

Palladium nanoparticles as efficient catalyst for C-S bond formation reactions

Mei-Na Zhang, Shahid Khan, Junjie Zhang and Ajmal Khan*

Department of Applied Chemistry, School of Science, and Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter Xi'an Jiaotong University, Xi'an 710049, P. R. China

E-mail: ajmalkhan@xjtu.edu.cn

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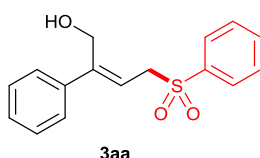
General experimental details

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. $\text{Pd}_2(\text{dba})_3$ and other palladium catalysts were purchased from Energy Chemicals and Aladin/Sigma-Aldrich companies and used as received. Substituted vinyl ethylene carbonates (VECs) were synthesized according to the previously reported procedure.¹ Sodium sulfinates were prepared according to a method reported in the literature.² All other chemicals were used as received from commercial resources.

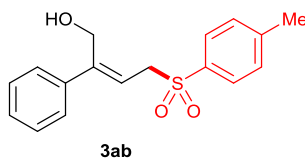
General procedure for PdNPs catalyzed cross coupling of allylic cyclic carbonate **1** with sodium sulfinates

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd₂(dba)₃ (2 mol%), allylic cyclic carbonate **1a** (0.2 mmol), sodium benzenesulfinate (0.3 mmol) and THF (1 mL) were added. The resulting mixture was stirred at room temperature for 15 hours. After the completion of reaction, the product **3aa** was isolated either by using flash column chromatography or by simple filtration. The *Z/E* ratio of the products were determined by ¹H-NMR analysis.

Scale-up Experiment: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd₂(dba)₃ (2 mol%), vinyl cyclic carbonate **1a** (5.0 mmol, 0.951g), sodium benzenesulfinate (7.5 mmol, 1.23g) and THF (10 mL) were added. The resulting mixture was stirred at room temperature for 15 hours. After the completion of reaction, the residue was purified by flash column chromatography to afford the product **3aa** in 90% yield (1.3g).

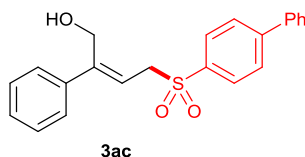


(Z)-2-phenyl-4-(phenylsulfonyl)but-2-en-1-ol (3aa) was prepared according to the general procedure from **1a** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (53.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.91–7.88 (m, 2H), 7.68–7.64 (m, 1H), 7.58–7.53 (m, 2H), 7.41–7.38 (m, 2H), 7.35–7.29 (m, 3H), 5.70 (t, *J* = 8.4 Hz, 1H), 4.37 (s, 2H), 4.14 (d, *J* = 8.4 Hz, 2H), 2.76 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 139.8, 138.5, 134.0, 129.3, 128.5, 128.2, 128.1, 126.3, 115.0, 60.0, 55.9; HRMS (ESI-MS): Calcd. for C₁₆H₁₆O₃S (M + Na): 311.0718, Found: 311.0724.

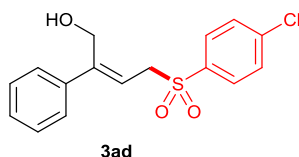


(Z)-2-phenyl-4-tosylbut-2-en-1-ol (3ab) was prepared according to the general procedure from **1a** and **2b**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 90% yield (44.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.80–7.77 (m, 2H), 7.44–7.41 (m, 2H), 7.38–7.31 (m, 5H), 5.71 (t, *J* = 8.4 Hz, 1H), 4.42 (d, *J* = 6.4 Hz, 2H), 4.12 (d, *J* = 8.4 Hz, 2H), 2.68 (brt, 1H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 145.2, 139.9, 135.7, 130.0, 128.5, 128.4,

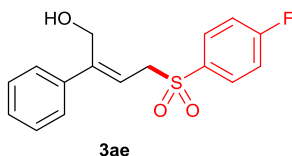
128.3, 126.4, 115.2, 60.2, 56.0, 21.6; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}O_3S$ ($M + Na$): 325.0874, Found: 325.0891.



(Z)-4-([1,1'-biphenyl]-4-ylsulfonyl)-2-phenylbut-2-en-1-ol (3ac) was prepared according to the general procedure from **1a** and **2c**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (67.8 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.96 (m, 2H), 7.80–7.77 (m, 2H), 7.63–7.60 (m, 2H), 7.52–7.43 (m, 5H), 7.37–7.32 (m, 3H), 5.76 (t, $J = 8.4$ Hz, 1H), 4.47 (d, $J = 6.4$ Hz, 2H), 4.19 (d, $J = 8.4$ Hz, 2H), 2.66 (brt, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 147.1, 139.9, 138.9, 137.2, 129.1, 128.9, 128.8, 128.6, 128.4, 127.9, 127.4, 126.5, 115.0, 60.4, 56.1; HRMS (ESI-MS): Calcd. for $C_{22}H_{20}O_3S$ ($M + Na$): 387.1031, Found: 387.1023.

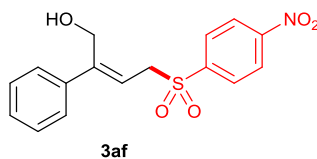


(Z)-4-((4-chlorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ad) was prepared according to the general procedure from **1a** and **2d**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 88% yield (56.8 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.84 (m, 2H), 7.58–7.54 (m, 2H), 7.44–7.42 (m, 2H), 7.39–7.33 (m, 3H), 5.70 (t, $J = 8.4$ Hz, 1H), 4.46 (d, $J = 6.4$ Hz, 2H), 4.16 (d, $J = 8.4$ Hz, 2H), 2.58 (brt, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 141.0, 139.7, 137.2, 129.9, 129.7, 128.7, 128.5, 126.4, 114.6, 60.4, 56.1; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}ClO_3S$ ($M + Na$): 345.0328, Found: 345.0336.

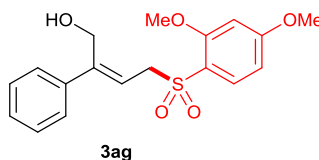


(Z)-4-((4-fluorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ae) was prepared according to the general procedure from **1a** and **2e**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 82% yield (50.2 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 2H), 7.43–7.39 (m, 2H), 7.37–7.31 (m, 3H), 7.27–7.22 (m, 2H), 5.69 (t, $J = 8.4$ Hz, 1H), 4.42 (s, 2H), 4.15 (d, $J = 8.4$ Hz, 2H), 2.71 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 164.7, 149.2, 139.7, 134.6,

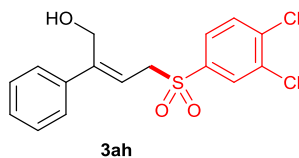
131.3, 131.2, 128.6, 128.4, 126.4, 116.8, 116.6, 114.8, 60.2, 56.1; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}FO_3S$ (M + Na): 329.0624, Found: 329.0632.



(Z)-4-((4-nitrophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3af) was prepared according to the general procedure from **1a** and **2f**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 94% yield (62.7 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.4 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H), 7.41–7.35 (m, 5H), 5.70 (t, J = 8.4 Hz, 1H), 4.46 (s, 2H), 4.25 (d, J = 8.4 Hz, 2H), 2.44 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 149.9, 144.3, 139.5, 130.0, 128.7, 128.6, 126.4, 124.5, 113.9, 60.6, 55.9; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}NO_5S$ (M + Na): 356.0569, Found: 356.0574.

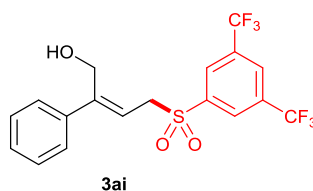


(Z)-4-((2,4-dimethoxyphenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ag) was prepared according to the general procedure from **1a** and **2g**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 95% yield (66.2 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 2.1, 8.4 Hz, 1H), 7.46–7.42 (m, 2H), 7.37–7.31 (m, 3H), 7.29 (d, J = 2.1 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 5.71 (t, J = 8.4 Hz, 1H), 4.43 (s, 2H), 4.14 (d, J = 8.4 Hz, 2H), 3.96 (s, 3H), 3.84 (s, 3H), 2.77 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.2, 148.7, 139.9, 130.1, 128.5, 128.3, 126.3, 122.5, 115.6, 110.8, 110.5, 60.1, 56.2, 56.1; HRMS (ESI-MS): Calcd. for $C_{18}H_{20}O_5S$ (M + Na): 371.0929, Found: 371.0937.

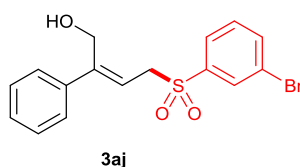


(Z)-4-((3,4-dichlorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ah) was prepared according to the general procedure from **1a** and **2h**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (65.7 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 2.1 Hz, 1H), 7.74 (dd, J = 2.1, 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.43–7.33 (m, 5H), 5.70 (t, J = 8.4 Hz, 1H), 4.46 (s, 2H), 4.18 (d, J = 8.3 Hz, 2H), 2.58 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7,

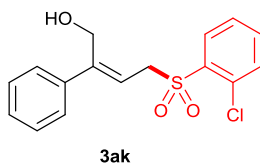
139.6, 139.3, 138.4, 134.2, 131.4, 130.4, 128.7, 128.5, 127.4, 126.4, 114.2, 60.5, 56.0; HRMS (ESI-MS): Calcd. for C₁₆H₁₄Cl₂O₃S (M + Na): 378.9938, Found: 378.9932.



(Z)-4-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ai) was prepared according to the general procedure from **1a** and **2i**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (78.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 2H), 8.20 (s, 1H), 7.43–7.31 (m, 5H), 5.72 (t, *J* = 8.4 Hz, 1H), 4.45 (s, 2H), 4.32 (d, *J* = 8.4 Hz, 2H), 2.31 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 141.4, 139.3, 133.4, 133.0, 129.0, 128.7, 127.6, 126.4, 123.7, 120.9, 113.9, 60.7, 55.9; HRMS (ESI-MS): Calcd. for C₁₈H₁₄F₆O₃S (M + Na): 447.0466, Found: 447.0473.

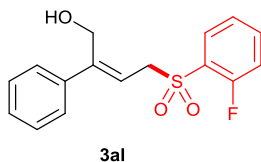


(Z)-4-((3-bromophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3aj) was prepared according to the general procedure from **1a** and **2j**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 82% yield (60.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (t, *J* = 1.8 Hz, 1H), 7.85–7.84 (m, 1H), 7.82–7.80 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.42–7.41 (m, 2H), 7.37–7.33 (m, 3H), 5.70 (t, *J* = 8.4 Hz, 1H), 4.43 (s, 2H), 4.17 (d, *J* = 8.4 Hz, 2H), 2.60 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 140.5, 139.7, 137.2, 131.3, 130.9, 128.6, 128.5, 126.9, 126.5, 123.4, 114.5, 60.3, 55.9; HRMS (ESI-MS): Calcd. for C₁₆H₁₅BrO₃S (M + Na): 388.9823, Found: 388.9831.

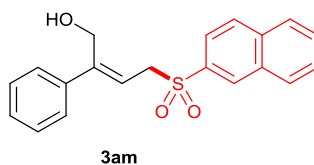


(Z)-4-((2-chlorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ak) was prepared according to the general procedure from **1a** and **2k**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 85% yield (54.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.7 Hz, 1H),

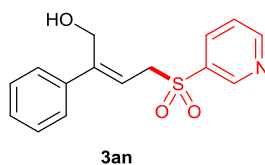
7.62–7.58 (m, 2H), 7.50–7.47 (m, 1H), 7.40–7.38 (m, 2H), 7.34–7.29 (m, 3H), 5.74 (t, $J = 8.4$ Hz, 1H), 4.52 (s, 2H), 4.47 (d, $J = 8.4$ Hz, 2H), 2.64 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 139.8, 136.4, 135.1, 132.7, 132.1, 132.0, 128.5, 128.4, 127.6, 126.5, 114.0, 60.3, 53.8; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{15}\text{ClO}_3\text{S}$ ($\text{M} + \text{Na}$): 345.0328, Found: 345.0336.



(Z)-4-((2-fluorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3al) was prepared according to the general procedure from **1a** and **2l**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 81% yield (49.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.94–7.91 (m, 1H), 7.70–7.66 (m, 1H), 7.41–7.39 (m, 2H), 7.36–7.27 (m, 5H), 5.76 (t, $J = 8.4$ Hz, 1H), 4.51 (s, 2H), 4.36 (d, $J = 8.4$ Hz, 2H), 2.64 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 158.7, 149.8, 139.8, 136.6, 130.9, 128.5, 128.4, 126.5, 124.9, 117.3, 117.2, 113.9, 60.3, 55.2; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{15}\text{FO}_3\text{S}$ ($\text{M} + \text{Na}$): 329.0624, Found: 329.0622.

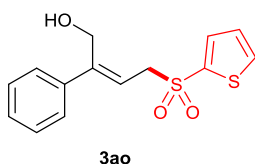


(Z)-4-(naphthalen-2-ylsulfonyl)-2-phenylbut-2-en-1-ol (3am) was prepared according to the general procedure from **1a** and **2m**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (62.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.03–7.87 (m, 4H), 7.72–7.63 (m, 2H), 7.43–7.39 (m, 2H), 7.36–7.30 (m, 3H), 5.74 (t, $J = 8.4$ Hz, 1H), 4.43 (d, $J = 8.0$ Hz, 2H), 4.22 (d, $J = 8.4$ Hz, 2H), 2.69 (brt, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 139.9, 135.5, 135.4, 132.1, 130.3, 129.6, 129.5, 129.4, 128.6, 128.3, 128.0, 127.9, 126.4, 122.8, 115.0, 60.3, 56.1; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 361.0874, Found: 361.0879.

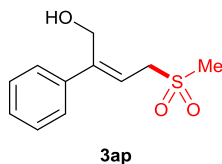


(Z)-2-phenyl-4-(pyridin-3-ylsulfonyl)but-2-en-1-ol (3an) was prepared according to the general procedure from **1a** and **2n**. The crude product was purified by flash column chromatog-

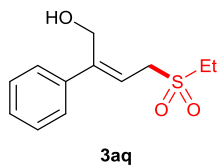
raphy (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (53.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.09 (d, $J = 2.0$ Hz, 1H), 8.86 (dd, $J = 1.5, 4.8$ Hz, 1H), 7.52–7.45 (m, 2H), 7.39–7.37 (m, 2H), 7.35–7.31 (m, 3H), 5.70 (t, $J = 8.4$ Hz, 1H), 4.39 (s, 2H), 4.23 (d, $J = 8.4$ Hz, 2H), 2.93 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 149.2, 139.6, 136.2, 135.1, 132.0, 128.6, 128.4, 126.4, 123.8, 114.3, 60.3, 56.2; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$ ($\text{M} + \text{Na}$): 312.0670, Found: 312.0678.



(Z)-2-phenyl-4-(thiophen-2-ylsulfonyl)but-2-en-1-ol (3ao) was prepared according to the general procedure from **1a** and **2o**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (66.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (dd, $J = 1.3, 5.0$ Hz, 1H), 7.69 (dd, $J = 1.3, 5.0$ Hz, 1H), 7.46–7.42 (m, 2H), 7.39–7.32 (m, 3H), 7.17 (dd, $J = 3.8, 5.2$ Hz, 1H), 5.77 (t, $J = 8.4$ Hz, 1H), 4.43 (s, 2H), 4.25 (d, $J = 8.4$ Hz, 2H), 2.53 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 139.7, 139.3, 134.7, 128.6, 128.3, 128.0, 126.5, 115.1, 60.2, 57.1; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}_2$ ($\text{M} + \text{Na}$): 317.0282, Found: 317.0276.

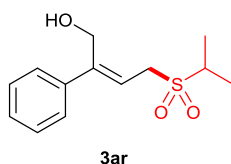


(Z)-4-(methylsulfonyl)-2-phenylbut-2-en-1-ol (3ap) was prepared according to the general procedure from **1a** and **2p**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 82% yield (37.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.50–7.46 (m, 2H), 7.38–7.32 (m, 3H), 5.92 (t, $J = 8.4$ Hz, 1H), 4.56 (s, 2H), 4.09 (d, $J = 8.4$ Hz, 2H), 3.07 (brs, 1H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.0, 139.9, 132.0, 128.6, 126.4, 115.1, 60.5, 54.4, 40.1; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 249.2798, Found: 249.2804.

