

CuCl₂-catalyzed highly stereoselective and chemoselective reduction of alkynyl amides into α , β - unsaturated amides using silanes as hydrogen donors

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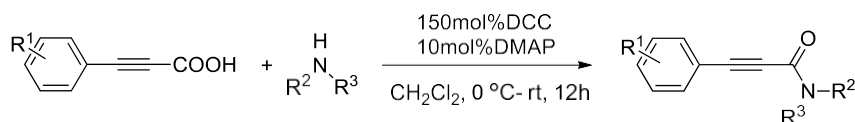
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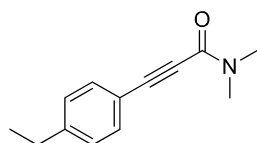
General information

Unless otherwise noted, all experiments were performed under N₂ atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. All reagents and starting materials were purchased from commercial suppliers and used as received. Infrared spectra (IR) were recorded on a Bruker TENSOR 27 FTIR spectrophotometer and were reported as wavelength numbers (cm⁻¹). ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F) recording in CDCl₃ as a solvent. Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The HRMS measurements were recorded on a TOF analyzer using an ESI source in the positive mode. Column chromatography was performed on silica gel (100–200 mesh) with mixtures of petroleum ether and ethyl acetate as the eluent.

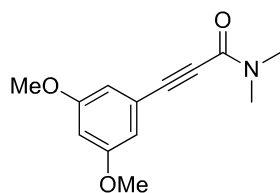
General Procedure for the synthesis of 1 and characterization data



To a mixture of amine (5 mmol) and propiolic acid (5 mmol) in CH₂Cl₂ (30 mL) was added a solution of DMAP (0.5 mmol, 10 mol%) and DCC (7.5 mmol, 1.5 equiv) in CH₂Cl₂ (20 mL) at 0°C. The reaction mixture was stirred for 12 hours at room temperature and filtered through a short plug of silica gel, which was rinsed with EtOAc. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether /ethyl acetate = 4/1).

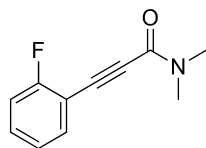


2-Propynamide, N,N-dimethyl-3-(4-ethylphenyl)- (1c); White solid was obtained in 70% (0.70 g) isolated yield; IR (KBr) ν : 2964, 2930, 2209, 1639, 1510, 1452, 1395, 1271, 1132, 1056, 835, 730, 667; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.18 (s, 3H), 2.92 (s, 3H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.75, 146.68, 132.36, 128.08, 117.64, 90.58, 81.14, 38.35, 34.09, 28.87, 15.18; HRMS (ESI) *m/z* calcd for C₁₃H₁₅NO [M+H]⁺ 202.1126, Found 202.1124.

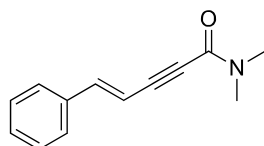


2-Propynamide, N,N-dimethyl-3-(3,5-dimethoxyphenyl)- (1f); White solid was obtained in 71% (0.83 g) isolated yield; IR (KBr) ν : 2934, 2220, 1632, 1592, 1457, 1396, 1351, 1264, 1203, 1157, 1061, 841, 732; ¹H NMR (400 MHz, CDCl₃) δ 6.65 (s, 2H), 6.48 (s, 1H), 3.74 (s, 6H), 3.25 (s, 3H), 2.99 (s,

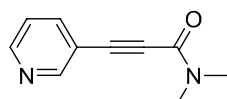
3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.58, 154.47, 121.77, 110.02, 103.27, 90.07, 80.95, 55.46, 38.36, 34.11; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 234.1125, Found 234.1121.



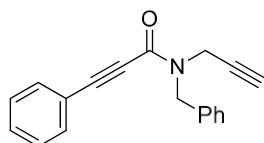
2-Propynamide, N,N-dimethyl-3-(2-fluorophenyl)- (1j); White solid was obtained in 75% (0.72 g) isolated yield; IR (KBr) ν : 2934, 2218, 1623, 1493, 1453, 1396, 1262, 1215, 1138, 770, 728, 685; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (t, $J = 7.2$ Hz, 1H), 7.41 (dd, $J = 14.2, 6.9$ Hz, 1H), 7.18-7.07 (m, 2H), 3.31 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.31 (d, $J = 254.0$ Hz), 154.28, 134.19, 131.92 (d, $J = 8.1$ Hz), 124.25 (d, $J = 3.7$ Hz), 115.68 (d, $J = 20.5$ Hz), 109.42 (d, $J = 15.2$ Hz), 86.42 (d, $J = 9.9$ Hz), 83.43, 38.33, 34.18; ^{19}F NMR (376MHz, CDCl_3) δ -108.42; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{FNO}$ $[\text{M}+\text{H}]^+$ 192.0819, Found 192.0817.



4-Pentenamide, 2-alkynyl-N,N-dimethyl-5-phenyl-, (4E)- (1m); White solid was obtained in 53% (1.08 g) isolated yield; IR (KBr) ν : 2926, 2192, 1624, 1488, 1441, 1391, 1268, 1184, 1069, 956, 730, 689; ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.31 (m, 5H), 7.17 (d, $J = 16.3$ Hz, 1H), 6.26 (d, $J = 16.3$ Hz, 1H), 3.26 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.70, 145.55, 135.37, 129.62, 128.87, 126.72, 105.62, 89.83, 83.41, 38.36, 34.15; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{NO}$ $[\text{M}+\text{Na}]^+$ 222.0889, Found 222.0892.



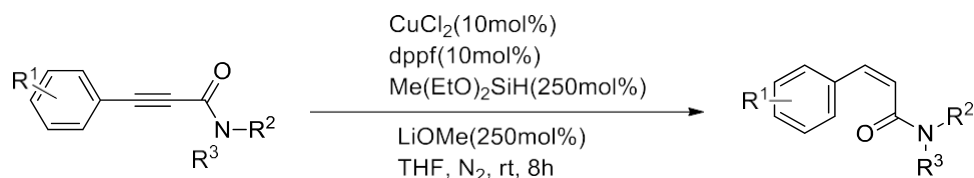
N,N-dimethyl-3-(pyridin-3-yl)propiolamide (1o); White solid was obtained in 62% (0.58 g) isolated yield; IR (KBr) ν : 3039, 2919, 2850, 2215, 1620, 1558, 1495, 1403, 1270, 1189, 1133, 1019, 704; ^1H NMR (400 MHz, CDCl_3) δ 8.77 (s, 1H), 8.63 (d, $J = 3.8$ Hz, 1H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.33 (dd, $J = 7.8, 5.0$ Hz, 1H), 3.30 (s, 1H), 3.05 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.03, 152.67, 150.14, 139.31, 123.19, 117.97, 86.61, 84.51, 38.40, 34.24; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 175.0866, Found 175.0863.



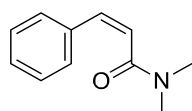
2-Propynamide, 3-phenyl-N-(phenylmethyl)-N-2-propyn-1-yl- (1v); Yellow oil was obtained in 79% (1.08 g) isolated yield; IR (KBr) ν : 3294, 3032, 2925, 2214, 1629, 1492, 1411, 1359, 1268, 1196, 1044, 920, 756, 688; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.24 (m, 10H), 5.00 (s, 1H), 4.80 (s, 1H), 4.33 (s, 1H), 4.19 (s, 1H), 2.31 (d, $J = 37.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.27, 135.58, 132.54,

130.32, 128.94, 128.79, 128.60, 128.19, 127.90, 120.20, 91.11, 81.28, 80.94, 73.24, 72.60, 51.59, 46.78, 37.65, 32.54; HRMS (ESI) m/z calcd for $C_{19}H_{15}NO$ $[M+Na]^+$ 296.1046, Found 296.1045.

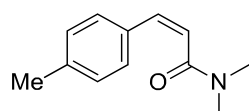
General procedure for the synthesis of **2** and characterization data



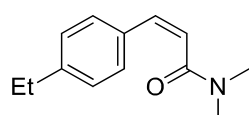
$CuCl_2$ (6.7 mg, 0.05 mmol, 10 mol%) and $dppf$ (27.8 mg, 0.05 mmol, 10 mol%) were dissolved in THF (2mL). Subsequently, **1** (0.5 mmol), $Me(EtO)_2SiH$ (167.8 mg, 1.25 mmol, 2.5 equiv.) and $LiOMe$ (47.5 mg, 1.25 mmol, 2.5 equiv.) were added in a Schlenk flask under nitrogen atmosphere. After being stirred at room temperature for 8 h, the resulting mixture was extracted with $AcOEt$ (3×5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 4/1) to give product **2**.



2-Propenamide, N,N-dimethyl-3-phenyl-, (Z)- (2a)¹; Colorless oil was obtained in 92% (81 mg) isolated yield; IR (KBr) ν : 3025, 2928, 1634, 1496, 1445, 1401, 1376, 1265, 1143, 782, 701; 1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 6.64 (d, $J = 12.6$ Hz, 1H), 6.03 (d, $J = 12.6$ Hz, 1H), 2.97 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.97, 135.64, 133.27, 128.56, 128.39, 128.15, 123.43, 37.46, 34.36.

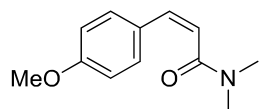


2-Propenamide, N,N-dimethyl-3-(4-methylphenyl)-, (Z)- (2b); Colorless oil was obtained in 96% (91 mg) isolated yield; IR (KBr) ν : 3019, 2964, 2930, 1642, 1512, 1454, 1402, 1374, 1266, 1141, 872, 837; 1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 6.60 (d, $J = 12.6$ Hz, 1H), 5.97 (d, $J = 12.6$ Hz, 1H), 2.98 (s, 3H), 2.83 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.21, 138.36, 133.25, 132.82, 129.26, 128.10, 122.40, 37.50, 34.37, 21.27; HRMS (ESI) m/z calcd for $C_{12}H_{15}NO$ $[M+H]^+$ 190.1226, Found 190.1225.

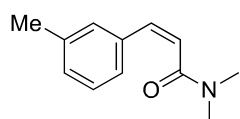


2-Propenamide, N,N-dimethyl-3-(4-ethylphenyl)-, (Z)- (2c); Colorless oil was obtained in 91% (92 mg) isolated yield; IR (KBr) ν : 3022, 2921, 1636, 1510, 1454, 1398, 1373, 1263, 1139, 869, 821; 1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 6.59 (d, $J = 12.6$ Hz, 1H),

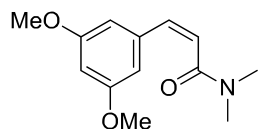
5.97 (d, $J = 12.6$ Hz, 1H), 2.98 (s, 3H), 2.83 (s, 3H), 2.62 (q, $J = 7.5$ Hz, 2H), 1.21 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.15, 144.65, 133.24, 133.01, 128.20, 128.03, 122.41, 37.47, 34.33, 28.95, 15.34; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$ 204.1383, Found 204.1384.



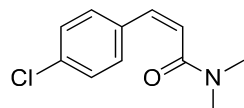
2-Propenamide, N,N-dimethyl-3-(4-methoxyphenyl)-, (2Z)-(2d)¹; Colorless oil was obtained in 93% (95 mg) isolated yield; IR (KBr) ν : 3012, 2923, 1630, 1510, 1456, 1399, 1255, 1178, 1141, 1031, 836; ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.24 (m, 2H), 6.86-6.77 (m, 2H), 6.56 (d, $J = 12.5$ Hz, 1H), 5.91 (d, $J = 12.5$ Hz, 1H), 3.78 (s, 3H), 2.98 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.23, 159.66, 132.93, 129.69, 128.29, 121.21, 113.91, 55.22, 55.19, 37.50, 34.35.



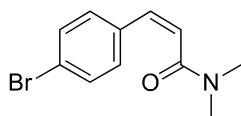
2-Propenamide, N,N-dimethyl-3-(3-methylphenyl)-, (2Z)-(2e); Colorless oil was obtained in 92% (81 mg) isolated yield; IR (KBr) ν : 3018, 2923, 1636, 1509, 1450, 1401, 1372, 1264, 1140, 972, 869, 822; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 6.60 (d, $J = 12.6$ Hz, 1H), 5.97 (d, $J = 12.6$ Hz, 1H), 2.98 (s, 3H), 2.83 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.20, 138.37, 133.24, 132.83, 129.27, 128.11, 122.43, 37.50, 34.38, 21.29; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$ $[\text{M}+\text{H}]^+$ 190.1126, Found 190.1124.



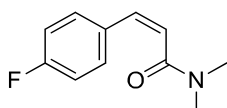
2-Propenamide, N,N-dimethyl-3-(3,5-dimethoxyphenyl)-, (2Z)-(2f)¹; Colorless oil was obtained in 95% (112 mg) isolated yield; IR (KBr) ν : 3001, 2935, 2838, 1621, 1594, 1457, 1406, 1373, 1307, 1264, 1201, 1156, 1062, 853, 684; ^1H NMR (400 MHz, CDCl_3) δ 6.56 (d, $J = 12.6$ Hz, 1H), 6.52 (s, 2H), 6.40 (s, 1H), 6.03 (d, $J = 12.5$ Hz, 1H), 3.76 (s, 6H), 2.98 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.96, 160.78, 137.53, 132.97, 123.89, 105.87, 100.96, 55.34, 37.54, 34.37; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 236.1281, Found 236.1277.



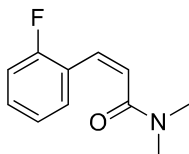
2-Propenamide, N,N-dimethyl-3-(4-chlorophenyl)-, (2Z)-(2g)¹; Colorless oil was obtained in 96% (100 mg) isolated yield; IR (KBr) ν : 3017, 928, 1637, 1492, 1453, 1399, 1373, 1263, 1142, 1091, 1013, 833, 780, 691; ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.21 (m, 4H), 6.60 (d, $J = 12.6$ Hz, 1H), 6.08 (d, $J = 12.6$ Hz, 1H), 2.99 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.57, 134.24, 134.04, 132.16, 129.53, 128.77, 124.03, 37.52, 34.44.



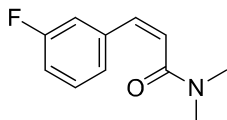
2-Propenamide, N,N-dimethyl-3-(4-bromophenyl)-, (2Z)-(2h); Colorless oil was obtained in 90% (113 mg) isolated yield; IR (KBr) ν : 3021, 2926, 1635, 1497, 1449, 1402, 1373, 1263, 1141, 1053, 779, 694; ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.23 (m, 5H), 6.63 (d, $J = 12.6$ Hz, 1H), 6.03 (d, $J = 12.6$ Hz, 1H), 2.97 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.97, 135.62, 133.27, 128.56, 128.39, 128.14, 123.41, 37.48, 34.36; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{BrNO}$ $[\text{M}+\text{H}]^+$ 256.0155, Found 256.0151.



2-Propenamide, N,N-dimethyl-3-(4-fluorophenyl)-, (2Z)-(2i)¹; Colorless oil was obtained in 98% (95 mg) isolated yield; IR (KBr) ν : 3008, 2930, 1625, 1508, 1402, 1373, 1229, 1141, 840, 721; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (dd, $J = 8.3, 5.6$ Hz, 2H), 6.99 (t, $J = 8.6$ Hz, 2H), 6.60 (d, $J = 12.6$ Hz, 1H), 6.03 (d, $J = 12.6$ Hz, 1H), 2.98 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.69, 162.59 (d, $J = 248.7$ Hz), 132.26, 131.75 (d, $J = 3.4$ Hz), 130.08 (d, $J = 8.2$ Hz), 123.20, 115.53 (d, $J = 21.6$ Hz), 37.48, 34.39; ^{19}F NMR (376MHz, CDCl_3) δ -112.66.

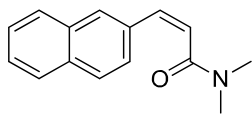


2-Propenamide, N,N-dimethyl-3-(2-fluorophenyl)-, (2Z)-(2j); Colorless oil was obtained in 99% (96 mg) isolated yield; IR (KBr) ν : 3029, 2929, 1635, 1488, 1454, 1408, 1374, 1238, 1142, 1097, 831, 761; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (t, $J = 7.7$ Hz, 1H), 7.32-7.20 (m, 1H), 7.10-6.98 (m, 2H), 6.82 (d, $J = 12.6$ Hz, 1H), 6.16 (d, $J = 12.6$ Hz, 1H), 2.95 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.44, 160.05 (d, $J = 249.5$ Hz), 130.15 (d, $J = 8.5$ Hz), 129.14 (d, $J = 2.8$ Hz), 126.02, 125.99 (d, $J = 5.3$ Hz), 124.15 (d, $J = 3.6$ Hz), 123.47 (d, $J = 12.7$ Hz), 115.42 (d, $J = 21.8$ Hz), 37.49, 34.39; ^{19}F NMR (376MHz, CDCl_3) δ -116.41; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{FNO}$ $[\text{M}+\text{H}]^+$ 194.0976, Found 194.0973.

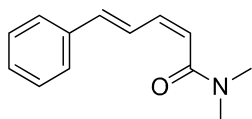


2-Propenamide, N,N-dimethyl-3-(3-fluorophenyl)-, (2Z)-(2k); Colorless oil was obtained in 93% (90 mg) isolated yield; IR (KBr) ν : 3011, 2929, 1629, 1580, 1490, 1445, 1405, 1373, 1253, 1151, 878, 792, 681; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (dd, $J = 14.8, 7.0$ Hz, 1H), 7.13 (d, $J = 7.7$ Hz, 1H), 7.07 (d, $J = 10.1$ Hz, 1H), 6.97 (t, $J = 8.3$ Hz, 1H), 6.59 (d, $J = 12.6$ Hz, 1H), 6.10 (d, $J = 12.6$ Hz, 1H), 2.99 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.40, 162.79 (d, $J = 245.9$ Hz), 137.69 (d, $J = 7.8$ Hz), 131.99 (d, $J = 2.4$ Hz), 130.06 (d, $J = 8.3$ Hz), 124.73, 124.05 (d, $J = 2.8$ Hz), 115.29 (d, $J =$

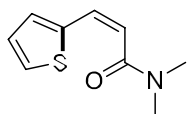
21.3 Hz), 114.79 (d, $J = 22.2$ Hz), 37.46, 34.39; ^{19}F NMR (376 MHz, CDCl_3) $\delta -112.91$; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{FNO}$ $[\text{M}+\text{H}]^+$ 194.0976, Found 194.0972.



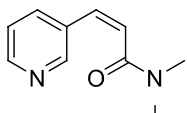
2-Propenamide, N,N-dimethyl-3-(2-naphthalenyl)-, (2Z)-(2l)⁴; Colorless oil was obtained in 99% (111 mg) isolated yield; IR (KBr) ν : 3052, 2928, 1634, 1500, 1451, 1406, 1377, 1264, 1142, 863, 821, 749; ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.72 (m, 4H), 7.55-7.42 (m, 3H), 6.81 (d, $J = 12.6$ Hz, 1H), 6.13 (d, $J = 12.6$ Hz, 1H), 3.02 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.10, 133.31, 133.23, 133.12, 128.31, 128.24, 128.13, 127.63, 126.38, 125.33, 123.68, 37.57, 34.43.



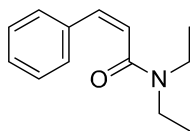
2,4-Pentadienamide, N,N-dimethyl-5-phenyl-, (2Z,4E)-(2m)¹; Colorless oil was obtained in 87% (87 mg) isolated yield; IR (KBr) ν : 3056, 2922, 1631, 1512, 1489, 454, 1397, 1365, 1259, 1138, 1051, 997, 958, 801, 753, 695; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 15.7, 11.2$ Hz, 1H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.36-7.23 (m, 3H), 6.74 (d, $J = 15.7$ Hz, 1H), 6.58 (t, $J = 11.3$ Hz, 1H), 6.05 (d, $J = 11.3$ Hz, 1H), 3.07 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.44, 139.32, 138.60, 136.65, 128.61, 128.44, 127.24, 125.37, 119.77, 37.87, 35.14.



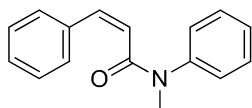
(Z)-N,N-dimethyl-3-(thiophen-2-yl)acrylamide (2n); Colorless oil was obtained in 92% (83 mg) isolated yield; IR (KBr) ν : 3058, 2929, 1635, 1496, 1455, 1373, 1266, 1214, 1135, 737, 699; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 4.8$ Hz, 1H), 7.14 (d, $J = 2.8$ Hz, 1H), 6.99 – 6.97 (m, 1H), 6.79 (d, $J = 12.4$ Hz, 1H), 5.95 (d, $J = 12.4$ Hz, 1H), 3.04 (s, 1H), 3.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.02, 138.24, 130.46, 128.36, 127.53, 126.89, 119.27, 37.59, 34.73; HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{11}\text{NOS}$ $[\text{M}+\text{H}]^+$ 182.0634, Found 182.0631.



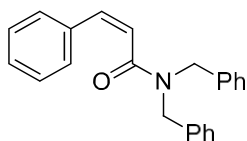
(Z)-N,N-dimethyl-3-(thiophen-2-yl)acrylamide (2o); Colorless oil was obtained in 42% (37 mg) isolated yield; IR (KBr) ν : 2925, 1635, 1540, 1496, 1456, 1143, 817, 737, 700; ^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1H), 8.51 (d, $J = 4.2$ Hz, 1H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.27 – 7.23 (m, 1H), 6.64 (d, $J = 12.6$ Hz, 1H), 6.22 (d, $J = 12.6$ Hz, 1H), 3.01 (s, 1H), 2.92 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.04, 149.76, 149.31, 135.05, 131.30, 130.13, 125.81, 123.45, 37.53, 34.48; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 177.1022, Found 177.1020.



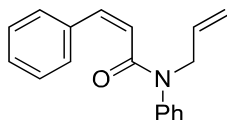
2-Propenamide, N,N-diethyl-3-phenyl-, (2Z)-(2p); Colorless oil was obtained in 91% (92 mg) isolated yield; IR (KBr) ν : 2972, 2931, 1615, 1431, 1380, 1269, 1140, 1072, 858, 778, 740, 697; ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.39 (m, 2H), 7.34-7.24 (m, 3H), 6.61 (d, $J = 12.7$ Hz, 1H), 6.07 (d, $J = 12.6$ Hz, 1H), 3.48 (q, $J = 7.1$ Hz, 2H), 3.27 (q, $J = 7.2$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.28, 135.53, 132.70, 128.45, 128.40, 128.33, 123.78, 42.58, 38.93, 13.98, 12.44; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$ 204.1383, Found 204.1380.



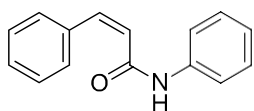
2-Propenamide, N-methyl-N,3-diphenyl-, (2Z)-(2q)²; Colorless oil was obtained in 94% (111 mg) isolated yield; IR (KBr) ν : 3035, 2917, 1634, 1493, 1452, 1424, 1374, 1240, 1079, 1047, 916, 735, 696; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.1$ Hz, 1.5H), 7.37-7.28 (m, 7H), 7.09 (d, $J = 6.7$ Hz, 1.5H), 6.70 (d, $J = 12.7$ Hz, 1H), 6.21 (d, $J = 12.7$ Hz, 1H), 4.62 (s, 1.5H), 4.42 (s, 1.5H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.22, 136.49, 136.26, 135.36, 133.98, 129.08, 128.87, 128.60, 128.58, 128.53, 127.70, 127.60, 127.19, 123.17, 50.50, 46.70.



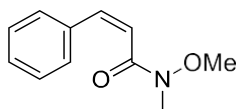
2-Propenamide, 3-phenyl-N,N-bis(phenylmethyl)-, (2Z)-(2r)³; Colorless oil was obtained in 99% (162 mg) isolated yield; IR (KBr) ν : 3028, 2926, 1638, 1493, 1450, 1426, 1215, 1077, 948, 737, 697; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 7.6$ Hz, 2H), 7.18-7.05 (m, 11H), 6.89 (d, $J = 7.1$ Hz, 2H), 6.49 (d, $J = 12.7$ Hz, 1H), 6.01 (d, $J = 12.7$ Hz, 1H), 4.44 (s, 2H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.24, 136.52, 136.27, 135.39, 134.02, 129.10, 128.90, 128.64, 128.61, 128.56, 127.73, 127.64, 127.23, 123.20, 50.54, 46.47.



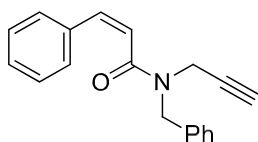
2-Propenamide, N,3-diphenyl-N-2-propenyl-, (2Z)- (2s); Colorless oil was obtained in 98% (129 mg) isolated yield; IR (KBr) ν : 3061, 3028, 2923, 1649, 1593, 1494, 1451, 1407, 1366, 1268, 1223, 1136, 991, 924, 771, 697; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 6.7$ Hz, 2H), 7.34 (d, $J = 7.0$ Hz, 3H), 7.29-7.22 (m, 3H), 6.95 (s, 2H), 6.41 (d, $J = 12.6$ Hz, 1H), 5.99-5.80 (m, 2H), 5.18-5.09 (m, 2H), 4.40 (d, $J = 6.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.46, 142.02, 135.59, 135.28, 132.85, 129.04, 128.98, 128.43, 128.22, 127.64, 127.52, 123.90, 118.10, 51.74; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$ 264.1383, Found 264.1380.



