Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synergistic Photoredox and Tertiary Amine Catalysis: Generation of Allylic Sulfones from Morita-Baylis-Hillman Acetates and Sulfur Dioxide

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Supporting Information

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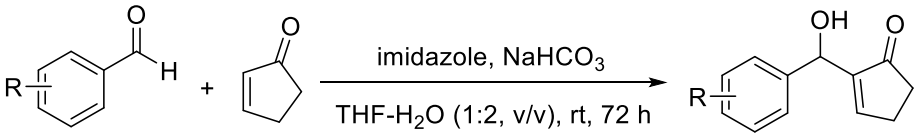
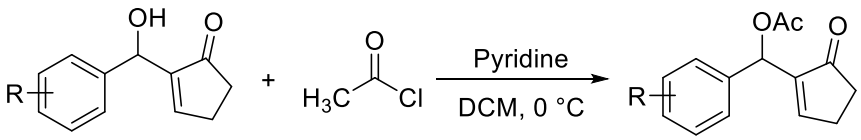
1. General methods

NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 100 MHz. Chemical shifts were given in parts per million (δ) from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI-HRMS was recorded on a Waters SYNAPT G2. Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and a solution of potassium permanganate were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted. Experiments involving moisture and/or air sensitive components were performed under glovebox. Dried solvents and liquid reagents were degassed before use and transferred by oven-dried syringes.

2. General procedure for the preparation of MBH acetates

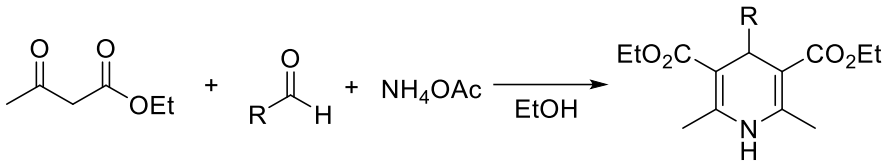


To solution of aromatic aldehyde (14.4 mmol), imidazole (12 mmol) and $NaHCO_3$ (38.4 mmol) in THF (19.2 mL) and water (38.4 mL) was added cyclopentenone (12 mmol) at room temperature. After full conversion, the reaction was quenched by 1M HCl and washed with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by column chromatography (*n*-hexane/EtOAc) affording MBH alcohol product. [1]



To a solution of MBH alcohol (5 mmol) in DCM (30 mL) was added pyridine (6.5 mmol) and AcCl (6.5 mmol) at 0 °C. After full conversion (TLC monitoring), the reaction mixture was quenched by addition of 1M HCl, extracted with DCM. The organic layer was washed with saturated brine, dried over $MgSO_4$, filtered and purified on silica gel affording the desired MBH acetate.[1]

3. General procedure for the preparation of 4-substituted Hantzsch esters

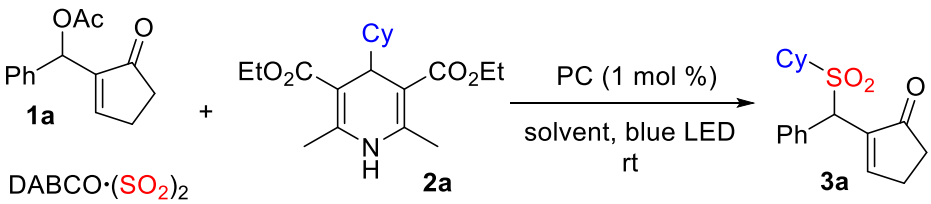


To a 250 mL round bottomed flask was charged ethyl acetoacetate (50 mmol), aldehyde (25 mmol), ammonium acetate (25 mmol) and ethanol (30 mL). The mixture was then heated to reflux overnight before being allowed to return to room temperature and concentrated in vacuo. The crude residue was diluted in CH_2Cl_2, washed with saturated brine. The organic phase was extracted with EtOAc, dried over $MgSO_4$ and concentrated in vacuo. The crude residue was then purified via silica gel column chromatography (EtOAc:pentane - 20:80 v:v) to give the desired 3-substituted Hantzsch ester.[2]

1 M. Kamlar, S. Hybelbauerová, I. Císařová and J. Veselý, Organocatalytic enantioselective allylic alkylation of MBH carbonates with β-keto esters, *Org. Biomol. Chem.* 2014, **12**, 5071.

2 T. Rossolini, J. A. Leitch, R. Grainger and D. J. Dixon, Photocatalytic Three-Component Umpolung Synthesis of 1,3-Diamines, *Org. Lett*. 2018, **20**, 6794.

4. Condition optimization for synergistic photoredox and tertiary amine catalyzed reaction of MBH acetate 1a, 4-substituted Hantzsch ester 2a and DABCO·$(SO_2)_2$.[a]

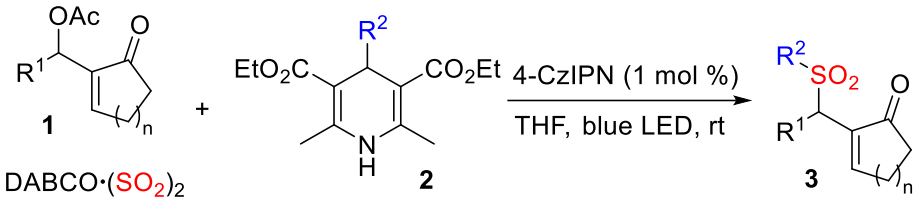


entry	Photocatalyst	Solvent	Yield[b] (%)
1	4-CzIPN	DCE	51
2	Rhodamine-6G	DCE	46
3	$Ru(bpy)_3Cl_2$	DCE	24
4	Eosin Y	DCE	34

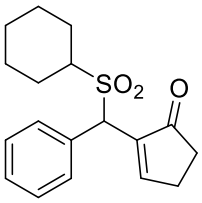
5	Fluorescein	DCE	31
6	Mes-Acr$^+$	DCE	46
7[c]	4-CzIPN	DCE	62
8[c]	4-CzIPN	EtOAc	70
9[c]	4-CzIPN	MeCN	70
10[c]	4-CzIPN	Toluene	64
11[c]	**4-CzIPN**	**THF**	**85**
12[c]	4-CzIPN	1,4-Dioxide	74
13[c]	4-CzIPN	DMSO	18
14[c]	4-CzIPN	MeOH	44

[a]Reaction conditions: MBH acetate **1a** (0.1 mmol), 4-substituted Hantzsch ester **2a** (0.1 mmol), DABCO·$(SO_2)_2$ (0.1 mmol), photocatalyst (0.001 mmol), solvent (1.0 mL), blue LED, rt, 48 h, under a N_2 atmosphere. [b]Isolated yield based on MBH acetate **1a**. [c]In the presence of 4-substituted Hantzsch ester **2a** (0.15 mmol).

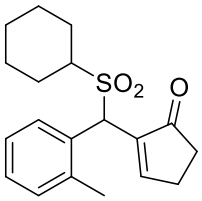
5. General procedure for the synergistic photoredox and tertiary amine catalyzed reaction



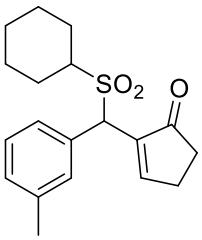
In glovebox, MBH acetate **1** (0.1 mmol), 4-substituted Hantzsch ester **2** (0.15 mmol), DABCO·$(SO_2)_2$ (0.1 mmol), 4-CzIPN (0.001 mmol) were added into a tube equipped with a magnetic stir bar. Then, THF (1.0 mL) was added and the mixture was stirred at room temperature for 48 h under blue LED irradiation. After completion, the resulting crude residue was concentrated in vacuum and purified by column chromatography on silica gel eluting with (EtOAc/*n*-hexane) to afford product **3**.



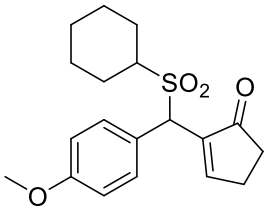
2-((Cyclohexylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3a), white solid, 85% yield; 33% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 206 nm, t (major) = 27.983 min, t (minor) = 35.90 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.55–7.53 (m, 2H), 7.41–7.37 (m, 3H), 5.38 (s, 1H), 2.84–2.66 (m, 3H), 2.44 (ddd, *J* = 44.8, 19.2, 6.4 Hz, 2H), 2.10 (dd, *J* = 45.2, 12.8 Hz, 2H), 1.87 (s, 2H), 1.64–1.49 (m, 3H), 1.23–1.09 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.7, 162.7, 138.5, 131.8, 129.7, 129.0, 59.4, 59.0, 33.4, 27.4, 25.6, 25.0, 25.0, 24.9, 24.3; ESI-HRMS: calcd. for $C_{18}H_{22}O_3S+Na^+$: 341.1187, found: 341.1196.



2-((Cyclohexylsulfonyl)(o-tolyl)methyl)cyclopent-2-en-1-one (3b), yellow oil, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.26 (t, *J* = 2.4 Hz, 1H), 7.73–7.69 (m, 1H), 7.25–7.19 (m, 3H), 5.73 (s, 1H), 2.85–2.66 (m, 3H), 2.54–2.36 (m, 5H), 2.11 (t, *J* = 14.8 Hz, 2H), 1.90–1.87 (m, 2H), 1.67 (d, *J* = 3.2 Hz, 1H), 1.57–1.51 (m, 1H), 1.22–1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.9, 163.3, 139.7, 137.9, 130.9, 129.9, 129.0, 128.8, 126.5, 60.2, 54.2, 33.5, 27.5, 25.5, 25.1, 25.0, 24.7, 120.0; ESI-HRMS: calcd. for $C_{19}H_{24}O_3S+Na^+$: 355.1344, found: 355.1350.

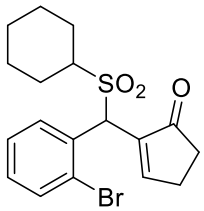


2-((Cyclohexylsulfonyl)(m-tolyl)methyl)cyclopent-2-en-1-one (3c), yellow oil, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (t, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28–7.25 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 5.34 (s, 1H), 2.84–2.66 (m, 3H), 2.53–2.39 (m, 2H), 2.36 (s, 3H), 2.17–2.05 (m, 2H), 1.88–1.85 (m, 2H), 1.66–1.64 (m, 1H), 1.60–1.51 (m, 2H), 1.22–1.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.8, 162.8, 138.8, 138.6, 131.7, 130.3, 129.9, 128.9, 126.8, 59.3, 58.9, 33.5, 27.4, 25.6, 25.1, 25.0, 24.9, 24.3, 21.5; ESI-HRMS: calcd. for $C_{19}H_{24}O_3S+Na^+$: 355.1344, found: 355.1346.

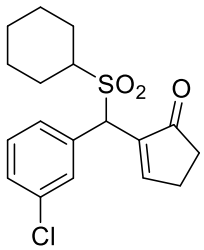


2-((Cyclohexylsulfonyl)(4-methoxyphenyl)methyl)cyclopent-2-en-1-one (3d), yellow solid, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.33 (s, 1H), 3.81 (s, 3H), 2.84–2.67 (m, 3H), 2.44 (ddd, *J* = 43.6, 19.2, 2.0 Hz, 2H), 2.09 (dd, *J* = 43.2, 12.8 Hz, 2H), 1.88 (s, 2H), 1.64–1.49 (m, 3H), 1.21–1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)

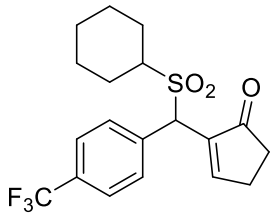
206.9, 162.4, 160.1, 138.8, 131.0, 123.5, 114.5, 59.0, 58.3, 55.3, 33.5, 27.4, 25.6, 25.1, 25.0, 24.9, 24.2; ESI-HRMS: calcd. for $C_{19}H_{24}O_4S+Na^+$: 371.1293, found: 371.1299.



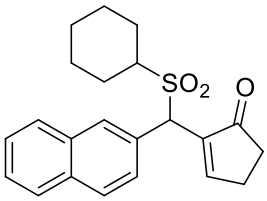
2-((2-Bromophenyl)(cyclohexylsulfonyl)methyl)cyclopent-2-en-1-one (3e), colourless oil, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (t, *J* = 2.8 Hz, 1H), 7.86 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 6.13 (s, 1H), 2.85–2.65 (m, 3H), 2.47 (qdd, *J* = 19.2, 6.8, 2.4 Hz, 2H), 2.28–2.10 (m, 2H), 1.89–1.87 (m, 2H), 1.68–1.66 (m, 1H), 1.59–1.51 (m, 2H), 1.24–1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.3, 163.6, 138.9, 133.5, 131.8, 130.9, 130.3, 127.9, 125.9, 60.7, 57.6, 33.5, 27.5, 25.3, 25.2, 25.1, 25.0; ESI-HRMS: calcd. for $C_{18}H_{21}Br^{79}O_3S+Na^+$: 419.0292, found: 419.0292; $C_{18}H_{21}Br^{81}O_3S+Na^+$: 421.0272, found: 421.0276.



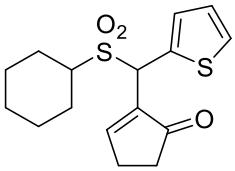
2-((3-Chlorophenyl)(cyclohexylsulfonyl)methyl)cyclopent-2-en-1-one (3f), white solid, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (t, *J* = 2.8 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.42 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.37–7.30 (m, 2H), 5.33 (s, 1H), 2.86–2.68 (m, 3H), 2.46 (qdd, *J* = 19.6, 6.4, 2.4 Hz, 2H), 2.16–2.05 (m, 2H), 1.89–1.88 (m, 2H), 1.67 (dd, *J* = 6.0, 4.4 Hz, 1H), 1.58–1.51 (m, 2H), 1.22–1.15 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.6, 163.1, 138.2, 134.9, 133.6, 130.2, 129.7, 129.3, 128.1, 59.7, 58.4, 33.4, 27.5, 25.4, 25.0, 25.0, 24.5; ESI-HRMS: calcd. for $C_{18}H_{21}Cl^{35}O_3S+Na^+$: 375.0798, found: 375.0806; $C_{18}H_{21}Cl^{37}O_3S+Na^+$: 377.0768, found: 377.0775.



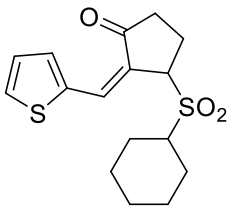
2-((Cyclohexylsulfonyl)(4-(trifluoromethyl)phenyl)methyl)cyclopent-2-en-1-one (3g), colourless oil, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (t, *J* = 2.8 Hz, 1H), 7.68–7.63 (m, 4H), 5.43 (s, 1H), 2.88–2.68 (m, 3H), 2.47 (qdd, *J* = 19.2, 6.4, 2.0 Hz, 2H), 2.17–2.06 (m, 2H), 1.90 (d, *J* = 2.8 Hz, 2H), 1.67–1.54 (m, 4H), 1.18–1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.6, 163.1, 138.2, 135.7, 131.2 (q, *J* = 32.6 Hz), 130.2, 126.0 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 270.6 Hz), 59.8, 58.4, 33.4, 27.5, 25.2, 25.0, 24.9, 24.9, 24.6; ESI-HRMS: calcd. for $C_{19}H_{21}F_3O_3S+Na^+$: 409.1061, found: 409.1064.



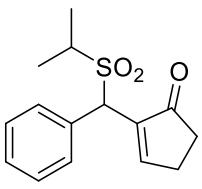
2-((Cyclohexylsulfonyl)(naphthalen-2-yl)methyl)cyclopent-2-en-1-one (3h), yellow solid, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.38 (t, *J* = 2.4 Hz, 1H), 8.00 (s, 1H), 7.88–7.83 (m, 3H), 7.67 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.54–7.50 (m, 2H), 5.56 (s, 1H), 2.87–2.68 (m, 3H), 2.45 (qdd, *J* = 19.2, 6.8, 2.0 Hz, 2H), 2.21 (d, *J* = 12.4 Hz, 1H), 2.07 (d, *J* = 12.8 Hz, 1H), 1.85 (t, *J* = 11.2 Hz, 2H), 1.67–1.54 (m, 4H), 1.17–1.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.8, 162.8, 138.6, 133.3, 133.2, 129.5, 129.4, 129.0, 128.2, 127.7, 126.9, 126.6, 126.5, 59.4, 59.1, 33.5, 27.4, 25.7, 25.0, 24.9, 24.2; ESI-HRMS: calcd. for $C_{18}H_{21}ClO_3S+Na^+$: 391.1344, found: 391.1351.



2-((Cyclohexylsulfonyl)(thiophen-2-yl)methyl)cyclopent-2-en-1-one (3i), yellow oil, 32% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.27 (t, *J* = 2.8 Hz, 1H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.03 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.71 (s, 1H), 2.86–2.69 (m, 3H), 2.49 (qdd, *J* = 19.2, 6.4, 2.4 Hz, 2H), 2.22–2.08 (m, 3H), 1.89–1.84 (m, 2H), 1.67 (d, *J* = 6.0 Hz, 1H), 1.55–1.51 (m, 1H), 1.23–1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.3, 164.1,138.3, 133.5, 129.3, 127.5, 127.2, 59.1, 54.3, 33.6, 27.4, 25.8, 25.1, 25.0, 24.9, 24.2; ESI-HRMS: calcd. for $C_{16}H_{20}O_3S_2+Na^+$: 347.0752, found: 347.0760.

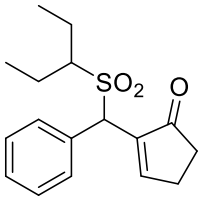


3-(cyclohexylsulfonyl)-2-(thiophen-2-ylmethylene)cyclopentan-1-one (3i'), yellow solid, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (s, 1H), 7.60 (d, *J* = 4.4 Hz, 1H), 7.52 (d, *J* = 2.8 Hz, 1H), 7.13 (t, *J* = 4 Hz, 1H), 4.90 (d, *J* = 7.2 Hz, 1H), 3.18–3.12 (m, 1H), 2.95–2.85 (m, 1H), 2.65 (dd, *J* = 14.0, 9.6 Hz, 1H), 2.38 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.24 (d, *J* = 6.4 Hz, 3H), 1.95 (s, 2H), 1.77–1.72 (m, 2H), 1.64–1.58 (m, 1H), 1.26–1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 204.0, 137.5, 136.0, 132.4, 131.7, 128.1, 124.9, 60.8, 59.8, 34.9, 26.2, 25.2, 25.1, 25.0, 24.5, 23.1. ESI-HRMS: calcd. For $C_{16}H_{20}O_3S_2+Na^+$:347.0752, found: 347.0753.

