

Supplementary Information

Nitrogen-Centered Radical-Mediated α -Sulfonimidation of Ketones

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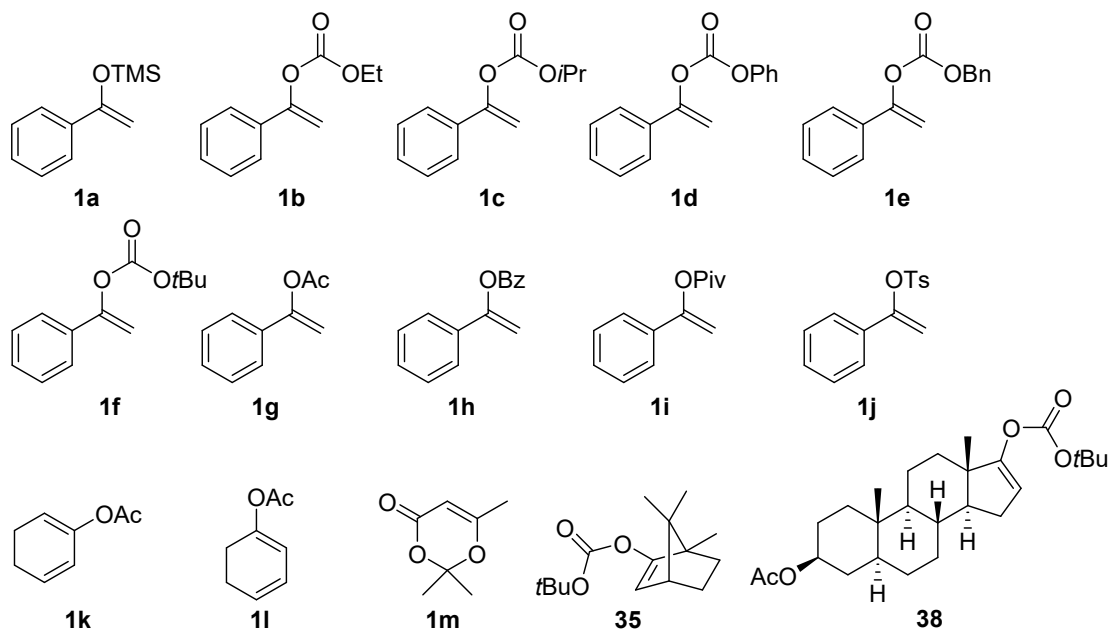
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1. General information

Anhydrous DCM, DCE and MeCN were refluxed with CaH₂ and freshly distilled prior to use; anhydrous THF were distilled over sodium and benzophenone ketyl under argon atmosphere; anhydrous EtOAc and MeNO₂ were dealt with fully dried 4Å molecular sieves; anhydrous MeOH was distilled over magnesium under argon atmosphere; all other solvents and reagents were used from commercial sources without further purifications. The silica gel (200-300 meshes) was used for column chromatography. Thin layer chromatographies (TLC) were carried out on GF254 plates (0.25 mm layer thickness).

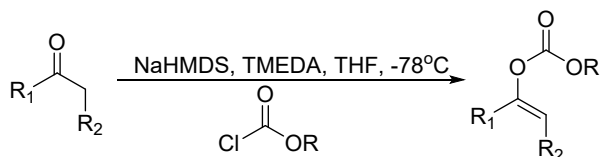
¹H NMR, ¹³C NMR experiments were performed on Bruker DRX-600 NMR or Bruker-500 spectrometer at ambient temperature. The residual solvent protons (¹H) or the solvent carbons (¹³C) were used as internal standards. ¹H NMR data were presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). Chemical shifts (δ) were given in ppm with reference to solvent signals [¹H NMR: CDCl₃ (7.26), DMSO-*d*₆ (2.50); ¹³C NMR: CDCl₃ (77.16), DMSO-*d*₆ (39.52)]. The following abbreviations are used in reporting NMR data: s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplet; m, multiplet. HRMS (ESI) was taken on Agilent 6540 Q-TOF spectrometer. The melting point test experiments were performed on microscopic visual melting point instrument (X-4A).

2. General procedure for the synthesis of enol ester substrates

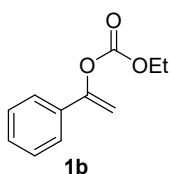


Enol ester substrates **1a**^[1], **1g**^[2], **1h**^[3], **1i**^[4], **1j**^[5], **1k**^[6] and **1l**^[6] were known compounds and prepared according to the reported literature procedures and the NMR and HRMS data were according with the reported literatures. Compound **1m** is commercially available.

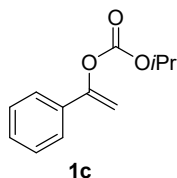
1b – 1f, **35**, and **38** were prepared according to the reported literature procedure^[7] as below:



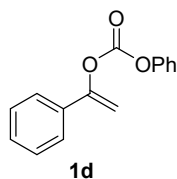
The ketone (5 mmol, 1.0 equiv.) was added dropwise over 10 min to a mixture of NaHMDS (1.0 M solution in THF, 1.0 equiv.) and TMEDA (1.0 equiv.) at -78°C to give a dark green solution. This solution was stirred for a further 20 min and then allowed to warm to 0°C. The enolate solution generated as above was diluted with THF (5 mLmmol⁻¹) and was added rapidly via syringe to a solution of the chloroformate ester (5 mmol, 1.0 equiv.) in THF (1 mLmmol⁻¹). After 1 min the reaction was quenched with sat. aq. NH₄Cl and extracted 3 times with Et₂O. The extracts were dried and concentrated *in vacuo*. The residue was further purified by flash chromatographic column to afford the corresponding enol esters.



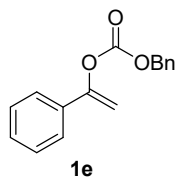
Following the general procedure, *O*-carbonylation reagent is ethyl chloroformate. After purification by flash chromatographic column (petroleum ether/EtOAc 50/1 as the eluent), **1b** was obtained as a colorless oil (595 mg, 62% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.51 (d, $J = 7.7$ Hz, 2H), 7.35 (p, $J = 6.5$ Hz, 3H), 5.45 (d, $J = 1.8$ Hz, 1H), 5.14 (d, $J = 1.8$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 153.5, 153.4, 134.2, 129.2, 128.7, 125.1, 101.8, 64.8, 14.3. HR-ESI-MS calcd. for $\text{C}_{11}\text{H}_{12}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 215.0679, found 215.0681.



Following the general procedure, *O*-carbonylation reagent is isopropyl chloroformate. After purification by flash chromatographic column (petroleum ether/EtOAc 50/1 as the eluent), **1c** was obtained as a colorless oil (381 mg, 37% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.50 (d, $J = 7.9$ Hz, 2H), 7.37 – 7.33 (m, 3H), 5.43 (d, $J = 2.3$ Hz, 1H), 5.13 (d, $J = 2.3$ Hz, 1H), 4.91 (dt, $J = 12.5, 6.2$ Hz, 1H), 1.33 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 153.6, 152.9, 129.2, 128.7, 125.1, 101.8, 73.0, 21.8. HR-ESI-MS calcd. for $\text{C}_{12}\text{H}_{14}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 229.0835, found: 229.0838.

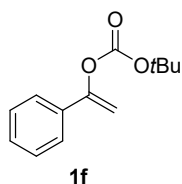


Following the general procedure, *O*-carbonylation reagent is phenyl chloroformate. After purification by flash chromatographic column (petroleum ether/EtOAc 40/1 as the eluent), **1d** was obtained as a colorless oil (696 mg, 58% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.61 (d, $J = 7.7$ Hz, 2H), 7.41 (dd, $J = 12.0, 6.2$ Hz, 5H), 7.30 (dd, $J = 15.2, 7.1$ Hz, 2H), 7.25 (s, 1H), 5.54 (d, $J = 2.3$ Hz, 1H), 5.30 (d, $J = 2.3$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 153.5, 151.7, 151.2, 133.9, 129.7, 129.7, 129.4, 128.8, 126.4, 126.4, 125.2, 121.1, 121.0, 102.1. HR-ESI-MS calcd. for $\text{C}_{15}\text{H}_{12}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 263.0679, found: 263.0679.

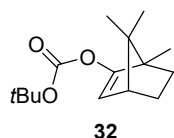


Following the general procedure, *O*-carbonylation reagent is benzyl chloroformate. After purification by flash chromatographic column (petroleum ether/EtOAc 40/1 as the eluent), **1e** benzyl chloroformate

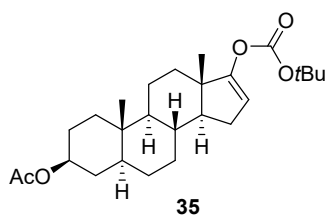
was obtained as a colorless oil (660 mg, 52% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.55 – 7.51 (m, 2H), 7.43 – 7.36 (m, 8H), 5.48 (d, $J = 1.8$ Hz, 1H), 5.25 (s, 2H), 5.19 (s, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 153.5, 153.3, 135.0, 134.0, 129.2, 128.8, 128.7, 128.7, 128.5, 128.4, 125.0, 101.9, 70.3. HR-ESI-MS calcd. for $\text{C}_{16}\text{H}_{14}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 277.0836, found: 277.0835.



Following the general procedure, *O*-carbonylation reagent is Boc_2O . After purification by flash chromatographic column (petroleum ether/EtOAc 50/1 as the eluent), **1f** was obtained as a colorless oil (803 mg, 73% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.51 (d, $J = 7.8$ Hz, 2H), 7.38 – 7.31 (m, 3H), 5.41 (s, 1H), 5.10 (s, 1H), 1.50 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): (150 MHz, CDCl_3) δ 153.6, 151.6, 134.6, 129.1, 128.6, 125.0, 101.7, 83.4, 27.8. HR-ESI-MS calcd. for $\text{C}_{13}\text{H}_{16}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 243.0992, found: 243.0992.



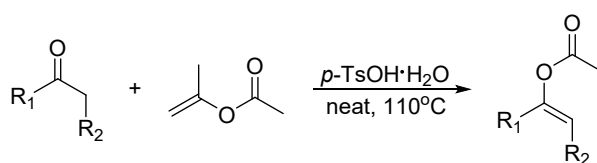
Following the general procedure, *O*-carbonylation reagent is Boc_2O . After purification by flash chromatographic column (petroleum ether/EtOAc 40/1 as the eluent), **32** was obtained as a colorless oil (718 mg, 57% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 5.49 (d, $J = 3.5$ Hz, 1H), 2.33 (t, $J = 3.4$ Hz, 1H), 1.85 (qd, $J = 8.0, 3.6$ Hz, 1H), 1.56 – 1.53 (m, 1H), 1.50 (s, 9H), 1.35 – 1.29 (m, 1H), 1.14 – 1.09 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 156.2, 151.4, 113.9, 82.8, 56.2, 53.5, 50.0, 31.4, 27.8, 26.1, 20.0, 19.6, 10.0. HR-ESI-MS calcd. for $\text{C}_{15}\text{H}_{24}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 275.1618, found: 275.1617.



Following the general procedure, *O*-carbonylation reagent is Boc_2O . After purification by flash chromatographic column (petroleum ether/EtOAc 40/1 as the eluent), **35** was obtained as a colorless oil (1.36 g, 63% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 5.41 (s, 1H), 4.68 (dt, $J = 11.3, 5.3$ Hz, 1H), 2.19 – 2.07 (m, 1H), 2.00 (s, 3H), 1.88 (t, $J = 12.4$ Hz, 1H), 1.80 (d, $J = 11.0$ Hz, 1H), 1.67 (dd, J

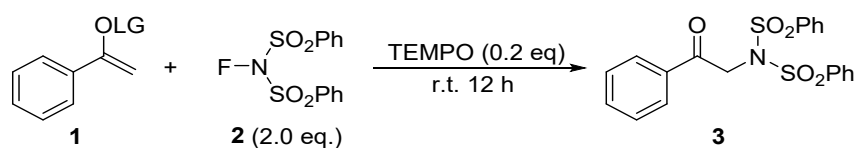
= 17.5, 3.6 Hz, 3H), 1.59 (d, $J = 3.4$ Hz, 2H), 1.53 (d, $J = 4.0$ Hz, 2H), 1.49 (s, 9H), 1.47 (s, 1H), 1.40 – 1.16 (m, 6H), 1.02 (dd, $J = 19.2, 8.9$ Hz, 1H), 0.97 – 0.92 (m, 1H), 0.90 (d, $J = 13.5$ Hz, 3H), 0.83 (s, 3H), 0.79 – 0.71 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 170.7, 160.3, 151.5, 110.2, 82.8, 73.7, 55.0, 54.4, 45.0, 44.9, 36.7, 35.9, 34.2, 33.7, 33.4, 31.2, 28.8, 28.5, 27.8, 27.6, 21.5, 20.8, 15.7, 12.3. HR-ESI-MS calcd. for $\text{C}_{26}\text{H}_{40}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 455.2766, found: 455.2768.

3. General procedure for the synthesis of enol acetates



A 15 mL sealed tube equipped with a magnetic stir bar was charged with ketone (5.0 mmol, 1.0 equiv), isopropenyl acetate (25 mmol, 5.0 equiv) and $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (0.5 mmol, 0.10 equiv). The reaction mixture was heated to 110°C for 12 h. Then the reaction mixture was allowed to cool to room temperature and the remaining isopropenyl acetate was subsequently evaporated under reduced pressure. The residue was dissolved in EtOAc (15 mL) and the resulting solution was washed with H_2O (3×15 mL) followed by saturated salt solution (20 mL) and dried over Na_2SO_4 . The solvent was evaporated *in vacuo* to give a dark brown oil, which was subjected to flash chromatographic column to afford the corresponding enol ester products (petroleum ether/EtOAc = 40:1). All enol acetates were synthesized and purified according to the above procedure and are in agreement with reported literature.

4. Optimization of reaction conditions

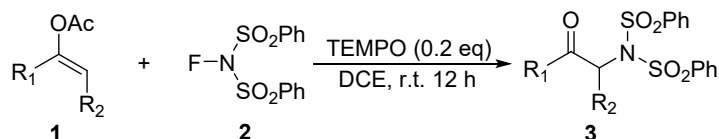


Entry ^a	Enol	LG	Solvents	Yield (%) ^b
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1	1a	TMS	DCE	n.d.
2	1b	CO ₂ Et	DCE	85
3	1c	CO ₂ <i>i</i> Pr	DCE	86
4	1d	CO ₂ Ph	DCE	81
5	1e	CO ₂ Bn	DCE	83
6	1f	CO ₂ <i>t</i> Bu	DCE	89
7	1g	Ac	DCE	93
8	1h	Bz	DCE	68
9	1i	Piv	DCE	60
10	1j	Ts	DCE	69
11	1f	Ac	DCM	65
12	1f	Ac	MeNO ₂	73
13	1f	Ac	EtOAc	62
14	1f	Ac	MeCN	83
15	1f	Ac	THF	35
16	1f	Ac	MeOH	23
17 ^c	1f	without TEMPO	DCE	n.r.
18 ^c	1f	50°C	DCE	91

^a Experiments were performed with **1** (0.3 mmol), NFSI **2** (0.6 mmol.), TEMPO (0.06 mmol) in solvent (1 mL) under Ar. ^b Isolated yields. ^cLG = Ac

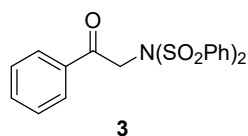
5. General procedure for the synthesis of α -sulfonimide ketones



To an oven-dried 15 mL reaction tube equipped with a stir bar, NFSI (0.60 mmol, 189 mg, 2.0 equiv) and TEMPO (0.06 mmol, 9.4 mg, 0.20 equiv) were added. Then dry DCE (500 μ L) was added to dissolve the reactants and reagents. The mixture was

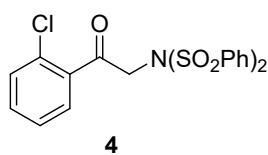
degassed 3 times by applying vacuum, and backfilling with Ar while stirring vigorously. Then the reaction tube was sealed. Enol ester **1** (0.30 mmol, 1.0 equiv) was dissolved in dry DCE (500 μ L) and added to the above reaction mixture at a constant speed by a syringe over 6 h. Then the reaction was stirred for additional 6 h at room temperature until enol ester was completely consumed (monitored by TLC). The reaction solution was concentrated *in vacuo* to give the residue, which was subjected to flash chromatographic column to afford the corresponding α -sulfonimide ketone products.

6. Characterization of α -sulfonimide ketone products



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **3** was obtained as a white powder (116 mg, 93% yield).

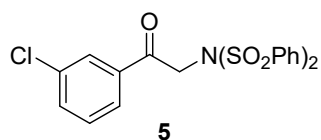
Mp = 188-190°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.08 (d, $J = 7.5$ Hz, 4H), 7.87 (d, $J = 7.3$ Hz, 2H), 7.67 (t, $J = 7.5$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 4H), 7.48 (t, $J = 7.8$ Hz, 2H), 5.19 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 191.0, 139.5, 134.6, 134.2, 134.1, 129.0, 128.95, 128.1, 53.8. HR-ESI-MS calcd. for $\text{C}_{20}\text{H}_{18}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 416.0521, found: 416.0518.



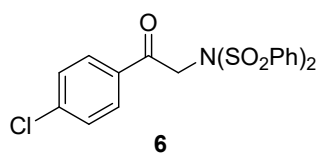
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **4** was obtained as a white powder (107 mg, 80% yield).

Mp = 170-172°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.07 (d, $J = 7.9$ Hz, 4H), 7.84 (s, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 7.0$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 5H), 7.42 (t, $J = 7.7$ Hz, 1H), 5.14 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 190.1, 139.3, 136.0, 135.4, 134.3, 134.0, 130.4, 129.1, 128.9, 128.2, 126.2, 53.7. HR-ESI-MS calcd. for $\text{C}_{20}\text{H}_{16}\text{ClNO}_5\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 472.0051, found: 472.0051.

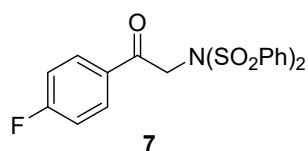
Following the general procedure: After purification by flash chromatographic column



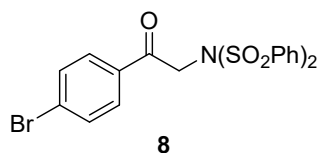
(petroleum ether/acetone 6/1 as the eluent), **5** was obtained as a white powder (101 mg, 75% yield). Mp = 131-133°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.08 (d, *J* = 8.0 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.59 – 7.51 (m, 5H), 7.46 – 7.40 (m, 2H), 7.34 (t, *J* = 6.6 Hz, 1H), 5.13 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 194.2, 139.4, 136.5, 134.2, 132.9, 131.2, 130.6, 130.1, 129.1, 128.9, 127.4, 56.4. HR-ESI-MS calcd. for C₂₀H₁₆ClNO₅S₂Na [M+Na]⁺: 472.0051, found: 472.0054.



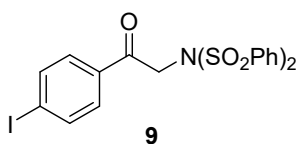
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **6** was obtained as a white powder (113 mg, 84% yield). Mp = 169-172°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.09 – 8.03 (m, 4H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 4H), 7.44 (d, *J* = 8.5 Hz, 2H), 5.14 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 190.1, 140.6, 139.4, 134.2, 132.8, 129.9, 129.6, 129.5, 129.4, 129.1, 128.9, 53.6. HR-ESI-MS calcd. for C₂₀H₁₇ClNO₅S₂ [M+H]⁺: 450.0231, found: 450.0234.



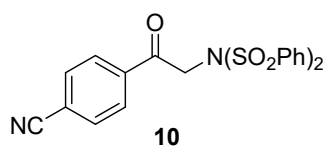
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **7** was obtained as a white powder (105 mg, 81% yield). Mp = 175-177°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.10 – 8.04 (m, 4H), 7.94 – 7.88 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 4H), 7.15 (t, *J* = 8.5 Hz, 2H), 5.15 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 189.58, 166.36 (d, *J*_{C-F} = 263.06 Hz), 139.4, 134.2, 131.0 (d, *J*_{C-F} = 2.88 Hz), 130.9 (d, *J*_{C-F} = 9.39 Hz), 129.1, 129.0, 116.3 (d, *J*_{C-F} = 21.92 Hz), 53.6. ¹⁹F NMR (565 MHz, CDCl₃) δ -103.11. HR-ESI-MS calcd. for C₂₀H₁₇FNO₅S₂ [M+H]⁺: 434.0527, found: 434.0530.



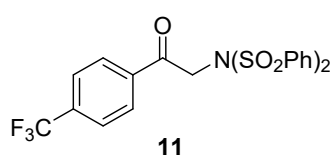
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **8** was obtained as a white powder (108 mg, 73% yield). Mp = 158-161°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.09 – 8.03 (m, 4H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.55 (t, *J* = 7.9 Hz, 4H), 5.13 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 190.3, 139.4, 134.2, 133.3, 132.4, 129.6, 129.1, 128.9, 53.57. HR-ESI-MS calcd. for C₂₀H₁₆BrNO₅S₂Na [M+Na]⁺: 515.9545, found: 515.9547.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **9** was obtained as a white powder (110 mg, 68% yield). Mp = 175-178°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.06 (d, *J* = 7.5 Hz, 4H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.60 – 7.54 (m, 6H), 5.12 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 190.4, 139.2, 138.3, 134.1, 129.2, 128.9, 128.8, 53.3. HR-ESI-MS calcd. for C₂₀H₁₇INO₅S₂ [M+H]⁺: 541.0587, found: 541.0583.

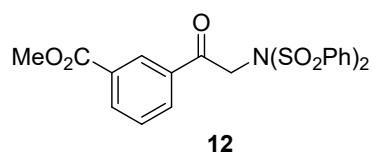


Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **10** was obtained as a light yellow powder (108 mg, 82% yield). Mp = 200-202°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.09 – 8.02 (m, 4H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.9 Hz, 4H), 5.15 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 190.4, 139.2, 137.6, 134.4, 132.9, 129.2, 128.9, 128.6, 117.7, 117.4, 53.8. HR-ESI-MS calcd. for C₂₁H₁₇N₂O₅S₂ [M+H]⁺: 441.0573, found: 441.0573.

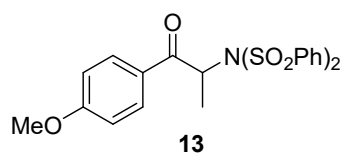


Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **11** was obtained as a white powder (126 mg, 87% yield). Mp = 195-197°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.09 – 8.03

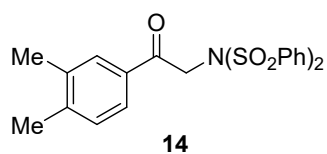
(m, 4H), 7.97 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.68 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.9$ Hz, 4H), 5.18 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 190.6, 139.3, 137.3, 135.3 (q, $J_{\text{C-F}} = 32.67$ Hz), 134.3, 129.1, 128.9, 128.5, 126.1 (q, $J_{\text{C-F}} = 3.59$ Hz), 123.5 (q, $J_{\text{C-F}} = 271.20$ Hz), 53.8. ^{19}F NMR (565 MHz, CDCl_3) δ -63.28. HR-ESI-MS calcd. for $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 484.0495, found: 484.0492.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **12** was obtained as a white powder (113 mg, 80% yield). Mp = 170-173°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.51 (s, 1H), 8.28 (d, $J = 7.7$ Hz, 1H), 8.09 – 8.07 (m, 5H), 7.68 (t, $J = 7.5$ Hz, 2H), 7.61 – 7.54 (m, 5H), 5.22 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 190.5, 166.0, 139.4, 134.8, 134.3, 132.3, 131.2, 129.4, 129.1, 129.1, 129.0, 53.8, 52.6. HR-ESI-MS calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_7\text{S}_2$ $[\text{M}+\text{H}]^+$: 474.0678, found: 474.0679.

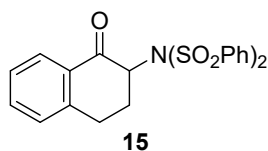


Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **13** was obtained as a white powder (90 mg, 65% yield). Mp = 96-98°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.99 (d, $J = 8.8$ Hz, 2H), 7.81 (d, $J = 7.8$ Hz, 4H), 7.60 (t, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.9$ Hz, 4H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.47 (q, $J = 6.9$ Hz, 1H), 3.87 (s, 3H), 1.45 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 193.3, 163.6, 139.8, 134.1, 131.5, 129.1, 128.9, 114.0, 61.9, 55.7, 16.3. HR-ESI-MS calcd. for $\text{C}_{22}\text{H}_{22}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$: 460.0883, found: 460.0882.



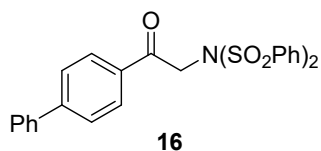
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **14** was obtained as a white powder (103 mg, 78% yield). Mp = 161-163°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.07 (d, $J = 7.7$ Hz, 4H), 7.71 – 7.63 (m, 3H), 7.60 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 4H), 7.22

(d, $J = 7.7$ Hz, 1H), 5.17 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 190.7, 139.6, 134.1, 130.2, 129.2, 129.0, 128.9, 125.7, 53.6, 20.2, 19.8. HR-ESI-MS calcd. for $\text{C}_{22}\text{H}_{22}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 444.0934, found: 444.0931.



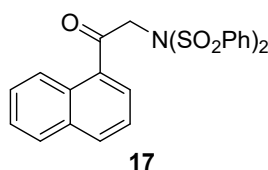
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **15** was obtained as a white powder (99 mg, 75% yield).

Mp = 195-197°C. ^1H NMR (600 MHz, d_6 -DMSO): δ (ppm): 8.11 (d, $J = 7.7$ Hz, 2H), 7.89 (t, $J = 7.6$ Hz, 3H), 7.83 – 7.75 (m, 2H), 7.71 (t, $J = 7.5$ Hz, 2H), 7.65 – 7.55 (m, 3H), 7.41 – 7.32 (m, 2H), 5.32 (dd, $J = 13.1, 4.8$ Hz, 1H), 3.29 – 3.20 (m, 1H), 3.02 – 2.94 (m, 1H), 2.78 (qd, $J = 13.1, 4.0$ Hz, 1H), 2.18 – 2.08 (m, 1H). ^{13}C NMR (150 MHz, d_6 -DMSO): δ (ppm): 190.8, 143.6, 140.4, 137.7, 134.5, 134.1, 134.0, 131.4, 129.1, 128.8, 128.4, 128.1, 127.2, 126.7, 65.2, 29.9, 28.2. HR-ESI-MS calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 442.0777, found: 442.0780.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **16** was obtained as a yellow powder (124 mg, 84% yield).

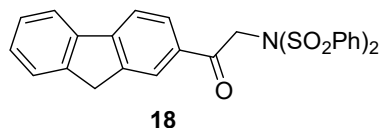
Mp = 133-135°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.10 (d, $J = 7.5$ Hz, 4H), 7.95 (d, $J = 8.3$ Hz, 2H), 7.72 – 7.65 (m, 4H), 7.64 – 7.61 (m, 2H), 7.57 (t, $J = 7.8$ Hz, 4H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 7.3$ Hz, 1H), 5.23 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 190.6, 146.8, 139.7, 139.5, 134.2, 133.2, 129.2, 129.0, 128.96, 128.7, 128.6, 127.6, 127.4, 53.7. HR-ESI-MS calcd. for $\text{C}_{26}\text{H}_{22}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 492.0934, found: 492.0939.



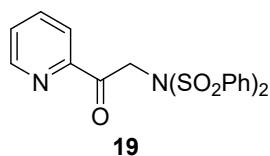
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **17** was obtained as a white powder (123 mg, 88% yield).

Mp = 164-166°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.36 (d, $J = 8.0$ Hz, 1H), 8.11 (dd, $J = 8.4, 1.0$ Hz, 4H), 8.03 (d, $J = 8.2$ Hz, 1H), 7.90 – 7.86 (m, 1H), 7.83 (d, $J = 7.1$

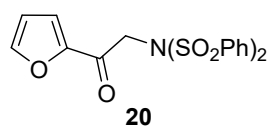
Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 2H), 7.60 – 7.53 (m, 6H), 7.53 – 7.49 (m, 1H), 5.18 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 194.8, 139.6, 134.2, 134.1, 133.5, 133.2, 130.2, 129.1, 129.0, 128.6, 128.4, 127.3, 127.0, 125.7, 124.4, 55.9. HR-ESI-MS calcd. for $\text{C}_{24}\text{H}_{20}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 466.0777, found: 466.0775.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **18** was obtained as a yellow oil (109 mg, 72% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.13 – 8.08 (m, 4H), 8.06 (s, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.85 (t, $J = 7.6$ Hz, 2H), 7.70 – 7.66 (m, 2H), 7.61 – 7.55 (m, 5H), 7.45 – 7.39 (m, 2H), 5.26 (s, 2H), 3.95 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 190.7, 147.5, 144.7, 143.7, 140.4, 139.6, 134.2, 132.9, 129.05, 129.0, 128.5, 127.4, 127.3, 125.5, 124.8, 121.2, 120.1, 53.8, 37.1. HR-ESI-MS calcd. for $\text{C}_{27}\text{H}_{22}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 504.0934, found: 504.0931.

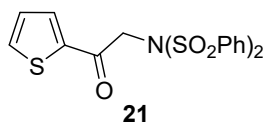


Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 4/1 as the eluent), **19** was obtained as a white powder (81 mg, 65% yield). Mp = 169-171°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.66 (d, $J = 4.6$ Hz, 1H), 8.12 (d, $J = 7.5$ Hz, 4H), 8.01 (d, $J = 7.8$ Hz, 1H), 7.85 (td, $J = 7.7, 1.6$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 2H), 7.57 (t, $J = 7.9$ Hz, 4H), 7.52 (ddd, $J = 7.5, 4.8, 0.9$ Hz, 1H), 5.50 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 192.6, 151.8, 149.2, 139.7, 137.3, 134.1, 129.0, 128.9, 128.09, 122.4, 53.9. HR-ESI-MS calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 417.0573, found: 417.0568.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 4/1 as the eluent), **20** was obtained as a yellow powder (82 mg, 67% yield). Mp = 154-156°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.11 – 8.07 (m, 4H), 7.67 (t, $J = 7.5$ Hz, 2H), 7.60 (d, $J = 1.0$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 4H), 7.25 (s, 1H), 6.58

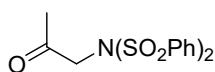
(dd, $J = 3.6, 1.6$ Hz, 1H), 5.04 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 180.6, 150.8, 147.0, 139.4, 134.2, 129.1, 129.0, 118.1, 112.9, 52.8. HR-ESI-MS calcd. for $\text{C}_{18}\text{H}_{16}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$: 406.0414, found 406.0414.



21

Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 4/1 as the eluent), **21** was obtained as a white powder (89 mg, 70% yield).

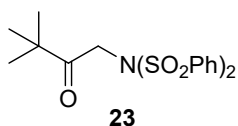
Mp = 173-175°C. ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.10 – 8.05 (m, 4H), 7.73 (d, $J = 3.8$ Hz, 1H), 7.71 (dd, $J = 4.9, 0.7$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.9$ Hz, 4H), 7.16 (dd, $J = 4.7, 4.0$ Hz, 1H), 5.09 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 184.0, 140.6, 139.3, 134.7, 134.2, 132.3, 129.1, 129.0, 128.5, 53.3. HR-ESI-MS calcd. for $\text{C}_{18}\text{H}_{16}\text{NO}_5\text{S}_3$ $[\text{M}+\text{H}]^+$: 422.0185, found: 422.0183.



22

Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 8/1 as the

eluent), **22** was obtained as a colorless oil (97 mg, 92% yield). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.02 (dd, $J = 8.4, 1.0$ Hz, 4H), 7.67 (t, $J = 7.5$ Hz, 2H), 7.55 (dd, $J = 8.1, 7.7$ Hz, 4H), 4.48 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 200.2, 139.2, 134.3, 129.1, 128.8, 56.3, 26.7. HR-ESI-MS calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_5\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 376.0284, found: 376.0284.

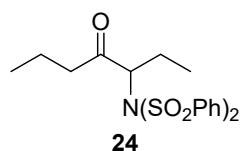


23

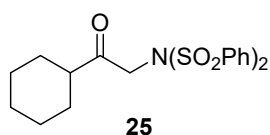
Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **23** was obtained as a white foam (102 mg, 86% yield).

^1H NMR (600 MHz, CDCl_3): δ (ppm): 8.08 – 8.00 (m, 4H), 7.66 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.9$ Hz, 4H), 4.71 (s, 2H), 1.17 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 206.2, 139.4, 134.1, 129.0, 128.9, 52.1, 43.2, 26.5. HR-ESI-MS calcd. for $\text{C}_{18}\text{H}_{22}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 396.0934, found: 396.0930.

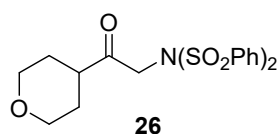
Following the general procedure: After purification by flash chromatographic column



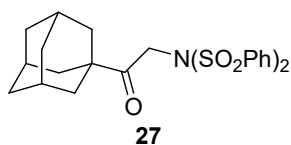
(petroleum ether/DCM 1/1 as the eluent), **24** was obtained as a colorless oil (102 mg, 83% yield). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.06 (d, *J* = 7.5 Hz, 4H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 4H), 4.32 – 4.26 (m, 1H), 2.41 – 2.29 (m, 2H), 1.92 – 1.80 (m, 2H), 1.49 – 1.39 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 204.1, 139.7, 134.3, 129.1, 71.0, 40.6, 23.4, 17.2, 13.6, 11.9. HR-ESI-MS calcd. for C₁₉H₂₄NO₅S₂ [M+H]⁺: 410.1090, found: 410.1093.



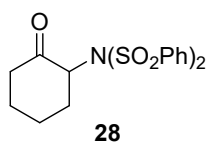
Following the general procedure: After purification by flash chromatographic column (petroleum ether/DCM 1/1 as the eluent), **25** was obtained as a colorless oil (104 mg, 82% yield). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.04 (d, *J* = 7.5 Hz, 4H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 4H), 4.57 (s, 2H), 2.41 – 2.35 (m, 1H), 1.79 (dd, *J* = 21.5, 8.8 Hz, 4H), 1.67 (d, *J* = 11.4 Hz, 1H), 1.35 (dd, *J* = 22.8, 11.1 Hz, 2H), 1.28 – 1.20 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 204.5, 139.2, 134.0, 128.9, 128.8, 54.3, 47.8, 28.3, 25.6, 25.4. HR-ESI-MS calcd. for C₂₀H₂₄NO₅S₂ [M+H]⁺: 422.1090, found: 422.1092.



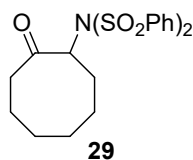
Following the general procedure: After purification by flash chromatographic column (petroleum ether/DCM 1/1 as the eluent), **26** was obtained as a pale yellow powder (100 mg, 79% yield). Mp = 113-116°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.03 (d, *J* = 7.5 Hz, 4H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 4H), 4.57 (s, 2H), 3.97 (dt, *J* = 11.5, 3.3 Hz, 2H), 3.44 – 3.34 (m, 2H), 2.69 – 2.59 (m, 1H), 1.74 – 1.66 (m, 4H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 203.0, 139.2, 134.3, 129.1, 129.0, 128.8, 67.0, 54.2, 44.8, 28.0. HR-ESI-MS calcd. for C₁₉H₂₂NO₆S₂ [M+H]⁺: 424.0883, found: 424.0881.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 8/1 as the eluent), **27** was obtained as a white powder (108 mg, 76% yield). Mp = 185-187°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.11 – 7.99 (m, 4H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 4H), 4.69 (s, 2H), 2.05 (s, 3H), 1.82 (t, *J* = 4.7 Hz, 6H), 1.75 (d, *J* = 12.4 Hz, 3H), 1.69 (d, *J* = 11.7 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 205.7, 139.6, 134.1, 129.3, 129.0, 128.9, 126.6, 52.1, 45.7, 38.3, 36.5, 27.9. HR-ESI-MS calcd. for C₂₄H₂₈NO₅S₂ [M+H]⁺: 474.1403, found: 474.1400.

