Supporting Information

An efficient and environmentally-friendly access to 4,5-unsaturated sulfonamides through a ligand-free copper-BF_3 catalyzed three-component alkene carbo-sulfonamidation

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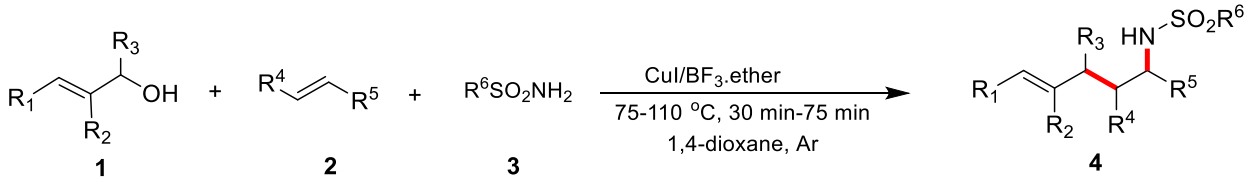
1. General Information

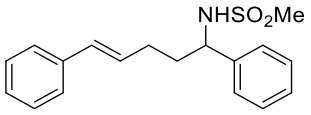
All the reactions were carried out in cleaned, oven dried sealed glass reactors fitted with stoppers. The commercially available chemicals were purchased from local vendors such as sigma-aldrich and TCI, and used directly without further purification. Solvents were used after drying through reported procedure. Broker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) was used for recording ^{1}H and ^{13}C NMR spectra with $CDCl_3$ as a solvent and TMS as an internal standard. The ppm (parts per million, δ) scale was used for reporting chemical shifts. The peak at 77.16 ppm was used as a reference (residual solvent signal of $CDCl_3$) for ^{13}C NMR and the single peak at 0.000 ppm originating from TMS was used as a reference for ^{1}H NMR. The coupling constant (J) was reported in Hertz (Hz); singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of triplet (dt), etc. The chemical shift values are given in (δ) in a descending order. IR spectra were recorded on Nicolet iS 50 FT-IR and the values were reported in cm^{-1} units. Molecular mass of the synthesized products was recorded on a Q-TOF mass spectrometry. The progress of the reaction was monitored by taking TLC (thin layer chromatography) and the position of the spot were seen under light (256 nm). The column chromatography with 80 mesh silica as stationary phase was used for the purification of the products.

2. General Procedure for Synthesis of Product 4



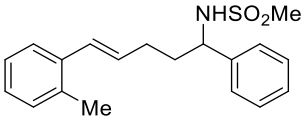
The general procedure for synthesis of product **4** is given here. Cleaned and dried glass reactor was charged with an sulfonamide (**3**, 1.5 equiv.) and BF_3·ether (5 to 20 mol%) After stirring at room temperature for 1 minute, CuI (7 mol%, 2.7 mg) was added and stirred for 2-3 minutes. Afterward, an allyl alcohol (**1,** 0.2 mmol) and alkene (**2**, 1 mmol) were added sucessively. The reaction mixture was allowed to stir for 30 to 75 minutes at 75-110 ^{o}C in an argon environment. The reaction mixture was concentrated on a rotary evaporator to remove the solvent. Then, the crude residue was purified through column chromatography (SiO_2) (petroleum ether/ethylacetate 8:2).

***(E)*-N-(1,5-diphenylpent-4-en-1-yl)methanesulfonamide (4aa)**



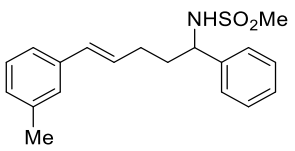
The compound **4aa** was synthesized following the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 75 minutes. The target compound was obtained as a colorless viscous oil (51.1 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.39 (m, 2H), 7.32–7.25 (m, 7H), 7.19 (t, J = 6.9 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 6.16 (dt, J = 15.8, 6.9 Hz, 1H), 5. 37 (d, J = 7.7 Hz, 1H), 5.02 (q, J = 7.5 Hz, 1H), 2.55 (s, 3H), 2.23–2.19 (m, 2H), 2.05-1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 137.5, 131.3, 129.2, 128.8, 128.6, 128.3, 127.2, 126.8, 126.2, 58.0, 42.0, 37.4, 29.6; HRMS (EI): calcd for $C_{18}H_{21}NO_2S$ $[M]^+$: 315.1293, Found 315.1296; IR (neat): 3275, 3056, 2930, 2876, 1600, 1508, 1494, 1449, 1319, 1070, 967, 820, 733 cm^{-1}.

***(E)*-N-(1-phenyl-5-(*o*-tolyl)pent-4-en-1-yl)acetamide (4ba)**



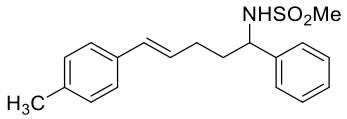
The compound **4ba** was synthesized as per the general procedure using **1b** (29.6 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL) BF_3.ether (0.04 mmol, 4.9 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 60 minutes. The target compound was obtained as colorless a viscous oil (52.7 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.35 (m, 6H), 7.18–7.15 (m, 3H), 6.61 (d, J = 15.9 Hz, 1H), 6.07 (dt, J = 15.9, 6.9 Hz, 1H), 5.29 (d, J= 7.9, 1H), 4.55 (q, J = 7.5 Hz, 1H), 2.58 (s, 3H), 2.35 (s, 3H), 2.35–2.28 (m, 2H), 2.09–1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 136.6, 135.2, 130.3, 130.2, 129.2, 128.2, 127.2, 126.8, 126.6, 126.1, 125.6, 58.0, 41.9, 37.4, 29.9, 19.9; HRMS (EI): $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1454; IR (neat): 3275, 3027, 2927, 2868, 1503, 1493, 1456, 1315, 1150, 1065, 1014, 974, 882, 756, 702 cm^{-1}.

***(E)*-N-(1-phenyl-5-(*m*-tolyl)pent-4-en-1-yl)acetamide (4ca)**



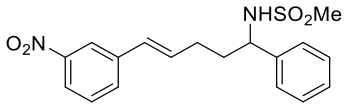
The compound **4ca** was synthesized as per the general procedure using **1c** (29.6 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL) BF_3.ether (0.04 mmol, 4.9 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 60 minutes. The target compound was obtained as a viscous colorless oil (54.0 mg, 82%; *E*/*Z* = 98:2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (m, 5H), 7.13–7.10 (m, 3H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.05 (d, *J* = 7.8 Hz, 1H), 4.49 (q, *J* = 7.5 Hz, 1H), 2.55 (s, 3H), 2.32 (s, 3H), 2.22–2.18 (m, 2H), 2.05–1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 138.2, 137.5, 131.4, 129.2, 128.5, 128.3, 128.0, 126.9, 126.8, 123.3, 58.0, 42.0, 37.4, 29.6, 21.5; HRMS (EI): calcd for $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1452; IR (KBr): 3275, 3027, 2926, 2867, 1602, 1493, 1456, 1314, 1153, 1061, 974, 886, 756, 702 cm^{-1}.

***(E)*-N-(1-phenyl-5-(p-tolyl)pent-4-en-1-yl)acetamide (4da)**



The compound **4da** was synthesized as per the general procedure using **1d** (29.6 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL) BF_3.ether (0.04 mmol, 4.9 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 30 minutes. The target compound was obtained as a viscous pale yellow oil (48.8 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44–7.39 (m, 2H), 7.35(dd, *J* = 10.6, 4.7 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.12 (d, 8.1 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.84 (d, *J* = 7.6 Hz, 1H), 4.52 (q, *J* = 7.4 Hz, 1H), 2.85 (s, 3H), 2.35 (s, 3H), 2.26–2.22 (m, 2H), 2.06–1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 137.0, 134.7, 131.2, 129.3, 129.2, 128.3, 127.7, 126.8, 126.1, 58.1, 42.0, 37.5, 29.6, 21.3; HRMS (EI): calcd for $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.14451; IR (neat): 3276, 3026, 2930, 2865, 1503, 1493, 1456, 1315, 1150, 1065, 1014, 974, 882, 756, 702 cm^{-1}

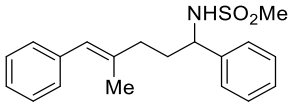
***(E)*-N-(5-(3-nitrophenyl)-1-phenylpent-4-en-1-yl)methanesulfonamide (4ea)**



The compound **4ea** was synthesized as per the general procedure using **1e** (35.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL) BF_3.ether (0.04 mmol, 4.9 µL), $MeSO_2NH_2$ (**3a**, 0.3

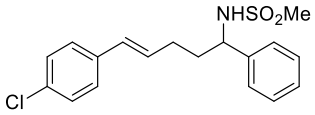
mmol, 28.5 mg). The reaction was carried out at 110 °C for 75 minutes. The target compound was obtained as a viscous pale yellow oil (51.2 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (t, J = 2.2 Hz, 1H), 8.04 (ddd, J = 8.1, 2.2, 0.9 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.47–7.41 (m, 1H), 7.43–7.39 (m, 3H), 7.36–7.31 (m, 2H), 6.43 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 6.8 Hz, 1H), 5.00 (d, J = 7.8 Hz, 1H), 4.50 (q, J = 7.8 Hz, 1H), 2.57 (s, 3H), 2.37–2.22 (m, 2H), 2.11–1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 132.3, 132.1, 129.5, 129.3, 129.1, 128.5, 127.5, 126.7, 126.1, 121.9, 120.7, 58.0, 42.1, 37.1, 29.6; HRMS (FAB): calcd for $C_{18}H_{21}N_2O_4S$ $[M+H]^+$: 361.1222, Found 361.1219; IR (neat): 3278, 3024, 2946, 2868, 1539, 1493, 1355, 1315, 1170, 1067, 1011, 972, 887, 756, 702 cm^{-1}

***(E)*-*N*-(4-methyl-1,5-diphenylpent-4-en-1-yl)methanesulfonamide (4fa)**



The compound **4fa** was synthesized as per the general procedure using **1f** (29.6 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL) BF_3.ether (0.04 mmol, 4.9 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 °C for 75 minutes. The target compound was obtained as viscous pale yellow oil (51.4 mg, 78%; E/Z = 97:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 7.0 Hz, 2H), 7.43–7.36 (m, 5H), 7.24–7.18 (m, 3H), 6.25 (s, 1H), 4.91 (d, J = 7.5 Hz, 1H), 4.49 (q, J = 7.2 Hz, 1H), 2.56 (s, 3H), 2.24–2.20 (m, 2H), 2.15–1.99 (m, 2H), 1.84 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 138.3, 137.3, 129.2, 128.9, 128.3, 128.2, 126.9, 127.3, 126.2, 126.2, 125.8, 125.3, 58.3, 42.1, 37.1, 36.1, 17.9; HRMS (EI): calcd for $C_{19}H_{23}NO$ $[M]^+$: 329.1449, Found 329.1447; IR (neat): 3276, 3026, 2929, 2850, 1590, 1493, 1455, 1316, 1150, 1071, 1030, 972, 918, 753, 701 cm^{-1}

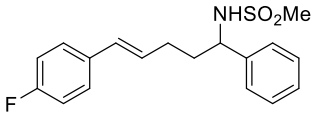
***(E)*-N-(5-(4-chlorophenyl)-1-phenylpent-4-en-1-yl)methanesulfonamide (4ga)**



The compound **4ga** was synthesized as per the general procedure using **1g** (33.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL) BF_3.ether (0.04 mmol, 4.9 µL), and $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 °C for 75 minutes. The target compound was obtained as a viscous colorless oil (59.5 mg, 85%). ^{1}H NMR (400 MHz,

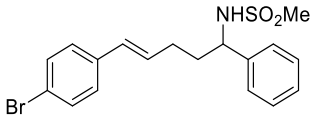
$CDCl_3$): δ 7.38 (dd, J = 7.5, 3.6 Hz, 2H), 6.33–7.30 (m, 3H), 7.27-7.23 (m, 4 H), 6.32 (d, J = 15.8 Hz, 1H), 6.13 (dt, J = 15.8, 6.4 Hz, 1H), 4.93 (d, J = 7.1 Hz, 1H), 4.49 (q, J = 7.5 Hz, 1 H), 2.55 (s, 3H), 2.26–2.19 (m, 2H), 2.01–1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 136.0, 132.8, 130.2, 129.25, 128.8, 128.4, 127.4, 126.8, 58.0, 42.0, 37.3, 29.6; HRMS (EI): calcd for $C_{18}H_{20}ClNO_2S$ $[M]^+$: 349.0903, Found 349.0900; IR (neat): 3275, 3027, 2919, 2881, 1586, 1494, 1477, 1455, 1324, 1265, 1159, 1086, 1014, 965, 826, 734 cm^{-1}.

***(E)*-N-(5-(4-fluorophenyl)-1-phenylpent-4-en-1-yl)methanesulfonamide (4ha)**



The compound **4ha** was synthesized as per the general procedure using **1h** (30.4 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), BF_3.ether (0.04 mmol, 4.9 µL), and $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 75 minutes. The target compound was obtained as a viscous colorless oil (58.0 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.36 (m, 2H), 7.35–7.29 (m, 3H), 7.29–7.24 (m, 2H), 7.00–6.94 (m, 2H), 6.33 (d, J = 15.9 Hz, 1H), 6.07 (dt, J = 15.9, 6.8 Hz, 1H), 5.01 (d, J = 7.7 Hz, 1H), 4.49 (q, J = 7.7 Hz, 1H), 2.55 (s, 3H), 2.28–2.15 (m, 2H), 2.07–1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 130.2, 129.2, 128.5 (d, $^3J_{C-F}$ = 9.5 Hz), 128.3, 127.6, 127.5, 127.3, 126.8, 115.3 (d, $^2J_{C-F}$ = 21.5 Hz), 58.0, 42.0, 37.4, 29.9; HRMS (EI): calcd for $C_{18}H_{20}FNO_2S$ $[M]^+$: 333.1199, Found 333.1197; IR (neat): 3272, 3026, 2915, 2859, 1566, 1492, 1476, 1459, 1320, 1264, 1159, 1082, 1012, 966, 824, 731 cm^{-1}

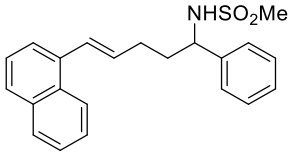
***(E)*-N-(5-(4-bromophenyl)-1-phenylpent-4-en-1-yl)methanesulfonamide (4ia)**



The compound **4ia** was synthesized as per the general procedure using **1i** (42.6 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), BF_3.ether (0.04 mmol, 4.9 µL), and $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 75 minutes. The target compound was obtained as a viscous light brown oil (65.5 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.95, 6.3 Hz, 4H), 7.36–7.27 (m, 3H), 7.19–7.14 (m, 2H), 6.31 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.8, 6.8 Hz, 1H), 4.95 (d, J = 7.7 Hz, 1H),

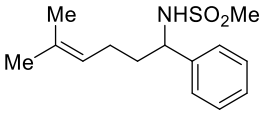
4.49 (q, *J* = 7.5 Hz, 1H), 2.55 (s, 3H), 2.29–2.18 (m, 2H), 2.07–1.90 (m,2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 136.5, 131.7, 130.2, 129.7, 129.3, 128.4, 127.7, 58.0, 42.0, 37.3, 29.6; HRMS (EI): calcd for $C_{18}H_{20}BrNO_2S$ $[M]^+$: 393.0398, and 395.0378 Found 393.0396 and 395.0406; IR (neat): 3270, 3027, 2918, 2856, 1586, 1498, 1467, 1450, 1325, 1268, 1145, 1060, 1015, 966, 826, 732 cm^{-1}

***(E)*-N-(5-(naphthalen-1-yl)-1-phenylpent-4-en-1-yl) methanesulfonamide (4ja)**



The compound **4ja** was synthesized as per the general procedure using **1j** (36.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), BF_3.ether (0.04 mmol, 4.9 µL), and $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 40 minutes. The target compound was obtained as a viscous light brown oil (57.7 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.86 (dd, *J* = 7.0, 2.48 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.56–7.42 (m, 6H), 7.38–7.33 (m, 3H), 7.15 (d, *J* = 15.6 Hz, 1H), 6.21 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.16 (d, *J* = 7.3 Hz, 1H), 4.59 (q, J = 7.5 Hz, 1H), 2.60 (s, 3H), 2.41–2.38 (m, 2H), 2.15–2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 135.3, 133.7, 132.1, 129.3, 128.6, 128.4, 127.7, 126.8, 126.6,126.1, 125.8,125.8, 124.0, 123.8, 123.5, 58.1, 42.1, 37.5, 30.1; HRMS (EI): calcd for $C_{22}H_{23}NO_2S$ $[M]^+$: 365.1449, Found 365.1452; IR (neat): 3276, 3026, 2929, 2854, 1600, 1493, 1456, 1315, 1150, 1070, 1028, 980, 918, 752, 700 cm^{-1}.

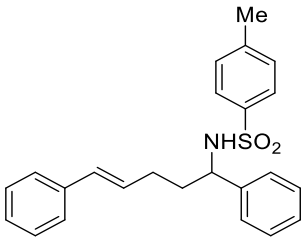
***(E)*-N-(1-phenyloct-4-en-1-yl)acetamide (4ka)**



The compound **4ka** was synthesized as per the general procedure using **1k** (20.0 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), and BF_3.ether (0.04 mmol, 4.9 µL), and $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg). The reaction was carried out at 110 ^oC for 75 minutes. The target compound was obtained as a viscous pale yellow oil (33.7 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.36 (m, 2H), 7.32–7.26 (m, 3H), 5.08 (t, *J* = 7.6 Hz, 1H), 4.79 (d, *J* = 7.2 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 1H), 2.52 (s, 3H), 2.04–1.98 (m, 2H), 1.88–1.77 (m, 2H), 1.68 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5,

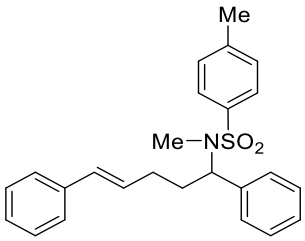
133.2, 129.1, 128.1, 126.9, 122.9, 58.2, 42.0, 37.8, 25.8, 24.8, 22.6, 17.9; HRMS (EI): calcd for $C_{14}H_{21}NO_2S$ $[M]^+$: 267.1293, found 267.1294; IR (KBr): 3276, 3026, 2918, 2865, 1586, 1494, 1476, 1455, 1324, 1265, 1159, 1086, 1068, 1014, 964, 826, 751, 734, 699 cm^{-1}

***(E)*-N-(1,5-diphenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (4la)**



The compound **4la** was synthesized as per the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), $TsNH_2$ (**3b**, 0.3 mmol, 51.4 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 30 minutes. The target compound was obtained as a viscous colorless oil (60.3 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.9 Hz, 2H), 7.29–7.26 (m, 4H), 7.21–7.16 (m, 4H), 7.21–7.18 (m, 1H), 7.09 (d, J = 7.9 Hz, 1H), 7.03–7.00 (m, 2H), 6.28 (d, J = 15.8 Hz, 1H), 6.07 (dt, J = 15.8, 6.8 Hz, 1H), 4.90 (d, J = 7.3 Hz, 1H), 4.31 (q, J = 7.3 Hz, 1H), 2.34 (s, 3H), 2.13–2.10 (m, 2H), 2.01–1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 140.8, 137.7, 137.6, 131.0, 130.7, 129.4, 129.1, 128.6, 127.5, 127.2, 127.1, 126.7, 126.1, 57.9, 37.2, 29.3, 21.5; HRMS (EI): calcd for $C_{24}H_{25}NO_2S$ $[M]^+$:391.1606, found 391.1609; IR (neat): 3275, 3060, 3027, 2929, 2856, 1601, 1494, 1455, 1401, 1317, 1264, 1156, 1055, 970, 889, 873, 733, 700 cm^{-1}

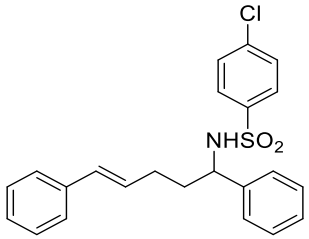
***(E)*-N-(1,5-diphenylpent-4-en-1-yl)-N,4-dimethylbenzenesulfonamide (4ma)**



The compound **4ma** was synthesized as per the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), TsNHMe (**3c**, 0.3 mmol, 55.6 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 30 minutes. The target compound was obtained as a viscous colorless oil (61.6 mg, 76%; E/Z = 97:3). ^1H NMR

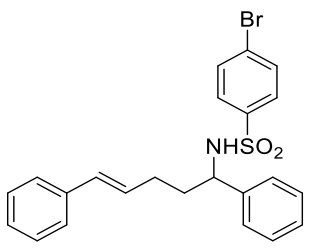
(400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.37–7.32 (m, 4H), 7.31–7.28 (m, 4H), 7.27–7.23 (m, 4H), 6.35 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 6.6 Hz, 1H), 5.17 (t, J = 7.5 Hz, 1H), 2.67 (s, 3H), 2.42 (s, 3H), 2.23–2.21 (m, 2H), 2.21–2.20 (m, 1H), 1.90–1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 138.2, 137.6, 137.4, 130.9, 129.8, 129.6, 129.3, 128.6, 128.5, 128.2, 127.9, 127.3, 127.3, 127.2, 126.1, 125.9, 59.6, 30.4, 30.0, 28.9, 21.6; HRMS (FAB+): calcd for $C_{25}H_{28}NO_2S$ $[M+H]^+$:406.1841, found 406.1839; IR (neat): 3277, 3061, 3021, 2912, 2832, 1603, 1491, 1456, 1401, 1315, 1261, 1157, 1042, 963, 885, 861, 731, 698 cm^{-1}

***(E)*-4-chloro-N-(1,5-diphenylpent-4-en-1-yl)benzenesulfonamide (4na)**



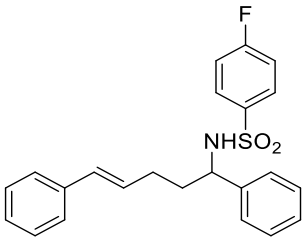
The compound **4na** was synthesized as per the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), *p*-chlorophenylsulfonamide (**3d**, 0.3 mmol, 57.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ºC for 30 minutes. The target compound was obtained as a viscous pale yellow oil (63.4 mg, 77%; E/Z = 96:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.8 Hz, 2H), 7.30–7.16 (m, 10H), 7.00–6.98 (m, 2H), 6.30 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.8 Hz, 1H), 5.13 (d, J = 7.6 Hz, 1H), 4.36 (q, J = 7.4 Hz, 1H), 2.16–2.13 (m, 2H), 1.91–1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 139.2, 138.8, 137.5, 133.9, 131.3, 129.0, 128.8, 128.7, 128.6, 127.9, 127.3, 126.7, 126.1, 58.1, 37.2, 29.4; HRMS (EI): calcd for $C_{23}H_{22}ClNO_2S$ $[M]^+$:411.1060, found 411.1058; IR (neat): 3275, 3060, 3027, 2929, 2855, 1601, 1494, 1455, 1401, 1317, 1265, 1150, 1065, 970, 889,873, 733, 700 cm^{-1}.

***(E)*-4-bromo-N-(1,5-diphenylpent-4-en-1-yl)benzenesulfonamide (4oa)**



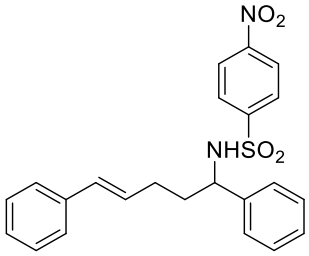
The compound **4oa** was synthesized as per the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene (**2a**, 1 mmol, 100 µL), *p*-bromophenylsulfonamide (**3e**, 0.3 mmol, 70.8 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 °C for 30 minutes. The target compound was obtained as a viscous pale yellow oil (68.5 mg, 75%; *E*/*Z* = 96:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.39–7.36 (m, 2H), 7.30–7.26 (m, 4H), 7.23–7.16 (m, 4H), 7.00–6.96 (m, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.03 (d, *J* = 7.5 Hz, 1H), 4.36 (q, *J* = 7.5 Hz, 1H), 2.16–2.11 (m, 2H), 2.01–1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 139.8, 137.5, 132.0, 131.3, 128.8, 128.7, 128.3, 127.9, 127.3, 126.7, 126.2, 58.2, 37.2, 29.4; HRMS (EI): calcd for $C_{23}H_{22}BrNO_2S$ $[M]^+$: 455.0555 and 457.0536 found 455.0552 and 457.0514; IR (neat): 3275, 3070, 3027, 2928, 2857, 1601, 1494, 1425, 1410, 1317, 1265, 1151, 1065, 970, 889,873, 733, 700 cm^{-1}.

***(E)*-N-(1,5-diphenylpent-4-en-1-yl)-4-fluorobenzenesulfonamide (4pa)**



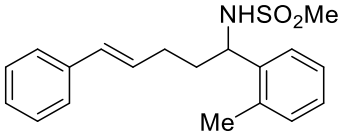
The compound **4pa** was synthesized as per the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene **2a** (1 mmol, 100 µL), *p*-flourophenylsulfonamide (**3f**, 0.3 mmol, 52.6 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 °C for 30 minutes. The target compound was obtained as a viscous pale yellow oil (62.5 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (ddd, *J* = 8.4, 5.1,1.9 Hz, 2H), 7.35–7.28 (m, 6H), 7.20–7.18 (m, 2H), 7.02–7.00 (m, 2H), 6.95 (ddd, *J* = 8.4, 5.1, 1.9 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.00 (d, *J* = 7.5 Hz, 1H), 4.39 (q, *J* = 7.5 Hz, 1H), 2.19–2.14 (m, 2H), 2.07–1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, $^1J_{C\text{-}F}$ = 235.5 Hz), 140.3, 137.5, 131.3, 129.6 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 128.9, 128.8, 128.8, 128.7, 127.9, 127.3, 127.2, 126.7, 126.1, 115.9 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 58.1, 37.2, 29.4. HRMS (EI): calcd for $C_{23}H_{22}FNO_2S$ $[M]^+$: 395.1355, found 395.1357. IR (neat): 3274, 3060, 3027, 2929, 2857, 1601, 1494, 1454, 1410, 1317, 1264, 1202, 1150, 1065, 970, 873, 733, 700 cm^{-1}.

***(E)*-N-(1,5-diphenylpent-4-en-1-yl)-4-nitrobenzenesulfonamide (4qa)**



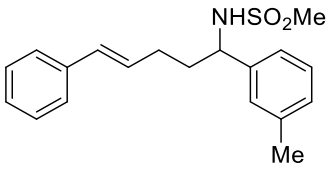
The compound **4qa** was synthesized as per the general procedure using **1a** (26.8 mg, 0.2 mmol), styrene **2a** (1 mmol, 100 µL), *p*-nitrophenylsulfonamide (**3g**, 0.3 mmol, 60.6 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 30 minutes. The target compound was obtained as a viscous pale yellow oil (60.0 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.9 Hz, 2H), 7.34–7.26 (m, 4H), 7.24–7.18 (m, 2H), 7.14–7.09 (m, 3H), 6.96 (dd, J = 7.7, 1.7 Hz, 1H), 6.32 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.8 Hz, 1H), 5.31 (d, J = 7.6 Hz, 1H), 4.44 (q, J = 7.4 Hz, 1H), 2.22–2.13 (m, 2H), 2.05–1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 146.5, 139.8, 137.4, 131.5, 128.8, 128.7, 128.3, 128.1, 127.4, 126.7, 126.1, 123.9, 58.4, 37.1, 29.4. HRMS (FAB+): calcd for $C_{23}H_{23}N_2O_4S$ $[M+H]^+$: 423.1379, found 423.1382. IR (neat): 3271, 3062, 3029, 2927, 1609, 1494, 1509, 1370, 1352, 1260, 1183, 991, 873, 731, 706 cm^{-1}.

***(E)*-N-(5-phenyl-1-(*o*-tolyl)pent-4-en-1-yl)methanesulfonamide (4ab)**



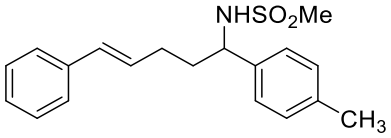
The compound **4ab** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2b,** 1 mmol, 130 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 75 minutes.The target compound was obtained as a viscous light brown oil (48.1 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 6H), 7.20–7.18 (m, 3H), 6.40 (d, J = 15.8 Hz, 1H), 6.17 (dt, J = 15.8, 6.7 Hz, 1H), 4.89 (d, J = 7.3 Hz, 1H), 4.83 (q, J = 7.3 Hz, 1H), 2.53 (s, 3H), 2.40 (s, 3H), 2.32–2.21 (m, 2H), 1.99–1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 139.6, 137.5, 135.5, 131.3, 131.1, 128.9, 128.7, 127.9, 127.0, 126.2, 125.6, 53.6, 42.0, 37.2, 29.6, 19.5. $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1449. IR (neat): 3274, 3065, 3033, 2927, 1591, 1504, 1488, 1432, 1403, 1343, 1248, 1150, 1131, 1066, 1024, 970, 889, 732, 700 cm^{-1}.

