

Supporting Information for

Cp₂TiCl₂-Catalyzed *cis*-Hydroalumination of Propargylic Amines with Red-Al: Stereoselective Synthesis of *Z*-Configured Allylic Amines

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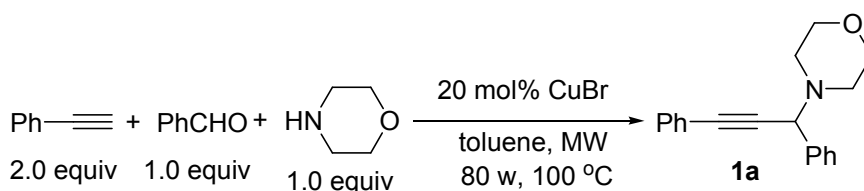
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General Methods.

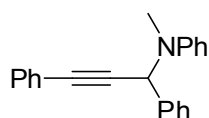
All reactions were carried out using standard Schlenk technique under argon. Toluene and THF were distilled from sodium and benzophenone. Titanocene dichloride and Red-Al were purchased from Aldrich Chemical Company. Unless noted, all commercial reagents were used without further purification. ¹H and ¹³C NMR spectra were recorded at room temperature in CDCl₃ (containing 0.03% TMS) or in C₆D₆ (containing 0.03% TMS) solutions on Varian XL-400 MHz or Agilent 400 MHz or Agilent 600 MHz Premium Shielded spectrometer. ¹H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ¹³C NMR spectra was recorded with CDCl₃ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra were obtained by using Waters Micromass GCT Premier or Agilent Technologies 6224 TOF LC/MS mass spectrometers. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. IR spectra were obtained by using a Nicolet iS10 spectrometer. Single crystal X-ray diffraction data were collected at 293(2) K for **7a** on Bruker SMART diffractometer, 130 K for **11** on Bruker APEX-II diffractometer.

Synthesis of propargylamine 1a, 1d^[1]

Typical procedure for the synthesis of allylamine 1a



To a microwave vial equipped with a magnetic stir bar were added benzaldehyde (2.0 mL, 20 mmol), ethynylbenzene (4.4 mL, 40 mmol), morpholine (1.7 mL, 20 mmol), copper bromide (574 mg, 4 mmol) and toluene (20 mL). The reaction vessel was sealed and irradiated in the cavity of CEM-Discover microwave reactor at a ceiling temperature of 100 °C and a maximum power of 80 W for 25 min. The resulting reaction mixture was cooled to ambient temperature, filtered over Celite, washed with dichloromethane. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1-5/1) to afford 4-(1,3-diphenylprop-2-ynyl)morpholine **1a** as a yellow solid in 59% yield (3.25 g). ¹H NMR (400 MHz, CDCl₃): δ 7.64-7.61 (m, 2H), 7.51-7.49 (m, 2H), 7.37-7.27 (m, 6H), 4.77 (s, 1H), 3.72-3.69 (m, 4H), 2.63-2.59 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 137.74, 131.76, 128.54, 128.27, 128.22, 128.19, 127.74, 122.91, 88.45, 84.99, 67.11, 61.97, 49.81. The spectroscopic data are in agreement with that previously reported.^[2]

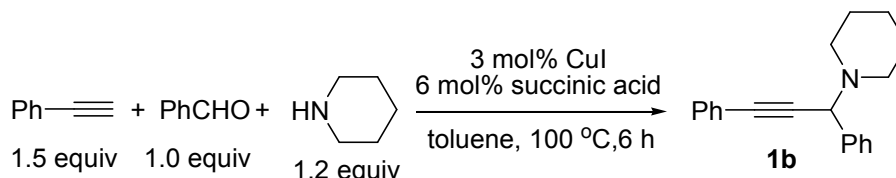


N-(1,3-Diphenylprop-2-ynyl)-N-methylaniline (1d). *N*-methylaniline (0.6 mL, 5.5 mmol), benzaldehyde (0.5 mL, 5 mmol), ethynylbenzene (0.55 mL, 5 mmol), copper bromide·dimethyl sulfide complex (103 mg, 0.5 mmol) and toluene (5 mL) were used in this reaction. The reaction proceeded at a ceiling temperature of 100 °C and a maximum power of 130 W for 3 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether) afforded the product as a pale yellow solid in 23% yield (340 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.63 (m, 2H), 7.48-7.47 (m, 2H), 7.41-7.29 (m, 8H), 7.05-7.03 (m, 2H), 6.88-6.86 (m, 1H), 6.01 (s, 1 H), 2.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 150.25, 138.51, 131.81, 129.15, 128.41, 128.26, 128.25, 127.72, 127.57, 122.88, 118.70, 115.26, 86.94, 85.69, 56.97, 33.77. IR (film): 3084, 3060, 3022, 2949, 2868, 2809, 2597, 2212, 1949, 1881, 1806, 1755, 1596, 1501, 1489, 1449, 1347, 1266, 1194, 1097, 1028, 992, 939, 913, 842, 750, 729, 688. HRMS(ESI) calcd for C₂₂H₂₀N

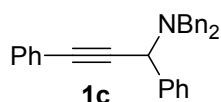
[M+H]⁺: 298.159, found 298.159.

Synthesis of propargylamine **1b-c**, **1f-r**^[3]

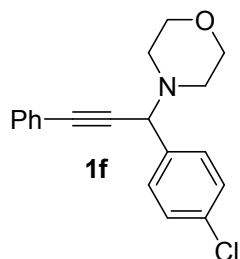
Typical procedure for the synthesis of allylamine **1b**



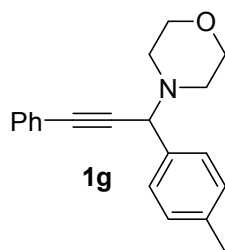
A mixture of benzaldehyde (0.3 mL, 3 mmol), toluene (1.5 mL), ethynylbenzene (0.49 mL, 4.5 mmol), piperidine (0.36 mL, 3.6 mmol), CuI (17 mg, 0.09 mmol), succinic acid (21 mg, 0.18 mmol), and was heated at 100 °C under argon for 6 h. After the reaction was complete as monitored by TLC, the reaction mixture was filtered over Celite and washed with ethyl acetate. The combined filtrates were concentrated under vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) followed by recrystallization from petroleum ether to afford **1b** as a yellow solid in 60% yield (498.7 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.64-7.62 (m, 2H), 7.52-7.48 (m, 2H), 7.37-7.26 (m, 6H), 4.79 (s, 1H), 2.55 (m, 4H), 1.62-1.56 (m, 4H), 1.44-1.43 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 138.60, 131.76, 128.46, 128.22, 128.00, 127.38, 123.31, 87.79, 86.05, 62.34, 50.64, 26.16, 24.41. The spectroscopic data are in agreement with that previously reported.^[2]



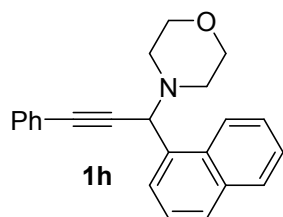
N,N-Dibenzyl-1,3-diphenylprop-2-yn-1-amine (1c). 1 equiv of CuI was used. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the product as a yellow solid in 80% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.72 (m, 2H), 7.64-7.62 (m, 2H), 7.44-7.29 (m, 13H), 7.27-7.20 (m, 3H), 4.94 (s, 1H), 3.80 (d, *J* = 13.6 Hz, 2H), 3.54 (d, *J* = 13.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 139.52, 139.15, 131.95, 128.88, 128.38, 128.27, 128.23, 128.10, 127.46, 126.99, 123.24, 88.64, 84.67, 56.02, 54.61. The spectroscopic data are in agreement with that previously reported.^[2]



4-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)morpholine (1f). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1-20/1) afforded the product as a yellow oil in 62% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.59-7.57 (m, 2H), 7.52-7.50 (m, 2H), 7.34-7.32 (m, 5H), 4.75 (s, 1H), 3.74-3.71 (m, 4H), 2.62-2.60 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 136.42, 133.51, 131.77, 129.84, 128.38, 128.34, 128.32, 122.66, 88.86, 84.30, 67.07, 61.32, 49.74. The spectroscopic data are in agreement with that previously reported.^[4]

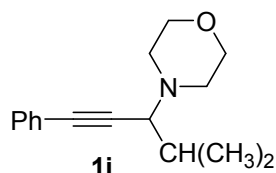


4-(3-Phenyl-1-(*p*-tolyl)prop-2-ynyl)morpholine (1g). 1 equiv of CuI was used. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1-20/1) afforded the product as a yellow solid in 92% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.51-7.49 (m, 4H), 7.31-7.29 (m, 3H), 7.17-7.15 (m, 2H), 4.73 (s, 1H), 3.73-3.70 (m, 4H), 2.62-2.59 (m, 4H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.32, 134.68, 131.68, 128.81, 128.40, 128.18, 128.09, 122.91, 88.14, 85.21, 67.03, 61.65, 49.55, 21.02. The spectroscopic data are in agreement with that previously reported.^[4]

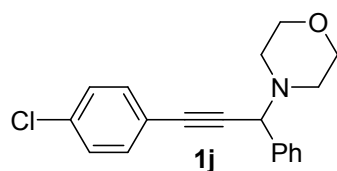


4-(1-(Naphthalen-1-yl)-3-phenylprop-2-ynyl)morpholine (1h). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =

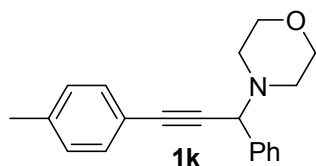
100/1-20/1) afforded the product as a yellow solid in 79% yield. ^1H NMR (400 MHz, CDCl_3): δ 8.36-8.34 (m, 1H), 7.91-7.90 (m, 1H), 7.82-7.76 (m, 2H), 7.53-7.49 (m, 3H), 7.47-7.39 (m, 2H), 7.28-7.27 (m, 3H), 5.39 (s, 1H), 3.67-3.60 (m, 4H), 2.67-2.66 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 133.92, 133.03, 131.70, 131.53, 128.79, 128.38, 128.21, 128.13, 126.98, 125.79, 125.58, 124.67, 124.61, 122.91, 88.94, 84.87, 67.04, 60.02, 49.69. HRMS(ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: 328.1696, found 328.1695.



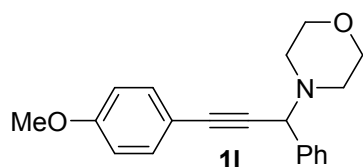
4-(4-Methyl-1-phenylpent-1-yn-3-yl)morpholine (1i). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1-20/1) afforded the product as a yellow solid in 78% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.43 (m, 2H), 7.31-7.25 (m, 3H), 3.77-3.73 (m, 4H), 3.01 (d, J = 10.0 Hz, 1H), 2.73-2.68 (m, 2H), 2.54-2.49 (m, 2H), 1.92-1.90 (m, 1H), 1.11 (d, J = 6.4, 3H), 1.03 (d, J = 6.4, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 131.65, 128.18, 127.82, 123.33, 86.66, 86.55, 67.17, 65.14, 49.97, 29.86, 20.29, 19.75. The spectroscopic data are in agreement with that previously reported.^[5]



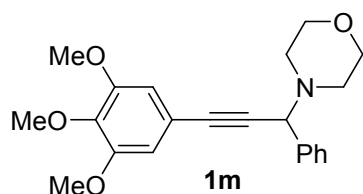
4-(3-(4-Chlorophenyl)-1-phenylprop-2-ynyl)morpholine (1j). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1-20/1) afforded the product as a yellow oil in 75% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.60 (m, 2H), 7.43-7.27 (m, 7H), 4.76 (s, 1H), 3.73-3.71 (m, 4H), 2.61-2.60 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.38, 134.14, 132.91, 128.52, 128.41, 128.17, 127.76, 121.27, 87.26, 86.03, 66.97, 61.89, 49.79. IR (film): 3059, 3030, 2956, 2853, 2820, 1952, 1898, 1649, 1593, 1489, 1450, 1397, 1322, 1276, 1247, 1207, 1115, 1090, 1071, 1030, 1014, 1003, 970, 936, 915, 865, 827, 798, 778, 732, 700. HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 312.1150, found 312.1152.



4-(1-Phenyl-3-*p*-tolylprop-2-ynyl)morpholine (1k). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a yellow oil in 48% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 2H), 7.30-7.26 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.76 (s, 1H), 3.76-3.67 (m, 4H), 2.66-2.57 (m, 4H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.21, 137.81, 131.58, 128.96, 128.50, 128.11, 127.64, 119.78, 88.47, 84.16, 67.05, 61.93, 49.74, 21.39. IR (film): 3084, 3062, 3028, 2955, 2852, 2820, 2740, 2685, 2209, 1976, 1901, 1802, 1720, 1647, 1601, 1509, 1492, 1450, 1391, 1321, 1284, 1247, 1206, 1178, 1157, 1115, 1072, 1030, 1021, 1002, 971, 936, 915, 865, 815, 798, 747, 713, 697, 663. HRMS(ESI) calcd for C₂₀H₂₂NO [M+H]⁺: 292.1696, found 292.1697.

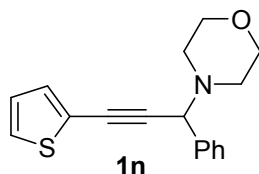


4-(3-(4-Methoxyphenyl)-1-phenylprop-2-ynyl)morpholine (1l). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1-20/1) afforded the product as a yellow solid in 69% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.61 (m, 2H), 7.45-7.43 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.26 (m, 1H), 6.85-6.83 (m, 2H), 4.76 (s, 1H), 3.78 (s, 3H), 3.73-3.71 (m, 4H), 2.62-2.60 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 159.42, 137.87, 133.08, 128.48, 128.08, 127.60, 114.94, 113.79, 88.18, 83.38, 67.03, 61.93, 55.14, 49.71. The spectroscopic data are in agreement with that previously reported.^[6]

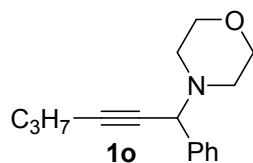


4-(1-Phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-ynyl)morpholine (1m). 1.1 equiv of morpholine and 1.1 equiv of 5-ethynyl-1,2,3-trimethoxybenzene were used. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl

acetate/dichloromethane = 5/1/1) afforded the product as a yellow oil in 89% yield. The product could be solidified upon standing. ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.62 (m, 2H), 7.39-7.27 (m, 3H), 6.74 (s, 2H), 4.78 (s, 1H), 3.87 (s, 6H), 3.86 (s, 3H), 3.76-3.74 (m, 4H), 2.64-2.63 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.96, 138.68, 137.62, 128.45, 128.14, 127.71, 117.87, 108.84, 88.28, 83.97, 67.01, 61.93, 60.84, 56.07, 49.80. IR (film): 2960, 2852, 2820, 2162, 1712, 1575, 1502, 1450, 1431, 1408, 1339, 1323, 1283, 1268, 1231, 1185, 1158, 1121, 1110, 1070, 1052, 1017, 998, 934, 914, 865, 838, 821, 799, 772, 742, 731, 700, 675. HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 368.1856, found 368.1857.

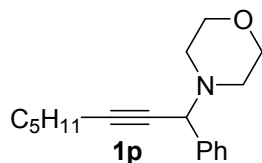


4-(1-Phenyl-3-(thiophen-2-yl)prop-2-ynyl)morpholine (1n). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the product as a yellow oil in 73% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.59 (m, 2H), 7.38-7.34 (m, 2H), 7.31-7.30 (m, 1H), 7.25-7.23 (m, 2H), 6.98-6.96 (m, 1H), 4.79 (s, 1H), 3.75-3.70 (m, 4H), 2.62-2.59 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.40, 131.94, 128.46, 128.20, 127.77, 126.87, 126.82, 122.74, 89.11, 81.42, 67.05, 62.17, 49.82. IR (film): 3061, 2956, 2915, 2852, 2684, 2753, 2211, 1602, 1517, 1492, 1450, 1425, 1392, 1339, 1286, 1178, 1114, 1044, 1001, 939, 865, 850, 829, 747, 695, 662. HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{NOS}$ $[\text{M}+\text{H}]^+$: 284.1104, found 284.1103.

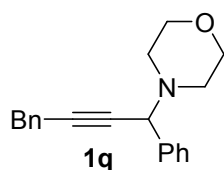


4-(1-Phenylhex-2-ynyl)morpholine (1o). 1.0 equiv of CuI was used. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the product as a yellow oil in 62% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.54 (m, 2H), 7.32-7.23 (m, 3H), 4.52 (s, 1H), 3.68-3.65 (m, 4H), 2.51-2.49 (m, 4H), 2.28 (td, J = 6.8, 2.0 Hz, 2H), 1.61-1.56 (m, 2H), 1.03 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 138.15, 128.26, 127.78, 127.24, 88.26, 75.24, 66.82, 61.34, 49.42, 22.20, 20.53, 13.39. IR (film): 3059, 2960, 2931, 2852, 2822, 2256, 1952, 1810,

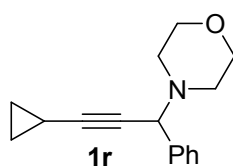
1662, 1601, 1493, 1450, 1379, 1338, 1322, 1285, 1270, 1246, 1206, 1115, 1072, 1028, 1000, 936, 915, 865, 820, 799, 766, 726, 698. HRMS(ESI) calcd for C₁₆H₂₂NO [M+H]⁺: 244.1696, found 244.1698.



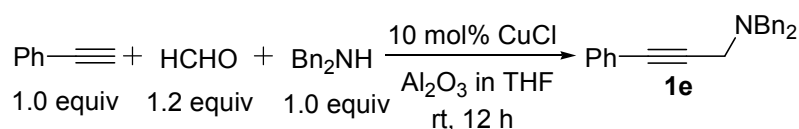
4-(1-Phenyl-2-octynyl)morpholine (1p). 1.0 equiv of CuI was used. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1-20/1) afforded the product as a colorless oil in 89% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.55 (m, 2H), 7.35-7.25 (m, 3H), 4.52 (s, 1H), 3.73-3.67 (m, 4H), 2.56-2.50 (m, 4H), 2.31 (t, *J* = 6.4 Hz, 2H), 1.60-1.55 (m, 2H), 1.46-1.32 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 138.40, 128.53, 128.02, 127.48, 88.72, 75.31, 67.13, 61.62, 49.27, 31.11, 28.67, 22.14, 18.72, 13.98. The spectroscopic data are in agreement with that previously reported.^[4]



4-(1,4-Diphenylbut-2-ynyl)morpholine (1q). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the product as a yellow oil in 61% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.59-7.57 (m, 2H), 7.40-7.38 (m, 2H), 7.35-7.23 (m, 6H), 4.60 (s, 1H), 3.75 (d, *J* = 1.2 Hz, 2H), 3.72-3.68 (m, 4H), 2.58-2.54 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 138.13, 136.84, 128.51, 128.49, 128.10, 127.84, 127.58, 126.54, 85.89, 77.79, 67.09, 61.67, 49.81, 25.16. IR (film): 3061, 3029, 2956, 2852, 2820, 2245, 1951, 1806, 1600, 1494, 1451, 1421, 1391, 1322, 1285, 1269, 1246, 1206, 1115, 1071, 1029, 1001, 936, 916, 863, 824, 799, 729, 697. HRMS(ESI) calcd for C₂₀H₂₂NO [M+H]⁺: 292.1696, found 292.1697.

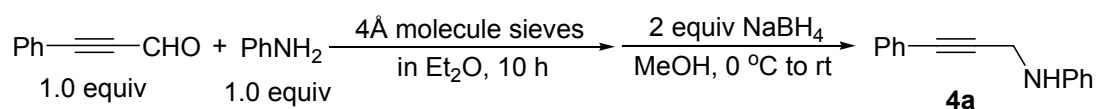


4-(3-Cyclopropyl-1-phenylprop-2-ynyl)morpholine (1r). 1.0 equiv of CuI was used. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow oil in 84% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.49 (m, 2H), 7.28-7.19 (m, 3H), 4.45 (s, 1H), 3.63-3.61 (m, 4H), 2.44-2.42 (m, 4H), 1.33-1.26 (m, 1H), 0.75-0.68 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 137.94, 127.94, 127.52, 126.98, 91.35, 70.11, 66.52, 61.01, 49.23, 8.02, -0.86. IR (film): 3062, 2960, 2932, 2853, 2822, 2264, 1949, 1806, 1598, 1493, 1450, 1379, 1338, 1322, 1285, 1246, 1206, 1115, 1072, 1028, 1001, 937, 915, 865, 820, 799, 766, 726, 698. HRMS(ESI) calcd for C₁₆H₂₀NO [M+H]⁺: 242.1539, found 242.1541.

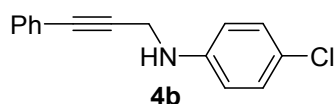


Synthesis of propargylamine 4a-c

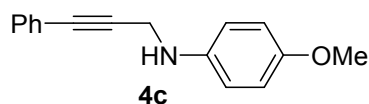
Typical procedure for the synthesis of allylamine 4a



period, the flask was evacuated and flushed with argon several times. After the Schlenk tube was cooled down, 3-phenylpropionaldehyde (650.7 mg, 5.0 mmol) and PhNH₂ (465.6 mg, 5 mmol) in Et₂O (20.0 mL) were added. The reaction mixture was stirred at room temperature for 10 h, then it was filtered through celite. The solvent was evaporated and the residue was used directly for the next step. To a solution of above residue in MeOH (20 mL) was added NaBH₄ (378.3 mg, 10 mmol). After stirring 2 h, the mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the *N*-(3-phenylprop-2-ynyl)benzenamine **4a** as a yellow oil in 71% yield (738.4 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.38 (m, 2H), 7.27-7.18 (m, 5H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.10 (s, 2H), 3.92 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.05, 131.62, 129.15, 128.18, 128.14, 122.78, 118.35, 113.47, 86.36, 83.17, 34.43. The spectroscopic data are in agreement with that previously reported.^[8]



4-Chloro-*N*-(3-phenylprop-2-ynyl)benzenamine (4b). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a yellow solid in 54% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.37 (m, 2H), 7.27-7.25 (m, 3H), 7.16-7.14 (m, 2H), 6.62-6.60 (m, 2H), 4.07 (s, 2H), 3.95 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 145.55, 131.61, 128.98, 128.27, 128.23, 122.98, 122.58, 114.59, 85.83, 83.39, 34.45. IR (film): 3415, 3056, 2842, 2557, 2234, 1954, 1859, 1753, 1597, 1497, 1489, 1441, 1402, 1351, 1311, 1293, 1260, 1178, 1122, 1094, 1071, 1028, 1004, 952, 916, 814, 755, 690, 671. HRMS(ESI) calcd for C₁₅H₁₃ClN [M+H]⁺: 242.0731, found 242.0735.