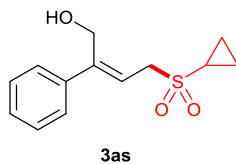


(Z)-4-(ethylsulfonyl)-2-phenylbut-2-en-1-ol (3aq) was prepared according to the general procedure from **1a** and **2q**. The crude product was purified by flash column chromatography

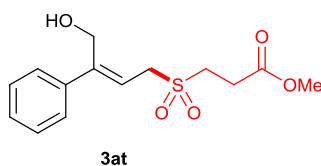
(Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 86% yield (41.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.49 (m, 2H), 7.39–7.31 (m, 3H), 5.90 (t, $J = 8.4$ Hz, 1H), 4.56 (s, 2H), 4.06 (d, $J = 8.4$ Hz, 2H), 3.07 (dd, $J = 7.5, 15.0$ Hz, 2H), 2.87 (brs, 1H), 1.44 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 140.0, 128.6, 128.4, 126.4, 114.5, 60.6, 51.9, 47.0, 6.53; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{S}$ (M + Na): 263.0718, Found: 263.0726.



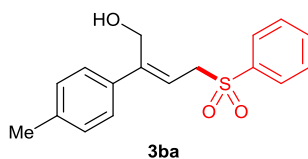
(Z)-4-(isopropylsulfonyl)-2-phenylbut-2-en-1-ol (3ar) was prepared according to the general procedure from **1a** and **2r**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 90% yield (45.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.49 (m, 2H), 7.38–7.31 (m, 3H), 5.89 (t, $J = 8.4$ Hz, 1H), 4.53 (s, 2H), 4.04 (d, $J = 8.4$ Hz, 2H), 3.25–3.15 (m, 1H), 3.10 (brs, 1H), 1.44 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 140.1, 128.5, 128.2, 126.4, 114.3, 60.4, 53.0, 49.4, 15.2; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{S}$ (M + Na): 277.0874, Found: 277.0878.



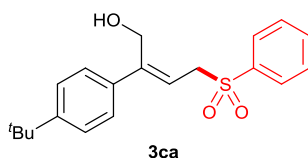
(Z)-4-(cyclopropylsulfonyl)-2-phenylbut-2-en-1-ol (3as) was prepared according to the general procedure from **1a** and **2s**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 87% yield (44.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.49 (m, 2H), 7.40–7.31 (m, 3H), 5.97 (t, $J = 8.4$ Hz, 1H), 4.57 (s, 2H), 4.11 (d, $J = 8.4$ Hz, 2H), 2.87 (brs, 1H), 2.51–2.45 (m, 1H), 1.33–1.26 (m, 2H), 1.12–1.06 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 140.0, 128.6, 128.3, 126.4, 114.9, 60.4, 29.7, 4.9; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$ (M + Na): 275.0718, Found: 275.0723.



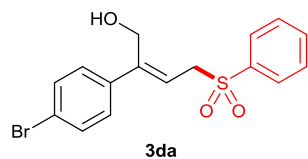
methyl (Z)-3-((4-hydroxy-3-phenylbut-2-en-1-yl)sulfonyl)propanoate (3at) was prepared according to the general procedure from **1a** and **2t**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 82% yield (49.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.47 (m, 2H), 7.38–7.33 (m, 3H), 5.93 (t, *J* = 8.4 Hz, 1H), 4.56 (s, 2H), 4.12 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H), 3.39 (t, *J* = 7.3 Hz, 2H), 3.05 (brs, 1H), 2.90 (t, *J* = 7.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 171.03, 149.1, 139.9, 132.0, 128.5, 126.4, 114.7, 60.5, 53.5, 52.5, 47.7, 26.8; HRMS (ESI-MS): Calcd. for C₁₄H₁₈O₅S (M + Na): 321.0773, Found: 321.0781.



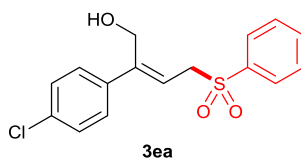
(Z)-4-(phenylsulfonyl)-2-(p-tolyl)but-2-en-1-ol (3ba) was prepared according to the general procedure from **1b** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (55.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.92–7.89 (m, 2H), 7.70–7.66 (m, 1H), 7.60–7.55 (m, 2H), 7.33–7.30 (m, 2H), 7.17–7.14 (m, 2H), 5.68 (t, *J* = 8.4 Hz, 1H), 4.38 (s, 2H), 4.13 (d, *J* = 8.4 Hz, 2H), 2.62 (brs, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 138.6, 138.3, 136.8, 134.0, 129.3, 129.2, 128.3, 126.3, 114.1, 60.1, 56.0, 21.1; HRMS (ESI-MS): Calcd. for C₁₇H₁₈O₃S (M + Na): 325.0874, Found: 325.0892.



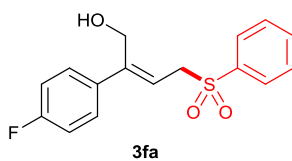
(Z)-2-(4-(tert-butyl)phenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ca) was prepared according to the general procedure from **1c** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 94% yield (64.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.90 (m, 2H), 7.71–7.66 (m, 1H), 7.61–7.56 (m, 2H), 7.41–7.34 (m, 4H), 5.70 (t, *J* = 8.4 Hz, 1H), 4.41 (s, 2H), 4.15 (d, *J* = 8.4 Hz, 2H), 2.58 (brs, 1H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 151.5, 148.7, 138.6, 136.7, 134.0, 129.3, 128.4, 126.1, 125.5, 114.1, 60.0, 56.0, 34.6, 31.2; HRMS (ESI-MS): Calcd. for C₂₀H₂₄O₃S (M + Na): 367.1344, Found: 367.1352.



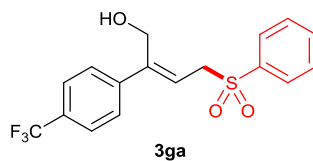
(Z)-2-(4-bromophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3da) was prepared according to the general procedure from **1d** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 88% yield (64.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.89 (m, 2H), 7.72–7.68 (m, 1H), 7.61–7.57 (m, 2H), 7.48–7.45 (m, 2H), 7.34–7.29 (m, 2H), 5.71 (t, *J* = 8.4 Hz, 1H), 4.39 (s, 2H), 4.13 (d, *J* = 8.4 Hz, 2H), 2.76 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 138.8, 138.6, 134.2, 131.6, 129.4, 128.3, 128.0, 122.5, 115.4, 59.9, 55.9; HRMS (ESI-MS): Calcd. for C₁₆H₁₅BrO₃S (M + Na): 388.9823, Found: 388.9826.



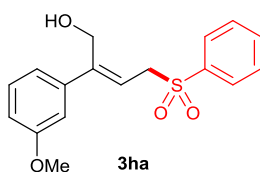
(Z)-2-(4-chlorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ea) was prepared according to the general procedure from **1e** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 91% yield (58.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.91–7.88 (m, 2H), 7.71–7.67 (m, 1H), 7.60–7.56 (m, 2H), 7.38–7.29 (m, 4H), 5.70 (t, *J* = 8.4 Hz, 1H), 4.38 (s, 2H), 4.13 (d, *J* = 8.4 Hz, 2H), 2.75 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.0, 138.6, 138.3, 134.2, 134.1, 129.4, 128.7, 128.3, 127.7, 115.4, 60.0, 55.9; HRMS (ESI-MS): Calcd. for C₁₆H₁₅ClO₃S (M + Na): 345.0328, Found: 345.0336.



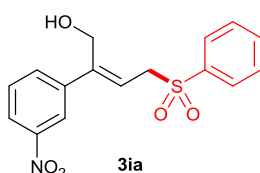
(Z)-2-(4-fluorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3fa) was prepared according to the general procedure from **1f** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 82% yield (50.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.92–7.89 (m, 2H), 7.71–7.66 (m, 1H), 7.60–7.56 (m, 2H), 7.43–7.39 (m, 2H), 7.06–6.99 (m, 2H), 5.67 (t, *J* = 8.4 Hz, 1H), 4.38 (s, 2H), 4.13 (d, *J* = 8.4 Hz, 2H), 2.82 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 161.5, 148.1, 138.5, 136.0, 135.9, 134.1, 129.4, 128.3, 128.2, 128.1, 115.5, 115.3, 114.8, 60.0, 55.9; HRMS (ESI-MS): Calcd. for C₁₆H₁₅FO₃S (M + Na): 329.0624, Found: 329.0628.



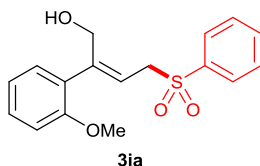
(Z)-4-(phenylsulfonyl)-2-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (3ga) was prepared according to the general procedure from **1g** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 82% yield (58.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.92–7.91 (m, 2H), 7.72–7.69 (m, 1H), 7.61–7.54 (m, 6H), 5.78 (t, *J* = 8.4 Hz, 1H), 4.44 (s, 2H), 4.15 (d, *J* = 8.4 Hz, 2H), 2.85 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 143.5, 138.5, 134.3, 129.5, 128.5, 128.3, 126.8, 125.5, 116.9, 59.9, 55.8; HRMS (ESI-MS): Calcd. for C₁₇H₁₅F₃O₃S (M + Na): 379.0592, Found: 379.0598.



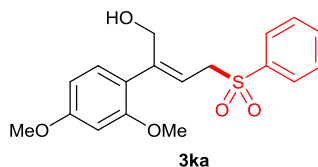
(Z)-2-(3-methoxyphenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ha) was prepared according to the general procedure from **1h** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (58.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.91 (m, 2H), 7.71–7.67 (m, 1H), 7.61–7.57 (m, 2H), 7.28–7.24 (m, 1H), 7.01–6.95 (m, 2H), 6.88–6.85 (m, 1H), 5.70 (t, *J* = 8.4 Hz, 1H), 4.40 (s, 2H), 4.14 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 2.61 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 149.1, 141.4, 138.6, 134.1, 129.6, 129.4, 128.4, 118.9, 115.2, 113.7, 112.2, 60.3, 55.9, 55.3; HRMS (ESI-MS): Calcd. for C₁₇H₁₈O₄S (M + Na): 341.0823, Found: 341.0816.



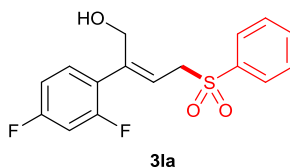
(Z)-2-(3-nitrophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ia) was prepared according to the general procedure from **1i** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 96% yield (64.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.27 (t, *J* = 2.0 Hz, 1H), 8.18–8.16 (m, 1H), 7.94–7.92 (m, 2H), 7.85–7.83 (m, 1H), 7.75–7.71 (m, 1H), 7.64–7.60 (m, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 5.82 (t, *J* = 8.4 Hz, 1H), 4.48 (s, 2H), 4.18 (d, *J* = 8.4 Hz, 2H), 3.01 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.3, 147.2, 141.6, 138.4, 134.4, 132.5, 129.6, 129.5, 128.2, 123.0, 121.4, 117.4, 59.8, 55.7; HRMS (ESI-MS): Calcd. for C₁₆H₁₅NO₅S (M + Na): 356.0569, Found: 356.0574.



(Z)-2-(2-methoxyphenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ja) was prepared according to the general procedure from **1j** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 87% yield (55.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.68–7.55 (m, 3H), 7.30–7.27 (m, 1H), 7.11–7.08 (m, 1H), 6.95–6.85 (m, 2H), 5.82 (t, *J* = 8.4 Hz, 1H), 4.15 (d, *J* = 8.4 Hz, 2H), 4.13, (s, 2H), 3.79 (s, 3H), 2.50 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.1, 148.4, 138.6, 133.7, 130.2, 129.9, 129.3, 129.0, 128.4, 120.9, 118.1, 110.5, 60.8, 55.6, 55.4; HRMS (ESI-MS): Calcd. for C₁₇H₁₈O₄S (M + Na): 341.0823, Found: 341.0831.

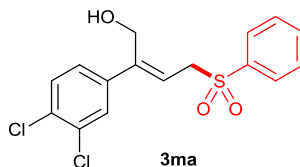


(Z)-2-(2,4-dimethoxyphenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ka) was prepared according to the general procedure from **1k** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (64.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.94 (m, 2H), 7.69–7.65 (m, 1H), 7.60–7.56 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.48–6.44 (m, 2H), 5.57 (t, *J* = 8.4 Hz, 1H), 4.15 (d, *J* = 8.4 Hz, 2H), 4.13, (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.33 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 157.2, 148.2, 138.8, 133.8, 130.6, 129.1, 128.5, 123.0, 117.4, 104.6, 98.7, 61.0, 55.8, 55.5, 55.4; HRMS (ESI-MS): Calcd. for C₁₈H₂₀O₅S (M + Na): 371.0929, Found: 371.0936.

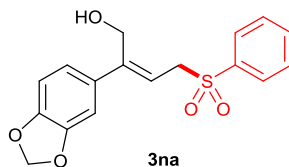


(Z)-2-(2,4-difluorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3la) was prepared according to the general procedure from **1l** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 91% yield (59.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.95–7.92 (m, 2H), 7.72–7.68 (m, 1H), 7.63–7.58 (m, 2H), 7.32–7.27 (m, 1H), 6.89–6.77 (m, 2H), 5.64 (t, *J* = 8.4 Hz, 1H),

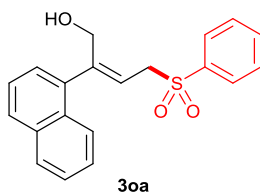
4.29 (s, 2H), 4.16 (d, $J = 8.4$ Hz, 2H), 2.46 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 163.8, 161.4, 161.3, 161.0, 160.9, 158.5, 158.4, 144.2, 138.4, 134.1, 131.0, 130.0, 129.3, 128.3, 118.9, 111.6, 111.4, 104.4, 104.1, 103.9, 60.8, 60.7, 50.6; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 347.0529, Found: 347.0534.



(Z)-2-(3,4-dichlorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ma) was prepared according to the general procedure from **1m** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 90% yield (64.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91–7.89 (m, 2H), 7.73–7.69 (m, 1H), 7.62–7.53 (m, 3H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.30–7.27 (m, 1H), 5.71 (t, $J = 8.4$ Hz, 1H), 4.38 (s, 2H), 4.13 (d, $J = 8.4$ Hz, 2H), 2.85 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 139.9, 138.5, 134.3, 132.6, 132.3, 130.4, 129.5, 128.4, 128.2, 125.7, 116.4, 59.8, 55.8; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 378.9938, Found: 378.9942.

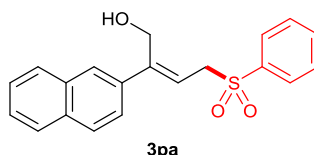


(Z)-2-(benzo[d][1,3]dioxol-5-yl)-4-(phenylsulfonyl)but-2-en-1-ol (3na) was prepared according to the general procedure from **1n** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 86% yield (57.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.92–7.90 (m, 2H), 7.72–7.67 (m, 1H), 7.62–7.57 (m, 2H), 6.94 (dd, $J = 1.8, 9.6$ Hz, 2H), 6.78 (d, $J = 8.1$ Hz, 1H), 5.97 (s, 2H), 5.61 (t, $J = 8.4$ Hz, 1H), 4.37 (s, 2H), 4.11 (d, $J = 8.4$ Hz, 2H), 2.63 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.7, 147.9, 147.8, 138.6, 134.1, 134.0, 129.4, 128.4, 120.3, 113.8, 108.3, 106.9, 101.2, 60.2, 56.0; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_5\text{S}$ ($\text{M} + \text{Na}$): 355.0616, Found: 355.0623.

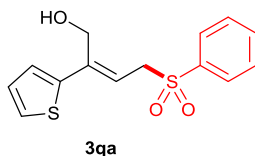


(Z)-2-(naphthalen-1-yl)-4-(phenylsulfonyl)but-2-en-1-ol (3oa) was prepared according to the general procedure from **1o** and **2a**. The crude product was purified by flash column chro-

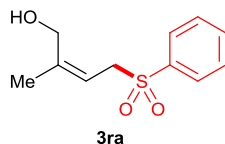
matography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 89% yield (60.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.98–7.96 (m, 2H), 7.86–7.82 (m, 1H), 7.80–7.78 (m, 2H), 7.69–7.65 (m, 1H), 7.59–7.55 (m, 2H), 7.50–7.39 (m, 3H), 7.26–7.24 (m, 1H), 5.55 (t, $J = 8.4$ Hz, 1H), 4.43 (s, 2H), 4.30 (d, $J = 8.4$ Hz, 2H), 2.59 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 138.7, 138.5, 134.0, 133.6, 131.3, 131.1, 129.3, 128.4, 128.3, 128.2, 126.3, 125.9, 125.8, 125.2, 117.8, 62.7, 55.5; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 361.0874, Found: 361.0876.