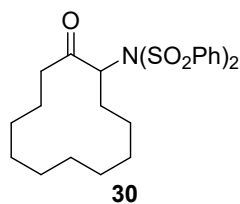


Following the general procedure: After purification by flash chromatographic column (petroleum ether/DCM 1/1 as the eluent), **28** was obtained as a white foam (86 mg, 73% yield). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.03 (s, 4H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H), 4.49 (dd, *J* = 12.3, 6.4 Hz, 1H), 2.68 – 2.56 (m, 2H), 2.26 – 2.15 (m, 2H), 2.05 – 1.93 (m, 2H), 1.74 (ddd, *J* = 13.4, 12.0, 3.8 Hz, 1H), 1.63 (t, *J* = 8.2 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 201.6, 134.0, 129.0, 67.7, 41.1, 32.8, 25.1, 24.4. HR-ESI-MS calcd. for C₁₈H₁₉NO₅S₂Na [M+Na]⁺: 416.0597, found: 416.0597.

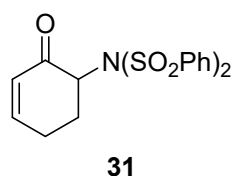


Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 8/1 as the eluent), **29** was obtained as a white foam (97 mg, 77% yield). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 7.96 (d, *J* = 7.6 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.9 Hz, 4H), 4.24 (d, *J* = 10.3 Hz, 1H), 3.15 (td, *J* = 12.2, 4.5 Hz, 1H), 2.71 (ddd, *J* = 14.6, 13.1, 2.5 Hz, 1H), 2.41 (dt, *J* = 12.2, 4.5 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.90 – 1.82 (m, 1H), 1.75 – 1.68 (m, 2H), 1.68 – 1.59 (m, 2H), 1.52 – 1.33 (m, 2H), 1.25 – 1.19 (m, 1H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 209.7, 139.5, 134.1, 129.0, 128.9, 69.1, 37.6, 32.45, 29.8, 27.1, 26.2, 25.8. HR-ESI-MS calcd. for C₂₀H₂₄NO₅S₂ [M+H]⁺: 422.1090, found: 422.1091.

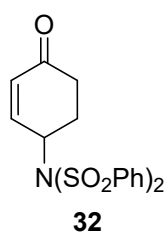
Following the general procedure: After purification by flash chromatographic column



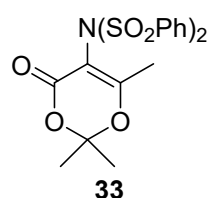
(petroleum ether/acetone 8/1 as the eluent), **30** was obtained as a white powder (109 mg, 76% yield). Mp = 180-182°C. ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.22 – 7.88 (m, 4H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 4H), 4.92 (dd, *J* = 10.0, 3.4 Hz, 1H), 2.66 – 2.51 (m, 1H), 2.48 – 2.39 (m, 1H), 2.12 (ddd, *J* = 12.9, 10.1, 5.5 Hz, 1H), 1.49 – 1.16 (m, 17H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 203.9, 140.0, 134.2, 129.2, 128.9, 63.4, 39.0, 28.4, 25.5, 25.3, 24.0, 23.5, 23.1, 23.0, 22.98. HR-ESI-MS calcd. for C₂₄H₃₂NO₅S₂ [M+H]⁺: 478.1716; found: 478.1717.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/DCM 1/1 as the eluent), **31** was obtained as a colorless oil (77 mg, 67% yield). ¹H NMR (600 MHz, *d*₆-DMSO) δ 8.09 (brs, 2H), 7.85 (brs, 2H), 7.77 (brs, 2H), 7.68 (brs, 2H), 7.60 (brs, 2H), 7.11 (m, 1H), 5.98 (dd, *J* = 10.0, 2.3 Hz, 1H), 5.01 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.66 (ddd, *J* = 24.2, 12.2, 4.5 Hz, 1H), 2.62 – 2.55 (m, 1H), 2.48 – 2.41 (m, 1H), 1.97 – 1.89 (m, 1H). ¹³C NMR (150 MHz, *d*₆-DMSO) δ 191.4, 152.0, 140.5, 137.7, 134.5, 134.1, 129.1, 128.5, 128.0, 128.0, 64.6, 29.0, 25.6. HR-ESI-MS calcd. for C₁₈H₁₇NO₅S₂Na [M+Na]⁺: 414.0446; found: 414.0449.



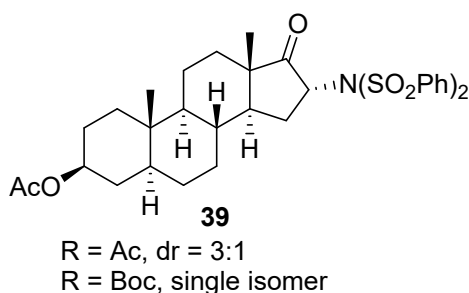
Following the general procedure: After purification by flash chromatographic column (DCM as the eluent), **31** was obtained as a colorless oil (75 mg, 64% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 4H), 7.72 – 7.68 (m, 2H), 7.61 (t, *J* = 7.8 Hz, 4H), 6.65 (d, *J* = 10.4 Hz, 1H), 5.95 – 5.86 (m, 1H), 5.17 – 5.00 (m, 1H), 2.88 (qd, *J* = 11.9, 4.3 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.41 (m, 1H), 2.14 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 196.5, 149.9, 134.4, 129.5, 129.1, 128.4, 59.3, 37.7, 29.8. HR-ESI-MS calcd. for C₁₈H₁₇NO₅S₂Na [M+Na]⁺: 414.0446; found: 414.0444.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 2/1 as the eluent), **33** was obtained as a white foam (80 mg, 61% yield). ¹H NMR (600

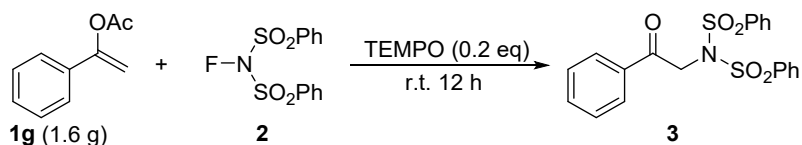
MHz, CDCl₃) δ 8.04 – 7.88 (m, 4H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 4H), 1.86 (s, 3H), 1.76 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 175.4, 158.5, 138.9, 134.4, 129.4, 129.0, 107.1, 104.6, 25.4, 18.1. HR-ESI-MS calcd. for C₁₉H₁₉NO₇S₂Na [M+Na]⁺: 460.0501; found: 460.0501.

Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 8/1 as the eluent), **36** was obtained as a white powder (R = Ac, 87 mg, 65% yield, dr = 10:1; R = Boc, 93 mg, 69% yield, dr = 25.5:1). Mp = 135-137°C. ¹H NMR (500 MHz, DMSO) δ 8.33 – 7.81 (m, 4H), 7.80 (d, *J* = 6.8 Hz, 2H), 7.67 (t, *J* = 6.8 Hz, 4H), 4.35 (d, *J* = 3.6 Hz, 1H), 2.01 (s, 1H), 1.73 – 1.58 (m, 4H), 0.95 (s, 3H), 0.84 (s, 3H), 0.80 (s, 3H). ¹³C NMR (125 MHz, DMSO) δ 208.9, 135.2, 129.9, 128.6, 128.3, 79.6, 66.7, 59.1, 47.9, 43.8, 30.3, 20.4, 19.6, 19.3, 10.1. HR-ESI-MS calcd. for C₂₂H₂₆NO₅S₂ [M+H]⁺: 448.1247, found: 448.1251.



Following the general procedure: After purification by flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), **39** was obtained as a white powder (R = Ac, 134 mg, 70% yield, dr = 3:1; R = Boc, 133 mg, 69% yield, single isomer). Mp = 132-135°C. ¹H NMR (600 MHz, CDCl₃) δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.65 (dd, *J* = 12.7, 7.1 Hz, 2H), 7.55 (dt, *J* = 15.9, 7.8 Hz, 4H), 4.88 (dd, *J* = 11.1, 3.5 Hz, 1H), 4.73 – 4.58 (m, 1H), 2.12 (d, *J* = 8.3 Hz, 1H), 2.01 (s, 3H), 1.87 – 1.77 (m, 4H), 1.73 – 1.59 (m, 4H), 1.53 – 1.42 (m, 4H), 1.38 – 1.25 (m, 5H), 1.23 – 1.16 (m, 2H), 0.94 (s, 3H), 0.82 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 212.2, 170.6, 140.6, 138.6, 134.2, 133.8, 129.1, 128.7, 128.4, 73.4, 61.4, 53.9, 47.0, 46.9, 44.6, 36.5, 35.6, 34.8, 33.9, 30.9, 30.3, 28.8, 28.2, 27.4, 21.4, 20.0, 15.8, 12.1. HR-ESI-MS calcd. for C₃₃H₄₁NO₇S₂Na [M+Na]⁺: 650.2218, found: 650.2218.

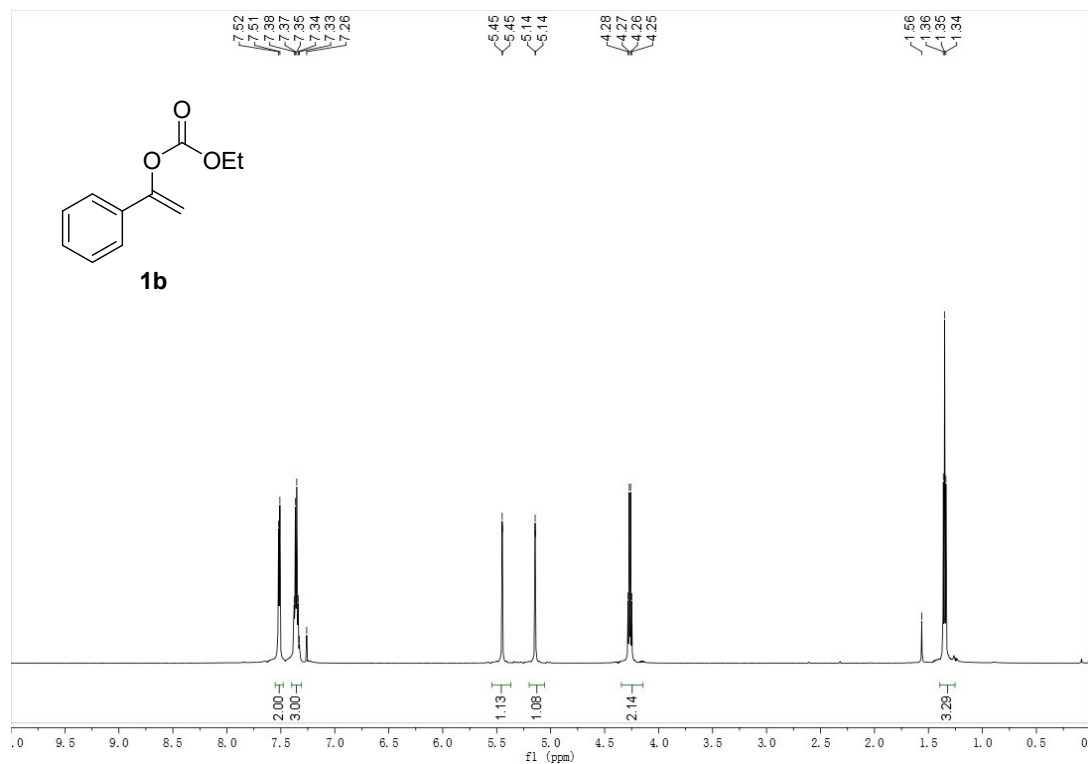
7. Gram scale experiment



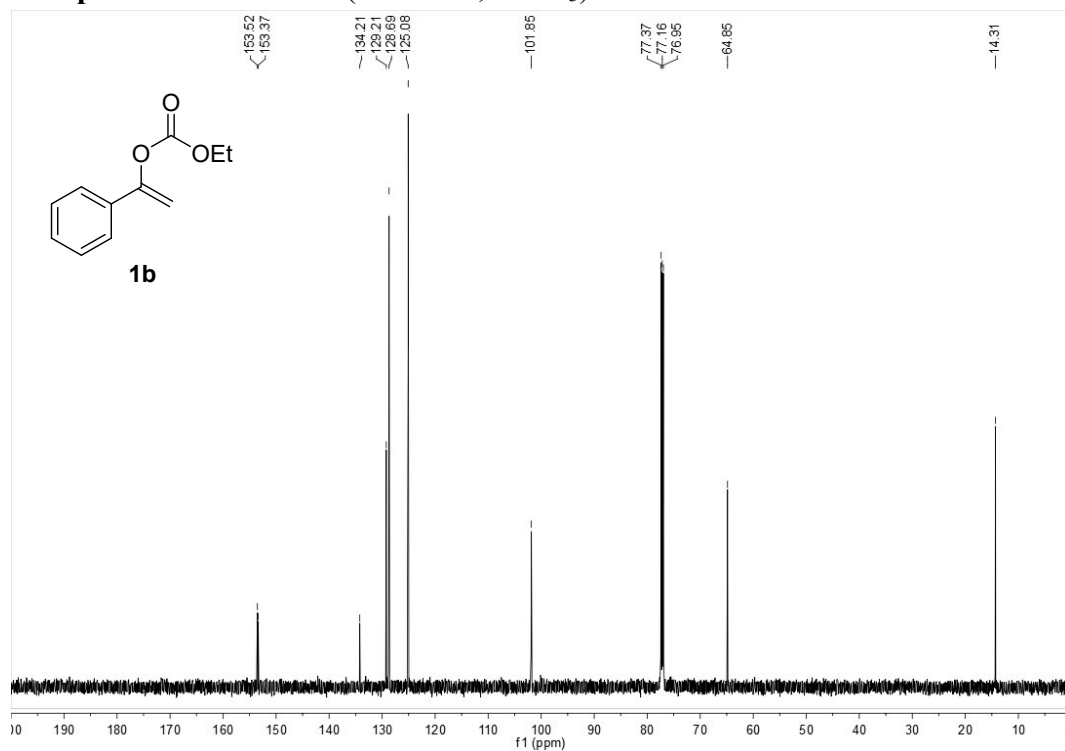
To an oven-dried 100 mL round bottom flask equipped with a stir bar, NFSI (20.0 mmol, 3.78 g, 2.0 equiv) and TEMPO (2.0 mmol, 312 mg, 0.20 equiv) were added. Then dry DCE (20 mL) was added to dissolve the reactants and reagents. The mixture was degassed 3 times by applying vacuum, and backfilling with Ar while stirring vigorously. Then the round bottom flask was sealed. 1-phenylvinyl acetate **1** (10.0 mmol, 1.60 g, 1.0 equiv) was dissolved in dry DCE (20 mL) and added to the above reaction mixture at a constant speed by a syringe over 10 h. Then the reaction was stirred for additional 14 h at room temperature until 1-phenylvinyl acetate **1** was completely consumed (monitored by TLC). The reaction solution was concentrated *in vacuo* to give the residue, which was subjected to flash chromatographic column (petroleum ether/acetone 6/1 as the eluent), compound **3** was obtained as a white powder (3.36 g, 81% yield).

8. Copies of NMR spectra

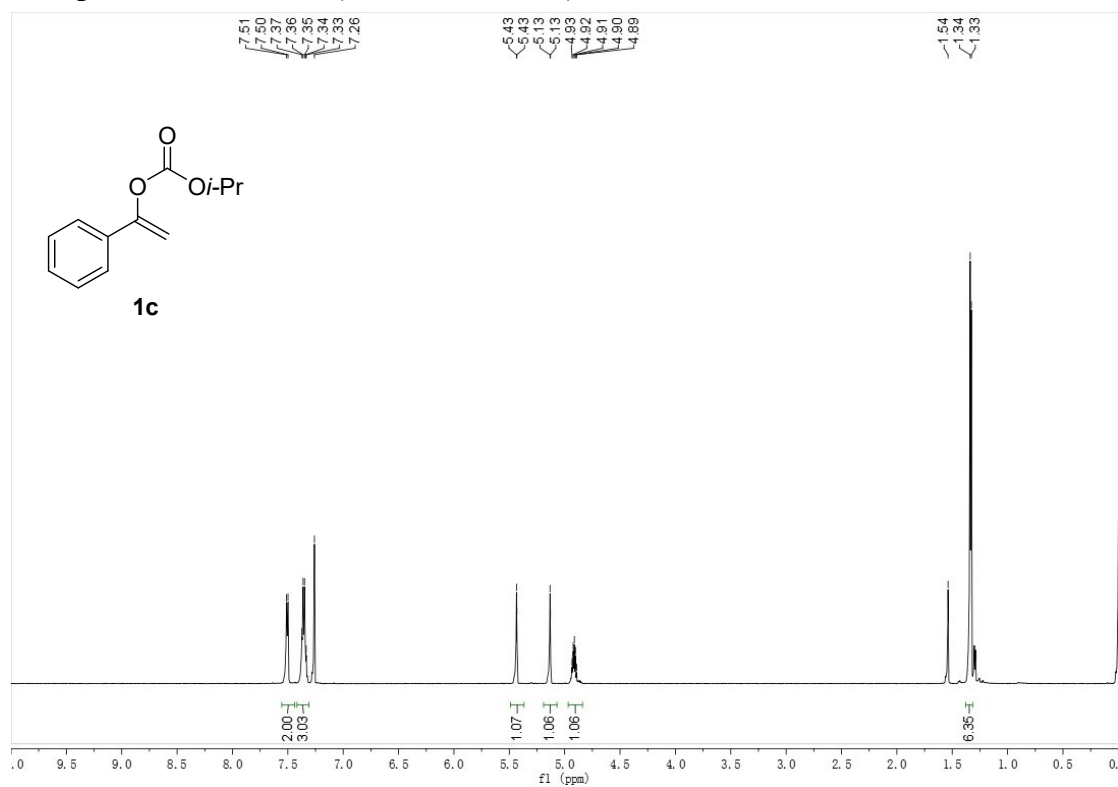
Compound 1b ^1H NMR (600 MHz, CDCl_3)



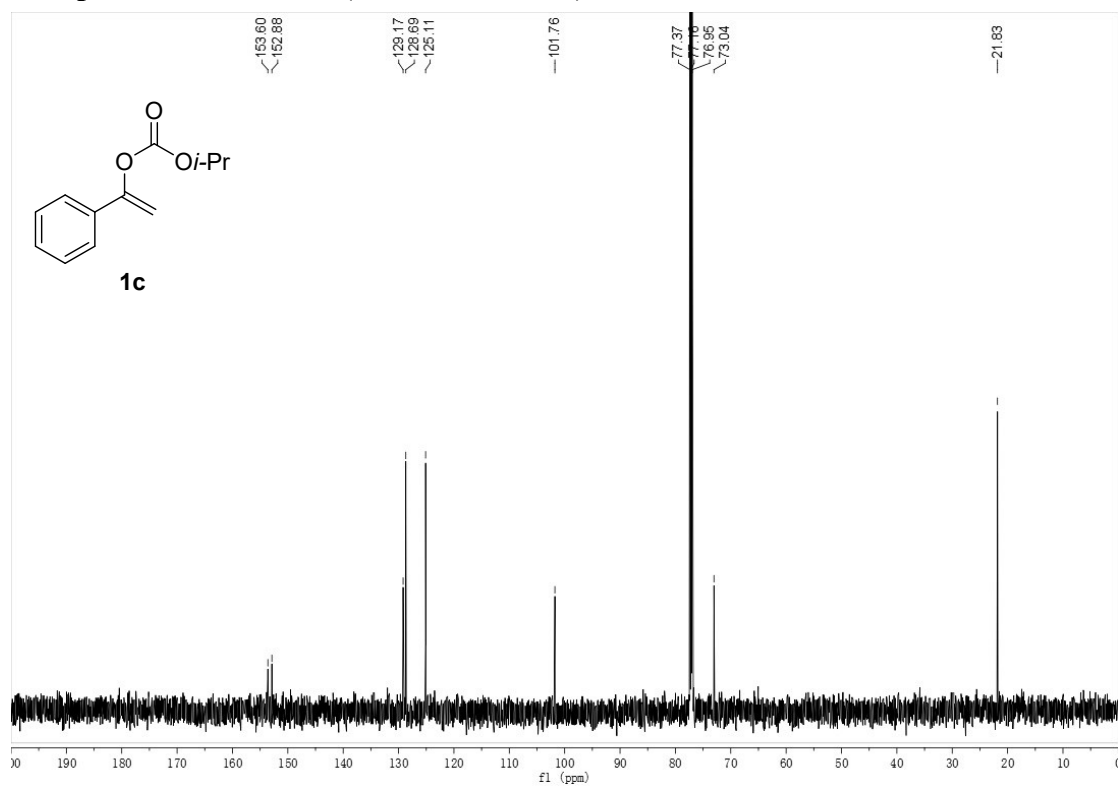
Compound 1b ^{13}C NMR (150 MHz, CDCl_3)



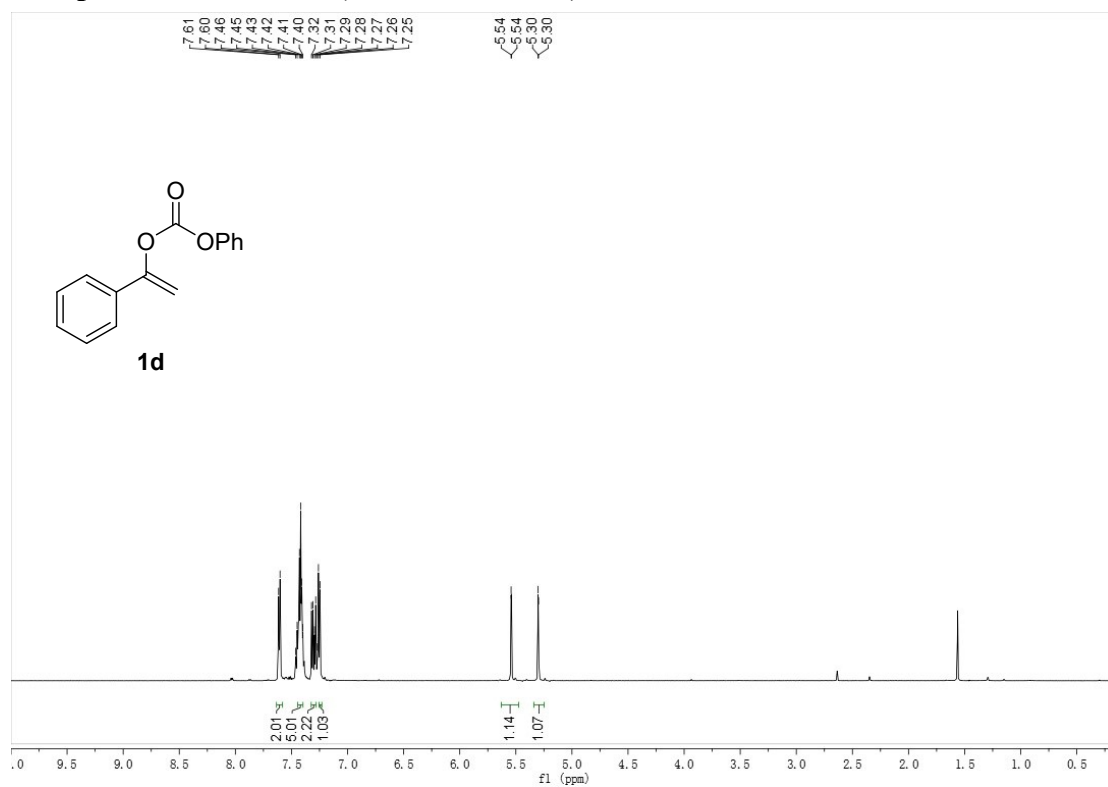
Compound **1c** ^1H NMR (600 MHz, CDCl_3)



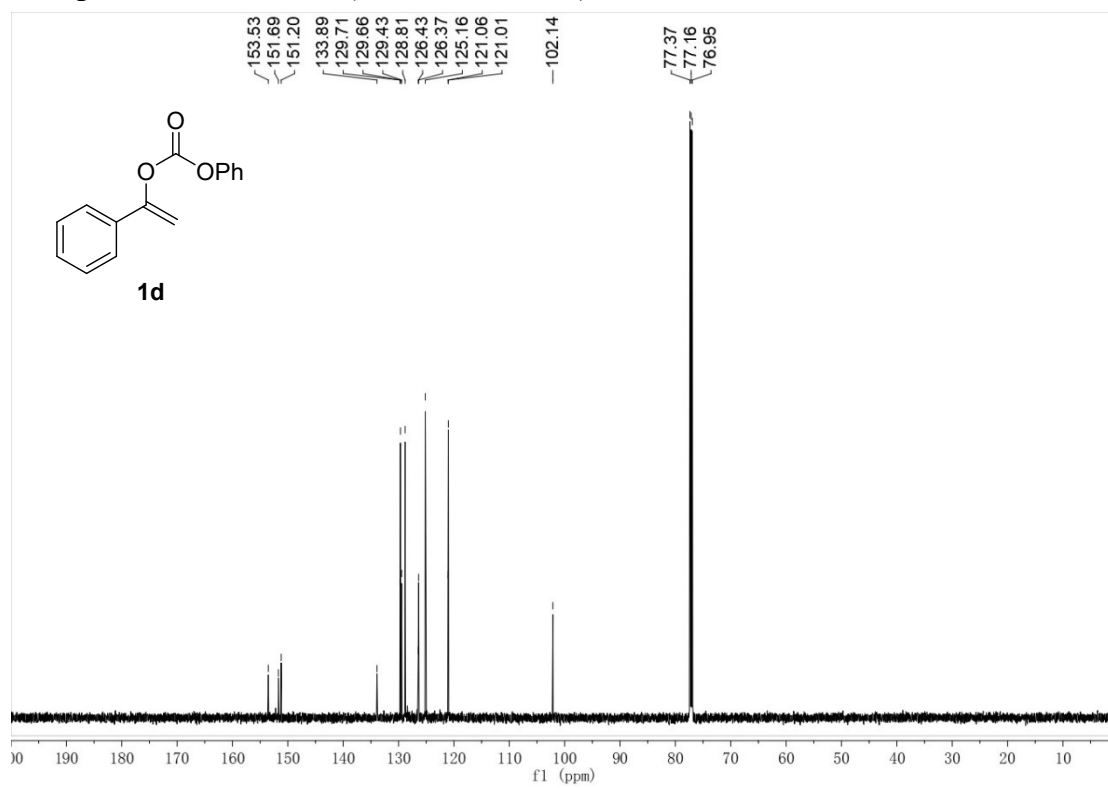
Compound **1c** ^{13}C NMR (150 MHz, CDCl_3)



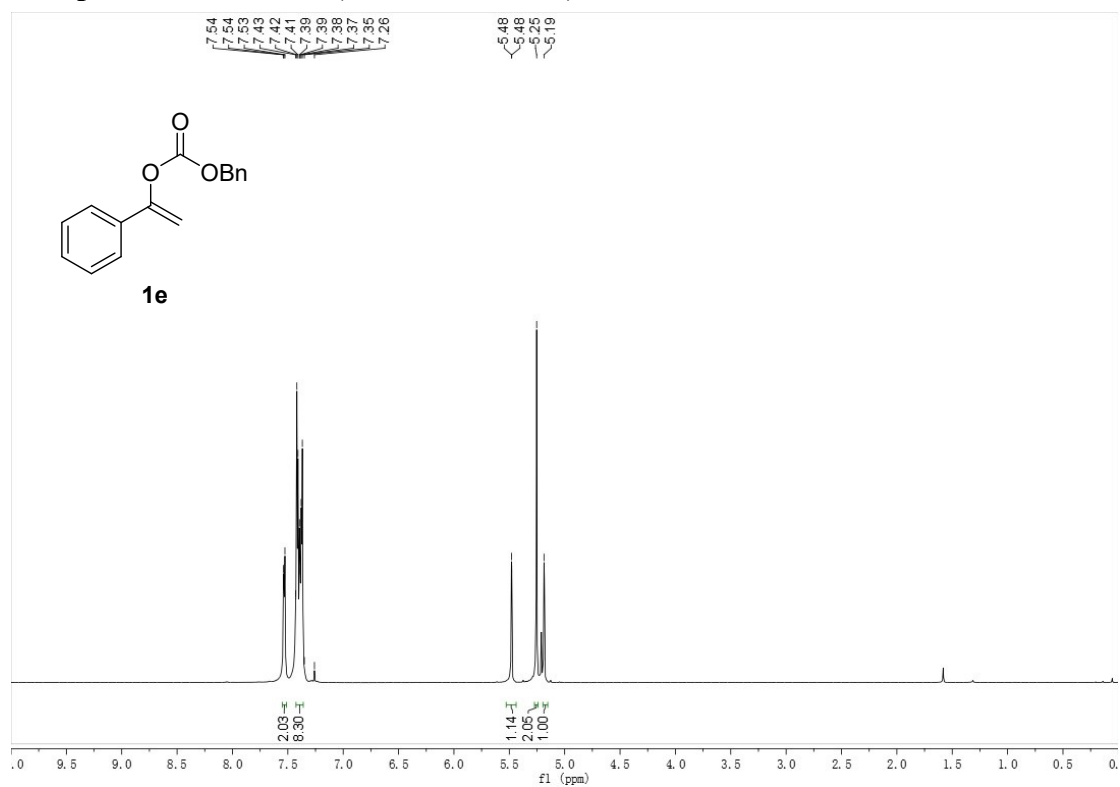
Compound 1d ^1H NMR (600 MHz, CDCl_3)



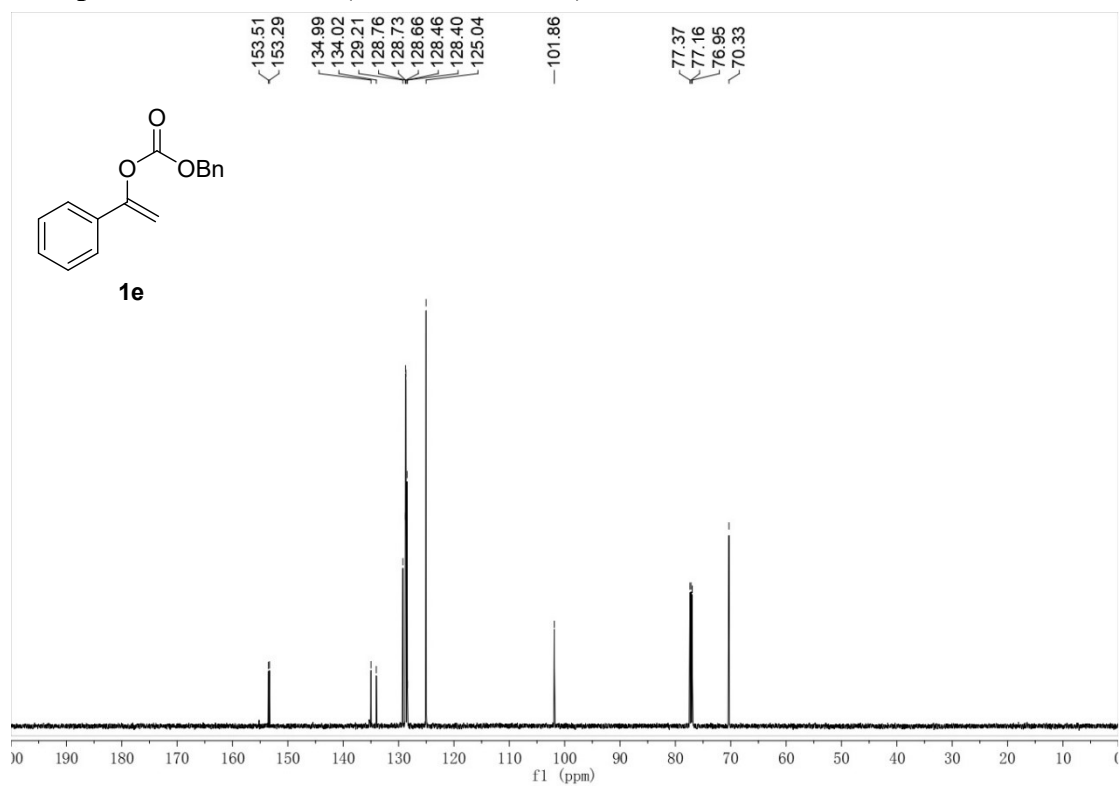
Compound 1d ^{13}C NMR (150 MHz, CDCl_3)



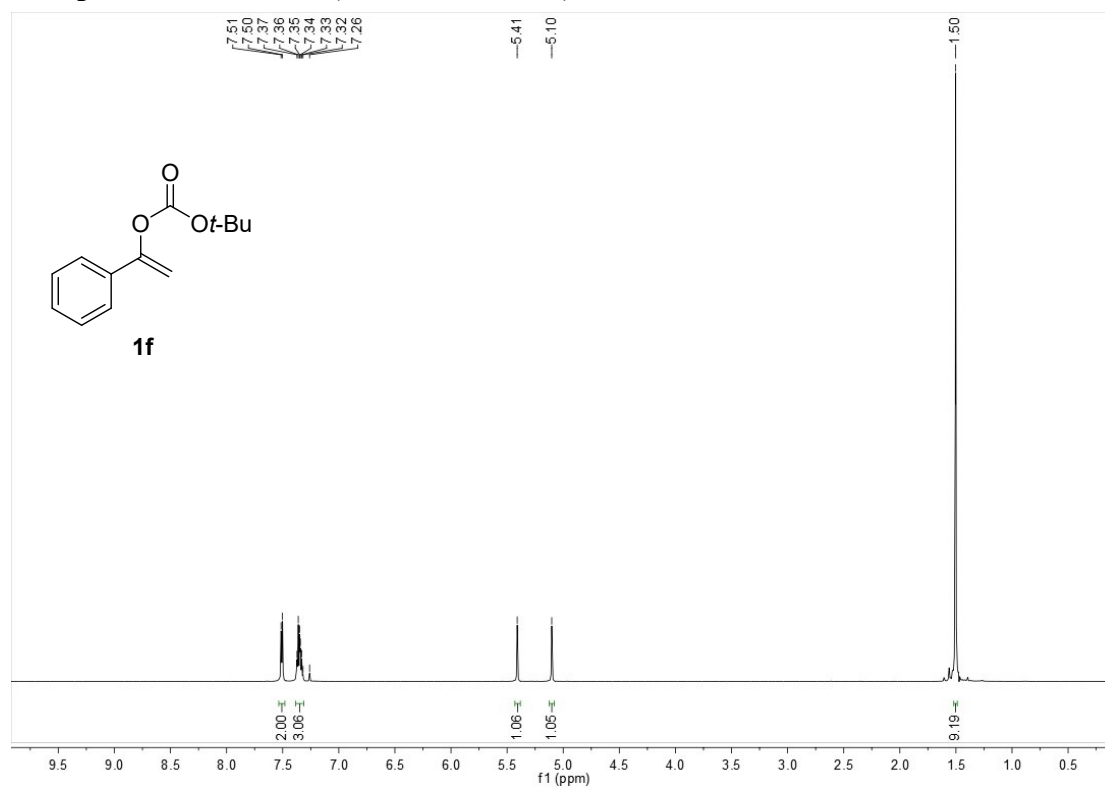
Compound **1e** ^1H NMR (600 MHz, CDCl_3)



