

Direct Synthesis of Allylic Sulfones via Hydrosulfonylation of 1,3-Dienes with Sulfinic Acids

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1. General Information

Reagents and Solvents: CYH refers to Cyclohexane, *m*-CPBA refers to 3-chloroperoxybenzoic acid, PE refers to petroleum ether (b.p. 60-90 °C), DCM refers to dichloromethane, MTBE refers to methyl tert-butyl ether, EA refers to ethyl acetate, NaOH refers to Sodium hydroxide, KO^tBu refers to potassium *t*-butoxide. Unless noted, commercially available reagents were used without further purification.

Chromatography: Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA which are listed as volume/volume ratios.

Data collection: ¹H and ¹³C NMR spectra were collected on BRUKER AV-600 (600 MHz) spectrometer using CDCl₃ as solvent. Chemical shifts of ¹H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as the internal standard (CDCl₃: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ¹³C NMR were reported in ppm with the solvent as the internal standard. High Resolution Mass measurement was performed on Waters Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.

2. Preparation of the Substrates

2.1 Involved substrates

1,3-dienes **1**

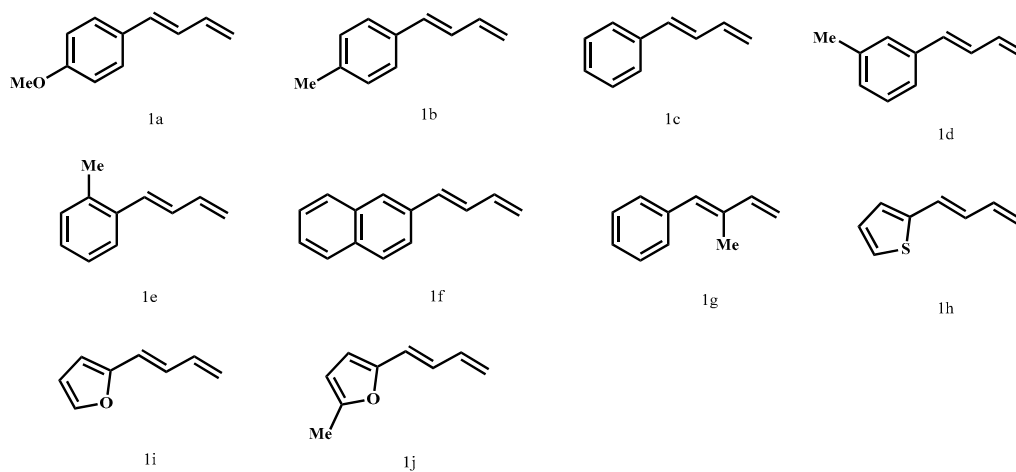


Figure S1. Structural formulas of substrate 1,3-dienes **1**

sulfinic acids **2**

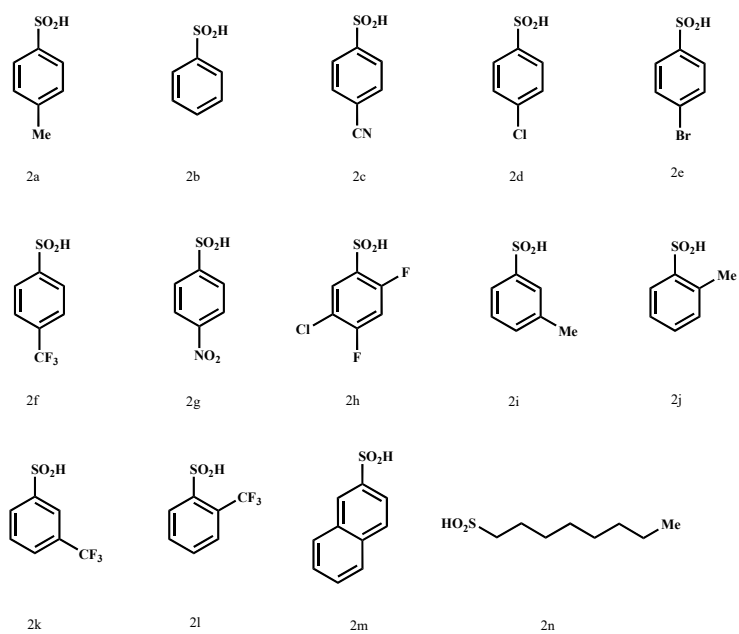
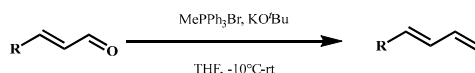


Figure S2. Structural formulas of substrate sulfinic acids **2**

2.2 General procedure for the synthesis of 1,3-dienes

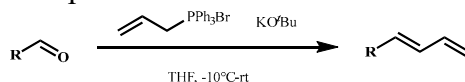
1,3-dienes were prepared by the Wittig-Olefin reaction according to the previously reported literature¹ (general procedures A and B).

The following scheme shows procedure A:



General Procedure A exemplified by the preparation of 1-(buta-1,3-dien-1-yl)4-methoxybenzene (**1a**): A stirred solution of Methyltriphenylphosphonium bromide (15 mmol, 1.5 equiv) in dry THF (25 mL) was slowly added the KOtBu (15 mmol, 1.5 equiv) at room temperature (RT). The mixture was stirred at RT for 30 min until all phosphonium bromide had been dissolved. Afterwards, the mixture was transferred to -10 °C, (E)-3-(4-methoxyphenyl)acrylaldehyde (10 mmol, 1.0 equiv) was slowly added and stirred, and the mixture was allowed to warm up to RT for 12 hours. After the reaction was completed, the mixture was diluted by adding PE (300 mL) and the solid phosphorus oxide precipitate was removed by filtration. Then the filtrate was concentrated *in vacuo* and the residue was purified by a silica gel to afford the desired 1,3-diene product.

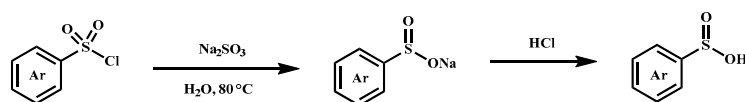
The following scheme shows procedure B:



General Procedure B exemplified by the preparation of 1-(*m*-methylphenyl)-1,3-butadiene (**1d**): A stirred solution of Allyl triphenylphosphonium bromide (15 mmol, 1.5 equiv) in dry THF (25 mL) was slowly added the KOtBu (15 mmol, 1.5 equiv) at -10 °C. The mixture was stirred at -10 °C for 30 min until all phosphonium bromide had been dissolved. Afterwards, *m*-Tolualdehyde (10 mmol, 1.0 equiv) was slowly added and stirred, and the mixture was allowed to warm up to RT for 12 hours. After the reaction was completed, the mixture was diluted by adding PE (300 mL) and the solid phosphorus oxide precipitate was removed by filtration. Then the filtrate was concentrated *in vacuo* and the residue was purified by a silica gel to afford the desired 1,3-diene product.

2.3 General procedure for the synthesis of sulfinic acid 2

Sulfinic acids were prepared according to the previously reported literature.²



To a 50 mL flask containing Na₂SO₃ (30 mmol, 3 equiv) was added, and the solid was completely dissolved in pure water. Then substituted benzenesulfonyl chloride (10 mmol, 1.0 equiv) was added into reaction system. The mixture was stirred and kept at 80 °C for 12 h. Then, this aqueous solution was washed with chloroform twice, acidified with excess concentrated HCl solution, cooled and filtered. The white precipitate was recrystallized from water to give substituted benzenesulfinic acid.

3. Experimental procedure

3.1 General Procedure for the Hydrosulfonylation Reaction.

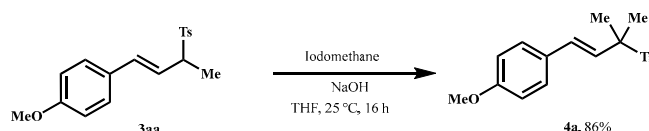
1,3-diene (0.20 mmol, 2 equiv), sulfinic acid (0.10 mmol, 1 equiv) were added to a 35 mL round bottom flask under air, followed by addition of DCM (3.0 mL). The formed mixture was stirred at room temperature for 8 h. Upon completion of the reaction, it was quenched with saturated ammonium chloride solution and the organic phase was washed with water and saturated sodium chloride solution sequentially. The solvent was then removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent in a ratio of PE/EA ranging from 10:1 to 4:1.

3.2 Procedure for the gram scale synthesis



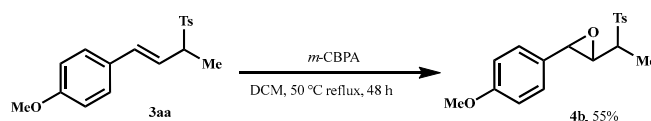
1,3-diene (10 mmol, 2 equiv), sulfinic acid (5 mmol, 1 equiv) were added to a 250 mL round bottomed flask under air, followed by addition of DCM (80 mL). The formed mixture was stirred and refluxed at room temperature for 48 h. When the reaction was finished, the solution was extracted with DCM (3×20 mL) and concentrated *in vacuo*. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (PE/EA = 10:1 to 4:1).

3.3 Further transformation of the product to obtain tertiary sulfone³



Typical procedure: To a stirred solution of **3aa** (0.1 mmol, 1.0 equiv) and NaOH (0.4 mmol, 4.0 equiv) in dry THF (1 mL) were slowly added the Iodomethane (0.12 mmol, 1.2 equiv.) at -10 °C. Then the mixture was allowed to warm up to RT for 16 hours. When the reaction was finished, the solution was diluted with DCM (3×5 mL), washed with water (30 mL), the combined organic layers were dried with anhydrous Na₂SO₄. The solvents were removed via rotary evaporator. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4:1) to afford of product **4a**.

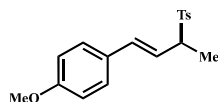
3.4 Epoxidation of allyl sulfone⁴



Procedure: To a 35 mL Schlenk tube were added **3aa** (0.2 mmol, 1.0 equiv), *m*-CBPA (0.4 mmol, 2.0 equiv) and DCM (2 mL). The resulting mixture was stirred under air at

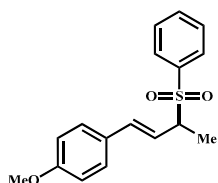
50 °C for 48 h and monitored by TLC. And then quenched by addition of saturated NH₄Cl aqueous. The layers were separated and the aqueous phase was extracted with DCM (3×5 mL). The combined organic layer was dried over Na₂SO₄. Product **4b** was isolated by flash column chromatography on silica gel (PE/EA = 4:1).

Characterization of the generated allylic sulfones.



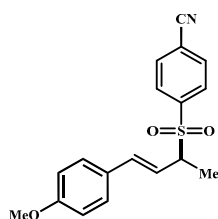
(*E*)-1-methoxy-4-(3-tosylbut-1-en-1-yl)benzene (**3aa**)

Yield 94%; White solid, m.p. 90-92 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.87 – 6.80 (m, 2H), 6.28 (d, *J* = 15.9 Hz, 1H), 5.92 (dd, *J* = 15.9, 8.3 Hz, 1H), 3.78- 3.83 (m, 4H), 2.42 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 159.7, 144.5, 135.7, 134.0, 129.4, 129.3, 128.7, 127.8, 119.8, 114.0, 64.1, 55.3, 21.6, 13.7. HRMS (ESI) calcd for [C₁₈H₂₀O₃S+Na]⁺: 339.1031, Found: 339.1035.



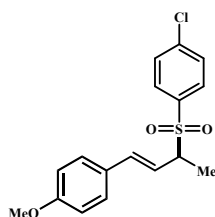
(*E*)-1-methoxy-4-(3-(phenylsulfonyl)but-1-en-1-yl)benzene (**3ab**)

Yield 90%; White solid, m.p. 81-82 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.22 (s, 2H), 6.84 (d, *J* = 7.0 Hz, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 5.92 (dd, *J* = 15.9, 8.2 Hz, 1H), 3.79-3.84 (m, 4H), 1.54 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 159.7, 136.9, 136.0, 133.6, 130.8, 129.3, 128.8, 127.8, 119.5, 114.0, 64.2, 55.3, 13.6. HRMS (ESI) calcd for [C₁₇H₁₈O₃S+Na]⁺: 325.0874, Found: 325.0859.



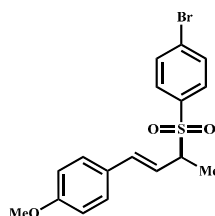
(*E*)-4-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)benzonitrile (**3ac**)

Yield 79%; Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.22 (d, *J* = 15.9 Hz, 1H), 5.89 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.81-3.87 (m, 4H), 1.57 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 160.1, 141.4, 136.8, 132.5, 130.1, 128.1, 127.9, 118.7, 117.4, 117.2, 114.2, 64.5, 55.3, 13.3. HRMS (ESI) calcd for [C₁₈H₁₇NO₃S+Na]⁺: 350.0827, Found: 350.0828.



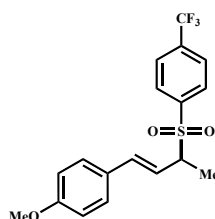
(*E*)-1-chloro-4-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)benzene (3ad)

Yield 76%; White solid, m.p. 76-77 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.26 (d, *J* = 15.9 Hz, 1H), 5.91 (dd, *J* = 15.9, 8.3 Hz, 1H), 3.80-3.82 (m, 4H), 1.54 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 159.9, 140.4, 136.3, 135.5, 130.8, 129.1, 128.4, 127.9, 119.3, 114.1, 64.3, 55.3, 13.6. HRMS (ESI) calcd for [C₁₇H₁₇ClO₃S+Na]⁺: 359.0485, Found: 359.0482.



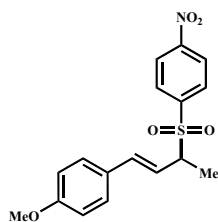
(*E*)-1-bromo-4-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)benzene (3ae)

Yield 94%; White solid, m.p. 87-88 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.78 – 7.57 (m, 4H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 15.9 Hz, 1H), 5.90 (dd, *J* = 15.9, 8.3 Hz, 1H), 3.80-3.83 (m, 4H), 1.53 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 159.9, 136.3, 132.1, 131.8, 130.9, 129.0, 128.4, 127.9, 119.2, 114.1, 64.3, 55.3, 13.5. HRMS (ESI) calcd for [C₁₇H₁₇BrO₃S+Na]⁺: 402.9979, Found: 402.9970.



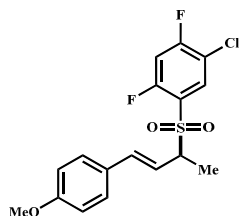
(*E*)-1-methoxy-4-(3-((4-(trifluoromethyl)phenyl)sulfonyl)but-1-en-1-yl)benzene (3af)

Yield 62%; White solid, m.p. 101-102 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 5.91 (dd, *J* = 15.9, 8.4 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.81 (s, 3H), 1.56 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 160.1, 140.7, 136.6, 135.4, 130.0, 128.3, 127.9, 125.9, 125.9, 118.9, 114.2, 64.4, 55.3, 13.5. HRMS (ESI) calcd for [C₁₈H₁₇F₃O₃S+Na]⁺: 393.0748, Found: 393.0753.



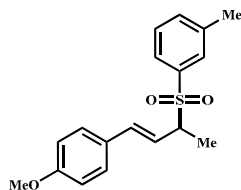
(*E*)-1-methoxy-4-(3-((4-nitrophenyl)sulfonyl)but-1-en-1-yl)benzene (3ag)

Yield 81%; yellow solid m.p. 151-153 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.34 (d, J = 9.0 Hz, 2H), 8.03 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.25 (d, J = 15.9 Hz, 1H), 5.91 (dd, J = 15.9, 8.4 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.81 (s, 3H), 1.58 (d, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.2, 150.8, 142.9, 136.9, 130.8, 128.0, 127.9, 123.9, 118.6, 114.2, 64.6, 55.3, 13.4. HRMS (ESI) calcd for $[\text{C}_{17}\text{H}_{17}\text{NO}_5\text{S}+\text{Na}]^+$: 370.0725, Found: 370.0688.



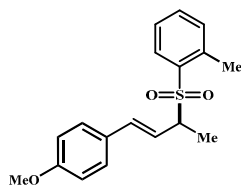
(*E*)-1-chloro-2,4-difluoro-5-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)benzene (3ah)

Yield 79%; White solid, m.p. 64-66 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.98 – 7.93 (t, J = 8.6 Hz, 1H), 7.22 (d, J = 8.9 Hz, 2H), 7.04 (t, J = 8.6 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 6.39 (d, J = 15.8 Hz, 1H), 5.96 – 5.90 (m, 1H), 4.11 – 4.03 (m, 1H), 3.80 (s, 3H), 1.61 (d, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 162.5, 160.1, 157.6, 136.9, 133.1, 128.2, 128.0, 118.6, 114.1, 106.9, 106.7, 106.5, 64.7, 55.3, 13.2. HRMS (ESI) calcd for $[\text{C}_{17}\text{H}_{15}\text{ClF}_2\text{O}_3\text{S}+\text{Na}]^+$: 395.0296, Found: 395.0278.



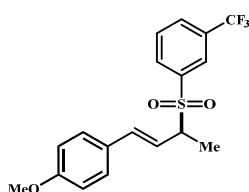
(*E*)-1-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)-3-methylbenzene (3ai)

Yield 74%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.63 (d, J = 8.9 Hz, 2H), 7.40 (s, 2H), 7.21 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 6.26 (d, J = 15.9 Hz, 1H), 5.91 (dd, J = 15.9, 8.3 Hz, 1H), 3.79-3.83 (m, 4H), 2.36 (s, 3H), 1.52 (d, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.8, 139.0, 136.8, 135.9, 134.4, 129.7, 128.7, 128.6, 127.8, 126.4, 119.7, 114.0, 64.2, 55.3, 21.2, 13.6. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_3\text{S}+\text{Na}]^+$: 339.1031, Found: 339.1030.



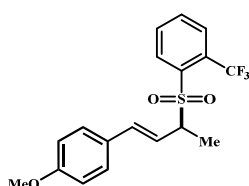
(*E*)-1-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)-2-methylbenzene (3aj)

Yield 83%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, $J = 6.3$ Hz, 1H), 7.46 (t, $J = 6.3$ Hz, 1H), 7.31 – 7.27 (m, 2H), 7.17 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 6.21 (d, $J = 15.9$ Hz, 1H), 5.91 (dd, $J = 15.9$, 8.7 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.79 (s, 3H), 2.68 (s, 3H), 1.55 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.8, 138.7, 136.0, 133.5, 132.6, 131.5, 129.4, 128.6, 127.9, 126.3, 119.7, 114.0, 63.8, 55.3, 20.8, 13.3. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_3\text{S}+\text{Na}]^+$: 339.1031, Found: 339.1031.



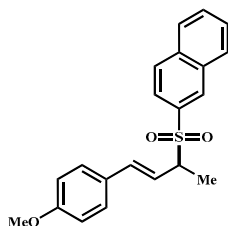
(*E*)-1-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)-3-(trifluoromethyl)benzene (3ak)

Yield 67%; White solid, m.p. 103-104 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.12 (s, 1H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.65 (t, $J = 7.9$ Hz, 1H), 7.20 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.24 (d, $J = 15.9$ Hz, 1H), 5.90 (dd, $J = 15.9$, 8.5 Hz, 1H), 3.83 – 3.88 (m, 1H), 3.81 (s, 3H), 1.56 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.0, 138.3, 136.7, 132.7, 131.7, 130.3, 129.6, 128.2, 127.9, 126.5, 126.5, 119.0, 114.1, 64.5, 55.3, 13.4. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_3\text{S}+\text{Na}]^+$: 393.0748, Found: 393.0745.