***(E)*-N-(5-phenyl-1-(*m*-tolyl)pent-4-en-1-yl)methanesulfonamide (4ac)**



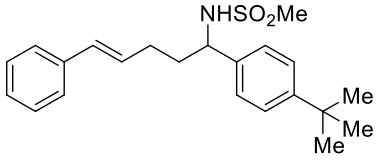
The compound **4ac** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2c,** 1 mmol, 131 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 50 minutes. The target compound was obtained as a viscous colourless oil (52.1 mg, 79%; *E*/*Z* = 98:2).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 6H), 7.13–7.11 (m, 3H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.93 (d, *J* = 7.8 Hz, 1H), 4.45 (q, *J* = 7.5 Hz, 1H), 2.57 (s, 3H), 2.36 (s, 3H), 2.25–2.19 (m, 2H), 2.03–1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 141.3, 138.9, 137.6, 131.2, 129.1, 129.0, 128.9, 128.6, 127.5, 127.2, 126.2, 123.7, 58.1, 42.0, 37.4, 29.7, 21.6. $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1453. IR (neat): 3275, 3066, 3028, 2929, 2856, 1589, 1502, 1472, 1430, 1412, 1316, 1250, 1151, 1123, 1055, 970, 889, 732, 700 cm^{-1}.

***(E)*-N-(5-phenyl-1-(*p*-tolyl)pent-4-en-1-yl)methanesulfonamide (4ad)**



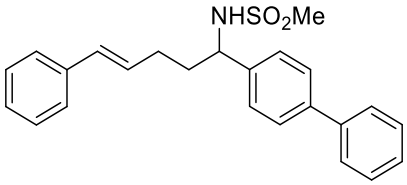
The compound **4ad** was synthesized as per general the procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2d,** 1 mmol, 132 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 30 minutes. The target compound was obtained as a viscous colorless oil (50.7 mg, 77%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 4H), 7.21–7.15 (m, 5H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.92 (d, *J* = 7.7 Hz, 1H), 4.45 (q, *J* = 7.5 Hz, 1H), 2.55 (s, 3H), 2.35 (s, 3H), 2.22–2.18 (m, 2H), 2.06–1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 138.2, `138.0, 137.5, 131.2, 129.9, 128.9, 128.6, 127.2, 126.5, 126.1, 57.8, 42.0, 37.4, 29.7, 21.2. HRMS (EI): calcd for $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1447. IR (neat): 3274, 3067, 3027, 2929, 2857, 1601, 1494, 1474, 1424, 1410, 1317, 1251, 1151, 1120, 1065, 1028, 970, 889, 732, 700 cm^{-1}.

***(E)*-N-(1-(4-(*tert*-butyl)phenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4ae)**



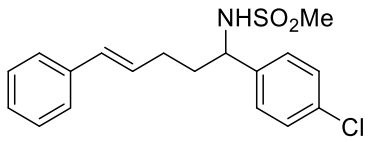
The compound **4ae** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2e,** 1 mmol, 181 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ºC for 30 minutes. The target compound was obtained as a viscous colorless oil (57.9 mg, 78%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.40 (m, 2H), 7.30–7.22 (m, 7H), 6.37 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 6.8 Hz, 1H), 4.99 (d, J = 7.8 Hz, 1H), 4.47 (q, J = 7.5 Hz, 1H), 2.57 (s, 3H), 2.28–2.18 (m, 2H), 2.05–1.91 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 138.1, 137.6, 131.1, 129.0, 128.6, 127.2, 126.5, 126.1, 126.0, 57.4, 42.0, 337.4, 34.7, 31.4, 29.7. HRMS (EI): calcd for $C_{22}H_{29}NO_2S$ $[M]^+$: 371.1919, Found 371.1920. IR (neat): 3275, 3059, 3027, 2929, 2855, 1601, 1494, 1455, 1425, 1410, 1317, 1264, 1150, 1121, 1065, 1028, 970, 914, 889, 732, 700 cm^{-1}.

***(E)*-N-(1-(4-(chloromethyl)phenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4af)**



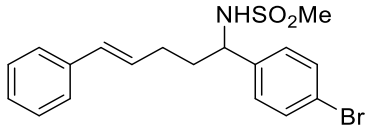
The compound **4af** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2f,** 1 mmol, 180 mg), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 95 ºC for 30 minutes with molecular sieves. The target compound was obtained as a viscous colorless oil (57.9 mg, 74%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.57 (m, 4H), 7.46–7.42 (m, 2H), 7.38 (d, J =7.8 Hz, 2H), 7.32–7.28 (m, 5H), 7.21–7.17 (m, 1H), 6.39 (d, J = 15.9 Hz, 1H), 6.18 (dt, J = 15.9, 6.9 Hz, 1H), 5.12 (d, J = 7.7 Hz, 1H), 4.55 (q, J = 7.5 Hz, 1H), 2.62 (s, 3H), 2.29–2.25 (m, 2H), 2.09–1.95 (m 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 141.1, 140.4, 140.3, 137.5, 131.3, 129.0, 128.8, 128.7, 127.8, 127.7, 127.3, 127.1, 126.2, 57.8, 42.1, 37.4, 29.7. HRMS (EI): calcd for $C_{24}H_{25}NO_2S$ $[M]^+$: 391.1606, Found 391.1605. IR (neat): 3275, 30260, 2929, 2870, 1601, 1494, 1454, 1317, 1265, 1151, 1065, 970, 827, 873, 732, 700 cm^{-1}.

***(E)*-N-(1-(4-chlorophenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4ag)**



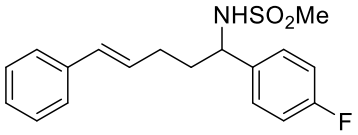
The compound **4ag** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2g,** 1 mmol, 132 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 °C for 50 minutes at 110 °C. The target compound was obtained as a viscous colorless oil (58.0 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.31–7.25 (m, 6H), 7.23–7.20 (m, 1H), 6.37 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.8, 6.9 Hz, 1H), 4.90 (d, J = 7.2 Hz, 1H), 4.50 (q, J = 7.3 Hz, 1H), 2.61 (s, 3H), 2.24–2.18 (m, 2H), 2.03–1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 139.9, 137.4, 134.0, 131.5, 129.4, 128.7, 128.5, 128.2, 127.3, 126.2, 57.3, 42.2, 37.3, 29.5. HRMS (EI): calcd for $C_{18}H_{20}ClNO_2S$ $[M]^+$: 349.0903, Found 349.0903. IR (neat): 3275, 3060, 3027, 2929 1601, 1494, 1454, 1401, 1317, 1265, 1151, 1121, 1065, 970, 889, 732, 700 cm^{-1}.

***(E)*-N-(1-(4-bromophenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4ah)**



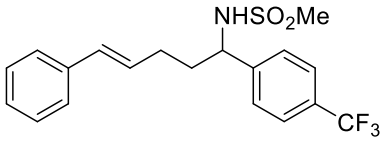
The compound **4ah** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2h,** 1 mmol, 131 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 °C for 50 minutes The target compound was obtained as a viscous colorless oil (63.9 mg, 81%; *E*/*Z* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 4H), 7.34–7.29 (m, 3H), 7.51 (dt, J = 8.4, 4.0 Hz, 2H), 6.31 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.8, 6.9 Hz, 1H), 4.95 (d, J = 7.4 Hz, 1H), 4.49 (q, J = 7.4 Hz, 1H), 2.55 (s, 3H), 2.29–2.19 (m, 2H), 2.05–1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 137.3, 132.2, 131.4, 130.7, 128.6, 128.5, 128.3, 127.2, 126.1, 122.0, 57.3, 42.1, 37.1, 29.4. HRMS (EI): calcd for $C_{18}H_{20}BrNO_2S$ $[M]^+$: 393.0398 and 395.0378, Found 393.402 and 395.0435. IR (neat): 3275, 3060, 3026, 2928, 1603, 1496, 1458, 1401, 1311, 1265, 1151, 1124, 1071, 981, 889, 738, 697 cm^{-1}.

***(E)*-N-(1-(4-fluorophenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4ai)**



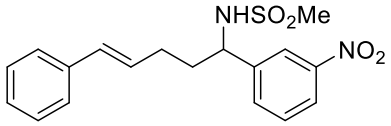
The compound **4ai** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2i,** 1 mmol, 116 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ºC for 50 minutes. The target compound was obtained as a viscous pale yellow oil (56.7 mg, 85%; *E*/*Z* = 94:6).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 6H), 7.21–7.18 (m, 1H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H), 4.50 (q, *J* = 7.4 Hz, 1H), 2.58 (s, 3H), 2.27–2.14 (m, 2H), 2.06–1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.5 (d, $^1J_{C–F}$ = 247.0 Hz), 137.4, 137.2 (d, $^4J_{C–F}$ = 3.3 Hz), 131.5, 128.6 (d, $^3J_{C–F}$ = 9.9 Hz), 128.5, 128.5, 127.3, 126.2, 116.2 (d, $^2J_{C–F}$ = 21.5 Hz), 57.3, 42.1, 37.4, 29.6. HRMS (EI): calcd for $C_{18}H_{20}FNO_2S$ $[M]^+$: 333.1199, Found 333.1201. IR (neat): 3274, 3060, 3026, 2925, 1609, 1491, 1462, 1403, 1318, 1303, 1256, 1204, 1145, 1107, 1020, 957, 738, 709 cm^{-1}.

***(E)*-N-(5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl)methanesulfonamide (4aj)**



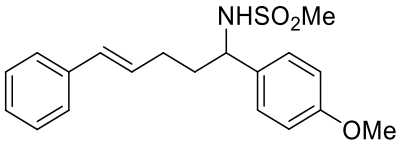
The compound **4aj** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2j,** 1 mmol, 148 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ºC for 50 minutes. The target compound was obtained as a viscous pale yellow oil (55.9 mg, 73%; *E/Z* = 94:6).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.38–7.29 (m, 4H), 7.26–7.21 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.23 (d, *J* = 7.5 Hz, 1H), 4.62 (q, *J* = 7.4 Hz, 1H), 2.66 (s, 3H), 2.31–2.24 (m, 2H), 2.09–1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.6, 137.3, 135.6, 131.7, 129.7, 128.7, 128.3, 127.4, 127.2, 126.2, 57.5, 42.2, 29.5, 29.6. HRMS (FAB+): calcd for $C_{19}H_{21}F_3NO_2S$ $[M+H]^+$: 384.1245, Found 384.1243. IR (neat): 3271, 3056, 3029, 2921, 1526, 1681, 1432, 1418, 1362, 1321, 1287, 1245, 1165, 1103, 981, 739, 711 cm^{-1}.

***(E)*-N-(1-(3-nitrophenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4ak)**



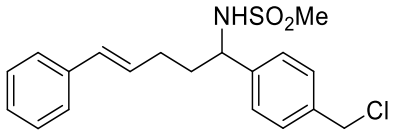
The compound **4ak** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2k,** 1 mmol, 128 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 °C for 50 minutes. The target compound was obtained as a viscous pale yellow oil (48.3 mg, 67%; E/Z = 95:5).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (t, J = 2.1 Hz, 2H), 8.19 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.38–7.31 (m, 2H), 7.26–7.21 (m, 2H), 6.40 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.8, 6.7 Hz, 1H), 5.01 (d, J = 7.2 Hz, 1H), 4.67 (q, J = 7.3 Hz, 1H), 2.72 (s, 3H), 2.31–2.23 (m, 2H), 2.08–1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.0, 137.2, 133.1, 132.0, 130.2, 127.9, 127.5, 126.2, 123.2, 121.6, 57.2, 42.3, 37.4, 29.5. HRMS (FAB+): calcd for $C_{18}H_{21}N_2O_4S$ $[M+H]^+$: 361.1222, Found 361.1224. IR (neat): 3273, 3051, 30261, 2929, 1584, 1502, 1453, 1388, 1331, 1250, 1201, 1141, 1123, 981, 738, 705 cm^{-1}.

***(E)-N*-(1-(4-(chloromethyl)phenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4al)**



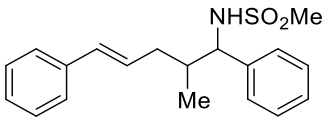
The compound **4al** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2l,** 1 mmol, 133 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.02 mmol, 2.4 µL). The reaction was carried out at 75 °C for 30 minutes with molecular sieves. The target compound was obtained as a viscous light brown oil (39.4 mg, 57%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.21 (m, 7H), 6.91 (d, J = 8.3 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 6.8 Hz, 1H), 4.73 (d, J = 7.4 Hz, 1H), 4.45 (q, J = 7.4 Hz, 1H), 3.81 (s, 3H), 2.55 (s, 3H), 2.16–2.06 (m, 2H), 2.94–1.81 (m 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.5, 137.5, 133.1, 131.3, 128.9, 128.7, 128.1, 127.3, 126.2, 114.5, 57.6, 55.4, 42.1, 37.3, 29.7. HRMS (EI): calcd for $C_{19}H_{23}NO_3S$ $[M]^+$: 345.1399, Found 345.1401. IR (neat): 3262, 3026, 3056, 2924, 2851, 1957, 1645, 1547, 1374, 1267, 1099, 966, 827, 743, 692 cm^{-1}

***(E)*-N-(1-(4-(chloromethyl)phenyl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4am)**



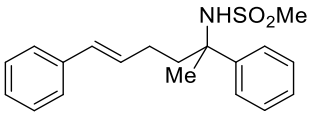
The compound **4am** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2m,** 1 mmol, 141 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ºC for 40 minutes. The target compound was obtained as a viscous brownish oil (52.2 mg, 72%; *E/Z* = 96:4).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.34–7.27 (m, 6H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.9, 6.9 Hz, 1H), 4.73 (d, *J* = 7.3 Hz, 1H), 4.59 (s, 2H), 4.53 (dd, *J* = 7.6 Hz, 7.2 1H), 2.60 (s, 3H), 2.27–2.14 (m, 2H), 2.06–1.91 (m 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 137.4, 131.4, 129.4, 128.6, 128.5, 127.3, 127.2, 127.2, 126.2, 57.7, 45.8, 42.1, 37.4, 29.6. HRMS (EI): calcd for $C_{19}H_{22}ClNO_2S$ $[M]^+$: 363.1060, Found 363.1060. IR (neat): 3262, 3026, 3056, 2924, 2851, 1957, 1645, 1547, 1374, 1267, 1099, 966, 827, 743, 692 cm^{-1}

***(E)*-N-(2-methyl-1,5-diphenylpent-4-en-1-yl)methanesulfonamide (4an)**



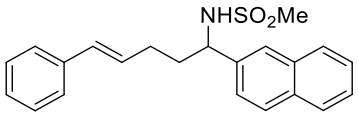
The compound **4an** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2n,** 1 mmol, 130 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ºC for 50 minutes.. The target compound was obtained as a viscous pale yellow oil (53.4 mg, 81%, dr 1:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) (Major isomer): δ 7.44–7.40 (m, 2 H), 7.37–7.33 (m, 7H), 7.25–7.21 (m, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.19 (dt, *J* = 15.7, 7.6 Hz, 1H), 5. 42 (d, *J* = 9.2 Hz, 1H), 4.43 (dd, *J* = 9.2, 6.3 Hz, 1H), 2.59 (s, 3H), 2.33–2.30 (m, 1H), 2.05–2.01 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (major isomer): δ 140.7, 137.6, 132.4, 128.6, 128.1, 128.0, 127.8, 127.2, 127.1, 126.2, 63.2, 41.8, 40.1, 37.2, 15.5. $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1452. IR (neat): 3275, 3026, 2929, 2856, 1602, 1494, 1454, 1411, 1317, 1265, 1065, 970, 873, 733, 699 cm^{-1}

***(E)*-N-(2,6-diphenylhex-5-en-2-yl)methanesulfonamide (4ao)**



The compound **4ao** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2o,** 1 mmol, 130 µL), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.ether (0.04 mmol, 4.9 µL). The reaction was carried out at 85 ^oC for 40 minutes with molecular sieves. The target compound was obtained as a viscous colorless oil (34.3 mg, 52%; *E*/*Z* = 93:7).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.43 (dd, *J* =8.4, 2.9 Hz, 2H), 7.33–7.28 (m, 5H), 7.23–7.20 (m, 1H), 5.36 (d, *J* = 15.9 Hz, 1H), 6.15 (d, *J* = 15.9, 7.6 Hz, 1H), 4.80 (s, 2H), 2.68 (s, 3H), 2.19 (d, *J* = 6.7 Hz, 2H), 2.08–2.00 (m, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 136.4, 134.8, 132.1, 131.0, 130.5, 129.2, 128.6, 128.5, 127.7, 127.1, 126.7, 126.1, 125.9, 61.2, 43.7, 42.7, 27.7, 25.7. $C_{19}H_{23}NO_2S$ $[M]^+$: 329.1449, Found 329.1446. IR (neat): 3274, 3027, 2929, 2855, 1601, 1494, 1454, 1411, 1316, 1265, 1064, 971, 873, 733, 699 cm^{-1}

***(E)*-N-(1-(naphthalen-2-yl)-5-phenylpent-4-en-1-yl)methanesulfonamide (4ap)**



The compound **4ap** was synthesized as per the general procedure using cinnamyl alcohol (**1a,** 0.2 mmol, 26.8 mg), alkene (**2p,** 1 mmol, 154 mg), $MeSO_2NH_2$ (**3a**, 0.3 mmol, 28.5 mg), and BF_3.Ether (0.04 mmol, 4.9 µL). The reaction was carried out at 110 ^oC for 40 minutes. The target compound was obtained as a viscous colorless oil (55.6 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 5.6, 3.5 Hz, 2H), 7.77 (s, 1H), 7.52 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.43 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.32–7.25 (m, 4H), 7.22–7.20 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.99 (d, *J* = 7.5 Hz, 1H), 4.68 (q, *J* = 7.5 Hz, 1H), 2.53 (s, 3H), 2.27–2.20 (m, 2H), 2.12–2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 138.4, 137.5, 133.4, 133.2, 131.4, 129.4, 128.7, 128.7, 128.1, 126.8, 126.6, 126.3, 126.2, 124.0, 58.2, 42.1, 37.3, 29.7. HRMS (EI): calcd for $C_{22}H_{23}NO_2S$ $[M]^+$: 365.1450, Found 365.1451. IR (neat): 3276, 3026, 2930, 2845, 1600, 1493, 1455, 1401, 1316, 1150, 1070, 1029, 979, 889, 918, 752, 700 cm^{-1}.

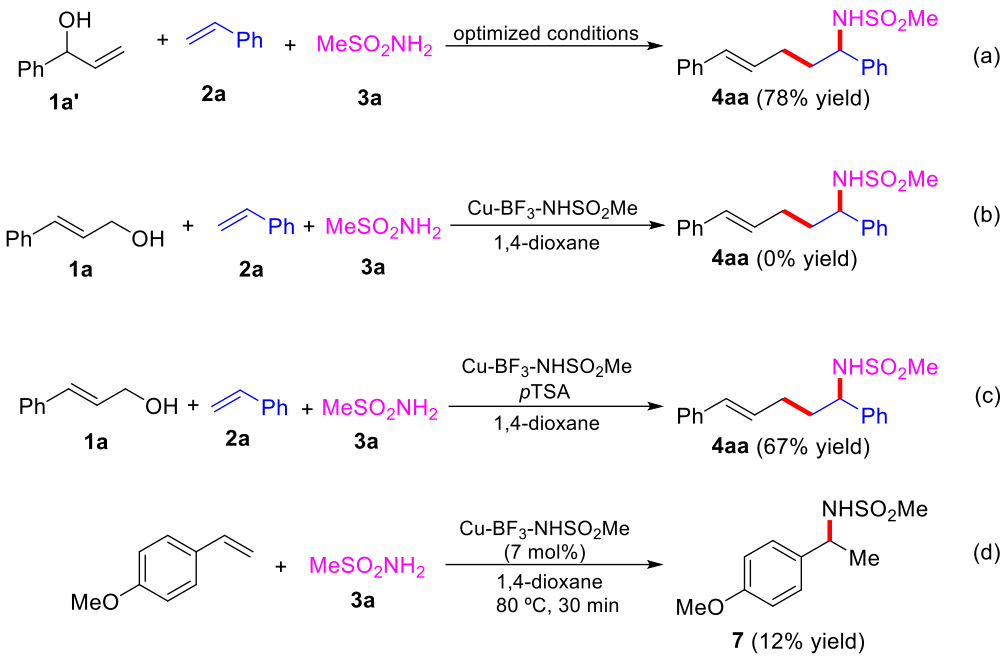
3. Procedure for synthesis of Cu-BF_3-$NHSO_2Me$.

To a clean oven dried flask, the $MeSO_2NH_2$ was added (1 mmol, 95.1 mg) in $CHCl_3$ and BF_3.ether (1 mmol, 123 μL) was transferred dropwise through needle. The mixture was stirred for 10 minutes, and the suspension of CuI (1 mmol, 190.5 mg) in $CHCl_3$ was added. The resulting mixture was sonicated for 1 hour under argon. Then, the solvent was removed, the crude mixture was washed with DCM, and the resulting dusty powder was dried under vacuum (168 mg, 74.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.83 (bs, 1H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): 43.5.

4. Procedure for gram-scale synthesis of compound 4ad

A cleaned and dried glass reactor was charged with sulfonamide (**3**, 11.2 mmol, 1.1 g) dissolved in 1,4-dioxane (7.5 mL). BF_3·ether (1.49 mol, 184 μL) was added and stirred for 1 minute. Then, CuI (0.52 mmol, 99 mg) was added to the reaction mixture, which was allowed to stir for 2 minutes. Next, cinnamyl alcohol (**1a,** 7.45 mmol, 1g), alkene (**2d**, 37.2 mmol, 4.9 mL), and molecular sieves (4Å) were added to remove water formed during alcohol activation. The reaction mixture was allowed to stir for 75 minutes at 110 ^{o}C in an argon environment. The reaction mixture was concentrated on a rotary evaporator to remove the volatile solvent. The crude residue was purified through column chromatography (SiO_2) (petroleum ether/ethylacetate 8:2) to obtain the desired product **4ad** (1.72 g, 70%).

5. Procedure for conducting control experiments



SCHEME 1. Control experiments for mechanistic detail.

Experiment (a):

The *α*-vinyl benzylalcohol (**1a′**) was added with styrene (**2a**) and $MeSO_2NH_2$ (**3a**) as per the standard procedure. The product **4aa** was obtained in 78% isolated yield.

Experiment (b):

The experiment was conducted with the allyl alcohol (**1a**), styrene (**2a**) and $MeSO_2NH_2$ (**3a**) added to Cu-BF_3-$NHSO_2Me$ (0.014 mmol, 3.2 mg) in 1,4-dioxane under argon. The reaction mixture was allowed to stir at 110 °C for 75 minutes. No desired product (**4aa**) was observed.

Experiment (c):

The experiment was conducted with allyl alcohol (**1a**), styrene (**2a**), and $MeSO_2NH_2$ (**3a**) added to Cu-BF_3-$NHSO_2Me$ (0.014 mmol, 3.2 mg) and *para*-toluenesulfonic acid (0.04 mmol, 6.9 mg) in 1,4-dioxane under argon. The reaction mixture was allowed to stir at 110 °C for 75 minutes. The desired product (**4aa**) was formed in 67% yield.

Experiment (d):

The experiment was conducted with *para*-methyoxystyrene **(2j,** 1.0 mmol) and $MeSO_2NH_2$ (**3a**, 1.5 mmol) added to Cu-BF_3-$NHSO_2Me$ (0.07 mmol, 15.8 mg) in 1,4-dioxane (1.0 M) under argon. The reaction mixture was allowed to stir at 80 °C for 30 minutes. The column chromatography of the reaction mixture provided the desired product (**7,** 27 mg, 12%).[1] ^{1}H

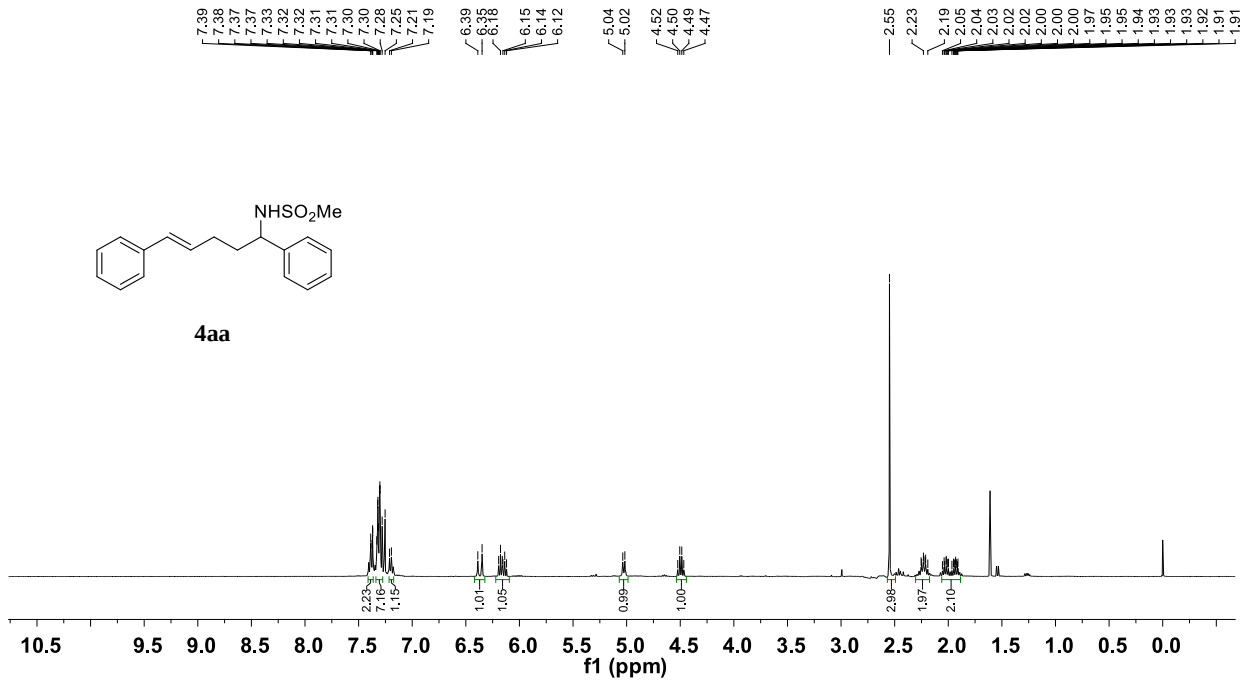
NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.63 (m, 1H), 4.57 (m, 1H), 3.81 (s, 3H), 2.62 (s, 3H), 1.53 (d, J = 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 134.3, 127.5, 114.3, 55.3, 53.3, 41.9, 23.9.

6. References

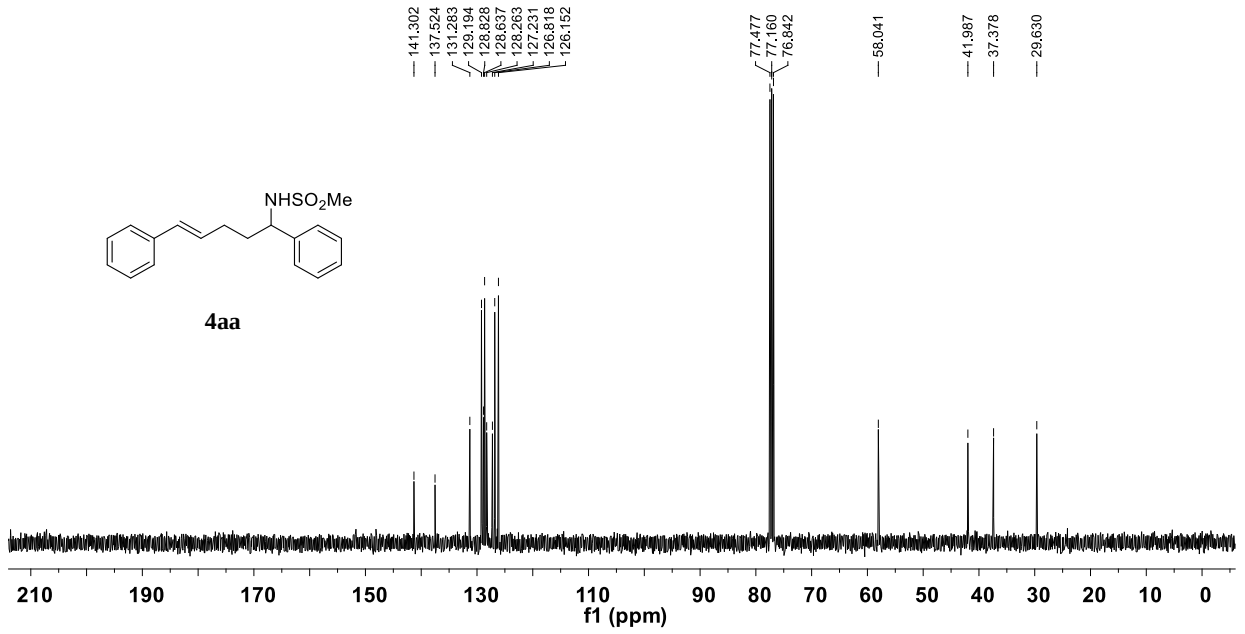
(1) Liang, J. L.; Huang, J. S.; Yu, X. Q.; Zhu, N.; Che, C. M. Metalloporphyrin-Mediated Asymmetric Nitrogen-Atom Transfer to Hydrocarbons: Aziridination of Alkenes and Amidation of Saturated C− H Bonds Catalyzed by Chiral Ruthenium and Manganese Porphyrins. *Eur. J. Chem.* **2002**, *8*, 1563-1572.

