Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Copper-Catalyzed Enantioconvergent Radical C(sp^3)–N Cross-Coupling: Access to α,α-Disubstituted Amino Acids

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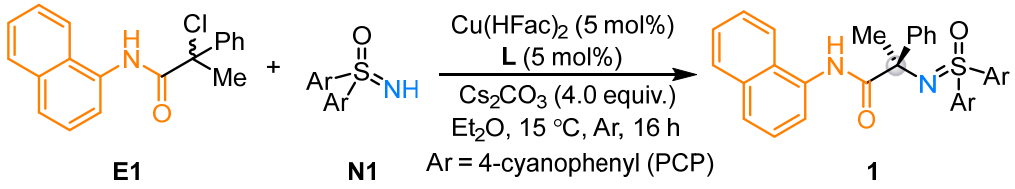
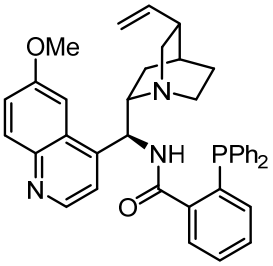
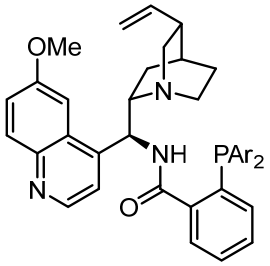


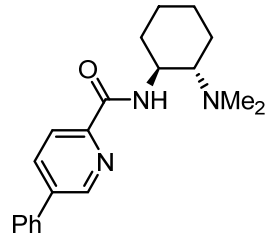
E1 **N1** **1**



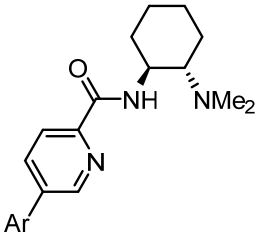
L1, trace



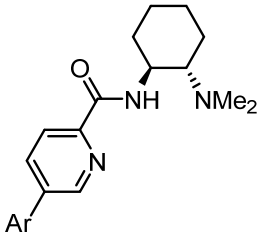
L2, Ar = 3,5-(3,5-$Me_2C_6H_3$)$_2C_6H_3$, trace



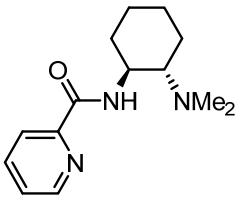
L3, R = Ph, 71%, 71% ee



L4, Ar = 1-naphthyl, 95%, 84% ee



L5, Ar = 9-anthryl, 92%, 92% ee

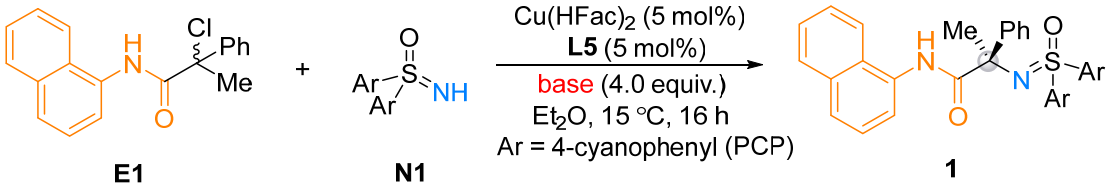


L6, R = H, 60%, 2% ee

[a] Reaction conditions: **E1** (0.05 mmol), **N1** (0.05 mmol), $Cu(HFac)_2$ (5 mol%), **L** (5 mol%) and Cs_2CO_3 (4.0 equiv.) in Et_2O (1.0 mL) at 15 °C for 16 h under argon (Ar). Yields were based on ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Ee values were based on HPLC analysis.

Scheme S1. Effect of ligands in the reaction.[a]

Table S1: Investigation of bases for the model reaction.[a]

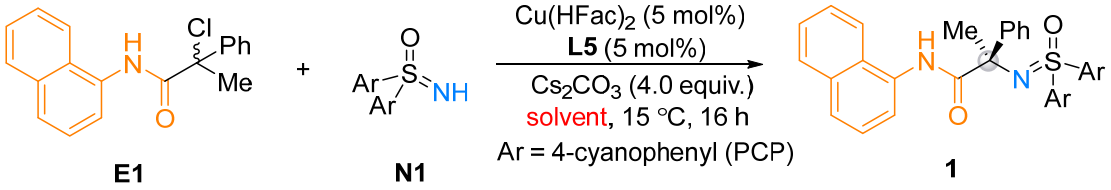


E1 **N1** **1**

Entry	Base	Conv. of **E1**	Yield of **1** [%]	Ee of **1** [%]
1	LiO^{t}Bu	87	78	93
2	NaO^{t}Bu	>99	65	87
3	KO^{t}Bu	>99	0	-
4	Na_2CO_3	0	0	-
5	K_2CO_3	30	28	95
6	Cs_2CO_3	>99	>95	93
7	K_3PO_4	79	73	93
8	LiOH	45	40	93
9	NaOH	55	50	93
10	Et_3N	0	0	-

[a] Reaction conditions: **E1** (0.05 mmol), **N1** (0.05 mmol), $Cu(HFac)_2$ (5 mol %), **L5** (5 mol %), and base (4.0 equiv.) in Et_2O (1.0 mL) at 15 °C for 16 h under argon; yield of **1** was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard; ee was determined by analysis of chiral HPLC measurement. HFac, hexafluoroacetylacetonate; PCP, 4-cyanophenyl.

Table S2: Investigation of solvents for the model reaction.[a]

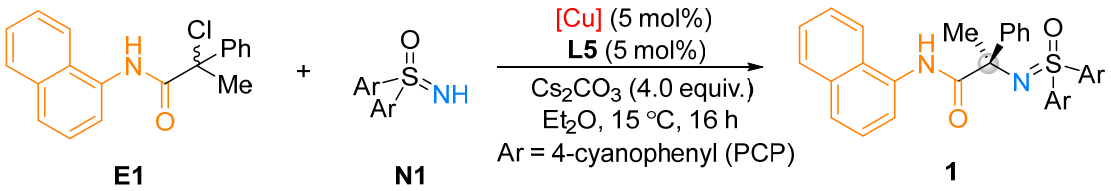


E1 **N1** **1**

Entry	Solvent	Conv. of **E1**	Yield of **1** [%]	Ee of **1** [%]
1	Et_2O	>99	>95	93
2	$^{i}Pr_2O$	42	39	95
3	$^{n}Bu_2O$	42	38	95
4	$PhCF_3$	50	49	89
5	toluene	25	25	91
6	EtOAc	96	87	90
7	THF	82	82	87
8	hexane	trace	0	-
9	DCM	24	24	76
10	DMF	>99	0	-

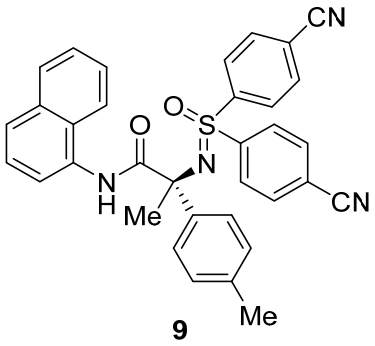
[a] Reaction conditions: **E1** (0.05 mmol), **N1** (0.05 mmol), $Cu(HFac)_2$ (5 mol %), **L5** (5 mol %), and Cs_2CO_3 (4.0 equiv.) in solvent (1.0 mL) at 15 °C for 16 h under argon; yield of **1** was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard; ee was determined by analysis of chiral HPLC measurement. HFac, hexafluoroacetylacetonate. PCP, 4-cyanophenyl. THF, tetrahydrofuran. DCM, dichloromethane; DMF, *N*,*N*-dimethyl formamide.

Table S3: Investigation of copper salts for the model reaction.[a]



Entry	[Cu]	Conv. of **E1**	Yield of **1** [%]	Ee of **1** [%]
1	$Cu(HFac)_2$	>99	>95	93
2	CuI	23	17	93
3	CuBr	45	31	93
4	CuTc	13	13	94
5	$Cu(PPh_3)_3Br$	29	20	60
6	$Cu(CH_3CN)_4PF_6$	10	10	94
7	$Cu(OTf)_2$	45	38	94
8	$Cu(OAc)_2$	37	30	94
9	$Cu(CO_2CF_3)_2$	62	62	94

[a] Reaction conditions: **E1** (0.05 mmol), **N1** (0.05 mmol), Cu (5 mol %), **L5** (5 mol %), and Cs_2CO_3 (4.0 equiv.) in Et_2O (1.0 mL) at 15 °C for 16 h under argon; yield of **1** was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard; ee was determined by analysis of chiral HPLC measurement. PCP, 4-cyanophenyl; HFac, hexafluoroacetylacetonate; Tc, thiophene-2-carboxylate; Tf, triflate.



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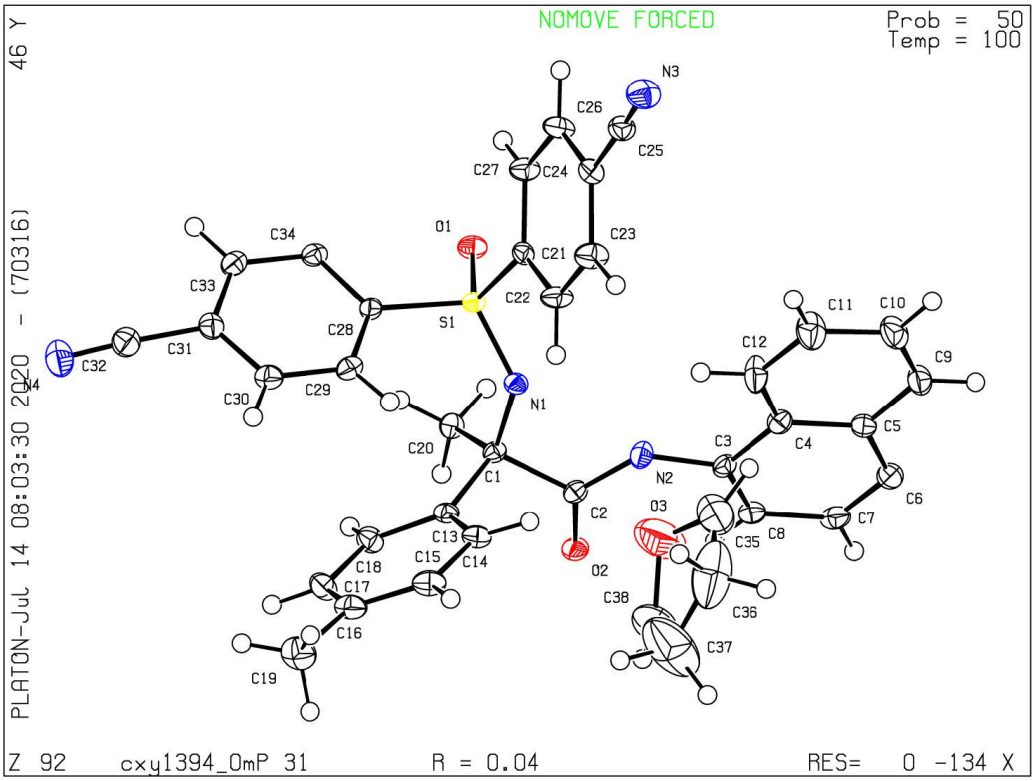


Figure S1. Crystal structure of **9**.

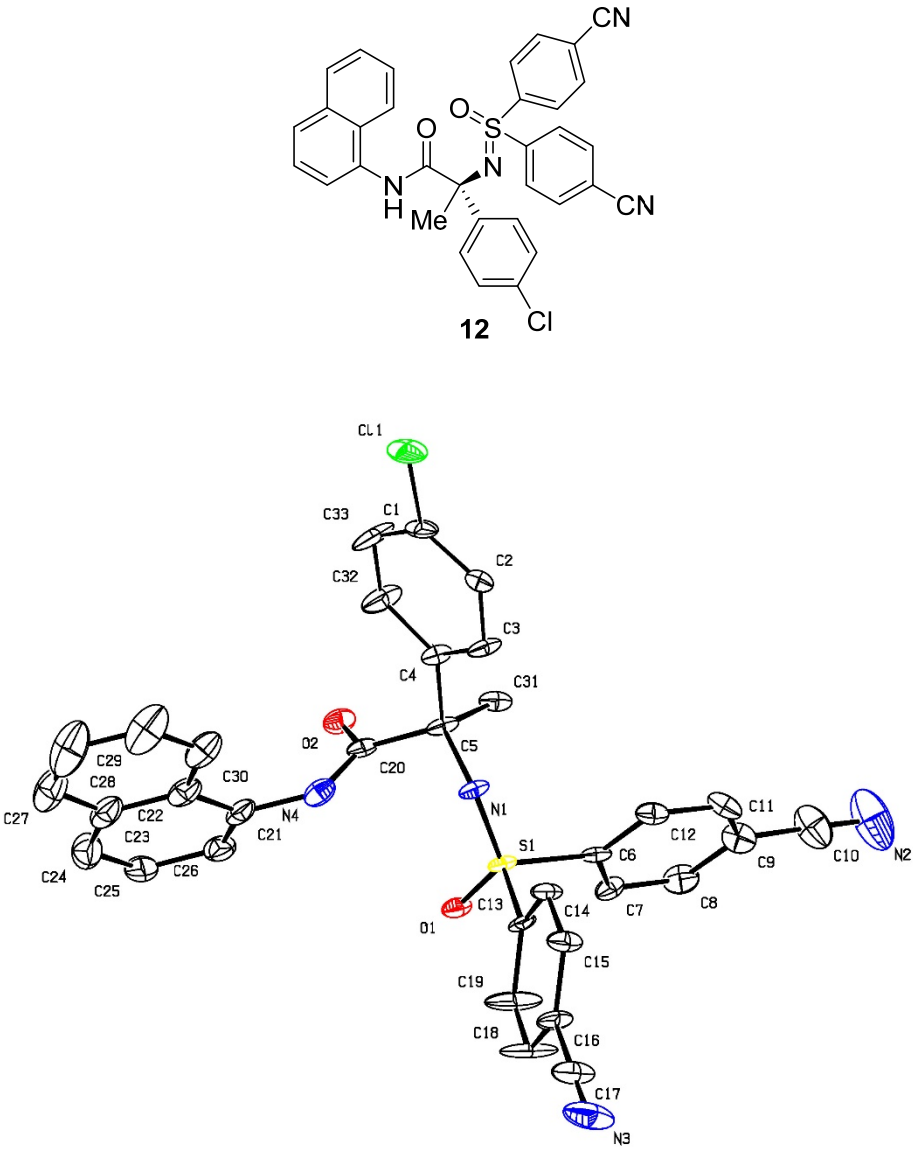
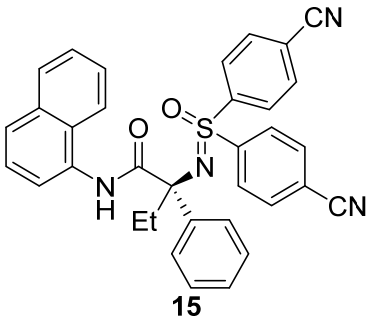


Figure S2. Crystal structure of **12**.



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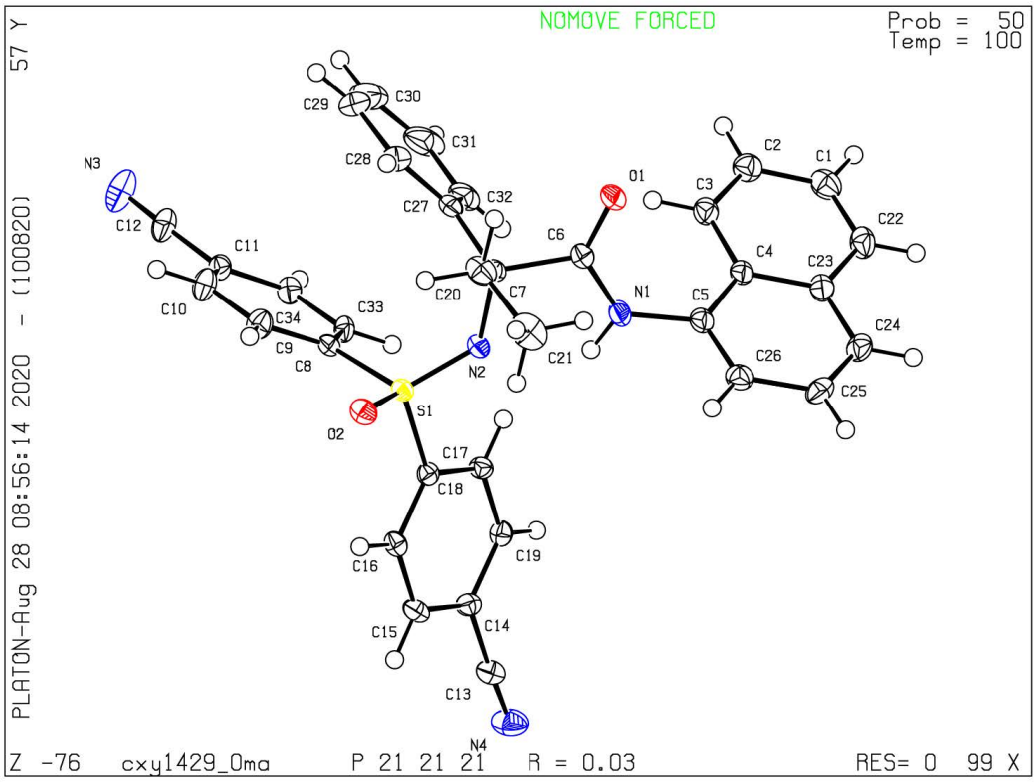


Figure S3. Crystal structure of **15**.

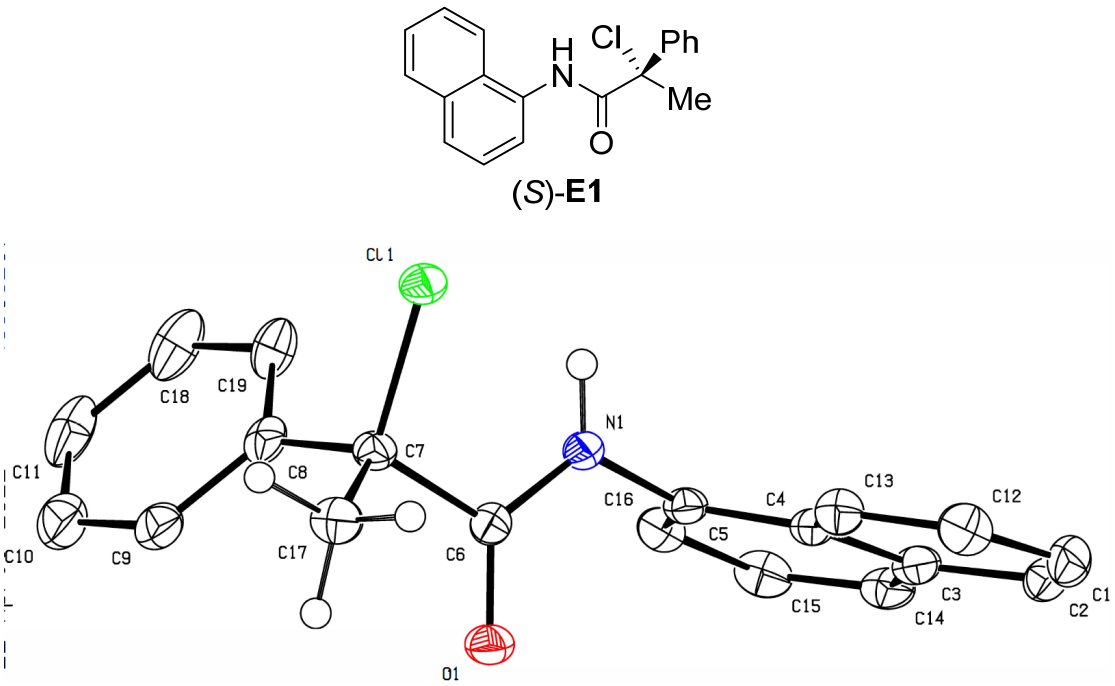


Figure S4. Crystal structure of (*S*)-**E1**.

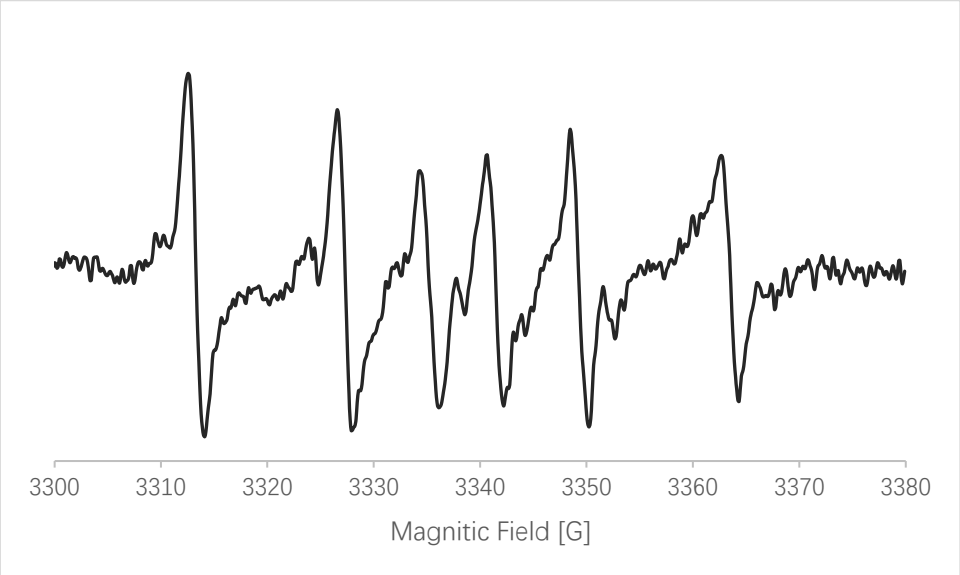


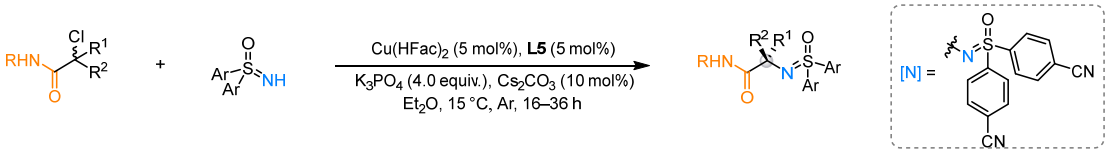
Figure S5. Spin trap study.

Room Temperature Q-band CW-EPR spectra of the spin trap study. g = 2.0061; A_H = 22.00 G; A_N = 14.11 G. EPR acquisition parameters: temperature = 298 K; MW power = 40 dB; modulation amplitude = 0.5 G. conversion time = 20 ms.

General information

Most of 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. CH_2Cl_2, THF and DMF were purified and dried using a solvent-purification system that contained activated alumina under argon. Copper(II) hexafluoroacetylacetonate ($Cu(HFac)_2$, CAS No. 14781-45-4) was purchased from TCI. K_3PO_4 was purchased from Shanghai Titan Scientific Co. Ltd. and Cs_2CO_3 was purchased from Leyan., both of them were treated by hot gun (approximate 500 to 600 °C) for 5 minutes in vacuum. Anhydrous diethyl ether (Et_2O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was treated by 4 Å Molecular sieve and distilled after refluxing with sodium and benzophenone. 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), hexane, ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2) 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 on silica gel or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^1H NMR, 100 or 150 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR and 162 MHz or 243 MHz for ^{31}P NMR, respectively, in $CDCl_3$, CD_3OD, C_6D_6, D_2O or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) value was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength) or SHIMADZU LC-20AD with SPD-20AV detector. Column conditions are reported in the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation. Q-band continuous-wave (CW) EPR spectra was recorded on a Bruker ELEXSYS-II spectrometer at room temperature.

Asymmetric cross-coupling of tertiary halides



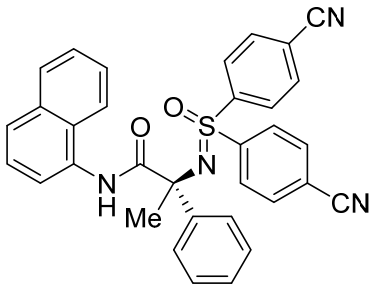
General procedure A: Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 4,4'-sulfonimidoyldibenzonitrile (53.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(HFac)_2$ (4.4 mg, 0.010 mmol, 5.0 mol%), **L5** (4.3 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (6.5 mg, 0.020 mmol, 10.0 mol%), K_3PO_4 (169.6 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). Then, tertiary halide (0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 16 to 36 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure B: Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 4,4'-sulfonimidoyldibenzonitrile (53.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(HFac)_2$ (4.4 mg, 0.010 mmol, 5.0 mol%), **L5** (4.3 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous $^iPr_2O$ (2.0 mL). Then, tertiary halide (0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 36 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

The synthesis of tertiary alkyl halides

All the tertiary alkyl halides were synthesized according to the reported literature.[1] All the characterization data are consistent with those in the reported literature.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-phenylpropanamide (1)



1

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide (61.8 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **1** as a white amorphous solid (99.4 mg, 92% yield, 92% ee).

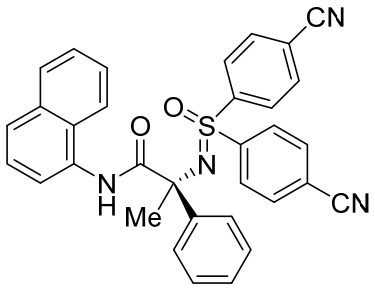
HPLC analysis: Chiralcel IE (hexane/*i*-PrOH = 40/60, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 26.19 min, t_R (minor) = 41.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.22 – 8.16 (m, 3H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.75 – 7.65 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.46 (m, 4H), 7.44 – 7.34 (m, 1H), 7.31 – 7.18 (m, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 145.9, 145.6, 143.2, 134.1, 133.3, 132.9, 132.3, 129.1, 128.8, 128.50, 128.47, 127.8, 126.5, 126.23, 126.15, 126.1, 125.9, 125.1, 119.8, 118.5, 117.1, 117.04, 116.97, 116.4, 67.4, 26.4.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{25}N_4O_2S$ $[M + H]^+$ 541.1693, found 541.1695.

(*S*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-phenylpropanamide (ent-1)

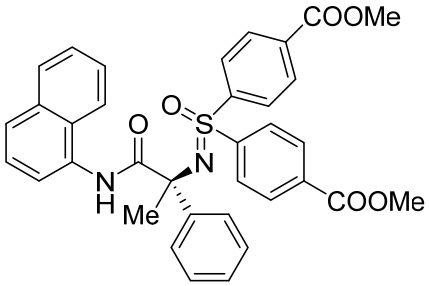


ent-1

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide (61.8 mg, 0.20 mmol, 1.0 equiv.) and (*R*, *R*)-**L$_5$** for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **ent-1** as a white amorphous solid (98.3 mg, 91% yield, –92% ee).

HPLC analysis: Chiralcel IE (hexane/*i*-PrOH = 40/60, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 28.55 min, t_R (major) = 45.47 min.

Dimethyl 4,4'-((1-(naphthalen-1-ylamino)-1-oxo-2-phenylpropan-2-yl)sulfonimidoyl)(*R*)-dibenzoate (2)



2

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide (61.8 mg, 0.20 mmol, 1.0 equiv.) and dimethyl 4,4'-sulfonimidoyldibenzoate (66.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **2** as a light yellow amorphous solid (99.4 mg, 82% yield, 88% ee).

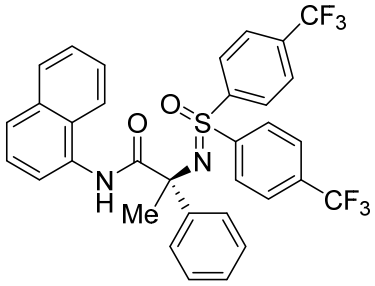
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.33 min, t_R (minor) = 21.80 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.31 – 8.25 (m, 1H), 8.23 – 8.14 (m, 4H), 8.02 – 7.92 (m, 2H), 7.90 – 7.85 (m, 1H), 7.83 – 7.73 (m, 3H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.45 (m, 2H), 7.39 – 7.33 (m, 1H), 7.29 – 7.17 (m, 3H), 3.98 (s, 3H), 3.94 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 165.5, 165.4, 146.3, 145.9, 143.8, 134.2, 134.0, 133.6, 132.6, 130.6, 130.2, 128.9, 128.3, 128.2, 127.9, 127.5, 126.4, 126.2, 126.08, 126.07, 125.8, 124.7, 120.0, 118.1, 67.1, 52.8, 52.7, 26.0.

HRMS (ESI) *m/z* calcd. for $C_{35}H_{31}N_2O_6S$ $[M + H]^+$ 607.1897, found 607.1892.

(*R*)-*N*-(Naphthalen-1-yl)-2-((oxobis(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)amino)-2-phenylpropanamide (3)



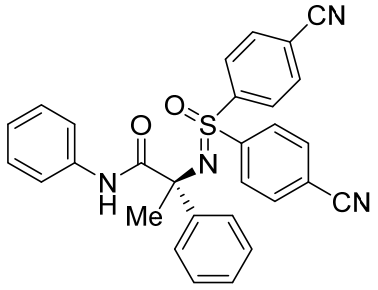
3

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide (61.8 mg, 0.20 mmol, 1.0 equiv.) and iminobis(4-(trifluoromethyl)phenyl)-λ^6-sulfanone (70.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **3** as a light yellow amorphous solid (108.9 mg, 87% yield, 88% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.70 min, t_R (major) = 13.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.40 – 8.10 (m, 3H), 7.93 – 7.73 (m, 6H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.46 (m, 6H), 7.39 – 7.33 (m, 1H), 7.28 – 7.16 (m, 3H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 145.7, 145.1, 143.4, 134.9 (d, *J* = 33.2 Hz), 134.2 (d, *J* = 34.2 Hz), 134.1, 132.5, 129.0, 128.7, 128.42, 128.35, 127.6, 126.7 (q, *J* = 3.7 Hz), 126.4, 126.3 (q, *J* = 3.7 Hz), 126.2, 126.1, 126.0, 125.9, 124.9, 123.09 (q, *J* = 272.9 Hz), 123.06 (q, *J* = 272.9 Hz), 119.9, 118.2, 67.3, 26.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.12, -63.25.
HRMS (ESI) *m/z* calcd. for $C_{33}H_{25}F_6N_2O_2S$ $[M + H]^+$ 627.1535, found 627.1530.

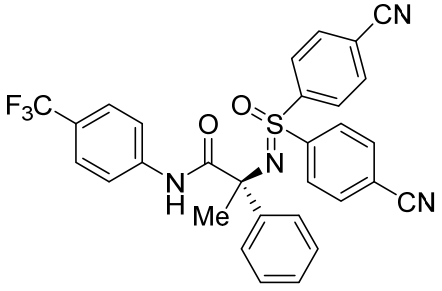
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*,2-diphenylpropanamide (4)



4

According to **General procedure A** with 2-chloro-*N*,2-diphenylpropanamide (51.8 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **4** as a white amorphous solid (64.7 mg, 66% yield, 77% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.11 min, t_R (minor) = 15.71 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.13 – 8.07 (m, 3H), 7.85 – 7.78 (m, 2H), 7.74 – 7.68 (m, 2H), 7.62 – 7.50 (m, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.30 (m, 2H), 7.25 – 7.18 (m, 3H), 7.22 – 7.10 (m, 1H), 1.98 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 145.8, 145.5, 143.2, 137.6, 133.3, 132.8, 129.1, 128.7, 128.44, 128.39, 127.7, 126.4, 124.5, 119.5, 117.03, 116.97, 116.4, 67.0, 26.5.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{23}N_4O_2S$ $[M + H]^+$ 491.1536, found 491.1532.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-phenyl-*N*-(4-(trifluoromethyl)phenyl)propenamide (5)



5

According to **General procedure A** with 2-chloro-2-phenyl-*N*-(4-

(trifluoromethyl)phenyl)propanamide (65.4 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **5** as a white amorphous solid (96.0 mg, 86% yield, 54% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 15.77 min, t_R (minor) = 28.07 min.

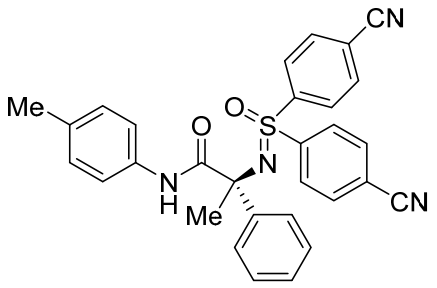
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.15 – 8.07 (m, 2H), 7.87 – 7.81 (m, 2H), 7.75 – 7.63 (m, 4H), 7.63 – 7.52 (m, 4H), 7.45 – 7.38 (m, 2H), 7.26 – 7.20 (m, 3H), 1.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 145. 6, 145.4, 142.9, 140.6, 133.3, 132.9, 128.8, 128.5, 128.4, 127.9, 126.31, 126.29 (m), 126.1 (q, J = 21.7 Hz), 124.1 (q, J = 271.6 Hz), 119.2, 117.2, 116.9 (d, J = 5.8 Hz), 116.5, 67.0, 26.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.06.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{22}F_3N_4O_2S$ $[M + H]^+$ 559.1410, found 559.1407.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-phenyl-*N*-(*p*-tolyl)propenamide (6)



6

According to **General procedure A** with 2-chloro-2-phenyl-*N*-(*p*-tolyl)propanamide (54.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **6** as a white amorphous solid (61.5 mg, 61% yield, 84% ee).

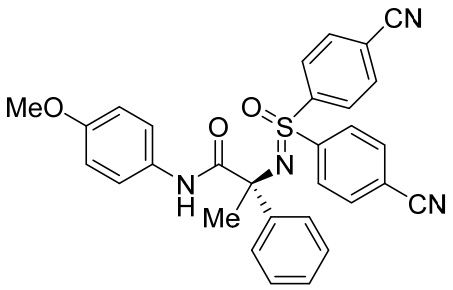
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.08 min, t_R (minor) = 41.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.10 – 8.03 (m, 2H), 7.81 – 7.75 (m, 2H), 7.72 – 7.65 (m, 2H), 7.58 – 7.51 (m, 2H), 7.43 – 7.36 (m, 4H), 7.21 – 7.14 (m, 3H), 7.11 (d, J = 8.2 Hz, 2H), 2.31 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 145.8, 145.5, 143.2, 135.1, 134.1, 133.3, 132.8, 129.5, 128.7, 128.5, 128.4, 127.7, 126.4, 119.5, 117.0, 116.3, 66.9, 26.6, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{25}N_4O_2S$ $[M + H]^+$ 505.1693, found 505.1688.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfanylidene)amino)-*N*-(4-methoxyphenyl)-2-phenylpropanamide (7)



7

According to **General procedure A** with 2-chloro-*N*-(4-methoxyphenyl)-2-phenylpropanamide (57.8 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **7** as a white amorphous solid (79.0 mg, 76% yield, 95% ee).

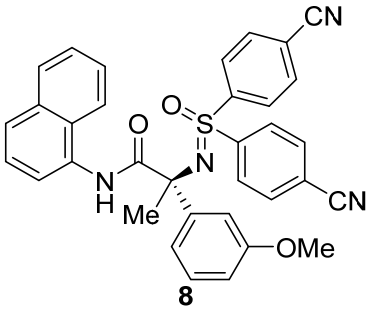
HPLC analysis: Chiralcel IF (hexane/*i*-PrOH = 30/70, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 23.59 min, t_R (minor) = 45.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.24 – 7.18 (m, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 156.5, 145.8, 145.5, 143.2, 133.3, 132.8, 130.8, 128.8, 128.5, 128.4, 127.7, 126.4, 121.2, 117.1, 117.0, 116.3, 114.2, 66.9, 55.5, 26.5.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{25}N_4O_3S$ $[M + H]^+$ 521.1642, found 521.1646.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(3-methoxyphenyl)-*N*-(naphthalen-1-yl)propenamide (8)



8

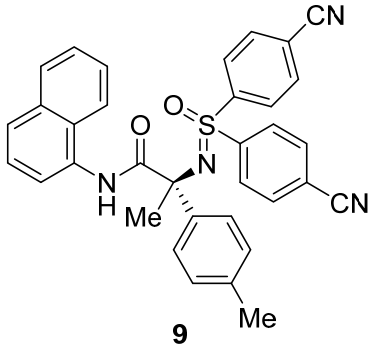
According to **General procedure A** with 2-chloro-2-(3-methoxyphenyl)-*N*-(naphthalen-1-yl)propanamide (67.8 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 30/1) to yield the product **8** as an amorphous solid (92.3 mg, 81% yield, 90% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.81 min, t_R (major) = 15.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.27 – 8.09 (m, 3H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 12.9, 8.5 Hz, 4H), 7.75 – 7.71 (m, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.45 (m, 2H), 7.40 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.22 – 7.09 (m, 2H), 6.99 (t, *J* = 2.1 Hz, 1H), 6.73 (ddd, *J* = 7.9, 2.5, 1.1 Hz, 1H), 3.76 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 159.5, 145.8, 145.5, 144.5, 134.1, 133.2, 132.8, 132.3, 129.6, 129.1, 128.8, 128.5, 126.3, 126.2, 126.1, 125.9, 125.1, 119.8, 119.0, 118.6, 117.07, 117.06, 117.0, 116.3, 113.4, 112.0, 67.3, 55.3, 26.5.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{27}N_4O_3S$ $[M + H]^+$ 571.1798, found 571.1796.

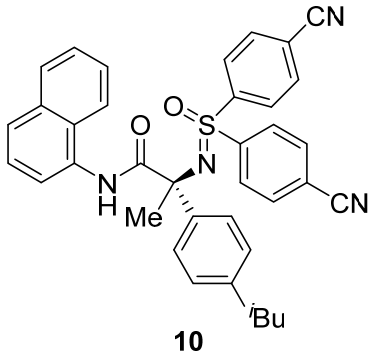
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-(*p*-tolyl)propenamide (9)



9

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-(*p*-tolyl)propanamide (64.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **9** as an white amorphous solid (102.9 mg, 93% yield, 93% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 30/70, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 19.90 min, t_R (major) = 29.01 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.17 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 3H), 7.75 – 7.68 (m, 3H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 6.98 (d, *J* = 8.1 Hz, 2H), 2.28 (s, 3H), 2.02 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 145.9, 145.7, 140.1, 137.6, 134.1, 133.2, 132.8, 132.4, 129.09, 129.05, 128.9, 128.5, 126.4, 126.2, 126.14, 126.08, 125.9, 125.1, 119.8, 118.5, 117.1, 117.01, 116.99, 116.2, 67.3, 26.5, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{26}N_4O_2SNa$ $[M + Na]^+$ 577.1669, found 577.1669.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(4-isobutylphenyl)-*N*-(naphthalen-1-yl)propenamide (10)

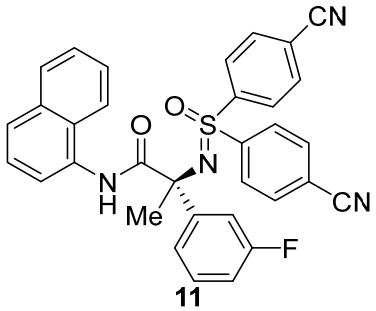


10

According to **General procedure A** with 2-chloro-2-(4-isobutylphenyl)-*N*-(naphthalen-1-yl)propanamide (73.0 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction

mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **10** as an white amorphous solid (113.0 mg, 98% yield, 90% ee).
HPLC analysis: Chiralcel IE (hexane/*i*-PrOH = 30/70, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 41.18 min, t_R (minor) = 66.94 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.22 – 8.08 (m, 3H), 7.85 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.76 (dd, *J* = 8.6, 1.9 Hz, 4H), 7.70 – 7.57 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.30 (m, 5H), 6.98 (d, *J* = 8.2 Hz, 2H), 2.40 (d, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.80 (dp, *J* = 13.5, 6.8 Hz, 1H), 0.90 (dd, *J* = 6.7, 1.1 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 146.0, 145.7, 141.4, 140.4, 134.1, 133.2, 132.8, 132.4, 129.14, 129.08, 128.9, 128.5, 126.3, 126.2, 126.13, 126.06, 125.9, 125.0, 119.0, 118.5, 117.1, 117.02, 116.96, 116.3, 67.3, 44.9, 30.1, 26.6, 22.4.
HRMS (ESI) *m/z* calcd. for $C_{37}H_{33}N_4O_2S$ $[M + H]^+$ 597.2319, found 597.2315.

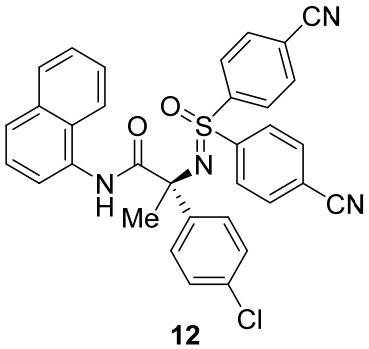
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)propenamide (11)



11

According to **General procedure B** with 2-chloro-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)propanamide (65.4 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **11** as a yellow oil (98.2 mg, 88% yield, 92% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.197 min, t_R (major) = 21.701 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.33 – 8.10 (m, 3H), 7.90 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.87 – 7.78 (m, 4H), 7.74 – 7.67 (m, 2H), 7.67 – 7.60 (m, 2H), 7.56 – 7.45 (m, 2H), 7.44 – 7.37 (m, 1H), 7.35 – 7.29 (m, 1H), 7.29 – 7.17 (m, 2H), 6.93 (tdd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 2.04 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 162.7 (d, *J* = 246.5 Hz), 145.9 (d, *J* = 6.6 Hz), 145.7, 145.5, 134.1, 133.4, 133.0, 132.2, 130.1 (d, *J* = 8.2 Hz), 129.1, 128.7, 128.5, 126.3, 126.3, 126.03, 126.00, 125.3, 122.2 (d, *J* = 2.9 Hz), 119.7, 118.7, 117.3, 116.94, 116.92, 116.7, 114.7 (d, *J* = 21.0 Hz), 113.8 (d, *J* = 22.7 Hz), 67.02, 67.00, 26.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ –112.0 – –112.2 (m).
HRMS (ESI) *m/z* calcd. for $C_{33}H_{24}FN_4O_2S$ $[M + H]^+$ 559.1599, found 559.1598.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)propenamide (12)



12

According to **General procedure A** with 2-chloro-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)propanamide (68.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **12** as a light yellow amorphous solid (101.1 mg, 88% yield, 90% ee).

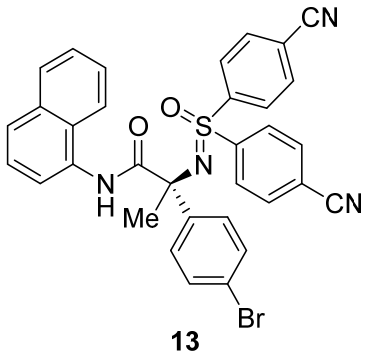
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 15.116 min, t_R (major) = 21.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.26 – 8.06 (m, 3H), 7.91 – 7.85 (m, 1H), 7.85 – 7.74 (m, 4H), 7.72 – 7.66 (m, 2H), 7.66 – 7.60 (m, 2H), 7.55 – 7.42 (m, 4H), 7.41 – 7.34 (m, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 145.8, 145.6, 141.8, 134.1, 133.8, 133.3, 133.0, 132.1, 129.2, 128.7, 128.48, 128.45, 128.0, 126.2, 126.1, 126.0, 125.3, 119.6, 118.6, 117.3, 116.9, 116.7, 67.0, 26.5.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{24}ClN_4O_2S$ $[M + H]^+$ 575.1303, found 575.1301.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(4-bromophenyl)-*N*-(naphthalen-1-yl)propenamide (13)



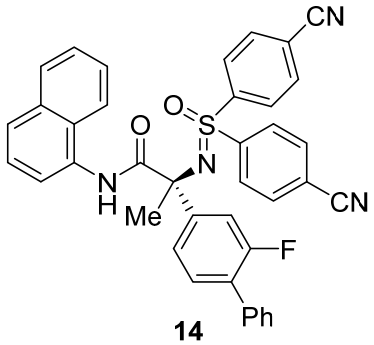
13

According to **General procedure A** with 2-(4-bromophenyl)-2-chloro-*N*-(naphthalen-1-yl)propanamide (77.4 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **13** as a white amorphous solid (111.1 mg, 90% yield, 91% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 30/70, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 21.64 min, t_R (major) = 32.35 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.22 – 8.10 (m, 3H), 7.91 – 7.86 (m, 1H), 7.83 – 7.79 (m, 2H), 7.78 – 7.74 (m, 2H), 7.73 – 7.65 (m, 2H), 7.64 – 7.59 (m, 2H), 7.53 – 7.44 (m, 2H), 7.42 – 7.28 (m, 5H), 2.00 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 145.7, 145.5, 142.3, 134.1, 133.3, 133.01, 132.97, 132.1, 131.4, 129.1, 128.7, 128.5, 128.3, 126.3, 126.1, 126.0, 125.3, 122.0, 119.7, 118.7, 117.2, 116.9, 116.7, 67.1, 26.4.
HRMS (ESI) *m/z* calcd. for $C_{33}H_{24}BrN_4O_2S$ $[M + H]^+$ 619.0798 & 621.0777, found 619.0796 & 621.0777.

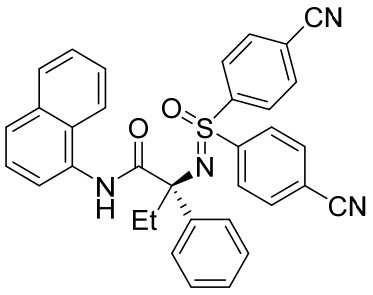
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)-*N*-(naphthalen-1-yl)propenamide (14)



14

According to **General procedure A** with 2-chloro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)-*N*-(naphthalen-1-yl)propanamide (80.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **14** as a white powder (114.1 mg, 90% yield, >99% ee).
HPLC analysis: Chiralcel ID (hexane/*i*-PrOH = 30/70, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 26.47 min, t_R (major) = 39.02 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.36 – 8.15 (m, 3H), 7.92 (d, *J* = 7.1 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 4H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.58 – 7.47 (m, 6H), 7.46 – 7.29 (m, 5H), 2.11 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.3 (d, *J* = 248.9 Hz), 145.7, 145.5, 144.5 (d, *J* = 6.9 Hz), 134.9, 134.1, 133.4, 132.9, 132.2, 130.7 (d, *J* = 3.8 Hz), 129.2, 128.84, 128.81, 128.79, 128.73, 128.68, 128.5, 128.4, 128.0, 126.27, 126.25, 126.1, 126.0, 125.3, 122.6 (d, *J* = 3.3 Hz), 119.7, 118.7, 117.3, 116.9 (d, *J* = 2.8 Hz), 116.6, 114.7 (d, *J* = 24.4 Hz), 67.0 (d, *J* = 1.4 Hz), 26.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ –116.94 (dd, *J* = 11.8, 8.0 Hz)
HRMS (ESI) *m/z* calcd. for $C_{39}H_{28}FN_4O_2S$ $[M + H]^+$ 635.1912, found 635.1916.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-phenylbutanamide (15)



15

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide (64.8 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **15** as a light yellow amorphous solid (85.3 mg, 77% yield, 91% ee).

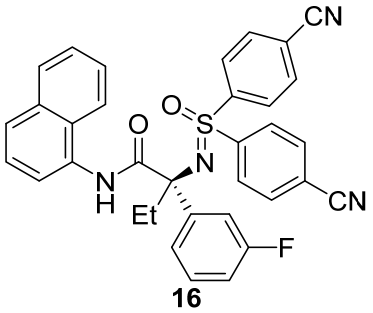
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.56 min, t_R (major) = 25.55 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.27 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.93 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.77 – 7.64 (m, 5H), 7.63 – 7.50 (m, 4H), 7.45 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.16 – 7.04 (m, 3H), 2.74 – 2.58 (m, 1H), 2.49 (dq, *J* = 14.0, 7.1 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 145.8, 145.1, 141.9, 134.1, 133.1, 132.6, 132.2, 129.2, 128.7, 128.31, 128.26, 127.8, 127.4, 126.3, 126.1, 126.0, 125.1, 119.7, 118.4, 117.1, 117.0, 116.8, 116.0, 71.8, 32.2, 9.2.

HRMS (ESI) *m/z* calcd. for $C_{34}H_{27}N_4O_2S$ $[M + H]^+$ 555.1849, found 555.1850.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)butanamide (16)



16

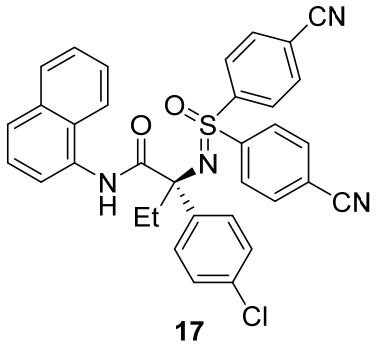
According to **General procedure A** with 2-chloro-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)butanamide (68.2 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **16** as a light yellow amorphous solid (75.5 mg, 66% yield, 89% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.55 min, t_R (major) = 28.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.11 – 8.05 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.76 (m, 3H), 7.76 – 7.69 (m, 3H), 7.62 – 7.41 (m,

5H), 7.20 – 6.99 (m, 3H), 6.85 – 6.77 (m, 1H), 2.61 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.47 (dq, *J* = 14.0, 7.1 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 162.4 (d, *J* = 246.9 Hz), 145.5, 145.0, 144.4 (d, *J* = 6.5 Hz), 134.1, 133.2, 132.7, 131.9, 129.9 (d, *J* = 8.1 Hz), 129.2, 128.6, 128.3, 126.3, 126.1, 126.0, 125.3, 123.1 (d, *J* = 2.9 Hz), 119.6, 118.5, 117.1, 117.0, 116.9, 116.3, 114.8 (d, *J* = 11.6 Hz), 114.6 (d, *J* = 10.2 Hz), 71.4 (d, *J* = 1.7 Hz), 32.3, 9.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ –112.22 (td, *J* = 9.6, 6.4 Hz).
HRMS (ESI) *m/z* calcd. for $C_{34}H_{26}FN_4O_2S$ $[M + H]^+$ 573.1755, found 573.1758.

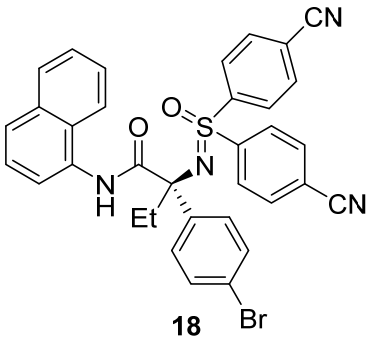
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)butanamide (17)



17

According to **General procedure A** with 2-chloro-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)butanamide (71.4 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **17** as a light yellow amorphous solid (82.3 mg, 70% yield, 88% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.64 min, t_R (major) = 24.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.26 – 8.20 (m, 1H), 8.04 – 7.98 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.73 – 7.64 (m, 3H), 7.60 – 7.56 (m, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.40 (m, 1H), 7.33 – 7.20 (m, 2H), 7.05 – 6.98 (m, 2H), 2.57 (dq, *J* = 14.2, 7.2 Hz, 1H), 2.45 (dq, *J* = 14.2, 7.2 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 145.6, 145.1, 140.4, 134.1, 133.9, 133.1, 132.7, 131.9, 129.2, 128.9, 128.7, 128.3, 128.2, 126.3, 126.12, 126.08, 126.0, 125.3, 119.5, 118.4, 117.0, 116.89, 116.86, 116.3, 71.3, 32.4, 9.2.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{26}ClN_4O_2S$ $[M + H]^+$ 589.1460, found 589.1456.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(4-bromophenyl)-*N*-(naphthalen-1-yl)butanamide (18)



18

According to **General procedure A** with 2-(4-bromophenyl)-2-chloro-*N*-(naphthalen-1-yl)butanamide (80.2 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **18** as a light yellow amorphous solid (93.5 mg, 74% yield, 88% ee).