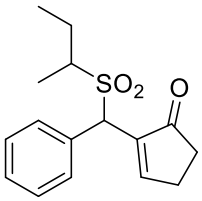


2-((Isopropylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3j), white solid, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.56–7.54 (m, 2H), 7.41–7.37 (m, 3H), 5.41 (s, 1H), 3.01–2.94 (m, 1H), 2.85–2.67 (m, 2H), 2.50 (ddd, *J* = 42.8, 18.8, 6.8 Hz, 2H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.31 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR

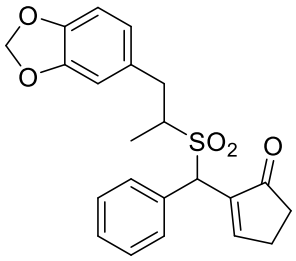
(100 MHz, $CDCl_3$): δ (ppm) 206.8, 162.8, 138.5, 131.8, 129.7, 129.1, 59.1, 51.4, 33.4, 27.4, 15.8, 14.8; ESI-HRMS: calcd. for $C_{15}H_{18}O_3S+Na^+$: 301.0874, found: 301.0877.



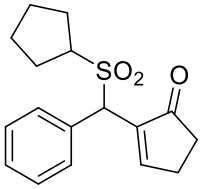
2-((Pentan-3-ylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3k), yellow oil, 90% yield; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.55–7.53 (m, 2H), 7.41–7.37 (m, 3H), 5.42 (s, 1H), 2.84–2.59 (m, 3H), 2.45 (ddd, *J* = 43.2, 19.2, 2.4 Hz, 2H), 1.98–1.71 (m, 4H), 0.98 (dd, *J* = 13.6, 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.8, 162.7, 138.6, 132.0, 129.8, 129.0, 129.0, 62.5, 60.2, 33.4, 27.4, 20.4, 19.5, 10.9, 10.8; ESI-HRMS: calcd. for $C_{17}H_{22}O_3S+Na^+$: 329.1187, found: 329.1189.



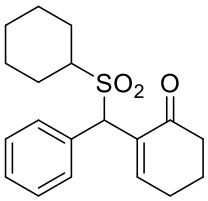
2-((Sec-butylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3l), (dr : 1:1), colourless oil, 90% yield; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (dt, *J* = 9.6, 2.4 Hz, 1H), 7.54 (td, *J* = 8.0, 2.4 Hz, 2H), 7.41–7.37 (m, 3H), 5.43 (d, *J* = 5.6 Hz, 1H), 2.85–2.66 (m, 3H), 2.54–2.35 (m, 2H), 2.09–1.95 (m, 1H), 1.59–1.53 (m, 1H), 1.32 (dd, *J* = 22.8, 6.8 Hz, 3H), 0.98–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.7, 206.7, 162.8, 162.7, 138.6, 138.4, 132.1, 131.6, 129.9, 129.7, 129.1, 129.1, 129.1, 129.0, 59.3, 59.3, 57.4, 57.3, 33.4, 33.4, 27.4, 27.4, 22.6, 21.5, 12.8, 11.7, 11.0, 10.9; ESI-HRMS: calcd. for $C_{16}H_{20}O_3S+Na^+$: 315.1031, found: 315.1029.



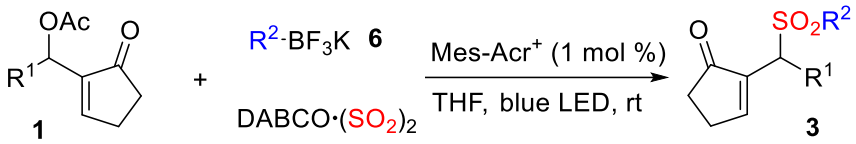
2-(((4-(Benzo[d][1,3]dioxol-4-yl)butan-2-yl)sulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3m), (dr : 1:1), yellow oil, 50% yield; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33–8.30 (m, 1H), 7.58–7.56 (m, 2H), 7.42–7.38 (m, 3H), 6.73–6.70 (m, 1H), 6.53–6.46 (m, 2H), 5.93–5.92 (m, 2H), 5.44 (d, *J* = 4.8 Hz, 1H), 3.35–3.26 (m, 1H), 3.02–2.94 (m, 1H), 2.86–2.68 (m, 2H), 2.56–2.37 (m, 3H), 1.26–1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.7, 206.6, 163.1, 163.0, 147.9, 147.9, 146.6, 146.6, 138.5, 138.4, 131.8, 131.7, 130.3, 130.2, 129.8, 129.7, 129.3, 129.2, 129.2, 129.2, 122.5, 122.4, 109.4, 109.3, 108.5, 108.4, 101.1, 101.0, 59.9, 59.8, 57.7, 57.7, 35.3, 34.2, 33.5, 33.4, 27.5, 12.6, 11.7; ESI-HRMS: calcd. for $C_{23}H_{24}O_5S+Na^+$: 421.1086, found: 421.1088.



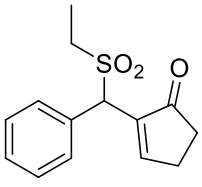
2-((Cyclopentylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3n), yellow solid, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.55–7.53 (m, 2H), 7.41–7.37 (m, 3H), 5.30 (s, 1H), 3.21–3.13 (m, 1H), 2.85–2.67 (m, 2H), 2.45 (ddd, *J* = 42.4, 17.6, 6.4 Hz, 2H), 2.16–1.90 (m, 3H), 1.85–1.71 (m, 3H), 1.62–1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.8, 162.6, 138.5, 132.0, 129.8, 129.1, 61.0, 59.6, 33.4, 27.5, 27.4, 26.4, 26.1, 26.0; ESI-HRMS: calcd. for $C_{17}H_{20}O_3S+Na^+$: 327.1031, found: 327.1033.



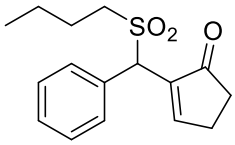
2-((Cyclohexylsulfonyl)(phenyl)methyl)cyclohex-2-en-1-one (3o), white solid, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (t, *J* = 4.4 Hz, 1H), 7.56 (dd, *J* = 8.0, 2.4 Hz, 2H), 7.40–7.35 (m, 3H), 5.90 (s, 1H), 2.75–2.41 (m, 5H), 2.16–1.94 (m, 4H), 1.87–1.84 (m, 2H), 1.65–1.47 (m, 4H), 1.15–1.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.3, 151.1, 133.1, 132.7, 129.7, 129.0, 128.7, 59.6, 58.3 37.8, 26.5, 25.7, 25.1, 25.0, 25.0, 24.2, 22.3; ESI-HRMS: calcd. for $C_{19}H_{24}O_3S+Na^+$: 355.1344, found: 355.1345.



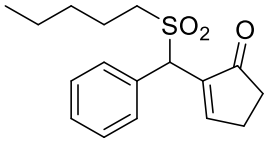
In glovebox, MBH acetate **1** (0.1 mmol), potassium alkyltrifluoroborate **6** (0.15 mmol), DABCO·$(SO_2)_2$ (0.1 mmol), 4-CzIPN (0.001 mmol) were added into a tube equipped with a magnetic stir bar. Then, THF (1.0 mL) was added and the mixture was stirred at room temperature for 48 h under blue LED irradiation. After completion, the resulting crude residue was concentrated in vacuum and purified by column chromatography on silica gel eluting with (EtOAc/*n*-hexane) to afford product **3**.



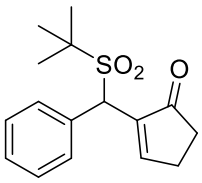
2-((Ethylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3p), colourless oil, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (t, *J* = 2.4 Hz, 1H), 7.56–7.53 (m, 2H), 7.41–7.37 (m, 3H), 5.30 (s, 1H), 2.90–2.68 (m, 4H), 2.55–2.37 (m, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.8, 162.8, 138.3, 131.6, 129.7, 129.2, 61.6, 46.1, 33.4, 27.4, 6.5; ESI-HRMS: calcd. for $C_{14}H_{16}O_3S+Na^+$: 287.0718, found: 287.0721.



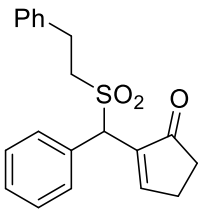
2-((Butylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3q), yellow oil, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (t, *J* = 2.6 Hz, 1H), 7.55–7.52 (m, 2H), 7.41–7.38 (m, 3H), 5.28 (s, 1H), 2.88–2.68 (m, 4H), 2.55–2.37 (m, 2H), 1.83–1.71 (m, 2H), 1.37 (dd, *J* = 14.8, 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) 206.8, 162.7, 138.3, 131.7, 129.7, 129.2, 129.1, 62.2, 51.4, 33.4, 27.4, 23.8, 21.7, 13.5; ESI-HRMS: calcd. for $C_{16}H_{20}O_3S+Na^+$: 315.1031, found: 315.1032.



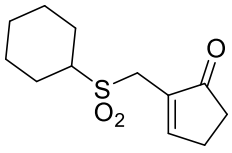
2-((Pentylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3r), yellow oil, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (s, 1H), 7.53 (d, *J* = 4.0 Hz, 2H), 7.39 (d, *J* = 3.6 Hz, 3H), 5.28 (s, 1H), 2.83–2.73 (m, 4H), 2.46 (ddd, *J* = 42.8, 18.8, 5.6 Hz, 2H), 1.79 (s, 2H), 1.30–1.26 (m, 4H), 0.88–0.87 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 206.8, 162.7, 138.4, 131.7, 129.7, 129.2, 129.1, 62.3, 51.7, 33.4, 30.5, 27.4, 22.1, 21.5, 13.7; ESI-HRMS: calcd. for $C_{17}H_{22}O_3S+Na^+$: 329.1187, found: 329.1193.



2-((Tert-butylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3s), white solid, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.26 (t, *J* = 2.8 Hz, 1H), 7.60–7.57 (m, 2H), 7.39–7.34 (m, 3H), 5.50 (s, 1H), 2.81–2.63 (m, 2H), 2.43 (ddd, *J* = 42.0, 19.2, 2.4 Hz, 2H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.6, 162.5, 139.8, 133.2, 129.8, 128.9, 129.0, 128.9, 62.7, 58.0, 33.4, 27.3, 24.4; ESI-HRMS: calcd. for $C_{16}H_{20}O_3S+Na^+$: 315.1031, found: 315.1037.



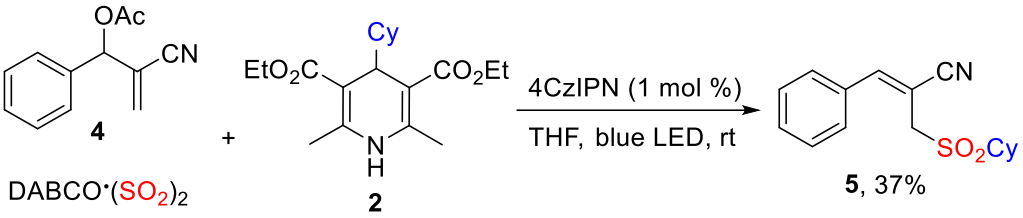
2-((Phenethylsulfonyl)(phenyl)methyl)cyclopent-2-en-1-one (3t), white solid, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (t, *J* = 2.0 Hz, 1H), 7.53–7.51 (m, 2H), 7.40–7.38 (m, 3H), 7.31–7.23 (m, 3H), 7.15–7.11 (m, 2H), 5.30 (s, 1H), 3.14–3.03 (m, 4H), 2.86–2.69 (m, 2H), 2.55–2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.7, 162.9, 138.2, 137.5, 131.5, 129.7, 129.3, 129.2, 128.9, 128.5, 127.1, 62.7, 53.2, 33.4, 28.1, 27.5; ESI-HRMS: calcd. for $C_{20}H_{20}O_3S+Na^+$: 315.1031, found: 315.1029.



2-((Cyclohexylsulfonyl)methyl)cyclopent-2-en-1-one (3u), white solid, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (s, 1H), 3.87 (d, *J* = 0.8 Hz, 2H),

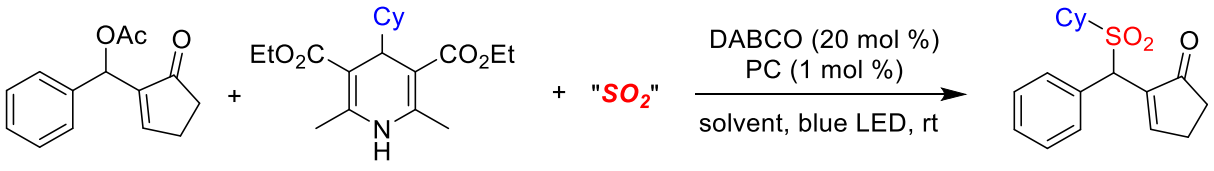
2.80–2.73 (m, 3H), 2.50–2.48 (m, 2H), 2.21 (d, *J* = 11.2 Hz, 2H), 1.94–1.91 (m, 2H), 1.73–1.67 (m, 2H), 1.59–1.49 (m, 2H), 1.26–1.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.3, 165.8, 133.8, 61.1, 44.9, 33.8, 27.5, 25.1, 25.0, 25.0; ESI-HRMS: calcd. for $C_{12}H_{18}O_3S+Na^+$: 265.0874, found: 265.0880.

6. Synergistic photoredox and tertiary amine catalyzed reaction with linear MBH acetates



In glovebox, MBH acetate **4** (0.1 mmol), 4-cyclohexyl Hantzsch ester **2** (0.15 mmol), DABCO·$(SO_2)_2$ (0.1 mmol), 4-CzIPN (0.001 mmol) were added into a tube equipped with a magnetic stir bar. Then, THF (1.0 mL) was added and the mixture was stirred at room temperature for 48 h under blue LED irradiation. After completion, the resulting crude residue was concentrated in vacuum and purified by column chromatography on silica gel eluting with (EtOAc/*n*-hexane) to afford (*Z*)-2-((cyclohexylsulfonyl)methyl)-3-phenylacrylonitrile **5,** white solid, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85–7.82 (m, 2H), 7.48–7.44 (m, 3H), 7.35 (s, 1H), 3.92 (s, 2H), 3.08–3.00 (m, 1H), 2.24 (d, *J* = 11.6 Hz, 2H), 2.00–1.96 (m, 2H), 1.77–1.59 (m, 3H), 1.39–1.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.4, 132.5, 131.7, 129.5, 129.1, 117.8, 97.1, 76.7, 60.9, 54.9, 25.1, 25.0; ESI-HRMS: calcd. for $C_{16}H_{19}NO_2S+Na^+$: 312.1034, found: 312.1034.

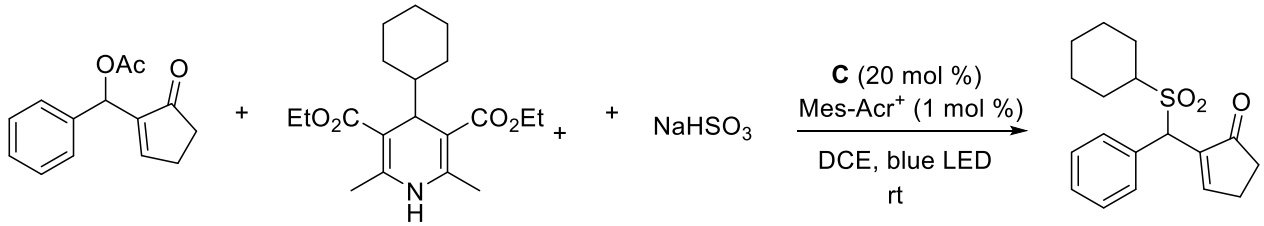
7. Condition optimization of synergistic photoredox and tertiary amine catalyzed reaction with inorganic sulfites as the source of sulfonyl group[a]



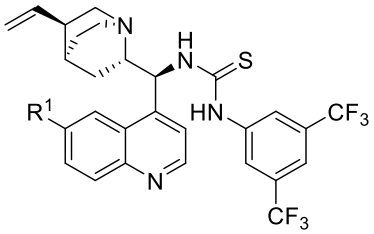
entry	Inorganic sulfites	Photocatalyst	Solvent	Yield[b] (%)
1	$NaHSO_3$	4-CzIPN	THF	/
2	$NaHSO_3$	4-CzIPN	DMF	/
3	$NaHSO_3$	4-CzIPN	EA	/
4	$NaHSO_3$	4-CzIPN	Xylene	/
5	$NaHSO_3$	4-CzIPN	MeCN	/
6	$NaHSO_3$	4-CzIPN	1,4-dioxane	/
7	$NaHSO_3$	4-CzIPN	DCE	24
8	$Na_2S_2O_5$	4-CzIPN	DCE	/
9	Na_2SO_3	4-CzIPN	DCE	/
10	K_2SO_3	4-CzIPN	DCE	3
11	$NaHSO_3$	$Ru(bpy)_3Cl_2$	DCE	23
12	$NaHSO_3$	Fluorescein	DCE	30
13	**$NaHSO_3$**	**Mes-Acr$^+$**	**DCE**	**53**
14	$NaHSO_3$	$Ir(ppy)_3$	DCE	20

[a]Reaction conditions: MBH acetate (0.1 mmol), 4-substituted Hantzsch ester (0.1 mmol), inorganic sulfites (0.1 mmol), photocatalyst (0.001 mmol), DABCO (0.002 mol), solvent (1.0 mL), blue LED, rt, 48 h, under a N_2 atmosphere. [b]Isolated yield based on MBH acetate.