7. ^{1}H and ^{13}C NMR spectra of target compounds

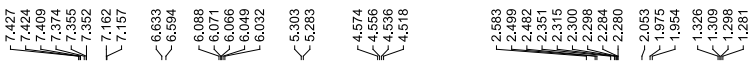
^{1}H NMR (400 MHz, $CDCl_3$)

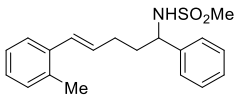


^{13}C NMR (100 MHz, $CDCl_3$)

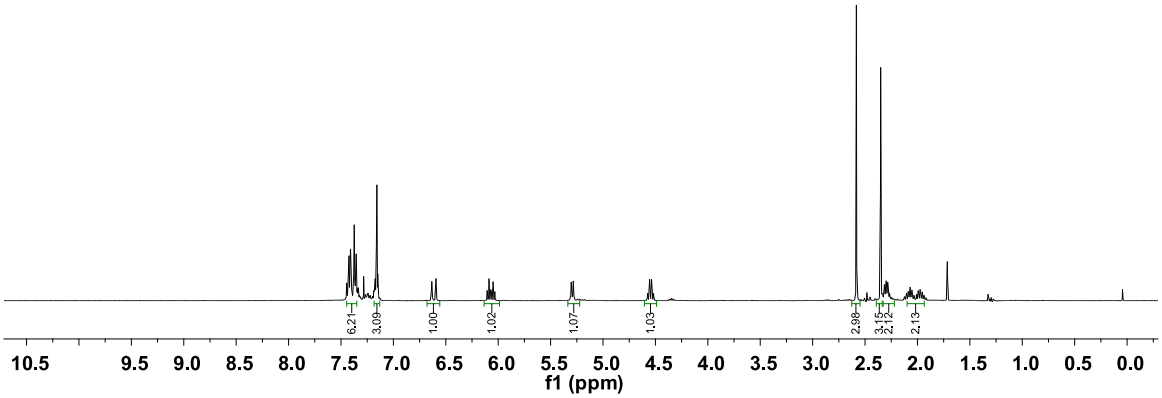


^{1}H NMR (400 MHz, $CDCl_3$)

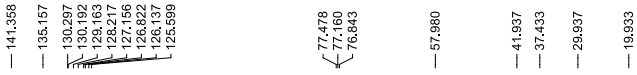


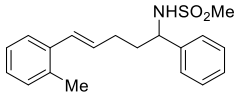


4ba



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





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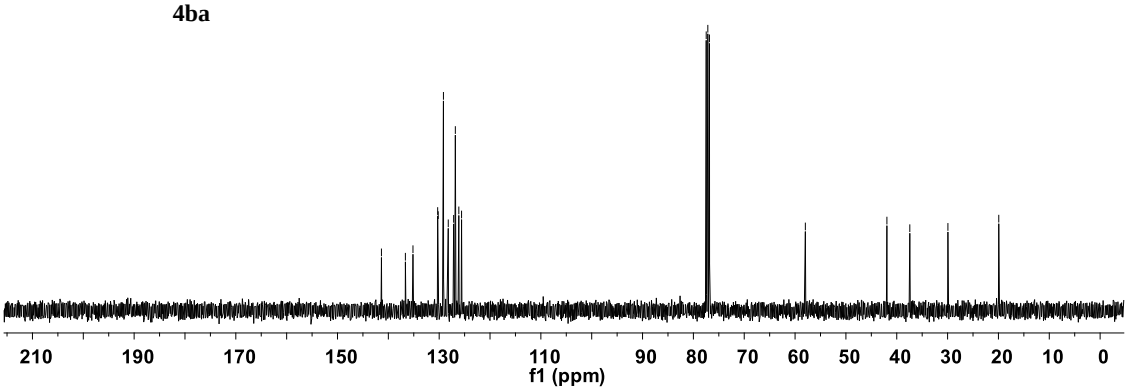
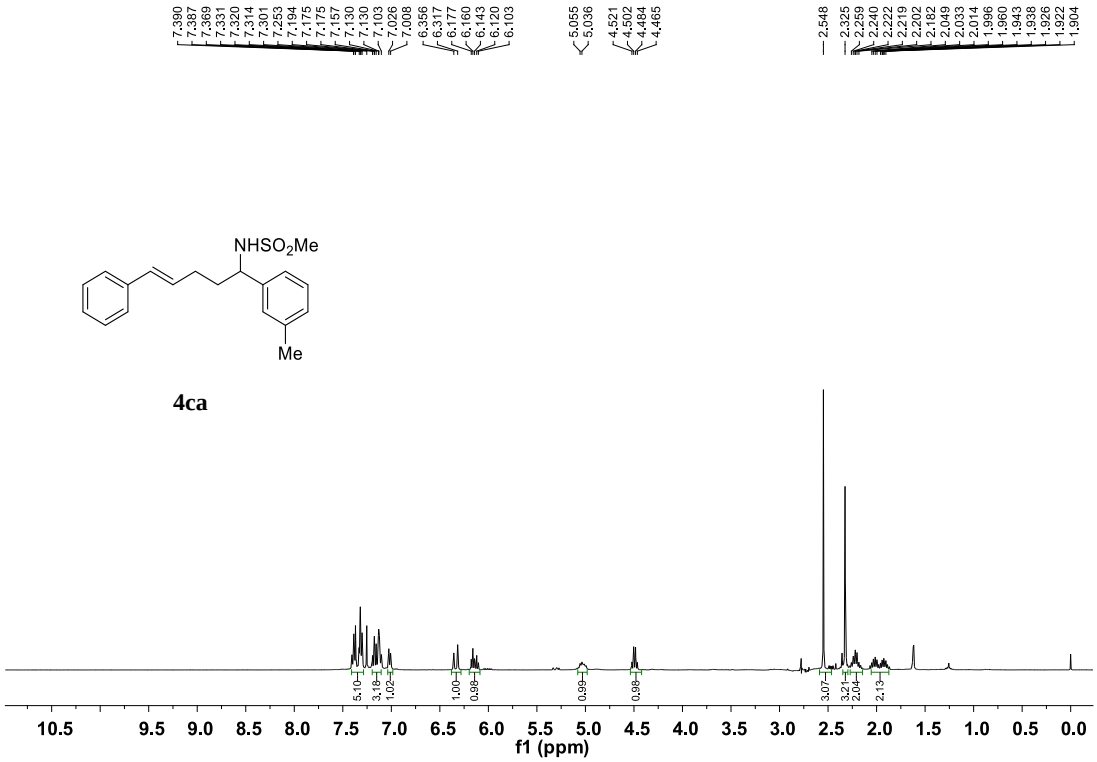
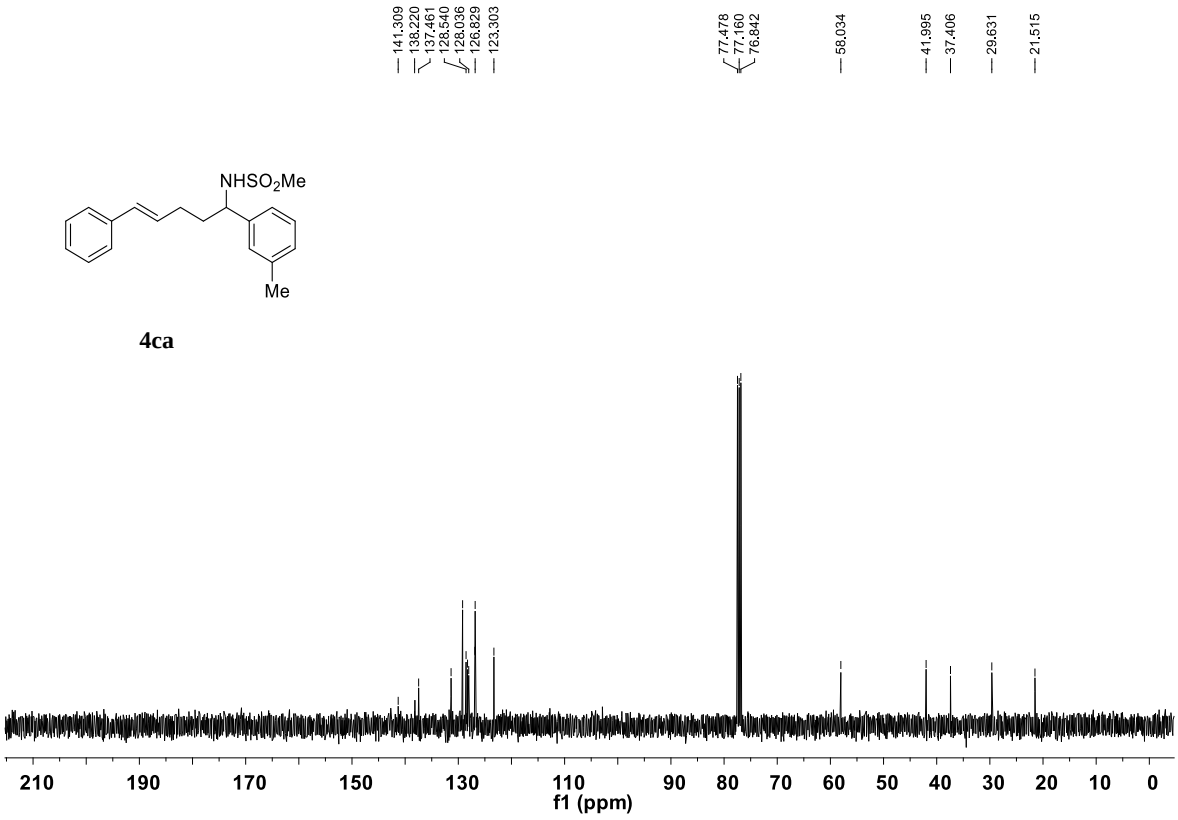


^{1}H NMR (400 MHz, $CDCl_3$)



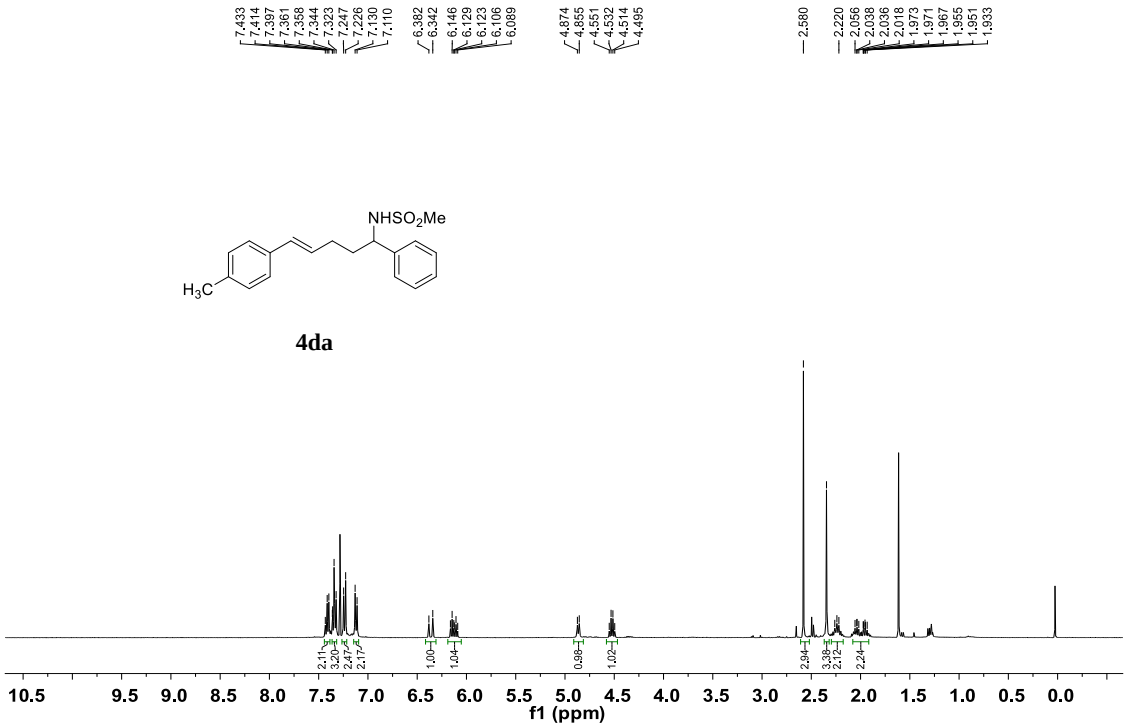
4ca

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



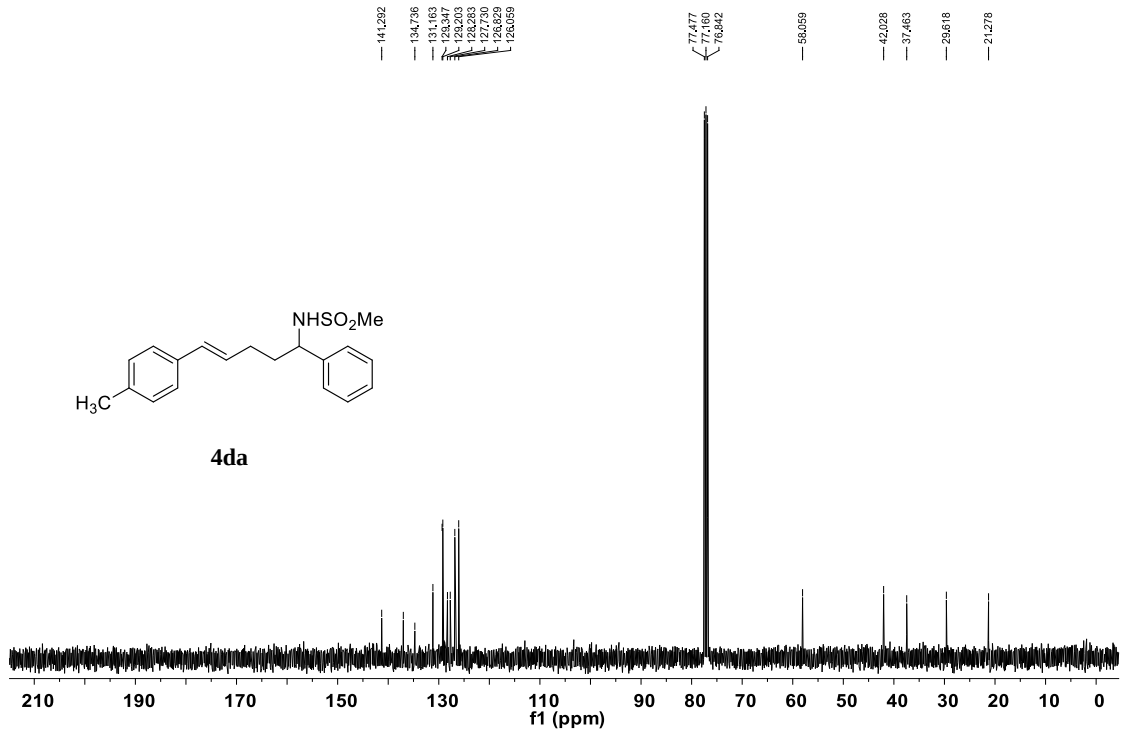
4ca

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



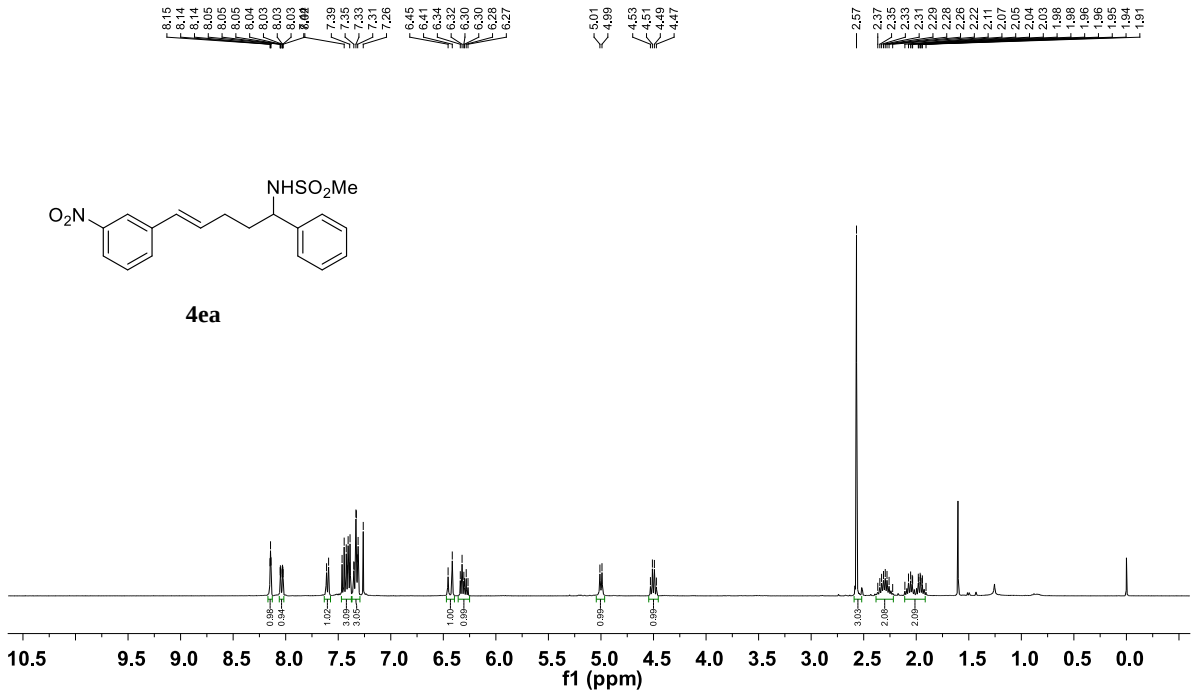
4da

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

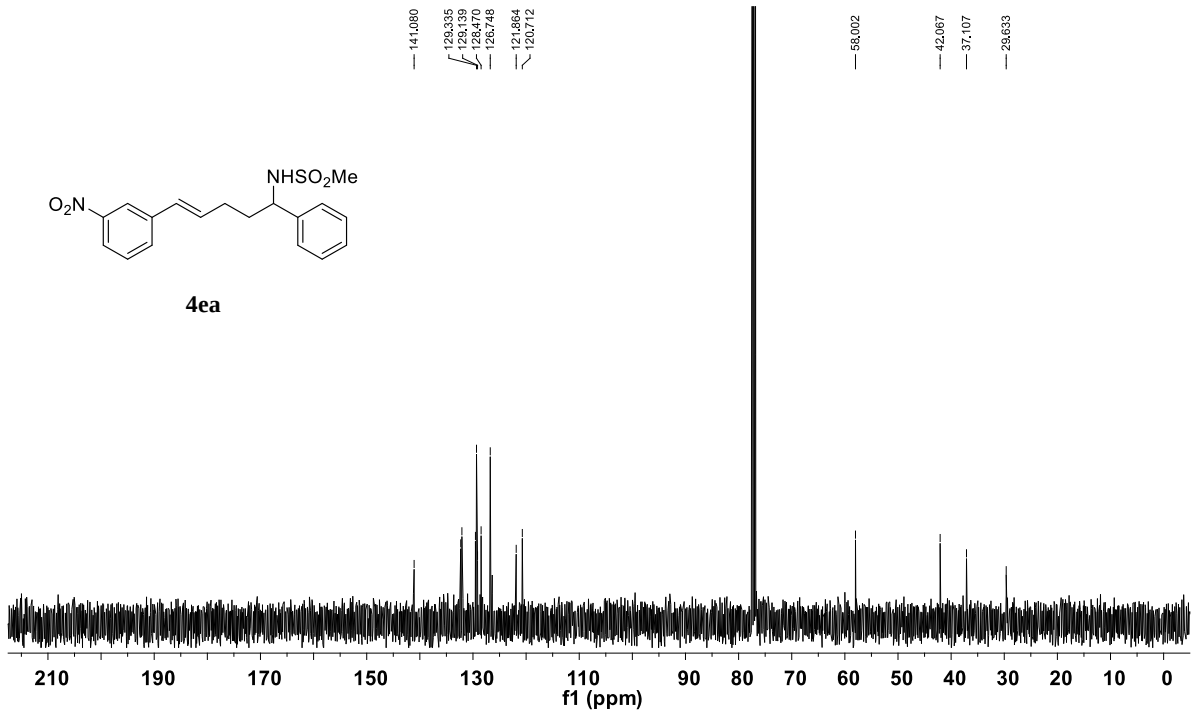


4da

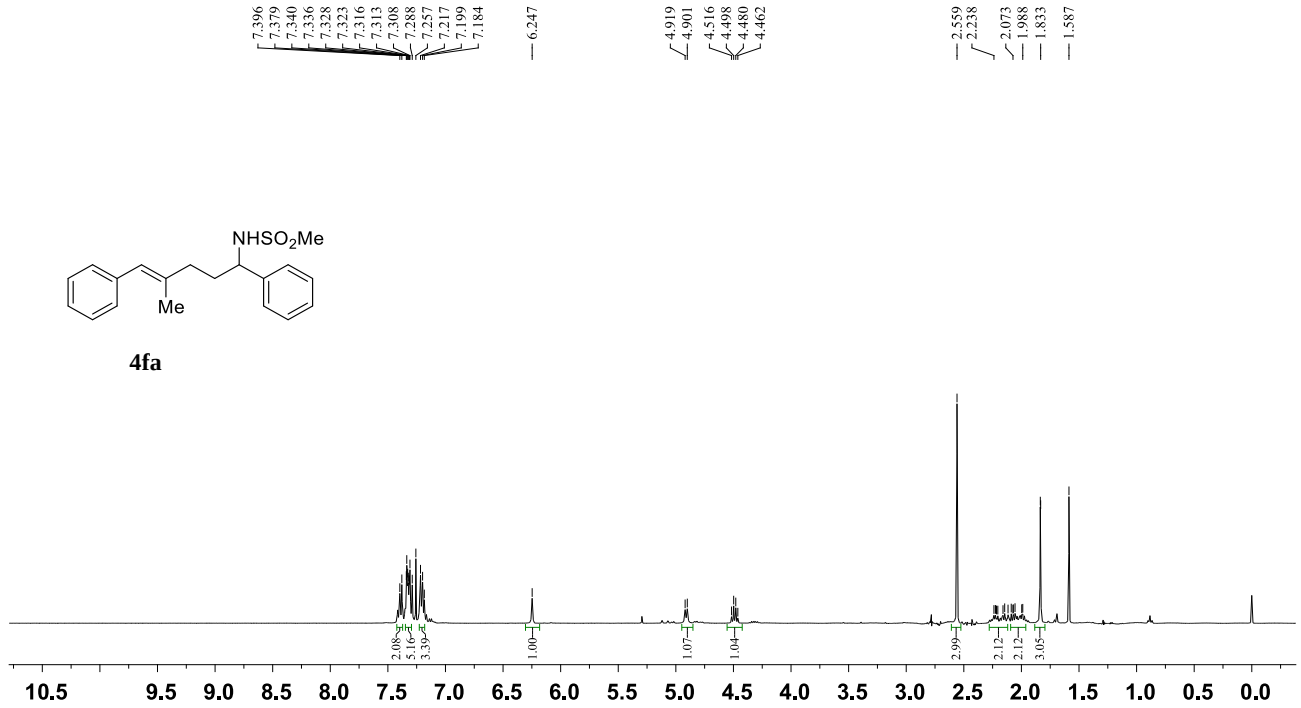
^{1}H NMR (400 MHz, $CDCl_3$)



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

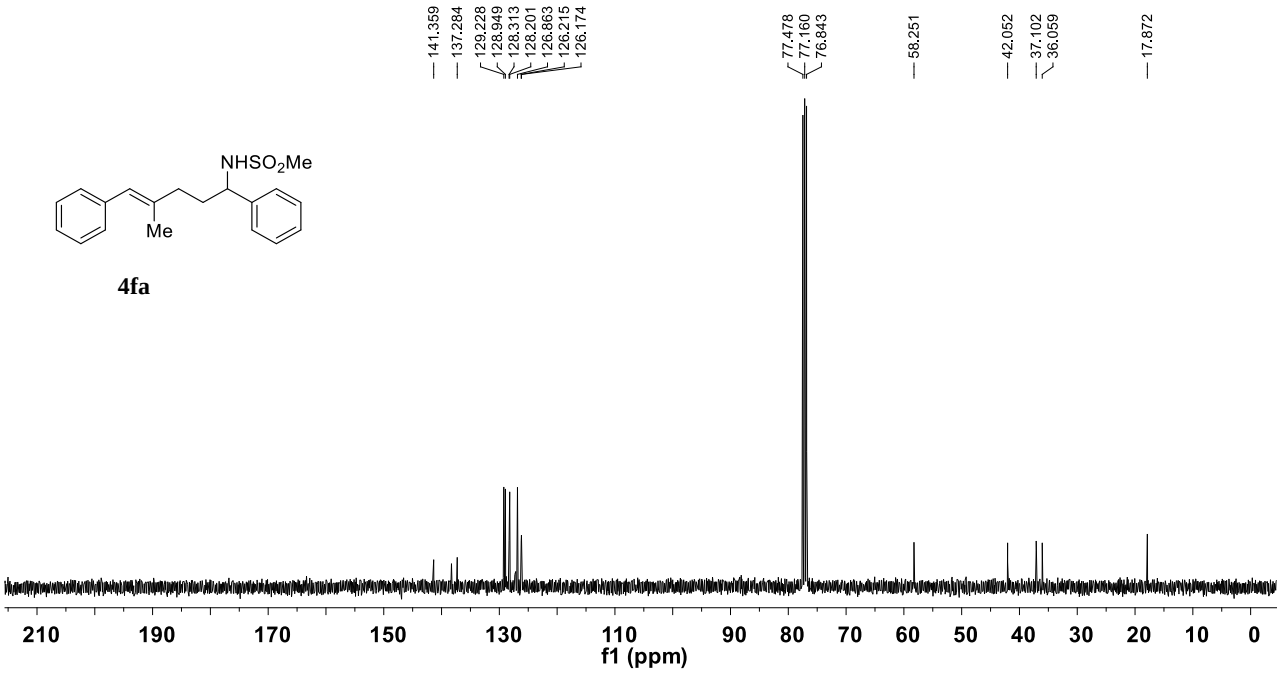


^{1}H NMR (400 MHz, $CDCl_3$)



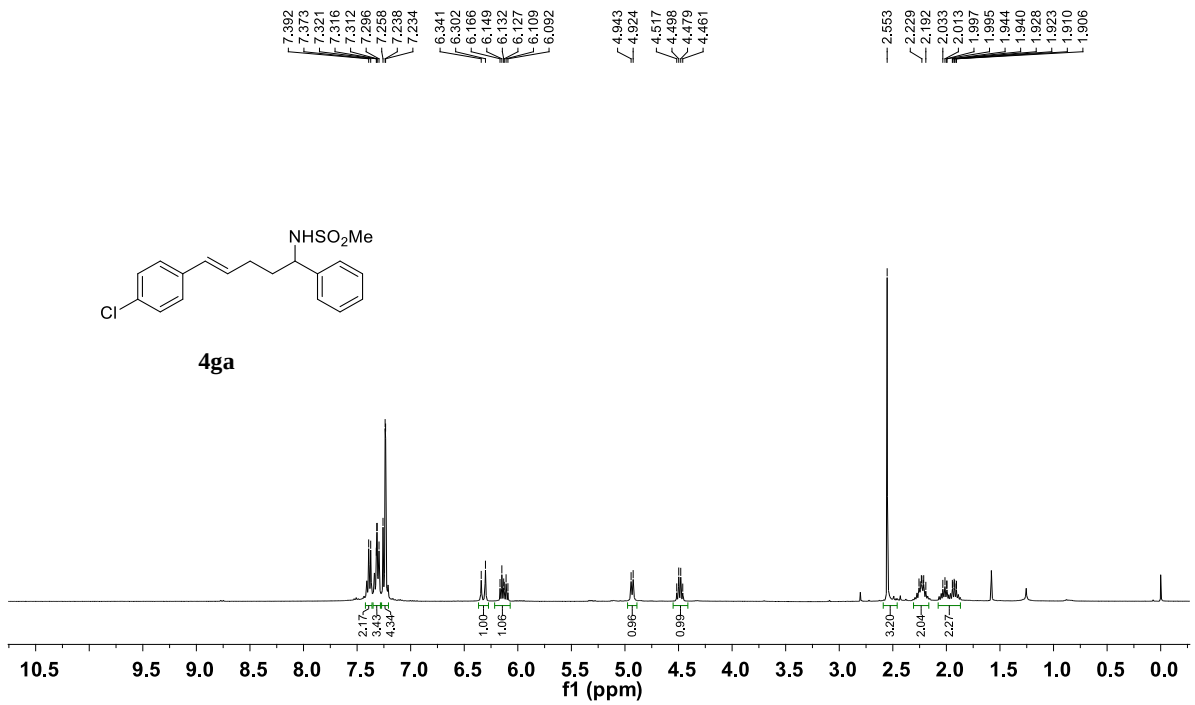
4fa

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



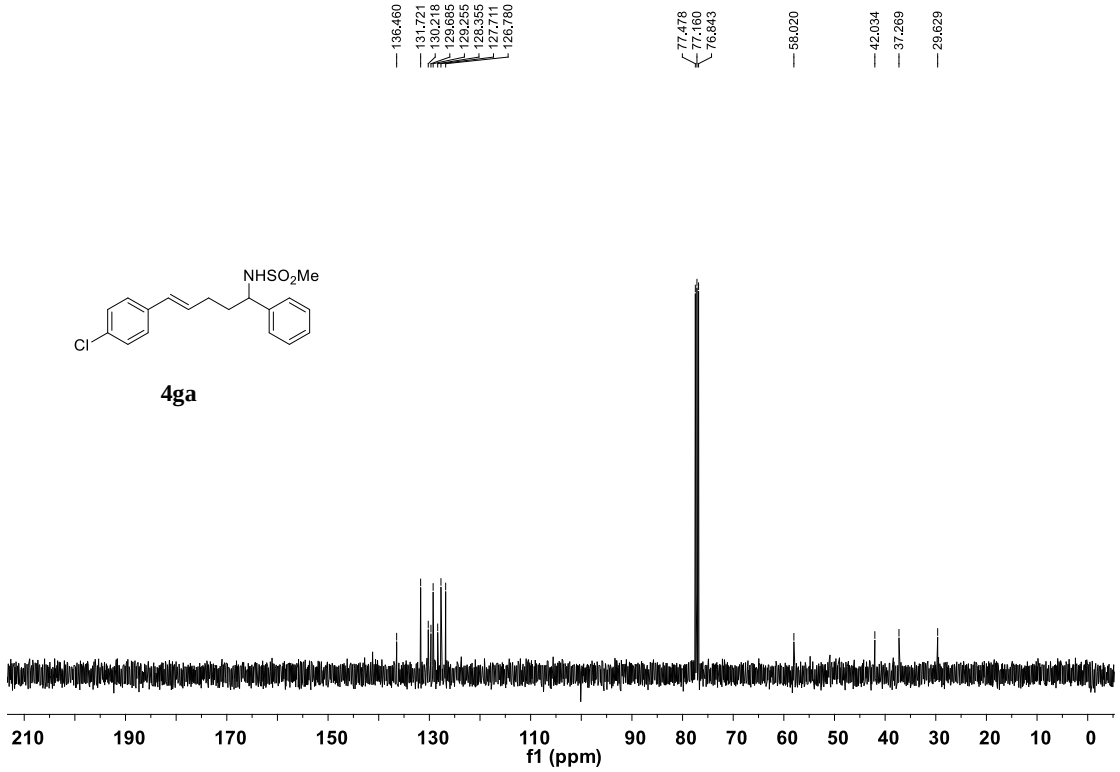
4fa

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



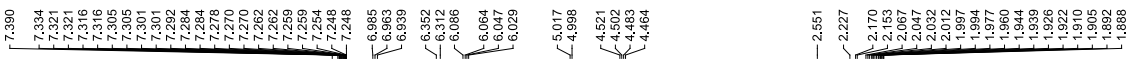
4ga

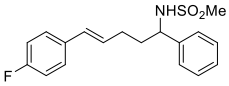
^{13}C NMR (100 MHz, $CDCl_3$)