(Z)-2-(naphthalen-2-yl)-4-(phenylsulfonyl)but-2-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 = 3:1) on silica gel to provide the title compound as a yellow solid in 85% yield (57.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.94–7.90 (m, 3H), 7.83–7.88 (m, 3H), 7.69–7.64 (m, 1H), 7.58–7.45 (m, 5H), 5.83 (t, $J = 8.4$ Hz, 1H), 4.51 (s, 2H), 4.18 (d, $J = 8.4$ Hz, 2H), 2.82 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 138.6, 137.0, 134.1, 133.2, 133.0, 129.3, 128.3, 128.2, 128.1, 127.5, 126.4, 126.3, 125.6, 124.1, 115.4, 60.1, 56.1; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 361.0874, Found: 361.0878.

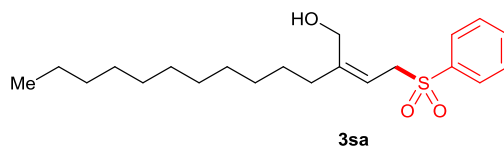


(E)-4-(phenylsulfonyl)-2-(thiophen-2-yl)but-2-en-1-ol (3qa) was prepared according to the general procedure from **1q** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 86% yield (50.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.92–7.89 (m, 2H), 7.72–7.67 (m, 1H), 7.61–7.56 (m, 2H), 7.24–7.21 (m, 2H), 7.02 (dd, $J = 3.7, 5.2$ Hz, 1H), 5.77 (t, $J = 8.4$ Hz, 1H), 4.46 (d, $J = 5.4$ Hz, 2H), 4.12 (d, $J = 8.4$ Hz, 2H), 2.77 (brt, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 142.5, 138.6, 134.1, 129.4, 128.4, 127.8, 125.6, 125.4, 112.7, 60.0, 55.8; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}_2$ ($\text{M} + \text{Na}$): 317.0282, Found: 317.0286.

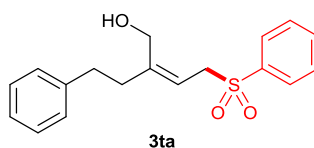


(Z)-2-methyl-4-(phenylsulfonyl)but-2-en-1-ol (3ra) was prepared according to the general procedure from **1r** and **2a**. The crude product was purified by flash column chromatography

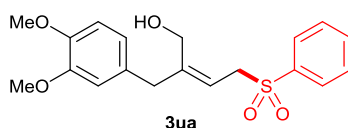
(Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 75% yield (33.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90–7.87 (m, 2H), 7.70–7.65 (m, 1H), 7.60–7.56 (m, 2H), 5.23 (t, $J = 8.4$ Hz, 1H), 3.98 (s, 2H), 3.94 (d, $J = 8.4$ Hz, 2H), 2.56 (brs, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 138.7, 133.8, 129.2, 128.2, 111.8, 67.9, 61.8, 25.5; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}$ (M + Na): 249.0561, Found: 249.0554.



(Z)-2-(2-(phenylsulfonyl)ethylidene)tridecan-1-ol (3sa) was prepared according to the general procedure from **1s** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 80% yield (58.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90–7.87 (m, 2H), 7.70–7.65 (m, 1H), 7.59–7.56 (m, 2H), 5.20 (t, $J = 8.4$ Hz, 1H), 4.01 (s, 2H), 3.97 (d, $J = 8.4$ Hz, 2H), 2.39 (brs, 1H), 2.15 (t, $J = 7.4$ Hz, 2H), 1.43–1.20 (m, 18H), 0.88 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.1, 138.7, 133.9, 129.2, 128.3, 111.8, 60.7, 55.3, 35.9, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.8, 22.6, 14.1; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{S}$ (M + Na): 389.2126, Found: 389.2134.

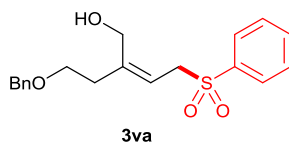


(Z)-2-phenethyl-4-(phenylsulfonyl)but-2-en-1-ol (3ta) was prepared according to the general procedure from **1t** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 82% yield (52.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.80 (m, 2H), 7.68–7.63 (m, 1H), 7.57–7.52 (m, 2H), 7.30–7.27 (m, 2H), 7.22–7.16 (m, 3H), 5.22 (t, $J = 8.4$ Hz, 1H), 4.04 (s, 2H), 3.94 (d, $J = 8.4$ Hz, 2H), 2.75 (t, $J = 7.4$ Hz, 2H), 2.53 (brs, 1H), 2.49 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 141.1, 138.6, 133.9, 129.2, 128.4, 128.3, 128.2, 126.0, 112.7, 60.6, 55.2, 37.5, 34.2; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{S}$ (M + Na): 339.1031, Found: 339.1026.

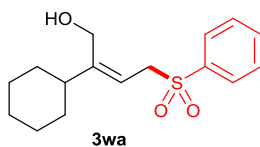


(Z)-2-(3,4-dimethoxybenzyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ua) was prepared according to the general procedure from **1u** and **2a**. The crude product was purified by flash col-

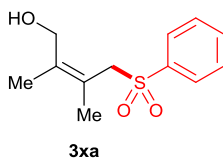
umn chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (66.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.83 (m, 2H), 7.66–7.63 (m, 1H), 7.54–7.51 (m, 2H), 6.78 (d, J = 8.0 Hz, 1H), 6.71–6.68 (m, 2H), 5.24 (t, J = 8.4 Hz, 1H), 3.99 (s, 2H), 3.98 (d, J = 8.4 Hz, 2H), 3.86 (s, 6H), 2.45 (s, 2H), 2.42 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 148.9, 147.6, 138.6, 133.9, 130.7, 129.2, 128.2, 121.1, 113.4, 112.2, 111.1, 60.1, 55.9, 55.2, 41.4; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_5\text{S}$ ($\text{M} + \text{Na}$): 385.1086, Found: 385.1082.



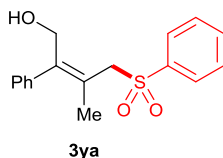
(Z)-2-(2-(benzyloxy)ethyl)-4-(phenylsulfonyl)but-2-en-1-ol (3va) was prepared according to the general procedure from **1v** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 86% yield (59.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.86–7.82 (m, 2H), 7.63–7.59 (m, 1H), 7.51–7.45 (m, 2H), 7.36–7.27 (m, 5H), 5.31 (t, J = 8.4 Hz, 1H), 4.48 (s, 2H), 3.92 (d, J = 8.4 Hz, 2H), 3.91 (m, 2H), 3.56 (t, J = 7.4 Hz, 2H), 2.99 (brs, 1H), 2.45 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 138.4, 137.6, 133.7, 129.0, 128.4, 128.3, 127.7, 127.6, 113.9, 73.1, 69.2, 60.2, 55.2, 36.0; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{S}$ ($\text{M} + \text{Na}$): 369.1136, Found: 369.1144.



(Z)-2-cyclohexyl-4-(phenylsulfonyl)but-2-en-1-ol (3wa) was prepared according to the general procedure from **1w** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 95% yield (55.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.87 (m, 2H), 7.69–7.67 (m, 1H), 7.59–7.57 (m, 2H), 5.19 (t, J = 8.4 Hz, 1H), 3.99 (s, 2H), 3.96 (d, J = 8.4 Hz, 2H), 2.39 (brs, 1H), 2.07 (t, J = 7.4 Hz, 2H), 1.78–1.67 (m, 4H), 1.31–1.08 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 138.5, 133.9, 129.2, 128.4, 111.1, 59.9, 55.4, 43.9, 32.1, 26.5, 26.1; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$): 317.1187, Found: 317.1193.



(*Z*)-2,3-dimethyl-4-(phenylsulfonyl)but-2-en-1-ol (**3xa**) was prepared according to the general procedure from **1x** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 77% yield (37.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.90 (m, 2H), 7.71–7.66 (m, 1H), 7.61–7.56 (m, 2H), 3.99 (s, 2H), 3.98 (s, 2H), 1.85 (s, 3H), 1.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.1, 140.4, 139.3, 133.9, 129.4, 128.3, 63.8, 61.2, 22.7, 14.1; HRMS (ESI-MS): Calcd. for C₁₂H₁₆O₃S (M + Na): 263.0718, Found: 263.726.



(*Z*)-3-methyl-2-phenyl-4-(phenylsulfonyl)but-2-en-1-ol (**3ya**) was prepared according to the general procedure from **1y** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 72% yield (43.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.00–7.97 (m, 2H), 7.73–7.69 (m, 1H), 7.65–7.60 (m, 2H), 7.38–7.33 (m, 2H), 7.30–7.27 (m, 1H), 7.17–7.14 (m, 2H), 4.19 (s, 2H), 4.14 (s, 2H), 1.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 140.4, 139.2, 134.1, 129.4, 128.4, 128.3, 128.2, 127.3, 122.5, 63.6, 61.0, 14.1; HRMS (ESI-MS): Calcd. for C₁₇H₁₈O₃S (M + Na): 325.0874, Found: 325.0886.

X-ray crystallography of **3ab**

A single-crystal of **3ab** was obtained from ethyl acetate/hexane solvent system at room temperature. A specimen of C₁₇H₁₈O₃S was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 1.34139 \text{ \AA}$). The total exposure time was 0.14 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 7276 reflections to a maximum θ angle of 56.67° (0.80 Å resolution), of which 2773 were independent (average redundancy 2.624, completeness = 99.3%, $R_{\text{int}} = 6.23\%$, $R_{\text{sig}} = 7.42\%$) and 2576 (92.90%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 5.5164(3) \text{ \AA}$, $b = 8.0709(5) \text{ \AA}$, $c = 17.2124(11) \text{ \AA}$, $\beta = 96.454(2)^\circ$, volume = 761.48(8) Å³, are based upon the refinement of the XYZ-centroids of 6767 reflections above $20 \sigma(I)$ with $8.996^\circ < 2\theta < 113.1^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.643. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 c 1, with $Z = 2$ for the formula unit, C₁₇H₁₈O₃S. The final anisotropic full-matrix least-squares refinement on F^2 with 192 variables converged at $R1 = 4.93\%$, for the observed data and $wR2 = 13.70\%$ for all data. The good-

ness-of-fit was 0.854. The largest peak in the final difference electron density synthesis was $0.308 \text{ e}/\text{\AA}^3$ and the largest hole was $-0.401 \text{ e}/\text{\AA}^3$ with an RMS deviation of $0.061 \text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was $1.319 \text{ g}/\text{cm}^3$ and $F(000)$, 320 e^- . The crystallographic data is summarized in Table F1 and the diagram is shown in Figure F1.

Table F1. Crystal data and structure refinement for **3ab**.

Identification code	xb2305_4
Empirical formula	C17H18O3S
Formula weight	302.37 g/mol
Temperature	186(2) K
Wavelength	1.34139 Å
Crystal system	Monoclinic
space group	P 1 c 1
Unit cell dimensions	a = 5.5164(3) Å $\alpha = 90^\circ$ b = 8.0709(5) Å $\beta = 96.454(2)^\circ$ c = 17.2124(11) Å $\gamma = 90^\circ$
Volume	761.48(8) Å ³
Z	2
Calculated density	1.319 g/m ³
Absorption coefficient	1.275 mm ⁻¹
F(000)	320
Crystal size	0.35 x 0.27 x 0.14mm ³
Theta range for data collection	4.50 to 56.67°
Index ranges	-6<=h<=6, -10<=k<=10, -21<=l<=21
Reflections collected	7276
Completeness to theta = 25.08	99.3 %
Absorption correction	Multi-Scan
Max. and min. transmission	0.9648 and 0.9159
Refinement method	Full-matrix least-squares on F ²

Data / restraints / parameters	2773 / 2 / 192
Goodness-of-fit on F^2	0.854
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0493, wR2 = 0.1311
R indices (all data)	R1 = 0.0553, wR2 = 0.1370
Absolute structure parameter	0.07(2)
Largest diff. peak and hole	0.308 and -0.401 $e\text{\AA}^{-3}$

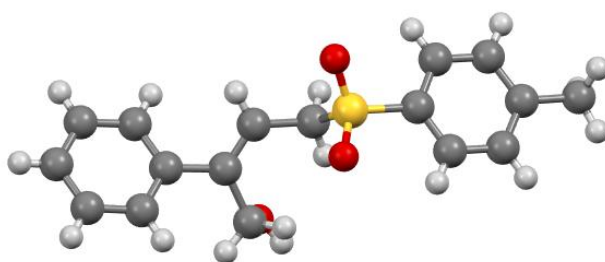


Figure F1. Molecular structure of **3ab**.

References:

1. (a) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 6439; (b) A. Khan, L. Yang, J. Xu, L. Y. Jin, Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 11257.
2. B. Du, P. Qian, Y. Wang, H. Mei, J. Han, Y. Pan, *Org. Lett.* **2016**, *18*, 4144.

TEM study of PdNPs for the coupling reaction of **1a** with **2a** in THF.

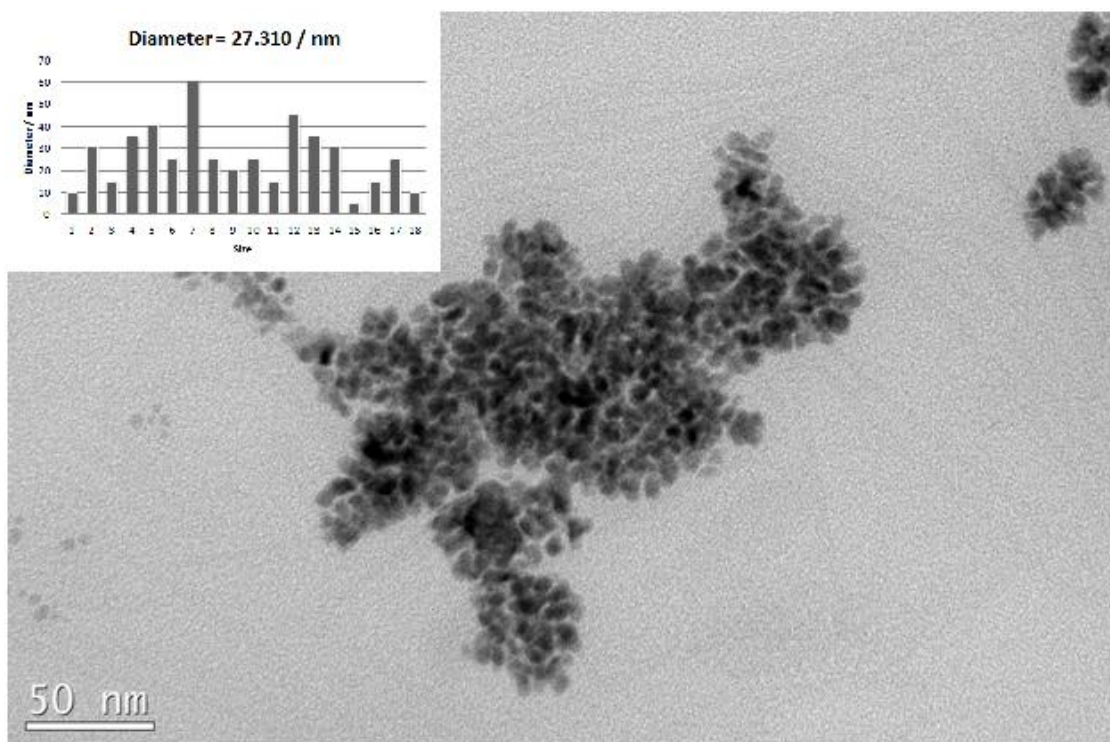


Figure S1. TEM image. A sample taken after 30 minutes of the reaction in THF.