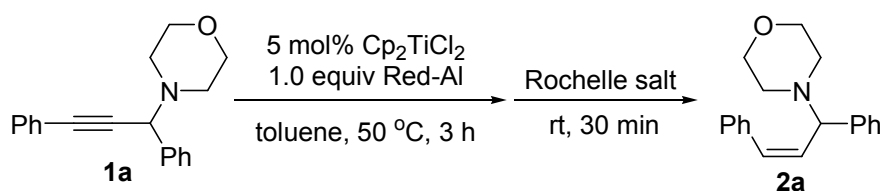


4-Methoxy-*N*-(3-phenylprop-2-ynyl)benzenamine (4c). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1-20/1) afforded the product as a yellow oil in 49% yield, which could be solidified upon standing in the refrigerator. ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.37 (m, 2H), 7.27-7.25 (m, 3H),

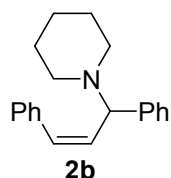
6.82-6.80 (m, 2H), 6.70-6.68 (m, 2H), 4.07 (s, 2H), 3.73 (s, 3H), 3.71 (br, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.71, 141.09, 131.55, 128.13, 128.05, 122.79, 115.05, 114.63, 86.71, 83.10, 55.54, 35.33. IR (film): 3382, 3059, 2989, 2931, 2831, 2557, 2330, 2066, 1958, 1881, 1680, 1597, 1509, 1489, 1463, 1441, 1408, 1348, 1310, 1232, 1178, 1117, 1070, 1034, 950, 915, 818, 755, 690. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 238.1226, found 238.1226.

Synthesis of allylamines **2a-r**, *Z* and *E* mixtures of **5a-c**

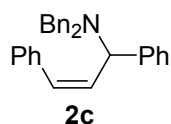
Typical procedure for the synthesis of allylamine **2a**



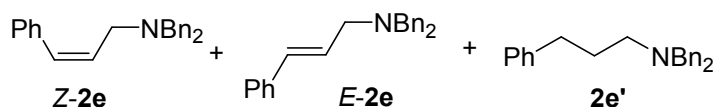
All the reactions were carried out on 0.3 mmol scale. To a solution of 4-(1,3-diphenylprop-2-ynyl)morpholine **1a** (83 mg, 0.3 mmol) in toluene (5 mL) were successively added Cp_2TiCl_2 (3.7 mg, 0.015 mmol) and Red-Al (98 μL , 0.3 mmol, 60% in toluene). The Schlenk tube was immersed into an oil bath preheated at 50 °C and stirred for 3 h. After the reaction was complete as monitored by TLC, the resulting mixture was cooled down to room temperature, quenched with saturated potassium sodium tartrate solution and stirred for 30 min. The mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo and the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate = 10/1) to afford (*Z*)-4-(1,3-diphenylallyl)morpholine **2a** as a colorless oil in 97% yield (81 mg), which could be solidified upon standing in the refrigerator. ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.31 (m, 6H), 7.26-7.21 (m, 4H), 6.65 (d, J = 11.6 Hz, 1H), 5.91 (t, J = 10.4 Hz, 1H), 4.22 (d, J = 10.0 Hz, 1H), 3.65-3.63 (m, 4H), 2.50-2.44 (m, 2H), 2.29-2.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.22, 136.93, 132.79, 131.10, 128.60, 128.56, 128.17, 128.10, 127.23, 126.89, 67.31, 67.08, 51.33. IR (film): 3055, 3024, 2851, 2807, 1949, 1883, 1804, 1599, 1492, 1450, 1393, 1276, 1115, 1071, 1029, 1004, 927, 875, 836, 797, 757, 734, 698. HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: 280.1696, found 280.1698.



(Z)-1-(1,3-Diphenylallyl)piperidine (2b). Purification of the crude product by preparative TLC on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product as a colorless oil in 74% yield (61.3 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.29 (m, 6H), 7.25-7.21 (m, 4H), 6.61 (d, J = 11.6 Hz, 1H), 5.96 (dd, J = 11.6, 10.0 Hz, 1H), 4.24 (d, J = 10.0 Hz, 1H), 2.46-2.45 (m, 2H), 2.27-2.23 (m, 2H), 1.54-1.48 (m, 4H), 1.40-1.36 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.12, 137.26, 133.45, 130.37, 128.70, 128.41, 128.18, 128.05, 126.93, 126.73, 67.54, 51.94, 26.14, 24.58. IR (film): 3059, 3024, 2931, 2851, 2790, 2747, 1943, 1879, 1804, 1599, 1491, 1451, 1397, 1304, 1274, 1256, 1211, 1153, 1115, 1100, 1072, 1029, 988, 912, 874, 794, 766, 738, 697. HRMS(ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$: 278.1903, found 278.1907.



(Z)-N,N-Dibenzyl-1,3-diphenylprop-2-en-1-amine (2c). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the product as a colourless oil in 78% yield (91.5 mg, containing a small amount of byproduct). ^1H NMR (400 MHz, CDCl_3): δ 7.63-7.61 (m, 2H), 7.36-7.32 (m, 2H), 7.25-7.21 (m, 1H), 7.12-7.09 (m, 13H), 7.02-6.99 (m, 3H), 6.06 (t, J = 11.8 Hz, 1H), 4.84 (d, J = 10.4 Hz, 1H), 3.71 (d, J = 13.2 Hz, 2H), 3.39 (d, J = 13.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.24, 139.72, 136.72, 133.94, 128.72, 128.42, 128.25, 128.16, 128.14, 127.88, 127.66, 127.00, 126.94, 126.52, 58.54, 53.54. IR (film): 3059, 3026, 2925, 2803, 2711, 1945, 1887, 1804, 1600, 1493, 1446, 1362, 1265, 1118, 1068, 1027, 964, 914, 802, 773, 743, 695. HRMS(ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$: 390.2216, found 390.2220.



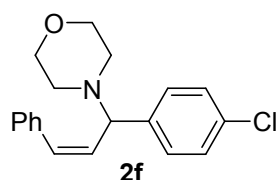
(Z)-N,N-Dibenzyl-3-phenylprop-2-en-1-amine (2e). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded a mixture of **Z-2e**, **E-2e** and **2e'** as a yellow oil in a combined yield of 83% (78.0

mg, *Z*-**2e**/*E*-**2e**/**2e'** = 20/1/3).

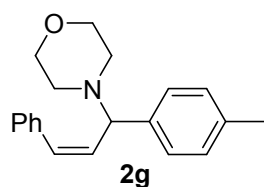
¹H NMR (400 MHz, CDCl₃) *Z*-**2e**: δ 7.40-7.15 (m, 15H), 6.56 (d, *J* = 12.0 Hz, 1H), 5.89 (dt, *J* = 11.6, 6.4 Hz, 1H), 3.54 (s, 4H), 3.33 (d, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) *Z*-**2e**: δ 139.37, 137.13, 131.19, 130.82, 128.85, 128.81, 128.12, 128.01, 126.79, 126.71, 58.05, 51.09. HRMS(ESI) calcd for C₂₃H₂₄N [M+H]⁺: 314.1903, found 314.1906.

¹H NMR (400 MHz, CDCl₃) *E*-**2e**: 6.29 (dt, *J* = 15.6, 6.4 Hz, 1H).

¹H NMR (400 MHz, CDCl₃) **2e'**: δ 2.57 (t, *J* = 7.6 Hz, 2H), 2.46 (t, *J* = 6.8 Hz, 2H), 1.84-1.77 (m, 2H), other peaks are overlapped with the signals of **2e**; ¹³C NMR (100 MHz, CDCl₃) **2e'**: δ 139.80, 128.79, 128.32, 128.20, 128.18, 126.74, 125.55, 58.28, 52.89, 33.49, 29.00. The characteristic spectroscopic data of **2e'** are in agreement with that previously reported.^[9]

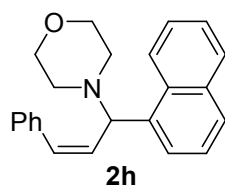


(Z)-4-(1-(4-Chlorophenyl)-3-phenylallyl)morpholine (2f). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a yellow solid in 81% yield (76.5 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.18 (m, 9H), 6.66 (d, *J* = 11.6 Hz, 1H), 5.84 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.22 (d, *J* = 10.0 Hz, 1H), 3.65-3.63 (m, 4H), 2.50-2.49 (m, 2H), 2.30-2.24 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 139.91, 136.76, 132.88, 132.15, 131.58, 129.44, 128.74, 128.53, 128.20, 127.04, 67.07, 66.56, 51.20. IR (film): 3023, 2955, 2852, 2810, 2363, 1958, 1898, 1726, 1674, 1598, 1488, 1451, 1408, 1326, 1287, 1270, 1117, 1091, 1071, 1014, 1005, 927, 879, 864, 815, 799, 769, 701, 668. HRMS(ESI) calcd for C₁₉H₂₁ClNO [M+H]⁺: 314.1306, found 314.1310.

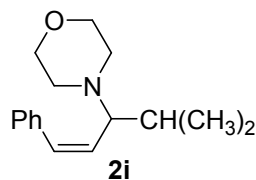


(Z)-4-(3-Phenyl-1-*p*-tolylallyl)morpholine (2g). Purification of the crude product by preparative TLC on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product as a white solid in 90% yield (79.2 mg, *Z*/*E* = 50/1). ¹H NMR (400 MHz, CDCl₃): δ 7.34-

7.31 (m, 2H), 7.27-7.21 (m, 5H), 7.16-7.14 (m, 2H), 6.63 (d, $J = 11.6$ Hz, 1H), 5.91 (dd, $J = 11.6, 10.4$ Hz, 1H), 4.19 (d, $J = 10.0$ Hz, 1H), 3.65-3.63 (m, 4H), 2.52-2.49 (m, 2H), 2.33 (s, 3H), 2.30-2.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 138.20, 137.00, 136.87, 133.01, 130.85, 129.28, 128.64, 128.08, 126.85, 67.10, 67.05, 51.36, 21.06. IR (film): 3059, 3022, 2954, 2851, 2806, 2359, 1958, 1899, 1802, 1599, 1511, 1493, 1450, 1397, 1330, 1301, 1273, 1207, 1176, 1116, 1070, 1030, 1004, 927, 878, 864, 842, 807, 764, 729, 698. HRMS(ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$: 294.1852, found 294.1855.

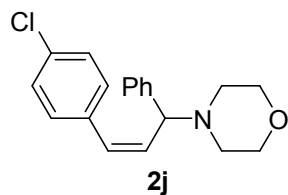


(Z)-4-(1-(Naphthalen-1-yl)-3-phenylallyl)morpholine (2h). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a white solid in 91% yield (89.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 8.22 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.58 (d, $J = 6.8$ Hz, 1H), 7.43-7.33 (m, 3H), 7.29-7.23 (m, 3H), 7.16-7.14 (m, 2H), 6.64 (d, $J = 11.6$ Hz, 1H), 6.15 (dd, $J = 11.6, 10.0$ Hz, 1H), 4.96 (d, $J = 10.0$ Hz, 1H), 3.66-3.57 (m, 4H), 2.59 (m, 2H), 2.40-2.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.15, 136.85, 134.05, 132.07, 131.62, 131.41, 128.72, 128.60, 128.11, 127.89, 126.93, 126.11, 125.47, 125.43, 125.36, 124.49, 67.25, 64.52, 51.21. IR (film): 3050, 2954, 2851, 2807, 2355, 2142, 1948, 1810, 1596, 1509, 1493, 1450, 1393, 1262, 1206, 1165, 1116, 1070, 1029, 1003, 990, 927, 879, 800, 776, 700. HRMS(ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$: 330.1852, found 330.1854.

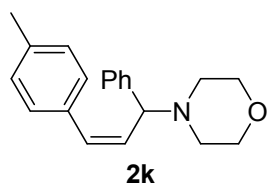


(Z)-4-(4-Methyl-1-phenylpent-1-en-3-yl)morpholine (2i). The reaction was carried out at 80 °C. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a colorless oil in 96% yield (70.6 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.21 (m, 5H), 6.76 (d, $J = 12.0$ Hz, 1H), 5.53 (t, $J = 11.6$ Hz, 1H), 3.67-3.59 (m, 4H), 3.09 (dd, $J = 10.8, 8.0$ Hz, 1H), 2.57-2.52 (m,

2H), 2.33-2.28 (m, 2H), 1.86-1.83 (m, 1H), 0.93 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.71, 132.88, 130.21, 128.57, 128.03, 126.52, 67.39, 66.41, 49.77, 28.52, 19.91, 18.69. IR (film): 3004, 2955, 2851, 2812, 2319, 1949, 1804, 1722, 1599, 1493, 1449, 1385, 1365, 1327, 1286, 1266, 1253, 1207, 1137, 1116, 1070, 1008, 939, 916, 875, 855, 819, 791, 766, 739, 698, 677. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$: 246.1852, found 246.1856.

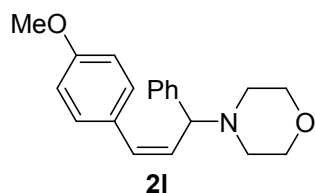


(Z)-4-(3-(4-Chlorophenyl)-1-phenylallyl)morpholine (2j). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a white solid in 72% yield (68.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.26 (m, 7H), 7.15-7.13 (m, 2H), 6.58 (d, $J = 11.6$ Hz, 1H), 5.94 (dd, $J = 11.2, 10.4$ Hz, 1H), 4.14 (d, $J = 10.0$ Hz, 1H), 3.66-3.63 (m, 4H), 2.51-2.48 (m, 2H), 2.29-2.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.93, 135.37, 133.61, 132.76, 129.95, 129.87, 128.65, 128.34, 128.17, 127.39, 67.38, 67.08, 51.35. IR (film): 3059, 3025, 2955, 2851, 2807, 1947, 1898, 1812, 1722, 1593, 1489, 1450, 1393, 1303, 1275, 1207, 1178, 1115, 1091, 1071, 1030, 1004, 926, 876, 844, 829, 794, 745, 720, 699. HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 314.1306, found 314.1309.

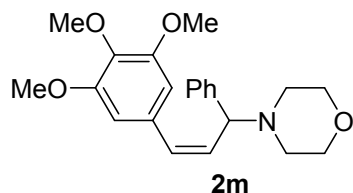


(Z)-4-(1-Phenyl-3-p-tolylallyl)morpholine (2k). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a colorless oil in 86% yield (75.8 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.31 (m, 4H), 7.27-7.23 (m, 1H), 7.16-7.11 (m, 4H), 6.61 (d, $J = 11.6$ Hz, 1H), 5.86 (dd, $J = 11.6, 10.0$ Hz, 1H), 4.24 (d, $J = 10.4$ Hz, 1H), 3.67-3.61 (m, 4H), 2.53-2.50 (m, 2H), 2.35 (s, 3H), 2.30-2.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.42, 136.61, 134.07, 132.28, 131.05, 128.84, 128.59, 128.56, 128.23, 127.20, 67.34, 67.16, 51.37, 21.17. IR (film): 3080, 3024, 2954, 2851, 2806, 2755, 2685, 2304, 1941, 1901, 1799,

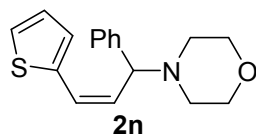
1731, 1600, 1510, 1489, 1450, 1396, 1276, 1207, 1115, 1070, 1029, 1004, 926, 876, 840, 820, 751, 737, 699. HRMS(ESI) calcd for C₂₀H₂₄NO [M+H]⁺: 294.1852, found 294.1852.



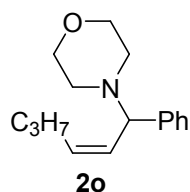
(Z)-4-(3-(4-Methoxyphenyl)-1-phenylallyl)morpholine (2l). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a colorless oil in 97% yield (90.0 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.37 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.24 (m, 1H), 7.18-7.16 (m, 2H), 6.87-6.85 (m, 2H), 6.58 (d, *J* = 11.6 Hz, 1H), 5.83 (dd, *J* = 11.6, 10.0 Hz, 1H), 4.25 (d, *J* = 10.0 Hz, 1H), 3.79 (s, 3H), 3.65-3.63 (m, 4H), 2.53-2.50 (m, 2H), 2.30-2.26 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 158.46, 141.31, 131.51, 130.62, 129.85, 129.42, 128.51, 128.19, 127.17, 113.48, 67.28, 67.09, 55.09, 51.28. IR (film): 3059, 3006, 2954, 2850, 2806, 2755, 2685, 1949, 1887, 1731, 1606, 1574, 1508, 1491, 1450, 1398, 1300, 1246, 1207, 1174, 1115, 1070, 1031, 1003, 926, 875, 842, 814, 755, 738, 699. HRMS(ESI) calcd for C₂₀H₂₄NO₂ [M+H]⁺: 310.1802, found 310.1802.



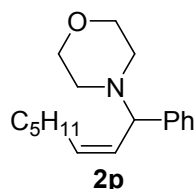
(Z)-4-(1-Phenyl-3-(3,4,5-trimethoxyphenyl)allyl)morpholine (2m). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) afforded the product as a yellow oil in 83% yield (91.8 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.31 (m, 4H), 7.28-7.24 (m, 1H), 6.60 (d, *J* = 11.6 Hz, 1H), 6.42 (s, 2H), 5.95 (t, *J* = 10.8 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 6H), 3.67-3.65 (m, 4H), 2.55-2.53 (m, 2H), 2.36-2.31 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 152.72, 140.97, 136.80, 132.43, 132.03, 131.04, 128.43, 128.27, 127.29, 105.63, 67.44, 67.00, 60.71, 55.85, 51.14. IR (film): 2955, 2851, 2826, 1725, 1578, 1505, 1450, 1400, 1328, 1275, 1236, 1183, 1115, 1070, 1030, 1004, 957, 923, 875, 848, 779, 753, 734, 700, 656. HRMS(ESI) calcd for C₂₂H₂₈NO₄ [M+H]⁺: 370.2013, found 370.2013.



(Z)-4-(1-Phenyl-3-(thiophen-2-yl)allyl)morpholine (2n). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the product as a colorless oil in 74% yield (63.5 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.47-7.45 (m, 2H), 7.33-7.22 (m, 4H), 7.00-6.97 (m, 2H), 6.63 (d, J = 11.6 Hz, 1H), 5.73 (t, J = 11.2 Hz, 1H), 4.59 (d, J = 10.4 Hz, 1H), 3.69-3.67 (m, 4H), 2.60-2.57 (m, 2H), 2.44-2.39 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.87, 139.22, 131.08, 128.89, 128.55, 128.07, 127.41, 126.73, 125.57, 123.20, 68.33, 67.11, 51.59. IR (film): 3062, 2955, 2851, 2807, 2757, 1599, 1491, 1450, 1393, 1304, 1275, 1215, 1116, 1071, 1004, 926, 876, 850, 751, 699. HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 286.1260, found 286.1259.

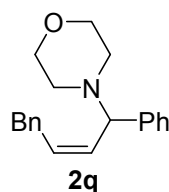
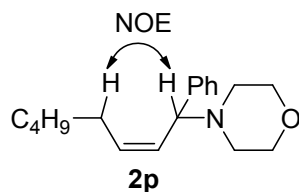


(Z)-4-(1-Phenylhex-2-enyl)morpholine (2o). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a colorless oil in 92% yield (67.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.28 (m, 4H), 7.23-7.21 (m, 1H), 5.53-5.49 (m, 2H), 3.98 (d, J = 8.4 Hz, 1H), 3.69-3.67 (m, 4H), 2.52 (m, 2H), 2.34-2.29 (m, 2H), 2.19-2.09 (m, 2H), 1.40-1.35 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.21, 131.79, 131.03, 128.47, 127.83, 126.95, 67.91, 67.12, 51.88, 29.78, 22.55, 13.85. IR (film): 3009, 2956, 2928, 2852, 2805, 1945, 1600, 1490, 1450, 1378, 1302, 1272, 1117, 1071, 1032, 1005, 922, 874, 832, 758, 732, 698, 657. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$: 246.1852, found 246.1855.

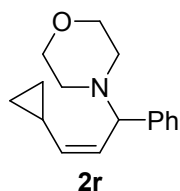


(Z)-4-(1-Phenyloct-2-enyl)morpholine (2p). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a colorless oil in 85% yield (70.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.27

(m, 4H), 7.23-7.21 (m, 1H), 5.52-5.49 (m, 2H), 3.97 (d, $J = 8.8$ Hz, 1H), 3.69-3.67 (m, 4H), 2.52 (m, 2H), 2.34-2.29 (m, 2H), 2.18-2.11 (m, 2H), 1.36-1.26 (m, 6H), 0.88 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.19, 132.03, 130.82, 128.46, 127.83, 126.95, 77.32, 77.00, 76.68, 67.93, 67.10, 51.88, 31.49, 29.02, 27.68, 22.46, 13.98. IR (film): 2955, 2924, 2852, 2802, 1597, 1490, 1450, 1301, 1278, 1117, 1066, 1008, 925, 876, 757, 738, 699. HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$: 274.2165, found 274.2168. The *cis*-geometry of **2p** was assigned on the basis of the following NOE result:

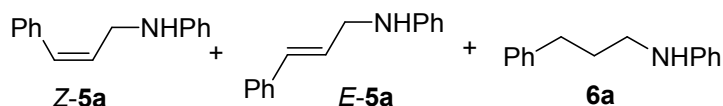


(Z)-4-(1,4-Diphenylbut-2-enyl)morpholine (2q). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the product as a colorless oil in 87% yield (76.6 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.36-7.10 (m, 10H), 5.69-5.68 (m, 2H), 4.10-4.09 (m, 1H), 3.69 (m, 4H), 3.59-3.46 (m, 2H), 2.55 (m, 2H), 2.37-2.34 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.76, 140.16, 131.95, 129.98, 128.56, 128.40, 128.27, 127.90, 127.14, 126.00, 67.98, 67.06, 51.90, 33.91. IR (film): 3059, 3025, 2955, 2851, 2808, 1945, 1876, 1810, 1678, 1601, 1493, 1450, 1397, 1304, 1277, 1207, 1116, 1070, 1030, 1010, 970, 922, 874, 855, 758, 736, 697. HRMS(ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$: 294.1852, found 294.1856.



