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SUPPLEMENTARY INFORMATION

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Cu-catalysed intramolecular radical enantioconvergent tertiary β-C(sp^3)–H amination of racemic ketones

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Supplementary Information

Cu-Catalysed intramolecular radical enantioconvergent tertiary β-C(sp^3)–H amination of racemic ketones

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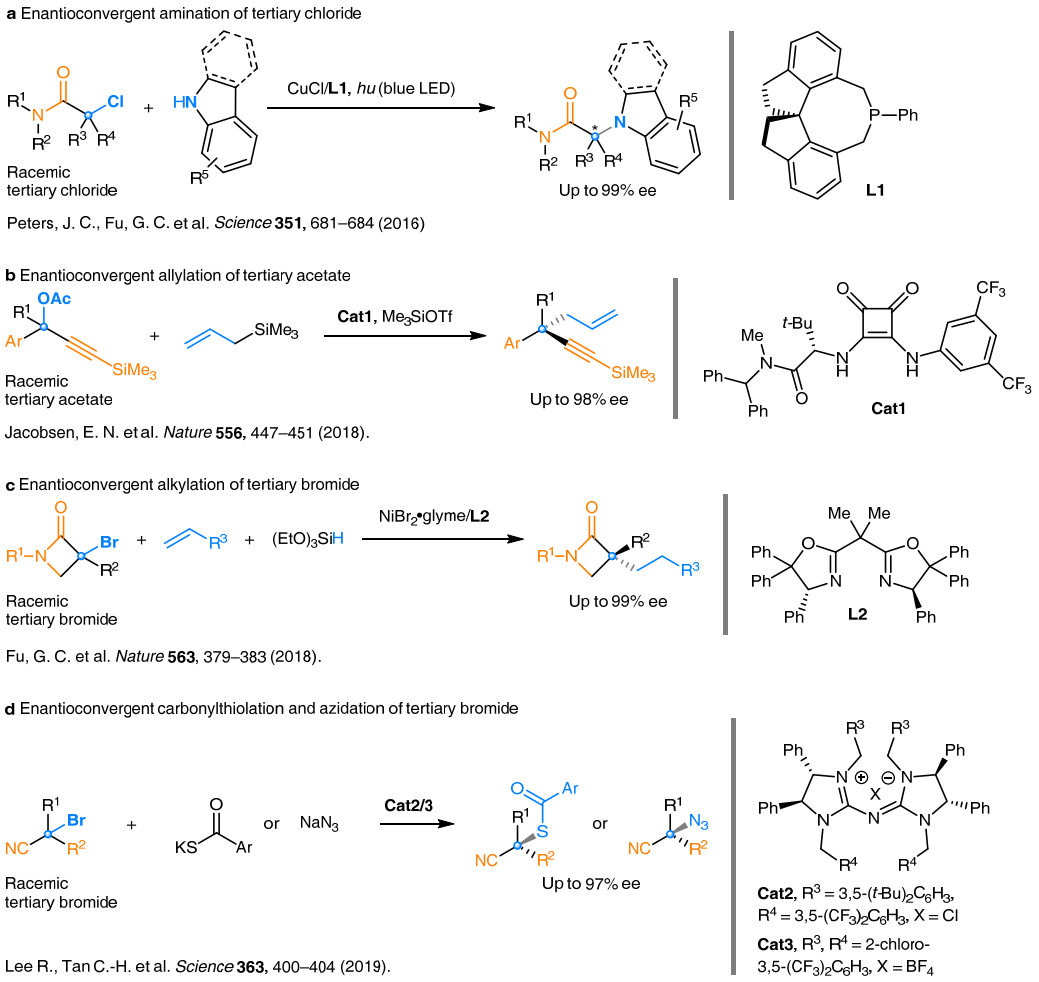
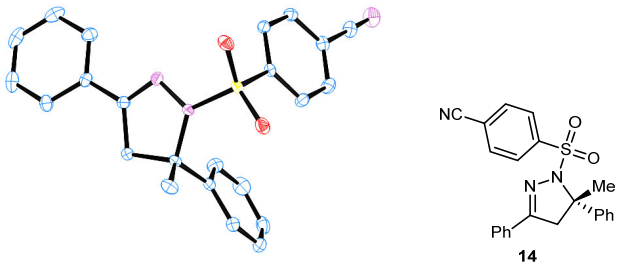
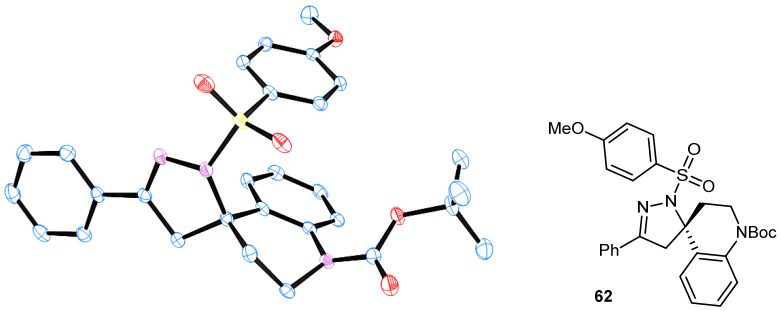


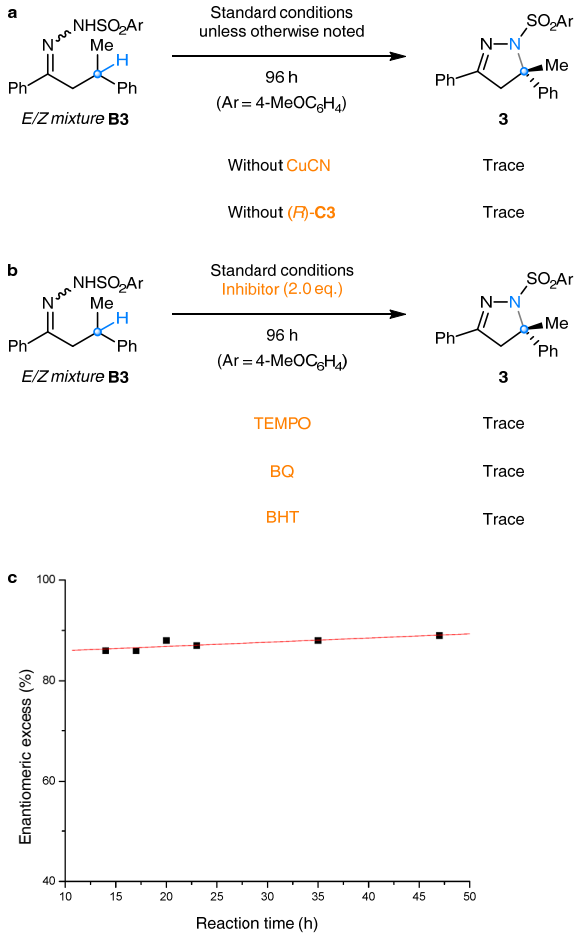
Supplementary Figure 1 Enantioconvergent transformations from racemic tertiary alkyl electrophiles. a, Fu and his coworkers reported the first radical enantioconvergent amination of racemic tertiary chloride with asymmetric copper catalysis under photochemical conditions. **b**, Jacobsen et al. achieved enantioconvergent allylation of racemic tertiary acetate with hydrogen-bonding organocatalysis together with Lewis acid via a unique S_N1 mechanism. **c**, Fu et al. reported radical enantioconvergent alkylation of racemic tertiary bromide with asymmetric nickel catalysis. **d**, Tan et al. disclosed enantioconvergent carbonylthiolation and azidation of tertiary bromide via an unusual S_N2X mechanism.



Supplementary Figure 2 The X-ray structure of chiral compound 14.



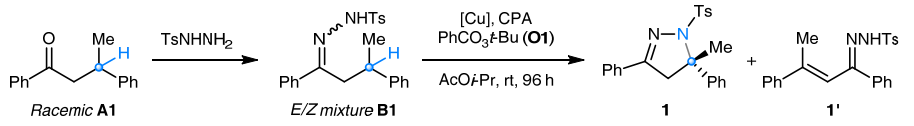
Supplementary Figure 3 The X-ray structure of chiral compound 62.

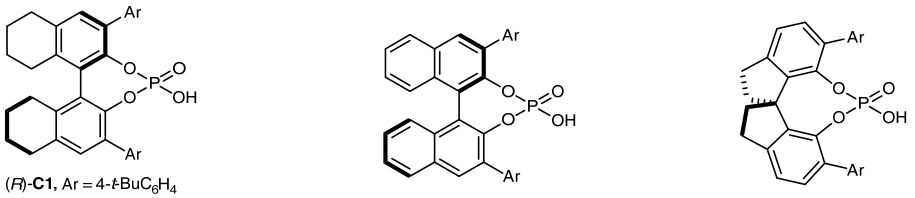


Supplementary Figure 4 Mechanistic experiments. a, The formation of product **3** was totally abolished in the absence of either CuCN or (*R*)-**C3**, thus suggesting both of the two are indispensable for the reaction initiation. **b**, The reaction was significantly inhibited in the presence of radical inhibitors 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), 1,4-benzoquinone (BQ), and butylated hydroxytoluene (BHT), respectively. Thus, the reaction likely proceeds through a radical mechanism. **c**, The enantiomeric excess of product did not significantly change during the reaction. Thus, the same reaction pathway with the same enantiodetermining transition state is likely involved.

Supplementary Tables

Supplementary Table 1 The effect of different CPAs and Cu salts in the model reaction





(*R*)-**C1**, Ar = 4-*t*-BuC_6H_4
(*R*)-**C2**, Ar = 3,5-$(Me)_2C_6H_3$
(*R*)-**C3**, Ar = 2,4,6-$(Me)_3C_6H_2$
(*R*)-**C4**, Ar = 3,5-$Ph_2C_6H_3$

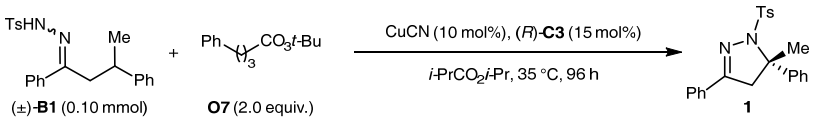
(*R*)-**C5**, Ar = 9-Phenanthryl
(*R*)-**C6**, Ar = 4-*t*-BuC_6H_4

(*S*)-**C7**, Ar = 4-*t*-BuC_6H_4
(*S*)-**C8**, Ar = 1-Naphthyl

Entry[a]	[Cu]	CPA	Yield (%)[b]		Ee (%)[c]
			1	**1'**	
1	CuI	(*R*)-**C1**	12	8	34
2	CuI	(*R*)-**C2**	15	13	51
3	CuI	(*R*)-**C3**	18	9	62
4	CuI	(*R*)-**C4**	18	12	48
5	CuI	(*R*)-**C5**	9	< 5	33
6	CuI	(*R*)-**C6**	13	11	40
7	CuI	(*S*)-**C7**	15	8	17
8	CuI	(*S*)-**C8**	12	10	31
9	CuCl	(*R*)-**C3**	15	11	53
10	CuBr	(*R*)-**C3**	18	9	54
11	CuCN	(*R*)-**C3**	21	< 5	71
12	CuSCN	(*R*)-**C3**	17	13	43
13	CuOAc	(*R*)-**C3**	17	11	52
14	CuTc	(*R*)-**C3**	21	9	53

[a]Reaction conditions: (±)-**B1** (0.10 mmol), $PhCO_3t$-Bu (**O1**, 0.20 mmol), [Cu] (10 mol%) and CPA (15 mol%) in dry AcO*i*-Pr (1.0 mL) at room temperature for 96 h under argon. [b]Isolated yield based on (±)-**B1** is given. [c]Ee value is based on HPLC analysis.

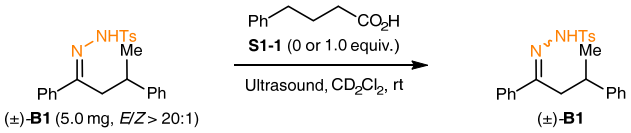
Supplementary Table 2 The effect of different *E*/*Z* ratios of hydrazone



E/*Z* ratio of (±)-**B1**	Yield of **1** (%)	Ee (%)
3.4:1	38	90
10.0:1	36	90
> 20:1	36	91

Reaction conditions: (±)-**B1** (0.10 mmol), $Ph(CH_2)_3CO_3t$-Bu (**O7**, 0.20 mmol), CuCN (10 mol%), and (*R*)-**C3** (15 mol%) in dry i-$PrCO_2i$-Pr (2.0 mL) at 35 °C for 96 h under argon; Isolated yield based on (±)-**B1** is given; Ee value is based on HPLC analysis.

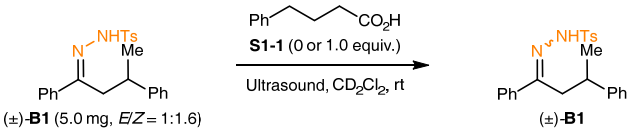
Supplementary Table 3 *E*/*Z* isomerization of (*E*)-hydrazone



Conditions	*E*/*Z* ratio of (±)-**B1**				
	0 h	1 h	2 h	4 h	8 h
With **S1-1**	> 20:1	20:1	15:1	6.5:1	4.1:1
Without **S1-1**	> 20:1	> 20:1	> 20:1	20:1	11:1

Conditions: (±)-(*E*)-**B1** (5.0 mg, 0.013 mmol, E/Z > 20:1) with or without **S1-1** (2.1 mg, 0.013 mmol, 1.0 equiv.) in CD_2Cl_2 (0.6 mL) while sonicating at room temperature.

Supplementary Table 4 *E*/*Z* isomerization of (*E*/*Z*)-hydrazone



Conditions	*E*/*Z* ratio of (±)-**B1**				
	0 h	1 h	2 h	4 h	8 h
With **S1-1**	1:1.6	1:1.4	1:1.3	1:1	1:0.9
Without **S1-1**	1:1.6	1:1.6	1:1.6	1:1.4	1:1.2

Conditions: (±)-(*E*/*Z*)-**B1** (5.0 mg, 0.013 mmol, E/Z 1:1.6) with or without **S1-1** (2.1 mg, 0.013 mmol, 1.0 equiv.) in CD_2Cl_2 (0.6 mL) while sonicating at room temperature.

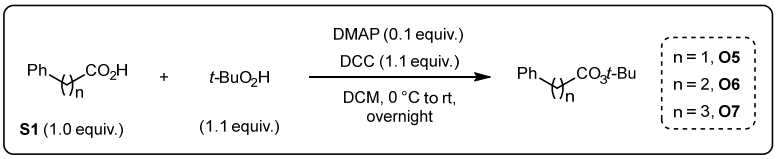
Supplementary Methods

General Information

All 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. CuCN and $(NH_4)_2CO_3$ were purchased from Aladdin. Chiral phosphoric acid (**CPA**) was purchased from Daicel Chiral Technologies (China). Isopropyl isobutyrate (*i*-PrCO_2*i*-Pr) was purchased from TCI and stored under argon atmosphere. 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). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on Bruker DPX-400 spectrometer at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR and 162 MHz for ^{31}P NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H 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) was determined using SHIMADZU LC-20AD with SPD-20AV detector or Agilent high-performance liquid chromatography (HPLC) with Hatachi detector (at appropriate wavelength). Column conditions are reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.

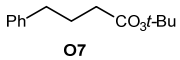
The Synthesis of Oxidants

The peroxides **O1**–**O4** were purchased from commercial sources. *tert*-Butyl peroxoates **O5**–**O7** were prepared from the corresponding carboxylic acid **S1** with *tert*-butyl hydroperoxide according to the literature procedure.[1]



General procedure for preparation of *tert*-butyl 4-phenylbutaneperoxoate (O7):

To a solution of 4-phenylbutanoic acid **S1-1** (n = 3, 1.64 g, 10 mmol, 1.0 equiv.) and 4-dimethylamino pyridine (DMAP, 0.12 g, 1.0 mmol, 0.1 equiv.) in DCM (40 mL) was dropwise added *tert*-butyl hydroperoxide (TBHP, 70% in H_2O, 1.42 g, 11 mmol, 1.1 equiv.) at 0 °C. The reaction mixture was stirred for 10 min and then dicyclohexyl carbodiimide (DCC, 2.27 g, 11 mmol, 1.1 equiv.) was added in one portion, the resulting mixture was warmed up to room temperature and stirred for overnight. Upon completion (monitored by TLC), the reaction mixture was filtered through a pad of anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30:1) to give **O7** as a colorless oil (1.98 g, 84% yield).



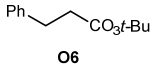
O7

***tert*-Butyl 4-Phenylbutaneperoxoate (O7)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 − 7.26 (m, 2H), 7.22 − 7.16 (m, 3H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 2.04 − 1.95 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 140.9, 128.4, 128.4, 126.0, 83.2, 34.9, 30.5, 26.4, 26.1.

Following the above general procedure, *tert*-butyl 3-phenylpropaneperoxoate **(O6)** was prepared from 3-phenylpropanoic acid **S1-2** (n = 2, 1.50 g, 10 mmol, 1.0 equiv.) with *tert*-butyl hydroperoxide (TBHP, 70% in H_2O, 1.42 g, 11 mmol, 1.1 equiv.) as a colorless oil (1.93 g, 87% yield).



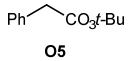
O6

3-Phenylpropaneperoxoate (O6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 − 7.27 (m, 2H), 7.23 − 7.18 (m, 3H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 139.8, 128.6, 128.3, 126.5, 83.4, 33.0, 30.8, 26.0.

Following the above general procedure, *tert*-butyl 2-phenylethaneperoxoate **(O5)** was prepared from 2-phenylacetic acid **S1-3** (n = 1, 1.36 g, 10 mmol, 1.0 equiv.) with *tert*-butyl hydroperoxide (TBHP, 70% in H_2O, 1.42 g, 11 mmol, 1.1 equiv.) as a colorless oil (1.68 g, 81% yield).



O5

***tert*-Butyl 2-Phenylethaneperoxoate (O5)**

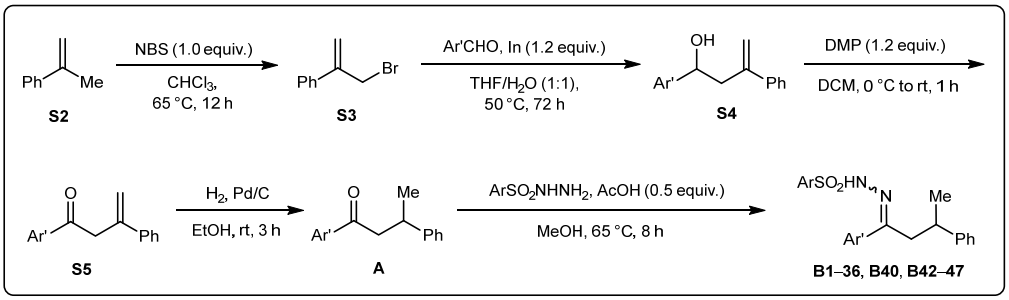
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 − 7.26 (m, 5H), 3.63 (s, 2H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 132.8, 129.1, 128.6, 127.3, 83.6, 31.1, 26.0.

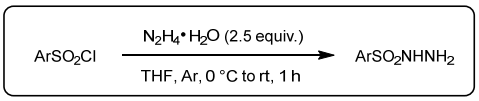
The Synthesis of Racemic Sulfonohydrazones

General procedure 1

Racemic sulfonohydrazones **B1**–**36**, **B40** and **B42**–**47** were prepared following the **general procedure 1**.

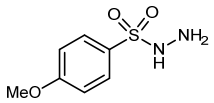


The arylsulfonohydrazides were prepared according to the literature method[2] from the corresponding commercially available sulfonyl chlorides with hydrazine monohydrate.



General procedure for preparation of 4-methoxybenzenesulfonohydrazide (Ar = 4-$MeOC_6H_4$) as the typical example:

To a cooled (0 °C) solution of 4-methoxybenzenesulfonyl chloride (2.07 g, 10 mmol, 1.0 equiv.) in THF (40 mL) was dropwise added hydrazine monohydrate (80% in H_2O, 1.56 g, 25 mmol, 2.5 equiv.) under argon atmosphere. The resulting mixture was warmed up to room temperature and stirred for 1 h. Then the reaction mixture was concentrated under reduced pressure. The residue was diluted with EtOAc (100 mL), washed with water (50 mL × 2) and brine (50 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recrystallization from EtOAc/petroleum ether to give 4-methoxybenzenesulfonohydrazide as a white solid (1.57 g, 78% yield).



4-Methoxybenzenesulfonohydrazide

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 5.73 (br s, 1H), 3.89 (s, 3H), 3.60 (br s, 2H).

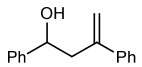
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 130.5, 127.5, 114.5, 55.7.

HRMS (ESI) *m/z* calcd. for $C_7H_{11}N_2O_3S$ $[M + H]^+$ 203.0485, found 203.0482.

General procedure for preparation of *N*'-(1,3-diphenylbutylidene)-4-methylbenzene sulfonohydrazide (**B1**, Ar = 4-MeC_6H_4, Ar' = Ph) as the typical example:

Synthesis of **S3**: To a solution of 2-phenyl-1-propene **S2** (11.82 g, 100 mmol) in $CHCl_3$ (150 mL) was added *N*-bromosuccinimide (NBS, 17.80 g, 100 mmol). The resulting mixture was stirred at 65 °C for 12 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether as eluent) to give the product **S3** as a pale-yellow oil (16.30 g, 83% yield).

Synthesis of **S4-1** (Ar' = Ph)[3]: To a stirring mixture of benzaldehyde (2.12 g, 20 mmol, 1.0 equiv.) and In powder (2.76 g, 24 mmol, 1.2 equiv.) in THF (30 mL) and H_2O (30 mL) was slowly added **S3** (4.73 g, 24 mmol, 1.2 equiv.). The resulting mixture was stirred at 50 °C for 72 h. After cooling down to room temperature, the reaction mixture was quenched by saturated $NaHCO_3$ (30 mL) and filtered through a short pad of celite. The filtrate was concentrated under reduced pressure to remove the organic solvent. Then the remaining aqueous phase was diluted with EtOAc (100 mL), washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50:1–20:1) to afford the desired product **S4-1** as a white solid (3.81 g, 85% yield).



S4-1

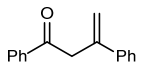
1,3-Diphenylbut-3-en-1-ol (S4-1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.36 – 7.23 (m, 8H), 5.39 (d, *J* = 1.2 Hz, 1H), 5.14 (d, *J* = 0.8 Hz, 1H), 4.70 (dd, *J* = 9.0, 4.4 Hz, 1H), 2.97 (ddd, *J* = 14.3, 4.4, 1.2 Hz, 1H), 2.84 (ddd, *J* = 14.3, 9.0, 0.8 Hz, 1H), 2.29 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.9, 140.3, 128.5, 128.3, 127.7, 127.5, 126.2, 125.8, 115.7, 72.0, 45.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}NaO$ $[M + Na]^+$ 247.1093, found 247.1093.

Synthesis of **S5-1** (Ar' = Ph)[3]: To a cooled (0 °C) solution of **S4-1** (2.24 g, 10 mmol, 1.0 equiv.) in anhydrous DCM (40 mL) was added Dess-Martin periodinane (DMP, 5.09 g, 12 mmol, 1.2 equiv.) in portions under argon atmosphere. Then the resulting mixture was warmed up to room temperature and stirred for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated $NaHCO_3$ (30 mL) and filtered through a short pad of celite. The organic layer was separated and the aqueous layer was extracted with DCM (20 mL × 2). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1) to give the product **S5-1** as a colorless oil (1.92 g, 87% yield).



S5-1

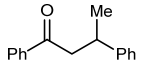
1,3-Diphenylbut-3-en-1-one (S5-1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.62 – 7.57 (m, 1H), 7.51 – 7.44 (m, 4H), 7.38 – 7.28 (m, 3H), 5.65 (br s, 1H), 5.22 (br s, 1H), 4.21 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 141.8, 140.2, 136.6, 133.1, 128.6, 128.4, 127.7, 125.8, 116.5, 45.2.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}O$ $[M + H]^+$ 223.1117, found 223.1111.

Synthesis of **A1** (Ar' = Ph): To a solution of **S5-1** (1.89 g, 8.5 mmol) in EtOH (20 mL) was added Pd/C (10% palladium on carbon, wet with ca. 50% water, 50 mg). Then the reaction flask was evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at room temperature for 3 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (20 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30:1) to give the product **A1** as a white solid (1.62 g, 85% yield).



A1

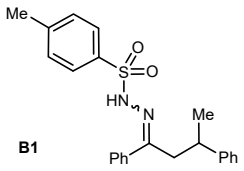
1,3-Diphenylbutan-1-one (A1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 7.32 – 7.25 (m, 4H), 7.21 – 7.16 (m, 1H), 3.56 – 3.46 (m, 1H), 3.30 (dd, J = 16.5, 5.7 Hz, 1H), 3.18 (dd, J = 16.5, 8.3 Hz, 1H), 1.34 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 146.5, 137.2, 132.9, 128.5, 128.5, 128.0, 126.8, 126.2, 47.0, 35.5, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{17}O$ $[M + H]^+$ 225.1274, found 225.1267.

Synthesis of **B1** (Ar = 4-MeC_6H_4, Ar' = Ph)[4]: To a solution of **A1** (0.45 g, 2.0 mmol, 1.0 equiv.) and 4-methylbenzenesulfonohydrazide (0.74 g, 4.0 mmol, 2.0 equiv.) in MeOH (15 mL) was added glacial acetic acid (57 μL, 1.0 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B1** as a white solid (0.70 g, 89% yield), an inseparable mixture of *E*/*Z* isomers (3.4:1).



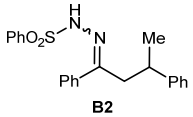
B1

***N*'-(1,3-Diphenylbutylidene)-4-methylbenzenesulfonohydrazide (B1)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 0.58H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.45 (br s, 0.29H), 7.39 – 7.32 (m, 3.87H), 7.29 – 7.24 (m, 2.58H), 7.19 – 7.11 (m, 3.87H), 7.08 – 7.04 (m, 2H), 7.01 – 6.97 (m, 0.58H), 6.91 – 6.87 (m, 0.58H), 6.85 (br s, 1H), 2.95 – 2.85 (m, 3H), 2.83 – 2.70 (m, 0.87H), 2.44 (s, 0.87H), 2.42 (s, 3H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 0.87H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 155.7, 145.9, 144.7, 143.9, 143.8, 136.4, 135.5, 134.9, 132.8, 129.7, 129.6, 129.5, 129.5, 129.1, 129.0, 128.4, 128.3, 128.3, 127.8, 127.3, 126.9, 126.5, 126.4, 126.1, 46.1, 37.6, 36.9, 36.9, 21.8, 21.6, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}N_2O_2S$ $[M + H]^+$ 393.1631, found 393.1620.



B2

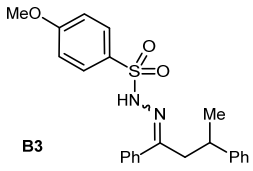
***N*'-(1,3-Diphenylbutylidene)benzenesulfonohydrazide (B2)**

White solid, as an inseparable mixture of *E*/*Z* isomers (3.5:1), 0.69 g, 91% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.3 Hz, 0.58H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.62 – 7.51 (m, 3.58H), 7.51 – 7.44 (m, 2.29H), 7.41 – 7.30 (m, 3.87 H), 7.20 – 7.09 (m, 3.87H), 7.07 – 7.01 (m, 2H), 7.01 – 6.97 (m, 0.58H), 6.94 (br s, 1H), 6.92 – 6.84 (m, 0.58H), 2.96 – 2.83 (m, 3.29H), 2.80 – 2.70 (m, 0.58H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 0.87H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.0, 145.8, 144.6, 138.4, 137.8, 136.3, 133.0, 132.9, 132.7, 129.7, 129.6, 129.5, 128.9, 128.9, 128.5, 128.4, 128.3, 128.2, 127.7, 127.3, 126.8, 126.5, 126.5, 126.4, 126.1, 46.0, 37.6, 36.9, 36.8, 21.7, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}N_2O_2S$ $[M + H]^+$ 379.1475, found 379.1465.



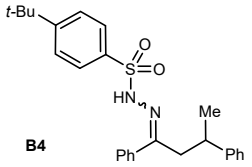
B3

***N*'-(1,3-Diphenylbutylidene)-4-methoxybenzenesulfonohydrazide (B3)**

White solid, as an inseparable mixture of *E*/*Z* isomers (3.0:1), 0.78 g, 95% yield in the final step.

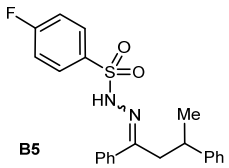
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 0.66H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.61 – 7.53 (m, 2H), 7.37 (m, 3.99H), 7.22 – 7.14 (m, 3.99H), 7.10 – 7.04 (m, 2H), 7.01 (d, *J* = 7.0 Hz, 0.66H), 6.99 – 6.92 (m, 2.66H), 6.92 – 6.86 (m, 0.66H), 6.63 (br s,

1H), 3.88 (s, 3.99H), 2.91 (m, 3.33H), 2.81 – 2.68 (m, 0.66H), 1.36 (d, *J* = 6.1 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 0.99H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 156.6, 155.7, 145.9, 144.7, 136.4, 132.8, 130.5, 129.9, 129.7, 129.7, 129.6, 129.5, 129.1, 128.4, 128.3, 127.4, 126.9, 126.5, 126.4, 126.1, 114.1, 113.6, 55.6, 46.1, 37.7, 37.1, 36.9, 21.9, 21.4.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}N_2O_3S$ $[M + H]^+$ 409.1580, found 409.1569.



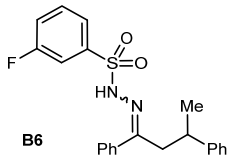
B4

4-(*tert*-Butyl)-*N*'-(1,3-diphenylbutylidene)benzenesulfonohydrazide (B4)
White solid, as an inseparable mixture of *E*/*Z* isomers (3.8:1), 0.62 g, 71% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 0.52H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.53 (d, *J* = 8.6 Hz, 0.52H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.33 (m, 3.78H), 7.20 – 7.14 (m, 0.78H), 7.13 – 7.09 (m, 3H), 7.07 – 7.03 (m, 2H), 7.02 – 6.99 (m, 0.52H), 6.91 – 6.86 (m, 1.52H), 2.96 – 2.85 (m, 3H), 2.85 – 2.70 (m, 0.78H), 1.36 (s, 11.34H), 1.34 (d, *J* = 6.5 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 0.78H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.7, 155.4, 145.9, 144.6, 136.5, 135.4, 134.9, 132.8, 129.7, 129.6, 129.5, 128.9, 128.4, 128.3, 128.1, 127.6, 127.3, 126.9, 126.6, 126.5, 126.4, 126.1, 125.9, 125.5, 46.1, 37.6, 36.9, 35.1, 31.1, 21.6, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{31}N_2O_2S$ $[M + H]^+$ 435.2101, found 435.2091.



B5

***N*'-(1,3-Diphenylbutylidene)-4-fluorobenzenesulfonohydrazide (B5)**
White solid, as an inseparable mixture of *E*/*Z* isomers (3.2:1), 0.67 g, 85% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 0.62H), 7.80 – 7.73 (m, 2H), 7.59 – 7.52 (m, 2H), 7.50 (s, 0.31H), 7.44 – 7.31 (m, 3.93H), 7.22 – 7.11 (m, 6.55H), 7.09 – 6.99 (m, 2.62H), 6.95 – 6.89 (m, 0.62H), 6.79 (br s, 1H), 2.98 – 2.82 (m, 3.31H), 2.82 – 2.69 (m, 0.62H), 1.35 (d, *J* = 6.5 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 0.93H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (d, *J* = 255.0 Hz), 165.3 (d, *J* = 255.2 Hz), 157.2, 156.4, 145.7, 144.7, 136.2, 134.4 (d, *J* = 3.1 Hz), 133.8 (d, *J* = 3.0 Hz), 132.6, 131.0 (d, *J* = 9.4 Hz), 130.5 (d, *J* = 9.4 Hz), 129.8, 129.6, 129.0, 128.5, 128.3, 127.3, 126.8, 126.5, 126.4, 126.1, 116.2 (d, *J* = 22.6 Hz), 115.7 (d, *J* = 22.5 Hz), 46.0, 37.7, 37.1, 36.8, 22.0, 21.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ −104.5 (s, 0.31F), −104.6 (s, 1F).
HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}FN_2O_2S$ $[M + H]^+$ 397.1381, found 397.1371.



B6

***N*'-(1,3-Diphenylbutylidene)-3-fluorobenzenesulfonohydrazide (B6)**

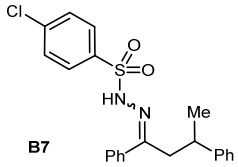
White solid, as a single isomer, *E*/*Z* > 20:1, 0.72 g, 91% yield in the final step.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.62 – 7.52 (m, 3H), 7.51 – 7.39 (m, 2H), 7.41 – 7.31 (m, 3H), 7.33 – 7.22 (m, 1H), 7.20 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 6.79 (br s, 1H), 2.96 – 2.84 (m, 3H), 1.41 – 1.31 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, *J* = 250.5 Hz), 156.6, 144.6, 139.6 (d, *J* = 6.9 Hz), 136.1, 130.2 (d, *J* = 7.5 Hz), 129.8, 129.0, 128.5, 127.4, 126.8, 126.5, 126.4, 124.1 (d, *J* = 3.4 Hz), 120.1 (d, *J* = 21.2 Hz), 115.6 (d, *J* = 24.5 Hz), 37.7, 37.2, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −110.4.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}FN_2O_2S$ $[M + H]^+$ 397.1381, found 397.1370.



B7

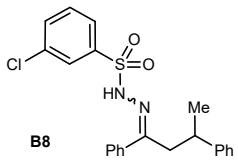
4-Chloro-*N*'-(1,3-diphenylbutylidene)benzenesulfonohydrazide (B7)

White solid, as an inseparable mixture of *E*/*Z* isomers (2.5:1), 0.72 g, 87% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.7 Hz, 0.80H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.49 (br s, 0.40H), 7.47 – 7.42 (m, 2.80H), 7.42 – 7.33 (m, 4.20H), 7.21 – 7.11 (m, 4.20H), 7.09 – 7.03 (m, 2H), 7.03 – 6.9 7 (m, 0.80H), 6.94 – 6.87 (m, 0.80H), 6.75 (br s, 1H), 2.95 – 2.86 (m, 3H), 2.85 – 2.71 (m, 1.20H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 1.20H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 156.5, 145.6, 144.6, 139.5, 139.5, 136.9, 136.3, 136.2, 132.6, 129.9, 129.8, 129.7, 129.6, 129.2, 129.2, 129.0, 128.7, 128.5, 128.3, 127.4, 126.8, 126.5, 126.5, 126.4, 126.1, 45.9, 37.7, 37.2, 36.8, 22.1, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}ClN_2O_2S$ $[M + H]^+$ 413.1085, found 413.1074.



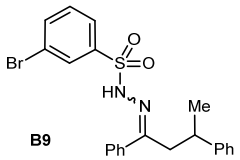
B8

3-Chloro-*N*'-(1,3-diphenylbutylidene)benzenesulfonohydrazide (B8)

Slightly yellow solid, as a single isomer, *E*/*Z* > 20:1, 0.76 g, 92% yield in the final step.

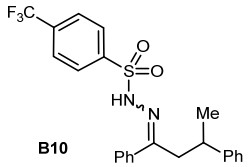
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.9 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.58 – 7.53 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.22 – 7.19 (m, 1H), 7.17 – 7.11 (m, 2H), 7.05 – 7.01 (m, 2H), 6.64 (br s, 1H), 2.98 – 2.82 (m, 3H), 1.37 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 144.5, 139.1, 136.1, 134.5, 133.0, 129.9, 129.7, 129.0, 128.5, 128.3, 127.4, 126.6, 126.5, 126.4, 37.7, 37.4, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}ClN_2O_2S$ $[M + H]^+$ 413.1085, found 413.1074.



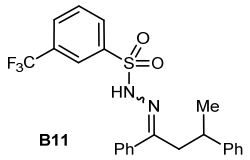
B9

3-Bromo-*N*'-(1,3-diphenylbutylidene)benzenesulfonohydrazide (B9)
White solid, as an inseparable mixture of *E*/*Z* isomers (1.7:1), 0.81 g, 89% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 0.59H), 7.88 (s, 1H), 7.81 – 7.76 (m, 0.59H), 7.73 – 7.68 (m, 2.59H), 7.60 – 7.53 (m, 2.59H), 7.42 – 7.34 (m, 6.36H), 7.24 – 7.19 (m, 1.77H), 7.17 – 7.10 (m, 3H), 7.07 – 6.99 (m, 3.18H), 6.95 – 6.89 (m, 1.18H), 6.62 (br s, 1H), 2.94 – 2.85 (m, 3H), 2.84 – 2.70 (m, 1.77H), 1.36 (d, *J* = 5.9 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 1.77H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 156.8, 145.6, 144.5, 140.1, 139.2, 136.1, 136.0, 135.9, 132.5, 131.1, 130.7, 130.5, 129.9, 129.9, 129.8, 129.5, 129.0, 128.5, 128.2, 127.4, 127.0, 126.8, 126.5, 126.4, 126.3, 126.2, 126.1, 122.8, 122.2, 46.0, 37.7, 37.4, 36.8, 21.8, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}BrN_2O_2S$ $[M + H]^+$ 457.0580, found 457.0579.



B10

***N*'-(1,3-Diphenylbutylidene)-4-(trifluoromethyl)benzenesulfonohydrazide (B10)**
White solid, as an inseparable mixture of *E*/*Z* isomers (3.0:1), 0.83 g, 93% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 0.66H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.73 (m, 2.66H), 7.60 – 7.54 (m, 2.33H), 7.44 – 7.35 (m, 3.99H), 7.19 – 7.09 (m, 3.99H), 7.06 – 6.99 (m, 2.66H), 6.94 – 6.91 (m, 0.66H), 6.76 (br s, 1H), 2.95 – 2.87 (m, 3H), 2.87 – 2.72 (m, 0.99H), 1.38 (d, *J* = 6.3 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 0.99H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 156.9, 145.5, 144.6, 142.0, 141.3, 136.1, 134.5 (q, *J* = 32.7 Hz), 134.5 (q, *J* = 33.0 Hz), 132.5, 130.0, 129.9, 129.7, 129.0, 128.8, 128.6, 128.3, 128.3, 127.5, 126.8, 126.5, 126.5, 126.4, 126.2, 126.1 (q, *J* = 3.7 Hz), 125.6 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 273.0 Hz), 123.2 (q, *J* = 273.1 Hz), 45.9, 37.8, 37.3, 36.8, 22.2, 21.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.0 (s, 3F), −63.1 (s, 0.99F).
HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}F_3N_2O_2S$ $[M + H]^+$ 447.1349, found 447.1339.



***N*'-(1,3-Diphenylbutylidene)-3-(trifluoromethyl)benzenesulfonohydrazide (B11)**

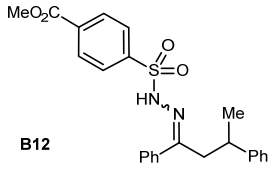
White solid, as an inseparable mixture of *E*/*Z* isomers (8.3:1), 0.76 g, 85% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 0.12H), 8.08 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 0.12H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 0.12H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.54 (br s, 0.12H), 7.44 – 7.35 (m, 3.36H), 7.17 – 7.07 (m, 3.36H), 7.04 – 6.99 (m, 2.24H), 6.94 – 6.90 (m, 0.24H), 6.46 (br s, 1H), 2.99 – 2.85 (m, 3H), 2.84 – 2.70 (m, 0.36H), 1.39 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 0.36H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.4, 145.7, 144.5, 139.6, 138.7, 136.0, 132.5, 131.7, 131.1, 131.0 (q, *J* = 33.3 Hz), 130.1, 130.0, 129.8, 129.7, 129.6 (q, *J* = 3.5 Hz), 129.2, 129.1, 128.6, 128.3, 127.5, 126.8, 126.5, 126.5, 126.4, 126.2, 125.6 (q, *J* = 3.9 Hz), 123.3 (q, *J* = 272.9 Hz), 46.0, 37.8, 37.7, 36.8, 21.8, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6 (s, 3F), −62.7 (s, 0.36F).

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}F_3N_2O_2S$ $[M + H]^+$ 447.1349, found 447.1340.



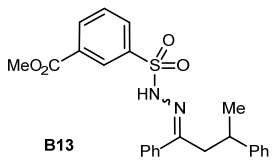
Methyl 4-((2-(1,3-Diphenylbutylidene)hydrazinyl)sulfonyl)benzoate (B12)

White solid, as an inseparable mixture of *E*/*Z* isomers (10:1), 0.83 g, 95% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 0.20H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.44 – 7.32 (m, 3.30H), 7.19 – 7.11 (m, 3.30H), 7.08 – 7.01 (m, 2H), 7.04 – 6.97 (m, 0.20H), 6.92 – 6.89 (m, 0.20H), 6.76 (br s, 1H), 3.97 (s, 3.30H), 2.97 – 2.87 (m, 3H), 2.84 – 2.71 (m, 0.30H), 1.37 (d, *J* = 6.1 Hz, 3H), 1.14 (d, *J* = 6.7 Hz, 0.30H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 157.5, 156.8, 145.6, 144.6, 142.3, 141.6, 136.1, 133.9, 132.5, 130.1, 129.9, 129.6, 129.1, 128.5, 128.3, 128.3, 127.7, 127.5, 126.8, 126.5, 126.5, 126.4, 126.1, 52.6, 46.0, 37.7, 37.3, 36.8, 22.0, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_4S$ $[M + H]^+$ 437.1530, found 437.1530.



Methyl 3-((2-(1,3-Diphenylbutylidene)hydrazinyl)sulfonyl)benzoate (B13)

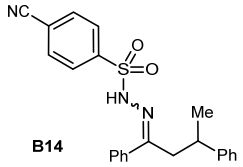
White solid, as an inseparable mixture of *E*/*Z* isomers (6.1:1), 0.80 g, 92% yield in the

final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 0.16H), 8.48 (s, 1H), 8.28 (d, *J* = 7.8 Hz, 0.16H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 0.16H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.54 (m, 3.32H), 7.44 – 7.34 (m, 3.48H), 7.17 – 7.06 (m, 3.48H), 7.04 – 6.99 (m, 2.32H), 6.95 – 6.92 (m, 0.32H), 6.55 (br s, 1H), 4.00 (s, 3H), 3.96 (s, 0.48H), 2.96 – 2.86 (m, 3H), 2.84 – 2.70 (m, 0.48H), 1.38 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 0.48H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.4, 157.3, 156.7, 145.7, 144.5, 139.0, 138.2, 136.1, 133.9, 133.8, 132.5, 132.5, 131.9, 131.1, 130.6, 129.9, 129.9, 129.6, 129.5, 129.2, 129.0, 128.9, 128.7, 128.5, 128.3, 127.5, 126.8, 126.6, 126.5, 126.3, 126.1, 52.6, 46.0, 37.7, 37.5, 36.8, 25.7, 21.8, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_4S$ $[M + H]^+$ 437.1530, found 437.1530.



B14

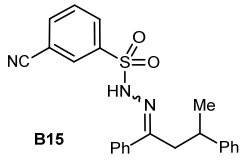
4-Cyano-*N*'-(1,3-diphenylbutylidene)benzenesulfonohydrazide (B14)

White solid, as an inseparable mixture of *E*/*Z* isomers (1.2:1), 0.70 g, 86% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.7 Hz, 1.66H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.79 – 7.75 (m, 3.66H), 7.57 – 7.53 (m, 2H), 7.53 (br s, 0.83H), 7.46 – 7.36 (m, 5.49H), 7.23 – 7.13 (m, 5.49H), 7.09 – 7.00 (m, 3.66H), 6.97 – 6.92 (m, 1.66H), 6.62 (br s, 1H), 2.96 – 2.89 (m, 3H), 2.88 – 2.82 (m, 1.66H), 2.75 (dd, *J* = 14.4, 7.0 Hz, 0.83H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 2.49H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.4, 145.5, 144.7, 142.6, 141.9, 135.9, 132.7, 132.3, 132.2, 130.1, 130.0, 129.7, 129.2, 129.0, 128.6, 128.4, 128.3, 127.5, 126.8, 126.5, 126.2, 117.3, 116.6, 116.5, 45.9, 37.9, 37.5, 36.8, 22.3, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}N_3O_2S$ $[M + H]^+$ 404.1427, found 404.1423.



B15

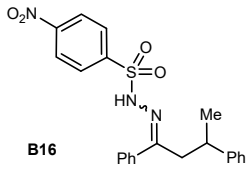
3-Cyano-*N*'-(1,3-diphenylbutylidene)benzenesulfonohydrazide (B15)

White solid, as a single isomer, *E*/*Z* > 20:1, 0.74 g, 91% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.93 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.46 – 7.34 (m, 3H), 7.30 – 7.21 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 2H), 6.62 (br s, 1H), 2.99 – 2.85 (m, 3H), 1.40 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 144.6, 139.1, 136.0, 135.8, 132.5, 131.8, 130.1, 129.4, 129.2, 128.6, 127.5, 126.5, 117.2, 113.0, 37.8, 37.5, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}N_3O_2S$ $[M + H]^+$ 404.1427, found 404.1427.



B16

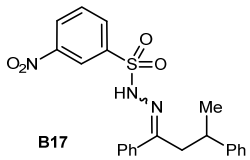
***N*'-(1,3-Diphenylbutylidene)-4-nitrobenzenesulfonohydrazide (B16)**

White solid, as an inseparable mixture of *E*/*Z* isomers (6.3:1), 0.64 g, 75% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2.32H), 7.99 (d, *J* = 8.9 Hz, 0.32H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.46 – 7.35 (m, 3.48H), 7.22 – 7.14 (m, 3.48H), 7.09 – 7.05 (m, 2H), 7.05 – 7.02 (m, 0.32H), 6.98 – 6.93 (m, 0.32H), 6.62 (br s, 1H), 2.98 – 2.88 (m, 3H), 2.86 – 2.73 (m, 0.48H), 1.41 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 0.48H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.6, 150.2, 150.2, 145.5, 144.7, 144.1, 143.3, 135.9, 132.3, 130.2, 130.1, 129.7, 129.7, 129.2, 129.0, 128.7, 128.4, 127.6, 126.9, 126.5, 126.5, 126.2, 124.1, 123.6, 45.9, 37.9, 37.6, 36.8, 22.5, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}N_3O_4S$ $[M + H]^+$ 424.1326, found 424.1313.



B17

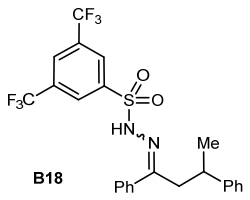
***N*'-(1,3-Diphenylbutylidene)-3-nitrobenzenesulfonohydrazide (B17)**

White solid, as an inseparable mixture of *E*/*Z* isomers (4.5:1), 0.69 g, 81% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 0.22H), 8.59 (s, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 0.22H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.68 (m, 1.22H), 7.63 (br s, 0.22H), 7.61 – 7.57 (m, 2H), 7.44 – 7.35 (m, 3.66H), 7.19 – 7.06 (m, 3.66H), 7.03 (d, *J* = 7.3 Hz, 2H), 7.01 – 6.96 (m, 0.88H), 6.54 (br s, 1H), 3.00 – 2.87 (m, 3H), 2.88 – 2.81 (m, 0.44H), 2.75 (dd, *J* = 14.5, 7.5 Hz, 0.22H), 1.40 (d, *J* = 5.9 Hz, 3H), 1.16 (d, *J* = 6.7 Hz, 0.66H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 157.7, 148.1, 147.7, 145.5, 144.6, 140.4, 139.5, 135.8, 134.0, 133.4, 132.3, 130.3, 130.2, 130.0, 129.7, 129.7, 129.1, 128.6, 128.2, 127.5, 127.4, 126.8, 126.5, 126.4, 126.1, 123.6, 123.0, 45.9, 37.9, 37.7, 36.7, 22.1, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}N_3O_4S$ $[M + H]^+$ 424.1326, found 424.1313.



B18

***N*'-(1,3-Diphenylbutylidene)-3,5-bis(trifluoromethyl)benzenesulfonohydrazide (B18)**

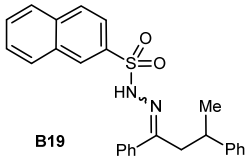
White solid, as an inseparable mixture of *E*/*Z* isomers (4.8:1), 0.87 g, 84% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 0.42H), 8.26 (s, 2H), 8.11 (s, 1H), 7.61 (br s, 0.21H), 7.59 – 7.51 (m, 2H), 7.47 – 7.37 (m, 3.63H), 7.18 – 7.04 (m, 3.63H), 7.03 – 6.99 (m, 2.42H), 6.98 – 6.95 (m, 0.42H), 6.24 (br s, 1H), 3.00 – 2.84 (m, 3H), 2.83 – 2.72 (m, 0.63H), 1.42 (d, *J* = 6.5 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 0.63H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 158.5, 145.5, 144.5, 141.1, 139.9, 135.7, 132.6 (q, *J* = 34.6 Hz), 132.3, 132.1 (q, *J* = 34.4 Hz), 130.4, 130.1, 129.7, 129.1, 128.9 (q, *J* = 3.0 Hz), 128.7, 128.3, 127.5, 126.8, 126.5, 126.5, 126.4, 126.4, 126.3, 122.6 (q, *J* = 273.3 Hz), 122.5 (q, *J* = 273.5 Hz), 46.0, 38.2, 37.9, 36.9, 21.7, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8 (s, 6F), −62.9 (s, 1.26F).

HRMS (ESI) *m/z* calcd. for $C_{24}H_{21}F_6N_2O_2S$ $[M + H]^+$ 515.1222, found 515.1219.



B19

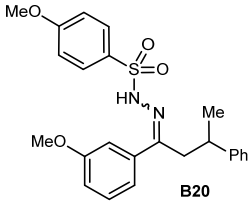
***N*'-(1,3-Diphenylbutylidene)naphthalene-2-sulfonohydrazide (B19)**

White solid, as an inseparable mixture of *E*/*Z* isomers (2.2:1), 0.69 g, 80% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.8 Hz, 0.45H), 8.40 (d, *J* = 1.8 Hz, 1H), 8.05 – 8.01 (m, 1.45H), 8.00 – 7.94 (m, 2.90H), 7.85 (dd, *J* = 8.7, 1.8 Hz, 0.45H), 7.82 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.74 – 7.64 (m, 2.90H), 7.63 (br s, 0.45H), 7.62 – 7.59 (m, 2H), 7.43 – 7.35 (m, 4.35H), 7.12 – 7.06 (m, 1.35H), 7.05 – 7.02 (m, 4.90H), 6.97 – 6.91 (m, 1.90H), 6.88 (br s, 1H), 2.99 – 2.87 (m, 3H), 2.86 – 2.72 (m, 1.35H), 1.38 (d, *J* = 6.1 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 1.35H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.0, 145.6, 144.5, 136.3, 135.2, 135.0, 134.9, 134.8, 132.7, 132.1, 131.9, 129.7, 129.7, 129.5, 129.5, 129.3, 129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.1, 127.9, 127.5, 127.4, 127.2, 126.7, 126.5, 126.5, 126.3, 126.0, 123.5, 122.6, 46.0, 37.6, 37.1, 36.8, 21.8, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}N_2O_2S$ $[M + H]^+$ 429.1631, found 429.1634.



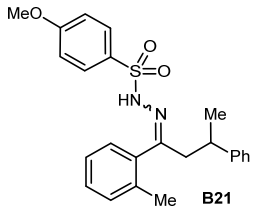
B20

4-Methoxy-*N*'-(1-(3-methoxyphenyl)-3-phenylbutylidene)benzenesulfonohydrazide (B20)

White solid, as an inseparable mixture of *E*/*Z* isomers (2.5:1), 0.47 g, 53% yield in the final step.

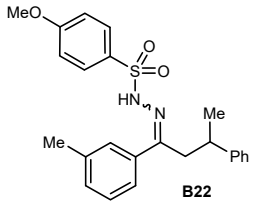
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 0.80H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.49 (m, 0.40H), 7.31 – 7.25 (m, 1H), 7.25 – 7.23 (m, 0.40H), 7.19 – 7.05 (m, 8.20H), 7.00 – 6.87 (m, 5.60H), 6.46 (d, *J* = 7.5 Hz, 0.40H), 6.35 (br s, 0.40H), 3.86

(s, 1.20H), 3.85 (s, 3H), 3.79 (s, 3H), 3.72 (s, 1.20H), 2.95 – 2.86 (m, 3H), 2.84 – 2.68 (m, 1.20H), 1.32 (d, J = 6.6 Hz, 3H), 1.14 (d, J = 6.9 Hz, 1.20H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 160.2, 159.4, 156.5, 155.4, 145.8, 144.7, 137.8, 134.0, 130.7, 130.4, 129.9, 129.8, 129.4, 129.3, 128.9, 128.2, 127.2, 126.8, 126.4, 126.0, 118.9, 118.4, 115.2, 115.1, 114.1, 113.6, 112.0, 111.9, 55.6, 55.5, 55.2, 55.1, 45.9, 37.5, 36.9, 36.8, 21.8, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_4S$ $[M + H]^+$ 439.1686, found 439.1687.



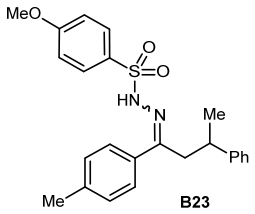
B21

4-Methoxy-*N*'-(3-phenyl-1-(*o*-tolyl)butylidene)benzenesulfonohydrazide (B21)
Slightly yellow solid, as a single isomer, *E*/*Z* > 20:1, 0.29 g, 34% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (br s, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.25 – 7.16 (m, 4H), 7.13 – 7.04 (m, 4H), 7.01 (d, J = 7.4 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.98 – 2.92 (m, 1H), 2.85 – 2.74 (m, 2H), 1.87 (s, 3H), 1.20 (d, J = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 158.0, 145.2, 137.1, 136.4, 130.9, 130.3, 129.8, 128.8, 128.3, 128.0, 126.9, 126.6, 125.4, 113.9, 55.6, 38.9, 37.1, 22.5, 20.0.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_3S$ $[M + H]^+$ 423.1737, found 423.1736.



B22

4-Methoxy-*N*'-(3-phenyl-1-(*m*-tolyl)butylidene)benzenesulfonohydrazide (B22)
White solid, as an inseparable mixture of *E*/*Z* isomers (1.4:1), 0.71 g, 84% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 1.40H), 7.71 (d, J = 8.3 Hz, 2H), 7.42 (br s, 0.70H), 7.37 – 7.33 (m, 2H), 7.28 – 7.21 (m, 2.10H), 7.20 – 7.16 (m, 5H), 7.16 – 7.11 (m, 1.40H), 7.09 – 7.05 (m, 2H), 7.01 (d, J = 7.0 Hz, 1.40H), 6.99 – 6.91 (m, 3.40H), 6.74 (br s, 1H), 6.69 – 6.62 (m, 1.40H), 3.87 (s, 5.10H), 2.98 – 2.83 (m, 3H), 2.81 – 2.68 (m, 2.10H), 2.36 (s, 3H), 2.30 (s, 2.10H), 1.34 (d, J = 5.7 Hz, 3H), 1.15 (d, J = 6.7 Hz, 2.10H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 157.1, 155.8, 146.0, 144.8, 139.4, 137.9, 136.4, 132.8, 130.5, 130.4, 130.4, 130.0, 129.9, 129.5, 129.4, 129.0, 128.3, 127.3, 127.2, 127.0, 126.9, 126.4, 126.0, 123.7, 123.4, 114.1, 113.6, 55.6, 55.6, 46.0, 37.6, 37.1, 36.9, 21.9, 21.5, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_3S$ $[M + H]^+$ 423.1737, found 423.1734.



B23

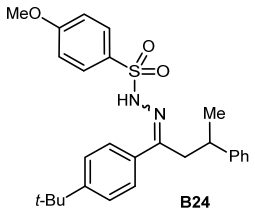
4-Methoxy-*N*'-(3-phenyl-1-(*p*-tolyl)butylidene)benzenesulfonohydrazide (B23)

White solid, as an inseparable mixture of *E*/*Z* isomers (4.2:1), 0.67 g, 79% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 0.48H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.28 – 7.18 (m, 0.48H), 7.20 – 7.11 (m, 5.96H), 7.10 – 7.04 (m, 2H), 7.03 – 6.96 (m, 0.72H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.81 (br s, 0.24H), 6.79 (br s, 1H), 3.85 (s, 3.72H), 2.93 – 2.84 (m, 3H), 2.81 – 2.68 (m, 0.72H), 2.35 (s, 3.72H), 1.33 (d, *J* = 5.9 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 0.72H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 163.1, 156.9, 155.7, 146.0, 144.8, 139.8, 139.7, 133.6, 130.4, 130.1, 130.0, 129.9, 129.6, 129.5, 129.1, 128.9, 128.2, 127.2, 126.8, 126.4, 126.4, 126.0, 114.0, 113.6, 55.5, 46.0, 37.6, 36.8, 21.7, 21.2, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_3S$ $[M + H]^+$ 423.1737, found 423.1736.



B24

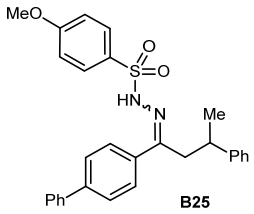
***N*'-(1-(4-(*tert*-Butyl)phenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B24)**

White solid, as a single isomer, *E*/*Z* > 20:1, 0.61 g, 66% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.16 (m, 3H), 7.09 – 7.06 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.91 (br s, 1H), 3.85 (s, 3H), 2.96 – 2.79 (m, 3H), 1.32 (d, *J* = 5.6 Hz, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 155.7, 152.8, 144.8, 133.5, 130.4, 129.5, 128.9, 127.2, 126.4, 126.2, 125.3, 113.6, 55.5, 37.6, 36.8, 34.6, 31.1, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{33}N_2O_3S$ $[M + H]^+$ 465.2206, found 465.2208.



B25

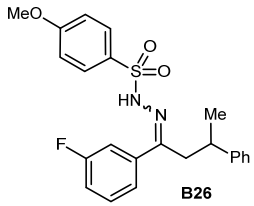
***N*'-(1-([1,1'-Biphenyl]-4-yl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B25)**

White solid, as an inseparable mixture of *E*/*Z* isomers (17.0:1), 0.67 g, 69% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 0.12H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.57 (m, 4H), 7.56 – 7.51 (m, 0.18H), 7.48 – 7.43 (m, 2H), 7.39 – 7.34 (m, 1H), 7.21 – 7.17 (m, 3H), 7.16 – 7.13 (m, 0.12H), 7.12 – 7.07 (m, 2H), 7.05 – 7.02 (m, 0.12H), 7.01 – 6.98 (m, 0.12H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.79 (br s, 1H), 3.88 (s, 0.18H), 3.87 (s, 3H), 3.00 – 2.88 (m, 3H), 2.83 – 2.73 (m, 0.18H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 0.18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 155.2, 145.9, 144.7, 142.6, 142.3, 140.2, 139.8, 135.3, 131.4, 130.5, 130.0, 129.5, 129.1, 128.9, 128.8, 128.3, 128.2, 127.9, 127.7, 127.4, 127.1, 127.1, 127.0, 126.9, 126.9, 126.5, 126.1, 114.1, 113.7, 55.6, 46.1, 37.7, 37.0, 29.7, 21.9, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{29}N_2O_3S$ $[M + H]^+$ 485.1893, found 485.1893.



B26

***N*'-(1-(3-Fluorophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B26)**

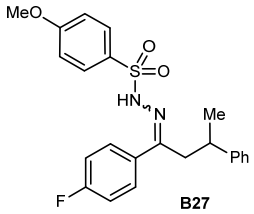
White solid, as an inseparable mixture of *E*/*Z* isomers (6.2:1), 0.80 g, 94% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 0.32H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.48 (br s, 0.16H), 7.38 – 7.34 (m, 0.16H), 7.33 – 7.29 (m, 2H), 7.28 – 7.25 (m, 0.48H), 7.25 – 7.22 (m, 0.48H), 7.20 – 7.13 (m, 3.48H), 7.09 – 7.02 (m, 4H), 7.01 – 6.94 (m, 3H), 6.69 (d, *J* = 7.6 Hz, 0.16H), 6.56 (d, *J* = 8.9 Hz, 0.16H), 3.88 (s, 0.48H), 3.87 (s, 3H), 2.96 – 2.83 (m, 3H), 2.81 – 2.70 (m, 0.48H), 1.34 (d, *J* = 6.5 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 0.48H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 163.0 (d, *J* = 249.9 Hz), 162.7 (d, *J* = 245.5 Hz), 155.0, 154.1 (d, *J* = 2.7 Hz), 145.6, 144.5, 138.8 (d, *J* = 7.6 Hz), 134.8 (d, *J* = 6.9 Hz), 131.4 (d, *J* = 8.2 Hz), 130.4, 130.0, 129.9 (d, *J* = 8.2 Hz), 129.8, 129.3, 129.0, 128.3, 127.3, 126.8, 126.4, 126.2, 122.3 (d, *J* = 3.1 Hz), 122.1 (d, *J* = 2.7 Hz), 116.8 (d, *J* = 20.9 Hz), 116.4 (d, *J* = 21.4 Hz), 114.2, 113.8 (d, *J* = 22.3 Hz), 113.7, 113.4 (d, *J* = 23.1 Hz), 55.6, 45.9, 37.5, 37.0, 36.9, 21.9, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −109.8 (s, 0.16F), −112.6 (s, 1F).

HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}FN_2O_3S$ $[M + H]^+$ 427.1486, found 427.1487.



B27

***N*'-(1-(4-Fluorophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B27)**

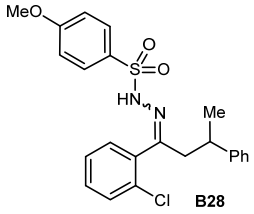
White solid, as an inseparable mixture of *E*/*Z* isomers (7.5:1), 0.73 g, 86% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 0.26H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.56 (br s, 0.13H), 7.53 – 7.48 (m, 2H), 7.24 (br s, 1H), 7.18 – 7.12 (m, 3.39H), 7.07 – 6.97 (m, 4.52H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.92 – 6.87 (m, 0.26H), 3.84 (s, 3.39H), 2.93 – 2.80 (m, 3H), 2.81 – 2.68 (m, 0.39H), 1.31 (d, *J* = 5.6 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 0.39H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 249.6 Hz), 163.2, 163.1, 162.9 (d, *J* = 250.6 Hz), 155.7, 154.5, 145.6, 144.5, 132.6 (d, *J* = 3.2 Hz), 130.3, 129.9, 129.7, 129.4, 128.8, 128.7, 128.4 (d, *J* = 8.3 Hz), 128.2, 127.1, 126.8, 126.4, 126.0, 116.5 (d, *J* = 21.8 Hz), 115.2 (d, *J* = 21.6 Hz), 114.1, 113.7, 55.5, 46.0, 37.4, 36.9, 36.6, 21.8, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ −109.9 (s, 0.13F), −111.4 (s, 1F).

HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}FN_2O_3S$ $[M + H]^+$ 427.1486, found 427.1487.



B28

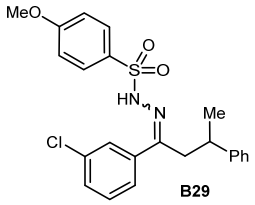
***N*'-(1-(2-Chlorophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B28)**

White solid, as a single isomer (*E*/*Z* > 20:1), 0.54 g, 60% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.61 (br s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.14 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.01 – 2.89 (m, 2H), 2.86 – 2.77 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 156.5, 144.9, 137.1, 132.1, 130.7, 130.3, 129.7, 129.7, 128.8, 126.9, 126.6, 126.5, 113.9, 55.6, 39.1, 36.9, 22.5.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}ClN_2O_3S$ $[M + H]^+$ 443.1191, found 443.1192.



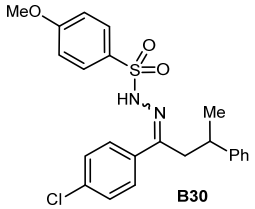
***N*'-(1-(3-Chlorophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B29)**

White solid, as a single isomer (*E*/*Z* = 20:1), 0.65 g, 73% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 0.10H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 0.10H), 7.48 (br s, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.10 (m, 4H), 7.08 – 7.02 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 0.10H), 3.87 (s, 3.15H), 2.95 – 2.81 (m, 3H), 2.80 – 2.73 (m, 0.15H), 1.33 (d, *J* = 5.8 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 0.15H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.6, 154.0, 144.4, 138.3, 134.4, 130.4, 130.0, 129.6, 129.4, 129.2, 129.0, 128.4, 128.3, 127.3, 126.8, 126.7, 126.5, 126.4, 124.5, 114.2, 113.8, 55.6, 37.5, 37.4, 37.0, 36.8, 21.9, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}ClN_2O_3S$ $[M + H]^+$ 443.1191, found 443.1189.



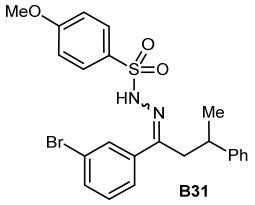
***N*'-(1-(4-Chlorophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B30)**

White solid, as a single isomer (*E*/*Z* > 20:1), 0.63 g, 71% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.08 – 7.02 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.91 (br s, 1H), 3.87 (s, 3H), 2.92 – 2.82 (m, 3H), 1.34 (d, *J* = 5.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 154.3, 144.5, 135.6, 134.9, 130.4, 129.4, 129.1, 128.6, 127.8, 127.4, 126.4, 113.7, 55.6, 37.6, 36.8, 21.3.

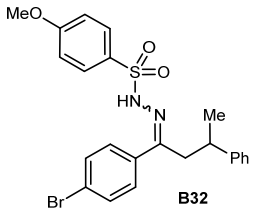
HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}ClN_2O_3S$ $[M + H]^+$ 443.1191, found 443.1192.



***N*'-(1-(3-Bromophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B31)**

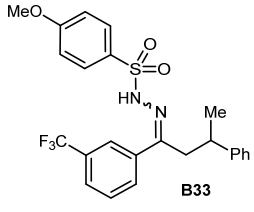
White solid, as an inseparable mixture of *E*/*Z* isomers (13.5:1), 0.83 g, 86% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 0.14H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.61 (s, 1H), 7.55 (br s, 0.07H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.34 (br s, 1H), 7.25 – 7.21 (m, 0.21H), 7.19 – 7.14 (m, 4H), 7.07 – 7.01 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 0.07H), 3.86 (s, 0.21H), 3.85 (s, 3H), 2.93 – 2.79 (m, 3H), 2.78 – 2.72 (m, 0.21H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 0.21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 153.8, 145.4, 144.4, 138.6, 134.8, 132.6, 132.2, 131.0, 130.3, 129.9, 129.8, 129.6, 129.3, 129.1, 128.9, 128.2, 127.2, 126.8, 126.4, 126.1, 125.2, 124.9, 123.5, 122.5, 114.1, 113.8, 55.5, 45.8, 37.3, 37.0, 36.6, 21.9, 21.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}BrN_2O_3S$ $[M + H]^+$ 487.0686, found 487.0684.



B32

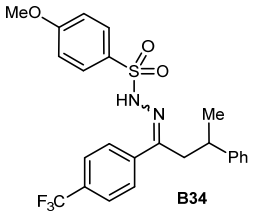
***N*'-(1-(4-Bromophenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B32)**
White solid, as a single isomer (*E*/*Z* > 20:1), 0.81 g, 83% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.14 (m, 3H), 7.07 – 7.03 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.82 (br s, 1H), 3.88 (s, 3H), 2.97 – 2.78 (m, 3H), 1.35 (d, *J* = 6.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 154.4, 144.5, 135.4, 131.6, 130.4, 129.3, 129.1, 128.0, 127.4, 126.4, 124.0, 113.7, 55.6, 37.6, 36.8, 21.4.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}BrN_2O_3S$ $[M + H]^+$ 487.0686, found 487.0685.



B33

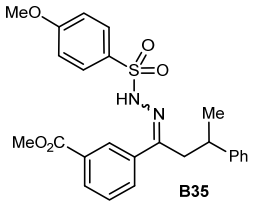
4-Methoxy-*N*'-(3-phenyl-1-(3-(trifluoromethyl)phenyl)butylidene)benzenesulfonohydrazide (B33)
White solid, as an inseparable mixture of *E*/*Z* isomers (10:1), 0.82 g, 86% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 0.20H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1.10H), 7.49 (br s, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.24 (br s, 0.10H), 7.18 – 7.12 (m, 3.30H), 7.09 (d, *J* = 7.6 Hz, 0.10H), 7.05 – 7.01 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 2.20H), 3.87 (s, 0.30H), 3.86 (s, 3H), 2.97 – 2.85 (m, 3H), 2.83 – 2.77 (m, 0.30H), 1.33 (d, *J* = 5.6 Hz, 3H), 1.18 (d, *J* = 6.5 Hz, 0.30H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 163.3, 155.3, 153.9, 145.3, 144.3, 137.4, 133.9, 130.6 (q, *J* = 32.7 Hz), 130.4, 130.1, 129.8 (q, *J* = 36.2 Hz), 129.5, 129.1, 128.9, 128.8, 128.3, 127.2, 126.8, 126.4, 126.2, 125.9 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 272.4 Hz), 123.5 (q, *J* = 3.8 Hz), 114.2, 113.8, 55.6, 55.5, 45.8, 37.3, 36.6, 22.0, 21.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6 (s, 3F), −62.7 (s, 0.30F).
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}F_3N_2O_3S$ $[M + H]^+$ 477.1454, found 477.1456.



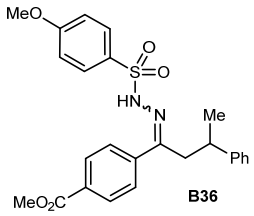
B34

4-Methoxy-*N*'-(3-phenyl-1-(4-(trifluoromethyl)phenyl)butylidene)benzenesulfonohydrazide (B34)
White solid, as a single isomer (*E*/*Z* > 20:1), 0.71 g, 75% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.21 – 7.16 (m, 3H), 7.06 – 7.04 (m, 2H), 7.03 (br s, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.94 – 2.87 (m, 3H), 1.36 (d, *J* = 6.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 153.8, 144.4, 139.9, 131.2 (q, *J* = 32.6 Hz), 130.4, 129.3, 129.1, 127.5, 126.8, 126.4, 125.4 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.2 Hz), 113.8, 55.6, 37.6, 36.9, 21.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}F_3N_2O_3S$ $[M + H]^+$ 477.1454, found 477.1455.



B35

Methyl 3-(1-(2-((4-Methoxyphenyl)sulfonyl)hydrazono)-3-phenylbutyl)benzoate (B35)
White solid, as a single isomer (*E*/*Z* > 20:1), 0.57 g, 61% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.72 (m, 3H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.18 – 7.15 (m, 3H), 7.10 (br s, 1H), 7.06 – 7.03 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 2.98 – 2.88 (m, 3H), 1.35 (d, *J* = 5.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 163.4, 154.6, 144.6, 137.0, 130.9, 130.6, 130.4, 129.3, 129.1, 128.7, 127.8, 127.4, 126.5, 113.9, 55.7, 52.3, 37.5, 36.9, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_5S$ $[M + H]^+$ 467.1635, found 467.1636.



B36

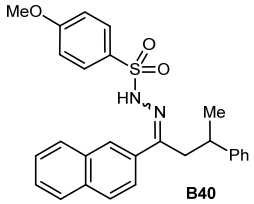
Methyl 4-(1-(2-((4-Methoxyphenyl)sulfonyl)hydrazono)-3-phenylbutyl)benzoate (B36)

White solid, as an inseparable mixture of *E*/*Z* isomers (10:1), 0.79 g, 85% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 0.20H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 0.20H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.15 (m, 3H), 7.18 – 7.13 (m, 0.30H), 7.07 – 7.03 (m, 2H), 7.00 (d, *J* = 8.7 Hz, 0.20H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.90 (br s, 1H), 3.93 (s, 3.30H), 3.90 (s, 0.30H), 3.88 (s, 3H), 2.94 – 2.87 (m, 3H), 2.85 – 2.77 (m, 0.30H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 0.30H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.3, 154.2, 144.5, 140.7, 130.8, 130.7, 130.5, 130.0, 129.7, 129.3, 129.1, 128.4, 127.5, 126.9, 126.8, 126.5, 126.5, 126.2, 114.2, 113.8, 55.6, 52.4, 52.2, 45.9, 37.6, 37.1, 37.0, 22.0, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_5S$ $[M + H]^+$ 467.1635, found 467.1636.



B40

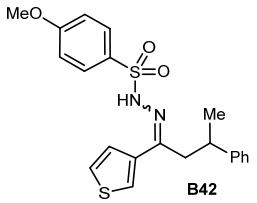
4-Methoxy-*N*'-(1-(naphthalen-2-yl)-3-phenylbutylidene)benzenesulfonohydrazide (B40)

White solid, as an inseparable mixture of *E*/*Z* isomers (5.9:1), 0.85 g, 92% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (br s, 1H), 7.84 – 7.78 (m, 6H), 7.77 – 7.71 (m, 1.02H), 7.63 – 7.56 (m, 0.17H), 7.51 – 7.45 (m, 2.34H), 7.39 – 7.33 (m, 0.17H), 7.24 – 7.19 (m, 1.17H), 7.18 – 7.12 (m, 3.51H), 7.09 – 7.04 (m, 2H), 7.01 – 6.96 (m, 0.68H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 0.51H), 3.81 (s, 3H), 3.06 – 2.91 (m, 3H), 2.90 – 2.79 (m, 0.51H), 1.35 (d, *J* = 5.6 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 0.51H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 156.8, 155.2, 145.8, 144.7, 133.8, 133.7, 132.7, 130.4, 129.9, 129.5, 129.4, 128.9, 128.5, 128.2, 128.1, 128.0, 127.7, 127.5, 127.3, 127.1, 126.9, 126.8, 126.8, 126.4, 126.3, 126.2, 126.0, 123.9, 123.3, 114.1, 113.7, 55.5, 55.5, 46.0, 37.6, 37.0, 36.5, 21.8, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{27}N_2O_3S$ $[M + H]^+$ 459.1737, found 459.1738.



B42

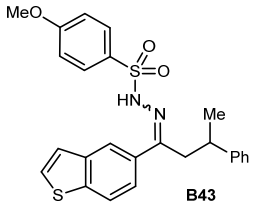
4-Methoxy-*N*'-(3-phenyl-1-(thiophen-3-yl)butylidene)benzenesulfonohydrazide (B42)

Yellow solid, as an inseparable mixture of *E*/*Z* isomers (4.5:1), 0.79 g, 95% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 0.44H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 – 7.15 (m, 3.66H), 7.12 (d, *J* = 7.0 Hz, 0.22H), 7.10 – 7.06 (m, 2H), 7.01 – 6.96 (m, 0.88H), 6.96 – 6.91 (m, 3H), 6.83 (d, *J* = 4.9 Hz, 0.22H), 3.84 (s, 3.66H), 3.05 – 2.95 (m, 1H), 2.93 – 2.88 (m, 0.22H), 2.86 – 2.78 (m, 2H), 2.77 – 2.67 (m, 0.44H), 1.34 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 0.66H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.1, 152.0, 151.8, 145.8, 144.7, 139.6, 132.7, 130.3, 130.0, 129.7, 129.3, 128.9, 128.2, 127.6, 127.1, 126.7, 126.4, 126.0, 125.8, 125.7, 125.6, 124.3, 114.0, 113.6, 55.5, 46.0, 37.8, 37.7, 37.3, 21.4, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}N_2O_3S_2$ $[M + H]^+$ 415.1145, found 415.1144.



B43

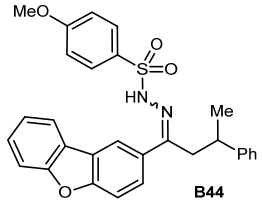
***N*'-(1-(Benzo[*b*]thiophen-5-yl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B43)**

White solid, as a single isomer (*E*/*Z* > 20:1), 0.81 g, 87% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 4H), 7.40 (s, 1H), 7.38 – 7.29 (m, 2H), 7.19 – 7.07 (m, 5H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.65 (br s, 1H), 3.87 (s, 3H), 3.14 – 3.04 (m, 1H), 2.98 – 2.82 (m, 2H), 1.43 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 151.5, 144.4, 142.7, 140.4, 139.5, 130.7, 129.1, 127.5, 126.4, 125.7, 124.4, 124.1, 123.4, 122.2, 113.6, 55.6, 38.2, 37.7, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_3S_2$ $[M + H]^+$ 465.1301, found 465.1305.

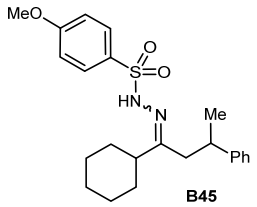


B44

***N*'-(1-(Dibenzo[*b*,*d*]furan-2-yl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B44)**

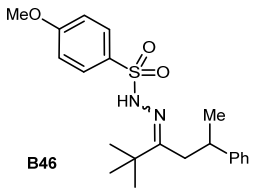
White solid, as an inseparable mixture of *E*/*Z* isomers (1.9:1), 0.95 g, 95% yield in the

final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.6 Hz, 1H), 7.95 – 7.90 (m, 1.04H), 7.86 – 7.81 (m, 1.56H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.66 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.56 – 7.52 (m, 1.56H), 7.51 – 7.48 (m, 1.56H), 7.47 – 7.44 (m, 1H), 7.39 – 7.33 (m, 2H), 7.20 – 7.13 (m, 4.56H), 7.10 – 7.06 (m, 2H), 7.02 – 6.99 (m, 1.56H), 6.98 – 6.94 (m, 4H), 3.88 (s, 1.56H), 3.86 (s, 3H), 3.06 – 2.94 (m, 3H), 2.93 – 2.84 (m, 1.56H), 1.38 (d, *J* = 6.3 Hz, 3H), 1.20 (d, *J* = 6.8 Hz, 1.56H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.2, 156.8, 156.7, 156.5, 156.4, 156.1, 155.8, 145.9, 144.7, 131.6, 130.4, 130.0, 129.9, 129.5, 129.0, 128.3, 128.0, 127.5, 127.3, 127.2, 126.9, 126.5, 126.1, 125.9, 125.4, 125.2, 124.2, 123.8, 123.1, 123.1, 122.9, 120.8, 120.6, 119.2, 119.0, 114.1, 113.7, 112.7, 111.8, 111.7, 111.4, 55.6, 55.5, 46.5, 37.6, 37.3, 37.2, 21.9, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{27}N_2O_4S$ $[M + H]^+$ 499.1686, found 499.1690.



B45

***N*'-(1-Cyclohexyl-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B45)**
Colorless oil, as an inseparable mixture of *E*/*Z* isomers (2.7:1), 0.63 g, 76% yield in the final step.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 0.74H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.15 (m, 4.11H), 7.14 – 7.11 (m, 0.37H), 7.07 – 7.02 (m, 2.74H), 6.97 (d, *J* = 8.9 Hz, 0.74H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.51 (br s, 1H), 3.88 (s, 3H), 3.87 (s, 1.11H), 3.23 – 3.11 (m, 0.37H), 2.99 – 2.82 (m, 1H), 2.43 – 2.36 (m, 2H), 2.35 – 2.27 (m, 0.74H), 1.93 – 1.82 (m, 1H), 1.76 – 1.52 (m, 7.22H), 1.30 (d, *J* = 7.0 Hz, 3H), 1.26 – 1.12 (m, 6.85H), 1.04 (d, *J* = 6.8 Hz, 1.11H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 163.1, 162.9, 162.4, 147.1, 144.9, 130.3, 130.2, 129.9, 129.7, 128.8, 128.1, 127.0, 126.9, 126.4, 125.8, 114.0, 113.5, 55.5, 45.2, 40.6, 38.7, 38.4, 37.0, 35.9, 30.5, 30.4, 28.5, 28.1, 26.2, 26.1, 25.9, 25.7, 25.5, 25.5, 21.6, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{31}N_2O_3S$ $[M + H]^+$ 415.2050, found 415.2048.



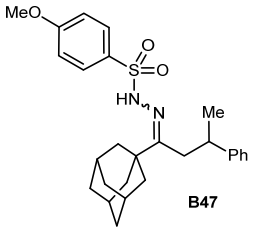
***N*'-(2,2-Dimethyl-5-phenylhexan-3-ylidene)-4-methoxybenzenesulfonohydrazide (B46)**

Colorless oil, as a single isomer (*E*/*Z* > 20:1), 0.25 g, 32% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.15 (m, 3H), 7.14 – 7.08 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.29 (br s, 1H), 3.87 (s, 3H), 3.06 – 2.95 (m, 1H), 2.51 – 2.40 (m, 2H), 1.33 (d, *J* = 6.7 Hz, 3H), 1.04 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 163.0, 145.1, 130.5, 129.6, 129.3, 127.4, 126.5, 113.3, 55.5, 39.3, 37.6, 36.8, 28.5, 22.1.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{29}N_2O_3S$ $[M + H]^+$ 389.1893, found 389.1891.



***N*'-(1-(Adamantan-1-yl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B47)**

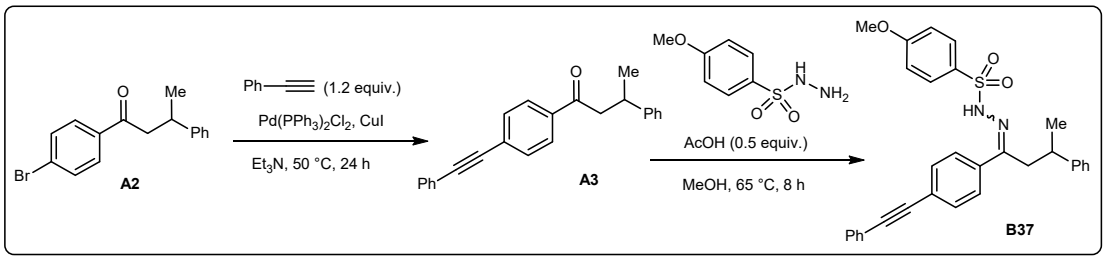
White solid, as a single isomer (*E*/*Z* > 20:1), 0.20 g, 21% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.17 (m, 3H), 7.13 – 7.08 (m, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.23 (br s, 1H), 3.88 (s, 3H), 3.02 – 2.89 (m, 1H), 2.49 – 2.38 (m, 2H), 2.02 – 1.97 (m, 3H), 1.79 – 1.68 (m, 6H), 1.66 – 1.61 (m, 6H), 1.33 (d, *J* = 7.0 Hz, 3H).

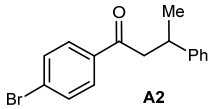
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 145.1, 130.5, 129.6, 129.2, 127.4, 126.5, 113.2, 55.5, 41.1, 40.1, 37.8, 36.5, 35.9, 28.2, 22.1.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{35}N_2O_3S$ $[M + H]^+$ 467.2363, found 467.2366.

General procedure for preparation of B37



According to the **general procedure 1**, substrate **A2** was prepared as a slightly yellow solid (2.0 g, 78% yield in the final step).



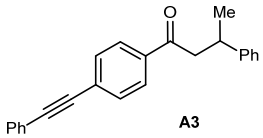
1-(4-Bromophenyl)-3-phenylbutan-1-one (A2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 3.55 – 3.43 (m, 1H), 3.26 (dd, *J* = 16.5, 5.9 Hz, 1H), 3.14 (dd, *J* = 16.5, 8.1 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 146.2, 135.8, 131.8, 129.5, 128.5, 126.8, 126.3, 46.9, 35.5, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}BrO$ $[M + H]^+$ 303.0379, found 303.0374.

Substrate **A3** was prepared according to a modified literature procedure[5]: To a stirring mixture of **A2** (0.45 g, 1.5 mmol, 1.0 equiv.), Pd $(PPh_3)_2Cl_2$ (21.0 mg, 0.03 mmol, 2 mol%) and CuI (2.9 mg, 0.015 mmol, 1 mol%) in Et_3N (10 mL) was added phenylacetylene (0.2 mL, 1.8 mmol, 1.2 equiv.) via syringe under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h. After cooling down to room temperature, the reaction mixture was quenched by water (10 mL), filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (20 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 80:1–50:1) to afford the product **A3** as a slightly yellow solid (0.39 g, 80% yield).

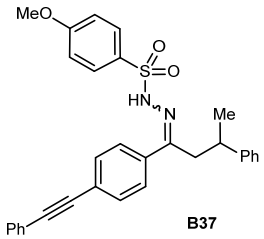


3-Phenyl-1-(4-(phenylethynyl)phenyl)butan-1-one (A3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.55 – 7.52 (m, 2H), 7.37 – 7.33 (m, 3H), 7.32 – 7.25 (m, 4H), 7.23 – 7.16 (m, 1H), 3.56 – 3.44 (m, 1H), 3.28 (dd, *J* = 16.5, 5.8 Hz, 1H), 3.16 (dd, *J* = 16.5, 8.2 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 146.4, 136.2, 131.7, 131.7, 128.8, 128.5, 128.4, 128.0, 126.8, 126.3, 122.6, 92.7, 88.6, 47.0, 35.6, 21.9.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{21}O$ $[M + H]^+$ 325.1587, found 325.1586.

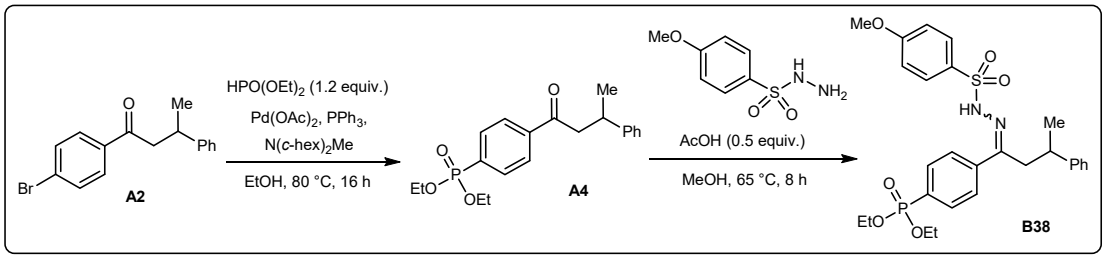
Synthesis of **B37**: To a solution of **A3** (0.32 g, 1.0 mmol, 1.0 equiv.) and 4-methoxy benzenesulfonohydrazide (0.40 g, 2.0 mmol, 2.0 equiv.) in MeOH (10 mL) was added glacial acetic acid (29 μL, 0.5 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B37** as a white solid (0.39 g, 76% yield), a single isomer (*E*/*Z* > 20:1).



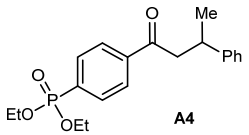
B37

4-Methoxy-*N*'-(3-phenyl-1-(4-(phenylethynyl)phenyl)butylidene)benzenesulfonohydrazide (B37)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.57 – 7.52 (m, 4H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.20 – 7.17 (m, 3H), 7.08 – 7.04 (m, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.92 (br s, 1H), 3.86 (s, 3H), 2.96 – 2.83 (m, 3H), 1.35 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 154.6, 144.6, 136.1, 131.6, 130.4, 129.4, 129.0, 128.5, 128.4, 127.3, 126.4, 126.4, 124.5, 122.9, 113.7, 91.1, 88.9, 55.6, 37.6, 36.7, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{31}H_{29}N_2O_3S$ $[M + H]^+$ 509.1893, found 509.1895.

General procedure for preparation of B38



Substrate **A4** was prepared according to a modified literature procedure[6]: To a stirring mixture of **A2** (0.45 g, 1.5 mmol, 1.0 equiv.), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 2 mol%), PPh_3 (23.6 mg, 0.09 mmol, 6 mol%) and dicyclohexylmethylamine (0.44 g, 2.25 mmol, 1.5 equiv.) in EtOH (6 mL) was added diethylphosphite (0.23 mL, 1.8 mmol, 1.2 equiv.) via syringe under argon atmosphere. The resulting mixture was stirred at 80 °C for 16 h. After cooling down to room temperature, the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL), and the filtrate was concentrated under reduced pressure. The residue was diluted with EtOAc (20 mL), washed with HCl (1 M, 20 mL), saturated $NaHCO_3$ (20 mL) and brine (20 mL × 2), respectively. The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to afford the product **A4** as a white solid (0.45 g, 83% yield).



Diethyl (4-(3-Phenylbutanoyl)phenyl)phosphonate (A4)

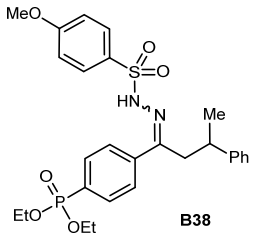
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.92 – 7.86 (m, 2H), 7.32 – 7.23 (m, 4H), 7.21 – 7.15 (m, 1H), 4.22 – 4.07 (m, 4H), 3.55 – 3.43 (m, 1H), 3.33 (dd, J = 16.7, 6.0 Hz, 1H), 3.21 (dd, J = 16.7, 7.9 Hz, 1H), 1.42 – 1.29 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 145.8, 139.6 (d, J = 3.0 Hz), 132.9 (d, J = 186.5 Hz), 131.7 (d, J = 9.9 Hz), 128.2, 127.5 (d, J = 15.0 Hz), 126.5, 126.0, 62.1, 62.0, 46.9, 35.2, 21.6, 16.0, 15.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 16.8.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}O_4P$ $[M + H]^+$ 361.1563, found 361.1561.

Synthesis of **B38**: To a solution of **A4** (0.43 g, 1.2 mmol, 1.0 equiv.) and 4-methoxy benzenesulfonohydrazide (0.49 g, 2.4 mmol, 2.0 equiv.) in MeOH (10 mL) was added glacial acetic acid (35 μL, 0.6 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 1:1–1:2) to afford the desired product **B38** as a white solid (0.47 g, 72% yield), a single isomer (E/Z > 20:1).



B38

Diethyl (4-(1-(2-((4-Methoxyphenyl)sulfonyl)hydrazono)-3-phenylbutyl)phenyl) phosphonate (B38)

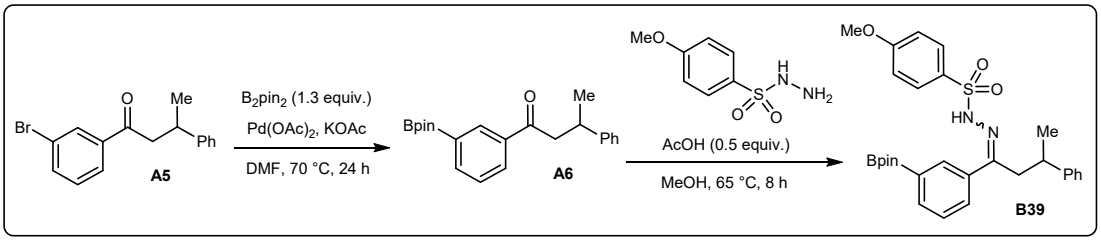
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.82 – 7.73 (m, 4H), 7.63 – 7.59 (m, 2H), 7.18 – 7.12 (m, 3H), 7.09 – 7.04 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 4.21 – 4.01 (m, 4H), 3.86 (s, 3H), 3.04 – 2.84 (m, 3H), 1.35 – 1.26 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 153.8, 144.5, 140.4 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 9.9 Hz), 130.2, 129.4, 128.9 (d, *J* = 188.5 Hz), 128.7, 127.0, 126.4, 126.3 (d, *J* = 15.0 Hz), 113.7, 62.1, 62.1, 55.5, 37.2, 36.3, 21.1, 16.2, 16.1.

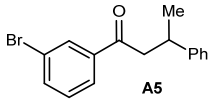
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.0.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{34}N_2O_6PS$ $[M + H]^+$ 545.1870, found 545.1867.

General procedure for preparation of B39



According to the **general procedure 1**, substrate **A5** was prepared as a slightly yellow solid (2.1 g, 81% yield in the final step).



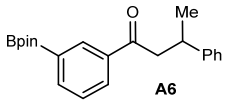
1-(3-Bromophenyl)-3-phenylbutan-1-one (A5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, *J* = 1.8 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.67 – 7.64 (m, 1H), 7.34 – 7.24 (m, 5H), 7.22 – 7.16 (m, 1H), 3.53 – 3.43 (m, 1H), 3.26 (dd, *J* = 16.6, 5.9 Hz, 1H), 3.14 (dd, *J* = 16.6, 8.0 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 146.2, 138.9, 135.8, 131.1, 130.1, 128.6, 126.8, 126.5, 126.4, 122.9, 47.1, 35.5, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}BrO$ $[M + H]^+$ 303.0379, found 303.0375.

Substrate **A6** was prepared according to a modified literature procedure[7]: To a mixture of **A5** (0.91 g, 3.0 mmol, 1.0 equiv.), $Pd(OAc)_2$ (33.7 mg, 0.15 mmol, 5 mol%) and KOAc (0.88 g, 9.0 mmol, 3.0 equiv.) in anhydrous DMF (12 mL) was added bis(pinacolato)diboron (0.99 g, 3.9 mmol, 1.3 equiv.) in one portion under argon atmosphere. The resulting mixture was stirred at 70 °C for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL), and the filtrate was diluted with water (20 mL) and extracted with EtOAc (10 mL × 2). The combined organic layers were washed with water (20 mL × 2) and brine (20 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50:1–30:1) to give the product **A6** as a colorless oil (0.76 g, 72% yield).



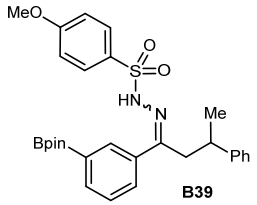
3-Phenyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butan-1-one (A6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.09 – 8.05 (m, 1H), 8.03 – 8.00 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.26 – 7.20 (m, 1H), 3.63 – 3.51 (m, 1H), 3.38 (dd, *J* = 16.8, 5.6 Hz, 1H), 3.27 (dd, *J* = 16.8, 8.3 Hz, 1H), 1.40 (s, 12H), 1.38 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 146.6, 139.2, 136.5, 134.3, 130.6, 128.5, 128.0, 126.9, 126.2, 84.1, 47.1, 35.3, 24.9, 24.8, 21.7.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{28}BO_3$ $[M + H]^+$ 351.2126, found 351.2127.

Synthesis of **B39**: To a solution of **A6** (0.70 g, 2.0 mmol, 1.0 equiv.) and 4-methoxy benzenesulfonohydrazide (0.81 g, 4.0 mmol, 2.0 equiv.) in MeOH (15 mL) was added glacial acetic acid (57 μL, 1.0 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B39** as a slightly yellow solid (0.84 g, 79% yield), an inseparable mixture of *E*/*Z* isomers (4.0:1).



B39

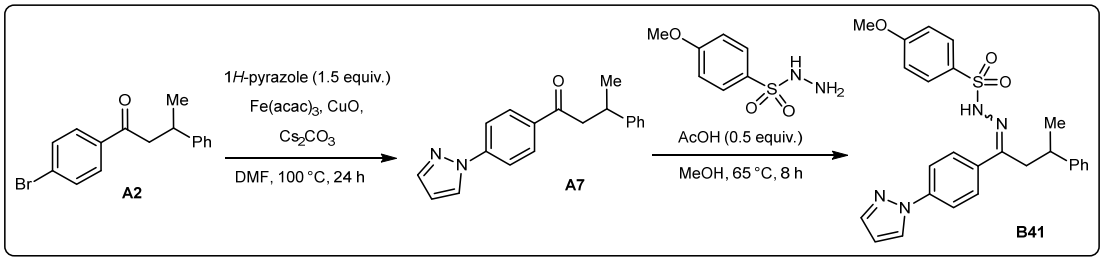
4-Methoxy-*N*'-(3-phenyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butylidene)benzenesulfonohydrazide (B39)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.83 – 7.76 (m, 3.75H), 7.66 – 7.61 (m, 1H), 7.40 – 7.37 (m, 0.75H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.14 (m, 3H), 7.14 – 7.11 (m, 0.50H), 7.08 – 7.04 (m, 2H), 7.03 – 6.99 (m, 0.50H), 6.99 – 6.95 (m, 2.50H), 6.91 (br s, 1H), 3.88 (s, 0.75H), 3.86 (s, 3H), 2.98 – 2.85 (m, 3H), 2.85 – 2.70 (m, 0.75H), 1.37 (s, 12H), 1.35 (s, 3.0H), 1.32 (d, *J* = 5.9 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 0.75H).

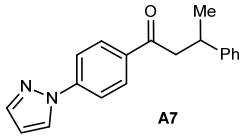
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 156.9, 155.8, 145.9, 144.7, 135.9, 135.7, 132.9, 132.5, 132.1, 130.5, 129.9, 129.8, 129.3, 129.2, 128.9, 128.7, 128.2, 127.8, 127.1, 126.8, 126.4, 126.0, 114.1, 113.6, 84.1, 83.8, 55.6, 55.5, 45.9, 37.4, 36.8, 36.7, 24.9, 24.8, 24.8, 24.7, 21.8, 21.1.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{36}BN_2O_5S$ $[M + H]^+$ 535.2432, found 535.2436.

General procedure for preparation of B41



Substrate **A7** was prepared according to a modified literature procedure[8]: To a mixture of **A2** (0.61 g, 2.0 mmol, 1.0 equiv.), ferric acetylacetonate (212.0 mg, 0.6 mmol, 30 mol%), CuO (15.9 mg, 0.2 mmol, 10 mol%) and Cs_2CO_3 (1.30 g, 4.0 mmol, 2.0 equiv.) in anhydrous DMF (5 mL) was added 1*H*-pyrazole (0.20 g, 3.0 mmol, 1.5 equiv.) in one portion under argon atmosphere. The resulting mixture was stirred at 100 °C for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL), and the filtrate was diluted with water (20 mL) and extracted with EtOAc (10 mL × 2). The combined organic layers were washed with water (20 mL × 2) and brine (20 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1–5:1) to give the product **A7** as a white solid (0.38 g, 66% yield).



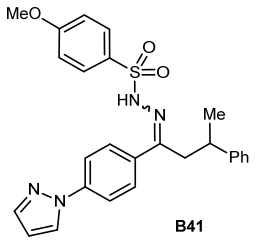
1-(4-(1*H*-Pyrazol-1-yl)phenyl)-3-phenylbutan-1-one (A7)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 2.5 Hz, 1H), 7.80 – 7.76 (m, 3H), 7.35 – 7.27 (m, 4H), 7.23 – 7.16 (m, 1H), 6.52 – 6.51 (m, 1H), 3.56 – 3.47 (m, 1H), 3.31 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.19 (dd, *J* = 16.4, 8.1 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 146.4, 143.2, 142.0, 134.8, 129.7, 128.5, 126.8, 126.3, 118.4, 108.5, 47.0, 35.7, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}N_2O$ $[M + H]^+$ 291.1492, found 291.1491.

Synthesis of **B41**: To a solution of **A7** (0.35 g, 1.2 mmol, 1.0 equiv.) and 4-methoxy benzenesulfonohydrazide (0.49 g, 2.4 mmol, 2.0 equiv.) in MeOH (10 mL) was added glacial acetic acid (35 μL, 0.6 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B41** as a white solid (0.31 g, 54% yield), an inseparable mixture of *E*/*Z* isomers (5.3:1).



B41

***N*'-(1-(4-(1*H*-Pyrazol-1-yl)phenyl)-3-phenylbutylidene)-4-methoxybenzenesulfonohydrazide (B41)**

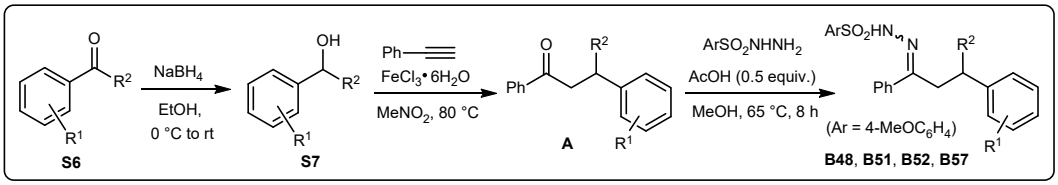
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.4 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 0.19H), 7.82 (d, *J* = 8.8 Hz, 0.38H), 7.76 – 7.62 (m, 7H), 7.45 (s, 0.19H), 7.20 – 7.18 (m, 3H), 7.17 – 7.13 (m, 0.38H), 7.08 – 7.04 (m, 2H), 7.02 – 6.98 (m, 0.95H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.76 (br s, 1H), 6.51 – 6.47 (m, 1H), 3.89 (s, 0.57H), 3.88 (s, 3H), 2.99 – 2.87 (m, 3H), 2.85 – 2.73 (m, 0.57H), 1.37 (d, *J* = 5.9 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 0.57H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 154.6, 145.7, 144.6, 141.5, 140.8, 134.4, 130.5, 130.0, 129.4, 129.1, 128.4, 128.1, 127.7, 127.4, 126.9, 126.7, 126.6, 126.4, 126.2, 119.8, 118.7, 114.1, 113.7, 108.3, 108.0, 55.6, 46.0, 37.6, 37.2, 36.9, 21.9, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{27}N_4O_3S$ $[M + H]^+$ 475.1798, found 475.1803.

General procedure 2

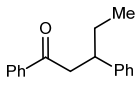
Racemic arylsulfonohydrazones **B48**, **B51**, **B52** and **B57** were prepared according to the **general procedure 2**.



General procedure for preparation of *N*'-(1,3-diphenylpentylidene)-4-methoxybenzene sulfonohydrazide (**B51**, R^1 = H, R^2 = Et) as the typical example:

Synthesis of **S7-1** (R^1 = H, R^2 = Et): To a solution of propiophenone **S6-1** (1.34 g, 10 mmol, 1.0 equiv.) in EtOH (20 mL) was added $NaBH_4$ (0.45 g, 12 mmol, 1.2 equiv.) in portions at 0 °C. Then the resulting mixture was stirred at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by water (10 mL), filtered through a short pad of celite and rinsed with EtOAc (20 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (20 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude alcohol **S7-1** (1.29 g), which was directly used in the next step without further purification.

Synthesis of **A8** (R^1 = H, R^2 = Et)[9]: To a solution of the crude alcohol **S7-1** obtained above and phenylacetylene (0.88 mL, 8.0 mmol, 1.0 equiv.) in nitromethane (30 mL) was added iron(III) chloride hexahydrate (0.32 g, 1.2 mmol, 0.15 equiv.) in one portion under argon atmosphere. The resulting mixture was stirred at 80 °C for 5 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure to remove the organic solvent. The residue was dissolved in EtOAc (30 mL), filtered through a short pad of celite and rinsed with EtOAc (20 mL). The filtrate was successively washed with water (50 mL) and brine (50 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100:1–50:1) to afford the product **A8** as a white solid (0.86 g, 45% yield).



A8

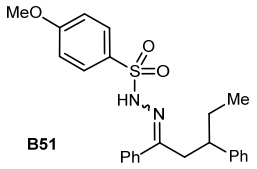
1,3-Diphenylpentan-1-one (A8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 3.35 – 3.19 (m, 3H), 1.85 – 1.72 (m, 1H), 1.71 – 1.62 (m, 1H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 144.6, 137.2, 132.9, 128.5, 128.4, 128.0, 127.6, 126.2, 45.6, 43.0, 29.2, 12.1.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}O$ $[M + H]^+$ 239.1430, found 239.1429.

Substrate **B51** (R^1 = H, R^2 = Et): To a solution of **A8** (0.48 g, 2.0 mmol, 1.0 equiv.) and 4-methoxybenzenesulfonohydrazide (0.81 g, 4.0 mmol, 2.0 equiv.) in MeOH (15 mL) was added glacial acetic acid (57 μL, 1.0 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B51** as a white solid (0.75 g, 88% yield), an inseparable mixture of *E*/*Z* isomers (2.1:1).



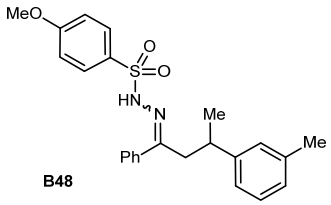
B51

***N*'-(1,3-Diphenylpentylidene)-4-methoxybenzenesulfonohydrazide (B51)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 9.0 Hz, 0.96H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.40 (br s, 0.48H), 7.37 – 7.32 (m, 4.44H), 7.20 – 7.11 (m, 4.44H), 7.02 – 6.99 (m, 2H), 6.98 – 6.95 (m, 0.96H), 6.94 – 6.91 (m, 2.96H), 6.85 – 6.80 (m, 0.96H), 6.71 (br s, 1H), 3.88 (s, 1.44H), 3.86 (s, 3H), 2.97 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.88 – 2.72 (m, 1.96H), 2.66 – 2.59 (m, 0.48H), 2.58 – 2.52 (m, 1H), 1.82 – 1.72 (m, 2H), 1.64 – 1.54 (m, 0.48H), 1.52 – 1.40 (m, 0.48H), 0.75 (t, *J* = 7.3 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 1.44H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 163.1, 156.8, 155.9, 143.1, 136.4, 132.8, 130.4, 129.9, 129.8, 129.6, 129.5, 129.4, 129.3, 129.0, 128.4, 128.1, 127.7, 127.3, 127.0, 126.5, 126.4, 126.0, 114.0, 113.6, 55.5, 45.2, 44.4, 44.2, 35.7, 29.0, 28.5, 12.2, 11.7.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_3S$ $[M + H]^+$ 423.1737, found 423.1735.



B48

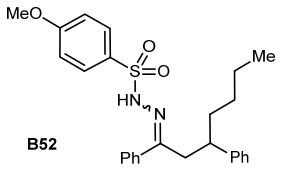
4-Methoxy-*N*'-(1-phenyl-3-(*m*-tolyl)butylidene)benzenesulfonohydrazide (B48)

White solid, as a single isomer (*E*/*Z* > 20:1), 0.67 g, 79% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.36 – 7.31 (m, 3H), 7.08 (br s, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 3.82 (s, 3H), 2.93 – 2.81 (m, 3H), 2.20 (s, 3H), 1.30 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 155.8, 144.7, 138.6, 136.4, 130.2, 129.4, 129.4, 128.8, 128.3, 127.9, 127.1, 126.4, 123.3, 113.6, 55.5, 37.5, 36.7, 21.3, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_3S$ $[M + H]^+$ 423.1737, found 423.1734.



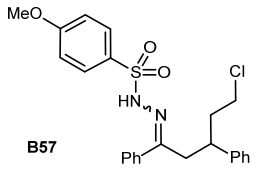
***N*'-(1,3-Diphenylheptylidene)-4-methoxybenzenesulfonohydrazide (B52)**

White solid, as an inseparable mixture of *E*/*Z* isomers (15.9:1), 0.60 g, 67% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.9 Hz, 0.12H), 7.67 (d, *J* = 8.9 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.39 – 7.32 (m, 3.18H), 7.20 – 7.13 (m, 3.18H), 7.04 – 6.98 (m, 2.12H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.84 – 6.81 (m, 0.12H), 6.70 (br s, 1H), 3.88 (s, 0.18H), 3.86 (s, 3H), 2.95 (dd, *J* = 13.9, 4.5 Hz, 1H), 2.88 – 2.81 (m, 1.12H), 2.76 – 2.71 (m, 0.06H), 2.68 – 2.59 (m, 1H), 1.82 – 1.64 (m, 2H), 1.55 – 1.44 (m, 0.12H), 1.27 – 0.98 (m, 4.24H), 0.79 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.3 Hz, 0.18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 155.9, 143.4, 136.4, 130.4, 129.8, 129.6, 129.4, 129.4, 129.0, 128.4, 128.1, 127.6, 127.3, 126.9, 126.5, 113.6, 55.6, 43.4, 42.6, 35.9, 35.8, 35.3, 29.6, 29.3, 22.5, 22.4, 13.9, 13.8.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{31}N_2O_3S$ $[M + H]^+$ 451.2050, found 451.2047.



***N*'-(5-Chloro-1,3-diphenylpentylidene)-4-methoxybenzenesulfonohydrazide (B57)**

Yellow oil, as an inseparable mixture of *E*/*Z* isomers (3.1:1), 0.65 g, 71% yield in the final step.

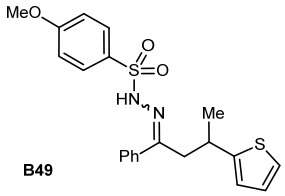
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 0.64H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.45 (m, 0.32H), 7.39 – 7.31 (m, 3.96H), 7.21 – 7.14 (m, 3.96H), 7.05 – 7.01 (m, 3H), 6.99 – 6.96 (m, 1.28H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.89 – 6.86 (m, 0.64H), 3.88 (s, 0.96H), 3.86 (s, 3H), 3.39 (dt, *J* = 11.3, 5.7 Hz, 1H), 3.30 (ddd, *J* = 11.0, 6.8, 4.6 Hz, 0.32H), 3.19 – 3.12 (m, 1H), 3.12 – 3.06 (m, 0.32H), 3.05 – 2.91 (m, 3H), 2.90 – 2.74 (m, 0.96H), 2.28 – 2.18 (m, 1H), 2.16 – 2.07 (m, 1H), 2.04 – 1.94 (m, 0.32H), 1.93 – 1.84 (m, 0.32H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 156.0, 155.0, 142.2, 141.3, 136.1, 132.5, 130.3, 129.9, 129.8, 129.6, 129.6, 129.3, 129.2, 128.5, 128.4, 127.8, 127.5, 127.1, 126.7, 126.5, 126.4, 114.2, 113.7, 55.6, 44.4, 42.6, 42.4, 40.4, 39.5, 38.2, 37.8, 34.9.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}ClN_2O_3S$ $[M + H]^+$ 457.1347, found 457.1345.

General procedure 3

Racemic arylsulfonohydrazones **B49**, **B50** and **B66** were prepared from the reaction of the corresponding arylketone (2.0 mmol, 1.0 equiv.) with 4-methoxybenzene sulfonohydrazide (0.81 g, 4.0 mmol, 2.0 equiv.). The corresponding arylketones are known compounds and were prepared according to the literature procedures[10,11].



B49

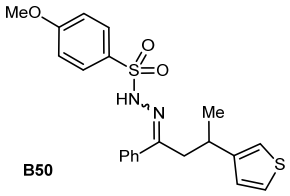
4-Methoxy-*N*'-(1-phenyl-3-(thiophen-2-yl)butylidene)benzenesulfonohydrazide (B49)

Slightly yellow solid, as an inseparable mixture of *E*/*Z* isomers (3.0:1), 0.38 g, 46% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2.66H), 7.59 – 7.54 (m, 2H), 7.49 (br s, 0.33H), 7.43 – 7.31 (m, 3.99H), 7.11 – 7.03 (m, 2.33H), 7.00 – 6.94 (m, 3.33H), 6.82 – 6.78 (m, 0.33H), 6.77 – 6.73 (m, 0.99H), 6.62 (br s, 1H), 3.87 (s, 3.99H), 3.31 – 3.19 (m, 1.33H), 2.95 – 2.87 (m, 2H), 2.87 – 2.81 (m, 0.33H), 2.79 – 2.68 (m, 0.33H), 1.39 (d, J = 6.5 Hz, 3H), 1.22 (d, J = 6.8 Hz, 0.99H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 155.9, 154.9, 150.0, 148.2, 136.3, 132.6, 130.4, 130.0, 129.9, 129.8, 129.6, 129.6, 129.5, 128.4, 127.1, 126.5, 126.3, 123.6, 122.8, 122.7, 114.1, 113.7, 55.6, 47.0, 37.5, 33.1, 32.2, 22.7.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}N_2O_3S_2$ $[M + H]^+$ 415.1145, found 415.1146.



B50

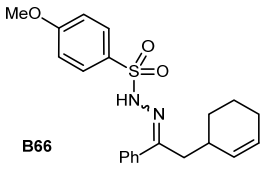
4-Methoxy-*N*'-(1-phenyl-3-(thiophen-3-yl)butylidene)benzenesulfonohydrazide (B50)

Slightly yellow solid, as an inseparable mixture of *E*/*Z* isomers (7.7:1), 0.42 g, 51% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2.26H), 7.61 – 7.54 (m, 2H), 7.45 (br s, 0.13H), 7.40 – 7.32 (m, 3.39H), 7.17 – 7.13 (m, 1H), 7.09 – 7.06 (m, 0.13H), 7.02 – 6.91 (m, 3.39H), 6.85 (d, J = 6.0 Hz, 2H), 6.81 – 6.70 (m, 0.39H), 3.89 (s, 0.39H), 3.87 (s, 3H), 3.13 – 2.99 (m, 1H), 2.88 (d, J = 7.3 Hz, 2H), 2.84 – 2.67 (m, 0.39H), 1.33 (d, J = 6.7 Hz, 3H), 1.14 (d, J = 6.6 Hz, 0.39H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 156.6, 155.7, 146.7, 145.6, 136.4, 132.7, 130.5, 130.0, 129.7, 129.6, 129.5, 128.4, 126.9, 126.7, 126.5, 125.9, 125.2, 123.6, 120.1, 119.3, 114.2, 113.8, 55.6, 45.8, 36.6, 32.9, 32.2, 21.7, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}N_2O_3S_2$ $[M + H]^+$ 415.1145, found 415.1147.



B66

***N*'-(2-(Cyclohex-2-en-1-yl)-1-phenylethylidene)-4-methoxybenzenesulfonohydrazide (B66)**

White solid, as an inseparable mixture of *E*/*Z* isomers (4.4:1), 0.54 g, 70% yield in the final step.

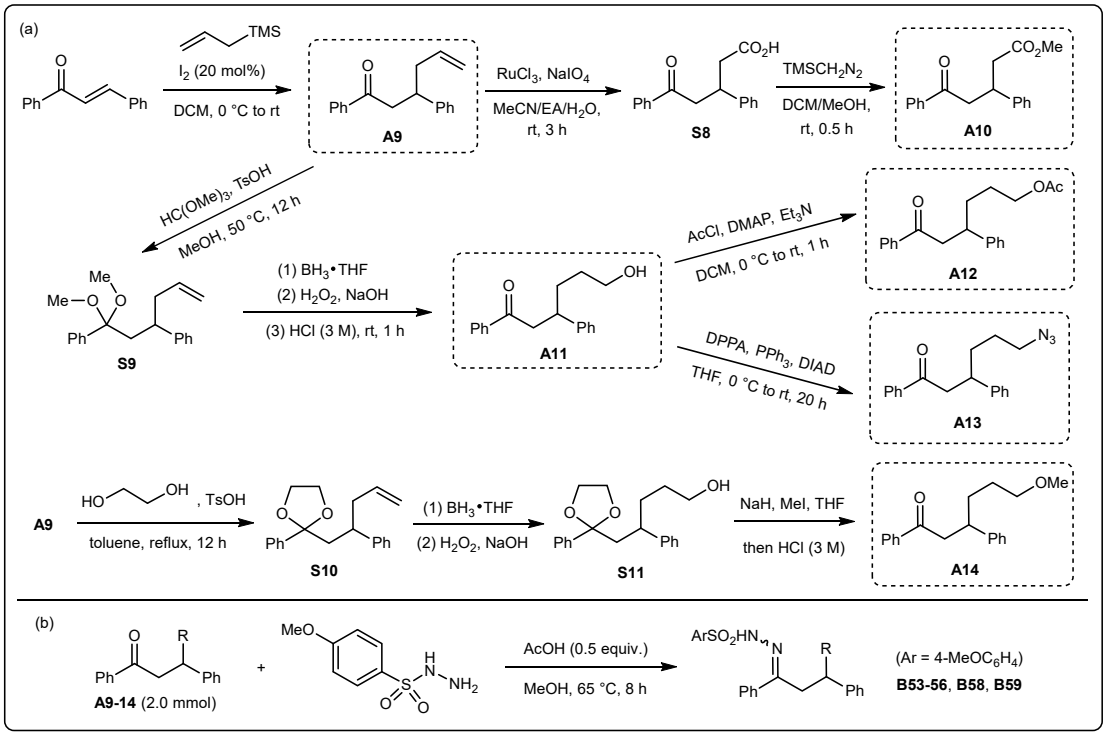
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2.46H), 7.91 (br s, 1H), 7.85 (d, *J* = 8.7 Hz, 0.46H), 7.67 – 7.61 (m, 2H), 7.45 – 7.40 (m, 0.92H), 7.37 – 7.31 (m, 3H), 7.05 (d, *J* = 6.6 Hz, 0.46H), 6.99 (d, *J* = 8.7 Hz, 2.46H), 5.70 – 5.64 (m, 1H), 5.63 – 5.58 (m, 0.23H), 5.36 – 5.30 (m, 0.23H), 5.19 – 5.12 (m, 1H), 3.88 (s, 0.69H), 3.85 (s, 3H), 2.60 (d, *J* = 8.2 Hz, 2H), 2.49 – 2.41 (m, 0.46H), 2.37 – 2.29 (m, 1H), 1.99 – 1.90 (m, 2H), 1.72 – 1.64 (m, 2.46H), 1.51 – 1.42 (m, 1.23H), 1.34 – 1.25 (m, 1.23H), 1.18 – 1.04 (m, 0.46H), 0.99 – 0.87 (m, 0.23H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 163.2, 156.9, 154.4, 136.5, 132.9, 130.2, 130.1, 129.8, 129.7, 129.6, 129.5, 128.9, 128.3, 127.7, 126.6, 126.4, 114.0, 55.6, 44.4, 33.0, 32.5, 32.0, 29.1, 28.6, 25.1, 25.0, 21.1, 20.6.

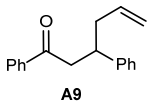
HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}N_2O_3S$ $[M + H]^+$ 385.1580, found 385.1581.

General procedure 4

Racemic arylsulfonohydrazones **B53**–**56**, **B58** and **B59** were prepared according to the **general procedure 4** from the corresponding racemic ketones **A9**–**14** with 4-methoxy benzenesulfonohydrazide.



Synthesis of **A9**[12]: To a solution of (*E*)-chalcone (10.41 g, 50 mmol, 1.0 equiv.) and iodine (2.54 g, 10 mmol, 0.2 equiv.) in DCM (200 mL) was slowly added allyl trimethylsilane (11.92 mL, 75 mmol, 1.5 equiv.) via syringe at 0 °C. Then the reaction mixture was stirred at room temperature for 12 h. Upon completion (monitored by TLC), the reaction mixture was quenched by water (100 mL), extracted with DCM (100 mL). The combined organic layers were washed with sodium thiosulphate (15% solution, 100 mL × 2) and brine (100 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50:1–30:1) to give the product **A9** as a white solid (10.36 g, 83% yield).



A9

1,3-Diphenylhex-5-en-1-one (A9)

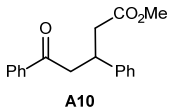
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.18 – 7.13 (m, 1H), 5.68 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.03 – 4.93 (m, 2H), 3.48 (p, *J* = 7.0 Hz, 1H), 3.33 – 3.24 (m, 2H), 2.53 – 2.39 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 144.3, 137.1, 136.2, 132.9, 128.4, 128.3, 127.9, 127.5, 126.3, 116.7, 44.4, 40.6, 40.6.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1430.

Synthesis of **A10**[13,14]: To a solution of **A9** (1.25 g, 5.0 mmol, 1.0 equiv.) in EtOAc (10 mL) and MeCN (10 mL) was successively added H_2O (15 mL), $NaIO_4$ (6.42 g, 30 mmol, 6.0 equiv.) and $RuCl_3$ (20.7 mg, 0.1 mmol, 2 mol%). The suspension was stirred vigorously at room temperature for 3 h. Then the reaction mixture was quenched by *i*-PrOH (2 mL) and filtered through a short pad of celite to remove the insoluble solids, and the filtrate was concentrated under reduced pressure to remove the organic solvents. The remaining aqueous phase was extracted with EtOAc (40 mL × 2), the combined organic layers were washed with brine (40 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 5:1–3:1) to give the carboxylic acid intermediate **S8** as a white solid (0.96 g, 72% yield).

To a stirring solution of **S8** (0.80 g, 3.0 mmol, 1.0 equiv.) in DCM (18 mL) and MeOH (2 mL) was slowly added $TMSCH_2N_2$ (2.0 M solution in hexane, 1.65 mL, 3.3 mmol, 1.1 equiv.) at room temperature under argon atmosphere. The resulting mixture was stirred at room temperature for 0.5 h. Then the reaction mixture was quenched by glacial acetic acid (2 mL), diluted with DCM (10 mL), washed with saturated $NaHCO_3$ (20 mL × 2) and brine (20 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 5:1–3:1) to afford the product **A10** as a white solid (0.65 g, 76% yield).



A10

Methyl 5-Oxo-3,5-diphenylpentanoate (A10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.41 (m, 2H), 7.31 – 7.25 (m, 4H), 7.22 – 7.17 (m, 1H), 3.88 (p, *J* = 7.1 Hz, 1H), 3.59 (s, 3H), 3.40 (dd, *J* = 16.9, 7.1 Hz, 1H), 3.33 (dd, *J* = 16.9, 7.1 Hz, 1H), 2.82 (dd, *J* = 15.4, 7.1 Hz, 1H), 2.69 (dd, *J* = 15.4, 7.1 Hz, 1H).

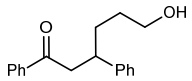
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 172.3, 143.3, 136.9, 133.1, 128.6, 128.6, 128.1, 127.3, 126.8, 51.6, 44.5, 40.6, 37.5.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O_3$ $[M + H]^+$ 283.1329, found 283.1329.

Synthesis of **A11**[15,16]: To a solution of **A9** (5.0 g, 20 mmol, 1.0 equiv.) and trimethyl orthoformate (3.28 mL, 30 mmol, 1.5 equiv.) in anhydrous methanol (100 mL) was added *p*-toluenesulfonic acid (34.4 mg, 0.2 mmol, 1 mol%) in one portion at room temperature under argon atmosphere. Then the resulting mixture was stirred at 50 °C for 12 h. After cooling down to room temperature, the reaction mixture was quenched by saturated Na_2CO_3 (20 mL) and concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (50 mL × 2). The combined organic layers were washed with brine (50 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to

afford the crude ketal **S9** (5.39 g), which was directly used in the next step without further purification.

To a cooled (0 °C) solution of the crude ketal **S9** in anhydrous THF (100 mL) was dropwise added borane-THF complex (1.0 M borane solution in THF, 30 mL, 30 mmol, 1.5 equiv.) via syringe under argon atmosphere. The resulting mixture was stirred at 0 °C for 4 h. Then NaOH (3 M, 20 mL) and H_2O_2 (30% in H_2O, 25 mL) were added into the reaction mixture, and the resulting solution was warmed up to room temperature and stirred for 3 h. The reaction mixture was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine (100 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in THF (100 mL), then HCl (3 M, 100 mL) was added into the reaction mixture. The resulting mixture was stirred vigorously at room temperature for 1 h. Then the reaction mixture was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (100 mL × 2). The combined organic layers were washed with brine (100 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 5:1–3:1) to afford the product **A11** as a colorless oil (3.12 g, 58% yield over three steps).



A11

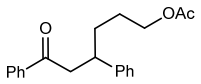
6-Hydroxy-1,3-diphenylhexan-1-one (A11)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.23 (m, 4H), 7.21 – 7.16 (m, 1H), 3.66 – 3.55 (m, 2H), 3.40 – 3.32 (m, 1H), 3.30 – 3.20 (m, 2H), 1.91 – 1.80 (m, 1H), 1.75 – 1.64 (m, 1H), 1.58 (br s, 1H), 1.52 – 1.38 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 144.4, 137.0, 133.0, 128.5, 128.5, 128.0, 127.6, 126.4, 62.5, 45.9, 40.6, 32.2, 30.4.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}O_2$ $[M + H]^+$ 269.1536, found 269.1536.

Synthesis of **A12**: To a solution of **A11** (0.81 g, 3.0 mmol, 1.0 equiv.), dimethyl aminopyridine (DMAP, 18.3 mg, 0.15 mmol, 5 mol%) and Et_3N (0.63 mL, 4.5 mmol, 1.5 equiv.) in anhydrous DCM (20 mL) was dropwise added acetyl chloride (0.26 mL, 3.6 mmol, 1.2 equiv.) via syringe at 0 °C under argon atmosphere. The resulting mixture was warmed up to room temperature and stirred for 1 h. Upon completion (monitored by TLC), the reaction mixture was washed with HCl (1 M, 30 mL × 2), and the aqueous phase was extracted with DCM (20 mL × 2). The combined organic layers were washed with brine (50 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the product **A12** as a colorless oil (0.87 g, 94% yield).



A12

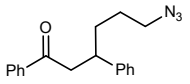
6-Oxo-4,6-diphenylhexyl Acetate (A12)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.55 – 7.48 (m, 1H), 7.44 – 7.38 (m, 2H), 7.31 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 3.99 (t, *J* = 6.7 Hz, 2H), 3.39 – 3.31 (m, 1H), 3.30 – 3.19 (m, 2H), 1.99 (s, 3H), 1.90 – 1.78 (m, 1H), 1.74 – 1.62 (m, 1H), 1.60 – 1.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 170.9, 144.1, 137.0, 132.9, 128.4, 128.4, 127.9, 127.4, 126.4, 64.2, 45.8, 40.7, 32.3, 26.5, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}O_3$ $[M + H]^+$ 311.1642, found 311,1642.

Synthesis of **A13**: To a solution of **A11** (1.07 g, 4.0 mmol, 1.0 equiv.) and Ph_3P (1.26 g, 4.8 mmol, 1.2 equiv.) in anhydrous THF (40 mL) was added diisopropyl azodicarboxylate (0.95 mL, 4.8 mmol, 1.2 equiv.) at 0 °C under argon atmosphere. The resulting mixture was stirred for 15 min. Then a solution of diphenylphosphoryl azide (1.03 mL, 4.8 mmol, 1.2 equiv.) in anhydrous THF (5 mL) was dropwise added into the reaction mixture over 30 min. The resulting mixture was warmed up to room temperature and stirred for 20 h. Upon completion (monitored by TLC), the reaction mixture was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) to afford the desired product **A13** as a colorless oil (0.91 g, 78% yield).



A13

6-Azido-1,3-diphenylhexan-1-one (A13)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.56 – 7.50 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.21 – 7.17 (m, 1H), 3.38 – 3.24 (m, 3H), 3.24 – 3.14 (m, 2H), 1.89 – 1.78 (m, 1H), 1.75 – 1.64 (m, 1H), 1.57 – 1.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 144.0, 137.0, 133.0, 128.6, 128.5, 128.0, 127.5, 126.5, 51.3, 45.8, 40.7, 33.1, 26.9.

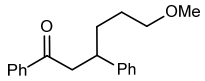
HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}N_3O$ $[M + H]^+$ 294.1601, found 294.1600.

Synthesis of **A14**[17]: To a solution of **A9** (1.25 g, 5.0 mmol, 1.0 equiv.) in anhydrous toluene (40 mL) was added ethylene glycol (1.40 mL, 25 mmol, 5.0 equiv.) and *p*-toluenesulfonic acid (86.1 mg, 0.5 mmol, 10 mol%). The resulting mixture was heated to reflux with azeotropic distillation of water via Dean-Stark trap for 12 h. After cooling down to room temperature, the reaction mixture was diluted with water (40 mL) and extracted with EtOAc (20 mL × 2). The combined organic layers were washed with water (50 mL) and brine (50 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100:1–50:1) to give the ketal **S10** as a colorless oil (1.35 g, 92% yield).

To a cooled (0 °C) solution of **S10** (1.32 g, 4.5 mmol, 1.0 equiv.) in anhydrous THF

(20 mL) was dropwise added borane-THF complex (1.0 M borane solution in THF, 6.75 mL, 6.75 mmol, 1.5 equiv.) via syringe under argon atmosphere. The resulting mixture was stirred at 0 °C for 4 h. Then NaOH (3 M, 5 mL) and H_2O_2 (30% in H_2O, 6 mL) were added into the reaction mixture, and the resulting mixture was warmed up to room temperature and stirred for 3 h. The reaction mixture was extracted with EtOAc (20 mL × 2), the combined organic layers were washed with brine (40 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–3:1) to give the product **S11** as a colorless oil (0.96 g, 68% yield).

To a cooled (0 °C) solution of **S11** (0.94 g, 3.0 mmol, 1.0 equiv.) in anhydrous THF (20 mL) was added NaH (60% dispersion in mineral oil, 0.18 g, 4.5 mmol, 1.5 equiv.) in portions under argon atmosphere. The resulting mixture was stirred at 0 °C for 15 min. Then MeI (0.28 mL, 4.5 mmol, 1.5 equiv.) was dropwise added into the reaction mixture, and the resulting mixture was warmed up to room temperature and stirred for 2 h. The reaction mixture was quenched by saturated NH_4Cl (10 mL) and concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (40 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in THF (10 mL), then HCl (3 M, 5 mL) was added, and the resulting mixture was stirred vigorously at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (40 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the product **A14** as a colorless oil (0.62 g, 72% yield over two steps).



A14

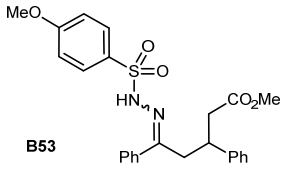
6-Methoxy-1,3-diphenylhexan-1-one (A14)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.55 – 7.50 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 3.38 – 3.25 (m, 5H), 3.26 (s, 3H), 1.87 – 1.76 (m, 1H), 1.74 – 1.63 (m, 1H), 1.56 – 1.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 144.5, 137.1, 132.9, 128.5, 128.5, 128.0, 127.5, 126.3, 72.6, 58.5, 45.9, 41.1, 32.8, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}O_2$ $[M + H]^+$ 283.1693, found 283.1691.

Substrates **B53**–**56**, **B58** and **B59** were prepared from the reactions of corresponding ketones **A9**–**14** (2.0 mmol, 1.0 equiv.) with 4-methoxybenzenesulfonohydrazide (0.81 g, 4.0 mmol, 2.0 equiv.).



B53

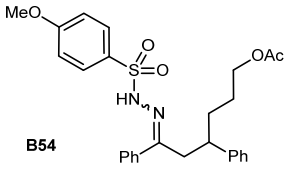
Methyl 5-(2-((4-Methoxyphenyl)sulfonyl)hydrazono)-3,5-diphenylpentanoate (B53)

Slightly yellow solid, as an inseparable mixture of *E*/*Z* isomers (5.9:1), 0.57 g, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 0.34H), 7.41 (d, *J* = 7.5 Hz, 0.34H), 7.39 (d, *J* = 7.5 Hz, 2.34H), 7.27 – 7.19 (m, 3H), 7.17 – 7.11 (m, 3.51H), 7.01 (d, *J* = 7.4 Hz, 0.34H), 6.99 – 6.93 (m, 4.68H), 6.91 – 6.89 (m, 0.34H), 3.88 (s, 0.51H), 3.86 (s, 3H), 3.70 (s, 3H), 3.53 (s, 0.51H), 3.37 – 3.29 (m, 0.17H), 3.25 – 3.16 (m, 1H), 3.08 (dd, *J* = 14.0, 4.3 Hz, 1H), 2.91 – 2.85 (m, 0.51H), 2.84 – 2.74 (m, 2H), 2.63 – 2.57 (m, 1H), 2.50 (dd, *J* = 15.5, 8.8 Hz, 0.17H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 172.1, 163.2, 163.1, 155.5, 153.5, 142.5, 141.7, 136.3, 132.4, 130.2, 130.1, 129.9, 129.8, 129.5, 129.2, 128.9, 128.3, 128.1, 127.5, 127.3, 126.9, 126.6, 126.5, 126.4, 114.1, 113.8, 55.6, 52.2, 51.4, 43.7, 40.3, 39.0, 38.7, 38.6, 34.2.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_5S$ $[M + H]^+$ 467.1635, found 467.1638.



B54

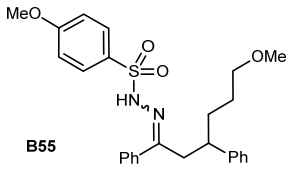
6-(2-((4-Methoxyphenyl)sulfonyl)hydrazono)-4,6-diphenylhexyl Acetate (B54)

Colorless oil, as an inseparable mixture of *E*/*Z* isomers (5.6:1), 0.85 g, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.9 Hz, 0.36H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.38 – 7.31 (m, 3.54H), 7.20 – 7.12 (m, 3.54H), 7.04 – 6.99 (m, 2H), 6.97 – 6.92 (m, 2.54H), 6.85 – 6.82 (m, 0.36H), 3.93 (t, *J* = 6.6 Hz, 2H), 3.89 (s, 0.54H), 3.87 (s, 3H), 3.01 – 2.84 (m, 2H), 2.84 – 2.76 (m, 0.54H), 2.76 – 2.65 (m, 1H), 1.98 (s, 3.54H), 1.89 – 1.71 (m, 2H), 1.70 – 1.61 (m, 0.36H), 1.58 – 1.49 (m, 0.36H), 1.46 – 1.33 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 163.1, 156.2, 155.5, 143.3, 142.5, 136.3, 132.7, 130.4, 129.9, 129.6, 129.4, 129.4, 129.1, 128.4, 128.3, 127.6, 127.5, 126.9, 126.5, 126.4, 114.1, 113.6, 64.2, 63.9, 55.6, 44.8, 43.0, 42.3, 35.8, 32.3, 31.7, 26.5, 26.2, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}N_2O_5S$ $[M + H]^+$ 495.1948, found 495.1950.



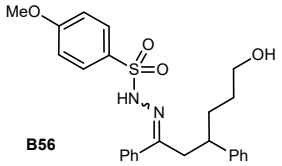
4-Methoxy-*N*'-(6-methoxy-1,3-diphenylhexylidene)benzenesulfonohydrazide (B55)

Yellow oil, as an inseparable mixture of *E*/*Z* isomers (3.4:1), 0.78 g, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.0 Hz, 0.58H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.38 – 7.33 (m, 3.87H), 7.18 – 7.12 (m, 3.87H), 7.02 – 6.99 (m, 2H), 6.98 – 6.95 (m, 0.87H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.84 – 6.81 (m, 0.58H), 6.61 (br s, 1H), 3.89 (s, 0.87H), 3.88 (s, 3H), 3.30 – 3.25 (m, 2H), 3.27 (s, 3H), 3.23 (s, 0.87H), 3.19 (t, *J* = 6.6 Hz, 0.58H), 2.97 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.91 – 2.76 (m, 1.58H), 2.75 – 2.64 (m, 1.29H), 1.87 – 1.80 (m, 2H), 1.66 – 1.60 (m, 0.29H), 1.56 – 1.47 (m, 0.29H), 1.40 (td, *J* = 13.8, 6.4 Hz, 2H), 1.33 – 1.26 (m, 0.58H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 163.1, 156.5, 155.7, 143.7, 143.1, 136.4, 132.8, 130.5, 129.9, 129.6, 129.5, 129.5, 129.2, 128.4, 128.2, 127.7, 127.5, 127.0, 126.5, 126.2, 114.1, 113.6, 72.4, 72.3, 58.6, 58.4, 55.6, 44.8, 43.3, 42.5, 36.0, 32.6, 32.5, 27.6, 27.3.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{31}N_2O_4S$ $[M + H]^+$ 467.1999, found 467.2004.



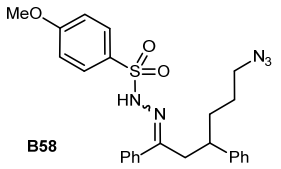
***N*'-(6-Hydroxy-1,3-diphenylhexylidene)-4-methoxybenzenesulfonohydrazide (B56)**

White solid, as an inseparable mixture of *E*/*Z* isomers (5.6:1), 0.71 g, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.9 Hz, 0.36H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.48 (br s, 0.18H), 7.46 – 7.43 (m, 2H), 7.37 – 7.26 (m, 4.72H), 7.16 – 7.09 (m, 3.54H), 6.99 – 6.93 (m, 4.72H), 6.87 – 6.83 (m, 0.36H), 3.88 (s, 0.54H), 3.86 (s, 3H), 3.84 – 3.82 (m, 0.36H), 3.60 – 3.50 (m, 2H), 3.46 (t, *J* = 6.5 Hz, 0.36H), 2.98 (dd, *J* = 13.4, 4.2 Hz, 1H), 2.87 – 2.73 (m, 2.54H), 1.94 (br s, 1H), 1.85 – 1.77 (m, 2H), 1.71 – 1.64 (m, 0.18H), 1.57 – 1.48 (m, 0.18H), 1.45 – 1.36 (m, 2H), 1.32 – 1.25 (m, 0.36H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 163.1, 156.6, 155.6, 143.7, 143.1, 136.5, 132.8, 130.3, 129.9, 129.8, 129.6, 129.5, 129.4, 129.4, 128.9, 128.2, 128.2, 127.6, 127.2, 127.0, 126.5, 126.2, 114.1, 113.7, 62.5, 62.4, 55.6, 55.6, 44.8, 42.8, 42.2, 35.5, 32.2, 32.0, 30.2, 30.1.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{29}N_2O_4S$ $[M + H]^+$ 453.1843, found 453.1840.



B58

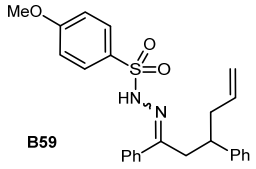
***N*'-(6-Azido-1,3-diphenylhexylidene)-4-methoxybenzenesulfonohydrazide (B58)**

Slightly yellow oil, as an inseparable mixture of *E*/*Z* isomers (4.8:1), 0.45 g, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 0.42H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.47 (br s, 0.21H), 7.38 – 7.31 (m, 3.63H), 7.19 – 7.14 (m, 3.63H), 7.02 – 6.99 (m, 2H), 6.97 – 6.91 (m, 3.63H), 6.86 – 6.83 (m, 0.42H), 3.88 (s, 0.63H), 3.86 (s, 3H), 3.19 – 3.10 (m, 2H), 3.10 – 3.04 (m, 0.42H), 2.95 (dd, *J* = 14.1, 5.0 Hz, 1H), 2.87 (dd, *J* = 14.0, 9.8 Hz, 1H), 2.82 – 2.77 (m, 0.42H), 2.75 – 2.62 (m, 1.21H), 1.88 – 1.72 (m, 2H), 1.69 – 1.59 (m, 0.21H), 1.58 – 1.48 (m, 0.21H), 1.41 – 1.26 (m, 2.42H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 156.2, 155.4, 143.1, 142.4, 136.3, 132.6, 130.3, 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 129.1, 128.4, 128.3, 127.5, 126.9, 126.5, 126.4, 126.3, 114.1, 113.6, 55.5, 51.1, 51.0, 44.8, 43.0, 42.2, 35.8, 32.9, 32.4, 26.8, 26.5.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{28}N_5O_3S$ $[M + H]^+$ 478.1907, found 478.1907.



B59

***N*'-(1,3-Diphenylhex-5-en-1-ylidene)-4-methoxybenzenesulfonohydrazide (B59)**

Yellow oil, as an inseparable mixture of *E*/*Z* isomers (2.9:1), 0.72 g, 83% yield.

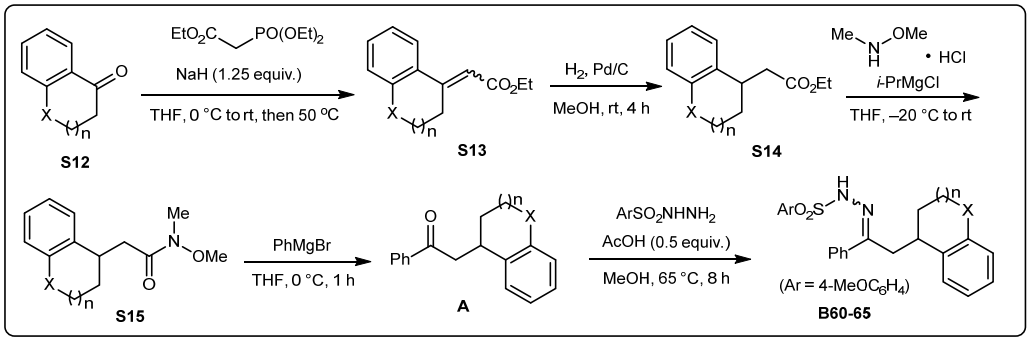
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.9 Hz, 0.70H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.38 – 7.33 (m, 4.05H), 7.35 – 7.32 (m, 0.35H), 7.22 – 7.12 (m, 4.05H), 7.03 – 7.00 (m, 2H), 6.98 – 6.96 (m, 0.70H), 6.97 – 6.92 (m, 2.70H), 6.84 – 6.81 (m, 0.70H), 6.51 (br s, 1H), 5.73 – 5.61 (m, 1H), 5.58 – 5.47 (m, 0.35H), 5.09 – 5.03 (m, 2H), 4.89 – 4.84 (m, 0.70H), 3.88 (s, 4.05H), 3.04 (dd, *J* = 13.6, 3.4 Hz, 1H), 2.98 – 2.88 (m, 0.35H), 2.88 – 2.69 (m, 2.70H), 2.56 – 2.43 (m, 2H), 2.31 – 2.18 (m, 0.70H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 156.4, 155.8, 143.4, 143.1, 136.2, 136.0, 135.6, 132.8, 130.5, 130.0, 129.9, 129.7, 129.5, 129.4, 129.2, 128.4, 128.2, 127.7, 127.6, 126.9, 126.6, 126.5, 126.2, 117.7, 116.5, 114.1, 113.6, 55.6, 43.7, 43.0, 42.2, 40.6, 39.9, 34.8.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_3S$ $[M + H]^+$ 435.1737, found 435.1742.

General procedure 5

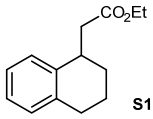
Racemic arylsulfonohydrazones **B60**–**65** were prepared according to the **general procedure 5**. The corresponding cyclic ketones **S12** are commercially available or were easily prepared through the reported procedures[18-20].



General procedure for preparation of 4-methoxy-*N*′-(1-phenyl-2-(1,2,3,4-tetrahydro naphthalen-1-yl)ethylidene)benzenesulfonohydrazide **B60** (n = 1, X = CH_2) as the typical example:

Synthesis of **S13-1** (n = 1, X = CH_2)[21]: To a suspension of NaH (60% dispersion in mineral oil, 0.50 g, 12.5 mmol, 1.25 equiv.) in anhydrous THF (40 mL) was dropwise added triethyl phosphonoacetate (2.69 g, 12 mmol, 1.2 equiv.) at 0 °C under argon atmosphere. The resulting mixture was warmed up to room temperature and stirred for 1 h. Then 1-tetralone **S12-1** (1.46 g, 10 mmol, 1.0 equiv.) was dropwise added into the reaction mixture, and the resulting mixture was heated to 50 °C and stirred for 8 h. After cooling down to room temperature, the reaction mixture was quenched by saturated NH_4Cl (20 mL), concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (40 mL × 2). The combined organic layers were washed with brine (40 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether /ethyl acetate 100:1–50:1) to afford the desired product **S13-1** as a colorless oil (1.77 g, 82% yield, as an inseparable mixture of *E*/*Z* isomers and the analytical data were in accordance with those reported in the literature report[22]).

Synthesis of **S14-1** (n = 1, X = CH_2): To a solution of **S13-1** (1.77 g, 8.2 mmol) in MeOH (20 mL) was added Pd/C (10% palladium on carbon, wet with ca. 50% water, 50 mg). Then the reaction flask was evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at room temperature for 4 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (20 mL). The filtrate was concentrated under reduced pressure to give **S14-1** as a colorless oil (1.75 g, 98% yield), which was pure enough and used without further purification.



S14-1

Ethyl 2-(1,2,3,4-Tetrahydronaphthalen-1-yl)acetate (S14-1)

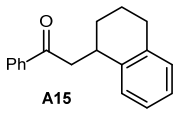
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.03 (m, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.40 - 3.33 (m, 1H), 2.80 – 2.68 (m, 3H), 2.53 (dd, *J* = 15.2, 9.9 Hz, 1H), 1.99–1.64 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 139.3, 137.1, 129.2, 128.2, 126.0, 125.8, 60.4, 42.0, 34.5, 29.5, 28.1, 19.5, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1381.