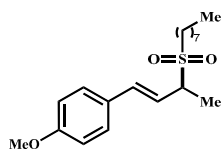
(*E*)-1-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)-2-(trifluoromethyl)benzene (3al)

Yield 64%; White solid, m.p. 100-101 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.12 (d, $J = 9.4$ Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 1H), 7.73 – 7.67 (m, 1H), 7.64 (t, $J = 7.7$ Hz, 1H), 7.17 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.9$ Hz, 2H), 6.19 (d, $J = 15.8$ Hz, 1H), 5.90 (dd, $J = 15.8$, 9.0 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.79 (s, 3H), 1.60 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.9, 136.6, 134.4, 133.5, 131.9, 129.4, 128.4, 128.3, 127.9, 123.6, 121.8, 119.6, 114.0, 64.6, 55.3, 13.4. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_3\text{S}+\text{Na}]^+$: 393.0748, Found: 393.0751.



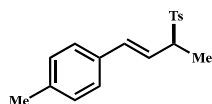
(*E*)-2-((4-(4-methoxyphenyl)but-3-en-2-yl)sulfonyl)naphthalene (3am)

Yield 81%; White solid, m.p. 119-120.5 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.43 (s, 1H), 7.92 (dd, J = 14.5, 8.7 Hz, 3H), 7.81 (dd, J = 8.7, 1.8 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.60 (td, J = 7.6, 1.8 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 6.28 (d, J = 15.9 Hz, 1H), 5.97 (dd, J = 15.9, 8.3 Hz, 1H), 3.89-3.94 (m, 1H), 3.79 (s, 3H), 1.56 (d, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.8, 136.0, 135.3, 134.1, 132.0, 131.2, 129.4, 129.2, 128.8, 128.6, 127.9, 127.9, 127.5, 124.1, 119.6, 114.0, 64.3, 55.3, 13.8. HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{20}\text{O}_3\text{S}+\text{Na}]^+$: 375.1031, Found: 375.1034.



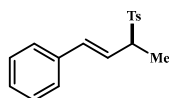
(*E*)-1-methoxy-4-(3-(octylsulfonyl)but-1-en-1-yl)benzene (3an)

Yield 68%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.35 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 6.60 (d, J = 15.8 Hz, 1H), 6.07 (dd, J = 15.9, 9.0 Hz, 1H), 3.82 (s, 3H), 3.74-3.78 (m, 1H), 2.99 – 2.90 (m, 2H), 1.88 – 1.78 (m, 2H), 1.58 (d, J = 6.9 Hz, 3H), 1.26 (q, J = 6.3 Hz, 10H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.0, 135.4, 128.3, 128.0, 120.7, 114.2, 61.7, 55.4, 49.6, 31.7, 29.0, 28.9, 28.6, 22.6, 21.4, 14.1, 12.6. HRMS (ESI) calcd for $[\text{C}_{19}\text{H}_{30}\text{O}_3\text{S}+\text{Na}]^+$: 361.1813, Found: 361.1825.



(*E*)-1-methyl-4-((4-(p-tolyl)but-3-en-2-yl)sulfonyl)benzene (3ba)

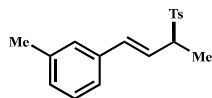
Yield 54%; White solid, m.p. 95-96 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 6.29 (d, J = 15.9 Hz, 1H), 6.02 (dd, J = 15.9, 8.2 Hz, 1H), 3.79-3.84 (m, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.52 (d, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.5, 138.3, 136.2, 134.0, 133.2, 129.4, 129.3, 126.5, 121.2, 64.1, 21.6, 21.2, 13.6. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}+\text{Na}]^+$: 323.1082, Found: 323.1089.



(*E*)-1-methyl-4-((4-phenylbut-3-en-2-yl)sulfonyl)benzene (3ca)

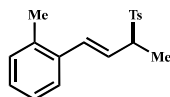
Yield 10%; White solid, m.p. 90-91 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, J = 8.2 Hz, 2H), 7.33 – 7.26 (m, 7H), 6.34 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 15.9, 8.2 Hz, 1H),

3.81-3.86 (m, 1H), 2.43 (s, 3H), 1.53 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.8, 136.9, 136.0, 133.6, 130.8, 129.3, 128.8, 127.9, 119.6, 114.0, 64.2, 55.3, 13.6. HRMS (ESI) calcd for $[\text{C}_{17}\text{H}_{18}\text{O}_2\text{S}+\text{Na}]^+$ 309.0925, Found: 309.0923.



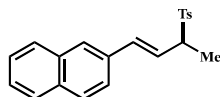
(E)-1-methyl-3-(3-tosylbut-1-en-1-yl)benzene (3da)

Yield 24%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.12 (s, 1H), 7.08 (t, $J = 7.6$ Hz, 2H), 6.29 (d, $J = 15.9$ Hz, 1H), 6.07 (dd, $J = 15.9, 8.2$ Hz, 1H), 3.80-3.85 (m, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.53 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.6, 138.2, 136.4, 135.9, 134.0, 129.5, 129.3, 129.1, 128.5, 127.2, 123.8, 122.0, 64.1, 21.6, 21.4, 13.6. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}+\text{Na}]^+$: 323.1082, Found: 323.1089.



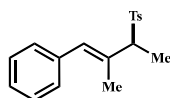
(E)-1-methyl-2-(3-tosylbut-1-en-1-yl)benzene (3ea)

Yield 27%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.37 – 7.32 (m, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 3.7$ Hz, 2H), 7.13 – 7.08 (m, 1H), 6.52 (d, $J = 15.8$ Hz, 1H), 5.94 (dd, $J = 15.8, 8.5$ Hz, 1H), 3.83-3.89 (m, 1H), 2.42 (s, 3H), 2.14 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.6, 135.6, 135.0, 134.4, 134.1, 130.3, 129.4, 129.3, 128.2, 126.2, 125.8, 123.8, 64.4, 21.6, 19.4, 13.6. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}+\text{Na}]^+$: 323.1082, Found: 323.1083.



(E)-2-(3-tosylbut-1-en-1-yl)naphthalene (3fa)

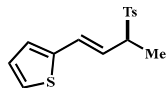
Yield 67%; White solid, m.p. 122-124 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.81 – 7.76 (m, 3H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.63 (s, 1H), 7.52 – 7.49 (m, 1H), 7.46 (m, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.21 (dd, $J = 15.9, 8.2$ Hz, 1H), 3.86-3.91 (m, 1H), 2.41 (s, 3H), 1.57 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.6, 136.3, 134.0, 133.4, 133.3, 133.2, 129.5, 129.3, 128.4, 128.1, 127.7, 126.9, 126.4, 126.3, 123.3, 122.6, 64.2, 21.6, 13.6. HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{20}\text{O}_2\text{S}+\text{Na}]^+$: 359.1082, Found: 359.1097.



(E)-1-methyl-4-((3-methyl-4-phenylbut-3-en-2-yl)sulfonyl)benzene (3ga)

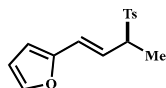
Yield 36%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.30 (dd, $J = 16.9, 8.1$ Hz, 4H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 7.5$ Hz, 2H), 6.10 (s,

1H), 3.80 (q, $J = 7.1$ Hz, 1H), 2.44 (s, 3H), 1.90 (d, $J = 1.5$ Hz, 3H), 1.62 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.5, 136.7, 134.3, 133.2, 131.4, 129.4, 129.2, 128.7, 128.1, 126.9, 69.3, 21.6, 15.8, 12.4. HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}+\text{Na}]^+$: 323.1082, Found: 323.1090.



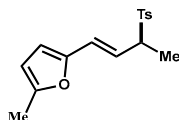
(E)-2-(3-tosylbut-1-en-1-yl)thiophene (3ha)

Yield 72%; White solid, m.p. 84-85 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.19 (s, 1H), 6.95 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.91 (d, $J = 3.4$ Hz, 1H), 6.48 (d, $J = 15.5$ Hz, 1H), 5.88 (dd, $J = 15.5, 8.2$ Hz, 1H), 3.76-3.82 (m, 1H), 2.43 (s, 3H), 1.50 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.7, 140.9, 133.9, 129.5, 129.4, 129.3, 127.5, 126.8, 125.3, 121.5, 63.9, 21.6, 13.6. HRMS (ESI) calcd for $[\text{C}_{15}\text{H}_{16}\text{O}_2\text{S}_2+\text{Na}]^+$: 315.0489, Found: 315.0492.



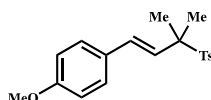
(E)-2-(3-tosylbut-1-en-1-yl)furan (3ia)

Yield 67%; Colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 1.3$ Hz, 1H), 7.31 (d, $J = 8.3$ Hz, 2H), 6.36 (dd, $J = 3.3, 1.3$ Hz, 1H), 6.26 – 6.17 (m, 2H), 6.01 (dd, $J = 15.8, 8.3$ Hz, 1H), 3.77-3.83 (m, 1H), 2.43 (s, 3H), 1.49 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 151.6, 144.7, 142.7, 133.9, 129.5, 129.4, 124.2, 120.4, 111.4, 109.4, 63.9, 21.6, 13.7. HRMS (ESI) calcd for $[\text{C}_{15}\text{H}_{16}\text{O}_3\text{S}+\text{Na}]^+$: 299.0718, Found: 299.0721.



(E)-2-methyl-5-(3-tosylbut-1-en-1-yl)furan (3ja)

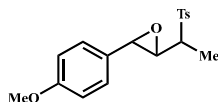
Yield 61%; White solid, m.p. 95-96 °C ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 6.13 – 6.06 (m, 2H), 5.99 – 5.91 (m, 2H), 3.72-3.80 (m, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 1.47 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 152.9, 150.1, 144.6, 134.1, 129.5, 129.4, 124.3, 118.5, 110.7, 107.6, 64.0, 21.7, 13.8, 13.7. HRMS (ESI) calcd for $[\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}+\text{Na}]^+$: 313.0874, Found: 313.0873.



(E)-1-methoxy-4-(3-methyl-3-tosylbut-1-en-1-yl)benzene (4a)

Yield 86%; White solid, m.p. 109-110 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, $J = 8.8$ Hz, 2H), 7.29 – 7.24 (m, 4H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.26 (d, $J = 16.3$ Hz, 1H), 6.13 (d, $J = 16.3$ Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H), 1.53 (s, 6H). ^{13}C NMR (150 MHz,

CDCl₃) δ 159.7, 144.5, 132.8, 132.4, 130.6, 129.5, 129.1, 128.9, 127.9, 127.0, 125.6, 114.1, 64.6, 55.3, 29.7, 21.7, 21.3. HRMS (ESI) calcd for [C₁₉H₂₂O₃S+Na]⁺: 353.1187, Found: 353.1186.



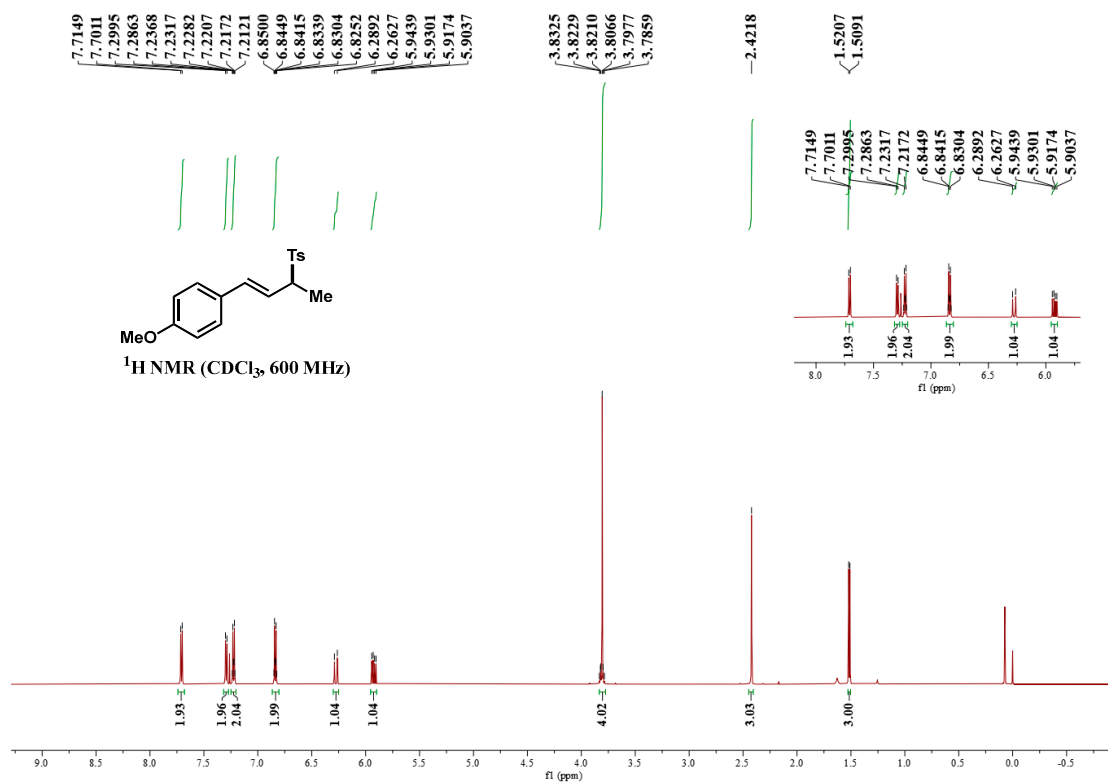
(*E*)-2-(4-methoxyphenyl)-3-(1-tosylethyl)oxirane (4b)

Yield 55%; White solid, m.p. 137-138 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.83 – 3.79 (m, 4H), 3.39 (dd, *J* = 7.5, 2.0 Hz, 1H), 2.75 (qd, *J* = 5.2, 2.0 Hz, 1H), 2.43 (s, 3H), 1.29 (d, *J* = 5.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 160.3, 145.0, 134.8, 131.3, 129.6, 129.1, 121.7, 114.1, 72.5, 56.3, 55.4, 55.3, 21.7, 17.1. HRMS (ESI) calcd for [C₁₈H₂₀O₄S+Na]⁺: 355.0980, Found: 355.0986.

4. ^1H and ^{13}C -NMR Spectra of the Title Compounds

3aa

^1H NMR



^{13}C NMR

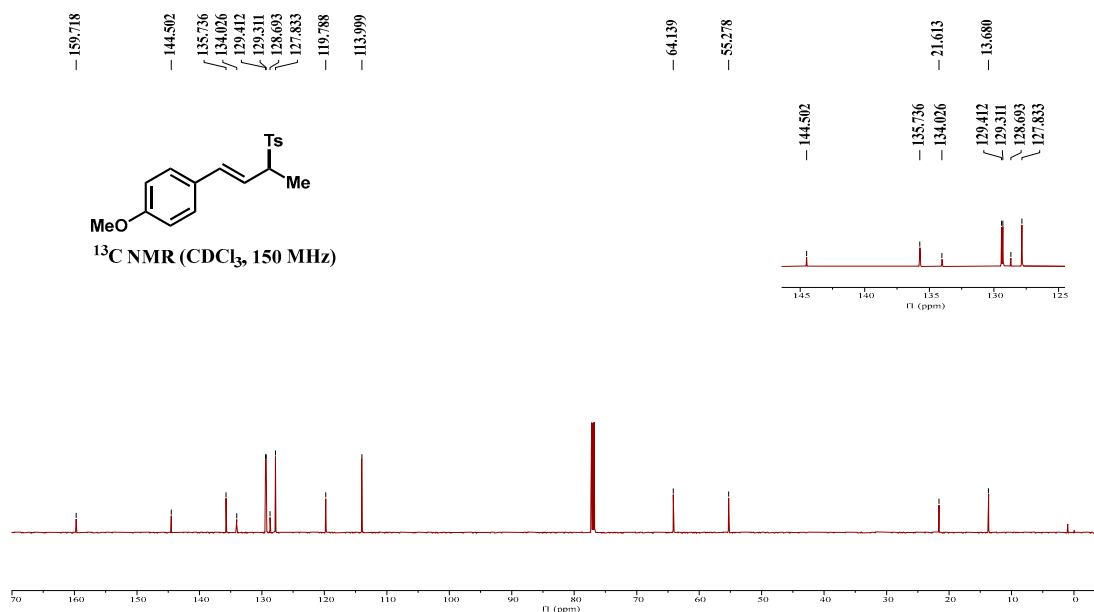
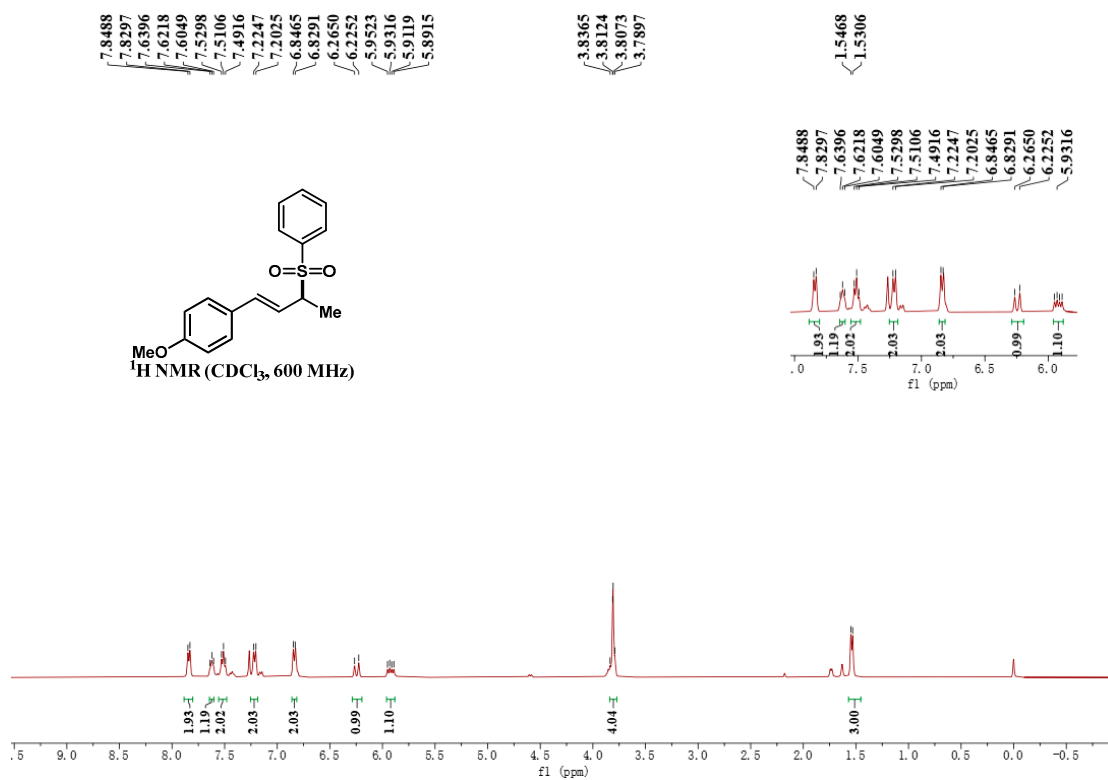