(Z)-4-(3-Cyclopropyl-1-phenylallyl)morpholine (2r). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product as a white solid in 86% yield (62.5 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.22 (m, 1H), 5.44 (t, $J = 10.4$ Hz, 1H), 4.87

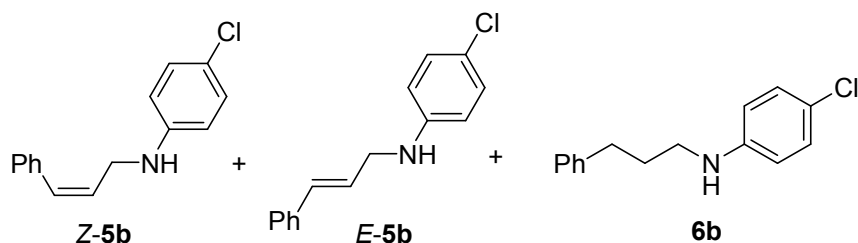
(t, $J = 10.8$ Hz, 1H), 4.13 (d, $J = 9.6$ Hz, 1H), 3.70-3.68 (m, 4H), 2.56 (m, 2H), 2.40-2.35 (m, 2H), 1.73-1.70 (m, 1H), 0.78-0.75 (m, 2H), 0.35-0.29 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.22, 135.99, 129.03, 128.48, 127.77, 126.94, 68.40, 67.12, 51.87, 9.86, 6.99. IR (film): 3077, 3005, 2955, 2851, 2805, 1945, 1877, 1806, 1651, 1600, 1491, 1450, 1393, 1295, 1279, 1207, 1116, 1071, 1018, 1004, 937, 875, 837, 810, 757, 739, 699, 662. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: 244.1696, found 244.1698.



(Z)-N-(3-Phenylallyl)benzenamine (Z-5a). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded a mixture of **Z-5a**, **E-5a** and **6a** as a yellow oil in 80% yield (50.1 mg, **Z-5a**/**E-5a**/**6a** = 8/1/3). ^1H NMR (400 MHz, CDCl_3) **Z-5a**: δ 7.36-7.32 (m, 2H), 7.27-7.25 (m, 2H), 7.19-7.13 (m, 3H), 6.72-6.68 (m, 1H), 6.60-6.54 (m, 3H), 5.77 (dt, $J = 11.6, 6.0$ Hz, 1H), 3.99 (d, $J = 6.8$ Hz, 2H), 3.71 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) **Z-5a**: δ 147.79, 136.60, 131.39, 129.66, 129.17, 128.75, 128.28, 127.14, 117.54, 112.97, 42.21. HRMS(ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 210.1277, found 210.1281.

^1H NMR (400 MHz, CDCl_3) **E-5a**: 6.29 (dt, $J = 16.0, 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) **E-5a**: 128.51, 127.45, 126.97, 126.26, 46.10.

^1H NMR (400 MHz, CDCl_3) **6a**: δ 3.11 (t, $J = 7.2$ Hz, 2H), 2.70 (t, $J = 7.6$ Hz, 2H), 1.93-1.91 (m, 2H), other peaks are overlapped with the signals of **5a**; ^{13}C NMR (100 MHz, CDCl_3) **6a**: δ 148.26, 141.60, 129.20, 128.37, 128.34, 125.89, 117.13, 112.67, 43.30, 33.31, 30.97. The characteristic spectroscopic data of **6a** are in agreement with that previously reported.^[10]



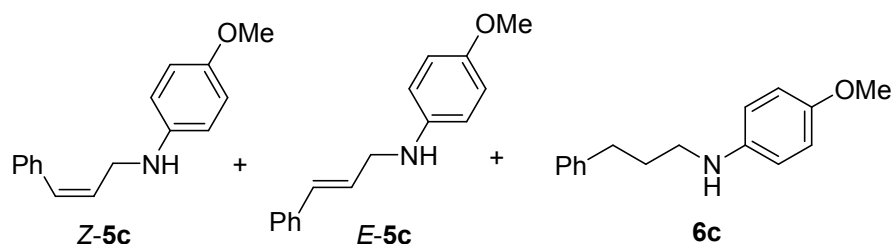
(Z)-4-Chloro-N-(3-phenylallyl)benzenamine (Z-5b). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded a mixture of **Z-5b**, **E-5b** and **6b** as a yellow oil in 92% yield (67.2 mg, **Z-5b**/**E-**

5b/6b = 8/1/3).

¹H NMR (400 MHz, CDCl₃) **Z-5b**: δ 7.37-7.33 (m, 2H), 7.30-7.24 (m, 3H), 7.10-7.07 (m, 2H), 6.61-6.53 (m, 1H), 6.47-6.43 (m, 2H), 5.73 (dt, *J* = 11.6, 6.4 Hz, 1H), 3.96 (dd, *J* = 6.4, 2.0 Hz, 2H), 3.74 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) **Z-5b**: δ 146.31, 136.47, 131.72, 129.15, 128.96, 128.73, 128.33, 127.26, 122.05, 114.01, 42.25. HRMS(ESI) calcd for C₁₅H₁₅ClN [M+H]⁺: 244.0888, found 244.0892.

¹H NMR (400 MHz, CDCl₃) **E-5b**: 6.26 (dt, *J* = 16.0, 5.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) **E-5b**: 131.64, 127.58, 126.39, 126.27, 46.13.

¹H NMR (400MHz, CDCl₃) **6b**: δ 3.07 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.94-1.87 (m, 2H), other peaks are overlapped with the signals of the product **5b**; ¹³C NMR (100 MHz, CDCl₃) **6b**: δ 146.79, 141.43, 129.00, 128.55, 128.41, 125.97, 121.57, 113.69, 43.39, 33.27, 30.79. The characteristic spectroscopic data of **6b** are in agreement with that previously reported.^[10]



(Z)-4-Methoxy-N-(3-phenylallyl)benzenamine (Z-5c). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded a mixture of **Z-5c**, **E-5c** and **6c** as a yellow oil in 80% yield (57.3 mg, **Z-5c/E-5c/6c** = 7/1/2).

¹H NMR (400 MHz, CDCl₃) **Z-5c**: δ 7.36-7.19 (m, 5H), 6.77-6.74 (m, 2H), 6.63-6.52 (m, 3H), 5.78 (dt, *J* = 11.6, 6.4 Hz, 1H), 3.97 (dd, *J* = 6.4, 2.0 Hz, 2H), 3.71 (s, 3H), 3.16 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) **Z-5c**: δ 152.18, 141.99, 136.66, 131.18, 129.98, 128.73, 128.25, 127.08, 114.76, 114.32, 55.67, 43.14. HRMS(ESI) calcd for C₁₆H₁₈NO [M+H]⁺: 240.1383, found 240.1388.

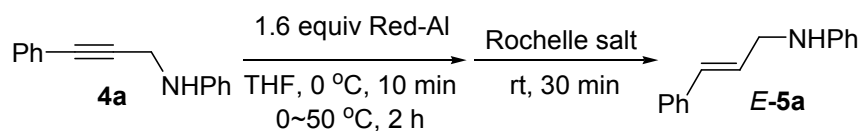
¹H NMR (400 MHz, CDCl₃) **E-5c**: 6.31 (dt, *J* = 15.6, 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) **E-5c**: 131.30, 128.48, 127.40, 127.29, 126.23, 114.79, 47.10.

¹H NMR (400MHz, CDCl₃) **6c**: δ 3.08 (t, *J* = 6.8 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.94-1.87 (m, 2H) other peaks are overlapped with the signals of **5c**; ¹³C NMR (100 MHz, CDCl₃) **6c**: δ 151.91, 142.55, 141.67, 128.33, 128.32, 125.84, 114.80, 114.01, 55.70, 44.34, 33.35, 31.09. The characteristic spectroscopic data of **6c** are in agreement with that

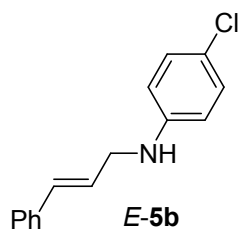
previously reported.^[10]

Synthesis of allylamine *E-5a* to *E-5c*

Typical procedure for the synthesis of allylamine *E-5a*.

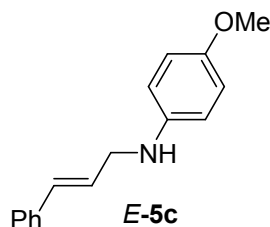


To a solution of *N*-(3-phenylprop-2-ynyl)benzenamine **4a** (62 mg, 0.3 mmol) in THF (5 mL) was added Red-Al (156 μ L, 0.48 mmol, 60% in toluene) at 0 °C and stirred for 10 min. Then the reaction mixture was warmed up to 50 °C and stirred for 2 h. After the reaction was complete as monitored by TLC, the resulting mixture was cooled down to room temperature, quenched with saturated potassium sodium tartrate solution and stirred for 30 min. The mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford *E*-**5a** as a yellow oil in 99% yield (62.3 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.27 (m, 4H), 7.22–7.16 (m, 3H), 6.71 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 16 Hz, 1H), 6.29 (dt, J = 16.0, 5.6 Hz, 1H), 3.89 (dd, J = 5.6, 1.6 Hz, 2H), 3.76 (br, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.95, 136.77, 131.38, 129.20, 128.50, 127.45, 126.96, 126.25, 117.52, 112.96, 46.09. IR (film): 3411, 3048, 3023, 2923, 2571, 1949, 1817, 1600, 1503, 1447, 1429, 1362, 1316, 1249, 1179, 1154, 1099, 1070, 1028, 964, 868, 745, 689. HRMS(ESI) calcd for C₁₅H₁₆N [M+H]⁺: 210.1277, found 210.1282.



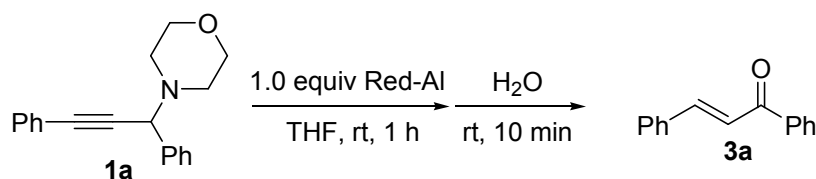
4-Chloro-*N*-cinnamylbenzenamine (*E*-5b). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the product as a yellow solid in 100% yield (76.6 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.27 (m, 4H), 7.23–7.21 (m, 1H), 7.11–7.09 (m, 2H), 6.56–6.52 (m, 3H), 6.24 (dt, J = 16.0, 5.6 Hz, 1H), 3.84 (dd, J = 5.6, 1.2 Hz, 2H), 3.83 (br, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.48, 136.59, 131.60, 128.98, 128.53, 127.56, 126.37, 126.25, 121.97, 113.99,

46.09. IR (film): 3416, 3330, 3025, 2851, 2579, 2136, 1947, 1863, 1674, 1597, 1496, 1315, 1177, 1122, 1092, 1002, 964, 813, 735, 692. HRMS(ESI) calcd for C₁₅H₁₅ClN [M+H]⁺: 244.0888, found 244.0892.



***N*-Cinnamyl-4-methoxybenzenamine (*E*-5c).** Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the product as a yellow oil in 98% yield (70.1 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.21 (m, 1H), 6.79-6.77 (m, 2H), 6.63-6.61 (m, 2H), 6.59 (d, *J* = 15.2 Hz, 1H), 6.31 (dt, *J* = 15.6, 6.0 Hz, 1H), 3.85 (dd, *J* = 5.8, 1.2 Hz, 2H), 3.72 (s, 3H), 3.43 (br, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 152.15, 142.17, 136.81, 131.29, 128.49, 127.40, 127.29, 126.23, 114.79, 114.31, 55.67, 47.09. IR (film): 3390, 3025, 2929, 2830, 2568, 1949, 1808, 1598, 1509, 1463, 1447, 1407, 1361, 1297, 1231, 1178, 1117, 1071, 1034, 965, 817, 741, 716, 692. HRMS(ESI) calcd for C₁₆H₁₈NO [M+H]⁺: 240.1383, found 240.1386.

synthesis of (*E*)-chalcone **3a**.

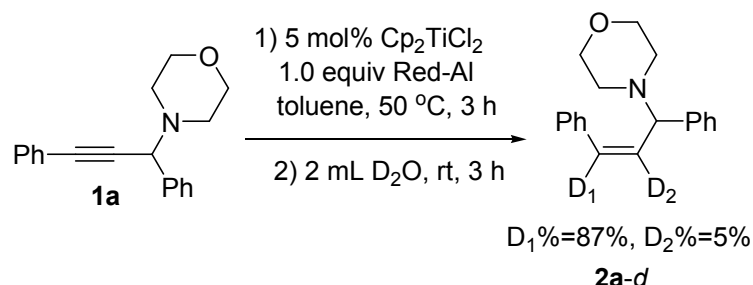


To a solution of 4-(1,3-diphenylprop-2-yn-1-yl)morpholine **1a** (83 mg, 0.3 mmol) in THF (5 mL) was added Red-Al (98 μL, 0.3 mmol, 60% in toluene) at room temperature and stirred for 1 h. After the reaction was complete as monitored by TLC, the resulting mixture was quenched with water and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the residue was purified by column chromatography on neutral Al₂O₃ (petroleum ether/ethyl acetate = 30/1) to afford (*E*)-chalcone **3a** in 80% yield (50 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.03-8.01 (m, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.64-7.63 (m, 2H), 7.57-7.47 (m, 4H), 7.41-7.40 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 190.43, 144.75, 138.09, 134.77,

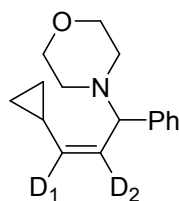
132.72, 130.48, 128.88, 128.55, 128.42, 128.38, 121.95. The spectroscopic data are in agreement with that previously reported.^[11]

Synthesis of allylamine **2a-d**, **2r-d**

Typical procedure for the synthesis of **2a-d**



To a solution of 4-(1,3-diphenylprop-2-ynyl)morpholine **1a** (83 mg, 0.3 mmol) in toluene (5 mL) were successively added Cp_2TiCl_2 (3.7 mg, 0.015 mmol) and Red-Al (98 μL , 0.3 mmol, 60% in toluene). The Schlenk tube was immersed into an oil bath preheated at 50 °C and stirred for 3 h. Then the resulting mixture was cooled down to room temperature, and D_2O (2 mL) was added. After stirred for 3 h, the reaction was quenched with saturated potassium sodium tartrate solution and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the product **2a-d** as a white solid in 87% yield (73.1 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.31 (m, 6H), 7.26-7.22 (m, 4H), 6.64 (d, J = 11.6 Hz, 0.13H), 5.90 (d, J = 10.4 Hz, 0.95H), 4.23 (d, J = 10.4 Hz, 1H), 3.65-3.63 (m, 4H), 2.52-2.50 (m, 2H), 2.30-2.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.25, 136.87, 132.68, 131.09, 128.62, 128.56, 128.18, 128.10, 127.22, 126.90, 67.28, 67.09, 51.34. IR (film): 3062, 3024, 2955, 2851, 2808, 2216, 1949, 1810, 1599, 1492, 1450, 1394, 1275, 1249, 1207, 1116, 1070, 1029, 1005, 940, 915, 873, 790, 756, 698. HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{DNO}$ $[\text{M}+\text{H}]^+$: 281.1759, found 281.176.

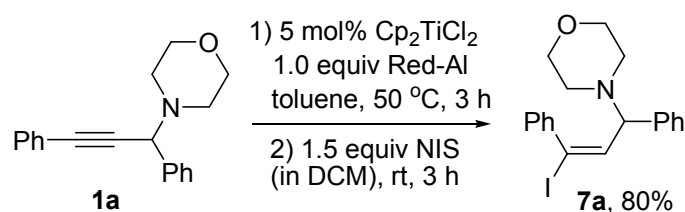


D₁%=72%, D₂%=25%
2r-d

Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the product **2r-d** in 81% yield (59.6 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.23 (m, 1H), 5.44 (d, *J* = 9.6 Hz, 0.75H), 4.91-4.85 (m, 0.28H), 4.13 (d, *J* = 9.6 Hz, 1H), 3.71-3.69 (m, 4H), 2.56 (m, 2H), 2.40-2.36 (m, 2H), 1.72-1.69 (m, 1H), 0.78-0.75 (m, 2H), 0.34-0.31 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 142.25, 135.93, 128.89, 128.51, 127.81, 126.98, 68.42, 67.16, 51.90, 9.82, 7.00. IR (film): 3077, 3003, 2955, 2851, 2805, 2220, 1945, 1806, 1641, 1600, 1491, 1450, 1394, 1275, 1250, 1207, 1116, 1070, 1047, 1005, 950, 926, 913, 872, 810, 755, 739, 700, 672. HRMS(ESI) calcd for C₁₆H₂₁DNO [M+H]⁺: 245.1759, found 245.1761.

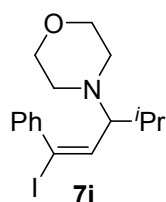
Synthesis of iodinated products 7.

Typical procedure for the synthesis of **7a**.



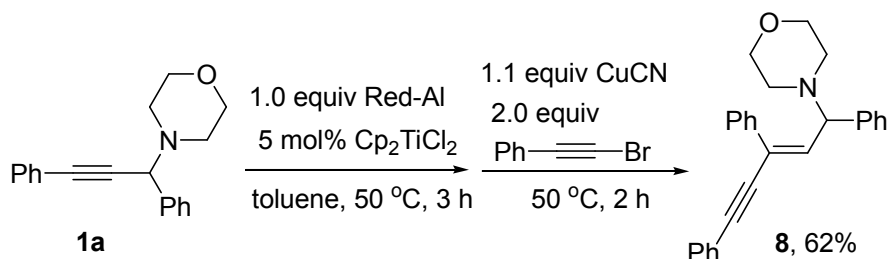
To a solution of 4-(1,3-diphenylprop-2-ynyl)morpholine **1a** (83 mg, 0.3 mmol) in toluene (5 mL) were successively added Cp₂TiCl₂ (3.7 mg, 0.015 mmol) and Red-Al (98 μL, 0.3 mmol, 65% in toluene). The Schlenk tube was immersed into an oil bath preheated at 50 °C and stirred for 3 h. Then the resulting mixture was cooled down to room temperature, NIS (101 mg, 0.45 mmol in DCM) was added and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with saturated potassium sodium tartrate solution and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the product **7a** as a yellow solid in 80% yield (96.9 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.20 (m, 10H), 6.64 (d, *J* = 10 Hz, 1H), 3.67-3.61 (m, 5H), 2.46 (m, 2H), 2.23-2.18 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 143.35, 141.74, 139.83, 128.69, 128.26, 128.24, 128.10, 127.97, 127.47, 96.72, 70.50, 66.96, 51.30. IR (film): 3055, 3027, 2955, 2851, 2807, 2363, 1954, 1808, 1599, 1489, 1450, 1393, 1336, 1274, 1247, 1173, 1116, 1070, 1028, 1005, 930, 873, 812, 766, 741, 698. HRMS(ESI)

calcd for $C_{19}H_{21}INO$ $[M+H]^+$: 406.0662, found 406.0661. The structure of **7a** was determined by X-ray single-crystal analysis.



(E)-4-(1-Iodo-4-methyl-1-phenylpent-1-en-3-yl)morpholine (7i). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product **7i** as a yellow solid in 89% yield (660.8 mg). 1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.23 (m, 5H), 6.37 (d, J = 10.4 Hz, 1H), 3.66-3.58 (m, 4H), 2.60-2.55 (m, 2H), 2.50 (dd, J = 10.8, 9.2 Hz, 1H), 2.28-2.23 (m, 2H), 1.78-1.76 (m, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.09, 141.80, 128.39, 128.06, 127.83, 96.92, 70.45, 67.23, 49.53, 28.29, 19.84, 19.38. IR (film): 2955, 2850, 2810, 1968, 1883, 1623, 1591, 1487, 1450, 1351, 1327, 1287, 1253, 1169, 1139, 1115, 1070, 1029, 1008, 940, 916, 872, 860, 818, 786, 763, 698, 685. HRMS(ESI) calcd for $C_{16}H_{23}INO$ $[M+H]^+$: 372.0819, found 372.0818.

Synthesis of alkynylated product **8**.