Synthesis of **S15-1** (n = 1, X = CH_2): To a solution of **S14-1** (0.87 g, 4 mmol, 1.0 equiv.) and *N*,*O*-dimethylhydroxylamine hydrochloride (0.78 g, 8 mmol, 2.0 equiv.) in anhydrous THF (20 mL) was dropwise added *i*-PrMgCl (1.3 M solution in THF, 12.3 mL, 16 mmol, 4.0 equiv.) at –20 °C under argon atmosphere. Then the resulting mixture was warmed up to room temperature and stirred for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (20 mL) and concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (20 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude **S15-1** (0.90 g), which was directly used in the next step without further purification.

Synthesis of **A15** (n = 1, X = CH_2): To a cooled (0 °C) solution of the crude **S15-1** obtained above in anhydrous THF (20 mL) was dropwise added PhMgBr (3.0 M solution in Et_2O, 2.67 mL, 8 mmol, 2.0 equiv.) under argon atmosphere. After being stirred at 0 °C for 1 h, the reaction mixture was quenched by saturated NH_4Cl (20 mL), filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (20 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100:1–50:1) to afford the product **A15** as a slightly yellow oil (0.72 g, 72% yield over two steps).



A15

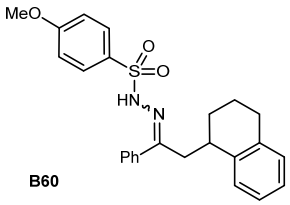
1-Phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethanone (A15)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.54 – 7.46 (m, 2H), 7.25 – 7.20 (m, 1H), 7.20 – 7.10 (m, 3H), 3.75 – 3.64 (m, 1H), 3.42 – 3.28 (m, 2H), 2.96 – 2.71 (m, 2H), 2.06 – 1.95 (m, 1H), 1.93 – 1.64 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 140.0, 137.2, 137.1, 133.0, 129.2, 128.5, 128.3, 128.0, 125.8, 46.1, 33.4, 29.5, 28.2, 19.6.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1430.

Synthesis of **B60**: To a solution of **A15** (0.50 g, 2.0 mmol, 1.0 equiv.) and 4-methoxybenzenesulfonohydrazide (0.81 g, 4.0 mmol, 2.0 equiv.) in MeOH (15 mL) was added glacial acetic acid (57 μL, 1.0 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B60** as a white solid (0.63 g, 72% yield), an inseparable mixture of *E*/*Z* isomers (3.2:1).



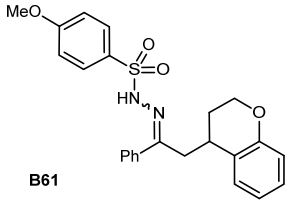
B60

4-Methoxy-*N*'-(1-phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethylidene)benzenesulfonohydrazide (B60)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2.62H), 7.70 – 7.63 (m, 2H), 7.55 (br s, 0.31H), 7.46 – 7.40 (m, 0.93H), 7.38 – 7.33 (m, 3H), 7.11 – 7.05 (m, 2H), 7.05 – 7.01 (m, 1.24H), 6.99 – 6.91 (m, 3.93H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 3.93H), 3.10 – 3.01 (m, 2H), 2.98 – 2.94 (m, 0.31H), 2.87 – 2.79 (m, 1.31H), 2.77 – 2.65 (m, 2.62H), 1.95 – 1.83 (m, 1H), 1.80 – 1.68 (m, 2.62H), 1.66 – 1.57 (m, 1.31H), 1.55 – 1.49 (m, 0.31H), 1.28 – 1.21 (m, 0.31H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 156.8, 156.1, 139.6, 138.0, 137.0, 136.5, 136.4, 132.7, 130.4, 130.0, 129.8, 129.7, 129.6, 129.5, 129.0, 128.4, 128.2, 128.0, 126.6, 126.5, 125.8, 125.6, 125.5, 114.0, 113.7, 55.5, 45.4, 35.0, 34.6, 34.1, 29.3, 28.9, 28.2, 26.8, 19.3, 19.0.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_3S$ $[M + H]^+$ 435.1737, found 435.1740.



B61

***N*'-(2-(Chroman-4-yl)-1-phenylethylidene)-4-methoxybenzenesulfonohydrazide (B61)**

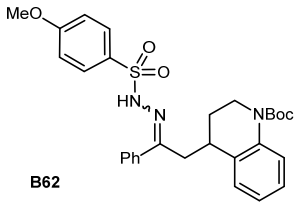
White solid, as an inseparable mixture of *E*/*Z* isomers (2.5:1), 0.49 g, 56% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2.80H), 7.70 – 7.64 (m, 2H), 7.54 (br s, 0.40H), 7.50 – 7.43 (m, 1.20H), 7.40 – 7.32 (m, 3H), 7.21 (br s, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.06 (dd, *J* = 14.1, 6.9 Hz, 1.40H), 6.98 (d, *J* = 8.8 Hz, 2.80H), 6.91 (d, *J* = 7.4 Hz, 0.40H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.79 – 6.72 (m, 1.60H), 6.52 (t, *J* = 7.4 Hz, 1H), 4.25 – 4.12 (m, 2H), 4.10 – 4.05 (m, 0.80H), 3.88 (s, 4.20H), 3.17 – 3.12 (m, 0.40H), 3.11 – 3.04 (m, 2H), 2.93 (dd, *J* = 15.5, 3.9 Hz, 0.40H), 2.81 (dd, *J* = 12.7,

5.9 Hz, 1H), 2.68 (dd, *J* = 15.5, 10.5 Hz, 0.40H), 2.05 – 1.93 (m, 1H), 1.92 – 1.85 (m, 0.40H), 1.76 – 1.70 (m, 1H), 1.69 – 1.63 (m, 0.40H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.5, 155.3, 154.5, 154.0, 136.4, 132.6, 130.4, 130.1, 130.0, 129.8, 129.7, 129.5, 128.7, 128.5, 128.5, 128.3, 127.5, 126.6, 126.5, 125.0, 123.4, 120.4, 120.2, 117.2, 116.8, 114.1, 113.9, 63.0, 62.8, 55.6, 44.8, 33.9, 30.8, 30.2, 27.2, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_4S$ $[M + H]^+$ 437.1530, found 437.1531.



B62

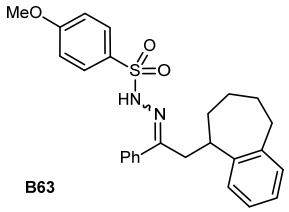
***tert*-Butyl 4-(2-(2-((4-Methoxyphenyl)sulfonyl)hydrazono)-2-phenylethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (B62)**

White solid, as an inseparable mixture of *E*/*Z* isomers (3.0:1), 0.72 g, 67% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 0.66H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.54 (m, 2.66H), 7.48 – 7.41 (m, 1H), 7.37 – 7.31 (m, 3.99H), 7.15 – 7.08 (m, 2H), 7.00 – 6.94 (m, 2.66H), 6.91 – 6.85 (m, 0.66H), 6.75 – 6.71 (m, 1H), 6.71 – 6.66 (m, 0.99H), 3.88 (s, 0.99H), 3.87 (s, 3H), 3.83 – 3.77 (m, 1H), 3.68 – 3.62 (m, 0.33H), 3.61 – 3.53 (m, 1.33H), 3.06 – 2.99 (m, 2H), 2.98 – 2.96 (m, 0.33H), 2.88 (dd, *J* = 15.4, 4.9 Hz, 0.33H), 2.83 – 2.74 (m, 1H), 2.65 (dd, *J* = 15.4, 9.8 Hz, 0.33H), 1.89 – 1.77 (m, 2.66H), 1.57 (s, 9H), 1.51 (s, 2.97H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 163.2, 155.7, 154.8, 153.8, 153.7, 138.1, 137.7, 136.3, 132.6, 132.6, 131.4, 130.4, 130.1, 130.0, 129.7, 129.7, 129.6, 128.5, 127.1, 127.0, 126.9, 126.6, 126.5, 126.1, 124.6, 124.2, 123.6, 123.3, 114.1, 113.9, 81.5, 80.8, 55.6, 43.3, 42.2, 42.0, 34.2, 33.4, 31.6, 28.8, 28.3, 28.3, 28.0.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{34}N_3O_5S$ $[M + H]^+$ 536.2214, found 536.2221.



B63

4-Methoxy-*N*'-(1-phenyl-2-(6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)ethylidene)benzenesulfonohydrazide (B63)

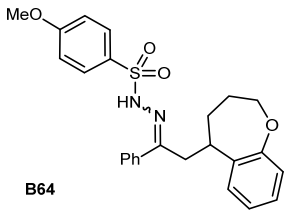
White solid, as an inseparable mixture of *E*/*Z* isomers (2.3:1), 0.58 g, 64% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 0.86H), 7.67 (d, *J* = 8.9 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.44 (br s, 0.43H), 7.43 – 7.39 (m, 1.29H), 7.38 – 7.32 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.13 – 7.09 (m, 1.29H), 7.05 – 7.00 (m, 1H), 6.99 – 6.96 (m, 1.29H), 6.93 (d, *J* = 8.9 Hz, 2.86H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.4 Hz, 1H),

6.44 (br s, 1H), 3.88 (s, 1.29H), 3.87 (s, 3H), 3.36 – 3.27 (m, 1H), 3.17 – 3.08 (m, 1H), 3.06 – 2.96 (m, 1.72H), 2.95 – 2.82 (m, 2.86H), 2.76 – 2.62 (m, 0.86H), 1.95 – 1.75 (m, 4.29H), 1.73 – 1.64 (m, 2H), 1.55 – 1.41 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.1, 157.3, 157.1, 144.2, 142.6, 142.4, 141.5, 136.3, 132.8, 131.1, 130.6, 130.0, 129.8, 129.7, 129.6, 129.5, 129.4, 128.4, 127.5, 126.6, 126.5, 126.0, 114.1, 113.6, 55.6, 55.6, 44.0, 41.7, 36.6, 35.7, 33.2, 32.4, 31.2, 28.0, 27.6, 26.9.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}N_2O_3S$ $[M + H]^+$ 449.1893, found 449.1892.



B64

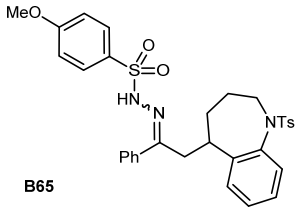
4-Methoxy-*N*'-(1-phenyl-2-(2,3,4,5-tetrahydrobenzo[*b*]oxepin-5-yl)ethylidene)benzenesulfonohydrazide (B64)

White solid, as an inseparable mixture of *E*/*Z* isomers (8.1:1), 0.75 g, 83% yield in the final step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 0.24H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.53 (br s, 1H), 7.46 – 7.42 (m, 2H), 7.38 – 7.28 (m, 3.36H), 7.08 – 7.03 (m, 0.12H), 6.99 (d, *J* = 8.9 Hz, 0.24H), 6.96 – 6.86 (m, 4.48H), 6.84 – 6.77 (m, 0.24H), 6.63 – 6.59 (m, 1H), 6.48 – 6.44 (m, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.20 – 4.11 (m, 0.12H), 3.88 (s, 0.36H), 3.86 (s, 3H), 3.70 – 3.63 (m, 0.12H), 3.61 – 3.52 (m, 2H), 3.13 – 3.07 (m, 0.12H), 3.06 – 3.00 (m, 1H), 2.97 – 2.87 (m, 0.12H), 2.75 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.47 – 2.33 (m, 1H), 2.11 – 1.99 (m, 1.12H), 1.83 – 1.70 (m, 2.24H), 1.71 – 1.63 (m, 0.48H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.9, 159.7, 158.8, 156.6, 155.2, 137.3, 136.3, 135.5, 132.8, 130.2, 130.2, 130.0, 129.9, 129.7, 129.5, 129.4, 128.5, 128.3, 127.6, 126.5, 123.9, 123.5, 122.1, 121.8, 114.1, 113.6, 74.0, 73.5, 55.6, 55.5, 42.0, 40.4, 30.6, 29.7, 29.6, 29.2, 27.5, 26.8.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_4S$ $[M + H]^+$ 451.1686, found 451.1685.



B65

4-Methoxy-*N*'-(1-phenyl-2-(1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-5-yl)ethylidene)benzenesulfonohydrazide (B65)

White solid, as an inseparable mixture of *E*/*Z* isomers (3.2:1), 0.63 g, 52% yield in the final step.

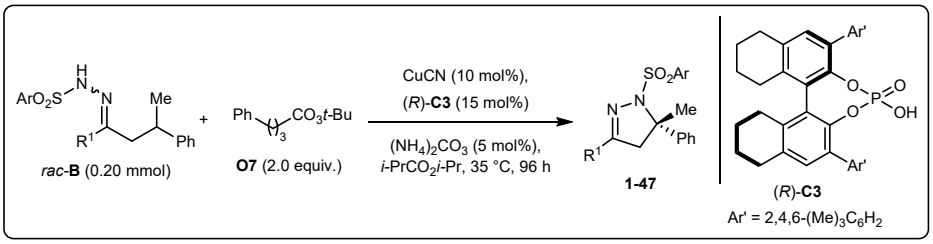
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (br s, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 0.62H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.66 – 7.61 (m, 2.62H), 7.45 – 7.35 (m, 5.24H), 7.10 – 6.94 (m, 3.93H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 6.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 4.39 – 4.31 (m, 1H), 3.88 (s, 0.93H), 3.84 (s, 3H), 3.48 – 3.37 (m, 1H), 3.07 – 2.96 (m, 2.62H), 2.95 – 2.90 (m, 1H), 2.49 (s, 3H), 2.42 (s, 0.93H), 2.35 – 2.20 (m, 1H), 2.10 – 2.01 (m, 1H), 1.82 – 1.68 (m, 2.62H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.6, 150.7, 143.7, 143.2, 142.5, 141.0, 139.1, 138.8, 137.0, 131.4, 131.0, 130.1, 130.0, 129.9, 129.6, 129.0, 128.4, 128.2, 128.0, 127.2, 127.1, 126.8, 126.4, 114.2, 113.7, 55.6, 55.5, 51.2, 43.2, 31.9, 30.9, 26.7, 21.57, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{34}N_3O_5S_2$ $[M + H]^+$ 604.1934, found 604.1935.

Enantioconvergent Amination of Racemic Tertiary C(sp^3)–H Bonds

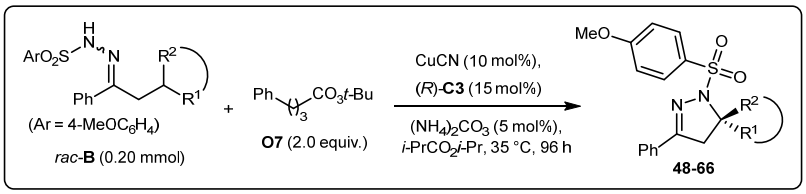
General procedure A: Substrate scope of the *N*-sulfonylhydrazone moiety (Fig. 2)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with *rac*-**B** (0.20 mmol, 1.0 equiv.), CuCN (1.8 mg, 0.020 mmol, 10 mol%), (*R*)-**C3** (17.8 mg, 0.030 mmol, 15 mol%), $(NH_4)_2CO_3$ (1.0 mg, 0.010 mmol, 5 mol%) and *i*-PrCO2*i*-Pr (4.0 mL). Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the reaction mixture was stirred at 35 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the desired products **1**–**47**.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

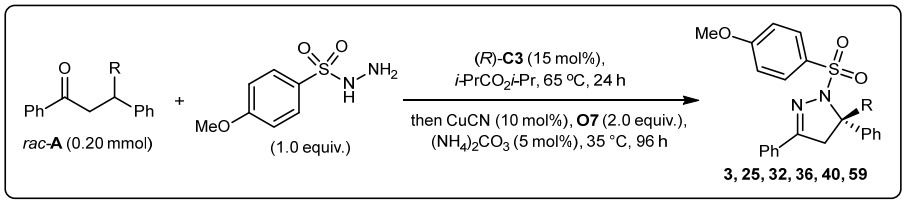
General procedure B: Substrate scope of the racemic tertiary C(sp^3)–H moiety (Fig. 3a)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with *rac*-**B** (0.20 mmol, 1.0 equiv.), CuCN (1.8 mg, 0.020 mmol, 10 mol%), (*R*)-**C3** (17.8 mg, 0.030 mmol, 15 mol%), $(NH_4)_2CO_3$ (1.0 mg, 0.010 mmol, 5 mol%) and *i*-PrCO2*i*-Pr (4.0 mL). Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the reaction mixture was stirred at 35 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1−5:1) to afford the desired products **48**–**66**.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

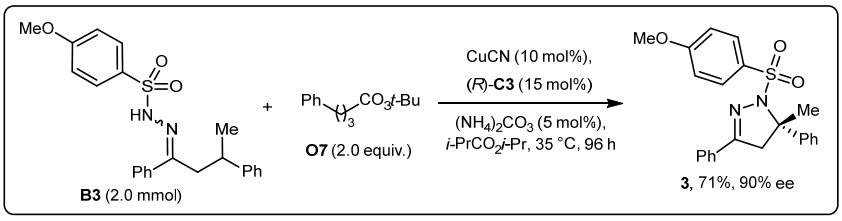
General procedure C: One-pot protocol for the enantioconvergent amination of tertiary *β*-C(sp^3)-H bonds starting from racemic ketones (Fig. 3b)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with *rac*-**A** (0.20 mmol, 1.0 equiv.), 4-methoxy benzenesulfonohydrazide (40.4 mg, 0.20 mmol, 1.0 equiv.), (*R*)-**C3** (17.8 mg, 0.030 mmol, 15 mol%) and *i*-PrCO$_2$*i*-Pr (4.0 mL), and the reaction mixture was stirred at 65 °C for 24 h. After cooling down to room temperature, CuCN (1.8 mg, 0.020 mmol, 10 mol%) and $(NH_4)_2CO_3$ (1.0 mg, 0.010 mmol, 5 mol%) were sequentially added into the reaction mixture under argon atmosphere. Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the resulting mixture was stirred at 35 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the desired products **3**, **25**, **32**, **36**, **40** and **59**.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

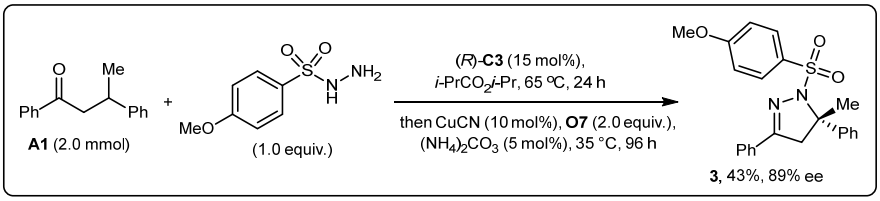
General procedure D: The large-scale reaction (Fig. 3c)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B3** (817.0 mg, 2.0 mmol, 1.0 equiv.), CuCN (17.9 mg, 0.20 mmol, 10 mol%), (*R*)-**C3** (177.8 mg, 0.30 mmol, 15 mol%), $(NH_4)_2CO_3$ (9.6 mg, 0.10 mmol, 5 mol%) and *i*-PrCO$_2$*i*-Pr (40 mL). Then **O7** (945.2 mg, 4.0 mmol, 2.0 equiv.) was slowly added into the mixture via syringe, and the resulting mixture was stirred at 35 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (50 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the desired product **3** as a white solid (576.7 mg, 71% yield, 90% ee).

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

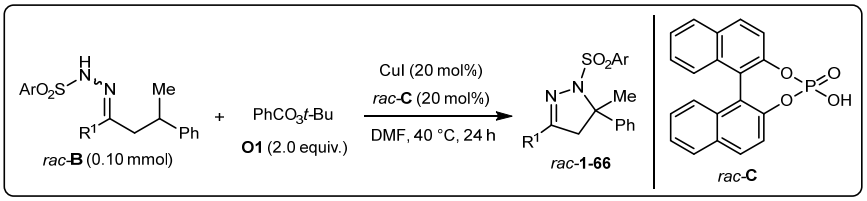
General procedure E: Large-scale reaction using the one-pot protocol (Fig. 3d)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **A1** (449.0 mg, 2.0 mmol, 1.0 equiv.), 4-methoxybenzenesulfonohydrazide (404.5 mg, 2.0 mmol, 1.0 equiv.), (*R*)-**C3** (177.8 mg, 0.30 mmol, 15 mol%) and *i*-PrCO2*i*-Pr (40 mL), and the reaction mixture was stirred at 65 °C for 24 h. After cooling down to room temperature, CuCN (17.9 mg, 0.20 mmol, 10 mol%) and $(NH_4)_2CO_3$ (9.6 mg, 0.10 mmol, 5 mol%) were sequentially added into the reaction mixture under argon atmosphere. Then **O7** (945.2 mg, 4.0 mmol, 2.0 equiv.) was slowly added into the mixture via syringe, and the resulting mixture was stirred at 35 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (50 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1–10:1) to afford the desired product **3** as a white solid (348.6 mg, 43% yield, 89% ee).

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

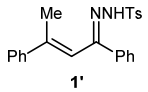
General procedure for the synthesis of racemates 1–66



The racemic products *rac*-**1**–**66** were prepared following the same procedure described above.

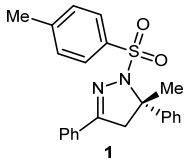
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with *rac*-**B** (0.10 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 20 mol%), *rac*-**C** (7.0 mg, 0.020 mmol, 20 mol%) and anhydrous DMF (2.0 mL). Then *tert*-butyl peroxybenzoate **O1** (38.8 mg, 0.20 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the resulting mixture was stirred at 40 °C for 24 h. Upon completion (monitored by TLC), the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with water (20 mL), saturated $NaHCO_3$ (20 mL × 2) and brine (20 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give the desired racemic products *rac*-**1**–**66**.

Analytical data for products 1' and 1–66



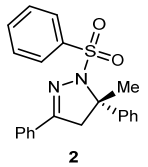
1'

(*E*)-*N*'-(1,3-Diphenylbut-2-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1')
The olefinic side product **1'** is a known compound, and the analytical data were in accordance with those reported in the literature.[23]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (br s, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.66 (m, 2H), 7.56 – 7.53 (m, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.30 (m, 5H), 6.20 (s, 1H), 2.41 (s, 3H), 1.86 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 146.1, 144.0, 139.6, 135.6, 135.5, 129.8, 129.5, 128.8, 128.6, 128.4, 127.9, 126.8, 125.8, 115.8, 21.5, 18.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}N_2O_2S$ $[M + H]^+$ 391.1475, found 391.1475.



1

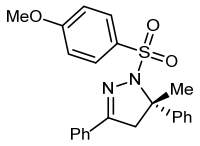
(*S*)-5-Methyl-3,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (1)
According to the **general procedure A**, substrate **B1** (78.5 mg, 0.20 mmol) was employed to yield the product **1** as a white solid (42.2 mg, 54% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 18.90 min, t_R (minor) = 26.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.38 (m, 3H), 7.34 – 7.31 (m, 2H), 7.25 – 7.19 (m, 3H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.49 (d, *J* = 17.2 Hz, 1H), 3.36 (d, *J* = 17.2 Hz, 1H), 2.36 (s, 3H), 2.02 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 143.4, 143.1, 136.9, 131.1, 130.1, 129.0, 128.6, 128.3, 127.6, 127.6, 126.5, 125.8, 71.8, 52.9, 25.3, 21.5.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}N_2O_2S$ $[M + H]^+$ 391.1475, found 391.1473.



2

(*S*)-5-Methyl-3,5-diphenyl-1-(phenylsulfonyl)-4,5-dihydro-1*H*-pyrazole (2)
According to the **general procedure A**, substrate **B2** (75.7 mg, 0.20 mmol) was employed to yield the product **2** as a white solid (44.3 mg, 59% yield, 92% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 9.77 min, t_R (major) = 17.11 min.

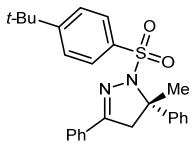
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.68 – 7.64 (m, 2H), 7.47 – 7.42 (m, 1H), 7.42 – 7.38 (m, 3H), 7.34 – 7.27 (m, 4H), 7.23 – 7.16 (m, 3H), 3.51 (d, *J* = 17.3 Hz, 1H), 3.38 (d, *J* = 17.3 Hz, 1H), 2.04 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 143.1, 139.8, 132.2, 131.0, 130.2, 128.6, 128.3, 128.2, 127.6, 127.4, 126.5, 125.8, 71.8, 52.8, 25.5.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{21}N_2O_2S$ $[M + H]^+$ 377.1318, found 377.1318.



3

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (3)

According to the **general procedure A**, substrate **B3** (81.7 mg, 0.20 mmol) was employed to yield the product **3** as a white solid (69.0 mg, 85% yield, 92% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 16.84 min, t_R (minor) = 25.44 min.
According to the **general procedure C**, substrate **A1** (44.9 mg, 0.20 mmol) was employed to yield the product **3** as a white solid (42.1 mg, 52% yield, 89% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 18.91 min, t_R (minor) = 29.20 min.
According to the **general procedure D**, substrate **B3** (817.0 mg, 0.20 mmol) was employed to yield the product **3** as a white solid (576.7 mg, 71% yield, 90% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 17.15 min, t_R (minor) = 25.88 min.
According to the **general procedure E**, substrate **A1** (449.0 mg, 0.20 mmol) was employed to yield the product **3** as a white solid (348.6 mg, 43% yield, 89% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 16.86 min, t_R (minor) = 25.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.49 (d, *J* = 17.2 Hz, 1H), 3.37 (d, *J* = 17.2 Hz, 1H), 2.03 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 152.5, 143.3, 131.5, 131.0, 130.0, 129.6, 128.5, 128.2, 127.5, 126.4, 125.7, 113.5, 71.7, 55.4, 52.7, 25.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}N_2O_3S$ $[M + H]^+$ 407.1424, found 407.1422.



4

(*S*)-1-((4-(*tert*-Butyl)phenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4)

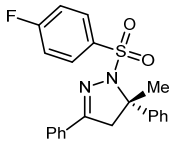
According to the **general procedure A**, substrate **B4** (86.9 mg, 0.20 mmol) was employed to yield the product **4** as a white solid (44.0 mg, 51% yield, 86% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 9.20 min, t_R (major) = 14.80 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.33 – 7.26 (m, 4H), 7.23 – 7.13 (m, 3H), 3.51 (d, *J* = 17.2 Hz, 1H), 3.39 (d, *J* = 17.2 Hz, 1H), 2.05 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 152.5, 143.1, 136.8, 131.2, 130.1, 128.6, 128.2, 127.6, 127.2, 126.6, 125.8, 125.3, 71.7, 52.8, 35.0, 31.1, 25.5.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}N_2O_2S$ $[M + H]^+$ 433.1944, found 433.1943.



5

(*S*)-1-((4-Fluorophenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (5)

According to the **general procedure A**, substrate **B5** (79.3 mg, 0.20 mmol) was employed to yield the product **5** as a slightly yellow solid (50.4 mg, 64% yield, 95% ee).

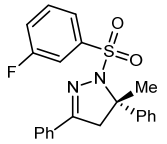
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 10.80 min, t_R (major) = 20.56 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.63 – 7.59 (m, 2H), 7.43 – 7.40 (m, 3H), 7.28 – 7.25 (m, 2H), 7.24 – 7.17 (m, 3H), 7.00 – 6.94 (m, 2H), 3.55 (d, *J* = 17.3 Hz, 1H), 3.42 (d, *J* = 17.3 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (d, *J* = 254.3 Hz), 153.1, 142.7, 135.7 (d, *J* = 3.2 Hz), 130.9, 130.3, 130.2 (d, *J* = 9.3 Hz), 128.7, 128.3, 127.8, 126.6, 125.9, 115.5 (d, *J* = 22.5 Hz), 71.7, 52.8, 25.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ −105.8.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}FN_2O_2S$ $[M + H]^+$ 395.1224, found 395.1224.



6

(*S*)-1-((3-Fluorophenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (6)

According to the **general procedure A**, substrate **B6** (79.3 mg, 0.20 mmol) was employed to yield the product **6** as a white solid (57.6 mg, 73% yield, 92% ee).

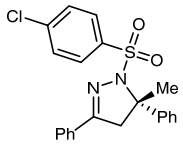
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 15.92 min, t_R (minor) = 20.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.46 – 7.40 (m, 4H), 7.31 – 7.27 (m, 1H), 7.26 – 7.18 (m, 5H), 7.17 – 7.10 (m, 2H), 3.57 (d, *J* = 17.4 Hz, 1H), 3.43 (d, *J* = 17.4 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 250.3 Hz), 153.3, 142.5, 141.5 (d, *J* = 7.0 Hz), 130.8, 130.4, 130.0 (d, *J* = 7.6 Hz), 128.7, 128.2, 128.0, 126.6, 125.8, 123.2 (d, *J* = 3.3 Hz), 119.4 (d, *J* = 21.3 Hz), 114.8 (d, *J* = 24.8 Hz), 71.7, 52.7, 25.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ −110.7.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}FN_2O_2S$ $[M + H]^+$ 395.1224, found 395.1225.



7

(*S*)-1-((4-Chlorophenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (7)

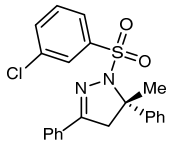
According to the **general procedure A**, substrate **B7** (82.6 mg, 0.20 mmol) was employed to yield the product **7** as a white solid (38.5 mg, 47% yield, 92% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 11.51 min, t_R (major) = 19.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.55 – 7.50 (m, 2H), 7.43 – 7.38 (m, 3H), 7.28 – 7.22 (m, 5H), 7.21 – 7.16 (m, 2H), 3.54 (d, *J* = 17.3 Hz, 1H), 3.41 (d, *J* = 17.3 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 142.7, 138.7, 138.1, 130.8, 130.4, 128.8, 128.7, 128.5, 128.3, 127.8, 126.6, 125.8, 71.7, 52.7, 25.7.

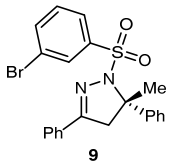
HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}ClN_2O_2S$ $[M + H]^+$ 411.0929, found 411.0929.



8

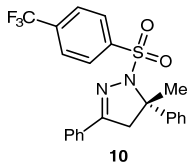
(*S*)-1-((3-Chlorophenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (8)

According to the **general procedure A**, substrate **B8** (82.6 mg, 0.20 mmol) was employed to yield the product **8** as a yellow solid (50.2 mg, 61% yield, 92% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 12.31 min, t_R (major) = 17.28 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.40 – 7.36 (m, 2H), 7.26 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 3.58 (d, *J* = 17.4 Hz, 1H), 3.44 (d, *J* = 17.4 Hz, 1H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 142.1, 141.1, 134.3, 132.3, 130.8, 130.4, 129.5, 128.7, 128.2, 128.1, 127.4, 126.6, 125.9, 125.5, 71.6, 52.7, 26.0.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}ClN_2O_2S$ $[M + H]^+$ 411.0929, found 411.0926.



9

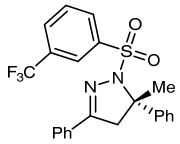
(*S*)-1-((3-Bromophenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (9)
According to the **general procedure A**, substrate **B9** (91.5 mg, 0.20 mmol) was employed to yield the product **9** as a white solid (60.2 mg, 66% yield, 93% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 11.47 min, t_R (major) = 16.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.63 – 7.60 (m, 1H), 7.56 – 7.51 (m, 2H), 7.45 – 7.40 (m, 3H), 7.28 – 7.23 (m, 1H), 7.22 – 7.14 (m, 5H), 3.57 (d, *J* = 17.4 Hz, 1H), 3.44 (d, *J* = 17.4 Hz, 1H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 142.0, 141.2, 135.1, 130.8, 130.4, 130.1, 129.8, 128.7, 128.3, 128.1, 126.6, 125.9, 125.8, 122.2, 71.6, 52.7, 26.0.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}BrN_2O_2S$ $[M + H]^+$ 455.0423, found 455.0424.



10

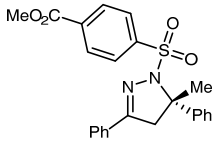
(*S*)-5-Methyl-3,5-diphenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-4,5-dihydro-1 *H*-pyrazole (10)
According to the **general procedure A**, substrate **B10** (89.3 mg, 0.20 mmol) was employed to yield the product **10** as a yellow solid (49.7 mg, 56% yield, 96% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 14.05 min, t_R (major) = 19.25 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 3H), 7.24 – 7.18 (m, 3H), 7.16 – 7.10 (m, 2H), 3.57 (d, *J* = 17.4 Hz, 1H), 3.45 (d, *J* = 17.4 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 142.9, 142.3, 133.7 (q, *J* = 32.9 Hz), 130.7, 130.5, 128.7, 128.2, 128.0, 127.7, 126.6, 125.8, 125.4 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 273.0 Hz), 71.7, 52.7, 25.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}F_3N_2O_2S$ $[M + H]^+$ 445.1192, found 445.1189.



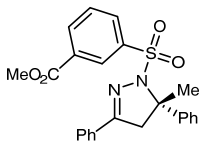
11

(*S*)-5-Methyl-3,5-diphenyl-1-((3-(trifluoromethyl)phenyl)sulfonyl)-4,5-dihydro-1*H*-pyrazole (11)
According to the **general procedure A**, substrate **B11** (89.3 mg, 0.20 mmol) was employed to yield the product **11** as a white solid (50.6 mg, 57% yield, 95% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 10.17 min, t_R (major) = 13.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.74 – 7.71 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.23 – 7.17 (m, 3H), 7.16 – 7.10 (m, 2H), 3.57 (d, *J* = 17.4 Hz, 1H), 3.45 (d, *J* = 17.4 Hz, 1H), 2.12 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 142.0, 140.5, 130.9 (q, *J* = 33.1 Hz), 130.7, 130.5, 129.1, 128.8 (q, *J* = 3.5 Hz), 128.7, 128.2, 128.1, 126.6, 125.8, 124.4 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 273.1 Hz), 71.7, 52.7, 26.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}F_3N_2O_2S$ $[M + H]^+$ 445.1192, found 445.1195.



12

Methyl (*S*)-4-((5-Methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)sulfonyl)benzoate (12)
According to the **general procedure A**, substrate **B12** (87.3 mg, 0.20 mmol) was employed to yield the product **12** as a white solid (49.5 mg, 71% yield, 94% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 19.58 min, t_R (minor) = 33.80 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.72 – 7.70 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.25 – 7.22 (m, 3H), 7.18 – 7.13 (m, 2H), 3.92 (s, 3H), 3.55 (d, *J* = 17.4 Hz, 1H), 3.42 (d, *J* = 17.4 Hz, 1H), 2.08 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 153.4, 143.4, 142.6, 133.1, 130.7, 130.4, 129.5, 128.7, 128.3, 127.9, 127.4, 126.6, 125.8, 71.7, 52.7, 52.5, 25.8.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + H]^+$ 435.1373, found 435.1373.



13

Methyl (*S*)-3-((5-Methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)sulfonyl)benzoate (13)

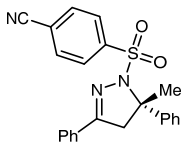
According to the **general procedure A**, substrate **B13** (87.3 mg, 0.20 mmol) was employed to yield the product **13** as a yellow solid (68.7 mg, 79% yield, 92% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 17.42 min, t_R (major) = 34.82 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.44 – 7.37 (m, 4H), 7.25 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 3.93 (s, 3H), 3.55 (d, *J* = 17.4 Hz, 1H), 3.43 (d, *J* = 17.4 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 153.4, 142.3, 140.0, 133.0, 131.3, 130.8, 130.5, 130.4, 128.7, 128.5, 128.5, 128.2, 127.8, 126.6, 125.8, 71.7, 52.6, 52.3, 25.8.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + H]^+$ 435.1373, found 435.1374.



14

(*S*)-4-((5-Methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)sulfonyl)benzonitrile (14)

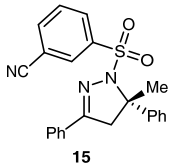
According to the **general procedure A**, substrate **B14** (80.7 mg, 0.20 mmol) was employed to yield the product **14** as a white solid (57.7 mg, 72% yield, 95% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 13.86 min, t_R (major) = 20.20 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.26 – 7.21 (m, 1H), 7.20 – 7.06 (m, 4H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.46 (d, *J* = 17.5 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 143.4, 142.2, 132.0, 130.6, 130.5, 128.8, 128.3, 128.1, 127.8, 126.6, 125.9, 117.4, 115.6, 71.7, 52.7, 26.0.

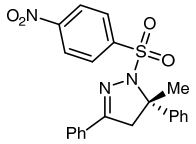
HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}N_3O_2S$ $[M + H]^+$ 402.1271, found 402.1271.



15

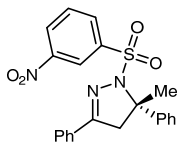
(*S*)-3-((5-Methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)sulfonyl)benzonitrile (15)

According to the **general procedure A**, substrate **B15** (80.7 mg, 0.20 mmol) was employed to yield the product **15** as a white solid (57.8 mg, 72% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 19.45 min, t_R (minor) = 28.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.35 – 7.26 (m, 1H), 7.18 – 7.09 (m, 4H), 3.62 (d, *J* = 17.5 Hz, 1H), 3.48 (d, *J* = 17.5 Hz, 1H), 2.16 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 141.4, 140.7, 135.1, 131.2, 130.7, 130.6, 130.5, 129.2, 128.8, 128.5, 128.2, 126.6, 125.9, 117.2, 112.8, 71.5, 52.5, 26.3.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}N_3O_2S$ $[M + H]^+$ 402.1271, found 402.1270.



16

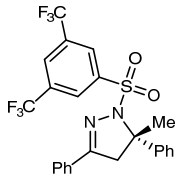
(*S*)-5-Methyl-1-((4-nitrophenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (16)
According to the **general procedure A**, substrate **B16** (84.7 mg, 0.20 mmol) was employed to yield the product **16** as a yellow solid (29.4 mg, 35% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 22.01 min, t_R (minor) = 64.51 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.74 – 7.68 (m, 4H), 7.46 – 7.40 (m, 3H), 7.25 – 7.18 (m, 3H), 7.17 – 7.11 (m, 2H), 3.60 (d, *J* = 17.5 Hz, 1H), 3.47 (d, *J* = 17.5 Hz, 1H), 2.13 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 149.5, 144.9, 142.2, 130.7, 130.5, 128.8, 128.5, 128.3, 128.2, 126.7, 125.9, 123.4, 71.7, 52.7, 26.1.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}N_3O_4S$ $[M + H]^+$ 422.1169, found 422.1159.



17

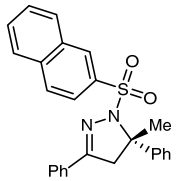
(*S*)-5-Methyl-1-((3-nitrophenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (17)
According to the **general procedure A**, substrate **B17** (84.7 mg, 0.20 mmol) was employed to yield the product **17** as a white solid (40.5 mg, 48% yield, 94% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 29.19 min, t_R (minor) = 36.94 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.16 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.51 – 7.43 (m, 4H), 7.16 – 7.11 (m, 3H), 7.09 – 7.03 (m, 2H), 3.61 (d, *J* = 17.5 Hz, 1H), 3.49 (d, *J* = 17.5 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 147.6, 141.4, 141.0, 132.6, 130.7, 130.4, 129.5, 128.8, 128.2, 128.1, 126.7, 126.2, 125.8, 122.5, 71.6, 52.4, 26.2.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}N_3O_4S$ $[M + H]^+$ 422.1169, found 422.1161.



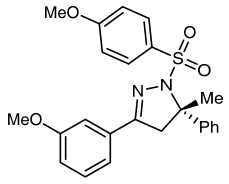
18

(*S*)-1-((3,5-Bis(trifluoromethyl)phenyl)sulfonyl)-5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (18)
According to the **general procedure A**, substrate **B18** (102.9 mg, 0.20 mmol) was employed to yield the product **18** as a yellow solid (44.1 mg, 43% yield, 86% ee).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 8.23 min, t_R (major) = 11.12 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.89 (s, 1H), 7.74 – 7.71 (m, 2H), 7.47 – 7.41 (m, 3H), 7.21 – 7.17 (m, 1H), 7.14 – 7.04 (m, 4H), 3.61 (d, *J* = 17.5 Hz, 1H), 3.52 (d, *J* = 17.5 Hz, 1H), 2.17 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 141.7, 141.2, 132.0 (q, *J* = 34.4 Hz), 130.8, 130.4, 128.9, 128.7, 128.2, 127.5 (q, *J* = 3.6 Hz), 126.6, 125.8, 125.7 (q, *J* = 3.5 Hz), 122.4 (q, *J* = 273.3 Hz), 71.8, 52.5, 26.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{19}F_6N_2O_2S$ $[M + H]^+$ 513.1066, found 513.1065.



19

(*S*)-5-Methyl-1-(naphthalen-2-ylsulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (19)
According to the **general procedure A**, substrate **B19** (85.7 mg, 0.20 mmol) was employed to yield the product **19** as a white solid (52.0 mg, 61% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 16.11 min, t_R (minor) = 20.70 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.82 – 7.79 (m, 3H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.59 – 7.49 (m, 2H), 7.40 – 7.37 (m, 3H), 7.28 – 7.24 (m, 2H), 7.13 – 7.04 (m, 3H), 3.50 (d, *J* = 17.3 Hz, 1H), 3.38 (d, *J* = 17.3 Hz, 1H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 142.6, 136.7, 134.5, 131.8, 131.0, 130.2, 129.4, 128.7, 128.6, 128.5, 128.3, 128.1, 127.8, 127.6, 126.9, 126.5, 125.8, 123.0, 71.7, 52.8, 25.7.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{23}N_2O_2S$ $[M + H]^+$ 427.1475, found 427.1473.



20

(*S*)-3-(3-Methoxyphenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (20)

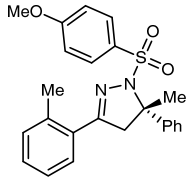
According to the **general procedure A**, substrate **B20** (87.7 mg, 0.20 mmol) was employed to yield the product **20** as a white solid (69.9 mg, 80% yield, 94% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 23.91 min, t_R (minor) = 35.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.24 – 7.20 (m, 4H), 6.95 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.49 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 17.2 Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 159.7, 152.4, 143.3, 132.5, 131.6, 129.7, 129.6, 128.3, 127.6, 125.8, 119.1, 116.0, 113.5, 111.5, 71.8, 55.5, 55.4, 52.9, 25.3.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_4S$ $[M + H]^+$ 437.1530, found 437.1529.



21

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(*o*-tolyl)-4,5-dihydro-1*H*-pyrazole (21)

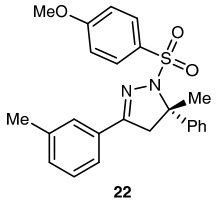
According to the **general procedure A**, substrate **B21** (84.5 mg, 0.20 mmol) was employed to yield the product **21** as a white solid (48.6 mg, 58% yield, 88% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 14.30 min, t_R (major) = 18.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.32 – 7.23 (m, 6H), 7.22 – 7.17 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.55 (d, *J* = 17.0 Hz, 1H), 3.42 (d, *J* = 17.0 Hz, 1H), 2.65 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 153.3, 143.6, 138.1, 131.8, 131.4, 130.1, 129.9, 129.3, 128.6, 128.3, 127.6, 125.8, 125.8, 113.4, 70.9, 55.5, 55.2, 25.0, 23.6.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_3S$ $[M + H]^+$ 421.1580, found 421.1580.

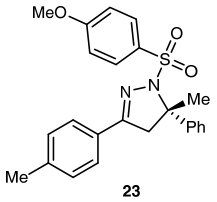


22

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (22)

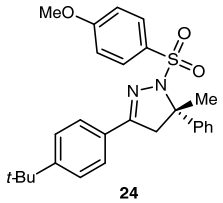
According to the **general procedure A**, substrate **B22** (84.5 mg, 0.20 mmol) was

employed to yield the product **22** as a white solid (63.7 mg, 76% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 21.56 min, t_R (minor) = 31.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.54 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.23 – 7.19 (m, 4H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.50 (d, *J* = 17.2 Hz, 1H), 3.37 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.03 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 152.7, 143.4, 138.3, 131.7, 131.1, 130.9, 129.7, 128.5, 128.3, 127.6, 127.1, 125.8, 123.7, 113.5, 71.6, 55.5, 53.0, 25.3, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_3S$ $[M + H]^+$ 421.1580, found 421.1579.



23

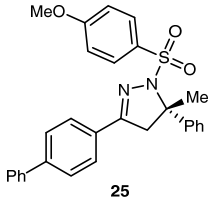
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole (23)
According to the **general procedure A**, substrate **B23** (84.5 mg, 0.20 mmol) was employed to yield the product **23** as a white solid (57.8 mg, 69% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 22.26 min, t_R (minor) = 32.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 4H), 7.34 – 7.29 (m, 2H), 7.23 – 7.19 (m, 5H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.48 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.02 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 152.6, 143.4, 140.4, 131.7, 129.7, 129.3, 128.4, 128.2, 127.5, 126.5, 125.8, 113.5, 71.6, 55.5, 52.9, 25.3, 21.4.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_3S$ $[M + H]^+$ 421.1580, found 421.1582.



24

(*S*)-3-(4-(*tert*-Butyl)phenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (24)
According to the **general procedure A**, substrate **B24** (92.9 mg, 0.20 mmol) was employed to yield the product **24** as a white solid (47.9 mg, 52% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 17.74 min, t_R (minor) = 23.78 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 3H), 6.77 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.49 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 17.2 Hz, 1H), 2.01 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 153.6, 152.5, 143.3, 131.6, 129.7, 128.3, 128.2, 127.5, 126.3, 125.8, 125.5, 113.4, 71.6, 55.5, 52.9, 34.8, 31.1, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}N_2O_3S$ $[M + H]^+$ 463.2050, found 463.2051.



25

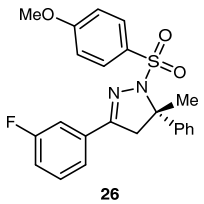
(*S*)-3-([1,1'-Biphenyl]-4-yl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (25)

According to the **general procedure A**, substrate **B25** (96.9 mg, 0.20 mmol) was employed to yield the product **25** as a slightly yellow solid (68.7 mg, 71% yield, 94% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 34.54 min, t_R (minor) = 47.57 min.

According to the **general procedure C**, substrate 1-([1,1'-biphenyl]-4-yl)-3-phenyl butan-1-one (60.1 mg, 0.20 mmol) was employed to yield the product **25** as a slightly yellow solid (52.0 mg, 54% yield, 92% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 34.33 min, t_R (minor) = 47.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.59 (m, 6H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.20 (m, 3H), 6.80 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 3.53 (d, *J* = 17.2 Hz, 1H), 3.40 (d, *J* = 17.2 Hz, 1H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 152.2, 143.3, 142.8, 140.1, 131.6, 130.0, 129.7, 128.9, 128.3, 127.8, 127.6, 127.2, 127.0, 125.8, 113.5, 71.8, 55.5, 52.8, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{27}N_2O_3S$ $[M + H]^+$ 483.1737, found 483.1734.



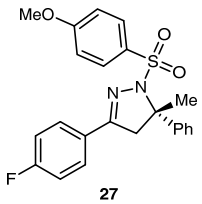
26

(*S*)-3-(3-Fluorophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (26)

According to the **general procedure A**, substrate **B26** (85.3 mg, 0.20 mmol) was employed to yield the product **26** as a white solid (70.2 mg, 83% yield, 92% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 10.03 min, t_R (major) = 18.11 min.

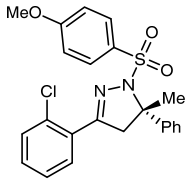
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.30 (m, 5H), 7.26 – 7.20 (m, 3H), 7.09 (t, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 3H), 3.47 (d, *J* = 17.2 Hz, 1H), 3.34 (d, *J* = 17.2 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.5 Hz), 162.7, 151.3 (d, *J* = 2.9 Hz), 143.2, 133.3 (d, *J* = 8.0 Hz), 131.4, 130.2 (d, *J* = 8.2 Hz), 129.8, 128.3, 127.7, 125.7, 122.2 (d, *J* = 2.8 Hz), 117.0 (d, *J* = 21.6 Hz), 113.6, 113.2 (d, *J* = 22.9 Hz), 72.1, 55.5, 52.7, 25.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ −112.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}FN_2O_3S$ $[M + H]^+$ 425.1330, found 425.1330.



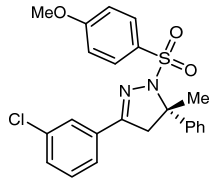
27

(*S*)-3-(4-Fluorophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (27)
According to the **general procedure A**, substrate **B27** (85.3 mg, 0.20 mmol) was employed to yield the product **27** as a white solid (69.5 mg, 82% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 17.29 min, t_R (minor) = 25.12 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 7.07 (t, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.46 (d, *J* = 17.2 Hz, 1H), 3.34 (d, *J* = 17.2 Hz, 1H), 2.02 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, *J* = 251.0 Hz), 162.7, 151.5, 143.3, 131.5, 129.7, 128.4 (d, *J* = 8.4 Hz), 128.3, 127.6, 127.4 (d, *J* = 3.1 Hz), 125.7, 115.7 (d, *J* = 22.0 Hz), 113.5, 71.9, 55.5, 52.9, 25.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ −109.7.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}FN_2O_3S$ $[M + H]^+$ 425.1330, found 425.1328.



28

(*S*)-3-(2-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (28)
According to the **general procedure A**, substrate **B28** (88.6 mg, 0.20 mmol) was employed to yield the product **28** as a white solid (45.7 mg, 52% yield, 81% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 21.98 min, t_R (minor) = 30.75 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.63 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.34 – 7.29 (m, 2H), 7.28 – 7.24 (m, 3H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.68 (d, *J* = 17.6 Hz, 1H), 3.55 (d, *J* = 17.6 Hz, 1H), 2.03 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 152.3, 143.2, 132.8, 131.5, 130.7, 130.7, 130.5, 130.5, 129.9, 128.3, 127.6, 126.9, 125.8, 113.5, 72.5, 55.6, 55.5, 24.8.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}ClN_2O_3S$ $[M + H]^+$ 441.1034, found 441.1035.



29

(*S*)-3-(3-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (29)

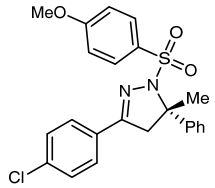
According to the **general procedure A**, substrate **B29** (88.6 mg, 0.20 mmol) was employed to yield the product **29** as a white solid (64.3 mg, 73% yield, 90% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 19.70 min, t_R (minor) = 27.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.38 – 7.29 (m, 4H), 7.26 – 7.21 (m, 3H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.47 (d, *J* = 17.3 Hz, 1H), 3.34 (d, *J* = 17.3 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 151.1, 143.2, 134.7, 133.0, 131.5, 130.0, 129.9, 129.7, 128.3, 127.7, 126.4, 125.7, 124.6, 113.6, 72.1, 55.5, 52.7, 25.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}ClN_2O_3S$ $[M + H]^+$ 441.1034, found 441.1034.



30

(*S*)-3-(4-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (30)

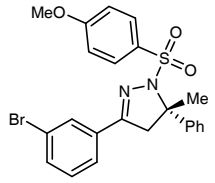
According to the **general procedure A**, substrate **B30** (88.6 mg, 0.20 mmol) was employed to yield the product **30** as a white solid (62.5 mg, 71% yield, 91% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 18.03 min, t_R (minor) = 24.59 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.46 (d, *J* = 17.2 Hz, 1H), 3.34 (d, *J* = 17.2 Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.3, 143.2, 136.0, 131.5, 129.7, 129.7, 128.9, 128.3, 127.7, 127.7, 125.7, 113.6, 72.0, 55.5, 52.7, 25.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}ClN_2O_3S$ $[M + H]^+$ 441.1034, found 441.1035.



31

(*S*)-3-(3-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (31)

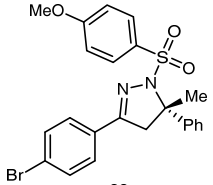
According to the **general procedure A**, substrate **B31** (97.5 mg, 0.20 mmol) was employed to yield the product **31** as a slightly yellow solid (75.6 mg, 78% yield, 90% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 20.70 min, t_R (minor) = 28.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 3H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.26 – 7.21 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.46 (d, *J* = 17.3 Hz, 1H), 3.34 (d, *J* = 17.3 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 150.9, 143.2, 133.2, 132.9, 131.5, 130.1, 129.7, 129.3, 128.3, 127.7, 125.7, 125.0, 122.8, 113.6, 72.1, 55.5, 52.7, 25.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}BrN_2O_3S$ $[M + H]^+$ 485.0529, found 485.0527.



32

(*S*)-3-(4-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (32)

According to the **general procedure A**, substrate **B32** (97.5 mg, 0.20 mmol) was employed to yield the product **32** as a white solid (71.0 mg, 73% yield, 93% ee).

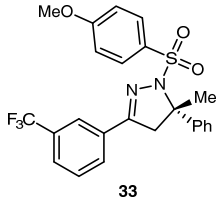
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 23.46 min, t_R (minor) = 31.95 min.

According to the **general procedure C**, substrate 1-(4-bromophenyl)-3-phenyl butan-1-one **A2** (60.6 mg, 0.20 mmol) was employed to yield the product **32** as a white solid (36.0 mg, 37% yield, 92% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 23.63 min, t_R (minor) = 32.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.56 – 7.49 (m, 4H), 7.32 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.45 (d, *J* = 17.2 Hz, 1H), 3.33 (d, *J* = 17.2 Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.4, 143.2, 131.8, 131.4, 130.1, 129.7, 128.3, 127.9, 127.7, 125.7, 124.3, 113.6, 72.1, 55.5, 52.6, 25.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}BrN_2O_3S$ $[M + H]^+$ 485.0529, found 485.0530.

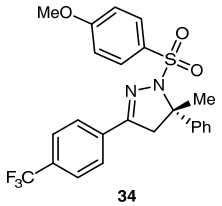


33

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-pyrazole (33)

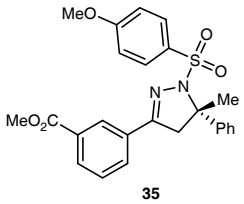
According to the **general procedure A**, substrate **B33** (95.3 mg, 0.20 mmol) was employed to yield the product **33** as a yellow solid (59.6 mg, 63% yield, 90% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 25.74 min, t_R (minor) = 37.10 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.88 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.27 – 7.22 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.52 (d, *J* = 17.3 Hz, 1H), 3.40 (d, *J* = 17.3 Hz, 1H), 2.06 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 150.9, 143.2, 132.1, 131.4, 131.2 (q, *J* = 32.7 Hz), 129.8, 129.5, 129.2, 128.4, 127.8, 126.5 (q, *J* = 3.6 Hz), 125.7, 123.7 (q, *J* = 272.5 Hz), 123.2 (q, *J* = 3.7 Hz), 113.6, 72.3, 55.5, 52.7, 25.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}F_3N_2O_3S$ $[M + H]^+$ 475.1298, found 475.1299.



34

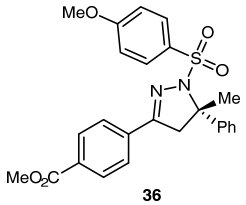
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-pyrazole (34)
According to the **general procedure A**, substrate **B34** (95.3 mg, 0.20 mmol) was employed to yield the product **34** as a white solid (59.5 mg, 63% yield, 90% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 15.12 min, t_R (minor) = 18.52 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H), 3.51 (d, *J* = 17.3 Hz, 1H), 3.39 (d, *J* = 17.3 Hz, 1H), 2.05 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 150.9, 143.1, 134.5, 131.5 (q, *J* = 32.9 Hz), 131.4, 129.7, 128.4, 127.8, 126.7, 125.7, 125.6 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.1 Hz), 113.6, 72.3, 55.5, 52.6, 25.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}F_3N_2O_3S$ $[M + H]^+$ 475.1298, found 475.1300.



35

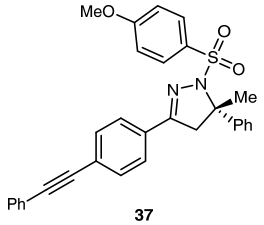
Methyl (*S*)-3-(1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)benzoate (35)
According to the **general procedure A**, substrate **B35** (93.3 mg, 0.20 mmol) was employed to yield the product **35** as a white solid (70.5 mg, 76% yield, 94% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 13.45 min, t_R (major) = 21.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.93 (s, 3H), 3.82 (s, 3H), 3.55 (d, *J* = 17.3 Hz, 1H), 3.42 (d, *J* = 17.3 Hz, 1H), 2.06 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.7, 151.6, 143.2, 131.6, 131.5, 131.0, 130.6, 130.6, 129.8, 128.8, 128.3, 127.7, 127.6, 125.8, 113.6, 72.1, 55.5, 52.8, 52.3, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_5S$ $[M + H]^+$ 465.1479, found 465.1479.



36

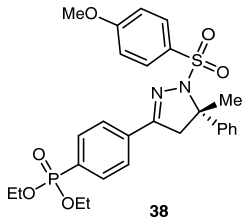
Methyl (*S*)-4-(1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)benzoate (36)
According to the **general procedure A**, substrate **B36** (93.3 mg, 0.20 mmol) was employed to yield the product **36** as a white solid (60.2 mg, 65% yield, 92% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 37.92 min, t_R (minor) = 53.90 min.
According to the **general procedure C**, substrate methyl 4-(3-phenylbutanoyl) benzoate (56.5 mg, 0.20 mmol) was employed to yield the product **36** as a white solid (43.8 mg, 47% yield, 89% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 38.36 min, t_R (minor) = 54.51 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.22 (m, 3H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.93 (s, 3H), 3.82 (s, 3H), 3.51 (d, *J* = 17.3 Hz, 1H), 3.39 (d, *J* = 17.3 Hz, 1H), 2.05 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.8, 151.3, 143.2, 135.3, 131.4, 131.1, 129.8, 129.8, 128.4, 127.7, 126.3, 125.7, 113.6, 72.3, 55.5, 52.7, 52.3, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_5S$ $[M + H]^+$ 465.1479, found 465.1479.



37

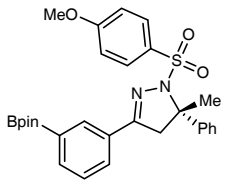
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(4-(phenylethynyl)phenyl)-4,5-dihydro-1*H*-pyrazole (37)
According to the **general procedure A**, substrate **B37** (101.7 mg, 0.20 mmol) was employed to yield the product **37** as a yellow solid (60.0 mg, 59% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 23.01 min, t_R (minor) = 33.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.55 – 7.52 (m, 4H), 7.36 – 7.31 (m, 5H), 7.26 – 7.23 (m, 3H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.47 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 17.2 Hz, 1H), 2.03 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.7, 143.3, 131.7, 131.6, 131.5, 130.8, 129.7, 128.5, 128.4, 128.3, 127.6, 126.4, 125.8, 124.9, 122.8, 113.6, 91.5, 89.0, 72.0, 55.5, 52.7, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{31}H_{27}N_2O_3S$ $[M + H]^+$ 507.1737, found 507.1737.



38

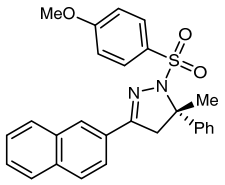
Diethyl (*S*)-(4-(1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenyl)phosphonate (38)
According to the **general procedure A**, substrate **B38** (108.9 mg, 0.20 mmol) was employed to yield the product **38** as a white solid (68.1 mg, 63% yield, 94% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 40/60, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 59.11 min, t_R (minor) = 87.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.79 – 7.75 (m, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H), 6.81 (d, *J* = 8.9 Hz, 2H), 4.23 – 4.01 (m, 4H), 3.82 (s, 3H), 3.50 (d, *J* = 17.3 Hz, 1H), 3.39 (d, *J* = 17.3 Hz, 1H), 2.04 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.2 (d, *J* = 1.1 Hz), 143.1, 134.7 (d, *J* = 3.3 Hz), 131.9 (d, *J* = 10.3 Hz), 131.3, 129.8 (d, *J* = 188.5 Hz), 129.6, 128.3, 127.6, 126.2 (d, *J* = 15.0 Hz), 125.6, 113.5, 72.2, 62.2, 62.2, 55.5, 52.5, 25.2, 16.3, 16.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ 17.7.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{32}N_2O_6PS$ $[M + H]^+$ 543.1713, found 543.1719.



39

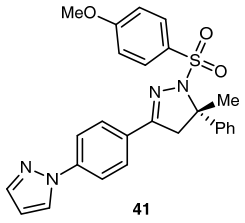
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4,5-dihydro-1*H*-pyrazole (39)
According to the **general procedure A**, substrate **B39** (106.9 mg, 0.20 mmol) was employed to yield the product **39** as a slightly yellow solid (70.5 mg, 66% yield, 80% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 22.08 min, t_R (minor) = 31.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.24 –

7.19 (m, 3H), 6.80 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.56 (d, *J* = 17.3 Hz, 1H), 3.43 (d, *J* = 17.3 Hz, 1H), 2.03 (s, 3H), 1.33 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 152.7, 143.4, 136.5, 132.9, 131.7, 130.5, 129.7, 129.1, 128.2, 128.0, 127.5, 125.8, 113.5, 84.0, 71.7, 55.5, 53.0, 25.3, 24.8, 24.8.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{34}BN_2O_5S$ $[M + H]^+$ 533.2276, found 533.2274.



40

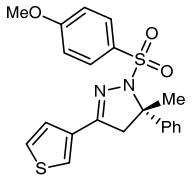
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-3-(naphthalen-2-yl)-5-phenyl-4,5-dihydro-1*H*-pyrazole (40)
According to the **general procedure A**, substrate **B40** (91.7 mg, 0.20 mmol) was employed to yield the product **40** as a white solid (70.5 mg, 77% yield, 94% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 24.16 min, t_R (minor) = 31.09 min.
According to the **general procedure C**, substrate 1-(naphthalen-2-yl)-3-phenylbutan-1-one (54.9 mg, 0.20 mmol) was employed to yield the product **40** as a white solid (41.3 mg, 51% yield, 90% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 23.23 min, t_R (minor) = 29.89 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.88 – 7.80 (m, 3H), 7.82 – 7.78 (m, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.55 – 7.46 (m, 2H), 7.38 – 7.33 (m, 2H), 7.25 – 7.21 (m, 3H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.63 (d, *J* = 17.1 Hz, 1H), 3.51 (d, *J* = 17.1 Hz, 1H), 2.08 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 152.6, 143.4, 134.0, 132.9, 131.6, 129.8, 128.8, 128.4, 128.3, 127.8, 127.6, 127.2, 126.7, 125.9, 123.5, 113.6, 72.0, 55.5, 52.9, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{25}N_2O_3S$ $[M + H]^+$ 457.1580, found 457.1580.



41

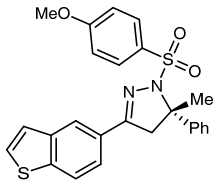
(*S*)-1-(4-(1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenyl)-1*H*-pyrazole (41)
According to the **general procedure A**, substrate **B41** (94.9 mg, 0.20 mmol) was employed to yield the product **41** as a white solid (52.2 mg, 55% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 45.76 min, t_R (minor) = 57.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.78 – 7.71 (m, 5H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.27 – 7.21 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H),

6.49 (br s, 1H), 3.81 (s, 3H), 3.50 (d, *J* = 17.2 Hz, 1H), 3.38 (d, *J* = 17.2 Hz, 1H), 2.04 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.6, 143.3, 141.5, 141.0, 131.5, 129.7, 129.1, 128.3, 127.7, 127.6, 126.6, 125.8, 118.8, 113.6, 108.1, 71.9, 55.5, 52.8, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}N_4O_3S$ $[M + H]^+$ 473.1642, found 473.1644.



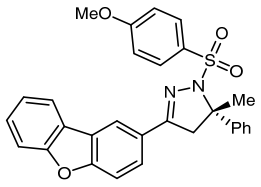
42

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-3-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrazole (42)
According to the **general procedure A**, substrate **B42** (82.9 mg, 0.20 mmol) was employed to yield the product **42** as a slightly red solid (35.5 mg, 43% yield, 78% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 26.48 min, t_R (minor) = 40.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 3H), 7.39 – 7.37 (m, 1H), 7.37 – 7.34 (m, 1H), 7.33 – 7.30 (m, 2H), 7.25 – 7.21 (m, 3H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.46 (d, *J* = 17.1 Hz, 1H), 3.33 (d, *J* = 17.1 Hz, 1H), 2.01 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 149.0, 143.3, 133.8, 131.6, 129.7, 128.3, 127.6, 126.6, 125.8, 125.8, 125.3, 113.5, 71.5, 55.5, 53.5, 25.2.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}N_2O_3S_2$ $[M + H]^+$ 413.0988, found 413.0986.



43

(*S*)-3-(Benzo[*b*]thiophen-5-yl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (43)
According to the **general procedure A**, substrate **B43** (92.9 mg, 0.20 mmol) was employed to yield the product **43** as a white solid (60.3 mg, 65% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 26.48 min, t_R (minor) = 34.77 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.40 – 7.29 (m, 5H), 7.26 – 7.21 (m, 3H), 6.80 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.55 (d, *J* = 17.0 Hz, 1H), 3.43 (d, *J* = 17.0 Hz, 1H), 2.05 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 148.6, 142.9, 140.6, 139.2, 135.0, 131.3, 129.8, 128.3, 127.7, 125.9, 125.8, 125.0, 124.7, 124.1, 122.4, 113.5, 72.5, 55.5, 53.0, 25.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{23}N_2O_3S_2$ $[M + H]^+$ 463.1145, found 463.1146.



44

(*S*)-3-(Dibenzo[*b*,*d*]furan-2-yl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (44)

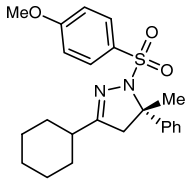
According to the **general procedure A**, substrate **B44** (99.7 mg, 0.20 mmol) was employed to yield the product **44** as a white solid (60.8 mg, 61% yield, 90% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 36.99 min, t_R (minor) = 50.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.5 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.84 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.51 – 7.46 (m, 1H), 7.39 – 7.35 (m, 3H), 7.26 – 7.23 (m, 3H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.62 (d, *J* = 17.1 Hz, 1H), 3.49 (d, *J* = 17.1 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 157.1, 156.6, 152.5, 143.3, 131.7, 129.7, 128.3, 127.7, 127.6, 126.2, 125.8, 124.6, 123.6, 123.1, 120.8, 119.0, 113.6, 111.9, 111.8, 71.8, 55.5, 53.2, 25.4.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{25}N_2O_4S$ $[M + H]^+$ 497.1530, found 497.1535.



45

(*S*)-3-Cyclohexyl-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (45)

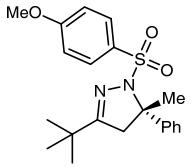
According to the **general procedure A**, substrate **B45** (82.9 mg, 0.20 mmol) was employed to yield the product **45** as a white solid (34.5 mg, 42% yield, 79% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 20.77 min, t_R (minor) = 28.53 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.0 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 3H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 3.04 (d, *J* = 17.4 Hz, 1H), 2.91 (d, *J* = 17.4 Hz, 1H), 2.42 – 2.35 (m, 1H), 1.88 (s, 3H), 1.87 – 1.65 (m, 5H), 1.39 – 1.16 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 161.1, 143.5, 131.7, 129.7, 128.1, 127.3, 125.7, 113.3, 70.6, 55.5, 53.3, 39.2, 30.1, 30.0, 25.8, 25.6, 25.6, 24.8.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{29}N_2O_3S$ $[M + H]^+$ 413.1893, found 413.1891.



46

(*S*)-3-(*tert*-Butyl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (46)

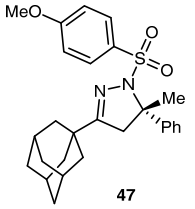
According to the **general procedure A**, substrate **B46** (77.7 mg, 0.20 mmol) was employed to yield the product **46** as a white solid (43.8 mg, 57% yield, 80% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.40 min, t_R (minor) = 20.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.25 – 7.21 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.07 (d, *J* = 17.2 Hz, 1H), 2.94 (d, *J* = 17.2 Hz, 1H), 1.85 (s, 3H), 1.18 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 162.5, 143.7, 131.8, 129.8, 128.1, 127.3, 125.7, 113.3, 71.5, 55.5, 52.2, 34.1, 27.9, 24.5.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}N_2O_3S$ $[M + H]^+$ 387.1737, found 387.1734.



47

(*S*)-3-(Adamantan-1-yl)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (47)

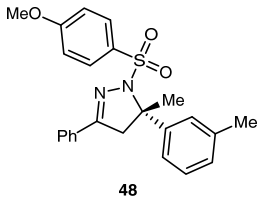
According to the **general procedure A**, substrate **B47** (93.3 mg, 0.20 mmol) was employed to yield the product **47** as a white solid (60.5 mg, 65% yield, 73% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 23.70 min, t_R (minor) = 30.03 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.0 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.20 (m, 3H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.05 (d, *J* = 17.2 Hz, 1H), 2.93 (d, *J* = 17.2 Hz, 1H), 2.07 – 2.01 (m, 3H), 1.85 (s, 3H), 1.81 – 1.61 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 162.4, 143.6, 131.7, 129.7, 128.1, 127.3, 125.7, 113.2, 70.8, 55.5, 51.3, 39.9, 36.5, 36.1, 27.9, 24.6.

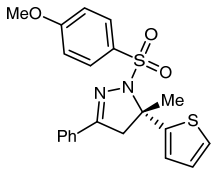
HRMS (ESI) *m/z* calcd. for $C_{27}H_{33}N_2O_3S$ $[M + H]^+$ 465.2206, found 465.2206.



48

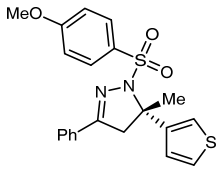
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-3-phenyl-5-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (48)

According to the **general procedure B**, substrate **B48** (84.5 mg, 0.20 mmol) was employed to yield the product **48** as a yellow solid (68.0 mg, 81% yield, 90% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 24.70 min, t_R (minor) = 34.79 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.41 – 7.38 (m, 3H), 7.17 – 7.10 (m, 2H), 7.05 – 7.01 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 3.48 (d, *J* = 17.3 Hz, 1H), 3.35 (d, *J* = 17.3 Hz, 1H), 2.20 (s, 3H), 2.02 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 152.4, 143.1, 137.8, 131.6, 131.1, 130.0, 129.6, 128.6, 128.3, 128.1, 126.6, 126.5, 122.8, 113.4, 71.6, 55.5, 52.9, 25.5, 21.4.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_3S$ $[M + H]^+$ 421.1580, found 421.1578.



49

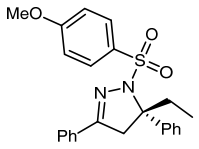
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-3-phenyl-5-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazole (49)
According to the **general procedure B**, substrate **B49** (82.9 mg, 0.20 mmol) was employed to yield the product **49** as a white solid (55.8 mg, 68% yield, 70% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 25.98 min, t_R (minor) = 39.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.61 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.39 (m, 3H), 7.08 (dd, *J* = 5.1, 0.8 Hz, 1H), 6.98 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.83 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.56 (d, *J* = 16.9 Hz, 1H), 3.41 (d, *J* = 16.9 Hz, 1H), 2.17 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 153.2, 146.3, 131.0, 130.9, 130.2, 129.8, 128.6, 126.6, 126.2, 125.5, 125.0, 113.4, 70.1, 55.5, 52.6, 26.6.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}N_2O_3S_2$ $[M + H]^+$ 413.0988, found 413.0983.



50

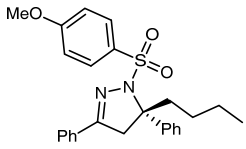
(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-methyl-3-phenyl-5-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrazole (50)
According to the **general procedure B**, substrate **B50** (82.9 mg, 0.20 mmol) was employed to yield the product **50** as a white solid (59.1 mg, 72% yield, 66% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 26.34 min, t_R (minor) = 37.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.18 (d, *J* = 3.0 Hz, 1H), 6.97 (dd, *J* = 4.8, 3.0 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 4.8 Hz, 1H), 3.80 (s, 3H), 3.47 (d, *J* = 17.0 Hz, 1H), 3.36 (d, *J* = 17.0 Hz, 1H), 2.12 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 153.1, 143.4, 131.1, 131.1, 130.2, 129.5, 128.6, 126.5, 125.8, 125.7, 122.2, 113.4, 69.2, 55.5, 51.2, 26.5.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}N_2O_3S_2$ $[M + H]^+$ 413.0988, found 413.0986.



51

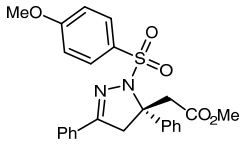
(*S*)-5-Ethyl-1-((4-methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (51)
According to the **general procedure B**, substrate **B51** (84.5 mg, 0.20 mmol) was employed to yield the product **51** as a white solid (59.6 mg, 71% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 19.55 min, t_R (minor) = 44.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.43 – 7.40 (m, 3H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.15 – 7.08 (m, 4H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 3H), 3.54 (d, *J* = 17.6 Hz, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 2.72 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.52 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.08 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 152.2, 141.4, 131.5, 131.0, 130.0, 129.2, 128.6, 128.1, 127.7, 126.5, 126.5, 113.2, 74.9, 55.4, 48.6, 30.2, 9.0.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_3S$ $[M + H]^+$ 421.1580, found 421.1572.



52

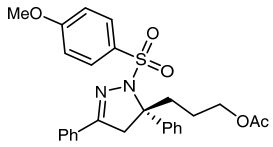
(*S*)-5-(*n*-Butyl)-1-((4-methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (52)
According to the **general procedure B**, substrate **B52** (90.1 mg, 0.20 mmol) was employed to yield the product **52** as a white solid (56.7 mg, 63% yield, 89% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 14.16 min, t_R (minor) = 24.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.43 – 7.40 (m, 3H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.08 (m, 5H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 3.56 (d, *J* = 17.6 Hz, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.57 – 2.46 (m, 1H), 1.53 – 1.24 (m, 4H), 0.95 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 152.2, 141.6, 131.5, 131.1, 130.0, 129.2, 128.6, 128.1, 127.7, 126.6, 126.5, 113.2, 74.5, 55.5, 49.1, 37.5, 26.8, 23.0, 14.1.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}N_2O_3S$ $[M + H]^+$ 449.1893, found 449.1886.



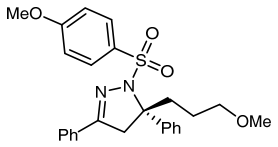
53

Methyl (*R*)-2-(1-((4-Methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetate (53)
According to the **general procedure B**, substrate **B53** (93.3 mg, 0.20 mmol) was employed to yield the product **53** as a white solid (60.2 mg, 65% yield, 96% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 22.24 min, t_R (major) = 33.12 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.44 – 7.42 (m, 3H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.09 – 7.02 (m, 4H), 6.62 (d, *J* = 9.0 Hz, 2H), 4.13 (d, *J* = 16.8 Hz, 1H), 3.95 (d, *J* = 18.0 Hz, 1H), 3.81 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.48 (d, *J* = 16.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 162.4, 154.1, 139.5, 130.8, 130.3, 129.2, 128.7, 128.2, 128.2, 126.7, 126.1, 113.3, 71.5, 55.5, 51.9, 50.5, 43.1.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_5S$ $[M + H]^+$ 465.1479, found 465.1478.



54

(*S*)-3-(1-((4-Methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl) propyl Acetate (54)
According to the **general procedure B**, substrate **B54** (98.9 mg, 0.20 mmol) was employed to yield the product **54** as a white solid (37.6 mg, 38% yield, 81% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 15.98 min, t_R (major) = 24.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.44 – 7.38 (m, 3H), 7.29 (d, *J* = 8.9 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.12 – 7.05 (m, 4H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.19 (t, *J* = 6.4 Hz, 2H), 3.76 (s, 3H), 3.53 (d, *J* = 17.7 Hz, 1H), 3.48 (d, *J* = 17.7 Hz, 1H), 2.74 (td, *J* = 13.4, 4.2 Hz, 1H), 2.54 (td, *J* = 13.4, 4.2 Hz, 1H), 2.06 (s, 3H), 1.92 – 1.80 (m, 1H), 1.79 – 1.67 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 162.4, 152.1, 141.2, 131.3, 130.9, 130.1, 129.2, 128.6, 128.2, 127.9, 126.5, 126.4, 113.3, 73.9, 64.1, 55.5, 49.2, 34.1, 24.1, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{29}N_2O_5S$ $[M + H]^+$ 493.1792, found 493.1797.



55

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-5-(3-methoxypropyl)-3,5-diphenyl-4,5-dihydr o-1*H*-pyrazole (55)

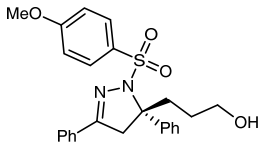
According to the **general procedure B**, substrate **B55** (93.3 mg, 0.20 mmol) was employed to yield the product **55** as a white solid (38.3 mg, 41% yield, 90% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 35.97 min, t_R (minor) = 44.74 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.43 – 7.39 (m, 3H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.07 (m, 5H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 3.60 – 3.45 (m, 4H), 3.37 (s, 3H), 2.78 – 2.55 (m, 2H), 1.85 – 1.76 (m, 1H), 1.74 – 1.62 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 152.2, 141.5, 131.5, 131.0, 130.0, 129.2, 128.6, 128.1, 127.7, 126.5, 126.5, 113.2, 74.3, 72.4, 58.6, 55.4, 49.3, 34.5, 25.0.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}N_2O_4S$ $[M + H]^+$ 465.1843, found 465.1846.



56

(*S*)-3-(1-((4-Methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl) propan-1-ol (56)

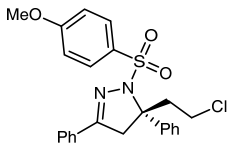
According to the **general procedure B**, substrate **B56** (90.5 mg, 0.20 mmol) was employed to yield the product **56** as a white solid (32.6 mg, 36% yield, 85% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 21.90 min, t_R (minor) = 26.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.43 – 7.39 (m, 3H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.15 – 7.07 (m, 4H), 6.67 (d, *J* = 9.0 Hz, 2H), 3.90 – 3.75 (m, 2H), 3.78 (s, 3H), 3.58 (d, *J* = 17.6 Hz, 1H), 3.48 (d, *J* = 17.6 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.65 – 2.53 (m, 1H), 1.87 – 1.76 (m, 2H), 1.75 – 1.64 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 152.3, 141.5, 131.4, 130.9, 130.1, 129.2, 128.6, 128.2, 127.8, 126.5, 126.4, 113.3, 74.2, 62.5, 55.5, 49.3, 34.0, 27.9.

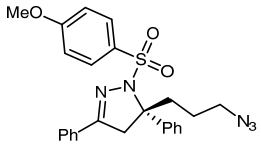
HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_2O_4S$ $[M + H]^+$ 451.1686, found 451.1680.



57

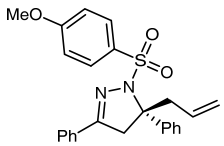
(*R*)-5-(2-Chloroethyl)-1-((4-methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1 *H*-pyrazole (57)

According to the **general procedure B**, substrate **B57** (91.4 mg, 0.20 mmol) was employed to yield the product **57** as a white solid (50.0 mg, 55% yield, 89% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 14.62 min, t_R (minor) = 23.58 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.44 – 7.42 (m, 3H), 7.35 (d, *J* = 8.9 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.18 – 7.07 (m, 4H), 6.69 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.77 – 3.61 (m, 3H), 3.53 (d, *J* = 17.6 Hz, 1H), 3.33 – 3.24 (m, 1H), 3.00 – 2.91 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 152.4, 140.7, 131.0, 130.6, 130.4, 129.3, 128.7, 128.4, 128.2, 126.6, 126.1, 113.4, 73.1, 55.5, 49.2, 40.6, 40.0.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}ClN_2O_3S$ $[M + H]^+$ 455.1191, found 455.1185.



58

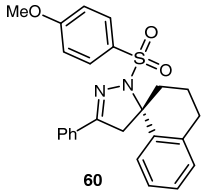
(*S*)-5-(3-Azidopropyl)-1-((4-methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (58)
According to the **general procedure B**, substrate **B58** (95.5 mg, 0.20 mmol) was employed to yield the product **58** as a white solid (59.7 mg, 63% yield, 78% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 20.02 min, t_R (minor) = 27.97 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 2H), 7.45 – 7.40 (m, 3H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.14 – 7.07 (m, 4H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 3.57 – 3.47 (m, 3H), 3.45 – 3.38 (m, 1H), 2.76 (td, *J* = 13.4, 4.2 Hz, 1H), 2.57 (td, *J* = 13.4, 4.2 Hz, 1H), 1.92 – 1.80 (m, 1H), 1.74 – 1.62 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 152.2, 141.2, 131.2, 130.8, 130.2, 129.2, 128.7, 128.2, 127.9, 126.5, 126.3, 113.3, 73.9, 55.5, 51.4, 49.2, 34.9, 24.4.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}N_5O_3S$ $[M + H]^+$ 476.1751, found 476.1745.



59

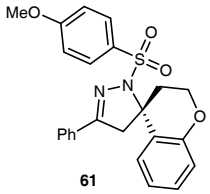
(*S*)-5-Allyl-1-((4-methoxyphenyl)sulfonyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (59)
According to the **general procedure B**, substrate **B59** (86.9 mg, 0.20 mmol) was employed to yield the product **59** as a slightly yellow solid (40.8 mg, 47% yield, 92% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 320 nm), t_R (major) = 17.01 min, t_R (minor) = 34.98 min.
According to the **general procedure C**, substrate 1,3-diphenylhex-5-en-1-one (50.1 mg, 0.20 mmol) was employed to yield the product **59** as a slightly yellow solid (27.8

mg, 32% yield, 90% ee). **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 320 nm), t_R (major) = 17.47 min, t_R (minor) = 36.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.43 – 7.39 (m, 3H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.09 (m, 5H), 6.68 (d, *J* = 8.9 Hz, 2H), 5.94 – 5.83 (m, 1H), 5.31 – 5.24 (m, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 3.79 (s, 3H), 3.65 (d, *J* = 17.6 Hz, 1H), 3.55 (dd, *J* = 14.3, 5.7 Hz, 1H), 3.41 (d, *J* = 17.6 Hz, 1H), 3.20 (dd, *J* = 14.3, 8.1 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 152.6, 141.3, 133.4, 131.4, 131.0, 130.1, 129.2, 128.6, 128.2, 127.9, 126.5, 126.5, 119.8, 113.3, 73.5, 55.5, 48.8, 42.1.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_3S$ $[M + H]^+$ 433.1580, found 433.1582.



60

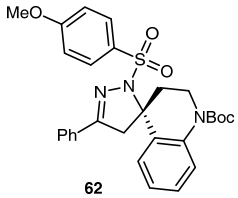
(*S*)-2'-((4-Methoxyphenyl)sulfonyl)-5'-phenyl-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole] (60)
According to the **general procedure B**, substrate **B60** (86.9 mg, 0.20 mmol) was employed to yield the product **60** as a white solid (45.6 mg, 53% yield, 89% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 24.84 min, t_R (minor) = 30.85 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.9 Hz, 2H), 7.68 – 7.64 (m, 2H), 7.39 – 7.35 (m, 3H), 7.17 – 7.12 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.46 (d, *J* = 17.2 Hz, 1H), 3.36 (d, *J* = 17.2 Hz, 1H), 3.05 – 2.93 (m, 1H), 2.85 – 2.76 (m, 2H), 2.10 – 1.97 (m, 2H), 1.84 – 1.71 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 151.2, 139.4, 136.4, 132.3, 131.3, 130.0, 129.9, 128.9, 128.5, 127.2, 126.6, 126.4, 126.4, 113.6, 73.2, 55.5, 52.6, 34.3, 29.2, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_3S$ $[M + H]^+$ 433.1580, found 433.1585.



61

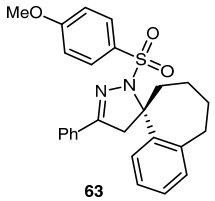
(*R*)-2'-((4-Methoxyphenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[chromane-4,3'-pyrazole] (61)
According to the **general procedure B**, substrate **B61** (87.3 mg, 0.20 mmol) was employed to yield the product **61** as a white solid (53.6 mg, 62% yield, 88% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 24.03 min, t_R (minor) = 29.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.68 – 7.65 (m, 2H), 7.40 – 7.36 (m, 3H), 7.17 – 7.11 (m, 1H), 7.02 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.86 – 6.83 (m, 1H), 6.74 – 6.70 (m, 1H), 4.53 (dt, *J* = 11.5, 4.0 Hz, 1H), 4.13 (td,

J = 11.5, 2.0 Hz, 1H), 3.83 (s, 3H), 3.55 (d, *J* = 17.2 Hz, 1H), 3.39 (d, *J* = 17.2 Hz, 1H), 3.17 – 3.08 (m, 1H), 2.07 – 1.99 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 154.1, 151.4, 131.6, 130.9, 130.2, 130.1, 129.1, 128.6, 127.0, 126.4, 124.7, 120.9, 117.2, 113.7, 68.5, 63.8, 55.5, 52.5, 33.5.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + H]^+$ 435.1373, found 435.1372.



62

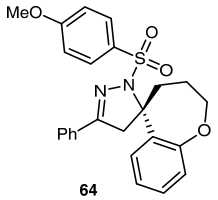
***tert*-Butyl (*S*)-2-((4-Methoxyphenyl)sulfonyl)-5-phenyl-2,2',3',4-tetrahydro-1'*H*-spiro[pyrazole-3,4'-quinoline]-1'-carboxylate (62)**
According to the **general procedure B**, substrate **B62** (107.1 mg, 0.20 mmol) was employed to yield the product **62** as a white solid (59.5 mg, 56% yield, 92% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 29.51 min, t_R (minor) = 39.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 5H), 7.42 – 7.35 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 4.36 (dt, *J* = 13.2, 4.2 Hz, 1H), 3.83 (s, 3H), 3.55 – 3.38 (m, 3H), 3.15 – 3.05 (m, 1H), 2.17 – 2.09 (m, 1H), 1.56 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 153.4, 151.7, 138.1, 131.7, 131.0, 130.9, 130.2, 129.9, 128.6, 127.4, 126.4, 126.2, 124.4, 123.8, 113.6, 81.3, 70.3, 55.5, 52.9, 42.5, 36.0, 28.3.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{31}N_3NaO_5S$ $[M + Na]^+$ 556.1877, found 556.1879.



63

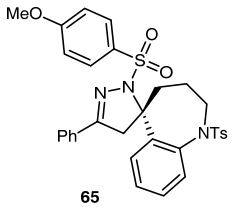
(*S*)-2'-((4-Methoxyphenyl)sulfonyl)-5'-phenyl-2',4',6,7,8,9-hexahydrospiro[benzo[7]annulene-5,3'-pyrazole] (63)
According to the **general procedure B**, substrate **B63** (89.7 mg, 0.20 mmol) was employed to yield the product **63** as a white solid (40.0 mg, 45% yield, 93% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 19.63 min, t_R (minor) = 24.02 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.41 – 7.34 (m, 4H), 7.15 – 7.08 (m, 2H), 7.08 – 7.02 (m, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.73 (d, *J* = 17.2 Hz, 1H), 3.32 (d, *J* = 17.2 Hz, 1H), 3.20 – 3.11 (m, 1H), 3.03 – 2.93 (m, 1H), 2.80 – 2.68 (m, 1H), 2.04 – 1.68 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.8, 143.2, 139.4, 132.4, 131.3, 131.1, 129.9, 129.8, 128.5, 128.2, 127.5, 126.4, 126.4, 113.7, 78.9, 55.5, 48.7, 35.3, 35.3, 26.4, 23.7.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{27}N_2O_3S$ $[M + H]^+$ 447.1737, found 447.1735.



64

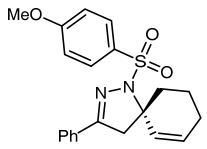
(*S*)-2'-((4-Methoxyphenyl)sulfonyl)-5'-phenyl-2',3,4,4'-tetrahydro-2*H*-spiro[benzo[*b*]oxepine-5,3'-pyrazole] (64)
According to the **general procedure B**, substrate **B64** (90.1 mg, 0.20 mmol) was employed to yield the product **64** as a white solid (48.2 mg, 54% yield, 89% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 17.73 min, t_R (minor) = 25.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.71 – 7.69 (m, 1H), 7.68 – 7.63 (m, 2H), 7.41 – 7.32 (m, 3H), 7.20 (t, *J* = 6.9 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.35 – 4.31 (m, 1H), 3.85 (s, 3H), 3.82 – 3.69 (m, 2H), 3.28 (d, *J* = 17.5 Hz, 1H), 2.91 (td, *J* = 13.0, 3.7 Hz, 1H), 2.21 – 2.09 (m, 1H), 2.02 – 1.89 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 156.9, 152.8, 137.5, 132.5, 131.1, 130.0, 129.9, 128.9, 128.5, 128.4, 126.4, 124.1, 122.3, 113.9, 77.2, 72.5, 55.6, 47.1, 33.1, 26.4.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O_4S$ $[M + H]^+$ 449.1530, found 449.1530.



65

(*S*)-2'-((4-Methoxyphenyl)sulfonyl)-5'-phenyl-1-tosyl-1,2,2',3,4,4'-hexahydrospiro[benzo[*b*]azepine-5,3'-pyrazole] (65)
According to the **general procedure B**, substrate **B65** (120.8 mg, 0.20 mmol) was employed to yield the product **65** as a white solid (25.4 mg, 21% yield, 86% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (major) = 32.45 min, t_R (minor) = 48.74 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.41 – 7.33 (m, 6H), 7.20 – 7.14 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.26 – 4.18 (m, 1H), 3.92 (d, *J* = 17.9 Hz, 1H), 3.87 (s, 3H), 3.72 (d, *J* = 17.9 Hz, 1H), 3.05 (t, *J* = 11.7 Hz, 1H), 2.74 (td, *J* = 13.4, 3.2 Hz, 1H), 2.48 (s, 3H), 2.38 – 2.26 (m, 1H), 2.08 – 2.02 (m, 1H), 1.91 – 1.81 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 153.8, 143.7, 143.6, 139.3, 137.6, 132.4, 130.9, 130.1, 130.0, 129.0, 128.5, 128.4, 128.2, 127.0, 126.7, 126.6, 114.0, 78.0, 55.6, 50.43, 33.9, 29.7, 26.2, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{32}H_{32}N_3O_5S_2$ $[M + H]^+$ 602.1778, found 602.1772.



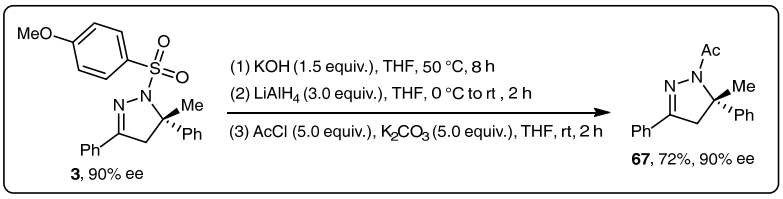
66

(*S*)-1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-1,2-diazaspiro[4.5]deca-2,6-diene (66)

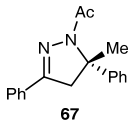
According to the **general procedure B**, substrate **B66** (76.9 mg, 0.20 mmol) was employed to yield the product **66** as a white solid (30.0 mg, 39% yield, 52% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 32.53 min, t_R (major) = 37.64 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.39 – 7.35 (m, 3H), 6.94 (d, *J* = 9.0 Hz, 2H), 5.81 (ddd, *J* = 9.6, 4.9, 2.0 Hz, 1H), 5.59 – 5.54 (m, 1H), 3.85 (s, 3H), 3.18 (d, *J* = 17.0 Hz, 1H), 3.14 (d, *J* = 17.0 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.26 – 2.16 (m, 1H), 2.07 – 1.99 (m, 1H), 1.97 – 1.85 (m, 2H), 1.65 – 1.53 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 153.3, 132.0, 131.3, 130.4, 130.0, 129.4, 129.1, 128.5, 126.5, 113.7, 71.4, 55.5, 48.5, 33.8, 24.3, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}N_2O_3S$ $[M + H]^+$ 383.1424, found 383.1424.

Procedure for Synthetic Applications

The synthesis of 67



To a solution of **3** (81.3 mg, 0.20 mmol, 1.0 equiv., 90% ee) in anhydrous THF (4 mL) was added KOH (16.8 mg, 0.30 mmol, 1.5 equiv.) under argon atmosphere. The resulting mixture was stirred at 50 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled to 0 °C, and $LiAlH_4$ (22.8 mg, 0.60 mmol, 3.0 equiv.) was added in portions under argon atmosphere. The resulting mixture was warmed up to room temperature and stirred for 2 h. Then K_2CO_3 (138.2 mg, 1.0 mmol, 5.0 equiv.) and acetyl chloride (71.4 μL, 1.0 mmol, 5.0 equiv.) were sequentially added into the reaction mixture under argon atmosphere. The resulting mixture was stirred at room temperature for 2 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5 mL), filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1–10:1) to give **67** as a white solid (39.8 mg, 72% yield, 90% ee).



67

(*S*)-1-(5-Methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethan-1-one (67)

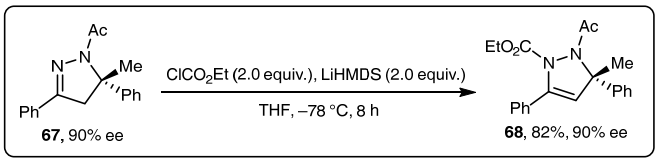
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R (minor) = 5.00 min, t_R (major) = 6.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.42 – 7.38 (m, 3H), 7.35 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 3.44 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* = 17.6 Hz, 1H), 2.41 (s, 3H), 2.06 (s, 3H).

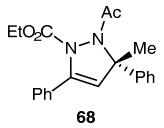
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 151.5, 144.9, 131.5, 130.1, 128.6, 128.6, 127.0, 126.3, 124.4, 67.5, 52.3, 24.5, 23.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found 279.1487.

The synthesis of 68



To a solution of **67** (55.7 mg, 0.20 mmol, 1.0 equiv., 90% ee) in anhydrous THF (4 mL) was added lithium bis(trimethylsilyl)amide (LiHMDS, 1.0 M solution in THF, 0.40 mL, 0.40 mmol, 2.0 equiv.) at −78 °C under argon atmosphere. The reaction mixture was stirred at −78 °C for 15 min. Then the solution of ethyl chloroformate (38.1 μL, 0.40 mmol, 2.0 equiv.) in anhydrous THF (0.6 mL) was dropwise added into the mixture via syringe. The resulting mixture was stirred at −78 °C for 8 h. After warming up to room temperature, the mixture was quenched by saturated NH_4Cl (10 mL), filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5 mL × 2). The combined organic layers were washed with brine (10 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to give **68** as a white solid (57.4 mg, 82% yield, 90% ee).



68

Ethyl (*S*)-2-Acetyl-3-methyl-3,5-diphenyl-2,3-dihydro-1*H*-pyrazole-1-carboxylate (68)

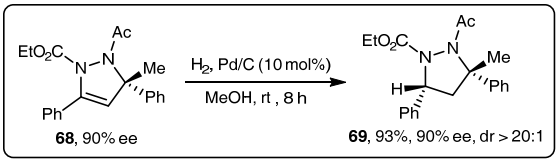
HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.05 min, t_R (major) = 10.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 4H), 7.39 – 7.30 (m, 5H), 7.26 – 7.21 (m, 1H), 6.02 (s, 1H), 3.94 (q, J = 6.4 Hz, 2H), 2.34 (s, 3H), 2.08 (s, 3H), 0.90 (t, J = 6.4 Hz, 3H).

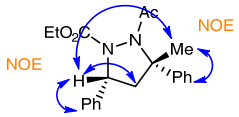
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 157.1, 143.2, 142.4, 131.3, 128.9, 128.5, 128.2, 127.4, 126.5, 125.7, 120.4, 73.2, 63.2, 26.8, 22.5, 13.7.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}N_2O_3$ $[M + H]^+$ 351.1703, found 351.1700.

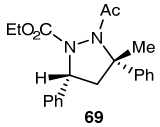
The synthesis of 69



To a solution of **68** (35.0 mg, 0.10 mmol, 90% ee) in MeOH (1 mL) was added Pd/C (10% palladium on carbon, wet with ca. 50% water, 10.6 mg, 10 mol%). Then the reaction flask was evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at room temperature for 8 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 5:1–3:1) to give the product **69** as a white solid (32.7 mg, 93% yield, 90% ee, dr > 20:1).

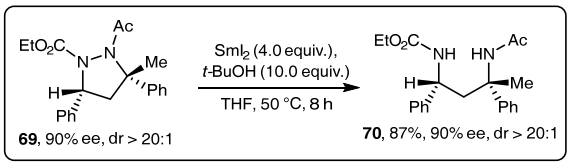


Supplementary Figure 5 The NOE of compound 69

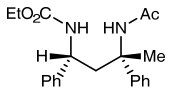


Ethyl (3*S*,5*R*)-2-Acetyl-3-methyl-3,5-diphenylpyrazolidine-1-carboxylate (69)
HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 9.32 min, t_R (minor) = 12.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 7.09 – 7.05 (m, 3H), 6.96 – 6.90 (m, 2H), 5.69 – 5.61 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.81 – 2.72 (m, 2H), 2.15 (s, 3H), 1.86 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 158.9, 143.2, 140.2, 128.6, 127.9, 127.4, 126.4, 125.7, 125.3, 66.9, 63.5, 61.3, 51.8, 24.3, 22.7, 14.4.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}N_2O_3$ $[M + H]^+$ 353.1860, found 353.1857.

The synthesis of 70



To a solution of **69** (35.2 mg, 0.10 mmol, 1.0 equiv., 90% ee) in anhydrous THF (2 mL) was added samarium (II) iodide (0.10 M solution in THF, 0.40 mL, 0.40 mmol, 4.0 equiv.) and *tert*-butanol (89.3 μL, 1.0 mmol, 10.0 equiv.) under argon atmosphere. The resulting mixture was stirred at 50 °C for 8 h. Upon completion (monitored by TLC), the mixture was quenched by saturated NH_4Cl (5 mL), filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) to give **70** as a white solid (30.7 mg, 87% yield, 90% ee, dr > 20:1).



70

Ethyl ((1*R*,3*S*)-3-Acetamido-1,3-diphenylbutyl)carbamate (70)

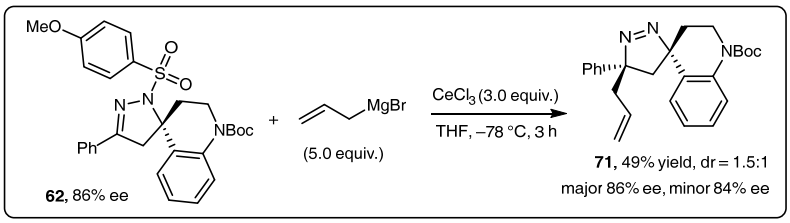
HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 7.05 min, t_R (major) = 8.98 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 720 (m, 10H), 6.85 (br s, 1H), 5.22 (d, *J* = 6.6 Hz, 1H), 4.82 – 4.74 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.72 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.33 (dd, *J* = 14.6, 4.5 Hz, 1H), 1.96 (s, 3H), 1.69 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

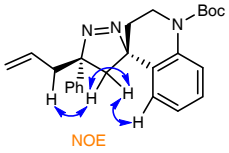
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.1, 146.2, 143.2, 129.0, 128.4, 127.6, 126.6, 124.6, 60.9, 58.1, 52.4, 47.7, 26.9, 24.1, 14.5.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{26}N_2NaO_3$ $[M + Na]^+$ 377.1836, found 377.1835.

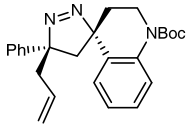
The synthesis of 71



To a mixture of **62** (81.3 mg, 0.20 mmol, 1.0 equiv., 86% ee) and cerium chloride (147.9 mg, 0.60 mmol, 3.0 equiv.) in anhydrous THF (2 mL) was dropwise added allylmagnesium bromide (1.0 M solution in Et_2O, 1.0 mL, 1.0 mmol, 5.0 equiv.) at −78 °C under argon atmosphere. The resulting mixture was stirred at −78 °C for 3 h. After warming up to room temperature, the reaction mixture was quenched by saturated NH_4Cl (5 mL), filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5 mL × 2). The combined organic layers were washed with brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100:1–50:1) to give **71** as two diastereoisomers (39.3 mg, dr = 1.5:1, 49% total yield).



Supplementary Figure 6 The NOE of 71-the major isomer



71-the major isomer

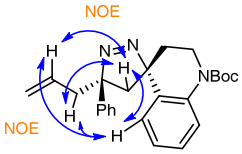
***tert*-Butyl (3*S*,5*R*)-5-Allyl-5-phenyl-2',3',4,5-tetrahydro-1'*H*-spiro[pyrazole-3,4'-quinoline]-1'-carboxylate**

(**71-the major isomer**: white powder, 23.9 mg, 30% yield, 86% ee)

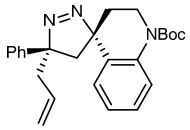
HPLC analysis: Chiralcel OD-3 (hexane/*i*-PrOH = 95/05, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 11.01 min, t_R (minor) = 13.67 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 7.16 – 7.09 (m, 1H), 6.78 – 6.70 (m, 1H), 6.14 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.64 – 5.51 (m, 1H), 5.15 – 5.05 (m, 2H), 4.17 – 4.05 (m, 1H), 4.01 – 3.89 (m, 1H), 2.88 – 2.72 (m, 2H), 2.38 (ddd, *J* = 13.6, 8.1, 3.6 Hz, 1H), 2.25 (d, *J* = 13.4 Hz, 1H), 2.09 (d, *J* = 13.4 Hz, 1H), 2.02 (ddd, *J* = 13.6, 7.8, 3.7 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.9, 137.8, 132.8, 129.6, 128.6, 127.6, 127.2, 126.9, 126.0, 124.2, 123.9, 119.6, 99.9, 93.8, 81.3, 47.8, 43.0, 42.2, 35.1, 28.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}N_3O_2$ $[M + H]^+$ 404.2333, found 404.2328.



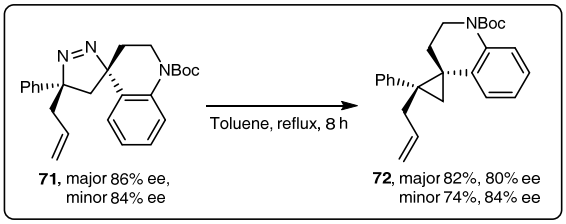
Supplementary Figure 7 The NOE of 71-the minor isomer



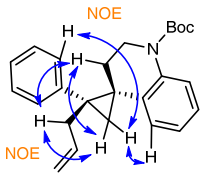
71-the minor isomer

***tert*-Butyl (3*S*,5*S*)-5-Allyl-5-phenyl-2',3',4,5-tetrahydro-1'*H*-spiro[pyrazole-3,4'-quinoline]-1'-carboxylate**
(**71-the minor isomer**: white powder, 15.4 mg, 19% yield, 84% ee)
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/01, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.51 min, t_R (minor) = 12.23 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.32 (m, 4H), 7.31 – 7.22 (m, 2H), 7.08 (td, *J* = 7.8, 1.1 Hz, 1H), 6.85 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.80 – 5.67 (m, 1H), 5.16 – 5.02 (m, 2H), 4.05 – 3.92 (m, 1H), 3.60 – 3.48 (m, 1H), 2.98 (dd, *J* = 14.0, 6.9 Hz, 1H), 2.88 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.29 (d, *J* = 13.3 Hz, 1H), 2.06 – 1.92 (m, 2H), 1.51 (s, 9H), 1.36 (ddd, *J* = 13.6, 5.4, 3.9 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.8, 137.9, 132.7, 130.2, 128.6, 127.7, 127.3, 126.8, 125.5, 124.1, 123.7, 119.6, 97.6, 92.4, 81.3, 47.1, 43.6, 41.9, 32.9, 28.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}N_3O_2$ $[M + H]^+$ 404.2333, found 404.2329.

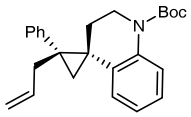
The synthesis of 72



Synthesis of **72-the major isomer**: Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **71-the major isomer** (23.9 mg, 0.06 mmol, 86% ee) and anhydrous toluene (1 mL). The reaction mixture was stirred at 110 °C for 8 h. After cooling down to room temperature, the reaction mixture was directly purified by flash column chromatography (using petroleum ether to remove the solvent, and then petroleum ether/ethyl acetate 100:1 as eluent) to give **72-the major isomer** as a colorless oil (18.4 mg, 82% yield, 80% ee).



Supplementary Figure 8 The NOE of 72-the major isomer



72-the major isomer

***tert*-Butyl (1*S*,2*R*)-2-Allyl-2-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-quinoline]-1'-carboxylate**

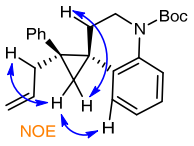
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/01, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.06 min, t_R (minor) = 6.41 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.98 – 6.88 (m, 4H), 6.62 (td, *J* = 7.6, 1.2 Hz, 1H), 6.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.75 – 5.62 (m, 1H), 4.96 – 4.84 (m, 2H), 4.17 – 4.06 (m, 1H), 3.69 (dt, *J* = 12.1, 5.0 Hz, 1H), 2.77 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.43 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.17 (d, *J* = 5.0 Hz, 1H), 2.15 (d, *J* = 5.0 Hz, 1H), 1.91 (d, *J* = 5.7 Hz, 1H), 1.58 (s, 9H), 0.95 (d, *J* = 5.7 Hz, 1H).

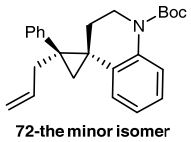
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 141.4, 139.0, 135.8, 133.6, 130.2, 127.4, 125.8, 125.4, 124.3, 124.2, 122.7, 116.2, 80.5, 44.7, 41.2, 38.3, 30.7, 29.9, 28.5, 20.3.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{29}NNaO_2$ $[M + Na]^+$ 398.2091, found 398.2086.

Synthesis of **72-the minor isomer**: Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **71-the minor isomer** (15.4 mg, 0.04 mmol, 84% ee) and anhydrous toluene (1 mL). The reaction mixture was stirred at 110 °C for 8 h. After cooling down to room temperature, the reaction mixture was directly purified by flash column chromatography (using petroleum ether to remove the solvent, and then petroleum ether/ethyl acetate 100:1 as eluent) to give **72-the minor isomer** as a colorless oil (10.6 mg, 74% yield, 84% ee).



Supplementary Figure 9 The NOE of 72-the minor isomer



72-the minor isomer

***tert*-Butyl (1*S*,2*S*)-2-Allyl-2-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-quinoline]-1'-carboxylate**

HPLC analysis: Chiralcel ID (hexane/*i*-PrOH = 99/01, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.97 min, t_R (minor) = 6.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.26 – 7.20 (m, 2H), 7.12 – 7.05 (m, 2H), 5.54 – 5.42 (m, 1H), 4.79 – 4.65 (m, 2H), 3.84 – 3.73 (m, 1H), 3.18 – 3.08 (m, 1H), 2.34 (dd, *J* = 14.8, 5.7 Hz, 1H), 1.94 (dt, *J* = 13.4, 9.4 Hz, 1H), 1.78 (dd, *J* = 14.8, 7.4 Hz, 1H), 1.58 (s, 9H), 1.51 (d, *J* = 5.7 Hz, 1H), 1.32 (dd, *J* = 5.7, 1.1 Hz, 1H), 1.30 – 1.24 (m, 1H).

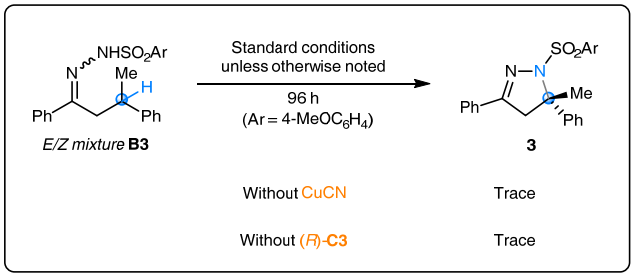
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 141.4, 140.4, 136.0, 134.1, 129.7, 128.0, 126.4, 126.3, 125.4, 124.9, 123.5, 115.8, 80.4, 42.1, 40.7, 37.7, 31.5, 30.8, 28.4, 17.6.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{29}NNaO_2$ $[M + Na]^+$ 398.2091, found 398.2086.

Mechanistic Study

(1) Control experiments

Control experiment A (Supplementary Figure 4a)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B3** (20.40 mg, 0.050 mmol, 1.0 equiv.), (*R*)-**C3** (4.45 mg, 0.0075 mmol, 15 mol%), $(NH_4)_2CO_3$ (0.24 mg, 0.0025 mmol, 5 mol%) and *i*-PrCO_2*i*-Pr (1.0 mL). Then **O7** (23.63 mg, 0.10 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the resulting mixture was stirred at 35 °C for 96 h.

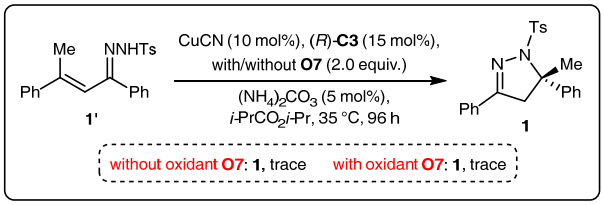
The desired product **3** was not obtained in the absence of CuCN.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B3** (20.40 mg, 0.050 mmol, 1.0 equiv.), CuCN (0.45 mg, 0.0050 mmol, 10 mol%), $(NH_4)_2CO_3$ (0.24 mg, 0.0025 mmol, 5 mol%) and *i*-PrCO_2*i*-Pr (1.0 mL). Then **O7** (23.63 mg, 0.10 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the resulting mixture was stirred at 35 °C for 96 h.

The desired product **3** was not obtained in the absence of (*R*)-**C3**.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

Control experiment B (Fig. 4f)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **1'** (19.52 mg, 0.050 mmol, 1.0 equiv.), CuCN (0.45 mg, 0.0050 mmol, 10 mol%), (*R*)-**C3** (4.45 mg, 0.0075 mmol, 15 mol%), $(NH_4)_2CO_3$ (0.24 mg, 0.0025 mmol, 5 mol%) and *i*-PrCO$_2$*i*-Pr (1.0 mL). Then **O7** (23.63 mg, 0.10 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the resulting mixture was stirred at 35 °C for 96 h.

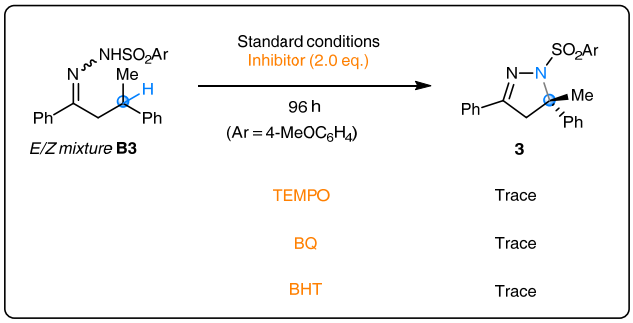
The desired product **1** was not obtained.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **1'** (19.52 mg, 0.050 mmol, 1.0 equiv.), CuCN (0.45 mg, 0.0050 mmol, 10 mol%), (*R*)-**C3** (4.45 mg, 0.0075 mmol, 15 mol%), $(NH_4)_2CO_3$ (0.24 mg, 0.0025 mmol, 5 mol%) and *i*-PrCO$_2$*i*-Pr (1.0 mL). The reaction mixture was stirred at 35 °C for 96 h.

The desired product **1** was not obtained.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

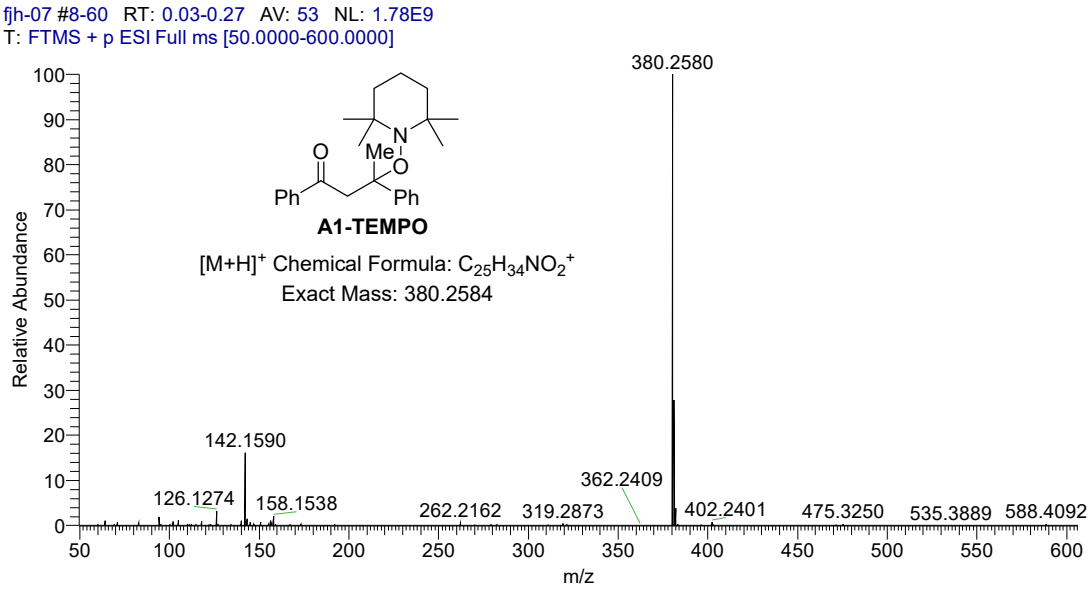
(2) Radical-inhibition experiments (Fig. 4a and Supplementary Figure 4b)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B3** (20.40 mg, 0.050 mmol, 1.0 equiv.), CuCN (0.45 mg, 0.0050 mmol, 10 mol%), (*R*)-**C3** (4.45 mg, 0.0075 mmol, 15 mol%), $(NH_4)_2CO_3$ (0.24 mg, 0.0025 mmol, 5 mol%), **radical inhibitor** (0.10 mmol, 2.0 equiv.) and *i*-PrCO_2*i*-Pr (1.0 mL). Then **O7** (23.63 mg, 0.10 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe, and the resulting mixture was stirred at 35 °C for 96 h.

In the presence of 2,2,6,6-tetramethylpiperidinooxy (**TEMPO**, 15.63 mg, 0.10 mmol, 2.0 equiv.) or 1,4-benzoquinone (**BQ**, 10.81 mg, 0.10 mmol, 2.0 equiv.) or butylated hydroxytoluene (**BHT**, 22.04 mg, 0.10 mmol, 2.0 equiv.), the desired reaction was inhibited and no desired product **3** was obtained.

When **TEMPO** used as radical inhibitor, the TEMPO-trapped hydrolyzed product **A1-TEMPO** was detected by HRMS analysis.

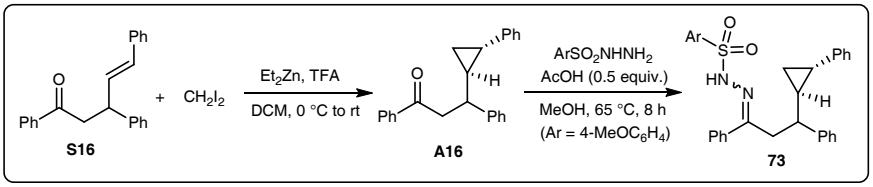


Supplementary Figure 10 The HRMS (ESI) spectrum of A1-TEMPO

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

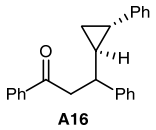
(3) Radical-clock experiment (Fig. 4b)

The synthesis of radical-clock substrate 73



Substrate **S16** is a known compound and was prepared according to the literature procedure[24].

Synthesis of **A16**: To a cooled (0 °C) solution of Et_2Zn (1.0 M solution in toluene, 4.0 mL, 4.0 mmol, 2.0 equiv.) in anhydrous DCM (6 mL) was dropwise added trifluoroacetic acid (TFA, 0.30 mL, 4.0 mmol, 2.0 equiv.). The resulting mixture was stirred at 0 °C for 20 minutes and a solution of CH_2I_2 (0.32 mL, 4.0 mmol, 2.0 equiv.) in DCM (2.0 mL) was added into the mixture via syringe. Then a solution of **S16** (0.6 g, 2.0 mmol, 1.0 equiv) in DCM (2 mL) was dropwise added into the reaction mixture, and the resulting mixture was warmed up to room temperature and stirred for 2 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (10 mL) and filtered through a pad of celite. The filtrate was concentrated under reduced pressure, and the residue was dissolved in DCM (20 mL), washed with water (20 mL) and brine (20 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100:1–50:1) to afford the product **A16** as a slightly yellow oil (0.46 g, 71% yield, as a single isomer, *trans*/*cis* > 20:1).



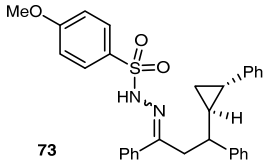
1,3-Diphenyl-3-(*trans*-2-phenylcyclopropyl)propan-1-one (A16)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 7.34 – 7.31 (m, 2H), 7.29 – 7.27 (m, 2H), 7.21 – 7.15 (m, 3H), 7.12 – 7.07 (m, 1H), 6.95 – 6.89 (m, 2H), 3.49 – 3.44 (m, 2H), 2.96 (dt, J = 9.3, 6.9 Hz, 1H), 1.80 – 1.72 (m, 1H), 1.46 – 1.37 (m, 1H), 1.03 – 0.97 (m, 1H), 0.95 – 0.88 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 144.1, 142.7, 137.2, 132.9, 128.5, 128.4, 128.1, 128.0, 127.4, 126.2, 126.0, 125.3, 45.7, 45.4, 28.8, 22.6, 15.9.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}O$ $[M + H]^+$ 327.1743, found 327.1745.

Synthesis of **73**: To a solution of **A16** (0.39 g, 1.2 mmol, 1.0 equiv.) and 4-methoxy benzenesulfonohydrazide (0.49 g, 2.4 mmol, 2.0 equiv.) in MeOH (10 mL) was added glacial acetic acid (35 μL, 0.6 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford **73** as a white solid (0.43 g, 70% yield, an inseparable mixture of *E*/*Z* isomers, *E*/*Z* = 8.5:1).



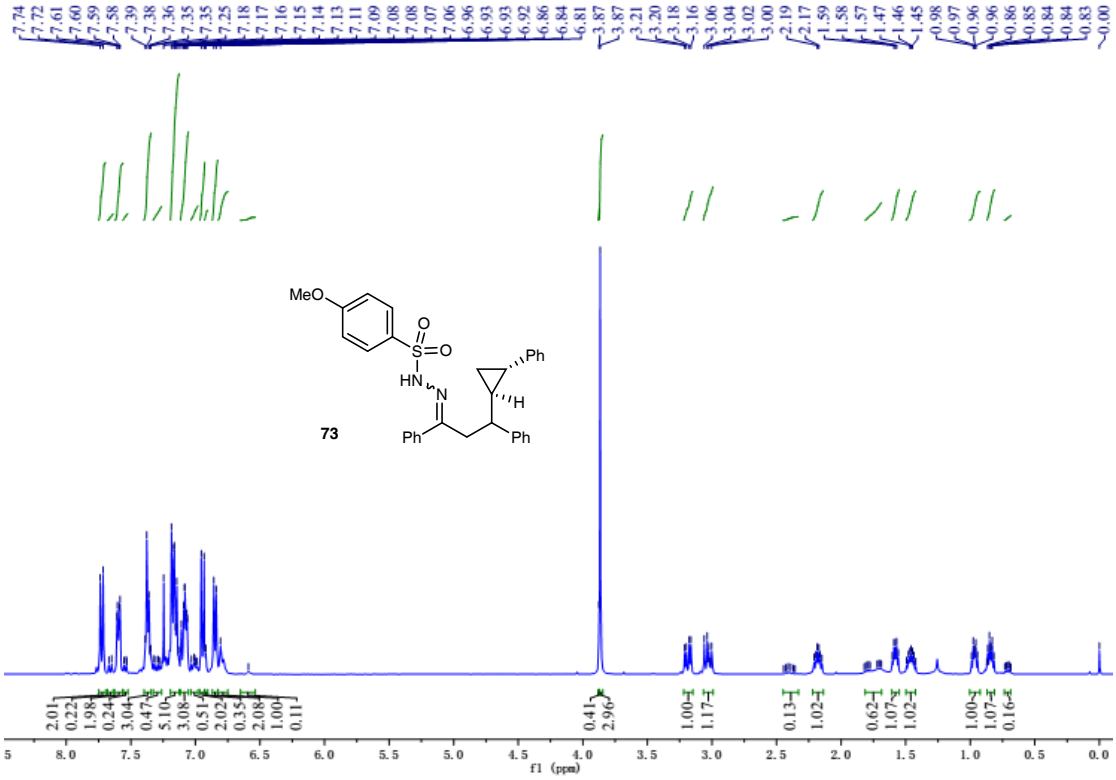
73

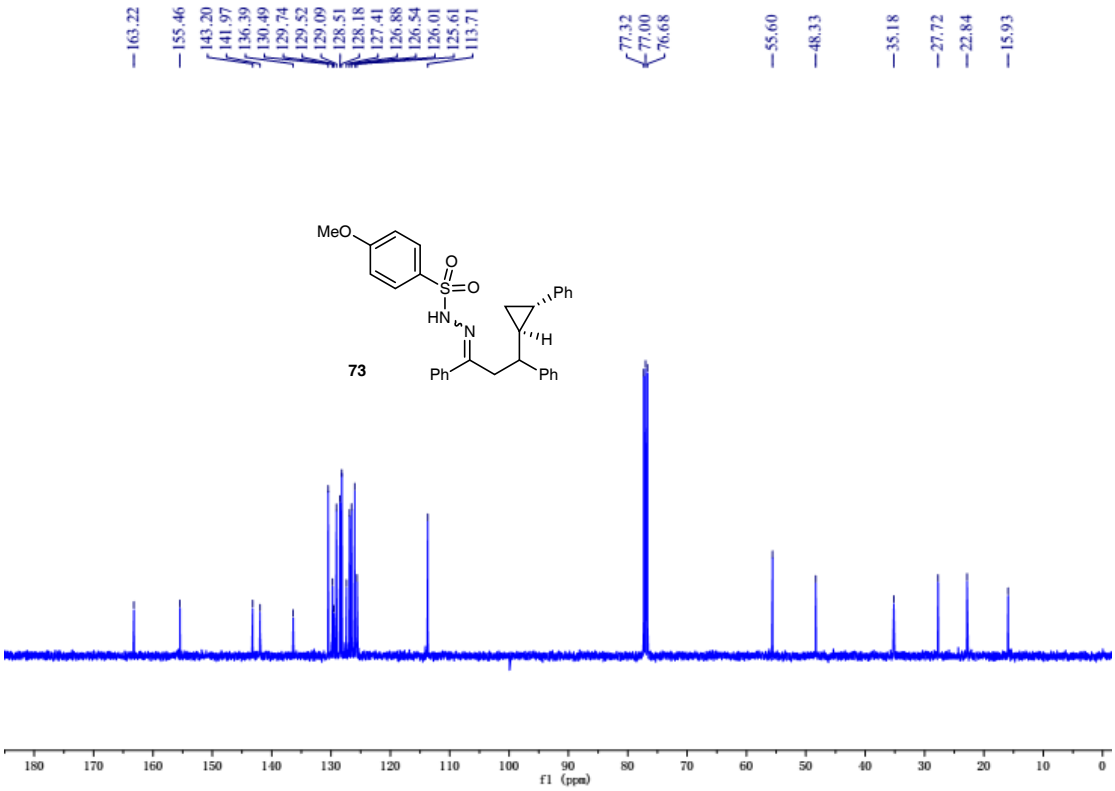
***N*'-(1,3-Diphenyl-3-(*trans*-2-phenylcyclopropyl)propylidene)-4-methoxybenzene sulfonohydrazide (73)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 0.24H), 7.62 – 7.57 (m, 2H), 7.56 – 7.53 (m, 0.24H), 7.40 – 7.34 (m, 3H), 7.33 – 7.27 (m, 0.48H), 7.19 – 7.13 (m, 5H), 7.11 – 7.06 (m, 3H), 7.03 – 6.98 (m, 0.48H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.93 – 6.92 (m, 0.36H), 6.87 – 6.83 (m, 2H), 6.81 (br s, 1H), 6.59 (br s, 0.12H), 3.87 (s, 0.36H), 3.87 (s, 3H), 3.19 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.06 – 2.99 (m, 1.12H), 2.46 – 2.35 (m, 0.12H), 2.18 (td, *J* = 9.3, 5.6 Hz, 1H), 1.84 – 1.68 (m, 0.60H), 1.62 – 1.55 (m, 1H), 1.50 – 1.42 (m, 1H), 0.97 (dt, *J* = 8.2, 5.2 Hz, 1H), 0.87 – 0.81 (m, 1H), 0.74 – 0.68 (m, 0.12H).

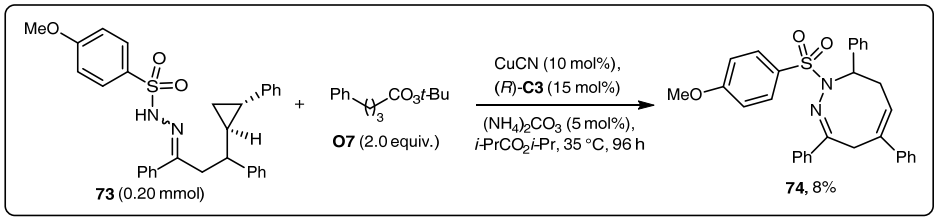
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 155.5, 143.2, 142.0, 136.4, 130.5, 129.7, 129.5, 129.1, 128.5, 128.2, 127.4, 126.9, 126.5, 126.0, 125.6, 113.7, 55.6, 48.3, 35.2, 27.7, 22.8, 15.9.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{31}N_2O_3S$ $[M + H]^+$ 511.2050, found 511.2054.

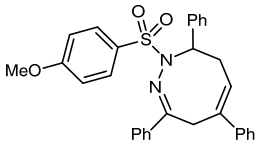

MeO
O
S=O
HN
N
Ph
H
Ph
Ph
73
f1 (ppm)


MeO
O
S=O
HN
N
Ph
H
Ph
Ph
73
f1 (ppm)

The radical-clock experiment



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **73** (102.1 mg, 0.20 mmol, 1.0 equiv.), CuCN (1.8 mg, 0.02 mmol, 10 mol%), (*R*)-**C3** (17.8 mg, 0.03 mmol, 15 mol%), $(NH_4)_2CO_3$ (1.0 mg, 0.01 mmol, 5 mol%) and *i*-PrCO_2*i*-Pr (4.0 mL). Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe and the reaction mixture was stirred at 35 °C for 96 h. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1–10:1) to afford the product **74** as a slightly yellow oil (8.1 mg, 8% yield).



74

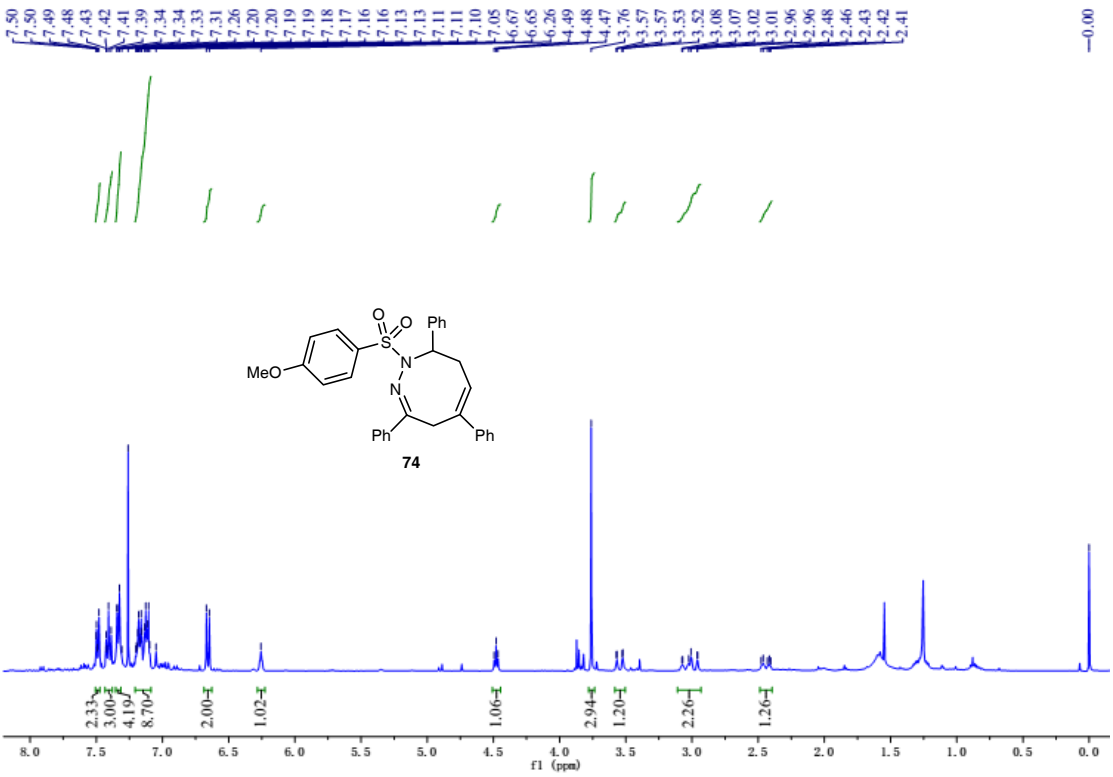
(2*E*,5*E*)-1-((4-Methoxyphenyl)sulfonyl)-3,5,8-triphenyl-1,4,7,8-tetrahydro-1,2-diazocine (74)

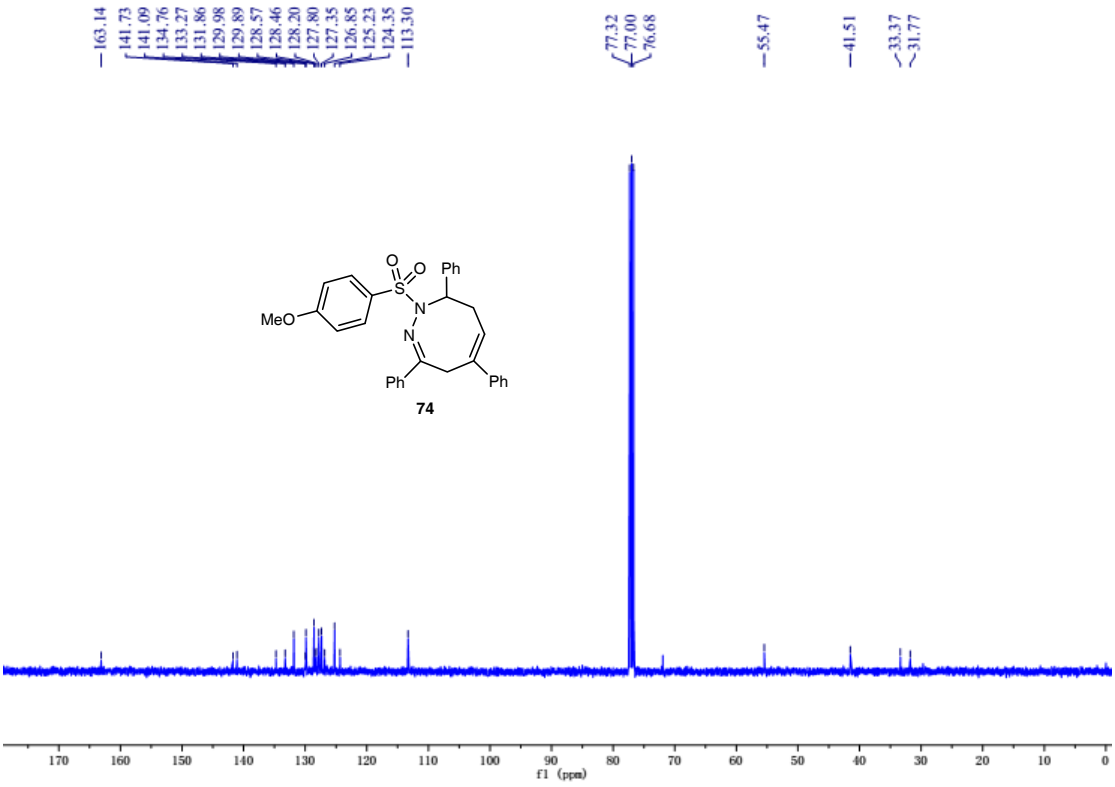
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.43 – 7.38 (m, 3H), 7.35 – 7.28 (m, 4H), 7.21 – 7.15 (m, 4H), 7.14 – 7.09 (m, 4H), 6.66 (d, *J* = 9.1 Hz, 2H), 6.28 – 6.22 (m, 1H), 4.48 (t, *J* = 5.9 Hz, 1H), 3.76 (s, 3H), 3.58 – 3.50 (m, 1H), 3.10 – 2.93 (m, 2H), 2.49 – 2.40 (m, 1H).

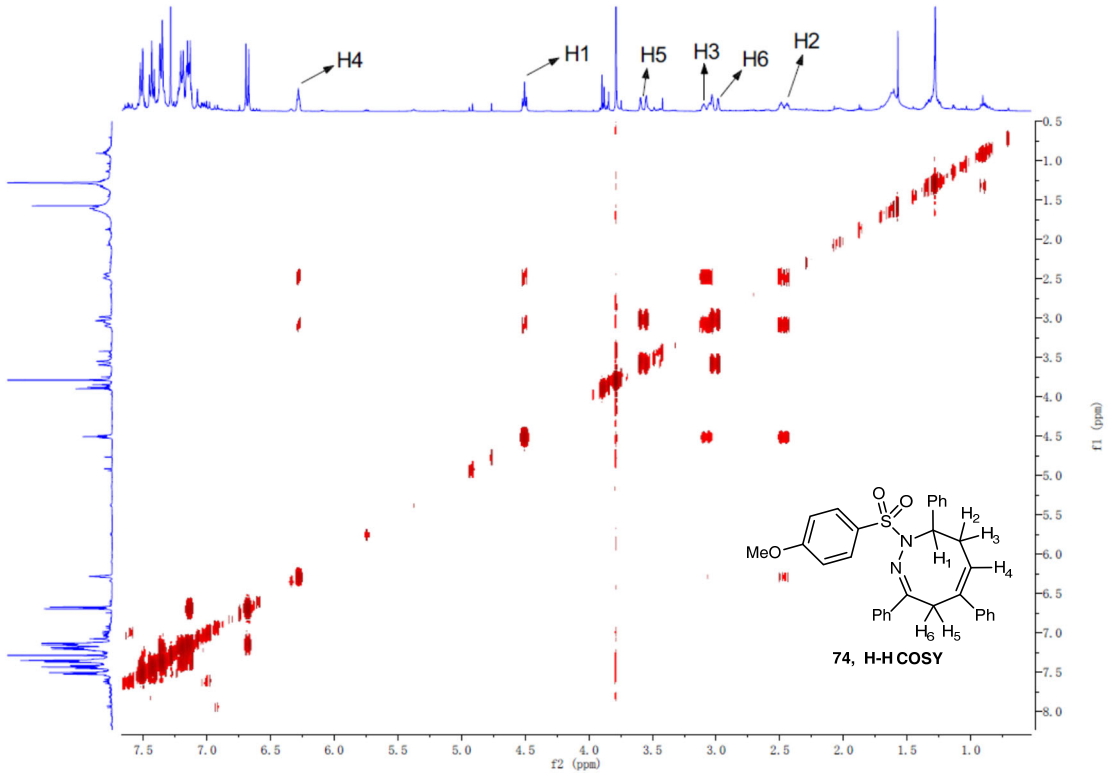
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 141.7, 141.1, 134.8, 133.3, 131.9, 130.0, 129.9, 128.6, 128.5, 128.2, 127.8, 127.4, 126.8, 125.2, 124.3, 113.3, 55.5, 41.5, 33.4, 31.8.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{29}N_2O_3S$ $[M + H]^+$ 509.1893, found 509.1899.

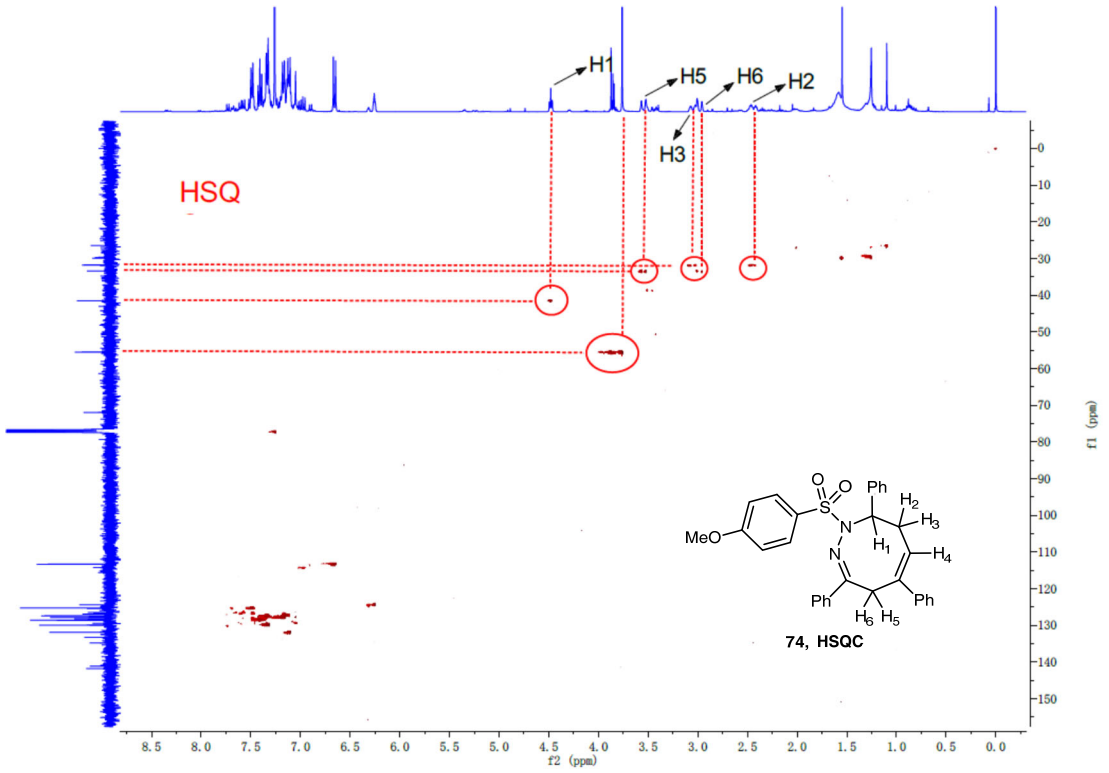
Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.


7.50
7.50
7.49
7.48
7.43
7.42
7.41
7.39
7.34
7.34
7.33
7.31
7.26
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.13
7.13
7.11
7.11
7.10
7.05
6.67
6.65
6.26
4.49
4.48
4.47
3.76
3.57
3.57
3.53
3.52
3.08
3.07
3.02
3.01
2.96
2.96
2.48
2.46
2.43
2.42
2.41
0.00
MeO
Ph
Ph
Ph
74
2.33
3.00
4.19
8.70
2.00
1.02
1.06
2.94
1.20
2.26
1.26
f1 (ppm)


163.14
141.73
141.09
134.76
133.27
131.86
129.98
129.89
128.57
128.46
128.20
127.80
127.35
126.85
125.23
124.35
113.30
77.32
77.00
76.68
55.47
41.51
33.37
31.77
MeO
Ph
Ph
Ph
74
f1 (ppm)



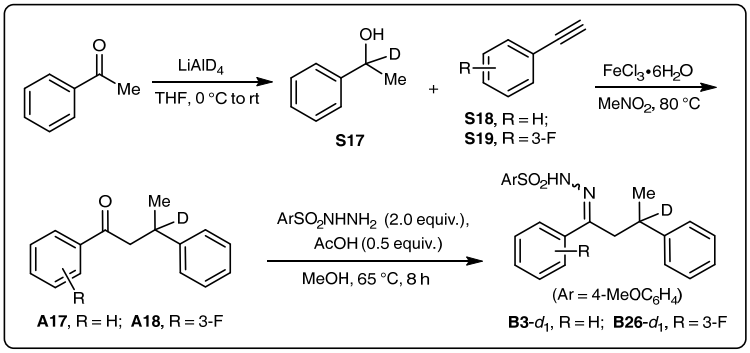
74, H-H COSY



74, HSQC

(4) Kinetic experiments

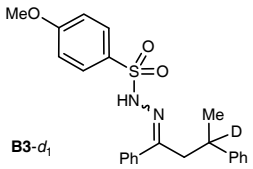
The synthesis of deuterated substrates B3-d_1 and B26-d_1



Synthesis of **S17**: To a cooled (0 °C) solution of acetophenone (1.17 mL, 10 mmol, 1.0 equiv.) in anhydrous THF (20 mL) was added lithium aluminum deuteride ($LiAlD_4$, 0.50 g, 12 mmol, 1.2 equiv.) in portions under argon atmosphere. Then the resulting mixture was warmed up to room temperature and stirred for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by water (10 mL), filtered through a short pad of celite and rinsed with EtOAc (20 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (20 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude alcohol **S17** (1.20 g), which was directly used in the next step without further purification.

Synthesis of **A17**: To a solution of the crude alcohol **S17** (0.60 g) obtained above and phenylacetylene **S18** (R = H) (0.44 mL, 4.0 mmol, 1.0 equiv.) in nitromethane (20 mL) was added iron(III) chloride hexahydrate (0.16 g, 0.6 mmol, 15 mol%) in one portion under argon atmosphere. The resulting mixture was stirred at 80 °C for 5 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure to remove the organic solvent. The residue was dissolved in EtOAc (20 mL), filtered through a short pad of celite and rinsed with EtOAc (20 mL). The filtrate was successively washed with water (30 mL) and brine (30 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100:1–50:1) to afford the product **A17** as a white solid (0.51 g, 57% yield).

Synthesis of **B3-d_1**: To a solution of **A17** (0.45 g, 2.0 mmol, 1.0 equiv.) and 4-methylbenzenesulfonohydrazide (0.74 g, 4.0 mmol, 2.0 equiv.) in MeOH (15 mL) was added glacial acetic acid (57 μL, 1.0 mmol, 0.5 equiv.) via microsyringe. The resulting mixture was stirred at 65 °C for 8 h. Upon completion (monitored by TLC), the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 10:1–5:1) to afford the desired product **B3-d_1** as a white solid (0.68 g, 83% yield), an inseparable mixture of *E*/*Z* isomers (*E*/*Z* = 4.0:1).

