

Regioselective molybdenum-catalyzed allylic sulfonylation of tertiary allylic electrophiles: methodology development and applications

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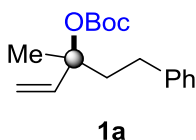
General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Xi'an Jiao Tong University using ESI method. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian Mercuryplus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling. $\text{Mo}(\text{CO})_6$, $(\text{C}_7\text{H}_8)_3\text{Mo}(\text{CO})_3$, $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$, and bipyridyne compounds were purchased from Energy Chemicals and Aladin/Sigma-Aldrich companies and used as received. Tertiary allylic carbonates were synthesized according to the previously reported procedure.¹ Sodium sulfinates were prepared according to a method reported in literature.² All other chemicals were used as received from commercial resources.

Synthesis and Characterization of Tertiary Allylic Carbonates

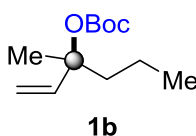
Tertiary allylic carbonates **1** were synthesized according to the previously reported procedures.¹ All characterization data are in accordance with the literature. New substrates have been fully characterized.

tert-butyl (3-methyl-5-phenylpent-1-en-3-yl) carbonate (**1a**)



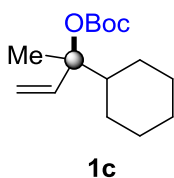
All spectral data matched the published values.^[1c]

tert-butyl (3-methylhex-1-en-3-yl) carbonate (**1b**)



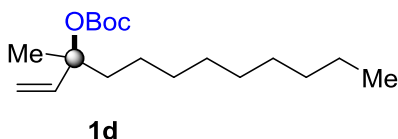
Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.93 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 1.72–1.67 (m, 2H), 1.45 (s, 3H), 1.38 (s, 9H), 0.83 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 140.7, 112.2, 82.5, 80.0, 40.9, 26.7, 22.0, 15.7, 13.1; HRMS (ESI-MS): Calcd. for C₁₂H₂₂O₃ (M + Na): 237.1461, Found: 237.1462.

tert-butyl (2-cyclohexylbut-3-en-2-yl) carbonate (**1c**)



Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.91 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.12 (d, *J* = 11.0 Hz, 1H), 5.05 (d, *J* = 17.6 Hz, 1H), 1.78–1.65 (m, 6H), 1.45 (s, 3H), 1.42–1.12 (m, 14H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 139.6, 111.1, 81.4, 78.9, 39.9, 25.6, 21.0, 14.7, 12.1; HRMS (ESI-MS): Calcd. for C₁₅H₂₆O₃ (M + Na): 277.1774, Found: 277.1773.

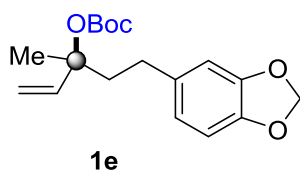
tert-butyl (3-methyldodec-1-en-3-yl) carbonate (**1d**)



Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.00 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.15 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 11.0 Hz, 1H), 1.81–1.77 (m, 2H), 1.52 (s, 3H), 1.46 (9H), 1.33–1.26 (m, 14H), 0.88 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.8, 141.7,

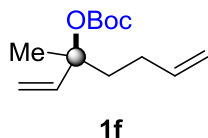
113.2, 83.6, 81.0, 39.7, 31.8, 29.7, 29.4, 29.2, 27.7, 23.4, 23.1, 22.6, 14.0; HRMS (ESI-MS): Calcd. for C₁₈H₃₄O₃ (M + Na): 321.2400, Found: 321.2399.

5-(benzo[d][1,3]dioxol-5-yl)-3-methylpent-1-en-3-yl tert-butyl carbonate (1e)



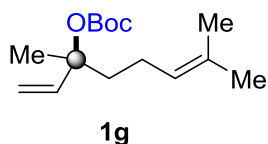
Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.70–6.59 (m, 3H), 6.05 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.88 (s, 2H), 5.21 (d, *J* = 17.8 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 2.57–2.53 (m, 2H), 2.10–2.05 (m, 2H), 1.58 (s, 3H), 1.48 (s, 9); ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 147.4, 145.4, 141.3, 135.5, 120.8, 113.5, 108.6, 107.9, 100.5, 82.9, 81.1, 41.7, 29.6, 27.6, 23.3; HRMS (ESI-MS): Calcd. for C₁₈H₂₄O₅ (M + Na): 343.1516, Found: 343.1508.

5-(benzo[d][1,3]dioxol-5-yl)-3-methylpent-1-en-3-yl tert-butyl carbonate (1f)



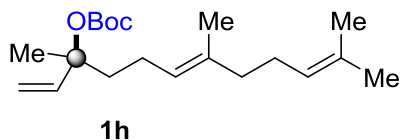
Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.01 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.85–5.75 (m, 1H), 5.20–5.14 (m, 2H), 5.00 (d, *J* = 17.8 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 2.12–2.06 (m, 2H), 1.91–1.87 (m, 2H), 1.55 (s, 3H), 1.47 (s, 9); ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 141.4, 138.0, 114.5, 113.5, 83.1, 81.2, 38.4, 27.8, 27.7, 23.2; HRMS (ESI-MS): Calcd. for C₁₃H₂₂O₃ (M + Na): 249.1461, Found: 249.1460.

tert-butyl (3,7-dimethylocta-1,6-dien-3-yl) carbonate (1g)



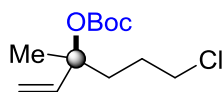
All spectral data matched the published values.^[1d]

tert-butyl (3,7,11-trimethyldodeca-1,6,10-trien-3-yl) carbonate (1h)



All spectral data matched the published values.^[1b]

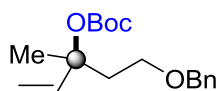
tert-butyl (6-chloro-3-methylhex-1-en-3-yl) carbonate (1i)



1i

Obtained as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.01 (dd, $J = 17.2, 11.3$ Hz, 1H), 5.19 (d, $J = 17.2$ Hz, 1H), 5.17 (d, $J = 11.3$ Hz, 1H), 3.56–3.51 (m, 2H), 1.98–1.92 (m, 2H), 1.87–1.79 (m, 2H), 1.56 (s, 3H), 1.46 (s, 9); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 141.0, 113.7, 82.7, 81.2, 44.7, 37.0, 27.6, 26.8, 23.3; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{21}\text{ClO}_3$ ($M + \text{Na}$): 271.1071, Found: 271.1059.

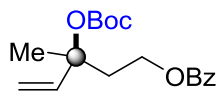
5-(benzyloxy)-3-methylpent-1-en-3-yl tert-butyl carbonate (1j)



1j

Obtained as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.25 (m, 5H), 6.03 (dd, $J = 17.5, 11.0$ Hz, 1H), 5.18 (d, $J = 17.5$ Hz, 1H), 5.15 (d, $J = 11.0$ Hz, 1H), 4.48 (s, 2H), 3.61–3.52 (m, 2H), 2.26–2.14 (m, 2H), 1.57 (s, 3H), 1.44 (s, 9); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 141.3, 138.3, 128.2, 127.5, 127.4, 113.5, 82.3, 81.3, 72.8, 65.9, 38.9, 27.7, 23.9; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_4$ ($M + \text{Na}$): 329.1723, Found: 329.1719.

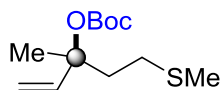
3-((tert-butoxycarbonyloxy)-3-methylpent-4-en-1-yl benzoate (1k)



1k

Obtained as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.05–8.02 (m, 2H), 7.57–7.53 (m, 1), 7.45–7.41 (m, 2H), 6.09 (dd, $J = 17.5, 11.0$ Hz, 1H), 5.25 (d, $J = 17.5$ Hz, 1H), 5.21 (d, $J = 11.0$ Hz, 1H), 4.48–4.38 (m, 2H), 2.33 (t, $J = 6.8$ Hz, 2H), 1.66 (s, 3H), 1.46 (s, 9); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 151.6, 140.8, 132.7, 130.0, 129.4, 128.2, 114.0, 81.8, 81.5, 60.7, 38.2, 27.6, 23.6; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_5$ ($M + \text{Na}$): 343.1515, Found: 343.1516.

tert-butyl (3-methyl-5-(methylthio)pent-1-en-3-yl) carbonate (1l)

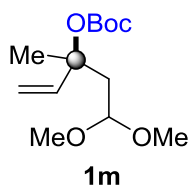


1l

Obtained as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.00 (dd, $J = 17.5, 11.0$ Hz, 1H), 5.20 (d, $J = 17.5$ Hz, 1H), 5.18 (d, $J = 11.0$ Hz, 1H), 2.51–2.47 (m, 2H), 2.14–2.09 (m, 5H), 1.56 (s, 3H), 1.47 (s, 9); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 140.9, 113.9, 82.7, 81.5, 39.5,

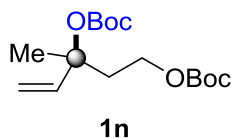
28.1, 27.7, 23.4, 15.4; HRMS (ESI-MS): Calcd. for C₁₂H₂₂O₃S (M + Na): 269.1182, Found: 269.1177.

tert-butyl (5,5-dimethoxy-3-methylpent-1-en-3-yl) carbonate (1m)



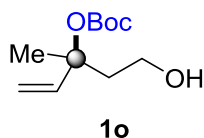
Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.04 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.21 (d, *J* = 17.5 Hz, 1H), 5.15 (d, *J* = 11.0 Hz, 1H), 4.52 (t, *J* = 6.8 Hz, 2H), 3.31 (s, 3H), 3.29 (m, 3H), 2.25–2.16 (m, 2H), 1.57 (s, 3H), 1.47 (s, 9); ¹³C NMR (100 MHz, CDCl₃) δ 151.5, 141.5, 113.3, 101.3, 81.3, 52.5, 52.2, 41.2, 27.6, 24.1; HRMS (ESI-MS): Calcd. for C₁₃H₂₄O₅ (M + Na): 283.1516, Found: 283.1510.

di-tert-butyl (3-methylpent-4-ene-1,3-diyl) bis(carbonate) (1n)



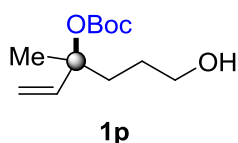
Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.02 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.22 (d, *J* = 17.6 Hz, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 4.21–4.11 (m, 2H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.59 (s, 3H), 1.53 (s, 3H), 1.48 (s, 9H), 1.47 (s, 9); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 151.6, 140.8, 114.1, 81.9, 81.7, 81.6, 62.8, 38.1, 27.8, 27.7, 27.3, 23.7; HRMS (ESI-MS): Calcd. for C₁₆H₂₈O₆ (M + Na): 339.1778, Found: 339.1774.

tert-butyl (5-hydroxy-3-methylpent-1-en-3-yl) carbonate (1o)



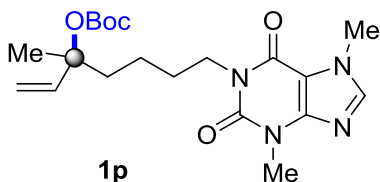
Obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.91 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.26 (d, *J* = 17.6 Hz, 1H), 5.07 (d, *J* = 11.0 Hz, 1H), 4.24–4.14 (m, 2H), 2.49 (brs, 1H), 1.99–1.84 (m, 2H), 1.56 (s, 3H), 1.47 (s, 9); ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 142.1, 112.1, 82.1, 81.9, 63.6, 40.0, 27.6, 23.6; HRMS (ESI-MS): Calcd. for C₁₁H₂₀O₄ (M + Na): 239.1254, Found: 239.1258.

tert-butyl (6-hydroxy-3-methylhex-1-en-3-yl) carbonate (1p)



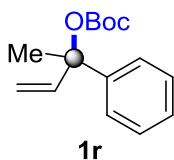
Obtained as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.01 (dd, $J = 17.6, 11.0$ Hz, 1H), 5.16 (d, $J = 17.6$ Hz, 1H), 5.14 (d, $J = 11.0$ Hz, 1H), 3.91–3.80 (m, 2H), 3.64 (brs, 1H), 1.92–1.78 (m, 4H), 1.54 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.8, 141.4, 113.6, 83.3, 81.2, 67.3, 41.5, 27.7, 26.0, 23.2; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_4$ ($\text{M} + \text{Na}$): 253.1410, Found: 253.1408.

tert-butyl(7-(3,7-dimethyl-2,6-dioxo-2,3,4,5,6,7-hexahydro-1H-purin-1-yl)-3-methylhept-1-en-3-yl) carbonate (1q)



Obtained as an orange solid; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (s, 1H), 6.01 (dd, $J = 11.0, 17.6$ Hz, 1H), 5.17 (d, $J = 11.0$ Hz, 1H), 5.14 (d, $J = 17.6$ Hz, 1H), 4.01–3.97 (m, 5H), 3.57 (s, 3H), 1.86–1.81 (m, 2H), 1.68–1.60 (m, 2H), 1.54 (s, 3H), 1.46 (s, 9H), 1.26 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.2, 151.8, 151.4, 148.7, 141.5, 141.3, 113.5, 107.6, 83.5, 81.3, 60.3, 41.1, 39.7, 33.5, 29.6, 27.8, 23.0, 21.0; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_4\text{O}_5$ ($\text{M} + \text{Na}$): 429.2108, Found: 429.2106.

tert-butyl (2-phenylbut-3-en-2-yl) carbonate (1r)



All spectral data matched the published values.^[1a]

Details for the Optimization Conditions

Table S1. Evaluation of ligand for the regioselective Mo-catalyzed sulfonylation of allylic carbonate **1a** with sodium sulfinate **2a**^a

Reaction scheme: **1a** (allylic carbonate) reacts with **2a** (sodium sulfinate) in the presence of $\text{Mo}(\text{CO})_6$ (10 mol%) and a ligand (15 mol%) in EtOH at 60 °C for 24 h to yield **3aa** (allylic sulfonate) and **4aa** (terminal sulfonate).

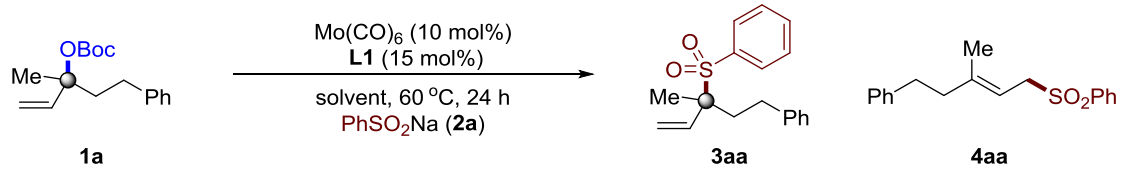
Chemical structures of ligands L1 through L7:

- L1**: 1,10-phenanthroline
- L2**: 2,9-dimethyl-1,10-phenanthroline
- L3**: 2,9-dicarboxylic acid-1,10-phenanthroline
- L4**: 2,9-dimethyl-4,7-dimethoxy-1,10-phenanthroline
- L5**: 1,10-phenanthroline
- L6**: 1,10-phenanthroline
- L7**: 1,10-phenanthroline

entry	ligand	3aa/4aa ^b	Yield (%) ^c
1	L1	99:1	92
2	L2	99:1	87
3	L3	99:1	35
4	L4	99:1	52
5	L5	25:1	16
6	L6	--	0
7	L7	--	< 10

^a Reaction conditions: $\text{Mo}(\text{CO})_6$ (10 mol%), mmol), ligand (15 mol%), **1a** (0.2 mmol), PhSO_2Na **2a** (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. ^b Determined by ¹H-NMR of the crude reaction mixture. ^c Isolated yields.

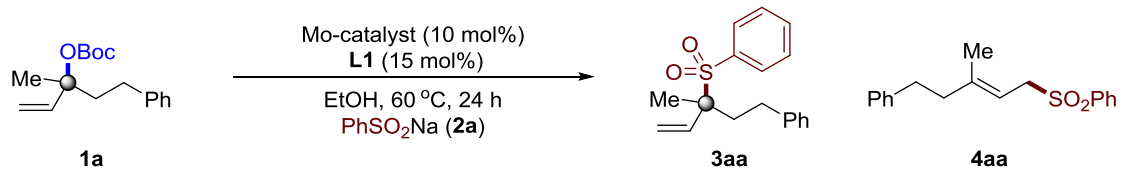
Table S2. Evaluation of solvent for the regioselective Mo-catalyzed sulfonylation of allylic carbonate **1a** with sodium sulfinate **2a**^a



entry	solvent	3aa/4aa ^b	Yield (%) ^c
1	CH ₃ CN	--	10
2	THF	--	< 5
3	DCE	25:1	35
4	1,4-dioxane	--	0
5	toluene	--	< 5
6	DCM	--	< 10
7	<i>i</i> PrOH	99:1	77
8	THF/EtOH (5:1)	25:1	25
9	DCE/EtOH (5:1)	25:1	63

^a Reaction conditions: Mo(CO)₆ (10 mol%), mmol), ligand (**L1**) (15 mol%), **1a** (0.2 mmol), PhSO₂Na **2a** (0.3 mmol), solvent (1.0 mL, 0.2 M), 60 °C, 24 hours. ^b Determined by ¹H-NMR of the crude reaction mixture. ^c Isolated yields.

Table S3. Evaluation of molybdenum-catalyst for Mo-catalyzed sulfonylation of allylic carbonate **1a** with sodium sulfinate **2a**^a



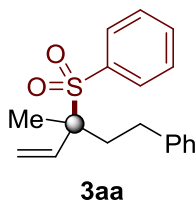
entry	Mo-catalyst	3aa/4aa ^b	Yield (%) ^c
1	Without molybdenum catalyst	--	--
2	Without ligand	--	--
3	(C ₇ H ₈) ₃ Mo(CO) ₃	99:1	82
4	(CH ₃ CN) ₃ Mo(CO) ₃	99:1	86

^a Reaction conditions: Mo-catalyst (10 mol%), mmol), ligand (**L1**) (15 mol%), **1a** (0.2 mmol), PhSO₂Na **2a** (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. ^b Determined by ¹H-NMR of the crude reaction mixture. ^c Isolated yields.

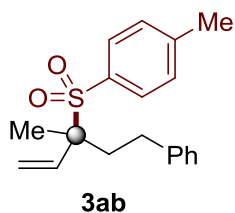
General procedure for the allylic sulfonylation of α,α -disubstituted allylic carbonate **1a** with sodium sulfinates **2**

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Mo}(\text{CO})_6$ (5.3 mg, 10 mol%), 2,2'-bipyridyne ligand (**L1**) (4.7 mg, 15 mol%), allylic carbonate **1a** (55.28 mg, 0.2 mmol), and sodium benzenesulfinate **2a** (49.25 mg, 0.3 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 1 mL) was added via syringe. The resulting mixture was stirred at 60 °C for 24 hours. The reaction mixture was cooled to room temperature and the residue was purified by flash column chromatography on silica gel to afford the pure tertiary allylic sulfone **3aa**.

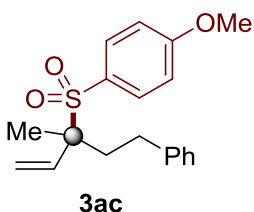
Scale-up Experiment: In a 100 mL round-bottom flask equipped with a magnetic stir bar, $\text{Mo}(\text{CO})_6$ (132.0 mg, 10 mol%), 2,2'-bipyridyne ligand (**L1**) (117.1 mg, 15 mol%), allylic carbonate **1g** (1.38 g, 5.0 mmol), and sodium benzenesulfinate **2a** (1.23 g, 7.5 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 25 mL) was added via syringe. The resulting mixture was stirred at 60 °C for 24 hours. The reaction mixture was cooled to room temperature and then quenched with water (10 mL). The organic portion was extracted with CH_2Cl_2 and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The obtained residue was purified by flash column chromatography on silica gel to afford the pure sulfone **3aa** in 87% isolated yield.



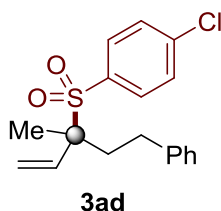
(3-methyl-3-(phenylsulfonyl)pent-4-en-1-yl)benzene (**3aa**) was prepared according to the general procedure from **1a** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 92% yield (55.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.81 (m, 2H), 7.64–7.61 (m, 1H), 7.53–7.49 (m, 2H), 7.30–7.26 (m, 2H), 7.21–7.14 (m, 3H), 6.00 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.43 (d, $J = 10.7$ Hz, 1H), 5.13 (d, $J = 17.4$ Hz, 1H), 2.60–2.48 (m, 2H), 2.25–2.21 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 135.2, 135.1, 133.6, 130.8, 128.5, 128.4, 128.3, 126.2, 120.6, 68.2, 34.7, 30.1, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 323.1082, Found: 323.1081.



1-methyl-4-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ab) was prepared according to the general procedure from **1a** and **2b**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 93% yield (58.4 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.69–7.67 (m, 2H), 7.30–7.26 (m, 4H), 7.21–7.14 (m, 3H), 5.99 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.42 (d, $J = 10.8$ Hz, 1H), 5.13 (d, $J = 17.5$ Hz, 1H), 2.59–2.49 (m, 2H), 2.43 (s, 3H), 2.24–2.19 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 141.1, 135.2, 132.2, 130.7, 129.0, 128.5, 128.3, 126.1, 120.7, 68.1, 34.7, 30.2, 21.6, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 337.1238, Found: 337.1232.

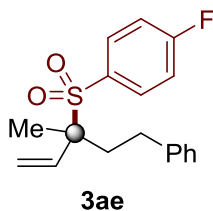


1-methoxy-4-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ac) was prepared according to the general procedure from **1a** and **2c**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 90% yield (59.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.74–7.72 (m, 2H), 7.30–7.26 (m, 2H), 7.21–7.14 (m, 3H), 6.97–6.95 (m, 2H), 5.99 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.42 (d, $J = 10.8$ Hz, 1H), 5.14 (d, $J = 17.5$ Hz, 1H), 3.87 (s, 3H), 2.61–2.47 (m, 2H), 2.23–2.17 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 141.1, 135.3, 132.8, 128.5, 128.3, 126.7, 126.1, 120.6, 113.6, 68.2, 55.6, 34.8, 30.2, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 353.1187, Found: 353.1188.

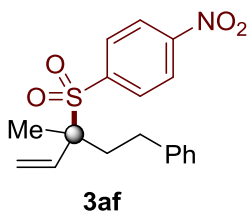


1-chloro-4-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ad) was prepared according to the general procedure from **1a** and **2d**. The crude product was purified by flash col-

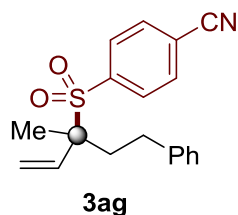
column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 87% yield (58.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.76–7.72 (m, 2H), 7.50–7.46 (m, 2H), 7.31–7.26 (m, 2H), 7.22–7.15 (m, 3H), 5.99 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.44 (d, $J = 10.8$ Hz, 1H), 5.14 (d, $J = 17.5$ Hz, 1H), 2.63–2.48 (m, 2H), 2.24–2.20 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.9, 140.4, 134.9, 133.7, 132.1, 128.8, 128.5, 128.3, 126.2, 121.2, 68.4, 34.6, 30.1, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{19}\text{ClO}_2\text{S}$ ($\text{M} + \text{Na}$): 357.0692, Found: 357.0686.



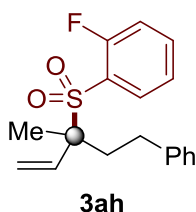
1-fluoro-4-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ae) was prepared according to the general procedure from **1a** and **2e**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 85% yield (54.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.84–7.80 (m, 2H), 7.30–7.26 (m, 2H), 7.22–7.14 (m, 5H), 6.00 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 1H), 5.13 (d, $J = 17.5$ Hz, 1H), 2.63–2.48 (m, 2H), 2.25–2.20 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 165.0, 140.9, 135.1, 133.5, 131.2, 131.1, 128.5, 128.3, 126.2, 121.0, 115.8, 115.7, 68.3, 34.6, 30.1, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{19}\text{FO}_2\text{S}$ ($\text{M} + \text{Na}$): 341.0982, Found: 341.0987.



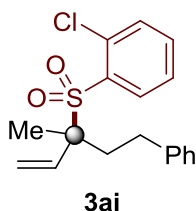
1-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)-4-nitrobenzene (3af) was prepared according to the general procedure from **1a** and **2f**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 75% yield (51.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.36–8.34 (m, 2H), 8.02–8.01 (m, 2H), 7.31–7.28 (m, 2H), 7.23–7.15 (m, 3H), 6.02 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.47 (d, $J = 10.8$ Hz, 1H), 5.14 (d, $J = 17.5$ Hz, 1H), 2.63–2.52 (m, 2H), 2.27–2.24 (m, 2H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 141.0, 140.6, 134.6, 132.2, 128.6, 128.3, 126.4, 123.5, 121.7, 68.9, 34.4, 30.0, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{S}$ ($\text{M} + \text{Na}$): 368.0927, Found: 368.0925.



4-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzonitrile (3ag) was prepared according to the general procedure from **1a** and **2g**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 72% yield (46.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.94–7.93 (m, 2H), 7.82–7.81 (m, 2H), 7.30–7.28 (m, 2H), 7.23–7.15 (m, 3H), 6.00 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.46 (d, $J = 10.8$ Hz, 1H), 5.14 (d, $J = 17.5$ Hz, 1H), 2.62–2.51 (m, 2H), 2.25–2.22 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 139.5, 134.7, 132.1, 131.4, 128.6, 128.3, 126.4, 121.6, 117.4, 117.2, 68.8, 34.6, 30.0, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$ ($\text{M} + \text{Na}$): 348.1034, Found: 348.1023.

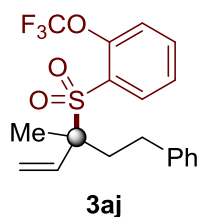


1-fluoro-2-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ah) was prepared according to the general procedure from **1a** and **2h**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 88% yield (56.0 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.77 (m, 1H), 7.64–7.59 (m, 1H), 7.30–7.25 (m, 3H), 7.21–7.15 (m, 4H), 6.07 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 1H), 5.15 (d, $J = 17.5$ Hz, 1H), 2.65–2.51 (m, 2H), 2.34–2.20 (m, 2H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.5, 159.0, 140.8, 136.3, 134.6, 133.8, 128.4, 128.2, 126.1, 124.1, 122.9, 122.8, 120.9, 117.4, 117.2, 69.4, 34.2, 30.0, 16.0; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{19}\text{FO}_2\text{S}$ ($\text{M} + \text{Na}$): 341.0980, Found: 341.0982.

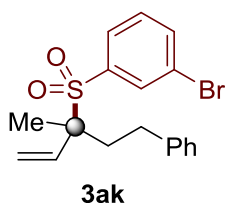


1-chloro-2-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ai) was prepared according to the general procedure from **1a** and **2i**. The crude product was purified by flash col-

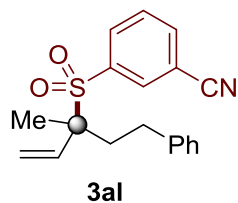
column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 87% yield (58.3 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.96–7.94 (m, 1H), 7.54–7.47 (m, 2H), 7.41–7.37 (m, 1H), 7.30–7.25 (m, 2H), 7.21–7.15 (m, 3H), 6.09 (dd, J = 10.8, 17.5 Hz, 1H), 5.43 (d, J = 10.8 Hz, 1H), 5.15 (d, J = 17.5 Hz, 1H), 2.64–2.50 (m, 2H), 2.36–2.24 (m, 2H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 135.2, 134.9, 134.8, 134.6, 133.0, 132.5, 128.4, 128.2, 126.6, 126.1, 121.0, 70.5, 34.5, 29.9, 16.3; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{19}\text{ClO}_2\text{S}$ ($M + \text{Na}$): 357.0686, Found: 357.0693.



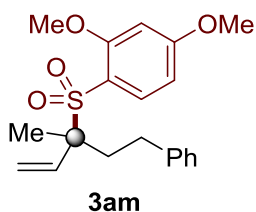
1-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)-2-(trifluoromethoxy)benzene (3aj) was prepared according to the general procedure from **1a** and **2j**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 72% yield (55.4 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.95–7.92 (m, 1H), 7.68–7.64 (m, 1H), 7.42–7.37 (m, 2H), 7.30–7.25 (m, 2H), 7.21–7.15 (m, 3H), 6.07 (dd, J = 10.8, 17.5 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H), 5.12 (d, J = 17.5 Hz, 1H), 2.64–2.51 (m, 2H), 2.34–2.20 (m, 2H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 147.8, 141.0, 135.7, 134.9, 134.9, 128.6, 128.4, 127.6, 126.3, 126.2, 120.8, 120.7, 120.6, 70.0, 34.4, 30.1, 16.2; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{O}_3\text{S}$ ($M + \text{Na}$): 407.0899, Found: 407.0903.



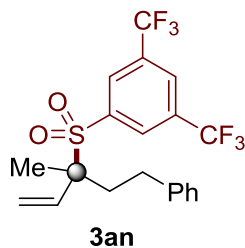
1-bromo-3-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ak) was prepared according to the general procedure from **1a** and **2k**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 82% yield (62.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.96–7.95 (m, 1H), 7.76–7.63 (m, 2H), 7.41–7.37 (m, 1H), 7.31–7.26 (m, 2H), 7.23–7.15 (m, 3H), 6.01 (dd, J = 10.8, 17.5 Hz, 1H), 5.46 (d, J = 10.8 Hz, 1H), 5.15 (d, J = 17.5 Hz, 1H), 2.64–2.50 (m, 2H), 2.28–2.19 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 137.0, 136.7, 134.9, 133.4, 129.9, 129.3, 128.5, 128.3, 126.3, 122.5, 121.2, 68.6, 34.5, 30.1, 16.5; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{19}\text{BrO}_2\text{S}$ ($M + \text{Na}$): 401.0181, Found: 401.0190.



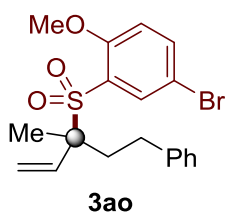
3-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzonitrile (3al) was prepared according to the general procedure from **1a** and **2l**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 78% yield (50.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.09 (m, 1H), 8.04–8.02 (m, 1H), 7.91–7.88 (m, 1H), 7.66 (t, $J = 7.8$ Hz, 1H), 7.31–7.26 (m, 2H), 7.23–7.15 (m, 3H), 6.01 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.47 (d, $J = 10.8$ Hz, 1H), 5.12 (d, $J = 17.5$ Hz, 1H), 2.64–2.50 (m, 2H), 2.28–2.21 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 137.0, 136.8, 134.7, 134.6, 134.2, 129.5, 128.6, 128.3, 126.4, 121.6, 117.1, 113.2, 68.8, 34.4, 30.1, 16.5; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$ ($\text{M} + \text{Na}$): 348.1029, Found: 348.1025.



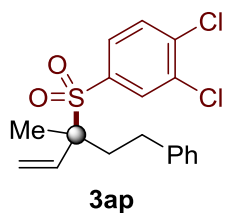
2,4-dimethoxy-1-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3am) was prepared according to the general procedure from **1a** and **2m**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 94% yield (67.7 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 1.4, 5.6$ Hz, 1H), 7.29–7.27 (m, 2H), 7.24 (d, $J = 1.4$ Hz, 1H), 7.21–7.18 (m, 1H), 7.16–7.15 (m, 2H), 6.94 (d, $J = 5.6$ Hz, 1H), 6.01 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 1H), 5.15 (d, $J = 17.5$ Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 2.61–2.50 (m, 2H), 2.26–2.18 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 148.4, 141.1, 135.4, 128.5, 128.3, 126.8, 126.1, 124.9, 120.6, 113.0, 110.0, 68.3, 56.2, 56.1, 34.8, 30.2, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{S}$ ($\text{M} + \text{Na}$): 383.1288, Found: 383.1297.



1-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)-3,5-bis(trifluoromethyl)benzene (3an) was prepared according to the general procedure from **1a** and **2n**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 95% yield (82.8 mg); ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 2H), 8.13 (s, 1H), 7.31–7.28 (m, 2H), 7.23–7.20 (m, 1H), 7.18–7.16 (m, 2H), 6.07 (dd, *J* = 10.8, 17.5 Hz, 1H), 5.47 (d, *J* = 10.8 Hz, 1H), 5.18 (d, *J* = 17.5 Hz, 1H), 2.67–2.55 (m, 2H), 2.34–2.26 (m, 2H), 1.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.4, 137.9, 134.8, 132.6, 132.3, 132.1, 131.9, 131.0, 130.9, 128.6, 128.2, 127.2, 126.4, 123.3, 121.7, 121.5, 67.0, 34.0, 30.0, 16.5; HRMS (ESI-MS): Calcd. for C₂₀H₁₈F₆O₂S (M + Na): 459.0824, Found: 459.0836.

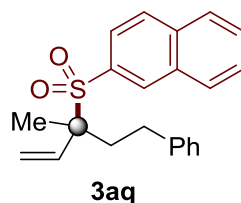


4-bromo-1-methoxy-2-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ao) was prepared according to the general procedure from **1a** and **2o**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 84% yield (68.8 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 1.7 Hz, 1H), 7.65 (dd, *J* = 1.7, 5.8 Hz, 1H), 7.33–7.27 (m, 3H), 7.21–7.15 (m, 3H), 6.06 (dd, *J* = 10.8, 17.5 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 17.5 Hz, 1H), 3.83 (s, 3H), 2.63–2.55 (m, 2H), 2.31–2.21 (m, 2H), 1.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 141.1, 138.3, 136.9, 136.5, 135.5, 128.5, 128.3, 126.1, 123.7, 121.1, 119.7, 70.1, 56.1, 34.7, 30.1, 16.4; HRMS (ESI-MS): Calcd. for C₁₉H₂₁BrO₃S (M + Na): 431.0287, Found: 431.0292.

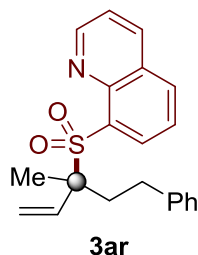


1,2-dichloro-4-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)benzene (3ap) was prepared according to the general procedure from **1a** and **2p**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 87% yield (64.2 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.64–7.58 (m, 2H), 7.31–7.26 (m, 2H), 7.23–7.15 (m, 3H), 6.00 (dd, *J* = 10.8, 17.5 Hz, 1H), 5.48 (d, *J* = 10.8 Hz, 1H), 5.16 (d, *J* = 17.5 Hz, 1H), 2.64–2.50 (m, 2H), 2.25–2.21 (m, 2H), 1.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 138.8, 135.0, 134.8, 133.3, 132.4, 130.4,

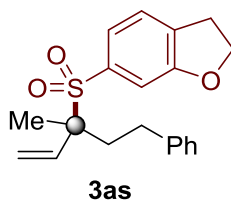
129.7, 128.6, 128.3, 126.3, 121.5, 68.7, 34.4, 30.1, 16.5; HRMS (ESI-MS): Calcd. for $C_{18}H_{18}Cl_2O_2S$ (M + Na): 391.0297, Found: 391.0294.



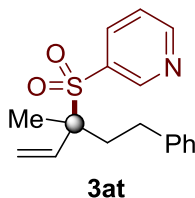
2-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)naphthalene (3aq) was prepared according to the general procedure from **1a** and **2q**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 82% yield (57.5 mg); 1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 1.6 Hz, 1H), 7.99–7.92 (m, 2H), 7.80 (dd, J = 1.7, 8.6 Hz, 1H), 7.70–7.60 (m, 2H), 7.30–7.26 (m, 3H), 7.21–7.15 (m, 3H), 6.07 (dd, J = 10.8, 17.5 Hz, 1H), 5.44 (d, J = 10.8 Hz, 1H), 5.13 (d, J = 17.5 Hz, 1H), 2.64–2.50 (m, 2H), 2.31–2.26 (m, 2H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 135.2, 135.1, 132.6, 132.4, 131.7, 129.5, 129.3, 128.5, 128.4, 128.3, 127.9, 127.4, 126.2, 125.5, 121.0, 68.5, 34.8, 30.2, 16.5; HRMS (ESI-MS): Calcd. for $C_{22}H_{22}O_2S$ (M + Na): 373.1233, Found: 373.1224.



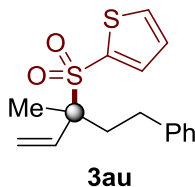
8-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)quinoline (3ar) was prepared according to the general procedure from **1a** and **2r**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 72% yield (54.8 mg); 1H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, J = 1.2, 2.8 Hz, 1H), 8.47 (d, J = 1.2, 4.8 Hz, 1H), 8.22 (d, J = 1.2, 4.8 Hz, 1H), 8.09 (d, J = 1.2, 4.8 Hz, 1H), 7.65 (t, J , 5.2 Hz, 1H), 7.50 (d, J = 2.8, 5.5 Hz, 1H), 7.27–7.24 (m, 2H), 7.19–7.14 (m, 3H), 6.18 (dd, J = 10.8, 17.5 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 5.08 (d, J = 17.5 Hz, 1H), 2.66–2.55 (m, 2H), 2.45–2.35 (m, 2H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 145.5, 141.3, 136.8, 136.4, 136.0, 135.0, 134.3, 129.0, 128.4, 128.3, 126.0, 125.2, 121.9, 119.8, 70.5, 35.5, 30.2, 17.0; HRMS (ESI-MS): Calcd. for $C_{21}H_{21}NO_2S$ (M + Na): 374.1185, Found: 374.1177.



6-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)-2,3-dihydrobenzofuran (3as) was prepared according to the general procedure from **1a** and **2s**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 92% yield (63.0 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59–7.57 (m, 2H), 7.30–7.26 (m, 2H), 7.21–7.15 (m, 3H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.00 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 1H), 5.16 (d, $J = 17.5$ Hz, 1H), 4.68 (t, $J = 8.8$ Hz, 2H), 3.25 (t, $J = 8.8$ Hz, 2H), 2.61–2.48 (m, 2H), 2.26–2.15 (m, 2H), 1.44 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.6, 141.1, 135.4, 132.4, 128.5, 128.3, 127.7, 127.6, 126.6, 126.1, 120.5, 109.0, 72.3, 68.1, 34.8, 30.2, 28.9, 16.4; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 365.1182, Found: 365.1184.

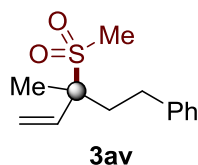


3-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)pyridine (3at) was prepared according to the general procedure from **1a** and **2t**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 82% yield (49.4 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.00 (d, $J = 2.1$ Hz, 1H), 8.83 (dd, $J = 2.1, 4.8$ Hz, 1H), 8.10–8.07 (m, 1H), 7.48–7.44 (m, 1H), 7.32–7.27 (m, 2H), 7.23–7.15 (m, 3H), 6.02 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.47 (d, $J = 10.8$ Hz, 1H), 5.13 (d, $J = 17.5$ Hz, 1H), 2.65–2.50 (m, 2H), 2.29–2.22 (m, 2H), 1.46 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 154.0, 151.0, 140.6, 138.3, 134.6, 131.6, 128.5, 128.2, 126.2, 123.1, 68.5, 34.2, 30.0, 16.3; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{S}$ ($\text{M} + \text{Na}$): 324.1029, Found: 324.1032.

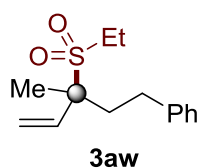


2-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)thiophene (3au) was prepared according to the general procedure from **1a** and **2u**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 86% yield (52.7 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 4.4$ Hz, 1H),

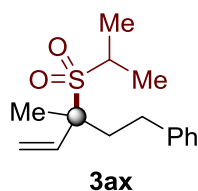
7.59 (d, $J = 4.4$ Hz, 1H), 7.30–7.24 (m, 3H), 7.21–7.11 (m, 3H), 6.04 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.50 (d, $J = 10.8$ Hz, 1H), 5.24 (d, $J = 17.5$ Hz, 1H), 2.65–2.51 (m, 2H), 2.32–2.19 (m, 2H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.9, 136.3, 136.0, 134.8, 134.5, 128.5, 128.3, 127.4, 126.2, 121.3, 68.7, 34.8, 30.3, 16.5; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2$ ($\text{M} + \text{Na}$): 329.0640, Found: 329.0645.