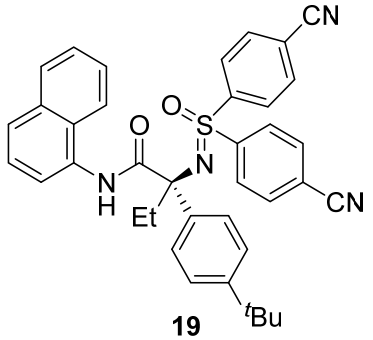
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.64 min, t_R (major) = 28.66 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.76 (m, 3H), 7.76 – 7.66 (m, 3H), 7.63 – 7.42 (m, 5H), 7.23 – 7.15 (m, 4H), 2.54 (ddq, *J* = 41.2, 14.0, 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 145.6, 145.0, 140.9, 134.1, 133.1, 132.7, 131.9, 131.2, 129.23, 129.21, 128.7, 128.2, 126.3, 126.13, 126.10, 126.0, 125.3, 122.1, 119.5, 118.5, 117.1, 116.91, 116.87, 116.2, 71.3, 32.3, 9.2.

HRMS (ESI) *m/z* calcd. for $C_{34}H_{26}BrN_4O_2S$ $[M + H]^+$ 633.0594, found 633.0597.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-(4-(*tert*-butyl)phenyl)-*N*-(naphthalen-1-yl)butanamide (19)



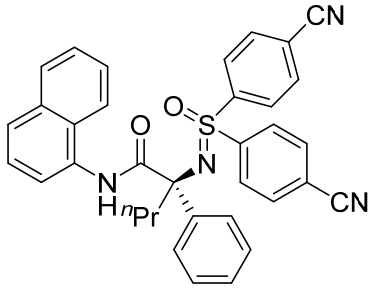
19

According to **General procedure A** with 2-(4-(*tert*-butyl)phenyl)-2-chloro-*N*-(naphthalen-1-yl)butanamide (75.8 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **19** as an amorphous solid (109.8 mg, 90% yield, 87% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.68 min, t_R (major) = 23.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.27 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.91 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.38 (m, 5H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 2.67 – 2.44 (m, 2H), 1.25 (t, *J* = 9.0 Hz, 3H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 150.7, 145.9, 145.2, 138.7, 134.1, 133.1, 132.5, 132.2, 129.2, 128.7, 128.3, 127.0, 126.20, 126.17, 126.1, 125.9, 125.1, 125.0, 119.7, 118.3, 117.03, 116.96, 116.8, 115.9, 71.6, 34.4, 32.3, 31.3, 9.3.
HRMS (ESI) *m/z* calcd. for $C_{38}H_{35}N_4O_2S$ $[M + H]^+$ 611.2475, found 611.2470.

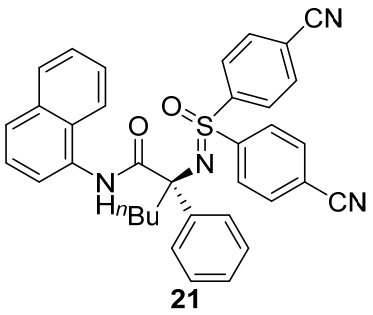
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-phenylpentanamide (20)



20

According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpentanamide (67.8 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **20** as an amorphous solid (97.7 mg, 86% yield, 89% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.32 min, t_R (major) = 12.80 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.25 (dd, *J* = 7.5, 1.1 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 1.3 Hz, 1H), 7.79 – 7.70 (m, 3H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.45 (m, 4H), 7.41 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.12 – 7.00 (m, 3H), 2.53 (td, *J* = 12.7, 4.5 Hz, 1H), 2.36 (td, *J* = 12.6, 3.9 Hz, 1H), 1.98 – 1.82 (m, 1H), 1.59 – 1.44 (m, 1H), 1.02 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 145.8, 145.0, 142.1, 134.1, 133.1, 132.6, 132.2, 129.2, 128.7, 128.33, 128.26, 127.8, 127.2, 126.24, 126.15, 126.1, 126.0, 125.0, 119.6, 118.2, 117.1, 117.0, 116.9, 116.0, 71.2, 41.4, 18.0, 14.5.
HRMS (ESI) *m/z* calcd. for $C_{35}H_{29}N_4O_2S$ $[M + H]^+$ 569.2006, found 569.2004.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-phenylhexanamide (21)



21

According to **General procedure B** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylhexanamide (70.2 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **21** as a light yellow amorphous solid (82.6 mg, 71% yield, 88% ee).

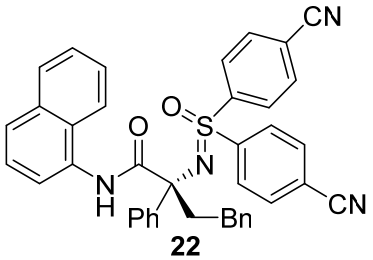
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 21.70 min, t_R (major) = 25.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.78 (dd, *J* = 8.4, 4.3 Hz, 3H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.50 (m, 4H), 7.44 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.16 – 7.04 (m, 3H), 2.64 – 2.53 (m, 1H), 2.48 – 2.36 (m, 1H), 1.95 – 1.81 (m, 1H), 1.56 – 1.39 (m, 3H), 0.96 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 145.8, 145.1, 142.2, 134.1, 133.1, 132.6, 132.2, 129.2, 128.7, 128.34, 128.27, 127.8, 127.2, 126.21, 126.17, 126.1, 126.0, 125.0, 119.6, 118.2, 117.1, 117.0, 116.9, 116.0, 71.2, 39.0, 26.6, 23.1, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{36}H_{31}N_4O_2S$ $[M + H]^+$ 583.2162, found 583.2160.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2,4-diphenylbutanamide (22)



22

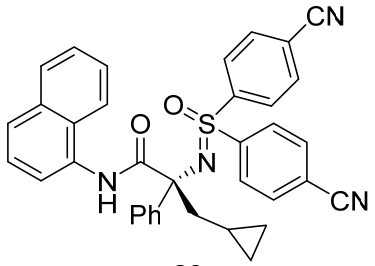
According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2,4-diphenylbutanamide (85.4 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **22** as an amorphous solid (110.9 mg, 88% yield, 91% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 19.17 min, t_R (minor) = 75.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.31 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 2H), 8.00 – 7.91 (m, 1H), 7.82 – 7.74 (m, 3H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.51 (m, 2H), 7.52 – 7.43 (m, 3H), 7.42 – 7.29 (m, 6H), 7.28

– 7.19 (m, 1H), 7.16 – 7.05 (m, 3H), 3.27 (td, *J* = 12.2, 3.5 Hz, 1H), 2.95 (td, *J* = 12.2, 4.1 Hz, 1H), 2.79 (dtd, *J* = 38.7, 12.0, 3.9 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 145.6, 144.8, 142.0, 141.9, 134.1, 133.2, 132.6, 132.1, 129.2, 128.7, 128.6, 128.5, 128.4, 127.9, 127.2, 126.3, 126.2, 126.1, 126.0, 125.2, 119.6, 118.4, 117.1, 117.03, 116.95, 116.0, 71.1, 41.6, 31.0.
HRMS (ESI) *m/z* calcd. for $C_{40}H_{31}N_4O_2S$ $[M + H]^+$ 631.2162, found 631.2162.

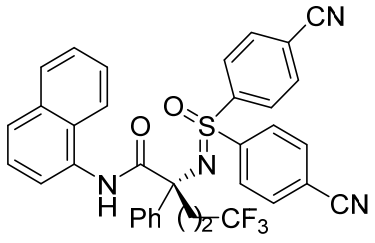
(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-3-cyclopropyl-*N*-(naphthalen-1-yl)-2-phenylpropanamide (23)



23

According to **General procedure A** with 2-chloro-3-cyclopropyl-*N*-(naphthalen-1-yl)-2-phenylpropanamide (69.8 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **23** as a light yellow amorphous solid (94.0 mg, 81% yield, 87% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 30/70, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 13.29 min, t_R (major) = 18.78 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.33 – 8.26 (m, 1H), 8.08 – 8.01 (m, 2H), 7.93 – 7.89 (m, 1H), 7.88 – 7.82 (m, 1H), 7.79 – 7.72 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.55 – 7.47 (m, 4H), 7.46 – 7.40 (m, 1H), 7.27 – 7.22 (m, 2H), 7.14 – 6.95 (m, 3H), 2.83 (dd, *J* = 13.5, 4.3 Hz, 1H), 2.11 (dd, *J* = 13.5, 8.9 Hz, 1H), 1.34 – 1.21 (m, 1H), 0.58 – 0.46 (m, 1H), 0.44 – 0.28 (m, 2H), 0.27 – 0.18 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 145.8, 145.1, 141.8, 134.1, 133.1, 132.6, 132.4, 129.2, 128.7, 128.3, 128.1, 127.8, 127.5, 126.3, 126.2, 126.1, 126.0, 124.9, 119.7, 118.3, 117.1, 117.0, 116.8, 115.9, 71.4, 43.7, 6.8, 5.0, 4.2.
HRMS (ESI) *m/z* calcd. for $C_{36}H_{29}N_4O_2S$ $[M + H]^+$ 581.2006, found 581.2003.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-5,5,5-trifluoro-*N*-(naphthalen-1-yl)-2-phenylpentanamide (24)



24

According to **General procedure B** with 2-chloro-5,5,5-trifluoro-*N*-(naphthalen-1-yl)-2-phenylpentanamide (78.2 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture

was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **24** as a light yellow oil (109.5 mg, 88% yield, 95% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.12 min, t_R (major) = 16.76 min.

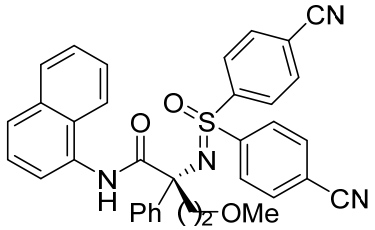
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.16 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.93 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.82 – 7.63 (m, 6H), 7.59 – 7.47 (m, 5H), 7.43 – 7.37 (m, 2H), 7.27 – 7.13 (m, 3H), 2.99 – 2.84 (m, 1H), 2.78 – 2.50 (m, 2H), 2.45 – 2.30 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 145.3, 144.8, 140.6, 134.1, 133.2, 132.8, 131.7, 129.3, 128.7, 128.6, 128.4, 128.3, 127.4 (q, *J* = 275.0 Hz), 127.0, 126.5, 126.1, 126.0, 125.9, 125.4, 119.3, 118.2, 117.0, 116.9, 116.4, 69.9, 32.0, 29.7 (q, *J* = 29.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –65.82 (t, *J* = 10.6 Hz).

HRMS (ESI) *m/z* calcd. for $C_{35}H_{26}F_3N_4O_2S$ $[M + H]^+$ 623.1723, found 623.1719.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-4-methoxy-*N*-(naphthalen-1-yl)-2-phenylbutanamide (25)



25

According to **General procedure A** with 2-chloro-4-methoxy-*N*-(naphthalen-1-yl)-2-phenylbutanamide (70.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **25** as an amorphous solid (82.9 mg, 71% yield, 92% ee).

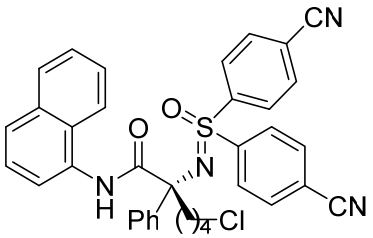
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 27.84 min, t_R (minor) = 37.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.23 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.94 – 7.88 (m, 1H), 7.83 – 7.66 (m, 6H), 7.61 – 7.38 (m, 5H), 7.34 (d, *J* = 6.4 Hz, 2H), 7.20 – 6.98 (m, 3H), 3.91 (ddd, *J* = 9.5, 8.4, 5.0 Hz, 1H), 3.76 (ddd, *J* = 9.4, 8.1, 6.2 Hz, 1H), 3.35 (s, 3H), 2.95 (ddd, *J* = 13.2, 8.4, 6.2 Hz, 1H), 2.74 (ddd, *J* = 13.3, 8.2, 5.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 145.7, 145.1, 141.3, 134.1, 133.1, 132.7, 132.1, 129.2, 128.7, 128.4, 128.3, 128.0, 127.2, 126.3, 126.14, 126.12, 126.0, 125.1, 119.7, 118.4, 117.1, 117.0, 116.8, 116.2, 69.4, 69.2, 58.8, 38.7.

HRMS (ESI) *m/z* calcd. for $C_{35}H_{29}N_4O_3S$ $[M + H]^+$ 585.1955, found 585.1951.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-6-chloro-*N*-(naphthalen-1-yl)-2-phenylhexanamide (26)



26

According to **General procedure B** with 2,6-dichloro-*N*-(naphthalen-1-yl)-2-phenylhexanamide (77.0 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **26** as a light yellow amorphous solid (94.9 mg, 77% yield, 87% ee).

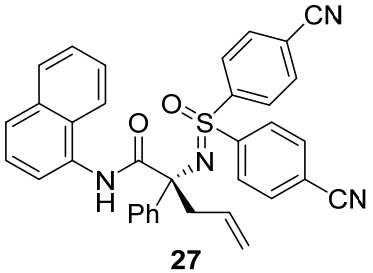
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 15.42 min, t_R (major) = 17.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.23 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.09 – 8.00 (m, 2H), 7.95 – 7.89 (m, 1H), 7.81 – 7.68 (m, 6H), 7.63 – 7.41 (m, 5H), 7.39 – 7.32 (m, 2H), 7.18 – 7.03 (m, 3H), 3.88 – 3.41 (m, 2H), 2.85 – 2.53 (m, 1H), 2.49 – 2.39 (m, 1H), 2.16 – 2.02 (m, 1H), 2.02 – 1.83 (m, 2H), 1.74 – 1.59 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 145.7, 145.0, 141.8, 134.1, 133.1, 132.7, 132.0, 129.2, 128.7, 128.4, 128.3, 127.9, 127.2, 126.3, 126.12, 126.10, 126.0, 125.2, 119.6, 118.4, 117.1, 117.0, 116.9, 116.1, 71.0, 44.9, 38.4, 32.8, 22.0.

HRMS (ESI) *m/z* calcd. for $C_{36}H_{30}ClN_4O_2S$ $[M + H]^+$ 617.1773, found 617.1769.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-*N*-(naphthalen-1-yl)-2-phenylpent-4-enamide (27)



27

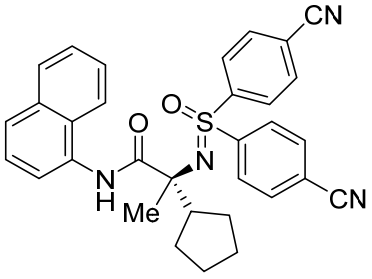
According to **General procedure A** with 2-chloro-*N*-(naphthalen-1-yl)-2-phenylpent-4-enamide (72.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **27** as an amorphous solid (83.8 mg, 74% yield, 92% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.40 min, t_R (major) = 19.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.20 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.92 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.80 – 7.68 (m, 6H), 7.62 – 7.40 (m, 5H), 7.39 – 7.31 (m, 2H), 7.18 – 7.05 (m, 3H), 6.18 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1H), 5.32 (dd, *J* = 17.2, 1.9 Hz, 1H), 5.19 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.49 – 3.09 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 145.9, 145.3, 141.2, 134.1, 133.3, 133.0, 132.7, 132.1, 129.1, 128.7, 128.3, 128.2, 128.0, 127.4, 126.3, 126.2, 126.1, 126.0, 125.2, 119.8, 119.4, 118.6, 117.1, 117.0, 116.8, 116.2, 71.0, 43.6.
HRMS (ESI) *m/z* calcd. for $C_{35}H_{27}N_4O_2S$ $[M + H]^+$ 567.1849, found 567.1849.

(*R*)-2-((Bis(4-cyanophenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-cyclopentyl-*N*-(naphthalen-1-yl)propenamide (28)

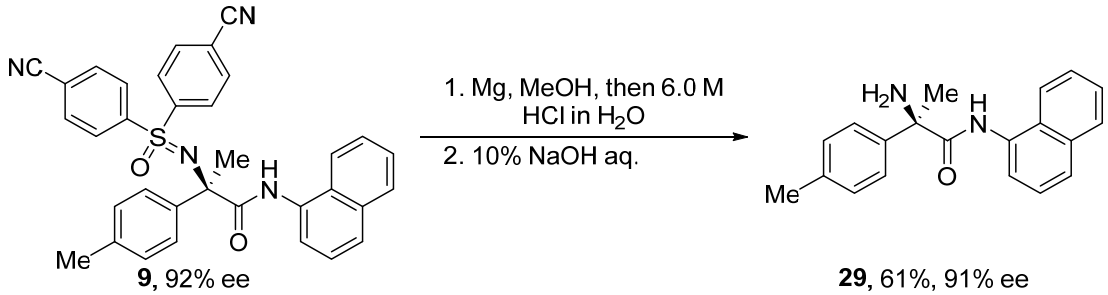


28

According to **General procedure B** with 2-bromo-2-cyclopentyl-*N*-(naphthalen-1-yl)propanamide (69.0 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to yield the product **28** as a yellow oil (70.2 mg, 66% yield, 64% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.02 min, t_R (minor) = 13.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 3H), 7.92 – 7.75 (m, 6H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.50 (td, *J* = 7.8, 4.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 2.47 (p, *J* = 8.6 Hz, 1H), 1.93 – 1.58 (m, 8H), 1.46 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 147.9, 146.9, 134.1, 133.4, 133.3, 132.5, 129.0, 128.7, 128.5, 126.7, 126.1, 126.0, 125.9, 125.2, 120.2, 119.2, 117.1, 117.0, 116.94, 116.90, 68.0, 51.3, 27.9, 27.5, 25.6, 25.4, 24.3.
HRMS (ESI) *m/z* calcd. for $C_{32}H_{28}N_4O_2SNa$ $[M + Na]^+$ 555.1825, found 555.1824.

Transformation

The synthesis of 29.



9, 92% ee

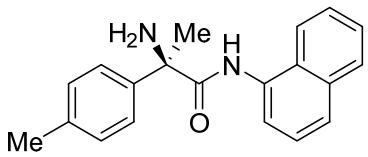
29, 61%, 91% ee

To a flamed flask charged with a stir bar were added **9** (83.1 mg, 0.15 mmol, 1.0 equiv.,

92% ee), Mg (36.0 mg, 1.5 mmol, 10.0 equiv.) and anhydrous MeOH (2.0 mL) under argon. The reaction was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.55 mL, 3.3 mmol, 22.0 equiv., 6.0 M in H_2O) was added at 0 °C, and the reaction mixture was stirred at room temperature to afford a homogenous solution in 0.5 h.

After completion (monitored by TLC), 10% aqueous NaOH solution was added to adjust the pH value to 10. Then, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the desired product **29** as a colorless oil (27.8 mg, 61% yield, 91% ee).

(*R*)-2-Amino-*N*-(naphthalen-1-yl)-2-(*p*-tolyl)propanamide (29)



29

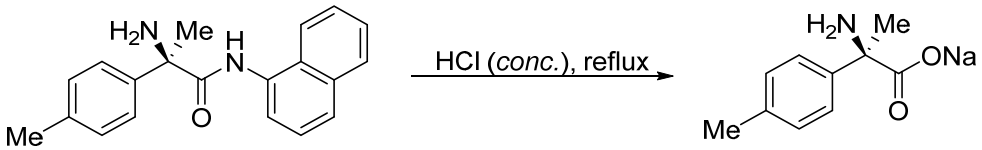
HPLC analysis: Chiralcel AD (hexane/^{i}PrOH = 75/25, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 7.47 min, t_R (minor) = 15.37 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.24 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.80 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.42 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.71 (brs, 2H), 2.36 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 140.9, 137.5, 134.0, 132.6, 129.5, 128.8, 126.2, 126.1, 126.0, 125.8, 125.3, 124.7, 120.2, 118.0, 61.2, 28.1, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}N_2O_2$ $[M + H]^+$ 305.1648, found 305.1654.

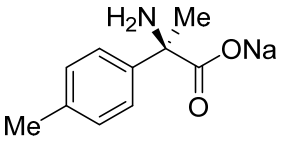
The synthesis of 30-1



29, 91% ee **30-1**, 92%

The compound of **29** (27.4 mg, 0.090 mmol, 1.0 equiv., 92% ee) in concentrated HCl (1.0 mL) was refluxed for 24 h. The reaction mixture was concentrated and adjusted pH to 10 with 10% aqueous NaOH solution, and extracted with CH_2Cl_2 three times. After that, the aqueous phase was evaporated to yield **30-1** as a white solid (16.6 mg, 92% yield) without further purification.

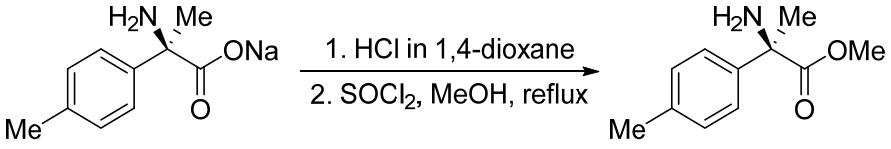
Sodium (*R*)-2-amino-2-(*p*-tolyl)propanoate (30-1)



30-1

^{1}H NMR (400 MHz, D_2O) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H), 1.78 (s, 3H).
^{13}C NMR (100 MHz, D_2O) δ 178.3, 138.9, 136.7, 129.5, 125.7, 62.4, 22.5, 20.2.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}NO_2$ $[M - Na]^-$ 178.0874, found 178.0869.

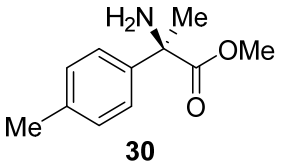
The synthesis of 30



30-1 **30**, 81%, 91% ee

To a solution of **30-1** (10.1 mg, 0.050 mmol, 1.0 equiv.) in MeOH (1.0 mL) was added HCl (15 μl, 0.06 mmol, 1.2 equiv., 4.0 M in 1,4-dioxane),the mixture was stirred for 5 min, then the mixture was added thionyl chloride (29.5 mg, 0.25 mmol, 5.0 equiv.) and the reaction mixture was refluxed for 3 h. The solvent was evaporated, followed by the addition of CH_2Cl_2. Then the solution was washed with saturated aqueous Na_2CO_3 solution, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the desired product **30** (7.8 mg, 81% yield, 91% ee) as a slight yellow oil.

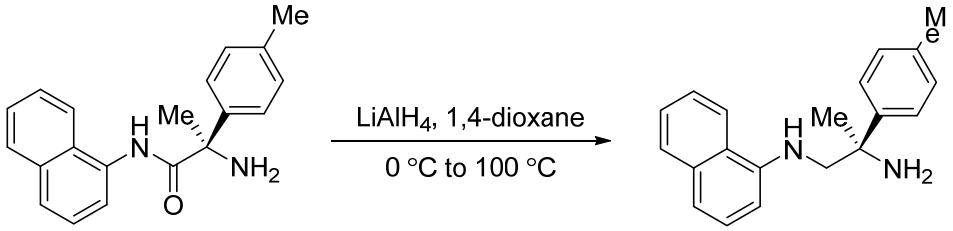
Methyl (*R*)-2-amino-2-(*p*-tolyl)propanoate (30)



30

HPLC analysis: Chiralcel OJH (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 7.79 min, t_R (major) = 10.71 min.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.70 (s, 3H), 2.33 (s, 3H), 2.11 (brs, 2H), 1.70 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.5, 140.8, 137.3, 129.2, 125.0, 60.5, 52.6, 27.2, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NO_2$ $[M + H]^+$ 194.1176, found 194.1182.

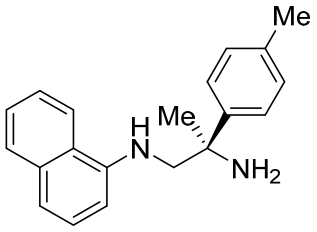
The synthesis of 31



29, 61%, 91% ee **31**, 92%, 91% ee

To a solution of $LiAlH_4$ (9.5 mg, 0.25 mmol, 2.5 equiv.) in 1,4-dioxane (2.0 ml) at 0 °C, **29** (30.4 mg, 0.10 mmol, 1.0 equiv.) was added and warmed up to 100 °C. After completion (monitored by TLC), the mixture was quenched by water at 0 °C and extracted with EtOAc three times. The organic phase was concentrated in vacuum and purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to yield the desired product **31** (26.7 mg, 92% yield, 91% ee) as a slight yellow oil.

(*R*)-N^1-(Naphthalen-1-yl)-2-(*p*-tolyl)propane-1,2-diamine (31)



31

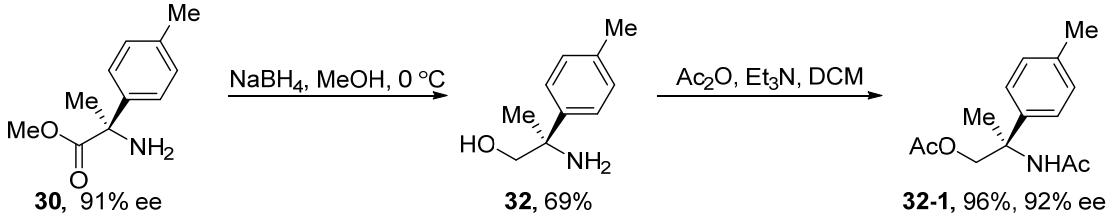
HPLC analysis: Chiralcel INB (hexane/^{i}PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.50 min, t_R (minor) = 28.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.32 (m, 5H), 7.26 (t, *J* = 8.2 Hz, 3H), 6.66 (d, *J* = 7.5 Hz, 1H), 4.70 (brs, 1H), 3.47 (q, *J* = 11.5 Hz, 2H), 2.40 (s, 3H), 1.87 (brs, 2H), 1.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.9, 136.6, 134.3, 129.4, 128.6, 126.7, 125.7, 125.2, 124. 7, 123.8, 120.1, 117.4, 104.6, 55.9, 55.4, 29.5, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}N$ $[M + H]^+$ 291.1856, found 291.1848.

The synthesis of 32

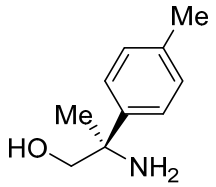


30, 91% ee **32**, 69% **32-1**, 96%, 92% ee

To a solution of **30** (19.3 mg, 0.10 mmol, 1.0 equiv.) in MeOH (1.0 ml) at 0 °C, $NaBH_4$ (7.6 mg, 0.2 mmol, 2.0 equiv.) was added and stirred at this temperature. After completion (monitored by TLC), the mixture was quenched by water at 0 °C and extracted with CH_2Cl_2 three times. The organic phase was concentrated in vacuum and purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to yield the desired product **32** (26.7 mg, 69% yield) as a yellow oil.

The ee value of **32** was determined by **32-1**.
To a solution of **32** (11.4 mg, 0.069 mmol, 1.0 equiv.) and Ac_2O (21.1 mg, 0.207 mmol, 3.0 equiv.) in CH_2Cl_2 (1.0 ml), Et_3N (20.9 mg, 0.207 mmol, 3.0 equiv.) was added dropwise and stirred at room temperature overnight. After concentration, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the desired product **32-1** (16.5 mg, 96% yield, 92% ee) as a white amorphous solid.

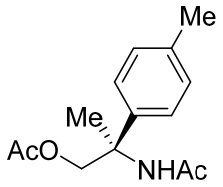
(*R*)-2-Amino-2-(*p*-tolyl)propan-1-ol (32)



32

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.24 – 7.12 (m, 2H), 3.70 – 3.53 (m, 2H), 2.36 (s, 3H), 2.10 (brs, 3H), 1.47 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 136.5, 129.2, 125.2, 71.7, 56.2, 27.0, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{16}NO$ $[M + H]^+$ 166.1226, found 166.1224.

(*R*)-2-Acetamido-2-(*p*-tolyl)propyl acetate (32-1)

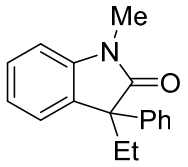


32-1

HPLC analysis: Chiralcel INA (hexane/^{i}PrOH = 95/05, flow rate 0.7 mL/min, λ = 214 nm), t_R (major) = 29.30 min, t_R (minor) = 38.53 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.34 (s, 1H), 4.41 (d, *J* = 11.3 Hz, 1H), 4.25 (d, *J* = 11.3 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.73 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 169.5, 139.3, 136.9, 129.2, 125.3, 70.1, 58.5, 24.2, 23.0, 21.0, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{20}NO_3$ $[M + H]^+$ 250.1438, found 250.1430.

Mechanism

3-Ethyl-1-methyl-3-phenylindolin-2-one (33)



33

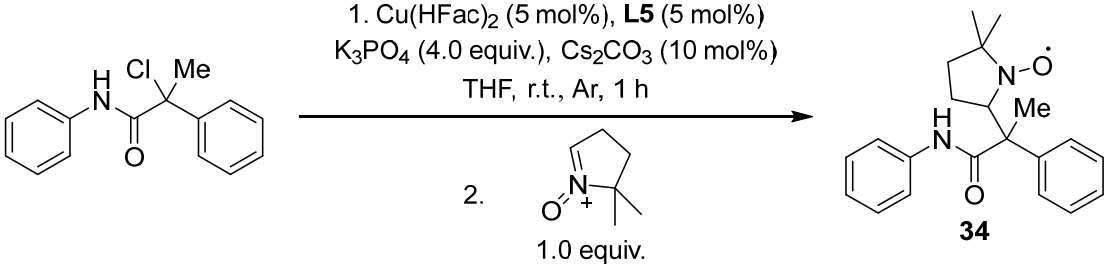
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 4,4'-sulfonimidoyldibenzonitrile (53.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(HFac)_2$ (4.4 mg, 0.010 mmol, 5.0 mol%), **L5** (4.3 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and $PhCF_3$ (2.0 mL). Then, 2-chloro-*N*-methyl-*N*,2-diphenylbutanamide (67.4 mg, 0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at 80 °C for 16 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc= 50/1) to afford the product **33** as a white amorphous solid (41.2 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.21 (m, 7H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.26 (s, 3H), 2.46 (dq, *J* = 13.5, 7.3 Hz, 1H), 2.27 (dq, *J* = 13.4, 7.4 Hz, 1H), 0.71 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 144.1, 140.3, 132.1, 128.5, 128.1, 127.2, 127.0, 124.8, 122.6, 108.2, 57.3, 30.9, 26.4, 9.1.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383, found 252.1386.

Spin trap Study.



34

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(HFac)_2$ (4.4 mg, 0.010 mmol, 5.0 mol%), **L5** (4.3 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (6.5 mg, 0.020 mmol, 10.0 mol%), K_3PO_4 (169.6 mg, 0.80 mmol, 4.0 equiv.) and anhydrous THF (2.0 mL). Then, 2-chloro-*N*,2-diphenylpropanamide (51 mmol, 0.2 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 1h. Then the reaction was transferred into the glove box and DMPO (2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 22mg, 0.2 mmol, 1.0 equiv.) was added, After that an aliquot (0.3 mL) was taken from the mixture for room temperature Q-band CW-EPR.

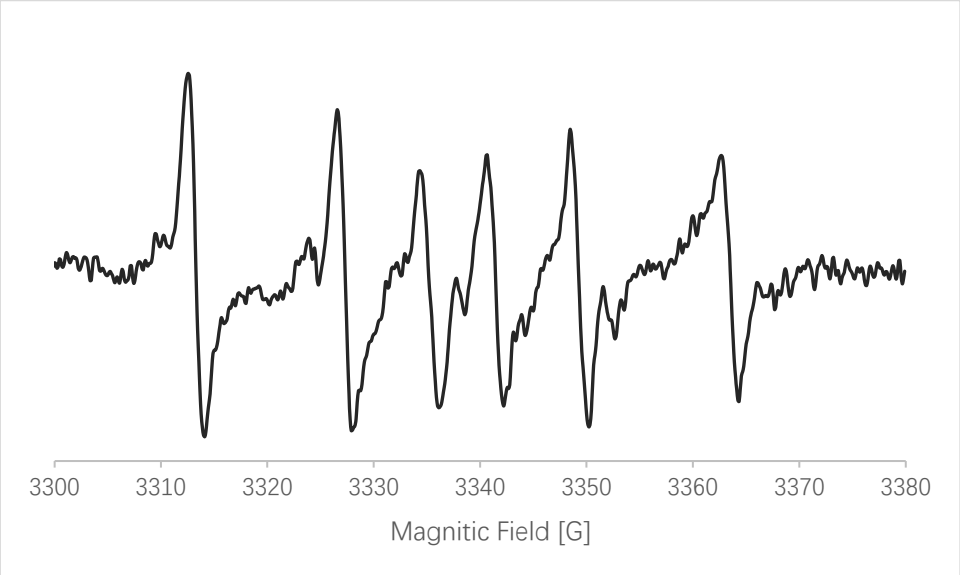


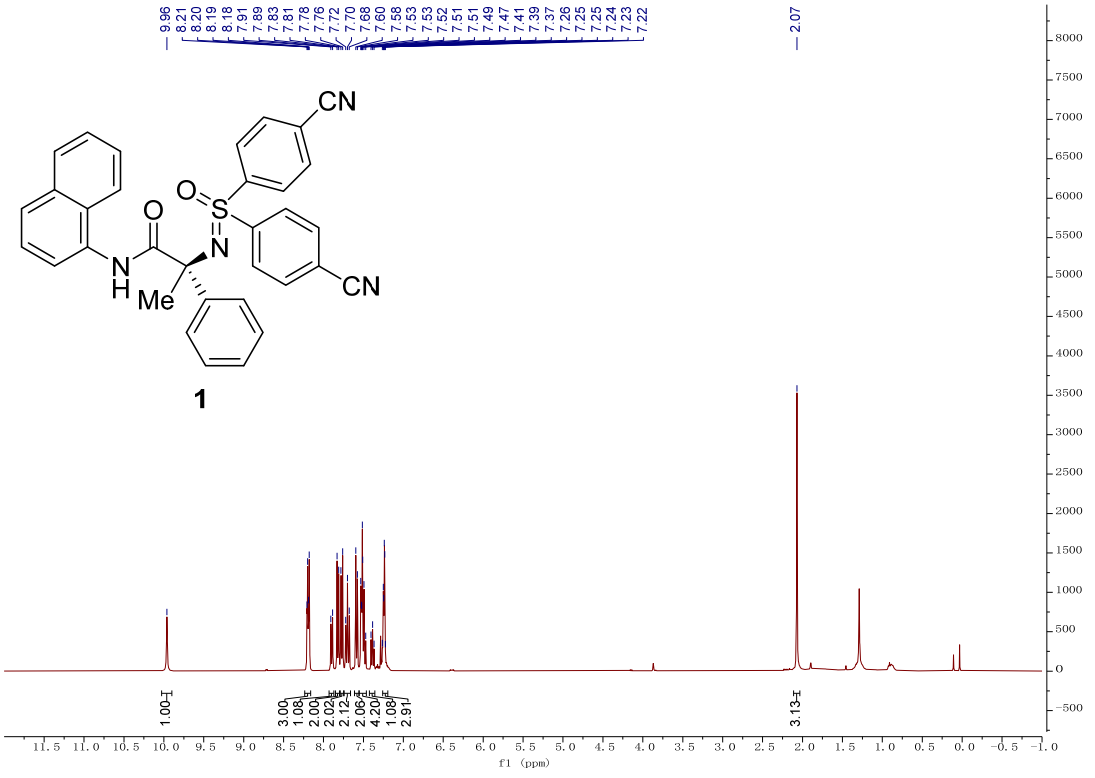
Figure S5. Spin trap study. Room Temperature Q-band CW-EPR spectra of the spin trap study. g = 2.0061; A_H = 22.00 G; A_N = 14.11 G. EPR acquisition parameters: temperature = 298 K; MW power = 40 dB; modulation amplitude = 0.5 G. conversion time = 20 ms.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}N_2O_2$ M^+ 337.1911, found 337.1897.

Reference

1. F.-L. Wang, C.-J. Yang, J.-R. Liu, N.-Y. Yang, X.-Y. Dong, R.-Q. Jiang, X.-Y. Chang, Z.-L. Li, G.-X. Xu, D.-L. Yuan, Y.-S. Zhang, Q.-S. Gu, X. Hong, X.-Y. Liu, *Nat. Chem.* **2022**, 949–957.