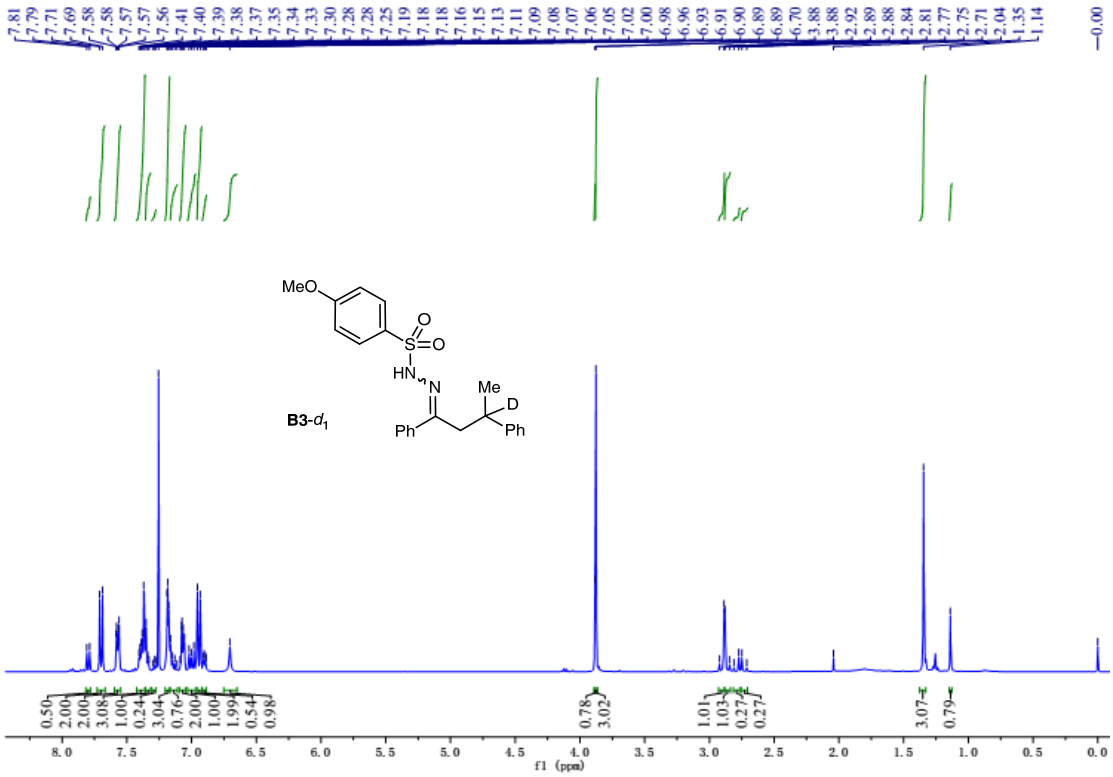


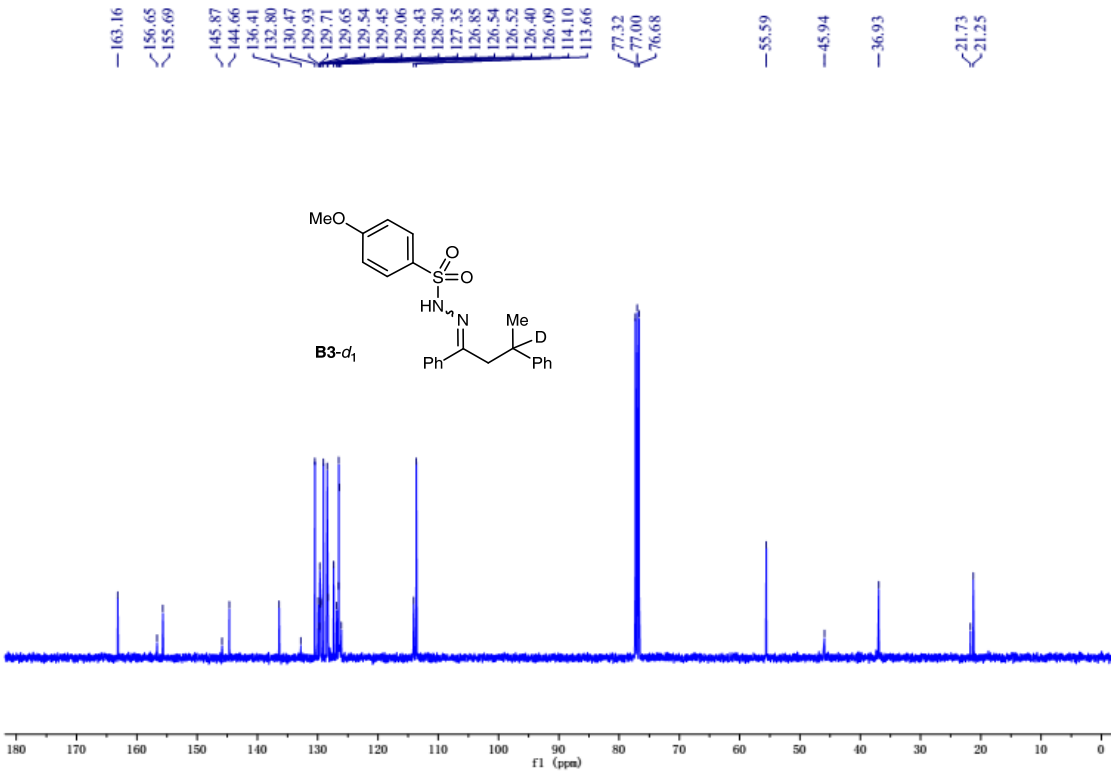
B3-d_1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.9 Hz, 0.50H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.41 – 7.36 (m, 3H), 7.36 – 7.32 (m, 1.0H), 7.31 – 7.28 (m, 0.25H), 7.20 – 7.16 (m, 3H), 7.15 – 7.11 (m, 0.75H), 7.09 – 7.04 (m, 2H), 7.03 – 6.97 (m, 1.0H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.91 – 6.89 (m, 0.50H), 6.70 (br s, 1H), 3.88 (s, 0.75H), 3.88 (s, 3H), 2.90 (d, *J* = 14.0 Hz, 1H), 2.86 (d, *J* = 14.0 Hz, 1H), 2.79 (d, *J* = 14.8 Hz, 0.25H), 2.73 (d, *J* = 14.8 Hz, 0.25H), 1.35 (s, 3H), 1.14 (s, 0.75H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 156.7, 155.7, 145.9, 144.7, 136.4, 132.8, 130.5, 129.9, 129.7, 129.7, 129.5, 129.5, 129.1, 128.4, 128.3, 127.4, 126.9, 126.5, 126.5, 126.4, 126.1, 114.1, 113.7, 55.6, 45.9, 36.9, 21.7, 21.3.

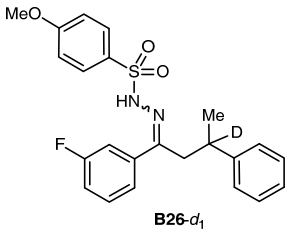
HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}DN_2O_3S$ $[M + H]^+$ 410.1643, found: 410.1646.





Synthesis of **A18**: According to the general procedure for **A17**, 3-fluorophenyl acetylene **S19** (R = 3-F) (0.46 mL, 4.0 mmol, 1.0 equiv.) was employed to afford substrate **A18** as a white solid (0.59 g, 61% yield).

Synthesis of **B26-*d*$_1$**: According to the general procedure for **B3-*d*$_1$**, substrate **A18** (0.49 g, 2.0 mmol, 1.0 equiv.) was employed to afford the product **B26-*d*$_1$** as a white solid (0.76 g, 86% yield), an inseparable mixture of *E*/*Z* isomers (*E*/*Z* = 9.1:1).



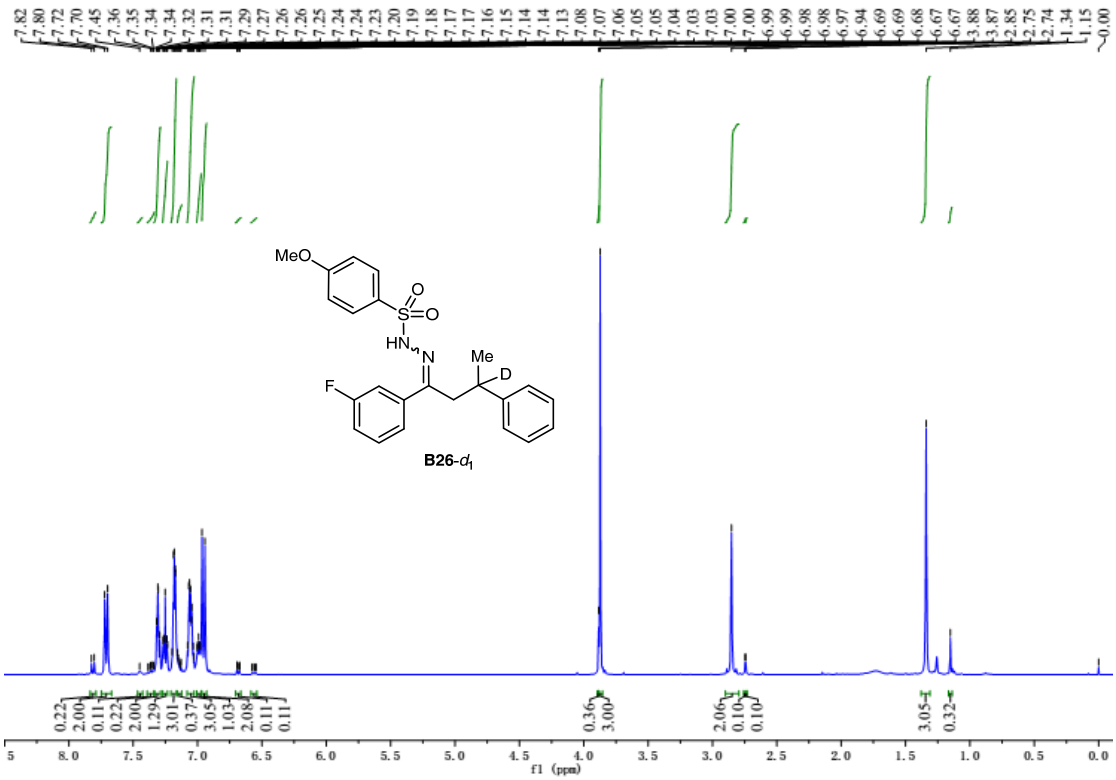
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 0.22H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.45 (br s, 0.11H), 7.40 – 7.34 (m, 0.22H), 7.33 – 7.29 (m, 2H), 7.27 – 7.24 (m, 1H), 7.20 – 7.16 (m, 3H), 7.16 – 7.13 (m, 0.33H), 7.08 – 7.03 (m, 3H), 7.01 – 6.98 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.70 – 6.67 (m, 0.11H), 6.58 – 6.54 (m, 0.11H), 3.88 (s, 0.33H), 3.87 (s, 3H), 2.85 (s, 2H), 2.75 (br s, 0.11H), 2.74 (br s, 0.11H), 1.34 (s, 3H), 1.15 (s, 0.33H).

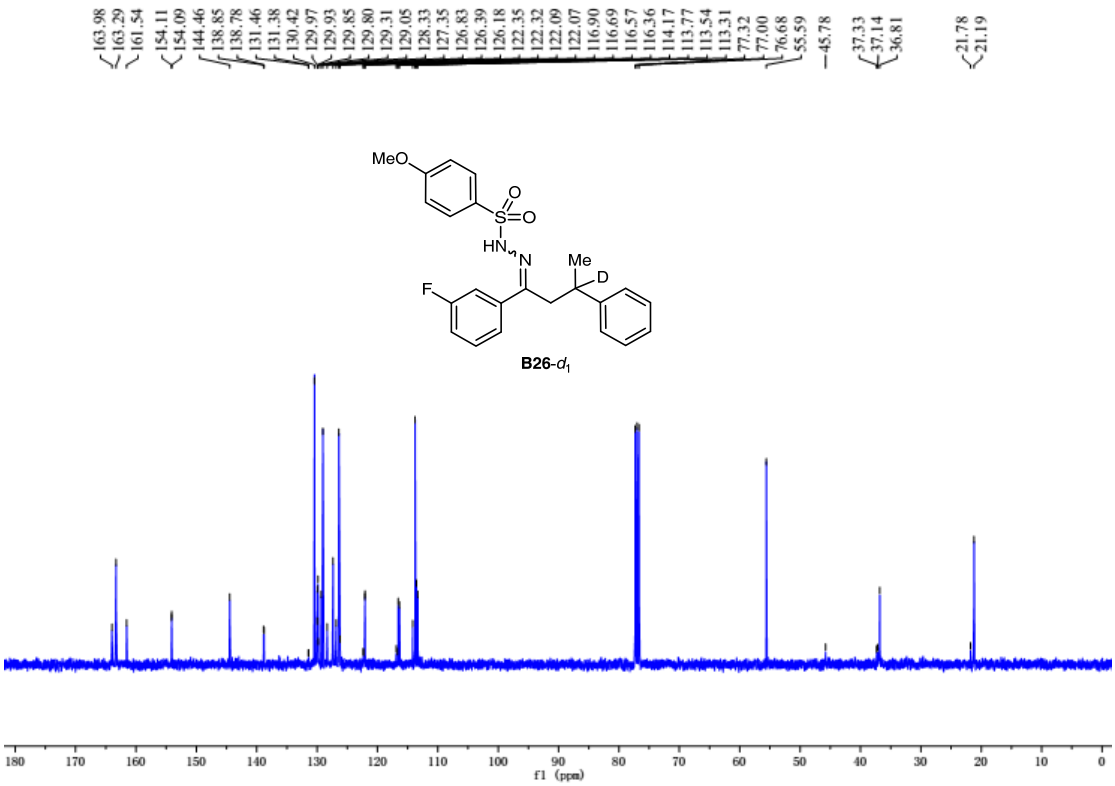
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.8 (d, *J* = 245.6 Hz), 154.1 (d, *J* = 2.5 Hz), 144.5, 138.8 (d, *J* = 7.5 Hz), 131.4 (d, *J* = 8.6 Hz), 130.4, 130.0, 129.9 (d, *J* = 8.2 Hz), 129.8, 129.3, 129.1, 128.3, 127.4, 126.8, 126.4, 126.2, 122.3 (d, *J* = 3.1 Hz), 122.1 (d,

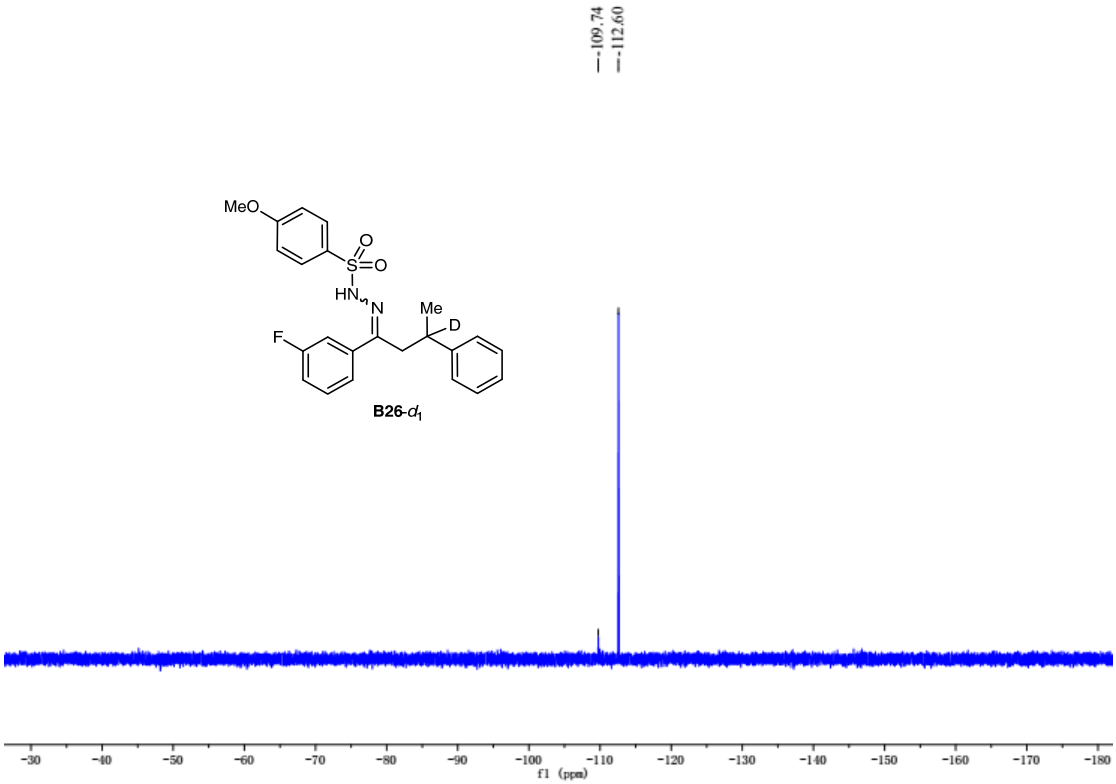
J = 2.6 Hz), 116.8 (d, J = 20.8 Hz), 116.5 (d, J = 21.6 Hz), 114.2, 113.8 (d, J = 22.5 Hz), 113.8, 113.4 (d, J = 23.1 Hz), 55.6, 45.8, 37.3, 37.1, 36.8, 21.8, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ −109.7 (s, 0.11F), −112.6 (s, 1F).

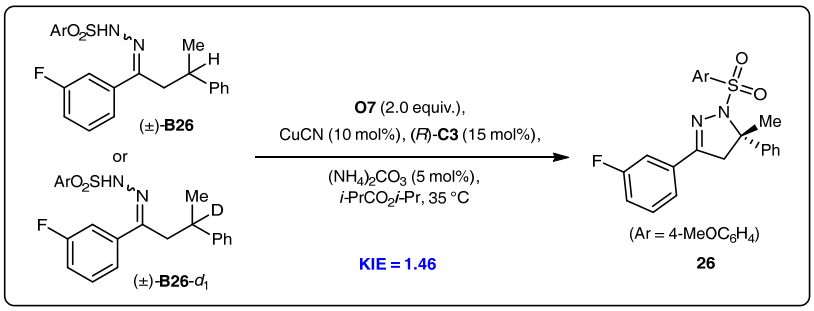
HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}DFN_2O_3S$ $[M + H]^+$ 428.1549, found 428.1553.






-109.74
-112.60
MeO
O
S
O
HN
N
Me
D
F
B26-d_1
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

The KIE experiments (Fig. 4c)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B26** (85.3 mg, 0.20 mmol, 1.0 equiv.) or **B26**-d_1 (85.5 mg, 0.20 mmol, 1.0 equiv.), CuCN (1.8 mg, 0.020 mmol, 10 mol%), (*R*)-**C3** (17.8 mg, 0.030 mmol, 15 mol%), $(NH_4)_2CO_3$ (1.0 mg, 0.010 mmol, 5 mol%) and *i*-PrCO_2*i*-Pr (4.0 mL). Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe. The resulting mixture was stirred at 35 °C.

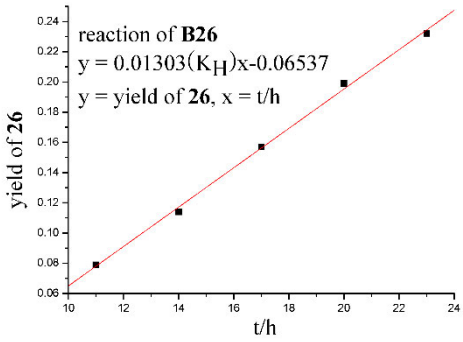
The reaction progress was monitored by ^{19}F NMR analysis to determine the yields of product **26**. At specific time intervals (11, 14, 17, 20, 23 h), 0.2 mL of the reaction mixture was taken out via syringe, filtered through a short pad of celite and rinsed with EtOAc (1 mL). The filtrate was concentrated under reduced pressure, and the residue was analyzed with ^{19}F NMR in $CDCl_3$ using **2-fluoroacetophenone** as the internal standard. The reaction rate constants were determined by plotting yield of the corresponding product over time (h) and extracting the slope after linear fitting.

KIE = K_H/K_D = 0.01303/0.0089 = 1.46.

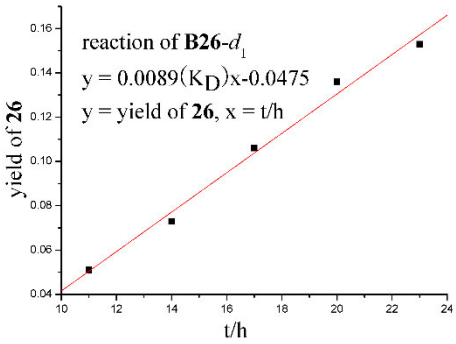
Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

Supplementary Table 5 Yields of product 26 monitored at specific time intervals during reaction

Time (h)	Yield of **26** (reaction of **B26**)	Yield of **26** (reaction of **B26**-d_1)
11	0.079	0.051
14	0.114	0.073
17	0.157	0.106
20	0.199	0.136
23	0.232	0.153

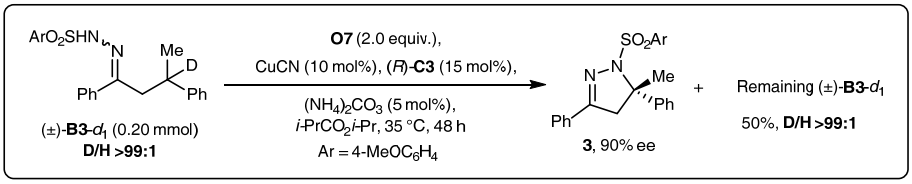


Supplementary Figure 11 Plots of yield versus reaction time for substrate B26



Supplementary Figure 12 Plots of yield versus reaction time for substrate B26-d_1

The reaction of B3-d_1 under standard condition (Fig. 4d)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B3-d_1** (81.9 mg, 0.20 mmol, 1.0 equiv.), CuCN (1.8 mg, 0.020 mmol, 10 mol%), (*R*)-**C3** (17.8 mg, 0.030 mmol, 15 mol%), $(NH_4)_2CO_3$ (1.0 mg, 0.010 mmol, 5 mol%) and *i*-$PrCO_2$*i*-Pr (4.0 mL). Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe. The reaction mixture was stirred at 35 °C.

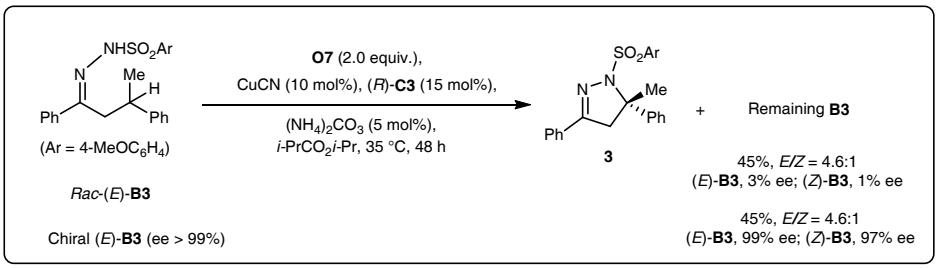
After 48 h, 0.5 mL of the reaction mixture was taken out via syringe, filtered through a short pad of celite and rinsed with EtOAc (2 mL). The filtrate was concentrated under reduced pressure, and the residue was firstly analyzed with ^{1}H NMR in $CDCl_3$ to determine the conversion of **B3-d_1** as 50%. Then the residue was purified by preparative TLC to give product **3** for HPLC analysis and the remaining **B3-d_1** for NMR analysis.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

The reactions of *rac*-(*E*)-B3 and chiral (*E*)-B3 under standard conditions (Fig. 4e)

The substrates *rac*-(*E*)-**B3** and chiral (*E*)-**B3** (ee > 99%) were separated from *rac*-**B3** (*E*/*Z* = 3.0:1) by PRE-HPLC analysis using a preparative Daicel Chiralcel AD-H column (hexane/*i*-PrOH = 60/40, flow rate 8.0 mL/min, λ = 239 nm).

HPLC analysis condition for the remaining material **B3**: Chiralcel AD-H (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 239 nm), t_R (minor for *Z*-isomer) = 8.47 min, t_R (major for *Z*-isomer) = 9.02 min, t_R (major for *E*-isomer) = 13.58 min, t_R (minor for *Z*-isomer) = 23.85 min.



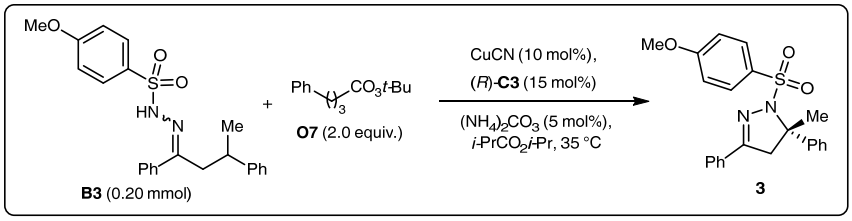
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with *rac*-(*E*)-**B3** (40.8 mg, 0.10 mmol, 1.0 equiv.), CuCN (0.9 mg, 0.010 mmol, 10 mol%), (*R*)-**C3** (8.9 mg, 0.015 mmol, 15 mol%), $(NH_4)_2CO_3$ (0.5 mg, 0.0050 mmol, 5 mol%) and *i*-PrCO_2*i*-Pr (2.0 mL). Then **O7** (47.3 mg, 0.20 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe. The resulting mixture was stirred at 35 °C.

After 48 h, 0.4 mL of the reaction mixture was taken out via syringe, filtered through a short pad of celite and rinsed with EtOAc (2 mL). The filtrate was concentrated under reduced pressure. The residue was firstly analyzed with ^{1}H NMR in $CDCl_3$ to determine the ratio of remaining **B3** as 45%. Then the residue was purified by preparative TLC to give the remaining **B3** for HPLC analysis.

The procedure for the reaction of chiral (*E*)-**B3** (ee > 99%) was the same with that described above except that chiral (*E*)-**B3** (40.8 mg, 0.10 mmol, 1.0 equiv.) was used.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

Experiment for determining the ee values during reaction (Supplementary Figure 4c)

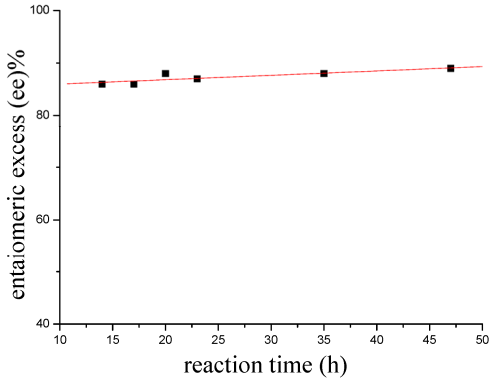


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B3** (81.7 mg, 0.20 mmol, 1.0 equiv.), CuCN (1.8 mg, 0.020 mmol, 10 mol%), (*R*)-**C3** (17.8 mg, 0.030 mmol, 15 mol%), $(NH_4)_2CO_3$ (1.0 mg, 0.010 mmol, 5 mol%) and *i*-$PrCO_2$*i*-Pr (4.0 mL). Then **O7** (94.5 mg, 0.40 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe. The reaction mixture was stirred at 35 °C.

At specific time intervals (14, 17, 20, 23, 35, 47 h), 0.2 mL of the reaction mixture was taken out via syringe, filtered through a short pad of celite and rinsed with EtOAc (1 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC to give the product **3** for HPLC analysis.

Supplementary Table 6 The ee values of product 3 at different time points during reaction

Time (h)	Ee of **3** (%)
14	86
17	86
20	88
23	87
35	88
47	89



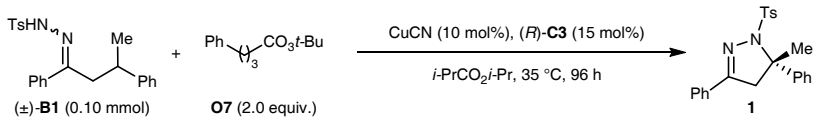
Supplementary Figure 13 Plots of ee values for 3 at different time points during reaction

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

(5) Control experiments on *E*/*Z* ratio of hydrazone

The hydrazones with different *E*/*Z* ratios were obtained by recrystallization of an *E*/*Z* mixture of **B1** (*E*/*Z* 3.4:1, solvent: petroleum ether/ethyl acetate), which was prepared according to the **general procedure 1**.

Experiment A (Supplementary Table 2)



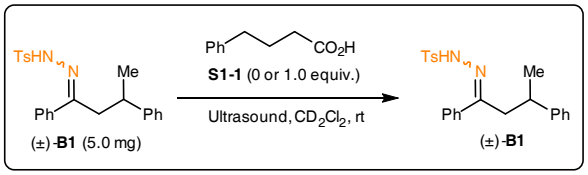
E/*Z* ratio of (±)-**B1**	Yield of **1** (%)	Ee (%)
3.4:1	38	90
10.0:1	36	90
> 20:1	36	91

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **B1** (39.3 mg, 0.10 mmol, 1.0 equiv.), CuCN (0.9 mg, 0.010 mmol, 10 mol%), (*R*)-**C3** (8.9 mg, 0.015 mmol, 15 mol%) and *i*-PrCO$_2$*i*-Pr (2.0 mL). Then **O7** (47.3 mg, 0.20 mmol, 2.0 equiv.) was slowly added into the mixture via microsyringe. The resulting mixture was stirred at 35 °C for 96 h. Then the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1).

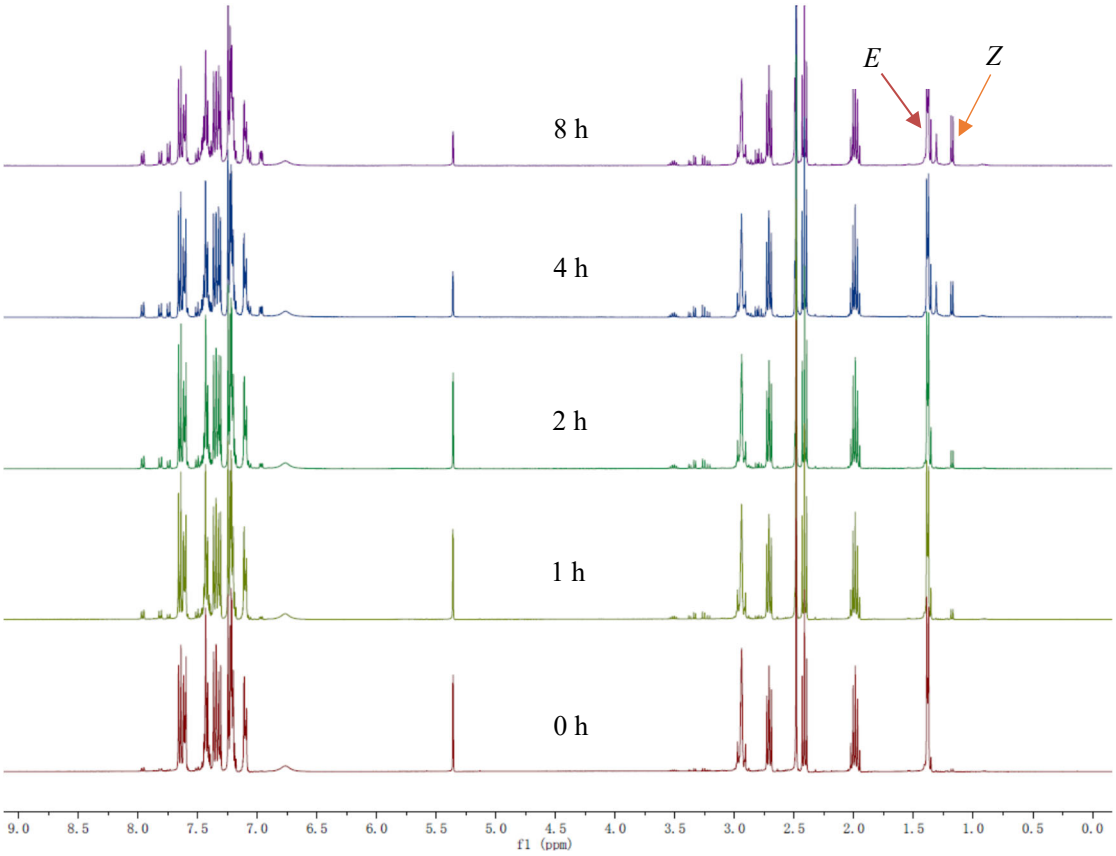
The results suggested that the *E*/*Z* ratios of substrate **B1** have no significant effects on the reaction outcomes.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

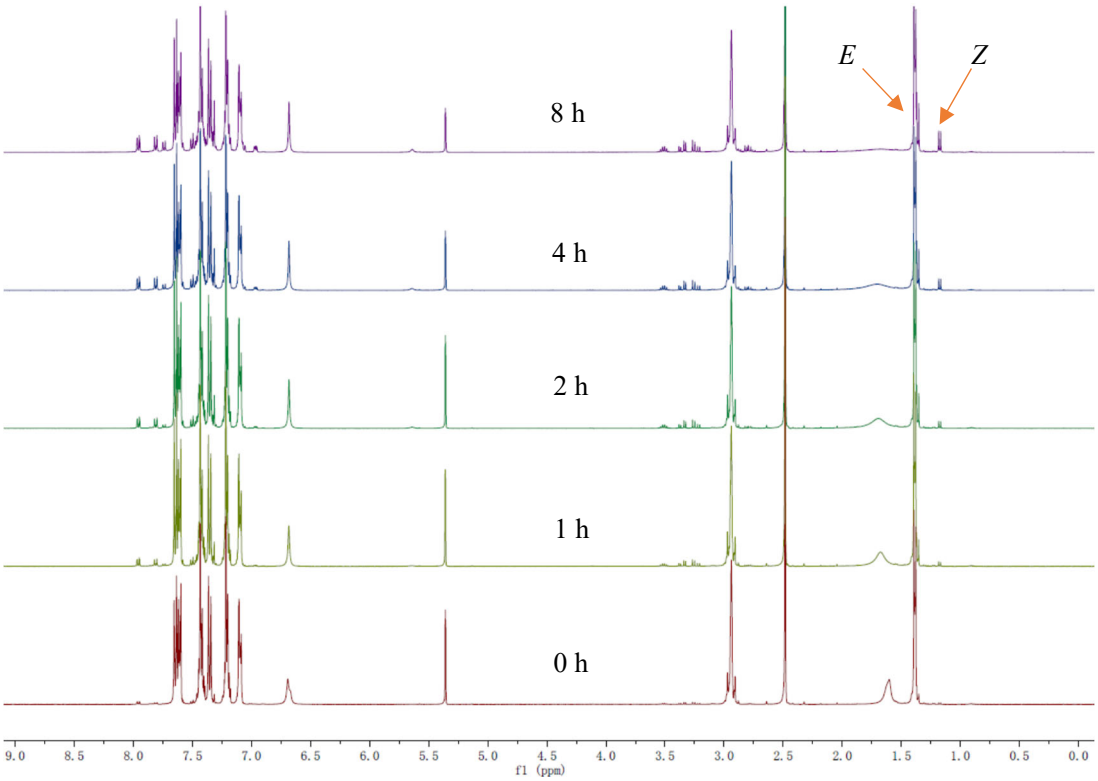
Experiment B (Supplementary Tables 3 and 4)



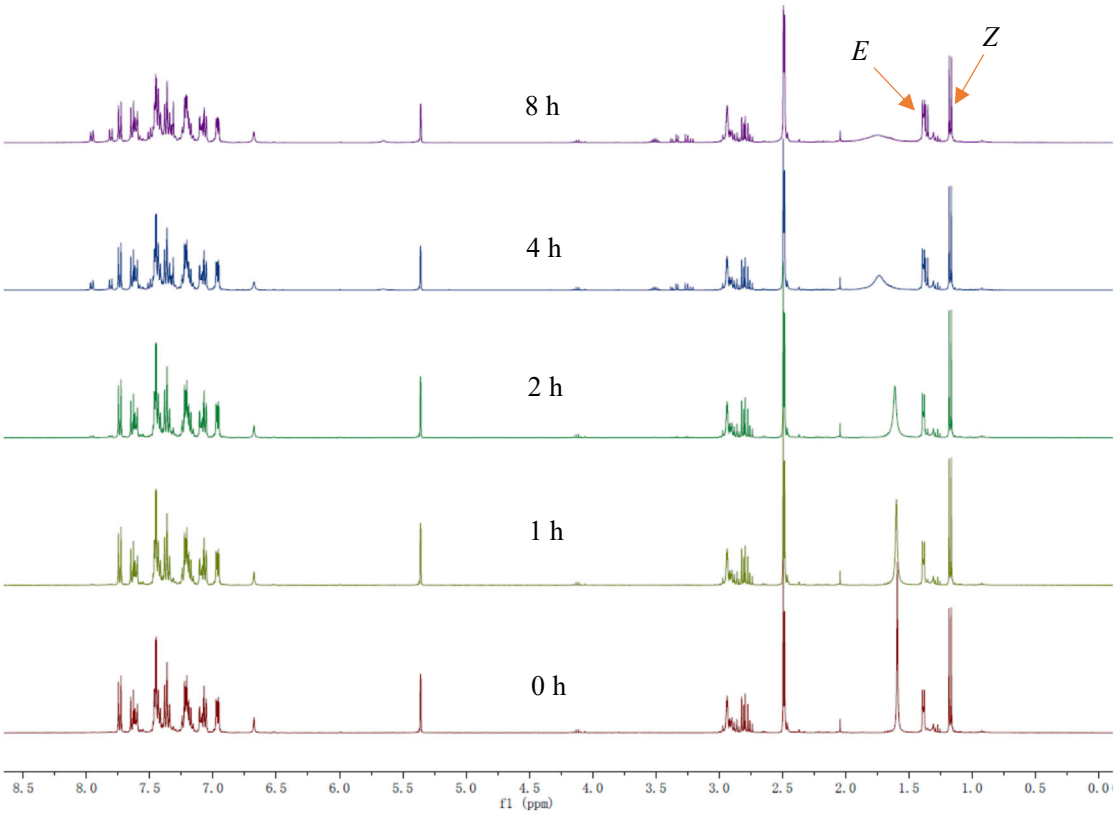
(±)-**B1** (5.0 mg, 0.0127 mmol, 1.0 equiv.) with or without 4-phenylbutanoic acid **S1-1** (2.1 mg, 0.0127 mmol, 1.0 equiv.) was dissolved in CD_2Cl_2 (0.6 mL) at room temperature in an NMR tube. The NMR tube was immersed in an ultrasonic cleaner filled with water, and sonicated at room temperature for a specified time. Then the mixture was applied to ^{1}H NMR analysis to obtain the *E*/*Z* ratio of **B1**. The sample was scanned at certain intervals as shown in the following stacking NMR spectra.



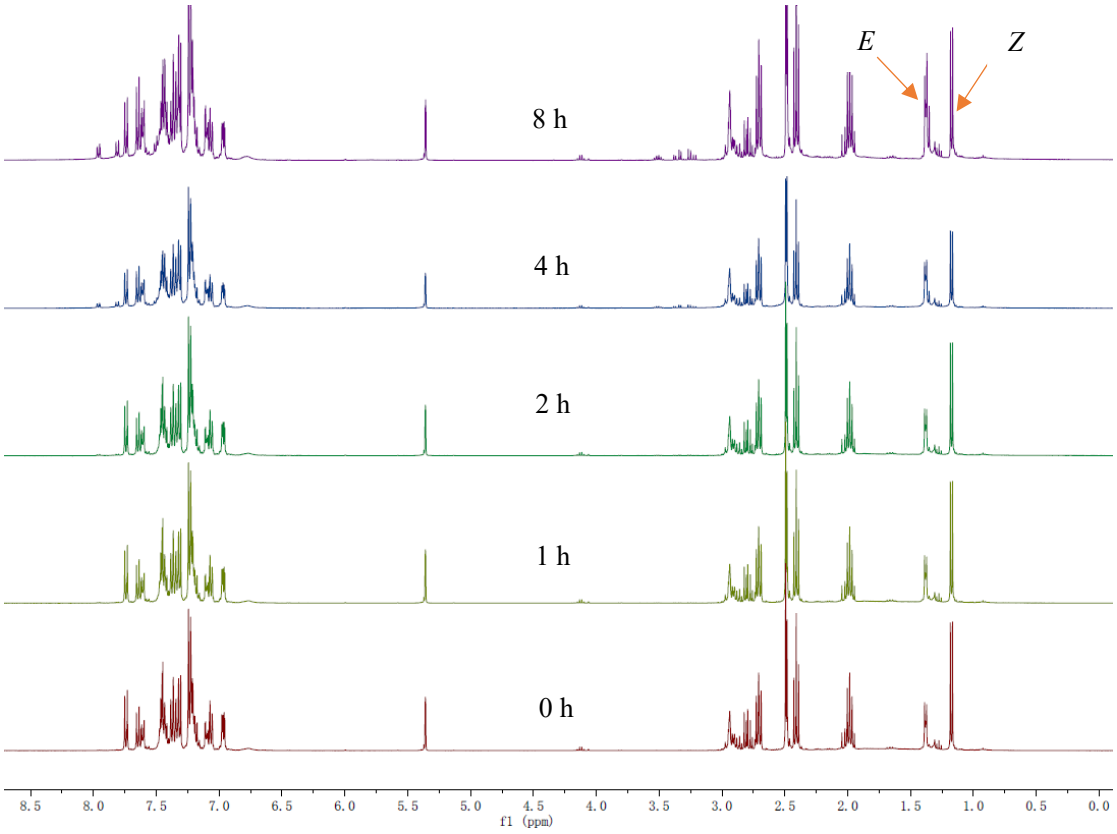
Supplementary Figure 14 The stacking ^{1}H NMR spectra of (±)-B1 (initial *E*/*Z* ratio > 20:1) with S1-1



Supplementary Figure 15 The stacking ^{1}H NMR spectra of (±)-B1 (initial E/Z ratio > 20:1) without S1-1

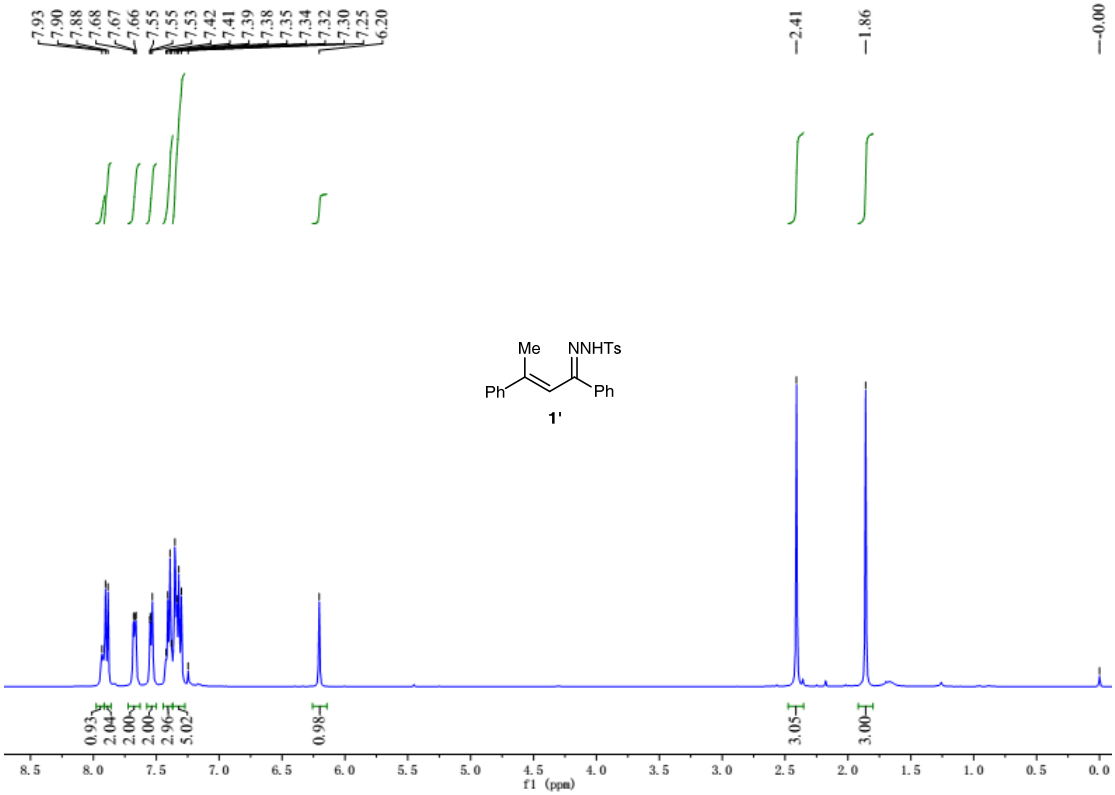


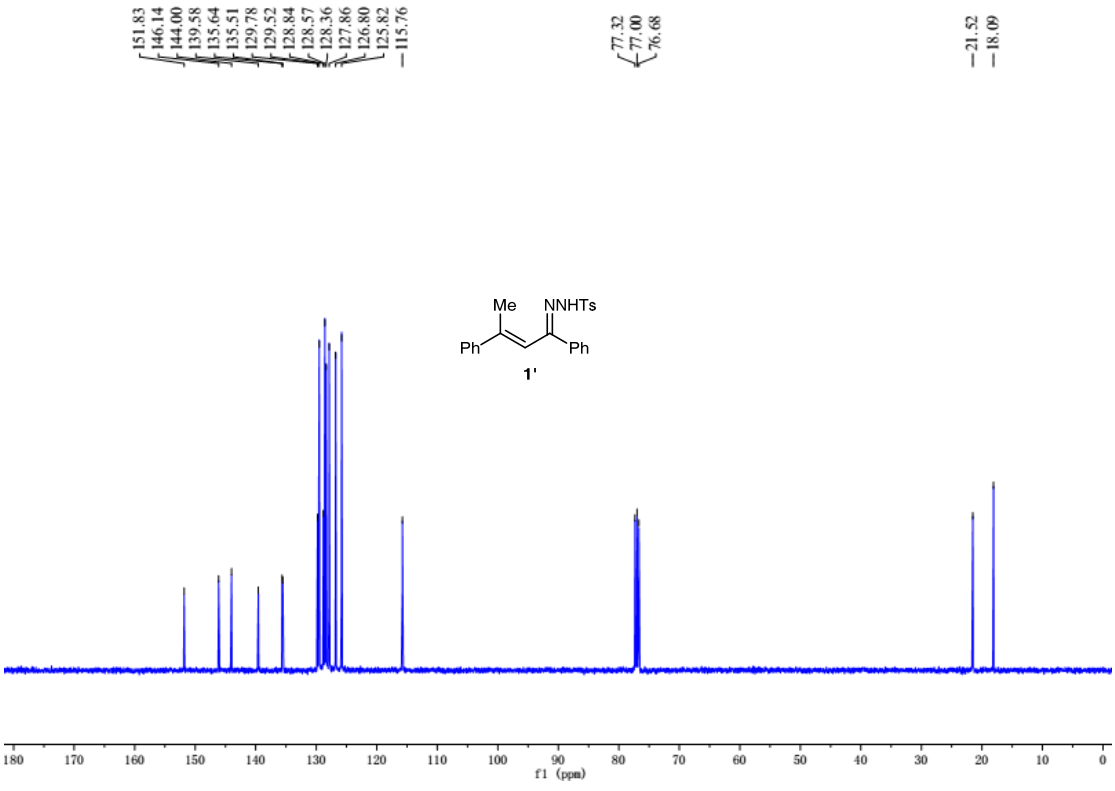
Supplementary Figure 16 The stacking ^{1}H NMR spectra of (±)-B1 (initial *E*/*Z* ratio > 1:1.6) with S1-1

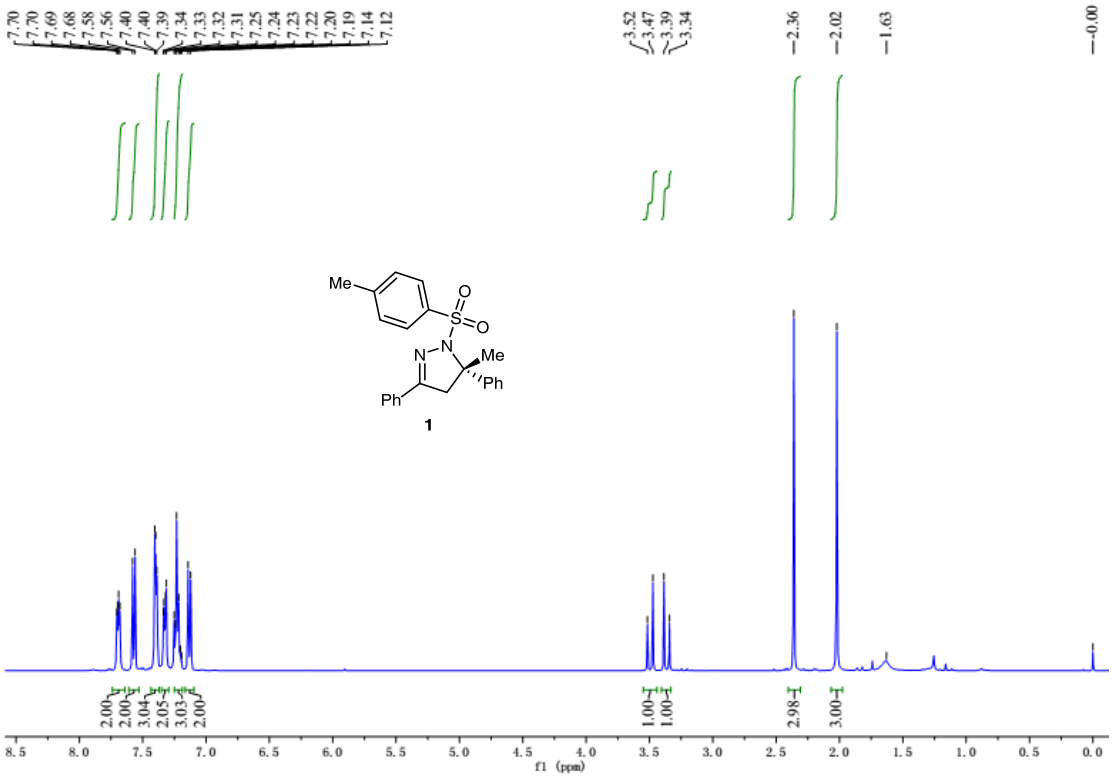


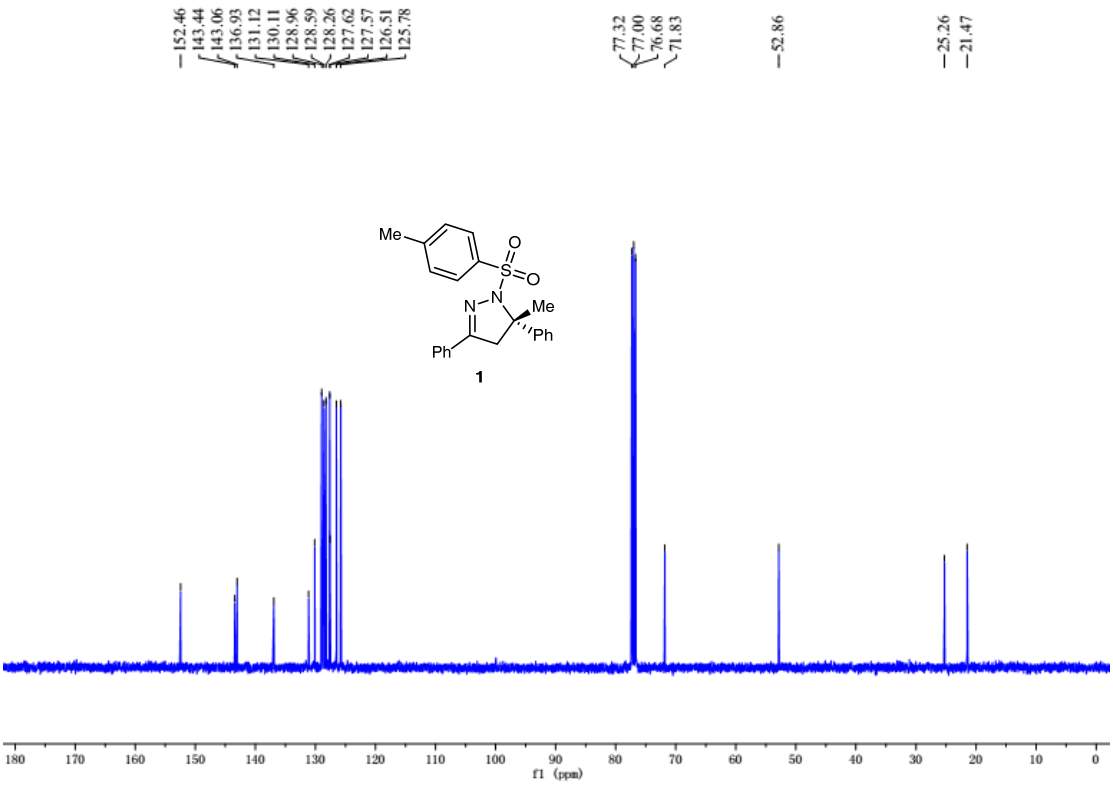
Supplementary Figure 17 The stacking ^{1}H NMR spectra of (±)-B1 (initial *E*/*Z* ratio > 1:1.6) without S1-1

NMR Spectra


7.93
7.90
7.88
7.68
7.67
7.66
7.55
7.55
7.53
7.42
7.41
7.39
7.38
7.35
7.34
7.32
7.30
7.25
6.20
2.41
1.86
0.00
Me
NNHTs
Ph
Ph
1'
0.93
2.04
2.00
2.00
2.96
5.02
0.98
3.05
3.00
f1 (ppm)


151.83
146.14
144.00
139.58
135.64
135.51
129.78
129.52
128.84
128.57
128.36
127.86
126.80
125.82
115.76
77.32
77.00
76.68
21.52
18.09
Me
NNHTs
Ph
Ph
1'
f1 (ppm)


7.70
7.70
7.69
7.68
7.58
7.56
7.40
7.40
7.39
7.34
7.33
7.32
7.31
7.25
7.24
7.23
7.22
7.20
7.19
7.14
7.12
3.52
3.47
3.39
3.34
2.36
2.02
1.63
0.00
Me
S
O
O
N
N
Me
Ph
Ph
1
2.00
2.00
3.04
2.05
3.03
2.00
1.00
1.00
2.98
3.00
f1 (ppm)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127.62
127.57
126.51
125.78
77.32
77.00
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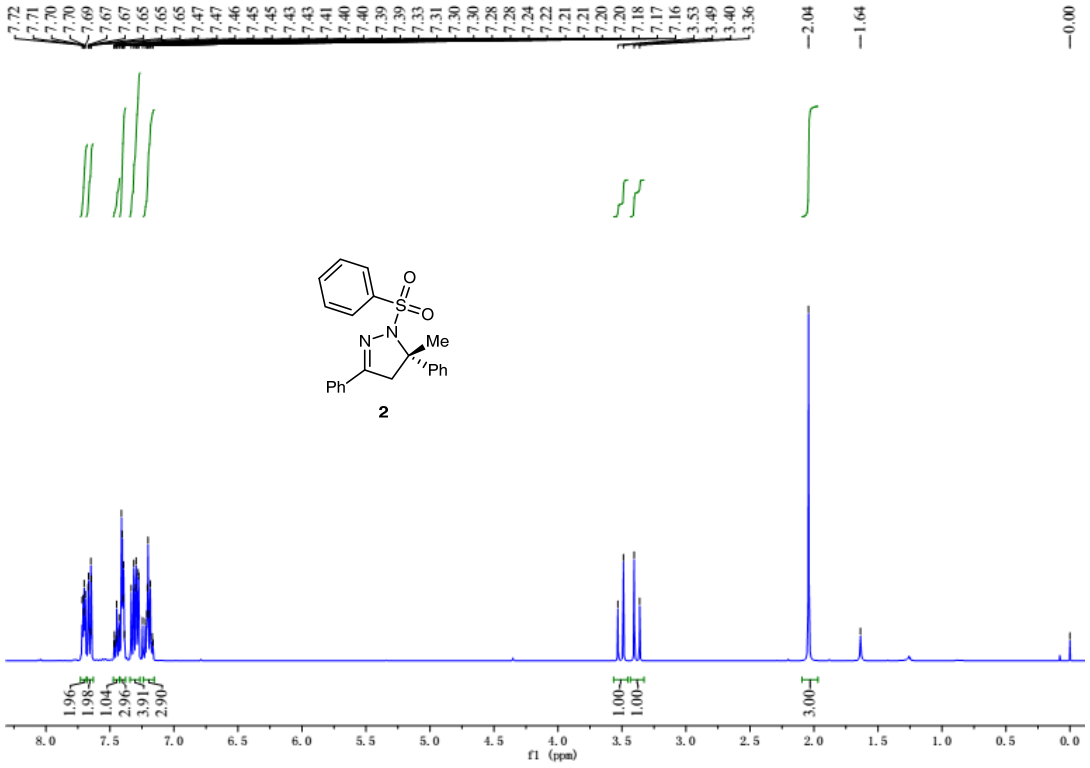
25.26
21.47
Me
S
O
O
N
N
Me
Ph
Ph
1
f1 (ppm)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7.45
7.45
7.43
7.43
7.41
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7.40
7.39
7.39
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7.31
7.30
7.30
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7.24
7.22
7.21
7.21
7.20
7.20
7.18
7.17
7.16
3.53
3.49
3.40
3.36
2.04
1.64
0.00
O
S
O
N
N
Me
Ph
Ph
2
1.96
1.98
1.04
2.96
3.91
2.90
1.00
1.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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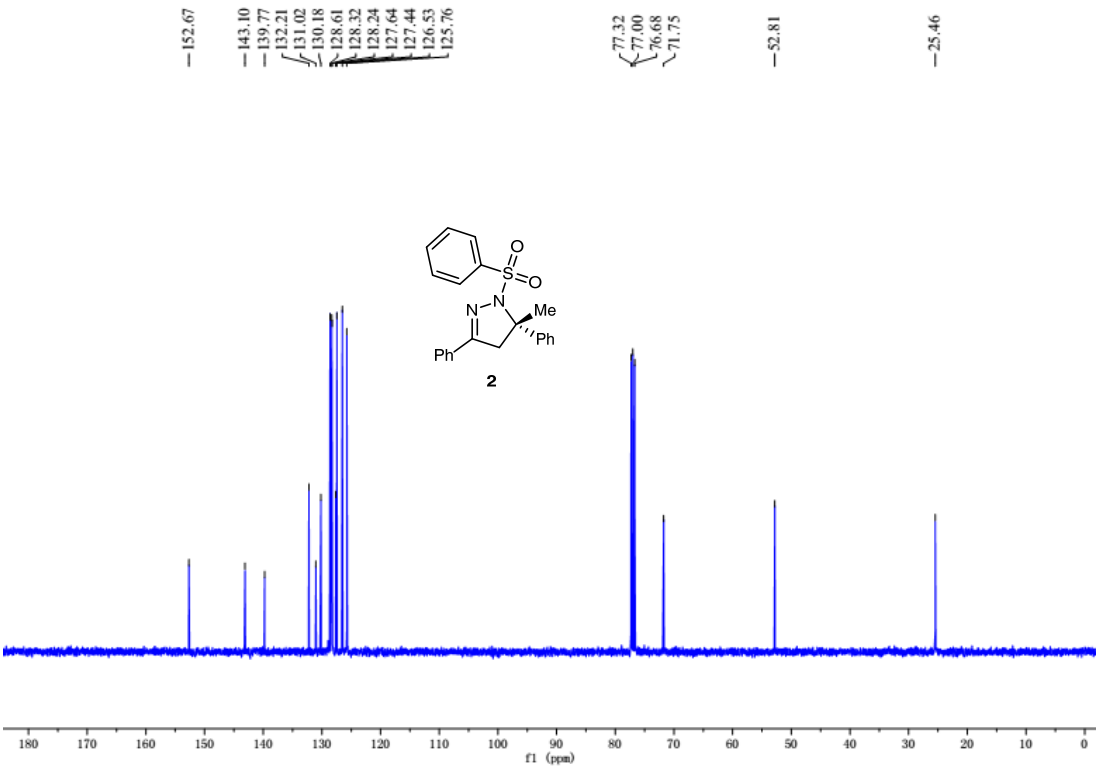
0.0
f1 (ppm)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130.18
128.61
128.32
128.24
127.64
127.44
126.53
125.76
77.32
77.00
76.68
71.75
52.81
25.46
O
S
O
N
N
Me
Ph
Ph
2
180
170
160
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140
130
120
110
100
90
80
70
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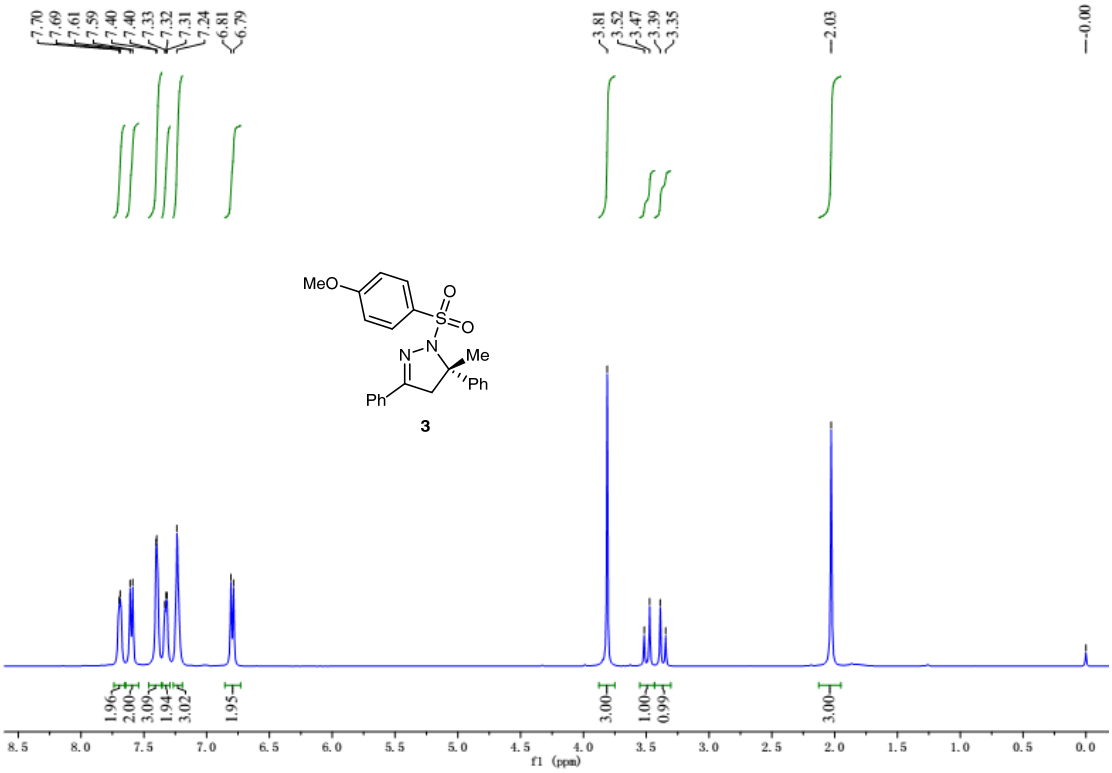
50
40
30
20
10
0
f1 (ppm)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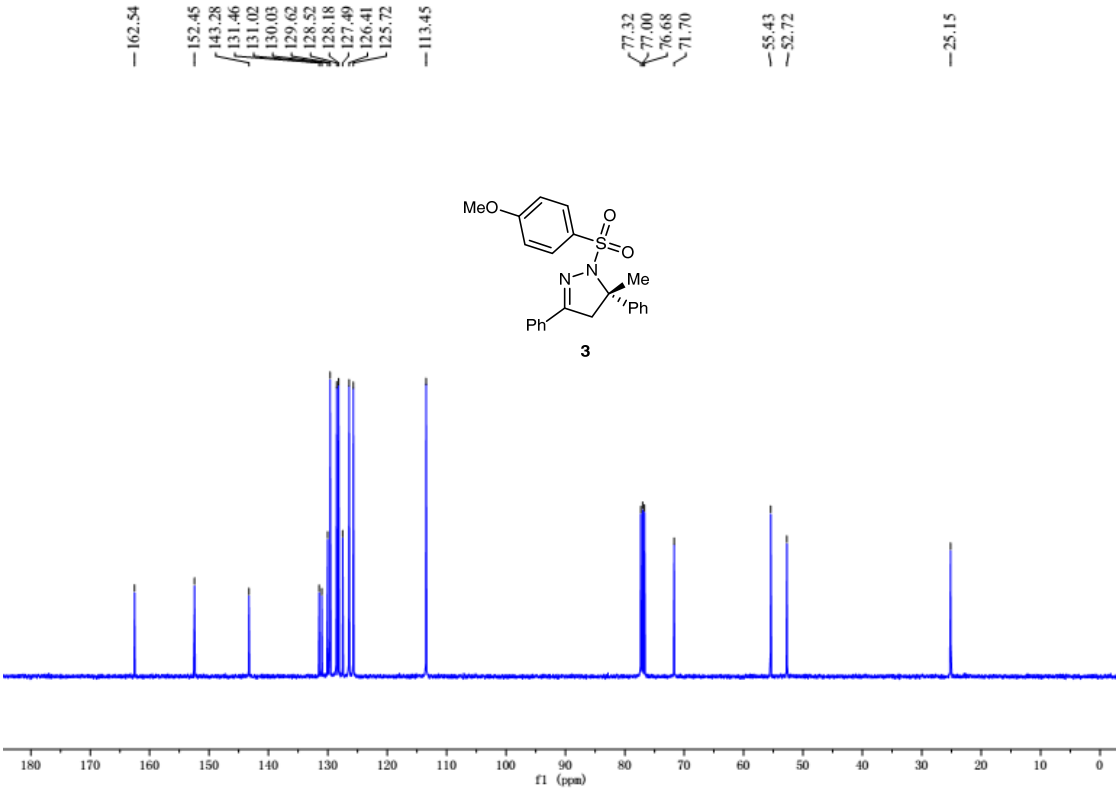
7.40
7.33
7.32
7.31
7.24
6.81
6.79
3.81
3.52
3.47
3.39
3.35
2.03
0.00
MeO
O
S
O
N
N
Me
Ph
Ph
3
1.96
2.00
3.09
1.94
3.02
1.95
3.00
1.00
0.99
3.00
f1 (ppm)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127.49
126.41
125.72
113.45
77.32
77.00
76.68
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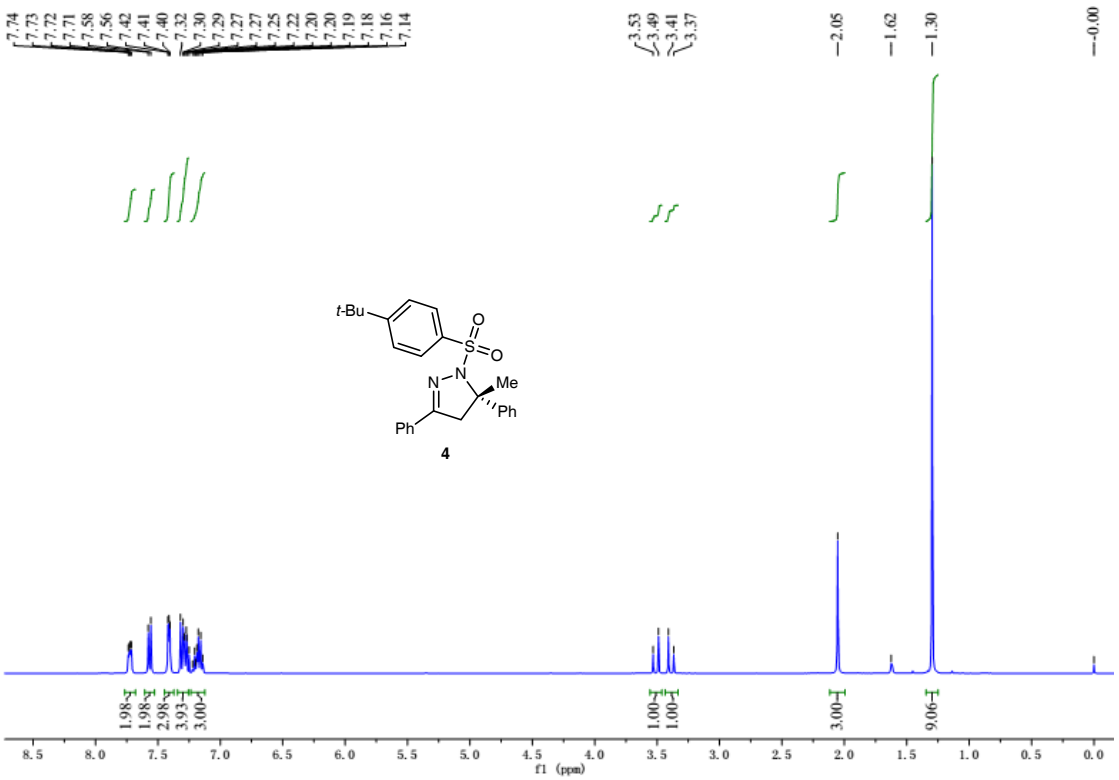
52.72
25.15
MeO
O
S
O
N
N
Me
Ph
Ph
3
f1 (ppm)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7.73
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7.41
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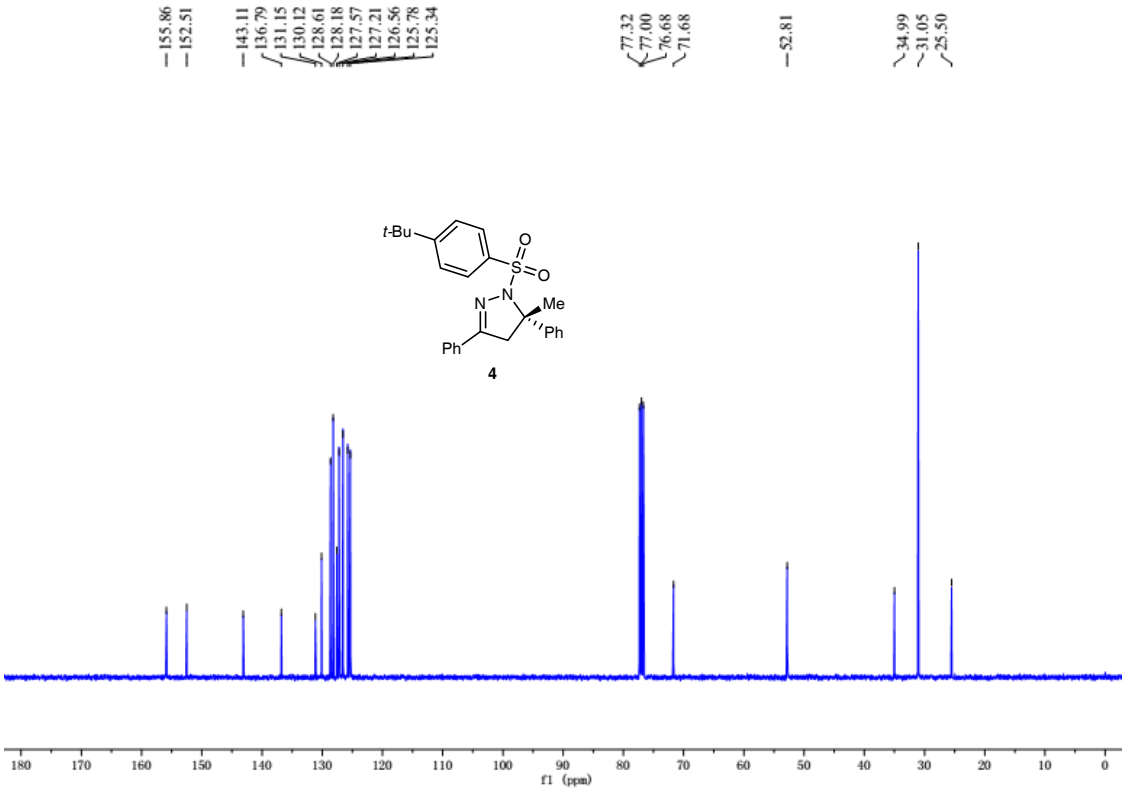
7.32
7.30
7.29
7.27
7.27
7.25
7.22
7.20
7.20
7.19
7.18
7.16
7.14
3.53
3.49
3.41
3.37
2.05
1.62
1.30
0.00
t-Bu
O
S
O
N
N
Me
Ph
Ph
4
1.98
1.98
2.98
3.93
3.00
1.00
1.00
3.00
9.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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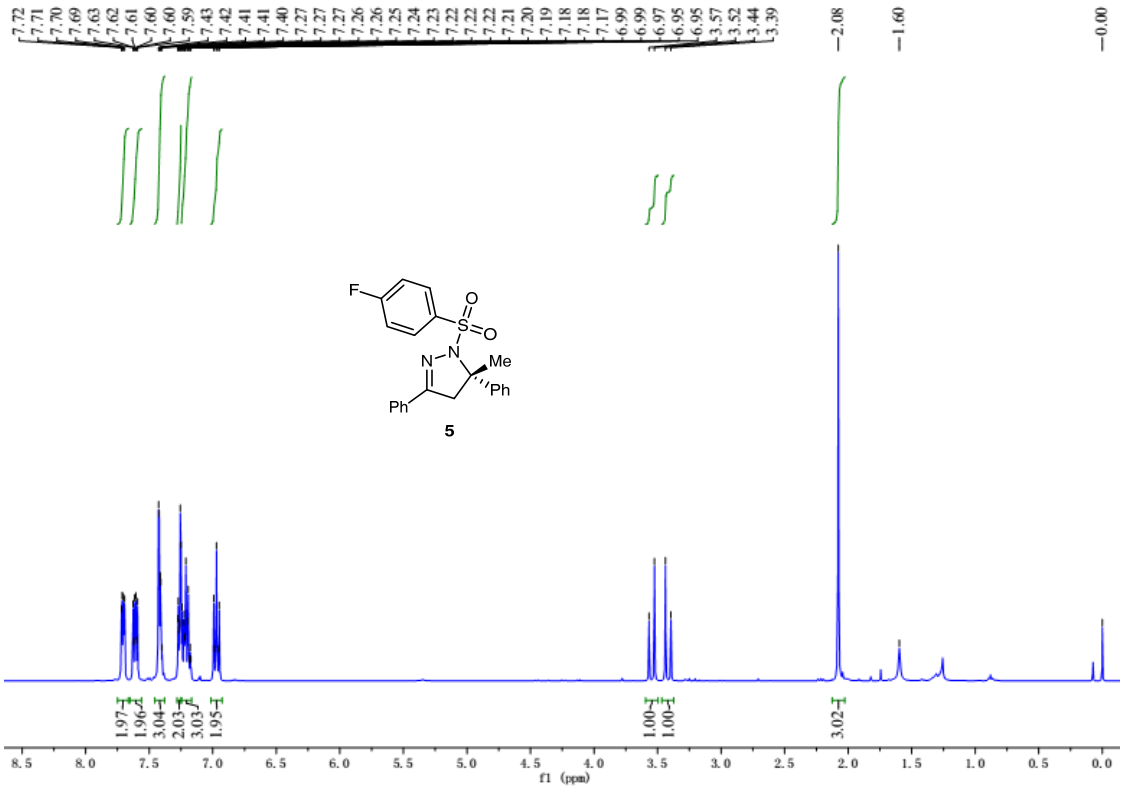
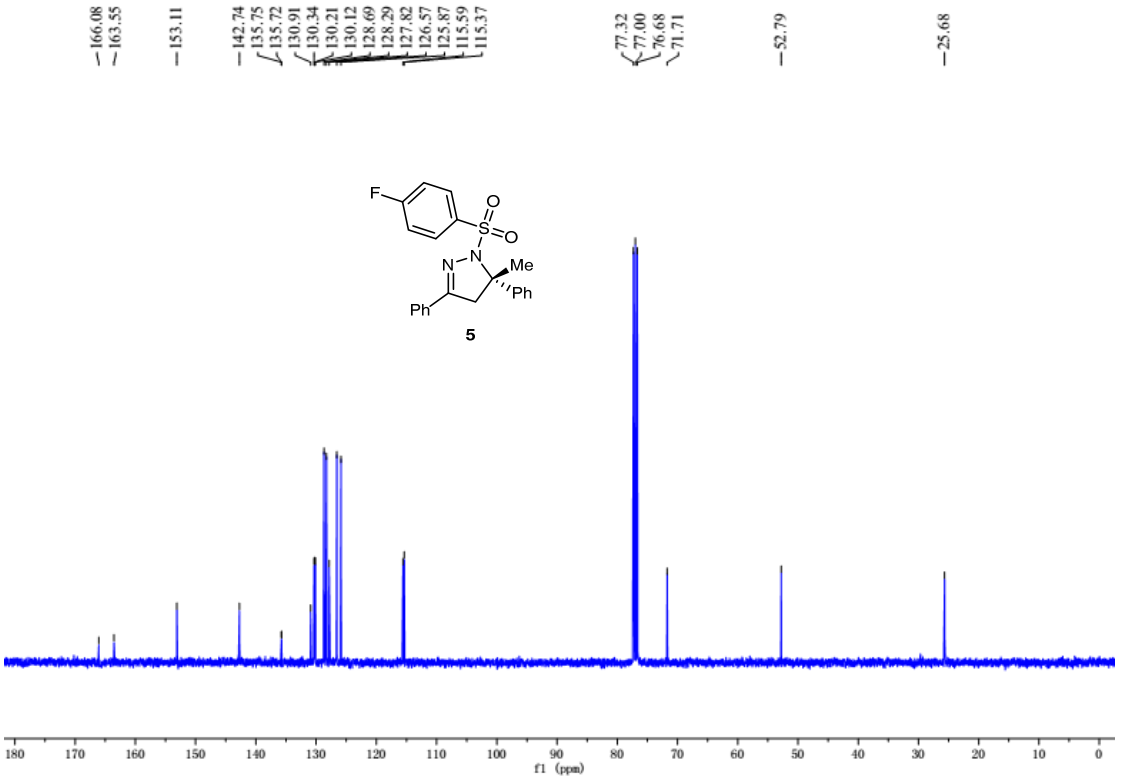
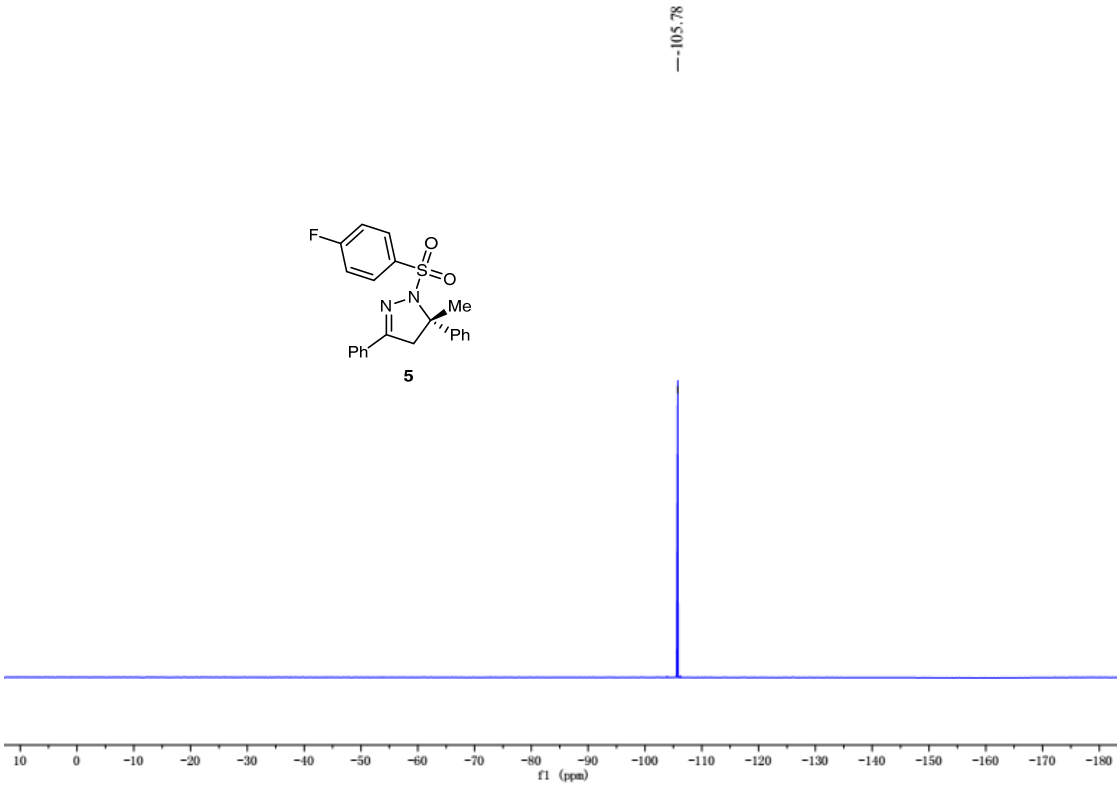
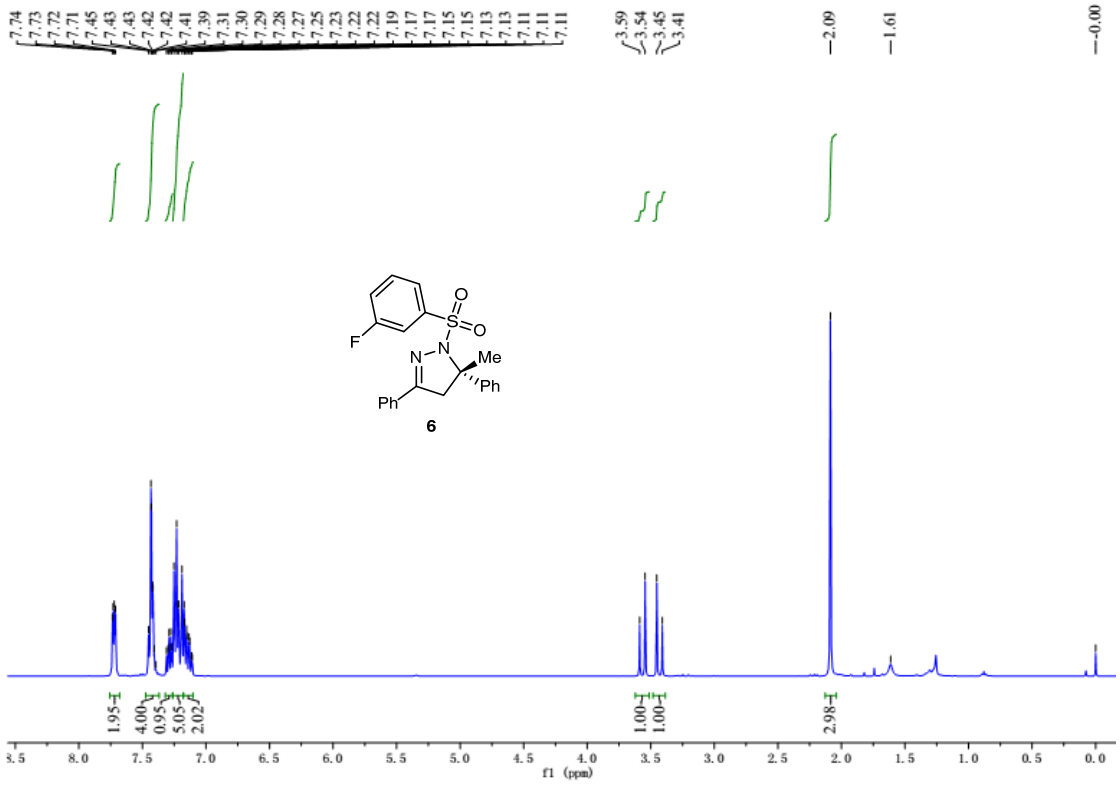
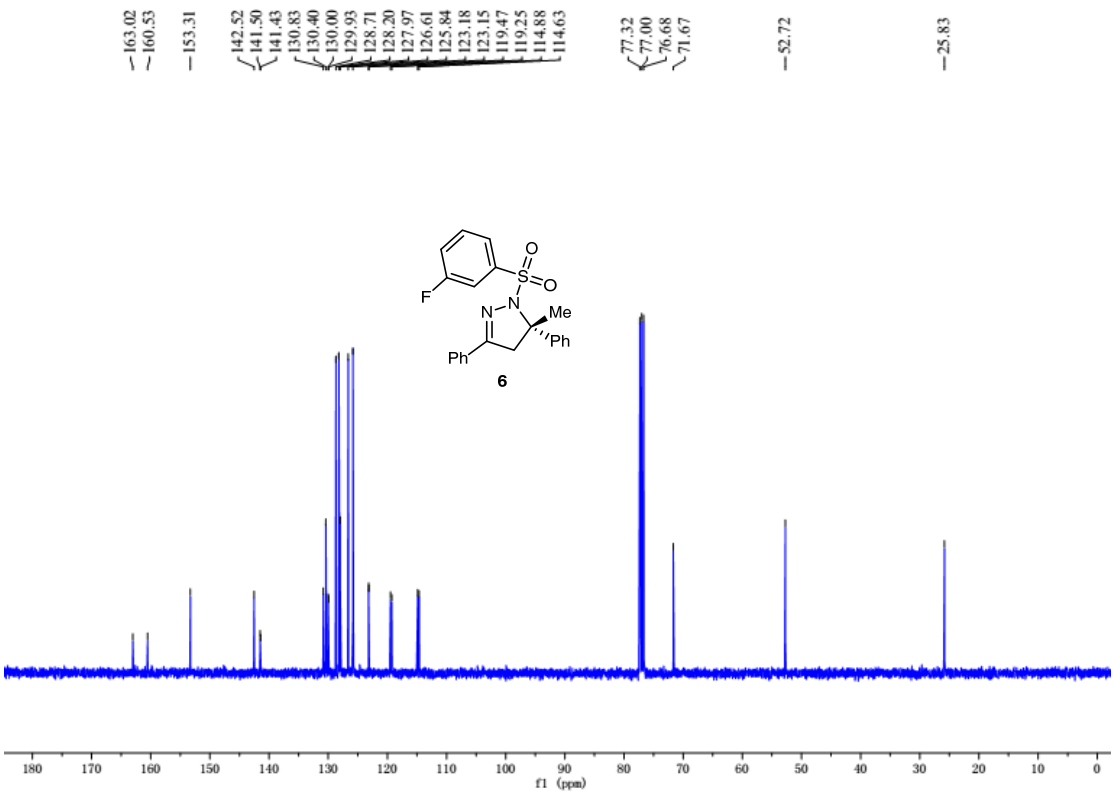
128.18
127.57
127.21
126.56
125.78
125.34
77.32
77.00
76.68
71.68
52.81
34.99
31.05
25.50
t-Bu
O
S
O
N
N
Me
Ph
Ph
4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.72 7.71 7.70 7.69 7.63 7.62 7.61 7.60 7.60 7.59 7.43 7.42 7.41 7.41 7.40 7.27 7.27 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.22 7.22 7.21 7.20 7.19 7.18 7.18 7.17 6.99 6.99 6.97 6.95 6.95 3.57 3.52 3.44 3.39
2.08
1.60
0.00
F
O
S
O
N
N
Me
Ph
Ph
5
1.97 1.96 3.04 2.03 3.03 1.95
1.00 1.00
3.02
f1 (ppm)


166.08 163.55
153.11
142.74 135.75 135.72 130.91 130.34 130.21 130.12 128.69 128.29 127.82 126.57 125.87 115.59 115.37
77.32 77.00 76.68 71.71
52.79
25.68
F
O
S
O
N
N
Me
Ph
Ph
5
f1 (ppm)


-105.78
F
O
S
O
N
N
Me
Ph
Ph
5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)


7.74 7.73 7.72 7.71 7.45 7.43 7.43 7.42 7.42 7.41 7.39 7.31 7.30 7.29 7.28 7.27 7.25 7.23 7.22 7.22 7.19 7.17 7.17 7.15 7.15 7.13 7.13 7.11 7.11 7.11
3.59 3.54 3.45 3.41
2.09
1.61
0.00
F
O
S
O
N
N
Me
Ph
Ph
6
1.95 4.00 0.95 5.05 2.02
1.00 1.00
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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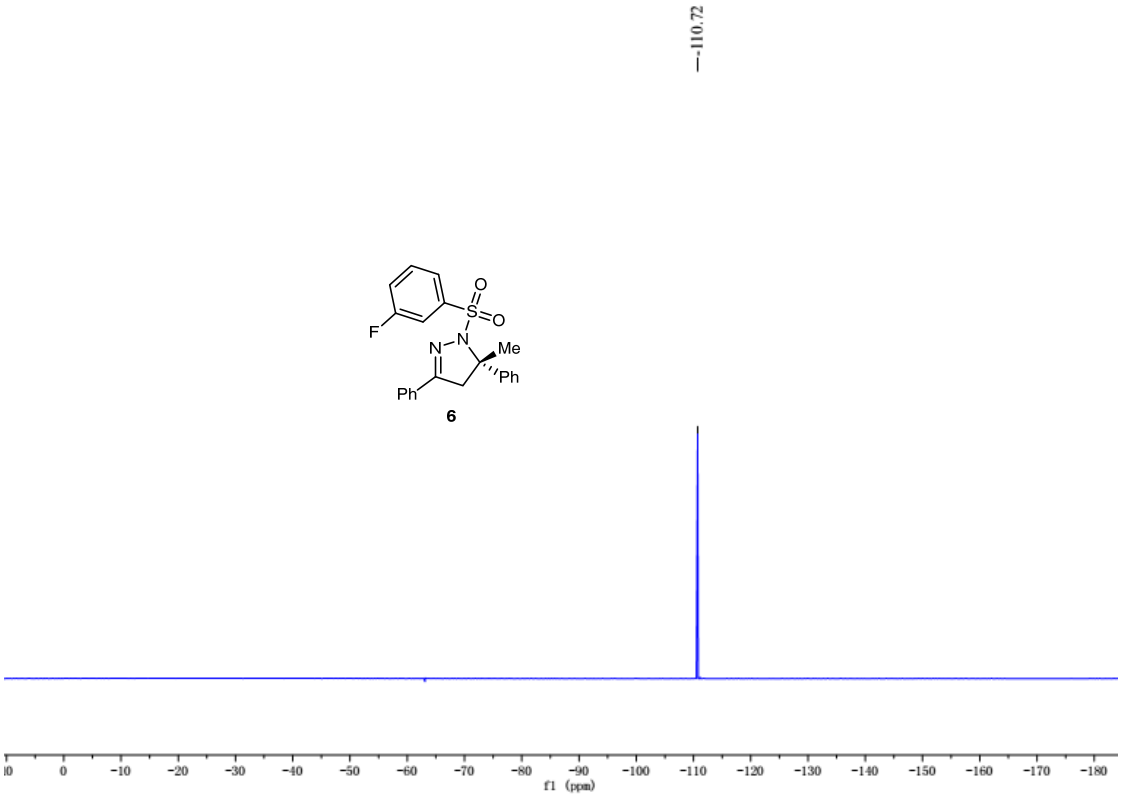
130.40
130.00
129.93
128.71
128.20
127.97
126.61
125.84
123.18
123.15
119.47
119.25
114.88
114.63
77.32
77.00
76.68
71.67
52.72
25.83
F
O
S
O
N
N
Me
Ph
Ph
6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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F
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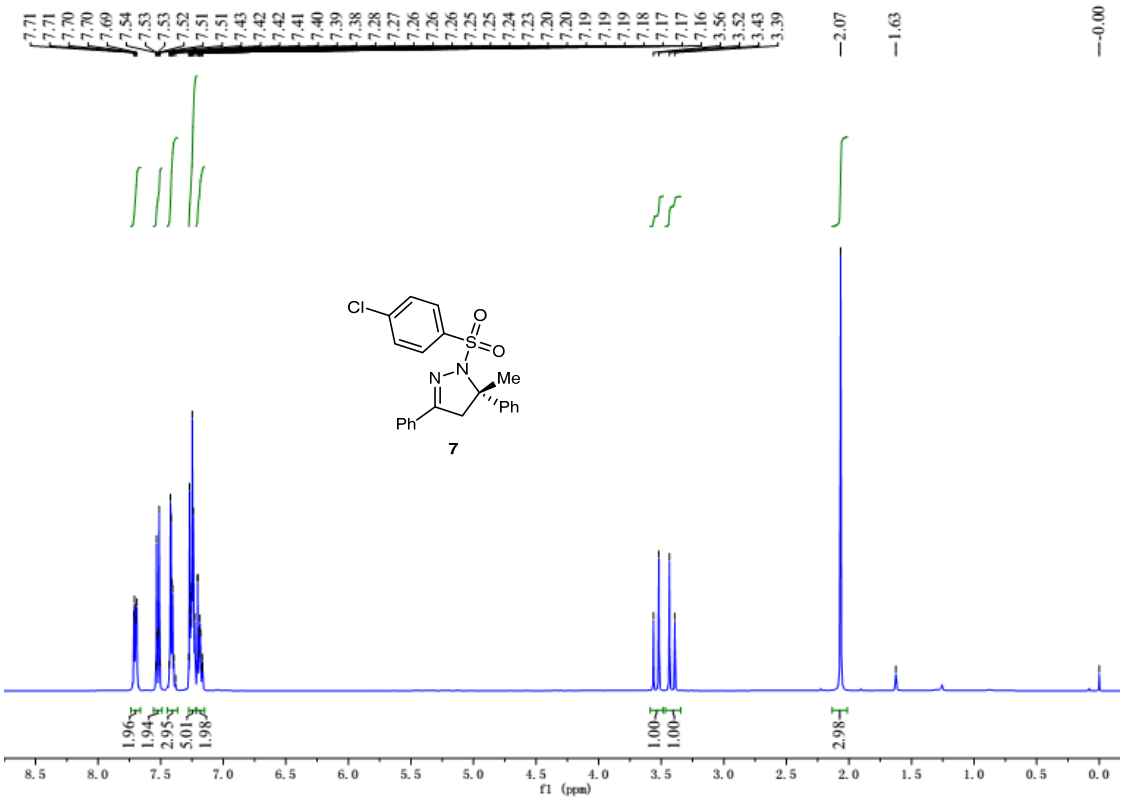
S
O
N
N
Me
Ph
Ph
6
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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7.51
7.43
7.42
7.42
7.41
7.40
7.39
7.38
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.20
7.20
7.19
7.19
7.19
7.18
7.17
7.17
7.16
3.56
3.52
3.43
3.39
2.07
1.63
0.00
Cl
O
S
O
N
N
Me
Ph
Ph
7
1.96
1.94
2.95
5.01
1.98
1.00
1.00
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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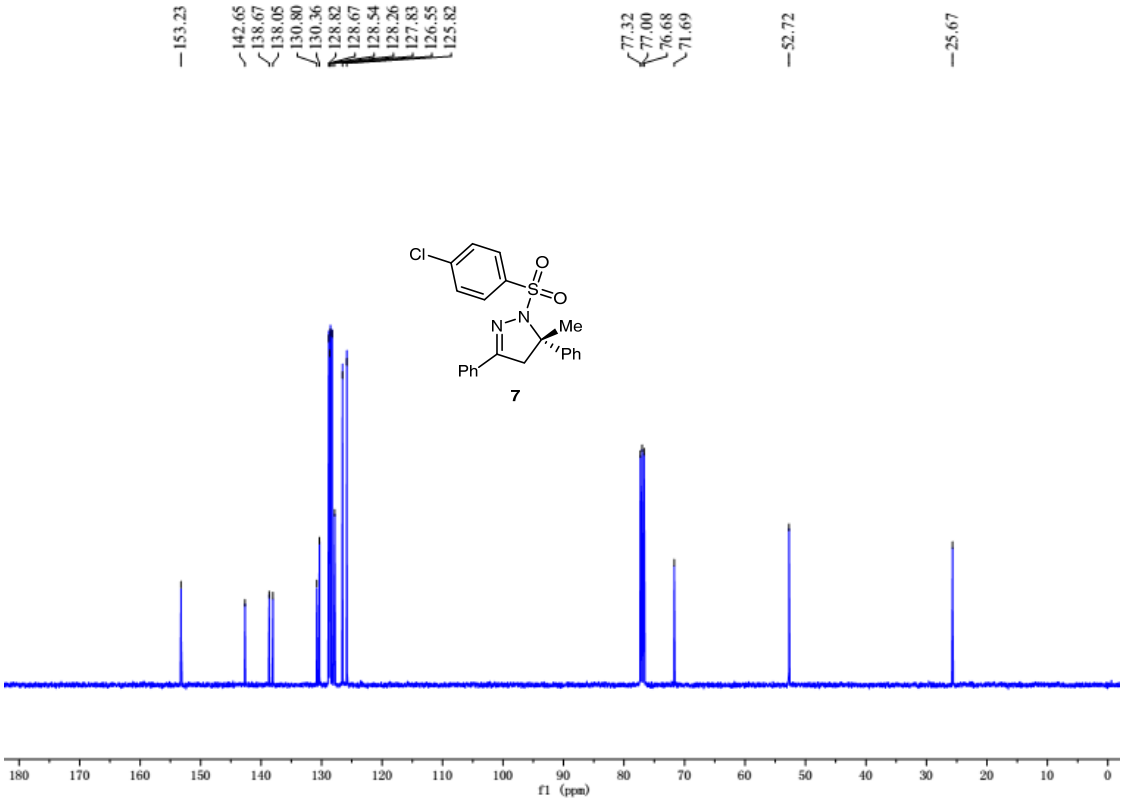
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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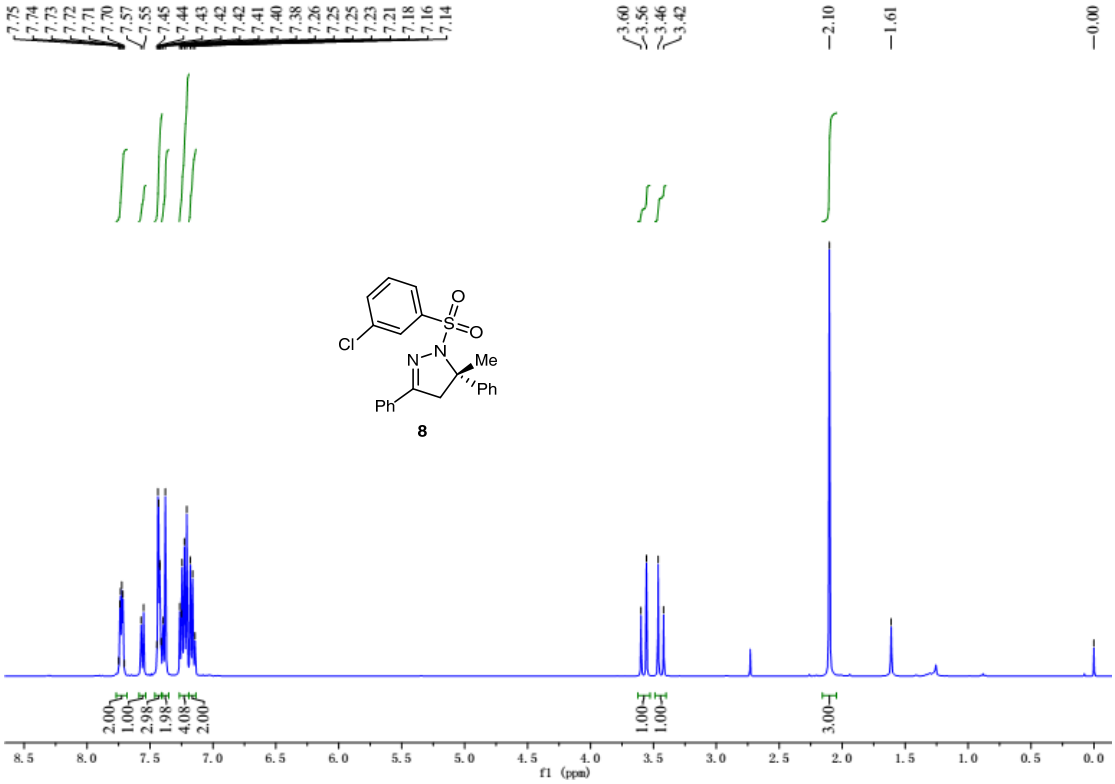
128.54
128.26
127.83
126.55
125.82
77.32
77.00
76.68
71.69
52.72
25.67
Cl
O
S
O
N
N
Me
Ph
Ph
7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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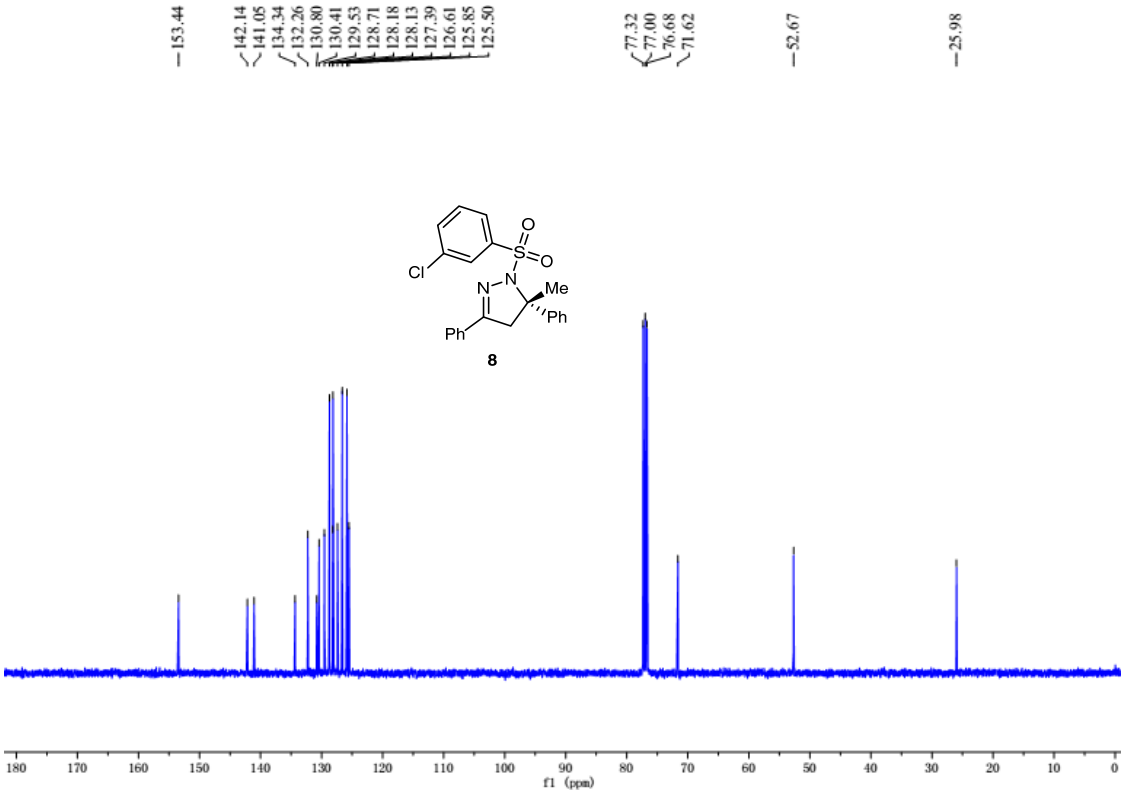
7.42
7.42
7.41
7.40
7.38
7.26
7.25
7.25
7.23
7.21
7.18
7.16
7.14
3.60
3.56
3.46
3.42
2.10
1.61
0.00
Cl
S
O
O
N
N
Me
Ph
Ph
8
2.00
1.00
2.98
1.98
4.08
2.00
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.53
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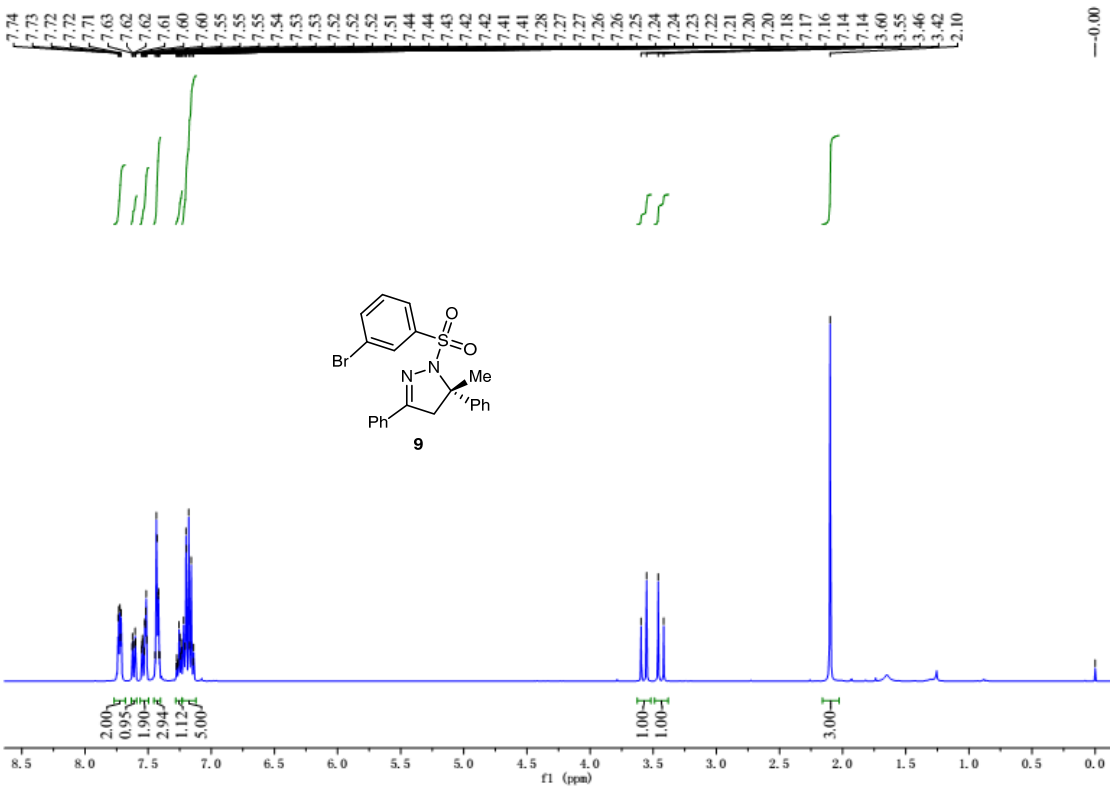
128.18
128.13
127.39
126.61
125.85
125.50
77.32
77.00
76.68
71.62
52.67
25.98
Cl
S
O
O
N
N
Me
Ph
Ph
8
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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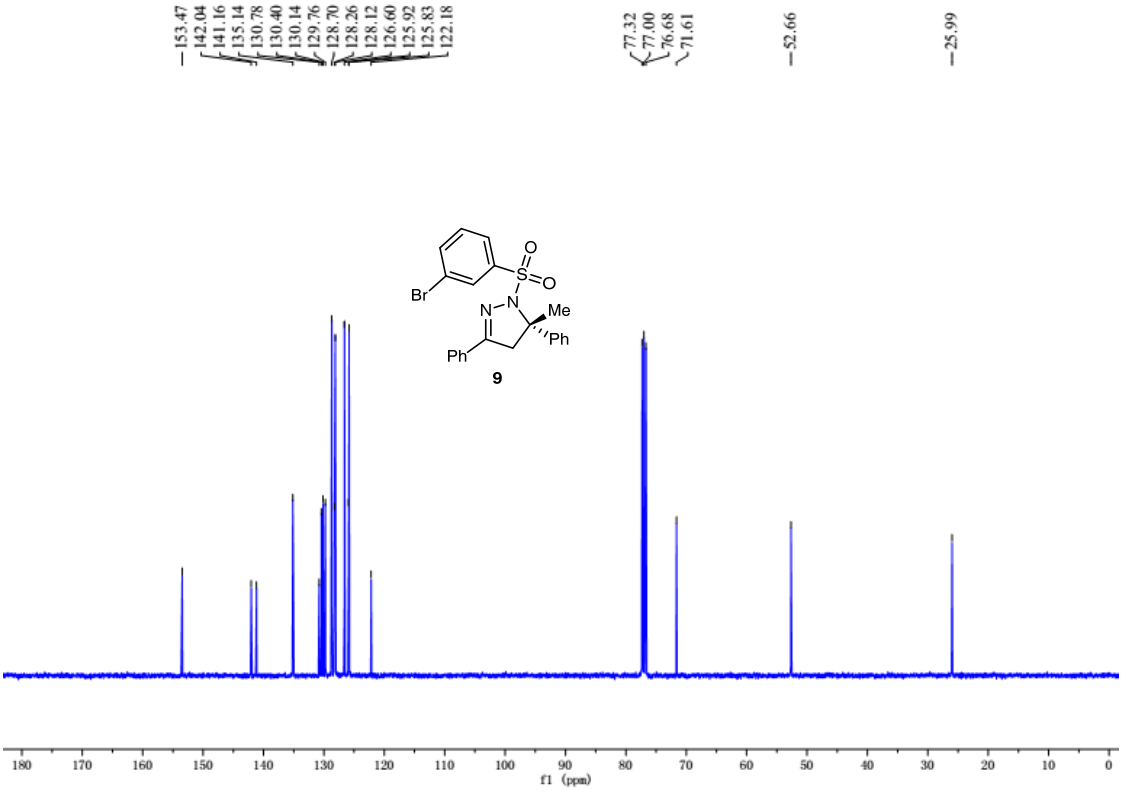
7.73
7.72
7.72
7.71
7.63
7.62
7.62
7.61
7.60
7.60
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.18
7.17
7.16
7.14
7.14
3.60
3.55
3.46
3.42
2.10
0.00
Br
O
S
O
N
N
Me
Ph
Ph
9
2.00
0.95
1.90
2.94
1.12
5.00
1.00
1.00
3.00
f1 (ppm)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129.76
128.70
128.26
128.12
126.60
125.92
125.83
122.18
77.32
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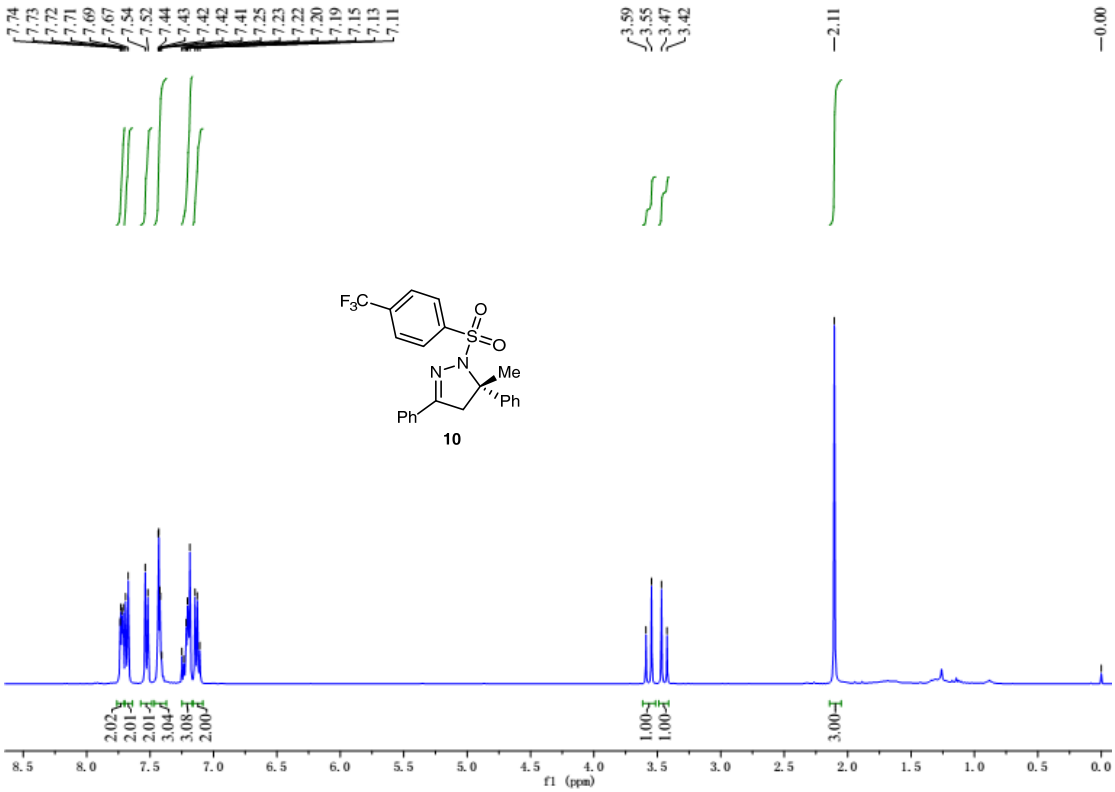
52.66
25.99
Br
O
S
O
N
N
Me
Ph
Ph
9
f1 (ppm)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7.73
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7.71
7.69
7.67
7.54
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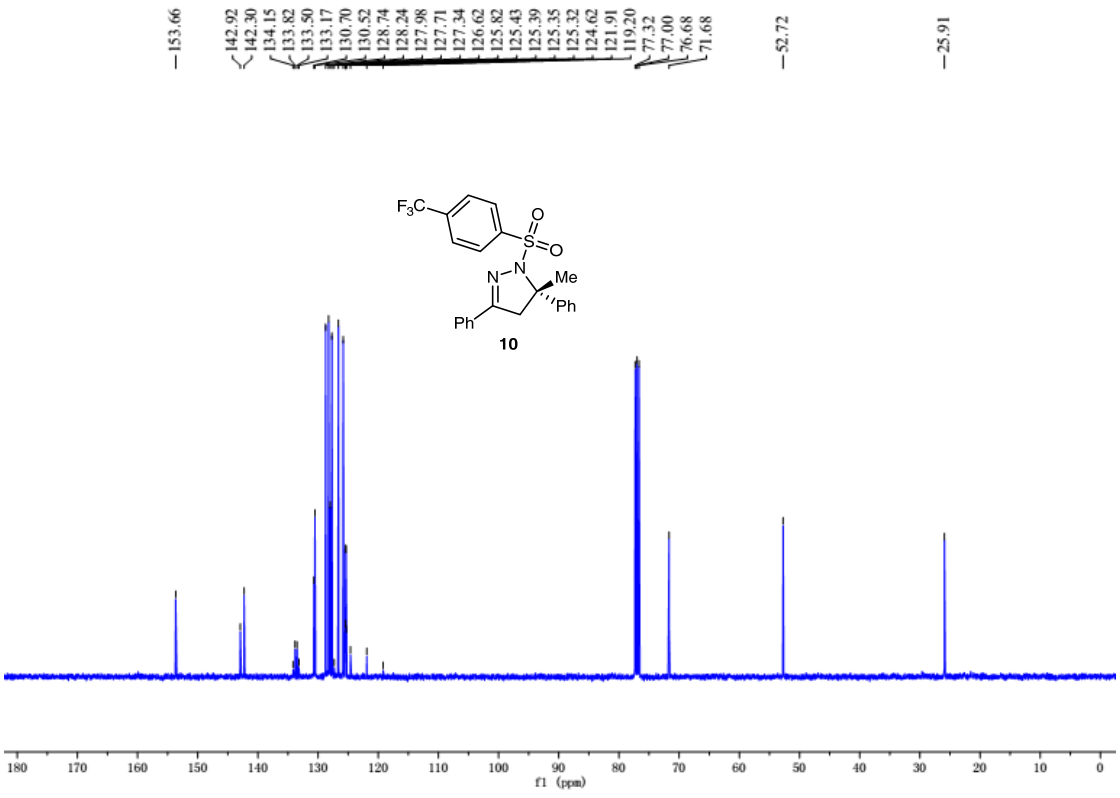
7.44
7.43
7.42
7.42
7.41
7.25
7.23
7.22
7.20
7.19
7.15
7.13
7.11
3.59
3.55
3.47
3.42
2.11
0.00
F3C
O
S
O
N
N
Me
Ph
Ph
10
2.02
2.01
2.01
3.04
3.08
2.00
1.00
1.00
3.00
f1 (ppm)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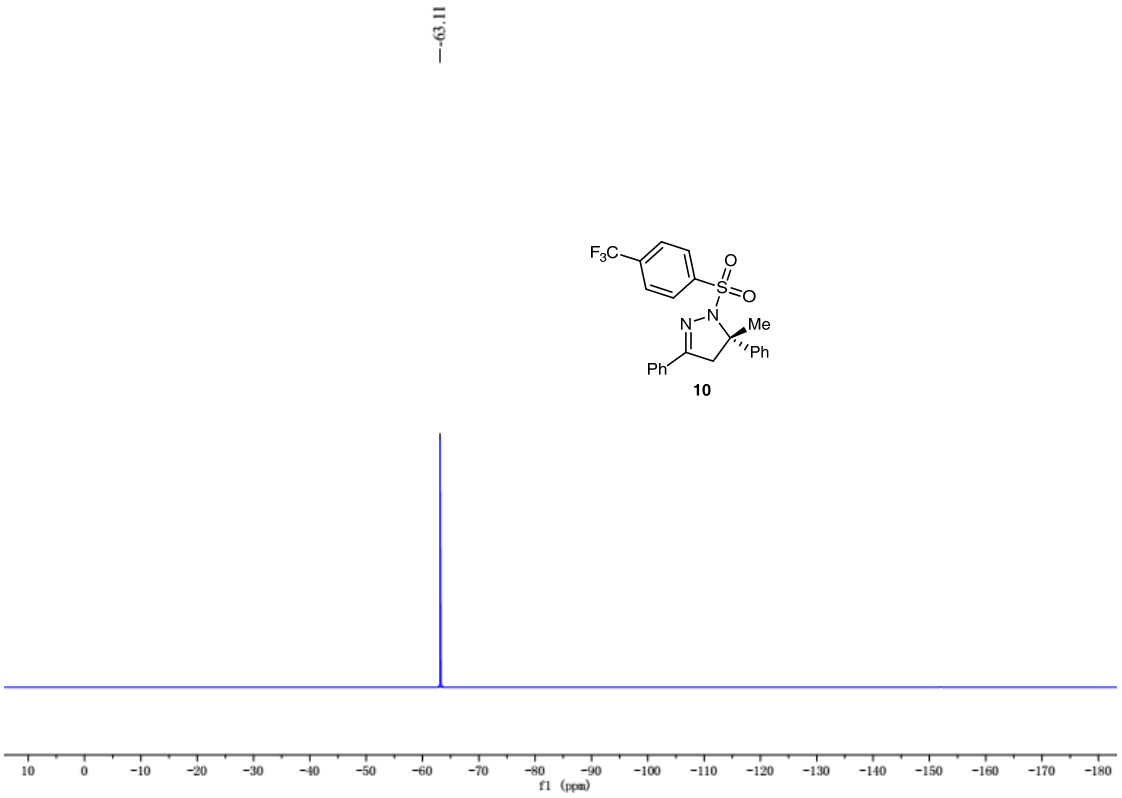
127.71
127.34
126.62
125.82
125.43
125.39
125.35
125.32
124.62
121.91
119.20
77.32
77.00
76.68
71.68
52.72
25.91
F3C
O
S
O
N
N
Me
Ph
Ph
10
f1 (ppm)