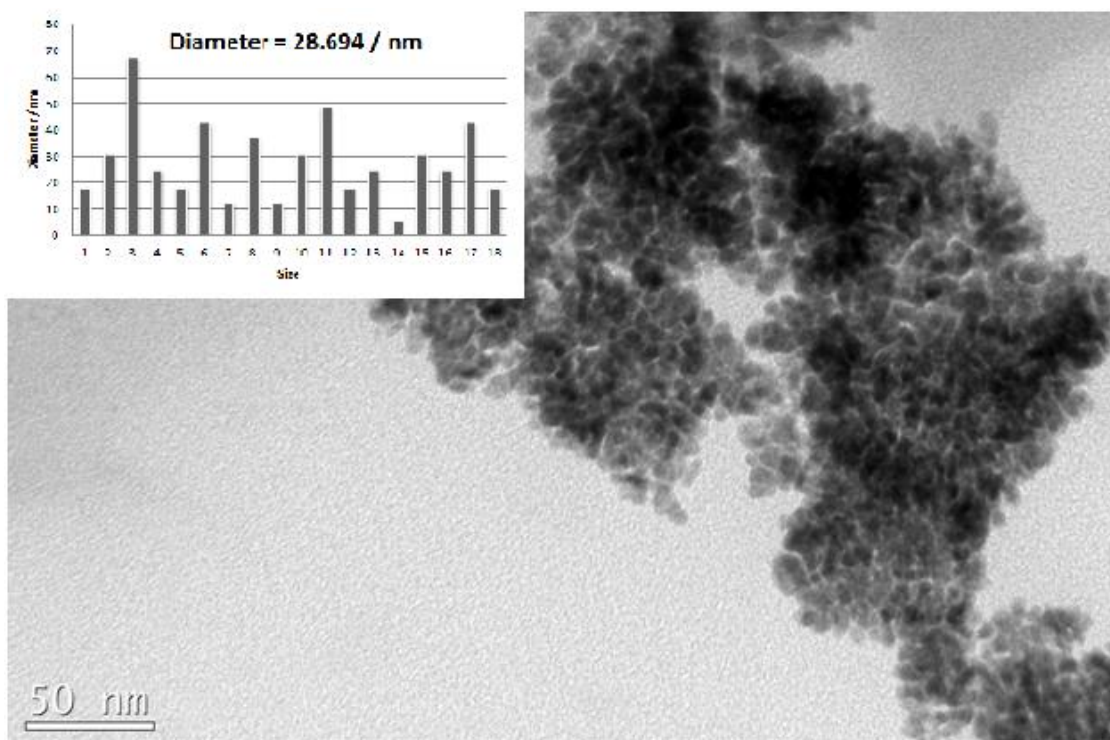
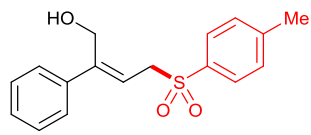
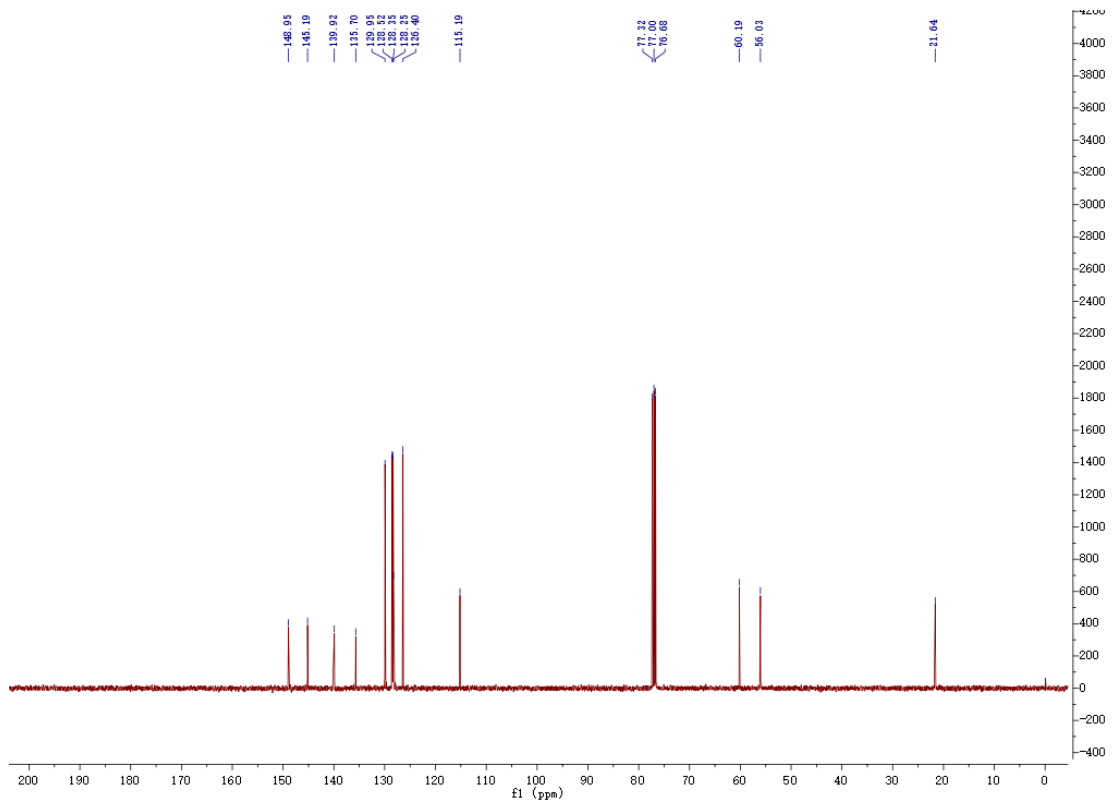
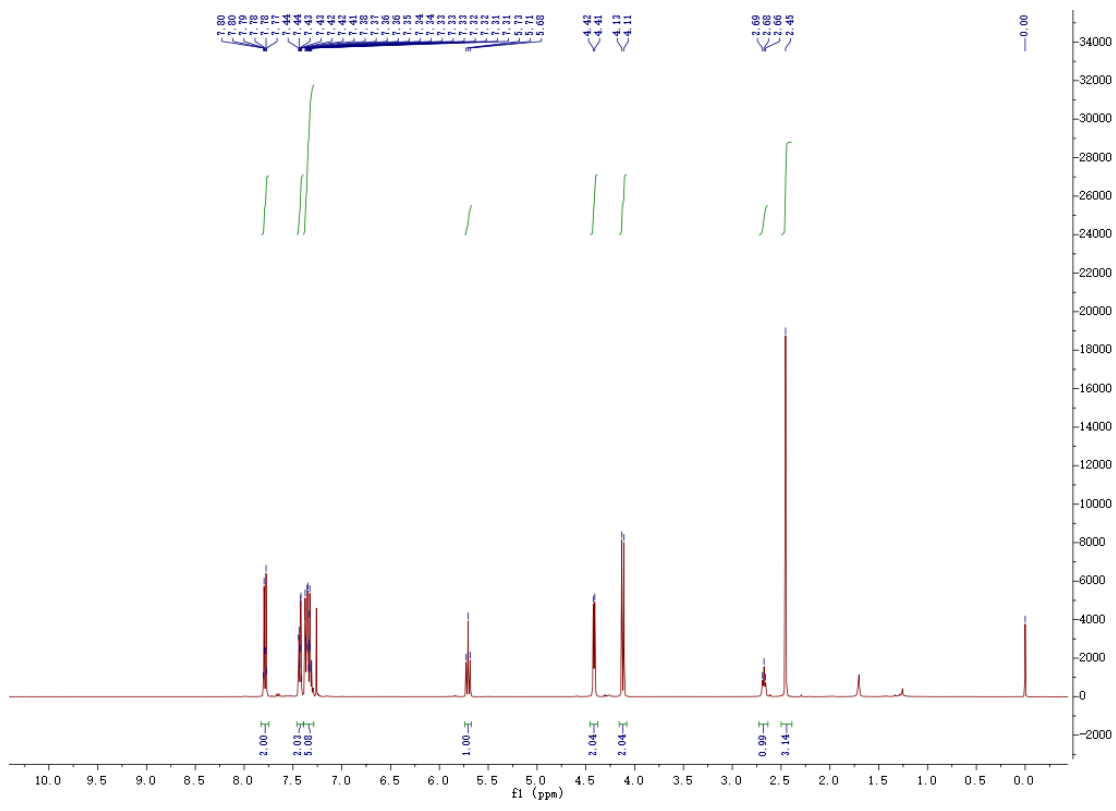
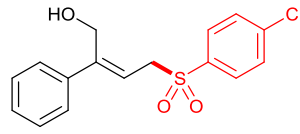


Figure S2. TEM image. A sample taken after 15 hours of the reaction in THF

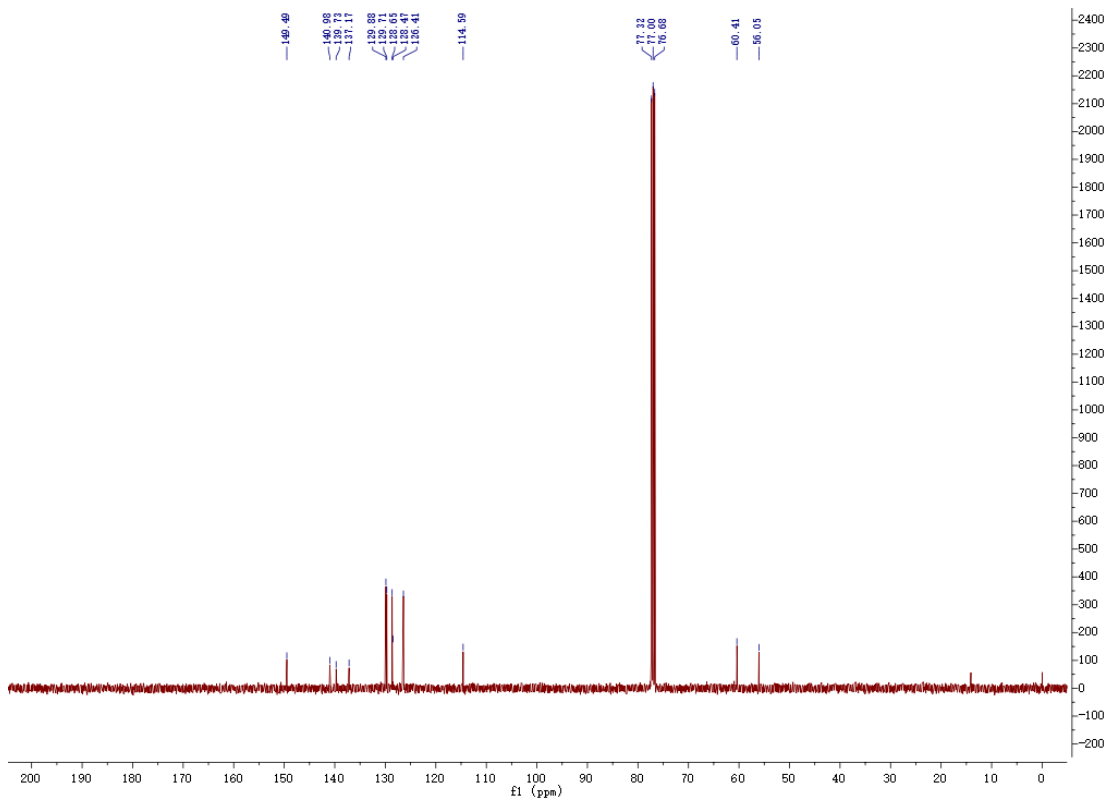
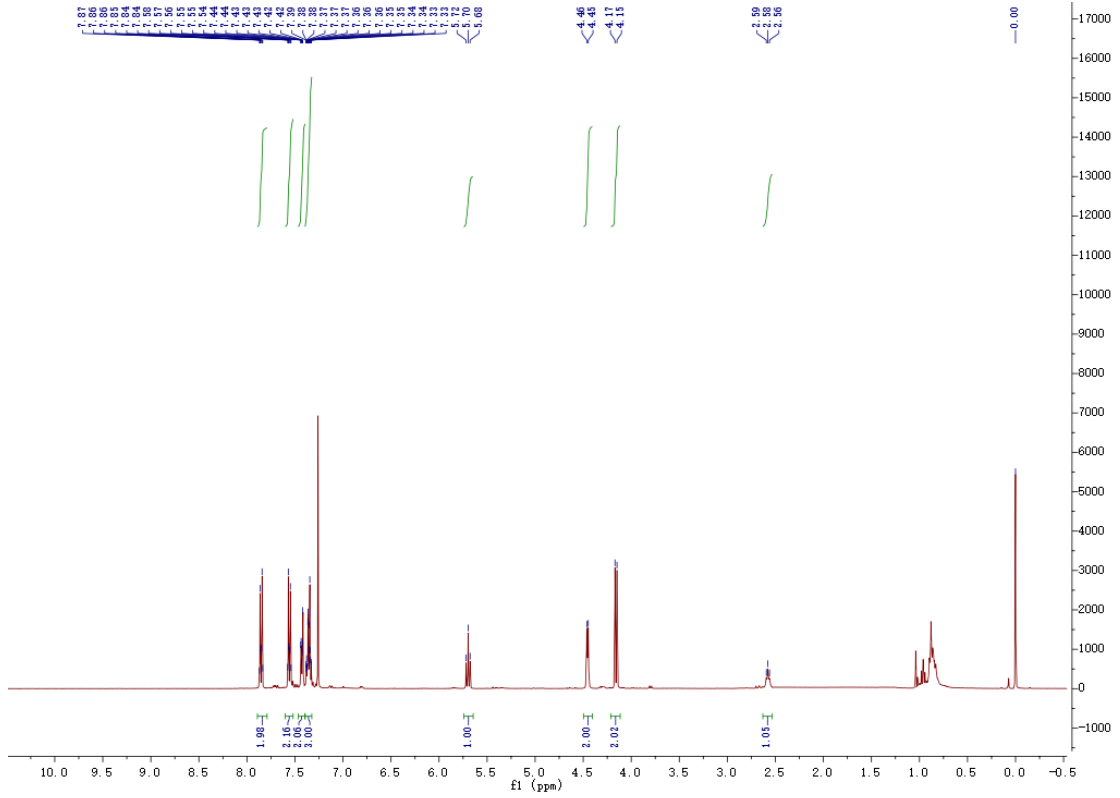