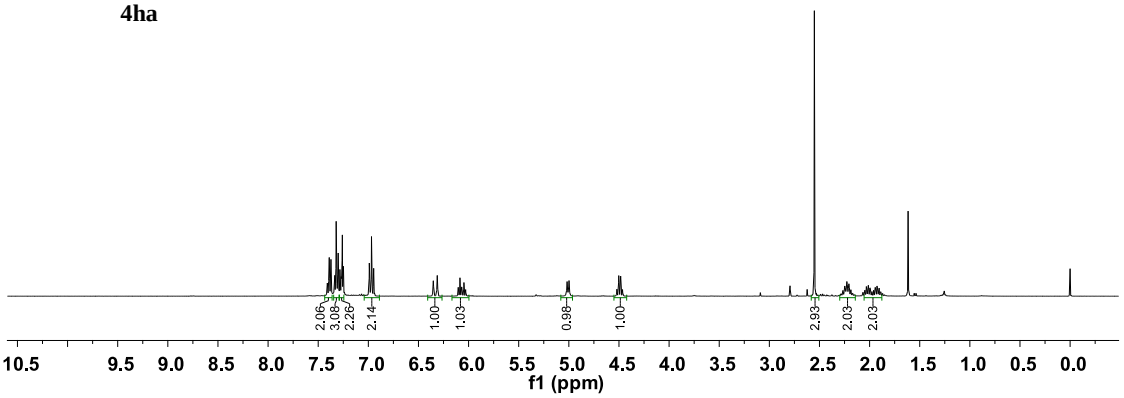
4ga

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

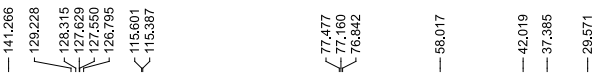


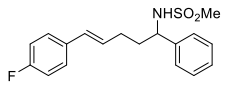


4ha



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





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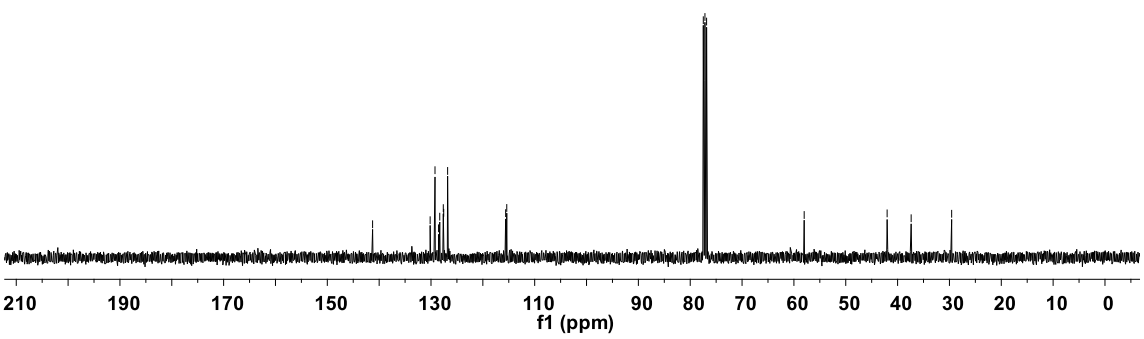
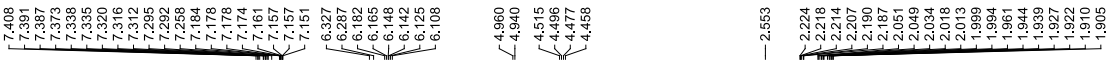
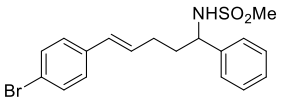
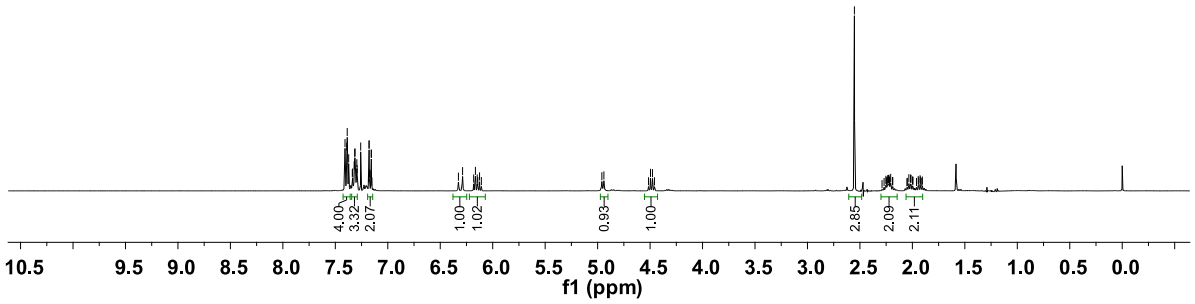


^{1}H NMR (400 MHz, $CDCl_3$)

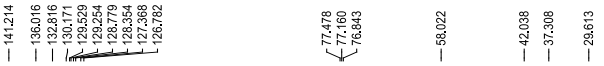


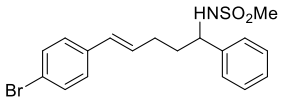


4ia

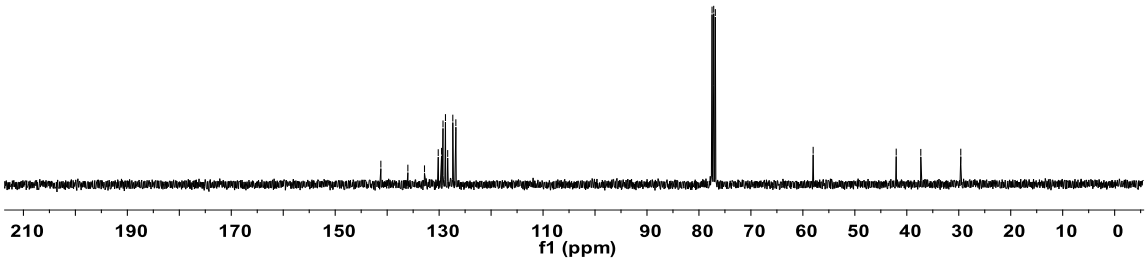


^{13}C NMR (100 MHz, $CDCl_3$)

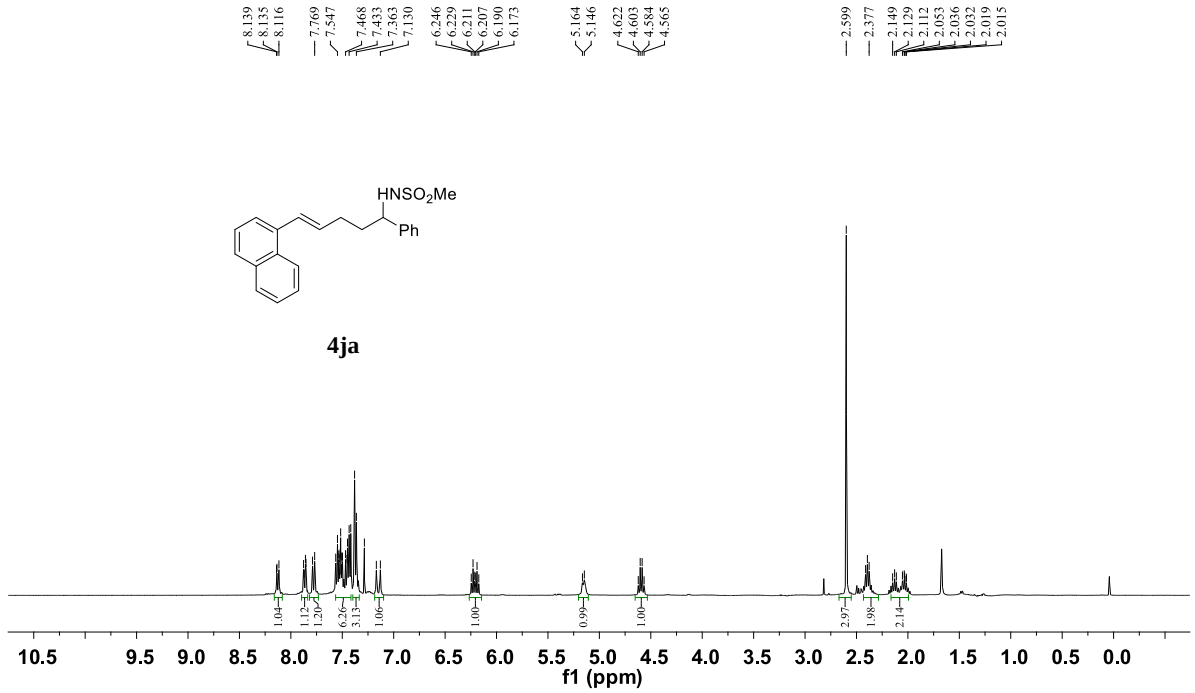




4ia

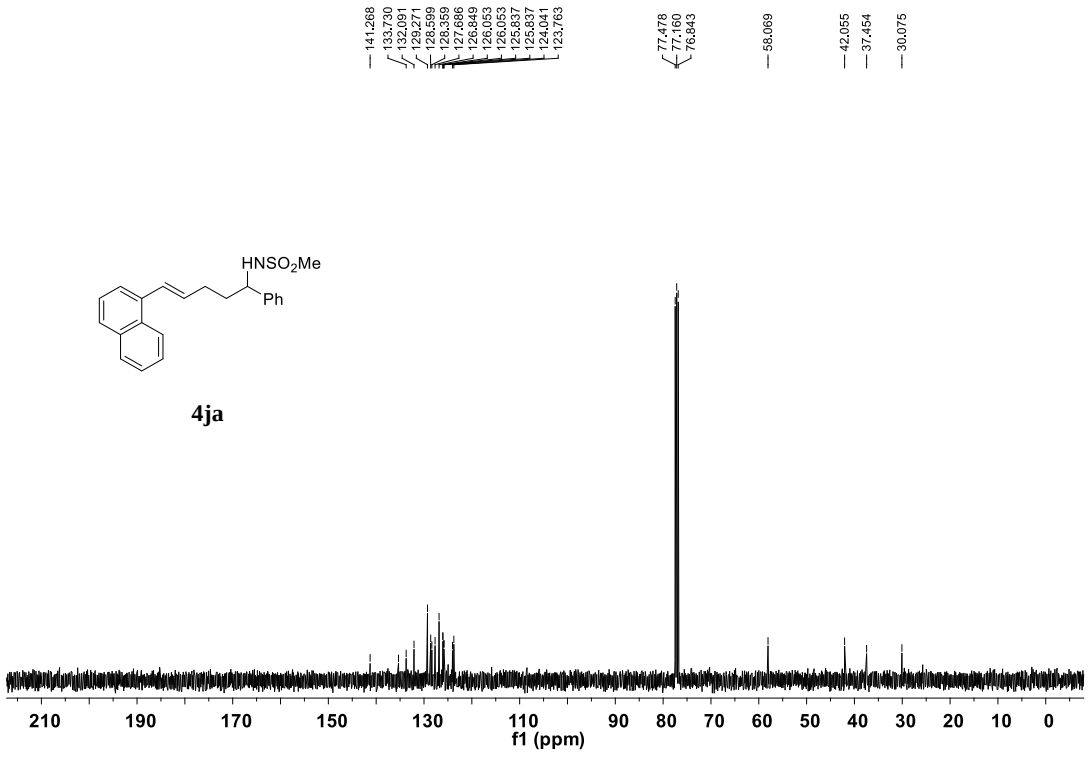


^{1}H NMR (400 MHz, $CDCl_3$)