NMR Spectra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7.60
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7.51
7.51
7.49
7.47
7.41
7.39
7.37
7.26
7.25
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7.24
7.23
7.22
2.07
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N
O
N
H
Me
CN
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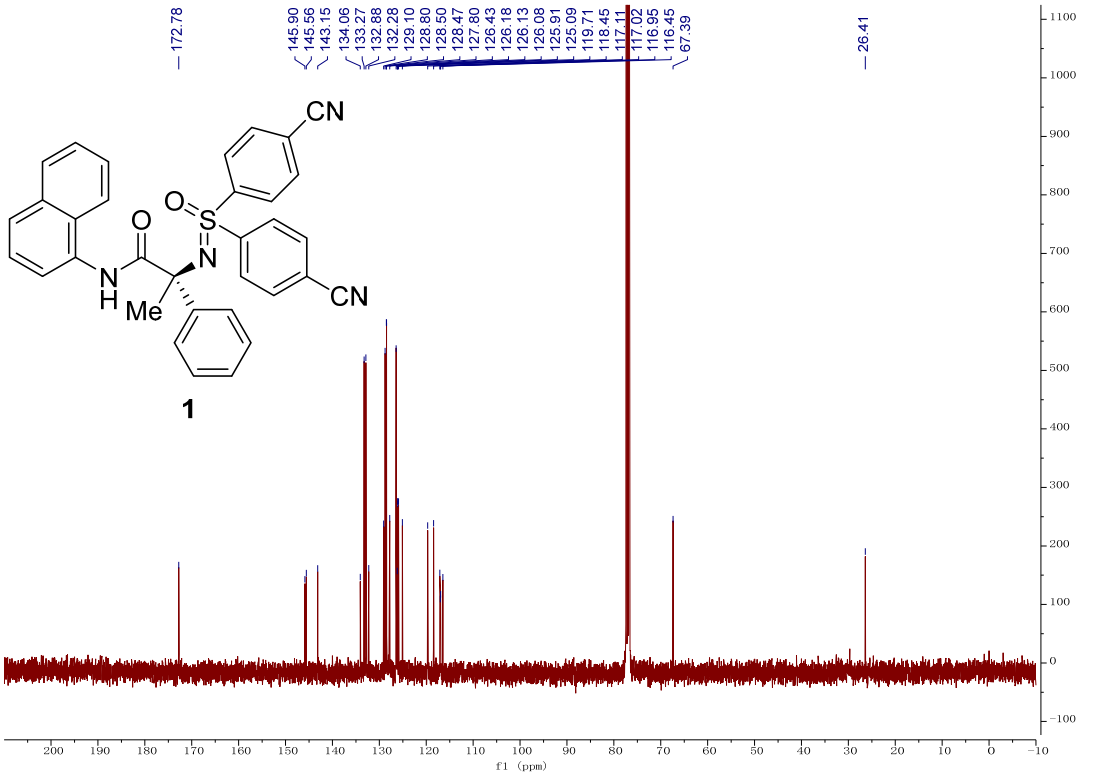
f1 (ppm)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126.13
126.08
125.91
125.09
119.71
118.45
117.11
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O
N
H
Me
CN
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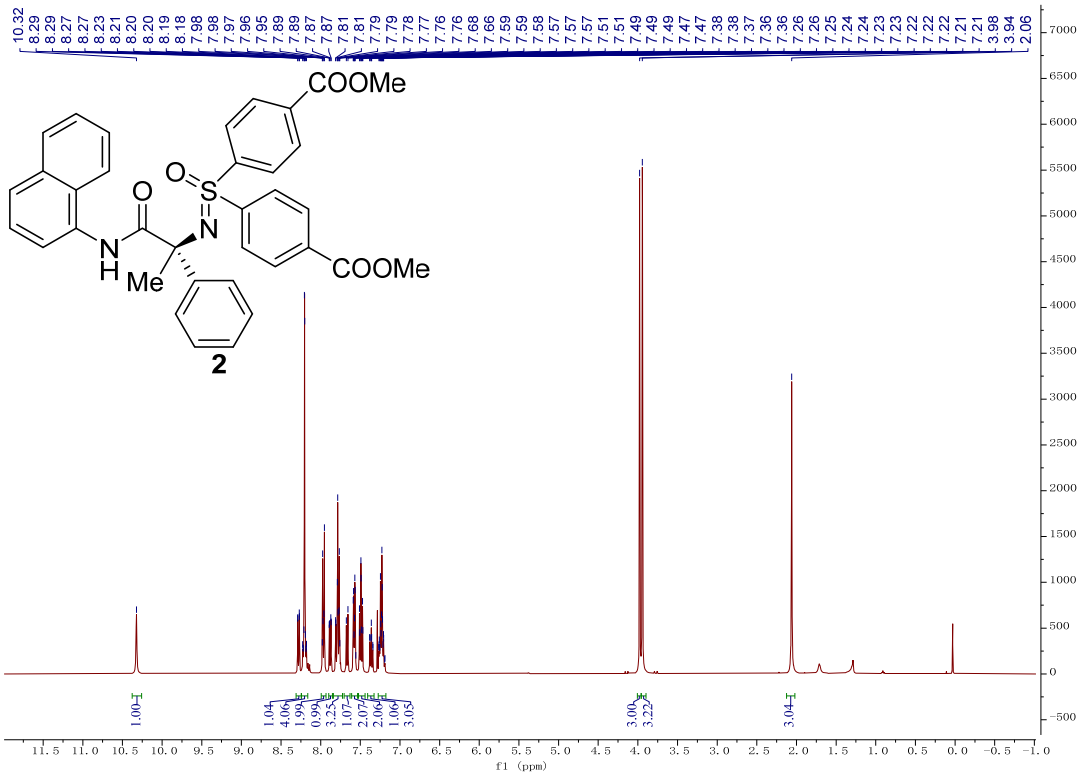
f1 (ppm)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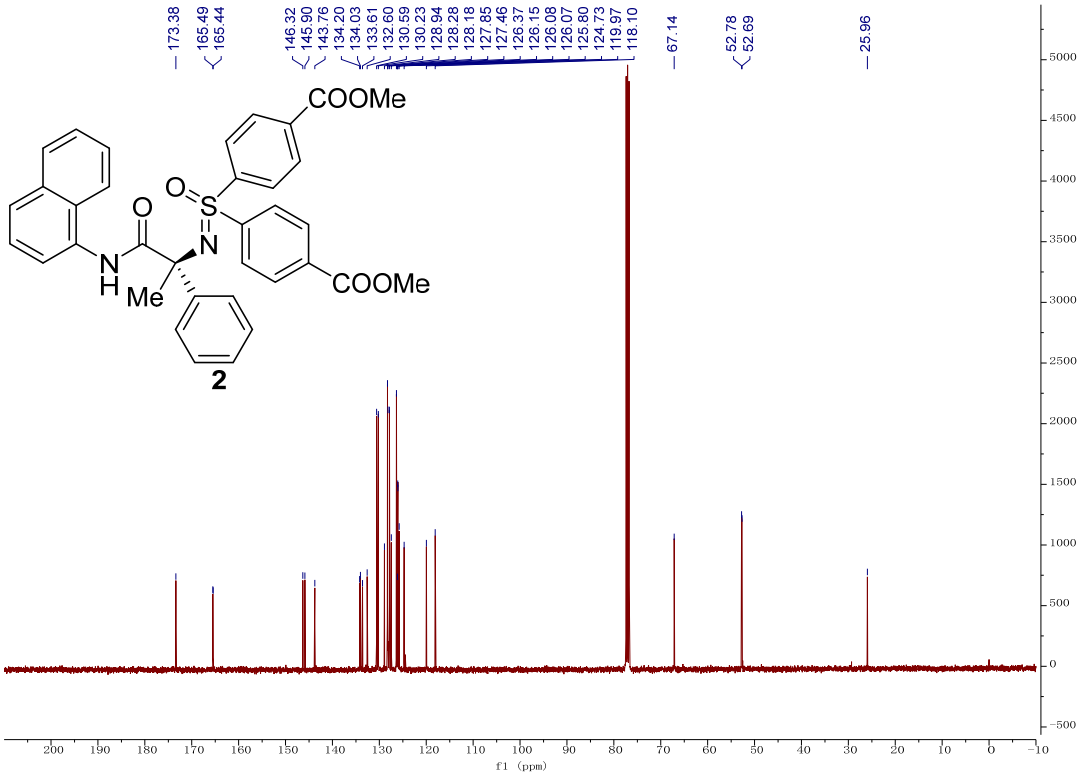
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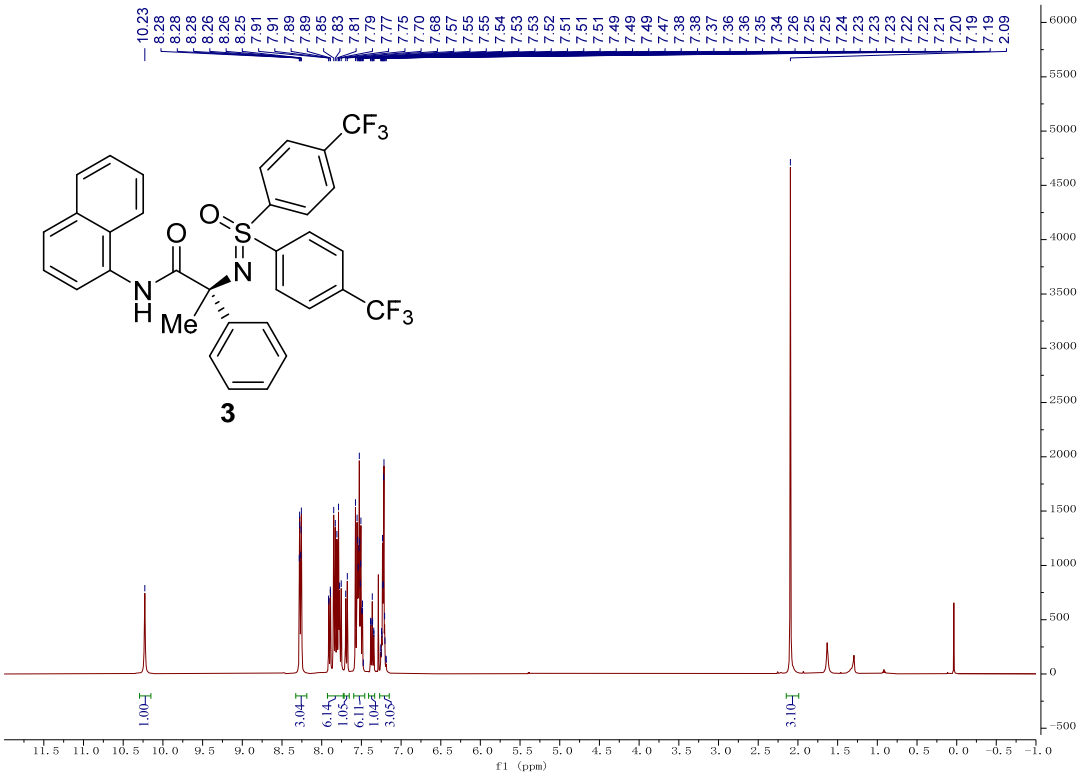
2
f1 (ppm)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7.22
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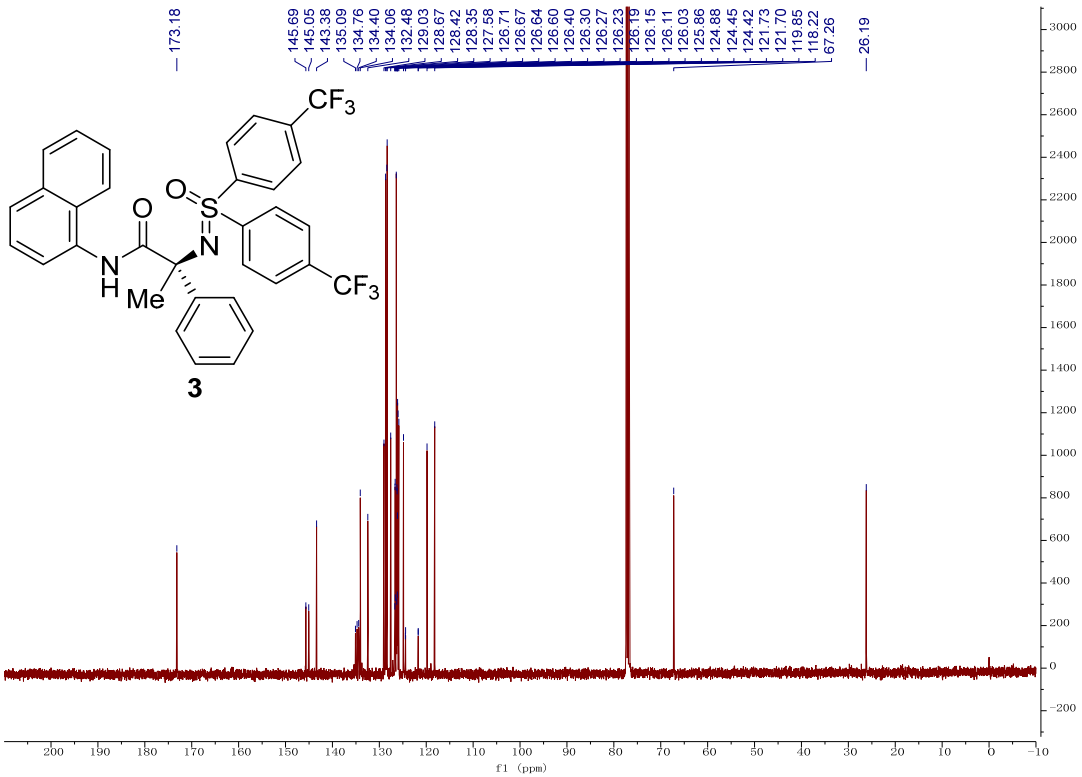
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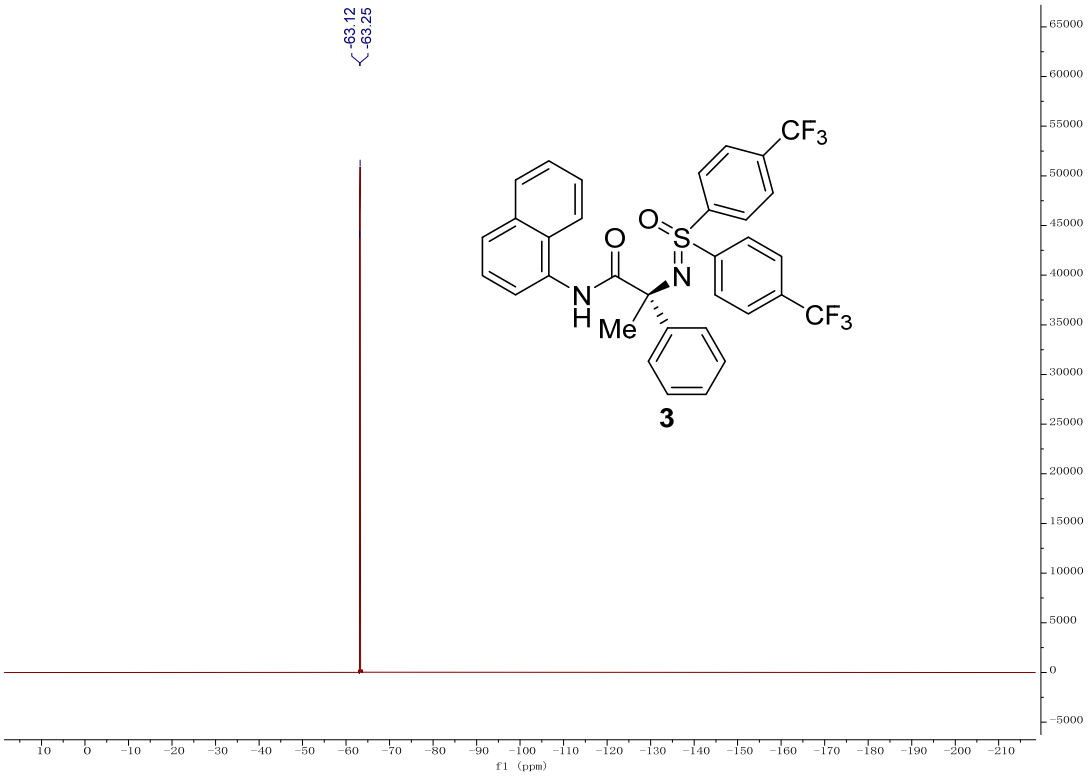
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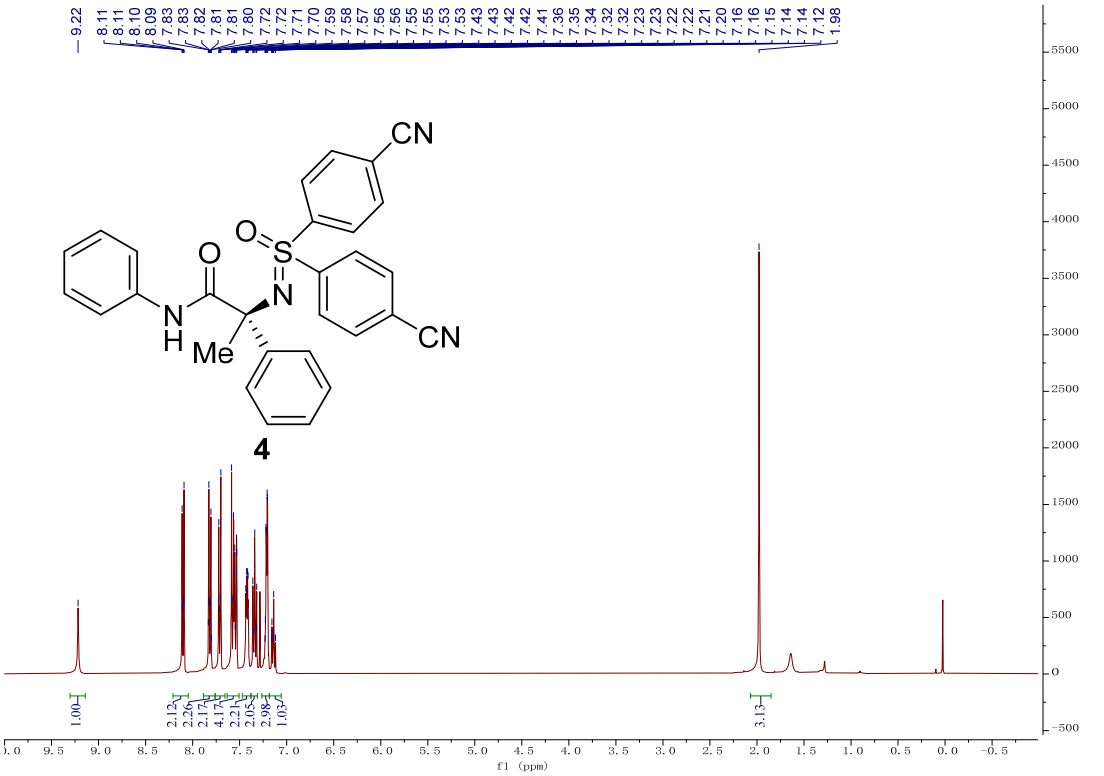
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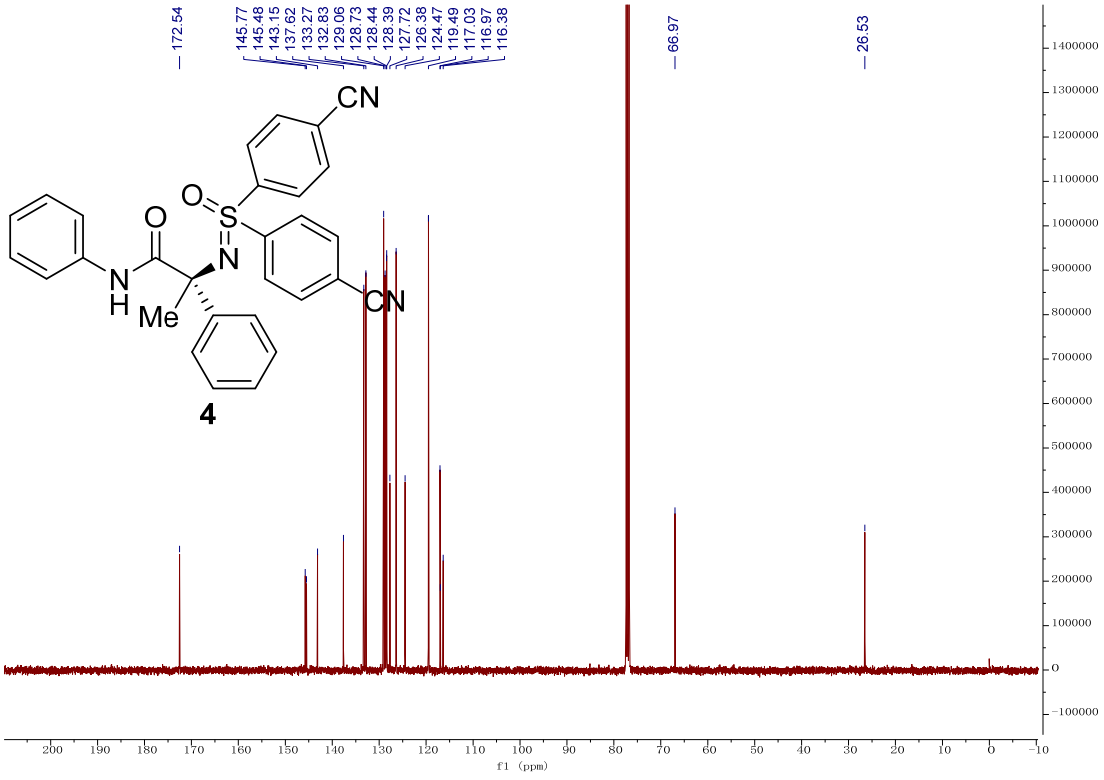
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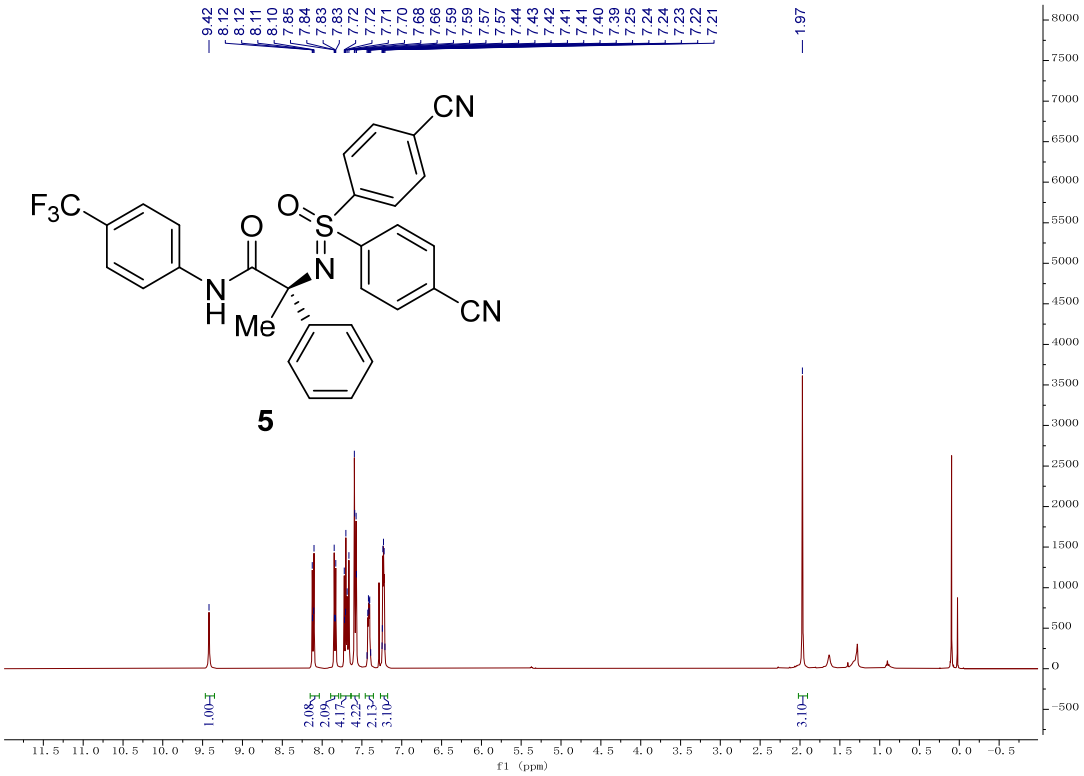
f1 (ppm)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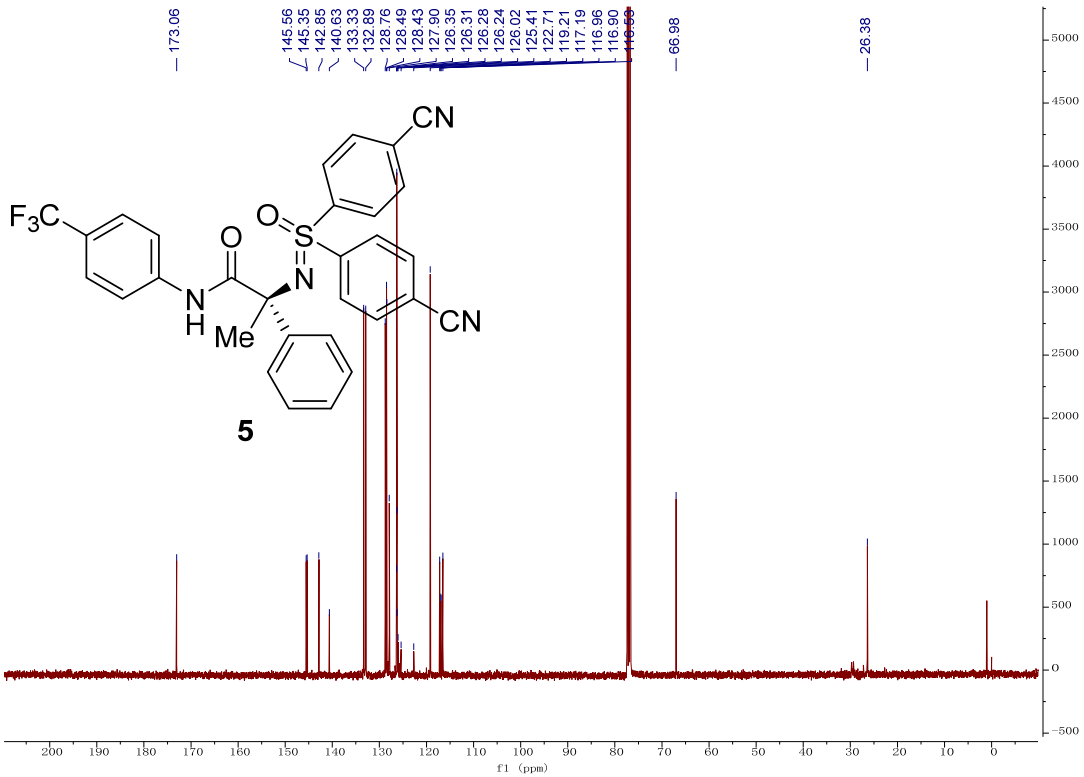
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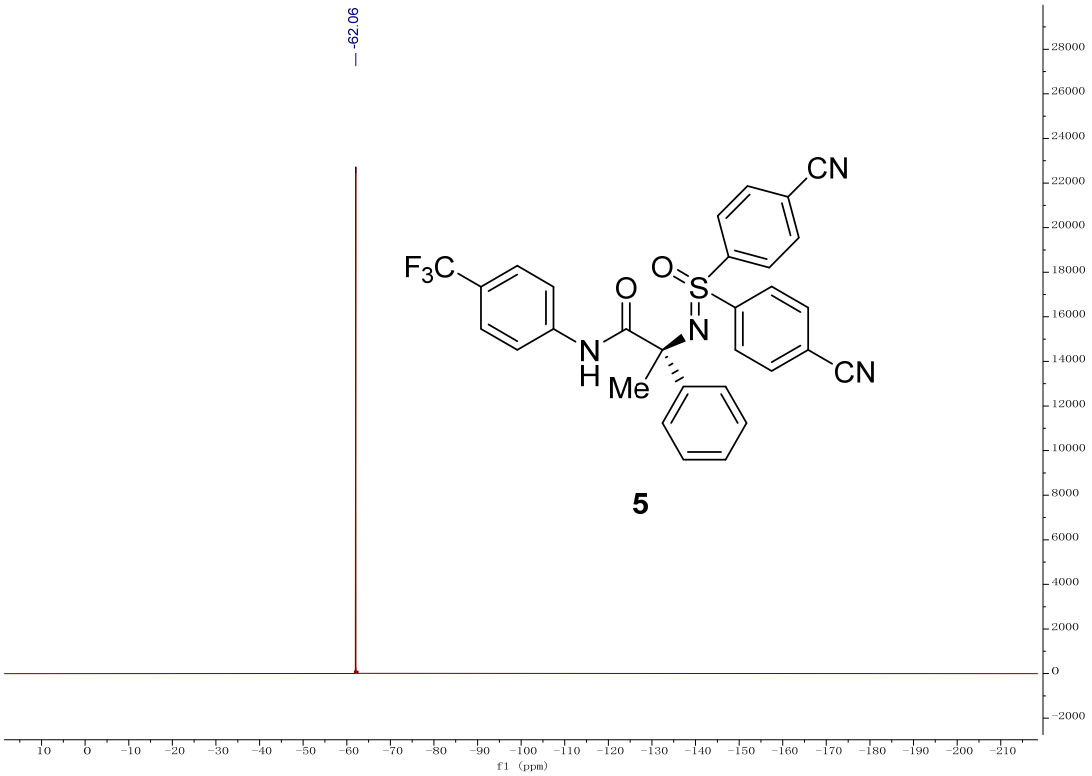
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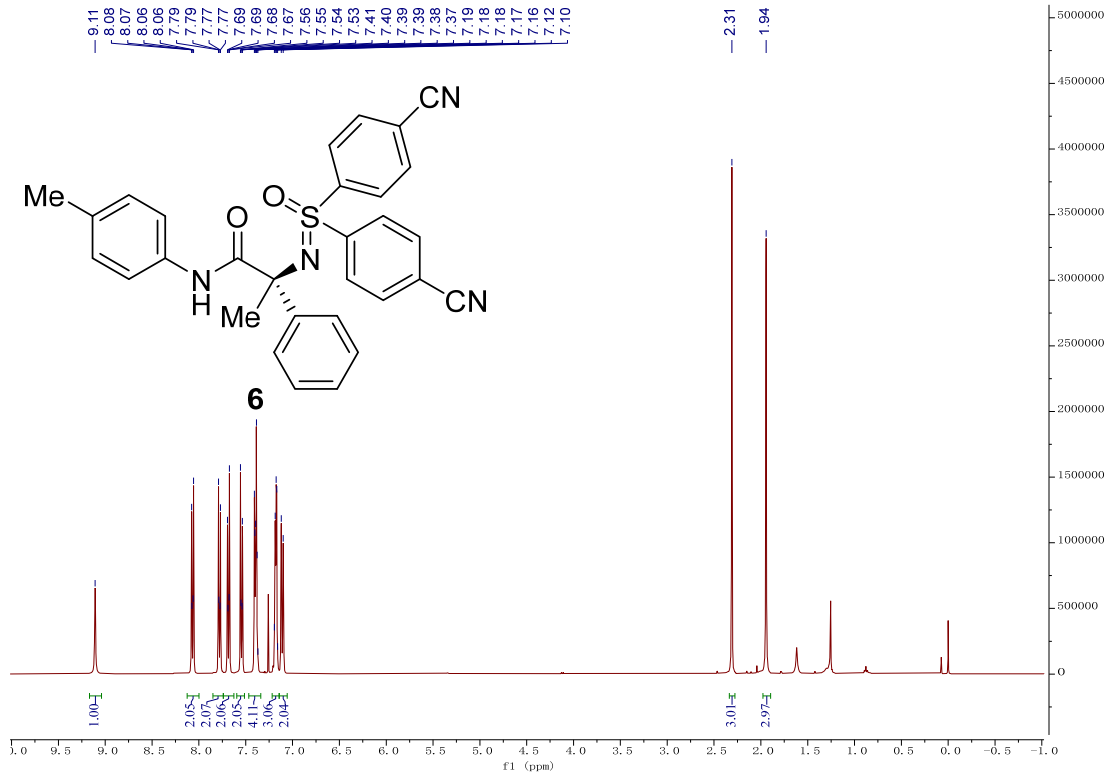
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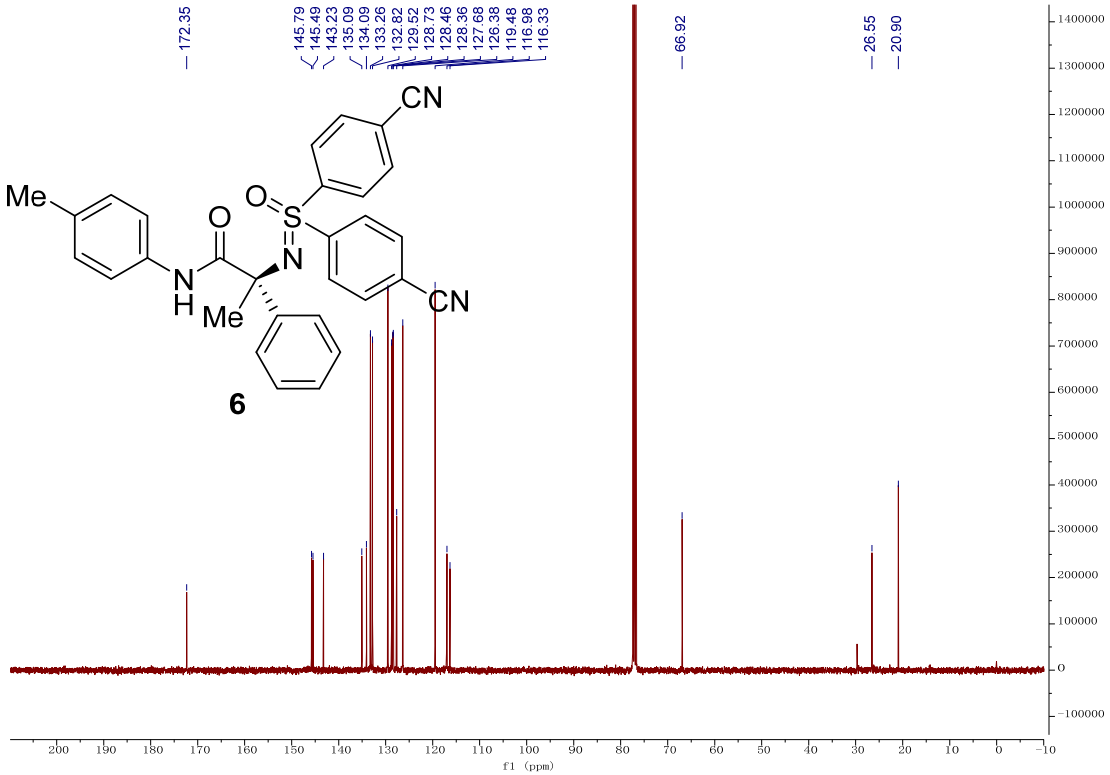
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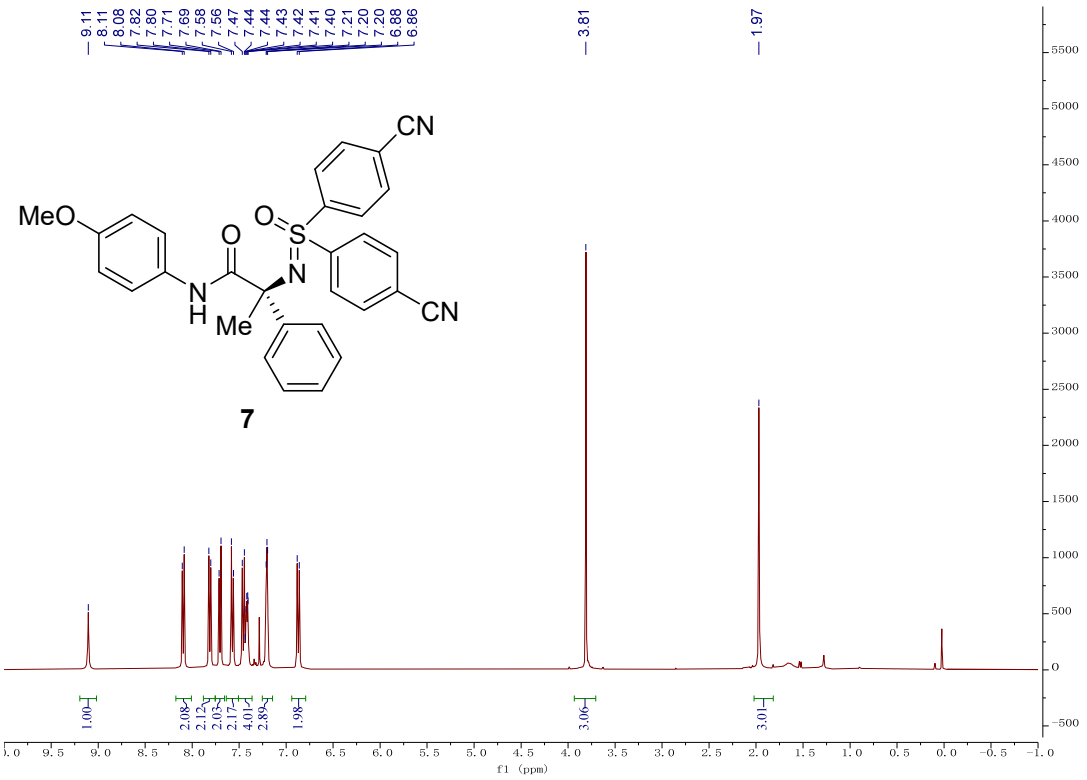
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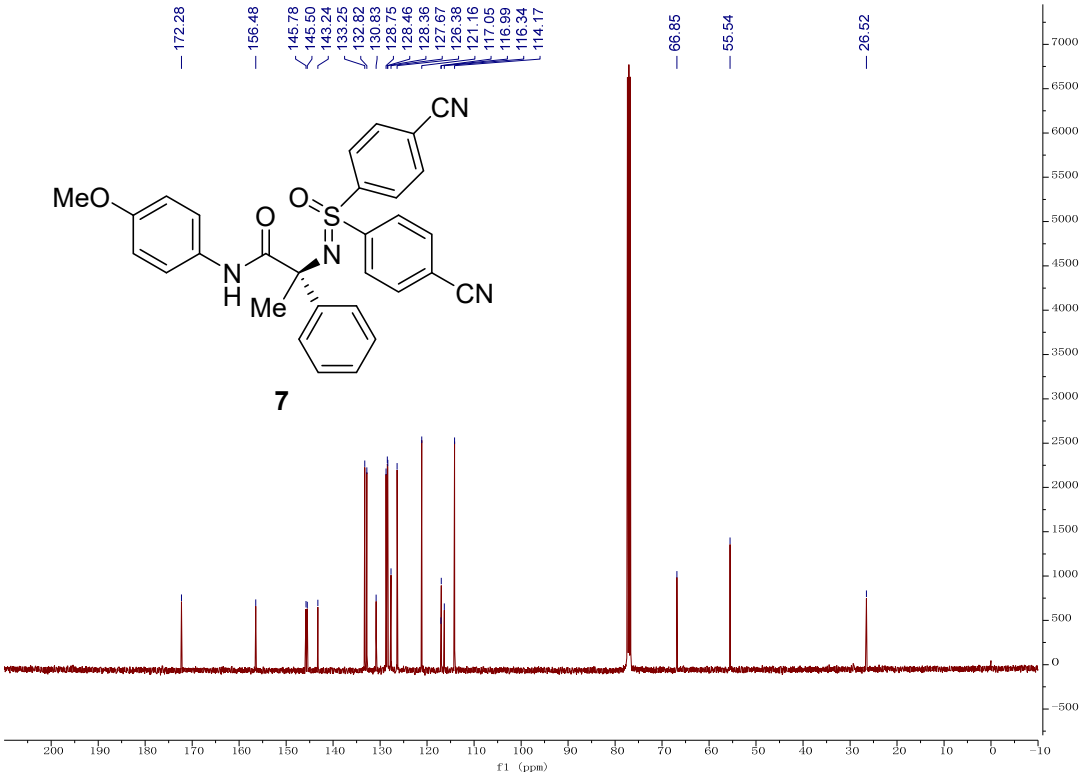
7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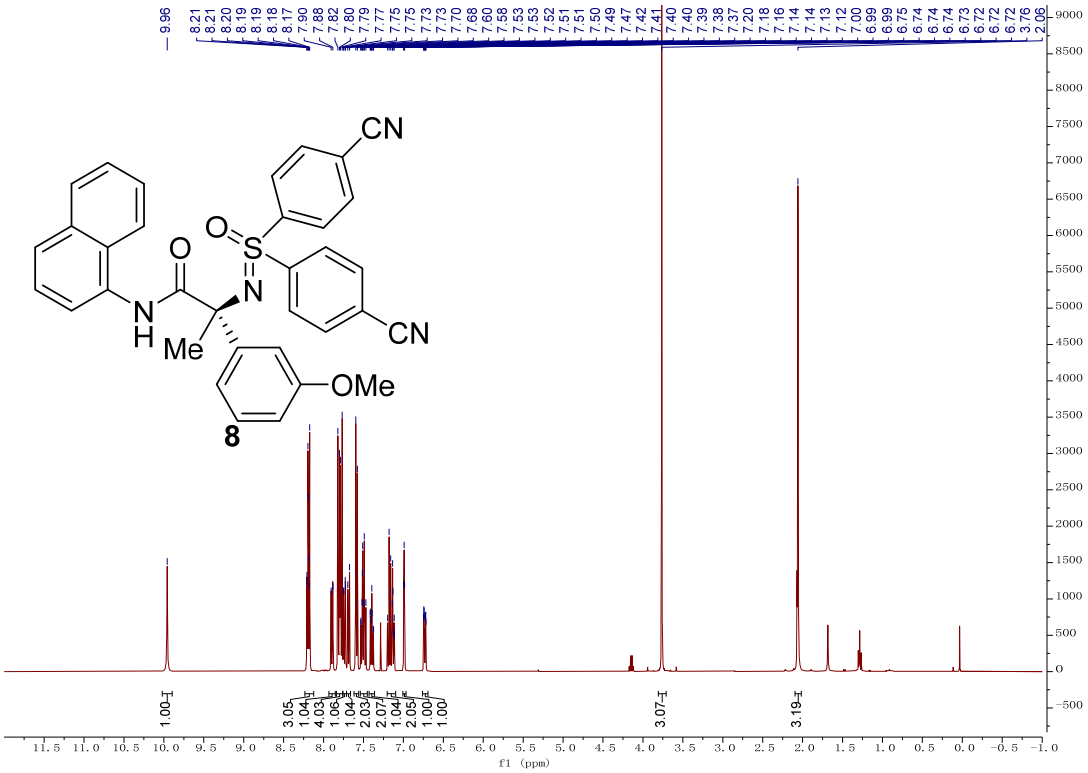
CN
f1 (ppm)

7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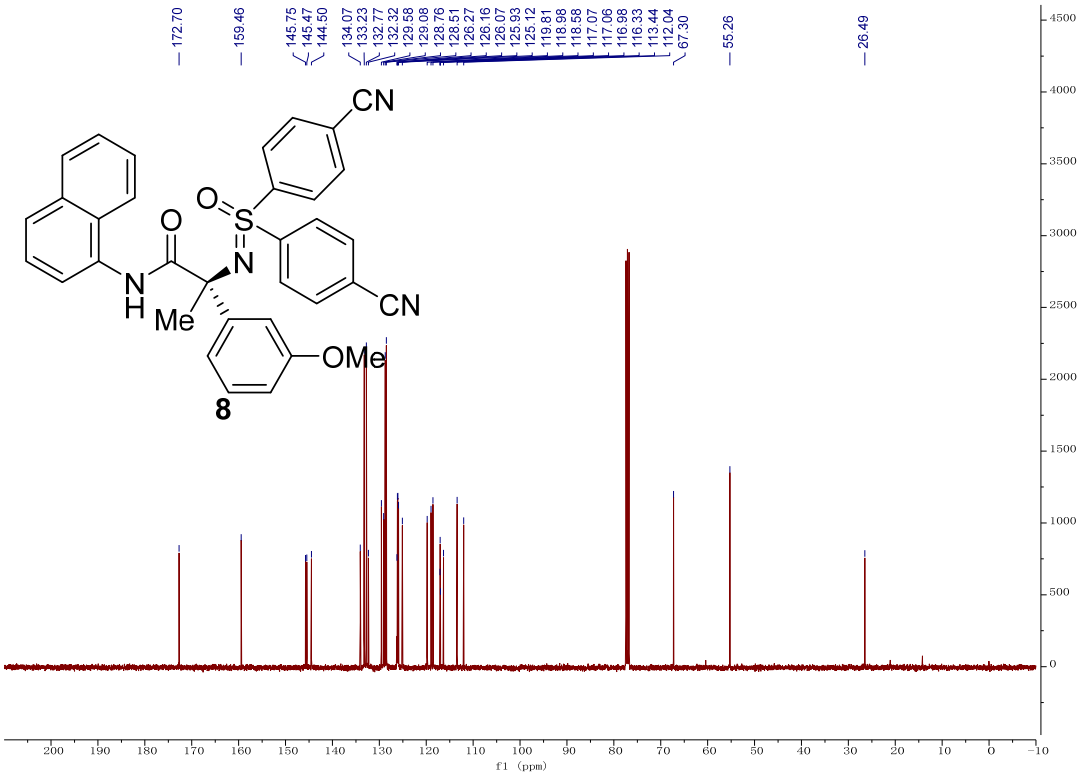
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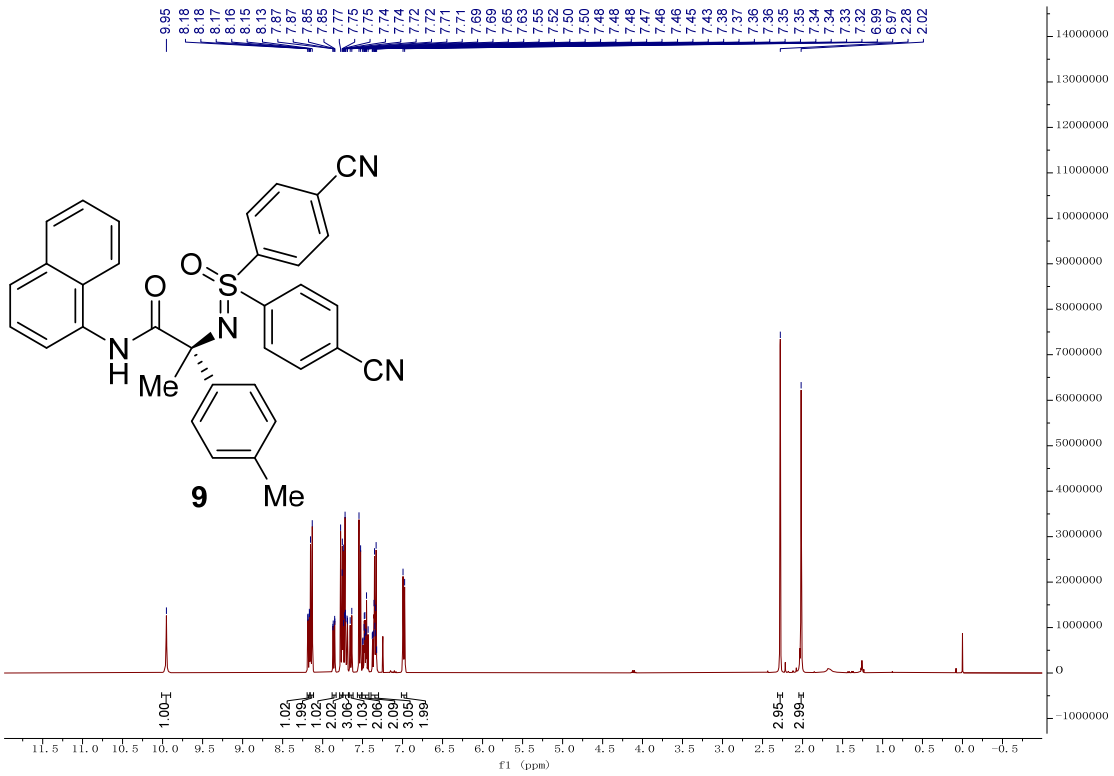
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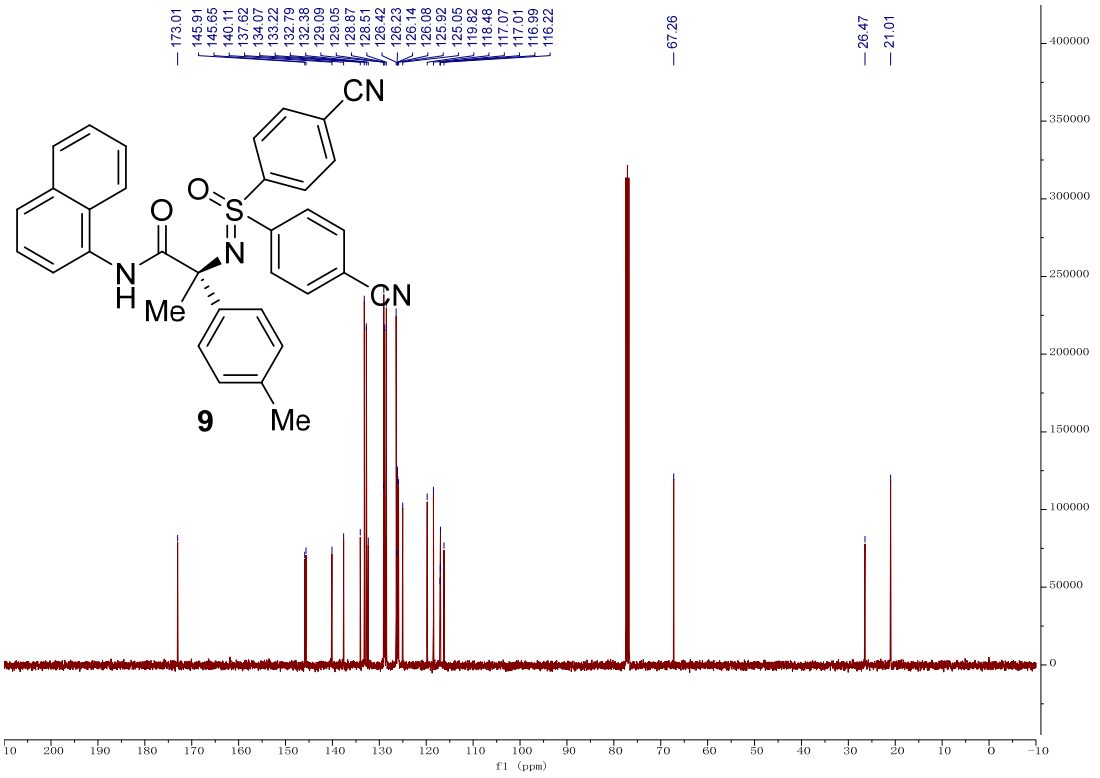
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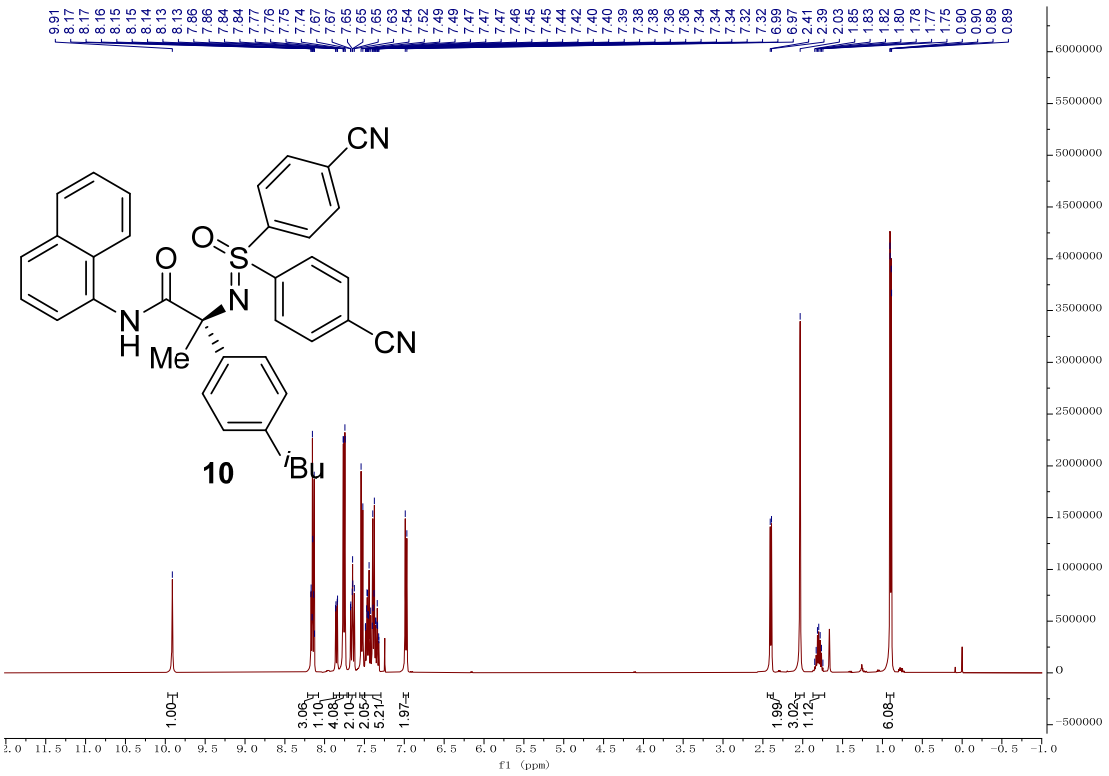
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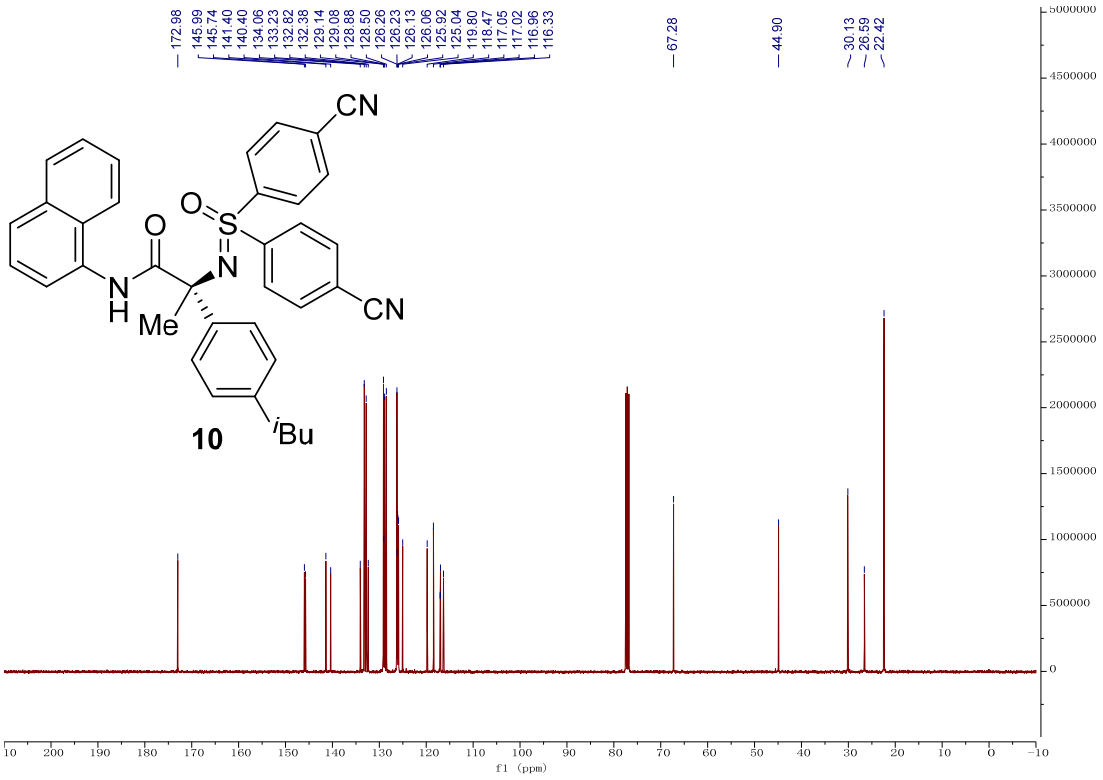
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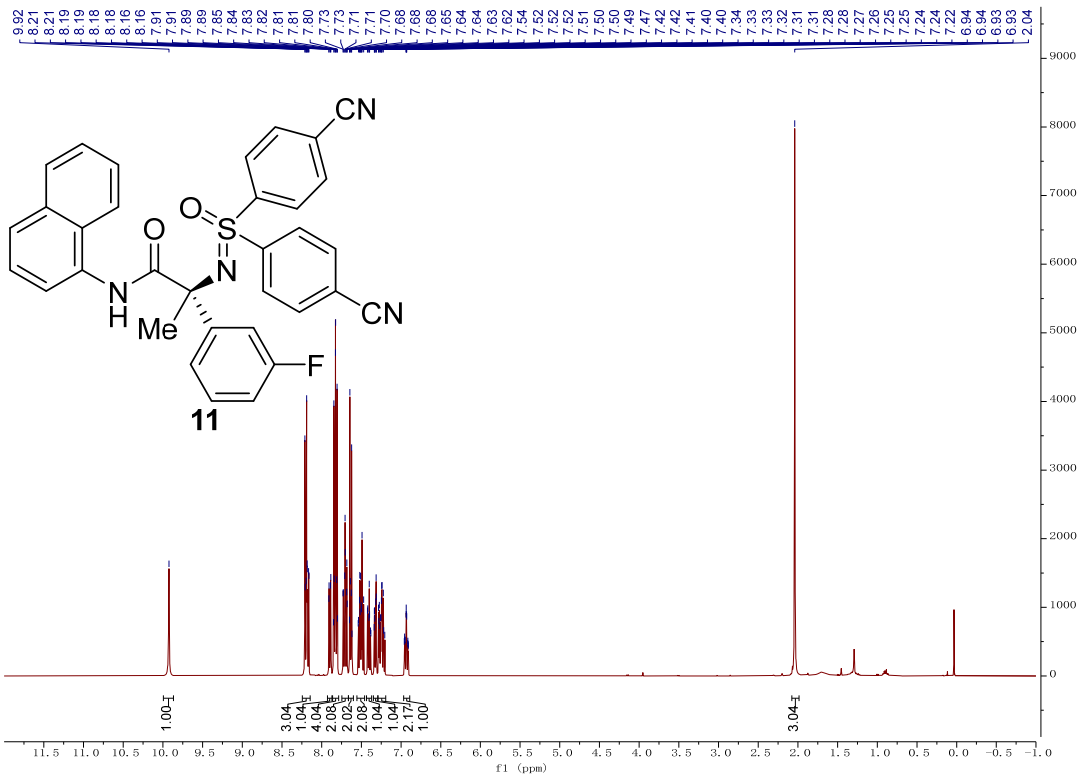
f1 (ppm)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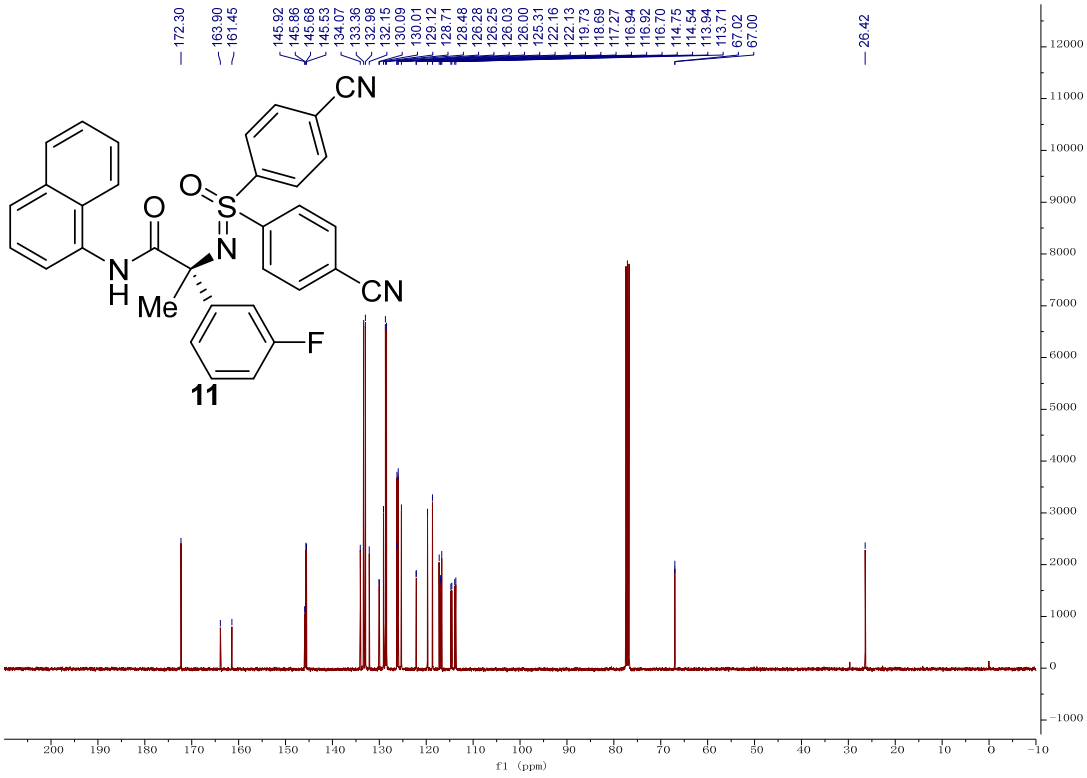
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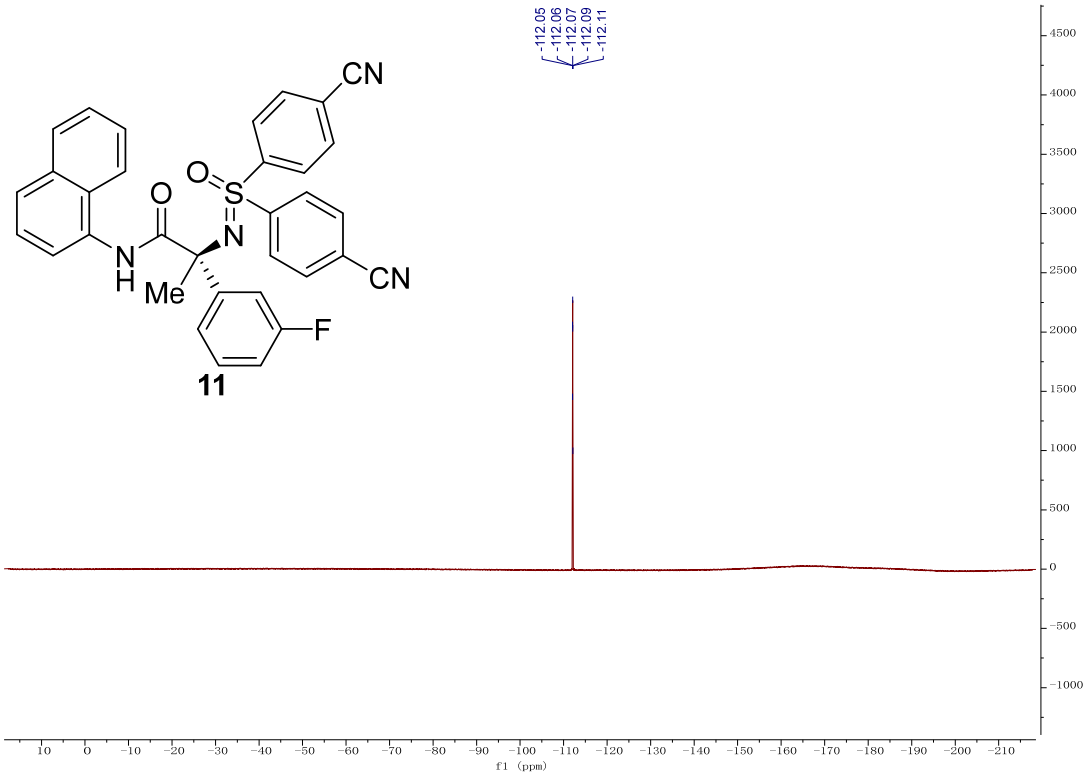
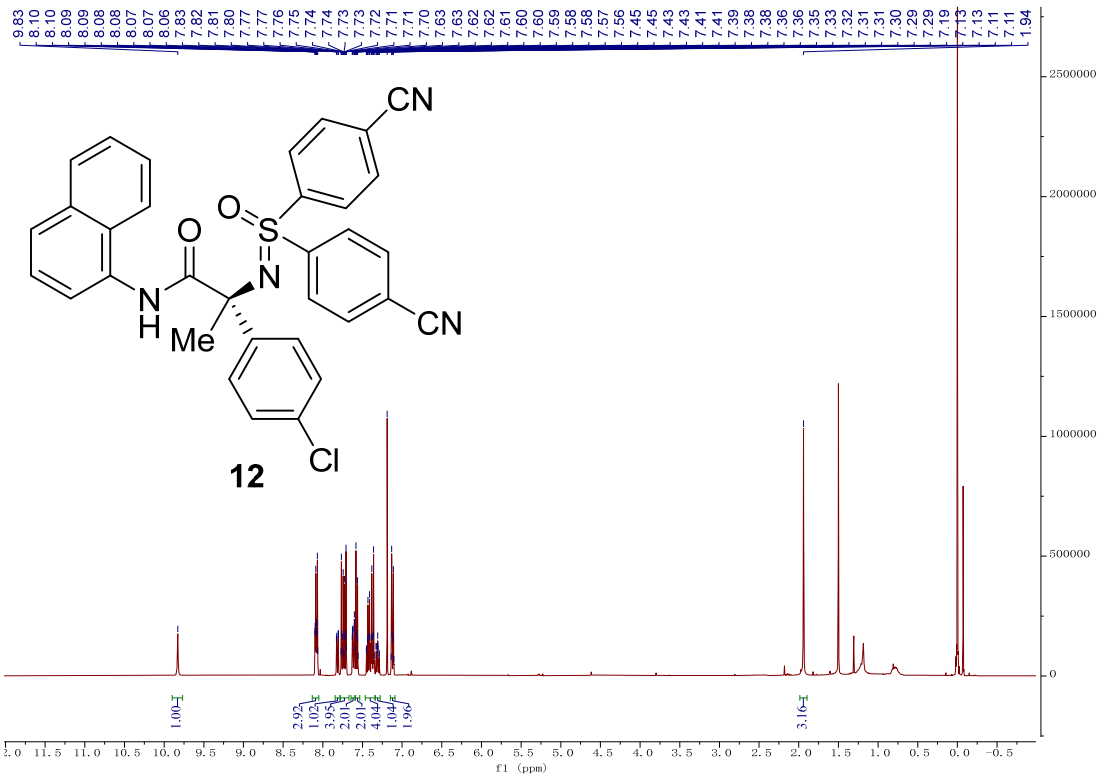
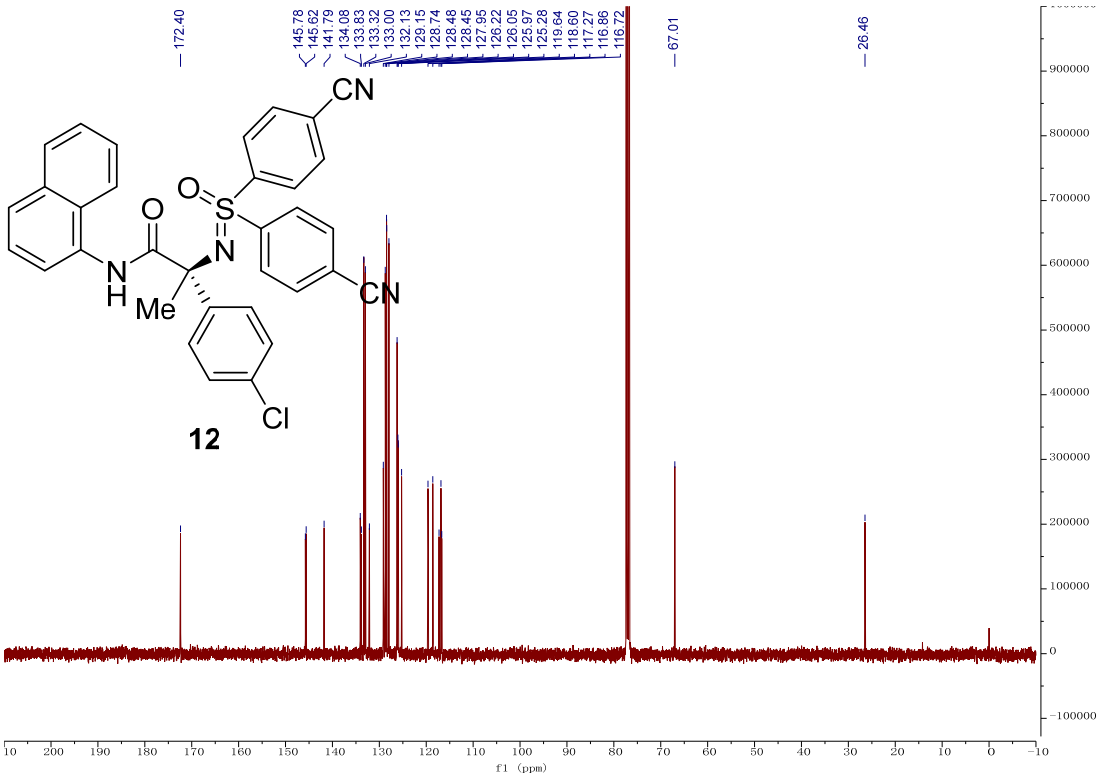
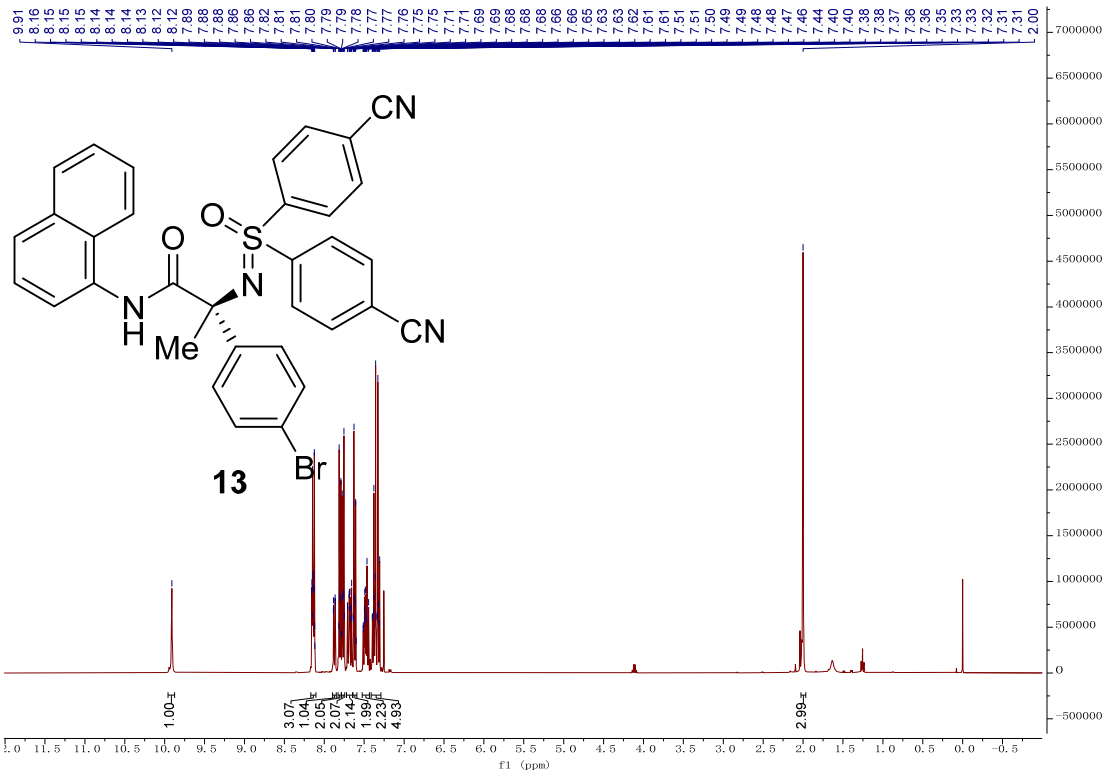
11
f1 (ppm)