Figure S3. ^1H NMR and ^{13}C NMR spectra of **3aa** in CDCl_3

3ab

^1H NMR



^{13}C NMR

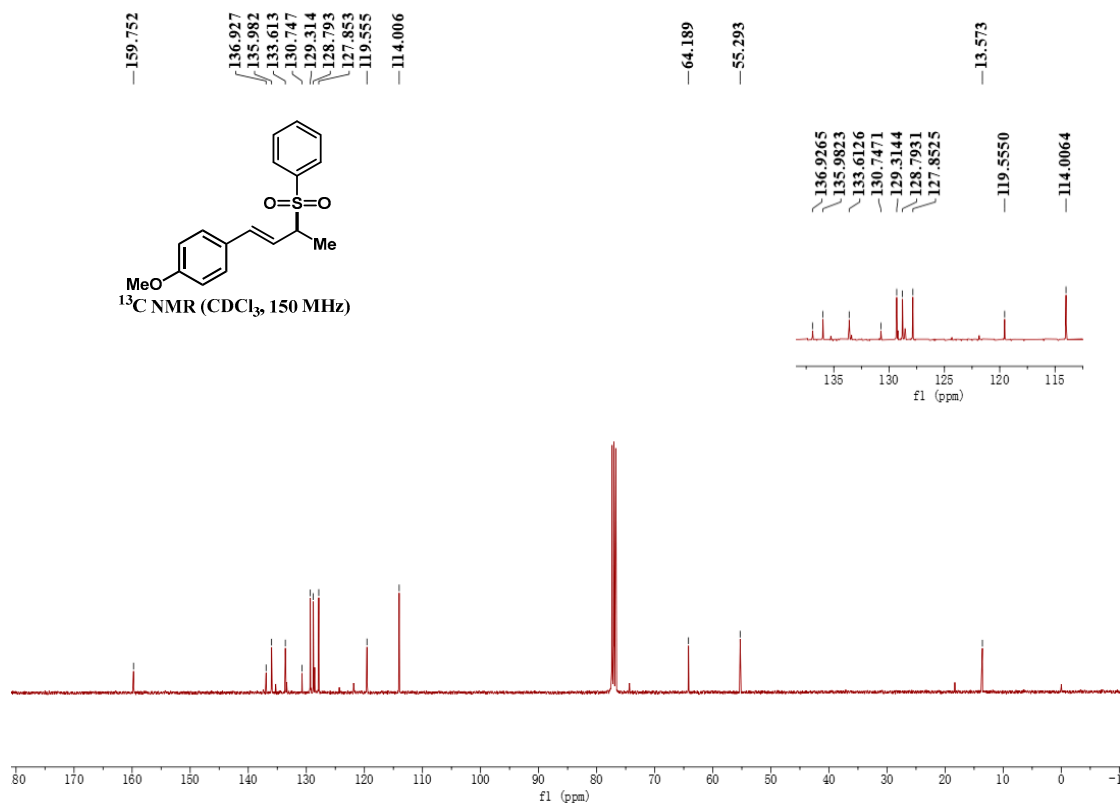
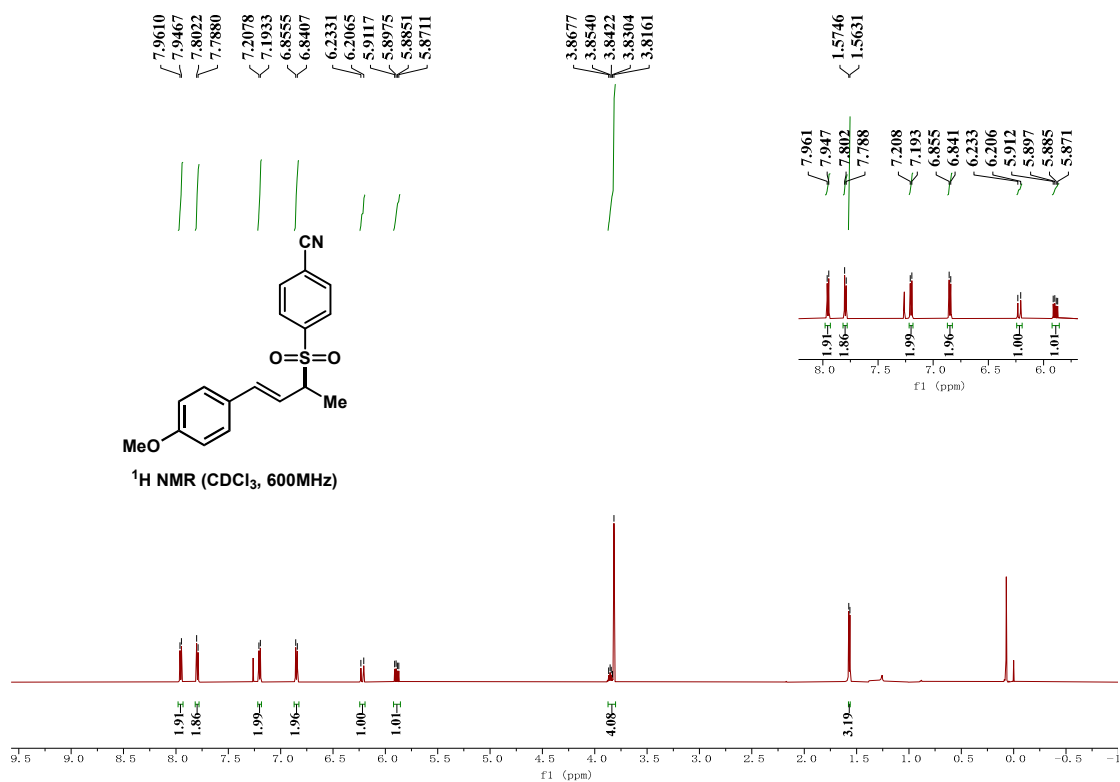


Figure S4. ^1H NMR and ^{13}C NMR spectra of **3ab** in CDCl₃

3ac

¹H NMR



¹³C NMR

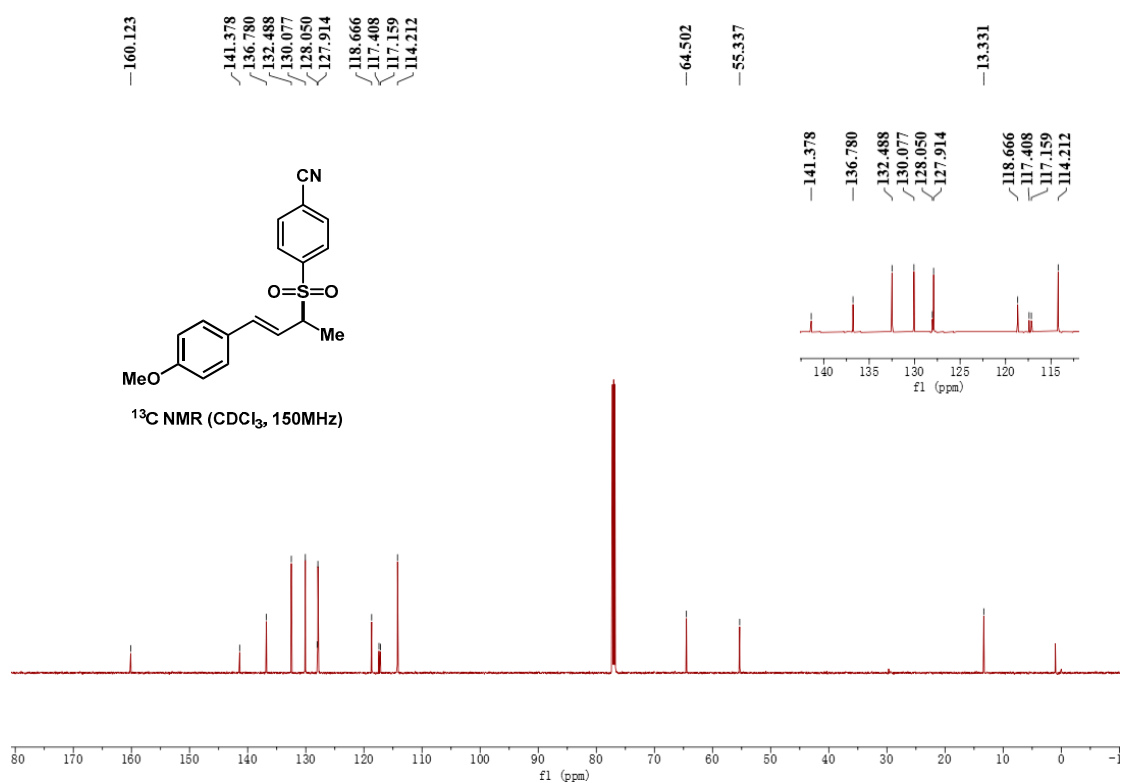
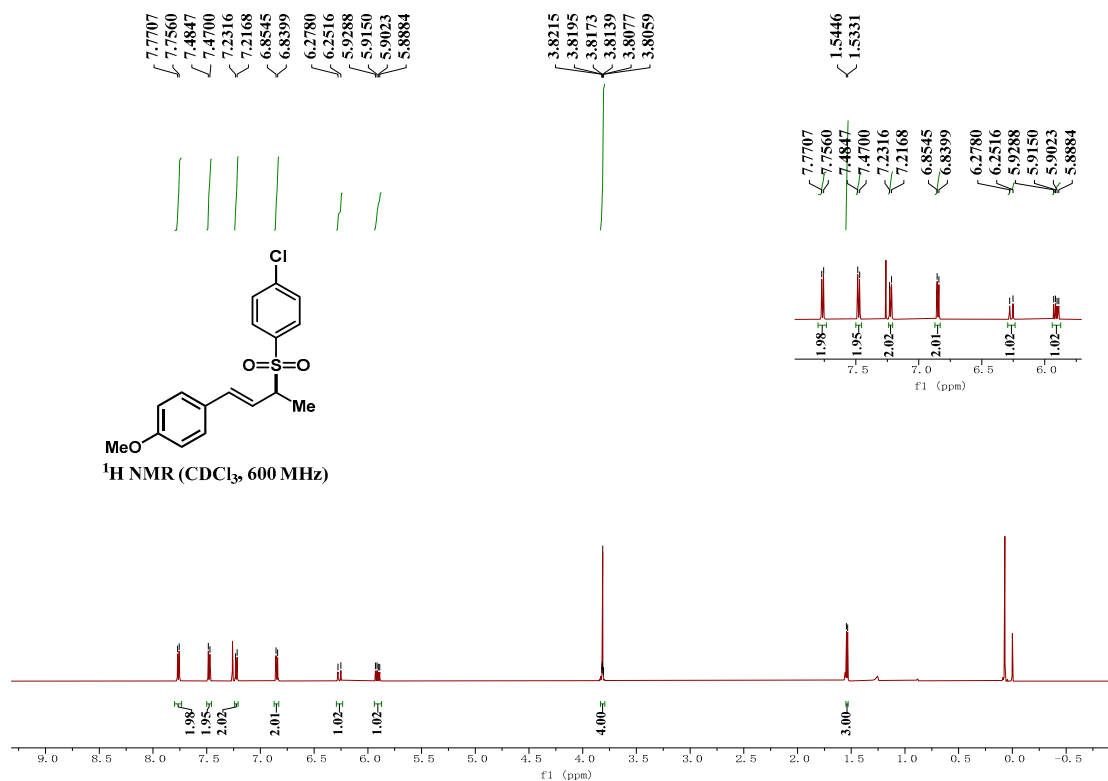


Figure S5. ¹H NMR and ¹³C NMR spectra of **3ac** in CDCl₃

3ad

^1H NMR



^{13}C NMR

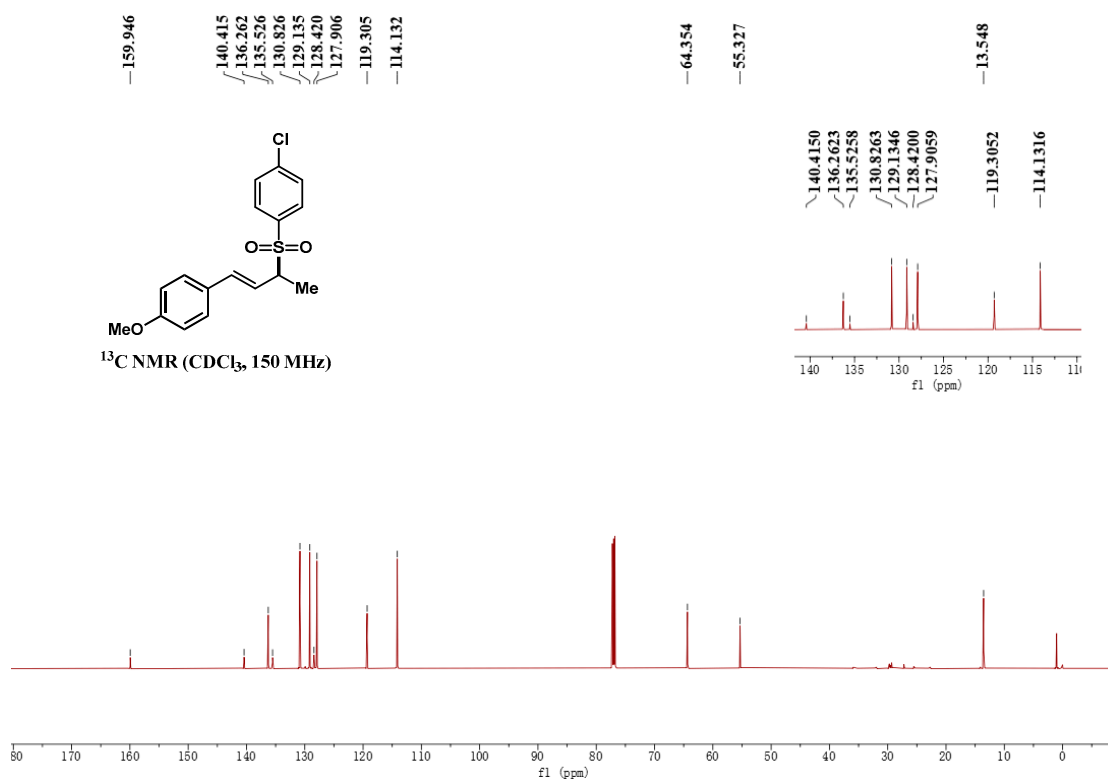


Figure S6. ^1H NMR and ^{13}C NMR spectra of 3ad in CDCl₃

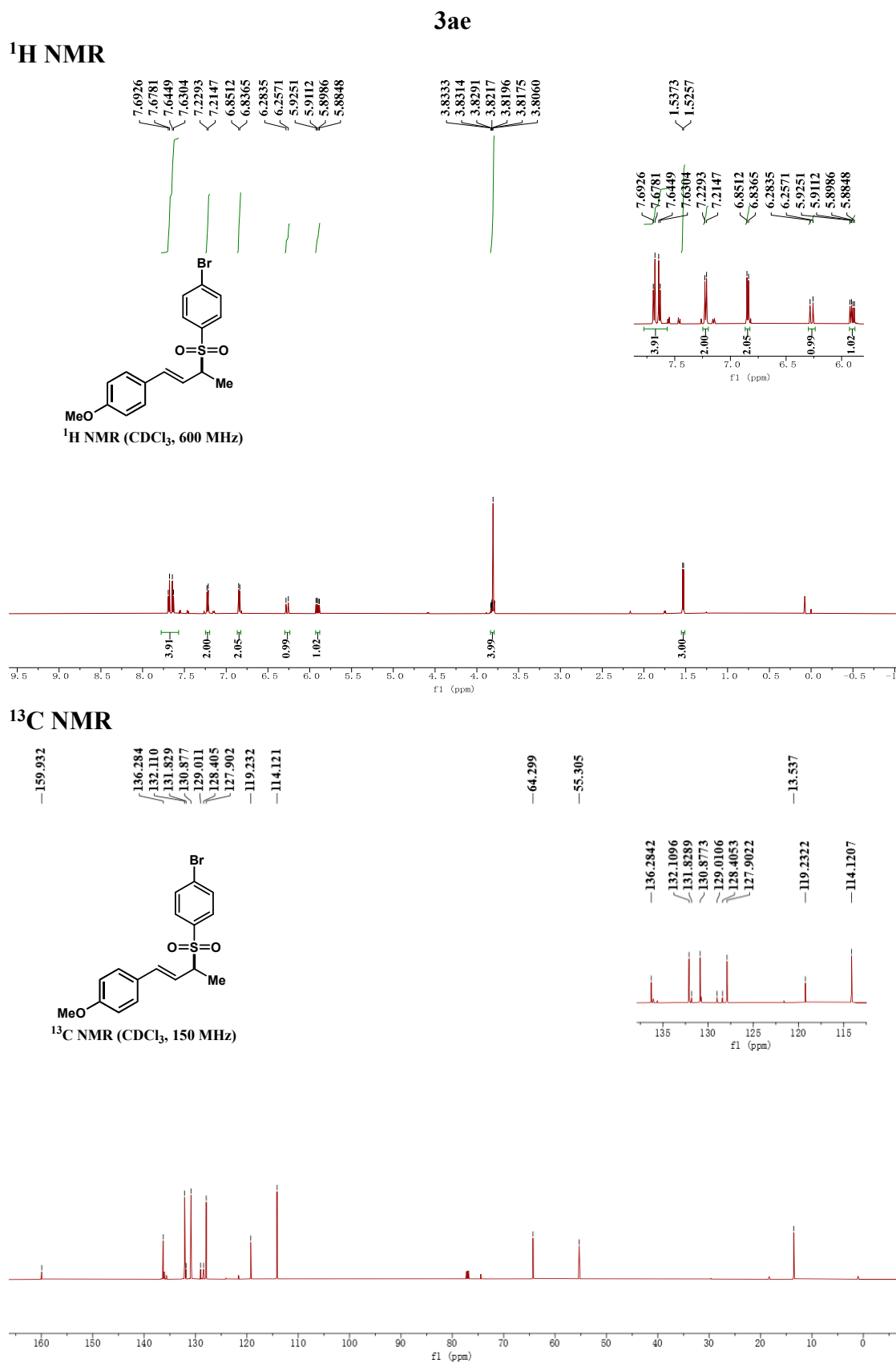
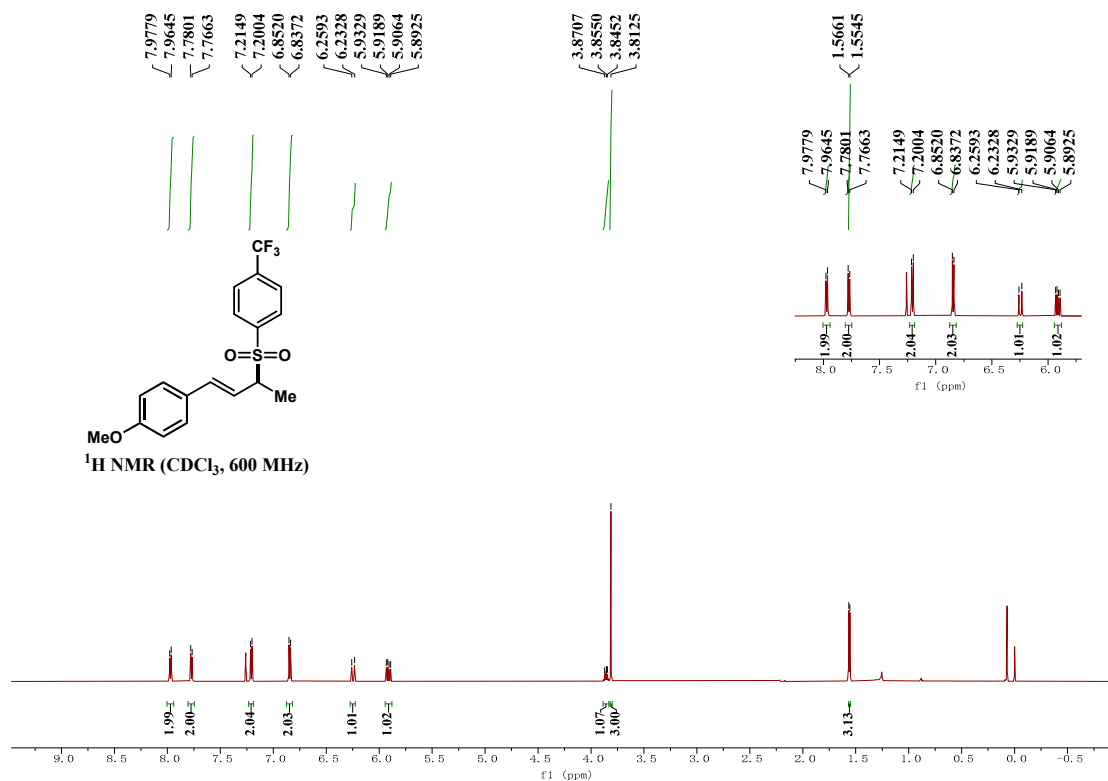