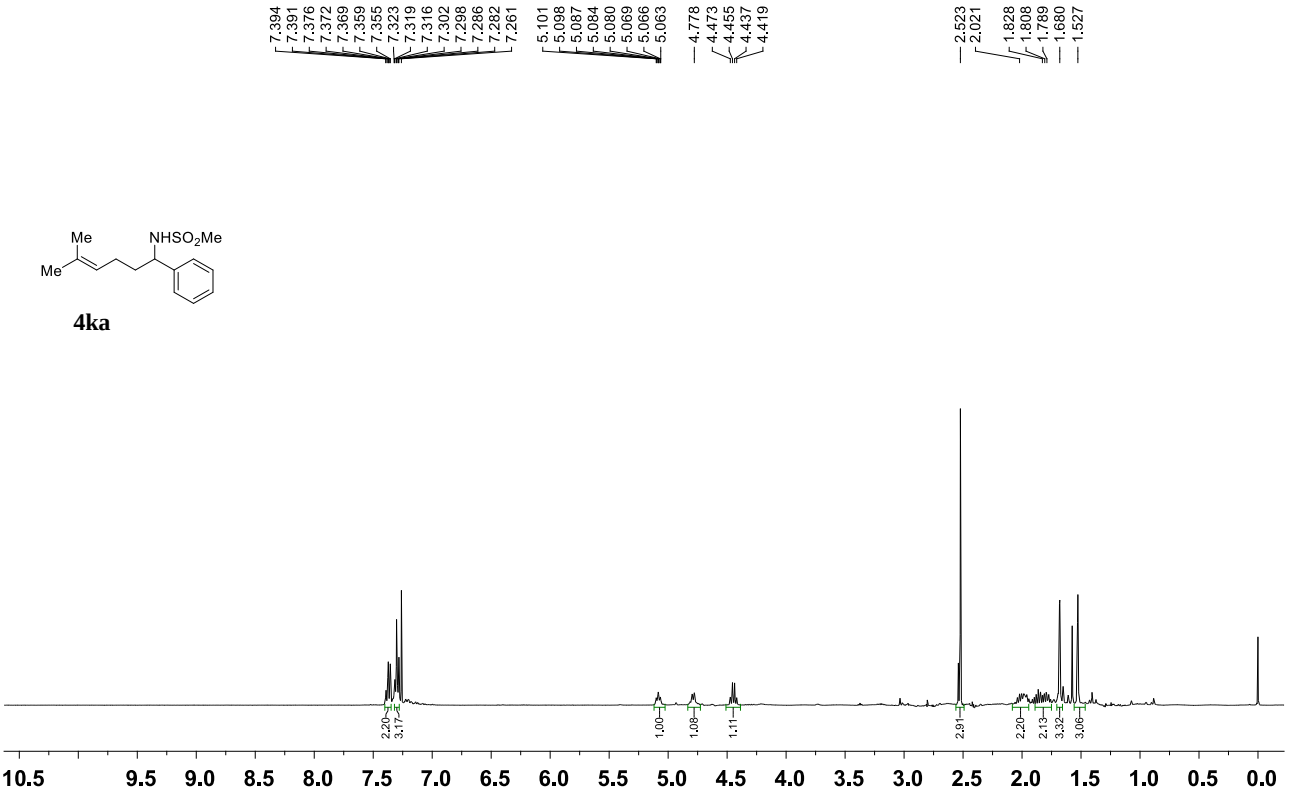
4ja

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



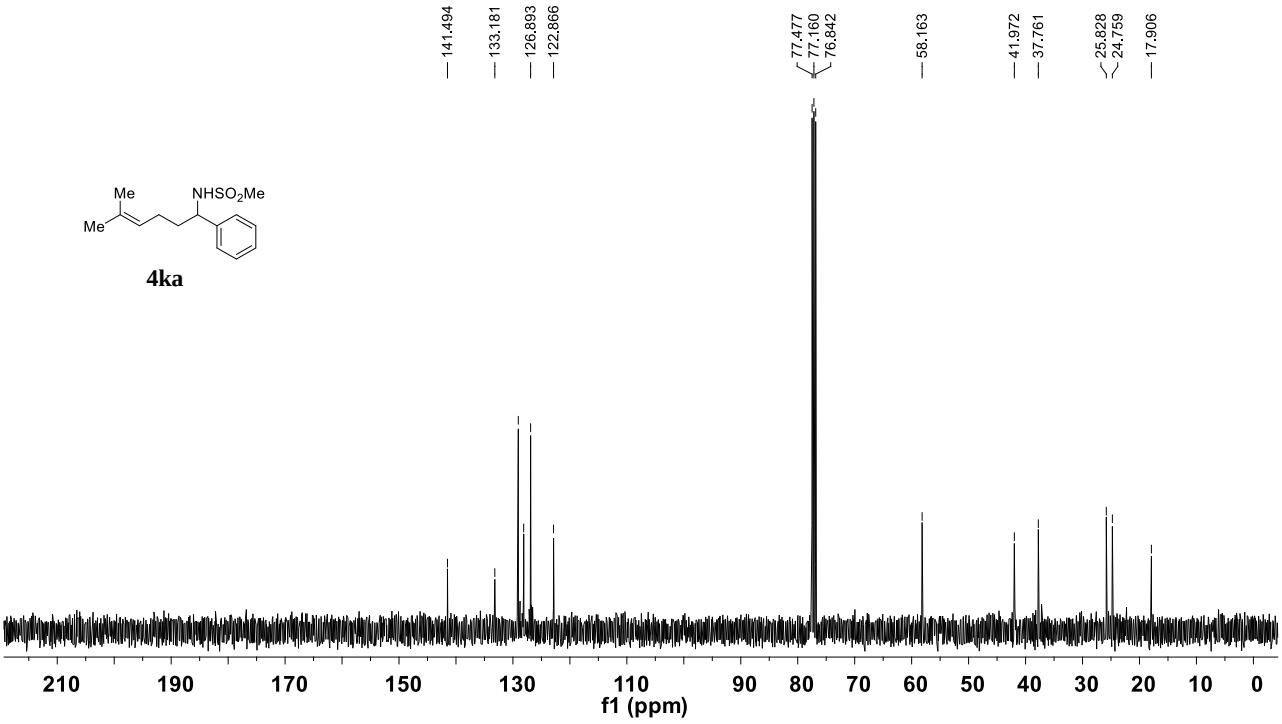
4ja

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



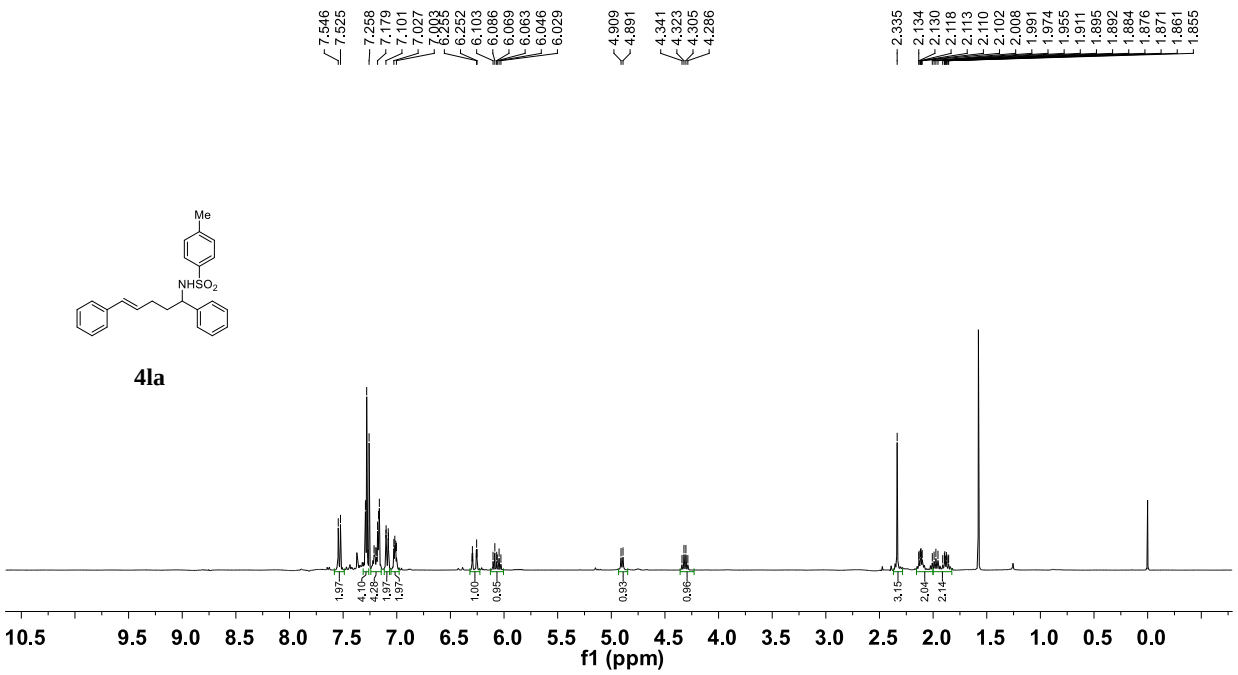
4ka

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



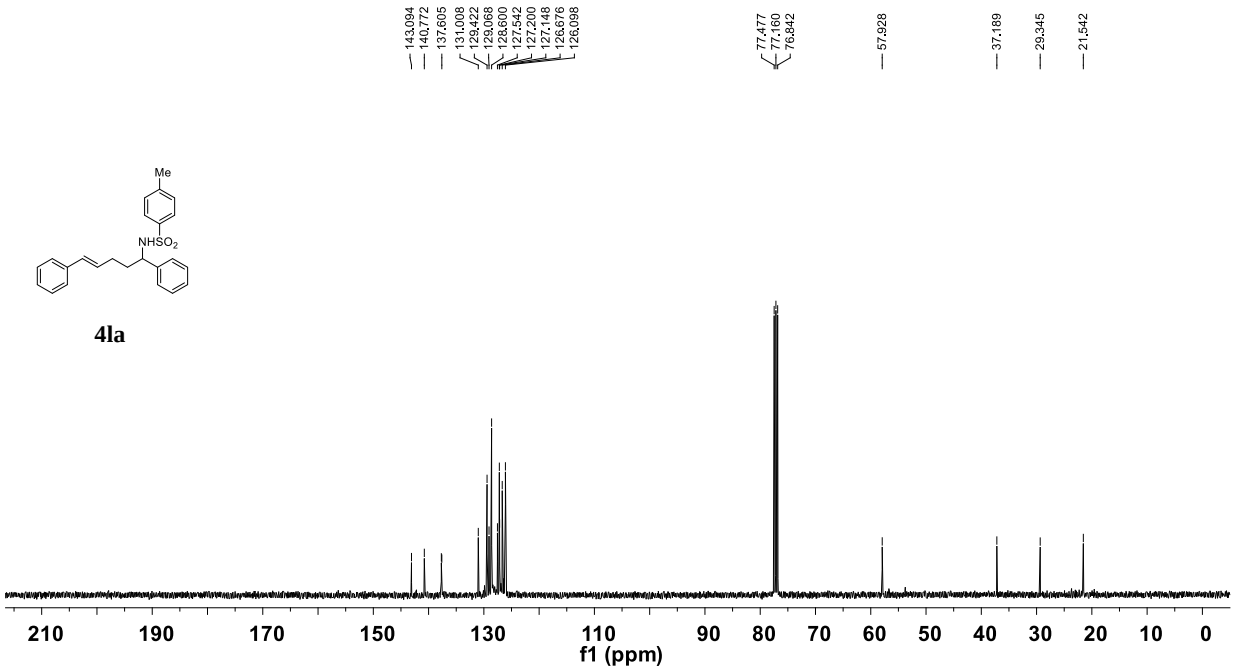
4ka

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



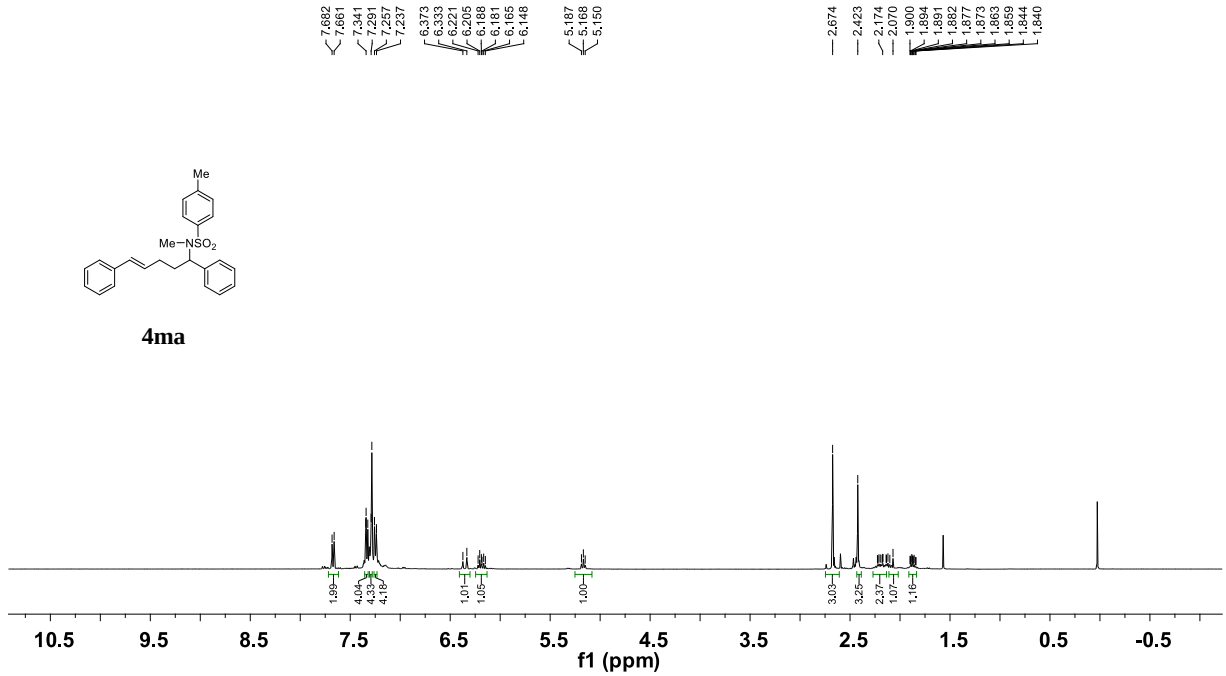
4la

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



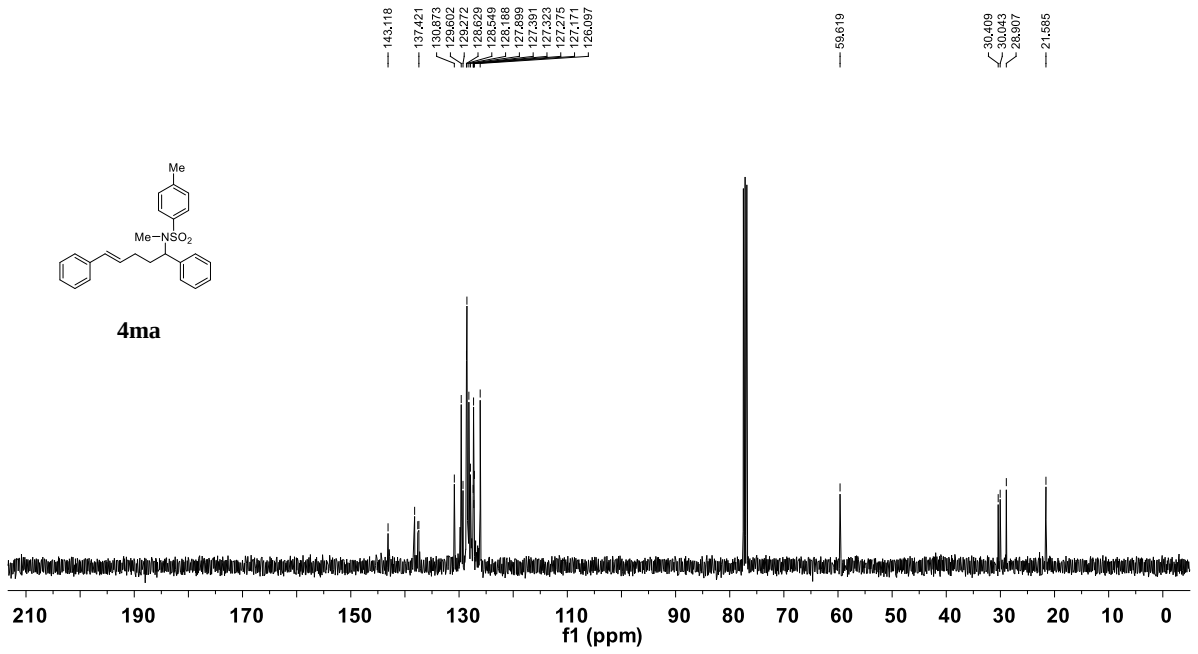
4la

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



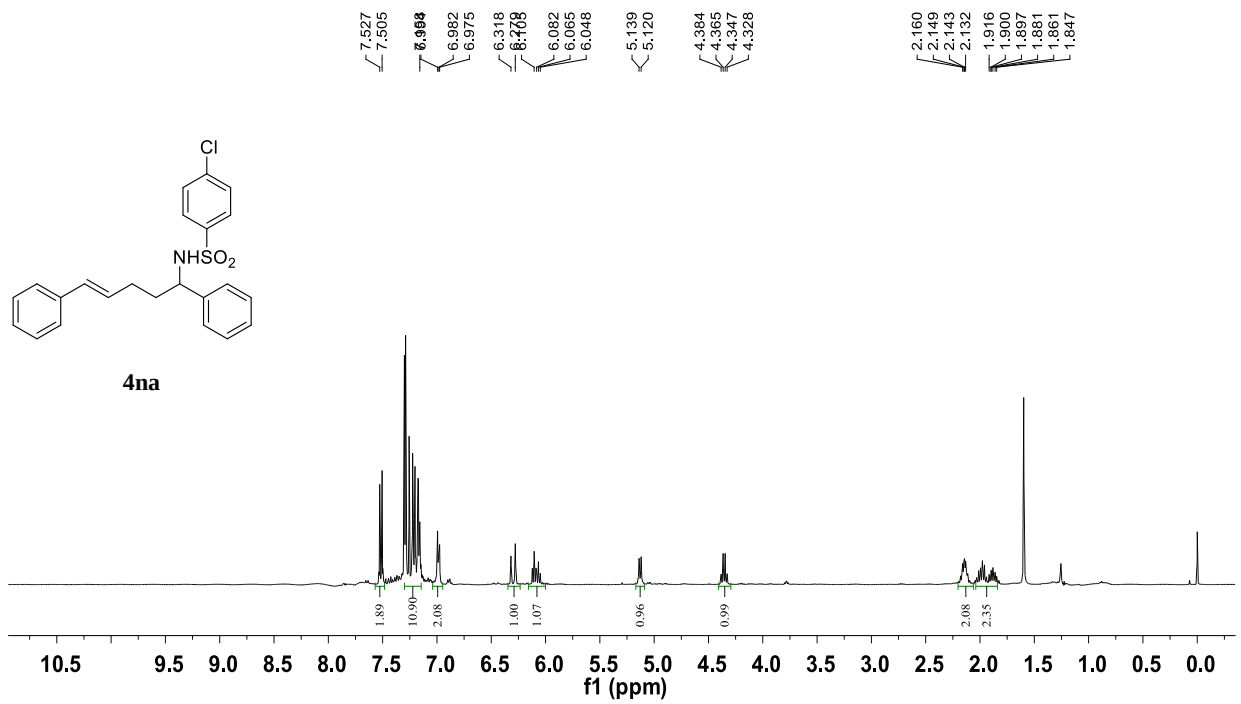
4ma

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

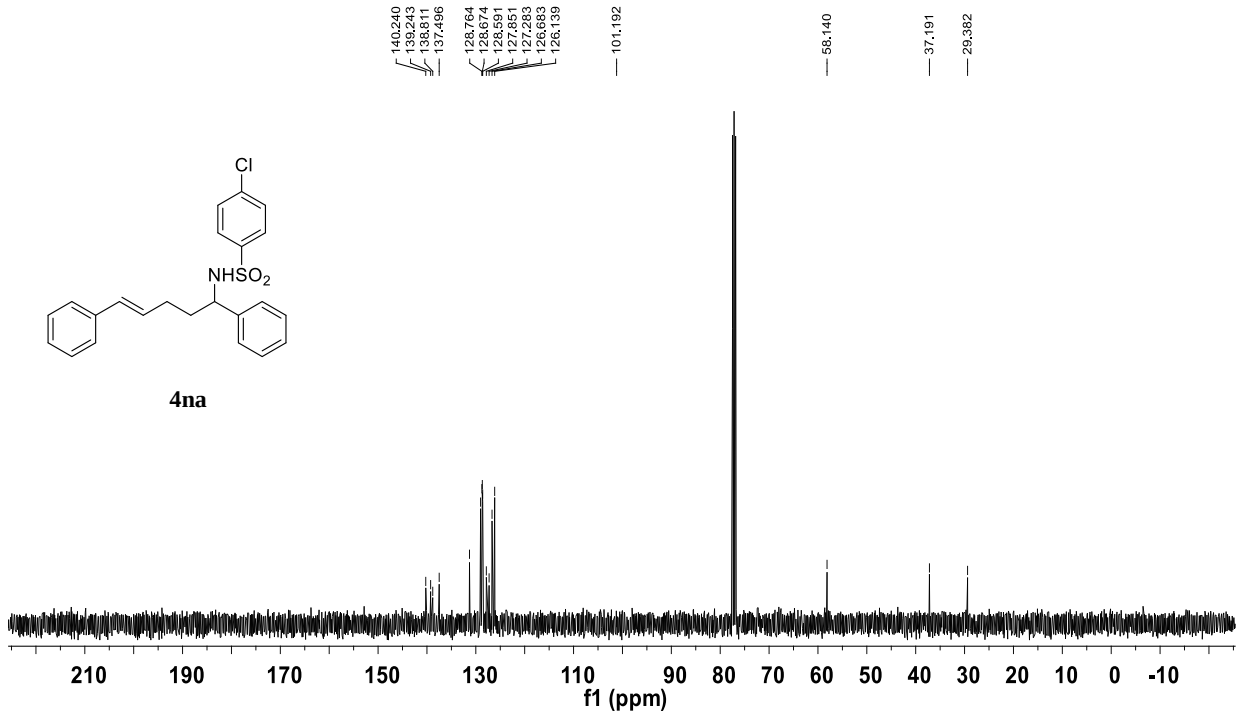


4ma

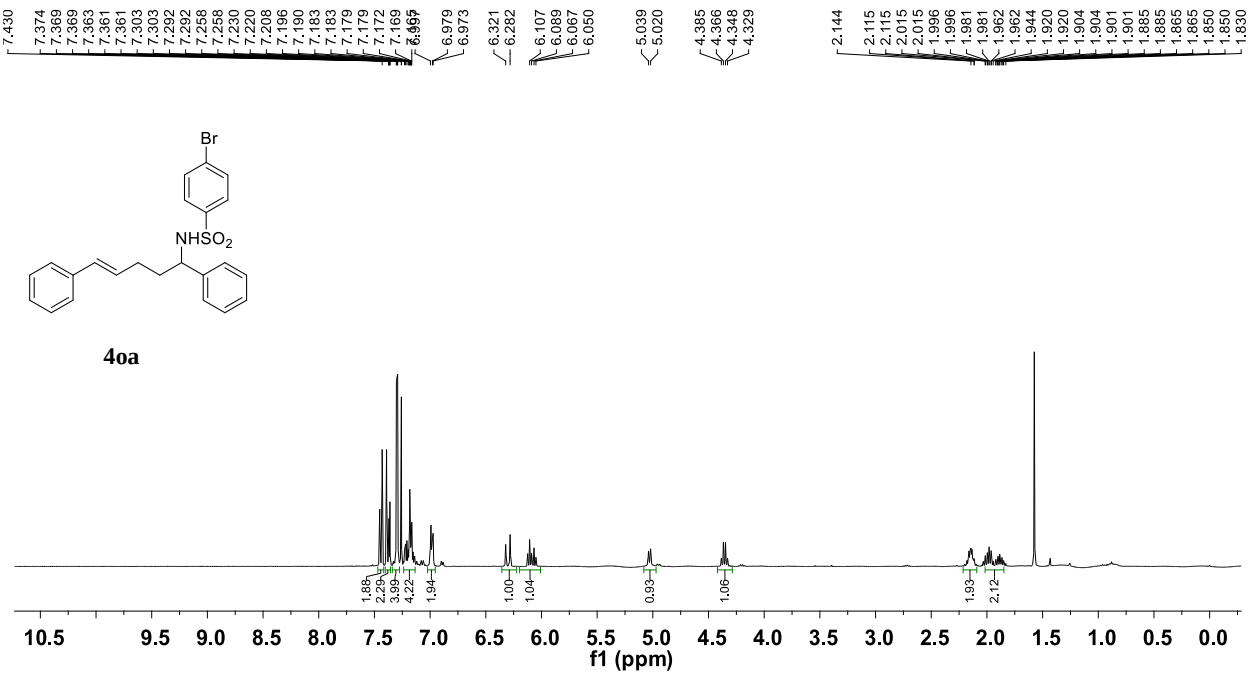
^{1}H NMR (400 MHz, $CDCl_3$)



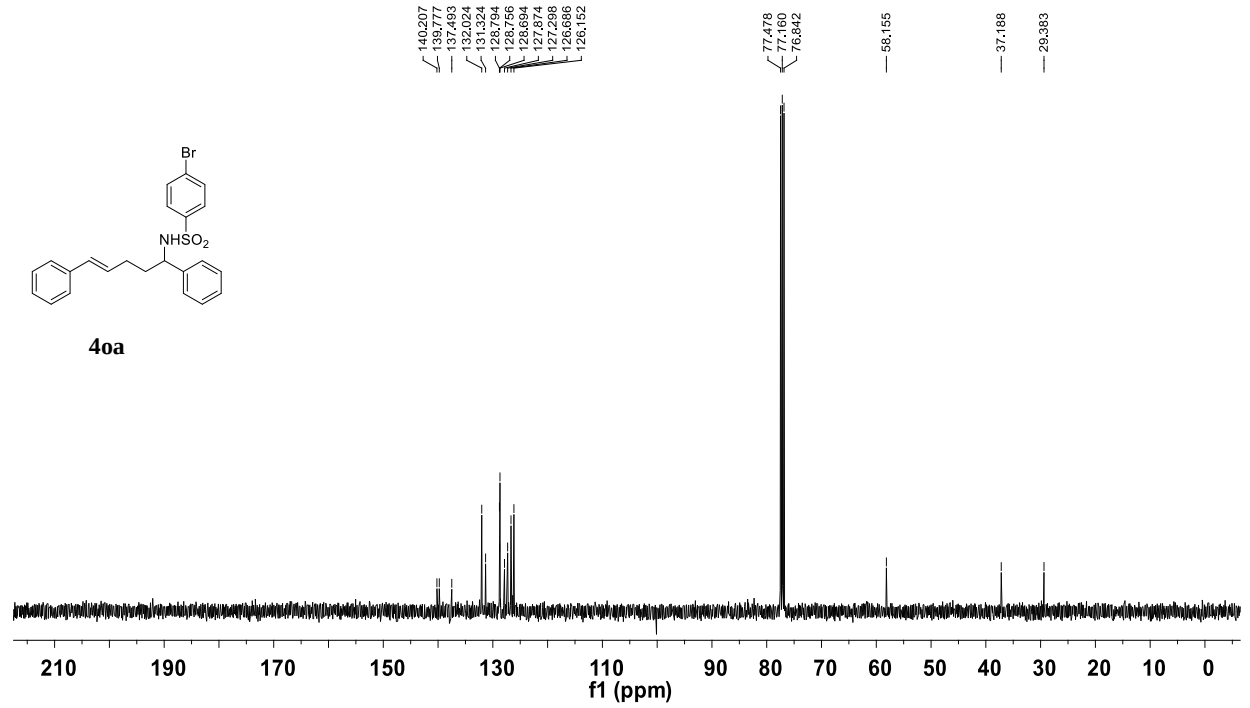
^{13}C NMR (100 MHz, $CDCl_3$)



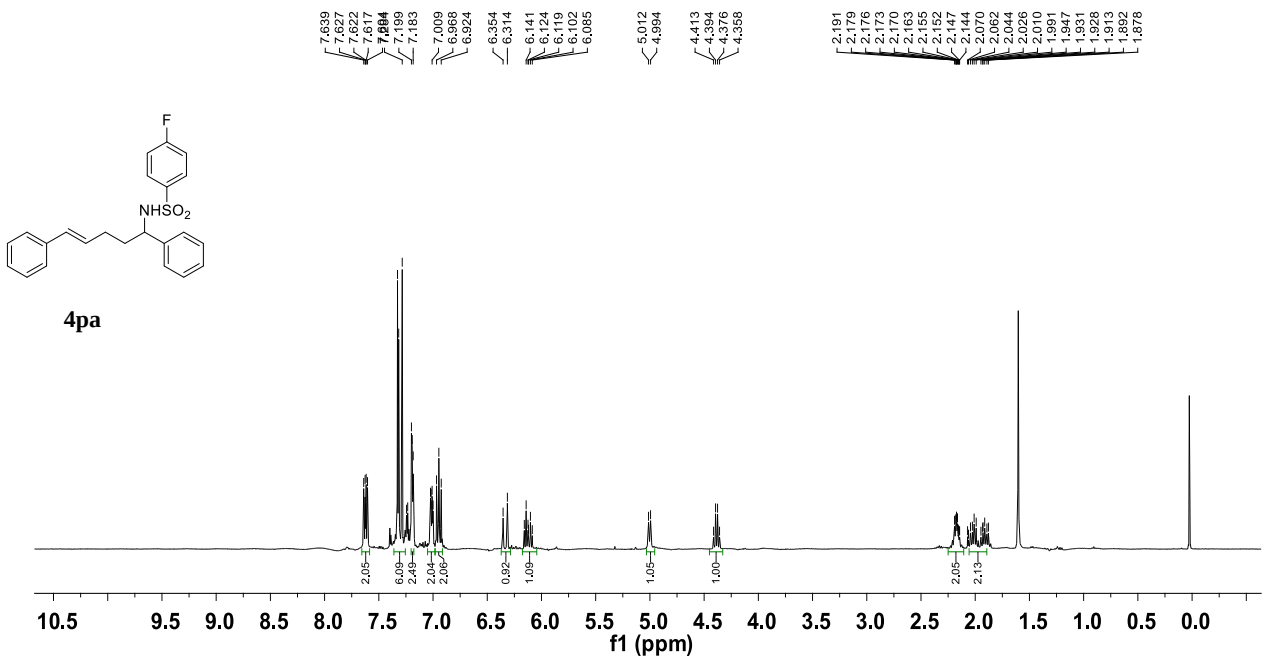
^{1}H NMR (400 MHz, $CDCl_3$)



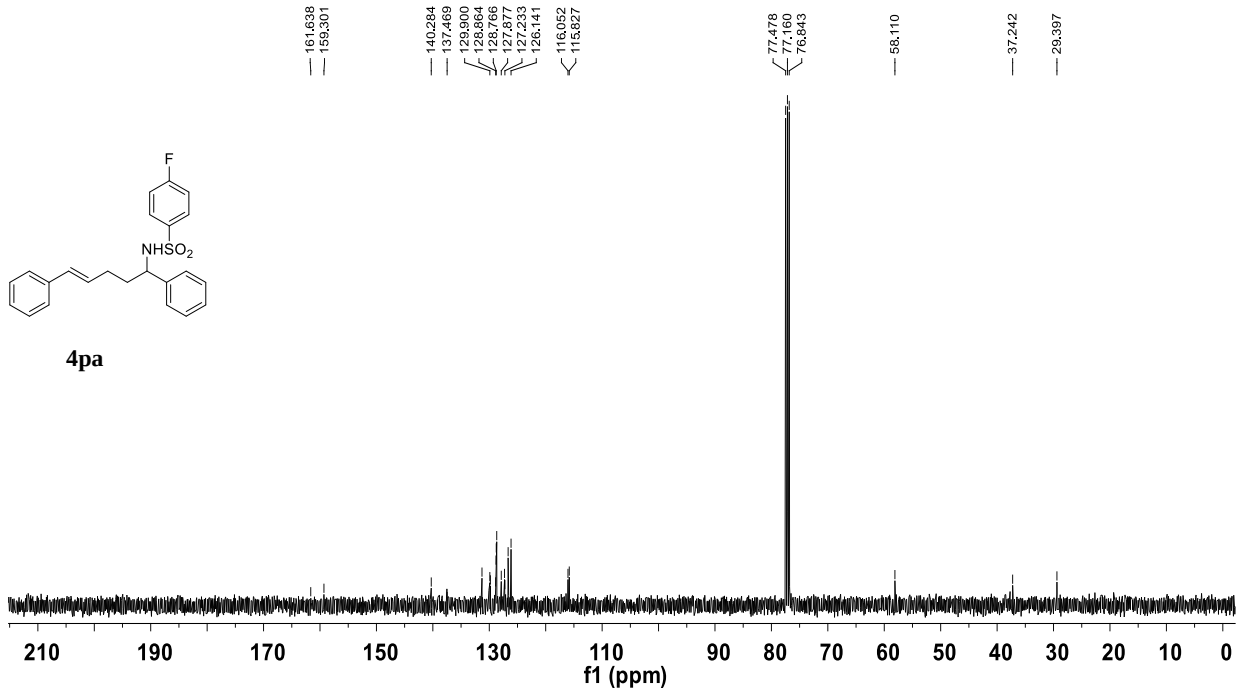
^{13}C NMR (100 MHz, $CDCl_3$)



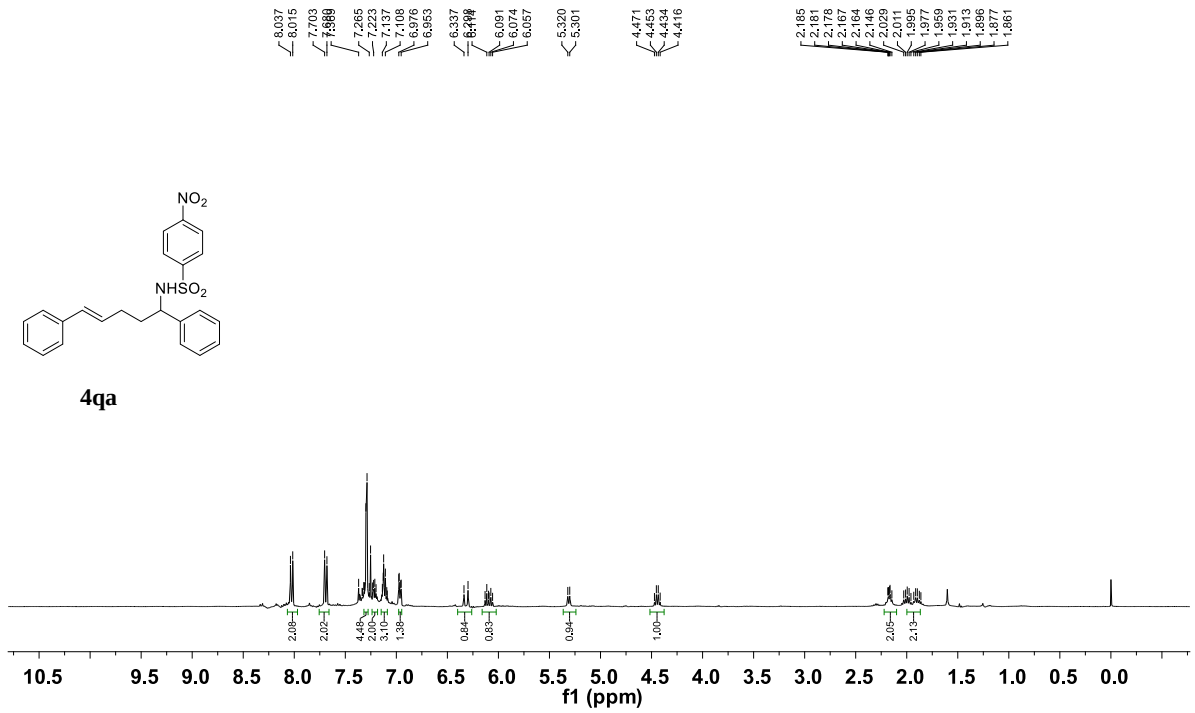
^{1}H NMR (400 MHz, $CDCl_3$)



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

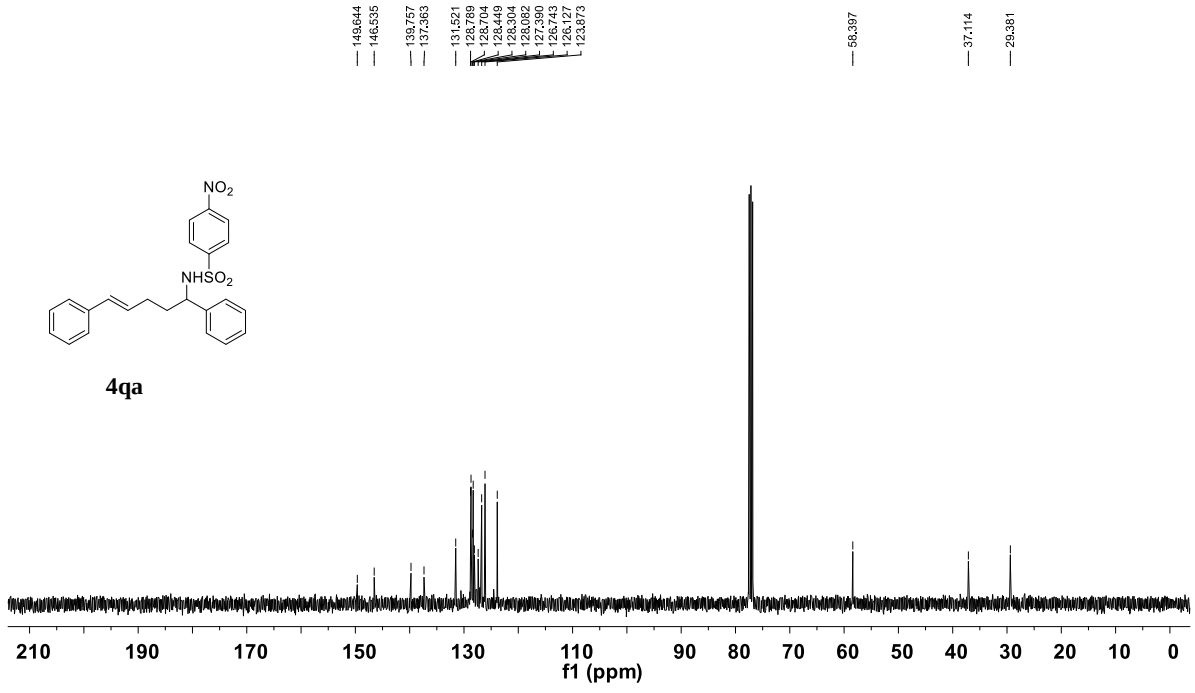


^{1}H NMR (400 MHz, $CDCl_3$)



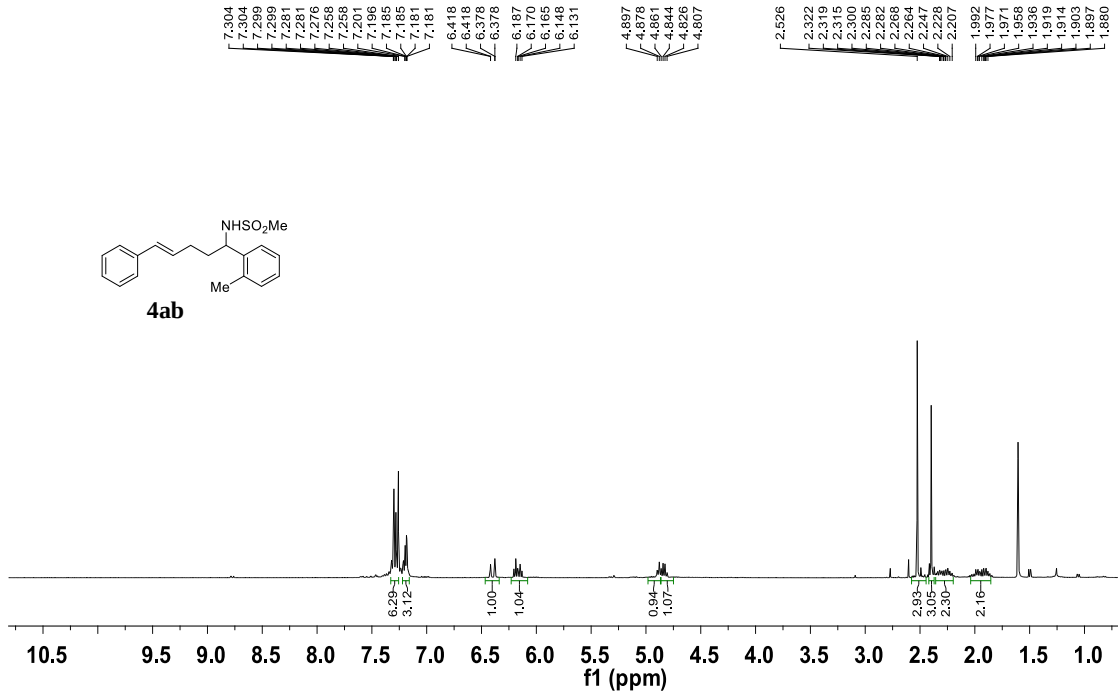
4qa

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

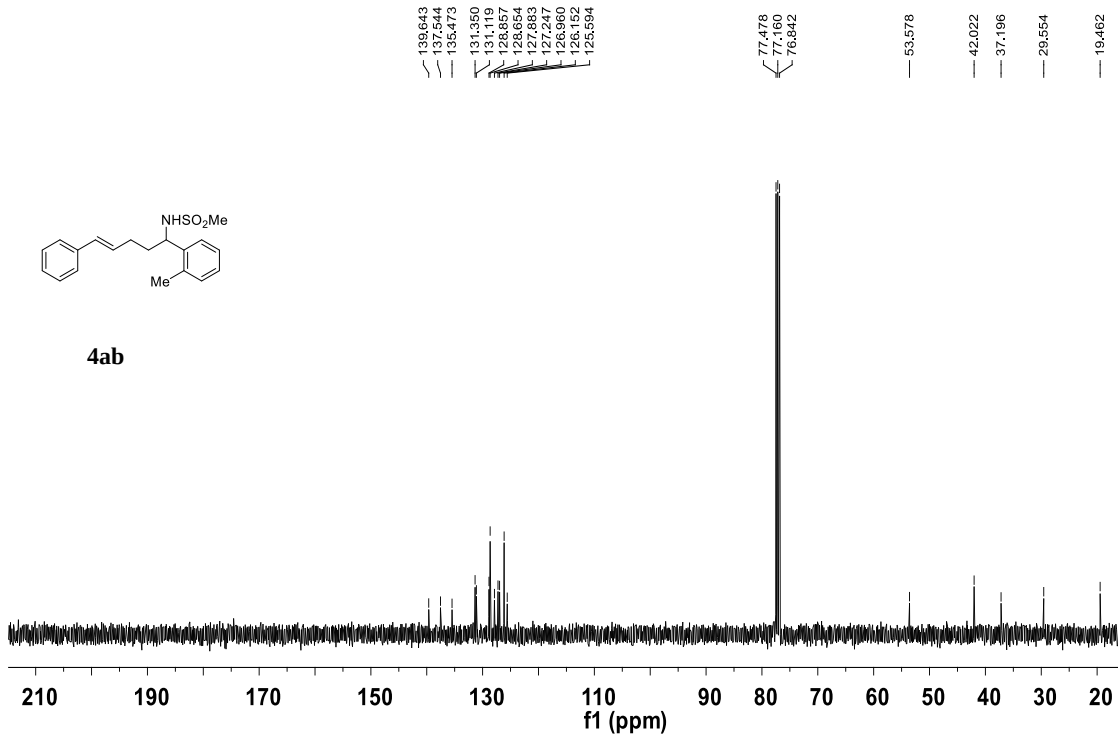


4qa

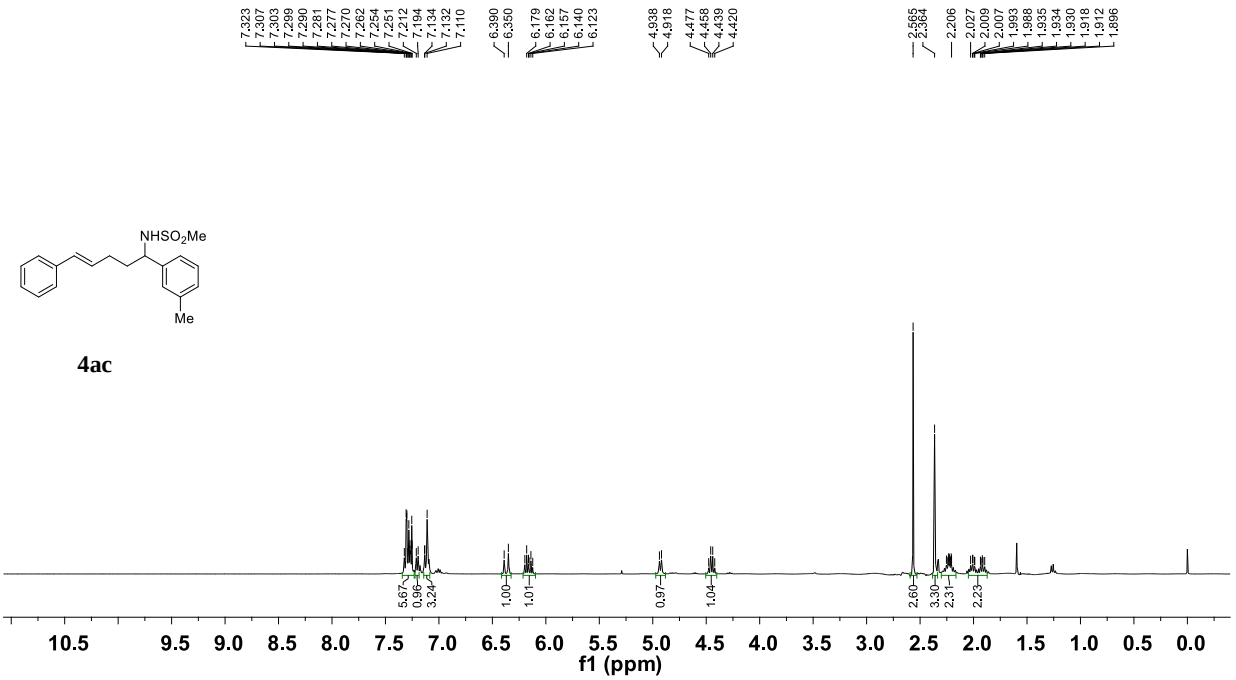
^{1}H NMR (400 MHz, $CDCl_3$)