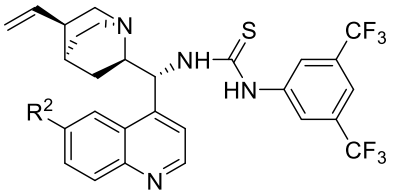
8. Condition optimization for asymmetric synergistic photoredox and tertiary amine catalyzed reaction of MBH acetate[a]



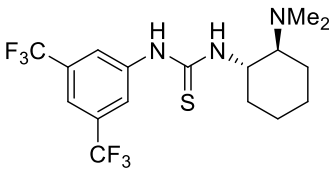
1a **2a** **3a**



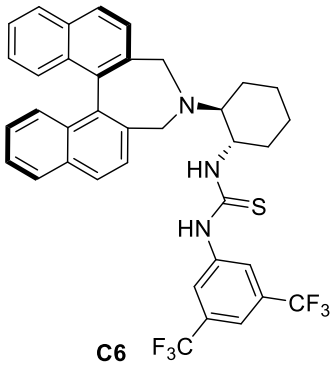
C1 R^1 = H
C4 R^1 = OCH_3



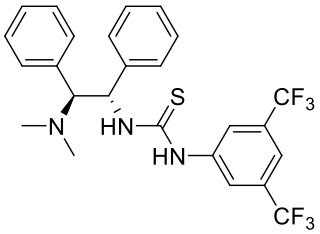
C2 R^2 = H
C3 R^2 = OCH_3



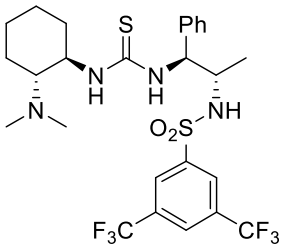
C5



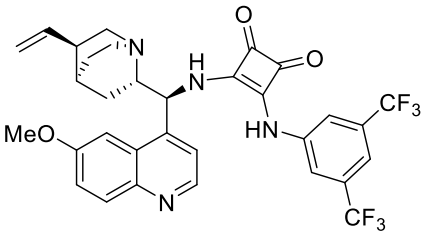
C6



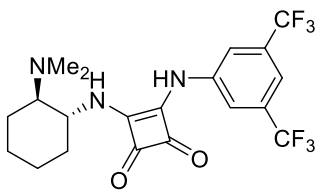
C7



C8



C9

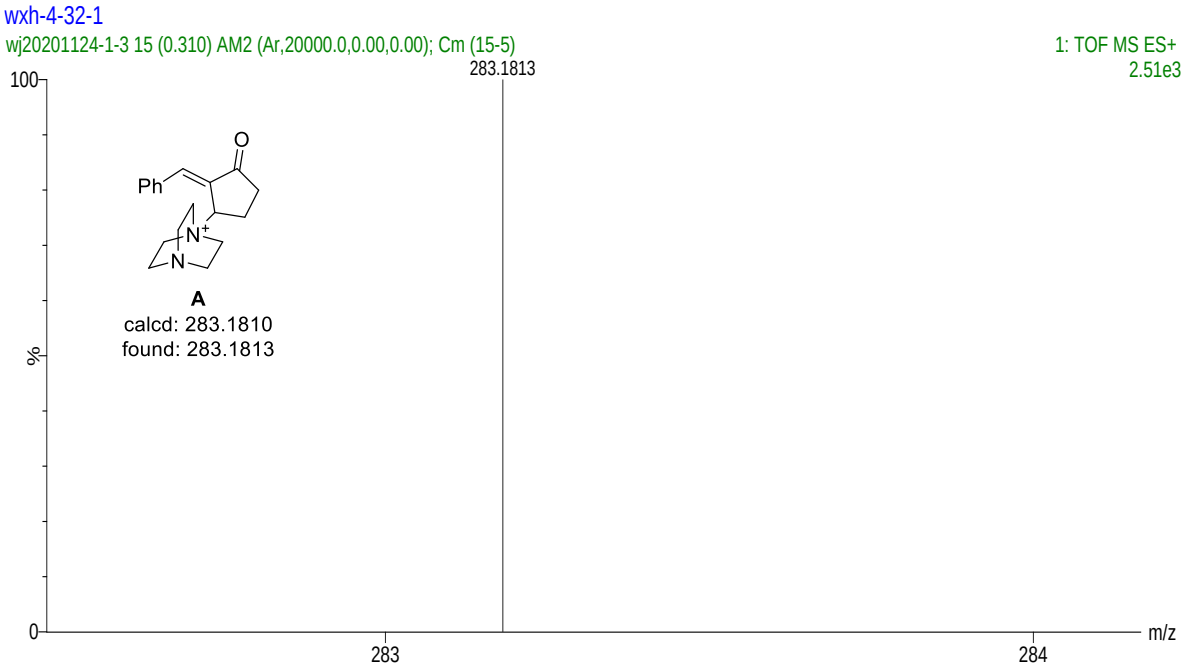


C10

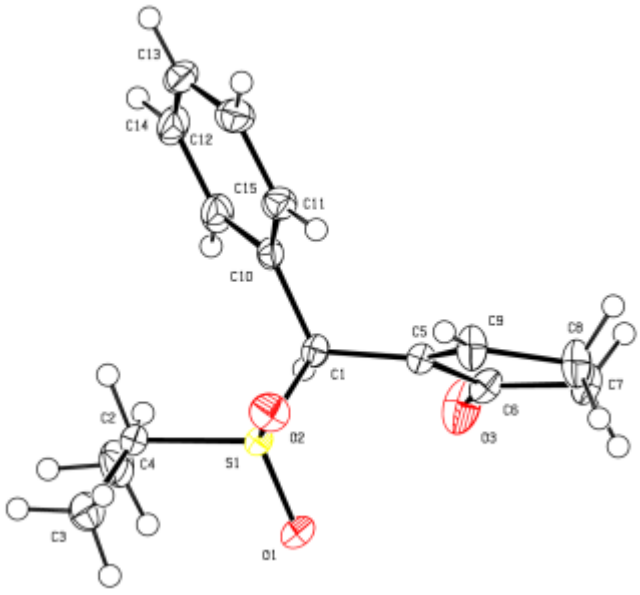
entry	Catalyst	Yield[b] (%)	Ee[c] (%)
1	**C1**	41	16
2	**C2**	35	/
3	**C3**	45	16
4	**C4**	**55**	**33**
5	**C5**	52	18
6	**C6**	6	/
7	**C7**	50	16
8	**C8**	48	8
9	**C9**	43	/
10	**C10**	45	/

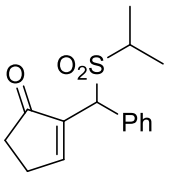
[a]Unless noted otherwise, reactions were performed with MBH acetate **1a** (0.1 mmol), 4-substituted Hantzsch ester **2a** (0.15 mmol), $NaHSO_3$ (0.1 mmol), Mes-Acr^+ (0.001 mmol), catalyst (0.02 mmol), DCE (1 mL), blue LED, rt, 48 h, under N_2 atmosphere. [b]Determined by ^{1}H-NMR spectroscopy. [c]Determined by HPLC analysis on chiral stationary phase.

9. HRMS spectrum of captured intermediate A



10. Crystal data and structural refinement for 3j



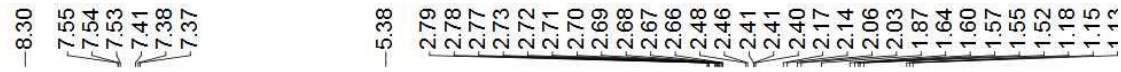


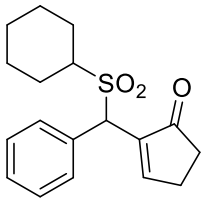
3j

Identification code	**3j**
Empirical formula	$C_{15}\ H_{18}\ O_3\ S$
Formula weight	278.35
Temperature	173(2) K

Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 13.5251(14) Å	= 90°.
	b = 10.9872(11) Å	= 100.546(4)°.
	c = 9.4818(9) Å	= 90°.
Volume	1385.2(2) $Å^3$	
Z	4	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	1.369 mm^{-1}	
F(000)	592	
Crystal size	0.270 x 0.210 x 0.080 mm^3	
Theta range for data collection	4.542 to 58.479°.	
Index ranges	-17<=h<=16, -13<=k<=13, -12<=l<=12	
Reflections collected	10335	
Independent reflections	2899 [R(int) = 0.0322]	
Completeness to theta = 53.594°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.752 and 0.634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2899 / 2 / 174	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0587	
R indices (all data)	R1 = 0.0240, wR2 = 0.0591	
Absolute structure parameter	0.032(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.215 and -0.171 $e.Å^{-3}$	

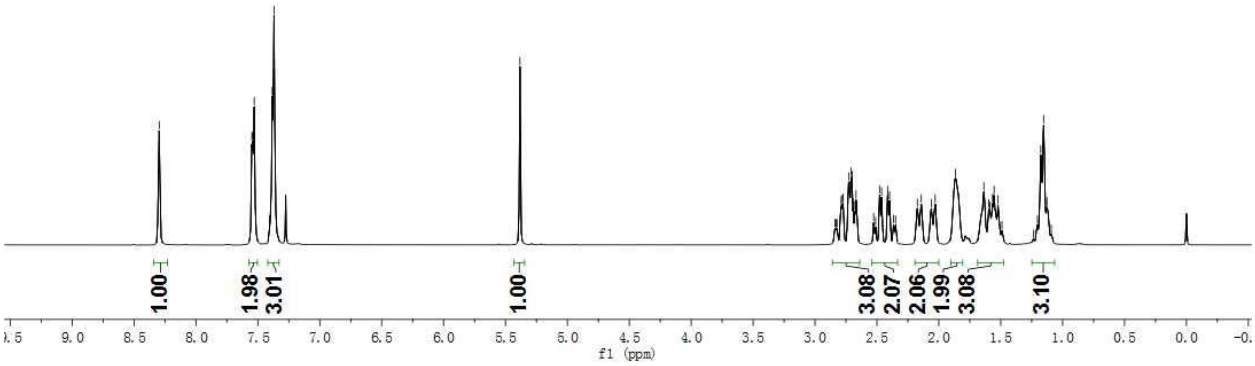
11. NMR spectra and HPLC chromatograph

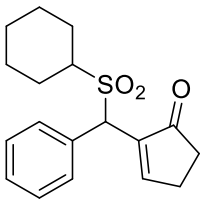




3a

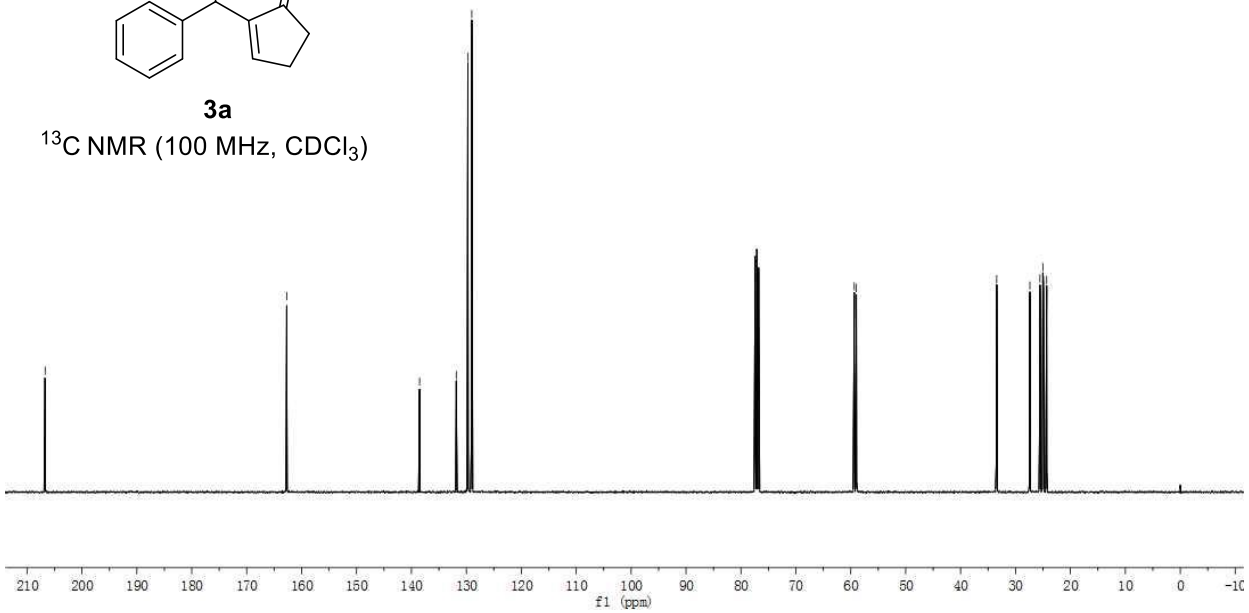
^{1}H NMR (400 MHz, $CDCl_3$)

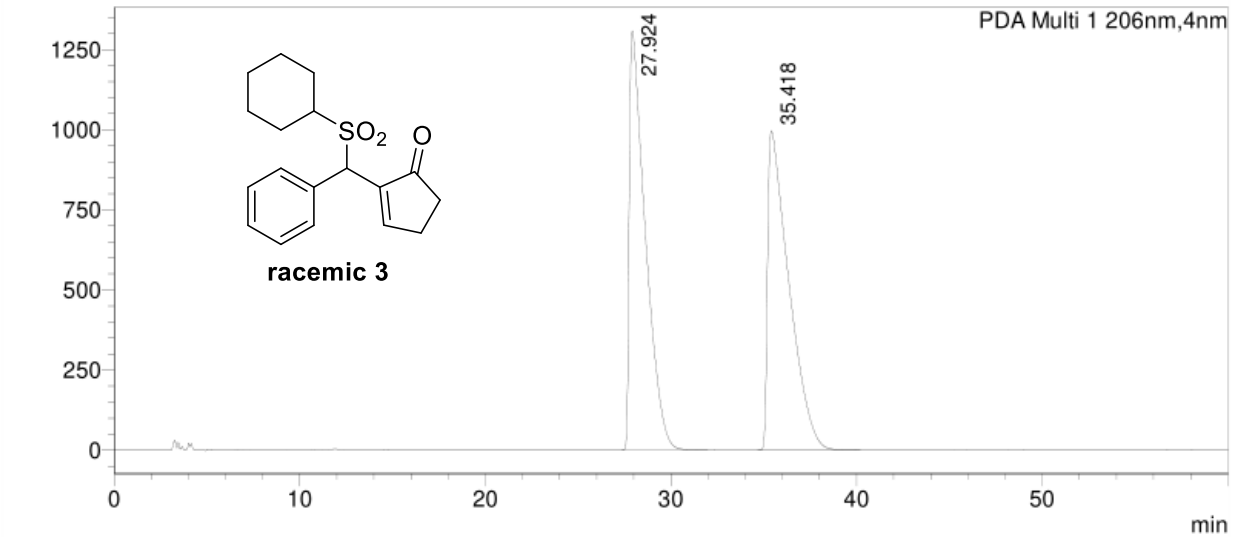




3a

^{13}C NMR (100 MHz, $CDCl_3$)

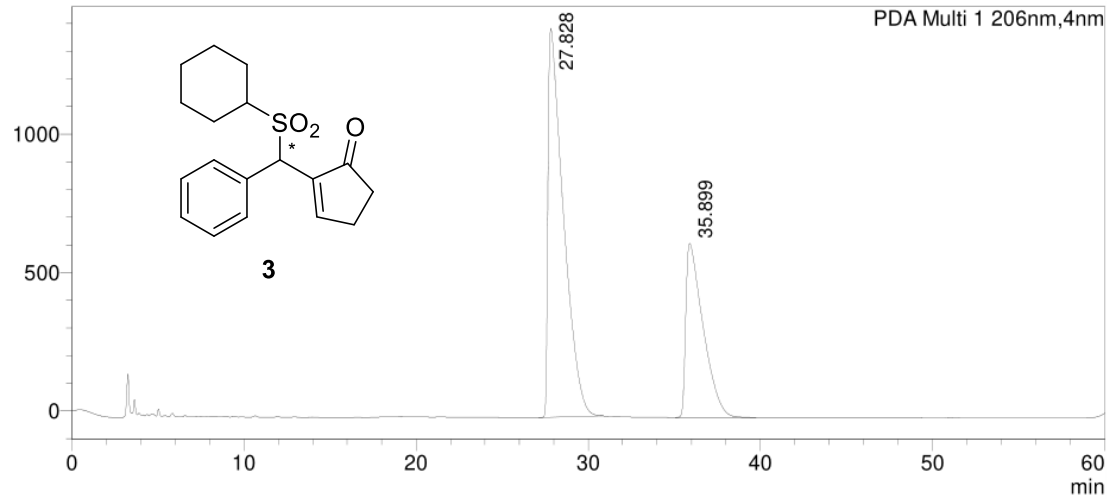




<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	27.924	78859860	1307806	49.811
2	35.418	79458776	995986	50.189