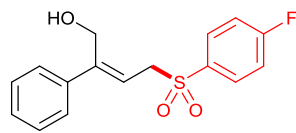
3ab



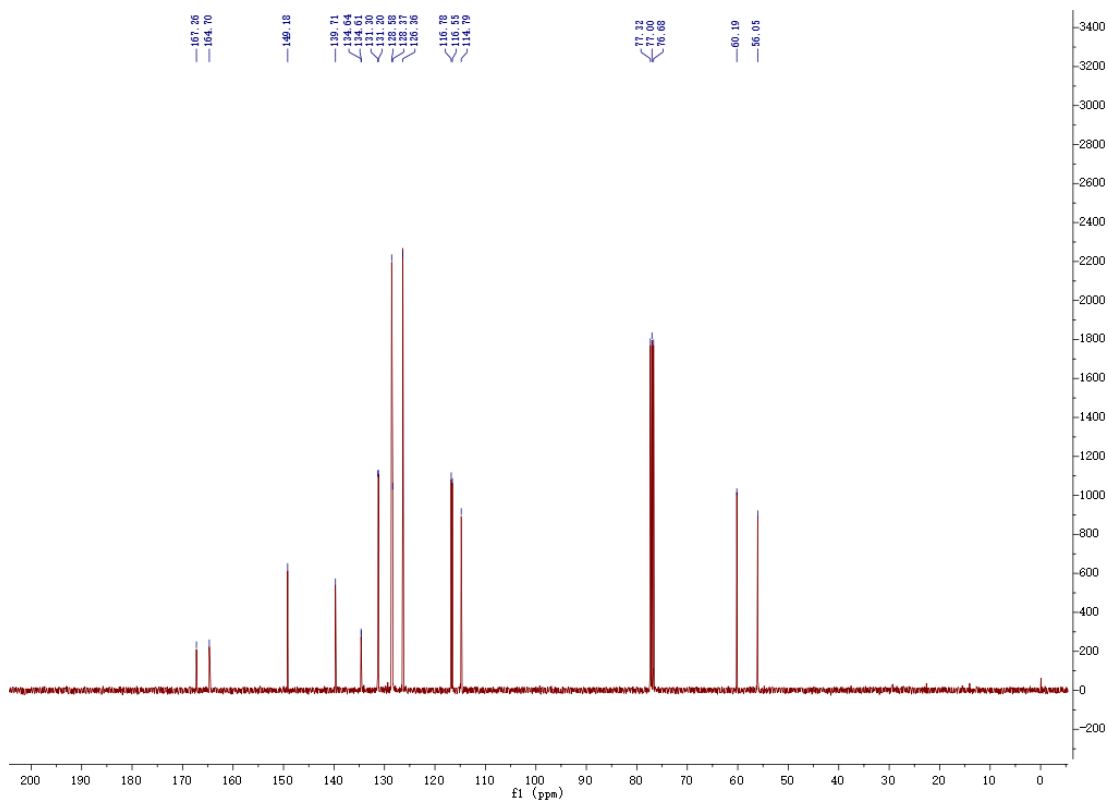
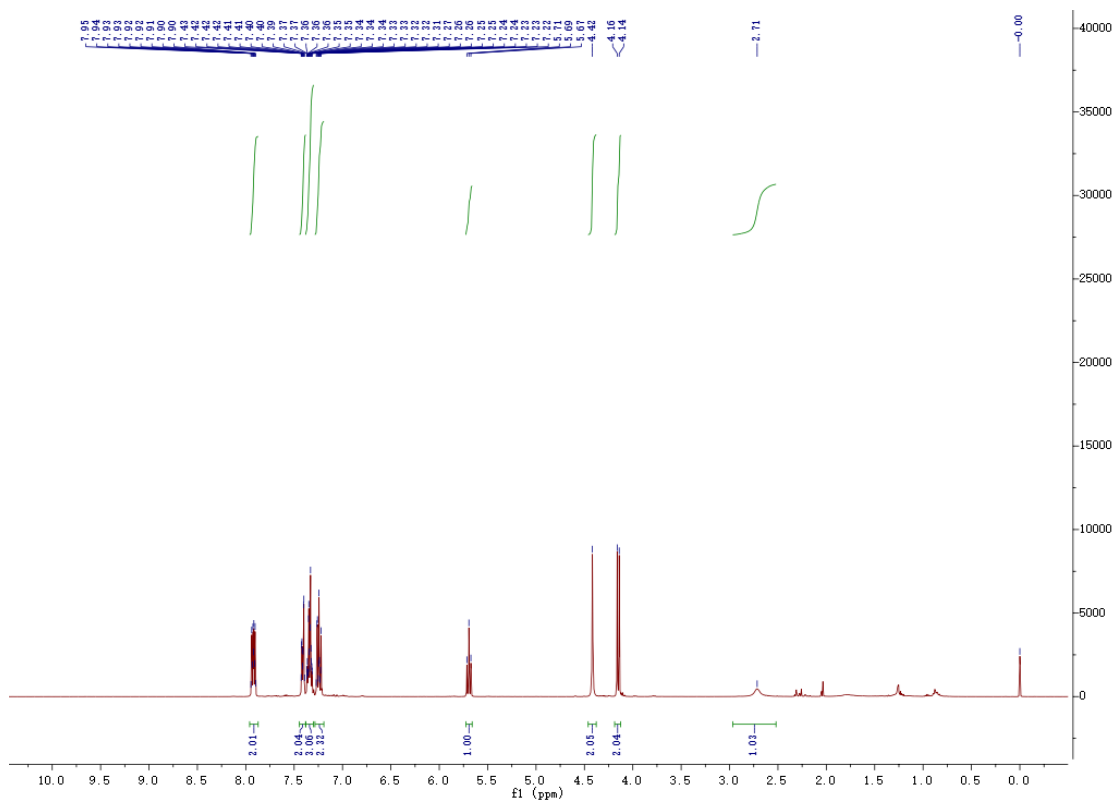


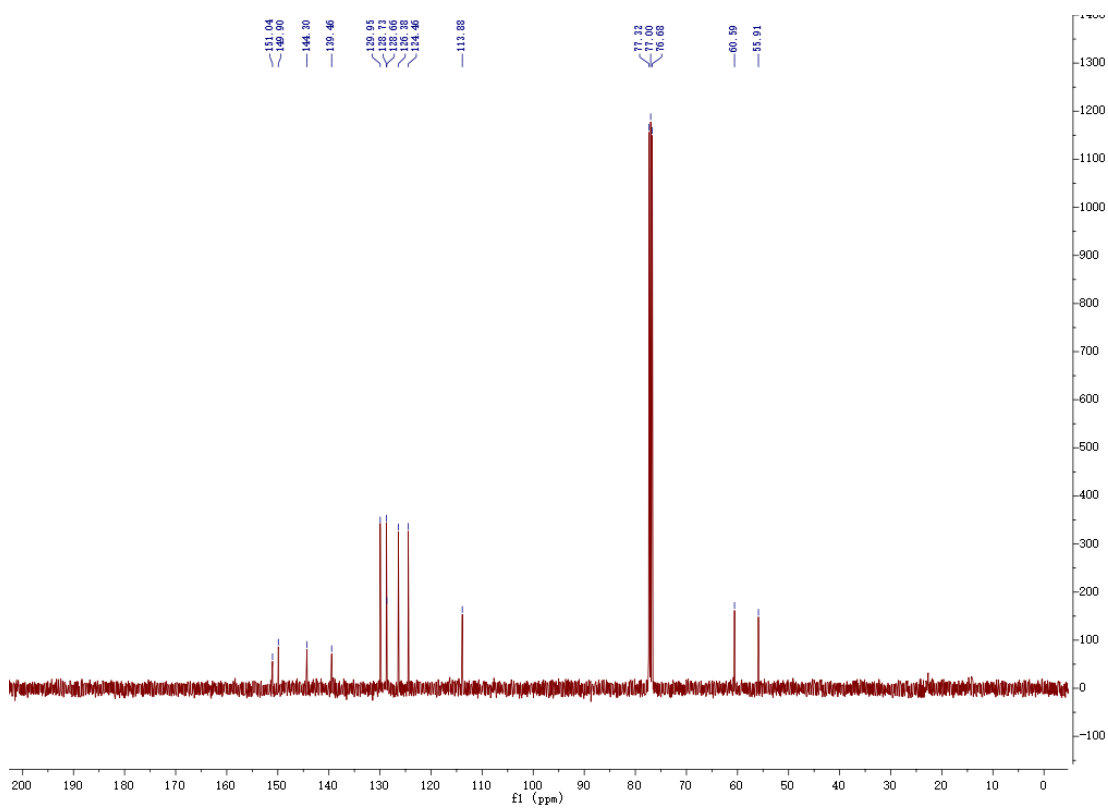
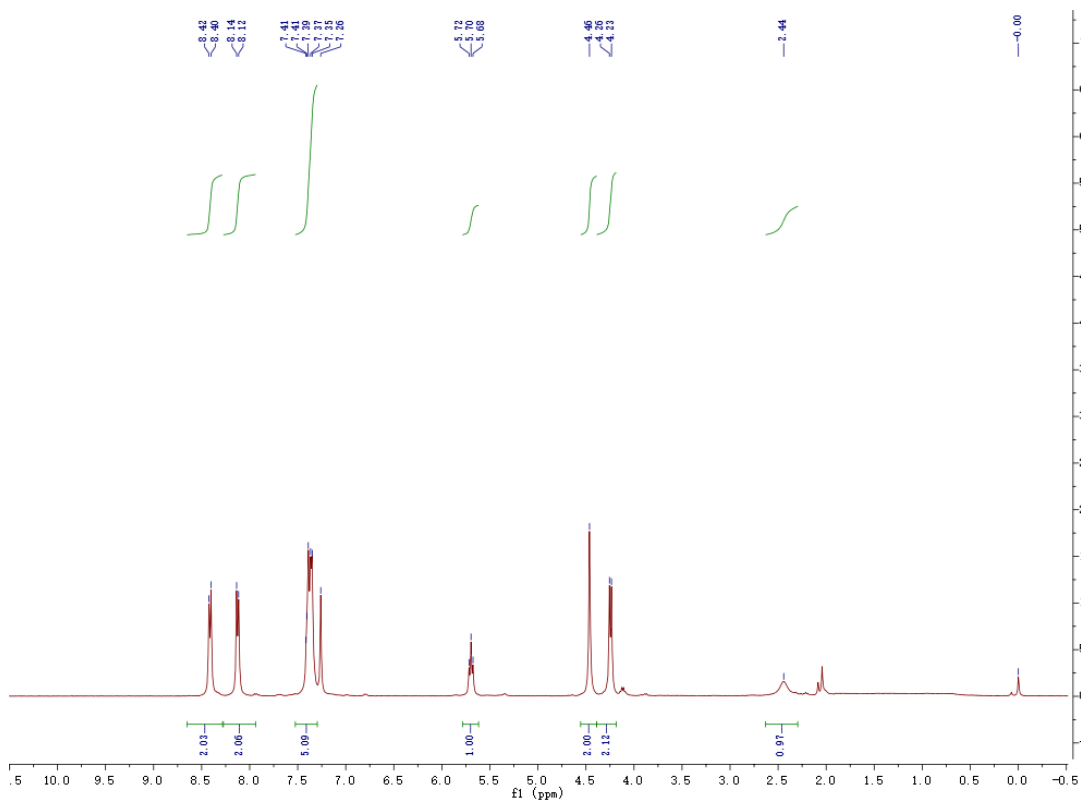
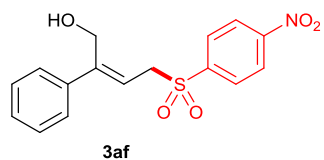
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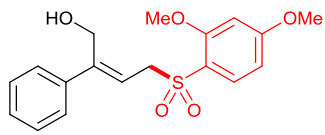




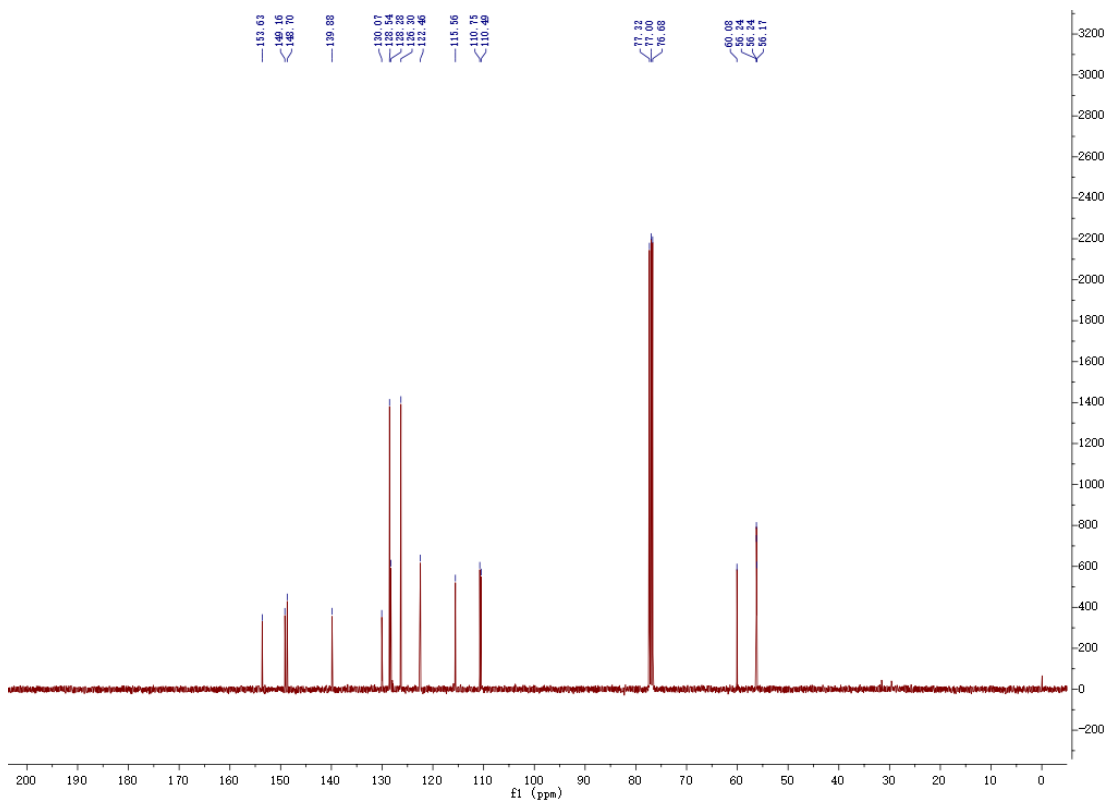
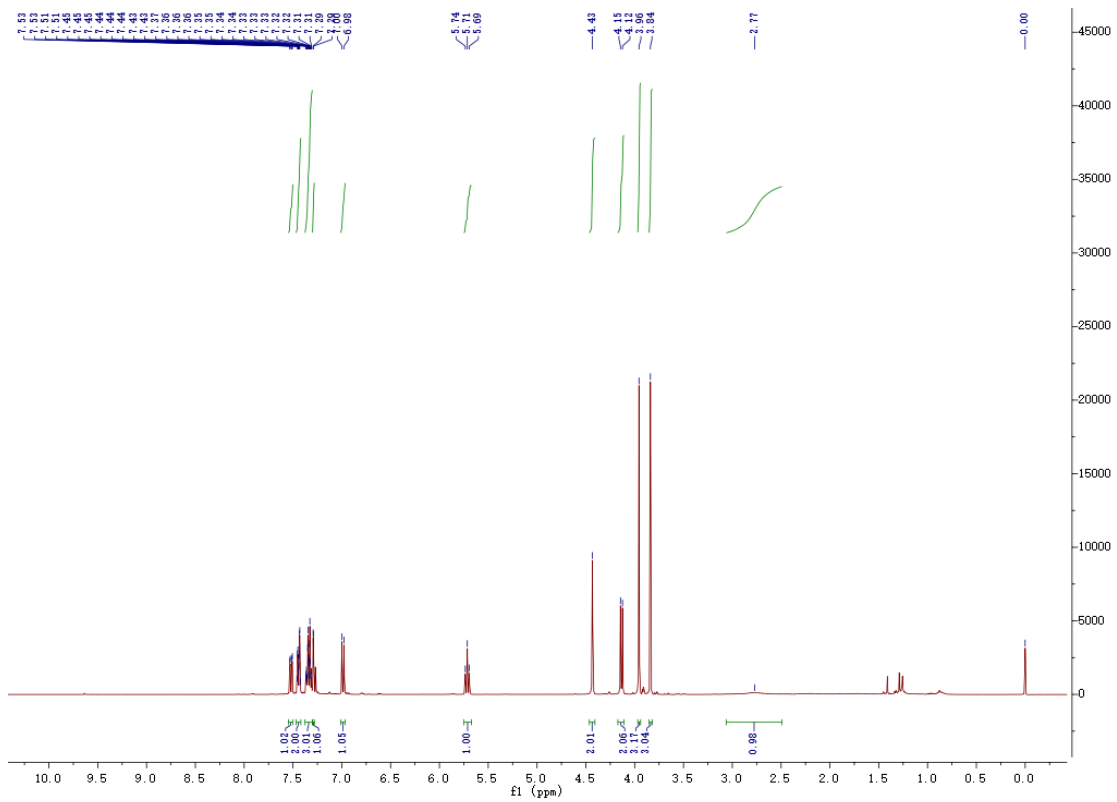
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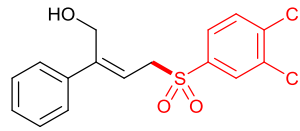