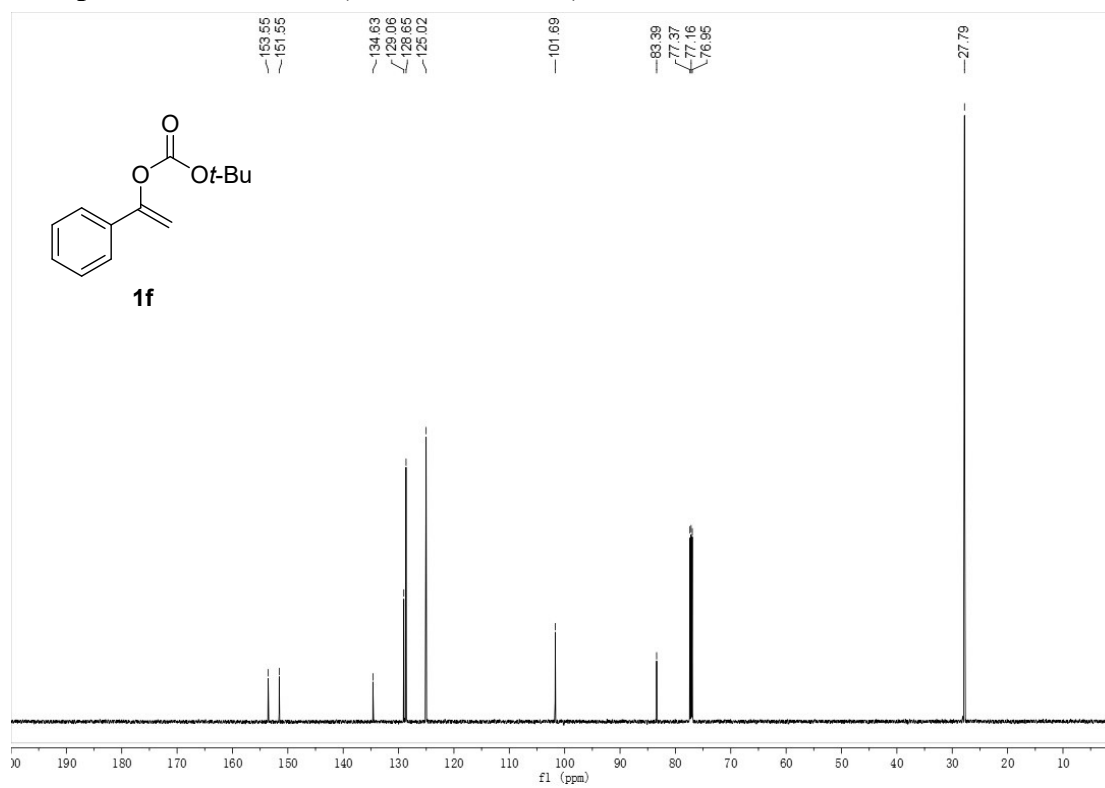
Compound **1e** ^{13}C NMR (150 MHz, CDCl_3)



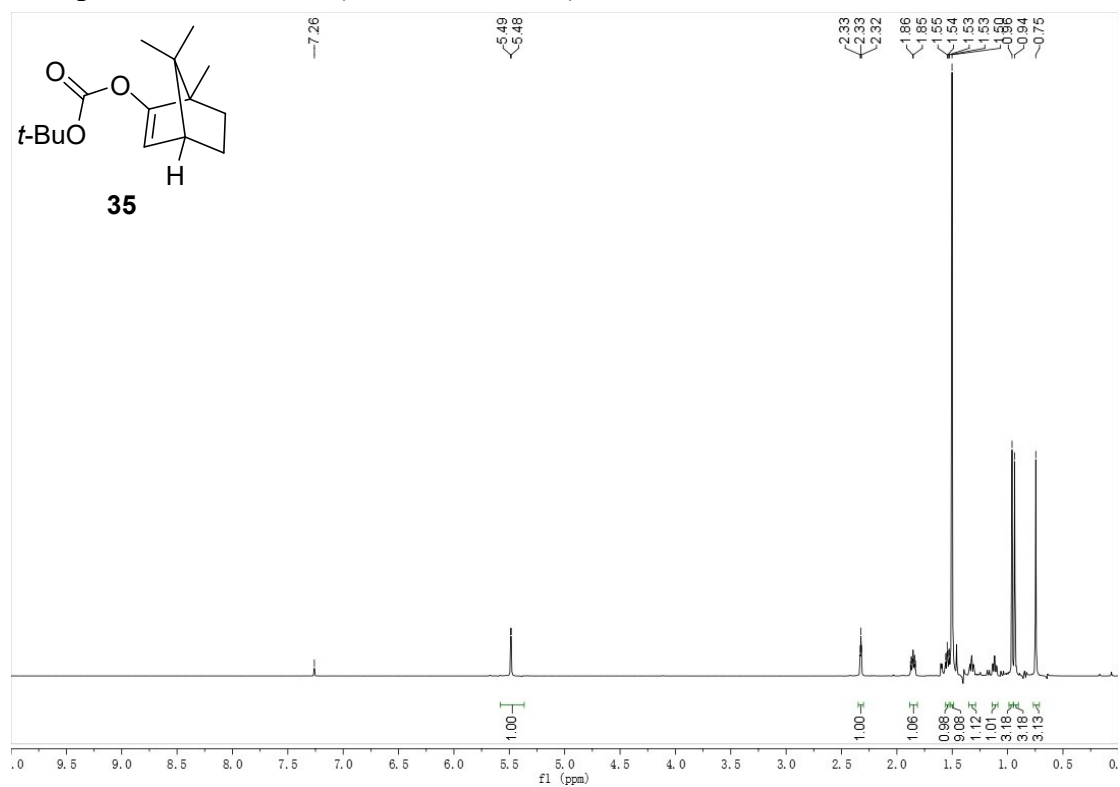
Compound 1f ^1H NMR (600 MHz, CDCl_3)



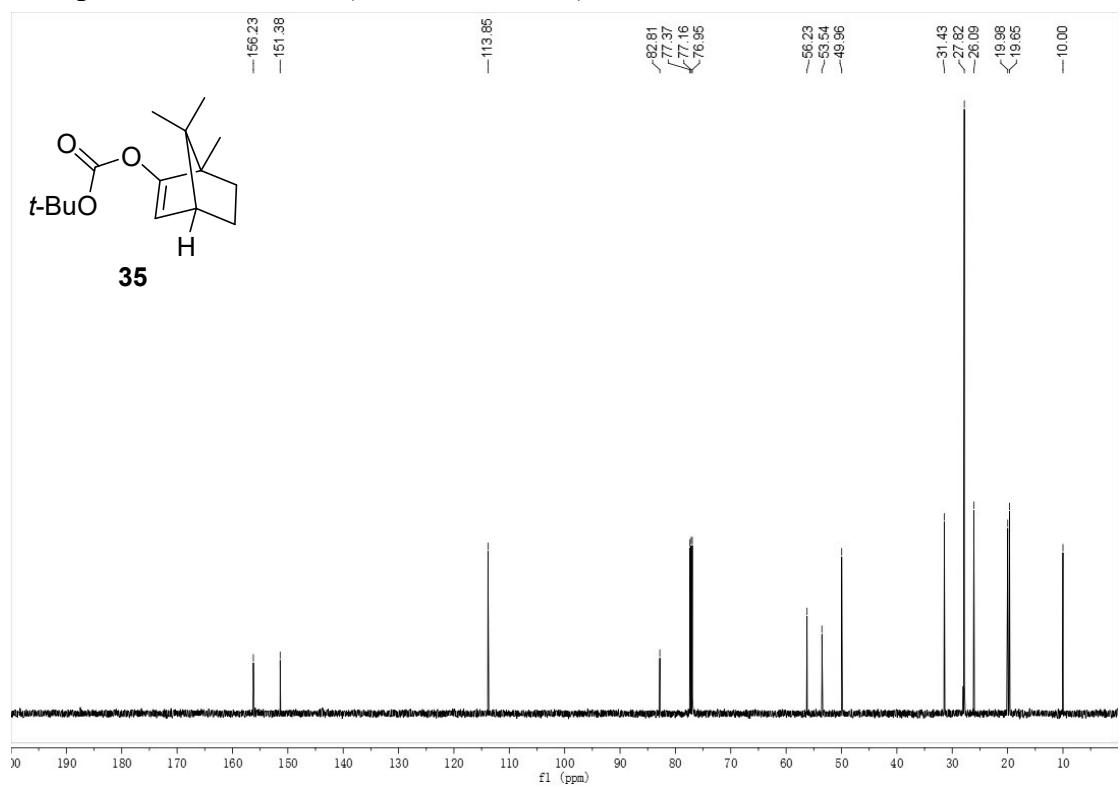
Compound 1f ^{13}C NMR (150 MHz, CDCl_3)



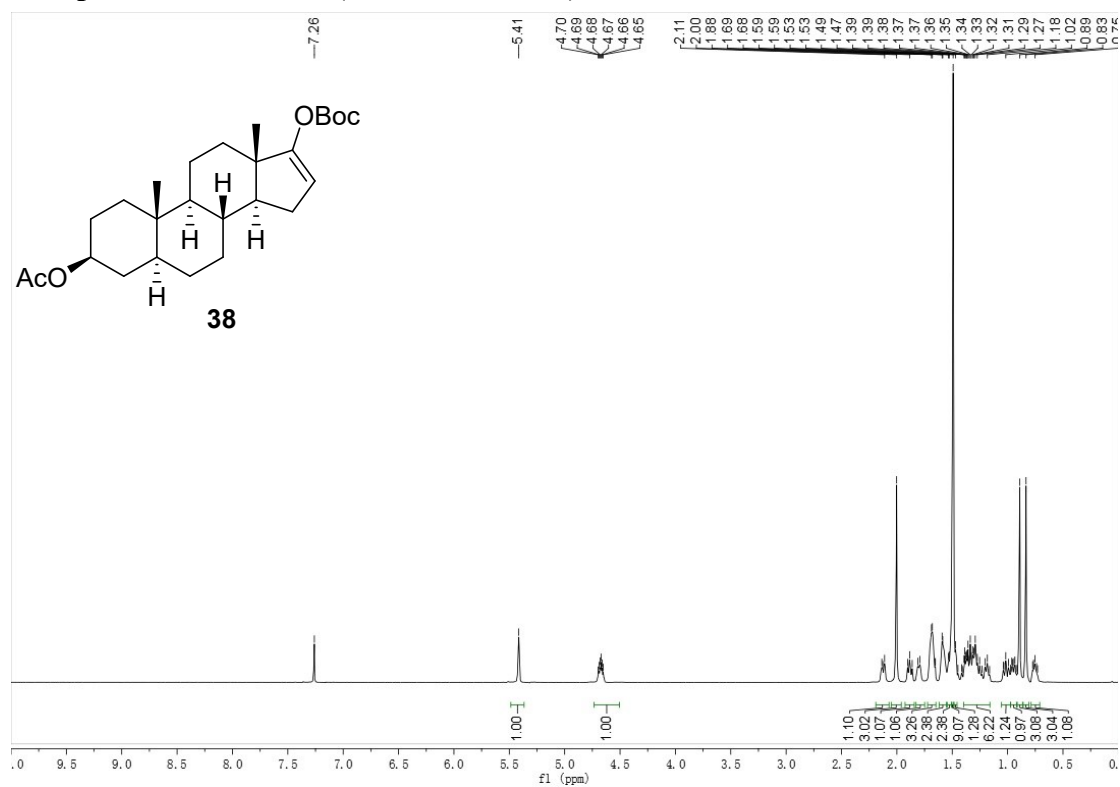
Compound 35 ^1H NMR (600 MHz, CDCl_3)



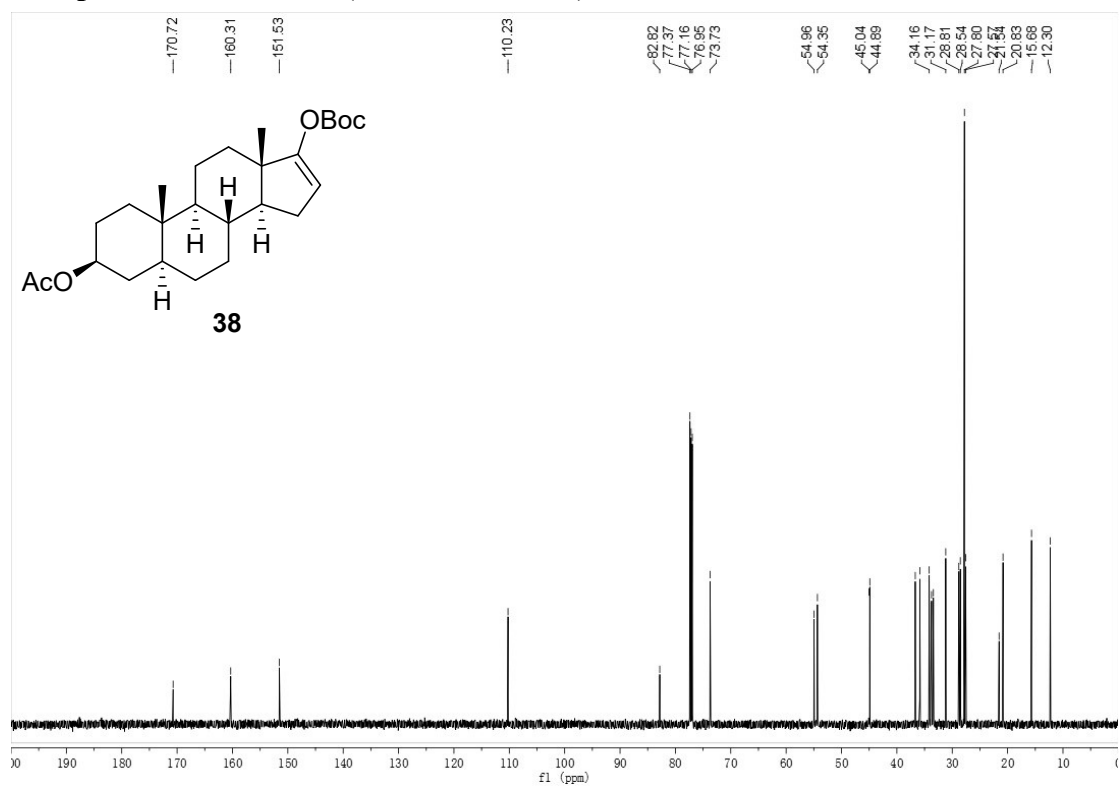
Compound 35 ^{13}C NMR (150 MHz, CDCl_3)



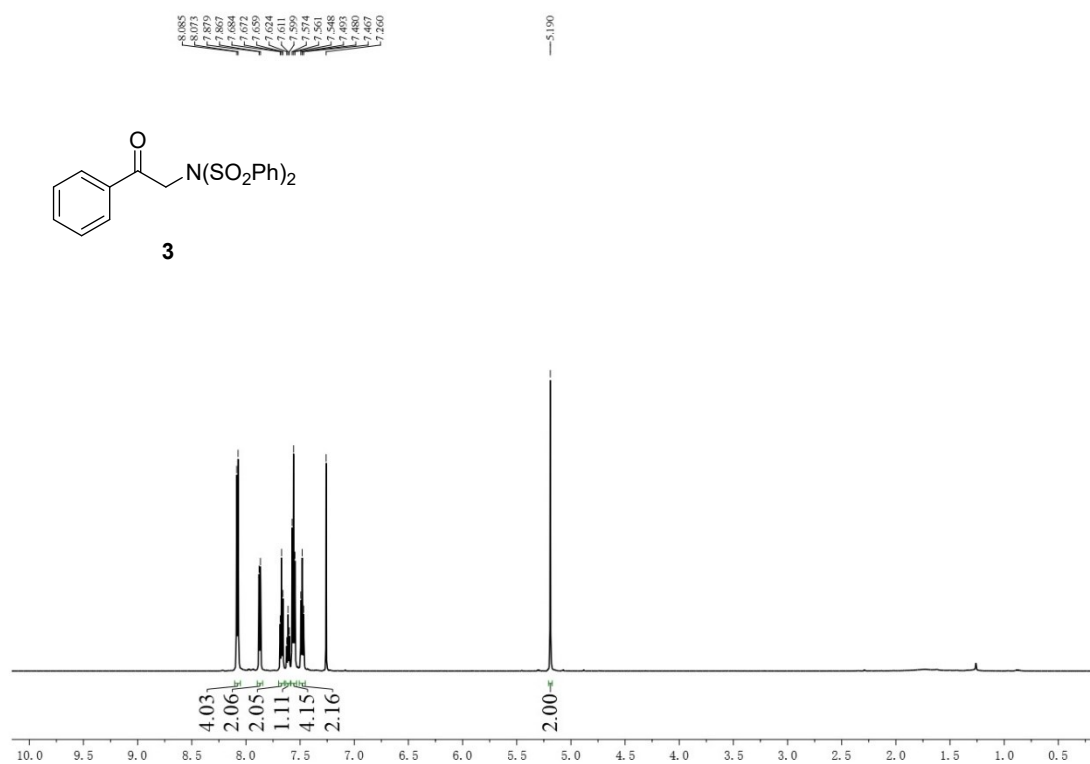
Compound 38 ^1H NMR (600 MHz, CDCl_3)



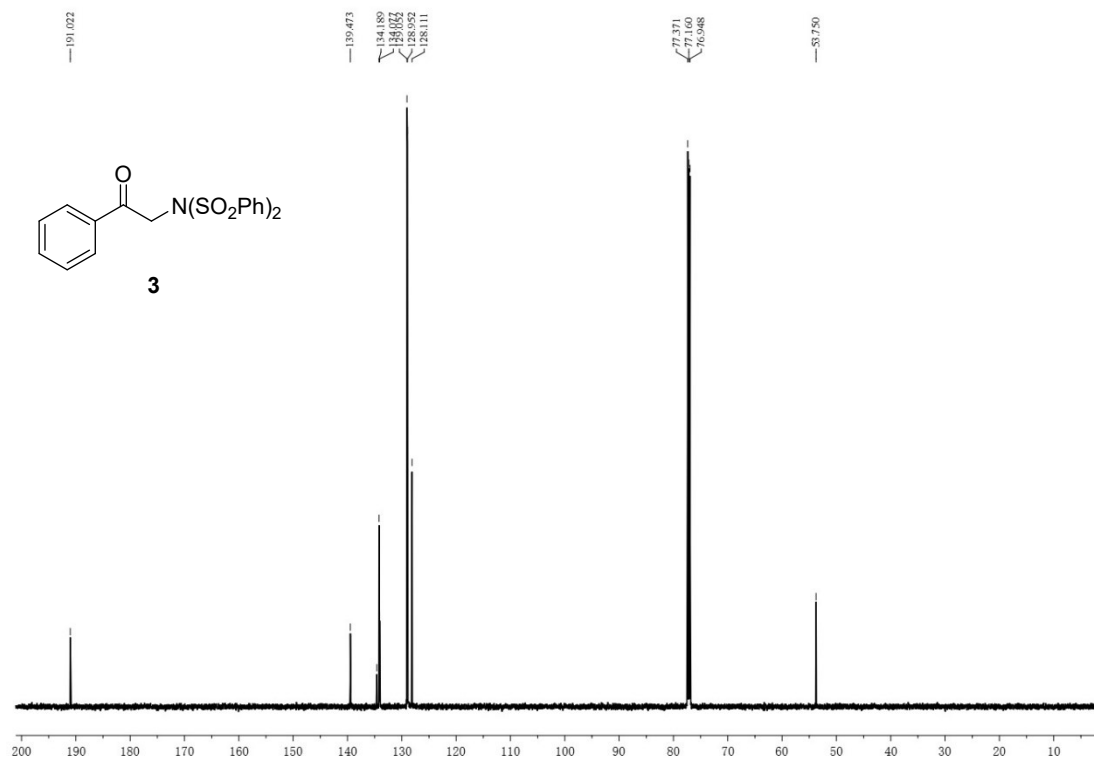
Compound 38 ^{13}C NMR (150 MHz, CDCl_3)



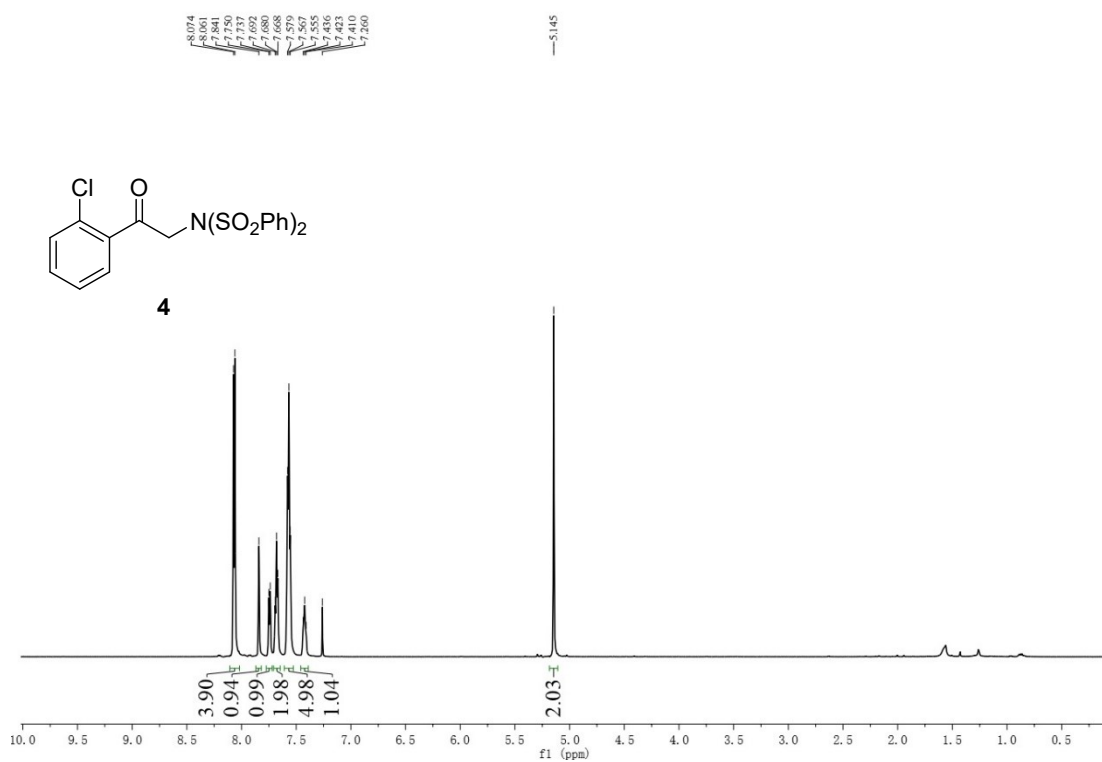
Compound 3 ¹H NMR (600 MHz, CDCl₃)



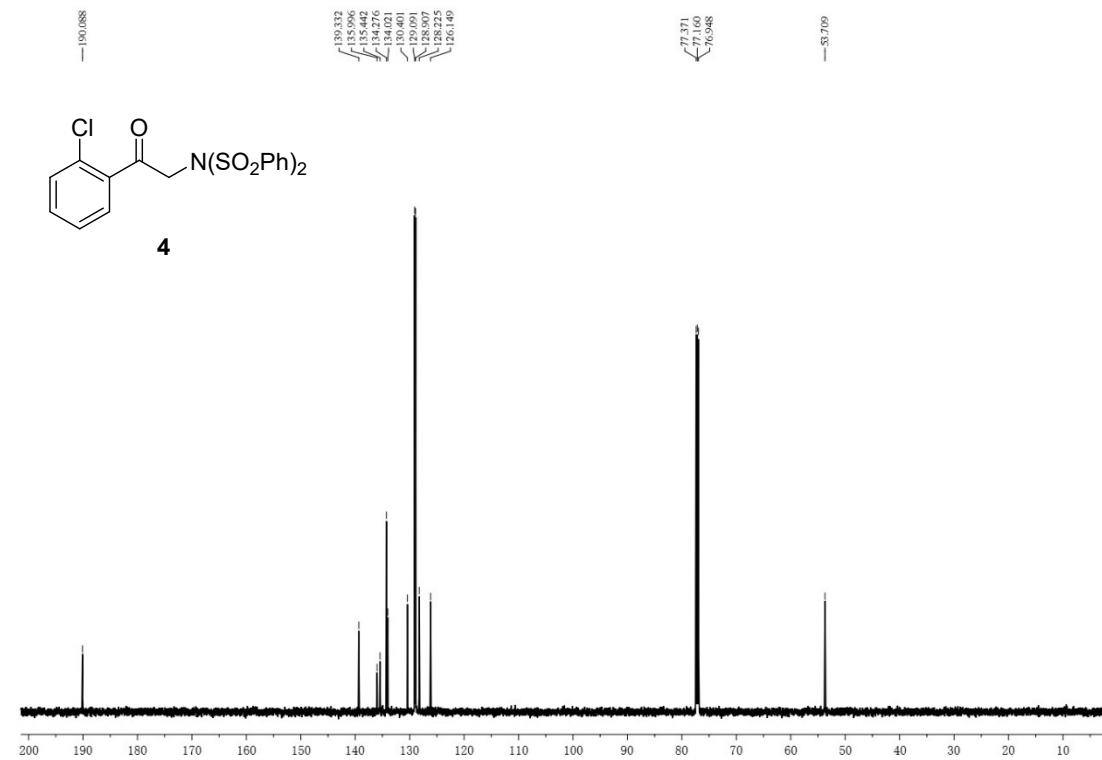
Compound 3 ¹³C NMR (150 MHz, CDCl₃)



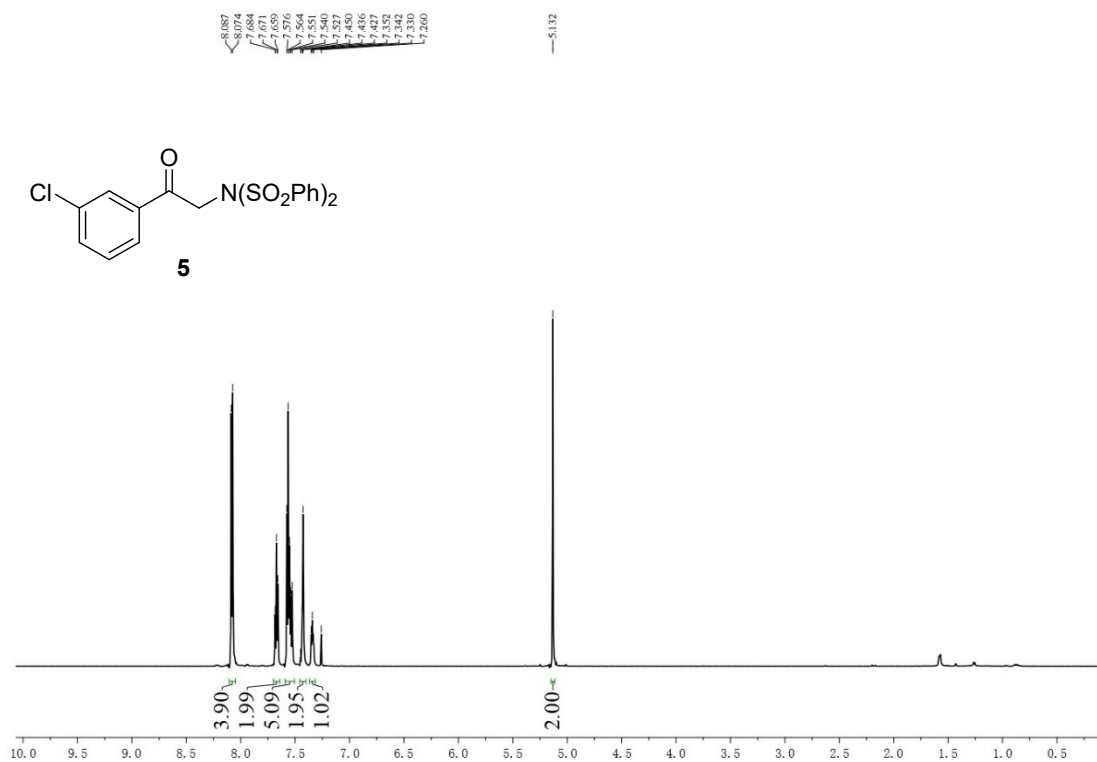
Compound 4 ¹H NMR (600 MHz, CDCl₃)



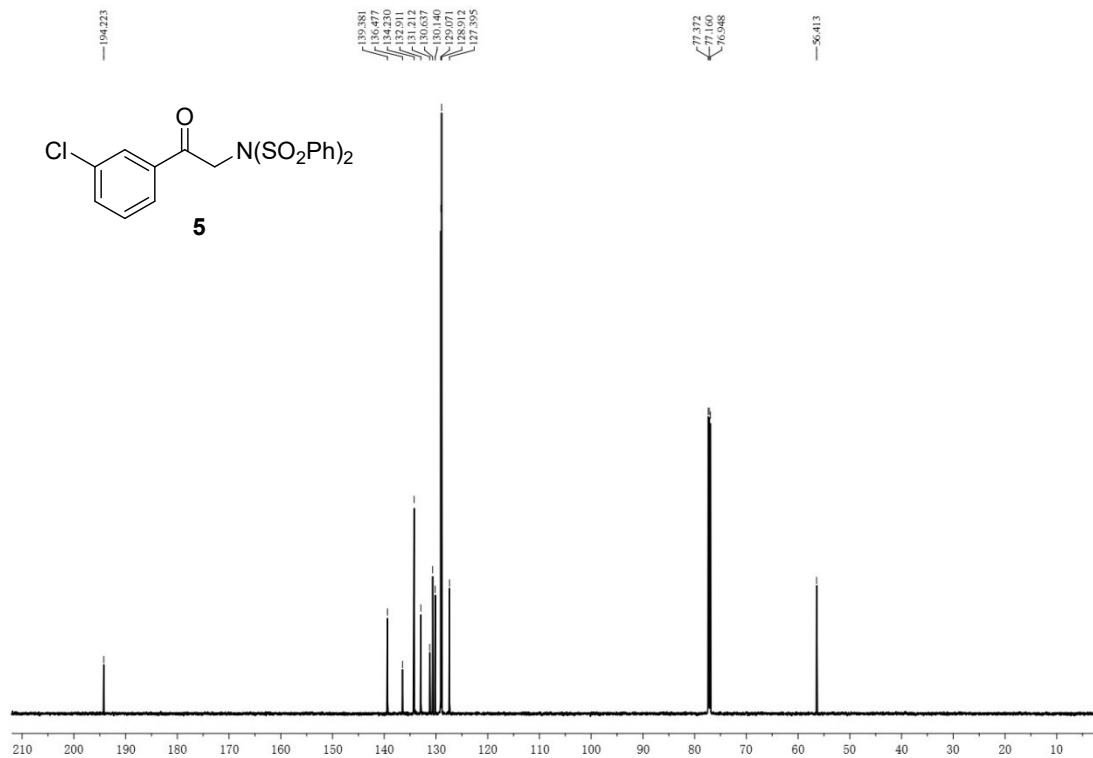
Compound 4 ¹³C NMR (150 MHz, CDCl₃)



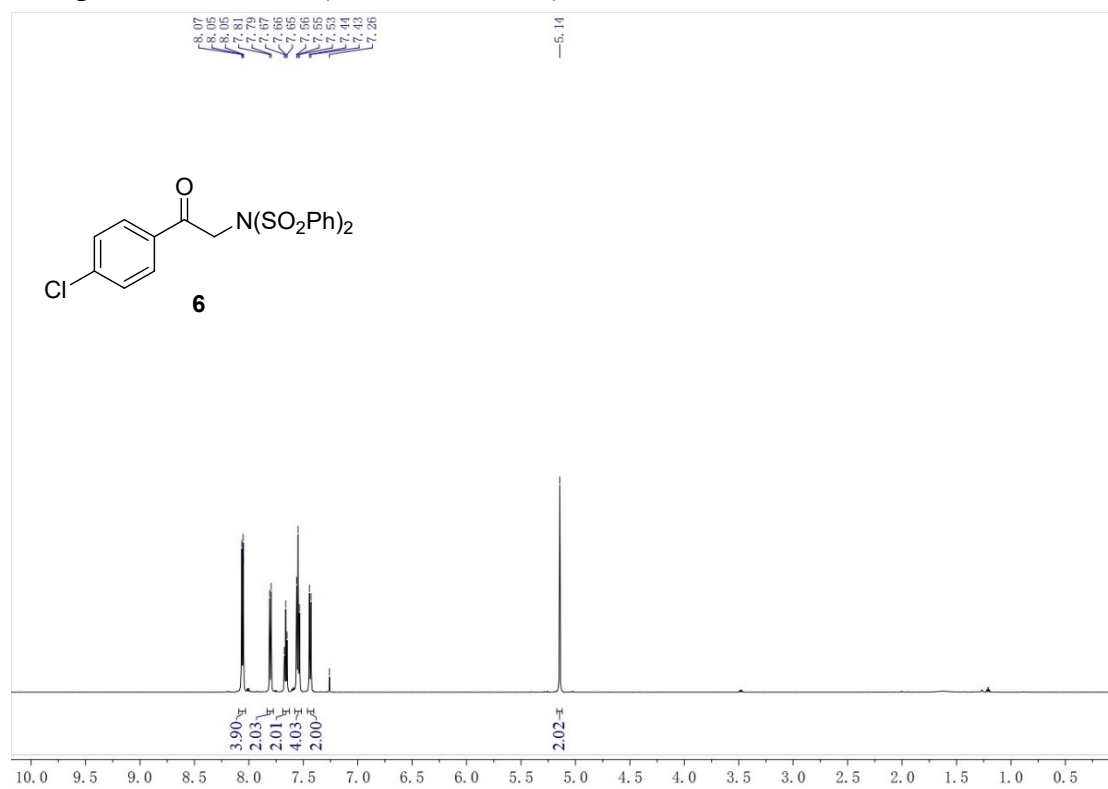
Compound 5 ¹H NMR (600 MHz, CDCl₃)



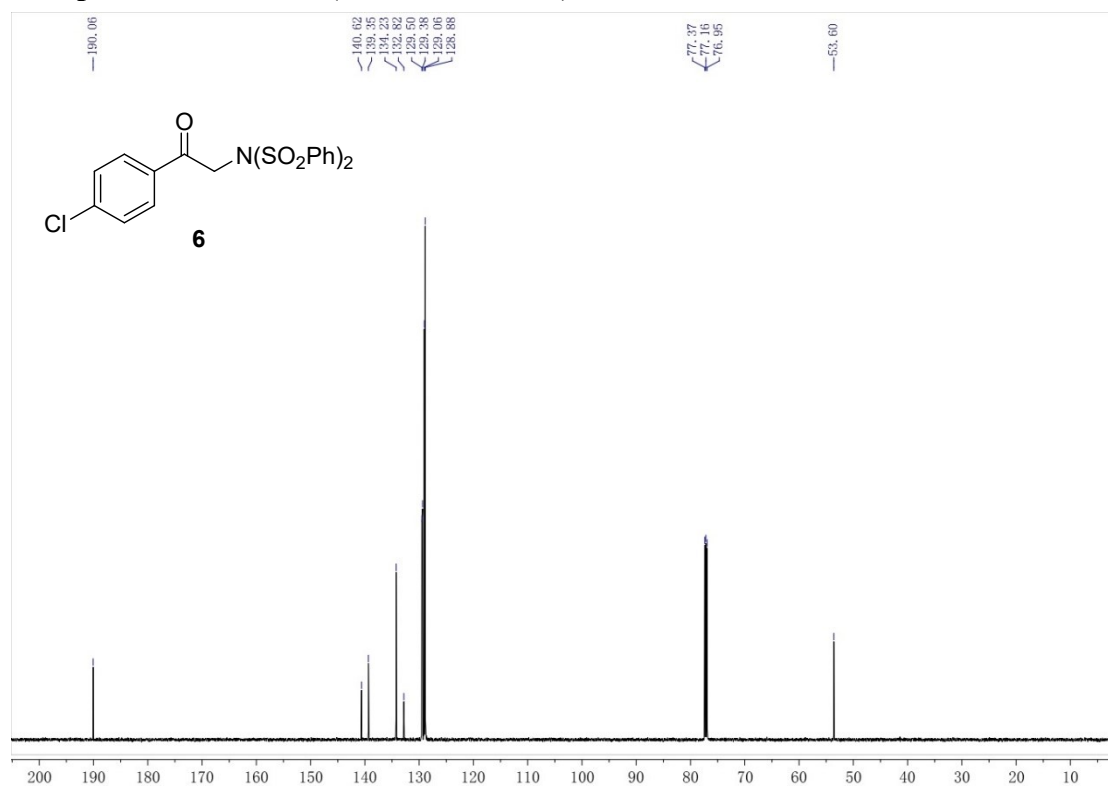
Compound 5 ¹³C NMR (150 MHz, CDCl₃)