Figure S7. ¹H NMR and ¹³C NMR spectra of **3ae** in CDCl₃

3af

¹H NMR



¹³C NMR

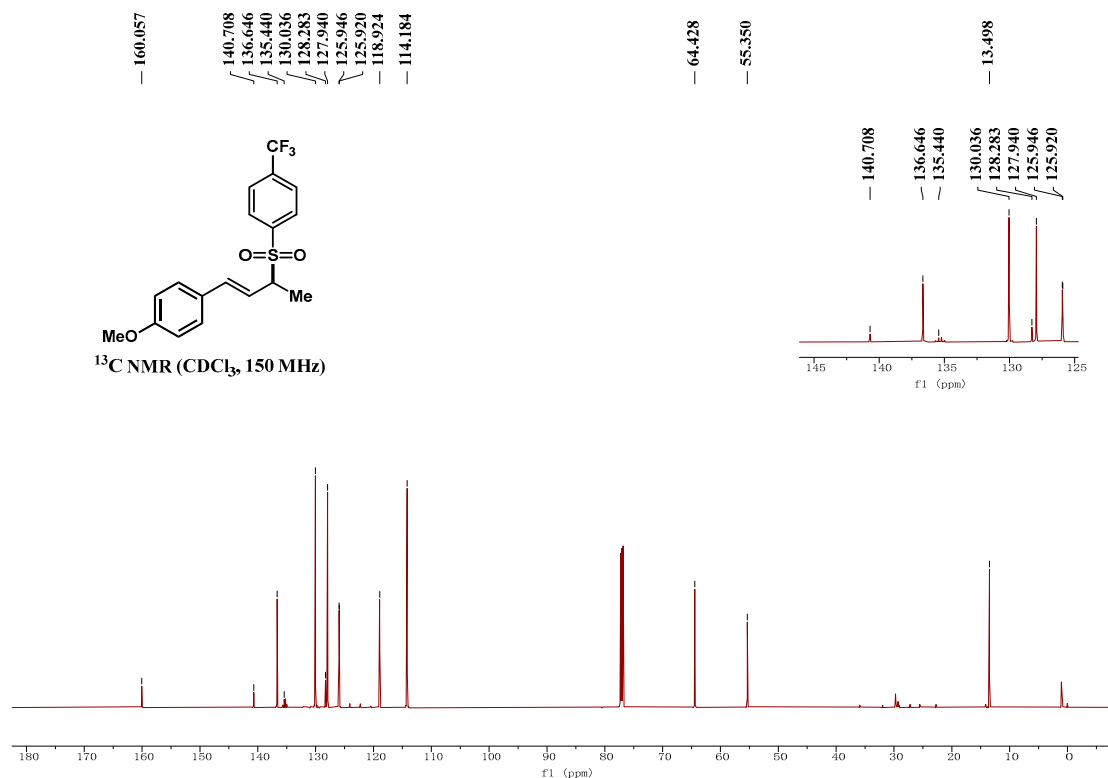
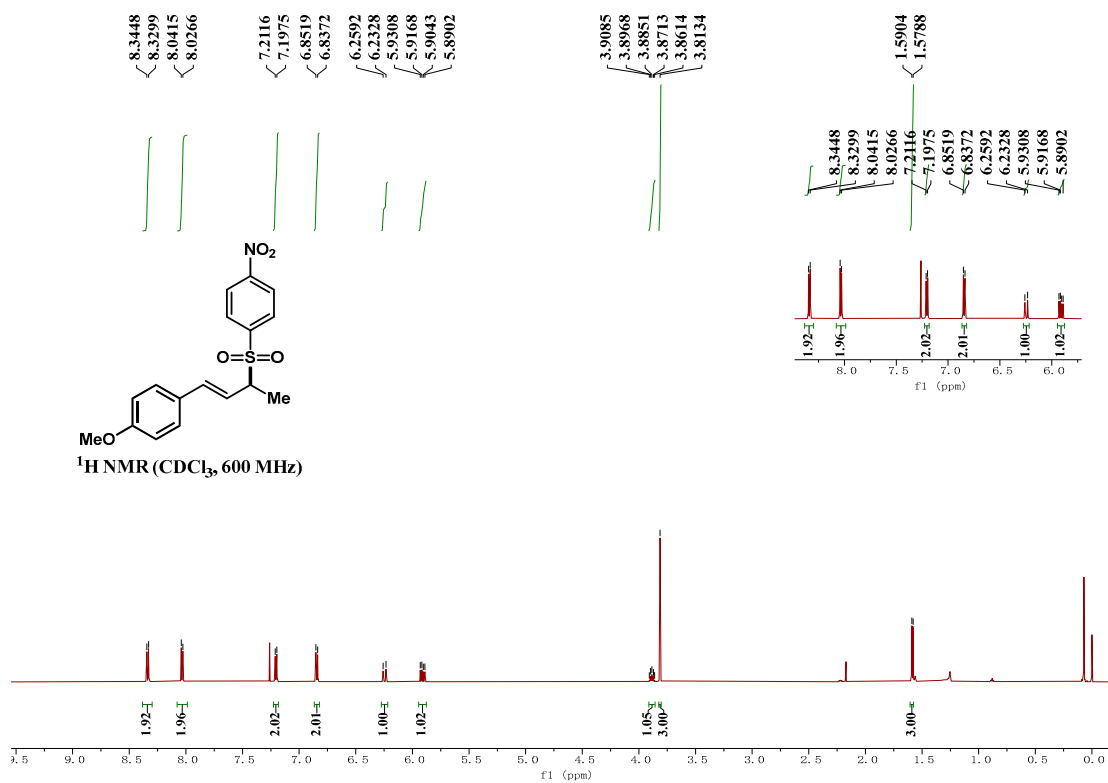


Figure S8. ¹H NMR and ¹³C NMR spectra of **3af** in CDCl₃

3ag

¹H NMR



¹³C NMR

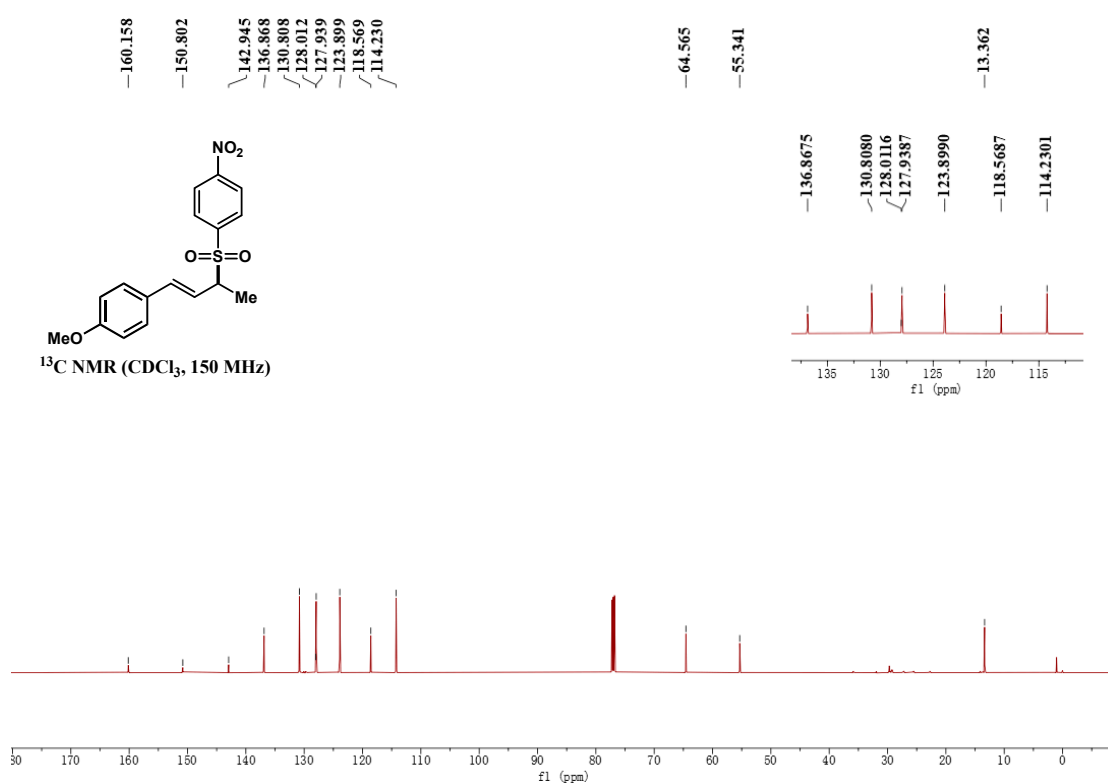
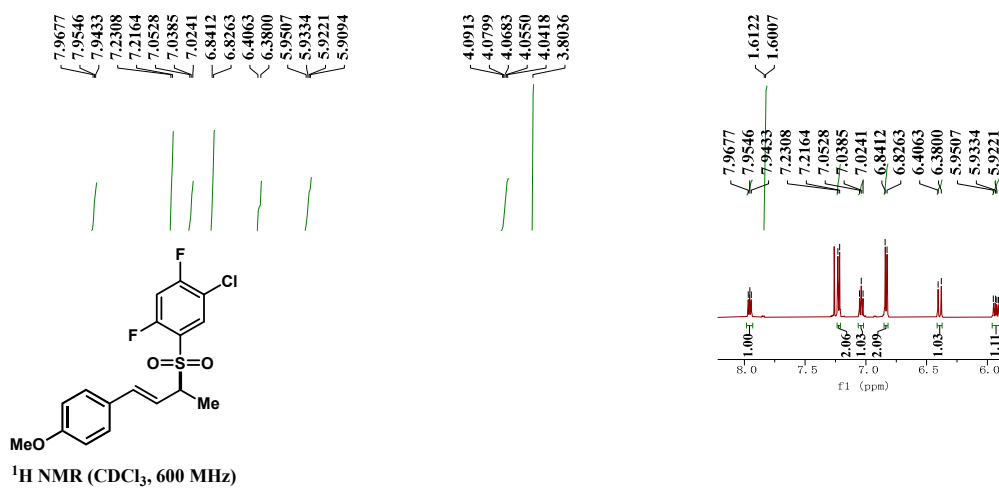


Figure S9. ¹H NMR and ¹³C NMR spectra of **3ag** in CDCl₃

3ah

¹H NMR



¹³C NMR

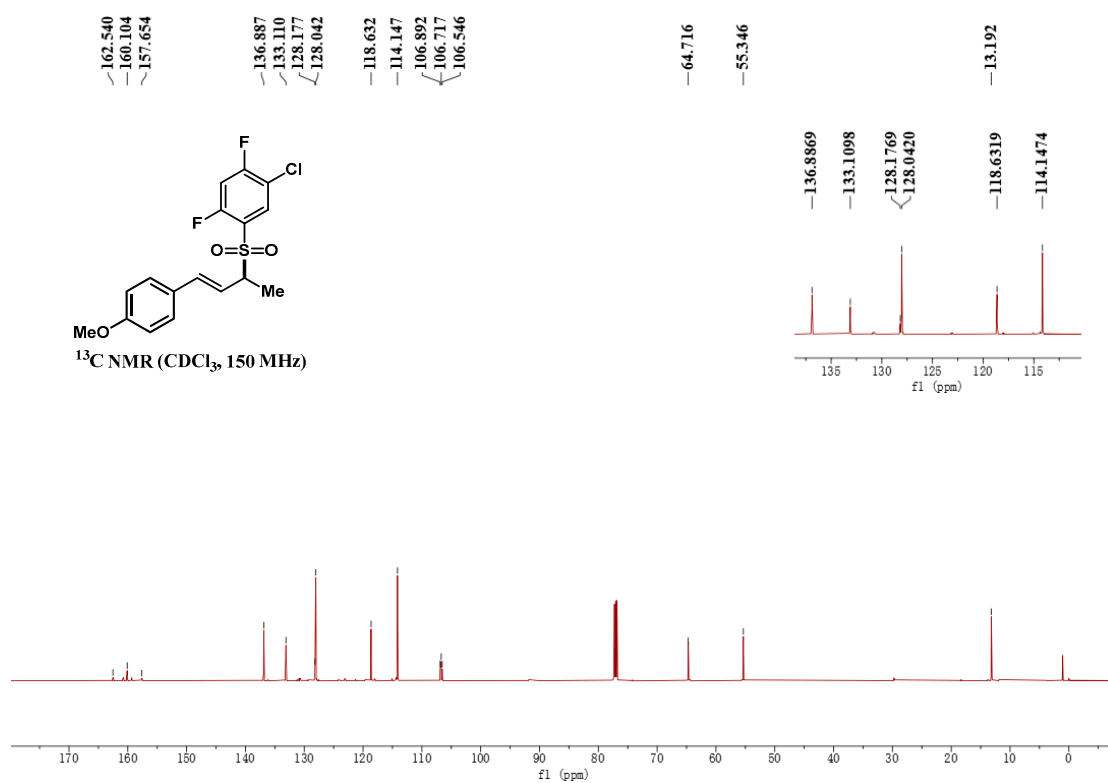
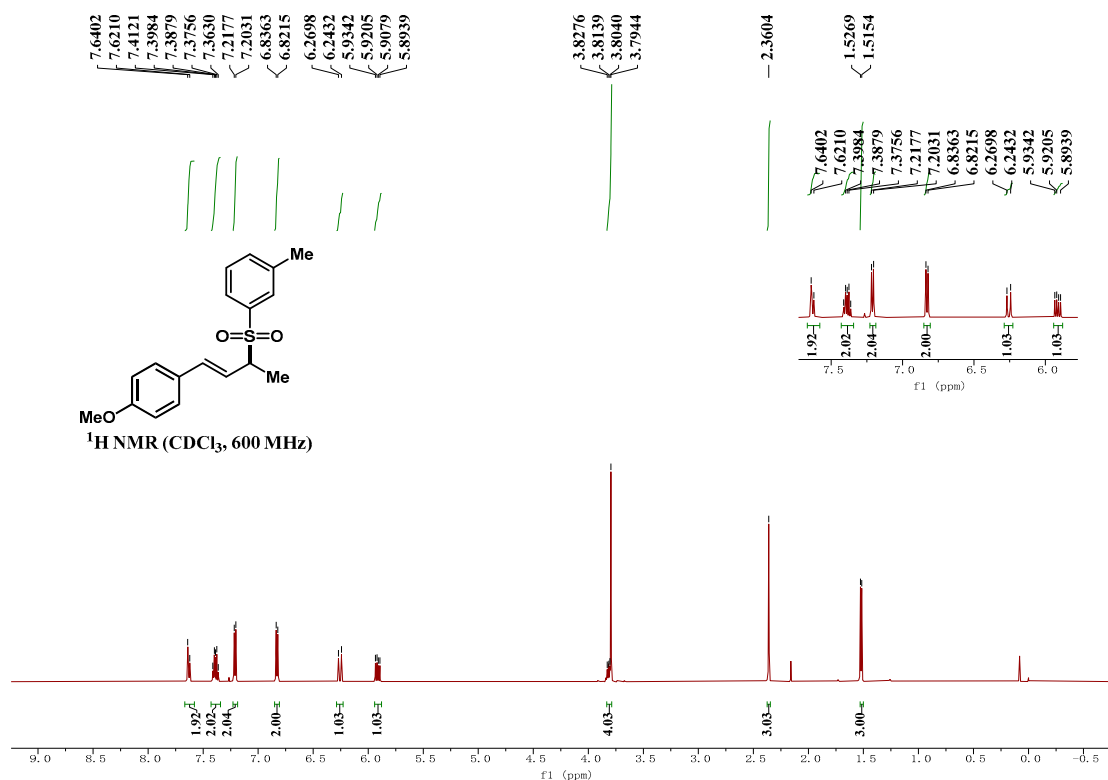


Figure S10. ¹H NMR and ¹³C NMR spectra of **3ah** in CDCl₃

3ai

^1H NMR



^{13}C NMR

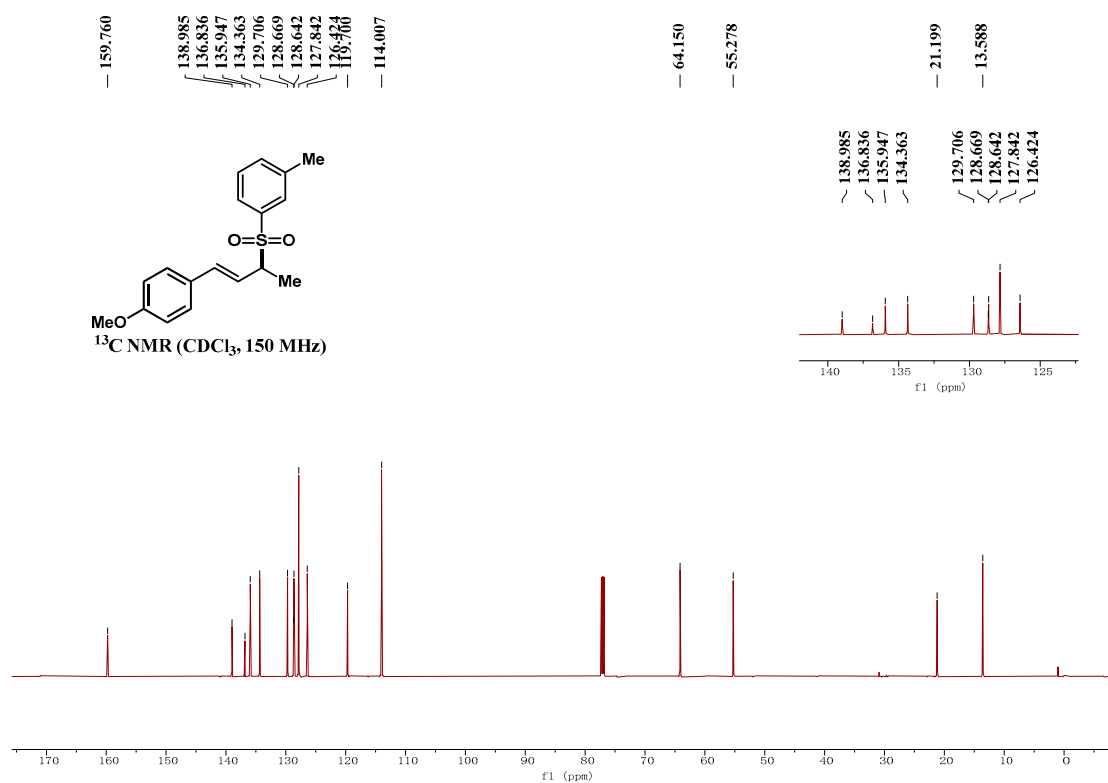
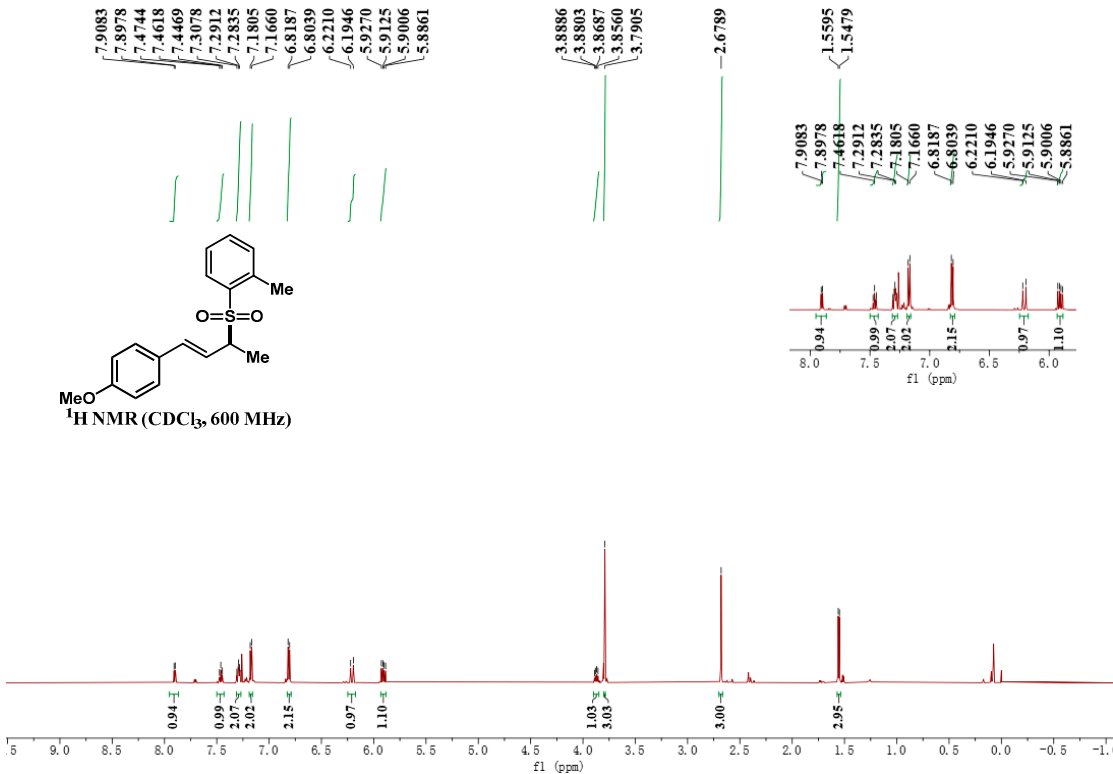