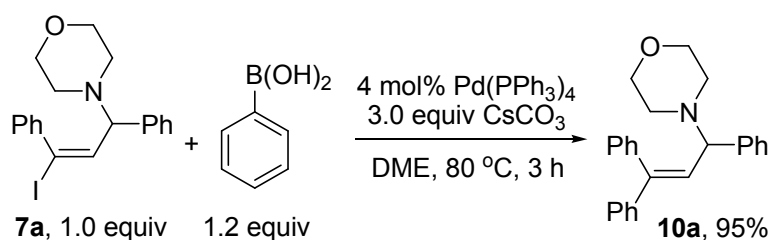


To a solution of **1a** (83 mg, 0.3 mmol) in toluene (5 mL) were successively added Cp_2TiCl_2 (3.7 mg, 0.015 mmol) and Red-Al (98 μ L, 0.3 mmol, 60% in toluene). The Schlenk tube was immersed into an oil bath preheated at 50 $^{\circ}C$ and stirred for 3 h. Then CuCN (30 mg, 0.33 mmol) and 1-bromo-2-phenylethyne (109 mg, 0.6 mmol) were added to the above mixture at 50 $^{\circ}C$. Then the mixture was stirred at 50 $^{\circ}C$ for additional 2 hours. After the reaction was complete as monitored by TLC, the resulting mixture was cooled down to room temperature, quenched with saturated potassium sodium tartrate solution and stirred for 30 min. The mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford **8**

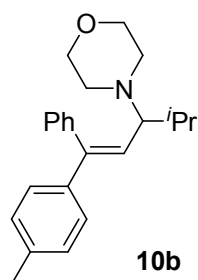
as a pale yellow oil in 62% yield (70 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.24 (m, 15H), 6.44 (d, J = 10.0 Hz, 1H), 3.98 (d, J = 10.4 Hz, 1H), 3.65-3.63 (m, 4H), 2.49 (m, 2H), 2.28-2.23 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.55, 139.65, 137.39, 131.45, 128.68, 128.64, 128.31, 128.21, 128.18, 128.12, 127.74, 127.44, 125.55, 123.08, 90.61, 89.19, 68.38, 67.11, 51.47. IR (film): 3084, 3057, 2958, 2853, 2798, 2689, 2300, 1951, 1881, 1806, 1598, 1489, 1450, 1443, 1394, 1356, 1265, 1115, 1069, 1027, 1002, 929, 915, 868, 774, 755, 735, 697. HRMS(EI) calcd for $\text{C}_{27}\text{H}_{25}\text{NO}$ [M]: 379.1936, found 379.1932.

Pd-catalyzed coupling reactions of alkenyl iodides **7** with arylboronic acids.

Typical procedure for the synthesis of **10a**.

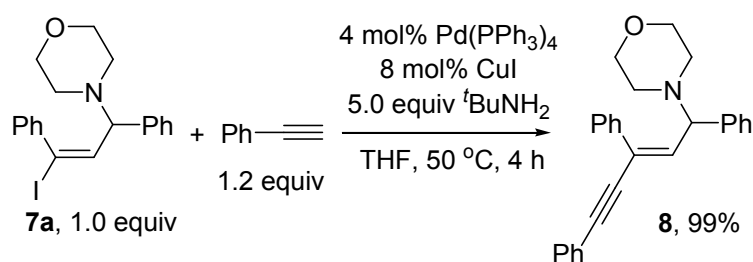


To a solution of (*E*)-4-(3-iodo-1,3-diphenylallyl)morpholine **7a** (122 mg, 0.3 mmol) in DME (5 mL) were successively added phenylboronic acid (44 mg, 0.36 mmol), cesium carbonate (293 mg, 0.9 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (14 mg, 0.012 mmol). Then the reaction mixture was heated up to 80 °C. After stirring 3 h, the resulting mixture was cooled down to room temperature, quenched with water and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the product **10a** as a yellow oil in 95% yield (101 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.35 (m, 3H), 7.30-7.19 (m, 10H), 7.14-7.12 (m, 2H), 6.32 (d, J = 9.6 Hz, 1H), 3.80 (d, J = 10.0 Hz, 1H), 3.66-3.65 (m, 4H), 2.52 (m, 2H), 2.30-2.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.91, 141.58, 141.54, 139.60, 129.92, 129.74, 128.55, 128.26, 128.10, 127.34, 127.22, 127.13, 127.01, 69.32, 67.15, 51.73. IR (film): 3055, 3025, 2954, 2851, 2806, 1947, 1883, 1808, 1733, 1598, 1572, 1491, 1445, 1393, 1356, 1270, 1115, 1070, 1030, 1005, 936, 898, 865, 779, 761, 727, 696. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{NO}$ [$\text{M}+\text{H}$] $^+$: 356.2009, found 356.201.



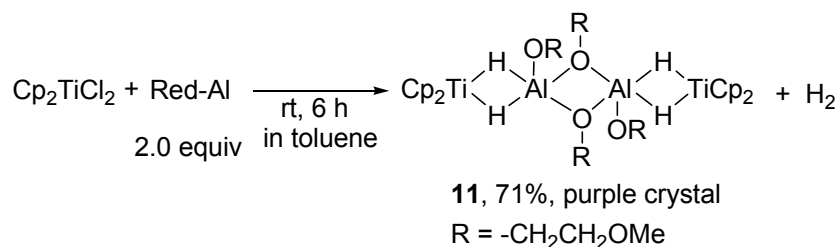
(E)-4-(4-Methyl-1-phenyl-1-*p*-tolylpent-1-en-3-yl)morpholine (10b). Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the product **10b** as a yellow oil in 91% yield (91.6 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.28 (m, 3H), 7.17-7.12 (m, 4H), 7.08-7.06 (m, 2H), 5.99 (d, *J* = 10.4 Hz, 1H), 3.64 (m, 4H), 2.66-2.61 (m, 3H), 2.37-2.33 (m, 2H), 2.31 (s, 3H), 1.90-1.88 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 144.83, 140.20, 139.63, 137.00, 130.02, 128.80, 127.96, 127.02, 126.76, 126.68, 68.18, 67.45, 50.10, 28.91, 21.01, 20.10, 19.10. IR (film): 3021, 2955, 2851, 2808, 2235, 1959, 1899, 1729, 1595, 1510, 1492, 1449, 1360, 1327, 1285, 1266, 1253, 1140, 1116, 1070, 1007, 944, 917, 895, 862, 842, 818, 773, 714, 701, 664. HRMS(ESI) calcd for C₂₃H₃₀NO [M+H]⁺: 336.2322, found 336.2322.

Pd-catalyzed coupling reactions of alkenyl iodide **7a** with alkyne.



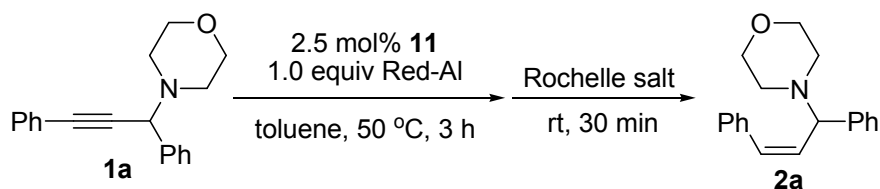
To a solution of (*E*)-4-(3-iodo-1,3-diphenylallyl)morpholine **7a** (122 mg, 0.3 mmol) in THF (5 mL) were successively added ethynylbenzene (40 μL, 0.36 mmol), ^{*t*}BuNH₂ (110 mg, 1.5 mmol), CuI (4.6 mg, 0.024 mmol) and Pd(PPh₃)₄ (14 mg, 0.012 mmol). Then the reaction mixture was stirred at 50 °C for 4 h. The resulting mixture was cooled down to room temperature, quenched with saturated ammonium chloride solution and extracted with ethyl acetate. The extract was washed with saturated NaHCO₃, brine, dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the product **8** as a yellow oil in 99% yield (113 mg).

Synthesis of the complex (C₆H₅)₂Ti(μ-H)₂Al(OCH₂CH₂OCH₃) **11**.



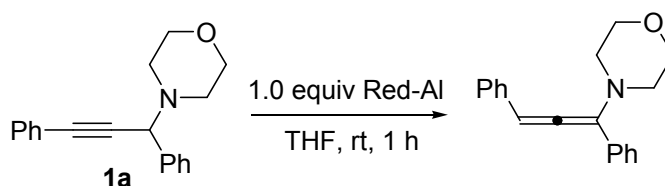
To a solution of Cp₂TiCl₂ (249 mg, 1.0 mmol) in toluene (5 mL) was added Red-Al (0.6 mL, 2.0 mmol, 65% in toluene) at room temperature and stirred for 6 h. Then the Schlenk tube was moved into the glove box and the reaction mixture was filtered. The solvent of the filtrate was removed under the reduced pressure, and the residue was added hexane to produce a purple powder. The powder was washed with hexane for two times. Then the powder was pumped dry, extracted with toluene and filtered. The solvent of the filtrate was partially removed under the reduced pressure and hexane was added. Under -40 °C, purple lumpy crystal was precipitated in 71% yield (253.6 mg). Anal. Calcd for C₃₂H₅₂Al₂O₈Ti₂: C, 53.80; H, 7.34. Found: C, 54.18; H, 7.14. The structure of **11** was determined by X-ray single-crystal analysis.

Formation of allylamine **2a** catalyzed by **11**.



In a glovebox, complex **11** (5.4 mg, 0.0075 mmol) was added to a Schlenk tube. Then the Schlenk tube was removed from the glovebox, and toluene (5 mL), Red-Al (98 μL, 0.3 mmol, 60% in toluene), 4-(1,3-diphenylprop-2-yn-1-yl)morpholine **1a** (83 mg, 0.3 mmol) were added sequentially. The resulting mixture was stirred at 50 °C for 3 h. Then the mixture was allowed to cool to room temperature, quenched with saturated potassium sodium tartrate solution and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na₂SO₄. Then the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford *Z*-**2a** in 98% yield (82 mg).

Trapping of the allene intermediate in the direct reaction of **1a** with Red-Al.



To a solution of **1a** (83 mg, 0.3 mmol) in THF (5 mL) was added Red-Al (98 μ L, 0.3 mmol, 60% in toluene) at room temperature and stirred for 1 h. The solvent was removed under the reduced pressure, and 1,3,5-trimethoxybenzene (50.5 mg, 0.3 mmol) was added as an internal standard. The ^1H NMR yield of 4-(1,3-diphenylpropa-1,2-dienyl)morpholine was 73% in C_6D_6 . In another reaction, after the reaction was complete, the solvent of the reaction mixture was removed under the reduced pressure, and hexane was added and stirred. The clear hexane layer was transferred to another tube. The solvent was removed under the reduced pressure, and the residue was used for NMR. The NMR data of this sample was shown as follows: ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.52 (m, 2H), 7.40-7.25 (m, 8H), 6.80 (s, 1H), 3.82-3.80 (m, 4H), 2.84-2.81 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 200.87, 135.37, 134.46, 128.69, 128.46, 128.04, 127.99, 127.41, 127.27, 126.87, 103.81, 67.02, 51.35. HRMS(EI) calcd for $\text{C}_{19}\text{H}_{19}\text{NO}$: 277.1467, found 277.1469. The product was unstable upon isolation on silica gel. The result indicated that allene was indeed formed before quenching the reaction mixture.

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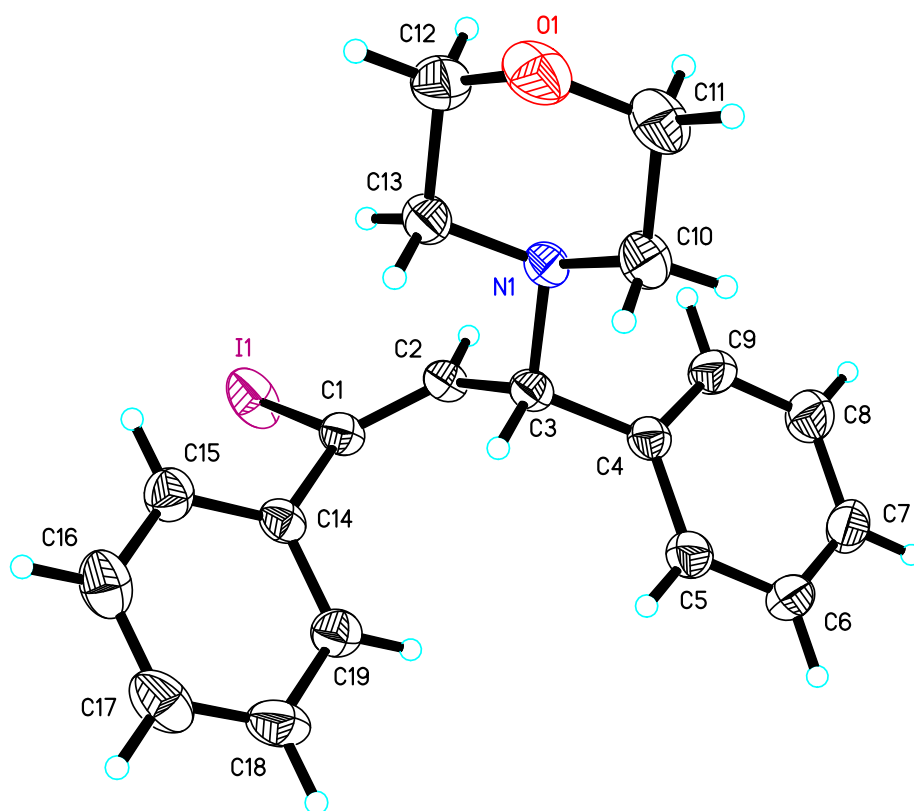