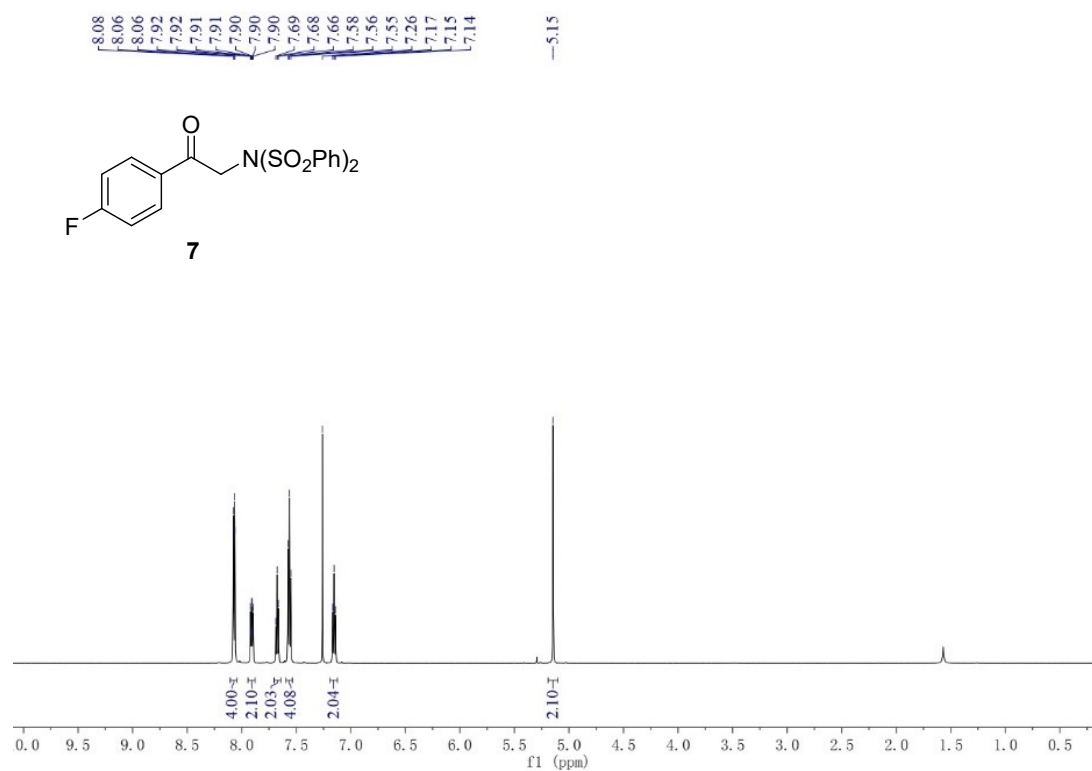
Compound 6 ^1H NMR (600 MHz, CDCl_3)



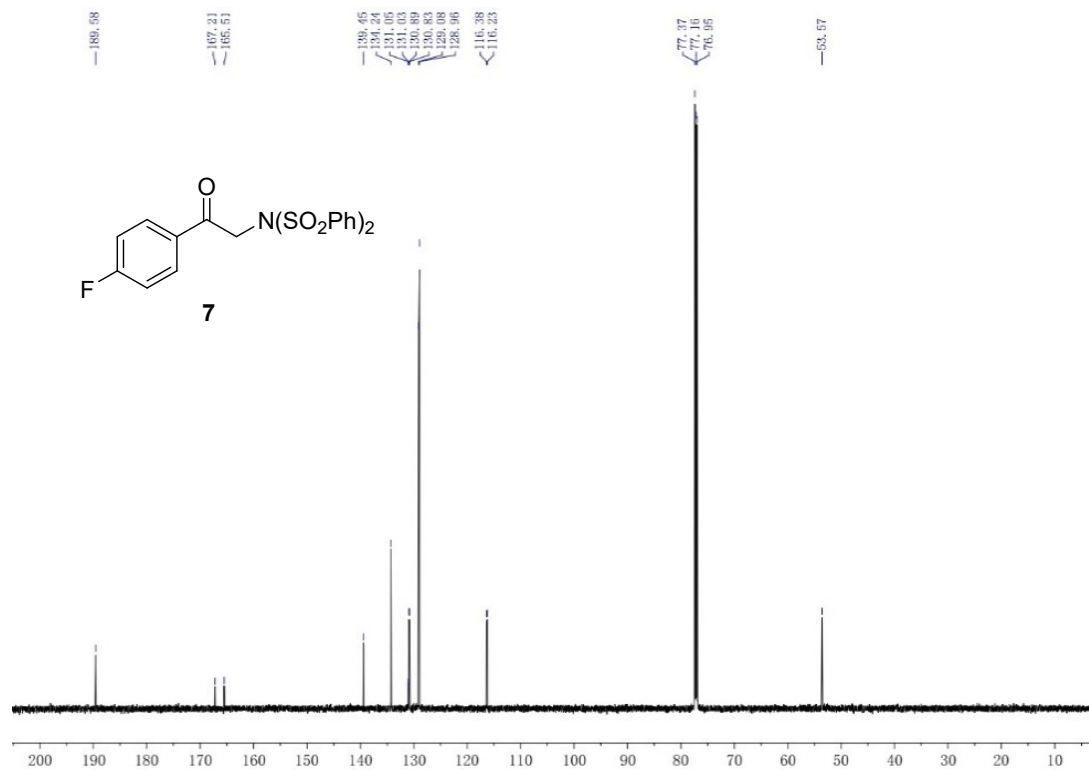
Compound 6 ^{13}C NMR (150 MHz, CDCl_3)



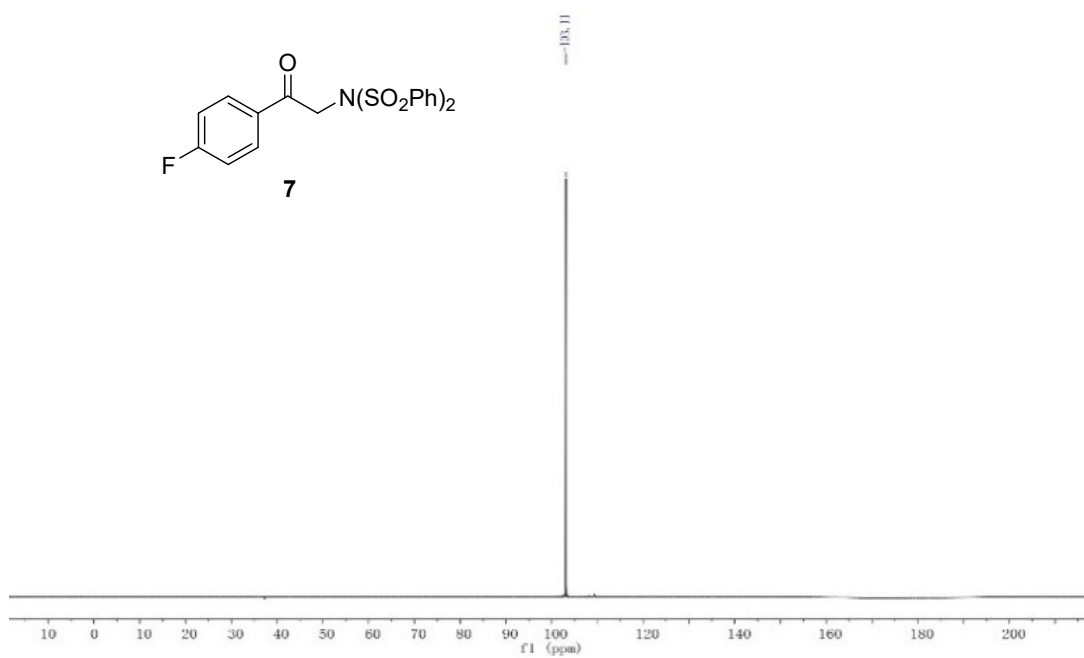
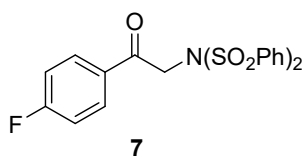
Compound 7 ^1H NMR (600 MHz, CDCl_3)



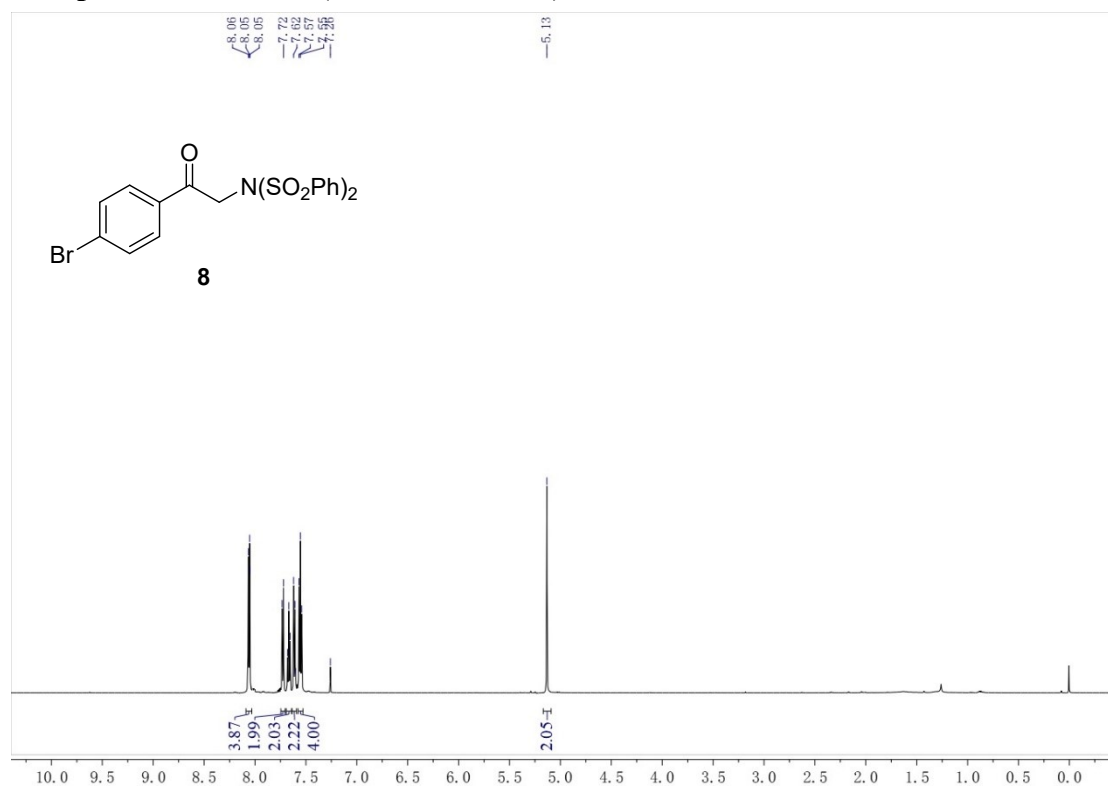
Compound 7 ^{13}C NMR (150 MHz, CDCl_3)



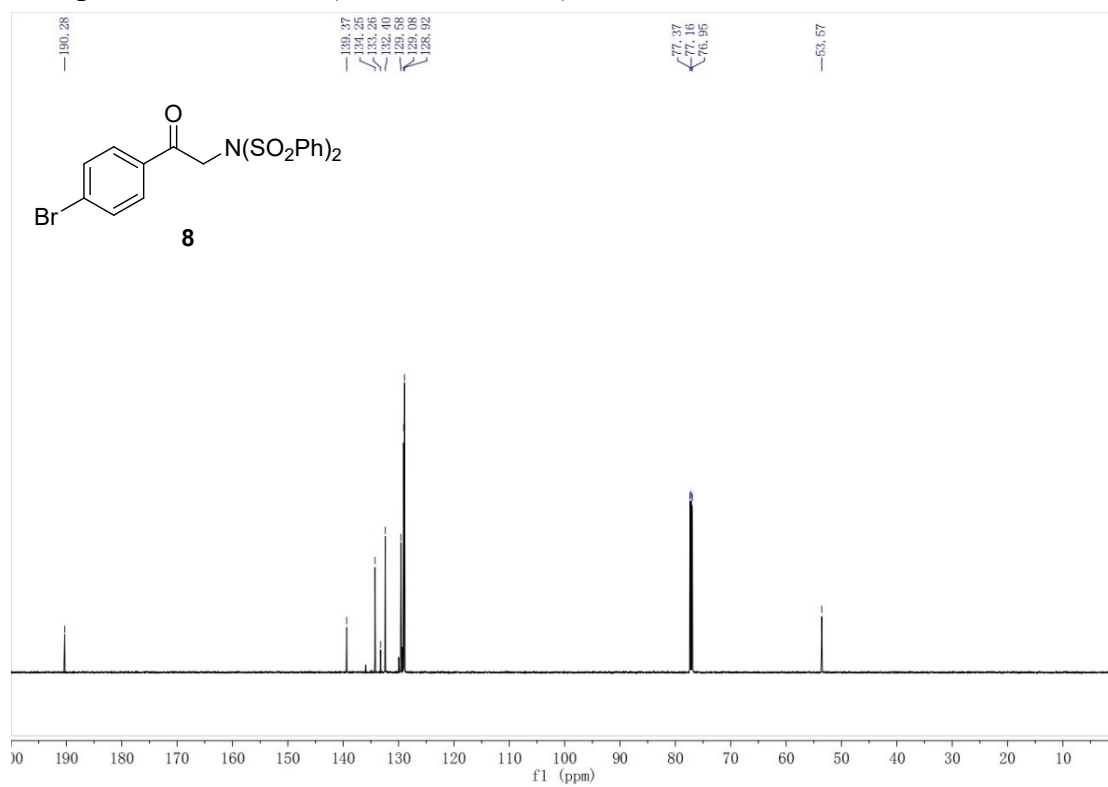
Compound 7 ^{19}F NMR (565 MHz, CDCl_3)



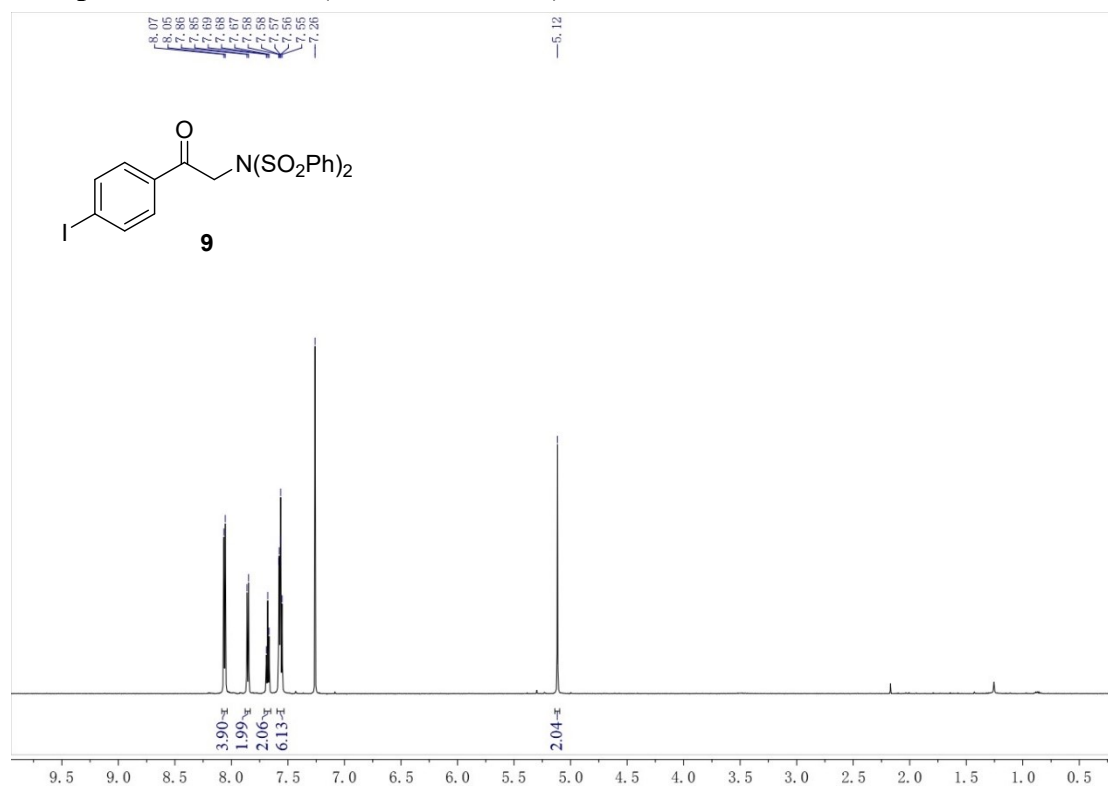
Compound 8 ^1H NMR (600 MHz, CDCl_3)



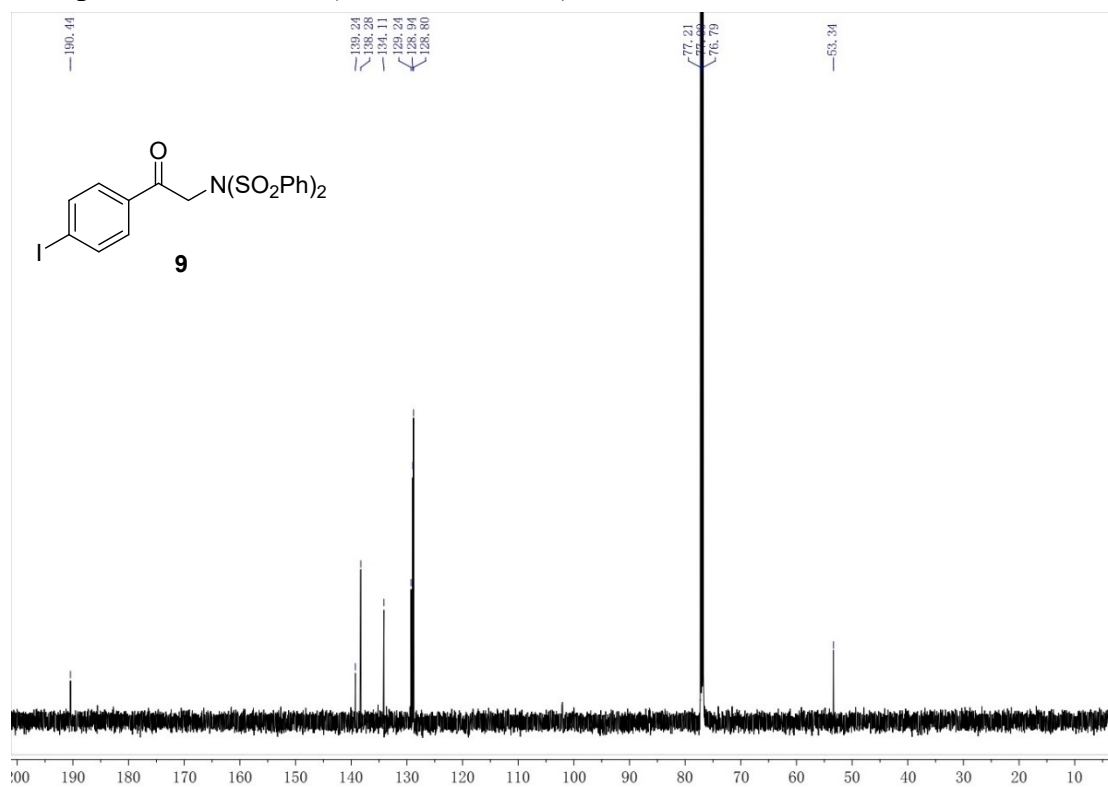
Compound 8 ^{13}C NMR (150 MHz, CDCl_3)



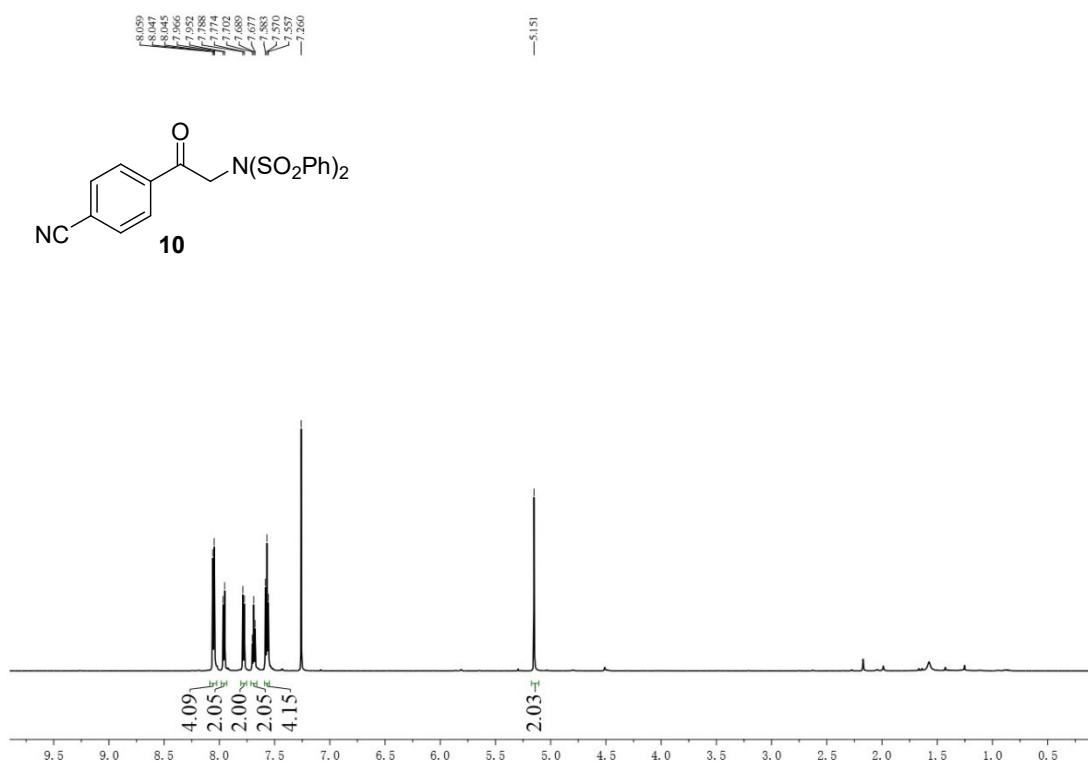
Compound 9 ¹H NMR (600 MHz, CDCl₃)



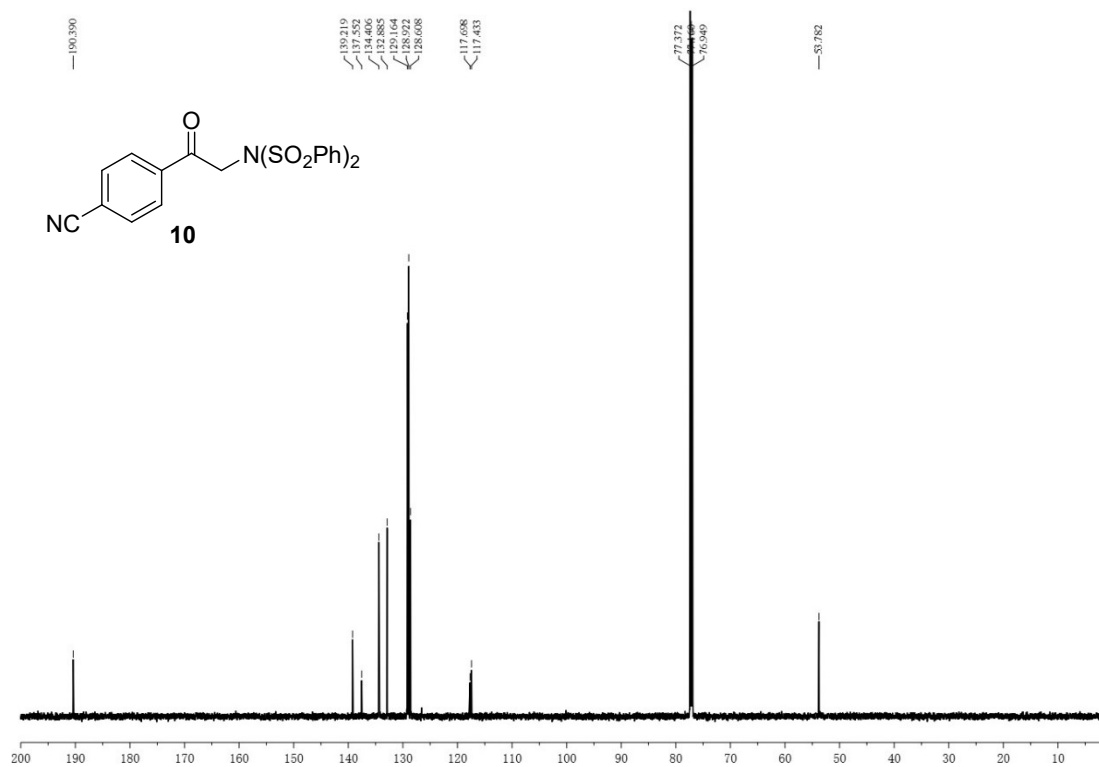
Compound 9 ¹³C NMR (150 MHz, CDCl₃)



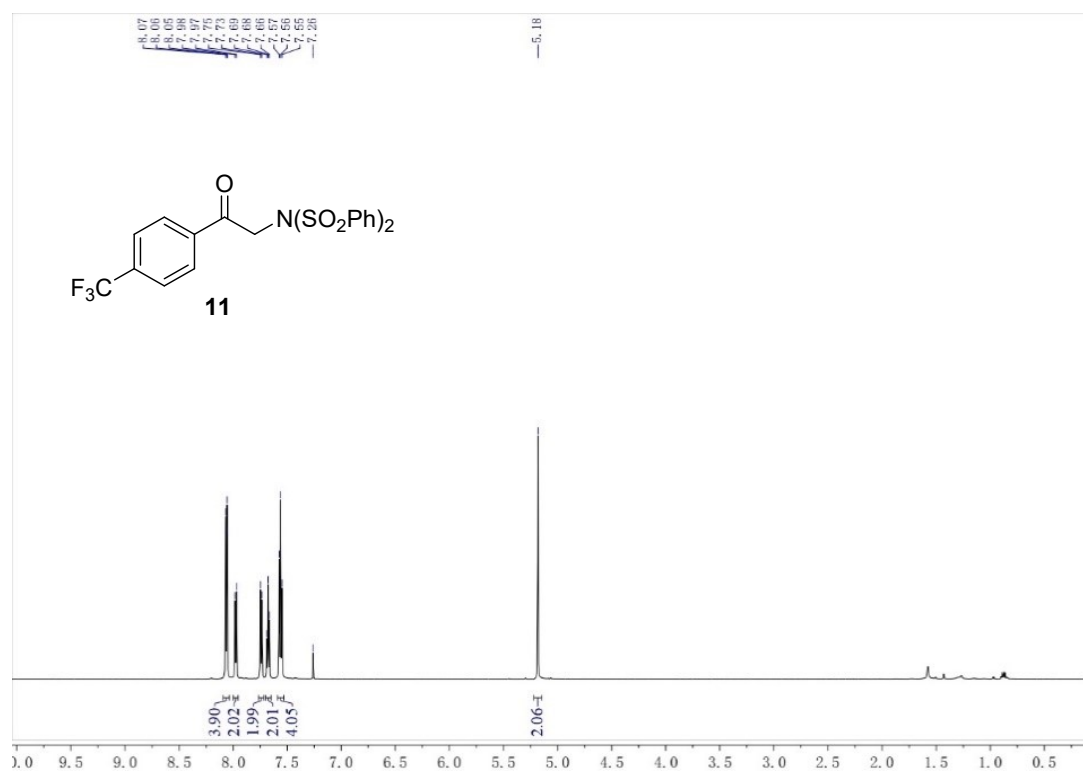
Compound 10 ¹H NMR (600 MHz, CDCl₃)



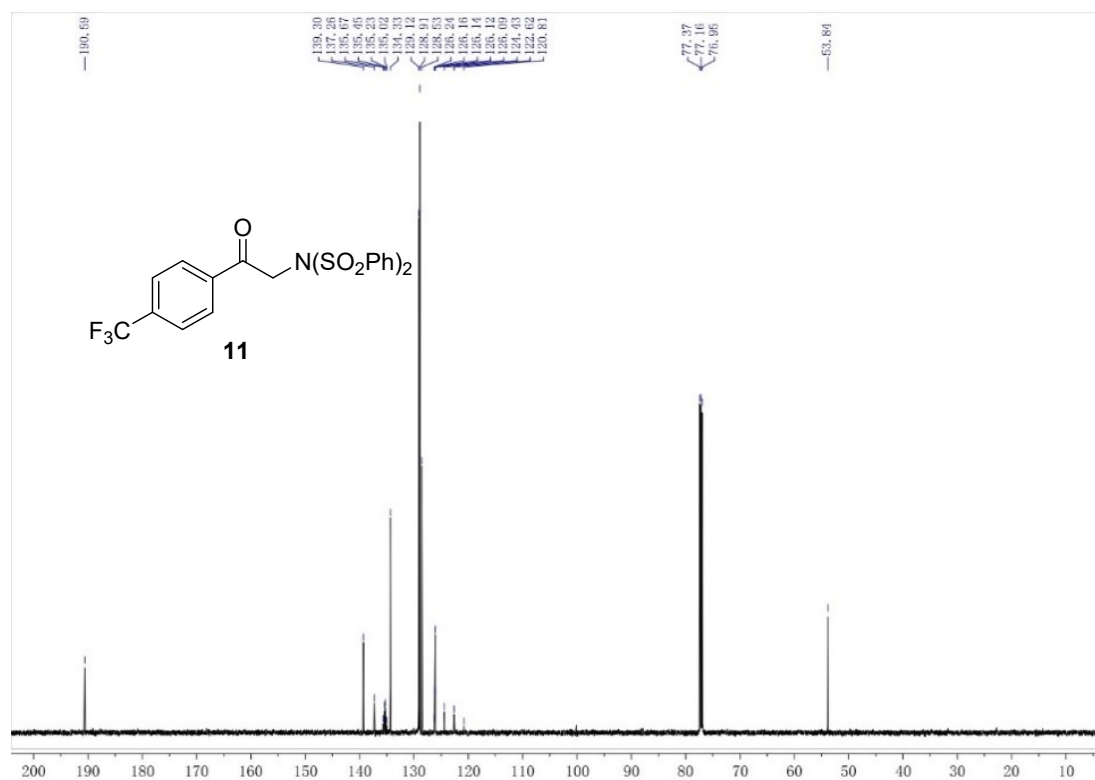
Compound 10 ¹³C NMR (150 MHz, CDCl₃)



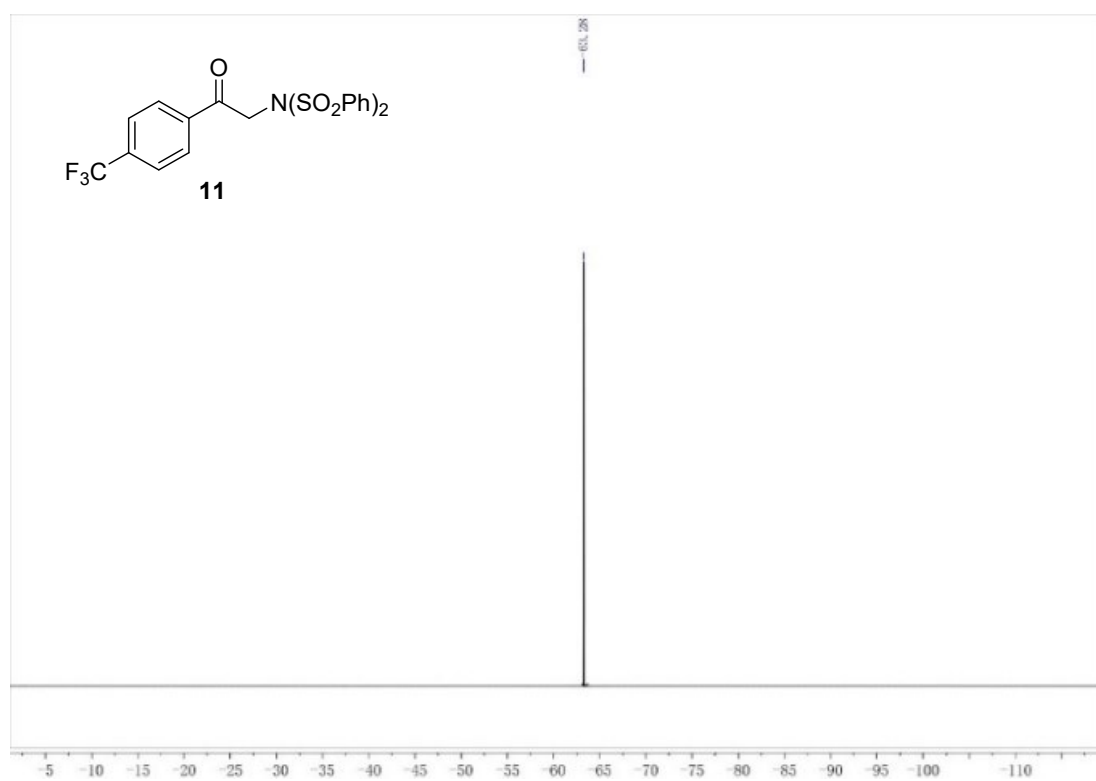
Compound 11 ^1H NMR (600 MHz, CDCl_3)