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

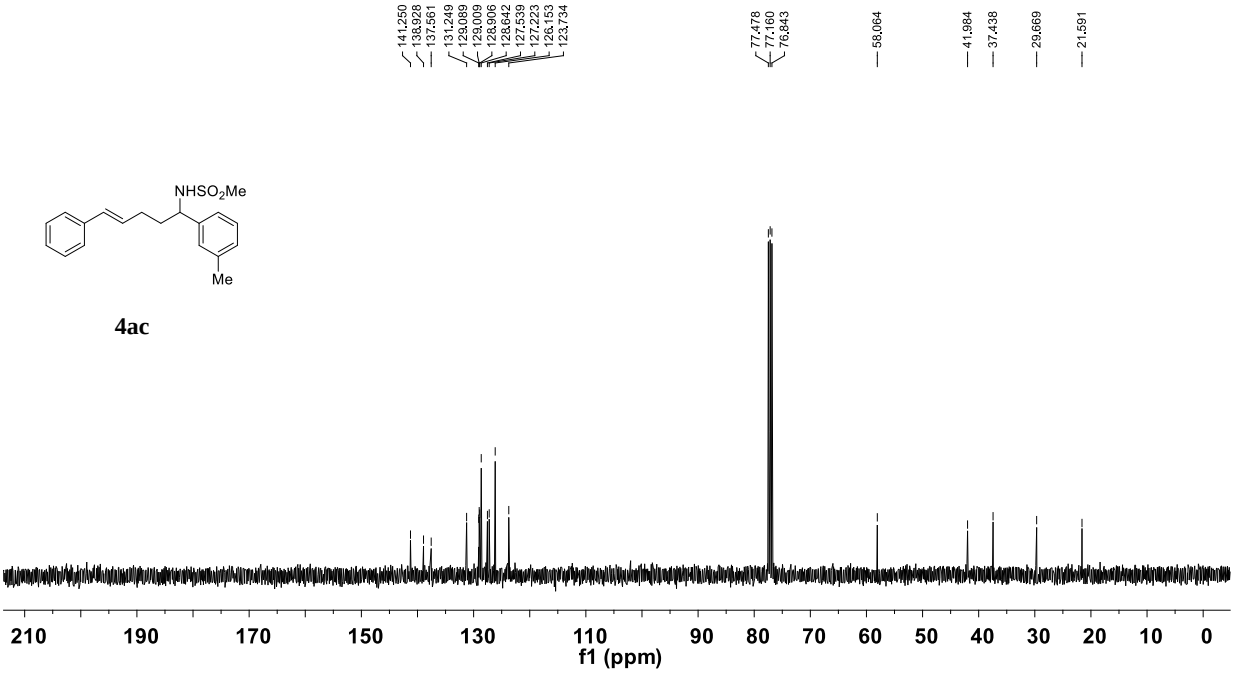


^{1}H NMR (400 MHz, $CDCl_3$)



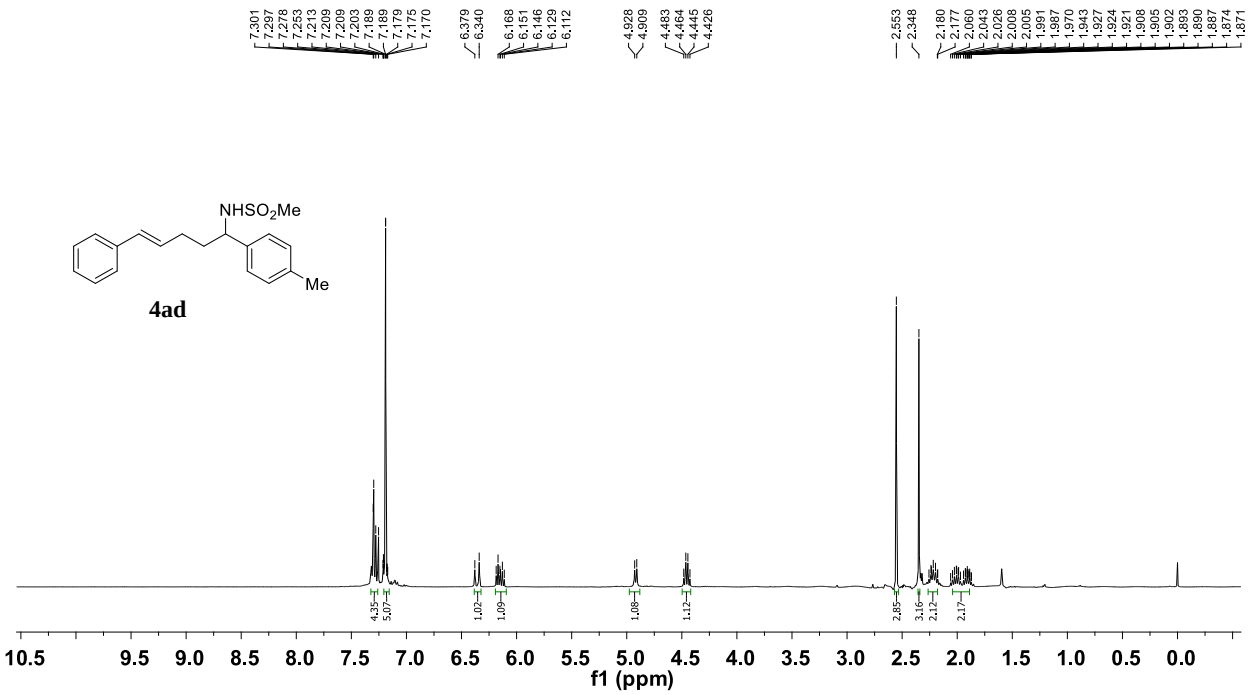
4ac

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

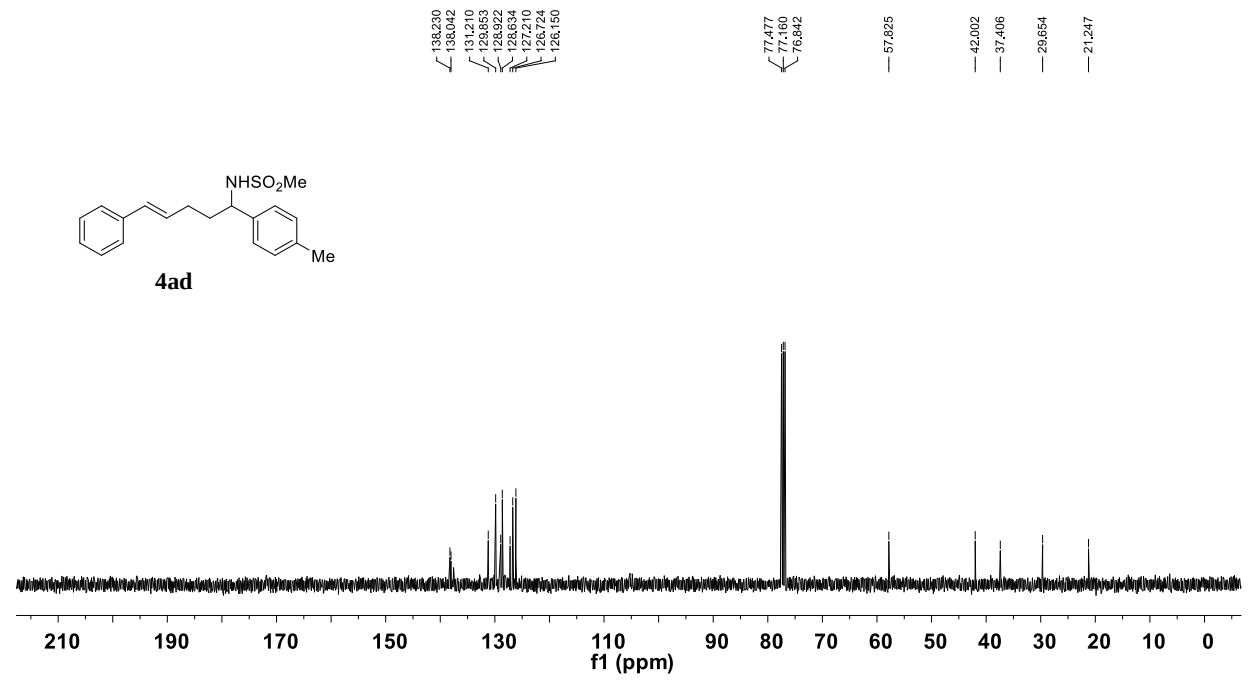


4ac

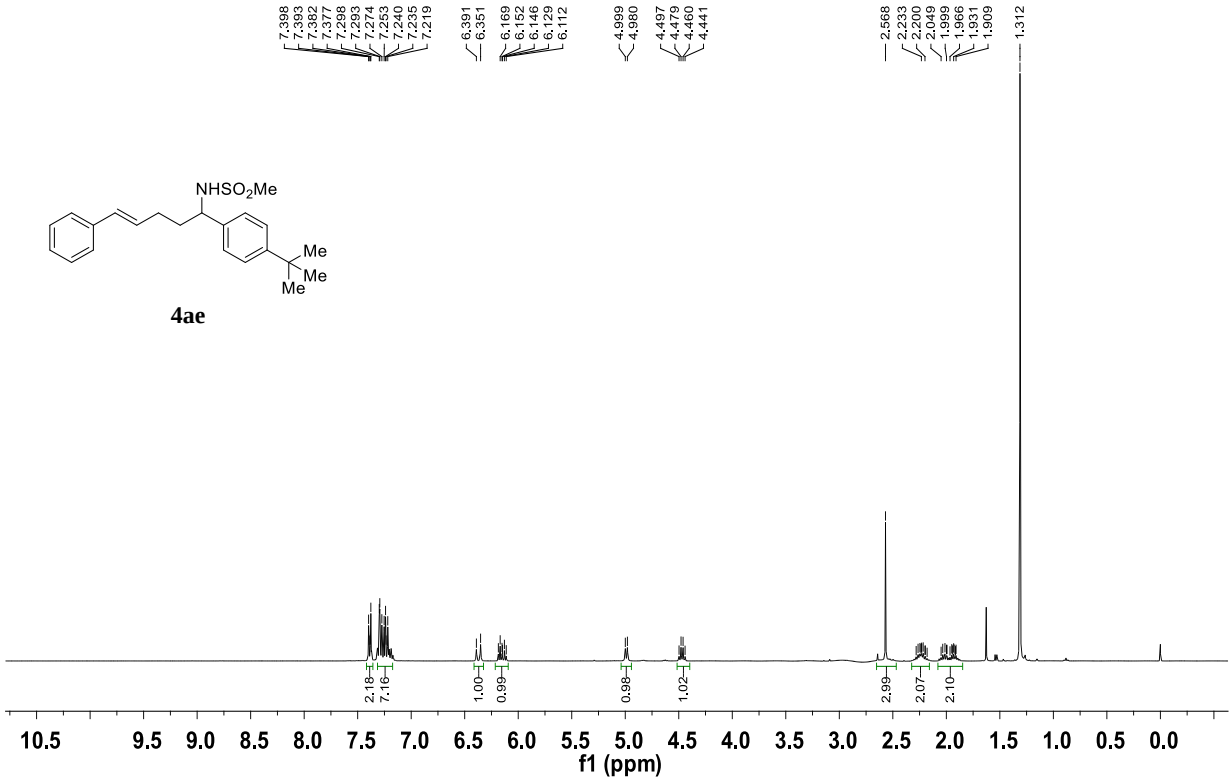
^{1}H NMR (400 MHz, $CDCl_3$)



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

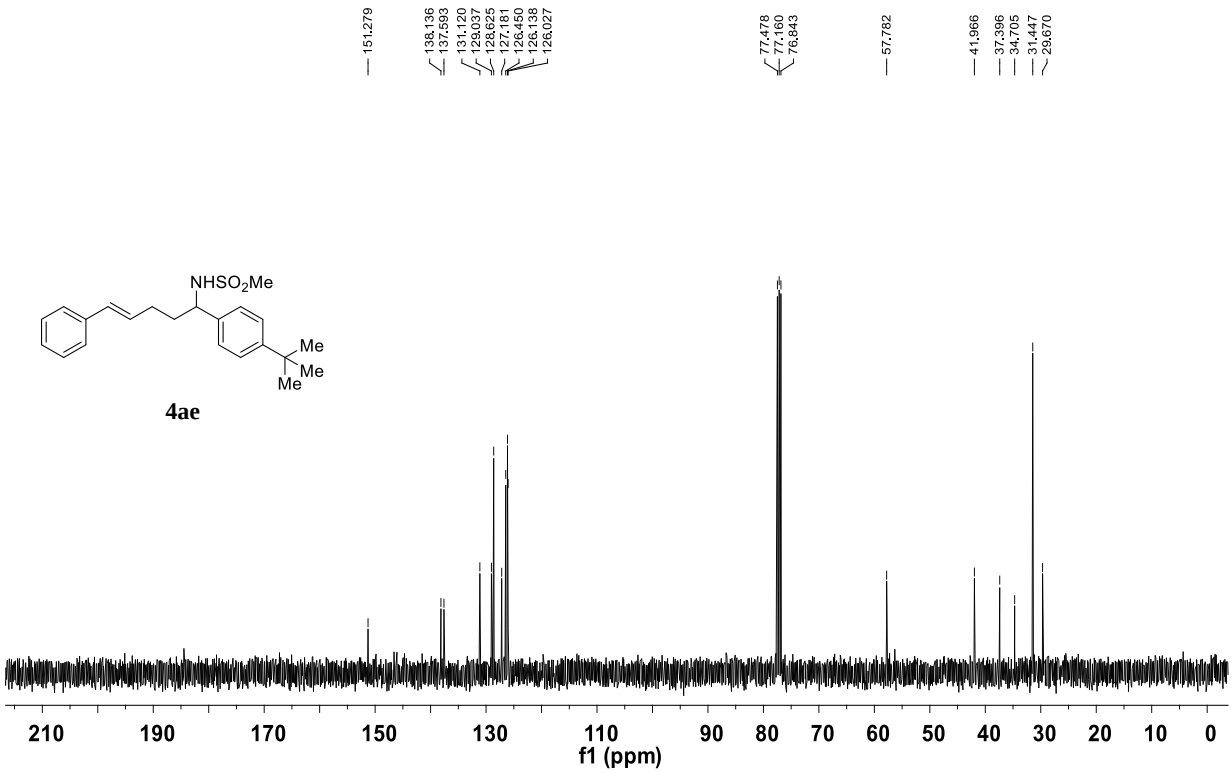


^{1}H NMR (400 MHz, $CDCl_3$)



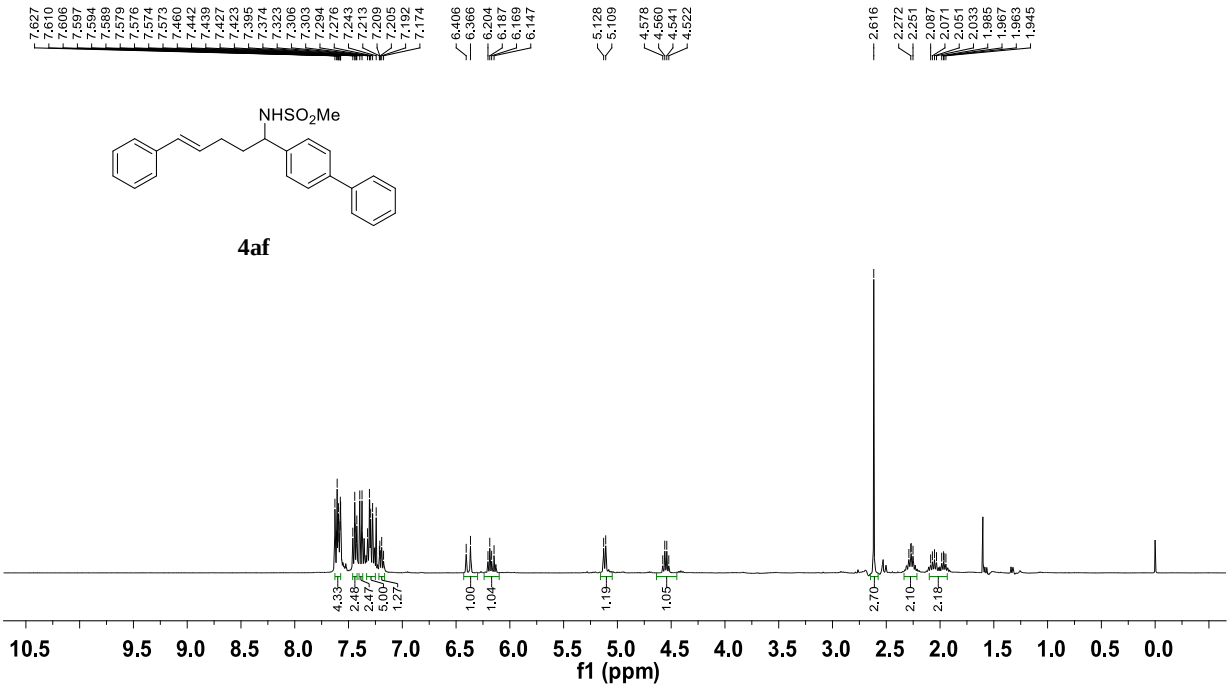
4ae

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

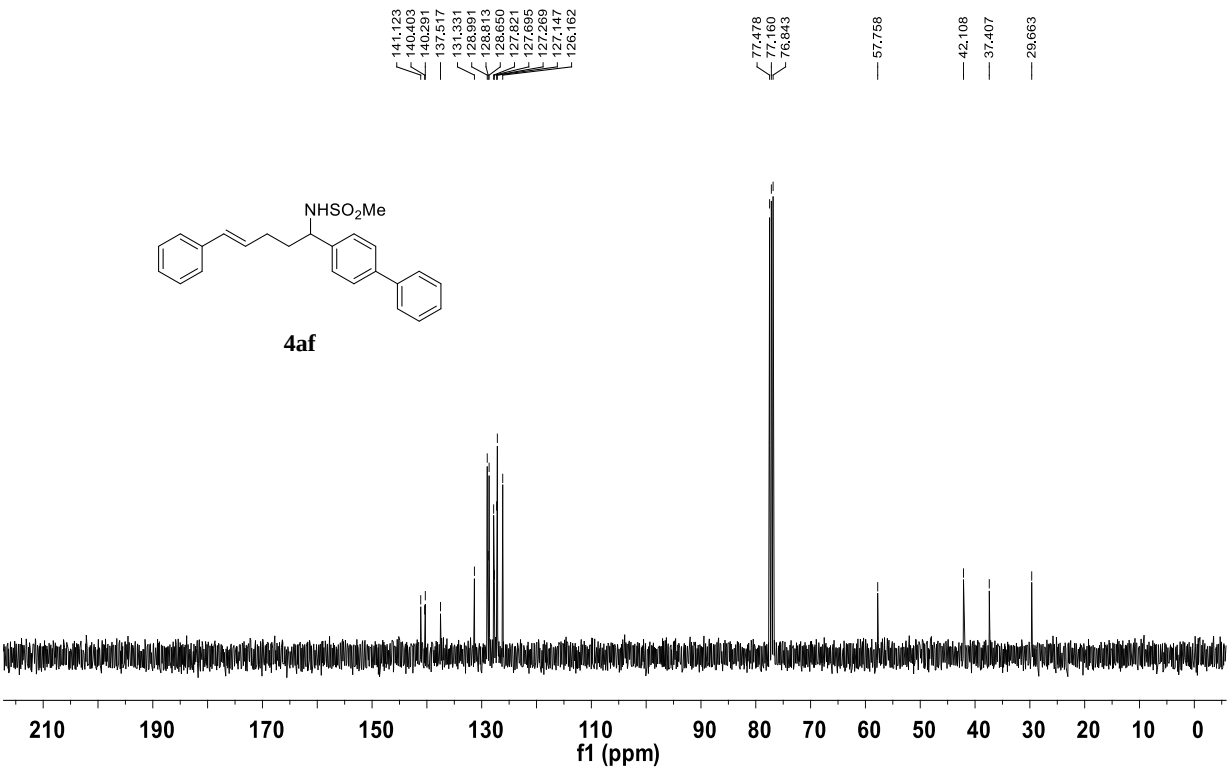


4ae

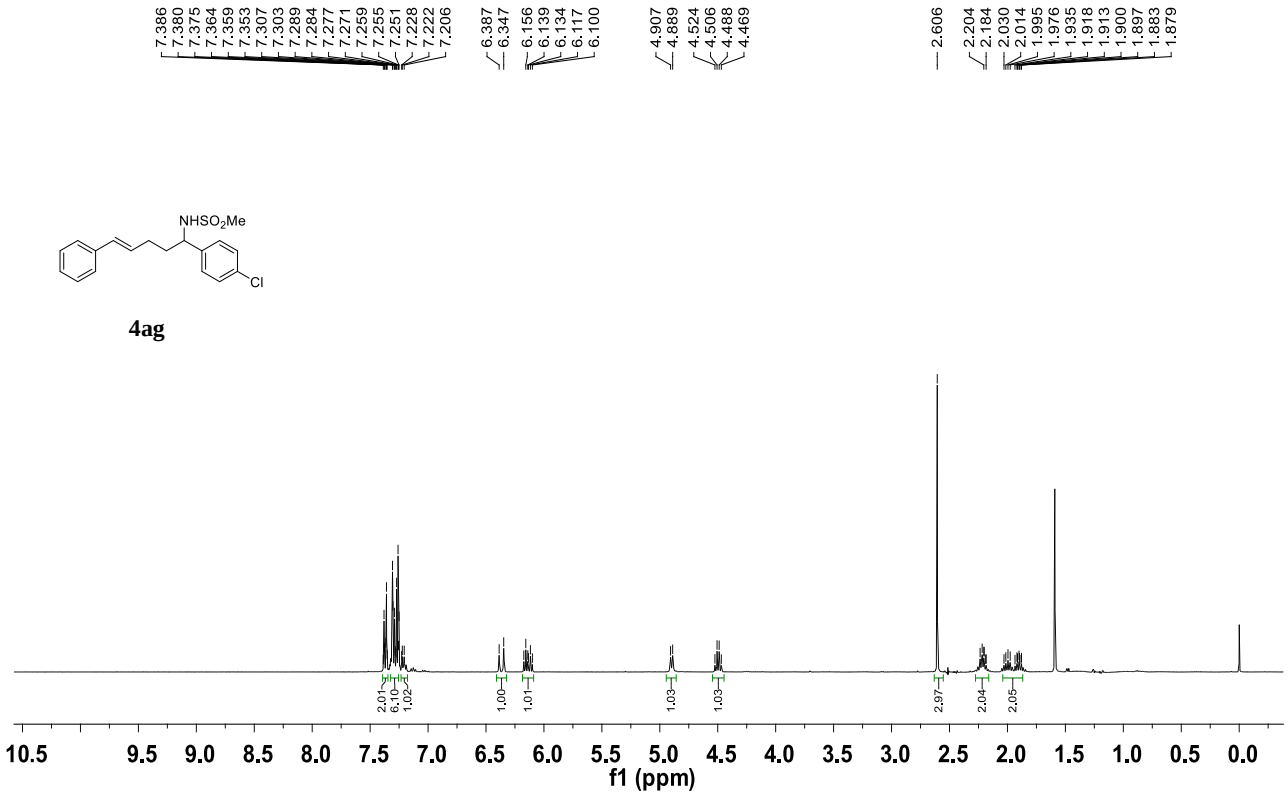
^{1}H NMR (400 MHz, $CDCl_3$)



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

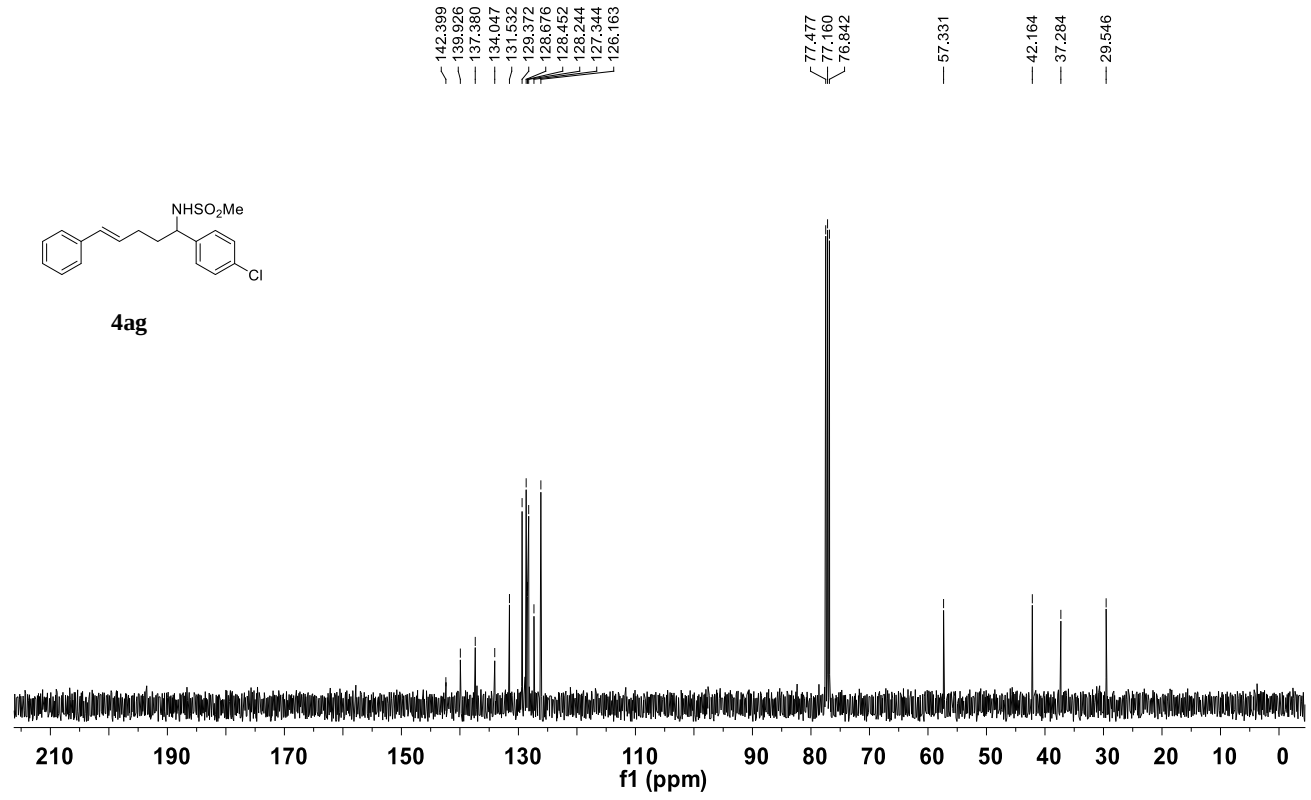


^{1}H NMR (400 MHz, $CDCl_3$)



