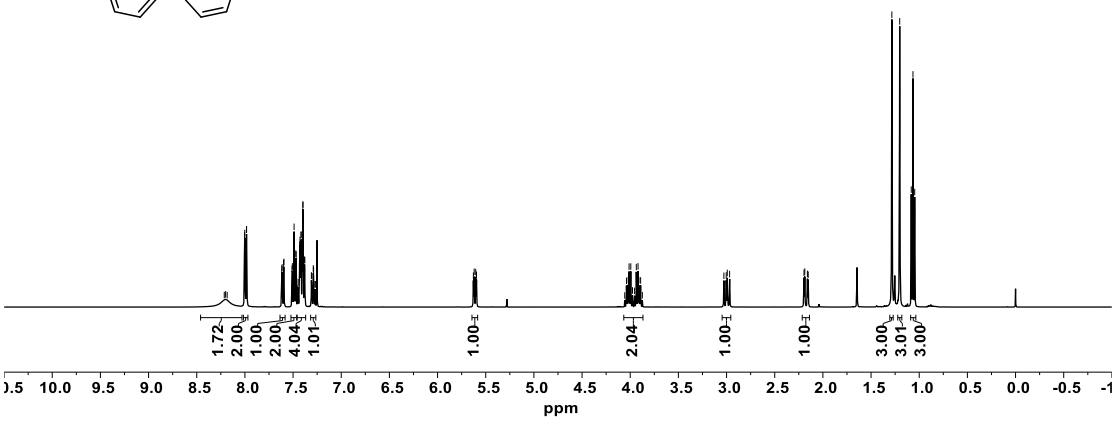


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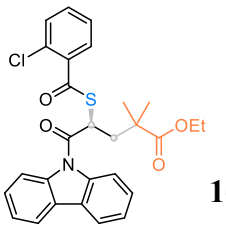




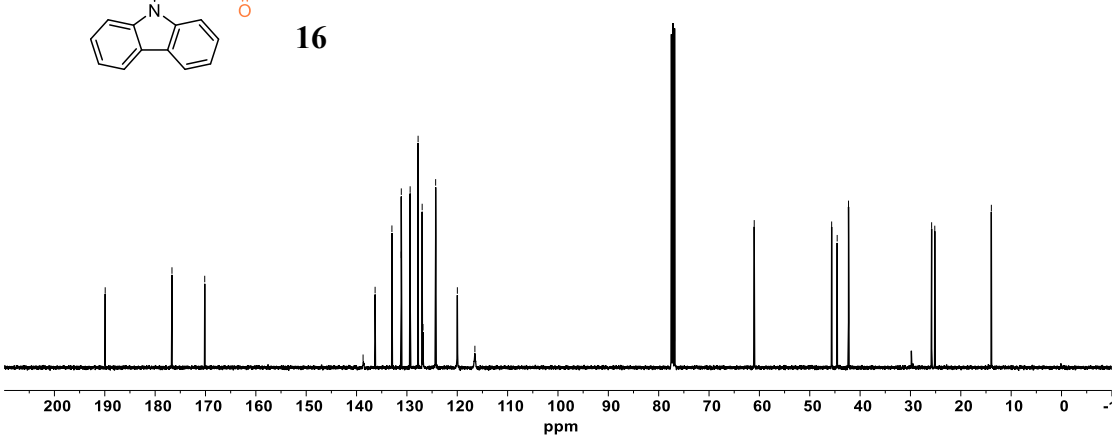
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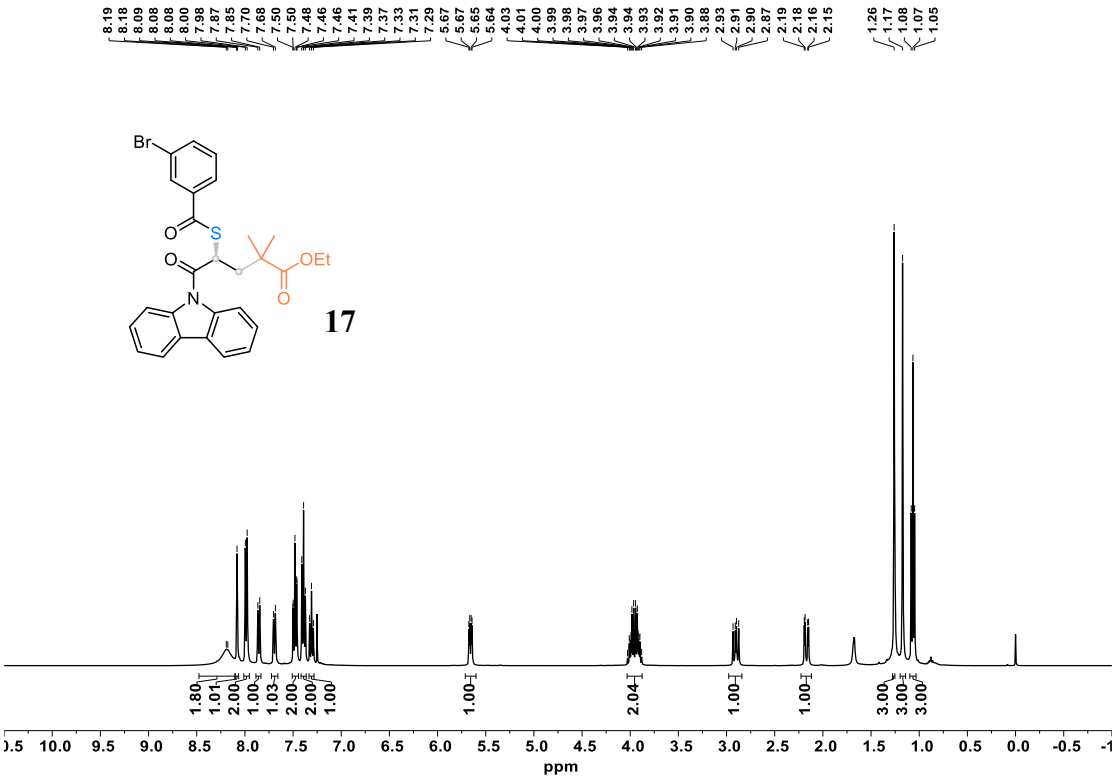


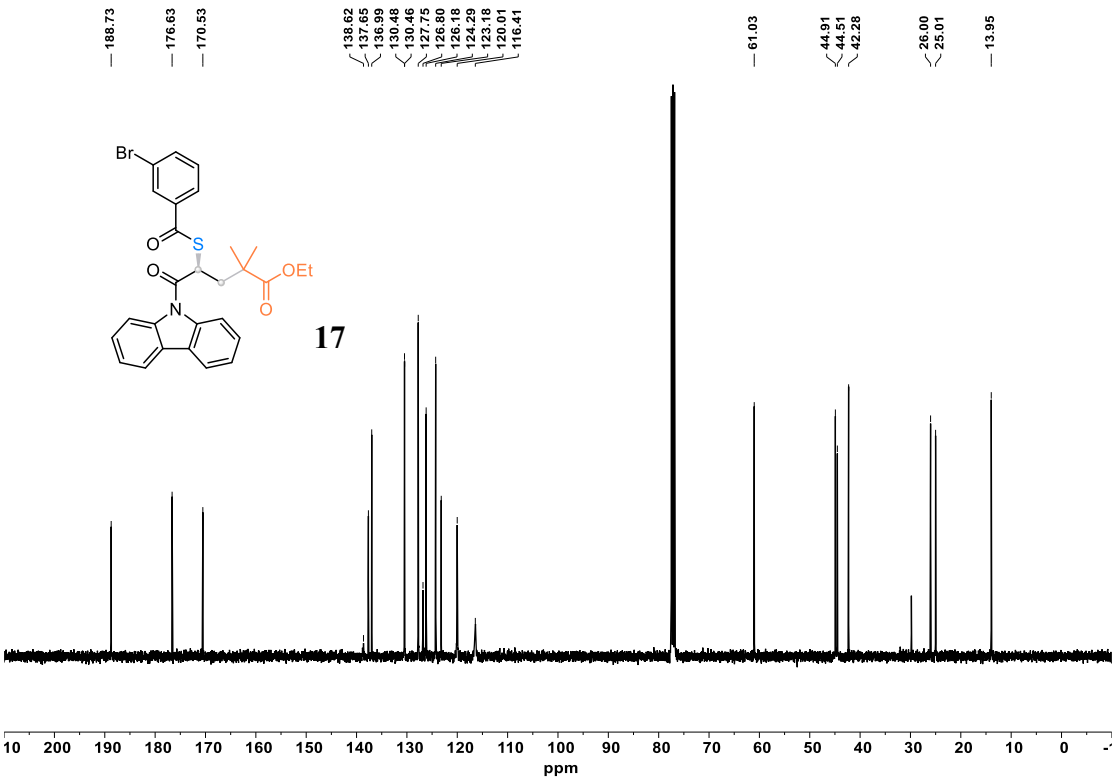


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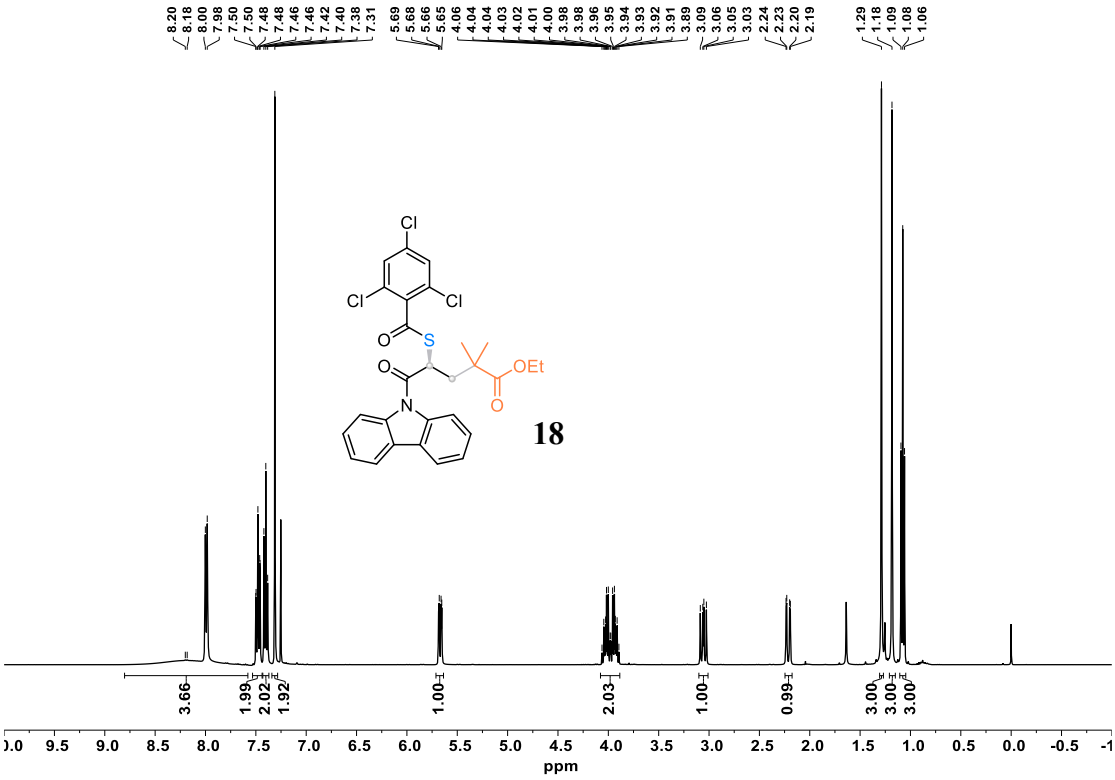


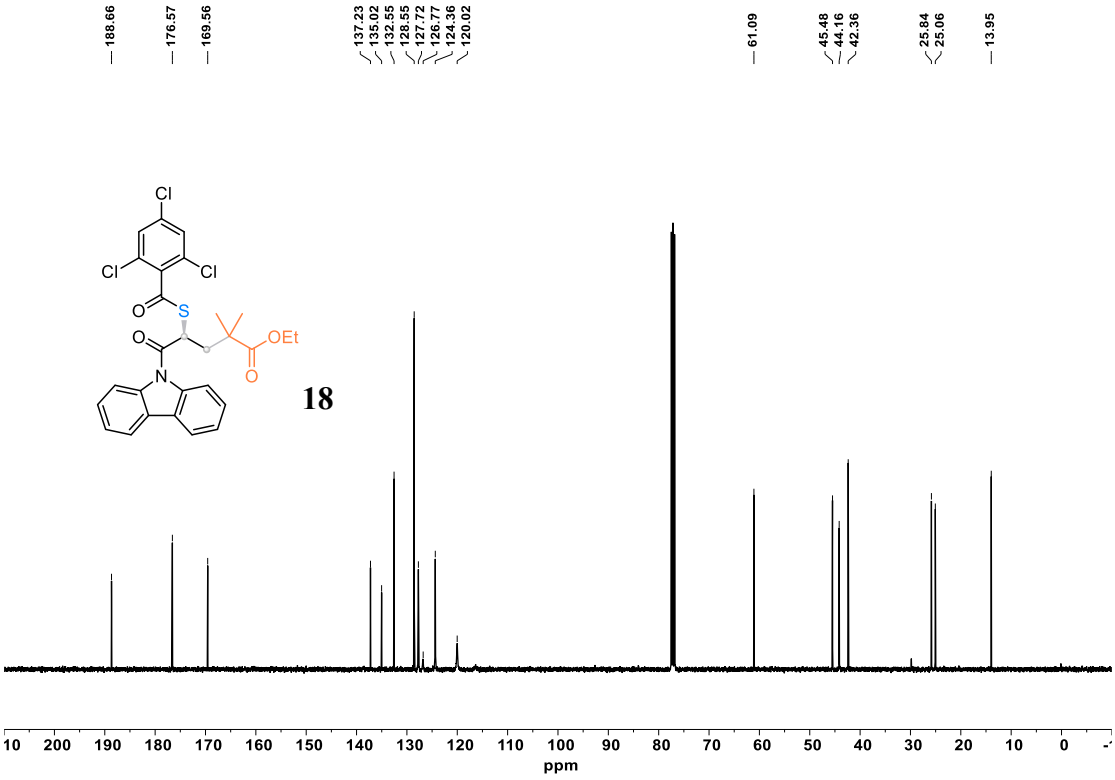
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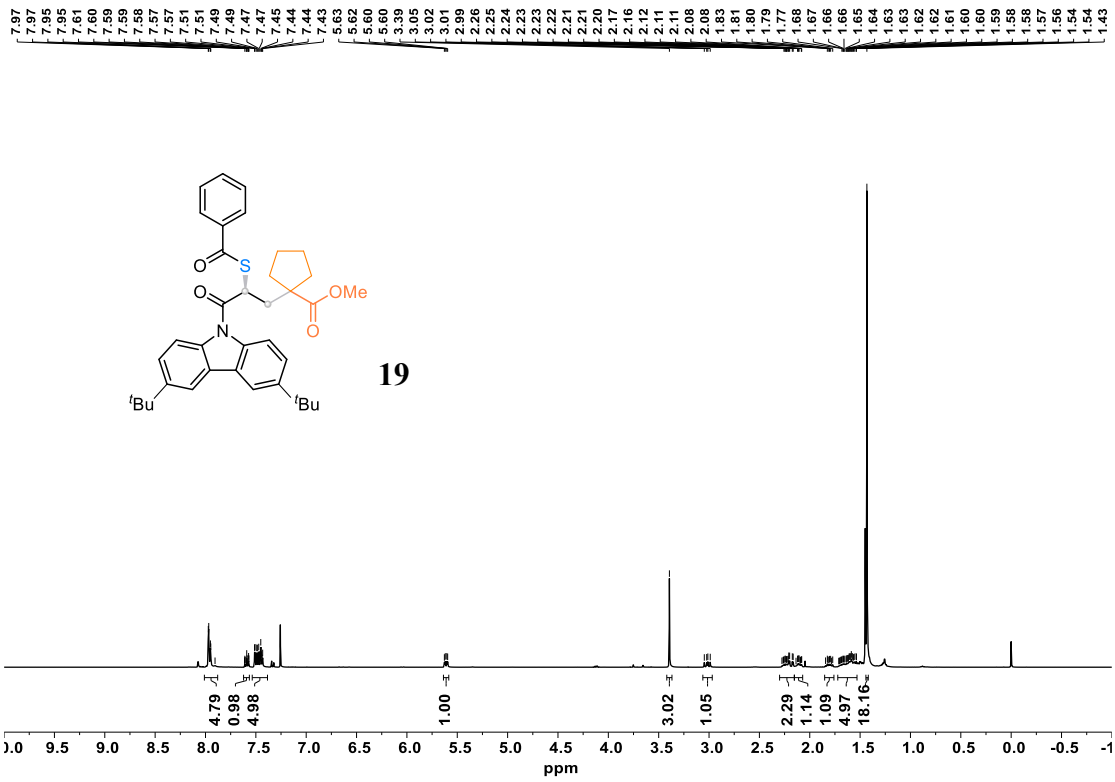


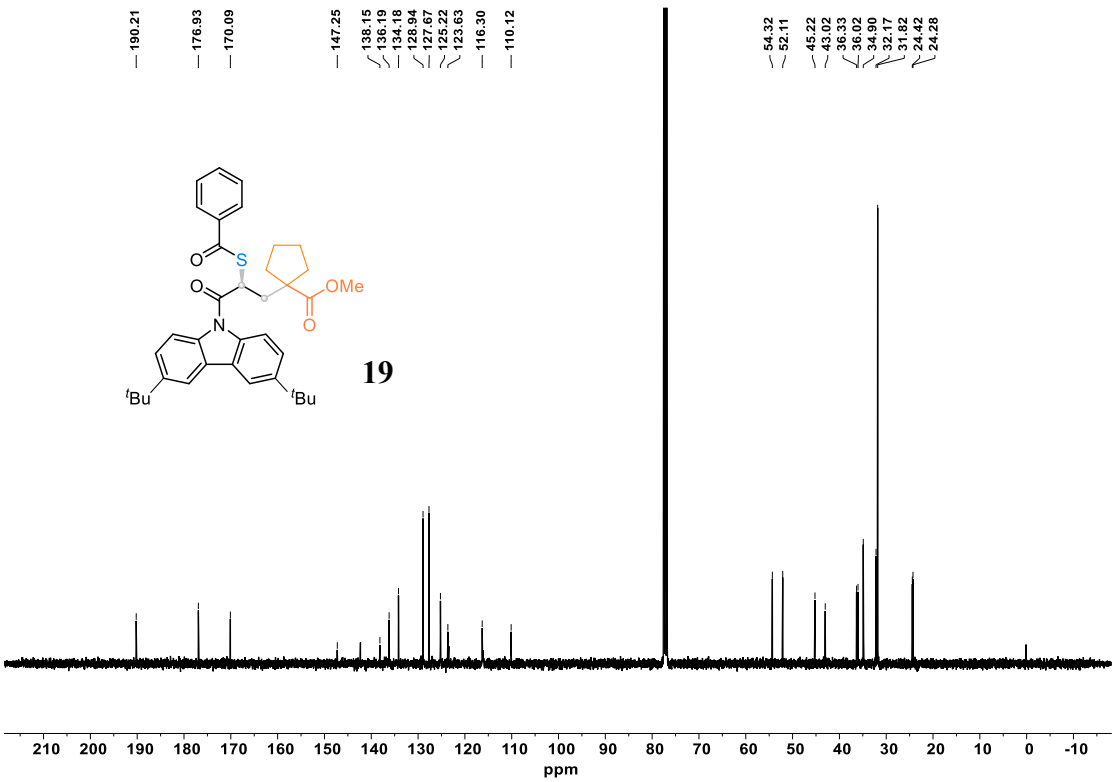
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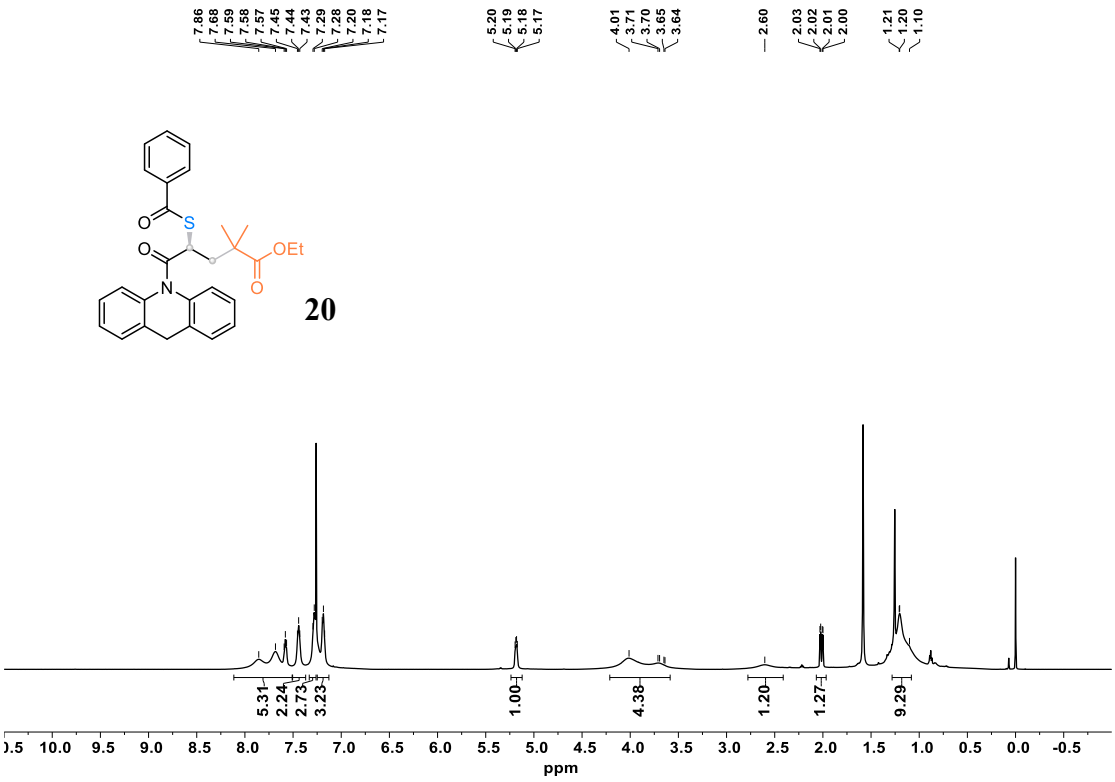


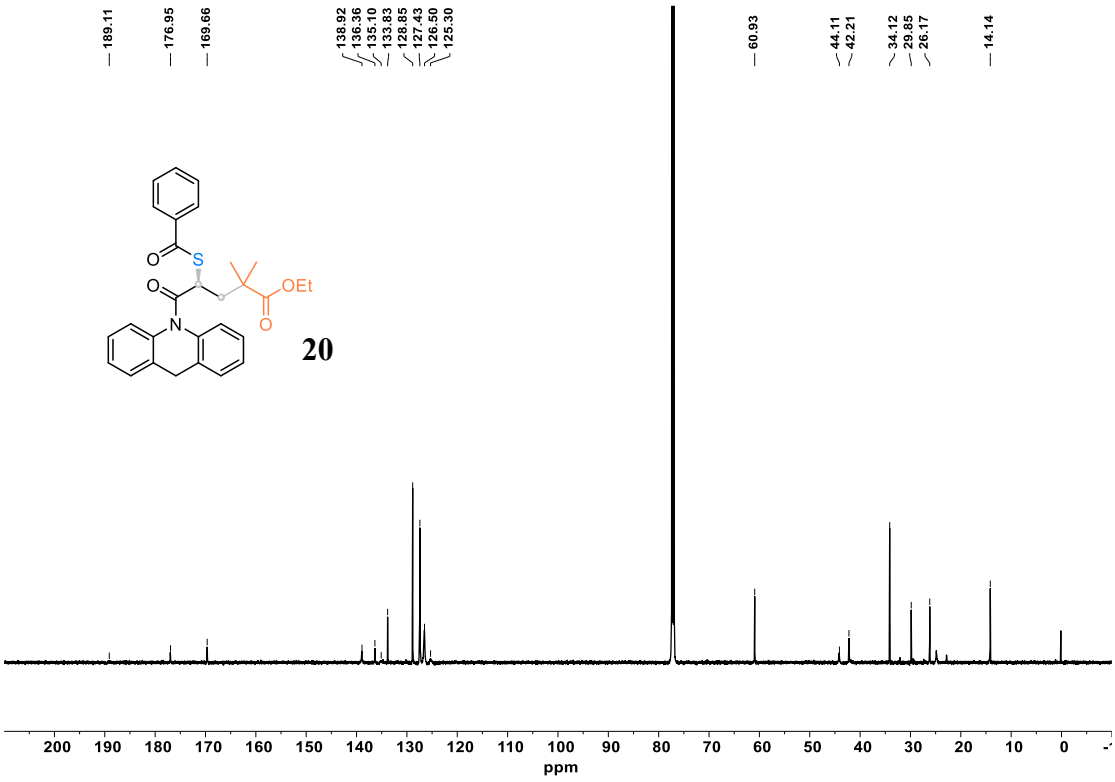
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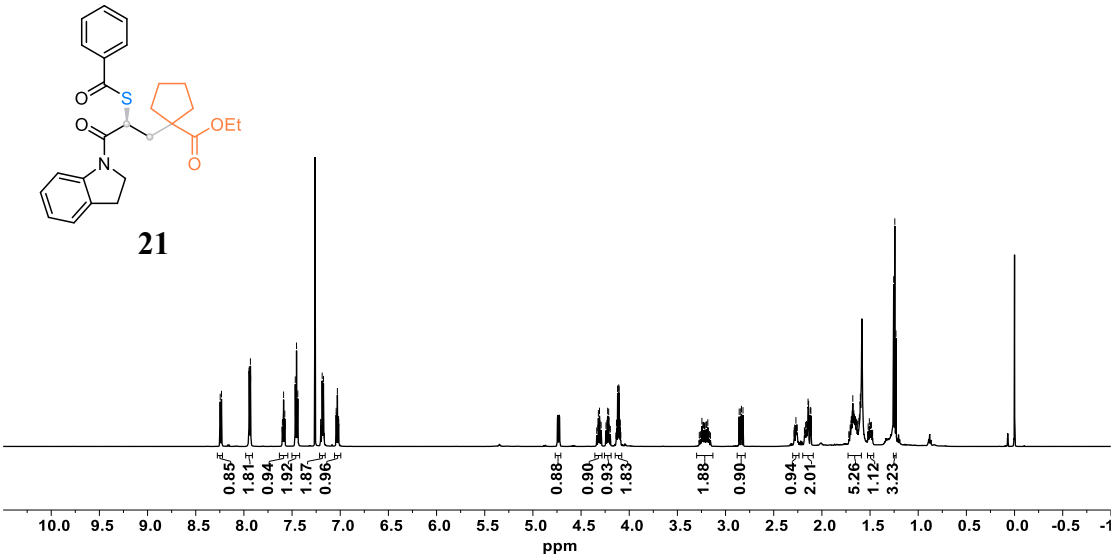
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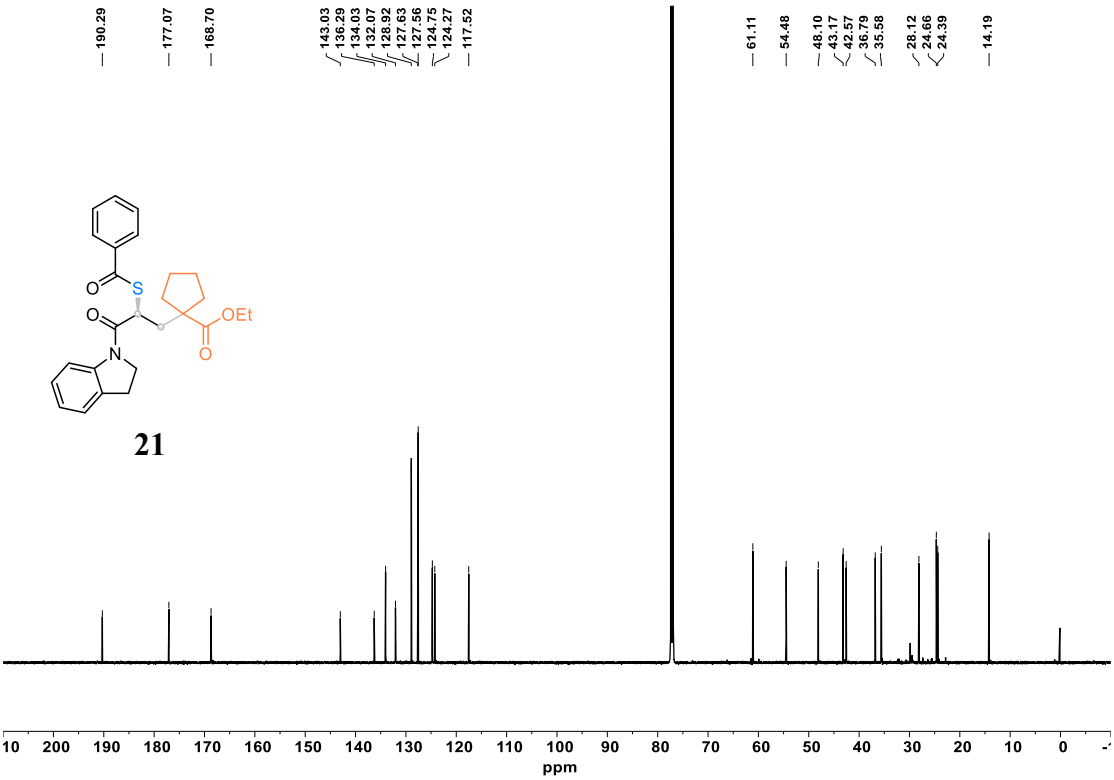




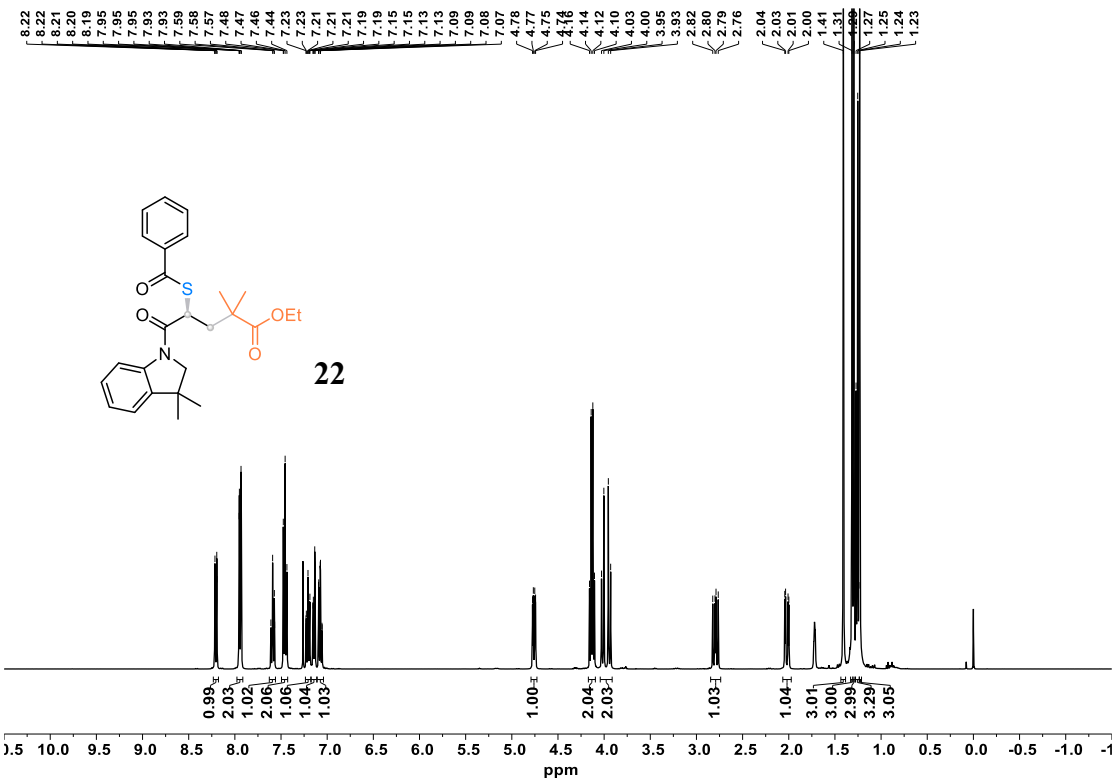
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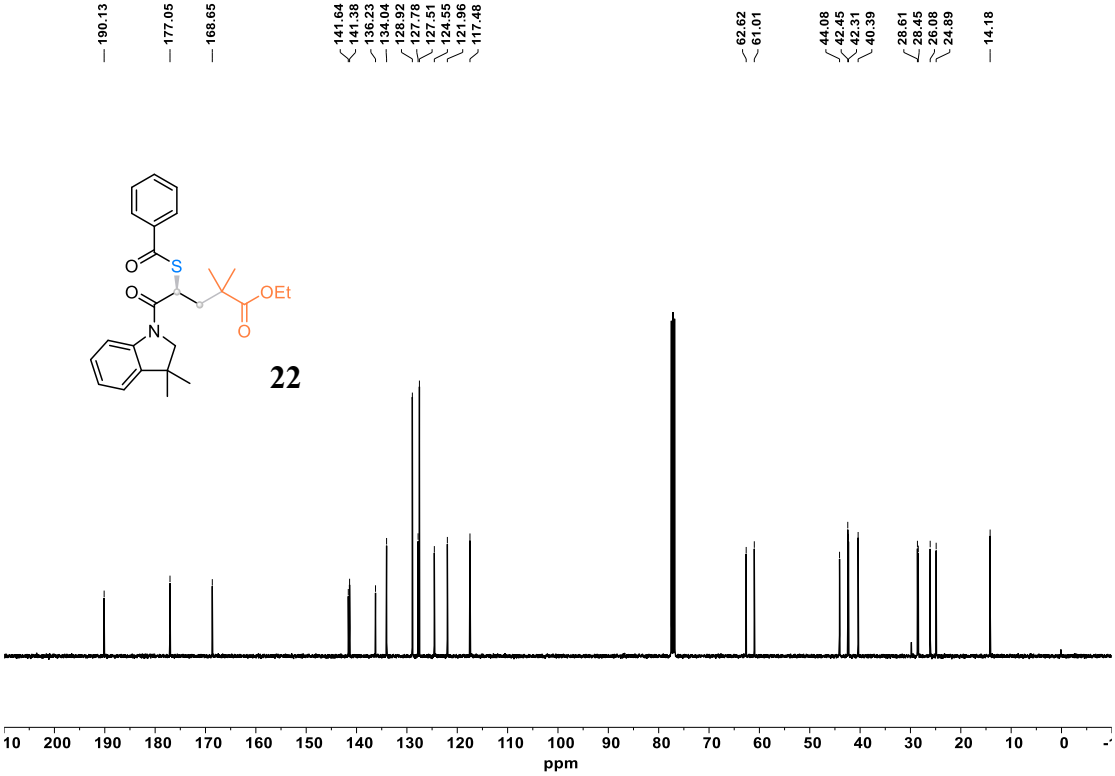




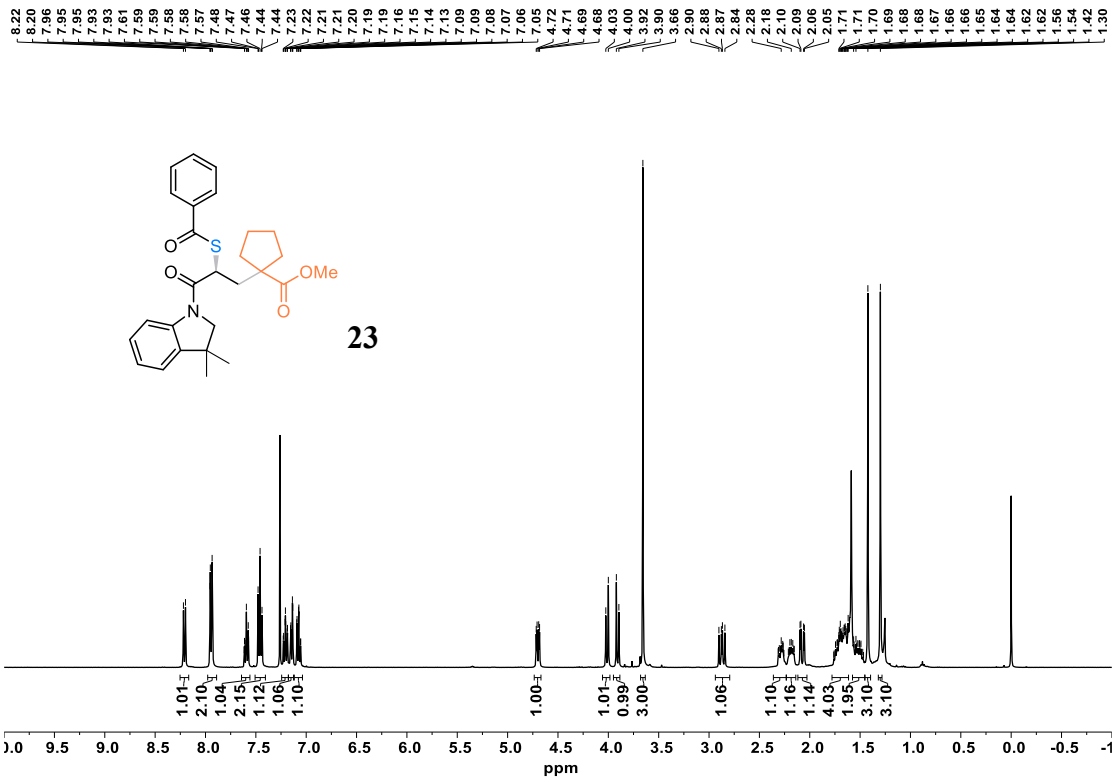


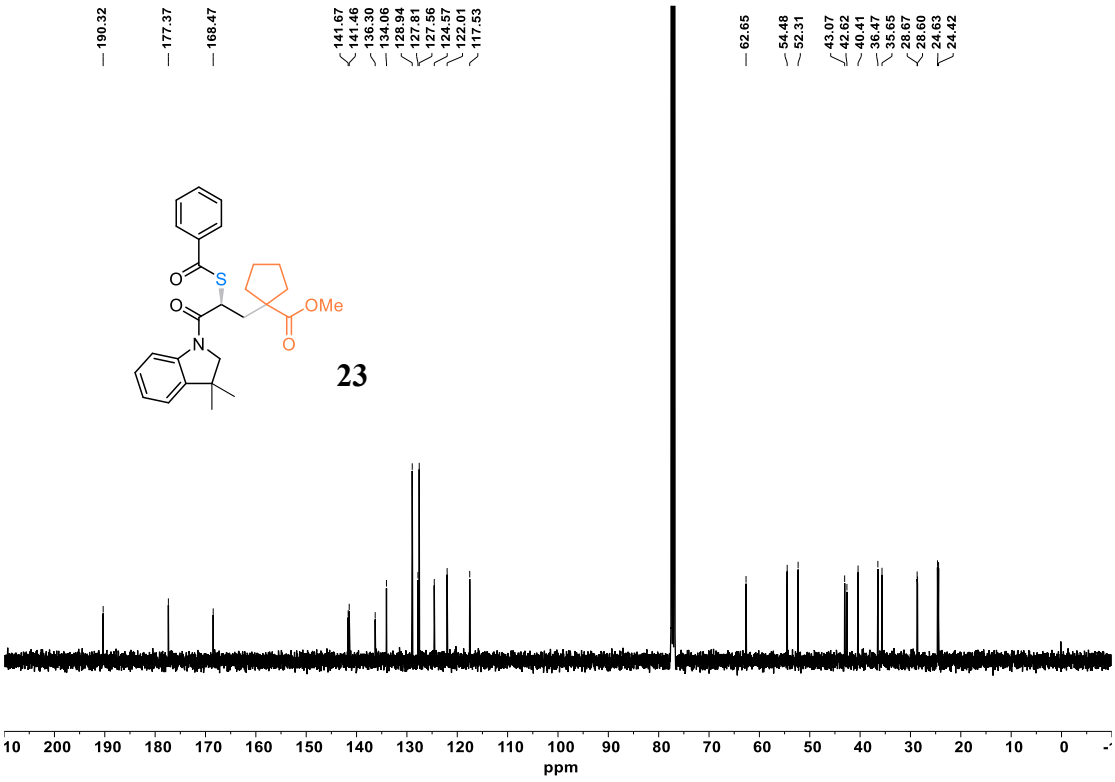
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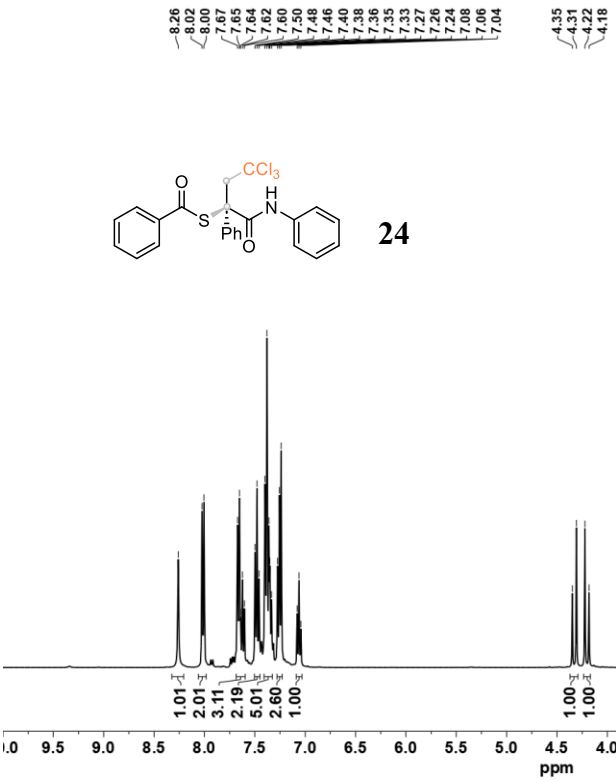


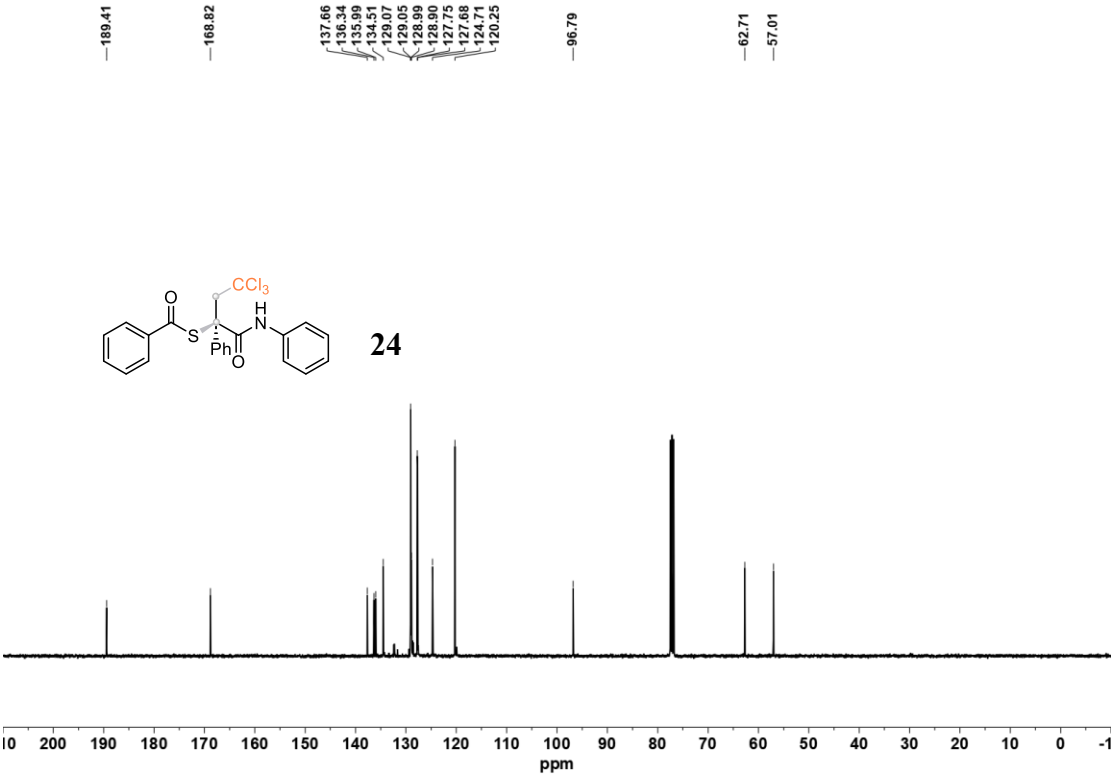
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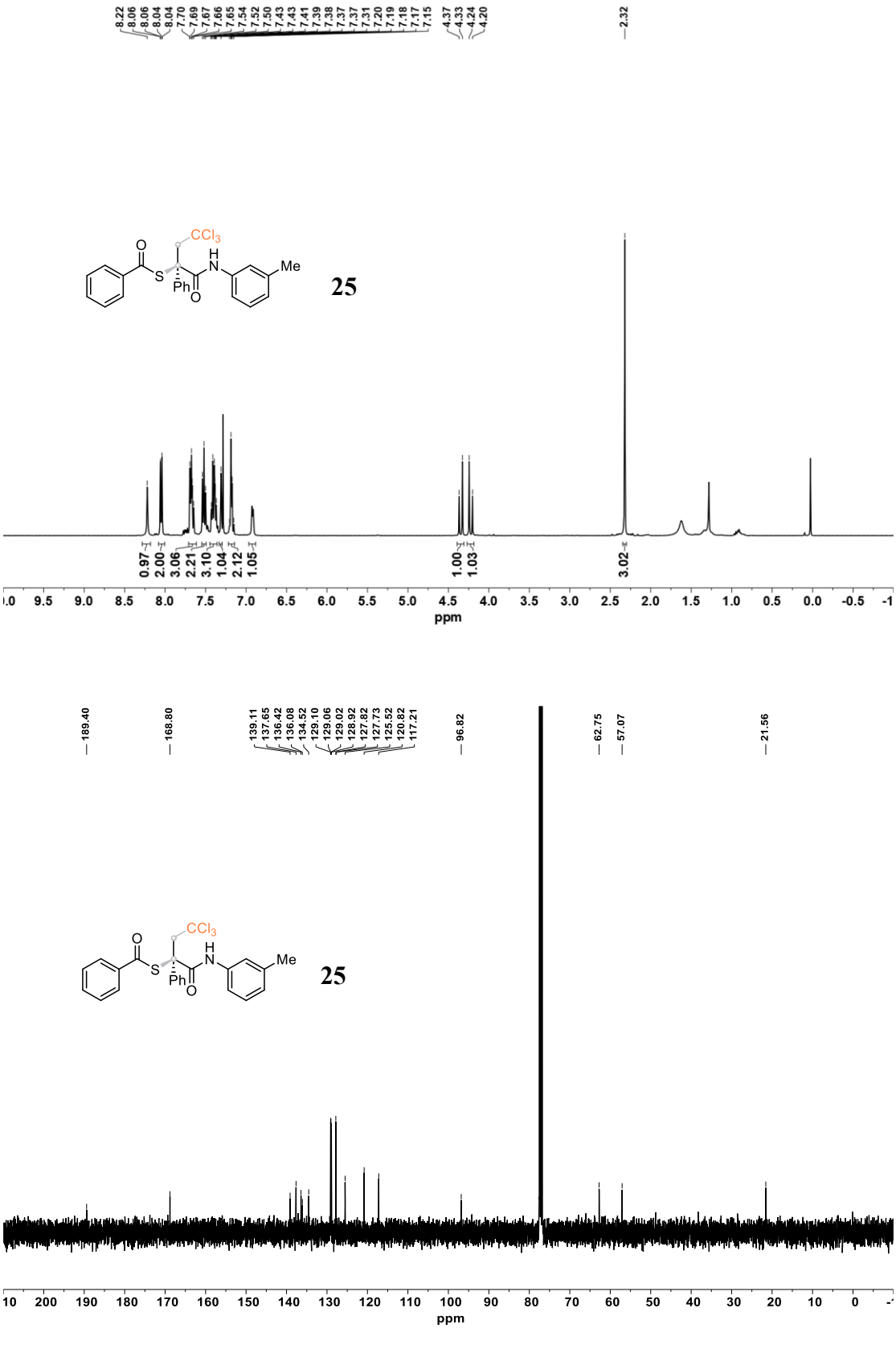


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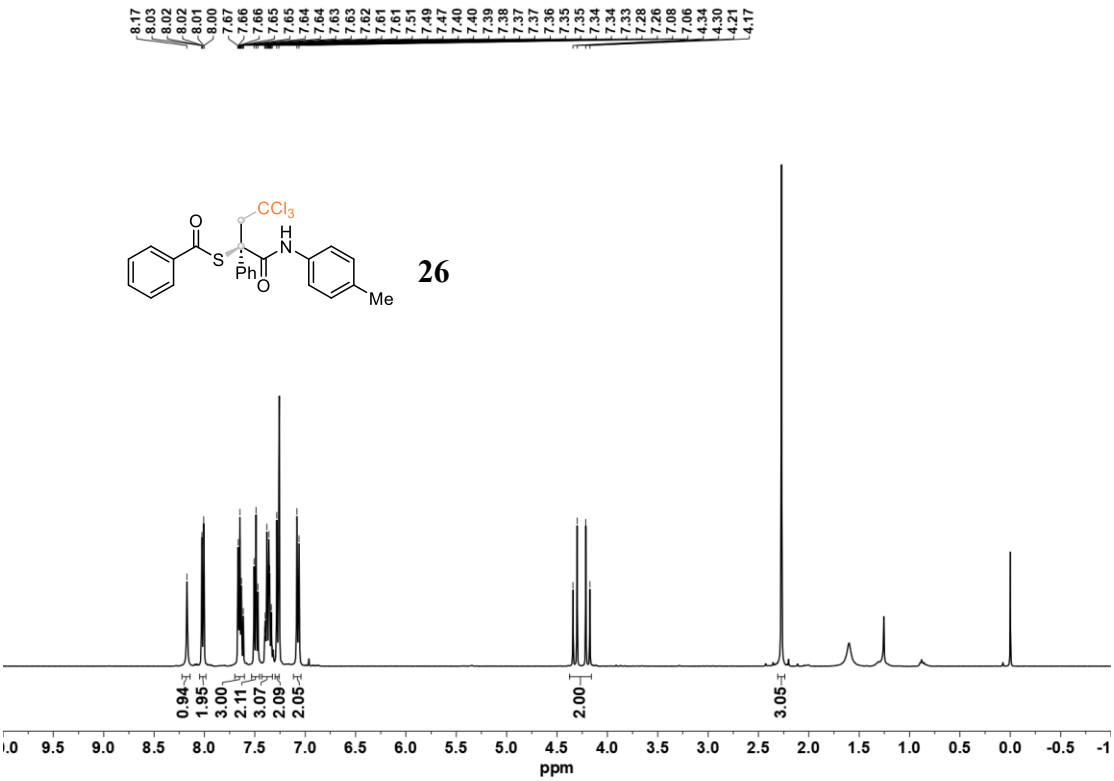


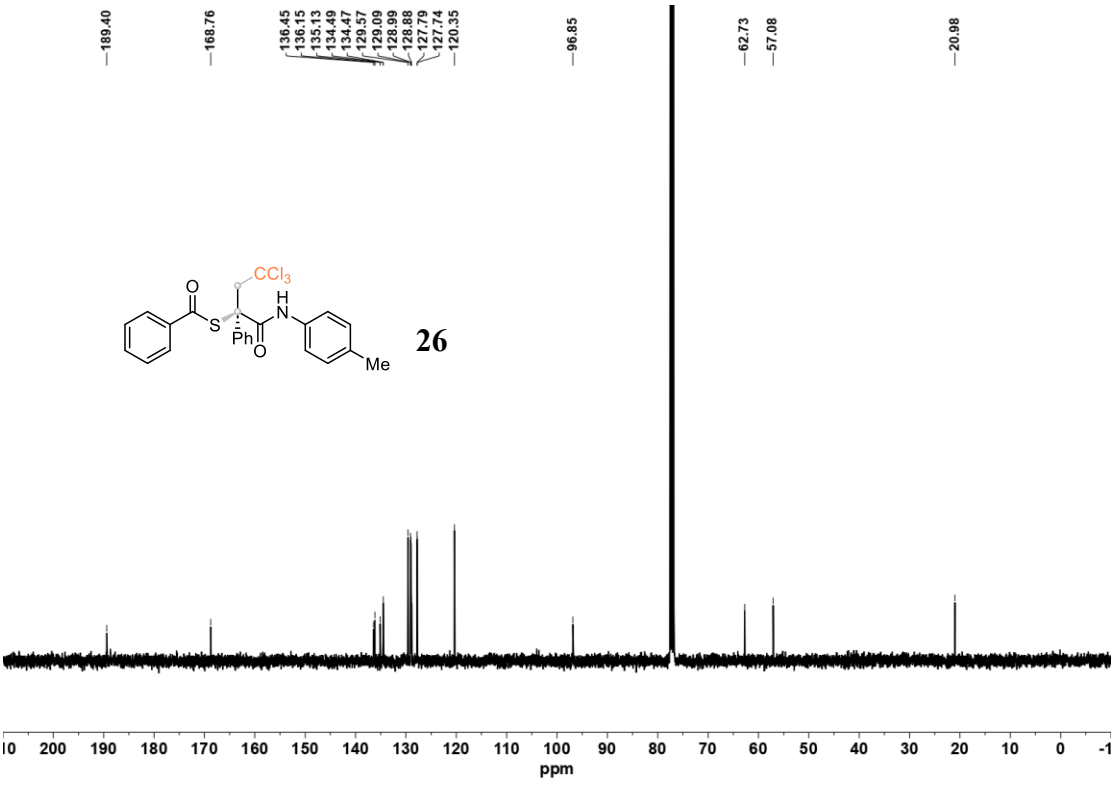


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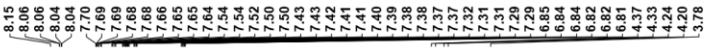


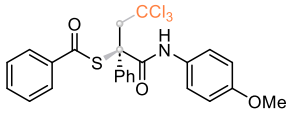
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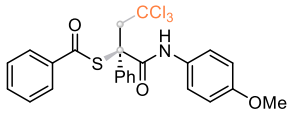
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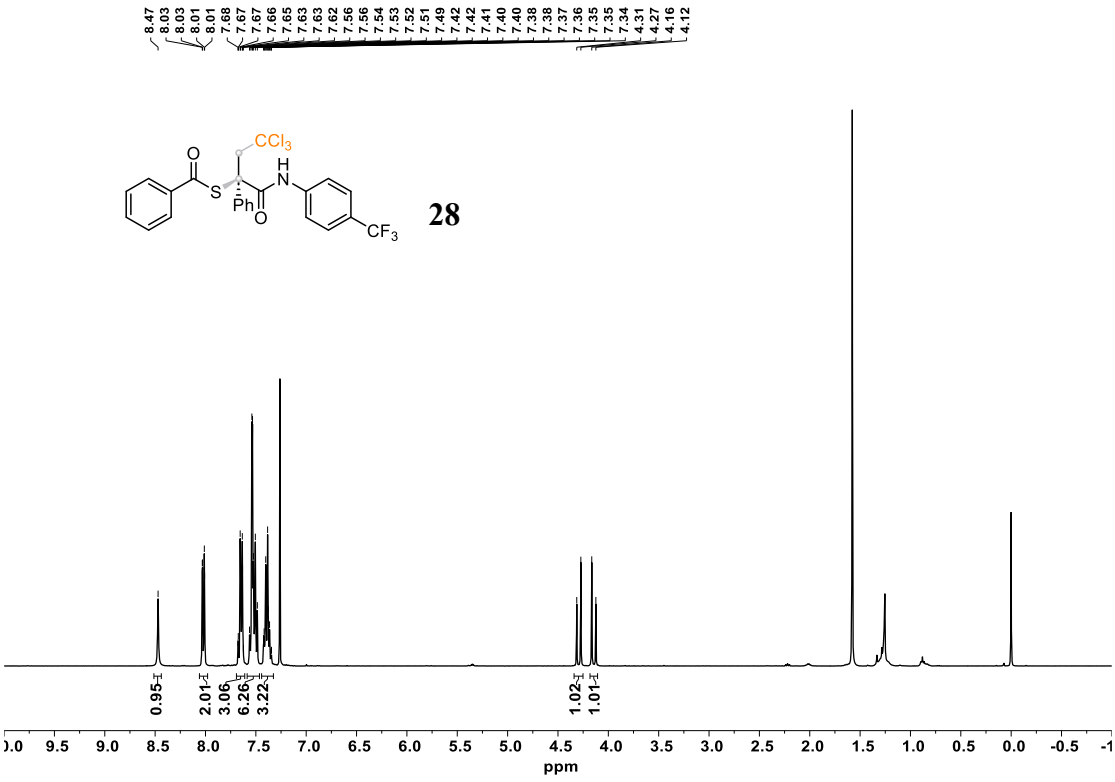
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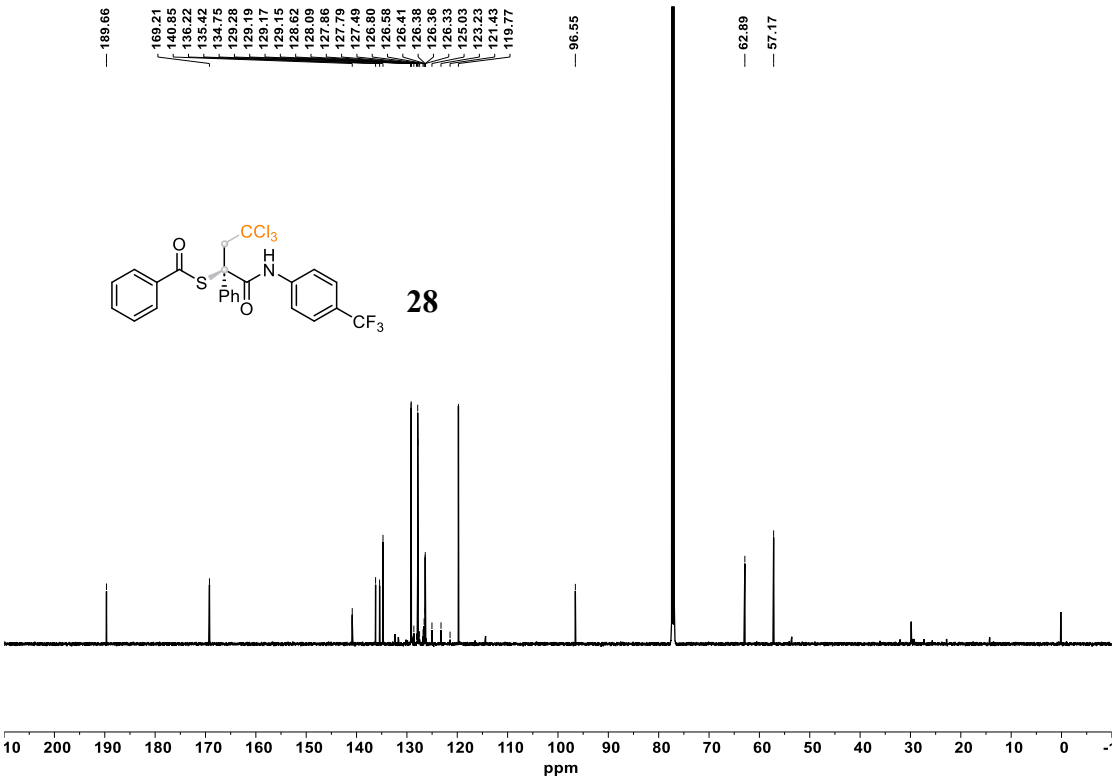