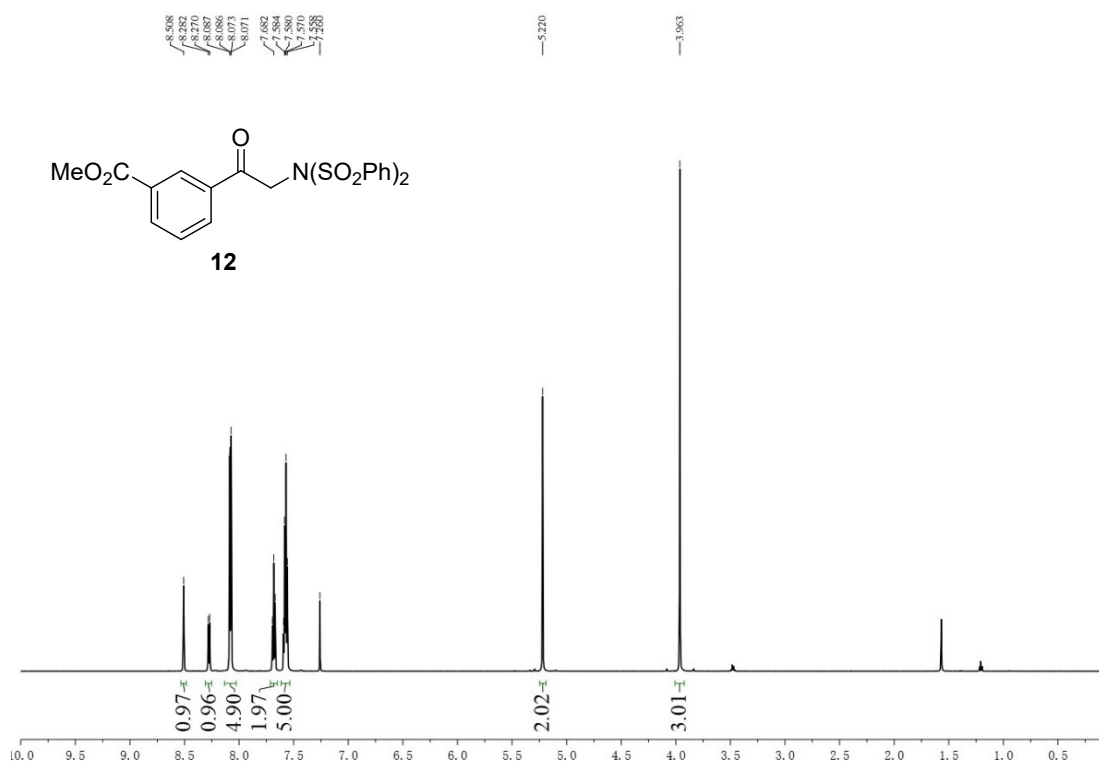
Compound 11 ^{13}C NMR (150 MHz, CDCl_3)



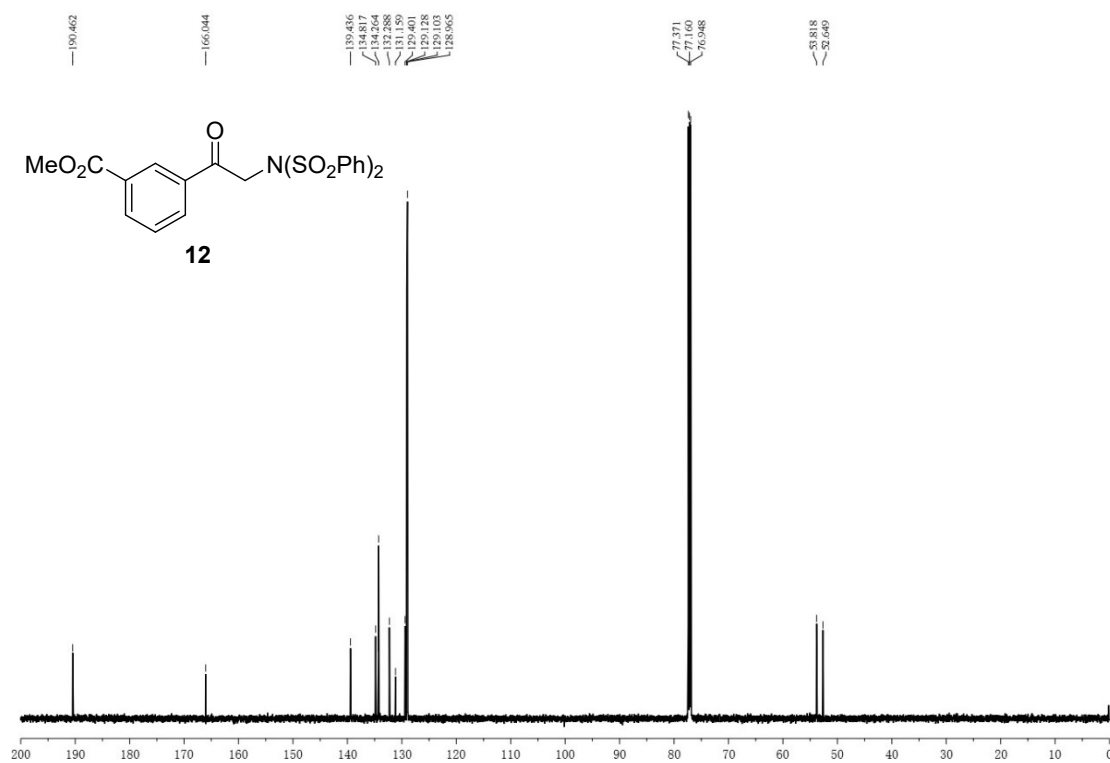
Compound 11 ^{19}F NMR (565 MHz, CDCl_3)



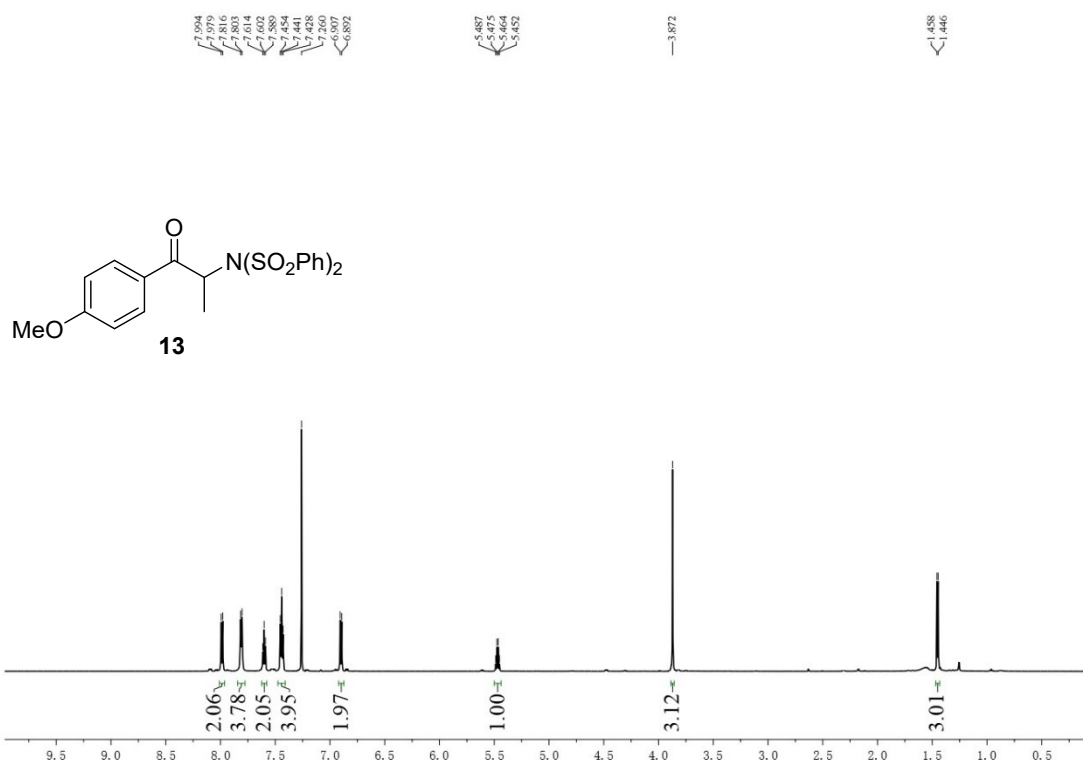
Compound 12 ¹H NMR (600 MHz, CDCl₃)



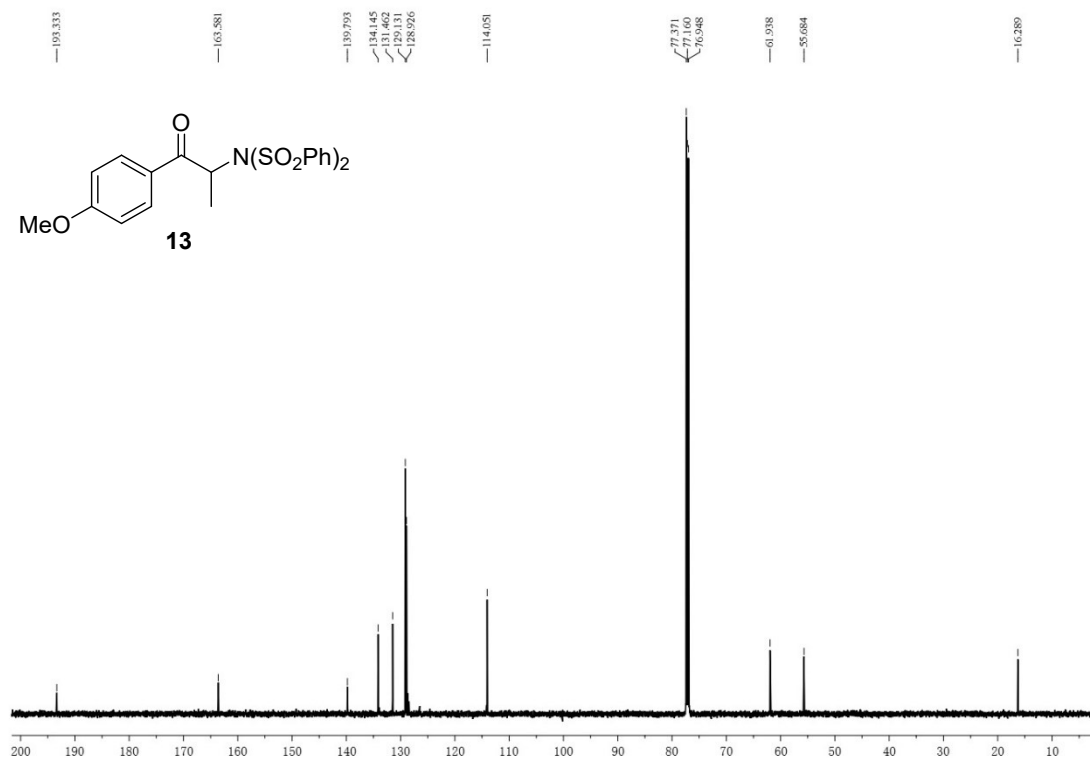
Compound 12 ¹³C NMR (150 MHz, CDCl₃)



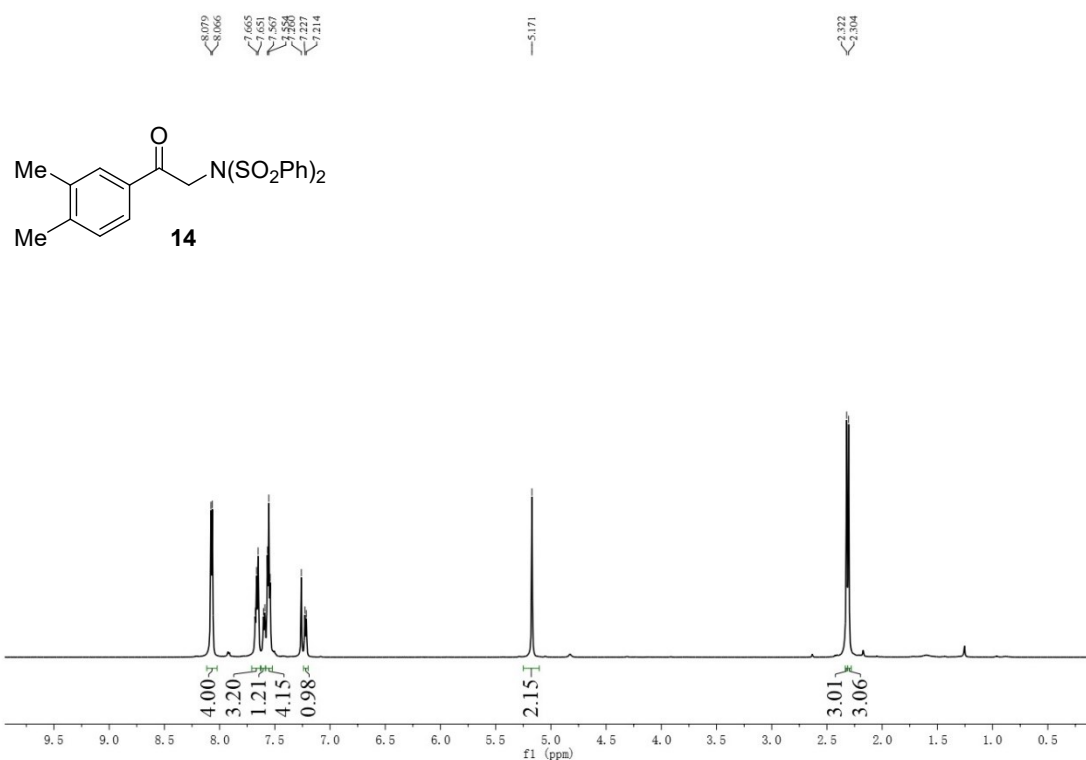
Compound 13 ¹H NMR (600 MHz, CDCl₃)



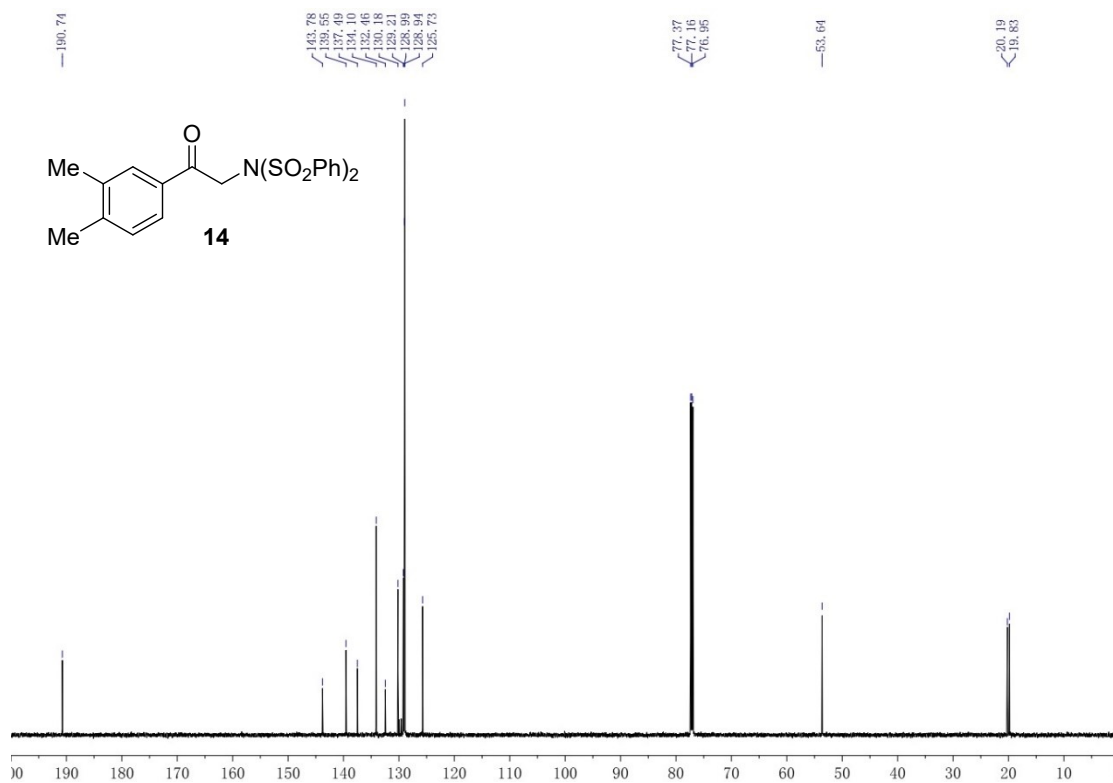
Compound 13 ¹³C NMR (150 MHz, CDCl₃)



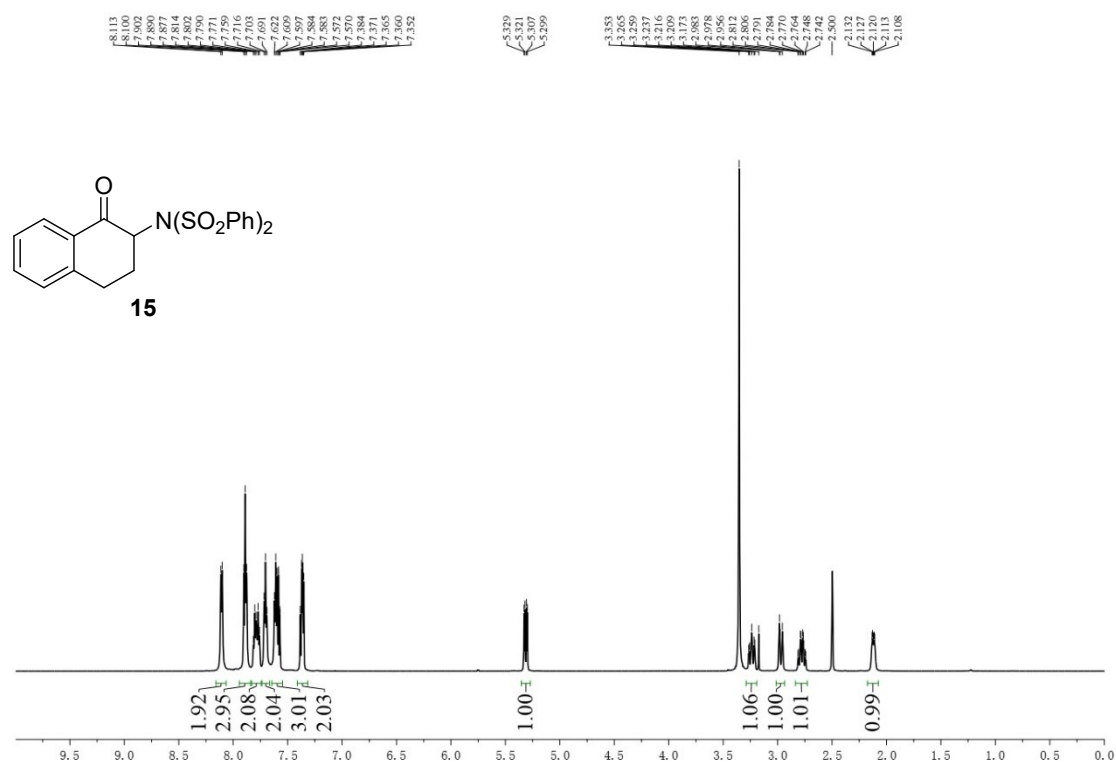
Compound 14 ¹H NMR (600 MHz, CDCl₃)



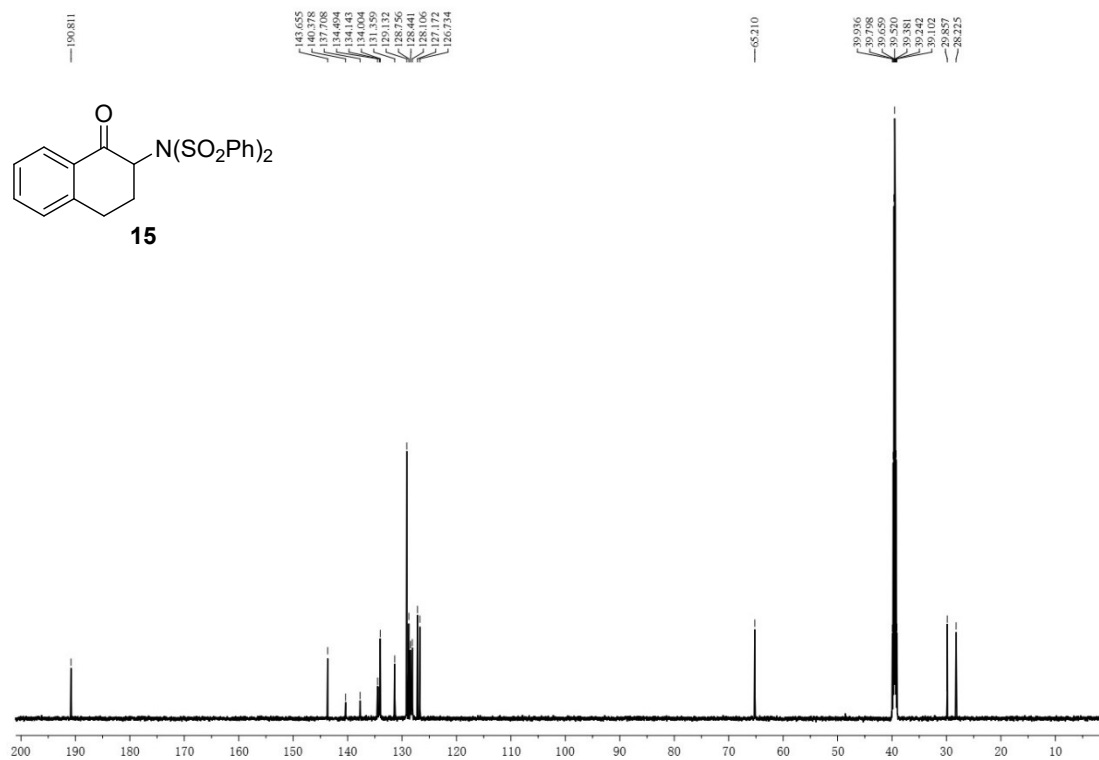
Compound 14 ¹³C NMR (150 MHz, CDCl₃)



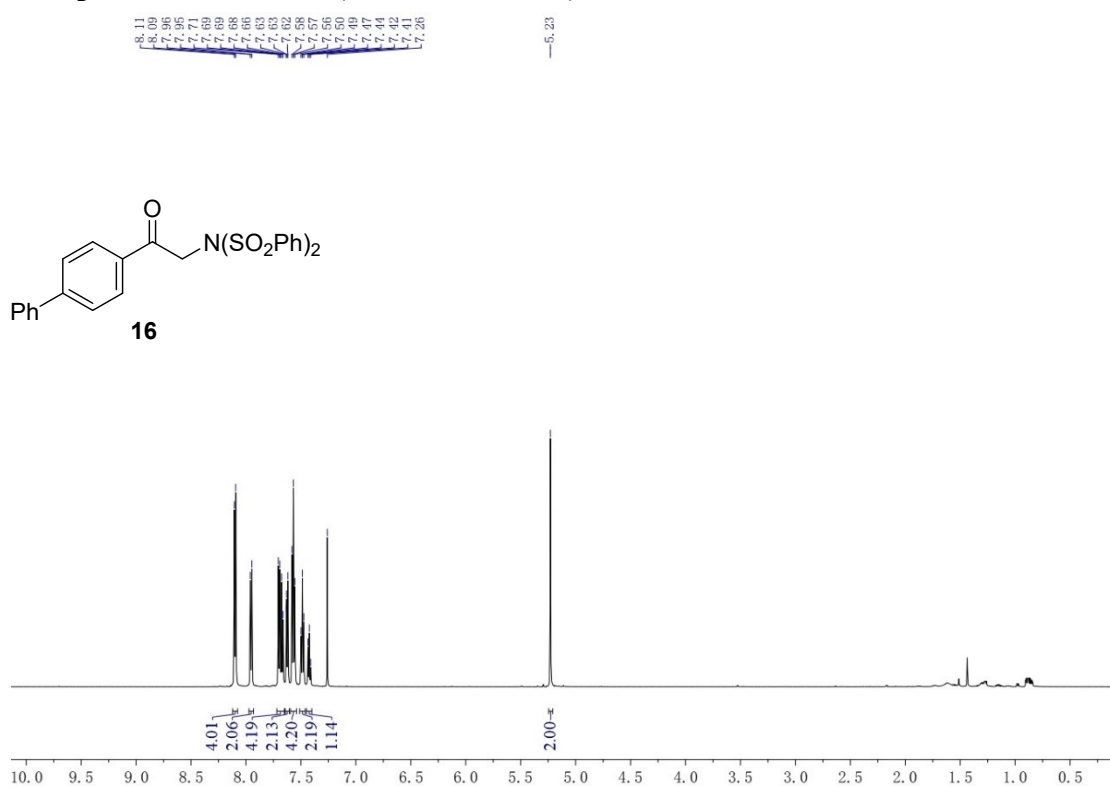
Compound 15 ^1H NMR (600 MHz, d_6 -DMSO)



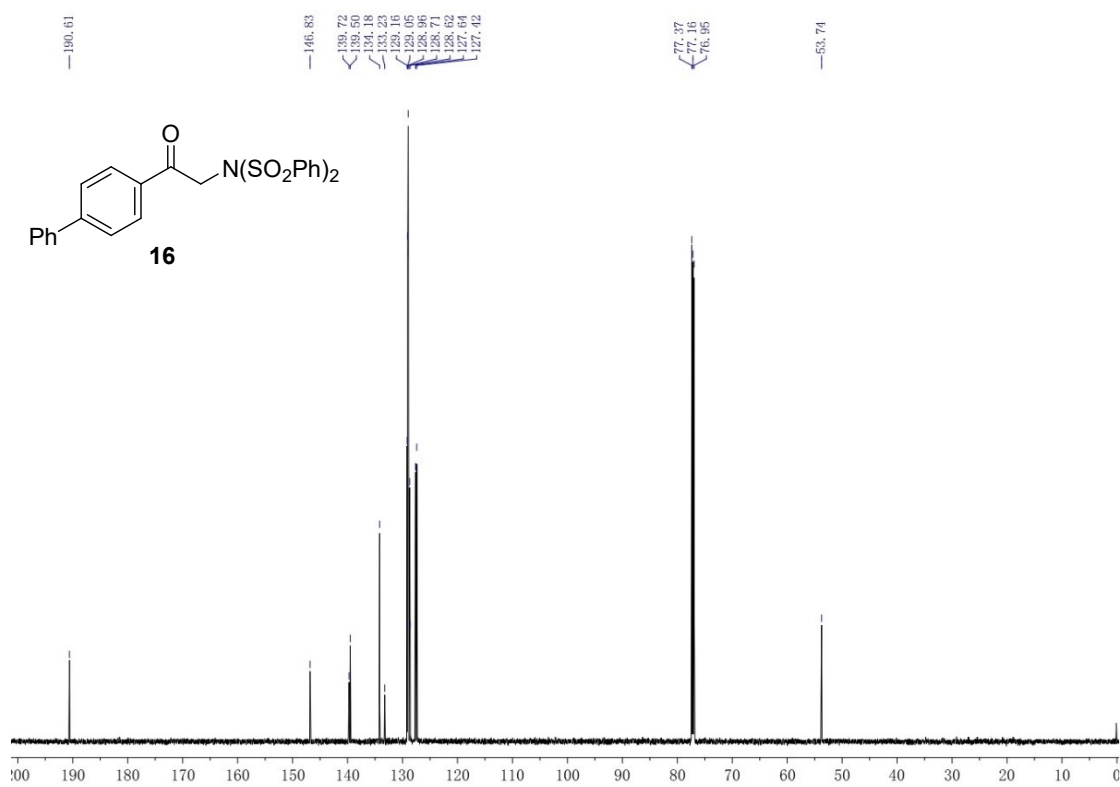
Compound 15 ^{13}C NMR (150 MHz, d_6 -DMSO)



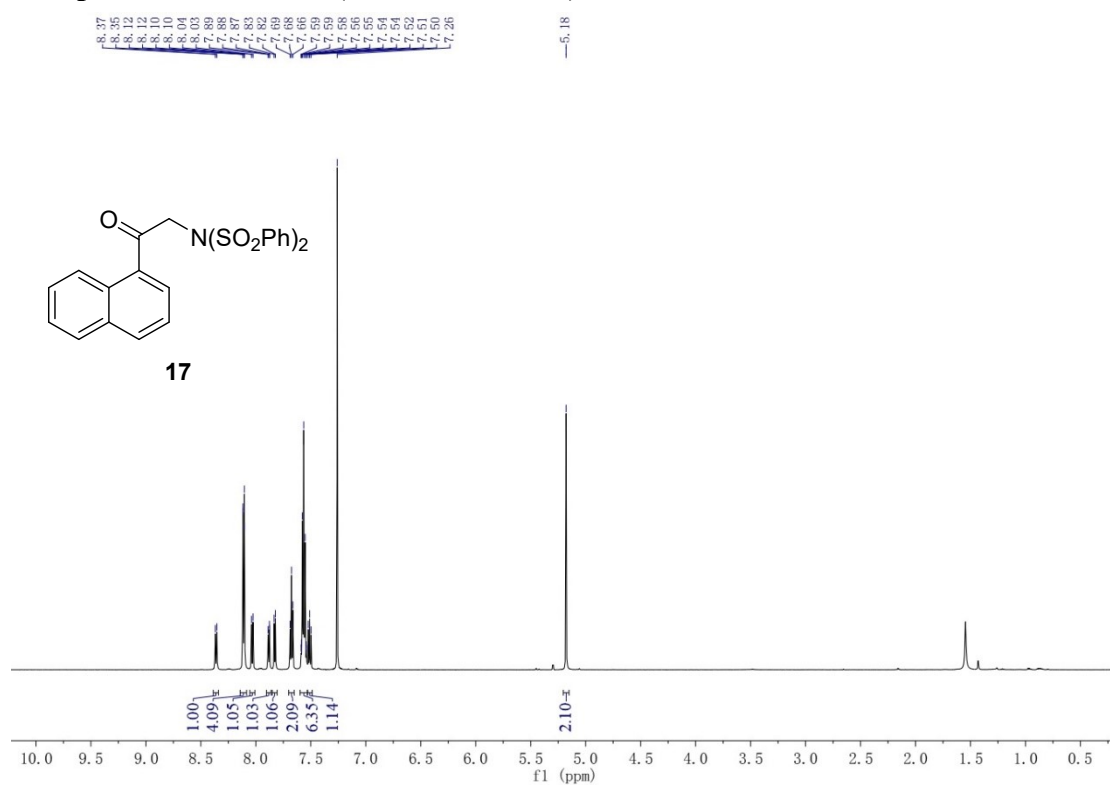
Compound 16 ^1H NMR (600 MHz, CDCl_3)



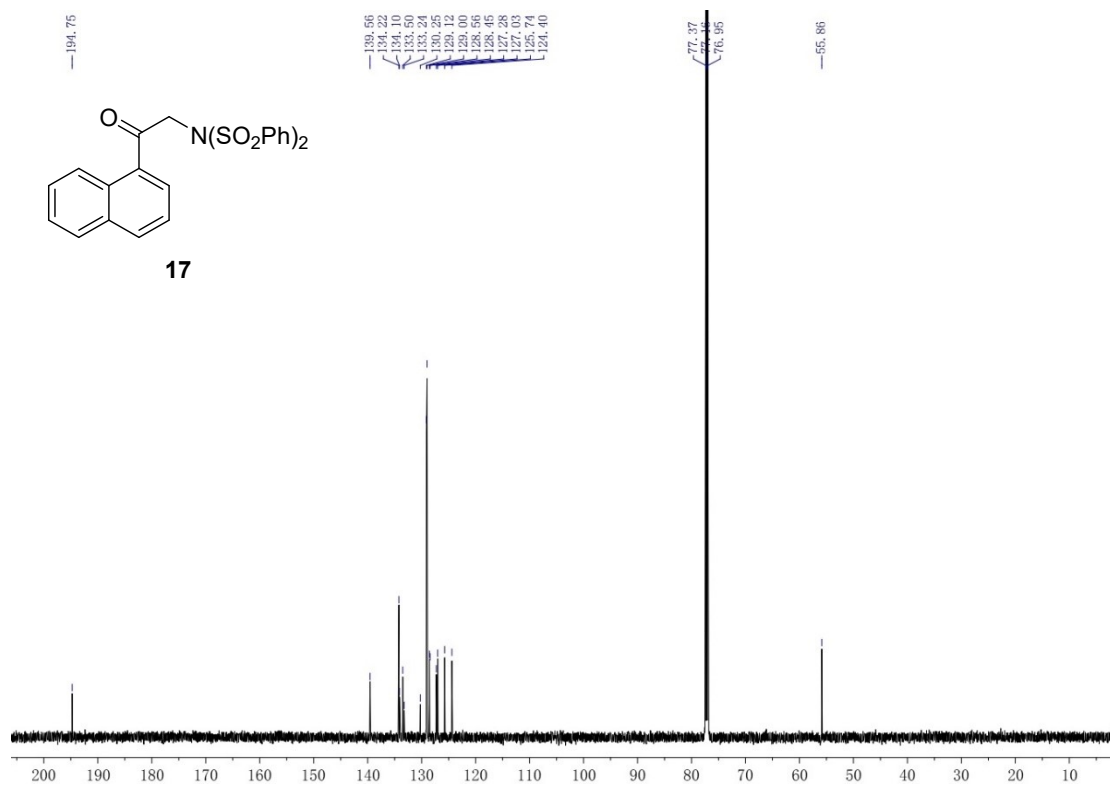
Compound 16 ^{13}C NMR (150 MHz, CDCl_3)



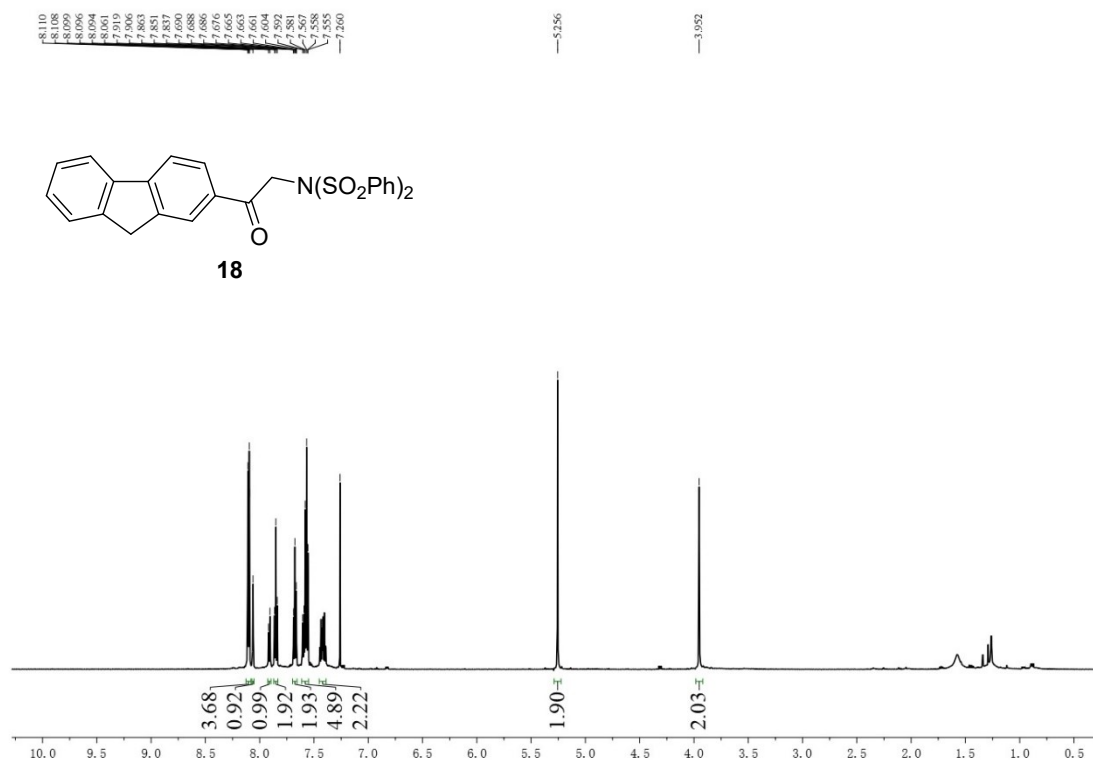
Compound 17 ¹H NMR (600 MHz, CDCl₃)