Figure S11. ^1H NMR and ^{13}C NMR spectra of **3ai** in CDCl₃

3aj

¹H NMR



¹³C NMR

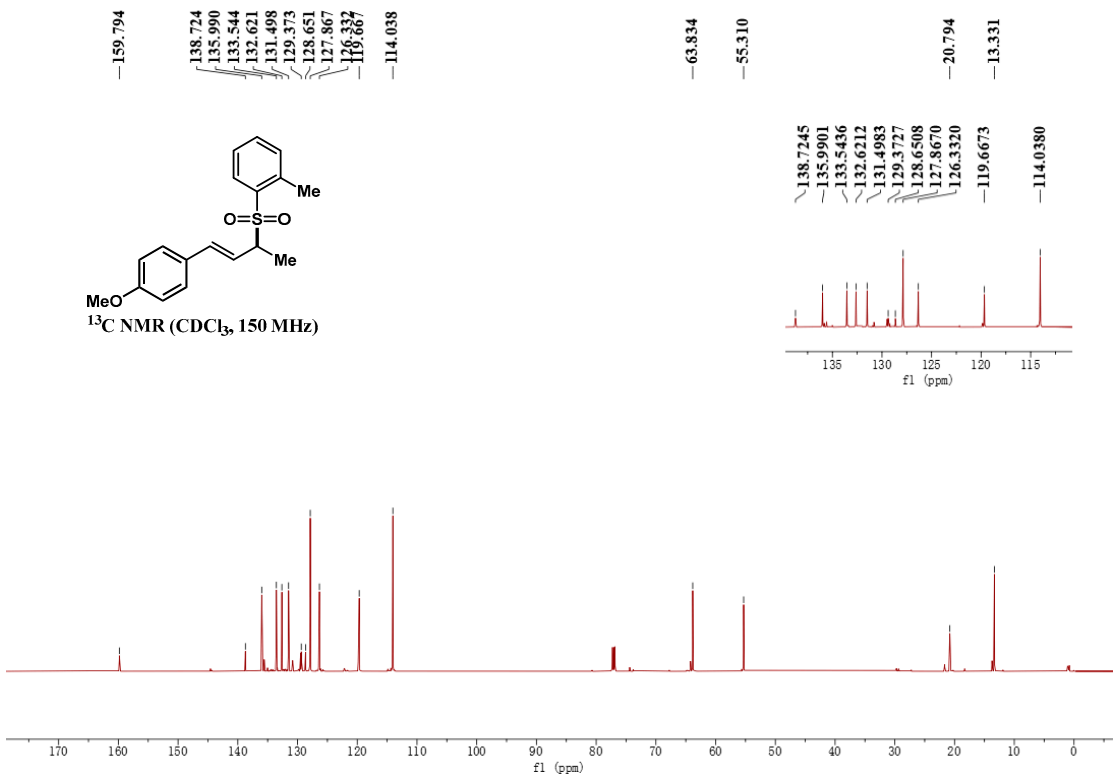


Figure S12. ^1H NMR and ^{13}C NMR spectra of **3aj** in CDCl_3

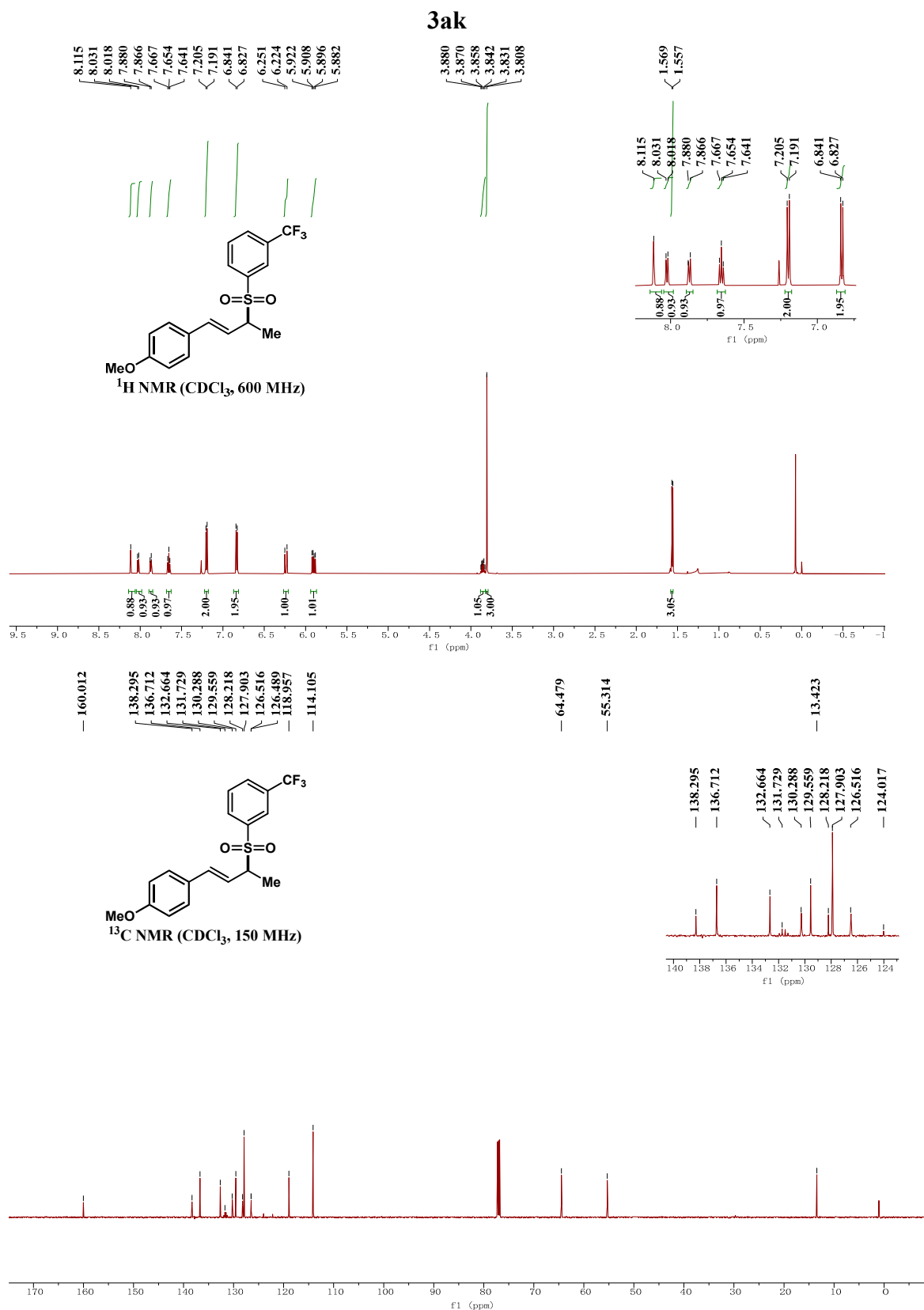


Figure S13. ¹H NMR and ¹³C NMR spectra of **3ak** in CDCl₃

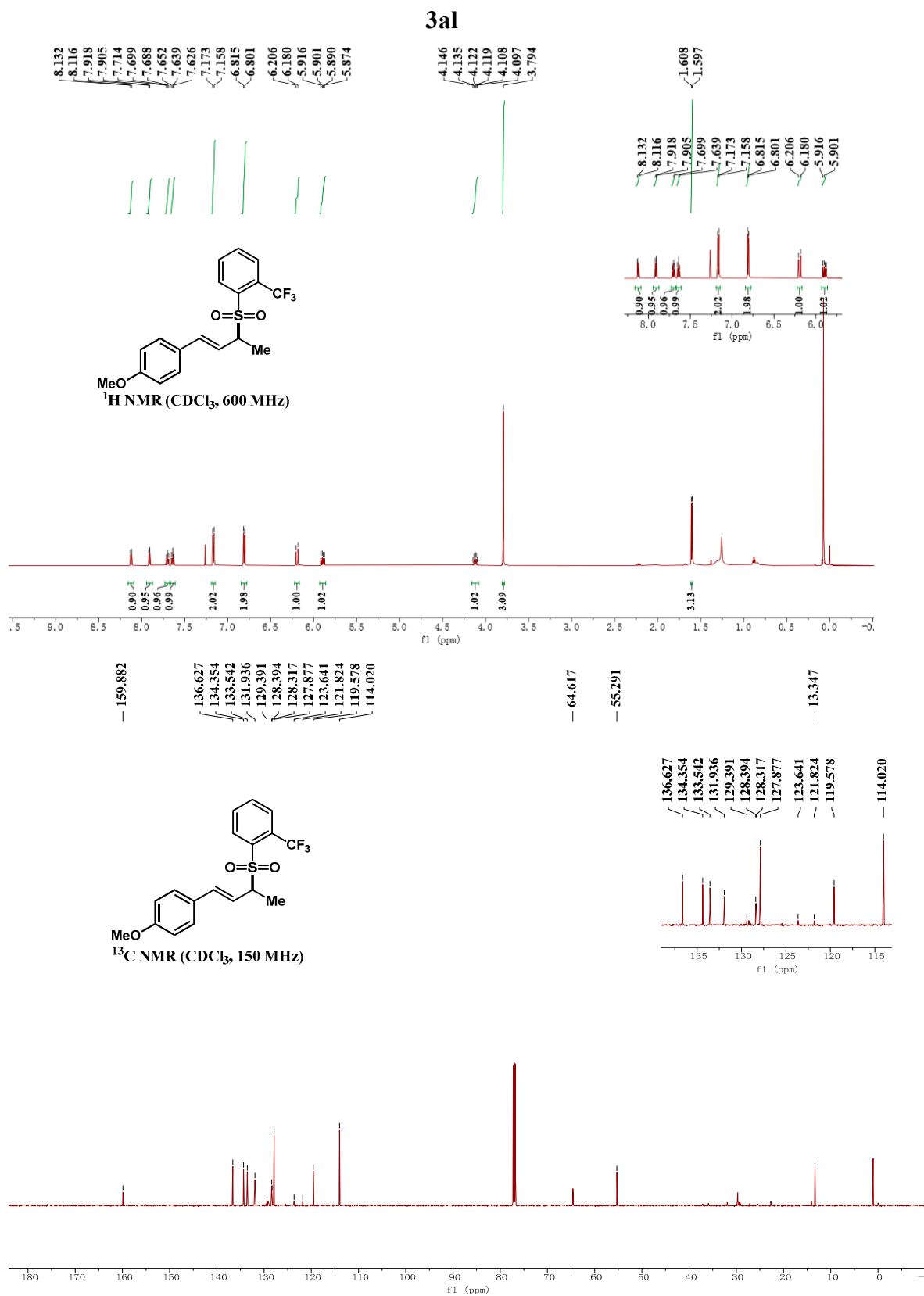


Figure S14. ¹H NMR and ¹³C NMR spectra of **3al** in CDCl₃

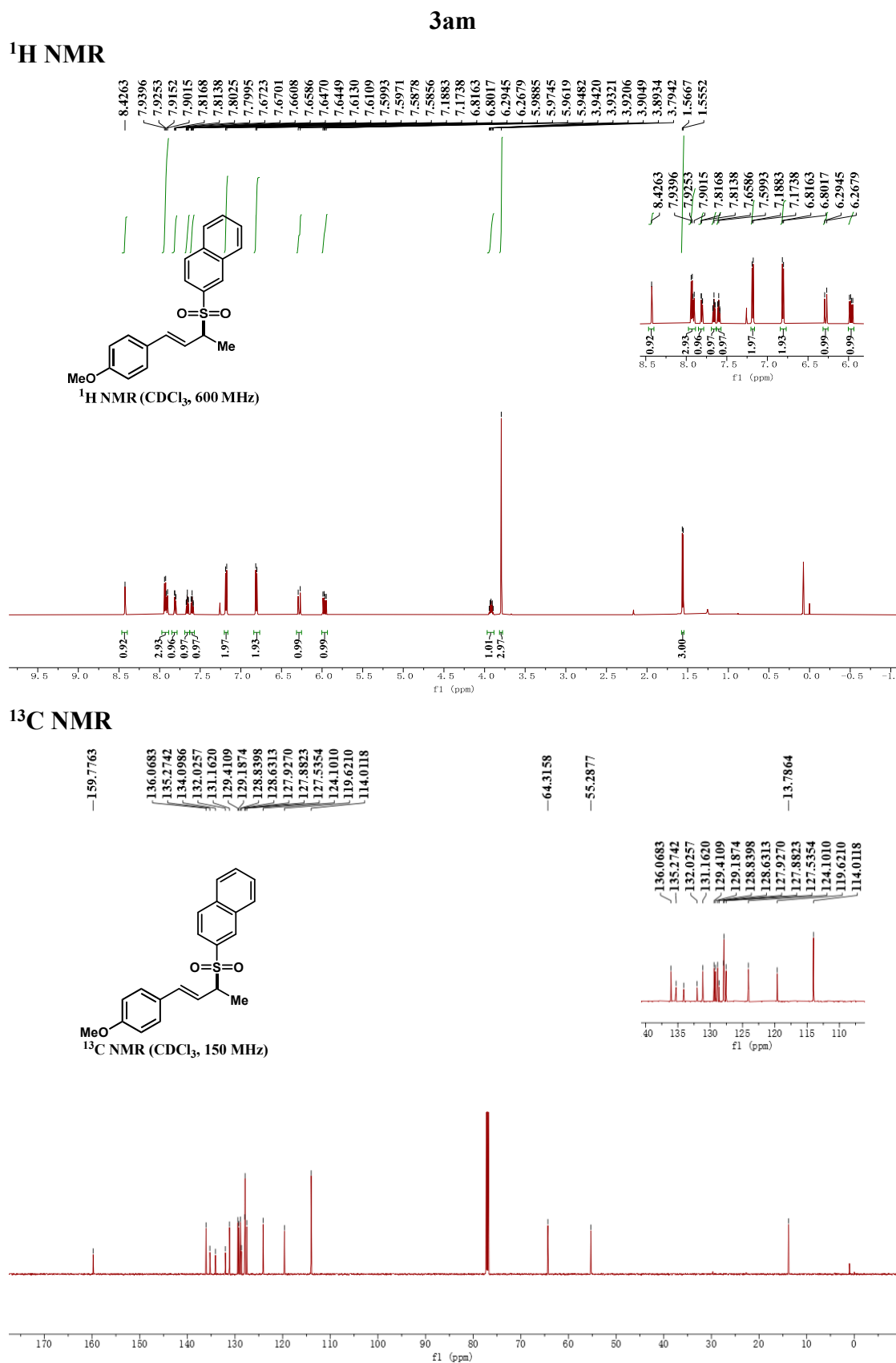
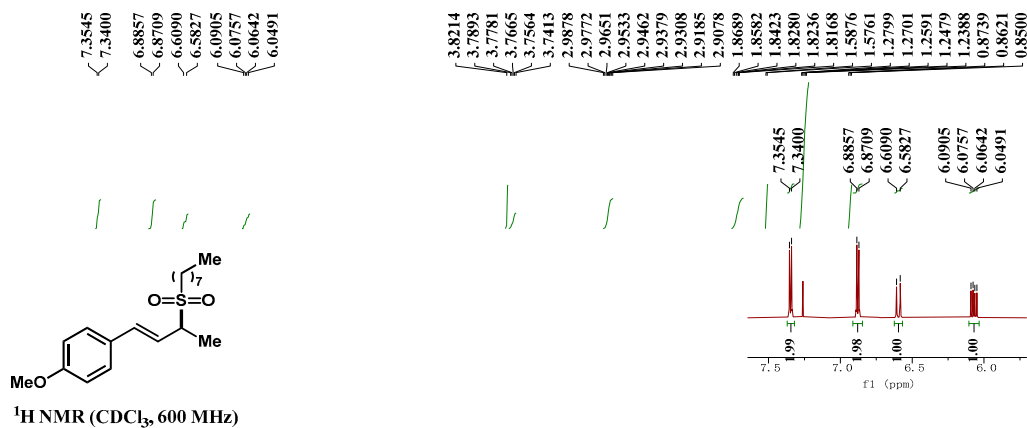