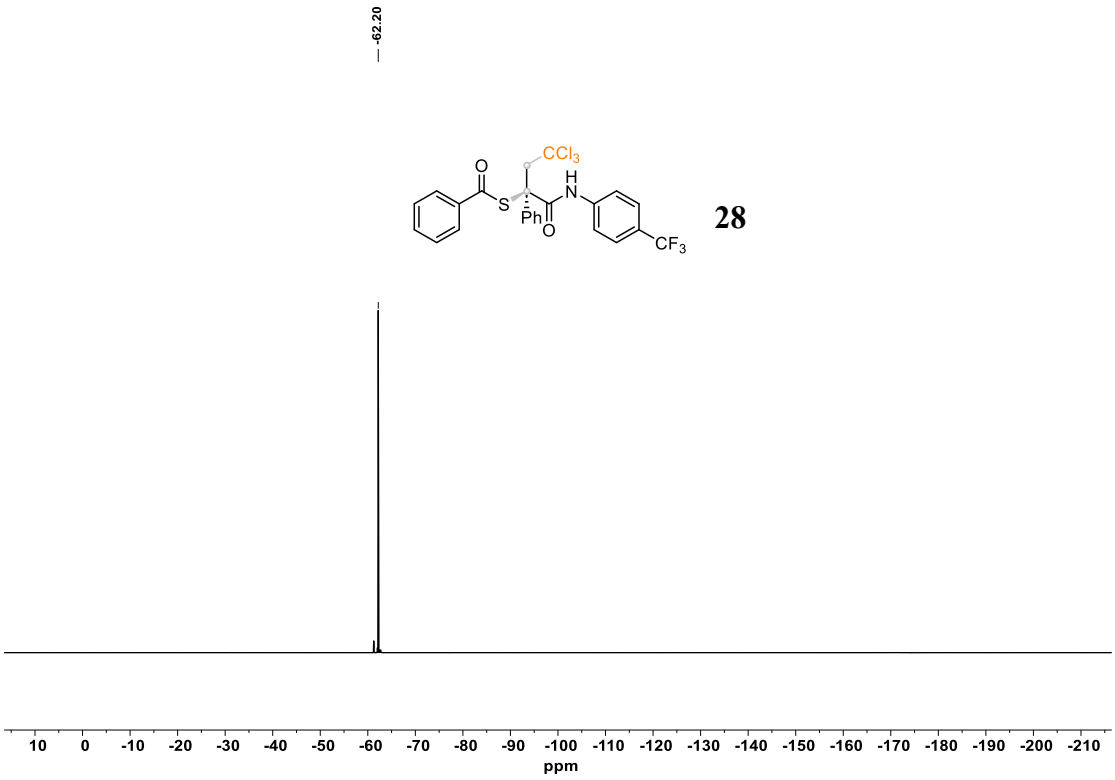
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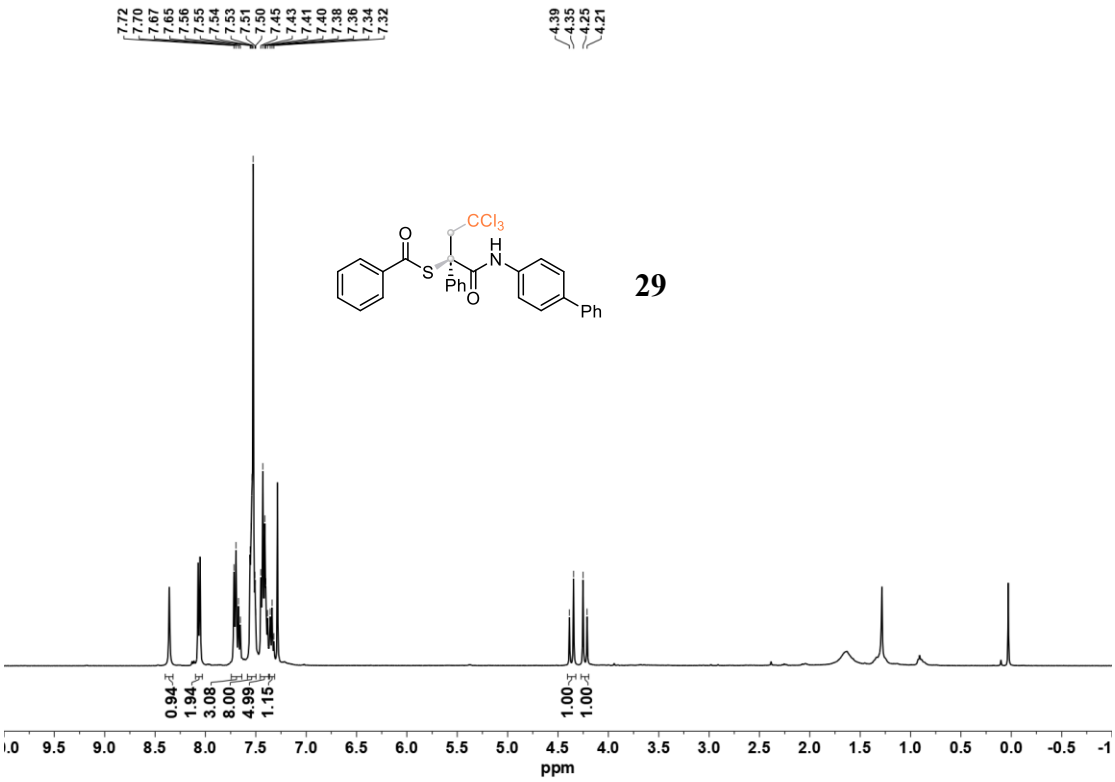




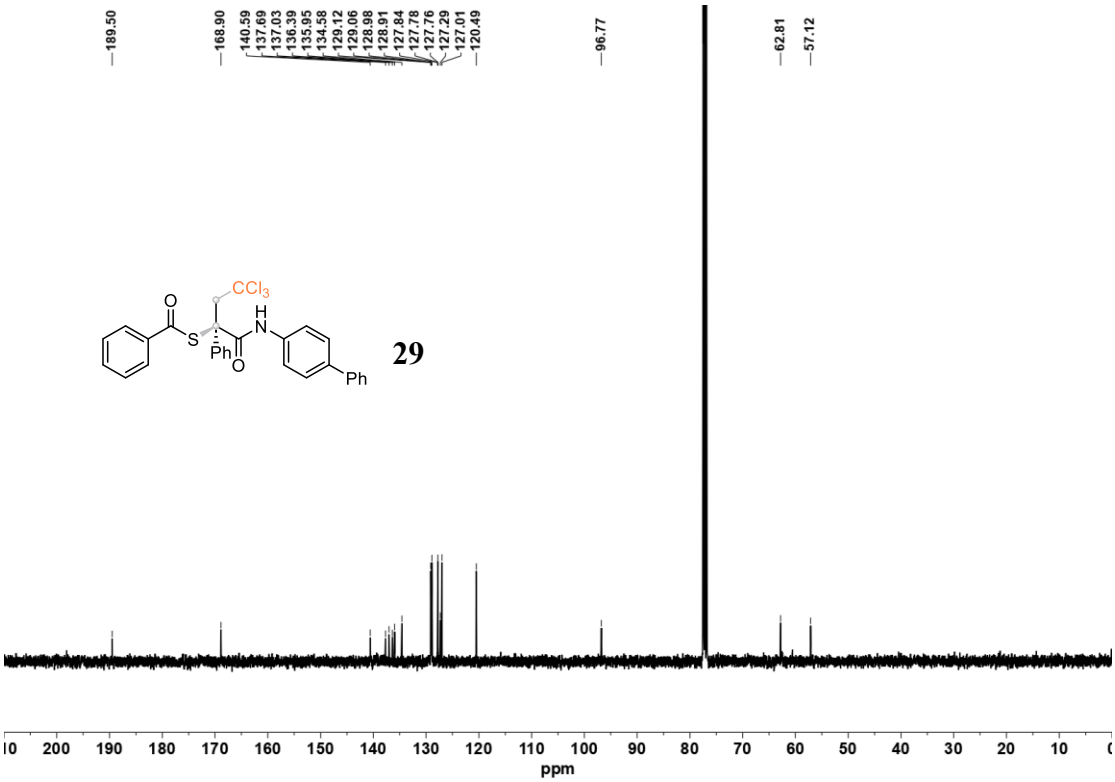
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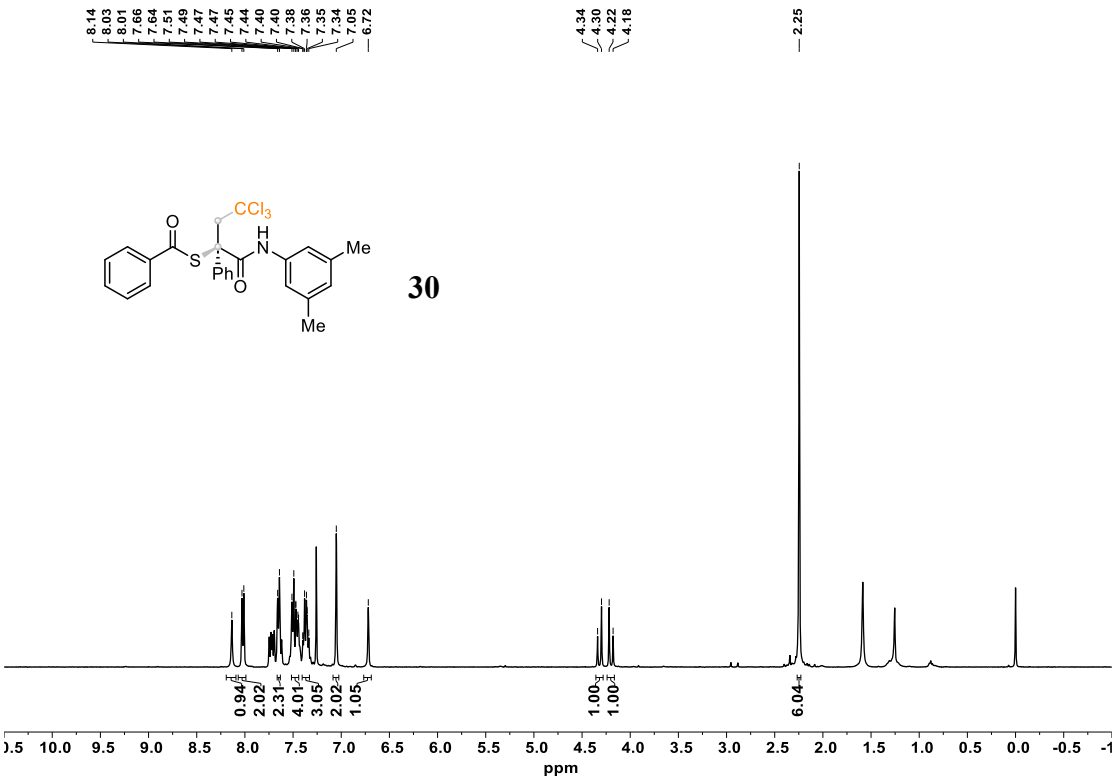


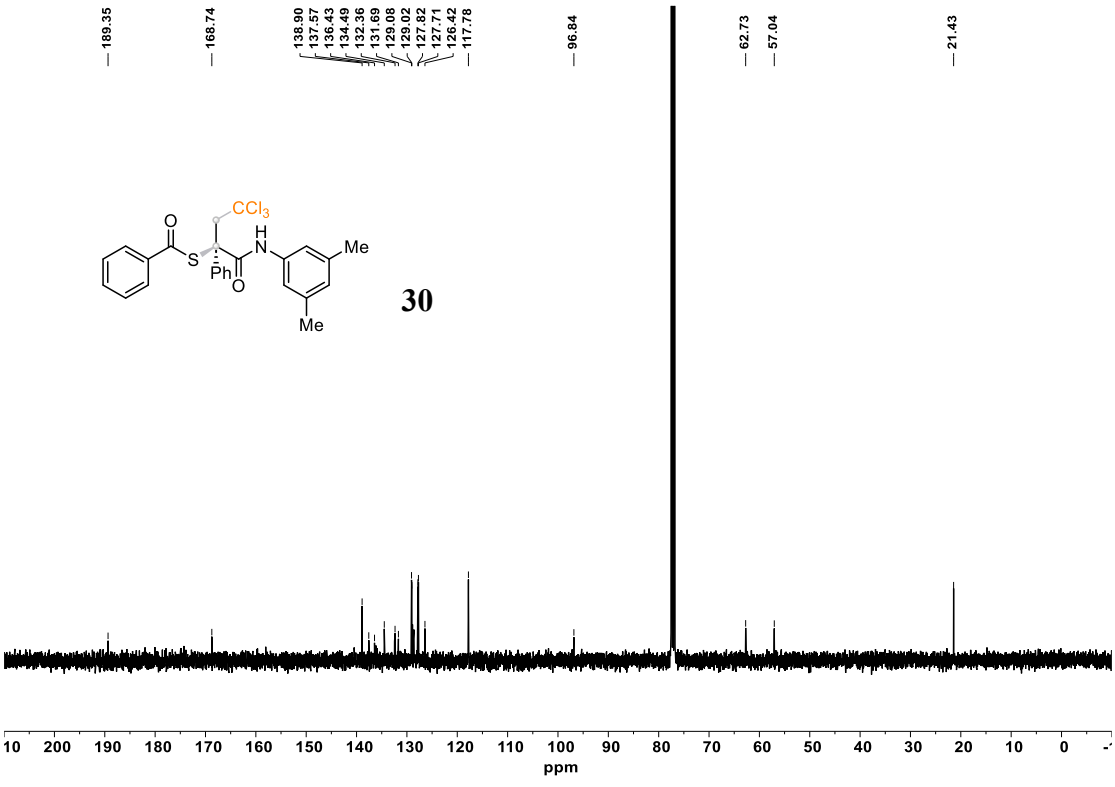
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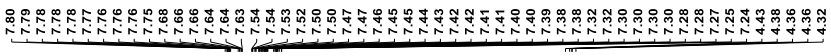
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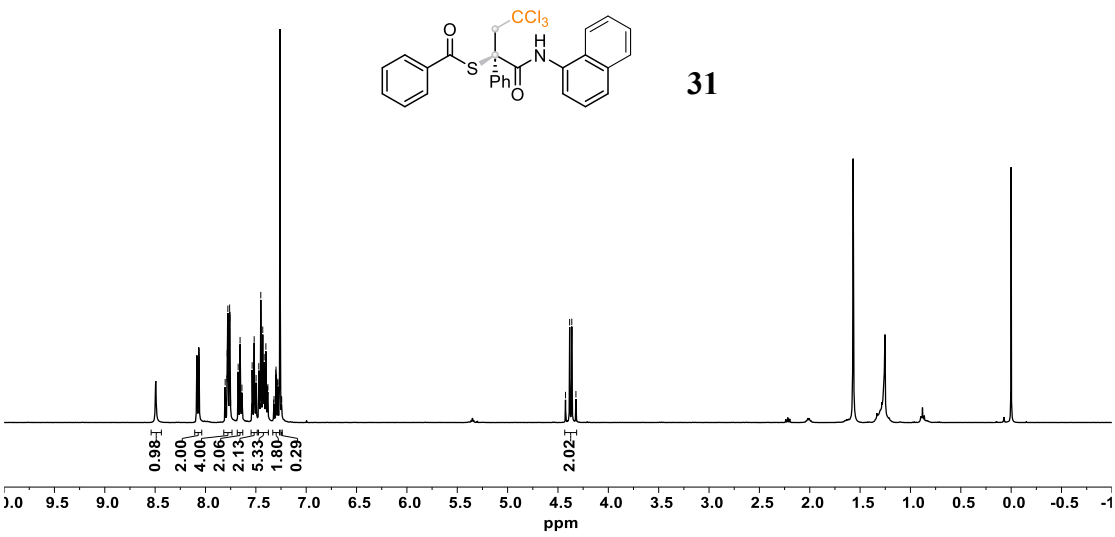
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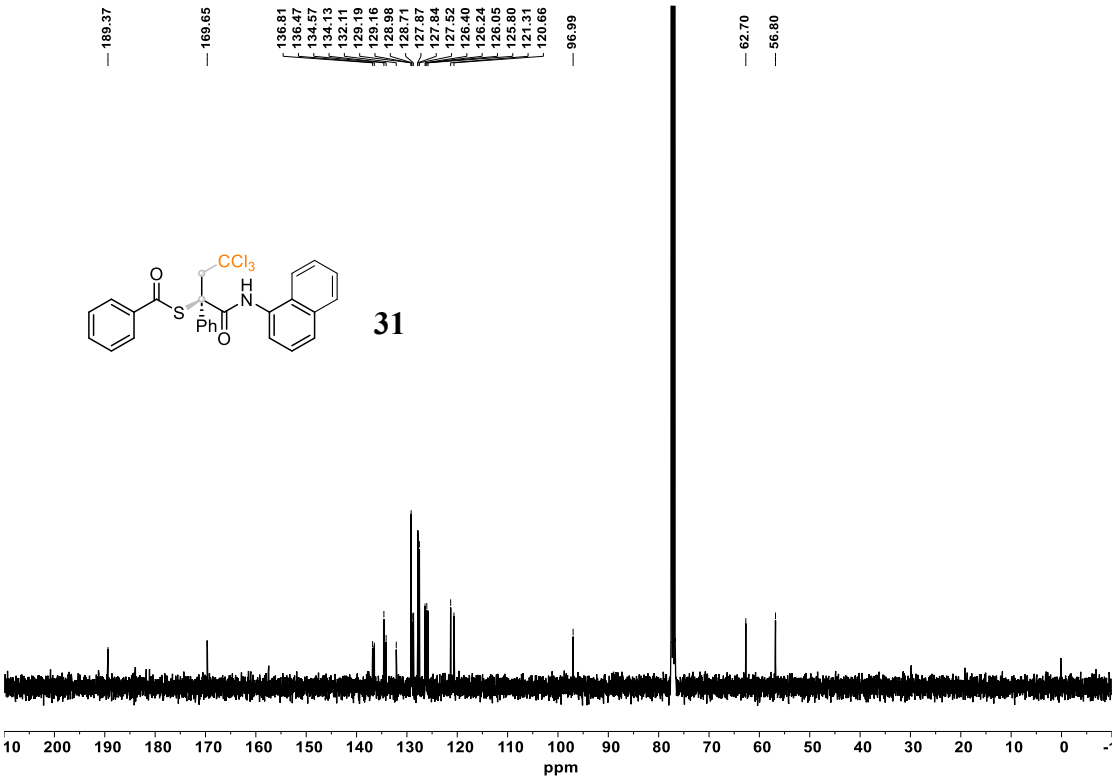




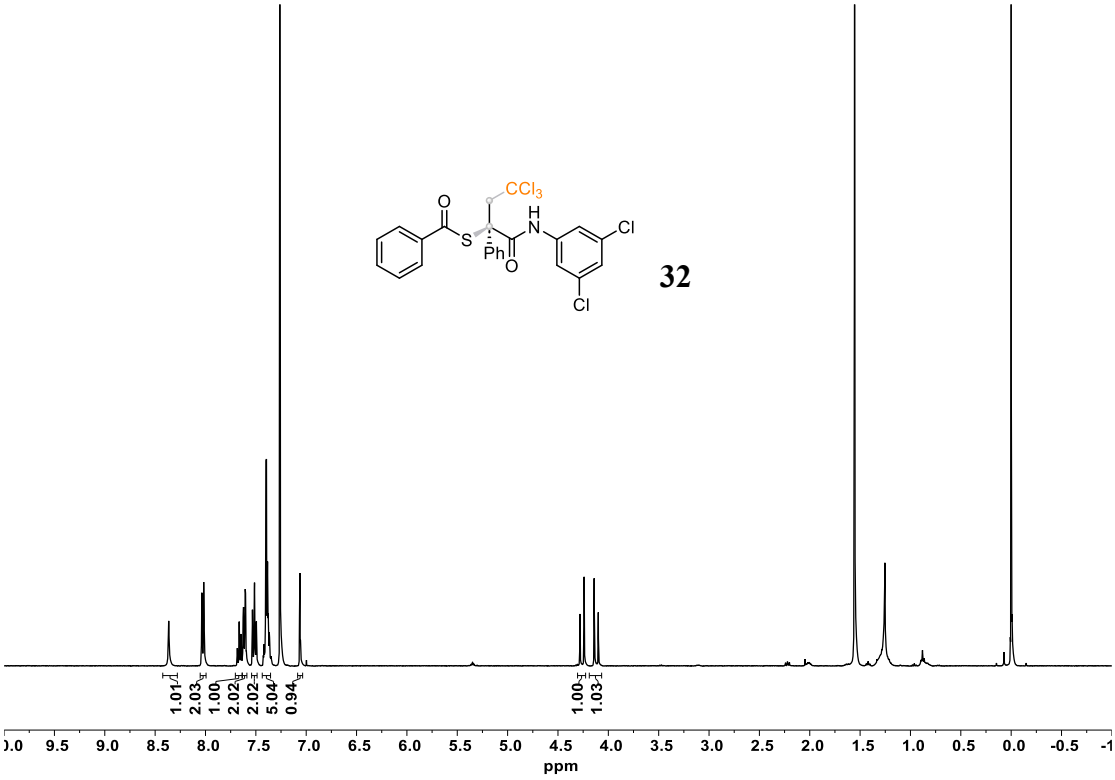
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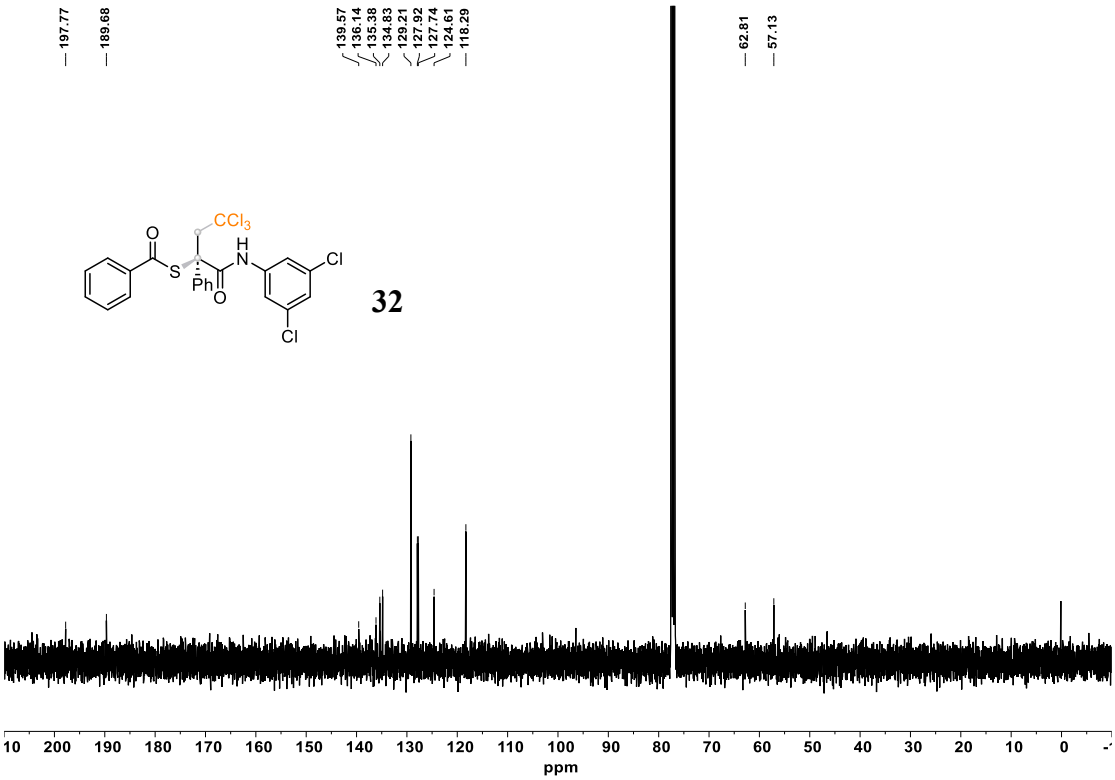




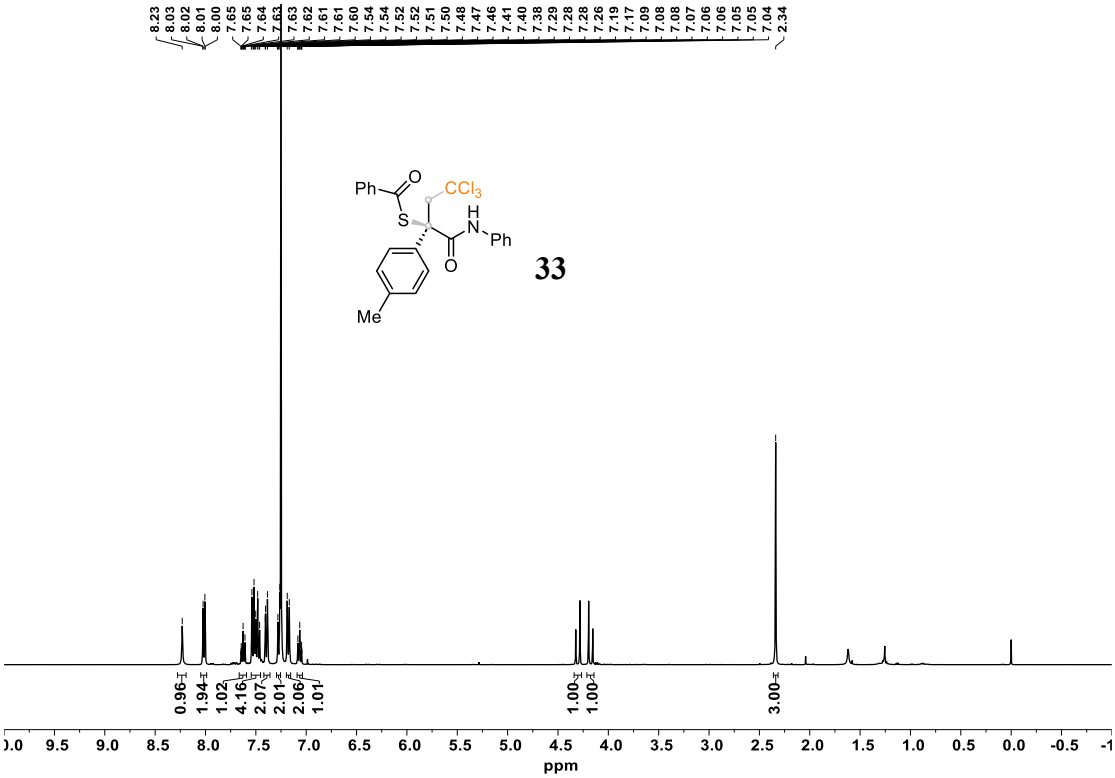


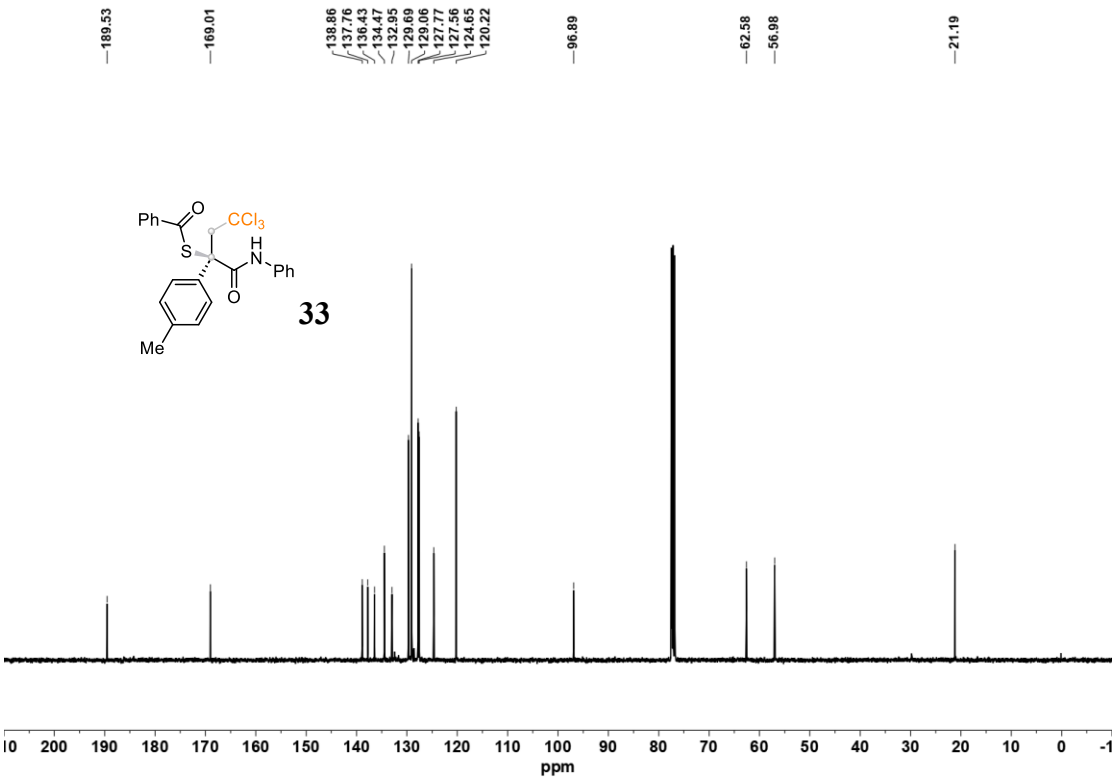
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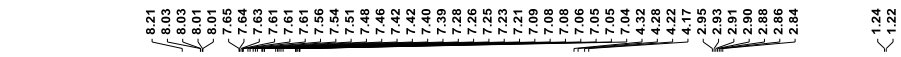


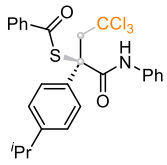
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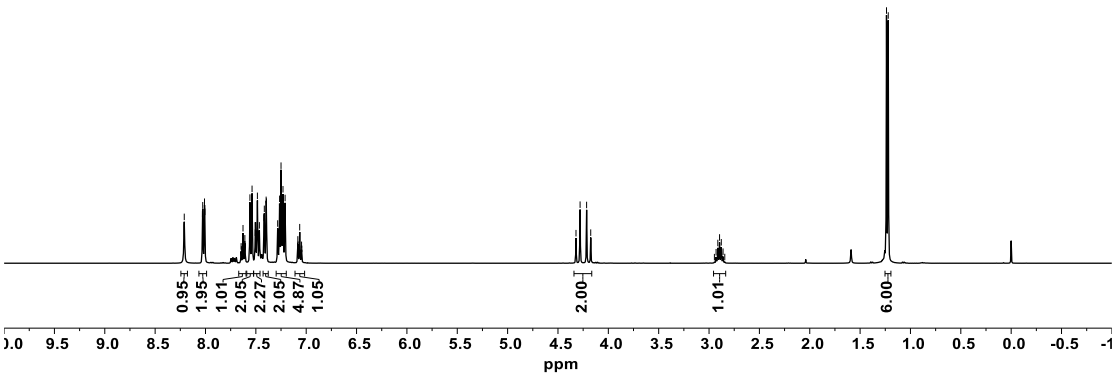


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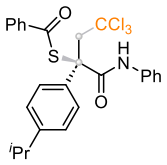




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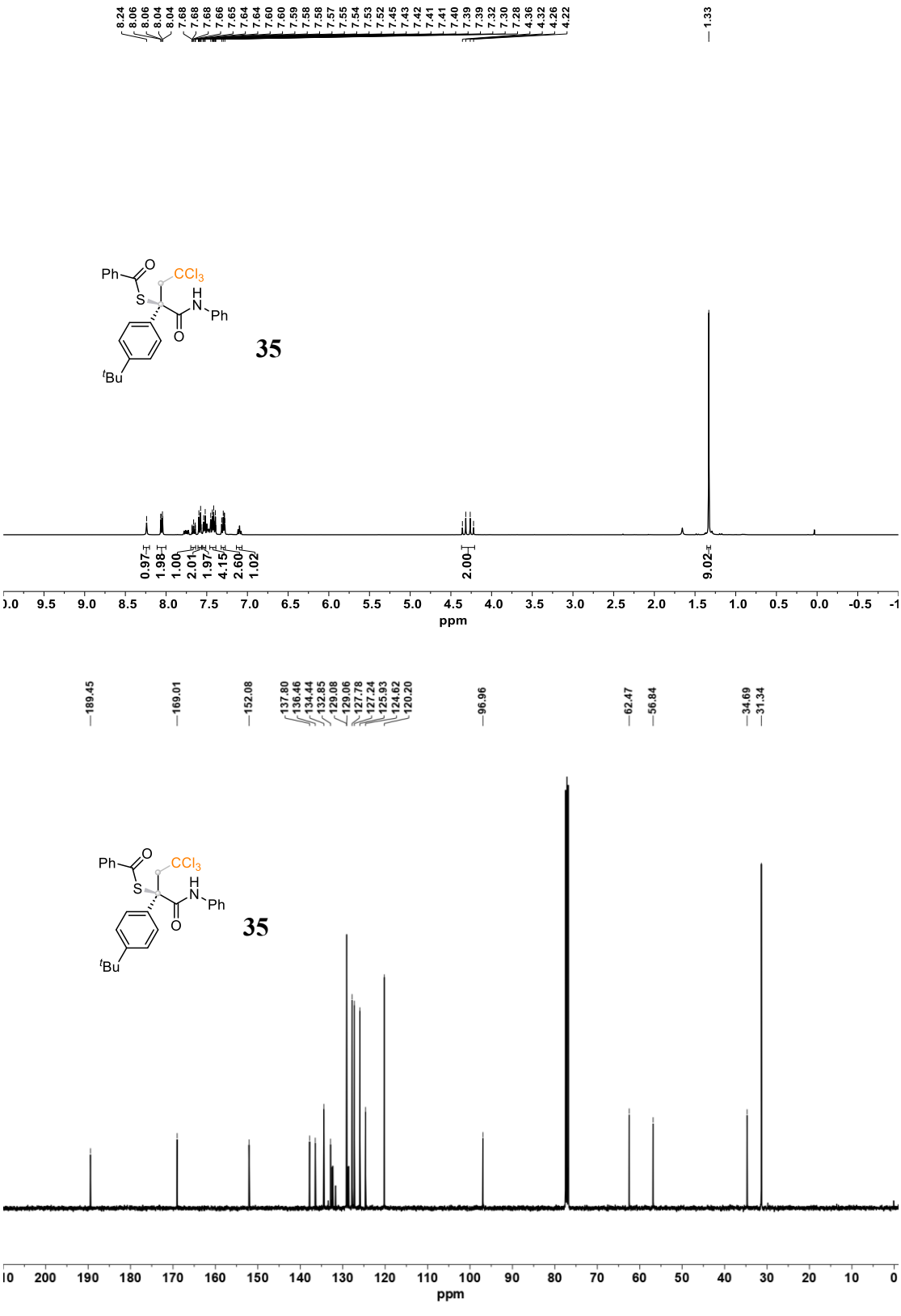




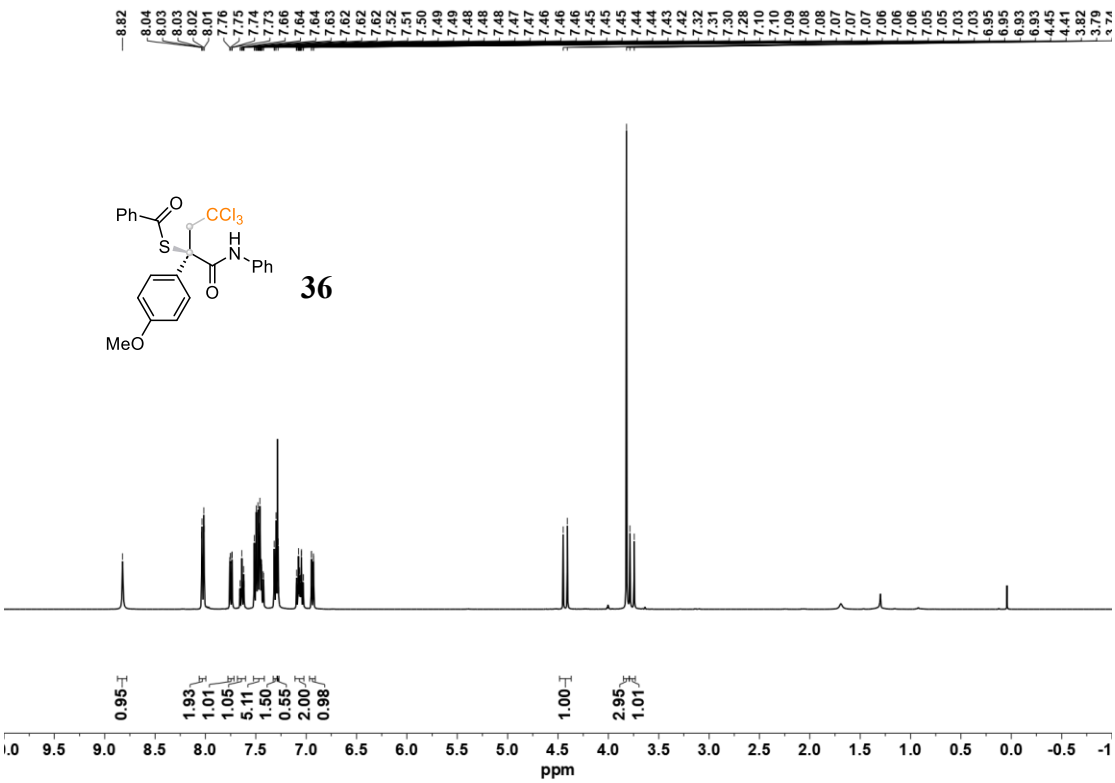


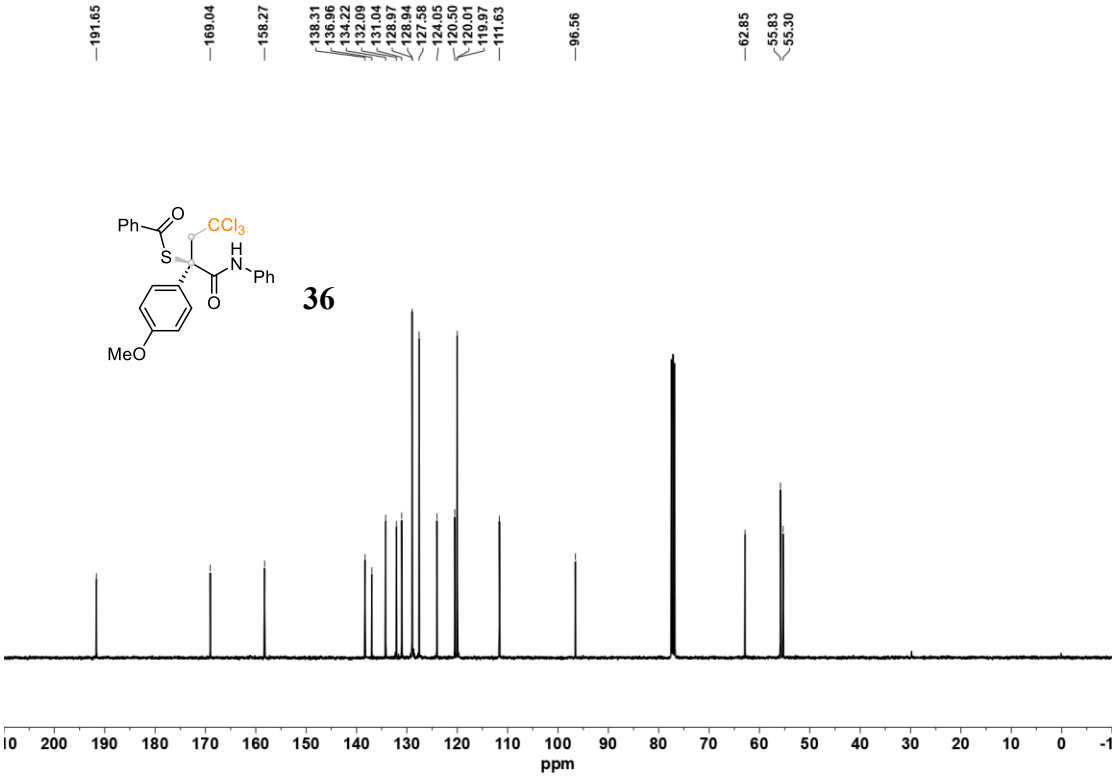
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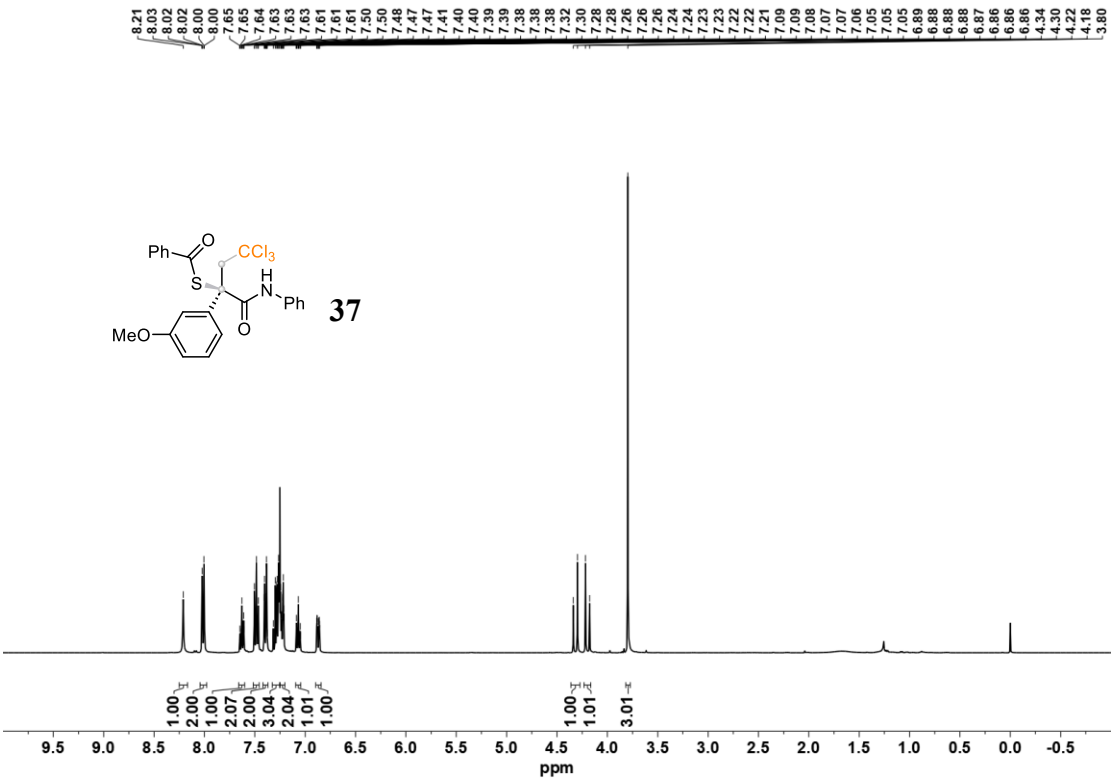


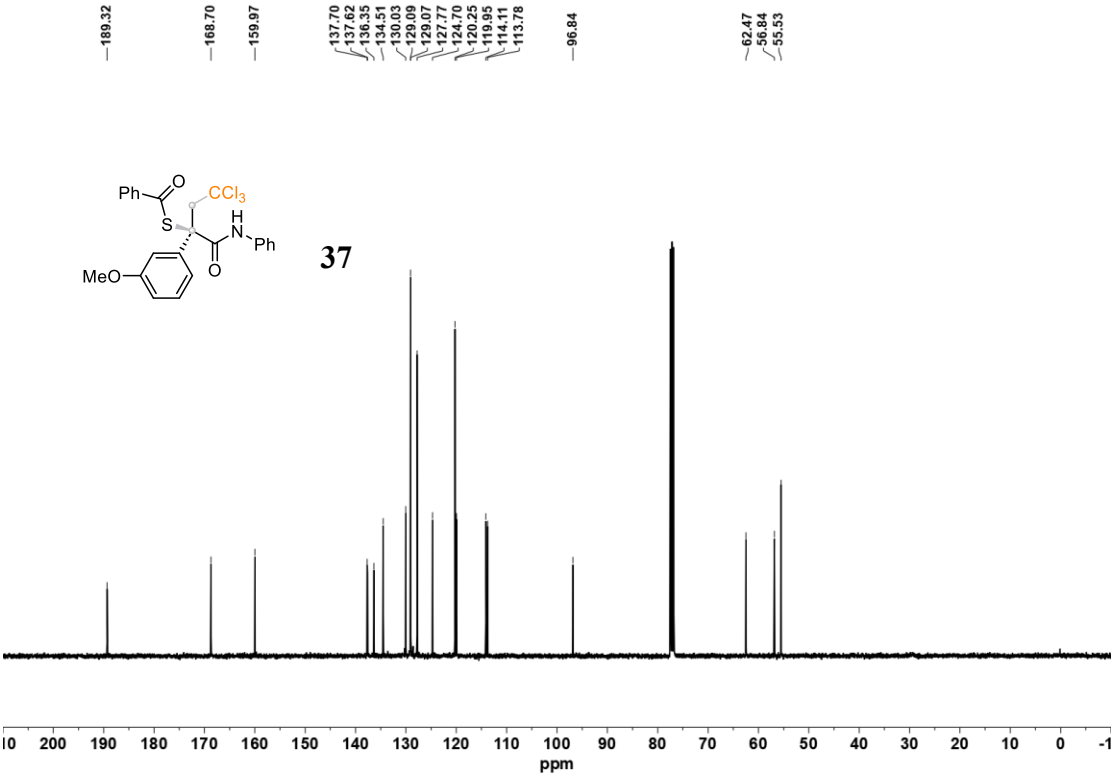
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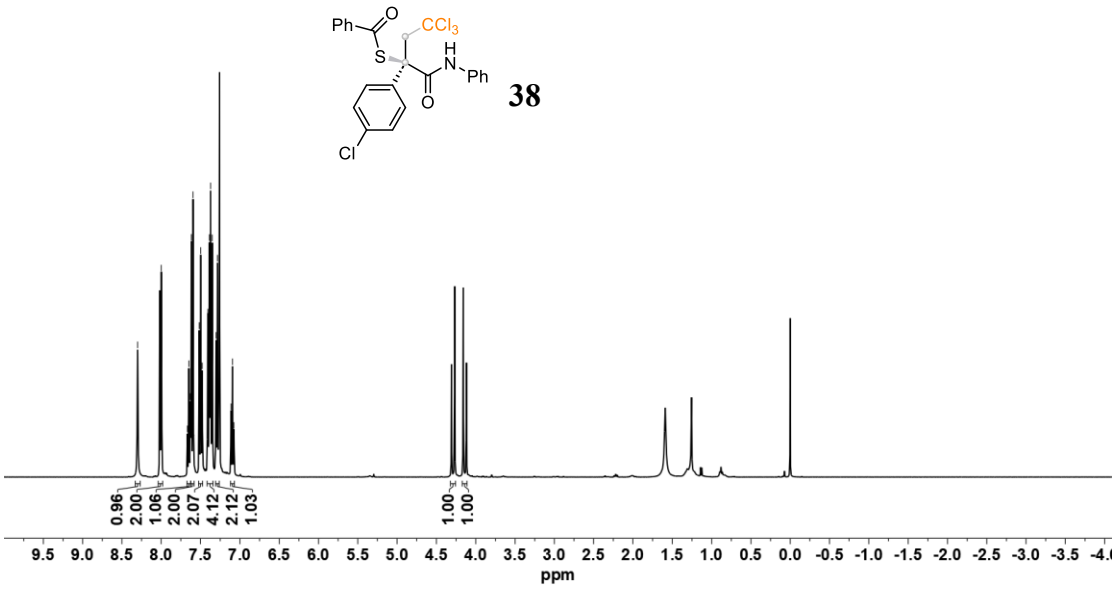
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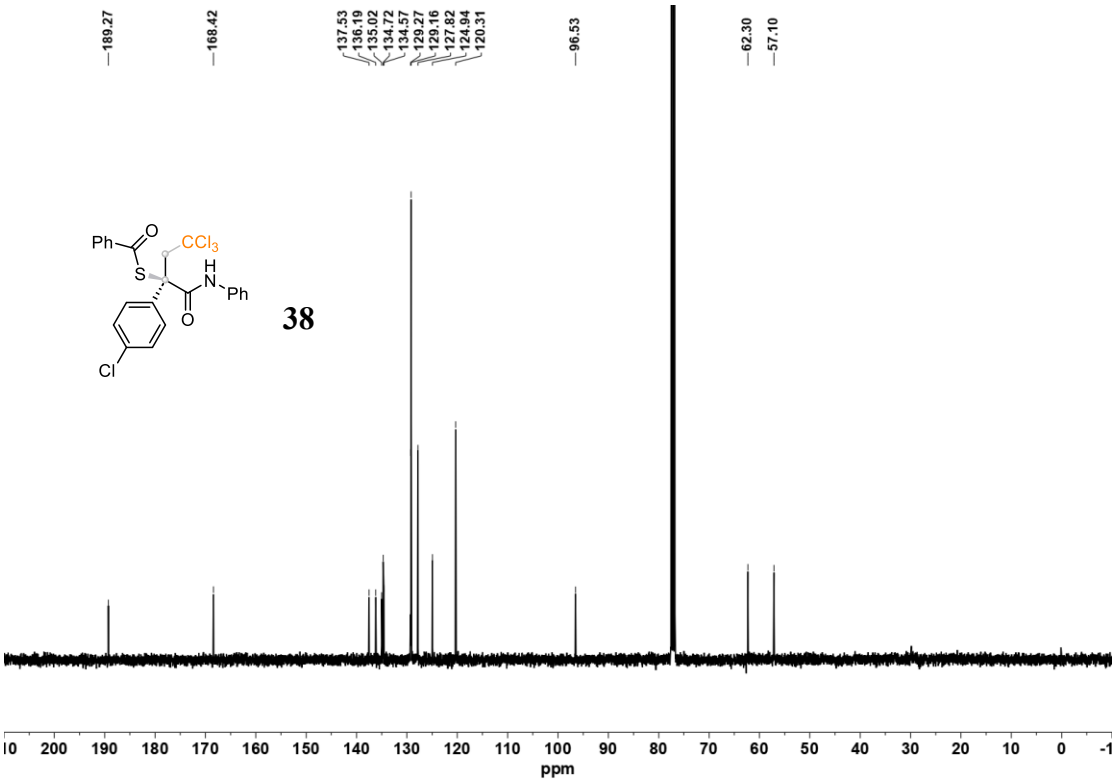




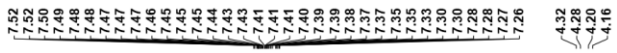
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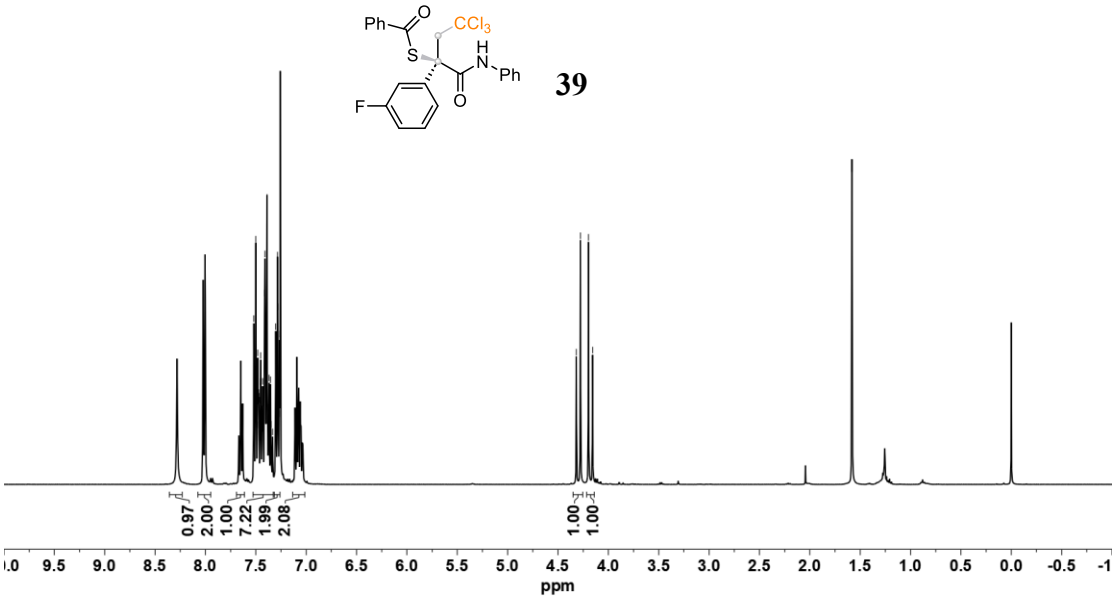


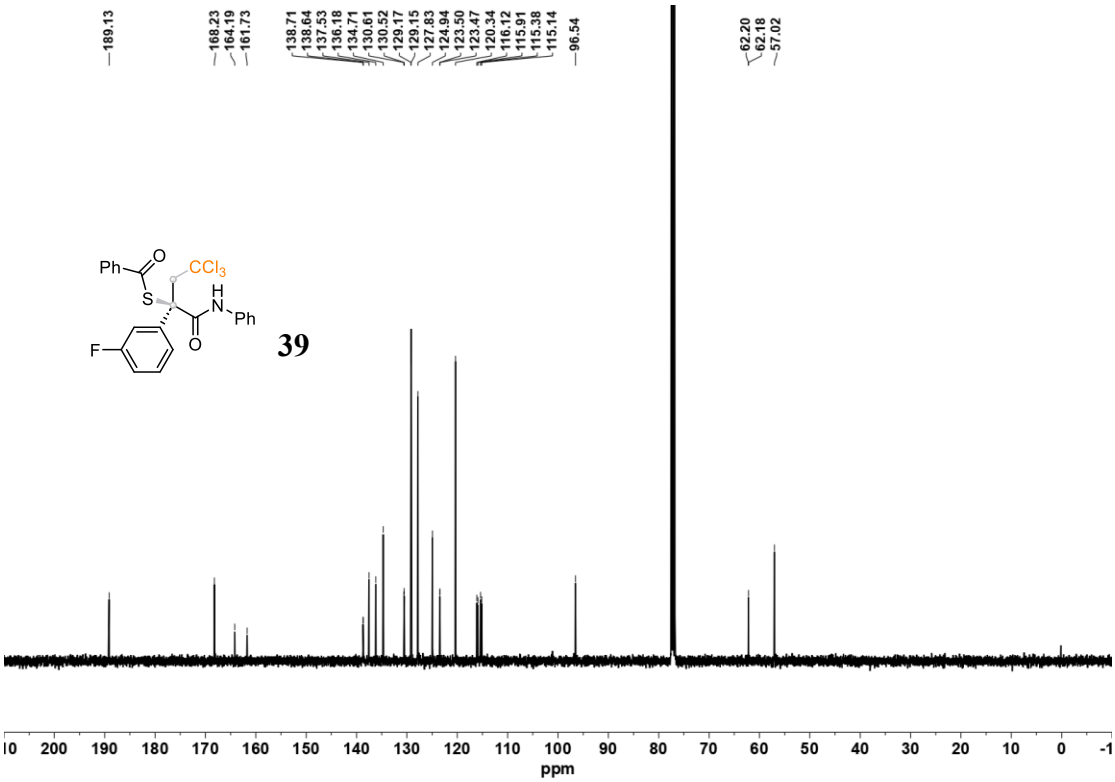




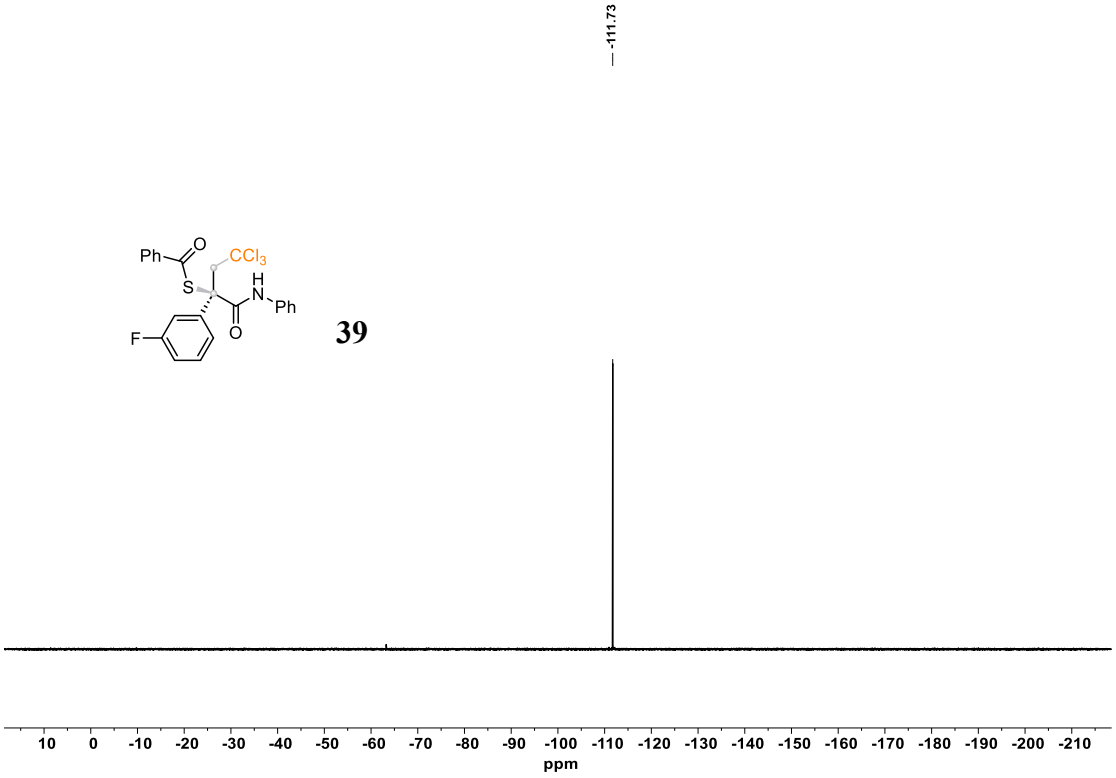
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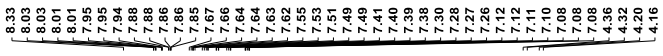


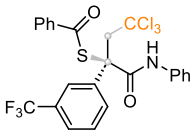


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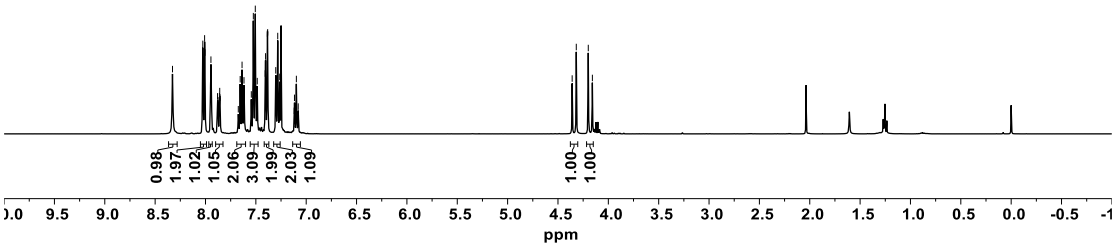


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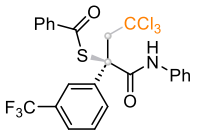




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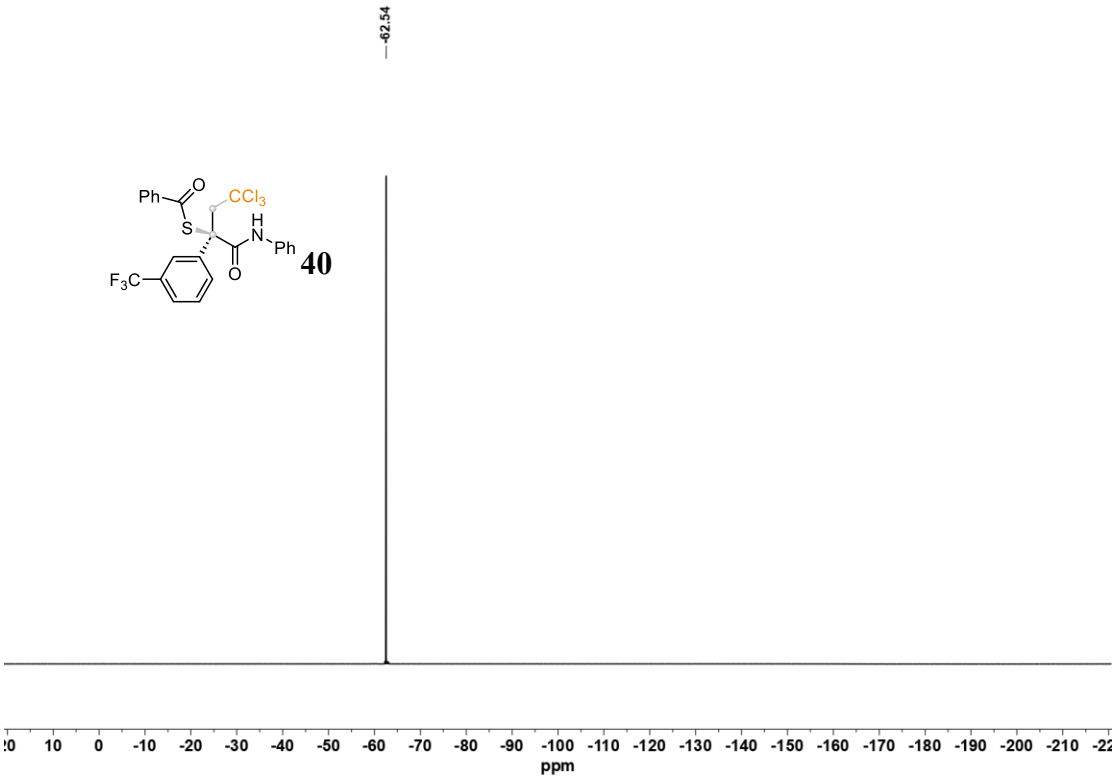