-112.05
-112.06
-112.07
-112.09
-112.11
CN
CN
O
S
N
N
H
Me
F
11
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


9.83 8.10 8.10 8.09 8.09 8.08 8.08 8.07 8.07 8.06 7.83 7.82 7.81 7.80 7.77 7.77 7.76 7.75 7.74 7.74 7.73 7.73 7.72 7.71 7.71 7.70 7.63 7.63 7.62 7.62 7.61 7.60 7.60 7.59 7.58 7.58 7.57 7.56 7.45 7.45 7.43 7.43 7.41 7.41 7.39 7.38 7.38 7.36 7.36 7.35 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.19 7.13 7.13 7.11 7.11 1.94
CN
O
S
N
O
N
H
Me
CN
Cl
12
2500000
2000000
1500000
1000000
500000
0
1.00 2.92 1.02 3.95 2.01 2.01 4.04 1.04 1.96 3.16
f1 (ppm)


172.40
145.78 145.62 141.79 134.08 133.83 133.32 133.00 132.13 129.15 128.74 128.48 128.45 127.95 126.22 126.05 125.97 125.28 119.64 118.60 117.27 116.86 116.72
67.01
26.46
CN
O
S
N
O
N
H
Me
CN
Cl
12
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
f1 (ppm)


CN
O
S
N
O
N
H
Me
CN
Br
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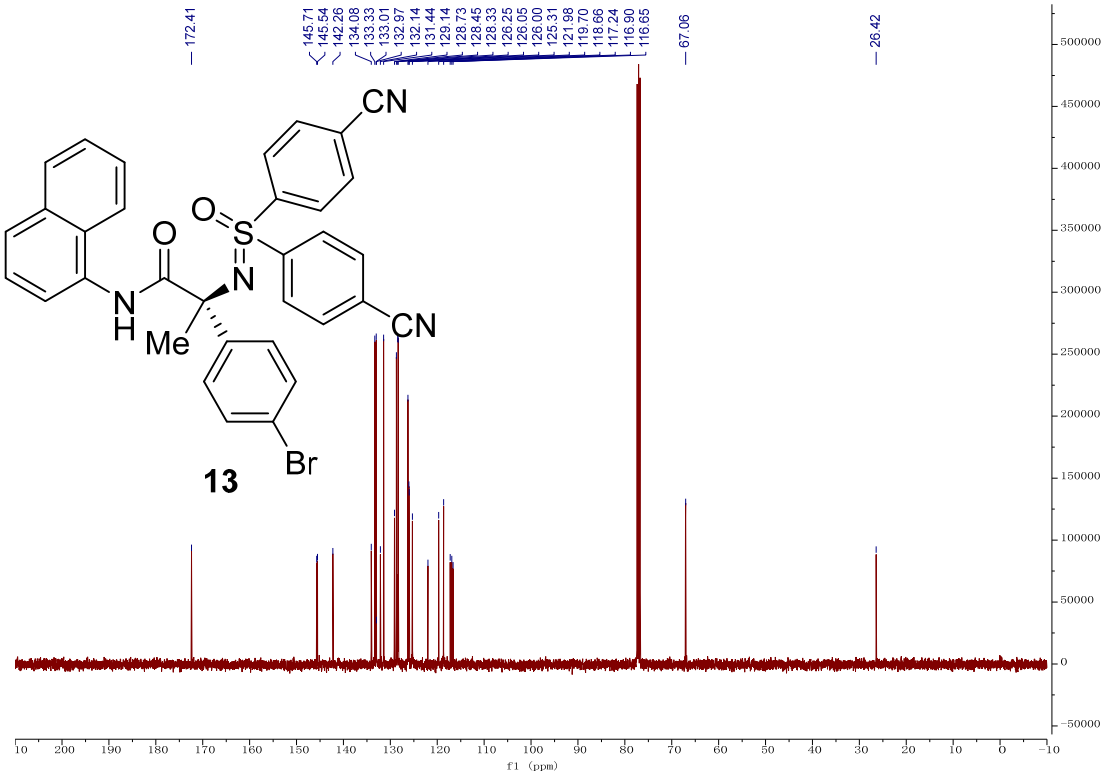
1.00
3.07
1.04
2.05
2.07
2.14
1.99
2.23
4.93
2.99
f1 (ppm)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145.54
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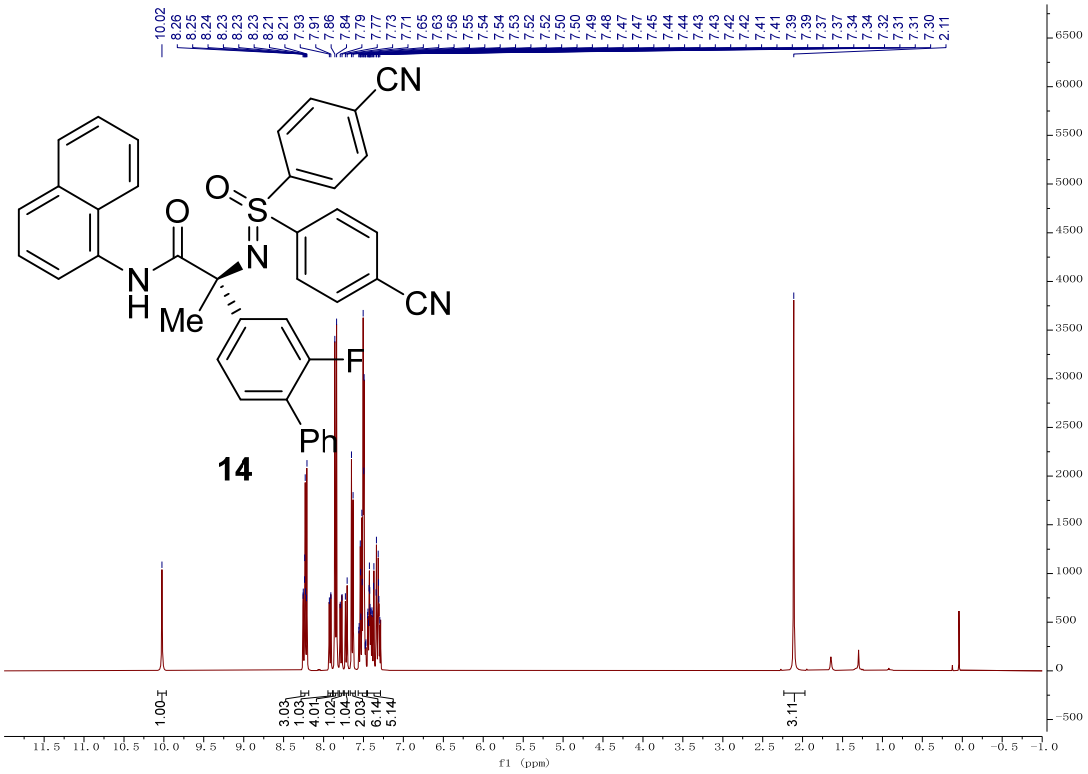
133.33
133.01
132.97
132.14
131.44
129.14
128.73
128.45
128.33
126.25
126.05
126.00
125.31
121.98
119.70
118.66
117.24
116.90
116.65
67.06
26.42
CN
O
S
N
O
N
H
Me
CN
Br
13
f1 (ppm)


10.02
8.26
8.25
8.24
8.23
8.23
8.23
8.21
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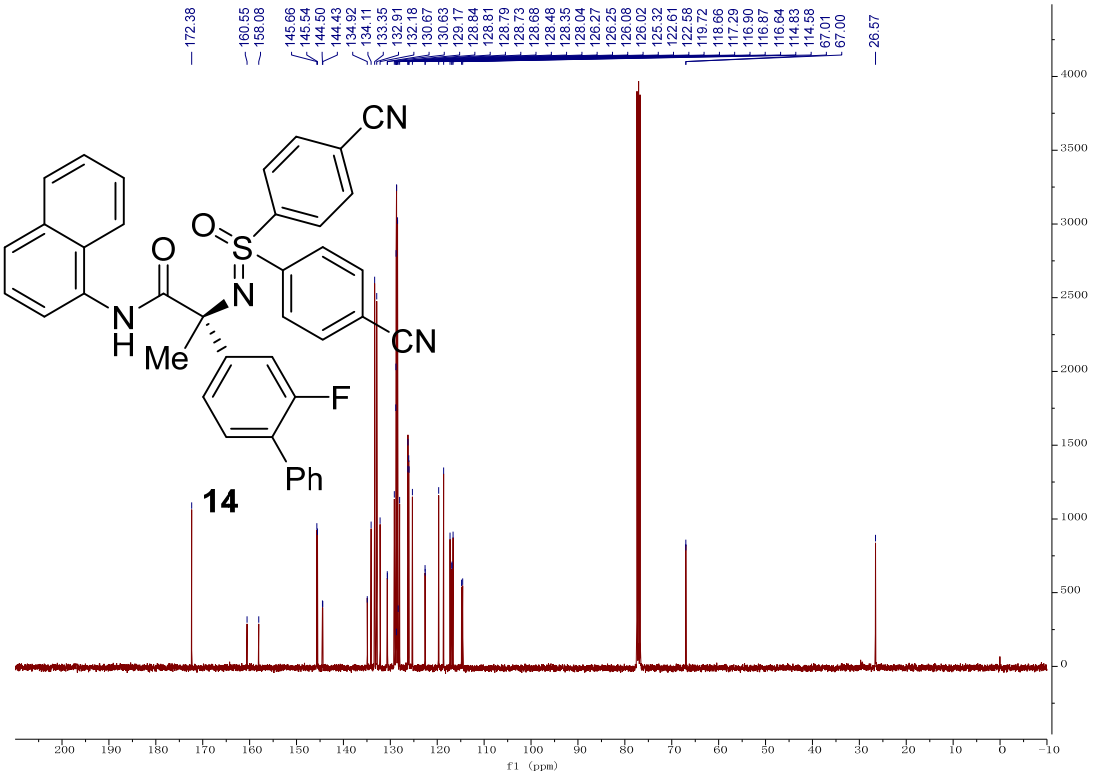
7.93
7.91
7.86
7.84
7.79
7.77
7.73
7.71
7.65
7.63
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.50
7.50
7.49
7.48
7.47
7.47
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.39
7.39
7.37
7.37
7.34
7.32
7.31
7.31
7.30
2.11
CN
O
S
N
O
N
H
Me
CN
F
Ph
14
1.00
3.03
1.03
4.01
1.02
1.04
2.03
6.14
5.14
3.11
f1 (ppm)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158.08
145.66
145.54
144.50
144.43
134.92
134.11
133.35
132.91
132.18
130.67
130.63
129.17
128.84
128.81
128.79
128.73
128.68
128.48
128.35
128.04
126.27
126.25
126.08
126.02
125.32
122.61
122.58
119.72
118.66
117.29
116.90
116.87
116.64
114.83
114.58
67.01
67.00
26.57
CN
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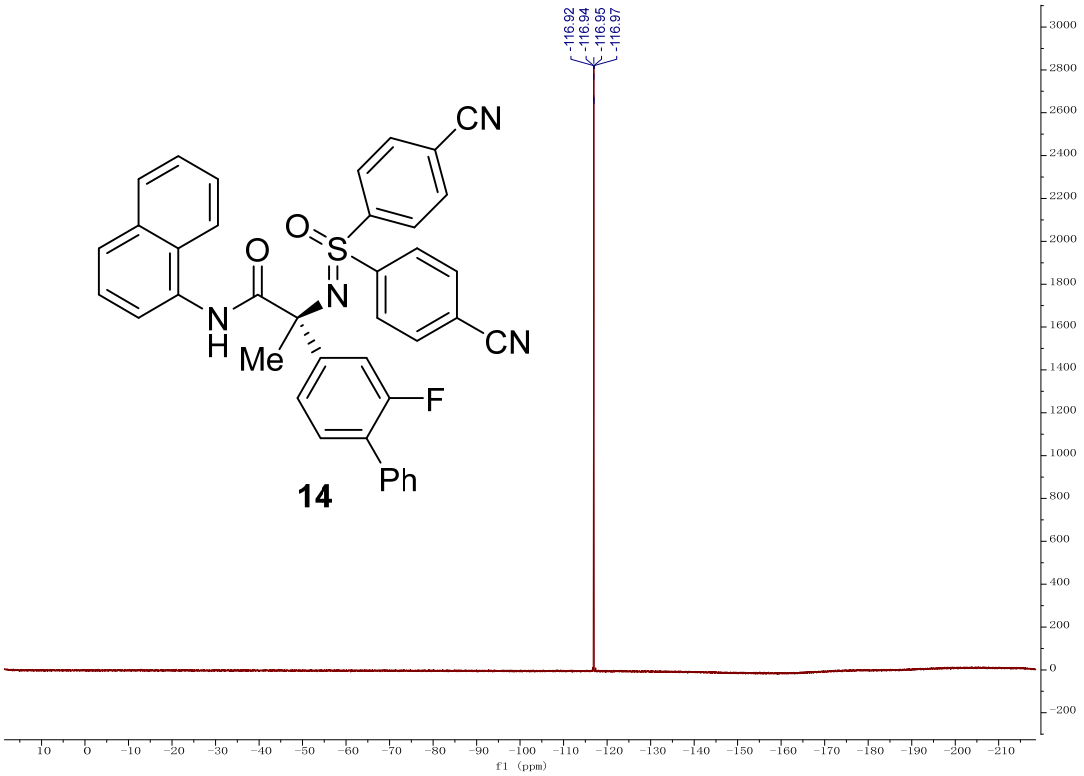
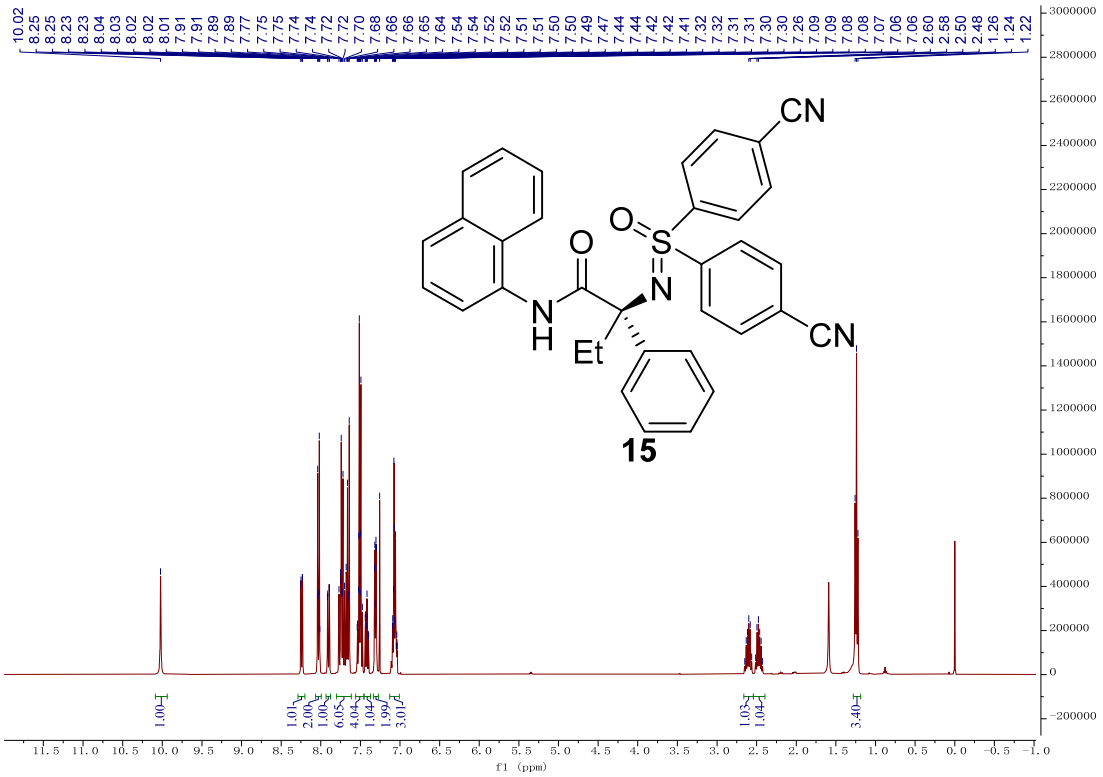
S
N
O
N
H
Me
CN
F
Ph
14
f1 (ppm)


-116.92
-116.94
-116.95
-116.97
CN
O
S
N
O
N
H
Me
CN
F
Ph
14
f1 (ppm)


CN
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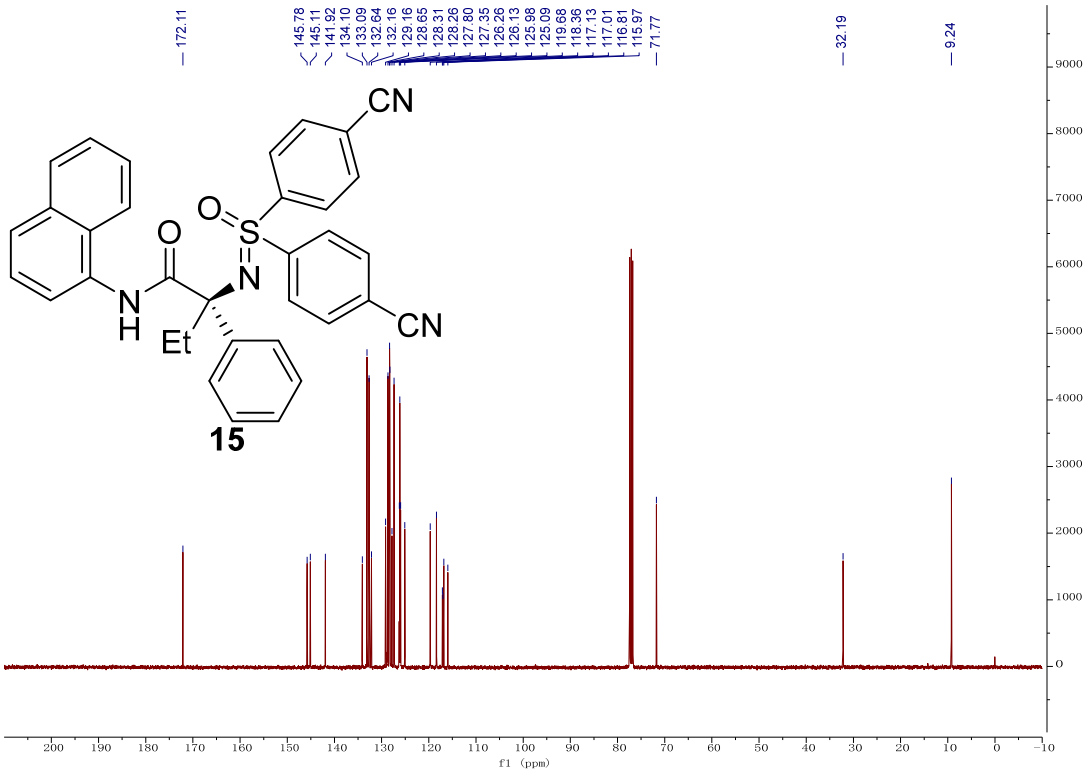
S
N
O
N
H
Et
CN
15
f1 (ppm)


CN
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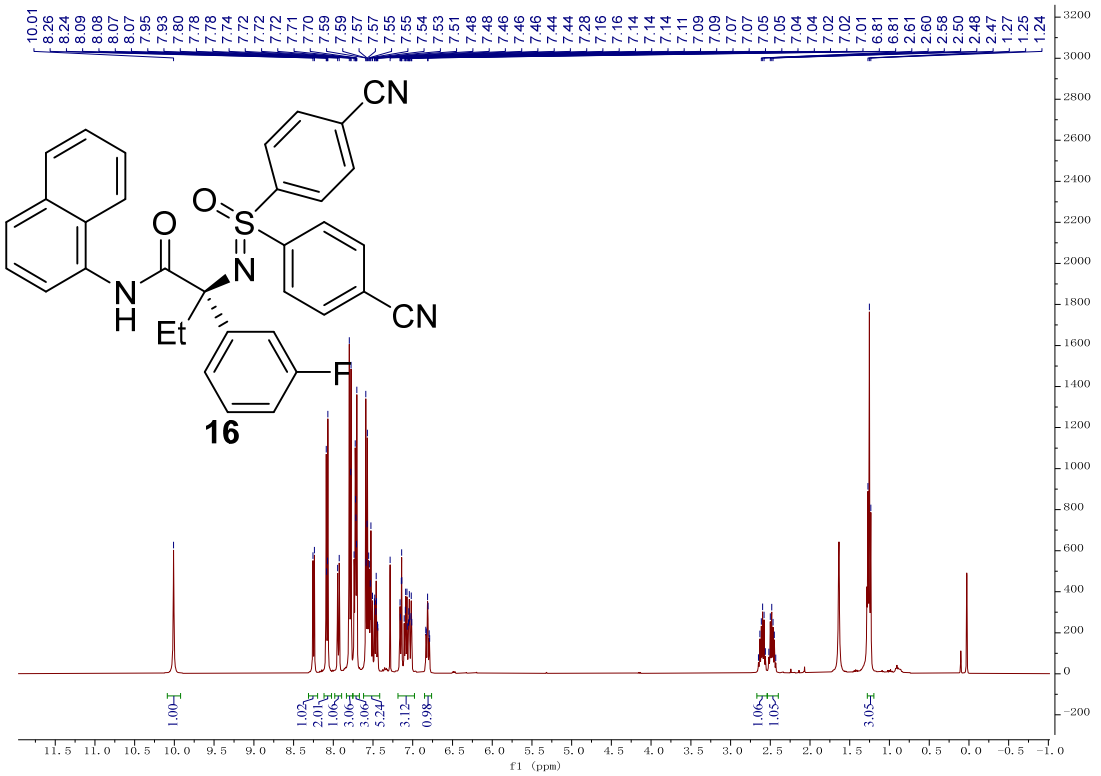
S
N
O
N
H
Et
CN
15
f1 (ppm)


CN
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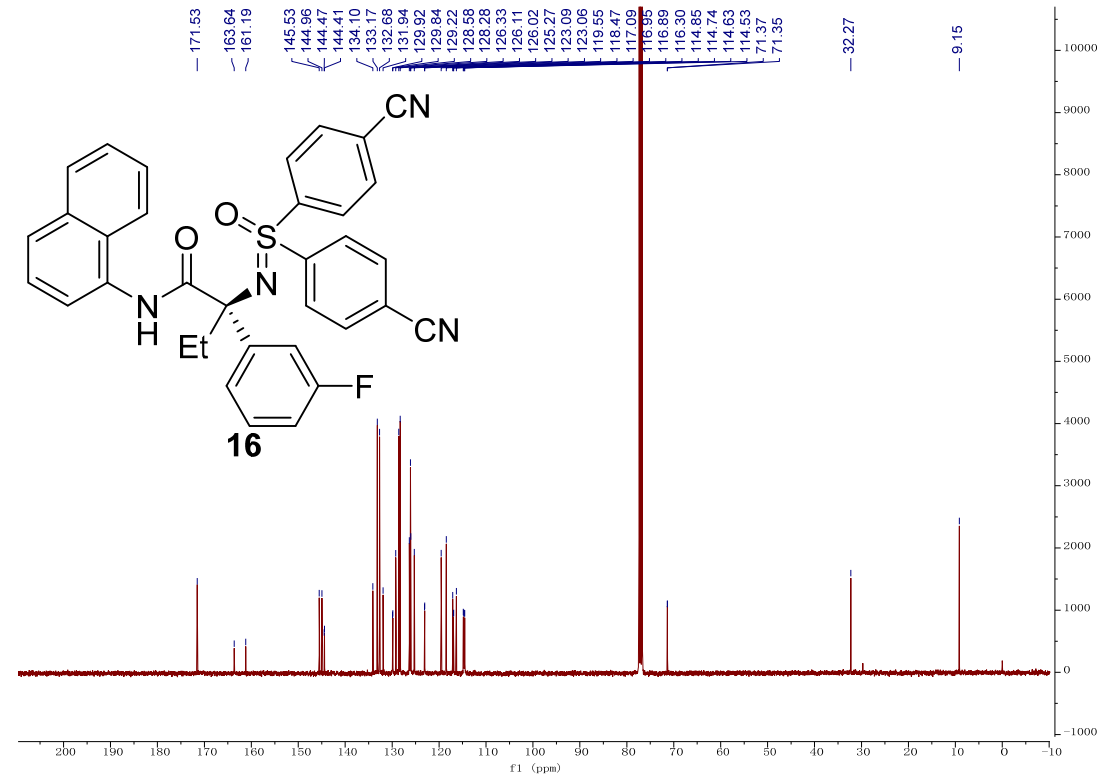
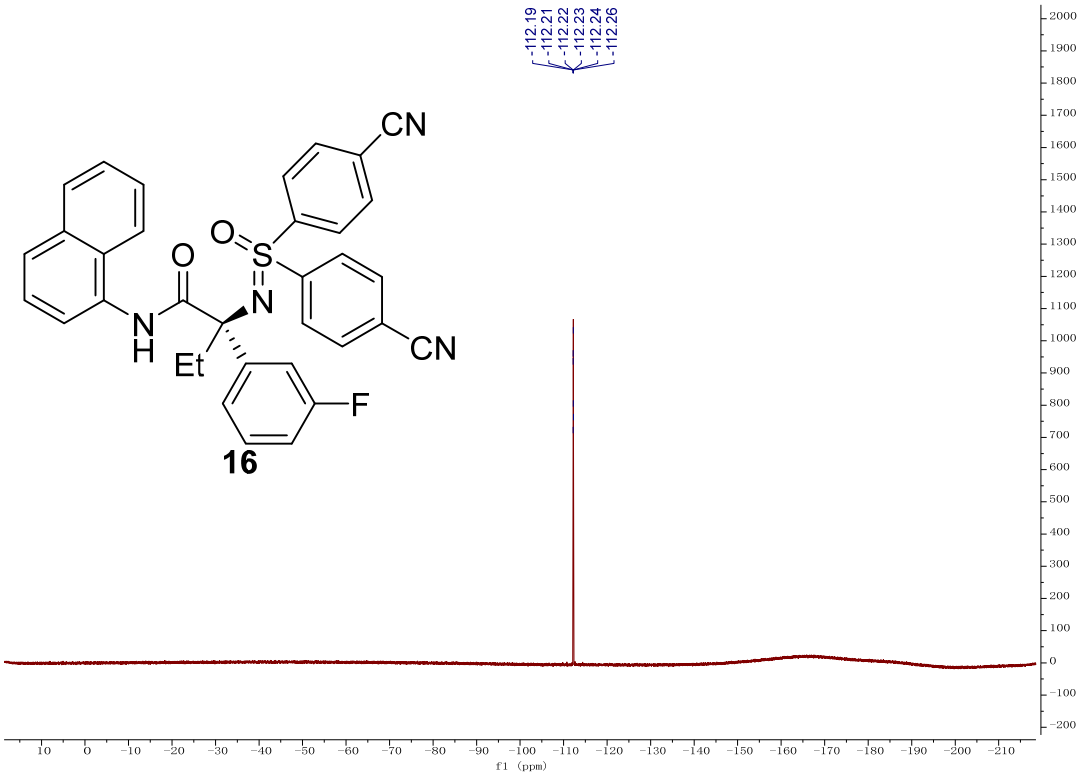
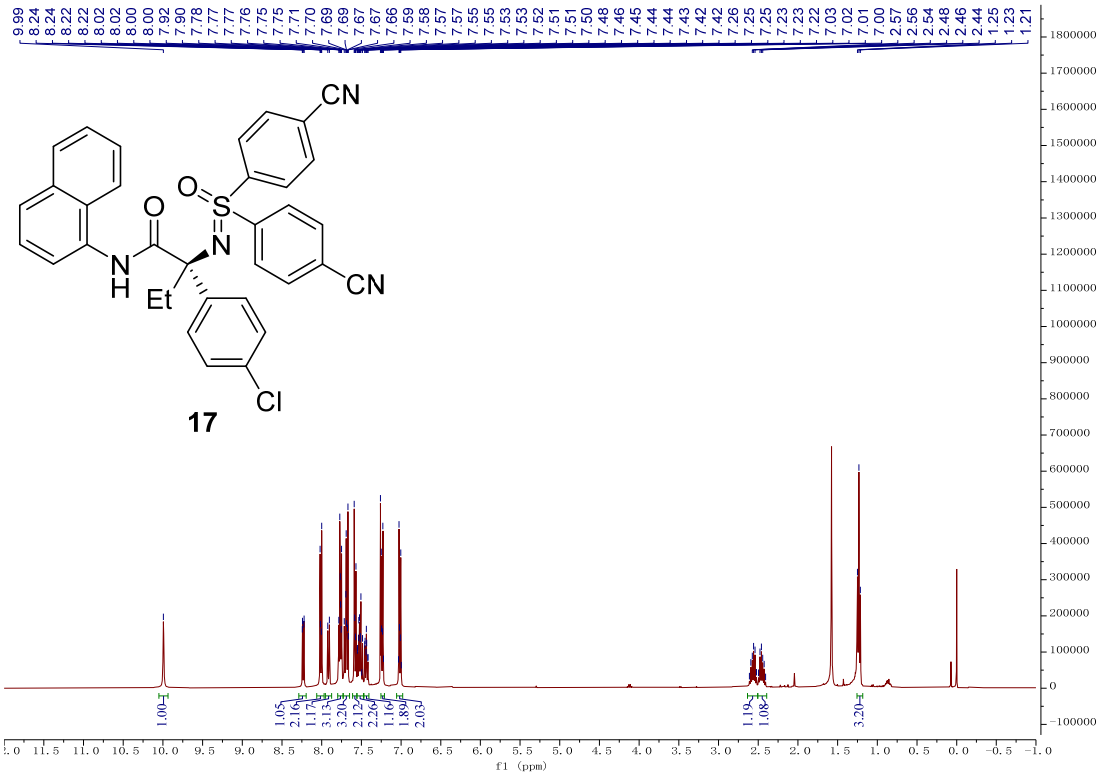
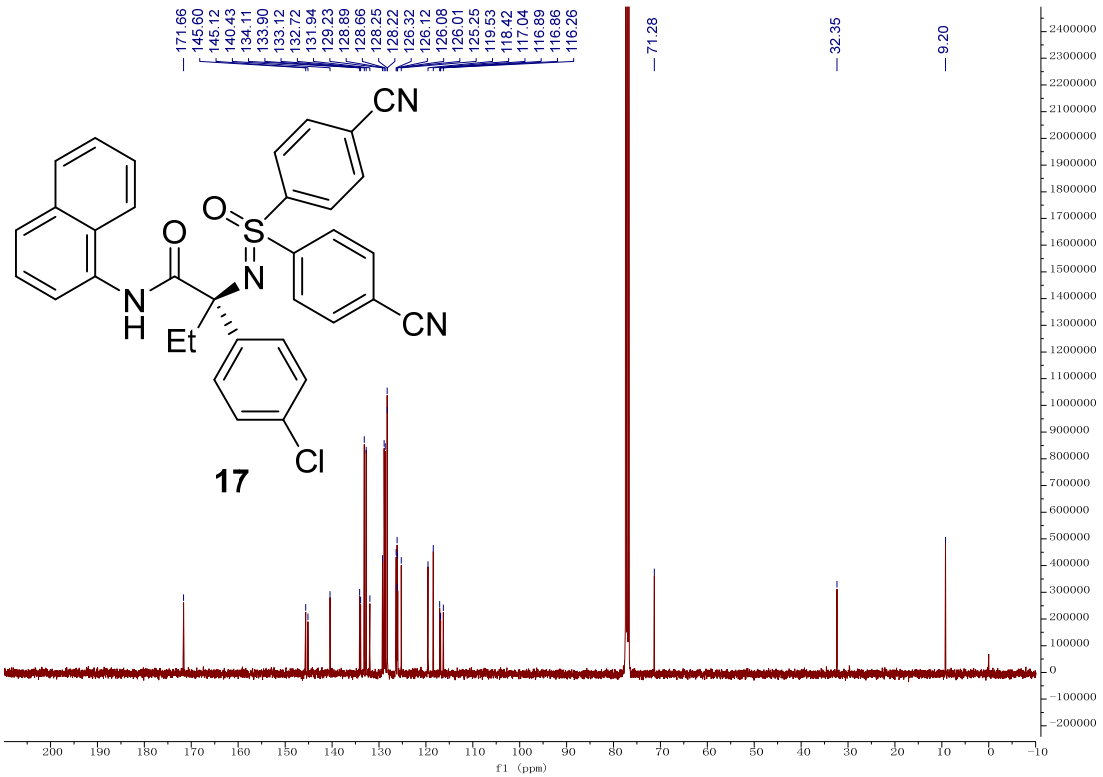
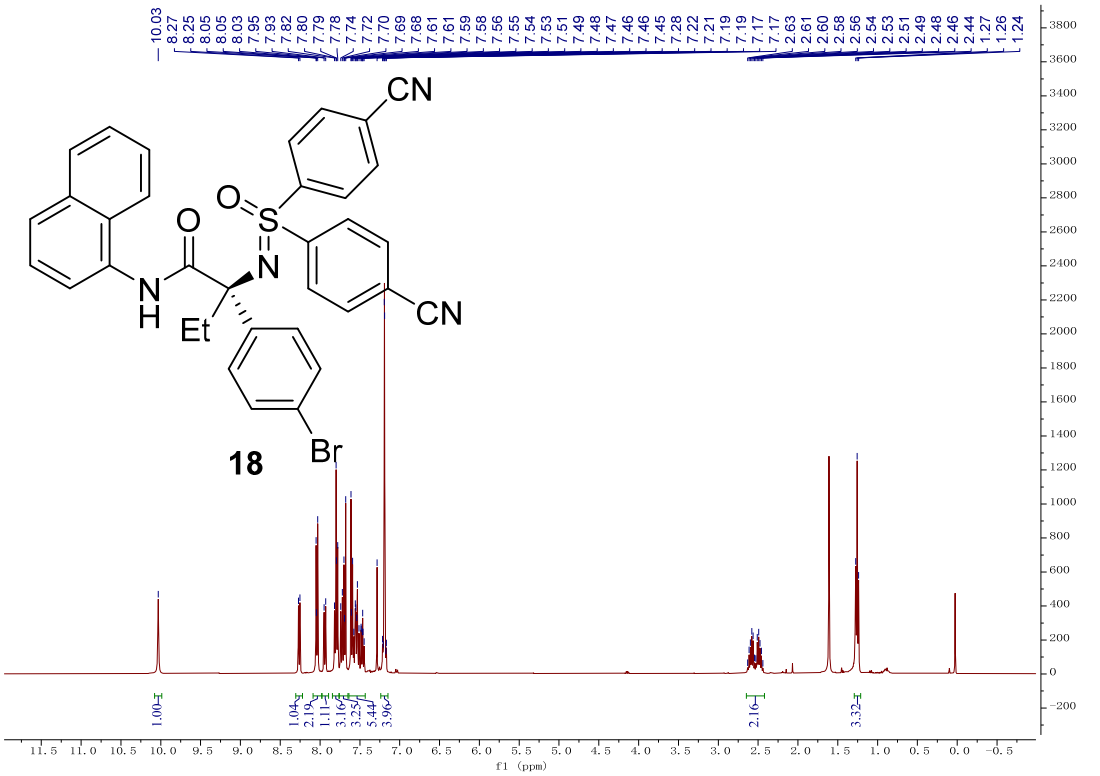
S
N
O
N
H
Et
CN
F
16
f1 (ppm)


CN
O
S
N
O
N
H
Et
CN
F
16
f1 (ppm)


-112.19
-112.21
-112.22
-112.23
-112.24
-112.26
CN
O
S
O
N
N
H
Et
CN
F
16
f1 (ppm)


9.99 8.24 8.24 8.22 8.22 8.02 8.02 8.00 8.00 7.92 7.90 7.78 7.77 7.77 7.76 7.75 7.75 7.71 7.70 7.69 7.69 7.67 7.67 7.66 7.59 7.58 7.57 7.57 7.55 7.55 7.53 7.53 7.52 7.51 7.51 7.50 7.48 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.26 7.25 7.25 7.23 7.23 7.22 7.03 7.02 7.01 7.00 2.57 2.56 2.54 2.48 2.46 2.44 1.25 1.23 1.21
CN
O
S
N
O
N
H
Et
CN
Cl
17
1.00 1.05 2.16 1.17 3.15 3.20 2.12 2.26 1.16 1.89 2.03 1.19 1.08 3.20
f1 (ppm)