Figure S1. X-ray crystal structure of compound **7a**

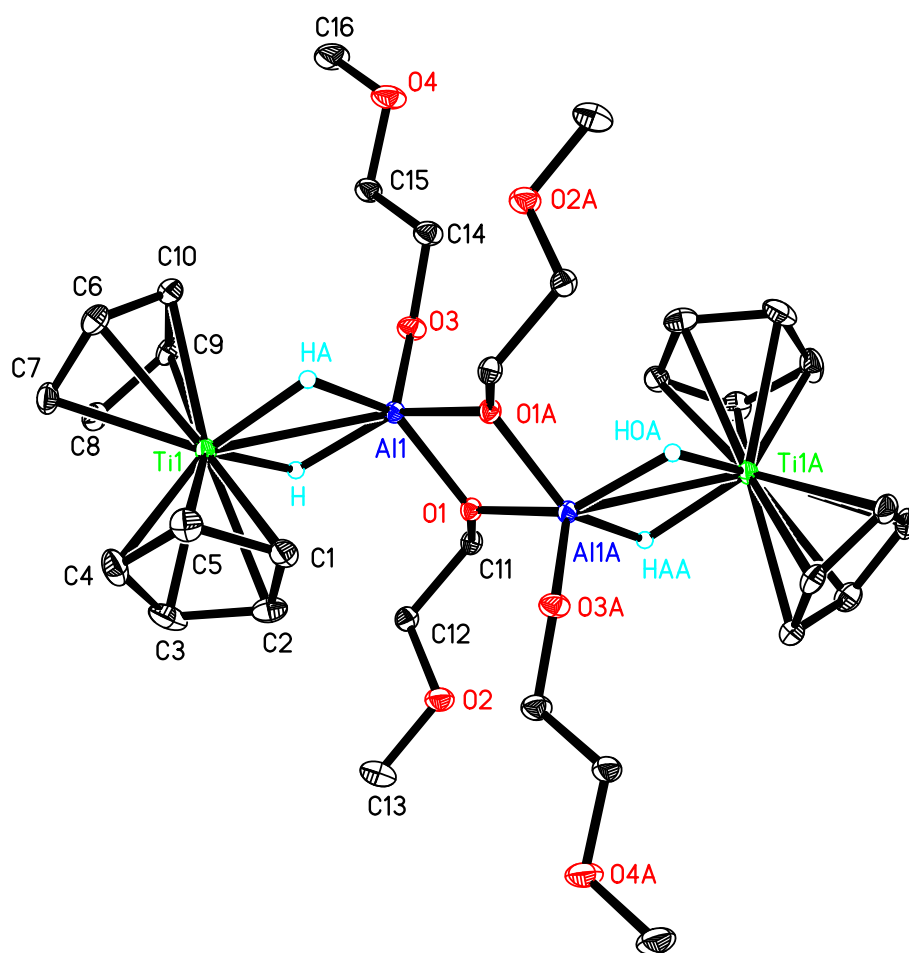
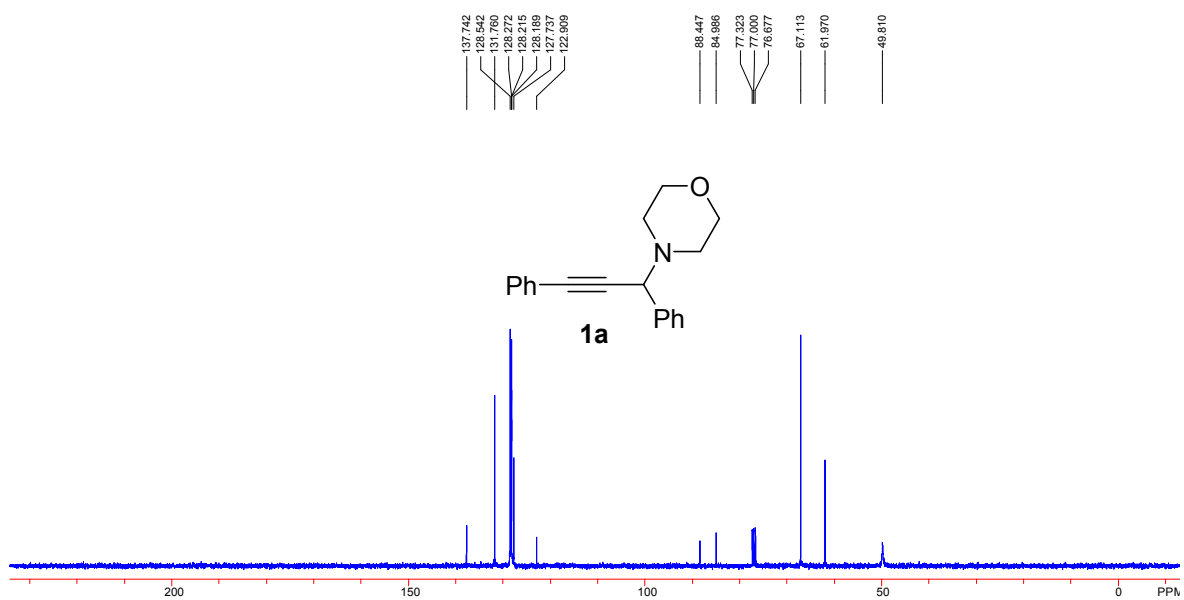
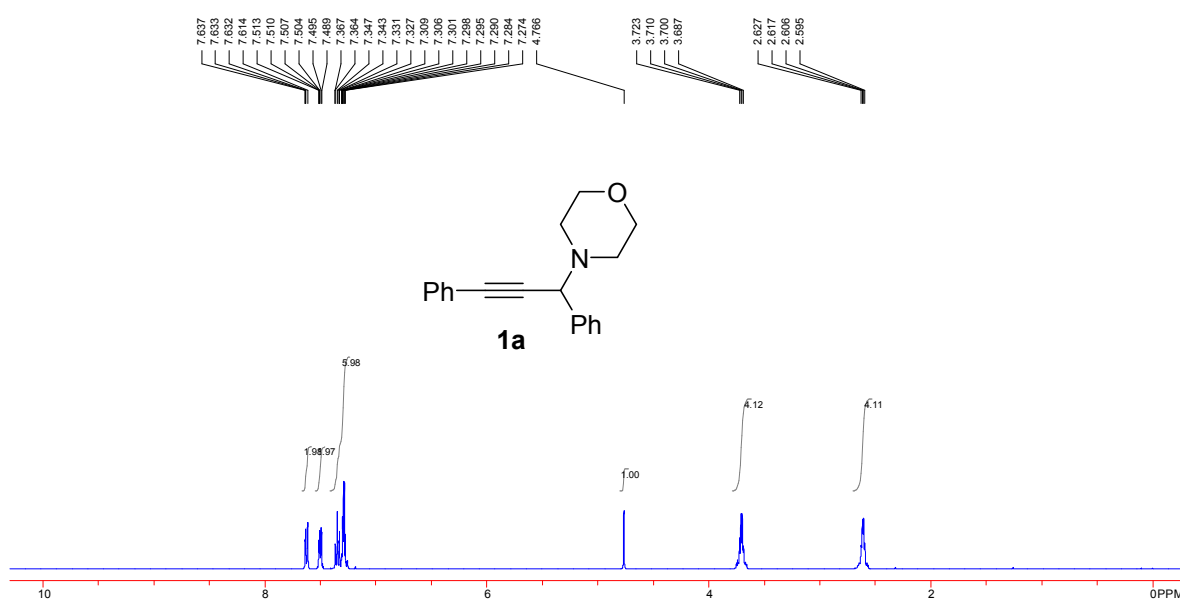
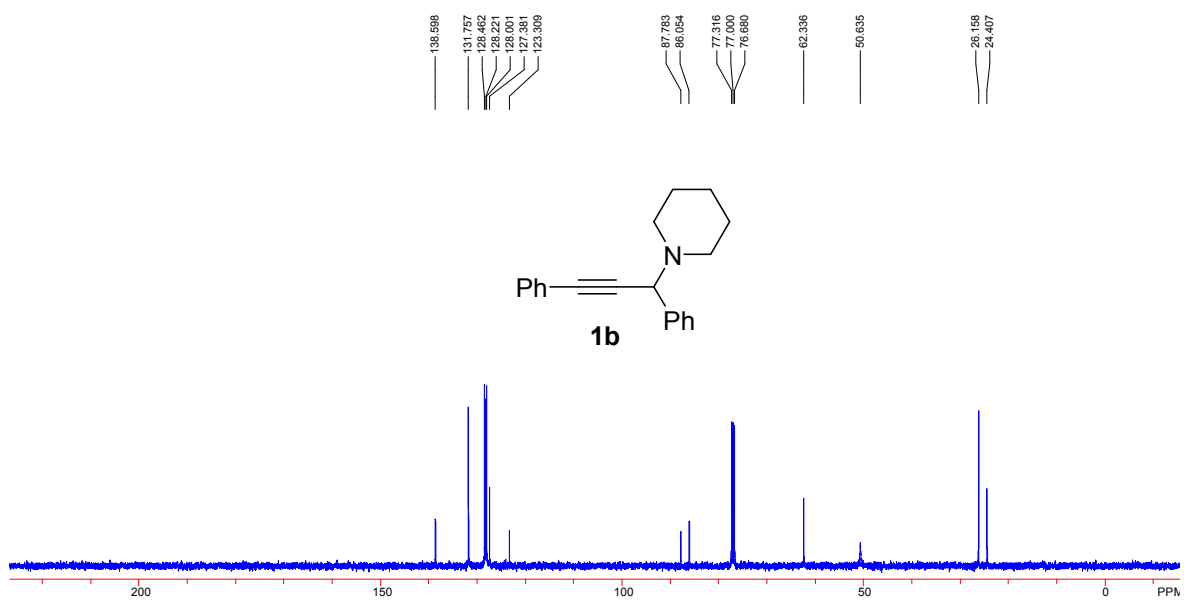
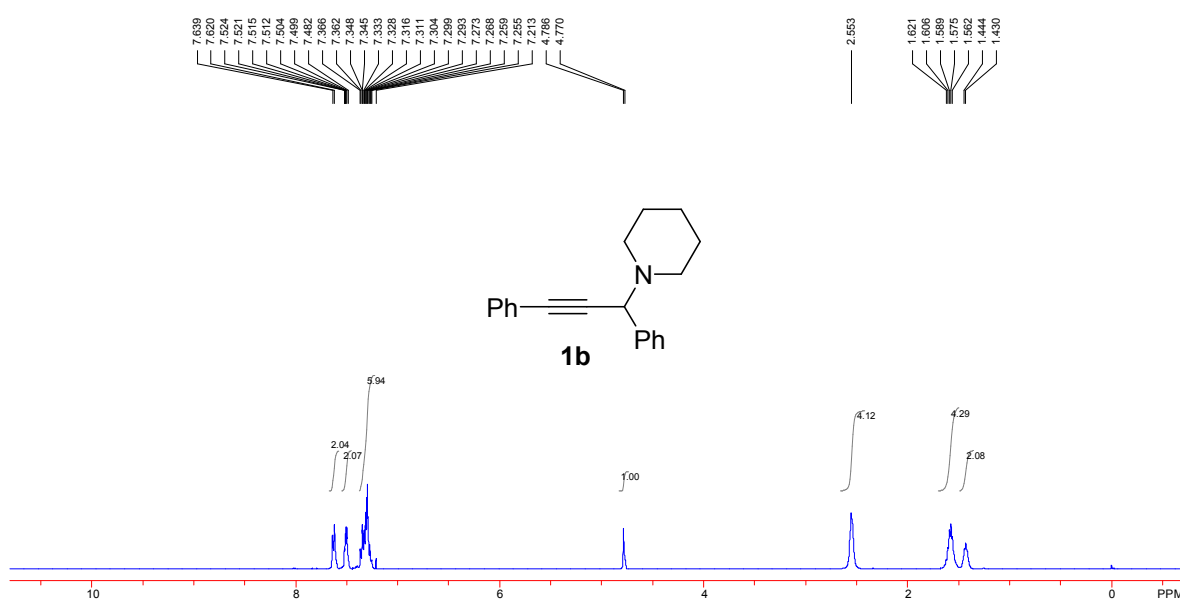
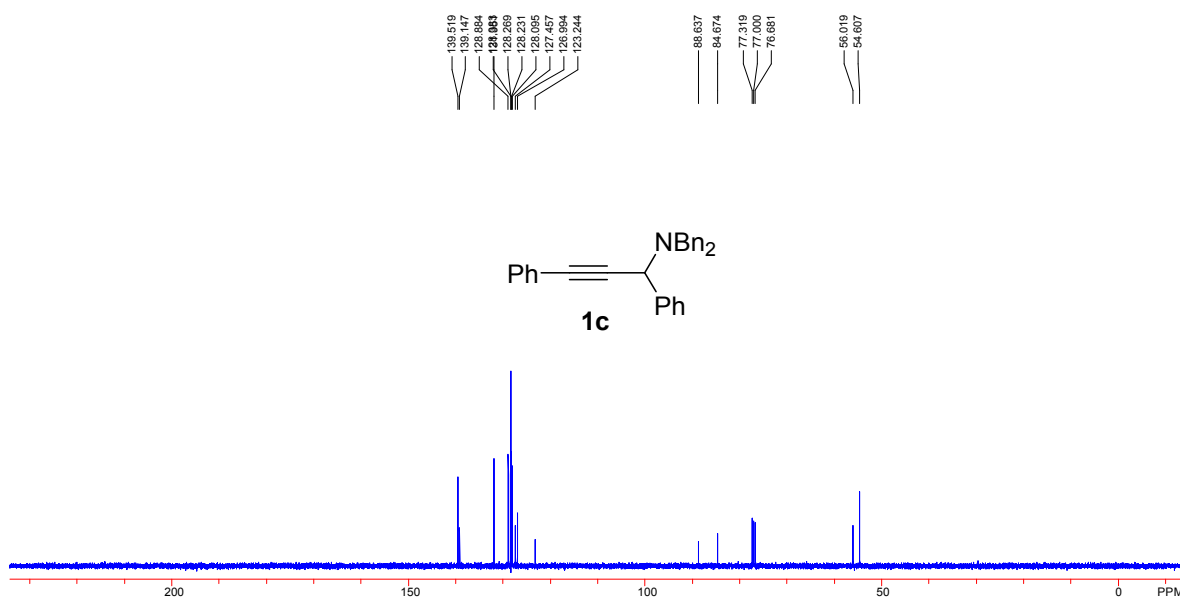
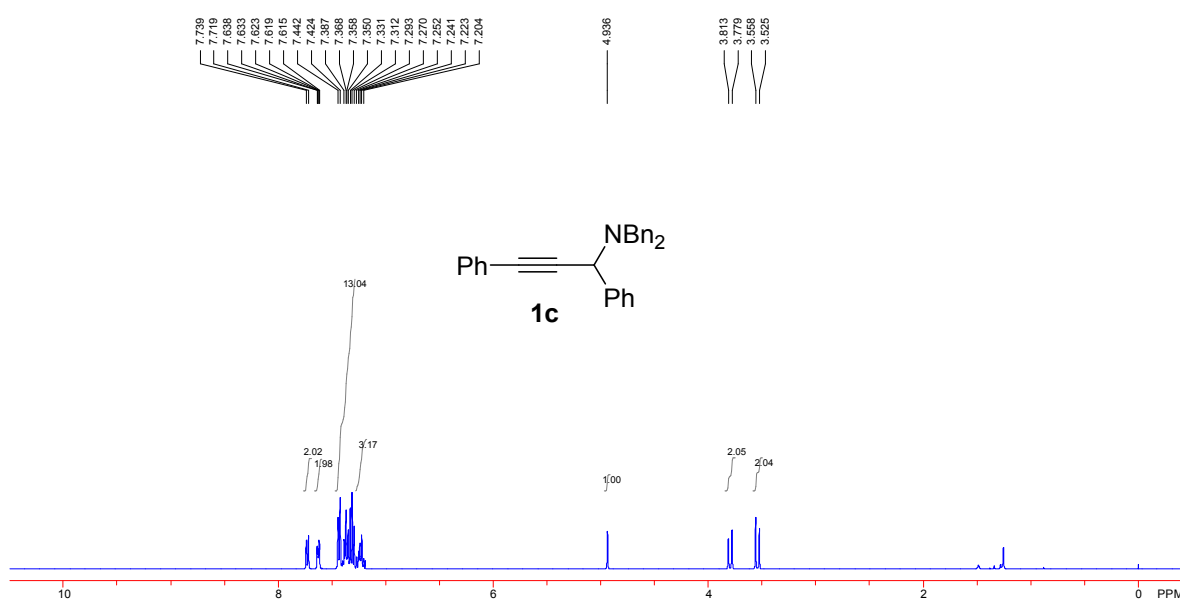
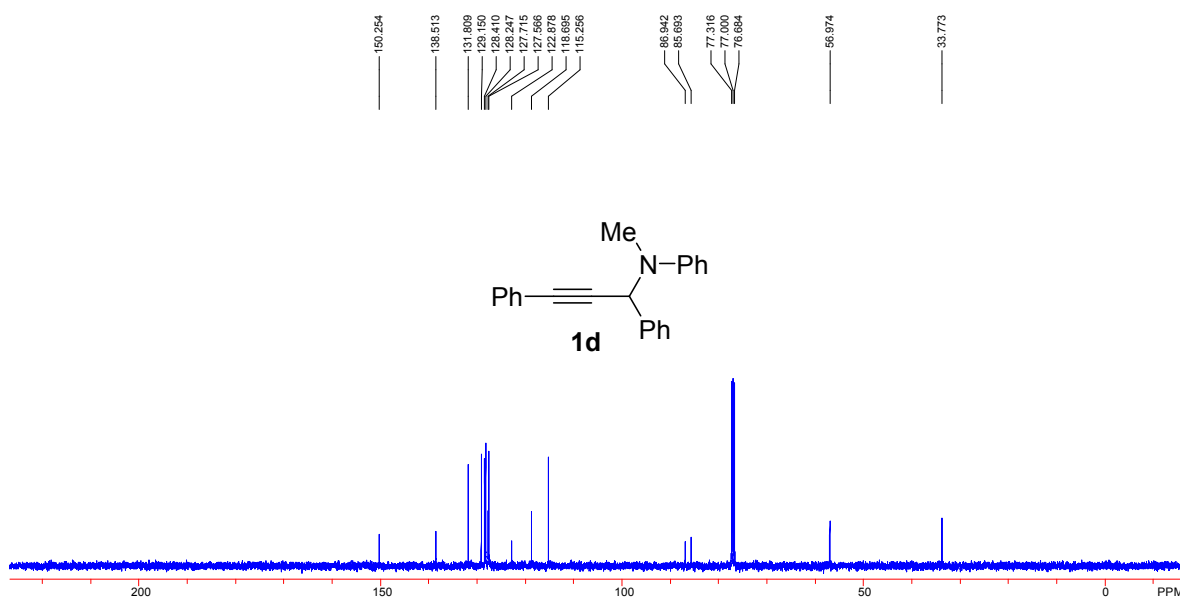
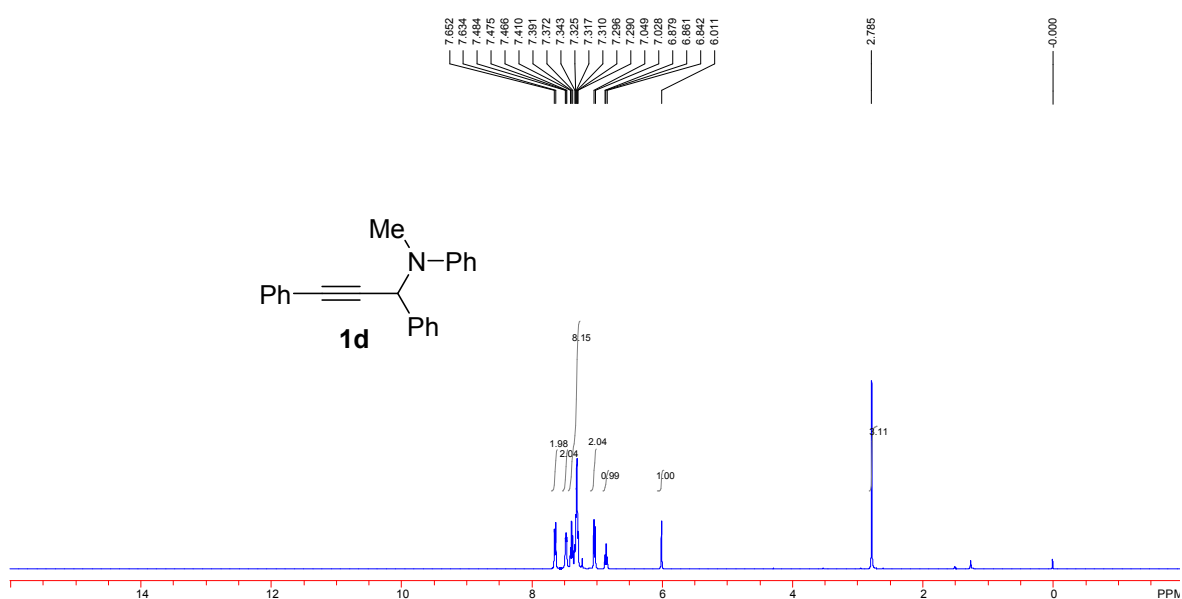


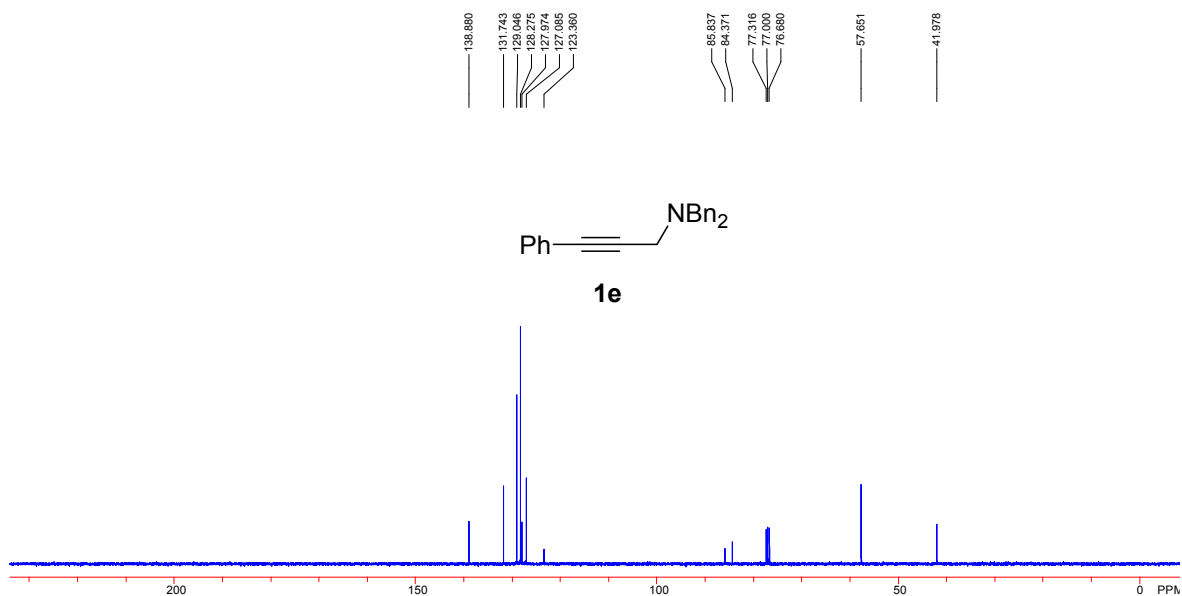
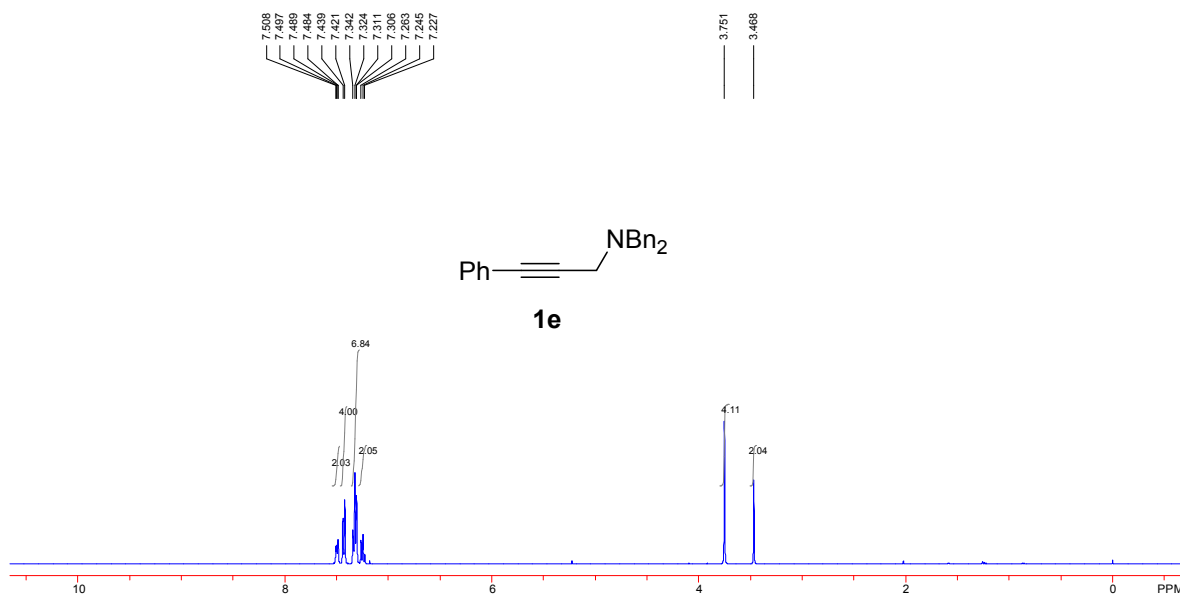
Figure S2. X-ray crystal structure of compound **11**

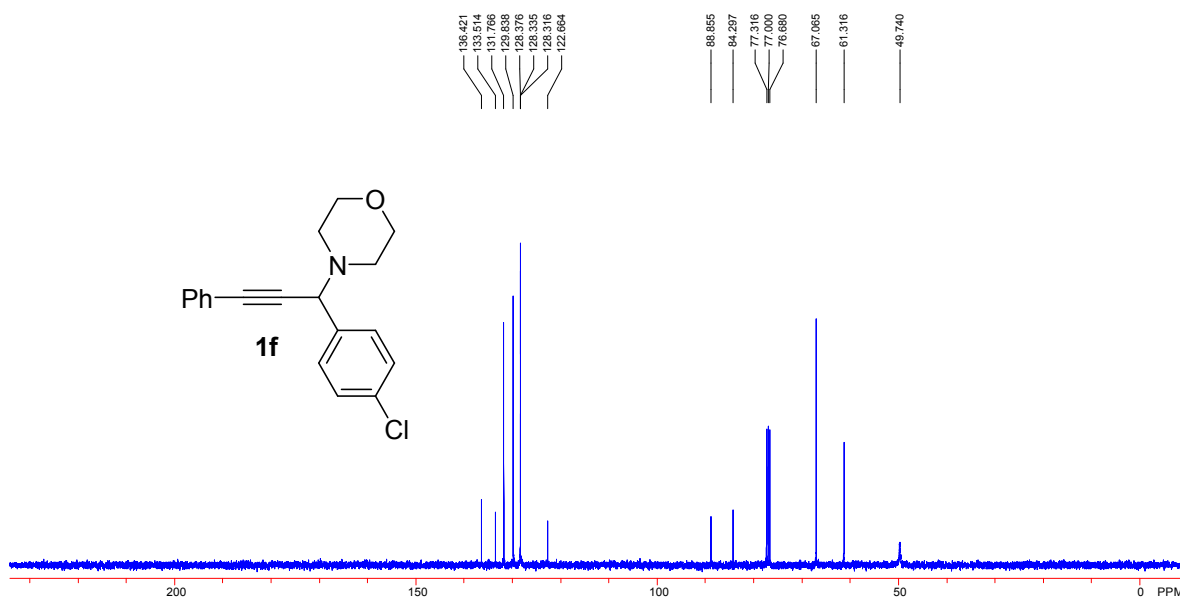
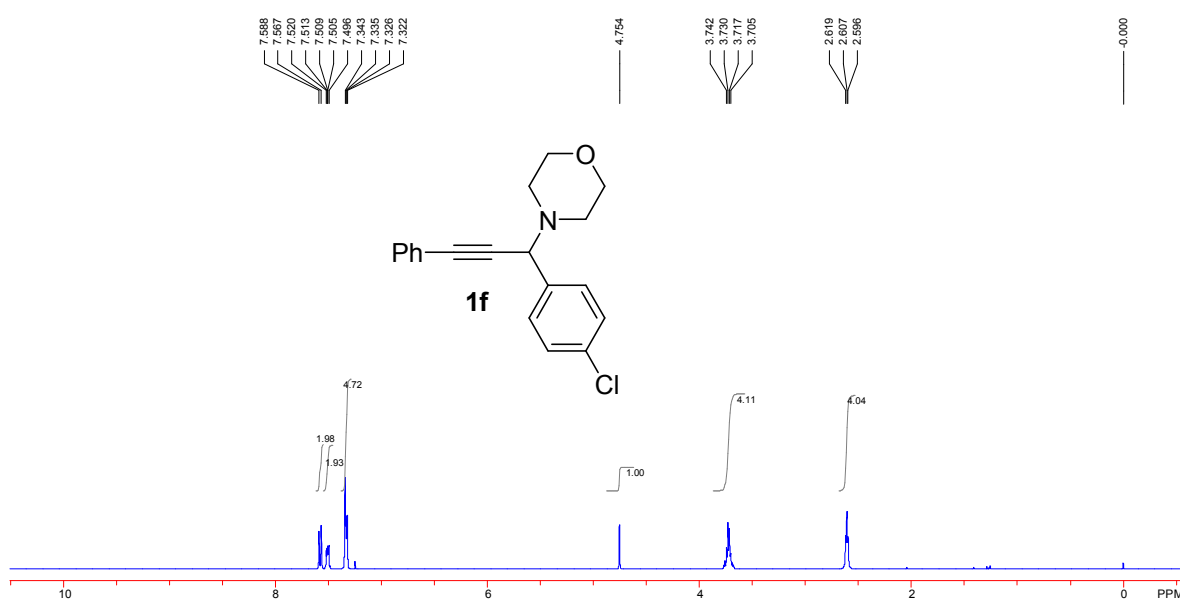