-63.11
F3C
O
S
O
N
N
Me
Ph
Ph
10
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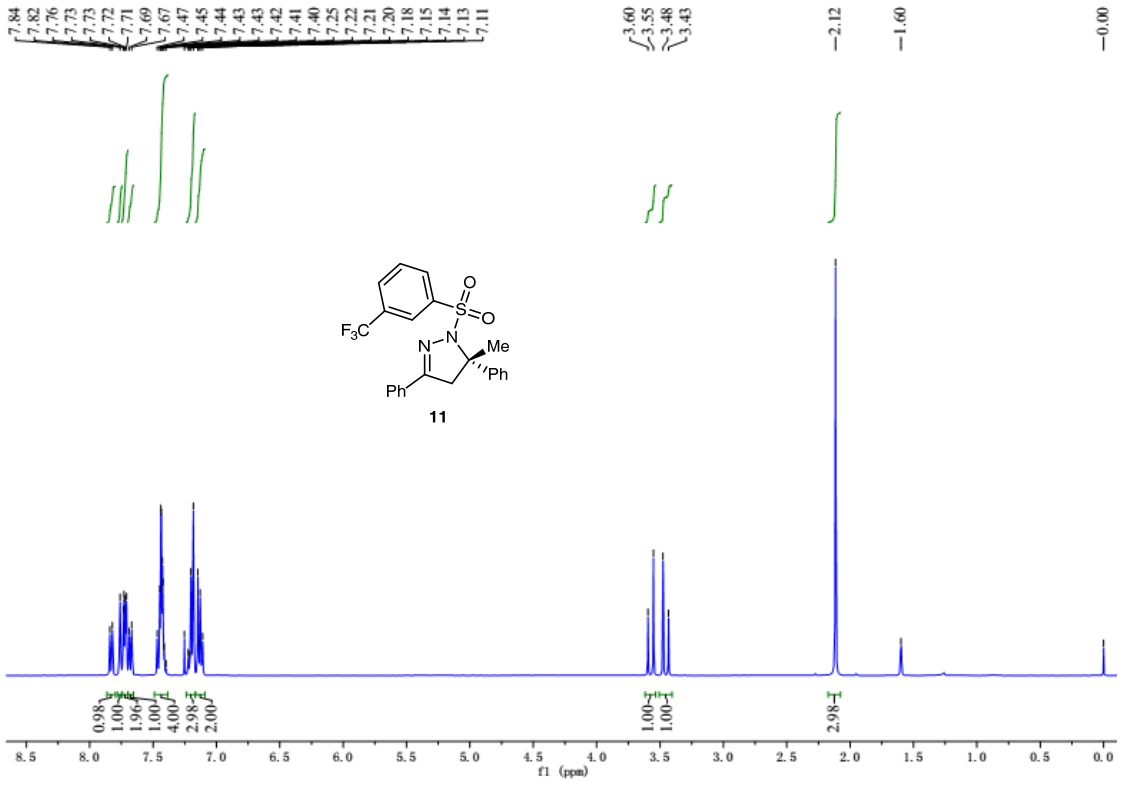
f1 (ppm)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7.67
7.47
7.45
7.44
7.43
7.43
7.42
7.41
7.40
7.25
7.22
7.21
7.20
7.18
7.15
7.14
7.13
7.11
3.60
3.55
3.48
3.43
2.12
1.60
0.00
F3C
O
S
O
N
N
Me
Ph
Ph
11
0.98
1.00
1.96
1.00
4.00
2.98
2.00
1.00
1.00
2.98
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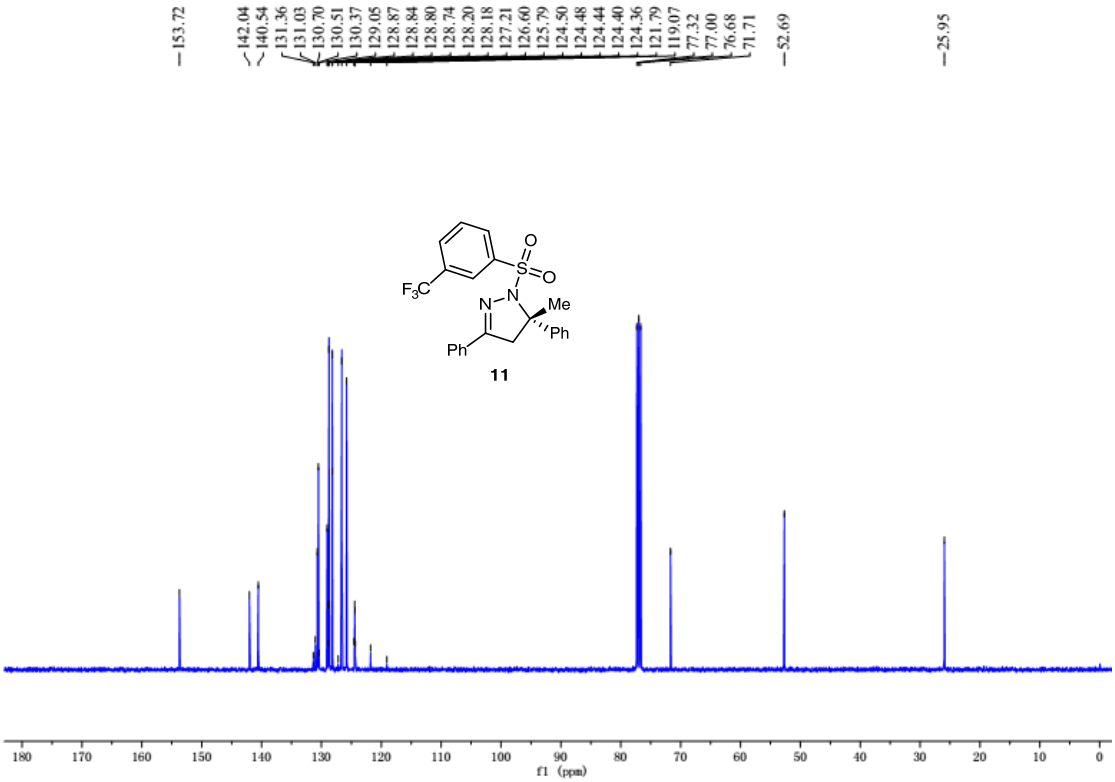
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128.74
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128.18
127.21
126.60
125.79
124.50
124.48
124.44
124.40
124.36
121.79
119.07
77.32
77.00
76.68
71.71
52.69
25.95
F3C
S
O
O
N
N
Me
Ph
Ph
11
180
170
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140
130
120
110
100
90
80
70
60
50
40
30
20
10
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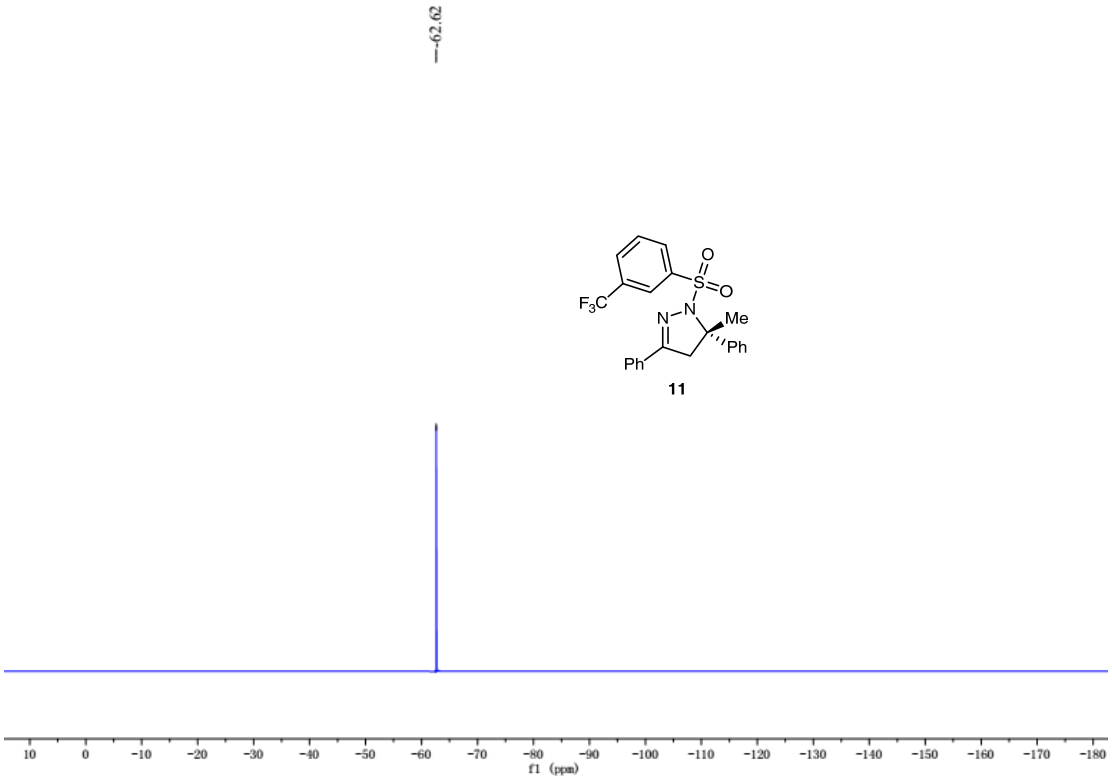
f1 (ppm)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F3C
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O
O
N
N
Me
Ph
Ph
11
10
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-10
-20
-30
-40
-50
-60
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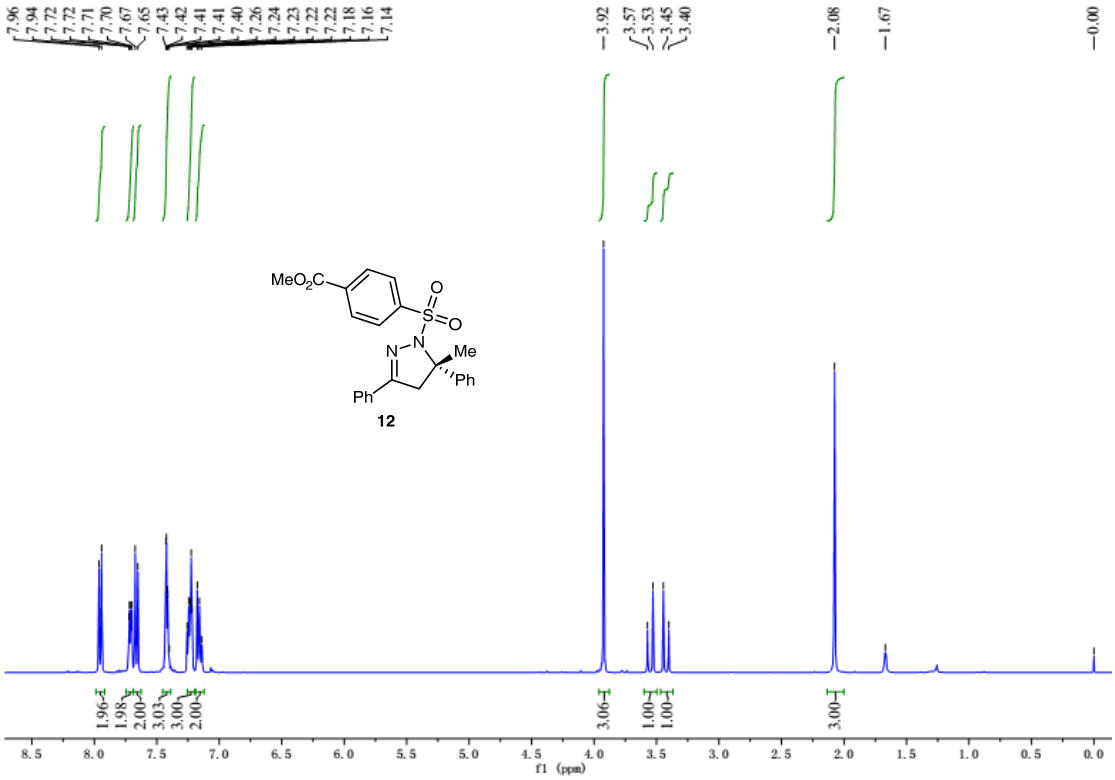
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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7.41
7.40
7.26
7.24
7.23
7.22
7.22
7.18
7.16
7.14
3.92
3.57
3.53
3.45
3.40
2.08
1.67
0.00
MeO2C
O
S
O
N
N
Me
Ph
Ph
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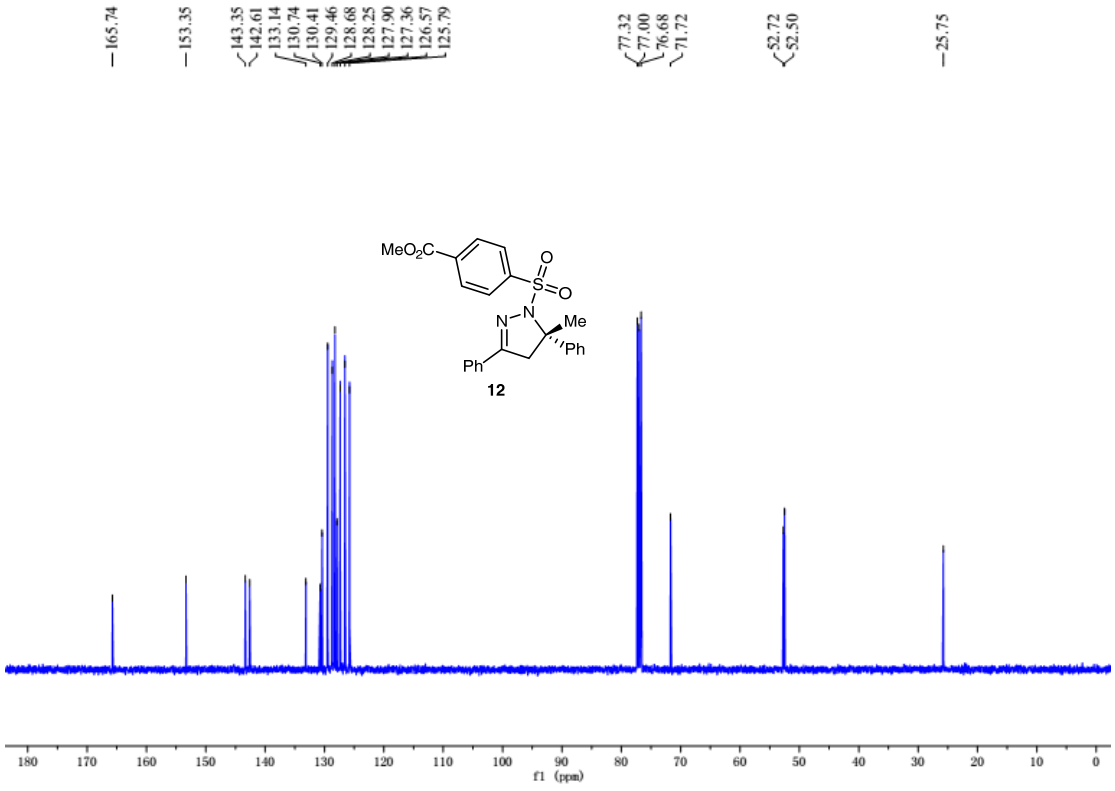
1.98
2.00
3.03
3.00
2.00
3.06
1.00
1.00
3.00
f1 (ppm)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128.25
127.90
127.36
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125.79
77.32
77.00
76.68
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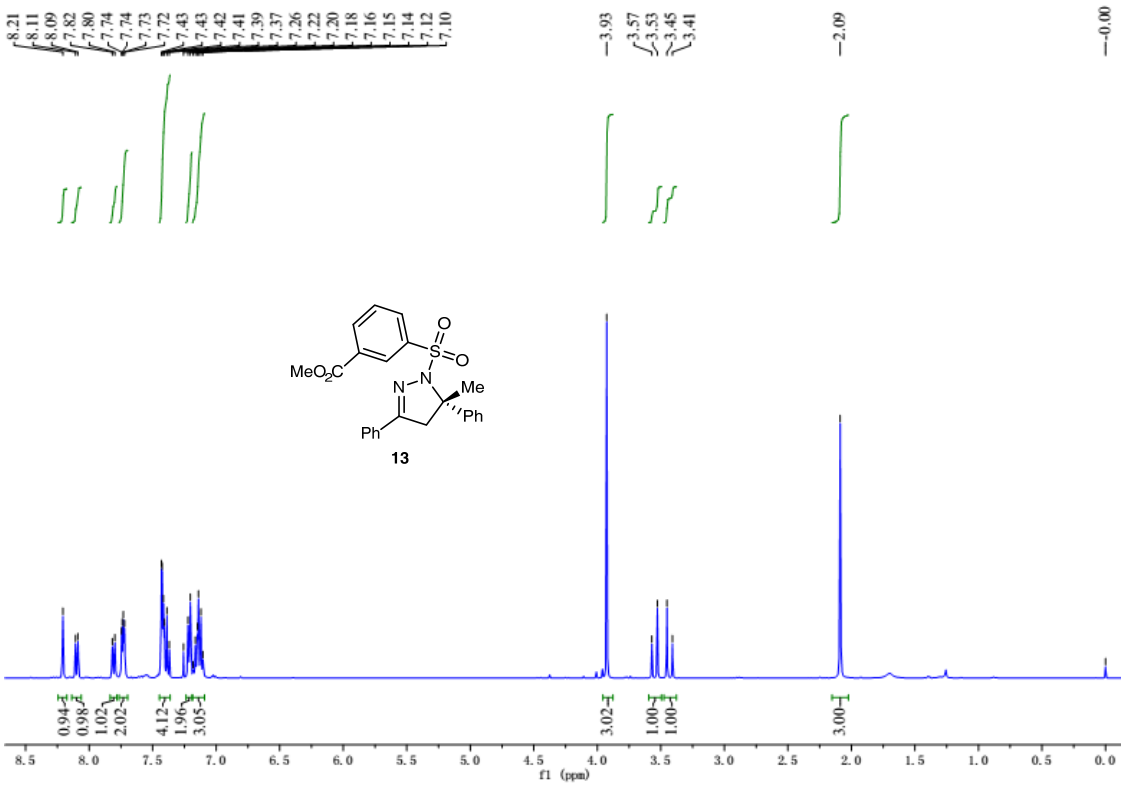
25.75
MeO2C
O
S
O
N
N
Me
Ph
Ph
12
f1 (ppm)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7.74
7.73
7.72
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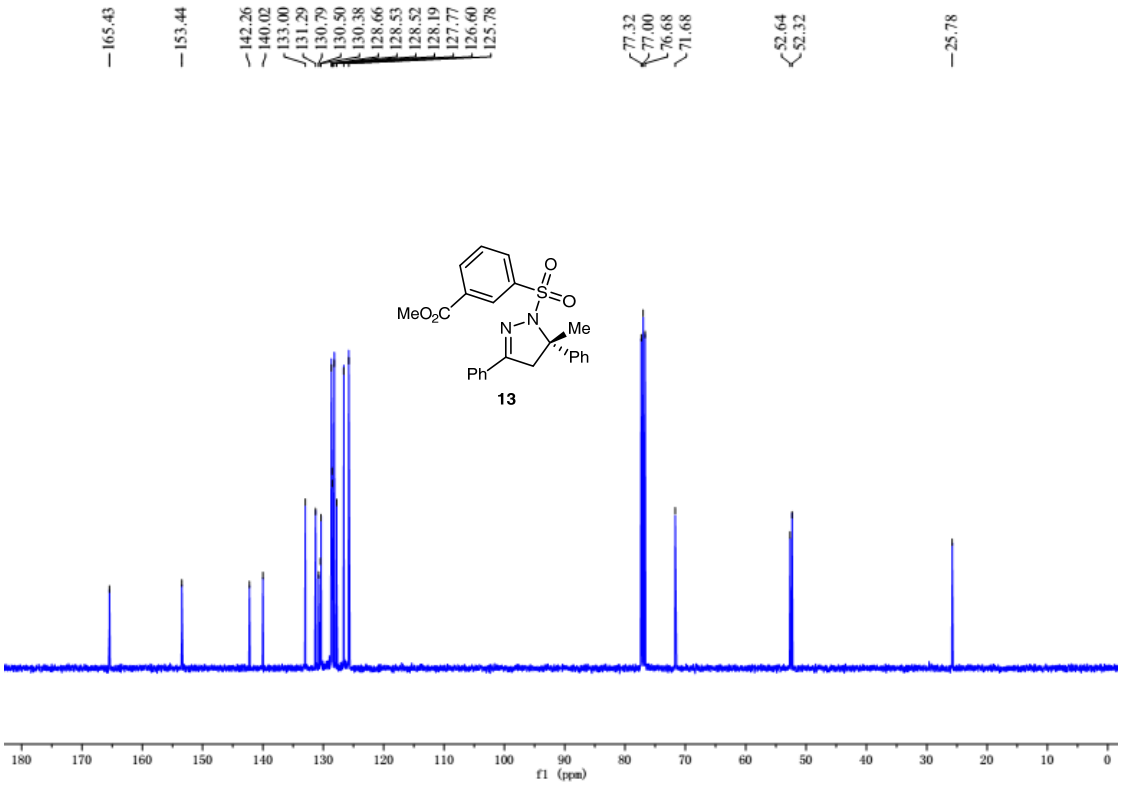
7.43
7.42
7.41
7.39
7.37
7.26
7.22
7.20
7.18
7.16
7.15
7.14
7.12
7.10
3.93
3.57
3.53
3.45
3.41
2.09
0.00
MeO2C
S
O
O
N
N
Me
Ph
Ph
13
0.94
0.98
1.02
2.02
4.12
1.96
3.05
3.02
1.00
1.00
3.00
f1 (ppm)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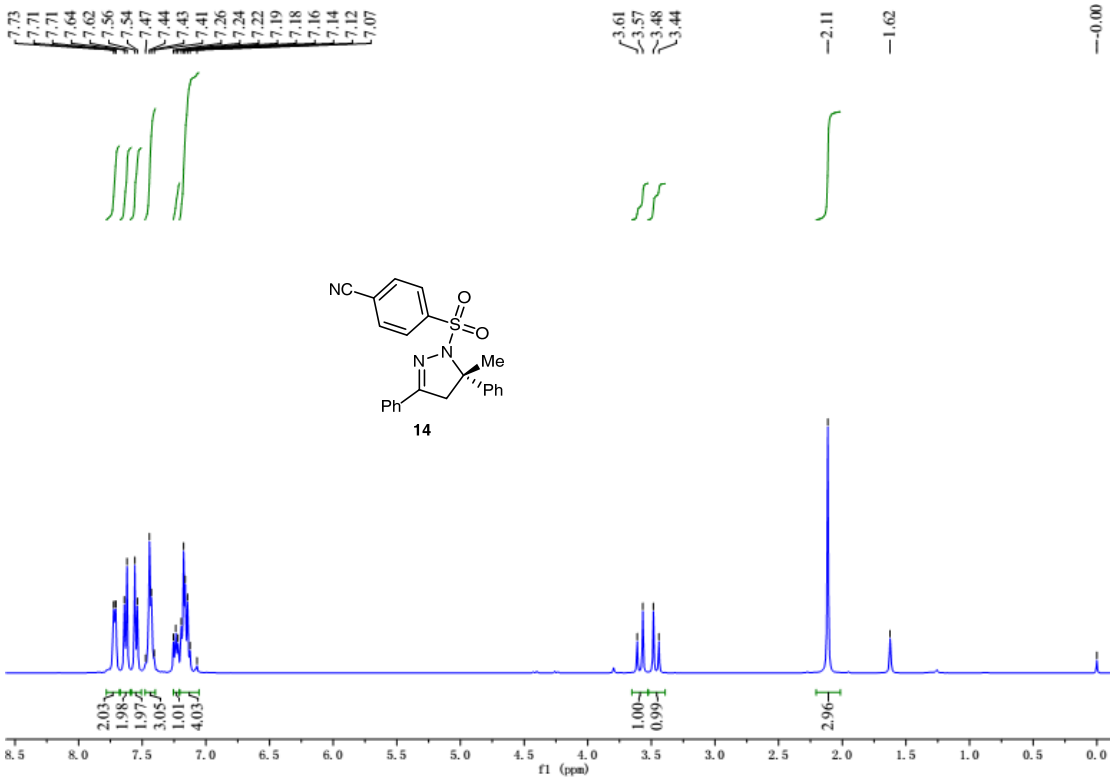
128.66
128.53
128.52
128.19
127.77
126.60
125.78
77.32
77.00
76.68
71.68
52.64
52.32
25.78
MeO2C
S
O
O
N
N
Me
Ph
Ph
13
f1 (ppm)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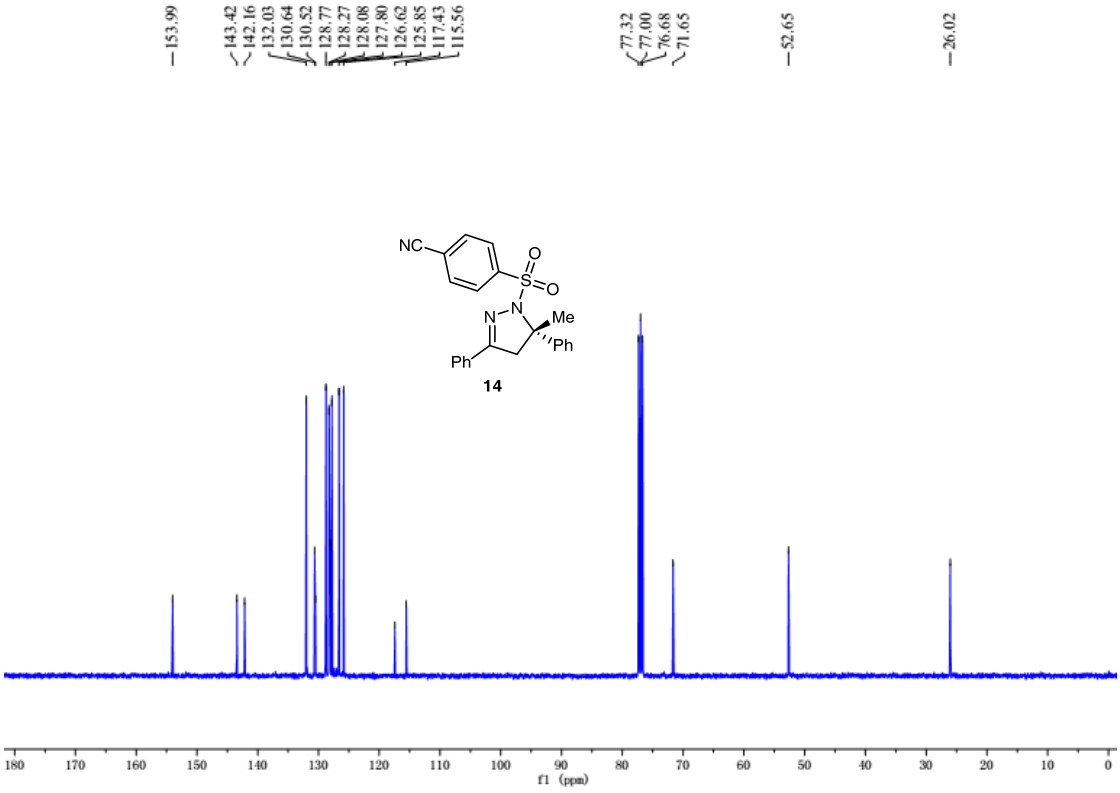
7.71
7.71
7.64
7.62
7.56
7.54
7.47
7.44
7.43
7.41
7.26
7.24
7.22
7.19
7.18
7.16
7.14
7.12
7.07
3.61
3.57
3.48
3.44
2.11
1.62
0.00
NC
O
S
O
N
N
Me
Ph
Ph
14
2.03
1.98
1.97
3.05
1.01
4.03
1.00
0.99
2.96
f1 (ppm)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143.42
142.16
132.03
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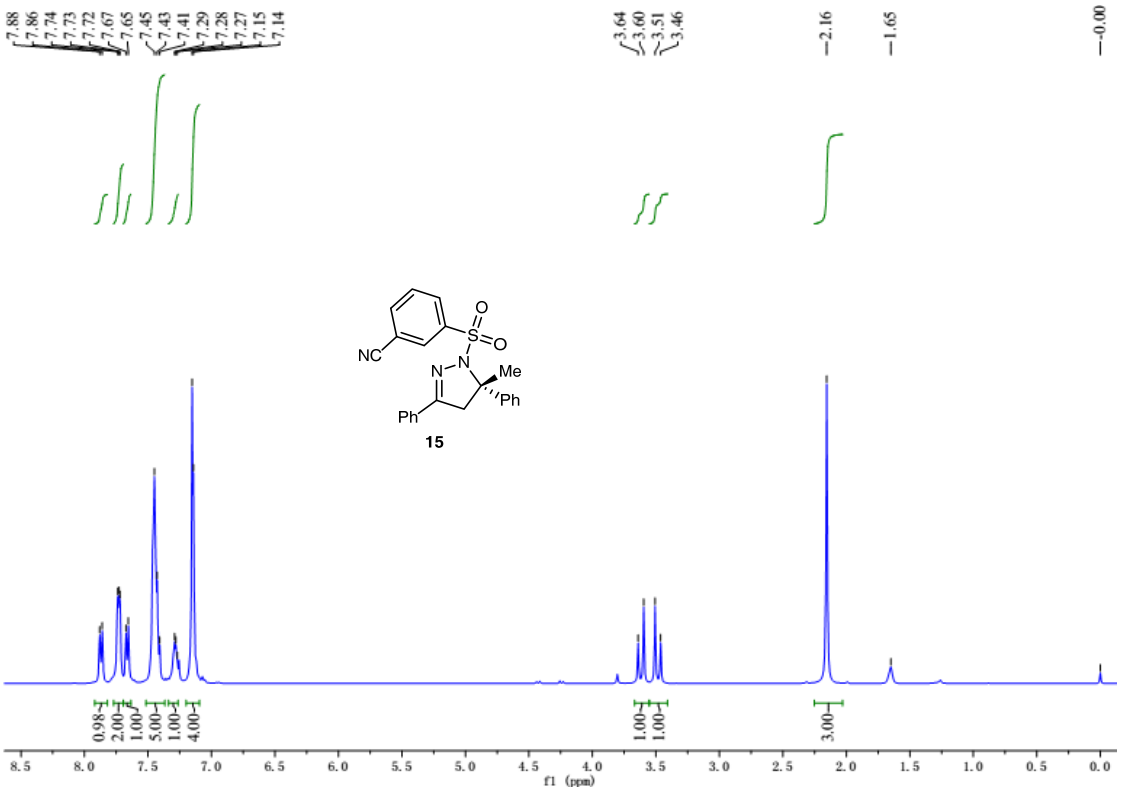
130.52
128.77
128.27
128.08
127.80
126.62
125.85
117.43
115.56
77.32
77.00
76.68
71.65
52.65
26.02
NC
O
S
O
N
N
Me
Ph
Ph
14
f1 (ppm)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7.67
7.65
7.45
7.43
7.41
7.29
7.28
7.27
7.15
7.14
3.64
3.60
3.51
3.46
2.16
1.65
0.00
NC
O
S
O
N
N
Me
Ph
Ph
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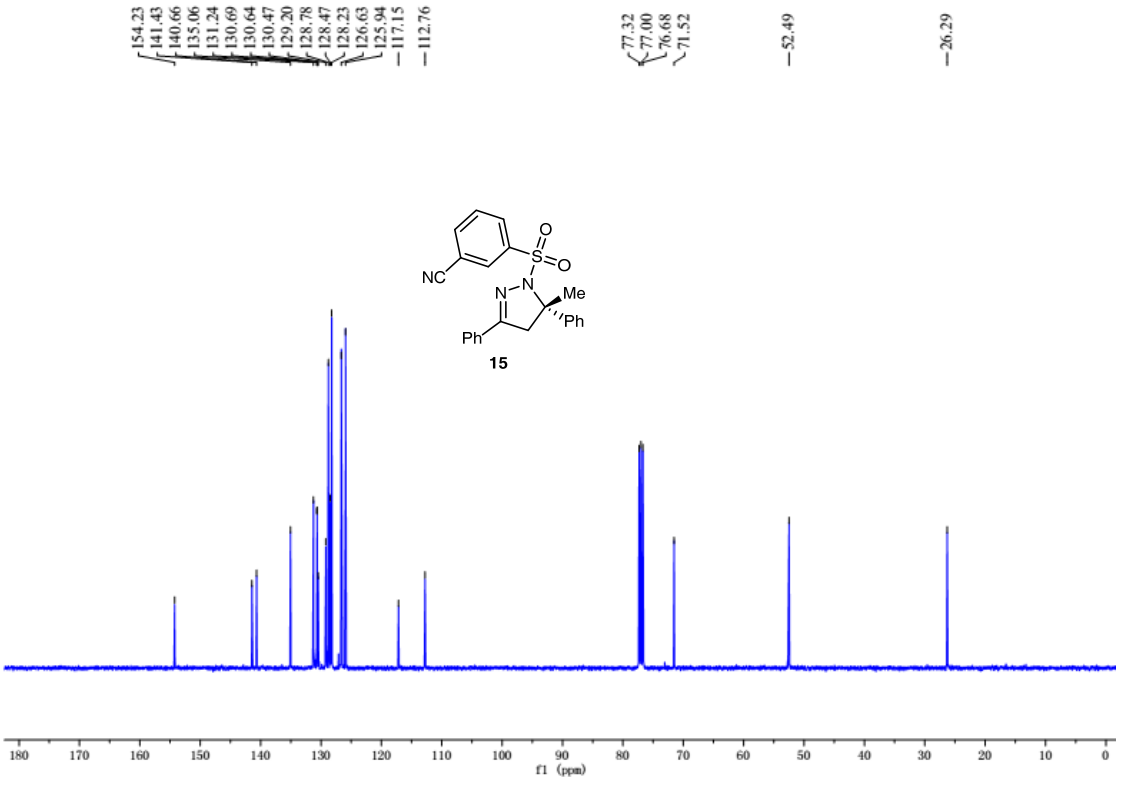
0.98
2.00
1.00
5.00
1.00
4.00
1.00
1.00
3.00
f1 (ppm)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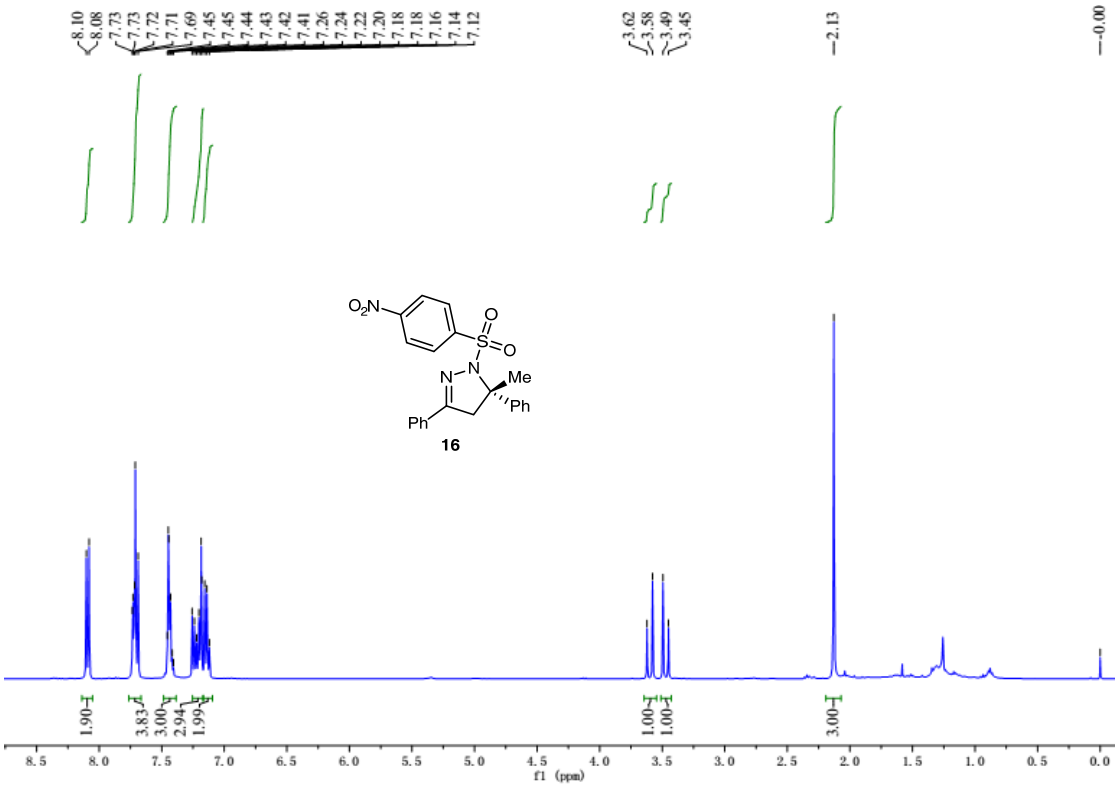
140.66
135.06
131.24
130.69
130.64
130.47
129.20
128.78
128.47
128.23
126.63
125.94
117.15
112.76
77.32
77.00
76.68
71.52
52.49
26.29
NC
O
S
O
N
N
Me
Ph
Ph
15
f1 (ppm)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8.08
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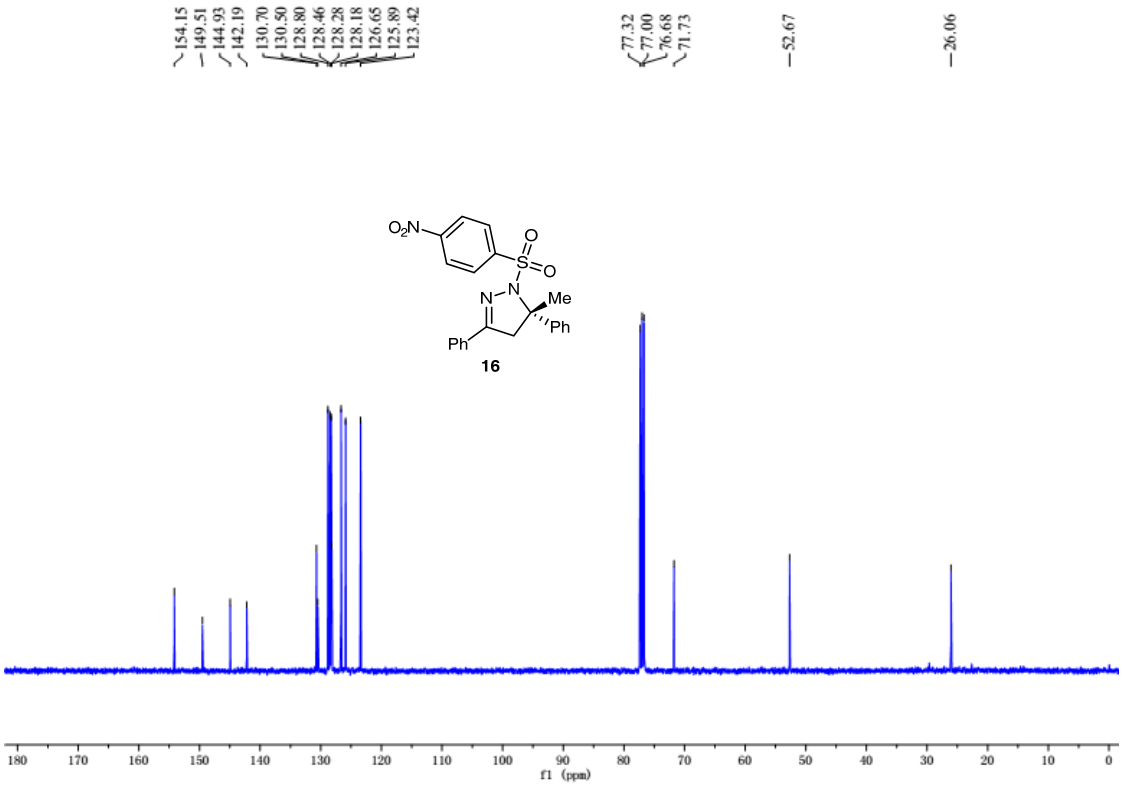
7.72
7.71
7.69
7.45
7.44
7.43
7.42
7.41
7.26
7.24
7.22
7.20
7.18
7.16
7.14
7.12
3.62
3.58
3.49
3.45
2.13
0.00
O2N
S
O
O
N
N
Me
Ph
Ph
16
1.90
3.83
3.00
2.94
1.99
1.00
1.00
3.00
f1 (ppm)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130.50
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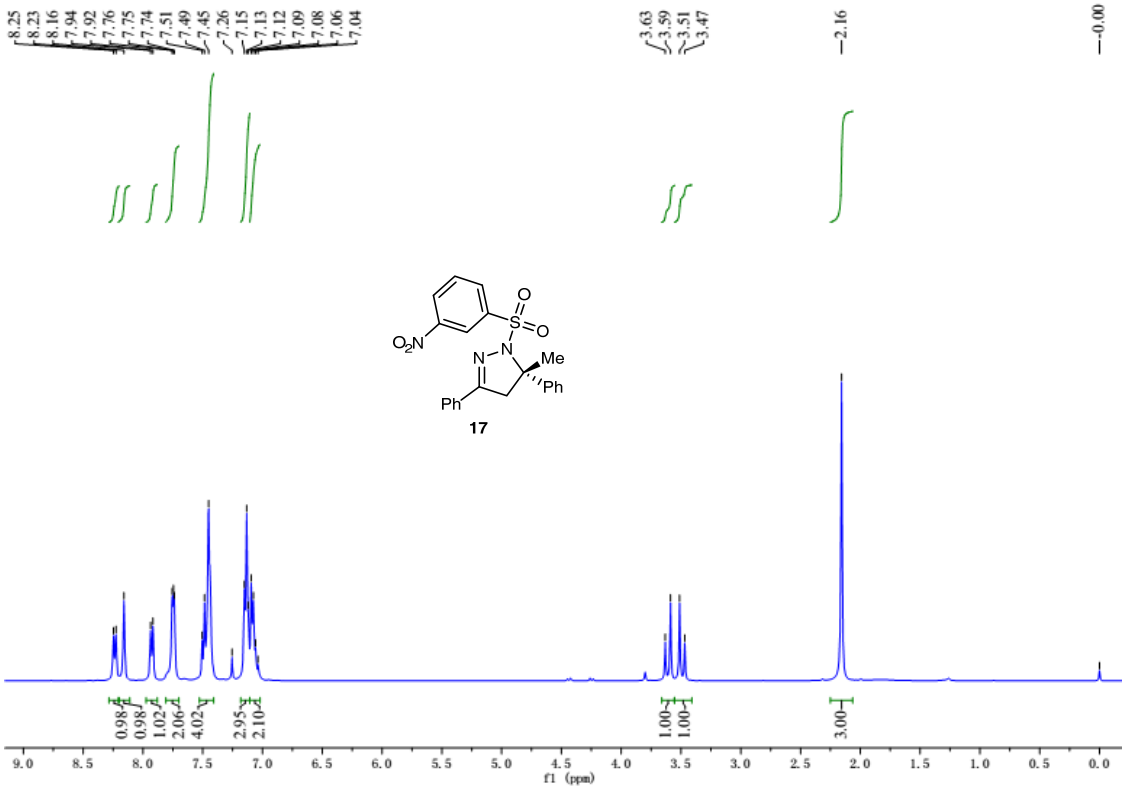
128.46
128.28
128.18
126.65
125.89
123.42
77.32
77.00
76.68
71.73
52.67
26.06
O2N
S
O
O
N
N
Me
Ph
Ph
16
f1 (ppm)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8.23
8.16
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7.92
7.76
7.75
7.74
7.51
7.49
7.45
7.26
7.15
7.13
7.12
7.09
7.08
7.06
7.04
3.63
3.59
3.51
3.47
2.16
-0.00
O2N
S
O
O
N
N
Me
Ph
Ph
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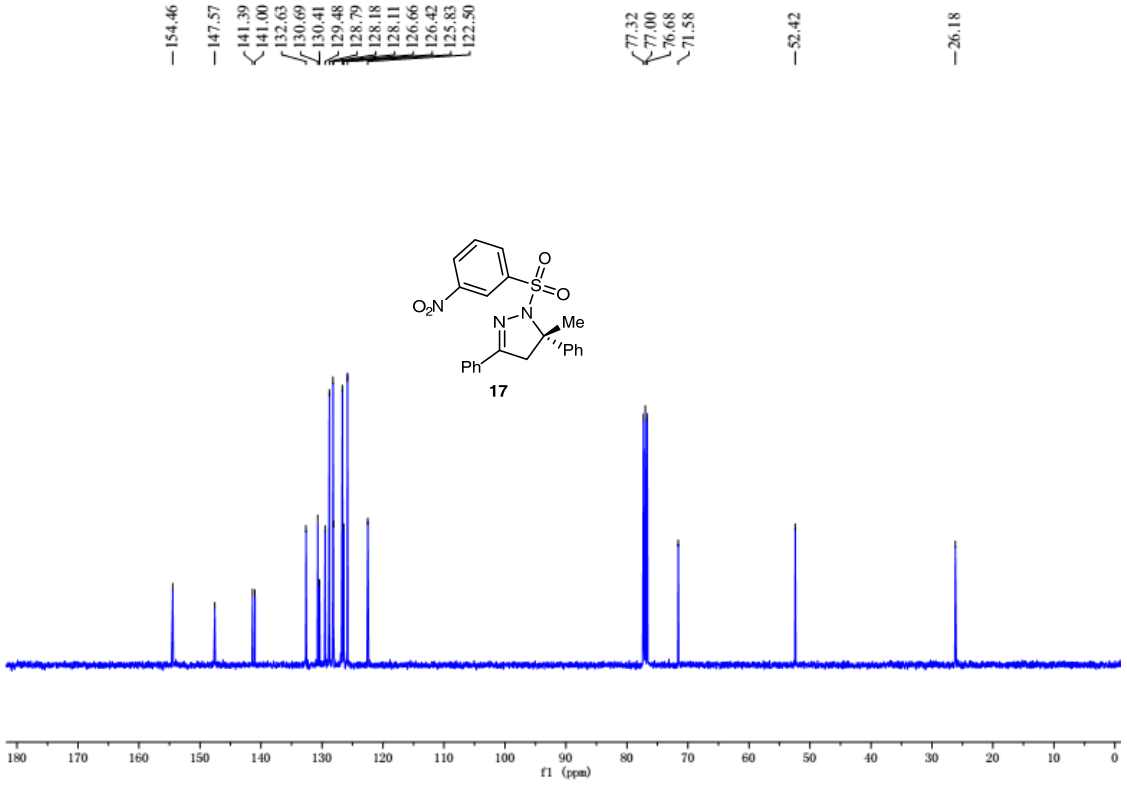
0.98
0.98
1.02
2.06
4.02
2.95
2.10
1.00
1.00
3.00
f1 (ppm)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130.41
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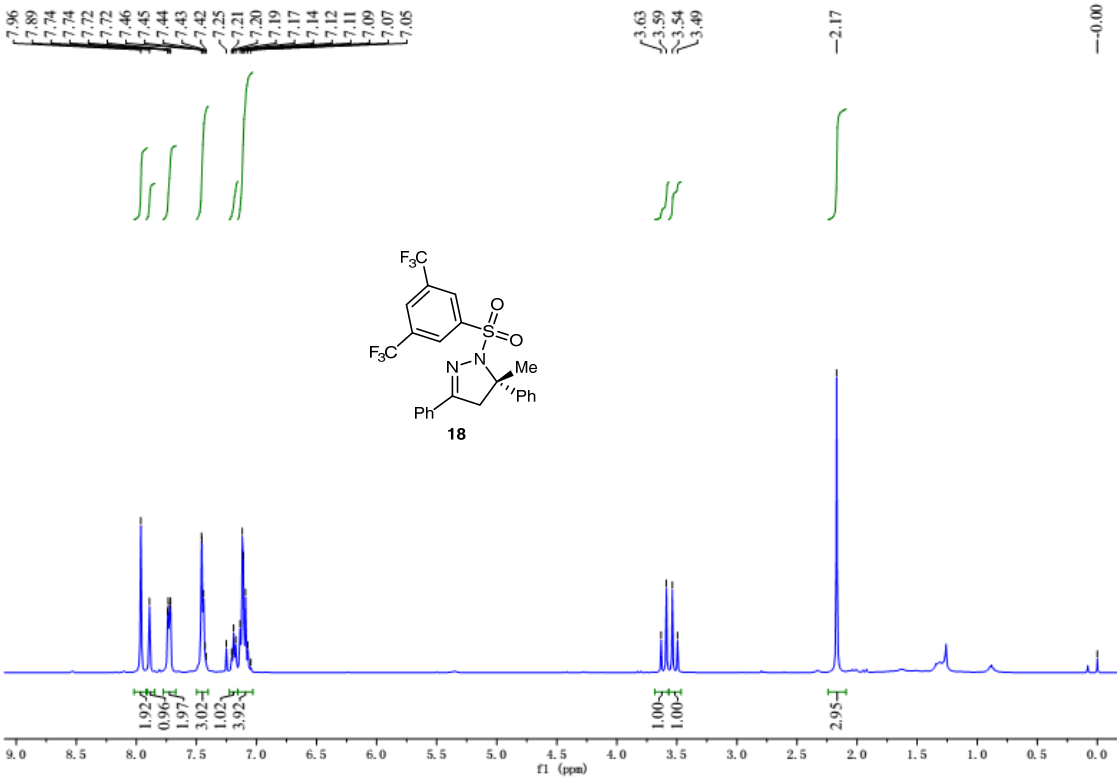
128.79
128.18
128.11
126.66
126.42
125.83
122.50
77.32
77.00
76.68
71.58
52.42
26.18
O2N
S
O
O
N
N
Me
Ph
Ph
17
f1 (ppm)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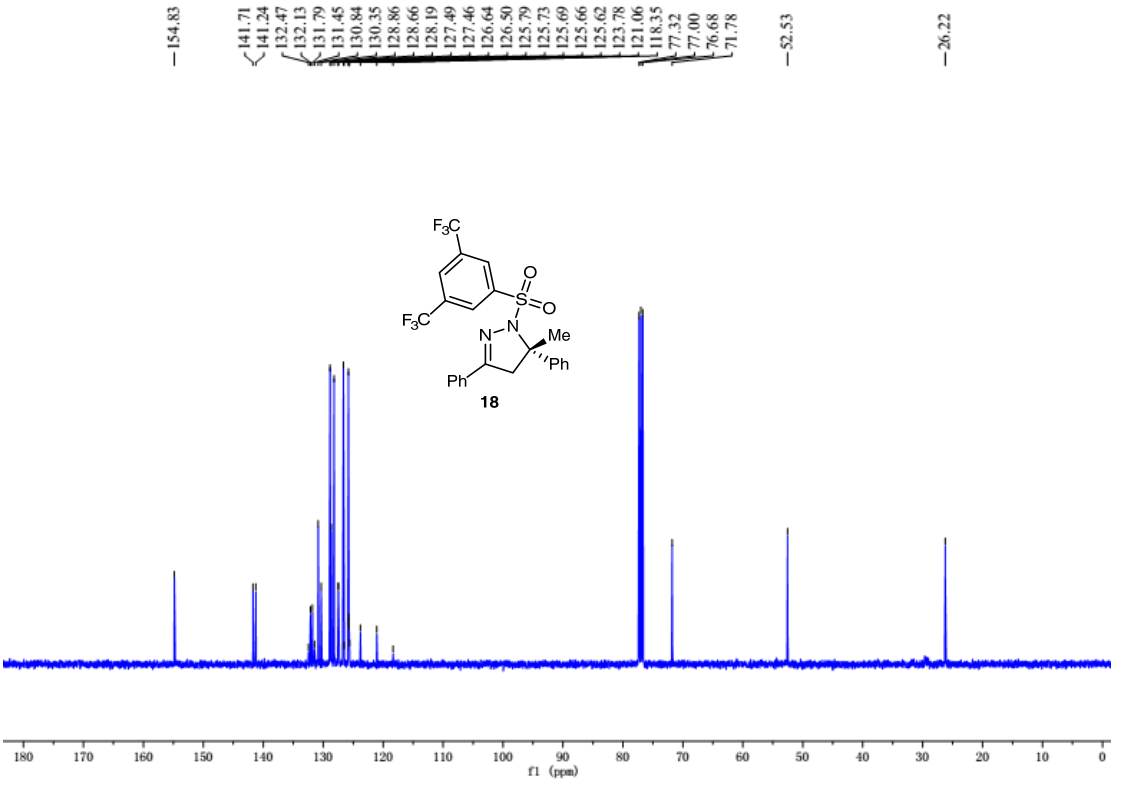
7.43
7.42
7.25
7.21
7.20
7.19
7.17
7.14
7.12
7.11
7.09
7.07
7.05
3.63
3.59
3.54
3.49
2.17
0.00
F3C
F3C
O
S
O
N
N
Me
Ph
Ph
18
1.92
0.96
1.97
3.02
1.02
3.92
1.00
1.00
2.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.79
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130.84
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128.66
128.19
127.49
127.46
126.64
126.50
125.79
125.73
125.69
125.66
125.62
123.78
121.06
118.35
77.32
77.00
76.68
71.78
52.53
26.22
F3C
F3C
O
S
O
N
N
Me
Ph
Ph
18
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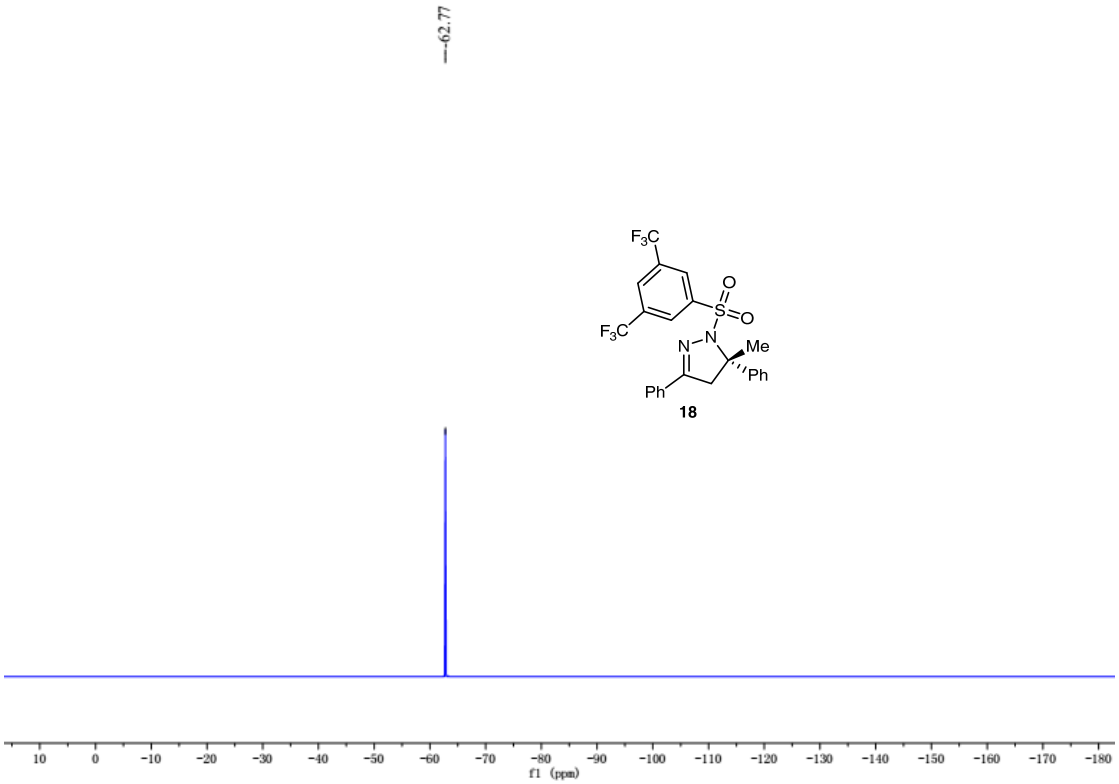
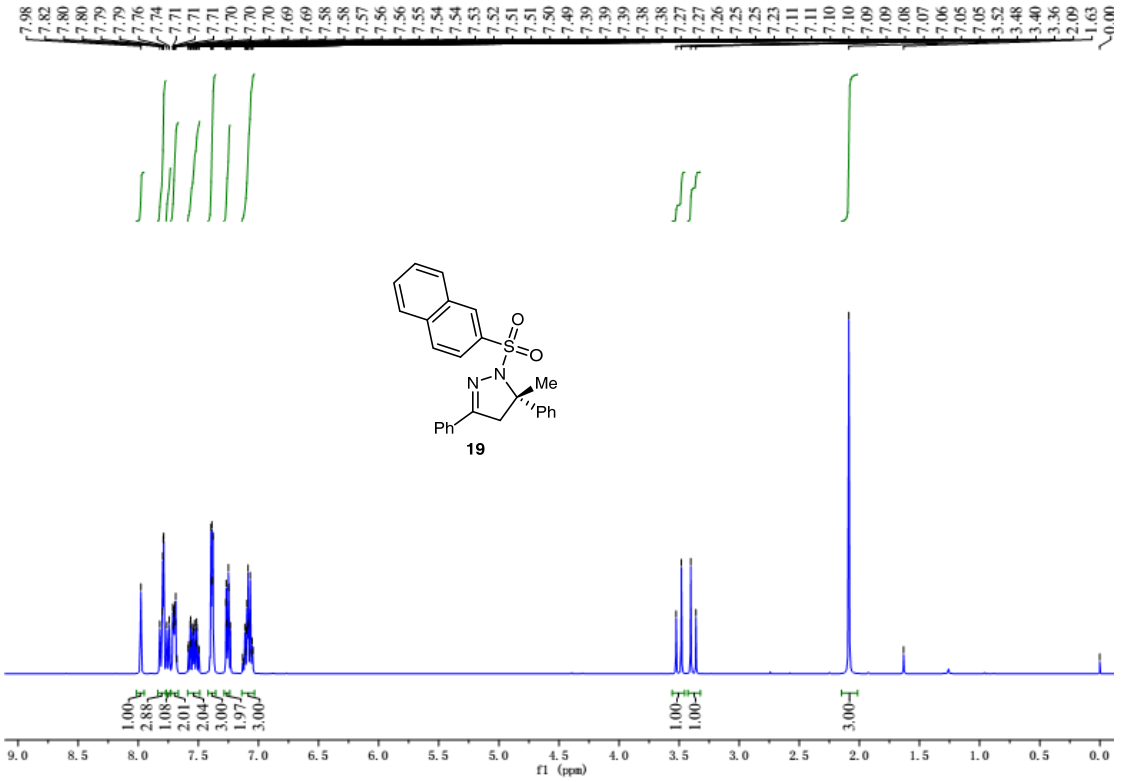
f1 (ppm)


-62.77
F3C
F3C
O
S
O
N
N
Me
Ph
Ph
18
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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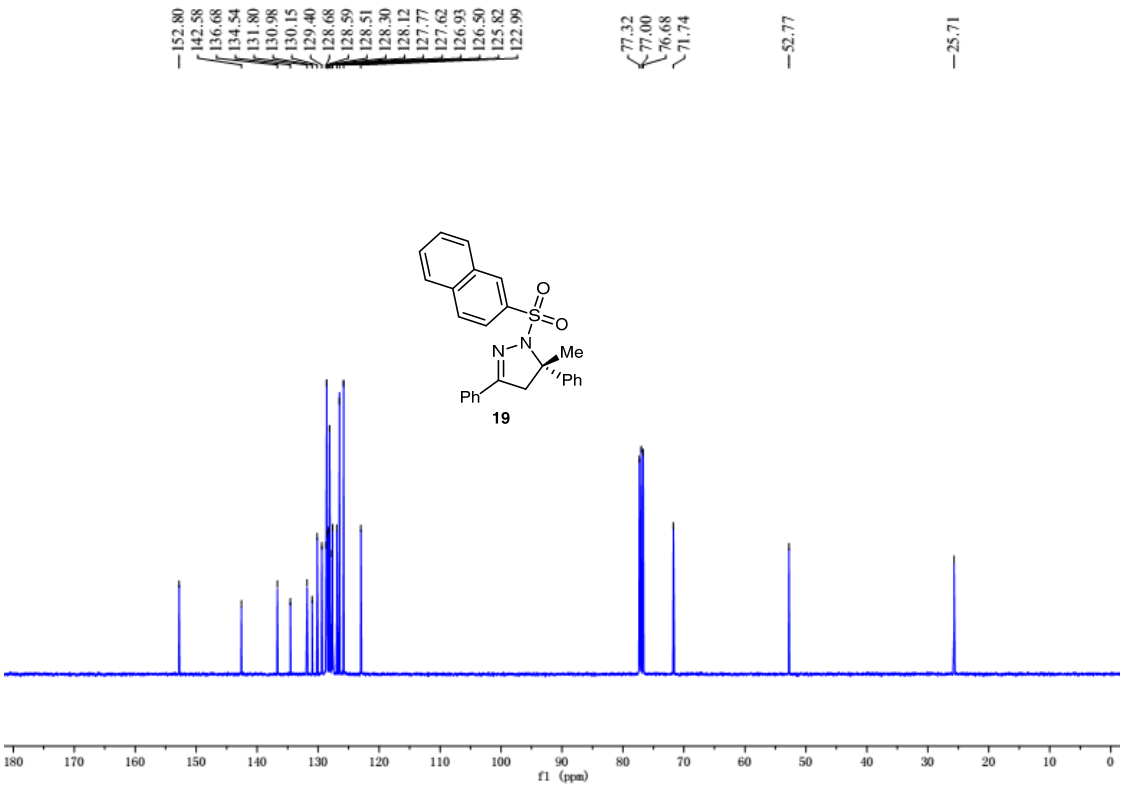
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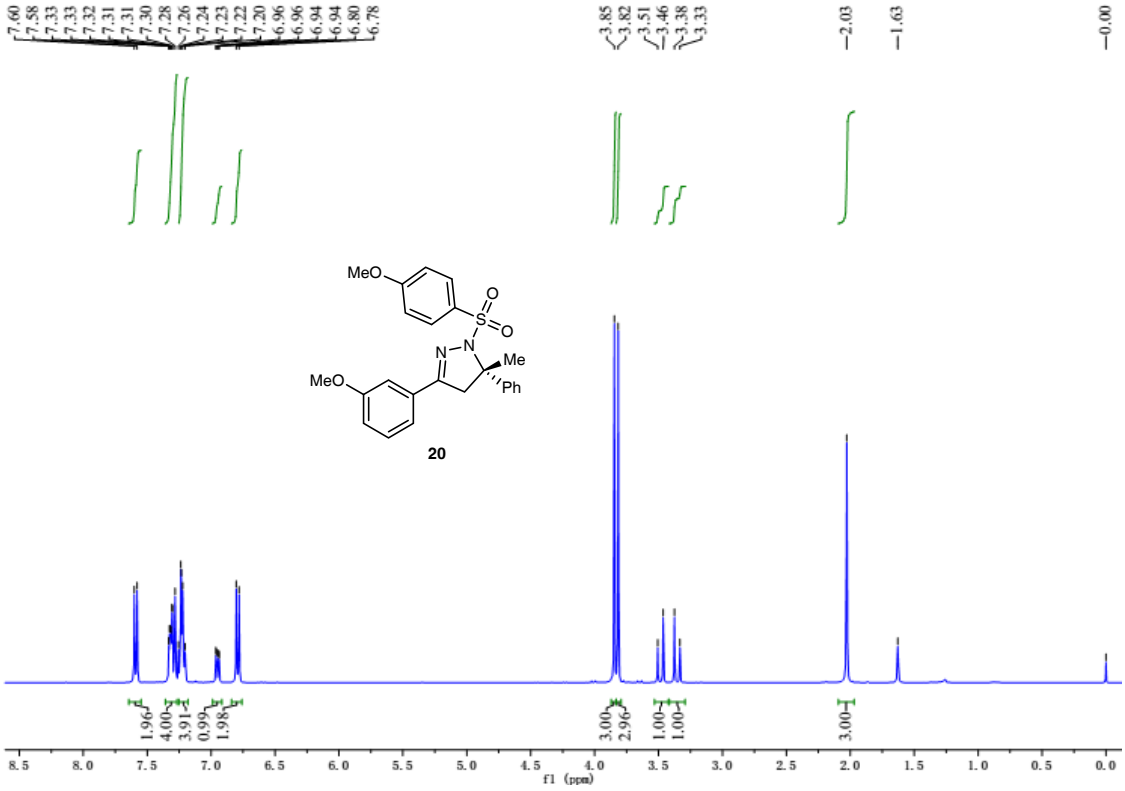
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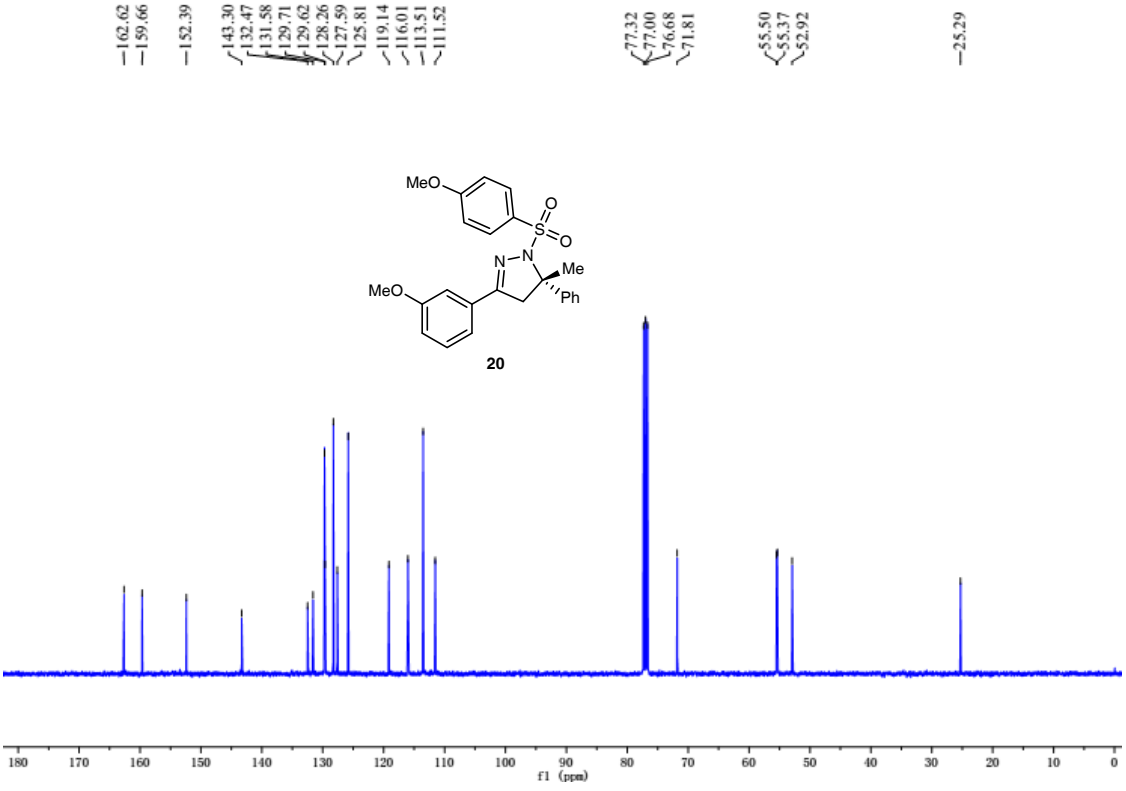
7.58
7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.26
7.24
7.23
7.22
7.20
6.96
6.96
6.94
6.94
6.80
6.78
3.85
3.82
3.51
3.46
3.38
3.33
2.03
1.63
0.00
MeO
O
S
O
N
N
Me
Ph
MeO
20
1.96
4.00
3.91
0.99
1.98
3.00
2.96
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.58
129.71
129.62
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127.59
125.81
119.14
116.01
113.51
111.52
77.32
77.00
76.68
71.81
55.50
55.37
52.92
25.29
MeO
O
S
O
N
N
Me
Ph
MeO
20
180
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130
120
110
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90
80
70
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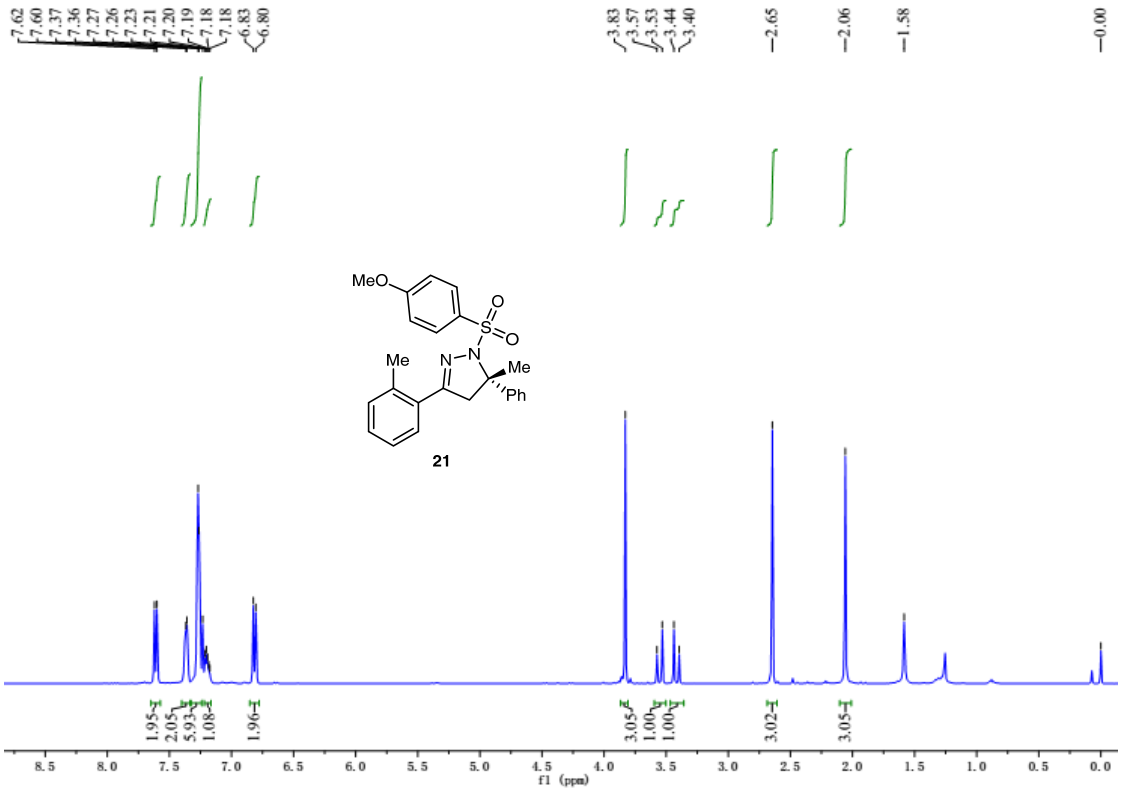
50
40
30
20
10
0
f1 (ppm)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7.36
7.27
7.26
7.23
7.21
7.20
7.19
7.18
7.18
6.83
6.80
3.83
3.57
3.53
3.44
3.40
2.65
2.06
1.58
0.00
MeO
Me
Me
Ph
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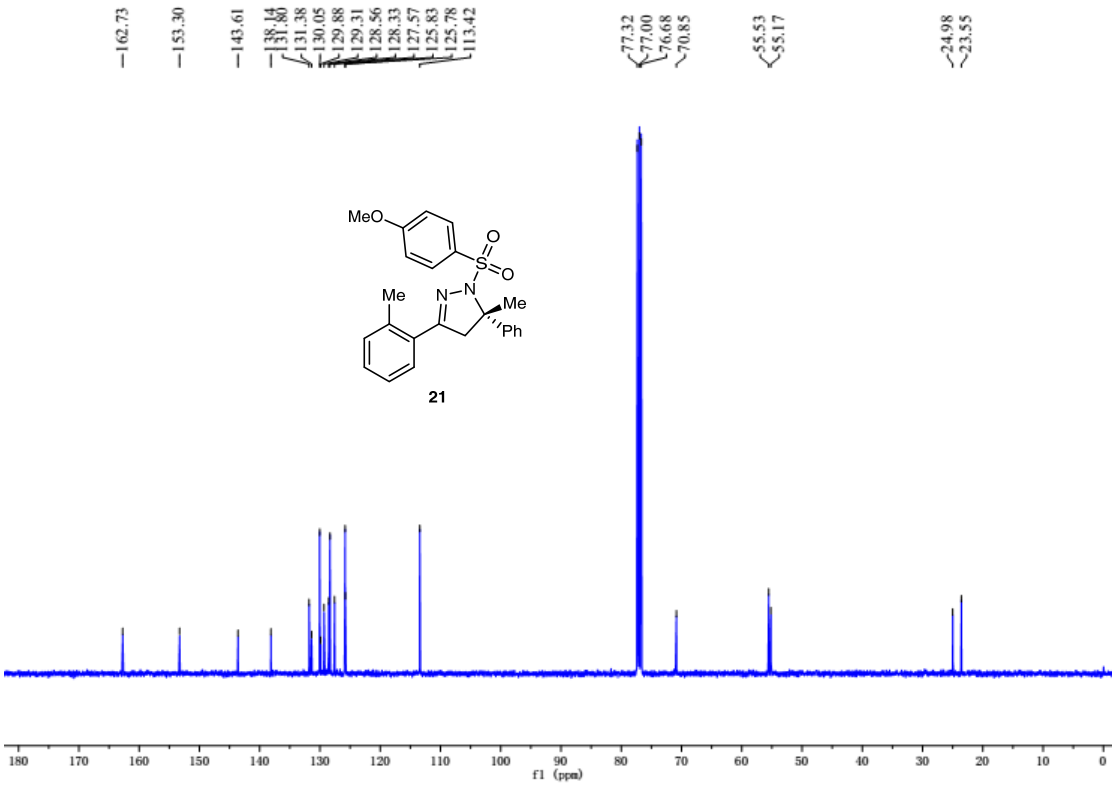
1.95
2.05
5.93
1.08
1.96
3.05
1.00
1.00
3.02
3.05
f1 (ppm)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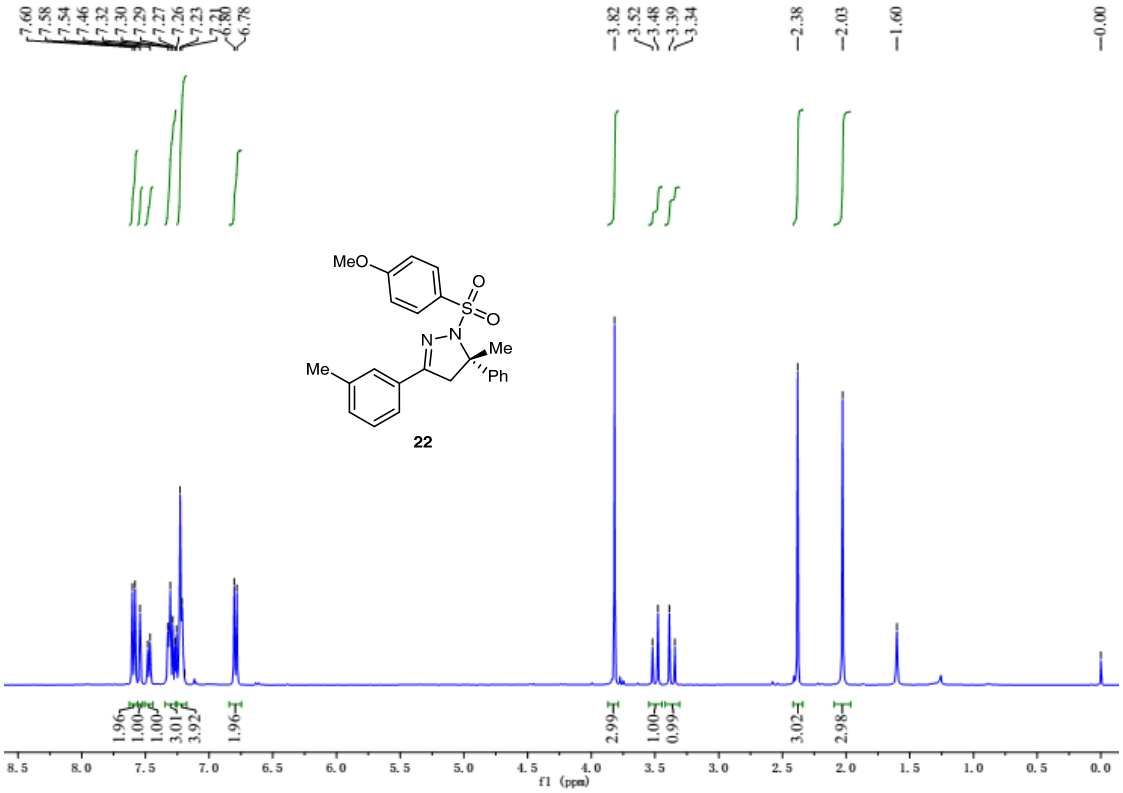
127.57
125.83
125.78
113.42
77.32
77.00
76.68
70.85
55.53
55.17
24.98
23.55
MeO
Me
Me
Ph
21
f1 (ppm)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7.54
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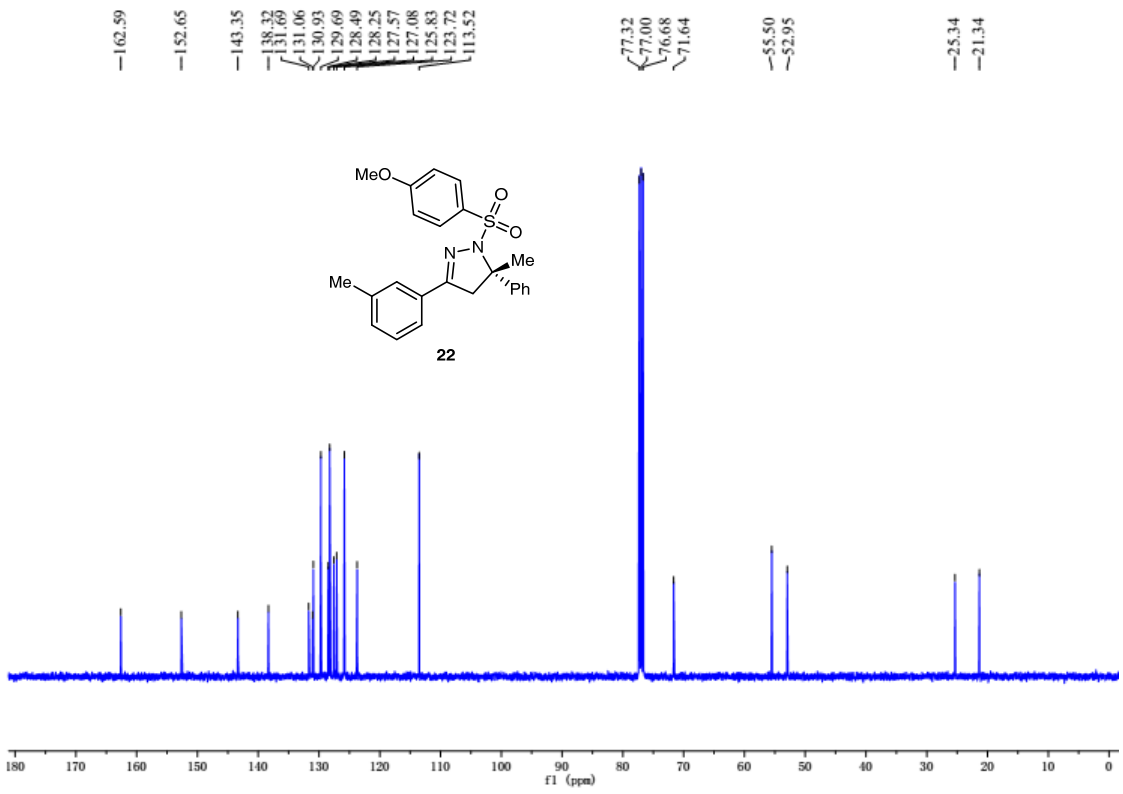
7.30
7.29
7.27
7.26
7.23
7.21
6.80
6.78
3.82
3.52
3.48
3.39
3.34
2.38
2.03
1.60
0.00
MeO
O
S
O
N
N
Me
Ph
Me
22
1.96
1.00
1.00
3.01
3.92
1.96
2.99
1.00
0.99
3.02
2.98
f1 (ppm)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129.69
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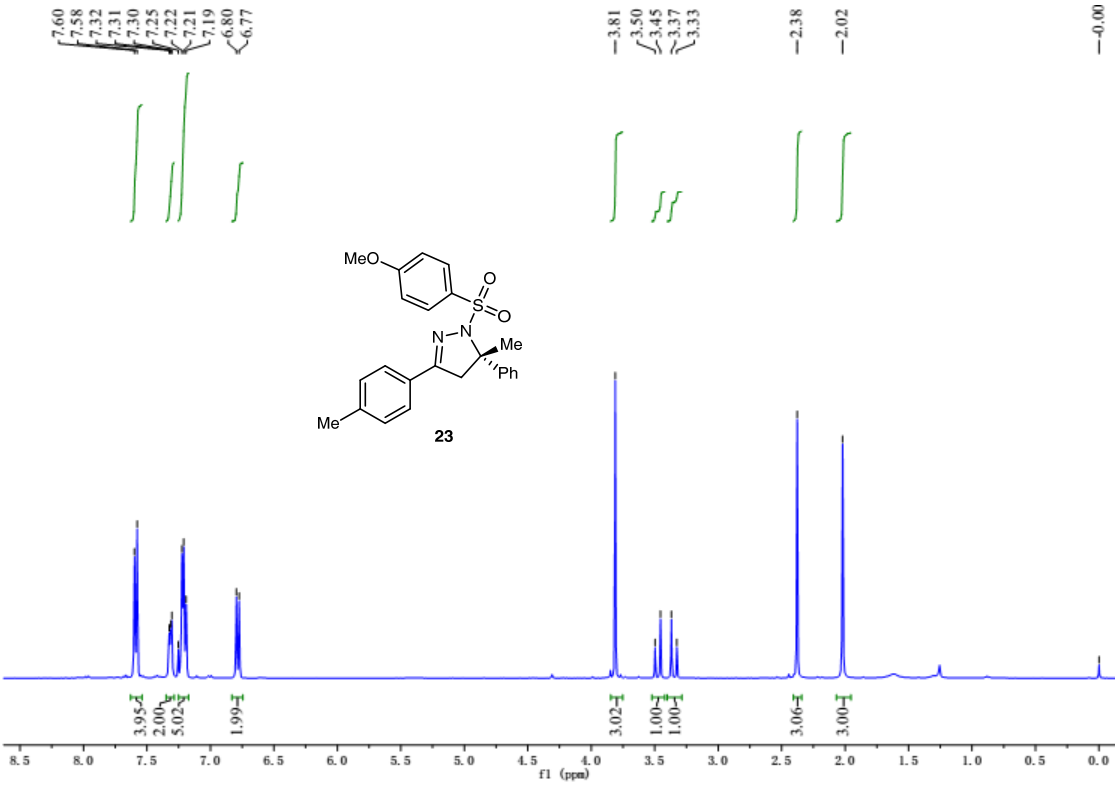
128.25
127.57
127.08
125.83
123.72
113.52
77.32
77.00
76.68
71.64
55.50
52.95
25.34
21.34
MeO
O
S
O
N
N
Me
Ph
Me
22
f1 (ppm)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7.19
6.80
6.77
3.81
3.50
3.45
3.37
3.33
2.38
2.02
0.00
MeO
O
S
O
N
N
Me
Ph
Me
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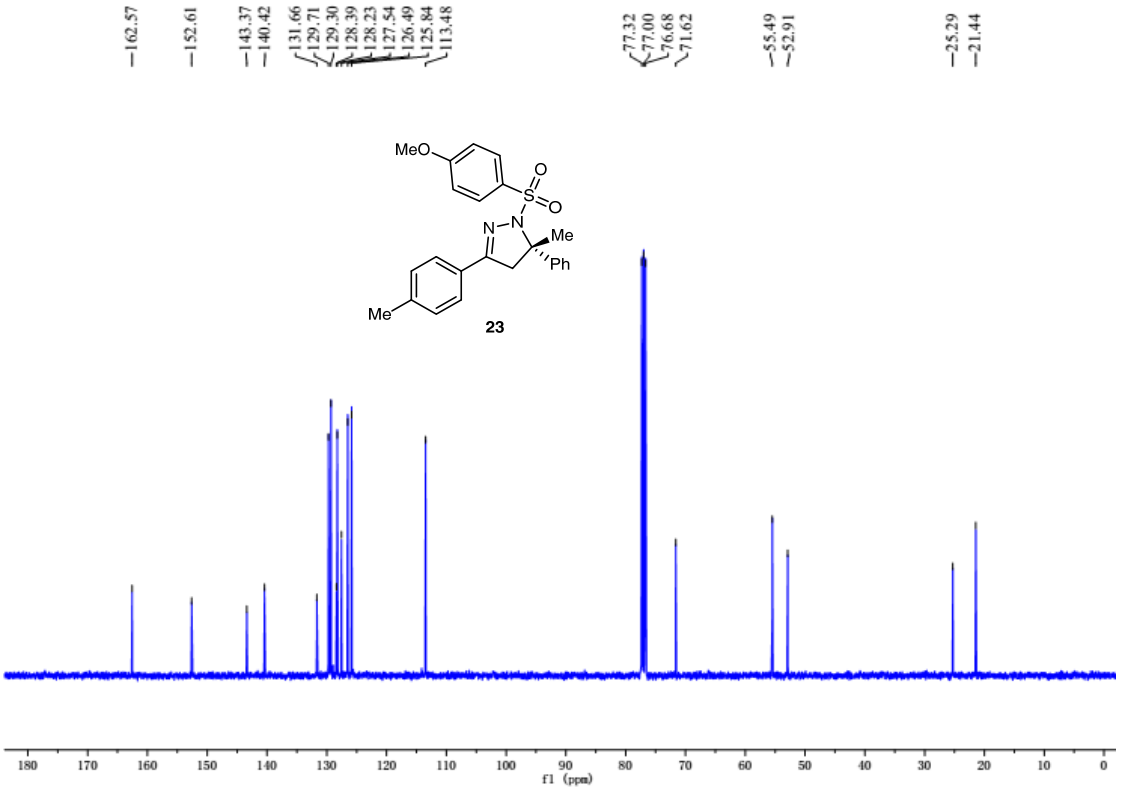
2.00
5.02
1.99
3.02
1.00
1.00
3.06
3.00
f1 (ppm)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128.39
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126.49
125.84
113.48
77.32
77.00
76.68
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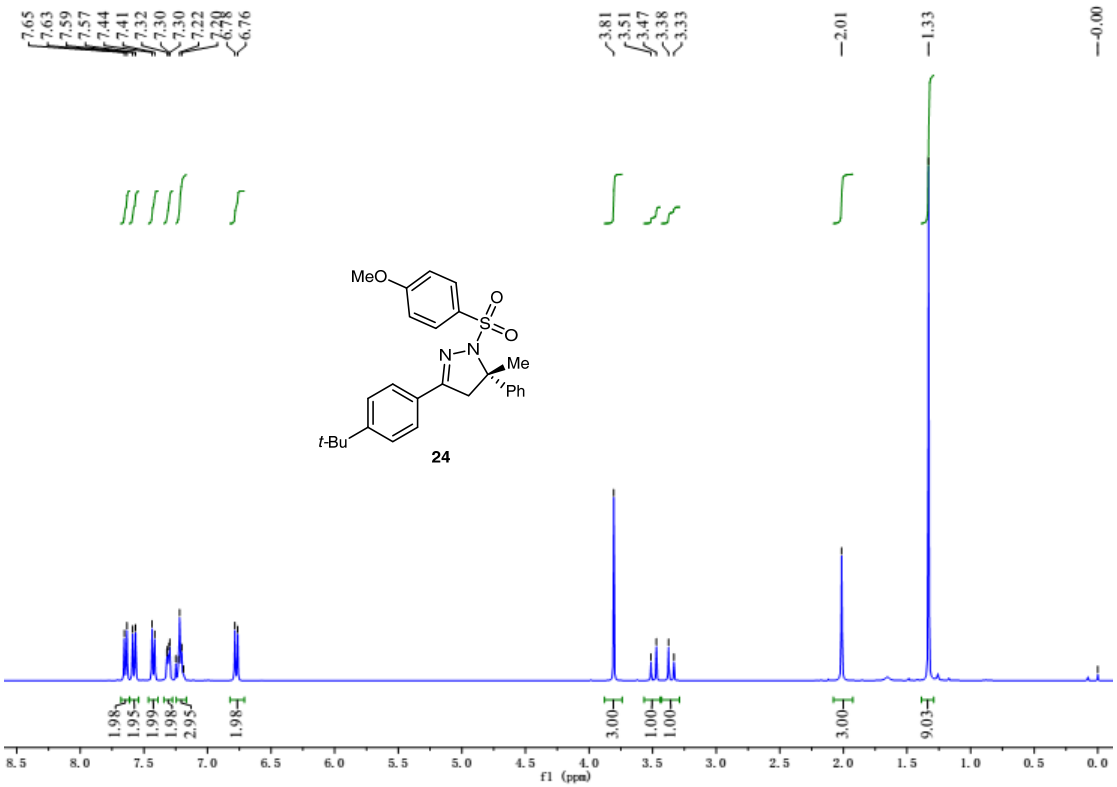
52.91
25.29
21.44
MeO
O
S
O
N
N
Me
Ph
Me
23
f1 (ppm)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7.63
7.59
7.57
7.44
7.41
7.32
7.30
7.30
7.22
6.78
6.76
3.81
3.51
3.47
3.38
3.33
2.01
1.33
0.00
MeO
S
O
O
N
N
Me
Ph
t-Bu
24
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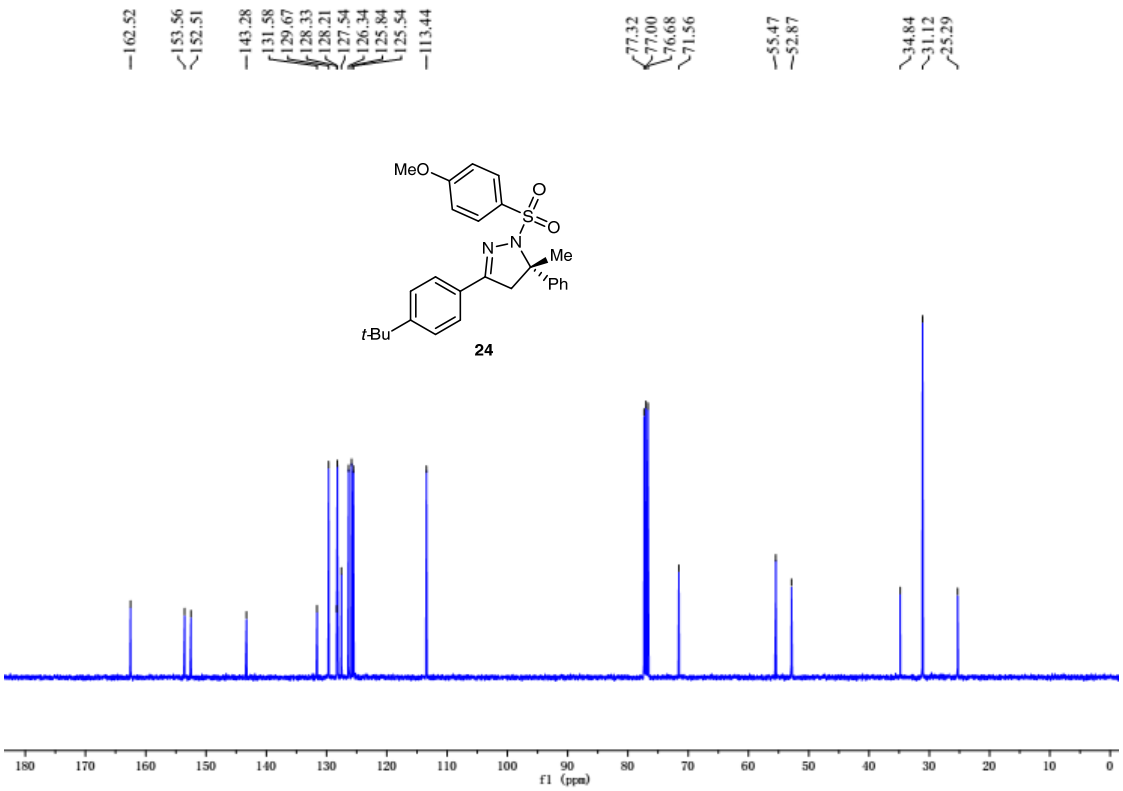
1.98
2.95
1.98
3.00
1.00
1.00
3.00
9.03
f1 (ppm)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126.34
125.84
125.54
113.44
77.32
77.00
76.68
71.56
55.47
52.87
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25.29
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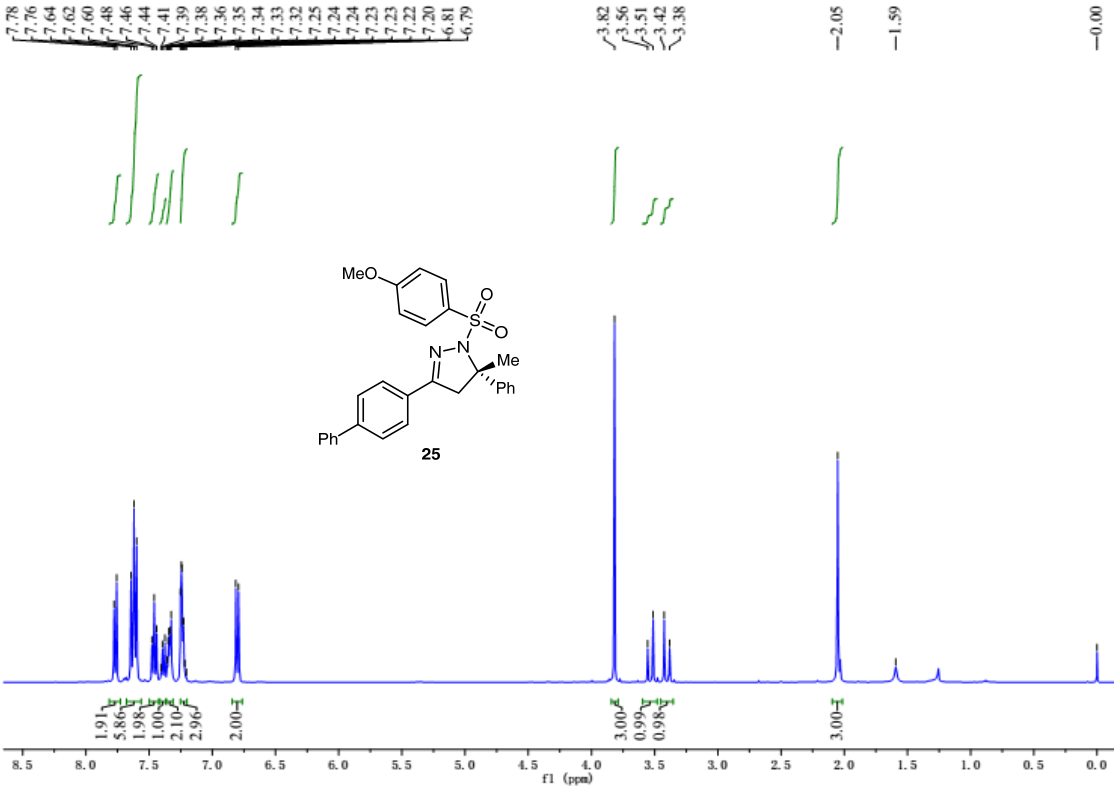
S
O
O
N
N
Me
Ph
t-Bu
24
f1 (ppm)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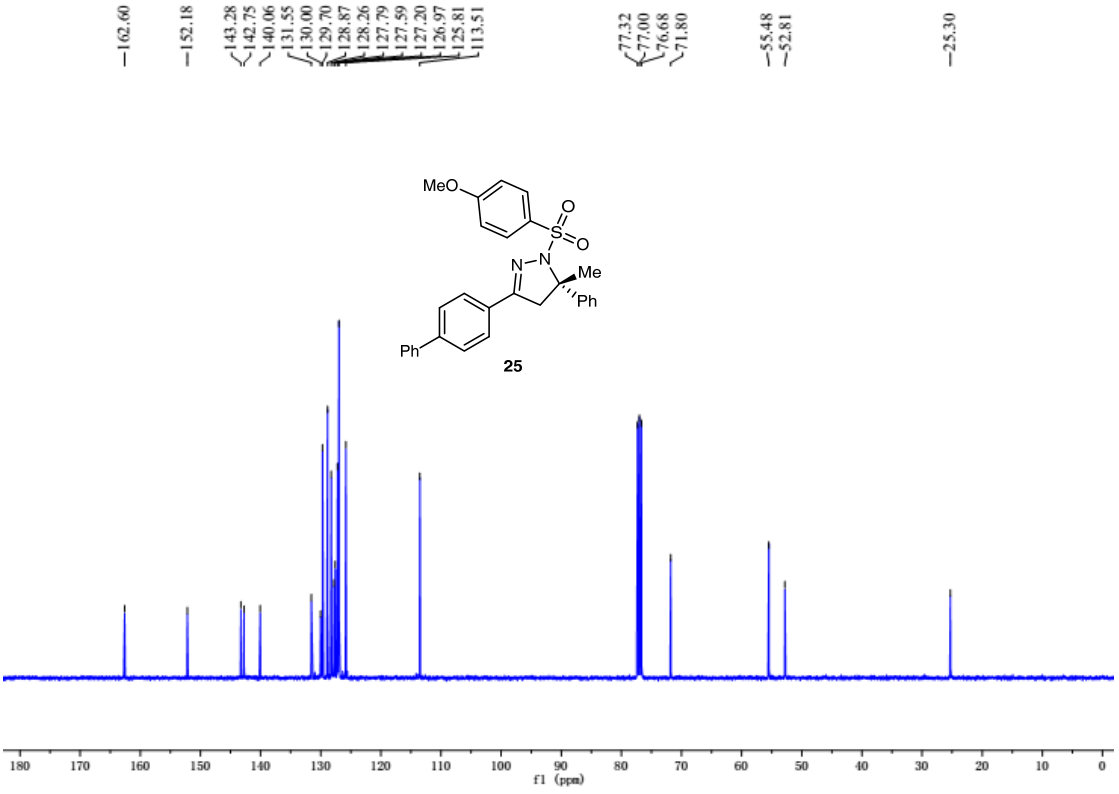
7.46
7.44
7.41
7.39
7.38
7.36
7.35
7.34
7.33
7.32
7.25
7.24
7.24
7.23
7.23
7.22
7.20
6.81
6.79
3.82
3.56
3.51
3.42
3.38
2.05
1.59
0.00
MeO
O
S
O
N
N
Me
Ph
Ph
25
1.91
5.86
1.98
1.00
2.10
2.96
2.00
3.00
0.99
0.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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143.28
142.75
140.06
131.55
130.00
129.70
128.87
128.26
127.79
127.59
127.20
126.97
125.81
113.51
77.32
77.00
76.68
71.80
55.48
52.81
25.30
MeO
O
S
O
N
N
Me
Ph
Ph
25
180
170
160
150
140
130
120
110
100
90
80
70
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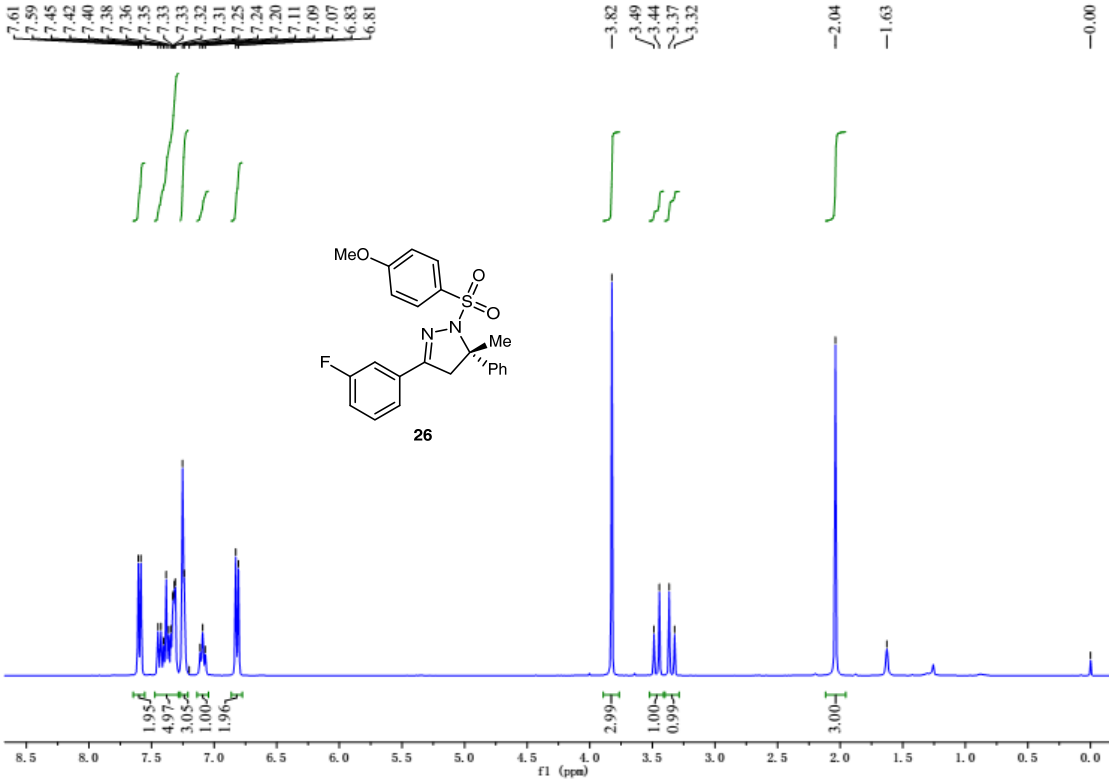
50
40
30
20
10
0
f1 (ppm)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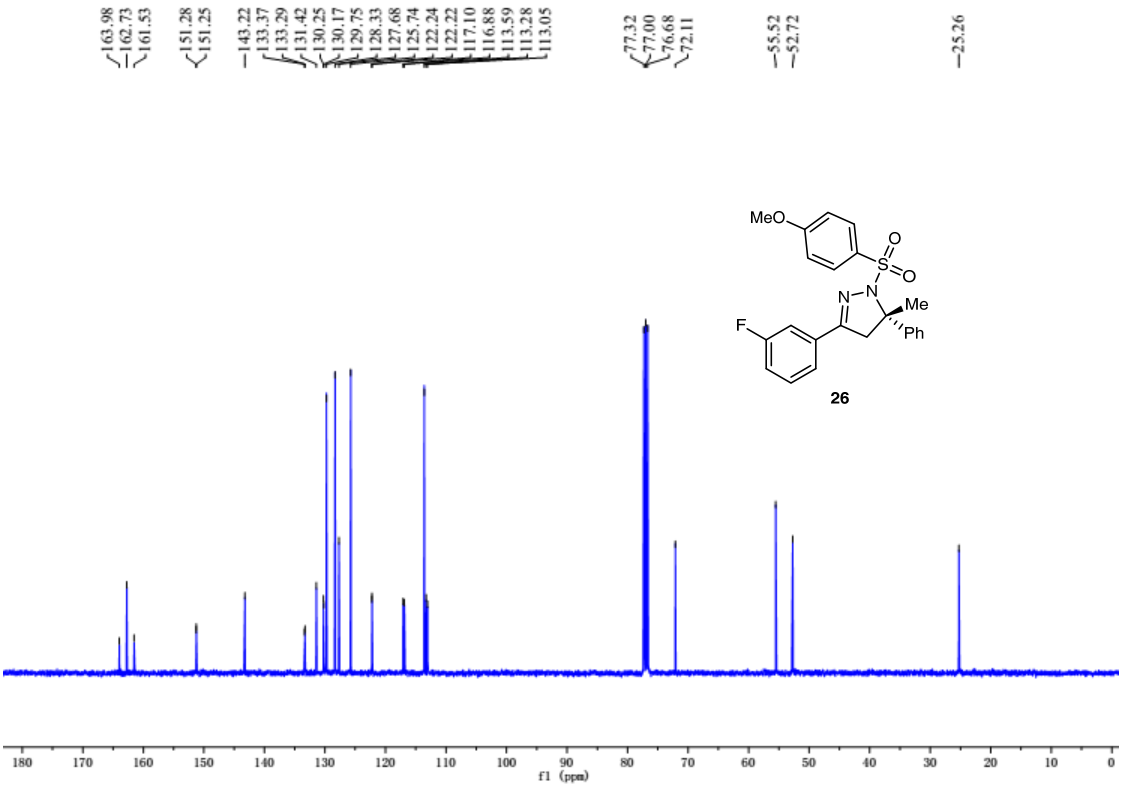
7.42
7.40
7.38
7.36
7.35
7.33
7.33
7.32
7.31
7.25
7.24
7.20
7.11
7.09
7.07
6.83
6.81
3.82
3.49
3.44
3.37
3.32
2.04
1.63
0.00
MeO
O
S
O
N
N
Me
Ph
F
26
1.95
4.97
3.05
1.00
1.96
2.99
1.00
0.99
3.00
f1 (ppm)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133.29
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130.25
130.17
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128.33
127.68
125.74
122.24
122.22
117.10
116.88
113.59
113.28
113.05
77.32
77.00
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52.72
25.26
MeO
O
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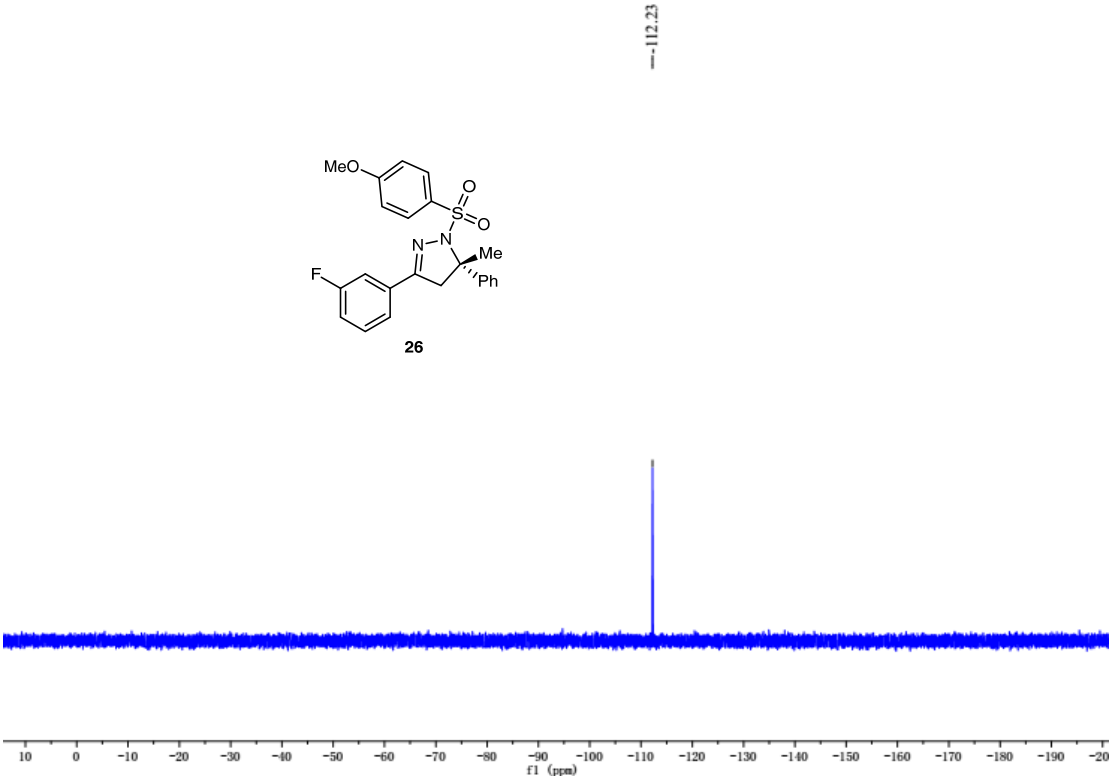
O
N
N
Me
Ph
F
26
f1 (ppm)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MeO
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N
Me
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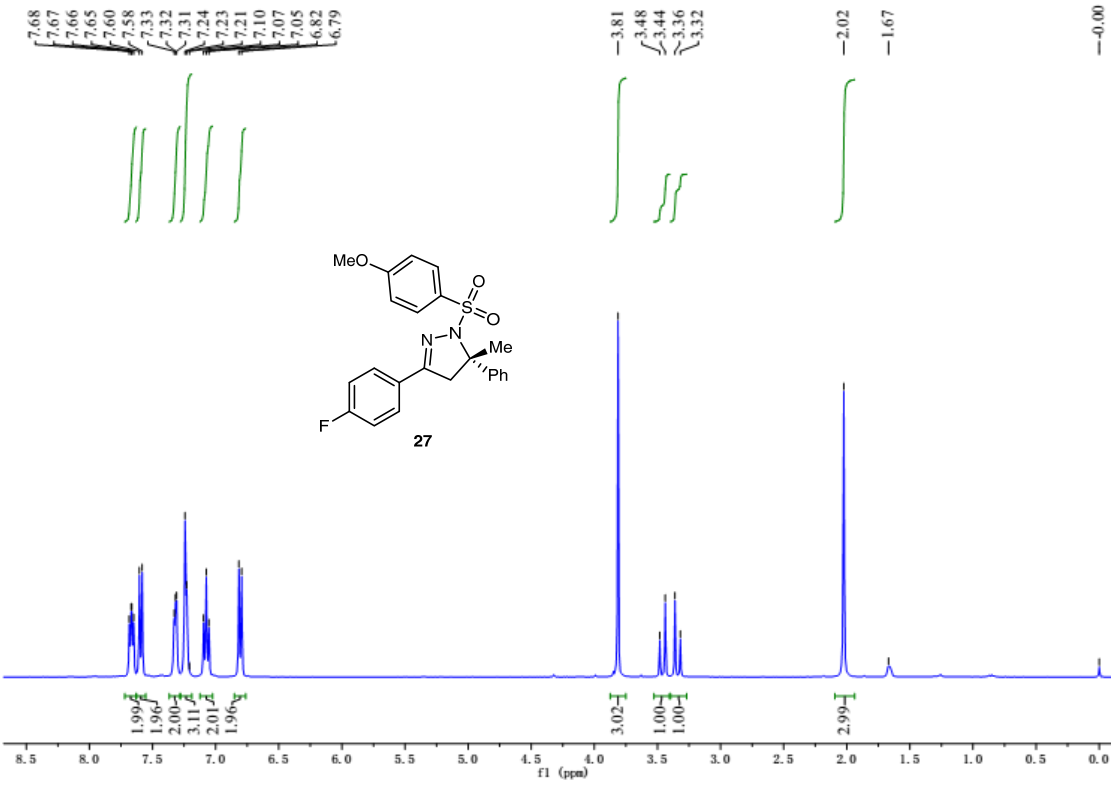
F
26
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)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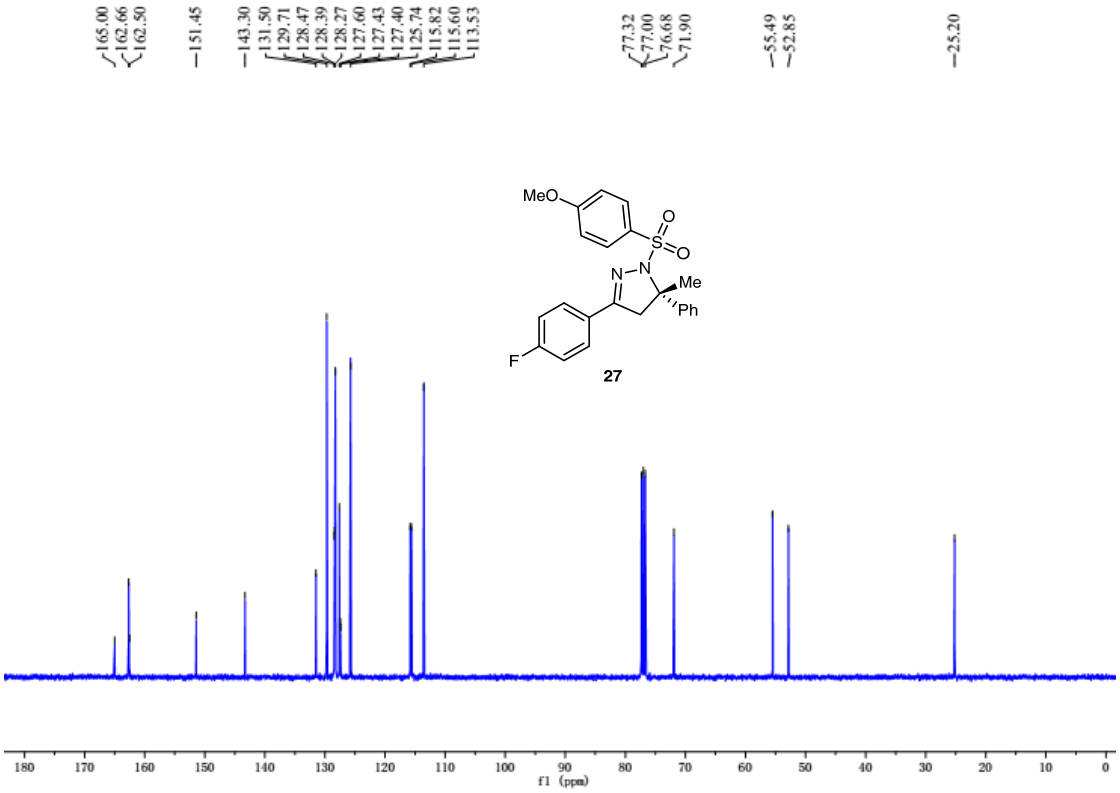
7.32
7.31
7.24
7.23
7.21
7.10
7.07
7.05
6.82
6.79
3.81
3.48
3.44
3.36
3.32
2.02
1.67
0.00
MeO
O
S
O
N
N
Me
Ph
F
27
1.99
1.96
2.00
3.11
2.01
1.96
3.02
1.00
1.00
2.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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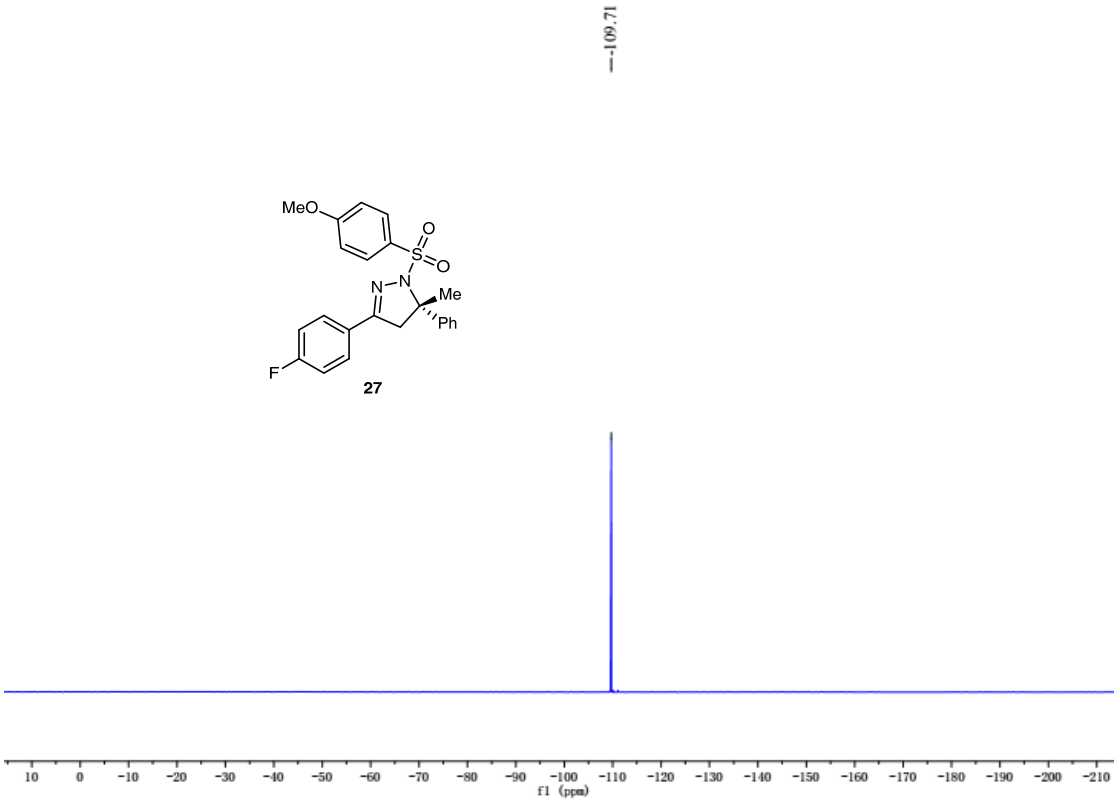
128.27
127.60
127.43
127.40
125.74
115.82
115.60
113.53
77.32
77.00
76.68
71.90
55.49
52.85
25.20
MeO
O
S
O
N
N
Me
Ph
F
27
f1 (ppm)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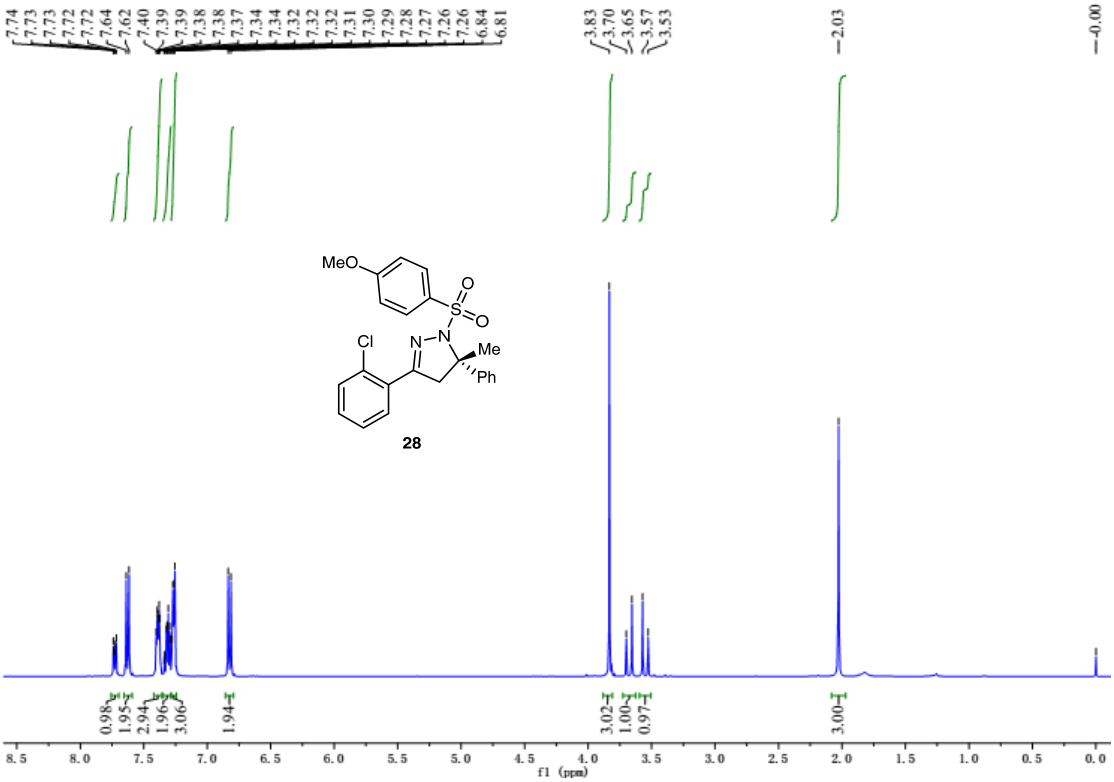
MeO
O
S
O
N
N
Me
Ph
F
27
f1 (ppm)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7.38
7.38
7.37
7.34
7.34
7.32
7.32
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.26
6.84
6.81
3.83
3.70
3.65
3.57
3.53
2.03
0.00
MeO
O
S
O
N
N
Cl
Me
Ph
28
0.98
1.95
2.94
1.96
3.06
1.94
3.02
1.00
0.97
3.00
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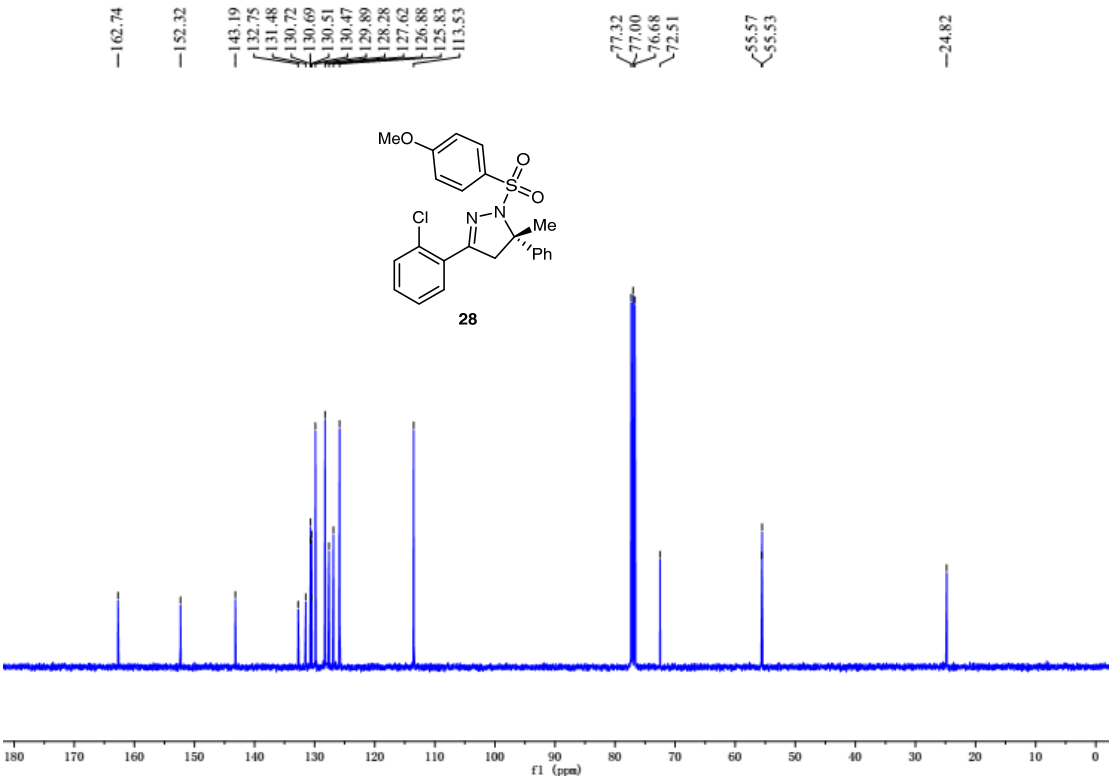
f1 (ppm)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127.62
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125.83
113.53
77.32
77.00
76.68
72.51
55.57
55.53
24.82
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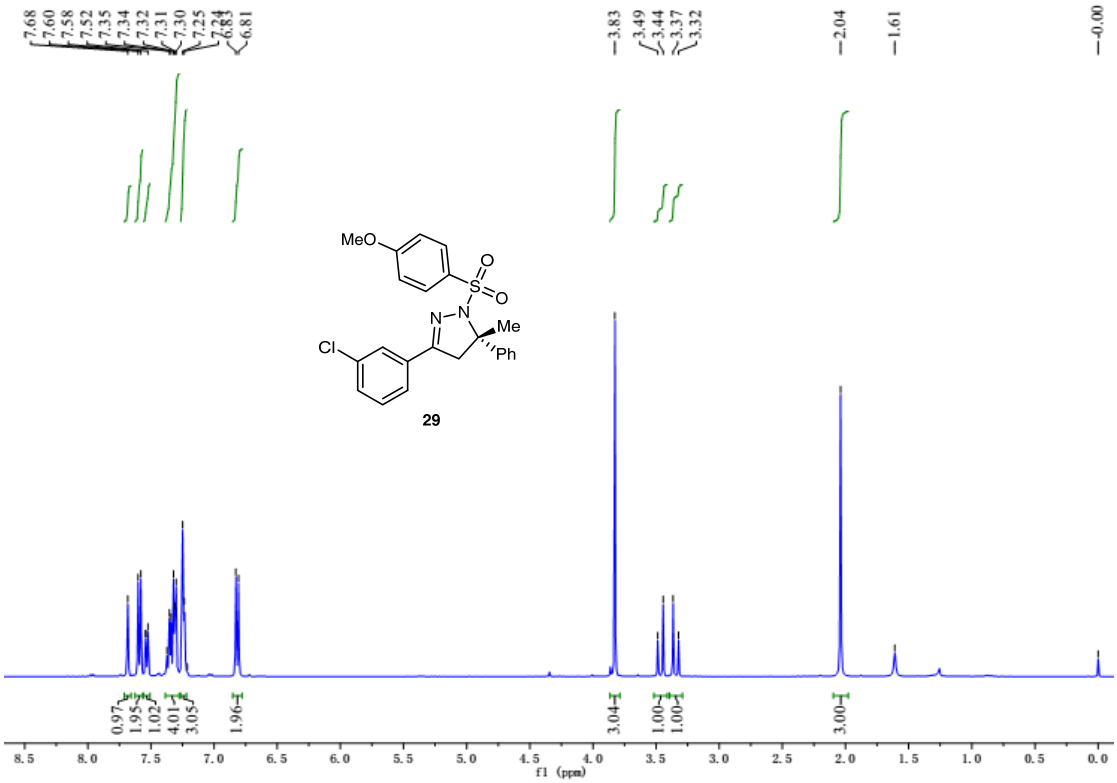
O
S
O
N
N
Cl
Me
Ph
28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.34
7.32
7.31
7.30
7.25
7.24
6.83
6.81
3.83
3.49
3.44
3.37
3.32
2.04
1.61
0.00
MeO
O
S
O
N
N
Me
Ph
Cl
29
0.97
1.95
1.02
4.01
3.05
1.96
3.04
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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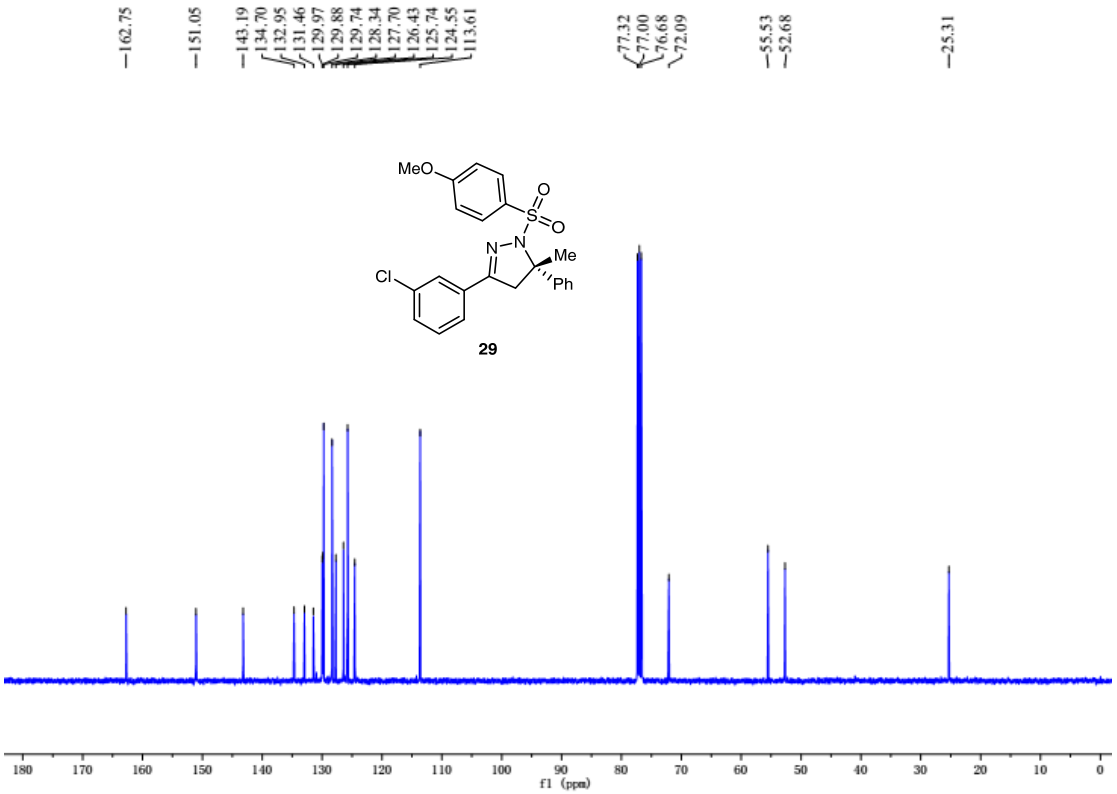
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.46
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129.88
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127.70
126.43
125.74
124.55
113.61
77.32
77.00
76.68
72.09
55.53
52.68
25.31
MeO
O
S
O
N
N
Me
Ph
Cl
29
180
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130
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110
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90
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50
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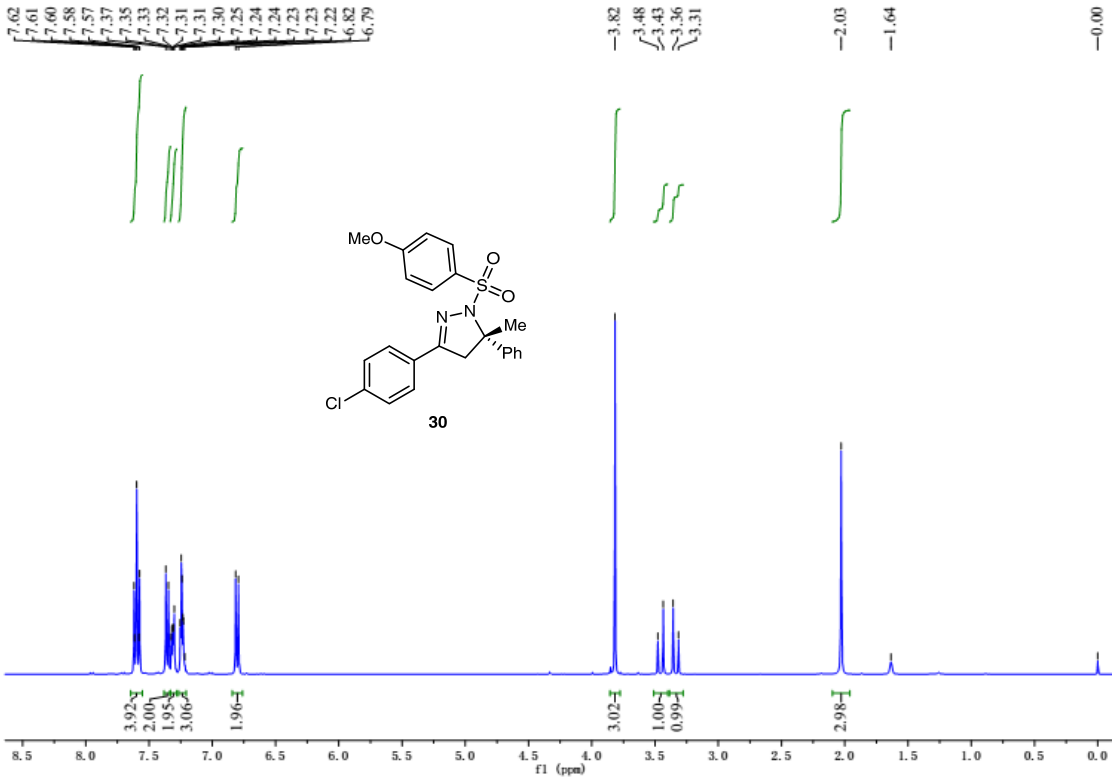
20
10
0
f1 (ppm)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7.32
7.31
7.31
7.30
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7.24
7.24
7.23
7.23
7.22
6.82
6.79
3.82
3.48
3.43
3.36
3.31
2.03
1.64
0.00
MeO
O
S
O
N
N
Me
Ph
Cl
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2.00
1.95
3.06
1.96
3.02
1.00
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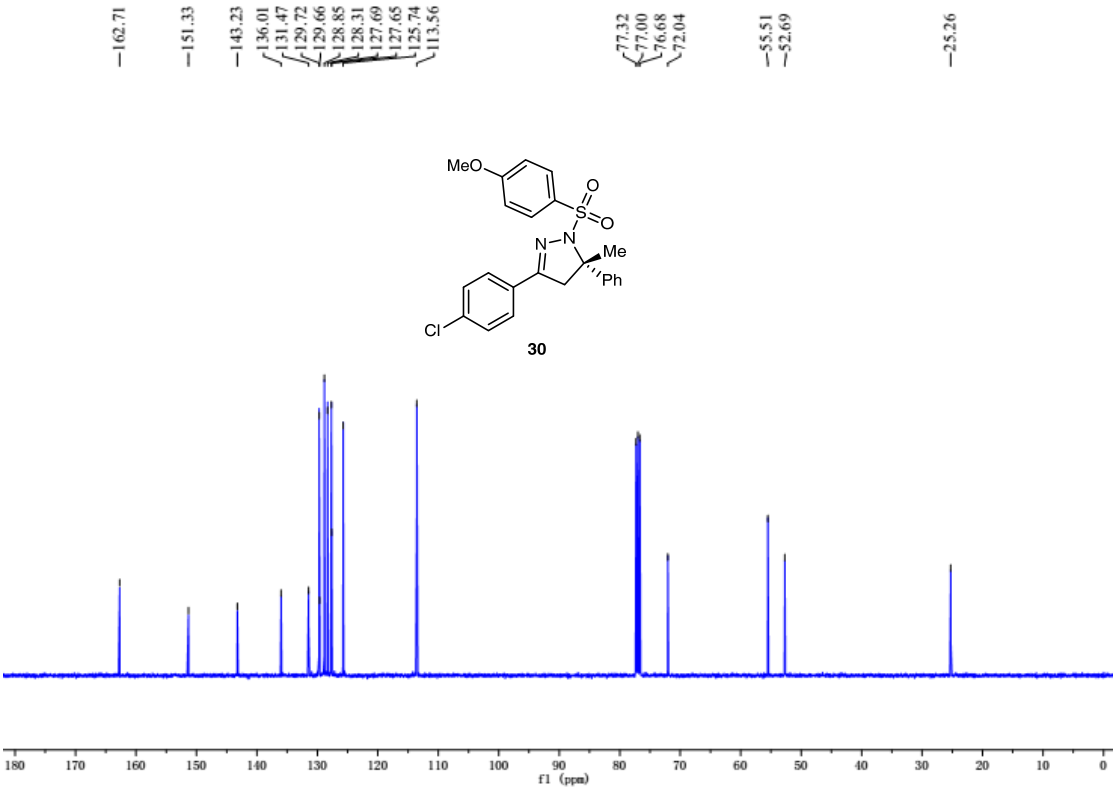
2.98
f1 (ppm)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127.69
127.65
125.74
113.56
77.32
77.00
76.68
72.04
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52.69
25.26
MeO
O
S
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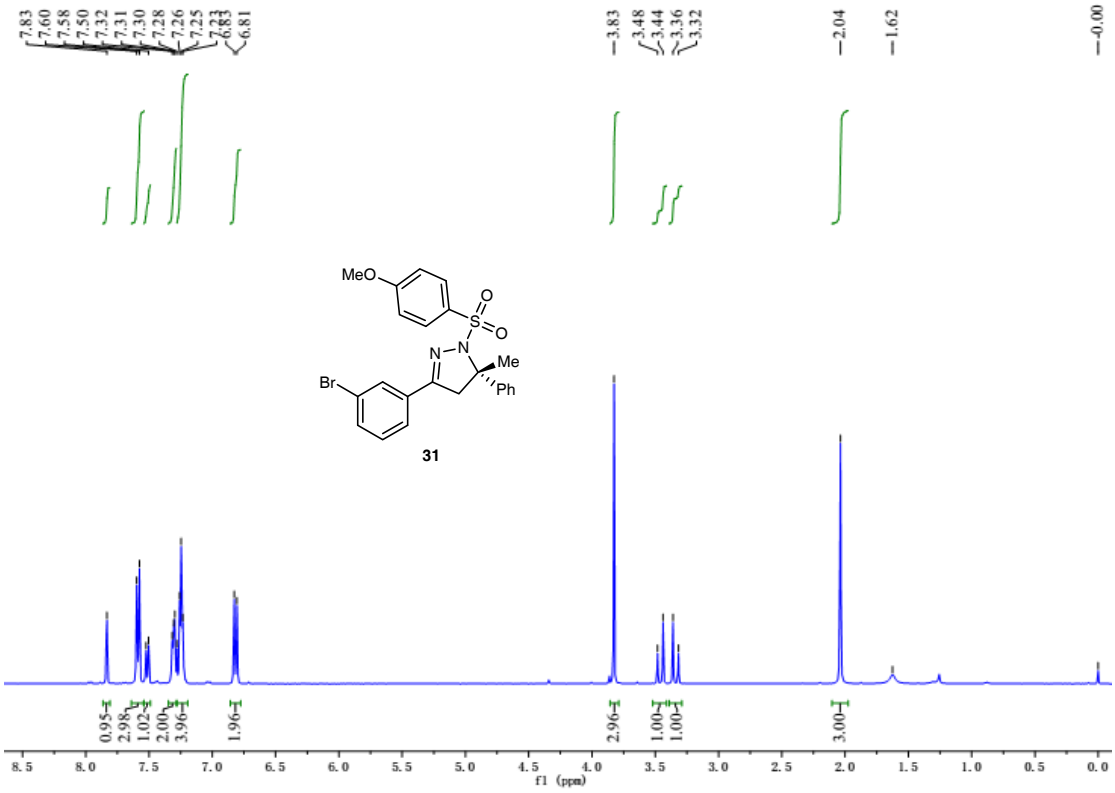
N
N
Me
Ph
Cl
30
f1 (ppm)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7.31
7.30
7.28
7.26
7.25
6.83
6.81
3.83
3.48
3.44
3.36
3.32
2.04
1.62
0.00
MeO
O
S
O
N
N
Me
Ph
Br
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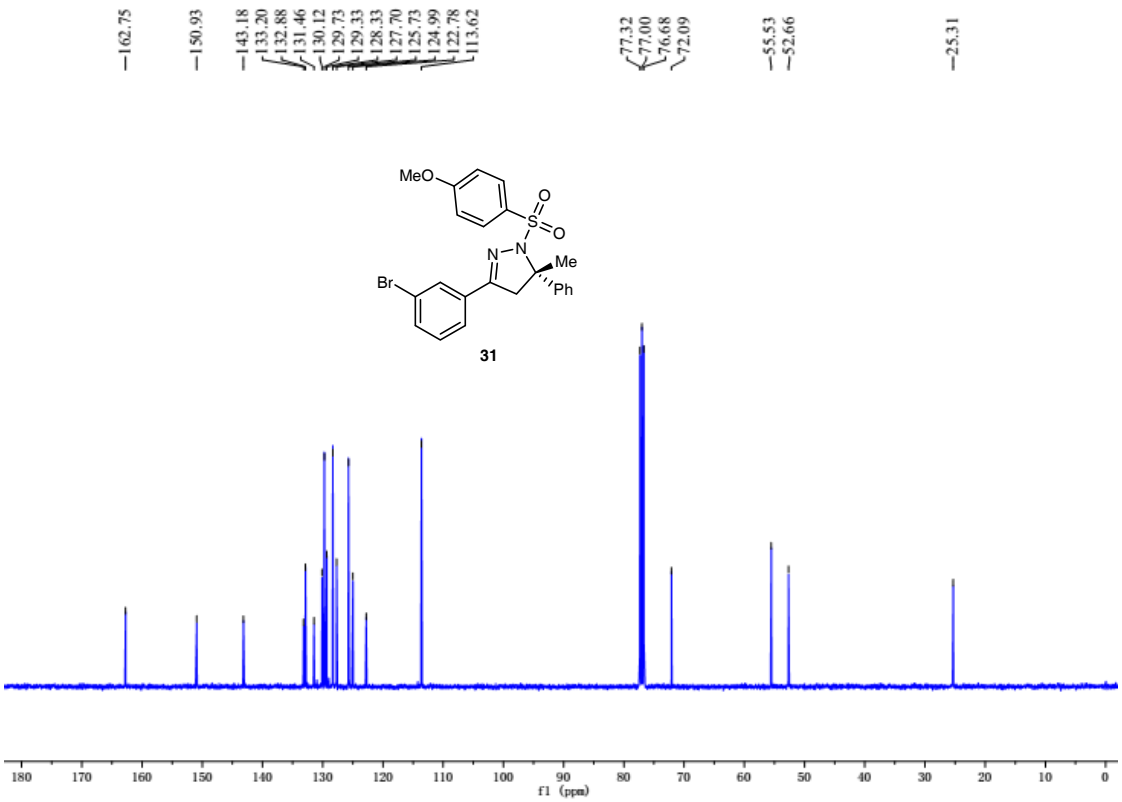
0.95
2.98
1.02
2.00
3.96
1.96
2.96
1.00
1.00
3.00
f1 (ppm)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131.46
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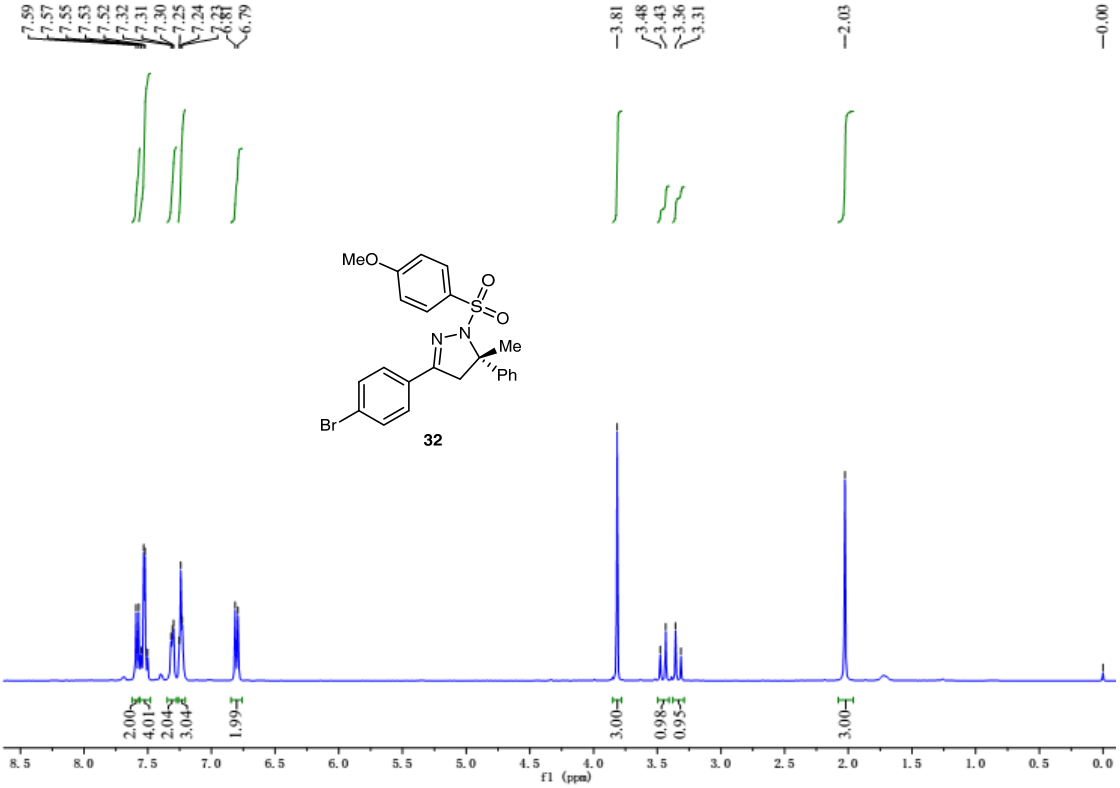
128.33
127.70
125.73
124.99
122.78
113.62
77.32
77.00
76.68
72.09
55.53
52.66
25.31
MeO
O
S
O
N
N
Me
Ph
Br
31
f1 (ppm)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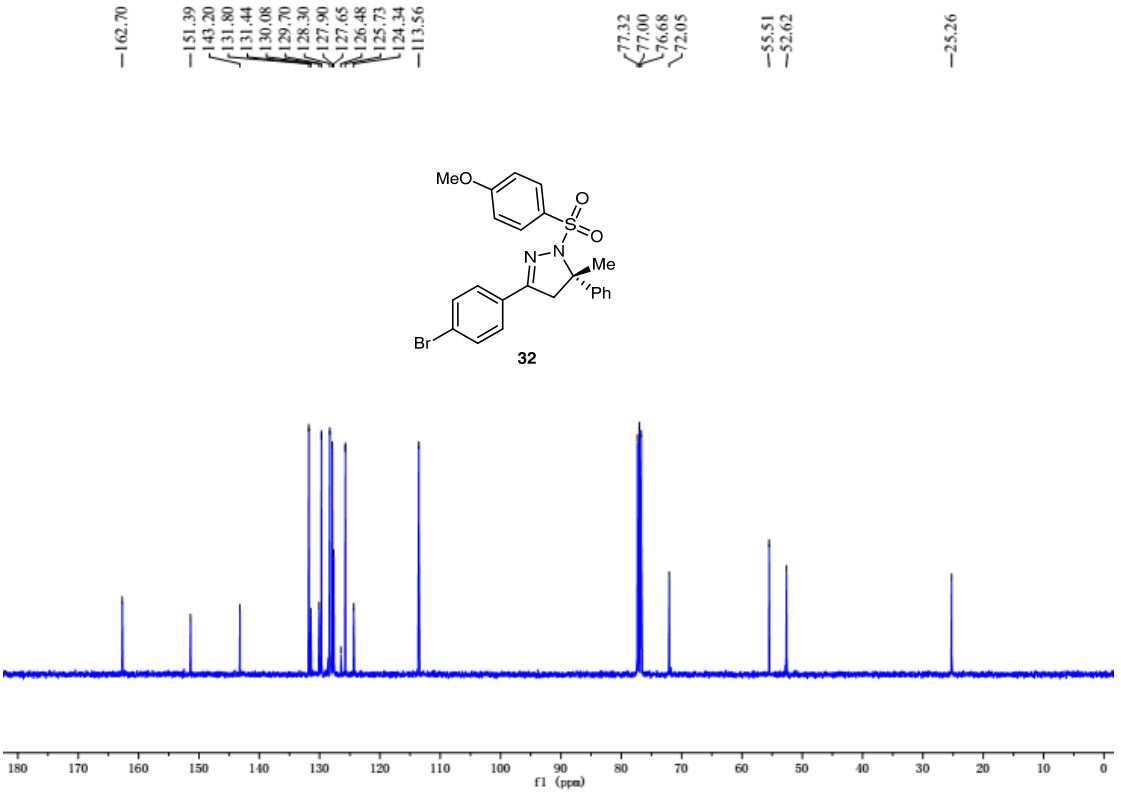
7.57
7.55
7.53
7.52
7.32
7.31
7.30
7.25
7.24
6.81
6.79
3.81
3.48
3.43
3.36
3.31
2.03
0.00
MeO
O
S
O
N
N
Me
Ph
Br
32
2.00
4.01
2.04
3.04
1.99
3.00
0.98
0.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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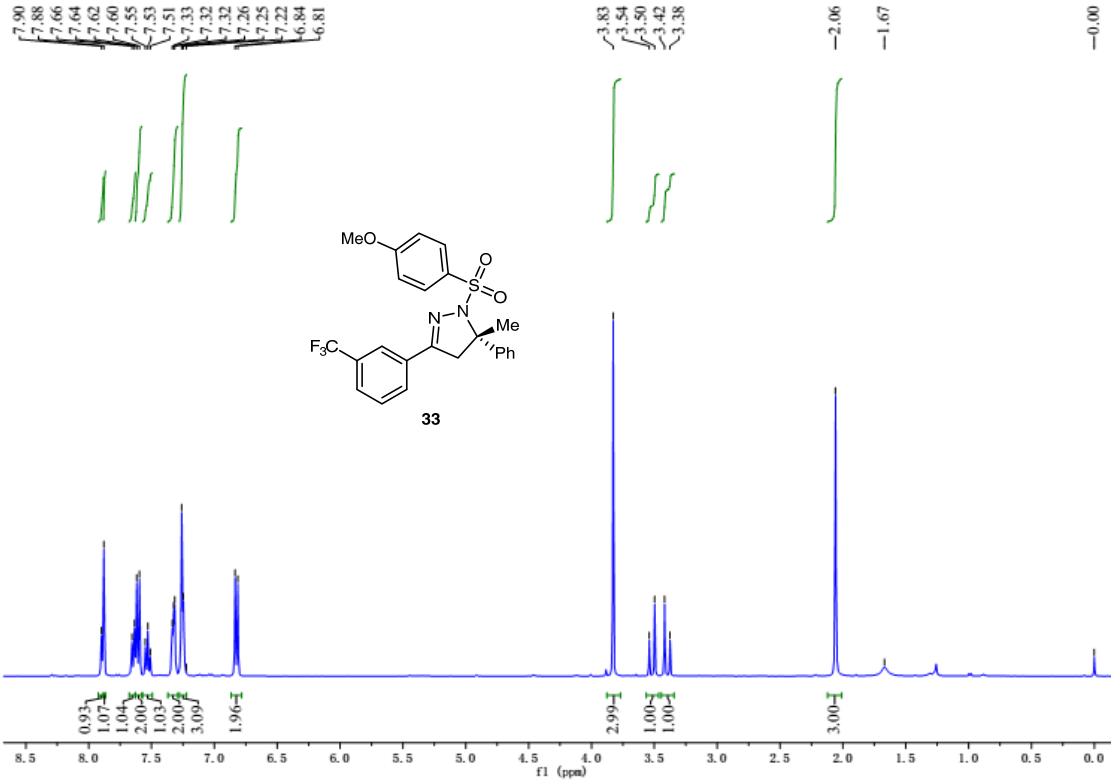
143.20
131.80
131.44
130.08
129.70
128.30
127.90
127.65
126.48
125.73
124.34
113.56
77.32
77.00
76.68
72.05
55.51
52.62
25.26
MeO
O
S
O
N
N
Me
Ph
Br
32
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.66
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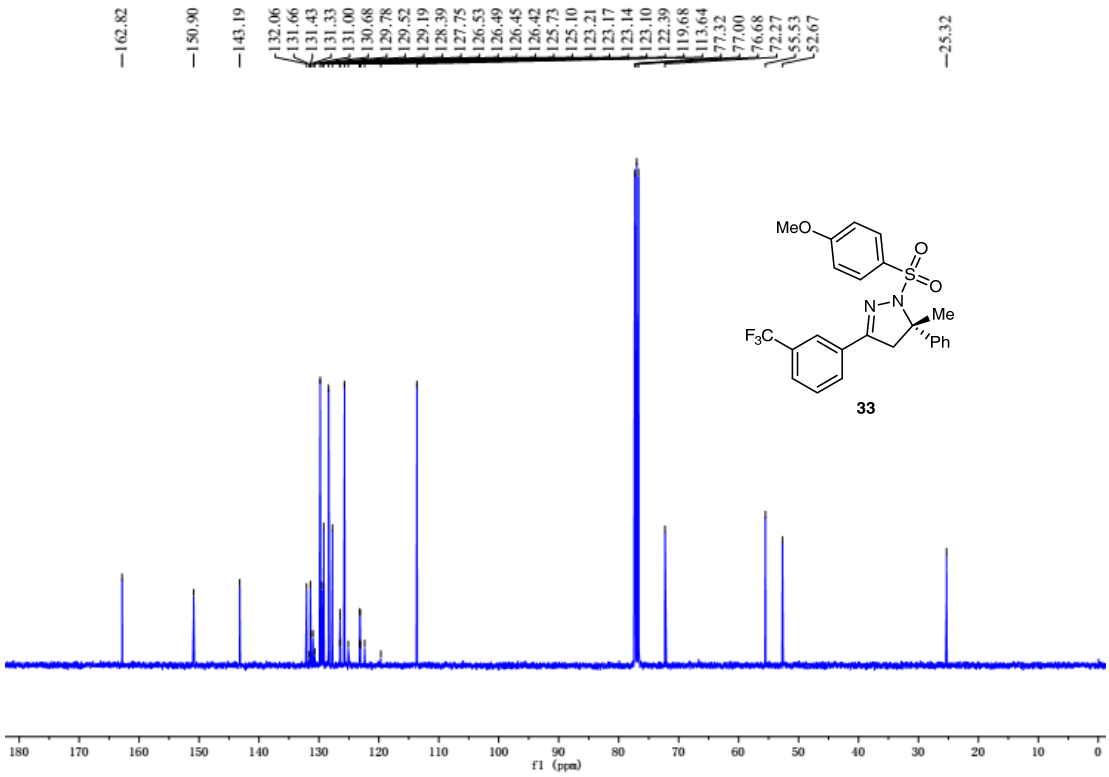
7.60
7.55
7.53
7.51
7.33
7.32
7.32
7.26
7.25
7.22
6.84
6.81
3.83
3.54
3.50
3.42
3.38
2.06
1.67
0.00
MeO
O
S
O
N
N
Me
Ph
F3C
33
0.93
1.07
1.04
2.00
1.03
2.00
3.09
1.96
2.99
1.00
1.00
3.00
f1 (ppm)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143.19
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131.43
131.33
131.00
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129.78
129.52
129.19
128.39
127.75
126.53
126.49
126.45
126.42
125.73
125.10
123.21
123.17
123.14
123.10
122.39
119.68
113.64
77.32
77.00
76.68
72.27
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52.67
25.32
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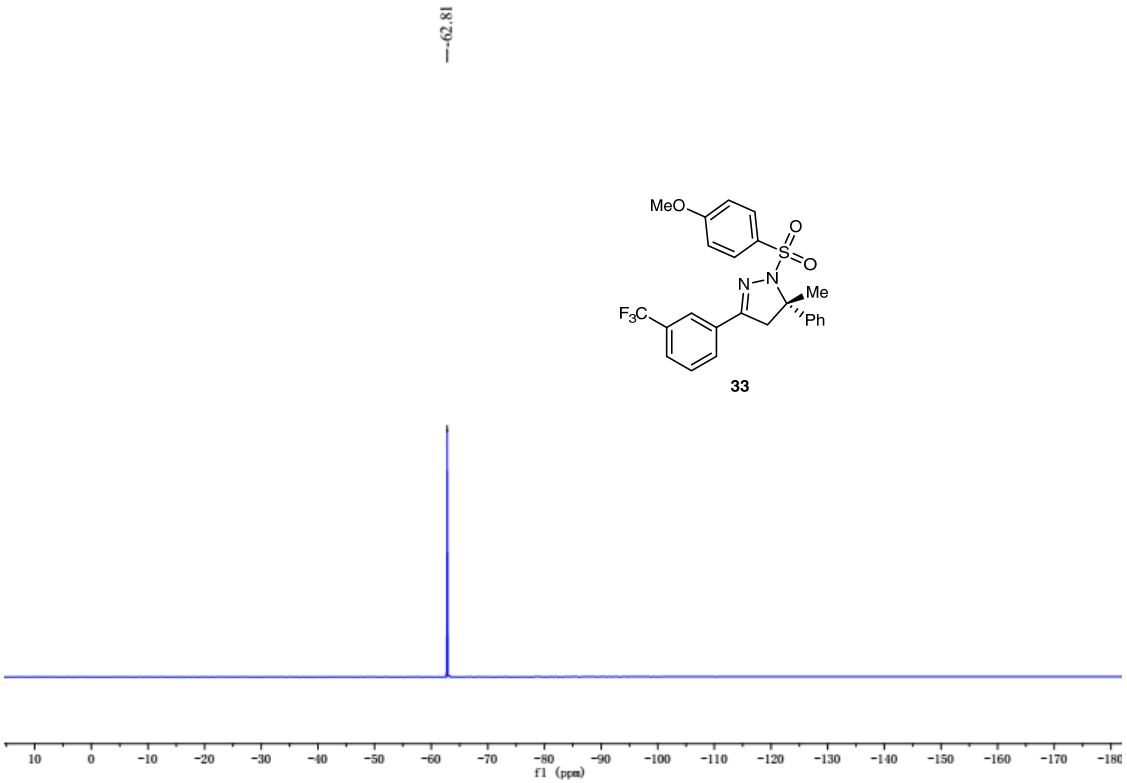
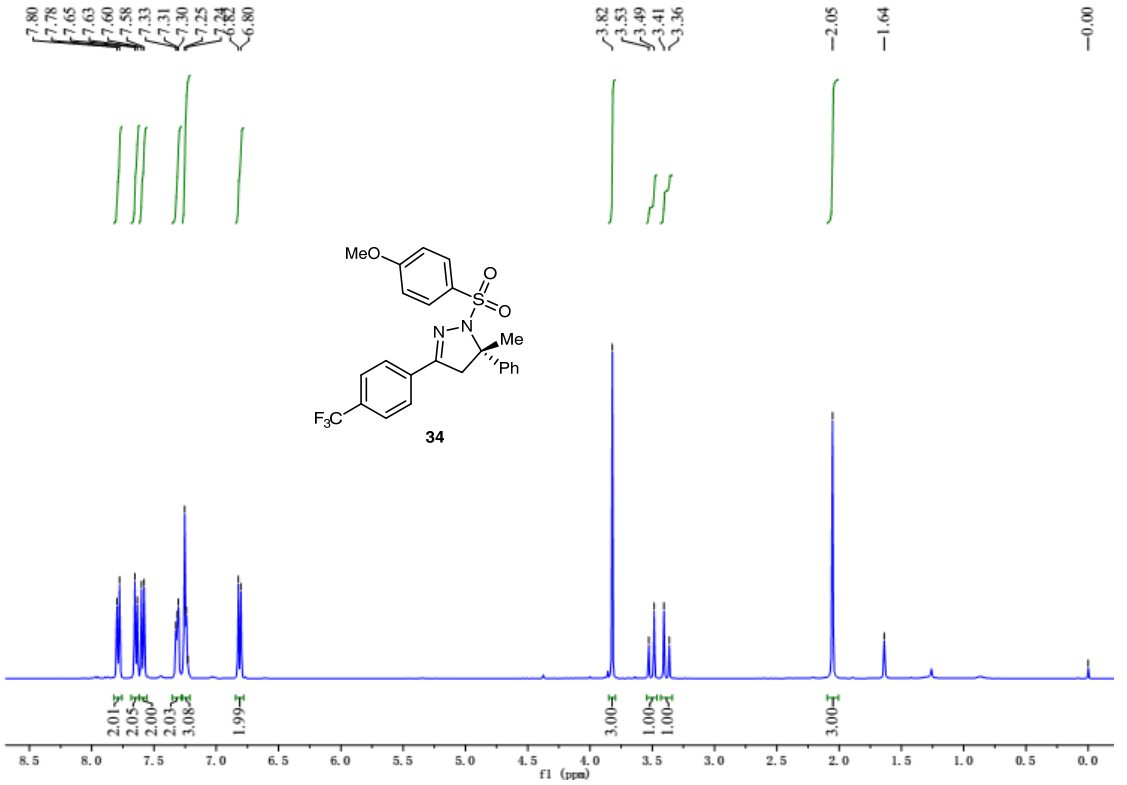
O
S
O
N
N
Me
Ph
F3C
33
f1 (ppm)