171.66 145.60 145.12 140.43 134.11 133.90 133.12 132.72 131.94 129.23 128.89 128.66 128.25 128.22 126.32 126.12 126.08 126.01 125.25 119.53 118.42 117.04 116.89 116.86 116.26
71.28
32.35
9.20
CN
O
S
N
O
N
H
Et
CN
Cl
17
f1 (ppm)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8.05
8.03
7.95
7.93
7.82
7.80
7.79
7.78
7.74
7.72
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7.69
7.68
7.61
7.61
7.59
7.58
7.56
7.55
7.54
7.53
7.51
7.49
7.48
7.47
7.46
7.46
7.45
7.28
7.22
7.21
7.19
7.19
7.17
7.17
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2.61
2.60
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2.54
2.53
2.51
2.49
2.48
2.46
2.44
1.27
1.26
1.24
CN
O
S
N
O
N
H
Et
CN
Br
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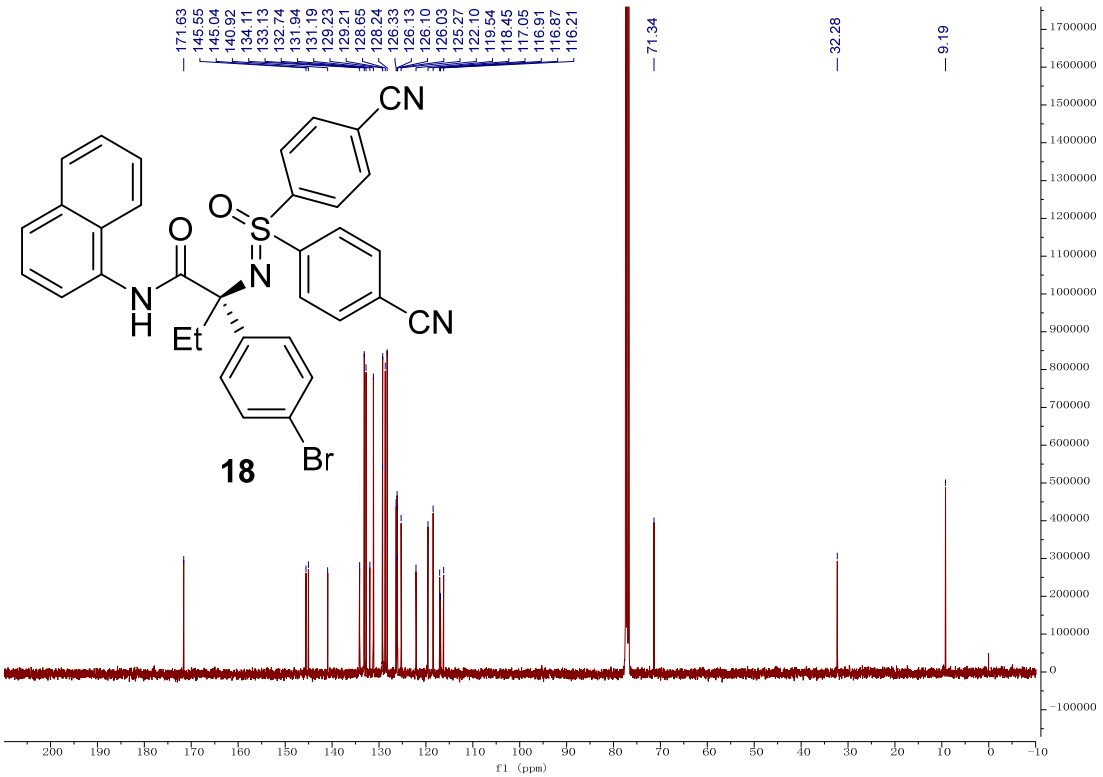
1.00
1.04
2.19
1.11
3.16
3.25
5.44
3.96
2.16
3.32
f1 (ppm)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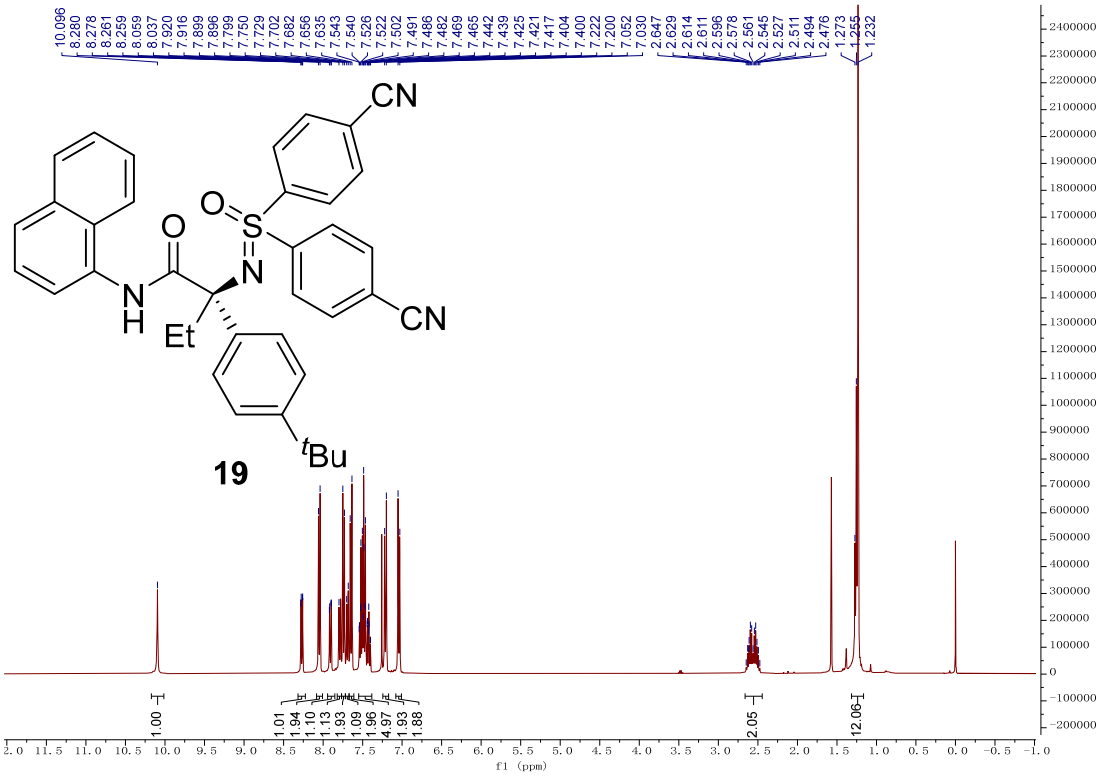
145.04
140.92
134.11
133.13
132.74
131.94
131.19
129.23
129.21
128.65
128.24
126.33
126.13
126.10
126.03
125.27
122.10
119.54
118.45
117.05
116.91
116.87
116.21
71.34
32.28
9.19
CN
O
S
N
O
N
H
Et
CN
Br
18
f1 (ppm)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7.899
7.896
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7.750
7.729
7.702
7.682
7.656
7.635
7.543
7.540
7.526
7.522
7.502
7.491
7.486
7.482
7.469
7.465
7.442
7.439
7.425
7.421
7.417
7.404
7.400
7.222
7.200
7.052
7.030
2.647
2.629
2.614
2.611
2.596
2.578
2.561
2.545
2.527
2.511
2.494
2.476
1.273
1.255
1.232
CN
O
S
N
O
N
H
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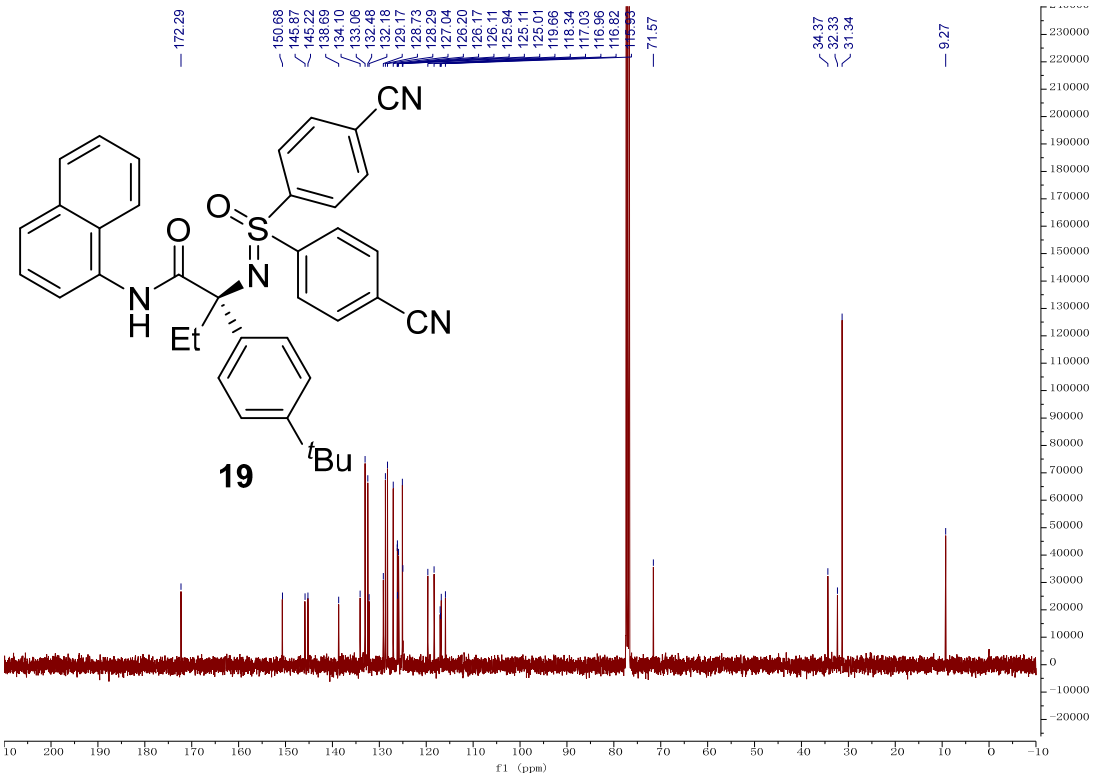
1.93
1.88
2.05
12.06
f1 (ppm)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129.17
128.73
128.29
127.04
126.20
126.17
126.11
125.94
125.11
125.01
119.66
118.34
117.03
116.96
116.82
116.68
71.57
34.37
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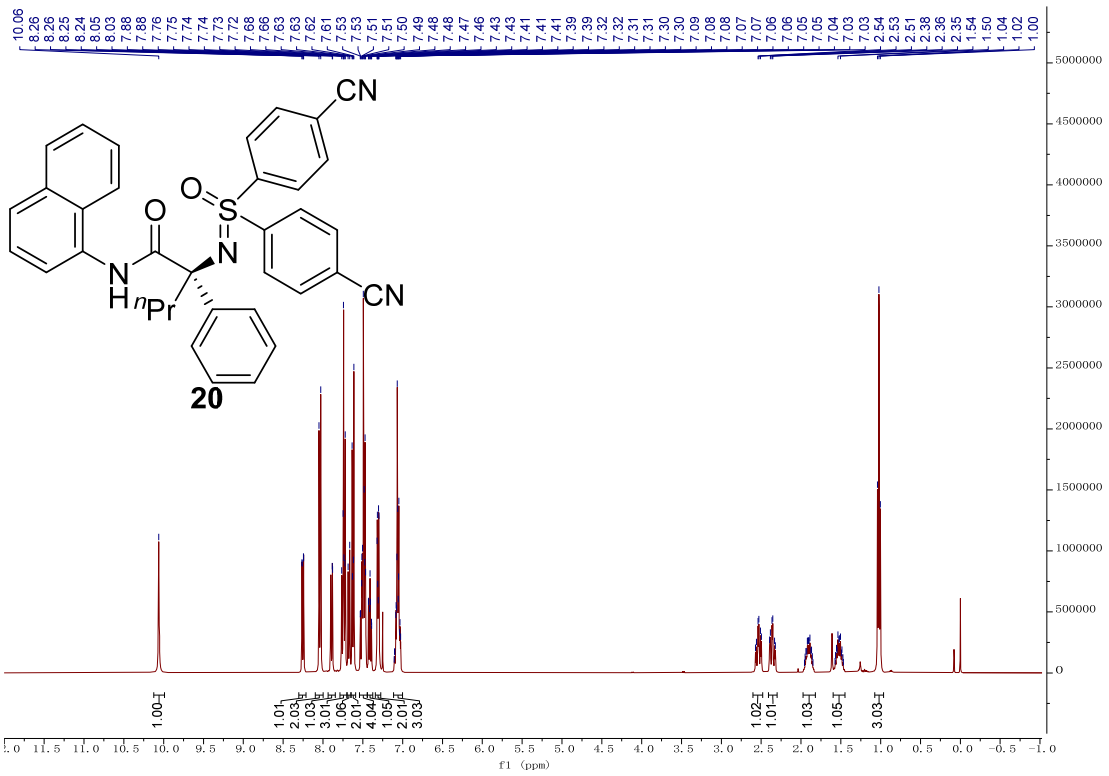
O
N
H
Et
CN
tBu
19
f1 (ppm)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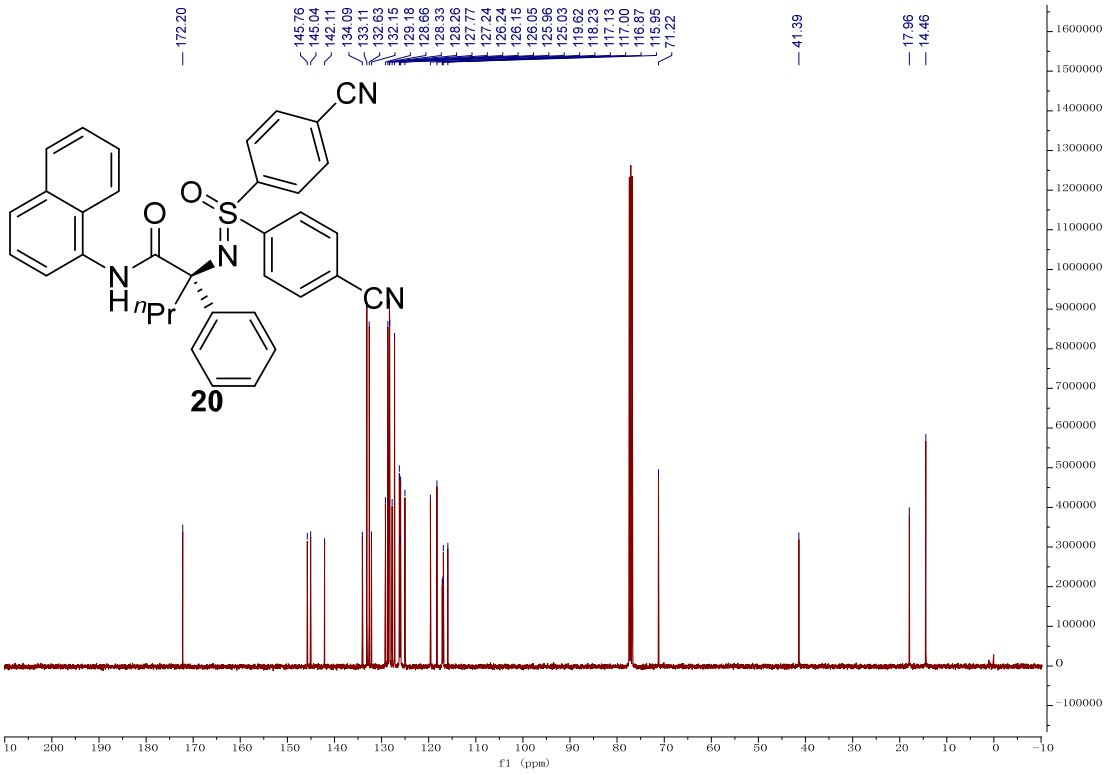
O
N
H
nPr
CN
20
f1 (ppm)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O
N
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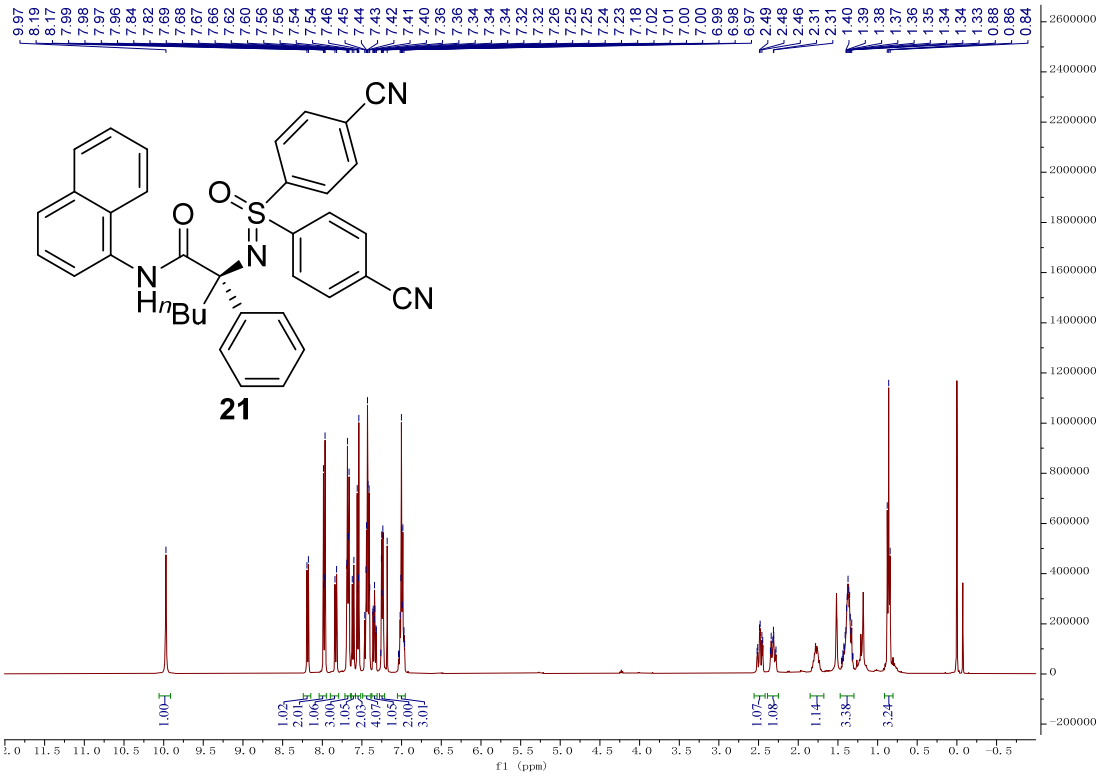
nPr
CN
20
f1 (ppm)


CN
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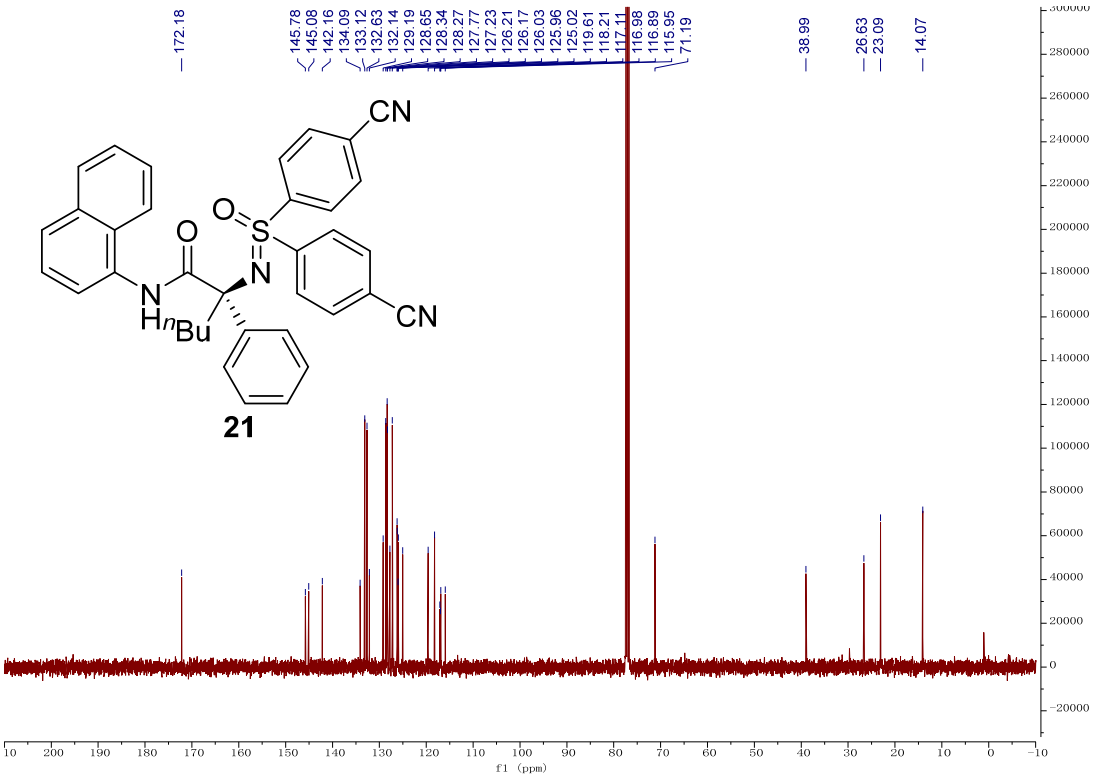
S
N
O
N
HnBu
CN
21
f1 (ppm)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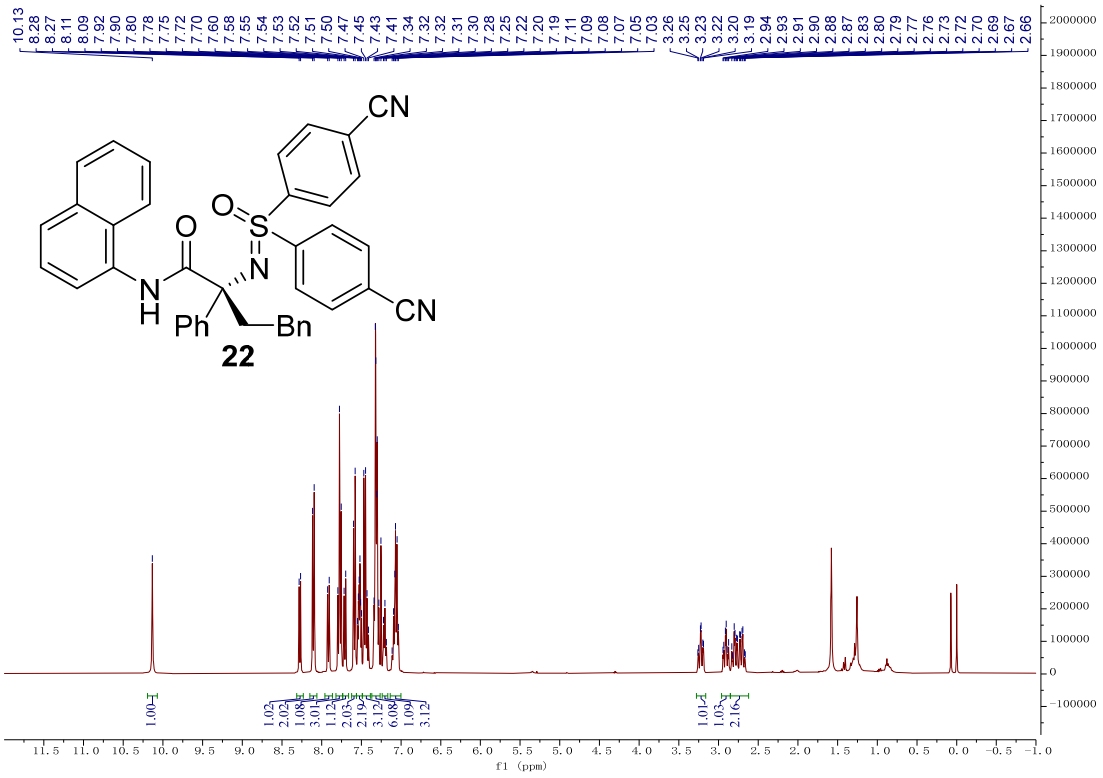
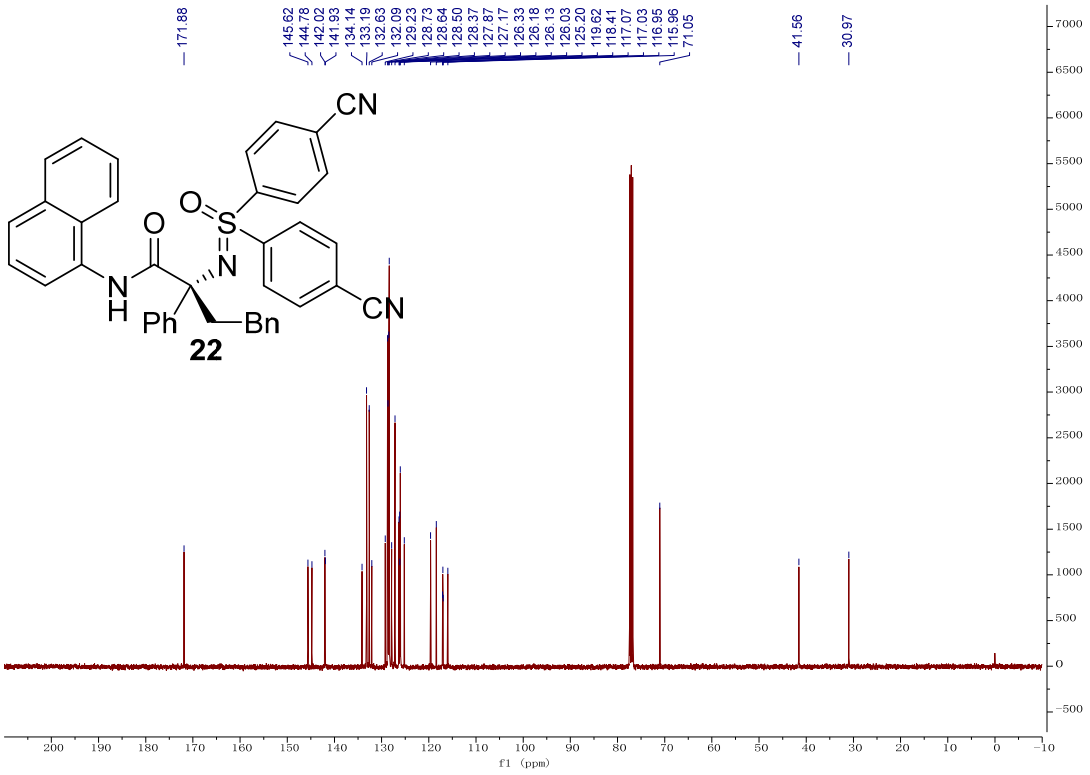
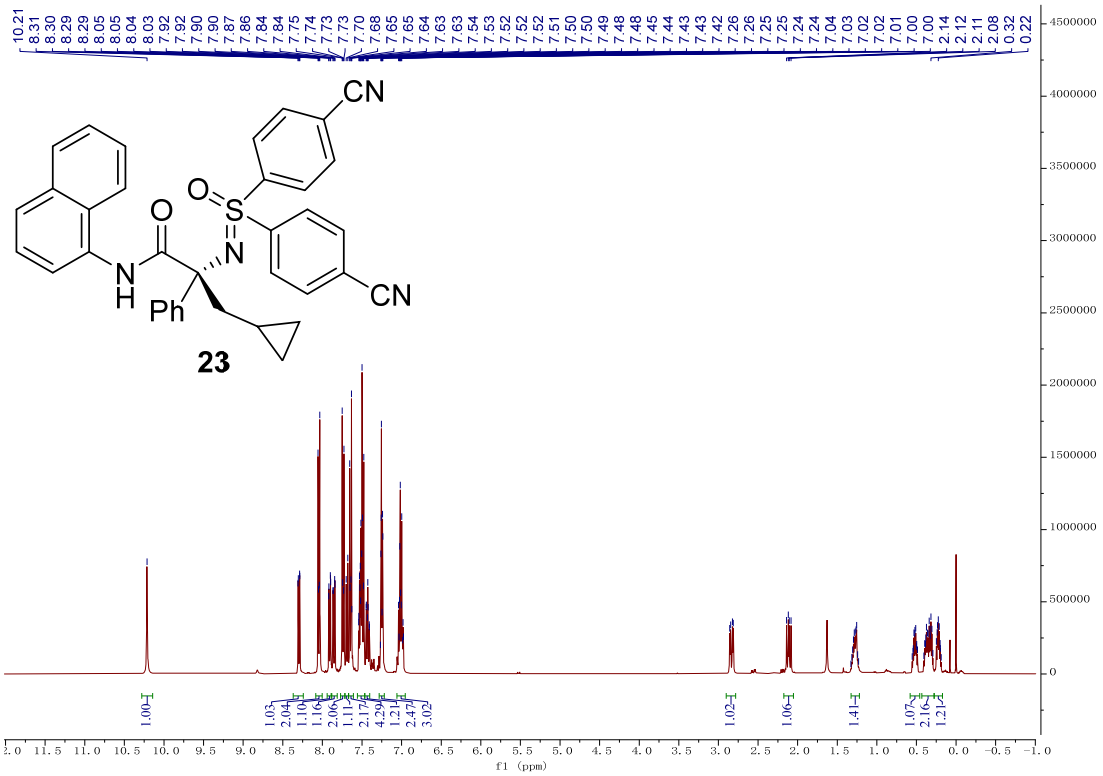
O
N
HnBu
CN
21
f1 (ppm)


22
f1 (ppm)


22
f1 (ppm)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7.24
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7.03
7.02
7.02
7.01
7.00
7.00
2.14
2.12
2.11
2.08
0.32
0.22
CN
O
S
N
O
N
H
Ph
CN
23
1.00
1.03
2.04
1.10
1.16
2.06
1.11
2.17
4.29
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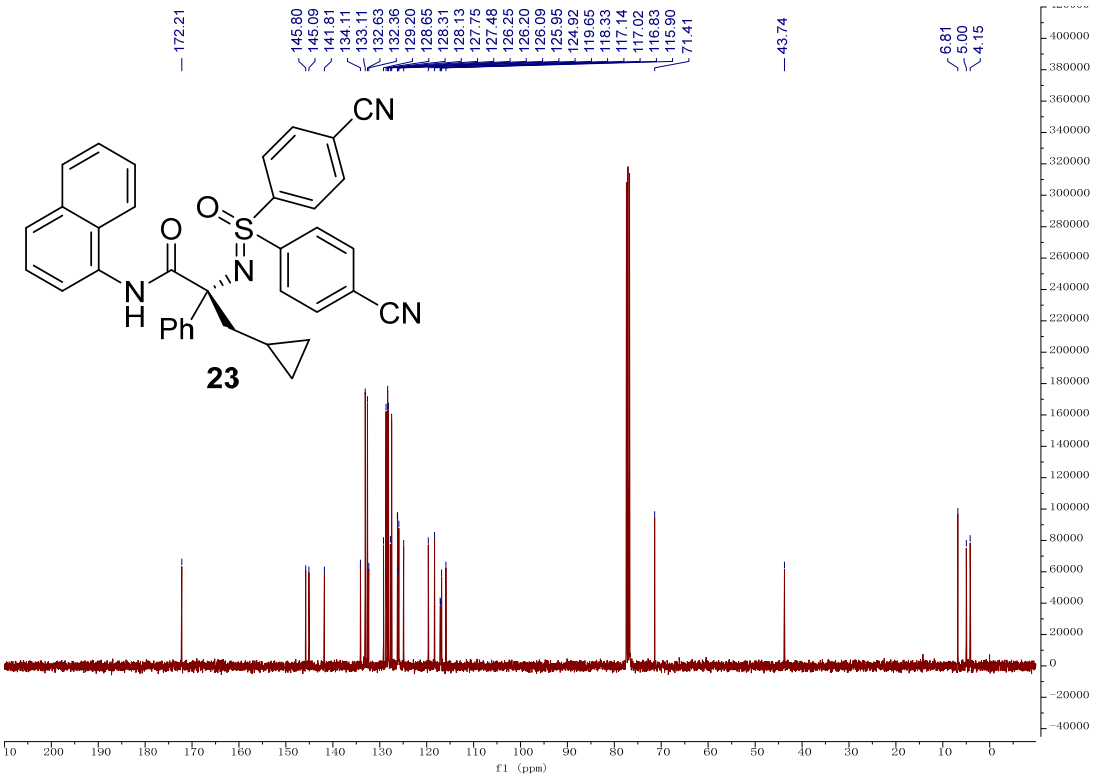
2.47
3.02
1.02
1.06
1.41
1.07
2.16
1.21
f1 (ppm)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133.11
132.63
132.36
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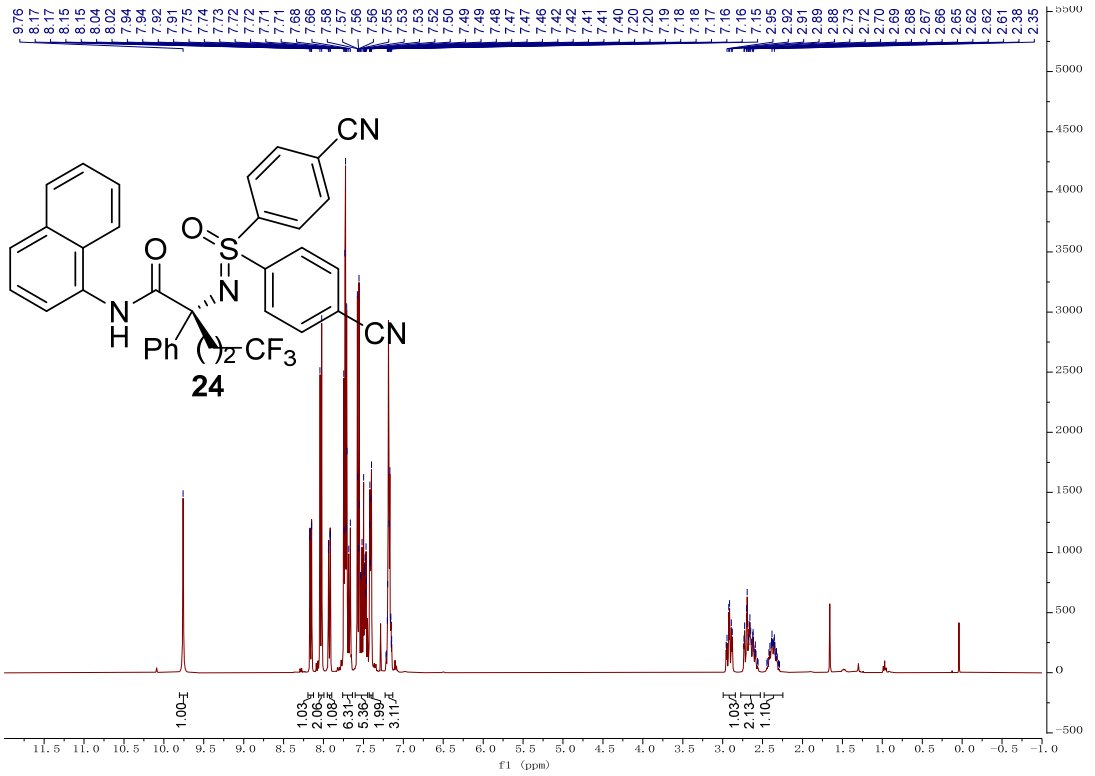
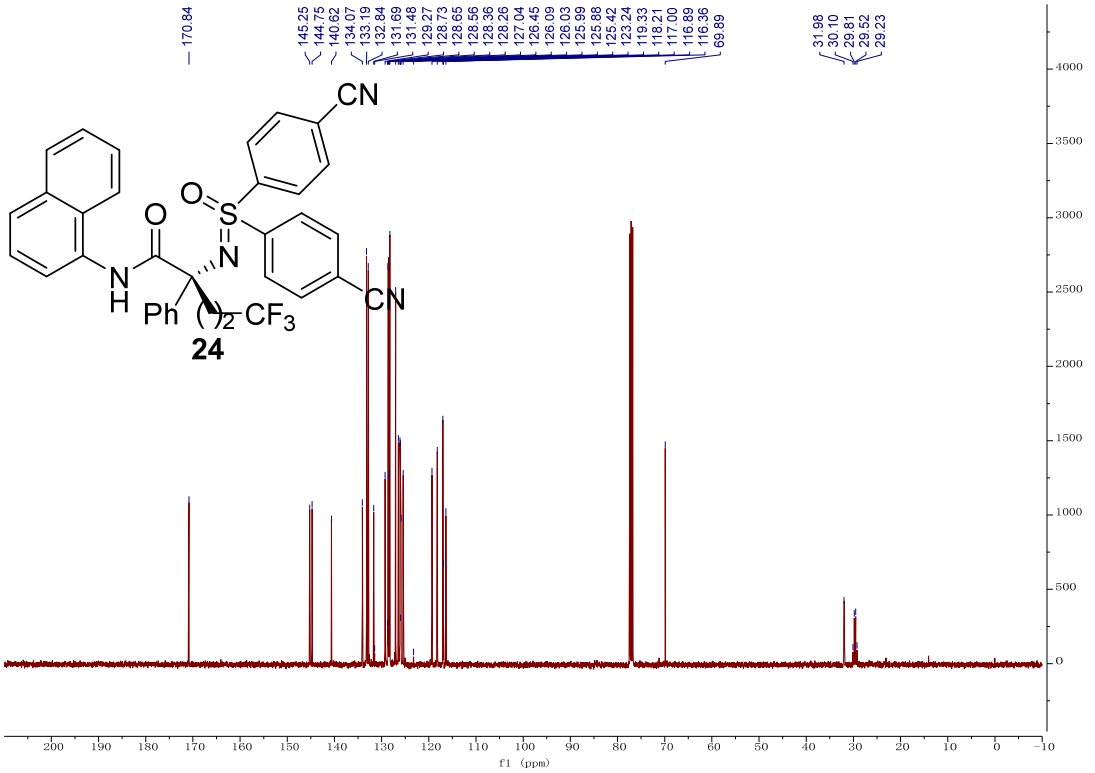
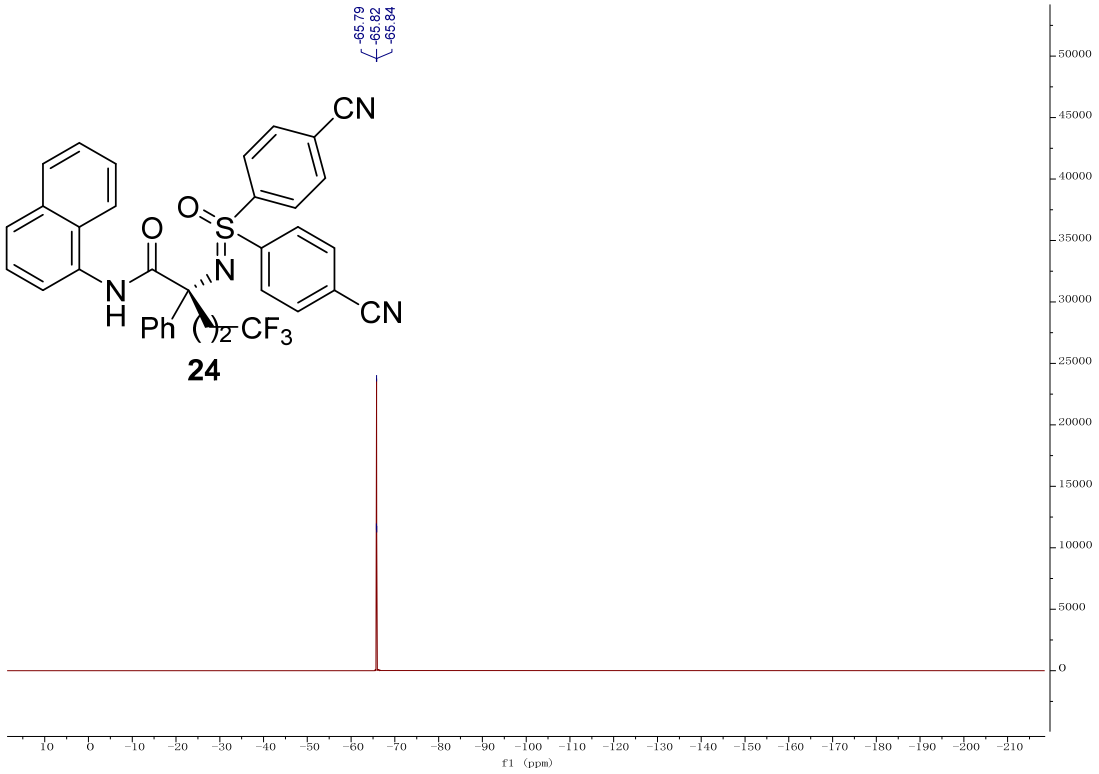
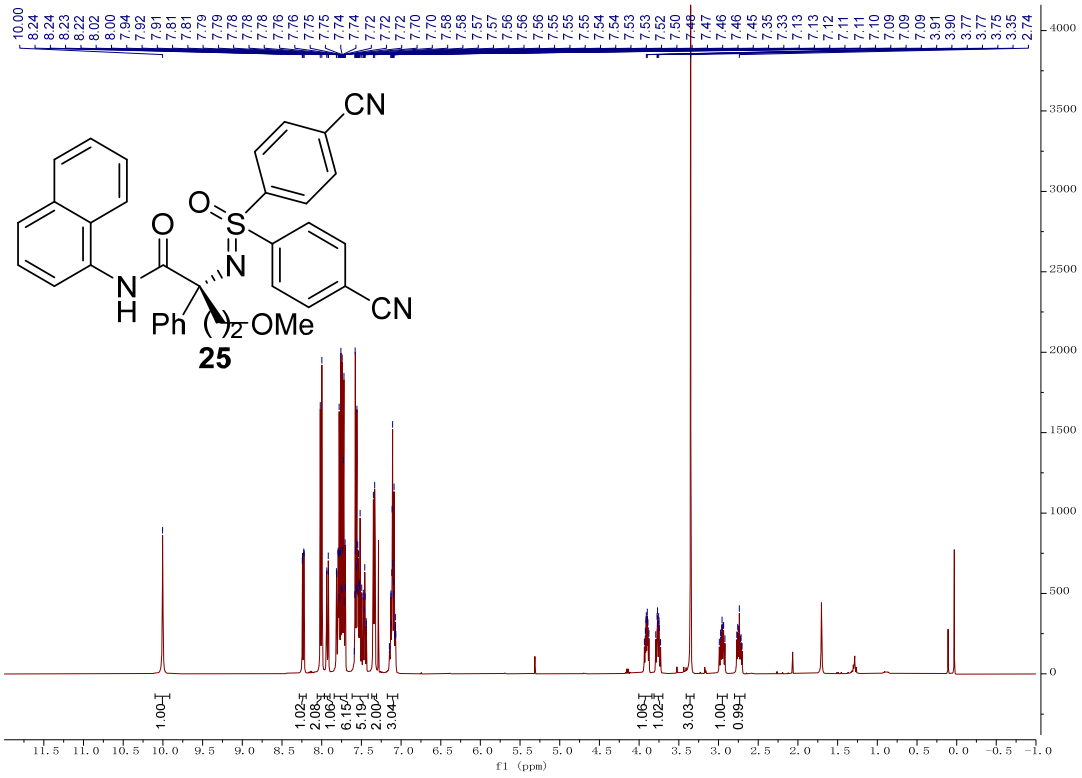
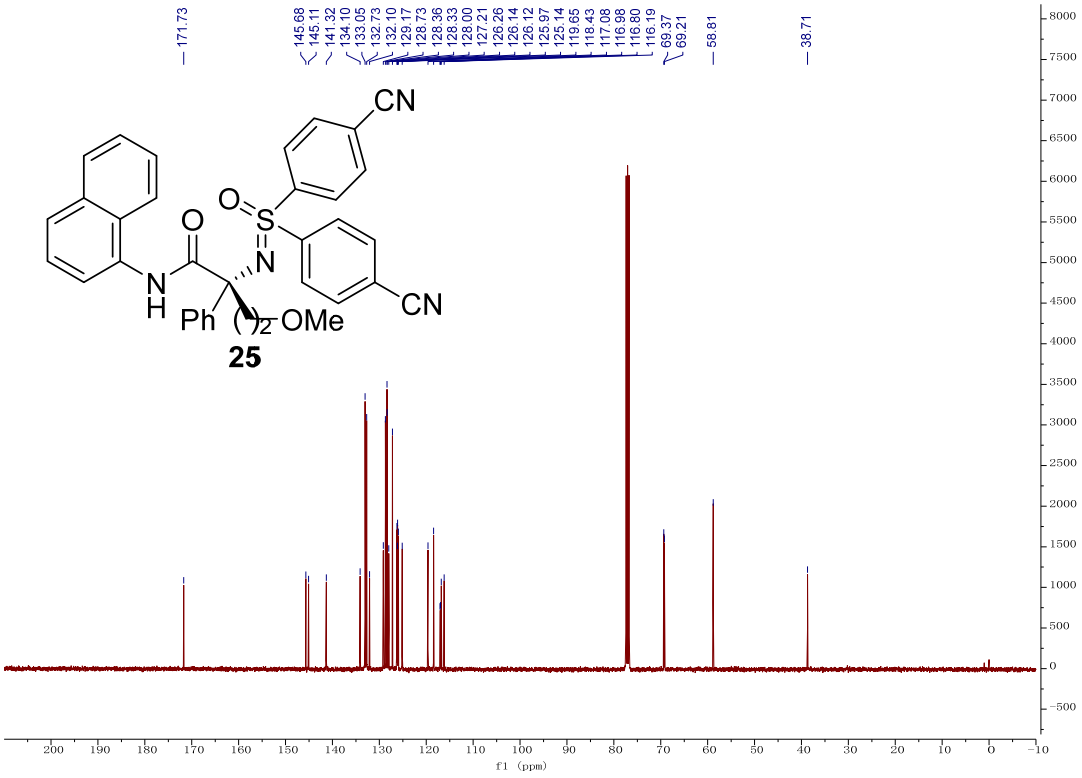
128.31
128.13
127.75
127.48
126.25
126.20
126.09
125.95
124.92
119.65
118.33
117.14
117.02
116.83
115.90
71.41
43.74
6.81
5.00
4.15
CN
O
S
N
O
N
H
Ph
CN
23
f1 (ppm)


CN
O
S
N
O
N
H
Ph
CF3
2
CN
24
f1 (ppm)


CN
O
S
N
O
N
H
Ph
CF3
2
CN
24
f1 (ppm)


-65.79
-65.82
-65.84
CN
O
S
N
O
N
H
Ph
CF3
CN
24
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


CN
O
S
N
O
N
H
Ph
OMe
CN
25
f1 (ppm)


CN
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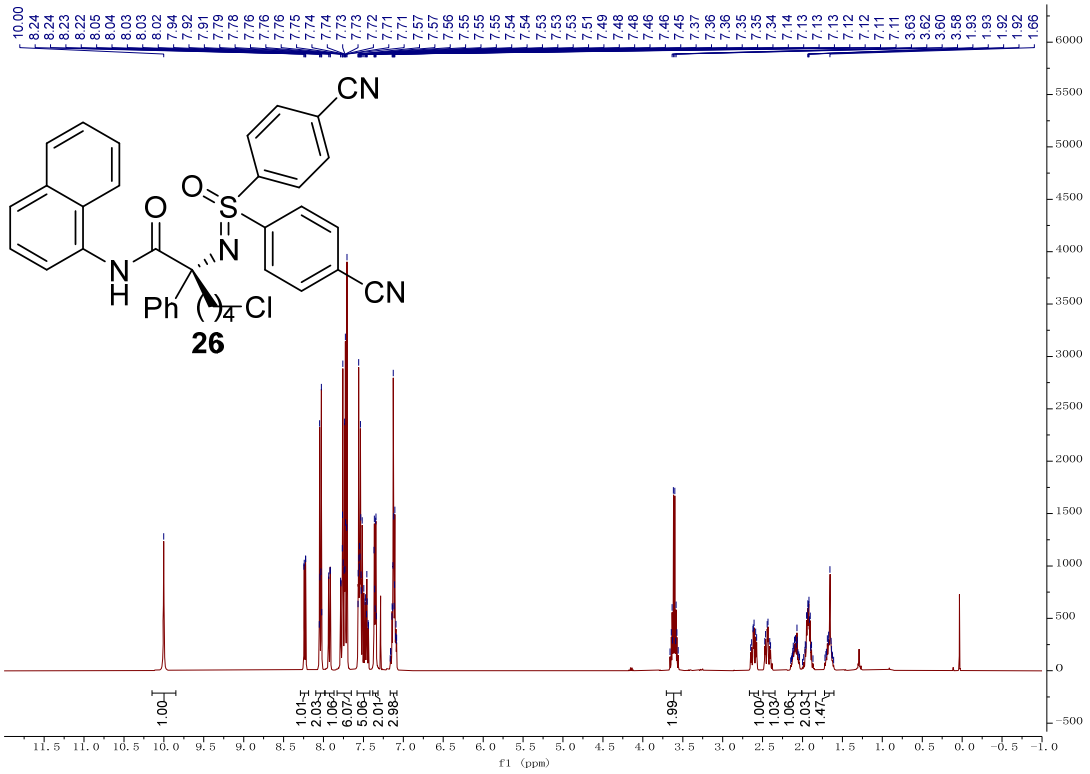
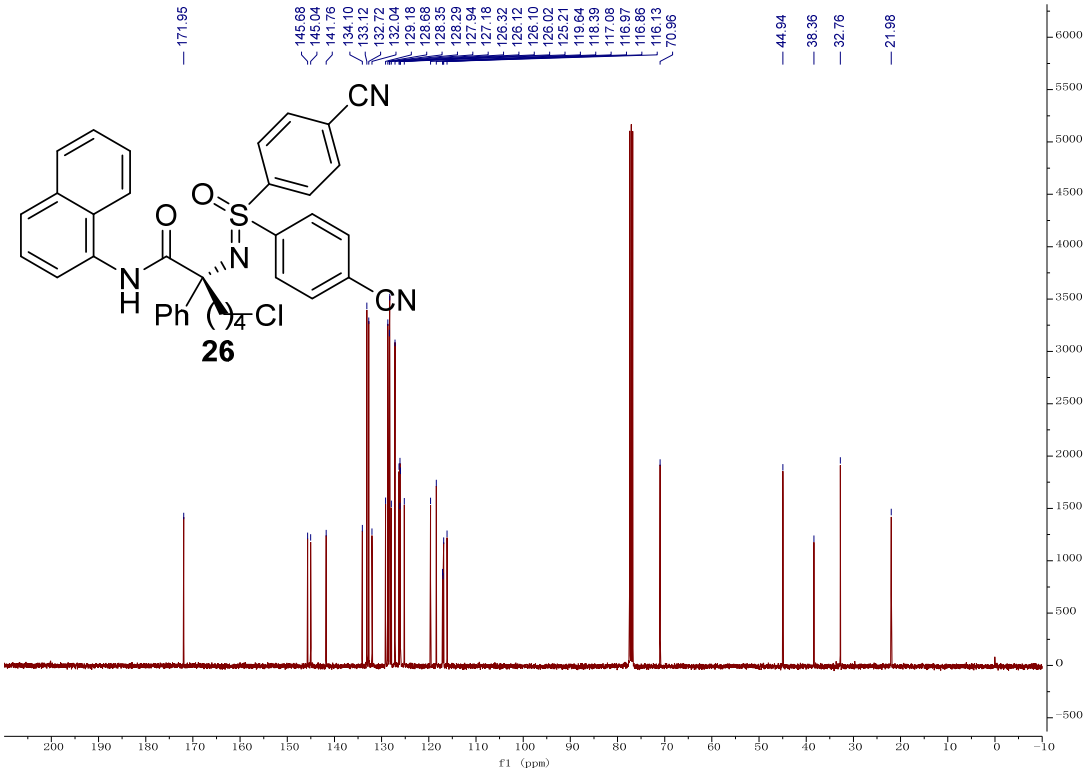
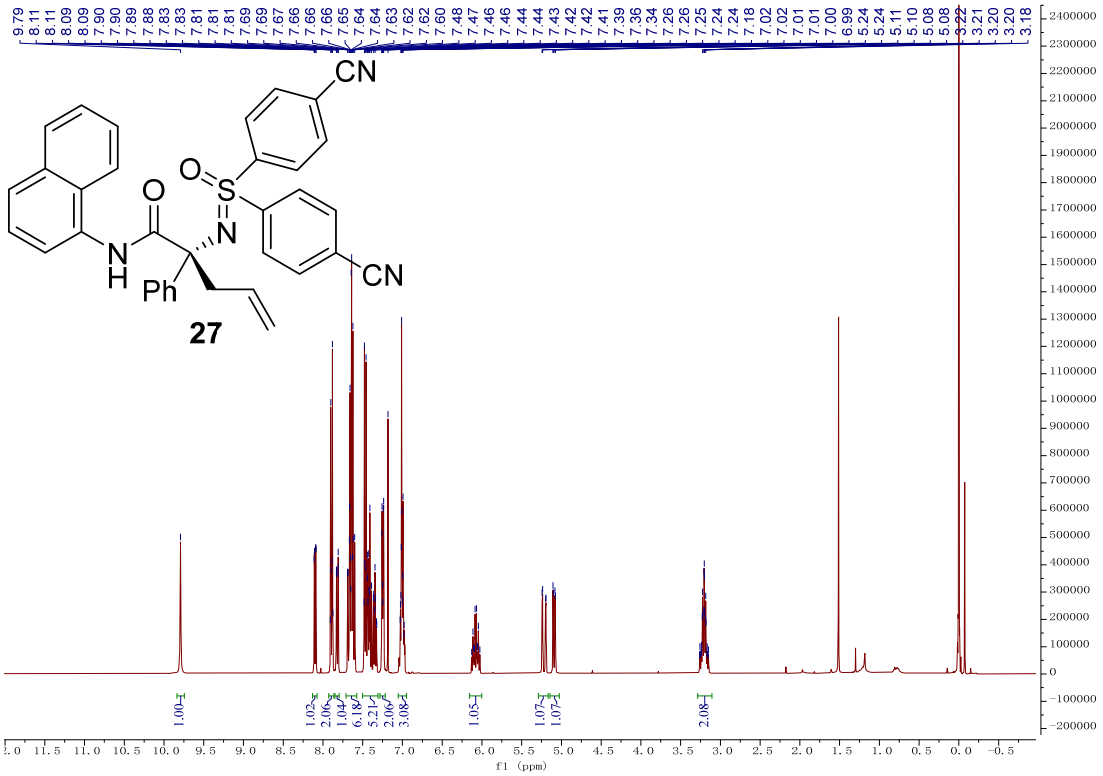
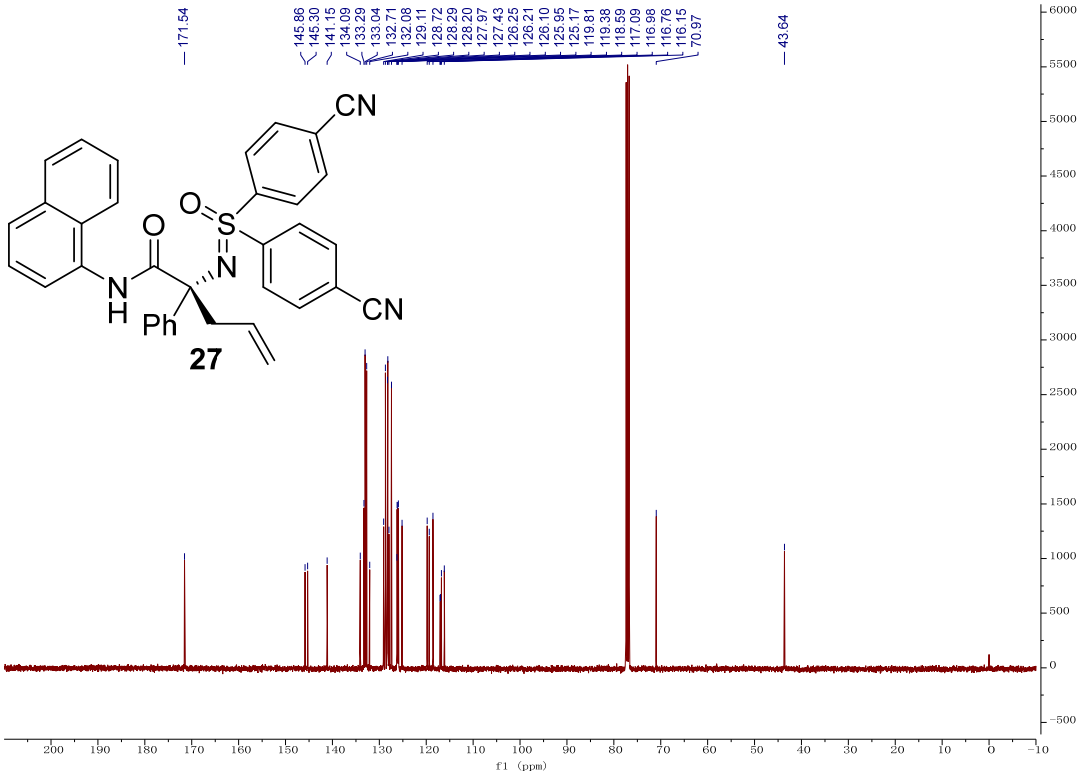
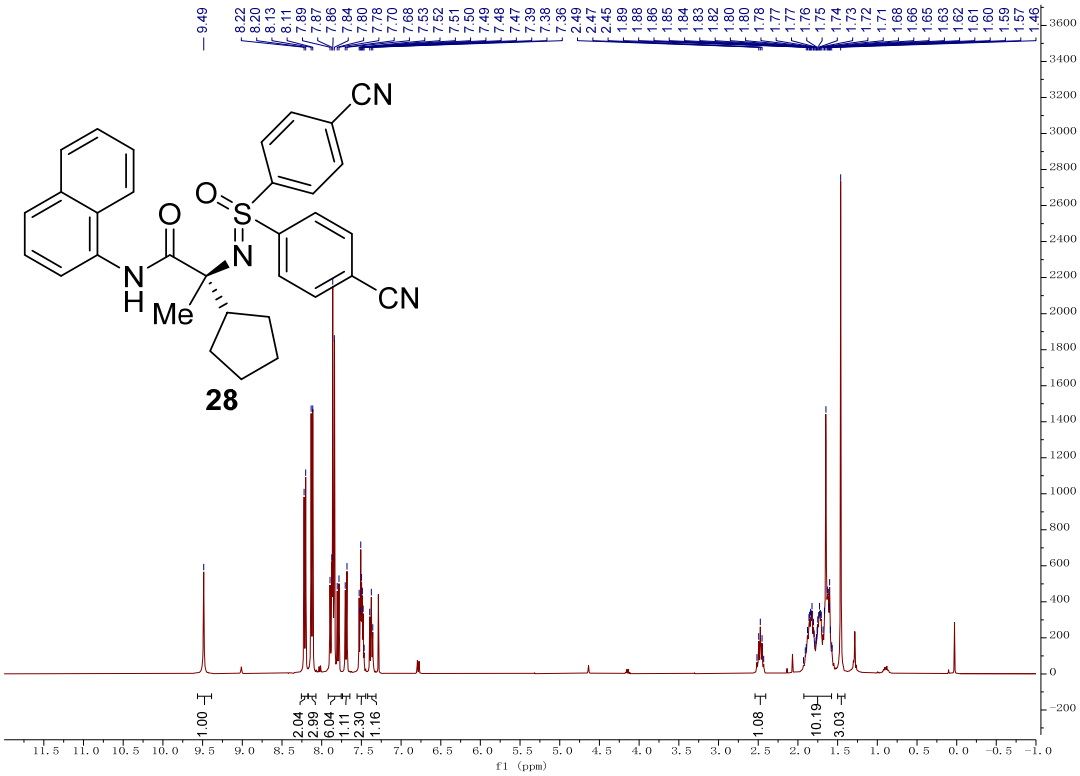
S
N
O
N
H
Ph
OMe
CN
25
f1 (ppm)