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
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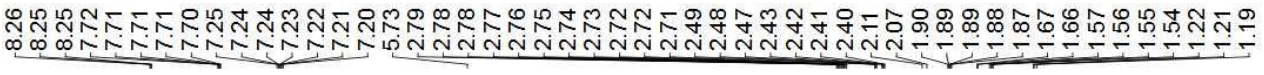
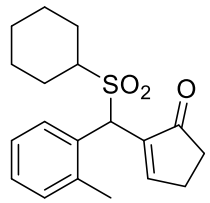
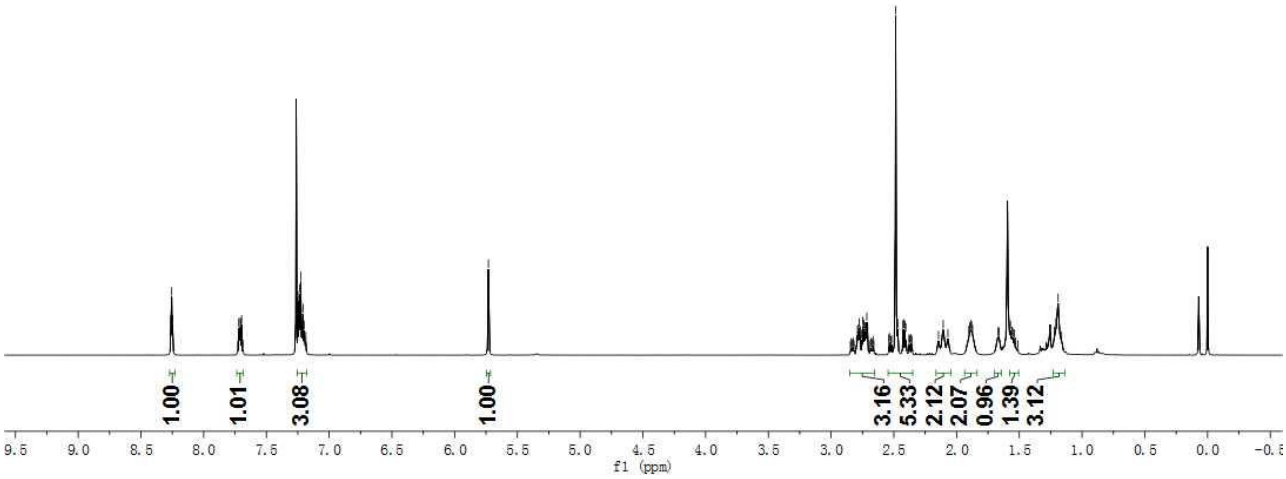
2	35.899	43924032	628778	33.410

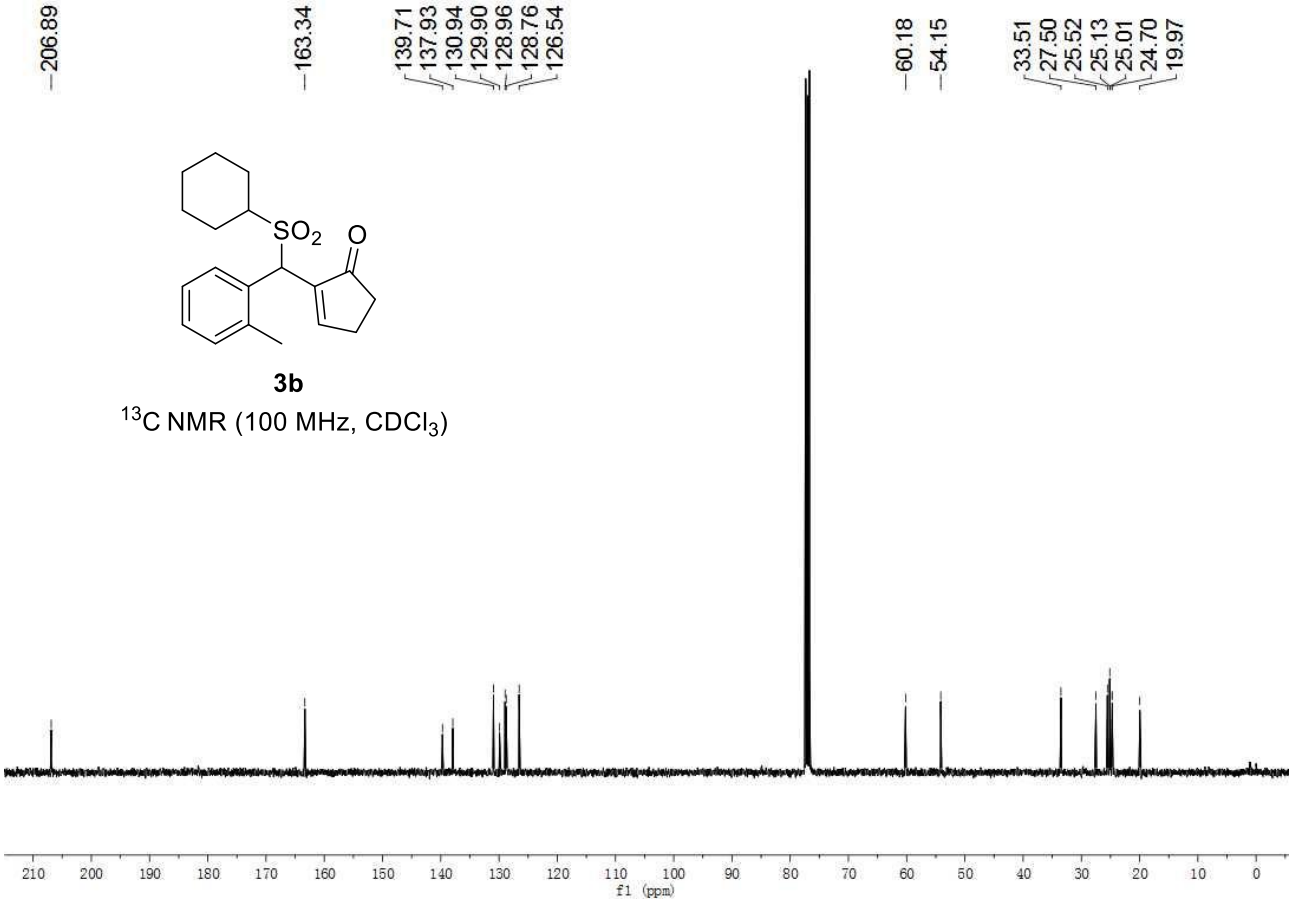




3b

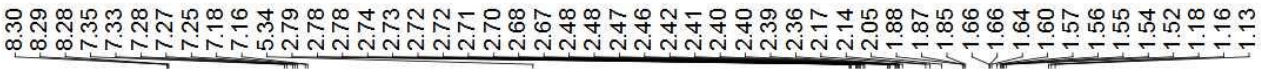
^{1}H NMR (400 MHz, $CDCl_3$)

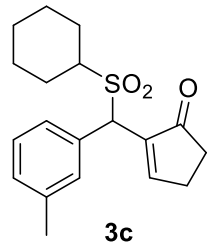




3b

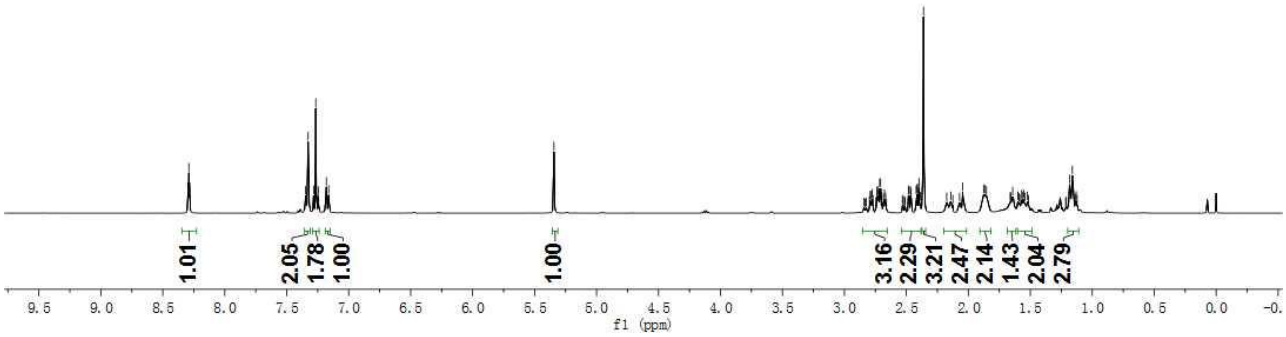
^{13}C NMR (100 MHz, $CDCl_3$)

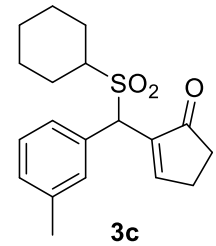




3c

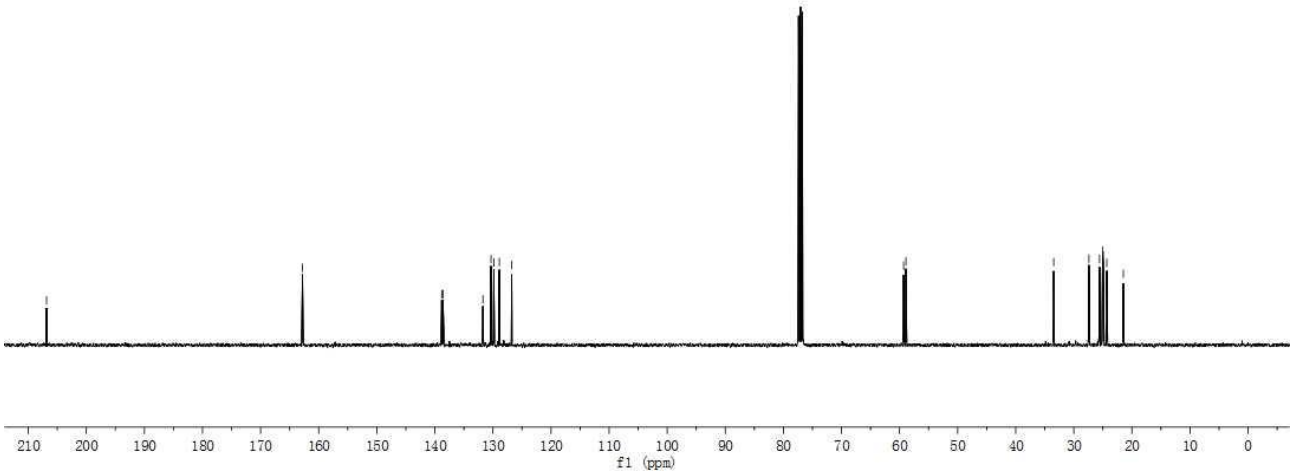
^{1}H NMR (400 MHz, $CDCl_3$)

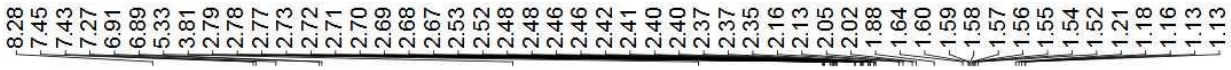


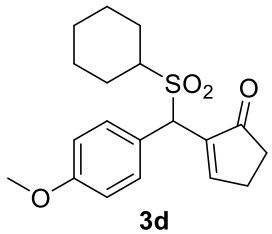


3c

^{13}C NMR (100 MHz, $CDCl_3$)

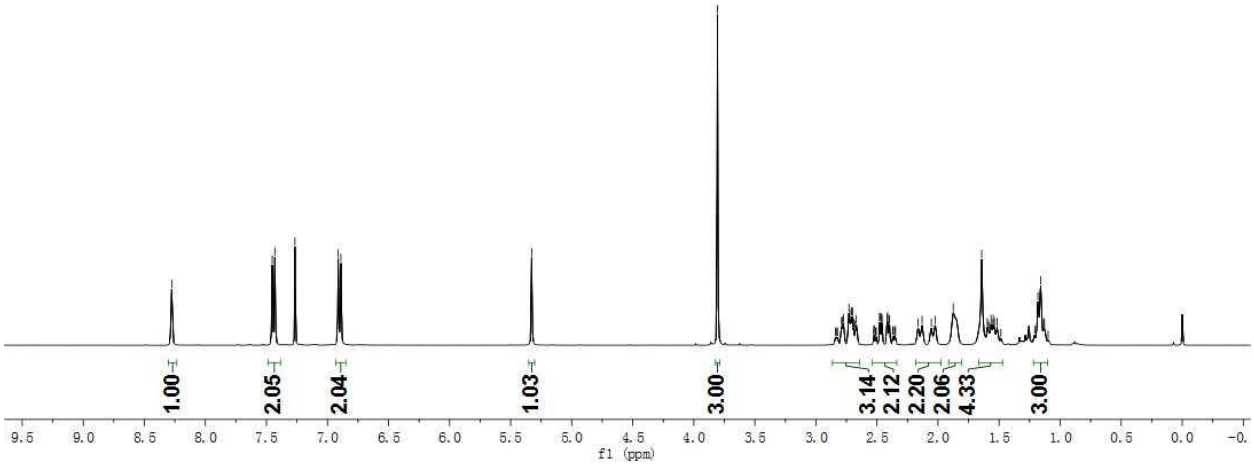


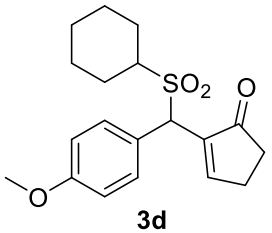




3d

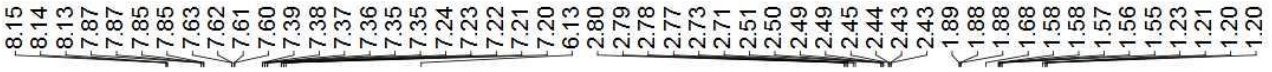
^{1}H NMR (400 MHz, $CDCl_3$)

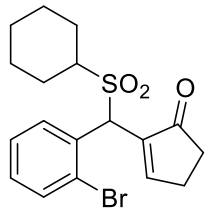




3d

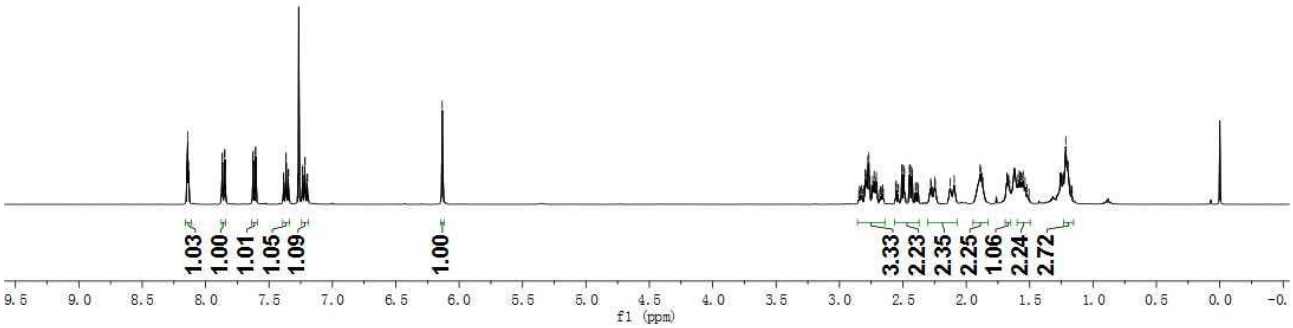
^{13}C NMR (100 MHz, $CDCl_3$)

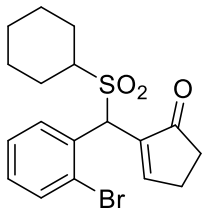




3e

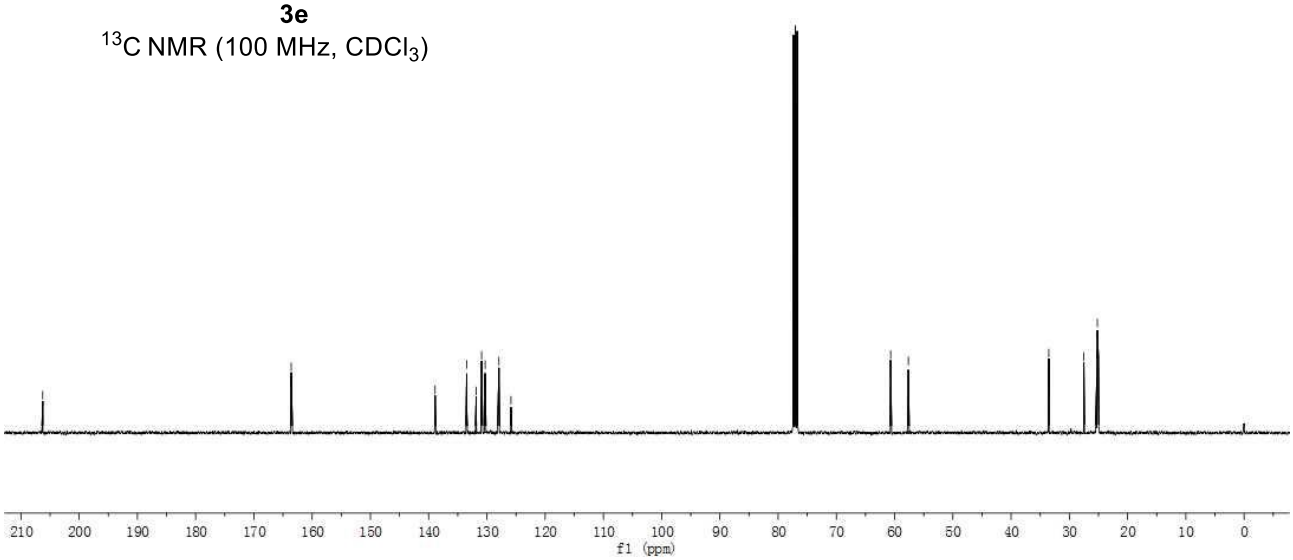
^{1}H NMR (400 MHz, $CDCl_3$)

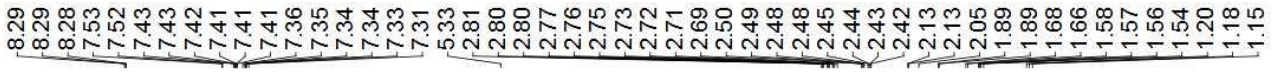


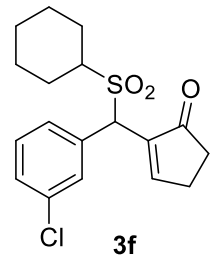


3e

^{13}C NMR (100 MHz, $CDCl_3$)