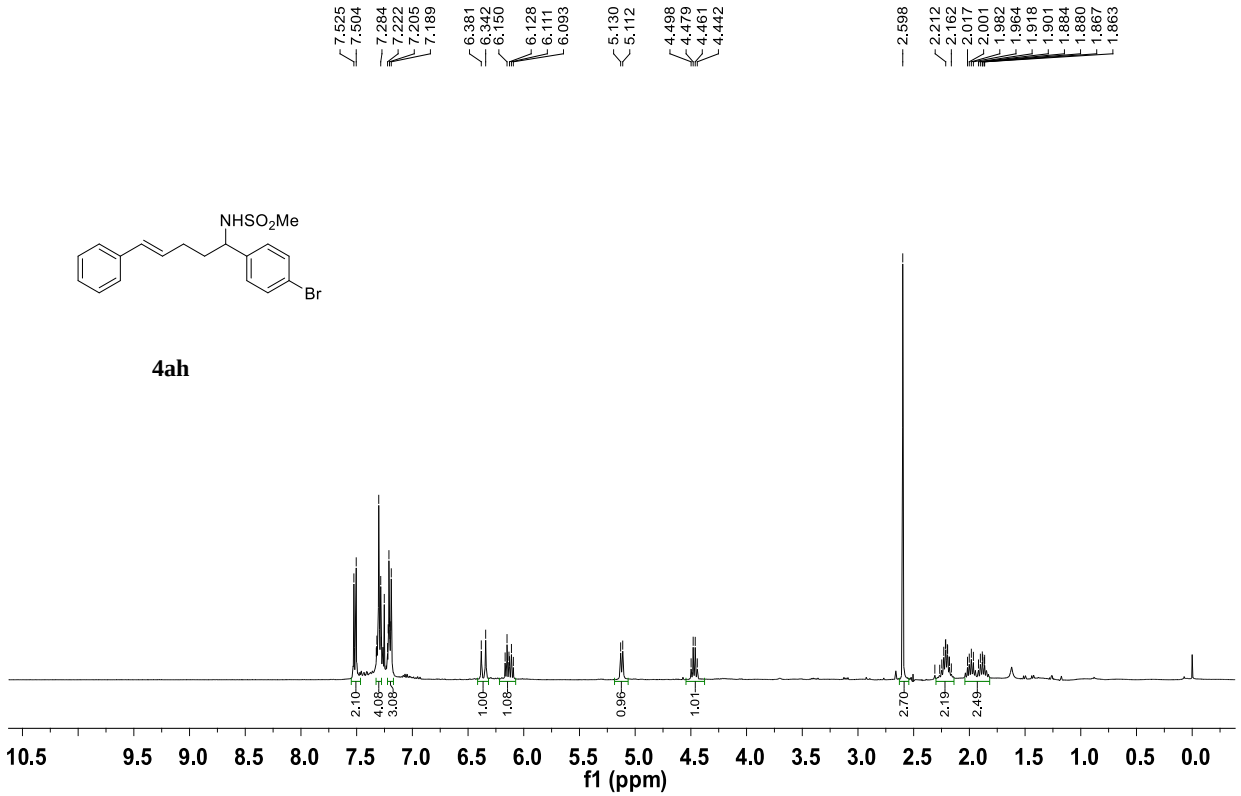
4ag

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



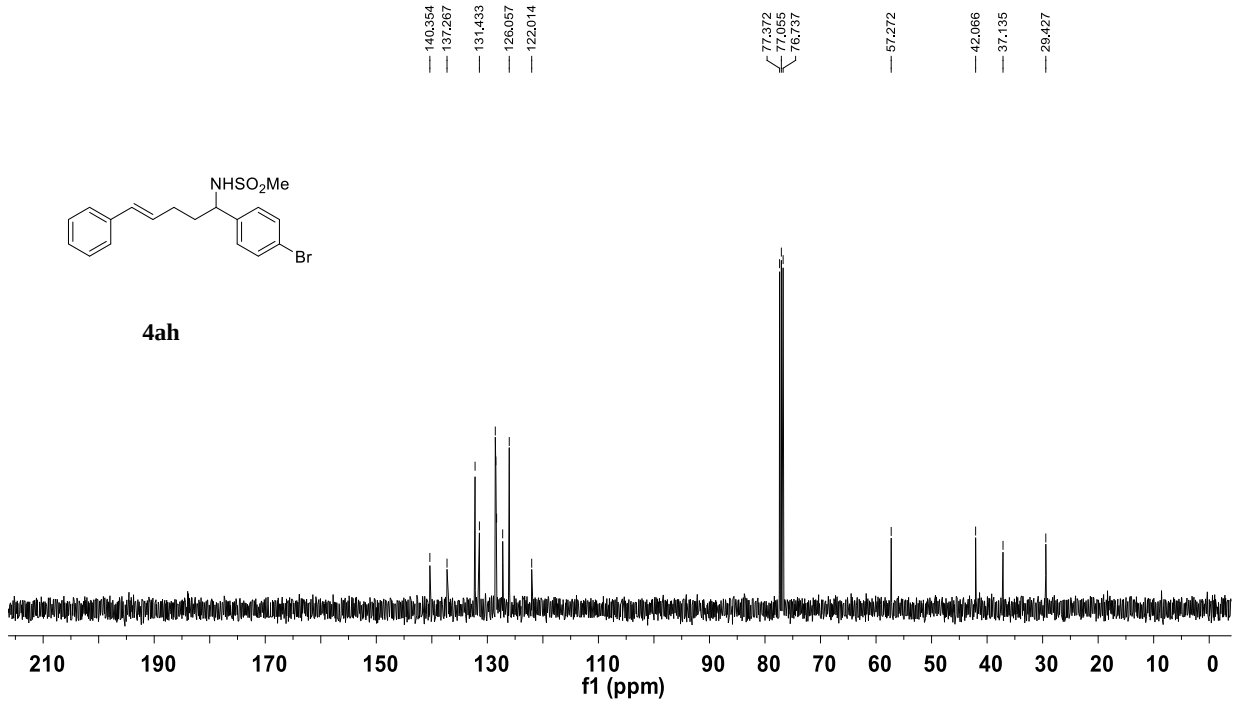
4ag

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



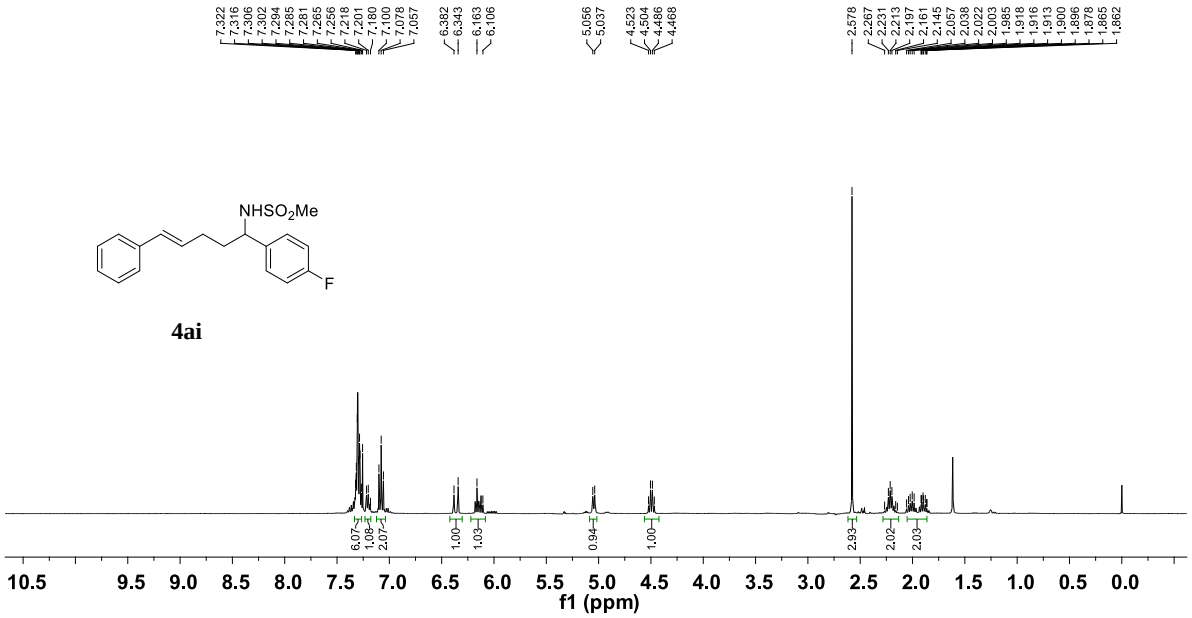
4ah

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

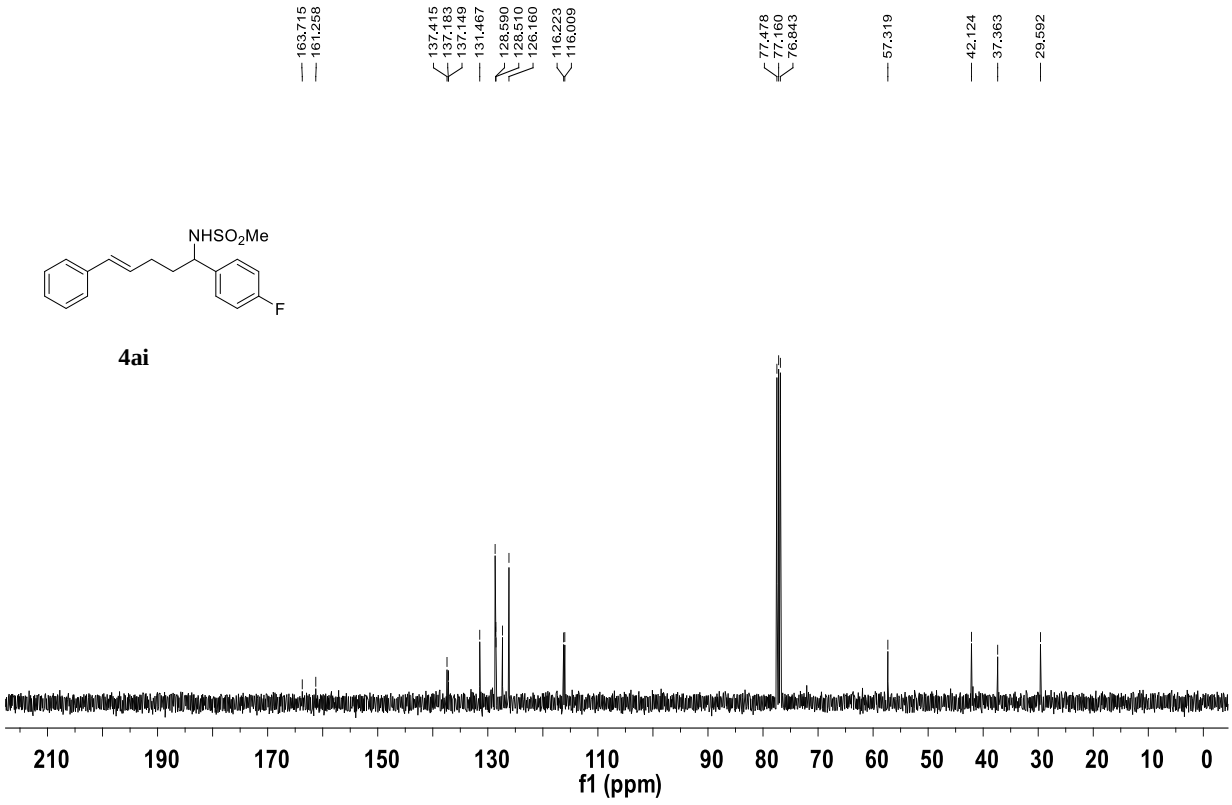


4ah

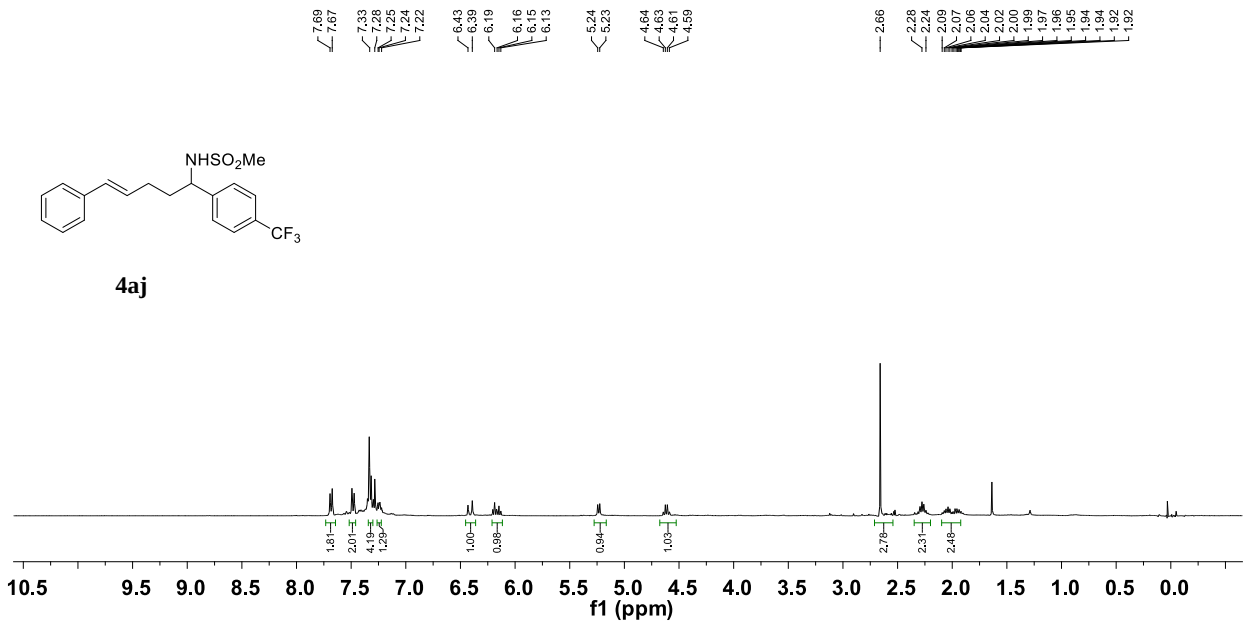
^{1}H NMR (400 MHz, $CDCl_3$)



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

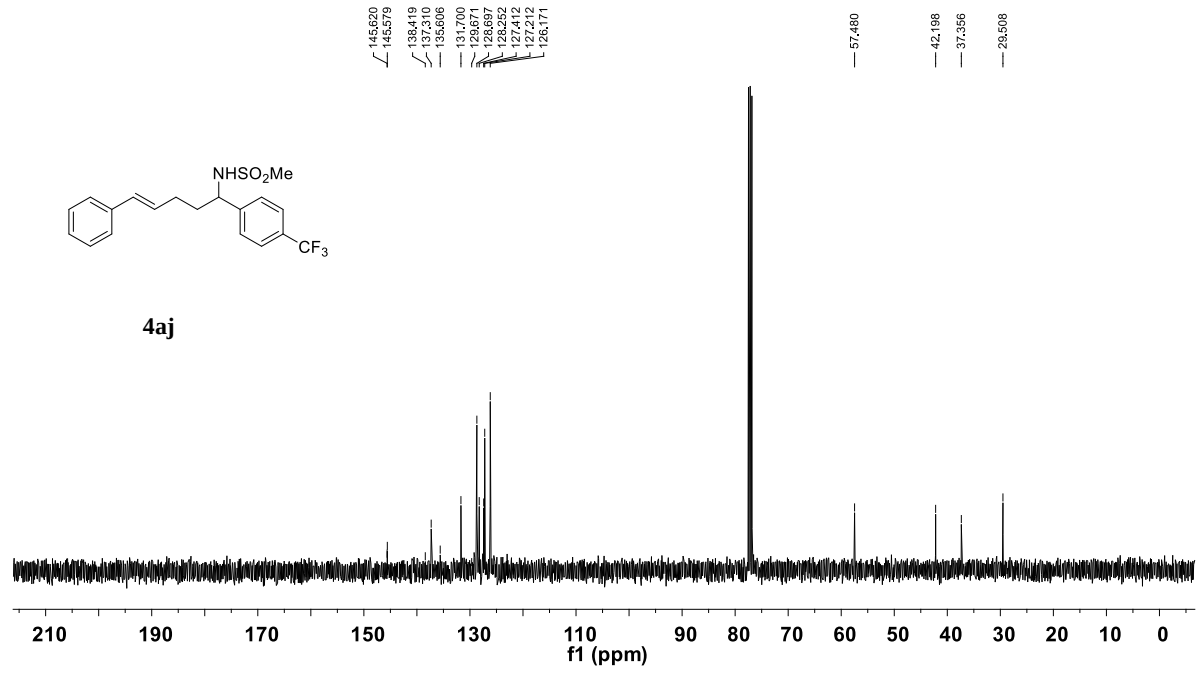


^{1}H NMR (400 MHz, $CDCl_3$)



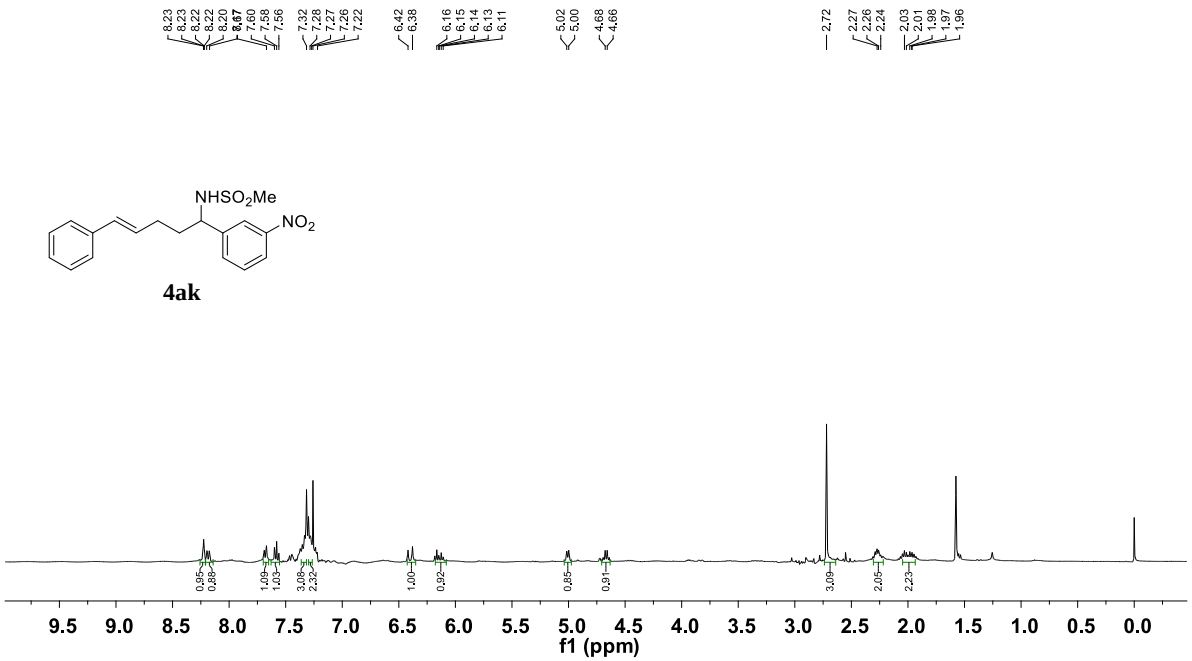
4aj

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

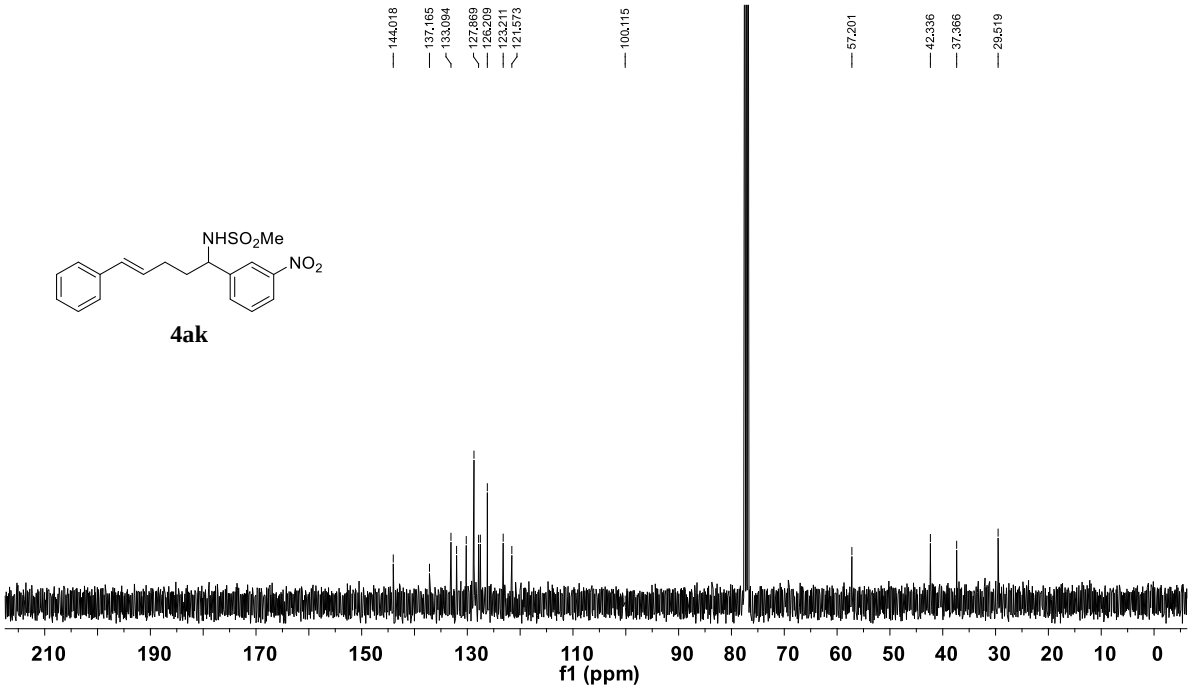


4aj

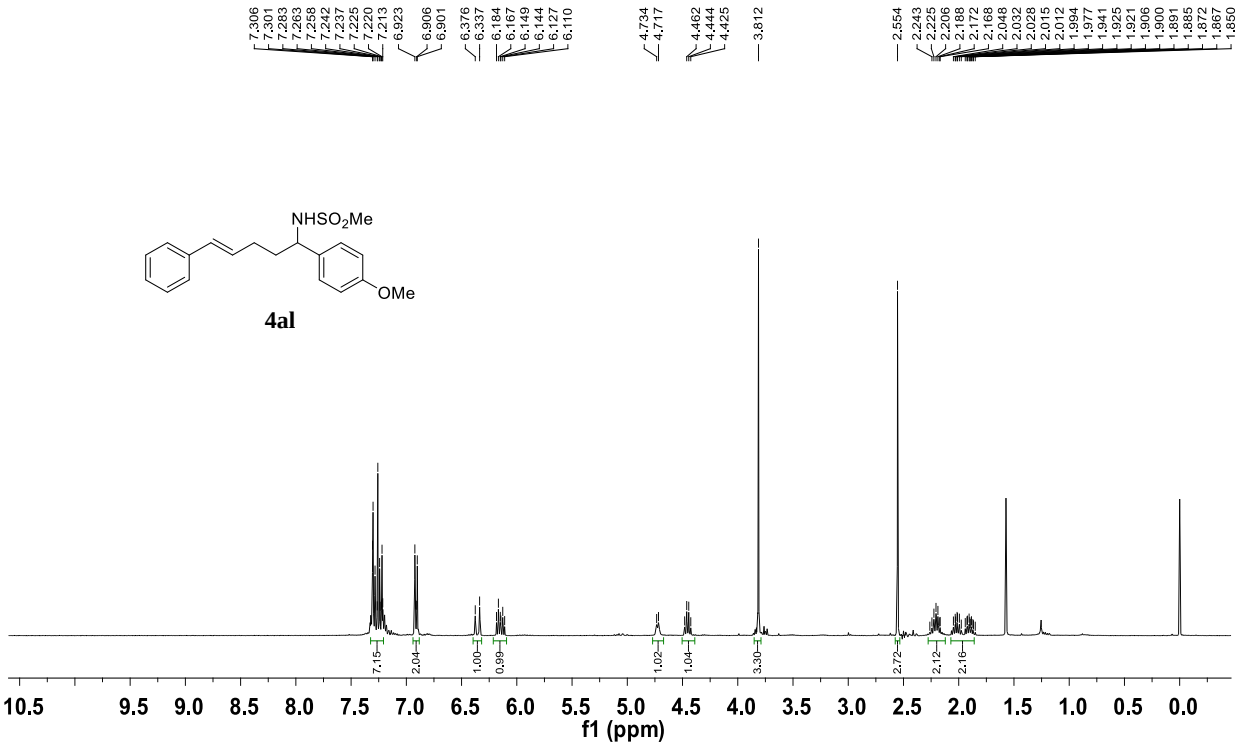
^{1}H NMR (400 MHz, $CDCl_3$)



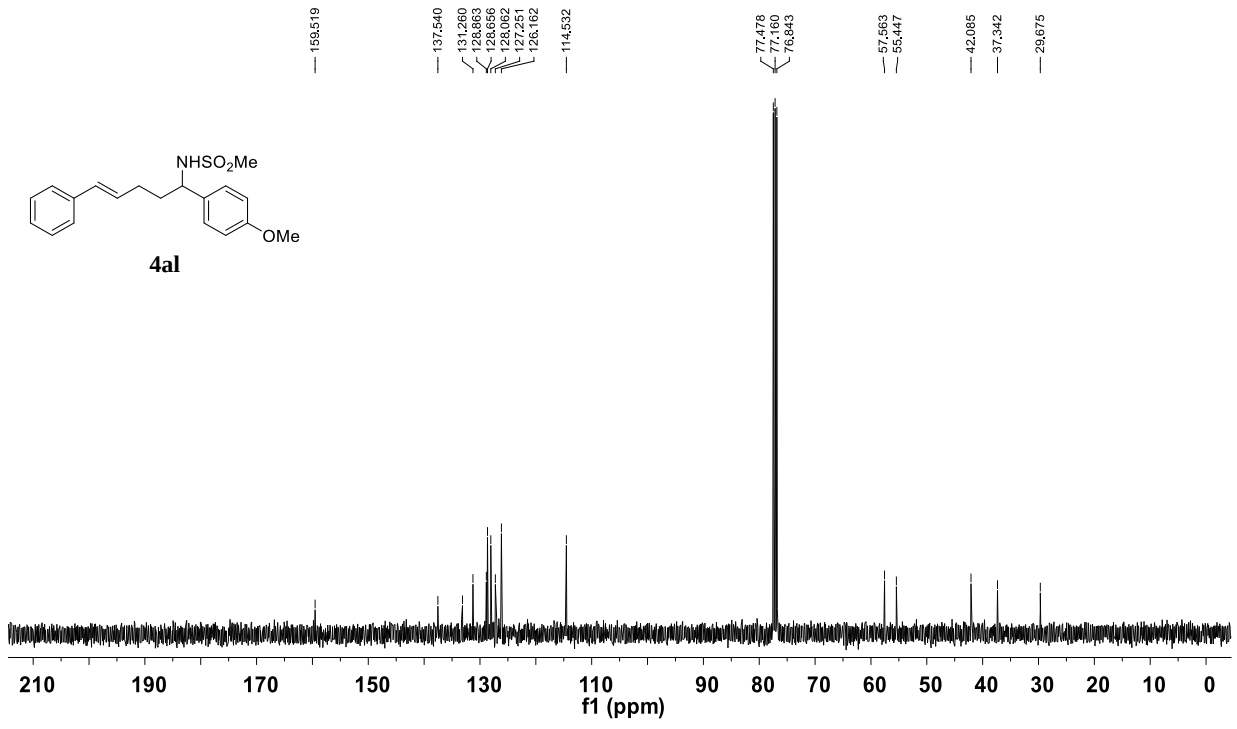
^{13}C NMR (100 MHz, $CDCl_3$)



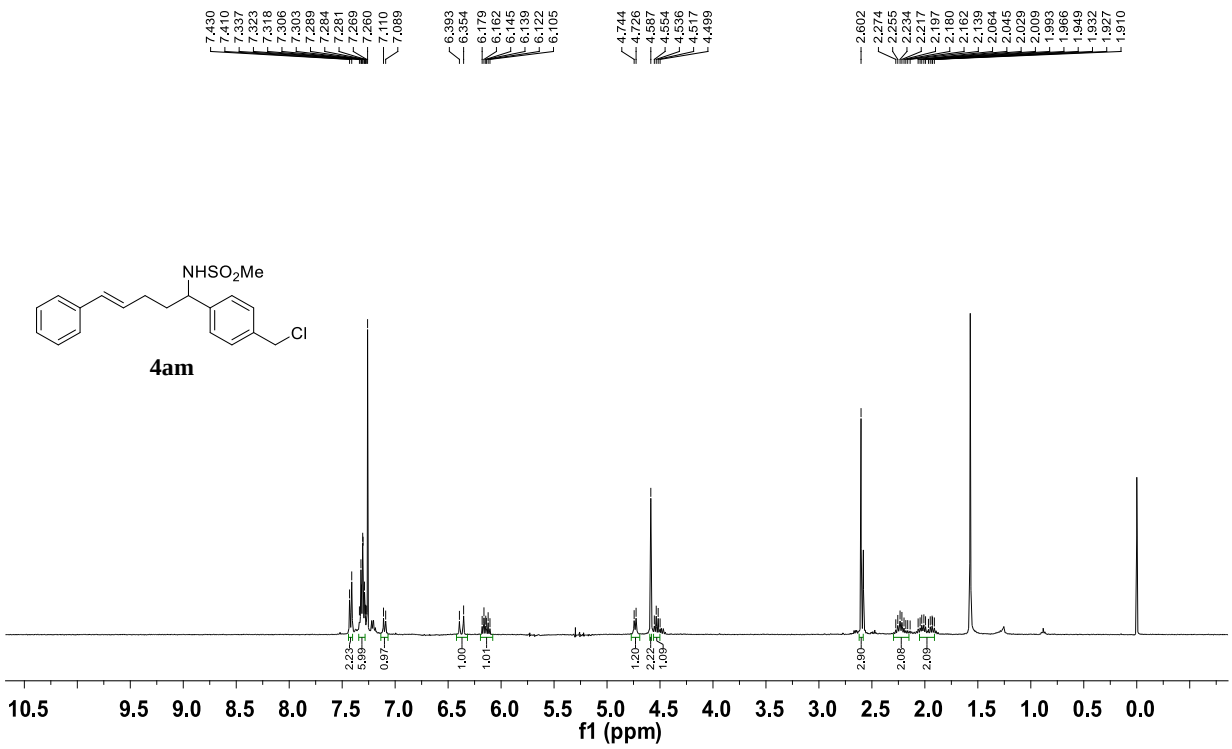
^{1}H NMR (400 MHz, $CDCl_3$)