Figure S15. ¹H NMR and ¹³C NMR spectra of **3am** in CDCl₃

3an

¹H NMR



¹³C NMR

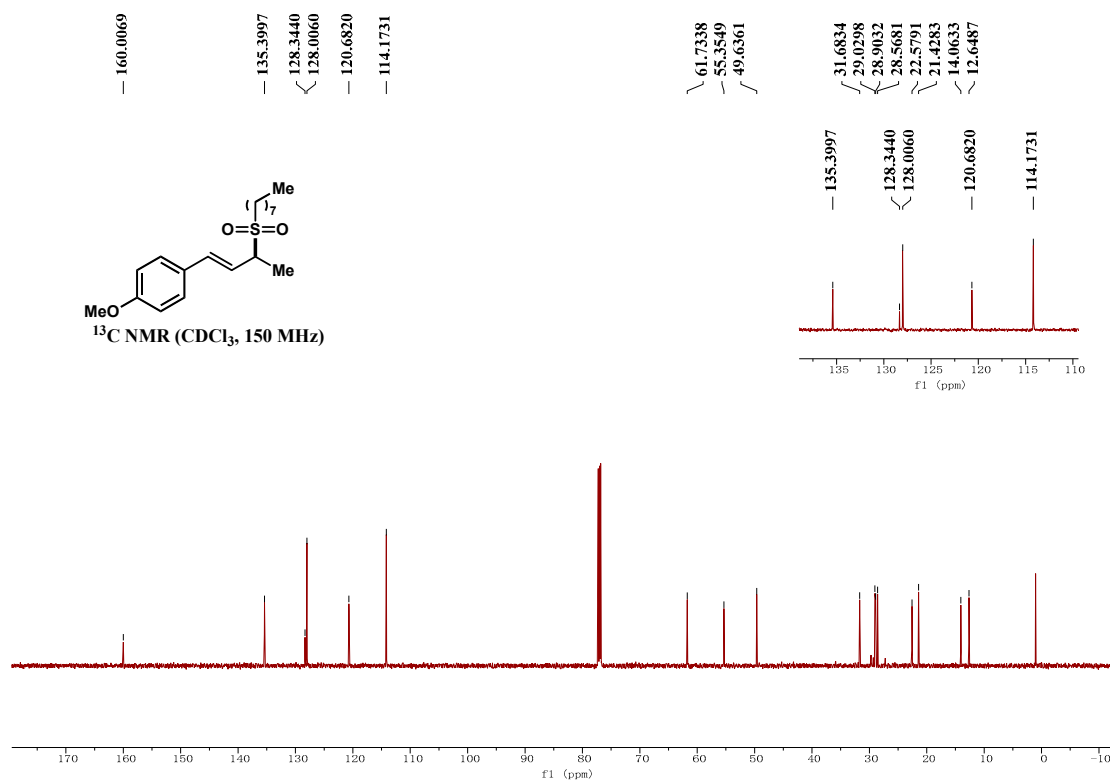
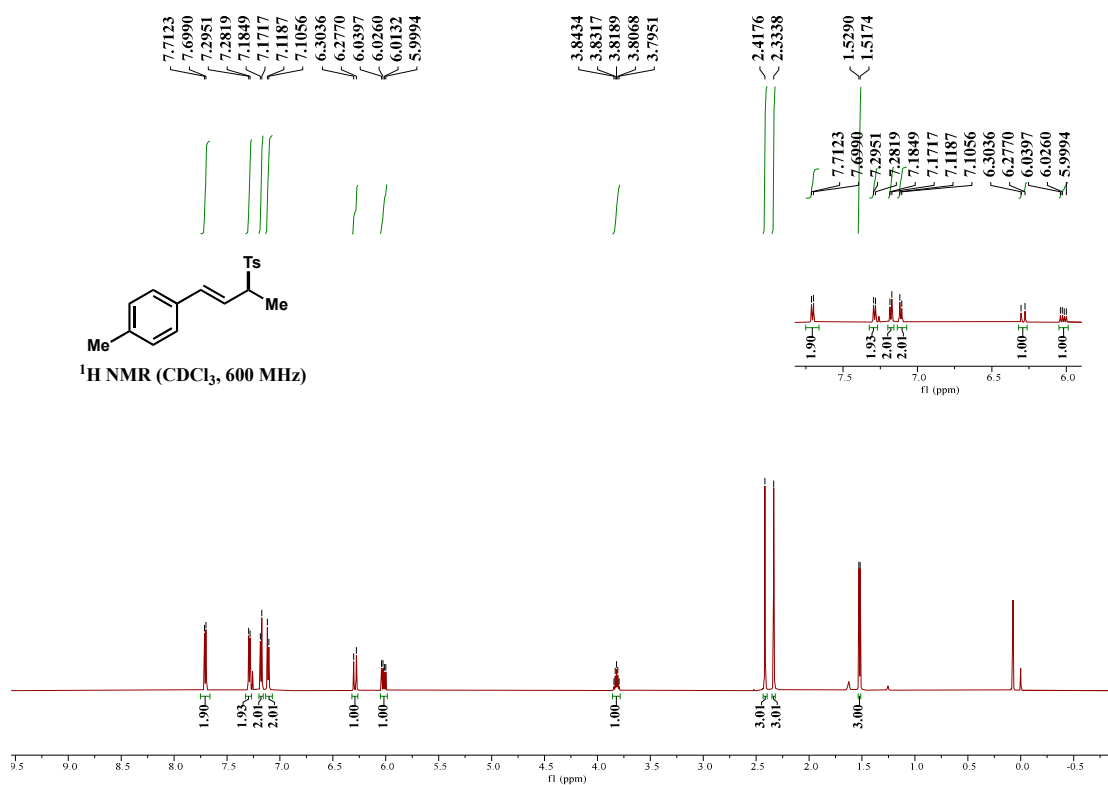


Figure S16. ¹H NMR and ¹³C NMR spectra of 3an in CDCl₃

3ba

¹H NMR



¹³C NMR

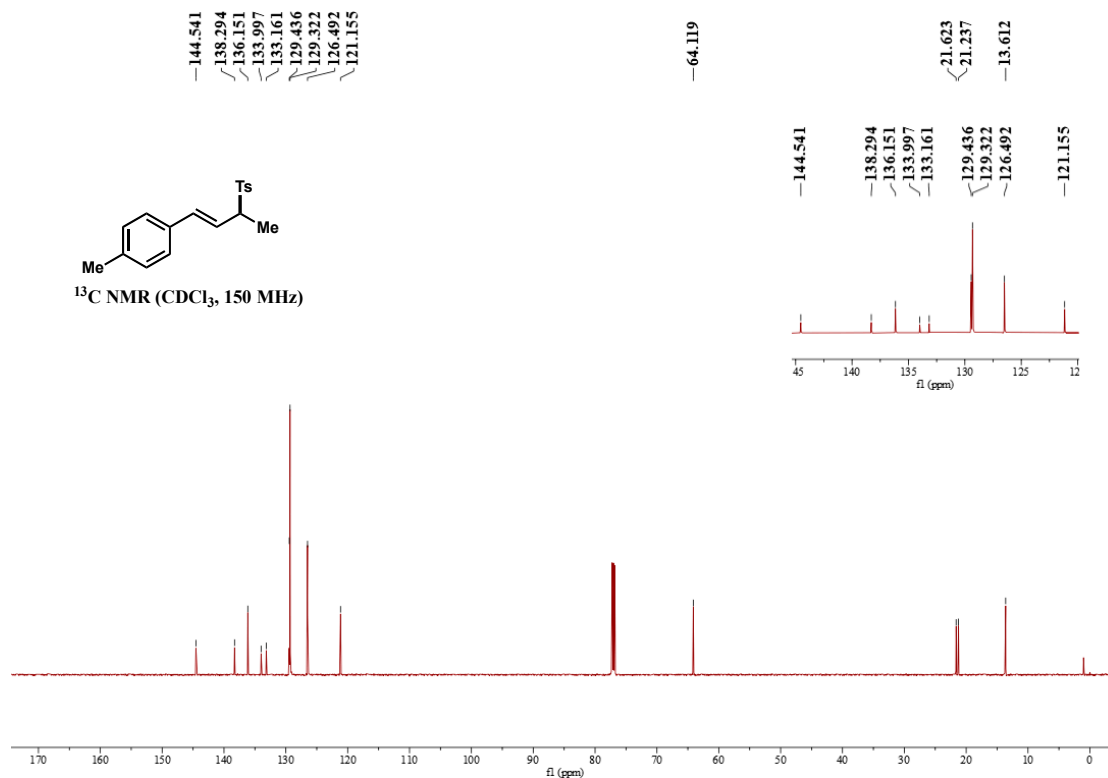


Figure S17. ¹H NMR and ¹³C NMR spectra of **3ba** in CDCl₃

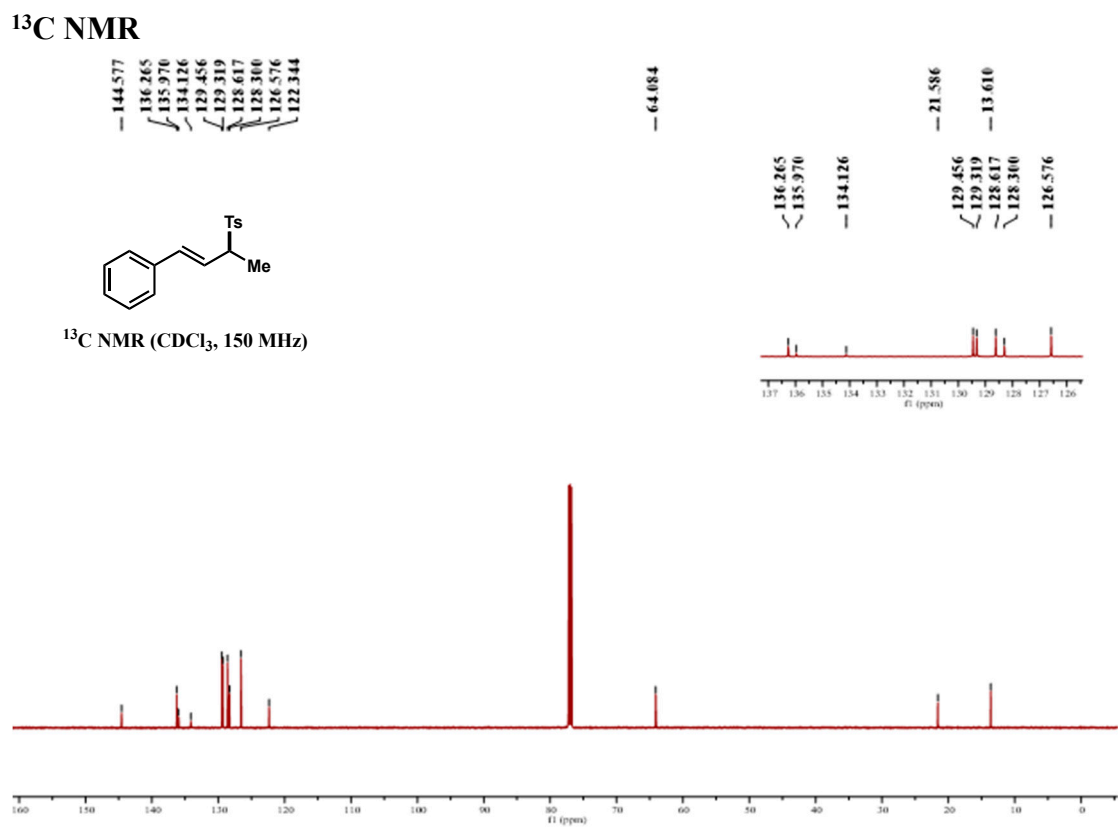
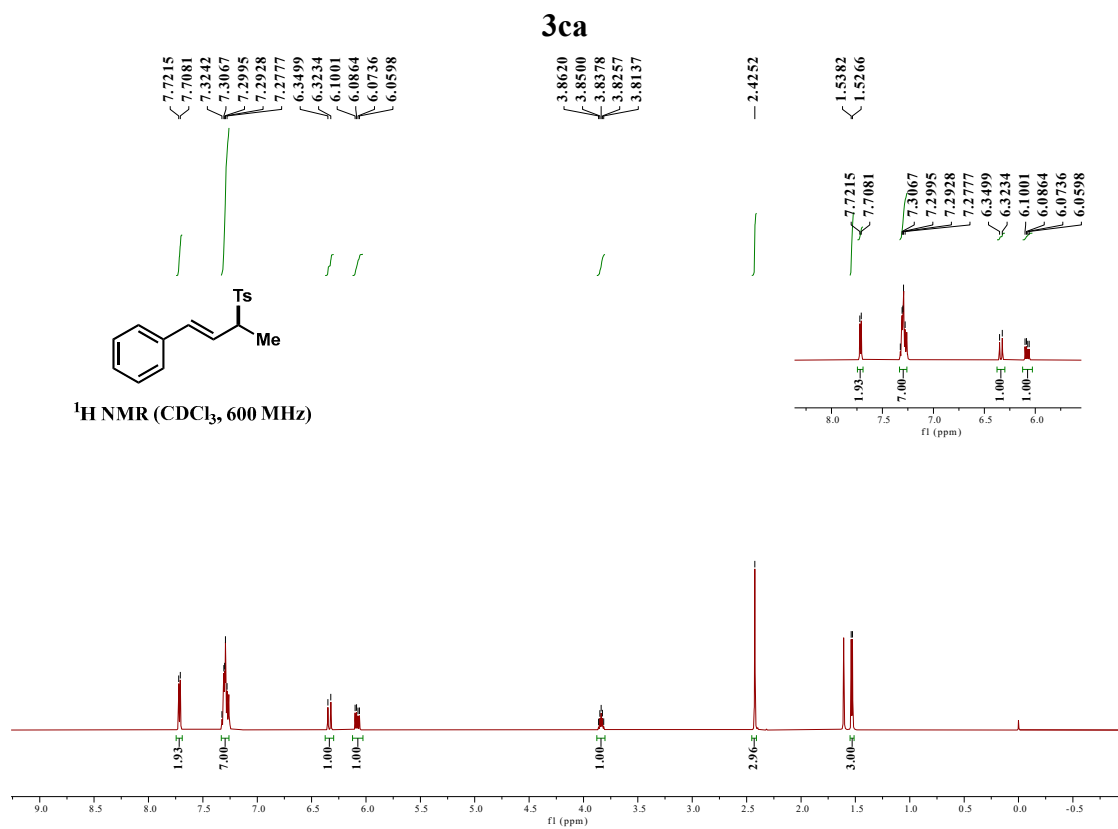
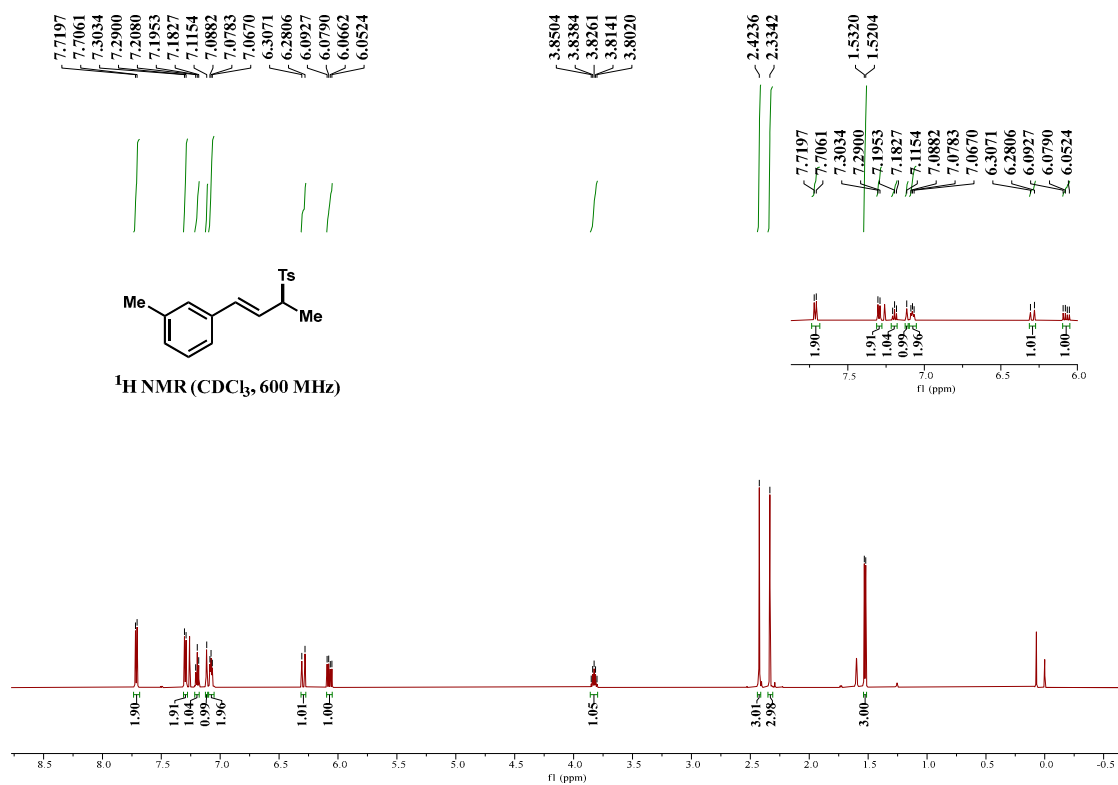


Figure S18. ¹H NMR and ¹³C NMR spectra of **3ca** in CDCl₃

3da

^1H NMR



^{13}C NMR

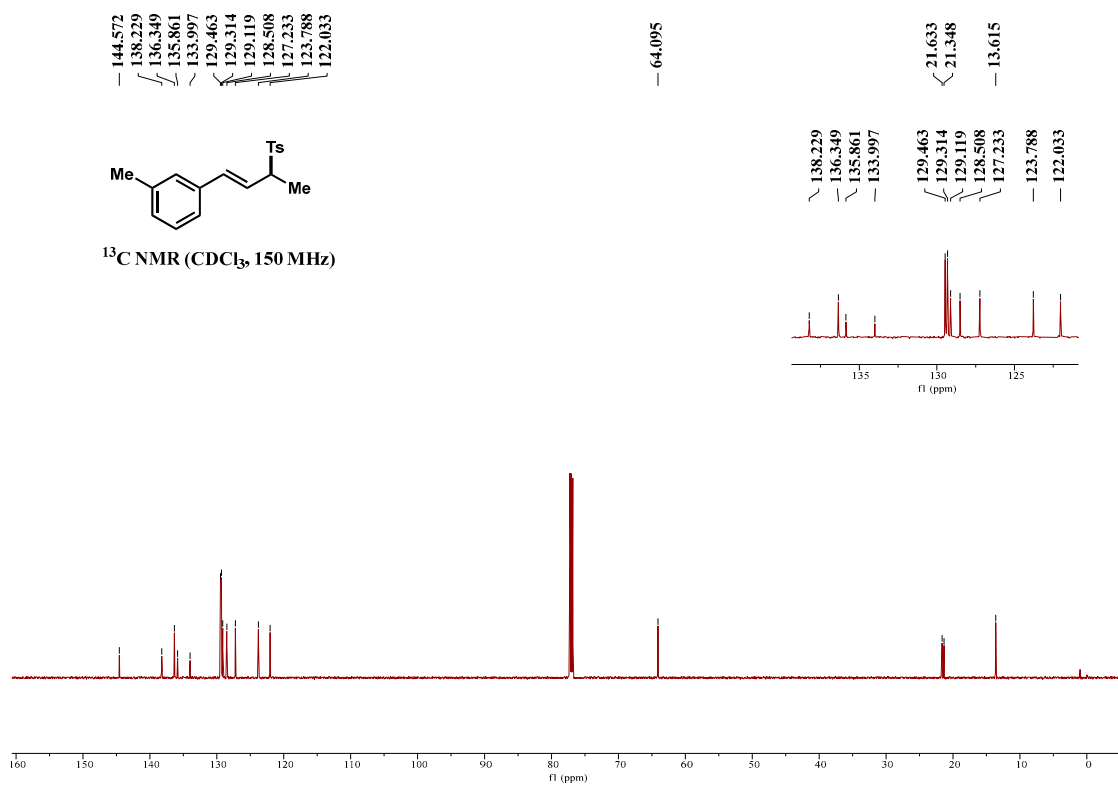


Figure S19. ^1H NMR and ^{13}C NMR spectra of 3da in CDCl₃

3ea

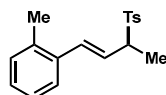
^1H NMR

7.7368
7.7233
7.3520
7.3415
7.3376
7.3146
7.3010
7.1719
7.1657
7.1603
7.1107
7.1070
7.0969
6.5310
6.5048
5.9559
5.9418
5.9297
5.9156