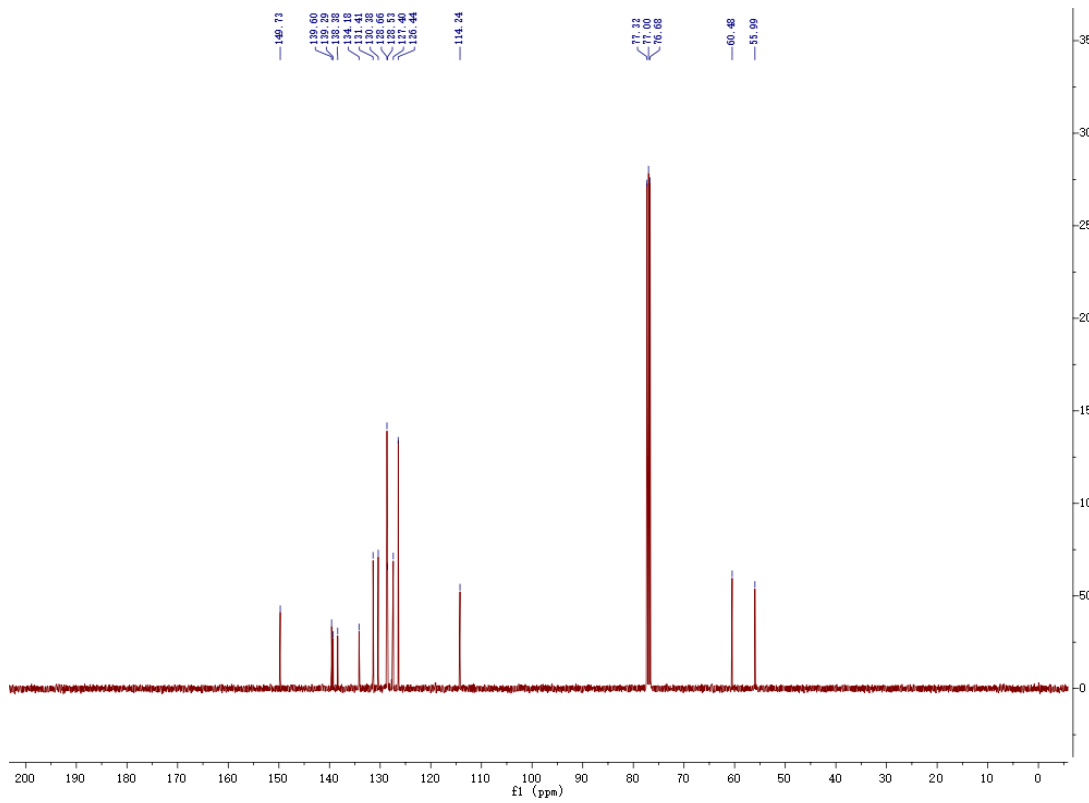
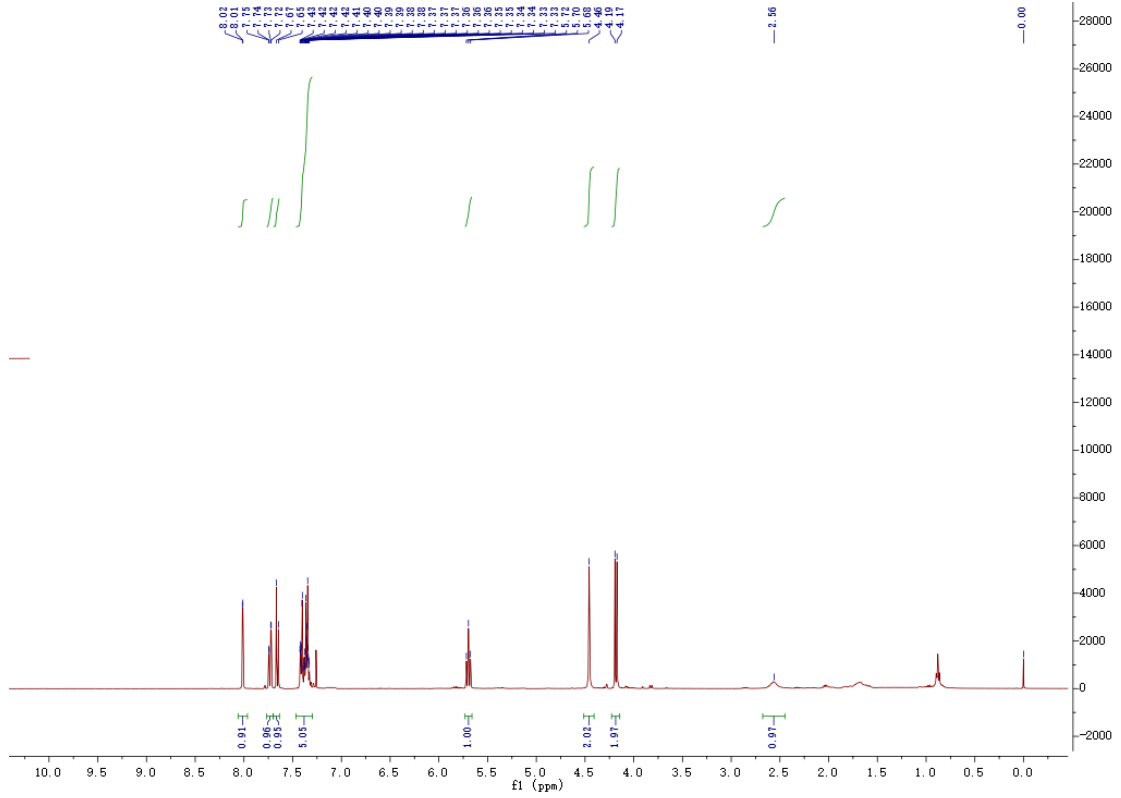


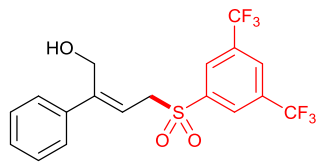
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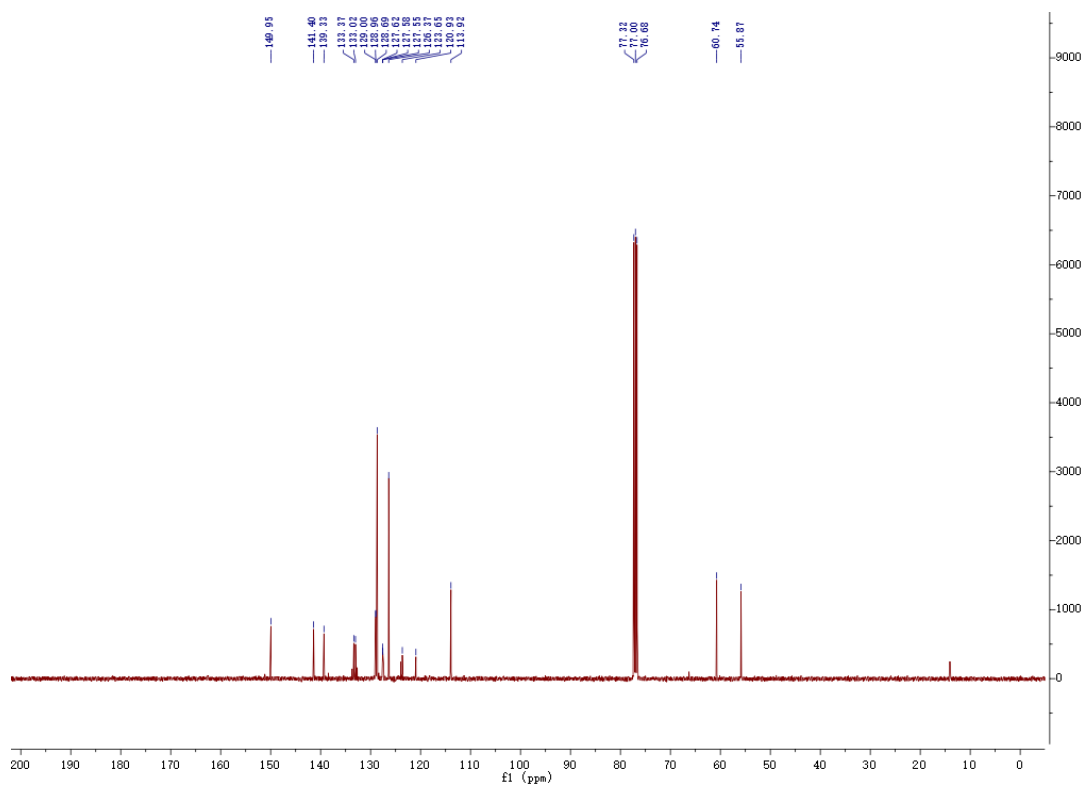
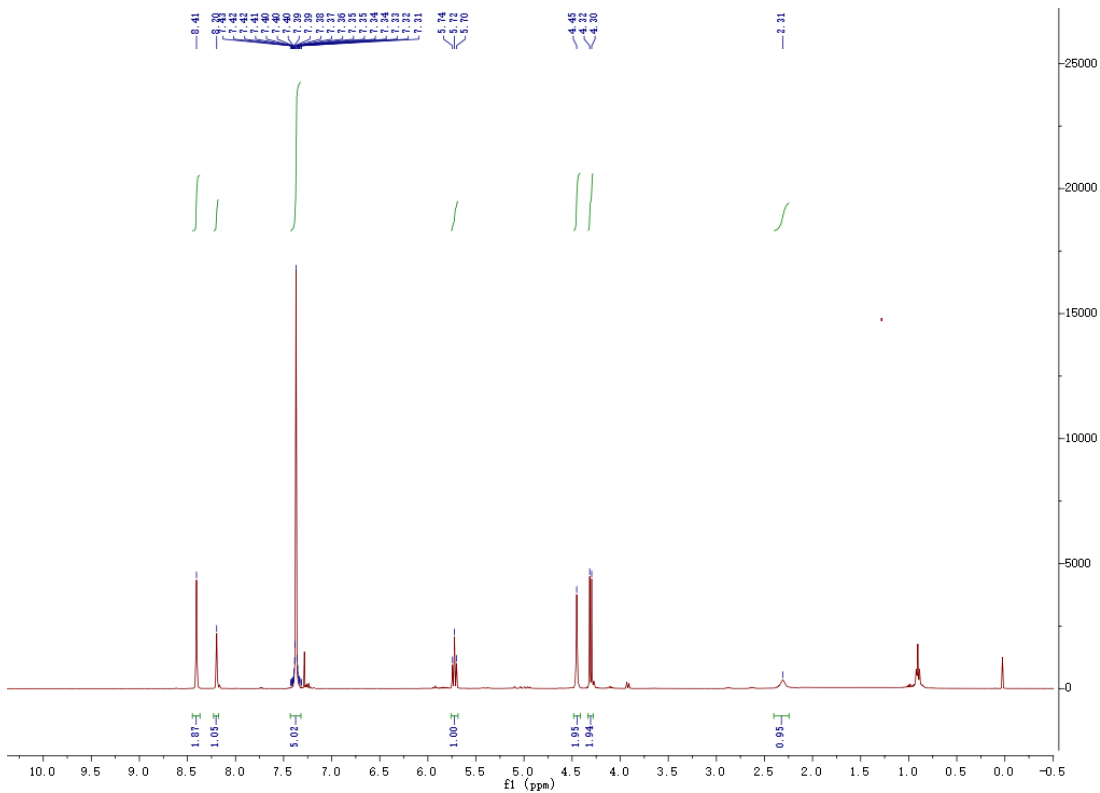


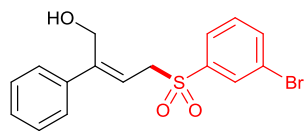
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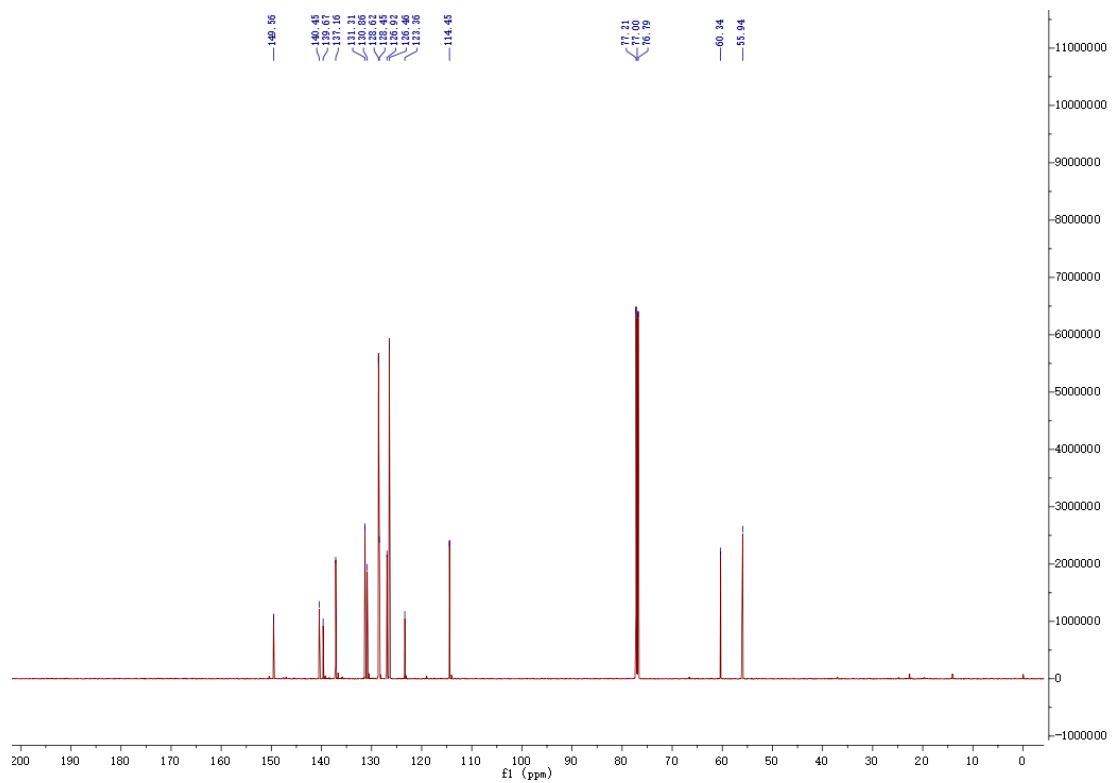
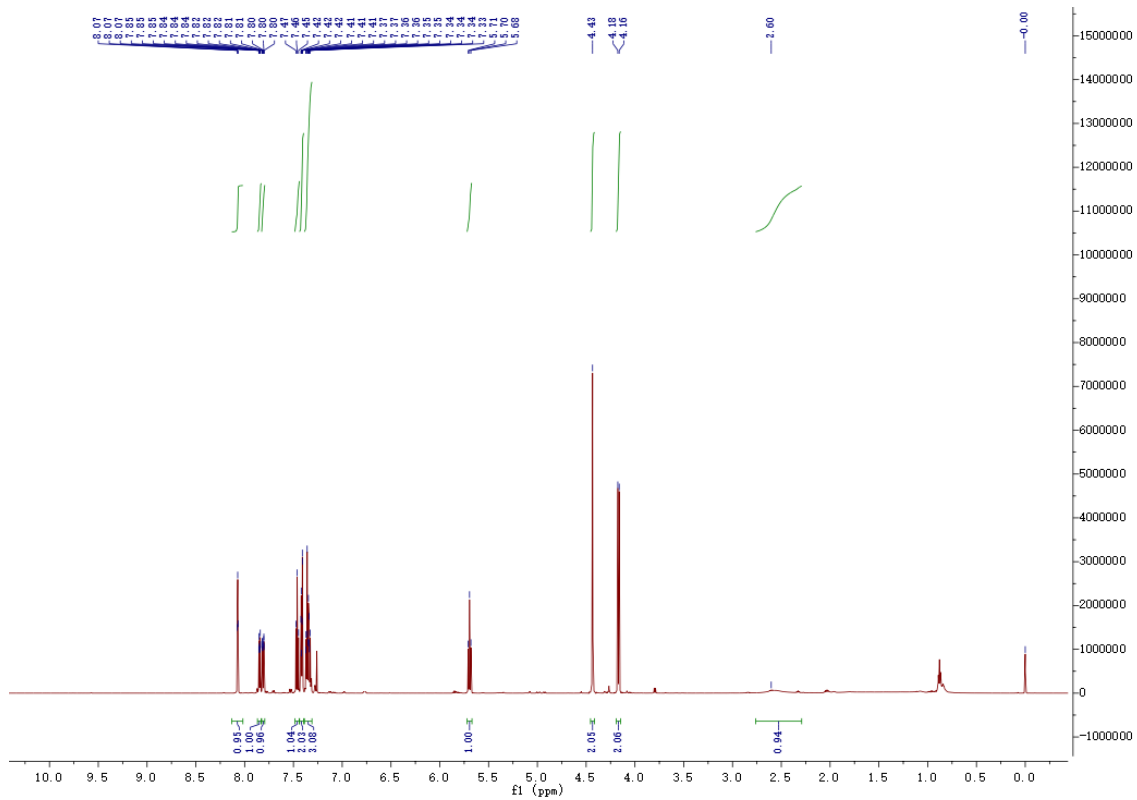