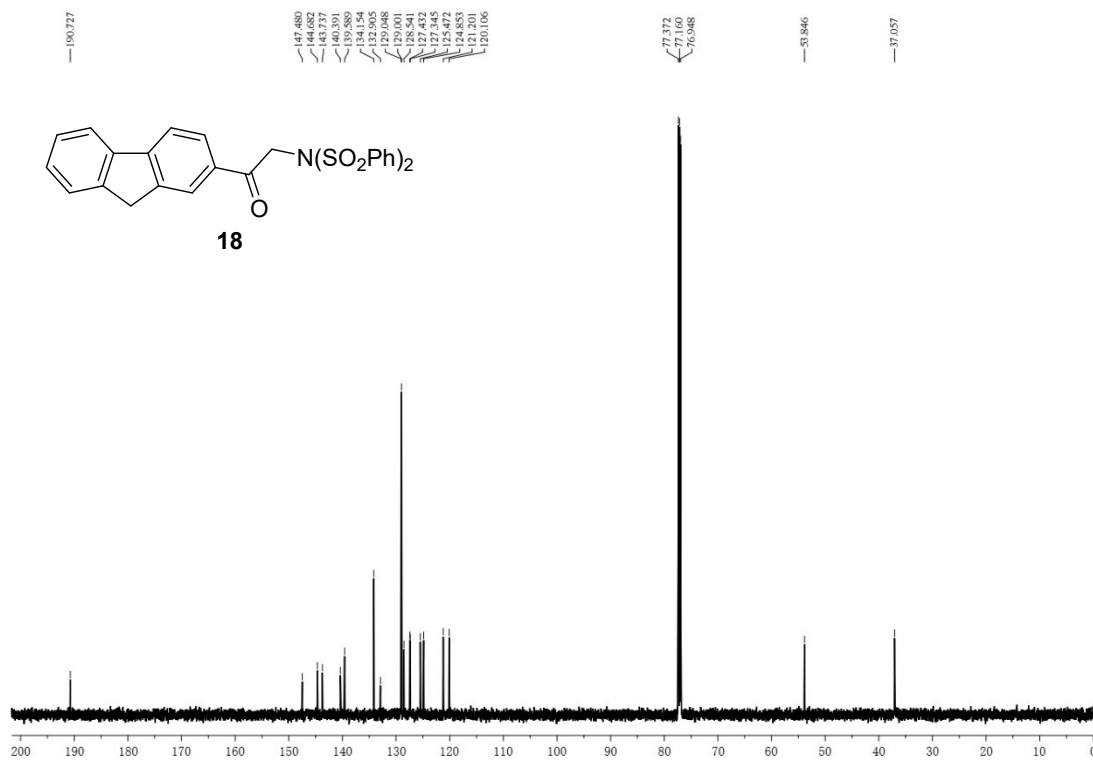
Compound 17 ¹³C NMR (150 MHz, CDCl₃)



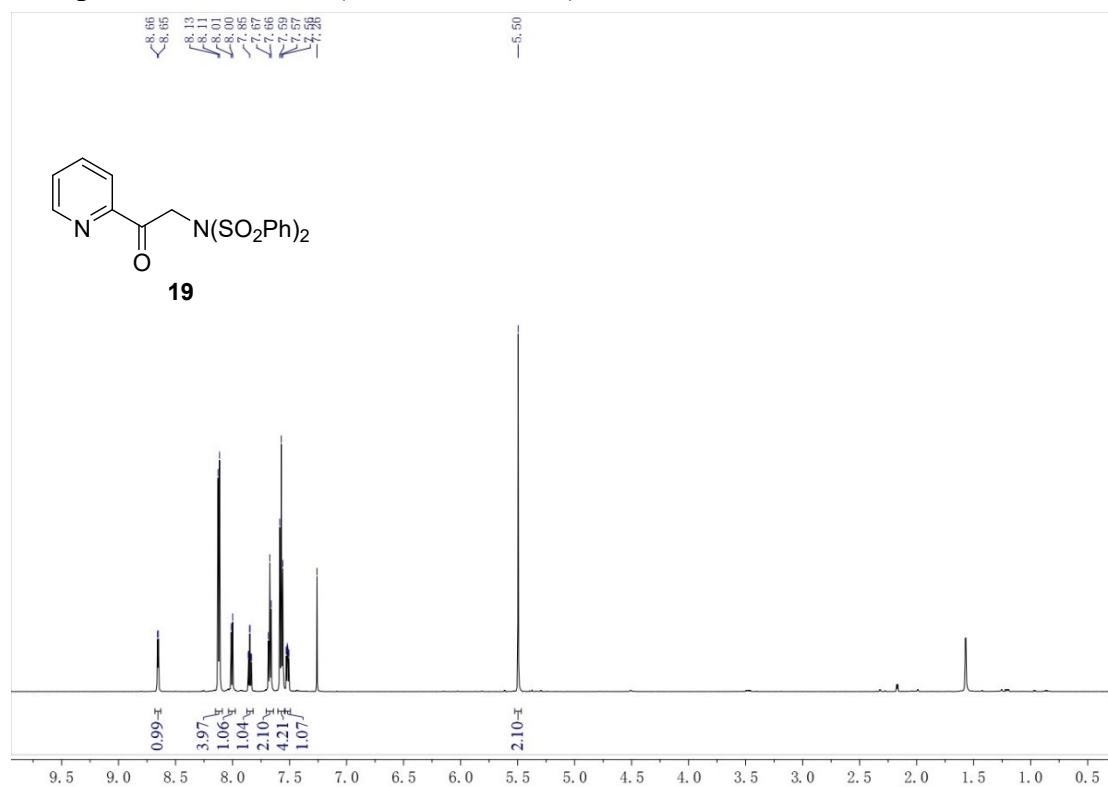
Compound 18 ¹H NMR (600 MHz, CDCl₃)



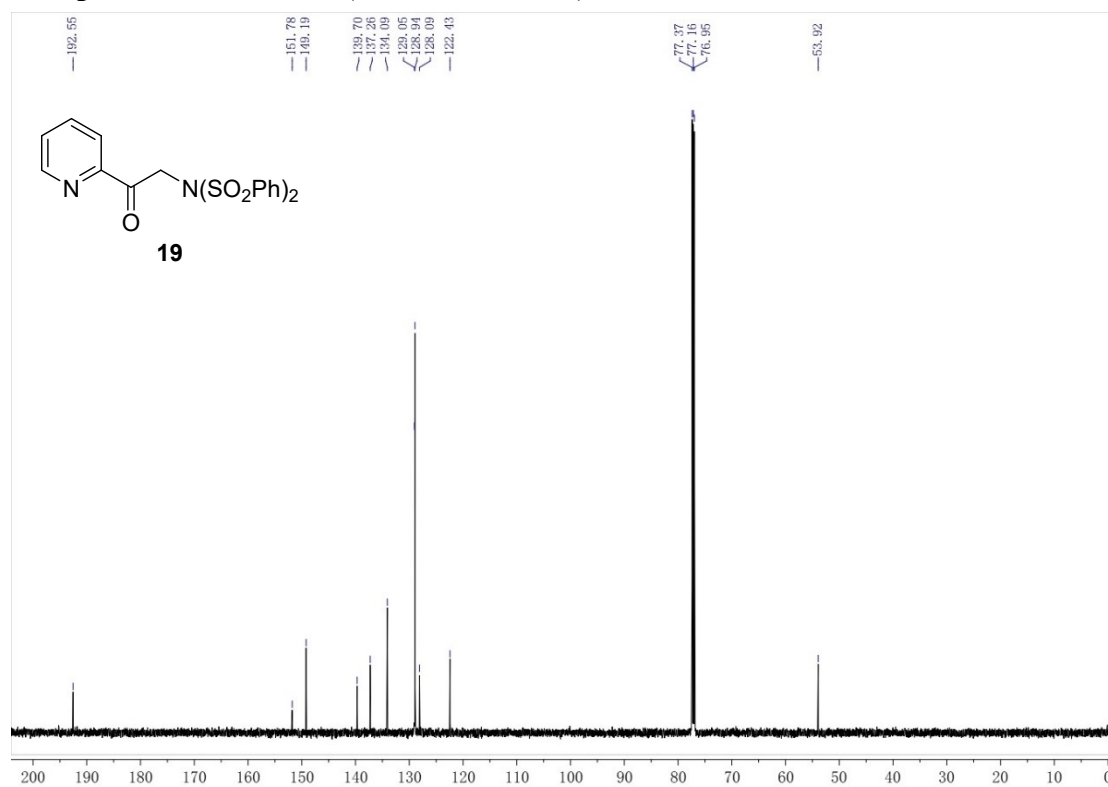
Compound 18 ¹³C NMR (150 MHz, CDCl₃)



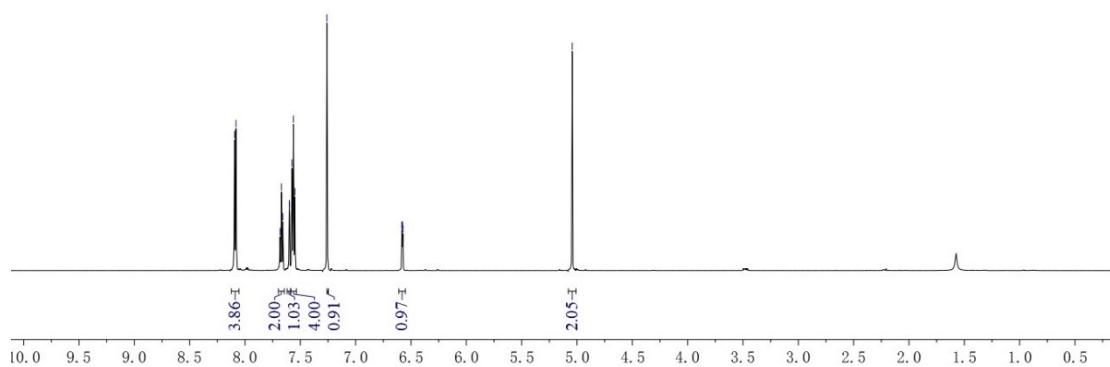
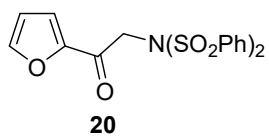
Compound 19 ¹H NMR (600 MHz, CDCl₃)



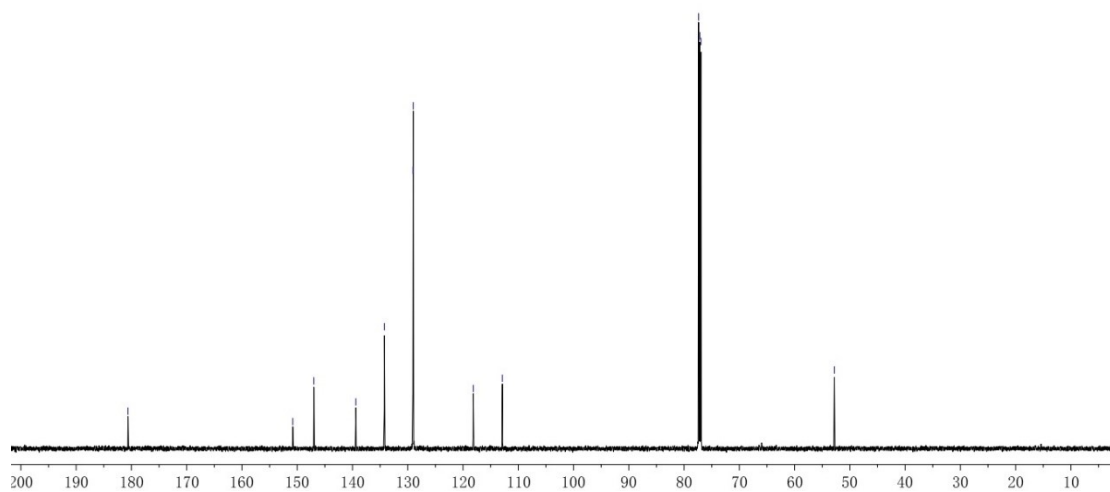
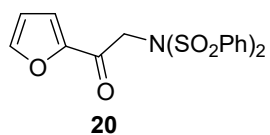
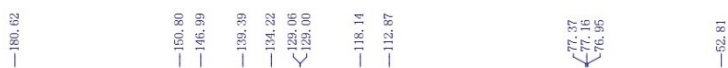
Compound 19 ¹³C NMR (150 MHz, CDCl₃)



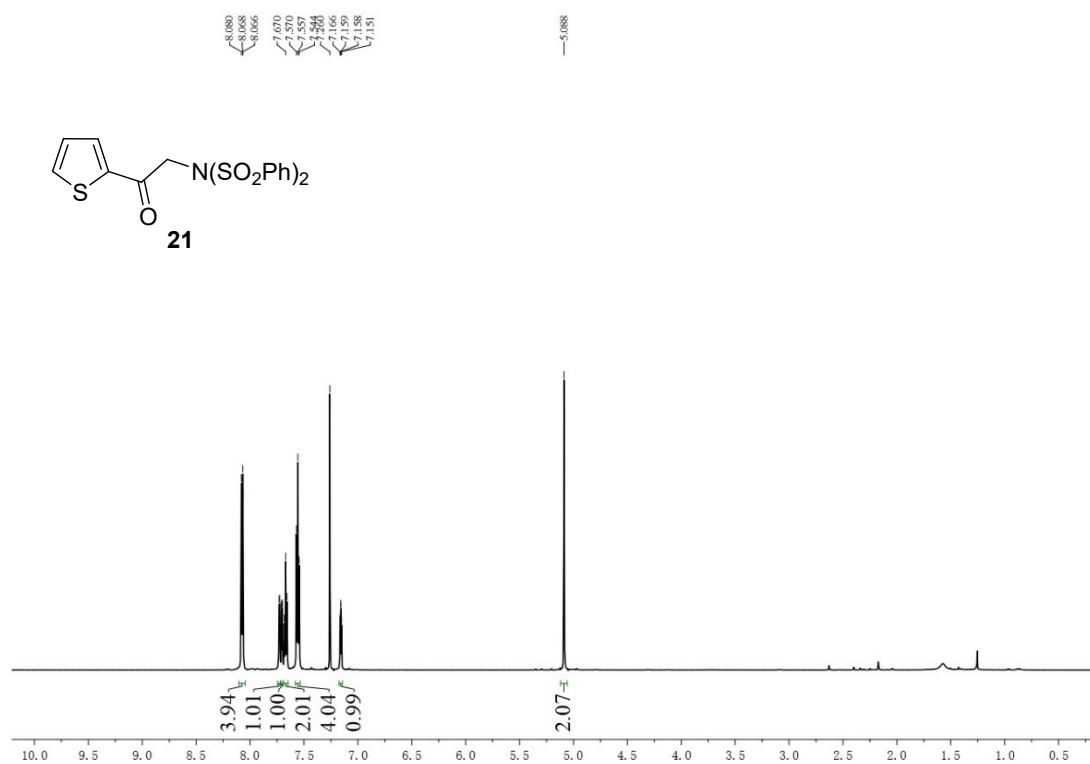
Compound 20 ^1H NMR (600 MHz, CDCl_3)



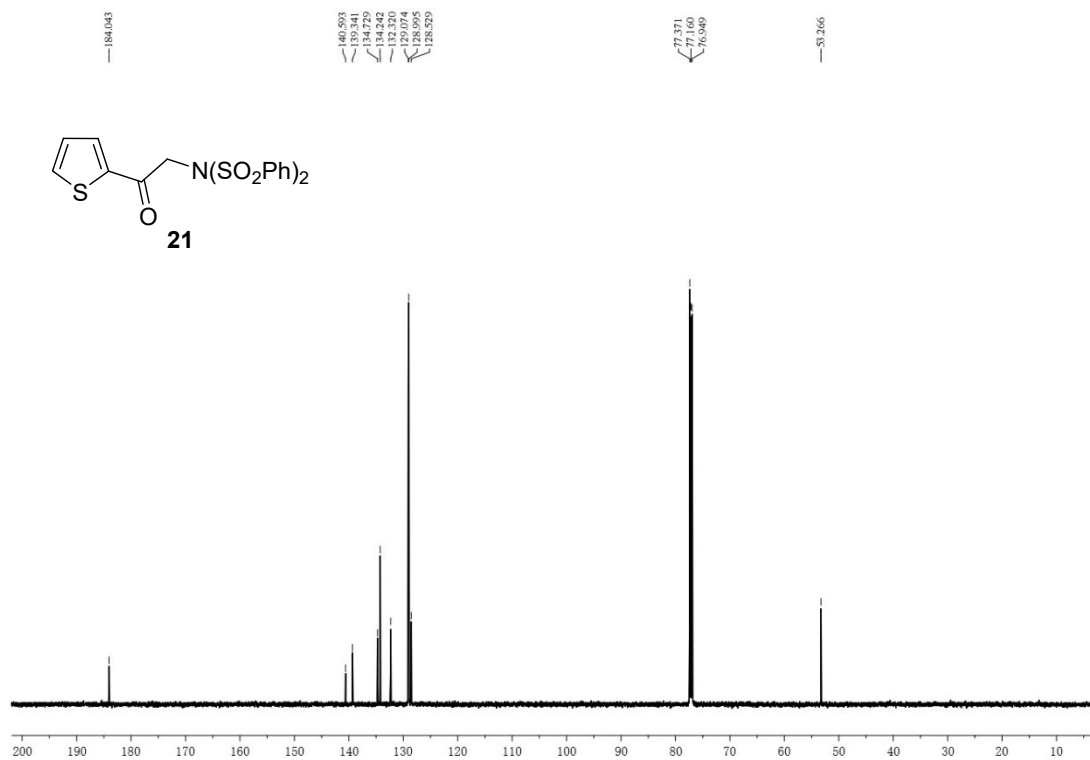
Compound 20 ^{13}C NMR (150 MHz, CDCl_3)



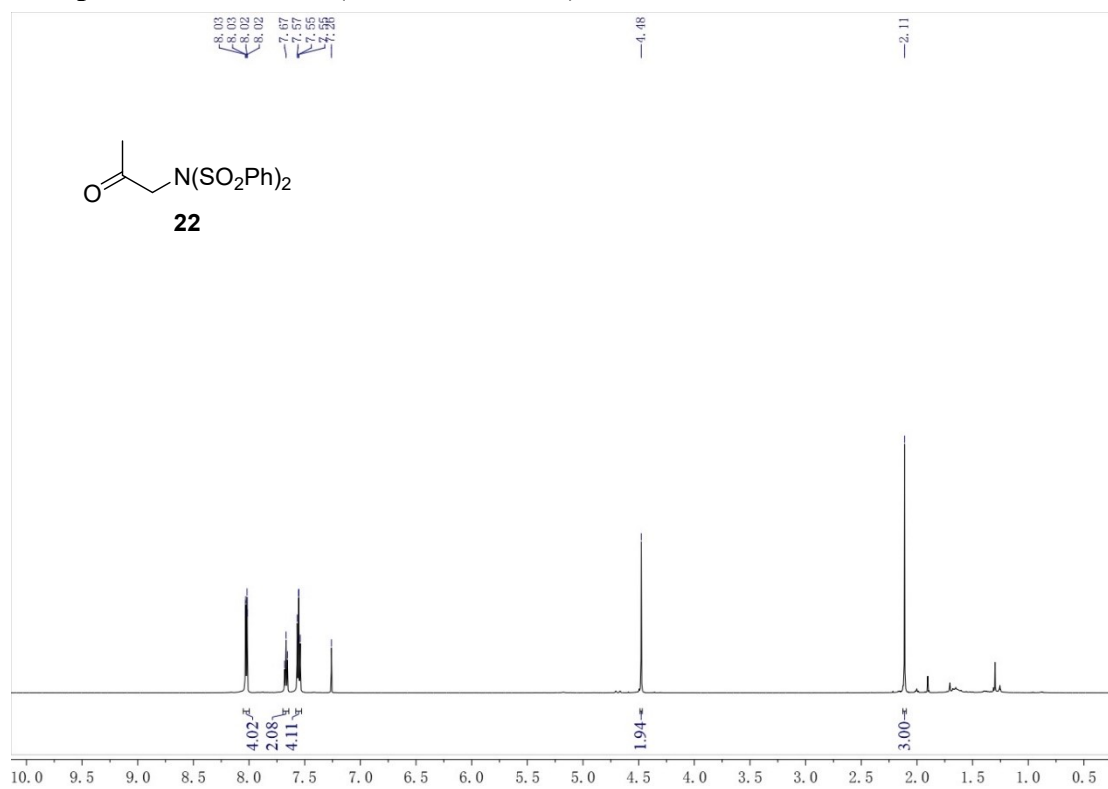
Compound 21 ^1H NMR (600 MHz, CDCl_3)



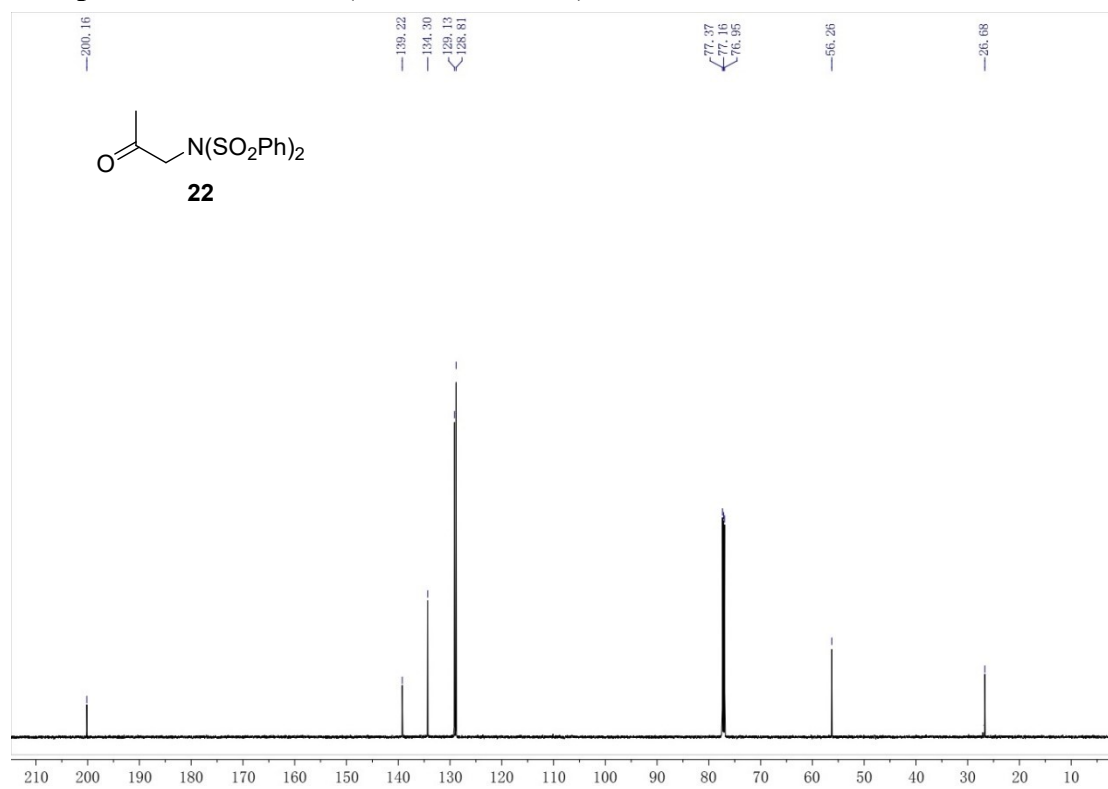
Compound 21 ^{13}C NMR (150 MHz, CDCl_3)



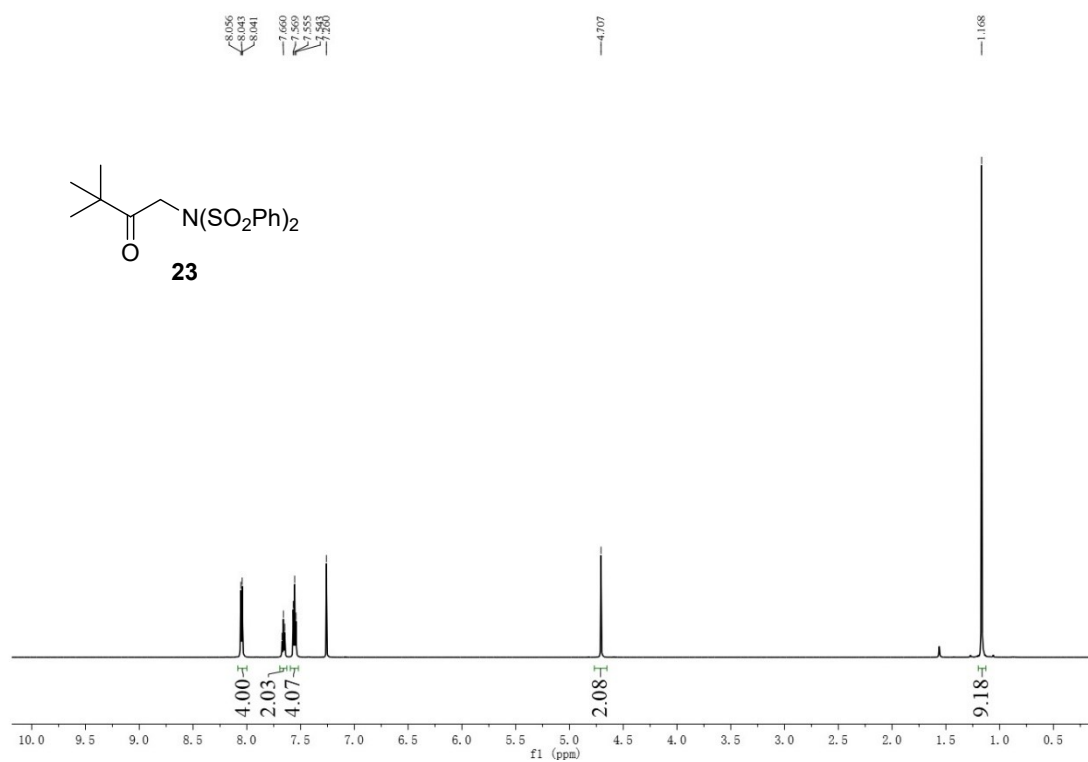
Compound 22 ^1H NMR (600 MHz, CDCl_3)



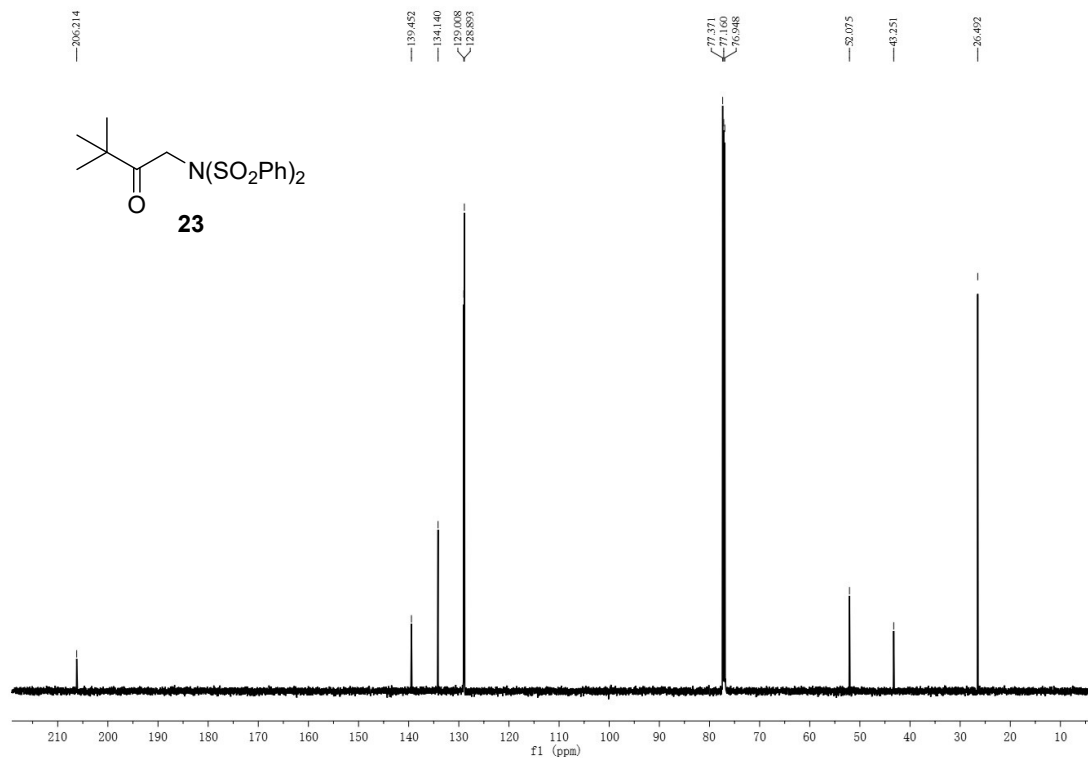
Compound 22 ^{13}C NMR (150 MHz, CDCl_3)



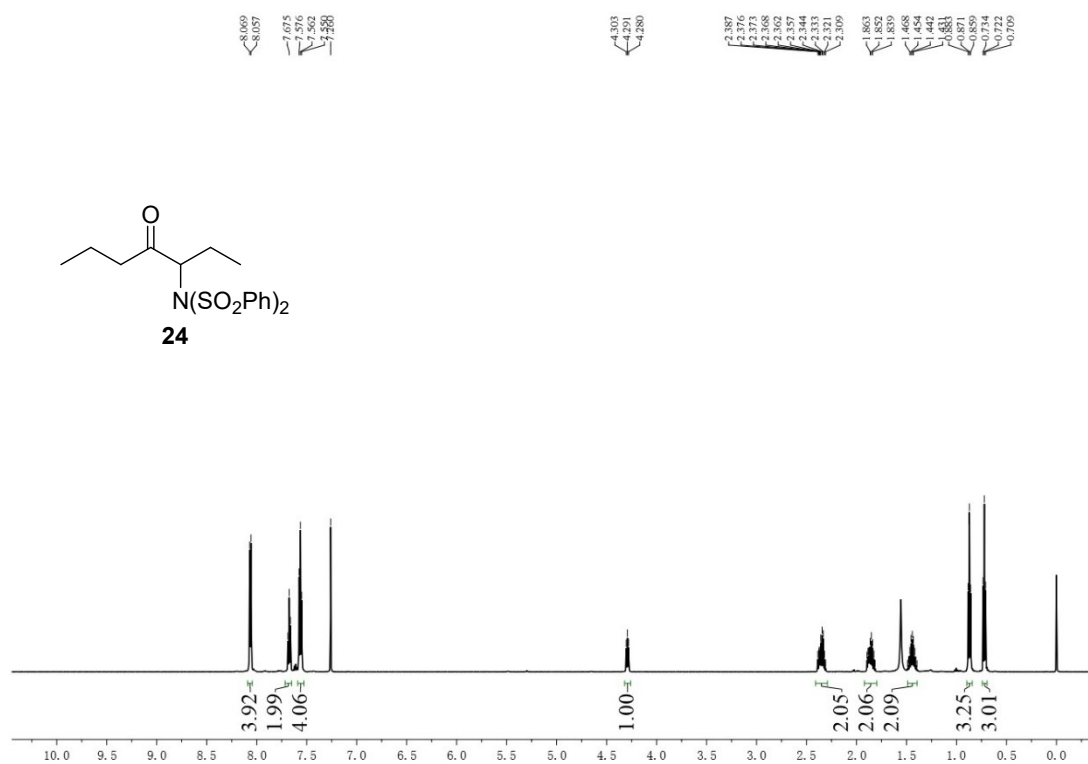
Compound 23 ¹H NMR (600 MHz, CDCl₃)



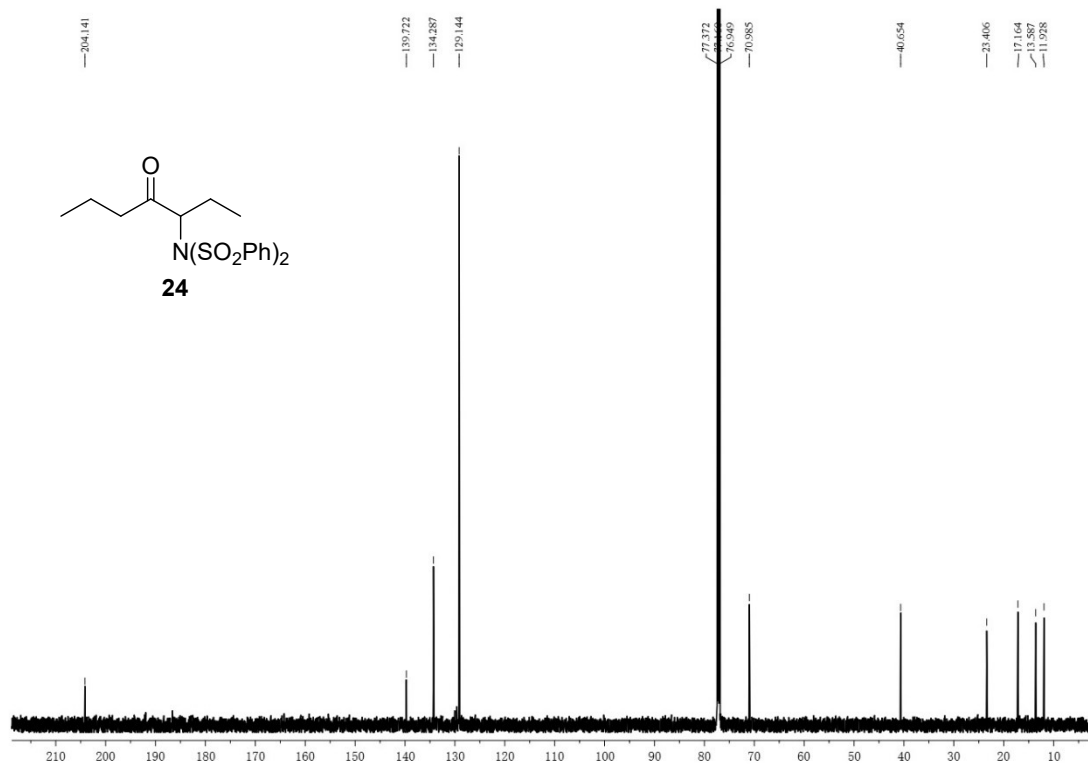
Compound 23 ¹³C NMR (150 MHz, CDCl₃)



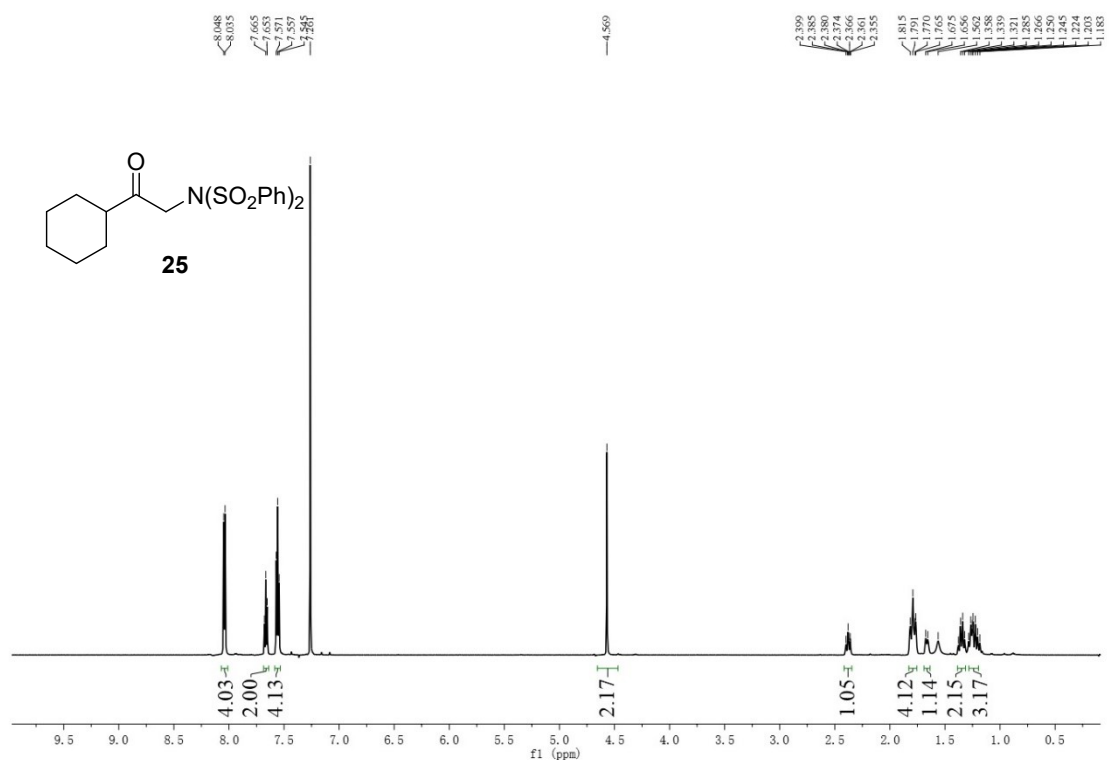
Compound 24 ¹H NMR (600 MHz, CDCl₃)