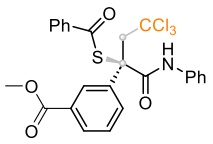
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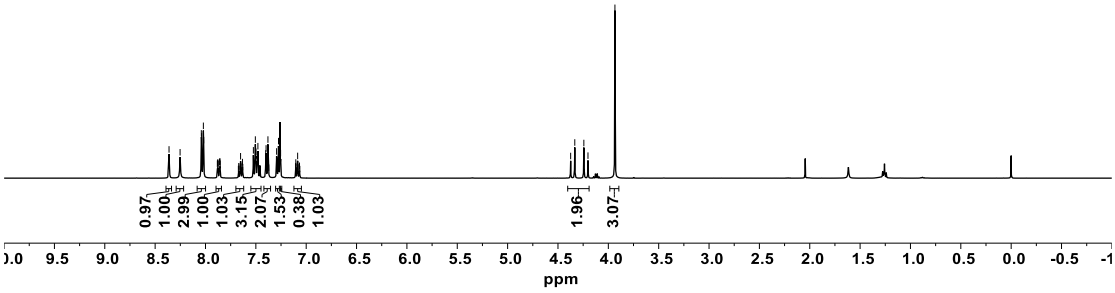


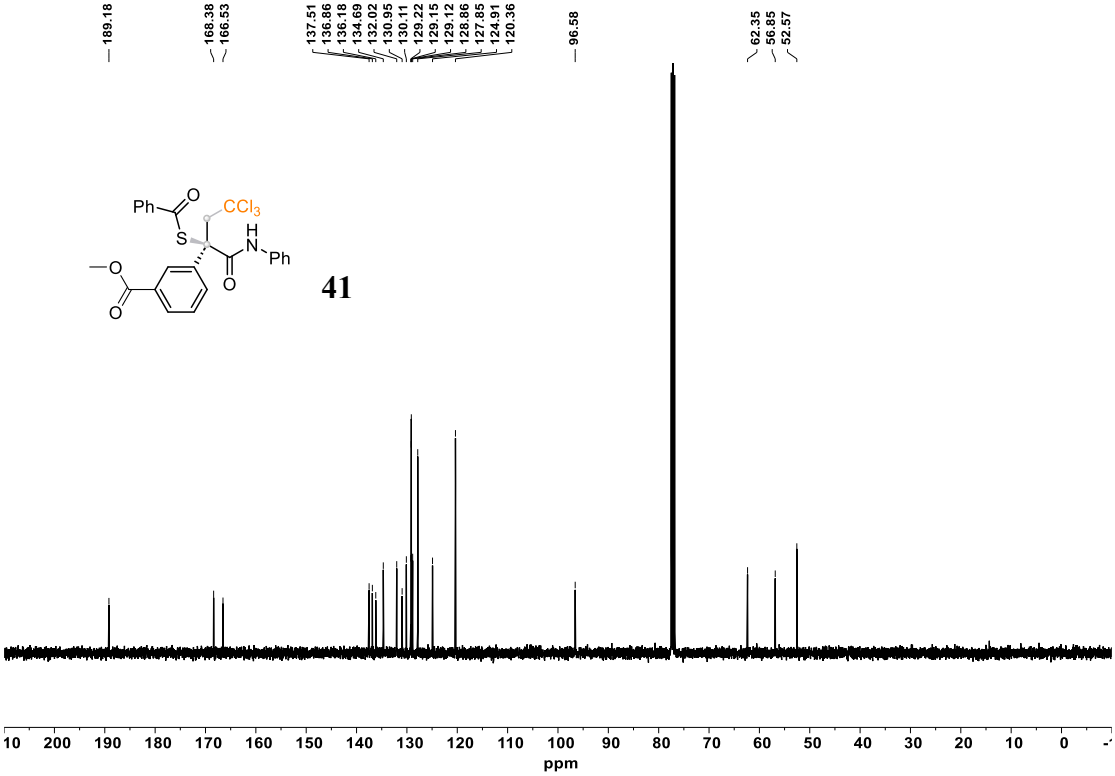
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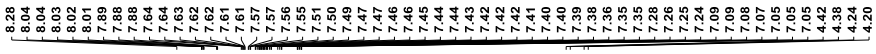
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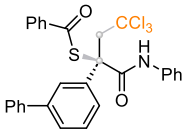




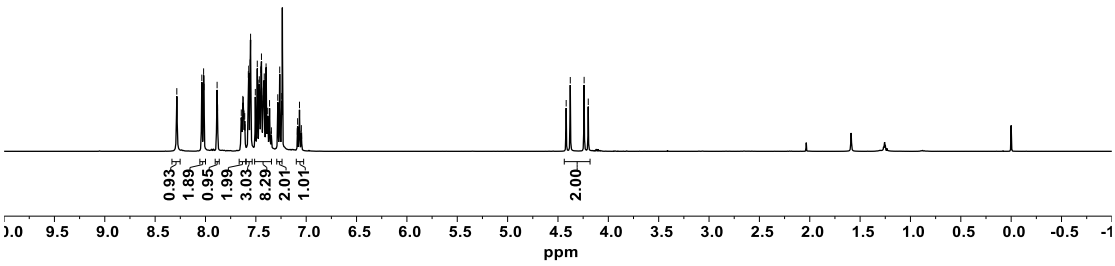
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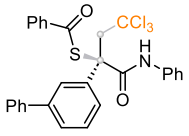




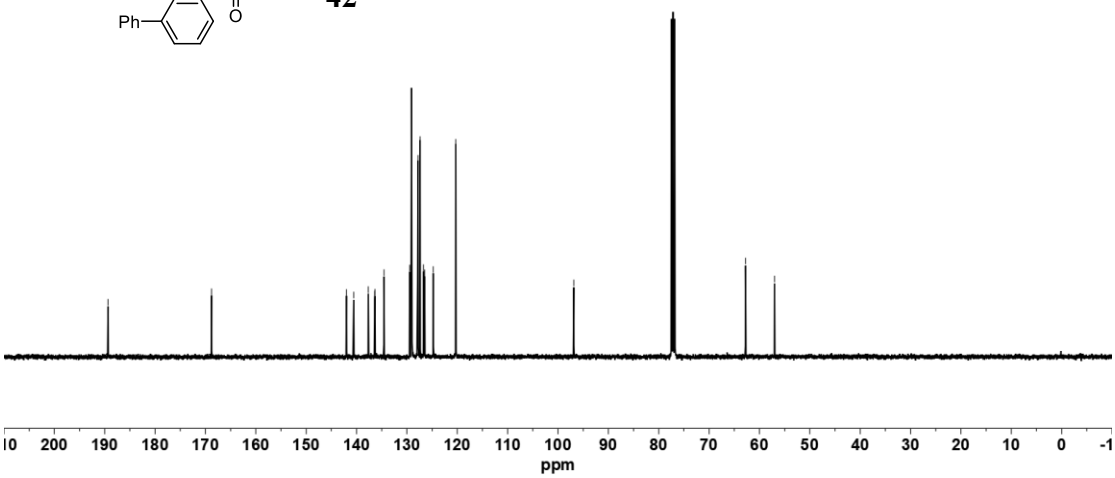
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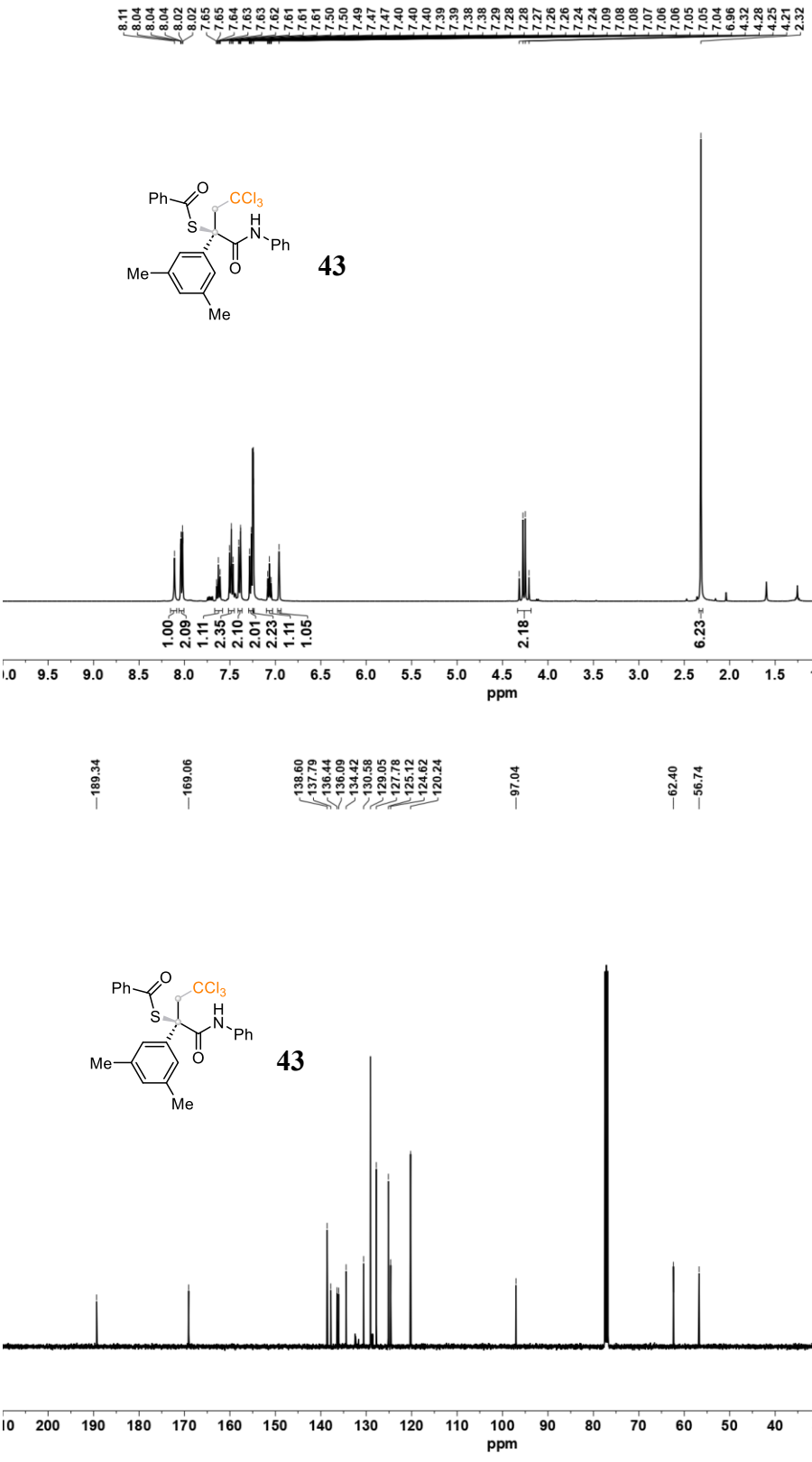




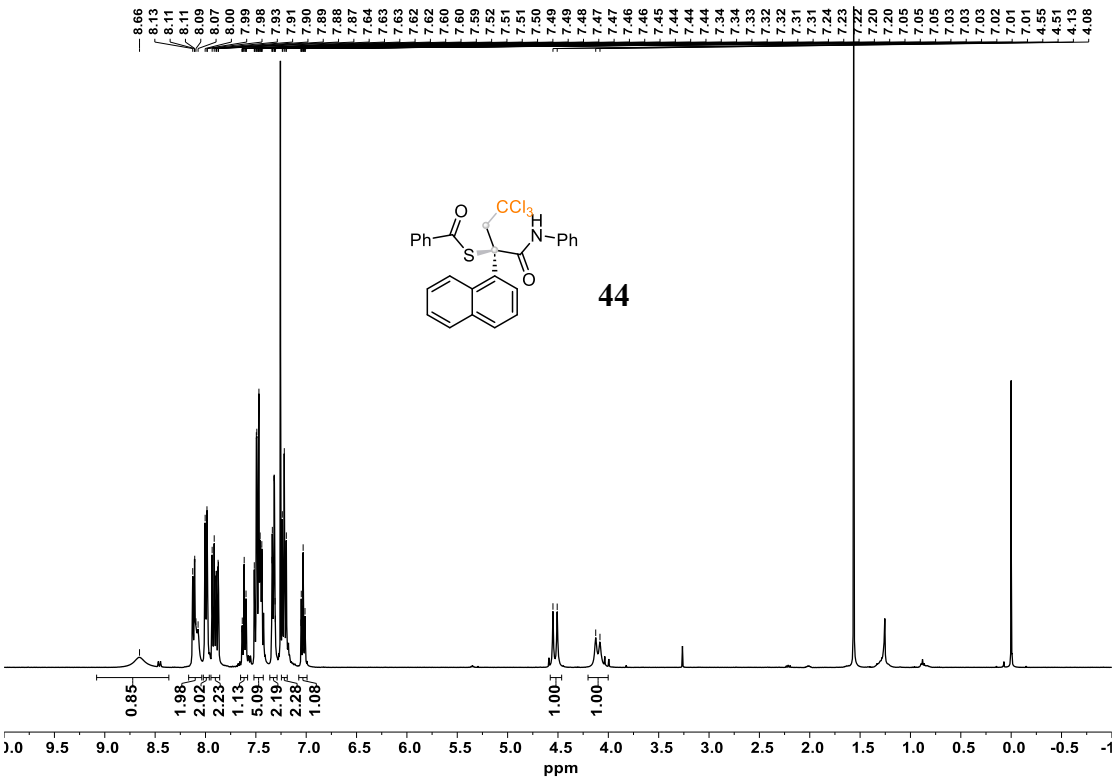
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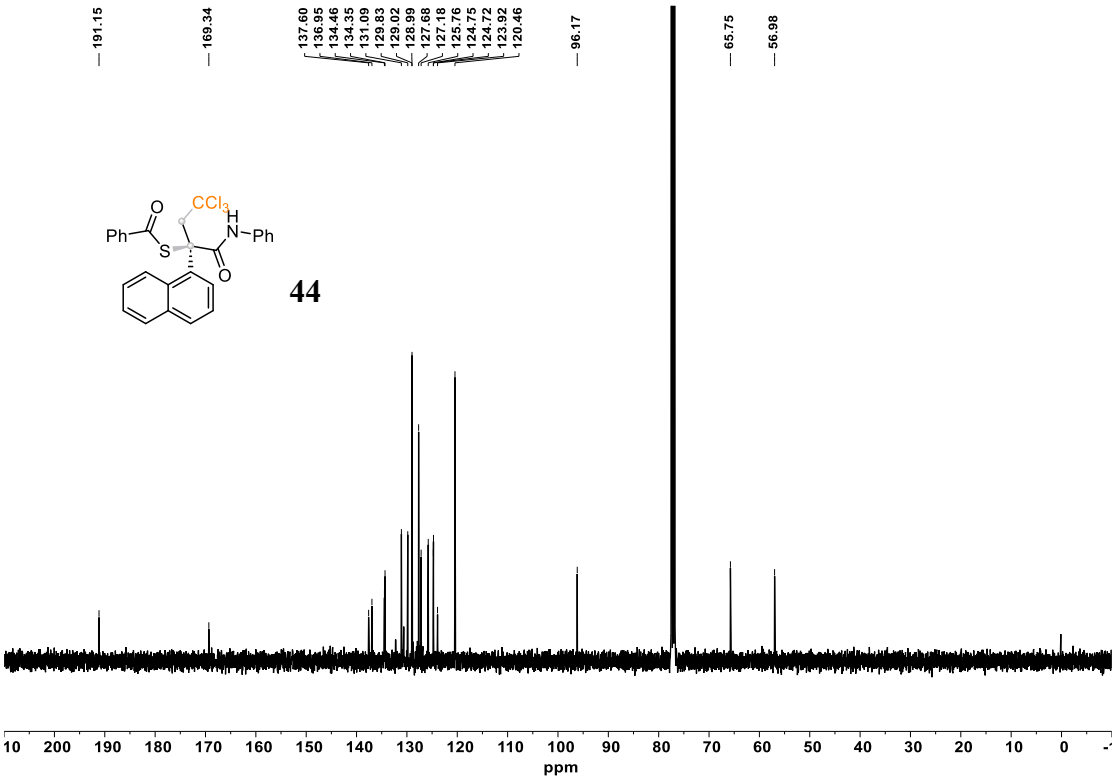


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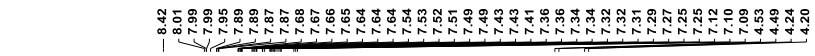


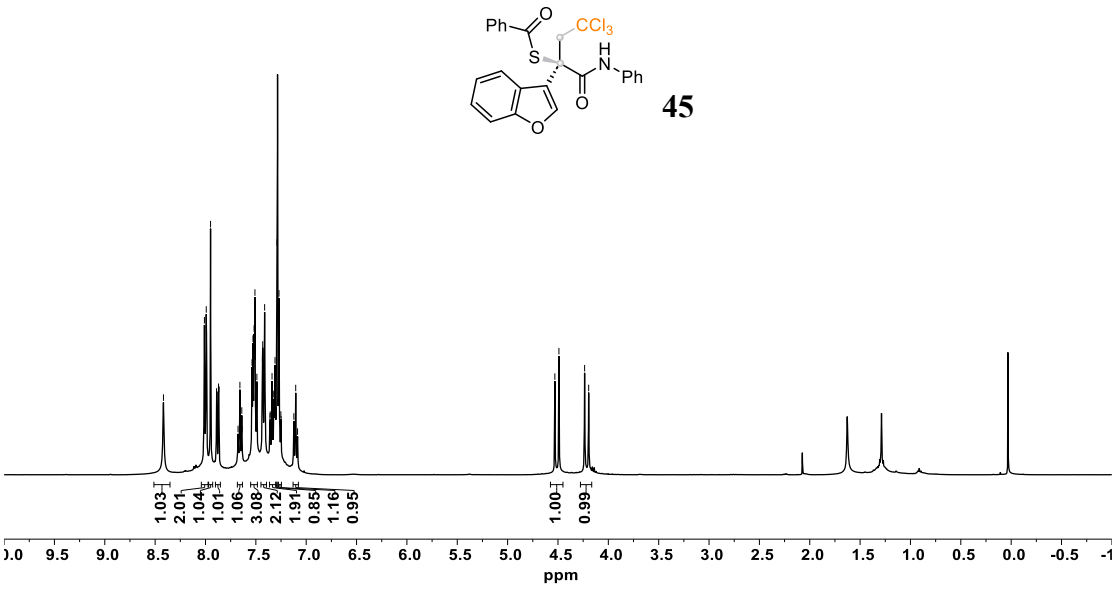
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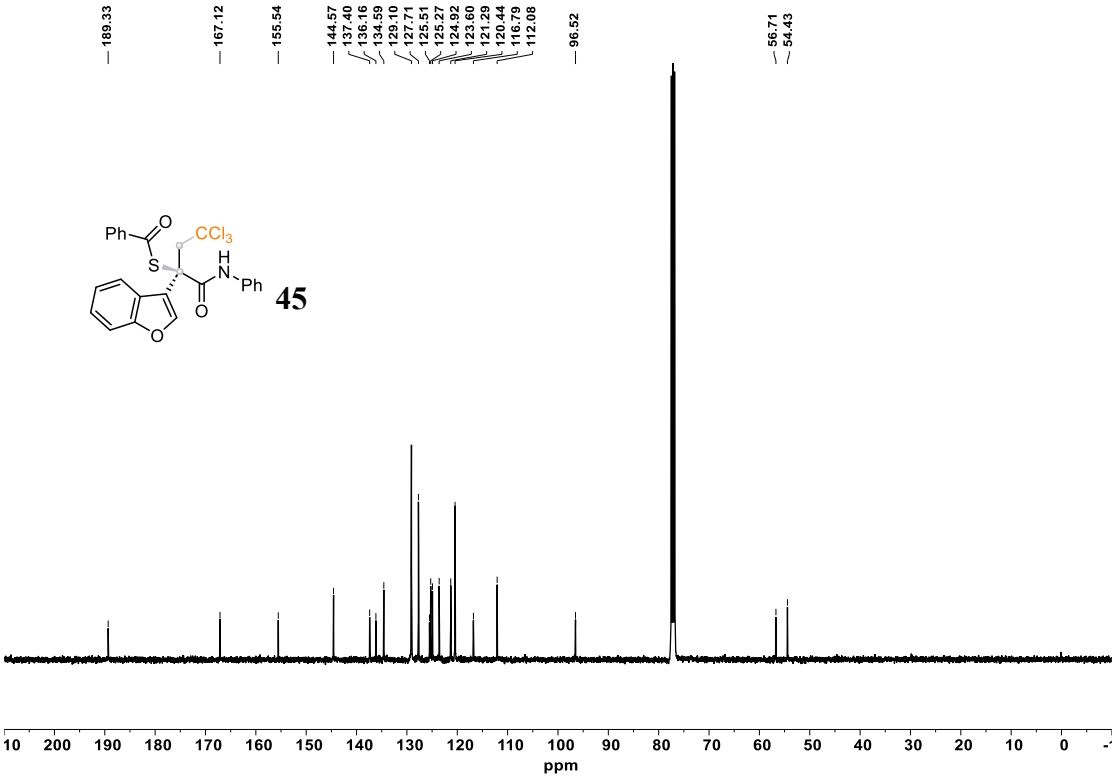




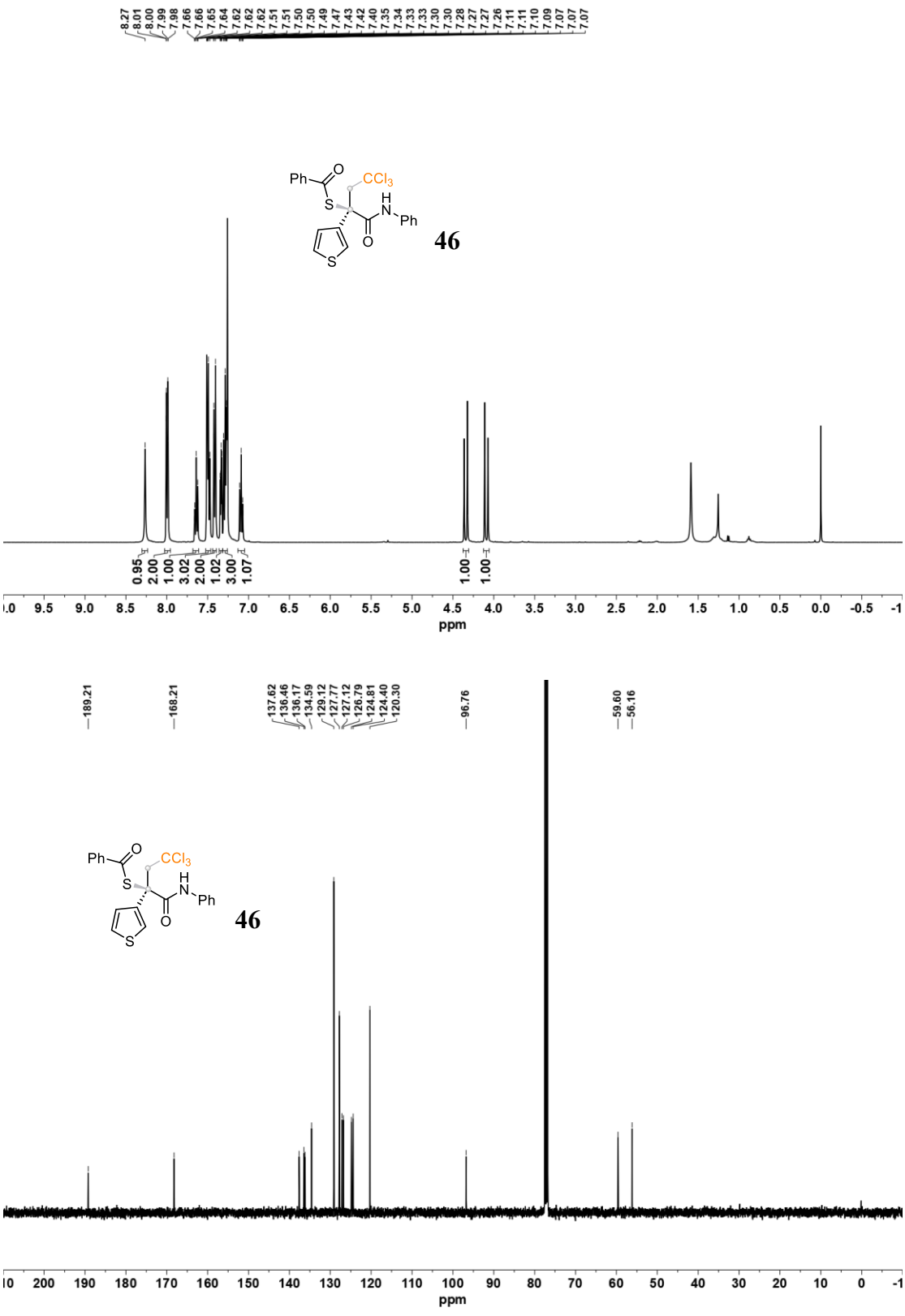
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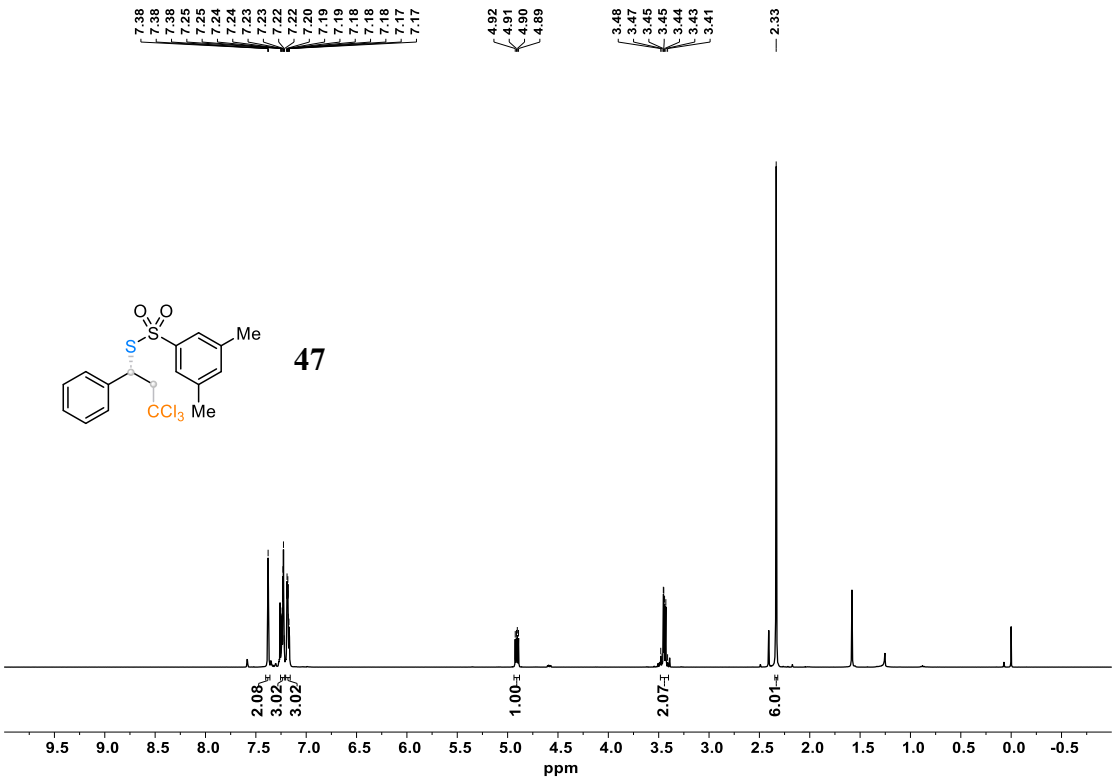


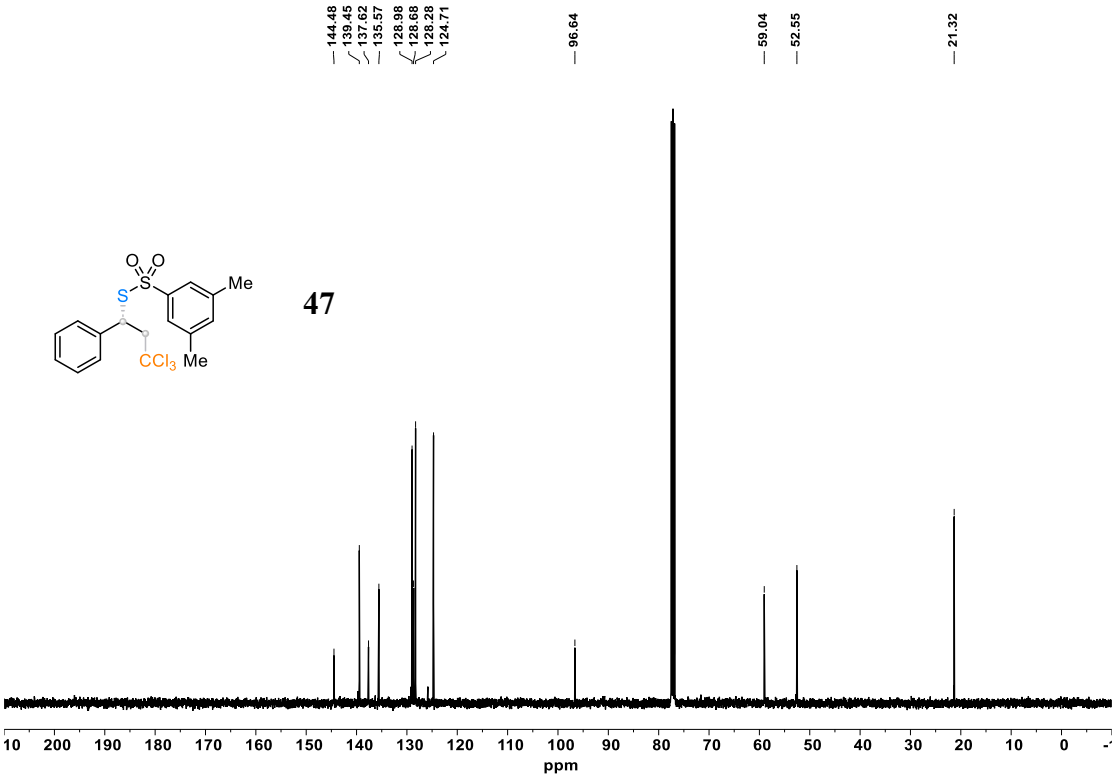


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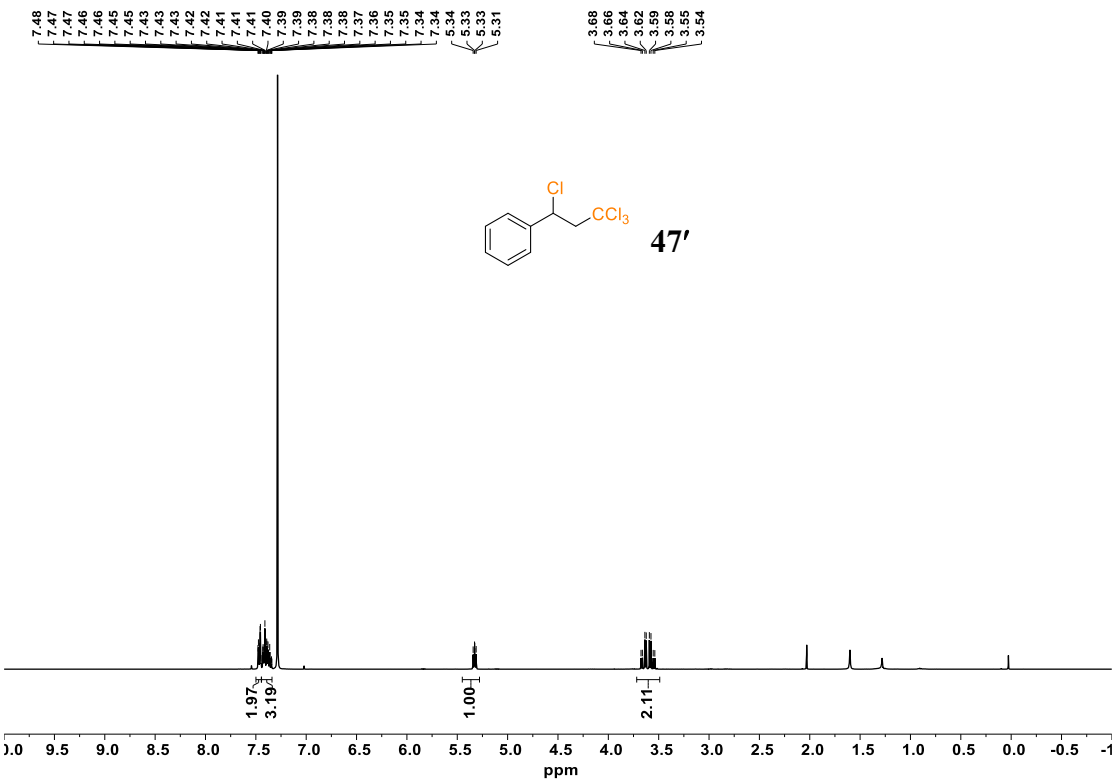


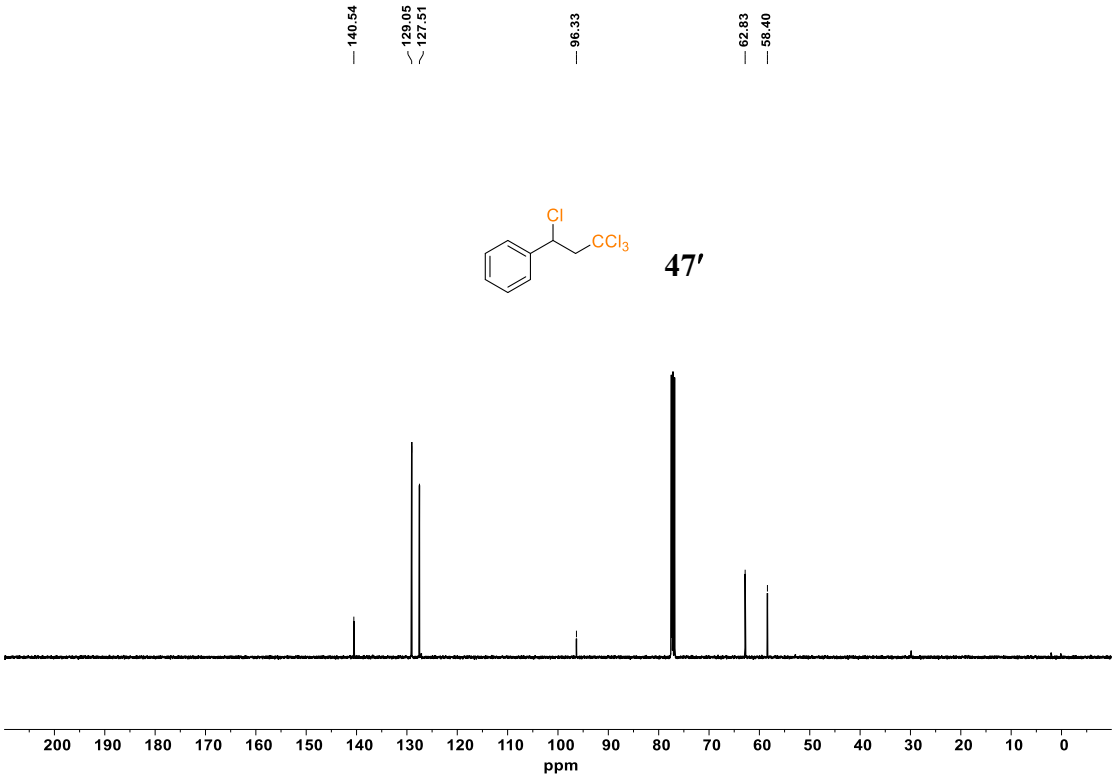
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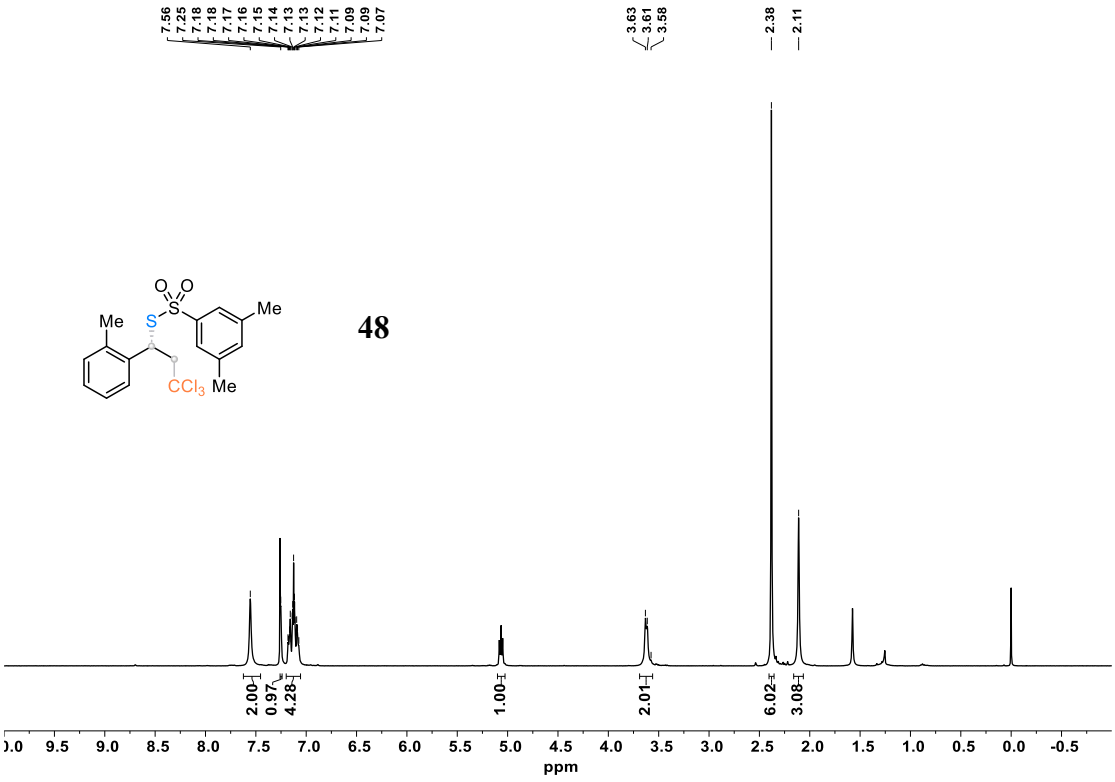


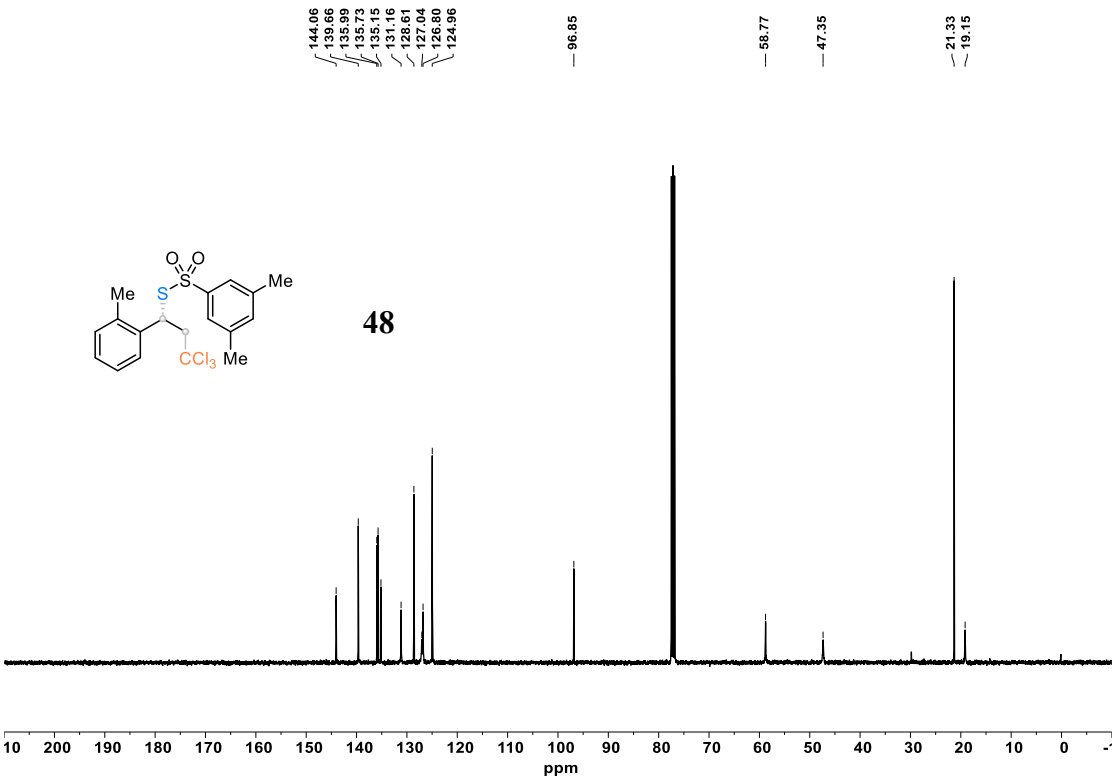
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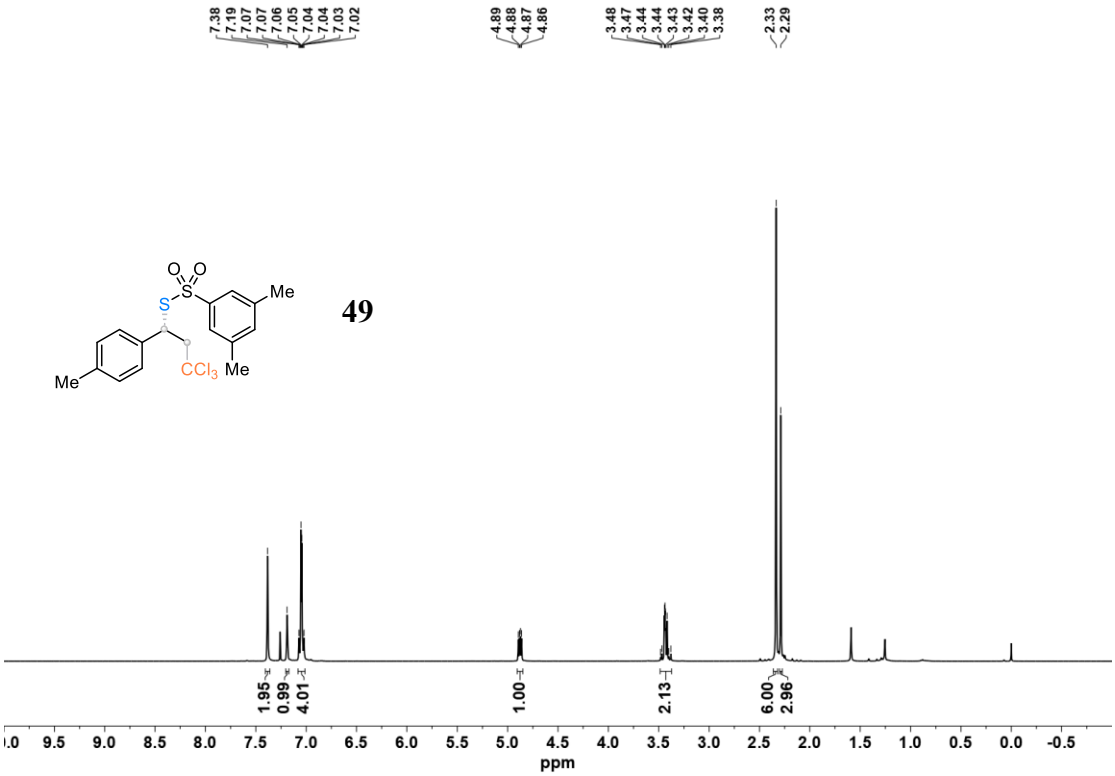


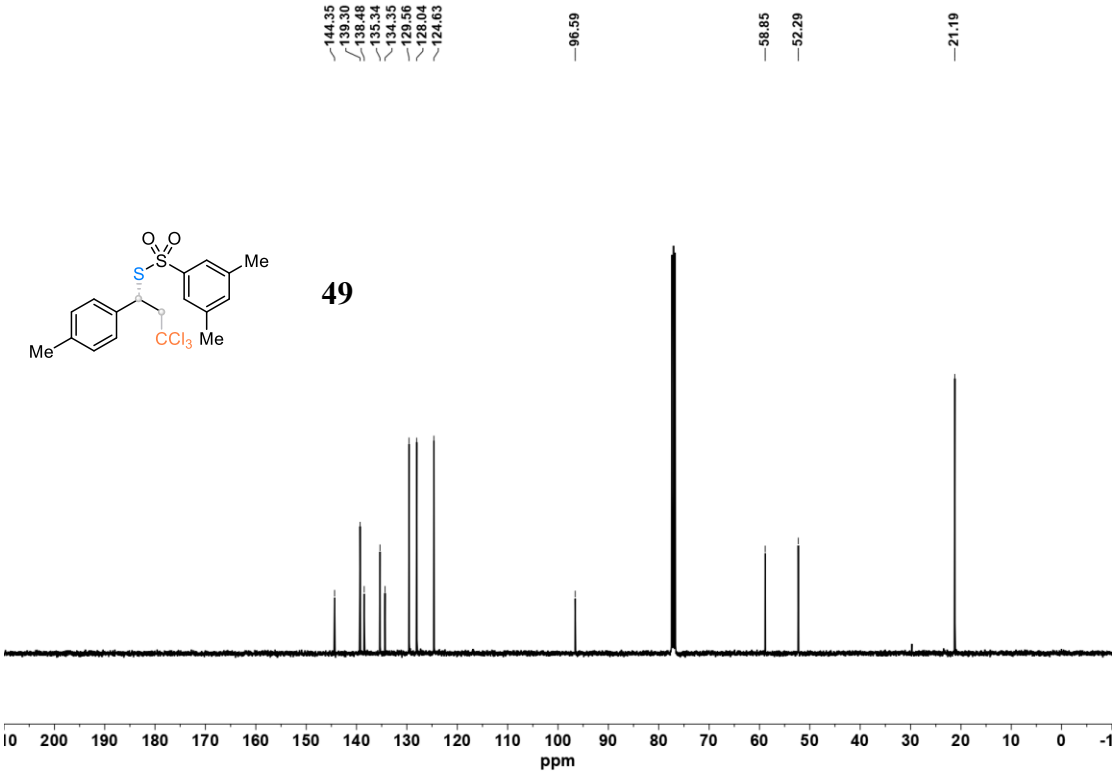
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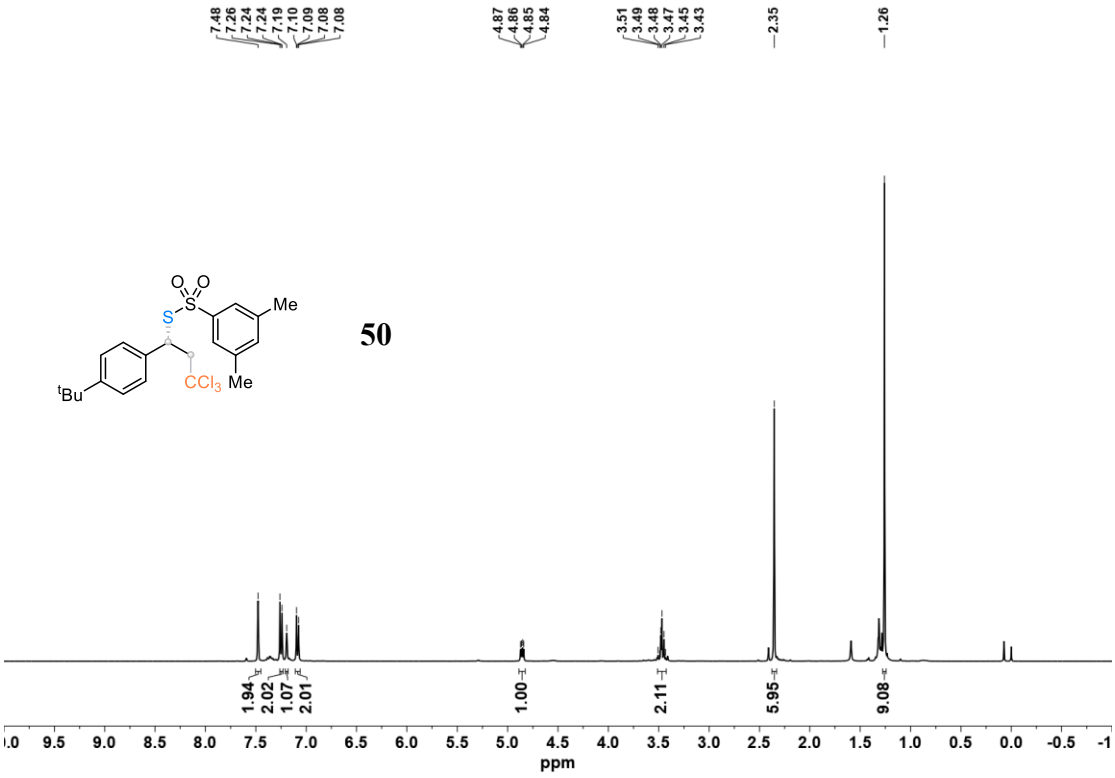


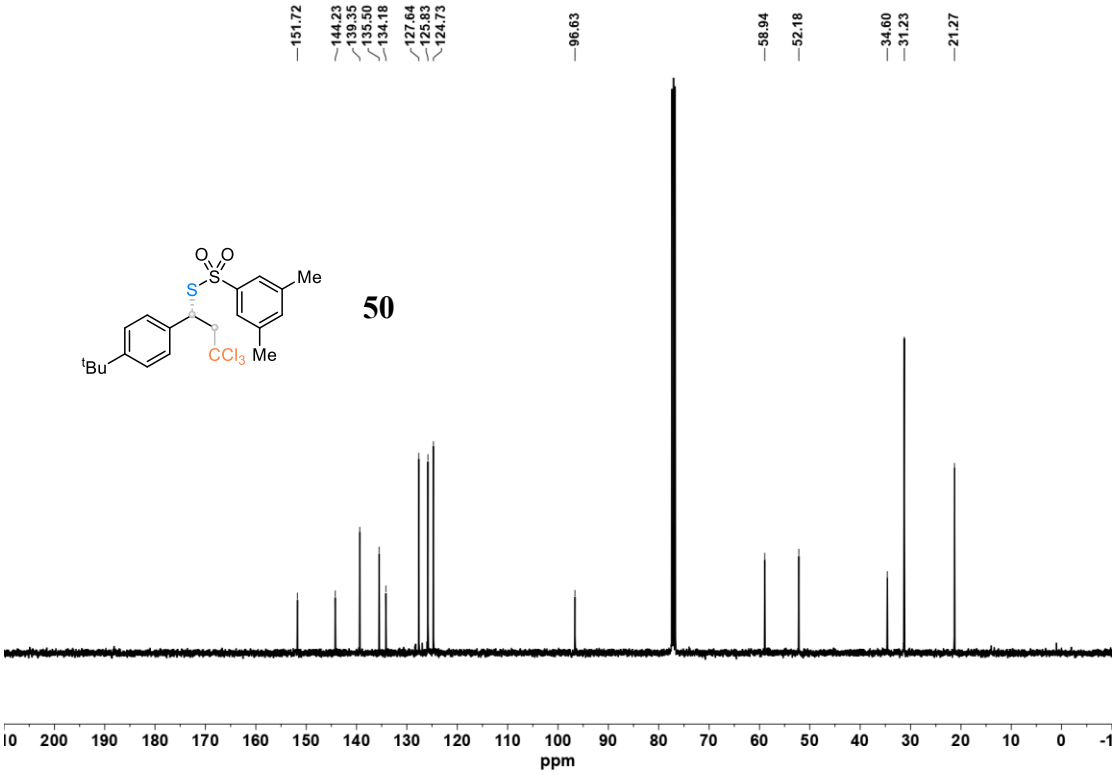
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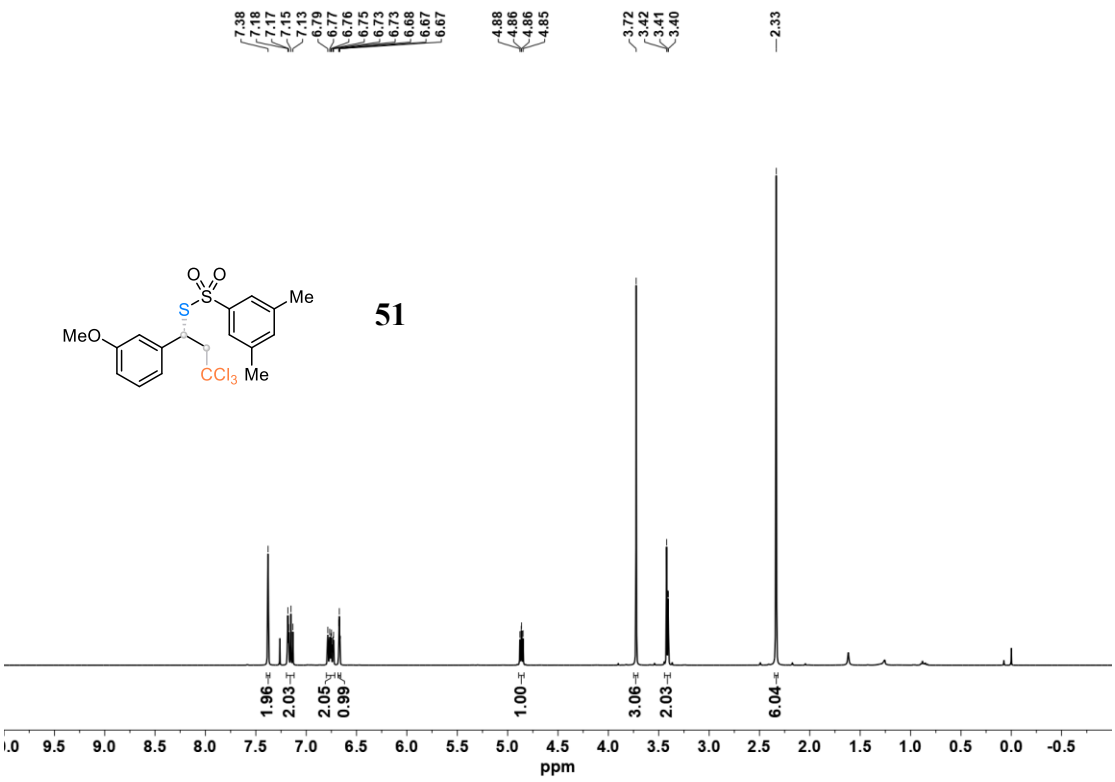


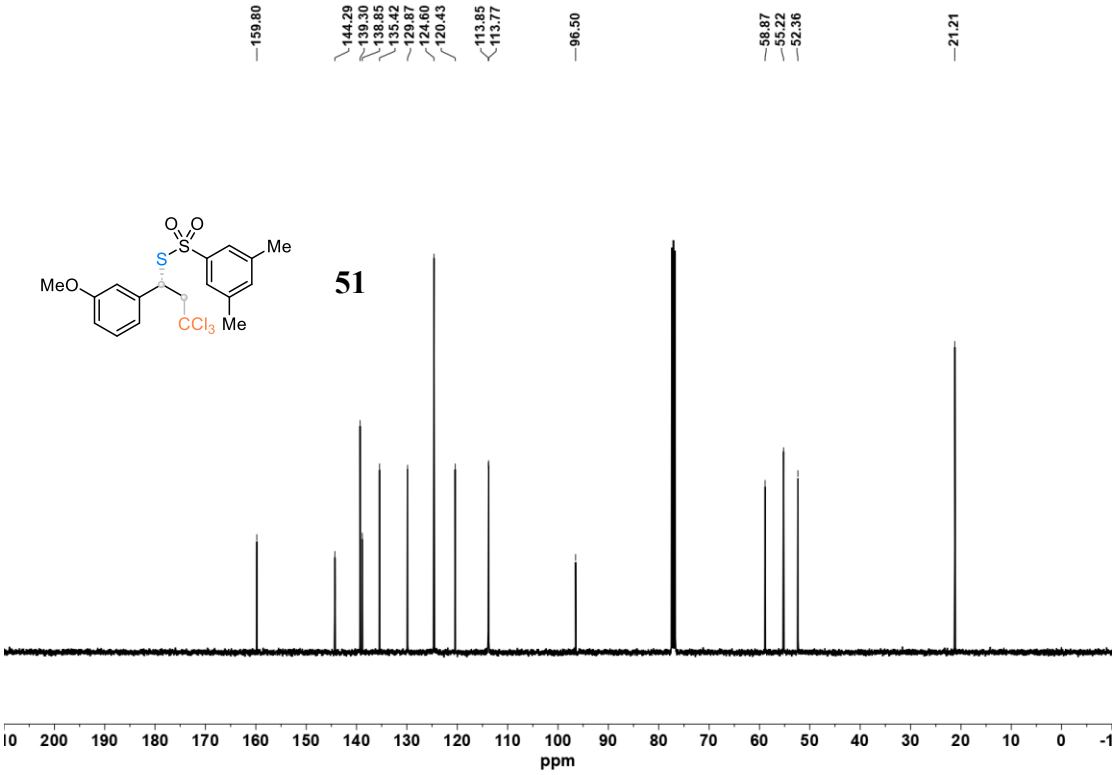
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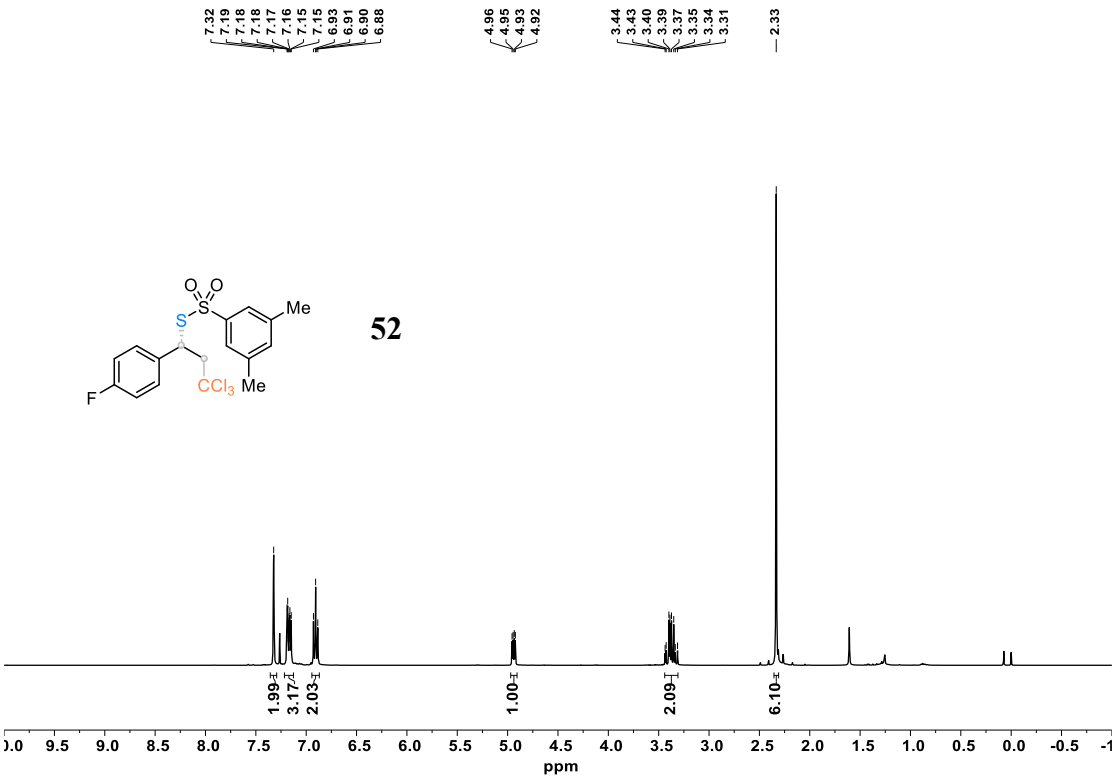