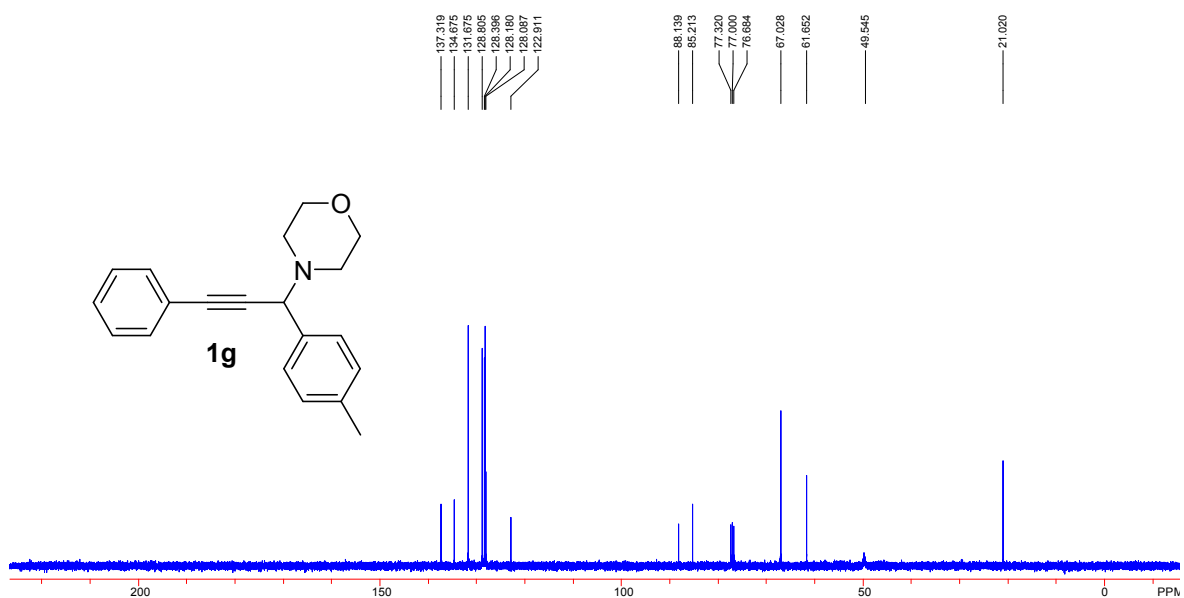
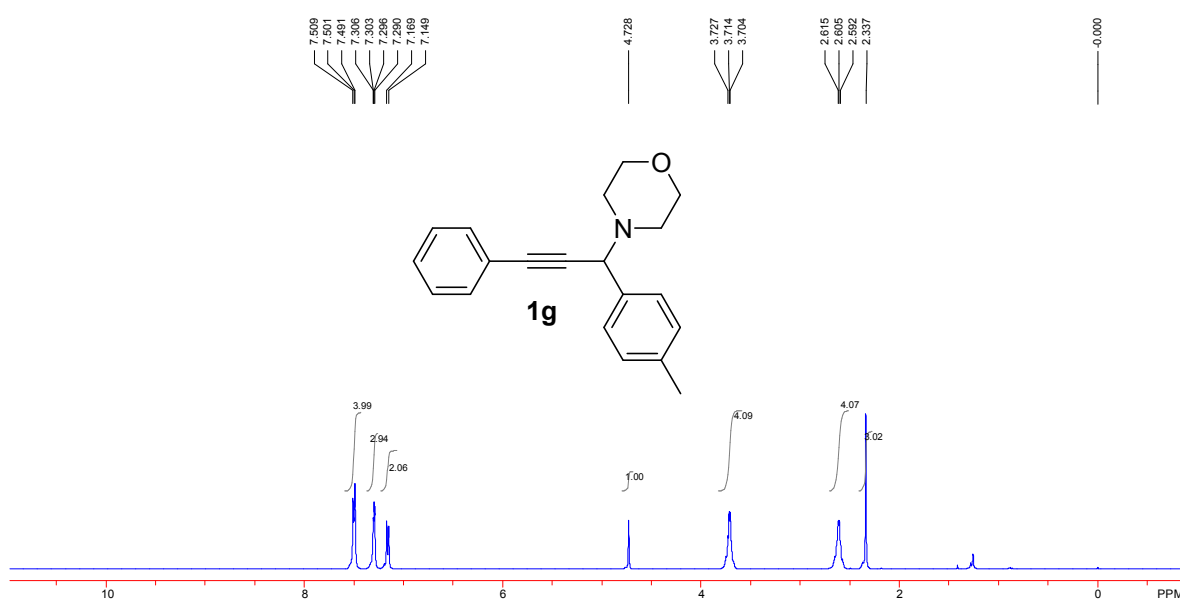


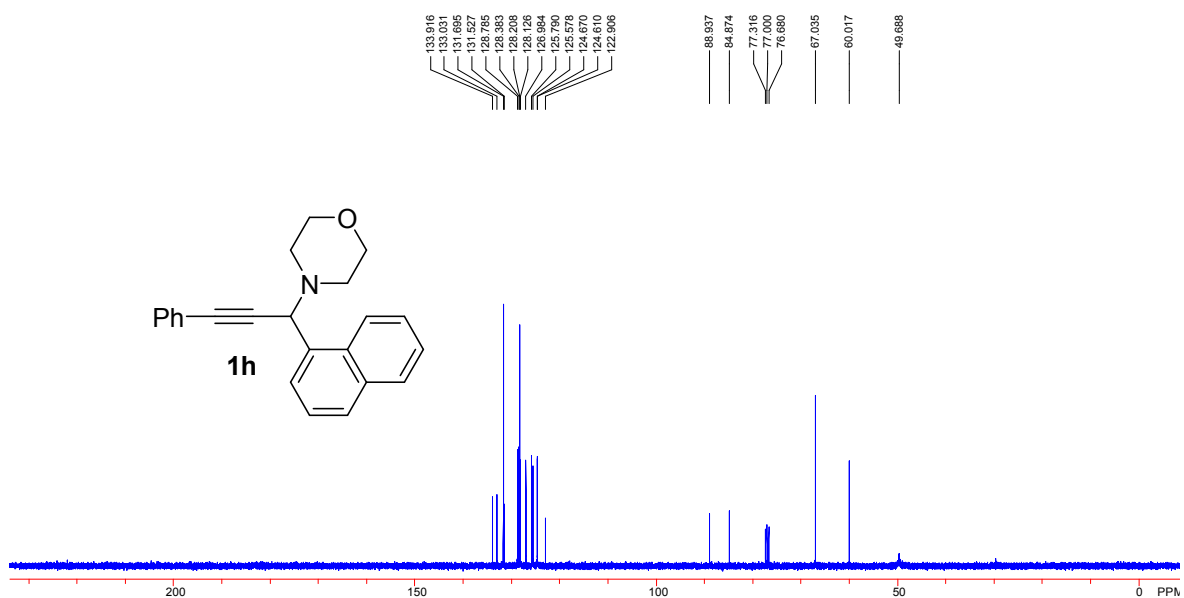
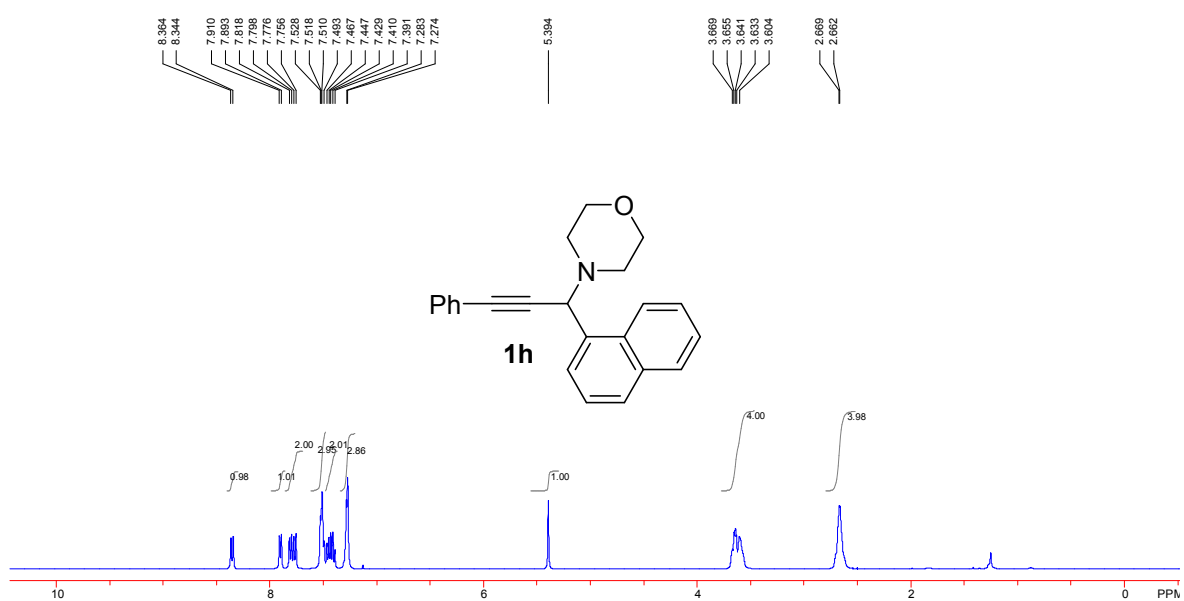


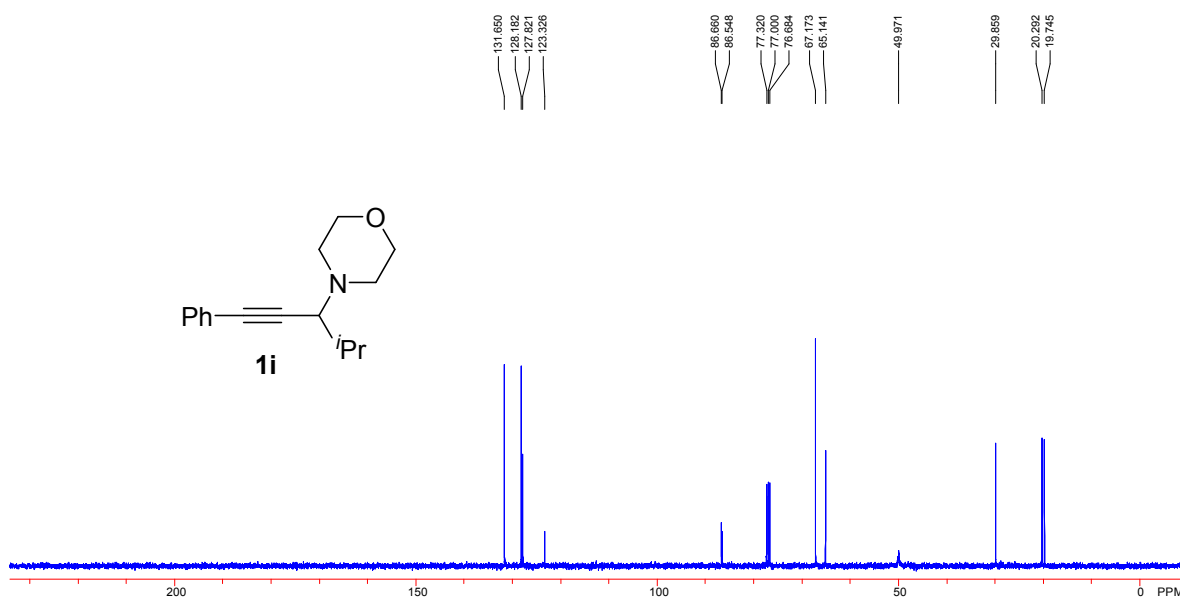
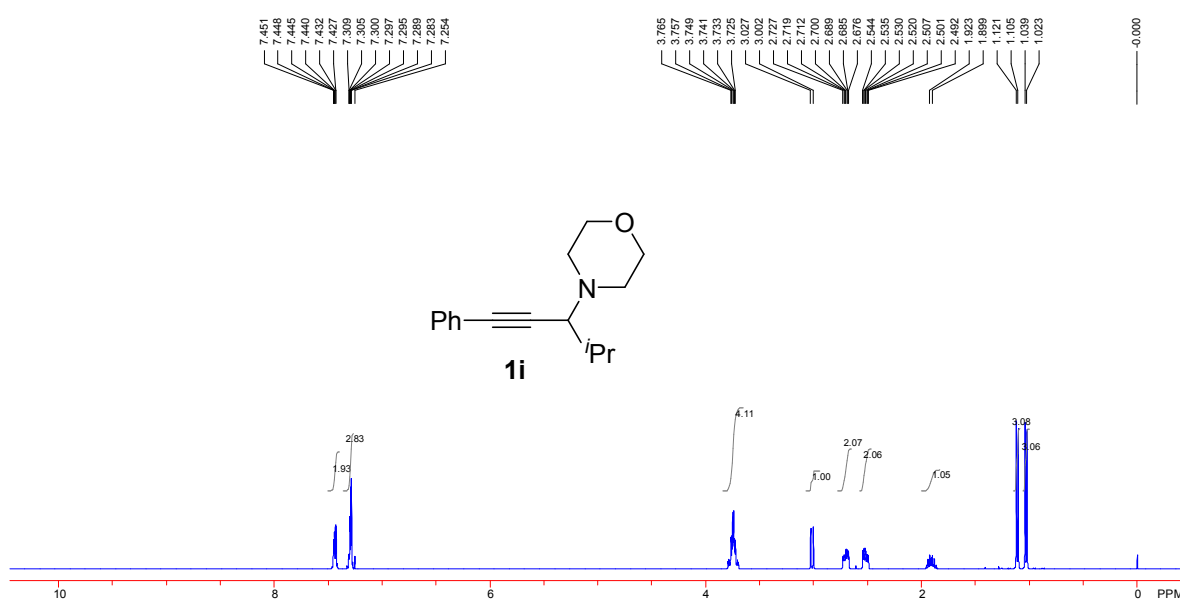


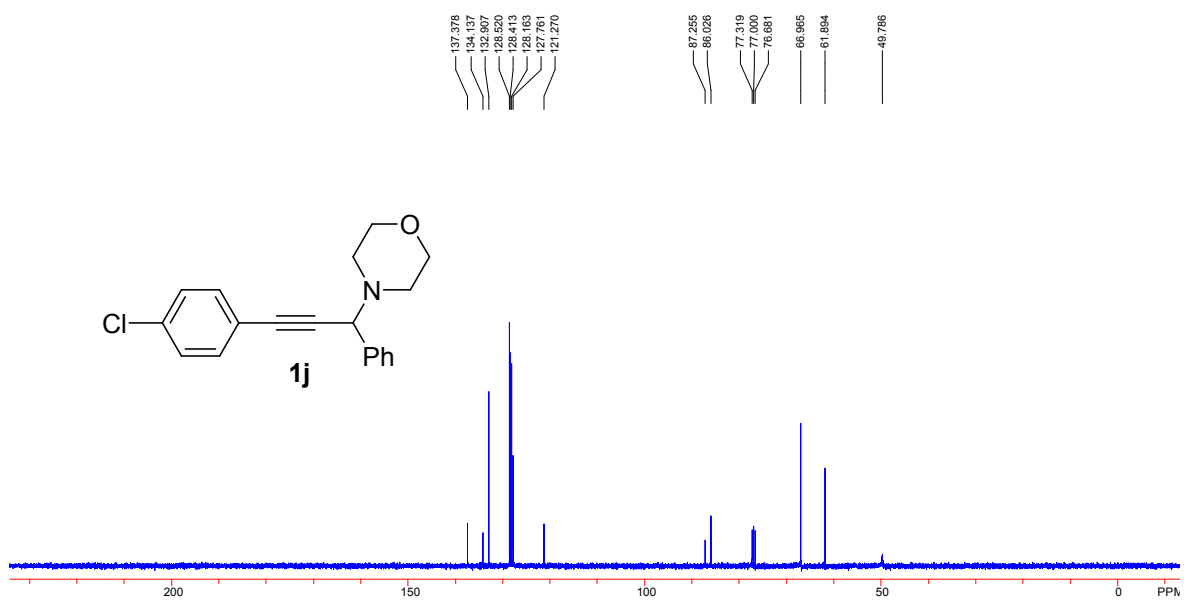
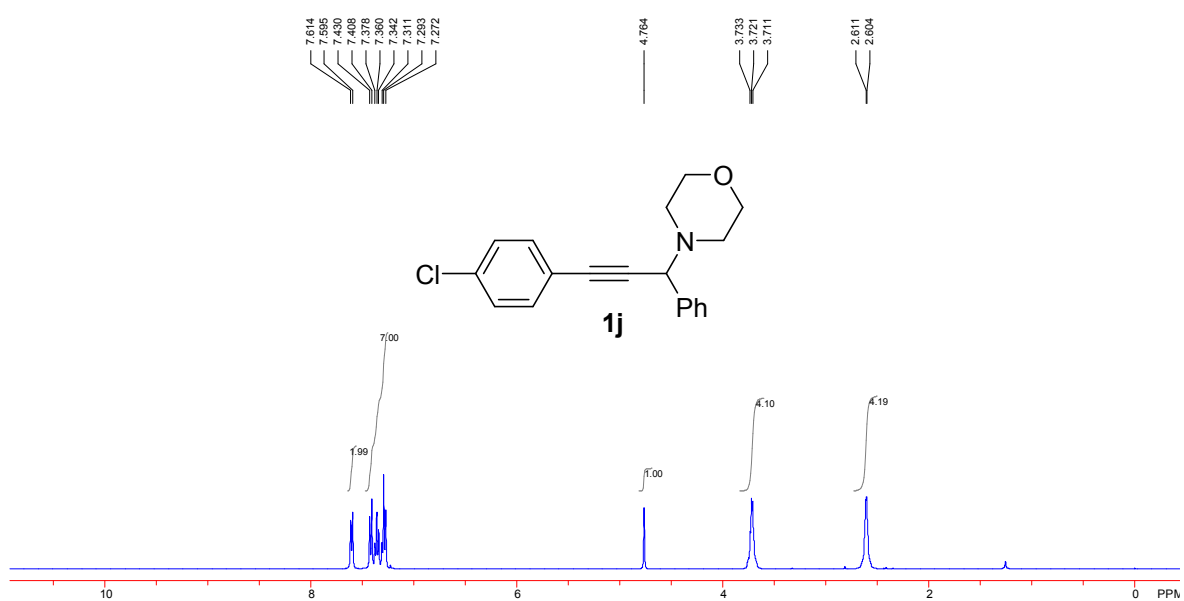


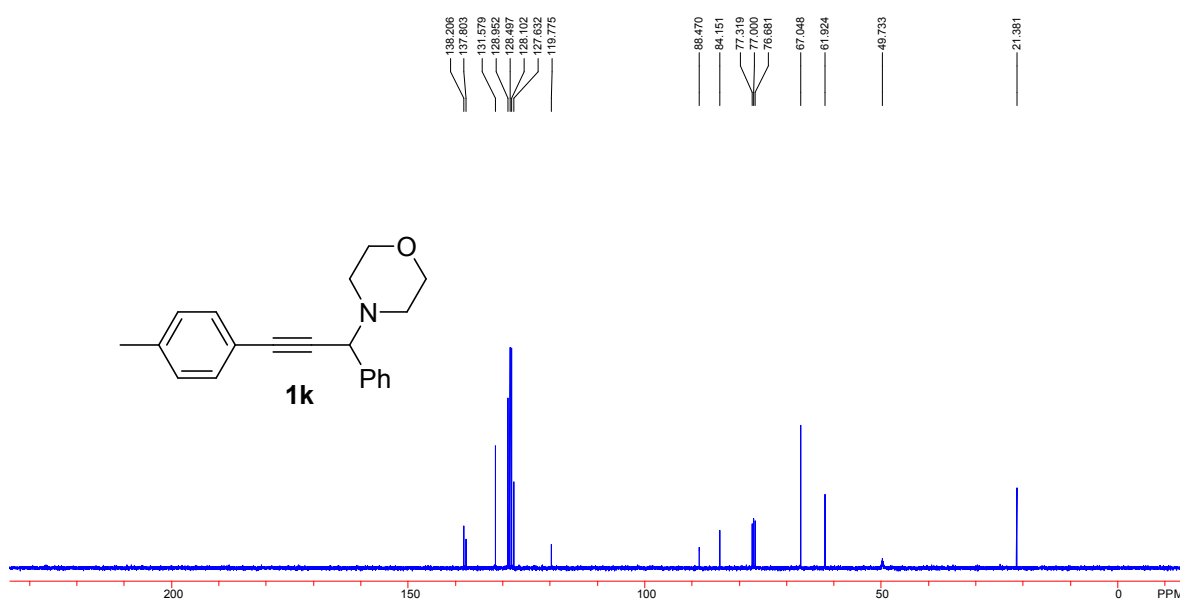
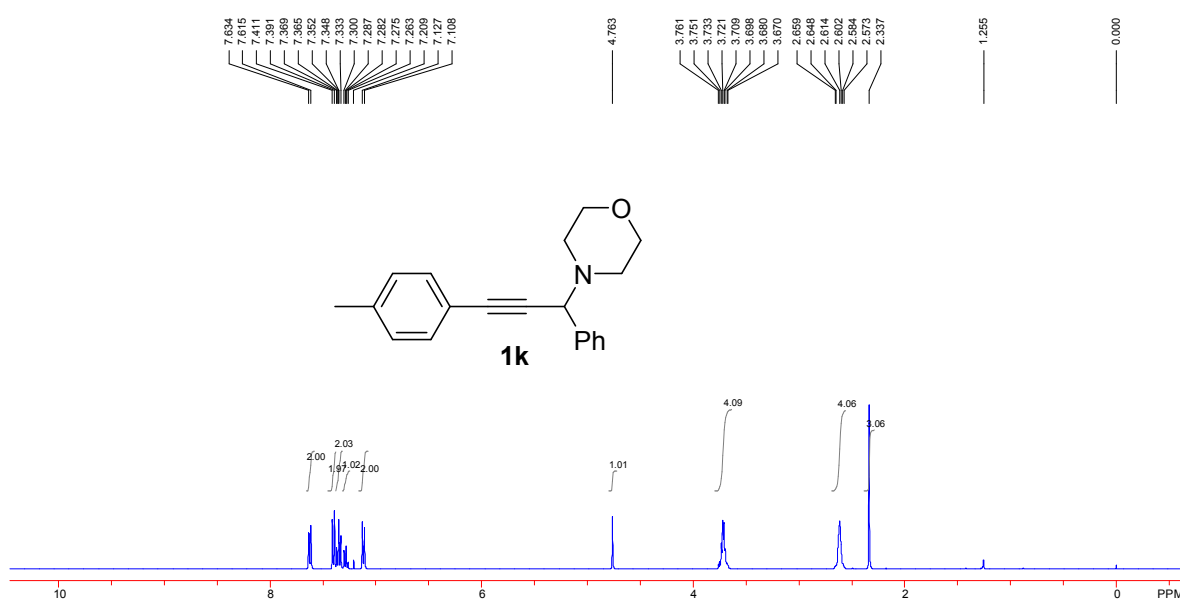