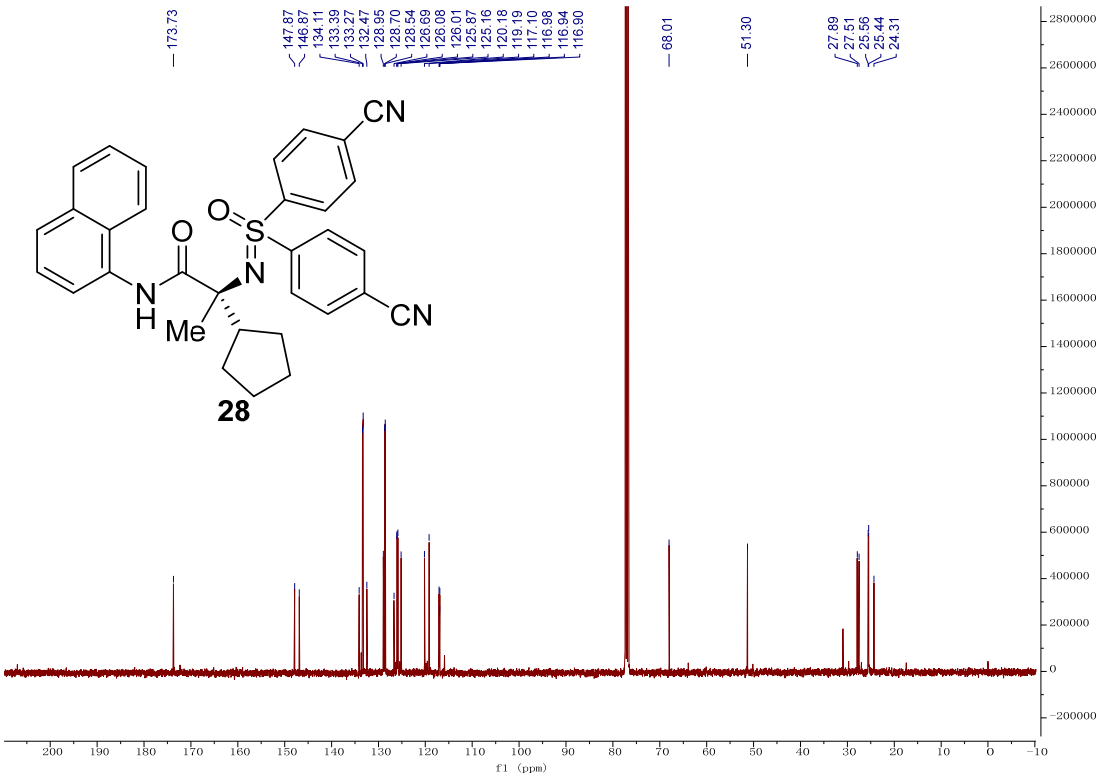

CN
O
S
N
O
N
H
Ph
4
Cl
CN
26
f1 (ppm)

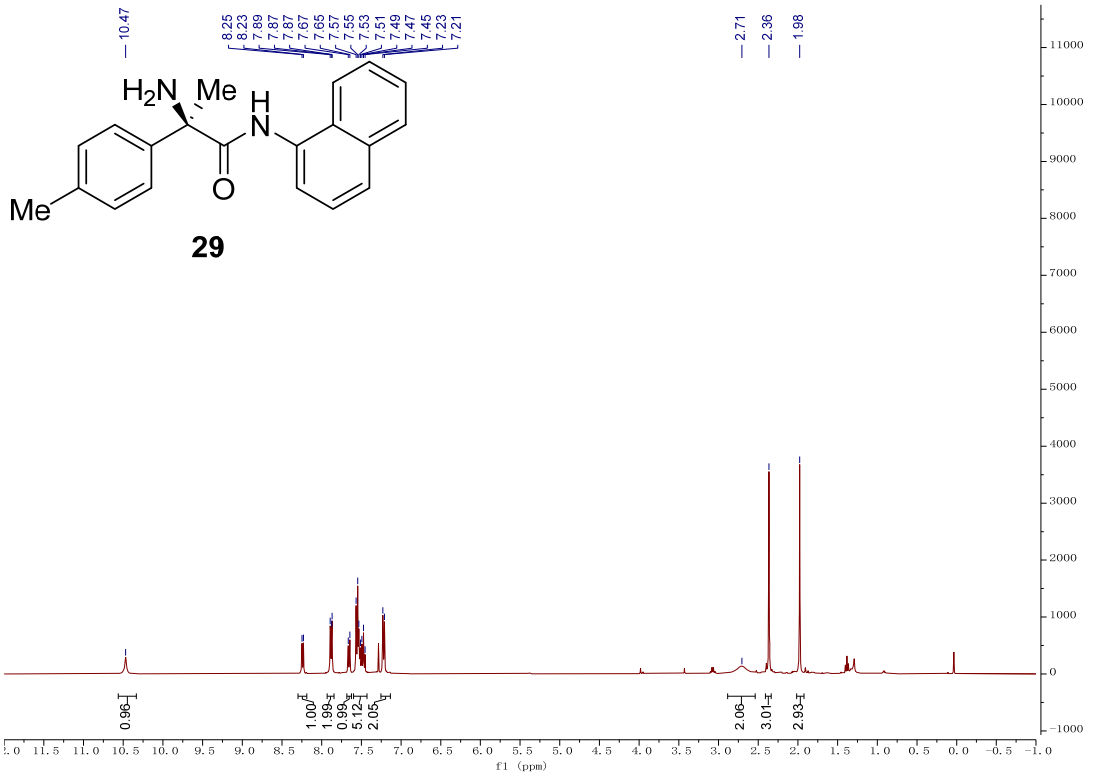

171.95
145.68
145.04
141.76
134.10
133.12
132.72
132.04
129.18
128.88
128.35
128.29
127.94
127.18
126.32
126.12
126.10
126.02
125.21
119.64
118.39
117.08
116.97
116.86
116.13
70.96
44.94
38.36
32.76
21.98
CN
O
S
N
O
N
H
Ph
4
Cl
CN
26
f1 (ppm)

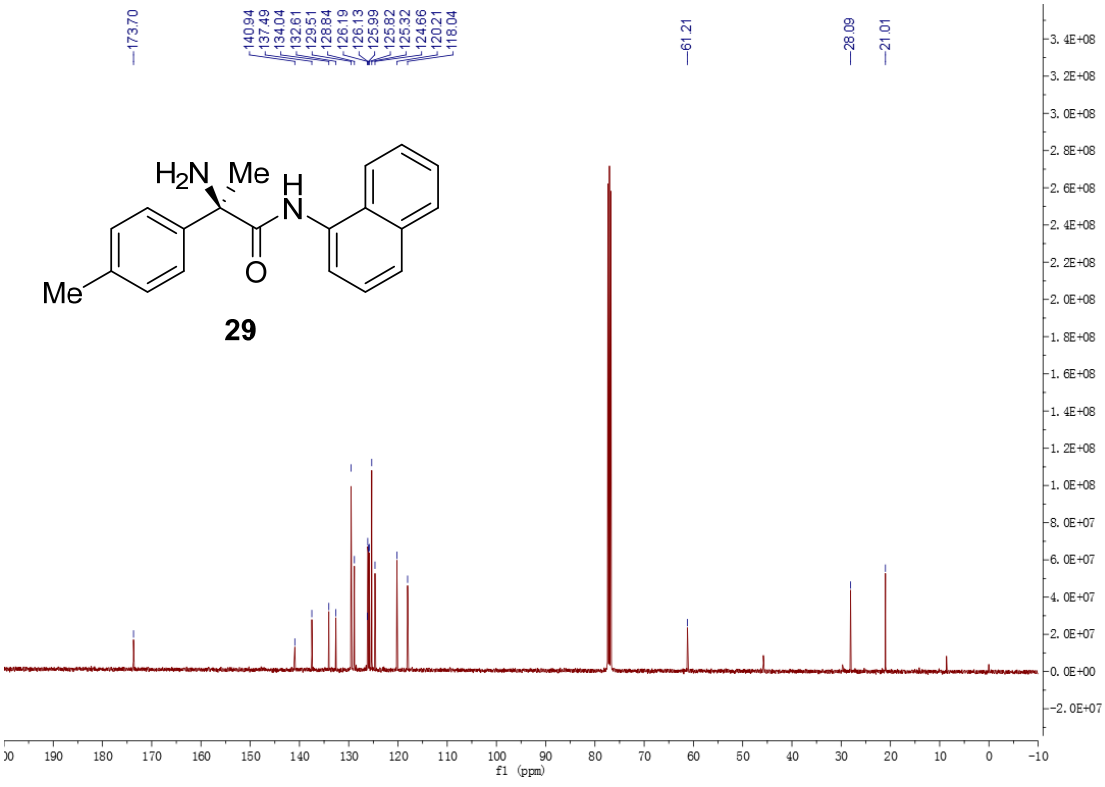

CN
O
S
N
O
N
H
Ph
CN
27
f1 (ppm)

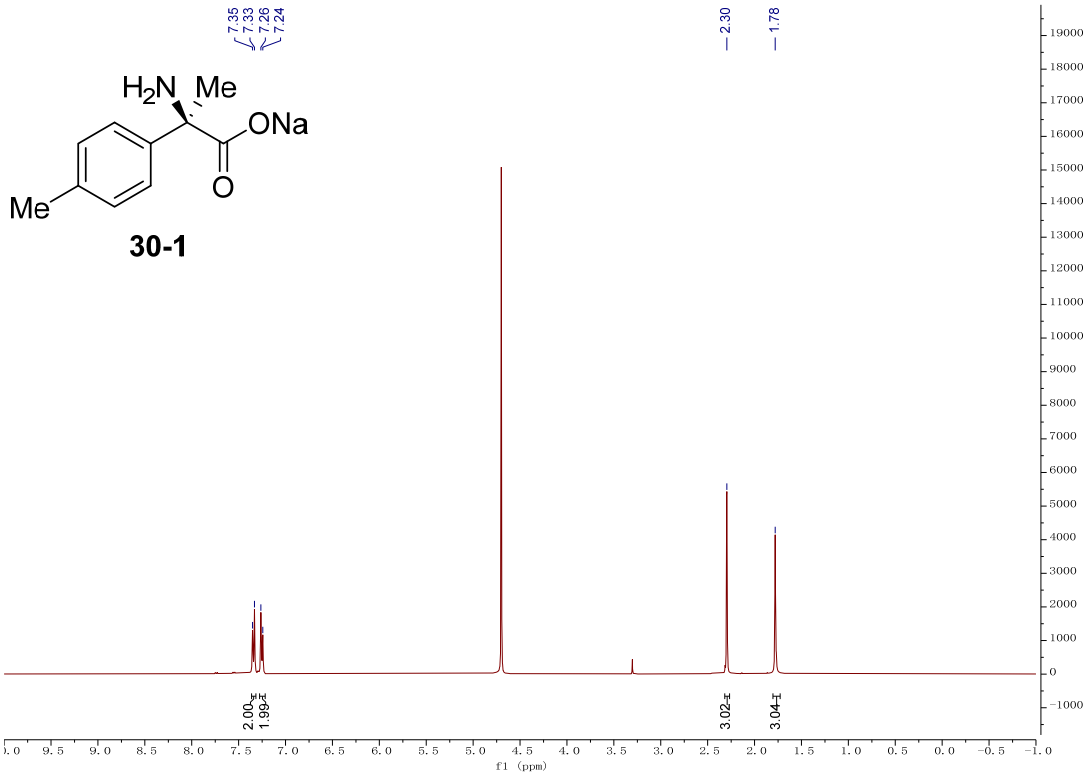

CN
O
S
N
O
N
H
Ph
CN
27
f1 (ppm)

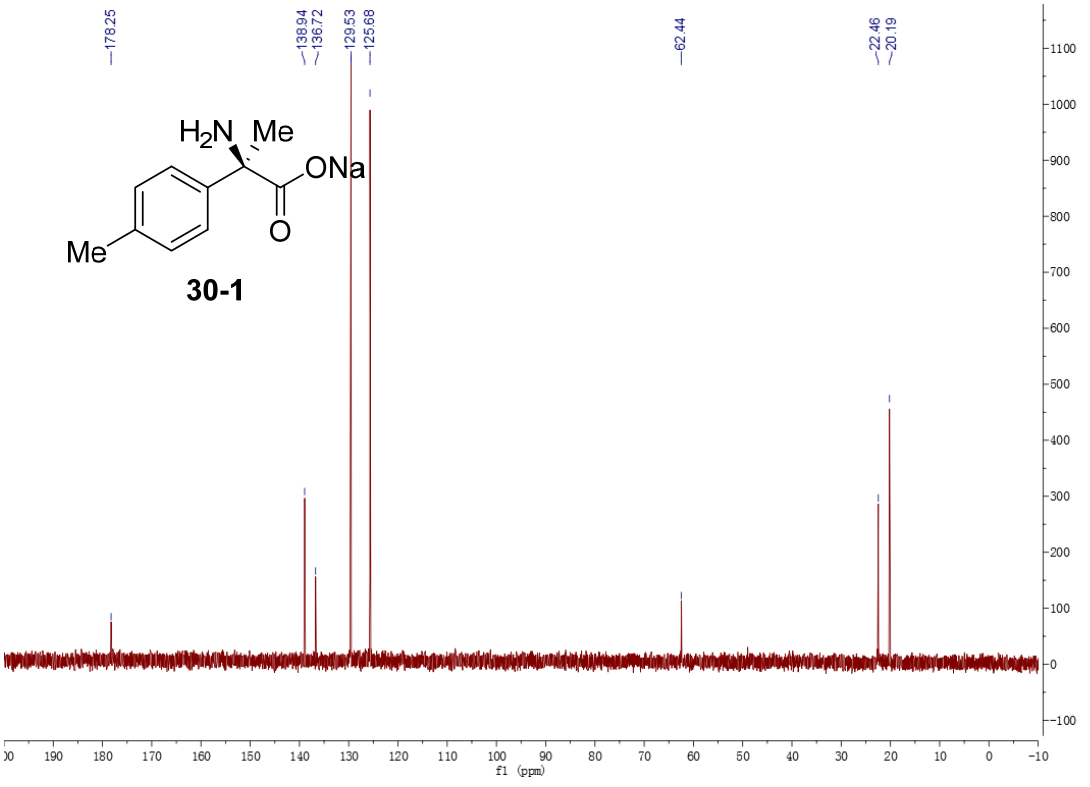

9.49
8.22
8.20
8.13
8.11
7.89
7.87
7.86
7.84
7.80
7.78
7.70
7.68
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.39
7.38
7.36
2.49
2.47
2.45
1.89
1.88
1.86
1.85
1.84
1.83
1.82
1.80
1.80
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.68
1.66
1.65
1.63
1.62
1.61
1.60
1.59
1.57
1.46
CN
O
S
N
O
N
H
Me
CN
28
1.00
2.04
2.99
6.04
1.11
2.30
1.16
1.08
10.19
3.03
f1 (ppm)

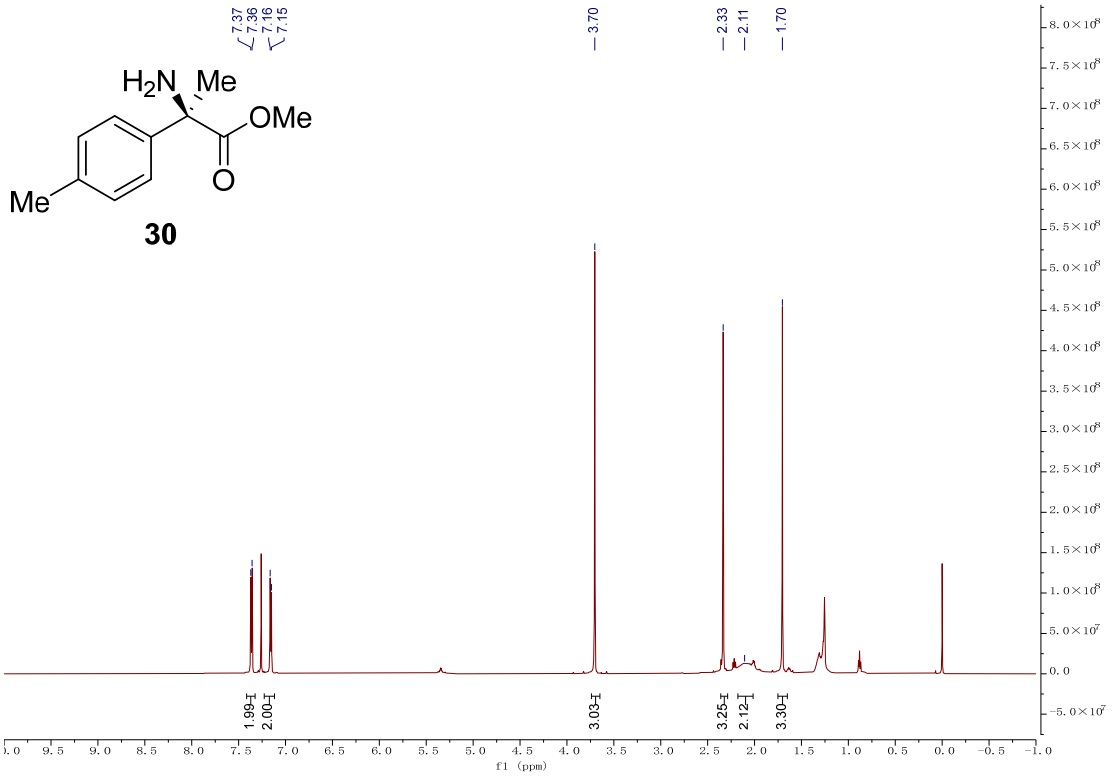

173.73
147.87
146.87
134.11
133.39
133.27
132.47
128.95
128.70
128.54
126.69
126.08
126.01
125.87
125.16
120.18
119.19
117.10
116.98
116.94
116.90
68.01
51.30
27.89
27.51
25.56
25.44
24.31
CN
O
S
N
O
N
H
Me
CN
28
f1 (ppm)

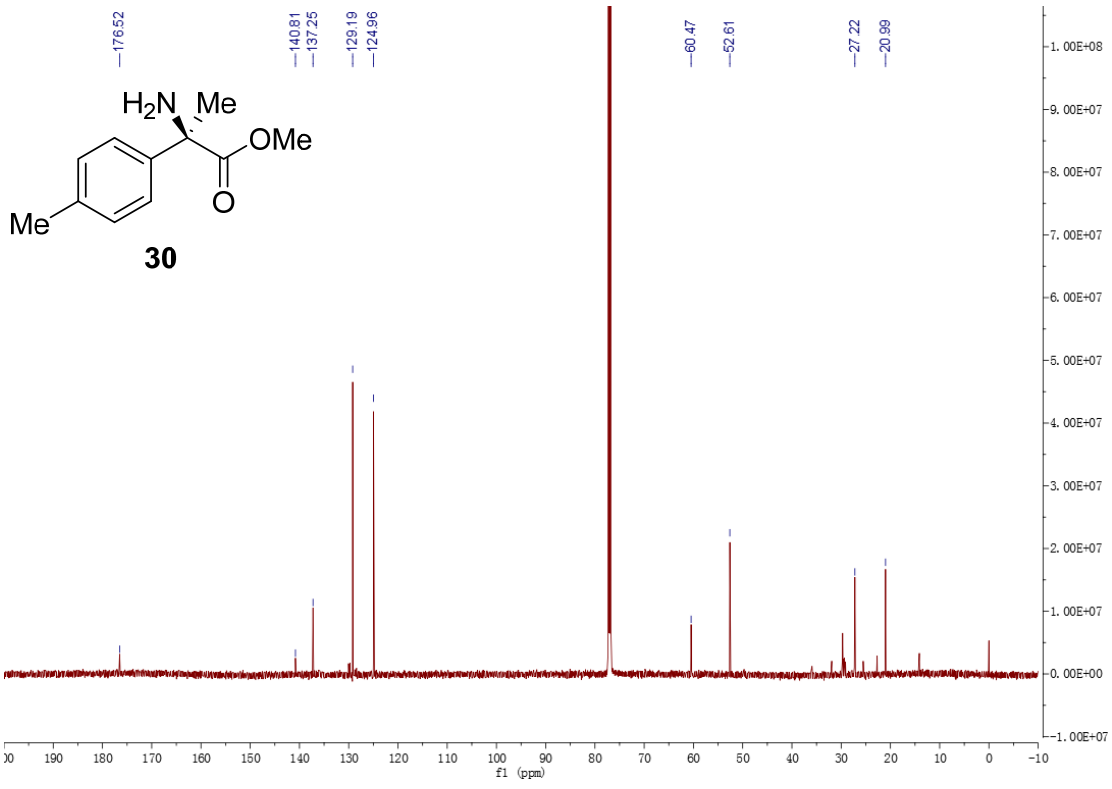

10.47
8.25
8.23
7.89
7.87
7.87
7.67
7.65
7.57
7.55
7.53
7.51
7.49
7.47
7.45
7.23
7.21
2.71
2.36
1.98
H2N
Me
H
N
O
Me
29
0.96
1.00
1.99
0.99
5.12
2.05
2.06
3.01
2.93
f1 (ppm)

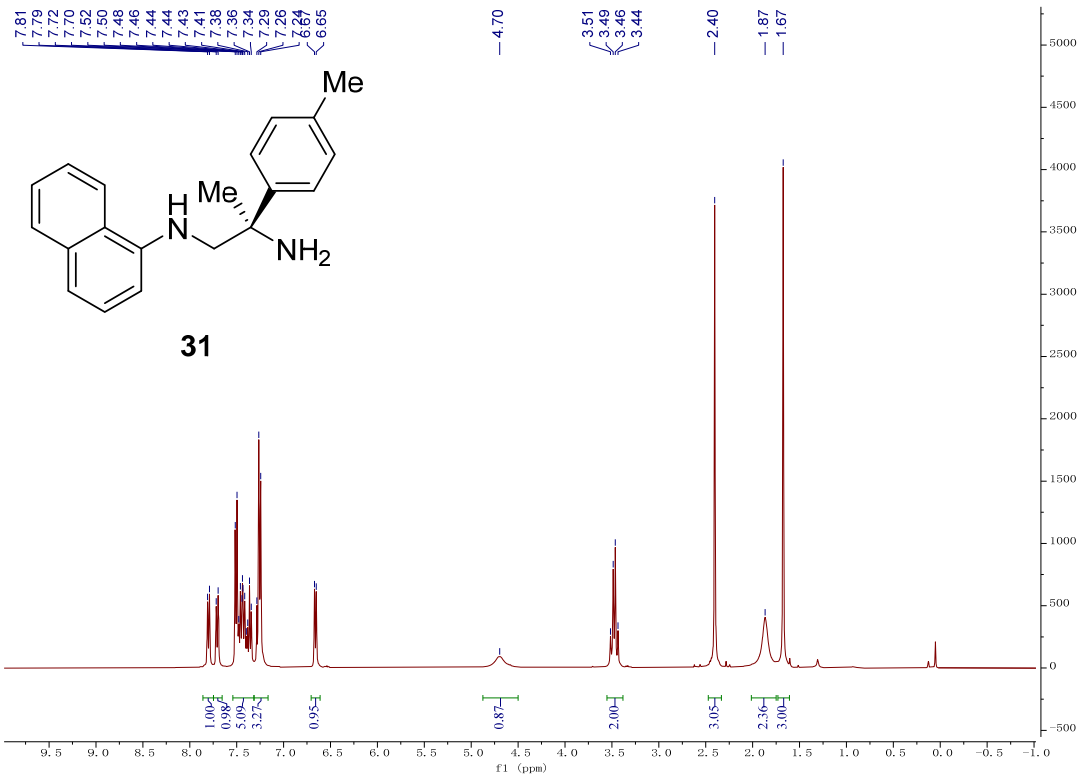

173.70
140.94
137.49
134.04
132.61
129.51
128.84
126.19
126.13
125.99
125.82
125.32
124.66
120.21
118.04
61.21
28.09
21.01
H2N
Me
H
N
O
Me
29
f1 (ppm)

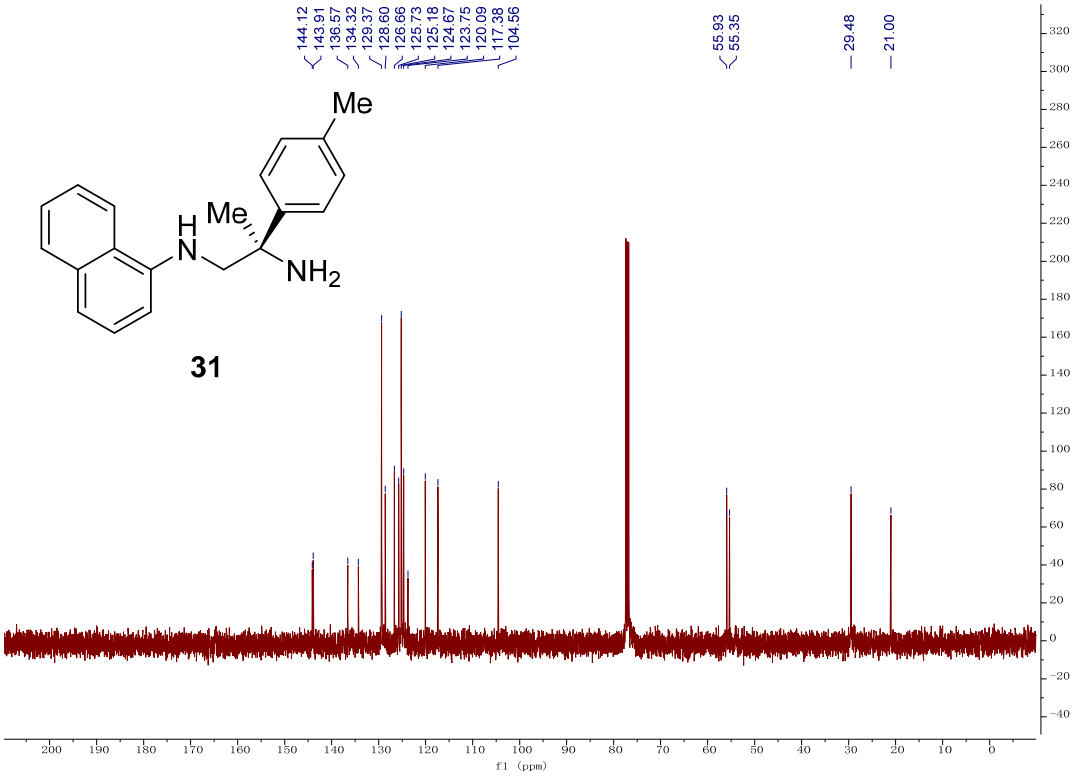

7.35
7.33
7.26
7.24
2.30
1.78
H2N Me
ONa
O
Me
30-1
2.00
1.99
3.02
3.04
f1 (ppm)

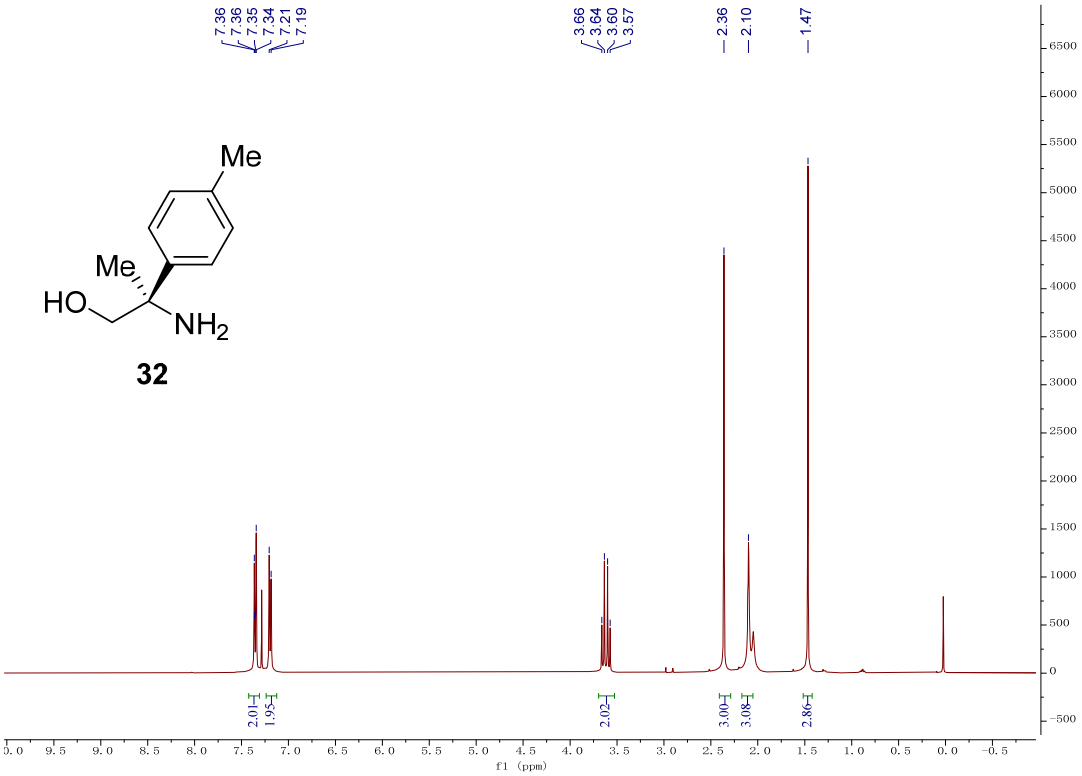

178.25
138.94
136.72
129.53
125.68
62.44
22.46
20.19
H2N Me
ONa
O
Me
30-1
f1 (ppm)

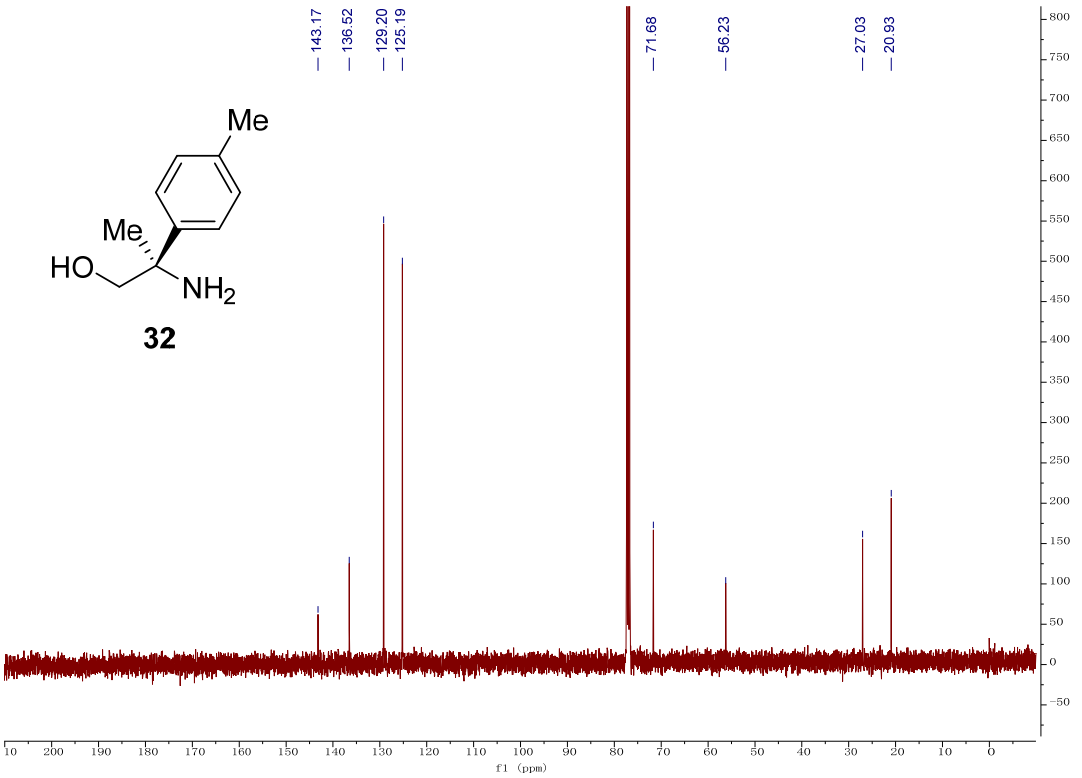

7.37
7.36
7.16
7.15
3.70
2.33
2.11
1.70
H2N Me
OMe
O
Me
30
1.99
2.00
3.03
3.25
2.12
3.30
f1 (ppm)

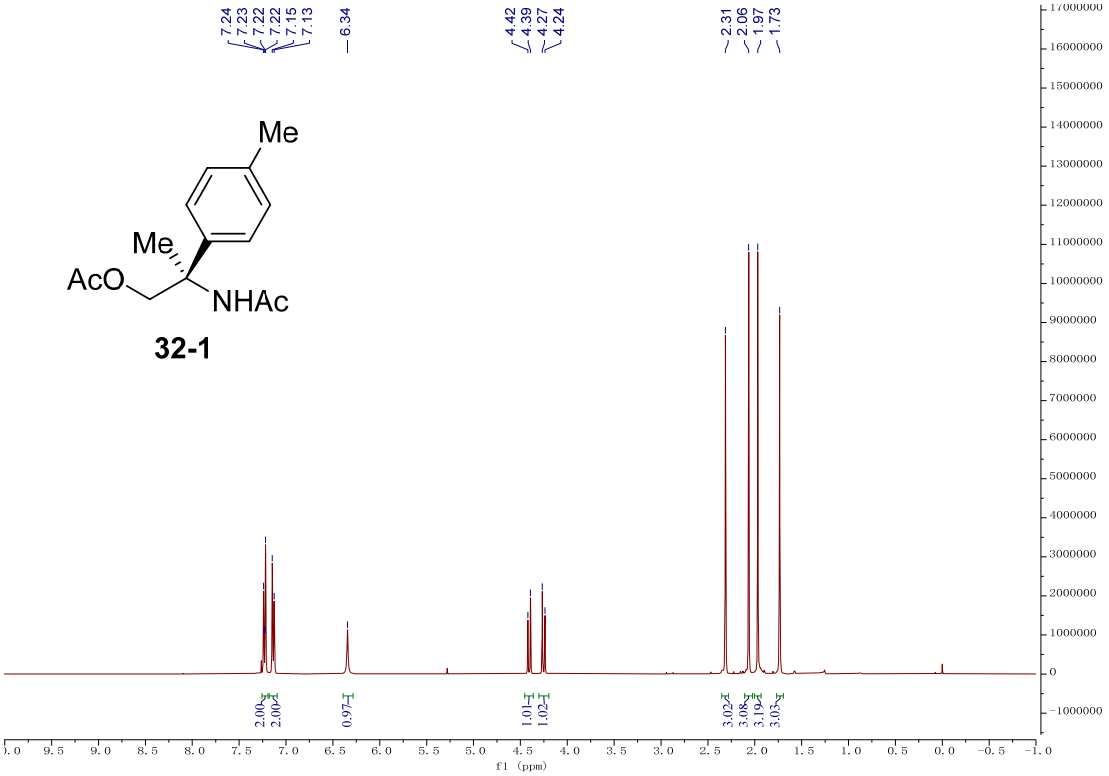

176.52
140.81
137.25
129.19
124.96
60.47
52.61
27.22
20.99
H2N Me
OMe
O
Me
30
f1 (ppm)

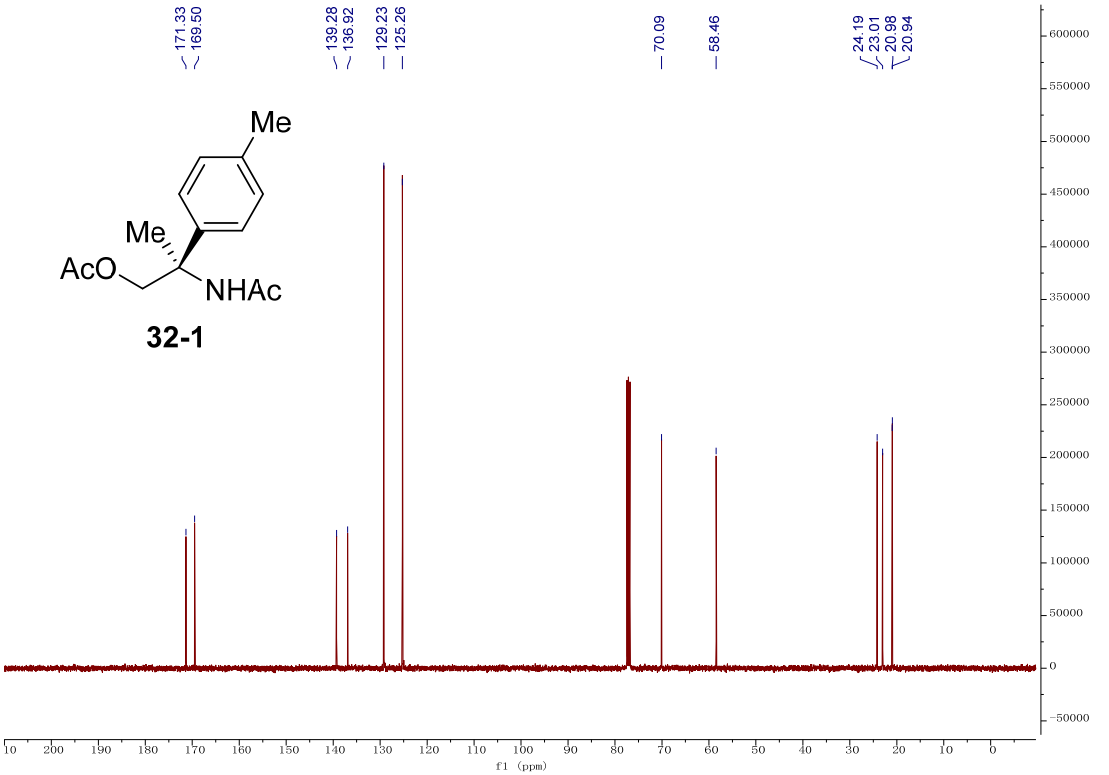

7.81
7.79
7.72
7.70
7.52
7.50
7.48
7.46
7.44
7.44
7.43
7.41
7.38
7.36
7.34
7.29
7.26
6.64
6.65
4.70
3.51
3.49
3.46
3.44
2.40
1.87
1.67
Me
H
N
Me
NH2
31
1.00
0.98
5.09
3.27
0.95
0.87
2.00
3.05
2.36
3.00
f1 (ppm)

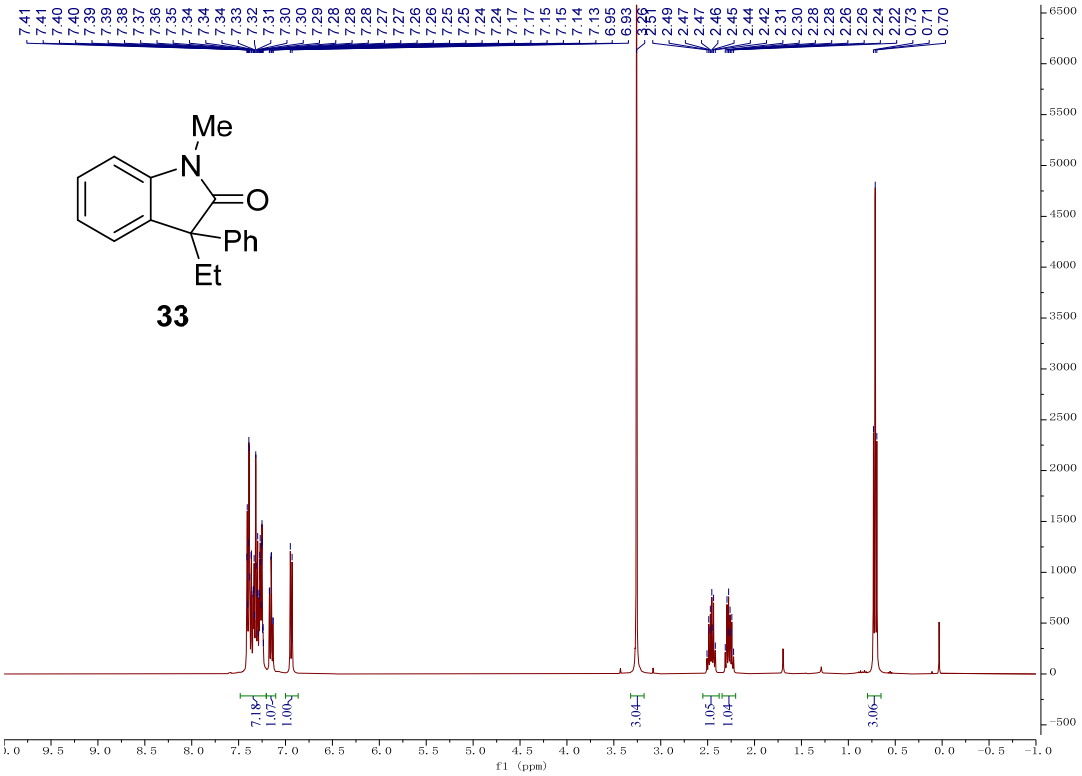

144.12
143.91
136.57
134.32
129.37
128.60
126.66
125.73
125.18
124.67
123.75
120.09
117.38
104.56
55.93
55.35
29.48
21.00
Me
H
N
Me
NH2
31
f1 (ppm)

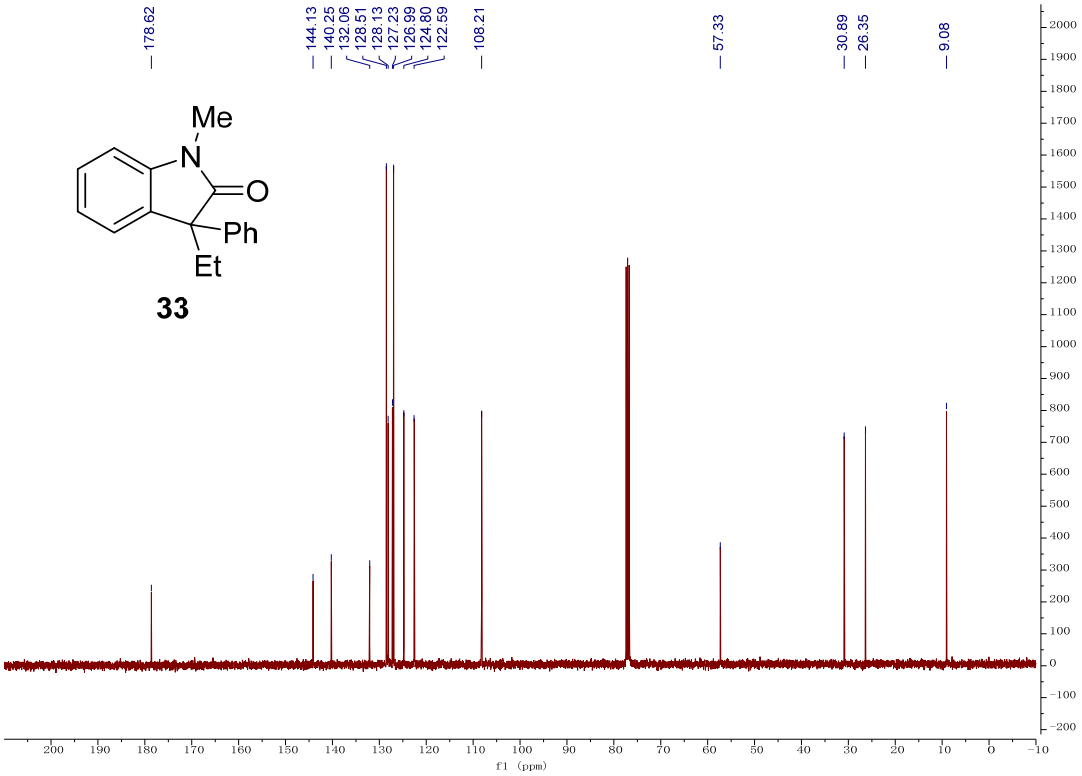

7.36
7.36
7.35
7.34
7.21
7.19
3.66
3.64
3.60
3.57
2.36
2.10
1.47
Me
Me
HO
NH2
32
2.01
1.95
2.02
3.00
3.08
2.86
f1 (ppm)


143.17
136.52
129.20
125.19
71.68
56.23
27.03
20.93
Me
Me
HO
NH2
32
f1 (ppm)

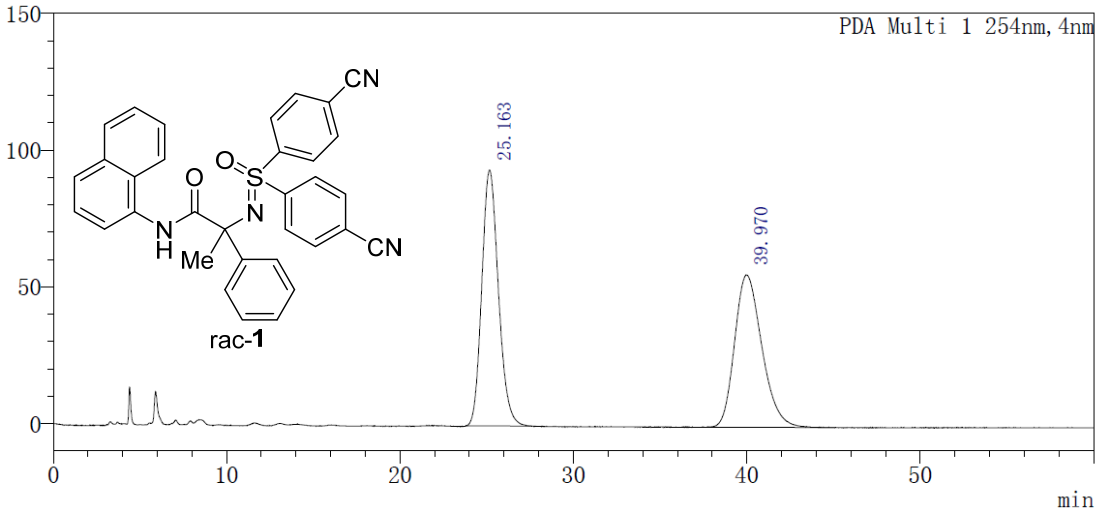

7.24
7.23
7.22
7.22
7.15
7.13
6.34
4.42
4.39
4.27
4.24
2.31
2.06
1.97
1.73
Me
Me
AcO
NHAc
32-1
2.00
2.00
0.97
1.01
1.02
3.02
3.08
3.19
3.03
f1 (ppm)


171.33
169.50
139.28
136.92
129.23
125.26
70.09
58.46
24.19
23.01
20.98
20.94
Me
Me
AcO
NHAc
32-1
f1 (ppm)


Me
N
O
Ph
Et
33
f1 (ppm)

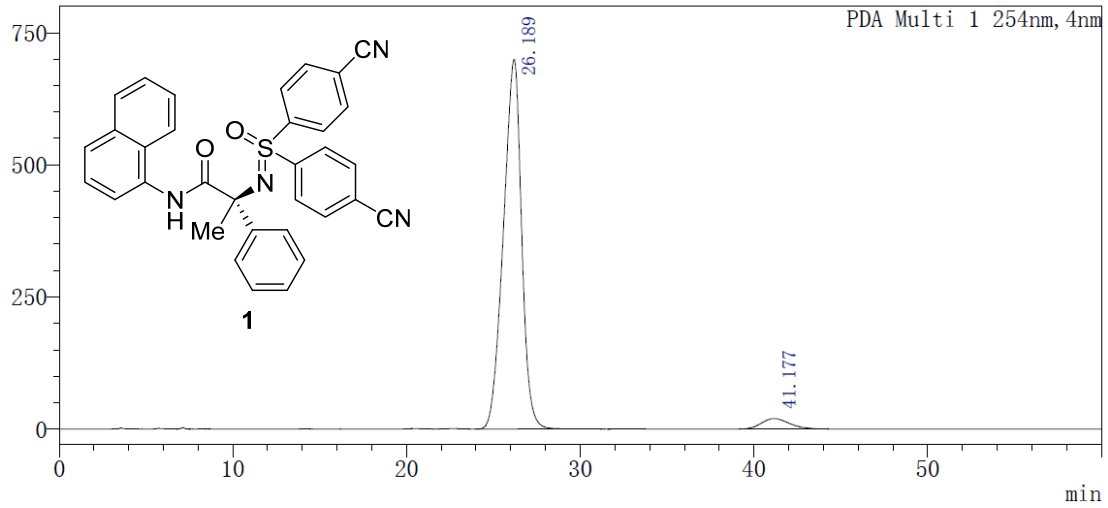

178.62
144.13
140.25
132.06
128.51
128.13
127.23
126.99
124.80
122.59
108.21
57.33
30.89
26.35
9.08
Me
N
O
Ph
Et
33
f1 (ppm)

HPLC Spectra



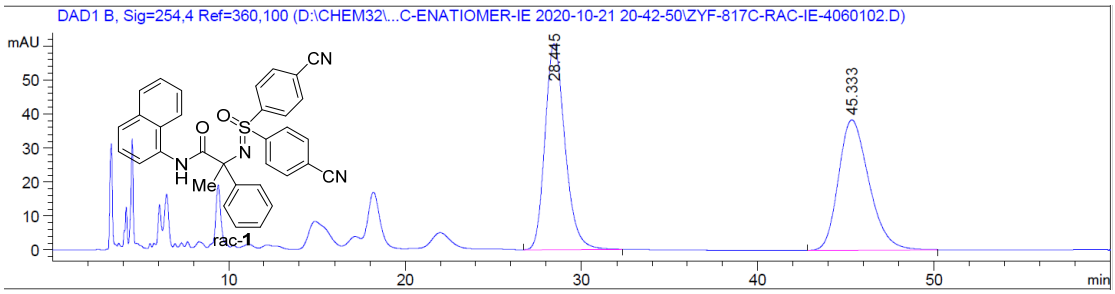
PDA Ch1 254nm

T	Hight	Area	Area%
25.163	93532	6218942	50.561
39.970	55687	6080990	49.439



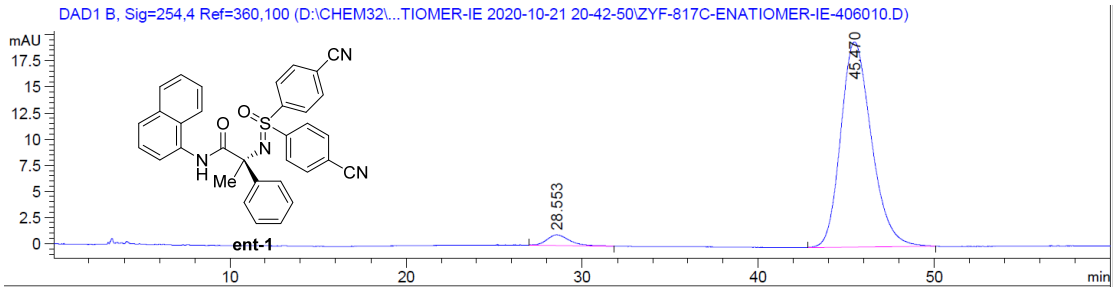
PDA Ch1 254nm

T	Hight	Area	Area%
26.189	699417	50832952	95.795
41.177	19817	2231232	4.205



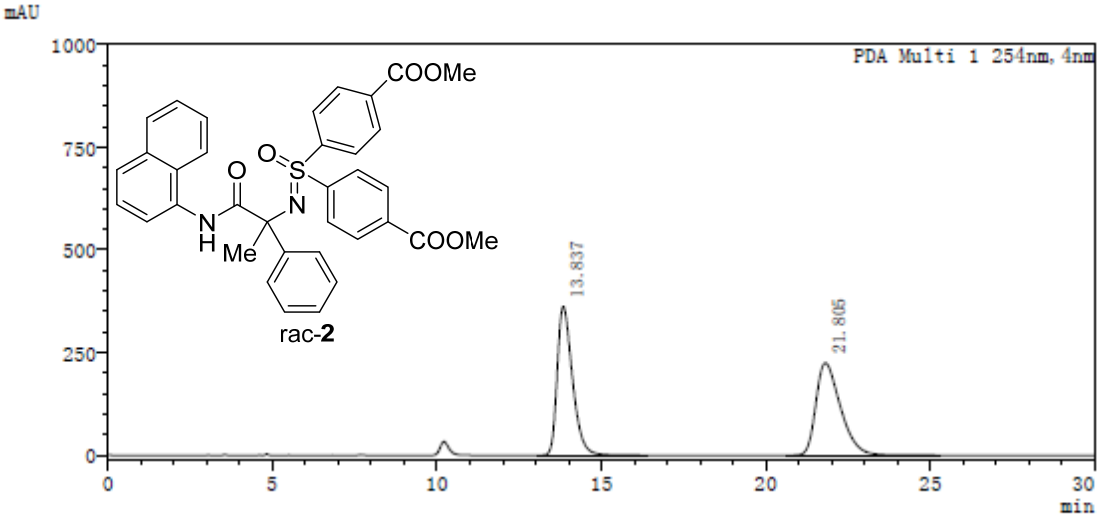
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.445	BB	1.1909	4770.96777	60.70808	50.8533
2	45.333	BB	1.6951	4610.86133	38.39438	49.1467
Totals :				9381.82910	99.10246	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