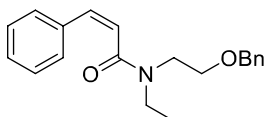
2-Propenamide, N,3-diphenyl-, (2Z)-(2t)⁵; Colorless oil was obtained in 99% (110 mg) isolated yield; IR (KBr) ν : 3266, 3129, 3057, 1654, 1597, 1538, 1495, 1440, 1312, 1257, 1183, 752, 691; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (br, 1H), 7.53 (d, J = 7.0 Hz, 2H), 7.44-7.33 (m, 5H), 7.30 (t, J = 7.8 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 12.5 Hz, 1H), 6.11 (d, J = 12.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.13, 137.83, 137.71, 134.77, 129.19, 128.98, 128.62, 124.80, 124.47, 120.07.



2-Propenamide, N-methoxy-N-methyl-3-phenyl-, (2Z)-(2u)⁶; Colorless oil was obtained in 99% (95 mg) isolated yield; IR (KBr) ν : 3024, 2921, 1650, 1514, 1453, 1369, 1176, 992, 758, 695; ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.47 (m, 2H), 7.40-7.27 (m, 3H), 6.78 (d, J = 12.7 Hz, 1H), 6.28 (br, 1H), 3.82-3.18 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 173.66, 171.62, 143.44, 137.74, 135.22, 129.15, 128.63, 128.48, 128.46, 128.30, 126.12, 120.66, 61.21, 33.80, 32.20, 30.71.



2-Propenamide, 3-phenyl-N-(phenylmethyl)-N-2-propyn-1-yl-, (2Z)-(2v); Colorless oil was obtained in 83% (114 mg) isolated yield; IR (KBr) ν : 3289, 3026, 1637, 1492, 1425, 1383, 1215, 1046, 918, 772, 734, 693; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 7.3 Hz, 1H), 7.39-7.22 (m, 8H), 7.10 (d, J = 7.1 Hz, 1H), 6.73 (d, J = 12.6 Hz, 1H), 6.16 (d, J = 12.6 Hz, 1H), 4.81 (s, 1H), 4.58 (s, 1H), 4.22 (s, 1H), 3.92 (s, 1H), 2.26 (d, J = 12.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 168.83, 168.61, 135.68, 135.08, 134.64, 129.00, 128.84, 128.73, 128.71, 128.68, 128.64, 128.52, 128.49, 127.90, 127.78, 127.48, 122.59, 122.18, 77.94, 77.84, 73.09, 72.08, 50.68, 46.76, 36.71, 32.64; HRMS (ESI) m/z calcd for C₁₉H₁₇NO [M+H]⁺ 276.1383, Found 276.1381.



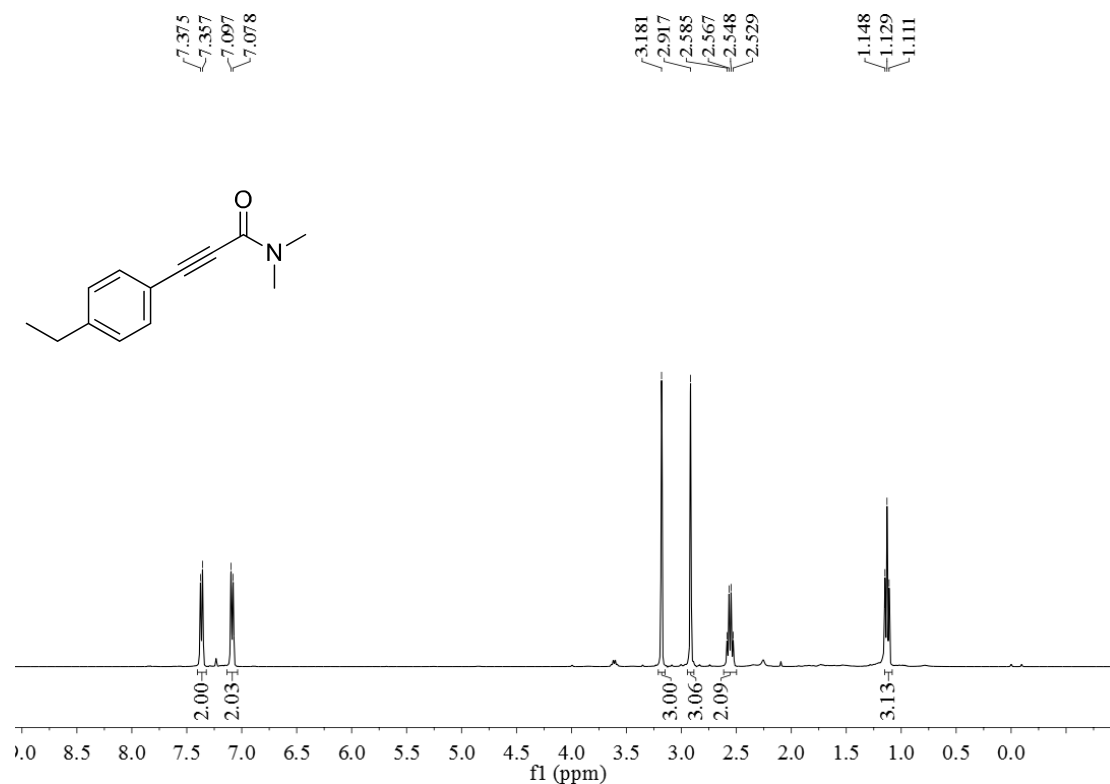
(Z)-N-(2-(benzyloxy)ethyl)-N-ethyl-3-phenylacrylamide (2w); Colorless oil was obtained in 98% (151 mg) isolated yield; IR (KBr) ν : 3059, 3028, 2974, 2932, 2864, 1626, 1494, 1432, 1362, 1269, 1107, 724, 699; ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.36 (m, 1H), 7.34 – 7.20 (m, 5H), 6.58 (dd, J = 16.6, 12.7 Hz, 1H), 6.07 (dd, J = 16.9, 9.2 Hz, 1H), 4.51 (s, 1H), 4.37 (s, 1H), 3.70 (t, J = 5.4 Hz, 1H), 3.64 (t, J = 5.3 Hz, 1H), 3.50 (q, J = 7.1 Hz, 1H), 3.43 – 3.33 (m, 2H), 1.14 (t, J = 7.1 Hz, 1H), 0.97 (t, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.93, 168.87, 138.18, 137.84, 135.54, 135.48, 133.17, 132.67, 128.50, 128.49, 128.46, 128.41, 127.77, 127.64, 127.56, 124.22, 123.48, 73.25, 73.23, 68.44, 68.22, 47.72, 44.37, 44.32, 40.20, 13.91, 12.25; HRMS (ESI) m/z calcd for C₂₀H₂₃NO₂ [M+H]⁺ 310.1802, Found 310.1796.

Reference

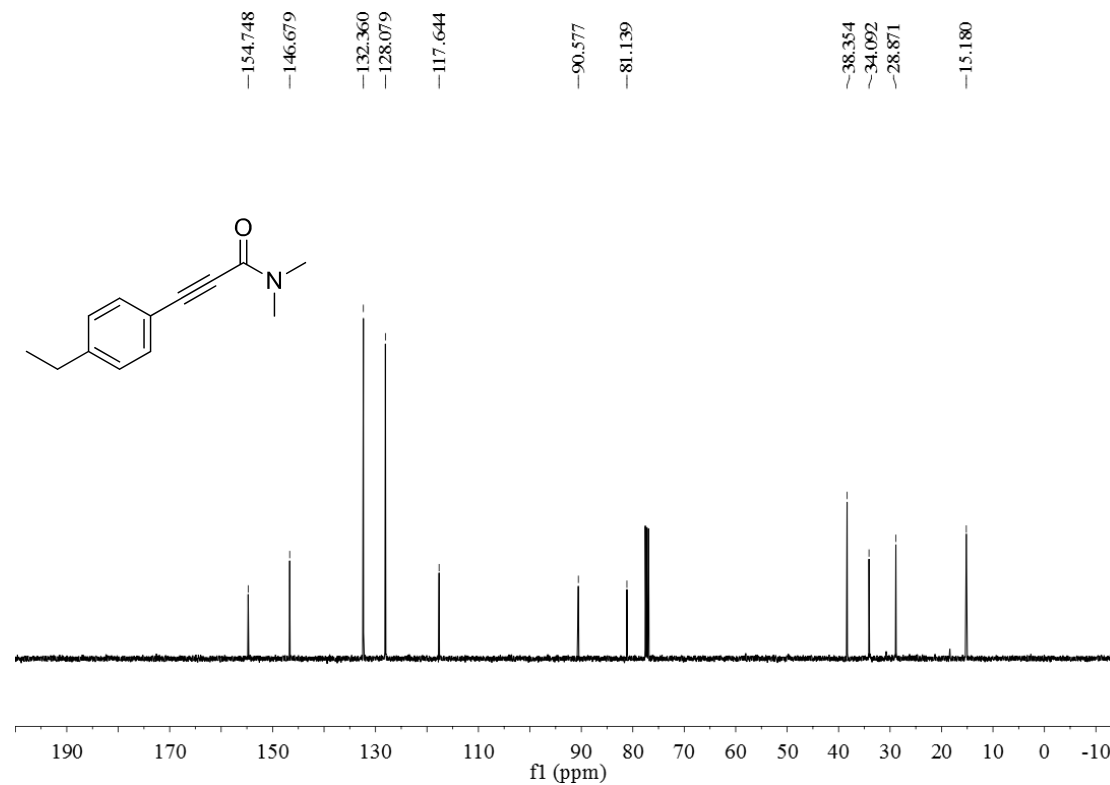
- [1] Satoshi, K.; Hiroki, I.; Tsugihiko, H.; Tomohide, F.; Katsuo, O. *J. Org. Chem.* **2002**, *67*, 4093–4099.
- [2] Wen-Peng, M.; Ji-Tao, W.; Yong-Mei, X.; Pu, M.; Kui, L. *Tetrahedron* **2015**, *71*, 8041–8051.
- [3] Satoshi, K.; Tsugihiko, H.; Yuko, O.; Katsuo, O. *Phosphorus, Sulfur and Silicon*, **2002**, *177*, 729–732.
- [4] Tianlong, Y.; Maojian, L.; Zhaowei, L.; Mingqiang, H.; Shunyou, C. *Org. Biomol. Chem.* **2019**, *17*, 449–453.
- [5] Kaori, A. *Synlett*, **2001**, *8*, 1272–1274.
- [6] Kaori, A.; Shigeo, N.; Yuko, T. *Tetrahedron Letters* **2009**, *50*, 5689–5691.

NMR spectra of substrates and products

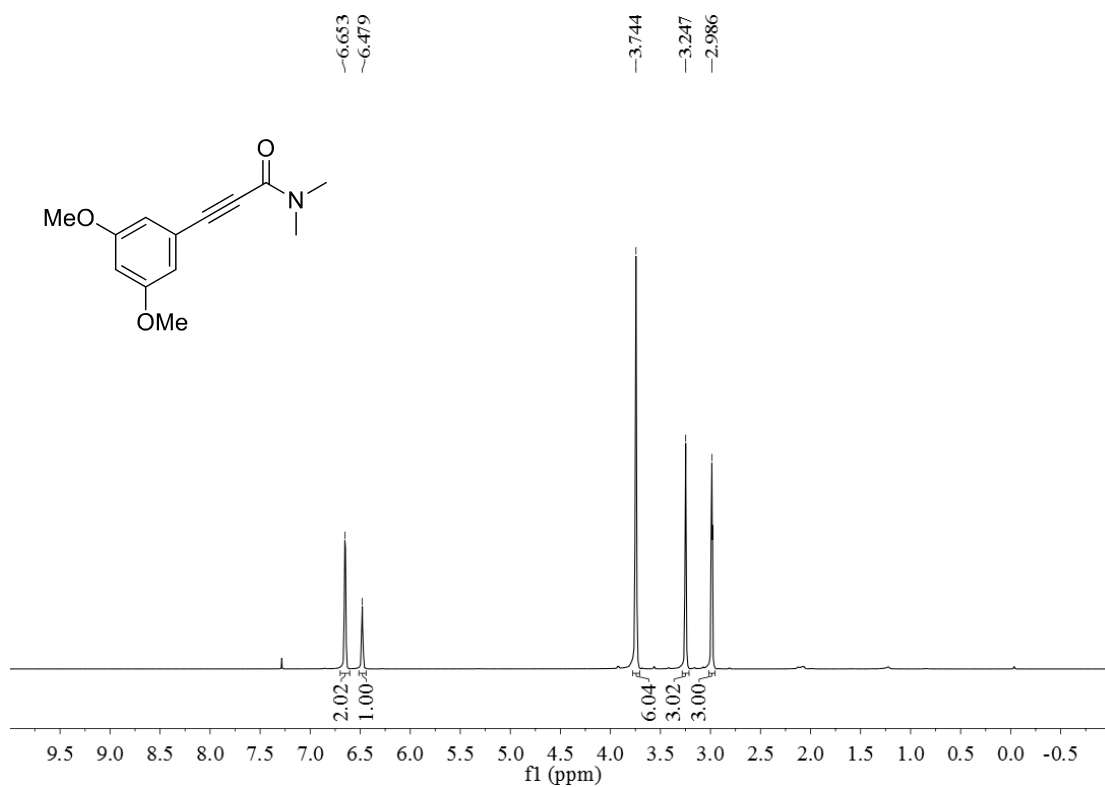
^1H NMR spectrum (400 MHz, CDCl_3) of **1c**



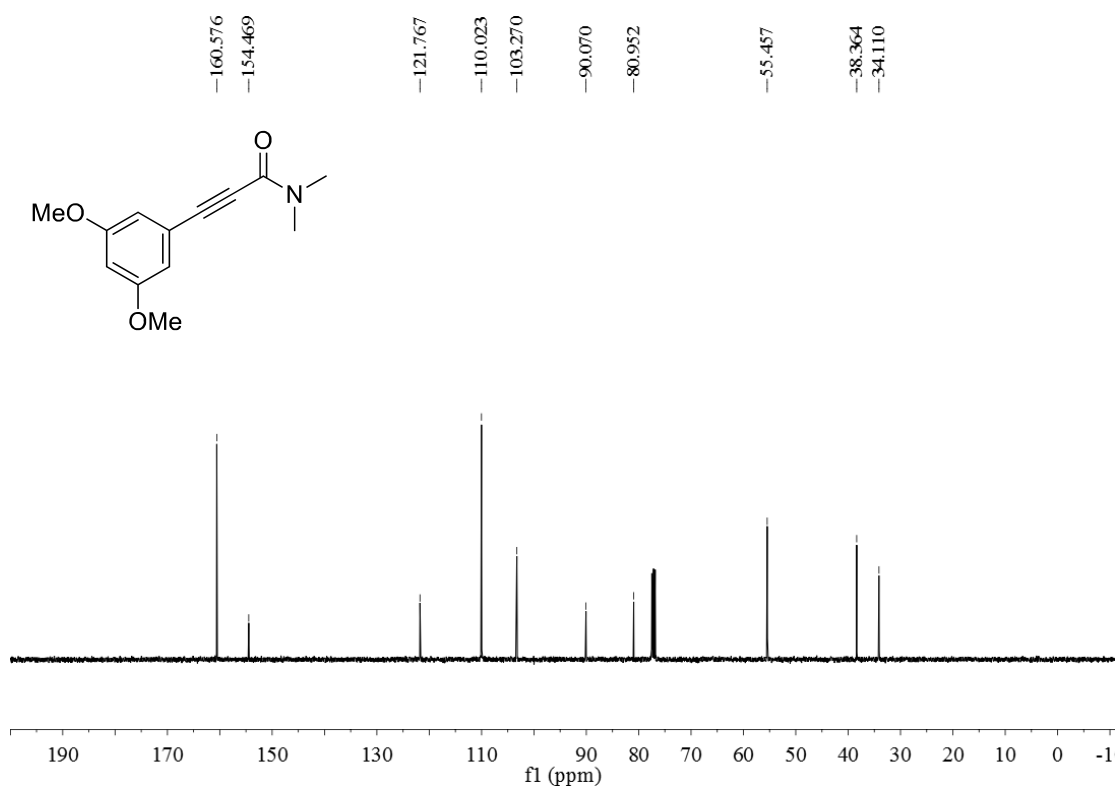
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1c**



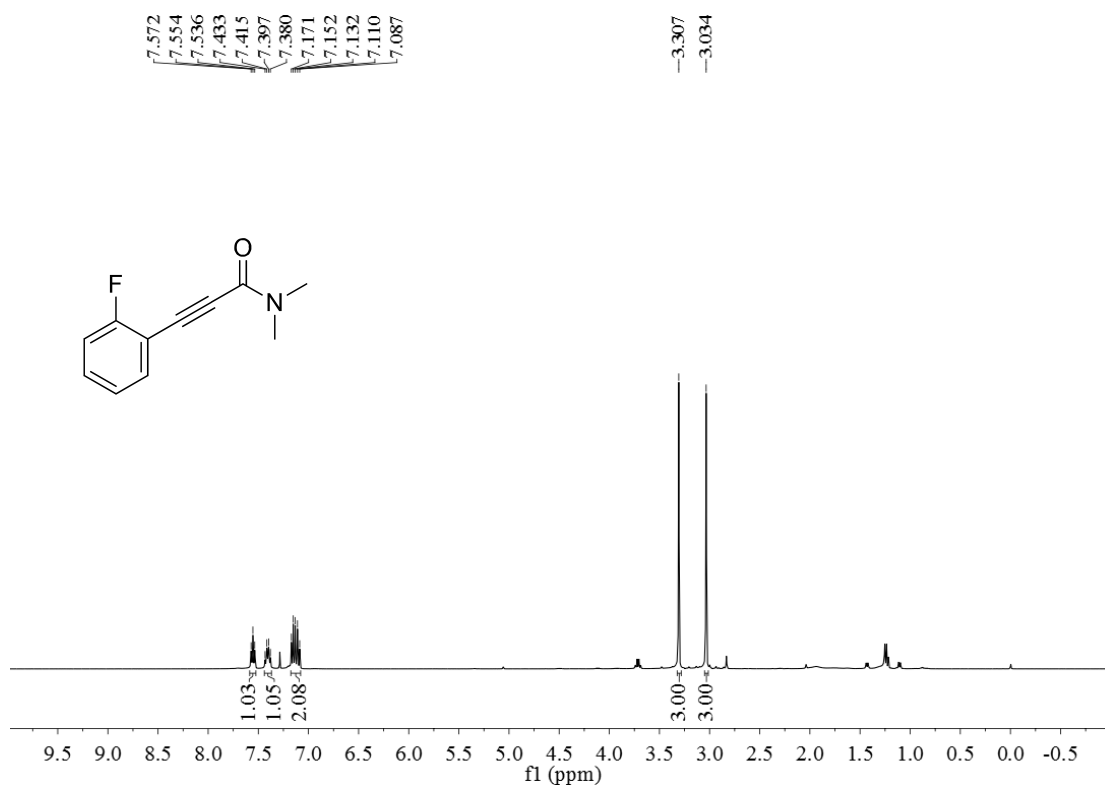
^1H NMR spectrum (400 MHz, CDCl_3) of **1f**



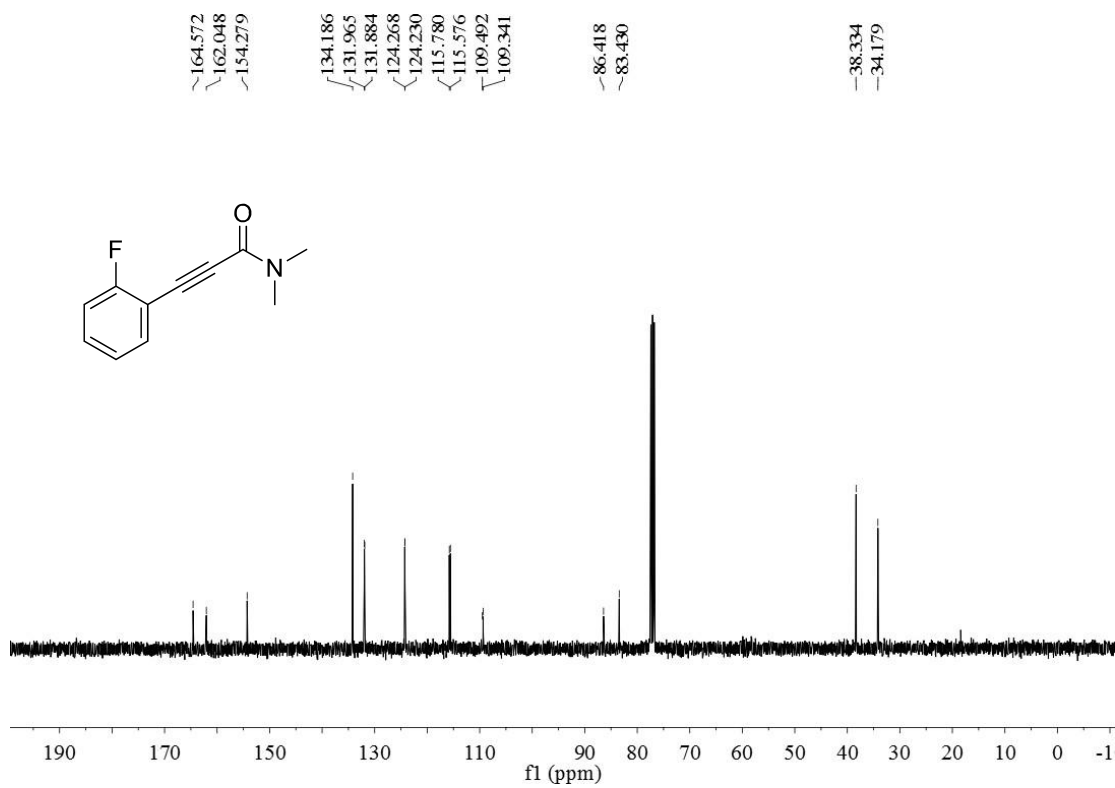
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1f**



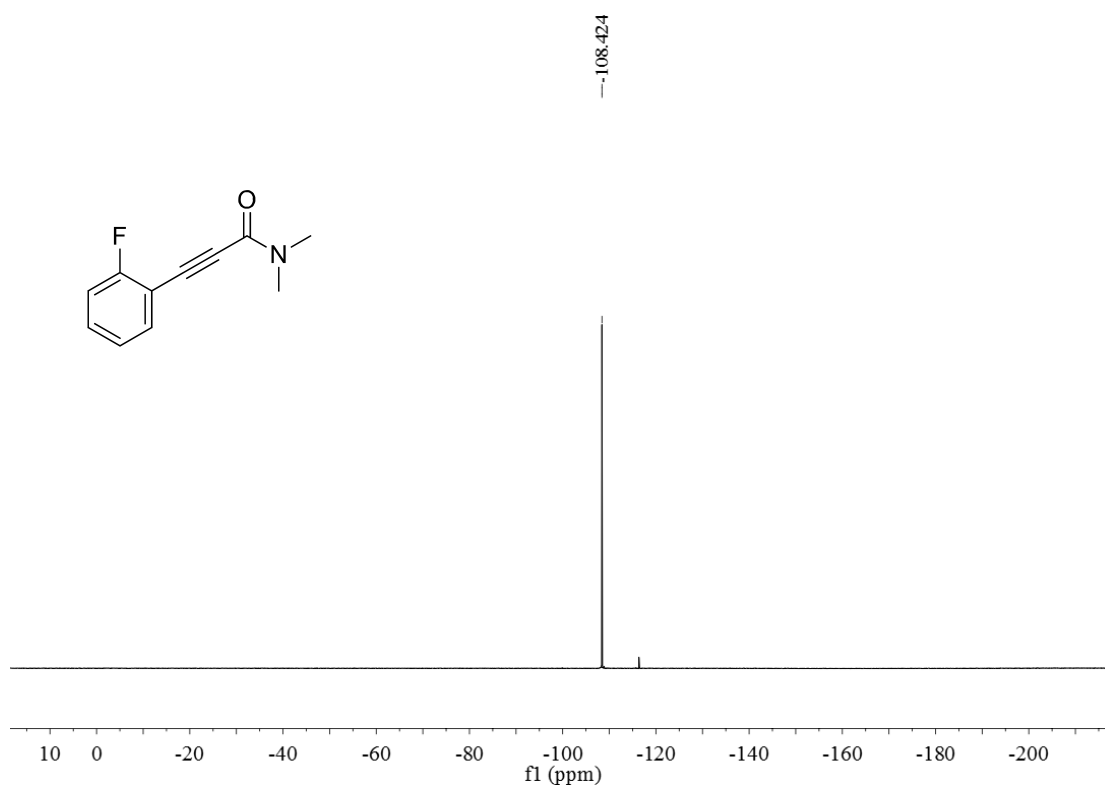
¹H NMR spectrum (400 MHz, CDCl₃) of **1j**