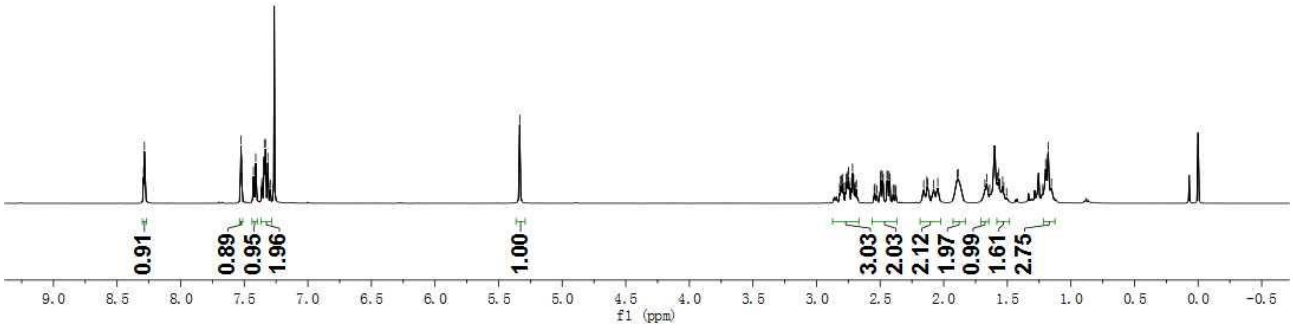


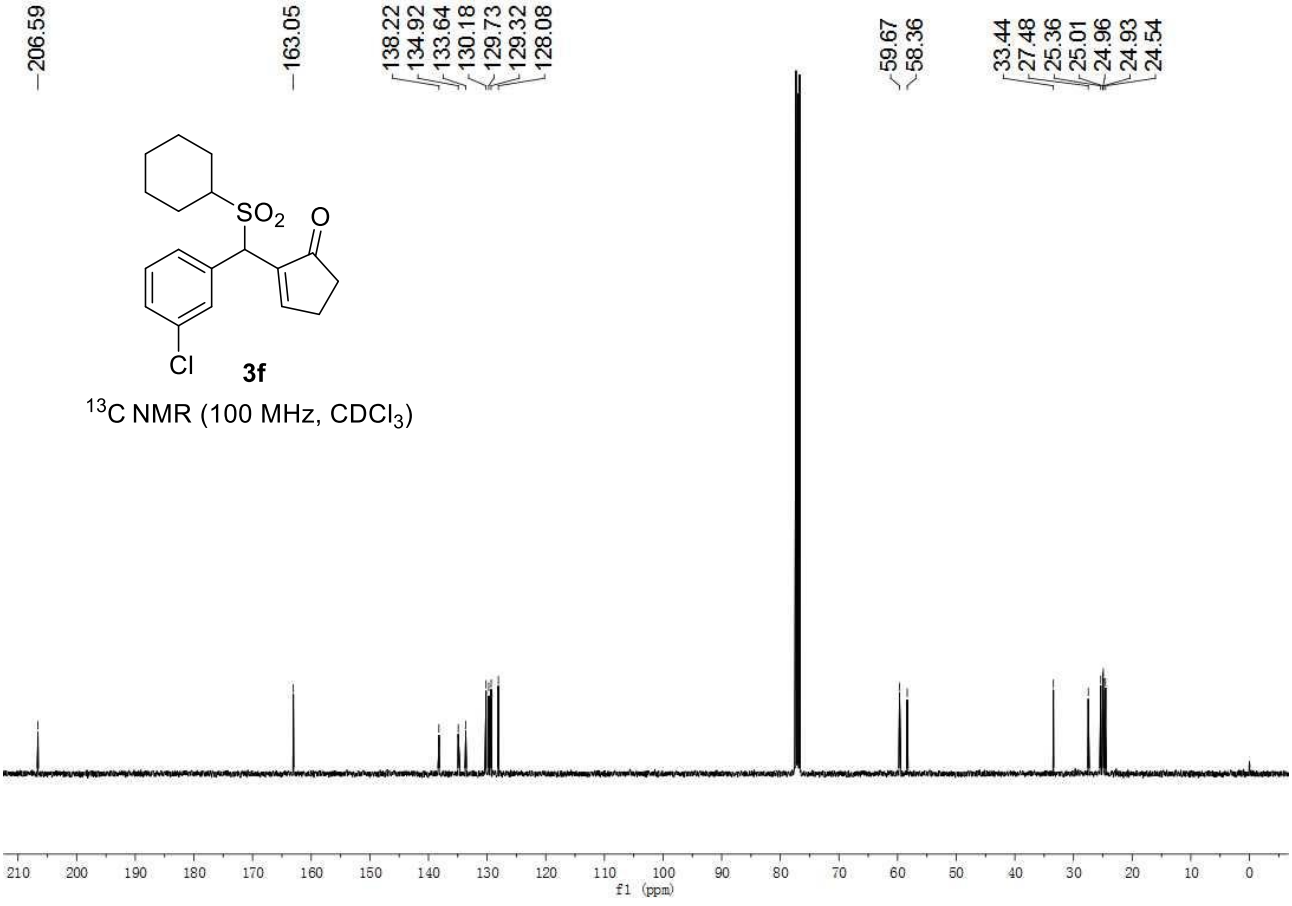




3f

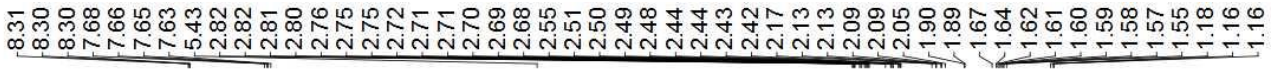
^{1}H NMR (400 MHz, $CDCl_3$)

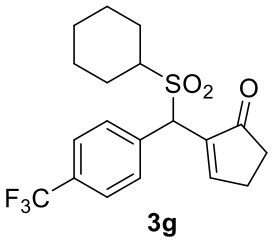




3f

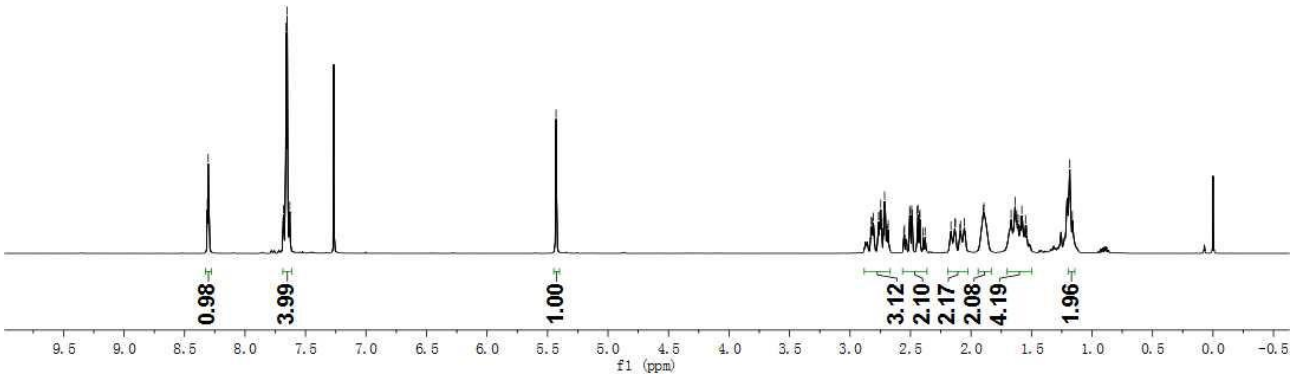
^{13}C NMR (100 MHz, $CDCl_3$)

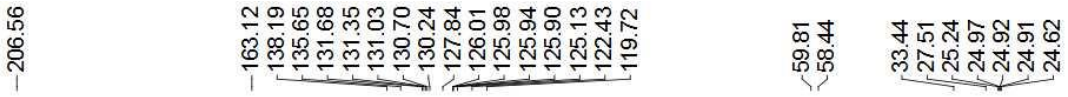


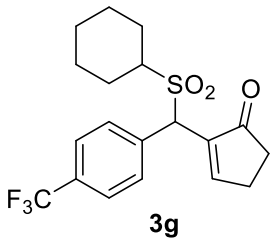


3g

^{1}H NMR (400 MHz, $CDCl_3$)

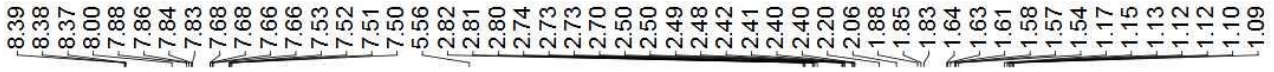


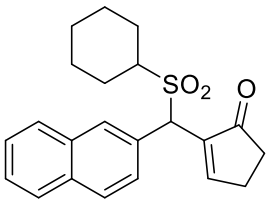




3g

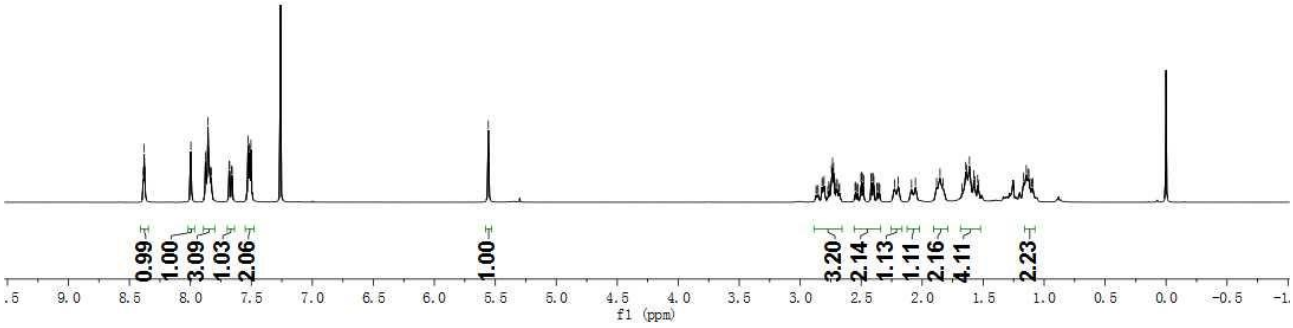
^{13}C NMR (100 MHz, $CDCl_3$)

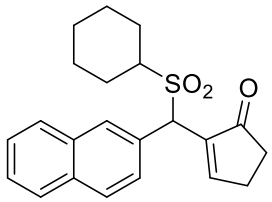




3h

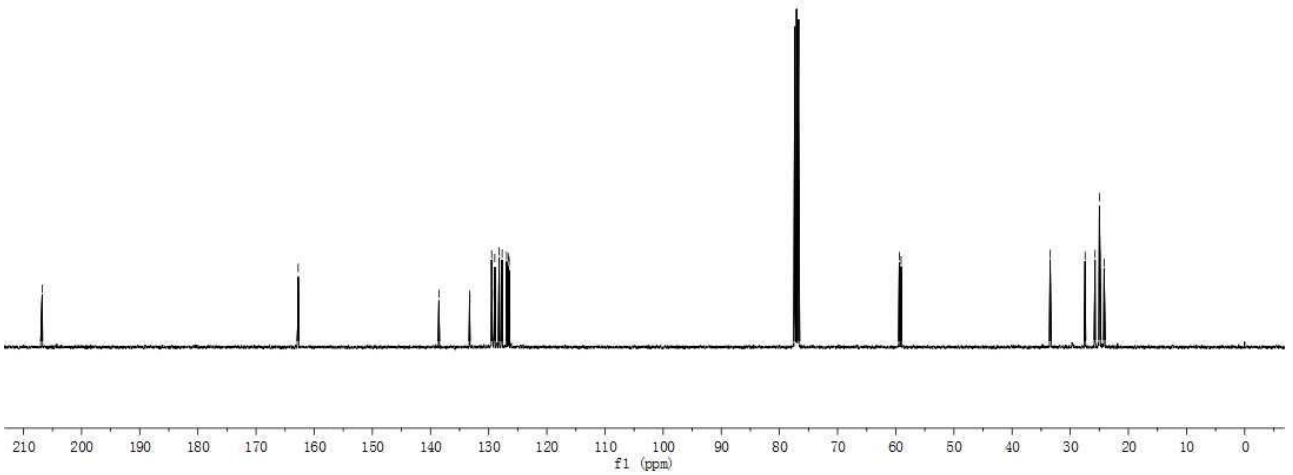
^{1}H NMR (400 MHz, $CDCl_3$)

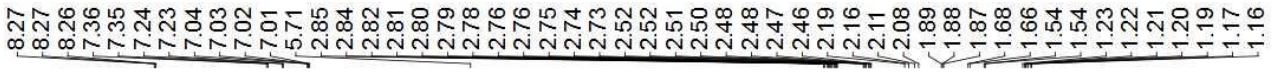


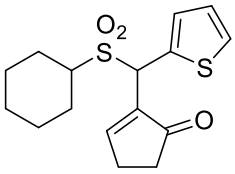


3h

^{13}C NMR (100 MHz, $CDCl_3$)

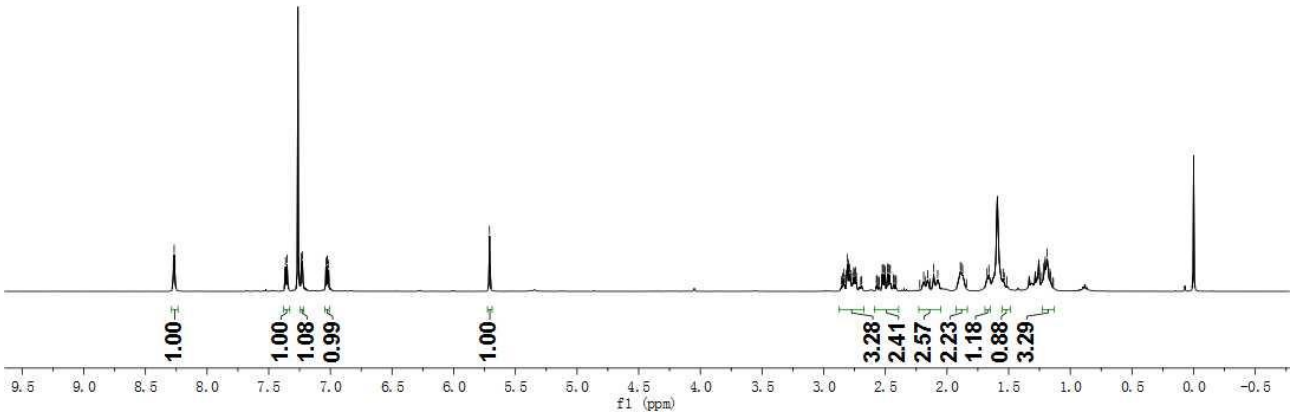


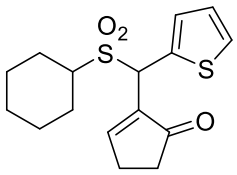




3i

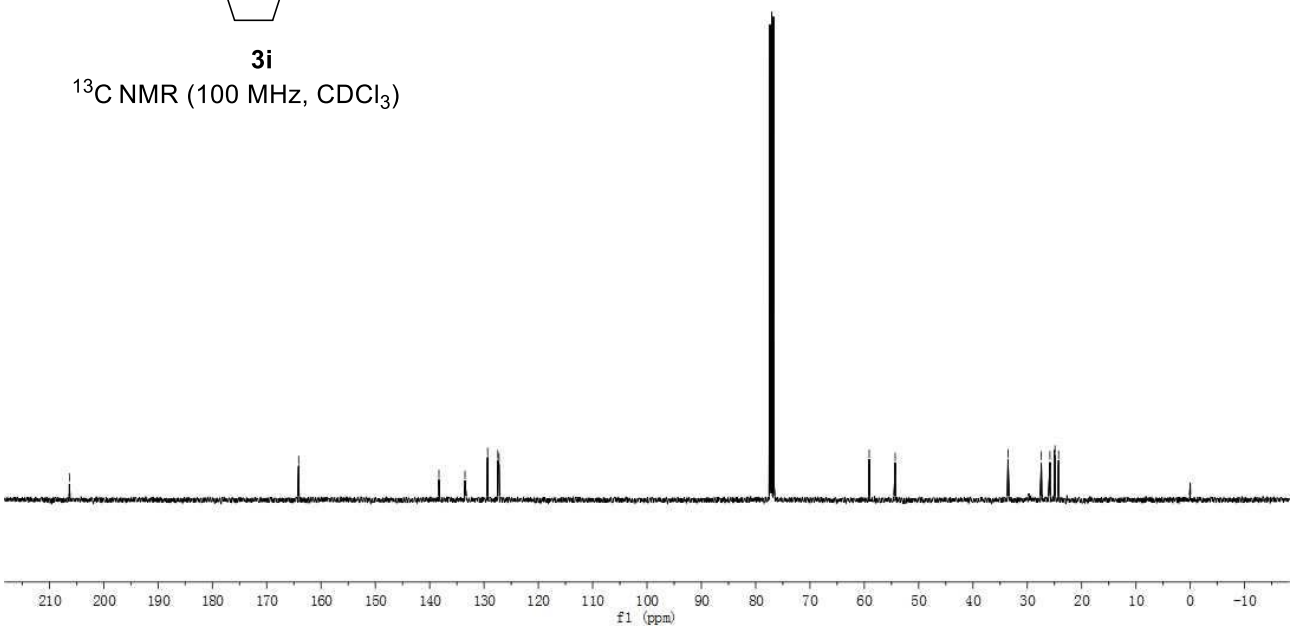
^{1}H NMR (400 MHz, $CDCl_3$)

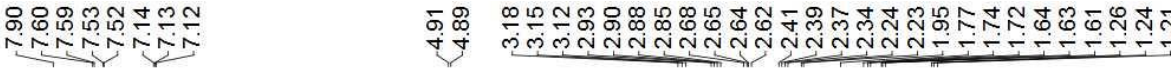


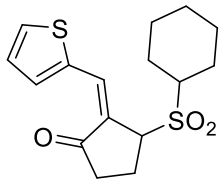


3i

^{13}C NMR (100 MHz, $CDCl_3$)