(3-methyl-3-(methylsulfonyl)pent-4-en-1-yl)benzene (3av) was prepared according to the general procedure from **1a** and **2v**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 72% yield (34.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.27 (m, 2H), 7.22–7.17 (m, 3H), 6.11 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.58 (d, $J = 10.8$ Hz, 1H), 5.47 (d, $J = 17.5$ Hz, 1H), 2.77 (s, 3H), 2.66–2.53 (m, 2H), 2.26–2.18 (m, 2H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 135.8, 128.5, 128.3, 126.3, 120.6, 67.1, 34.6, 33.8, 29.9, 16.2; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 261.0920, Found: 261.0924.

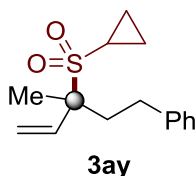


(3-(ethylsulfonyl)-3-methylpent-4-en-1-yl)benzene (3aw) was prepared according to the general procedure from **1a** and **2w**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 78% yield (39.4 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.26 (m, 2H), 7.22–7.17 (m, 3H), 6.09 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.54 (d, $J = 10.8$ Hz, 1H), 5.44 (d, $J = 17.5$ Hz, 1H), 2.99–2.90 (m, 2H), 2.66–2.51 (m, 2H), 2.29–2.18 (m, 2H), 1.58 (s, 3H), 1.37 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.9, 135.8, 128.5, 128.3, 126.2, 120.3, 67.1, 40.7, 34.0, 29.8, 16.1, 5.1; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 275.1076, Found: 275.1079.

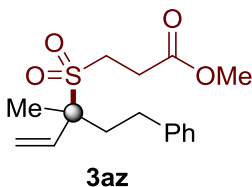


(3-(isopropylsulfonyl)-3-methylpent-4-en-1-yl)benzene (3ax) was prepared according to the general procedure from **1a** and **2x**. The crude product was purified by flash column chro-

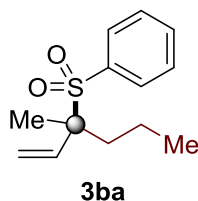
matography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 82% yield (43.7 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.26 (m, 2H), 7.21–7.17 (m, 3H), 6.15 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.50 (d, $J = 10.8$ Hz, 1H), 5.42 (d, $J = 17.5$ Hz, 1H), 3.44–3.37 (m, 1H), 2.63–2.52 (m, 2H), 2.26–2.21 (m, 2H), 1.59 (s, 3H), 1.38–1.35 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 136.6, 128.5, 128.4, 126.2, 119.3, 68.6, 50.2, 34.92, 29.8, 17.6, 17.3, 16.7; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 289.1238, Found: 289.1244.



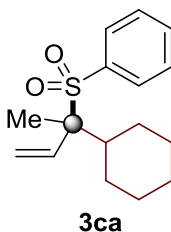
(3-(cyclopropylsulfonyl)-3-methylpent-4-en-1-yl)benzene (3ay) was prepared according to the general procedure from **1a** and **2y**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 78% yield (41.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.25 (m, 2H), 7.21–7.17 (m, 3H), 6.11 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.54 (d, $J = 10.8$ Hz, 1H), 5.45 (d, $J = 17.5$ Hz, 1H), 2.65–2.51 (m, 2H), 2.39–2.30 (m, 1H), 2.28–2.19 (m, 2H), 1.60 (s, 3H), 1.20–1.17 (m, 2H), 1.03–0.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 135.7, 128.4, 128.2, 126.1, 120.2, 67.6, 34.5, 29.7, 24.6, 16.2, 5.2, 4.1; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 287.1076, Found: 287.1082.



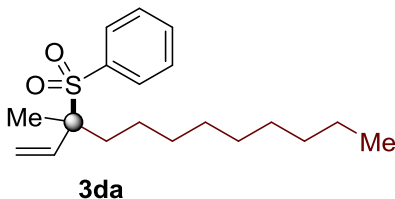
methyl 3-((3-methyl-5-phenylpent-1-en-3-yl)sulfonyl)propanoate (3az) was prepared according to the general procedure from **1a** and **2z**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 50:1) on silica gel to provide the title compound as a white solid in 72% yield (44.7 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.27 (m, 2H), 7.22–7.17 (m, 3H), 6.08 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.59 (d, $J = 10.8$ Hz, 1H), 5.48 (d, $J = 17.5$ Hz, 1H), 3.72 (s, 3H), 3.27–3.22 (m, 2H), 2.85 (t, $J = 5.4$ Hz, 2H), 2.65–2.53 (m, 2H), 2.27–2.19 (m, 2H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 140.8, 135.3, 128.6, 128.3, 126.3, 121.0, 67.6, 52.3, 41.9, 33.9, 29.8, 25.6, 16.1; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{S}$ ($\text{M} + \text{Na}$): 333.1131, Found: 333.1134.



((3-methylhex-1-en-3-yl)sulfonyl)benzene (3ba) was prepared according to the general procedure from **1b** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a colorless oil in 87% yield (41.5 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83–7.80 (m, 2H), 7.64–7.61 (m, 1H), 7.53–7.50 (m, 2H), 5.92 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.34 (d, $J = 10.7$ Hz, 1H), 5.03 (d, $J = 17.4$ Hz, 1H), 1.93–1.85 (m, 2H), 1.34 (s, 3H), 1.31–1.21 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 136.9, 135.4, 133.5, 130.8, 128.3, 120.3, 68.4, 34.7, 17.1, 16.2, 14.4; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 261.0920, Found: 261.0926.

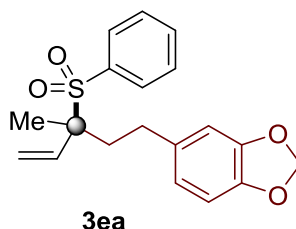


((2-cyclohexylbut-3-en-2-yl)sulfonyl)benzene (3ca) was prepared according to the general procedure from **1c** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a colorless oil in 24% yield (13.4 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80–7.78 (m, 2H), 7.63–7.58 (m, 1H), 7.51–7.47 (m, 2H), 6.04 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.21 (d, $J = 10.8$ Hz, 1H), 4.85 (d, $J = 17.5$ Hz, 1H), 2.34–2.18 (m, 2H), 1.92–1.67 (m, 4H), 1.39–1.04 (m, 8H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 136.7, 134.8, 133.2, 130.5, 128.1, 119.2, 72.0, 41.5, 28.8, 28.3, 26.8, 26.5, 26.3, 13.9; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 301.1238, Found: 301.1246.

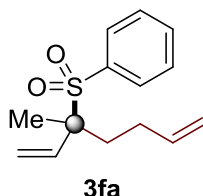


((3-methyldodec-1-en-3-yl)sulfonyl)benzene (3da) was prepared according to the general procedure from **1d** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a colorless oil in 91% yield (58.7 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82–7.80 (m, 2H), 7.63–7.61 (m, 1H),

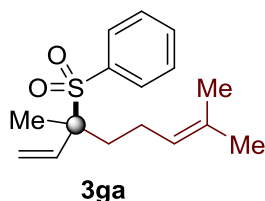
7.53–7.49 (m, 2H), 5.91 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.34 (d, $J = 10.7$ Hz, 1H), 5.02 (d, $J = 17.4$ Hz, 1H), 1.96–1.86 (m, 2H), 1.34 (s, 3H), 1.30–1.25 (m, 14H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.4, 135.3, 133.4, 130.7, 128.2, 120.3, 68.4, 32.5, 31.8, 29.9, 29.4, 29.3, 29.2, 23.7, 22.6, 16.2, 14.1; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 345.1859, Found: 345.1866.



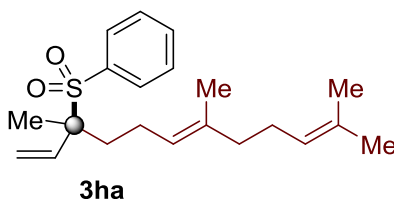
5-(3-methyl-3-(phenylsulfonyl)pent-4-en-1-yl)benzo[d][1,3]dioxole (3ea) was prepared according to the general procedure from **1e** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 96% yield (66.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.79 (m, 2H), 7.65–7.60 (m, 1H), 7.53–7.49 (m, 2H), 6.73–6.58 (m, 3H), 5.98 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.91 (s, 2H), 5.42 (d, $J = 10.7$ Hz, 1H), 5.11 (d, $J = 17.4$ Hz, 1H), 2.54–2.40 (m, 2H), 2.23–2.13 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.5, 145.8, 135.0, 134.9, 134.7, 133.6, 130.6, 128.3, 121.0, 120.8, 108.7, 108.2, 100.8, 68.0, 34.9, 29.8, 16.3; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{S}$ ($\text{M} + \text{Na}$): 367.0980, Found: 367.0984.



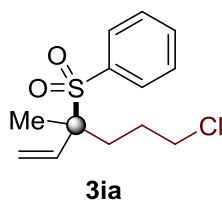
((3-methylhepta-1,6-dien-3-yl)sulfonyl)benzene (3fa) was prepared according to the general procedure from **1f** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 85% yield (42.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.81 (m, 2H), 7.64–7.61 (m, 1H), 7.53–7.50 (m, 2H), 5.93 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.81–5.75 (m, 1H), 5.37 (d, $J = 10.7$ Hz, 1H), 5.07 (d, $J = 17.4$ Hz, 1H), 5.03 (d, $J = 17.4$ Hz, 1H), 4.98 (d, $J = 10.5$ Hz, 1H), 2.06–1.96 (m, 4H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 135.2, 135.0, 133.6, 130.7, 128.3, 120.7, 115.3, 68.1, 31.9, 28.0, 16.2; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$): 273.0920, Found: 273.0924.



((3,7-dimethylocta-1,6-dien-3-yl)sulfonyl)benzene (3ga) was prepared according to the general procedure from **1g** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 92% yield (51.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.80 (m, 2H), 7.64–7.61 (m, 1H), 7.53–7.50 (m, 2H), 5.92 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.37 (d, $J = 10.7$ Hz, 1H), 5.08–5.05 (m, 2H), 1.96–1.86 (m, 4H), 1.67 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.3, 135.2, 133.5, 132.6, 130.8, 128.3, 123.0, 120.5, 68.2, 32.7, 25.6, 22.4, 17.6, 16.2; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_2\text{S}$ (M + Na): 301.1238, Found: 301.1245.

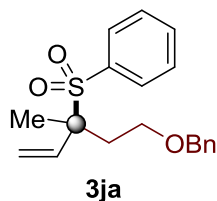


(E)-((3,7,11-trimethyldodeca-1,6,10-trien-3-yl)sulfonyl)benzene (3ha) was prepared according to the general procedure from **1h** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 86% yield (59.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.80 (m, 2H), 7.64–7.61 (m, 1H), 7.52–7.50 (m, 2H), 5.93 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.37 (d, $J = 10.7$ Hz, 1H), 5.09–5.05 (m, 3H), 2.07–1.87 (m, 8H), 1.67 (s, 3H), 1.60 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 136.3, 135.3, 135.2, 133.5, 130.8, 128.3, 124.1, 123.7, 120.5, 68.3, 39.6, 31.9, 26.5, 25.7, 23.3, 22.3, 17.7, 16.2; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{30}\text{O}_2\text{S}$ (M + Na): 369.1859, Found: 369.1864.

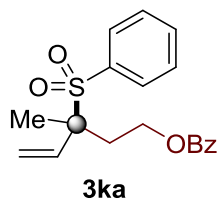


((6-chloro-3-methylhex-1-en-3-yl)sulfonyl)benzene (3ia) was prepared according to the general procedure from **1i** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 82% yield (44.7 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.81 (m, 2H), 7.65–7.62 (m, 1H), 7.54–7.51 (m, 2H), 5.93 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.37 (d, $J = 10.7$ Hz, 1H), 5.07 (d, $J = 17.4$ Hz, 1H), 3.53 (t, $J = 6.4$ Hz, 2H), 2.11–2.02 (m, 2H), 1.82–1.96 (m, 2H), 1.36 (s, 3H); ^{13}C

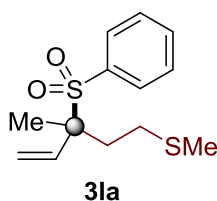
NMR (100 MHz, CDCl₃) δ 136.9, 134.9, 133.9, 130.7, 128.4, 120.9, 67.7, 44.6, 30.4, 27.2, 16.4;
HRMS (ESI-MS): Calcd. for C₁₃H₁₇ClO₂S (M + Na): 295.0535, Found: 295.0530.



((5-(benzyloxy)-3-methylpent-1-en-3-yl)sulfonyl)benzene (3ja) was prepared according to the general procedure from **1j** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 92% yield (60.8 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.79 (m, 2H), 7.64–7.60 (m, 1H), 7.52–7.48 (m, 2H), 7.35–7.25 (m, 5H), 5.94 (dd, *J* = 10.7, 17.4 Hz, 1H), 5.36 (d, *J* = 10.7 Hz, 1H), 5.09 (d, *J* = 17.4 Hz, 1H), 4.46 (d, *J* = 12.4 Hz, 1H), 4.42 (d, *J* = 12.4 Hz, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.29–2.22 (m, 2H), 1.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 134.8, 134.7, 133.6, 130.7, 128.4, 128.3, 127.6, 127.5, 120.6, 72.9, 67.2, 65.9, 32.7, 16.8; HRMS (ESI-MS): Calcd. for C₁₉H₂₂O₃S (M + Na): 353.1182, Found: 353.1177.

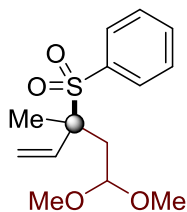


3-methyl-3-(phenylsulfonyl)pent-4-en-1-yl benzoate (3ka) was prepared according to the general procedure from **1k** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 94% yield (64.7 mg); ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.98 (m, 2H), 7.84–7.82 (m, 2H), 7.67–7.63 (m, 1H), 7.59–7.51 (m, 3H), 7.46–7.42 (m, 2H), 6.02 (dd, *J* = 10.7, 17.4 Hz, 1H), 5.39 (d, *J* = 10.7 Hz, 1H), 5.12 (d, *J* = 17.4 Hz, 1H), 4.45–4.31 (m, 2H), 2.52–2.38 (m, 2H), 1.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 134.6, 134.5, 133.8, 133.1, 130.8, 129.8, 129.5, 128.4, 128.3, 121.0, 67.0, 60.6, 31.8, 16.7; HRMS (ESI-MS): Calcd. for C₁₉H₂₀O₄S (M + Na): 367.0975, Found: 367.0977.



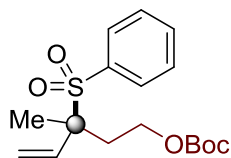
methyl(3-methyl-3-(phenylsulfonyl)pent-4-en-1-yl)sulfane (3la) was prepared according to the general procedure from **1l** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a

white solid in 88% yield (47.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.81 (m, 2H), 7.65–7.63 (m, 1H), 7.54–7.51 (m, 2H), 5.93 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.39 (d, $J = 10.7$ Hz, 1H), 5.09 (d, $J = 17.4$ Hz, 1H), 2.46–2.38 (m, 2H), 2.26–2.18 (m, 2H), 2.11 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 134.6, 133.7, 130.7, 128.4, 121.0, 67.8, 33.1, 28.5, 16.4, 15.5; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}_2$ (M + Na): 293.0640, Found: 293.0539.



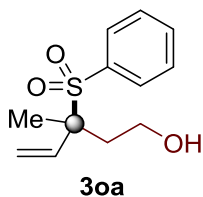
3ma

((5,5-dimethoxy-3-methylpent-1-en-3-yl)sulfonyl)benzene (3ma) was prepared according to the general procedure from **1m** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 86% yield (48.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.80 (m, 2H), 7.66–7.62 (m, 1H), 7.54–7.50 (m, 2H), 6.00 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.38 (d, $J = 10.7$ Hz, 1H), 5.10 (d, $J = 17.4$ Hz, 1H), 4.40–4.38 (m, 1H), 3.27 (s, 6H), 2.31–2.18 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.9, 134.7, 133.7, 130.8, 128.4, 120.4, 101.5, 66.8, 52.7, 52.4, 35.7, 16.7; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{S}$ (M + Na): 307.0975, Found: 307.0973.

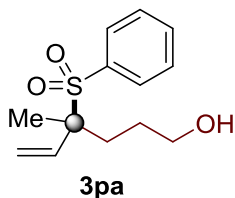


3na

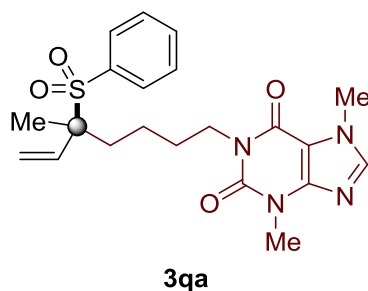
tert-butyl (3-methyl-3-(phenylsulfonyl)pent-4-en-1-yl) carbonate (3na) was prepared according to the general procedure from **1n** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 87% yield (59.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.80 (m, 2H), 7.67–7.63 (m, 1H), 7.55–7.51 (m, 2H), 5.94 (dd, $J = 10.8, 17.5$ Hz, 1H), 5.40 (d, $J = 10.8$ Hz, 1H), 5.13 (d, $J = 17.5$ Hz, 1H), 4.15–4.04 (m, 2H), 2.36–2.22 (m, 2H), 1.46 (s, 9H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 134.7, 134.3, 133.8, 130.8, 128.5, 121.1, 82.4, 66.7, 62.6, 31.9, 27.7, 16.6; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_5\text{S}$ (M + Na): 363.1242, Found: 363.1239.



3-methyl-3-(phenylsulfonyl)pent-4-en-1-ol (3oa) was prepared according to the general procedure from **1o** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 78% yield (37.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.84–7.80 (m, 2H), 7.67–7.62 (m, 1H), 7.56–7.50 (m, 2H), 6.01 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.37 (d, $J = 10.7$ Hz, 1H), 5.10 (d, $J = 17.4$ Hz, 1H), 3.74 (t, $J = 6.4$ Hz, 2H), 2.30–2.15 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.1, 134.1, 132.8, 130.4, 128.7, 121.1, 68.2, 58.3, 34.4, 17.4; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{S}$ ($M + \text{Na}$): 263.0718, Found: 263.0724.

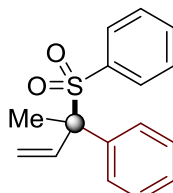


4-methyl-4-(phenylsulfonyl)hex-5-en-1-ol (3pa) was prepared according to the general procedure from **1p** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 78% yield (39.7 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.80 (m, 2H), 7.64–7.61 (m, 1H), 7.53–7.49 (m, 2H), 5.90 (dd, $J = 10.7, 17.4$ Hz, 1H), 5.37 (d, $J = 10.7$ Hz, 1H), 5.07 (d, $J = 17.4$ Hz, 1H), 3.91–3.78 (m, 1H), 3.65 (brs, 1H), 2.01–1.95 (m, 2H), 1.49–1.43 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 135.1, 133.5, 130.7, 128.3, 121.0, 67.5, 60.4, 26.1, 23.3, 14.1; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{S}$ ($M + \text{Na}$): 277.0869, Found: 277.0871.



3,7-dimethyl-1-(5-methyl-5-(phenylsulfonyl)hept-6-en-1-yl)-3,4,5,7-tetrahydro-1H-purine-2,6-dione (3qa) was prepared according to the general procedure from **1q** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a white solid in 92% yield (79.0 mg); ^1H NMR (400 MHz,

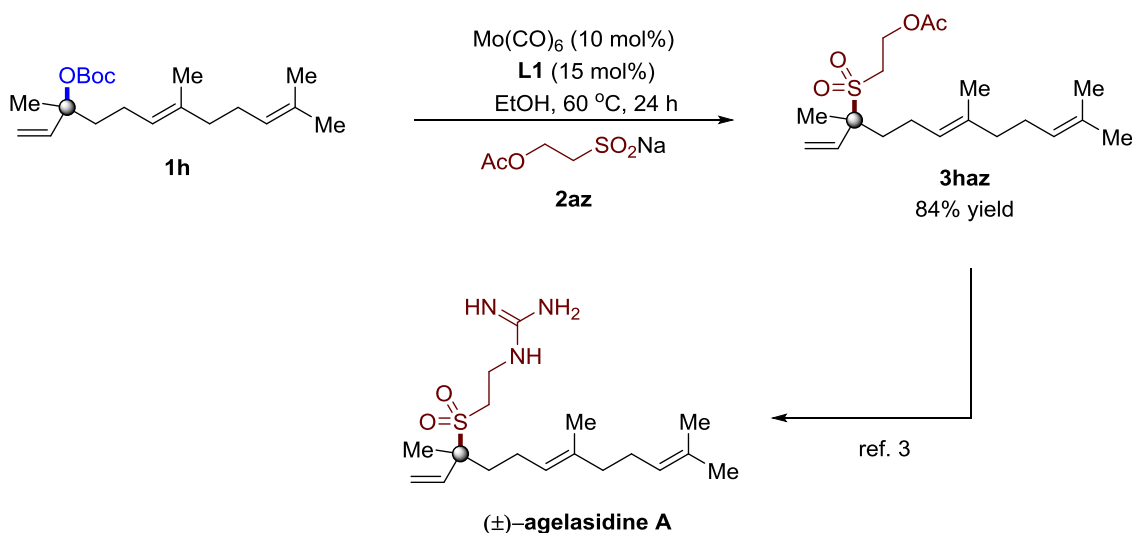
CDCl₃) δ 7.81–7.79 (m, 2H), 7.64–7.61 (m, 1H), 7.54–7.49 (m, 3H), 5.90 (dd, *J* = 10.7, 17.4 Hz, 1H), 5.36 (d, *J* = 10.7 Hz, 1H), 5.07 (d, *J* = 17.4 Hz, 1H), 4.00–3.95 (m, 5H), 3.56 (s, 3H), 1.99–1.89 (m, 2H), 1.68–1.63 (m, 2H), 1.36 (s, 3H), 1.36–1.26 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 155.1, 151.3, 148.6, 141.4, 135.2, 135.0, 133.5, 130.7, 128.3, 120.6, 107.5, 68.2, 41.0, 33.5, 32.5, 29.6, 28.3, 21.3, 16.1; HRMS (ESI-MS): Calcd. for C₂₁H₂₆N₄O₄S (M + Na): 453.1567, Found: 453.1570.



3ra

((2-phenylbut-3-en-2-yl)sulfonyl)benzene (**3ra**) was prepared according to the general procedure from **1r** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 60:1) on silica gel to provide the title compound as a yellow solid in 15% yield (8.2 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.57–7.26 (m, 10H), 6.70 (dd, *J* = 10.7, 17.4 Hz, 1H), 5.53 (d, *J* = 10.7 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 1.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 135.6, 135.5, 133.9, 130.2, 129.9, 128.9, 128.4, 128.3, 120.2, 71.6, 19.4; Other spectroscopic data for this compound matches with that reported in the literature.^{1b}

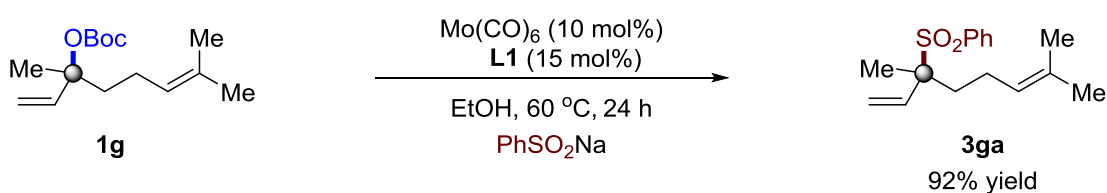
Formal synthesis of (±)-agelasidine A



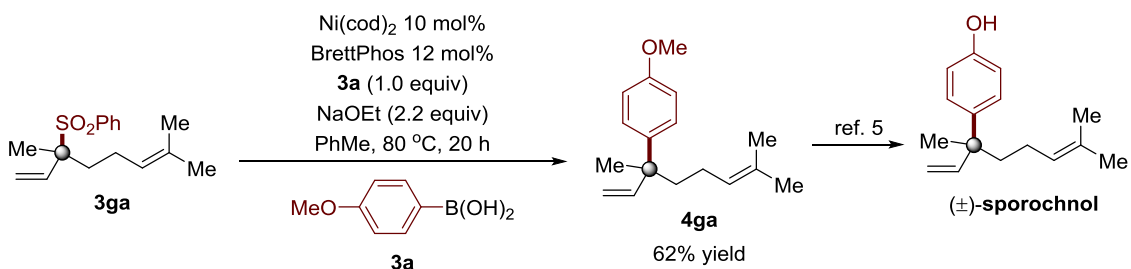
Compound **3haz** was prepared according to the general procedure from **1h** and **2az**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 20:1) on silica gel to provide the title compound as a colorless oil in 84% yield (58.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 6.01 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.52 (d, *J* = 10.8 Hz, 1H), 5.39 (d, *J* = 17.6 Hz, 1H), 5.11–5.04

(m, 2H), 4.50 (t, $J = 6.6$ Hz, 1H), 3.25 (t, $J = 6.6$ Hz, 2H), 2.07–1.87 (m, 11H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 136.6, 135.6, 131.6, 124.2, 122.7, 120.8, 68.3, 57.0, 45.7, 31.7, 26.7, 25.8, 22.2, 20.9, 17.8, 16.2, 16.0; The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^{1b,3} This compound could be directly converted to (\pm)-agelasidine **A** by following the previously reported literature procedures.³

Synthesis of (\pm)-Sporochnol methyl ether and (\pm)-Bakuchiol methyl ether

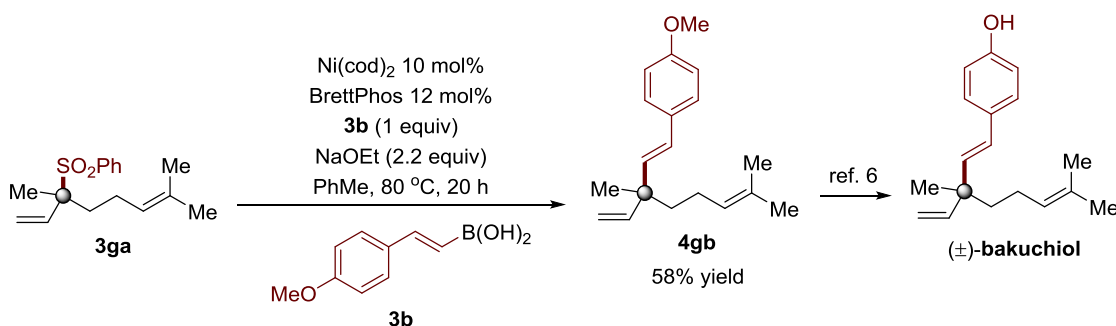


((3,7-dimethylocta-1,6-dien-3-yl)sulfonyl)benzene (3ga): To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Mo}(\text{CO})_6$ (26.4 mg, 10 mol%), 2,2'-bipyridyne ligand (**L1**) (23.5 mg, 15 mol%), allylic carbonate **1g** (254.4 mg, 1.0 mmol), and sodium benzenesulfinate **2a** (246.23 mg, 0.3 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 5 mL) were added via syringe. The resulting mixture was stirred at 60 °C for 24 hours. The reaction mixture was warm to room temperature and then quenched with water (5 mL). The organic portion was extracted with CH_2Cl_2 and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The obtained residue was purified by flash column chromatography on silica gel to afford the pure tertiary allylic sulfone **3ga** in 85% of isolated yield (236.6 mg) as a colorless oil.



Following the literature procedure⁴ with few modifications, describe by C. M. Crudden et. al. as follows: under nitrogen atmosphere, to an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Ni}(\text{cod})_2$ (10 mol %), BrettPhos (12 mol %), and NaOEt (2.2 equiv) were added. Then, ter-

tertiary allylic sulfone (**3ga**) (0.2 mmol), boronic acid **3a** (1.0 equiv) and toluene (0.2 M) were added. The reaction tube was capped and sealed, and was stirred at 80 °C for 20 h. The reaction mixture was cooled to room temperature and then diluted with EtOAc and saturated aqueous NH₄Cl (0.2 mL) was added. The mixture was filtered and washed with EtOAc. The obtained residue was concentrated and purified by flash column chromatography on silica gel to afford the pure **4ga** as a light-yellow oil (30.3 mg, 62%). This compound can be converted to (±)-**bakuchiol** by following the reported literature procedures.⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.27 (d, *J* = 16.2 Hz, 1H), 6.05 (d, *J* = 16.2 Hz, 1H), 5.87 (dd, *J* = 10.6, 17.4 Hz, 1H), 5.11 (t, *J* = 7.2 Hz, 1H), 5.04 (d, *J* = 10.6 Hz, 1H), 5.01 (d, *J* = 17.4 Hz, 1H), 3.80 (s, 3H), 1.95–1.88 (m, 2H), 1.67 (s, 3H), 1.56 (s, 3H), 1.51–1.45 (m, 2H), 1.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 146.2, 135.9, 131.5, 130.9, 127.3, 126.7, 125.0, 114.0, 112.1, 55.5, 42.7, 41.5, 25.9, 23.5, 23.4, 17.8. The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.⁵



Following the literature procedure⁴ with some modifications, describe by C. M. Crudden et. al. as follows: Under nitrogen atmosphere, to an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Ni(cod)₂ (10 mol %), BrettPhos (12 mol %), NaOEt (2.2 equiv) were added. Then, tertiary allylic sulfone (**3ga**) (0.2 mmol), boronic acid **3b** (1.0 equiv) and toluene (0.2 M) were added. The reaction tube was capped and sealed, and was stirred at 80 °C for 20 h. The reaction mixture was cooled to room temperature and then diluted with EtOAc and saturated aqueous NH₄Cl (0.2 mL) was added. The mixture was filtered and washed with EtOAc. The obtained residue was concentrated and purified by flash column chromatography on silica gel to afford **4gb** as a colorless oil (31.4 mg, 58%). This compound can be converted to (±)-**sporochnol** by following the reported literature.⁶ ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.03 (dd, *J* = 10.6, 17.4 Hz, 1H), 5.08–5.00 (m, 3H), 3.79 (s, 3H), 1.90–1.69 (m, 4H), 1.67 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 147.2, 139.5, 131.3, 127.6, 124.7, 113.4, 111.4,

55.2, 43.7, 41.1, 25.6, 25.1, 23.3, 17.6. The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.⁶

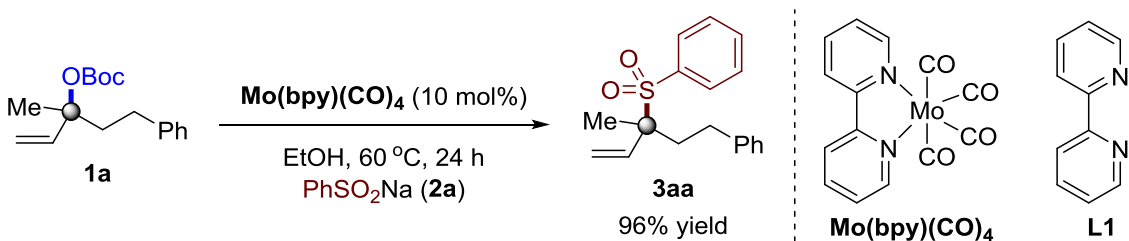
Synthesis of Mo-complex [Mo(bpy)(CO)₄]



In a 100 mL round-bottom flask equipped with a magnetic stir bar, a mixture of Mo(CO)₆ (1.0 mmol, 264.0 mg) and 2,2'-bipyridyne (**L1**) (1.0 mmol, 156.2 mg) in anhydrous THF were stirred at 60 °C for 12 hours under nitrogen atmosphere. After few minutes, the solution turned orange and slowly becoming dark red (picture A, left). After 12 h, the reaction mixture was cool to room temperature, filtered and washed with anhydrous hexane. The upper solid portion was scratched with spatula and collected as a dark red crystalline solid (picture B, middle) affording Mo(bpy)(CO)₄ complex (262.2 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.17–9.15 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.94 (ddd, *J* = 1.6, 7.8, 15.7 Hz, 1H), 7.42–7.38 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 204.7, 154.5, 153.1, 137.2, 125.2, 121.9; Other spectroscopic data for this compound matches with that reported in the literature.⁷

Preliminary Mechanistic Experiments

(1) Mechanistic experiments with Mo(bpy)(CO)₄

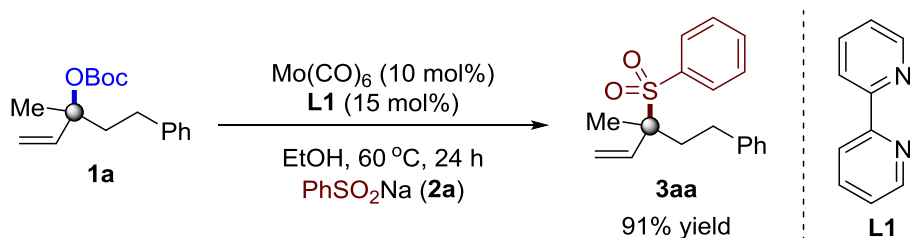


- **Without L1.** Following the standard procedure, to an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Mo(bpy)(CO)₄ (7.3 mg, 10 mol%), allylic carbonate **1a** (55.28 mg, 0.2 mmol), and sodium benzenesulfinate **2a** (49.25 mg, 0.3 mmol) were added. The reaction tube was

sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 1 mL) were added via syringe. The resulting mixture was stirred at 60 °C for 24 hours. Interestingly, the reaction proceeded smoothly to provide the title compound **3aa** in 96% of isolated yield.

- **With L1.** Following the standard procedure, to an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Mo(bpy)(CO)₄ (7.3 mg, 10 mol%), **L1** (4.7 mg, 15 mmol), allylic carbonate **1a** (55.28 mg, 0.2 mmol), and sodium benzenesulfinate **2a** (49.25 mg, 0.3 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 1 mL) were added via syringe. The resulting mixture was stirred at 60 °C for 24 hours afforded **3aa** in 89% of isolated yield.