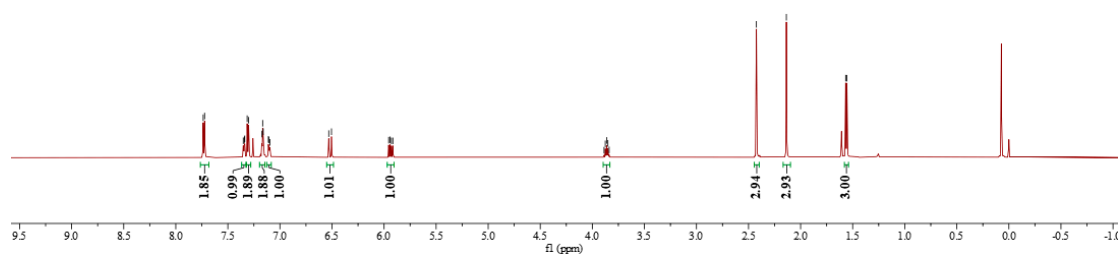
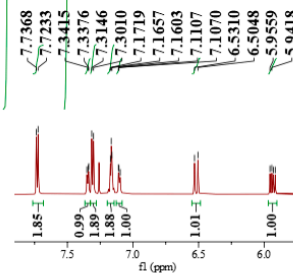
3.8873
3.8756
3.8625
3.8503
3.8386

2.4244
2.1369

1.5674
1.5559



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

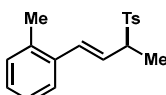


^{13}C NMR

144.581
135.568
135.051
134.385
134.097
130.263
129.454
129.319
128.185
126.187
125.795
123.760

64.353

21.610
19.443
13.581



^1H NMR (CDCl_3 , 600 MHz)

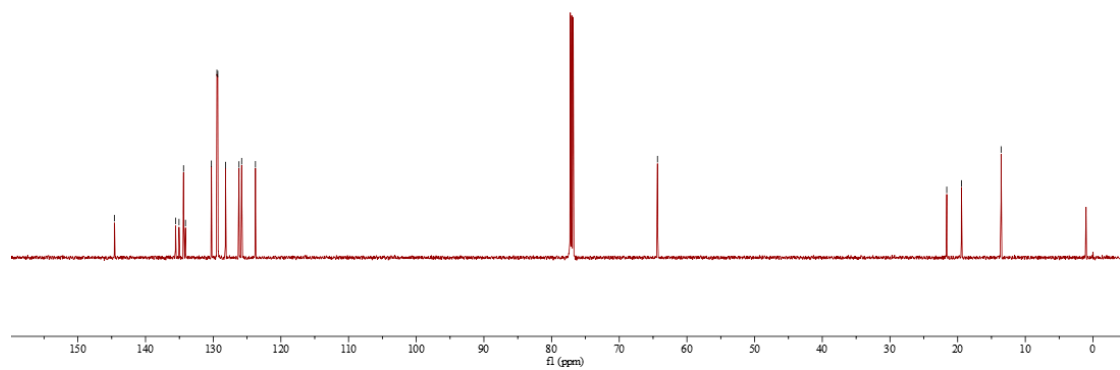
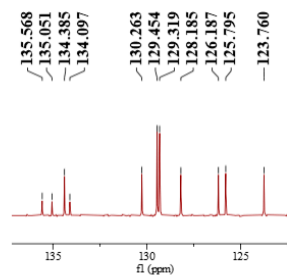
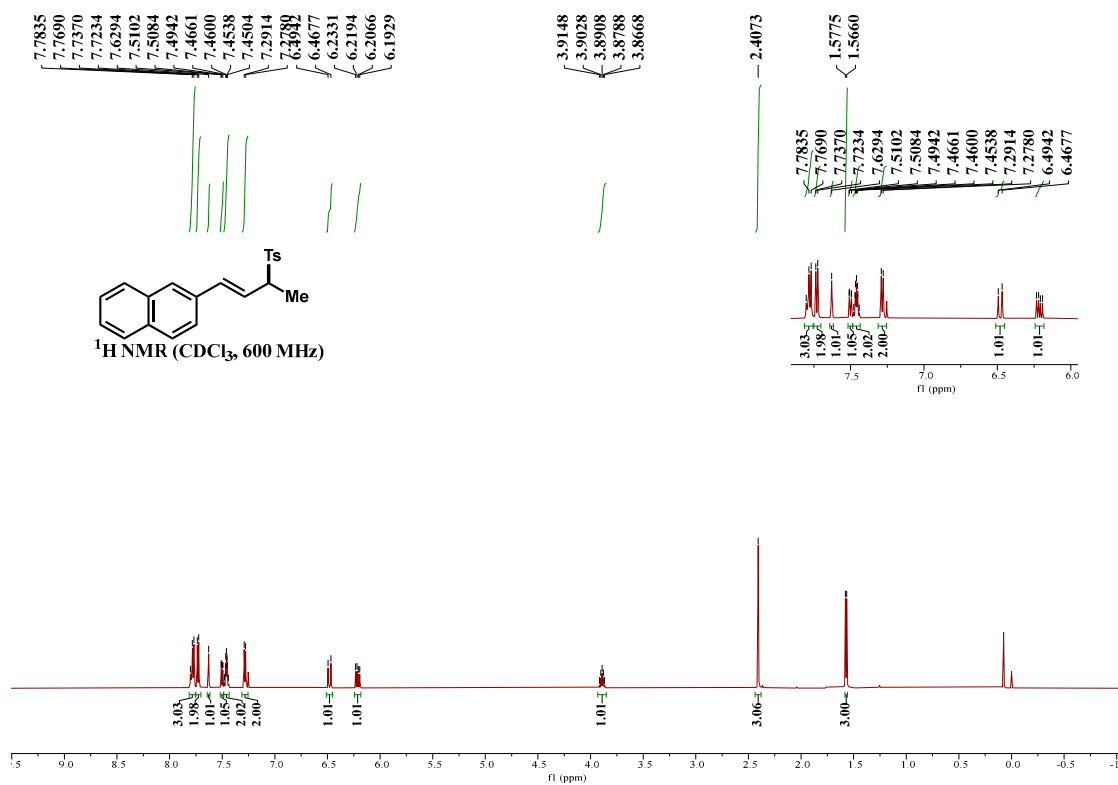


Figure S20. ^1H NMR and ^{13}C NMR spectra of **3ea** in CDCl_3

3fa

^1H NMR



^{13}C NMR

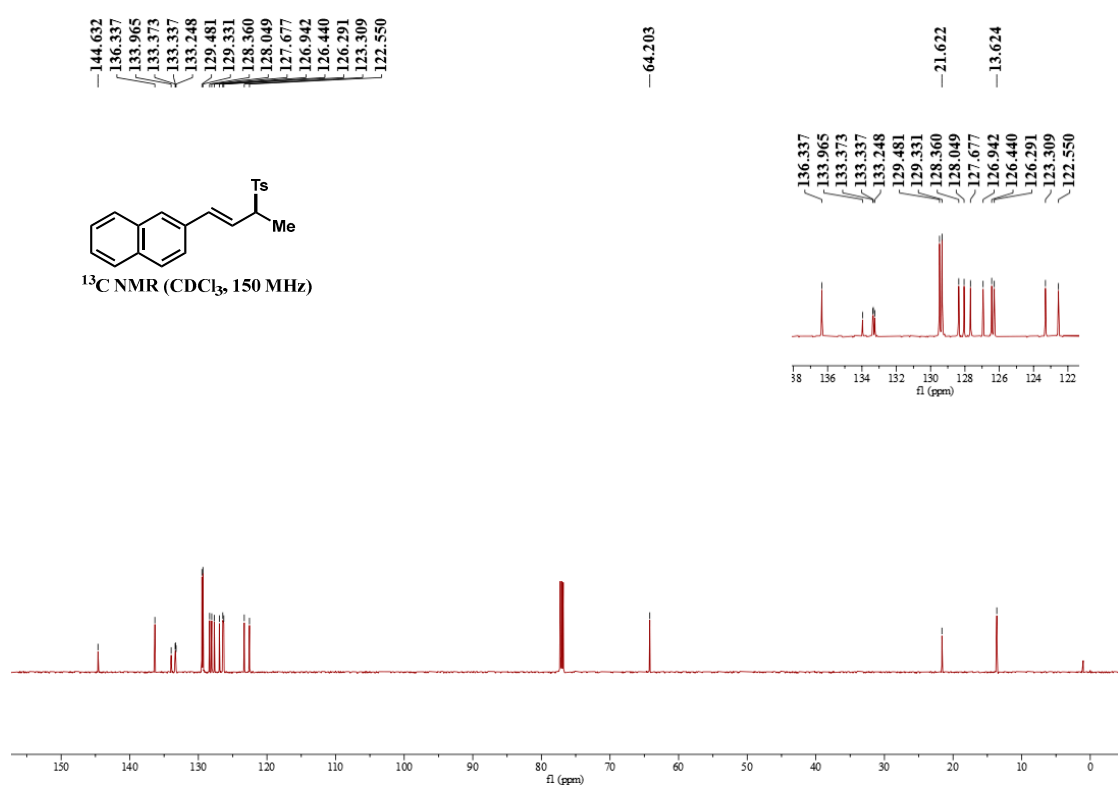
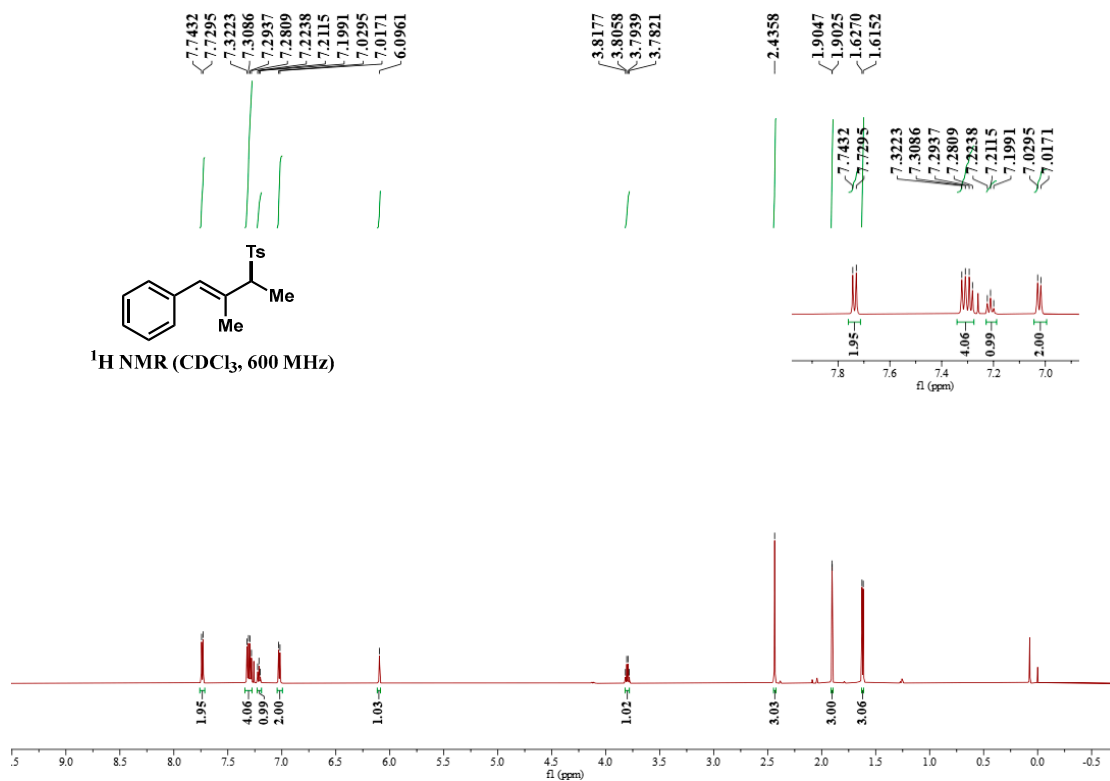


Figure S21. ^1H NMR and ^{13}C NMR spectra of **3fa** in CDCl_3

3ga

^1H NMR



^{13}C NMR

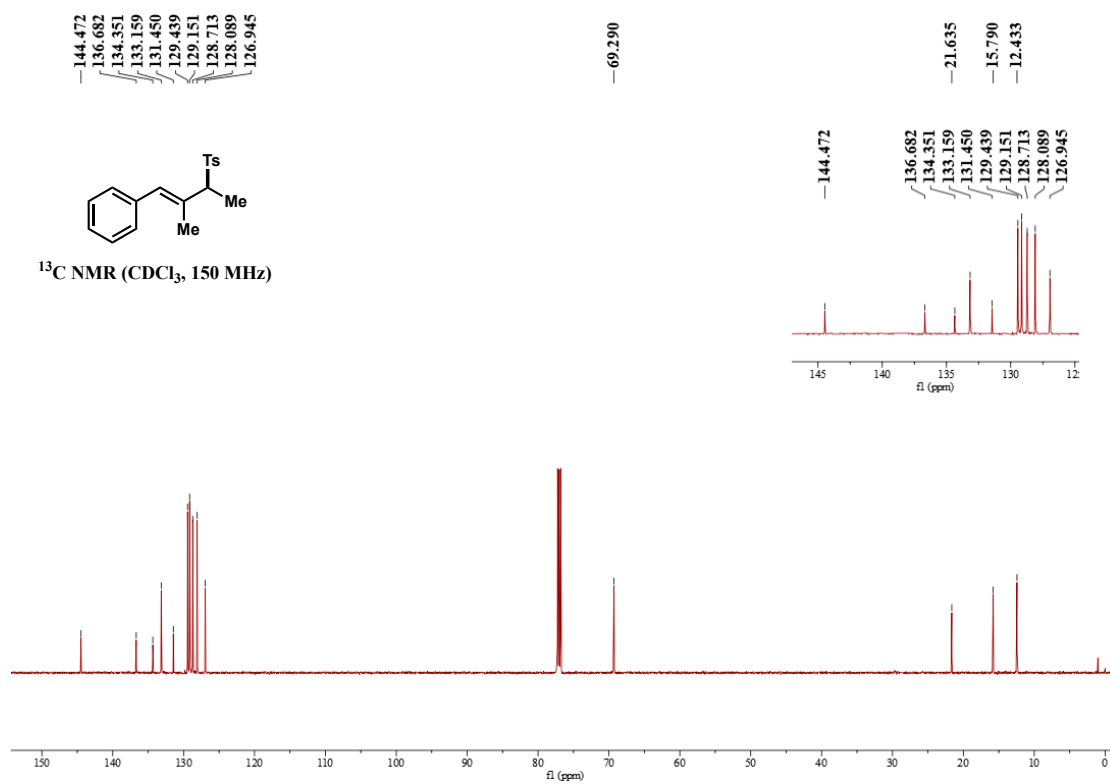
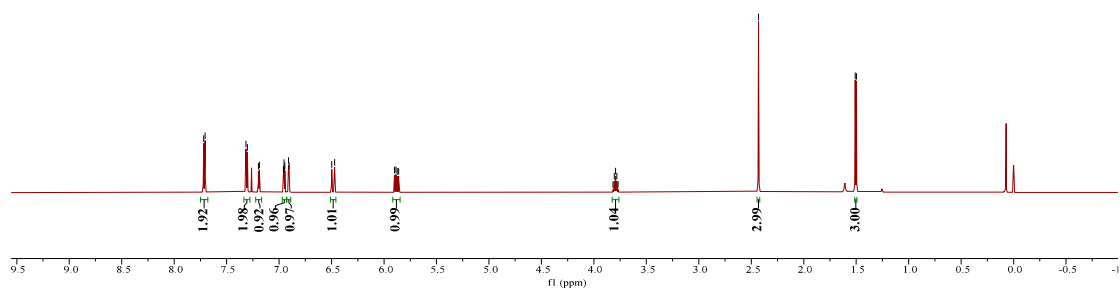
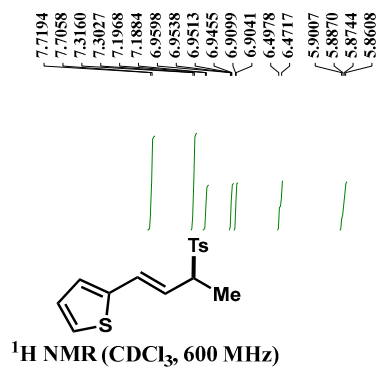


Figure S22. ^1H NMR and ^{13}C NMR spectra of **3ga** in CDCl_3

3ha

¹H NMR



¹³C NMR

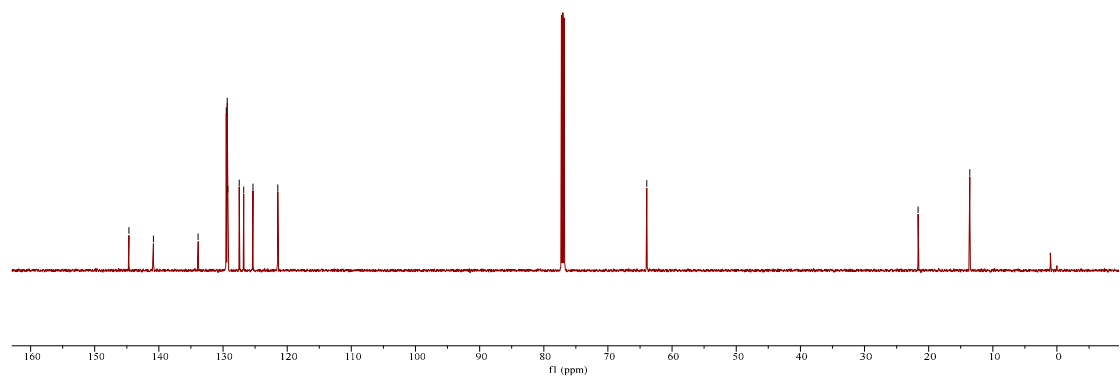
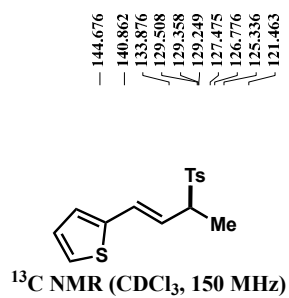
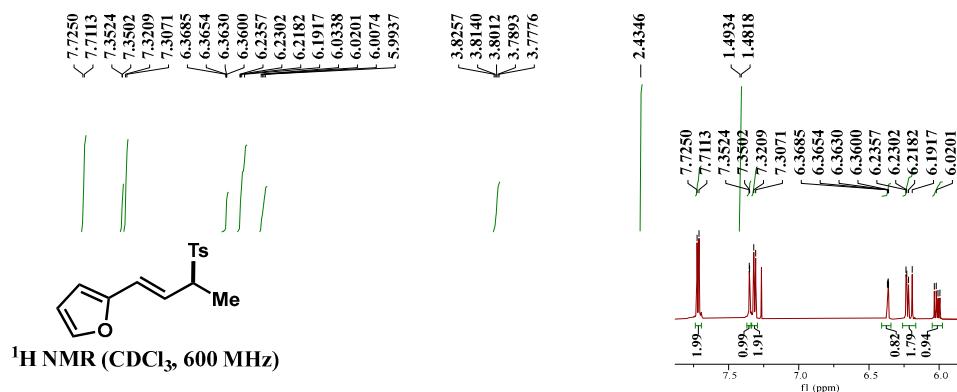