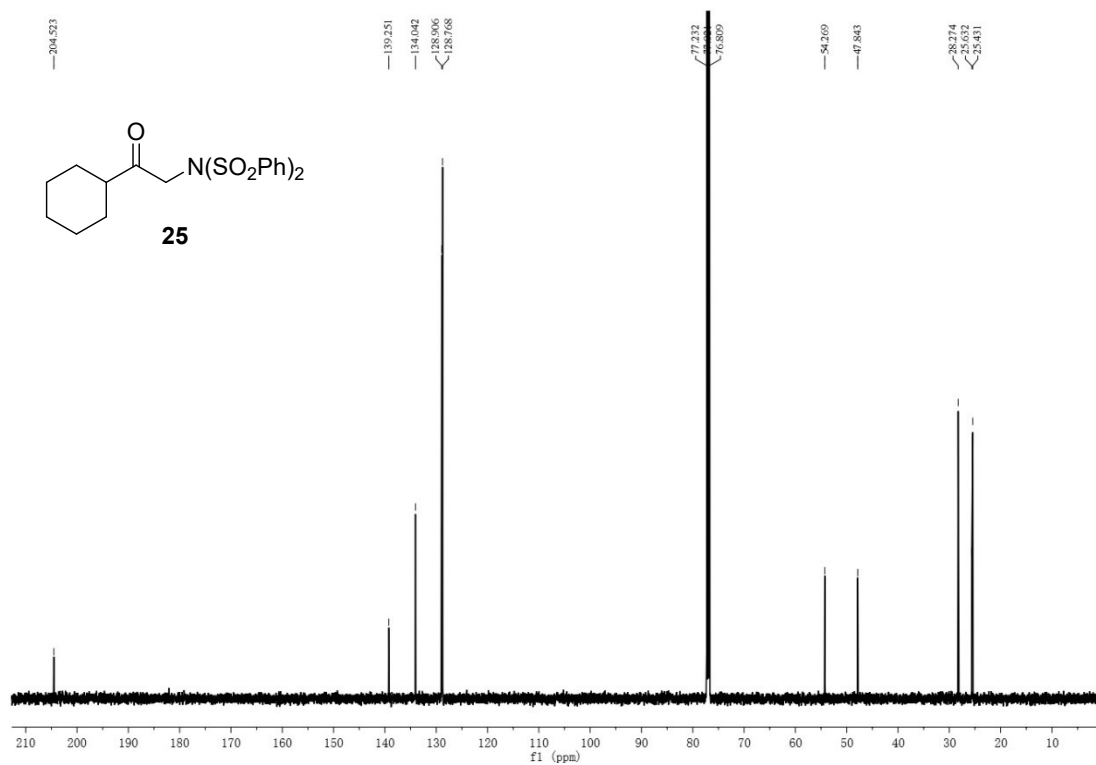
Compound 24 ¹³C NMR (150 MHz, CDCl₃)



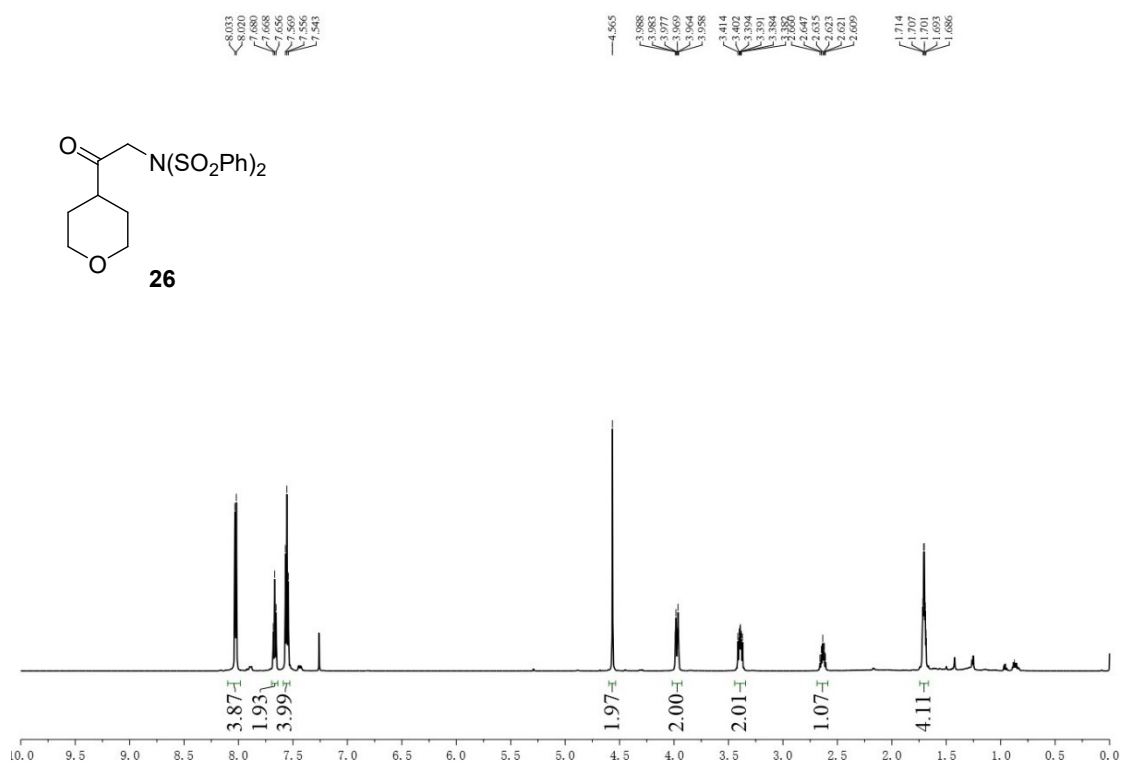
Compound 25 ^1H NMR (600 MHz, CDCl_3)



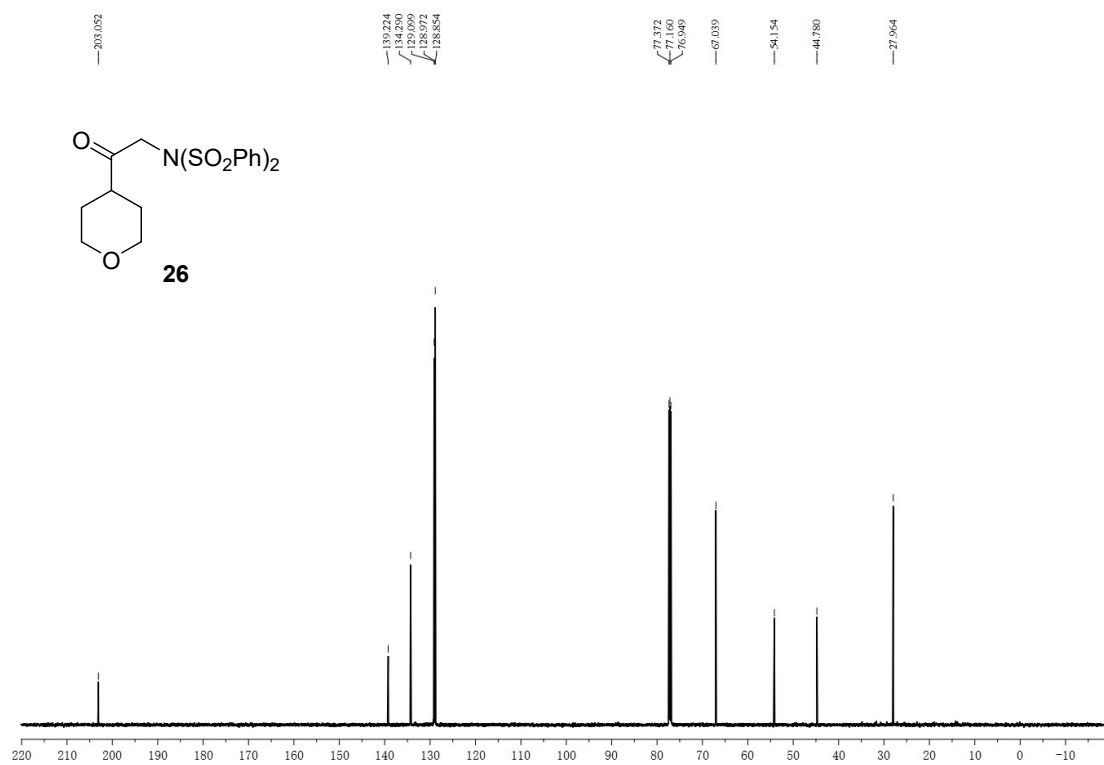
Compound 25 ^{13}C NMR (150 MHz, CDCl_3)



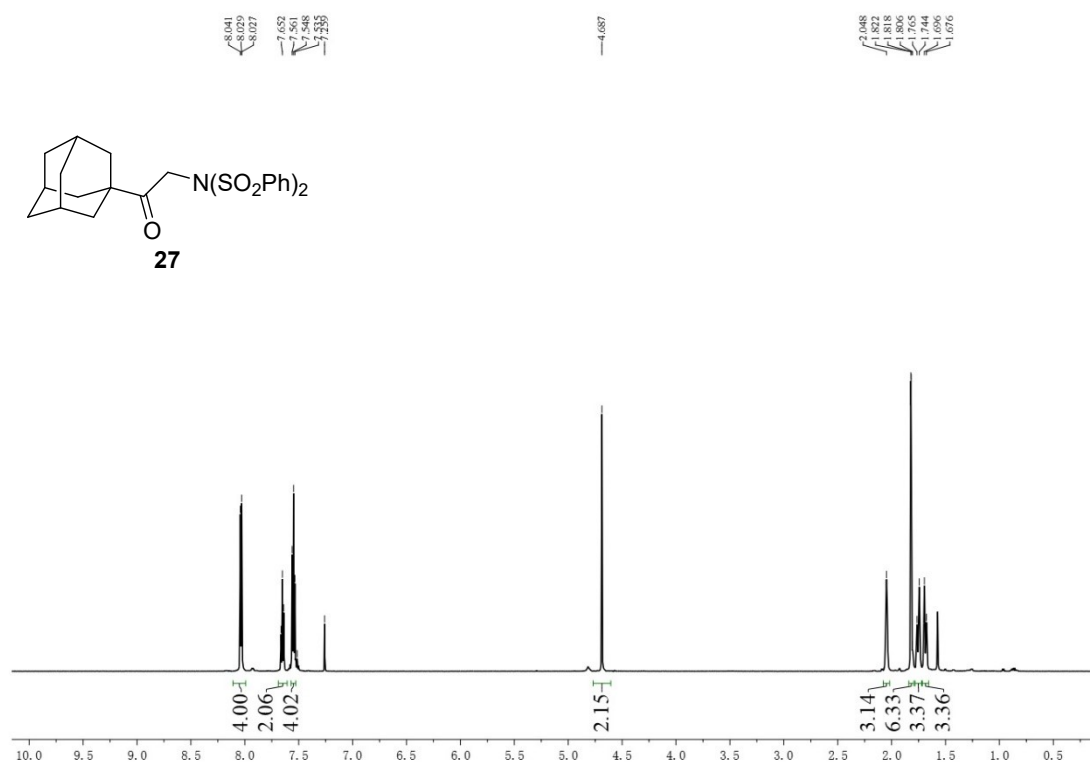
Compound 26 ¹H NMR (600 MHz, CDCl₃)



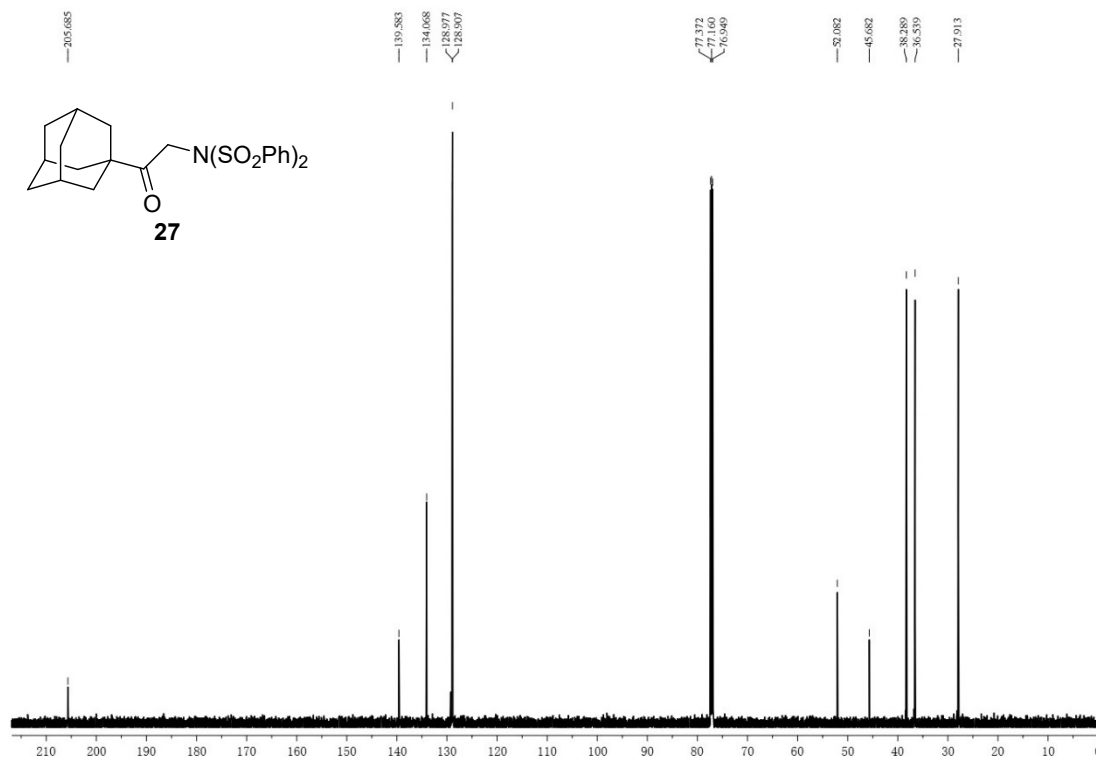
Compound 26 ¹³C NMR (150 MHz, CDCl₃)



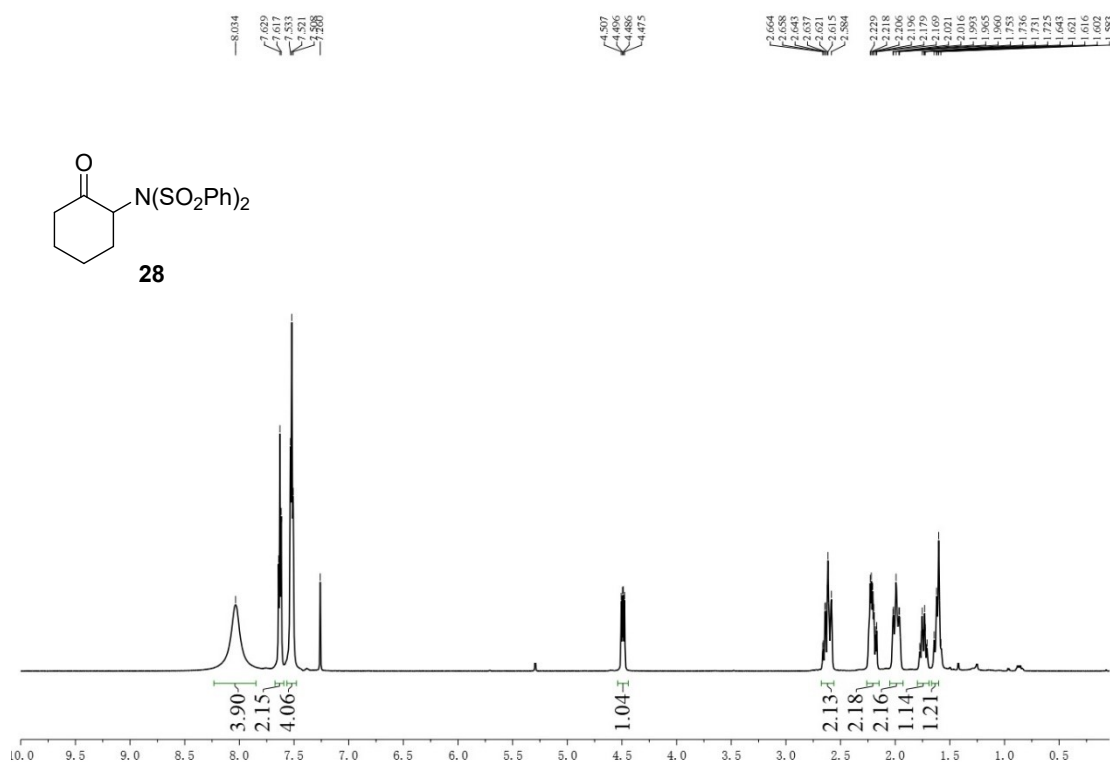
Compound 27 ^1H NMR (600 MHz, CDCl_3)



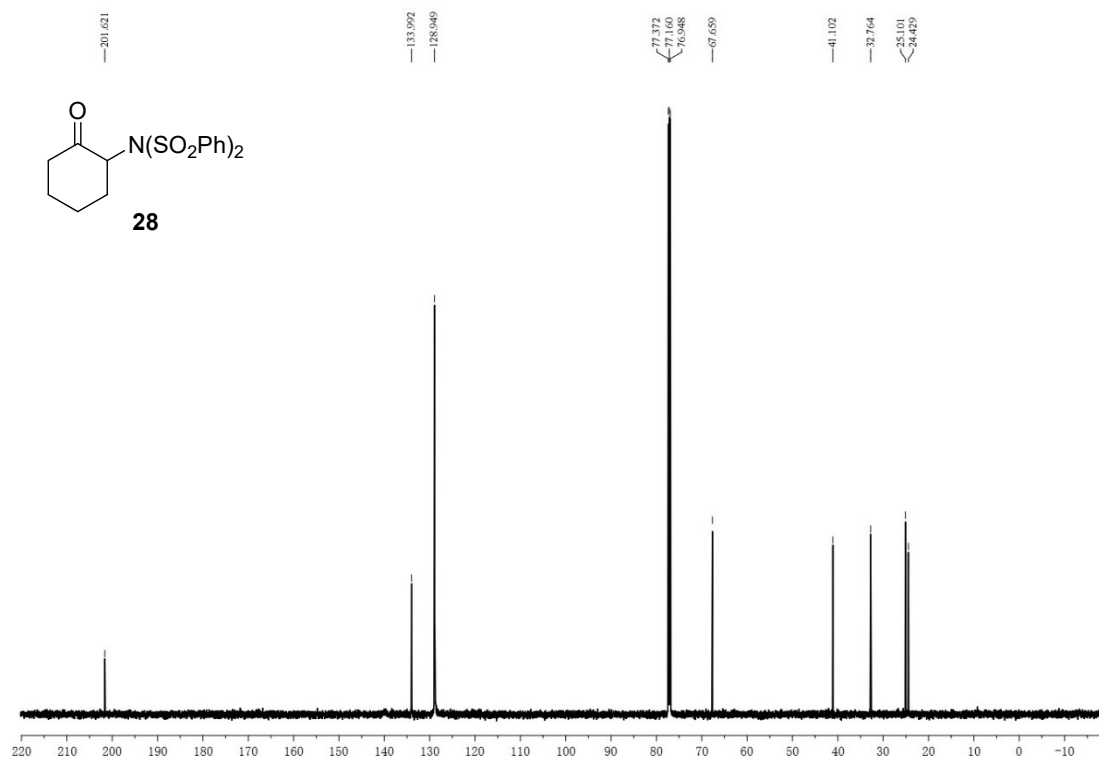
Compound 27 ^{13}C NMR (150 MHz, CDCl_3)



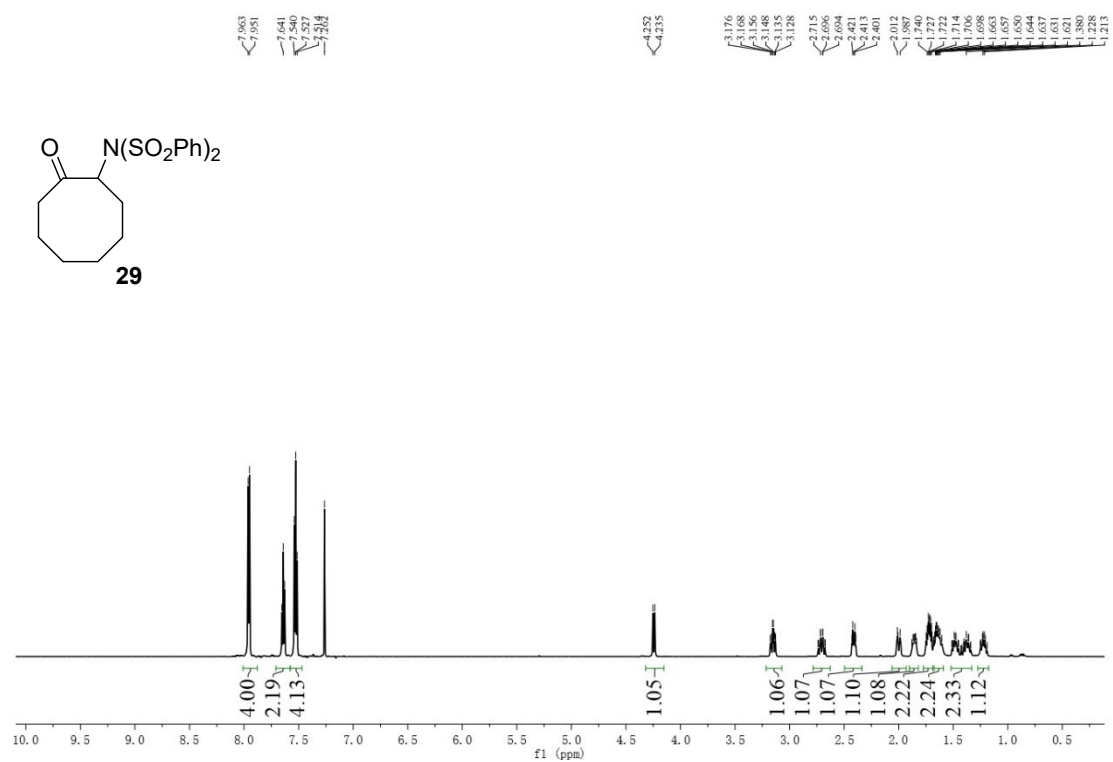
Compound 28 ¹H NMR (600 MHz, CDCl₃)



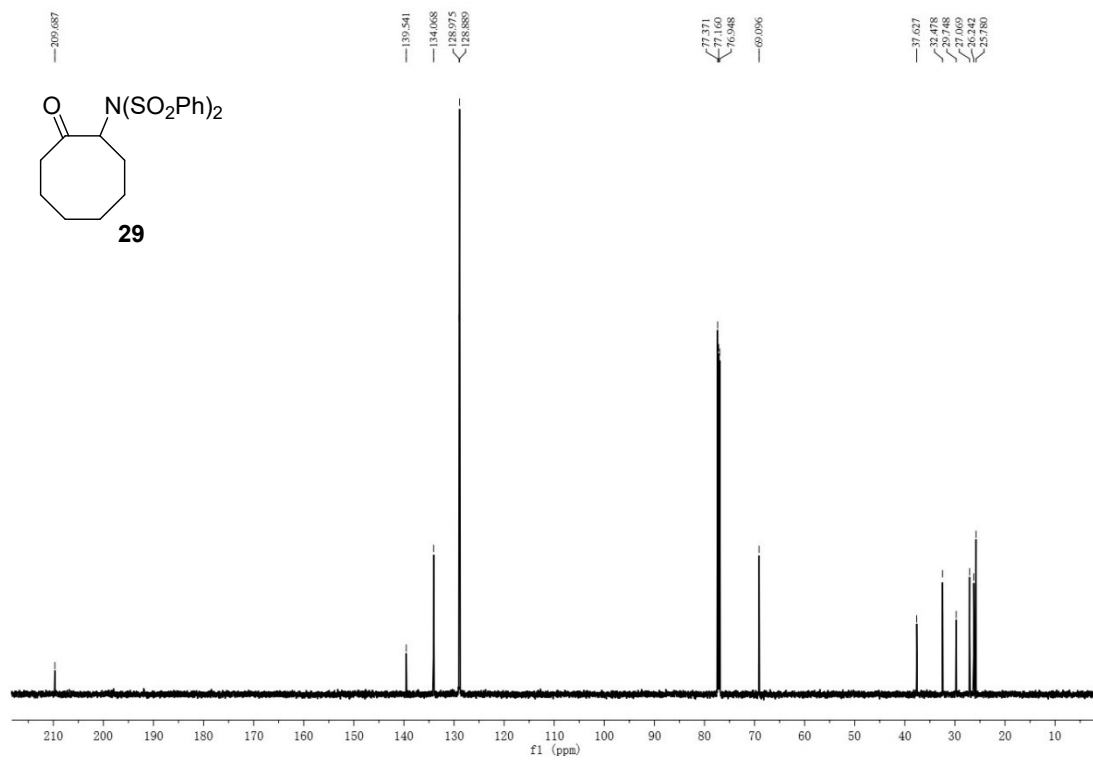
Compound 28 ¹³C NMR (150 MHz, CDCl₃)



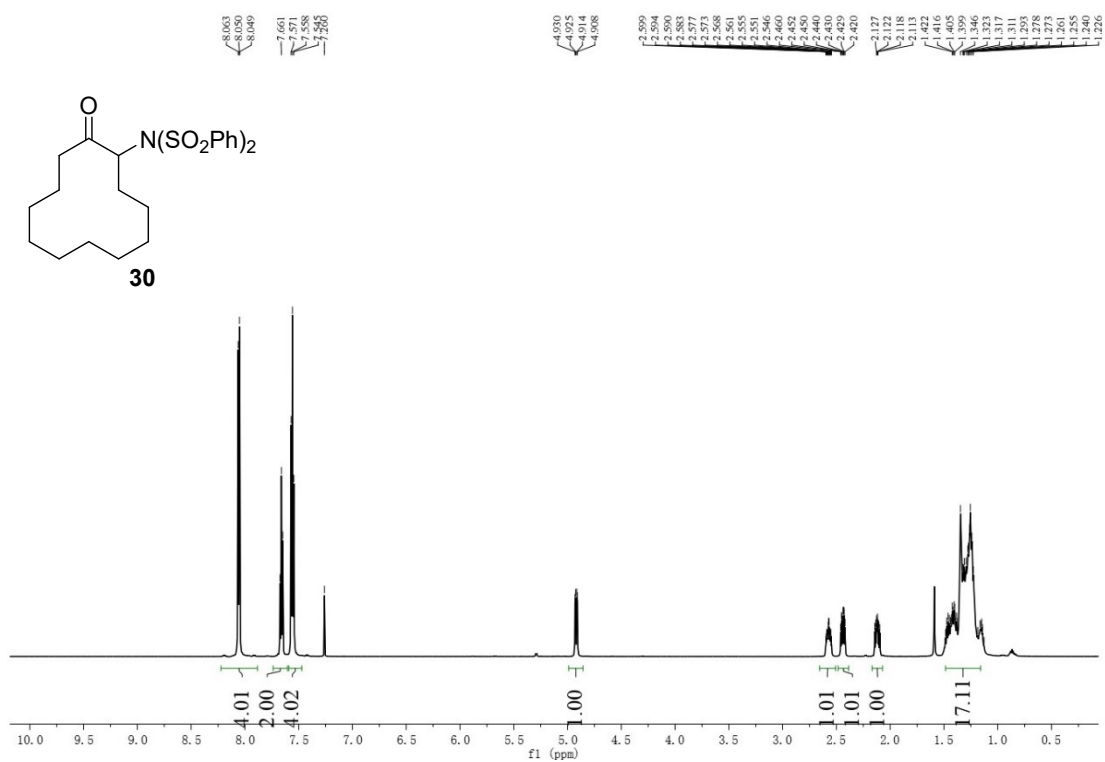
Compound 29 ^1H NMR (600 MHz, CDCl_3)



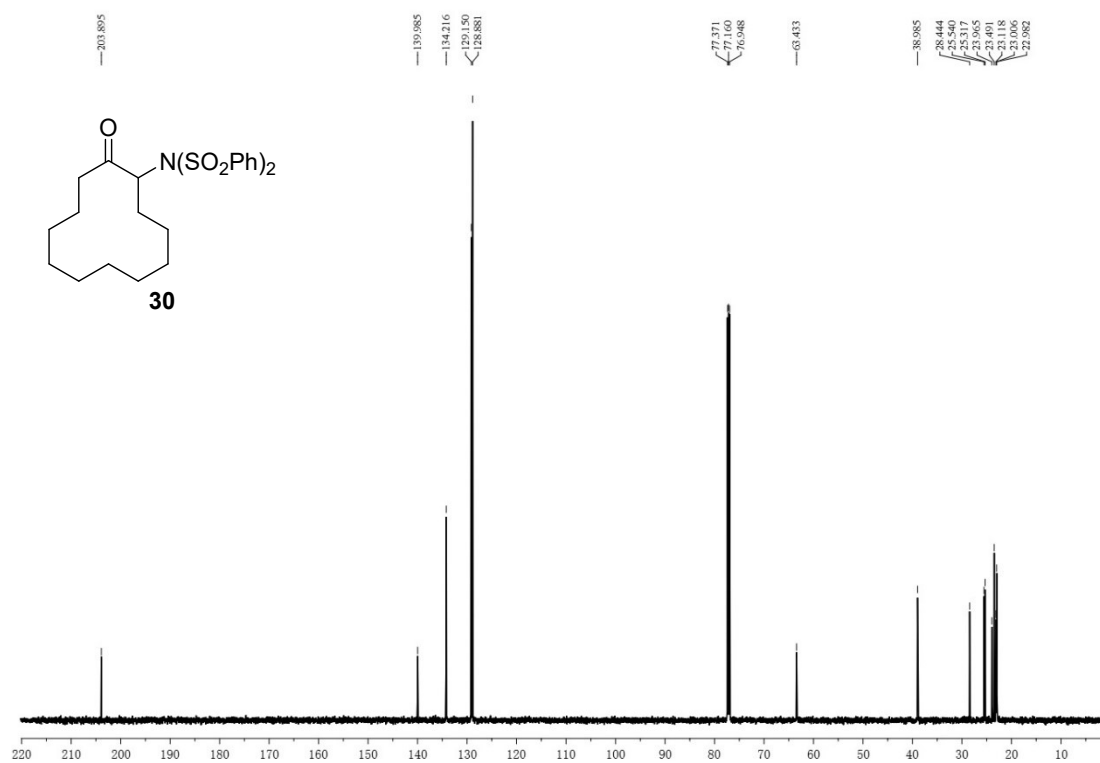
Compound 29 ^{13}C NMR (150 MHz, CDCl_3)



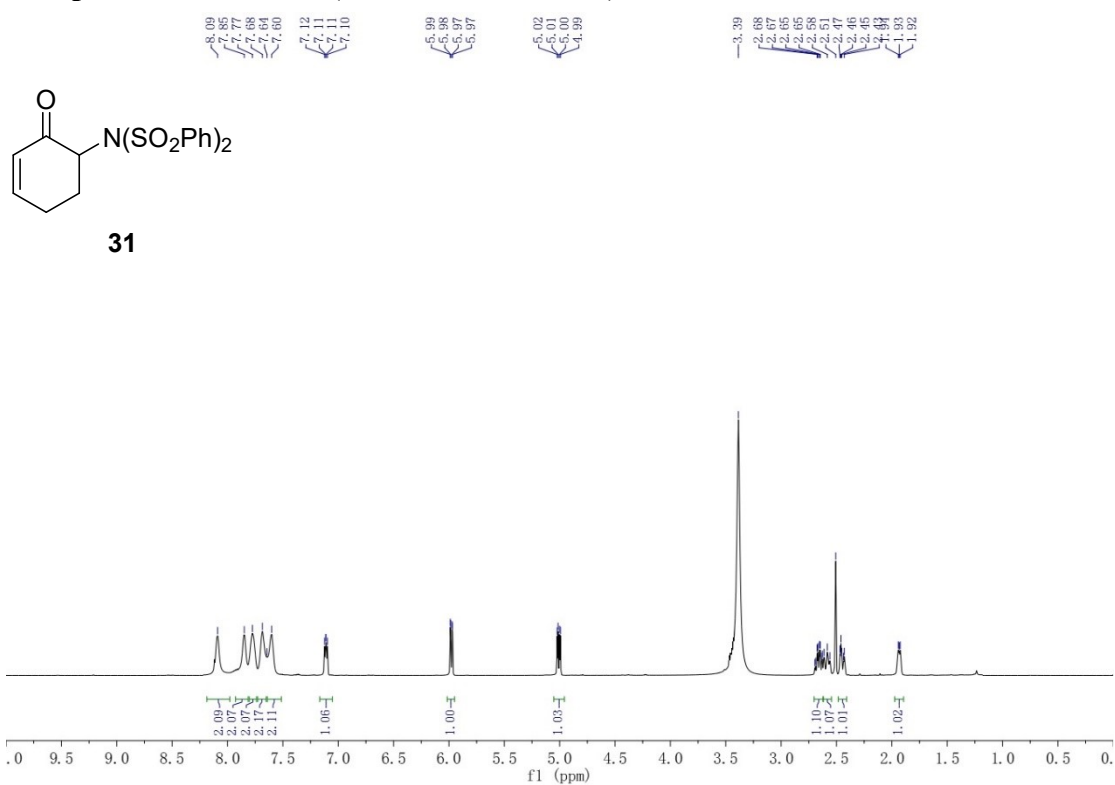
Compound 30 ^1H NMR (600 MHz, CDCl_3)