(2) Mechanistic experiments with Mo(CO)₆

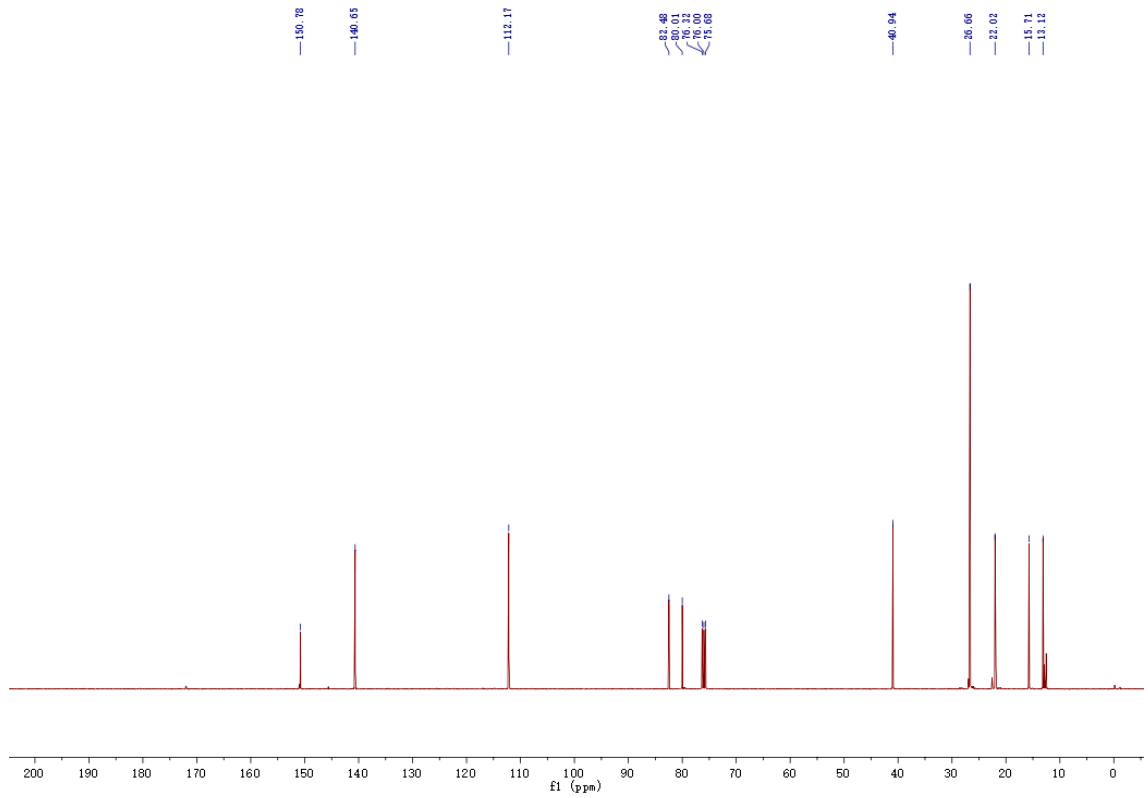
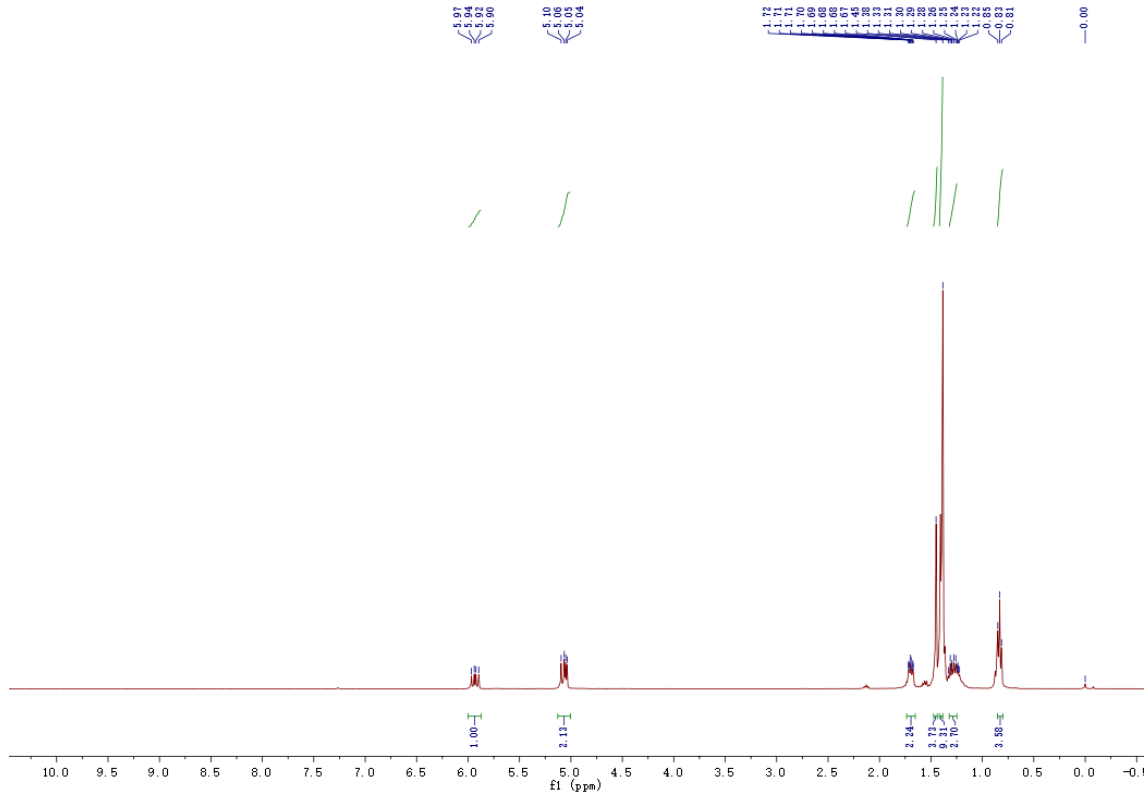
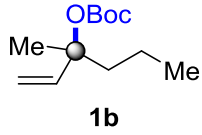


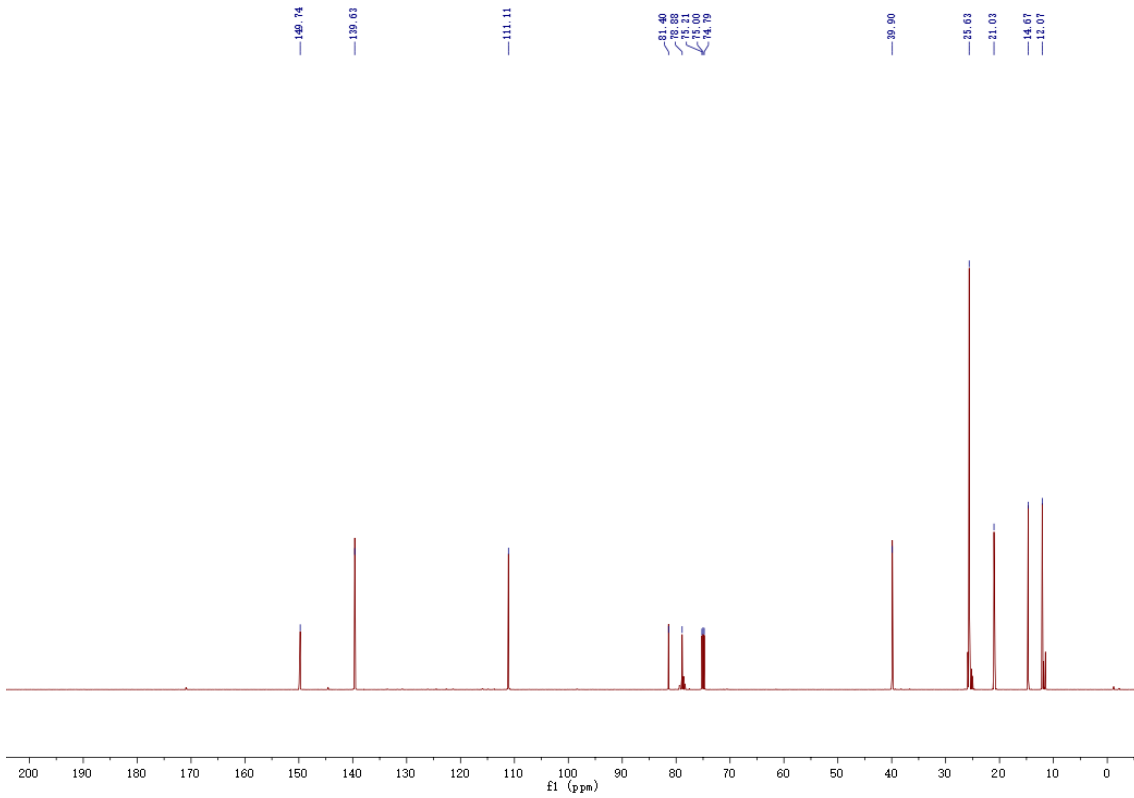
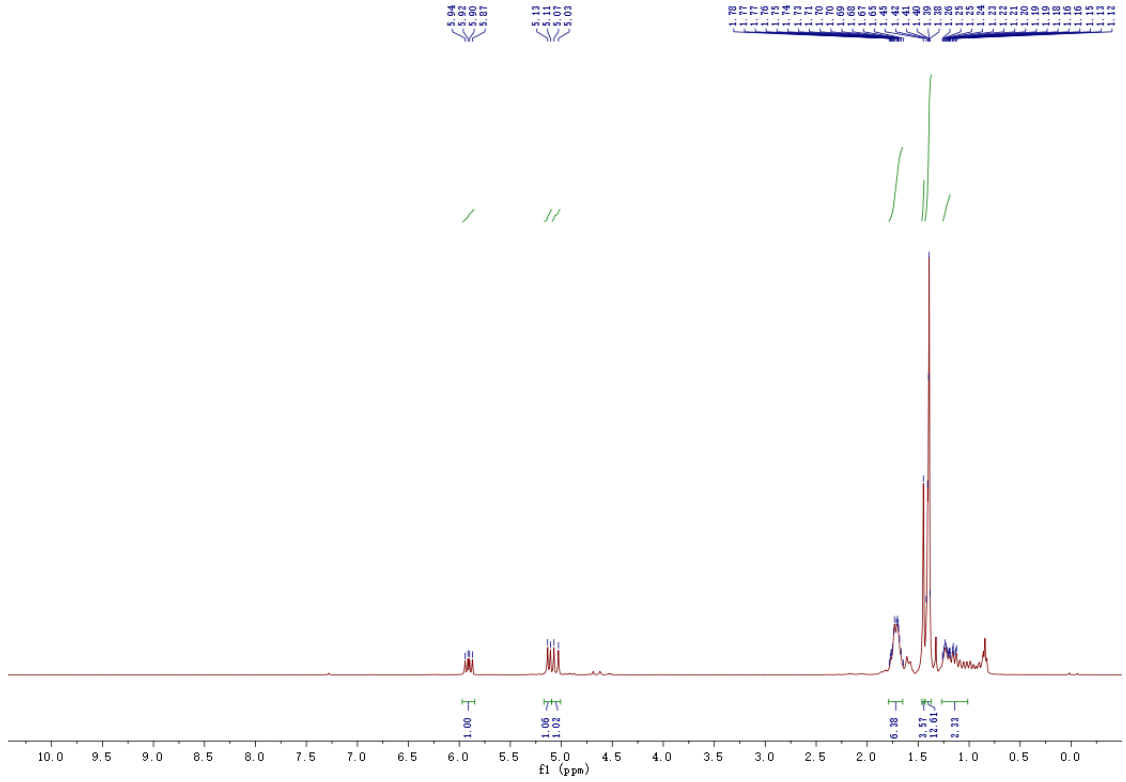
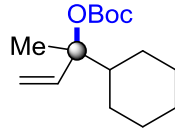
- **Without L1.** Following the standard procedure, using allylic carbonate **1a** (55.28 mg, 0.2 mmol), and sodium benzenesulfinate **2a** (49.25 mg, 0.3 mmol), and Mo(CO)₆ (5.3 mg, 10 mol%), did not provide any conversion to **3aa** as judged by ¹H NMR analysis.

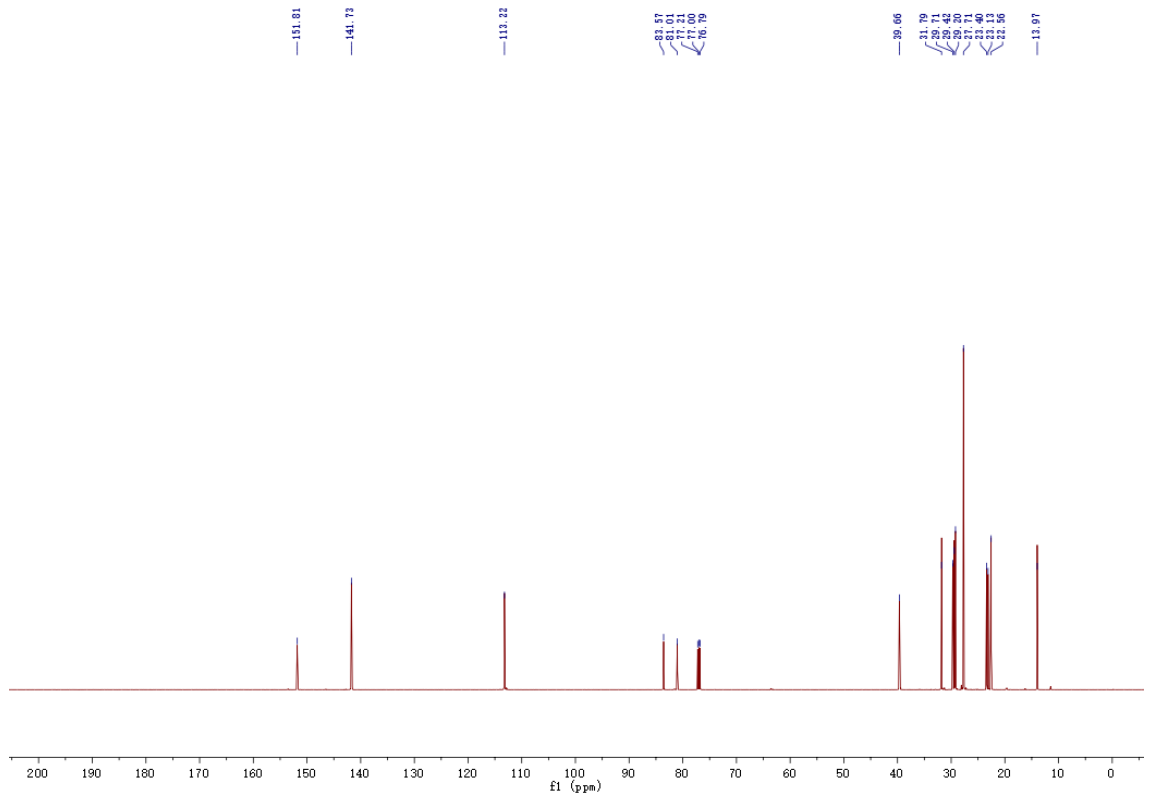
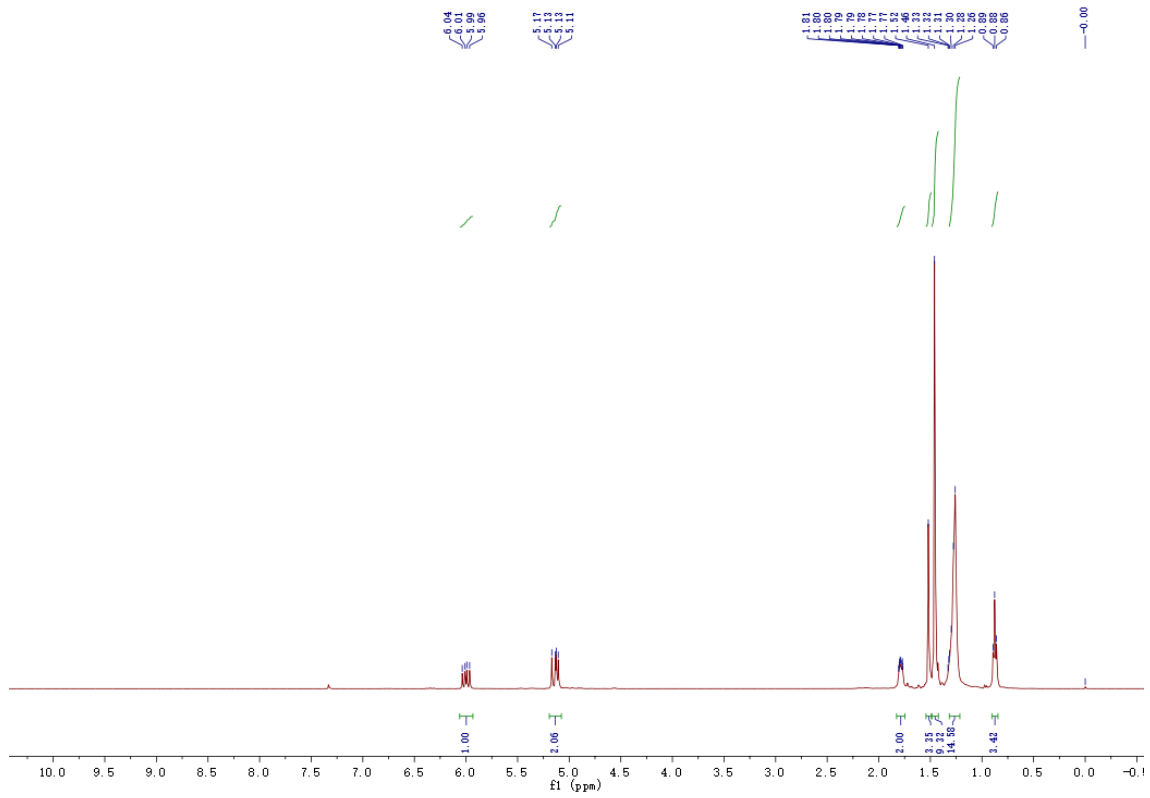
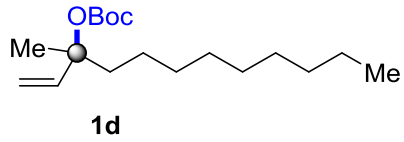
- **With L1.** Following the standard procedure, using allylic carbonate **1a** (55.28 mg, 0.2 mmol), and sodium benzenesulfinate **2a** (49.25 mg, 0.3 mmol), and Mo(CO)₆ (5.3 mg, 10 mol%), **L1** (4.7 mg, 15 mmol) afforded **3aa** in 91% of isolated yield. A small decline in yield of **3aa** under [Mo(CO)₆]/**L1** catalyst system, thus providing evidence and implicit that a [Mo(bpy)(CO)₄] complex is likely the active catalyst species in this allylic sulfonation reaction.

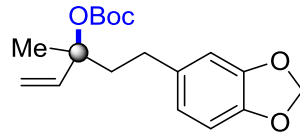
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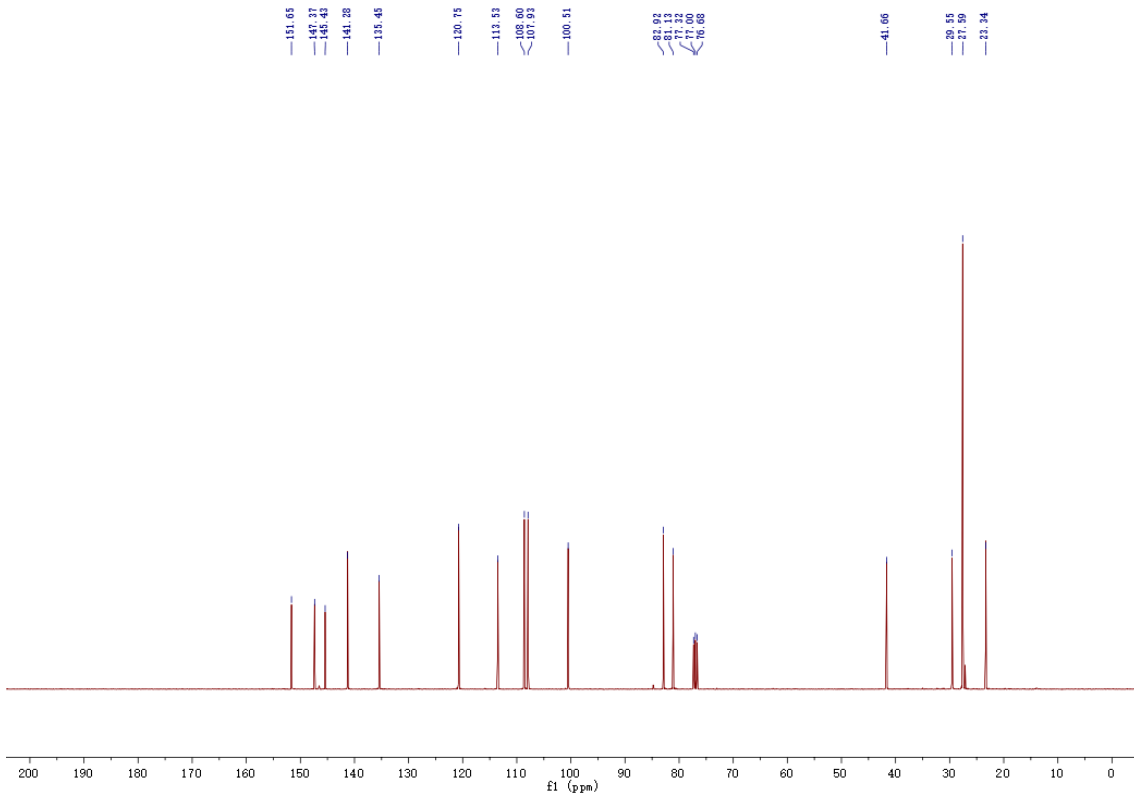
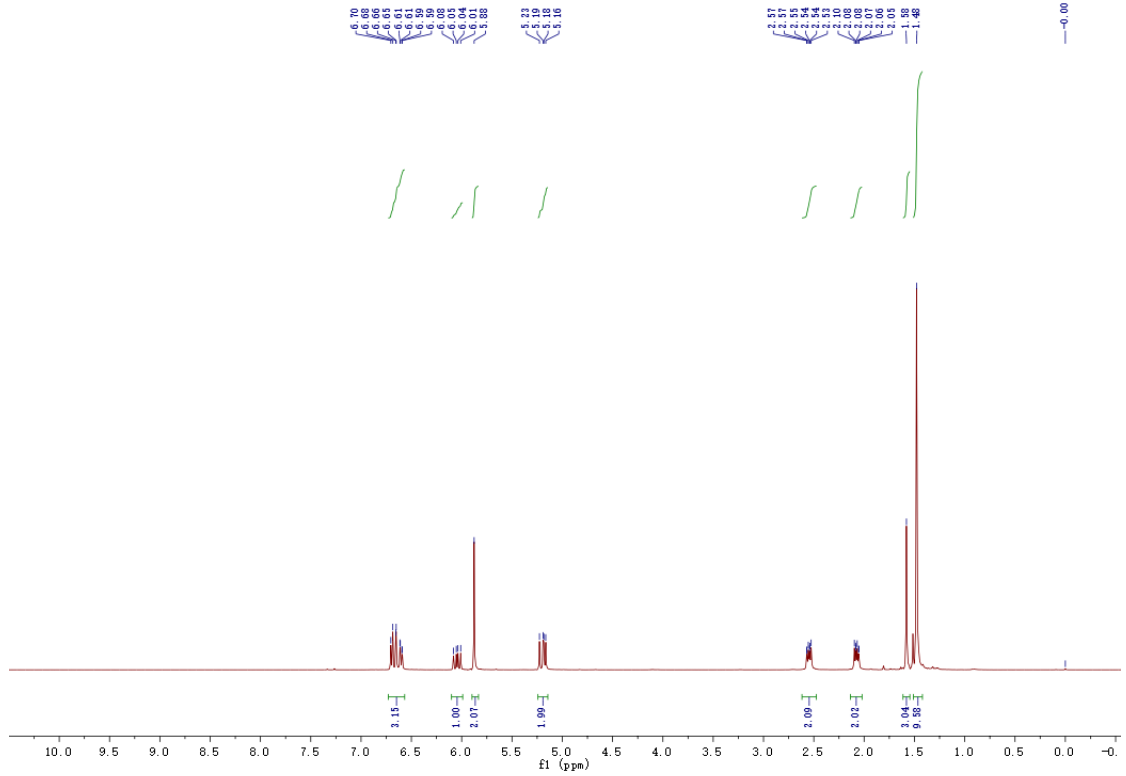


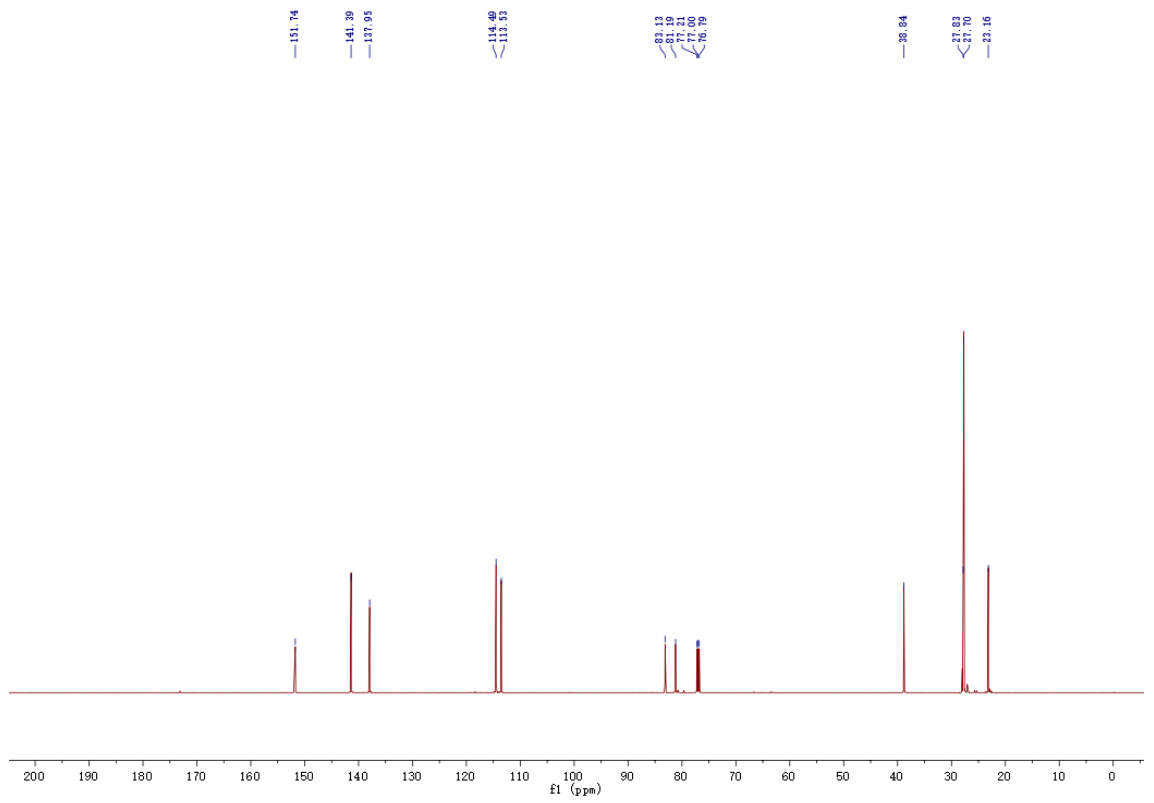
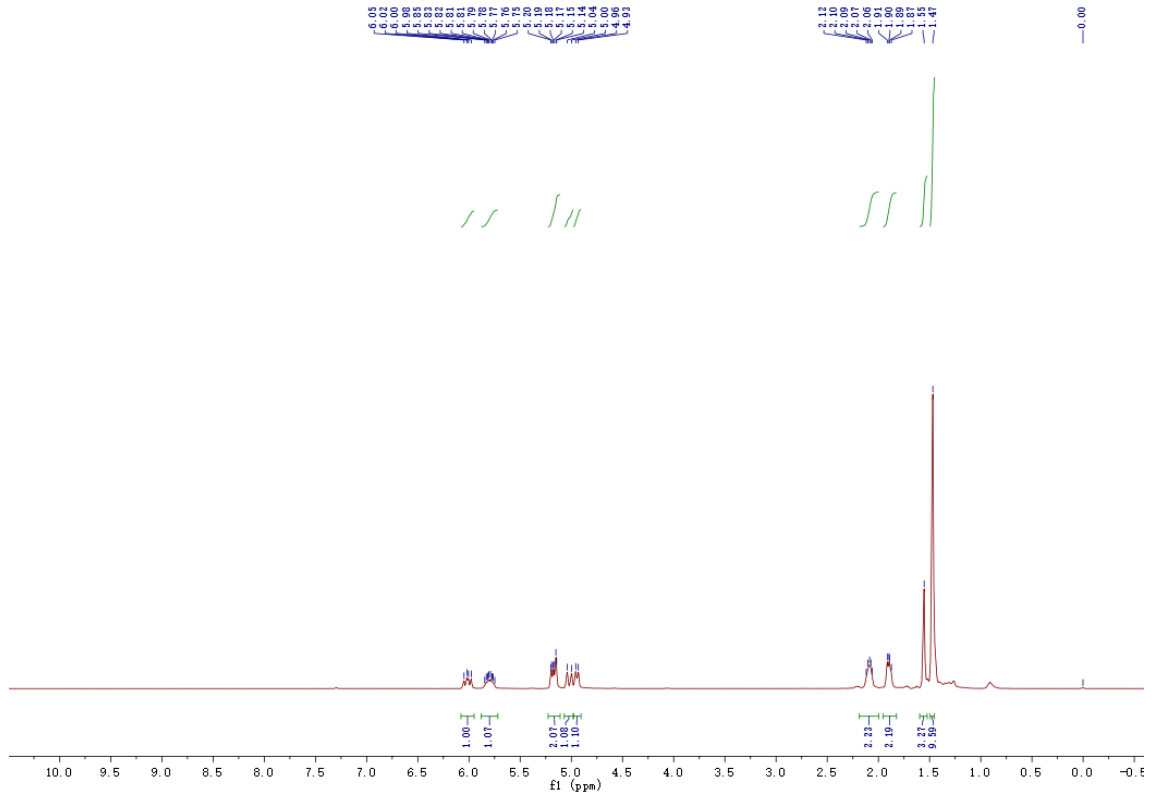
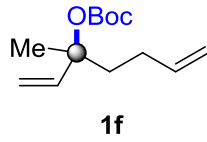


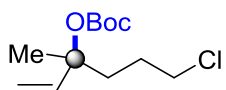




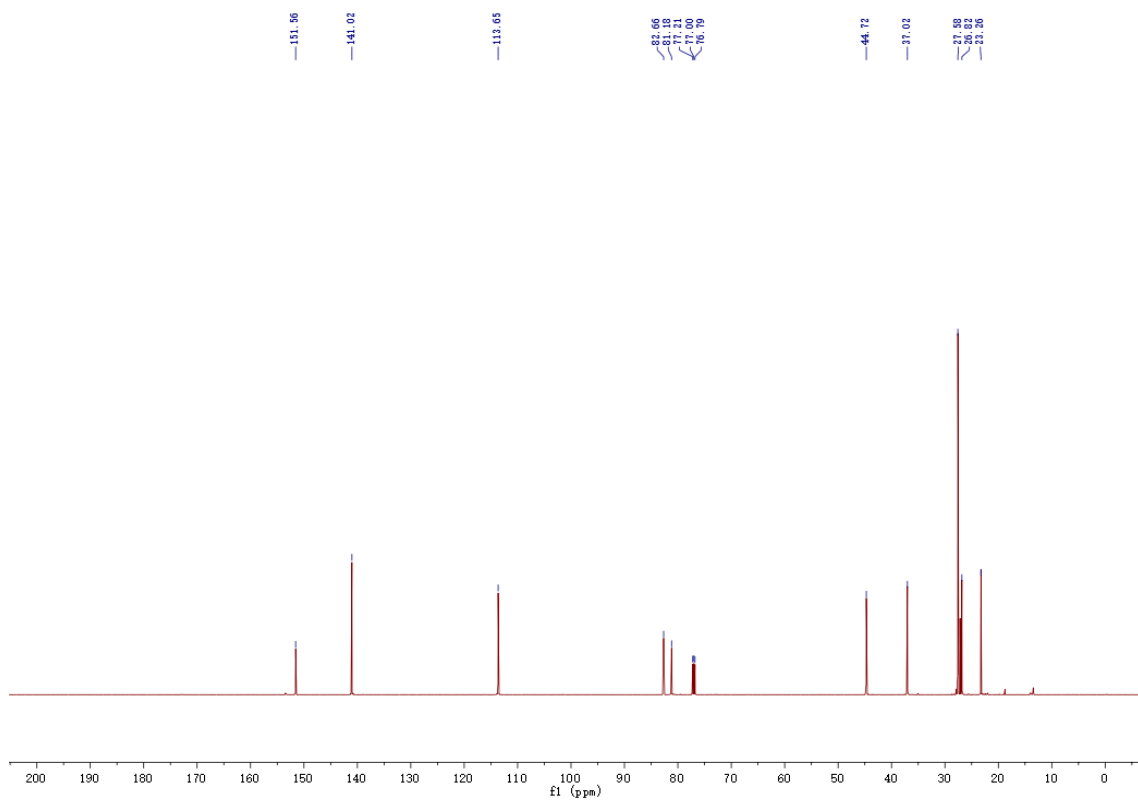
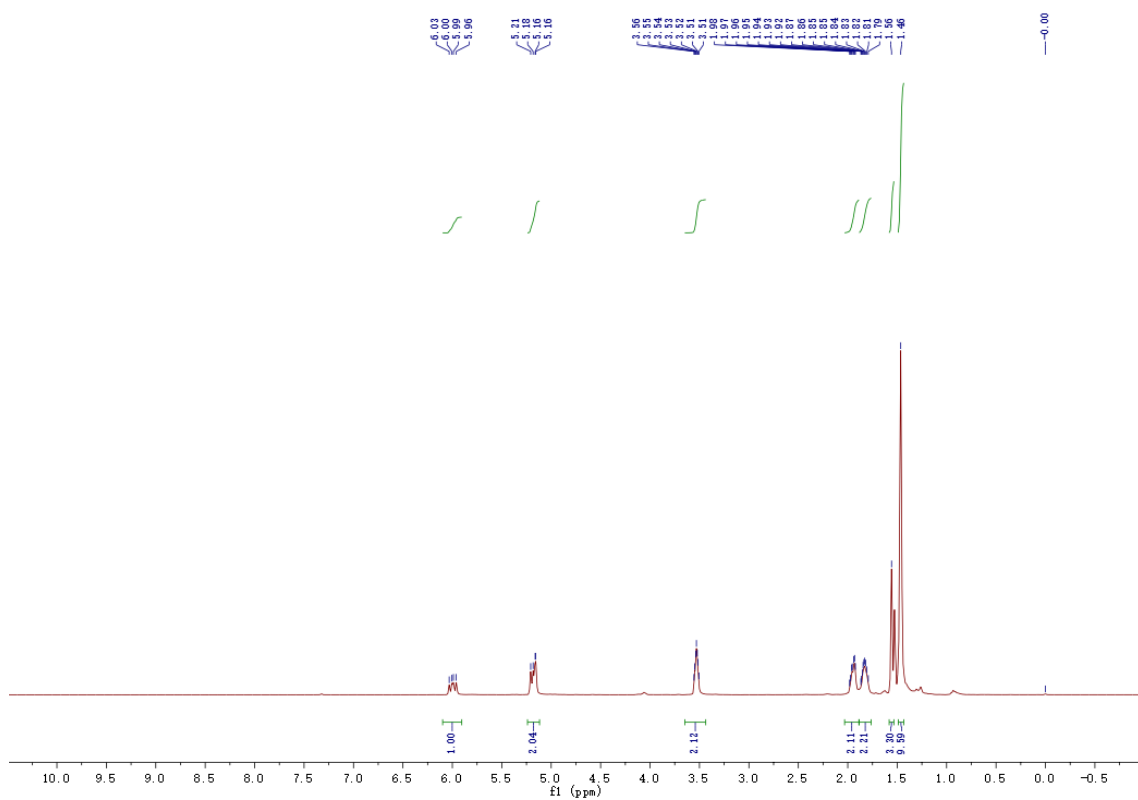
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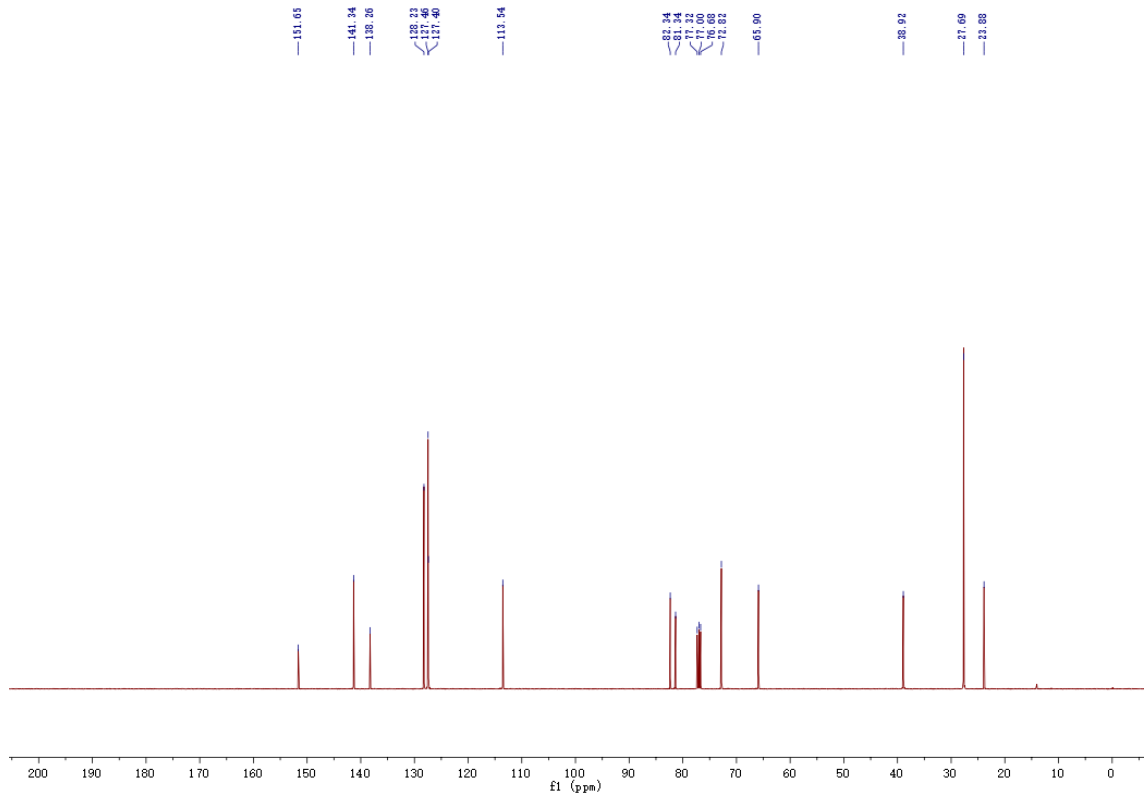
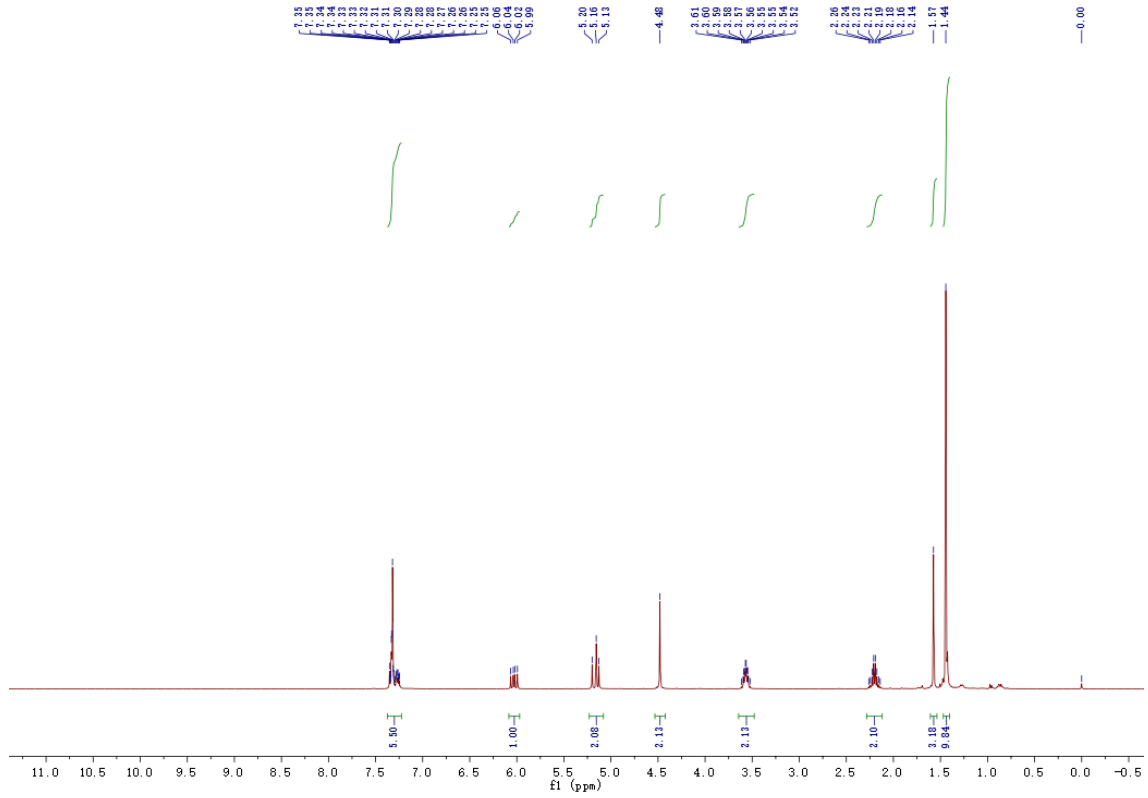
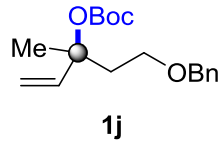


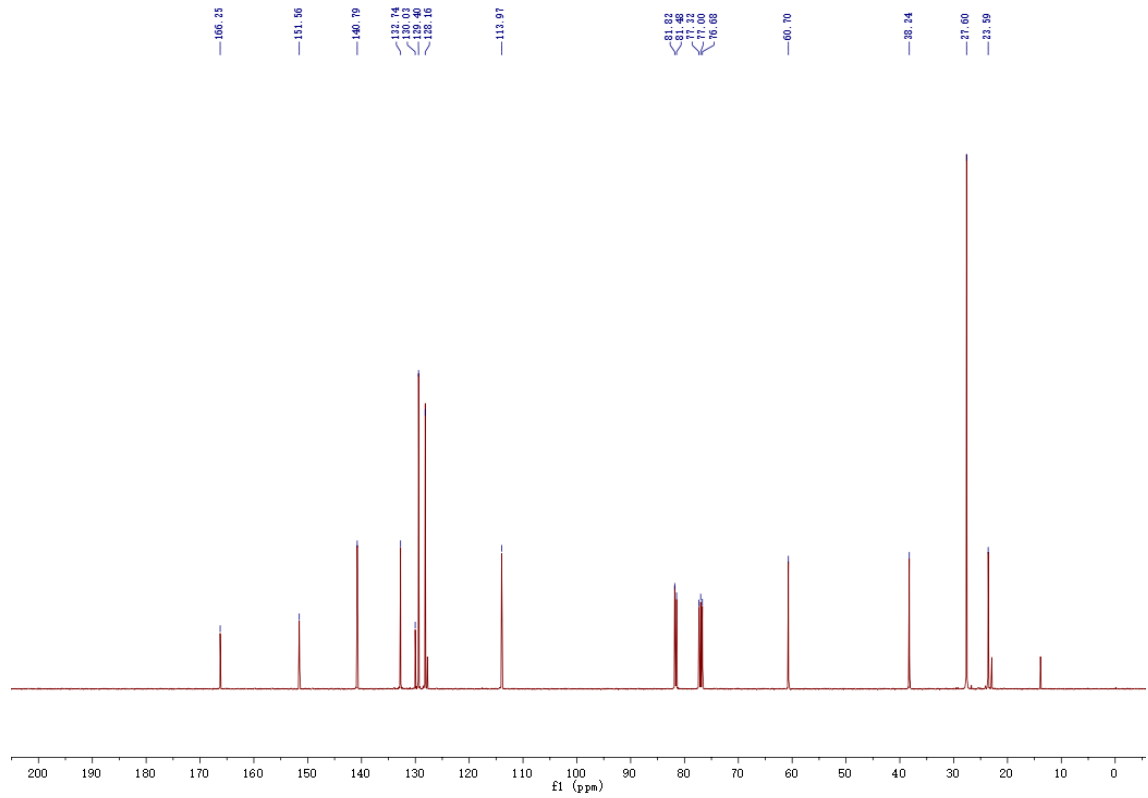
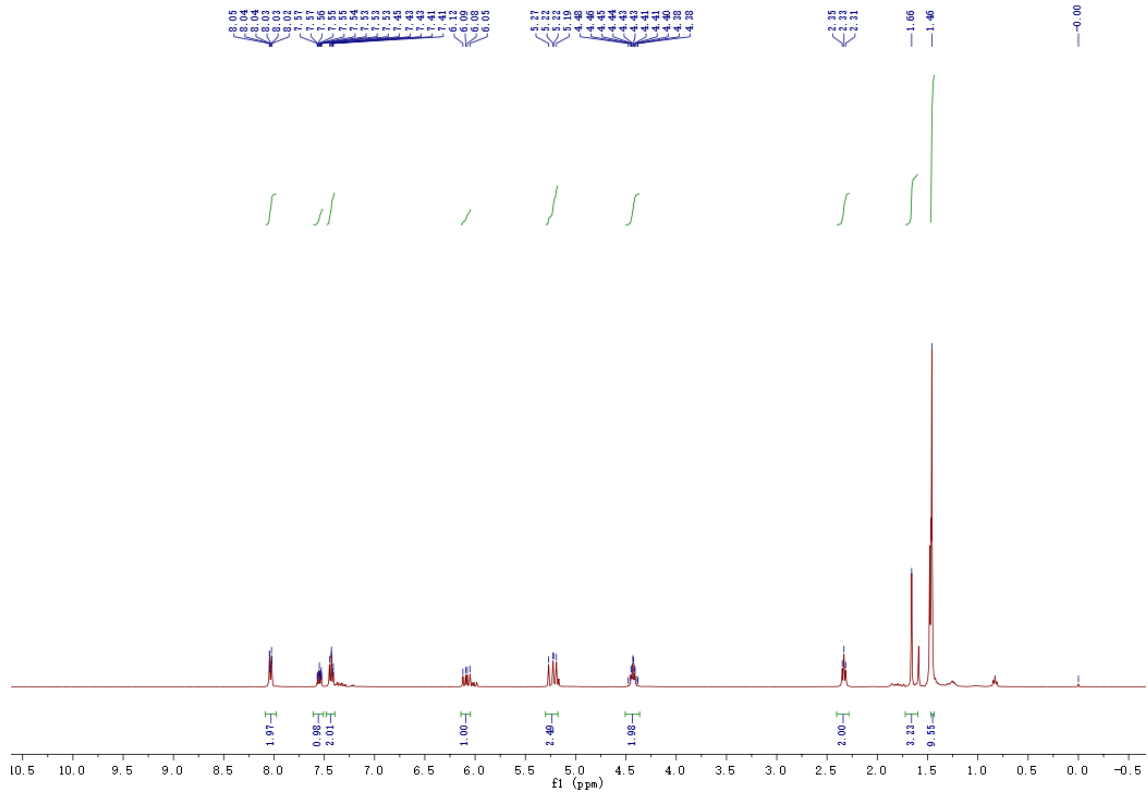
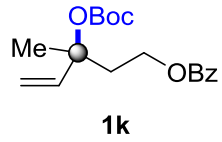