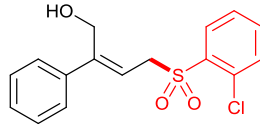
3ai



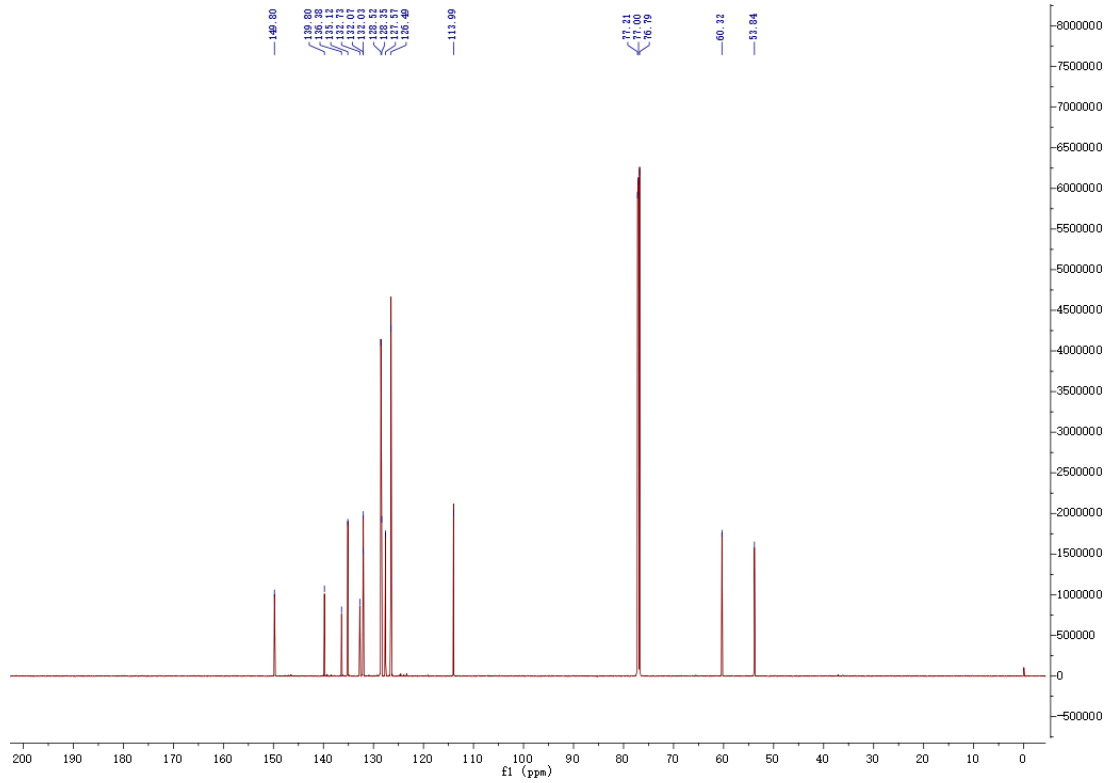
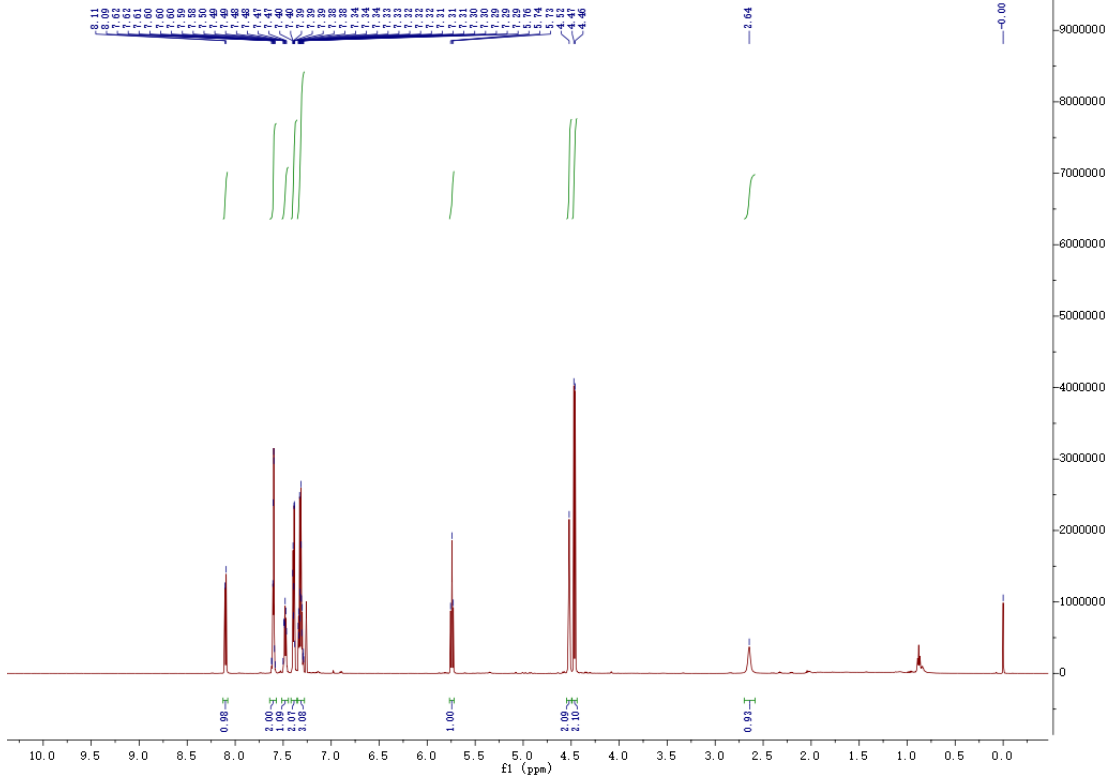


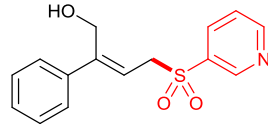
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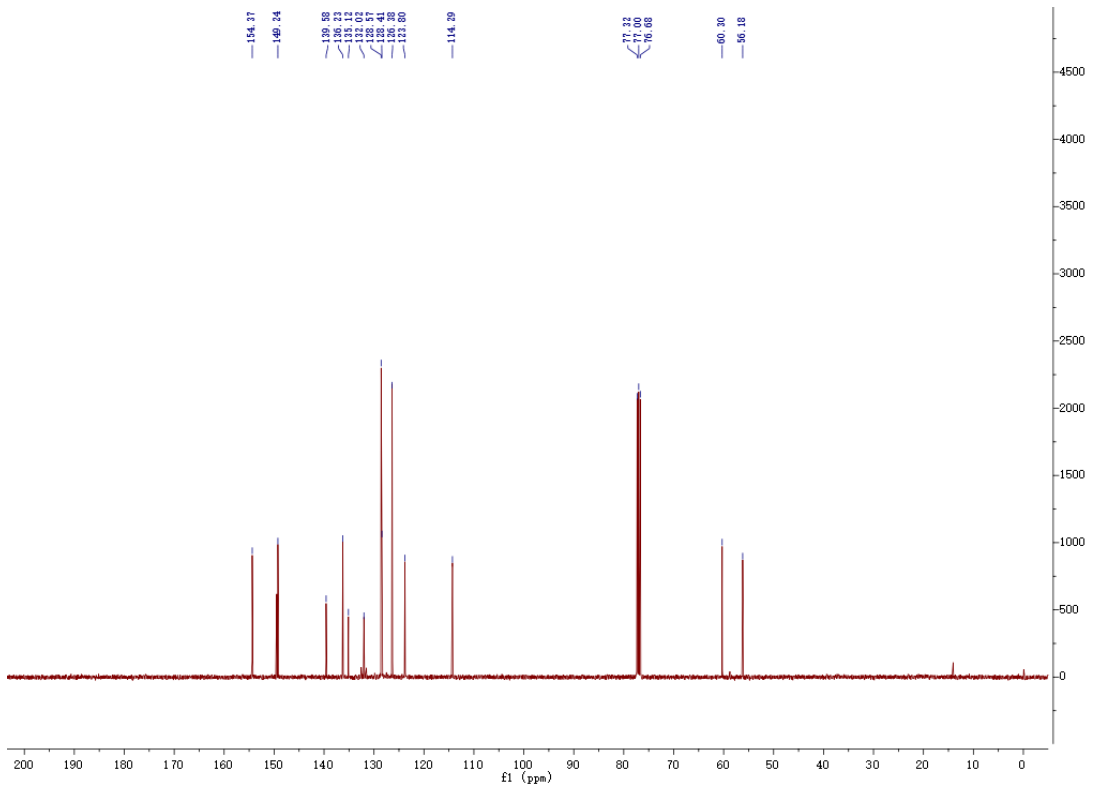
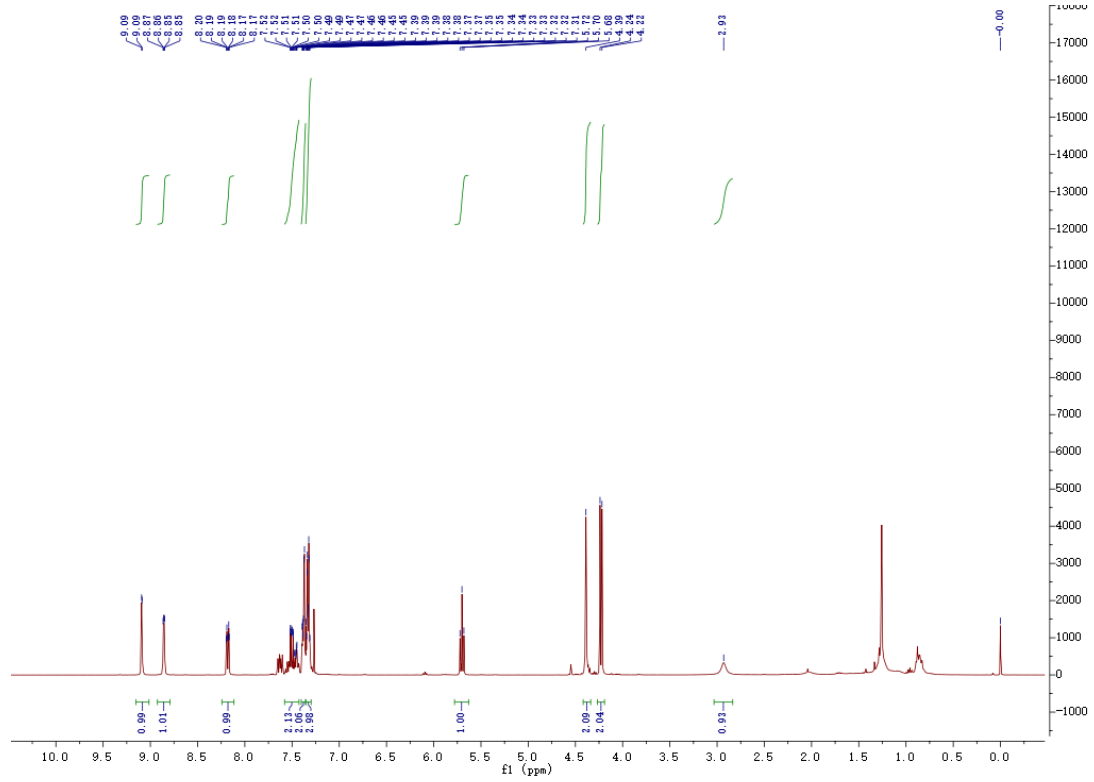


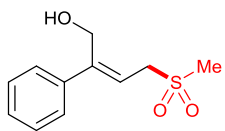
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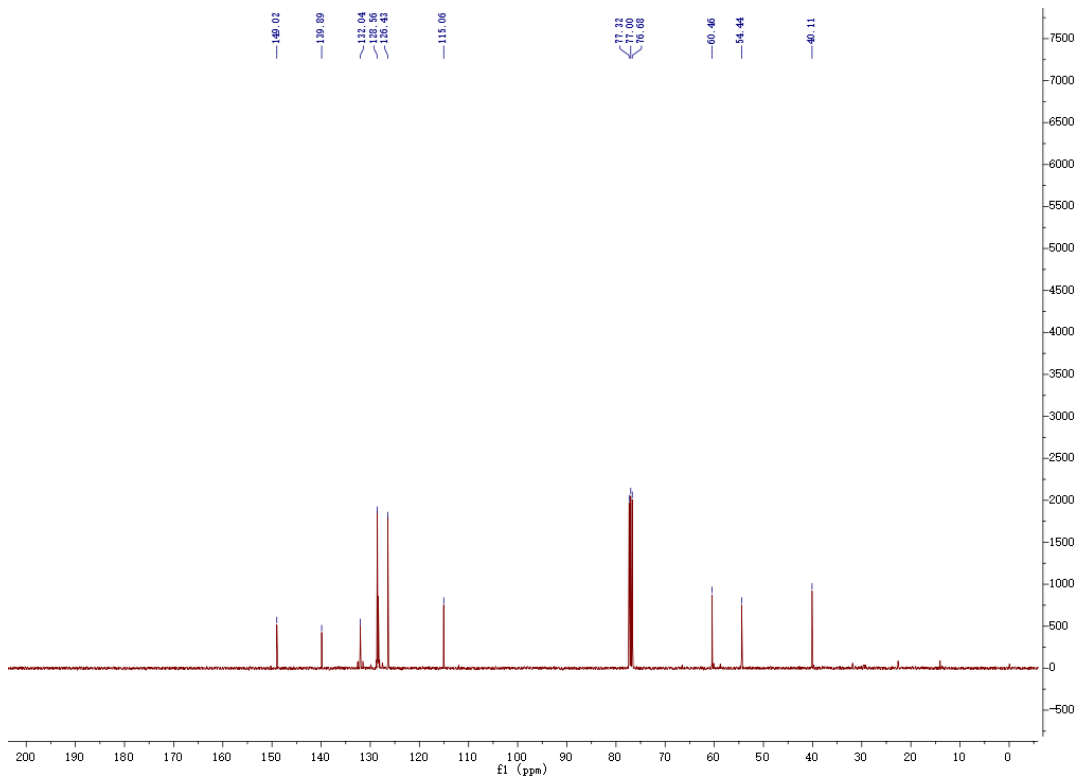
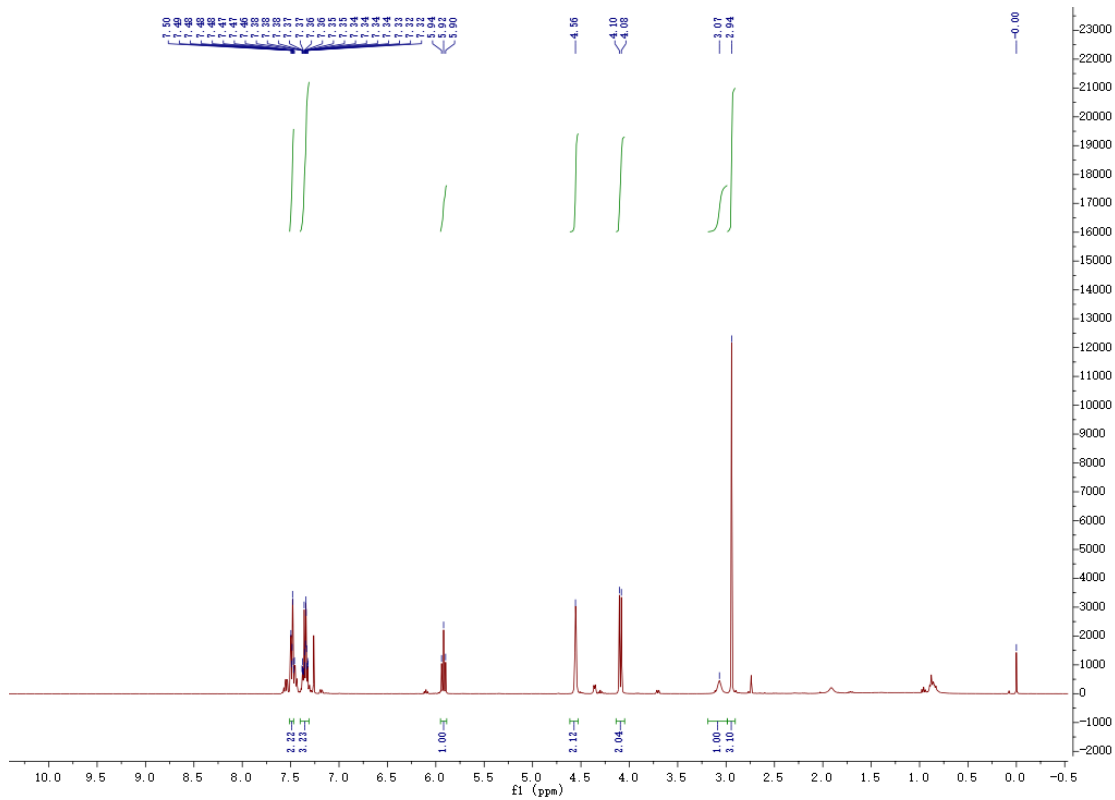