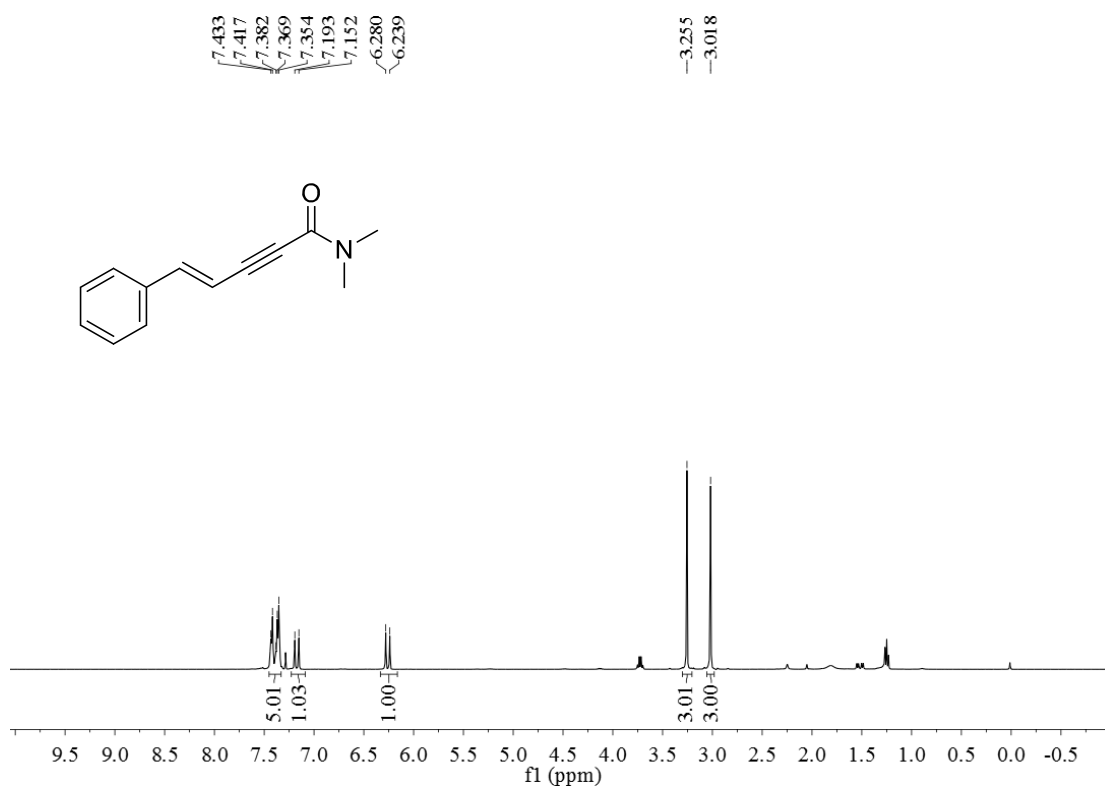
¹³C NMR spectrum (100 MHz, CDCl₃) of **1j**



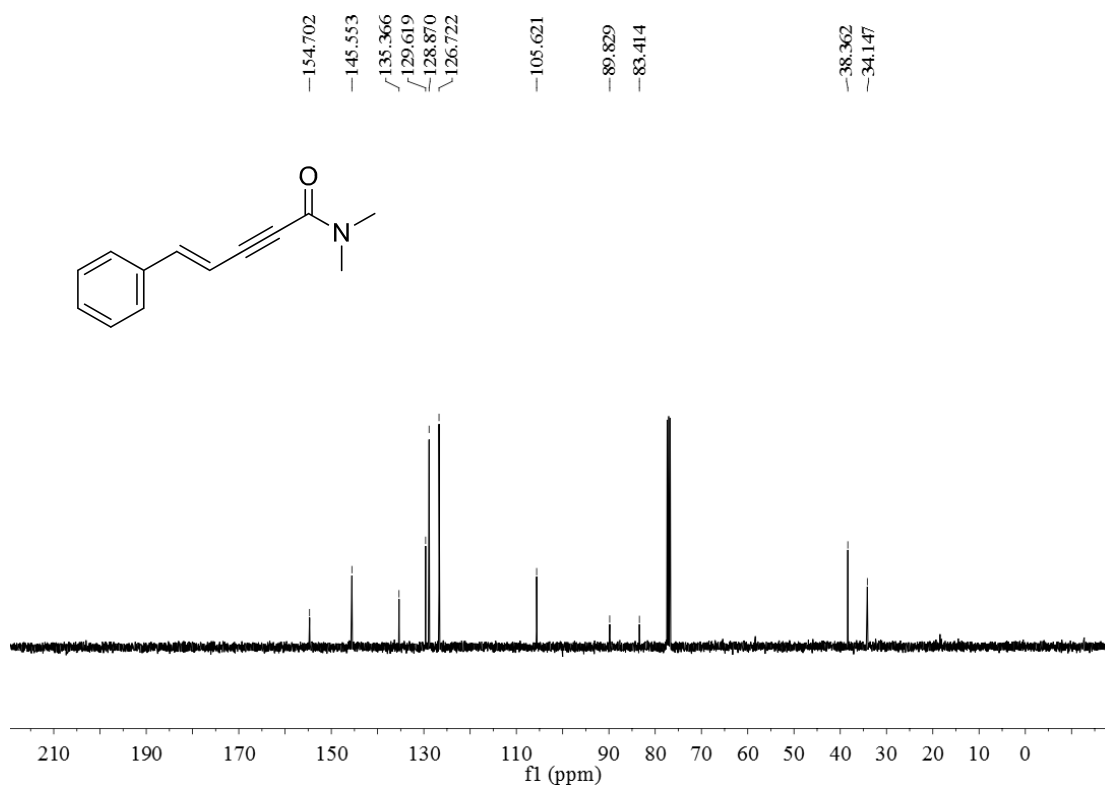
^{19}F NMR spectrum (376 MHz, CDCl_3) of **1j**



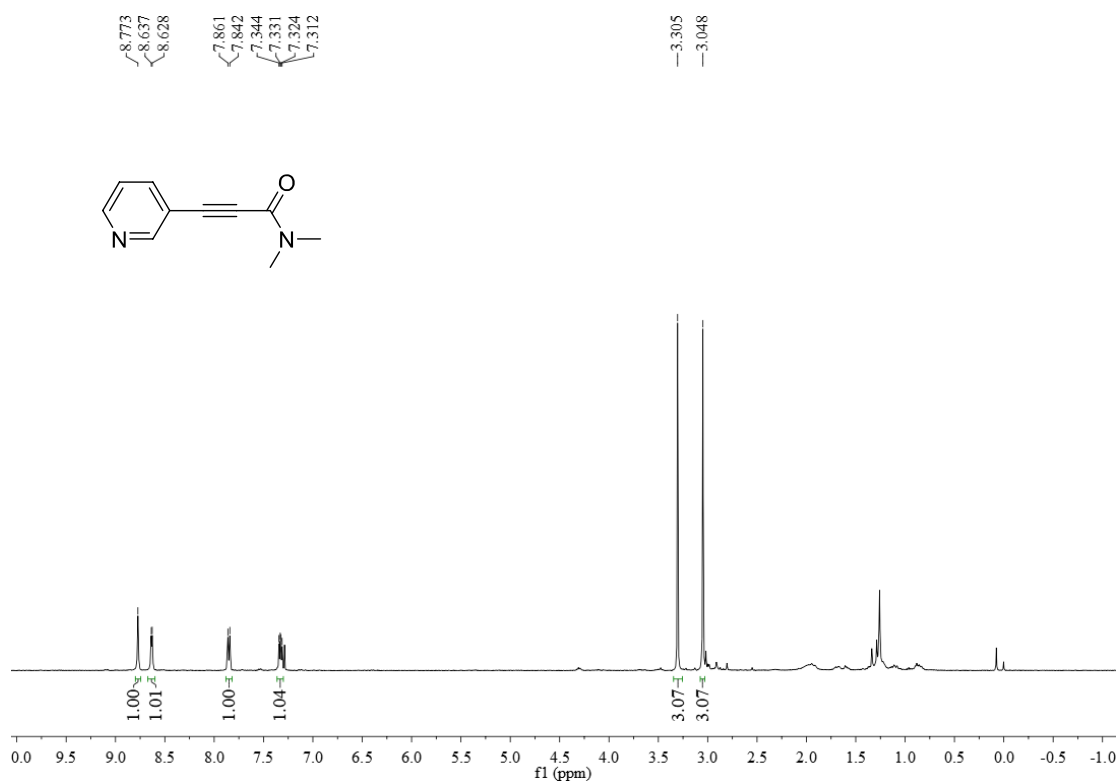
^1H NMR spectrum (400 MHz, CDCl_3) of **1m**



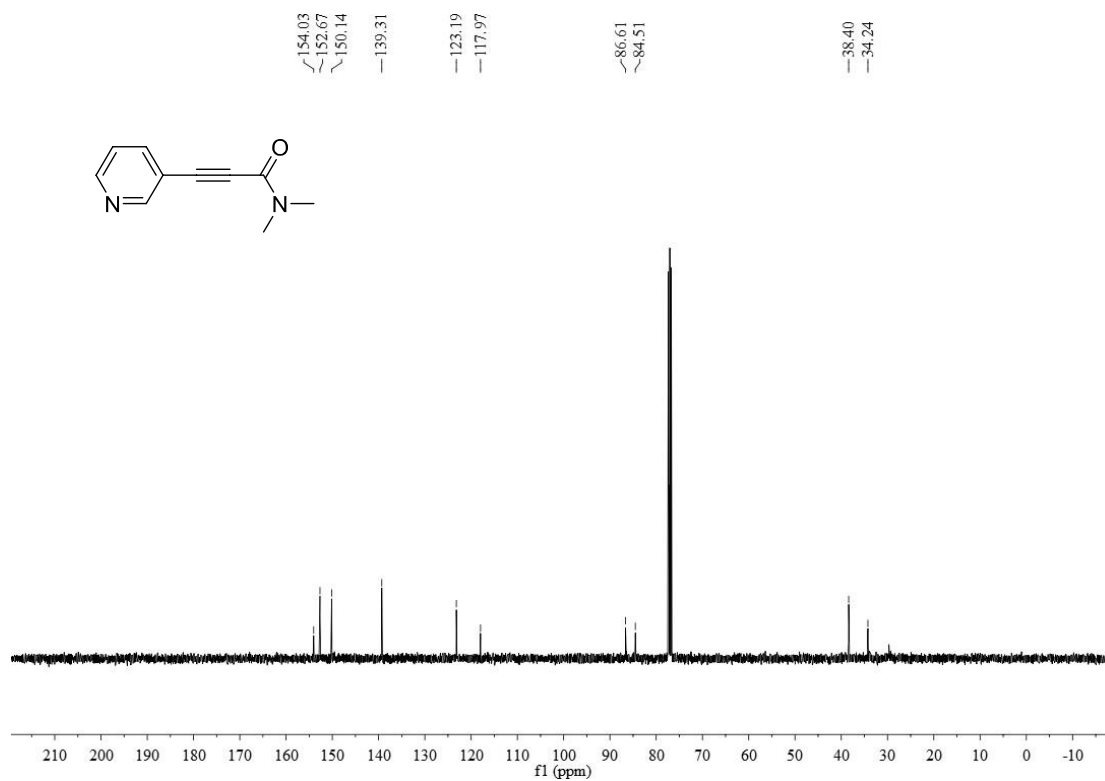
¹³C NMR spectrum (100 MHz, CDCl₃) of **1m**



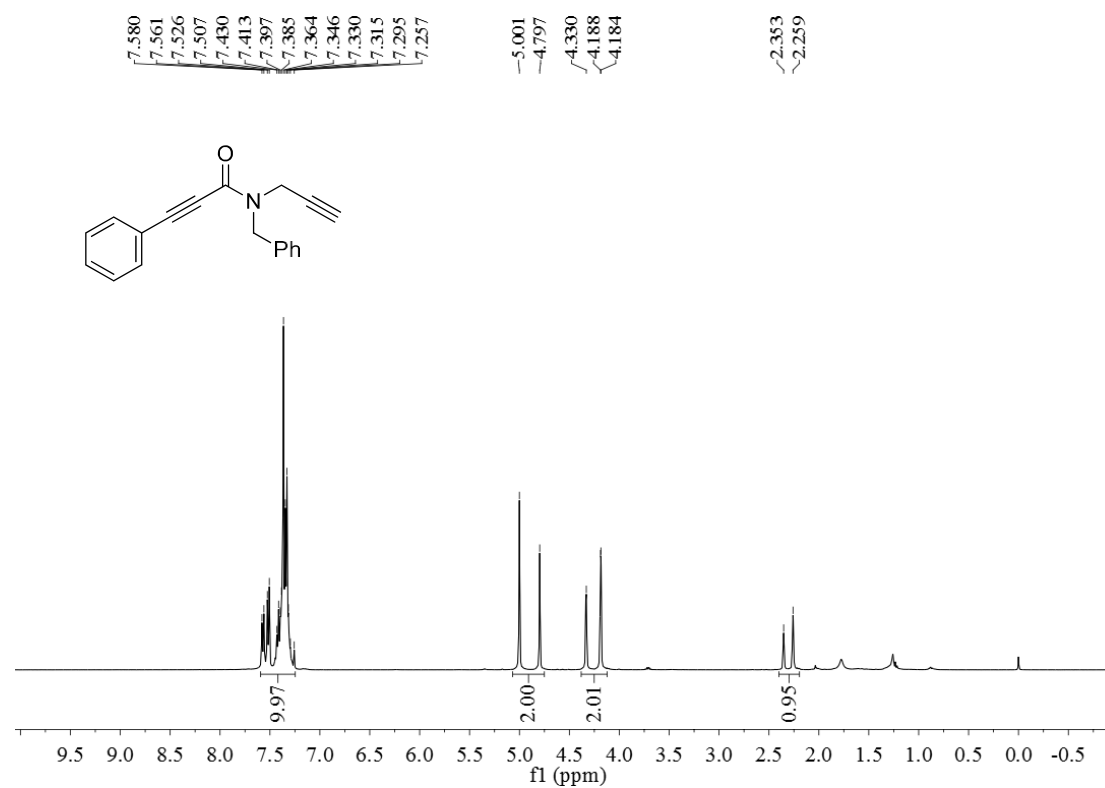
¹H NMR spectrum (400 MHz, CDCl₃) of **1o**



¹³C NMR spectrum (100 MHz, CDCl₃) of **1o**

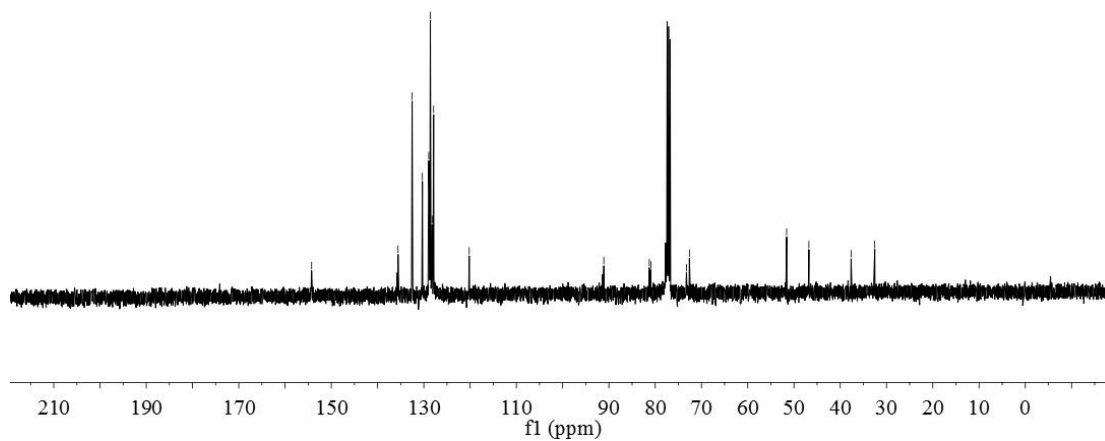
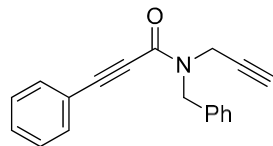


¹H NMR spectrum (400 MHz, CDCl₃) of **1v**



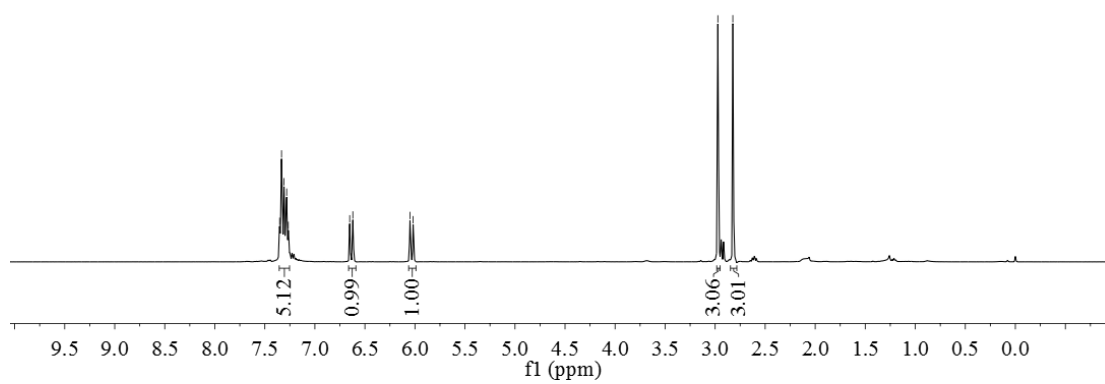
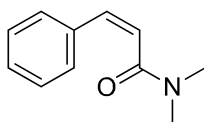
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1v**

154.267
135.578
132.540
130.324
128.944
128.785
128.599
128.188
127.900
120.197
-91.105
-81.275
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-73.236
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-51.589
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-37.654
-32.544

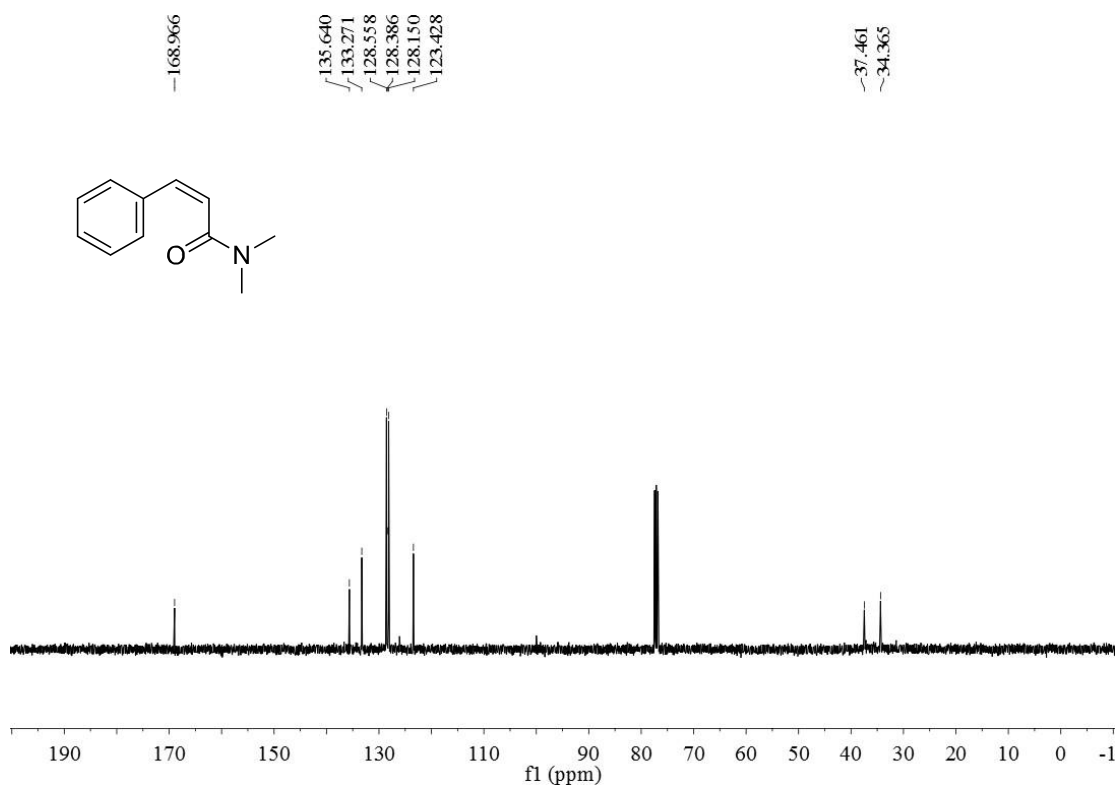


^1H NMR spectrum (400 MHz, CDCl_3) of **2a**

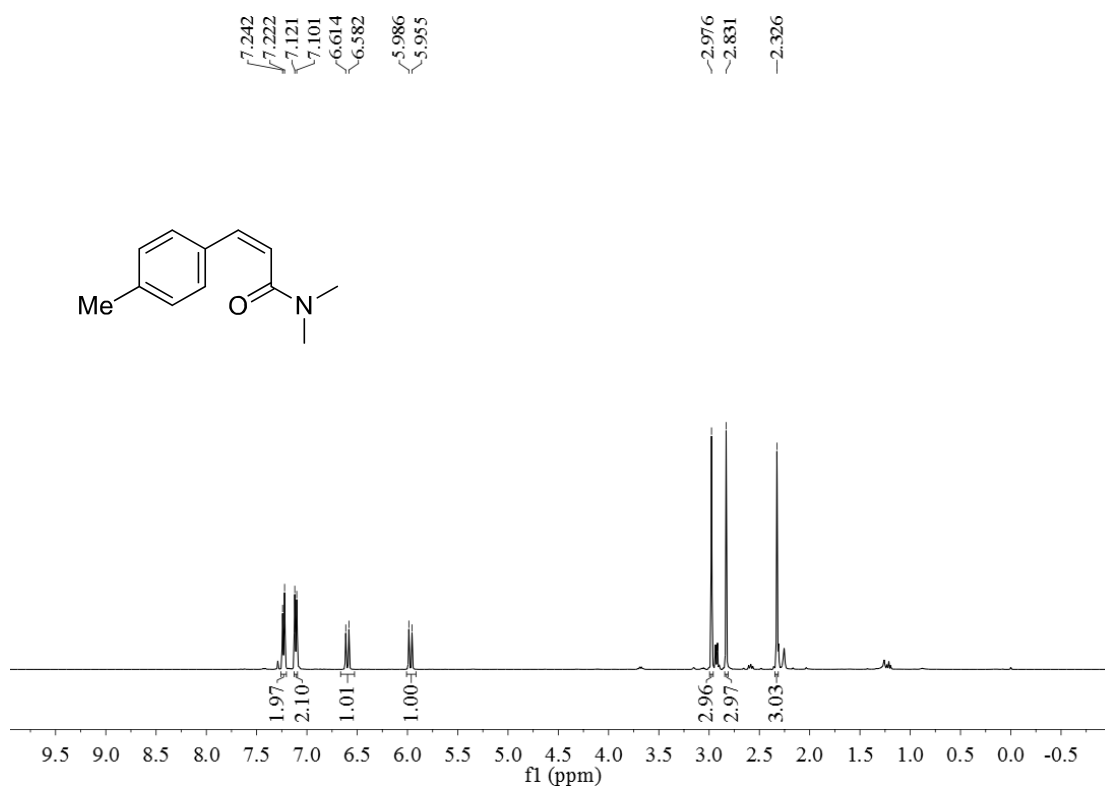
7.352
7.333
7.308
7.282
7.265
6.652
6.621
6.049
6.018
-2.973
-2.823



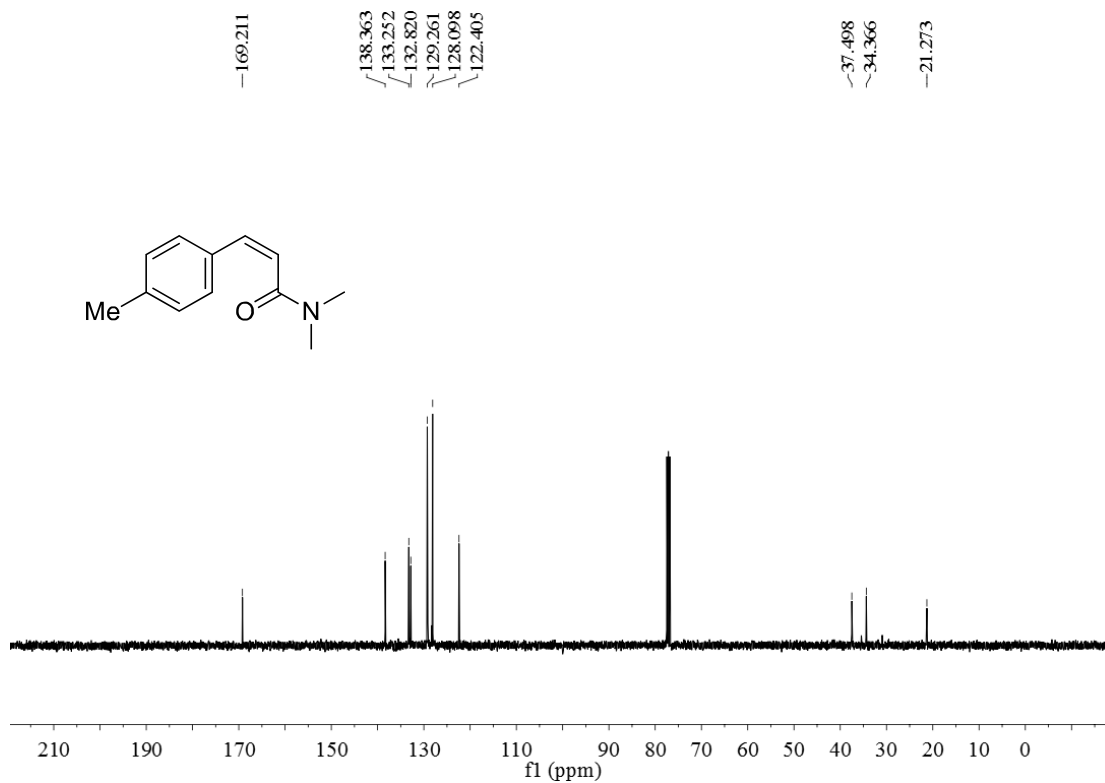
¹³C NMR spectrum (100 MHz, CDCl₃) of **2a**