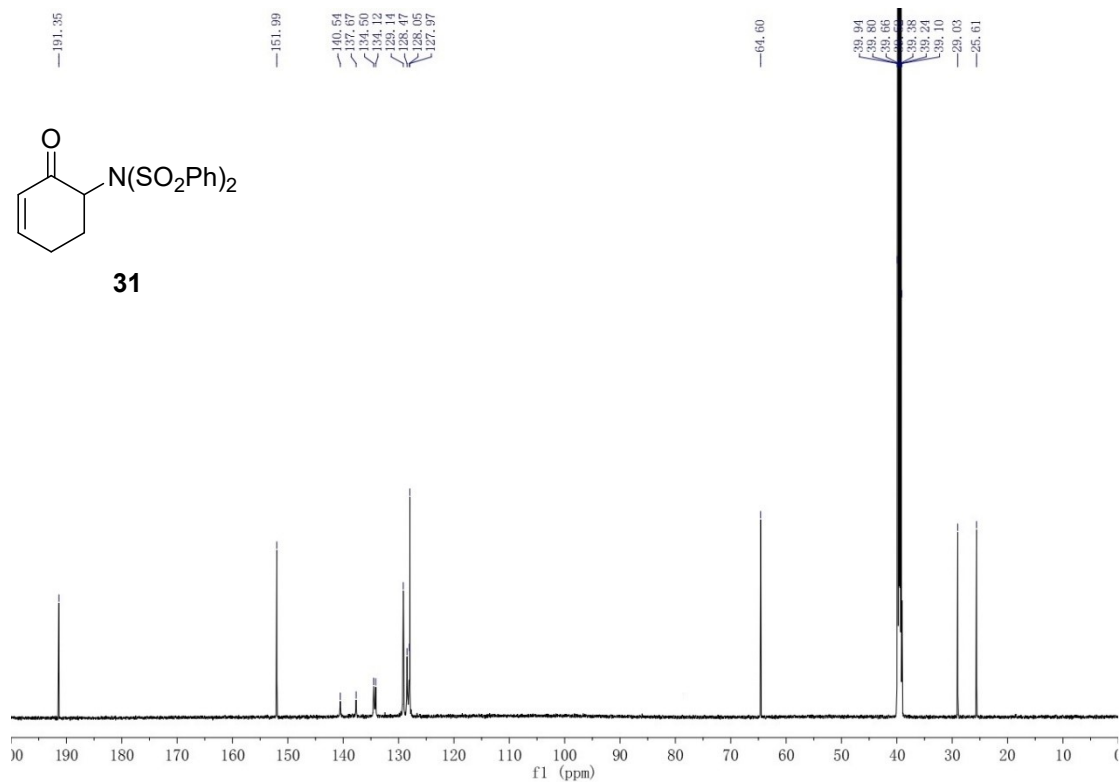
Compound 30 ^{13}C NMR (150 MHz, CDCl_3)



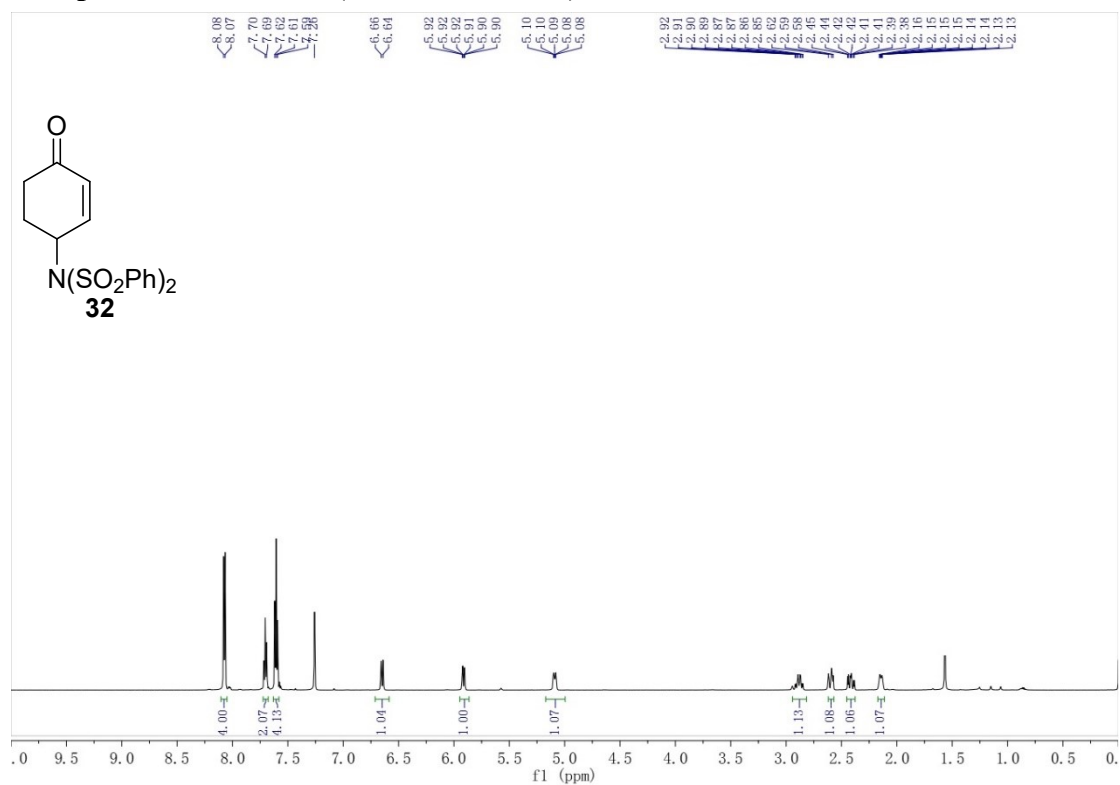
Compound 31 ^1H NMR (600 MHz, d_6 -DMSO)



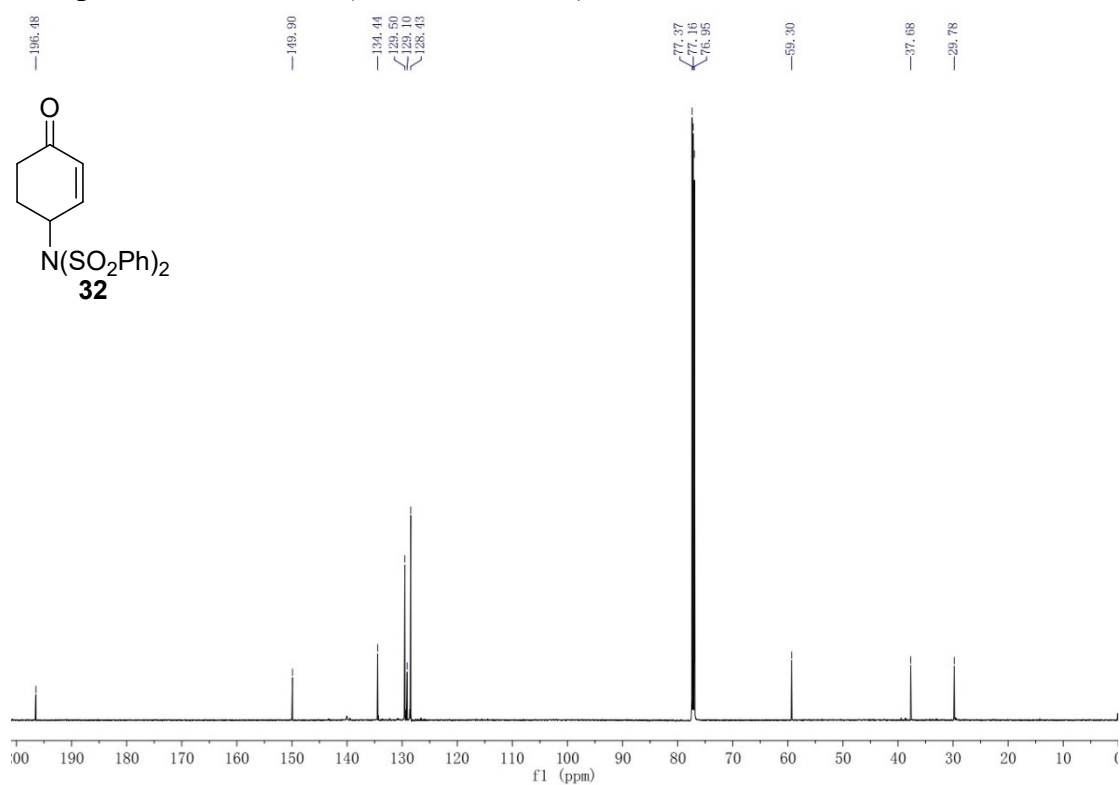
Compound 31 ^{13}C NMR (150 MHz, d_6 -DMSO)



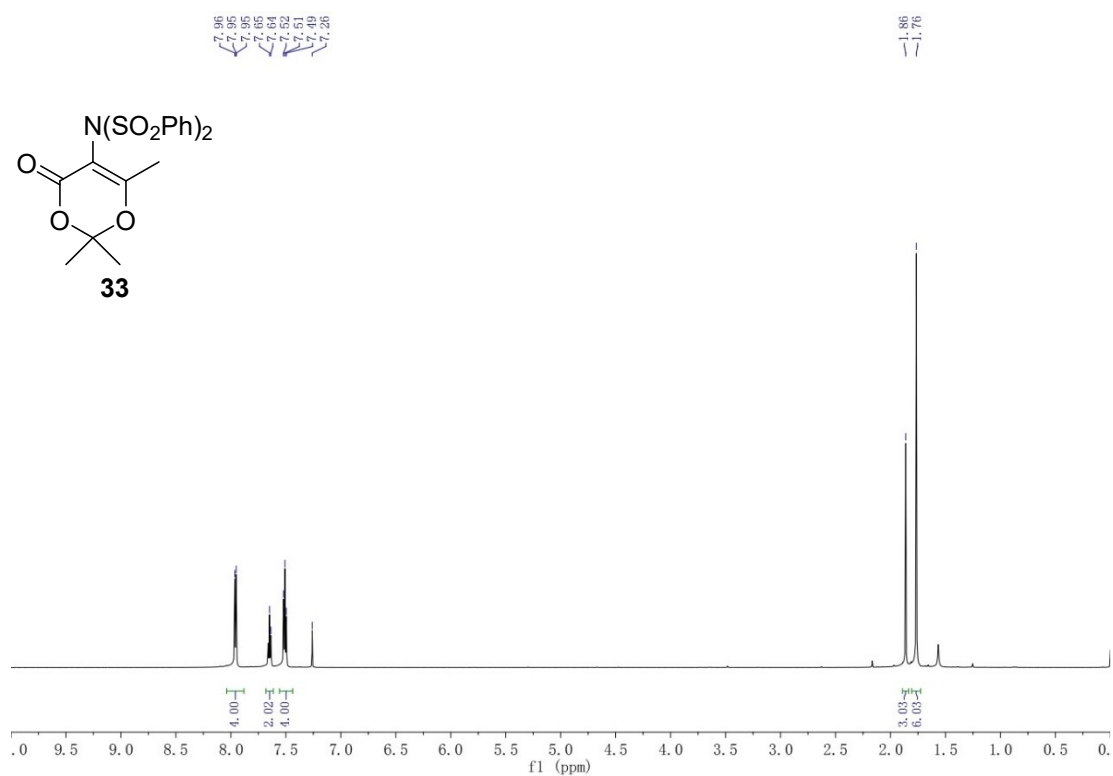
Compound 32 ^1H NMR (600 MHz, CDCl_3)



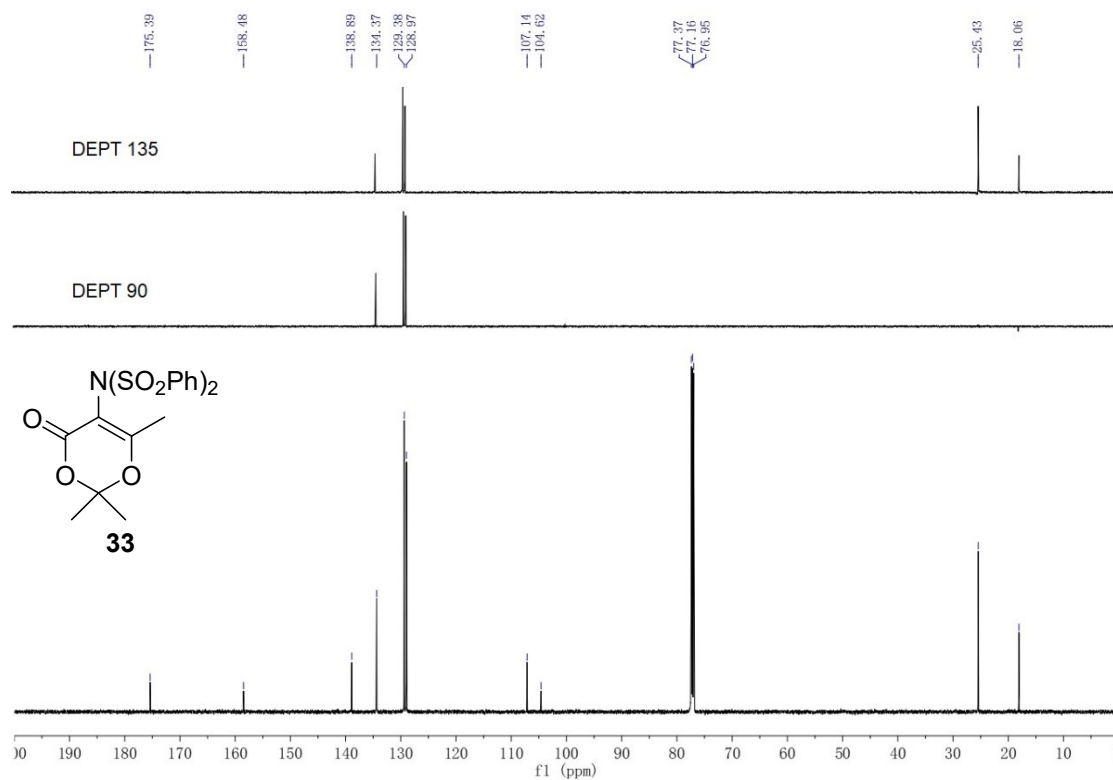
Compound 32 ^{13}C NMR (150 MHz, CDCl_3)



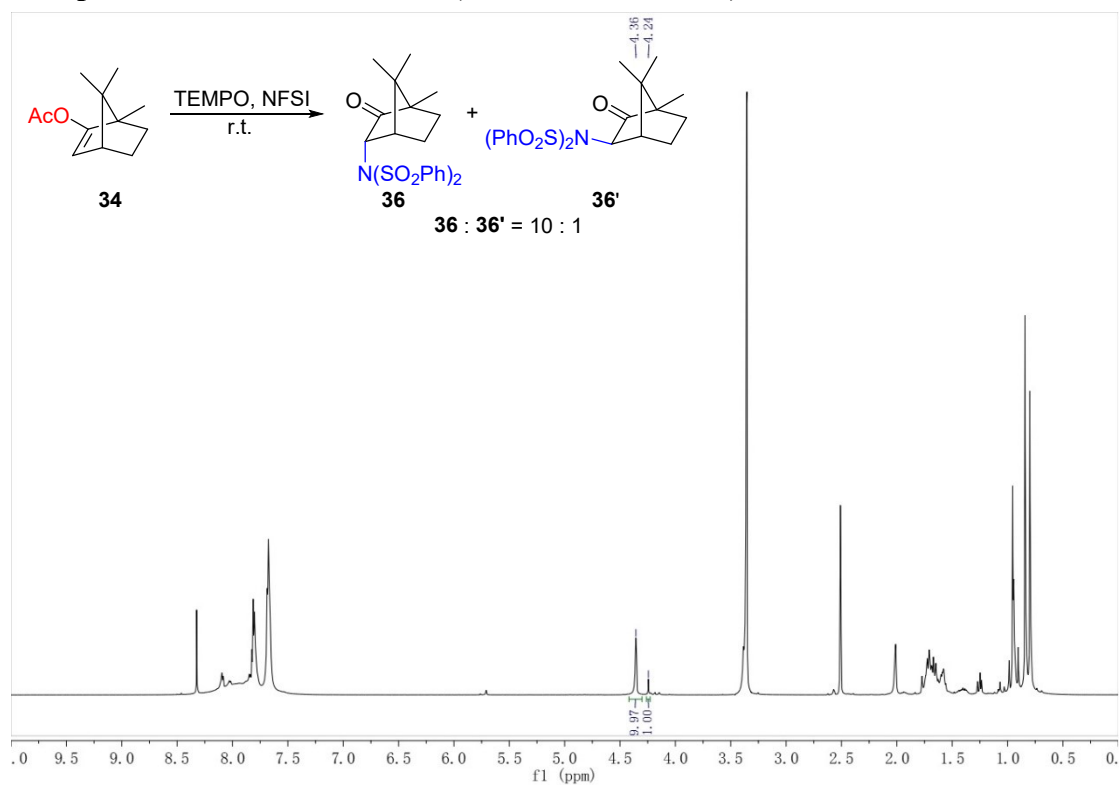
Compound 33 ^1H NMR (600 MHz, CDCl_3)



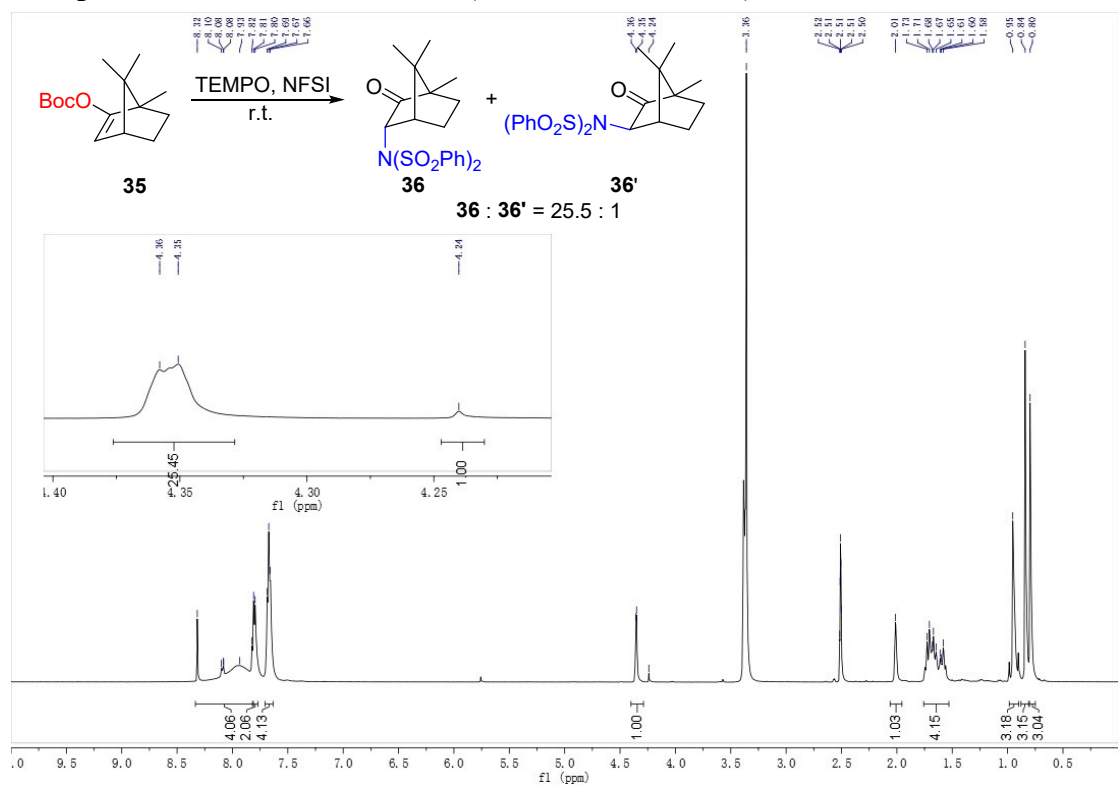
Compound 33 ^{13}C NMR (150 MHz, CDCl_3)



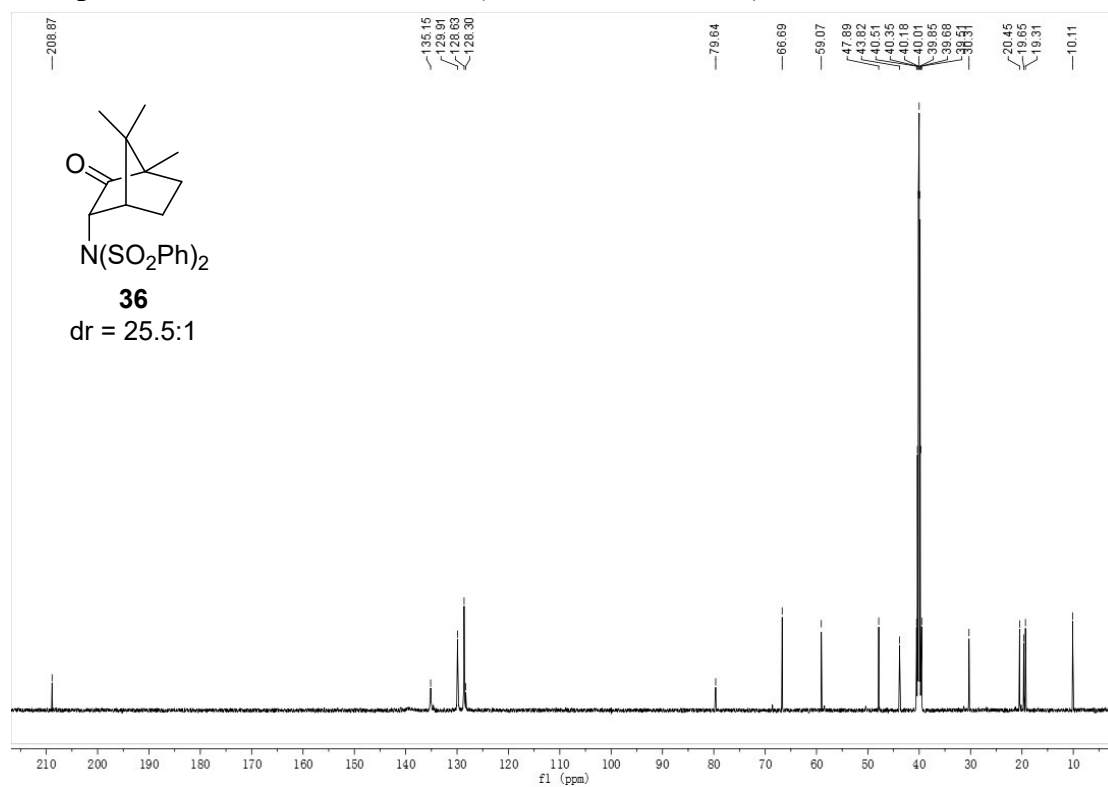
Compound 36, R = Ac, ^1H NMR (500 MHz, d_6 -DMSO)



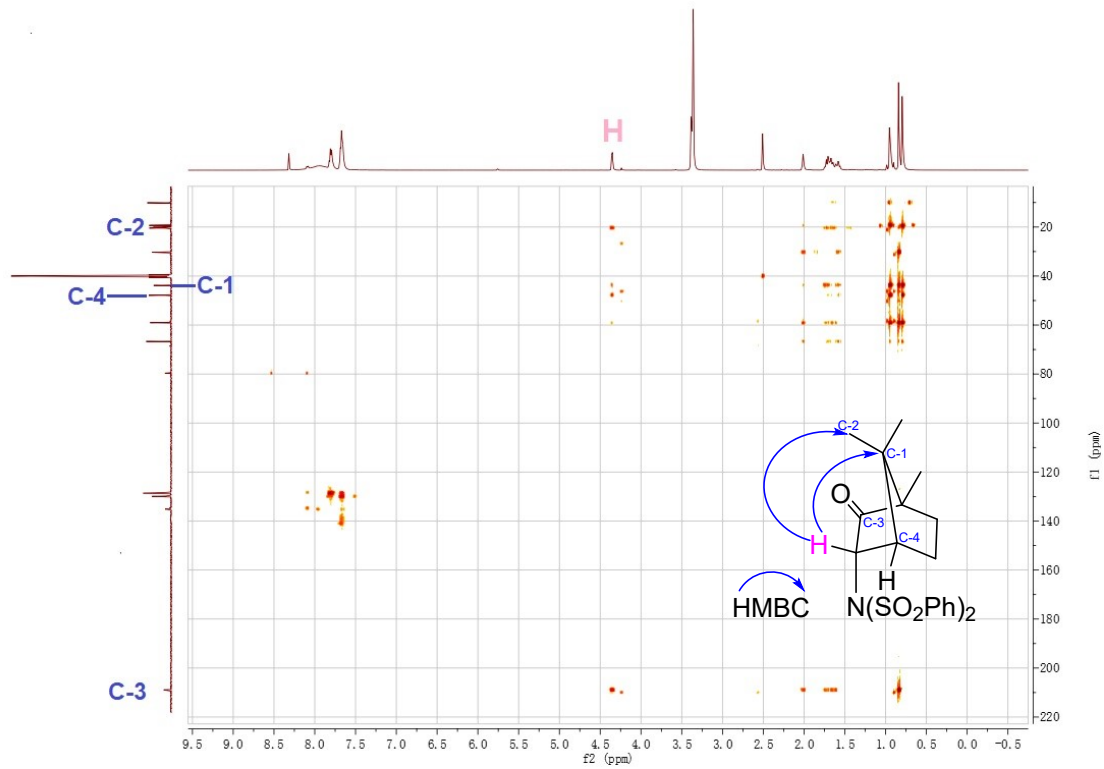
Compound 36, R = Boc, ^1H NMR (500 MHz, d_6 -DMSO)



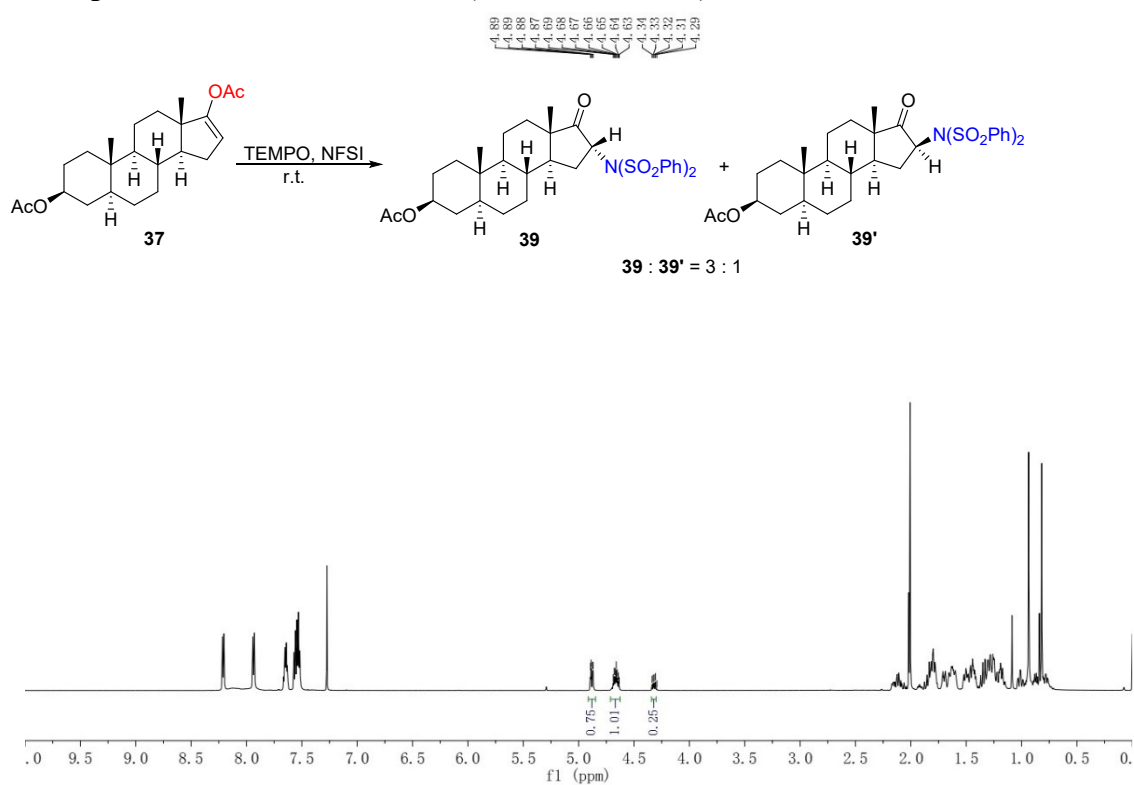
Compound 36, R = Boc, ^{13}C NMR (125 MHz, d_6 -DMSO)



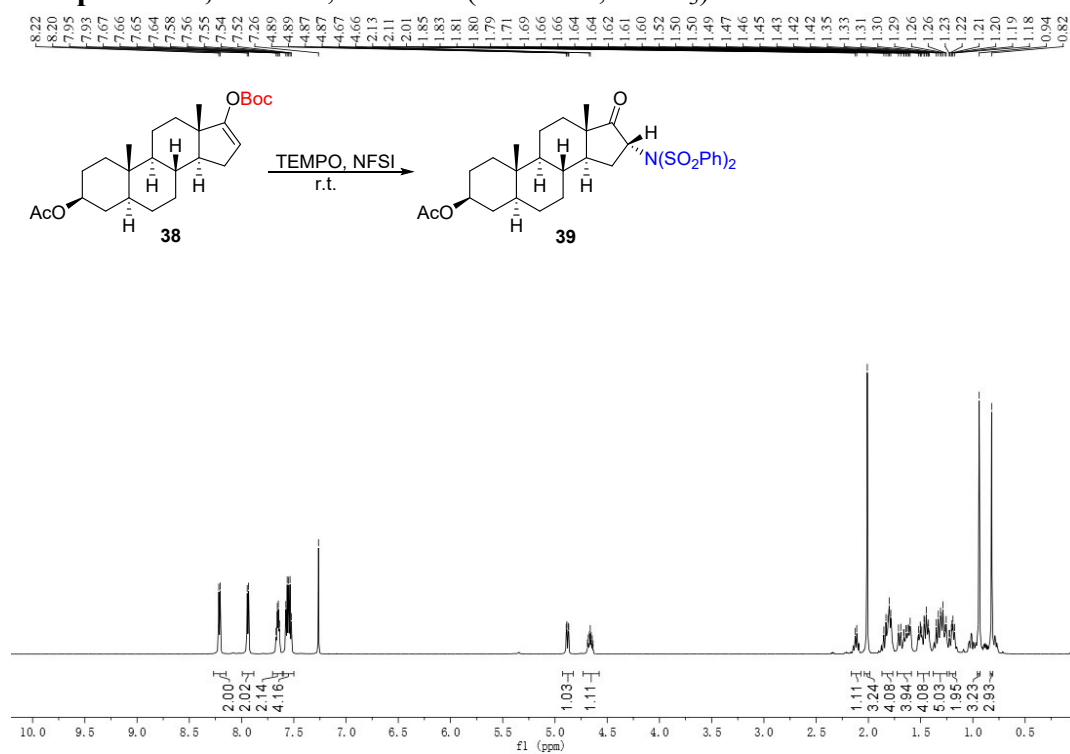
Compound 36, R = Boc, HMBC (500 MHz, d_6 -DMSO)



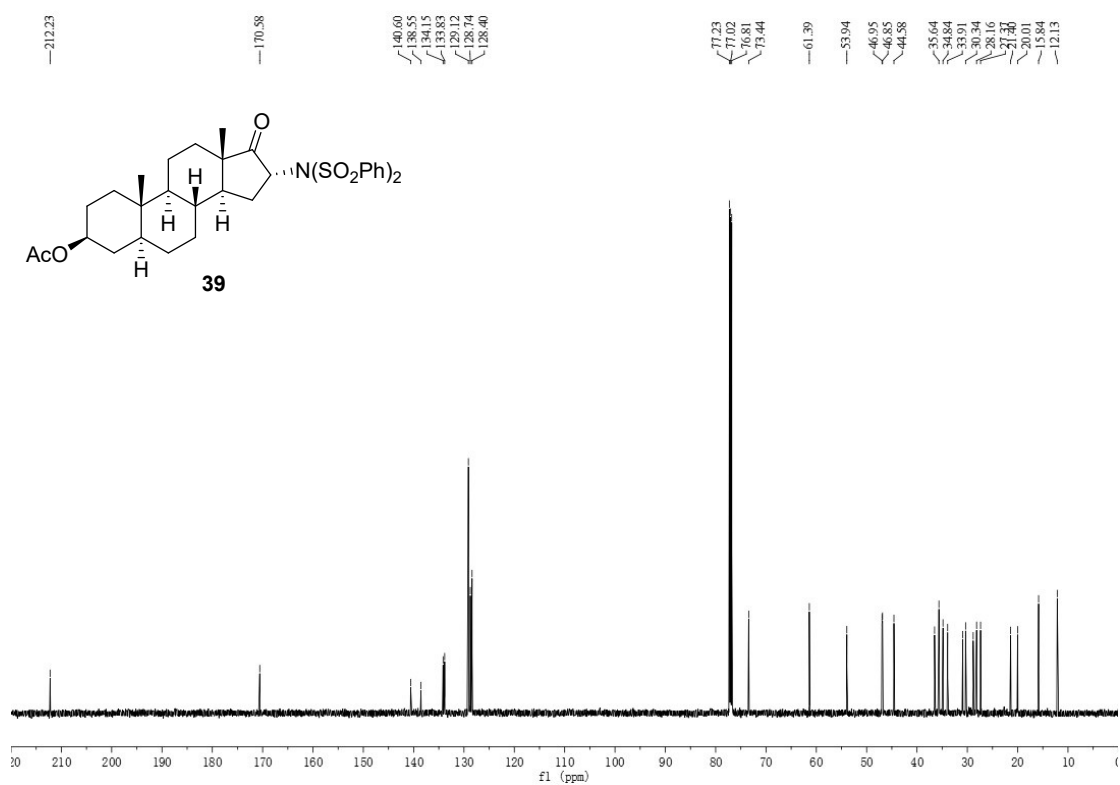
Compound 39, R = Ac, ^1H NMR (600 MHz, CDCl_3)



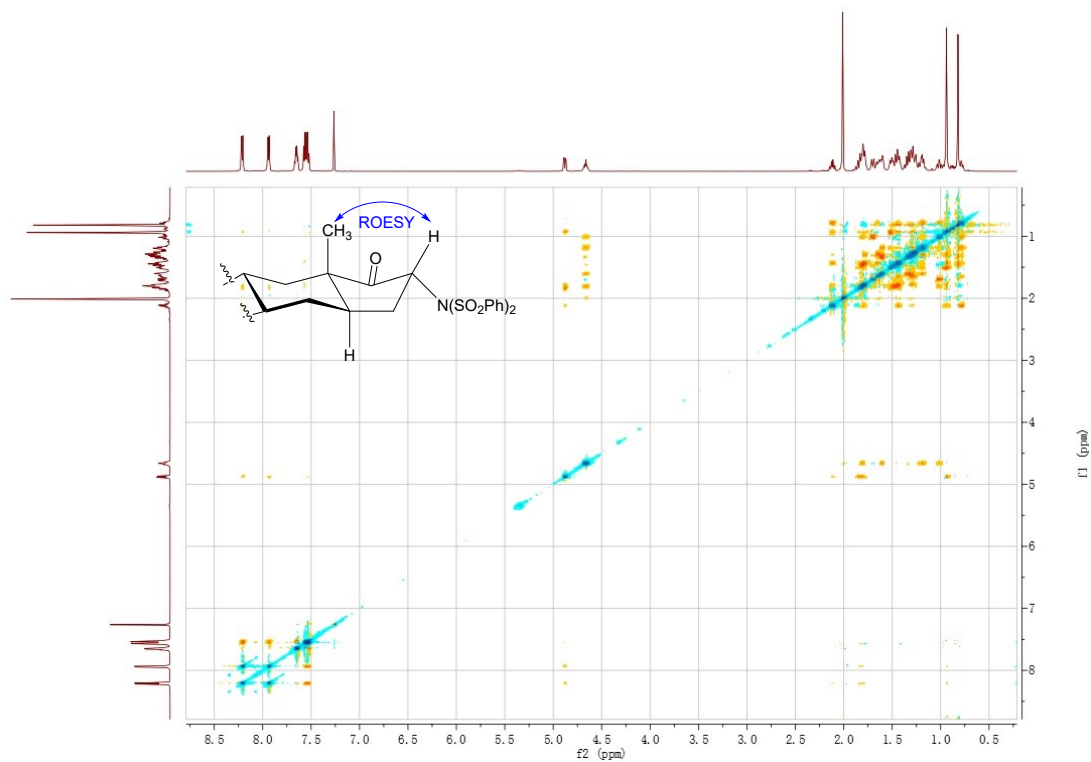
Compound 39, R = Boc, ^1H NMR (500 MHz, CDCl_3)



Compound 39, R = Boc, ^{13}C NMR (125 MHz, CDCl_3)



Compound 39, R = Boc, ROESY (500 MHz, CDCl_3)



9. References

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