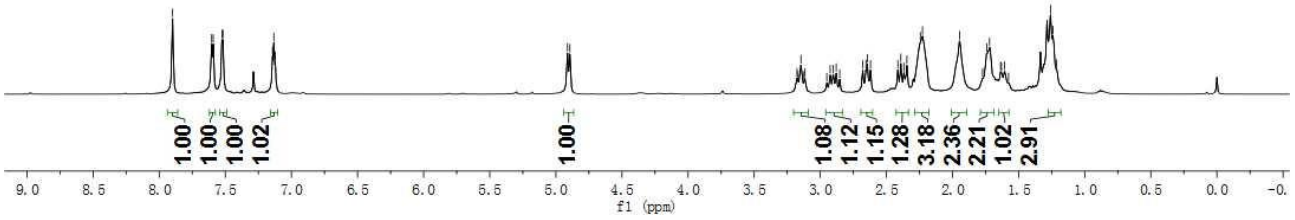


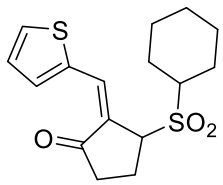




3i'

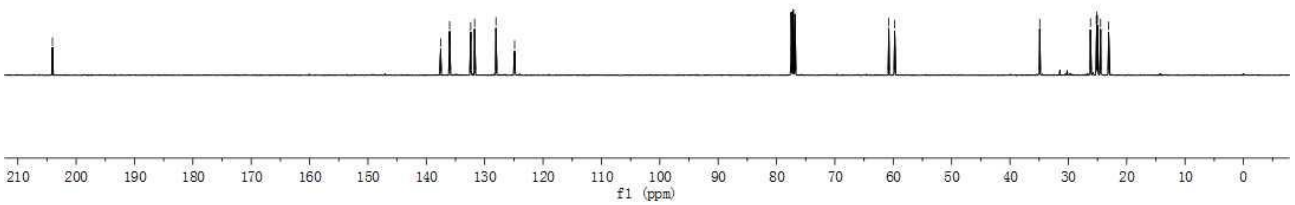
^{1}H NMR (400 MHz, $CDCl_3$)

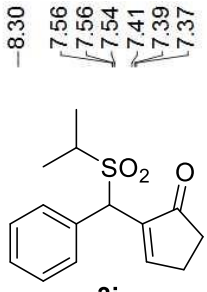




3i'

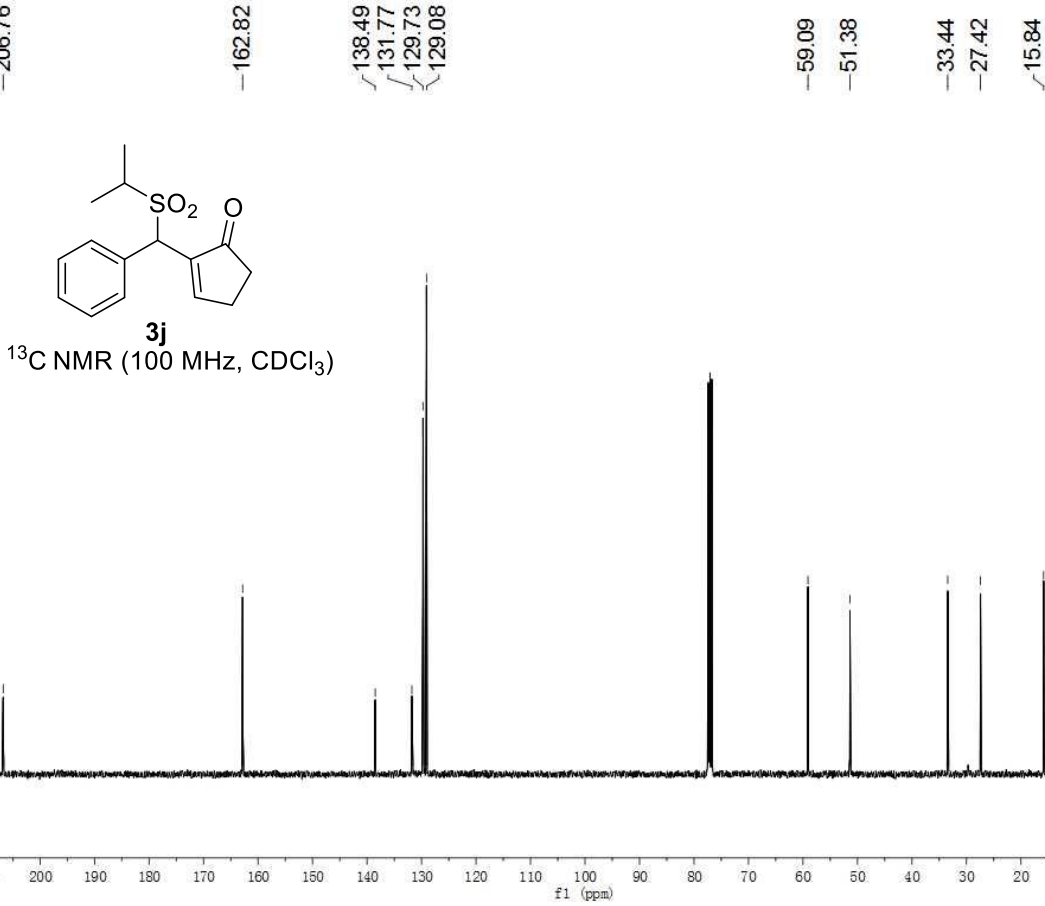
^{13}C NMR (100 MHz, $CDCl_3$)





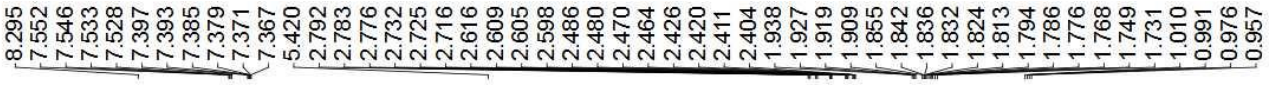
3j

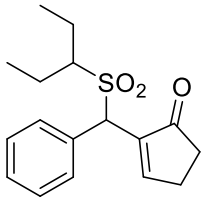
^{1}H NMR (400 MHz, $CDCl_3$)



3j

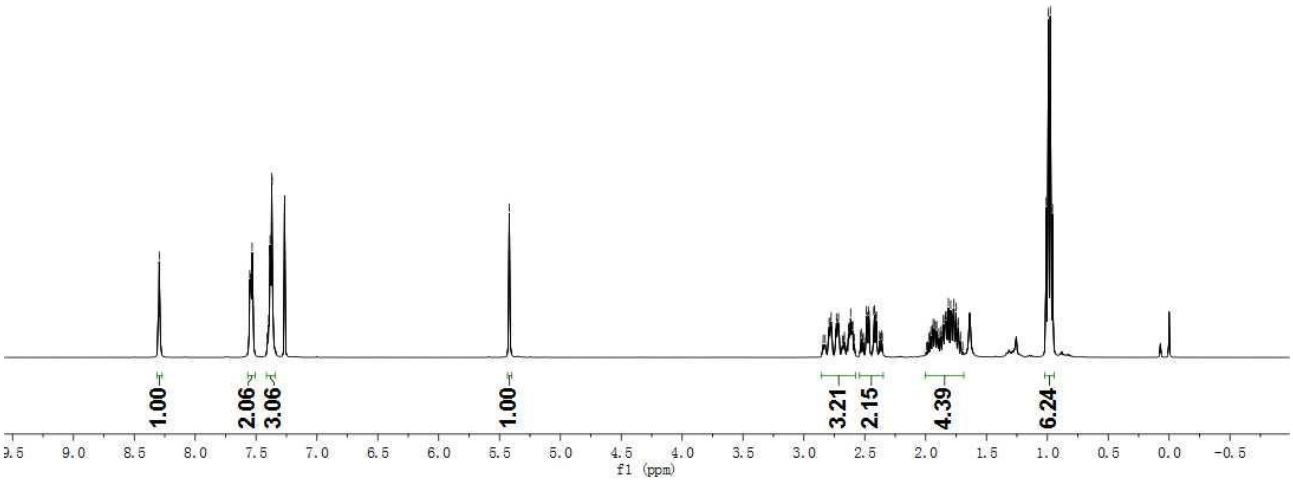
^{13}C NMR (100 MHz, $CDCl_3$)

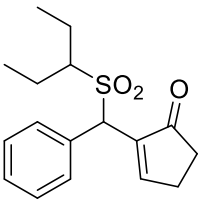




3k

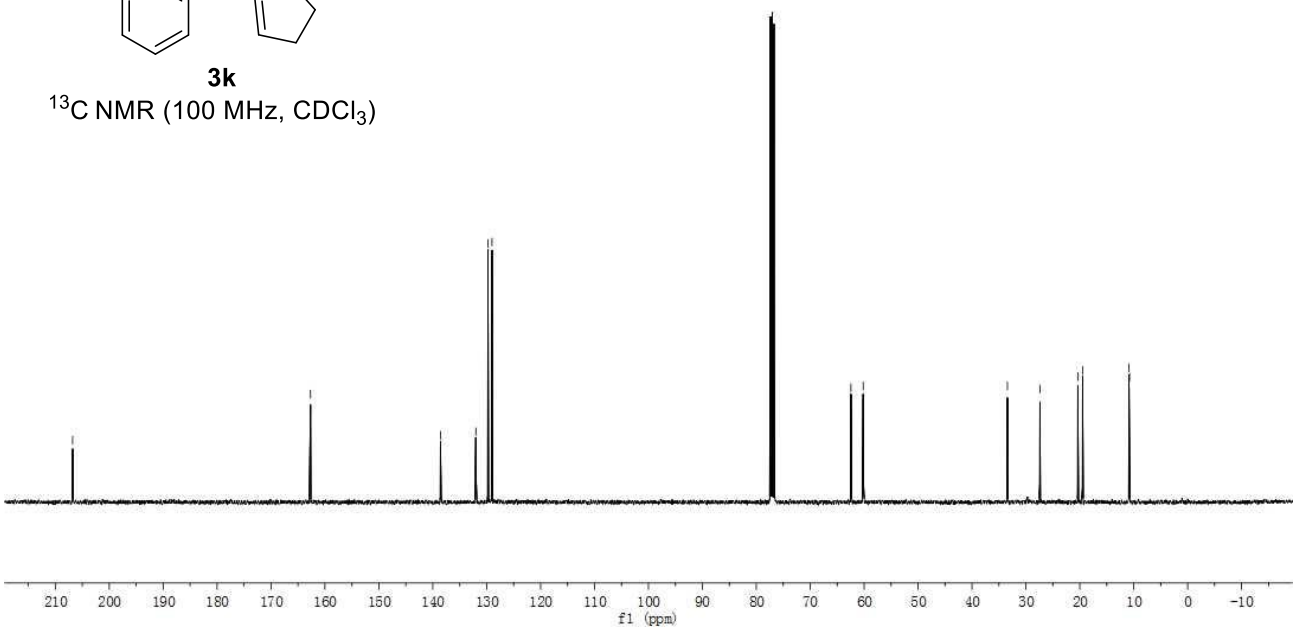
^{1}H NMR (400 MHz, $CDCl_3$)

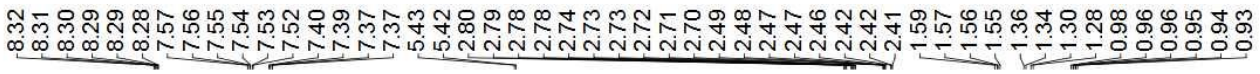


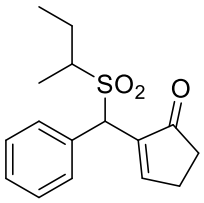


3k

^{13}C NMR (100 MHz, $CDCl_3$)

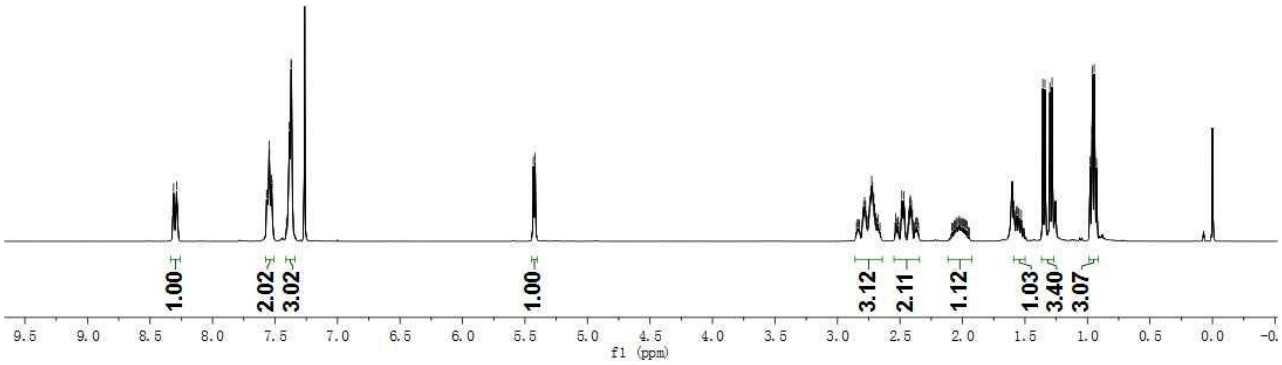


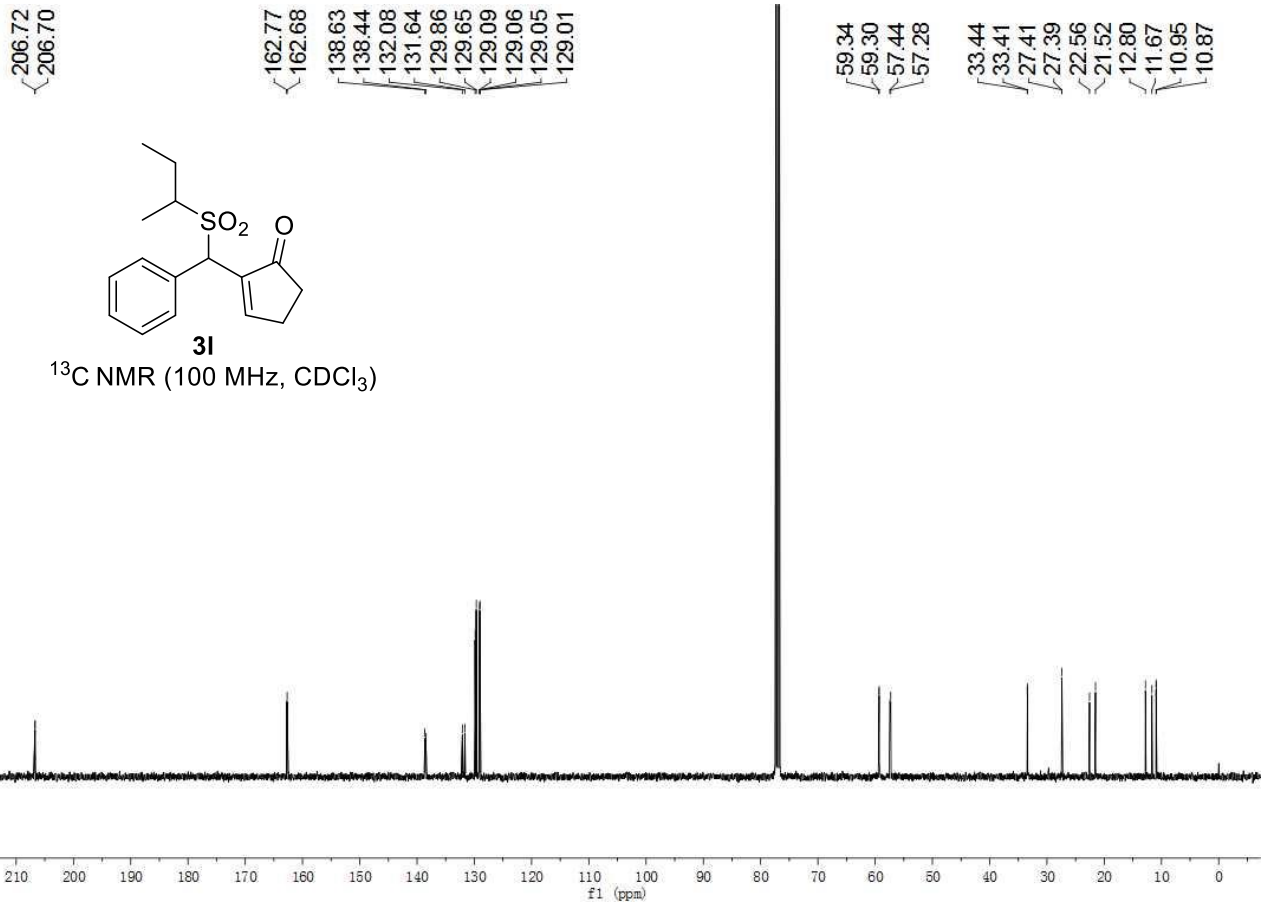




3l

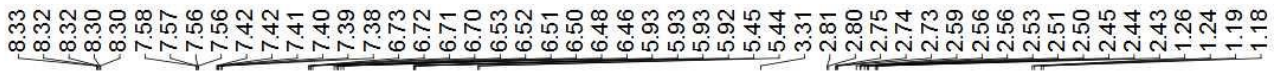
^{1}H NMR (400 MHz, $CDCl_3$)

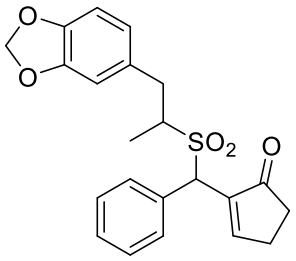




3l

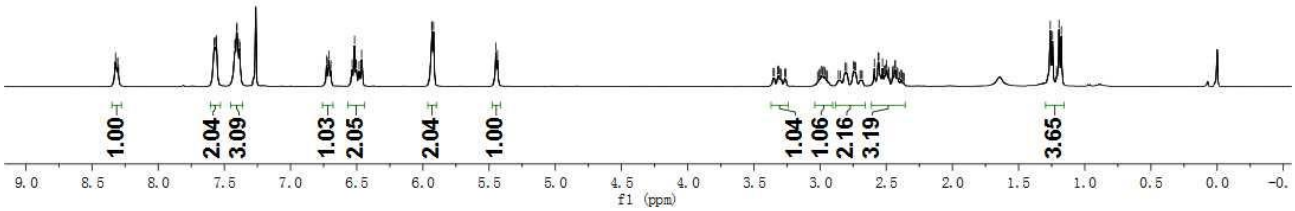
^{13}C NMR (100 MHz, $CDCl_3$)