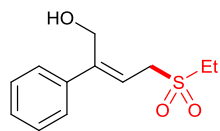
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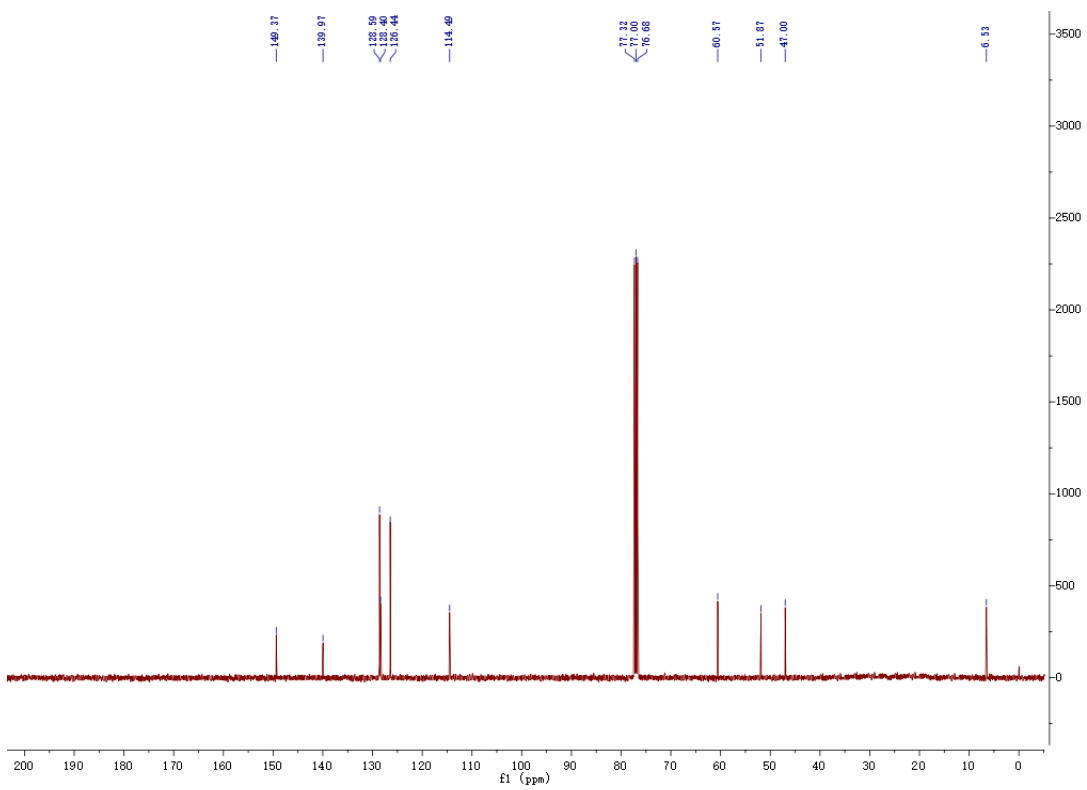
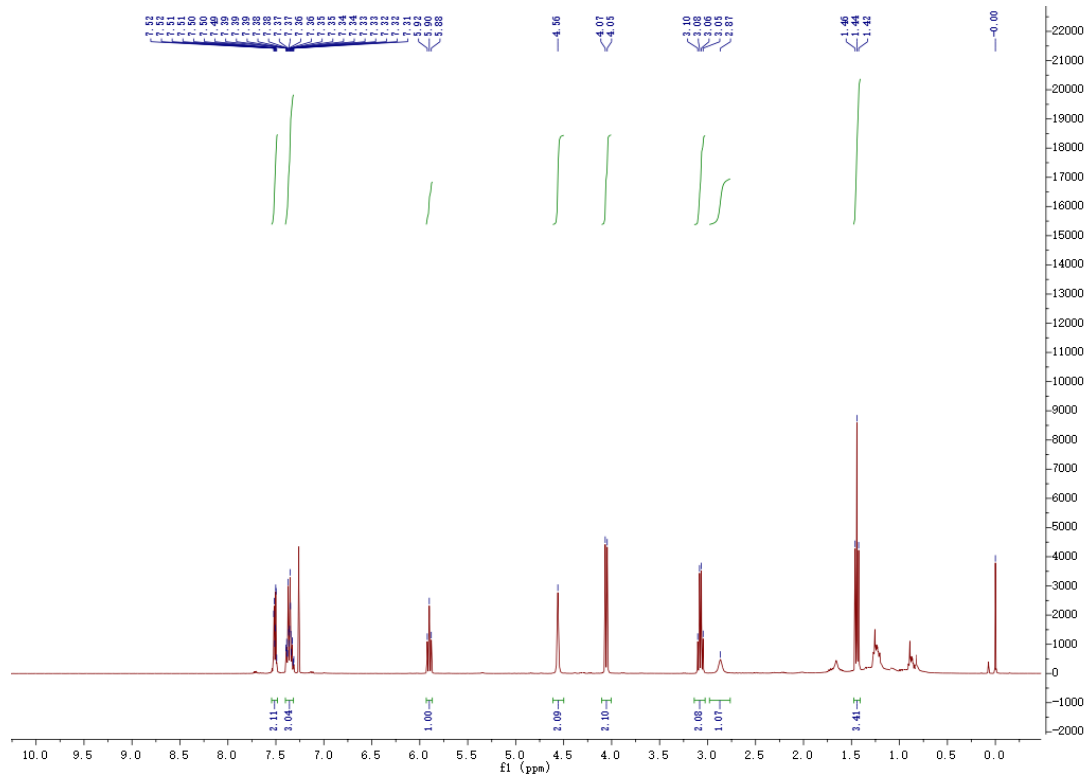


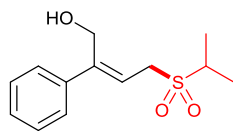
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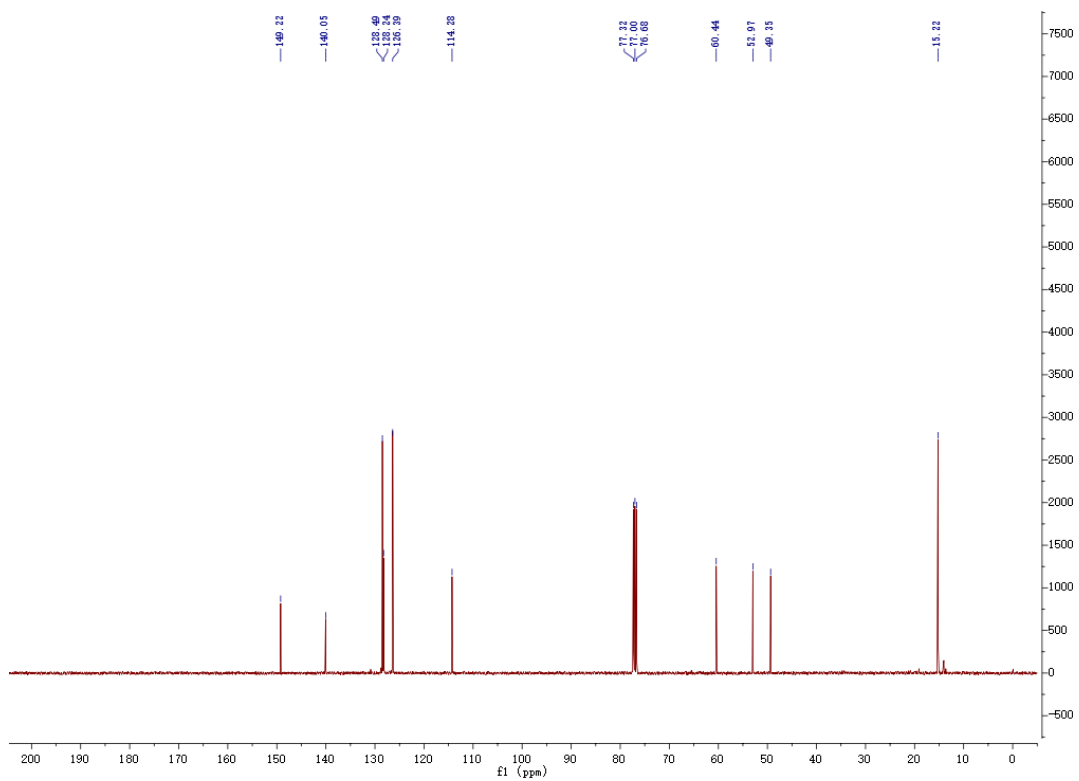
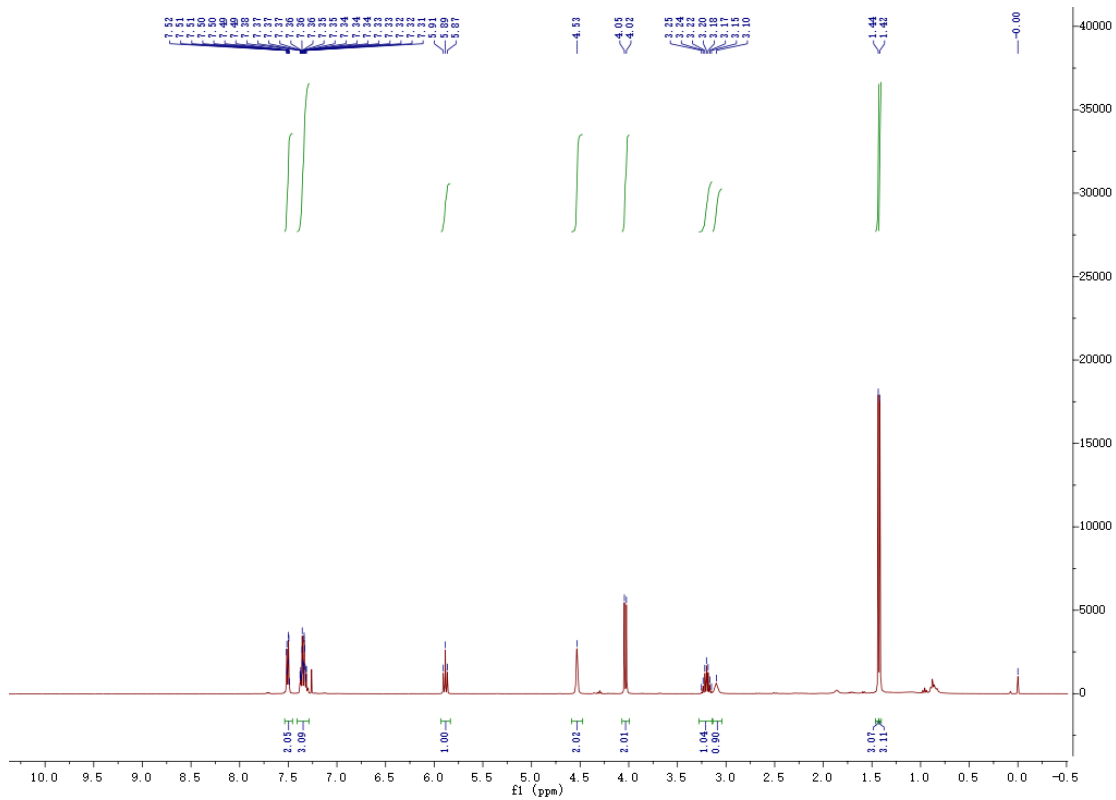


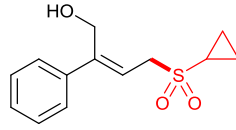
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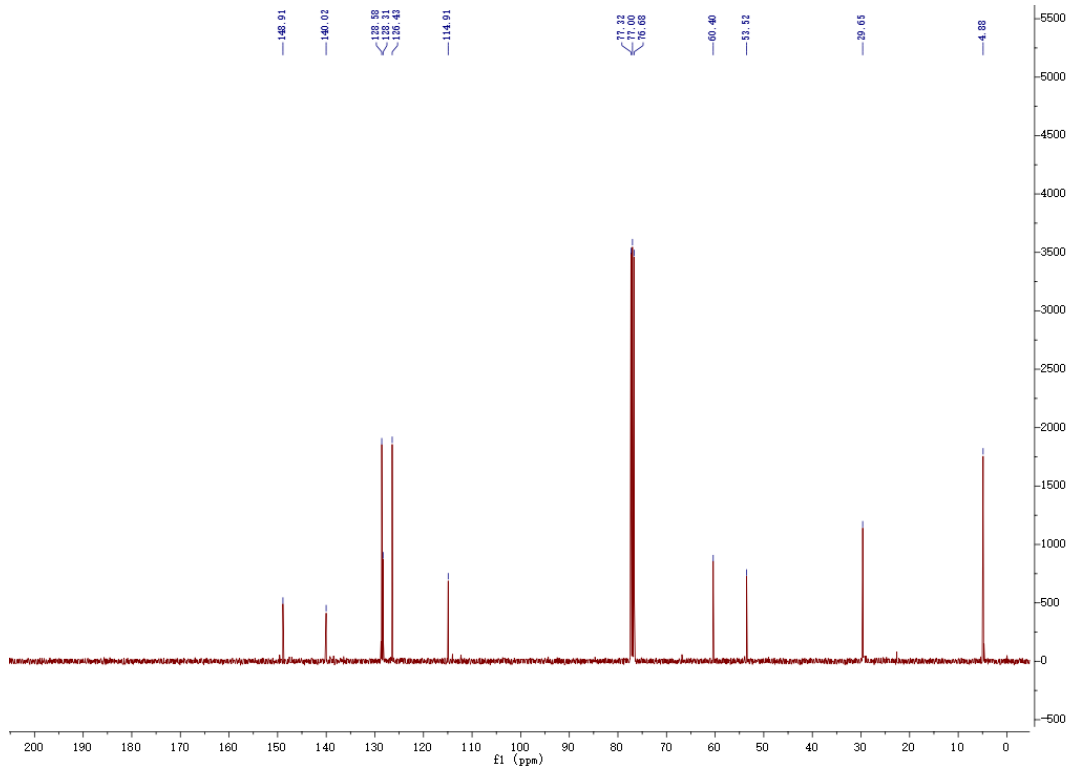
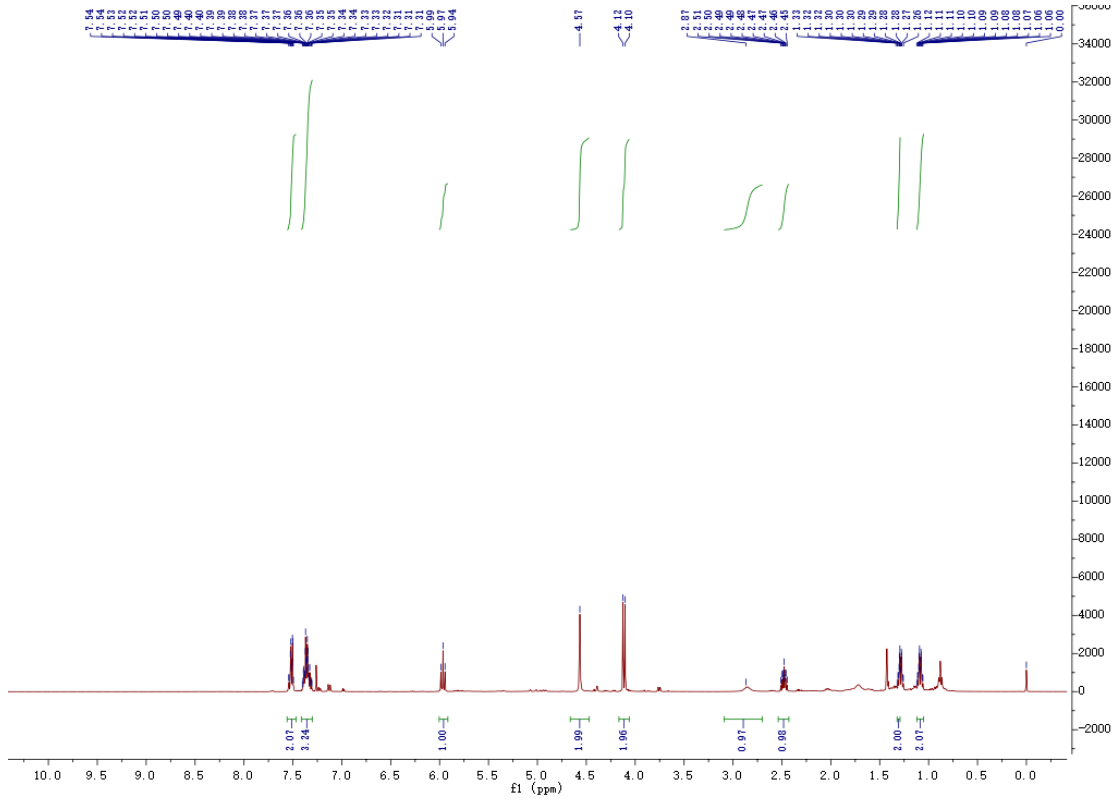


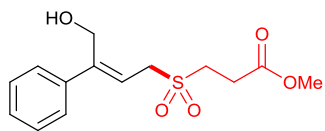
3ar





3as





3at