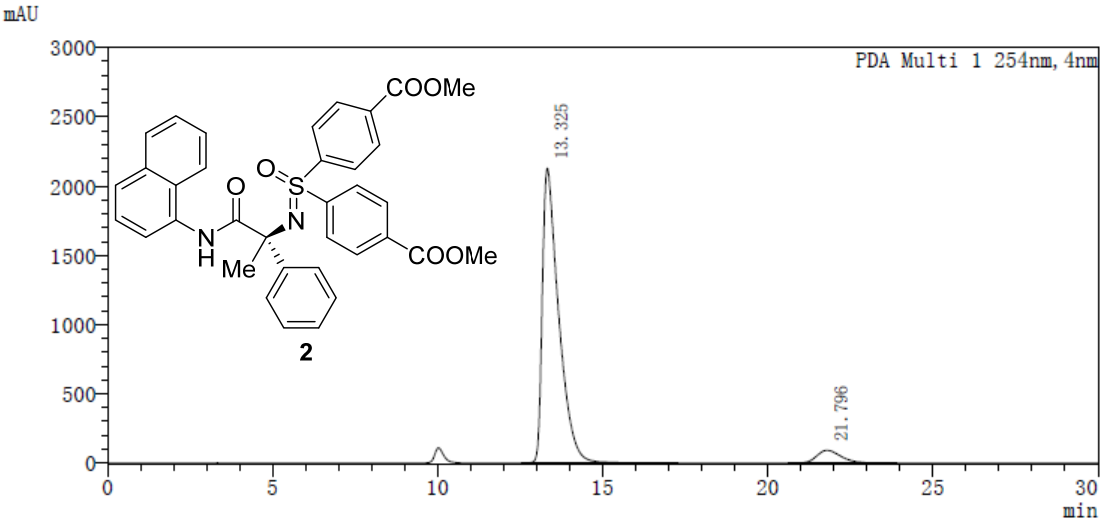
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.553	MM R	1.5080	93.17999	1.02984	3.7624
2	45.470	BB	1.4626	2383.42773	19.62934	96.2376
Totals :				2476.60773	20.65918	



Peak Table

PDA Ch1 254nm

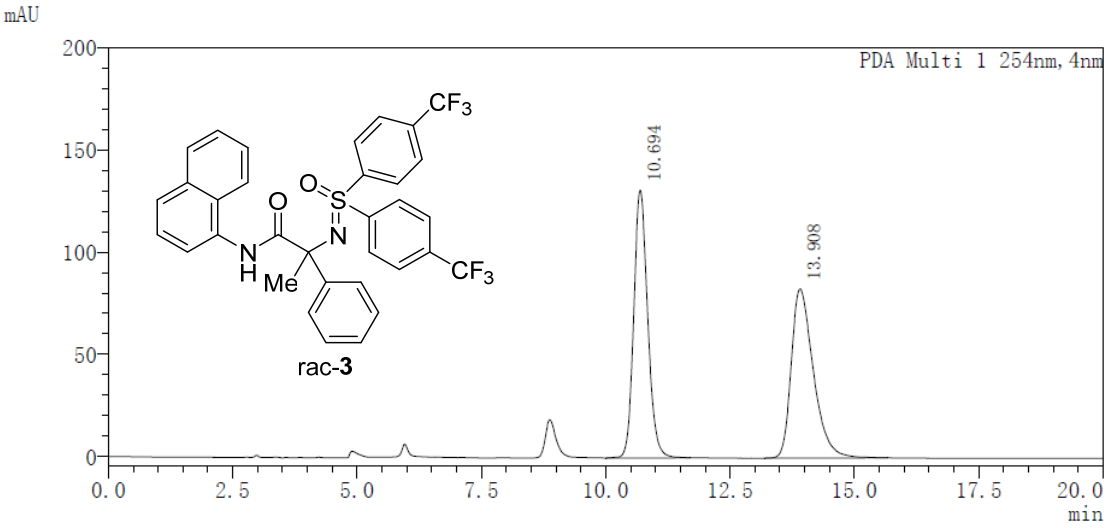
Peak#	Ret. Time	Area	Area%
1	13.837	11775710	50.092
2	21.805	11732389	49.908



Peak Table

PDA Ch1 254nm

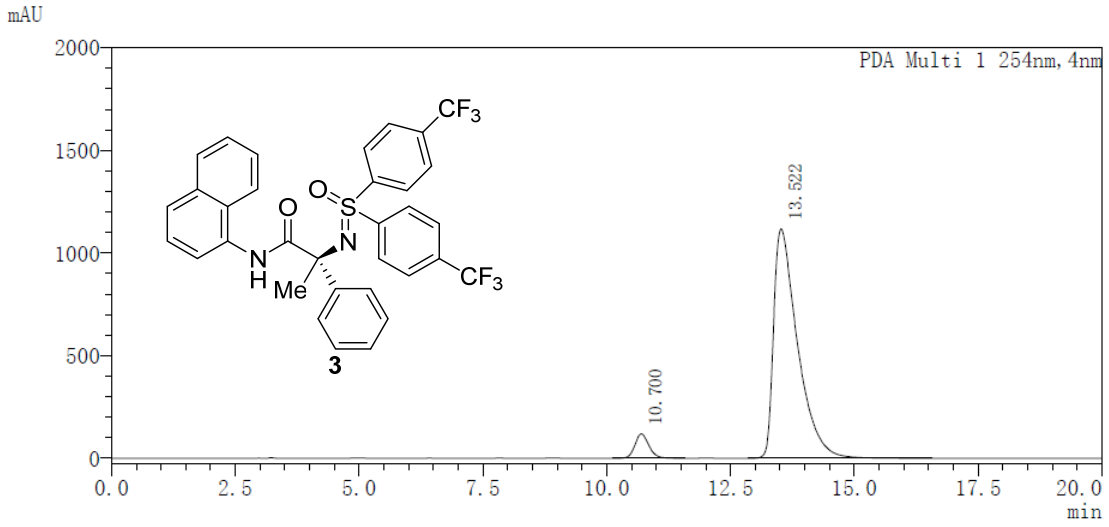
Peak#	Ret. Time	Area	Area%
1	13.325	73284200	94.025
2	21.796	4656645	5.975



Peak Table

PDA Ch1 254nm

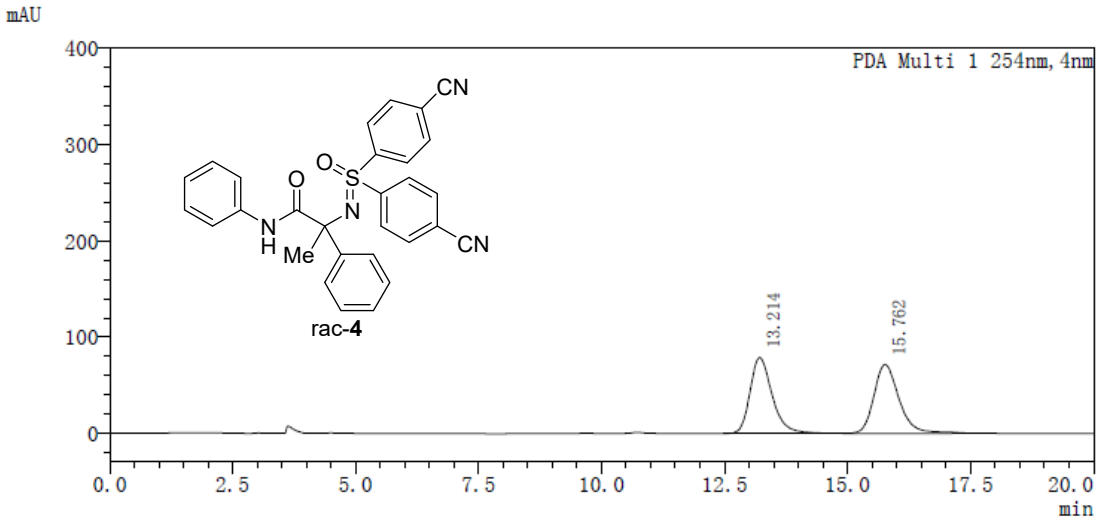
Peak#	Ret. Time	Area	Area%
1	10.694	2556136	49.862
2	13.908	2570250	50.138



Peak Table

PDA Ch1 254nm

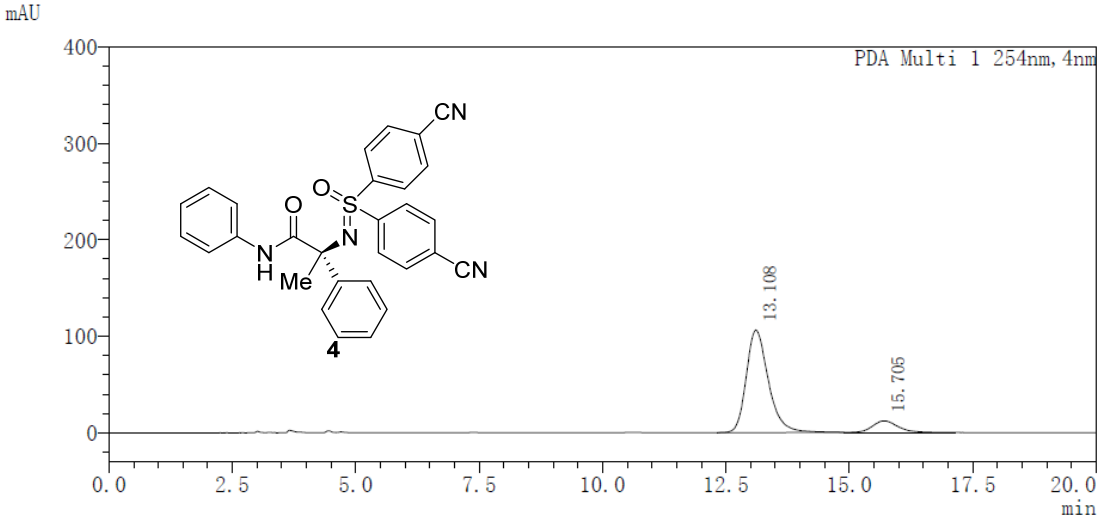
Peak#	Ret. Time	Area	Area%
1	10.700	2308687	5.784
2	13.522	37604420	94.216



Peak Table

PDA Ch1 254nm

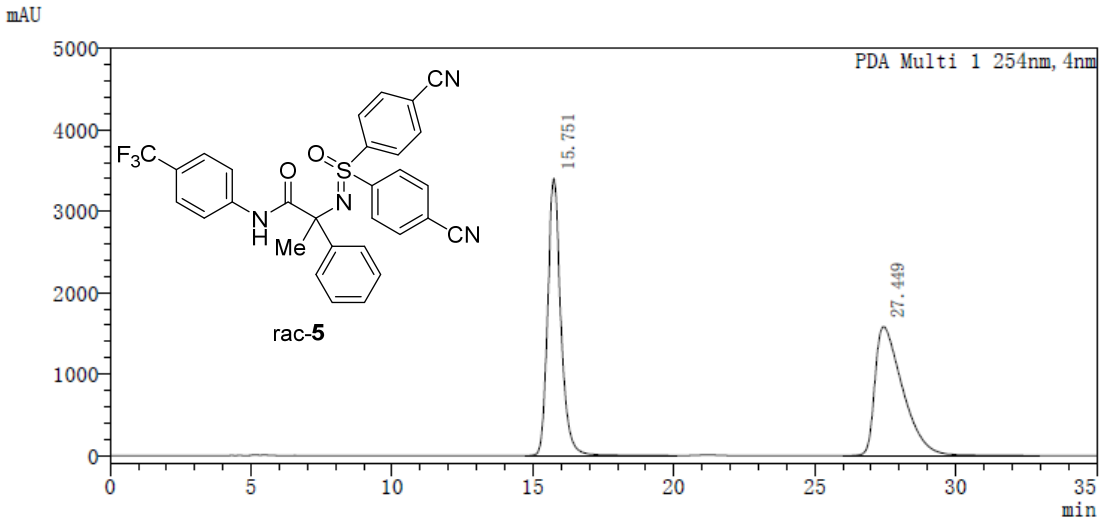
Peak#	Ret. Time	Area	Area%
1	13.214	2495395	49.225
2	15.762	2573970	50.775



Peak Table

PDA Ch1 254nm

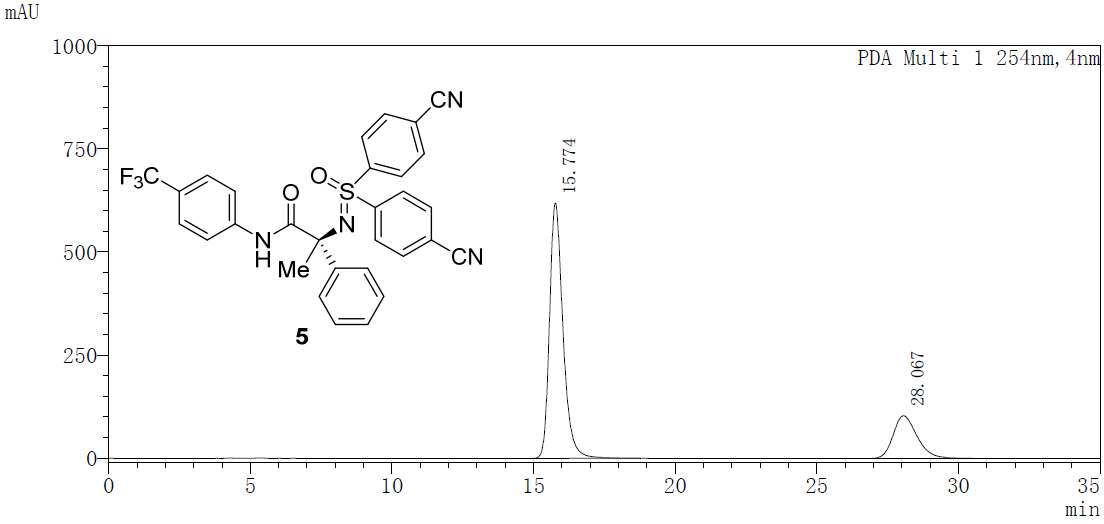
Peak#	Ret. Time	Area	Area%
1	13.108	3327114	88.302
2	15.705	440769	11.698



Peak Table

PDA Ch1 254nm

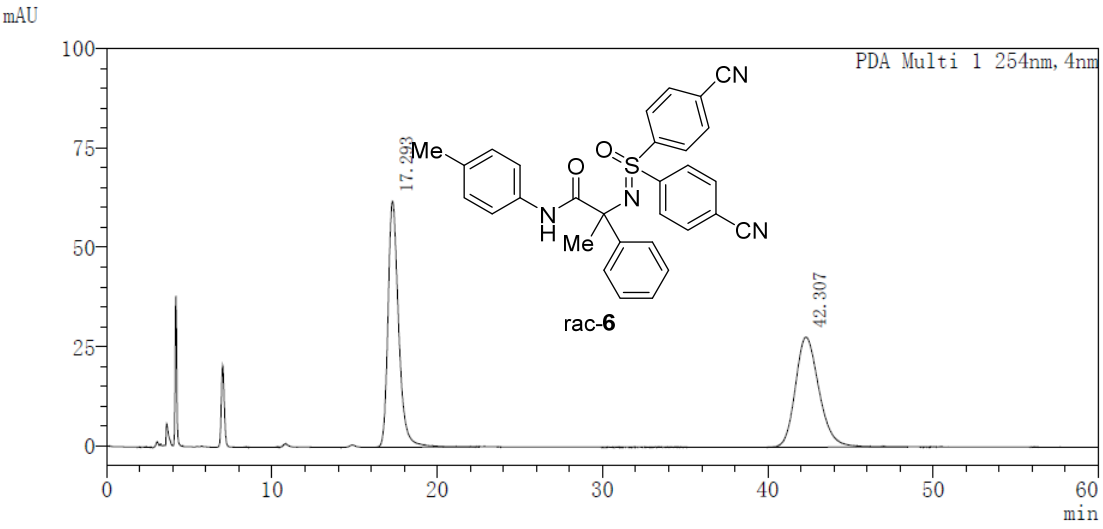
Peak#	Ret. Time	Area	Area%
1	15.751	109897219	50.366
2	27.449	108298765	49.634



Peak Table

PDA Ch1 254nm

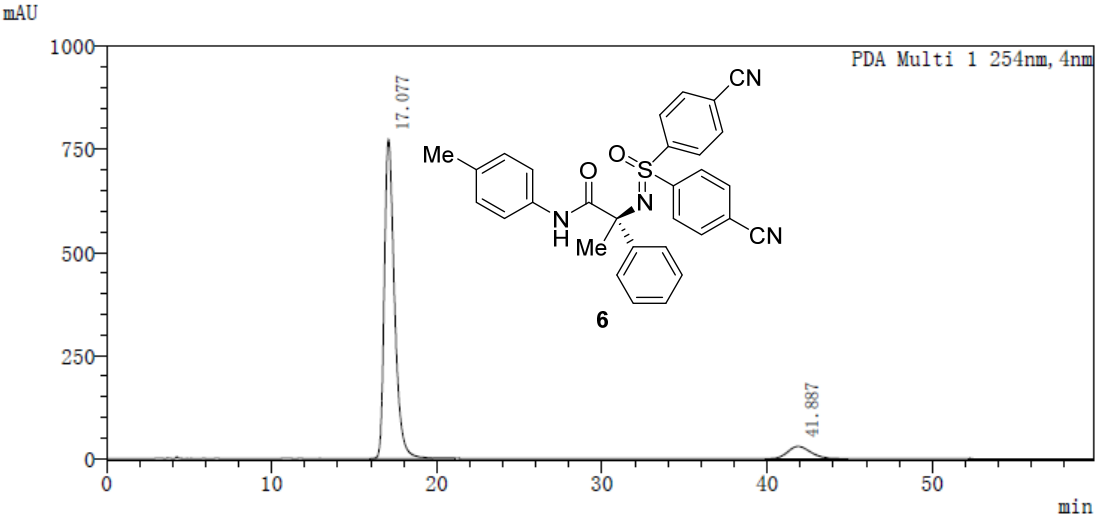
Peak#	Ret. Time	Area	Area%
1	15.774	20465820	77.098
2	28.067	6079270	22.902



Peak Table

PDA Ch1 254nm

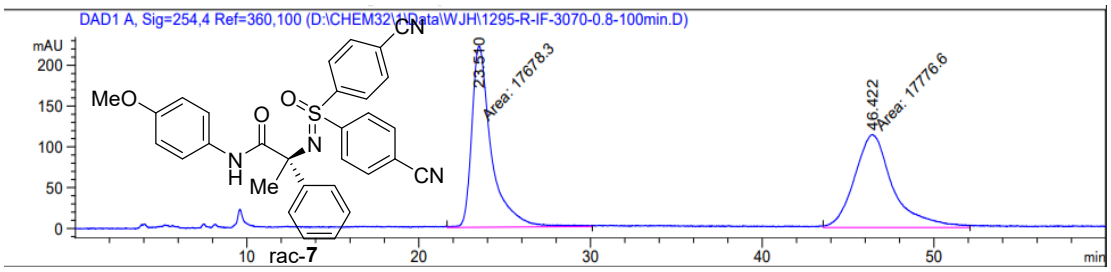
Peak#	Ret. Time	Area	Area%
1	17.293	2772534	50.060
2	42.307	2765834	49.940



Peak Table

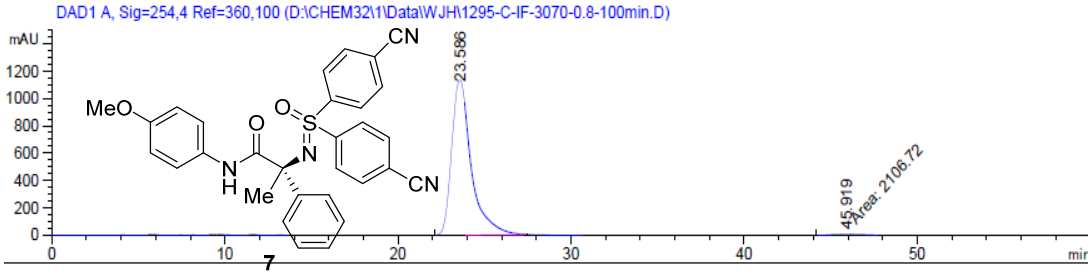
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.077	33137078	91.976
2	41.887	2890819	8.024



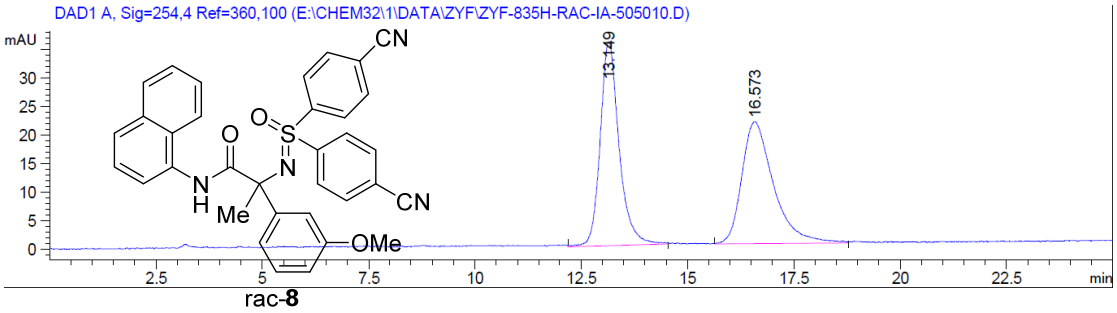
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.510	MM	1.3273	1.76783e4	221.98308	49.8615
2	46.422	MM	2.5955	1.77766e4	114.14861	50.1385
Totals :				3.54549e4	336.13169	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

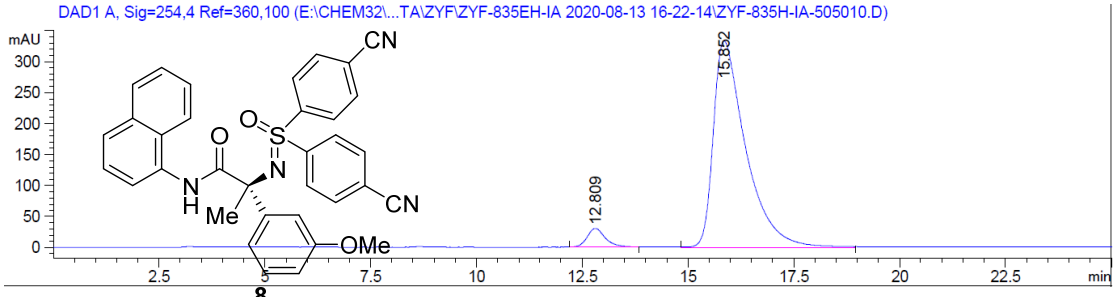
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.586	BV R	0.9295	8.88058e4	1136.64563	97.6827
2	45.919	MM	2.6512	2106.71973	13.24364	2.3173
Totals :				9.09125e4	1149.88927	



rac-**8**

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

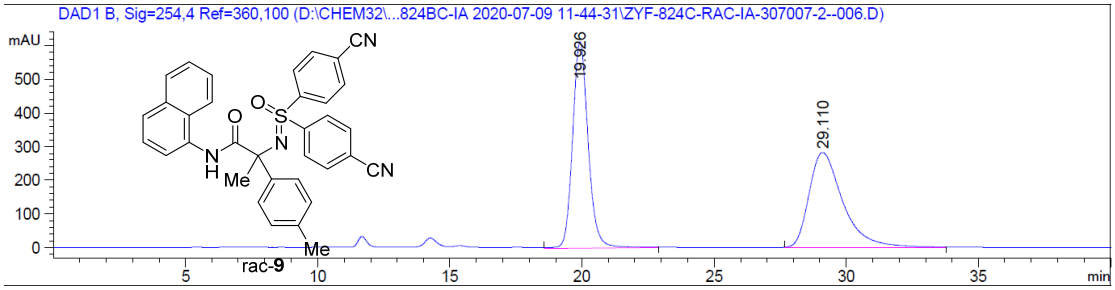
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.149	MM R	0.5131	1101.85181	35.78836	49.8572
2	16.573	MM R	0.8641	1108.16541	21.37340	50.1428
Totals :				2210.01721	57.16176	



8

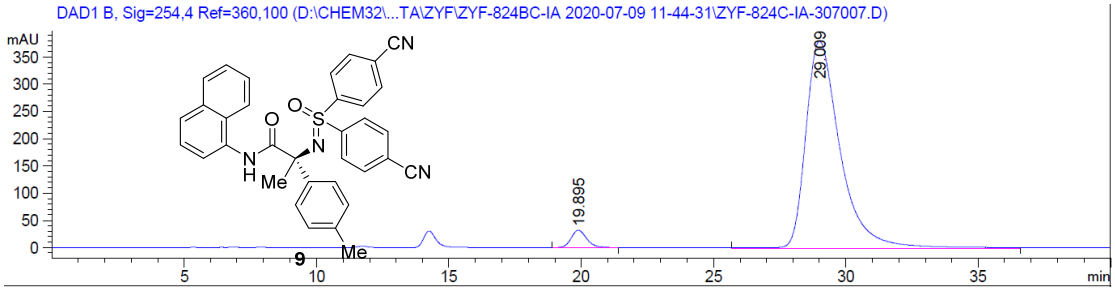
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.809	BB	0.4236	888.89850	30.18337	4.7745
2	15.852	MM R	0.8862	1.77287e4	333.42511	95.2255
Totals :				1.86176e4	363.60848	



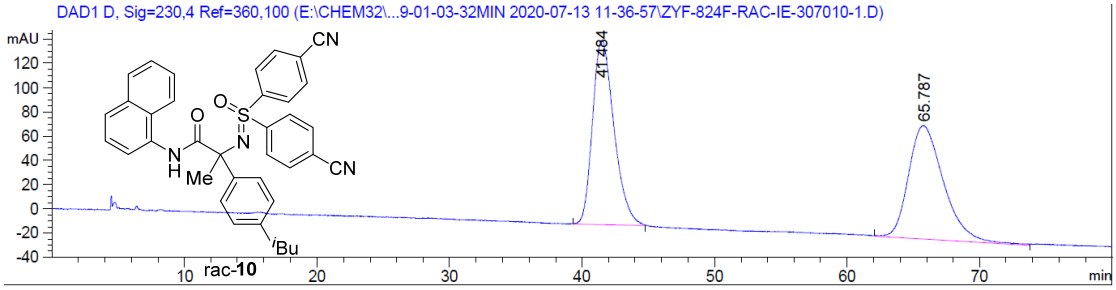
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.926	MM R	0.6829	2.51603e4	614.03613	49.8012
2	29.110	MM R	1.4925	2.53611e4	283.21234	50.1988
Totals :				5.05214e4	897.24847	



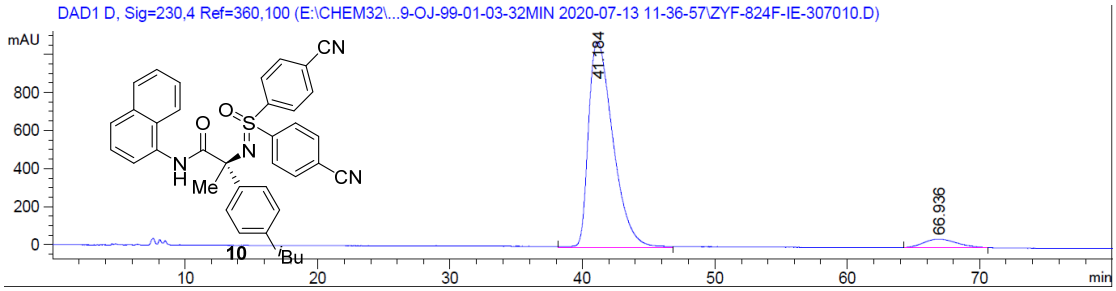
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.895	BB	0.6101	1299.21606	31.83745	3.6172
2	29.009	MM R	1.5161	3.46180e4	380.57184	96.3828
Totals :				3.59173e4	412.40928	



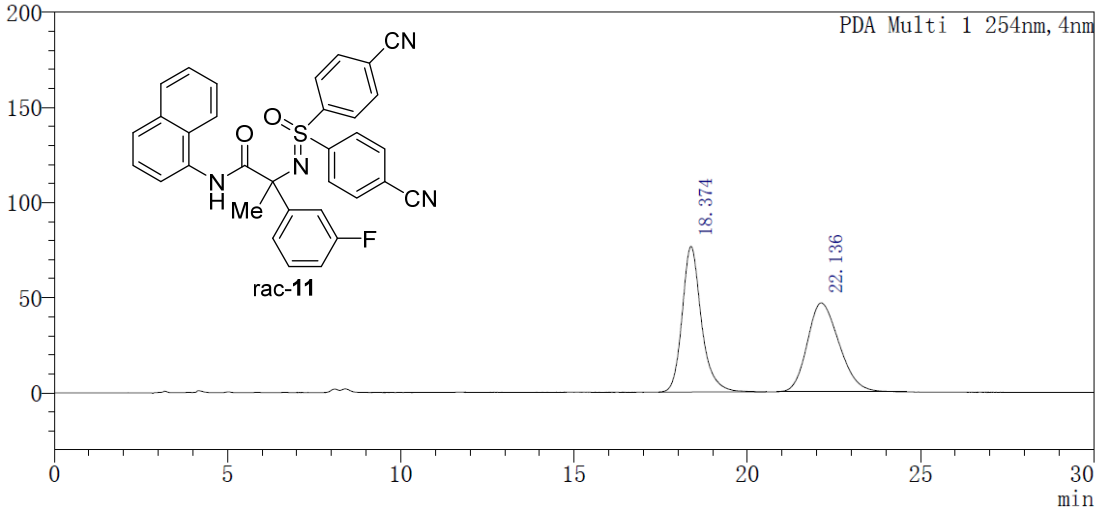
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.484	VV R	1.3253	1.71483e4	152.09937	49.9755
2	65.787	MM R	3.0587	1.71652e4	93.53107	50.0245
Totals :				3.43135e4	245.63043	



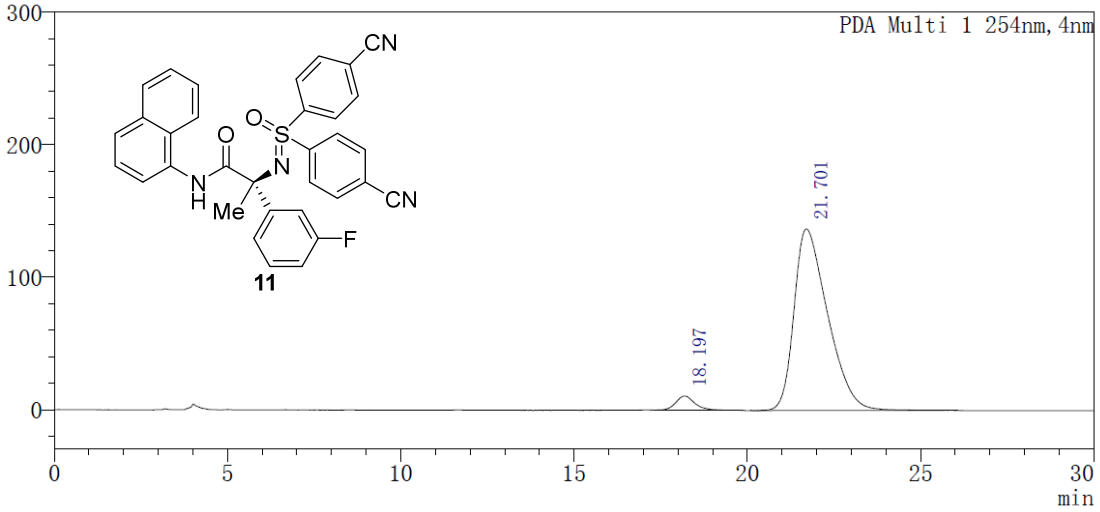
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.184	MM R	2.1393	1.38809e5	1081.42053	94.7657
2	66.936	VV R	2.0192	7667.04102	44.56421	5.2343
Totals :				1.46476e5	1125.98474	



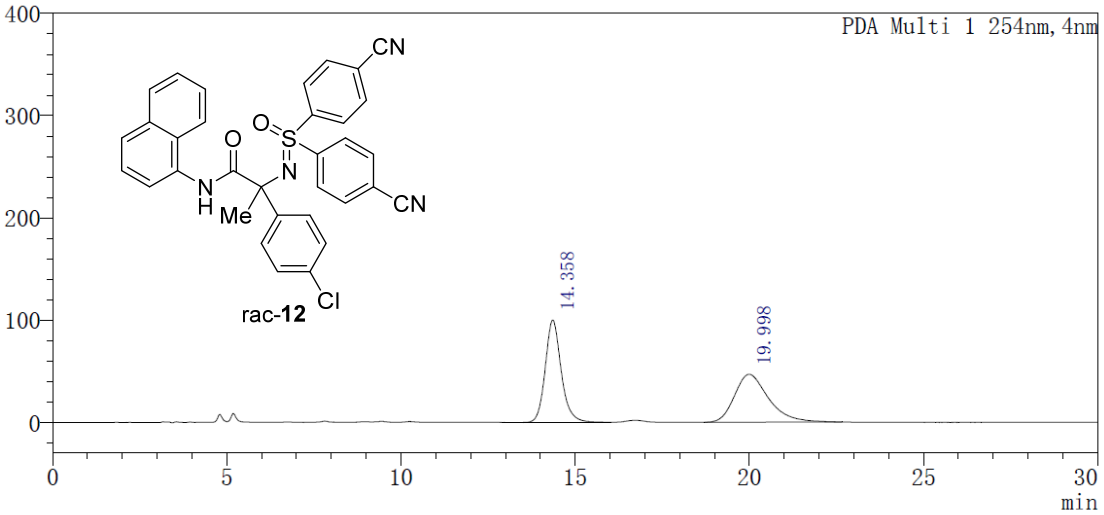
PDA Ch1 254nm

T	Hight	Area	Area%
18.374	76516	2964754	49.699
22.136	46790	3000685	50.301



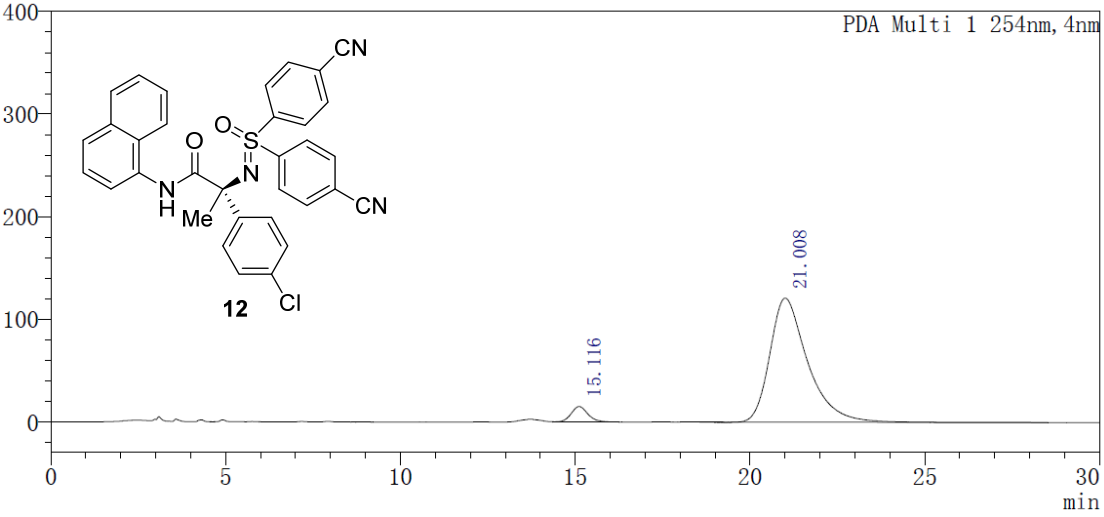
PDA Ch1 254nm

T	Hight	Area	Area%
18.197	10697	403221	4.187
21.701	137100	9227045	95.813



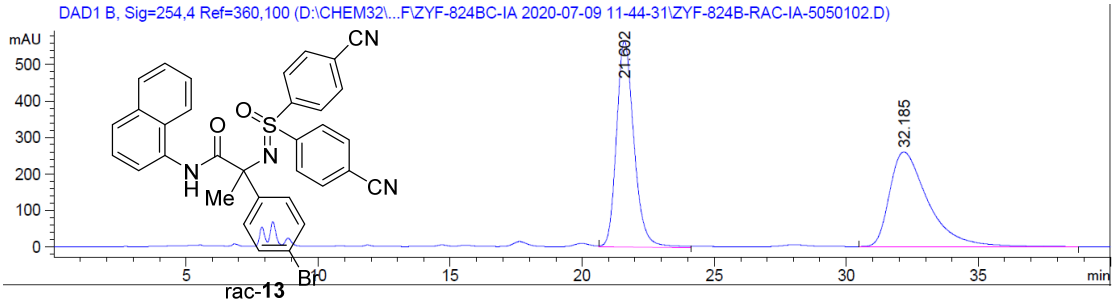
PDA Ch1 254nm

T	Hight	Area	Area%
14.358	100048	3185039	50.087
19.998	46811	3173917	49.913



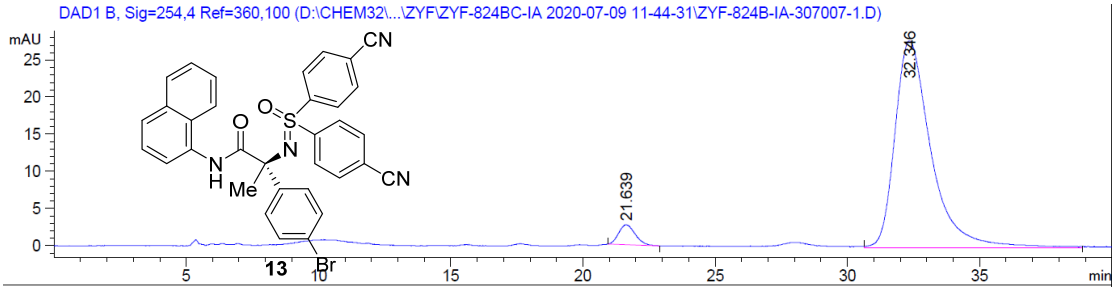
PDA Ch1 254nm

T	Hight	Area	Area%
15.116	14933	487614	5.094
21.008	120937	9085429	94.906



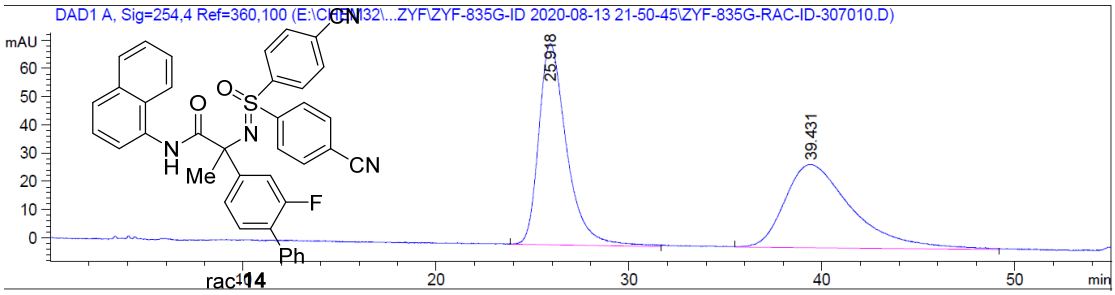
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.602	MM R	0.7691	2.61297e4	566.22473	49.9234
2	32.185	BB	1.4948	2.62100e4	259.83215	50.0766
Totals :				5.23397e4	826.05688	



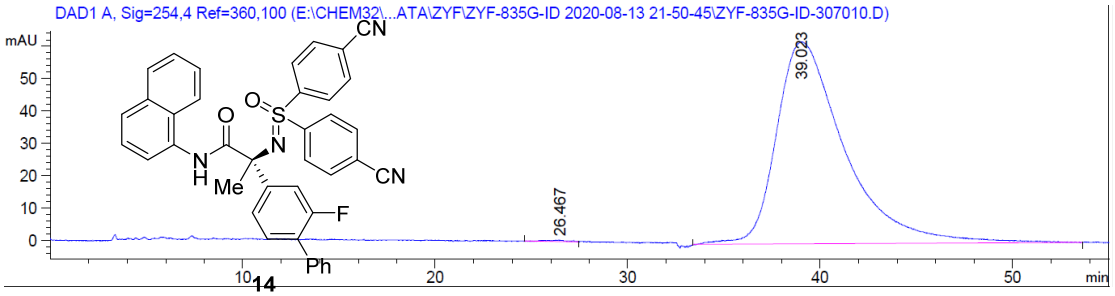
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.639	BB	0.5212	117.49535	2.70282	4.2766
2	32.346	MM R	1.5764	2629.93579	27.80507	95.7234
Totals :				2747.43114	30.50789	



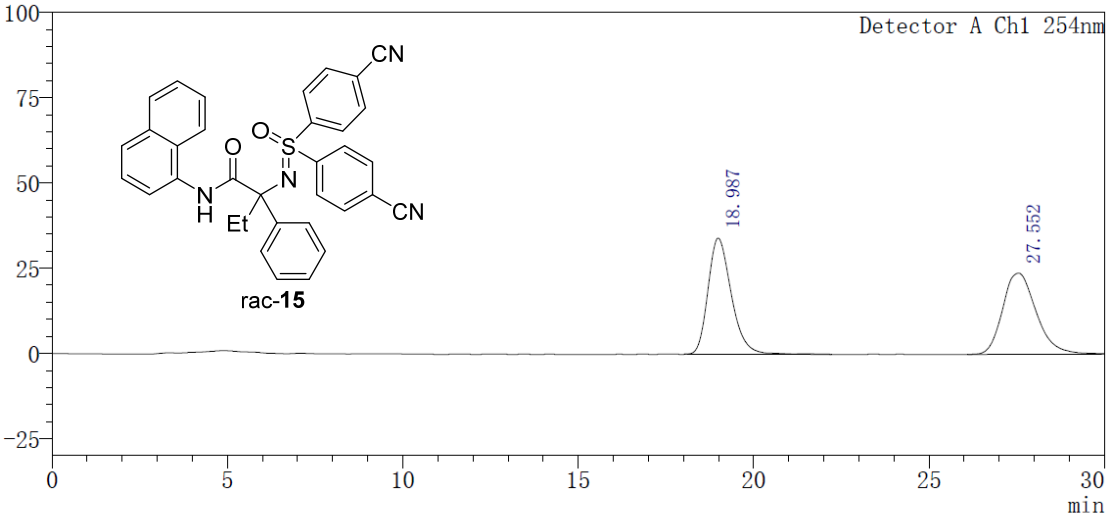
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.918	MM R	1.6710	7152.39697	71.33807	49.9408
2	39.431	MM R	4.0426	7169.35400	29.55756	50.0592
Totals :				1.43218e4	100.89564	



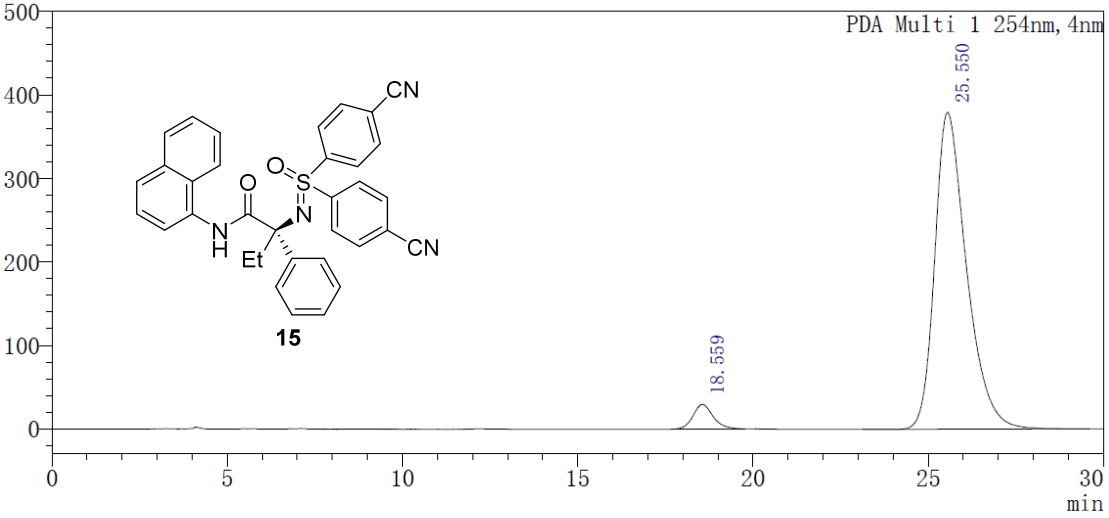
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.467	MM R	1.1152	29.54226	4.41522e-1	0.1918
2	39.023	MM R	4.1035	1.53757e4	62.44929	99.8082
Totals :				1.54052e4	62.89081	



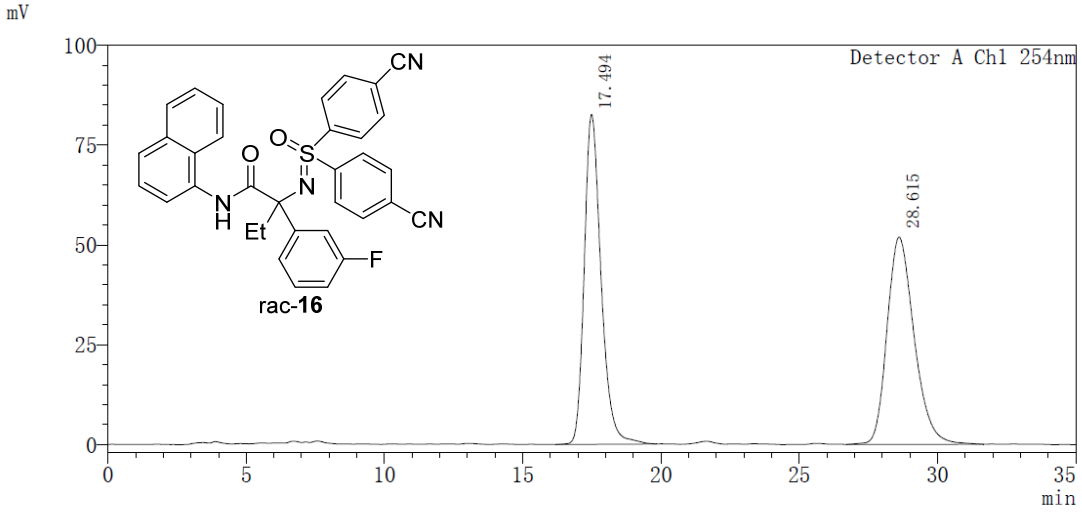
Detector A Ch1 254nm

T	Hight	Area	Area%
18.987	34083	1582438	49.737
27.552	23814	1599168	50.263



PDA Ch1 254nm

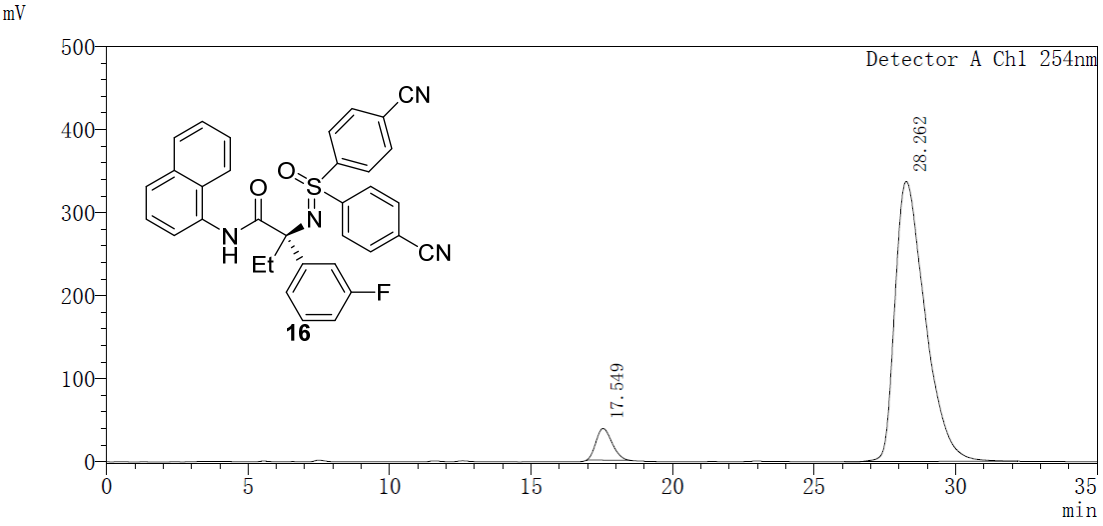
T	Hight	Area	Area%
18.559	29322	1150241	4.583
25.550	379465	23947347	95.417



Peak Table

Detector A Ch1 254nm

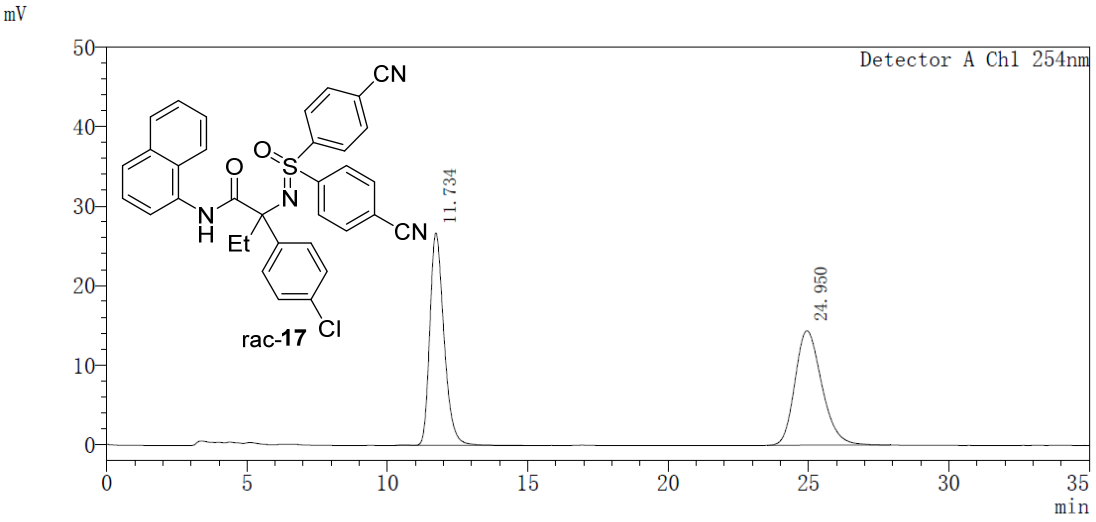
Peak#	Ret. Time	Area	Area%
1	17.494	3498879	49.689
2	28.615	3542713	50.311