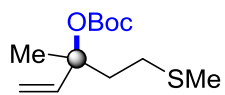


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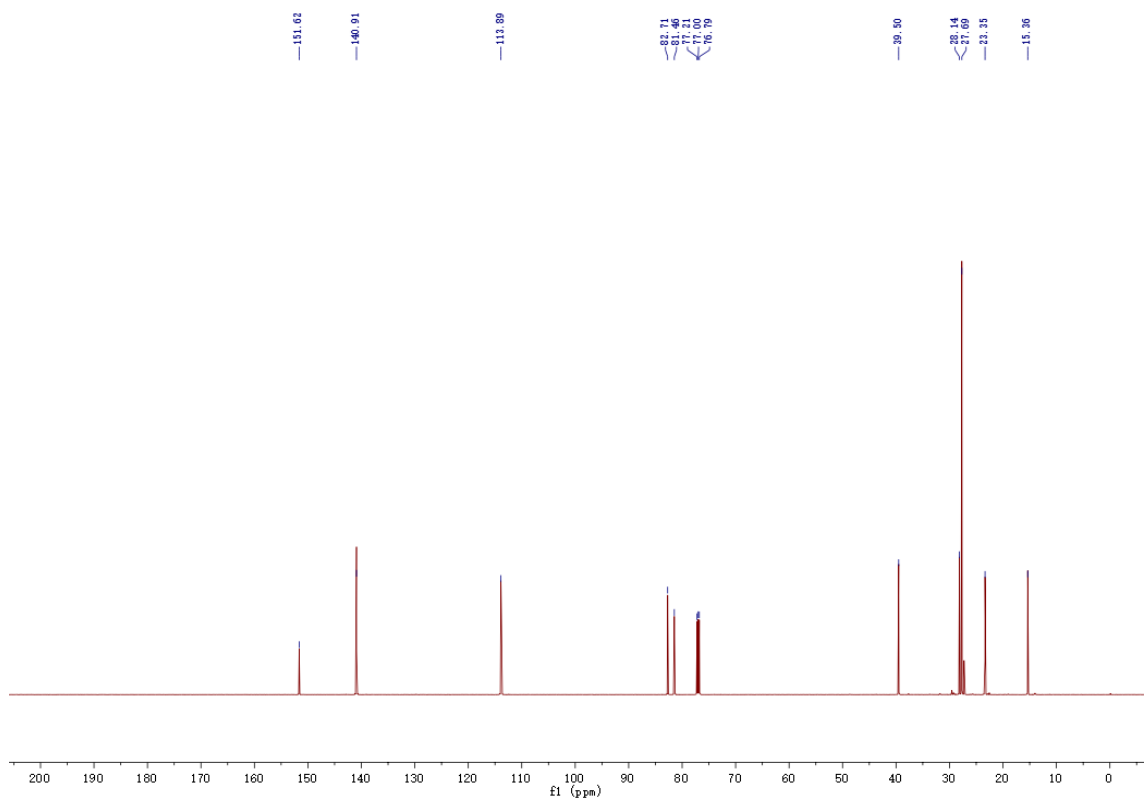
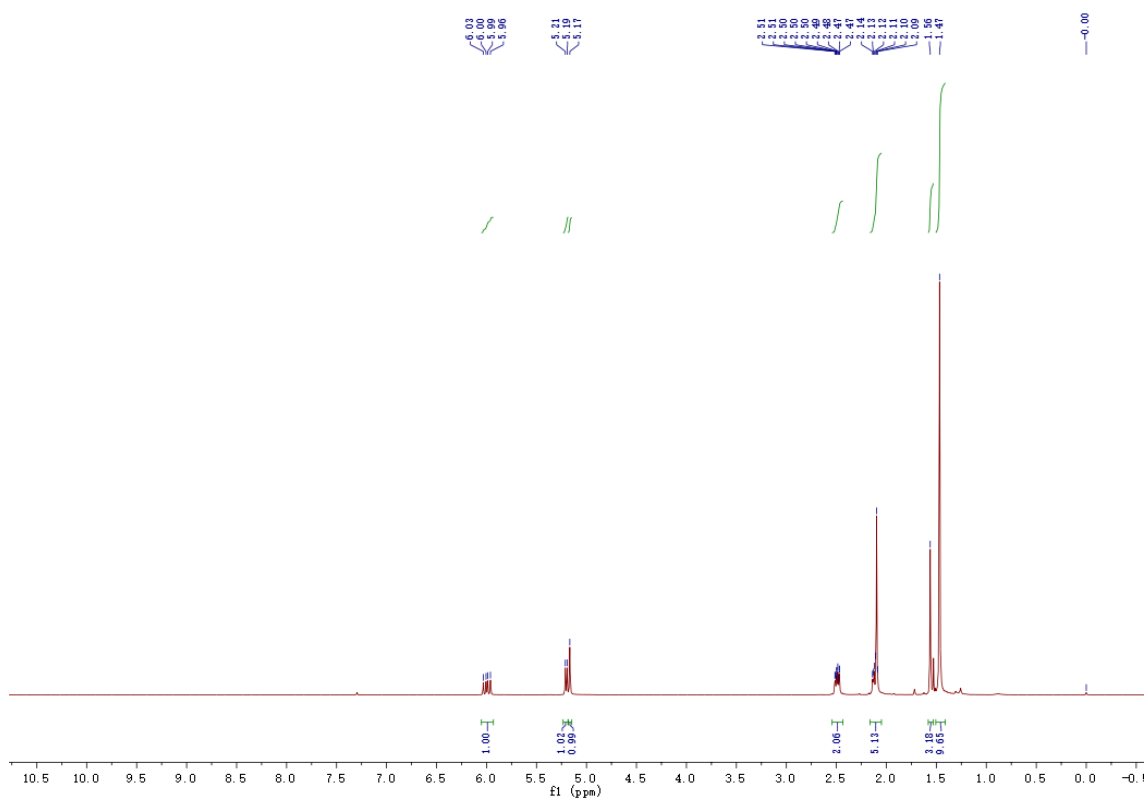


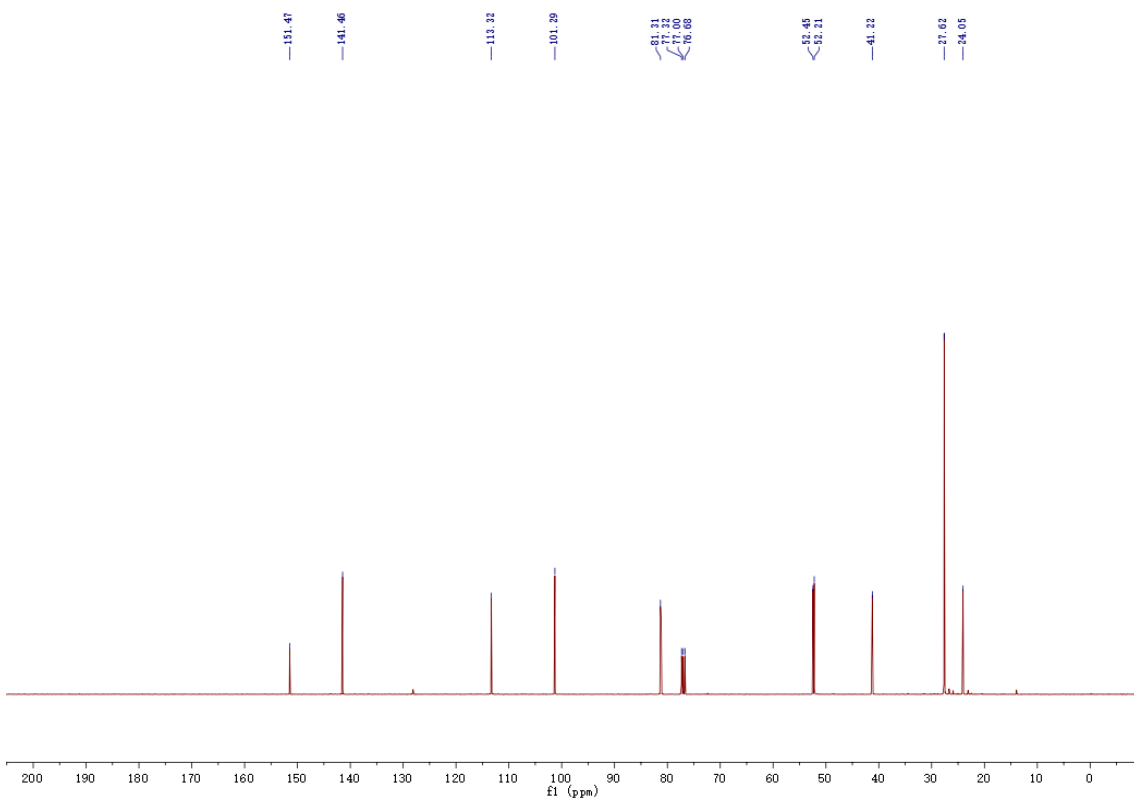
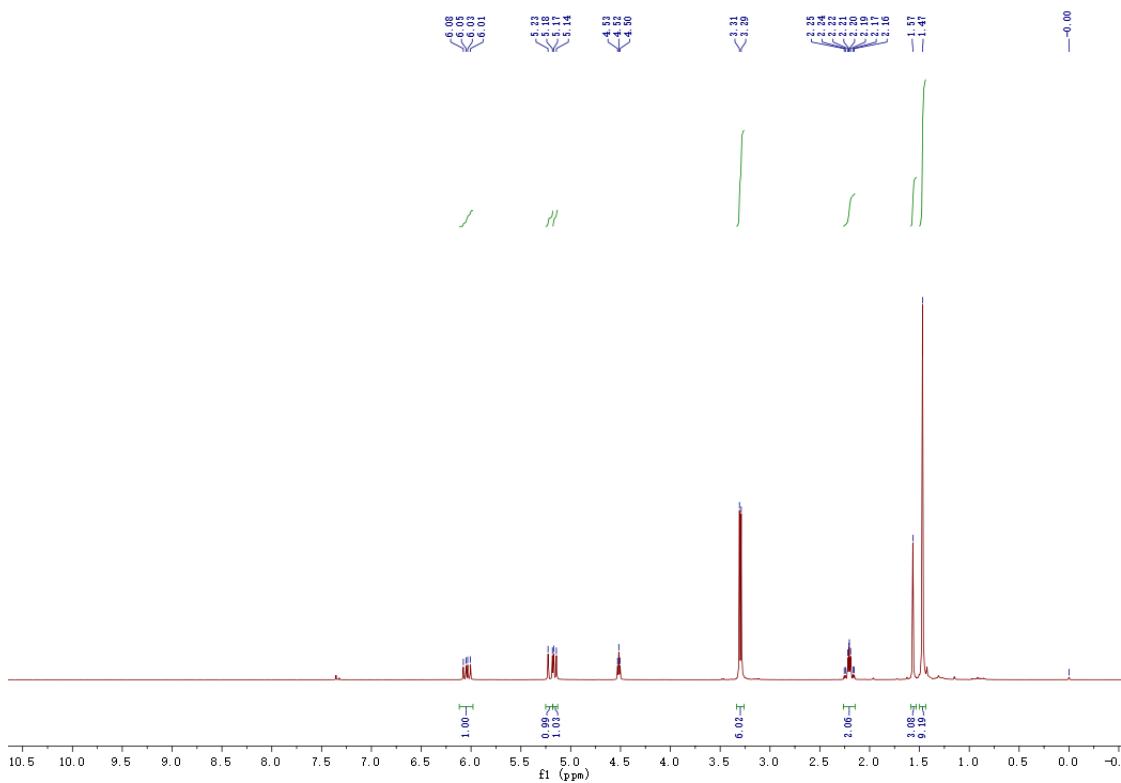
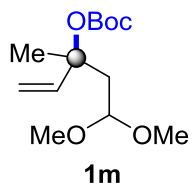


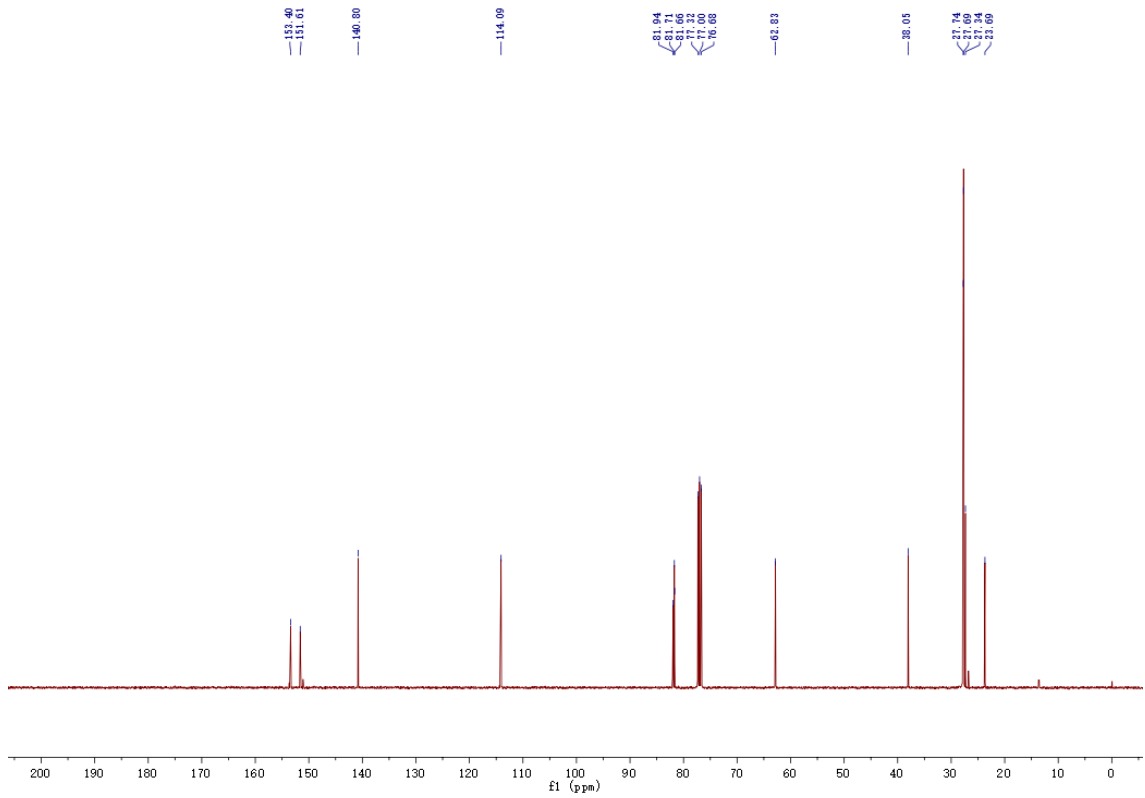
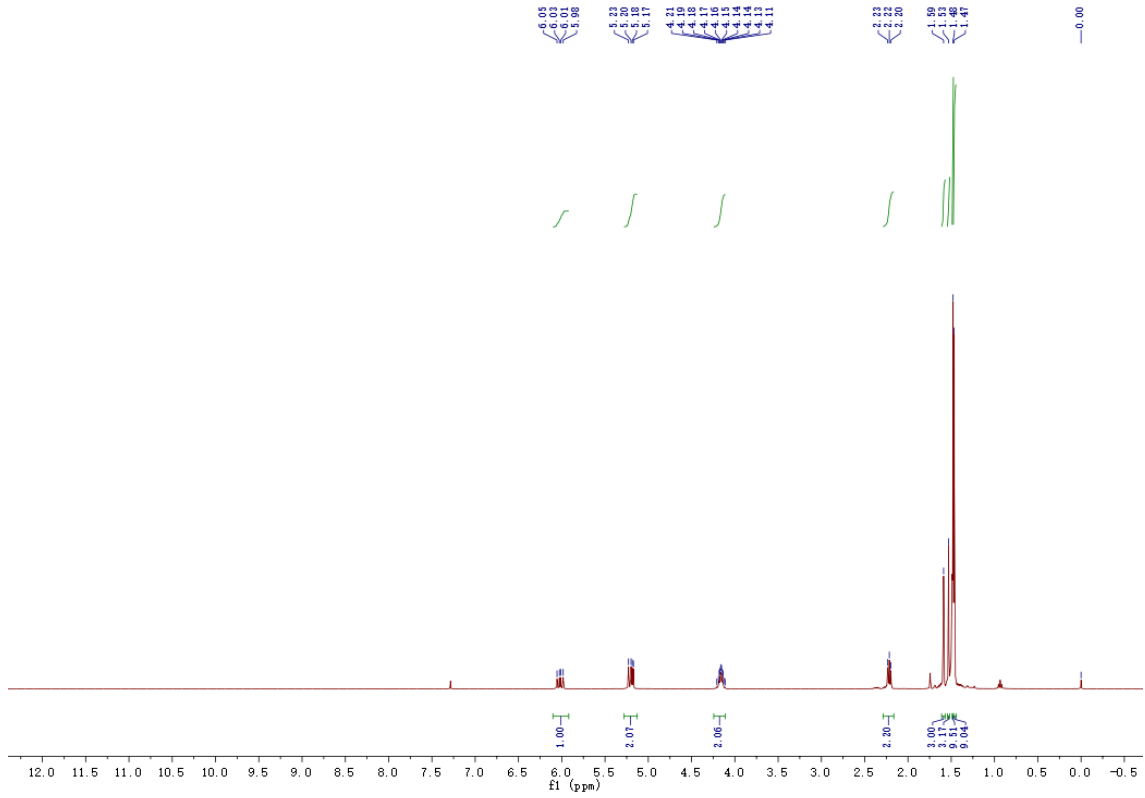
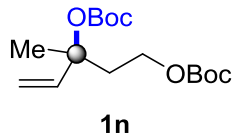


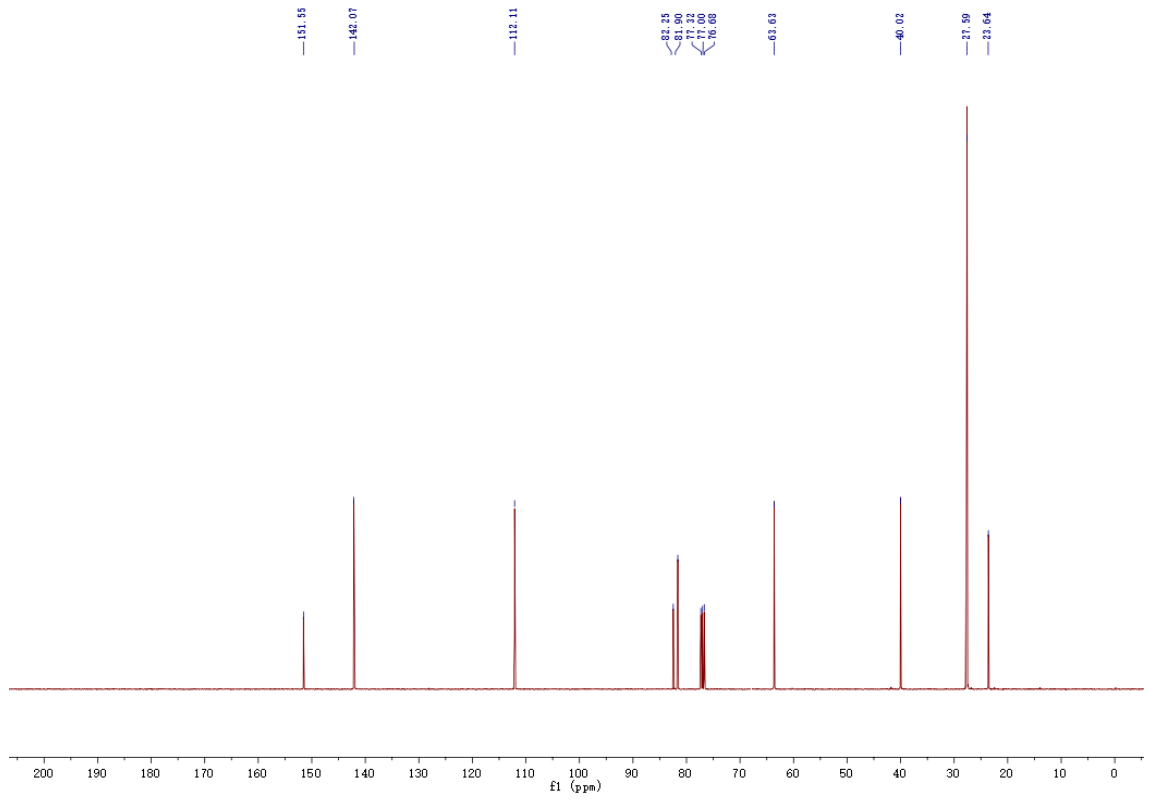
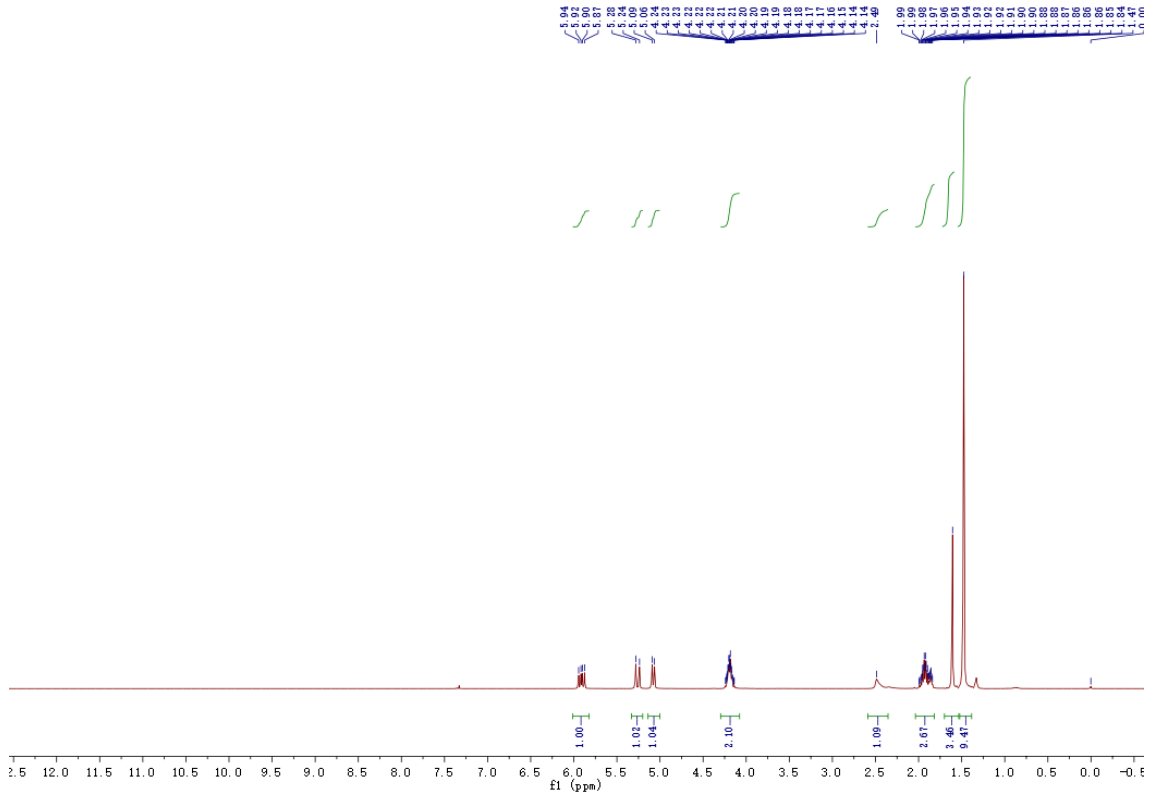
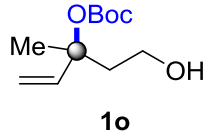


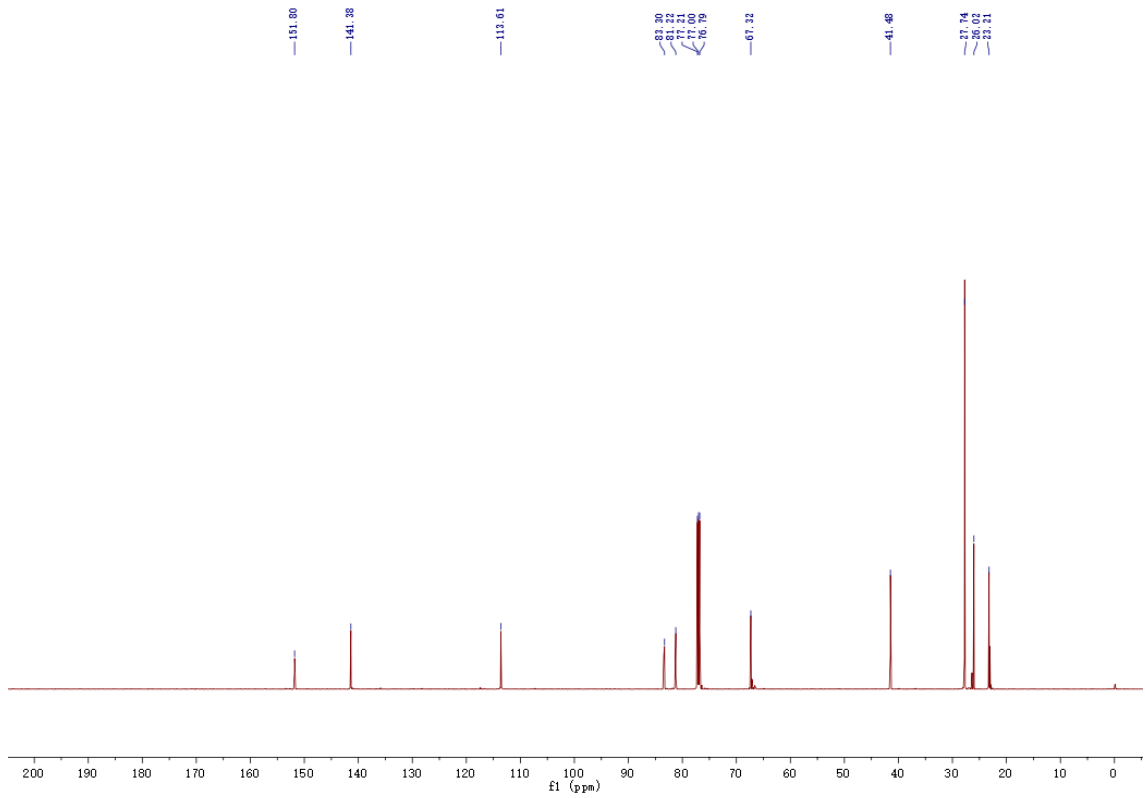
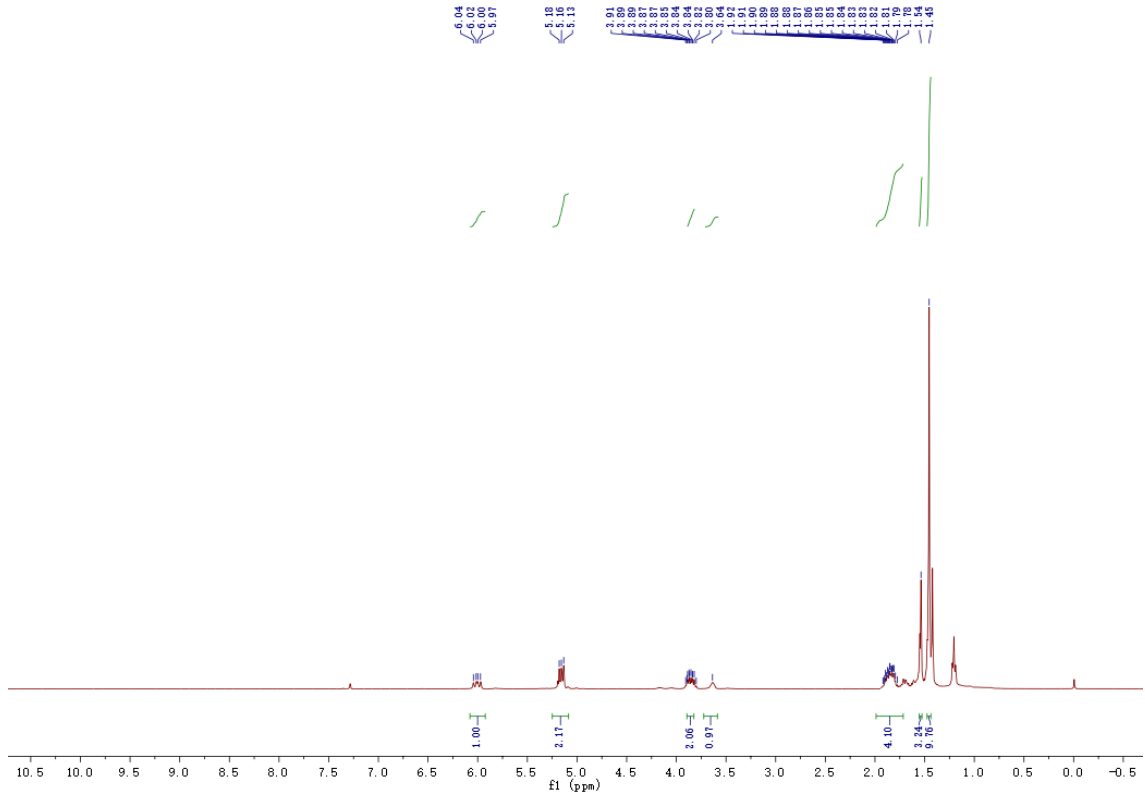
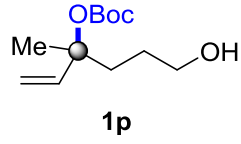
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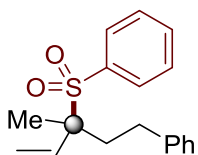




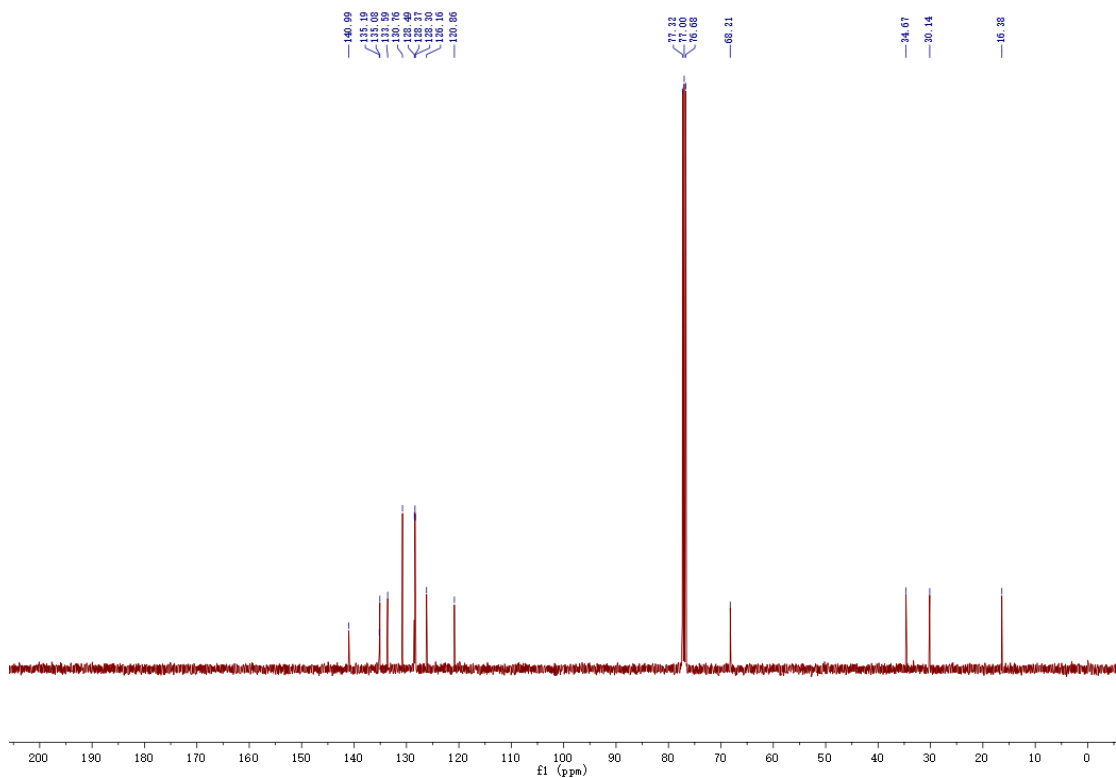
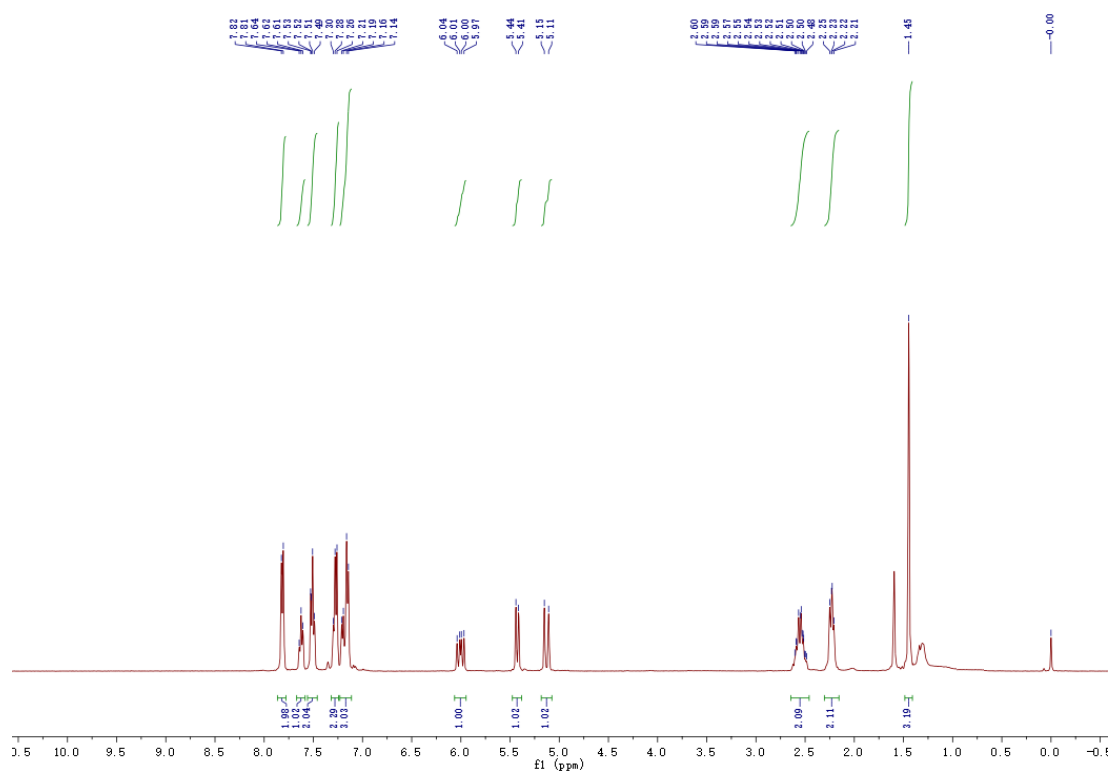