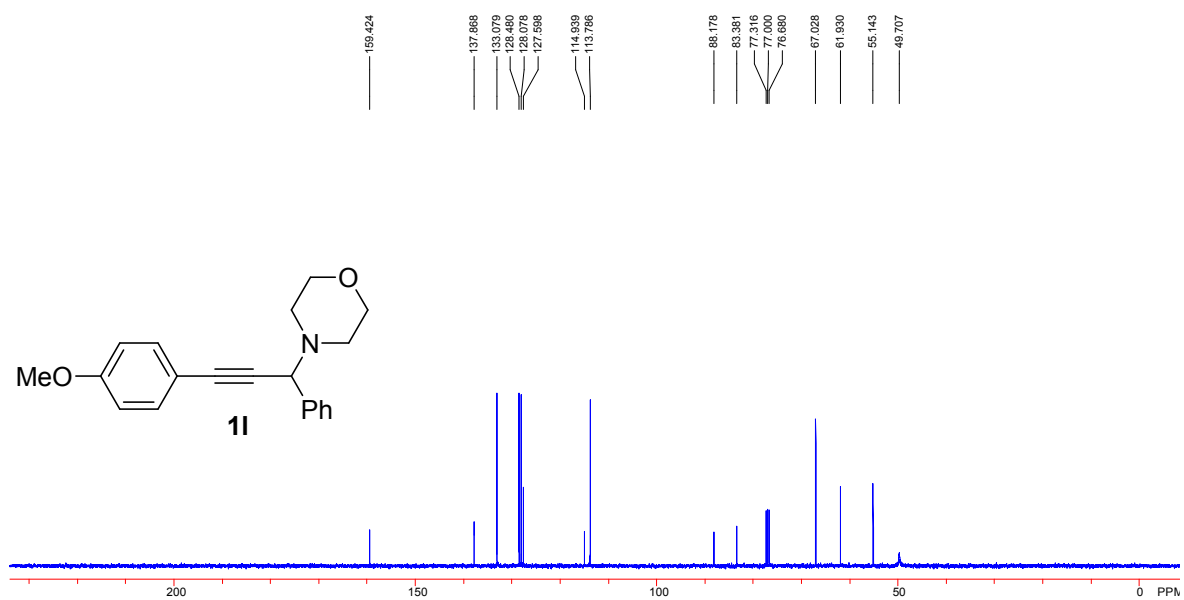
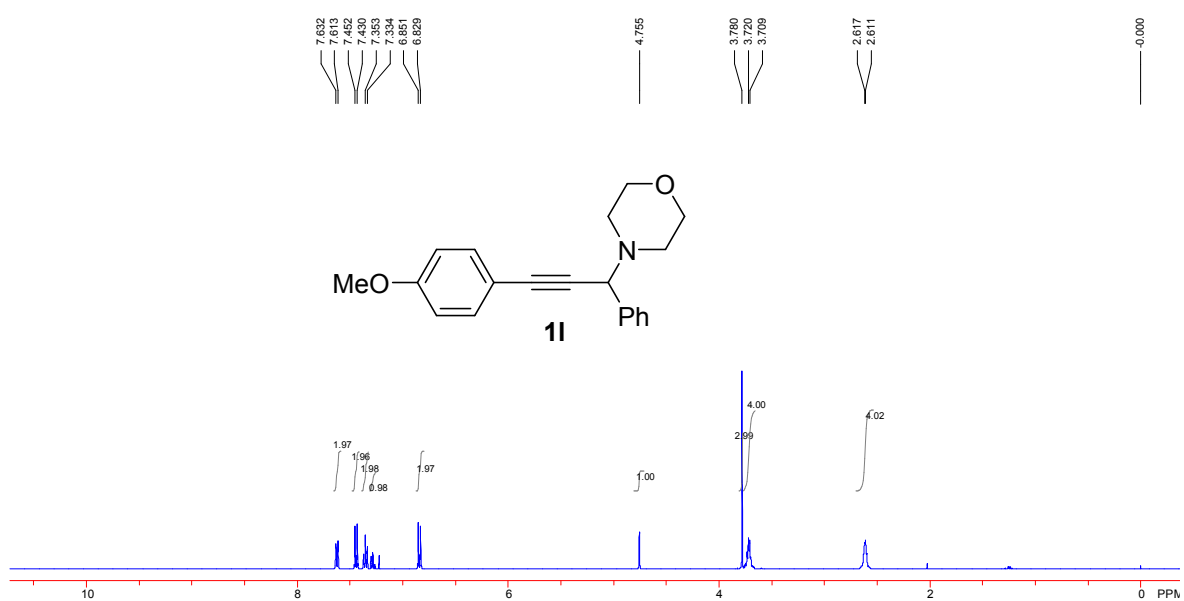


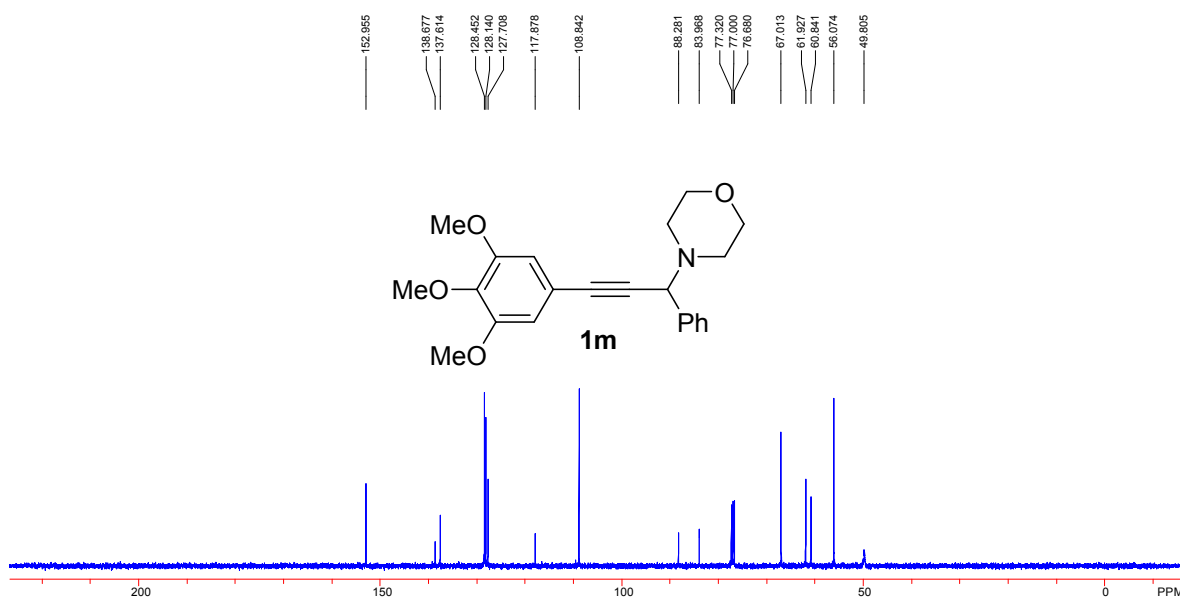
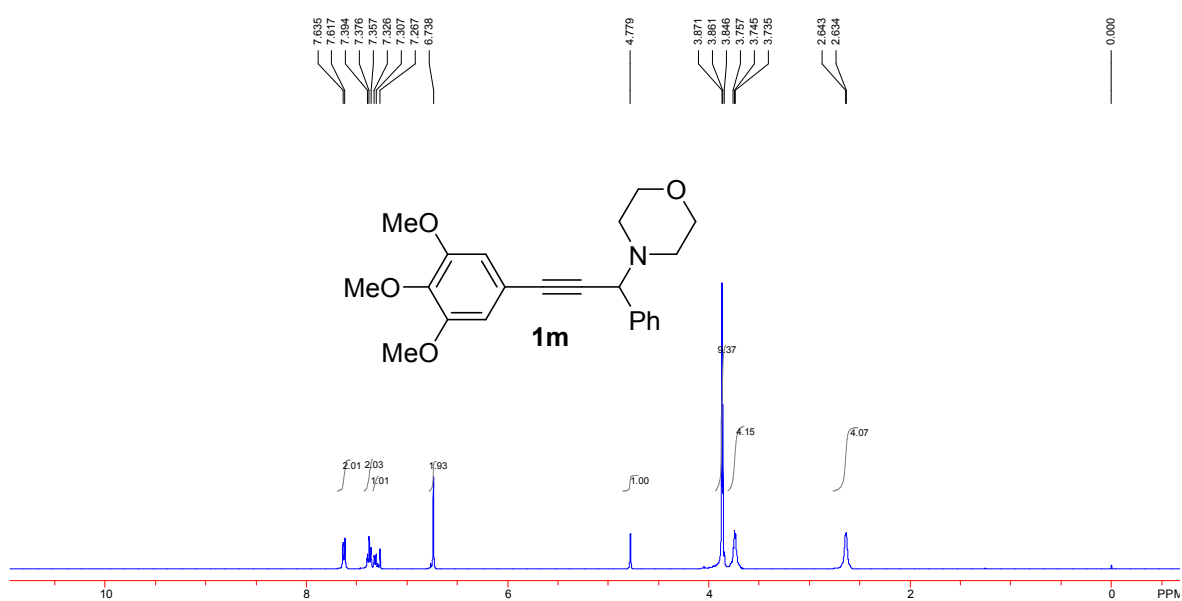


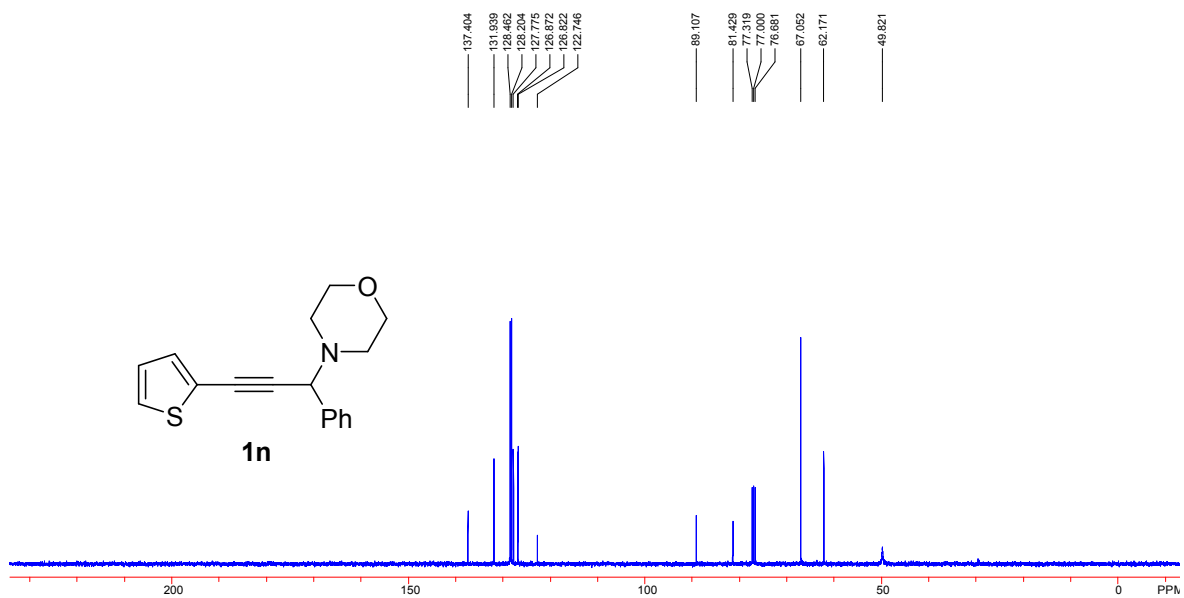
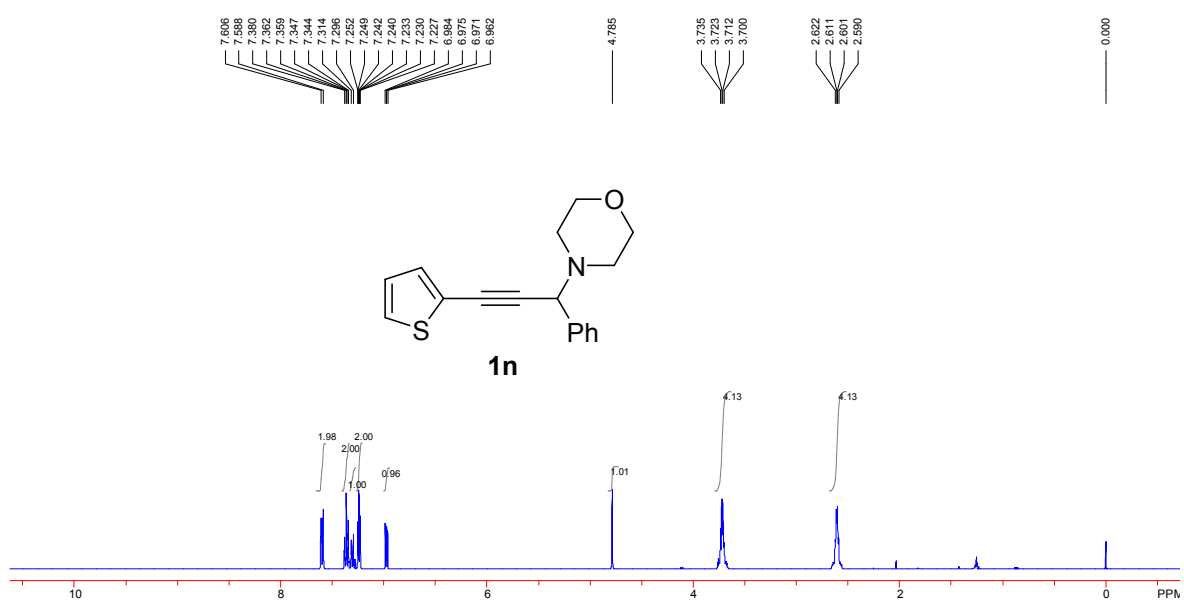


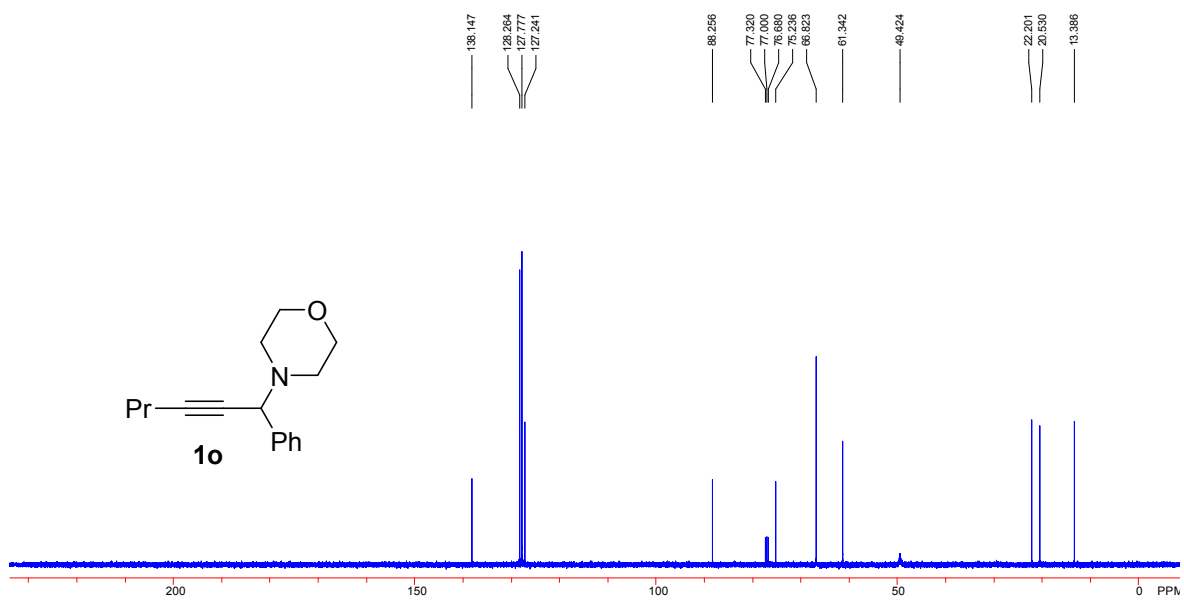
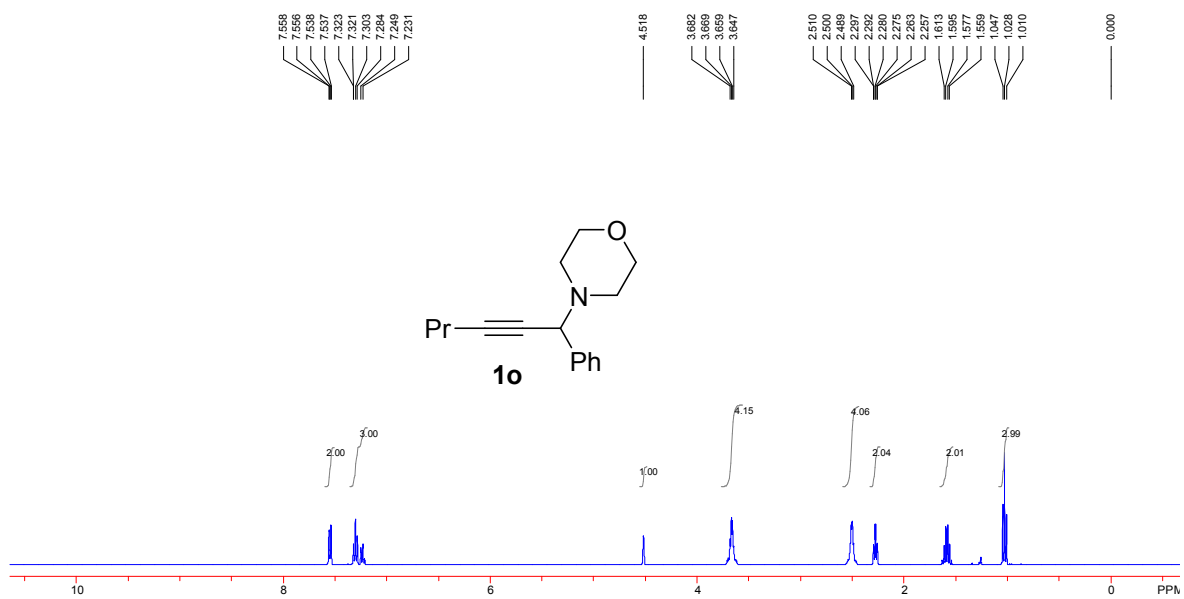


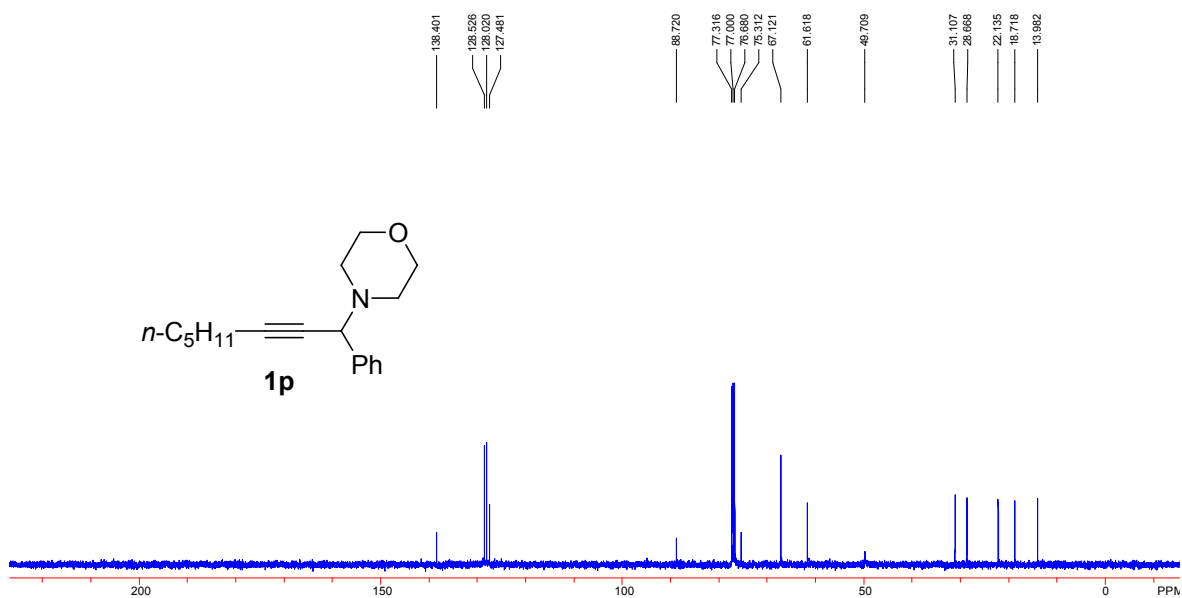
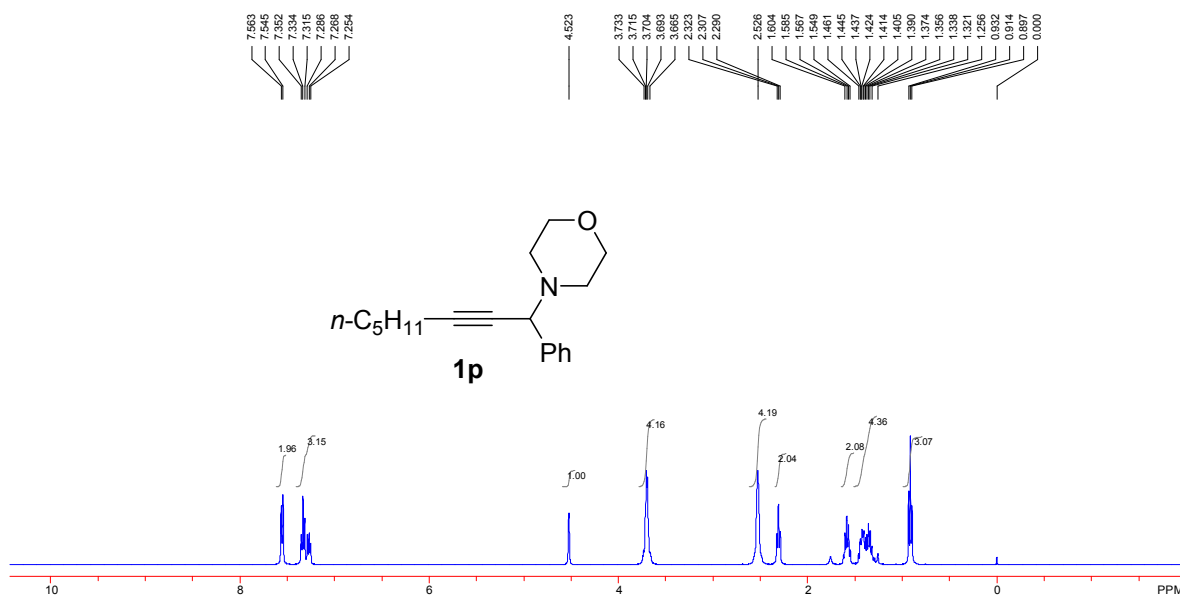