-62.81
MeO
O
S
O
N
N
Me
Ph
F3C
33
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)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7.78
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7.63
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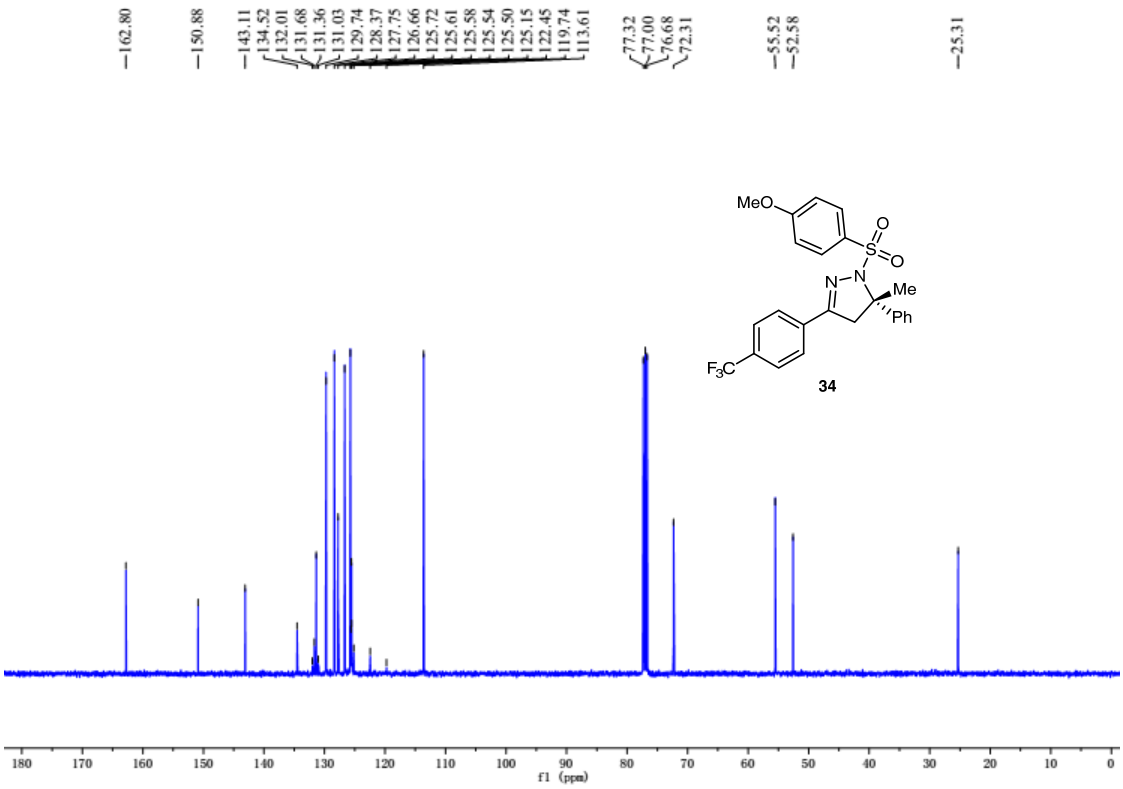
7.58
7.33
7.31
7.30
7.25
7.24
6.82
6.80
3.82
3.53
3.49
3.41
3.36
2.05
1.64
0.00
MeO
O
S
O
N
N
Me
Ph
F3C
34
2.01
2.05
2.00
2.03
3.08
1.99
3.00
1.00
1.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.03
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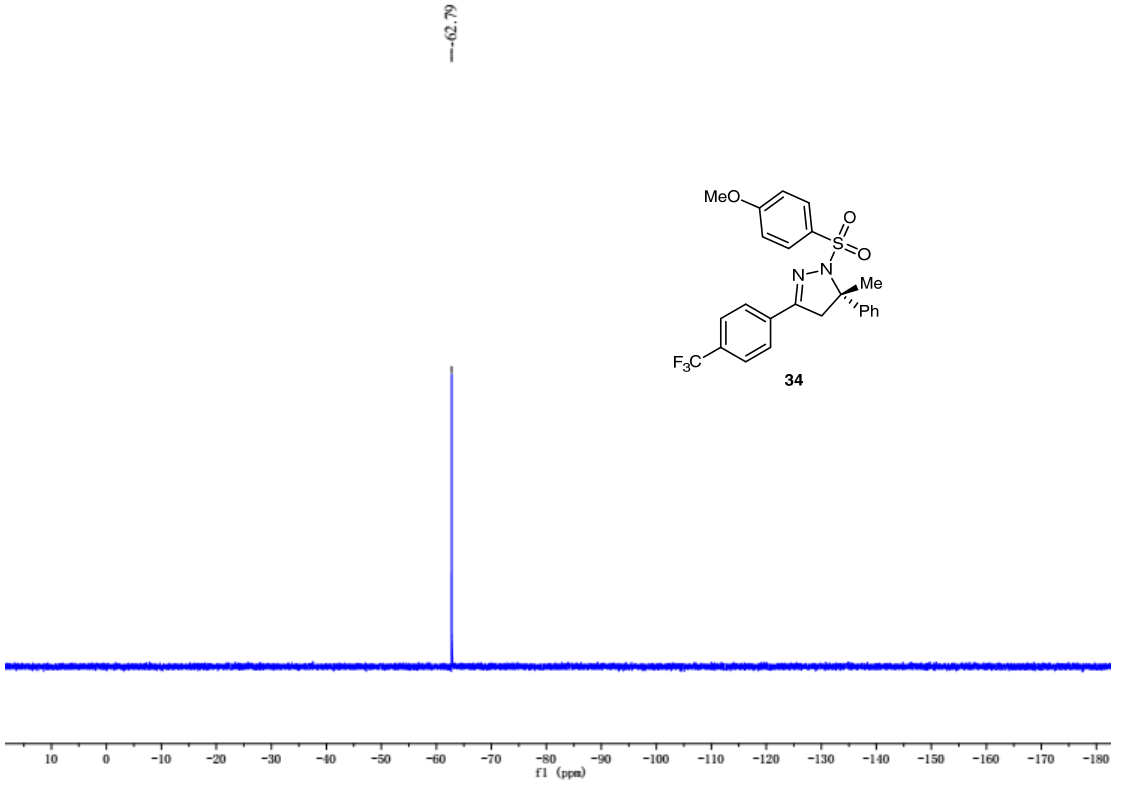
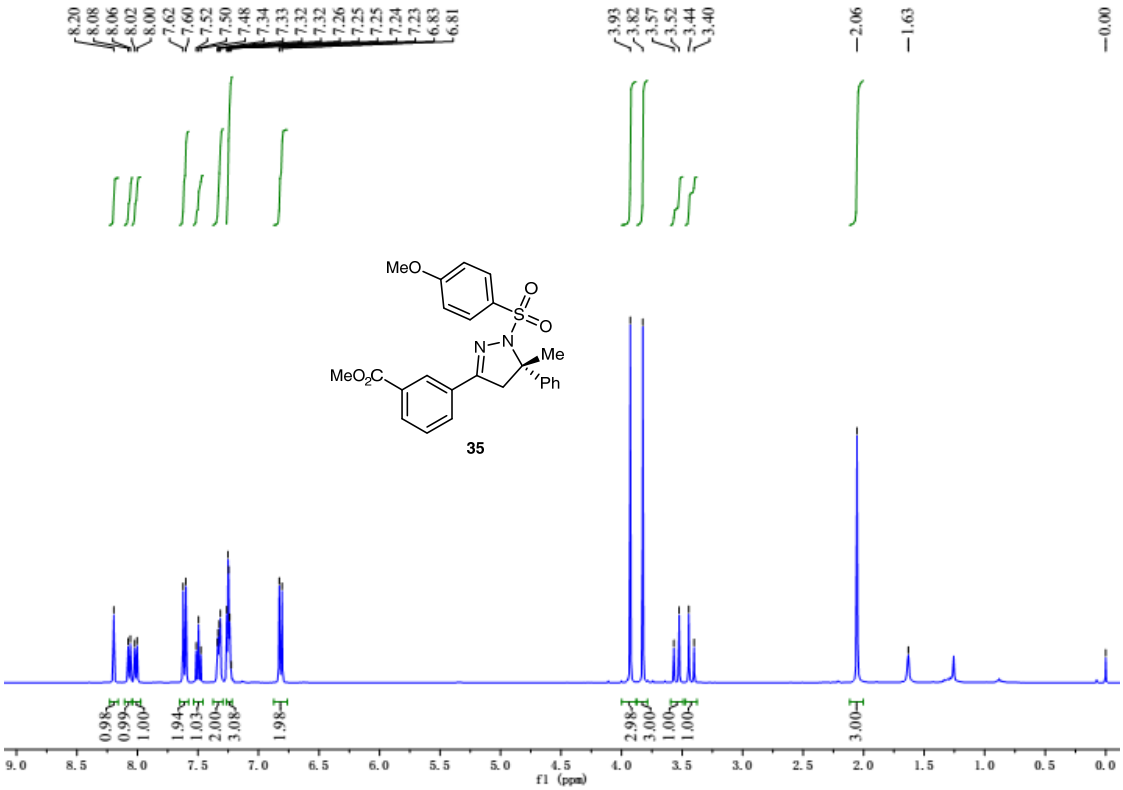
128.37
127.75
126.66
125.72
125.61
125.58
125.54
125.50
125.15
122.45
119.74
113.61
77.32
77.00
76.68
72.31
55.52
52.58
25.31
MeO
O
S
O
N
N
Me
Ph
F3C
34
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.79
MeO
O
S
O
N
N
Me
Ph
F3C
34
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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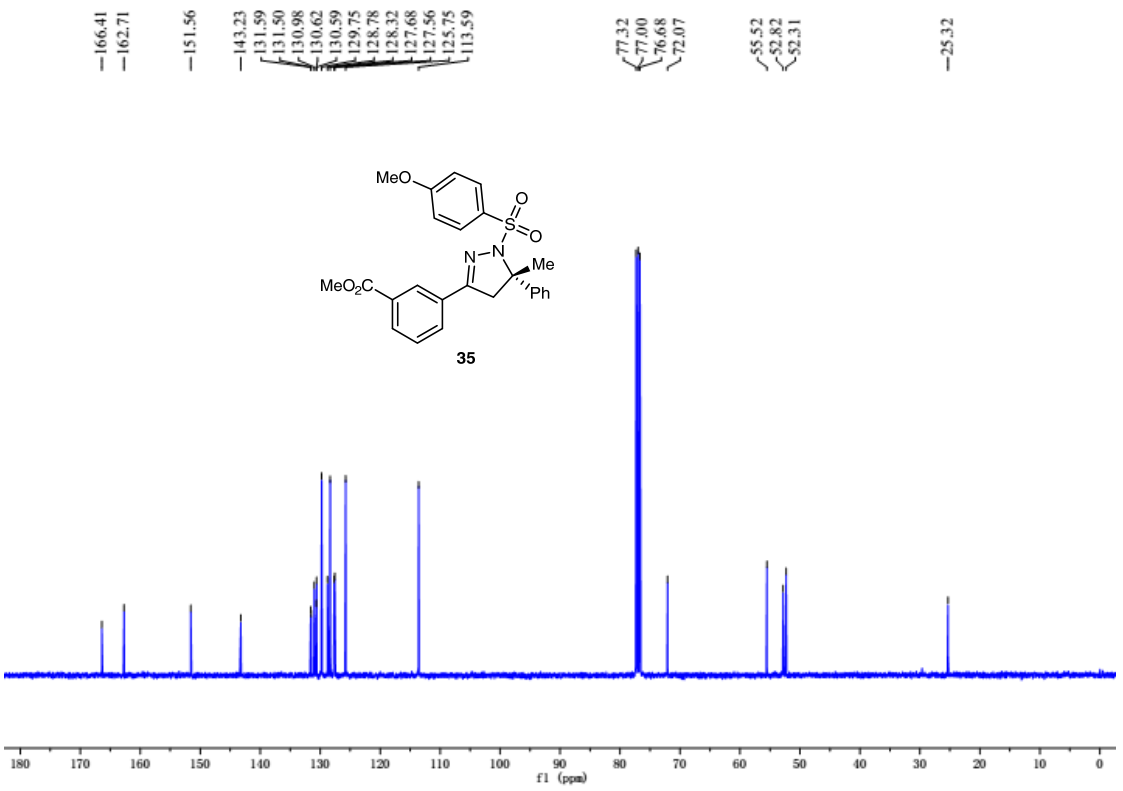
8.08
8.06
8.02
8.00
7.62
7.60
7.52
7.50
7.48
7.34
7.33
7.32
7.32
7.26
7.25
7.25
7.24
7.23
6.83
6.81
3.93
3.82
3.57
3.52
3.44
3.40
2.06
1.63
0.00
MeO
O
S
O
N
N
Me
Ph
MeO2C
35
0.98
0.99
1.00
1.94
1.03
2.00
3.08
1.98
2.98
3.00
1.00
1.00
3.00
f1 (ppm)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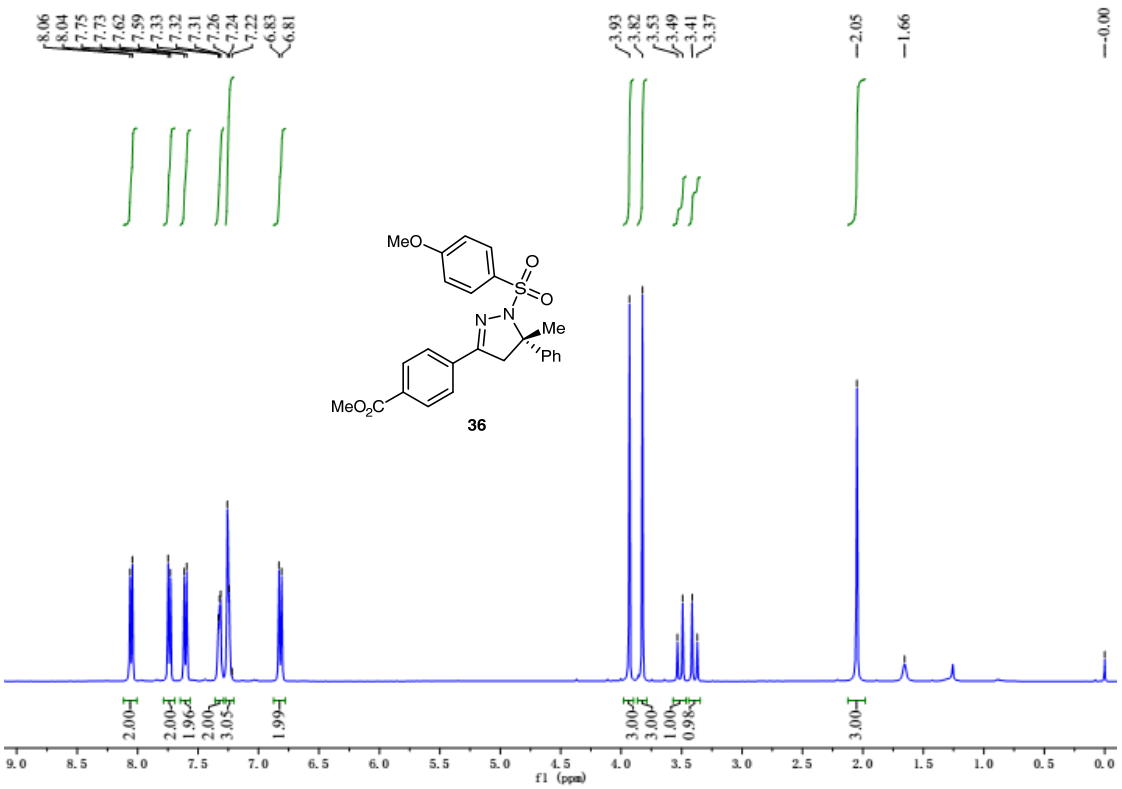
151.56
143.23
131.59
131.50
130.98
130.62
130.59
129.75
128.78
128.32
127.68
127.56
125.75
113.59
77.32
77.00
76.68
72.07
55.52
52.82
52.31
25.32
MeO
O
S
O
N
N
Me
Ph
MeO2C
35
f1 (ppm)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8.04
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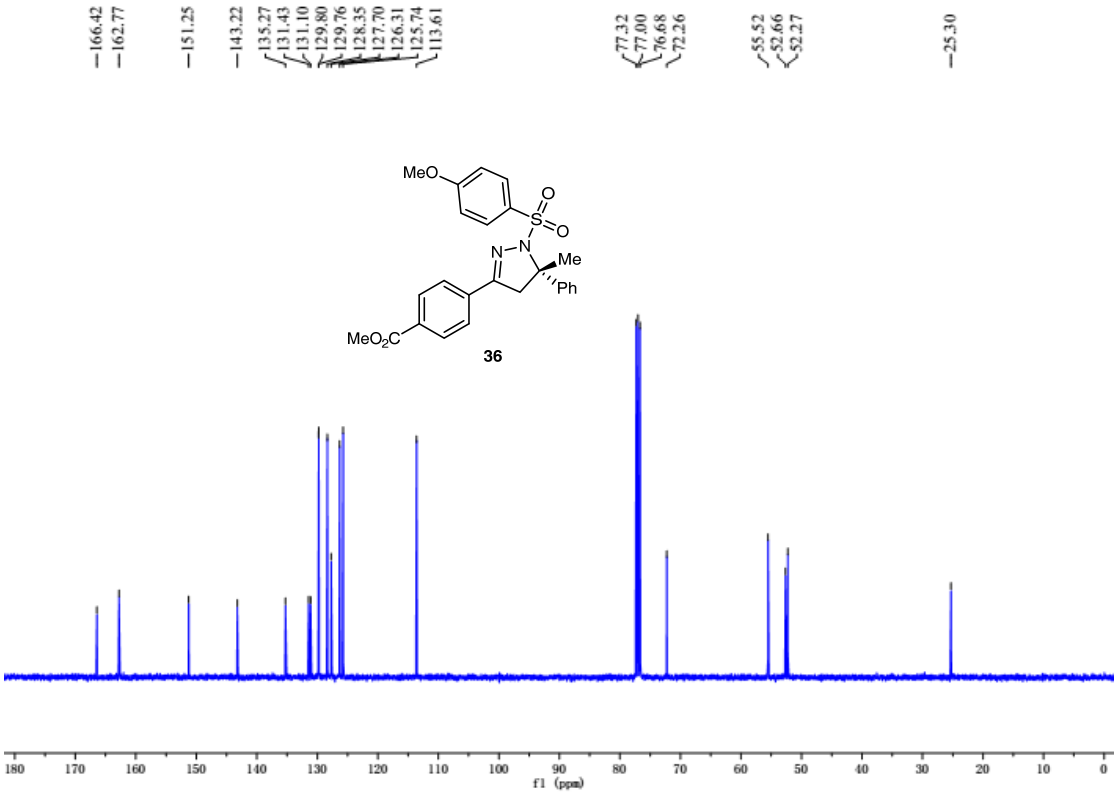
7.59
7.33
7.32
7.31
7.26
7.24
7.22
6.83
6.81
3.93
3.82
3.53
3.49
3.41
3.37
2.05
1.66
0.00
MeO
O
S
O
N
N
Me
Ph
MeO2C
36
2.00
2.00
1.96
2.00
3.05
1.99
3.00
3.00
1.00
0.98
3.00
f1 (ppm)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131.43
131.10
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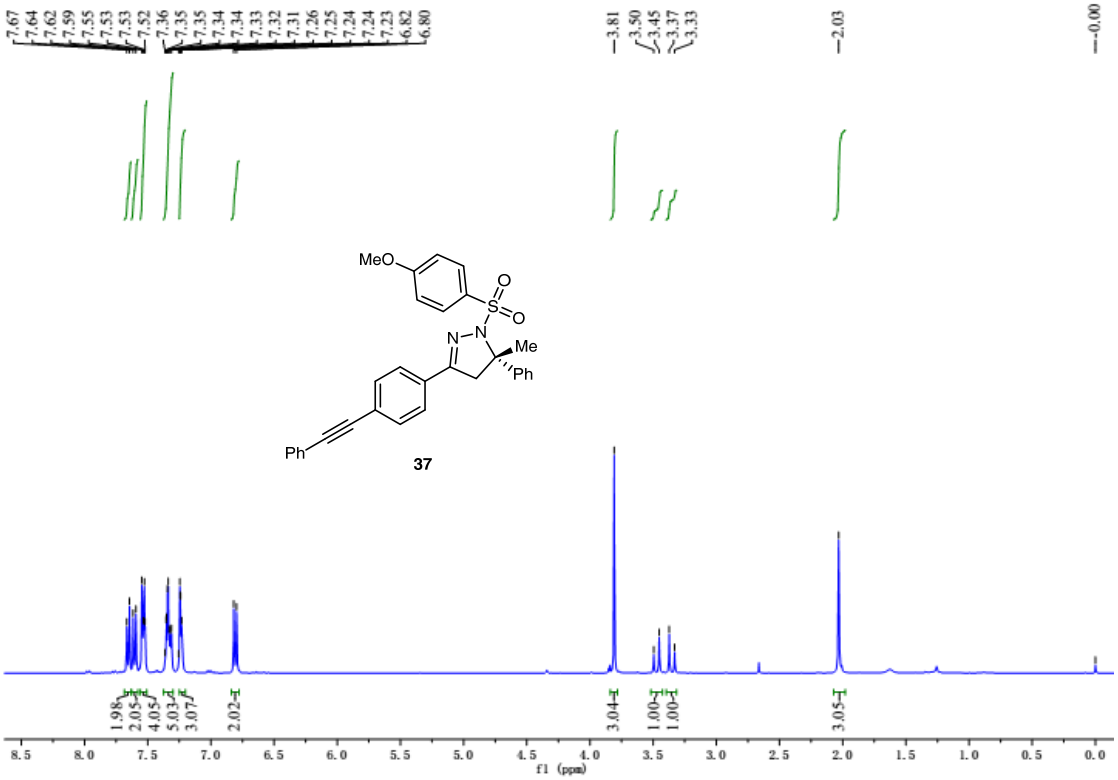
129.76
128.35
127.70
126.31
125.74
113.61
77.32
77.00
76.68
72.26
55.52
52.66
52.27
25.30
MeO
O
S
O
N
N
Me
Ph
MeO2C
36
f1 (ppm)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7.53
7.53
7.52
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.26
7.25
7.24
7.24
7.23
6.82
6.80
3.81
3.50
3.45
3.37
3.33
2.03
0.00
MeO
S
O
O
N
N
Me
Ph
Ph
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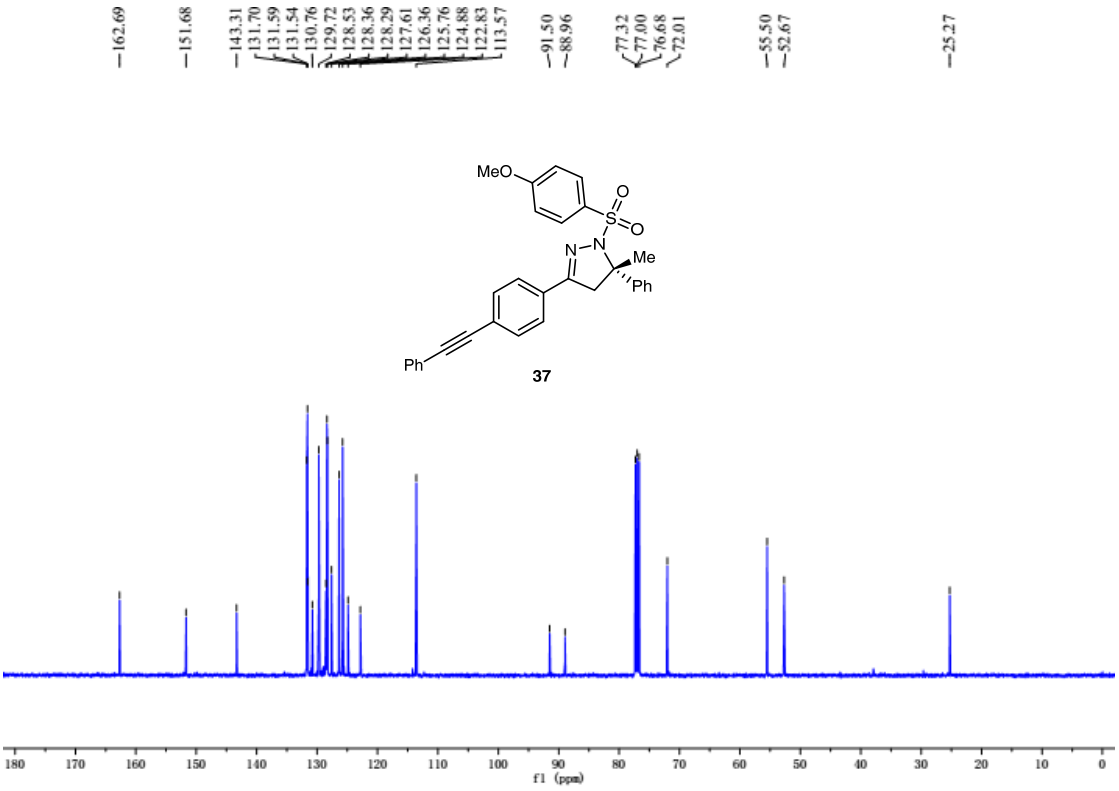
1.98
2.05
4.05
5.03
3.07
2.02
3.04
1.00
1.00
3.05
f1 (ppm)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131.54
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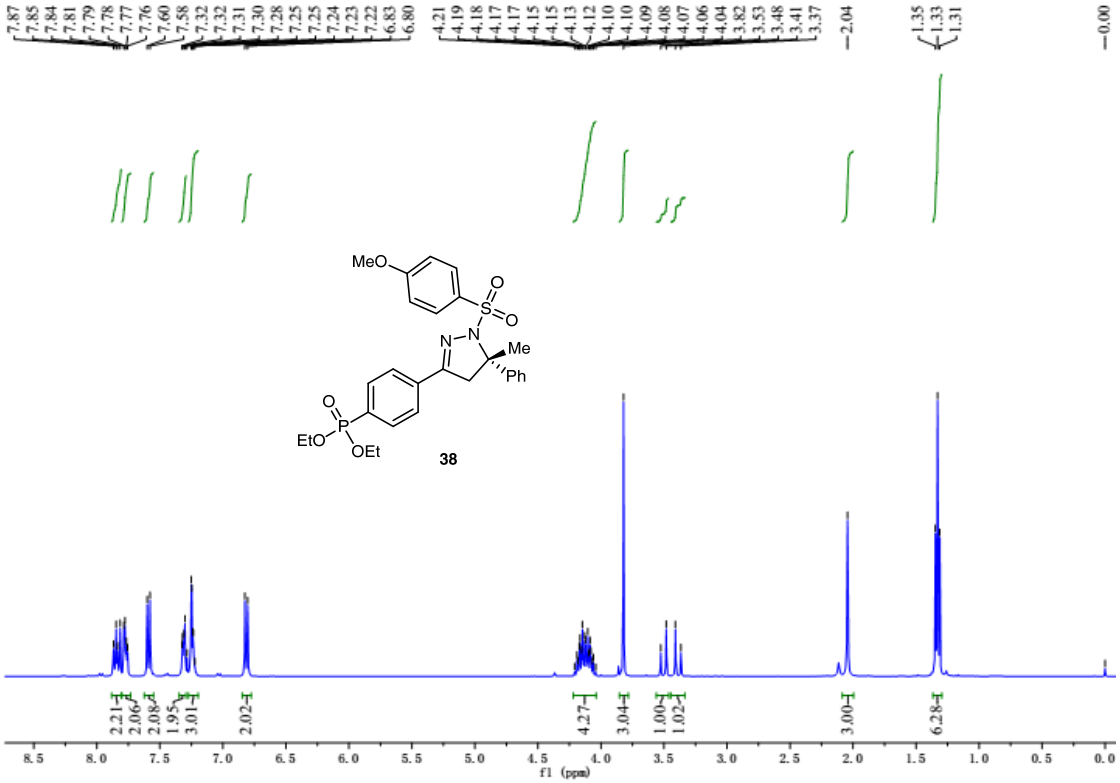
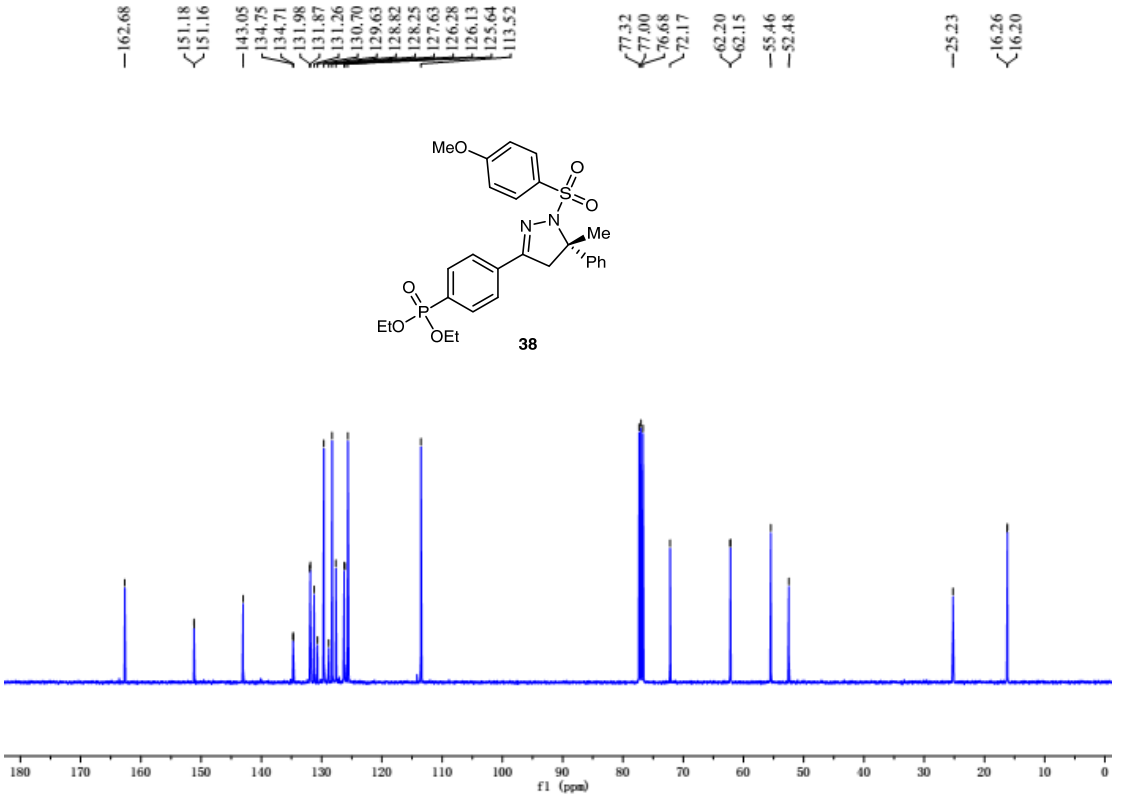
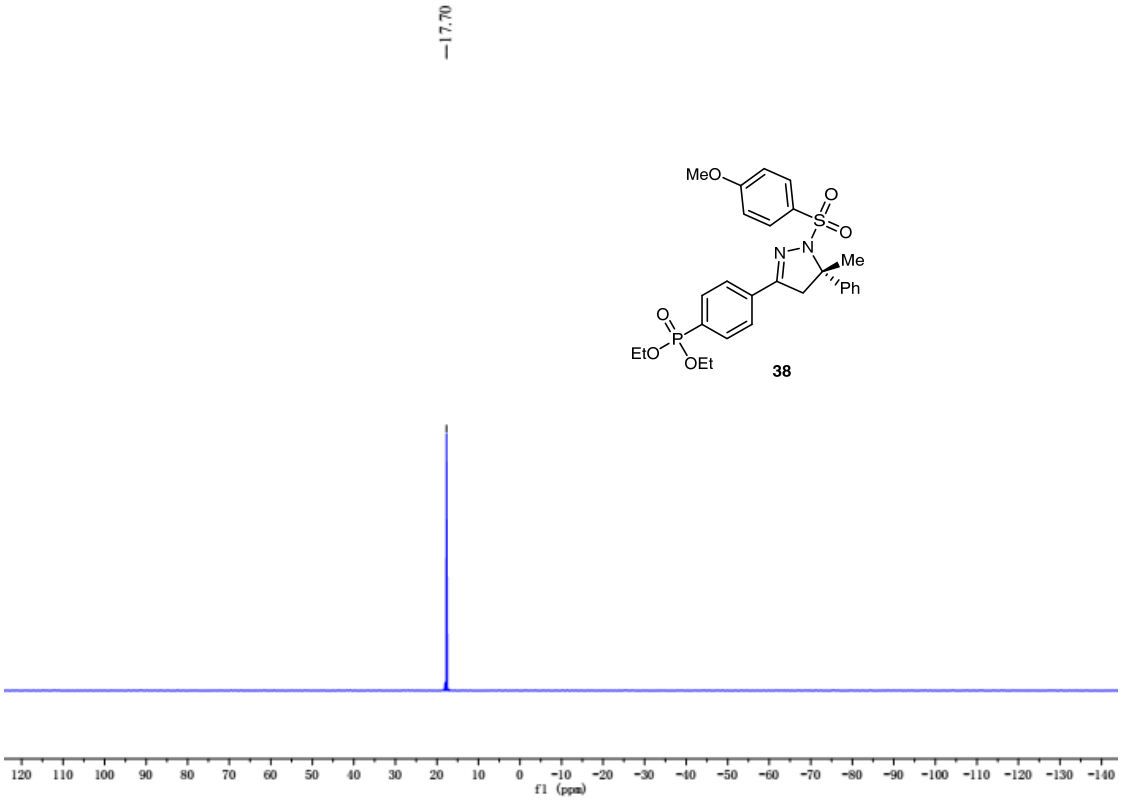
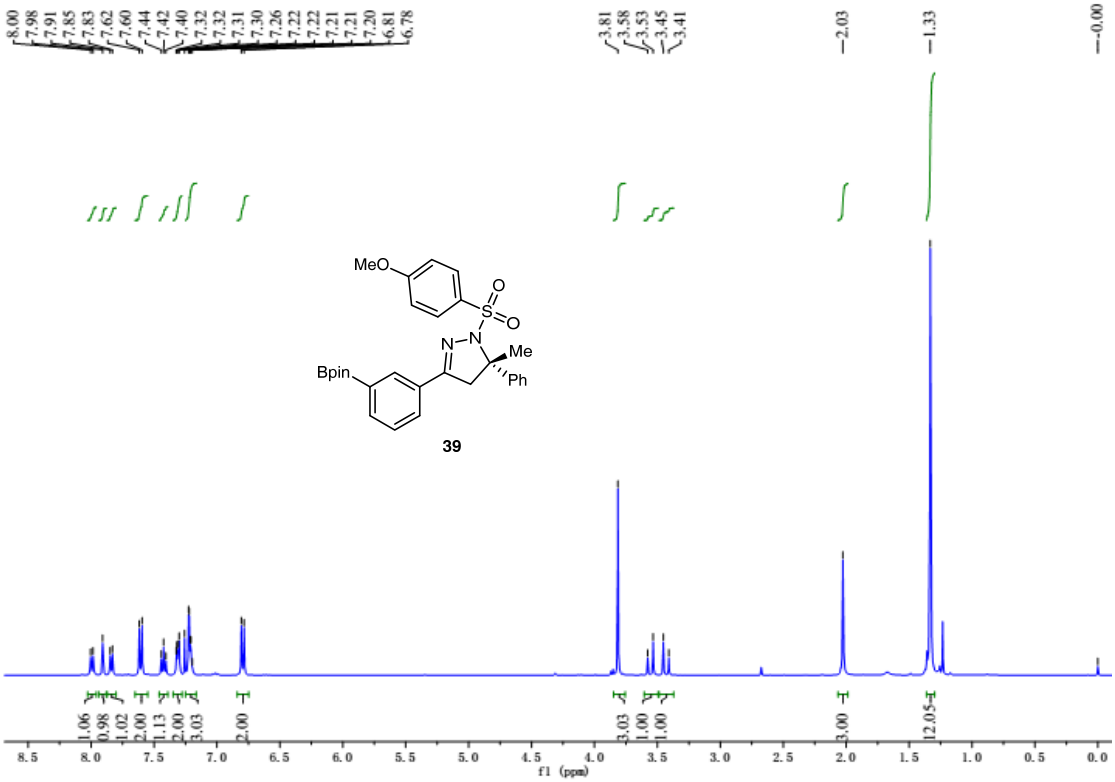
129.72
128.53
128.36
128.29
127.61
126.36
125.76
124.88
122.83
113.57
91.50
88.96
77.32
77.00
76.68
72.01
55.50
52.67
25.27
MeO
S
O
O
N
N
Me
Ph
Ph
37
f1 (ppm)


MeO
S
O
O
N
N
Me
Ph
O
P
EtO
OEt
38


MeO
S
O
O
N
N
Me
Ph
O
P
EtO
OEt
38


17.70
MeO
O
S
O
N
N
Me
Ph
O
P
EtO
OEt
38
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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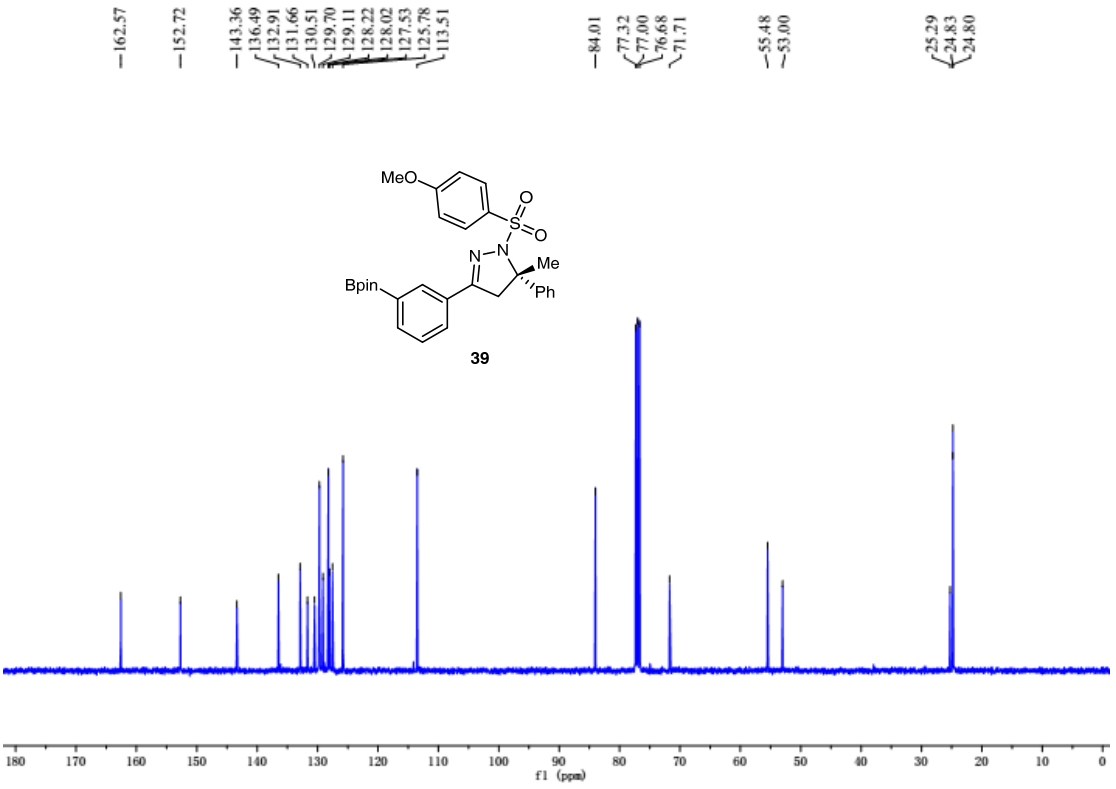
7.91
7.85
7.83
7.62
7.60
7.44
7.42
7.40
7.32
7.32
7.31
7.30
7.26
7.22
7.22
7.21
7.21
7.20
6.81
6.78
3.81
3.58
3.53
3.45
3.41
2.03
1.33
0.00
MeO
O
S
O
N
N
Me
Ph
Bpin
39
1.06
0.98
1.02
2.00
1.13
2.00
3.03
2.00
3.03
1.00
1.00
3.00
12.05
f1 (ppm)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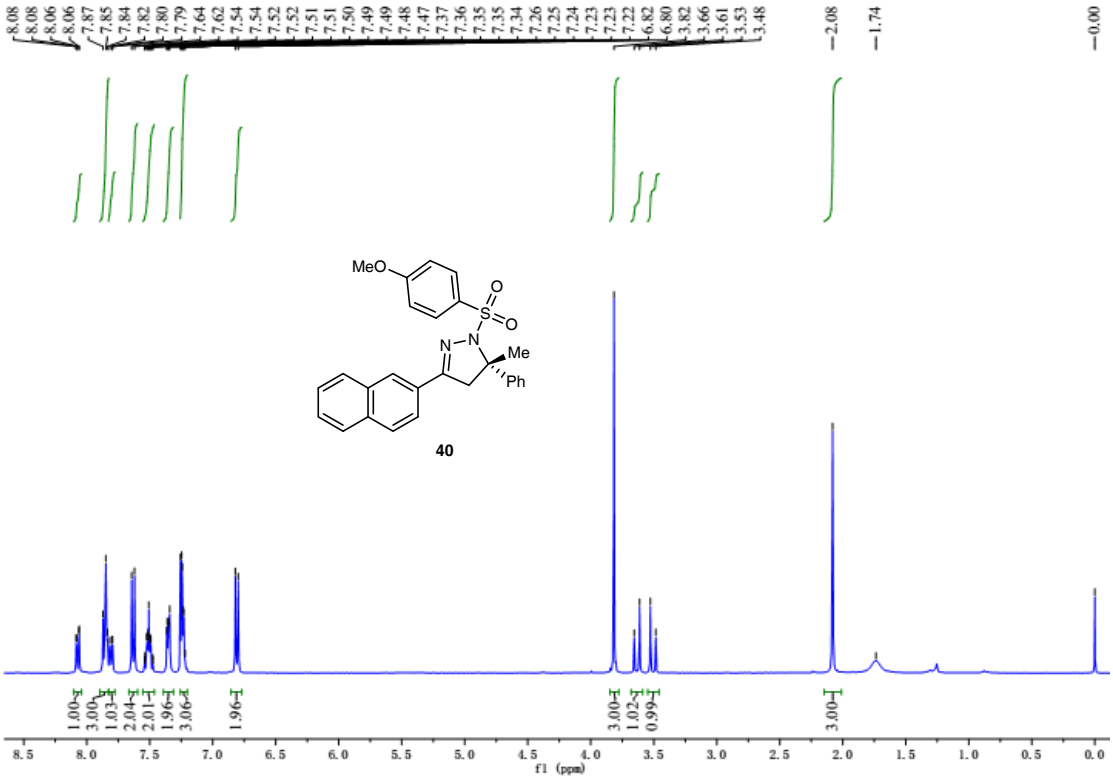
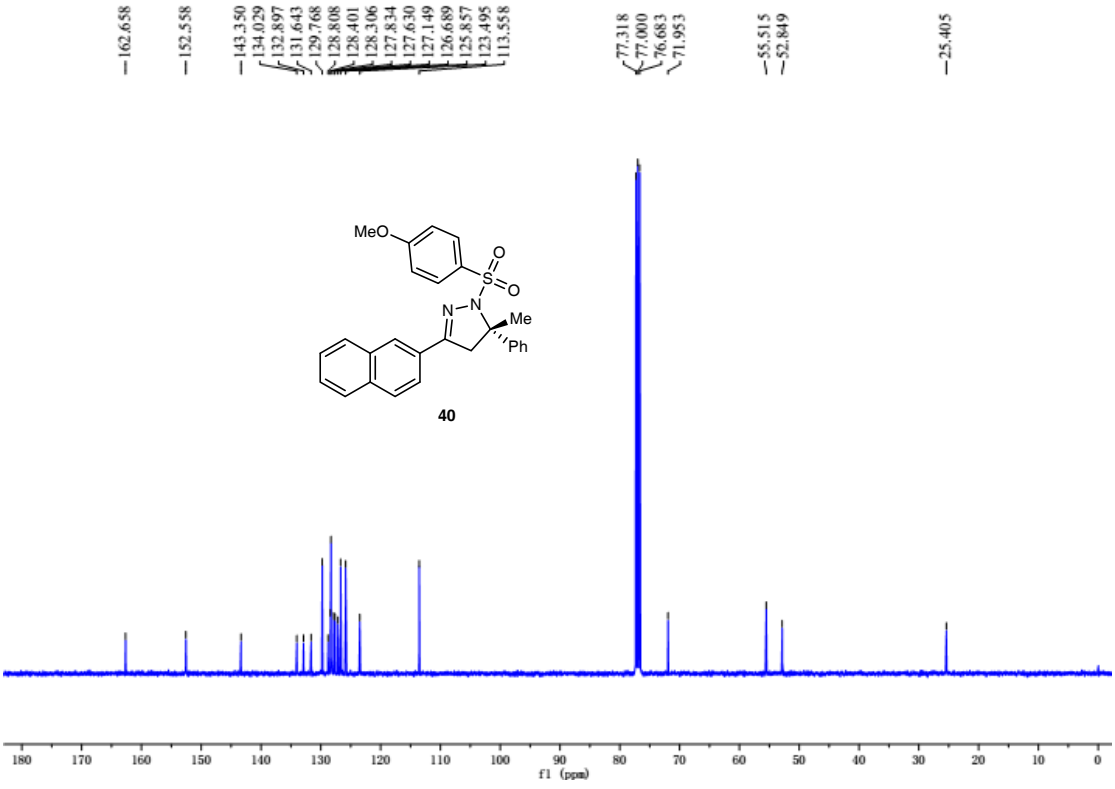
143.36
136.49
132.91
131.66
130.51
129.70
129.11
128.22
128.02
127.53
125.78
113.51
84.01
77.32
77.00
76.68
71.71
55.48
53.00
25.29
24.83
24.80
MeO
O
S
O
N
N
Me
Ph
Bpin
39
f1 (ppm)


8.08
8.08
8.06
8.06
7.87
7.85
7.84
7.82
7.80
7.79
7.64
7.62
7.54
7.54
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.37
7.36
7.35
7.35
7.34
7.26
7.25
7.24
7.23
7.23
7.22
6.82
6.80
3.82
3.66
3.61
3.53
3.48
2.08
1.74
0.00
MeO
O
S
O
N
N
Me
Ph
40
1.00
3.00
1.03
2.04
2.01
1.96
3.06
1.96
3.00
1.02
0.99
3.00
f1 (ppm)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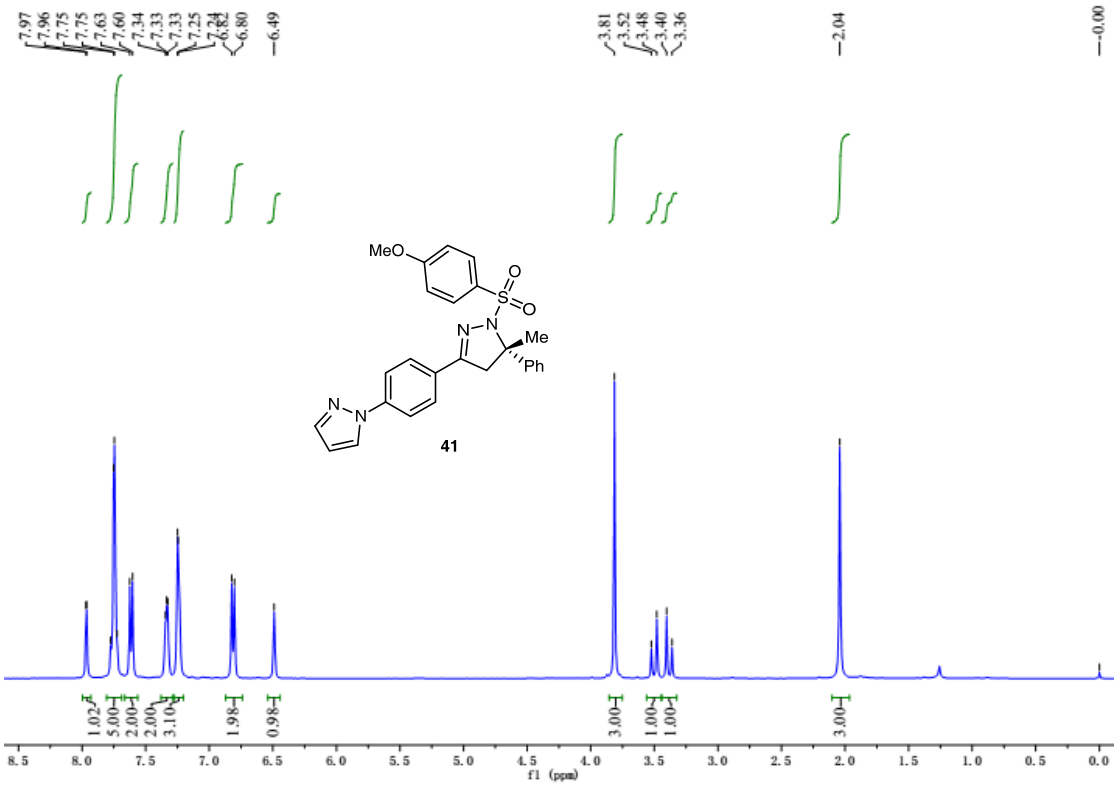
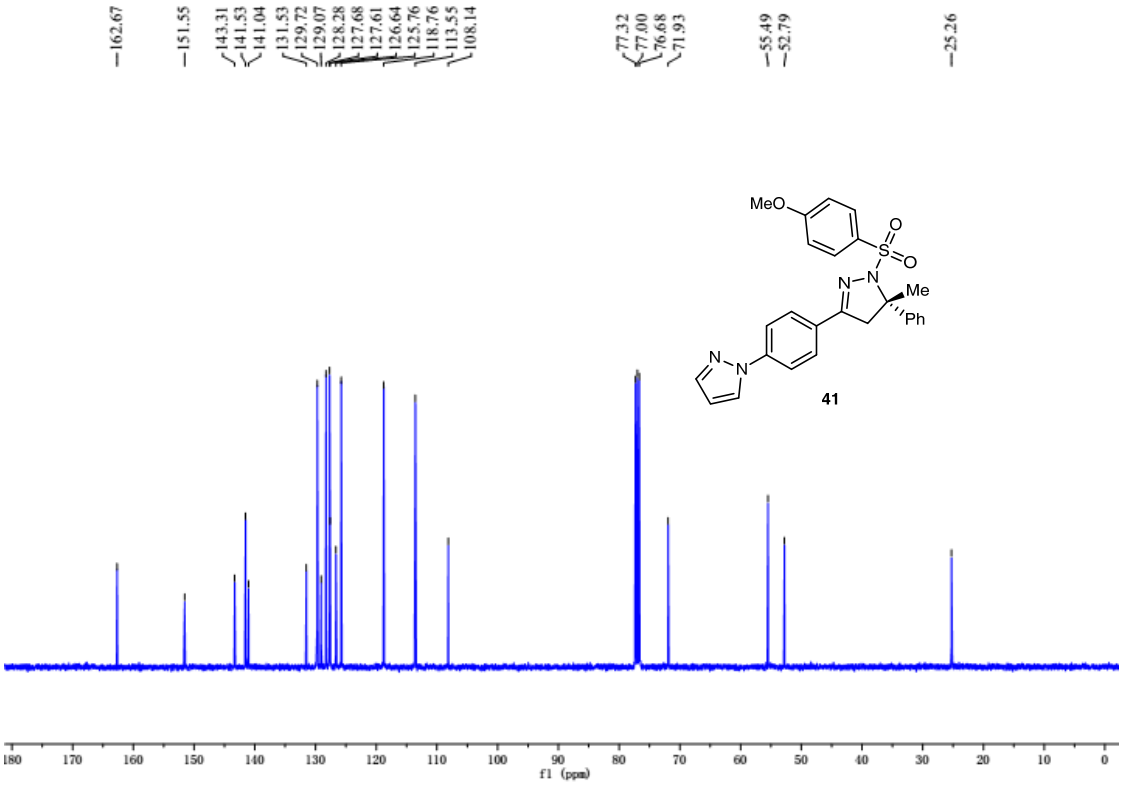
128.808
128.401
128.306
127.834
127.630
127.149
126.689
125.857
123.495
113.558
77.318
77.000
76.683
71.953
55.515
52.849
25.405
MeO
O
S
O
N
N
Me
Ph
40
f1 (ppm)


7.97
7.96
7.75
7.75
7.63
7.60
7.34
7.33
7.33
7.25
6.82
6.80
6.49
3.81
3.52
3.48
3.40
3.36
2.04
0.00
MeO
O
S
O
N
N
Me
Ph
N
N
41
1.02
5.00
2.00
2.00
3.10
1.98
0.98
3.00
1.00
1.00
3.00
f1 (ppm)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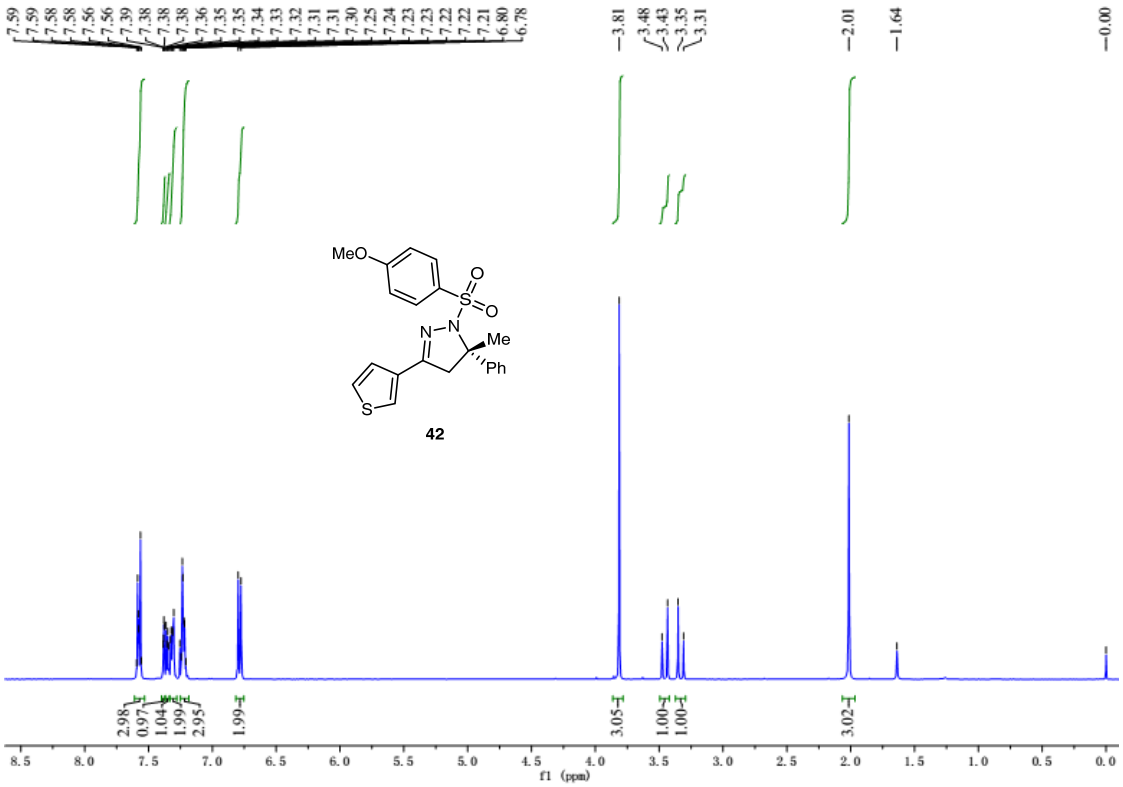
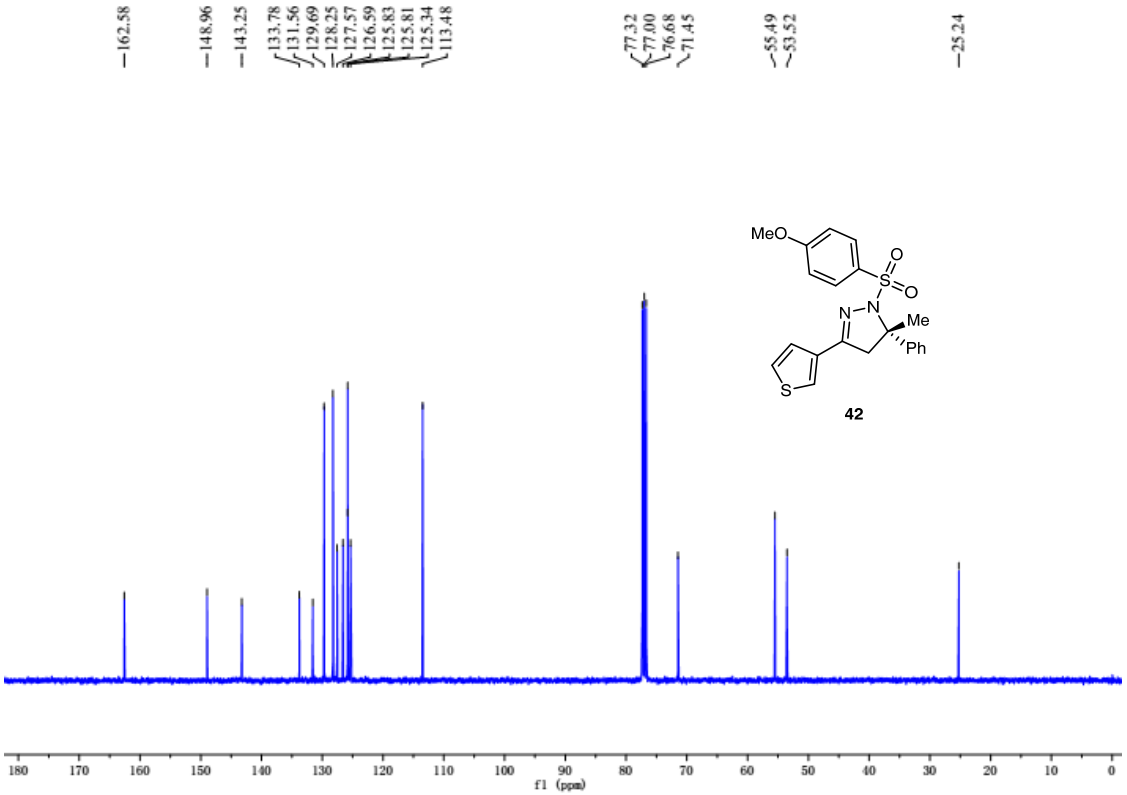
129.07
128.28
127.68
127.61
126.64
125.76
118.76
113.55
108.14
77.32
77.00
76.68
71.93
55.49
52.79
25.26
MeO
O
S
O
N
N
Me
Ph
N
N
41
f1 (ppm)


7.59
7.59
7.58
7.58
7.56
7.56
7.39
7.38
7.38
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.25
7.24
7.23
7.23
7.22
7.22
7.21
6.80
6.78
3.81
3.48
3.43
3.35
3.31
2.01
1.64
0.00
MeO
O
S
O
N
N
Me
Ph
S
42
2.98
0.97
1.04
1.99
2.95
1.99
3.05
1.00
1.00
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.56
129.69
128.25
127.57
126.59
125.83
125.81
125.34
113.48
77.32
77.00
76.68
71.45
55.49
53.52
25.24
MeO
O
S
O
N
N
Me
Ph
S
42
180
170
160
150
140
130
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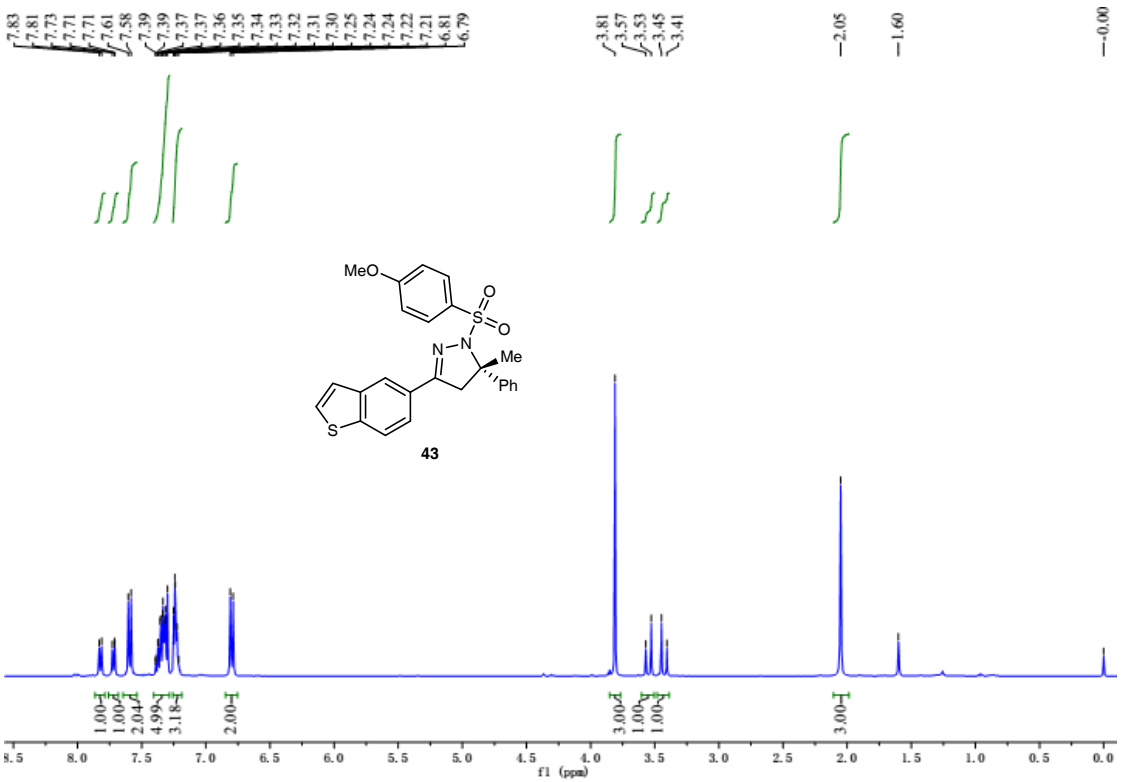
f1 (ppm)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7.34
7.33
7.32
7.31
7.30
7.25
7.24
7.24
7.22
7.21
6.81
6.79
3.81
3.57
3.53
3.45
3.41
2.05
1.60
0.00
MeO
O
S
O
N
N
Me
Ph
S
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2.04
4.99
3.18
2.00
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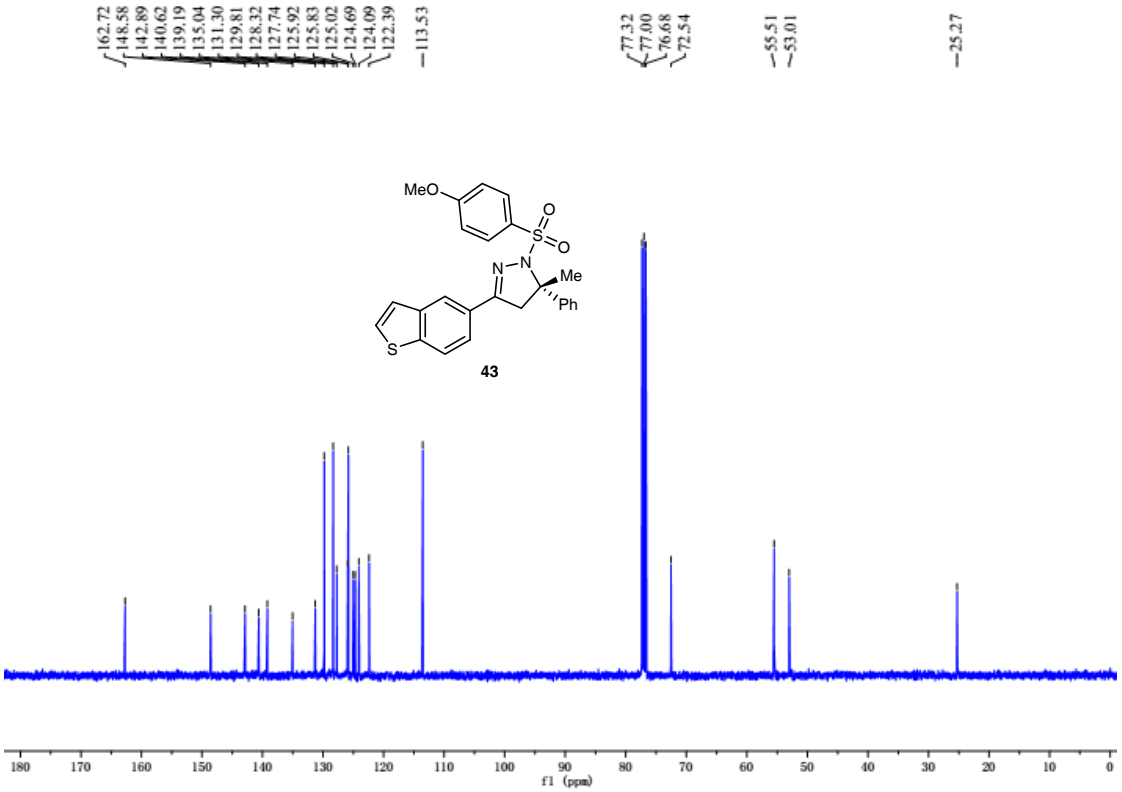
3.00
f1 (ppm)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127.74
125.92
125.83
125.02
124.69
124.09
122.39
113.53
77.32
77.00
76.68
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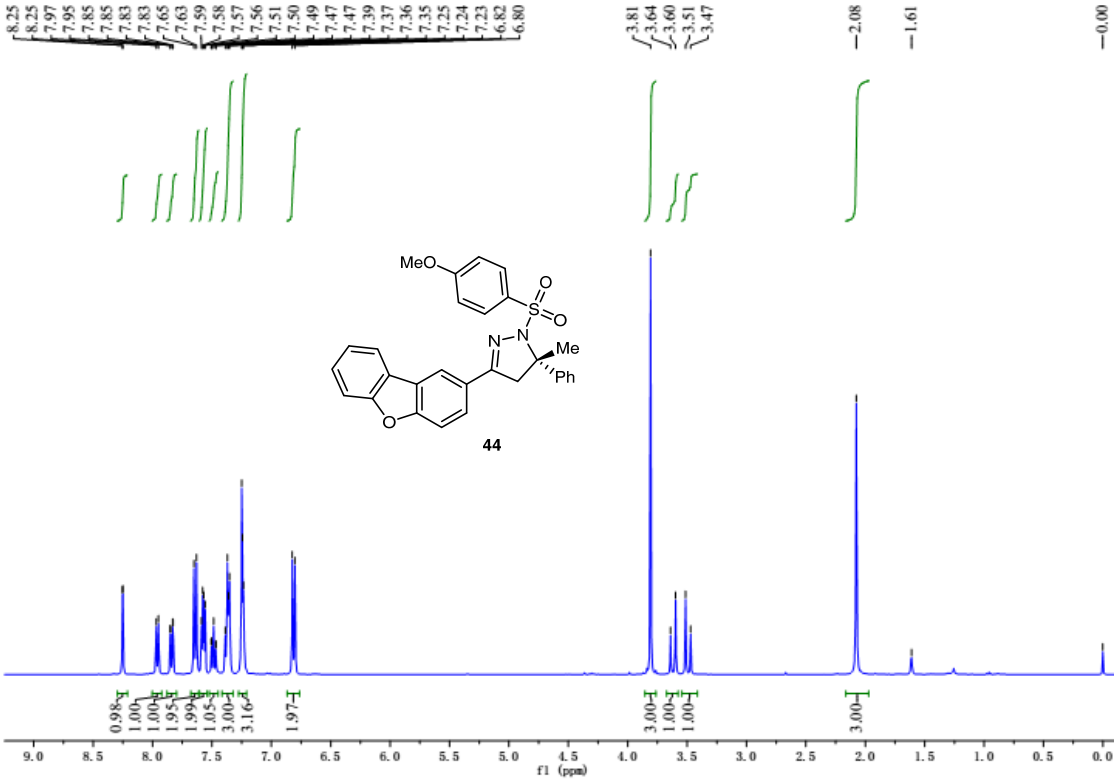
53.01
25.27
MeO
O
S
O
N
N
Me
Ph
S
43
f1 (ppm)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7.83
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7.63
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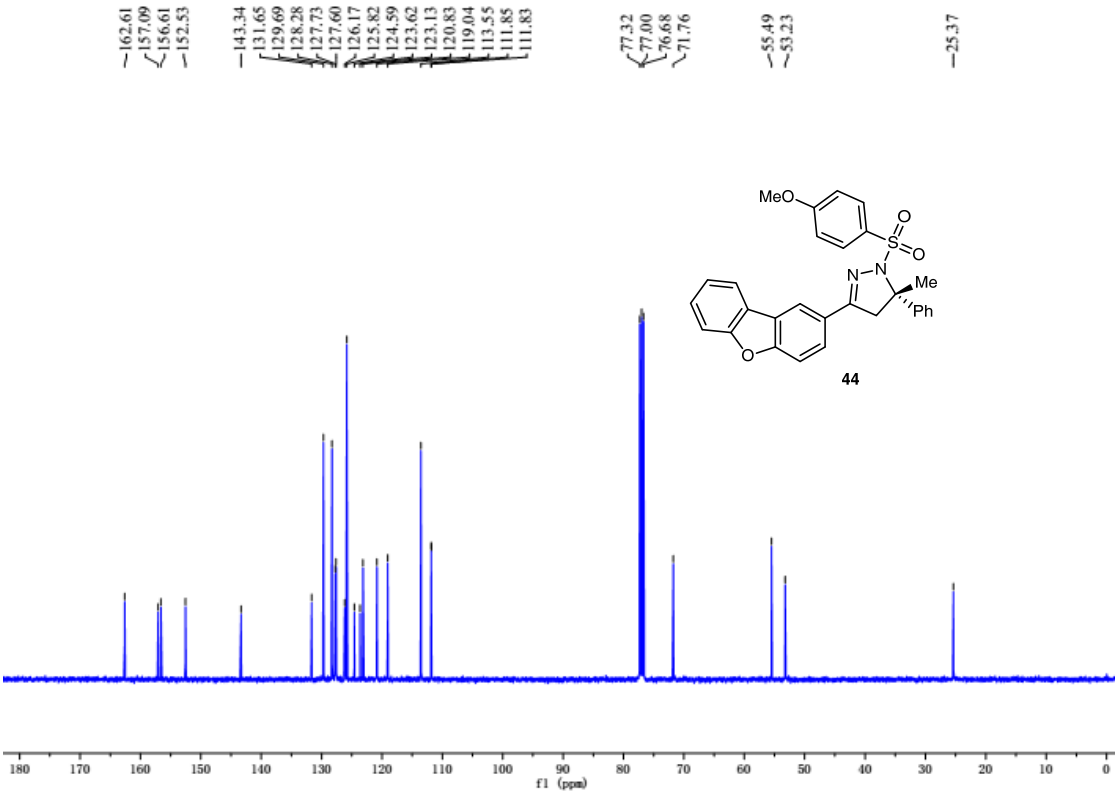
7.57
7.56
7.51
7.50
7.49
7.47
7.47
7.39
7.37
7.36
7.35
7.25
7.24
7.23
6.82
6.80
3.81
3.64
3.60
3.51
3.47
2.08
1.61
0.00
MeO
O
S
O
N
N
Me
Ph
O
44
0.98
1.00
1.00
1.95
1.99
1.05
3.00
3.16
1.97
3.00
1.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.60
126.17
125.82
124.59
123.62
123.13
120.83
119.04
113.55
111.85
111.83
77.32
77.00
76.68
71.76
55.49
53.23
25.37
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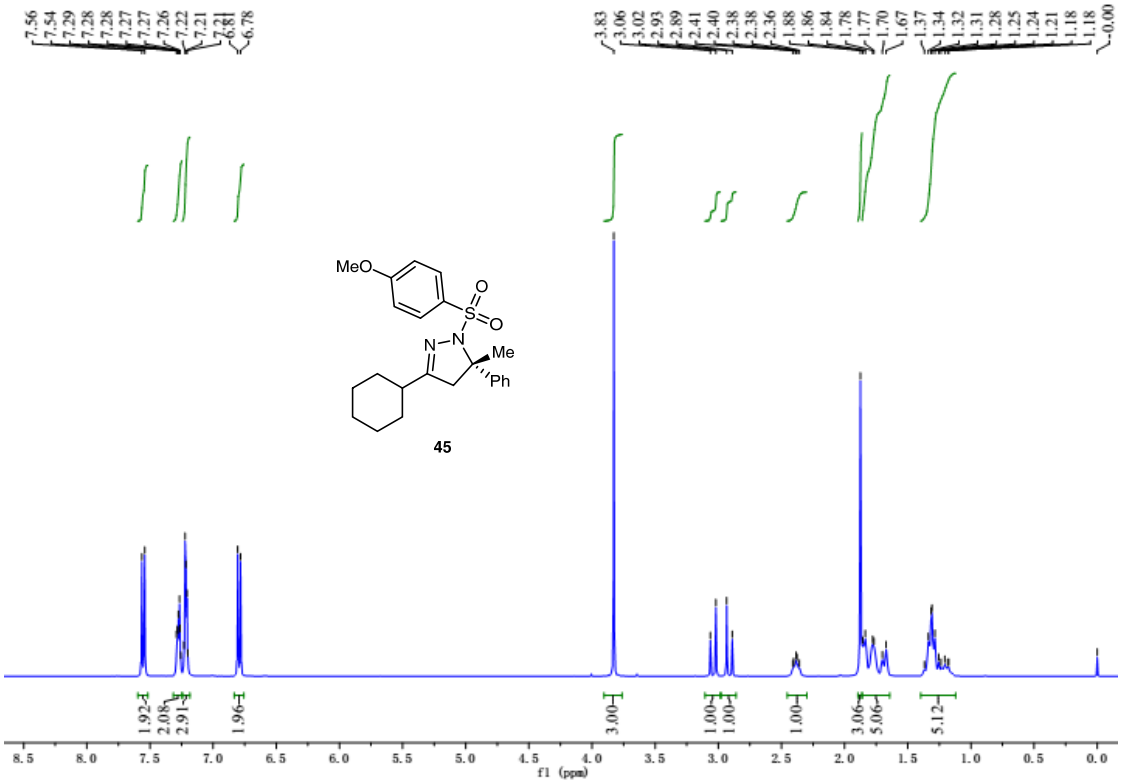
O
N
N
Me
Ph
O
44
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.22
7.21
7.21
6.81
6.78
3.83
3.06
3.02
2.93
2.89
2.41
2.40
2.38
2.38
2.36
1.88
1.86
1.84
1.78
1.77
1.70
1.67
1.37
1.34
1.32
1.31
1.28
1.25
1.24
1.21
1.18
1.18
0.00
MeO
O
S
O
N
N
Me
Ph
45
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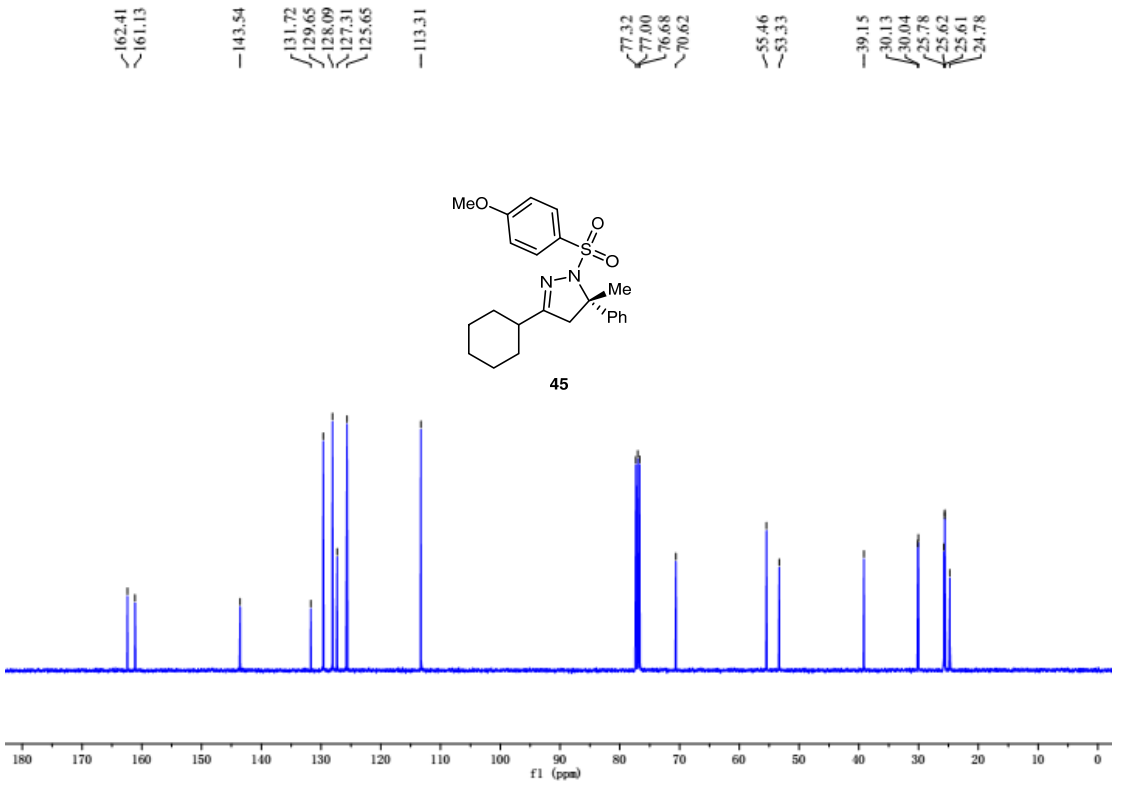
1.96
3.00
1.00
1.00
1.00
3.06
5.06
5.12
f1 (ppm)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127.31
125.65
113.31
77.32
77.00
76.68
70.62
55.46
53.33
39.15
30.13
30.04
25.78
25.62
25.61
24.78
MeO
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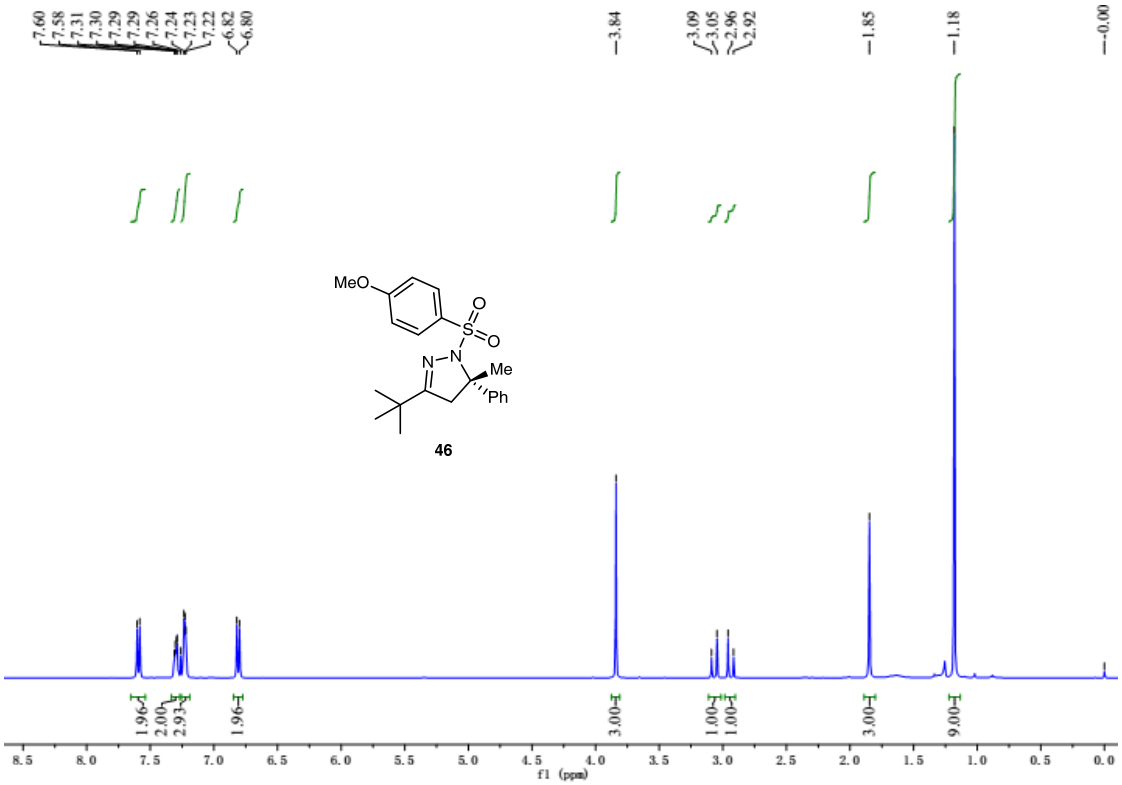
S
O
N
N
Me
Ph
45
f1 (ppm)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7.58
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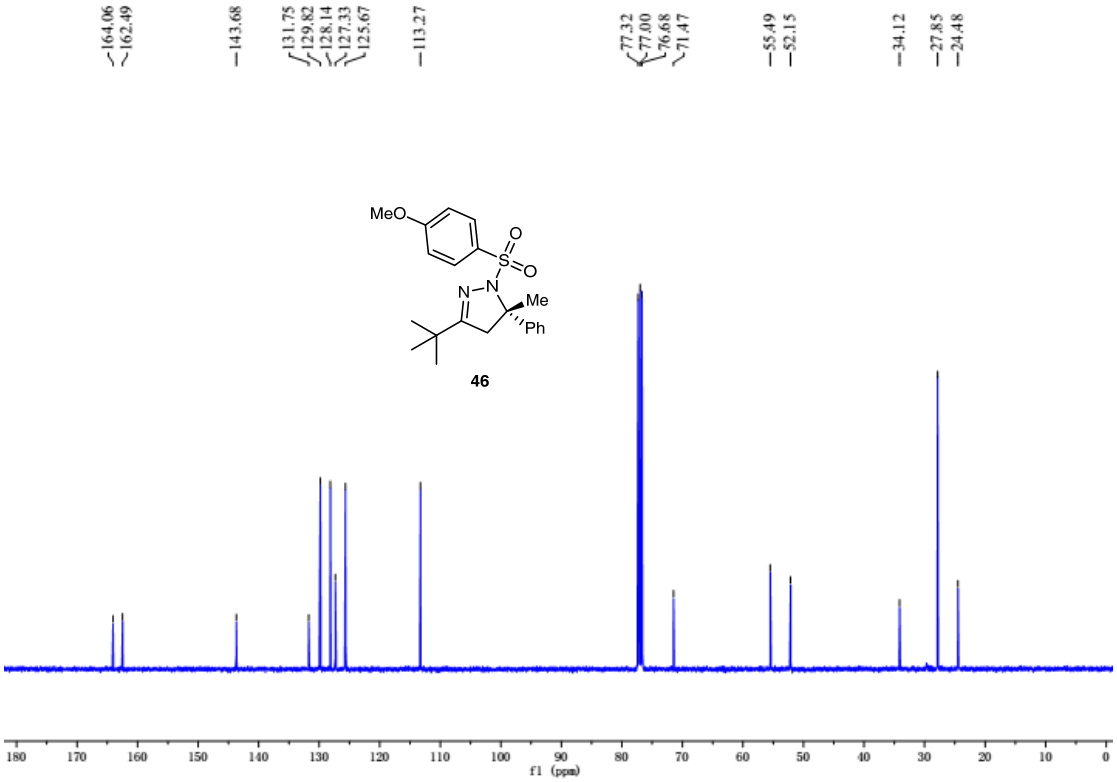
7.23
7.22
6.82
6.80
3.84
3.09
3.05
2.96
2.92
1.85
1.18
0.00
MeO
O
O
S
N
N
Me
Ph
46
1.96
2.00
2.93
1.96
3.00
1.00
1.00
3.00
9.00
f1 (ppm)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162.49
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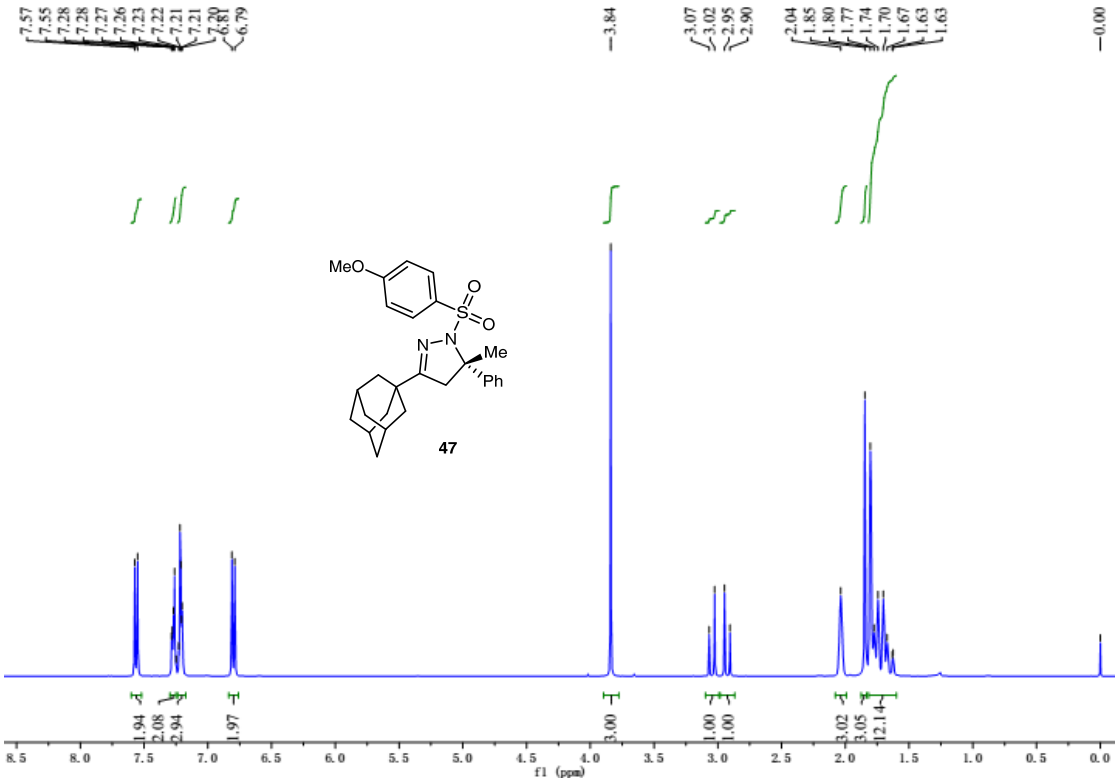
128.14
127.33
125.67
113.27
77.32
77.00
76.68
71.47
55.49
52.15
34.12
27.85
24.48
MeO
O
O
S
N
N
Me
Ph
46
f1 (ppm)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7.27
7.26
7.23
7.22
7.21
7.21
7.20
6.81
6.79
3.84
3.07
3.02
2.95
2.90
2.04
1.85
1.80
1.77
1.74
1.70
1.67
1.63
1.63
0.00
MeO
O
S
O
N
N
Me
Ph
47
1.94
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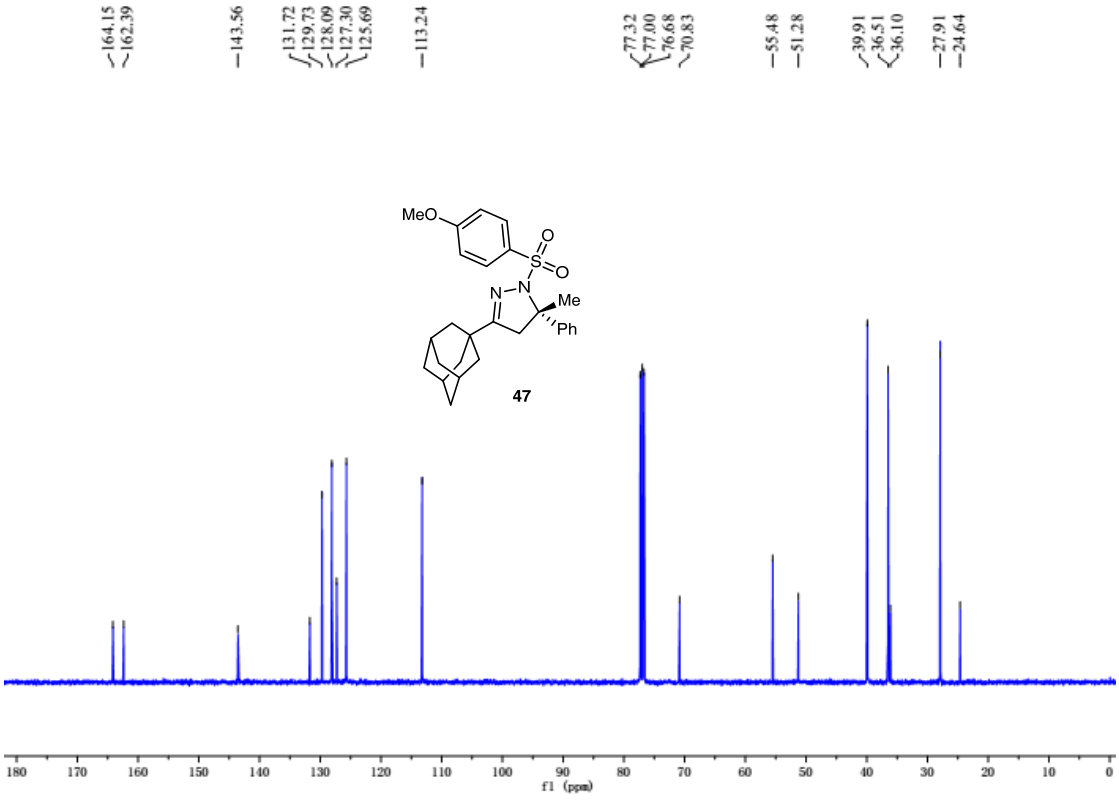
2.94
1.97
3.00
1.00
1.00
3.02
3.05
12.14
f1 (ppm)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128.09
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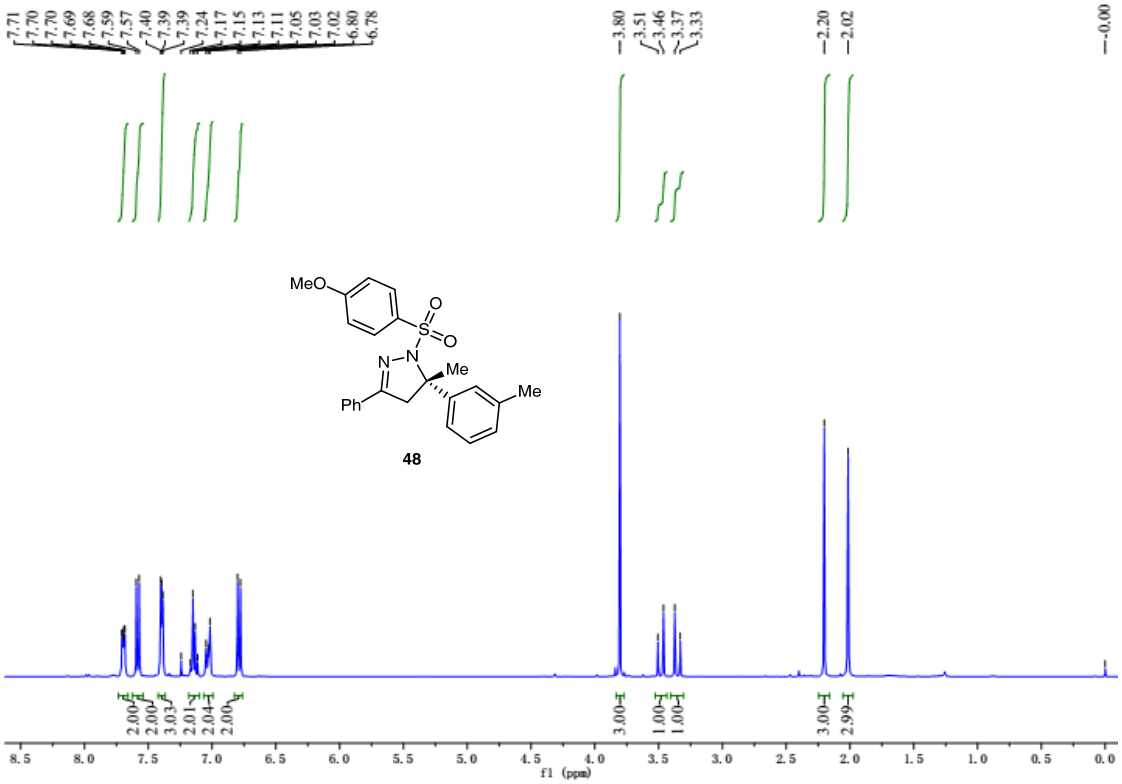
113.24
77.32
77.00
76.68
70.83
55.48
51.28
39.91
36.51
36.10
27.91
24.64
MeO
O
S
O
N
N
Me
Ph
47
f1 (ppm)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7.57
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7.39
7.39
7.24
7.17
7.15
7.13
7.11
7.05
7.03
7.02
6.80
6.78
3.80
3.51
3.46
3.37
3.33
2.20
2.02
0.00
MeO
O
S
O
N
N
Me
Ph
Me
48
2.00
2.00
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2.01
2.04
2.00
3.00
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1.00
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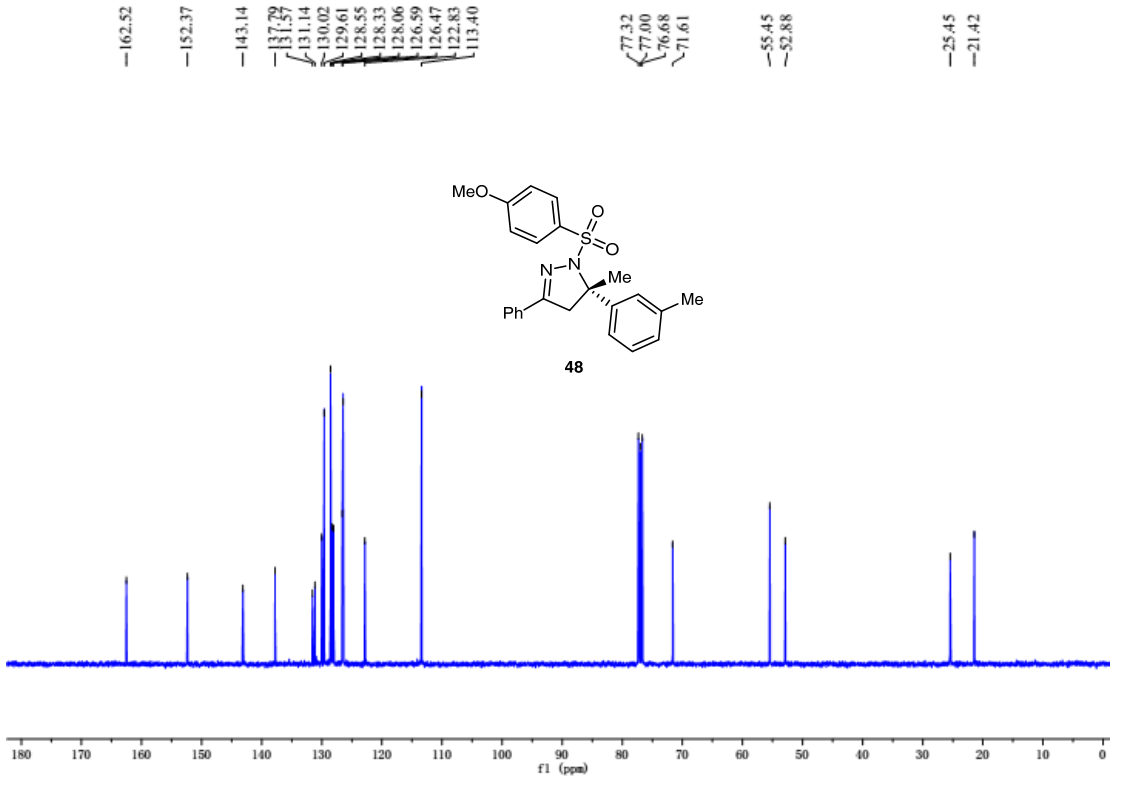
2.99
f1 (ppm)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128.33
128.06
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126.47
122.83
113.40
77.32
77.00
76.68
71.61
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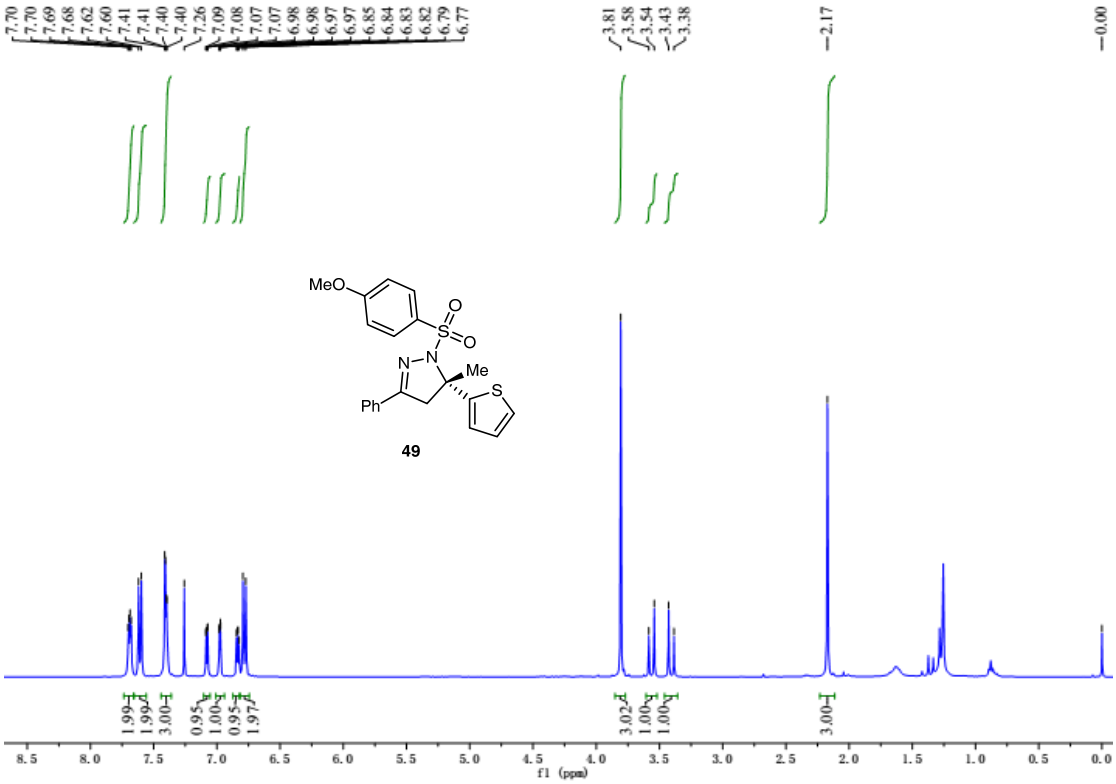
25.45
21.42
MeO
O
S
O
N
N
Me
Ph
Me
48
f1 (ppm)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7.40
7.26
7.09
7.08
7.07
7.07
6.98
6.98
6.97
6.97
6.85
6.84
6.83
6.82
6.79
6.77
3.81
3.58
3.54
3.43
3.38
2.17
0.00
MeO
O
S
O
N
N
Me
Ph
S
49
1.99
1.99
3.00
0.95
1.00
0.95
1.97
3.02
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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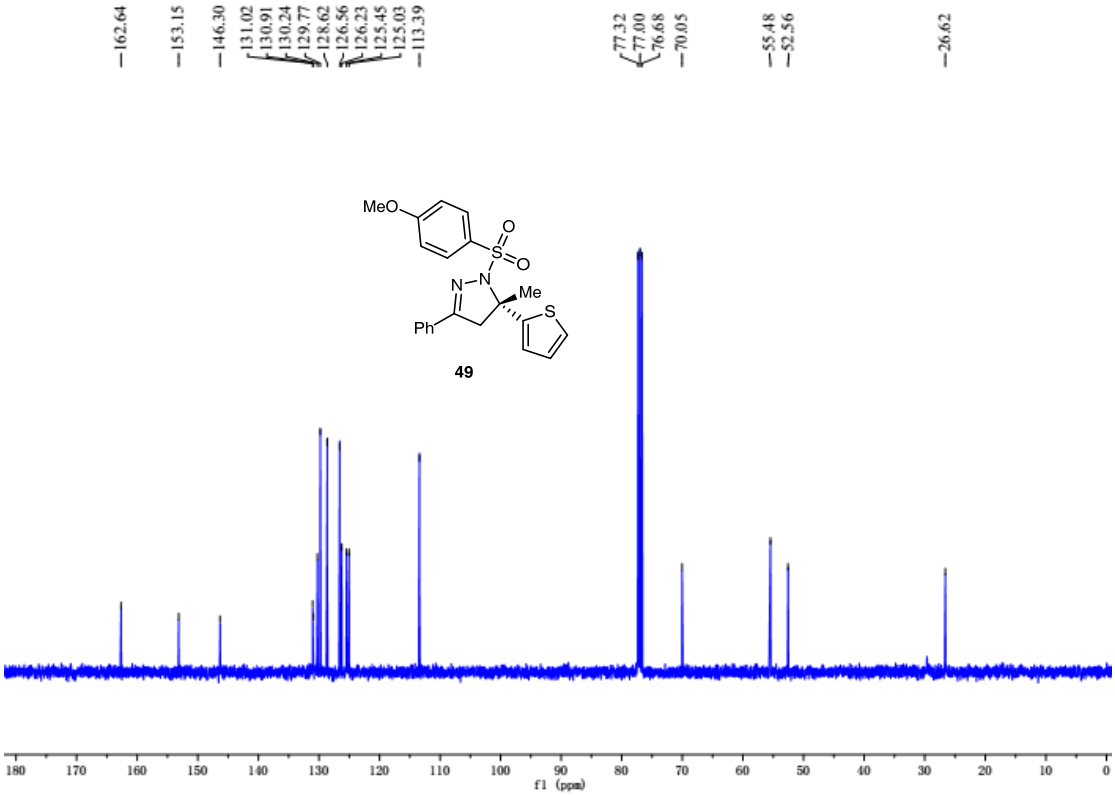
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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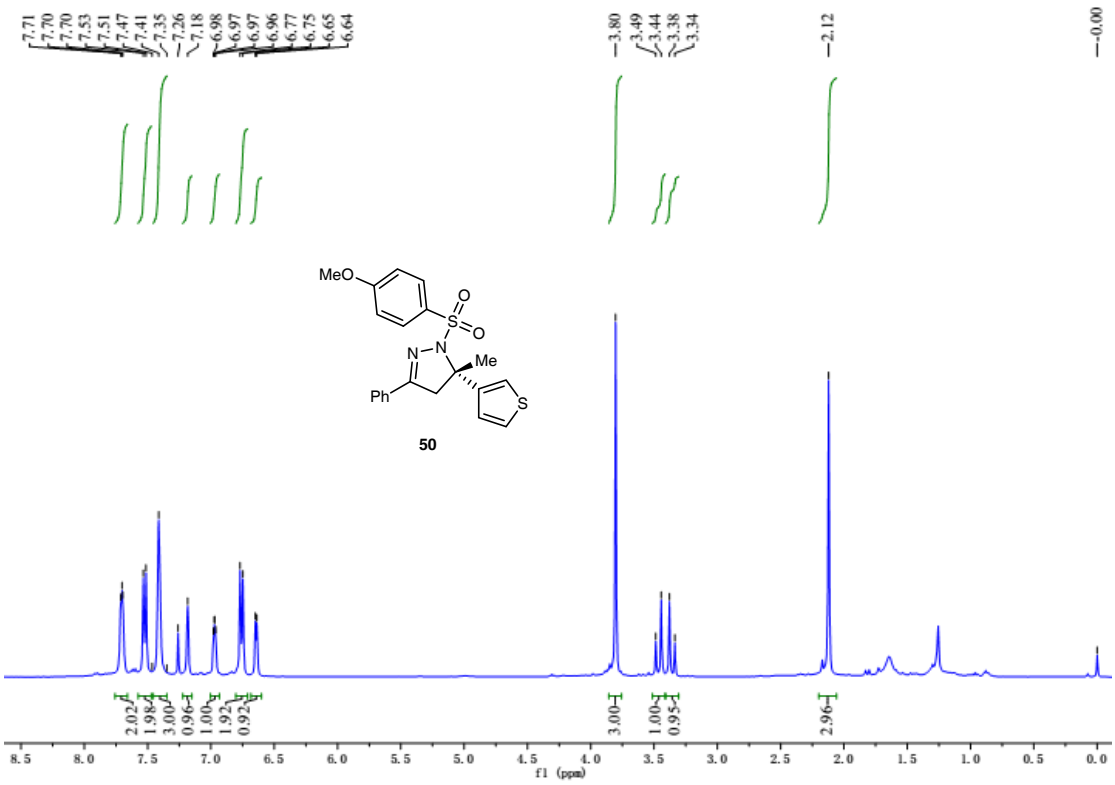
126.56
126.23
125.45
125.03
113.39
77.32
77.00
76.68
70.05
55.48
52.56
26.62
MeO
O
S
O
N
N
Me
Ph
S
49
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
7.18
6.98
6.97
6.97
6.96
6.77
6.75
6.65
6.64
3.80
3.49
3.44
3.38
3.34
2.12
0.00
MeO
O
S
O
N
N
Me
Ph
S
50
2.02
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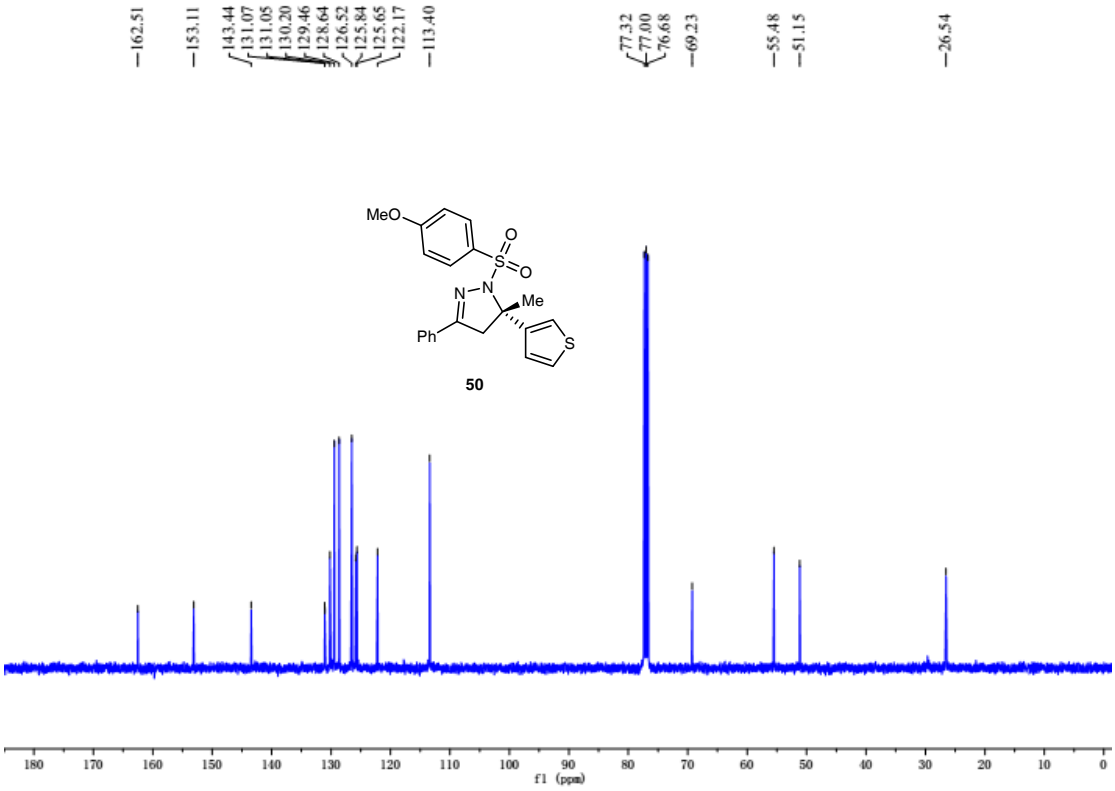
0.96
1.00
1.92
0.92
3.00
1.00
0.95
2.96
f1 (ppm)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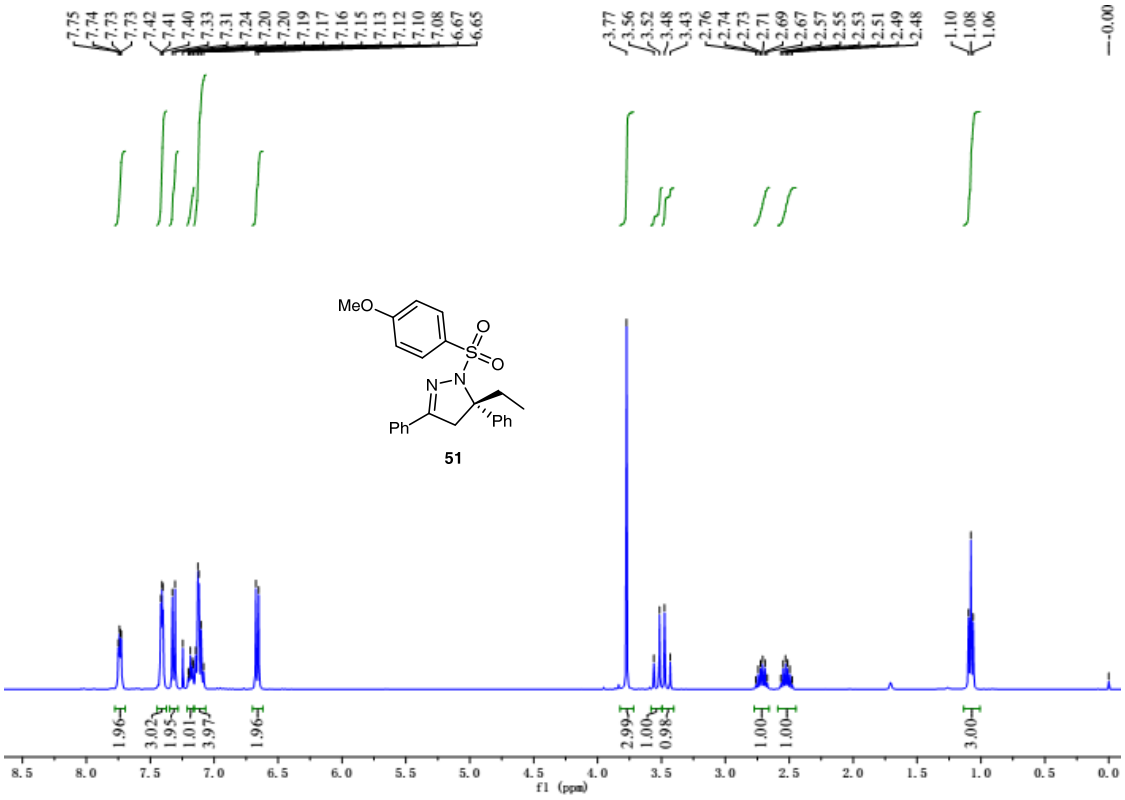
130.20
129.46
128.64
126.52
125.84
125.65
122.17
113.40
77.32
77.00
76.68
69.23
55.48
51.15
26.54
MeO
O
S
O
N
N
Me
Ph
S
50
f1 (ppm)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7.24
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7.19
7.17
7.16
7.15
7.13
7.12
7.10
7.08
6.67
6.65
3.77
3.56
3.52
3.48
3.43
2.76
2.74
2.73
2.71
2.69
2.67
2.57
2.55
2.53
2.51
2.49
2.48
1.10
1.08
1.06
-0.00
MeO
O
S
O
N
N
Ph
Ph
51
1.96
3.02
1.95
1.01
3.97
1.96
2.99
1.00
0.98
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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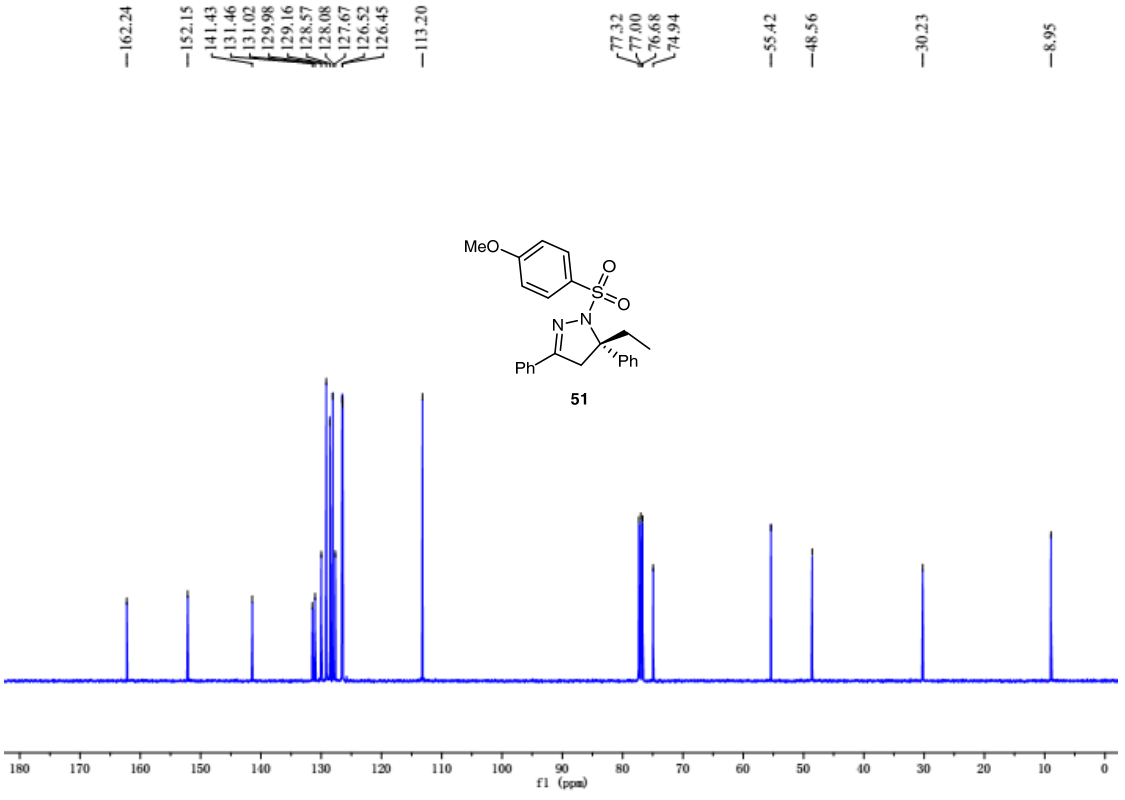
0.0
f1 (ppm)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127.67
126.52
126.45
113.20
77.32
77.00
76.68
74.94
55.42
48.56
30.23
8.95
MeO
O
S
O
N
N
Ph
Ph
51
180
170
160
150
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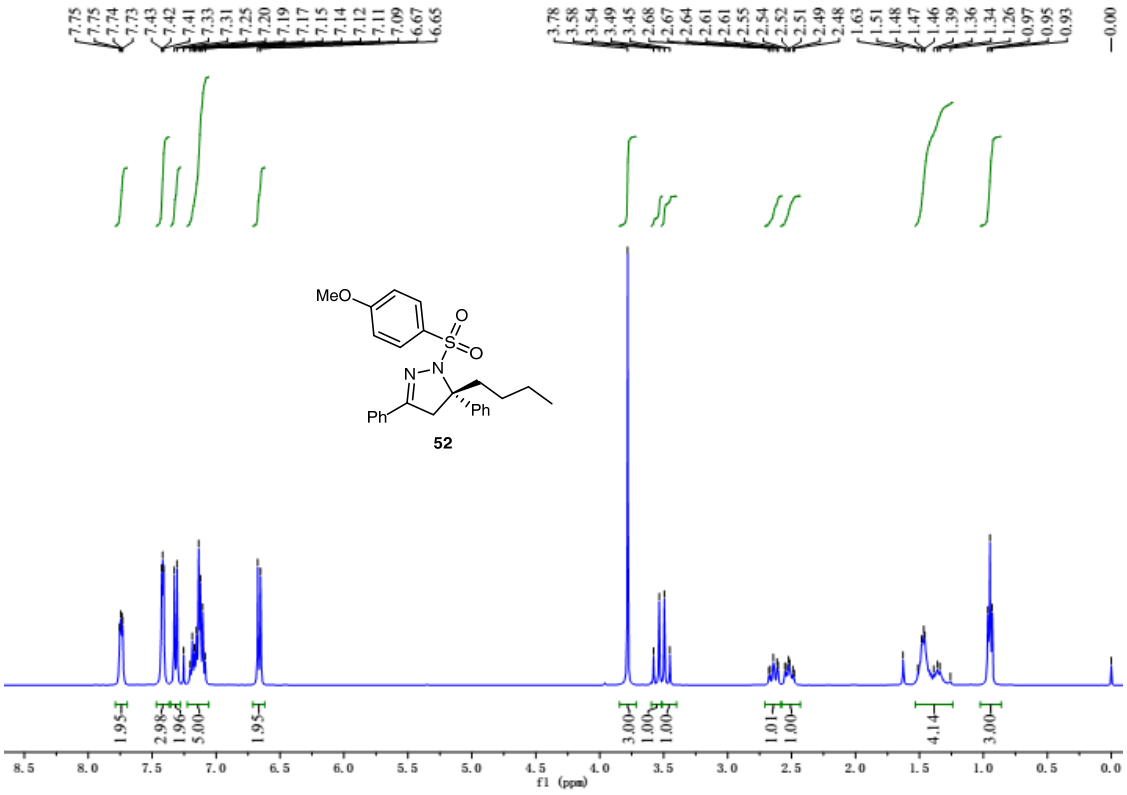
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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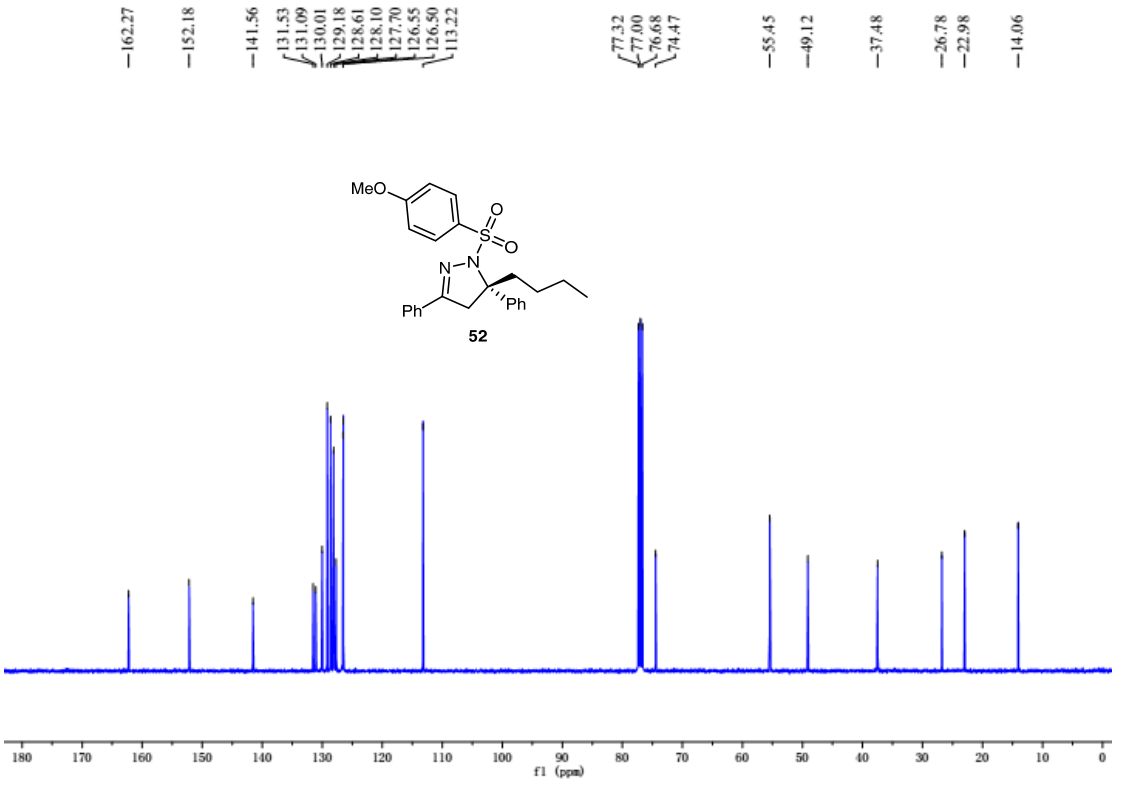
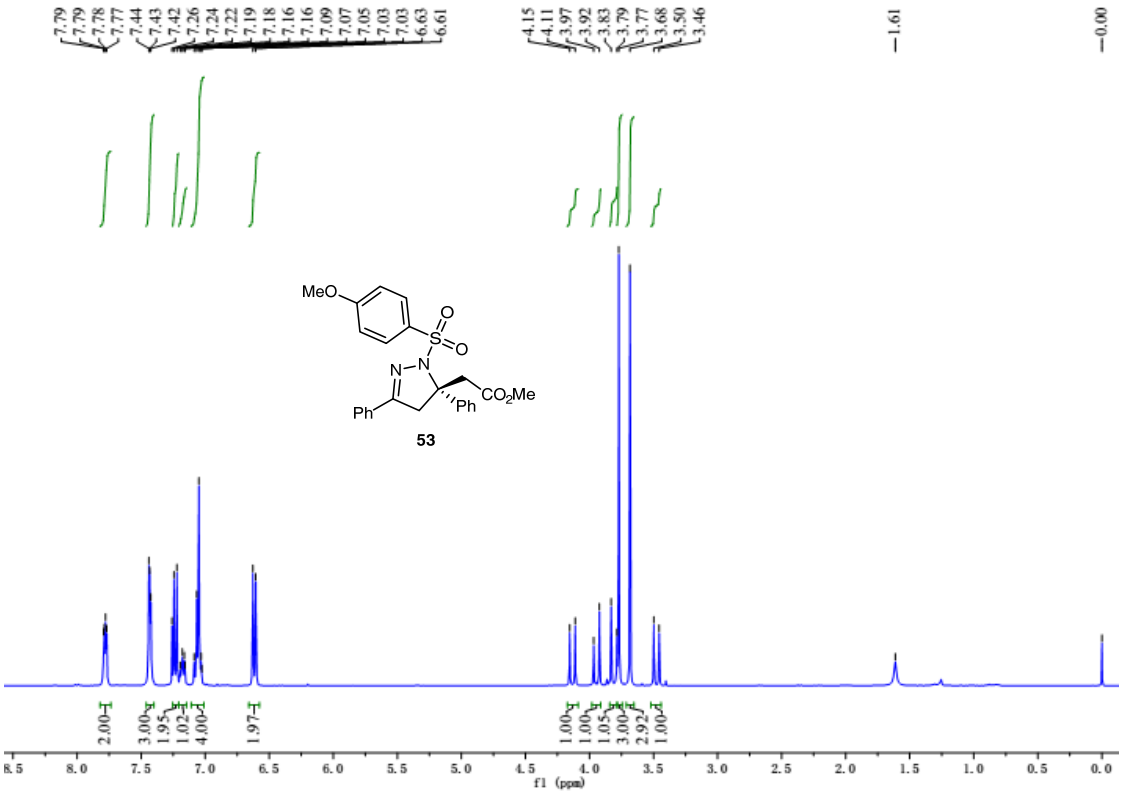
O
N
N
Ph
Ph
52


MeO
O
S
O
N
N
Ph
Ph
52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7.43
7.42
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7.22
7.19
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7.16
7.09
7.07
7.05
7.03
7.03
6.63
6.61
4.15
4.11
3.97
3.92
3.83
3.79
3.77
3.68
3.50
3.46
1.61
0.00
MeO
O
S
O
N
N
Ph
Ph
CO2Me
53
2.00
3.00
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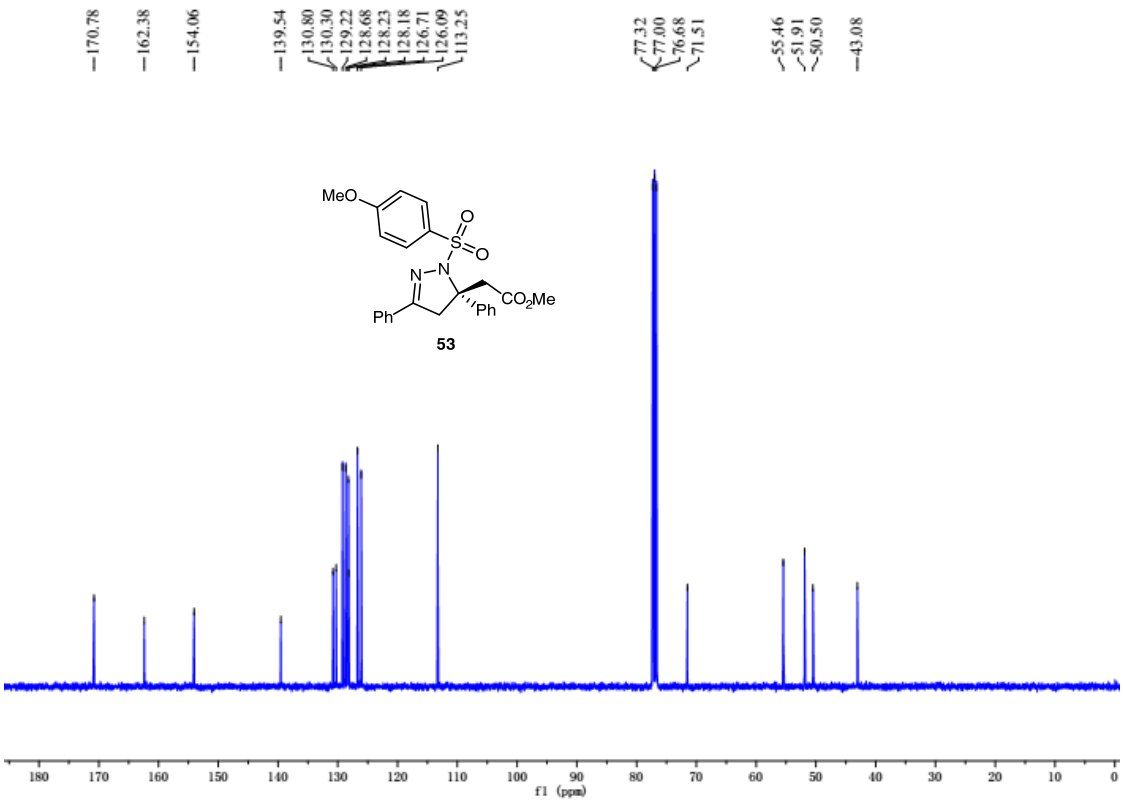
4.00
1.97
1.00
1.00
1.05
3.00
2.92
1.00
f1 (ppm)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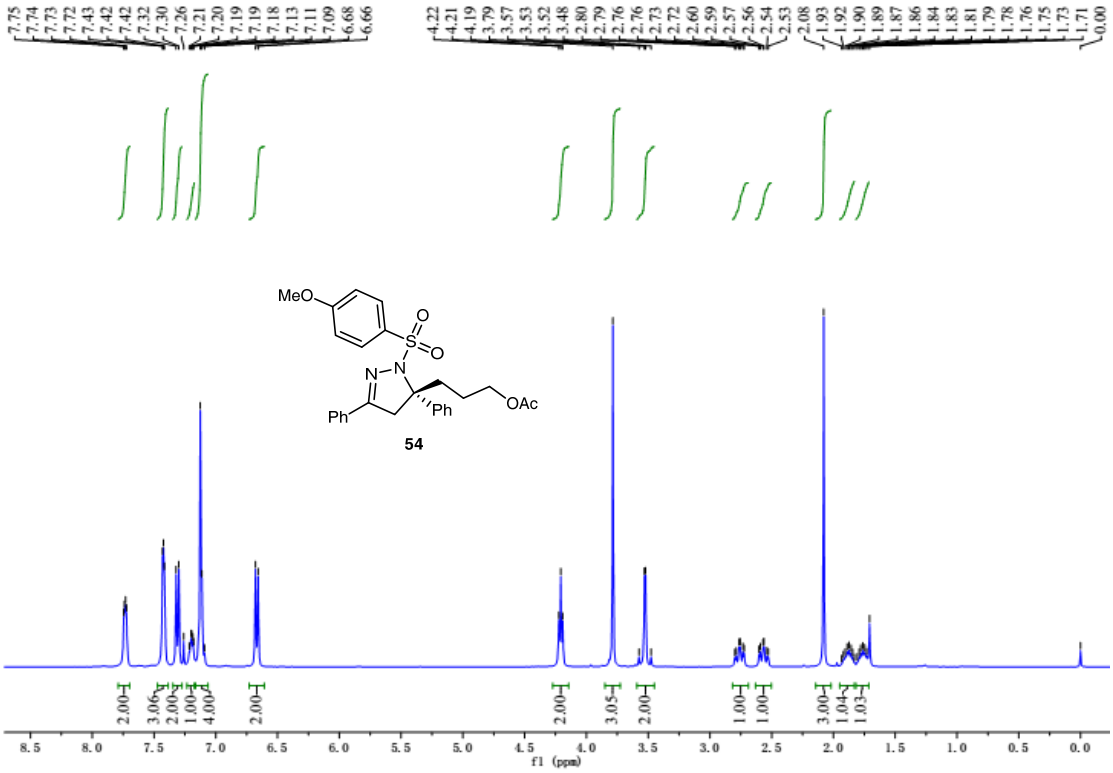
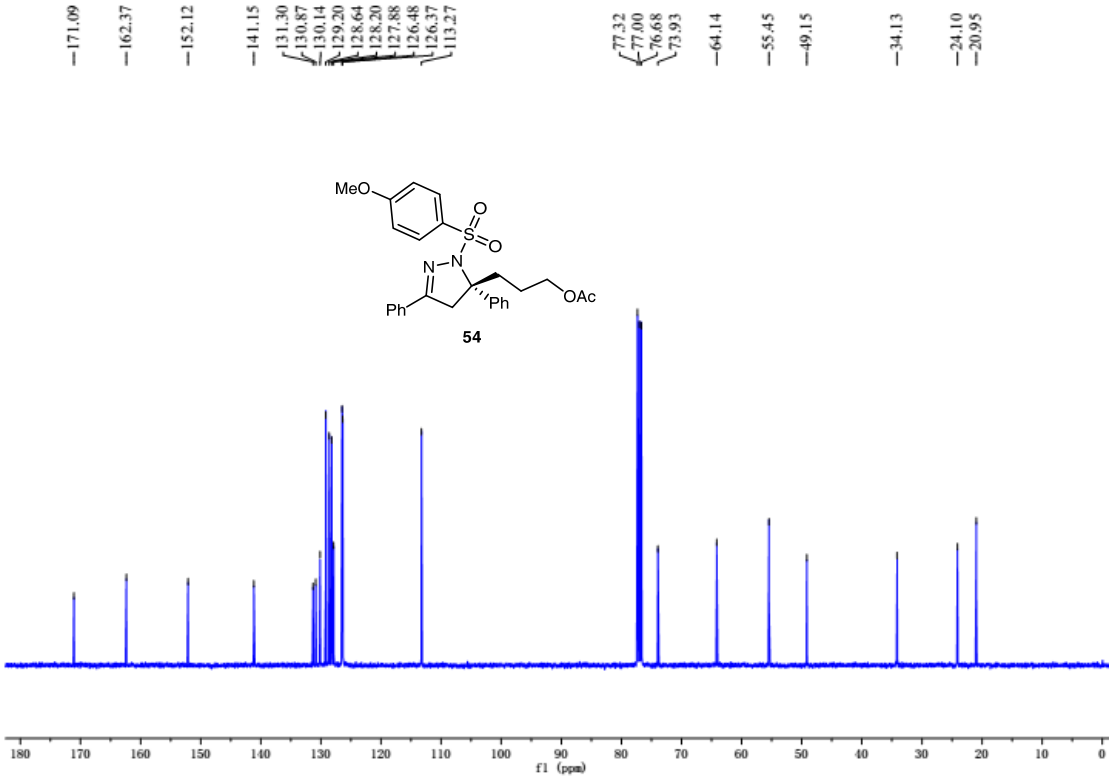
130.30
129.22
128.68
128.23
128.18
126.71
126.09
113.25
77.32
77.00
76.68
71.51
55.46
51.91
50.50
43.08
MeO
O
S
O
N
N
Ph
Ph
CO2Me
53
f1 (ppm)


7.75 7.74 7.73 7.72 7.43 7.42 7.42 7.32 7.30 7.26 7.21 7.20 7.19 7.19 7.18 7.13 7.11 7.09 6.68 6.66
4.22 4.21 4.19 3.79 3.57 3.53 3.52 3.48 2.80 2.79 2.76 2.76 2.73 2.72 2.60 2.59 2.57 2.56 2.54 2.53 2.08 1.93 1.92 1.90 1.89 1.87 1.86 1.84 1.83 1.81 1.79 1.78 1.76 1.75 1.73 1.71 0.00
MeO
O
S
O
N
N
Ph
Ph
OAc
54
2.00 3.06 2.00 1.00 4.00 2.00 2.00 3.05 2.00 1.00 1.00 3.00 1.04 1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.09 162.37 152.12 141.15 131.30 130.87 130.14 129.20 128.64 128.20 127.88 126.48 126.37 113.27
77.32 77.00 76.68 73.93 64.14 55.45 49.15 34.13 24.10 20.95
MeO
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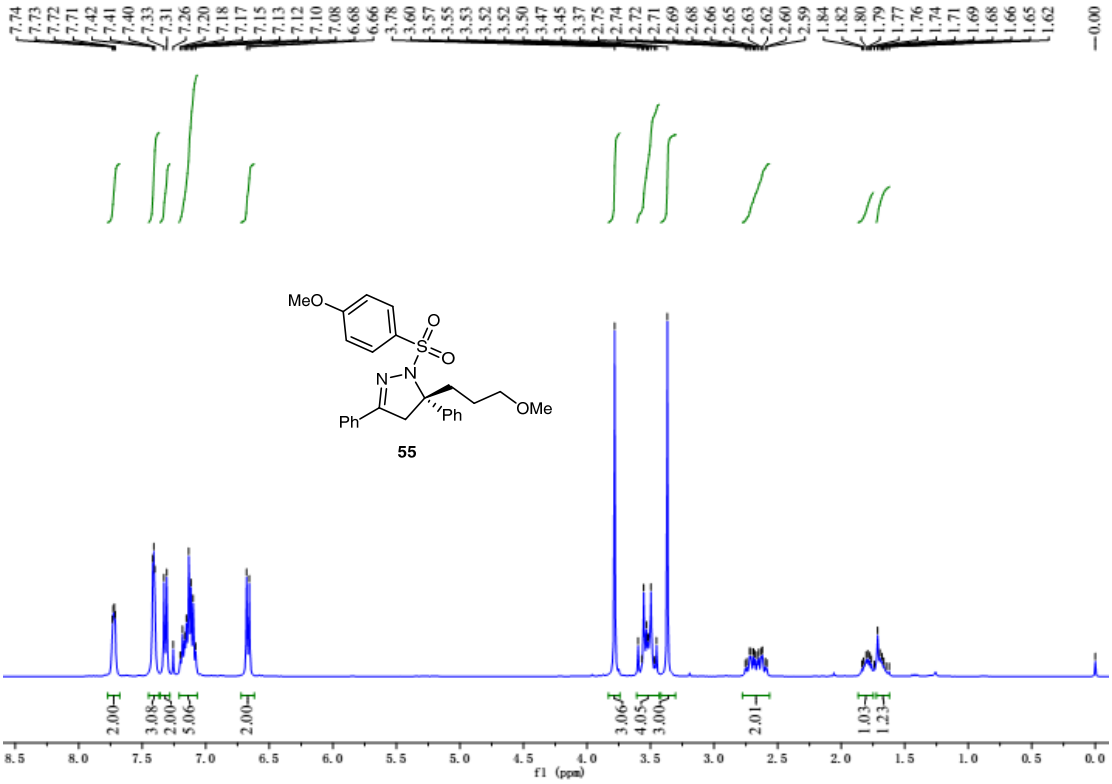
O
N
N
Ph
Ph
OAc
54
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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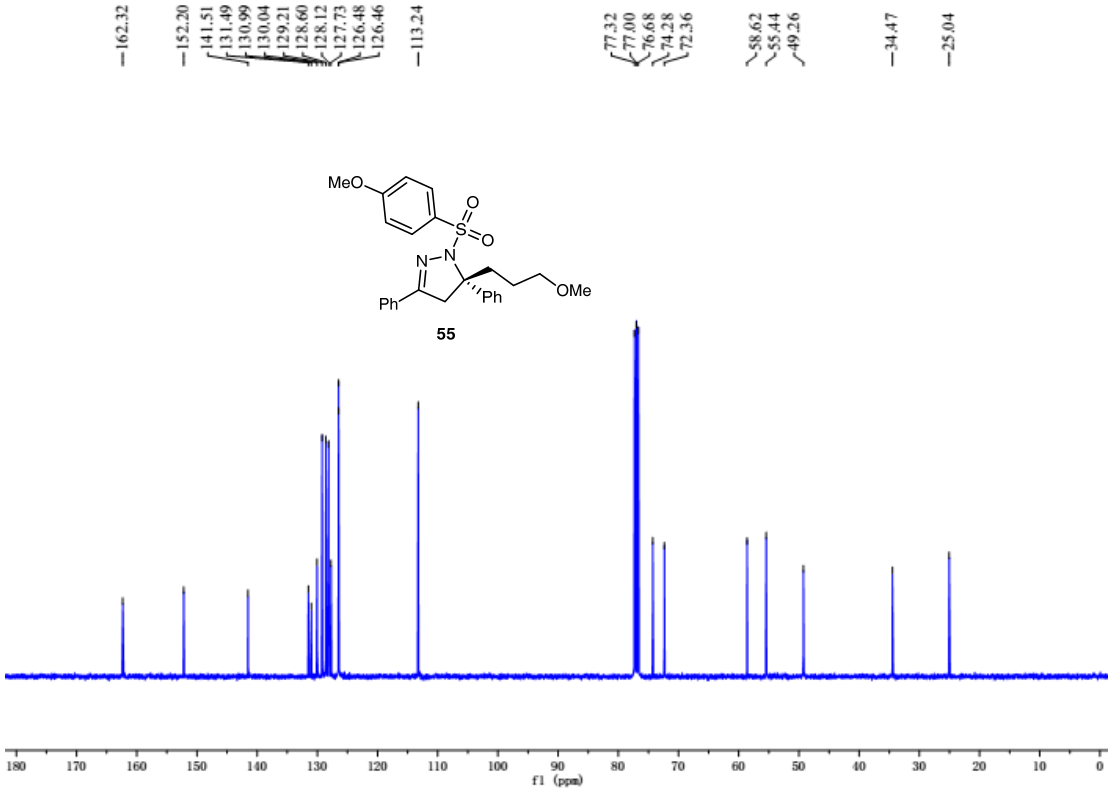
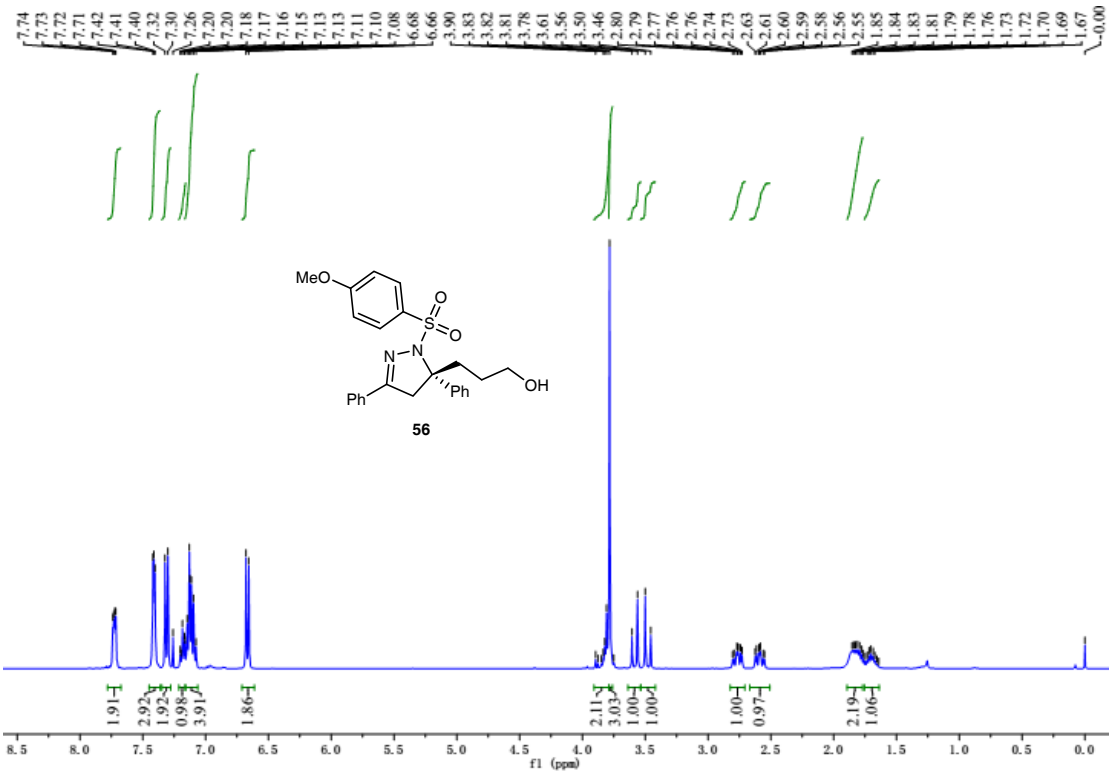
3.78 3.60 3.57 3.55 3.53 3.52 3.52 3.50 3.47 3.45 3.37 2.75 2.74 2.72 2.71 2.69 2.68 2.66 2.65 2.63 2.62 2.60 2.59
1.84 1.82 1.80 1.79 1.77 1.76 1.74 1.71 1.69 1.68 1.66 1.65 1.62
0.00
MeO
O
S
O
N
N
Ph
Ph
OMe
55
2.00 3.08 2.00 5.06 2.00 3.06 4.05 3.00 2.01 1.03 1.23
f1 (ppm)


162.32 152.20 141.51 131.49 130.99 130.04 129.21 128.60 128.12 127.73 126.48 126.46 113.24
77.32 77.00 76.68 74.28 72.36 58.62 55.44 49.26 34.47 25.04
MeO
O
S
O
N
N
Ph
Ph
OMe
55
f1 (ppm)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N
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Ph
Ph
OH
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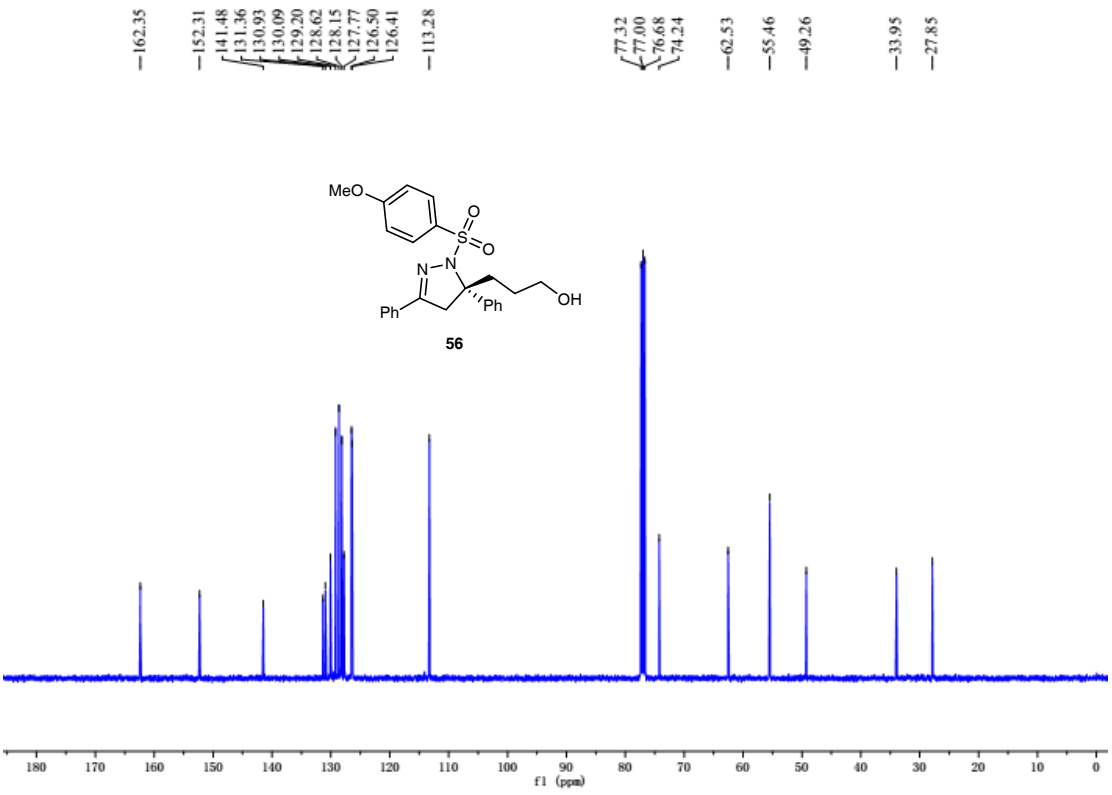
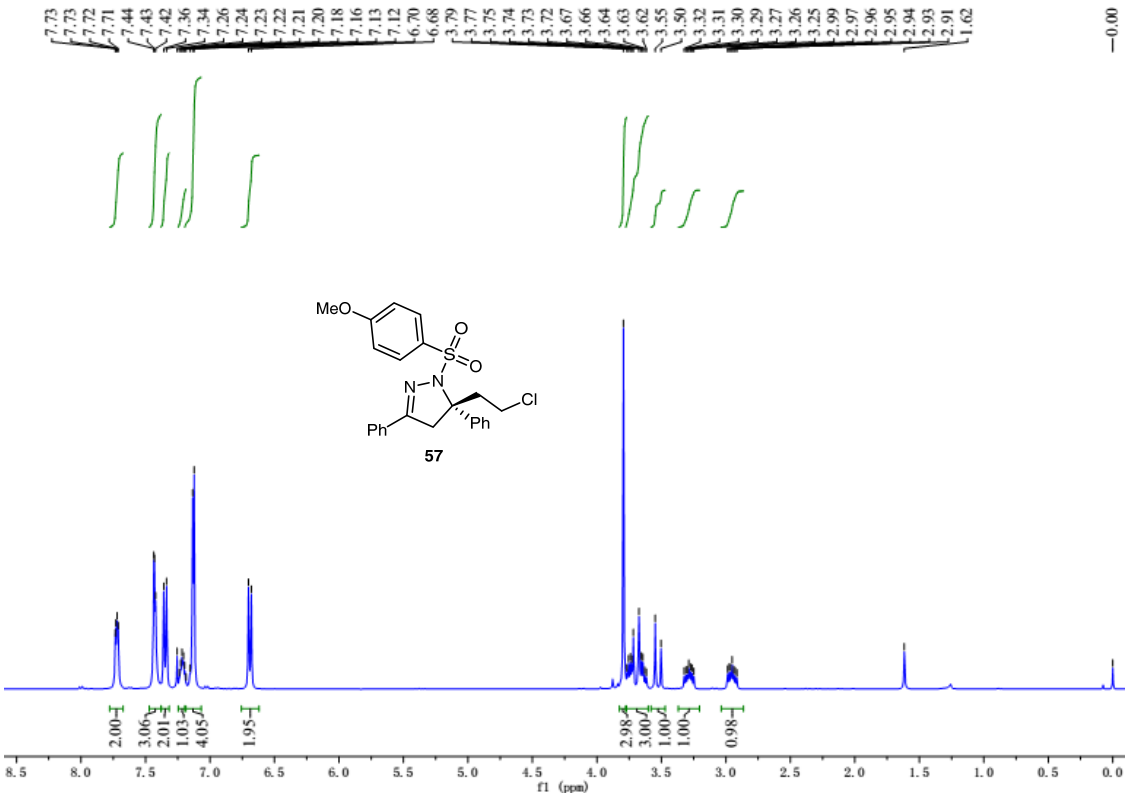
f1 (ppm)