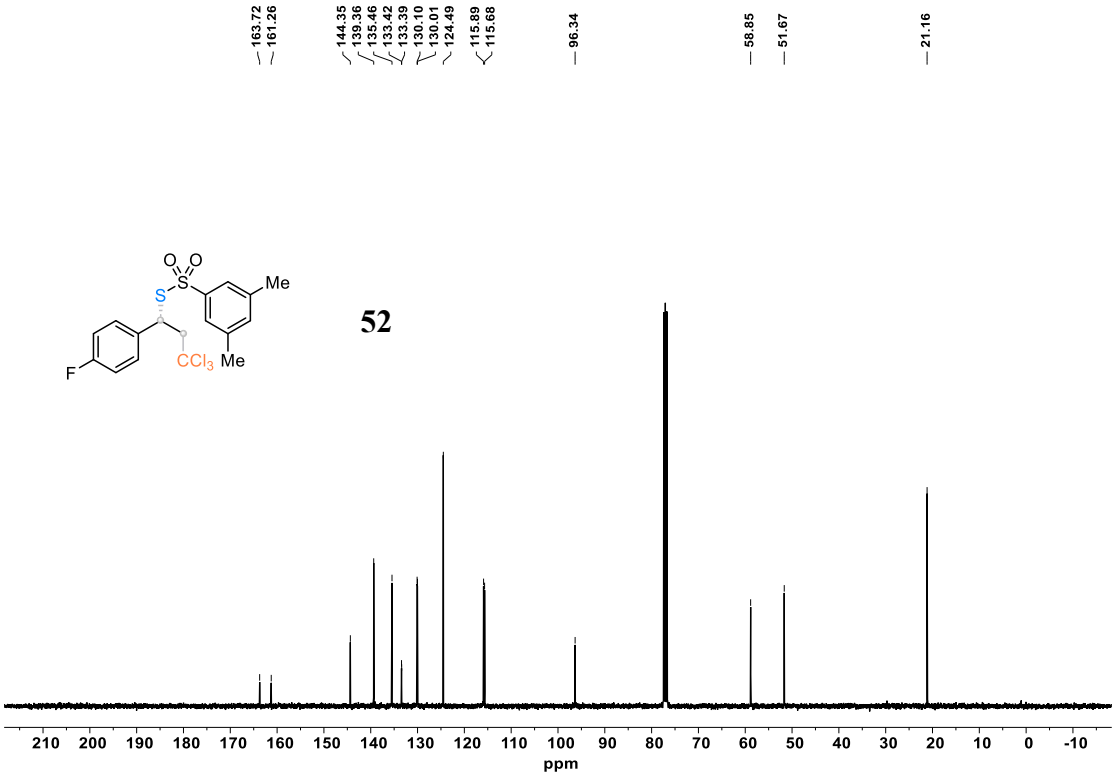
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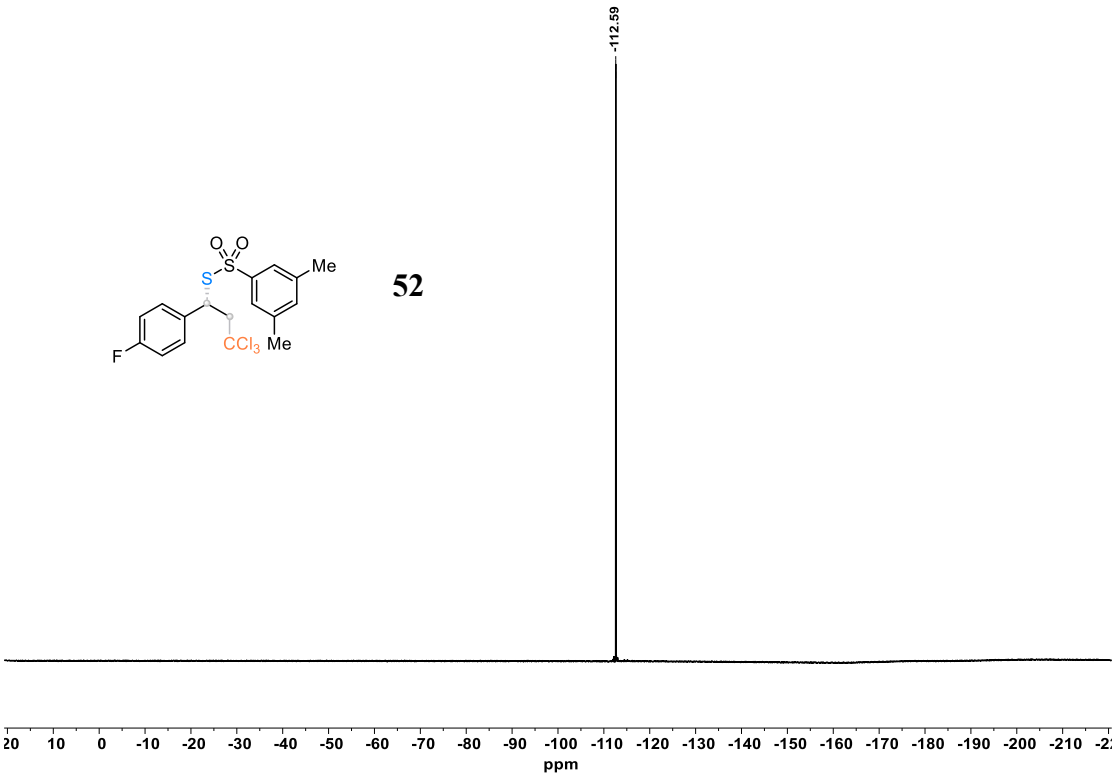


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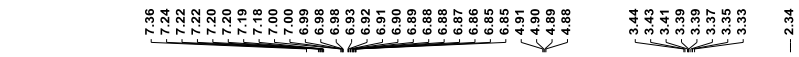


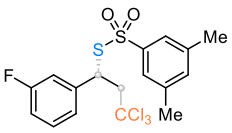


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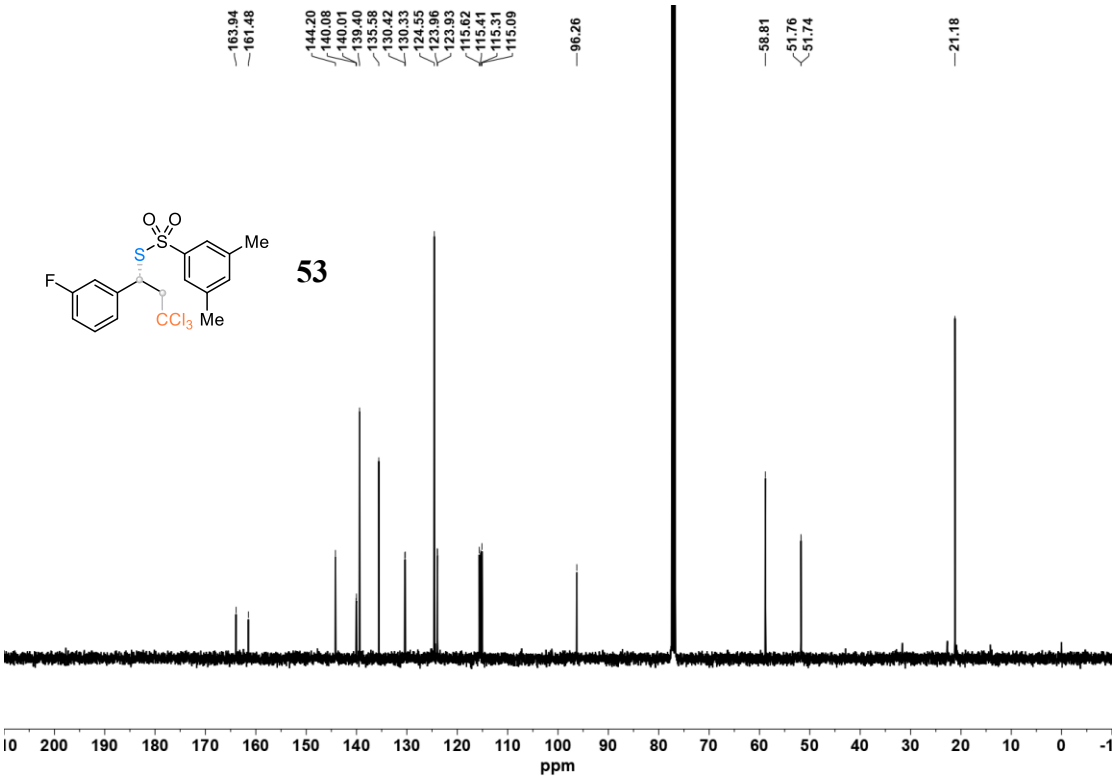


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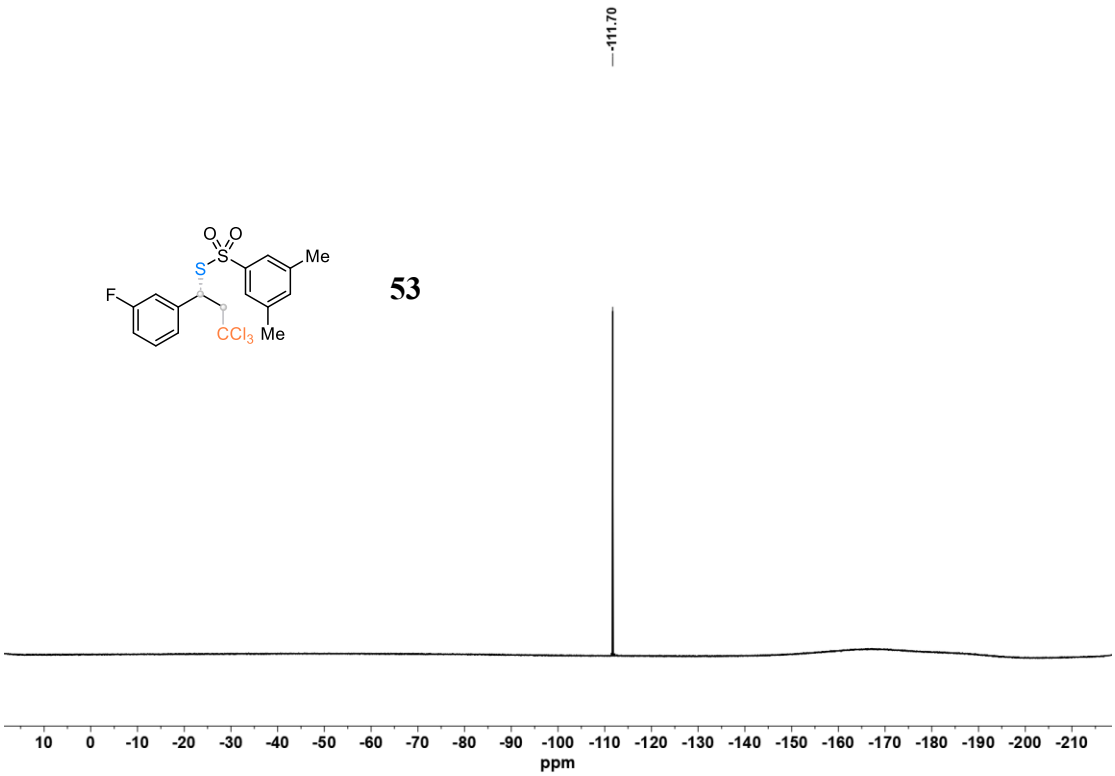


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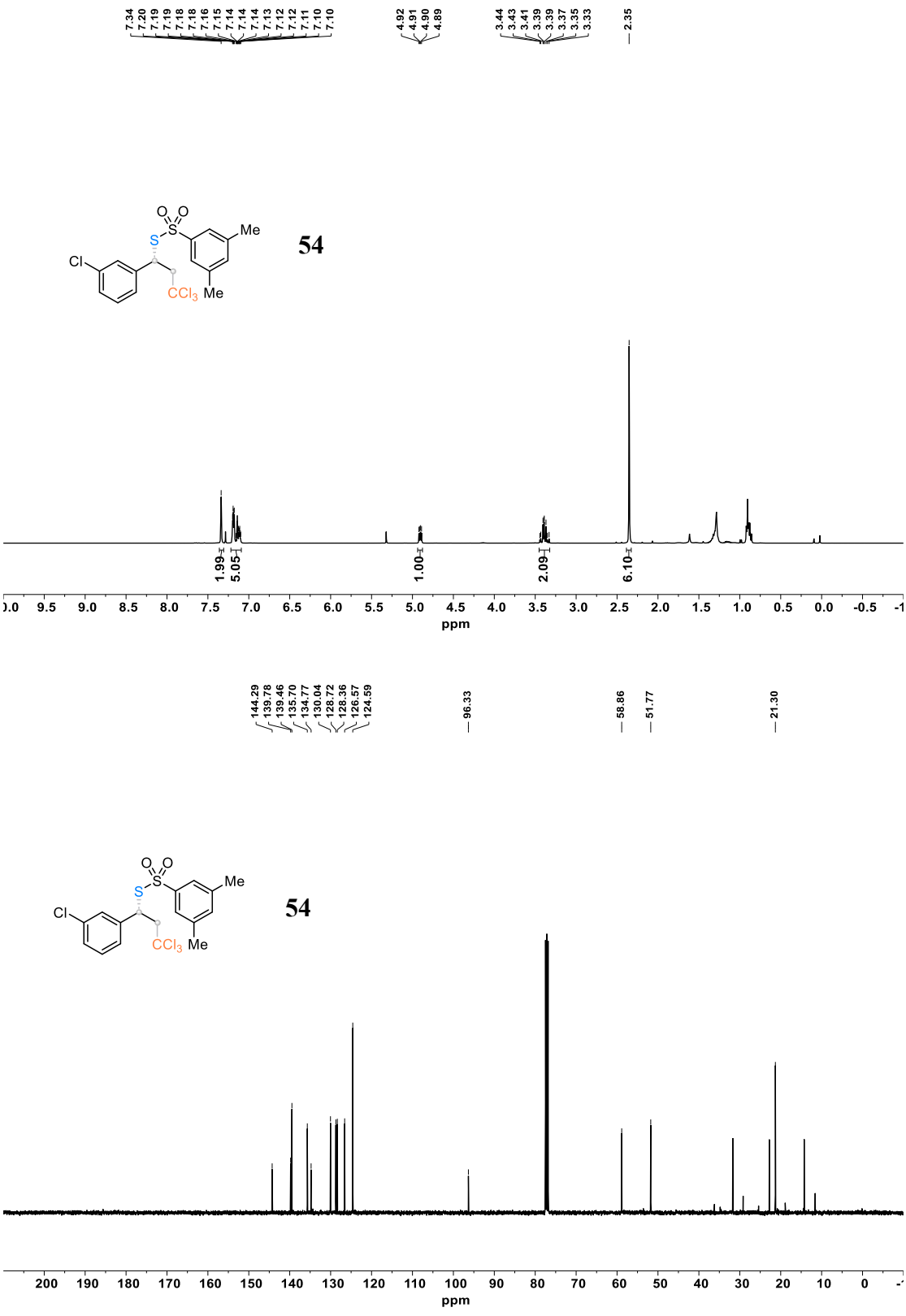


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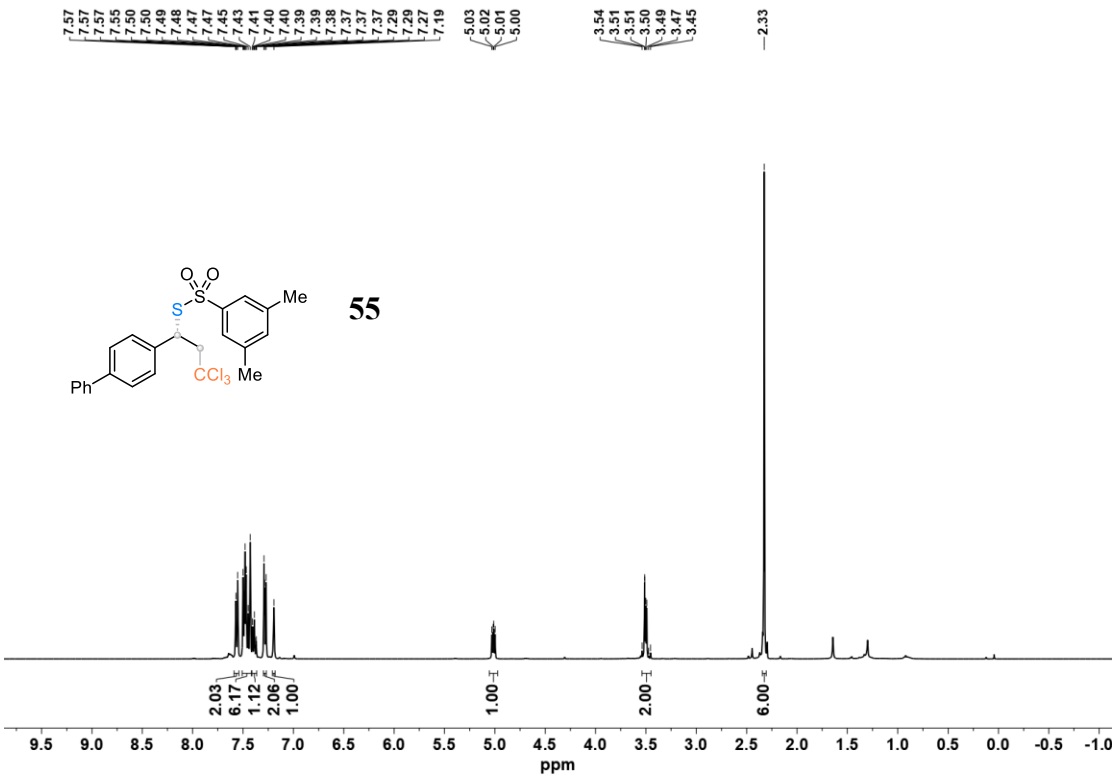
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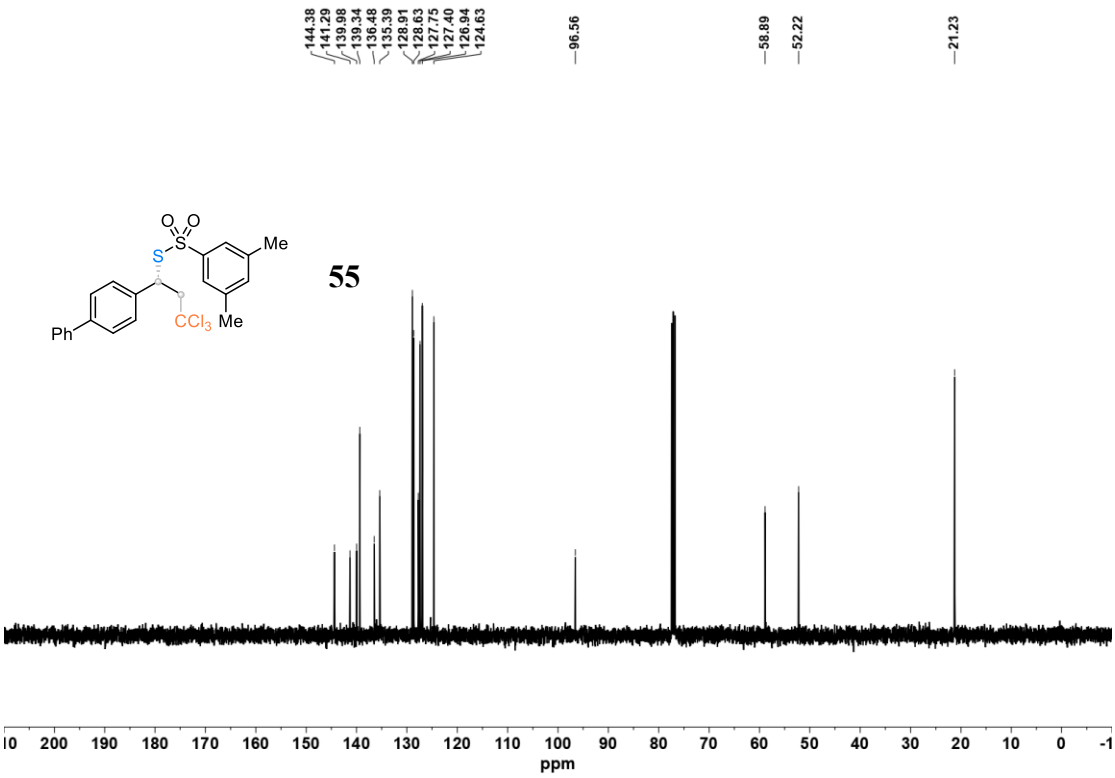


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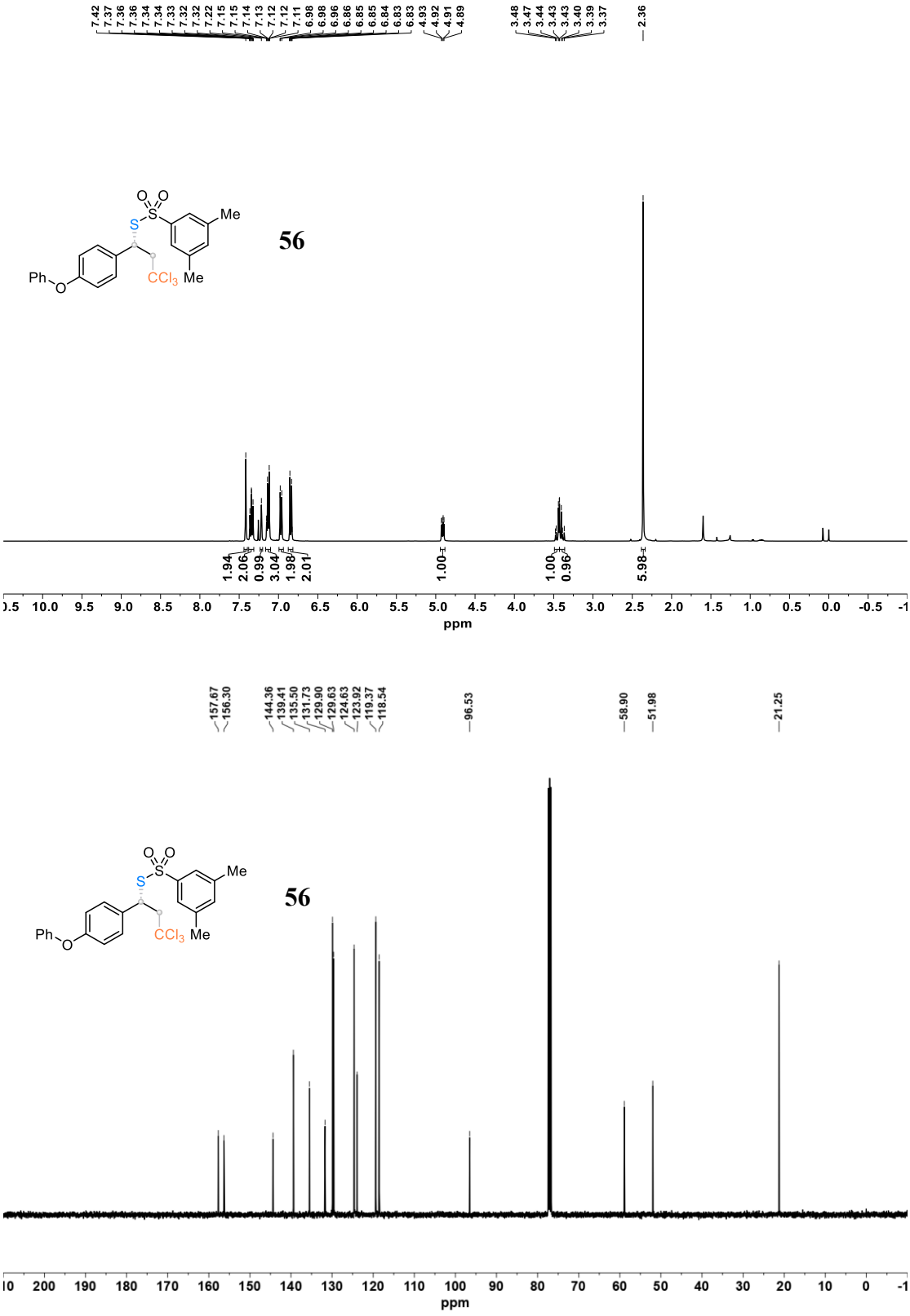


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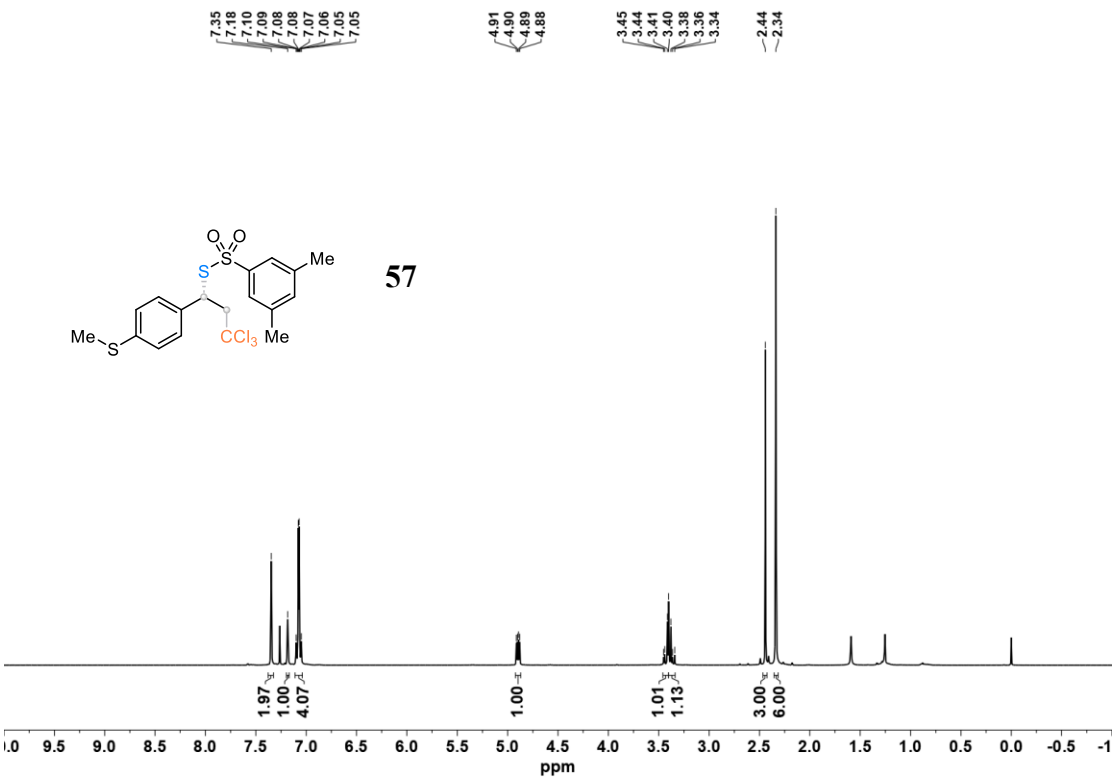


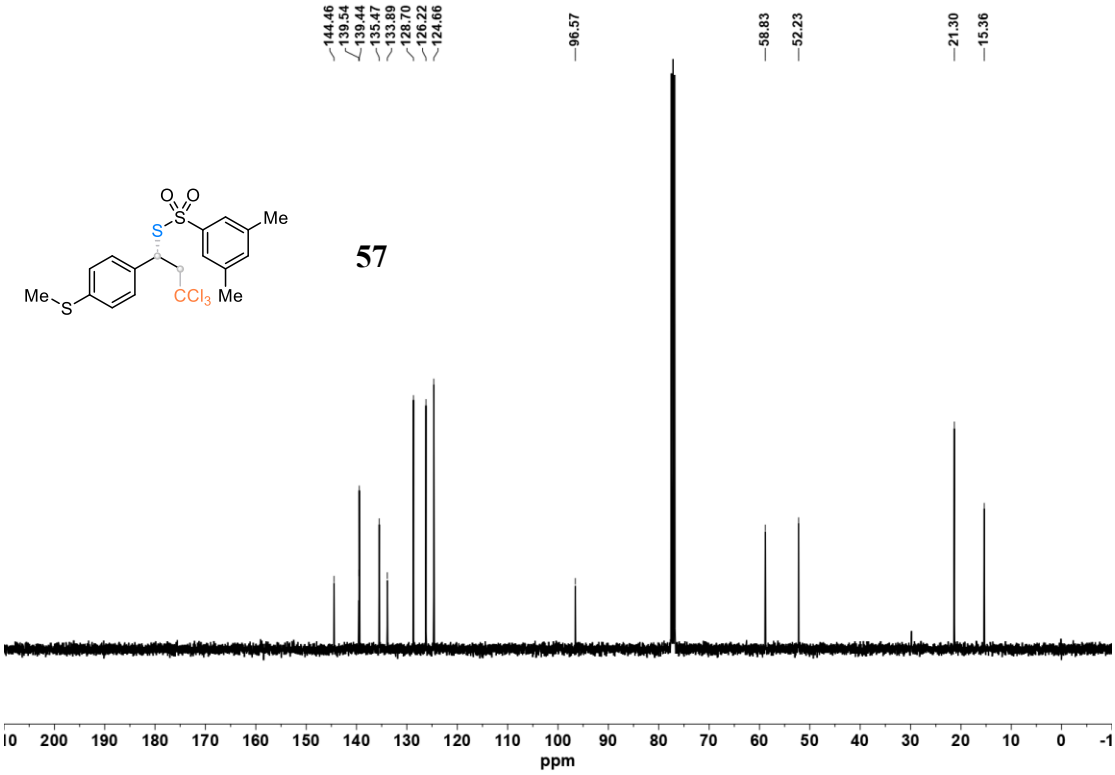


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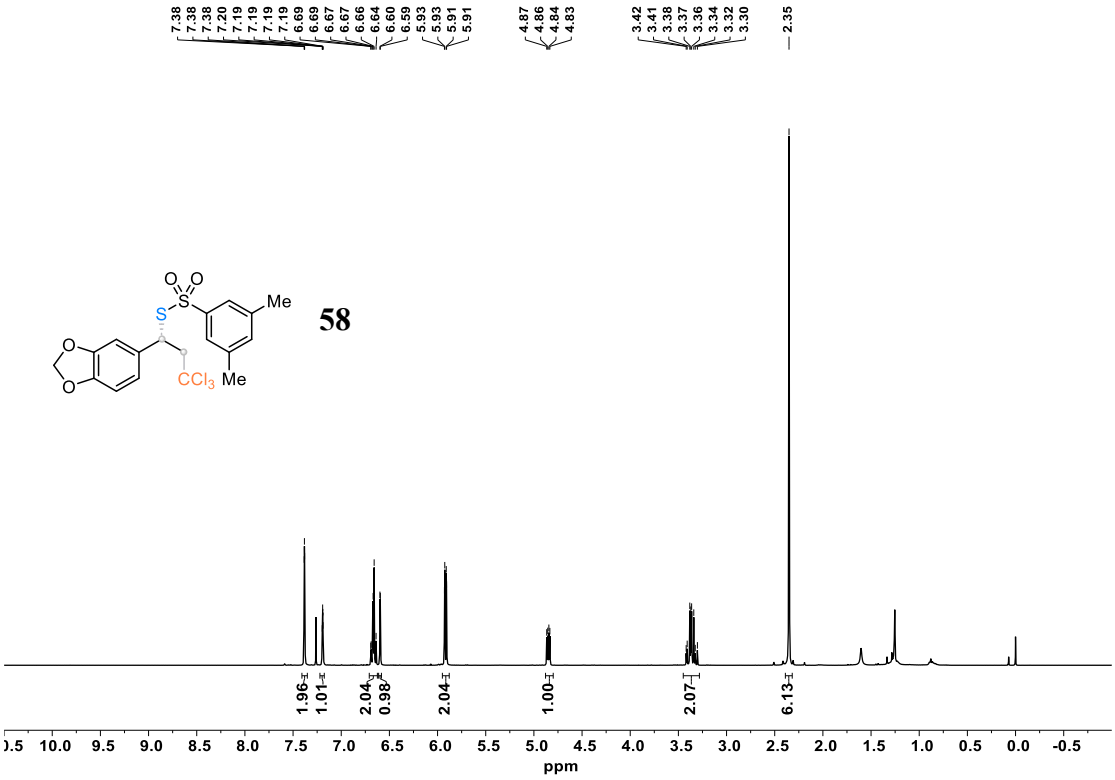


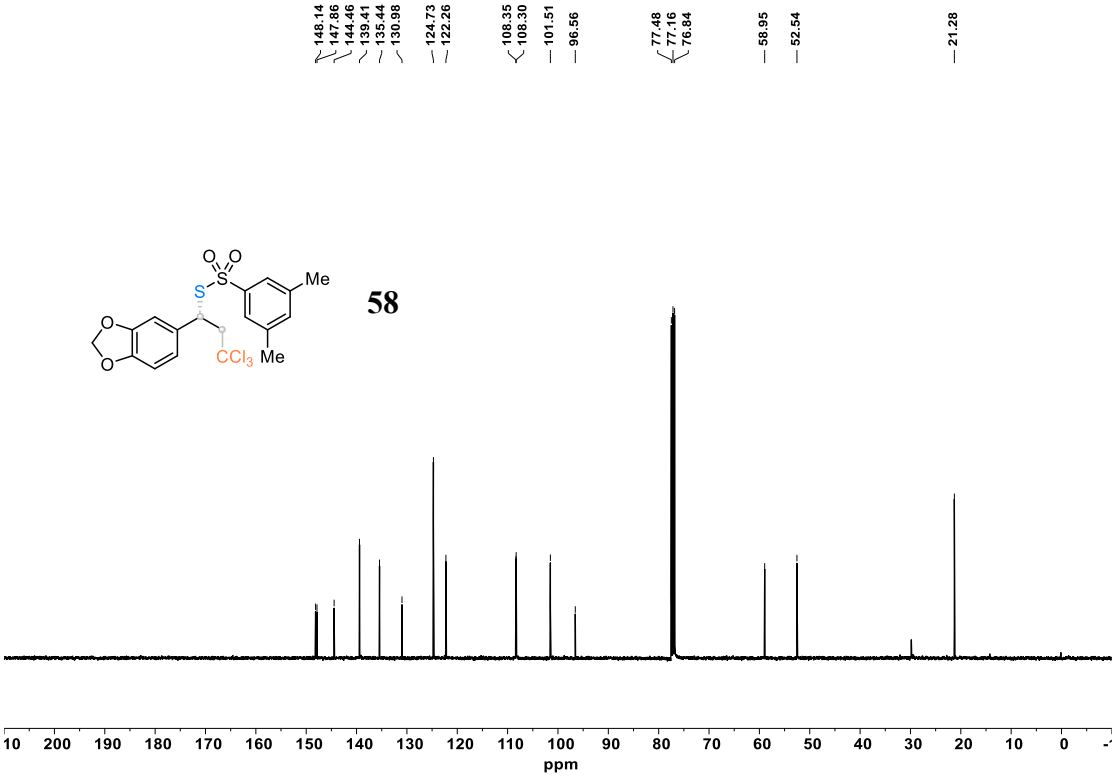
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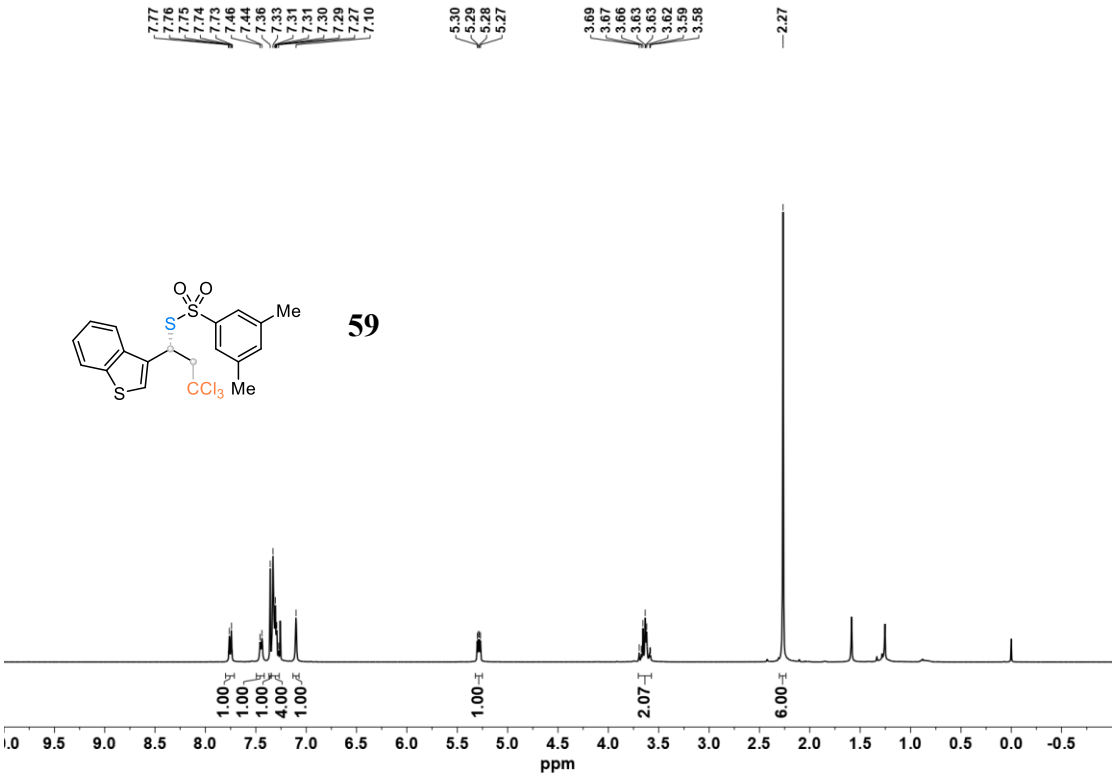


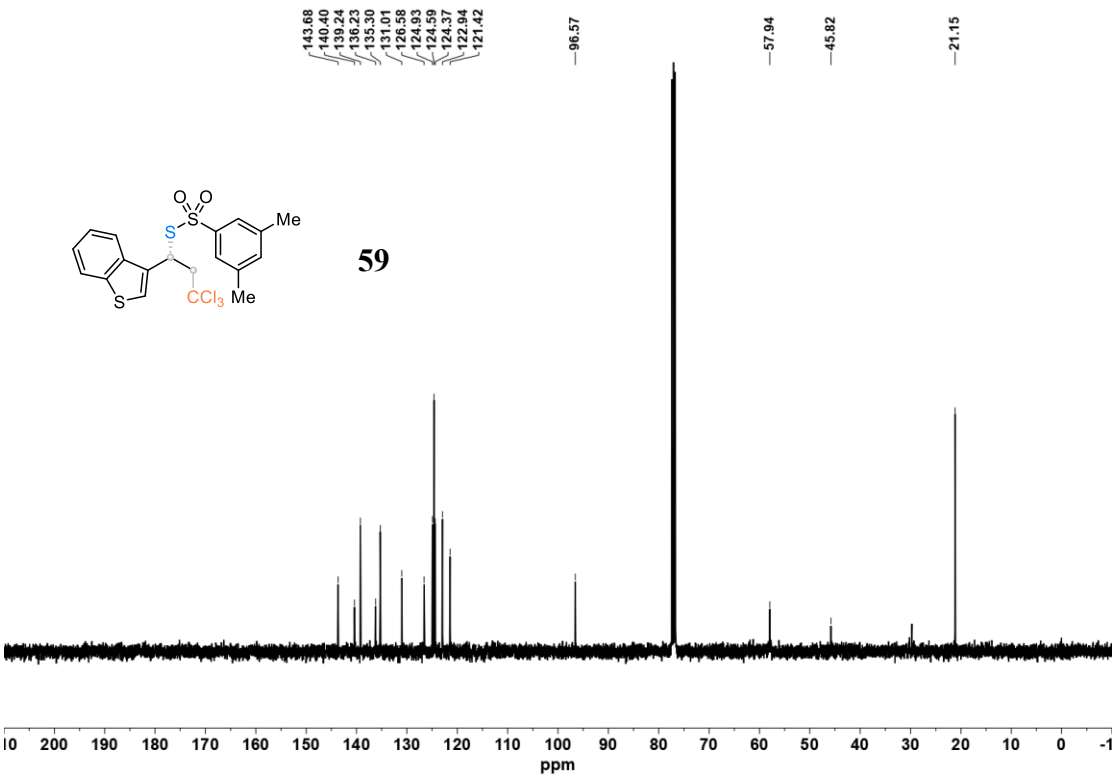
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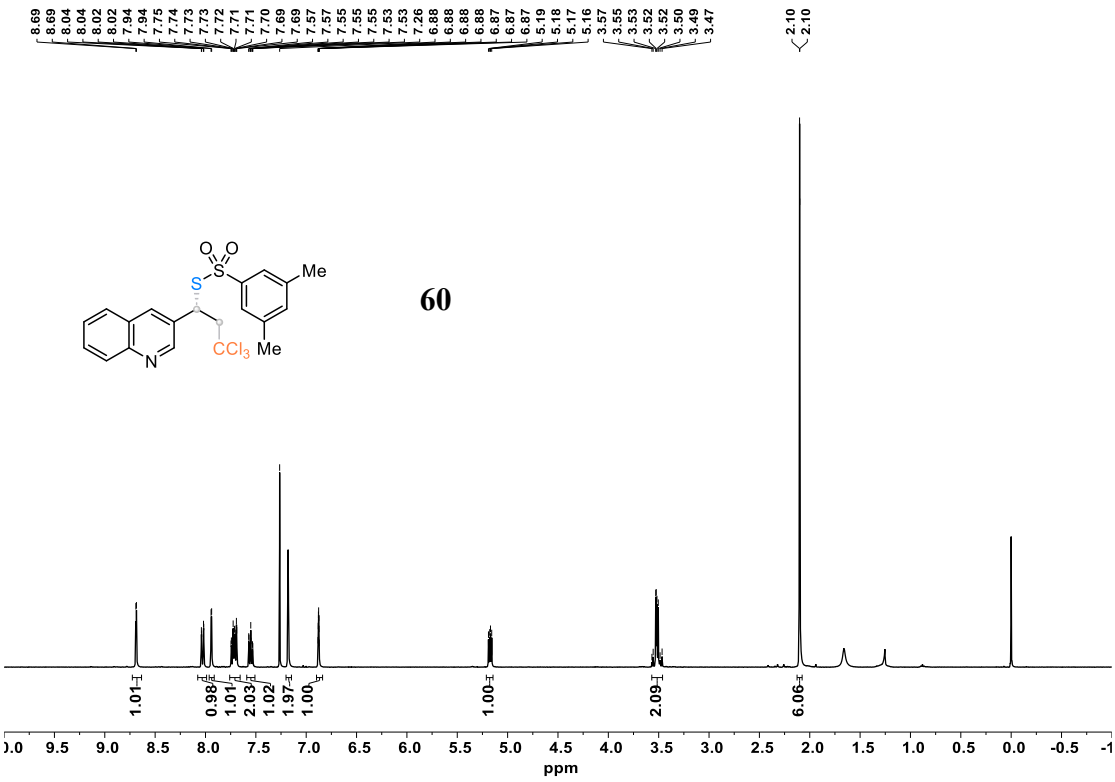


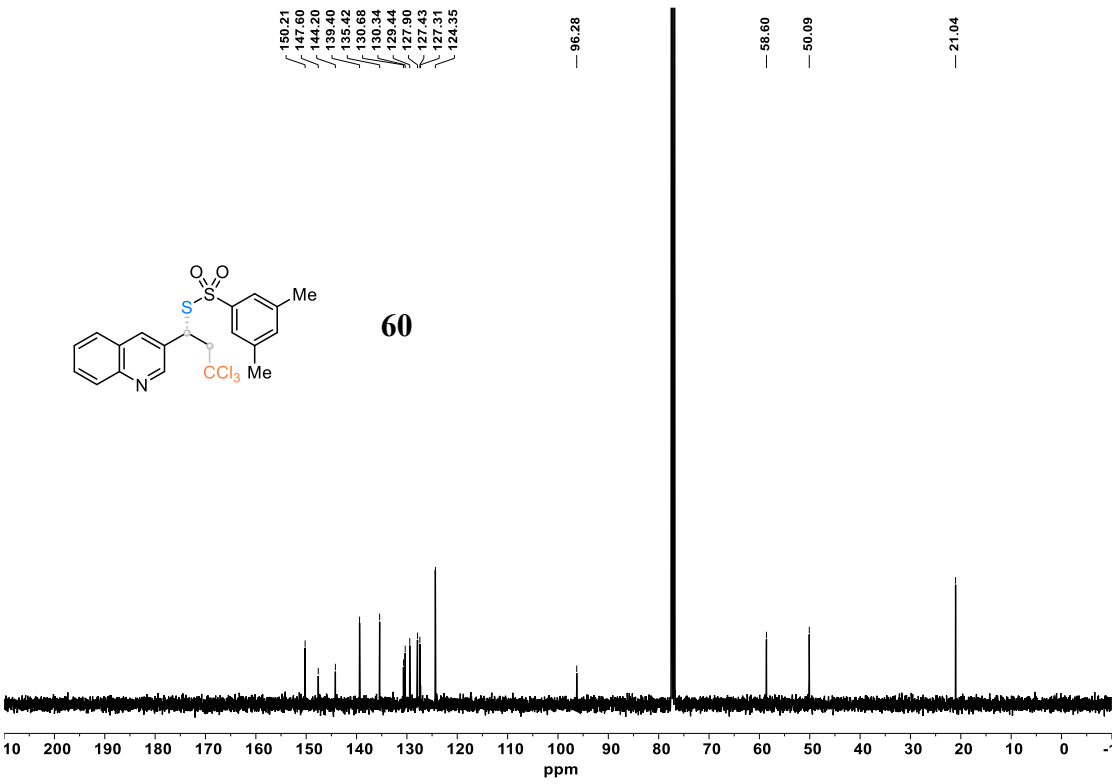
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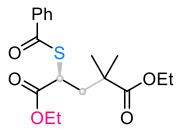
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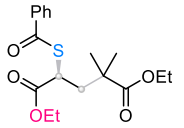


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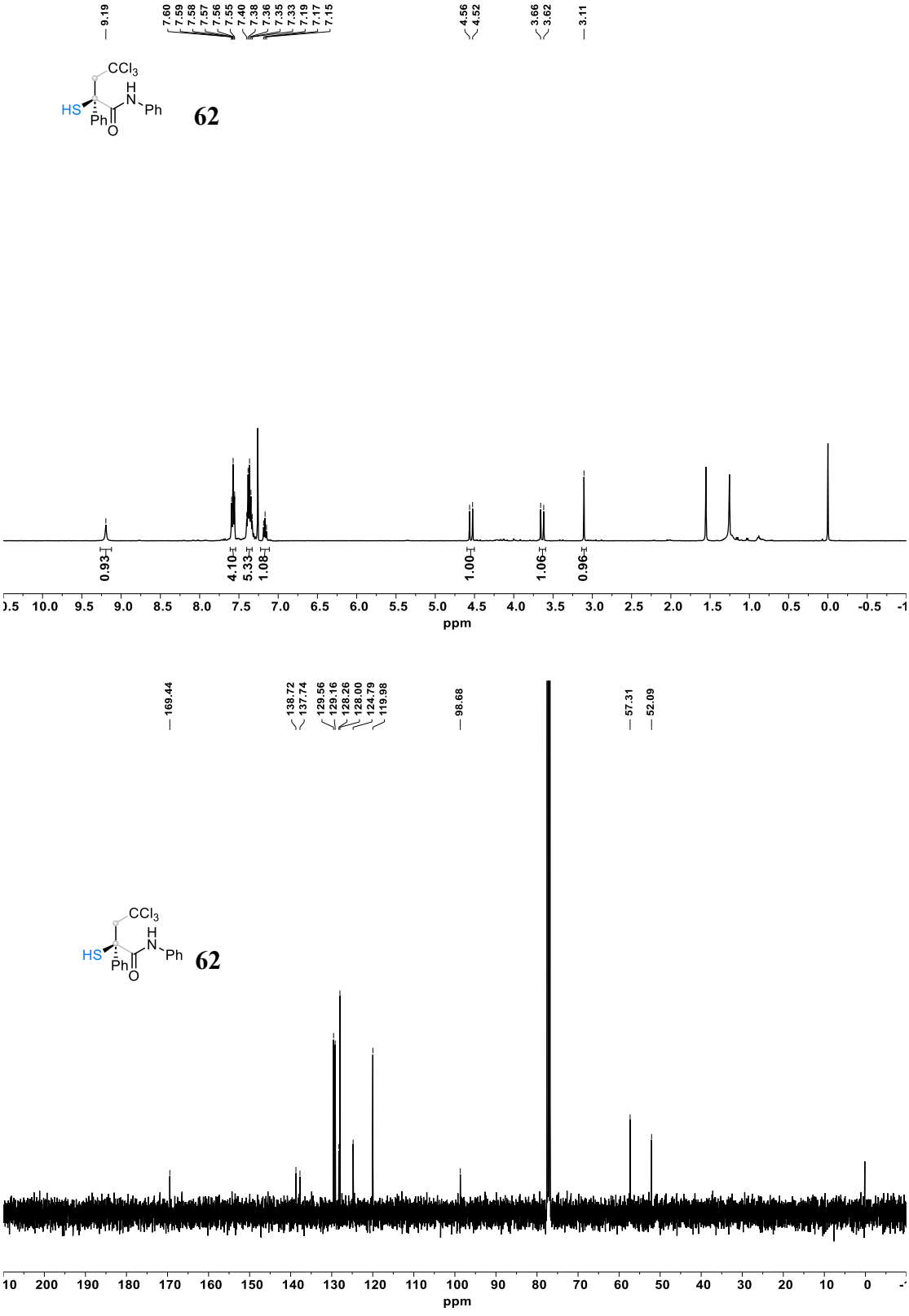


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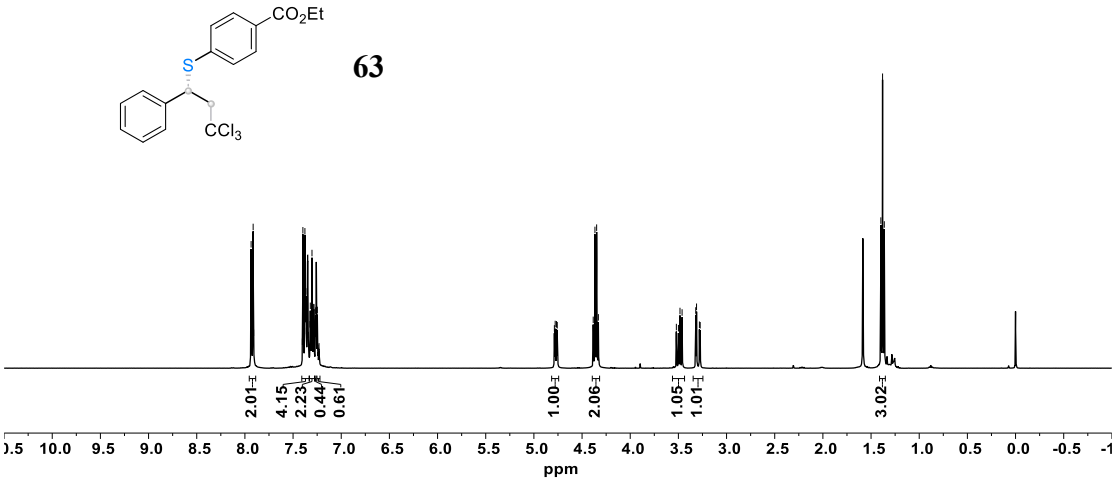
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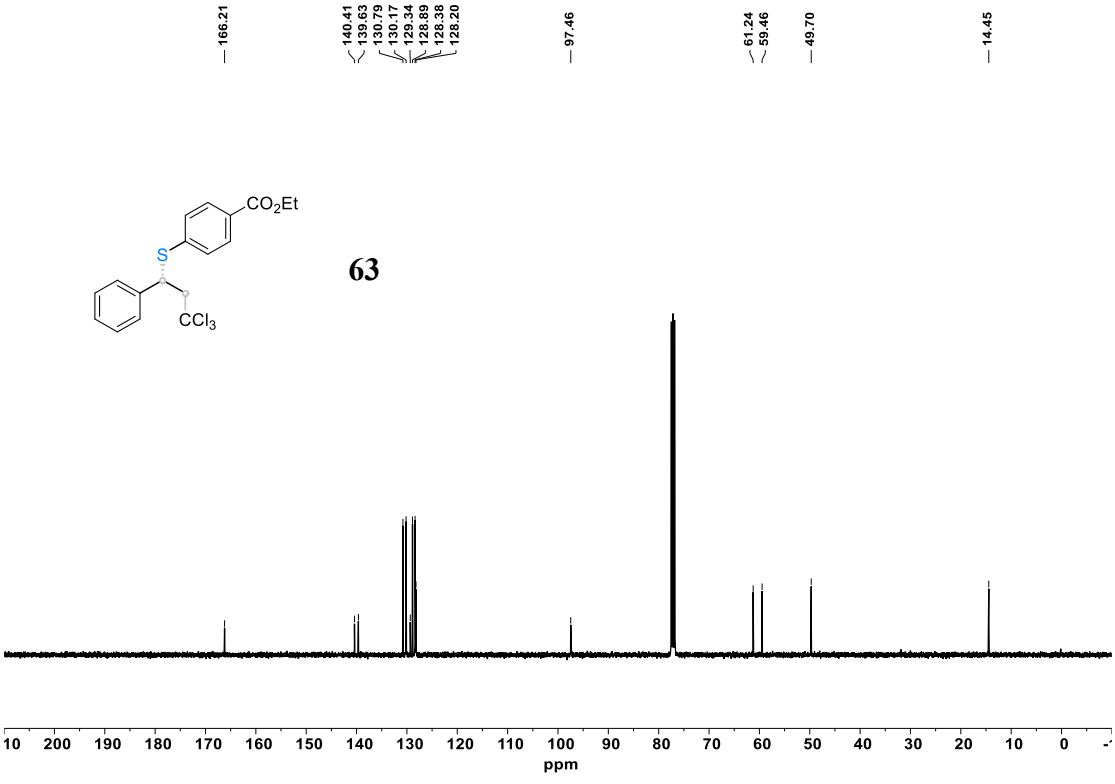
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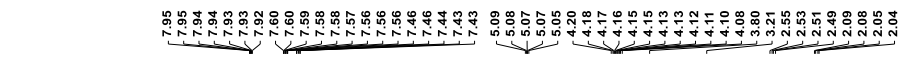
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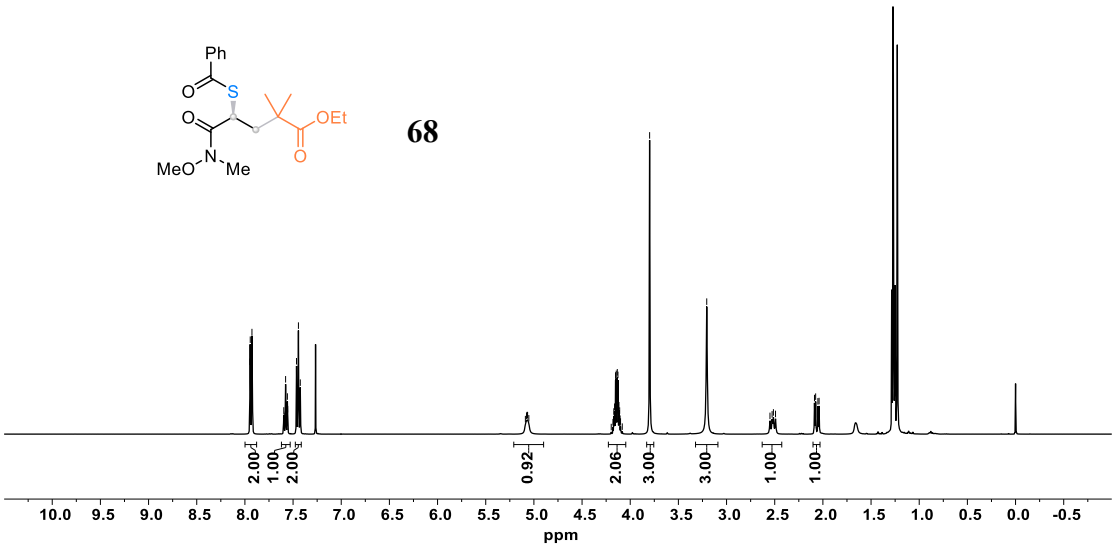


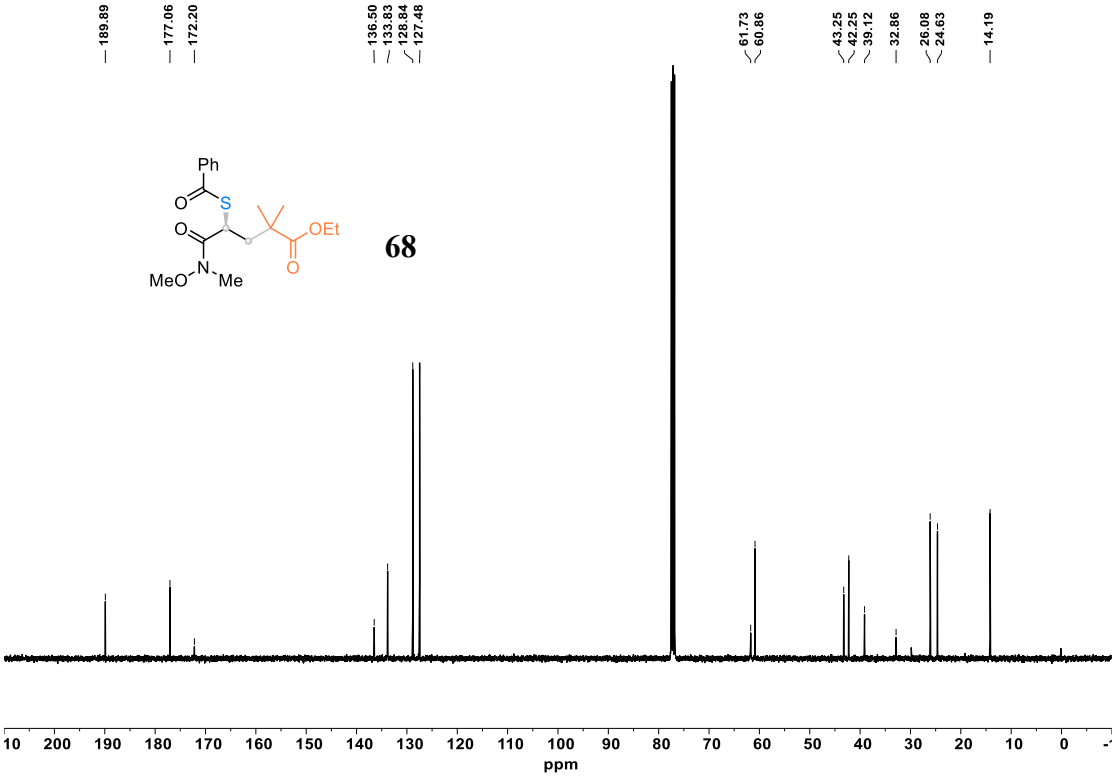




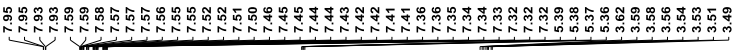
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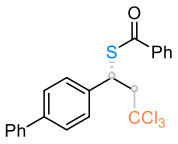




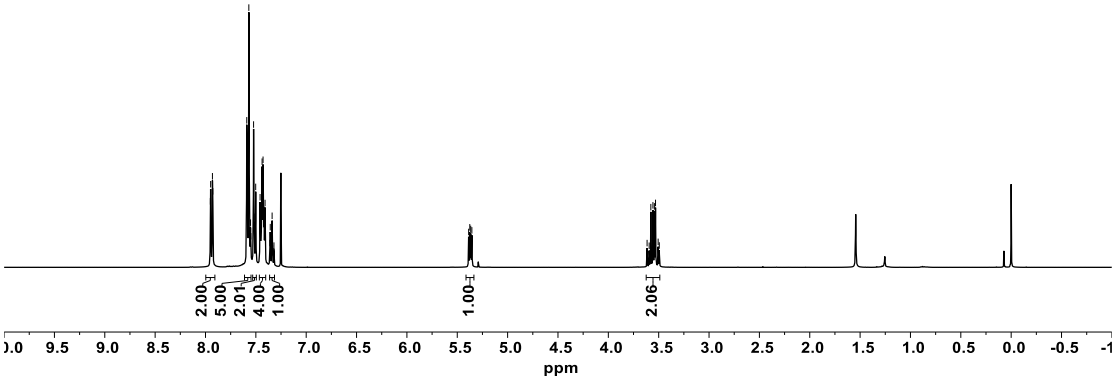


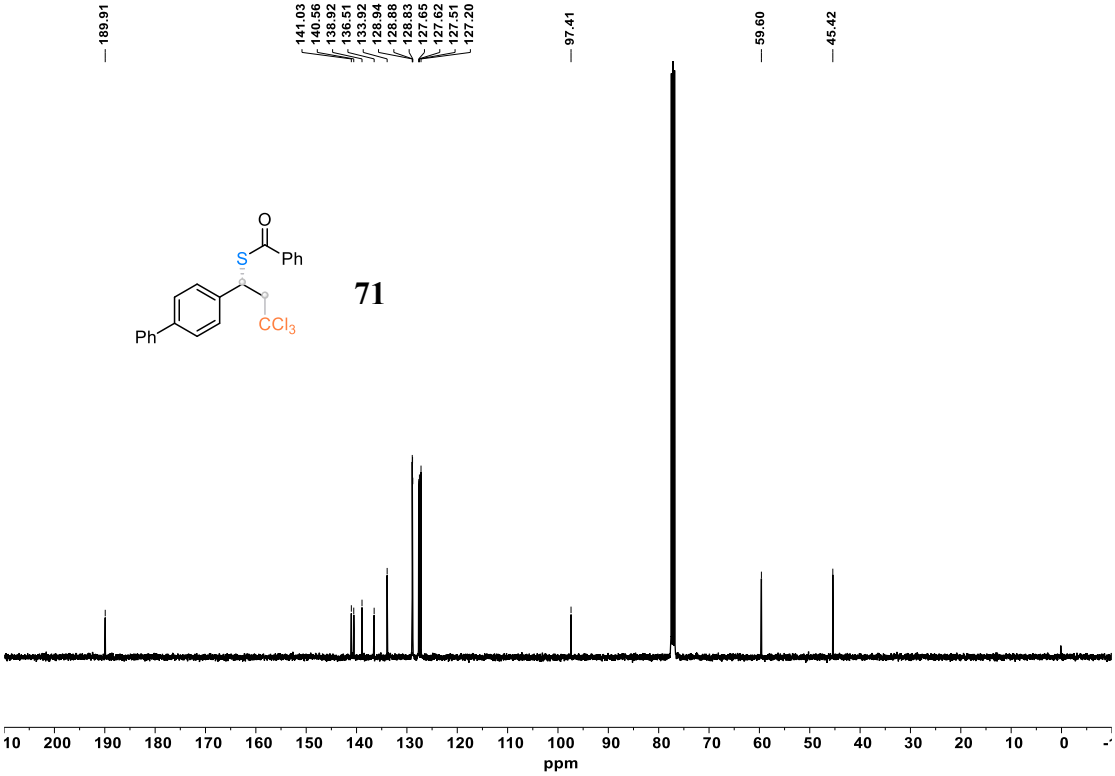
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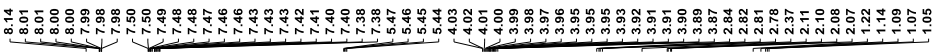
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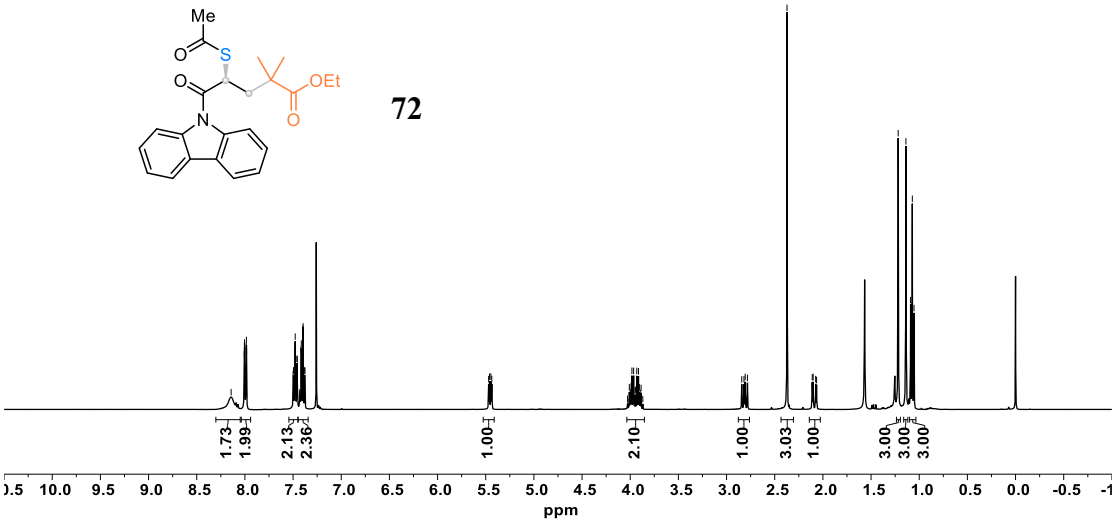