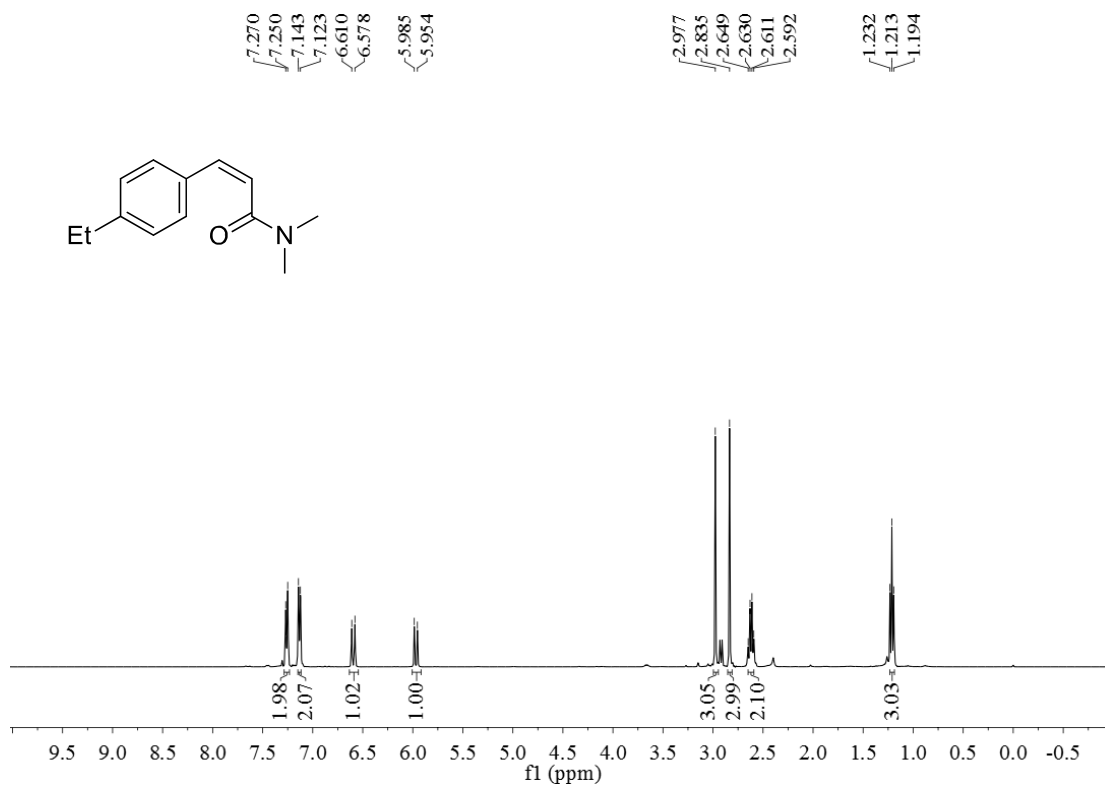
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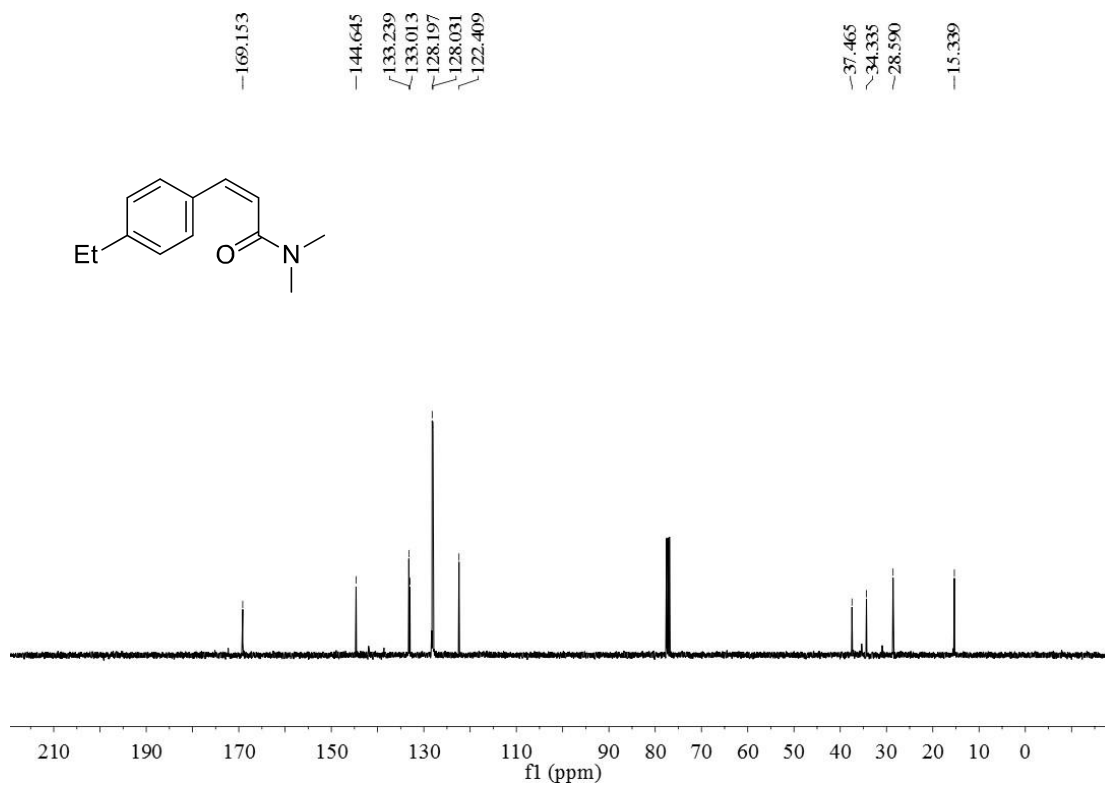
¹³C NMR spectrum (100 MHz, CDCl₃) of **2b**



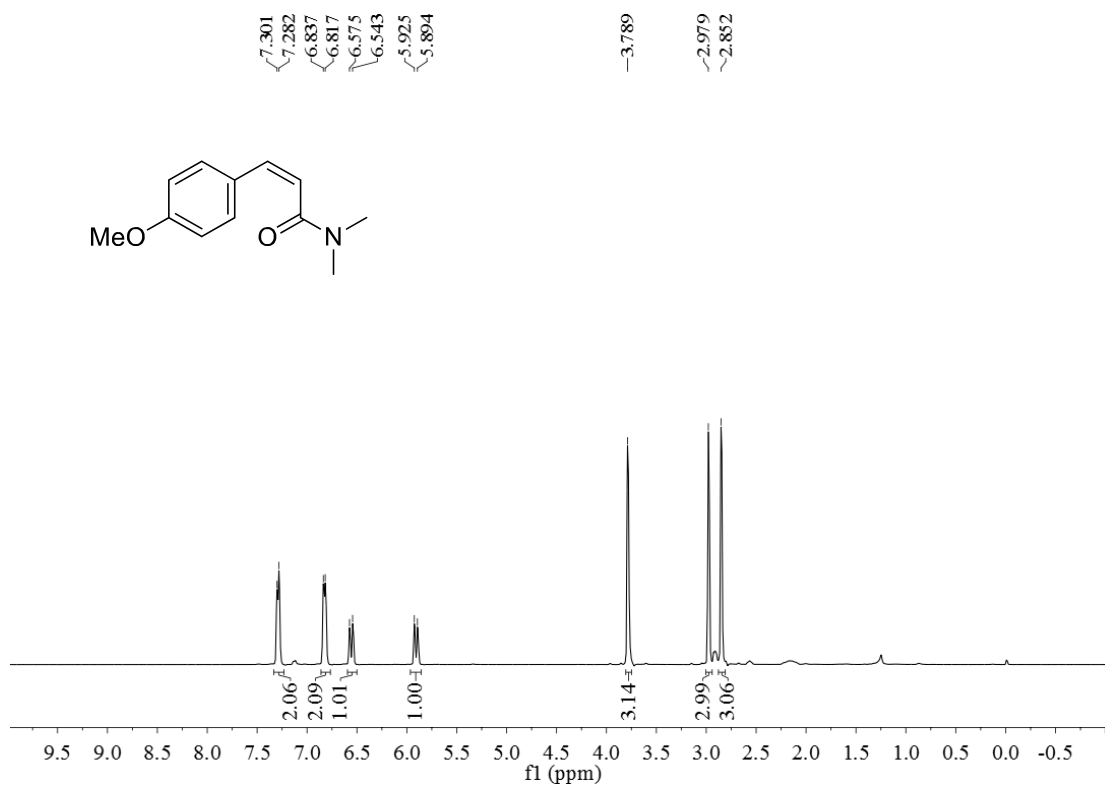
¹H NMR spectrum (400 MHz, CDCl₃) of **2c**



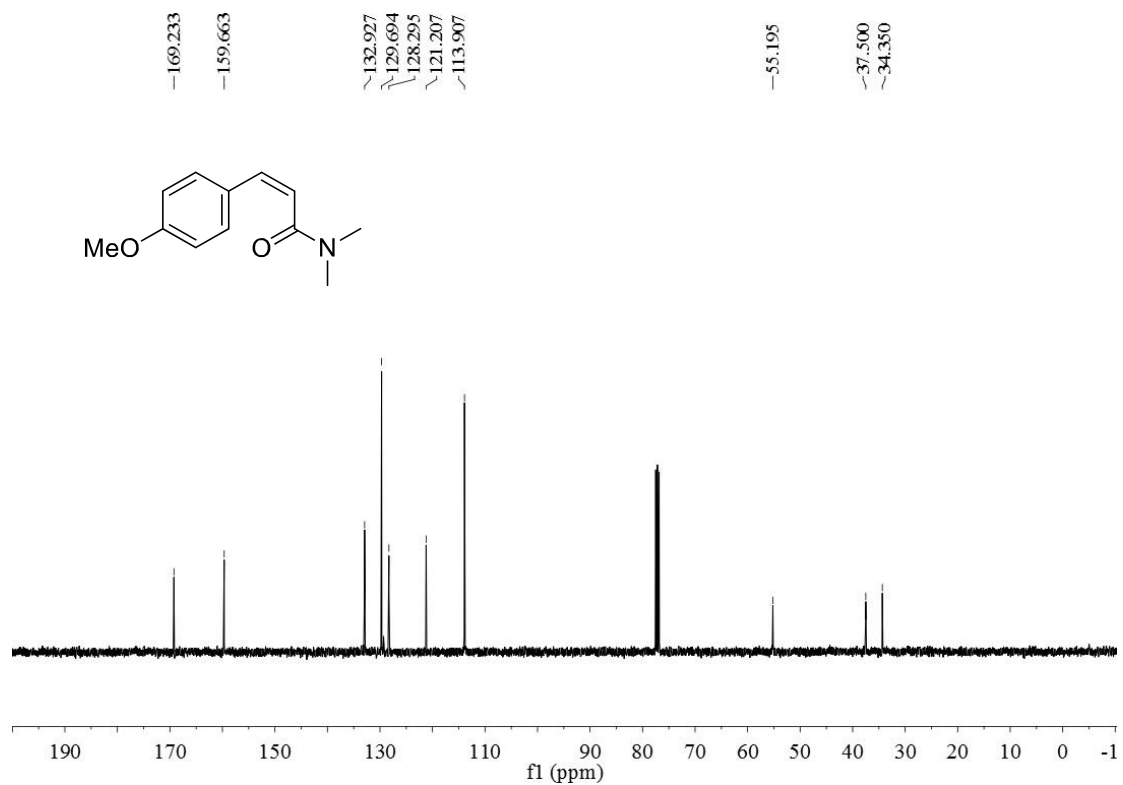
¹³C NMR spectrum (100 MHz, CDCl₃) of **2c**



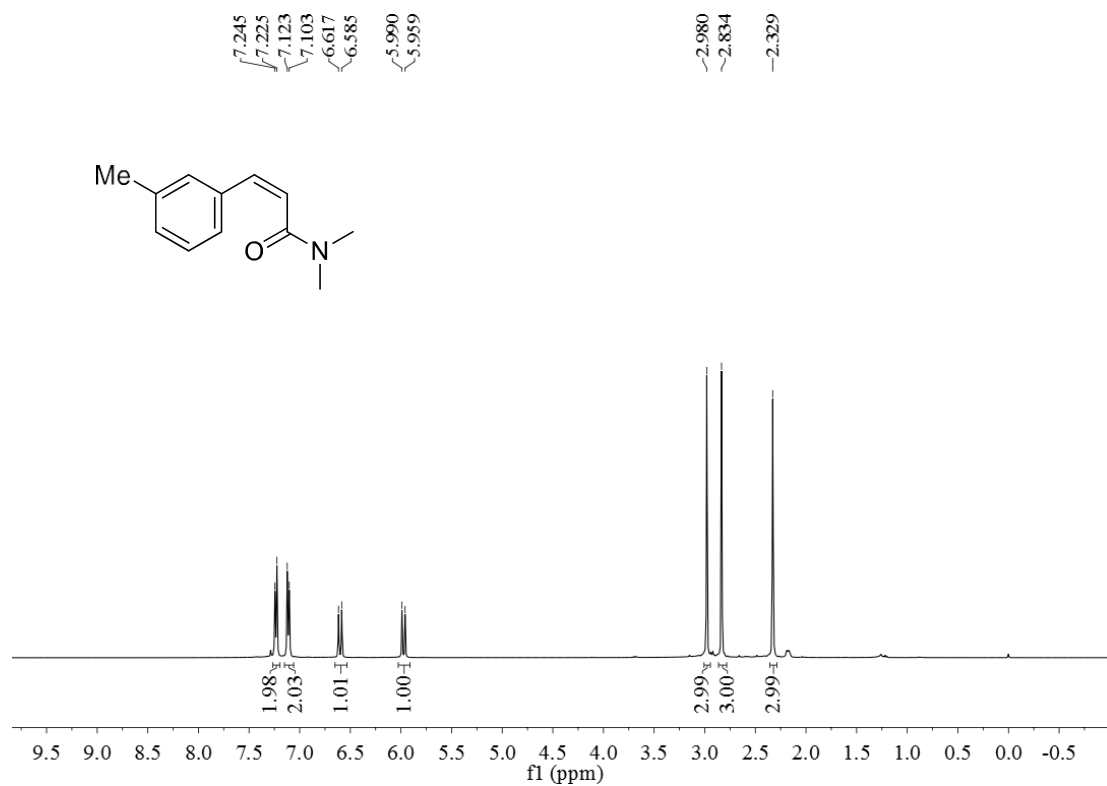
¹H NMR spectrum (400 MHz, CDCl₃) of **2d**



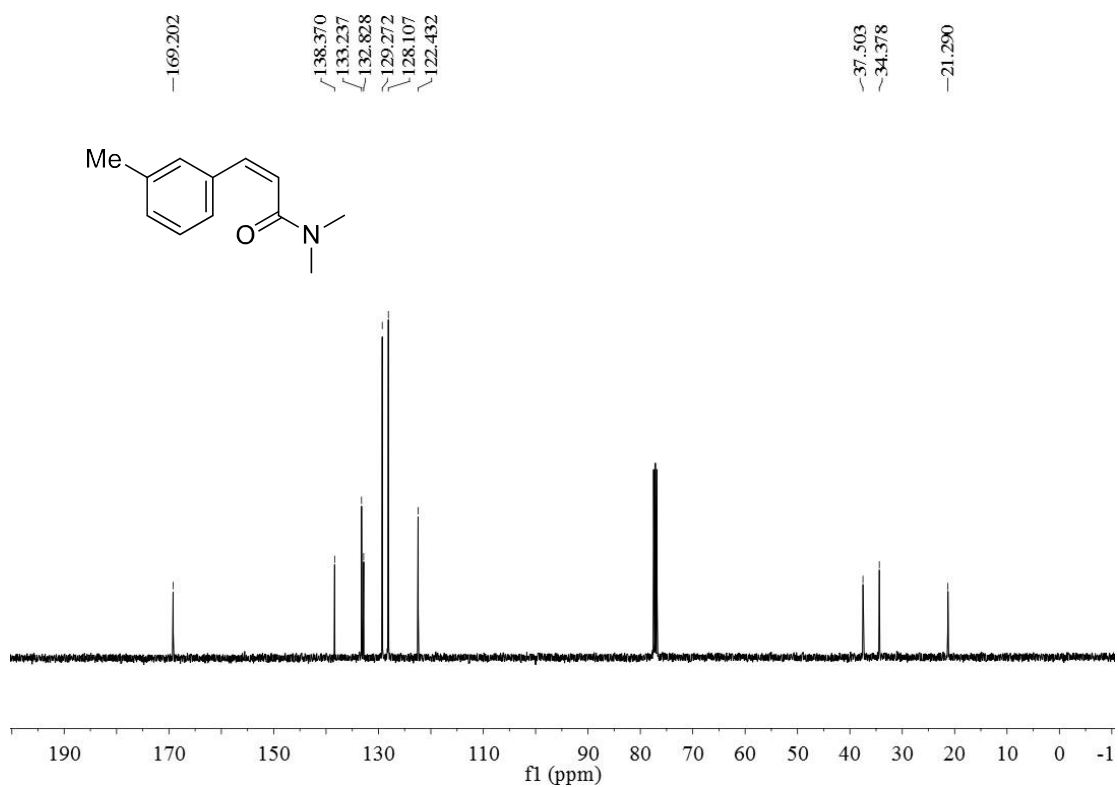
¹³C NMR spectrum (100 MHz, CDCl₃) of **2d**



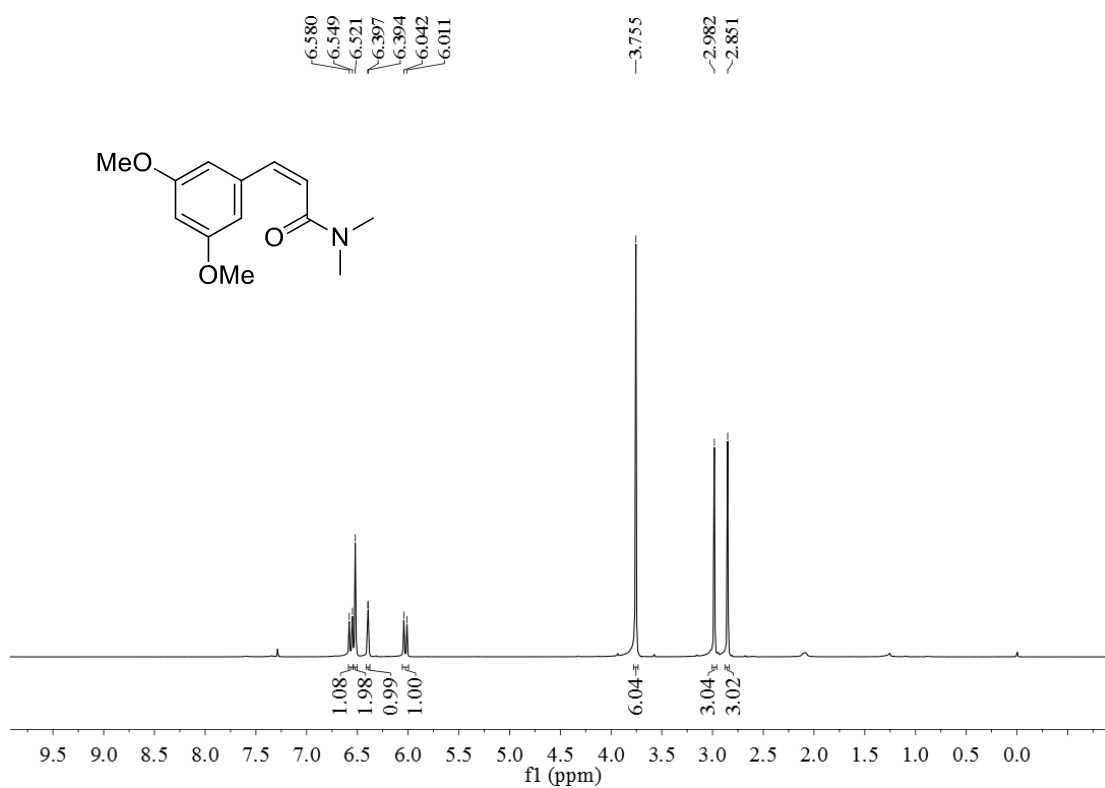
¹H NMR spectrum (400 MHz, CDCl₃) of **2e**



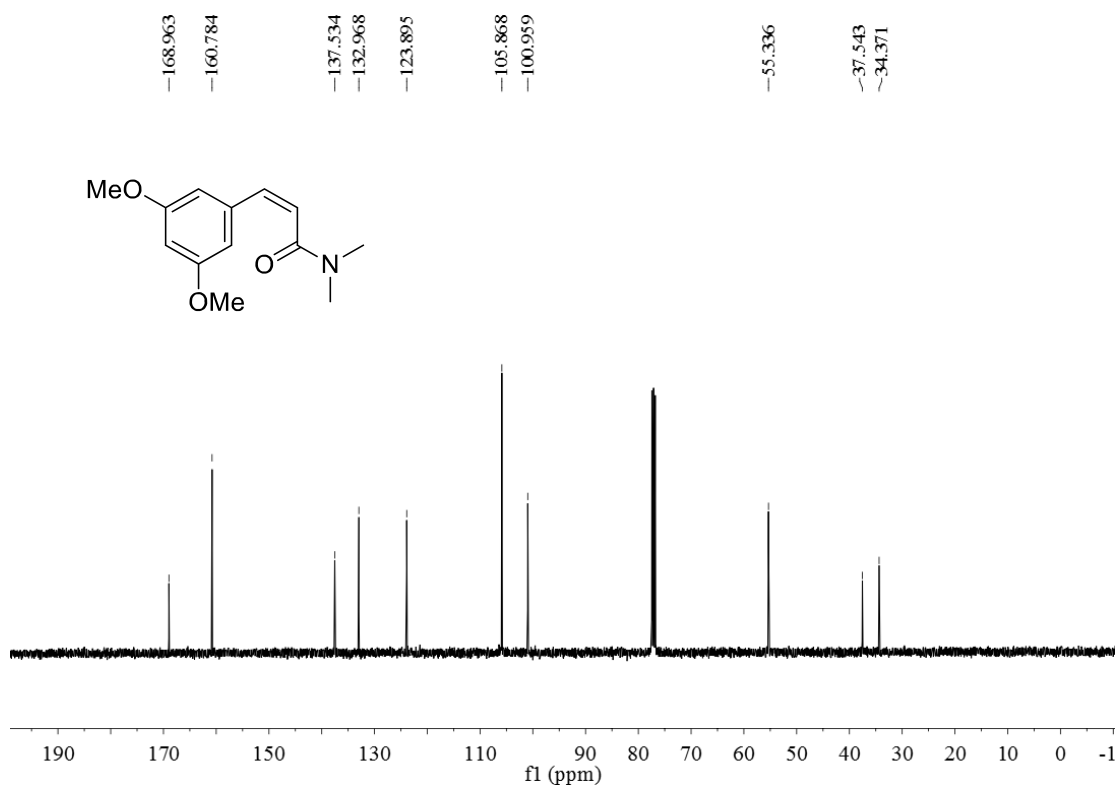
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2e**