MeO
O
S
O
N
N
Ph
Ph
OH
56
f1 (ppm)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7.72
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7.43
7.42
7.36
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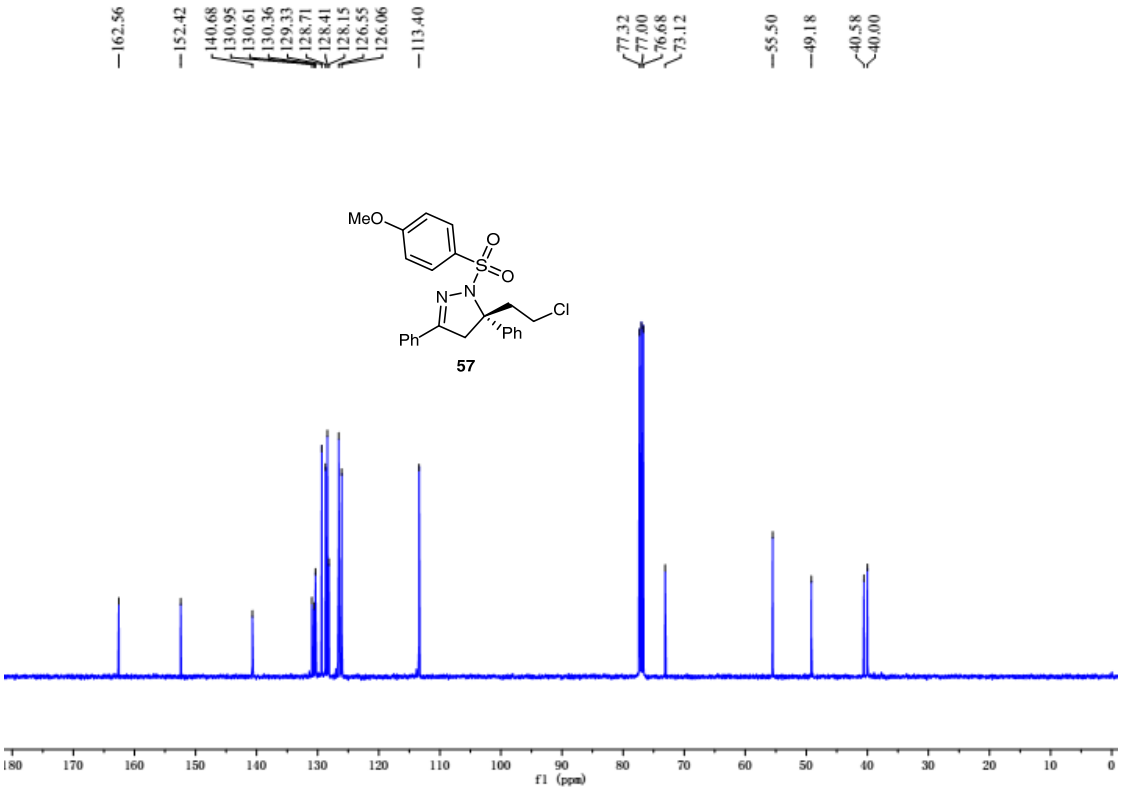
7.24
7.23
7.22
7.21
7.20
7.18
7.16
7.13
7.12
6.70
6.68
3.79
3.77
3.75
3.74
3.73
3.72
3.67
3.66
3.64
3.63
3.62
3.55
3.50
3.32
3.31
3.30
3.29
3.27
3.26
3.25
2.99
2.97
2.96
2.95
2.94
2.93
2.91
1.62
0.00
MeO
O
S
O
N
N
Cl
Ph
Ph
57
2.00
3.06
2.01
1.03
4.05
1.95
2.98
3.00
1.00
1.00
0.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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140.68
130.95
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130.36
129.33
128.71
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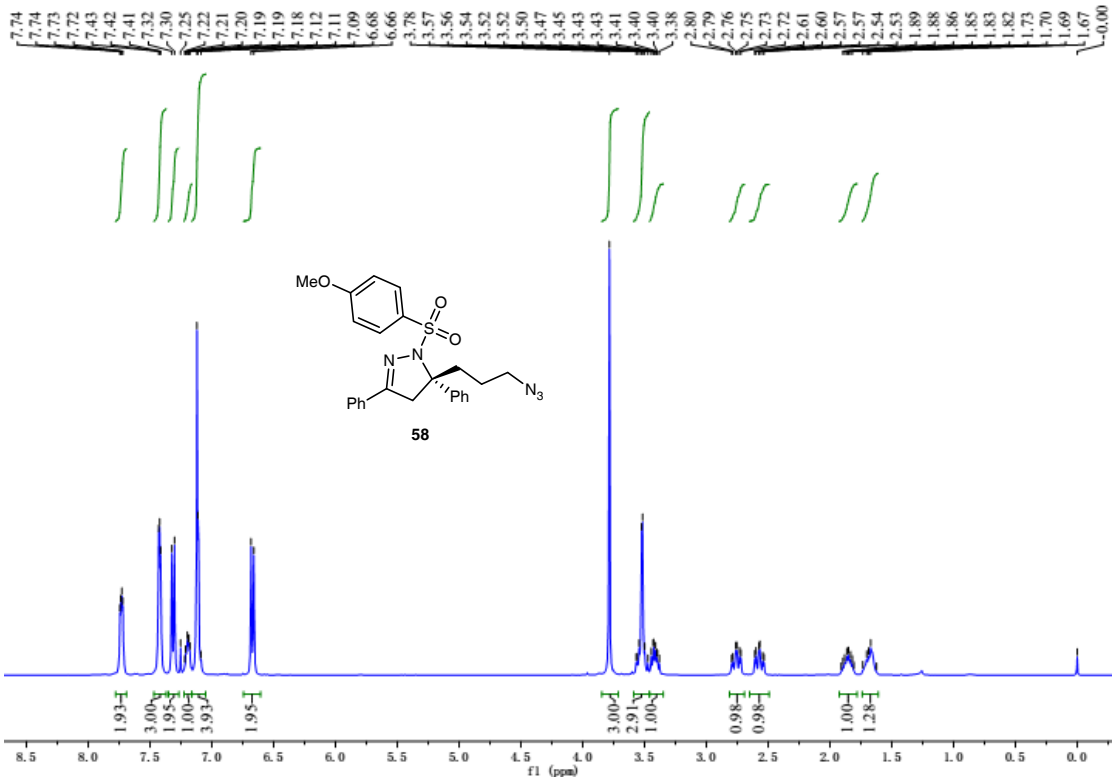
128.15
126.55
126.06
113.40
77.32
77.00
76.68
73.12
55.50
49.18
40.58
40.00
MeO
O
S
O
N
N
Cl
Ph
Ph
57
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
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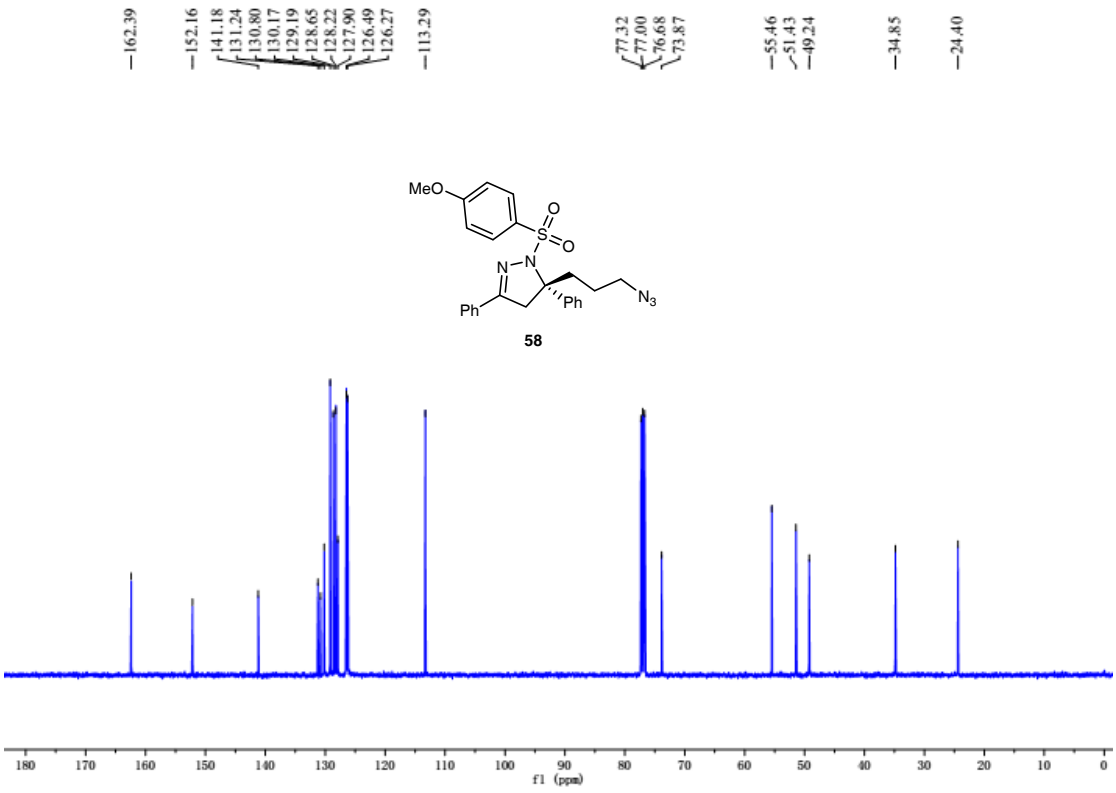
S
O
N
N
Ph
Ph
N3
58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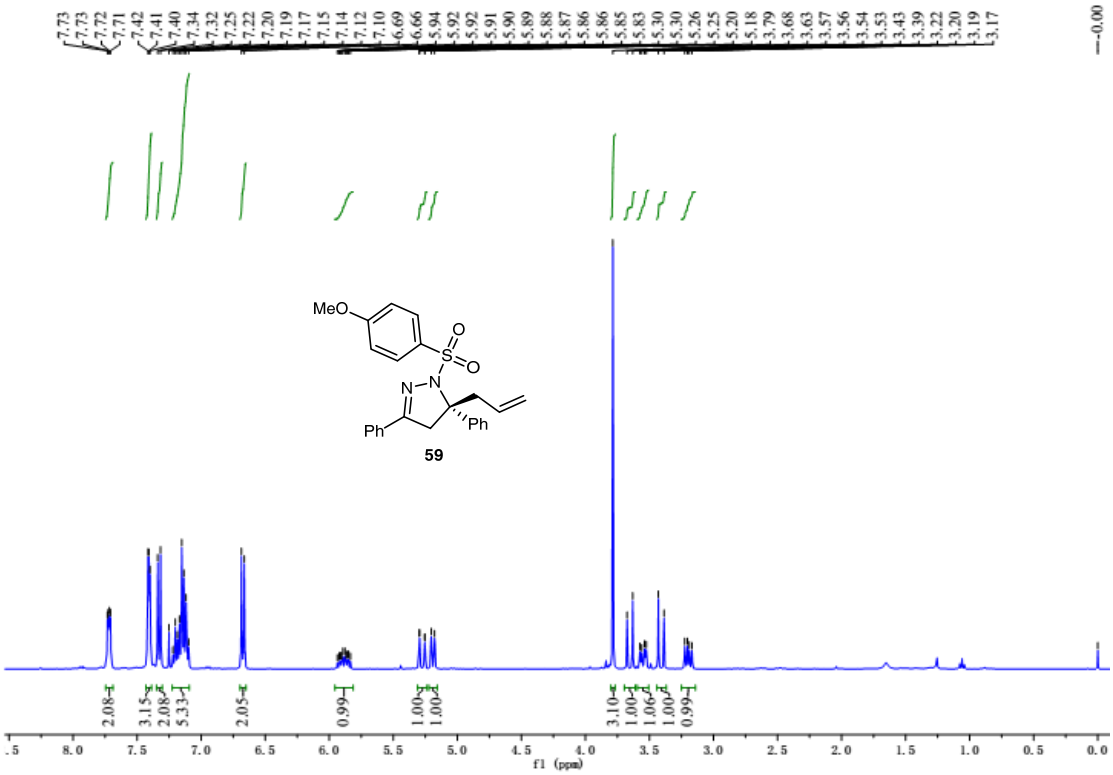
O
S
O
N
N
Ph
Ph
N3
58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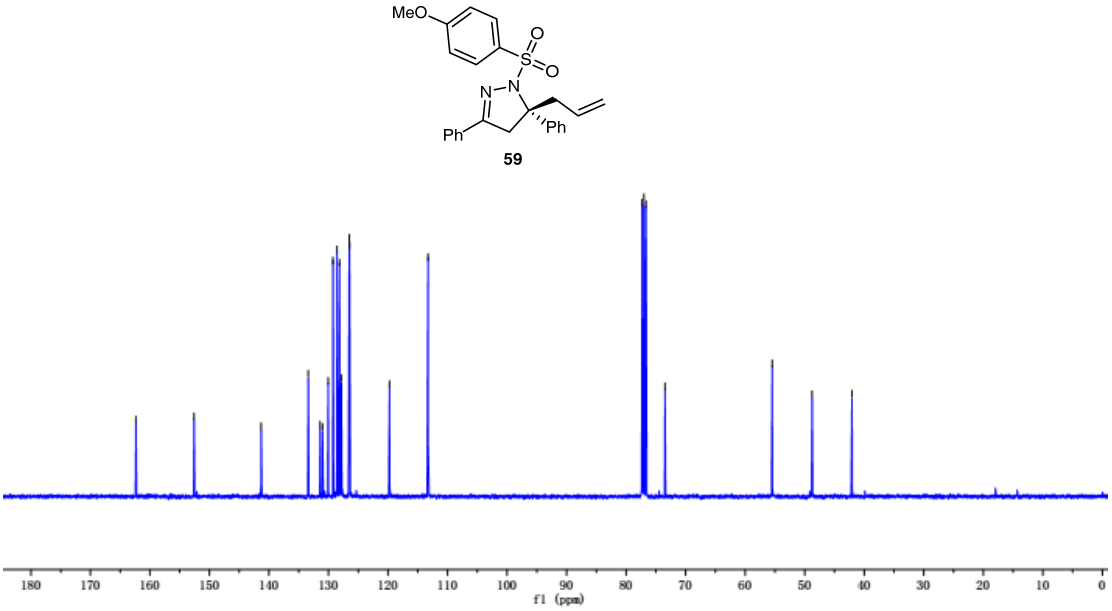
O
S
O
N
N
Ph
Ph
59
f1 (ppm)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S
O
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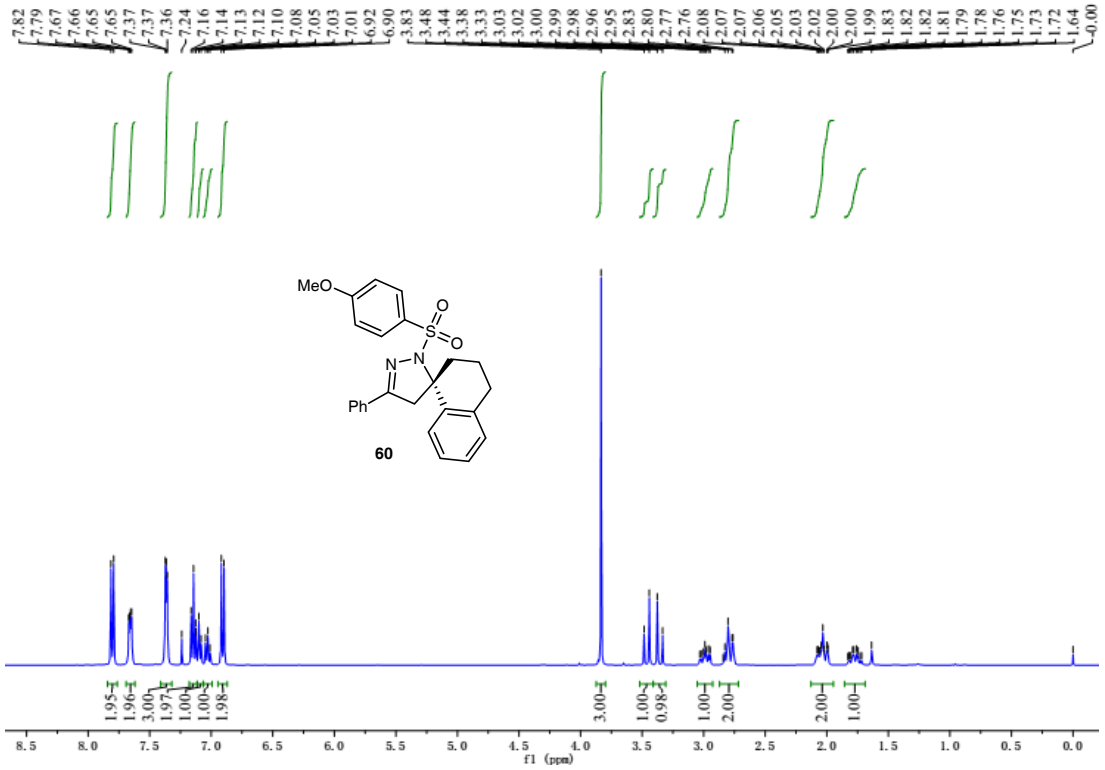
N
Ph
Ph
59
f1 (ppm)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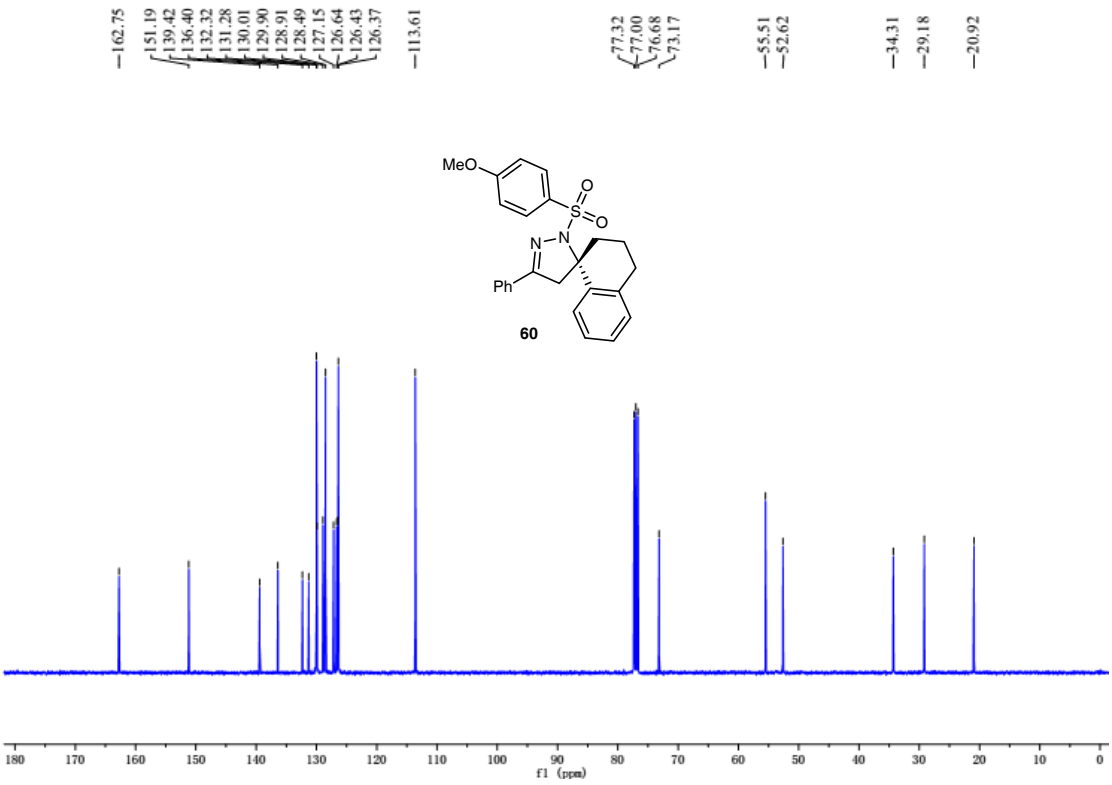
S
O
N
N
Ph
60
f1 (ppm)


MeO
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S
O
N
N
Ph
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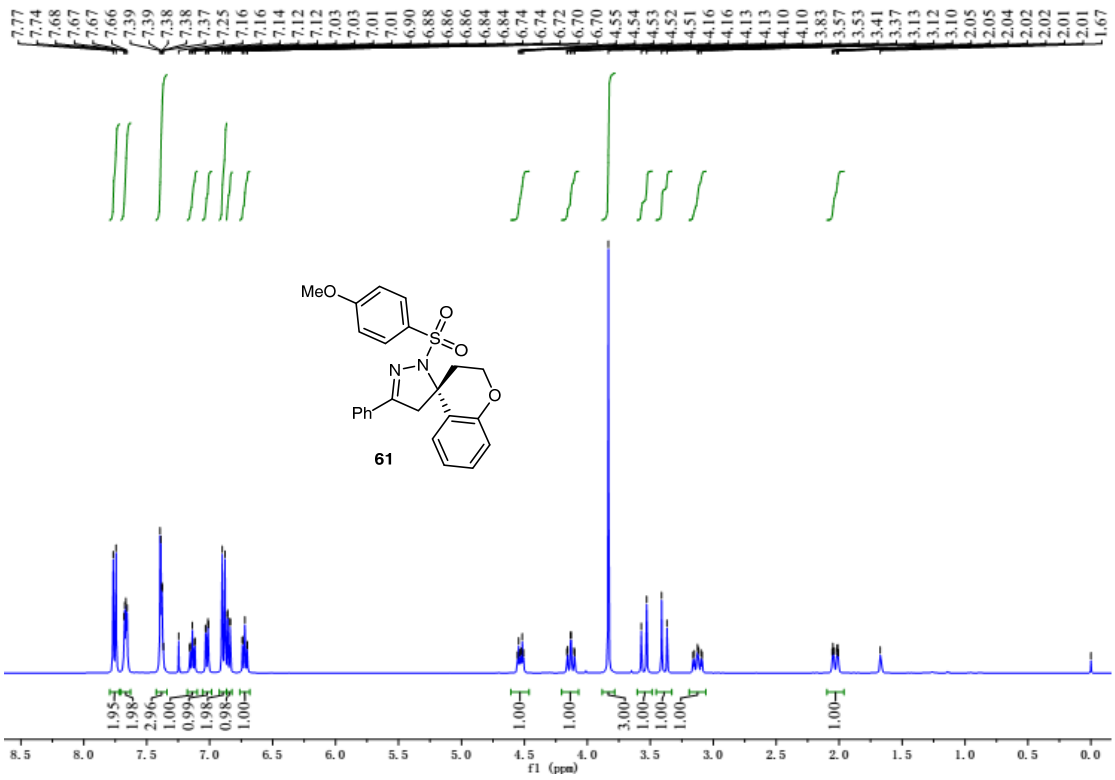
f1 (ppm)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S
O
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Ph
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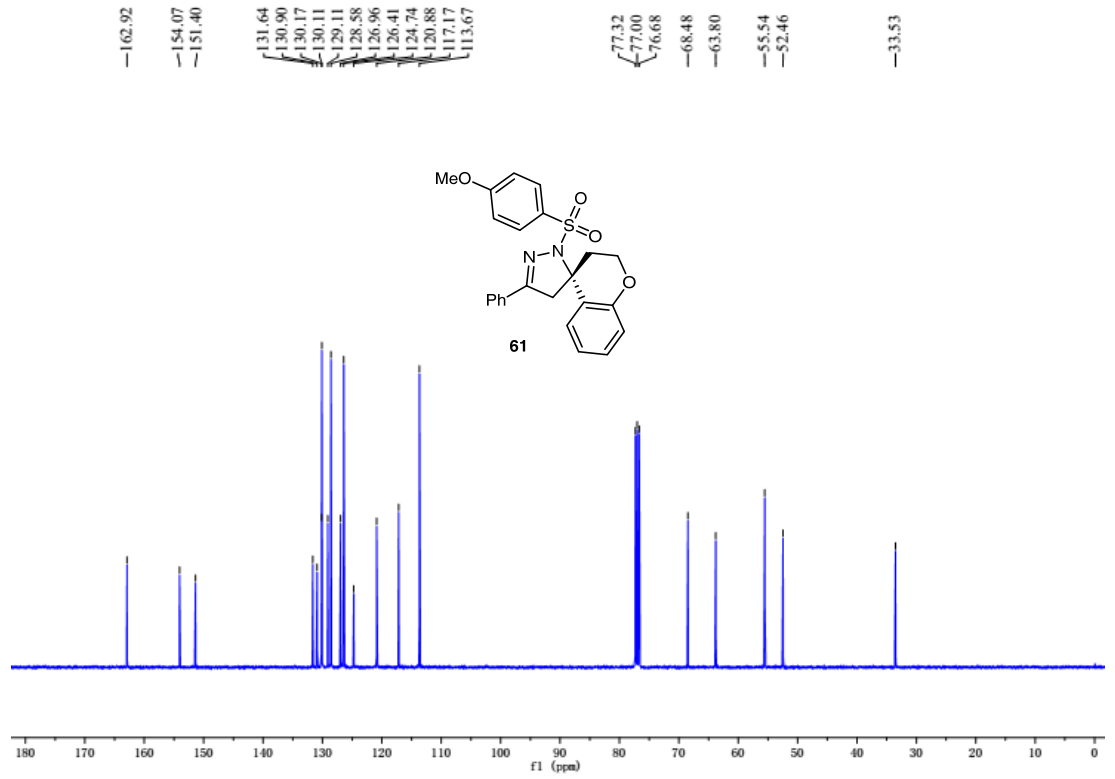
f1 (ppm)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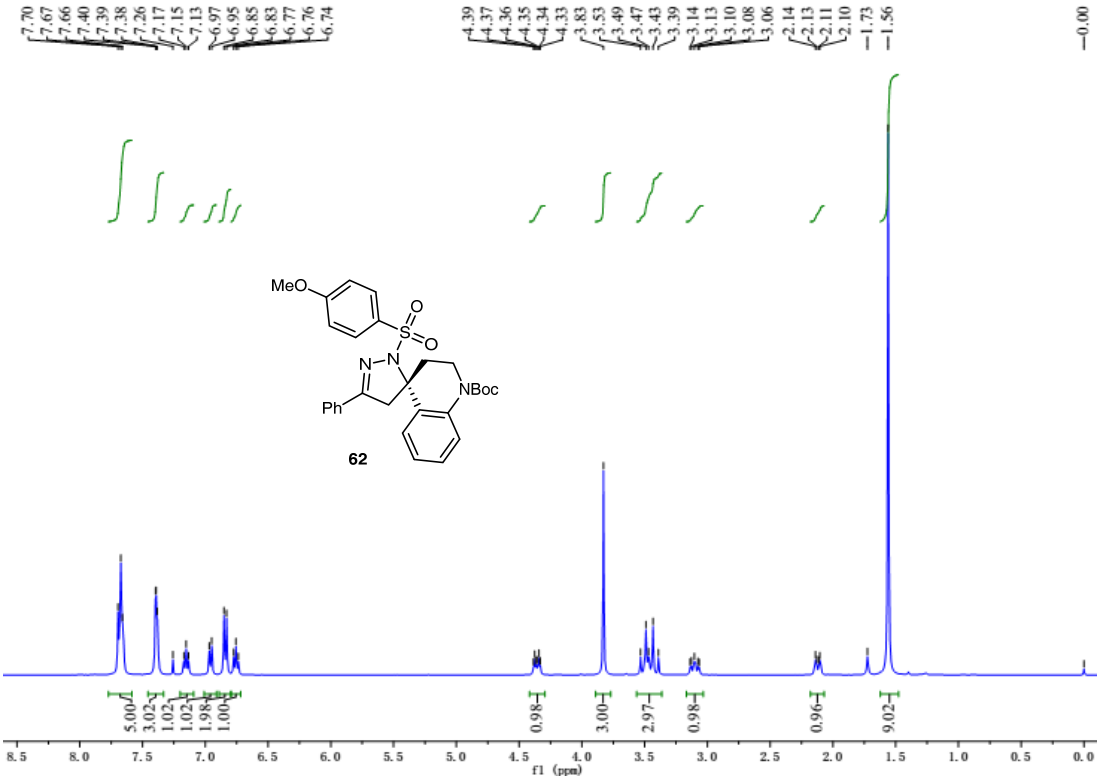
S
O
N
N
Ph
O
61
f1 (ppm)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7.17
7.15
7.13
6.97
6.95
6.85
6.83
6.77
6.76
6.74
4.39
4.37
4.36
4.35
4.34
4.33
3.83
3.53
3.49
3.47
3.43
3.39
3.14
3.13
3.10
3.08
3.06
2.14
2.13
2.11
2.10
1.73
1.56
0.00
MeO
S
O
O
N
N
Ph
NBoc
62
5.00
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1.98
1.00
0.98
3.00
2.97
0.98
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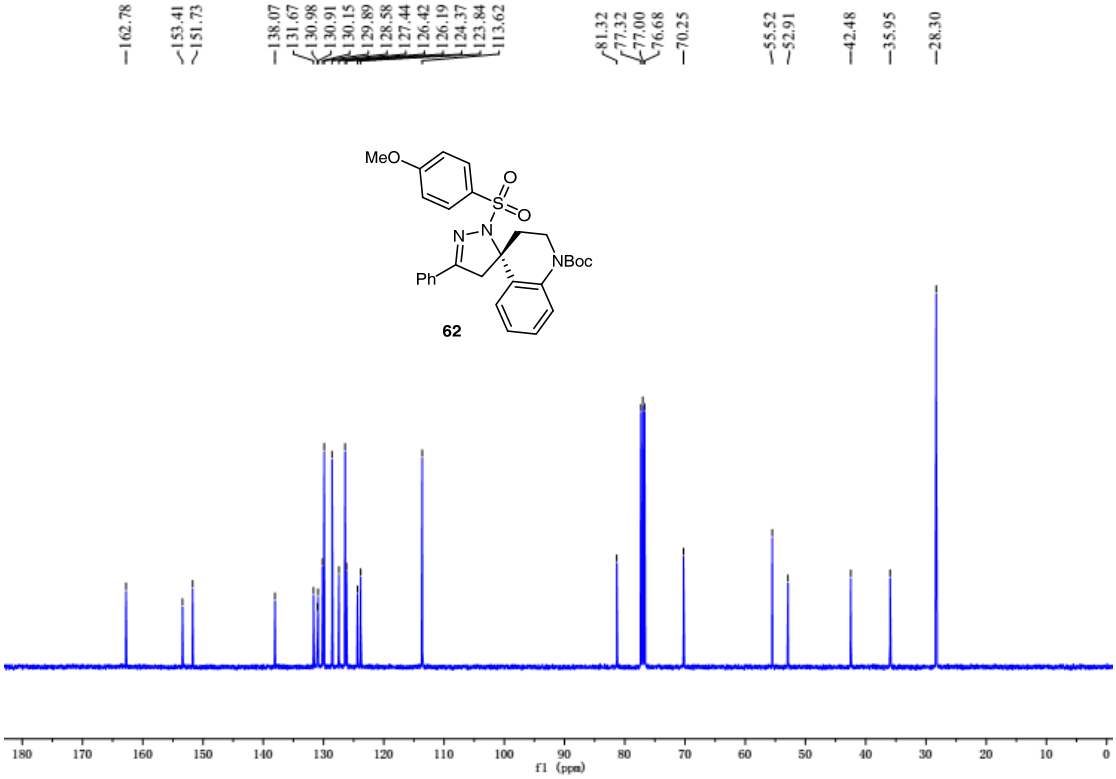
9.02
f1 (ppm)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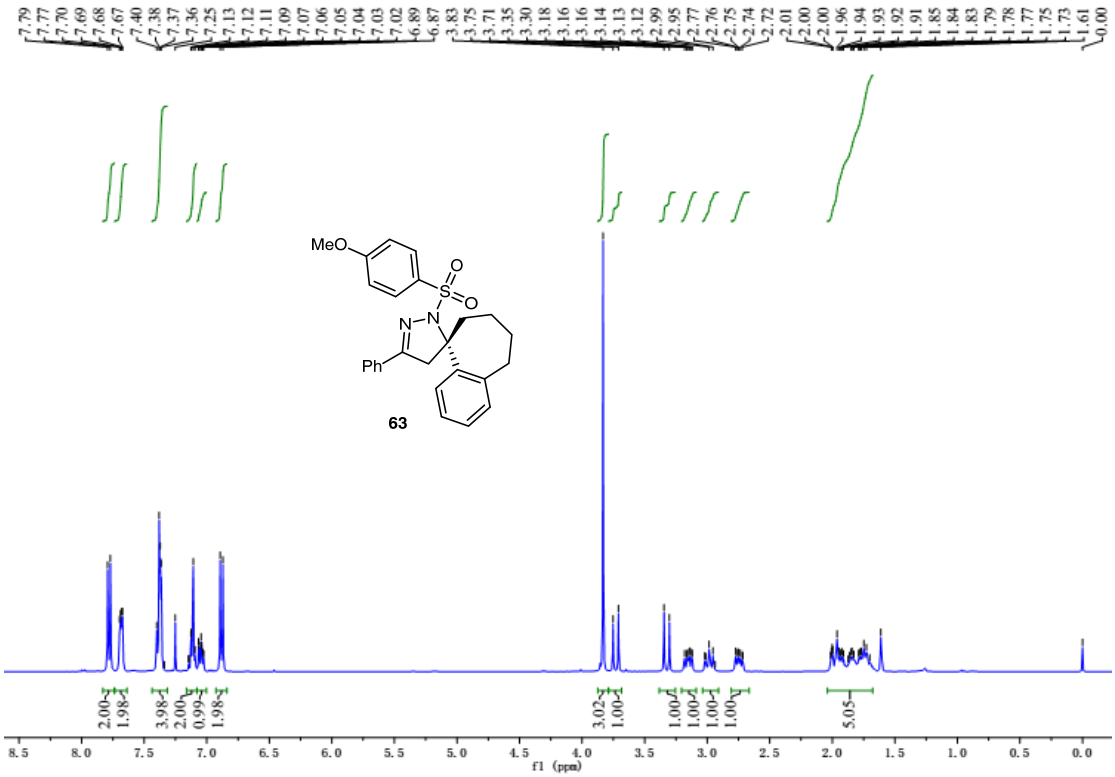
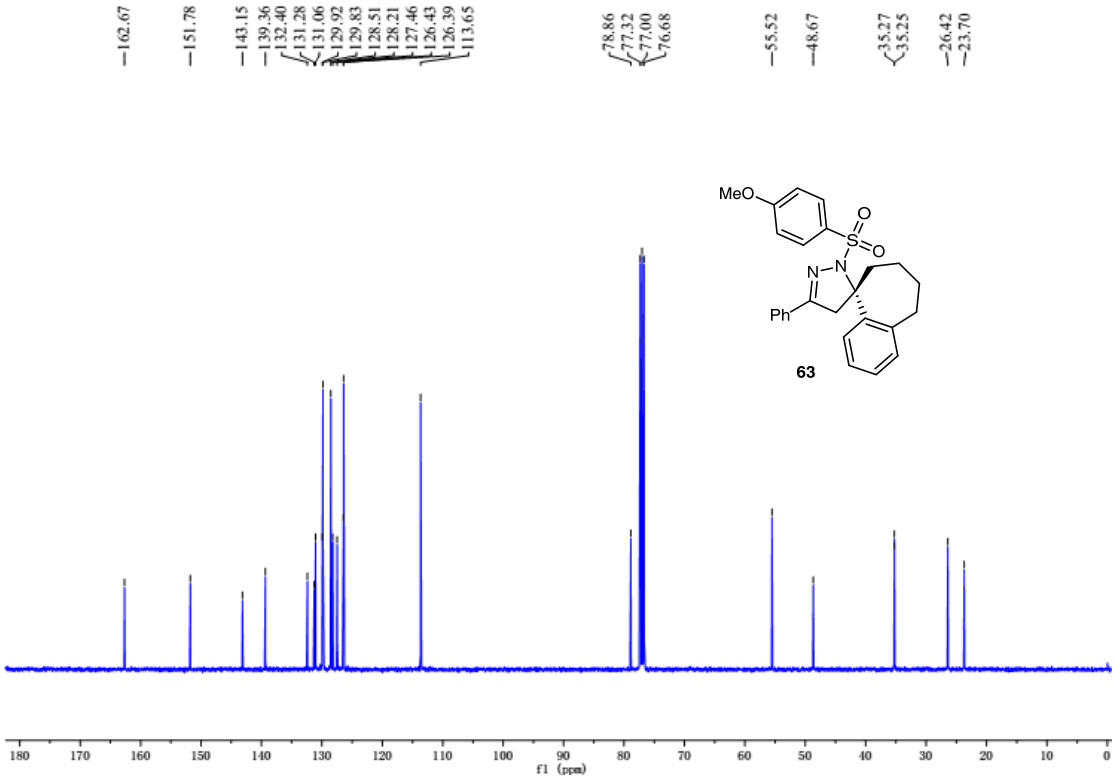
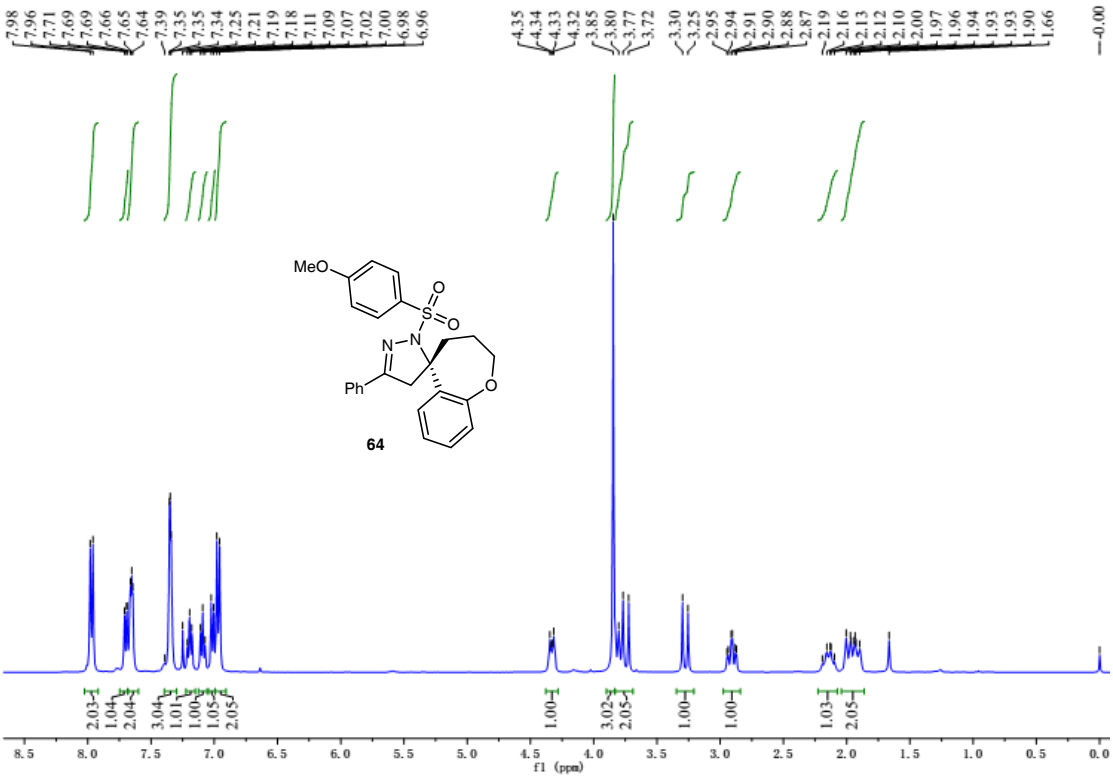
128.58
127.44
126.42
126.19
124.37
123.84
113.62
81.32
77.32
77.00
76.68
70.25
55.52
52.91
42.48
35.95
28.30
MeO
S
O
O
N
N
Ph
NBoc
62
f1 (ppm)


MeO
Ph
63
f1 (ppm)


MeO
Ph
63
f1 (ppm)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7.35
7.35
7.34
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7.21
7.19
7.18
7.11
7.09
7.07
7.02
7.00
6.98
6.96
4.35
4.34
4.33
4.32
3.85
3.80
3.77
3.72
3.30
3.25
2.95
2.94
2.91
2.90
2.88
2.87
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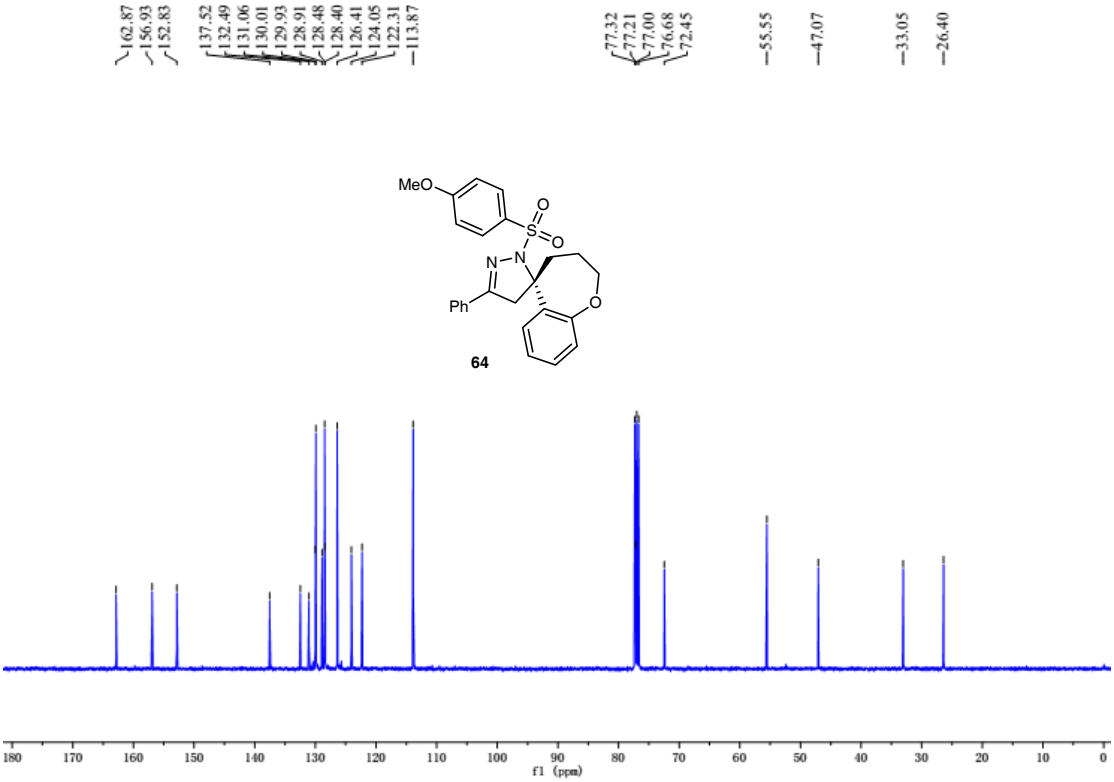
2.16
2.13
2.12
2.10
2.00
1.97
1.96
1.94
1.93
1.93
1.90
1.66
0.00
MeO
O
S
O
N
N
Ph
O
64
2.03
1.04
2.04
3.04
1.01
1.00
1.05
2.05
1.00
3.02
2.05
1.00
1.00
1.03
2.05
f1 (ppm)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130.01
129.93
128.91
128.48
128.40
126.41
124.05
122.31
113.87
77.32
77.21
77.00
76.68
72.45
55.55
47.07
33.05
26.40
MeO
O
S
O
N
N
Ph
O
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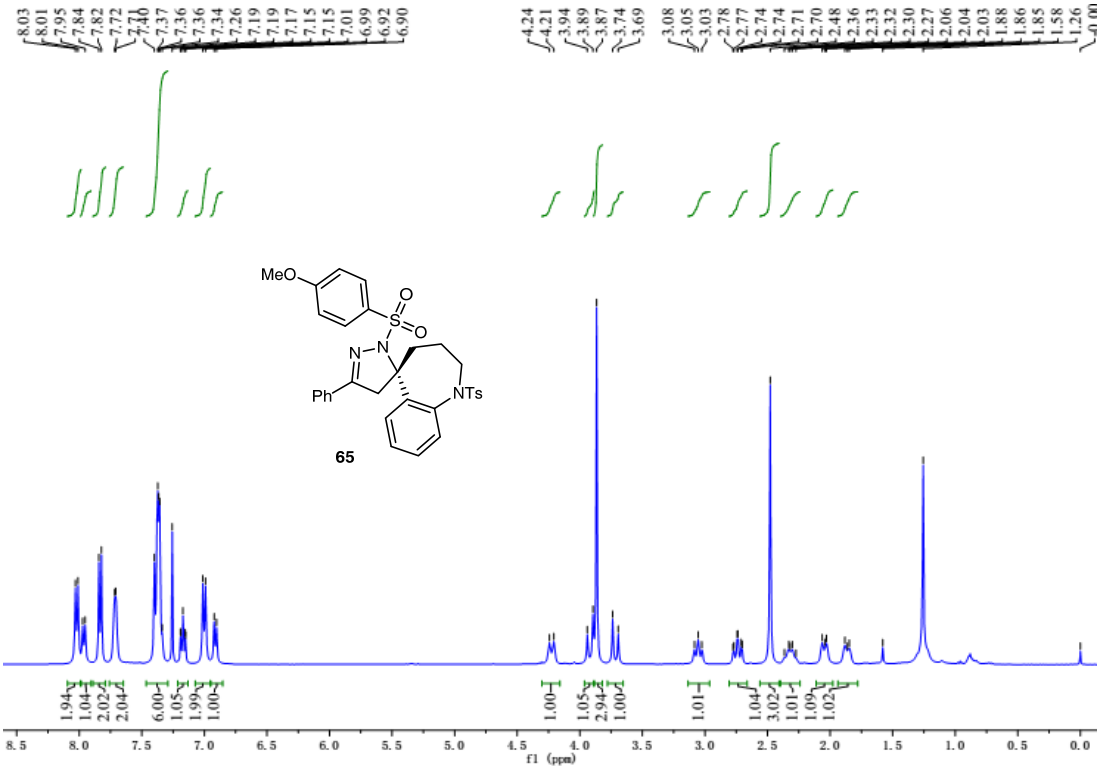
f1 (ppm)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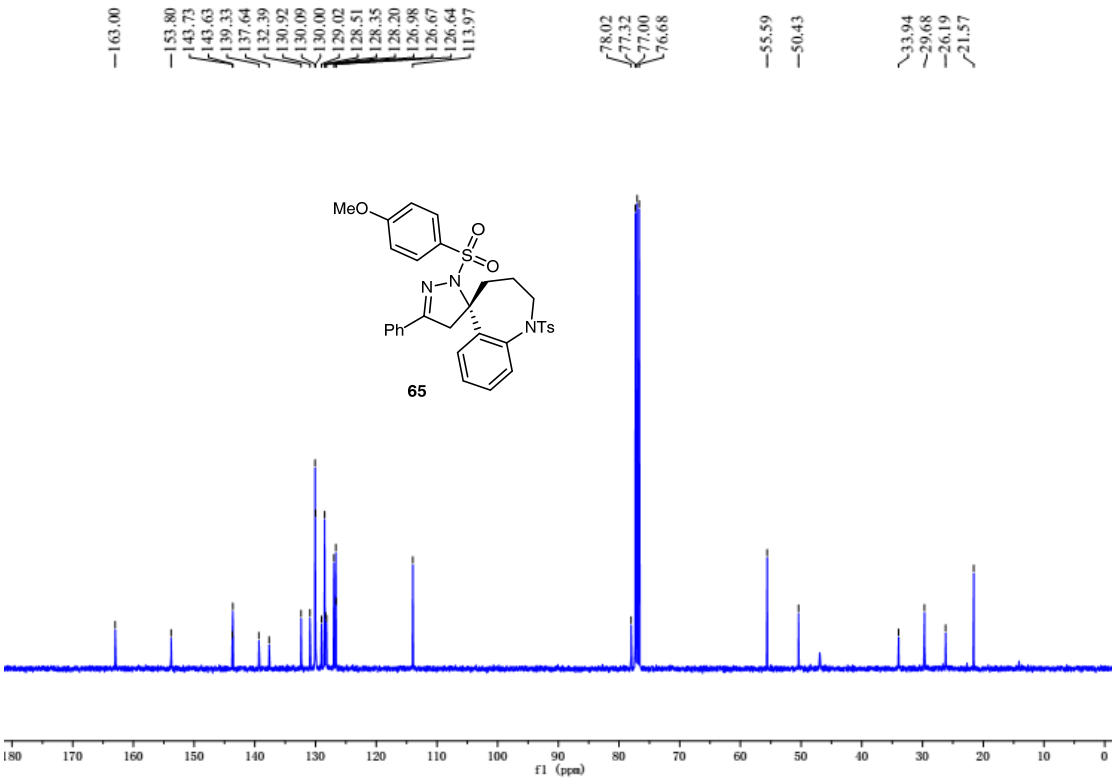
S
O
N
N
Ph
NTs
65
f1 (ppm)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O
S
O
N
N
Ph
NTs
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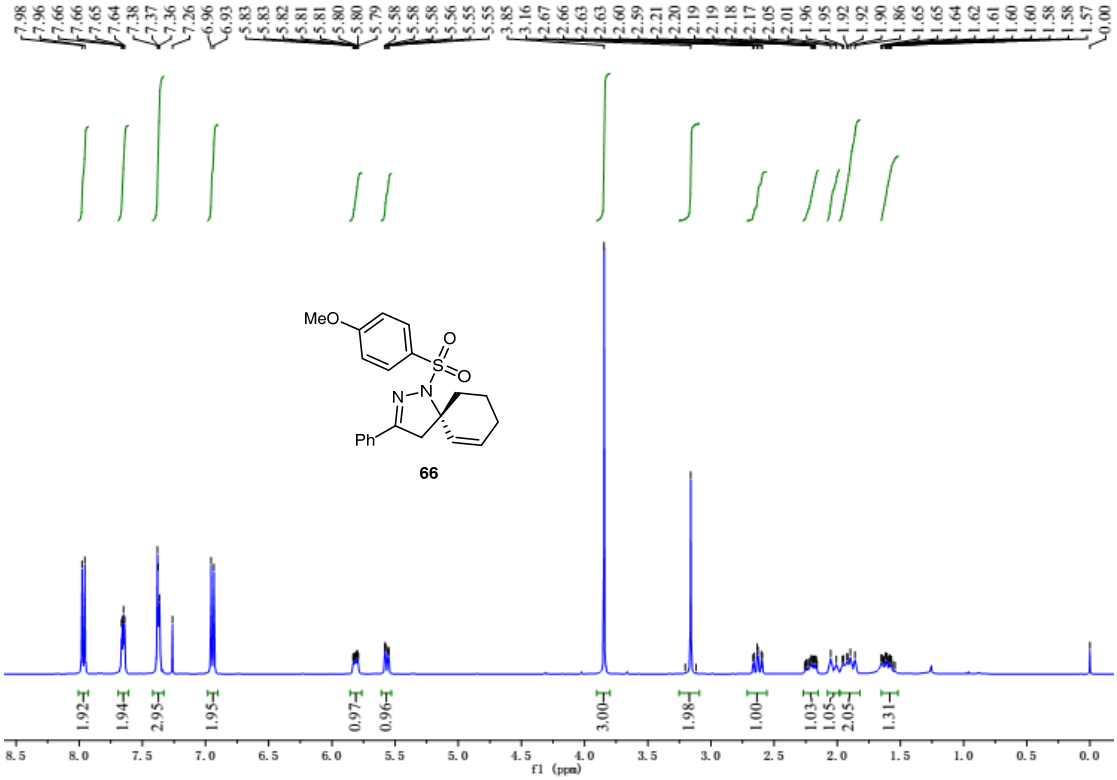
f1 (ppm)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7.66
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7.37
7.36
7.26
6.96
6.93
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5.83
5.82
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5.80
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5.79
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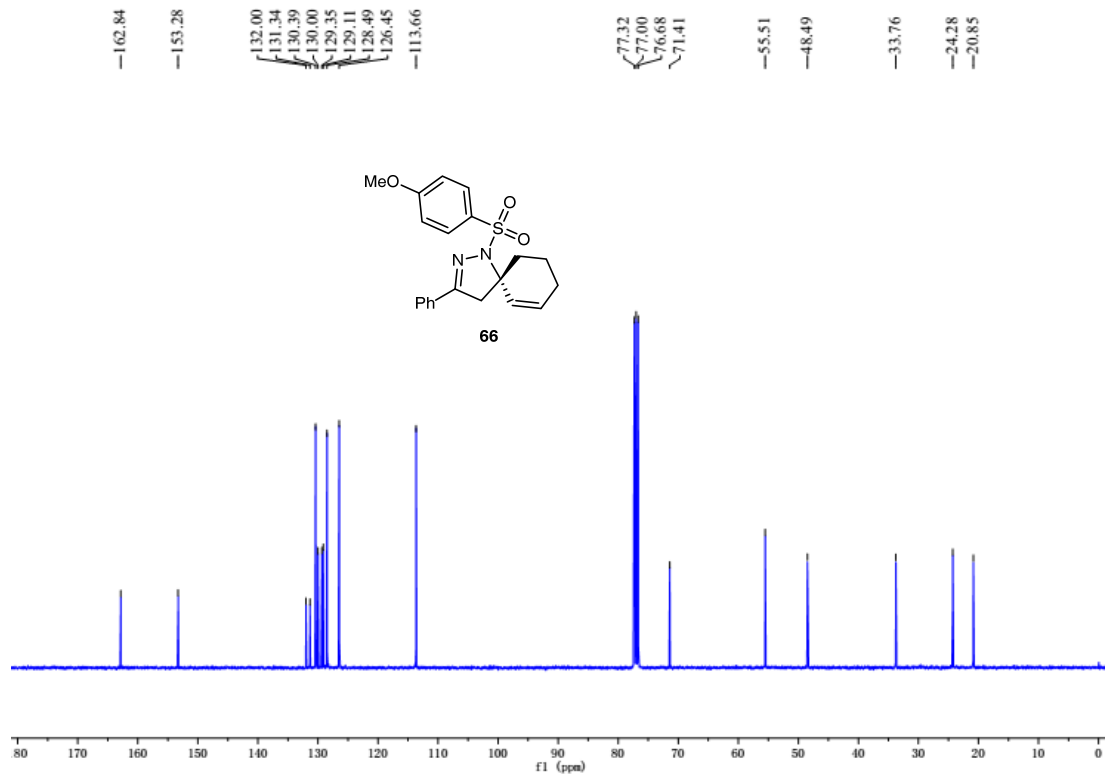
5.58
5.58
5.56
5.55
5.55
3.85
3.16
2.67
2.66
2.63
2.63
2.60
2.59
2.21
2.20
2.19
2.19
2.18
2.17
2.05
2.01
1.96
1.95
1.92
1.92
1.90
1.86
1.65
1.65
1.64
1.62
1.61
1.60
1.60
1.58
1.58
1.57
0.00
MeO
O
S
O
N
N
Ph
66
1.92
1.94
2.95
1.95
0.97
0.96
3.00
1.98
1.00
1.03
1.05
2.05
1.31
f1 (ppm)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128.49
126.45
113.66
77.32
77.00
76.68
71.41
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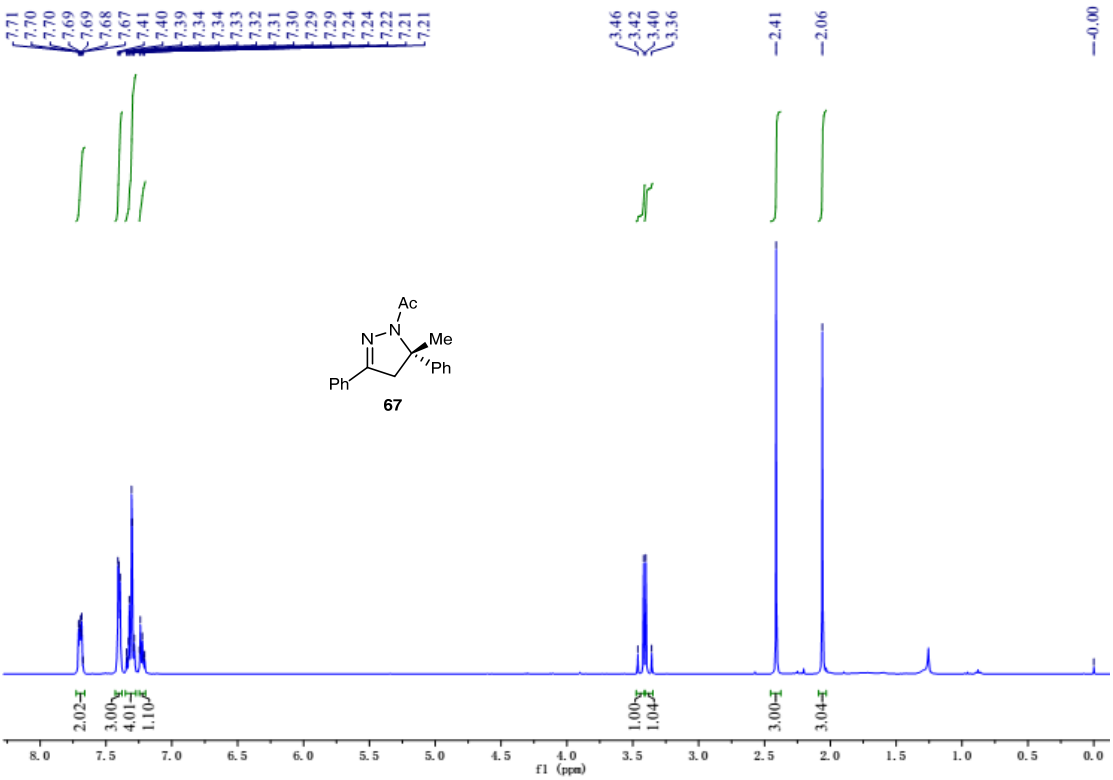
48.49
33.76
24.28
20.85
MeO
O
S
O
N
N
Ph
66
f1 (ppm)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7.70
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7.68
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7.41
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7.39
7.34
7.34
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7.32
7.31
7.30
7.29
7.29
7.24
7.24
7.22
7.21
7.21
3.46
3.42
3.40
3.36
2.41
2.06
0.00
Ac
N
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Me
Ph
Ph
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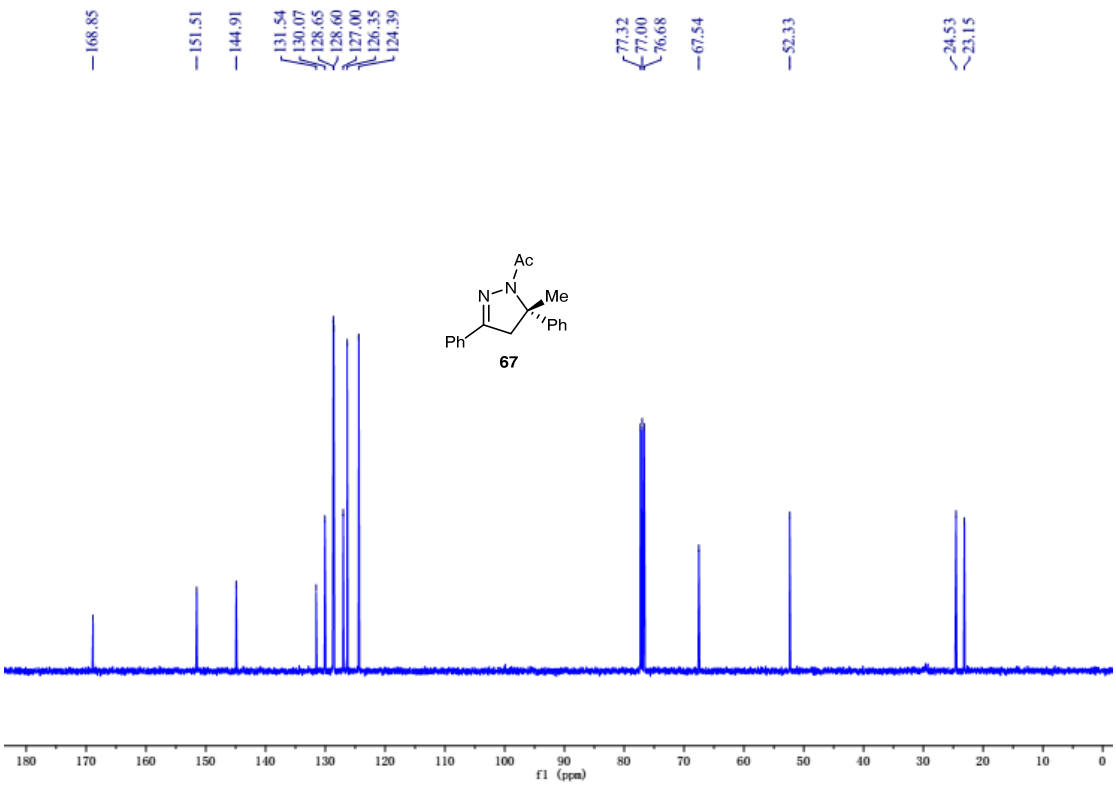
1.10
1.00
1.04
3.00
3.04
f1 (ppm)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151.51
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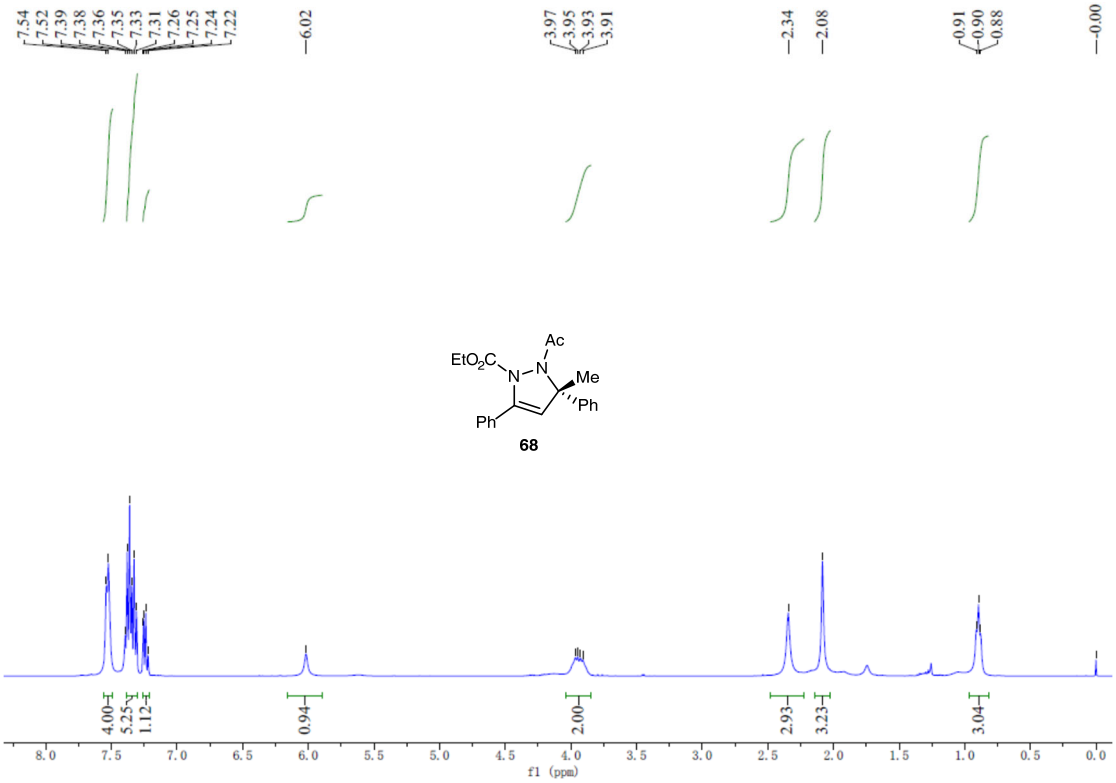
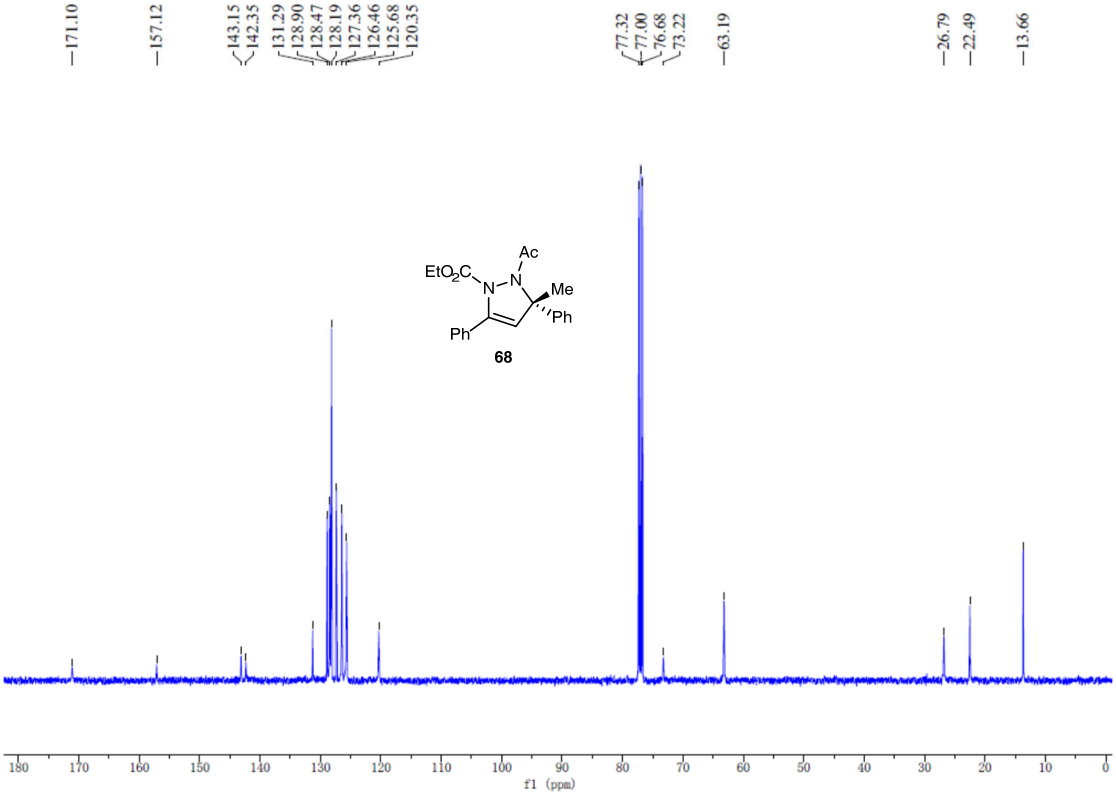
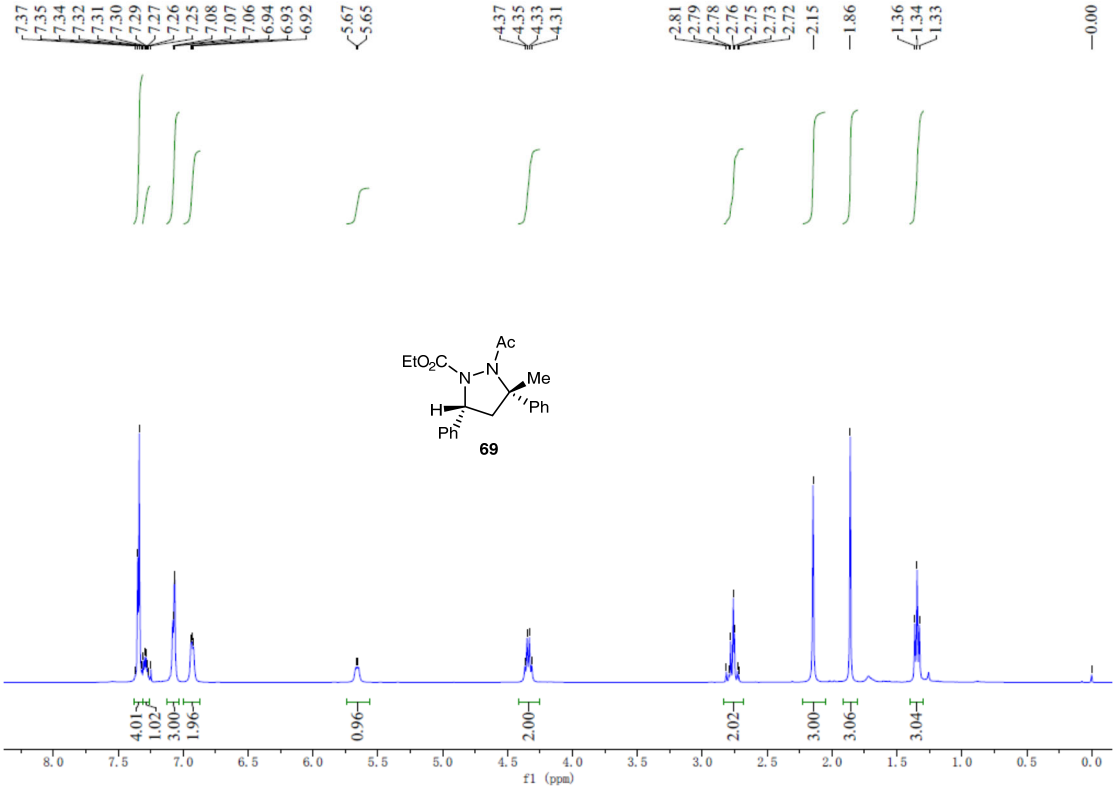
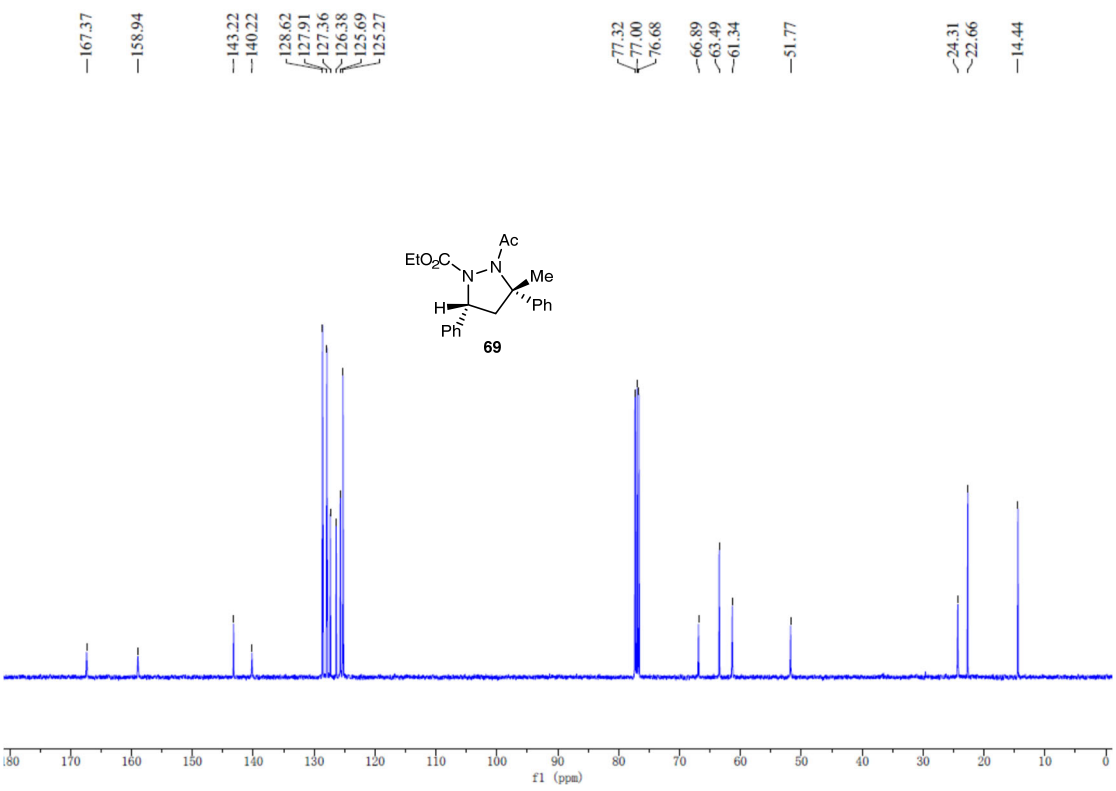
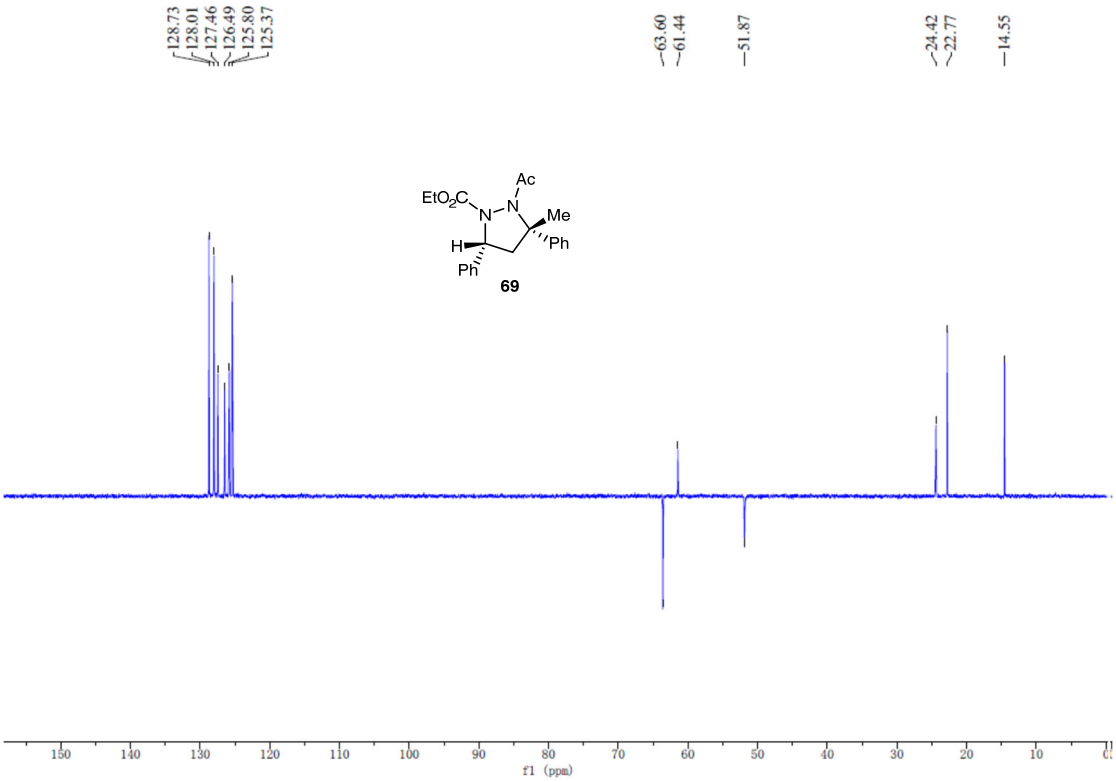
131.54
130.07
128.65
128.60
127.00
126.35
124.39
77.32
77.00
76.68
67.54
52.33
24.53
23.15
Ac
N
N
Me
Ph
Ph
67
f1 (ppm)

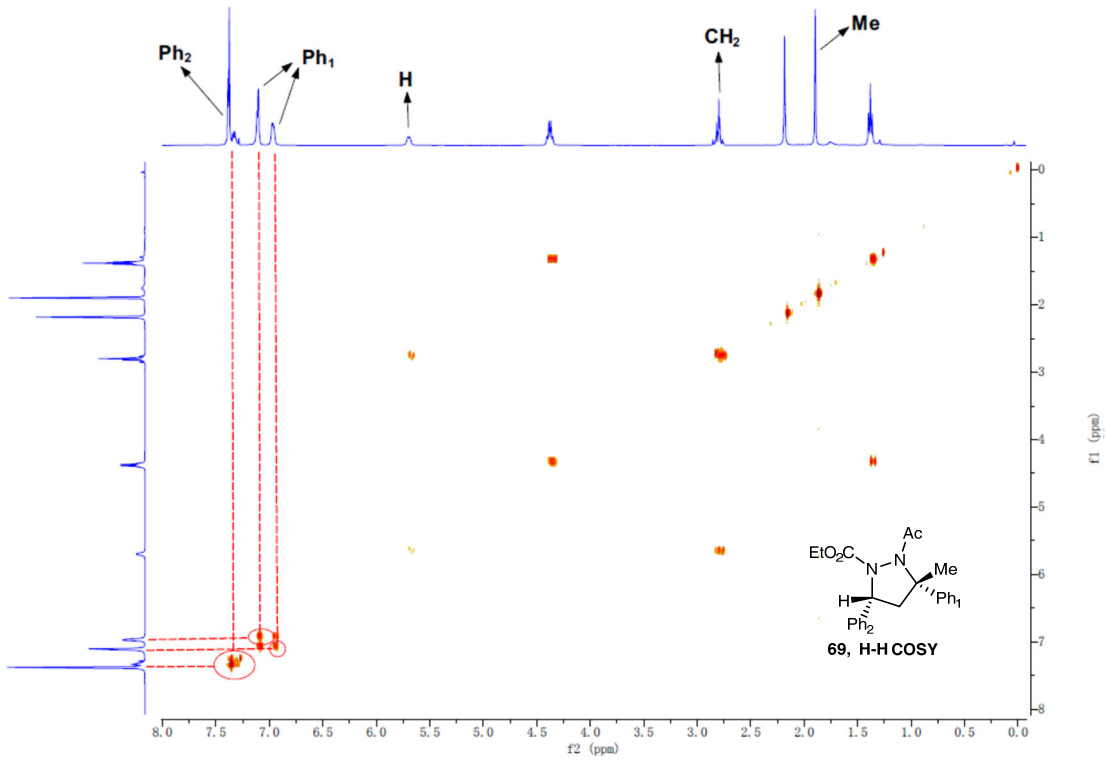

7.54
7.52
7.39
7.38
7.36
7.35
7.33
7.31
7.26
7.25
7.24
7.22
6.02
3.97
3.95
3.93
3.91
2.34
2.08
0.91
0.90
0.88
0.00
Ac
EtO2C
N
N
Me
Ph
Ph
68
4.00
5.25
1.12
0.94
2.00
2.93
3.23
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

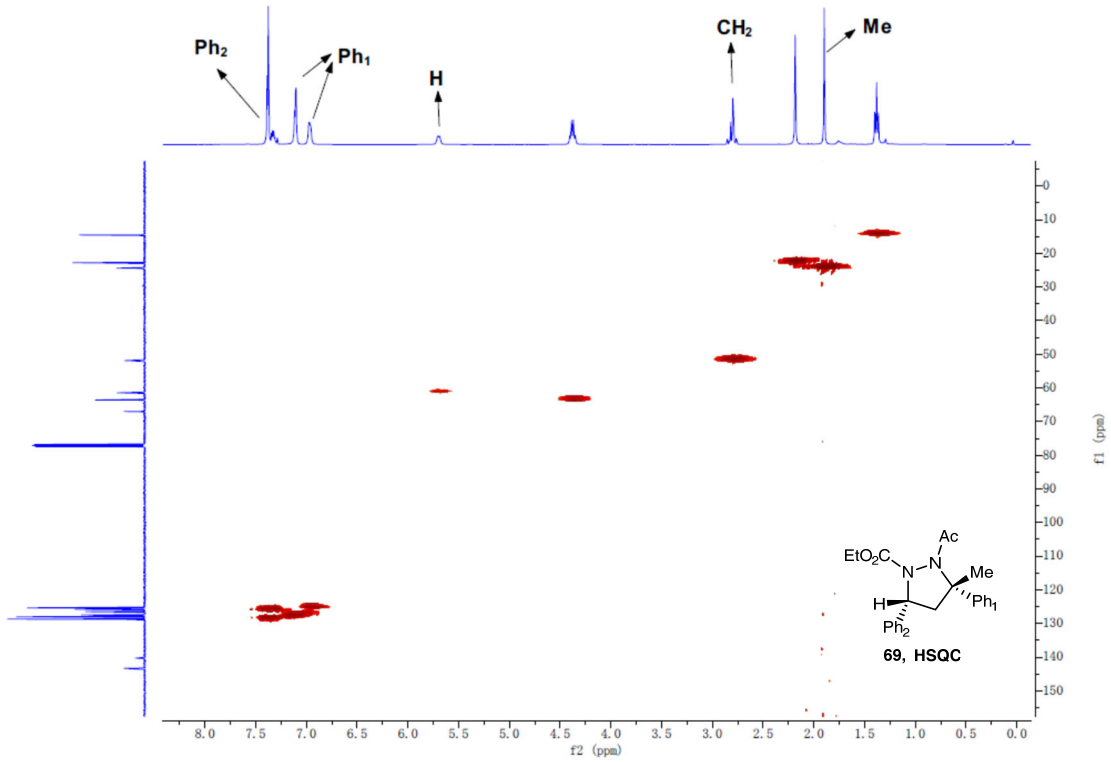

171.10
157.12
143.15
142.35
131.29
128.90
128.47
128.19
127.36
126.46
125.68
120.35
77.32
77.00
76.68
73.22
63.19
26.79
22.49
13.66
Ac
EtO2C
N
N
Me
Ph
Ph
68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

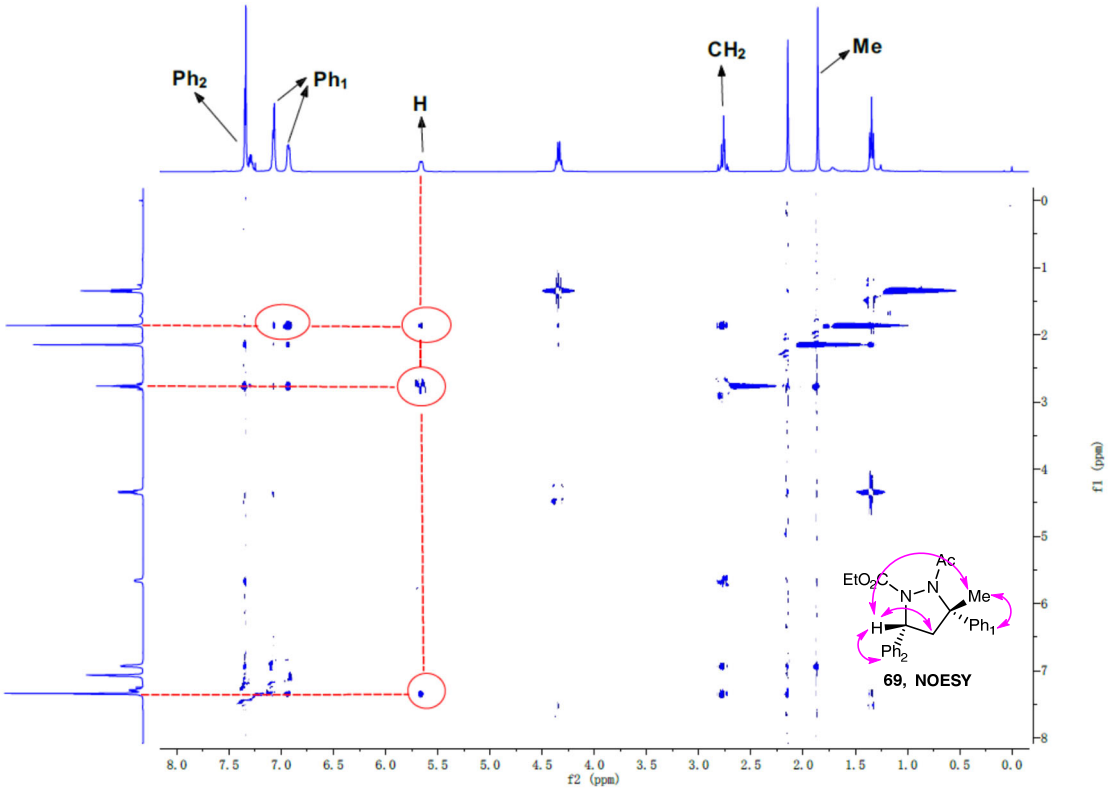

7.37
7.35
7.34
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.08
7.07
7.06
6.94
6.93
6.92
5.67
5.65
4.37
4.35
4.33
4.31
2.81
2.79
2.78
2.76
2.75
2.73
2.72
2.15
1.86
1.36
1.34
1.33
0.00
Ac
EtO2C
N
N
Me
H
Ph
Ph
69
4.01
1.02
3.00
1.96
0.96
2.00
2.02
3.00
3.06
3.04
f1 (ppm)

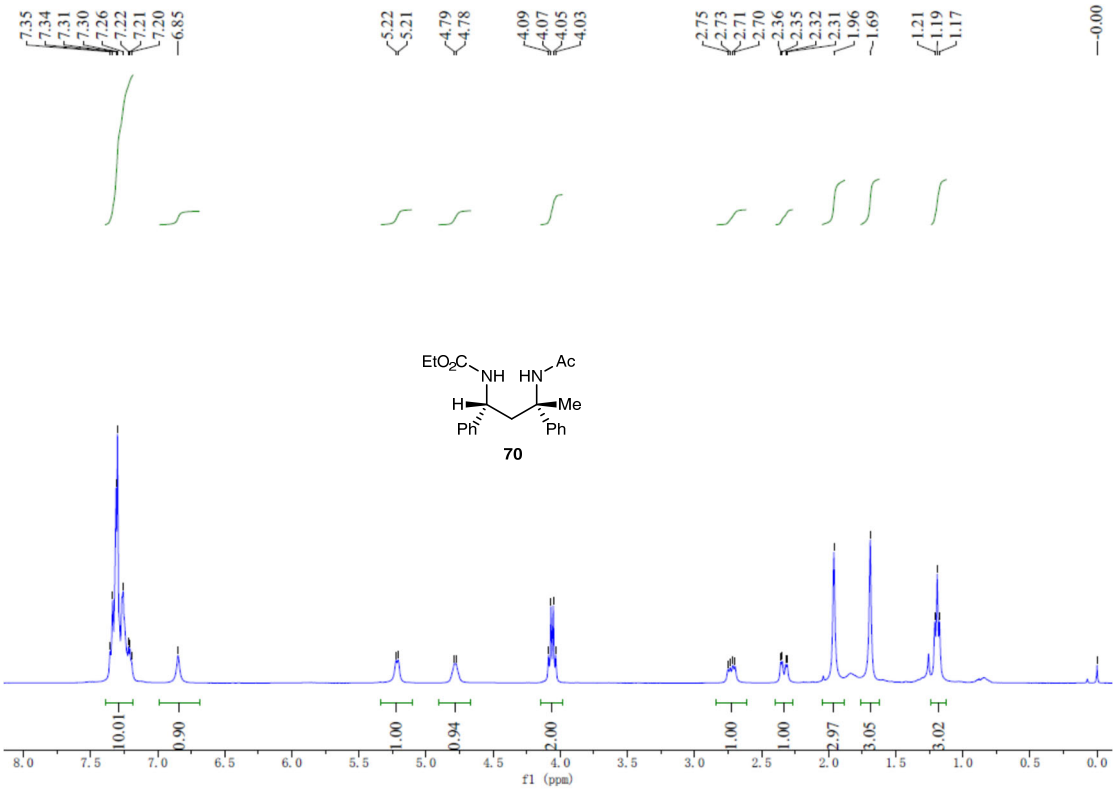

167.37
158.94
143.22
140.22
128.62
127.91
127.36
126.38
125.69
125.27
77.32
77.00
76.68
66.89
63.49
61.34
51.77
24.31
22.66
14.44
Ac
EtO2C
N
N
Me
H
Ph
Ph
69
f1 (ppm)

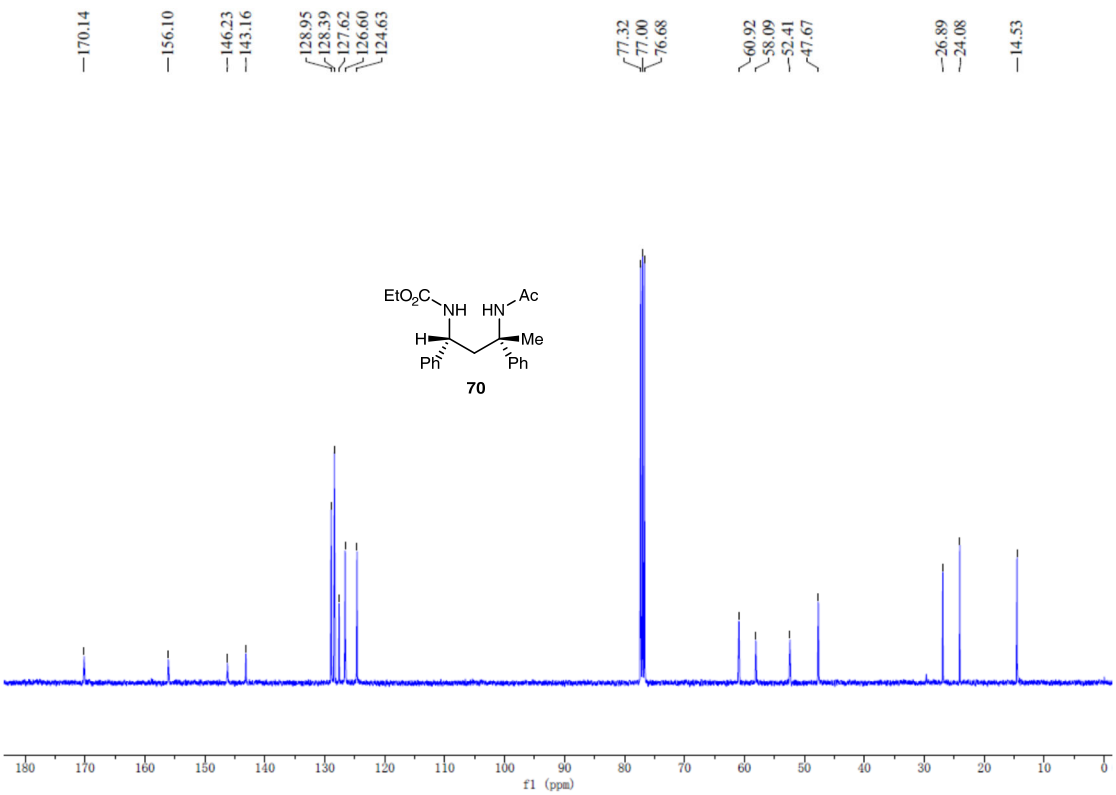

128.73
128.01
127.46
126.49
125.80
125.37
63.60
61.44
51.87
24.42
22.77
14.55
Ac
EtO2C
N
N
Me
H
Ph
Ph
69
f1 (ppm)

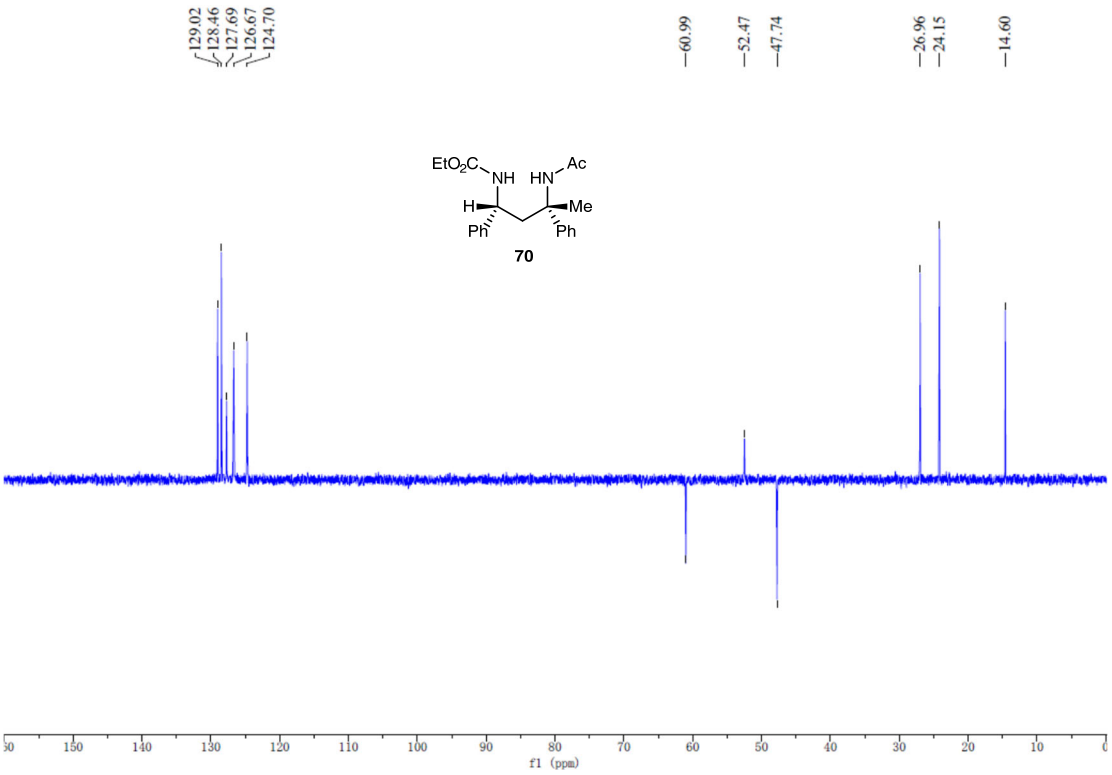

Ph2
Ph1
H
CH2
Me
Ac
EtO2C
N
N
Me
H
Ph1
Ph2
69, H-H COSY
f2 (ppm)
f1 (ppm)

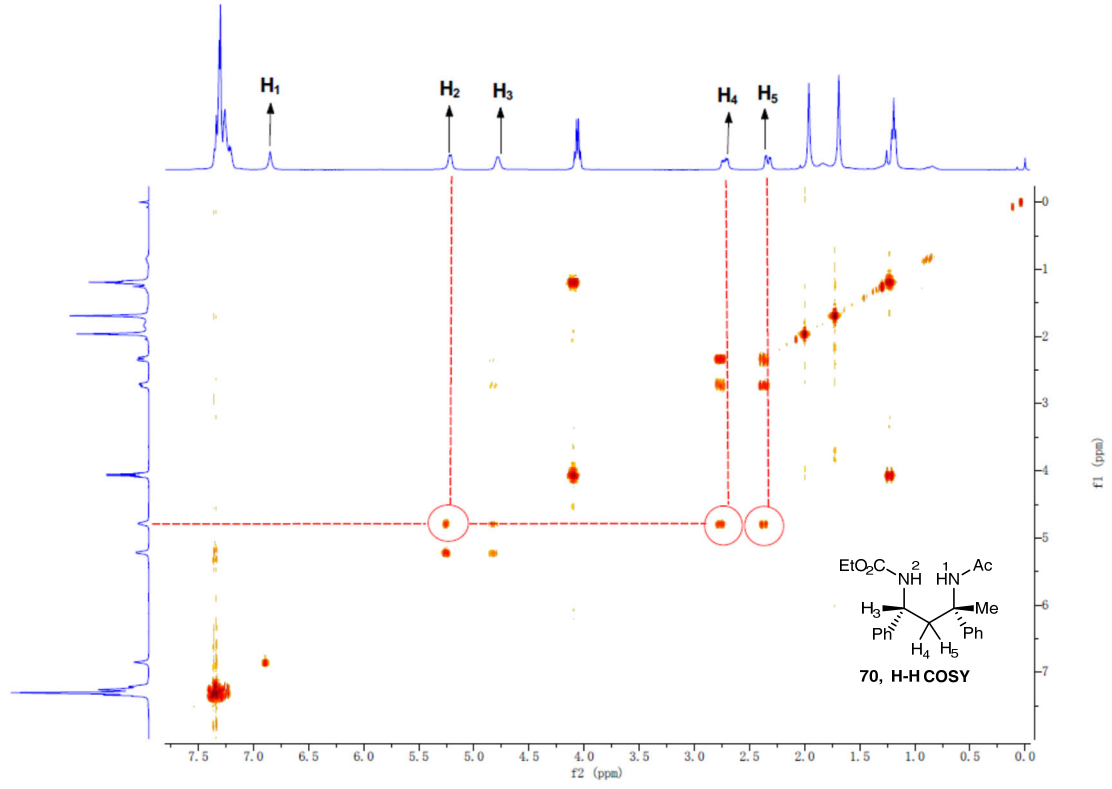

Ph2
Ph1
H
CH2
Me
f2 (ppm)
f1 (ppm)
EtO2C
Ac
N
Me
Ph1
H
Ph2
69, HSQC

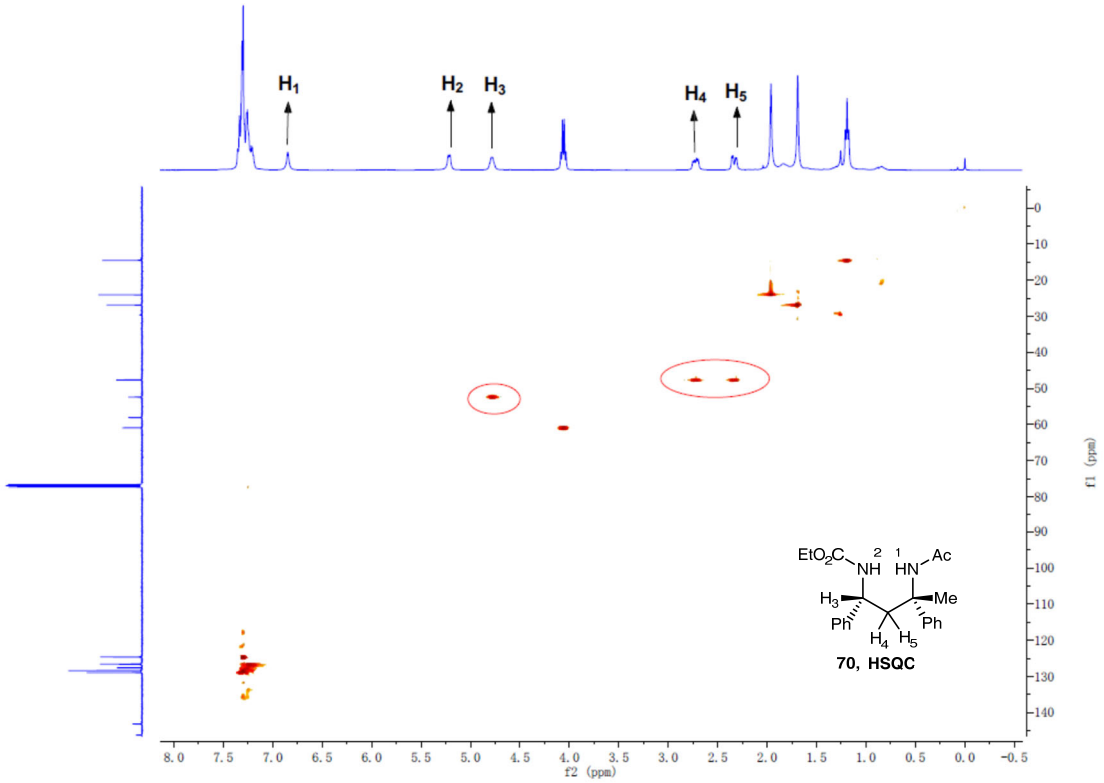

Ph2
Ph1
H
CH2
Me
f2 (ppm)
f1 (ppm)
EtO2C
Ac
N
Me
Ph1
H
Ph2
69, NOESY

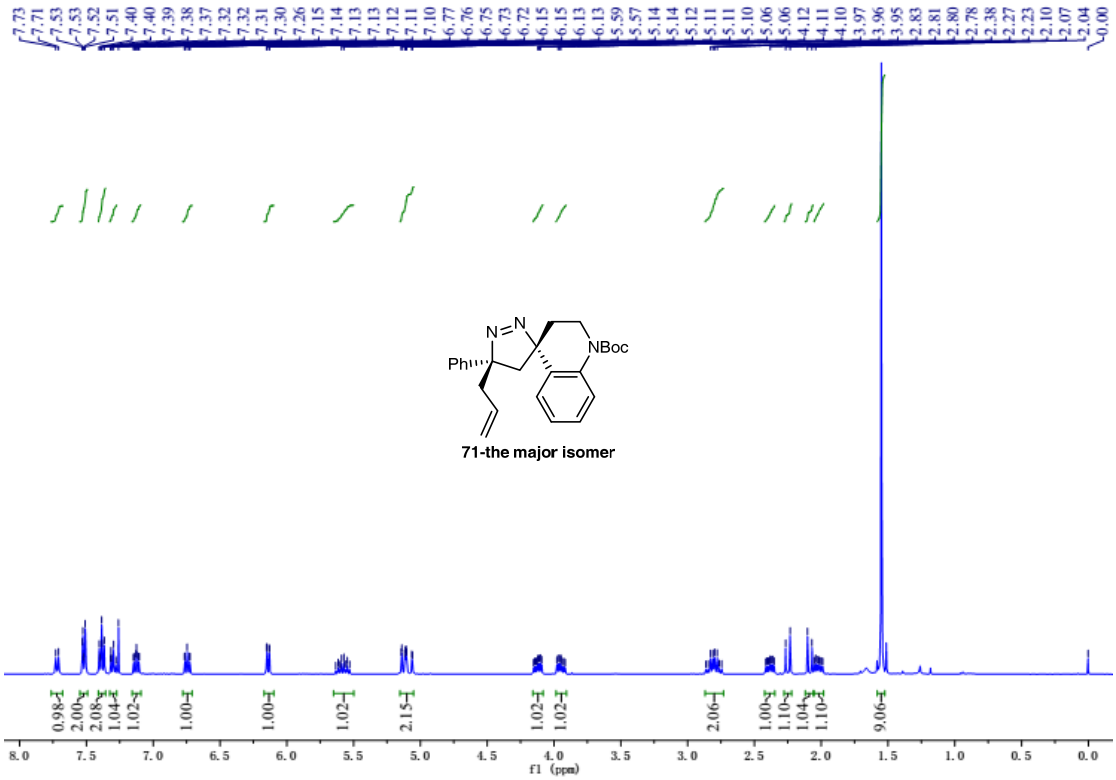

7.35
7.34
7.31
7.30
7.26
7.22
7.21
7.20
6.85
5.22
5.21
4.79
4.78
4.09
4.07
4.05
4.03
2.75
2.73
2.71
2.70
2.36
2.35
2.32
2.31
1.96
1.69
1.21
1.19
1.17
0.00
EtO2C
NH
HN
Ac
H
Me
Ph
Ph
70
10.01
0.90
1.00
0.94
2.00
1.00
1.00
2.97
3.05
3.02
f1 (ppm)

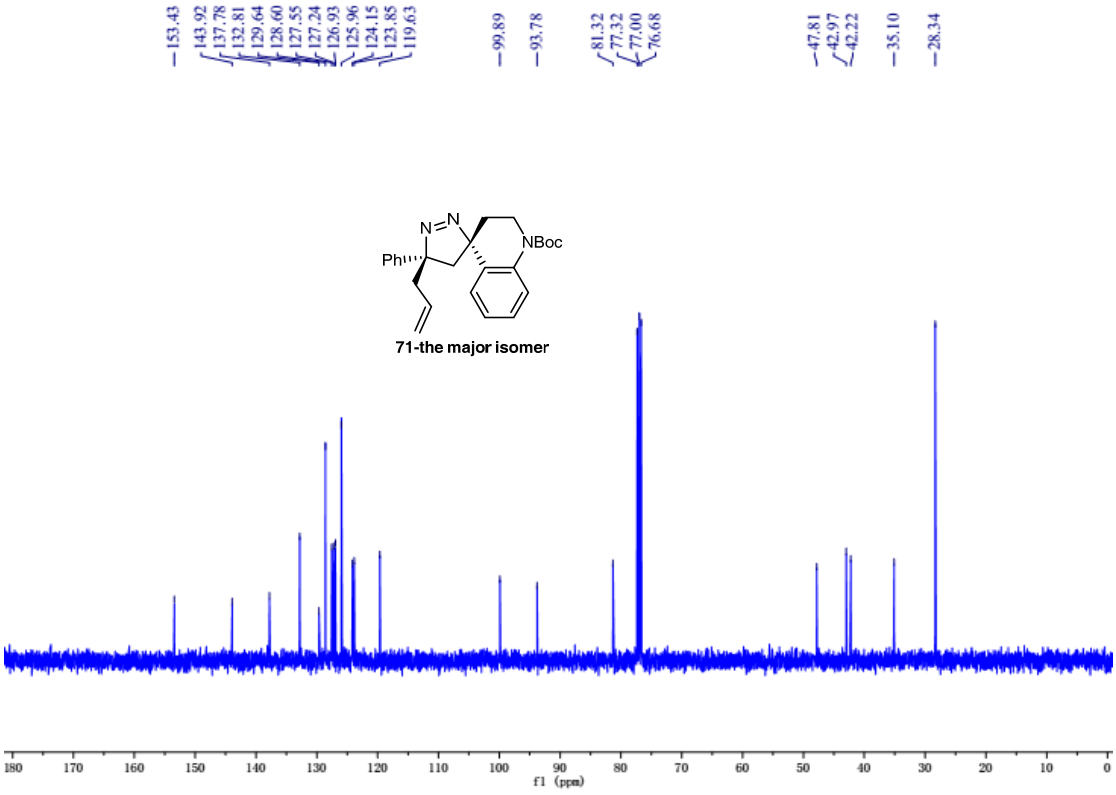

170.14
156.10
146.23
143.16
128.95
128.39
127.62
126.60
124.63
77.32
77.00
76.68
60.92
58.09
52.41
47.67
26.89
24.08
14.53
EtO2C
NH
HN
Ac
H
Me
Ph
Ph
70
f1 (ppm)

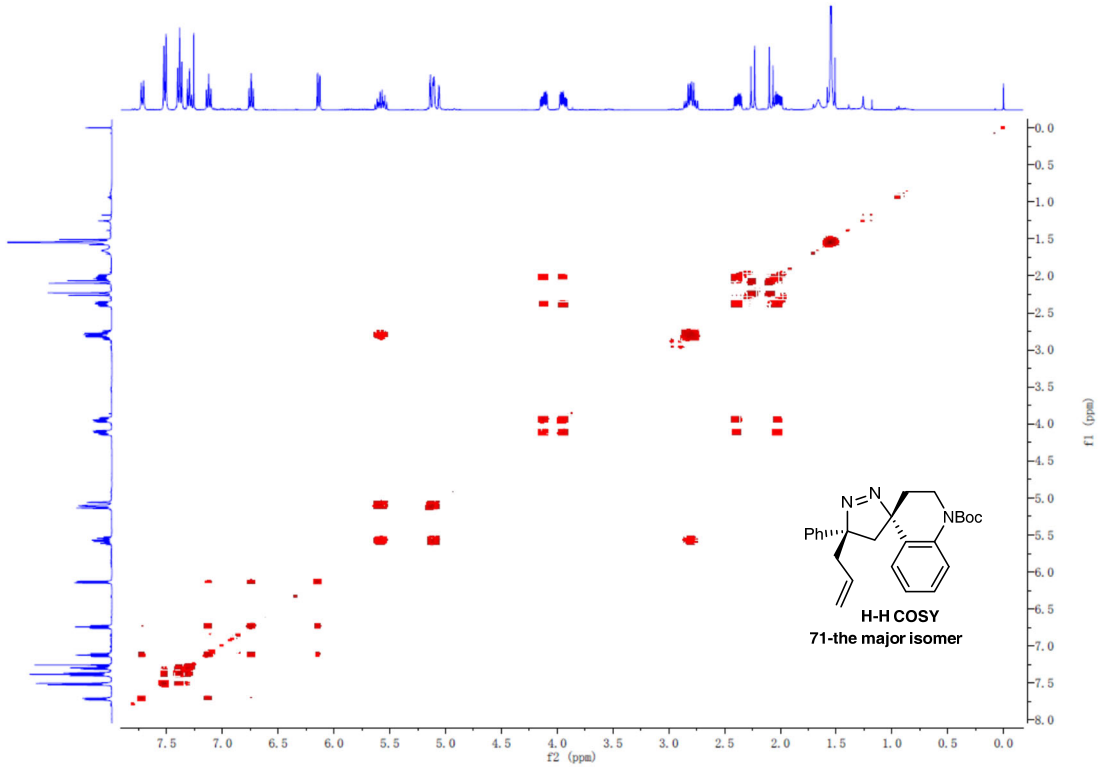

129.02
128.46
127.69
126.67
124.70
60.99
52.47
47.74
26.96
24.15
14.60
EtO2C
NH
HN
Ac
H
Me
Ph
Ph
70
f1 (ppm)

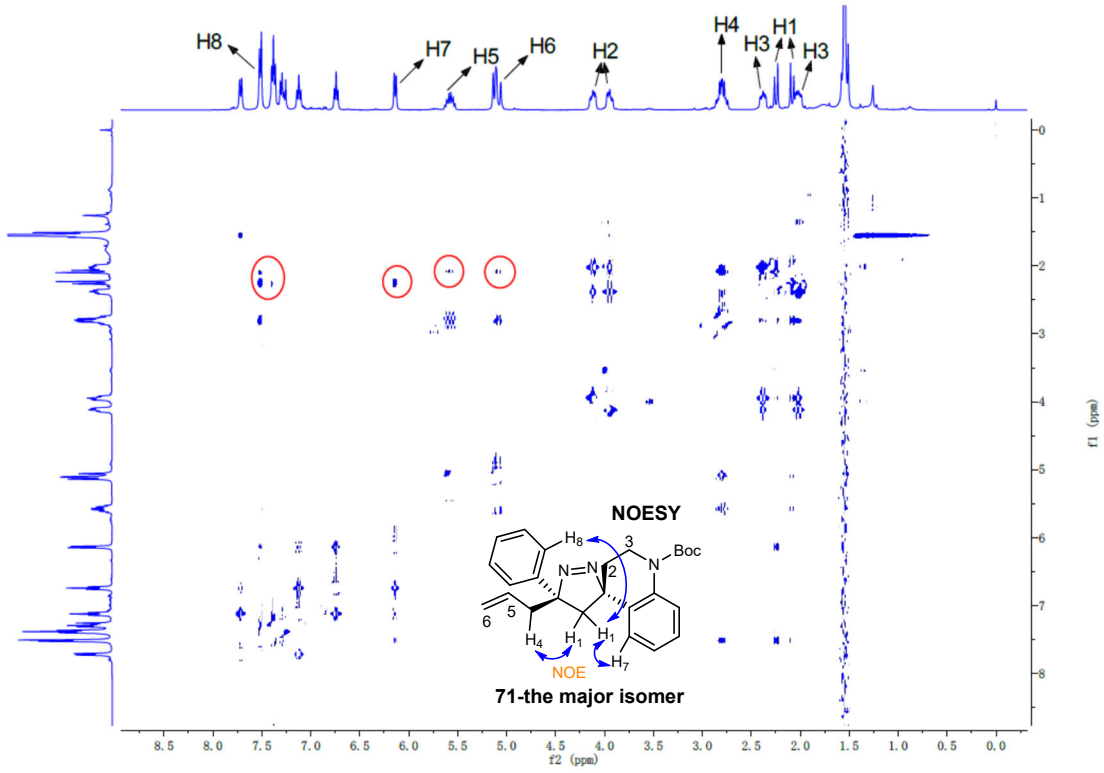

H1
H2
H3
H4
H5
f2 (ppm)
f1 (ppm)
EtO2C
NH
HN
Ac
H3
Me
Ph
Ph
H4
H5
70, H-H COSY

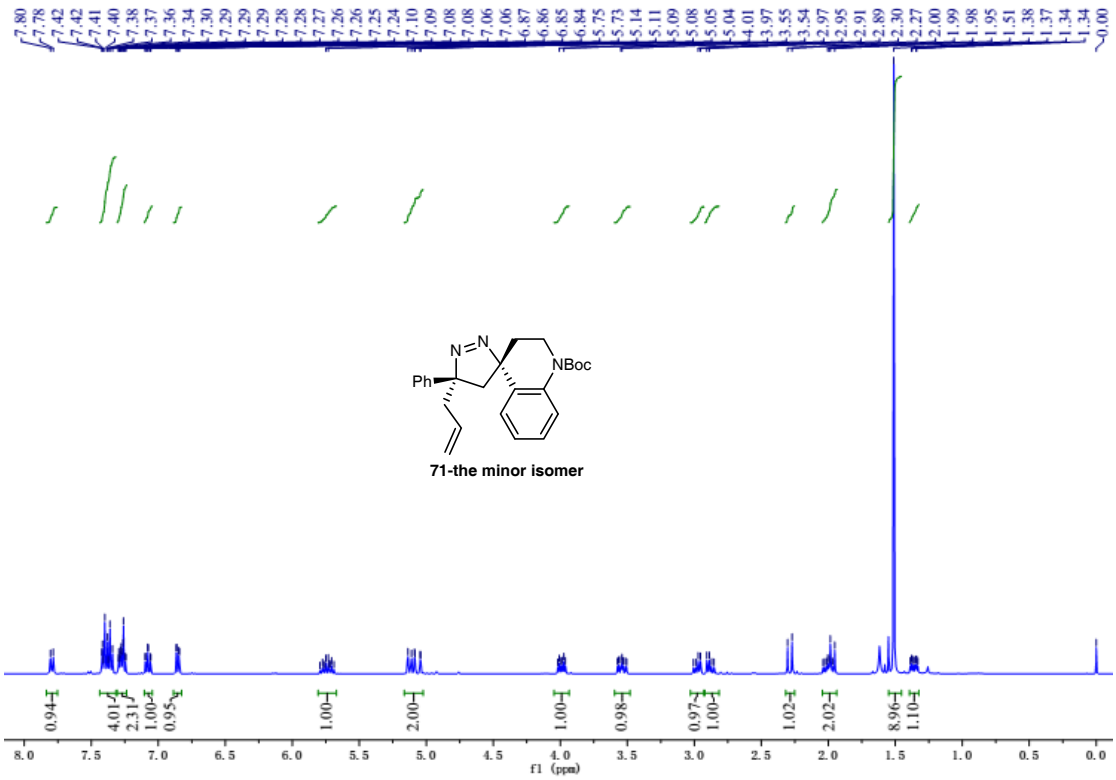

H1
H2
H3
H4
H5
EtO2C
NH
2
1
HN
Ac
H3
Ph
Me
Ph
H4
H5
70, HSQC
f2 (ppm)
f1 (ppm)

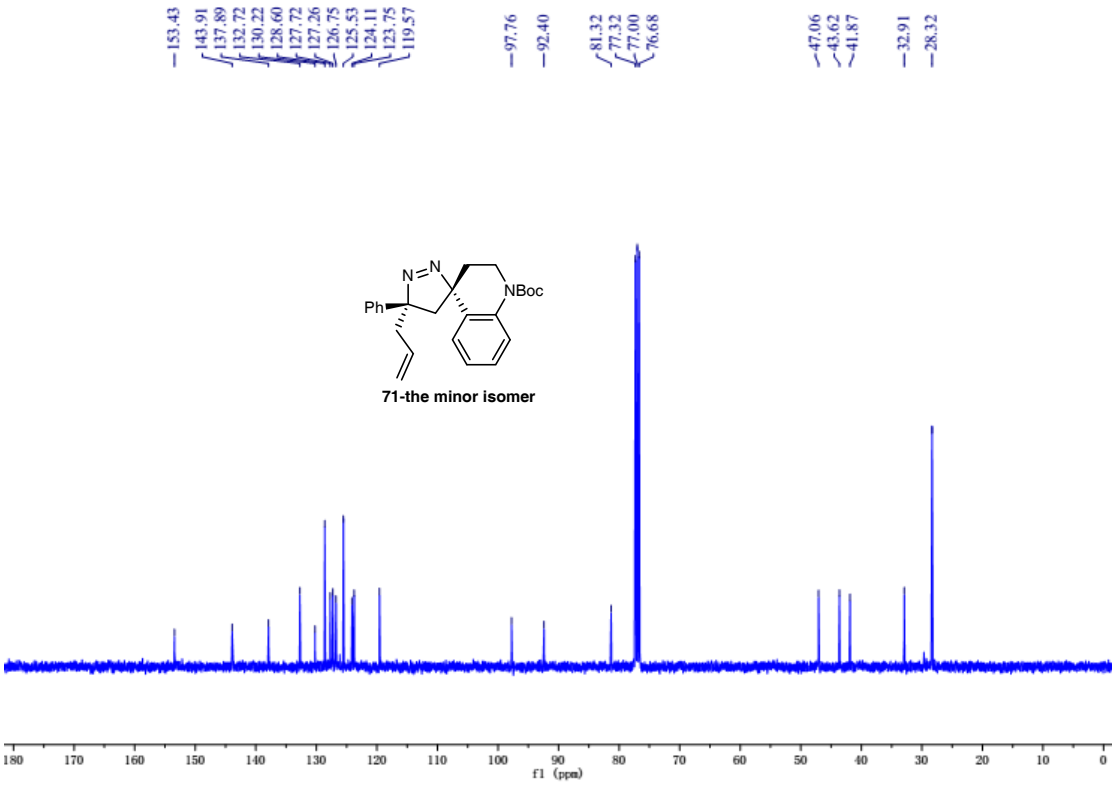

7.73
7.71
7.53
7.53
7.52
7.51
7.40
7.40
7.39
7.38
7.37
7.32
7.31
7.30
7.26
7.15
7.14
7.13
7.13
7.12
7.11
7.10
6.77
6.76
6.75
6.73
6.72
6.15
6.15
6.13
6.13
5.59
5.57
5.14
5.14
5.12
5.11
5.11
5.10
5.06
5.06
4.12
4.11
4.10
3.97
3.96
3.95
2.83
2.81
2.80
2.78
2.38
2.27
2.23
2.10
2.07
2.04
0.00
N
N
Ph
NBoc
71-the major isomer
0.98
2.00
2.08
1.04
1.02
1.00
1.00
1.02
2.15
1.02
1.02
2.06
1.00
1.10
1.04
1.10
9.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

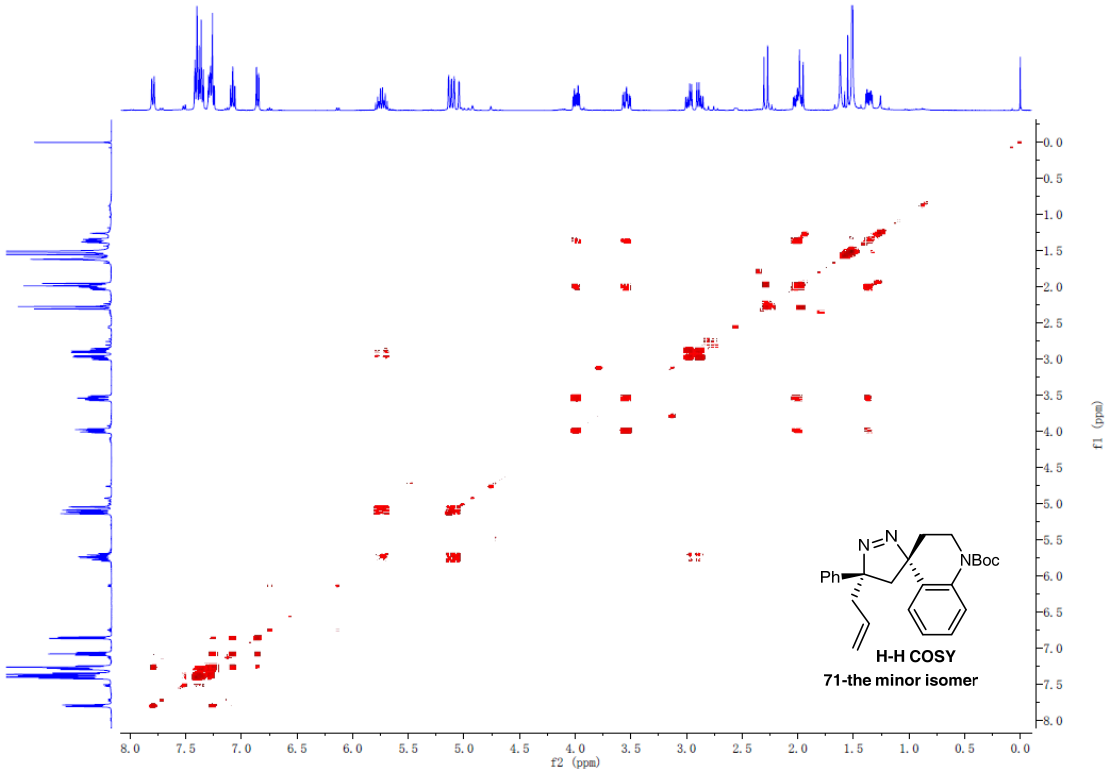

153.43
143.92
137.78
132.81
129.64
128.60
127.55
127.24
126.93
125.96
124.15
123.85
119.63
99.89
93.78
81.32
77.32
77.00
76.68
47.81
42.97
42.22
35.10
28.34
N
N
Ph
NBoc
71-the major isomer
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

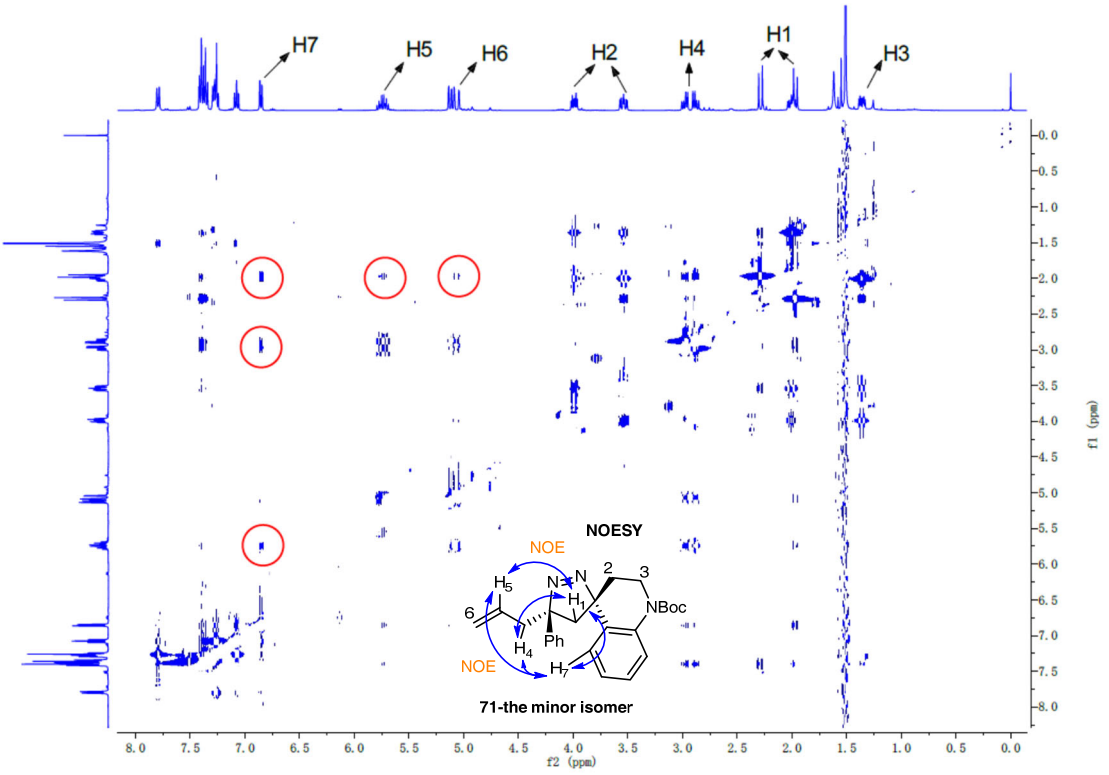

Ph
N=N
NBoc
H-H COSY
71-the major isomer
f2 (ppm)
f1 (ppm)

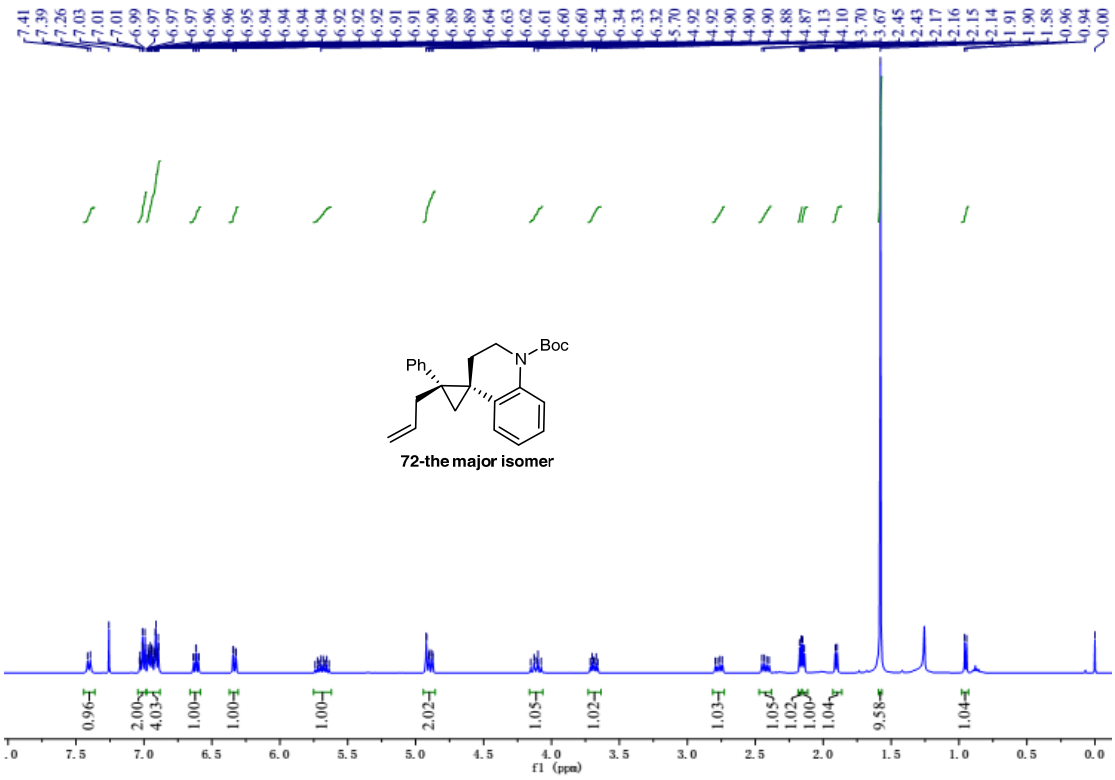

H8
H7
H5
H6
H2
H4
H3
H1
H3
NOESY
Boc
NOE
71-the major isomer
f2 (ppm)
f1 (ppm)

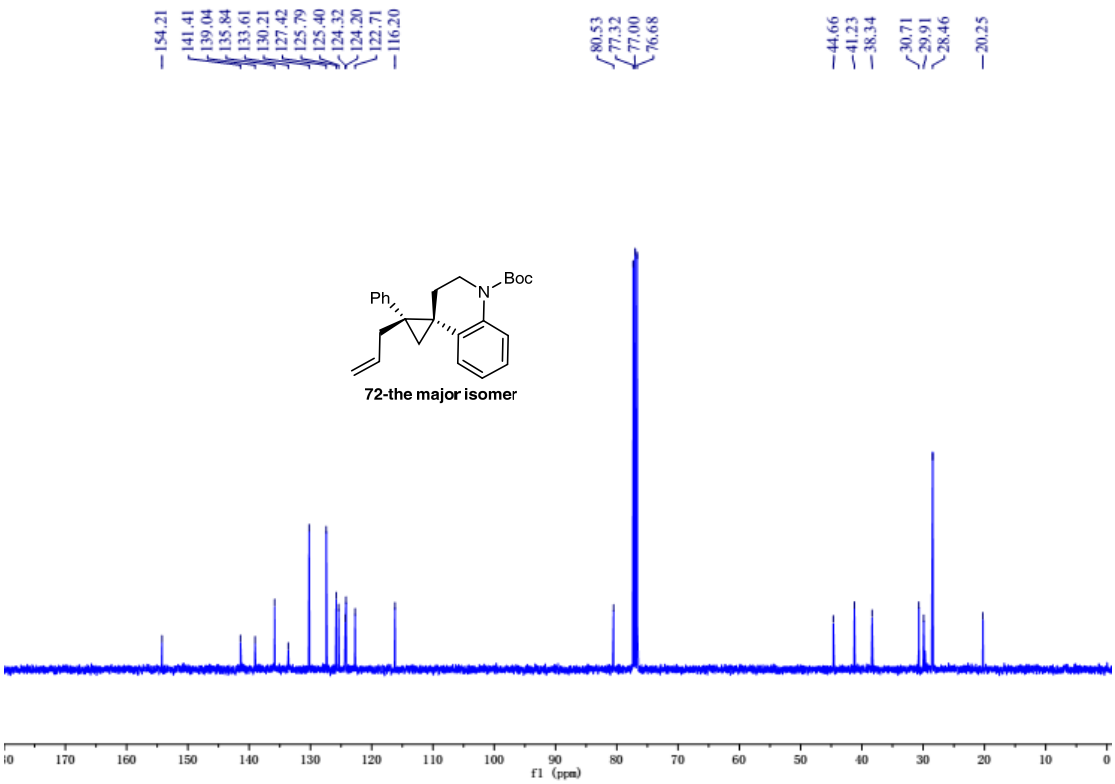

7.80 7.78 7.42 7.41 7.40 7.38 7.37 7.36 7.34 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.10 7.09 7.08 7.08 7.06 7.06 6.87 6.86 6.85 6.84 5.75 5.73 5.14 5.11 5.09 5.08 5.05 5.04 4.01 3.97 3.55 3.54 2.97 2.95 2.91 2.89 2.30 2.27 2.00 1.99 1.98 1.95 1.51 1.38 1.37 1.34 1.34 0.00
N
N
Ph
NBoc
71-the minor isomer
0.94 4.01 2.31 1.00 0.95 1.00 2.00 1.00 0.98 0.97 1.00 1.02 2.02 8.96 1.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

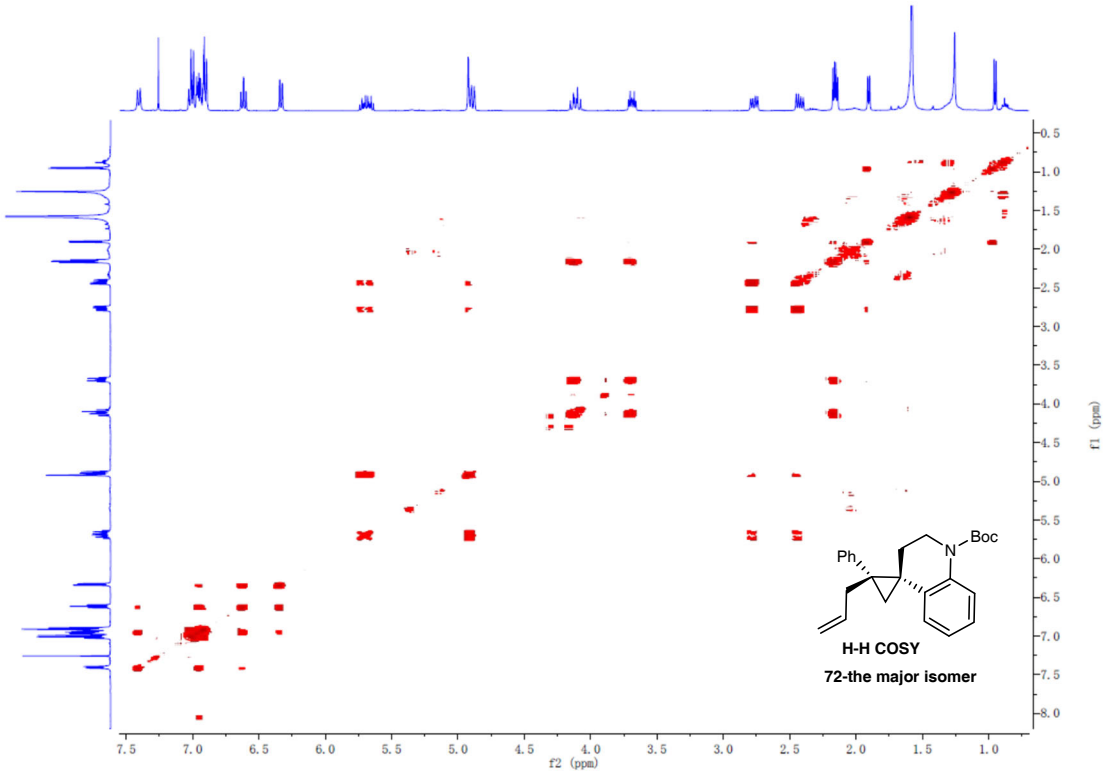

153.43 143.91 137.89 132.72 130.22 128.60 127.72 127.26 126.75 125.53 124.11 123.75 119.57
97.76 92.40
81.32 77.32 77.00 76.68
47.06 43.62 41.87
32.91 28.32
N
N
Ph
NBoc
71-the minor isomer
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

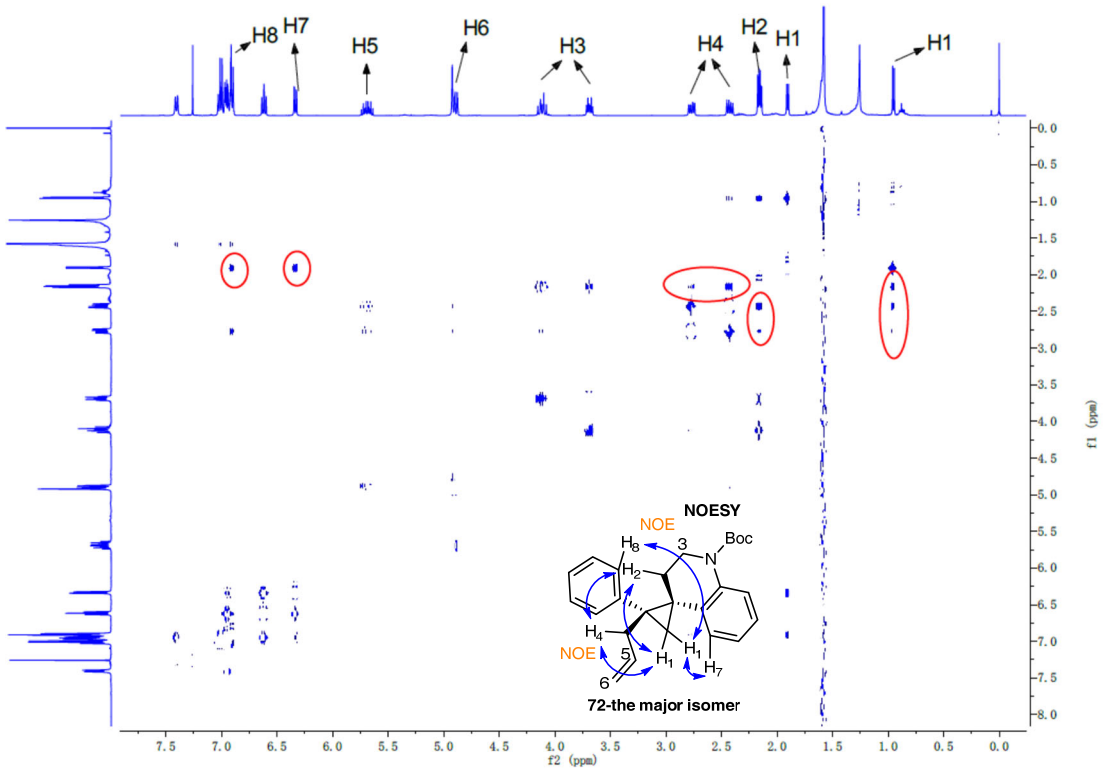

Ph
N
N
NBoc
H-H COSY
71-the minor isomer
f2 (ppm)
f1 (ppm)

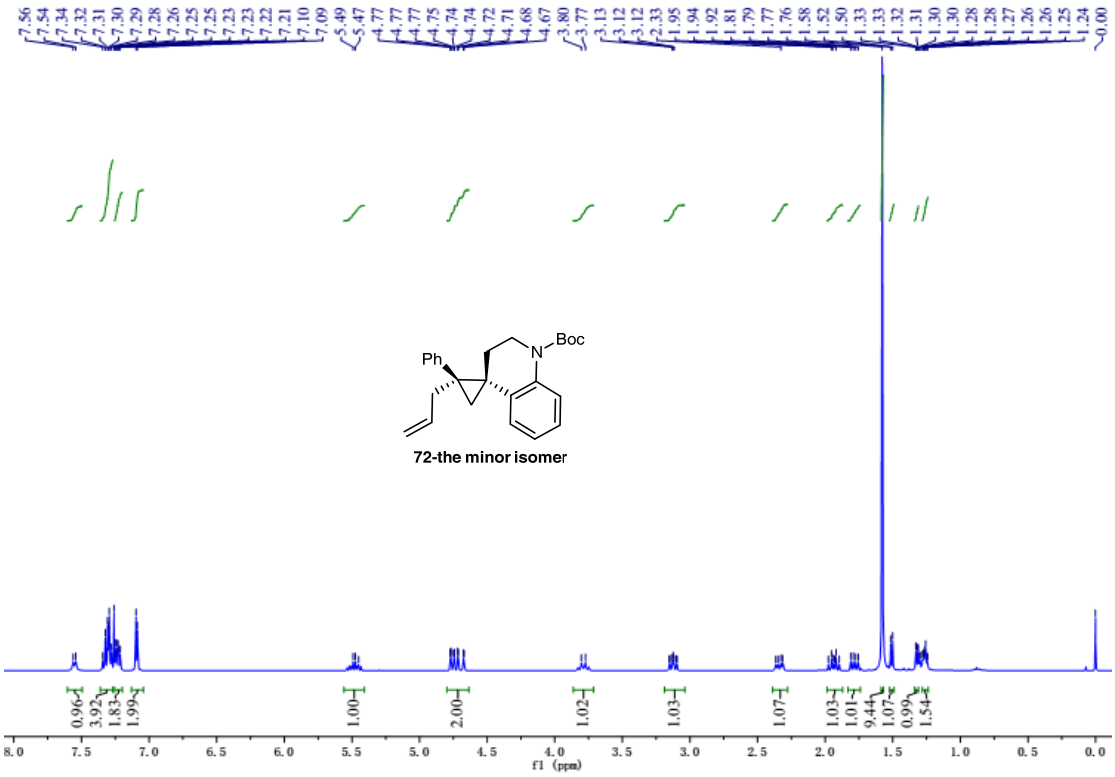

H7
H5
H6
H2
H4
H1
H3
NOESY
NOE
NOE
Ph
NBoc
71-the minor isomer
f2 (ppm)
f1 (ppm)

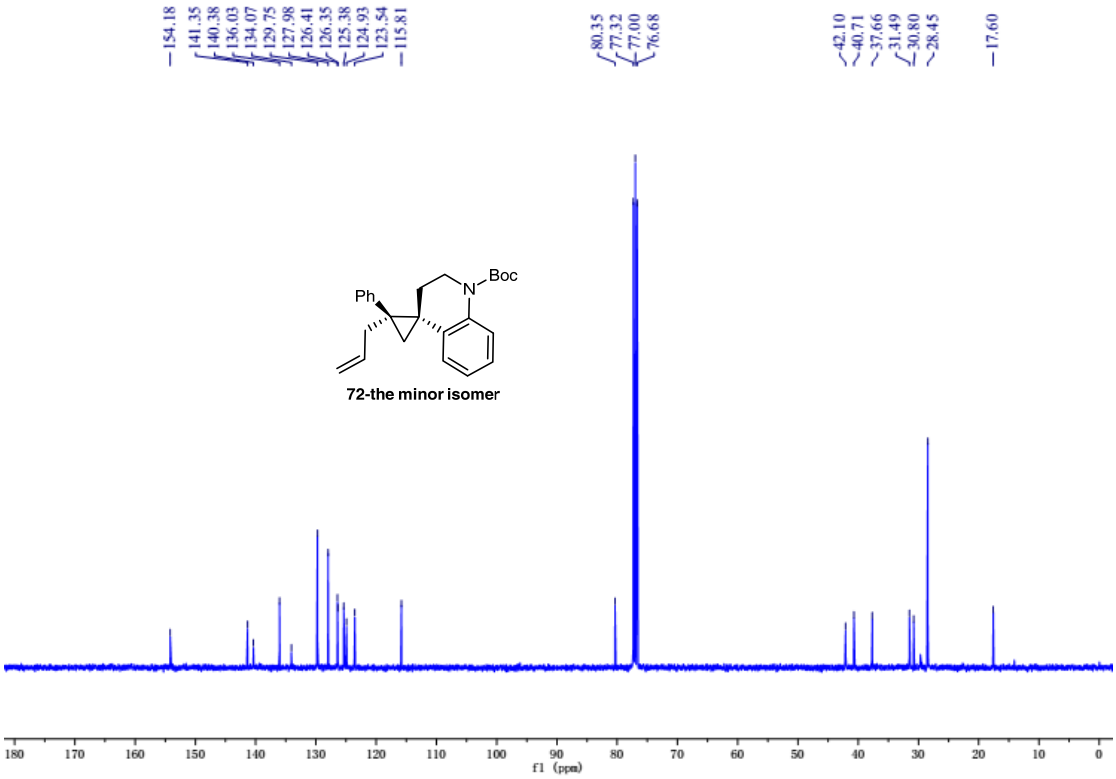

Ph
N
Boc
72-the major isomer
f1 (ppm)

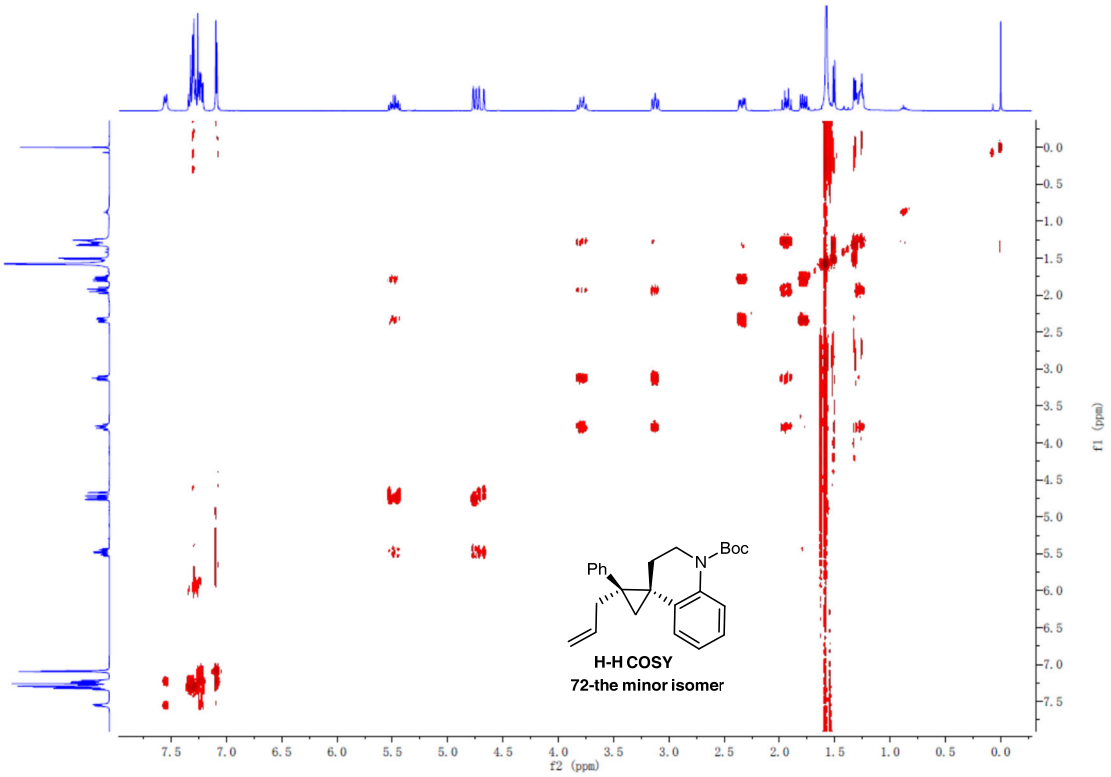

Ph
N
Boc
72-the major isomer
f1 (ppm)

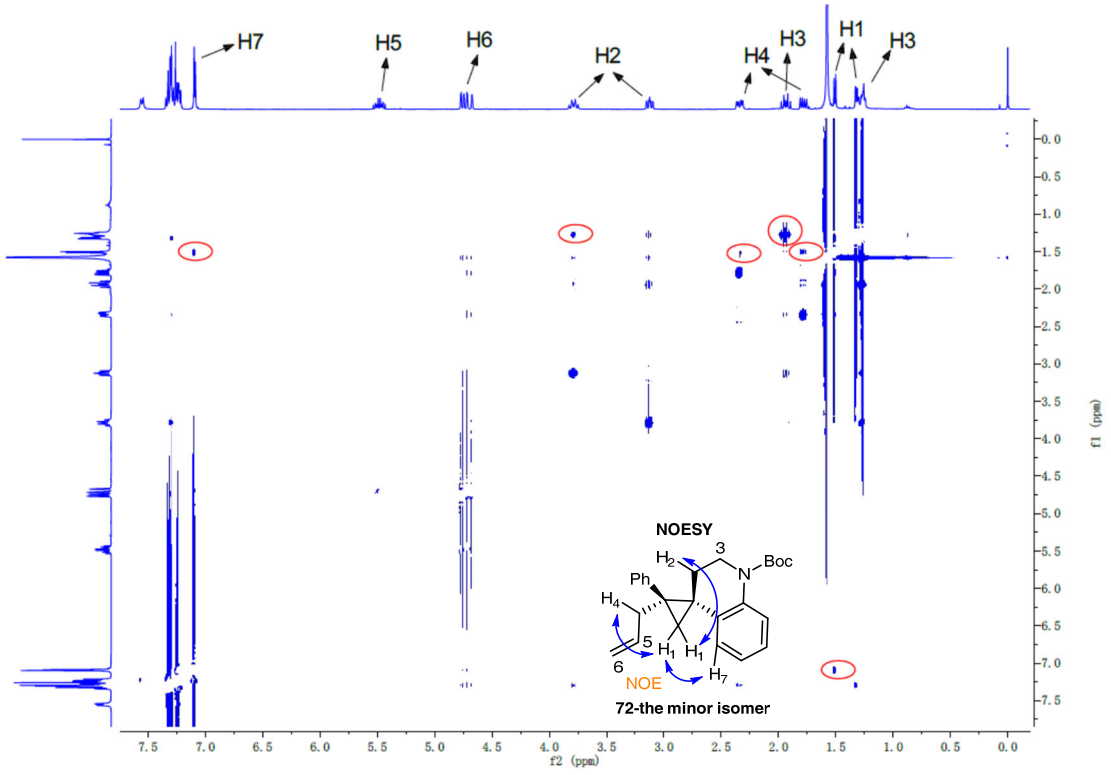

Ph
N
Boc
H-H COSY
72-the major isomer
f2 (ppm)
f1 (ppm)


H8
H7
H5
H6
H3
H4
H2
H1
H1
NOESY
NOE
NOE
Boc
72-the major isomer
f2 (ppm)
f1 (ppm)

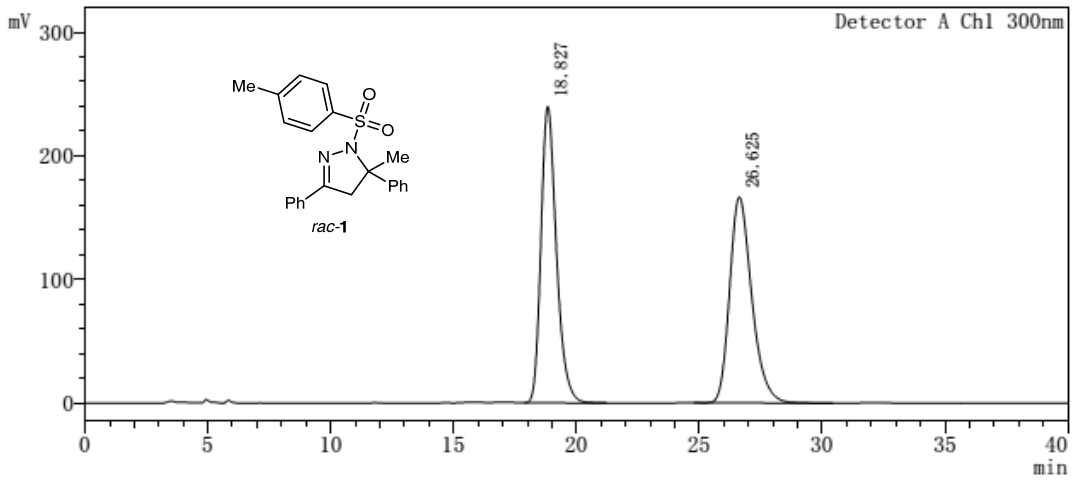

Ph
N
Boc
72-the minor isomer
f1 (ppm)


Ph
N
Boc
72-the minor isomer
f1 (ppm)


Ph
N
Boc
H-H COSY
72-the minor isomer
f2 (ppm)
f1 (ppm)


H7
H5
H6
H2
H4
H3
H1
H3
NOESY
Ph
N
Boc
NOE
72-the minor isomer
f2 (ppm)
f1 (ppm)

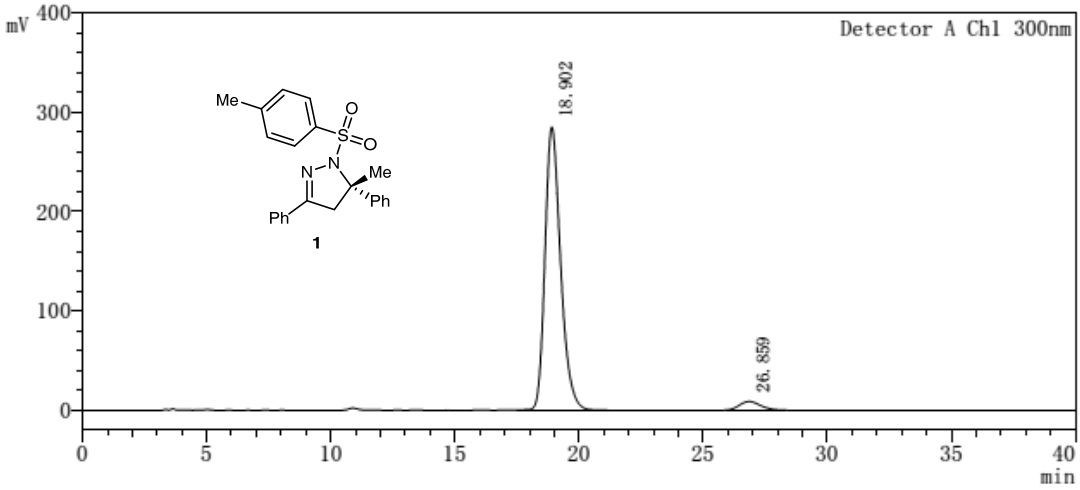
HPLC Spectra



Peak Table

Detector A Ch1 300nm

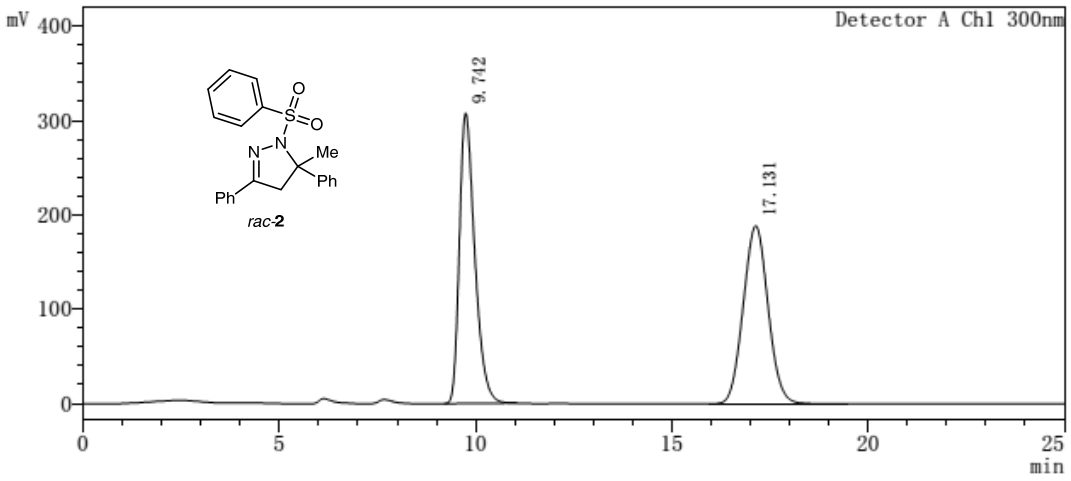
Peak#	Ret. Time	Area	Area%
1	18.827	10501154	50.136
2	26.625	10444351	49.864