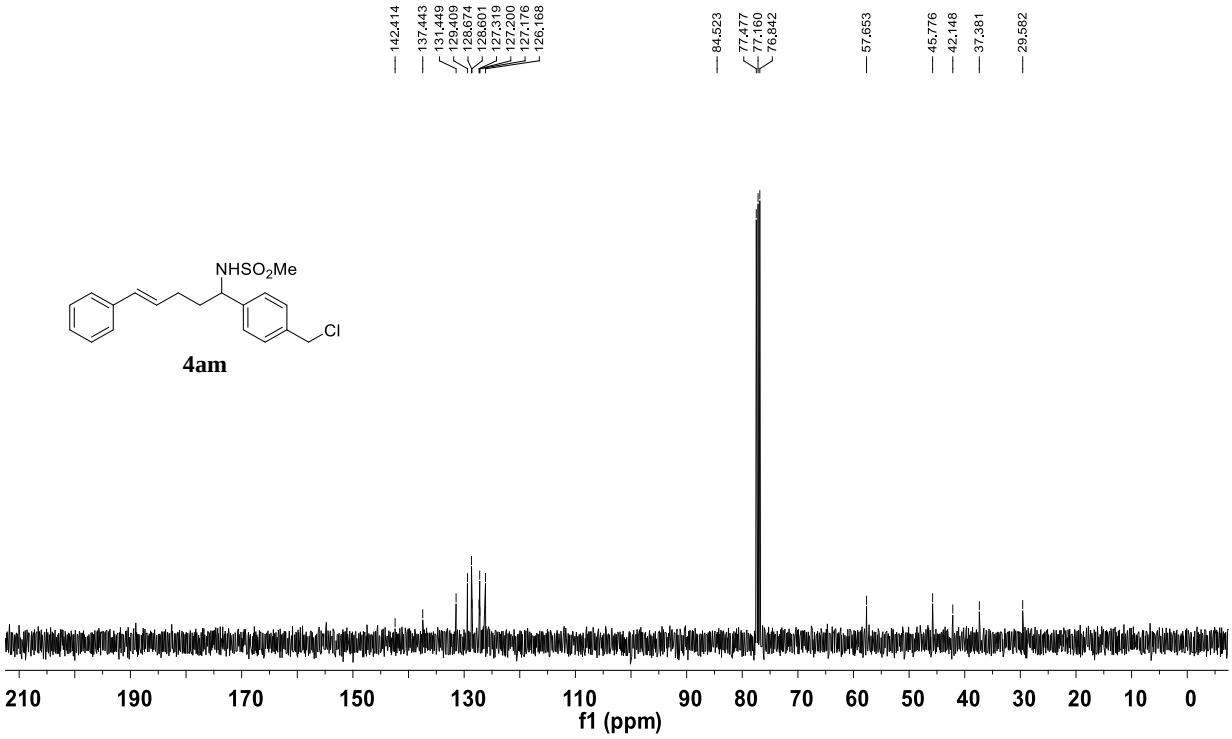
^{13}C NMR (100 MHz, $CDCl_3$)



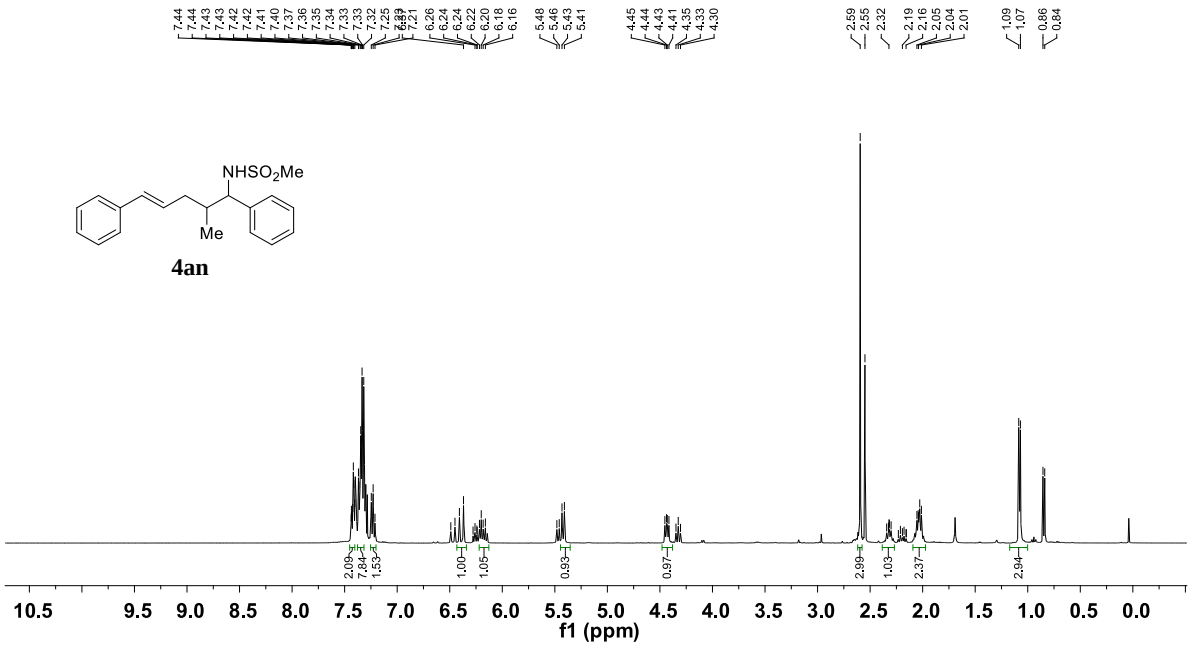
^{1}H NMR (400 MHz, $CDCl_3$)



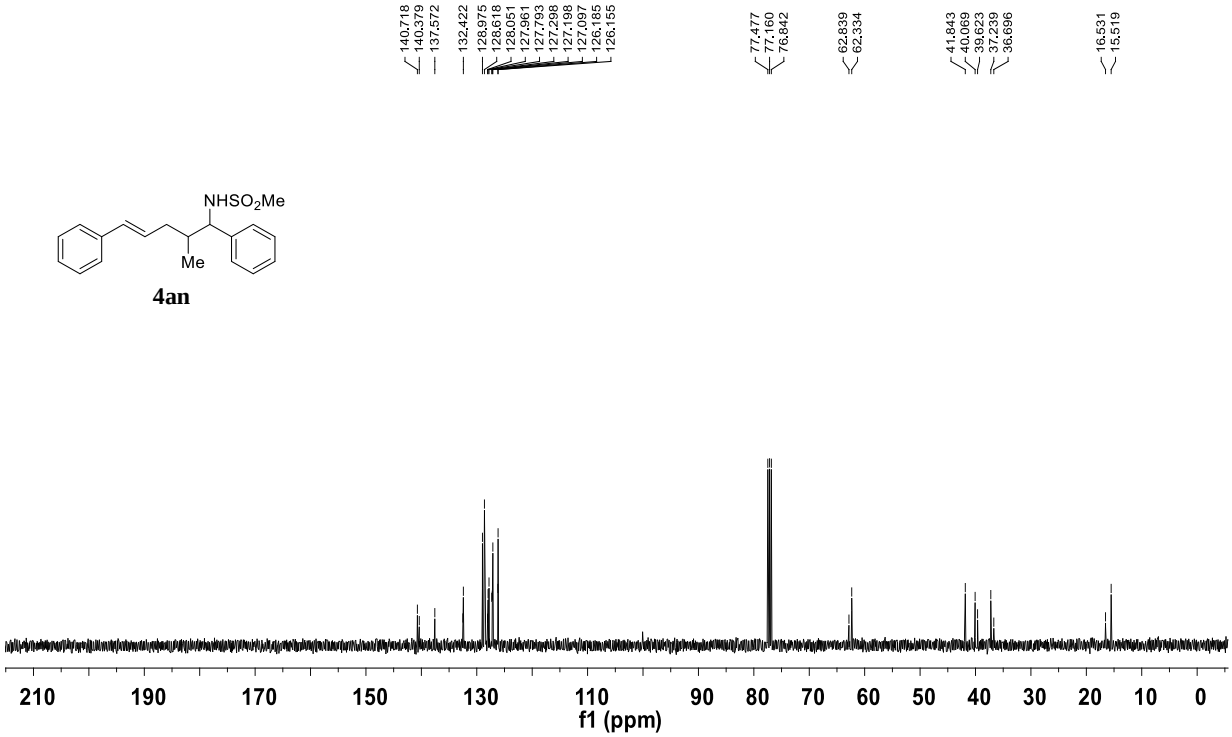
^{13}C NMR (100 MHz, $CDCl_3$)



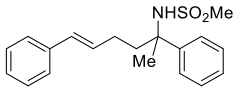
^{1}H NMR (400 MHz, $CDCl_3$)



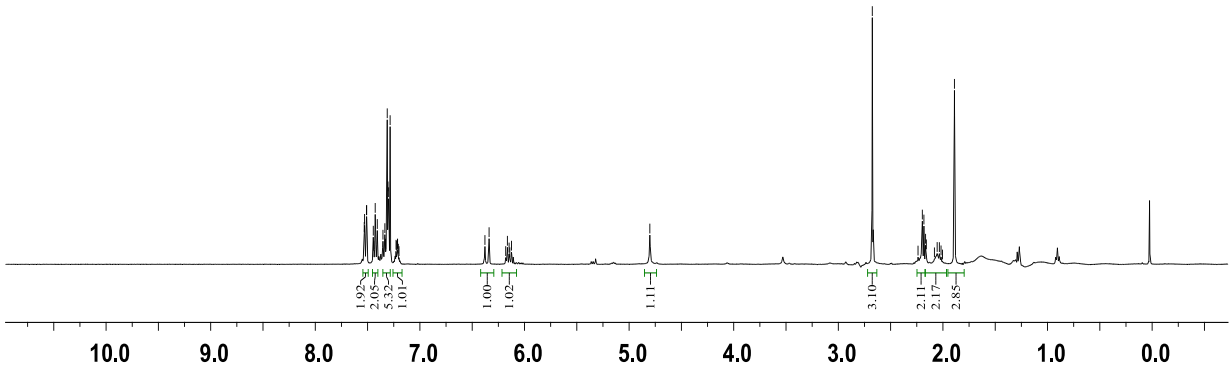
^{13}C NMR (100 MHz, $CDCl_3$)



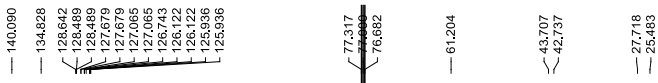
^{1}H NMR (400 MHz, $CDCl_3$)

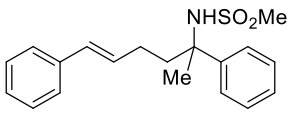


4ao



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





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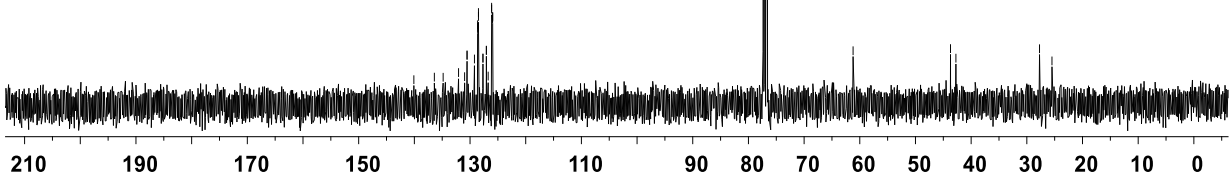
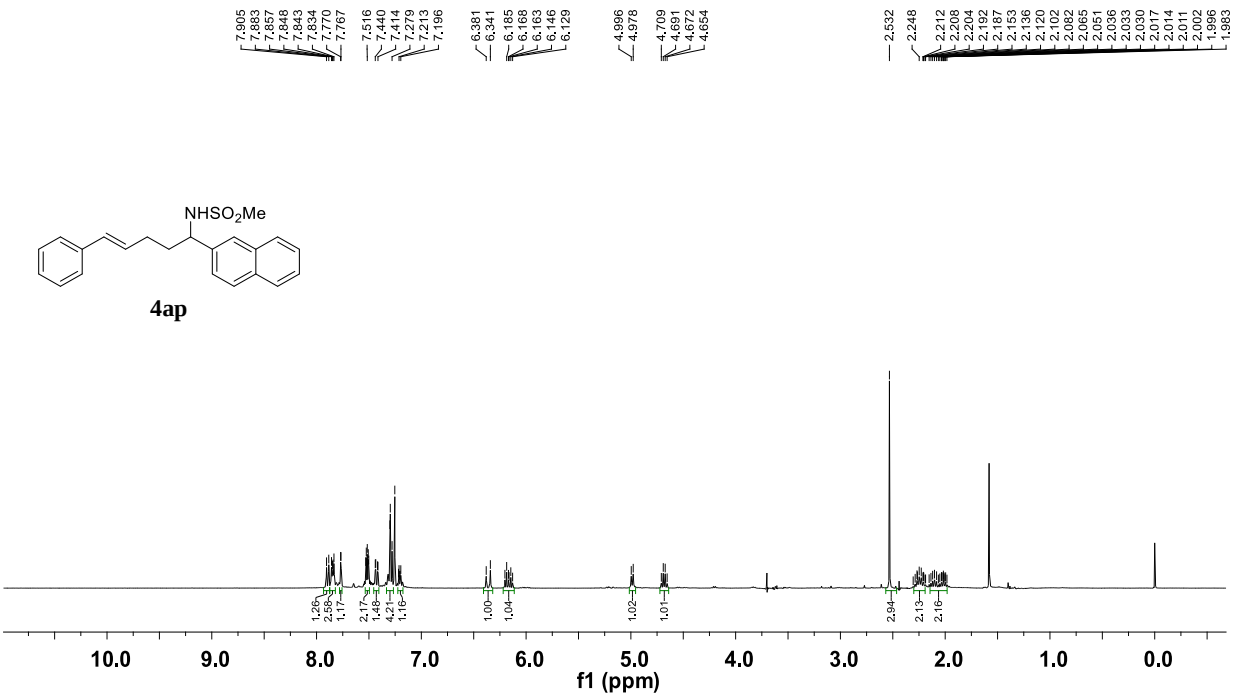
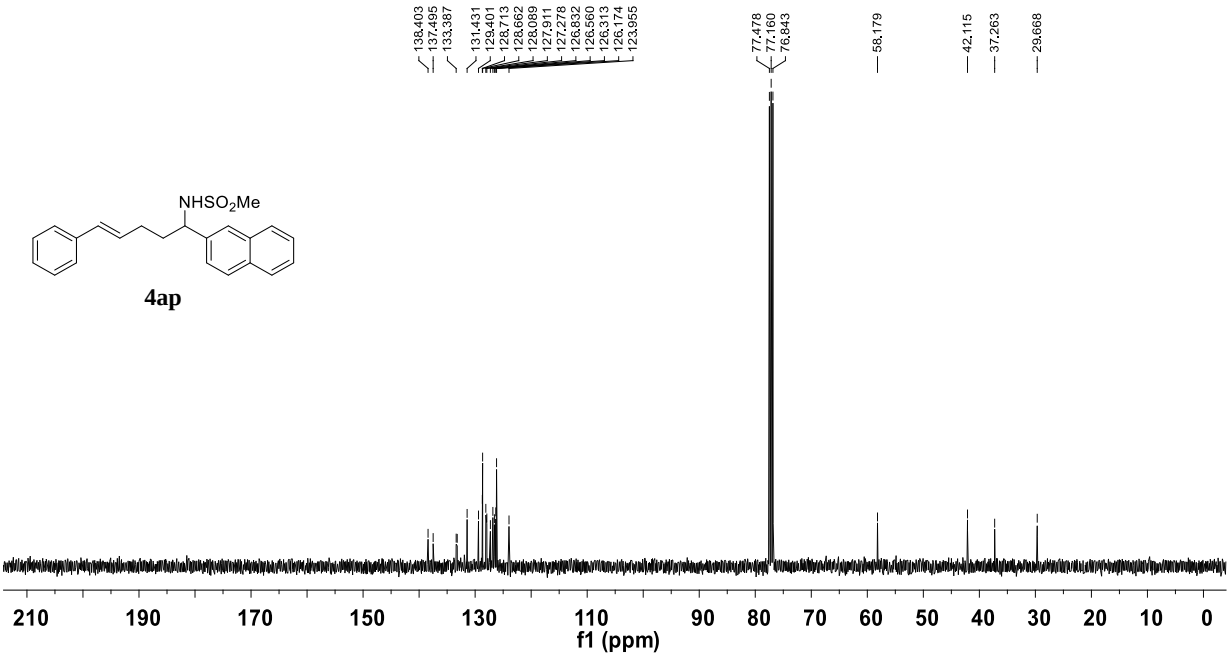


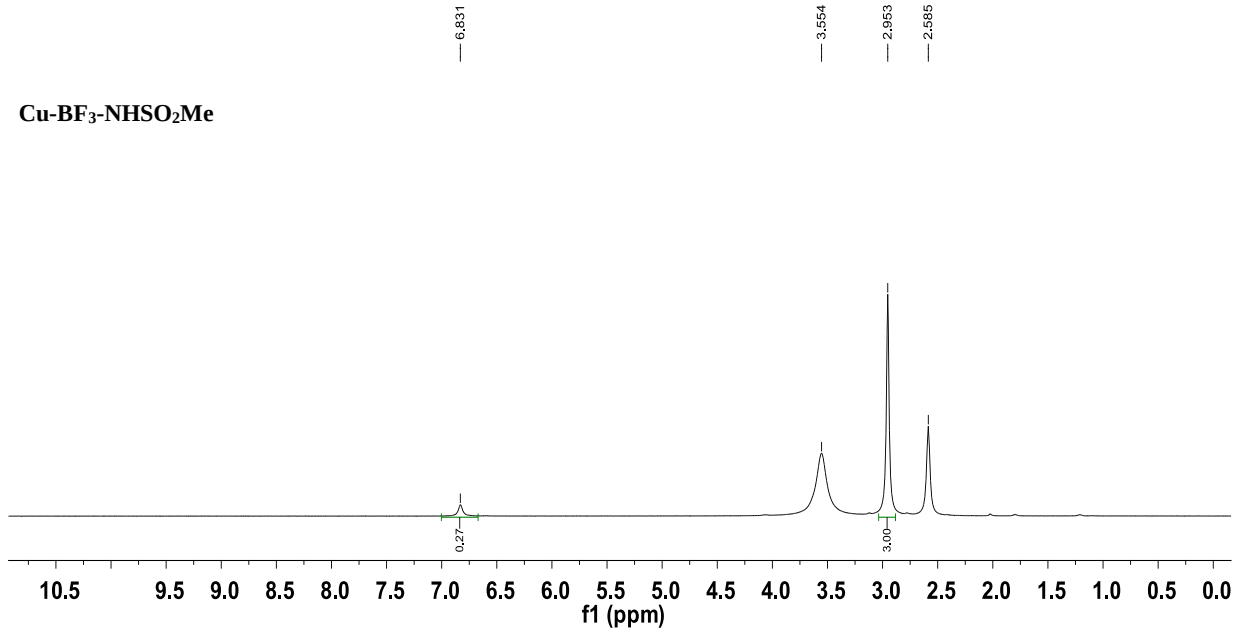
^{1}H NMR (400 MHz, $CDCl_3$)



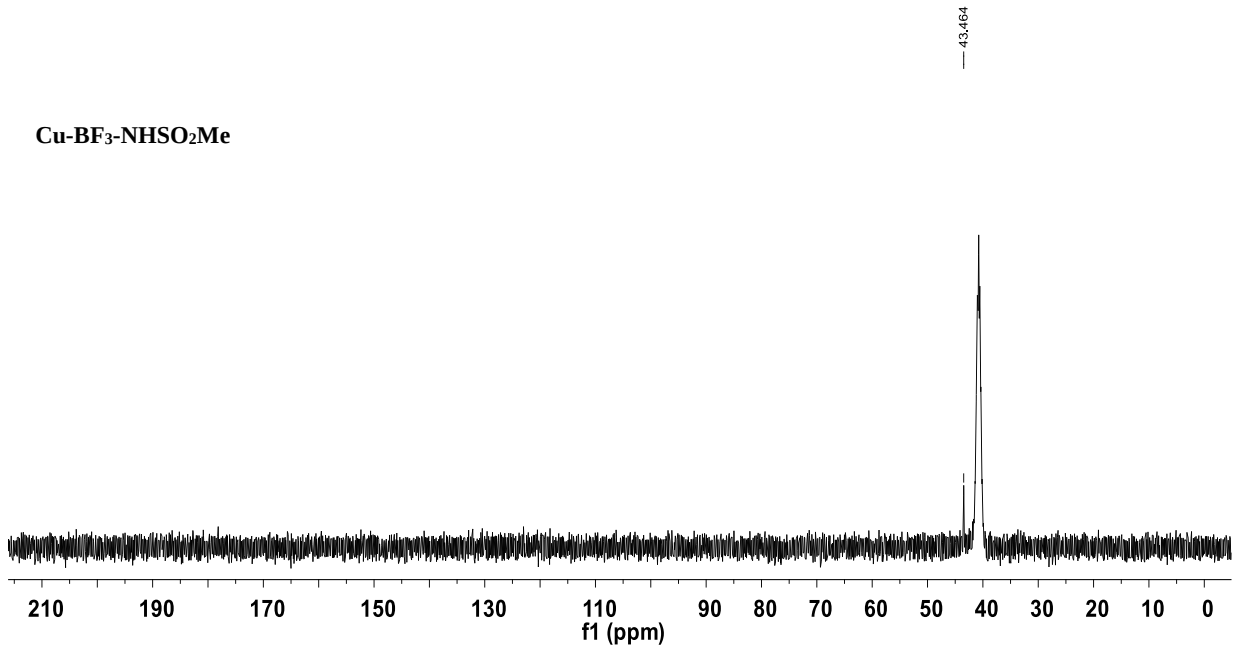
^{13}C NMR (100 MHz, $CDCl_3$)



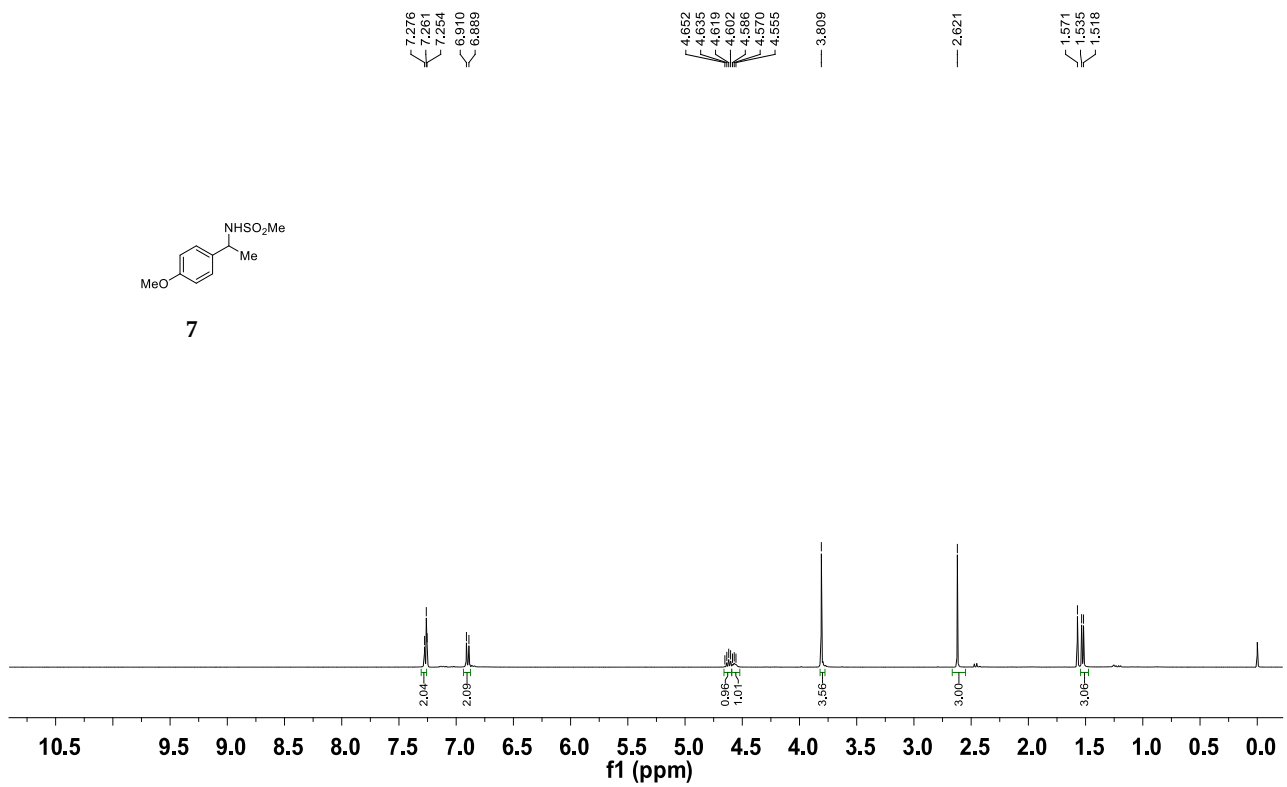
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)

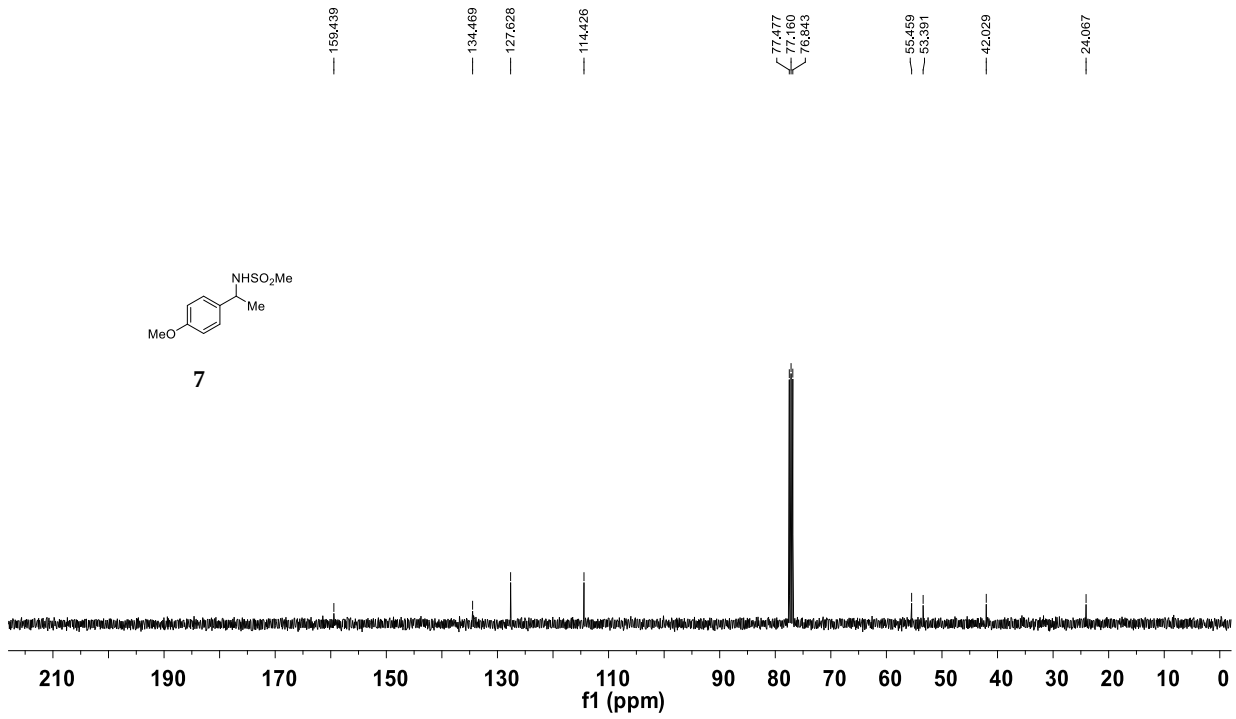


^{1}H NMR (400 MHz, $CDCl_3$)



7

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



7

^{1}H NMR (400 MHz, DMSO-d_6) of the crude mixture of styrene (2a) and complex Cu-BF_3NHSO_3Me