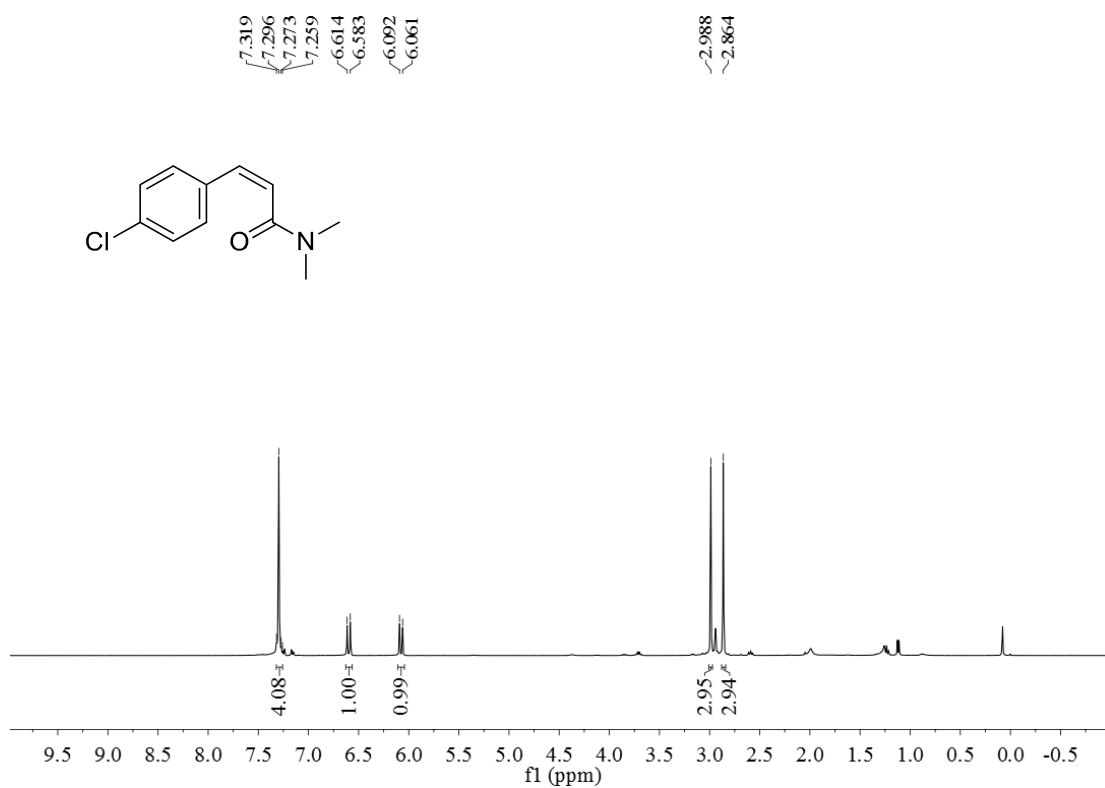
^1H NMR spectrum (400 MHz, CDCl_3) of **2f**



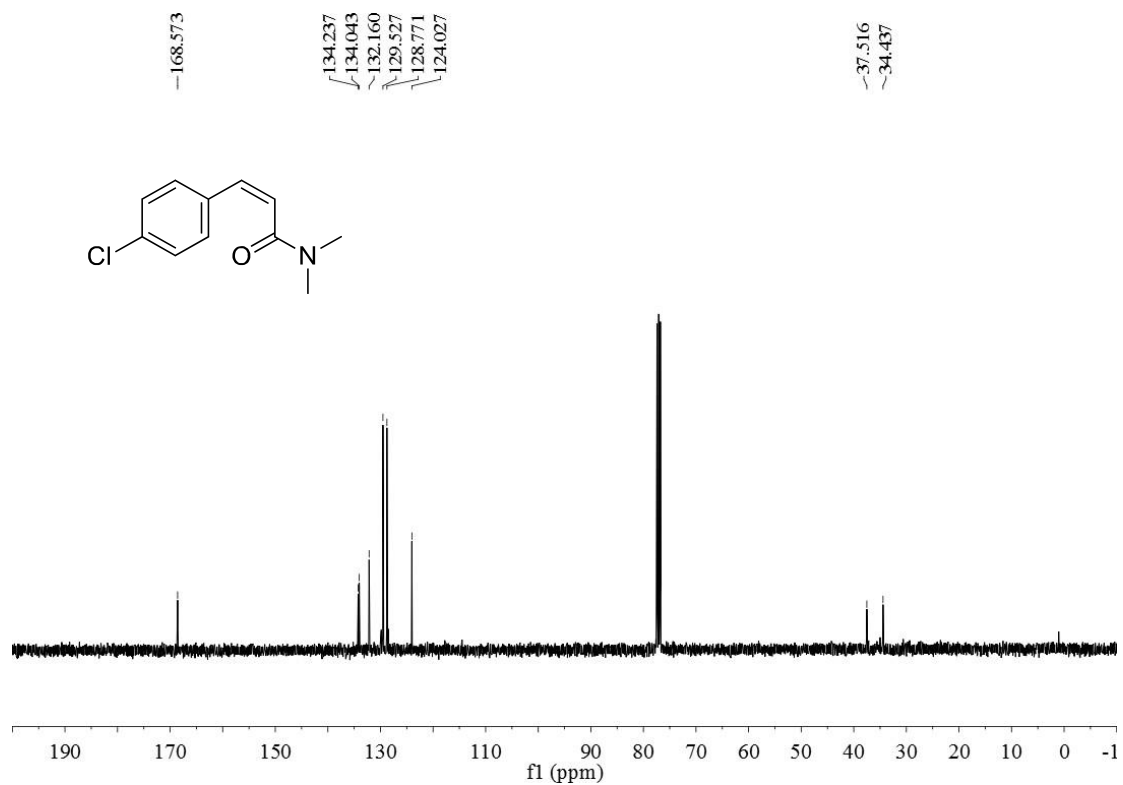
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2f**



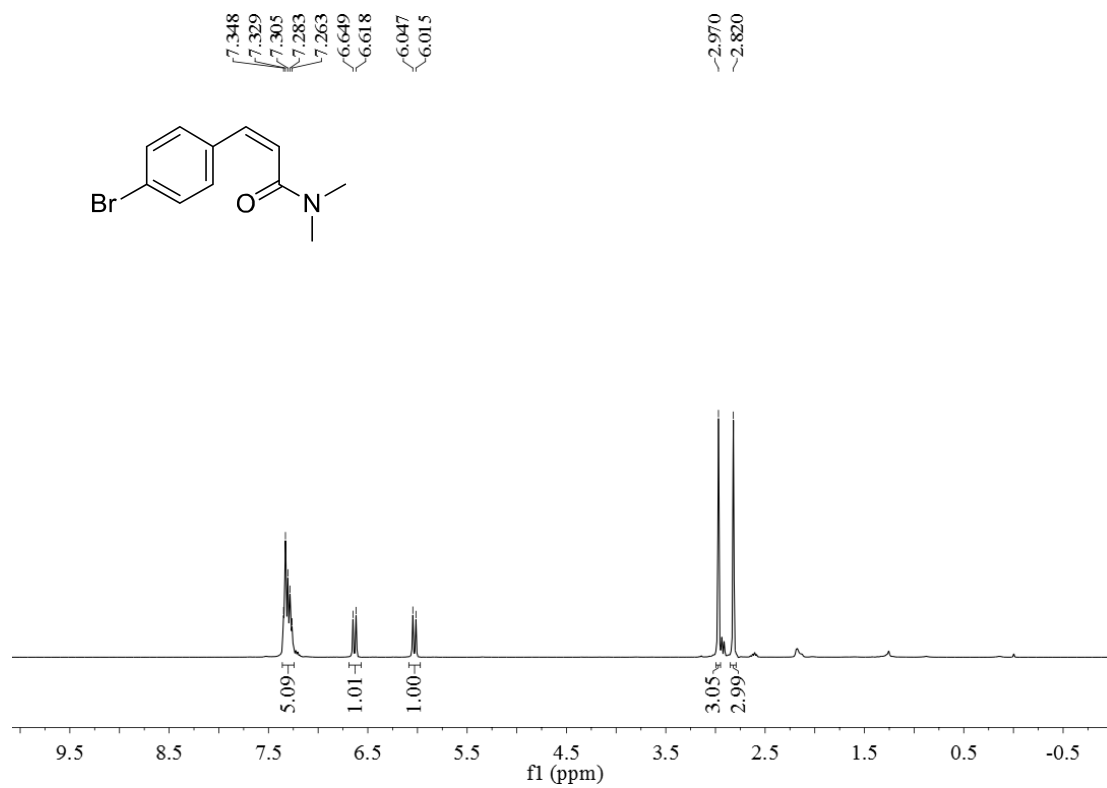
^1H NMR spectrum (400 MHz, CDCl_3) of **2g**



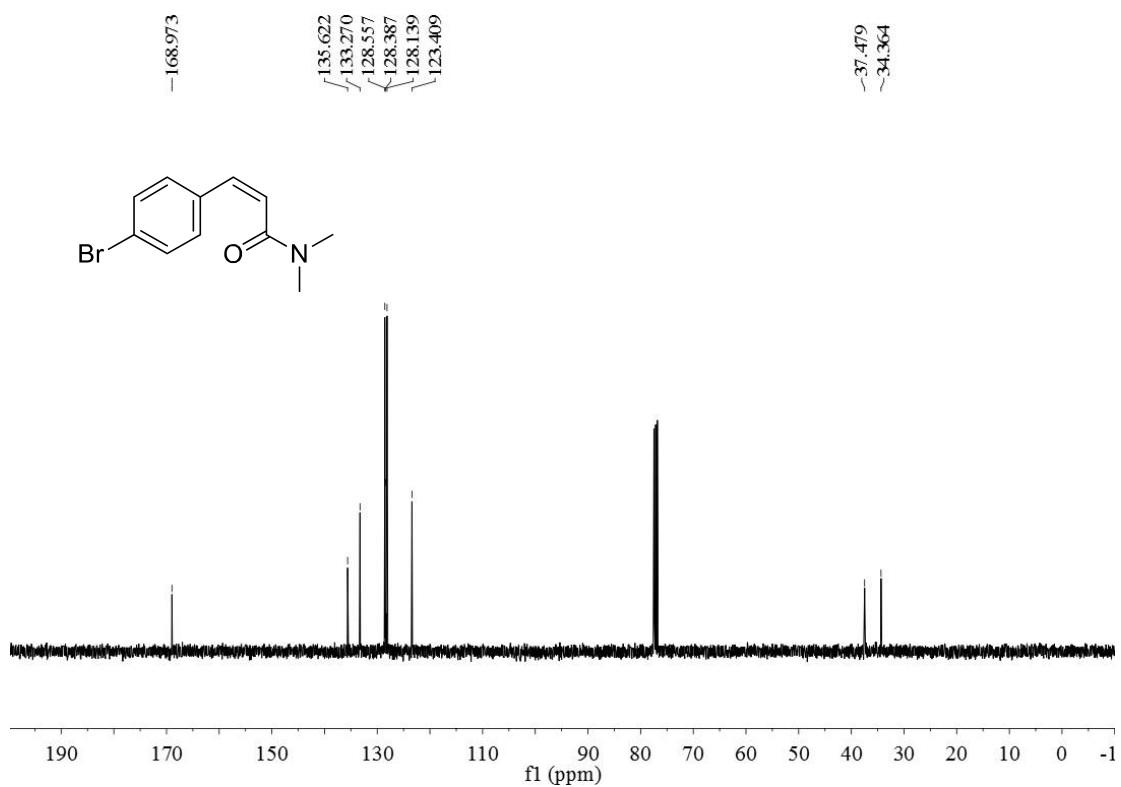
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2g**



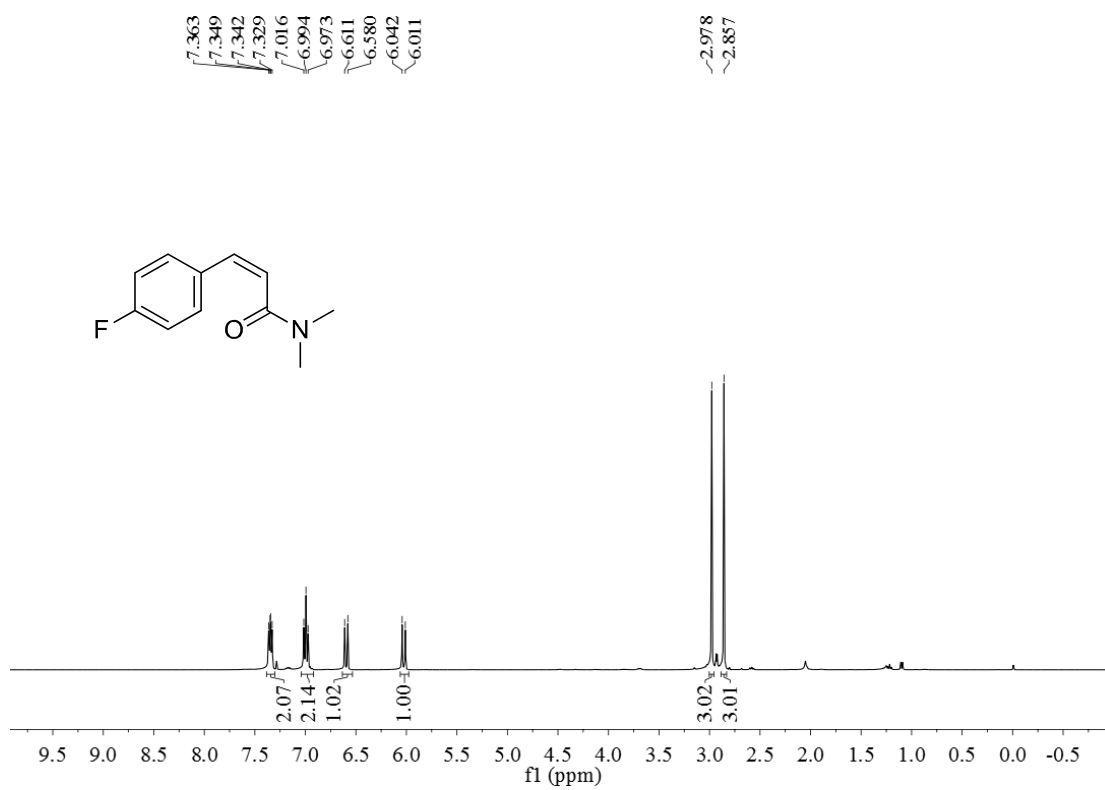
^1H NMR spectrum (400 MHz, CDCl_3) of **2h**



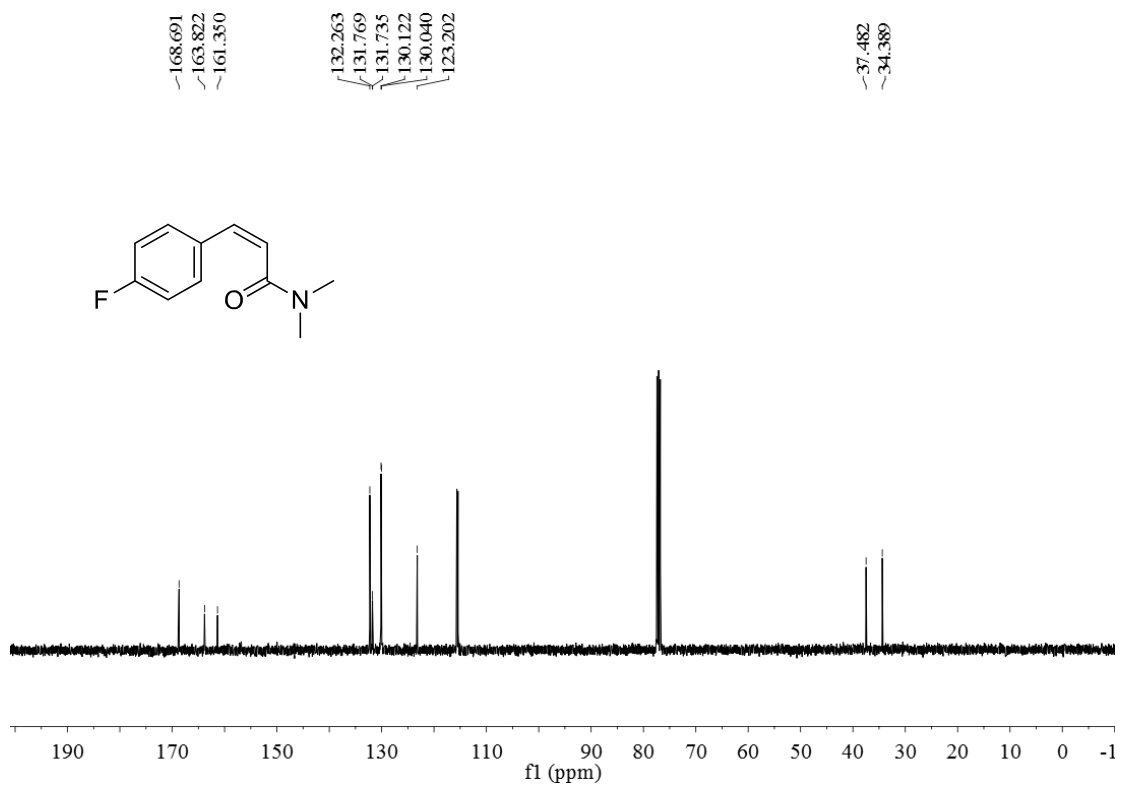
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2h**



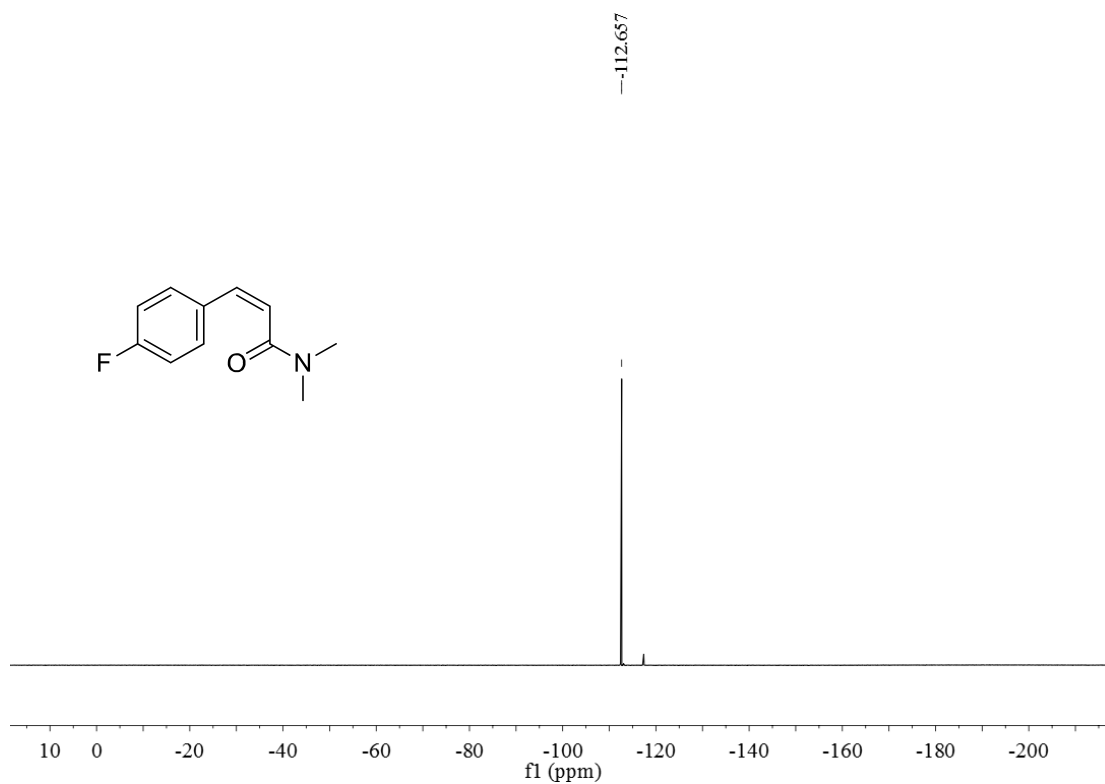
^1H NMR spectrum (400 MHz, CDCl_3) of **2i**



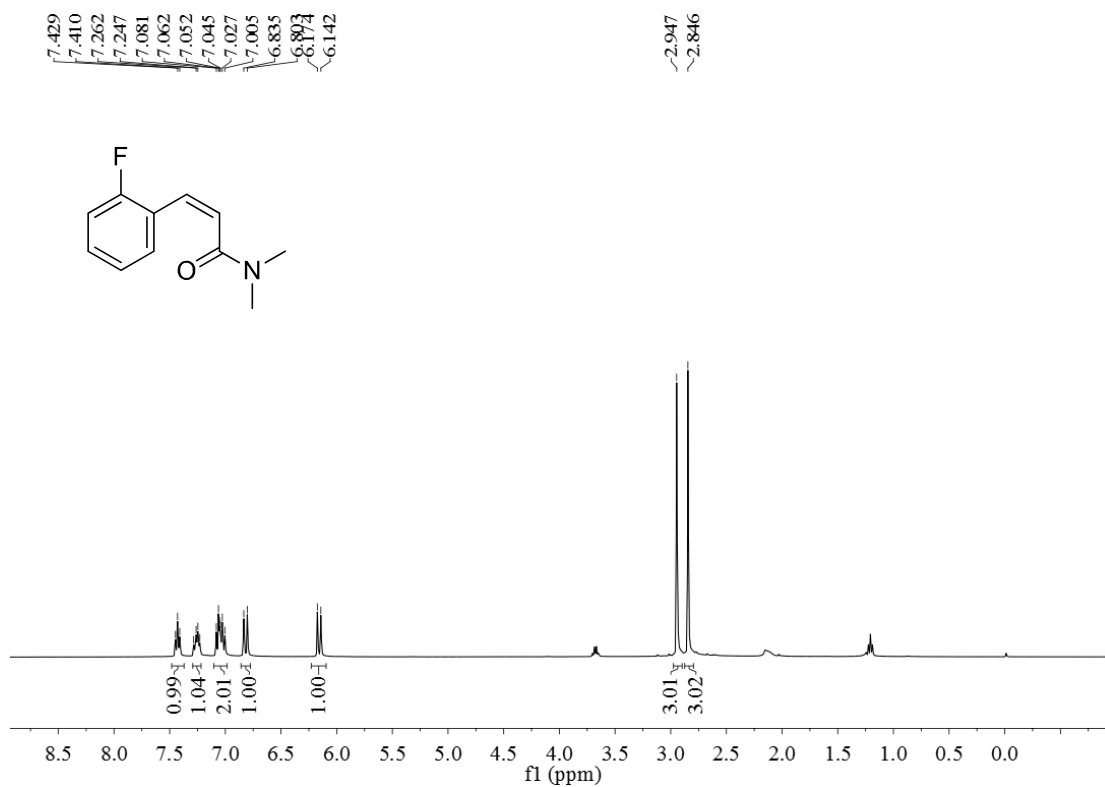
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2i**



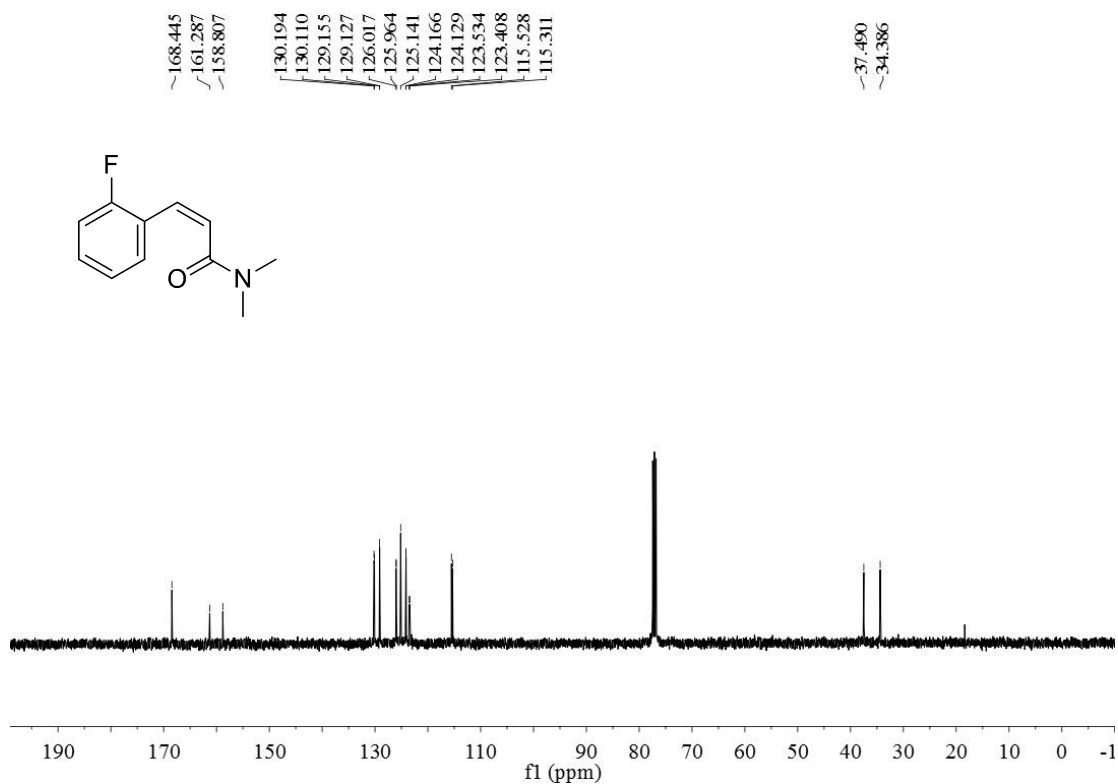
^{19}F NMR spectrum (376 MHz, CDCl_3) of **2i**