Figure S23. ¹H NMR and ¹³C NMR spectra of **3ha** in CDCl₃

3ia

^1H NMR



^{13}C NMR

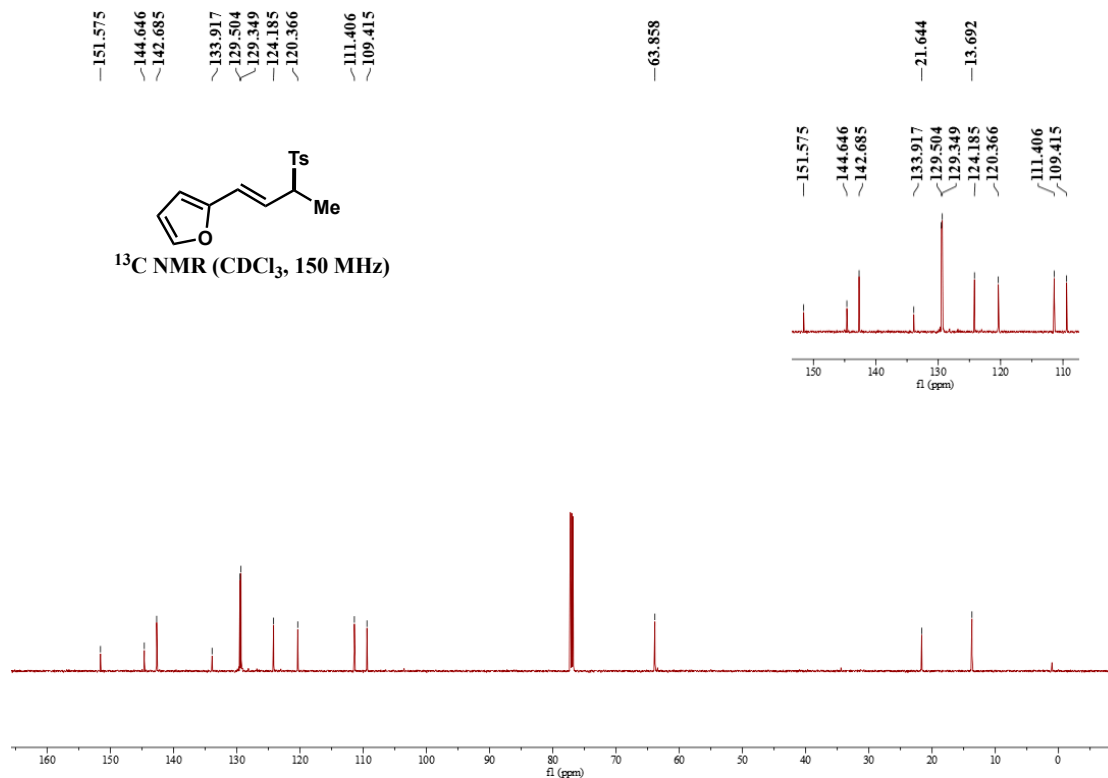
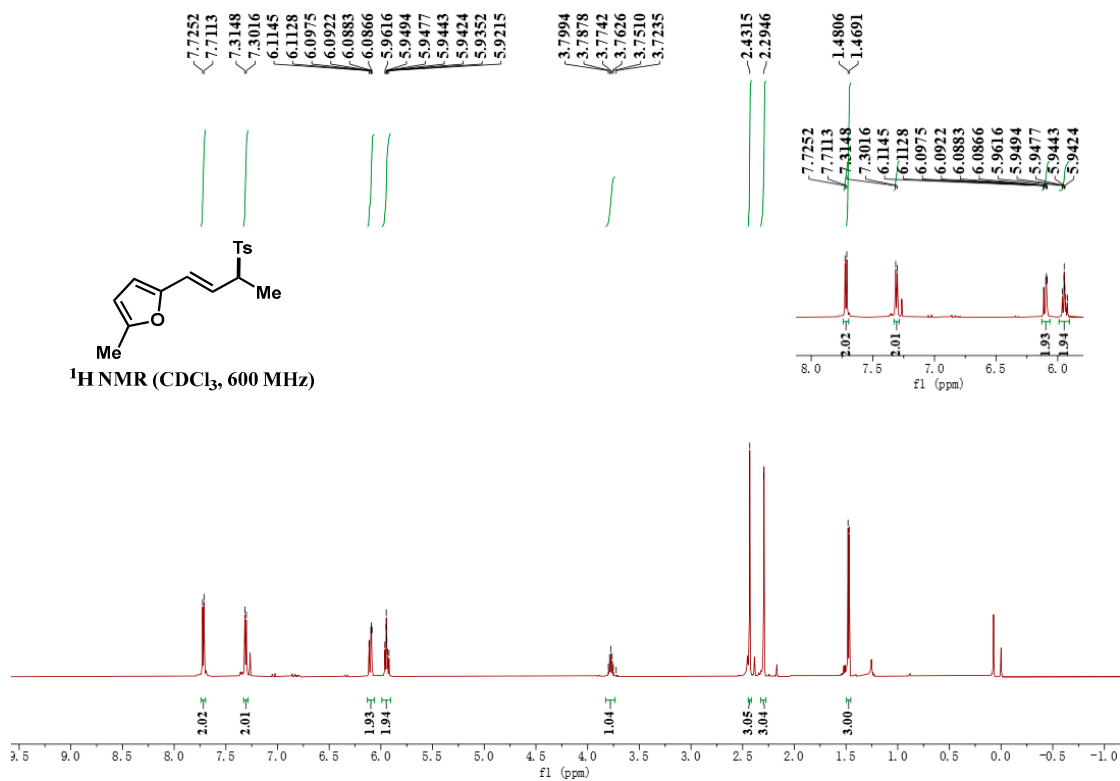


Figure S24. ^1H NMR and ^{13}C NMR spectra of **3ia** in CDCl_3

3ja

^1H NMR



^{13}C NMR

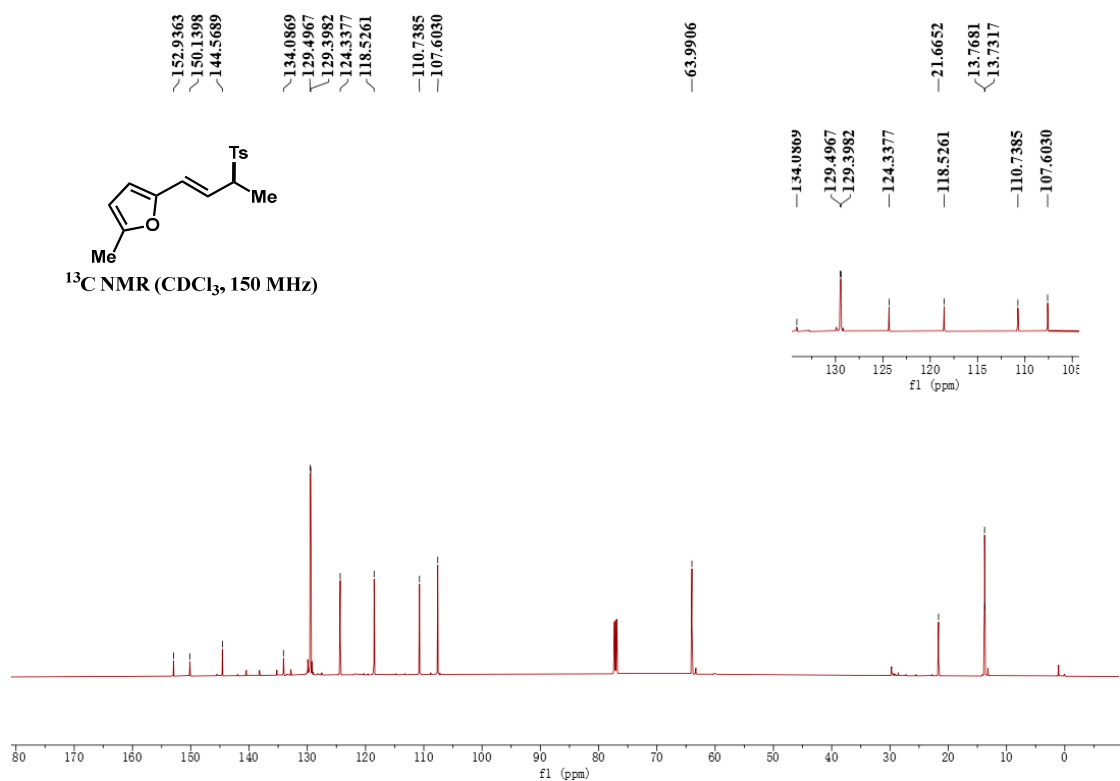


Figure S25. ^1H NMR and ^{13}C NMR spectra of **3ja** in CDCl₃

4a

¹H NMR

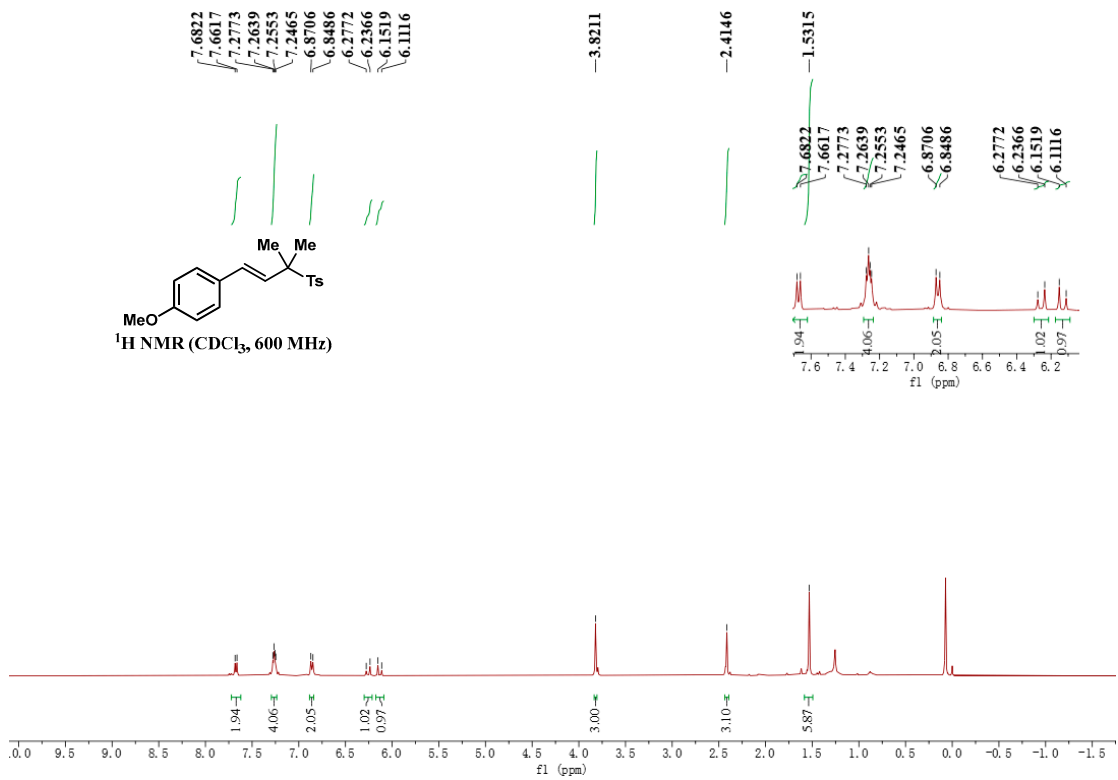
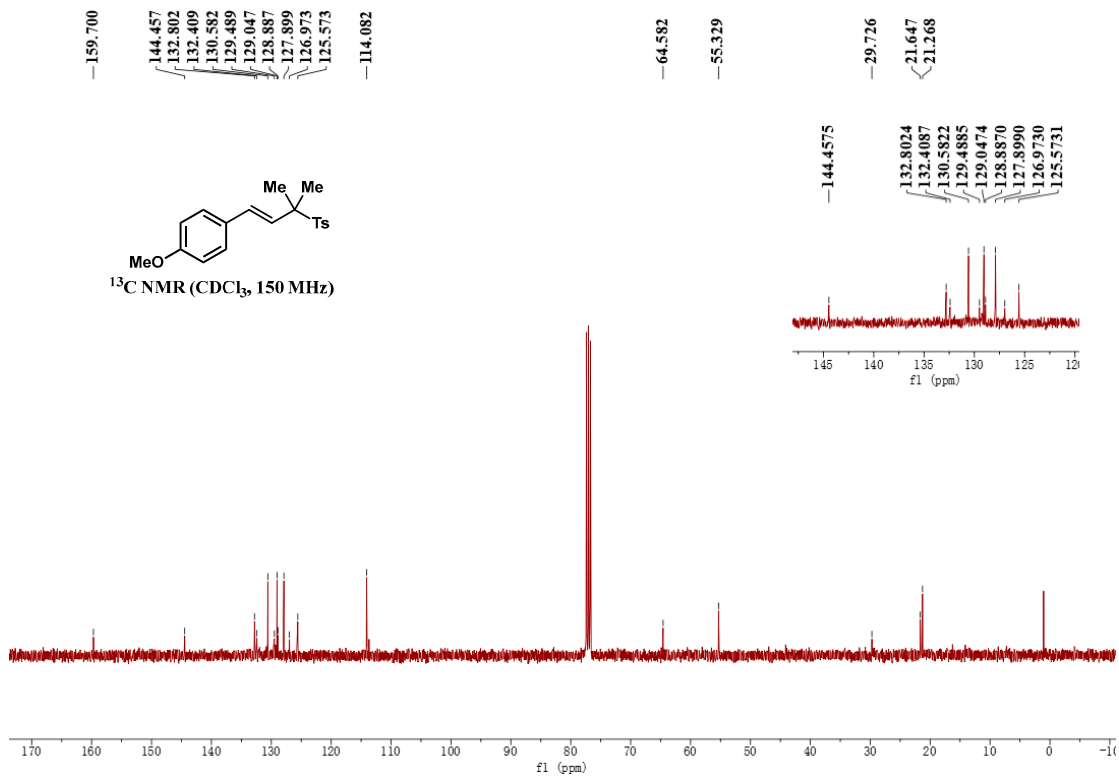
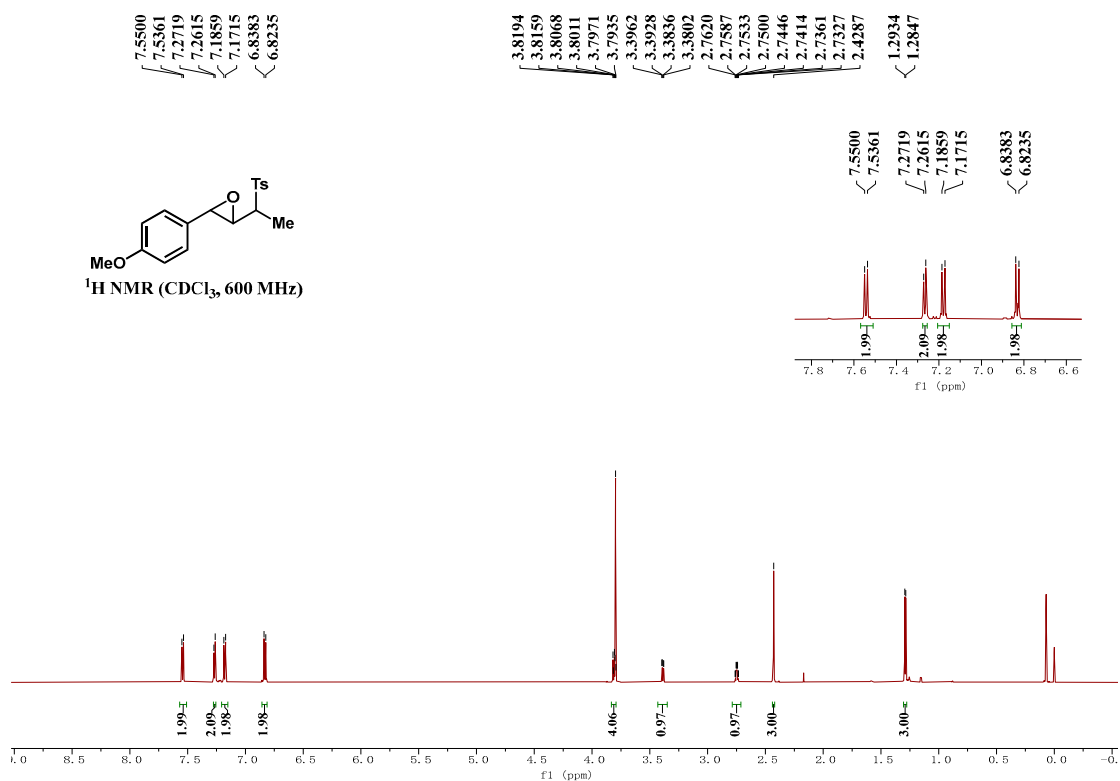
¹³C NMR

Figure S26. ^1H NMR and ^{13}C NMR spectra of **4a** in CDCl_3

4b

¹H NMR



¹³C NMR

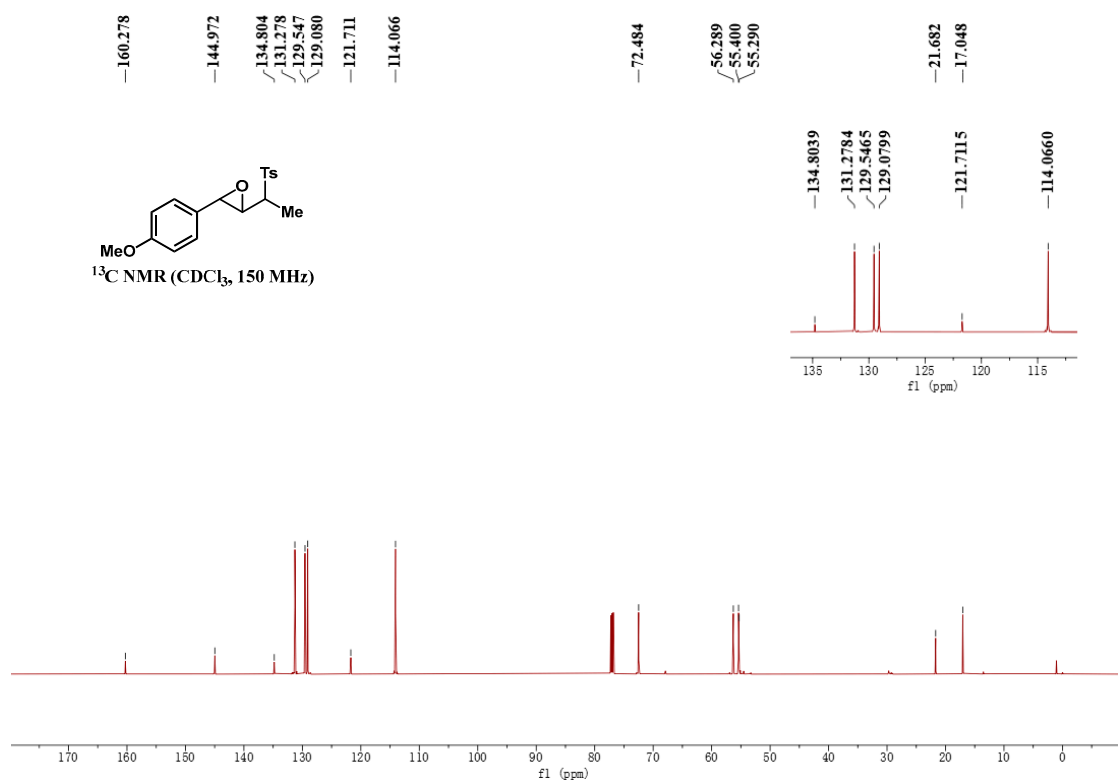


Figure S27. ¹H NMR and ¹³C NMR spectra of **4b** in CDCl₃

5. References

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