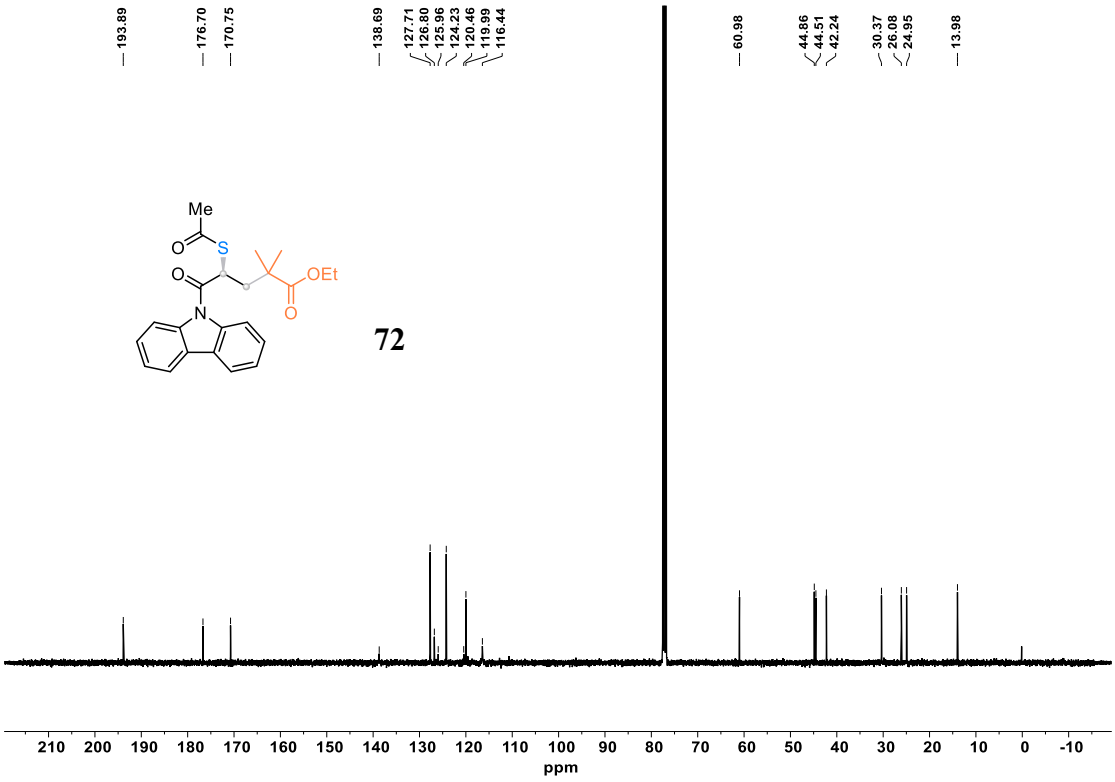


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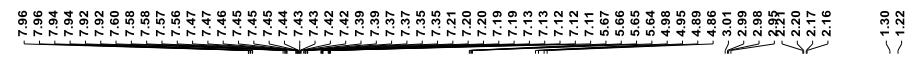
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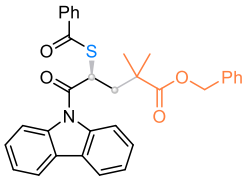




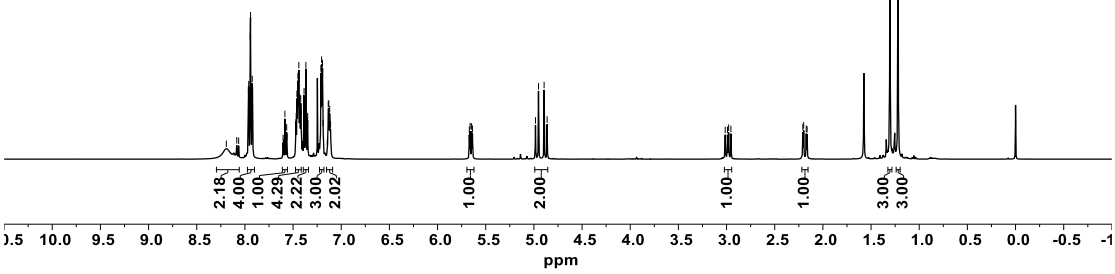


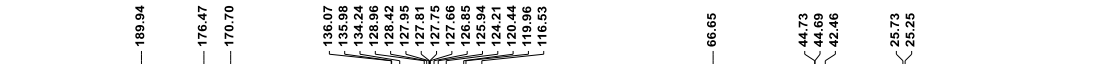
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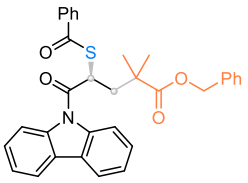




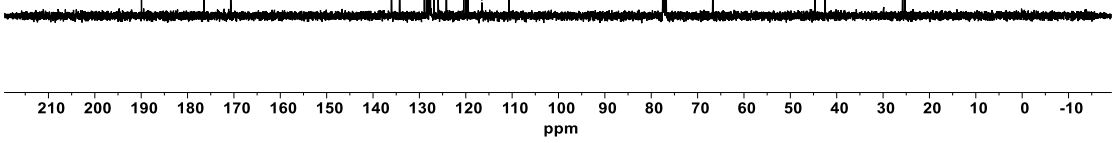
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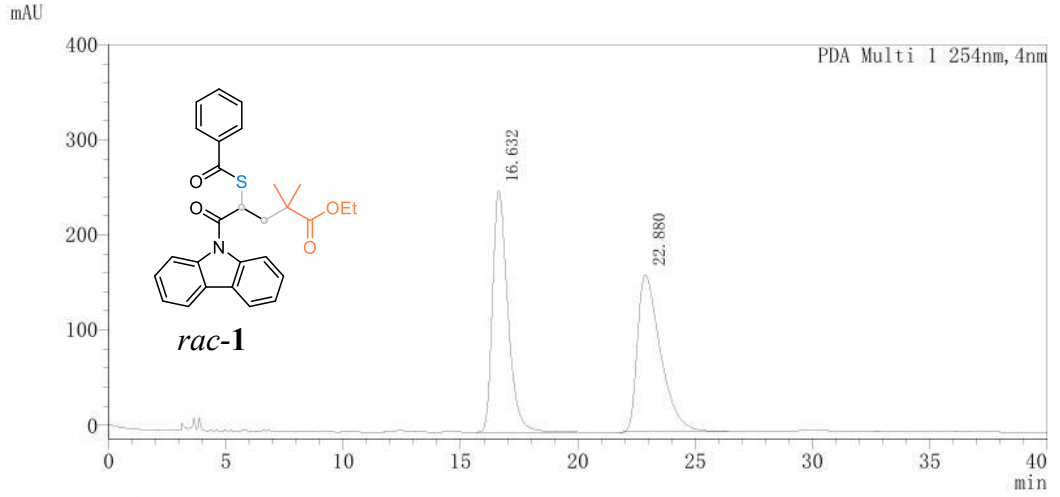


74



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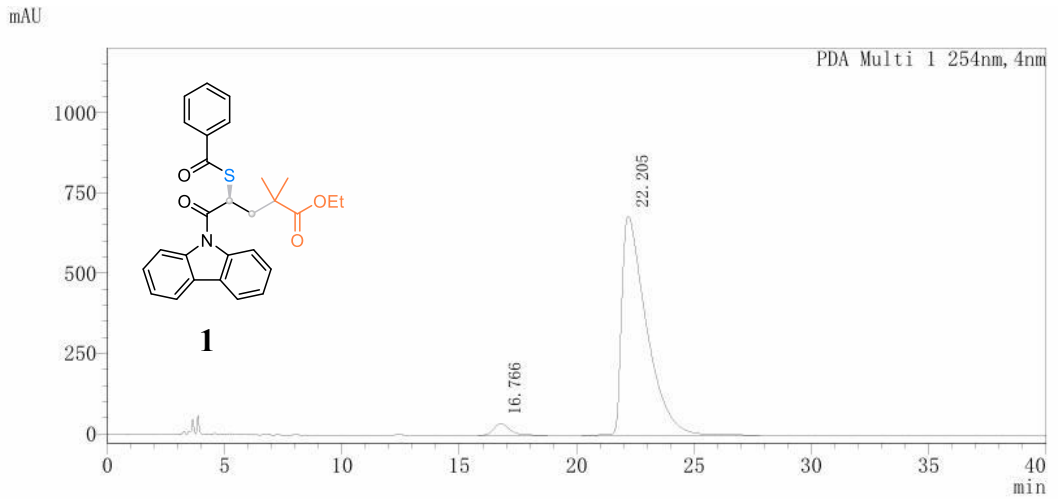
13. HPLC spectra



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.632	11469519	50.263
2	22.880	11349493	49.737

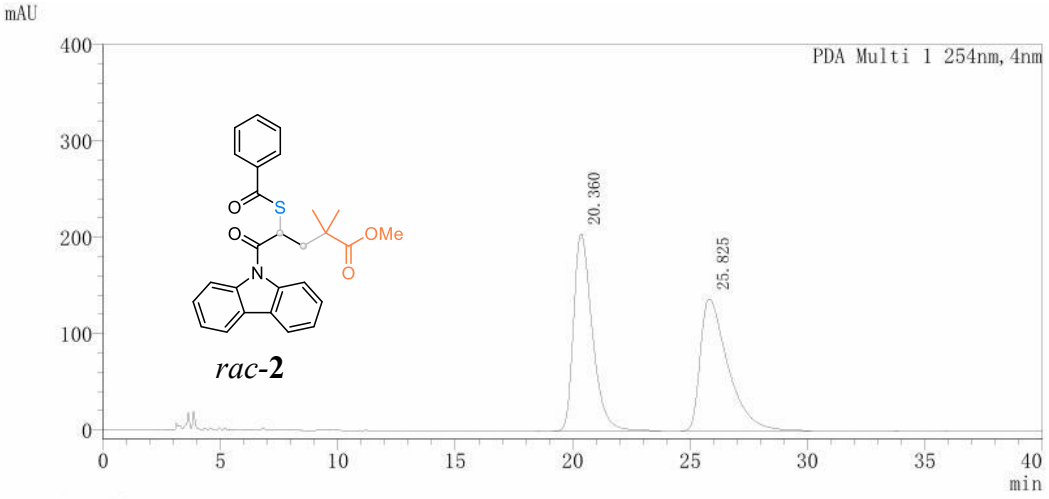


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.766	1669893	3.249
2	22.205	49726705	96.751

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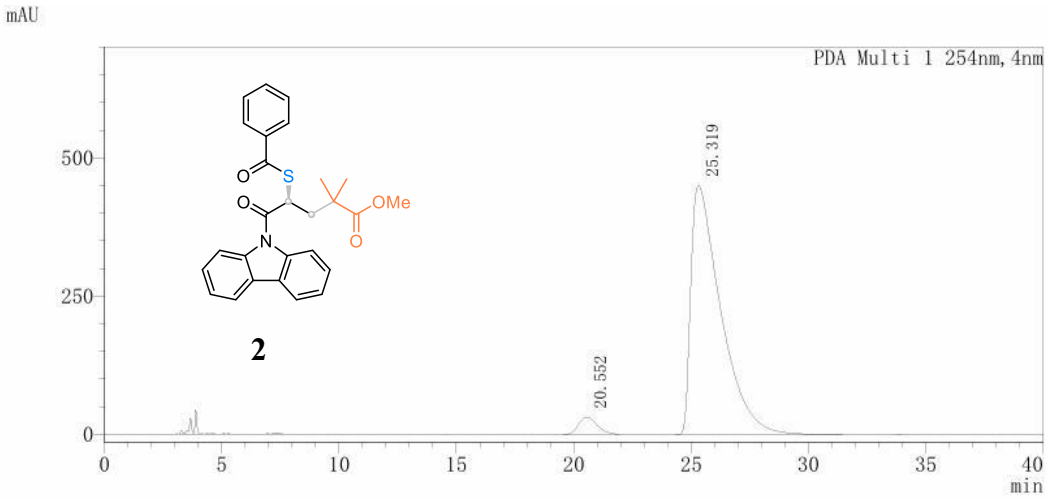


rac-**2**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.360	11303859	50.205
2	25.825	11211329	49.795



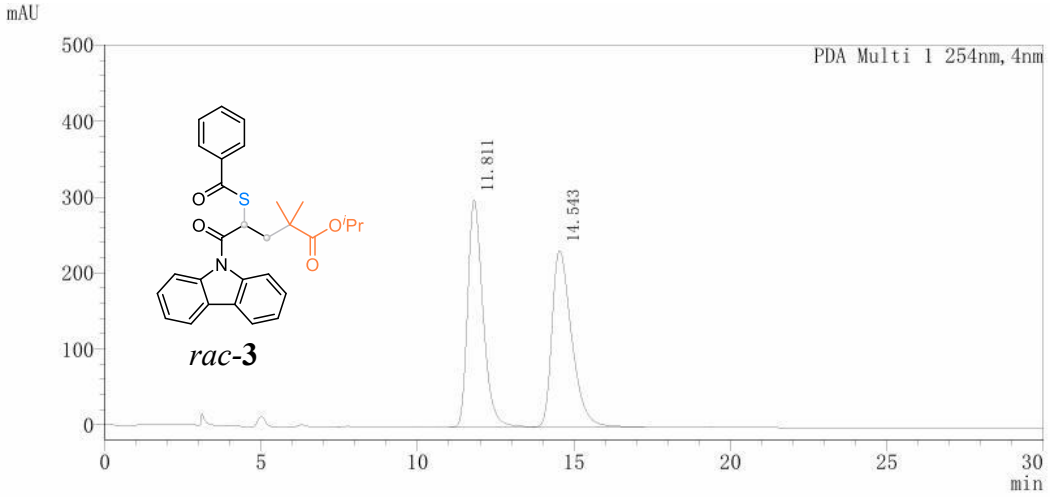
2

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.552	1699423	4.077
2	25.319	39982364	95.923

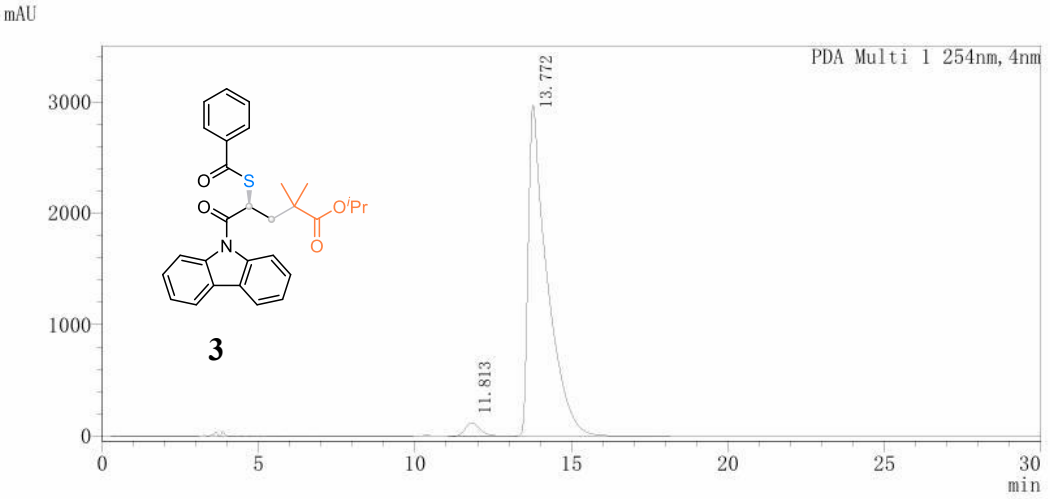
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.811	10136856	49.902
2	14.543	10176661	50.098

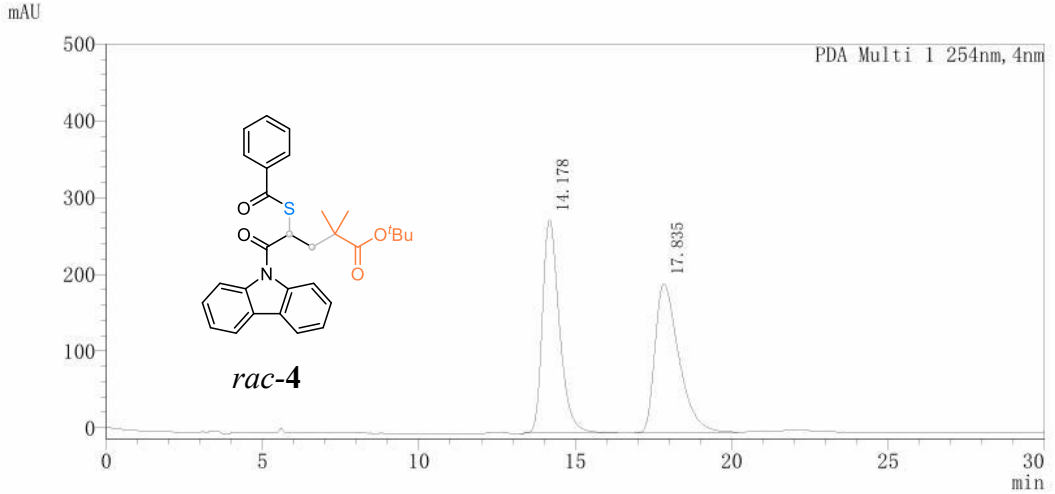


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.813	3998771	3.109
2	13.772	124629399	96.891

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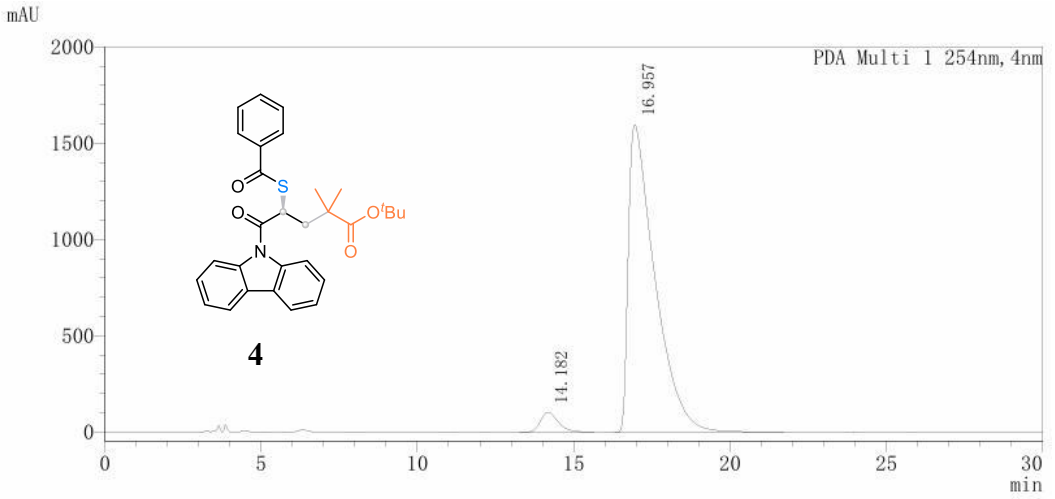


rac-**4**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.178	10428509	50.310
2	17.835	10300140	49.690



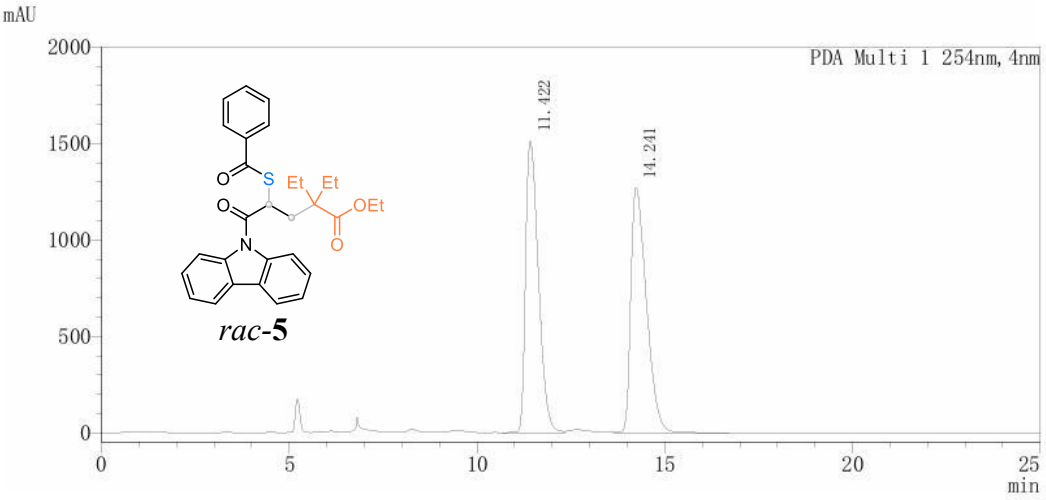
4

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.182	4011894	4.080
2	16.957	94320080	95.920

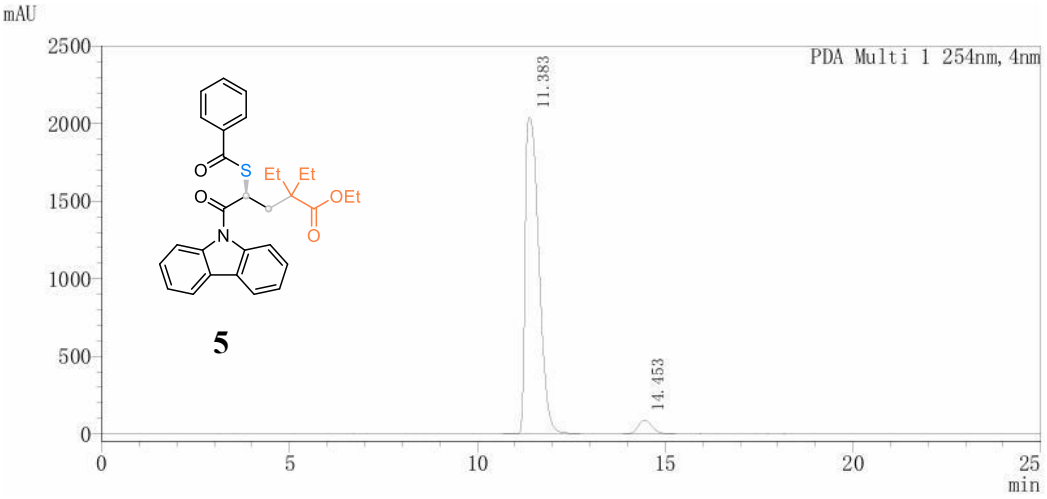
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.422	35972775	49.561
2	14.241	36610743	50.439

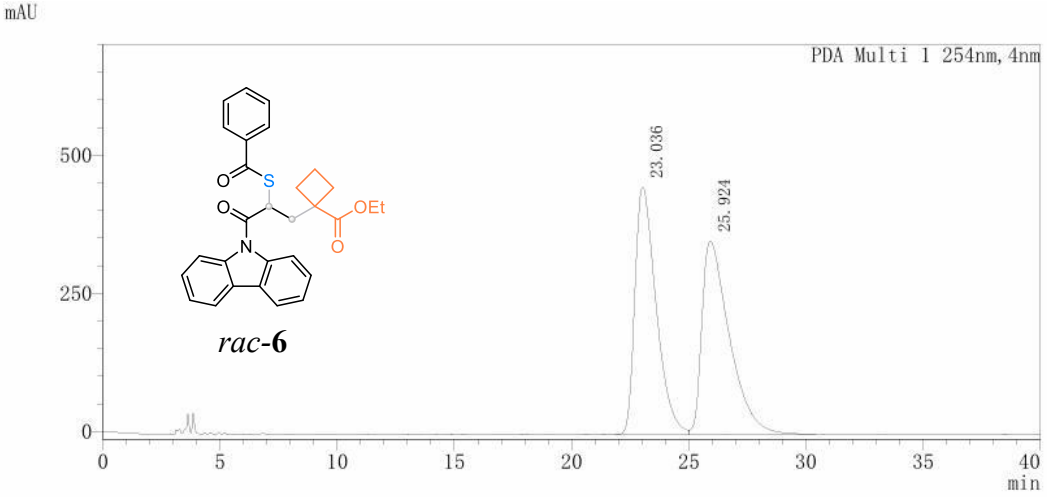


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.383	51259514	95.922
2	14.453	2179399	4.078

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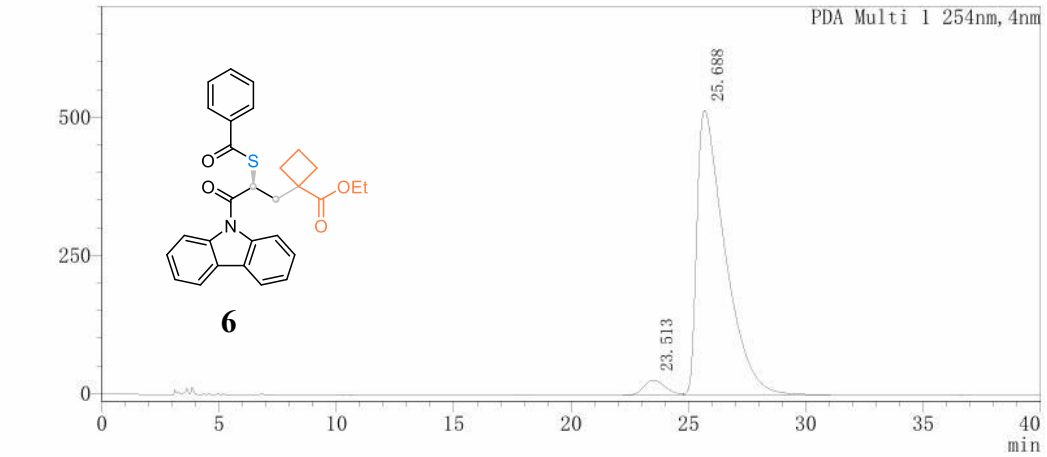


rac-**6**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.036	28241915	49.657
2	25.924	28631717	50.343



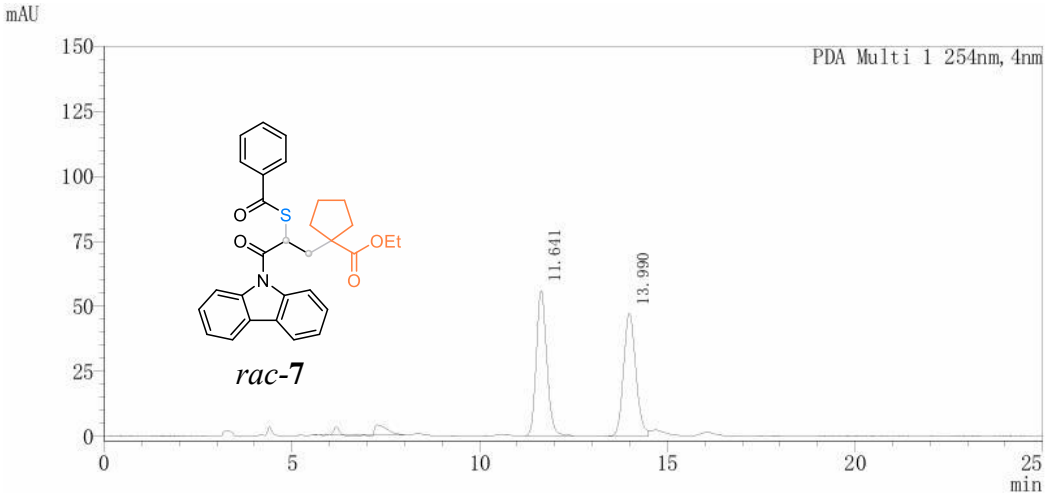
6

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.513	1730616	3.869
2	25.688	42997507	96.131

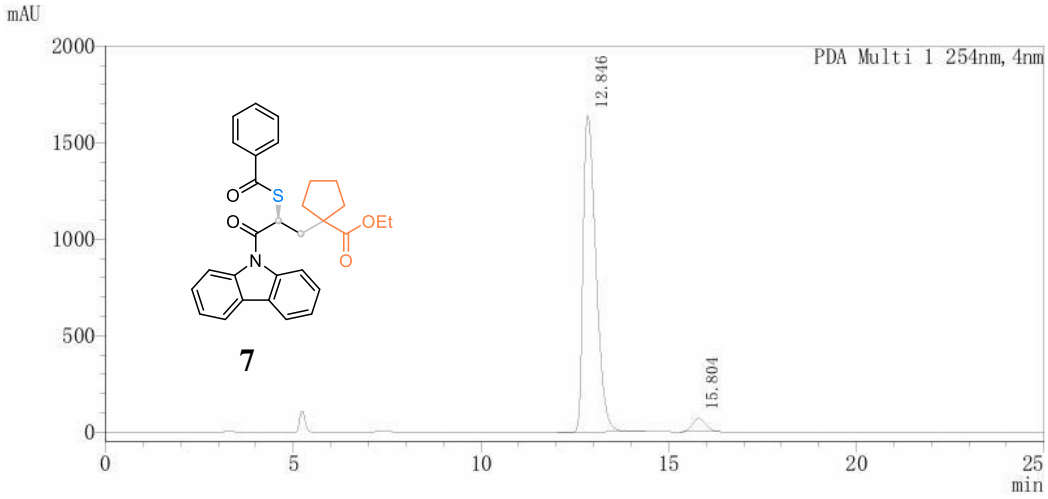
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.641	1075748	50.064
2	13.990	1073008	49.936

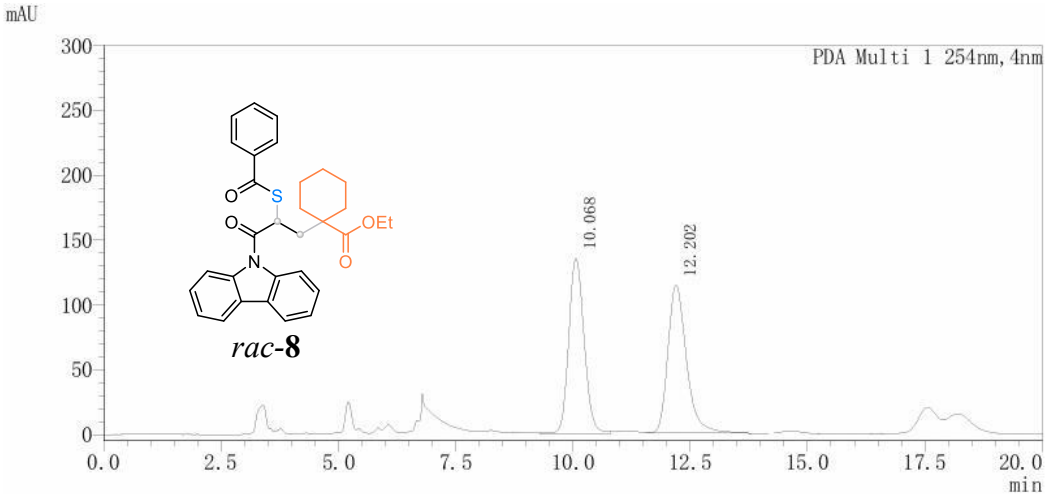


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.846	38752684	95.853
2	15.804	1676737	4.147

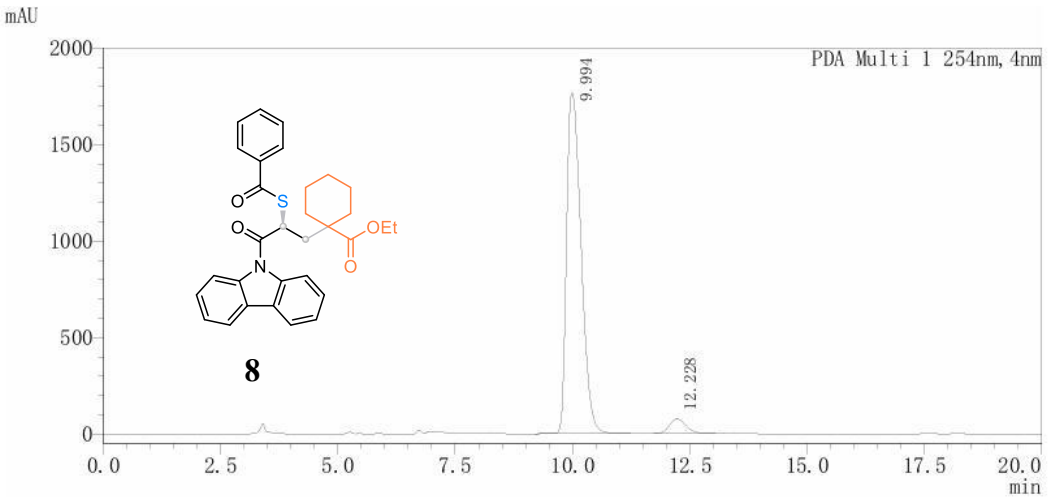
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.068	3130891	50.077
2	12.202	3121207	49.923

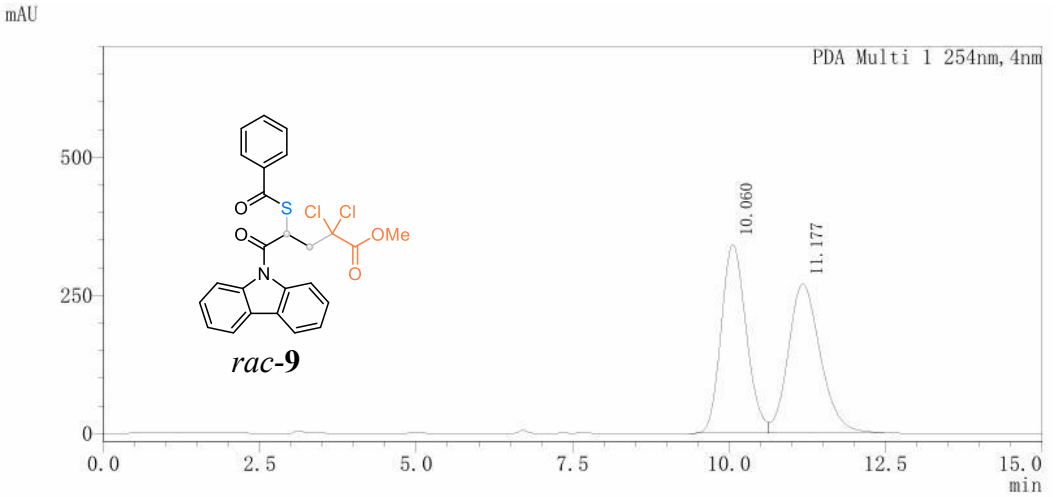


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.994	38010549	95.212
2	12.228	1911600	4.788

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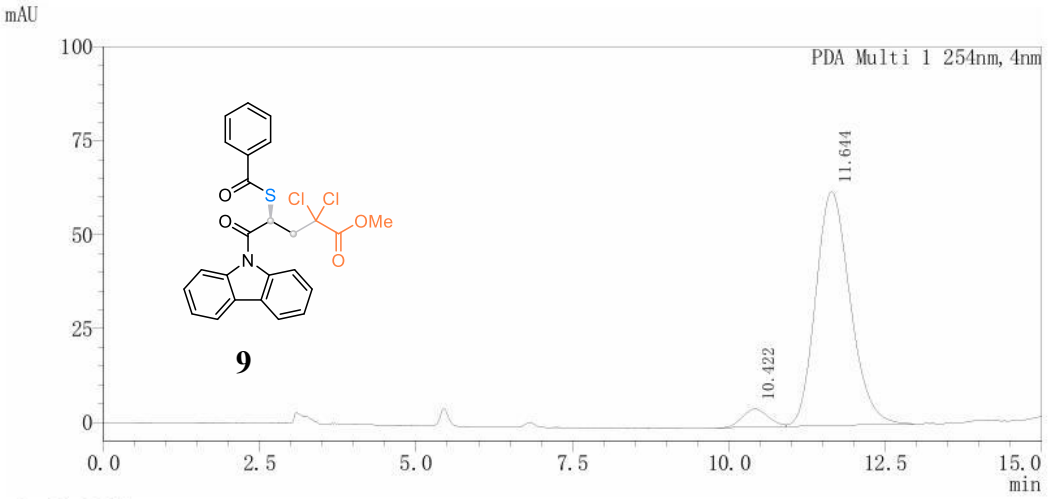


rac-**9**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.060	9503383	49.806
2	11.177	9577455	50.194



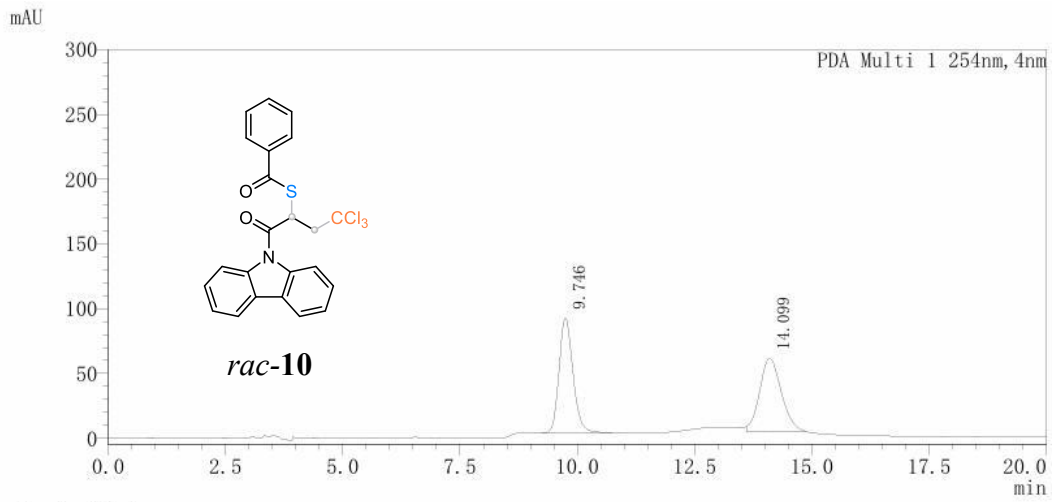
9

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.422	140036	5.538
2	11.644	2388428	94.462

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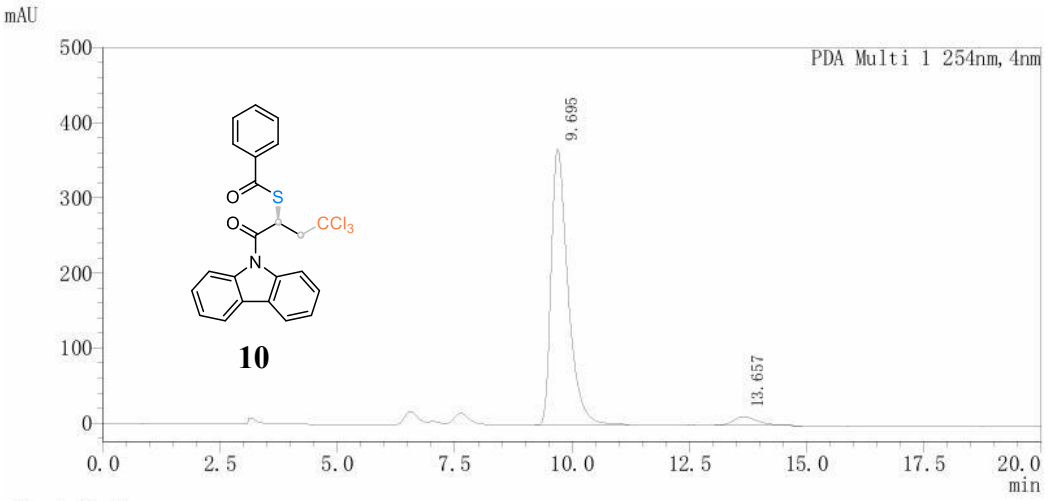


rac-**10**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.746	1813964	50.158
2	14.099	1802508	49.842



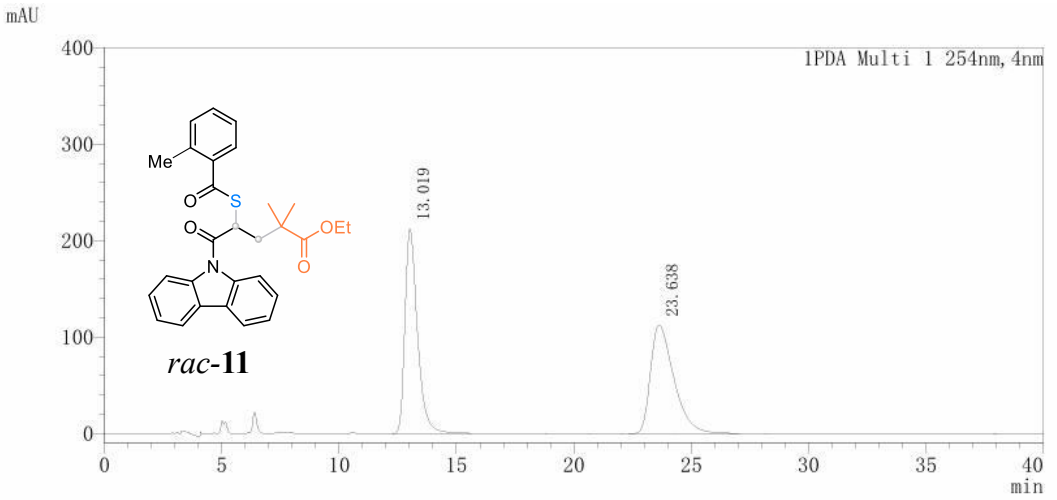
10

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.695	9137340	95.450
2	13.657	435594	4.550

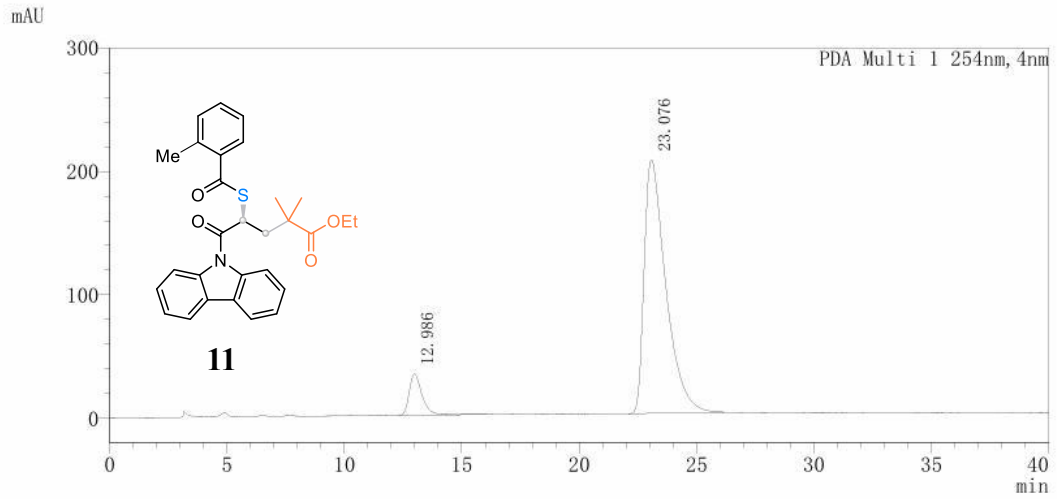
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.019	7816367	50.097
2	23.638	7785970	49.903

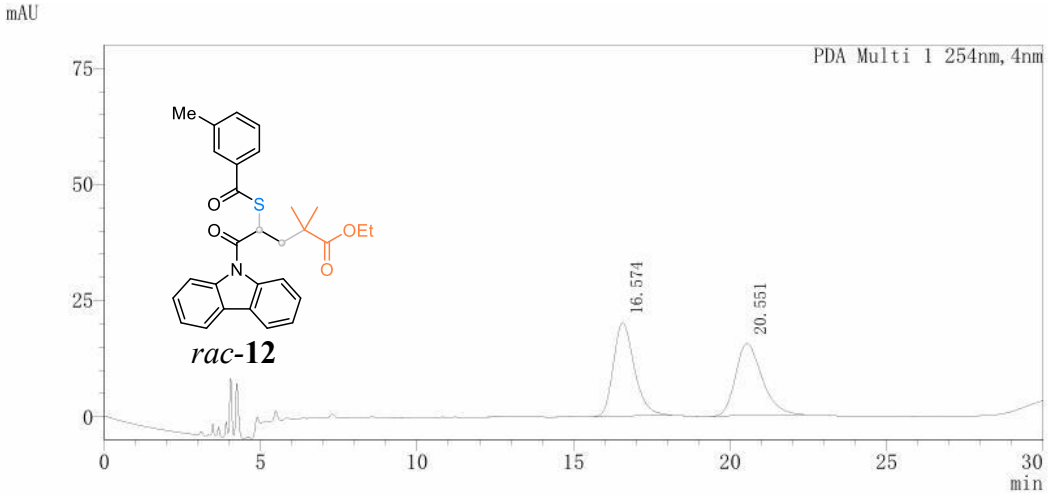


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.986	1249845	8.667
2	23.076	13170088	91.333

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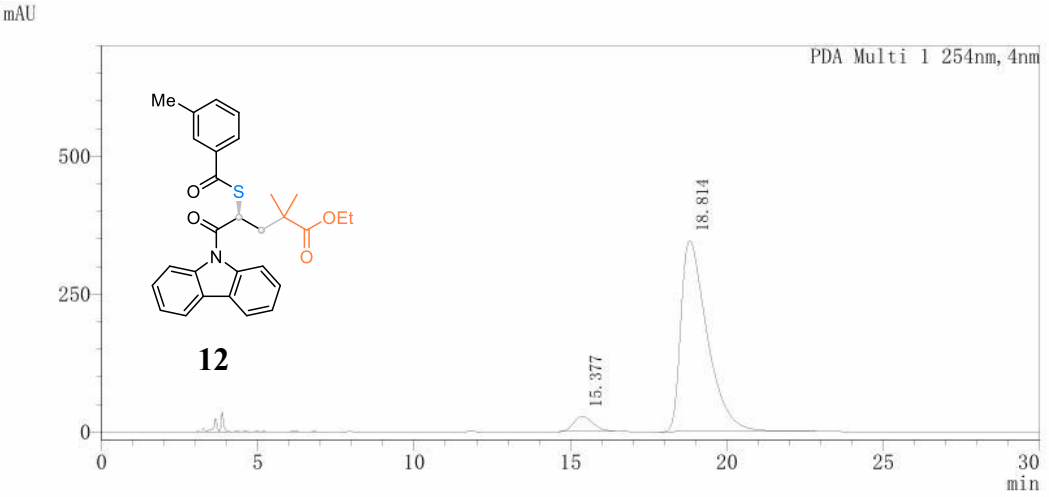


rac-**12**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.574	933183	50.449
2	20.551	916563	49.551



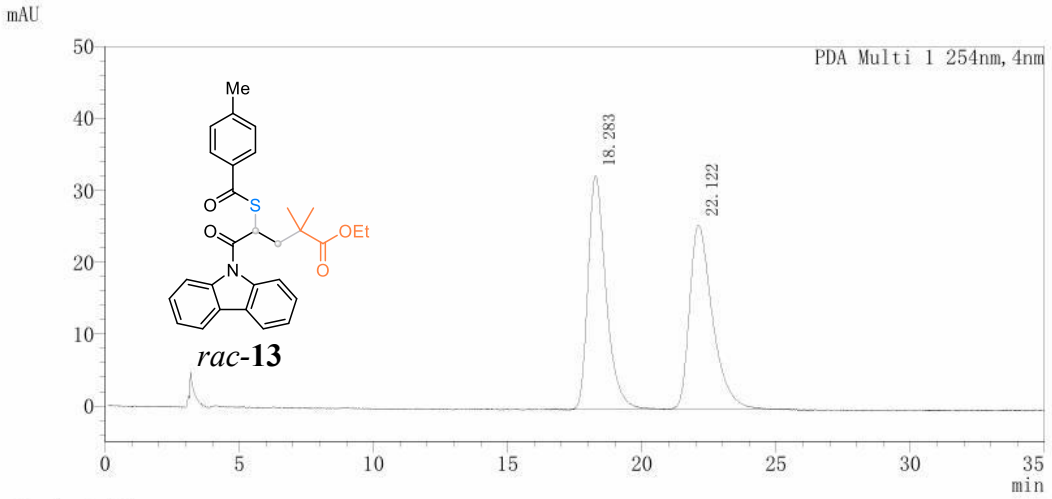
12

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.377	1164917	5.410
2	18.814	20365791	94.590

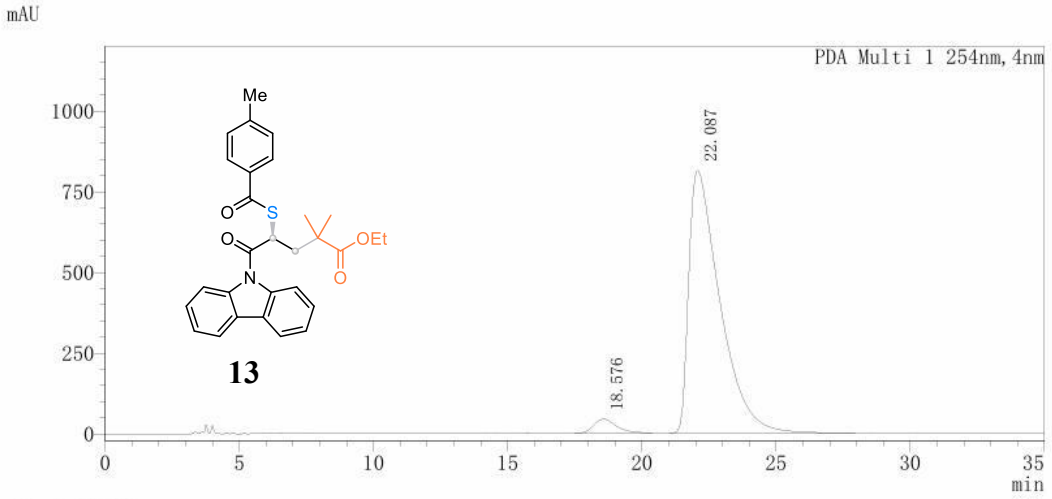
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.283	1529207	49.773
2	22.122	1543158	50.227

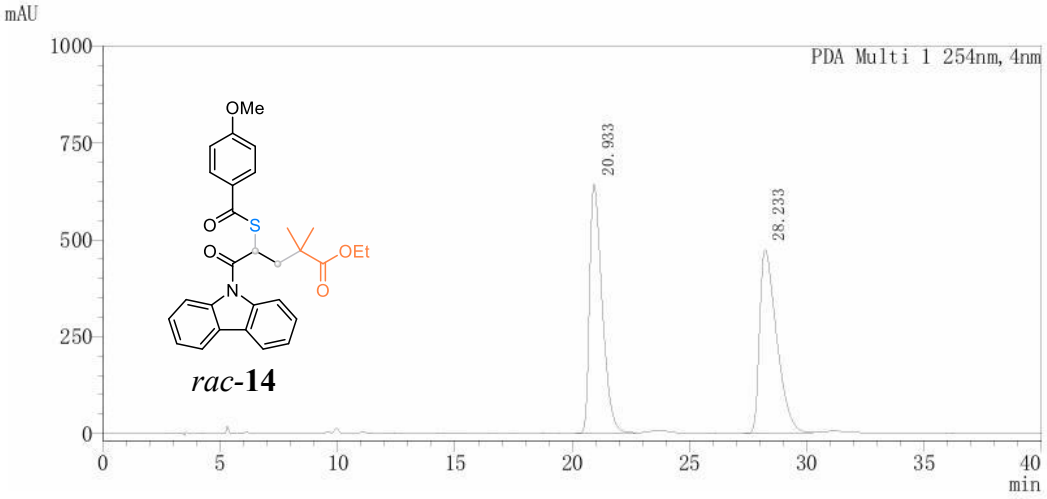


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.576	2490873	3.660
2	22.087	65565042	96.340

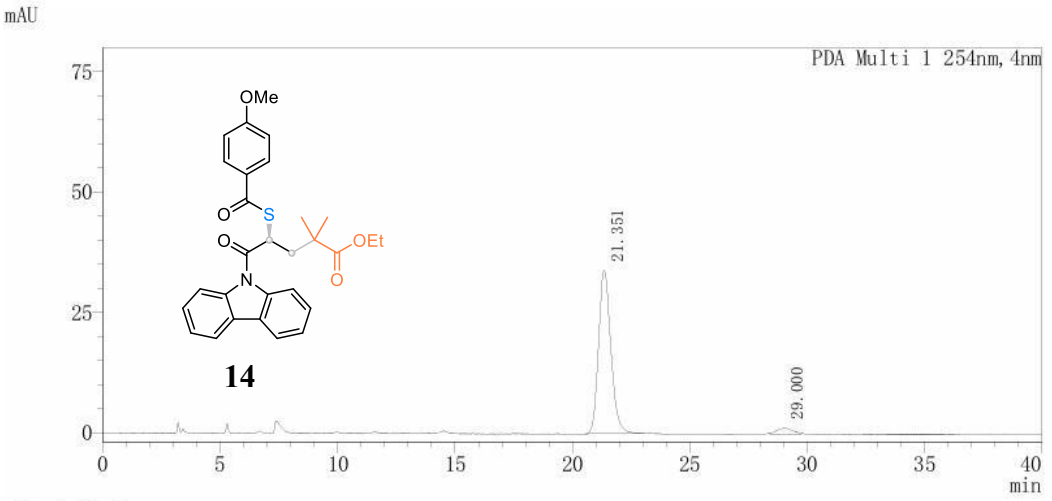
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.933	23878235	49.825
2	28.233	24046422	50.175

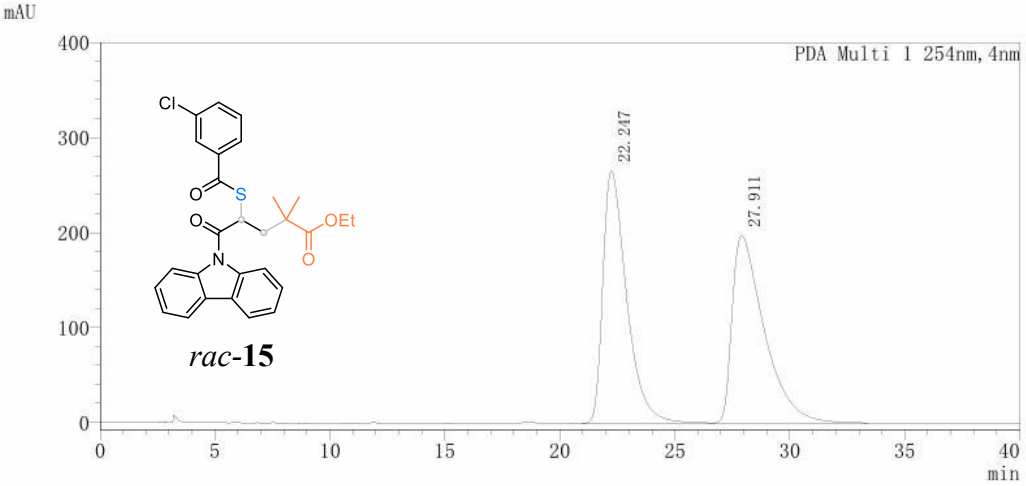


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.351	1233701	95.693
2	29.000	55525	4.307

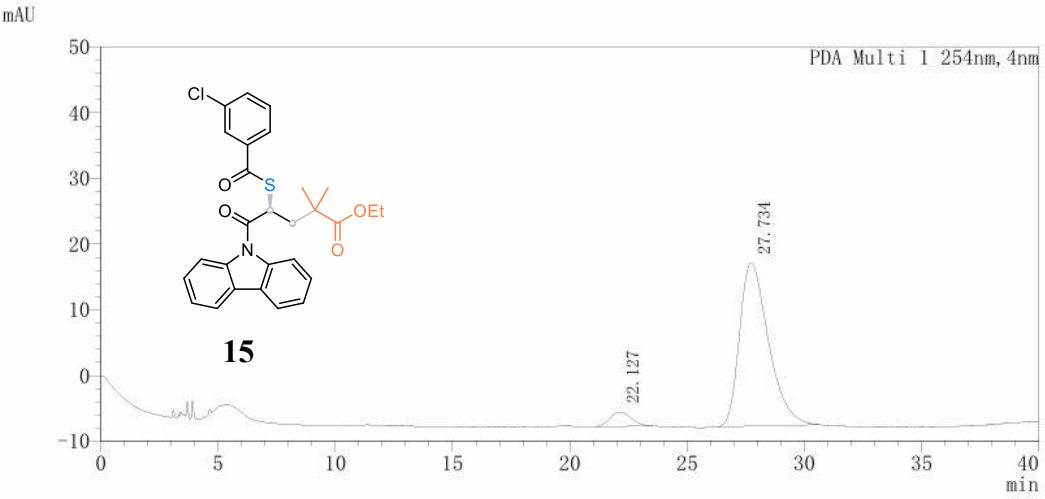
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.247	19107871	49.886
2	27.911	19195551	50.114

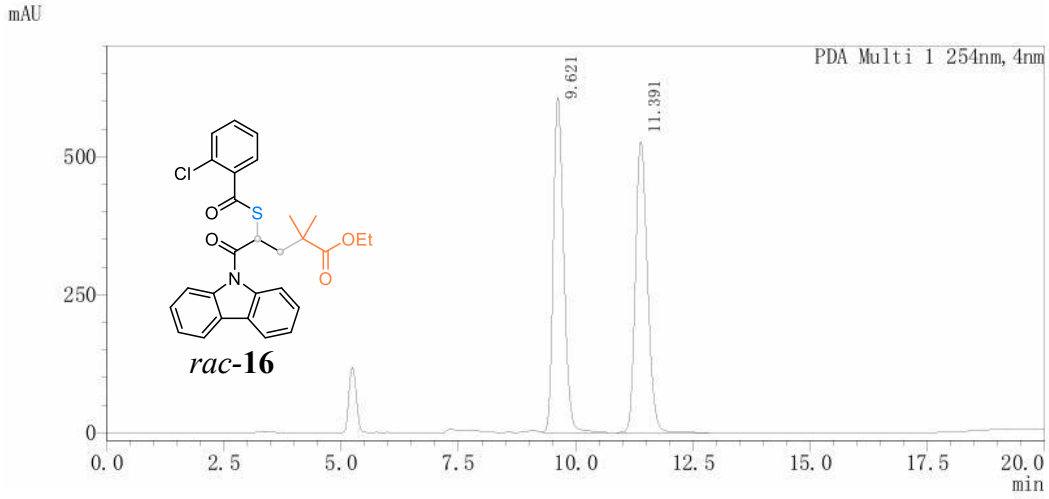


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.127	135790	5.968
2	27.734	2139326	94.032