Peak Table

Detector A Ch1 300nm

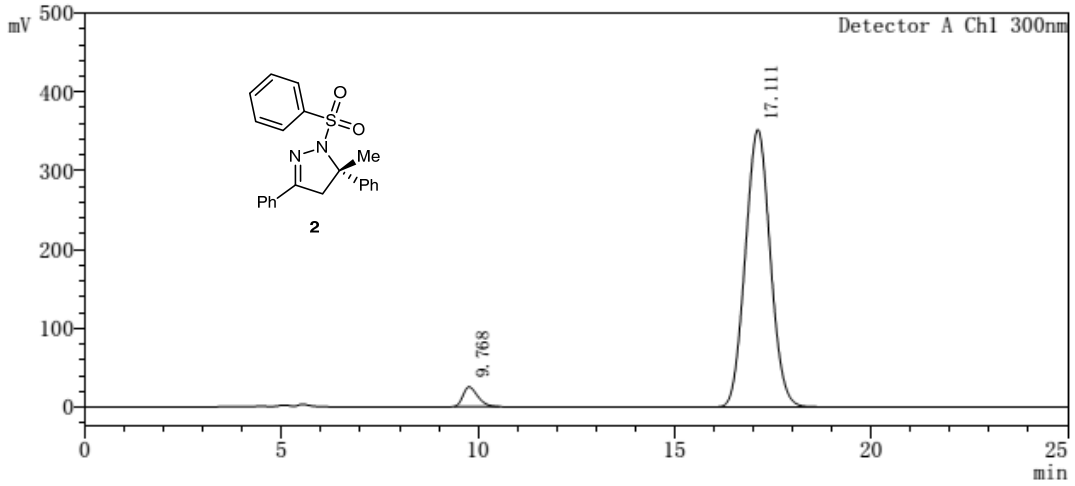
Peak#	Ret. Time	Area	Area%
1	18.902	12524064	95.960
2	26.859	527207	4.040



Peak Table

Detector A Ch1 300nm

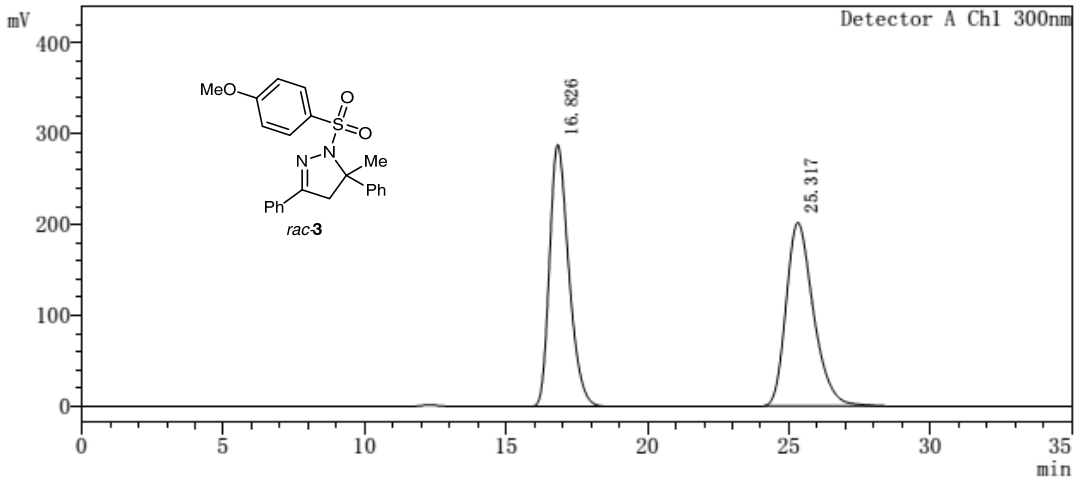
Peak#	Ret. Time	Area	Area%
1	9.742	8363665	50.273
2	17.131	8272889	49.727



Peak Table

Detector A Ch1 300nm

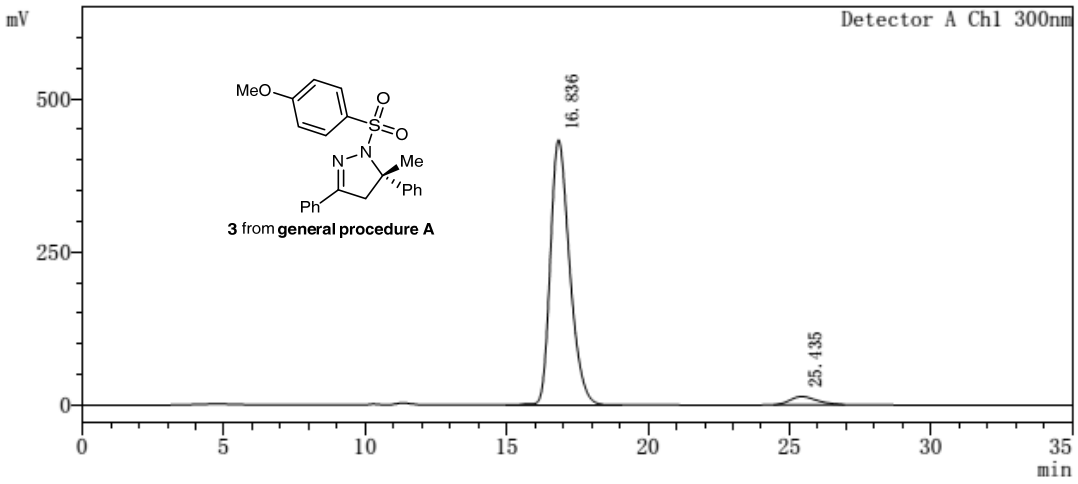
Peak#	Ret. Time	Area	Area%
1	9.768	651083	4.018
2	17.111	15554545	95.982



Peak Table

Detector A Ch1 300nm

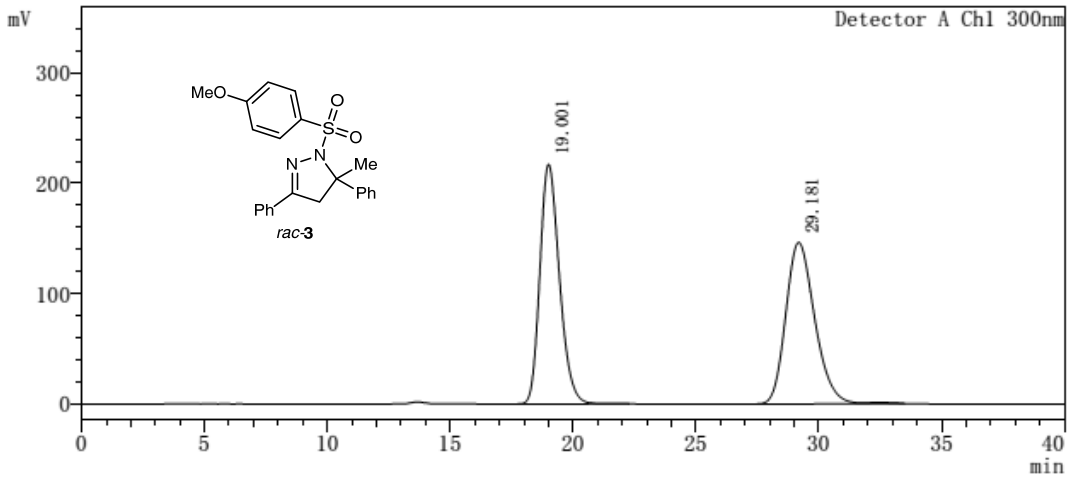
Peak#	Ret. Time	Area	Area%
1	16.826	13602864	50.074
2	25.317	13562902	49.926



Peak Table

Detector A Ch1 300nm

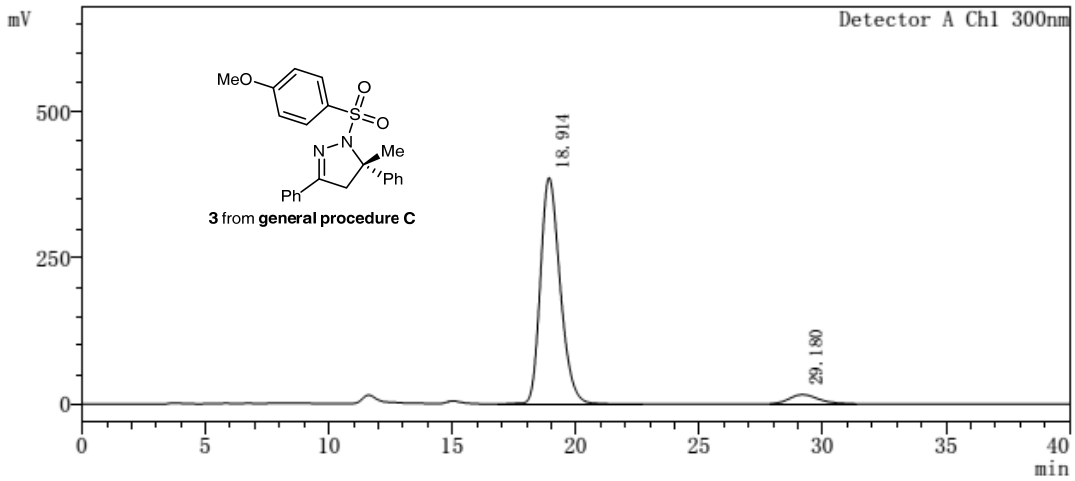
Peak#	Ret. Time	Area	Area%
1	16.836	20557256	95.933
2	25.435	871536	4.067



Peak Table

Detector A Ch1 300nm

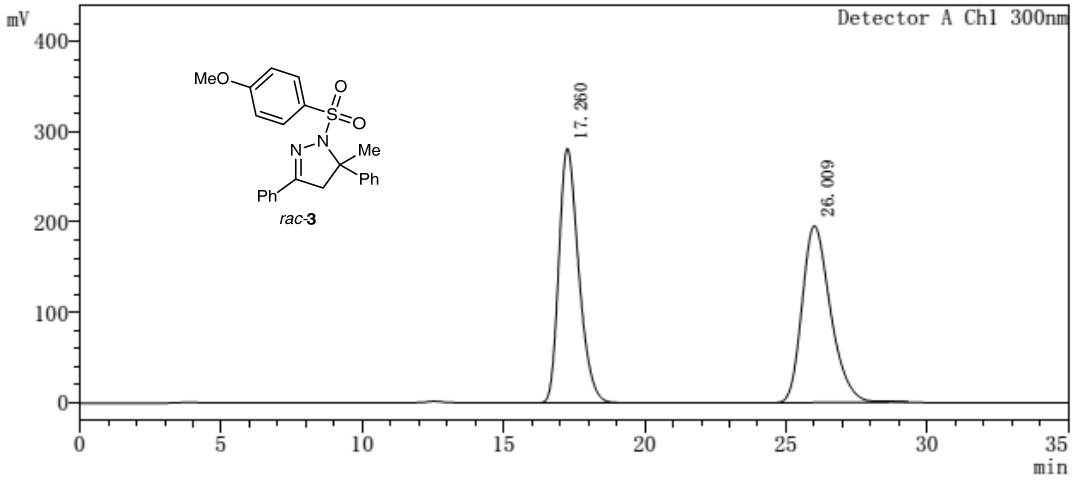
Peak#	Ret. Time	Area	Area%
1	19.001	12038831	50.005
2	29.181	12036255	49.995



Peak Table

Detector A Ch1 300nm

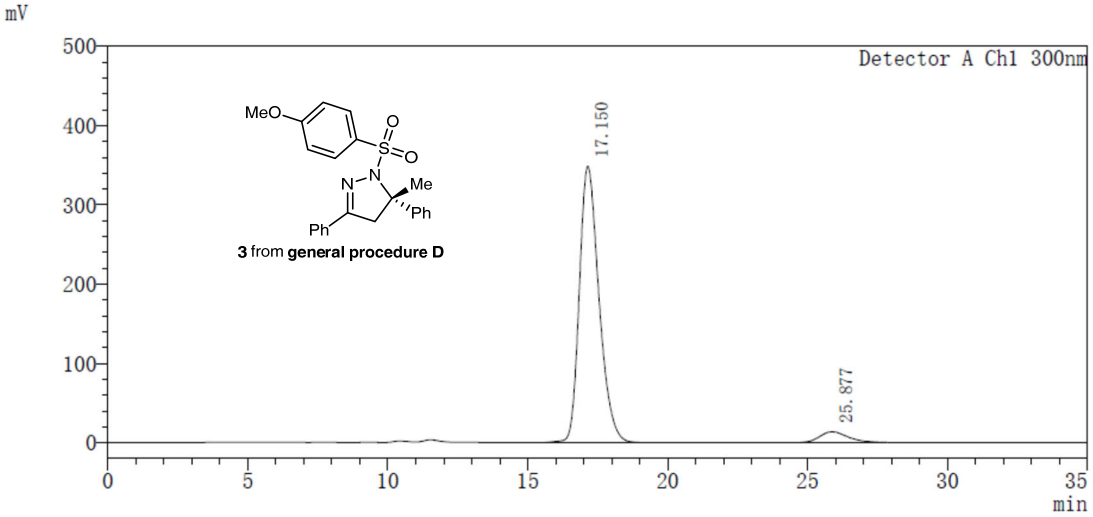
Peak#	Ret. Time	Area	Area%
1	18.914	21547698	94.425
2	29.180	1272192	5.575



Peak Table

Detector A Ch1 300nm

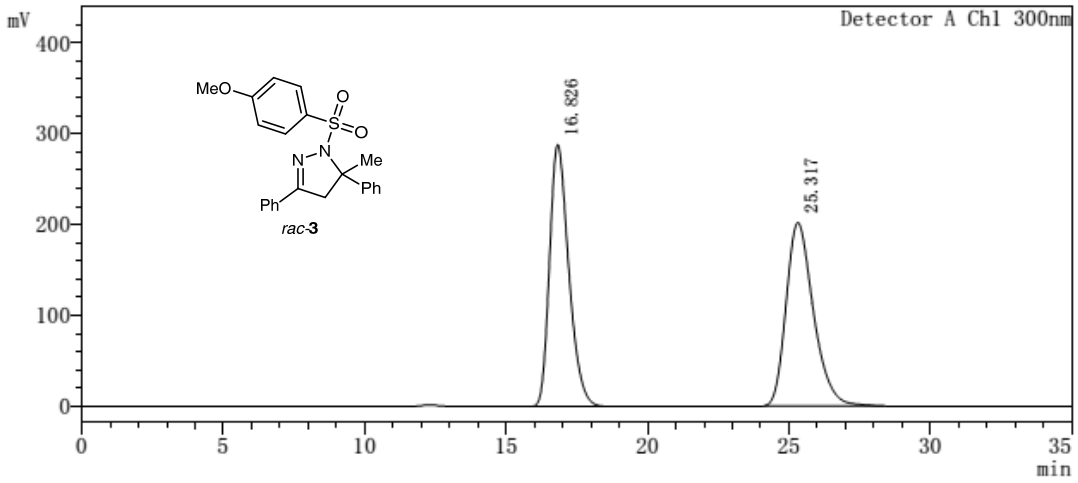
Peak#	Ret. Time	Area	Area%
1	17.260	13755210	50.008
2	26.009	13750923	49.992



Peak Table

Detector A Ch1 300nm

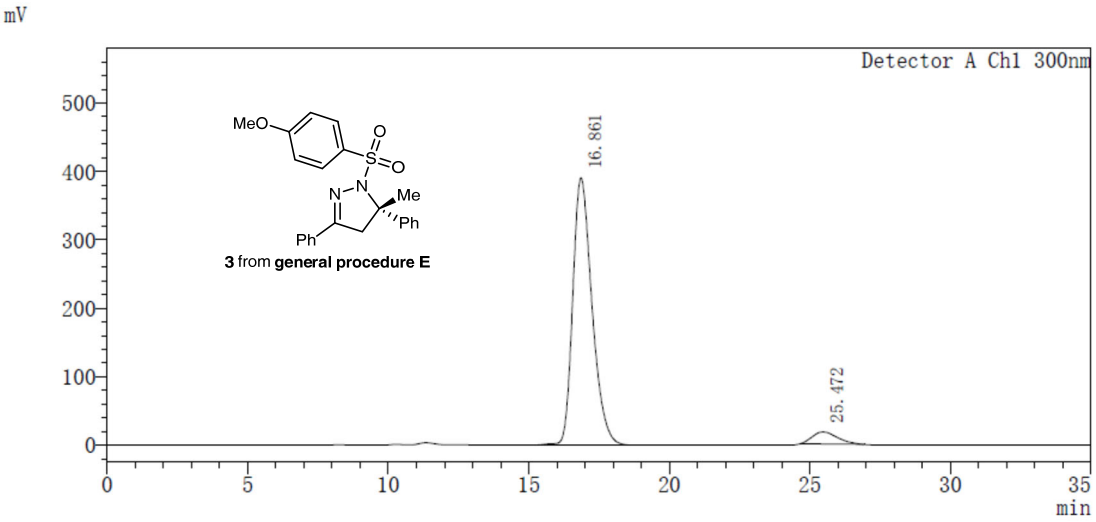
Peak#	Ret. Time	Area	Area%
1	17.150	17015859	94.822
2	25.877	929105	5.178



Peak Table

Detector A Ch1 300nm

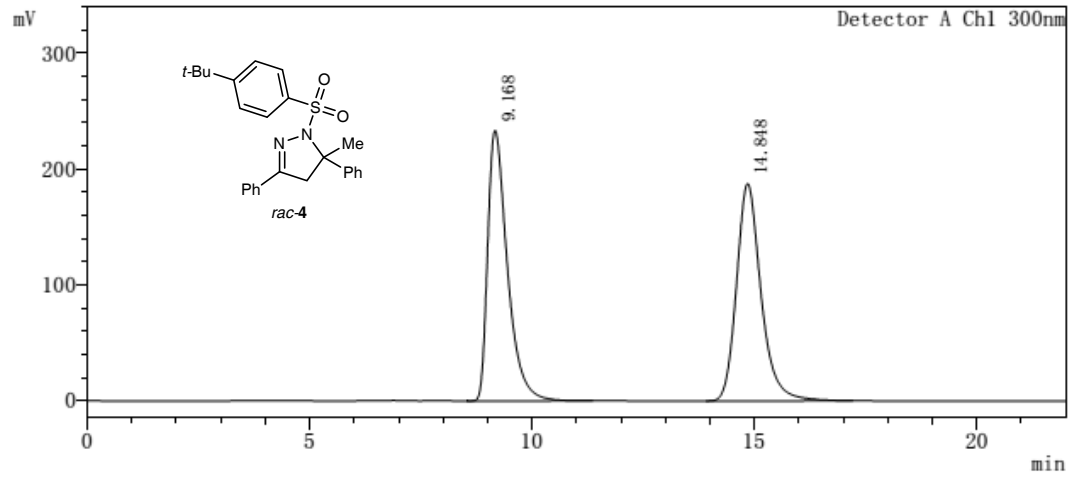
Peak#	Ret. Time	Area	Area%
1	16.826	13602864	50.074
2	25.317	13562902	49.926



Peak Table

Detector A Ch1 300nm

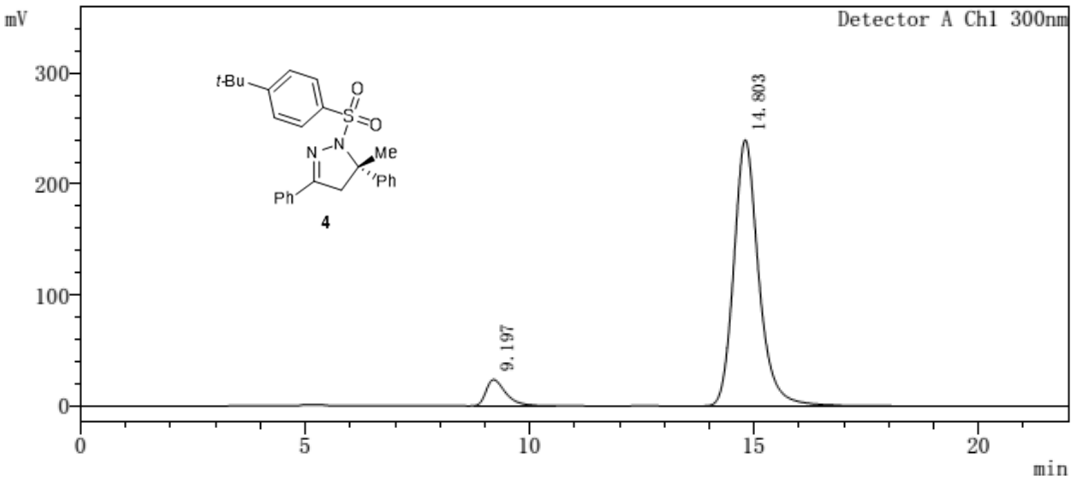
Peak#	Ret. Time	Area	Area%
1	16.861	18585045	94.428
2	25.472	1096663	5.572



Peak Table

Detector A Ch1 300nm

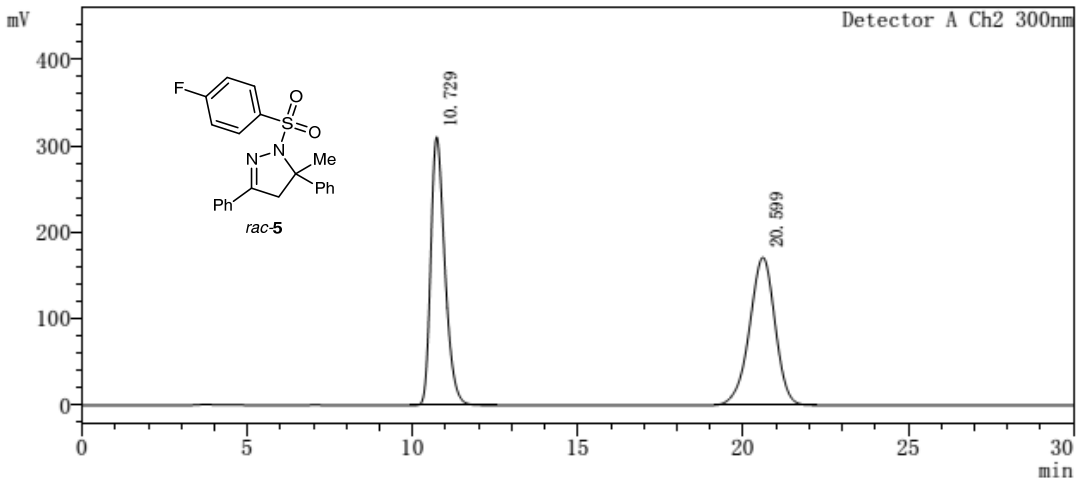
Peak#	Ret. Time	Area	Area%
1	9.168	7192282	49.972
2	14.848	7200207	50.028



Peak Table

Detector A Ch1 300nm

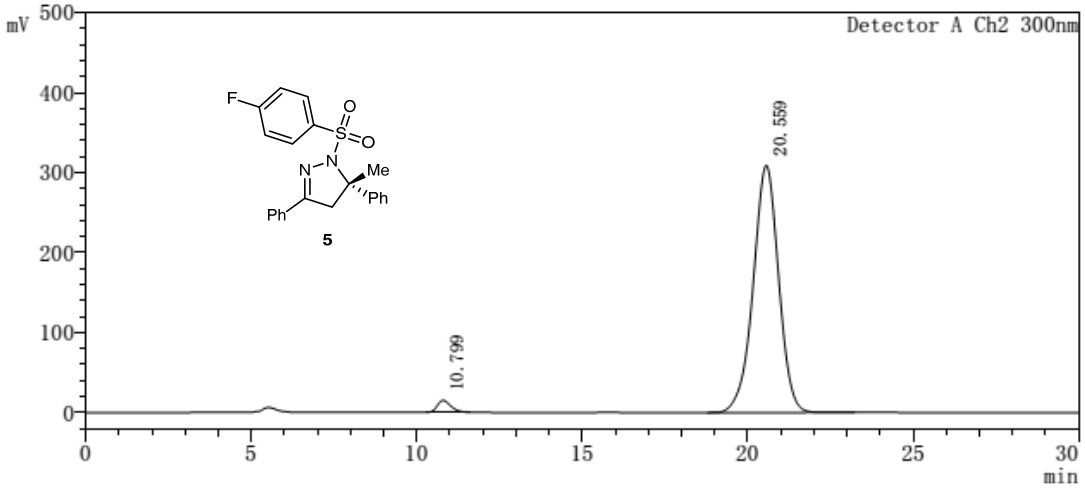
Peak#	Ret. Time	Area	Area%
1	9.197	714416	7.162
2	14.803	9261044	92.838



Peak Table

Detector A Ch2 300nm

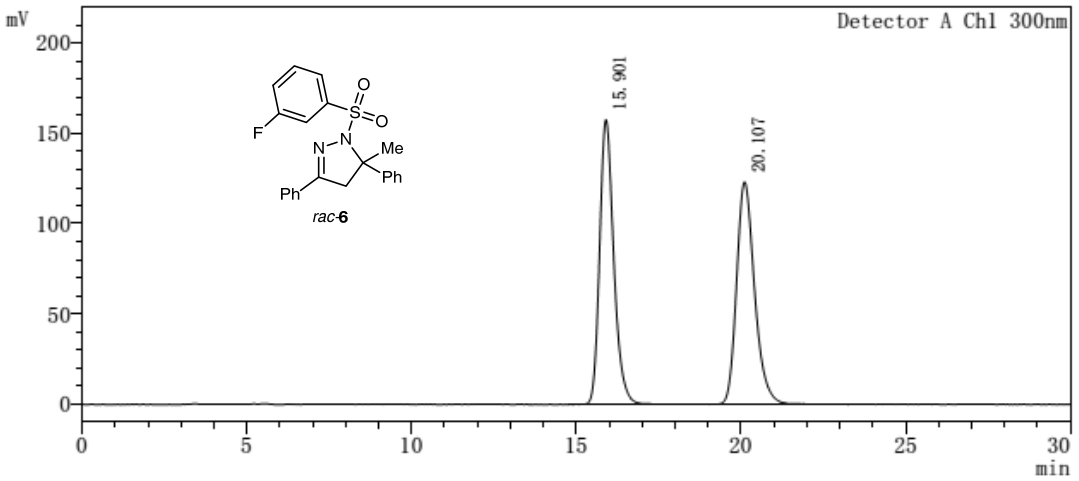
Peak#	Ret. Time	Area	Area%
1	10.729	9227800	49.991
2	20.599	9230941	50.009



Peak Table

Detector A Ch2 300nm

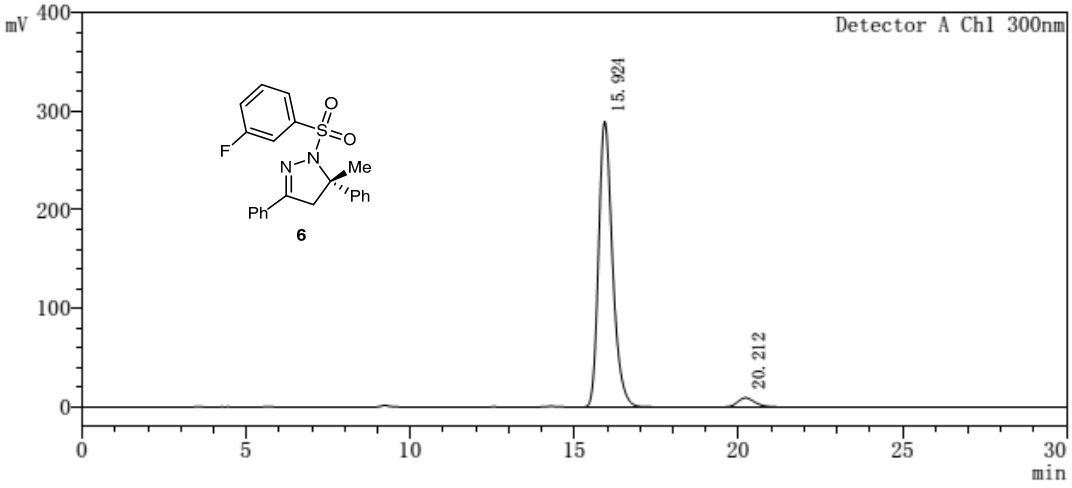
Peak#	Ret. Time	Area	Area%
1	10.799	429502	2.528
2	20.559	16559012	97.472



Peak Table

Detector A Ch1 300nm

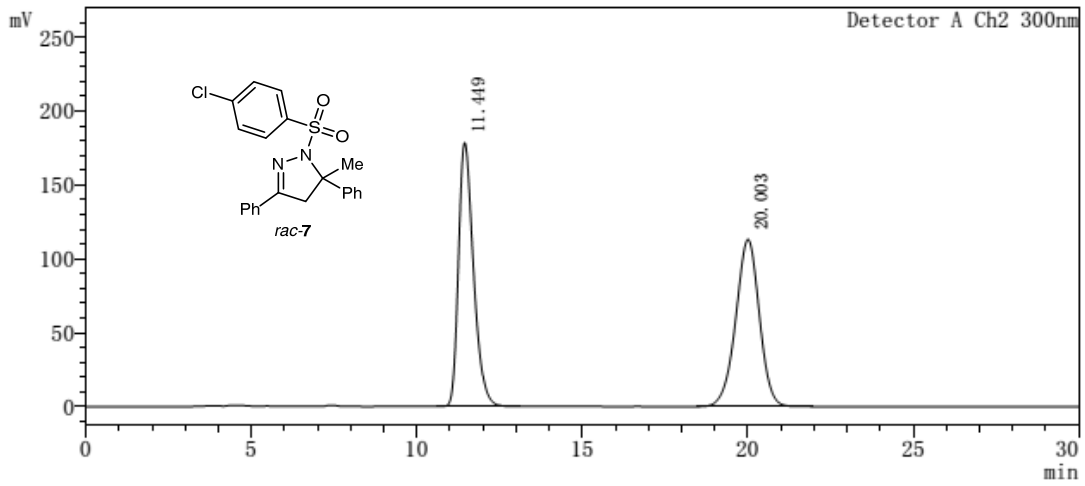
Peak#	Ret. Time	Area	Area%
1	15.901	4692427	50.005
2	20.107	4691561	49.995



Peak Table

Detector A Ch1 300nm

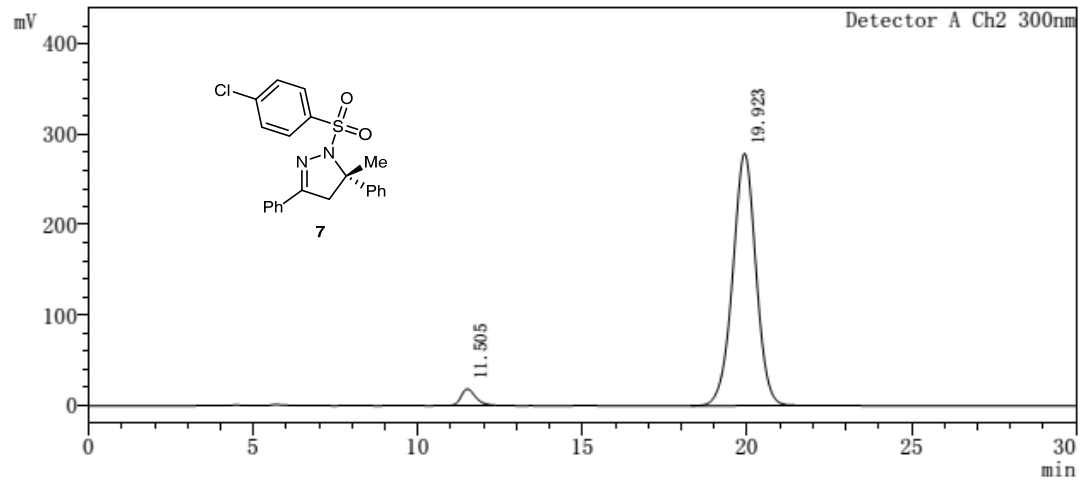
Peak#	Ret. Time	Area	Area%
1	15.924	8558385	95.907
2	20.212	365282	4.093



Peak Table

Detector A Ch2 300nm

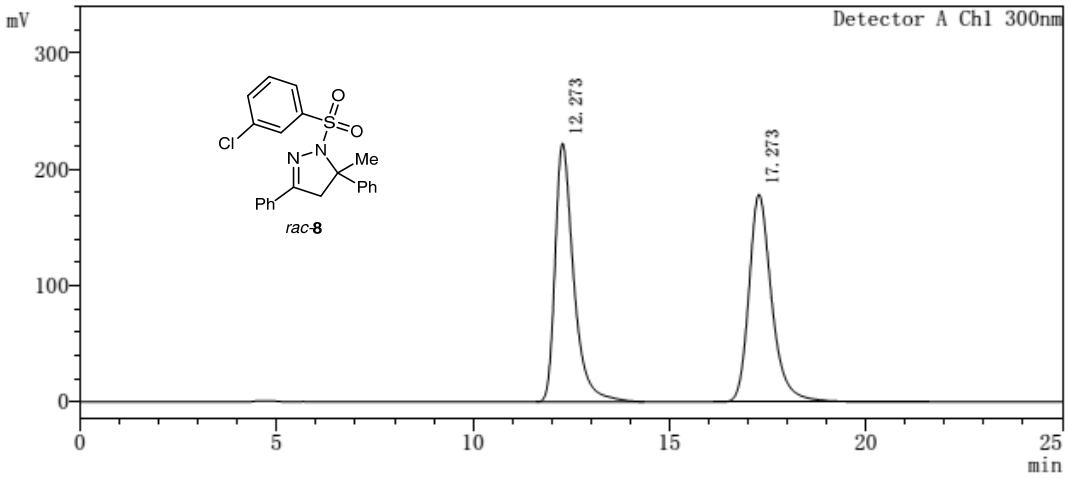
Peak#	Ret. Time	Area	Area%
1	11.449	5631984	49.988
2	20.003	5634790	50.012



Peak Table

Detector A Ch2 300nm

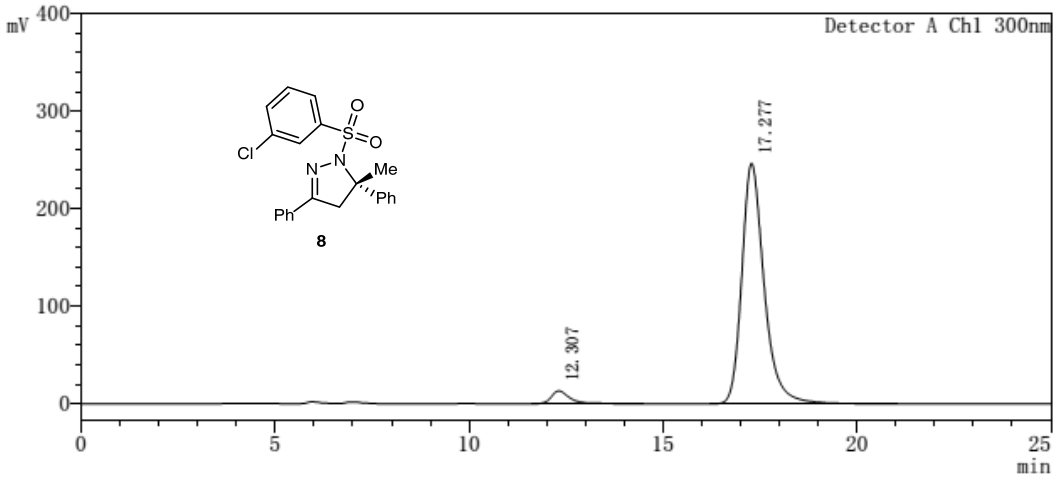
Peak#	Ret. Time	Area	Area%
1	11.505	544483	3.823
2	19.923	13697904	96.177



Peak Table

Detector A Ch1 300nm

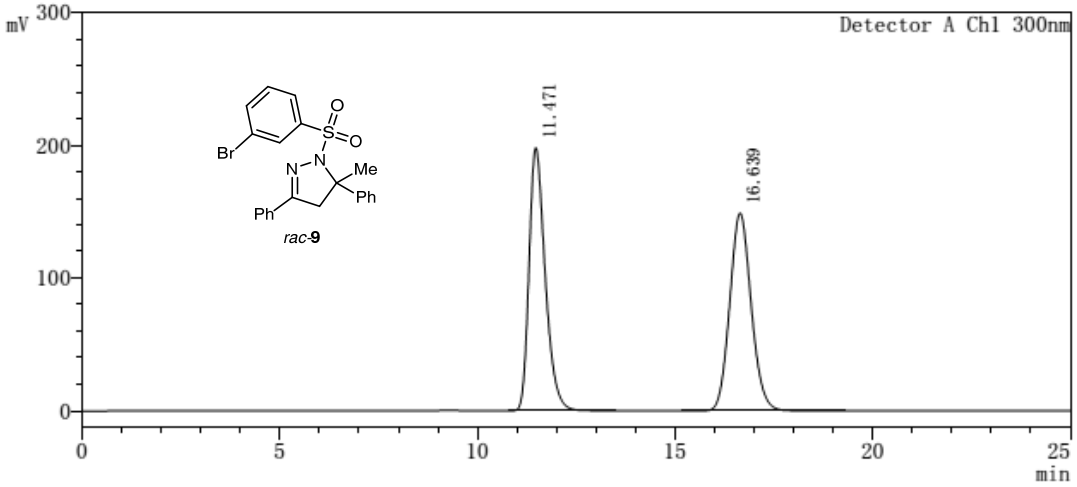
Peak#	Ret. Time	Area	Area%
1	12.273	7307118	50.280
2	17.273	7225733	49.720



Peak Table

Detector A Ch1 300nm

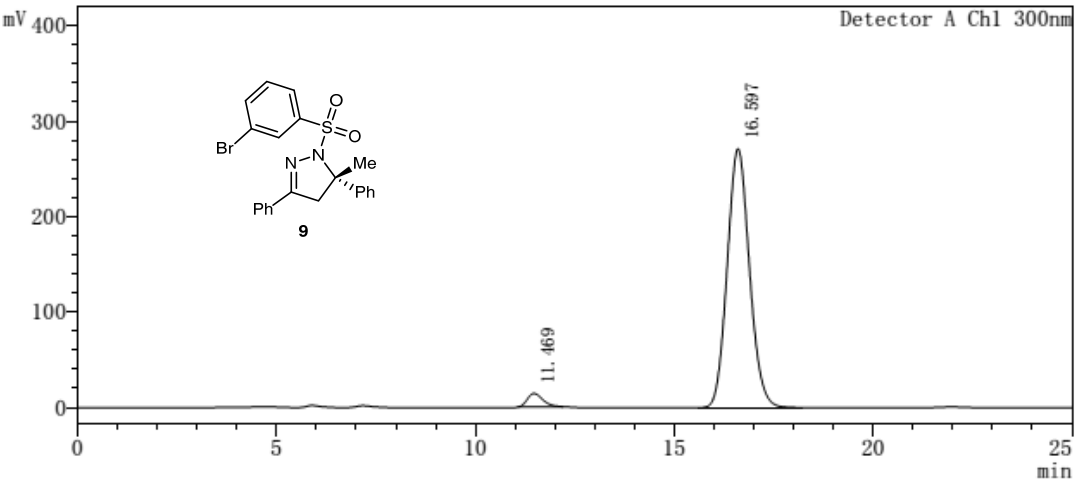
Peak#	Ret. Time	Area	Area%
1	12.307	436230	4.225
2	17.277	9887648	95.775



Peak Table

Detector A Ch1 300nm

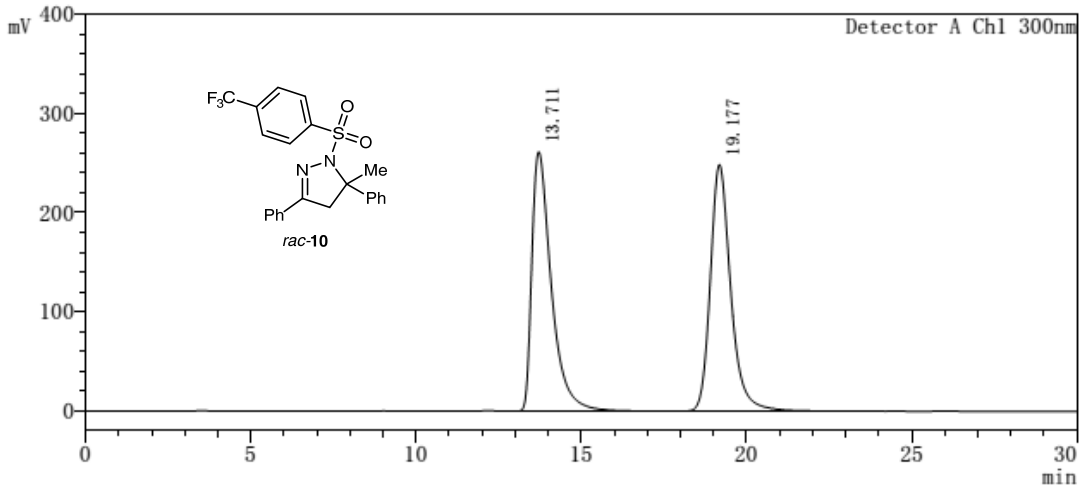
Peak#	Ret. Time	Area	Area%
1	11.471	5641928	50.031
2	16.639	5634852	49.969



Peak Table

Detector A Ch1 300nm

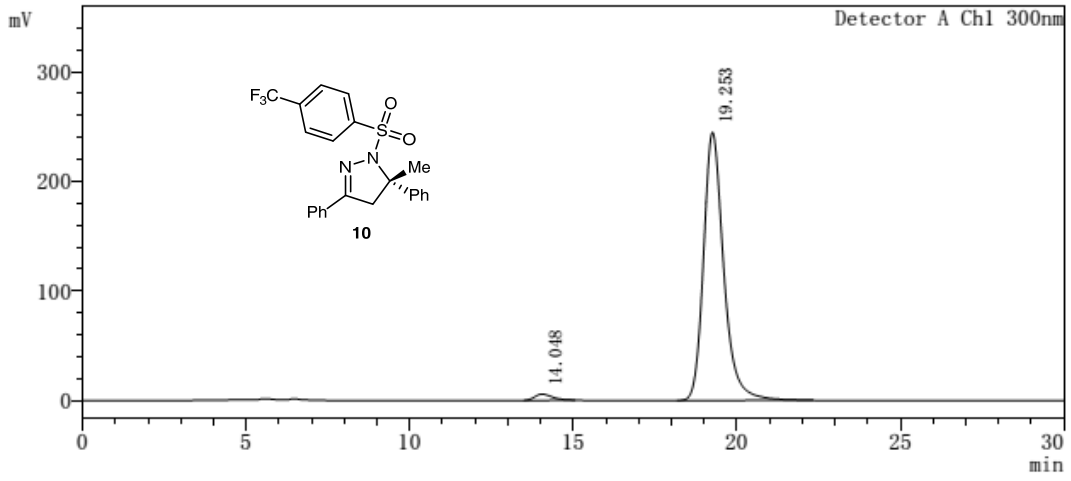
Peak#	Ret. Time	Area	Area%
1	11.469	384892	3.524
2	16.597	10538157	96.476



Peak Table

Detector A Ch1 300nm

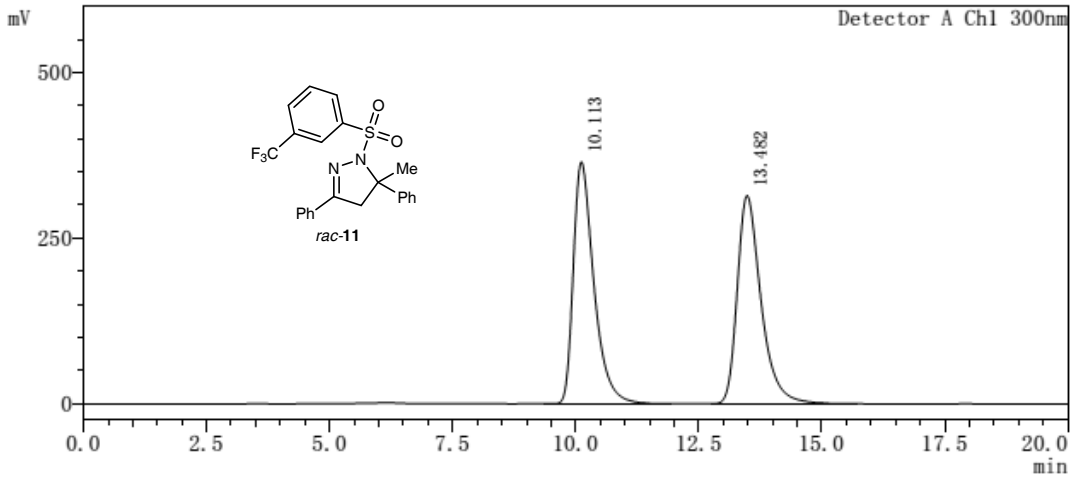
Peak#	Ret. Time	Area	Area%
1	13.711	10710393	50.058
2	19.177	10685458	49.942



Peak Table

Detector A Ch1 300nm

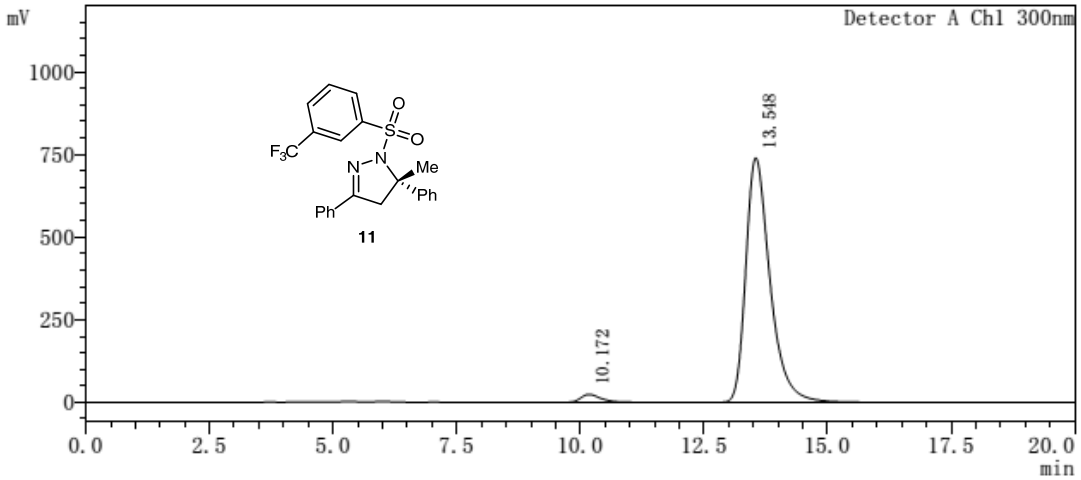
Peak#	Ret. Time	Area	Area%
1	14.048	210913	1.965
2	19.253	10520209	98.035



Peak Table

Detector A Ch1 300nm

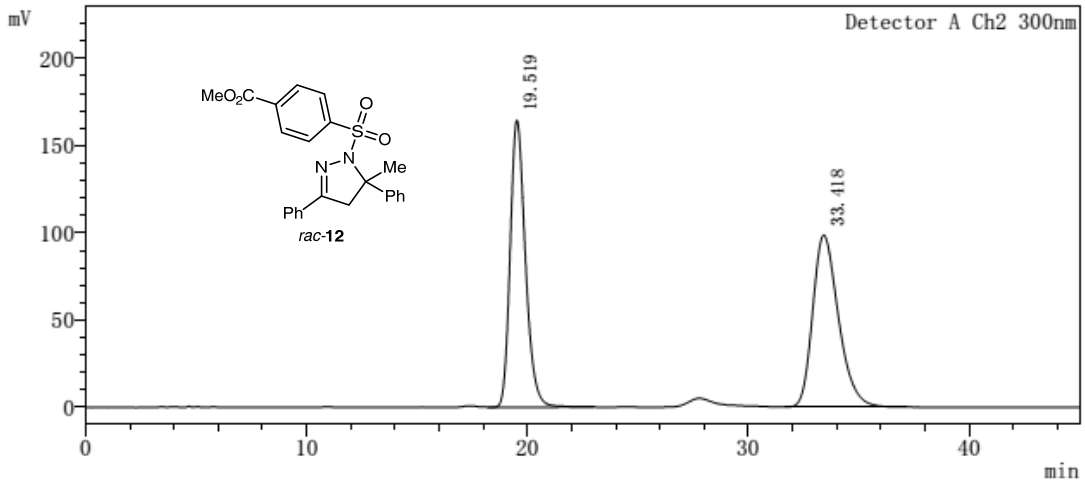
Peak#	Ret. Time	Area	Area%
1	10.113	10576512	49.980
2	13.482	10584865	50.020



Peak Table

Detector A Ch1 300nm

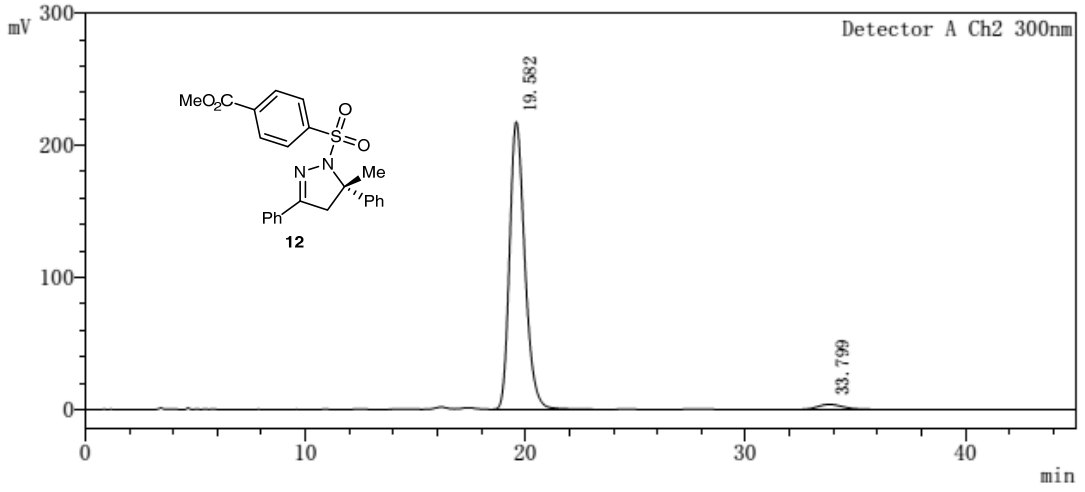
Peak#	Ret. Time	Area	Area%
1	10.172	668093	2.571
2	13.548	25319530	97.429



Peak Table

Detector A Ch2 300nm

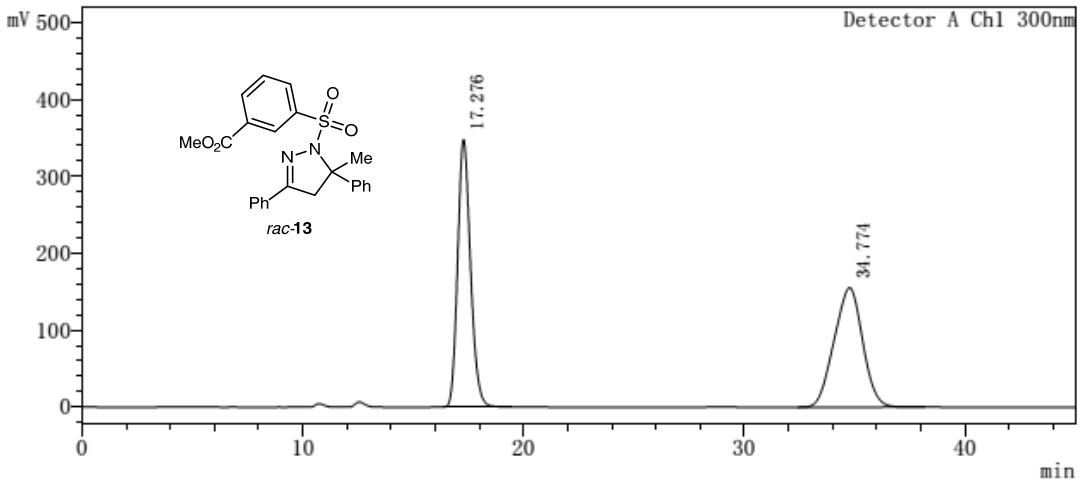
Peak#	Ret. Time	Area	Area%
1	19.519	7895170	49.672
2	33.418	7999517	50.328



Peak Table

Detector A Ch2 300nm

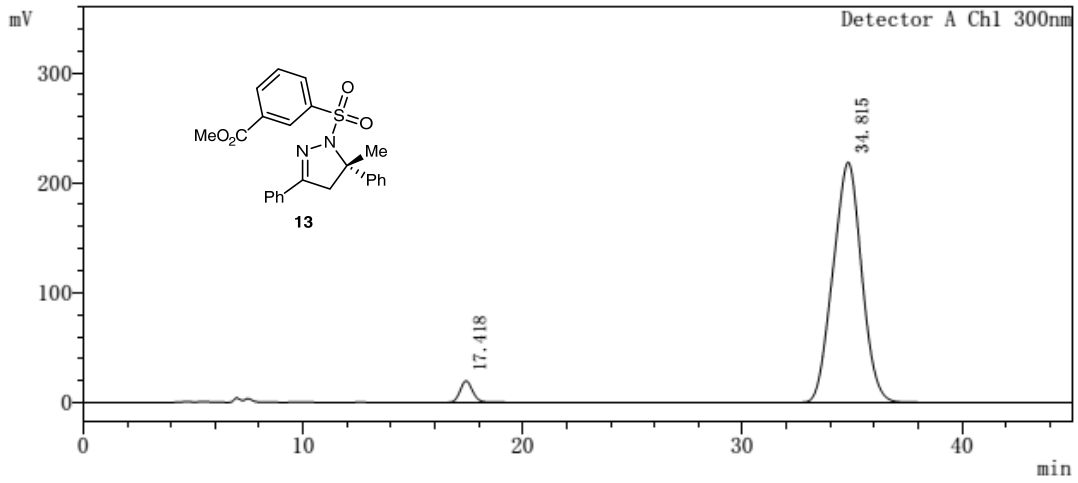
Peak#	Ret. Time	Area	Area%
1	19.582	10506920	96.888
2	33.799	337523	3.112



Peak Table

Detector A Ch1 300nm

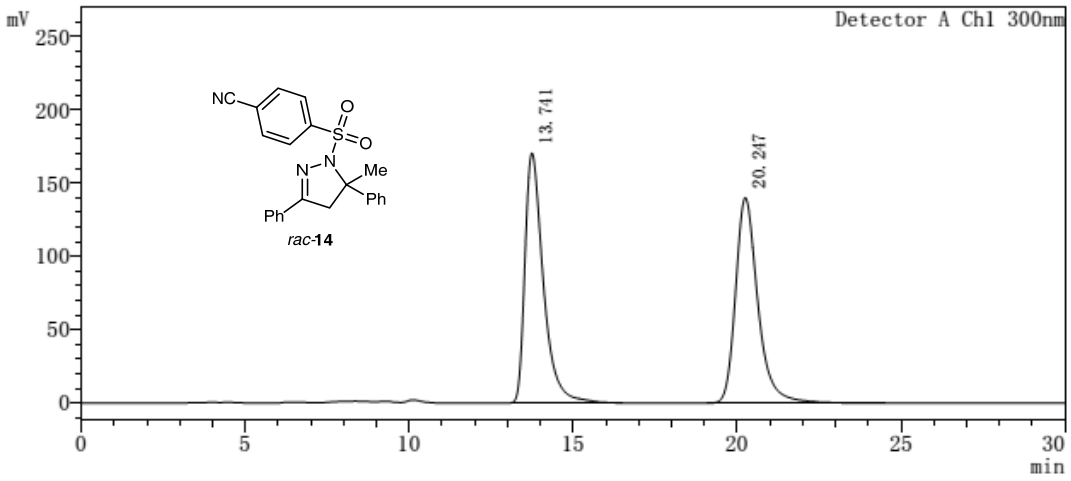
Peak#	Ret. Time	Area	Area%
1	17.276	14128548	50.179
2	34.774	14027778	49.821



Peak Table

Detector A Ch1 300nm

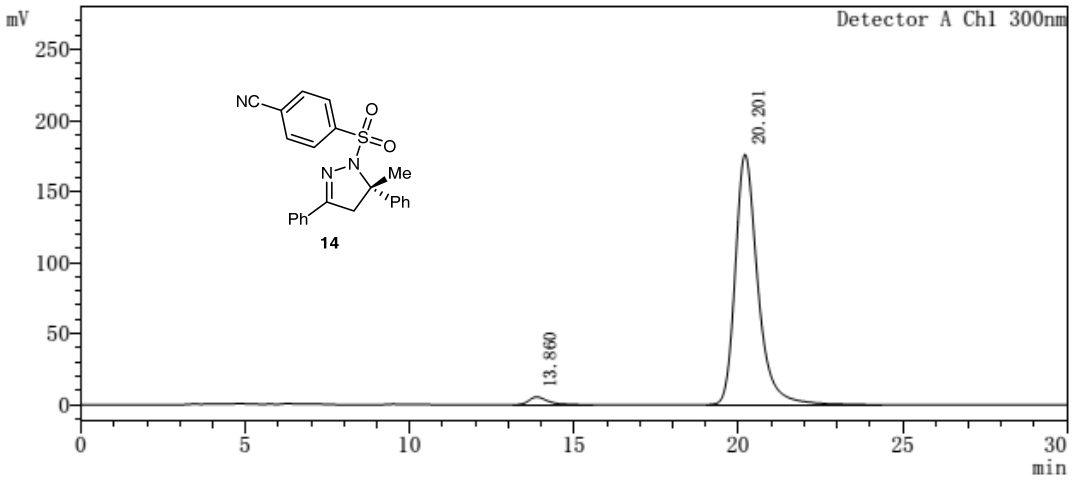
Peak#	Ret. Time	Area	Area%
1	17.418	817330	3.956
2	34.815	19842768	96.044



Peak Table

Detector A Ch1 300nm

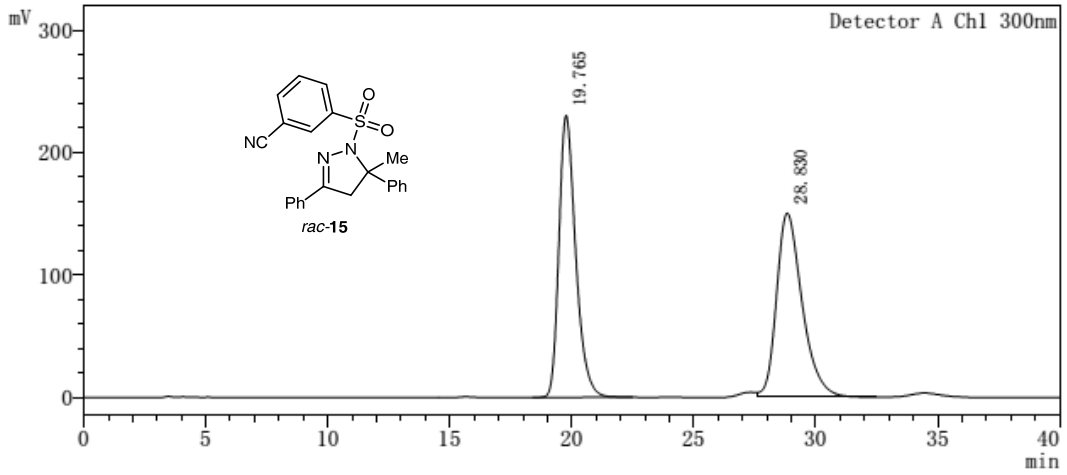
Peak#	Ret. Time	Area	Area%
1	13.741	6662588	50.004
2	20.247	6661530	49.996



Peak Table

Detector A Ch1 300nm

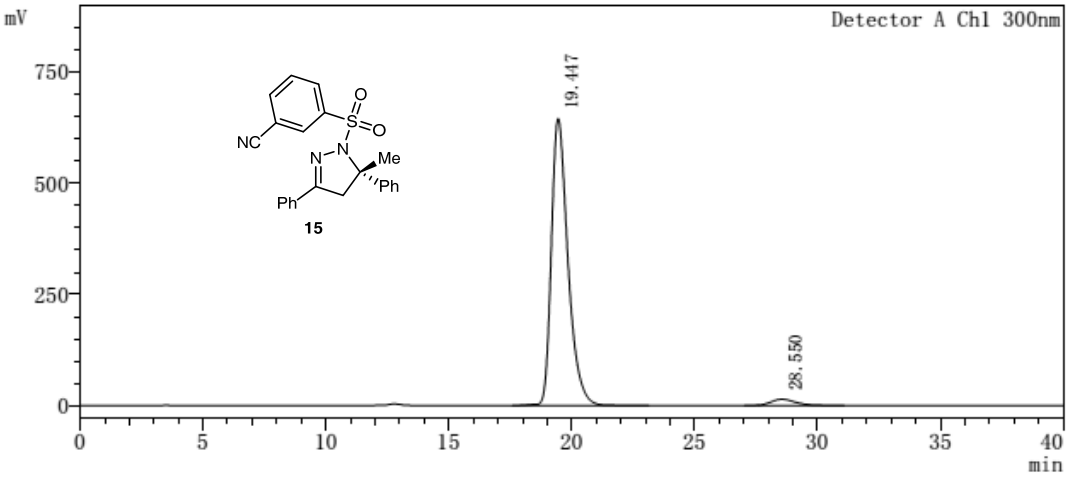
Peak#	Ret. Time	Area	Area%
1	13.860	208493	2.433
2	20.201	8362493	97.567



Peak Table

Detector A Ch1 300nm

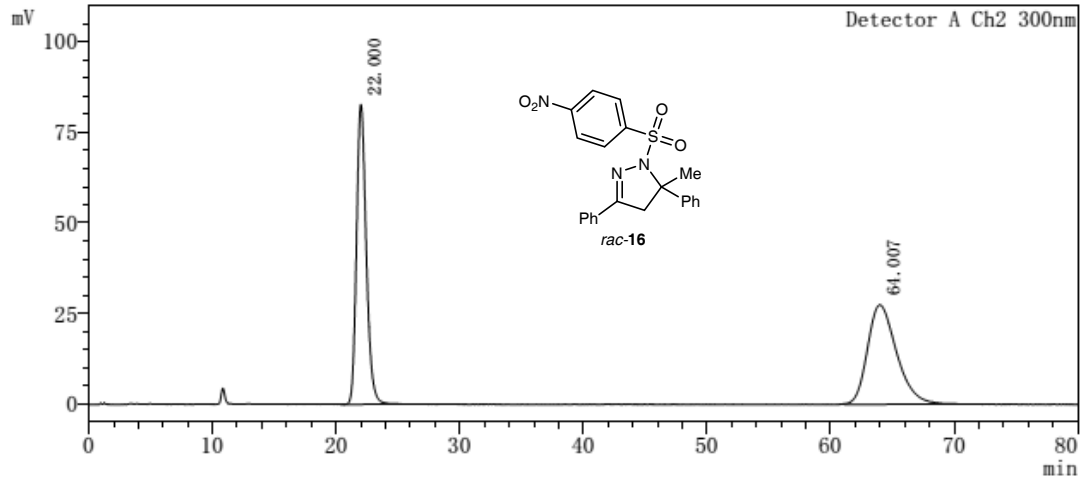
Peak#	Ret. Time	Area	Area%
1	19.765	10968525	49.874
2	28.830	11023815	50.126



Peak Table

Detector A Ch1 300nm

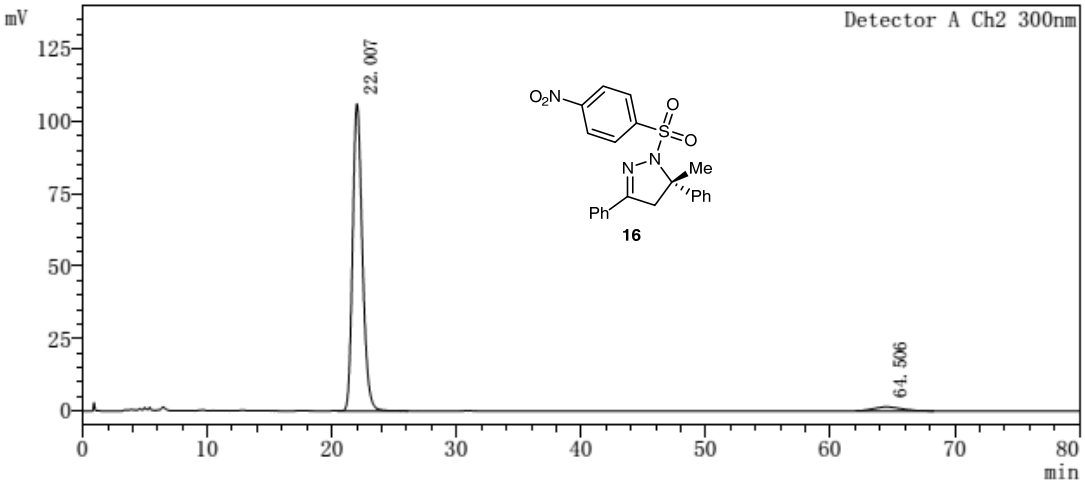
Peak#	Ret. Time	Area	Area%
1	19.447	30368632	96.656
2	28.550	1050566	3.344



Peak Table

Detector A Ch2 300nm

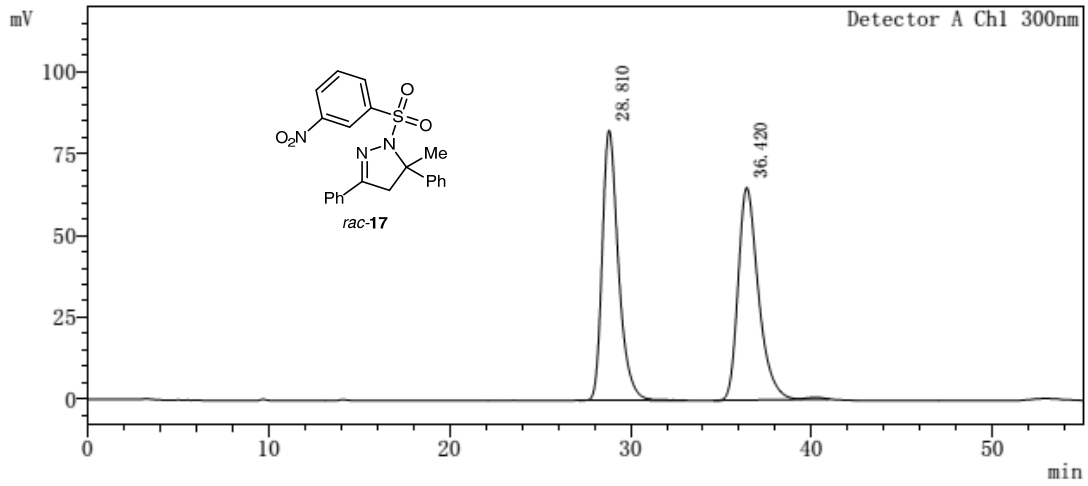
Peak#	Ret. Time	Area	Area%
1	22.000	4505843	49.998
2	64.007	4506246	50.002



Peak Table

Detector A Ch2 300nm

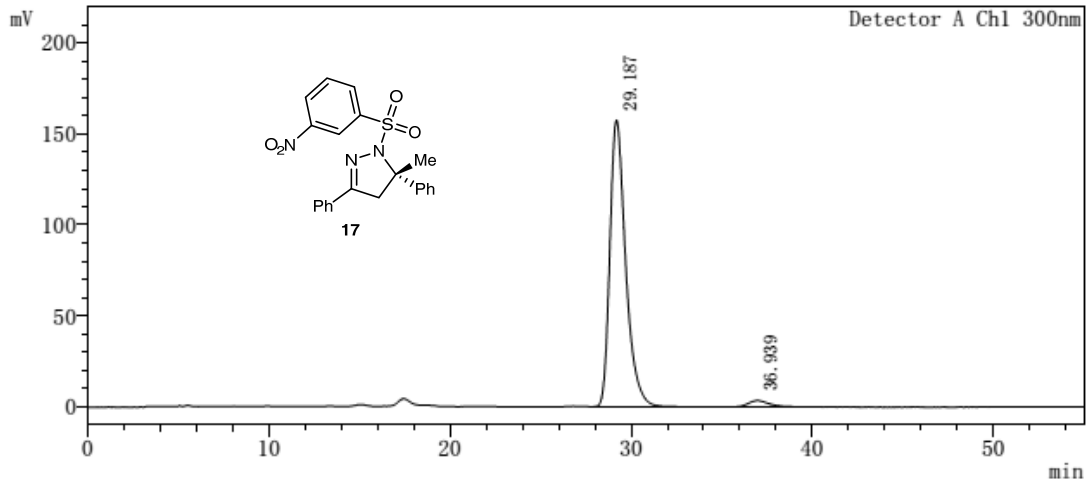
Peak#	Ret. Time	Area	Area%
1	22.007	5753983	96.412
2	64.506	214144	3.588



Peak Table

Detector A Ch1 300nm

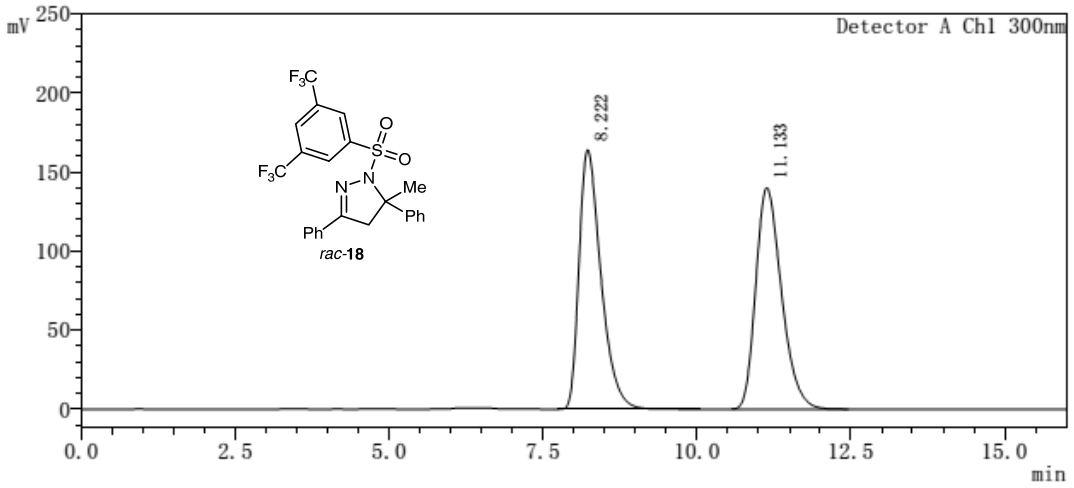
Peak#	Ret. Time	Area	Area%
1	28.810	5123523	50.100
2	36.420	5103088	49.900



Peak Table

Detector A Ch1 300nm

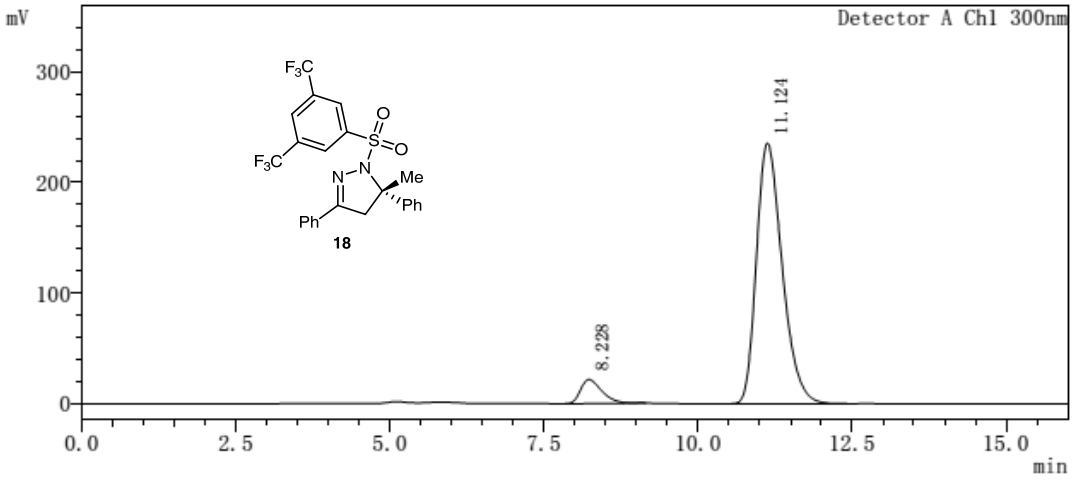
Peak#	Ret. Time	Area	Area%
1	29.187	9560963	97.198
2	36.939	275584	2.802



Peak Table

Detector A Ch1 300nm

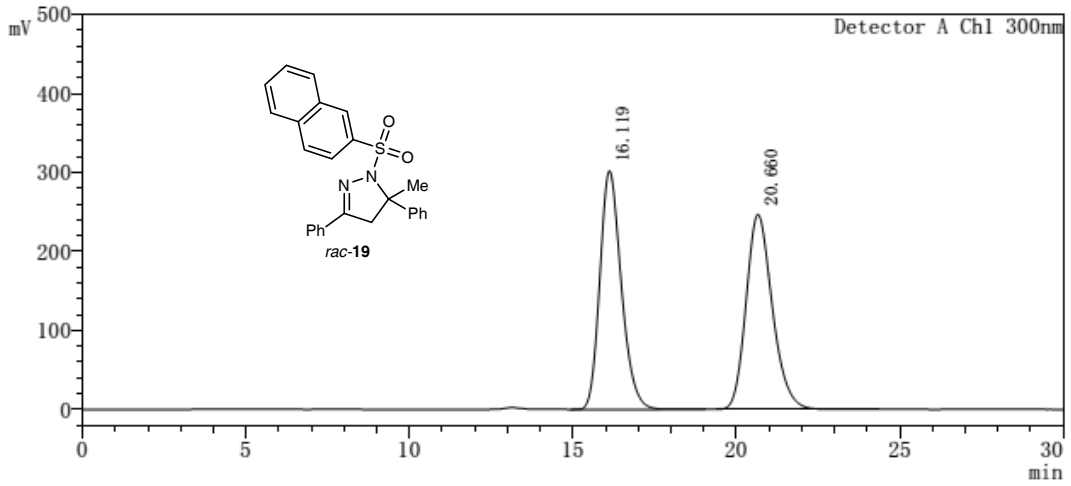
Peak#	Ret. Time	Area	Area%
1	8.222	4069602	49.885
2	11.133	4088349	50.115



Peak Table

Detector A Ch1 300nm

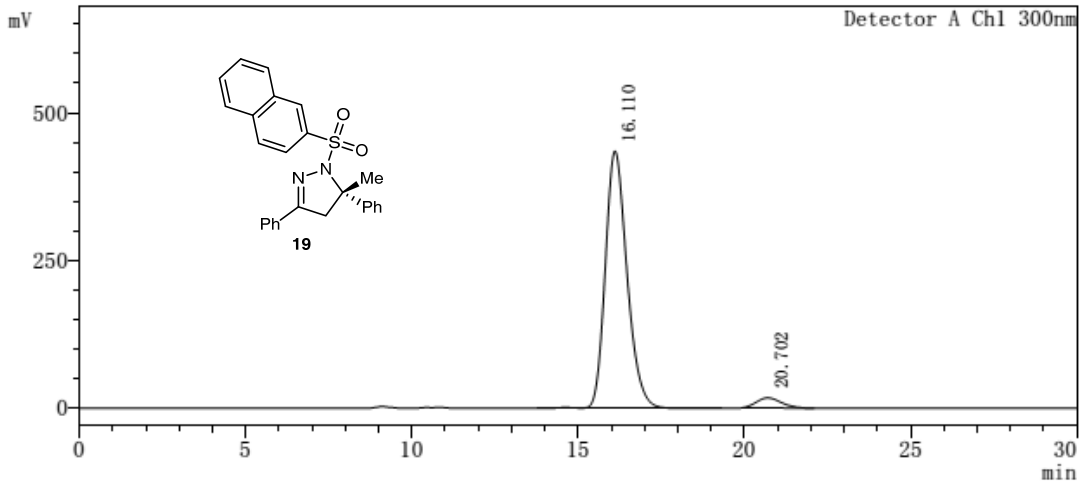
Peak#	Ret. Time	Area	Area%
1	8.228	516764	7.015
2	11.124	6850271	92.985



Peak Table

Detector A Ch1 300nm

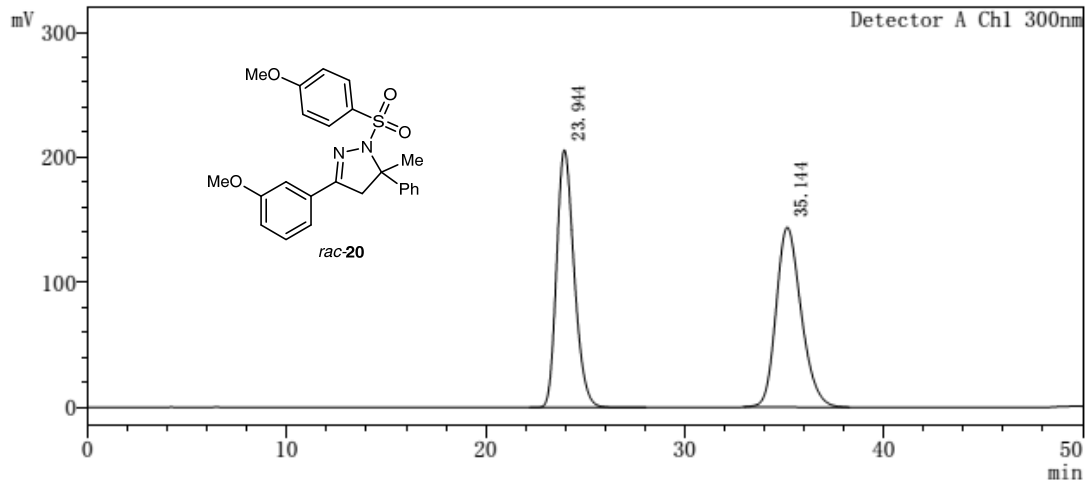
Peak#	Ret. Time	Area	Area%
1	16.119	13816697	50.002
2	20.660	13815496	49.998



Peak Table

Detector A Ch1 300nm

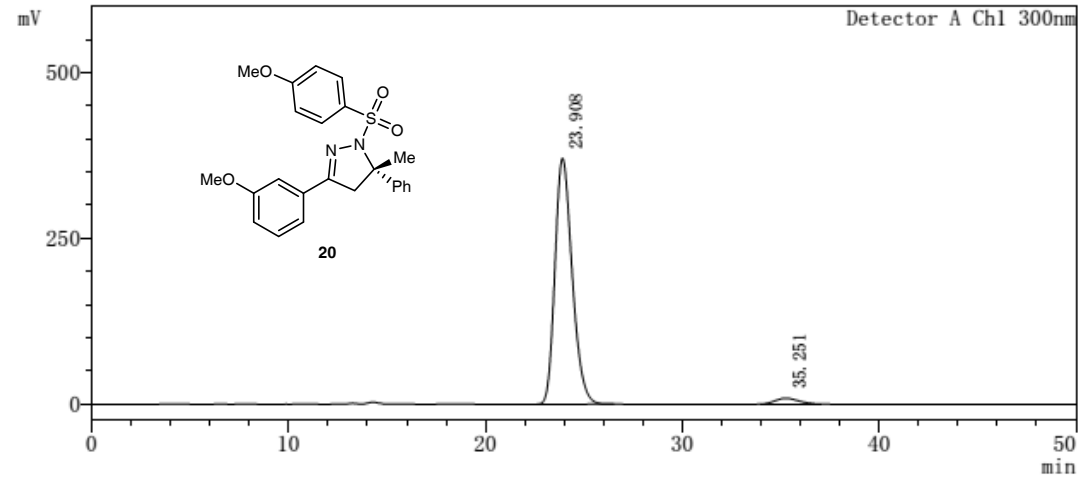
Peak#	Ret. Time	Area	Area%
1	16.110	19867808	95.755
2	20.702	880769	4.245



Peak Table

Detector A Ch1 300nm

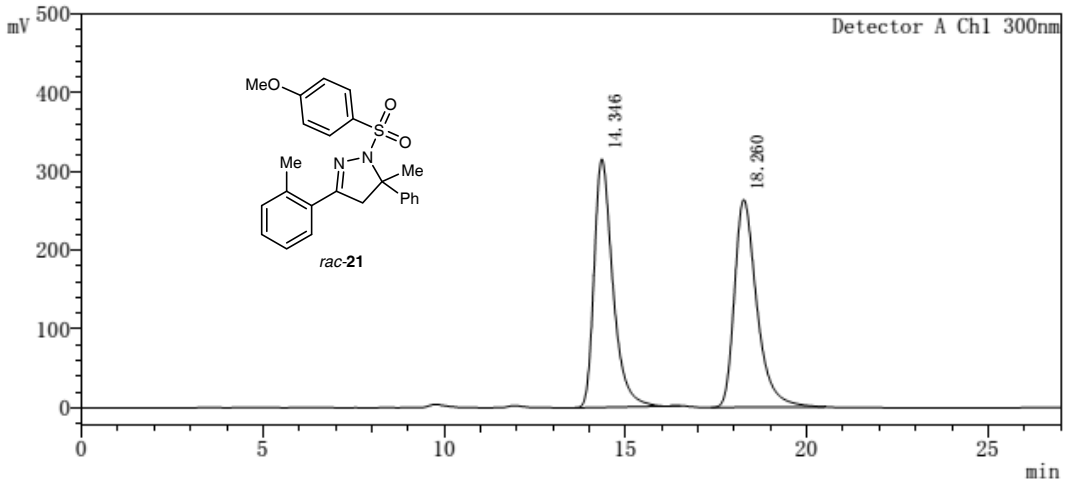
Peak#	Ret. Time	Area	Area%
1	23.944	12612629	49.982
2	35.144	12621885	50.018



Peak Table

Detector A Ch1 300nm

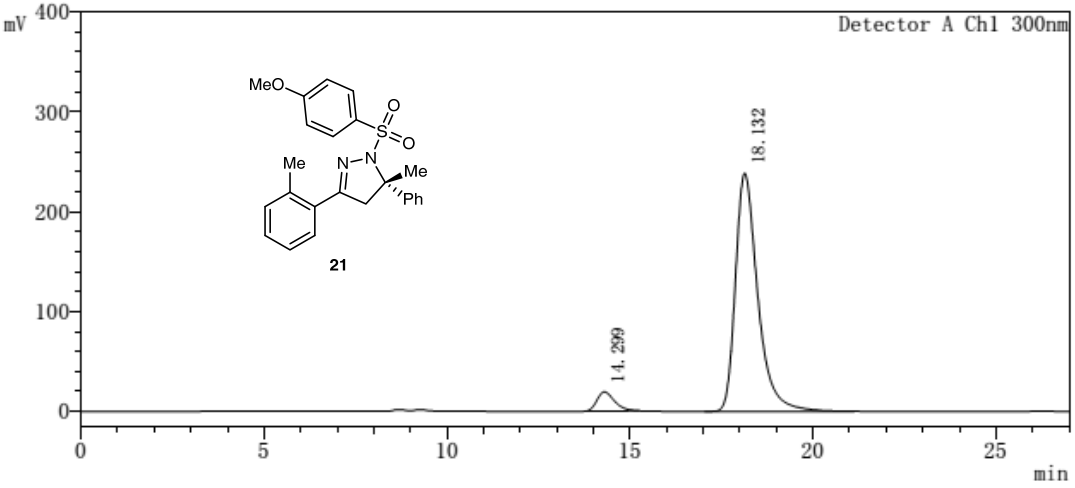
Peak#	Ret. Time	Area	Area%
1	23.908	22554770	96.946
2	35.251	710604	3.054



Peak Table

Detector A Ch1 300nm

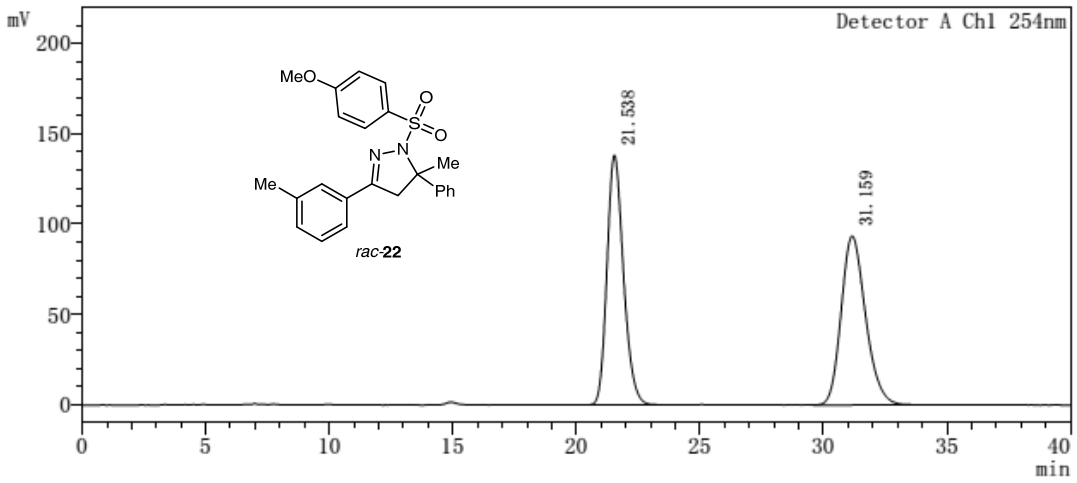
Peak#	Ret. Time	Area	Area%
1	14.346	11318632	49.917
2	18.260	11356314	50.083



Peak Table

Detector A Ch1 300nm

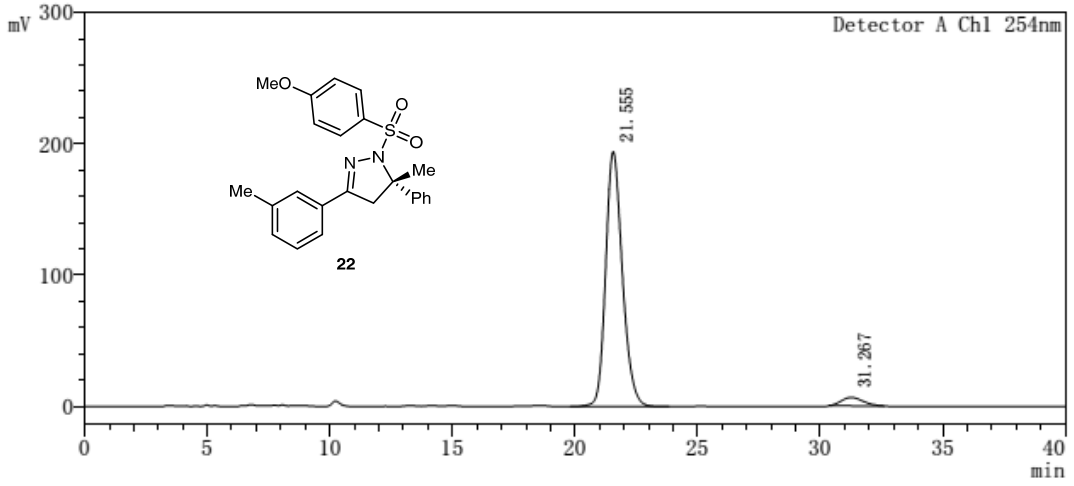
Peak#	Ret. Time	Area	Area%
1	14.299	649324	6.008
2	18.132	10157470	93.992



Peak Table

Detector A Ch1 254nm

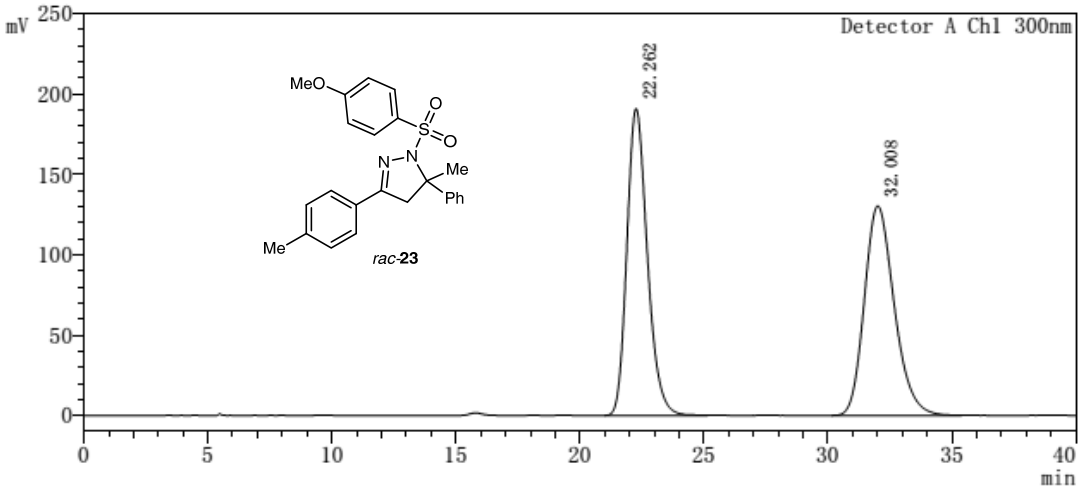
Peak#	Ret. Time	Area	Area%
1	21.538	6421011	49.958
2	31.159	6431858	50.042



Peak Table

Detector A Ch1 254nm

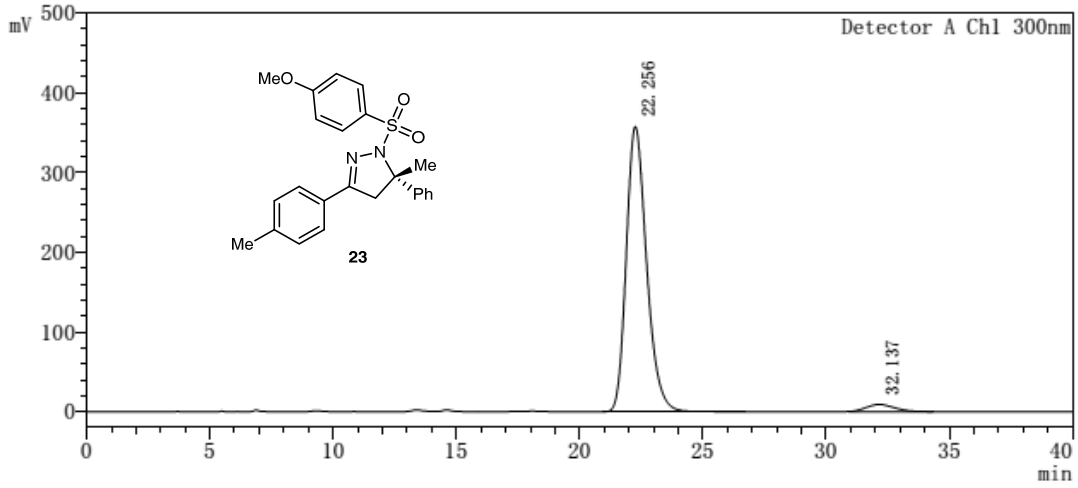
Peak#	Ret. Time	Area	Area%
1	21.555	9206797	95.904
2	31.267	393264	4.096



Peak Table

Detector A Ch1 300nm

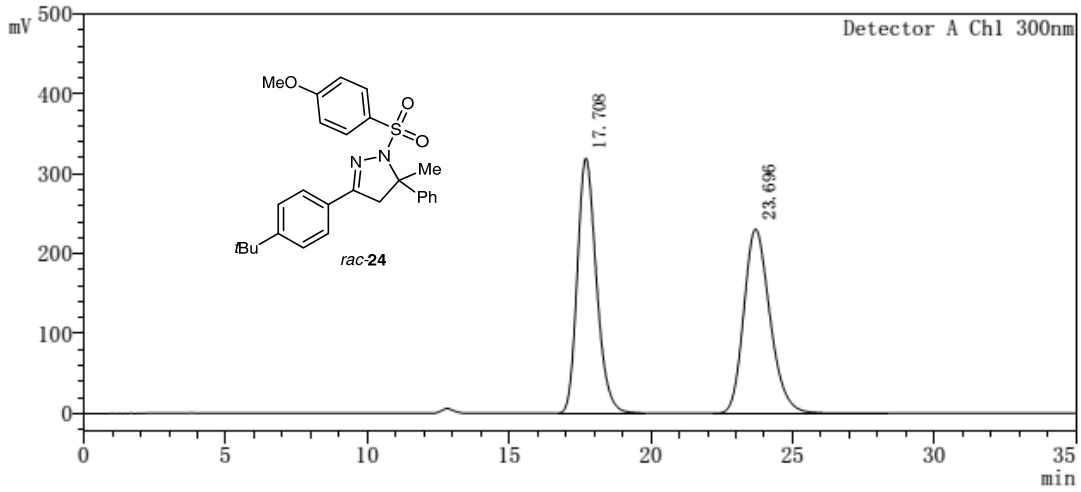
Peak#	Ret. Time	Area	Area%
1	22.262	10937410	50.040
2	32.008	10919890	49.960



Peak Table

Detector A Ch1 300nm

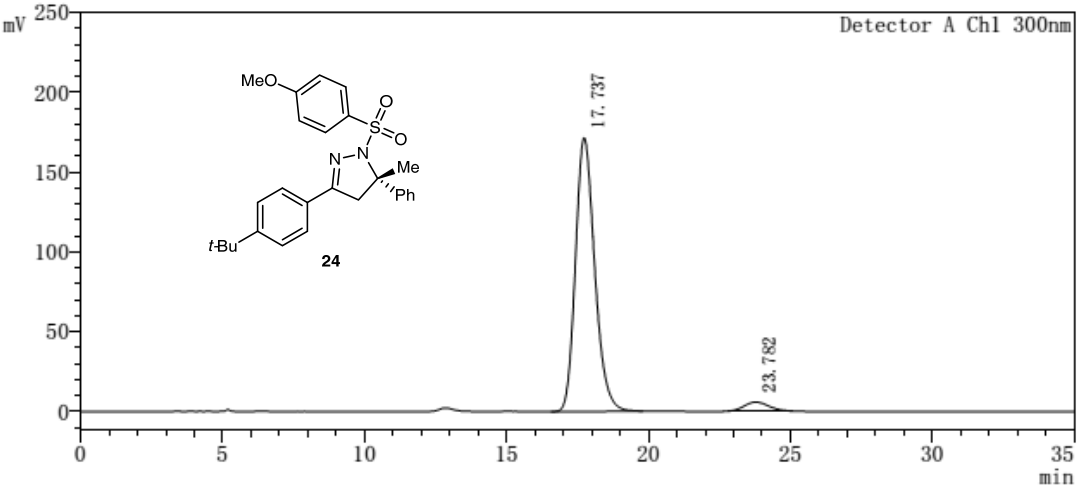
Peak#	Ret. Time	Area	Area%
1	22.256	20522604	96.600
2	32.137	722408	3.400



Peak Table

Detector A Ch1 300nm

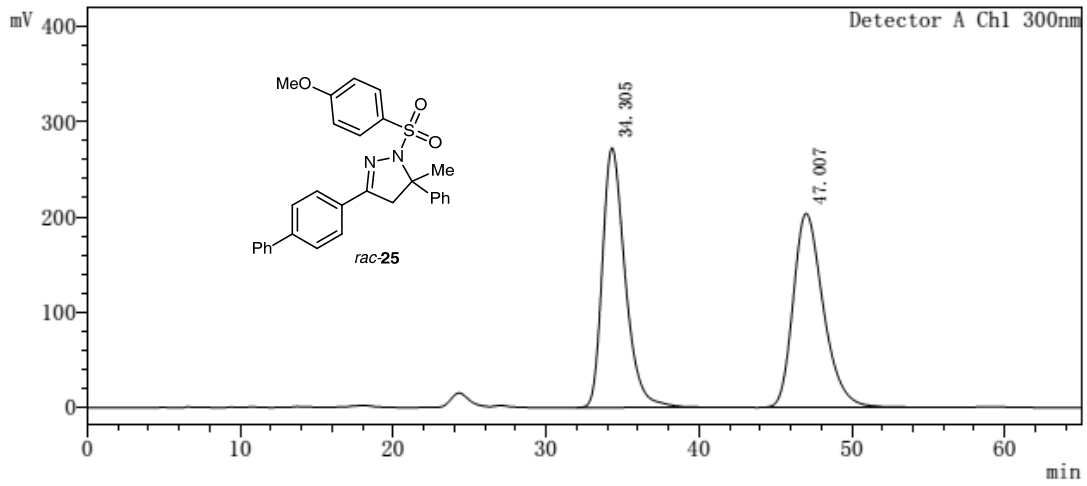
Peak#	Ret. Time	Area	Area%
1	17.708	14980376	50.153
2	23.696	14889040	49.847



Peak Table

Detector A Ch1 300nm

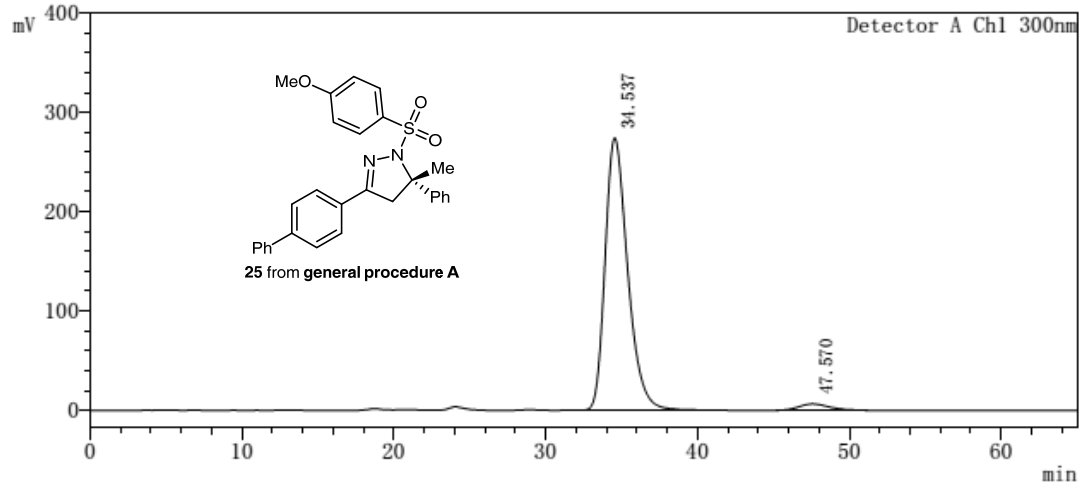
Peak#	Ret. Time	Area	Area%
1	17.737	8102321	95.905
2	23.782	345949	4.095



Peak Table

Detector A Ch1 300nm

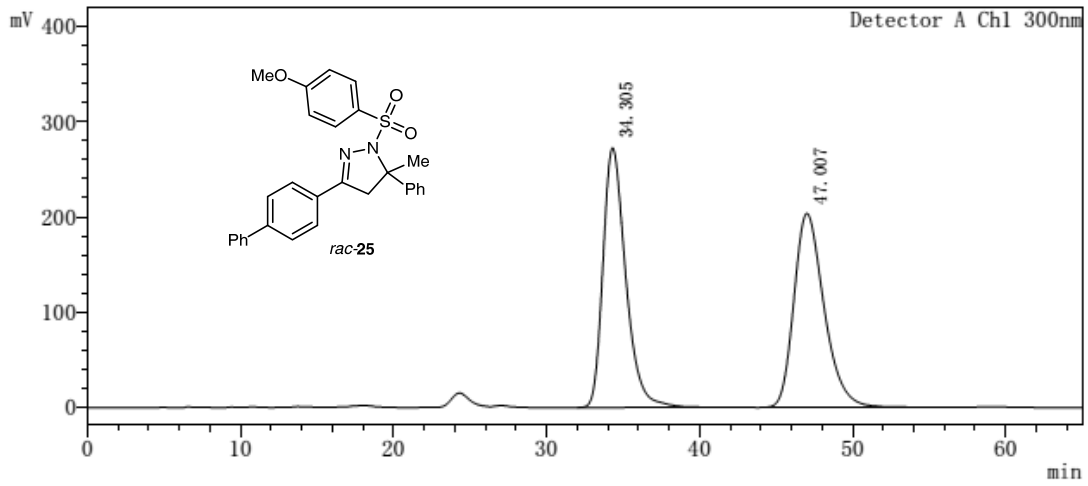
Peak#	Ret. Time	Area	Area%
1	34.305	28181971	50.232
2	47.007	27921452	49.768



Peak Table

Detector A Ch1 300nm

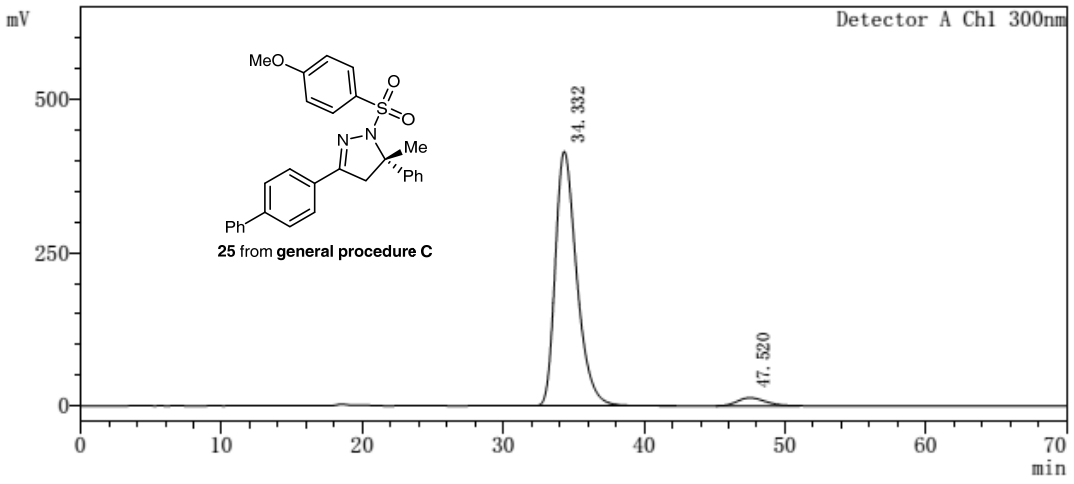
Peak#	Ret. Time	Area	Area%
1	34.537	28290481	96.992
2	47.570	877240	3.008



Peak Table

Detector A Ch1 300nm

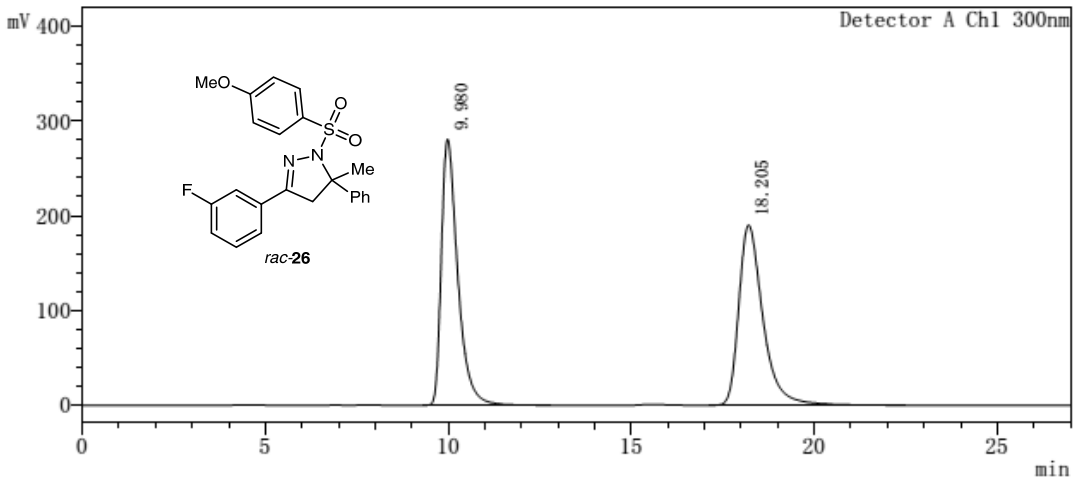
Peak#	Ret. Time	Area	Area%
1	34.305	28181971	50.232
2	47.007	27921452	49.768



Peak Table

Detector A Ch1 300nm

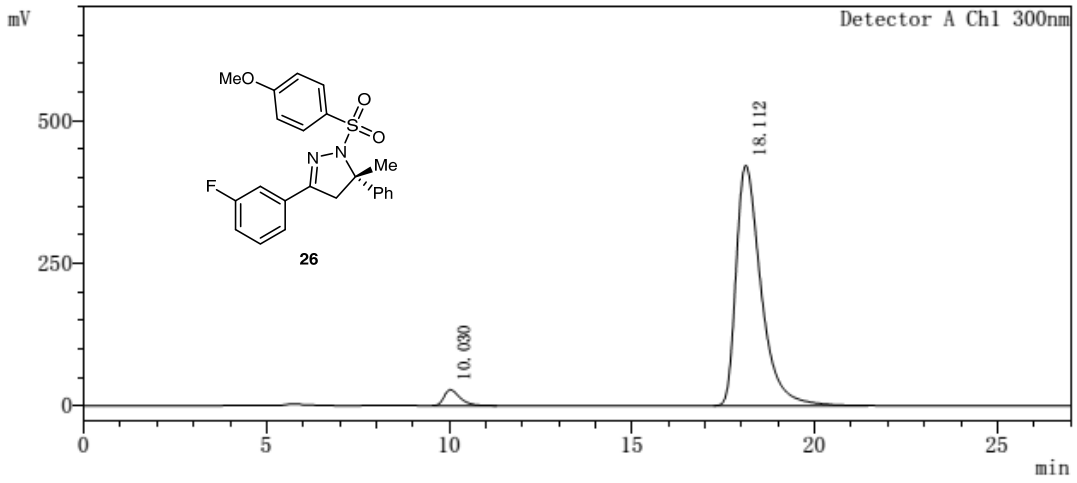
Peak#	Ret. Time	Area	Area%
1	34.332	44033090	95.925
2	47.520	1870758	4.075



Peak Table

Detector A Ch1 300nm

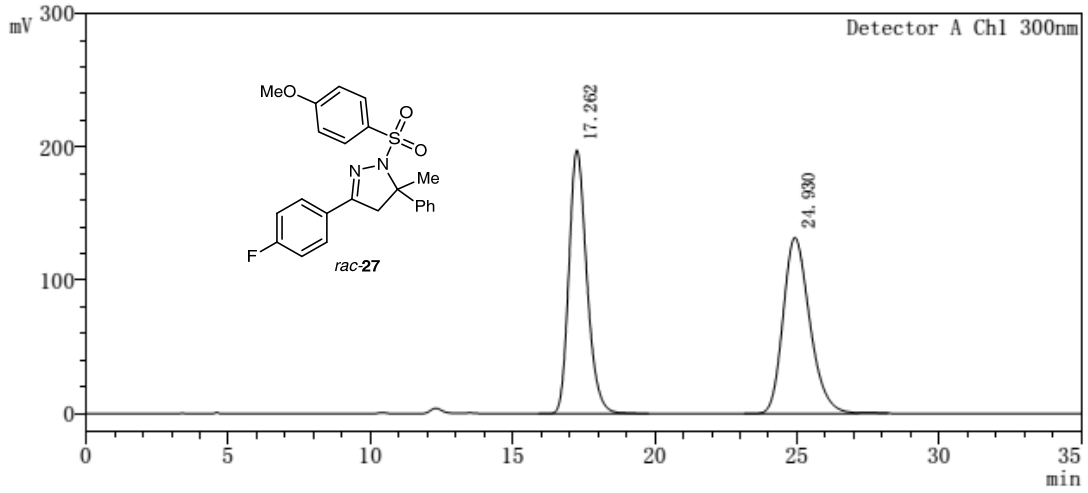
Peak#	Ret. Time	Area	Area%
1	9.980	8728772	50.001
2	18.205	8728313	49.999



Peak Table

Detector A Ch1 300nm

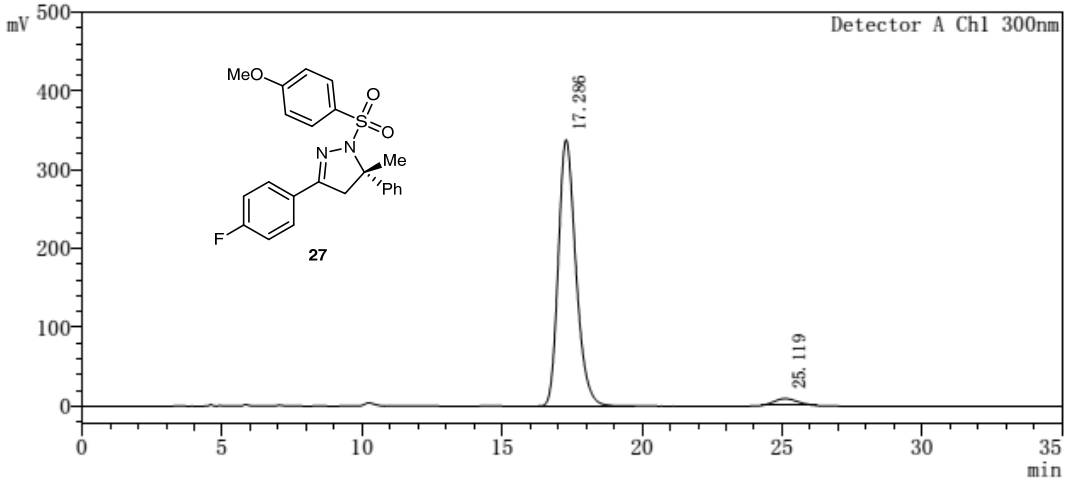
Peak#	Ret. Time	Area	Area%
1	10.030	858208	4.110
2	18.112	20022521	95.890



Peak Table

Detector A Ch1 300nm

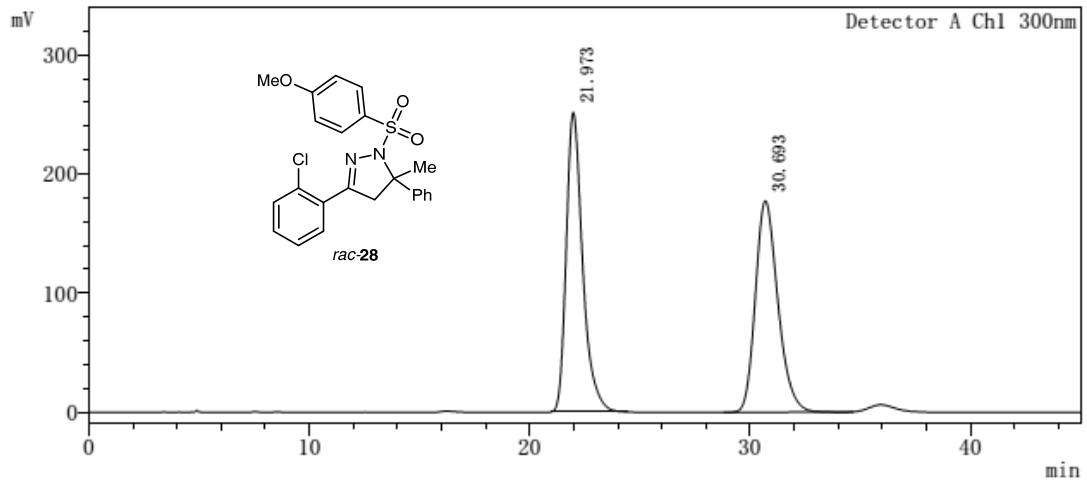
Peak#	Ret. Time	Area	Area%
1	17.262	8641358	50.021
2	24.930	8634168	49.979



Peak Table

Detector A Ch1 300nm

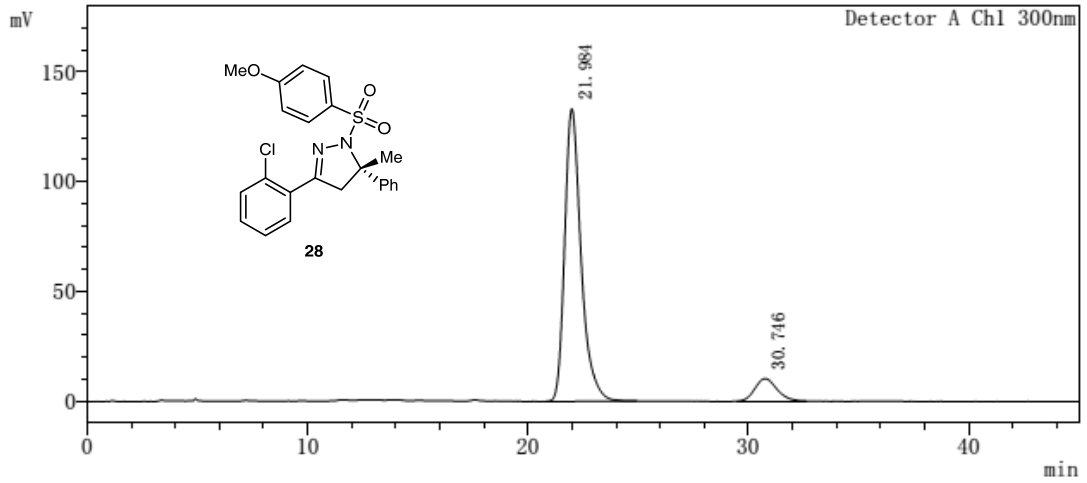
Peak#	Ret. Time	Area	Area%
1	17.286	14781118	96.668
2	25.119	509466	3.332



Peak Table

Detector A Ch1 300nm

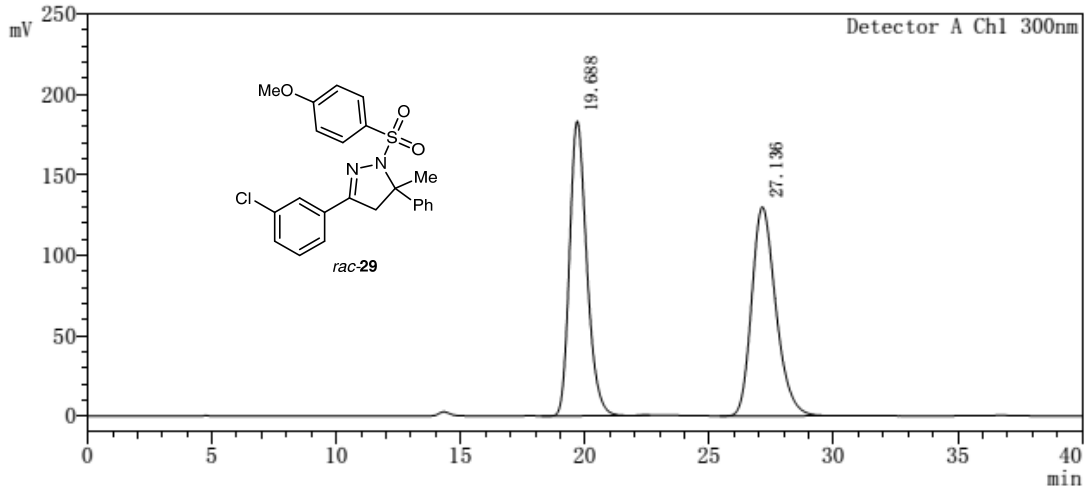
Peak#	Ret. Time	Area	Area%
1	21.973	13039248	50.879
2	30.693	12588718	49.121



Peak Table

Detector A Ch1 300nm

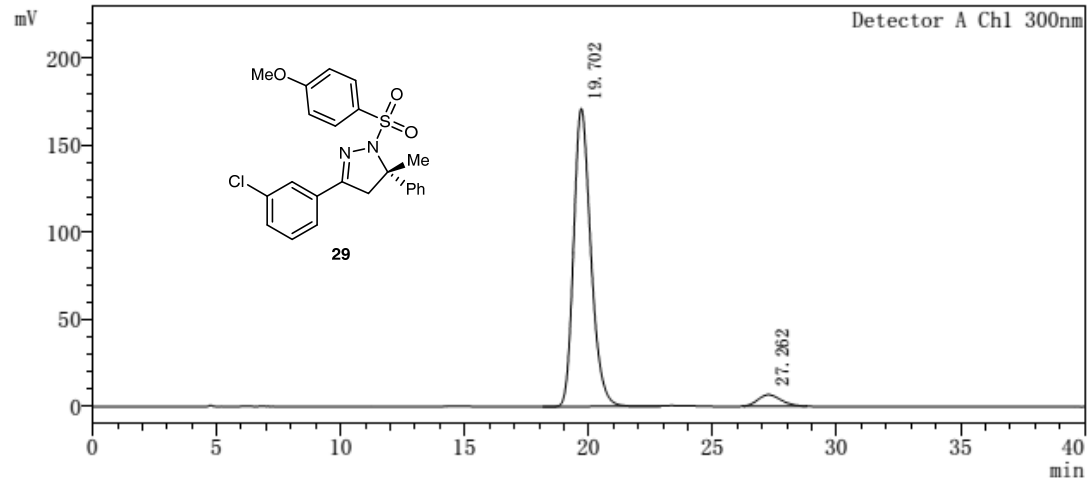
Peak#	Ret. Time	Area	Area%
1	21.984	6899260	90.543
2	30.746	720596	9.457



Peak Table

Detector A Ch1 300nm

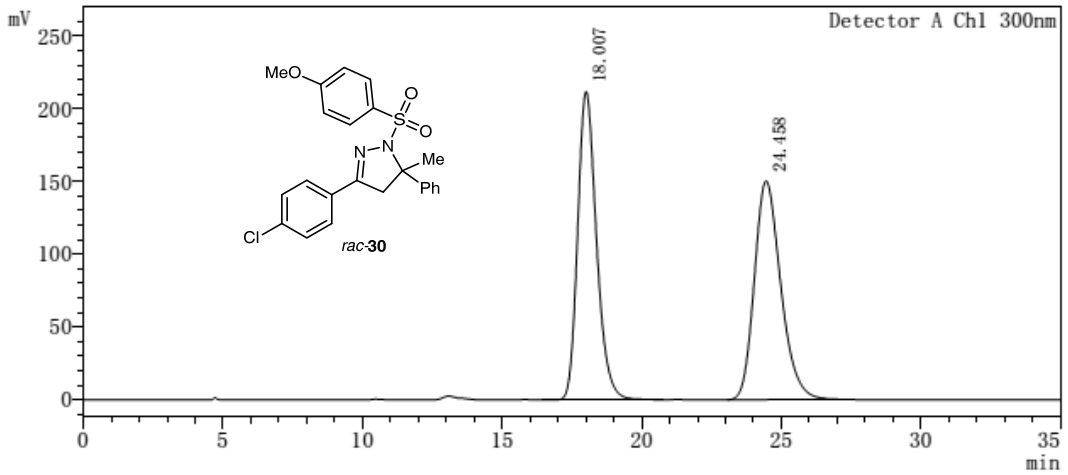
Peak#	Ret. Time	Area	Area%
1	19.688	8796984	49.985
2	27.136	8802108	50.015



Peak Table

Detector A Ch1 300nm

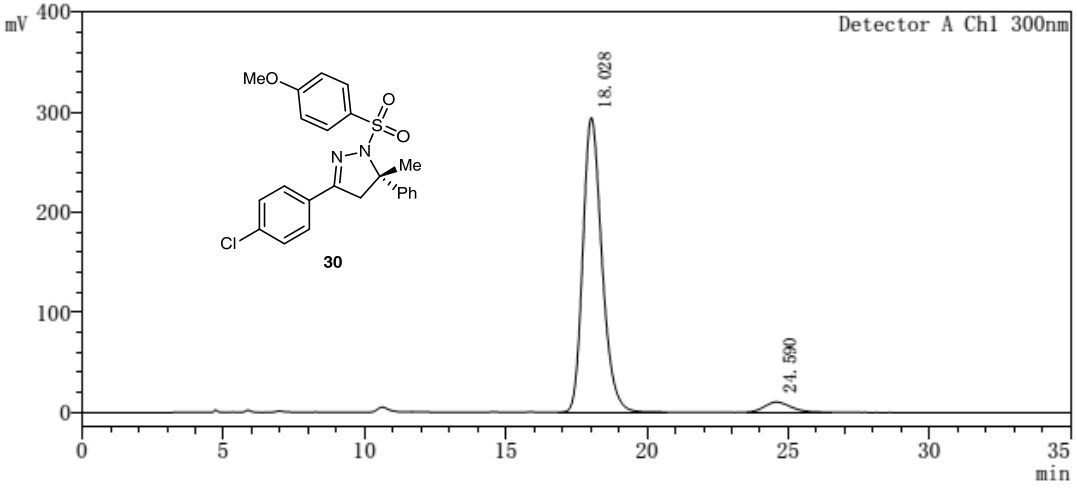
Peak#	Ret. Time	Area	Area%
1	19.702	8226320	95.065
2	27.262	427083	4.935



Peak Table

Detector A Ch1 300nm

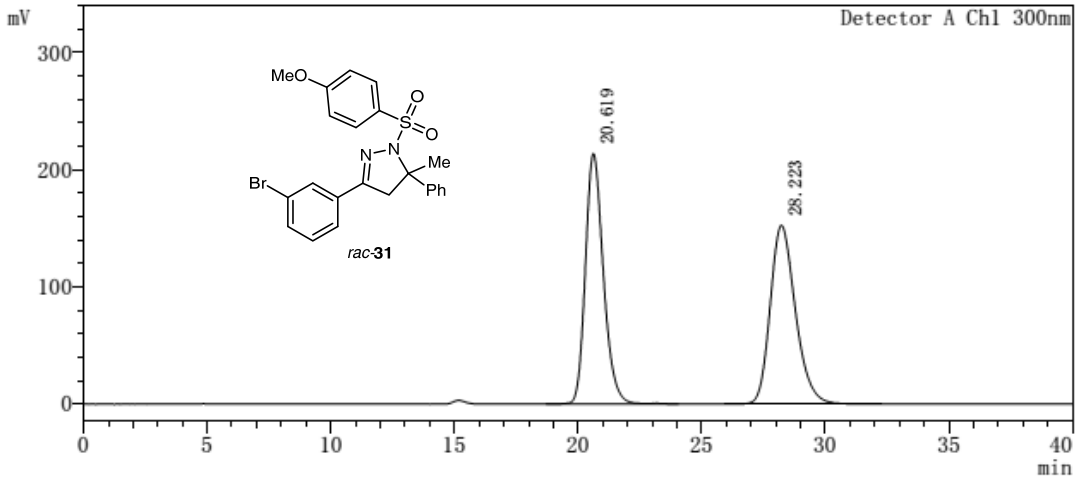
Peak#	Ret. Time	Area	Area%
1	18.007	9911563	50.046
2	24.458	9893283	49.954



Peak Table

Detector A Ch1 300nm

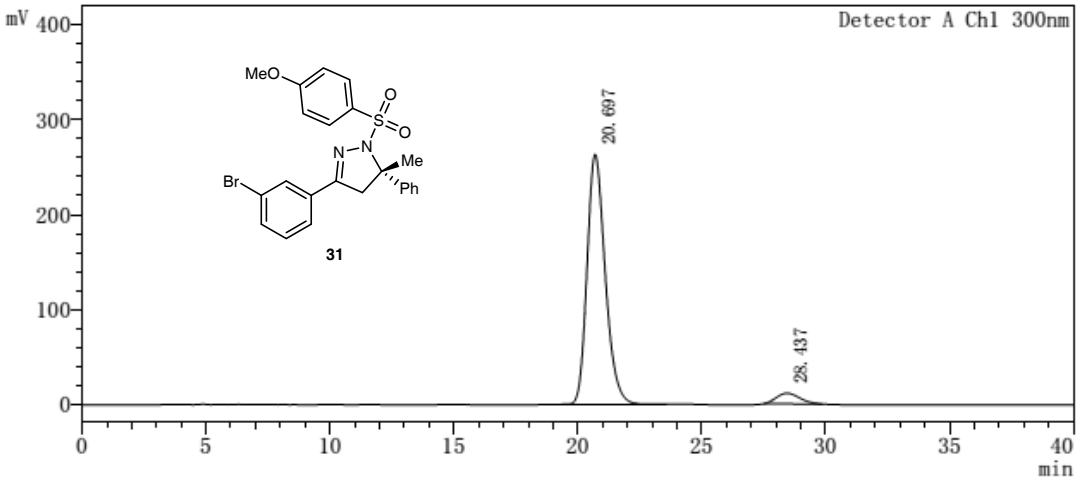
Peak#	Ret. Time	Area	Area%
1	18.028	13850017	95.397
2	24.590	668256	4.603



Peak Table

Detector A Ch1 300nm

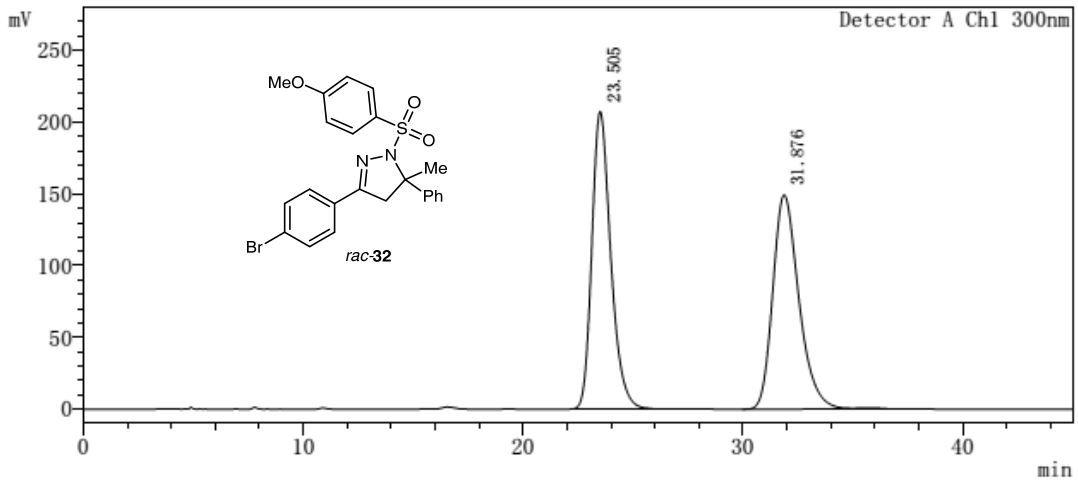
Peak#	Ret. Time	Area	Area%
1	20.619	10839552	49.964
2	28.223	10855040	50.036



Peak Table

Detector A Ch1 300nm

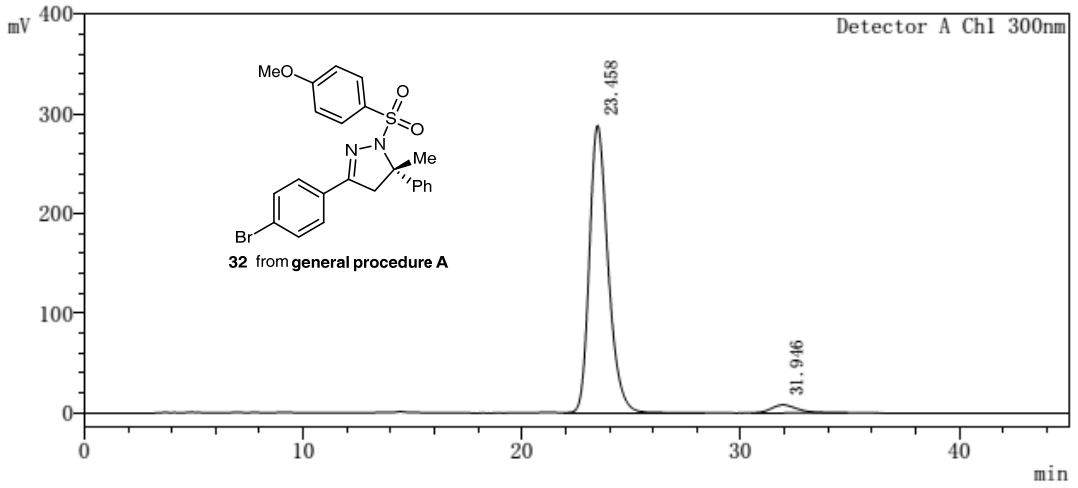
Peak#	Ret. Time	Area	Area%
1	20.697	13411110	94.818
2	28.437	732999	5.182



Peak Table

Detector A Ch1 300nm

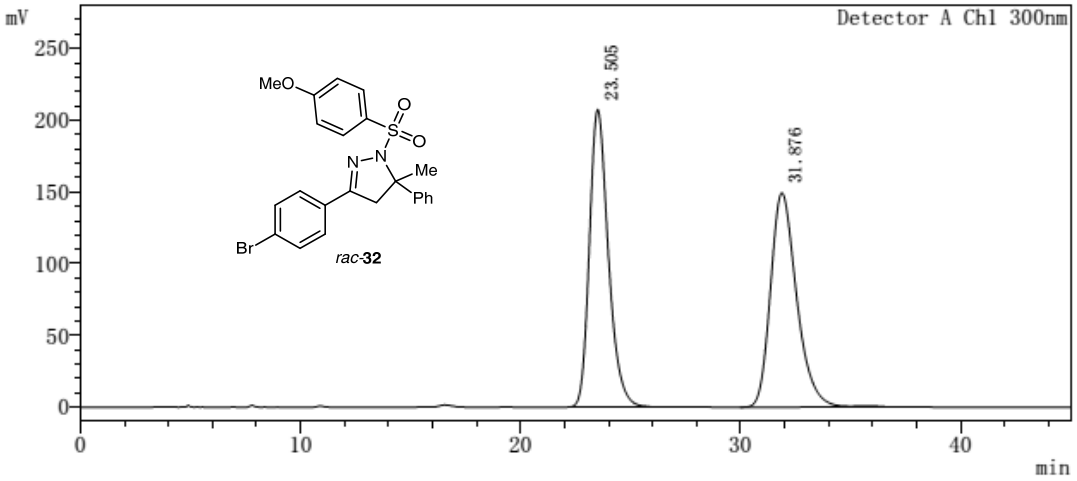
Peak#	Ret. Time	Area	Area%
1	23.505	12398446	50.069
2	31.876	12364445	49.931



Peak Table

Detector A Ch1 300nm

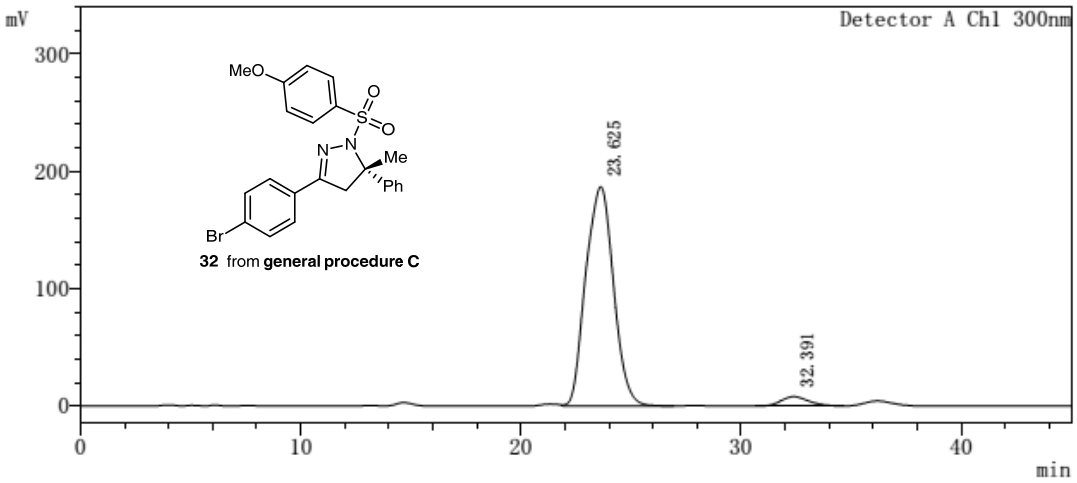
Peak#	Ret. Time	Area	Area%
1	23.458	17175910	96.261
2	31.946	667226	3.739



Peak Table

Detector A Ch1 300nm

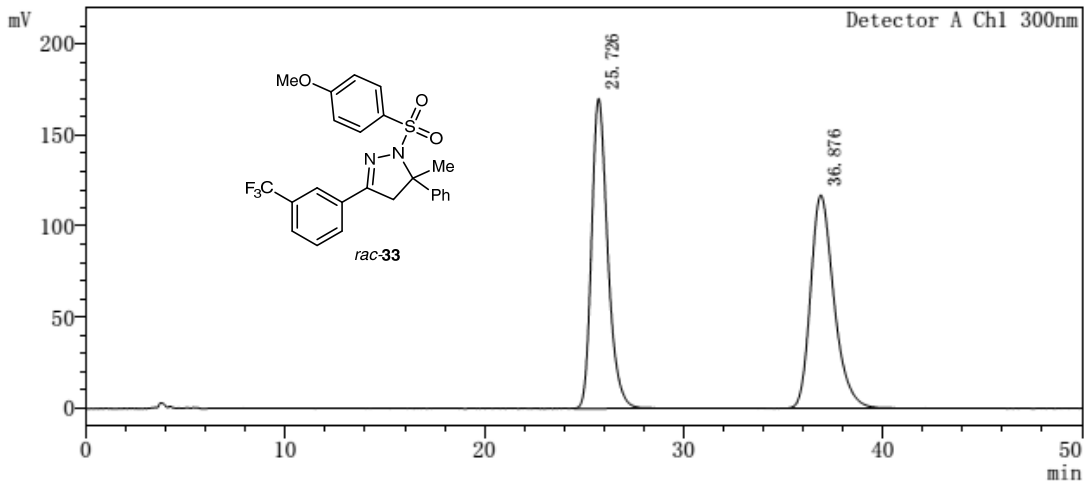
Peak#	Ret. Time	Area	Area%
1	23.505	12398446	50.069
2	31.876	12364445	49.931



Peak Table

Detector A Ch1 300nm

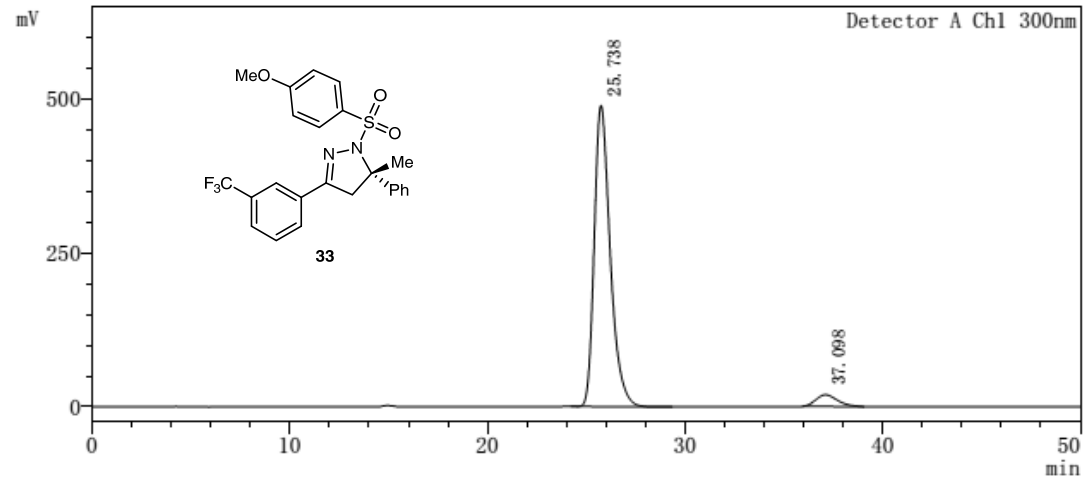
Peak#	Ret. Time	Area	Area%
1	23.625	16394274	95.764
2	32.391	725214	4.236



Peak Table

Detector A Ch1 300nm

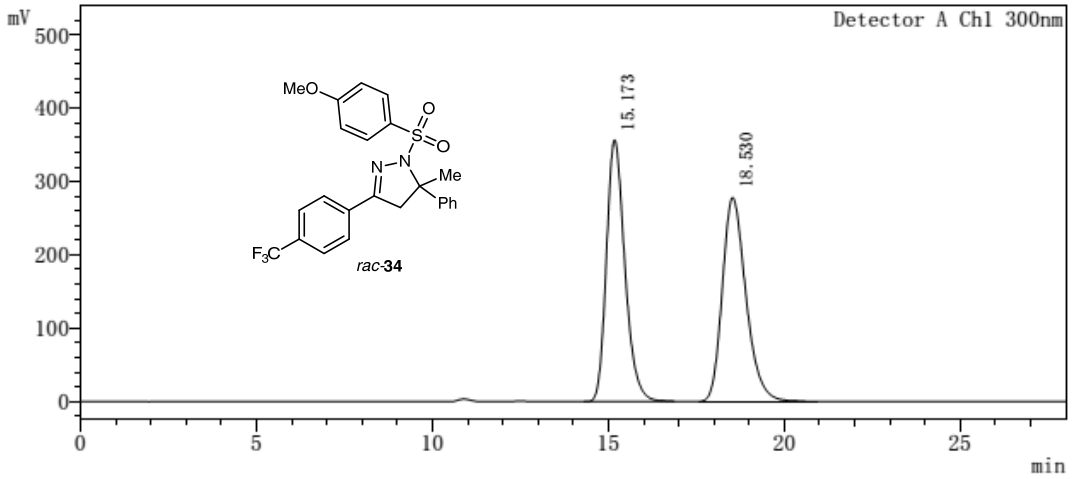
Peak#	Ret. Time	Area	Area%
1	25.726	9546005	50.007
2	36.876	9543486	49.993



Peak Table

Detector A Ch1 300nm

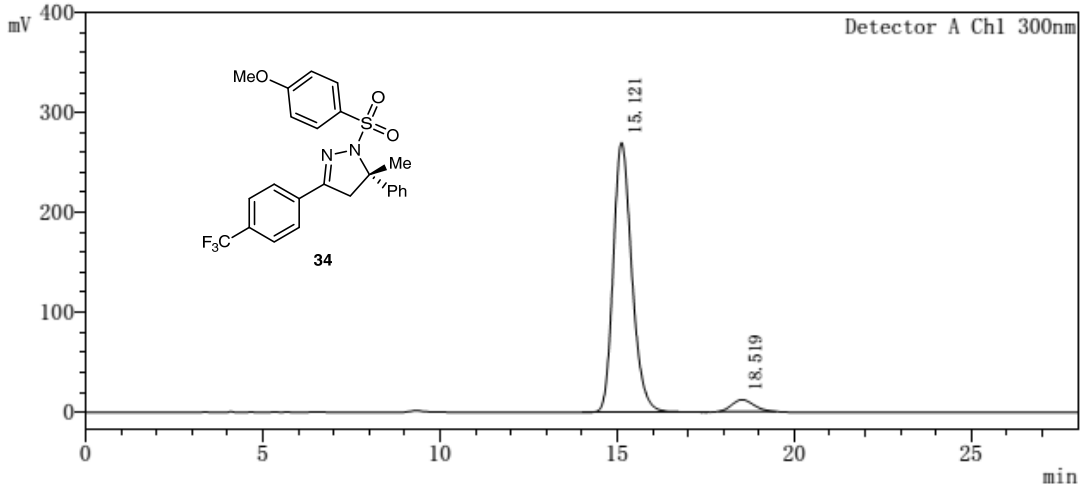
Peak#	Ret. Time	Area	Area%
1	25.738	27417217	94.963
2	37.098	1454165	5.037



Peak Table

Detector A Ch1 300nm

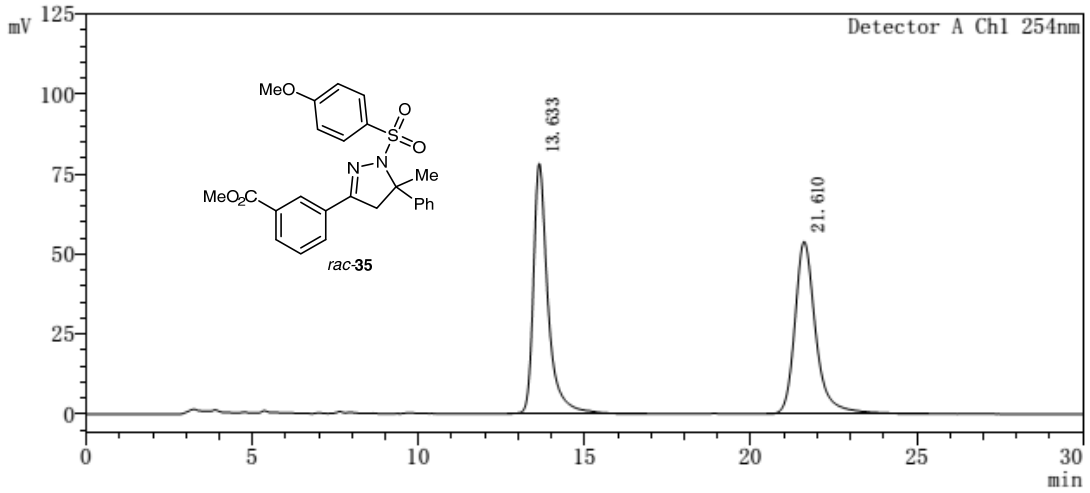
Peak#	Ret. Time	Area	Area%
1	15.173	13024230	50.015
2	18.530	13016512	49.985



Peak Table

Detector A Ch1 300nm

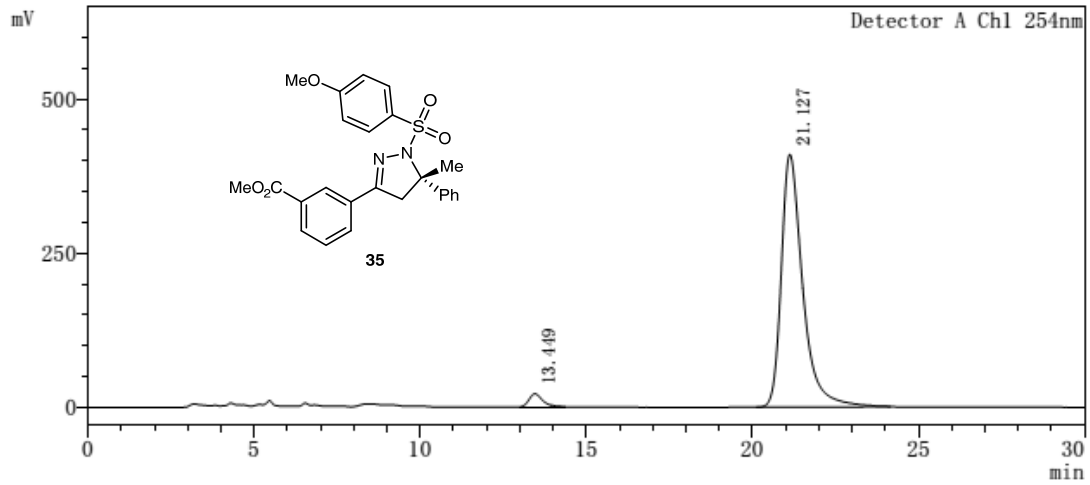
Peak#	Ret. Time	Area	Area%
1	15.121	9857126	95.103
2	18.519	507573	4.897