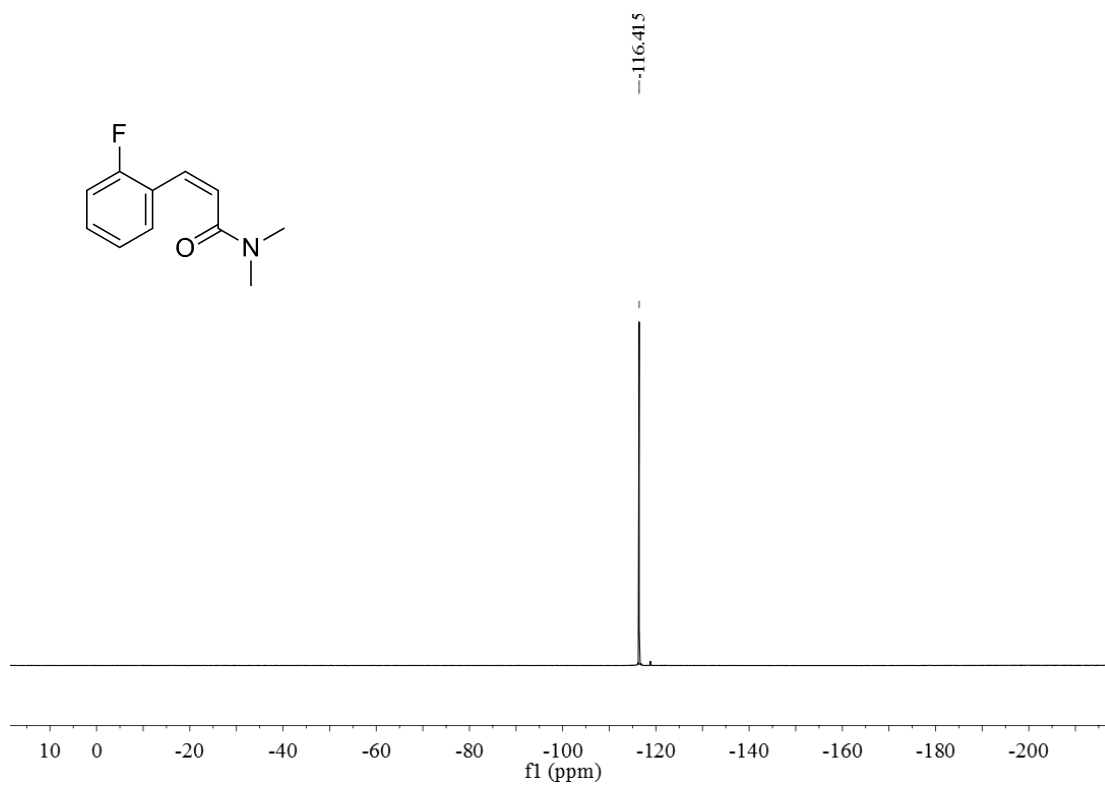
¹H NMR spectrum (400 MHz, CDCl₃) of **2j**



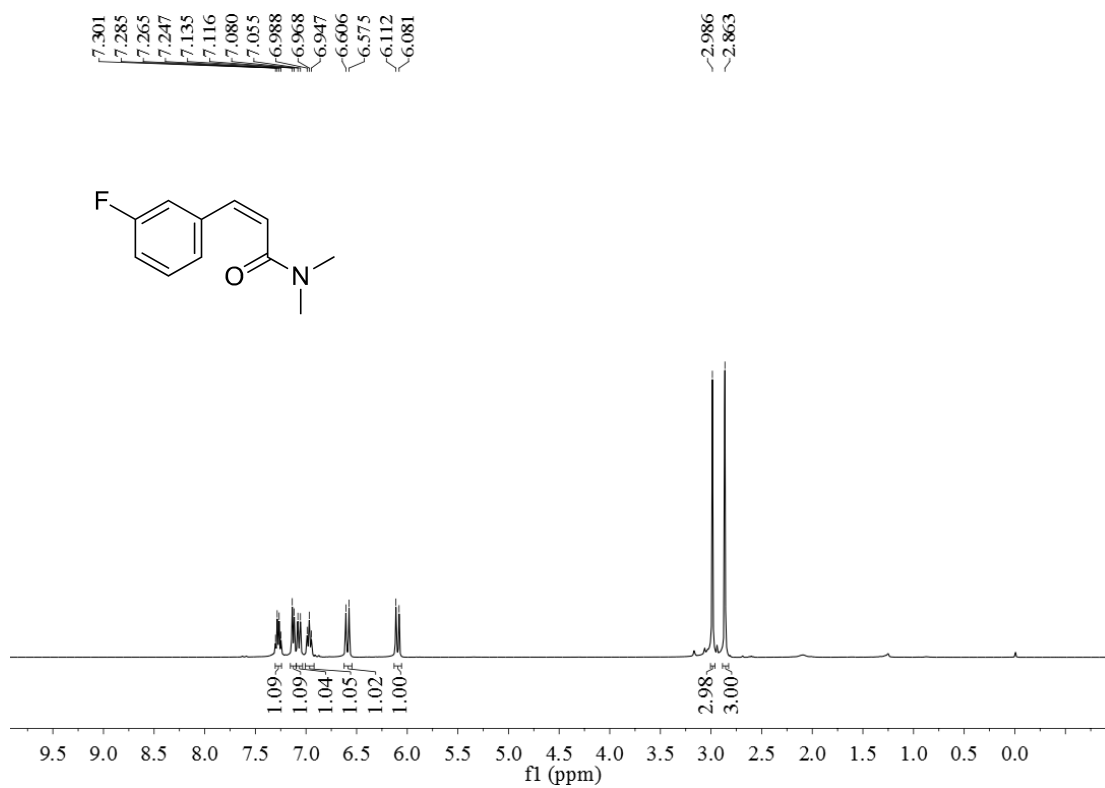
¹³C NMR spectrum (100 MHz, CDCl₃) of **2j**



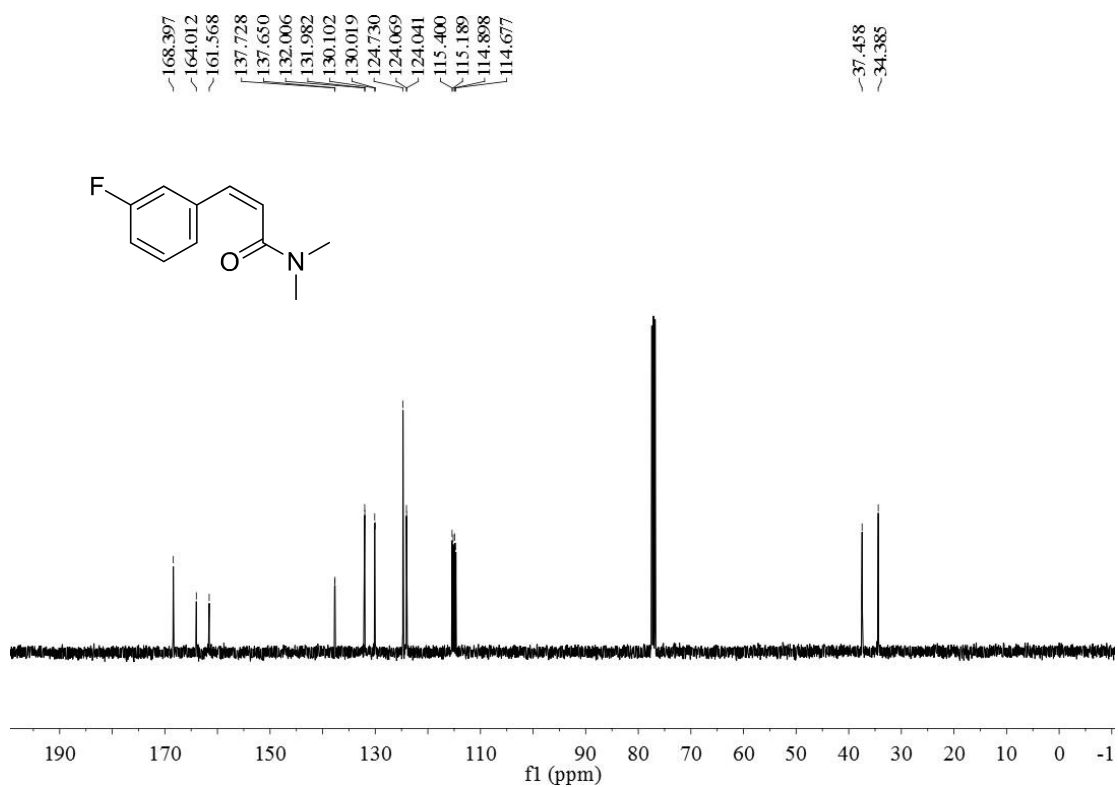
^{19}F NMR spectrum (376 MHz, CDCl_3) of **2j**



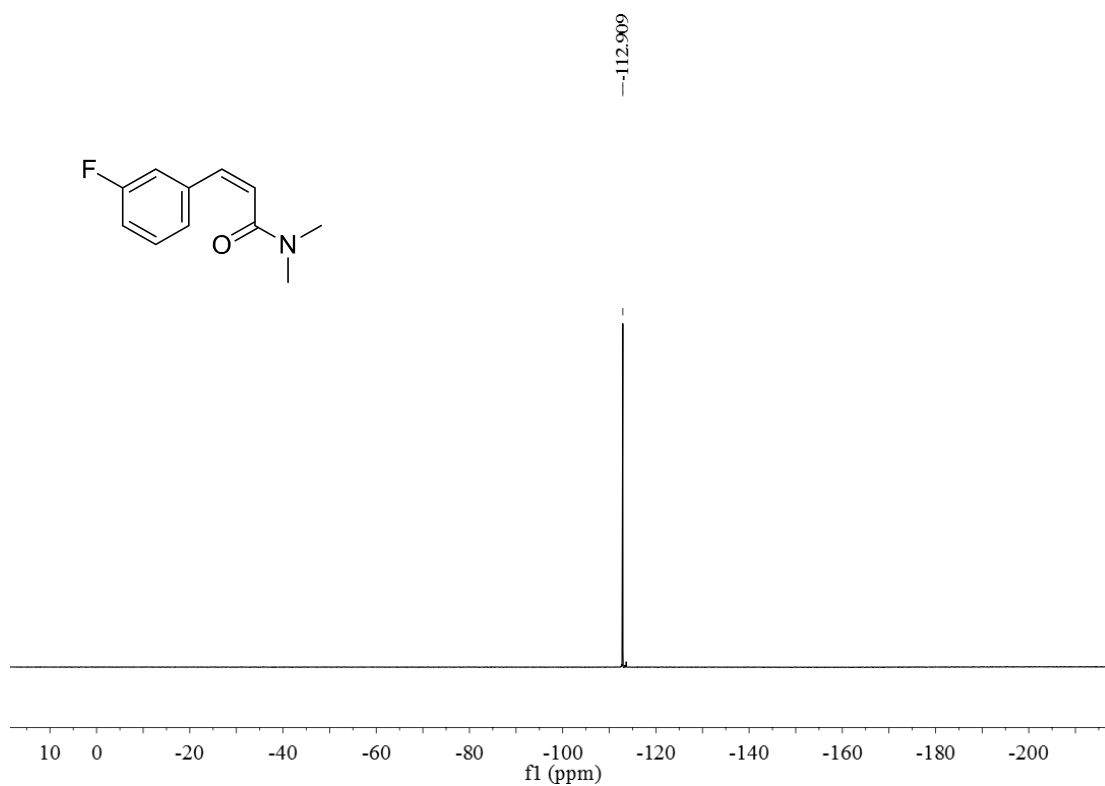
^1H NMR spectrum (400 MHz, CDCl_3) of **2k**



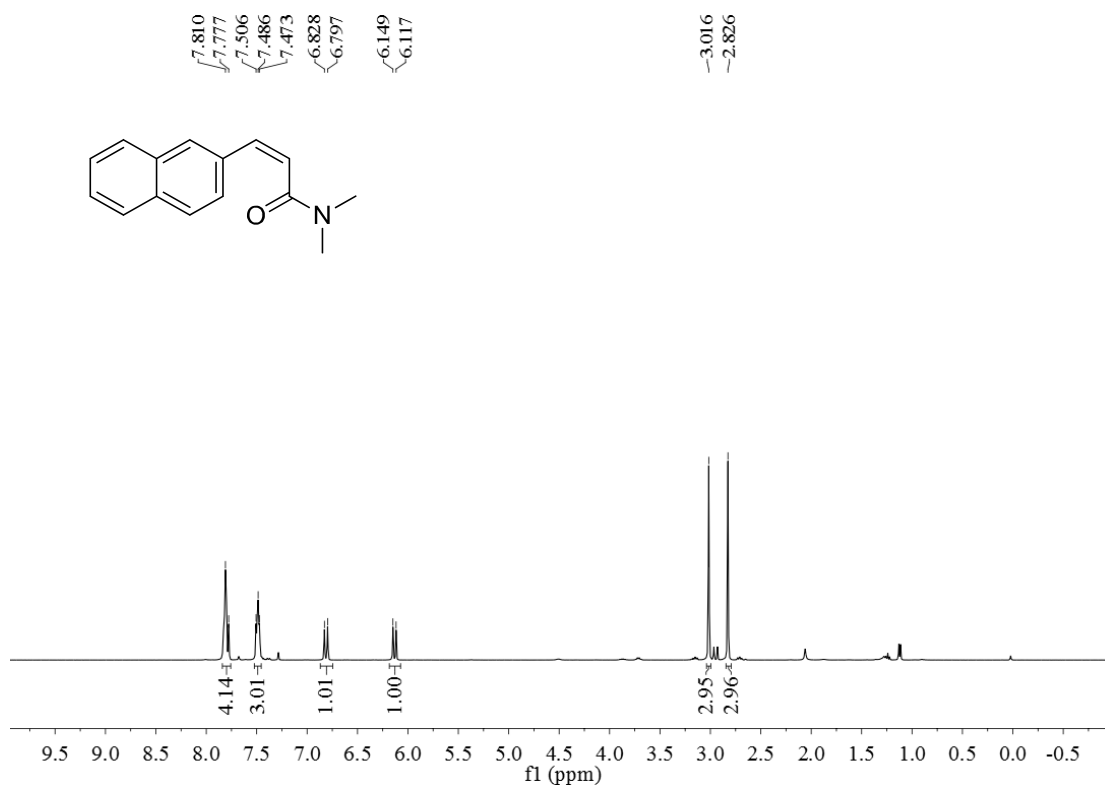
¹³C NMR spectrum (100 MHz, CDCl₃) of **2k**



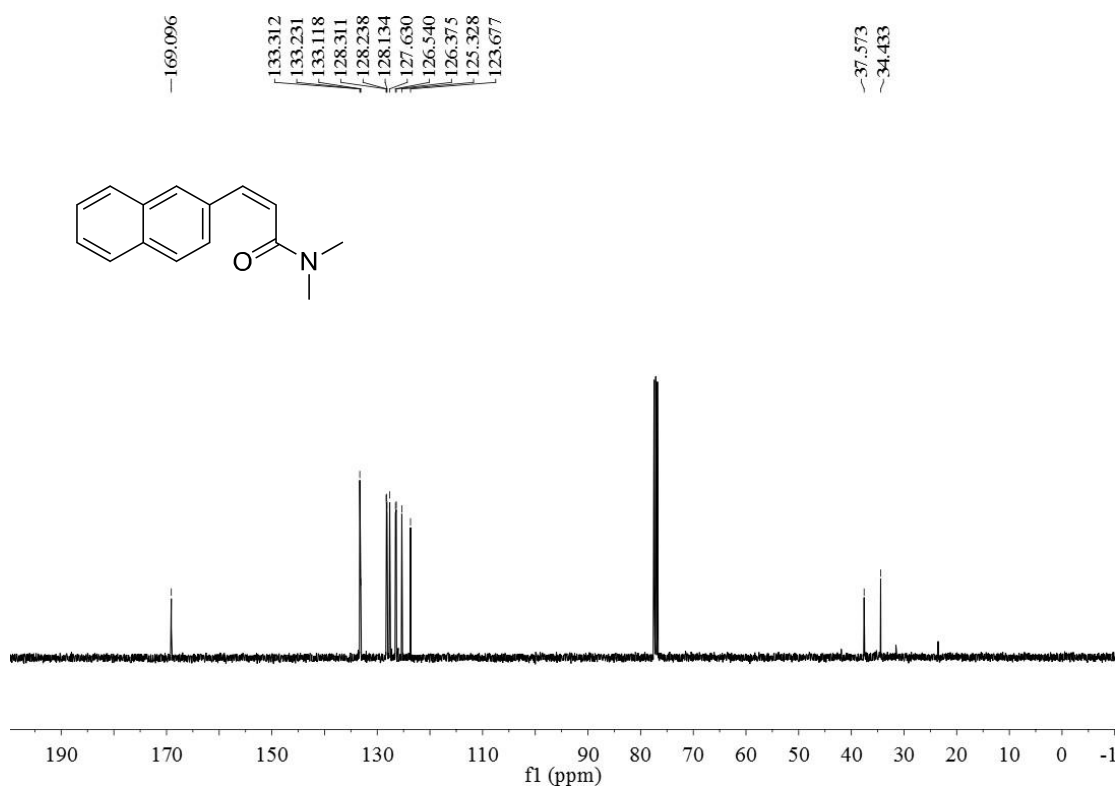
¹⁹F NMR spectrum (376 MHz, CDCl₃) of **2k**



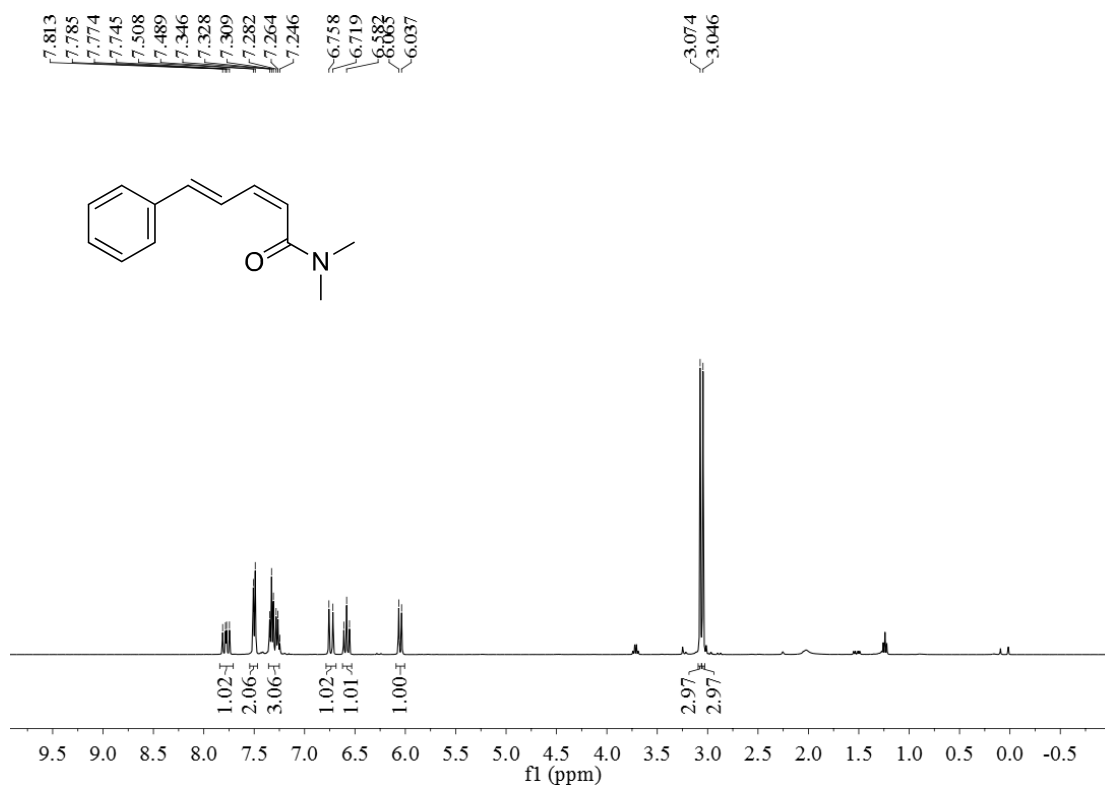
¹H NMR spectrum (400 MHz, CDCl₃) of **21**



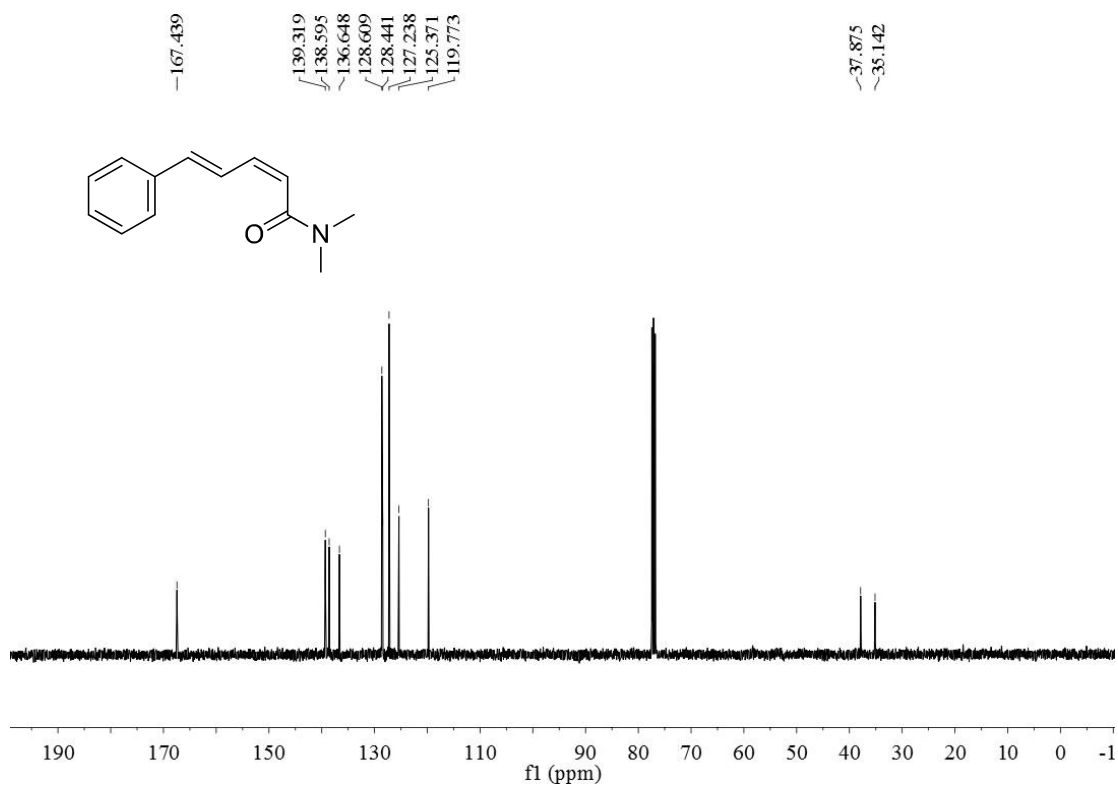
¹³C NMR spectrum (100 MHz, CDCl₃) of **21**



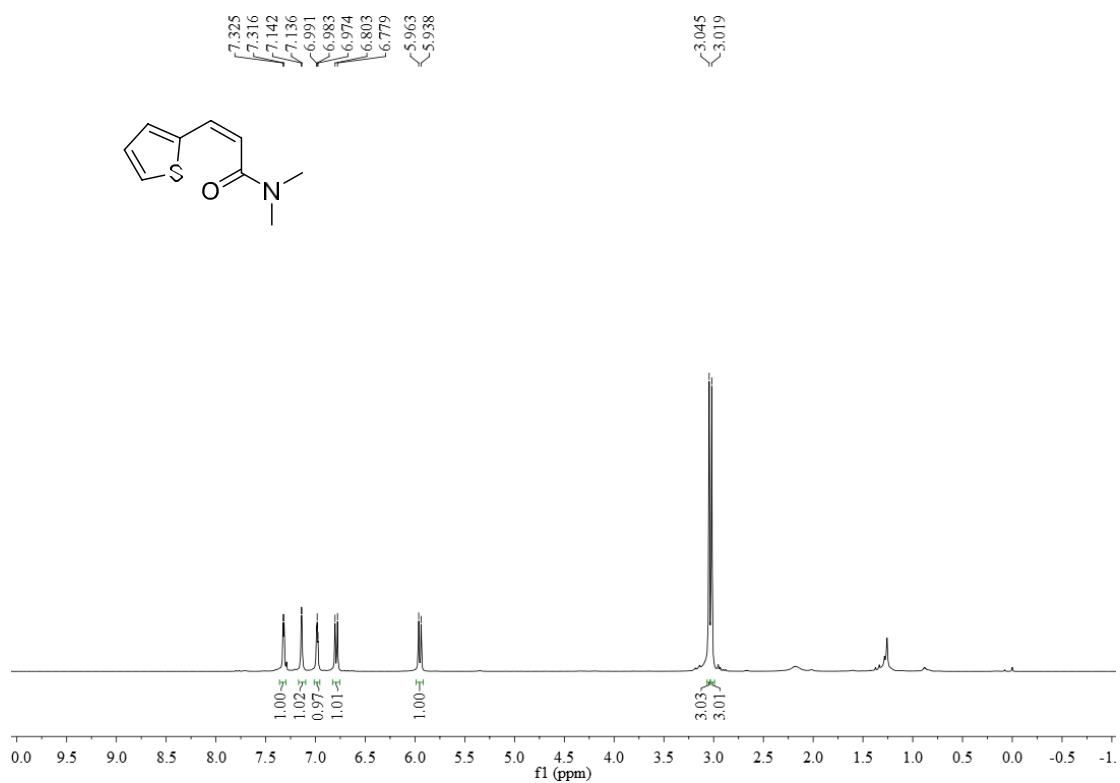
¹H NMR spectrum (400 MHz, CDCl₃) of **2m**