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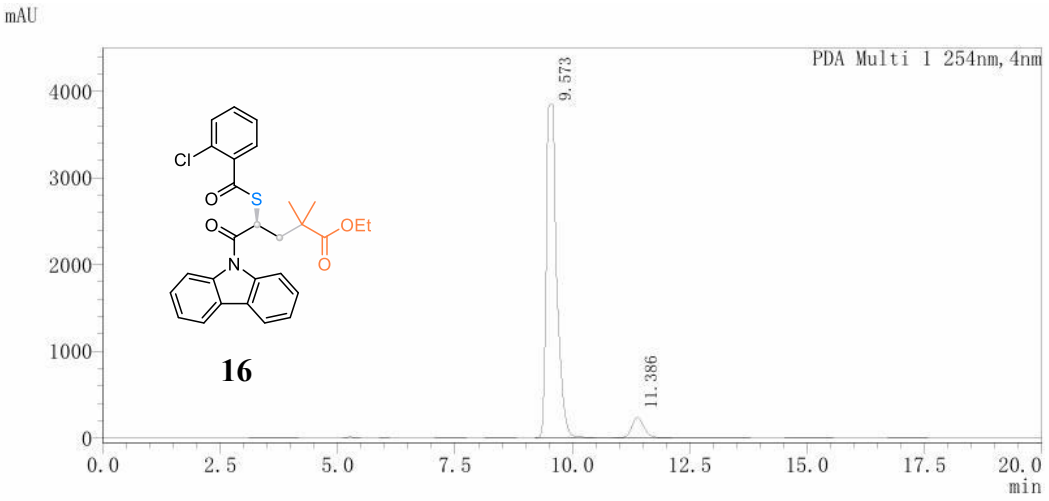


rac-**16**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.621	9345596	49.955
2	11.391	9362468	50.045



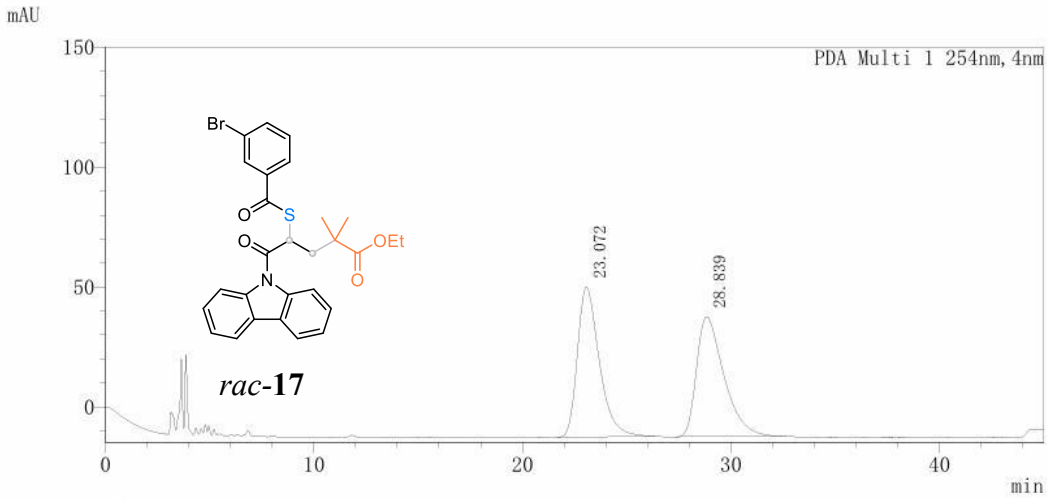
16

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.573	59586425	93.488
2	11.386	4150790	6.512

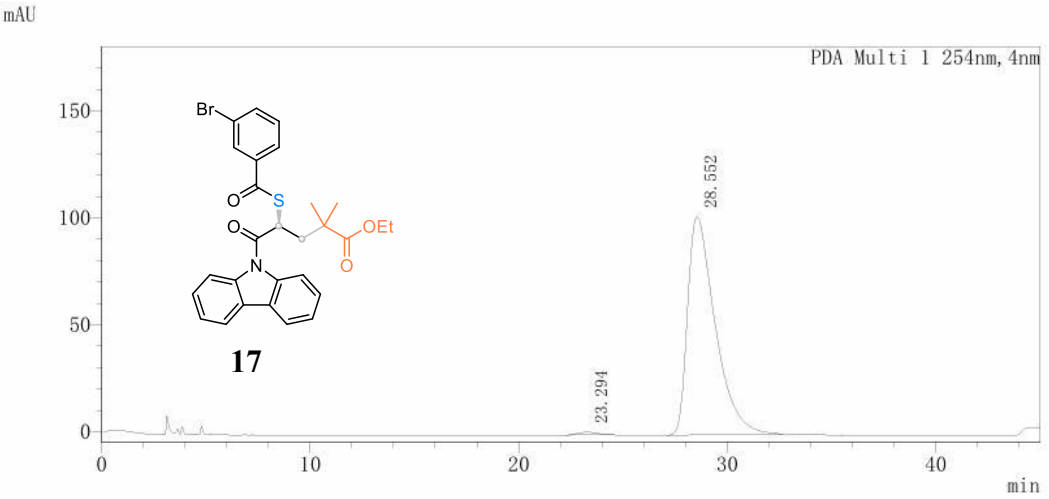
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.072	4588433	50.029
2	28.839	4583114	49.971

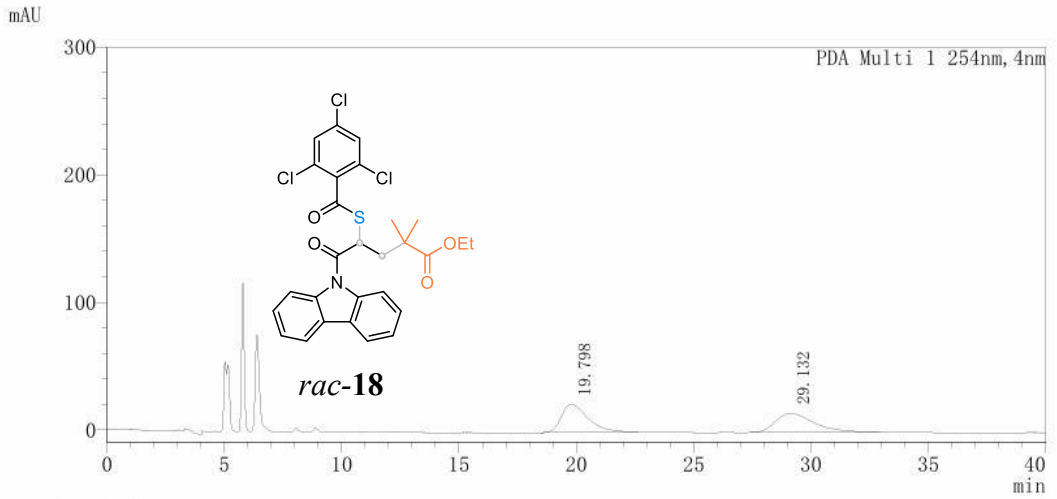


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.294	88015	0.930
2	28.552	9375187	99.070

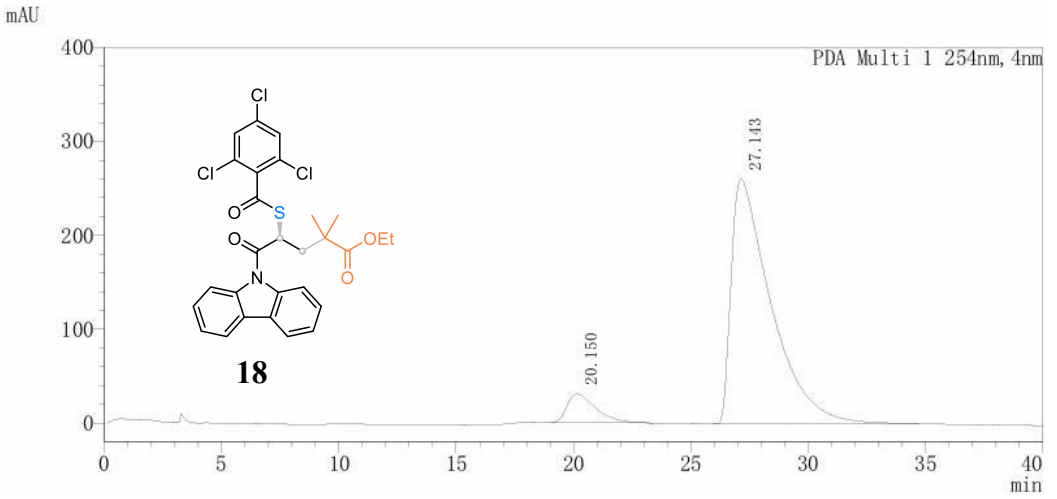
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.798	1741247	50.506
2	29.132	1706357	49.494

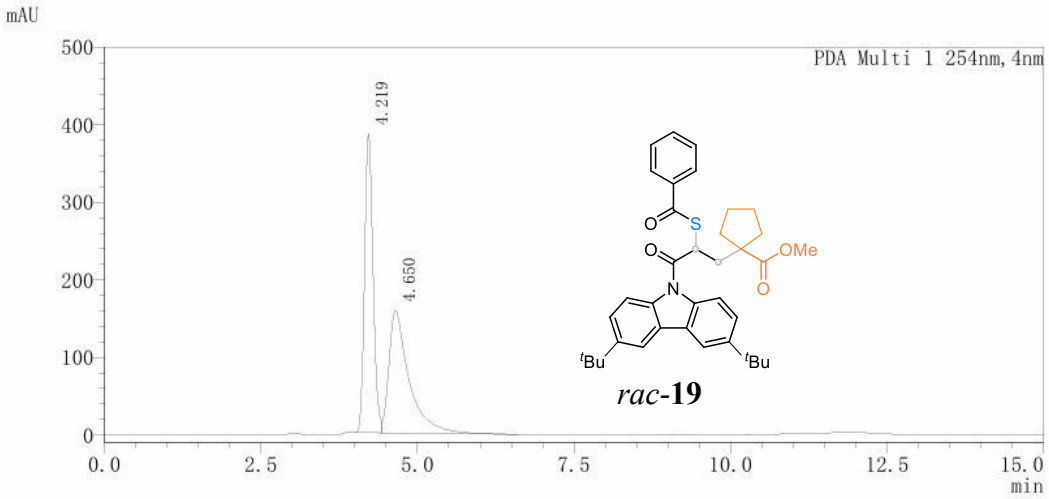


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.150	2553890	7.637
2	27.143	30886225	92.363

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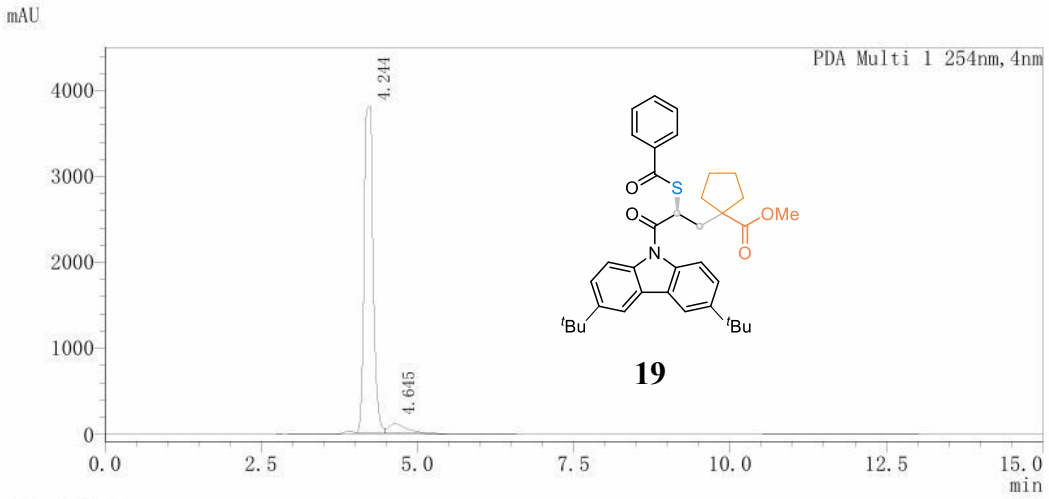


rac-**19**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.219	3640898	50.661
2	4.650	3545856	49.339



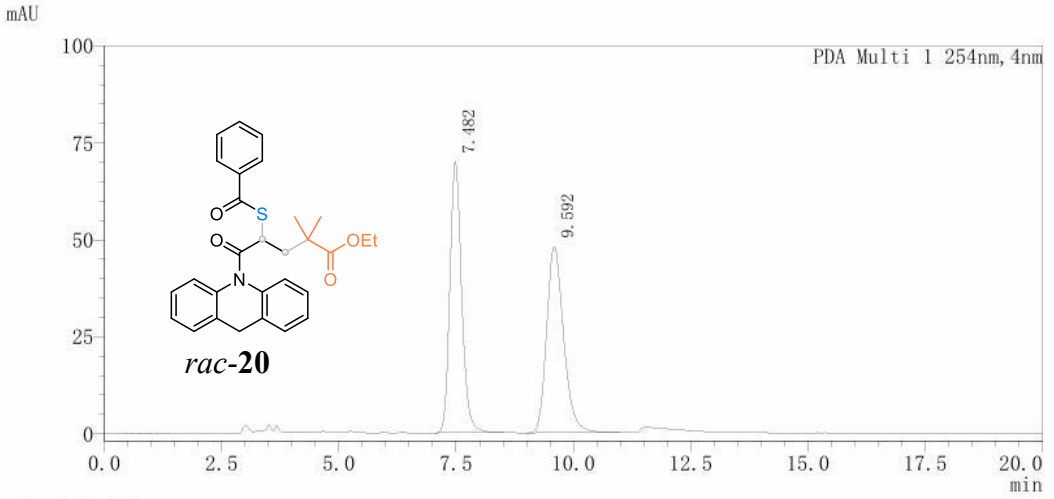
19

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.244	37913018	94.553
2	4.645	2184251	5.447

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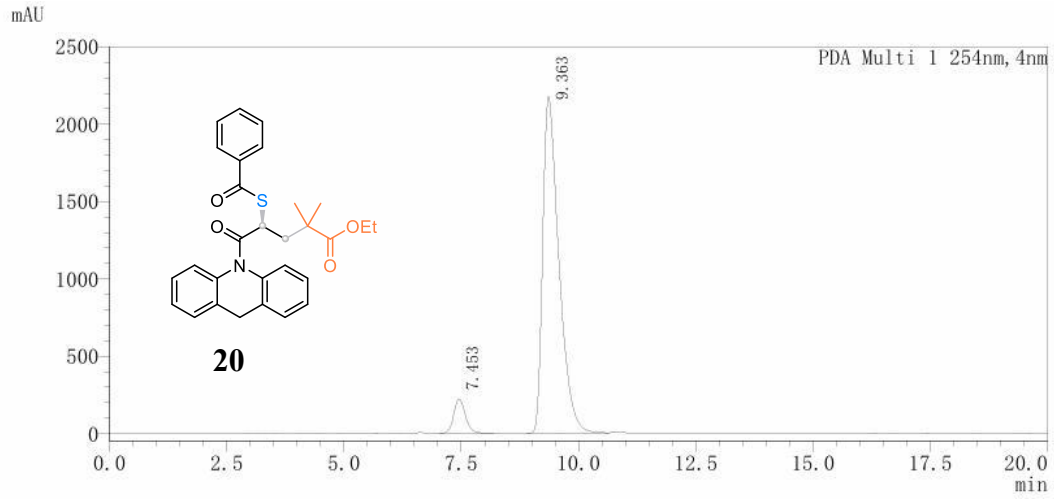


rac-**20**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.482	1222101	50.153
2	9.592	1214631	49.847



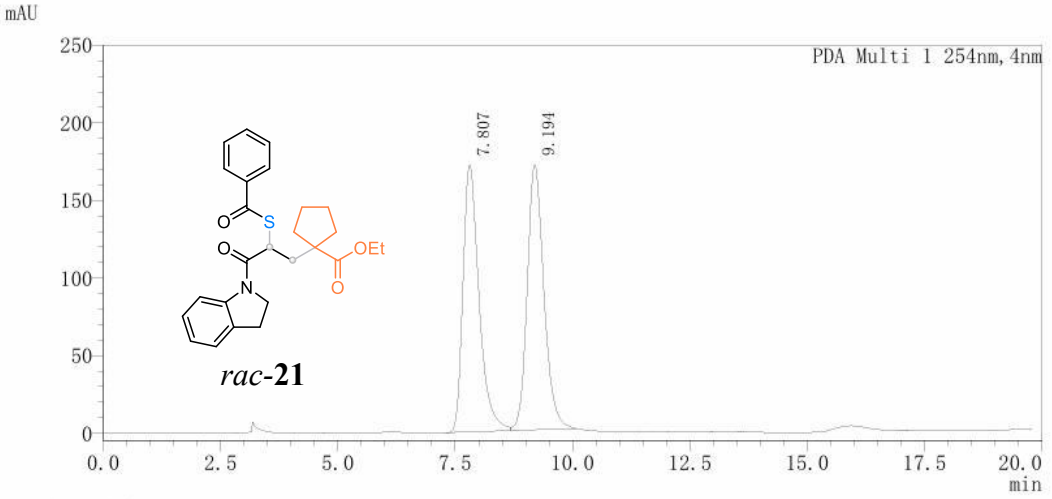
20

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.453	3814769	6.826
2	9.363	52069979	93.174

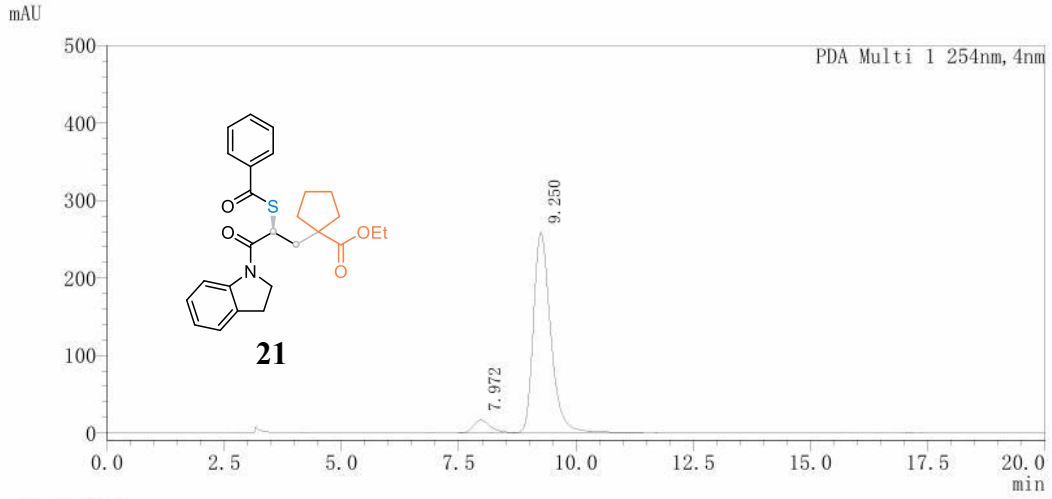
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.807	4108240	49.212
2	9.194	4239773	50.788

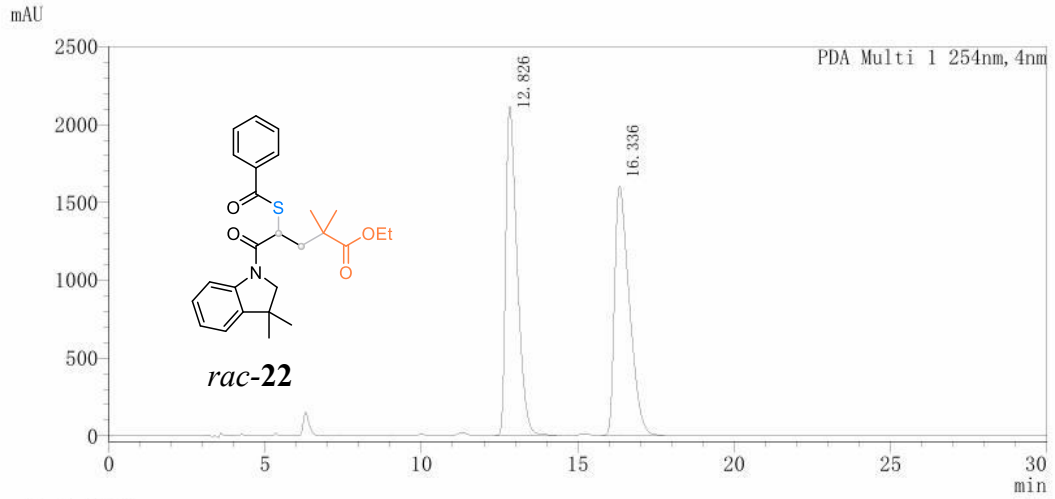


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.972	424547	6.018
2	9.250	6630095	93.982

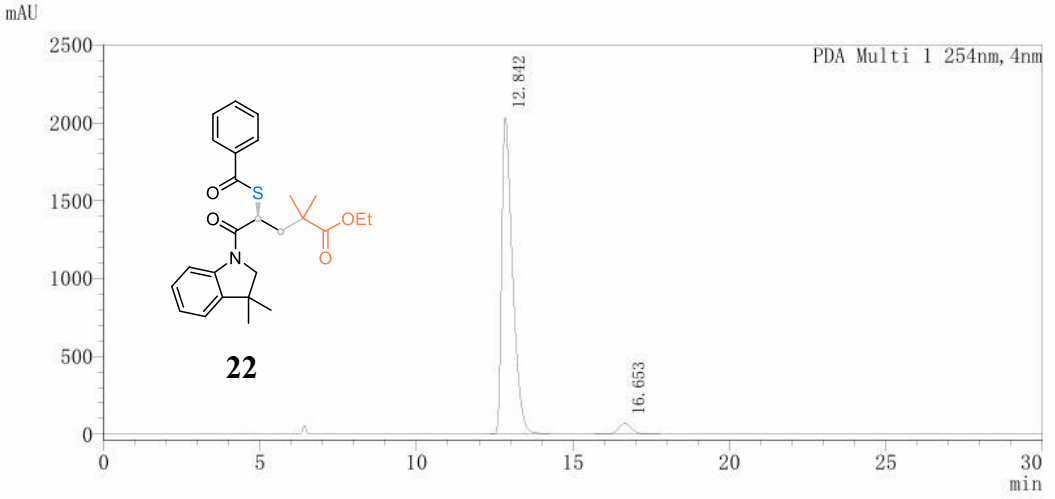
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.826	53469249	50.473
2	16.336	52466930	49.527

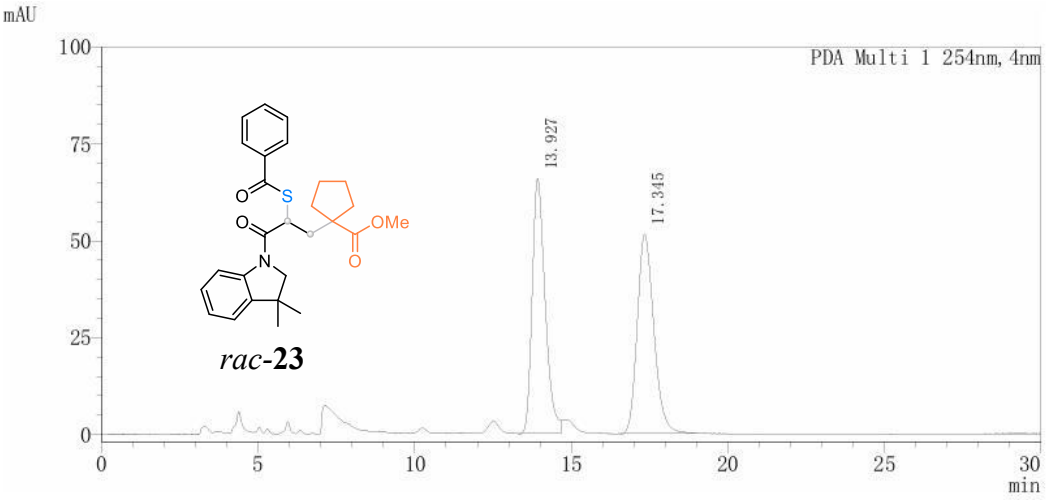


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.842	48519549	96.107
2	16.653	1965312	3.893

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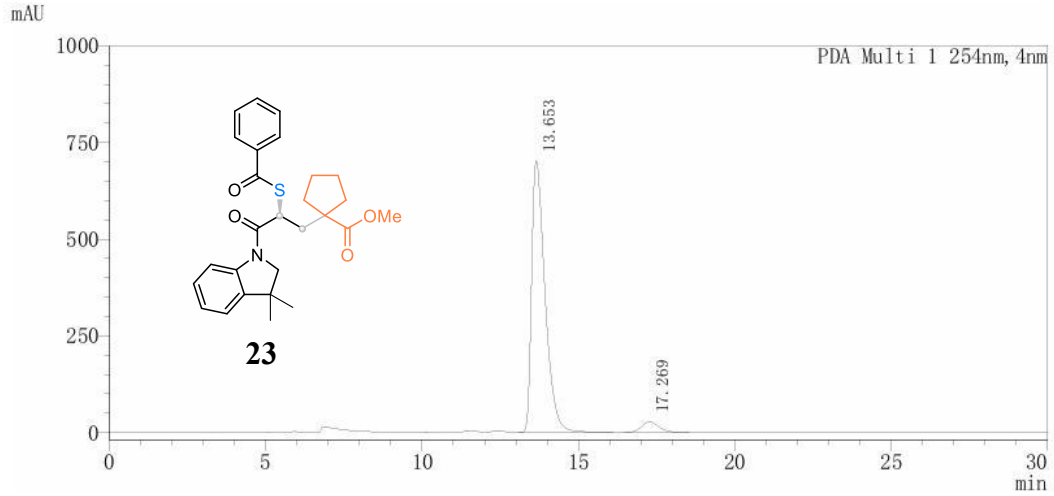
rac-**23**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.927	1894613	49.942
2	17.345	1898982	50.058

Z



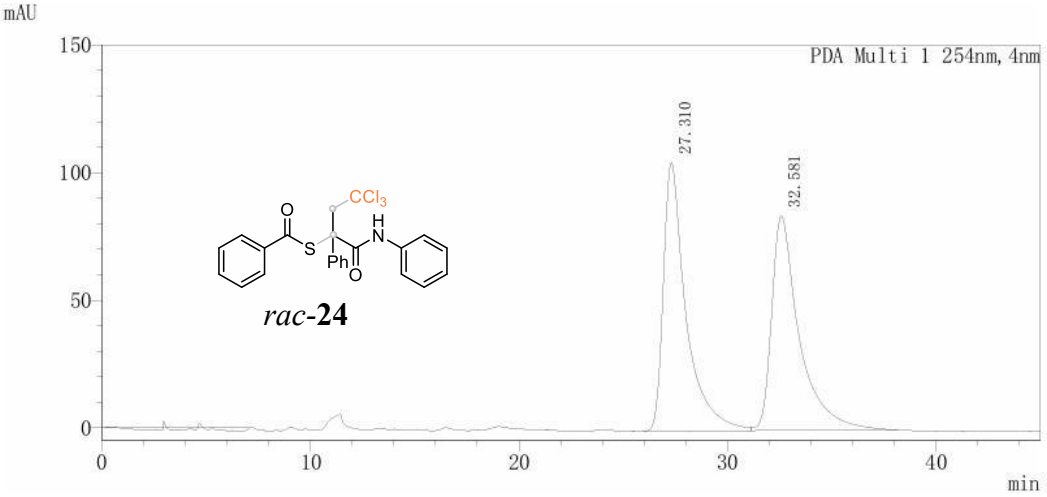
23

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.653	20896390	95.325
2	17.269	1024930	4.675

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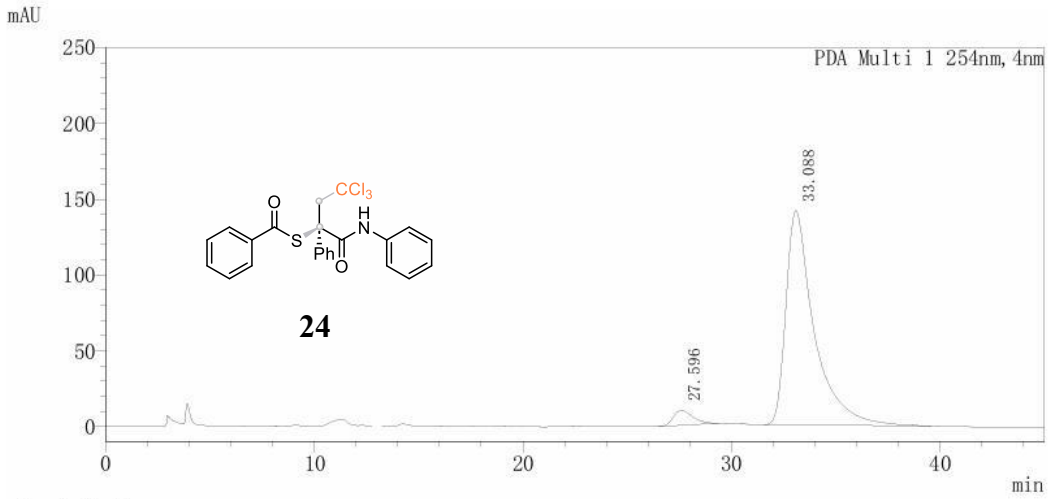


rac-**24**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.310	7927540	50.459
2	32.581	7783284	49.541



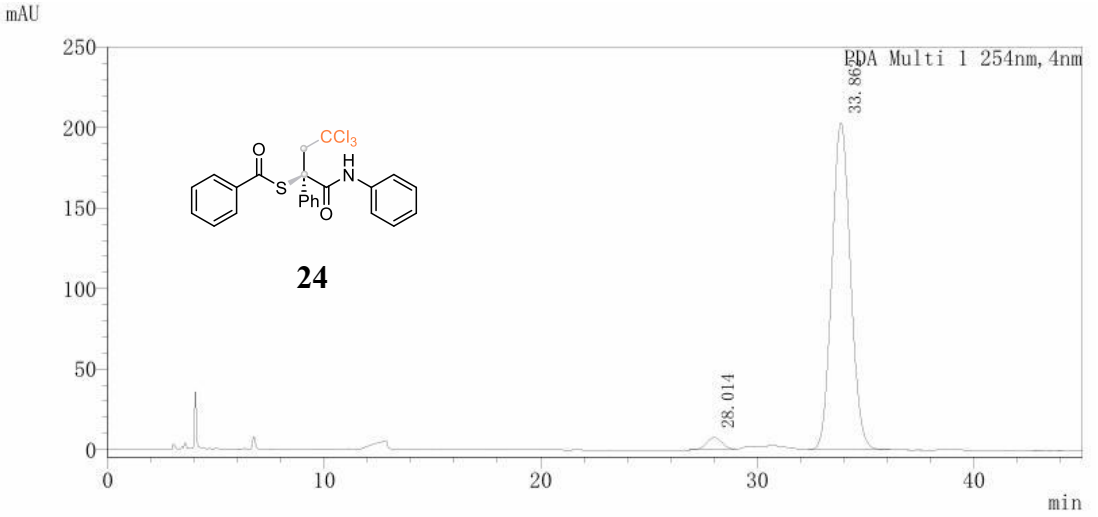
24

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.596	643102	4.593
2	33.088	13359499	95.407

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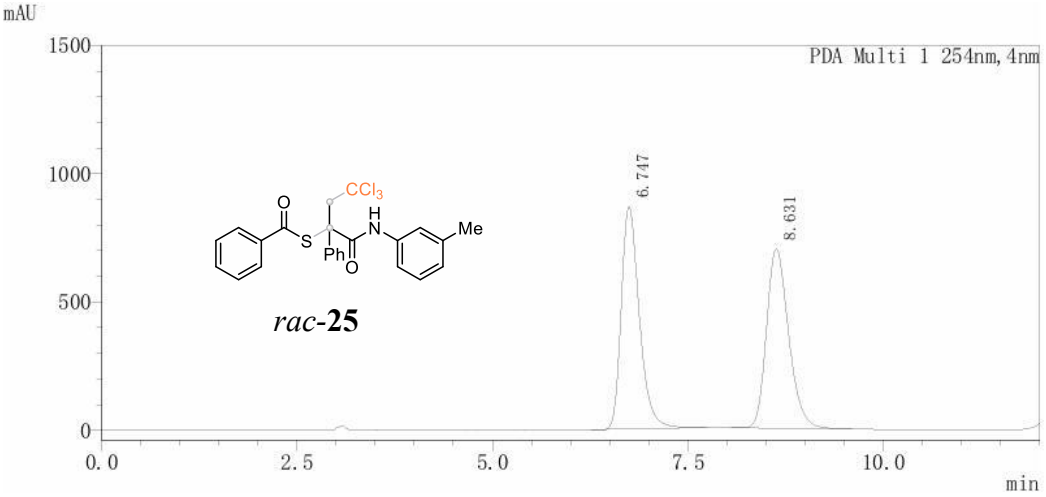
24

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.014	362159	2.895
2	33.862	12146561	97.105

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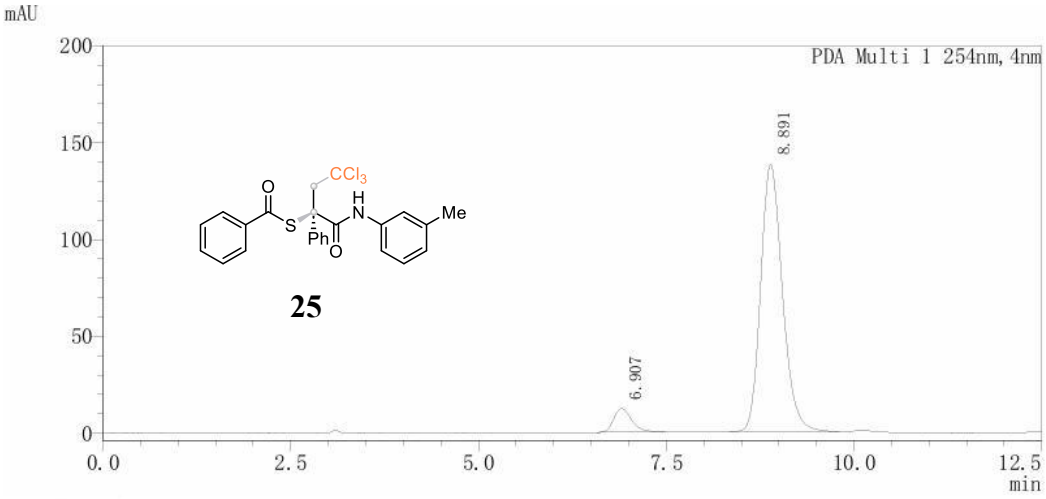


rac-**25**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.747	13867834	50.241
2	8.631	13734972	49.759



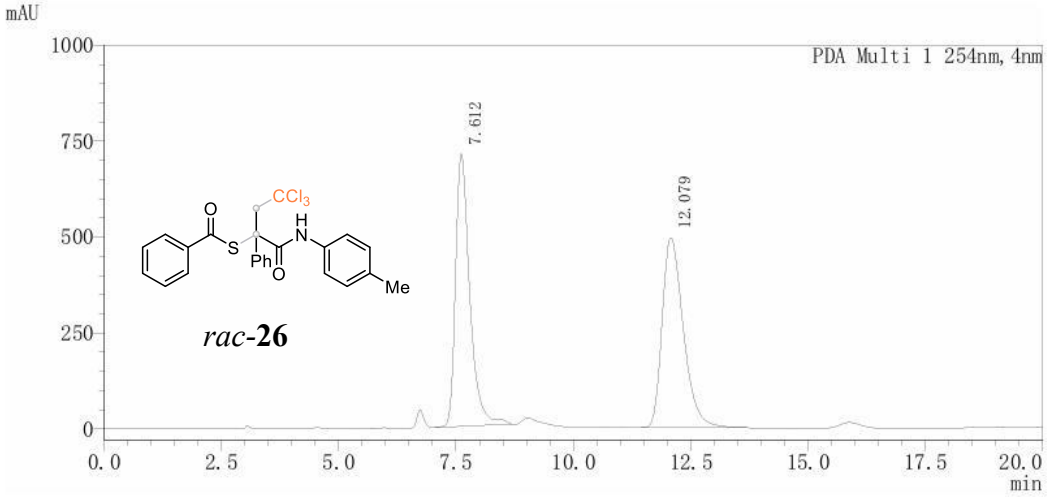
25

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.907	201854	6.777
2	8.891	2776874	93.223

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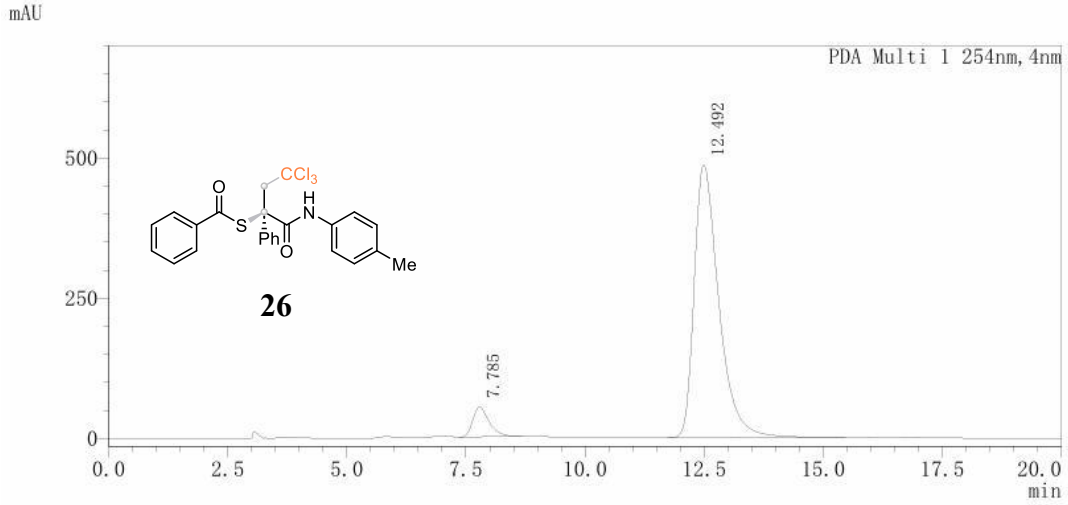


rac-**26**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.612	14997668	49.087
2	12.079	15555489	50.913



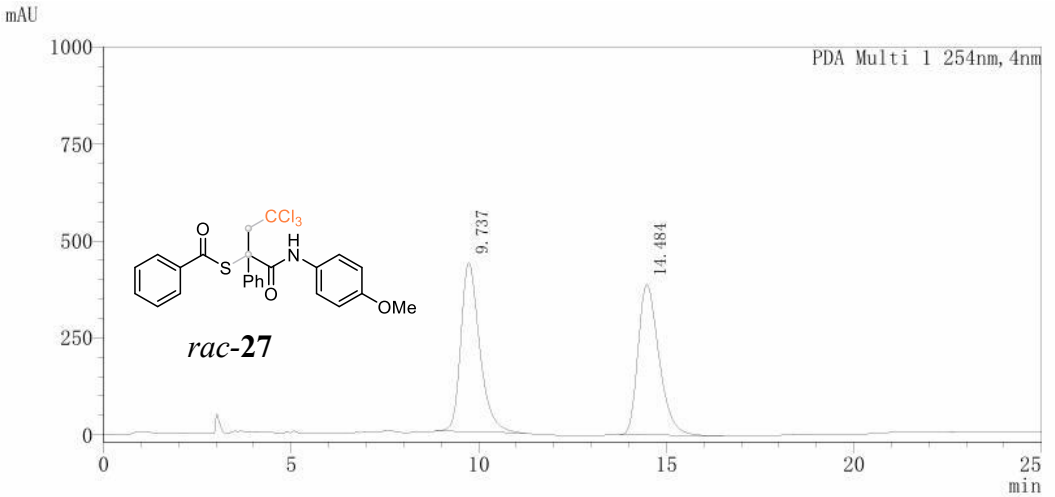
26

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.785	1251548	6.701
2	12.492	17426609	93.299

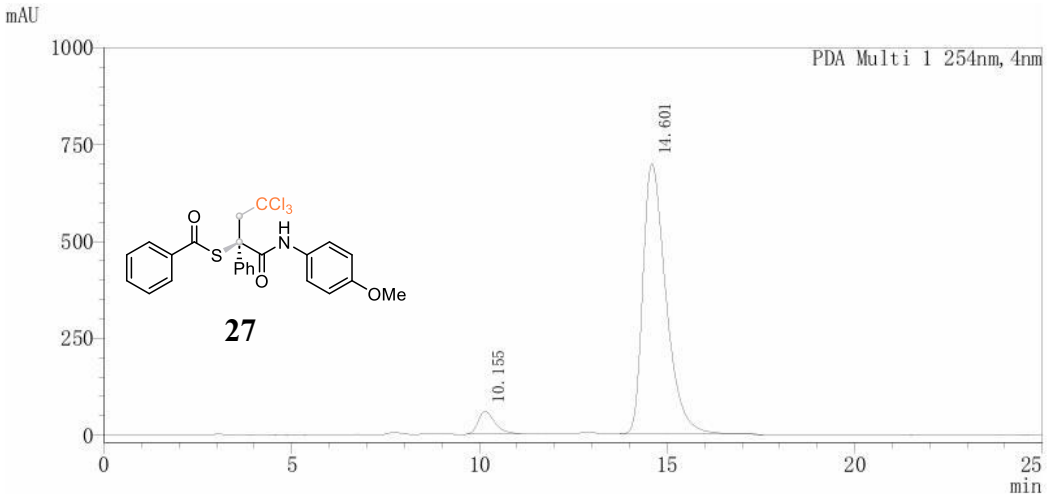
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.737	15250985	50.221
2	14.484	15116708	49.779

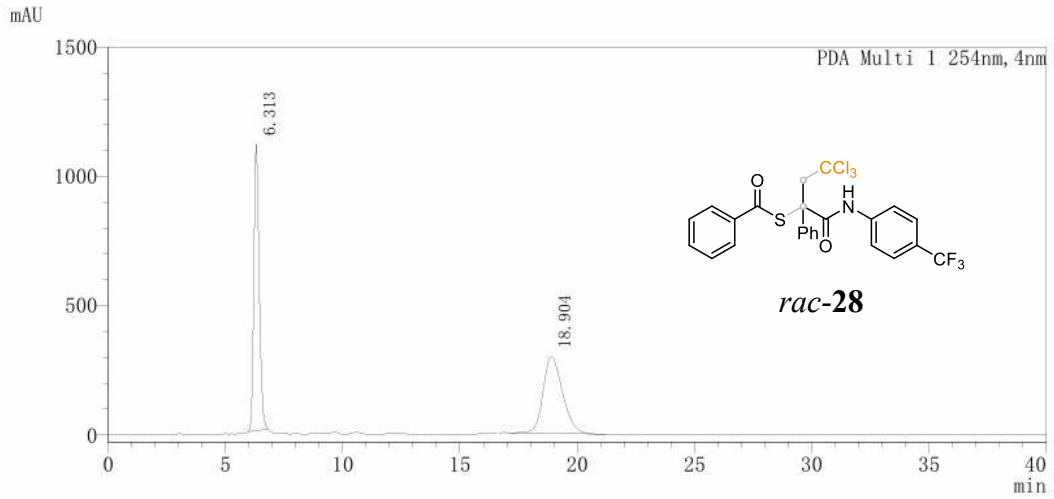


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.155	1758060	5.566
2	14.601	29825778	94.434

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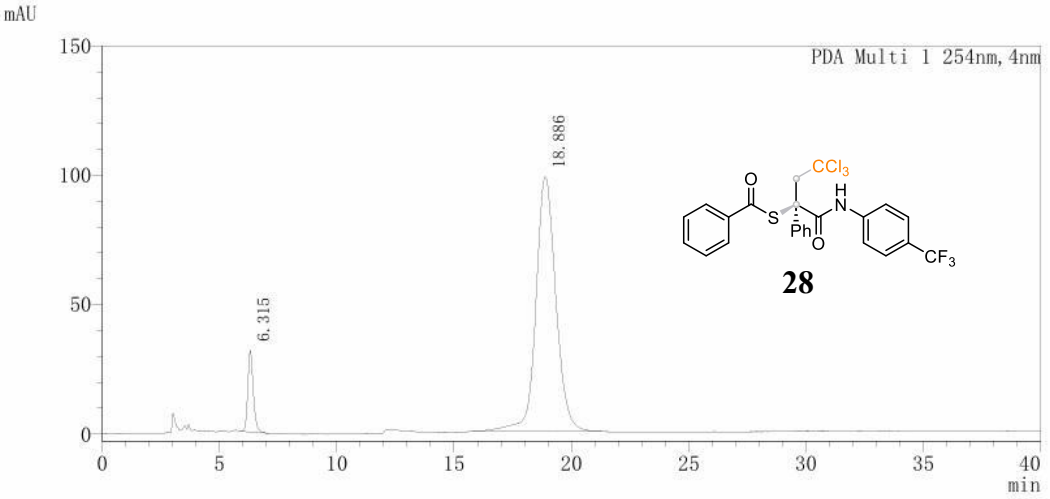


rac-**28**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.313	17513126	50.536
2	18.904	17141550	49.464



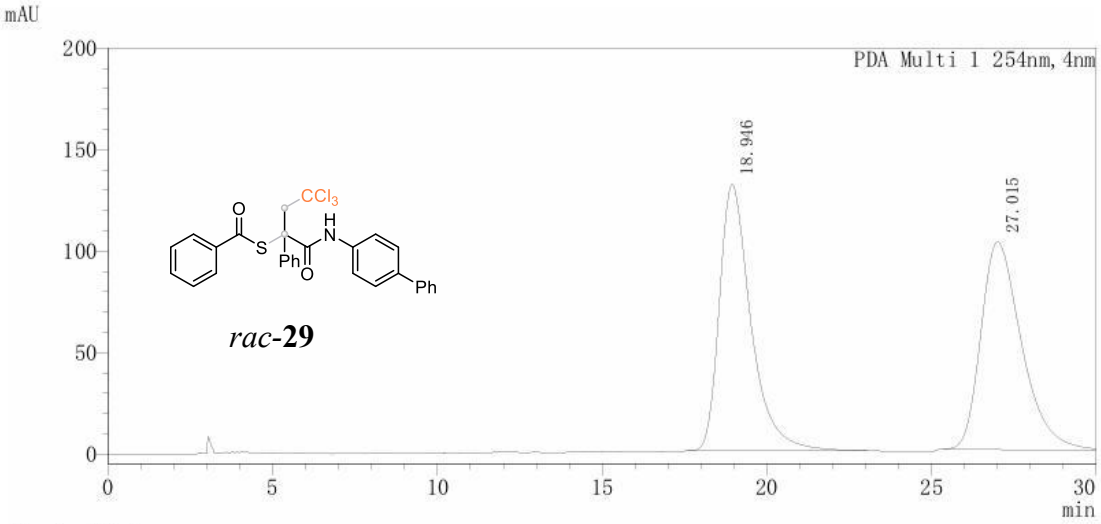
28

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.315	513021	8.064
2	18.886	5848899	91.936

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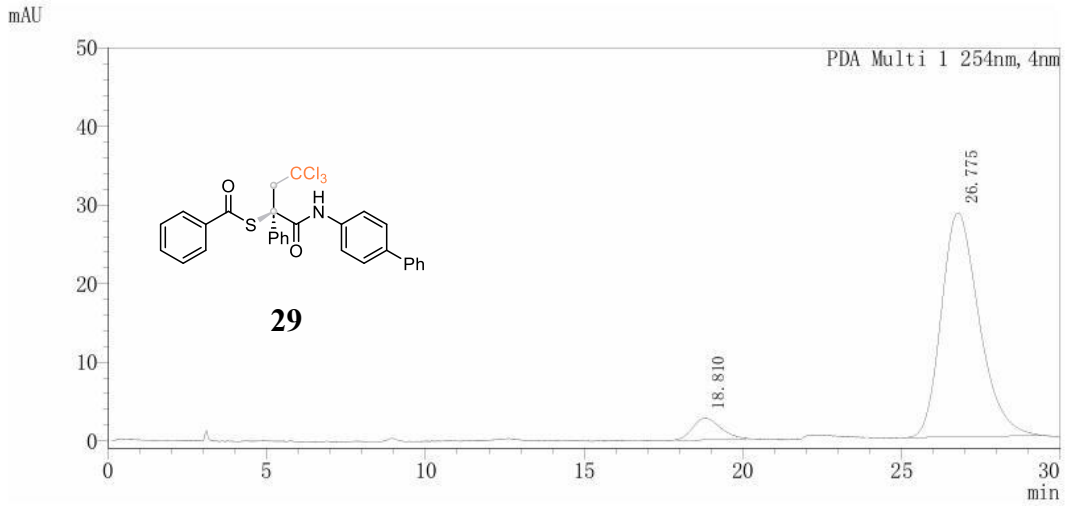


rac-**29**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.946	8805899	49.735
2	27.015	8899880	50.265



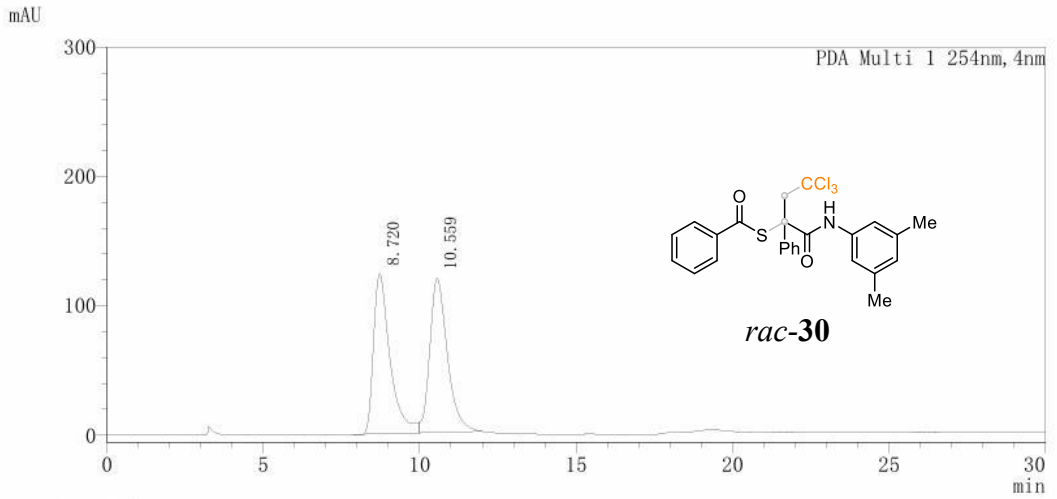
29

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.810	170552	6.731
2	26.775	2363176	93.269

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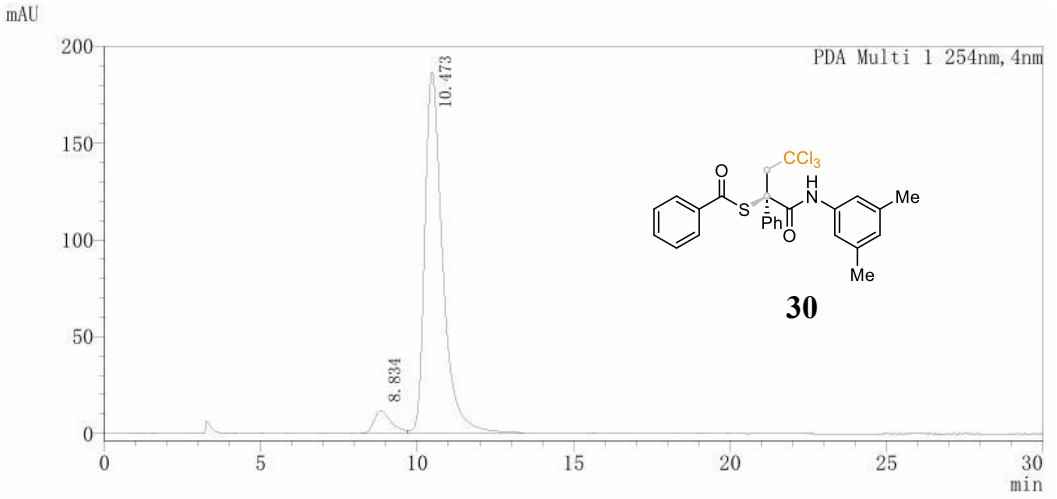


rac-**30**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.720	4575412	49.494
2	10.559	4668984	50.506



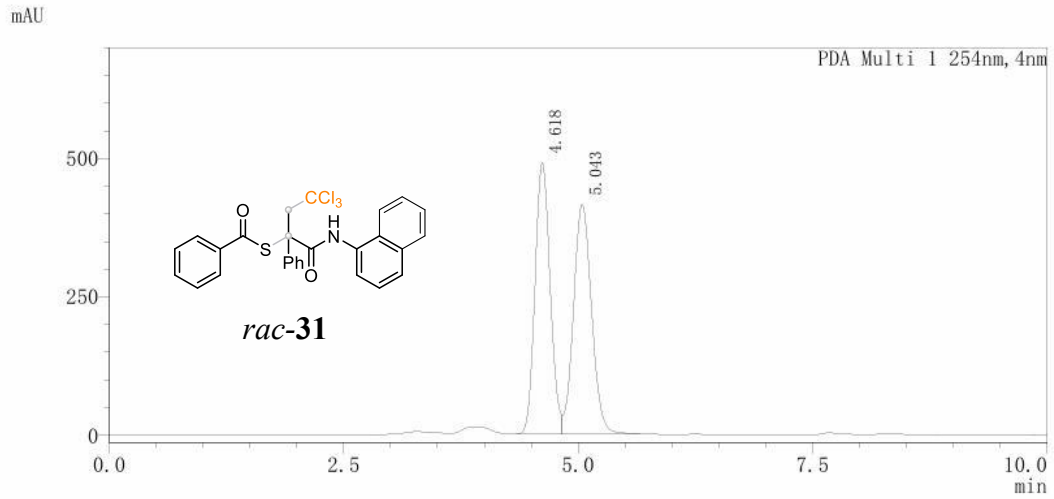
30

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.834	451355	5.783
2	10.473	7353539	94.217

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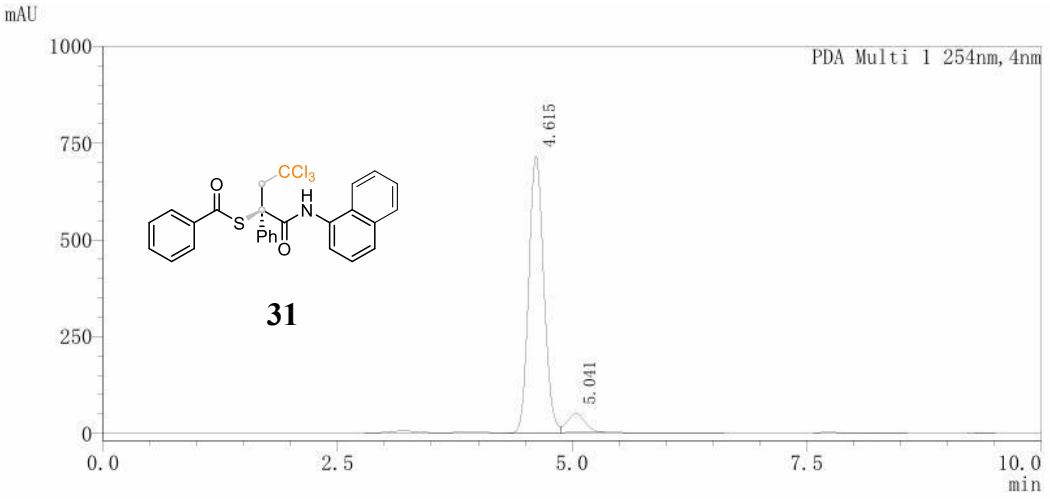


rac-**31**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.618	5513267	49.839
2	5.043	5548970	50.161



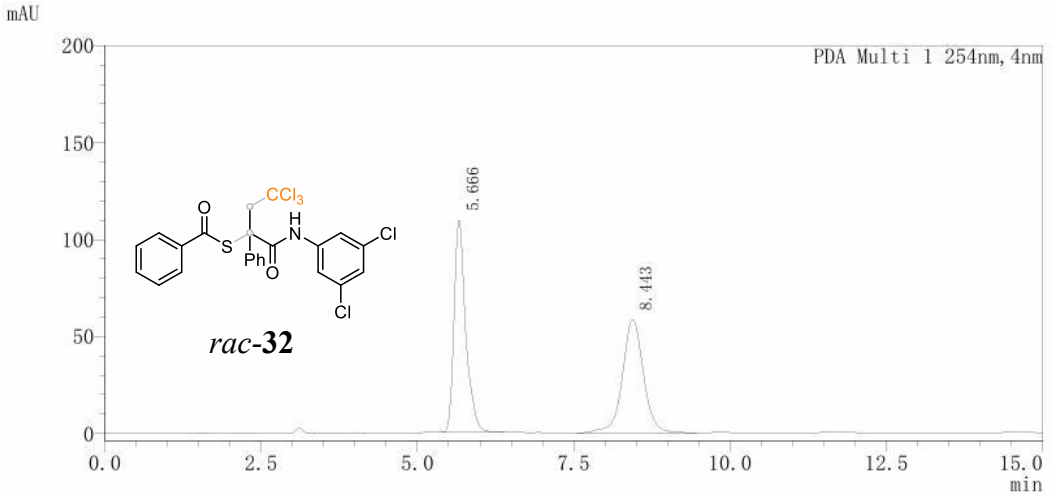
31

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.615	7939358	92.700
2	5.041	625248	7.300

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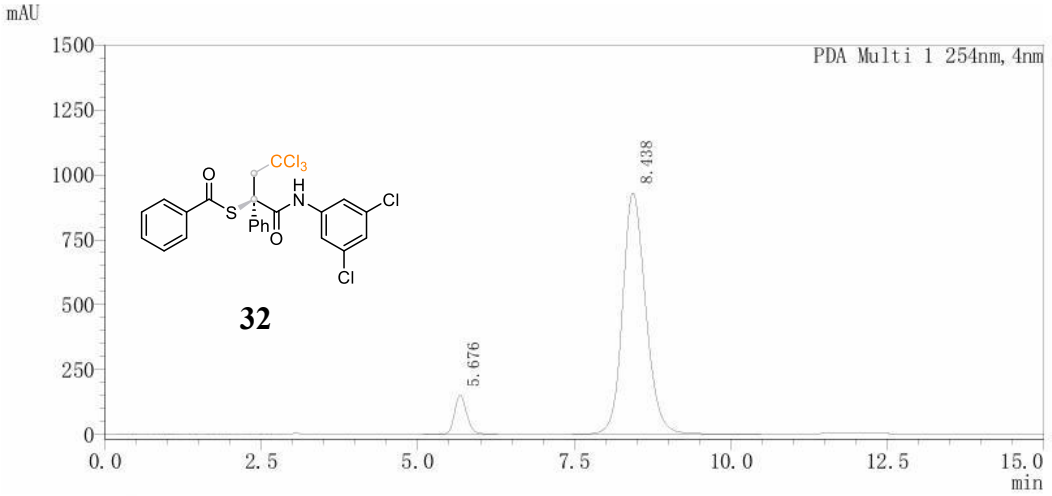


rac-**32**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.666	1420800	51.082
2	8.443	1360628	48.918



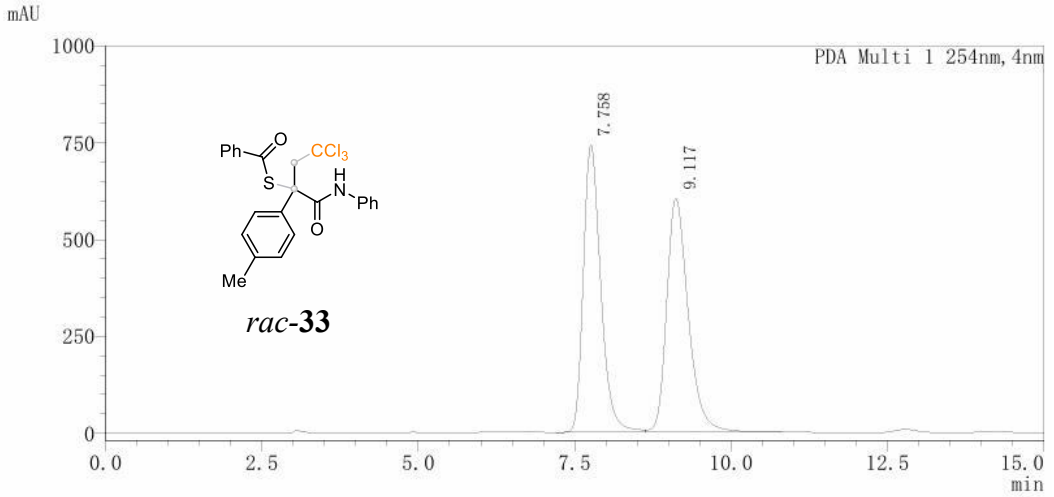
32

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.676	2004933	7.735
2	8.438	23915576	92.265