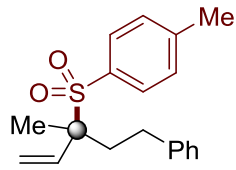




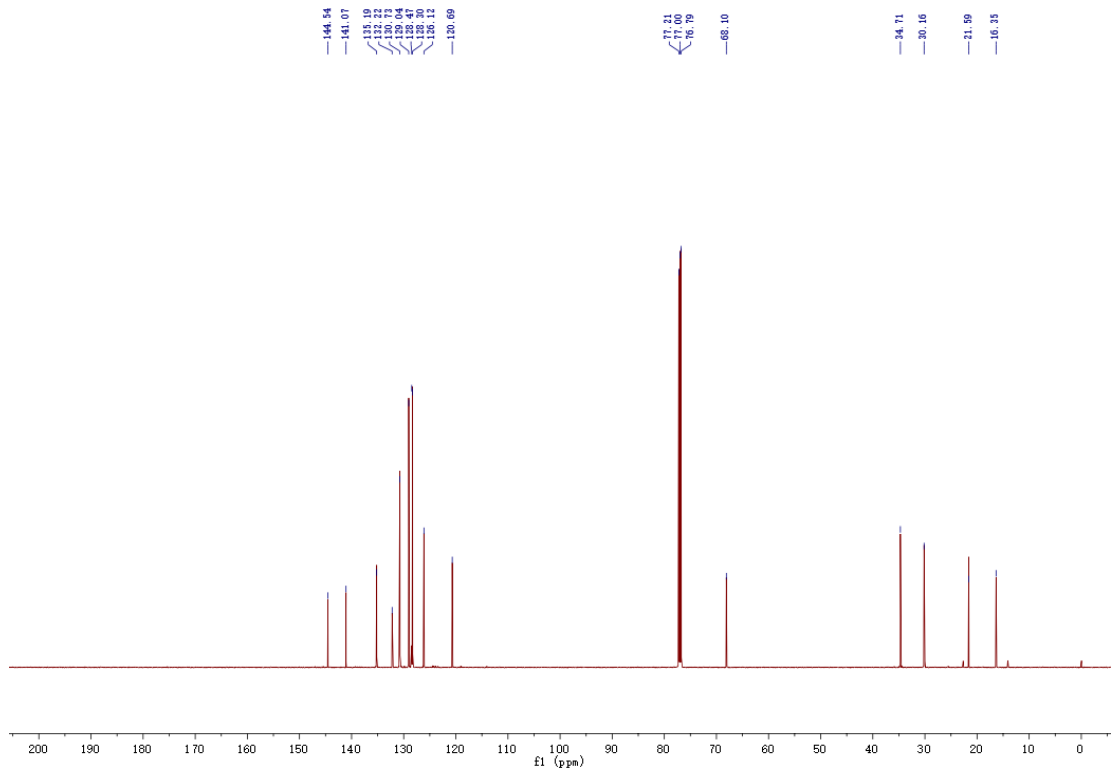
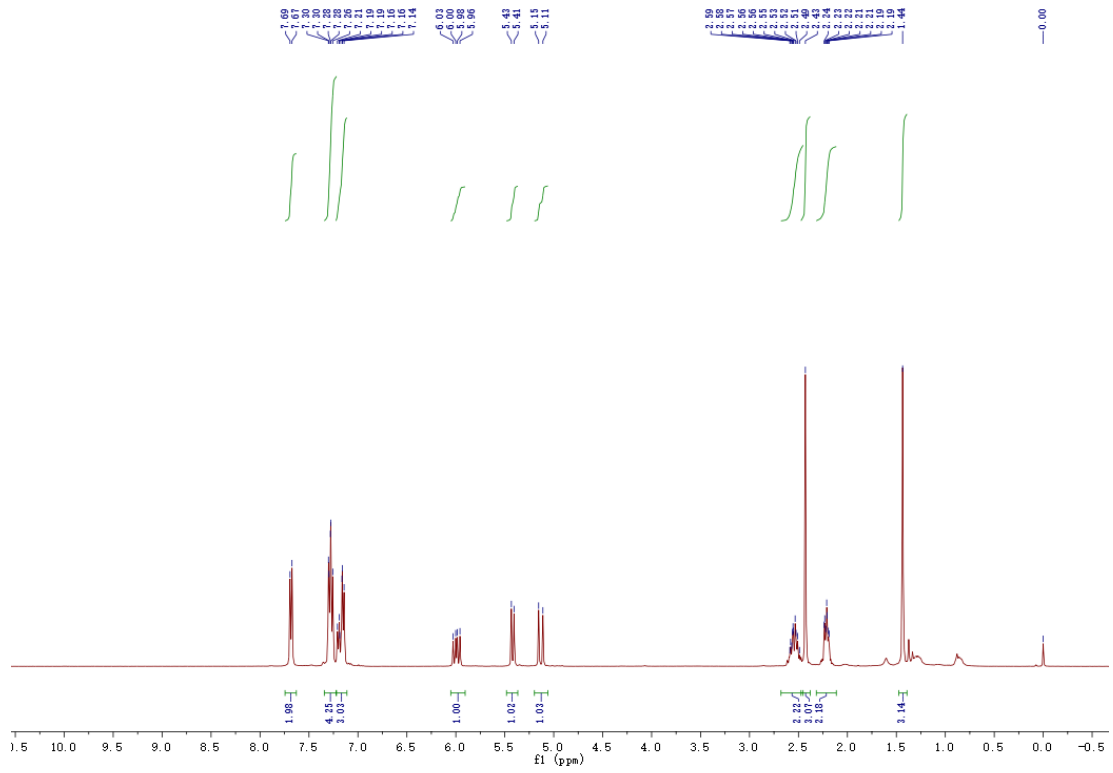


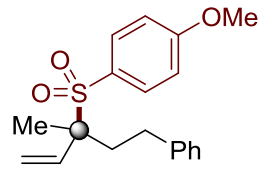
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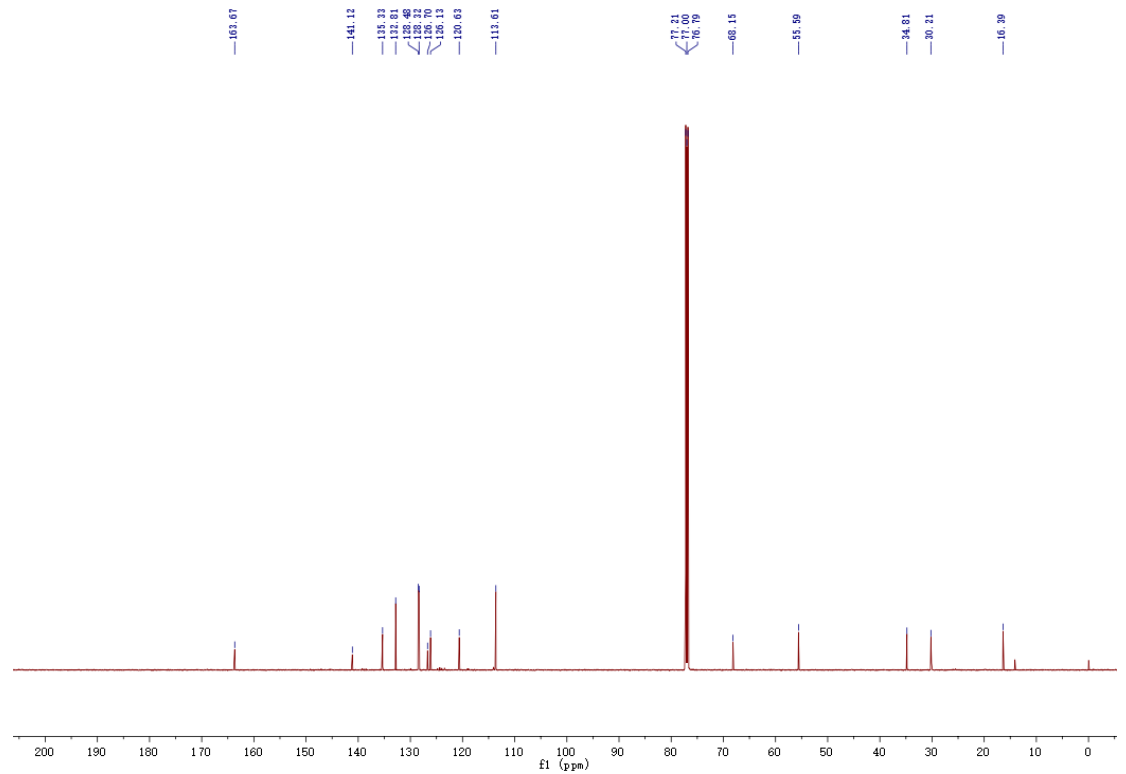
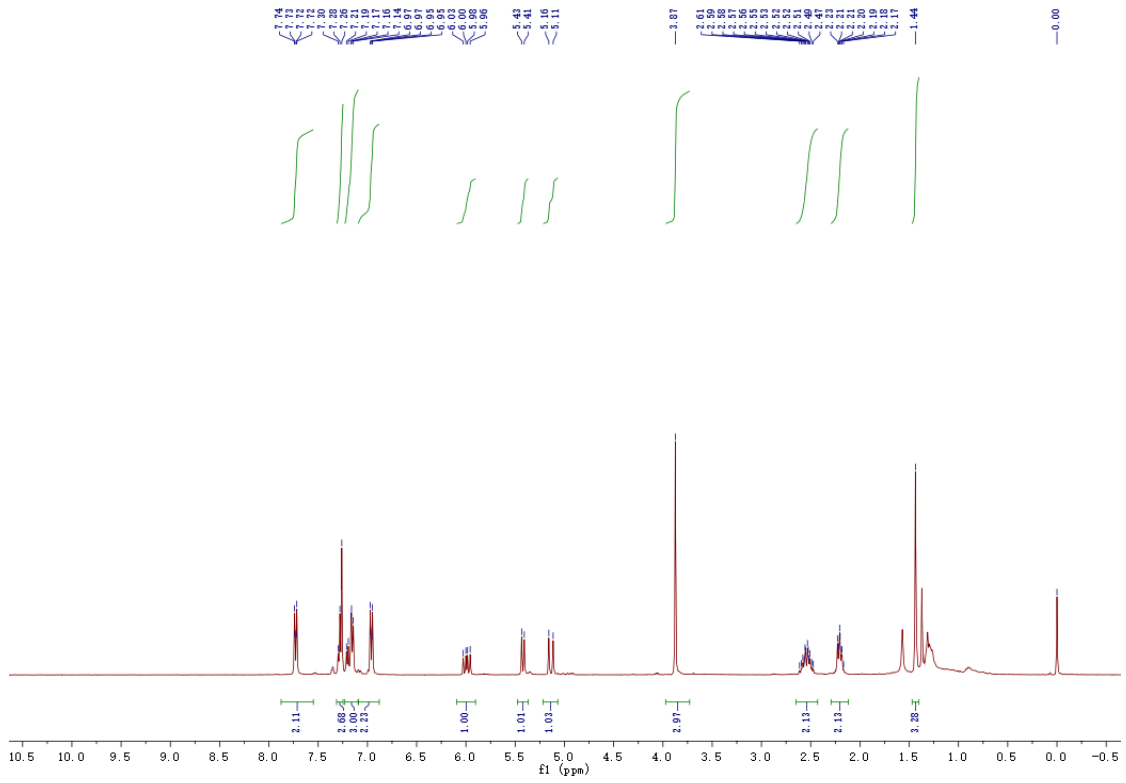


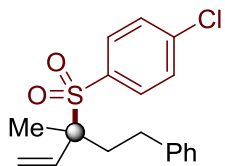
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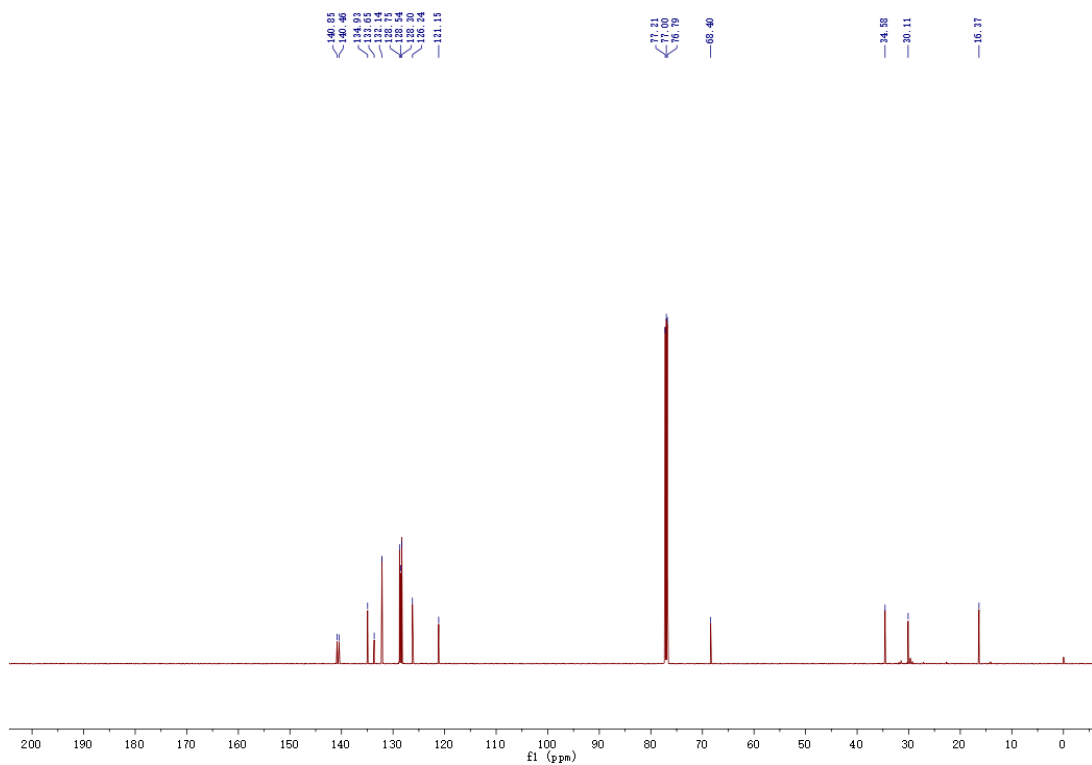
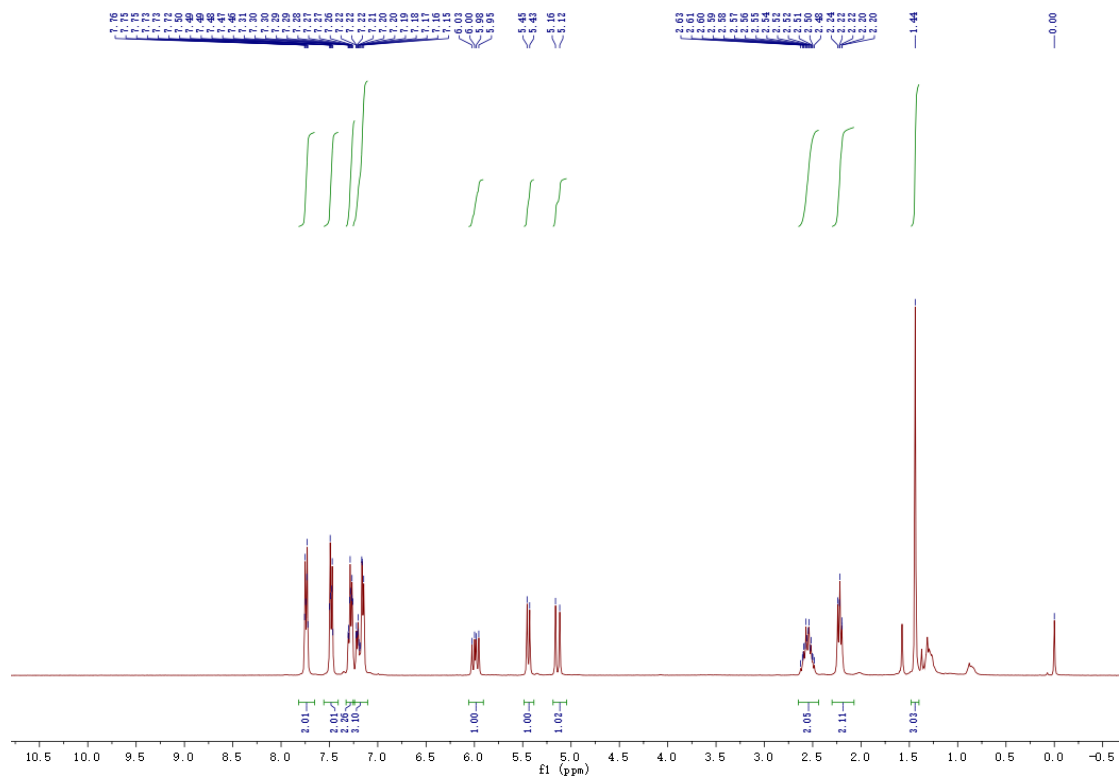


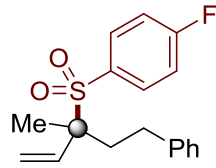
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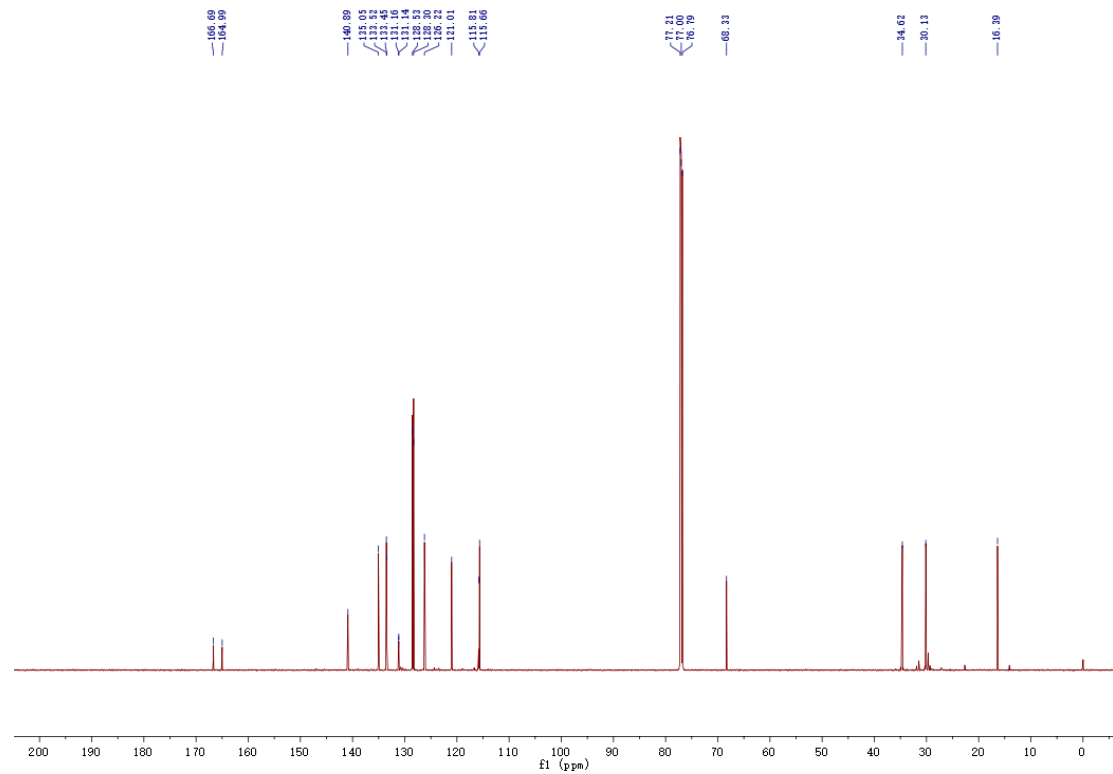
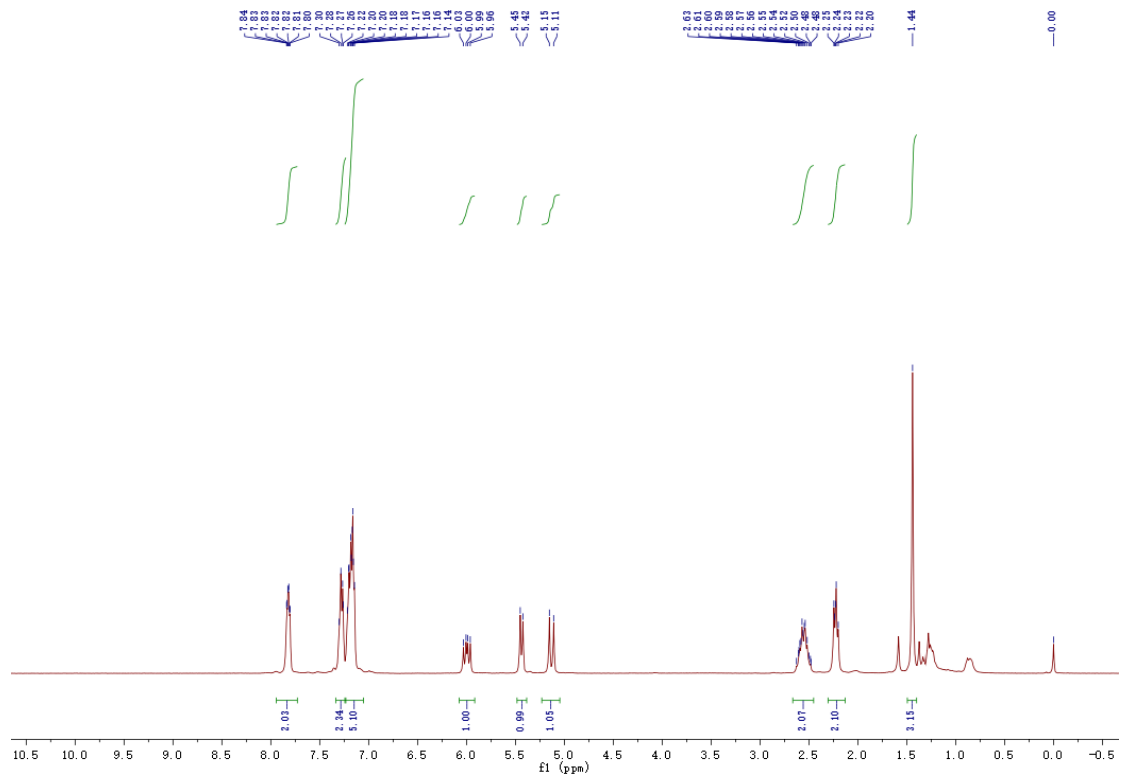


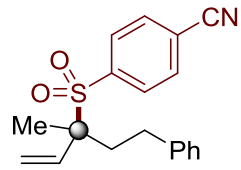
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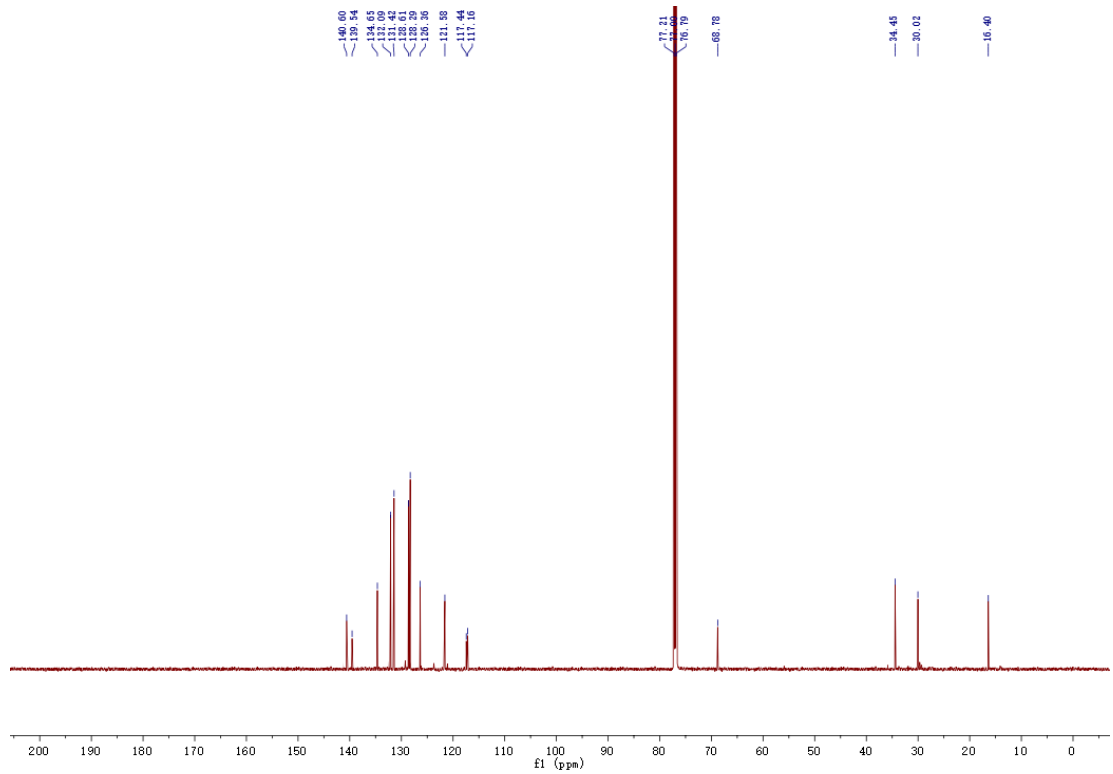
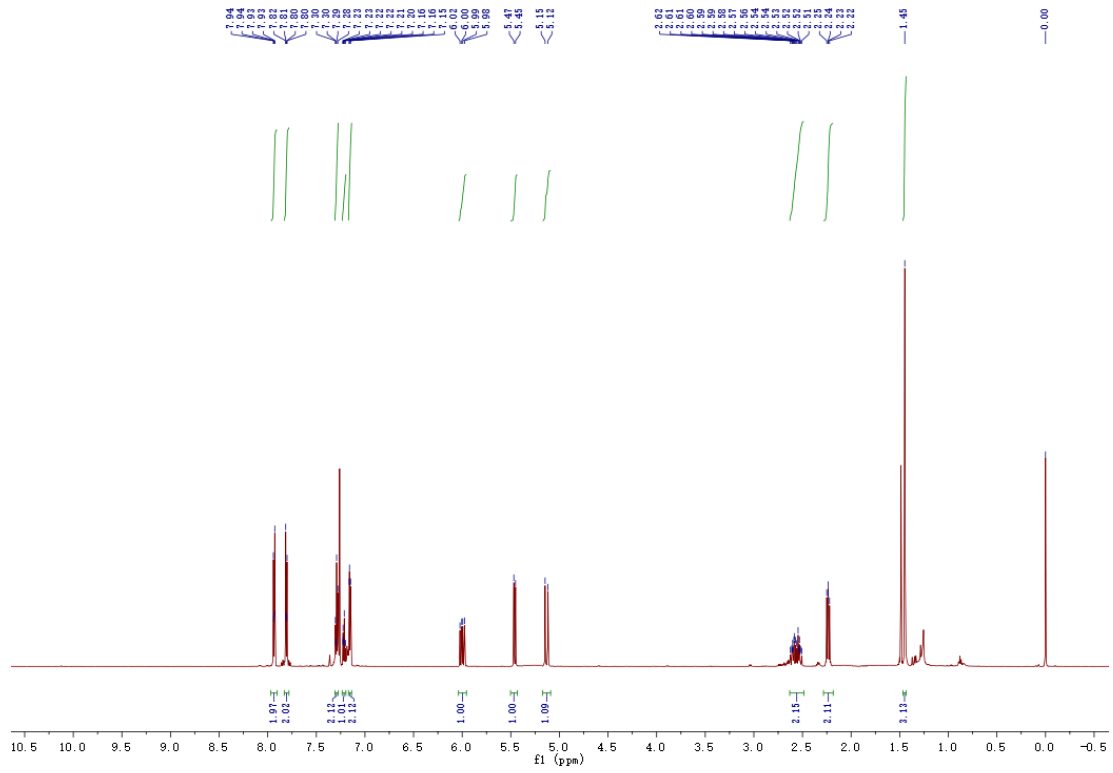


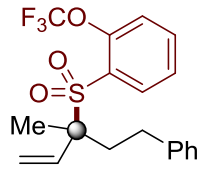
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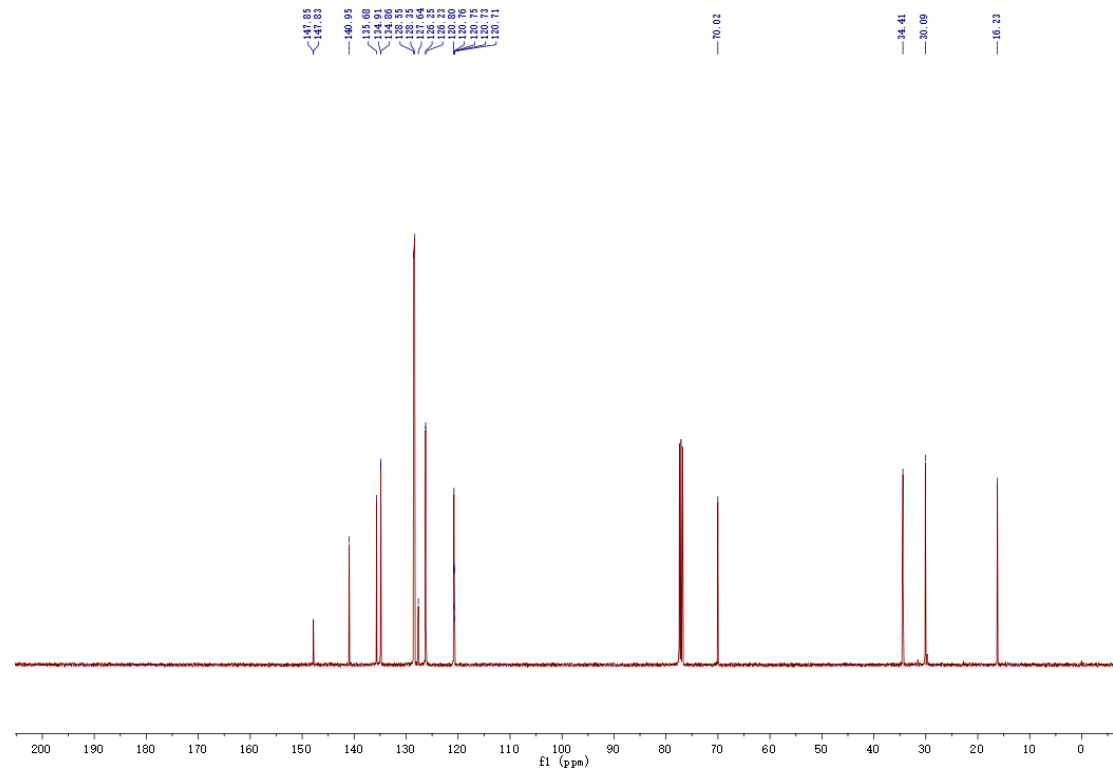
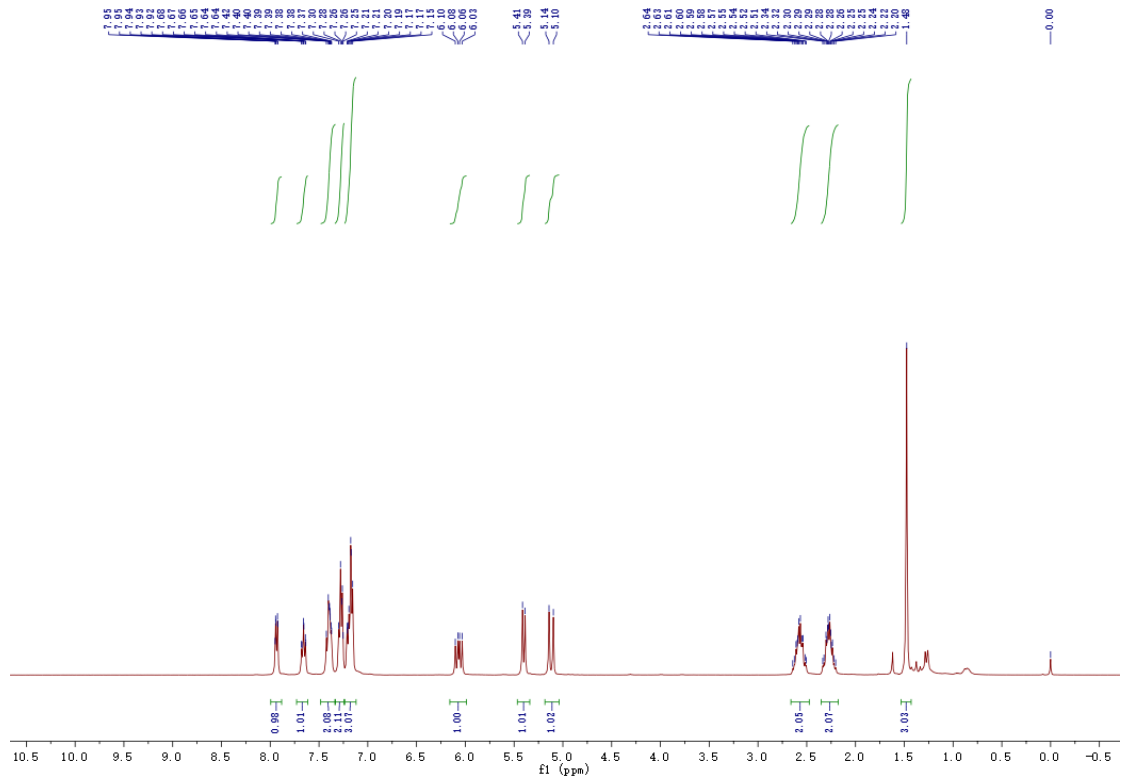


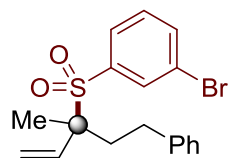
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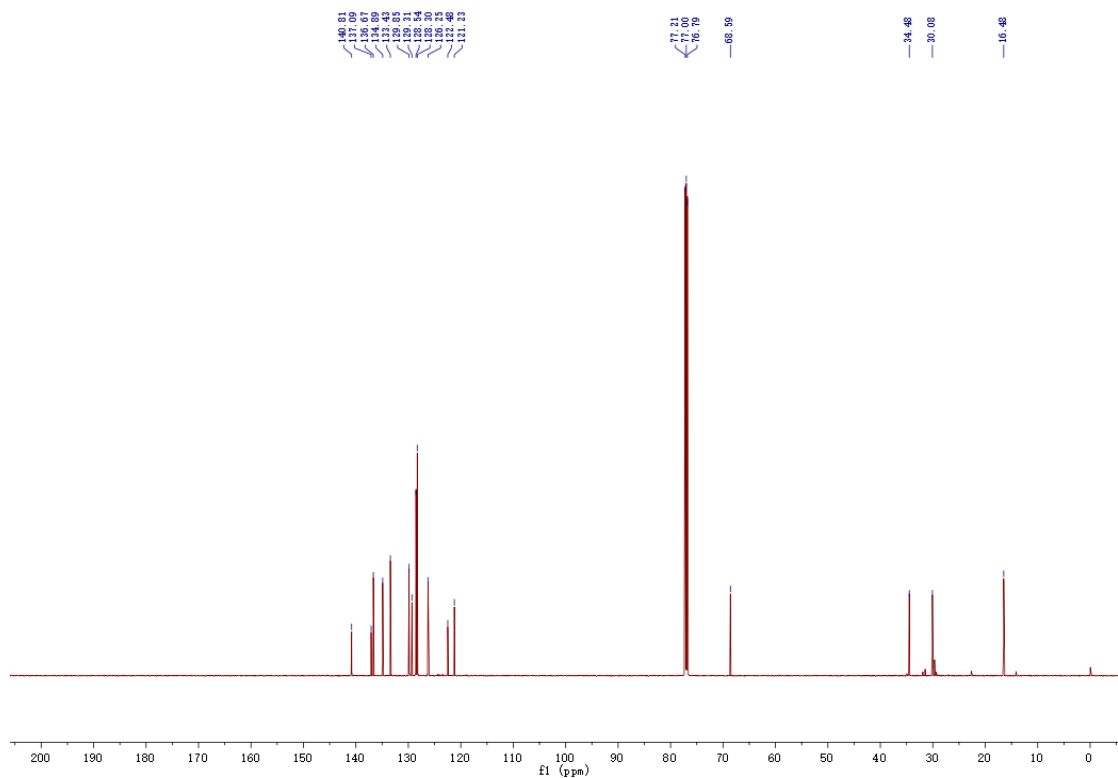
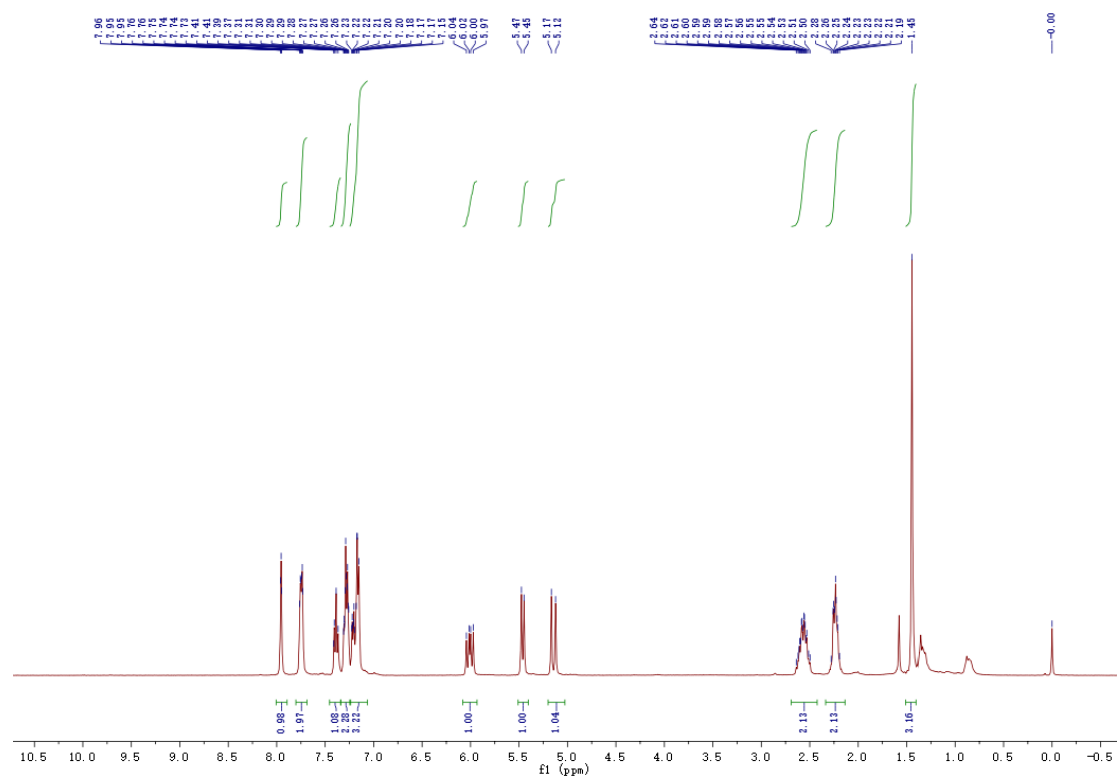


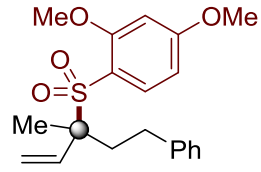
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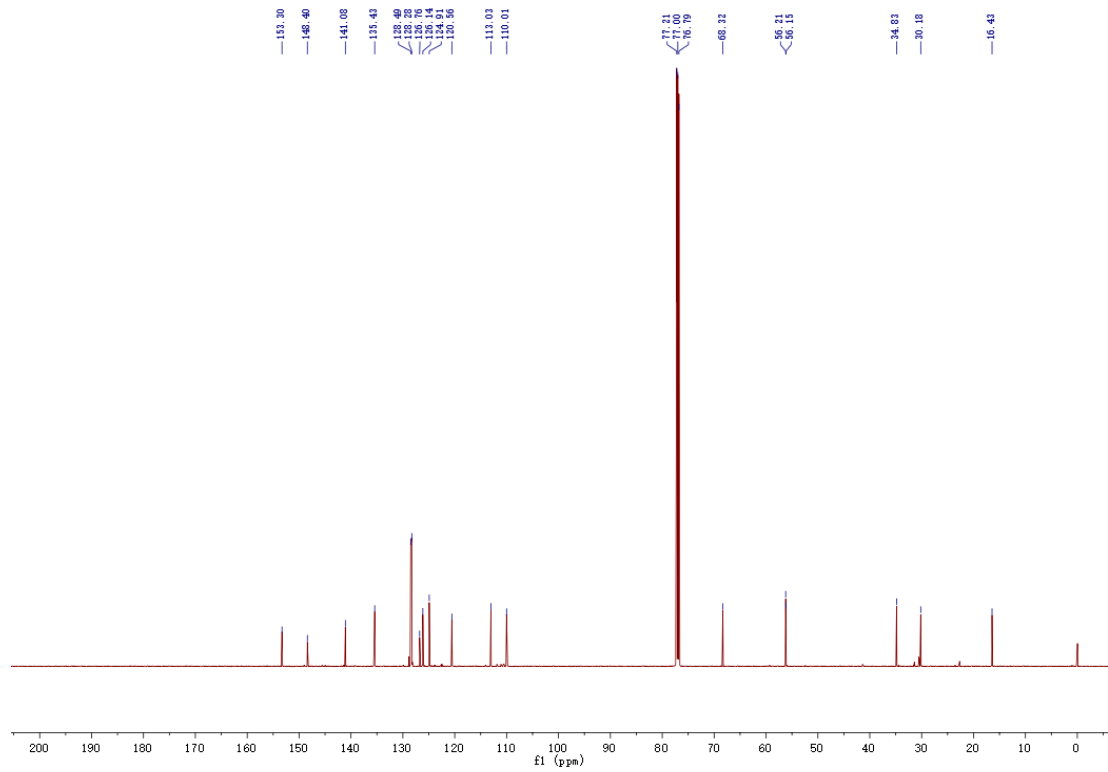
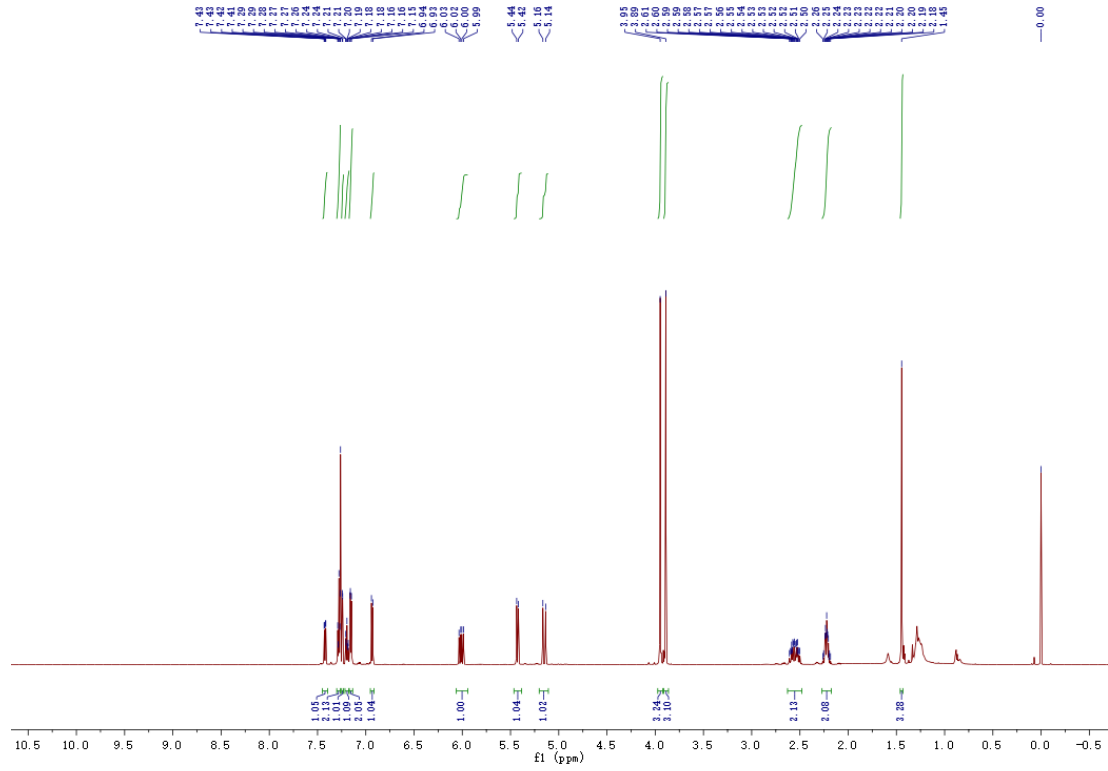