Peak Table

Detector A Ch1 254nm

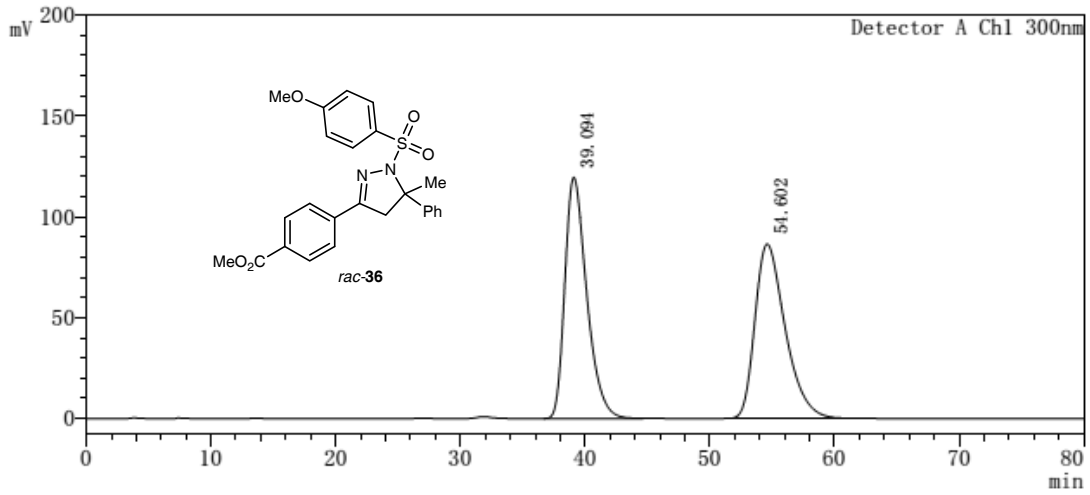
Peak#	Ret. Time	Area	Area%
1	13.633	2391155	50.231
2	21.610	2369203	49.769



Peak Table

Detector A Ch1 254nm

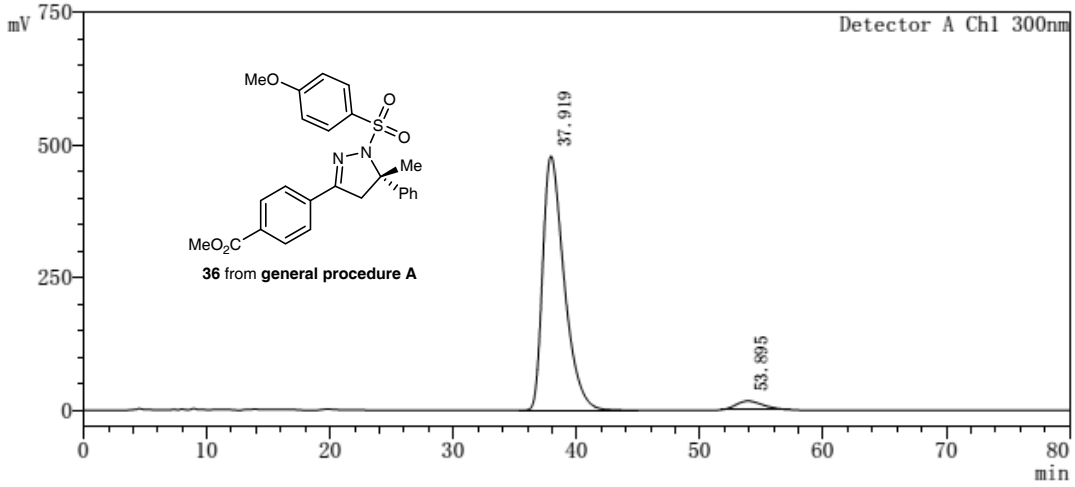
Peak#	Ret. Time	Area	Area%
1	13.449	613406	3.230
2	21.127	18377657	96.770



Peak Table

Detector A Ch1 300nm

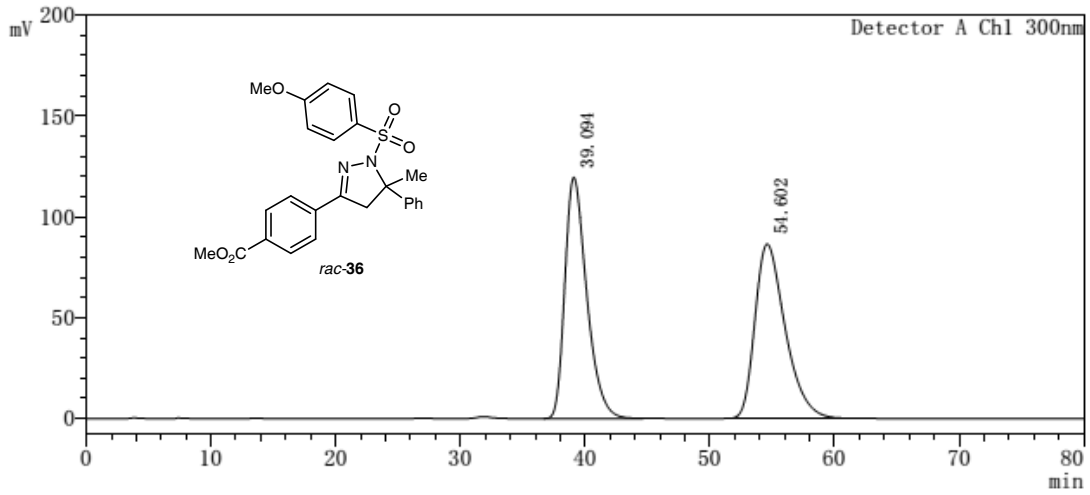
Peak#	Ret. Time	Area	Area%
1	39.094	14608455	50.007
2	54.602	14604350	49.993



Peak Table

Detector A Ch1 300nm

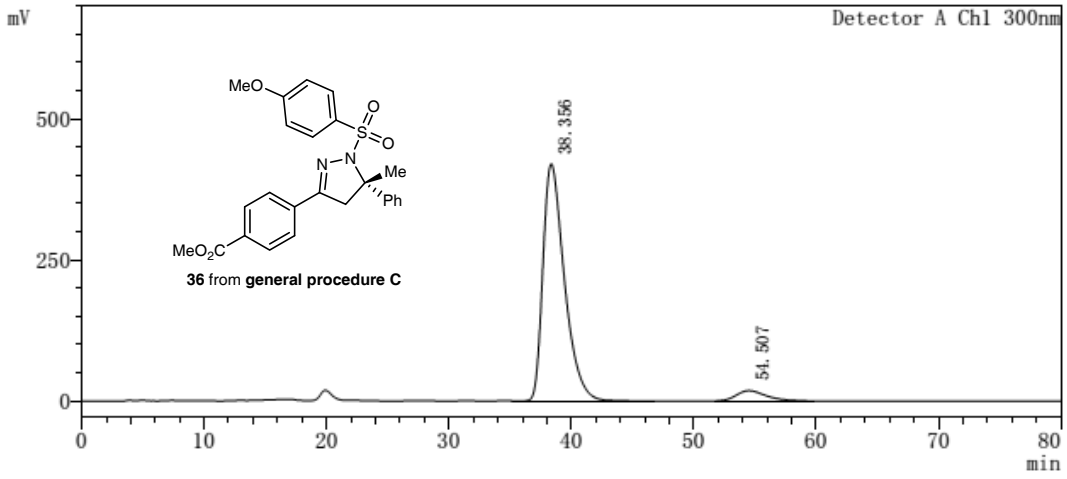
Peak#	Ret. Time	Area	Area%
1	37.919	57788203	95.905
2	53.895	2467207	4.095



Peak Table

Detector A Ch1 300nm

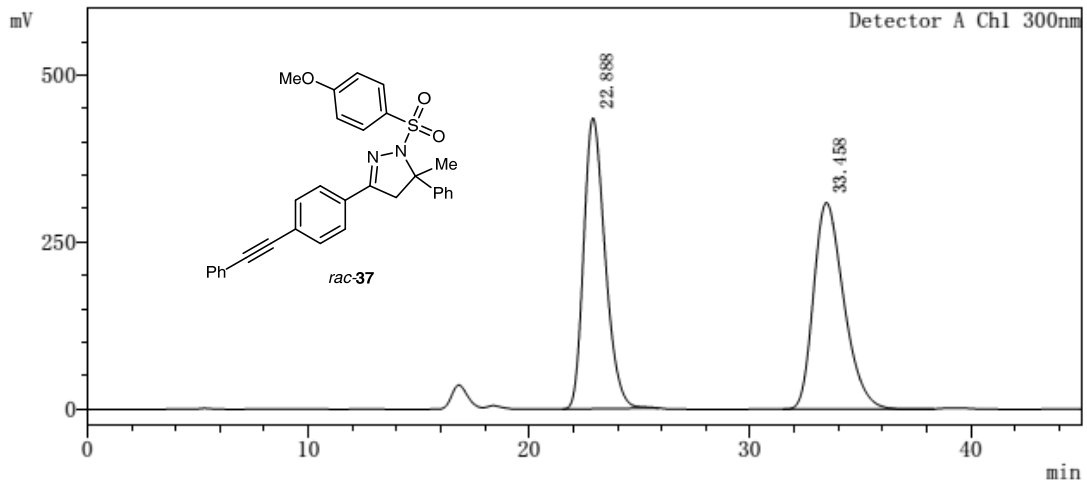
Peak#	Ret. Time	Area	Area%
1	39.094	14608455	50.007
2	54.602	14604350	49.993



Peak Table

Detector A Ch1 300nm

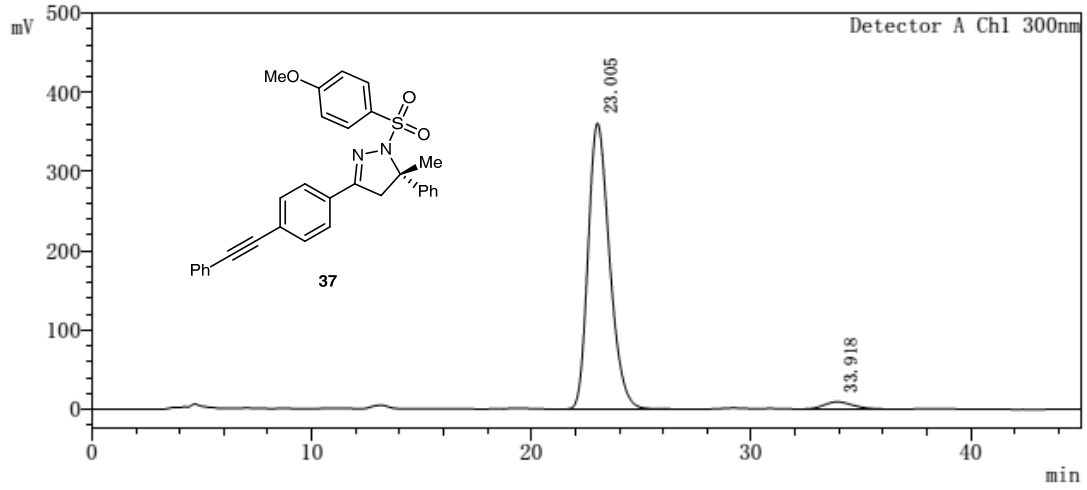
Peak#	Ret. Time	Area	Area%
1	38.356	51189196	94.429
2	54.507	3019993	5.571



Peak Table

Detector A Ch1 300nm

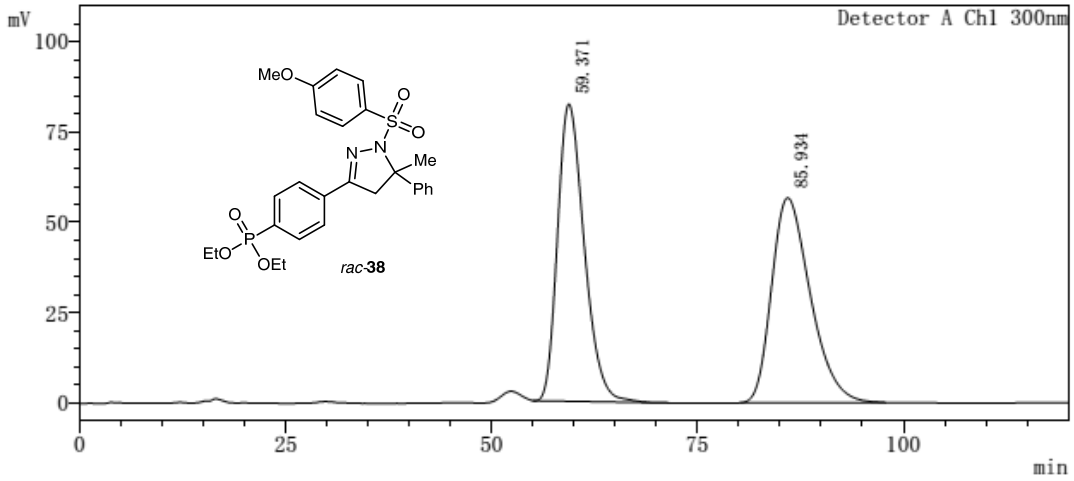
Peak#	Ret. Time	Area	Area%
1	22.888	29379355	49.994
2	33.458	29386515	50.006



Peak Table

Detector A Ch1 300nm

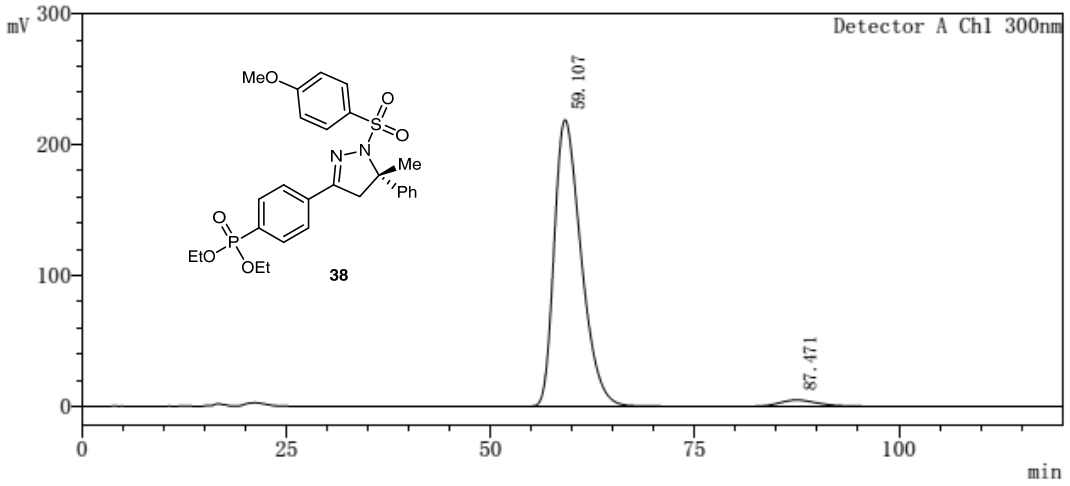
Peak#	Ret. Time	Area	Area%
1	23.005	24547512	96.614
2	33.918	860306	3.386



Peak Table

Detector A Ch1 300nm

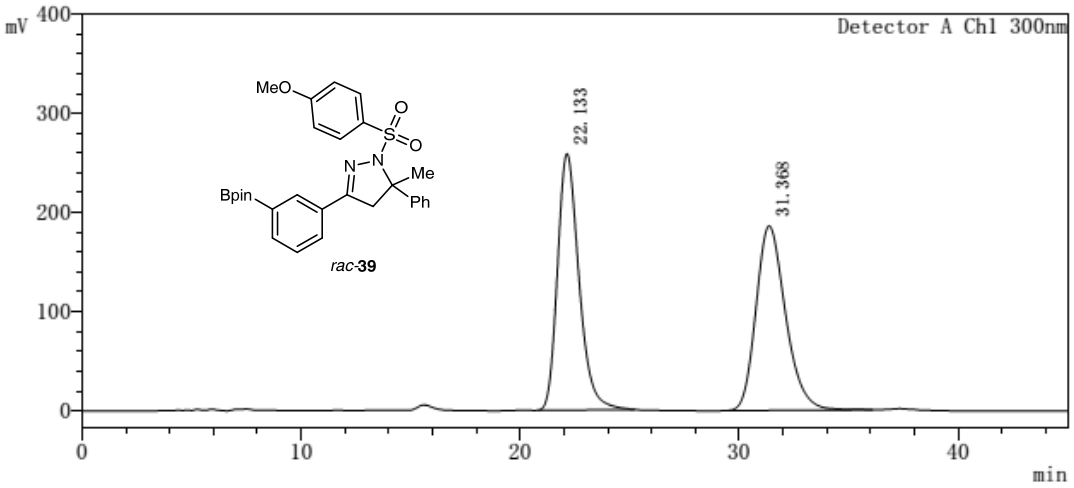
Peak#	Ret. Time	Area	Area%
1	59.371	18531109	49.963
2	85.934	18558311	50.037



Peak Table

Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	59.107	50183991	97.052
2	87.471	1524612	2.948



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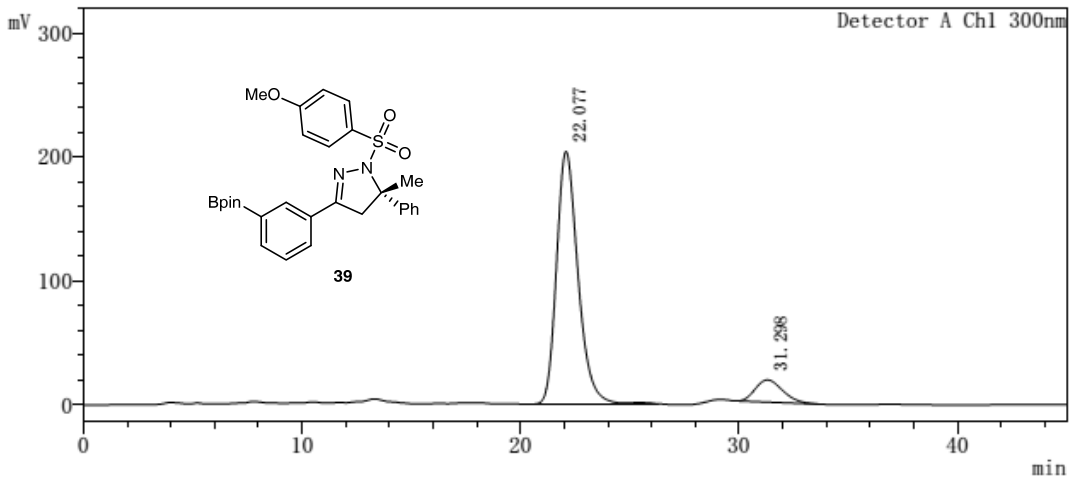
Peak Table

Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	22.133	17649853	50.175
2	31.368	17526458	49.825



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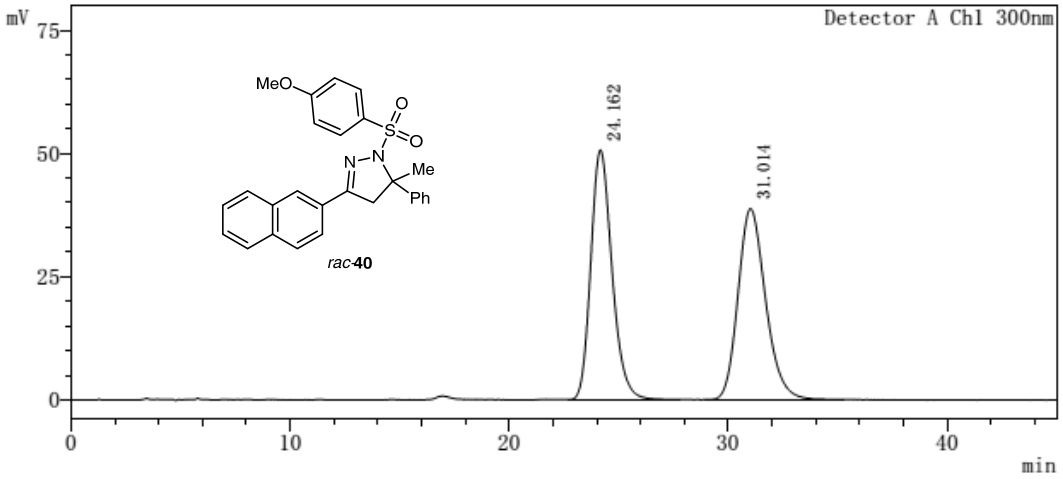
Peak Table

Detector A Ch1 300nm

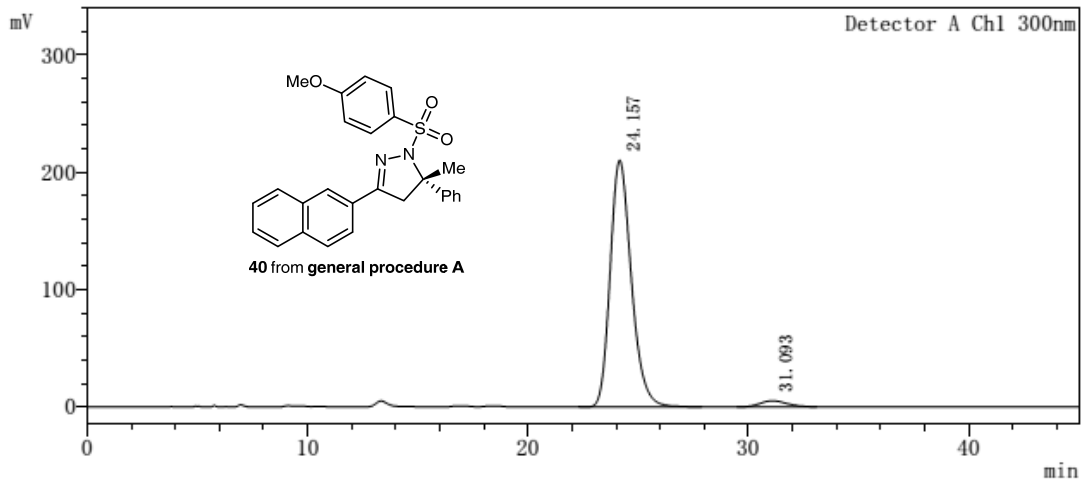
Peak#	Ret. Time	Area	Area%
1	22.077	13983986	89.973
2	31.298	1558375	10.027



Peak Table

Detector A Ch1 300nm

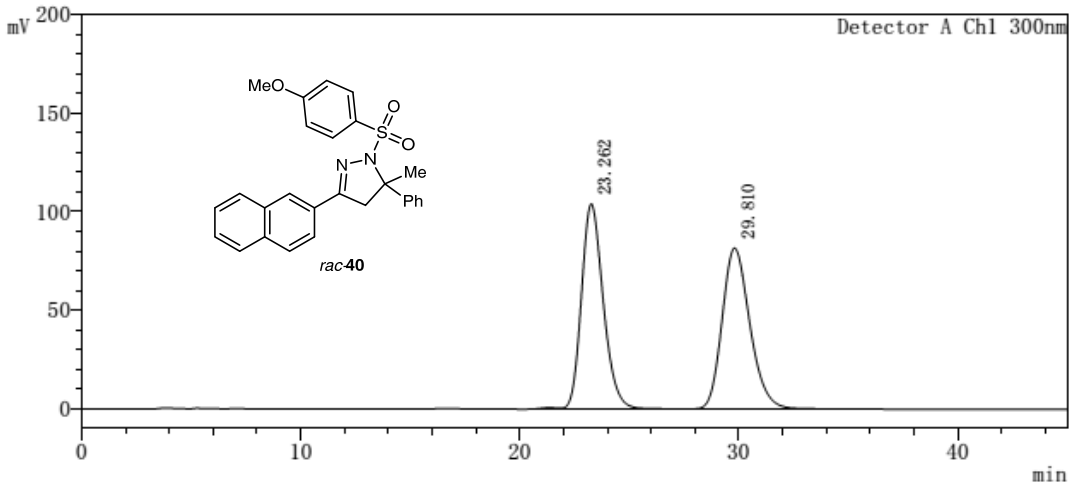
Peak#	Ret. Time	Area	Area%
1	24.162	3405864	50.012
2	31.014	3404208	49.988



Peak Table

Detector A Ch1 300nm

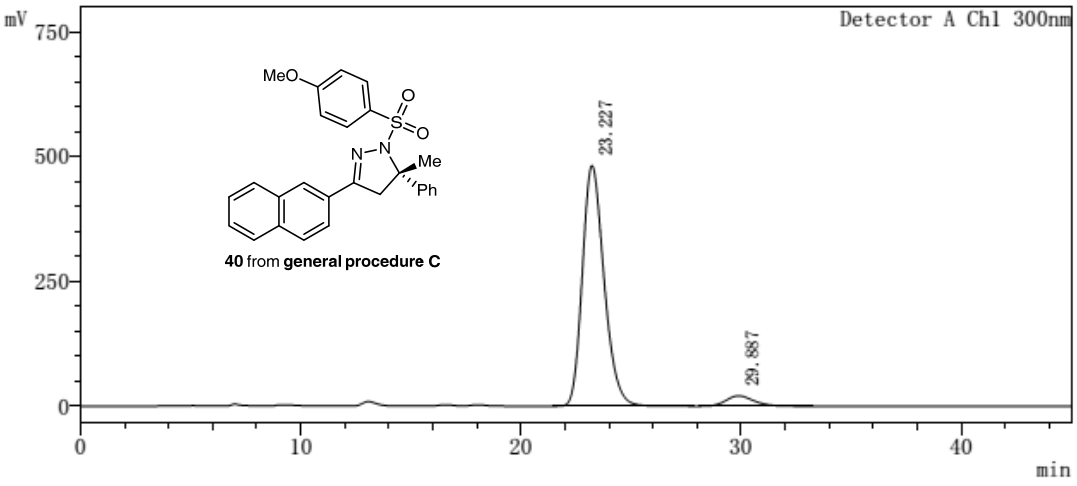
Peak#	Ret. Time	Area	Area%
1	24.157	14033837	96.922
2	31.093	445737	3.078



Peak Table

Detector A Ch1 300nm

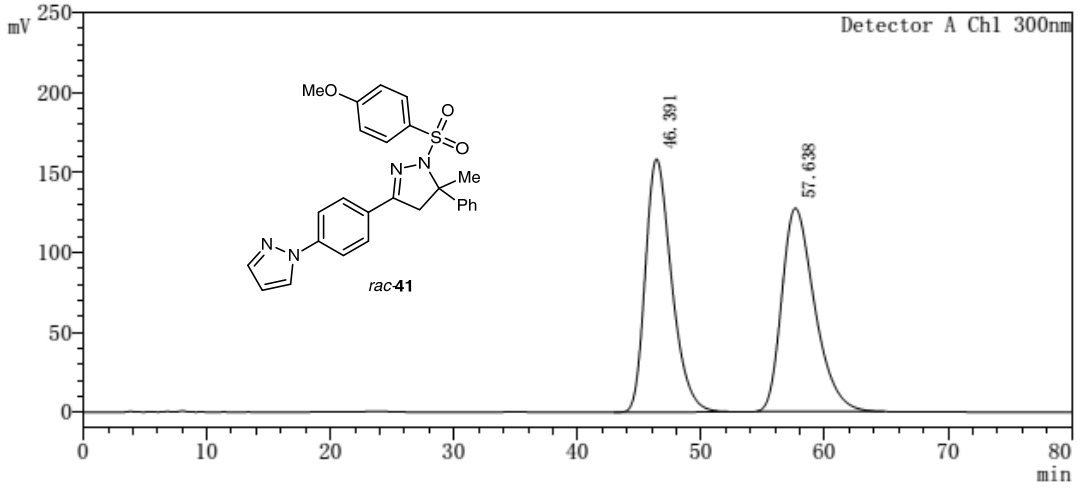
Peak#	Ret. Time	Area	Area%
1	23.262	7224292	50.064
2	29.810	7205687	49.936



Peak Table

Detector A Ch1 300nm

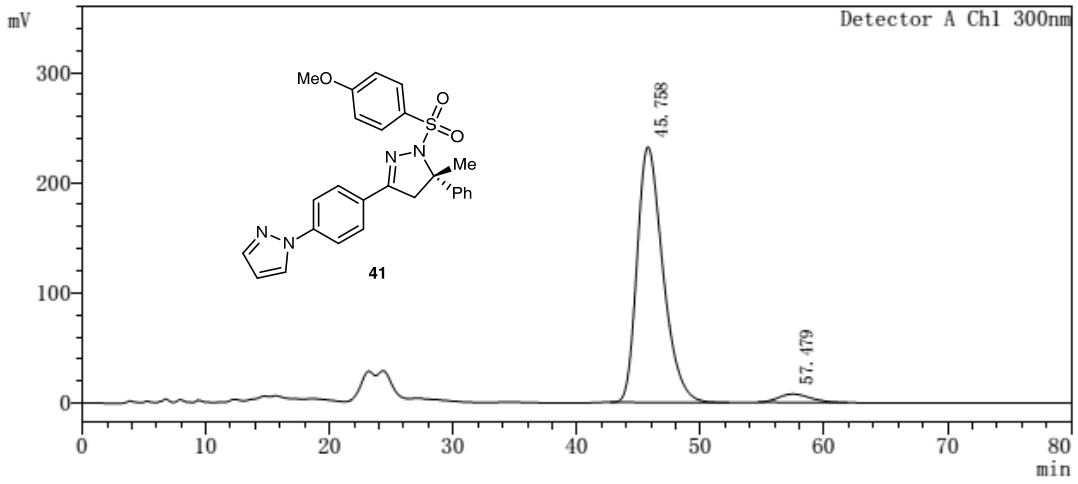
Peak#	Ret. Time	Area	Area%
1	23.227	33138522	94.815
2	29.887	1812181	5.185



Peak Table

Detector A Ch1 300nm

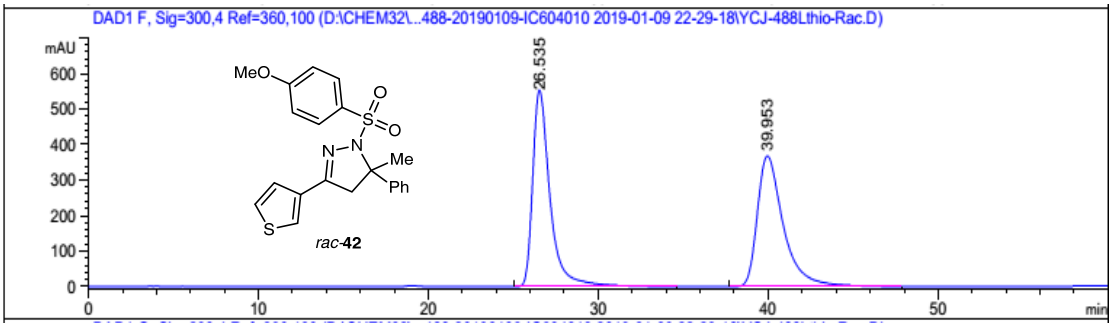
Peak#	Ret. Time	Area	Area%
1	46.391	23467222	49.913
2	57.638	23549111	50.087



Peak Table

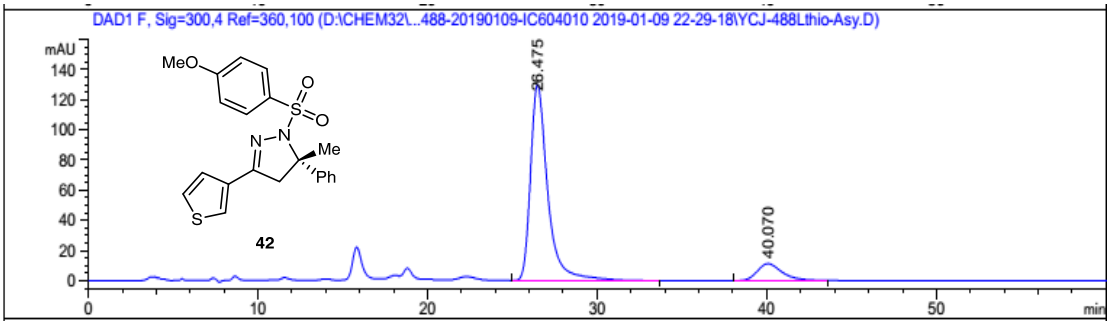
Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	45.758	33695174	96.046
2	57.479	1387003	3.954



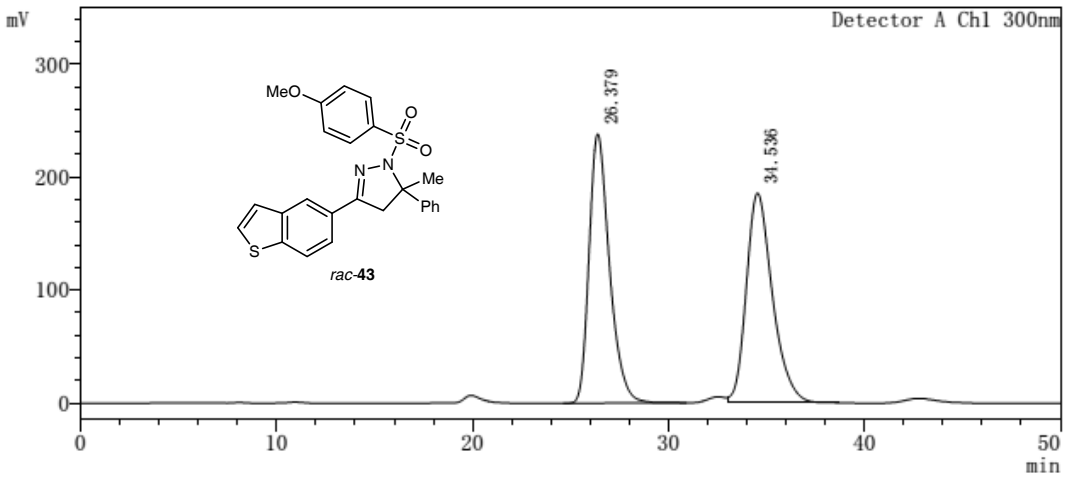
Signal 6: DAD1 F, Sig=300,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.535	BV	1.0659	3.94327e4	552.97876	49.9979
2	39.953	VV	1.5984	3.94360e4	367.94131	50.0021
Totals :				7.88687e4	920.92007	



Signal 6: DAD1 F, Sig=300,4 Ref=360,100

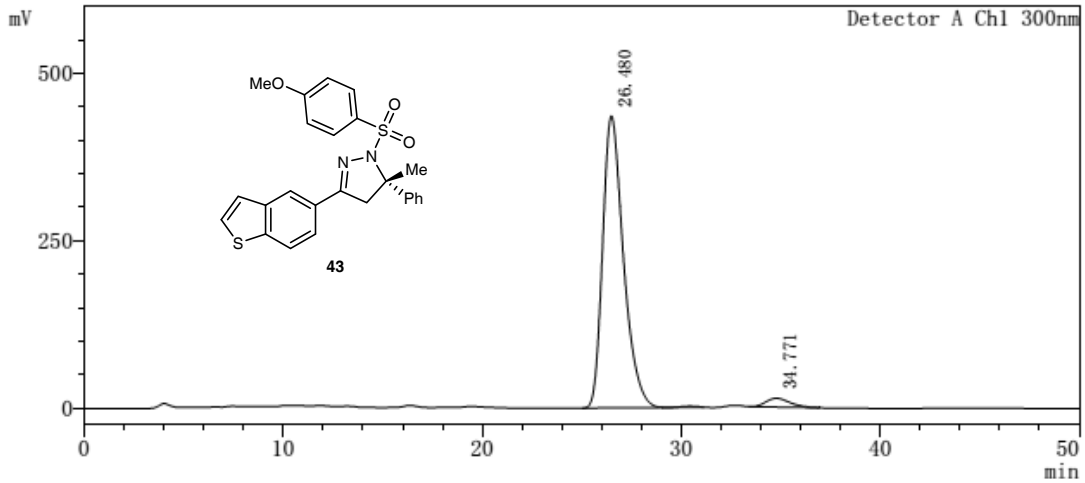
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.475	MM R	1.2101	9459.30859	130.28084	88.9409
2	40.070	VV	1.2619	1176.18848	11.26697	11.0591
Totals :				1.06355e4	141.54781	



Peak Table

Detector A Ch1 300nm

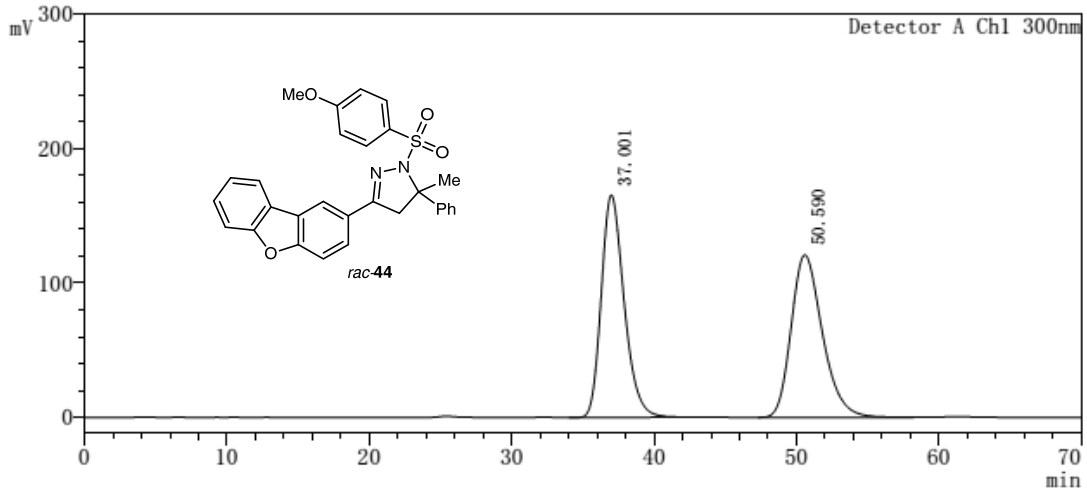
Peak#	Ret. Time	Area	Area%
1	26.379	17239124	49.969
2	34.536	17260831	50.031



Peak Table

Detector A Ch1 300nm

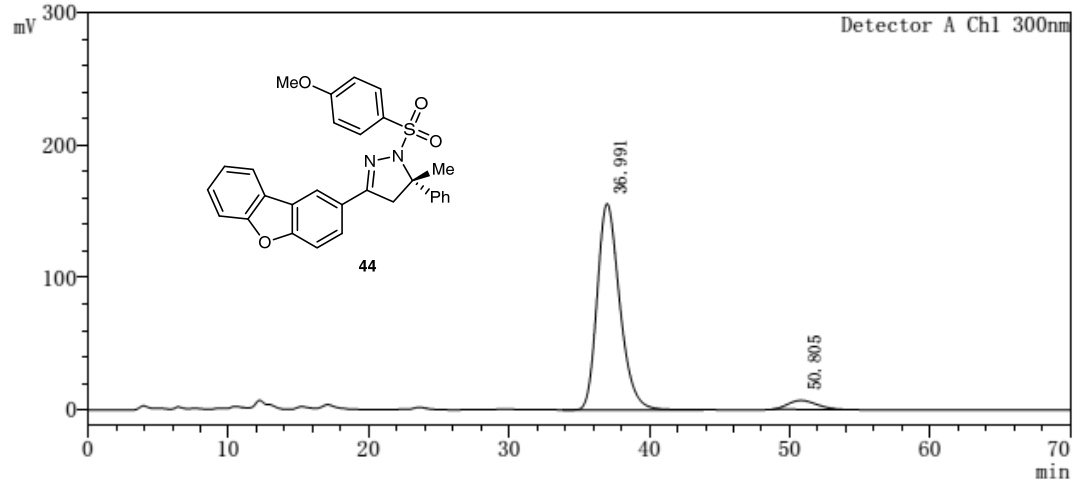
Peak#	Ret. Time	Area	Area%
1	26.480	31712810	96.660
2	34.771	1095924	3.340



Peak Table

Detector A Ch1 300nm

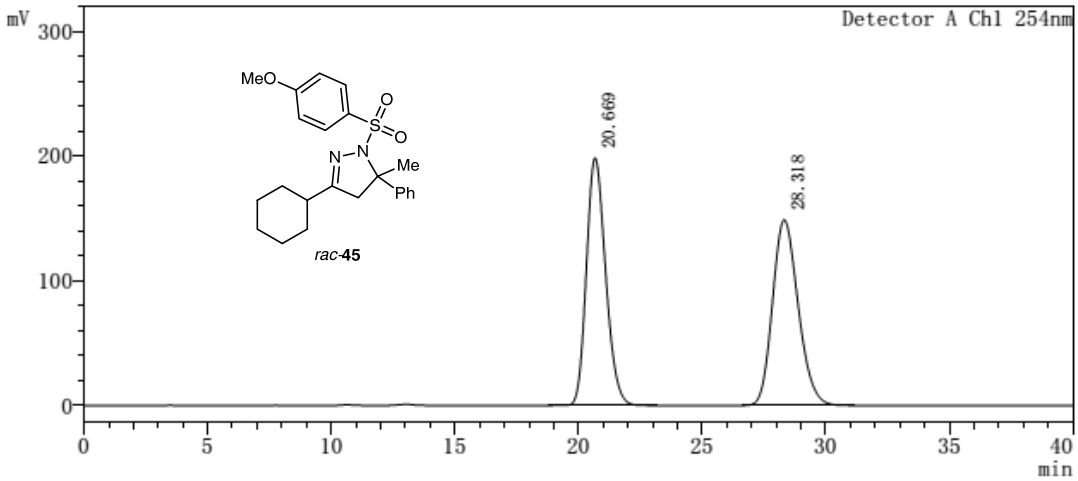
Peak#	Ret. Time	Area	Area%
1	37.001	18479092	49.997
2	50.590	18480984	50.003



Peak Table

Detector A Ch1 300nm

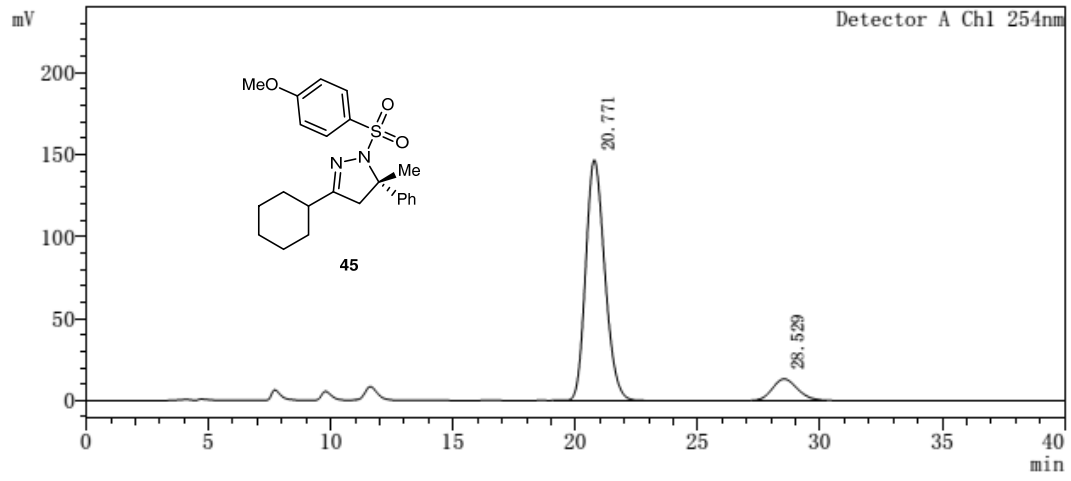
Peak#	Ret. Time	Area	Area%
1	36.991	17473779	94.768
2	50.805	964700	5.232



Peak Table

Detector A Ch1 254nm

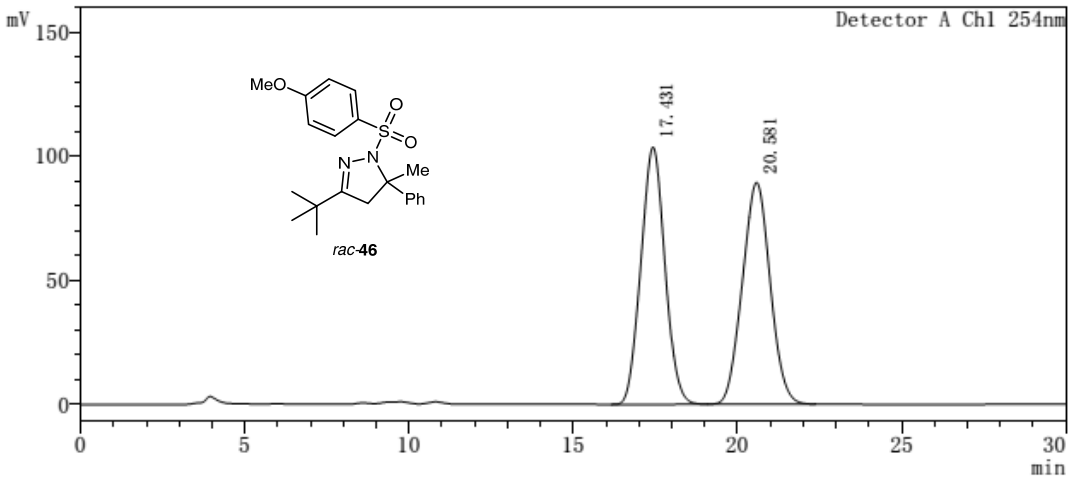
Peak#	Ret. Time	Area	Area%
1	20.669	10741261	50.005
2	28.318	10739288	49.995



Peak Table

Detector A Ch1 254nm

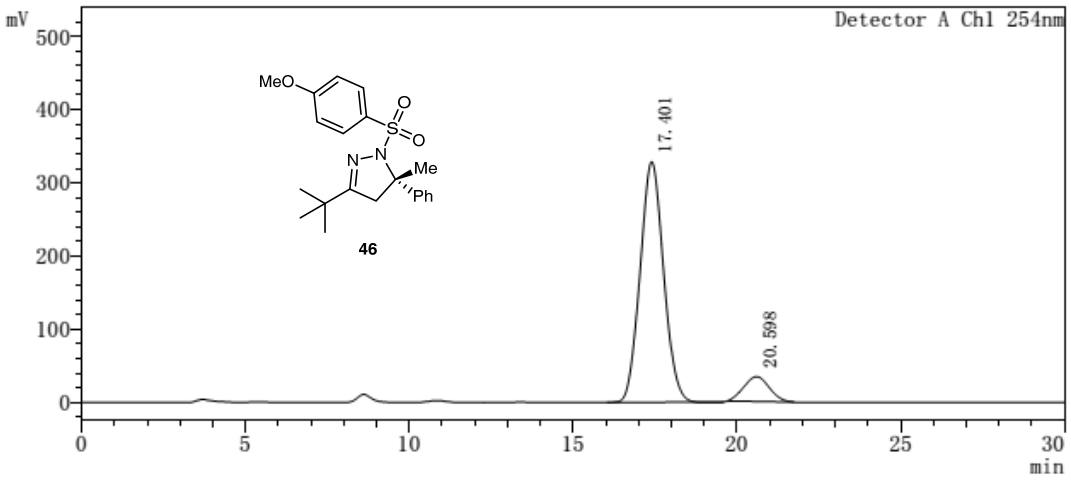
Peak#	Ret. Time	Area	Area%
1	20.771	7990897	89.584
2	28.529	929116	10.416



Peak Table

Detector A Ch1 254nm

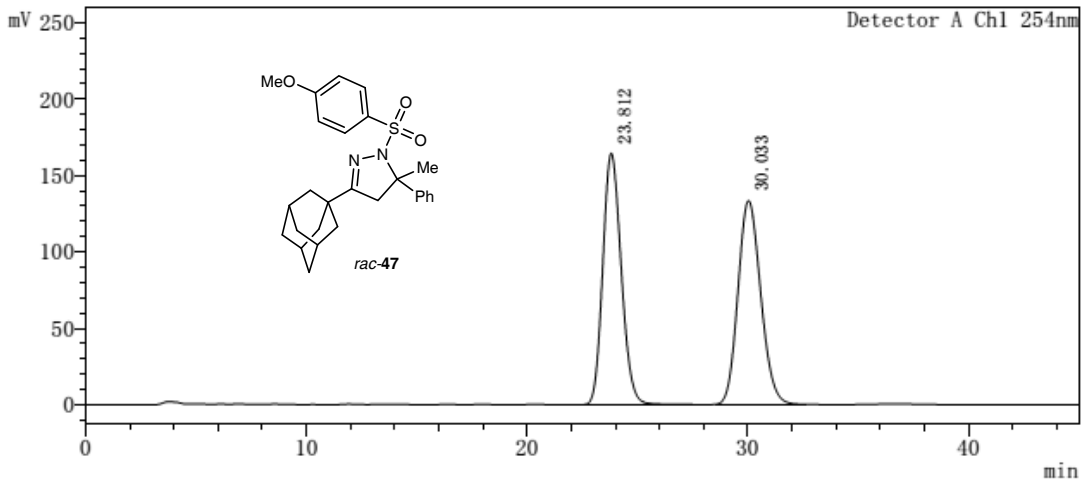
Peak#	Ret. Time	Area	Area%
1	17.431	5271976	50.029
2	20.581	5265855	49.971



Peak Table

Detector A Ch1 254nm

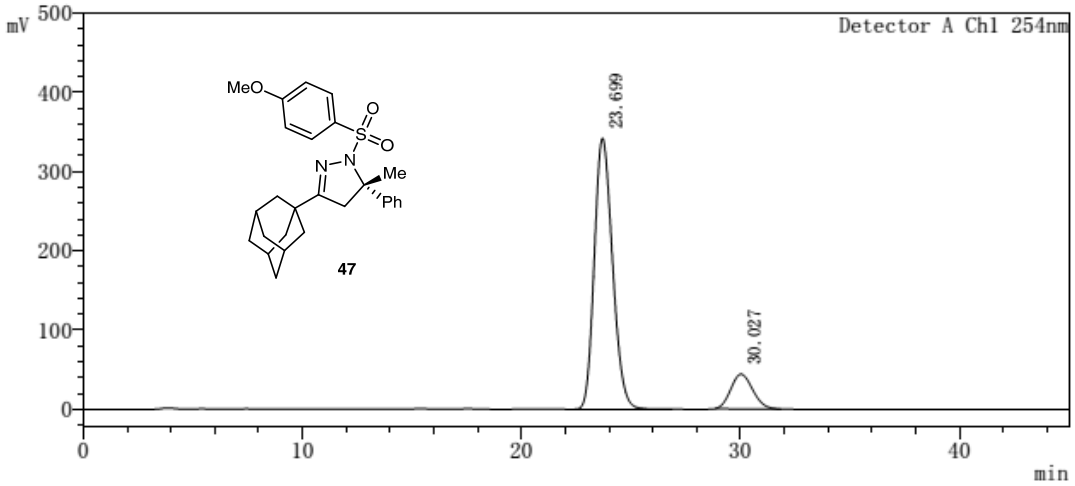
Peak#	Ret. Time	Area	Area%
1	17.401	16305098	89.834
2	20.598	1845240	10.166



Peak Table

Detector A Ch1 254nm

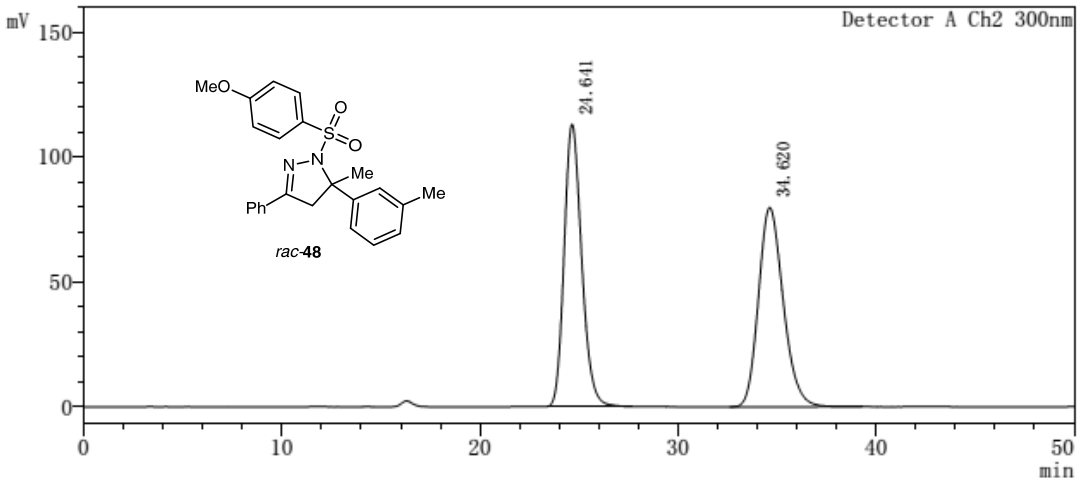
Peak#	Ret. Time	Area	Area%
1	23.812	9556490	49.987
2	30.033	9561425	50.013



Peak Table

Detector A Ch1 254nm

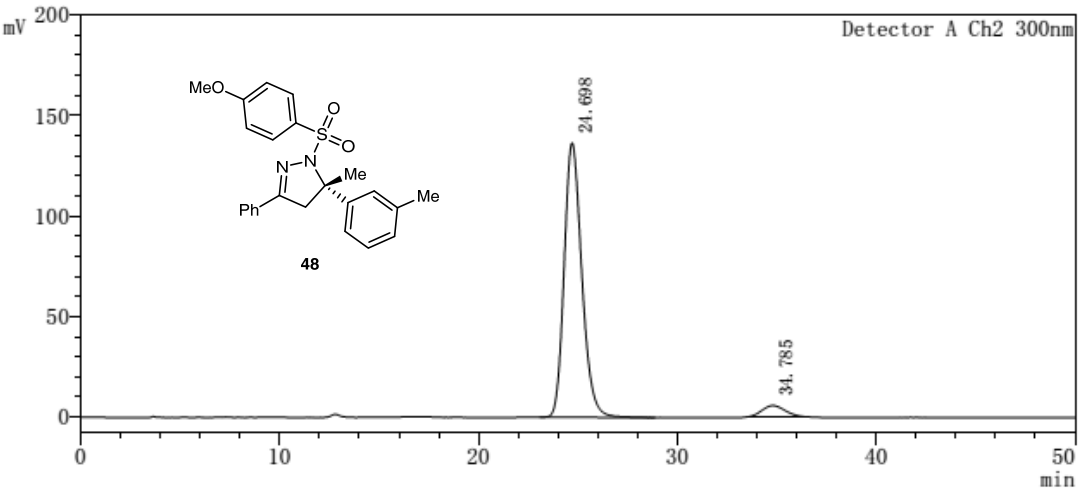
Peak#	Ret. Time	Area	Area%
1	23.699	19801681	86.714
2	30.027	3033996	13.286



Peak Table

Detector A Ch2 300nm

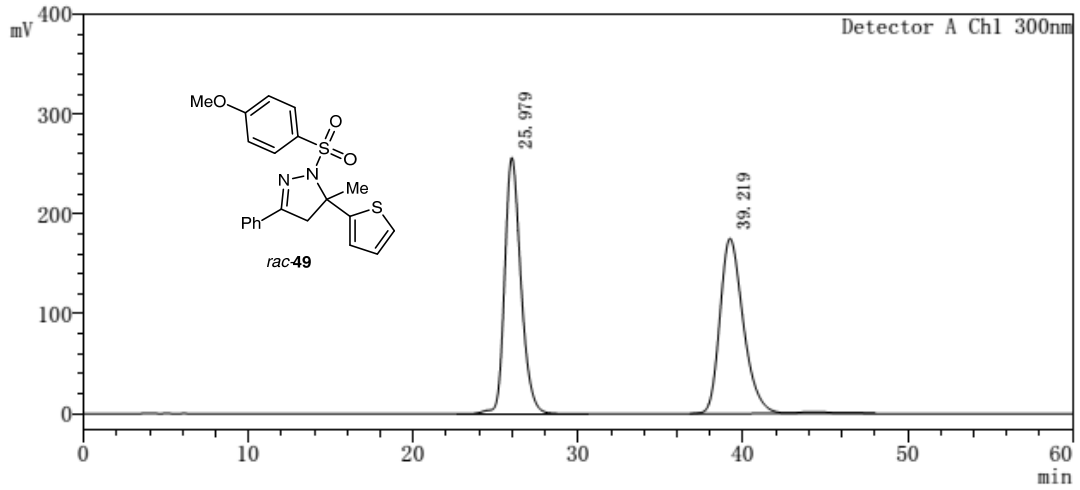
Peak#	Ret. Time	Area	Area%
1	24.641	6950427	49.999
2	34.620	6950678	50.001



Peak Table

Detector A Ch2 300nm

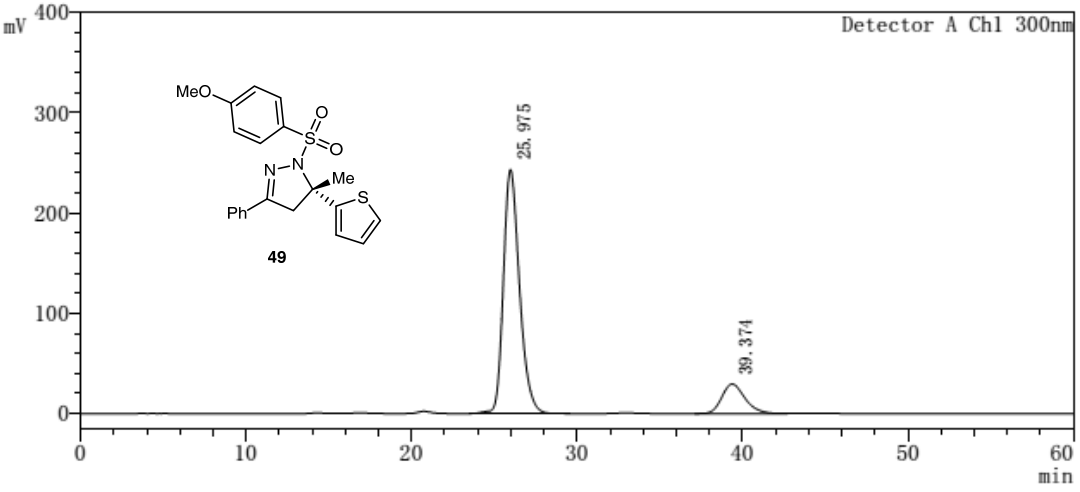
Peak#	Ret. Time	Area	Area%
1	24.698	8432217	94.978
2	34.785	445846	5.022



Peak Table

Detector A Ch1 300nm

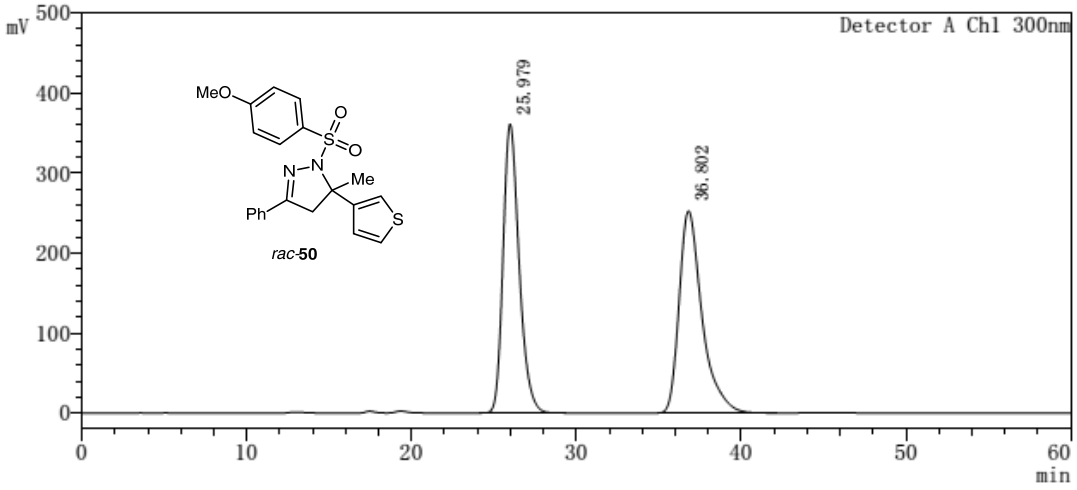
Peak#	Ret. Time	Area	Area%
1	25.979	17553692	49.973
2	39.219	17572482	50.027



Peak Table

Detector A Ch1 300nm

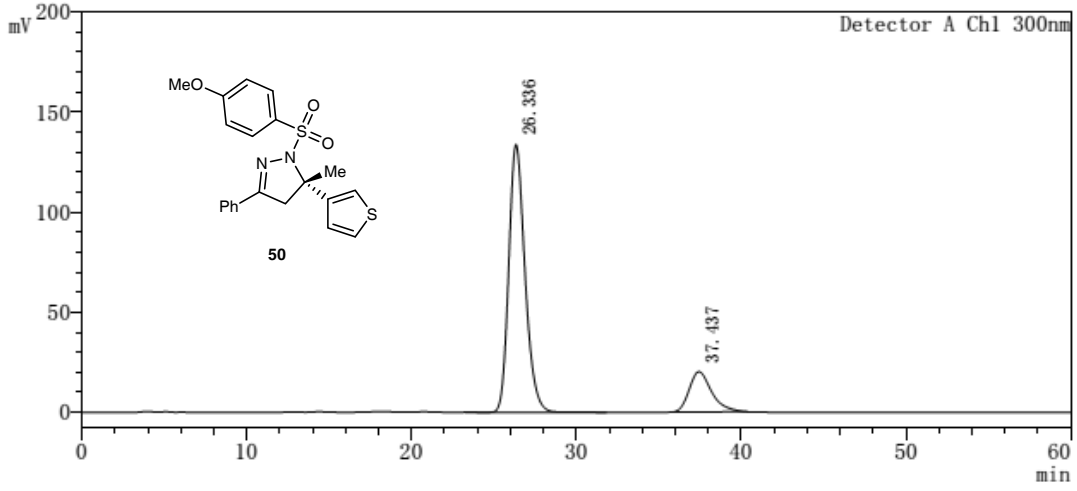
Peak#	Ret. Time	Area	Area%
1	25.975	16534331	85.100
2	39.374	2894925	14.900



Peak Table

Detector A Ch1 300nm

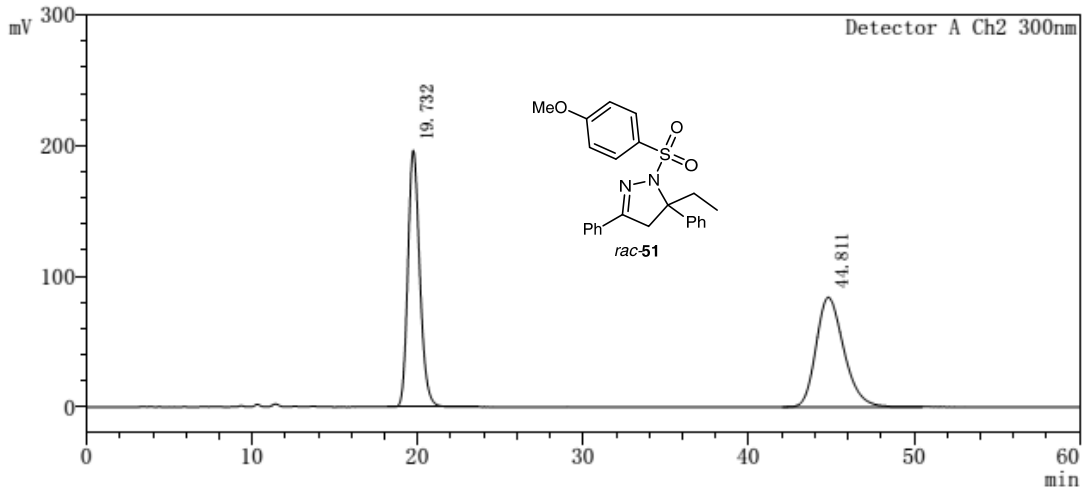
Peak#	Ret. Time	Area	Area%
1	25.979	24482725	50.008
2	36.802	24474409	49.992



Peak Table

Detector A Ch1 300nm

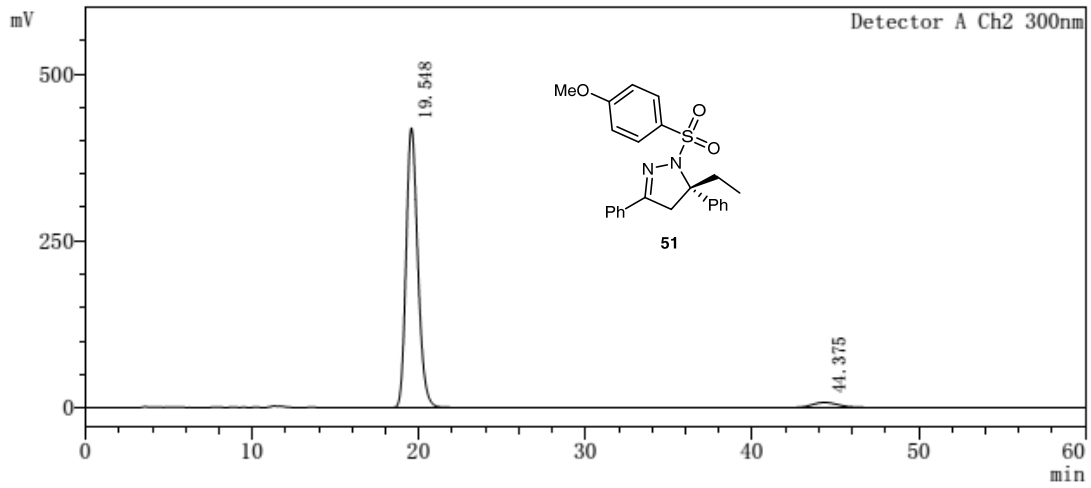
Peak#	Ret. Time	Area	Area%
1	26.336	9175954	82.789
2	37.437	1907529	17.211



Peak Table

Detector A Ch2 300nm

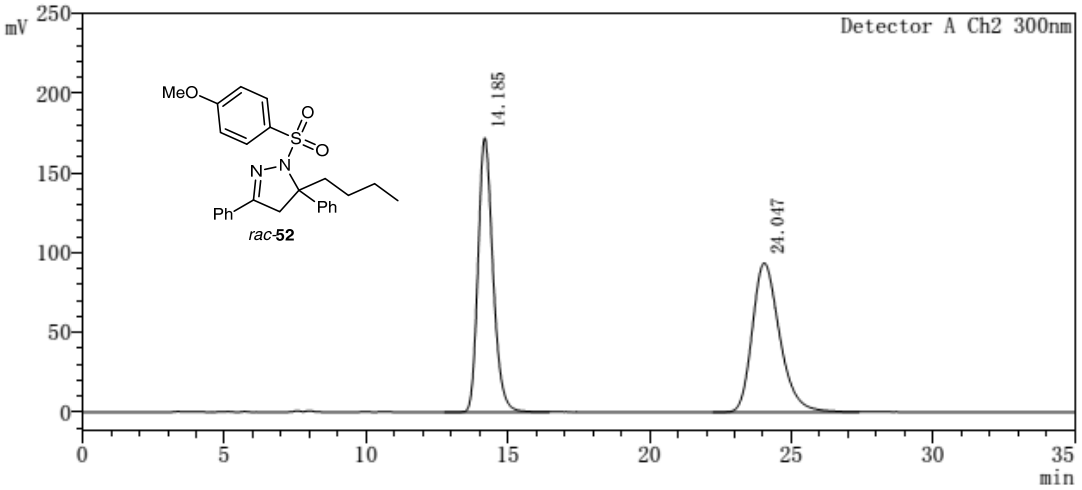
Peak#	Ret. Time	Area	Area%
1	19.732	9819079	50.000
2	44.811	9819198	50.000



Peak Table

Detector A Ch2 300nm

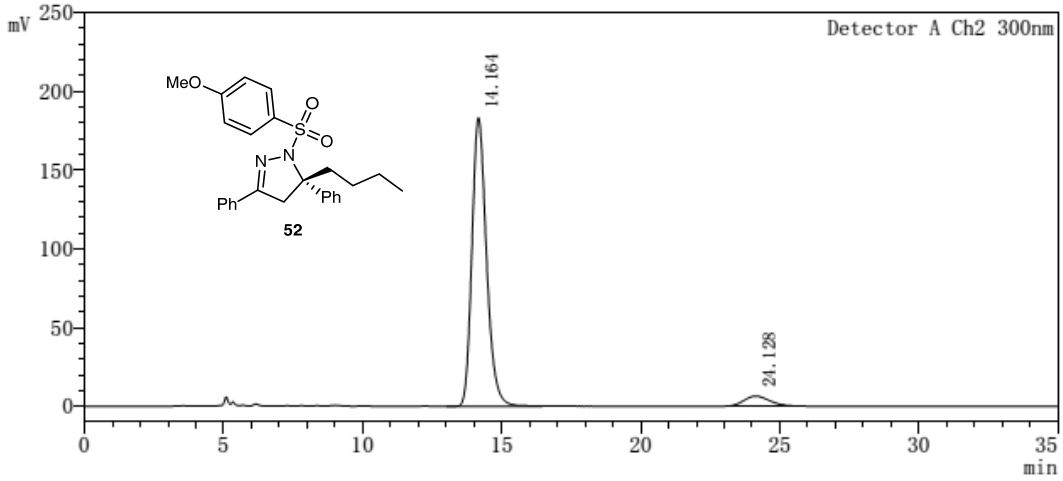
Peak#	Ret. Time	Area	Area%
1	19.548	20522697	96.034
2	44.375	847626	3.966



Peak Table

Detector A Ch2 300nm

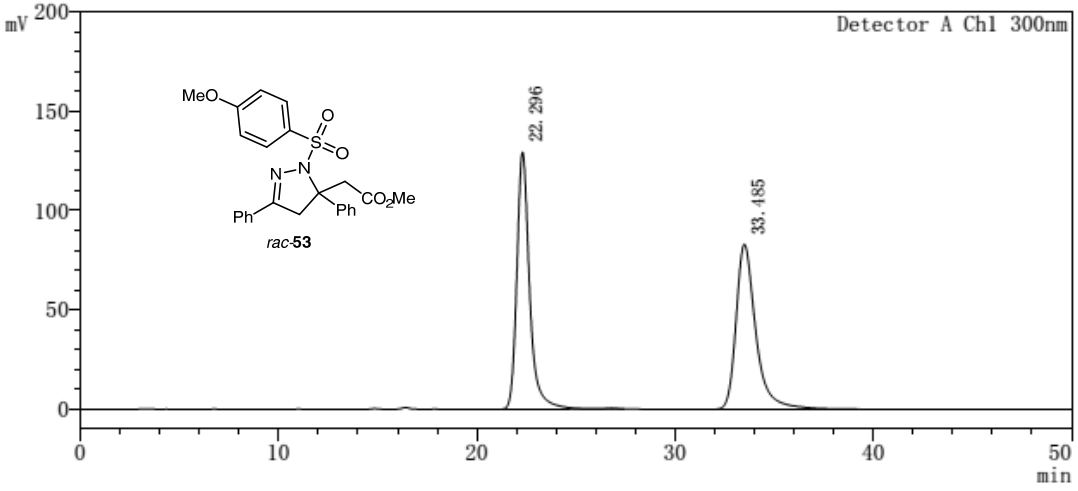
Peak#	Ret. Time	Area	Area%
1	14.185	6284167	49.980
2	24.047	6289150	50.020



Peak Table

Detector A Ch2 300nm

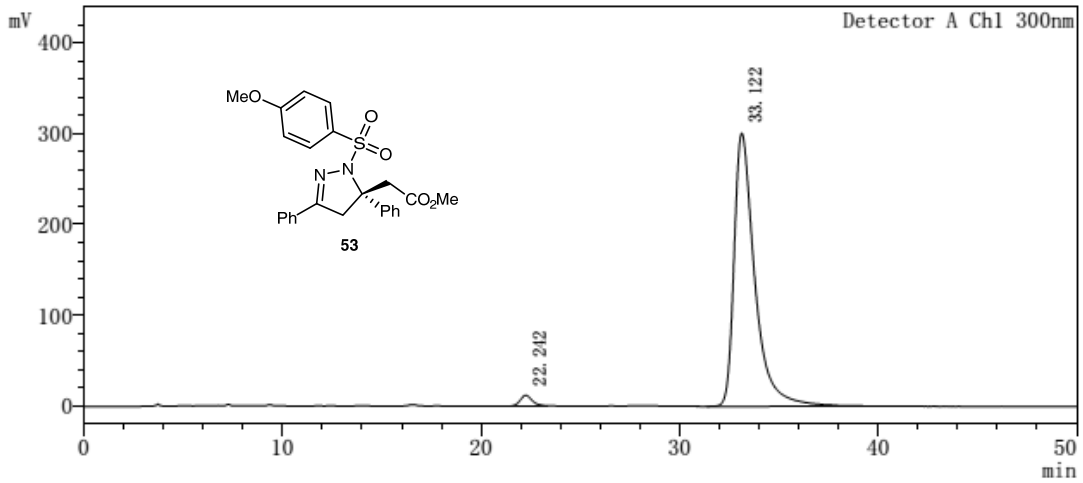
Peak#	Ret. Time	Area	Area%
1	14.164	6674588	94.316
2	24.128	402218	5.684



Peak Table

Detector A Ch1 300nm

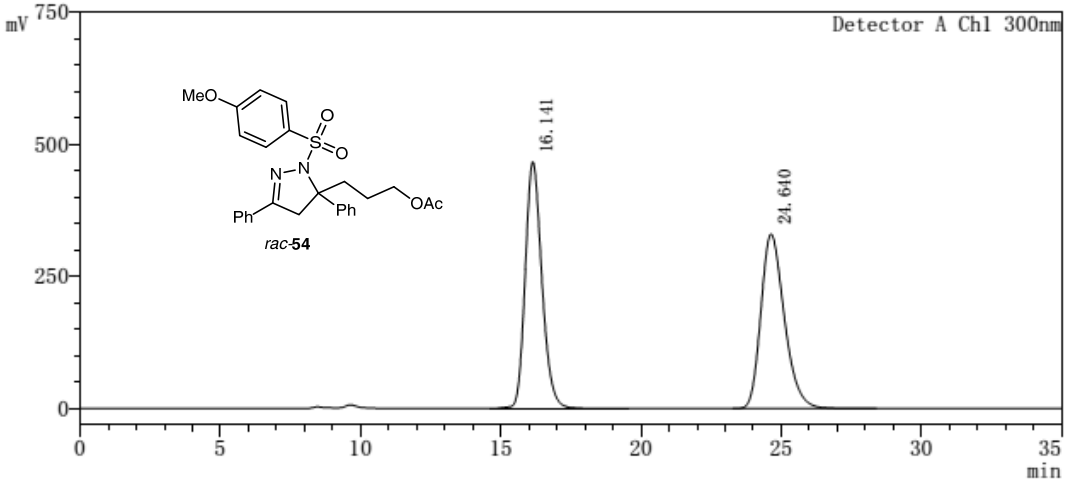
Peak#	Ret. Time	Area	Area%
1	22.296	5793688	50.067
2	33.485	5778141	49.933



Peak Table

Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	22.242	476209	2.134
2	33.122	21838512	97.866



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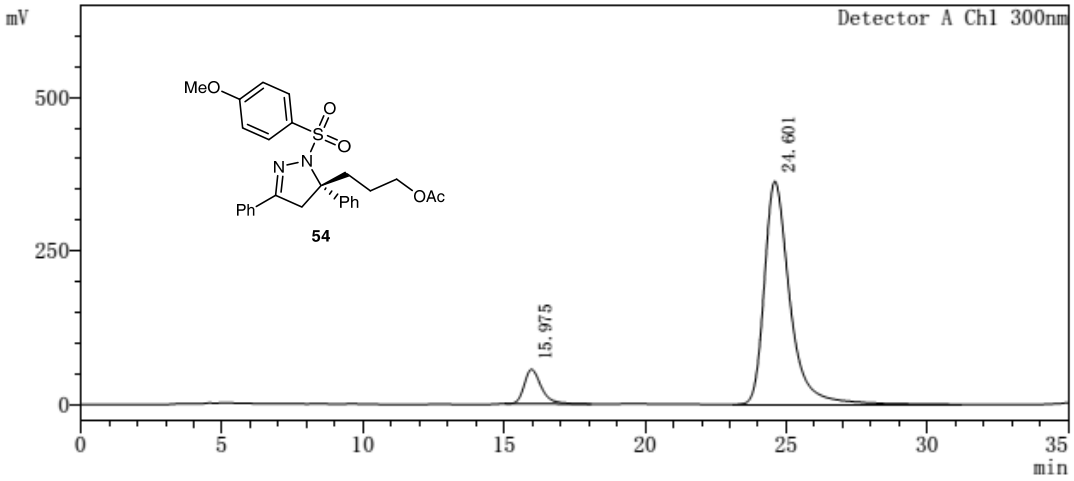
Peak Table

Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	16.141	19312547	50.153
2	24.640	19194683	49.847



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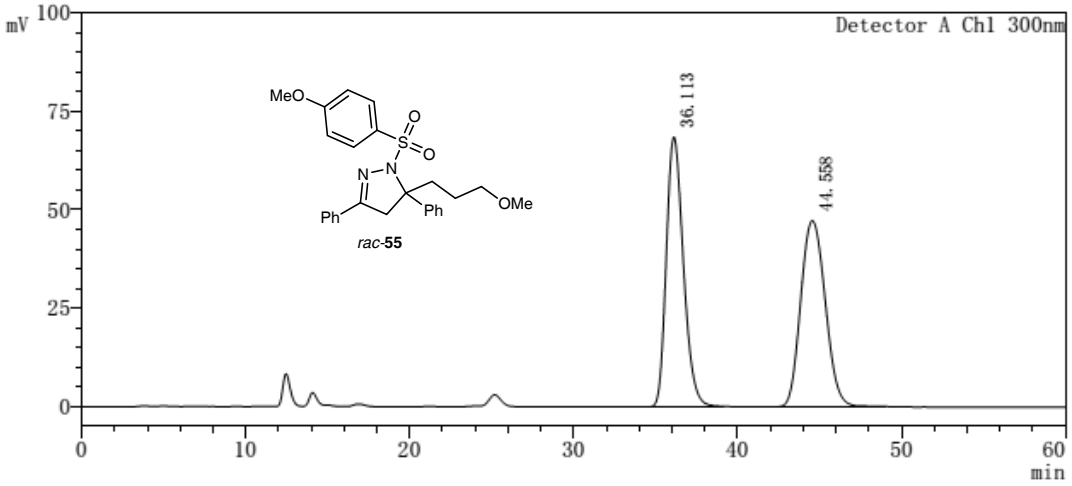
Peak Table

Detector A Ch1 300nm

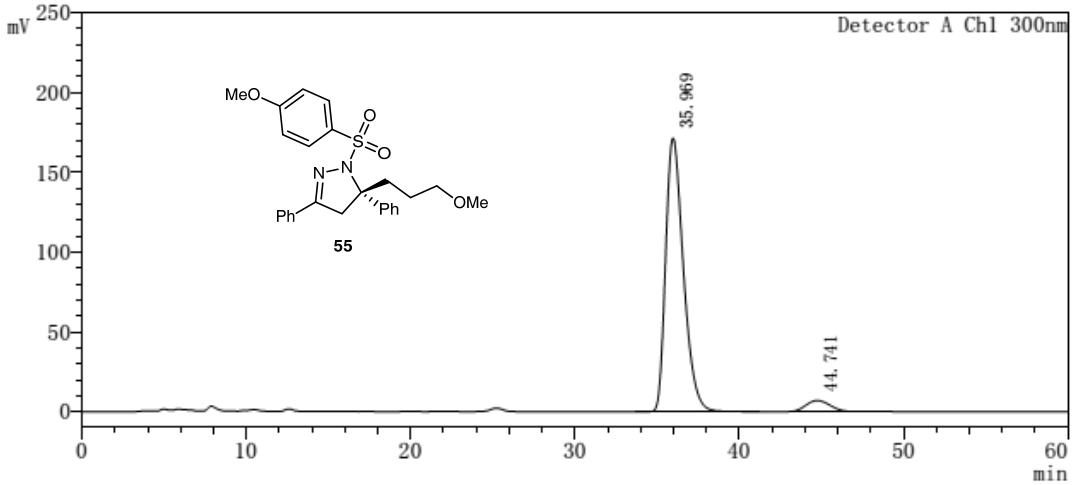
Peak#	Ret. Time	Area	Area%
1	15.975	2347358	9.338
2	24.601	22790414	90.662



Peak Table

Detector A Ch1 300nm

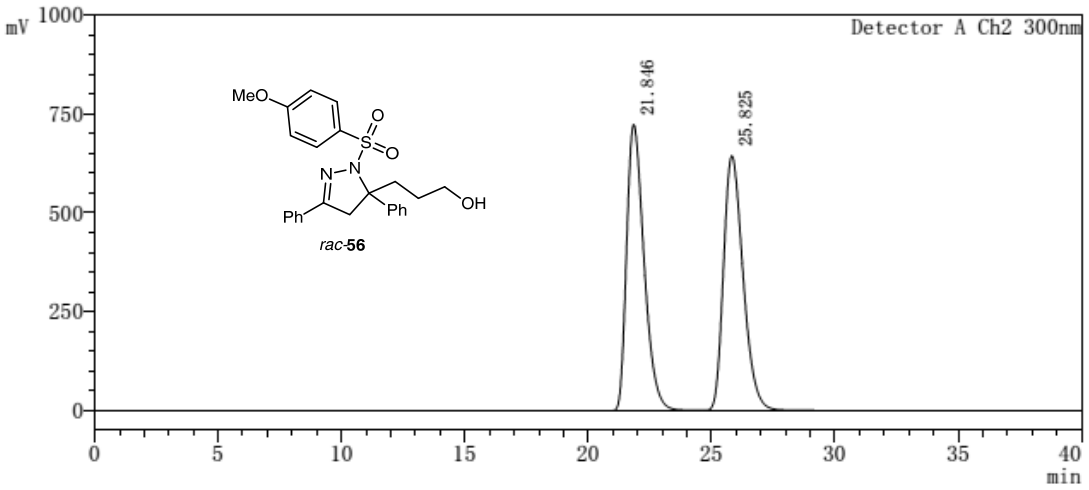
Peak#	Ret. Time	Area	Area%
1	36.113	4934019	50.003
2	44.558	4933434	49.997



Peak Table

Detector A Ch1 300nm

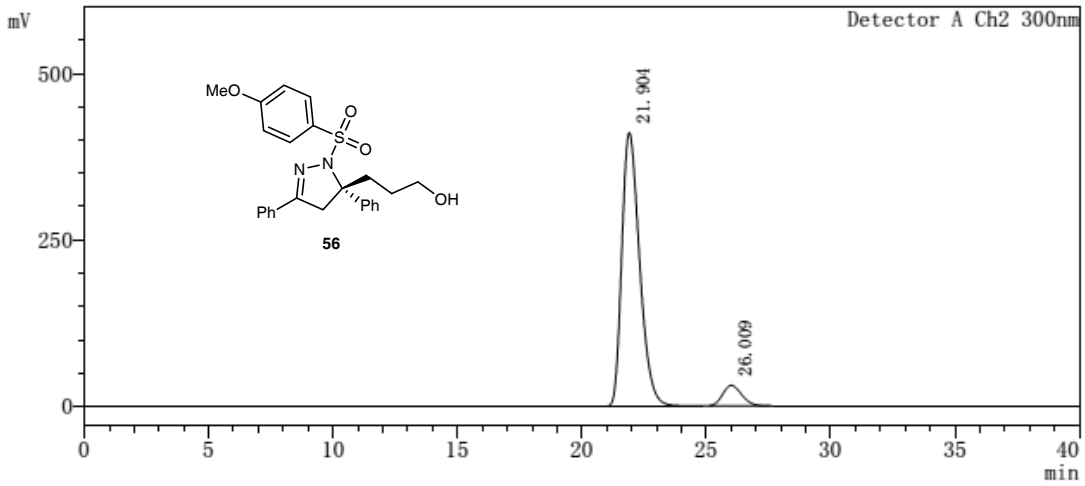
Peak#	Ret. Time	Area	Area%
1	35.969	12813676	94.809
2	44.741	701576	5.191



Peak Table

Detector A Ch2 300nm

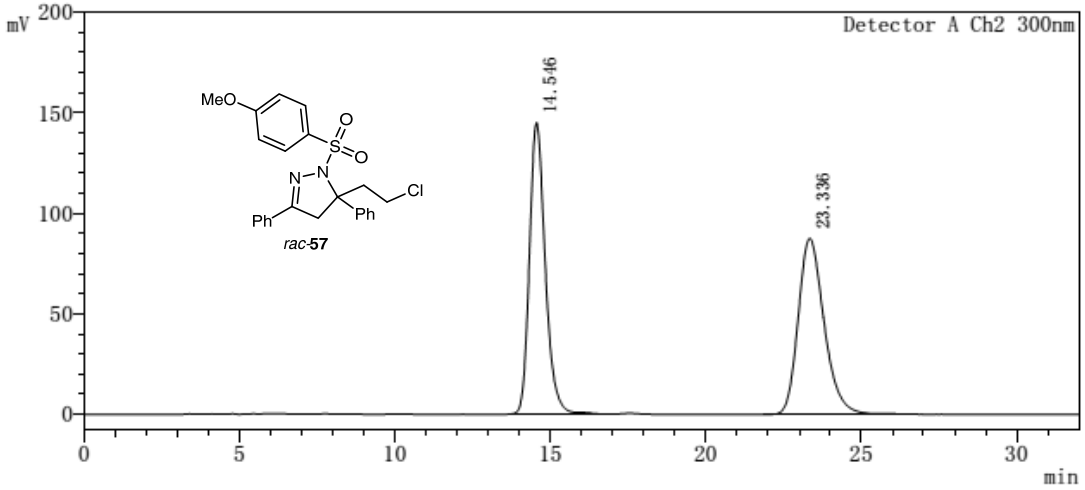
Peak#	Ret. Time	Area	Area%
1	21.846	35512132	49.987
2	25.825	35529904	50.013



Peak Table

Detector A Ch2 300nm

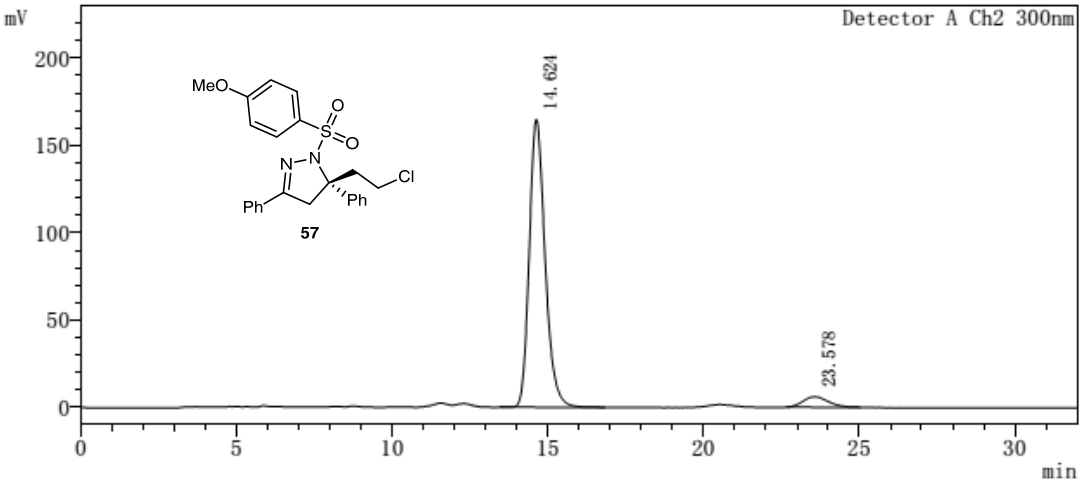
Peak#	Ret. Time	Area	Area%
1	21.904	20456793	92.503
2	26.009	1657903	7.497



Peak Table

Detector A Ch2 300nm

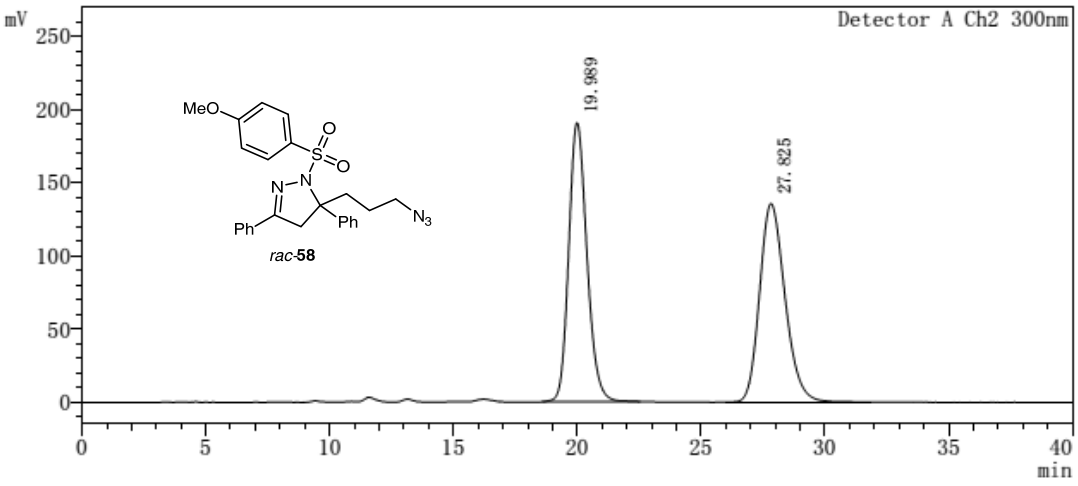
Peak#	Ret. Time	Area	Area%
1	14.546	5131878	50.134
2	23.336	5104538	49.866



Peak Table

Detector A Ch2 300nm

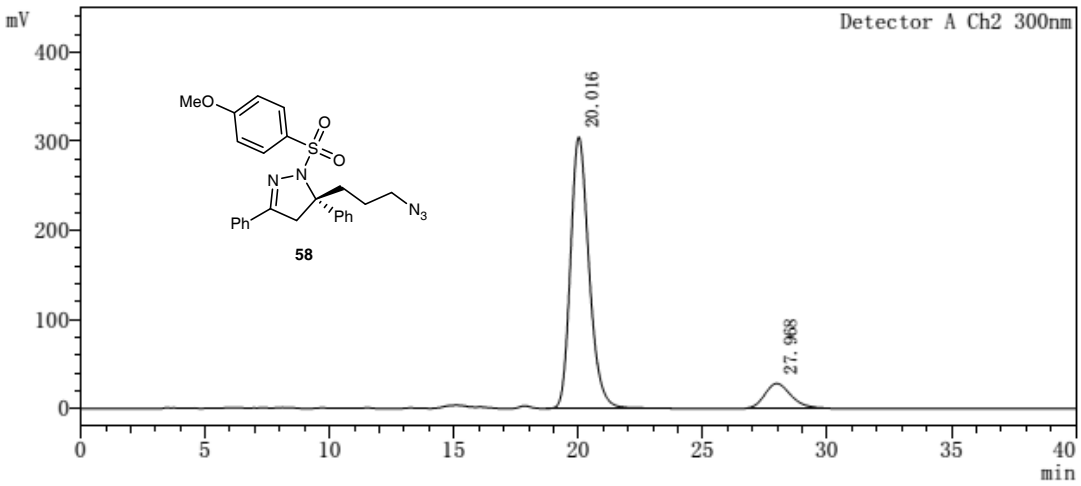
Peak#	Ret. Time	Area	Area%
1	14.624	5828562	94.493
2	23.578	339718	5.507



Peak Table

Detector A Ch2 300nm

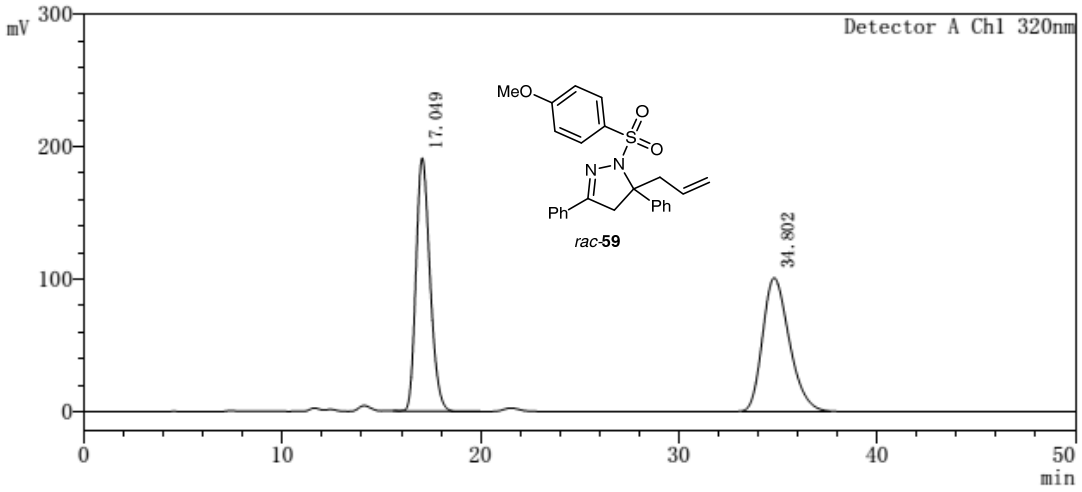
Peak#	Ret. Time	Area	Area%
1	19.989	9716176	50.089
2	27.825	9681466	49.911



Peak Table

Detector A Ch2 300nm

Peak#	Ret. Time	Area	Area%
1	20.016	15754215	88.857
2	27.968	1975680	11.143



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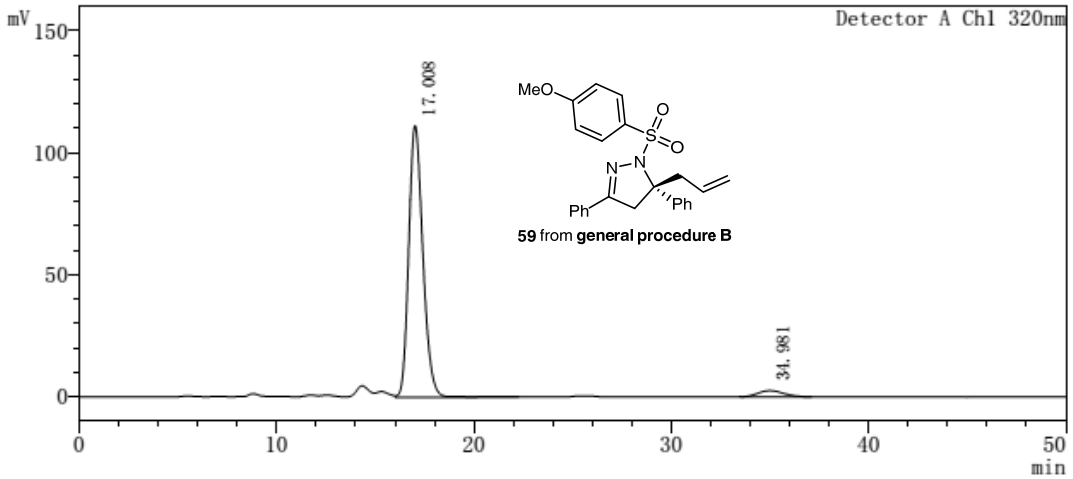
Peak Table

Detector A Ch1 320nm

Peak#	Ret. Time	Area	Area%
1	17.049	9387711	49.901
2	34.802	9425080	50.099



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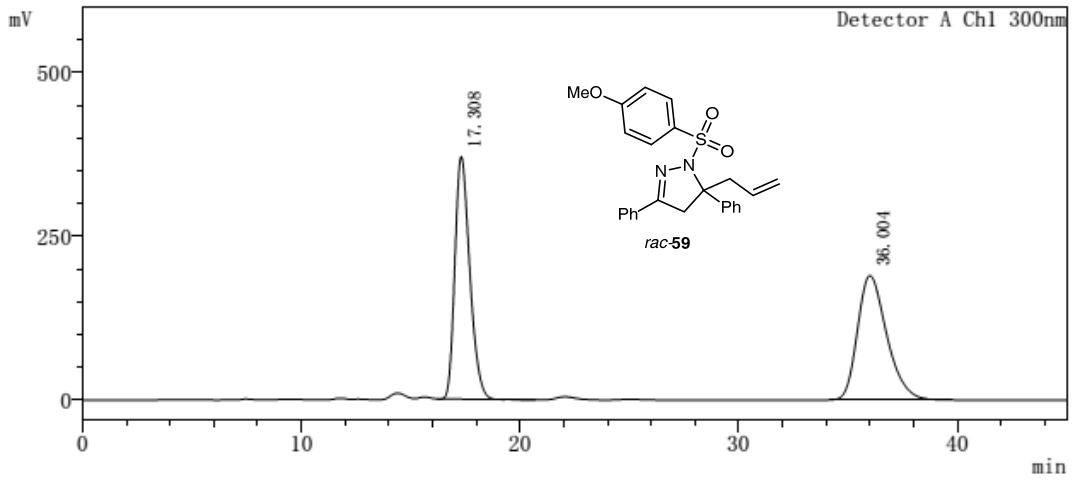
Peak Table

Detector A Ch1 320nm

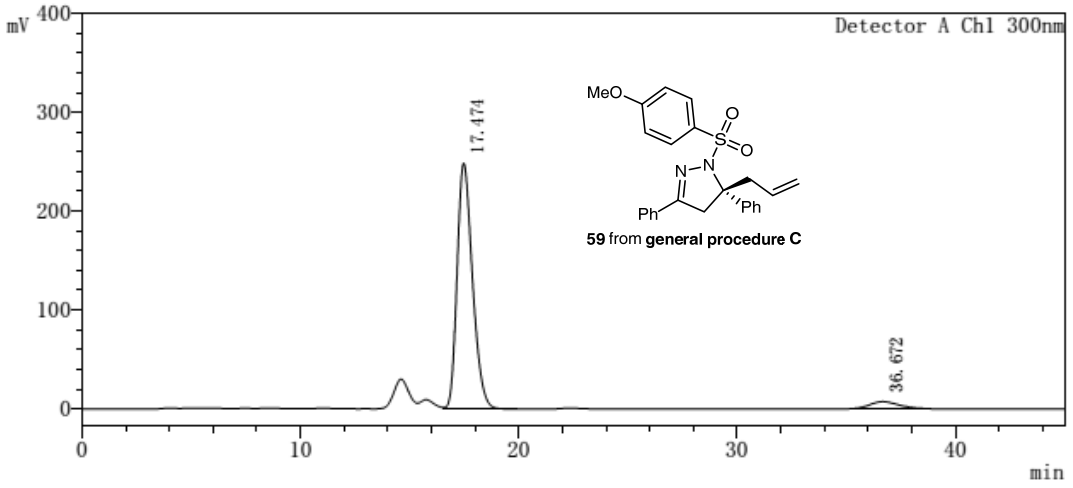
Peak#	Ret. Time	Area	Area%
1	17.008	5531451	95.948
2	34.981	233588	4.052



Peak Table

Detector A Ch1 300nm

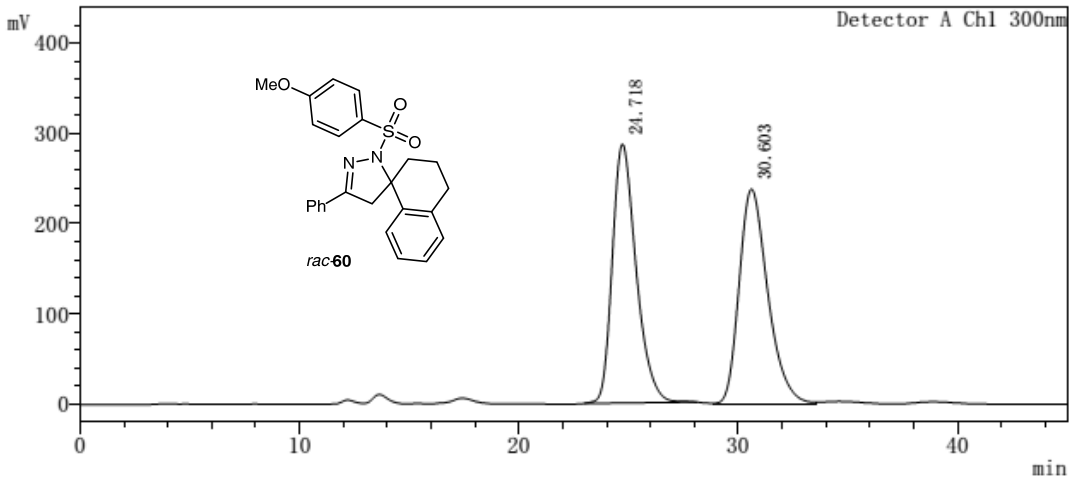
Peak#	Ret. Time	Area	Area%
1	17.308	17616993	49.955
2	36.004	17648450	50.045



Peak Table

Detector A Ch1 300nm

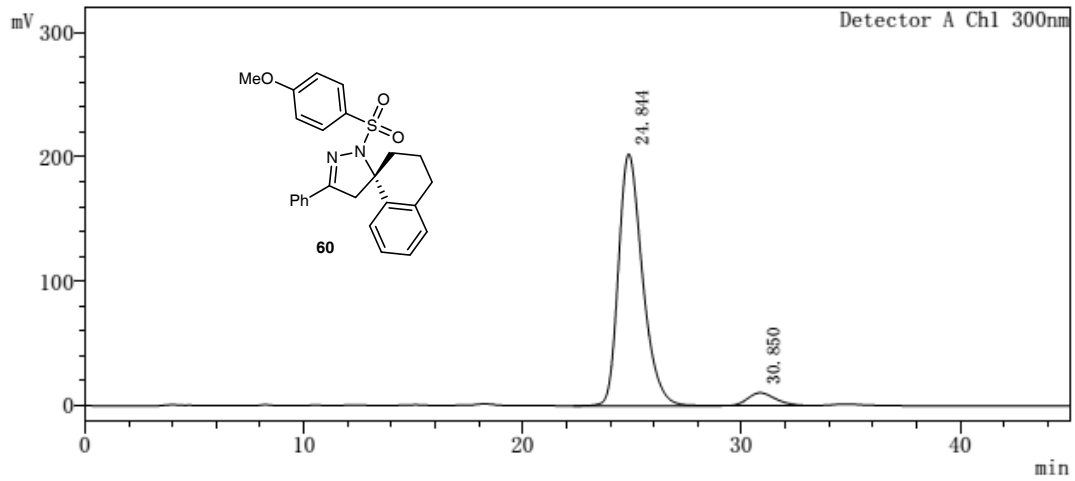
Peak#	Ret. Time	Area	Area%
1	17.474	12146541	94.943
2	36.672	647001	5.057



Peak Table

Detector A Ch1 300nm

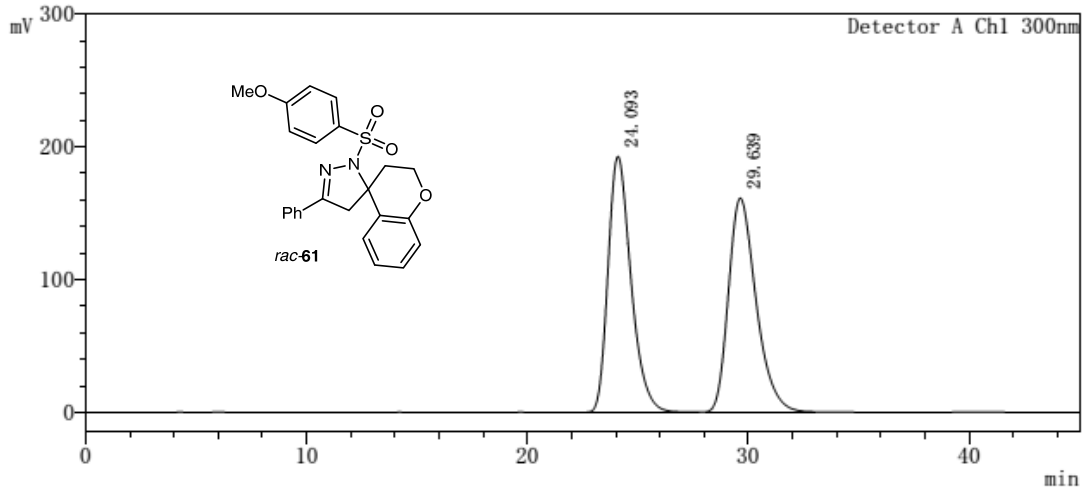
Peak#	Ret. Time	Area	Area%
1	24.718	21708117	49.966
2	30.603	21737589	50.034



Peak Table

Detector A Ch1 300nm

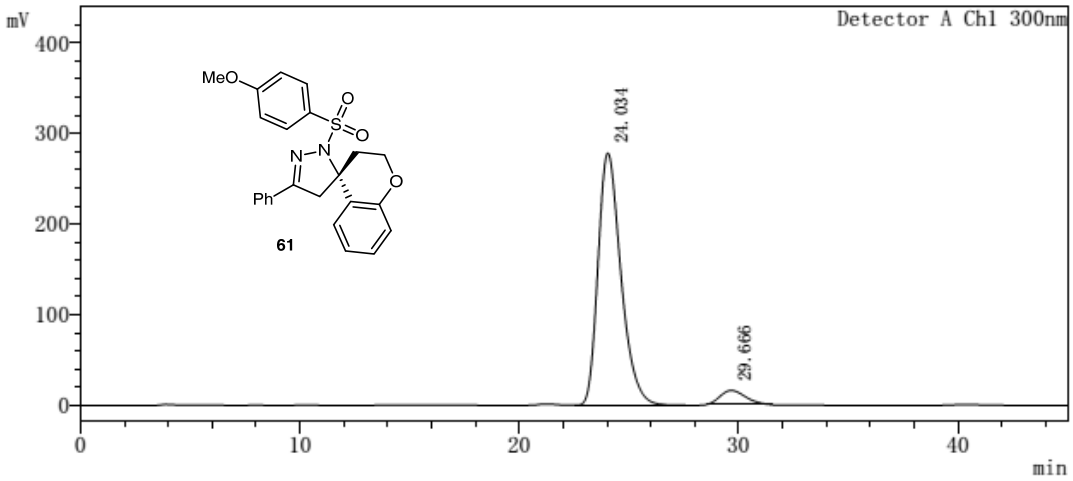
Peak#	Ret. Time	Area	Area%
1	24.844	15481160	94.540
2	30.850	894059	5.460



Peak Table

Detector A Ch1 300nm

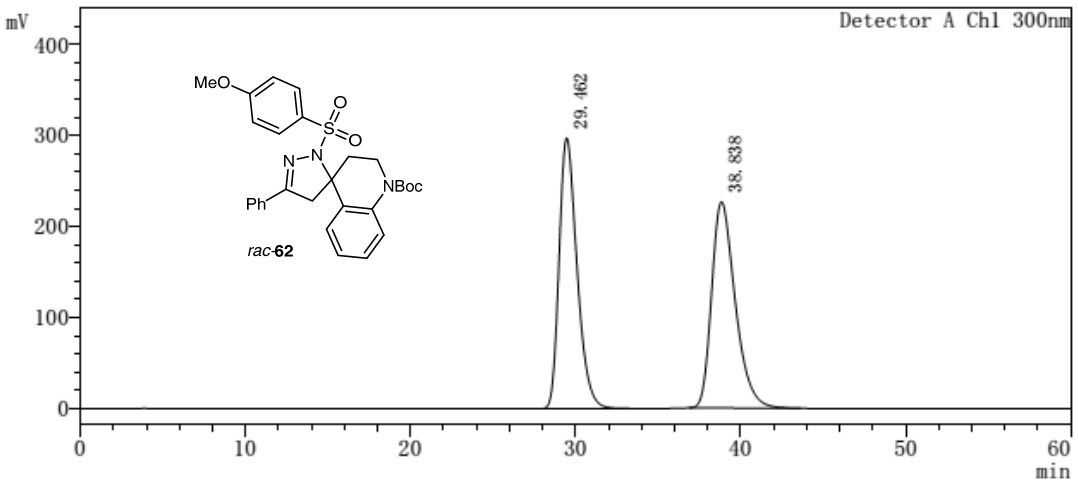
Peak#	Ret. Time	Area	Area%
1	24.093	13930984	49.873
2	29.639	14001817	50.127



Peak Table

Detector A Ch1 300nm

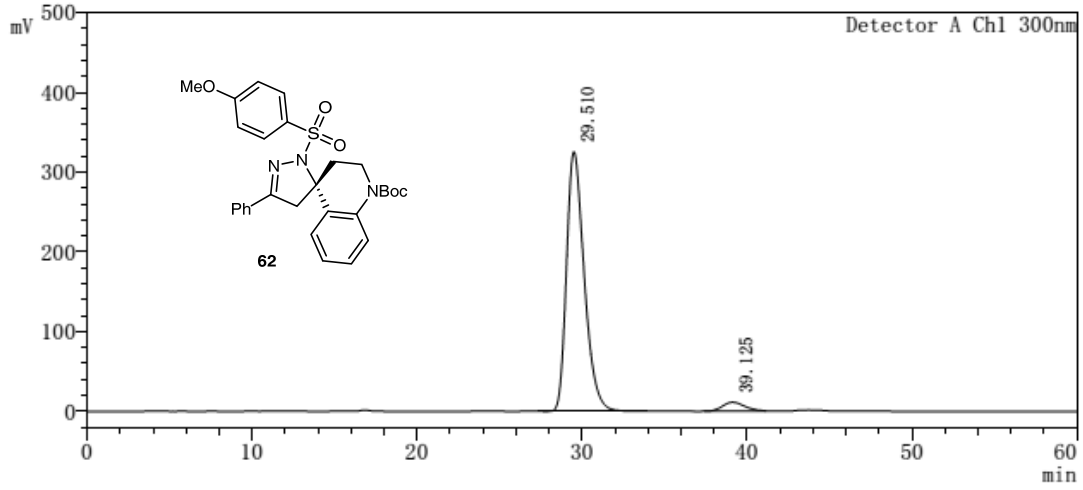
Peak#	Ret. Time	Area	Area%
1	24.034	20218567	94.065
2	29.666	1275649	5.935



Peak Table

Detector A Ch1 300nm

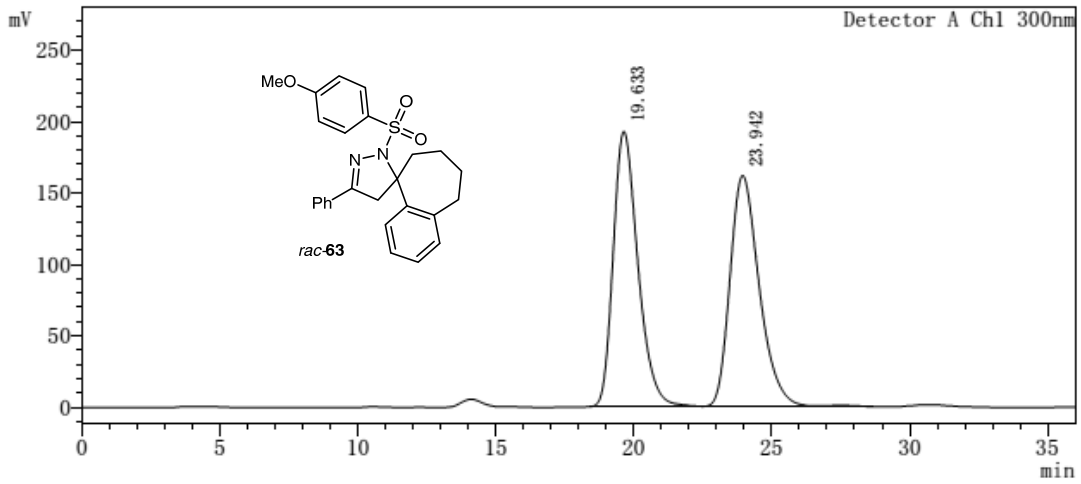
Peak#	Ret. Time	Area	Area%
1	29.462	22393964	49.808
2	38.838	22566222	50.192



Peak Table

Detector A Ch1 300nm

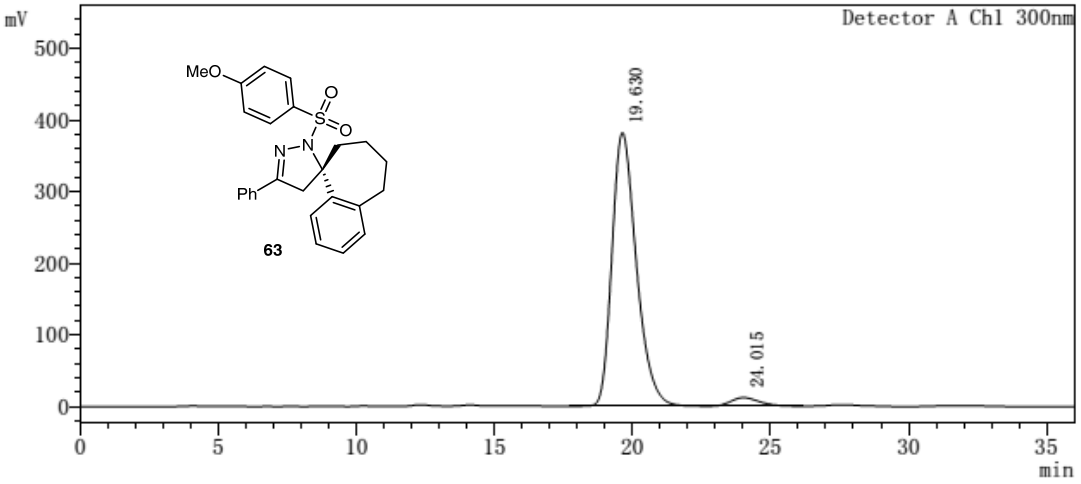
Peak#	Ret. Time	Area	Area%
1	29.510	24252973	95.935
2	39.125	1027540	4.065



Peak Table

Detector A Ch1 300nm

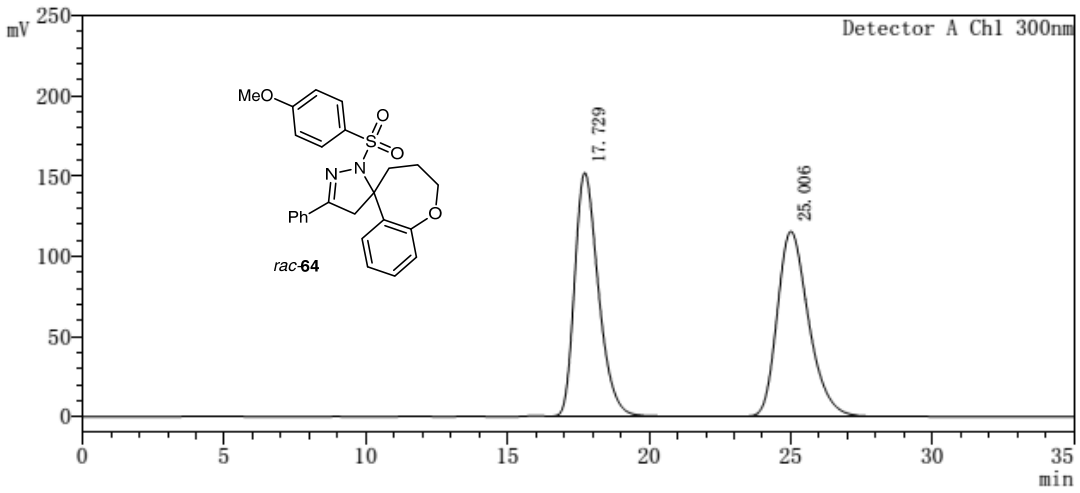
Peak#	Ret. Time	Area	Area%
1	19.633	11973190	50.050
2	23.942	11949144	49.950



Peak Table

Detector A Ch1 300nm

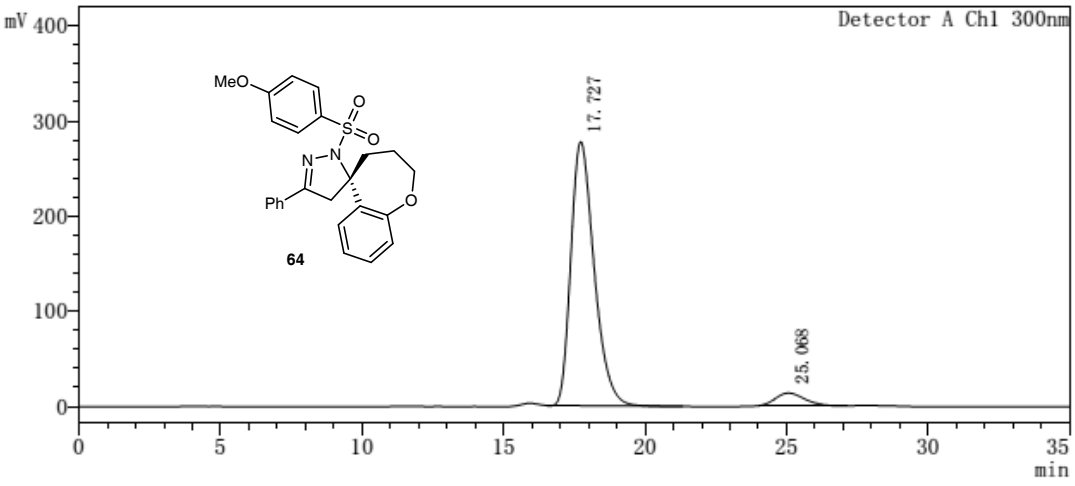
Peak#	Ret. Time	Area	Area%
1	19.630	23529843	96.446
2	24.015	866959	3.554



Peak Table

Detector A Ch1 300nm

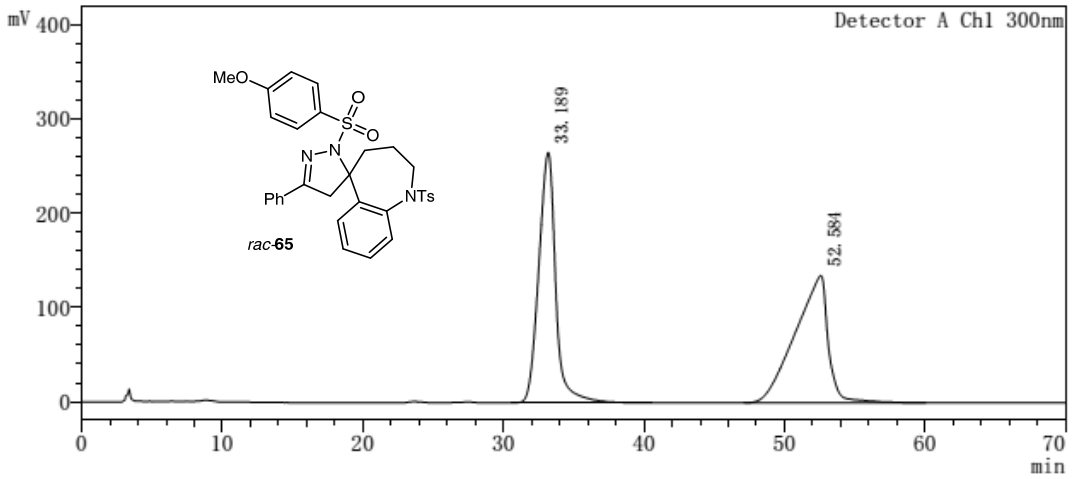
Peak#	Ret. Time	Area	Area%
1	17.729	8865059	49.900
2	25.006	8900690	50.100



Peak Table

Detector A Ch1 300nm

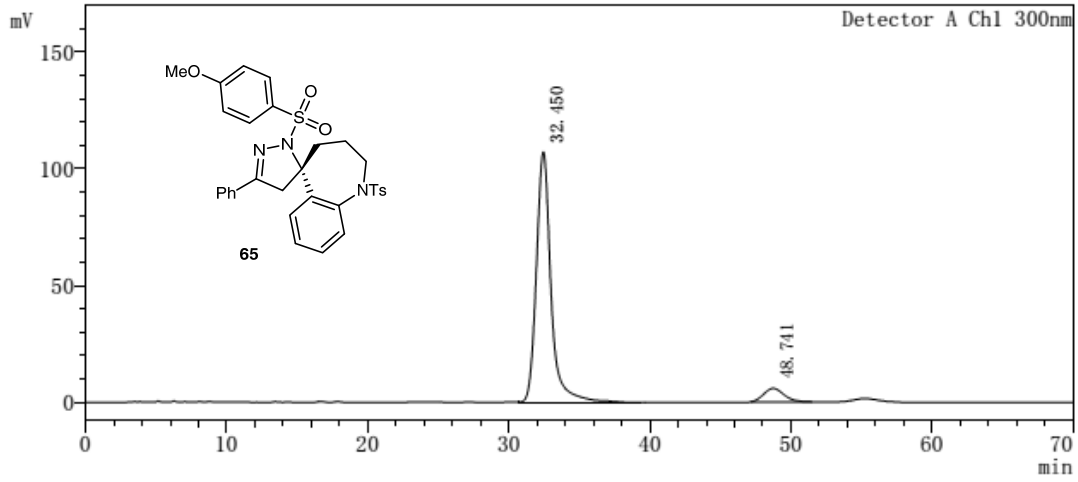
Peak#	Ret. Time	Area	Area%
1	17.727	15886244	94.400
2	25.068	942430	5.600



Peak Table

Detector A Ch1 300nm

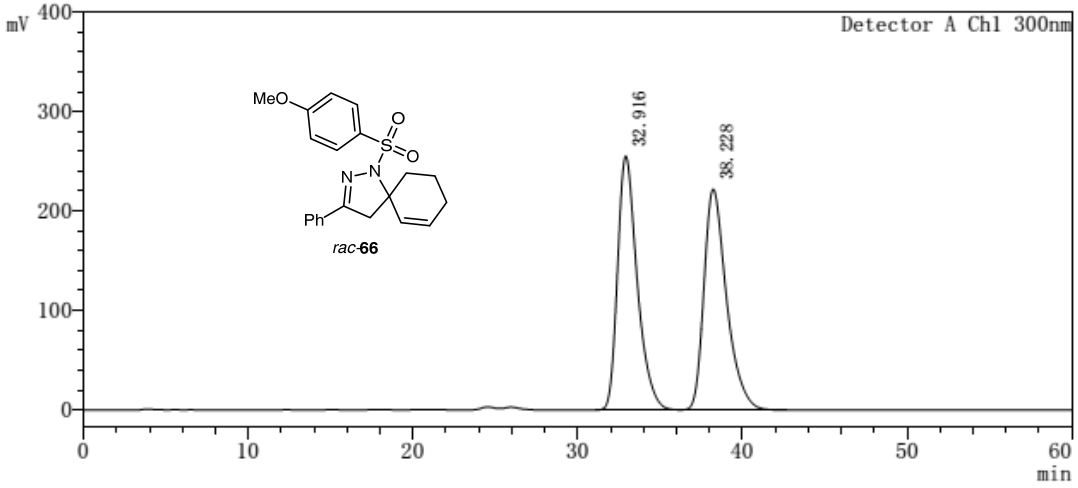
Peak#	Ret. Time	Area	Area%
1	33.189	22209048	50.000
2	52.584	22209389	50.000



Peak Table

Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	32.450	7762909	93.094
2	48.741	575839	6.906



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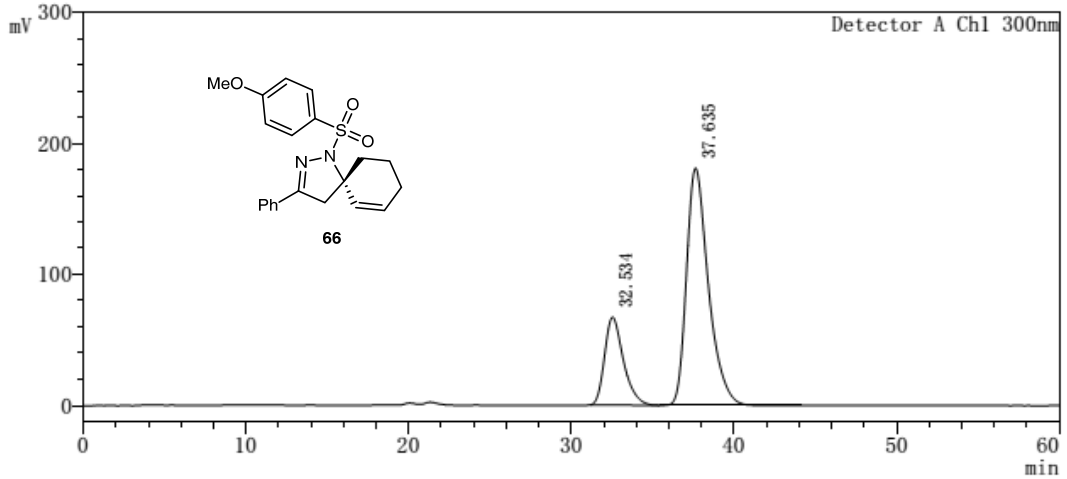
Peak Table

Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	32.916	21191883	50.002
2	38.228	21189904	49.998



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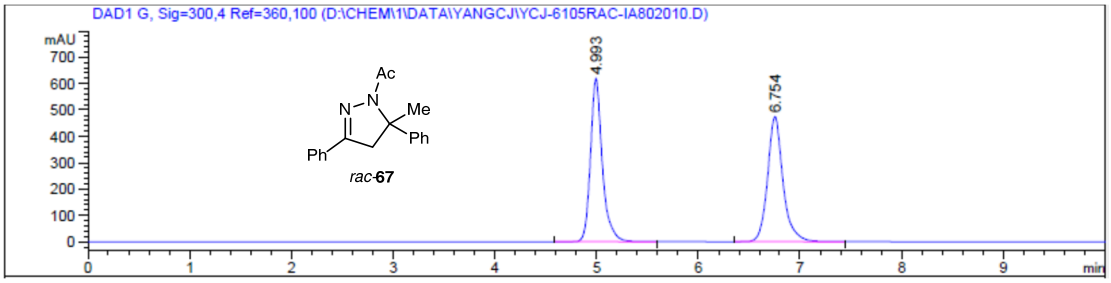
Peak Table

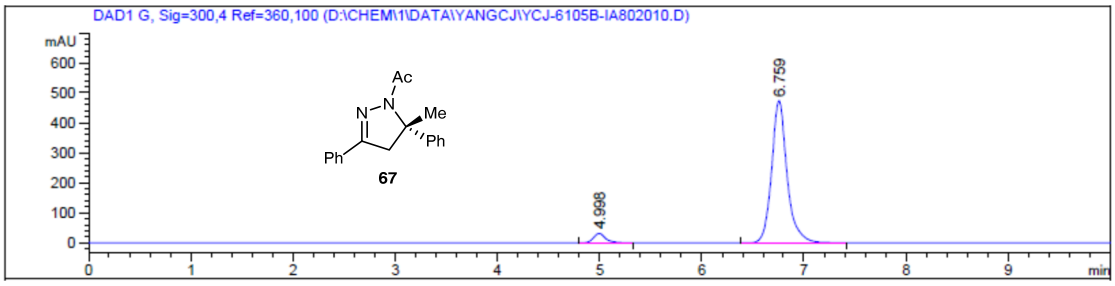
Detector A Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	32.534	5413626	24.182
2	37.635	16973811	75.818



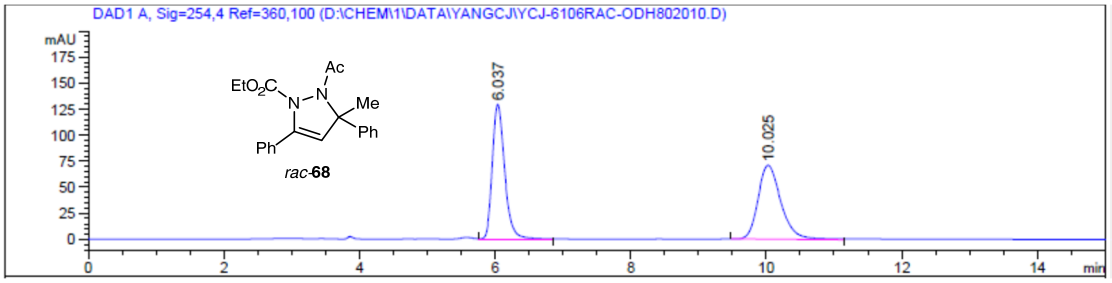
Signal 7: DAD1 G, Sig=300,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.993	MM R	0.1359	5046.91748	618.93799	50.0113
2	6.754	MM R	0.1771	5044.64355	474.83377	49.9887
Totals :				1.00916e4	1093.77176	



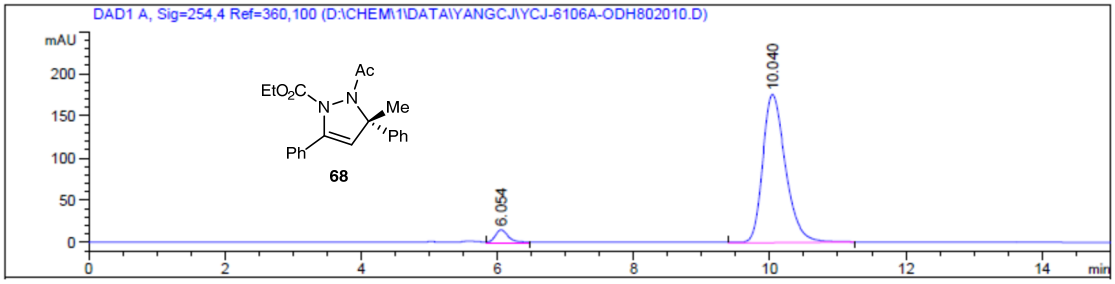
Signal 7: DAD1 G, Sig=300,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.998	MM R	0.1428	277.39359	32.38056	5.0949
2	6.759	MM R	0.1809	5167.17236	476.04031	94.9051
Totals :				5444.56595	508.42087	



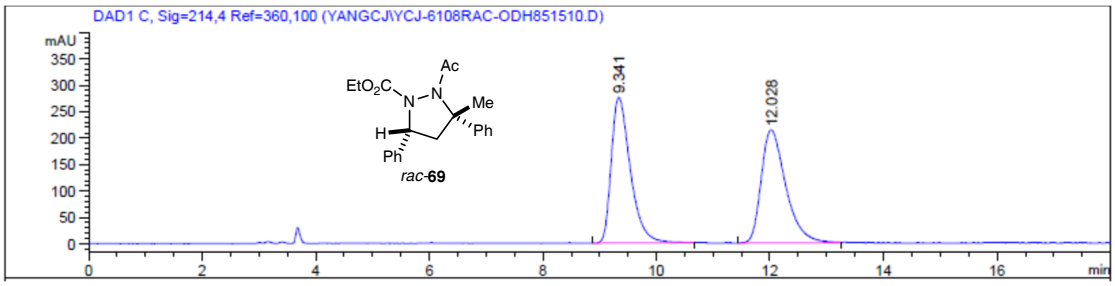
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.037	MM R	0.2137	1666.33423	129.97499	50.0435
2	10.025	MM R	0.3911	1663.43774	70.89042	49.9565
Totals :				3329.77197	200.86541	



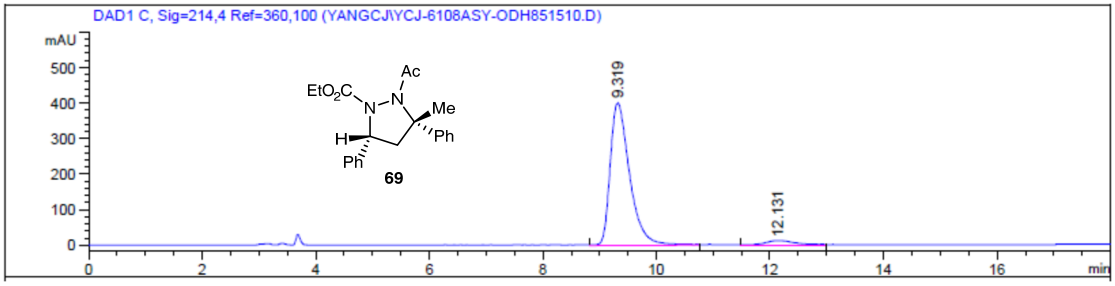
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.054	MM R	0.2358	217.70305	15.38709	5.0439
2	10.040	MM R	0.3886	4098.46191	175.75856	94.9561
Totals :				4316.16496	191.14565	



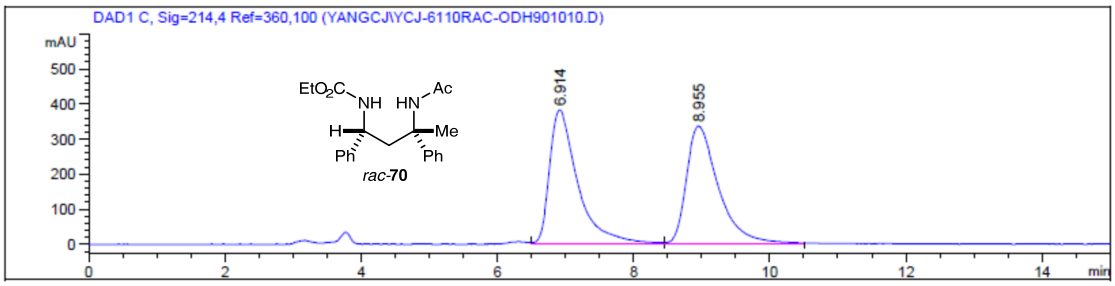
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.341	BB	0.3614	6457.67285	275.60062	50.0775
2	12.028	BV	0.4372	6437.68604	213.88199	49.9225
Totals :				1.28954e4	489.48260	



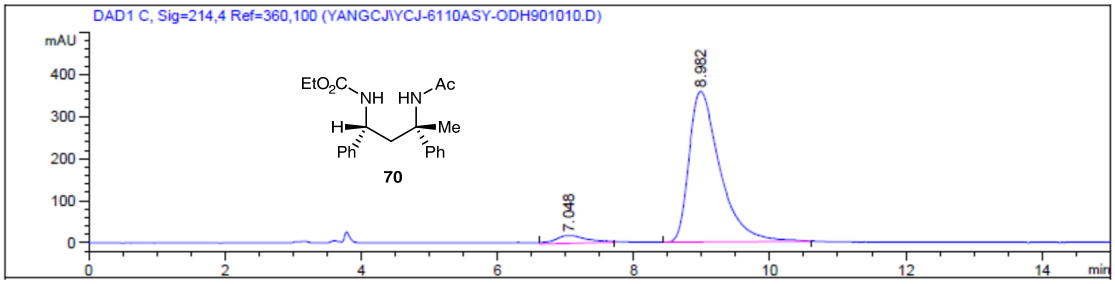
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.319	MM R	0.3987	9599.21680	401.31674	94.8819
2	12.131	MM R	0.6332	517.80170	13.62902	5.1181
Totals :				1.01170e4	414.94577	



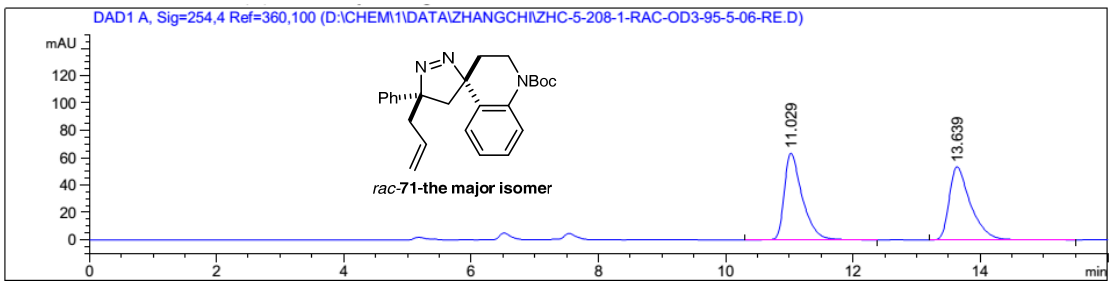
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.914	MM R	0.4829	1.10790e4	382.36566	49.9949
2	8.955	MM R	0.5489	1.10812e4	336.43750	50.0051
Totals :				2.21602e4	718.80316	



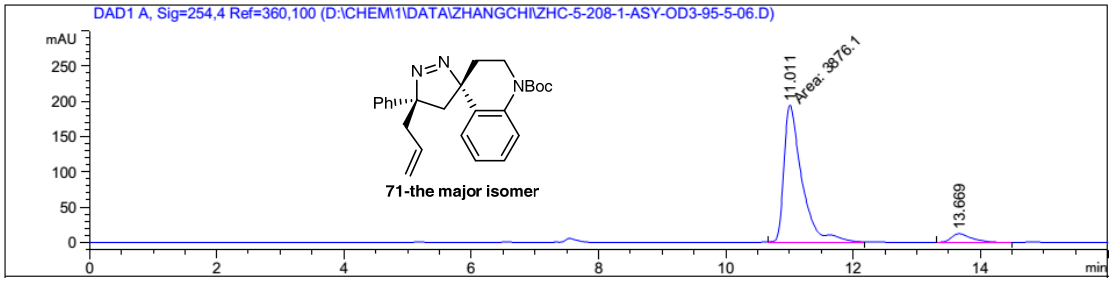
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.048	MM R	0.5339	591.06030	18.45221	4.9490
2	8.982	BV	0.4778	1.13519e4	358.14877	95.0510
Totals :				1.19430e4	376.60098	



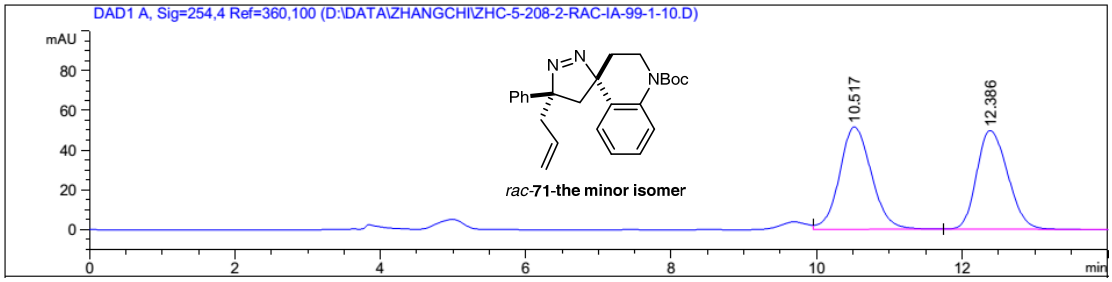
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.029	BV	0.2939	1255.36230	63.70195	50.1069
2	13.639	BB	0.3446	1250.00586	53.50371	49.8931
Totals :				2505.36816	117.20566	



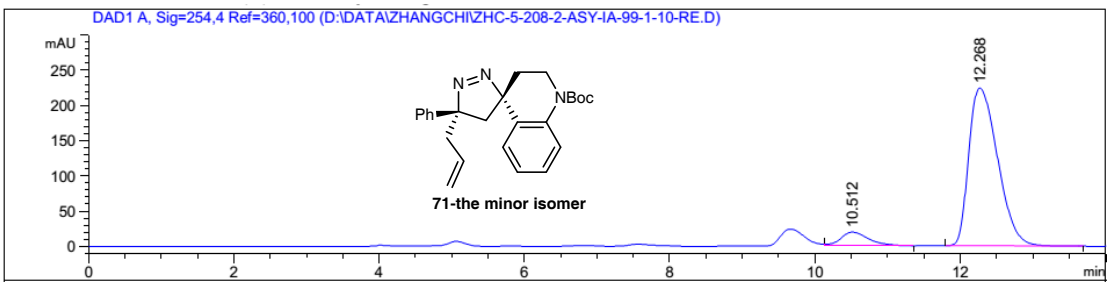
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.011	MM	0.3309	3876.09546	195.20370	93.1891
2	13.669	VV	0.3335	283.29224	12.44654	6.8109
Totals :				4159.38770	207.65025	



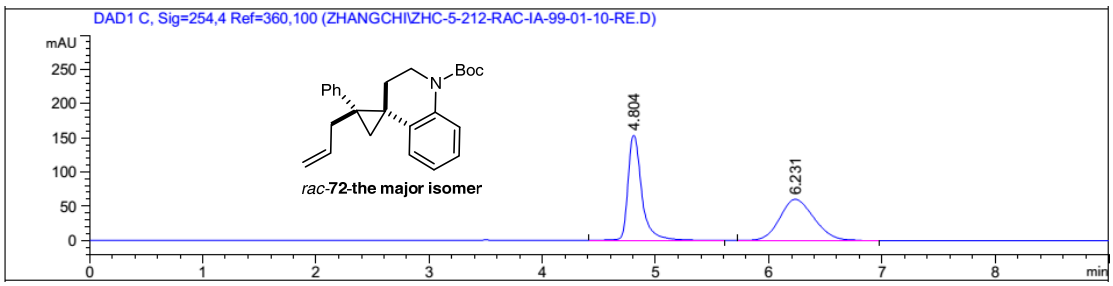
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.517	VB	0.4730	1578.72046	51.58894	51.5856
2	12.386	BBA	0.4720	1481.67188	49.67340	48.4144
Totals :				3060.39233	101.26235	



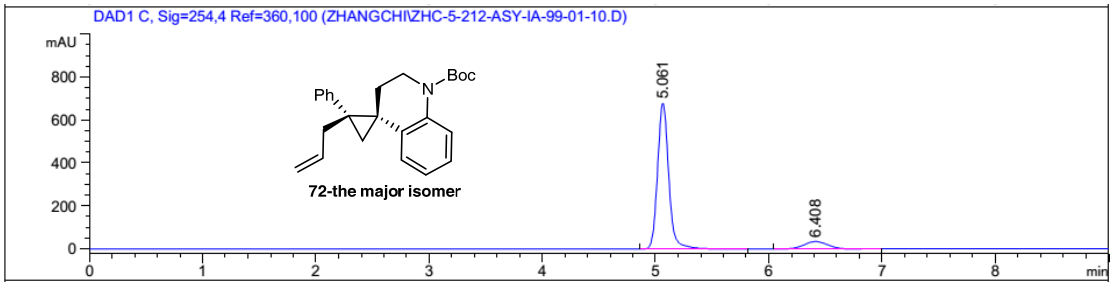
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.512	VB	0.4125	528.95630	19.50029	7.8937
2	12.268	BB	0.4398	6172.04297	223.75766	92.1063
Totals :				6700.99927	243.25795	



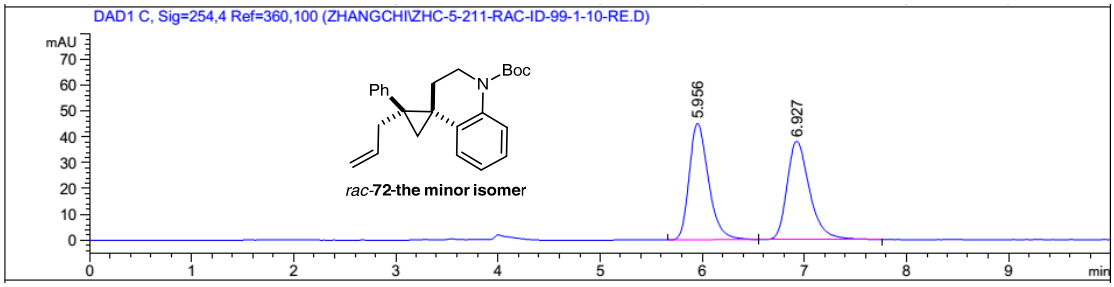
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.804	BB	0.1284	1297.47888	153.88597	50.7697
2	6.231	BB	0.3239	1258.13538	60.18726	49.2303
Totals :				2555.61426	214.07323	



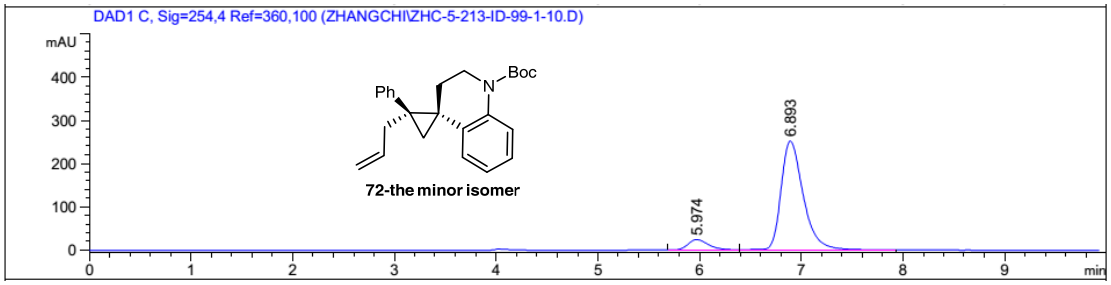
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.061	BB	0.1059	4636.16309	677.26105	90.1340
2	6.408	BB	0.2284	507.46854	34.73858	9.8660
Totals :				5143.63162	711.99963	



Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.956	BB	0.2010	591.40784	45.09174	50.4834
2	6.927	BB	0.2338	580.08276	38.06323	49.5166
Totals :				1171.49060	83.15497	



Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.974	BB	0.2111	331.63525	24.01363	8.0127
2	6.893	BB	0.2303	3807.25513	251.97247	91.9873
Totals :				4138.89038	275.98610	

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