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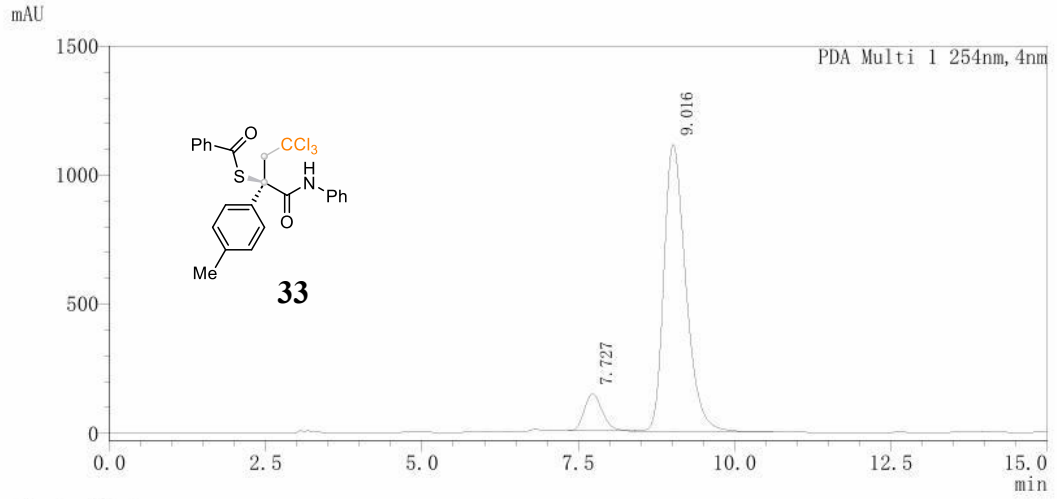


rac-**33**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.758	14398194	49.797
2	9.117	14515445	50.203



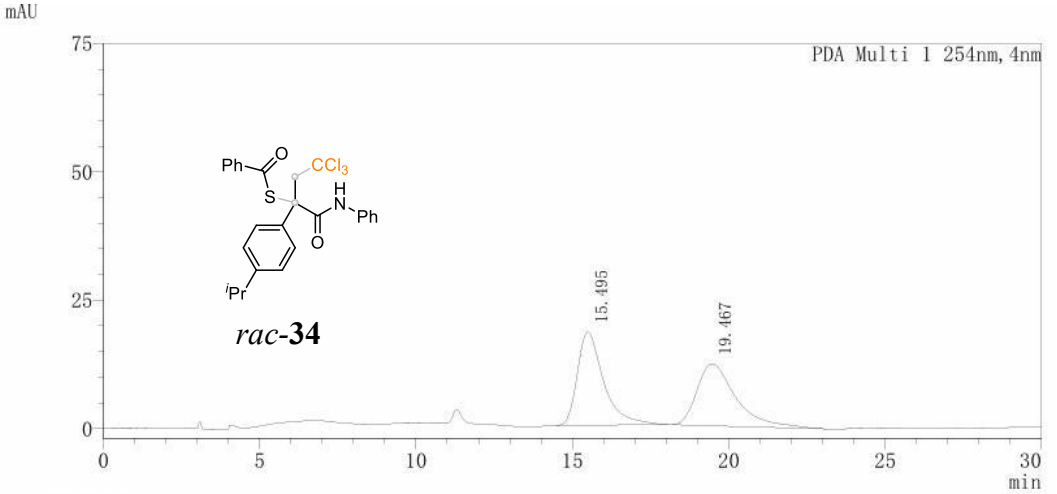
33

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.727	2893631	9.628
2	9.016	27160120	90.372

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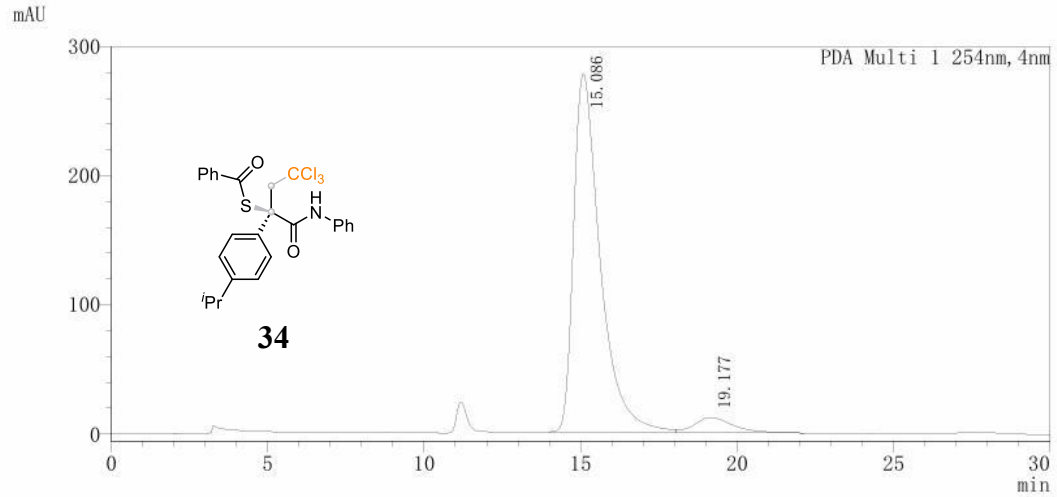


rac-**34**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.495	1060928	50.421
2	19.467	1043195	49.579



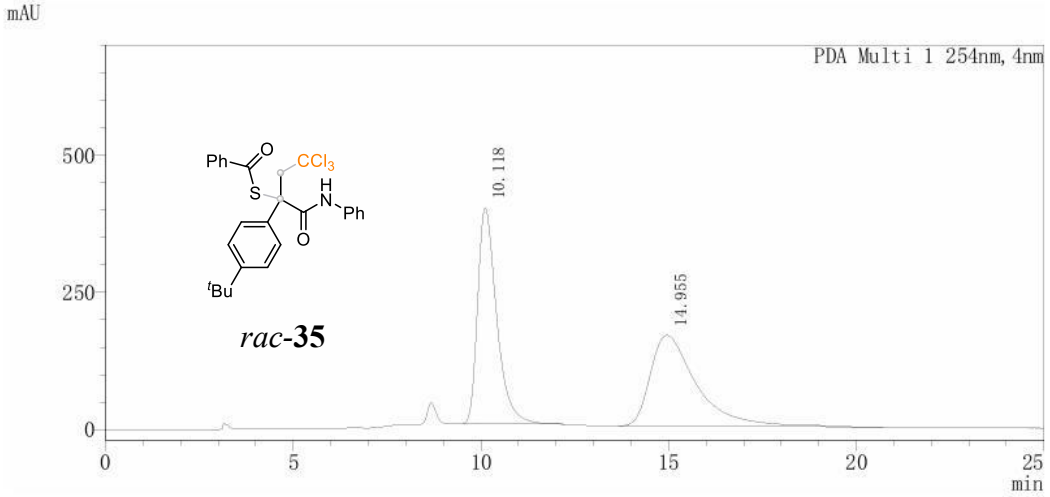
34

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.086	16374945	94.252
2	19.177	998604	5.748

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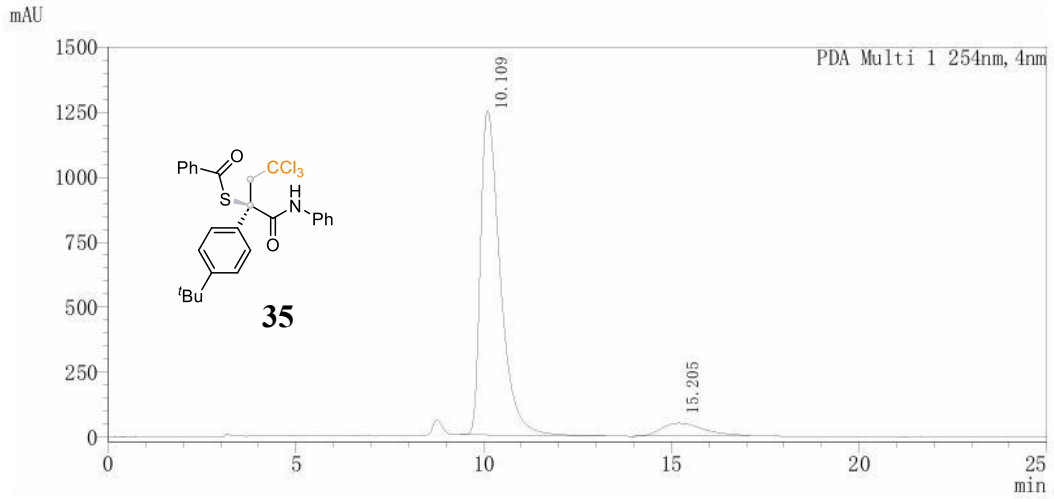
rac-**35**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.118	13891926	49.452
2	14.955	14200036	50.548

Z



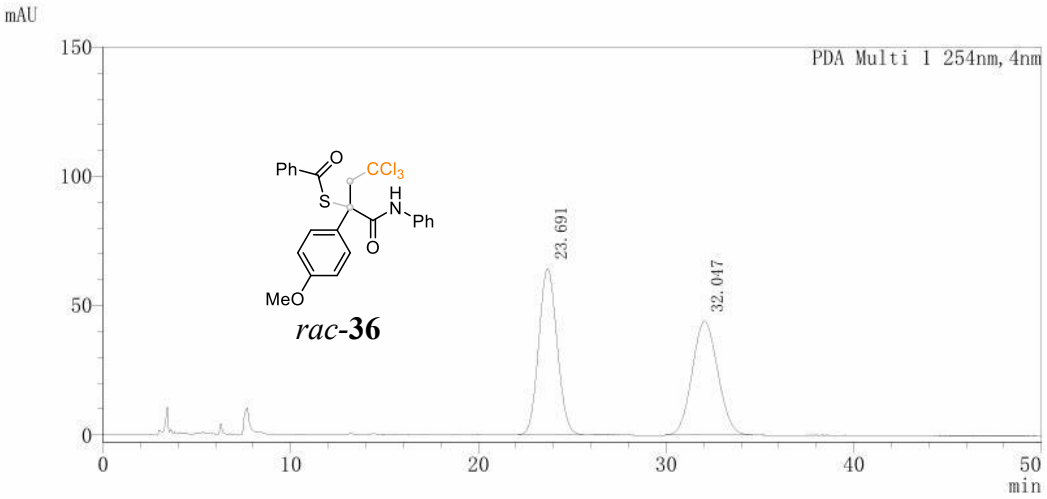
35

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.109	45762907	92.400
2	15.205	3763854	7.600

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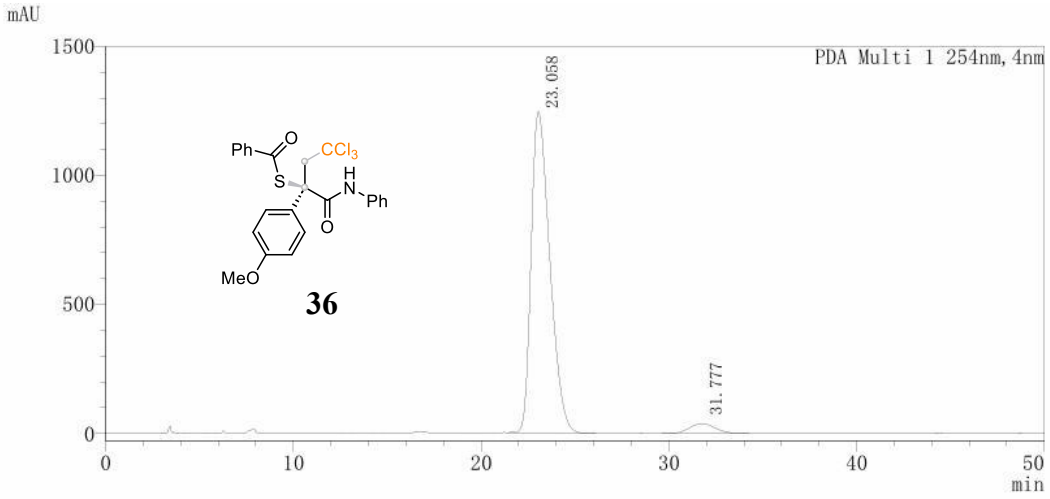


rac-**36**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.691	4372643	51.130
2	32.047	4179431	48.870



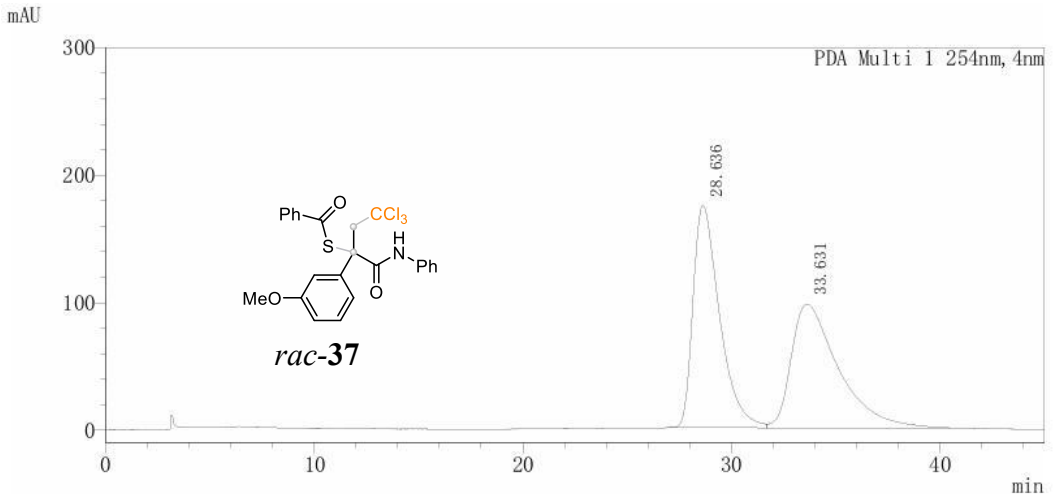
36

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.058	85924234	96.068
2	31.777	3516915	3.932

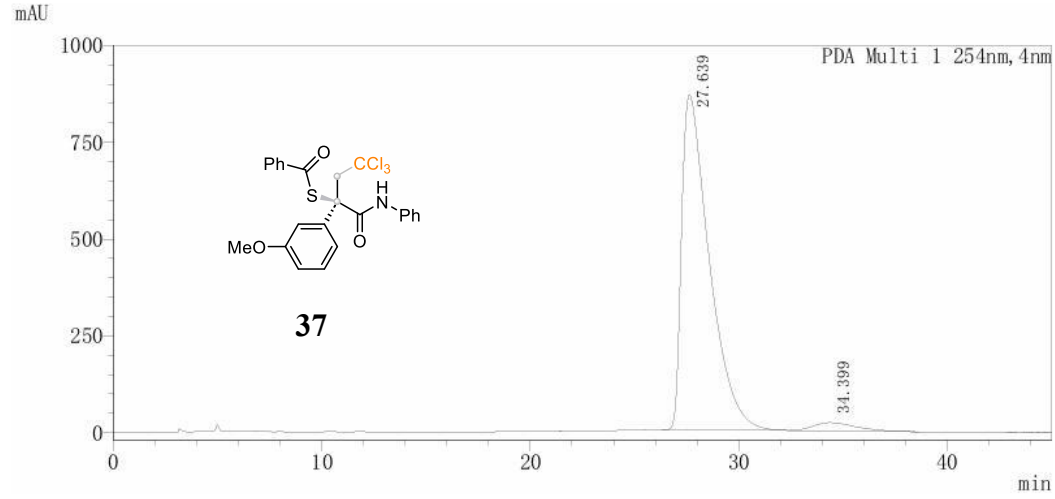
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.636	15474580	50.447
2	33.631	15200484	49.553

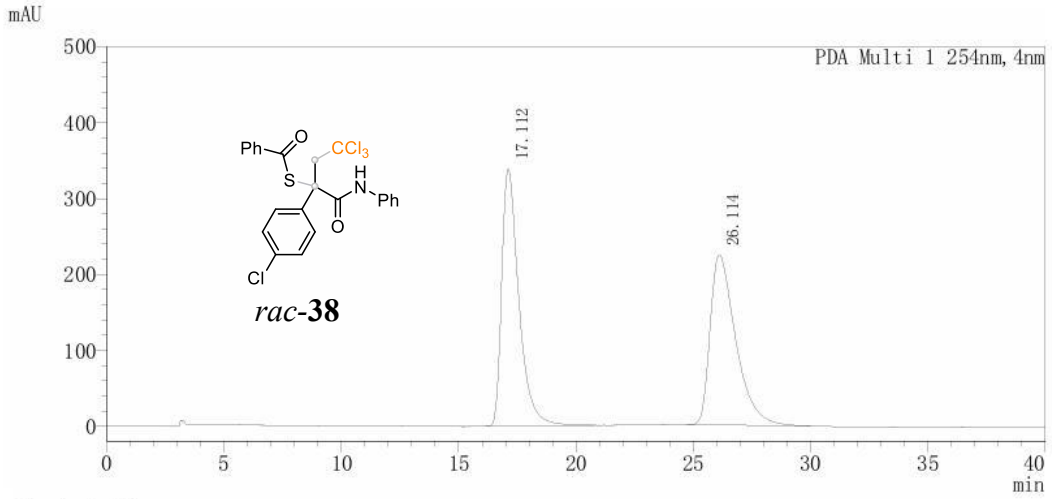


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.639	79888996	96.269
2	34.399	3096476	3.731

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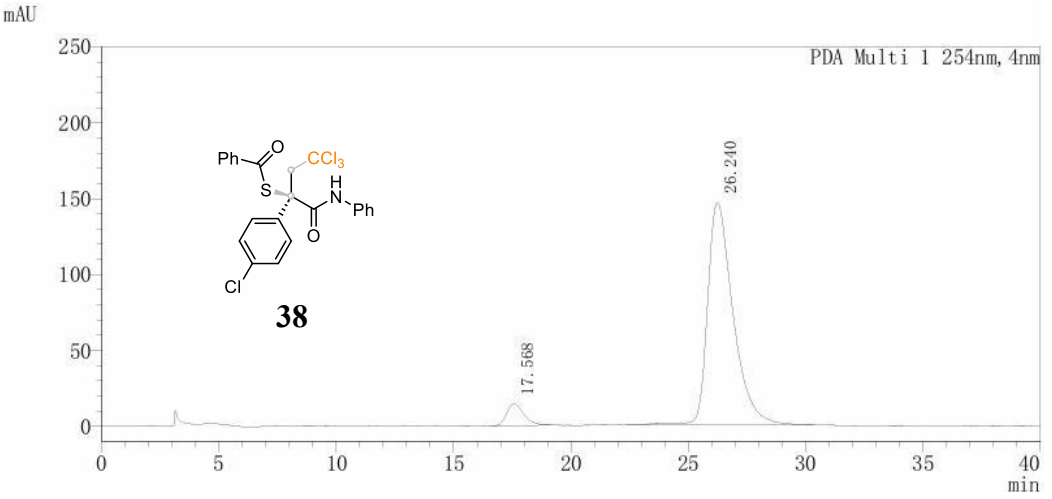


rac-**38**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.112	17233876	50.297
2	26.114	17030384	49.703



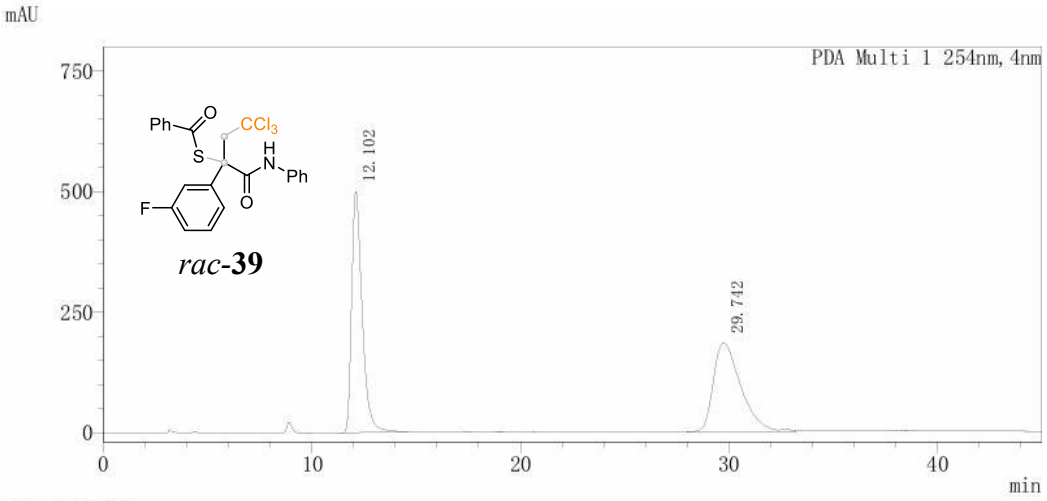
38

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.568	732593	6.233
2	26.240	11021017	93.767

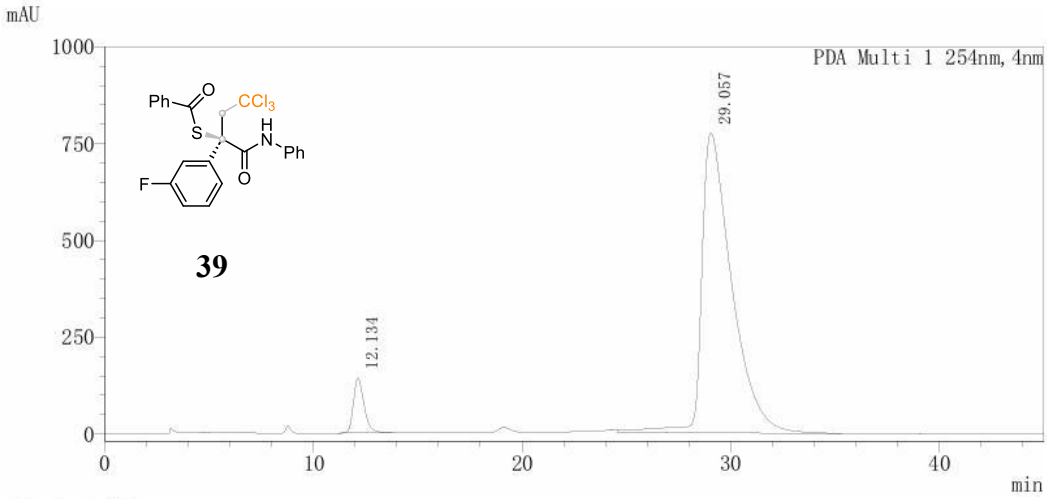
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.102	17563799	50.374
2	29.742	17302831	49.626

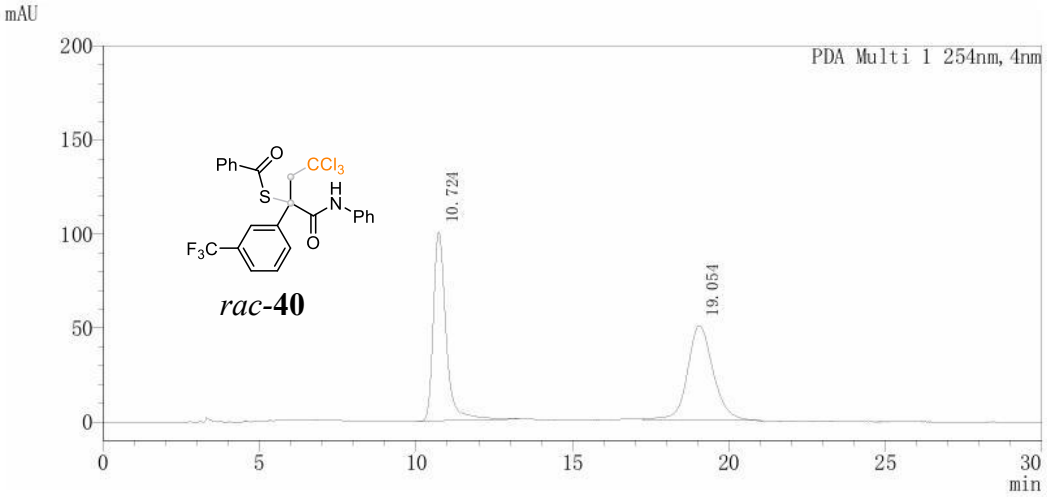


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.134	4977418	6.009
2	29.057	77851871	93.991

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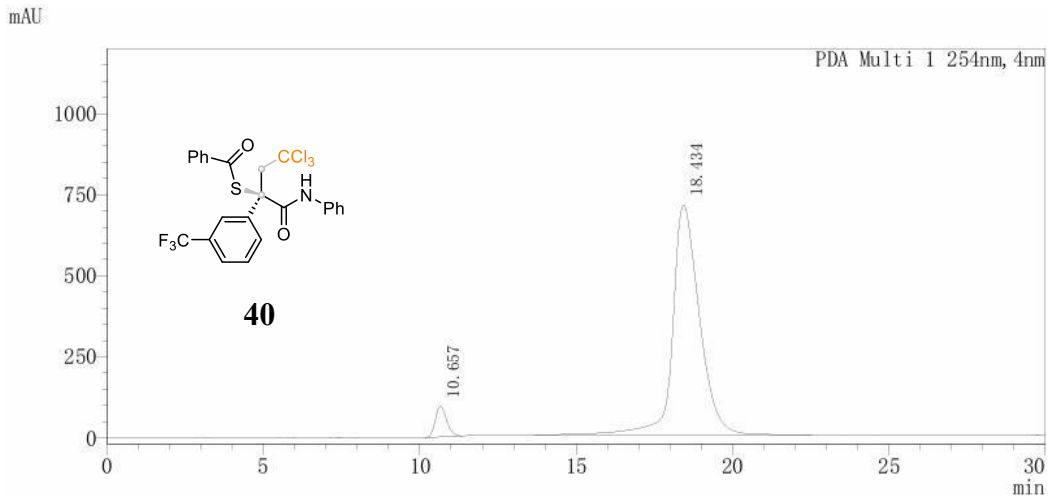


rac-**40**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.724	2835267	49.478
2	19.054	2895068	50.522



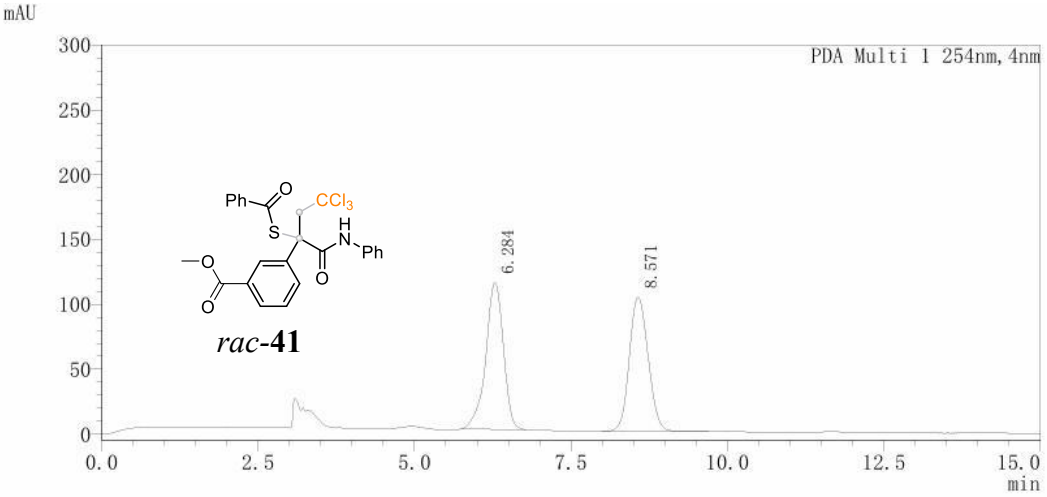
40

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.657	2355332	5.225
2	18.434	42719195	94.775

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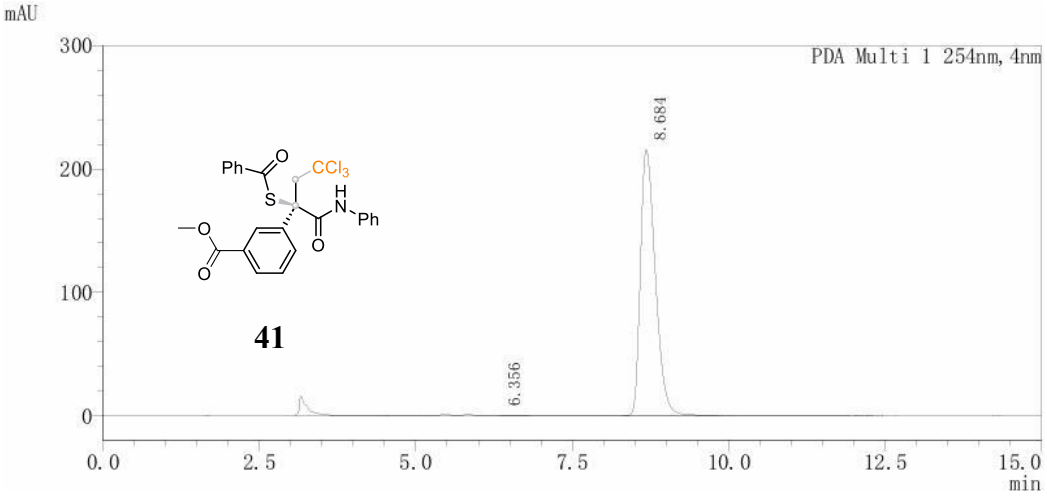


rac-**41**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.284	2227340	50.646
2	8.571	2170518	49.354



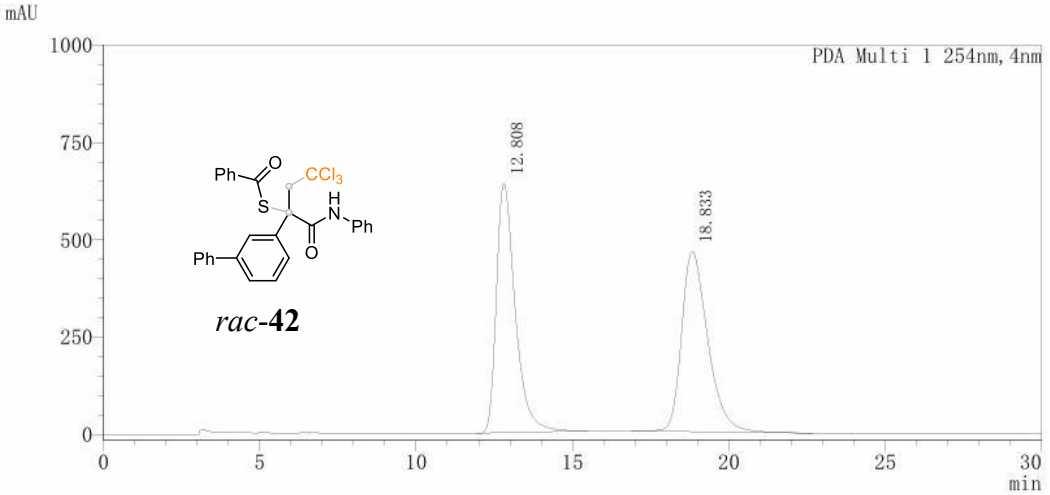
41

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.356	11948	0.335
2	8.684	3559964	99.665

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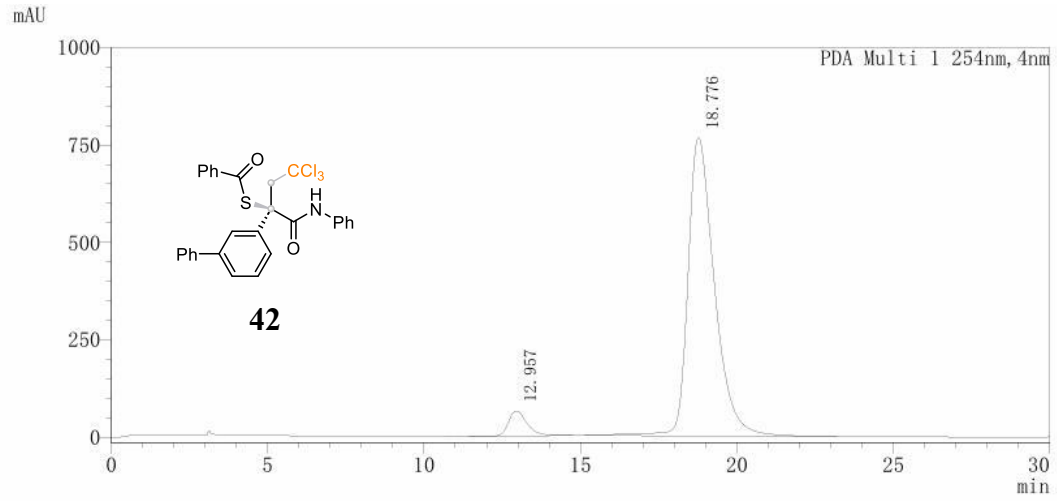


rac-**42**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.808	26899247	49.863
2	18.833	27046717	50.137



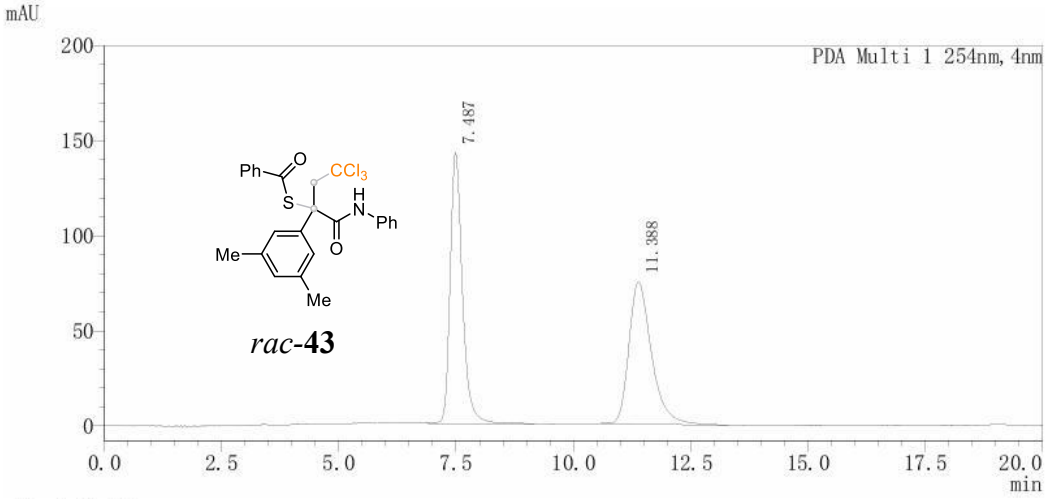
42

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.957	2726362	5.668
2	18.776	45371476	94.332

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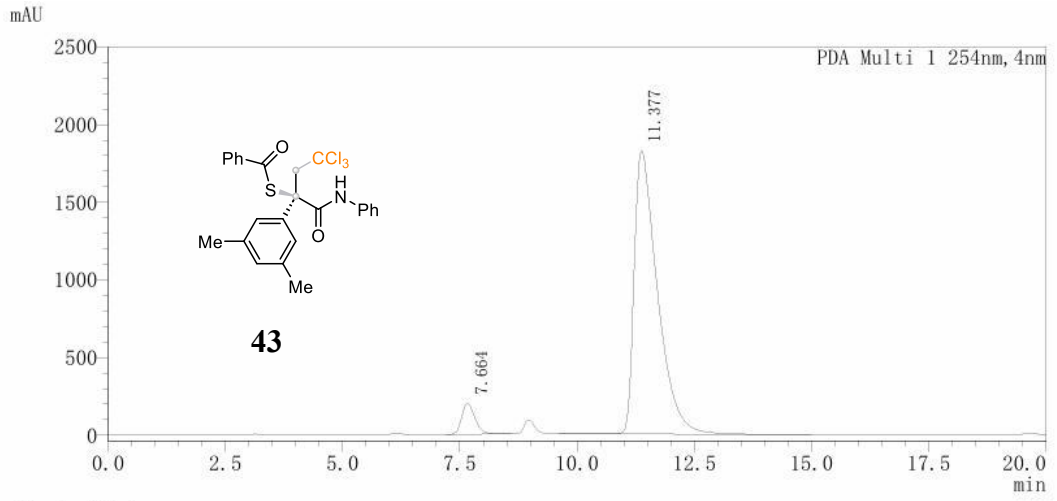


rac-**43**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.487	2590942	50.619
2	11.388	2527595	49.381



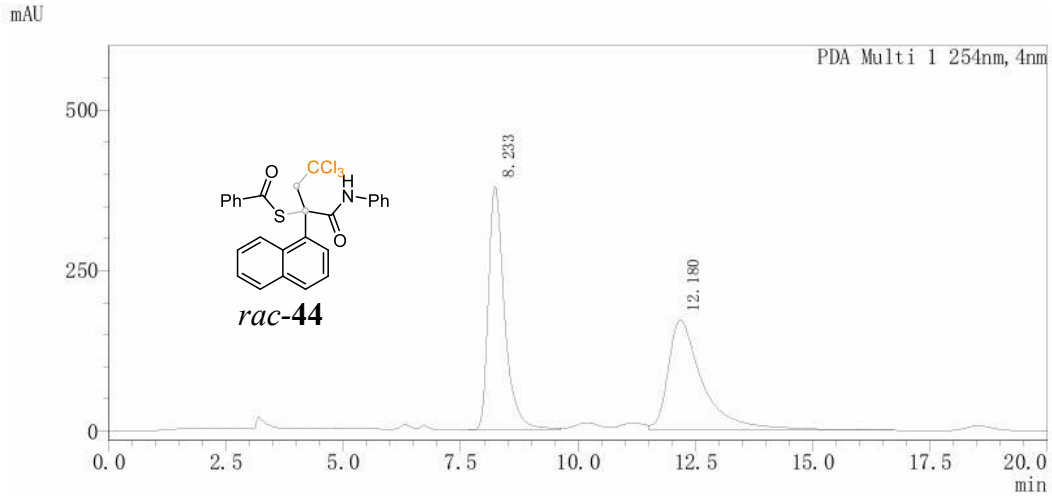
43

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.664	3897504	5.812
2	11.377	63167162	94.188

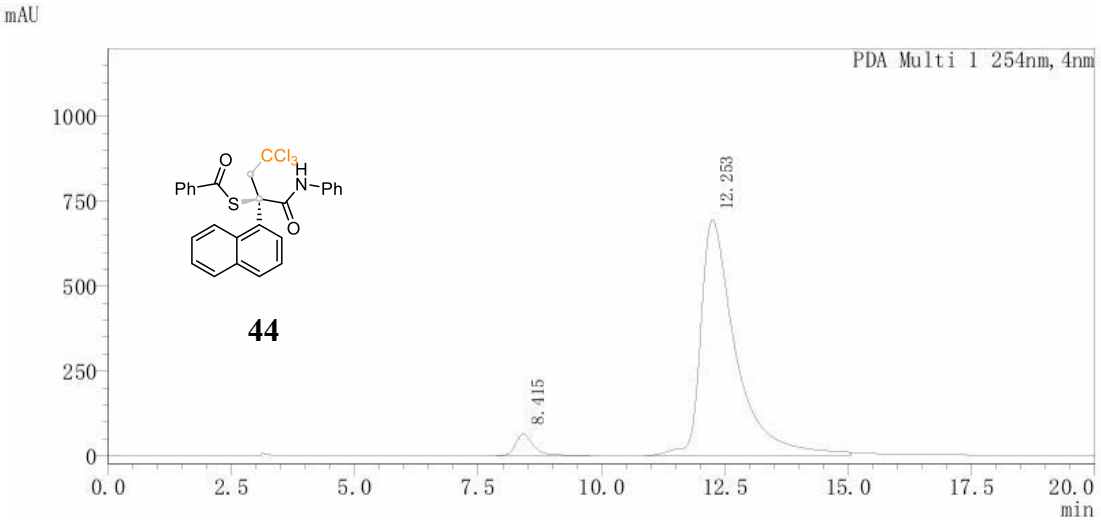
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.233	9107434	50.720
2	12.180	8848719	49.280

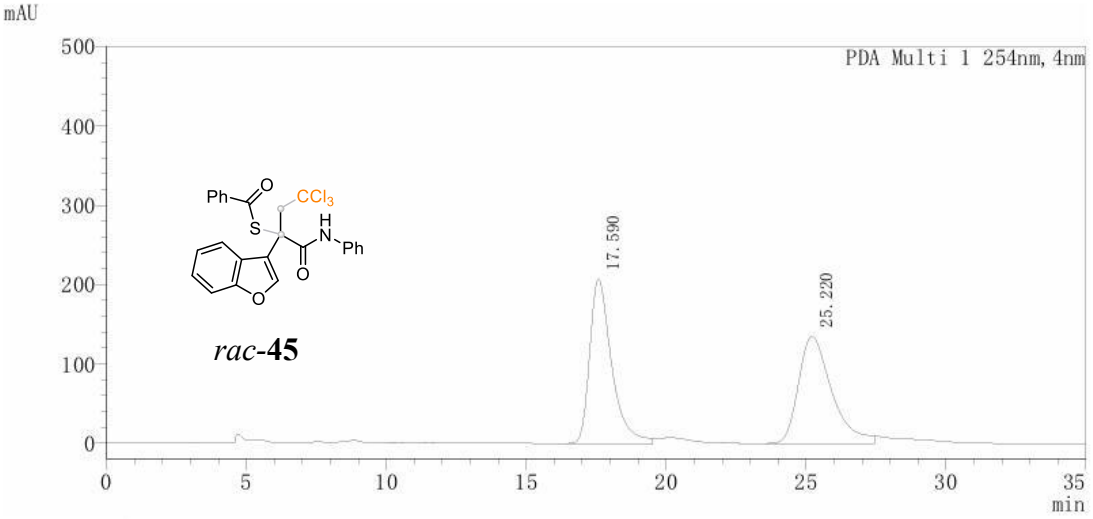


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.415	1562122	4.360
2	12.253	34262364	95.640

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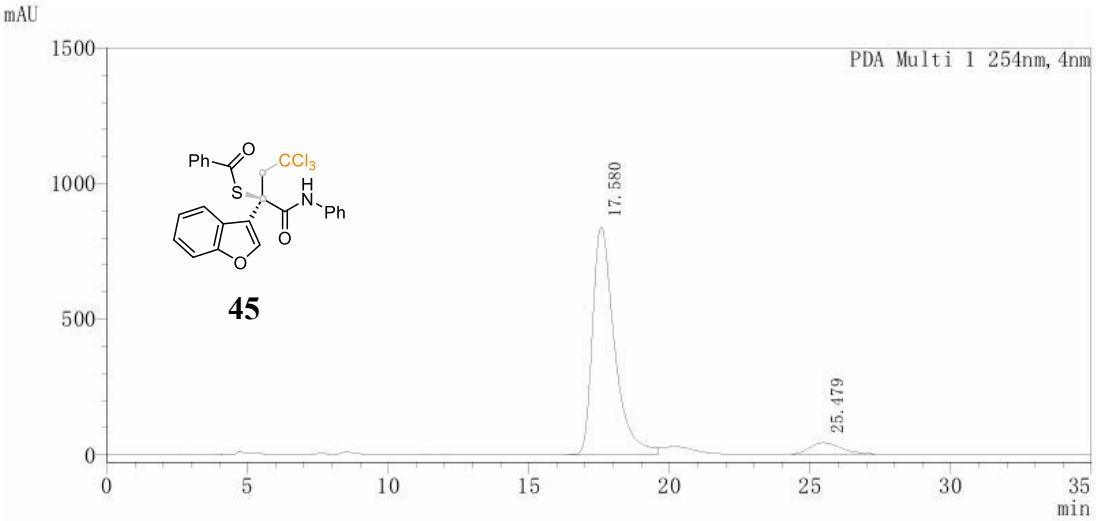


rac-**45**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.590	11248510	50.289
2	25.220	11119296	49.711



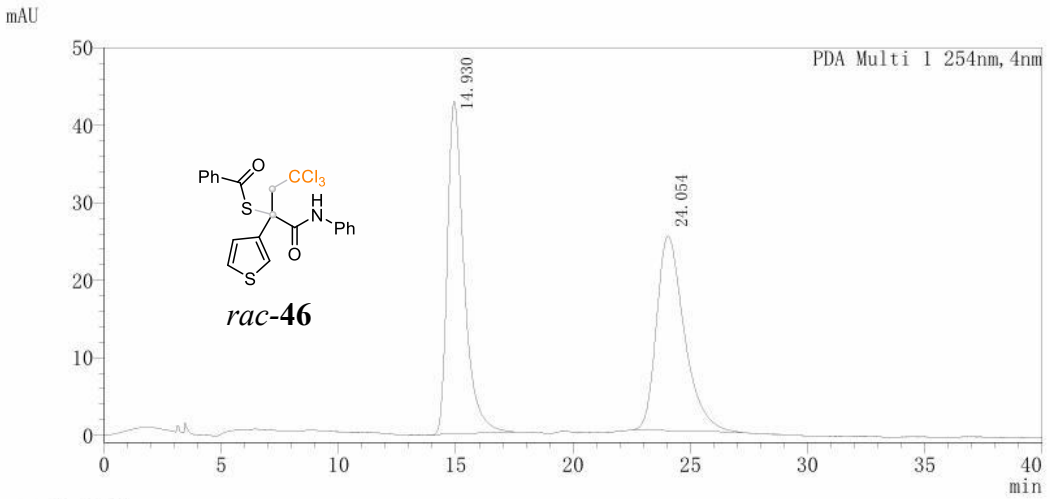
45

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.580	45606036	92.957
2	25.479	3455374	7.043

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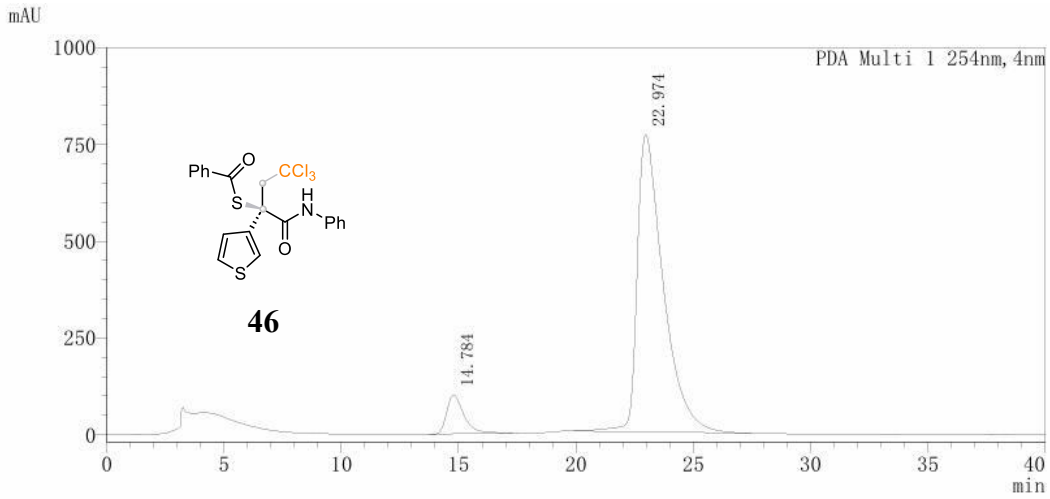


rac-**46**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.930	2126334	50.643
2	24.054	2072314	49.357



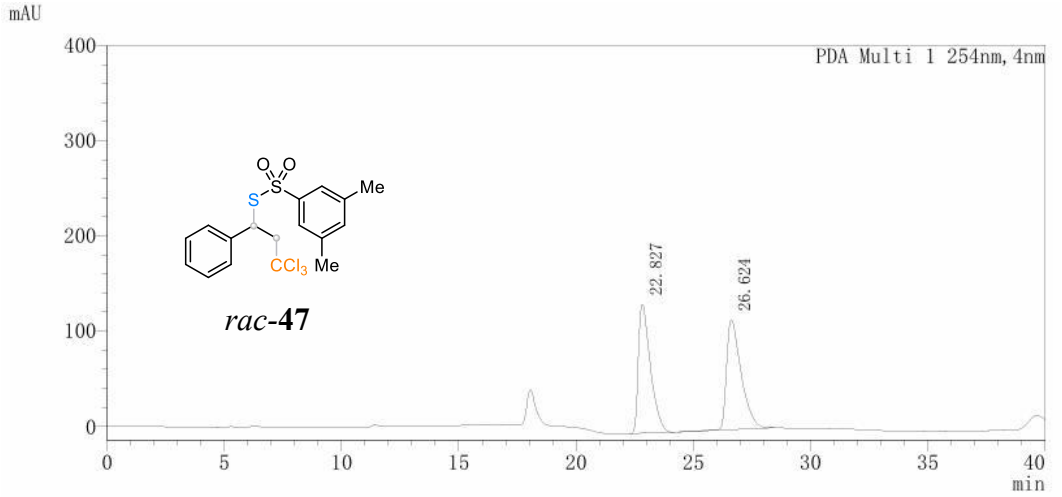
46

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.784	5083534	7.856
2	22.974	59622392	92.144

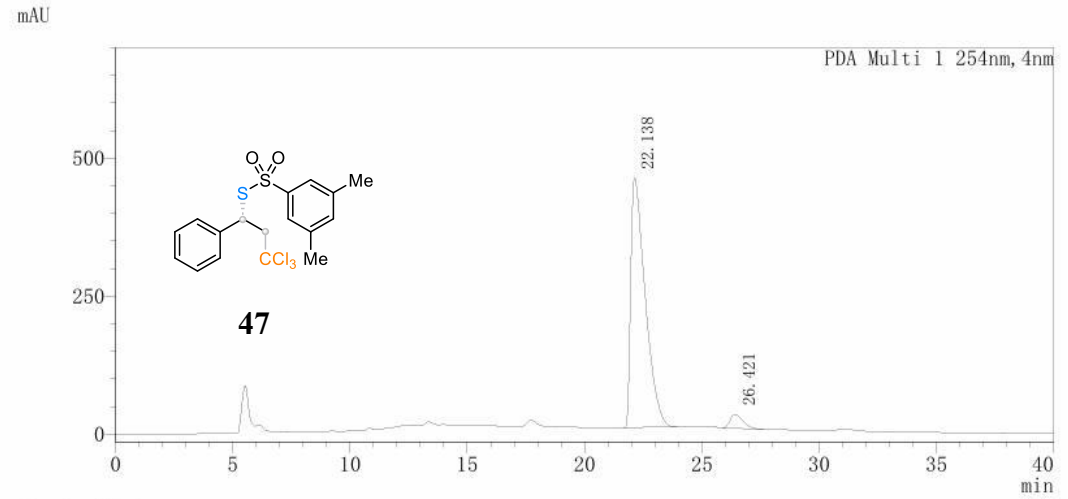
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.827	4826101	49.146
2	26.624	4993898	50.854

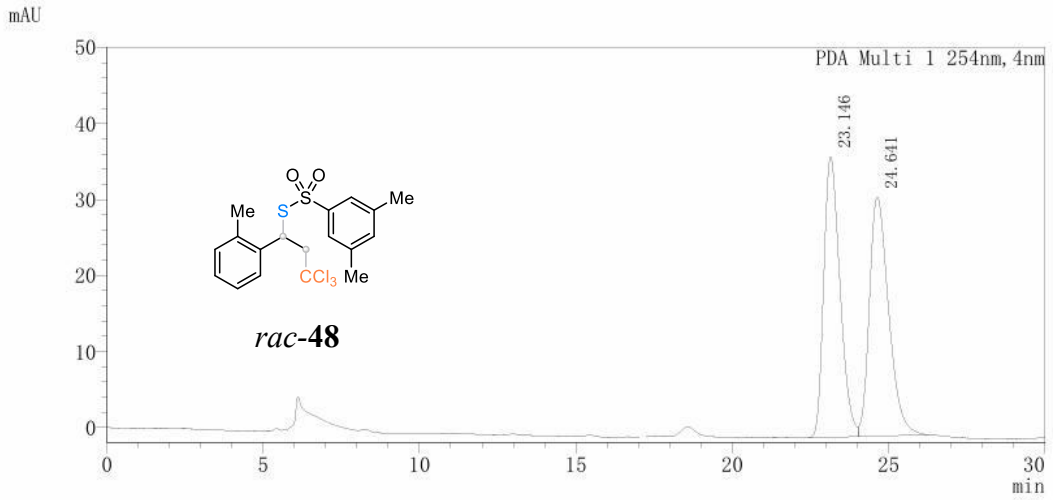


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.138	19343611	95.354
2	26.421	942470	4.646

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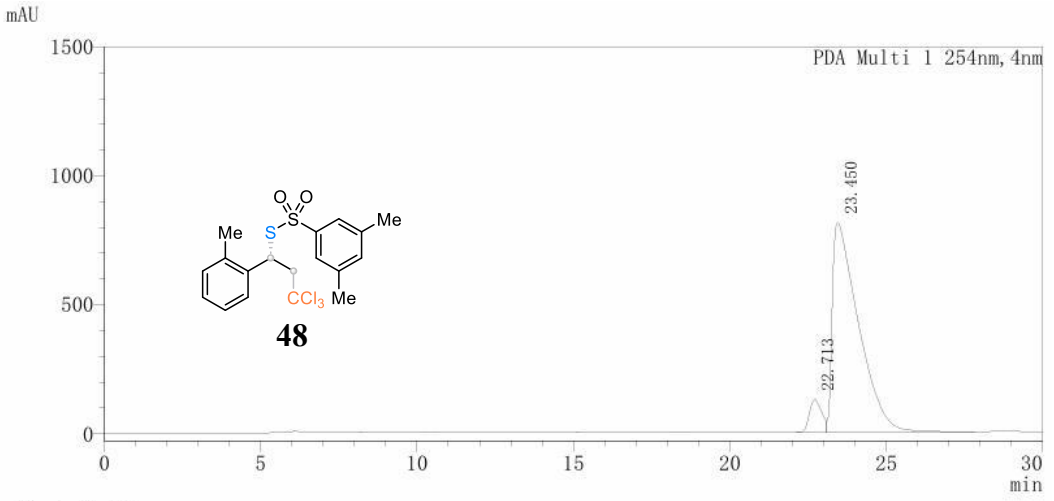


rac-**48**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.146	1328944	49.646
2	24.641	1347908	50.354



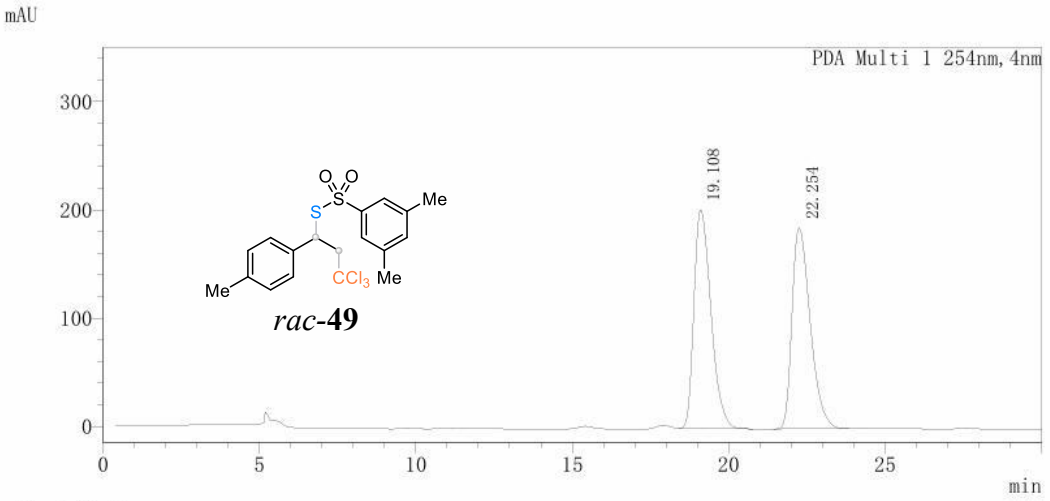
48

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.713	3531621	6.929
2	23.450	47439293	93.071

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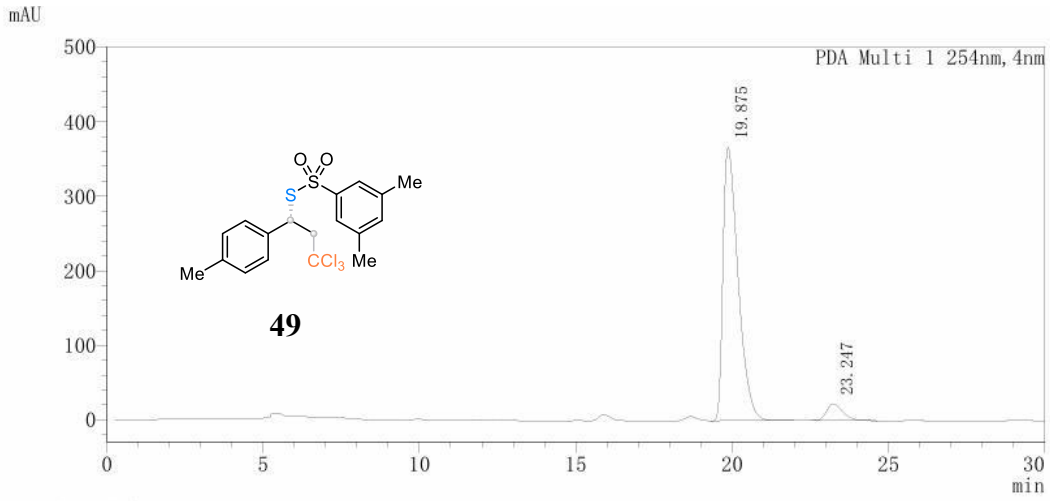


rac-**49**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.108	7635008	50.300
2	22.254	7544054	49.700



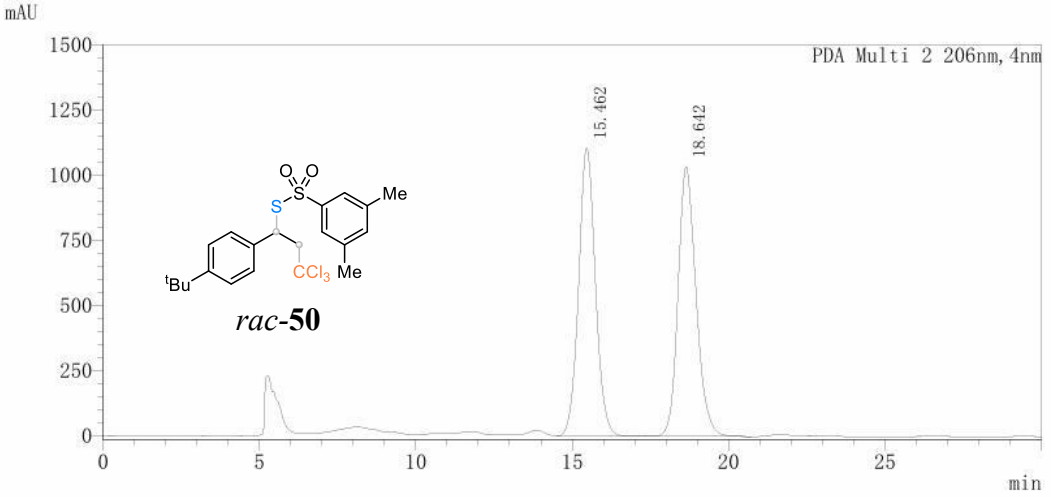
49

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.875	12312687	93.893
2	23.247	800865	6.107

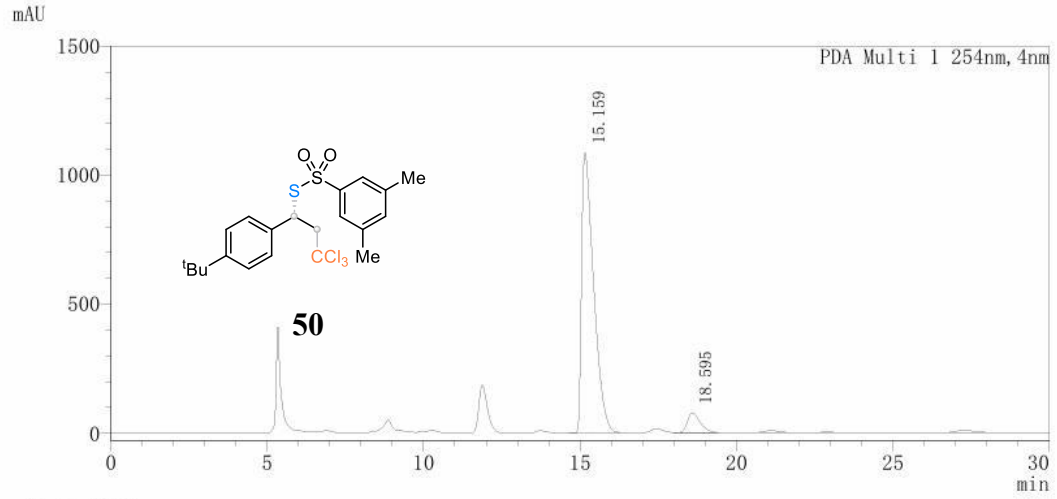
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Peak Table