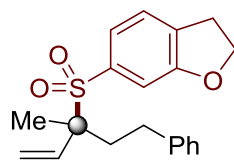
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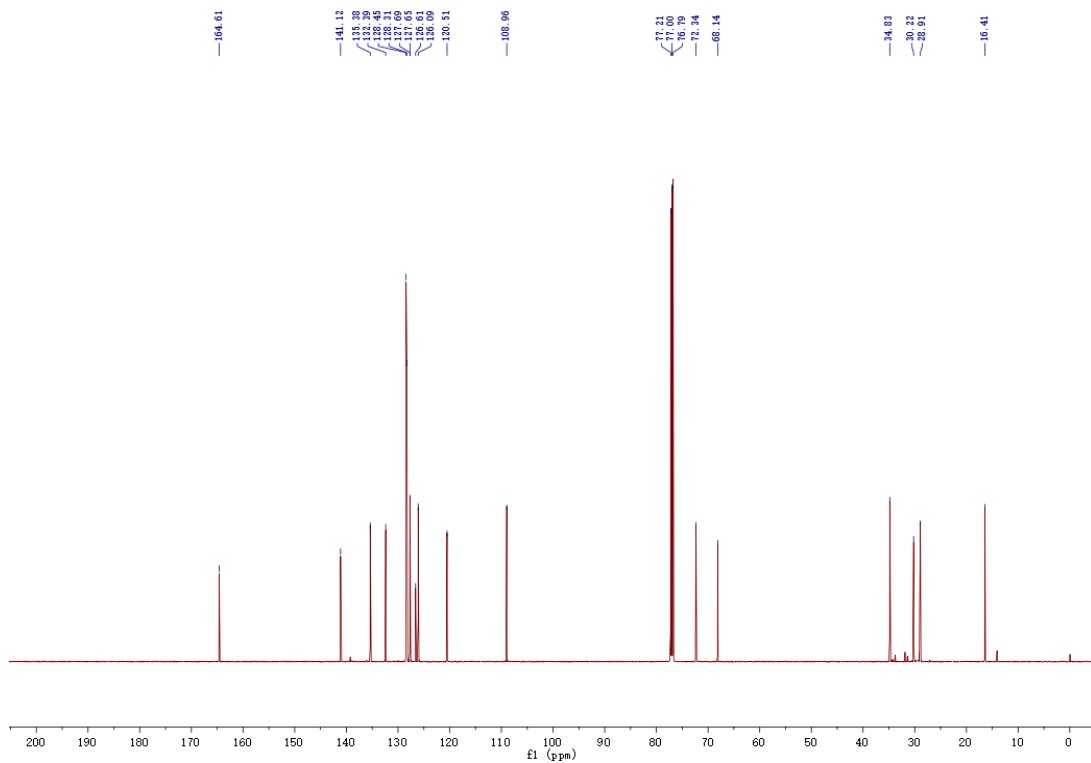
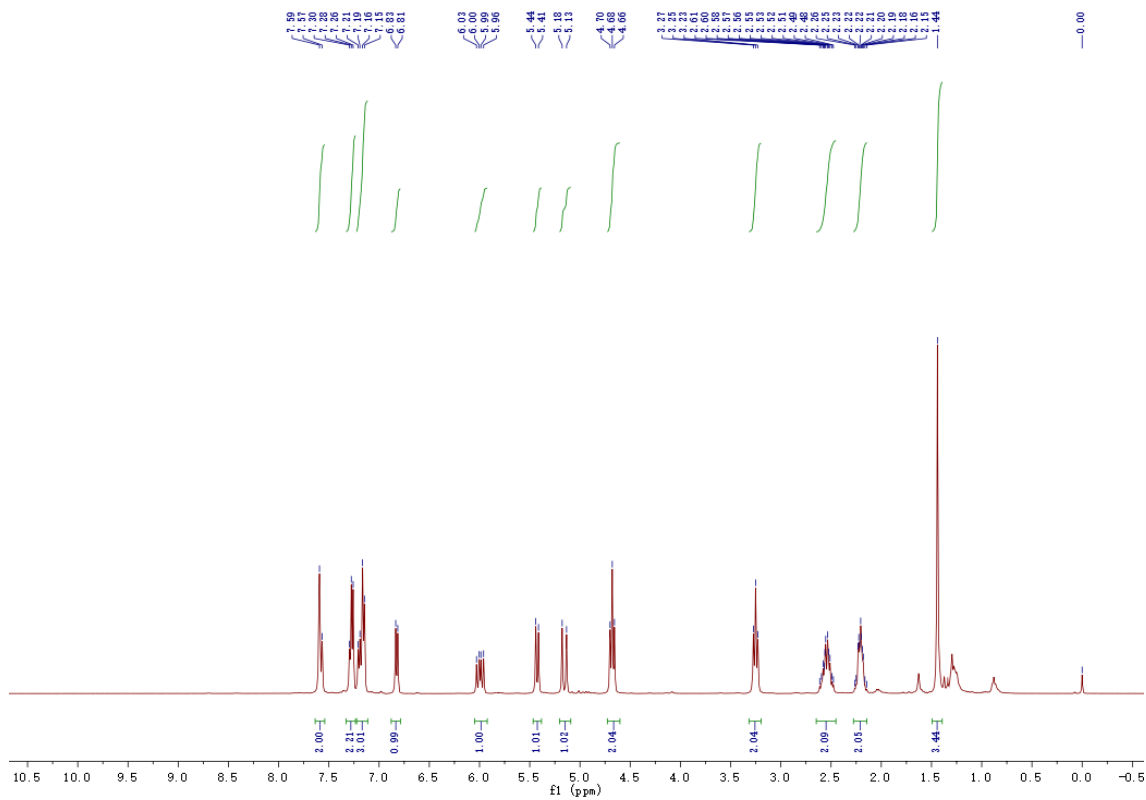


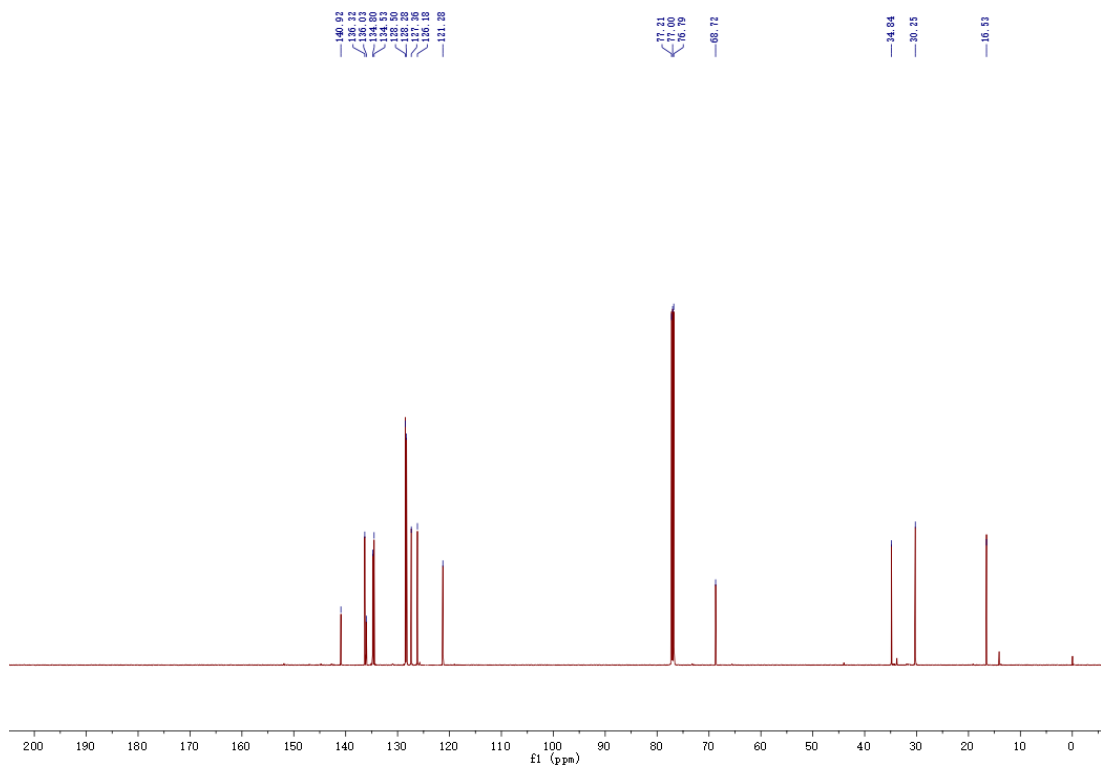
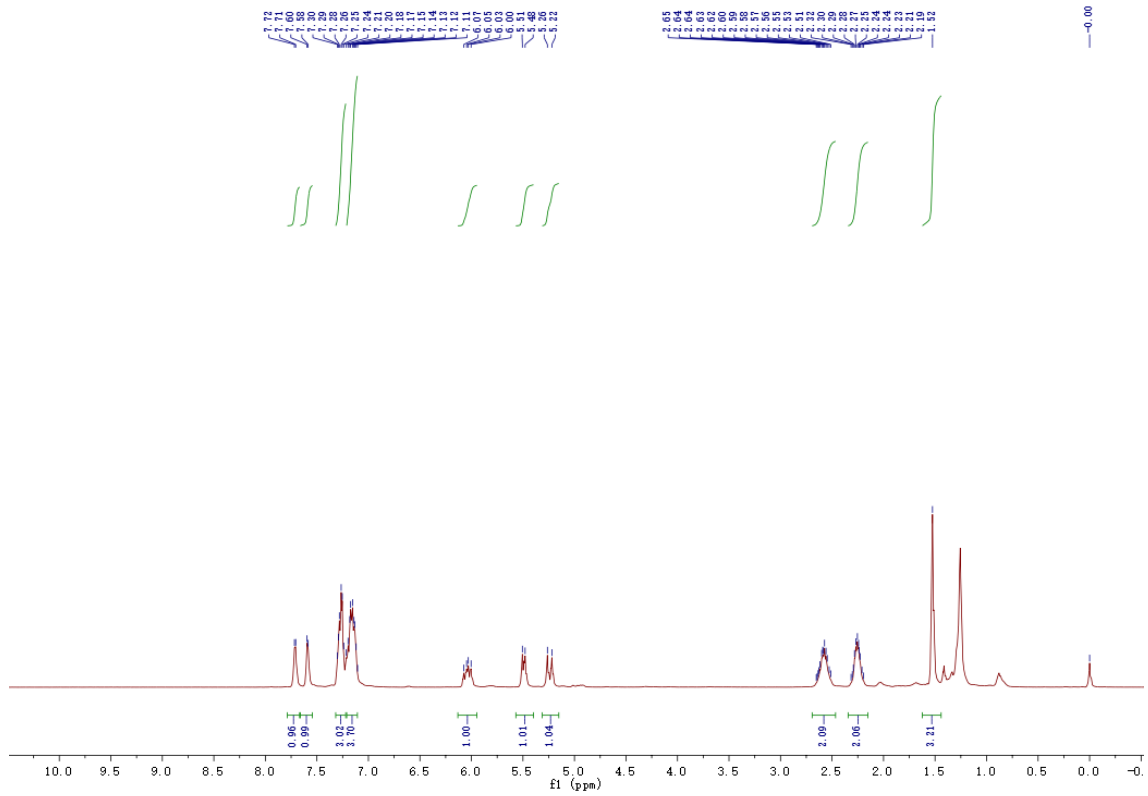
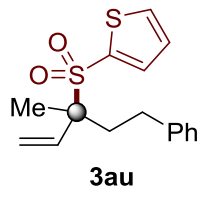
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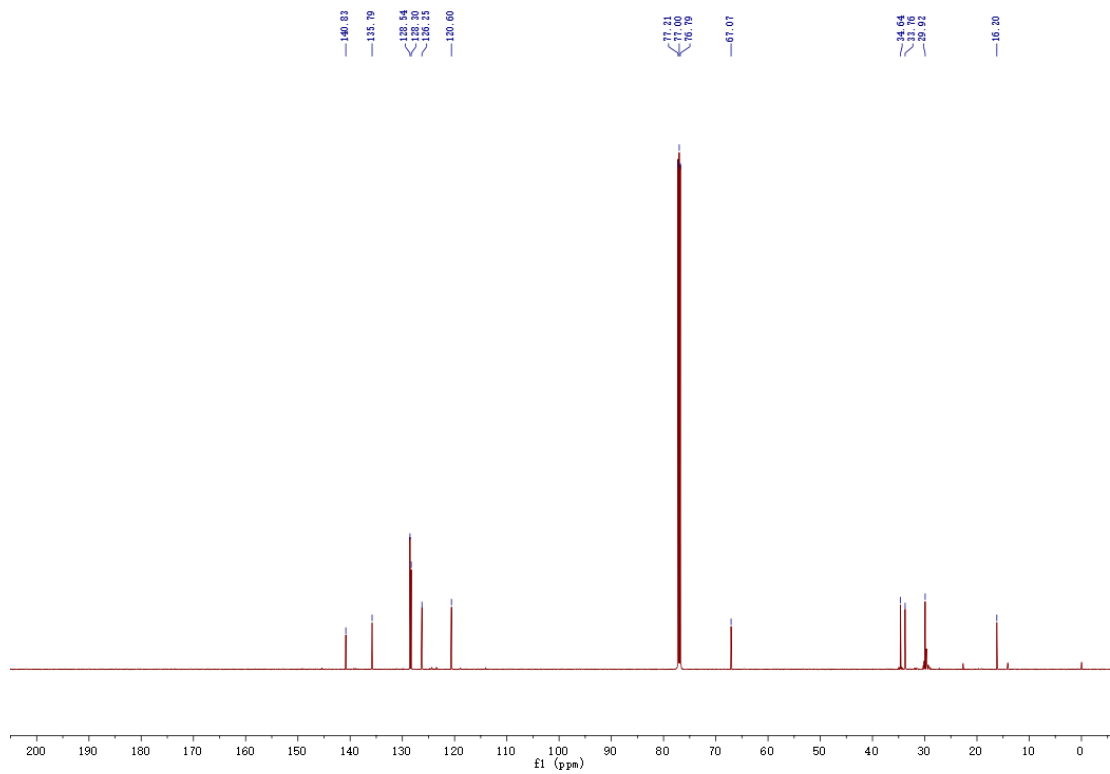
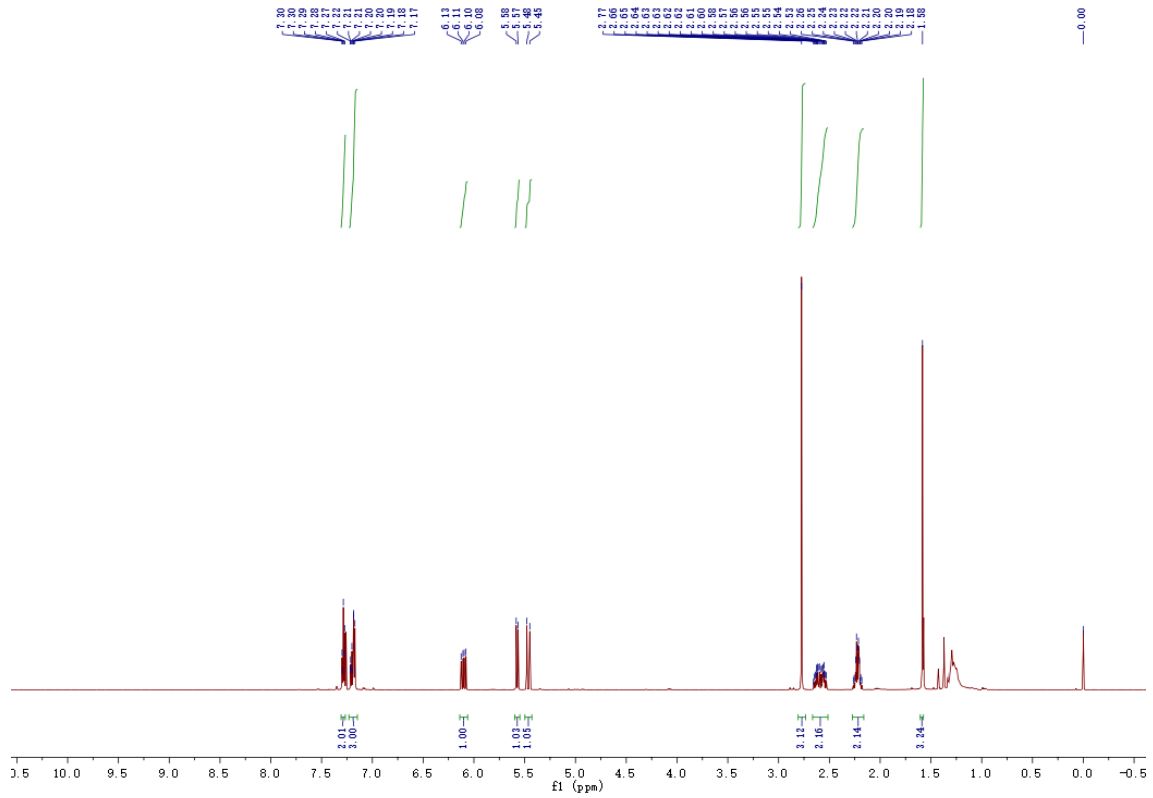
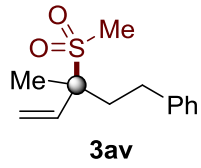


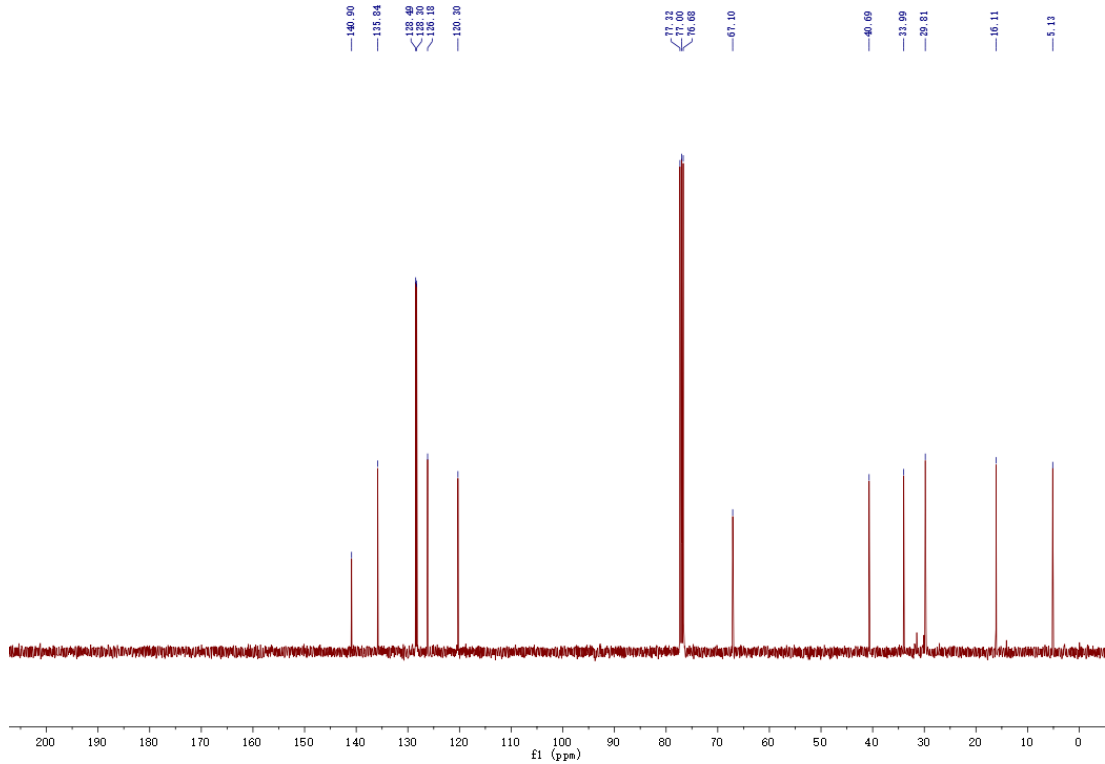
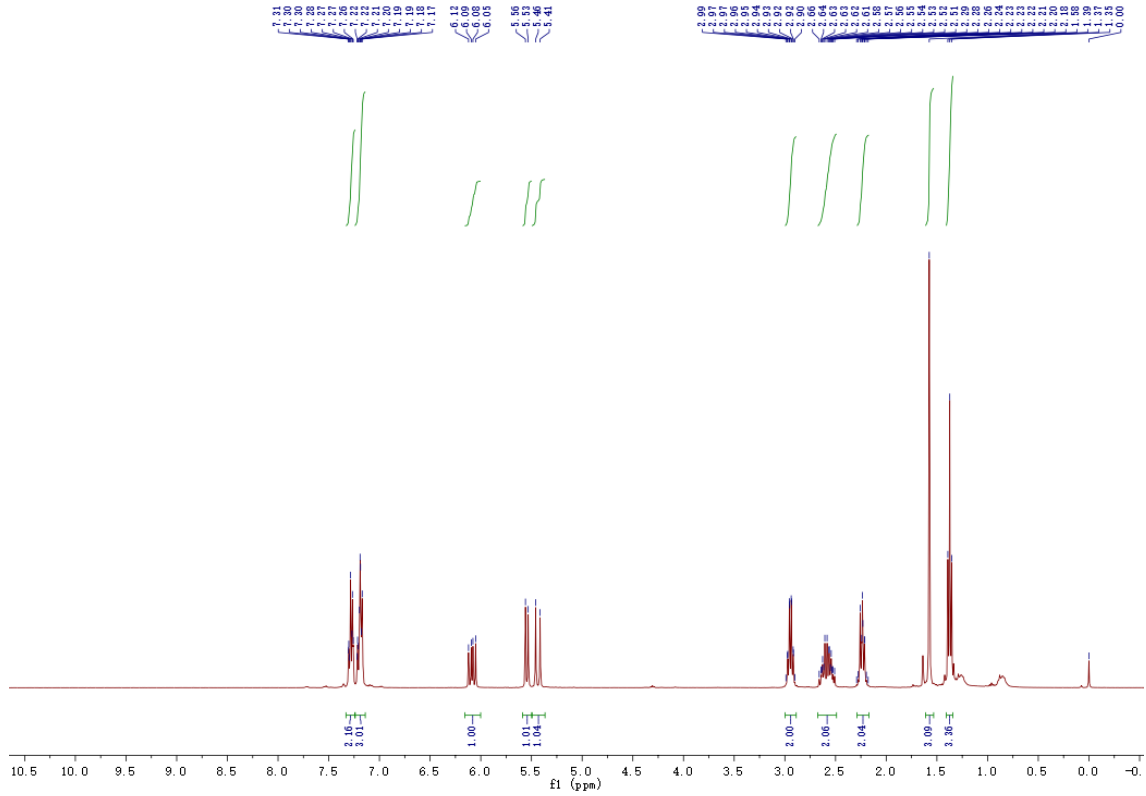
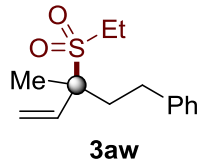


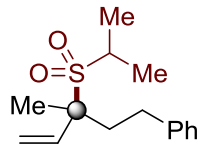
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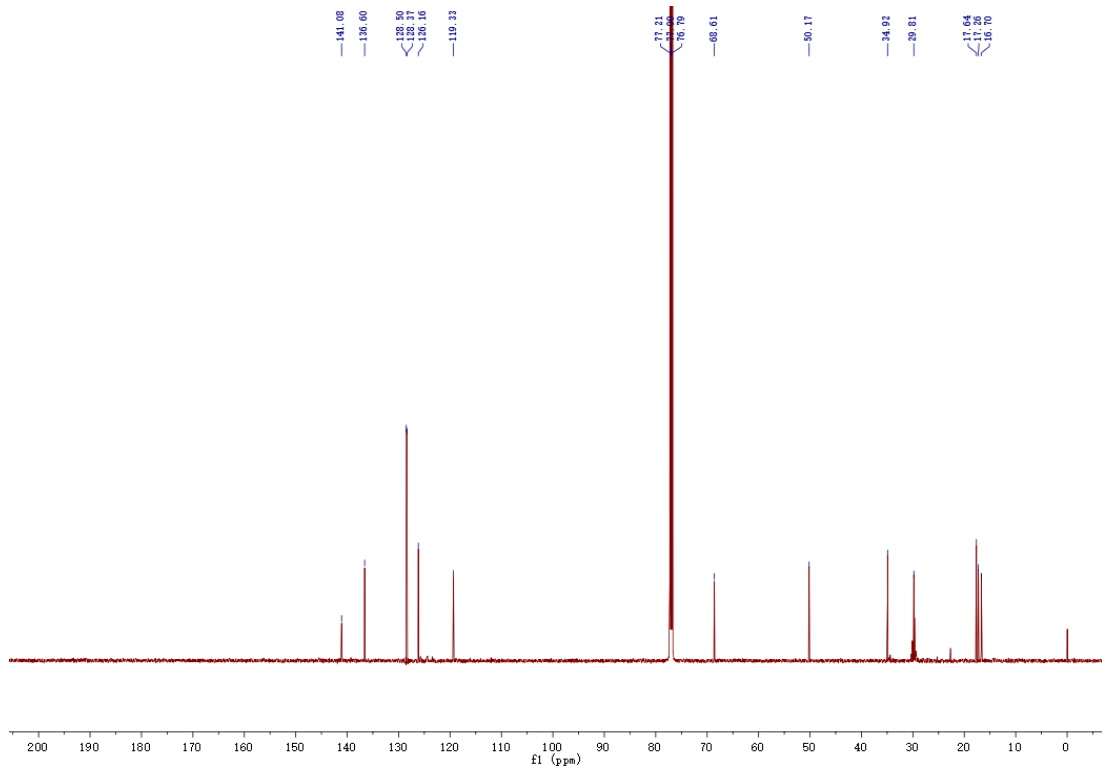
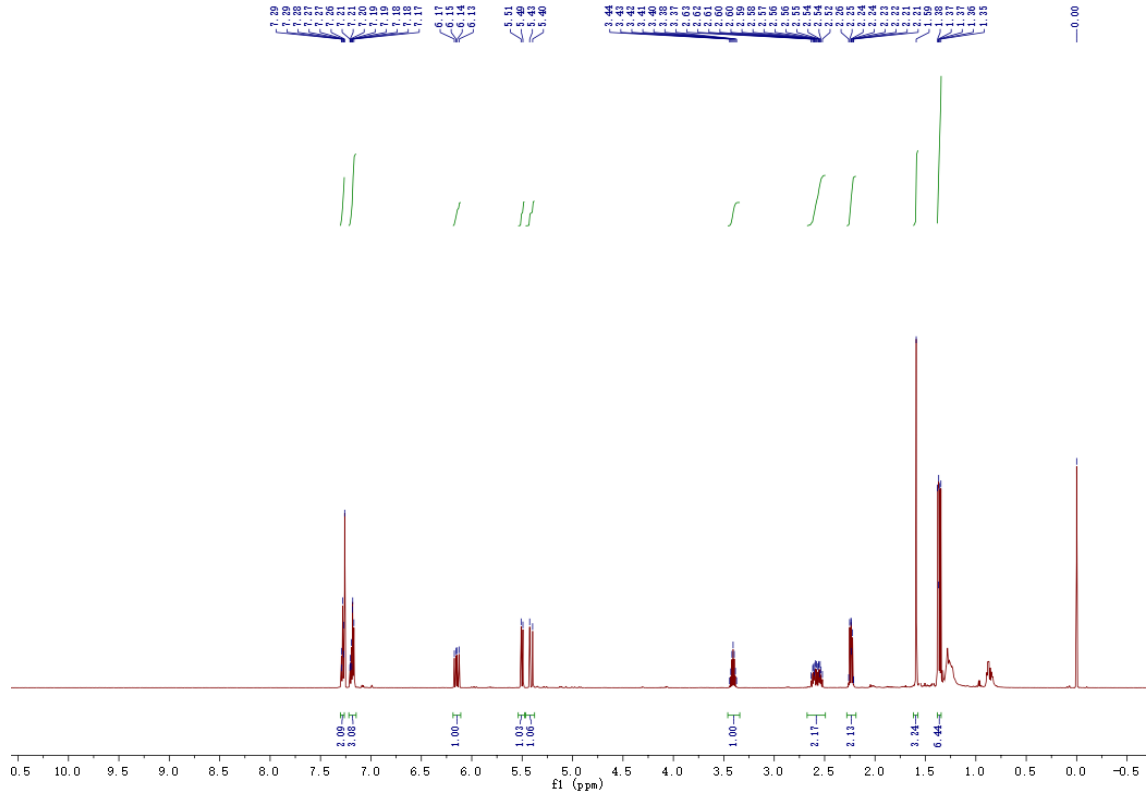


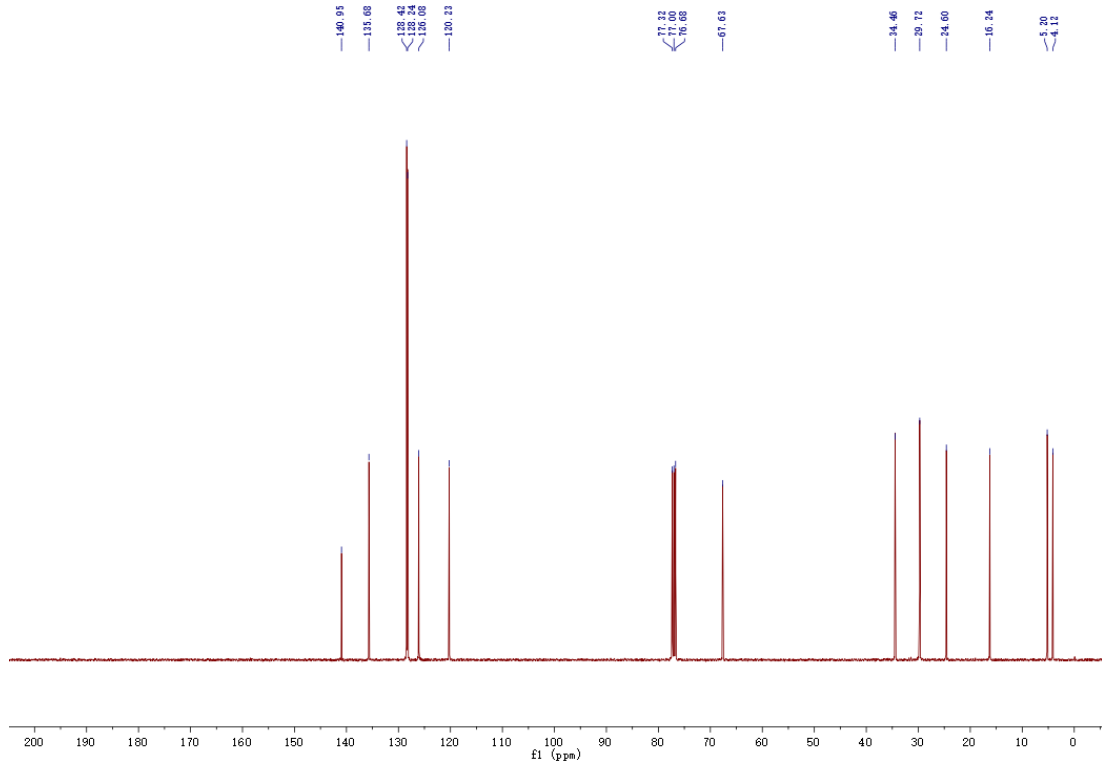
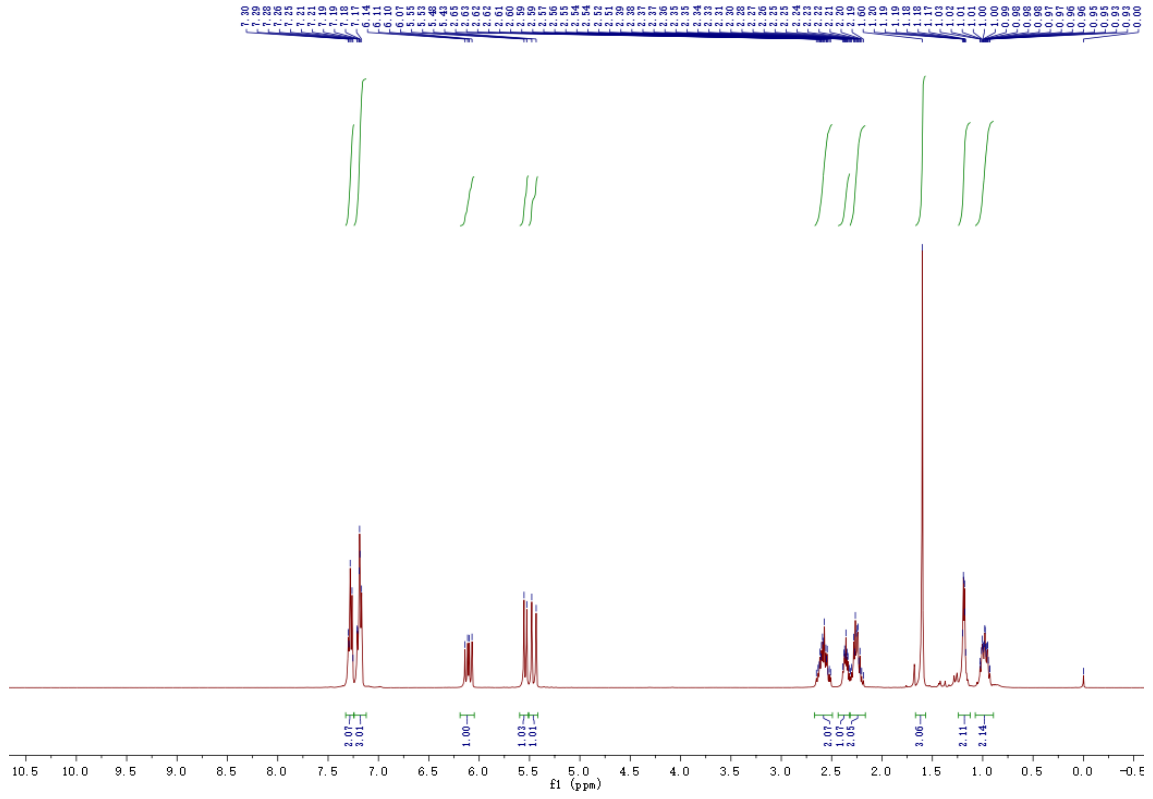
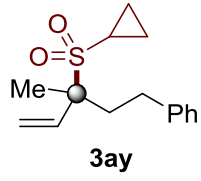


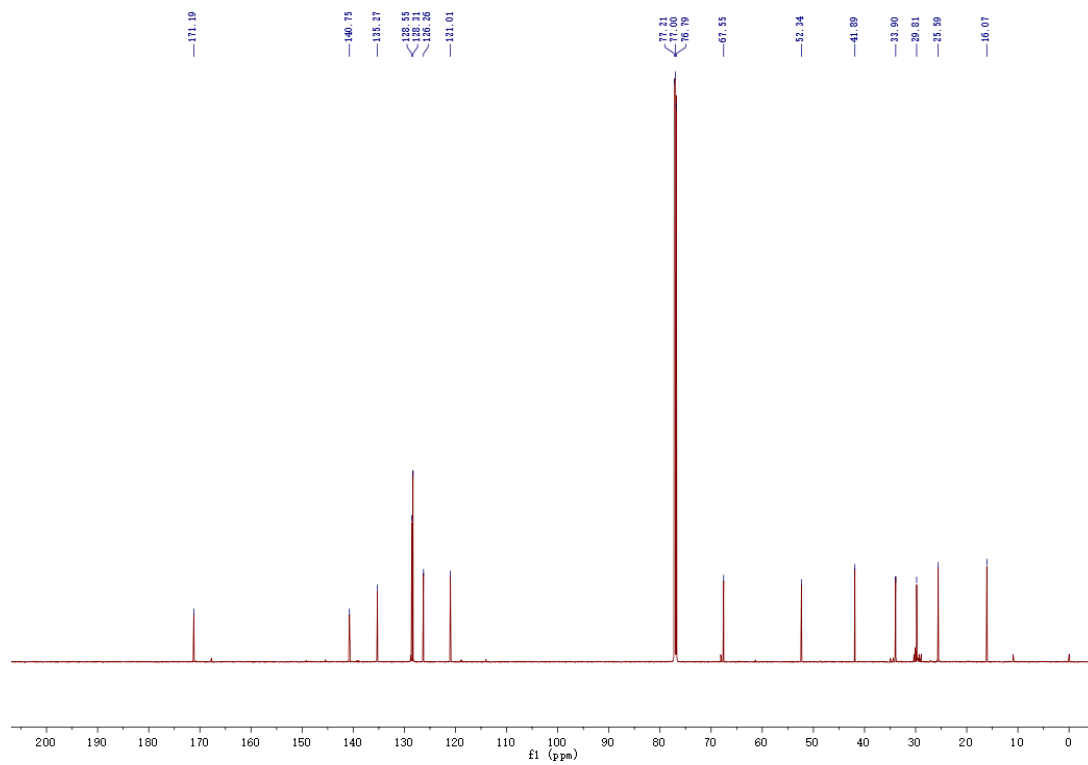
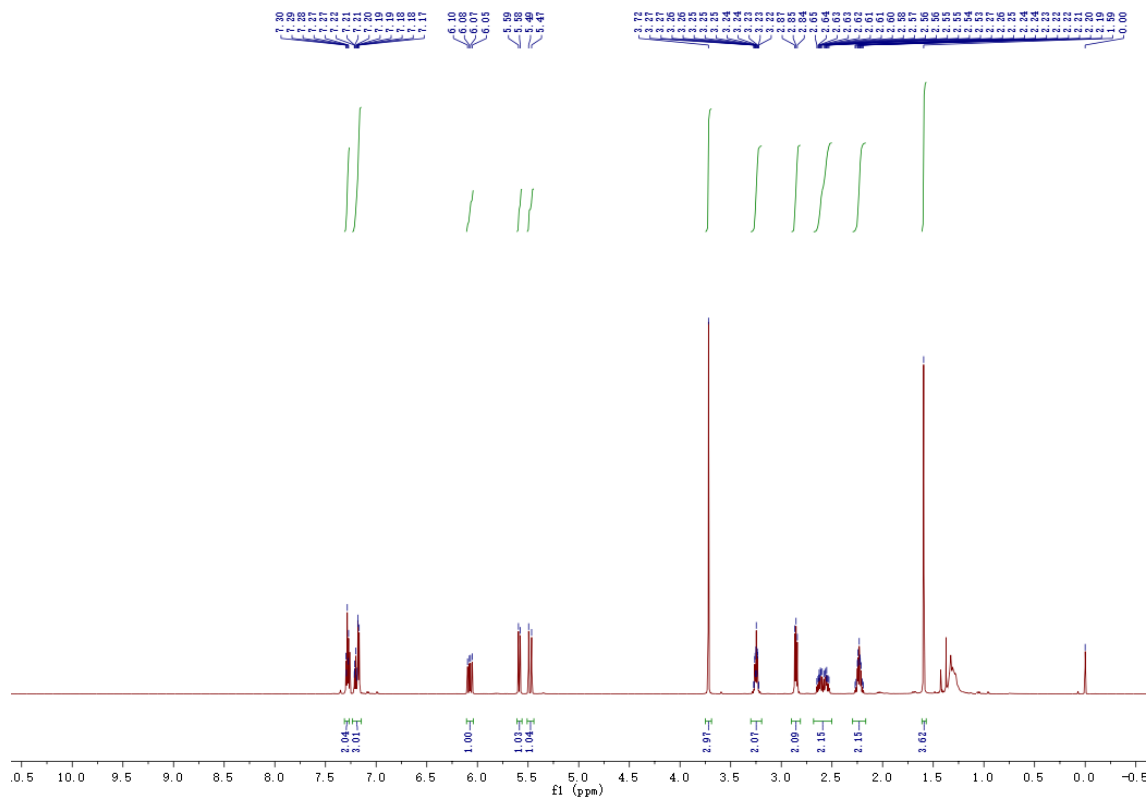
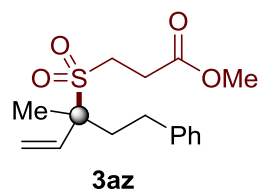