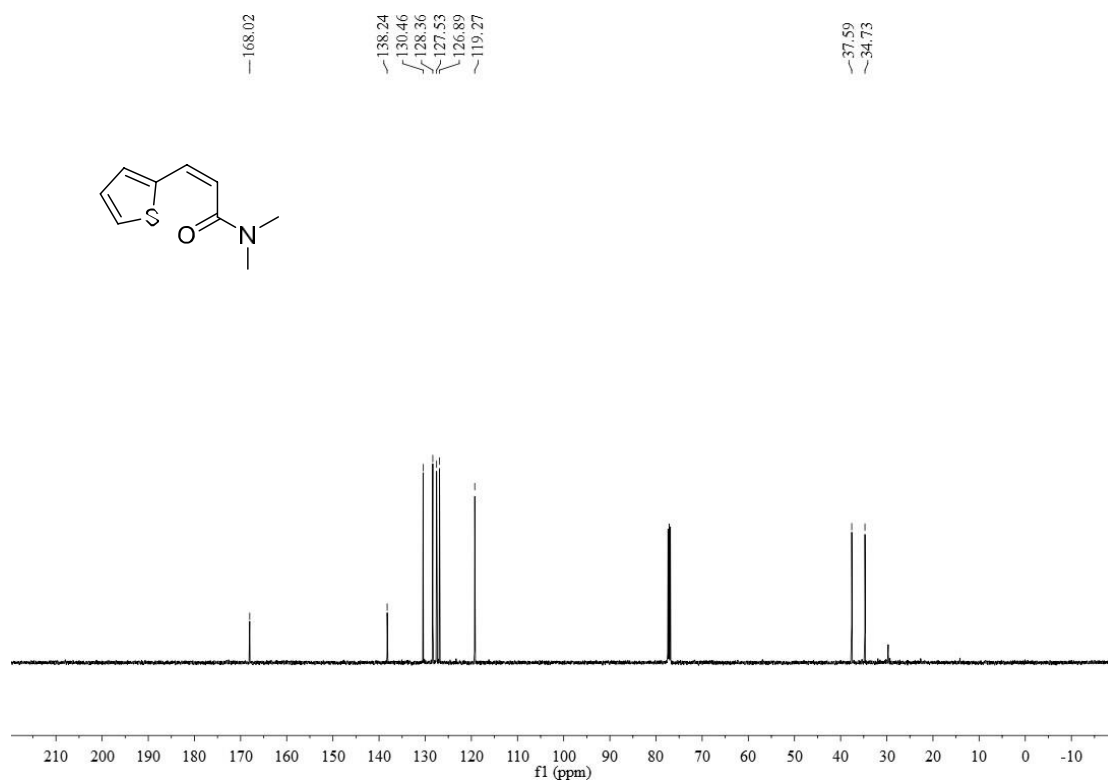
¹³C NMR spectrum (100 MHz, CDCl₃) of **2m**



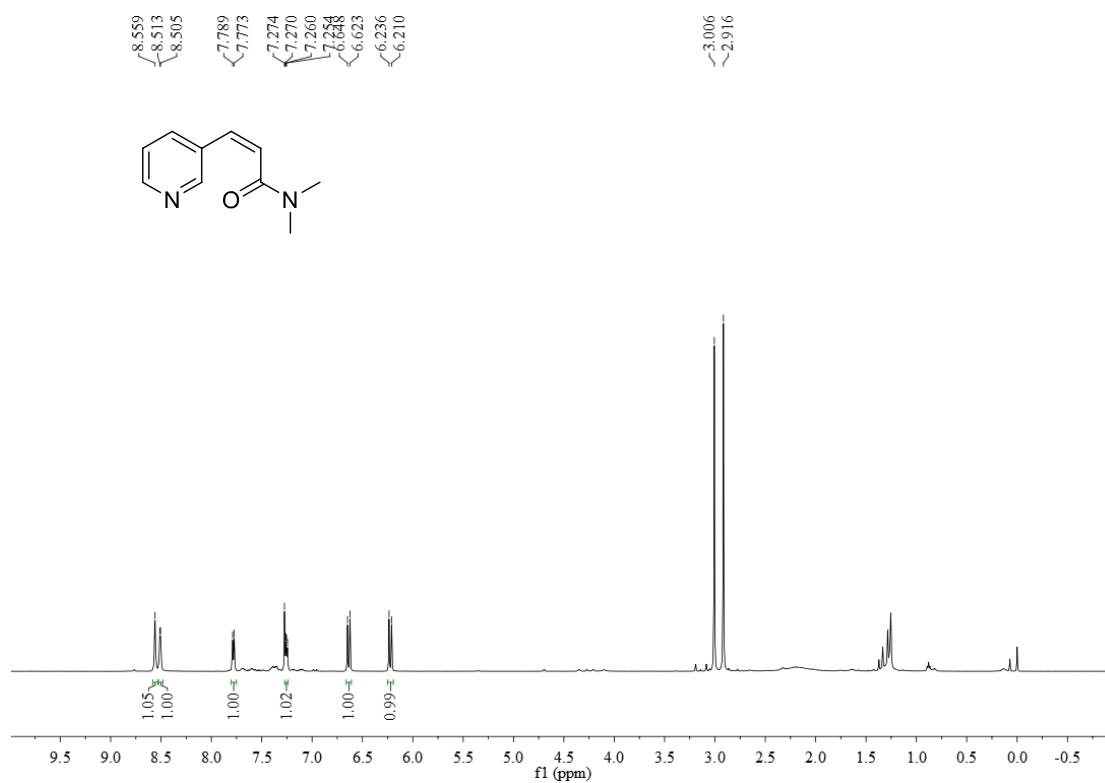
¹H NMR spectrum (400 MHz, CDCl₃) of **2n**



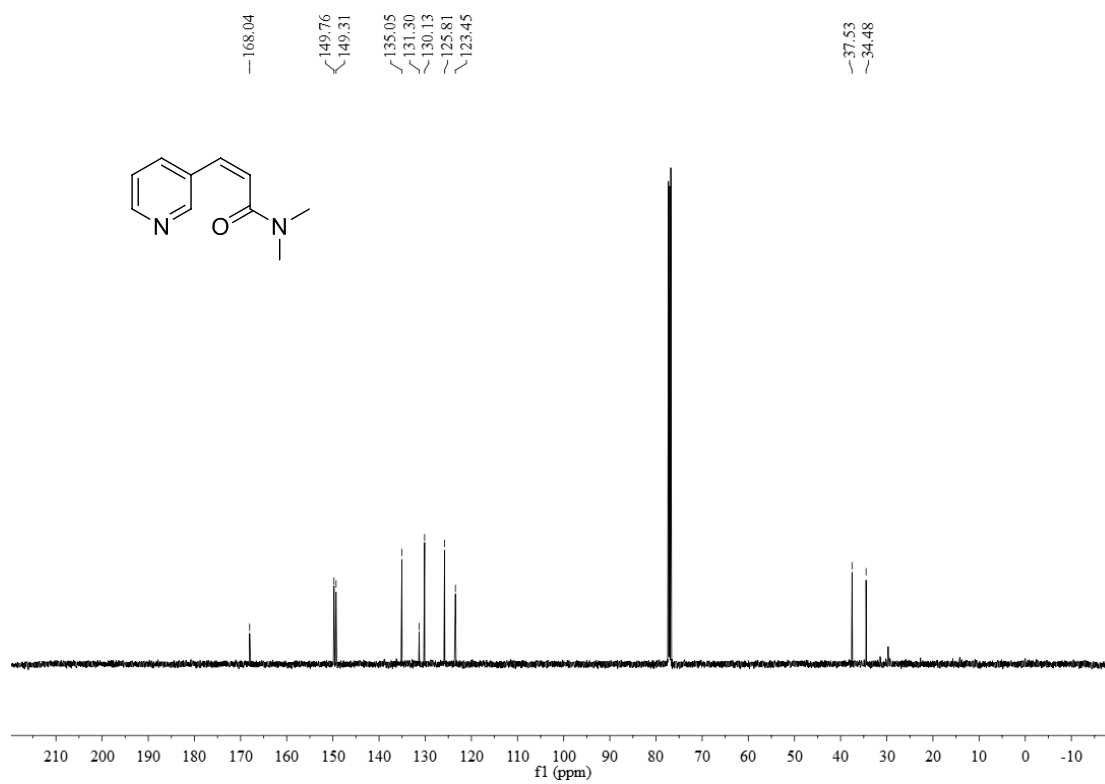
¹³C NMR spectrum (100 MHz, CDCl₃) of **2n**



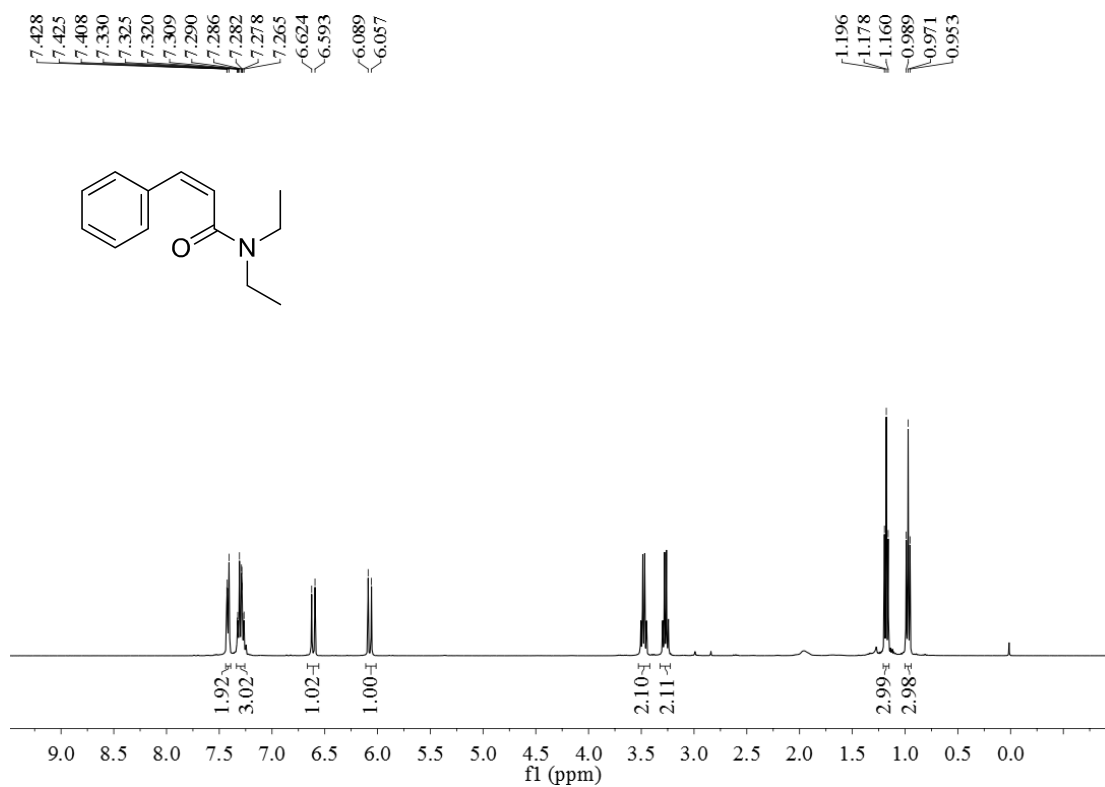
¹H NMR spectrum (400 MHz, CDCl₃) of **2o**



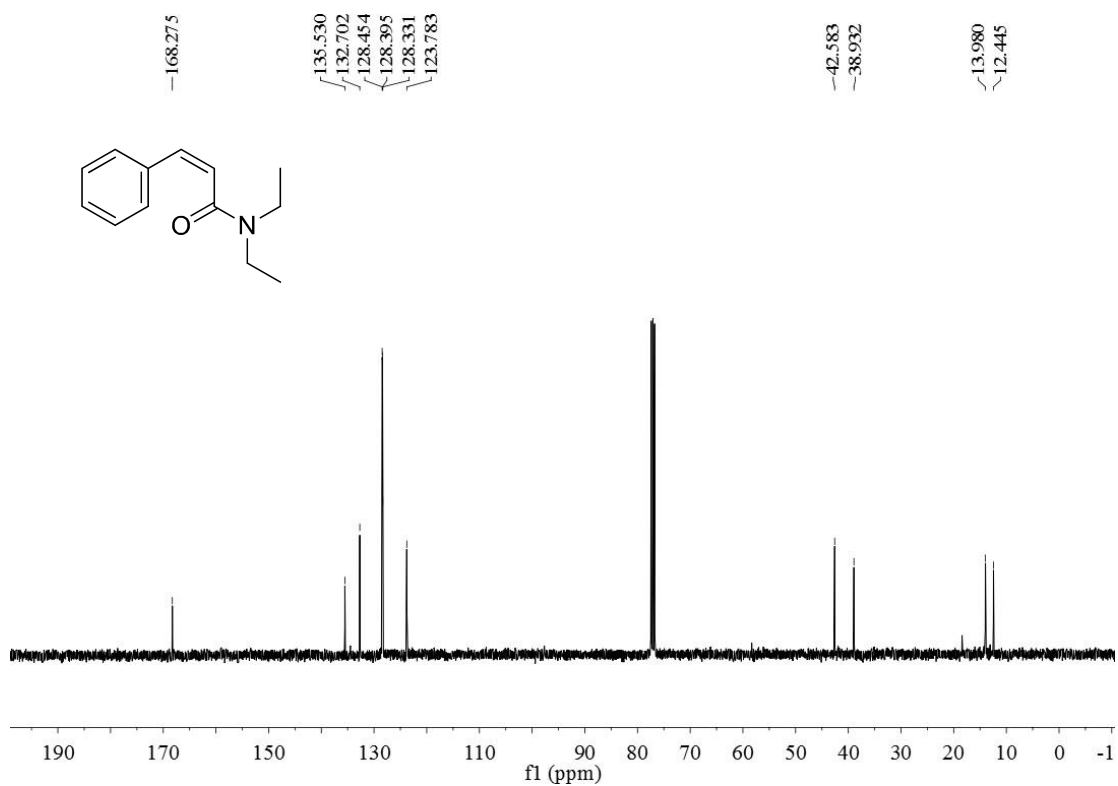
¹³C NMR spectrum (100 MHz, CDCl₃) of **2o**



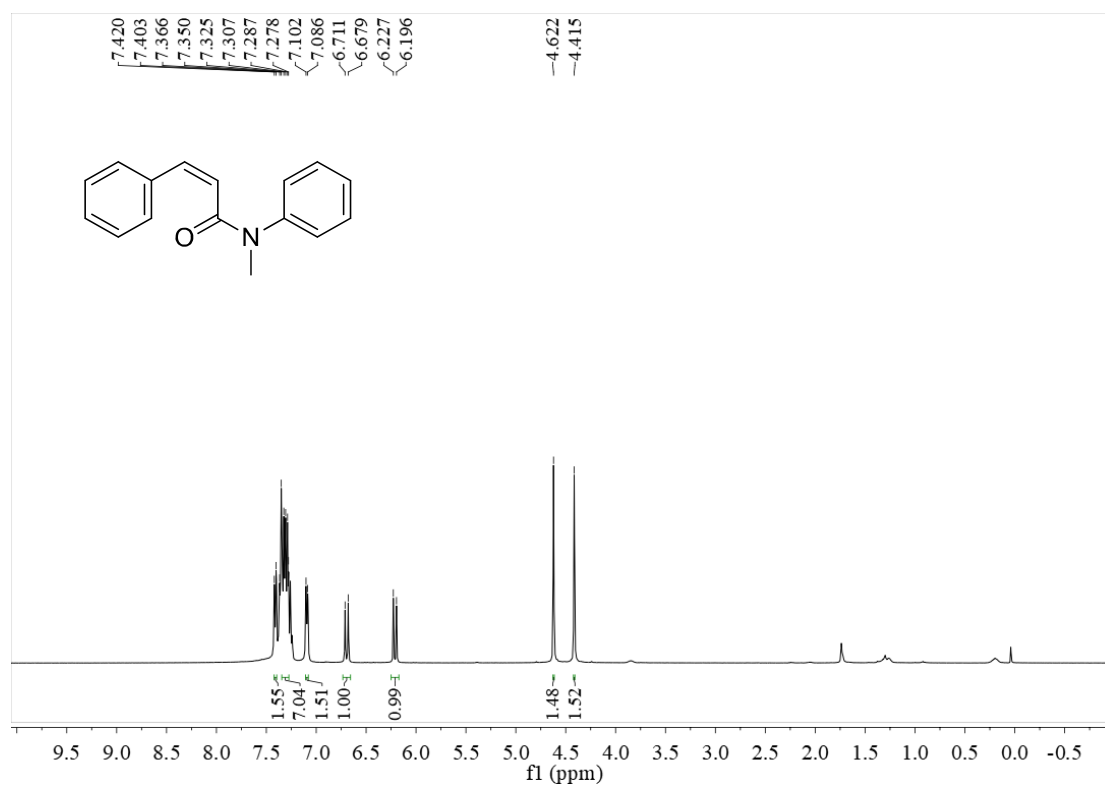
¹H NMR spectrum (400 MHz, CDCl₃) of **2p**



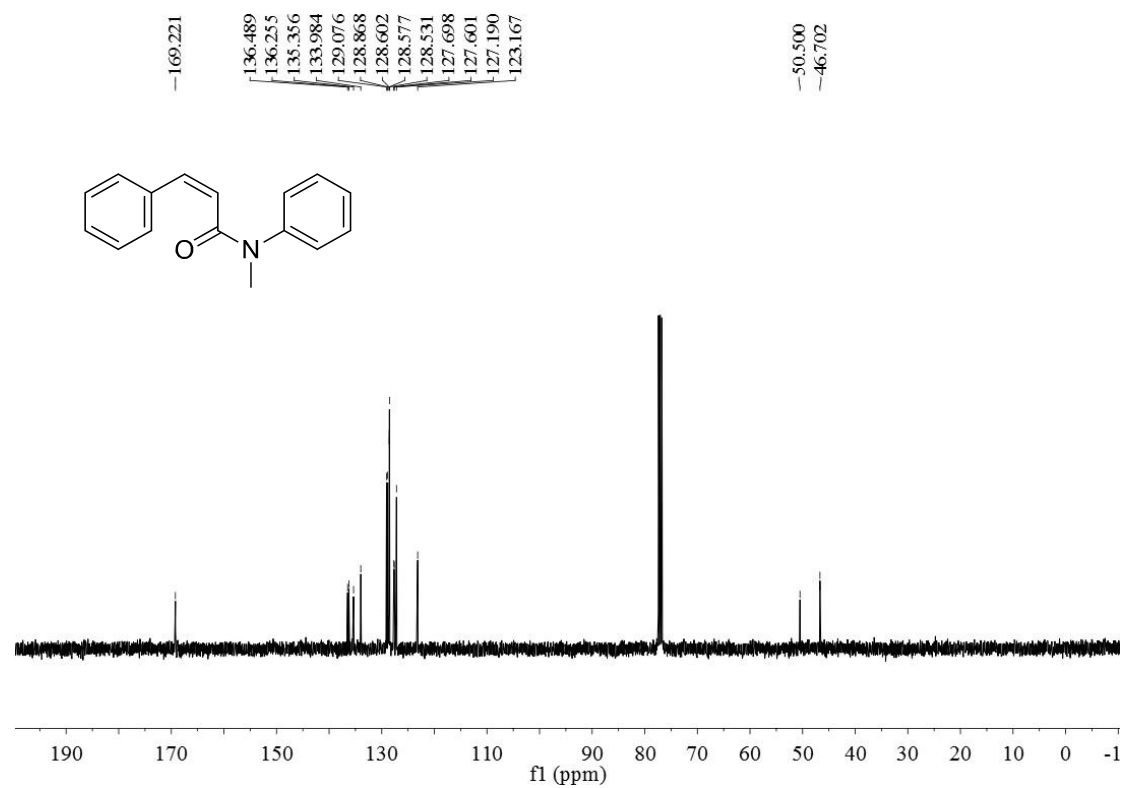
¹³C NMR spectrum (100 MHz, CDCl₃) of **2p**



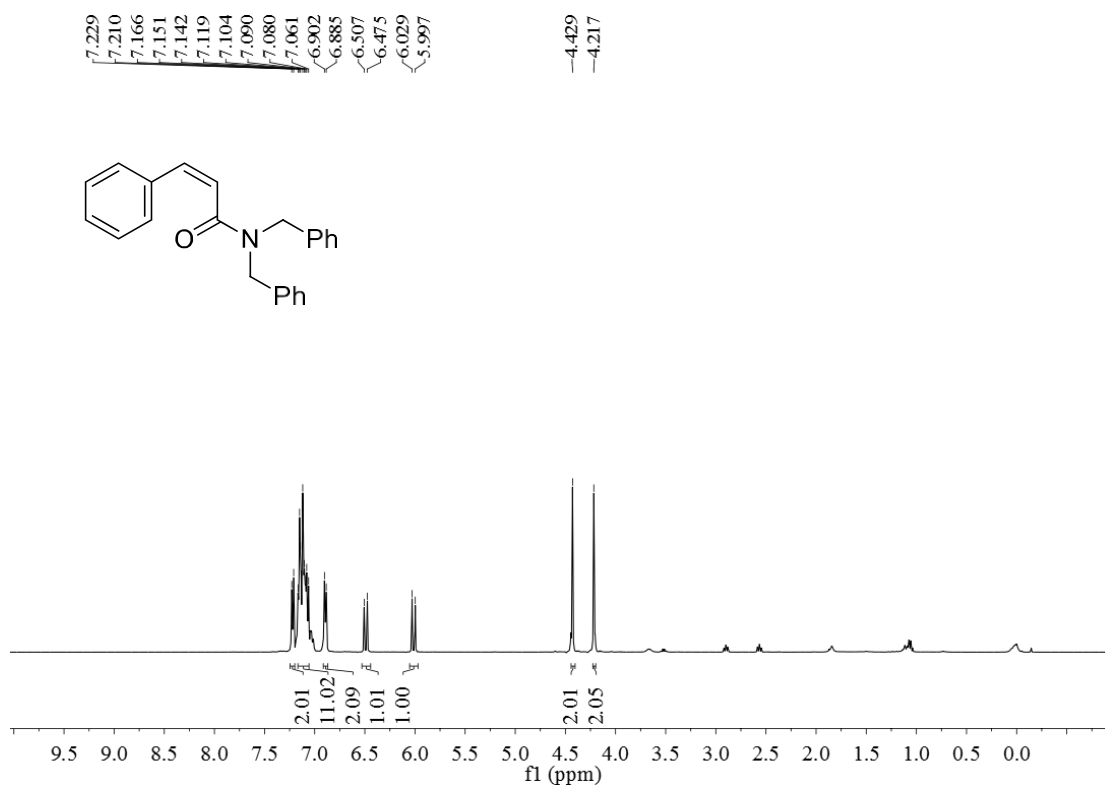
¹H NMR spectrum (400 MHz, CDCl₃) of **2q**



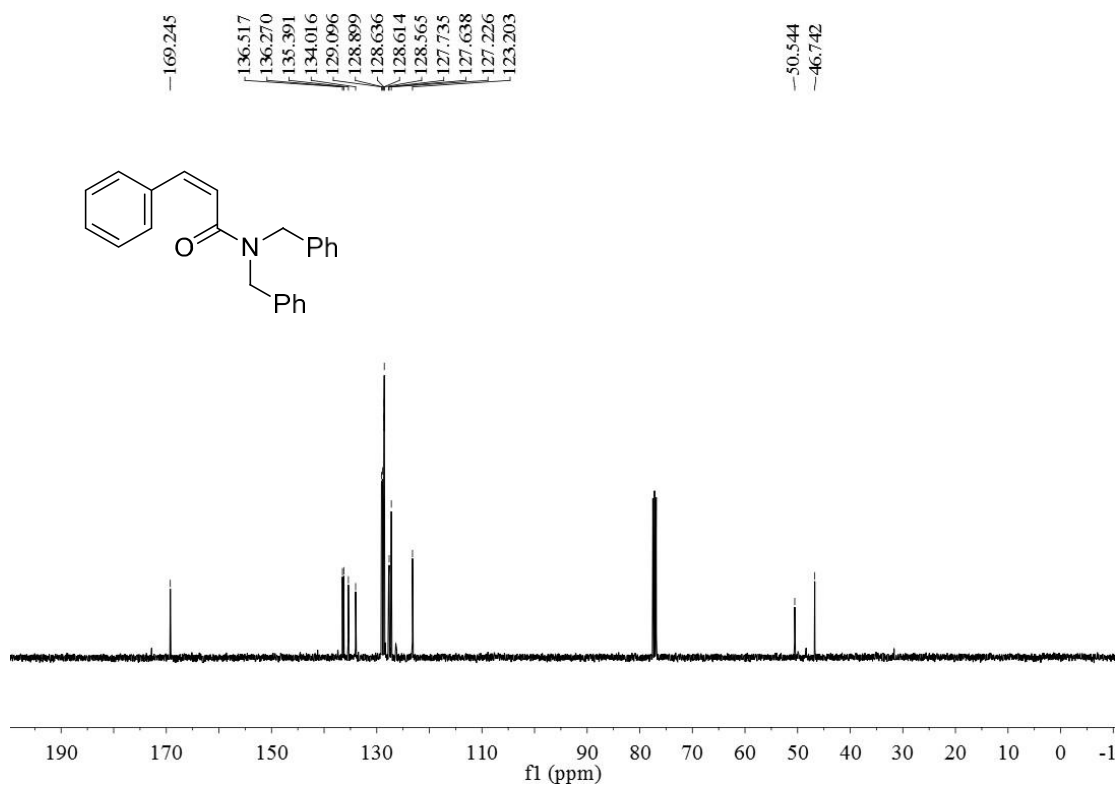
¹³C NMR spectrum (100 MHz, CDCl₃) of **2q**