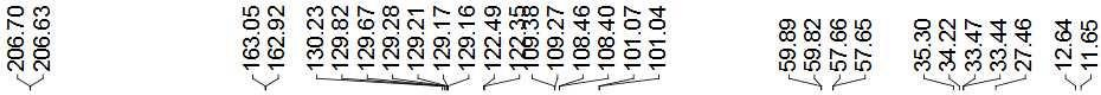


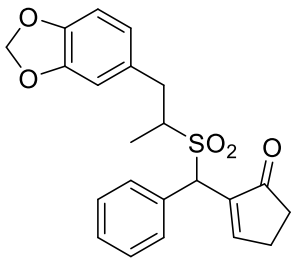


3m

^{1}H NMR (400 MHz, $CDCl_3$)

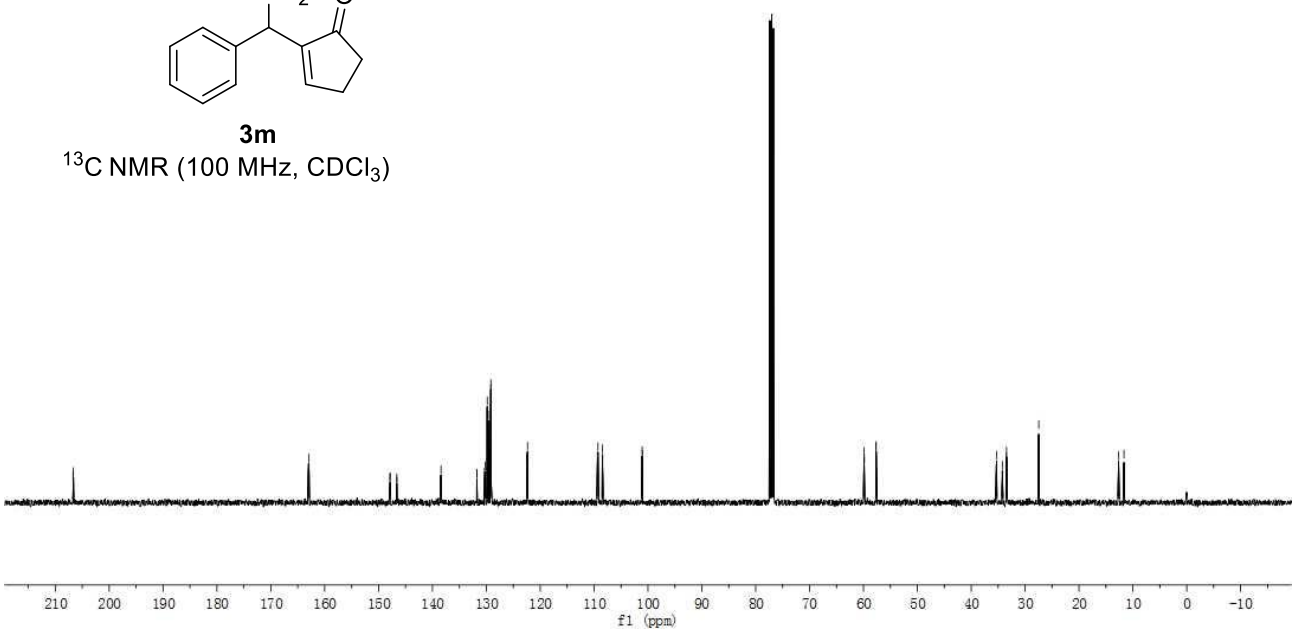


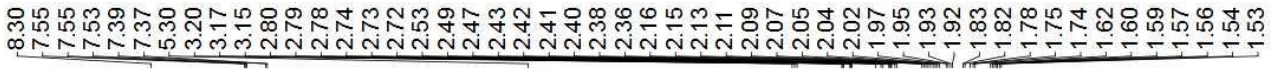


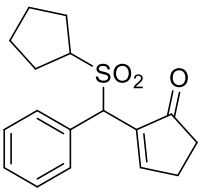


3m

^{13}C NMR (100 MHz, $CDCl_3$)

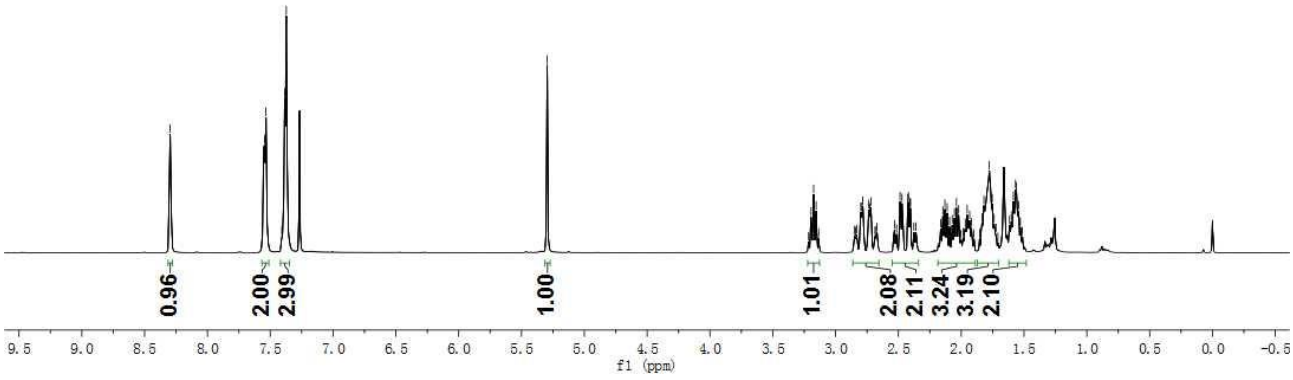


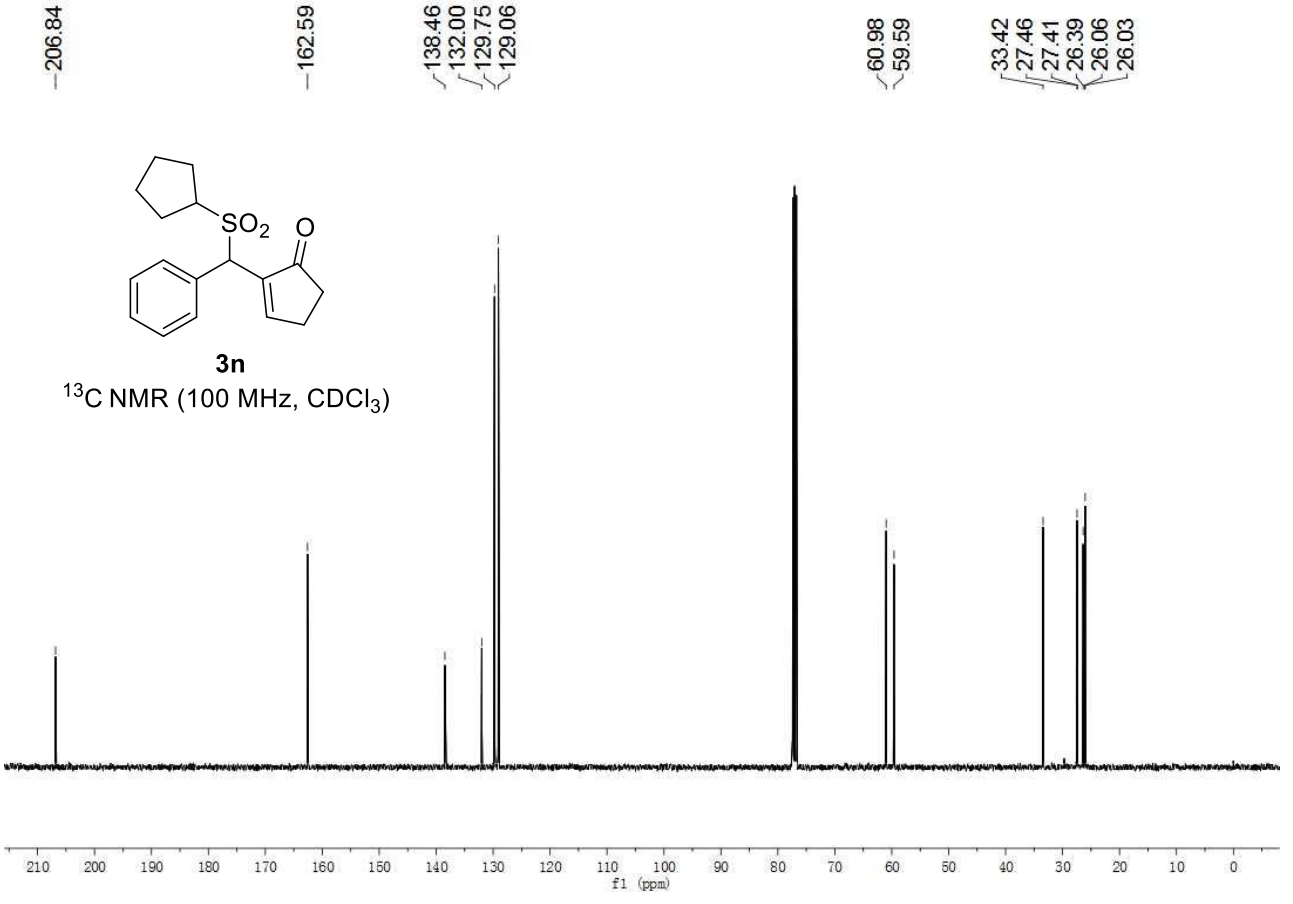




3n

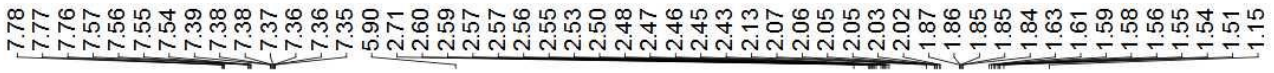
^{1}H NMR (400 MHz, $CDCl_3$)

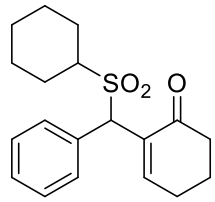




3n

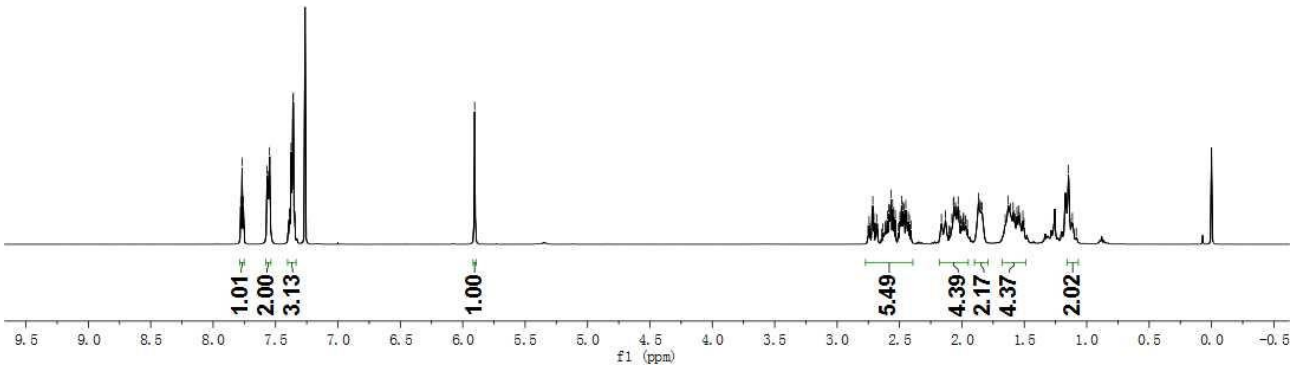
^{13}C NMR (100 MHz, $CDCl_3$)

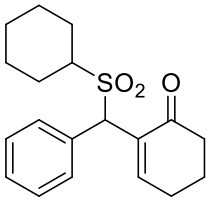




3o

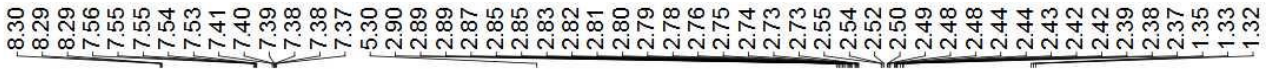
^{1}H NMR (400 MHz, $CDCl_3$)

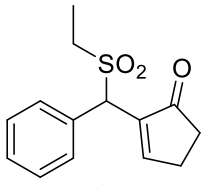




3o

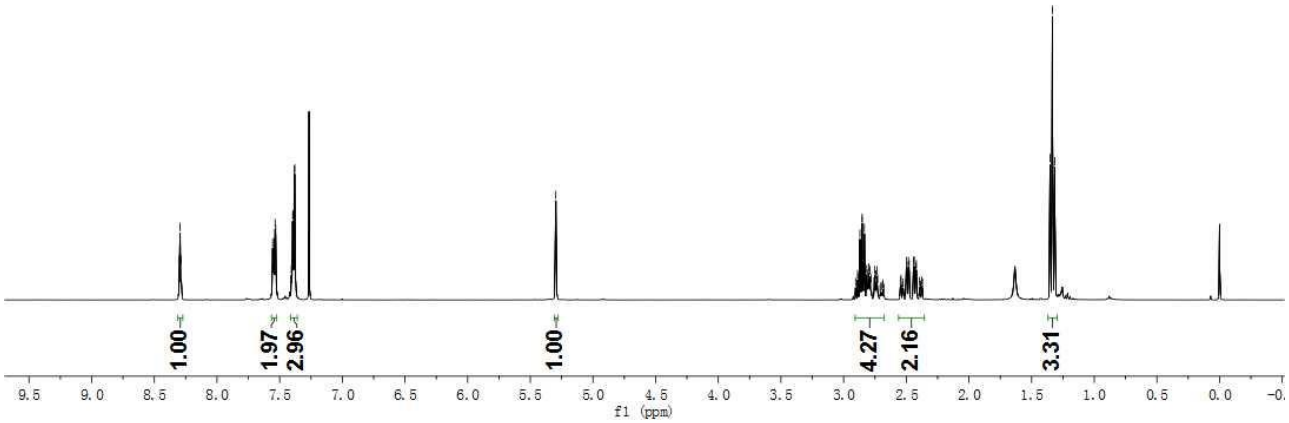
^{13}C NMR (100 MHz, $CDCl_3$)

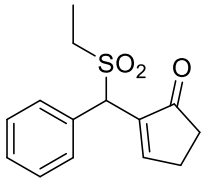




3p

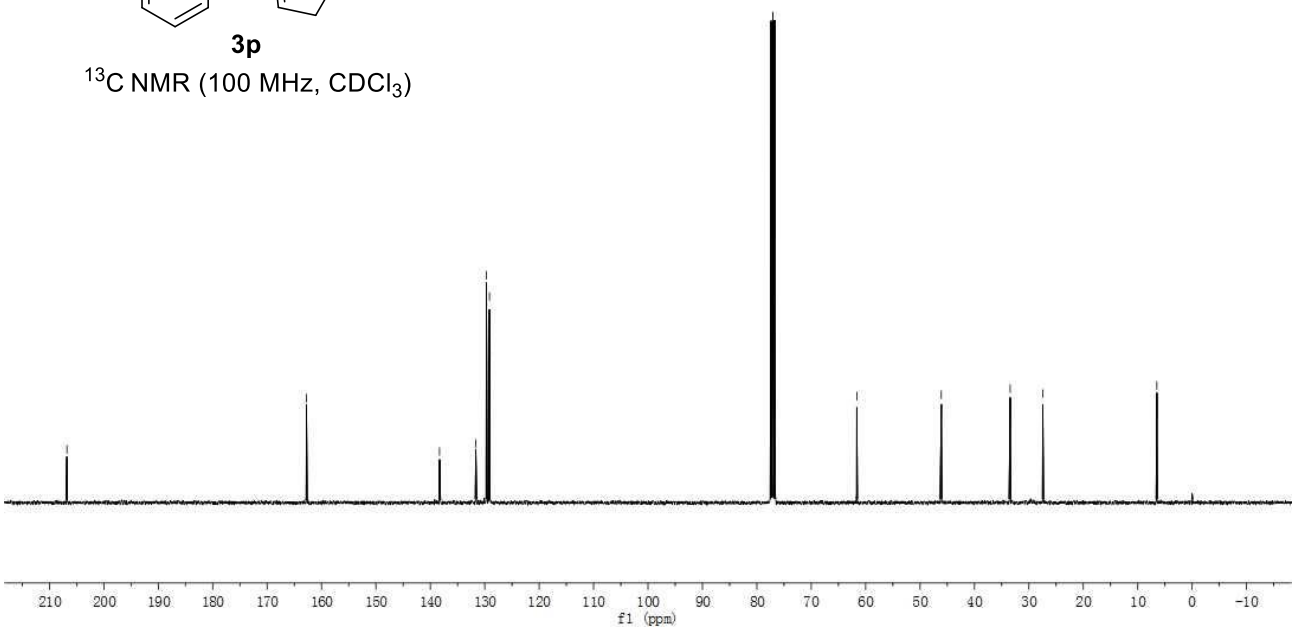
^{1}H NMR (400 MHz, $CDCl_3$)

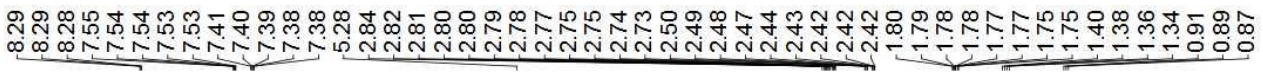


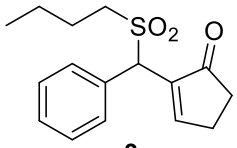


3p

^{13}C NMR (100 MHz, $CDCl_3$)