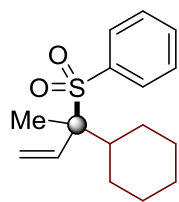


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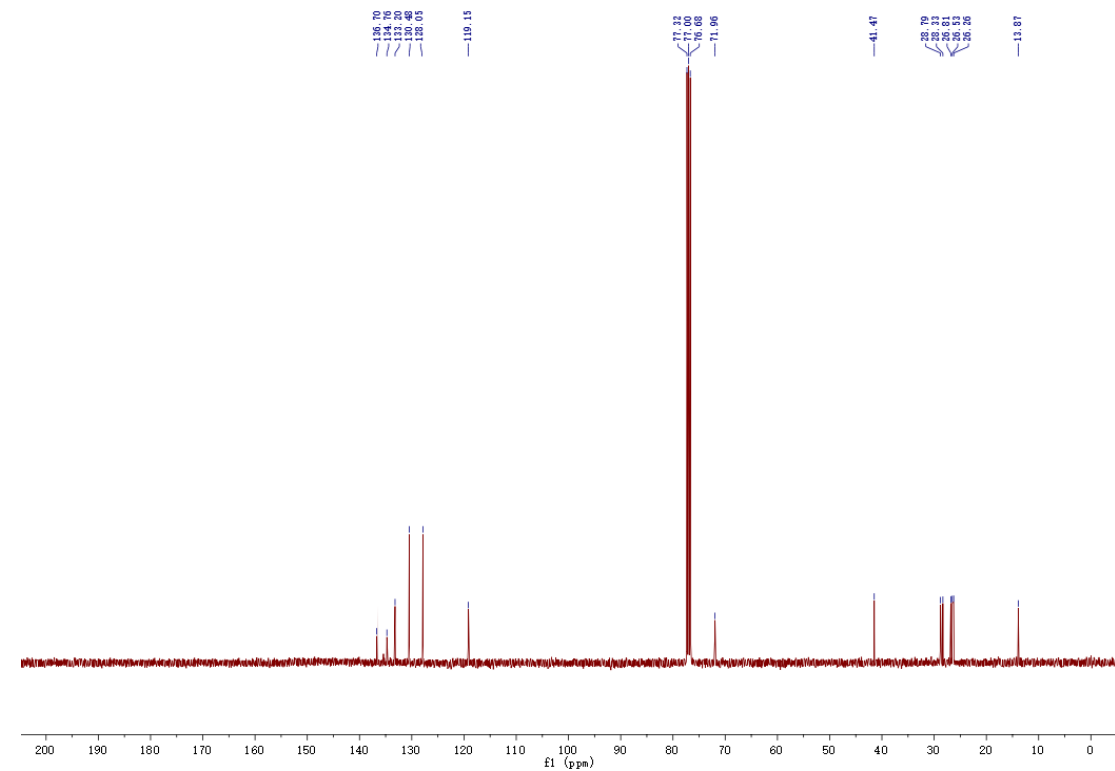
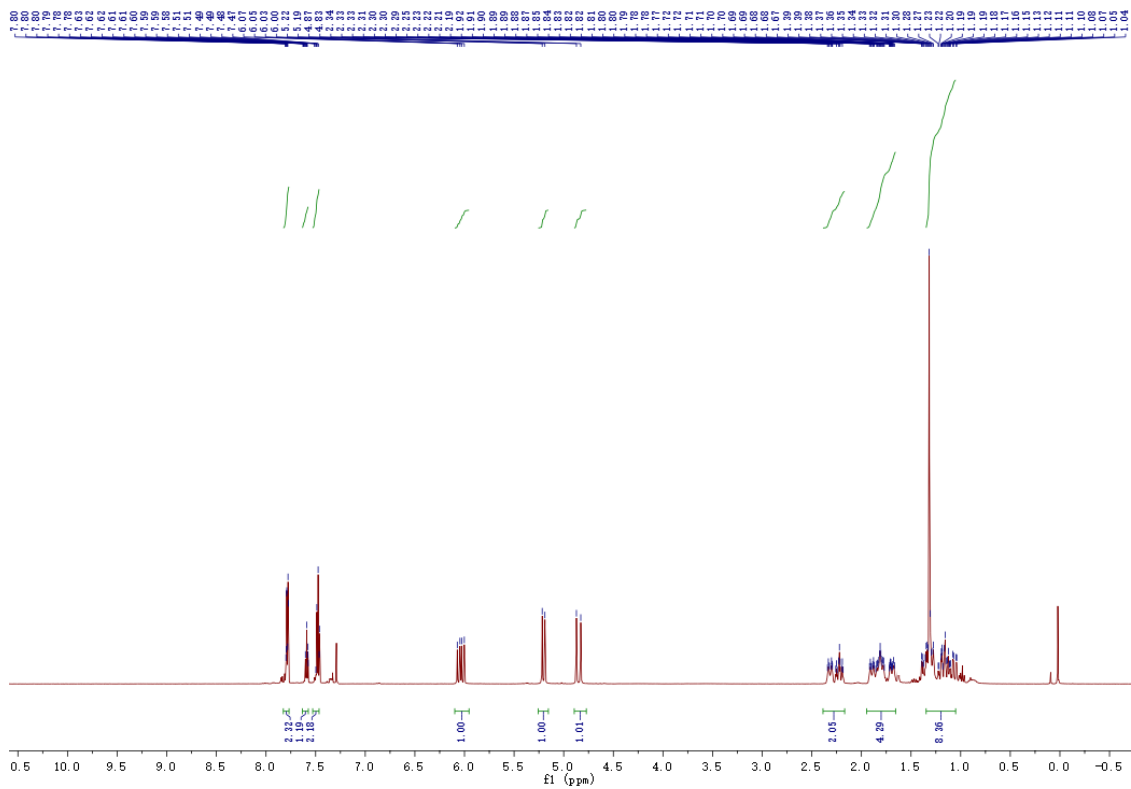


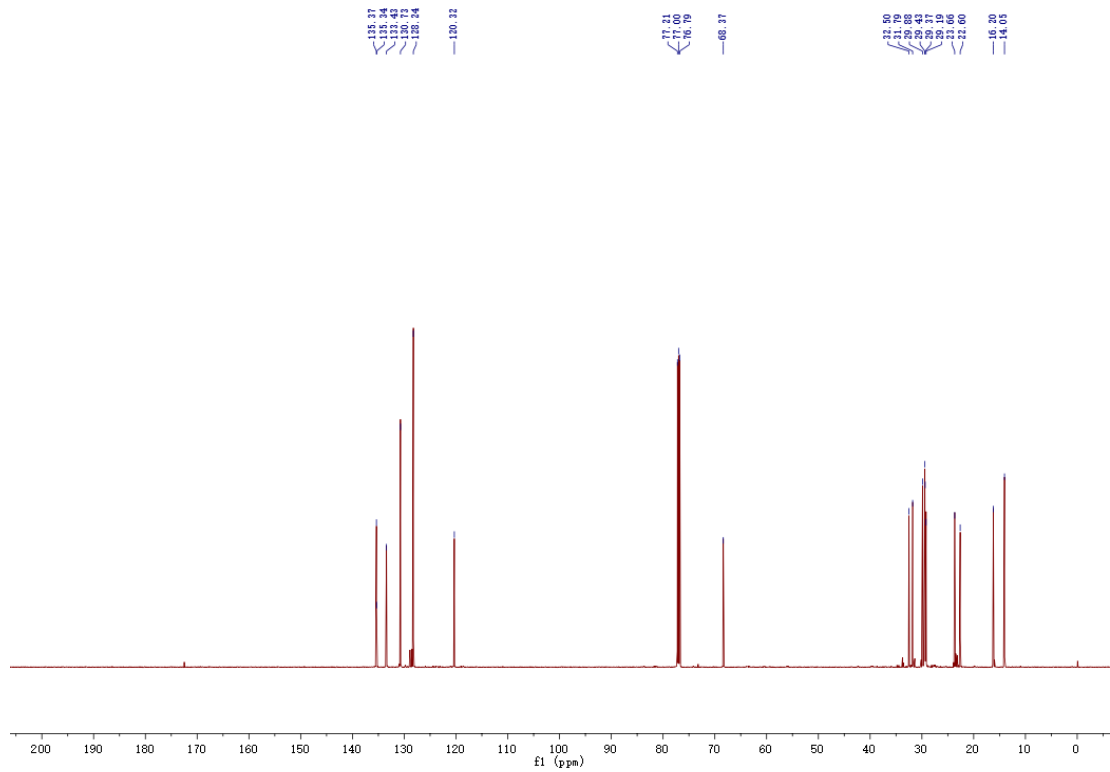
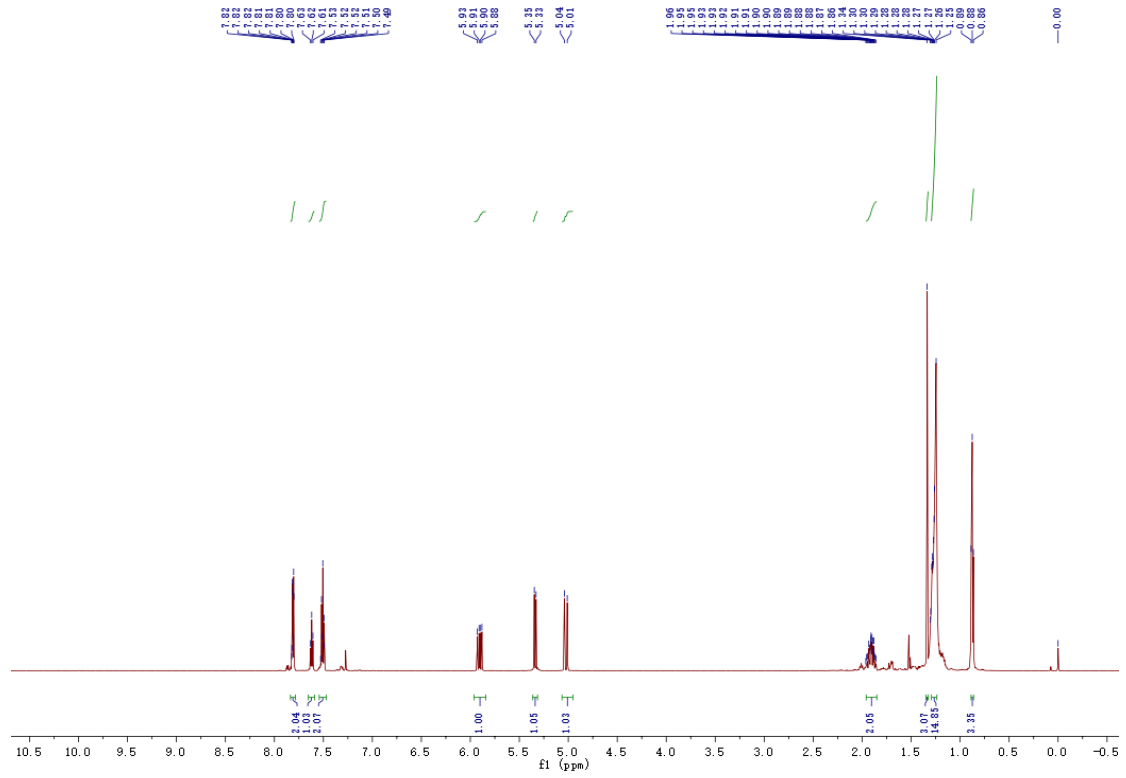
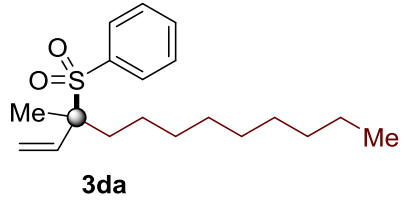


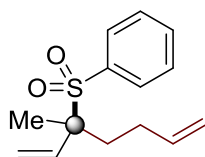




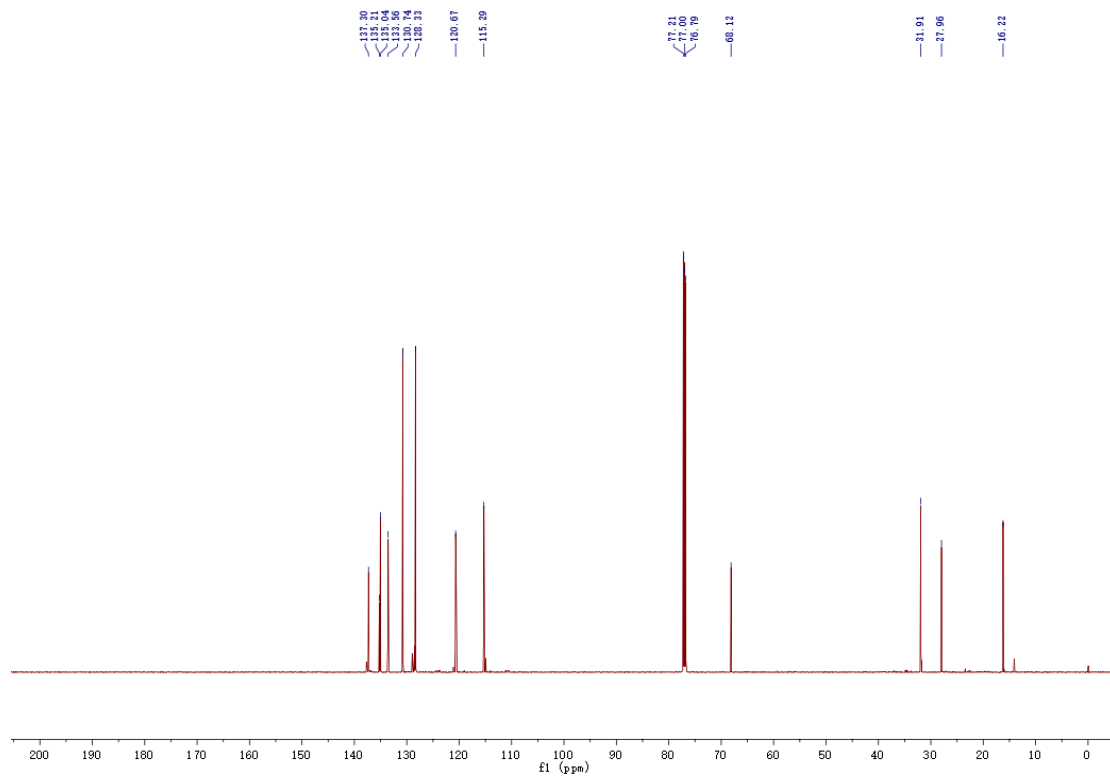
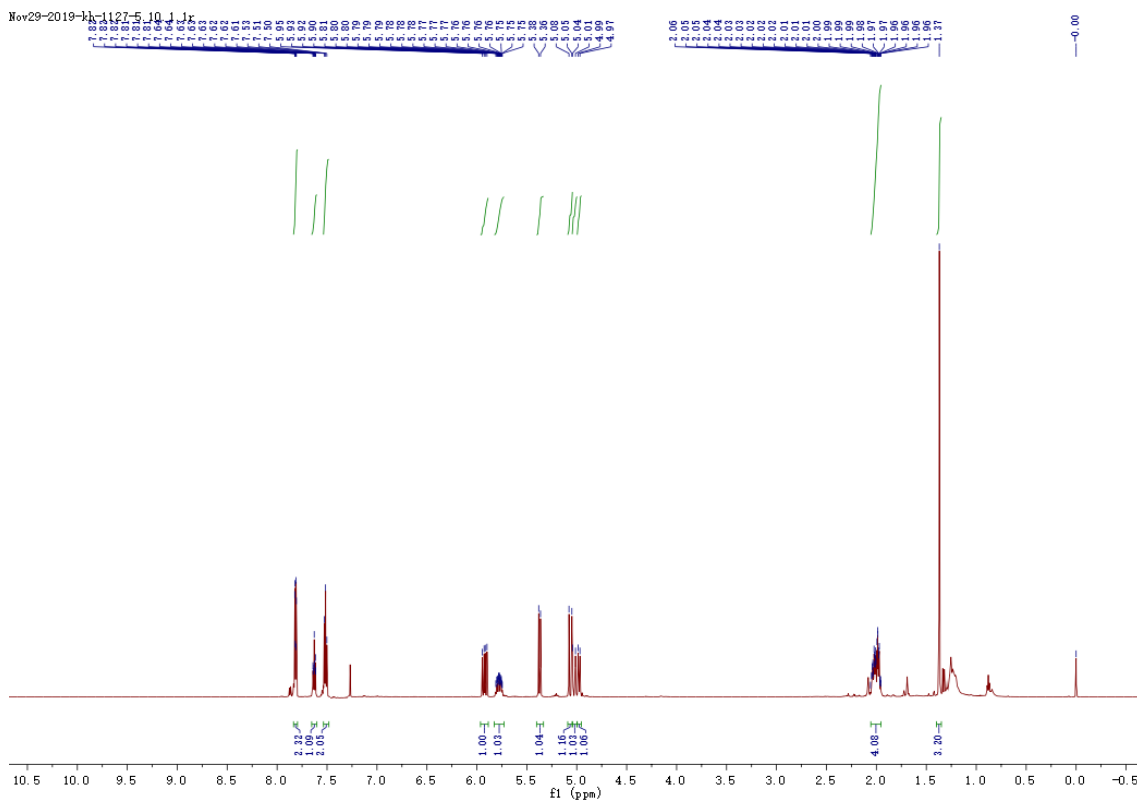
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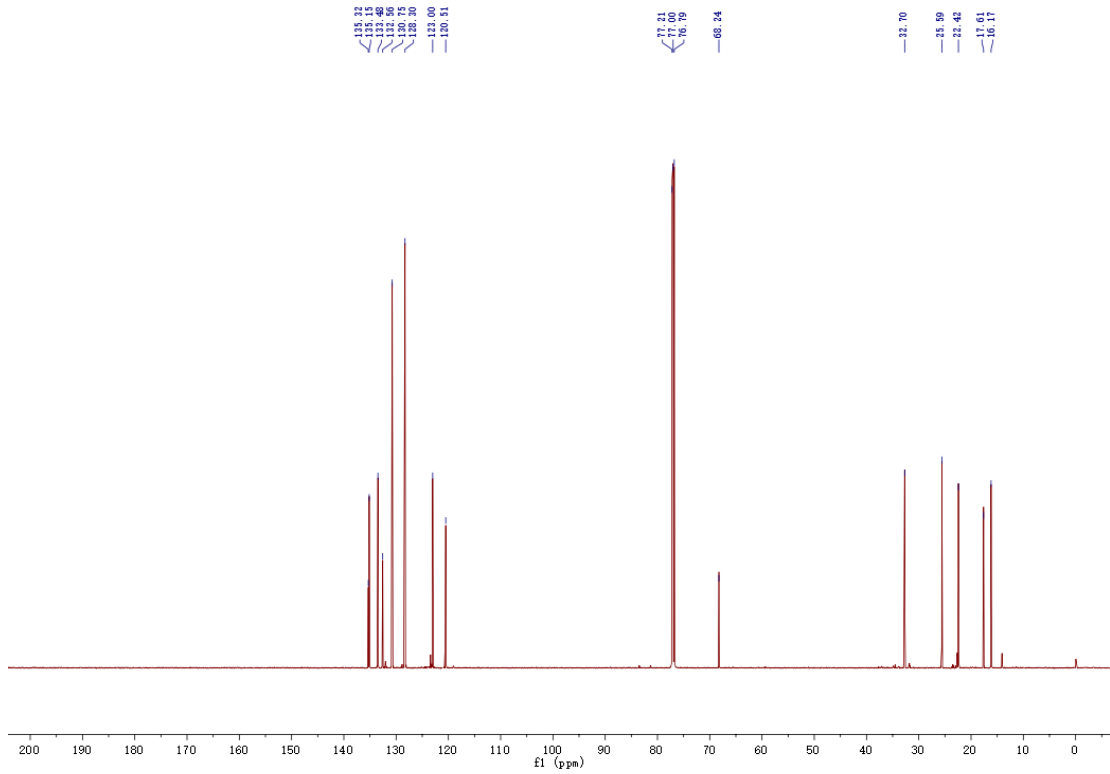
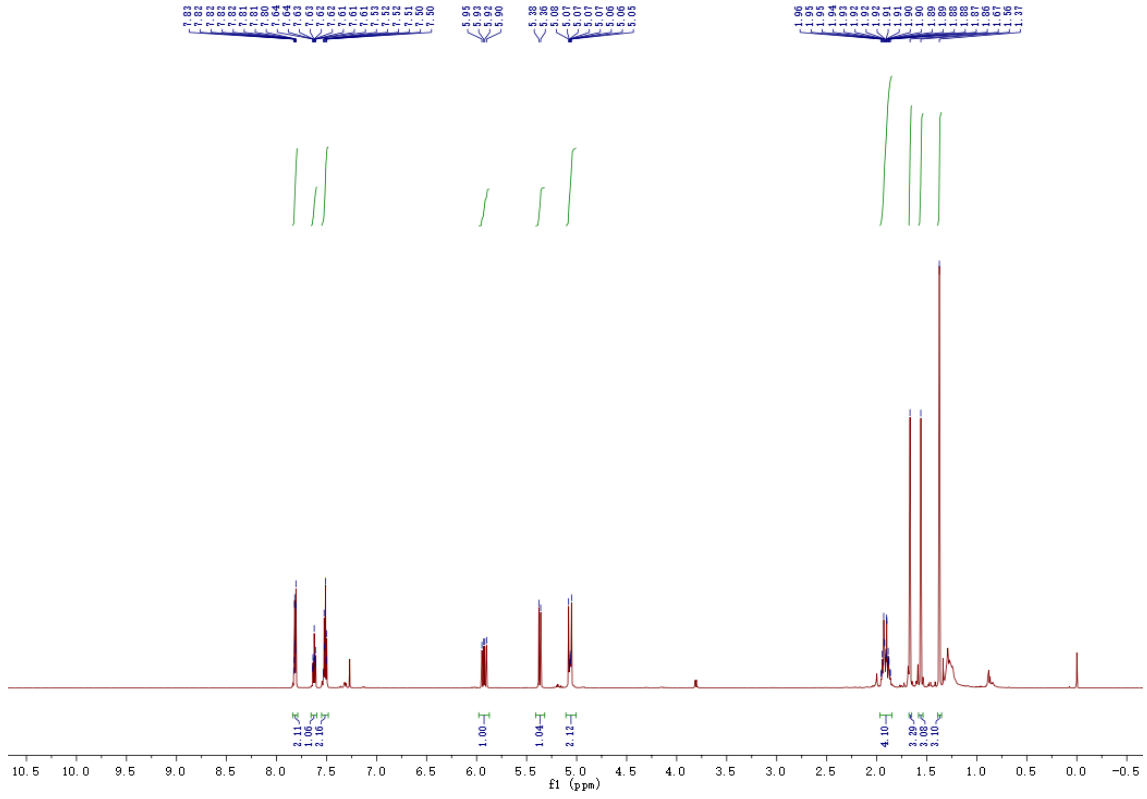
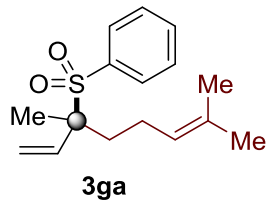


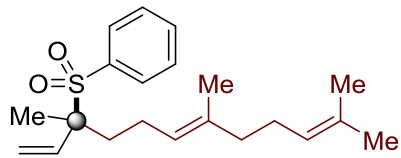




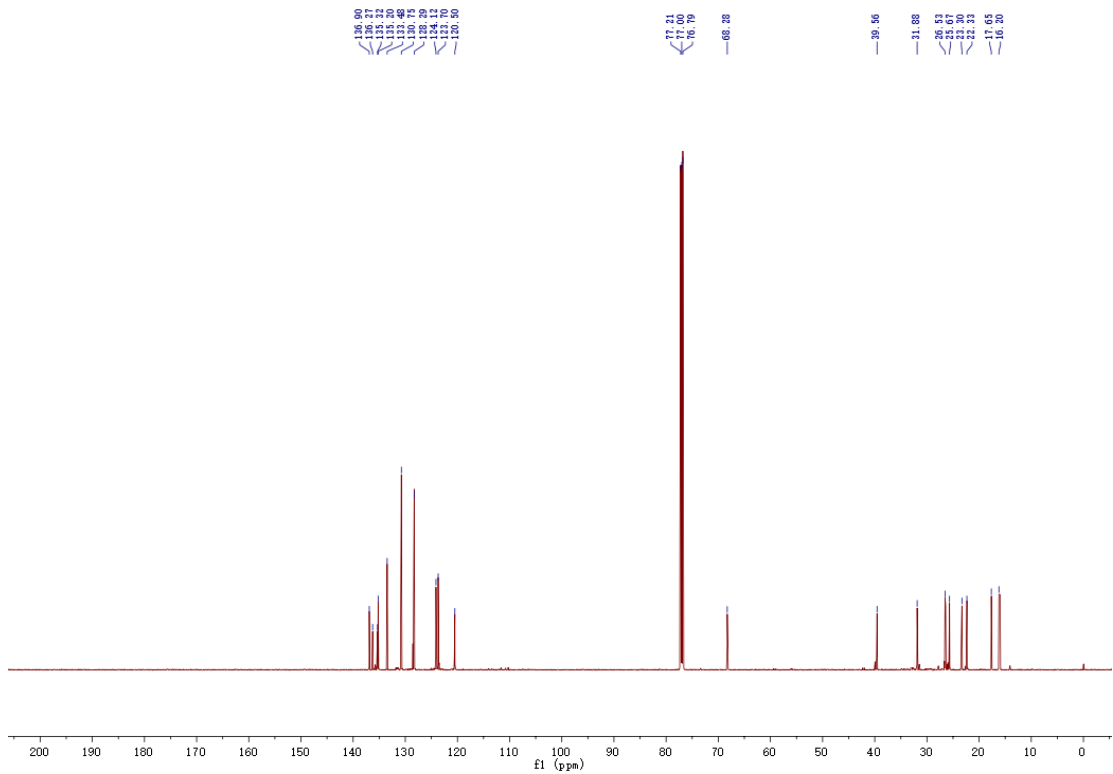
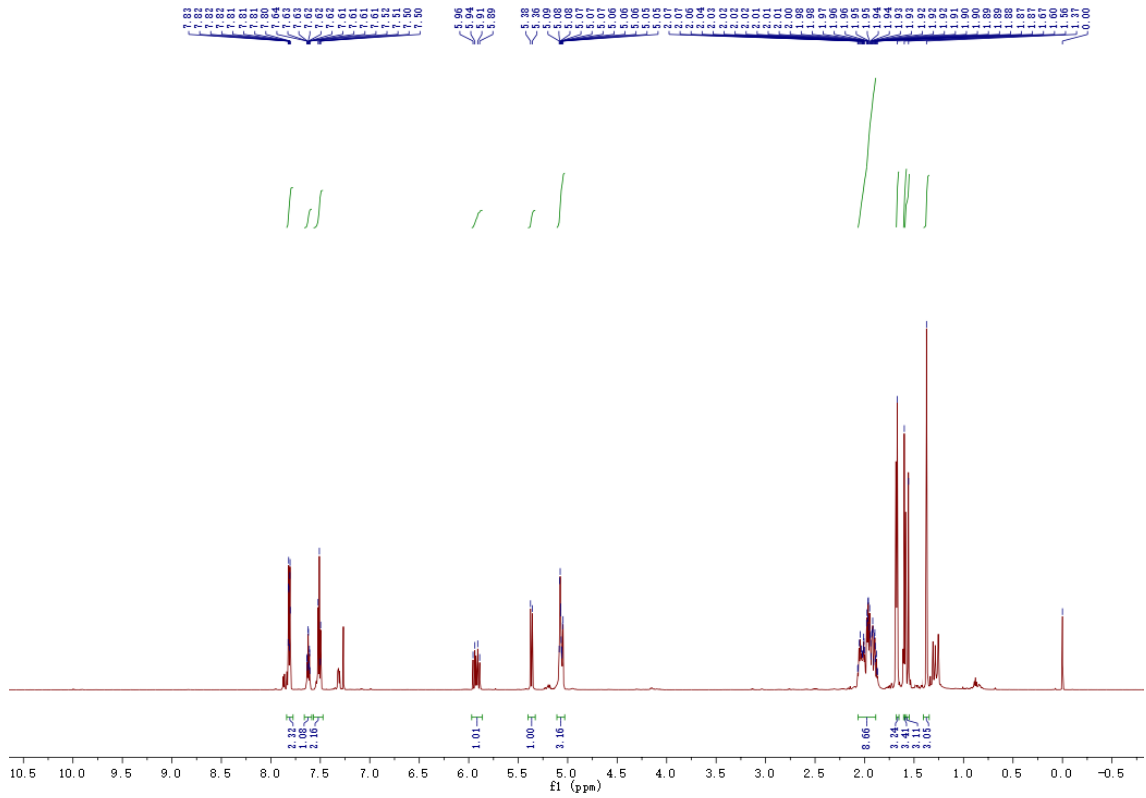
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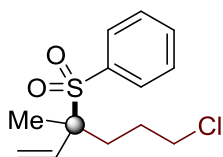




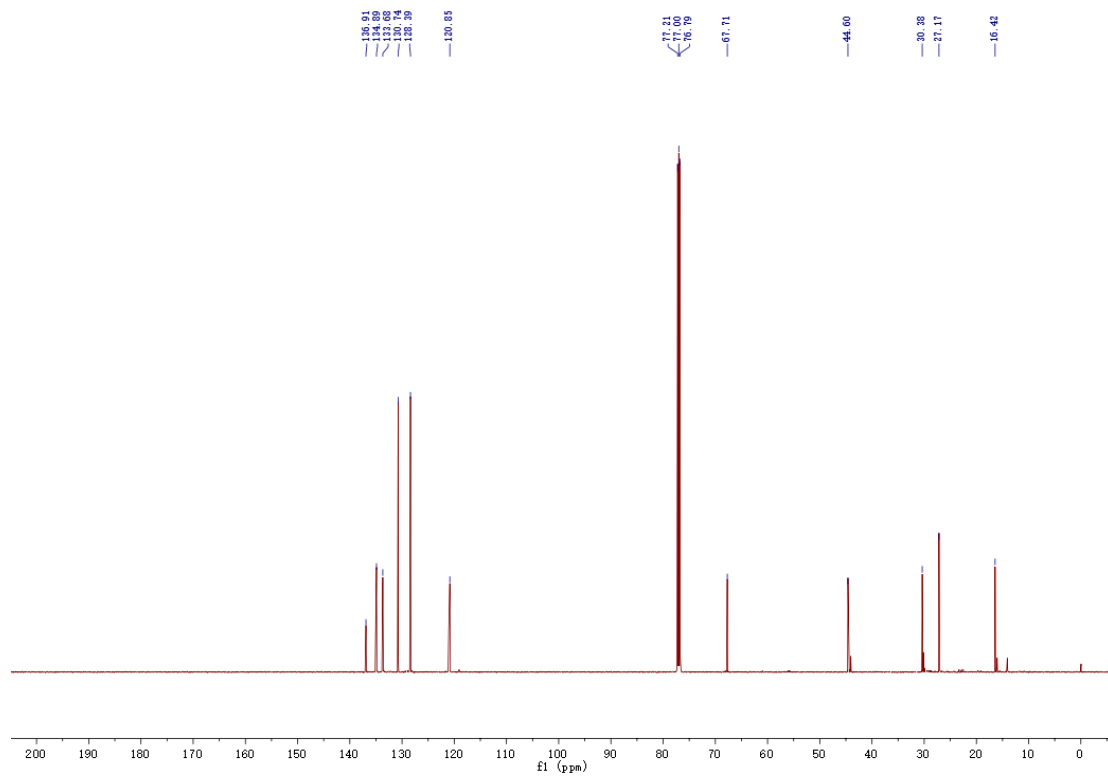
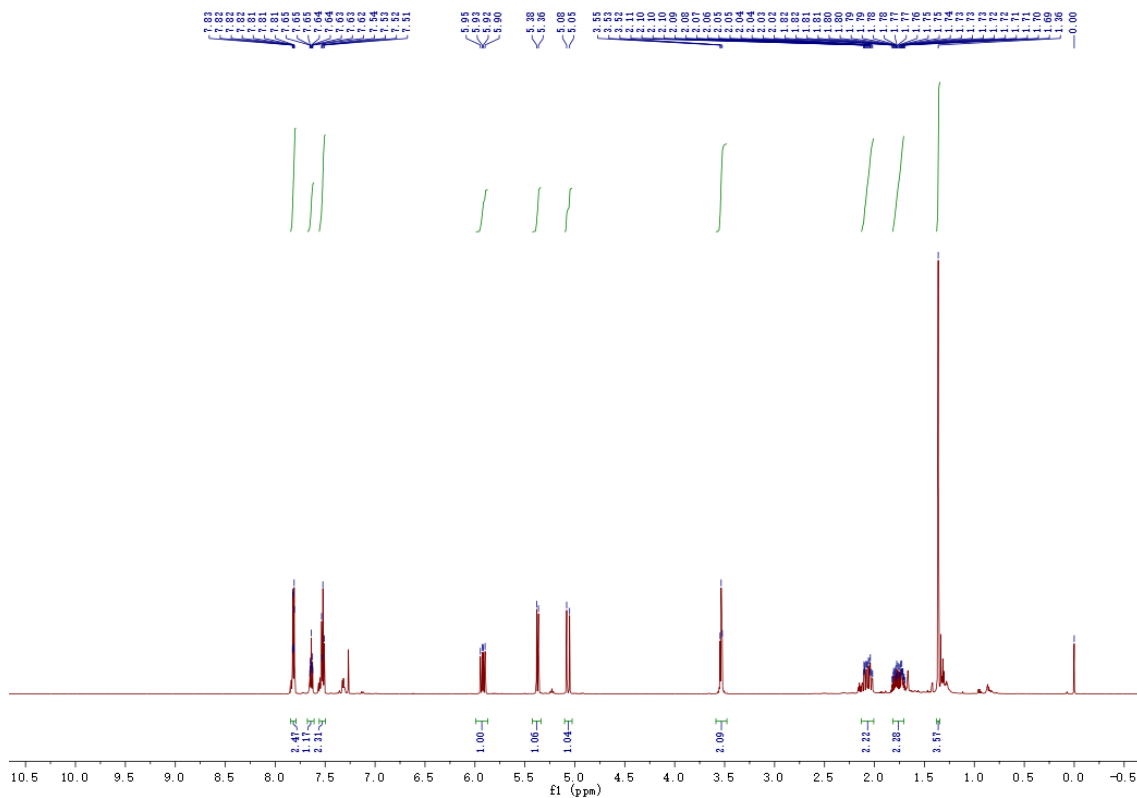


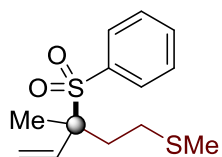
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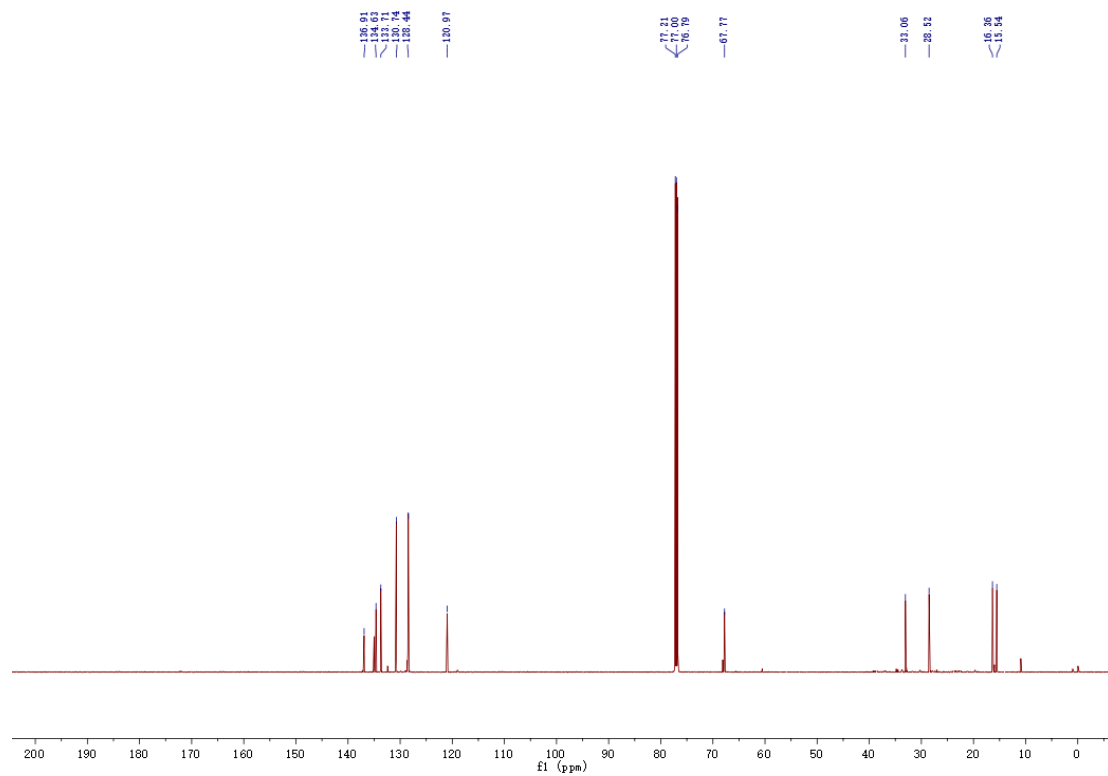
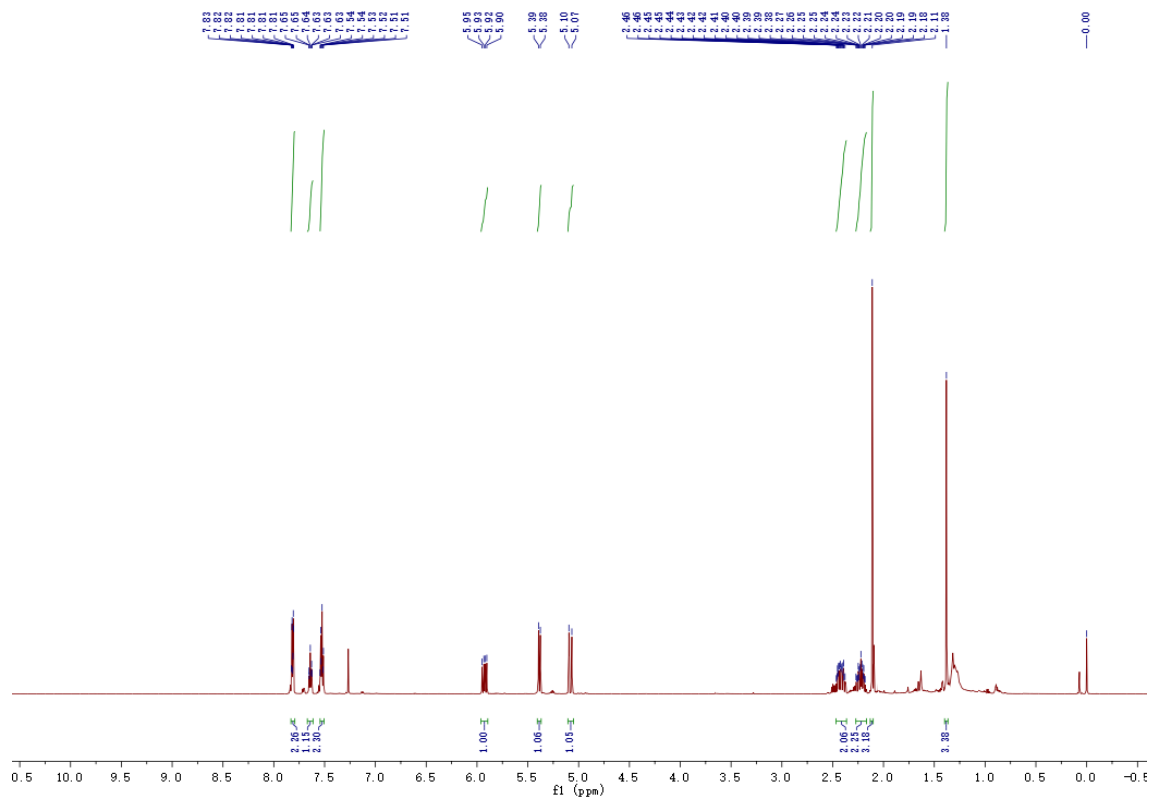