PDA Ch2 206nm

Peak#	Ret. Time	Area	Area%
1	15.462	41216033	49.888
2	18.642	41401610	50.112

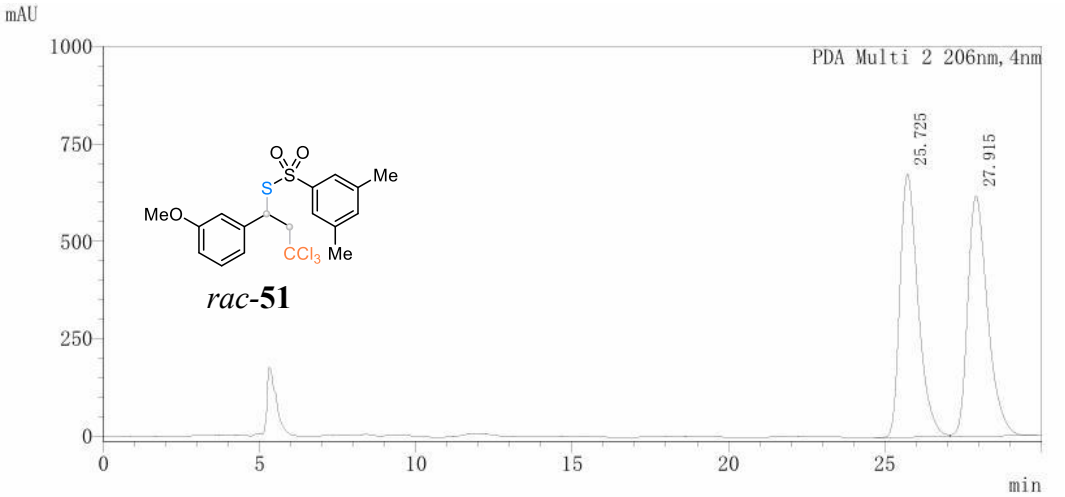


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.159	29069390	93.259
2	18.595	2101162	6.741

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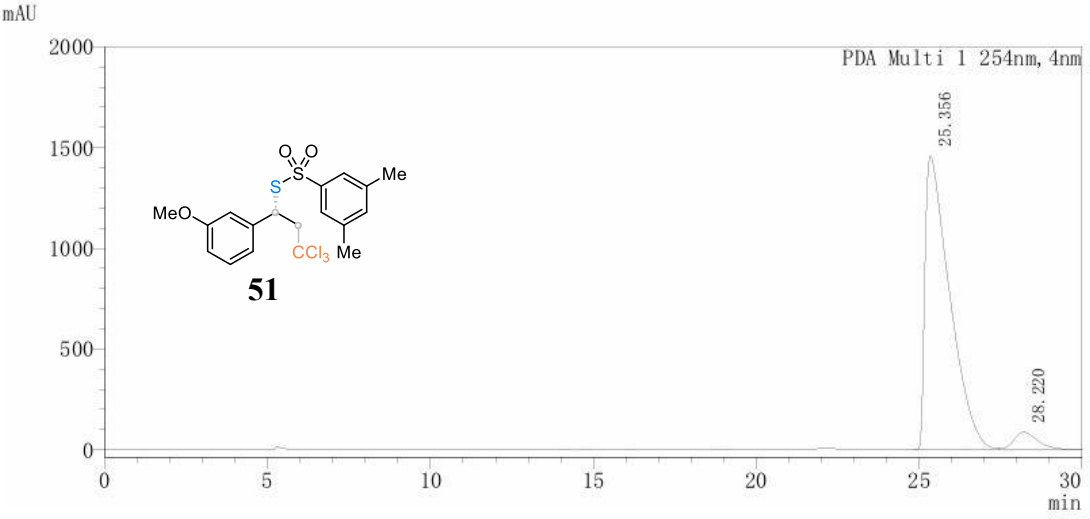


rac-**51**

Peak Table

PDA Ch2 206nm

Peak#	Ret. Time	Area	Area%
1	25.725	27245496	49.951
2	27.915	27299042	50.049



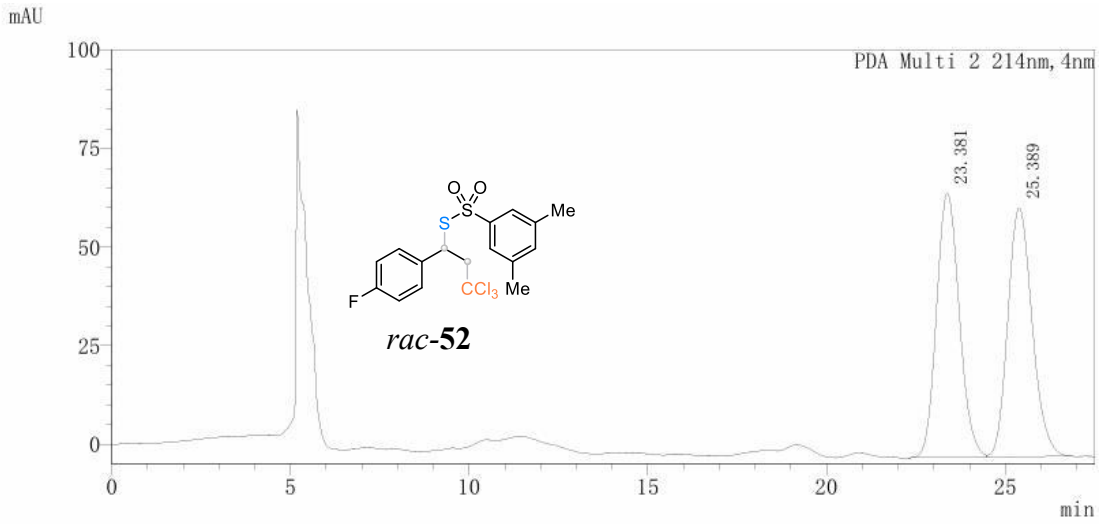
51

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.356	76594480	94.669
2	28.220	4312888	5.331

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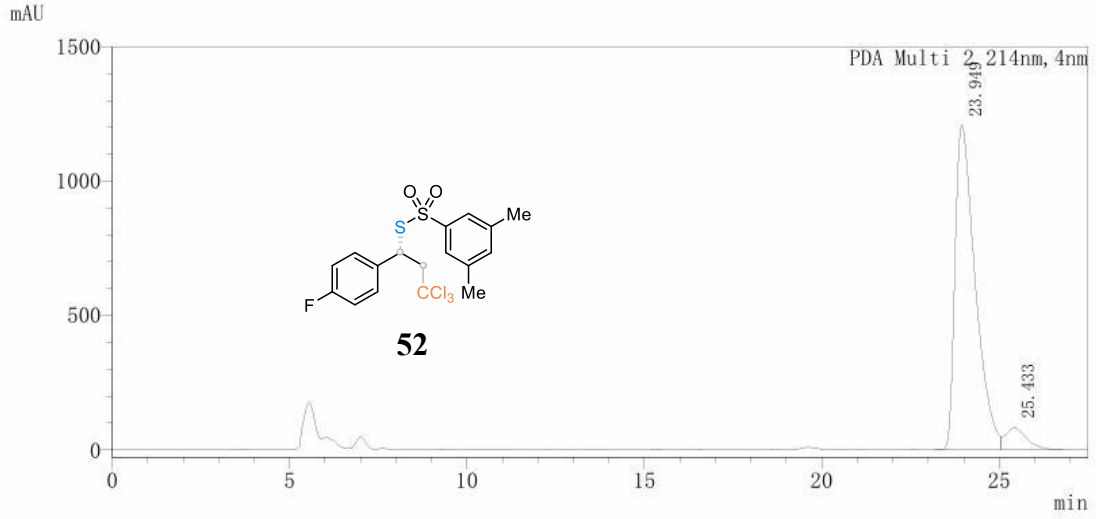


rac-**52**

Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	23.381	2969466	49.801
2	25.389	2993229	50.199



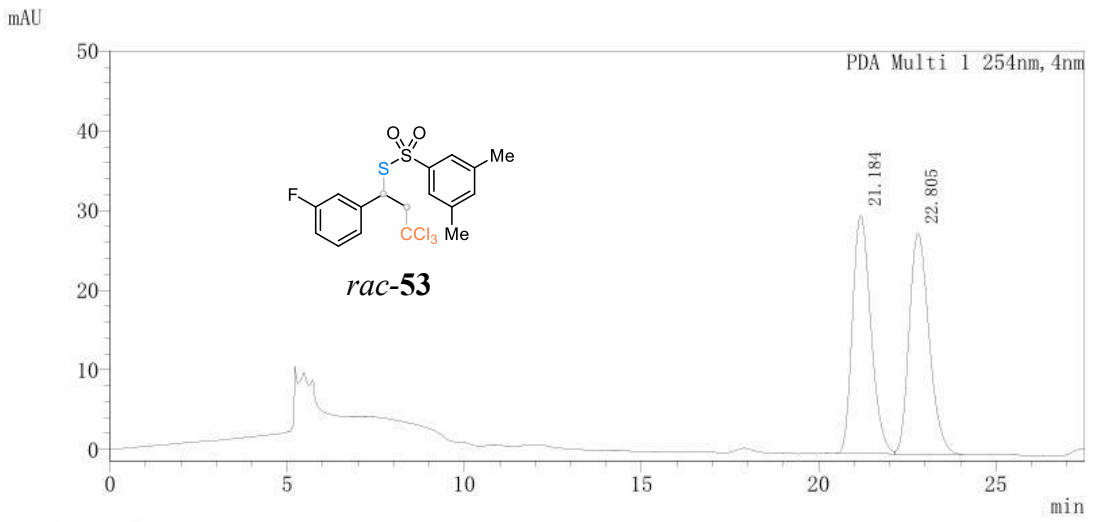
52

Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	23.949	47845233	93.571
2	25.433	3287424	6.429

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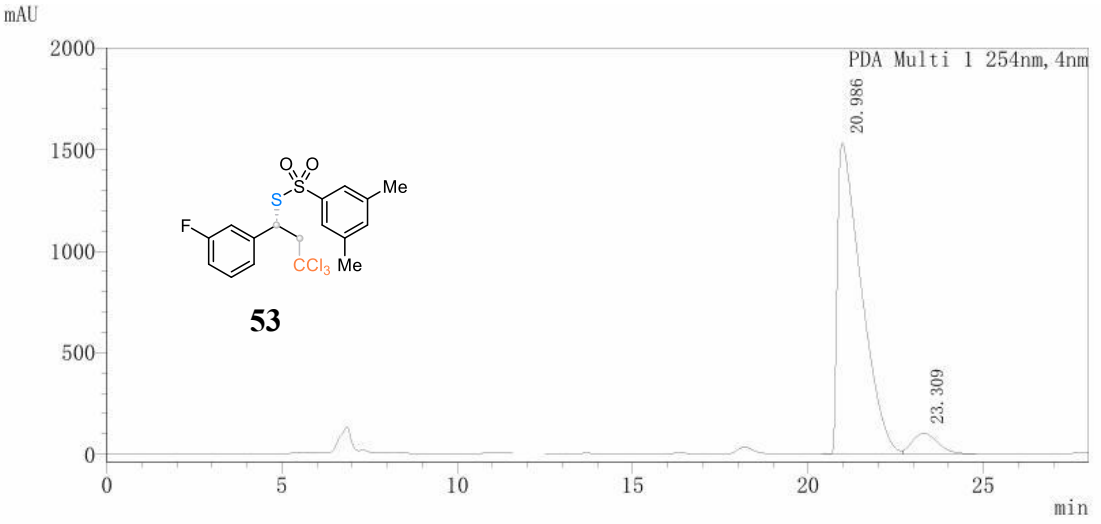


rac-**53**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.184	1079656	49.931
2	22.805	1082640	50.069



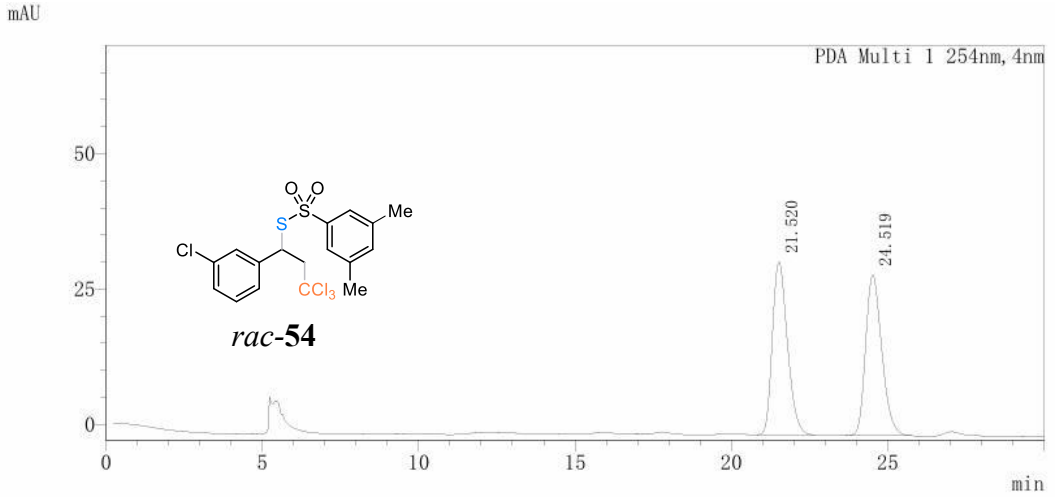
53

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.986	72596640	93.468
2	23.309	5073533	6.532

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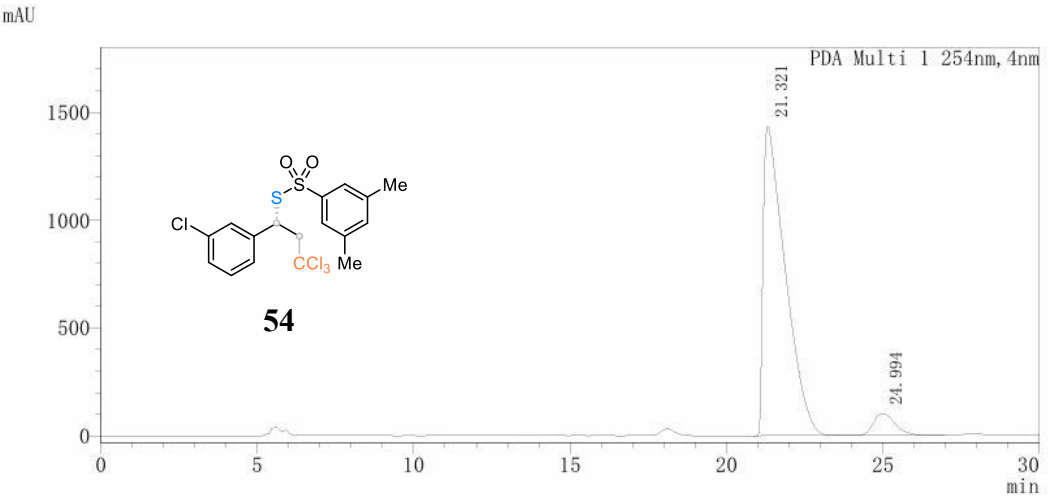


rac-**54**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.520	1066966	50.051
2	24.519	1064802	49.949



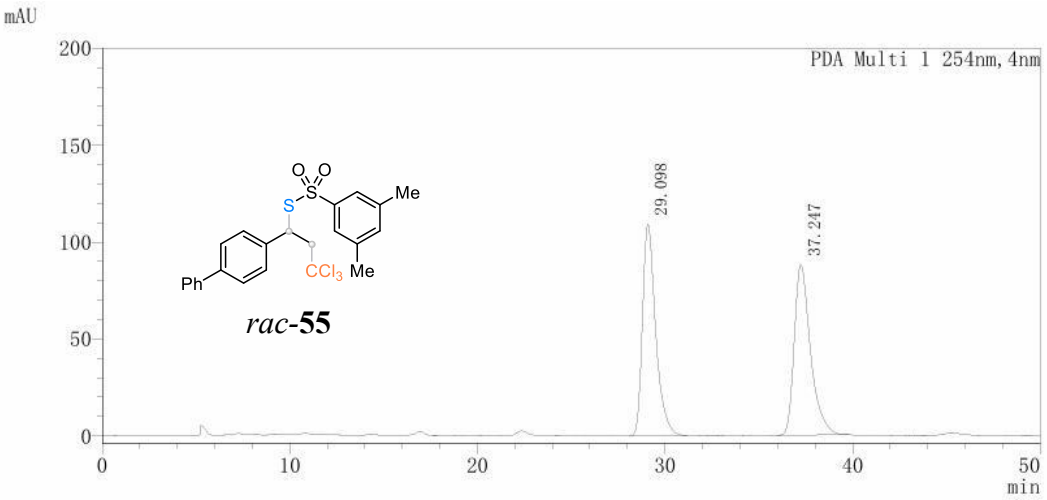
54

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.321	70553067	93.233
2	24.994	5120486	6.767

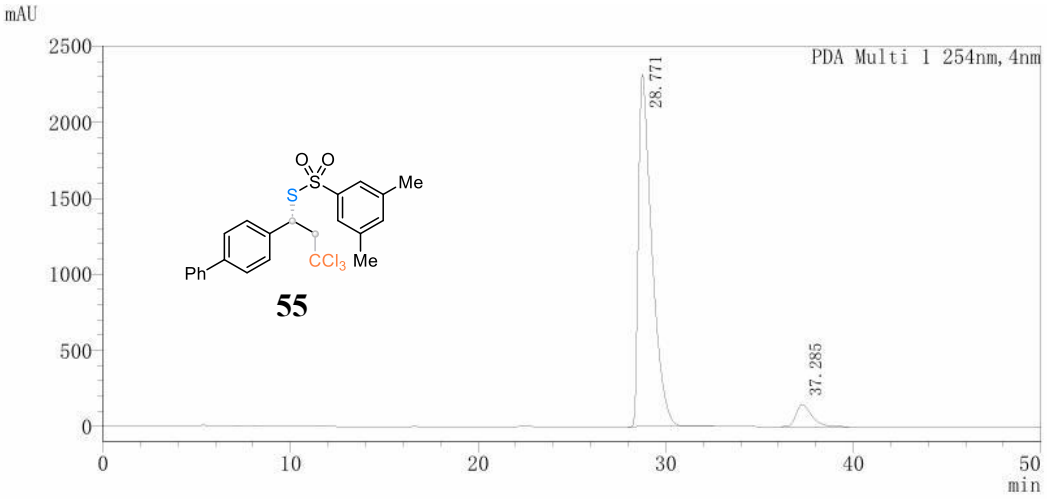
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.098	5318283	50.038
2	37.247	5310255	49.962

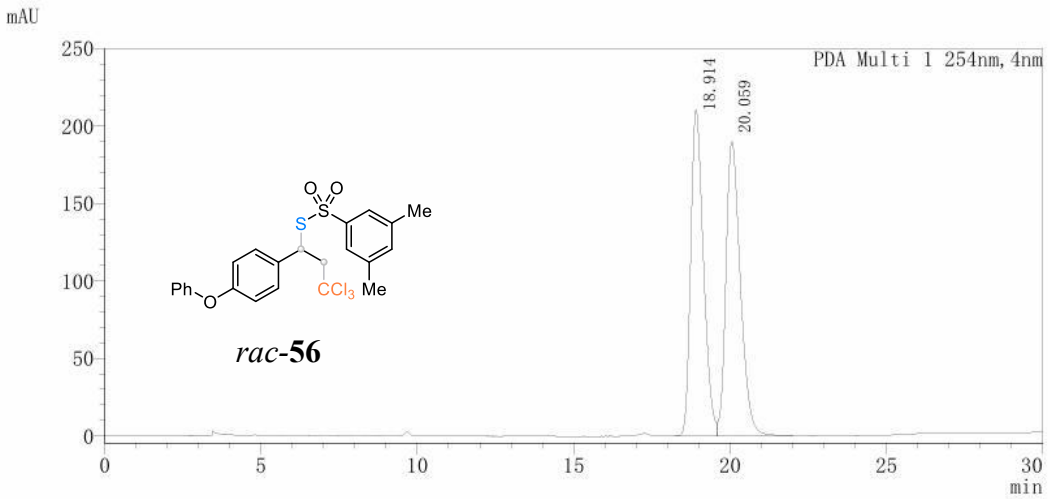


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.771	115536928	93.393
2	37.285	8173638	6.607

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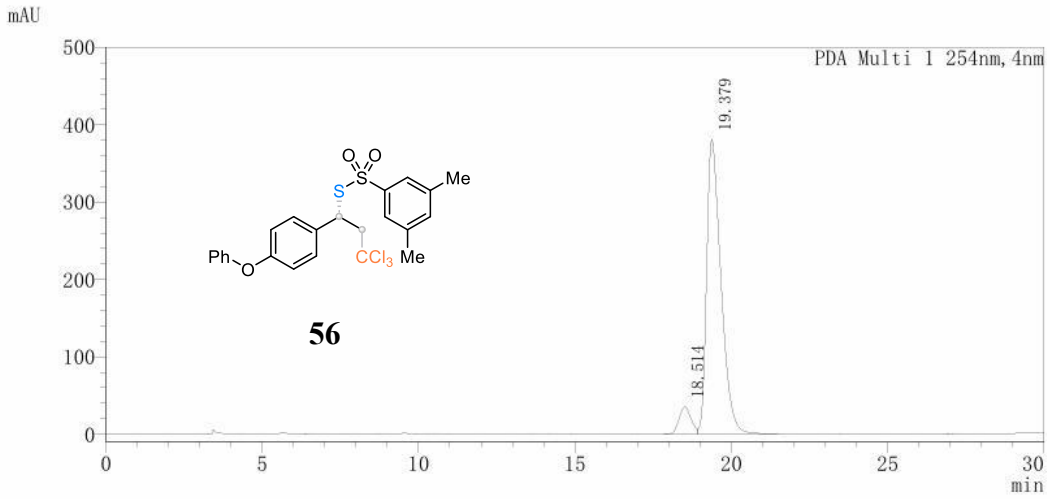


rac-**56**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.914	5974536	49.427
2	20.059	6112967	50.573



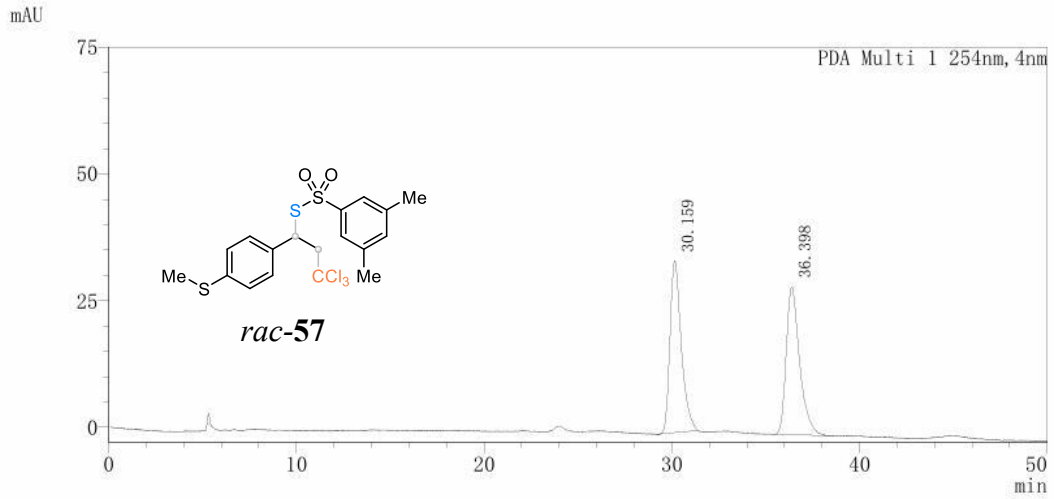
56

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.514	933610	7.168
2	19.379	12090303	92.832

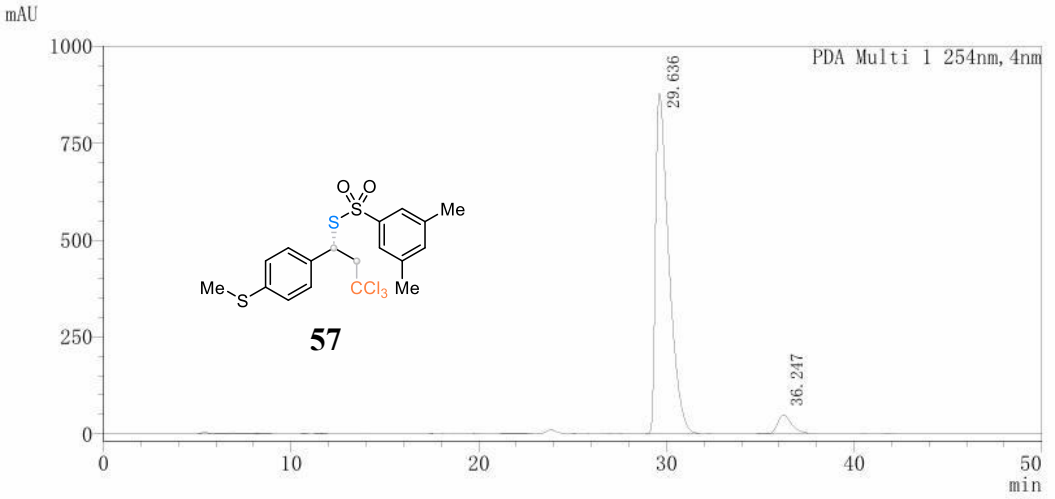
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.159	1415880	49.526
2	36.398	1442956	50.474

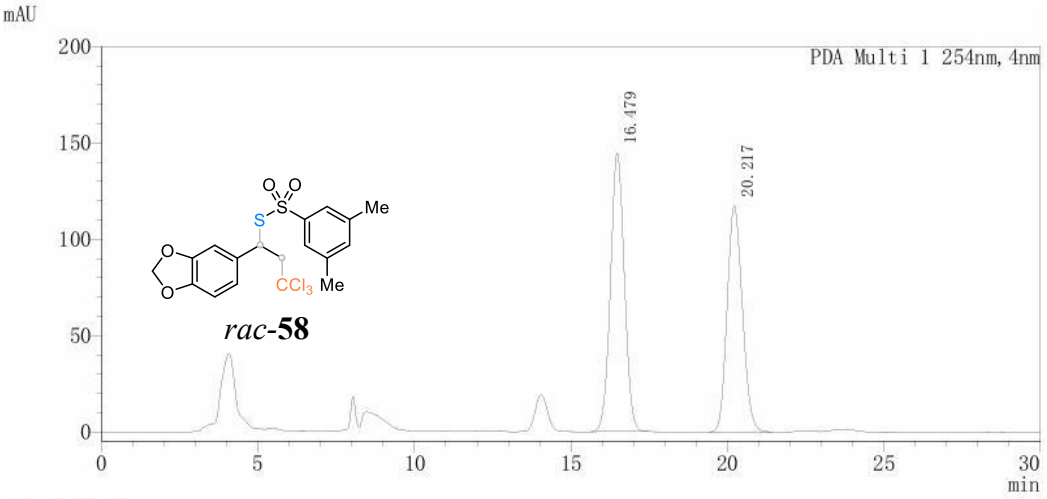


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.636	43180937	94.908
2	36.247	2316918	5.092

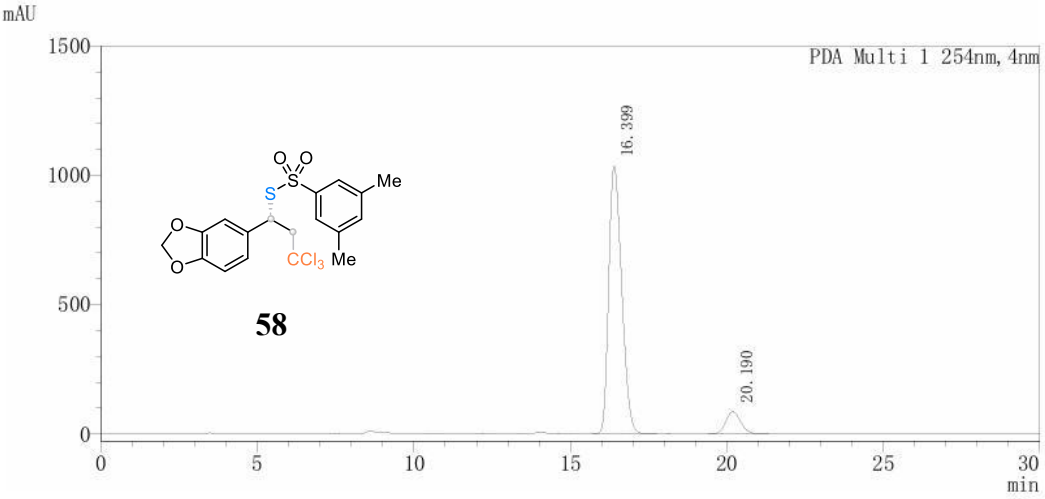
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.479	4477172	53.083
2	20.217	3957133	46.917

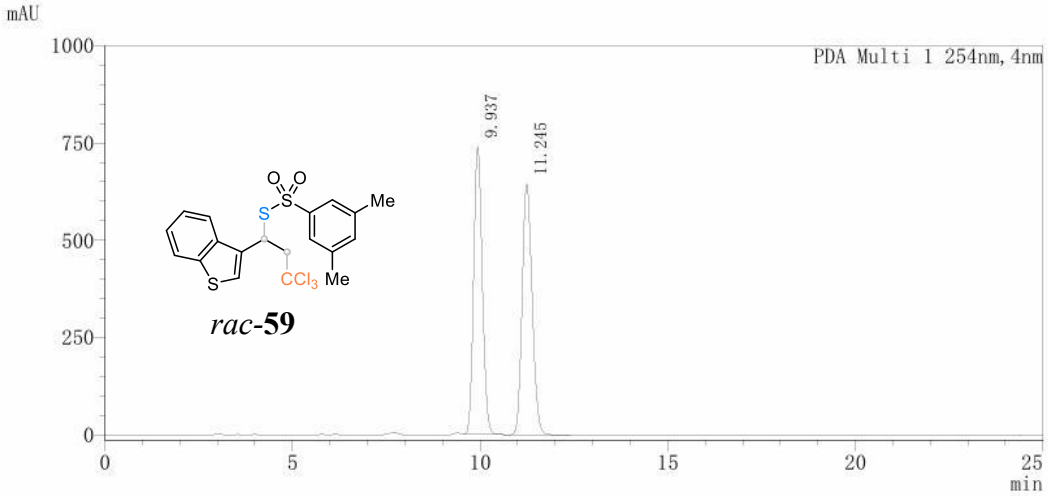


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.399	29799417	91.365
2	20.190	2816501	8.635

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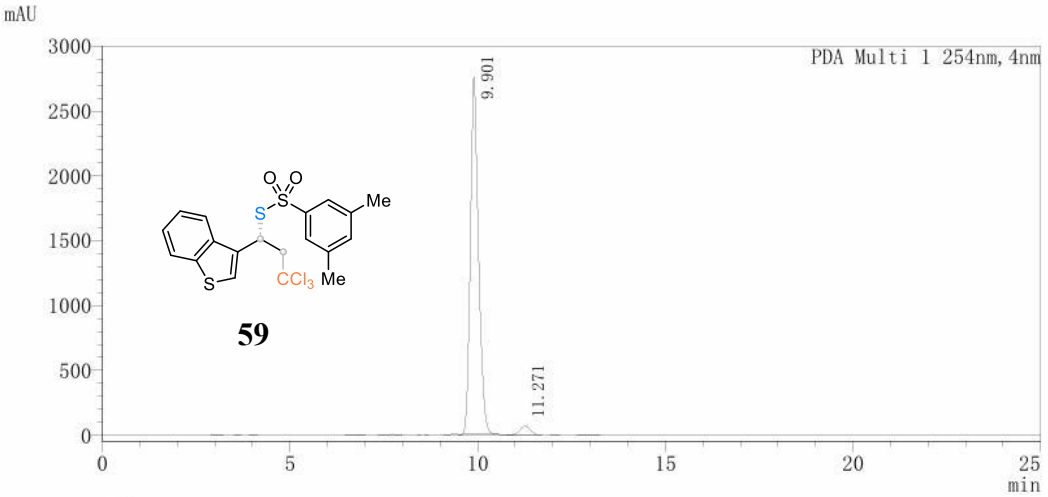


rac-**59**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.937	11896863	49.915
2	11.245	11937418	50.085



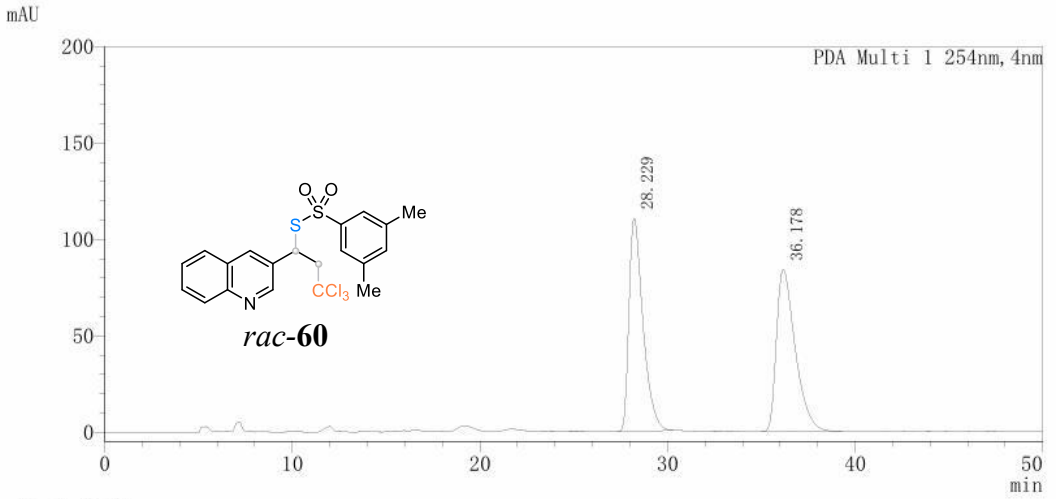
59

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.901	41355512	97.213
2	11.271	1185750	2.787

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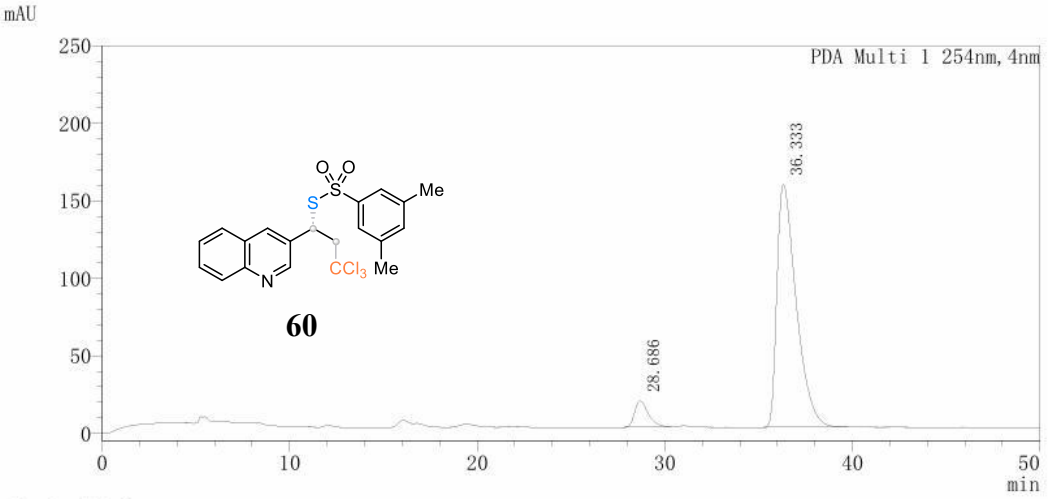


rac-**60**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.229	5747479	49.501
2	36.178	5863260	50.499



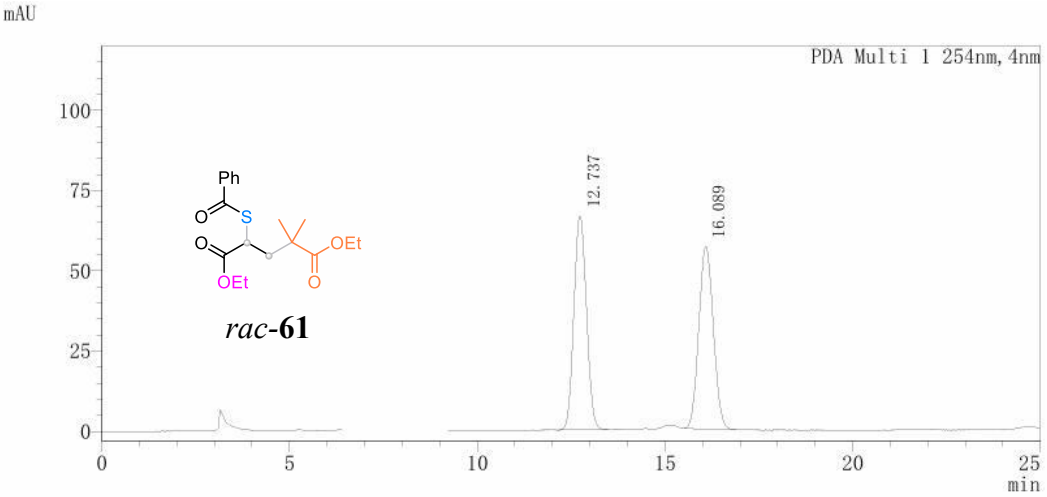
60

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.686	866374	7.185
2	36.333	11191892	92.815

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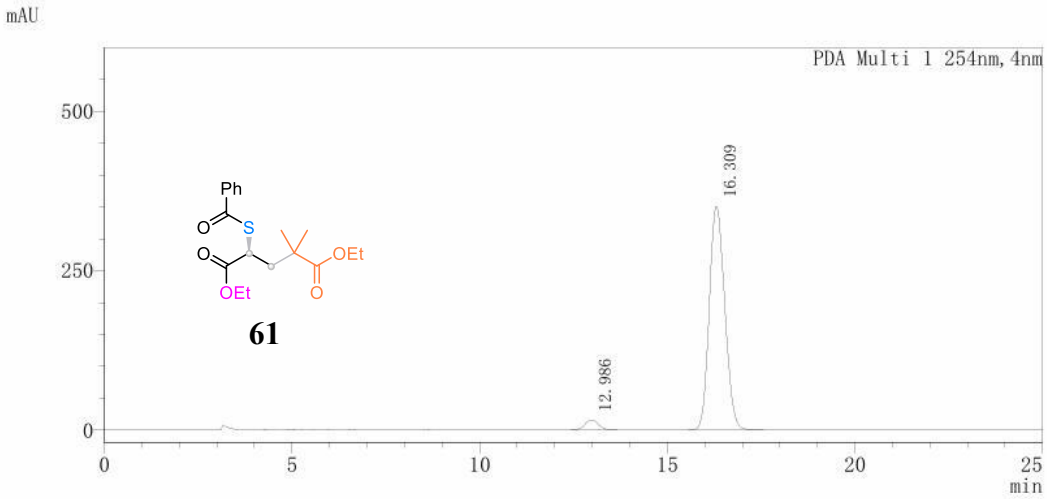


rac-**61**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.737	1549196	50.375
2	16.089	1526140	49.625



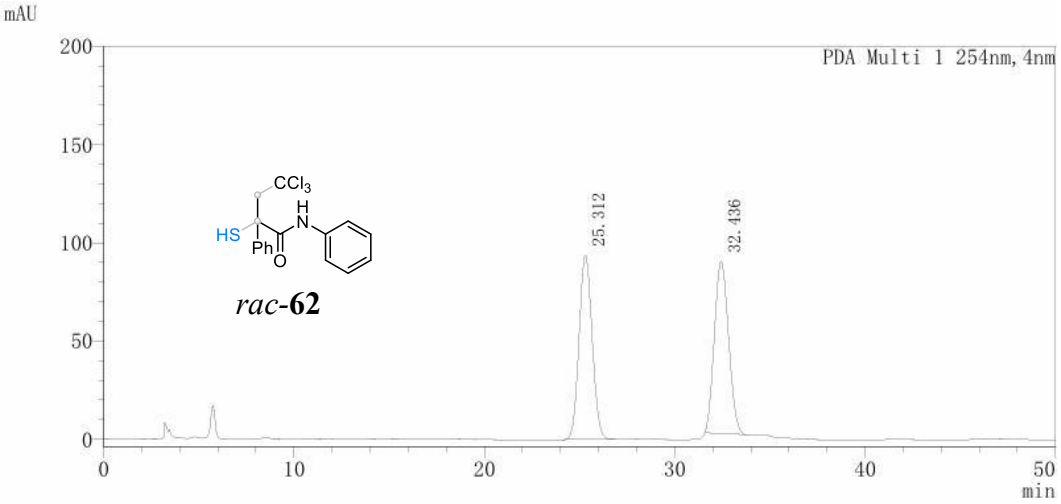
61

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.986	372150	3.588
2	16.309	9999201	96.412

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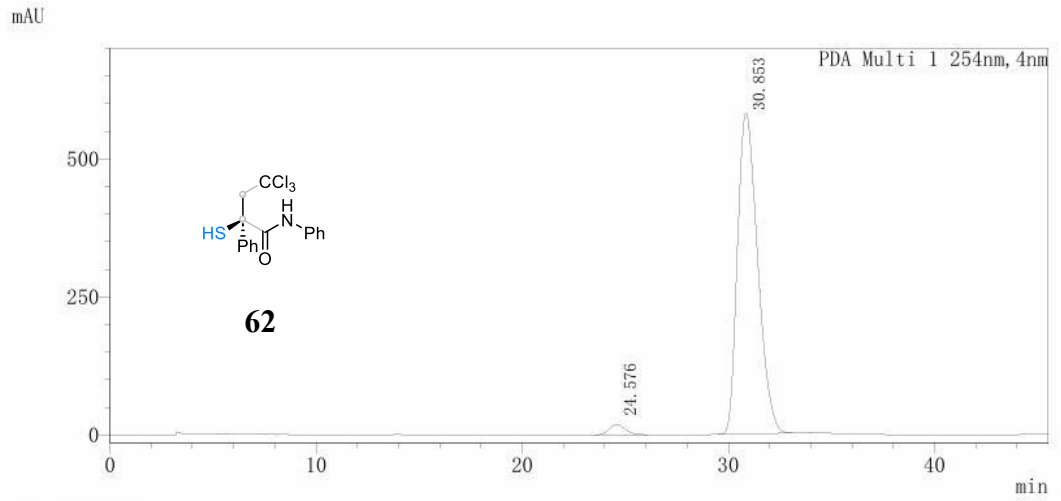


rac-**62**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.312	4487304	49.555
2	32.436	4567965	50.445



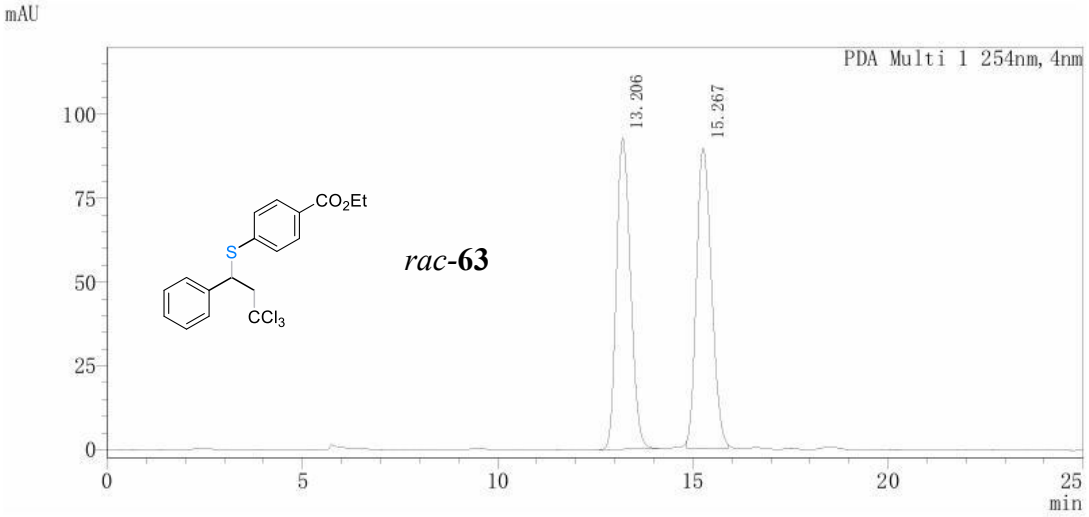
62

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.576	969089	2.394
2	30.853	39513549	97.606

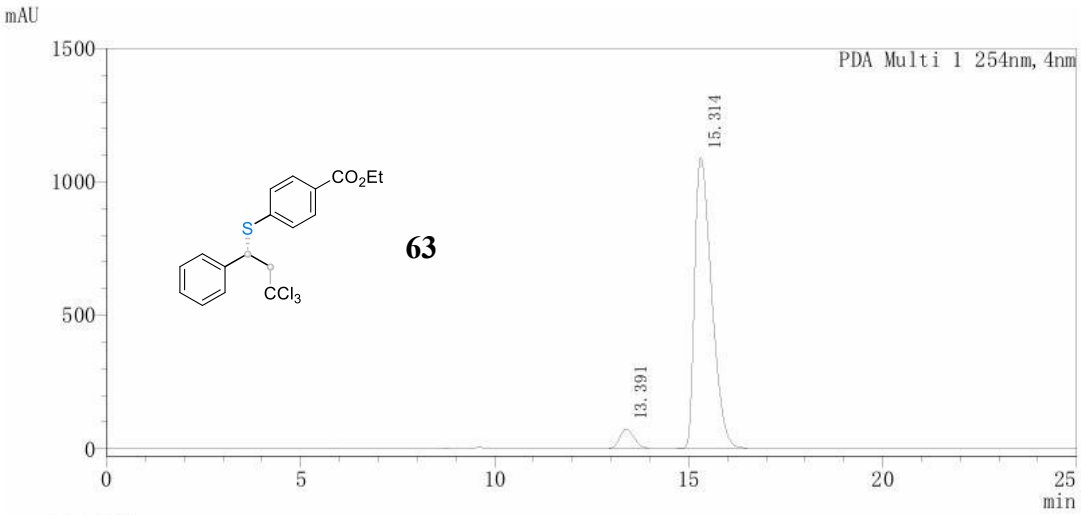
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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.206	2325468	49.098
2	15.267	2410953	50.902

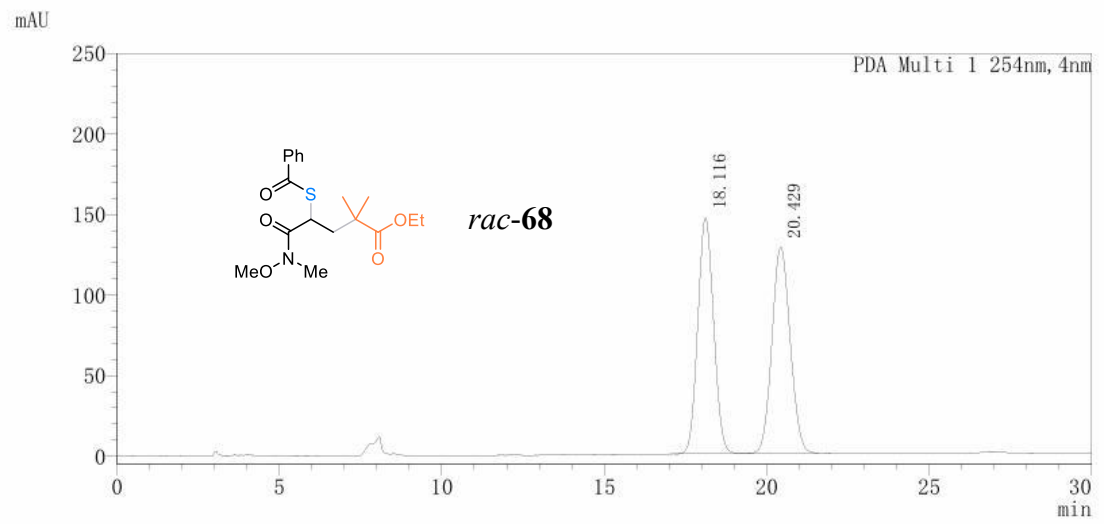


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.391	1843842	5.273
2	15.314	33125756	94.727

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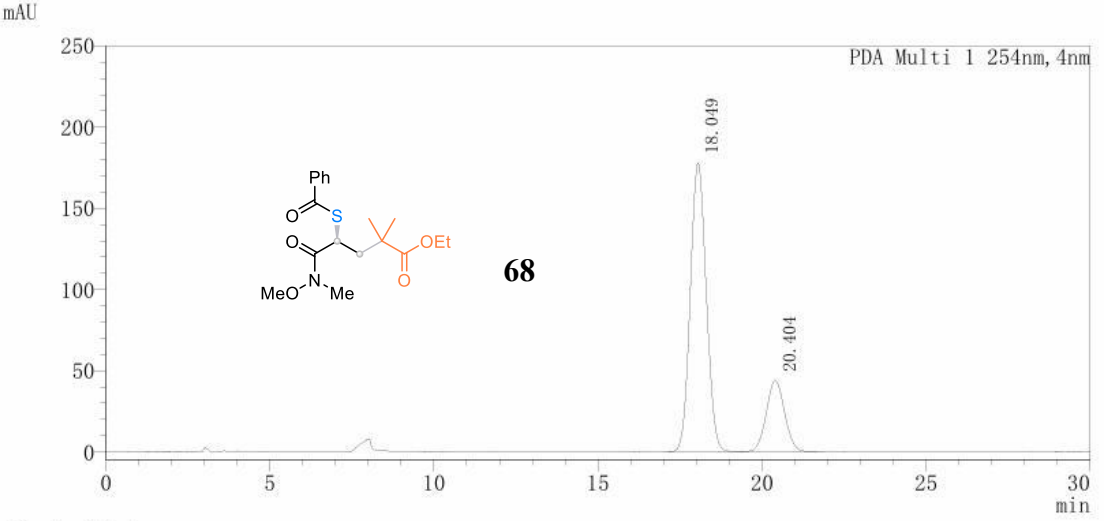


rac-**68**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.116	4976801	49.854
2	20.429	5006001	50.146



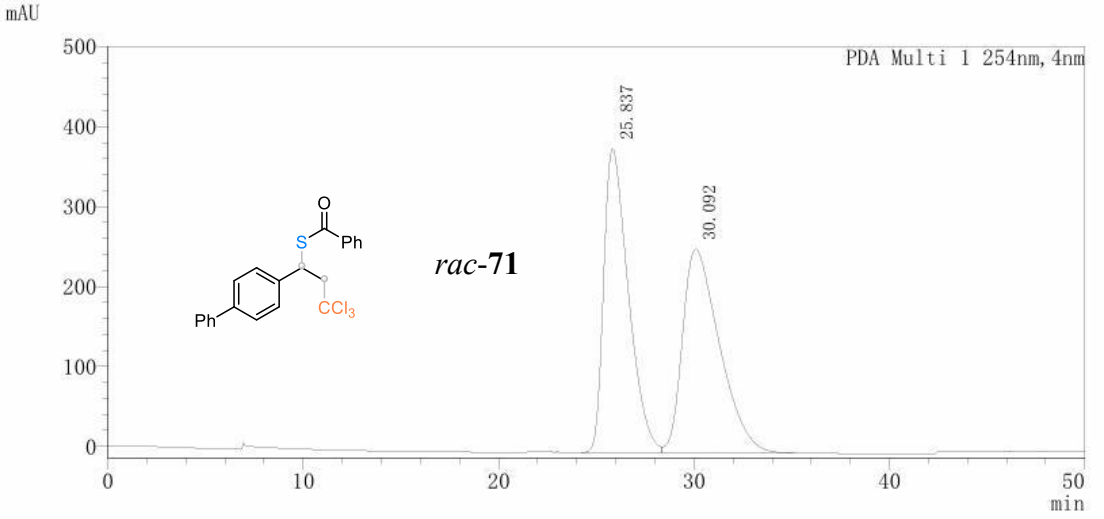
68

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.049	5998874	77.970
2	20.404	1694968	22.030

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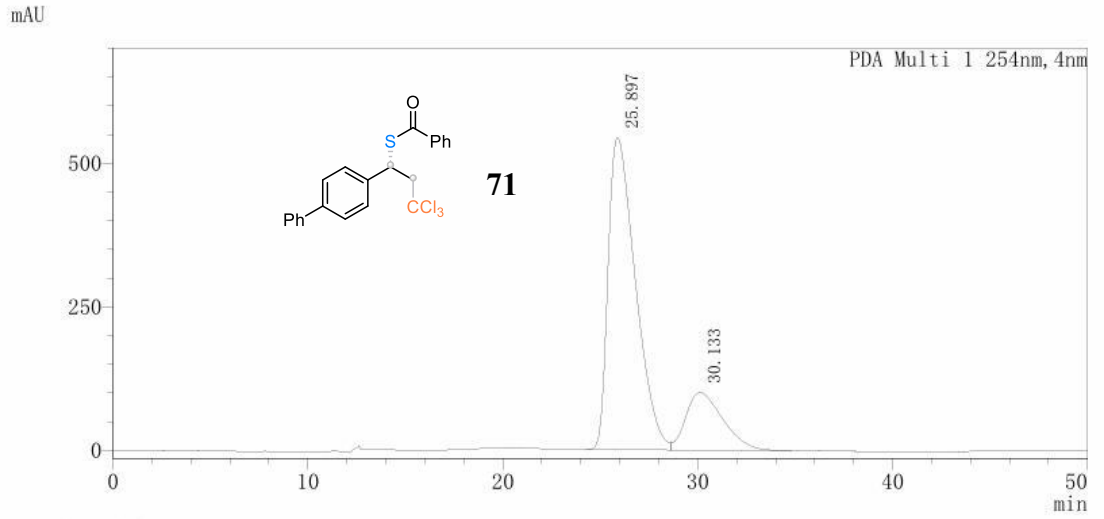


rac-**71**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.837	33343523	49.889
2	30.092	33491431	50.111



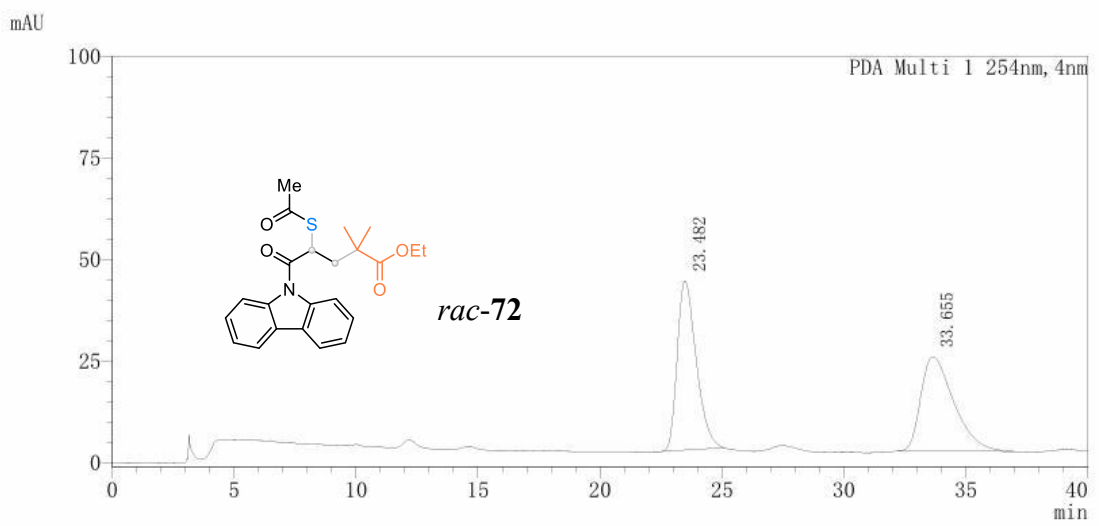
71

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.897	53003739	79.987
2	30.133	13261410	20.013

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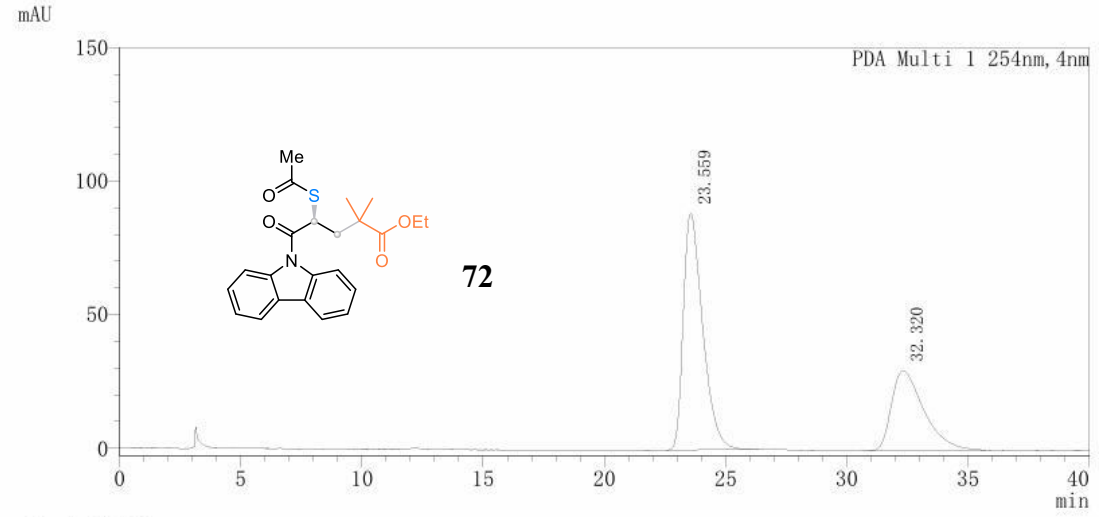


rac-**72**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.482	2257759	50.749
2	33.655	2191098	49.251



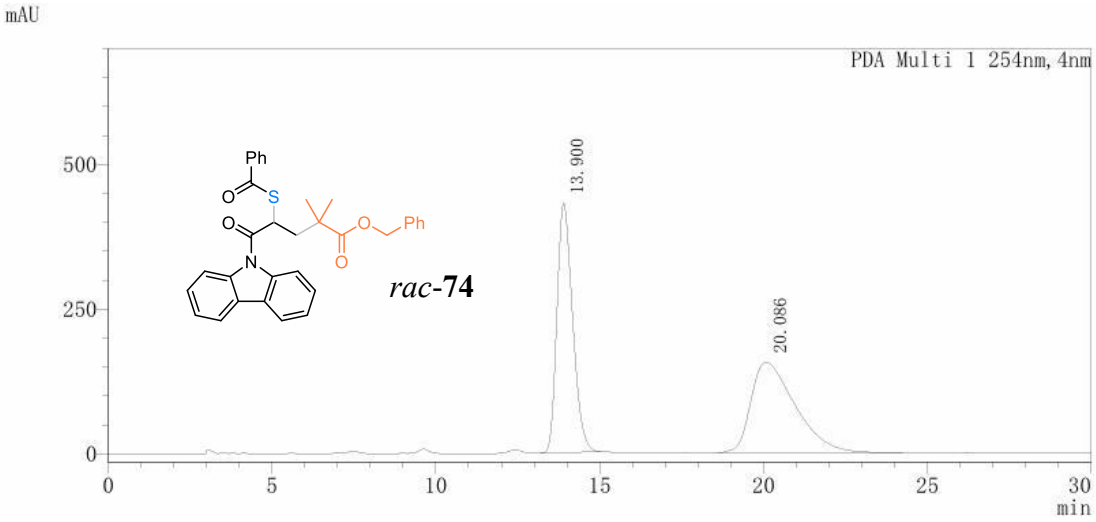
72

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.559	4930982	63.865
2	32.320	2789951	36.135

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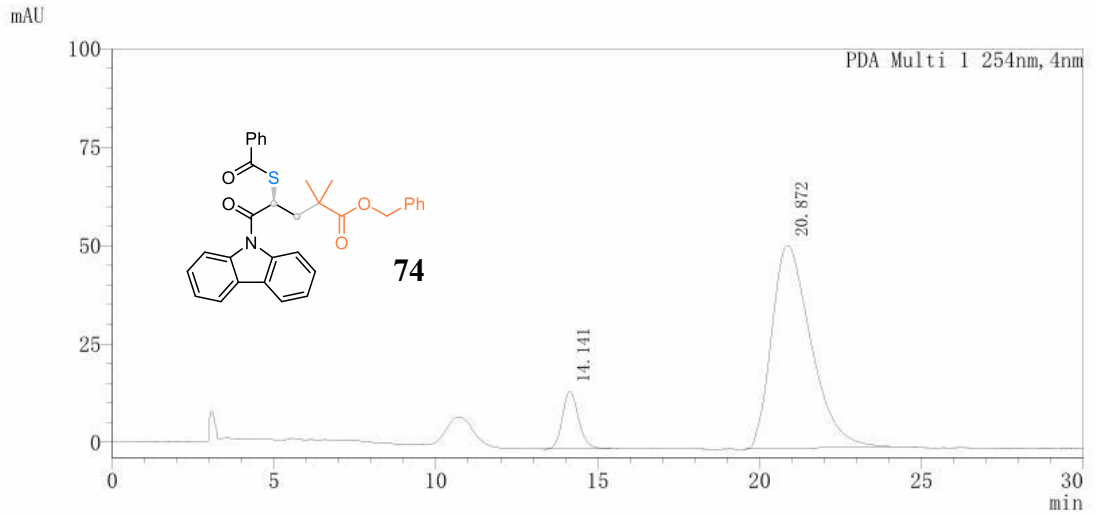


rac-**74**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.900	14309771	49.313
2	20.086	14708710	50.687



74

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.141	505200	10.401
2	20.872	4351949	89.599

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