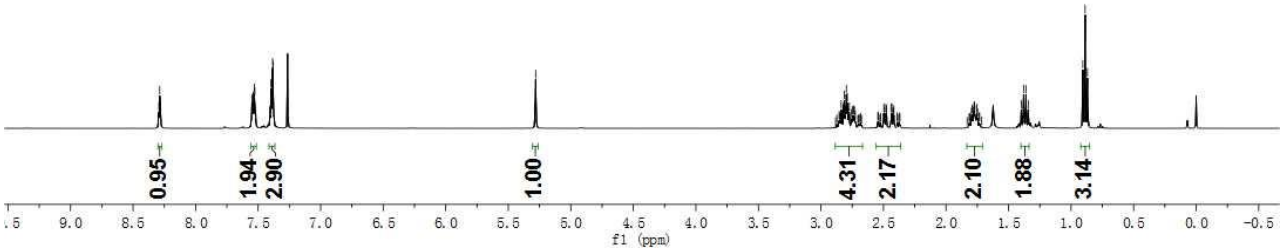


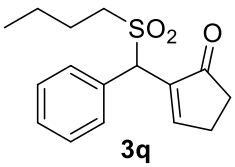




3q

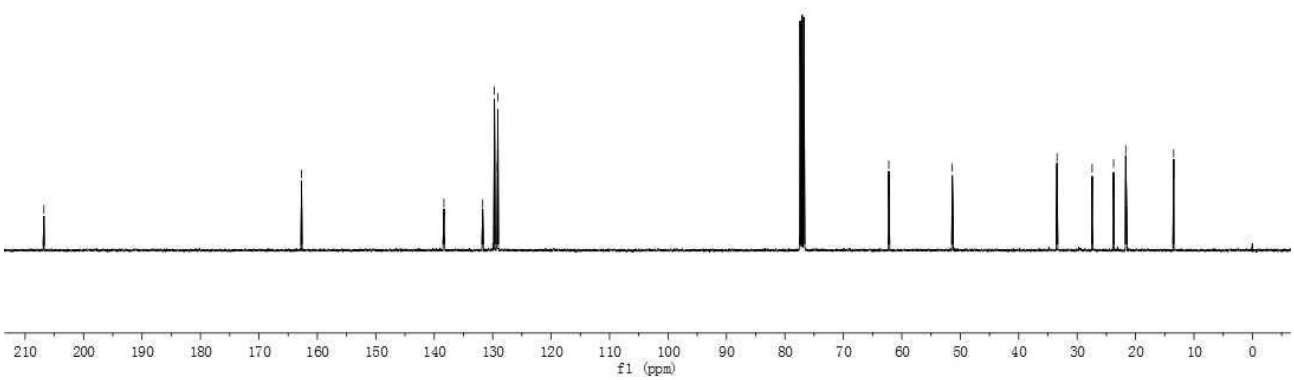
^{1}H NMR (400 MHz, $CDCl_3$)

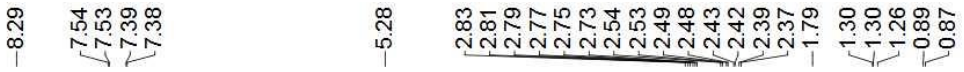


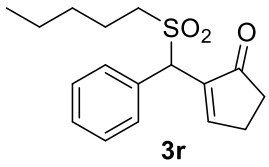


3q

^{13}C NMR (100 MHz, $CDCl_3$)

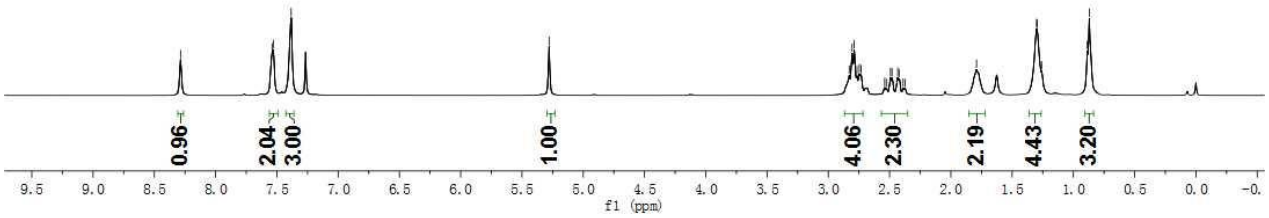


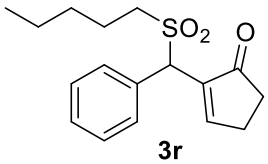




3r

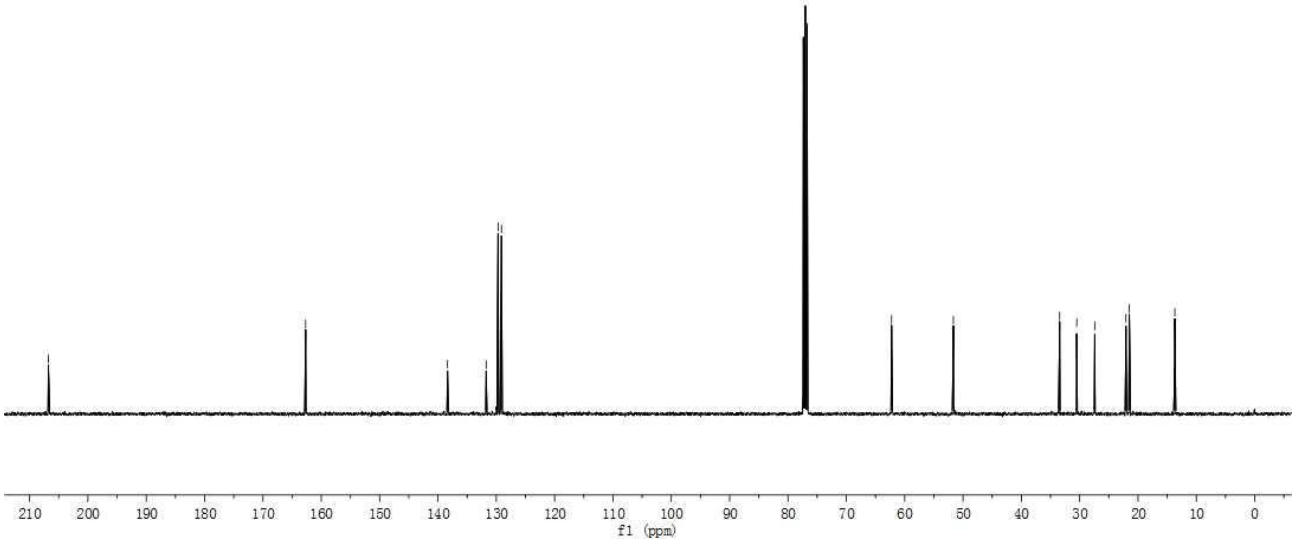
^{1}H NMR (400 MHz, $CDCl_3$)

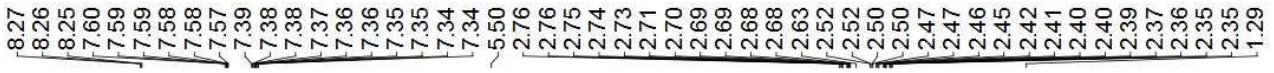


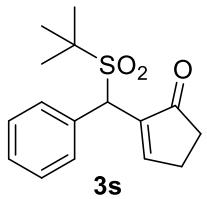


3r

^{13}C NMR (100 MHz, $CDCl_3$)

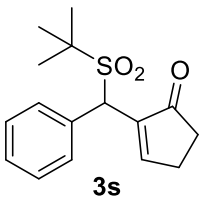






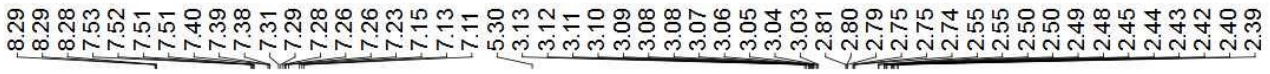
3s

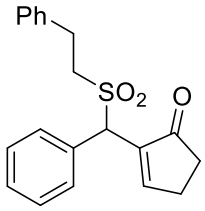
^{1}H NMR (400 MHz, $CDCl_3$)



3s

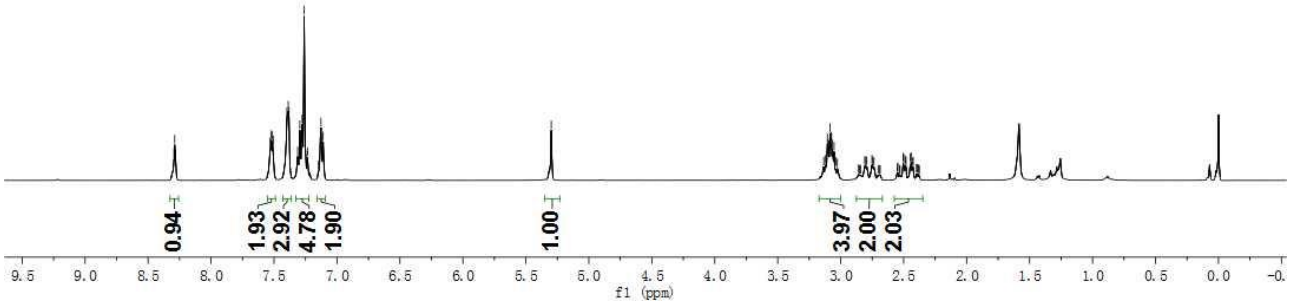
^{13}C NMR (100 MHz, $CDCl_3$)

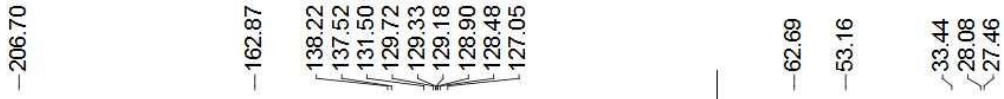


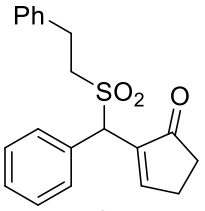


3t

^{1}H NMR (400 MHz, $CDCl_3$)

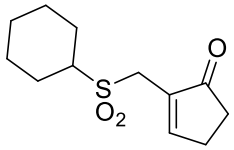






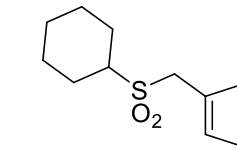
3t

^{13}C NMR (100 MHz, $CDCl_3$)



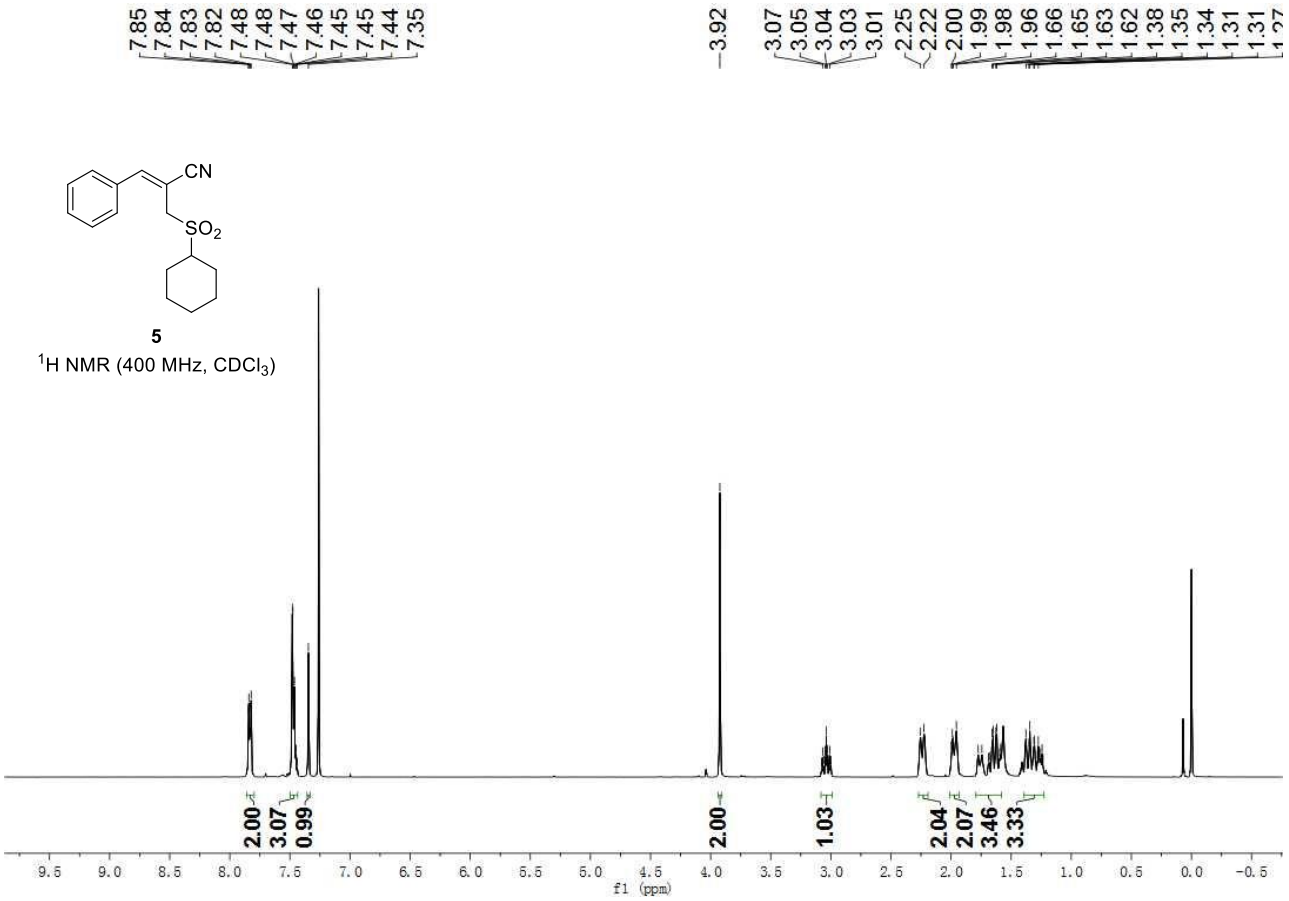
3u

^{1}H NMR (400 MHz, $CDCl_3$)



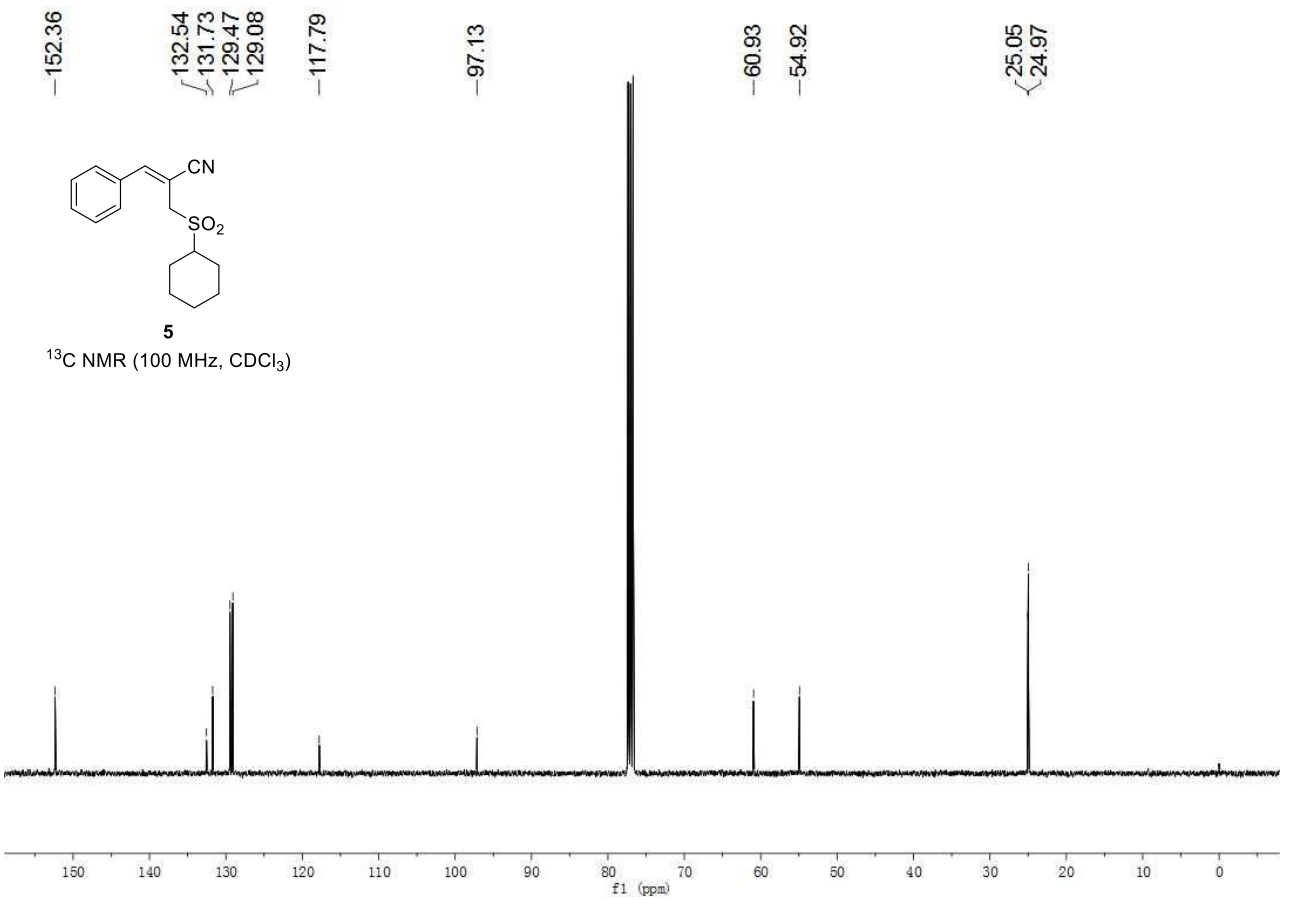
3u

^{13}C NMR (100 MHz, $CDCl_3$)



5

^{1}H NMR (400 MHz, $CDCl_3$)



5

^{13}C NMR (100 MHz, $CDCl_3$)