¹H NMR spectrum (400 MHz, CDCl₃) of **2r**

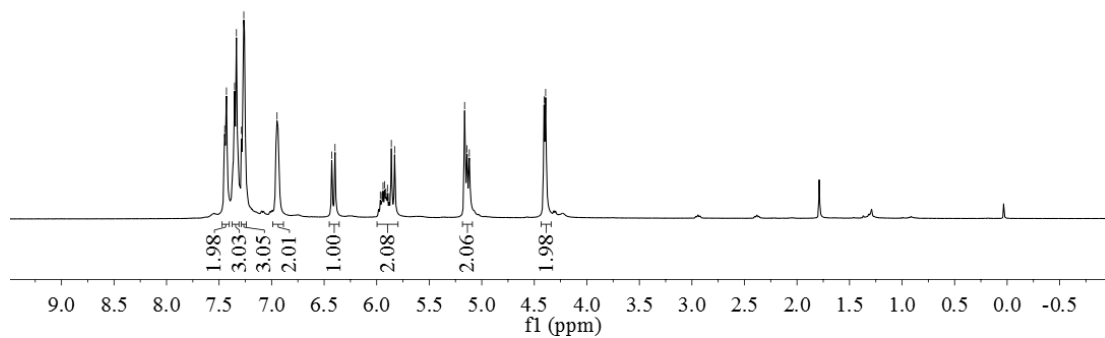
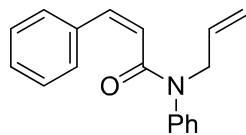


¹³C NMR spectrum (100 MHz, CDCl₃) of **2r**



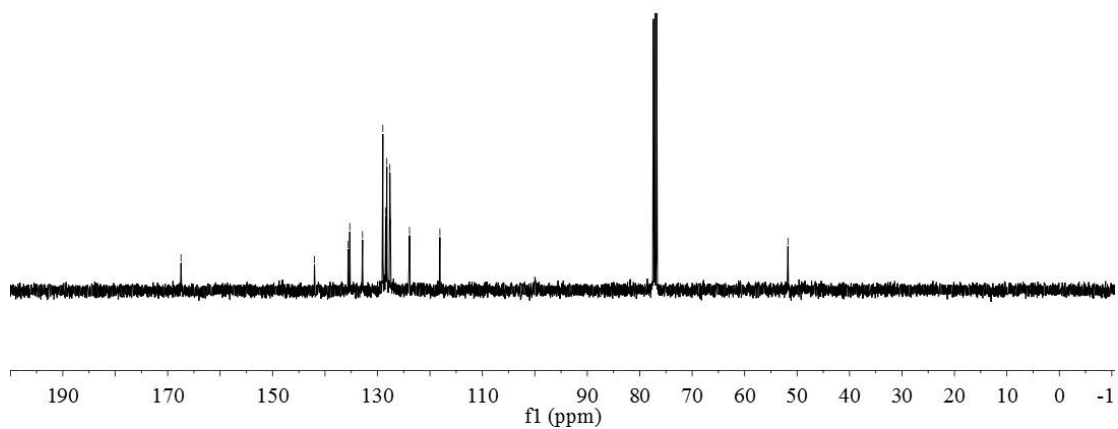
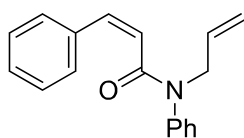
¹H NMR spectrum (400 MHz, CDCl₃) of **2s**

7.446
7.430
7.352
7.335
7.287
7.265
7.259
6.948
6.428
6.396
5.924
5.861
5.829
5.163
5.140
5.118
4.407
4.392

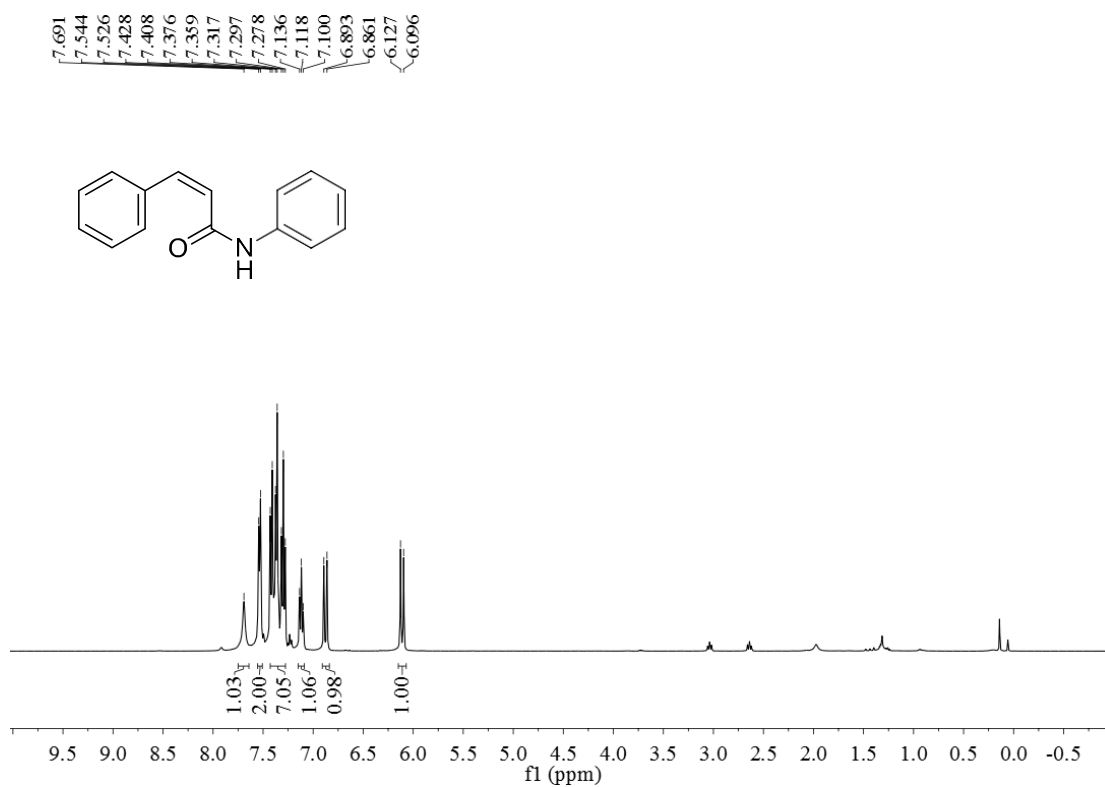


¹³C NMR spectrum (100 MHz, CDCl₃) of **2s**

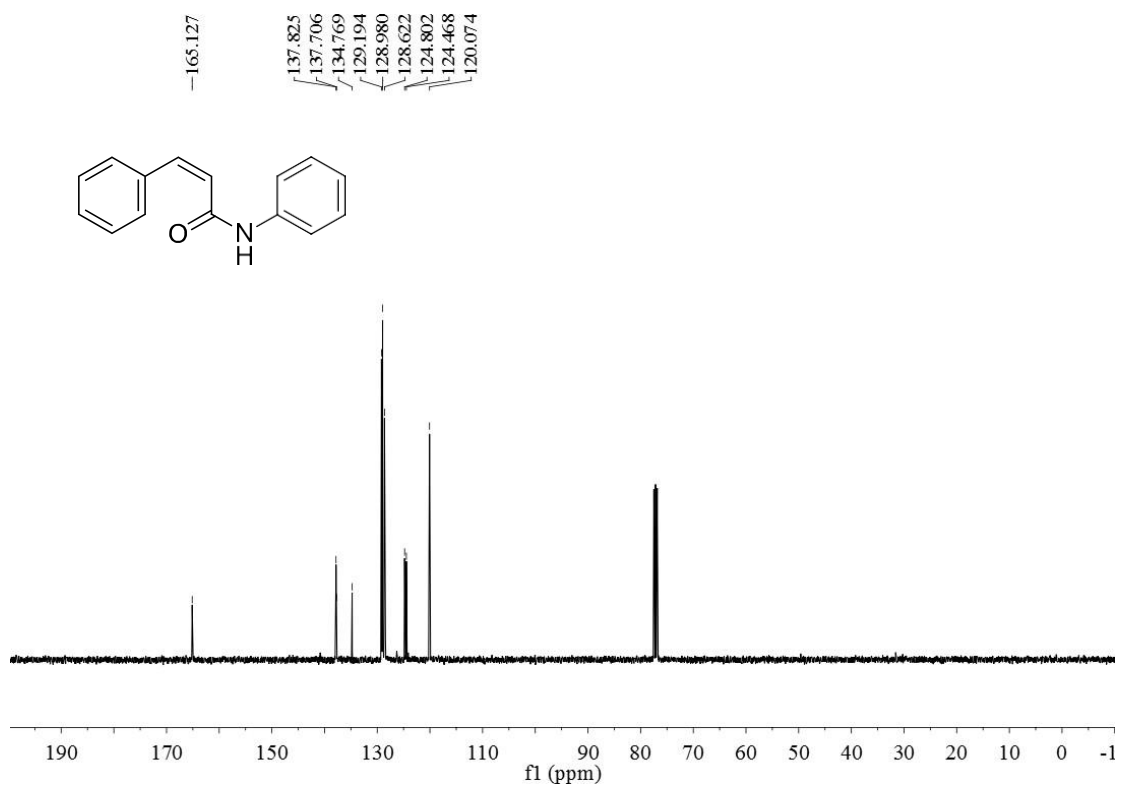
167.459
142.015
135.591
135.284
132.845
129.037
128.977
128.432
128.216
127.640
127.520
123.896
118.103
51.743



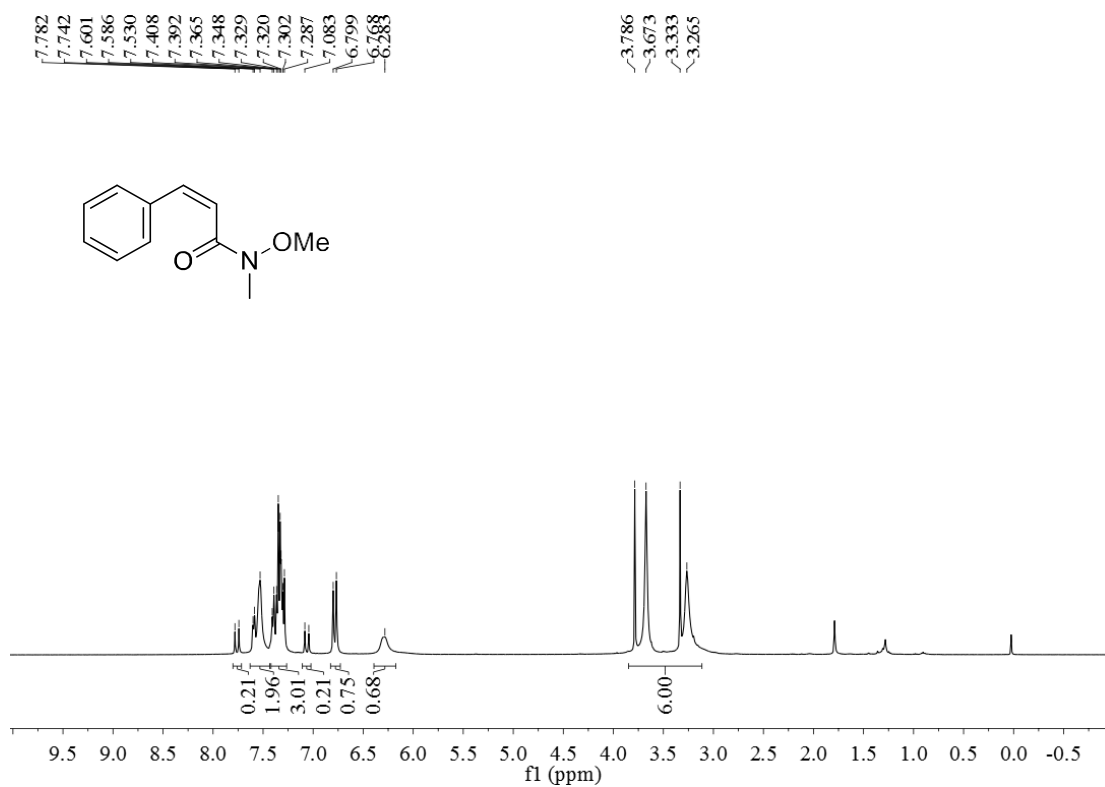
¹H NMR spectrum (400 MHz, CDCl₃) of **2t**



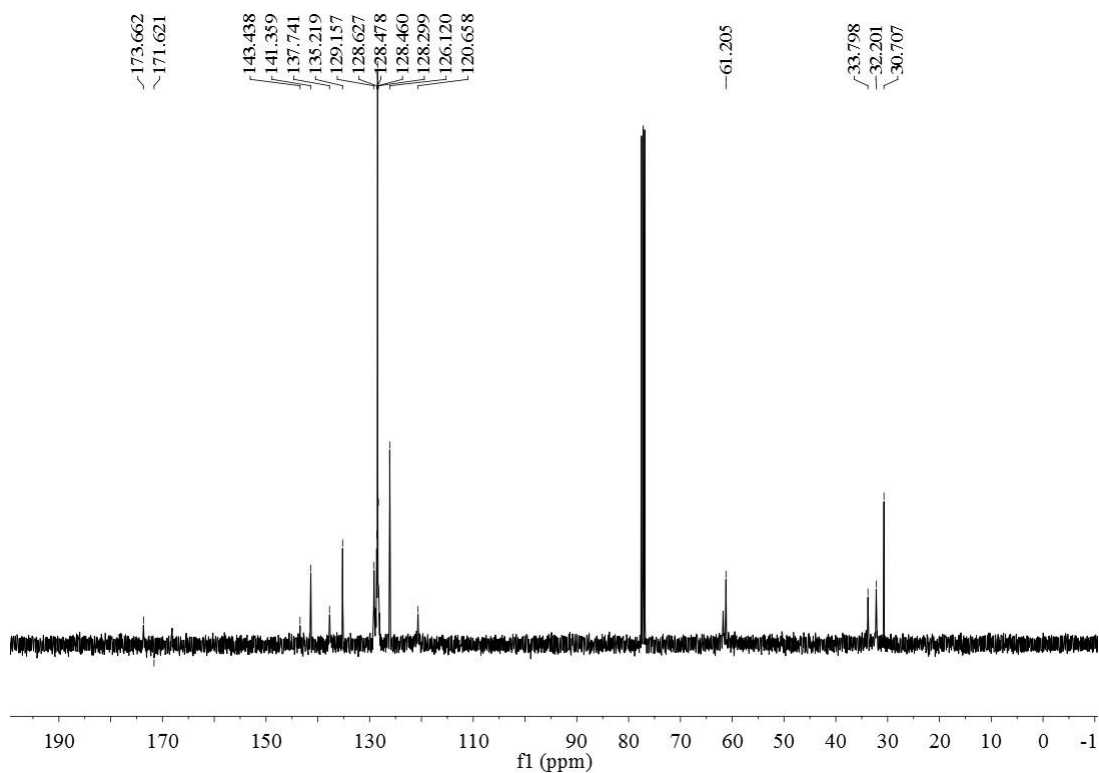
¹³C NMR spectrum (100 MHz, CDCl₃) of **2t**



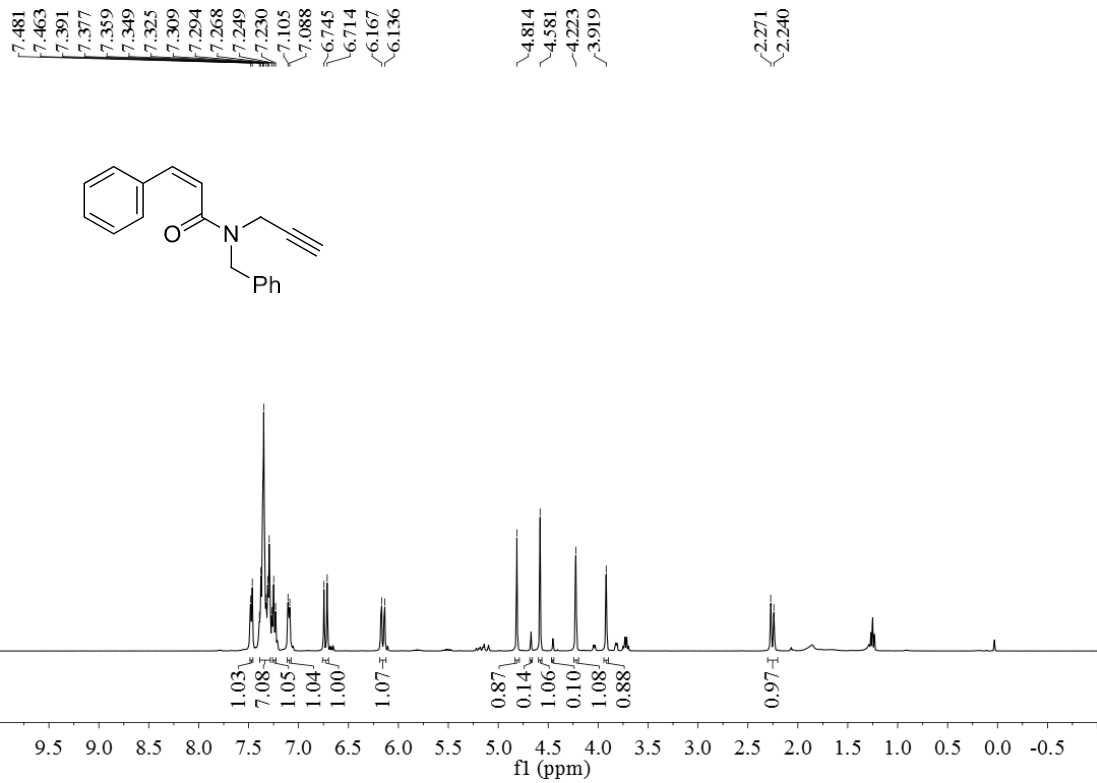
¹H NMR spectrum (400 MHz, CDCl₃) of **2u**



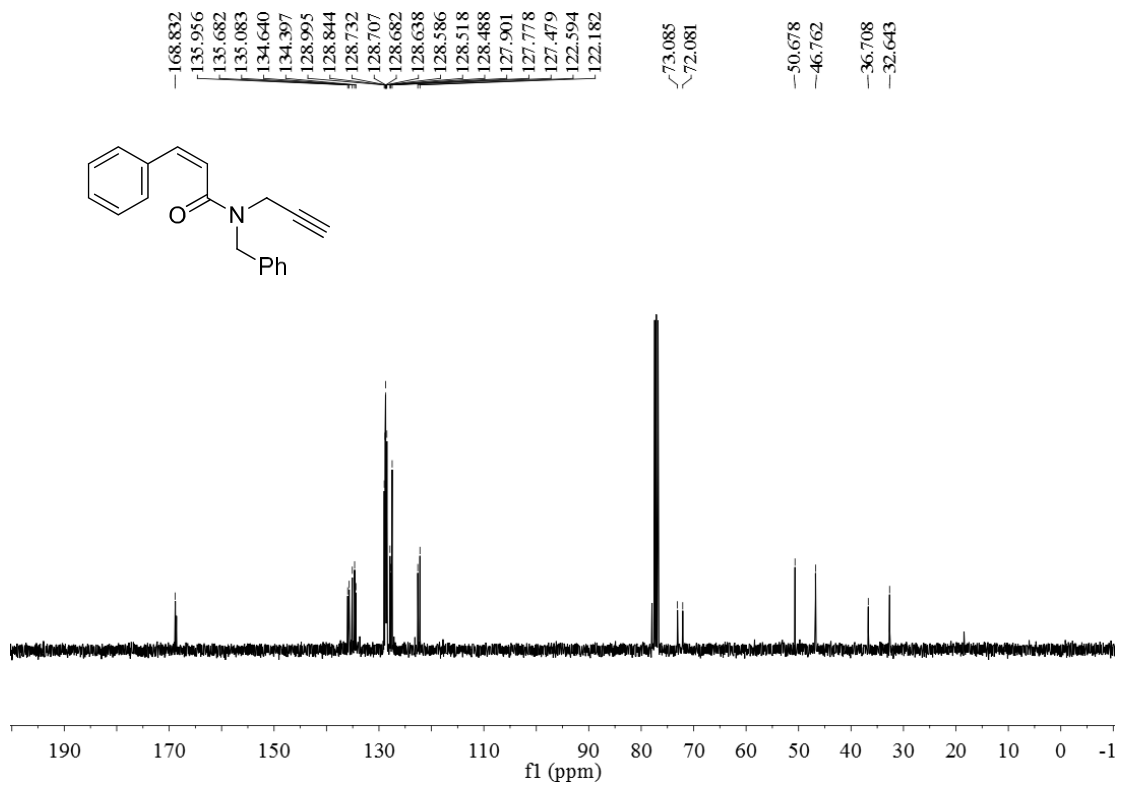
¹³C NMR spectrum (100 MHz, CDCl₃) of **2u**



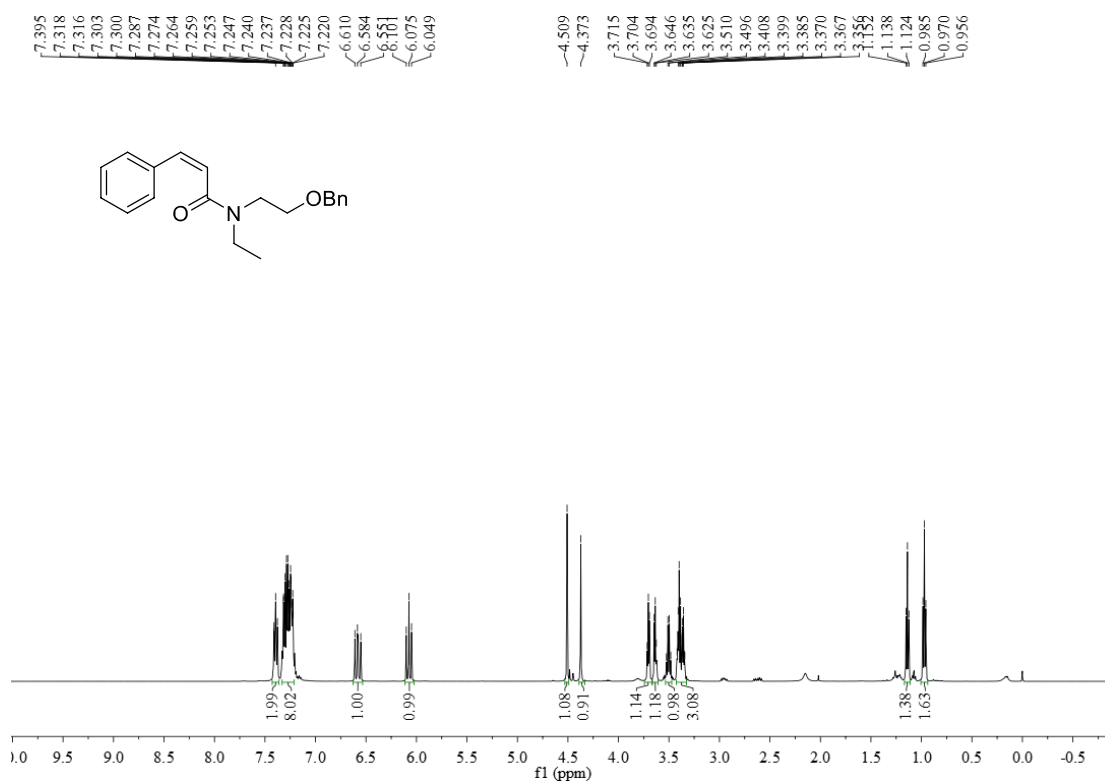
¹H NMR spectrum (400 MHz, CDCl₃) of **2v**



¹³C NMR spectrum (100 MHz, CDCl₃) of **2v**



¹H NMR spectrum (400 MHz, CDCl₃) of **2w**



¹³C NMR spectrum (100 MHz, CDCl₃) of **2w**