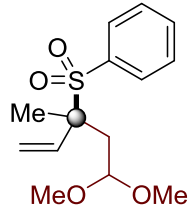
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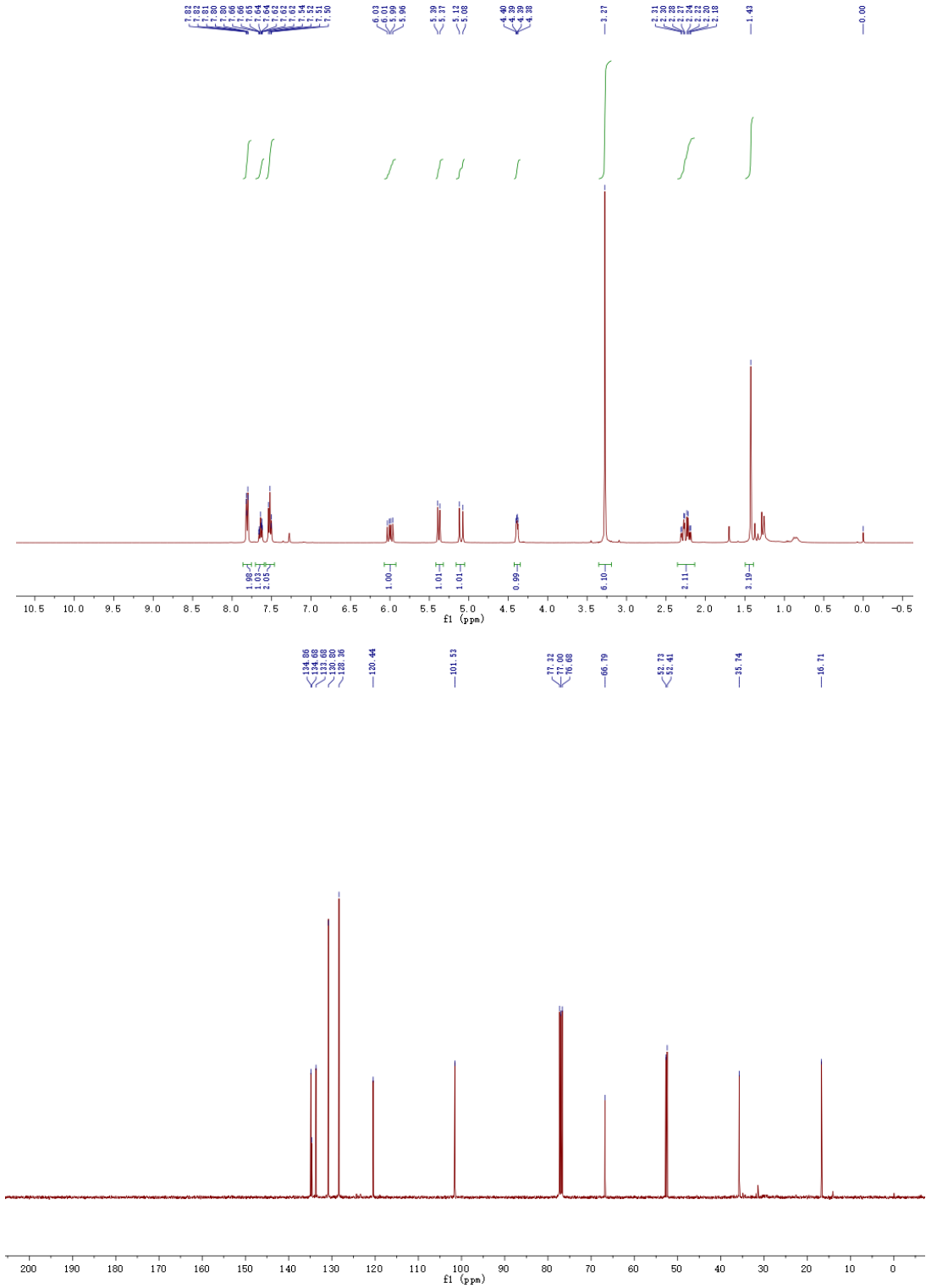


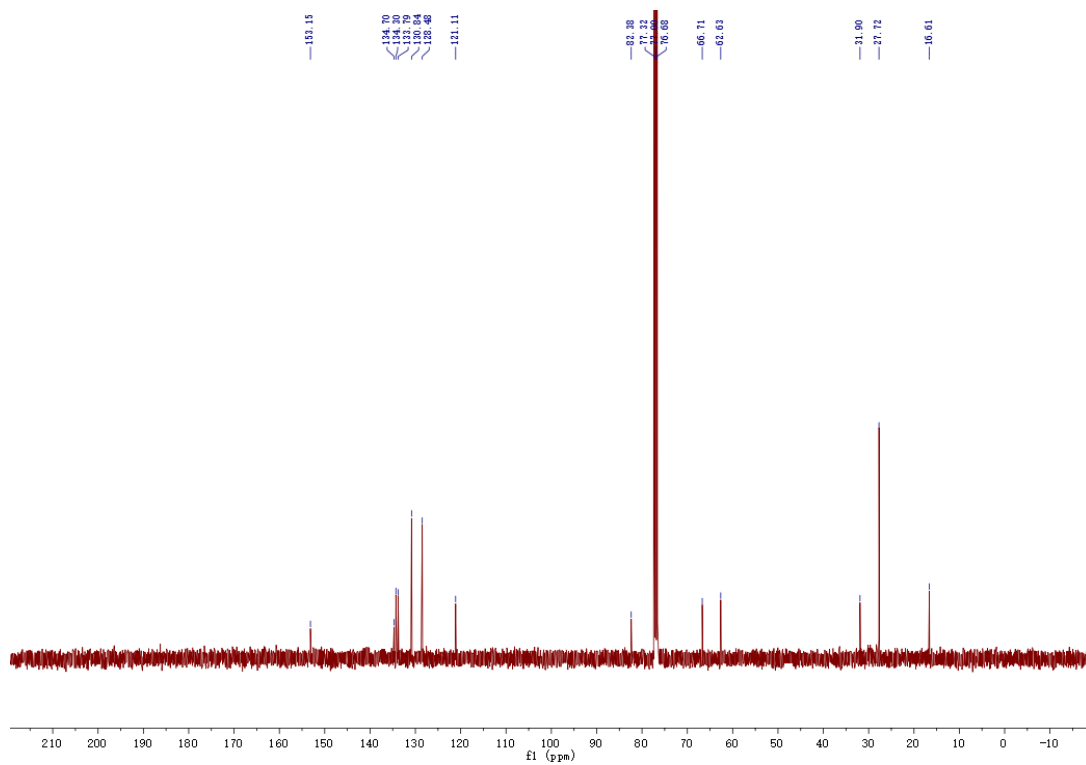
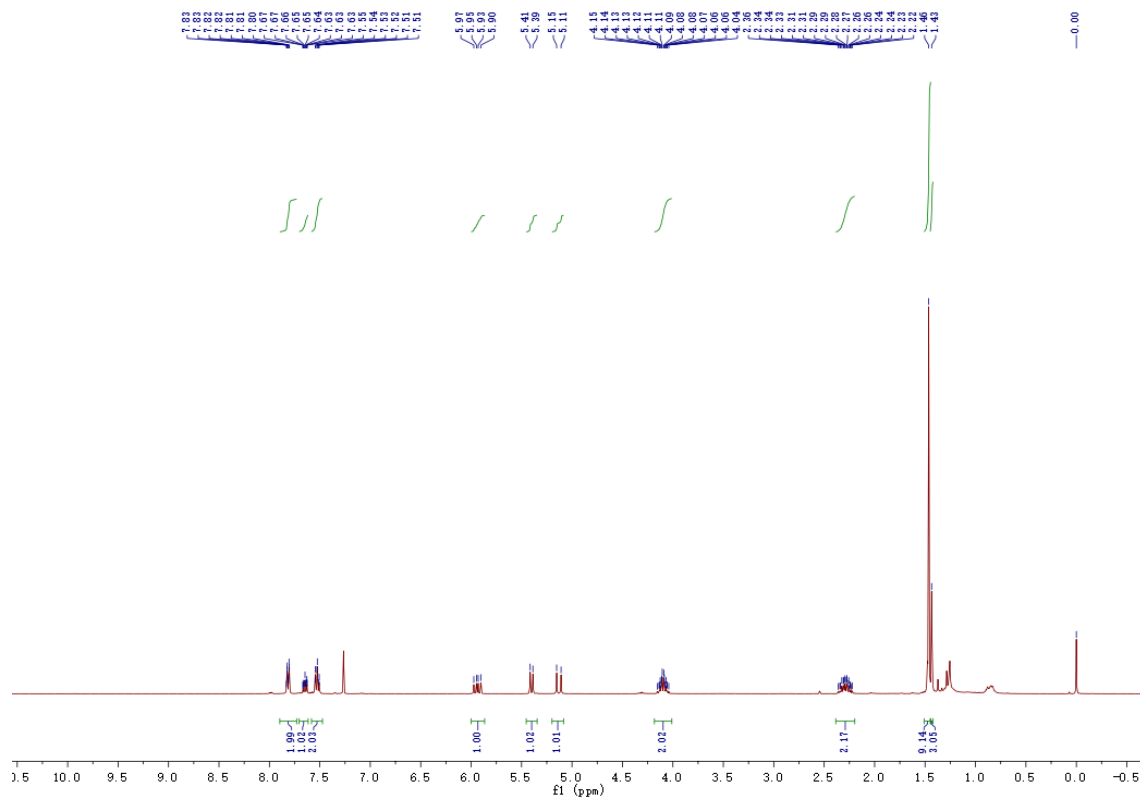
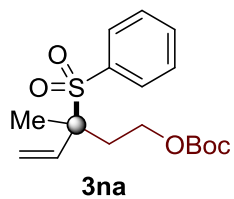
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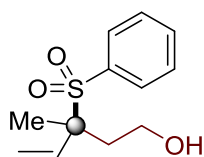




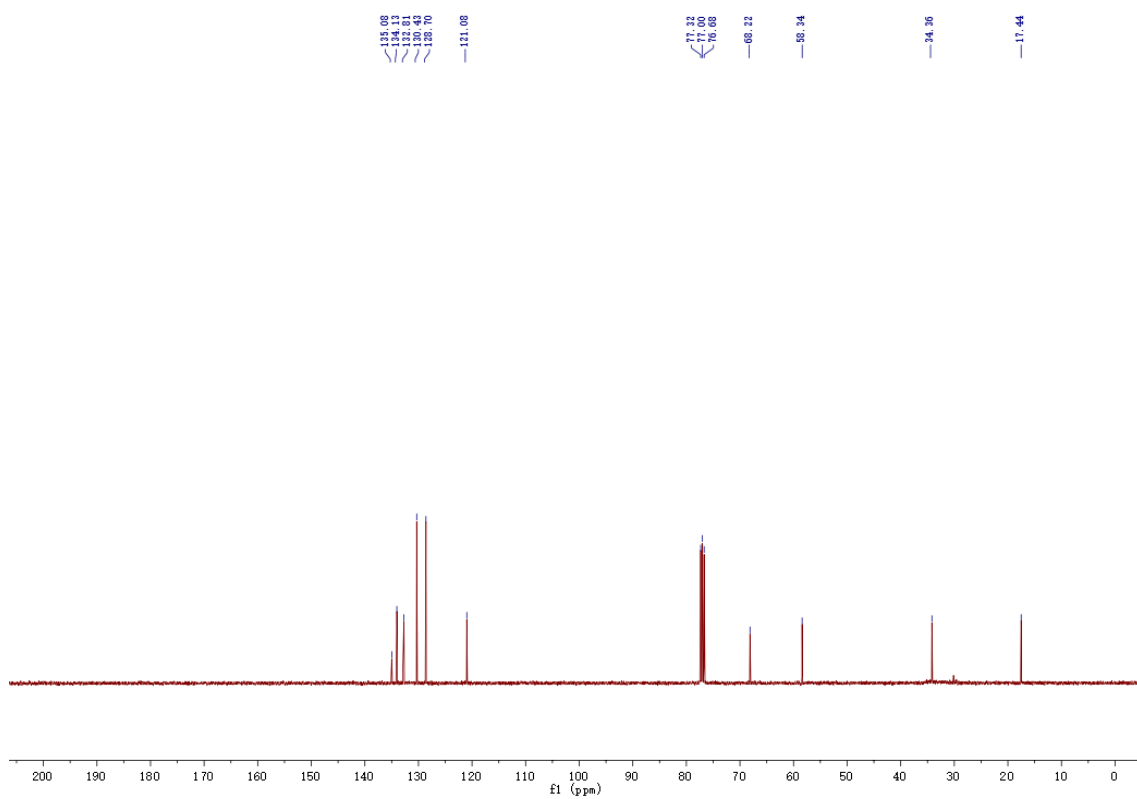
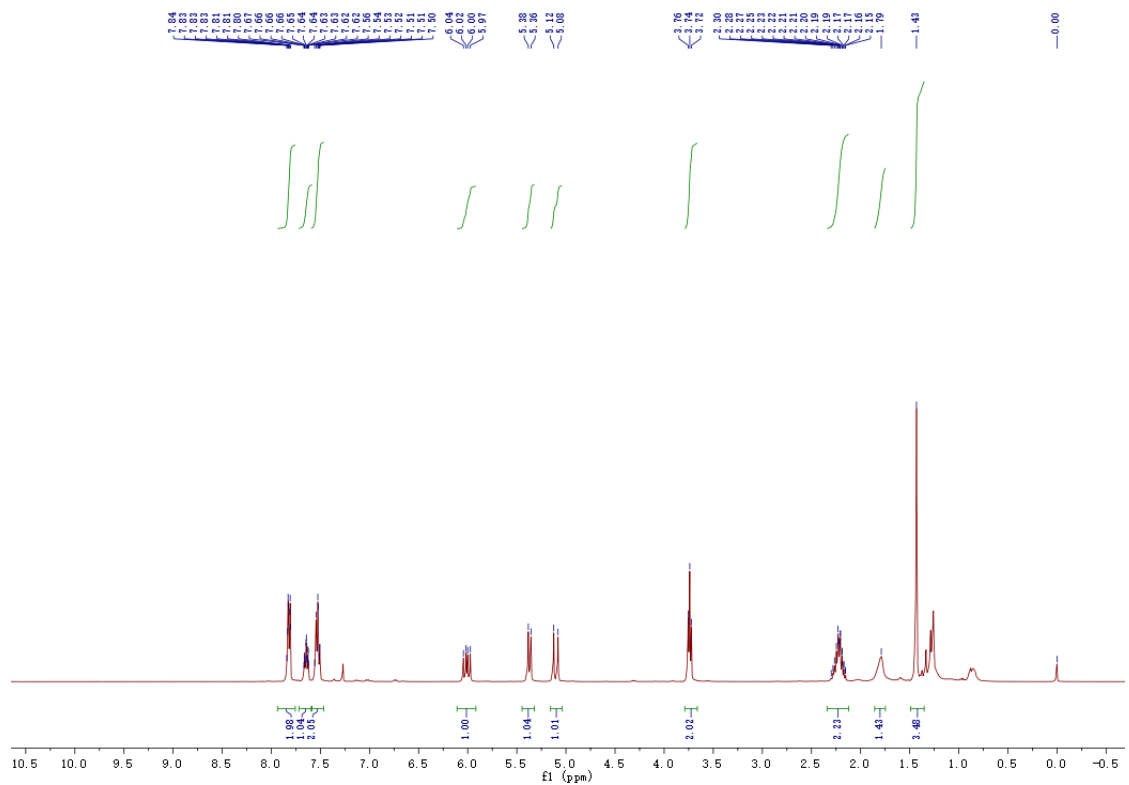
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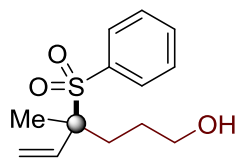




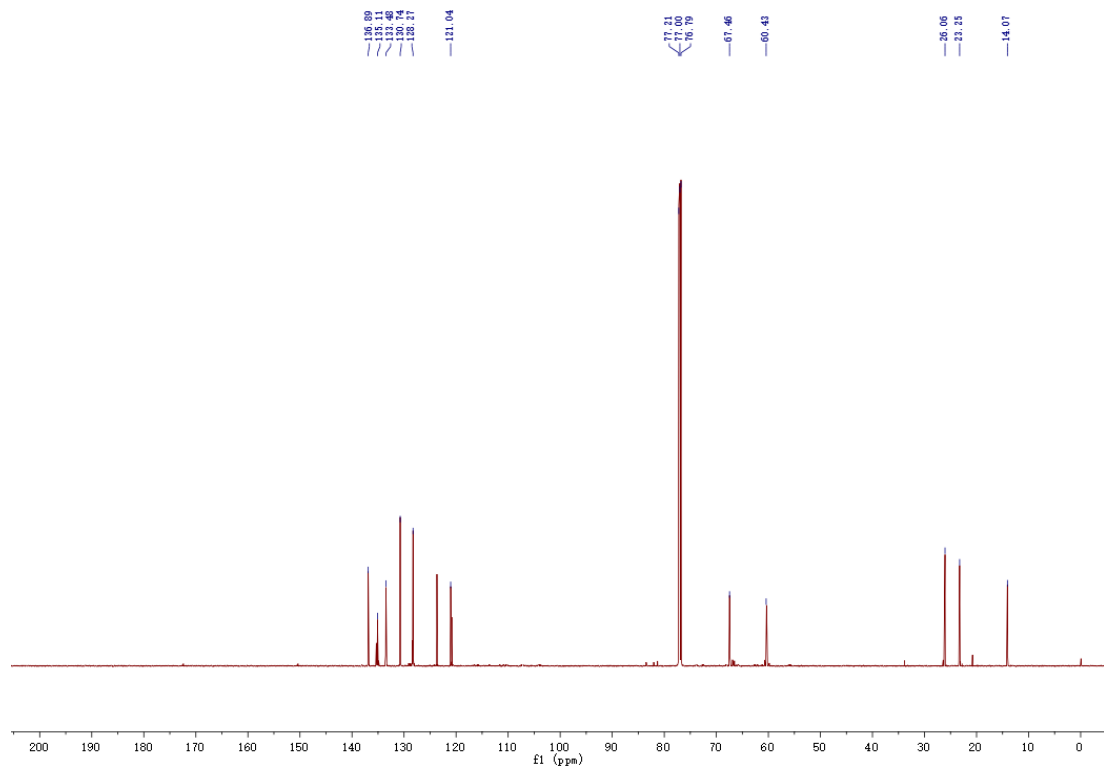
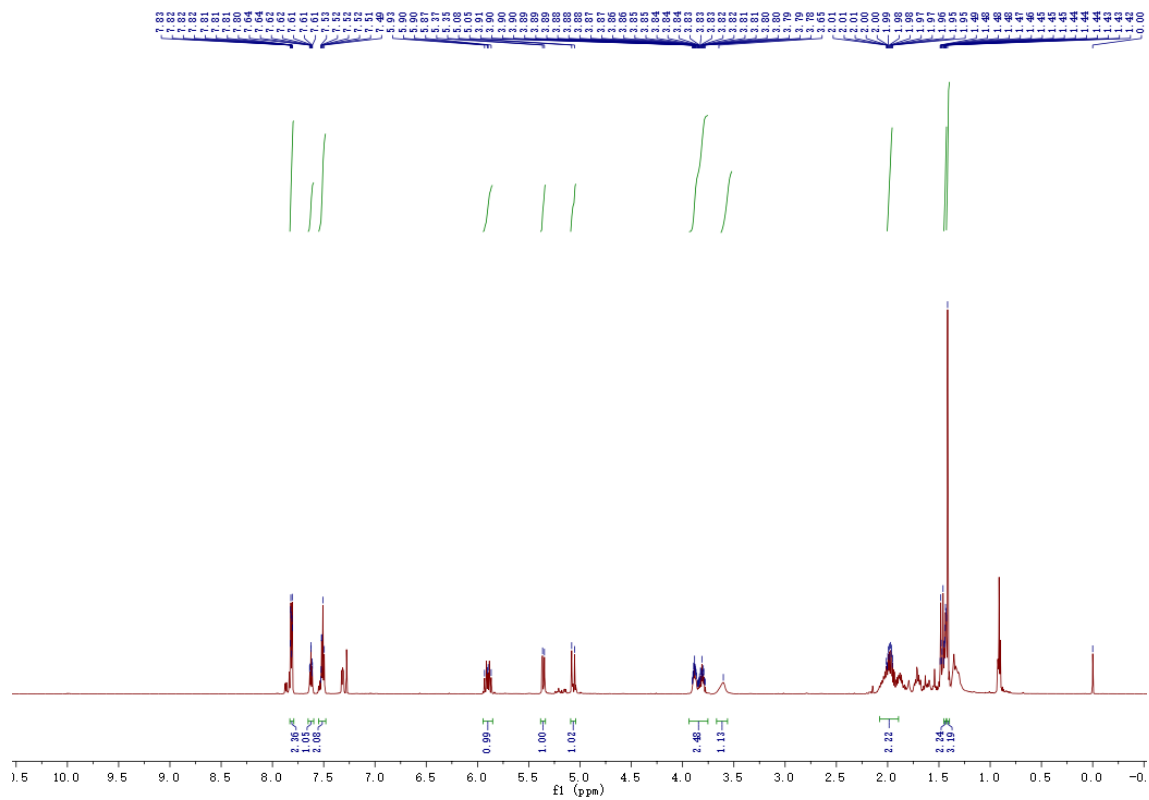


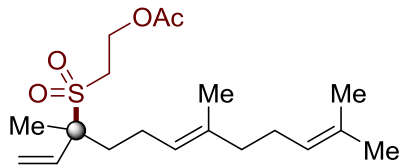
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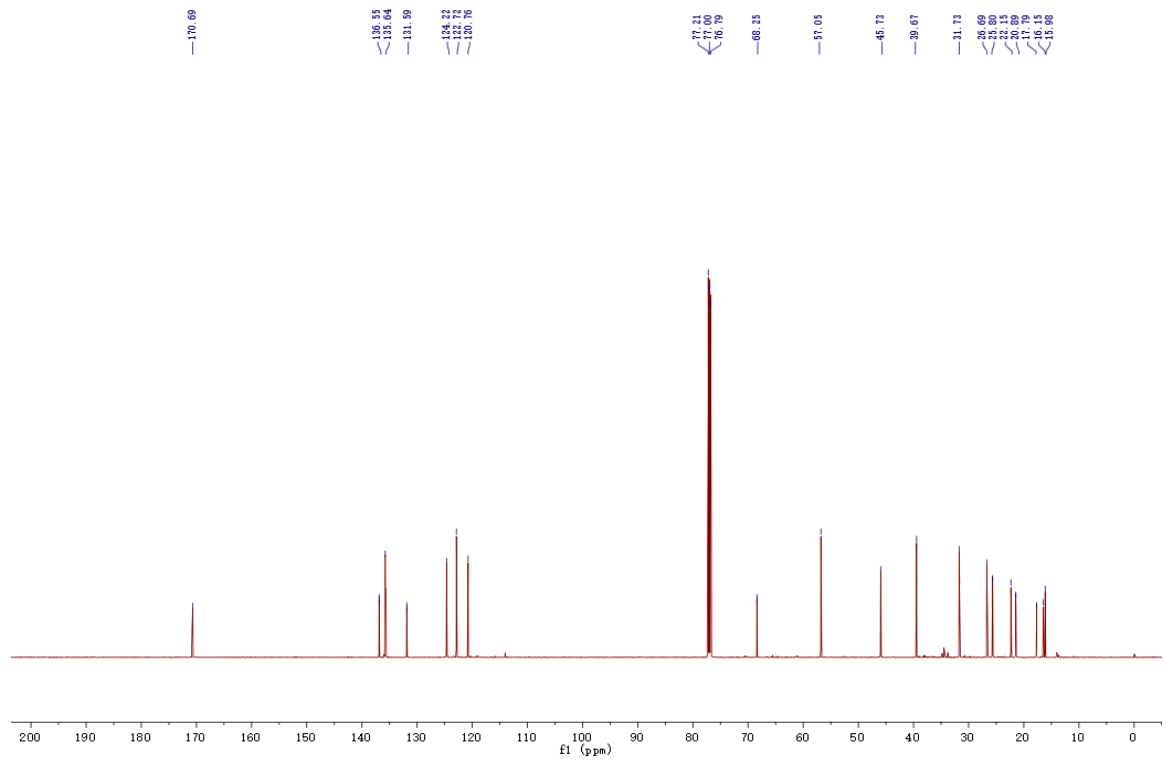
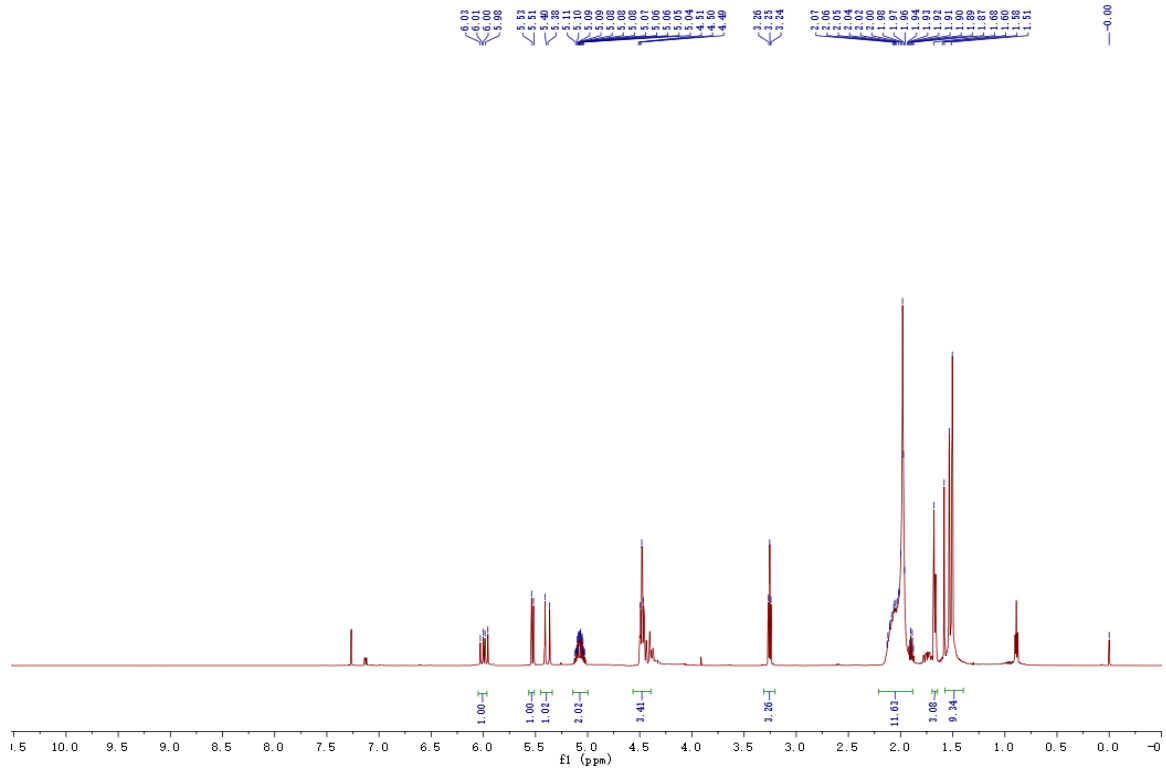


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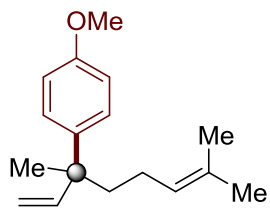




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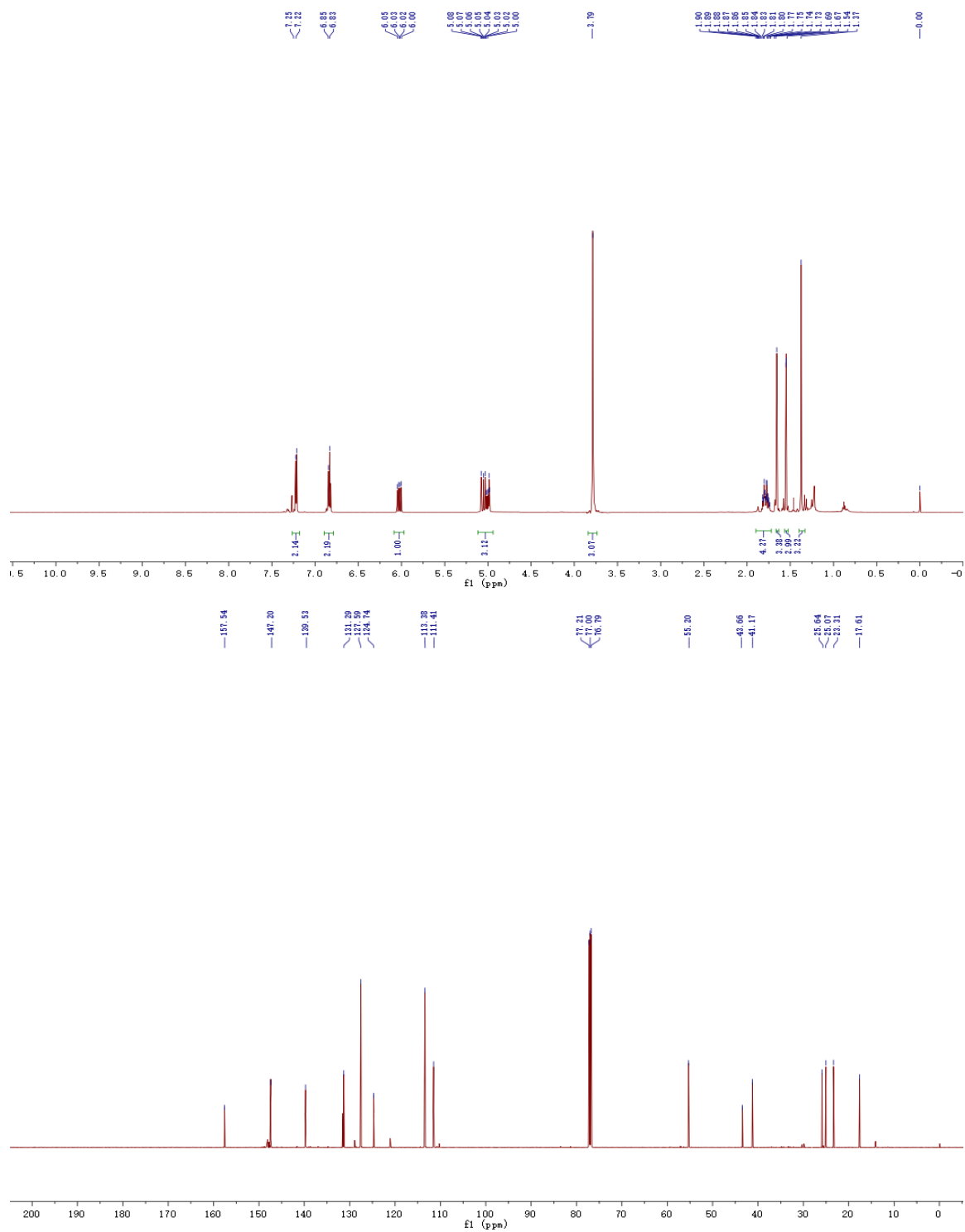


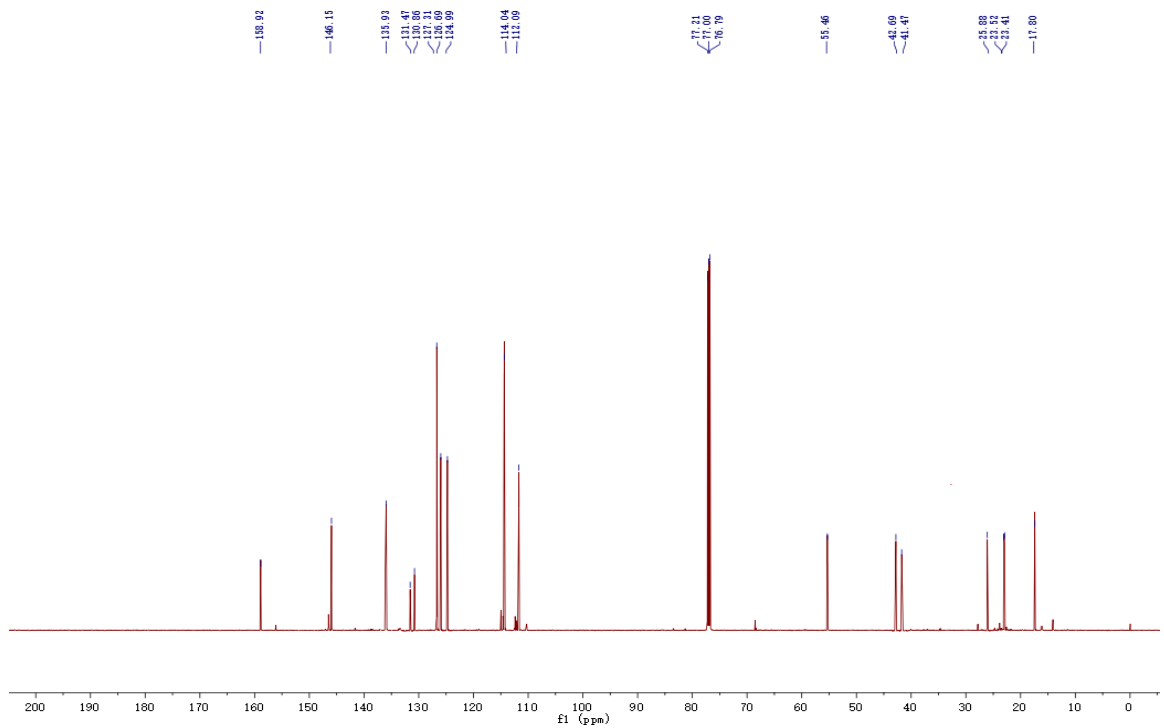
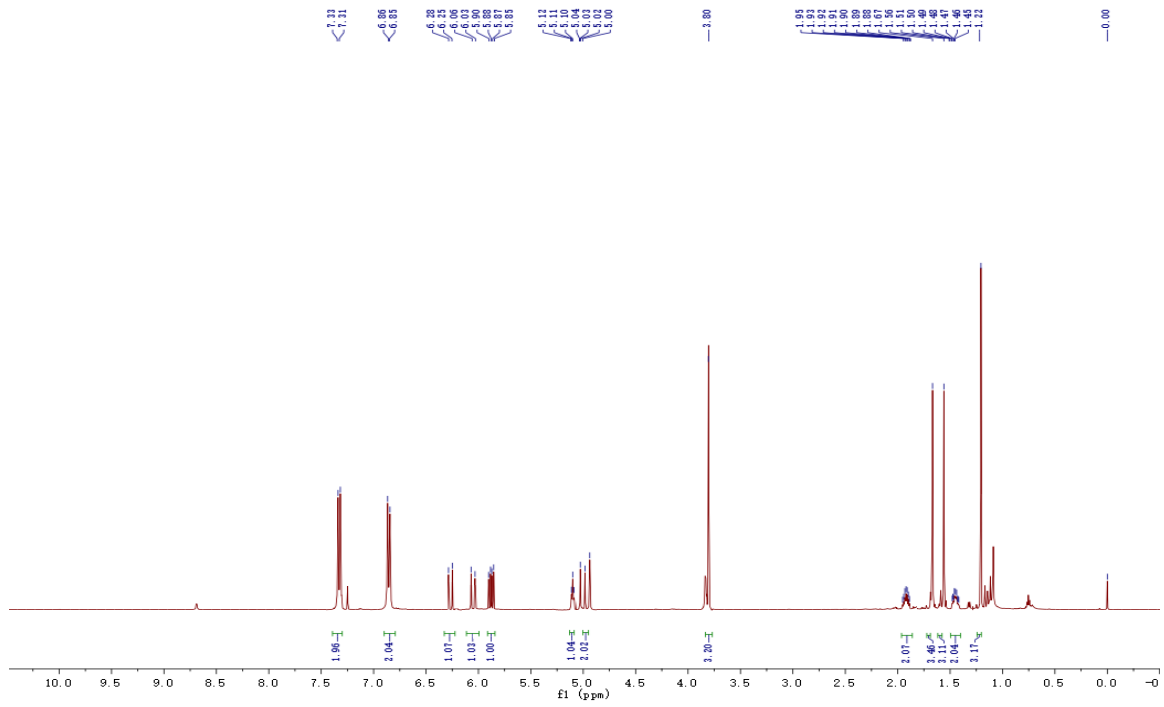
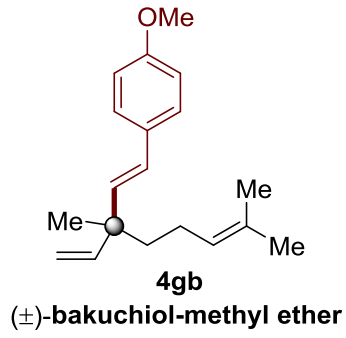
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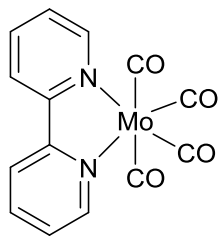


4ga

(±)-sporochnol-methyl ether







Mo(bpy)(CO)₄