Peak Table

Detector A Ch1 254nm

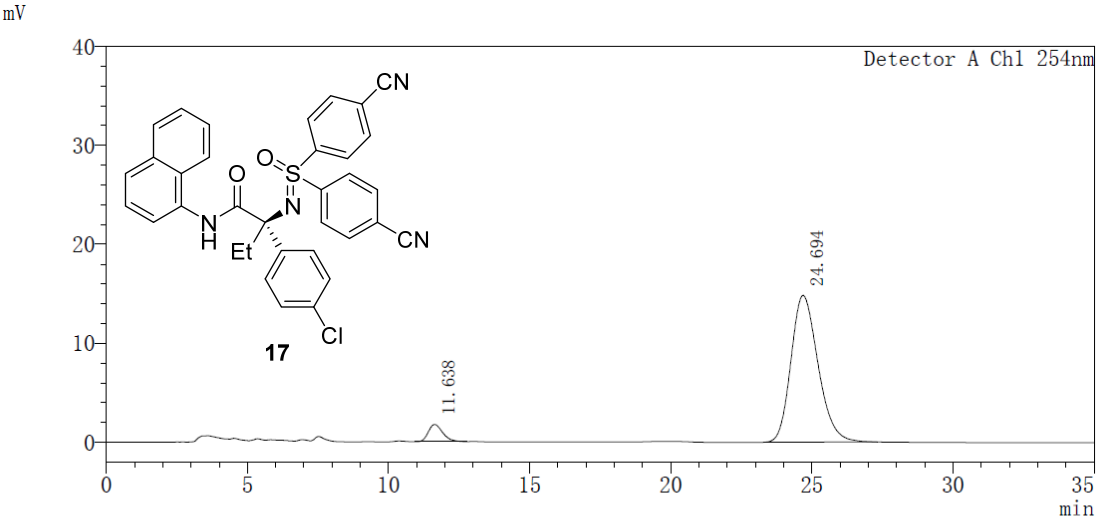
Peak#	Ret. Time	Area	Area%
1	17.549	1493264	5.628
2	28.262	25039997	94.372



Peak Table

Detector A Ch1 254nm

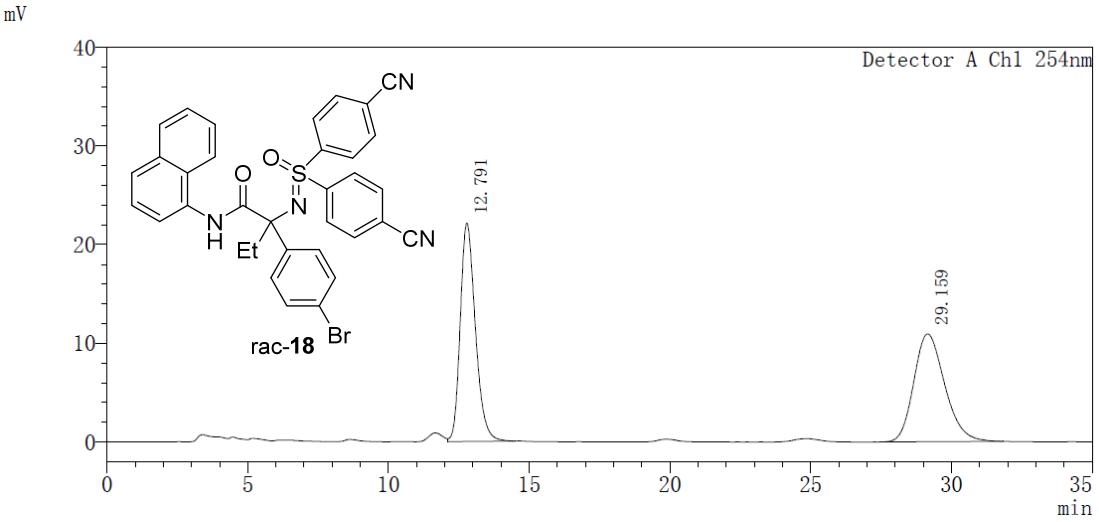
Peak#	Ret. Time	Area	Area%
1	11.734	939360	49.477
2	24.950	959217	50.523



Peak Table

Detector A Ch1 254nm

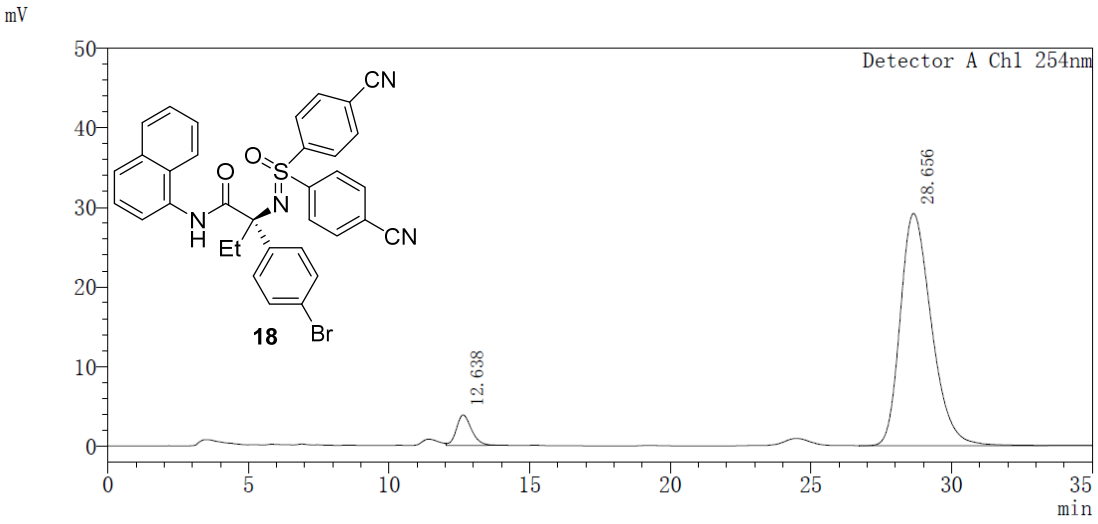
Peak#	Ret. Time	Area	Area%
1	11.638	62198	5.902
2	24.694	991660	94.098



Peak Table

Detector A Ch1 254nm

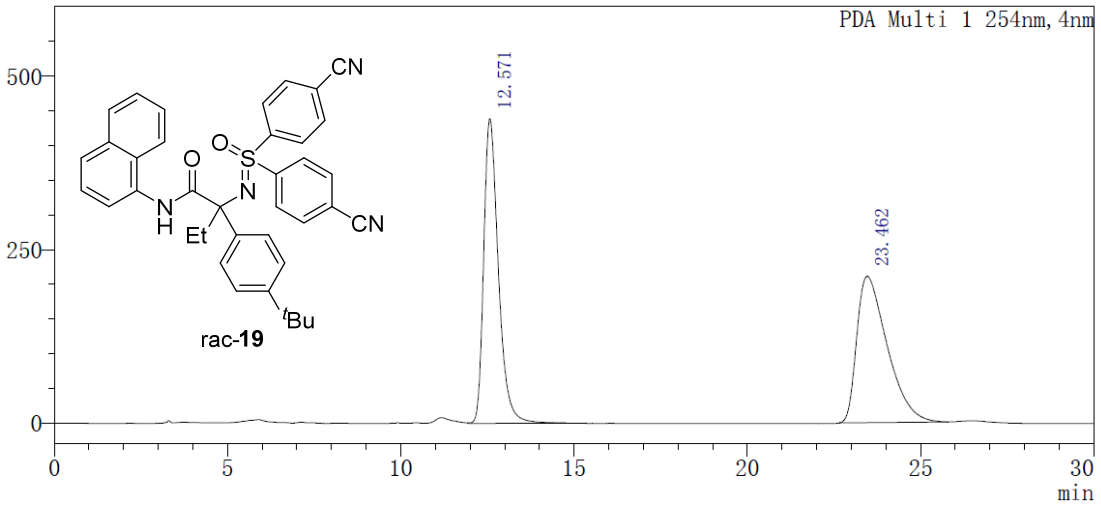
Peak#	Ret. Time	Area	Area%
1	12.791	825063	49.739
2	29.159	833739	50.261



Peak Table

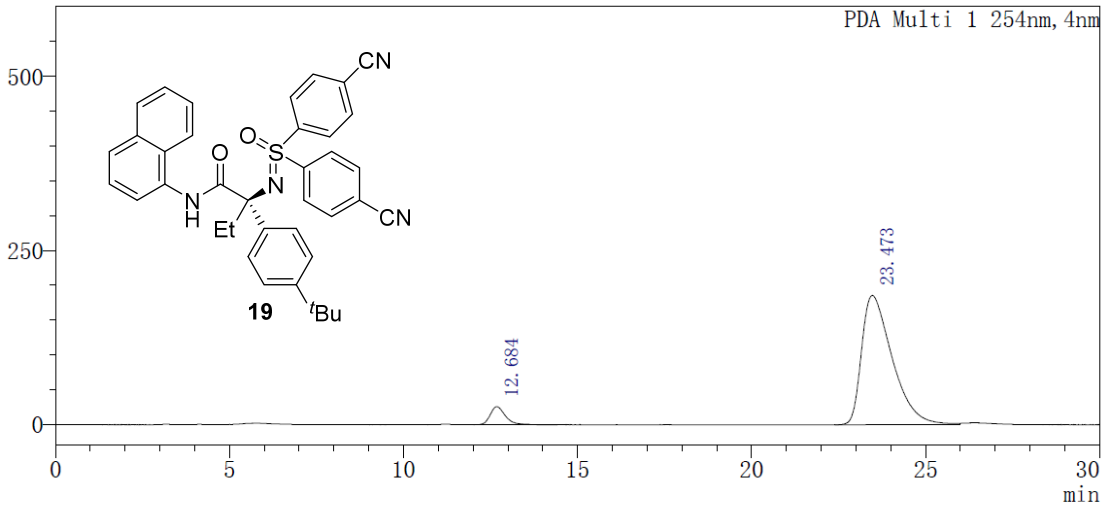
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.638	143511	5.985
2	28.656	2254474	94.015



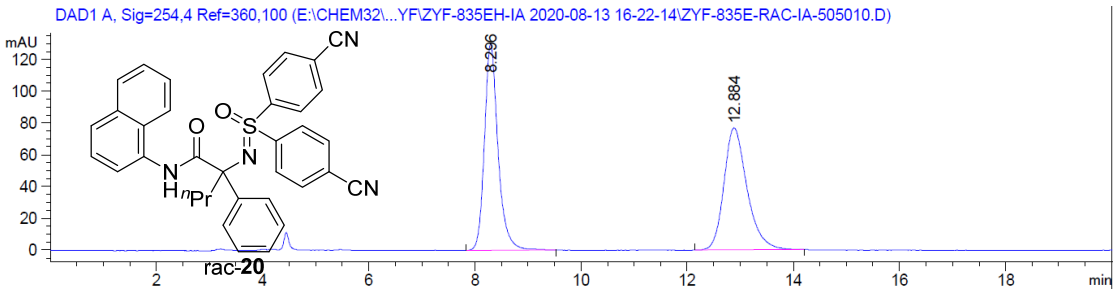
PDA Ch1 254nm

T	Hight	Area	Area%
12.571	438871	12908275	50.082
23.462	210672	12865905	49.918



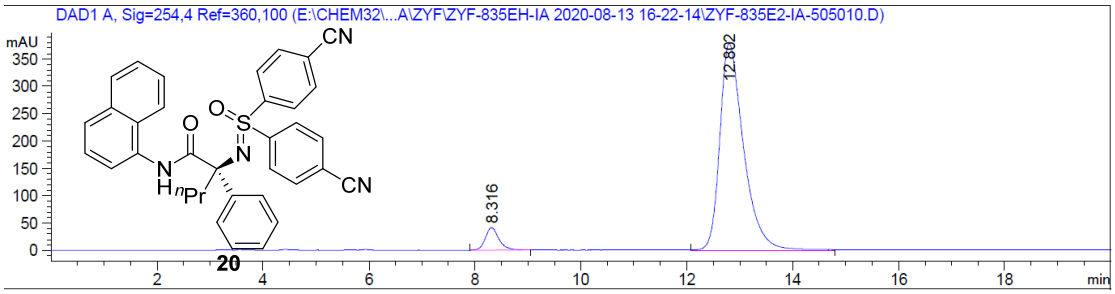
PDA Ch1 254nm

T	Hight	Area	Area%
12.684	25844	777658	6.407
23.473	185510	11359908	93.593



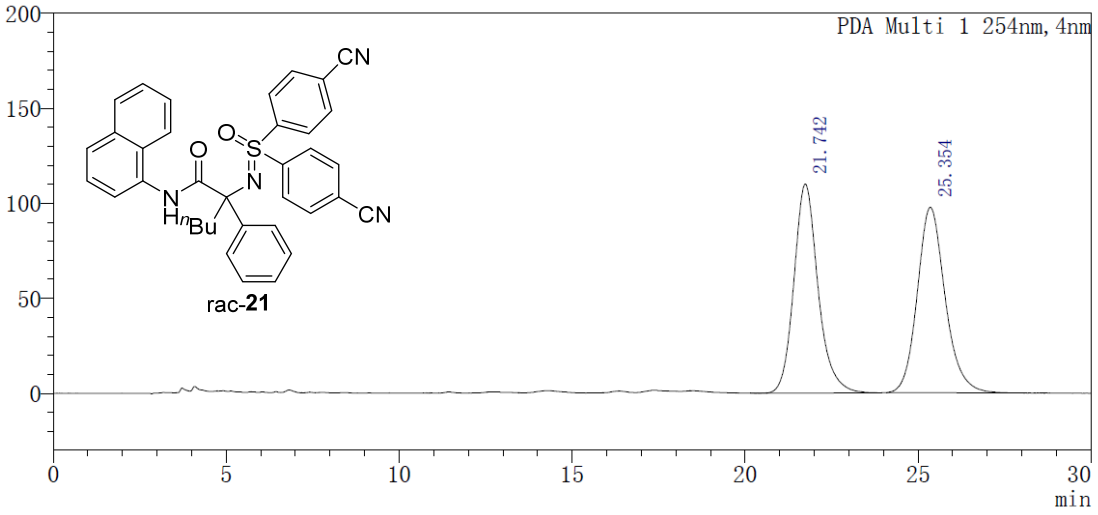
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.296	BB	0.2674	2311.95264	130.03482	49.7802
2	12.884	BB	0.4460	2332.36475	76.86443	50.2198
Totals :				4644.31738	206.89925	



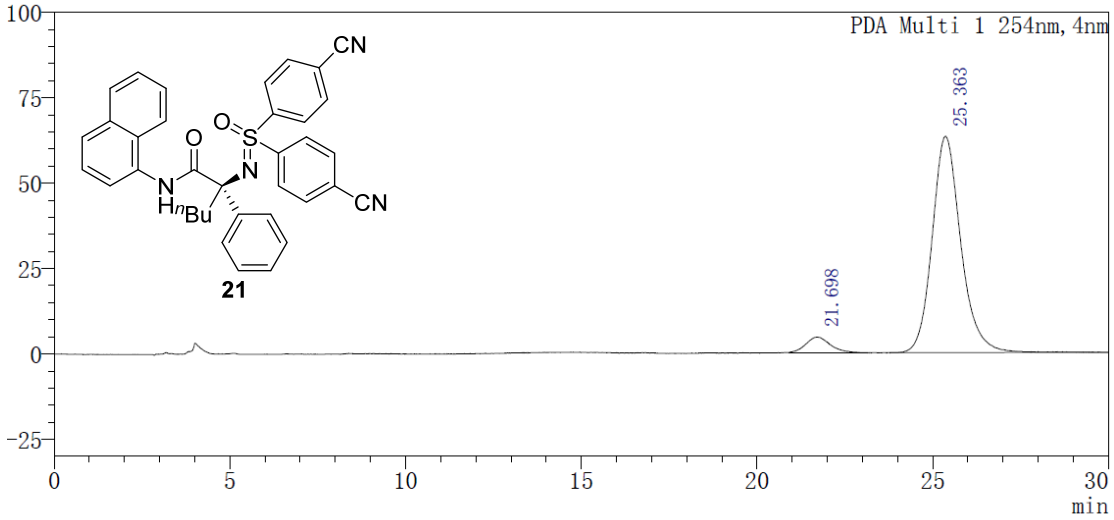
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.316	BB	0.2683	730.57251	40.90911	5.7395
2	12.802	MM R	0.5272	1.19984e4	379.33862	94.2605
Totals :				1.27290e4	420.24773	



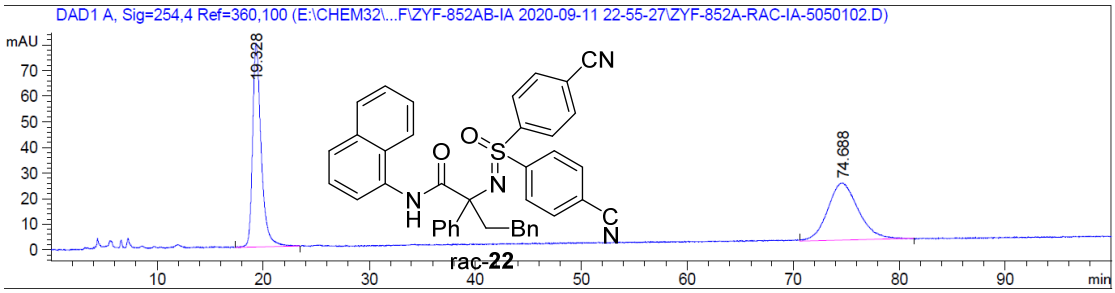
PDA Ch1 254nm

T	Hight	Area	Area%
21.742	109966	5341815	49.402
25.354	97602	5471053	50.598



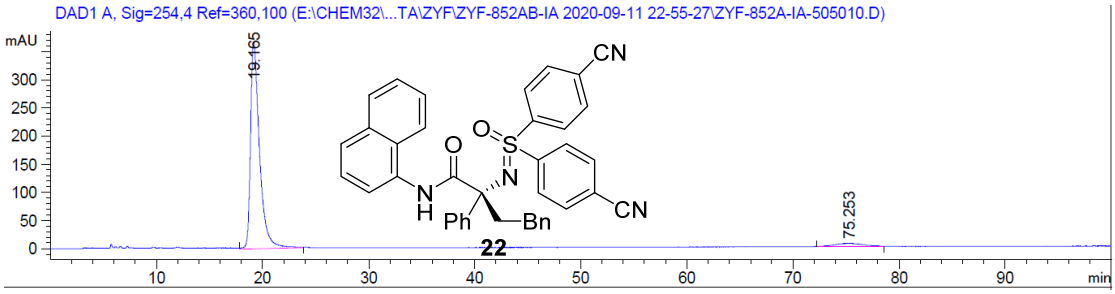
PDA Ch1 254nm

T	Hight	Area	Area%
21.698	4622	226532	5.924
25.363	63341	3597716	94.076



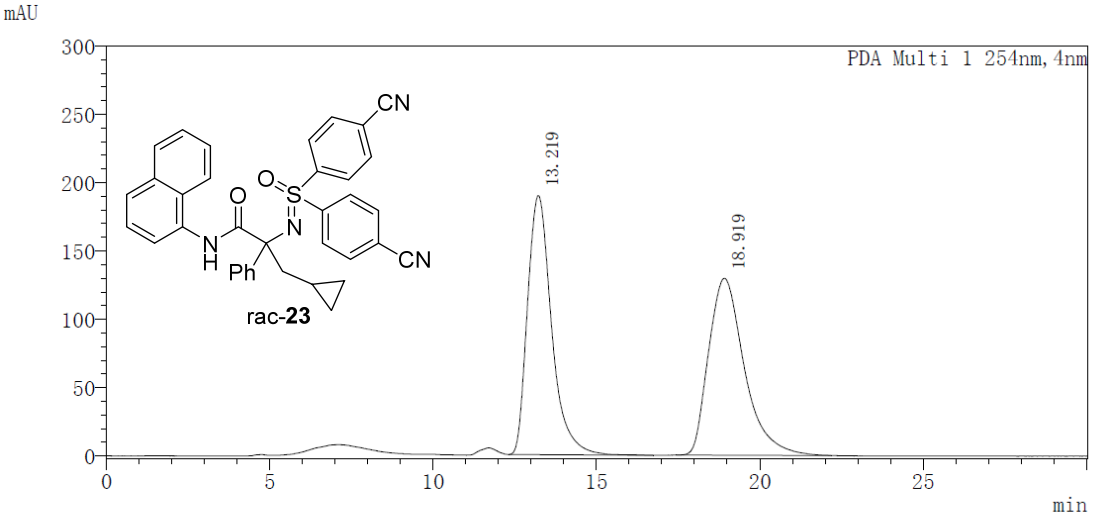
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.328	MM R	0.9394	4486.34521	79.59953	50.0603
2	74.688	MM R	3.3370	4475.53857	22.35321	49.9397
Totals :				8961.88379	101.95274	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

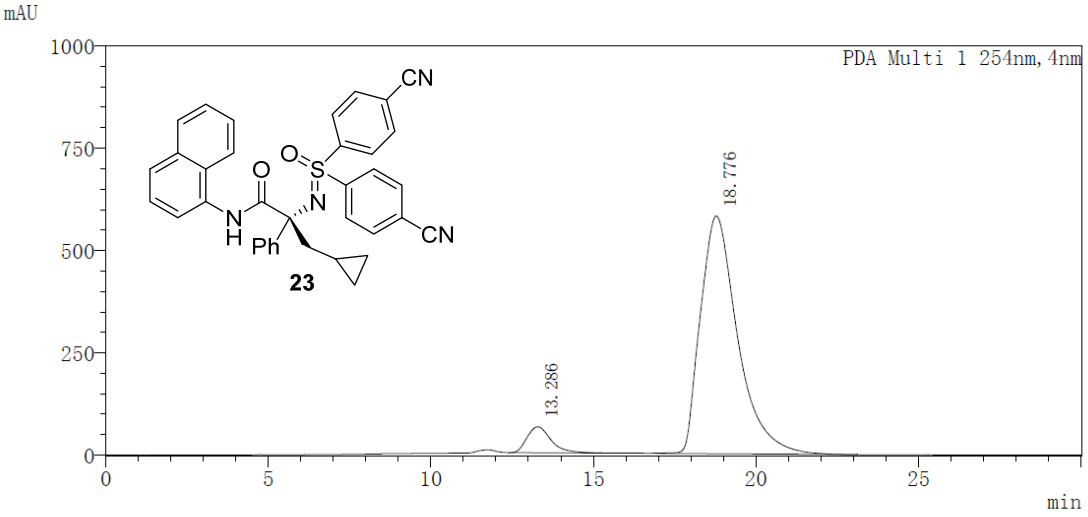
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.165	MM R	0.9802	2.16186e4	367.57486	95.3100
2	75.253	MM R	3.0835	1063.79956	5.74996	4.6900
Totals :				2.26824e4	373.32482	



Peak Table

PDA Ch1 254nm

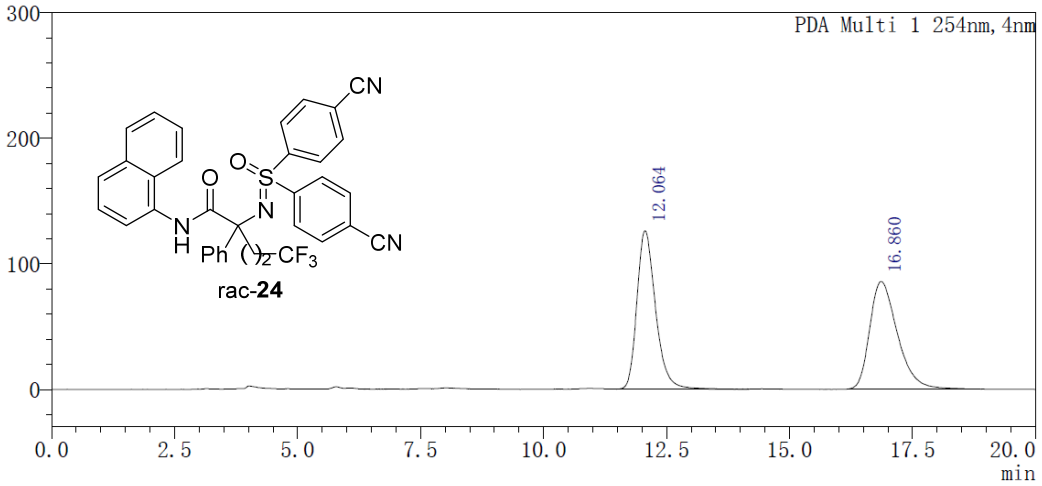
Peak#	Ret. Time	Area	Area%
1	13.219	9726175	49.644
2	18.919	9865703	50.356



Peak Table

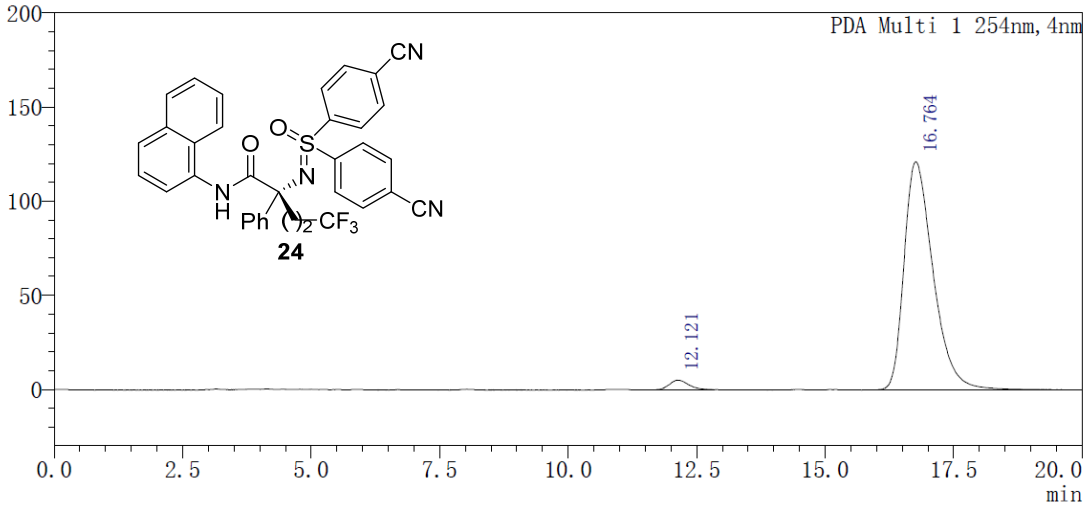
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.286	3266530	6.594
2	18.776	46274461	93.406



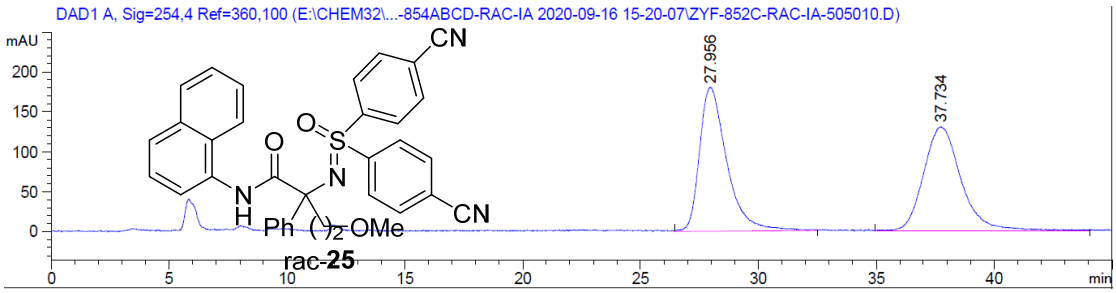
PDA Ch1 254nm

T	Hight	Area	Area%
12.064	126063	3325025	49.932
16.860	85624	3334053	50.068



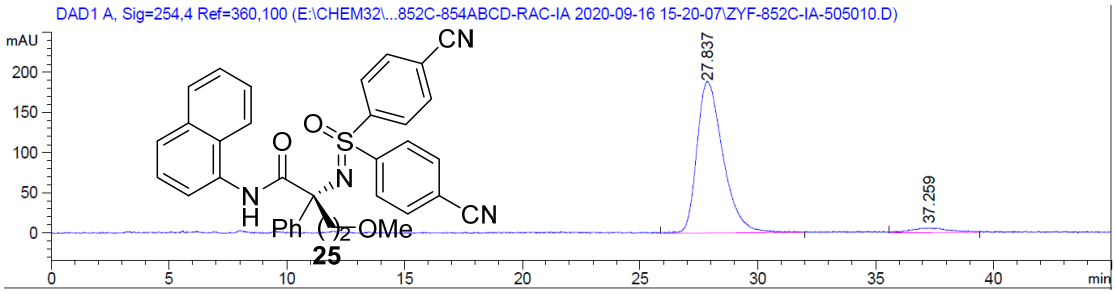
PDA Ch1 254nm

T	Hight	Area	Area%
12.121	5091	133458	2.720
16.764	121086	4772725	97.280



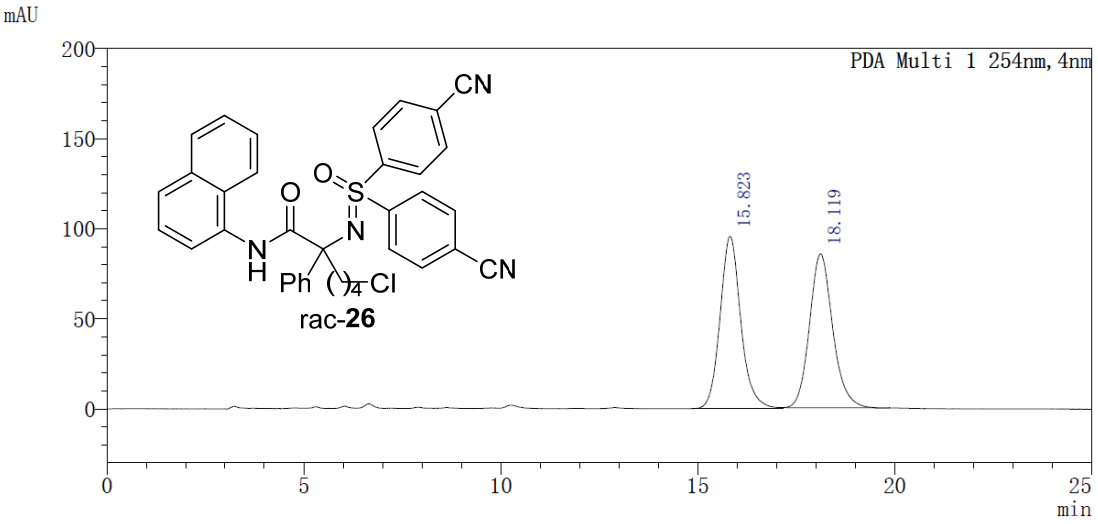
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.956	MM R	1.3450	1.45055e4	179.74248	50.4092
2	37.734	MM R	1.8343	1.42700e4	129.65741	49.5908
Totals :				2.87755e4	309.39989	



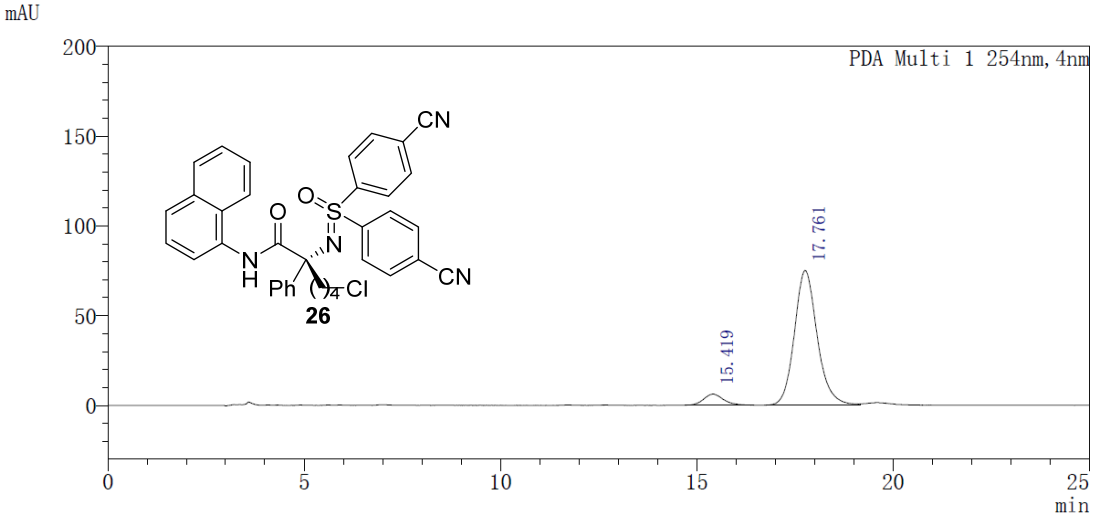
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.837	MM R	1.2856	1.45605e4	188.76358	95.9090
2	37.259	MM R	1.7927	621.06989	5.77400	4.0910
Totals :				1.51815e4	194.53758	



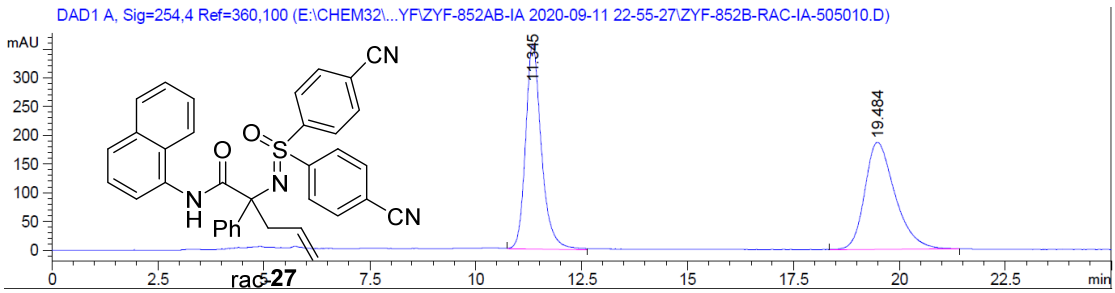
PDA Ch1 254nm

T	Hight	Area	Area%
15.823	95600	3511174	50.058
18.119	85406	3503008	49.942



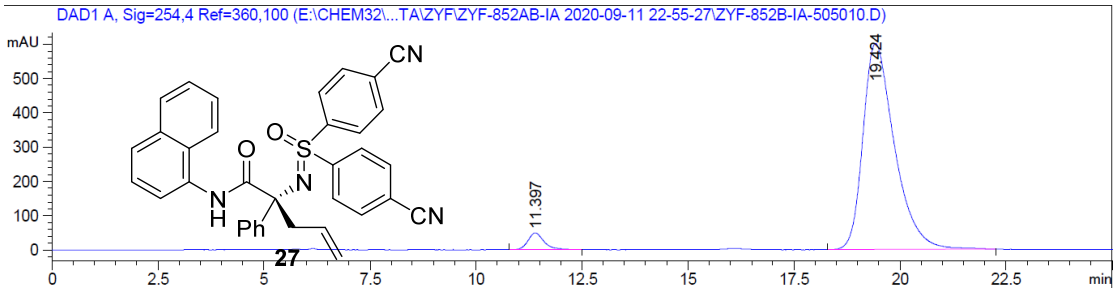
PDA Ch1 254nm

T	Hight	Area	Area%
15.419	6219	218335	6.732
17.761	74912	3024678	93.268



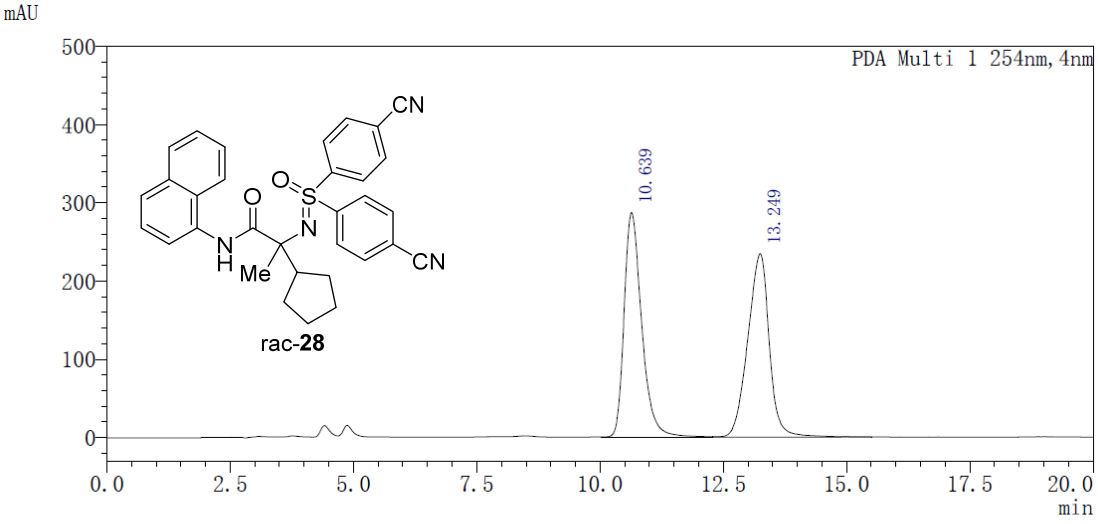
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.345	MM R	0.4332	9290.48535	357.46802	50.1069
2	19.484	BV R	0.7035	9250.84277	186.23959	49.8931
Totals :				1.85413e4	543.70761	



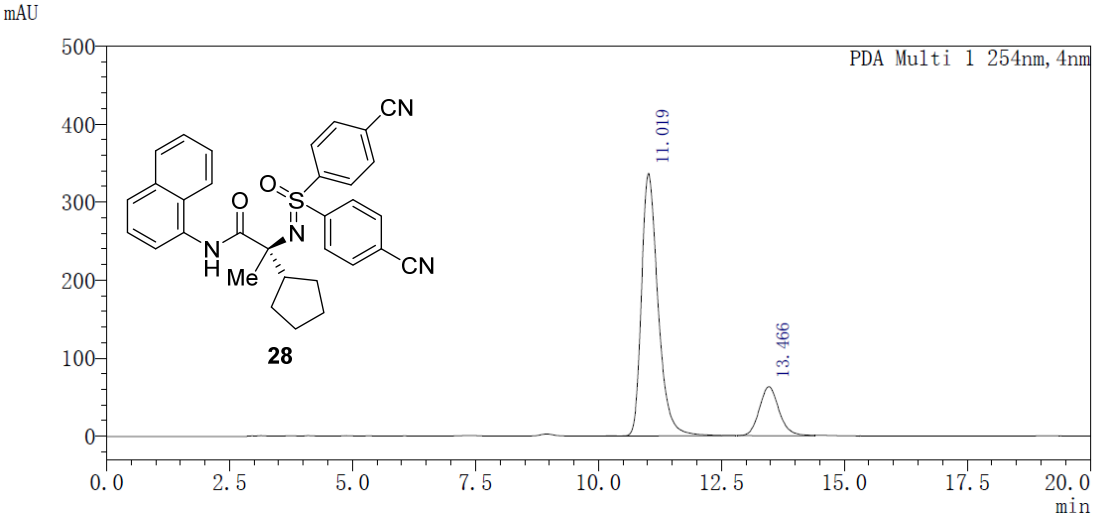
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.397	BB	0.3829	1299.19897	48.75248	4.0077
2	19.424	BV R	0.7404	3.11187e4	600.67297	95.9923
Totals :				3.24179e4	649.42545	



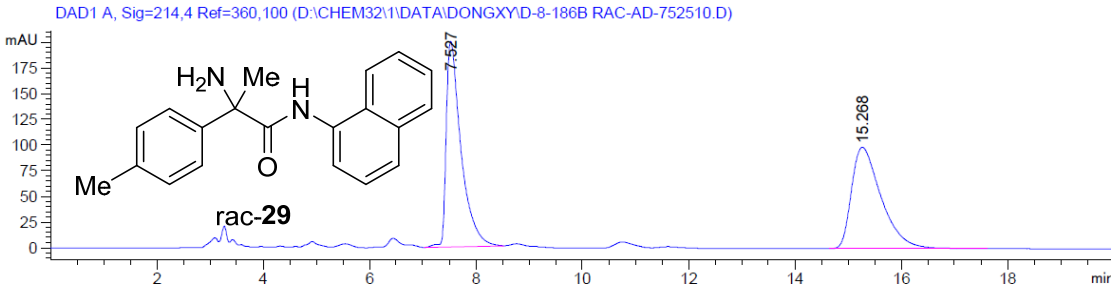
PDA Ch1 254nm

T	Hight	Area	Area%
10.639	286936	7141798	50.115
13.249	234414	7109071	49.885



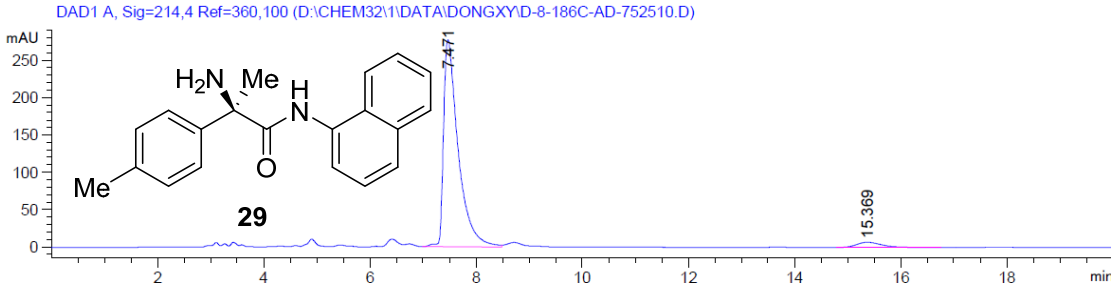
PDA Ch1 254nm

T	Hight	Area	Area%
11.019	336392	7886148	81.809
13.466	62761	1753599	18.191



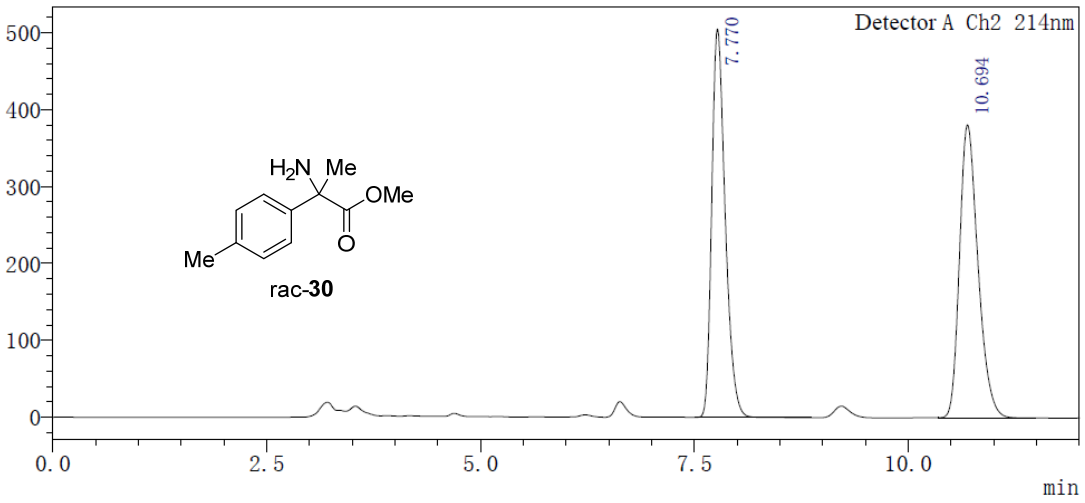
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.527	BB	0.2853	3864.03564	200.08275	50.2452
2	15.268	BB	0.5803	3826.31519	98.69917	49.7548
Totals :				7690.35083	298.78191	



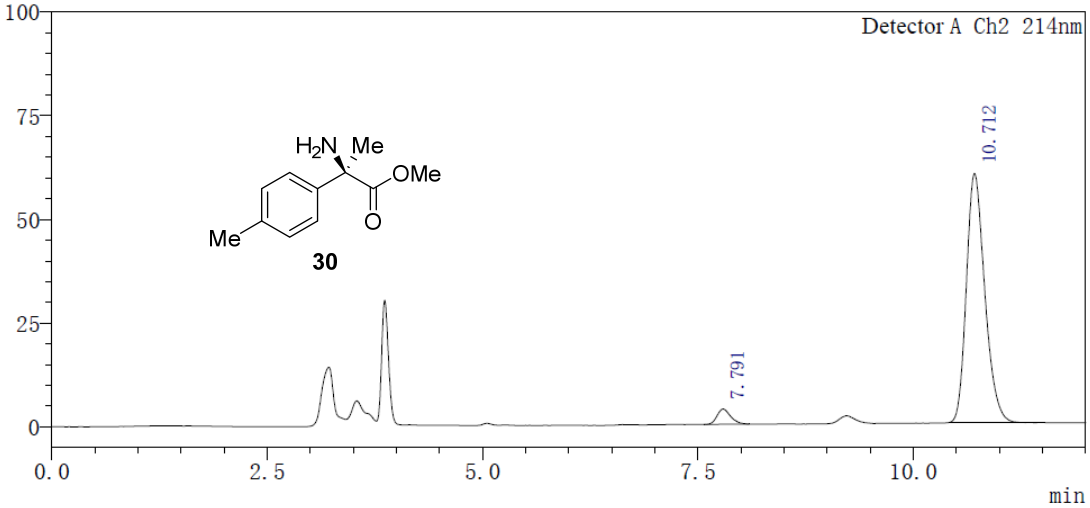
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.471	BV	0.2814	5306.15479	277.10092	95.6885
2	15.369	BB	0.4398	239.08099	7.08251	4.3115
Totals :				5545.23578	284.18343	



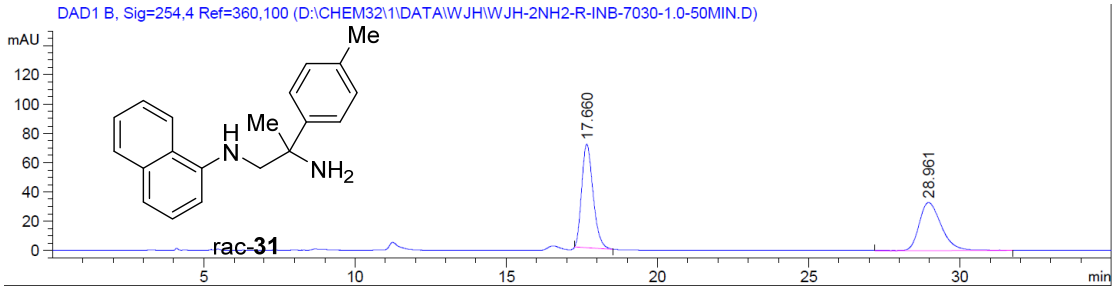
Detector A Ch2 214nm

T	Hight	Area	Area%
7.770	505470	5573435	49.356
10.694	381328	5718864	50.644



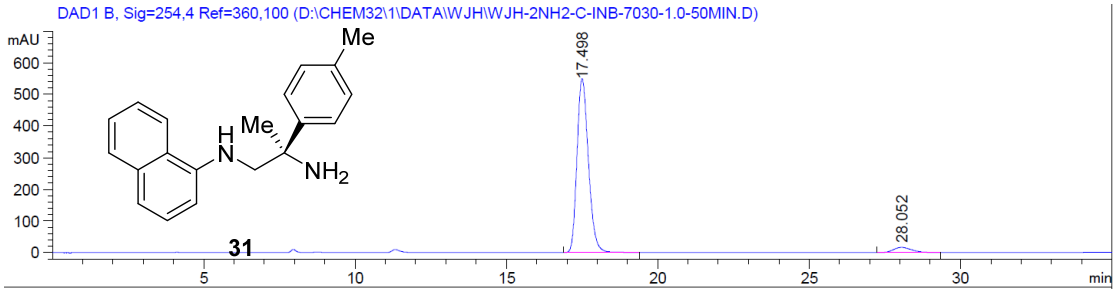
Detector A Ch2 214nm

T	Hight	Area	Area%
7.791	3693	40084	4.315
10.712	60008	888818	95.685
			100.000



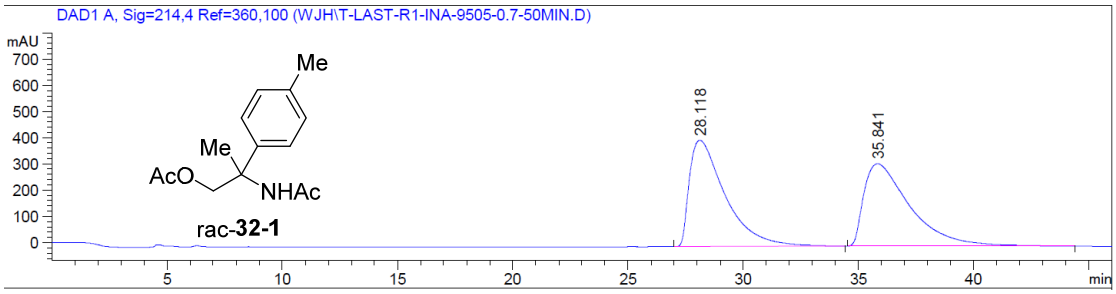
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.660	MM R	0.4366	1850.22595	70.62350	52.4332
2	28.961	MM R	0.8510	1678.50574	32.87244	47.5668
Totals :				3528.73169	103.49594	



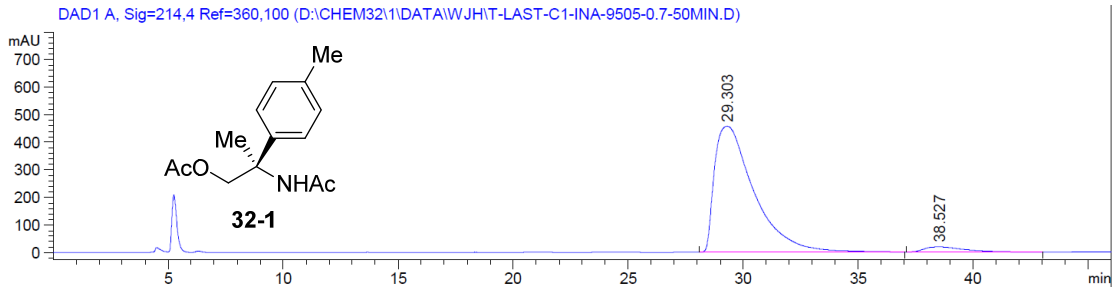
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.498	BB	0.4053	1.43747e4	549.30121	95.2739
2	28.052	BB	0.5294	713.06238	16.65885	4.7261
Totals :				1.50878e4	565.96006	



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.118	BB	1.6015	4.38098e4	404.53345	49.9457
2	35.841	MM R	2.3278	4.39049e4	314.35239	50.0543
Totals :				8.77147e4	718.88583	



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.303	BB	1.7742	5.47107e4	456.49927	95.8778
2	38.527	BB	1.4690	2352.22241	18.83489	4.1222
Totals :				5.70629e4	475.33415	