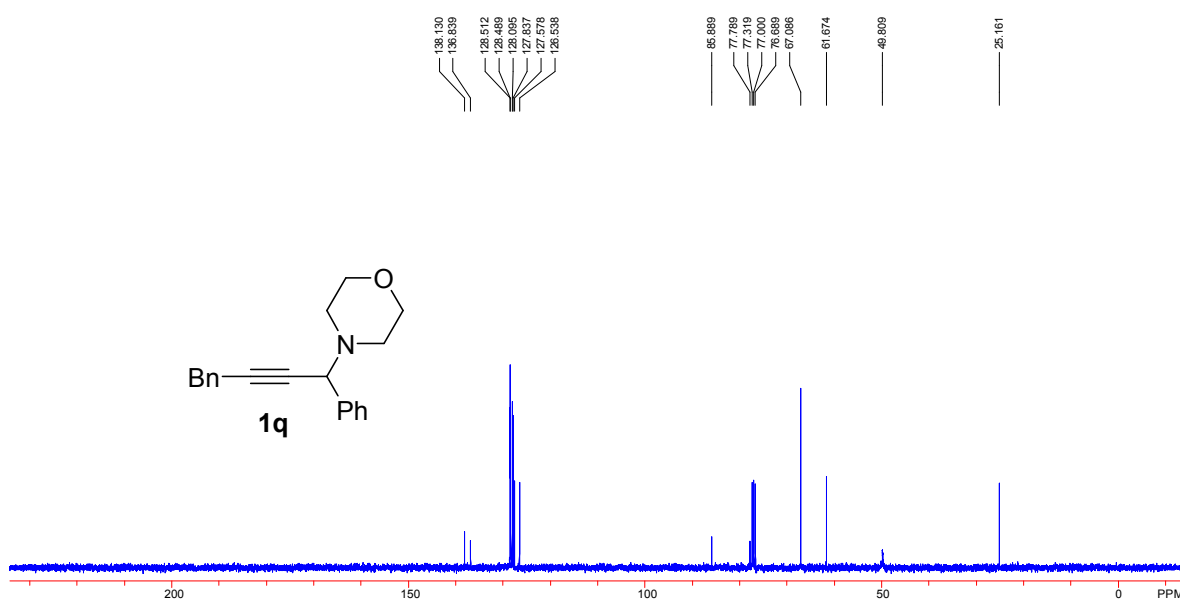
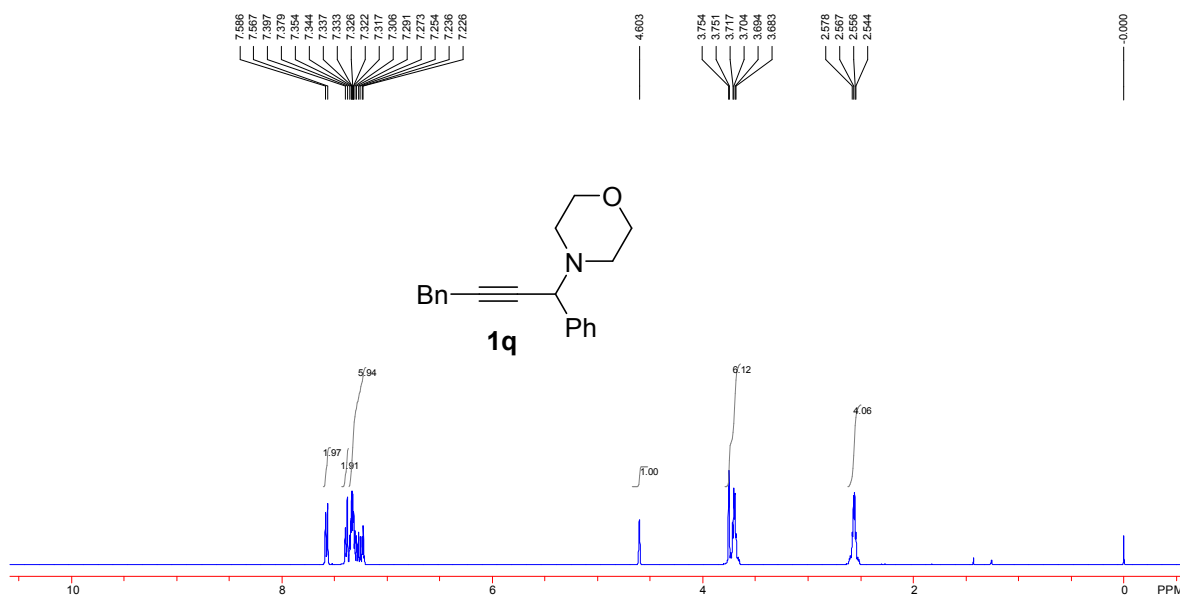


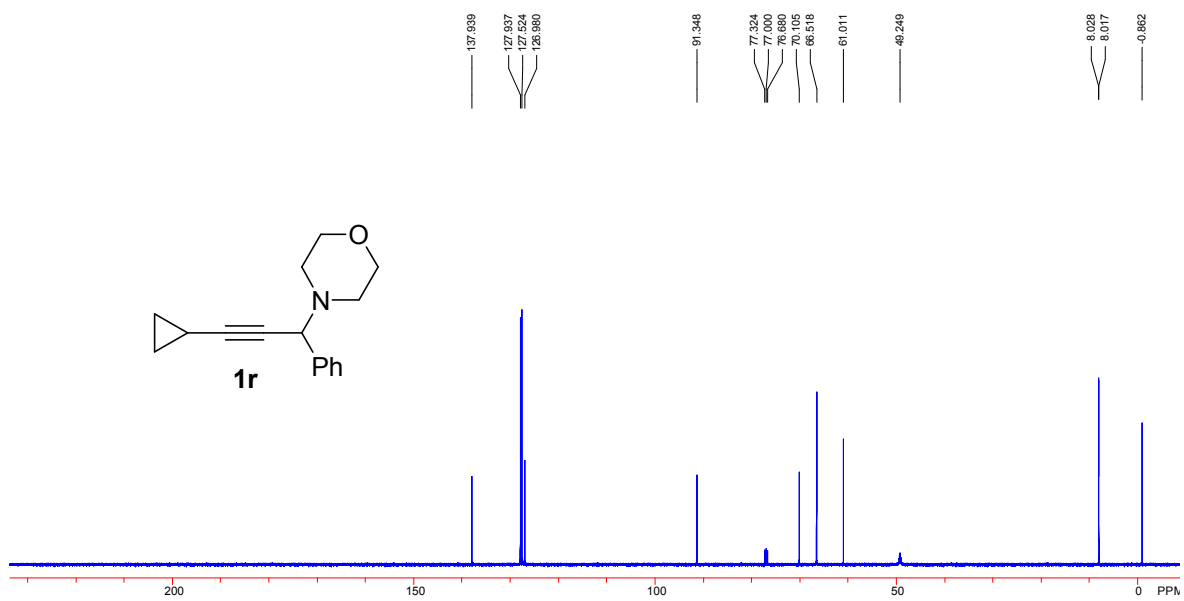
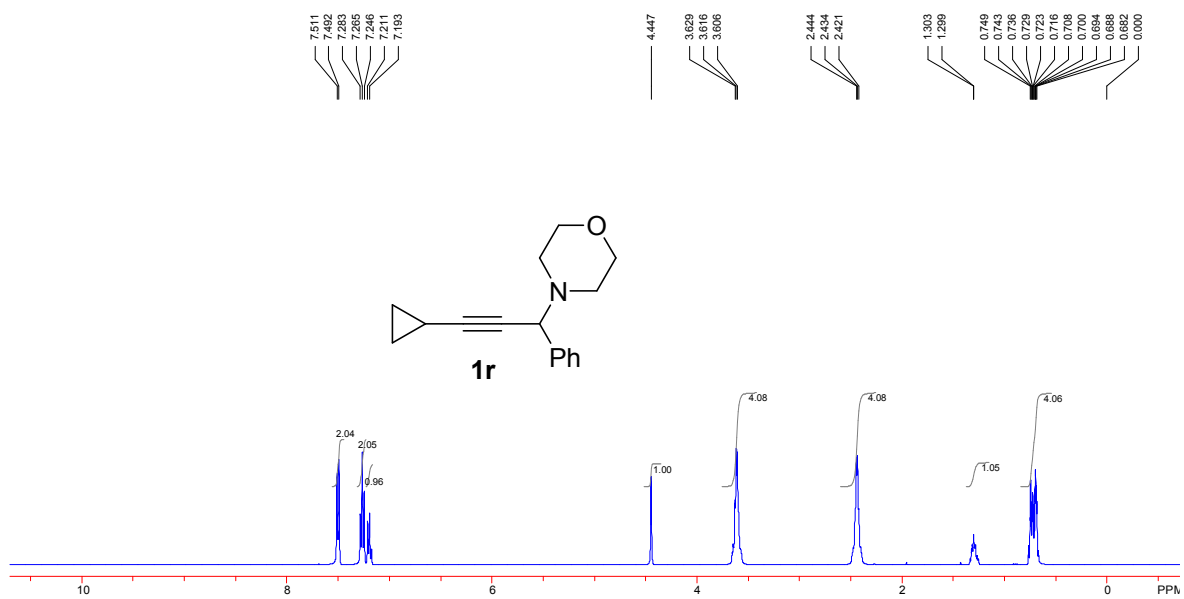


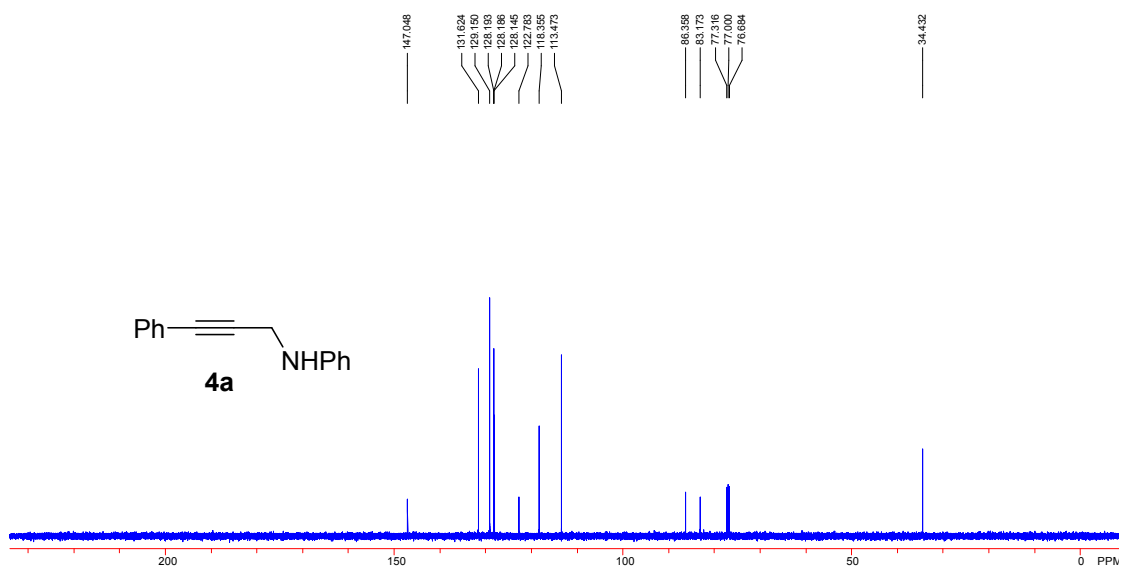
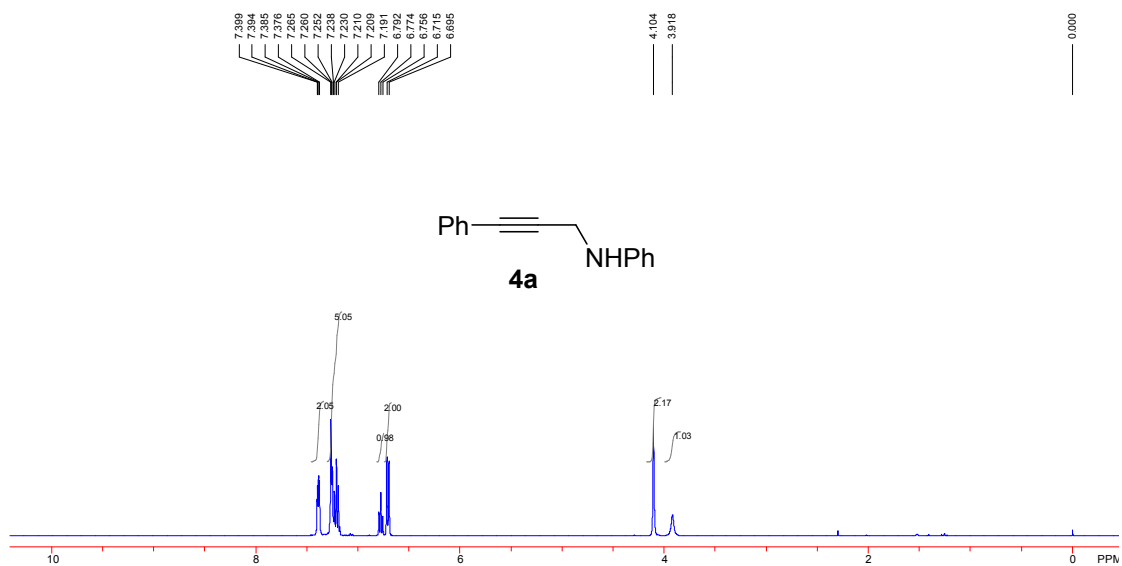


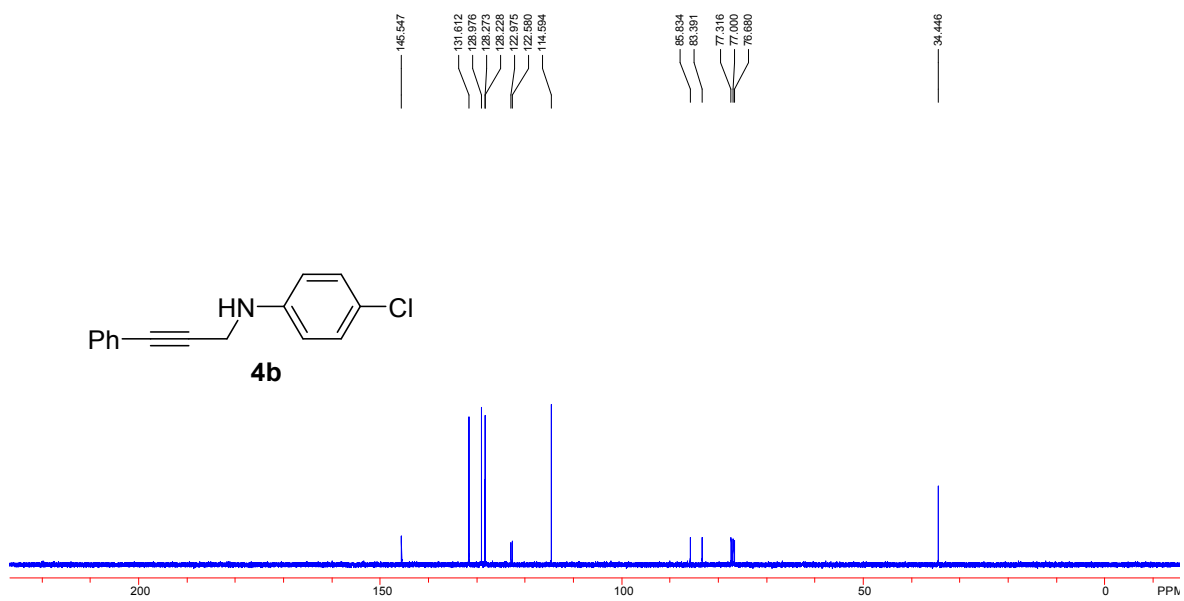
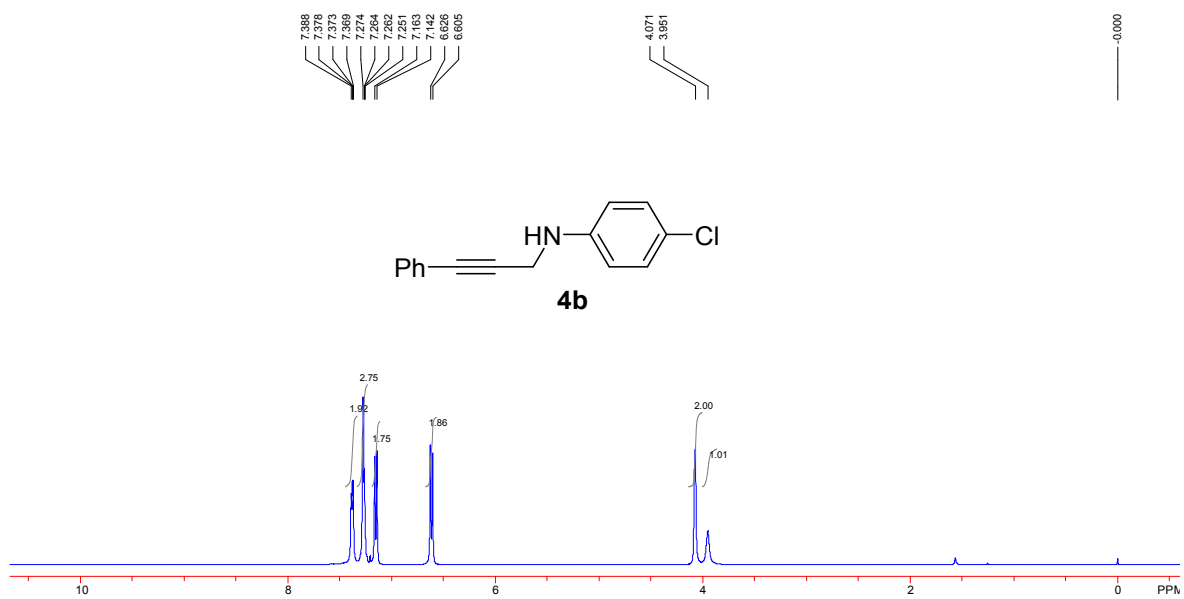


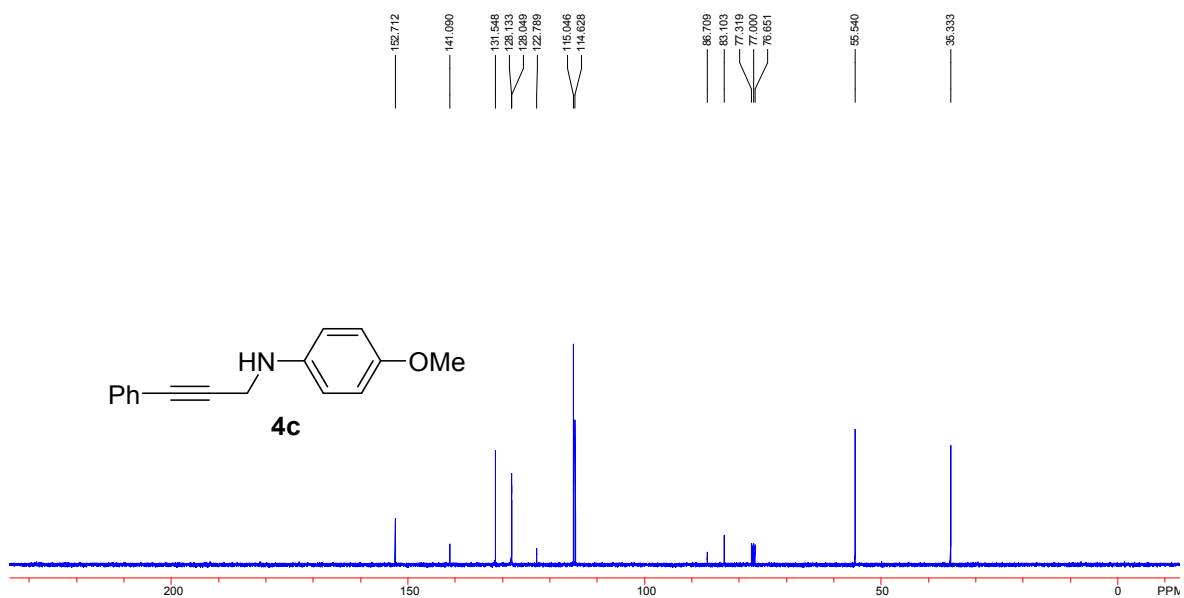
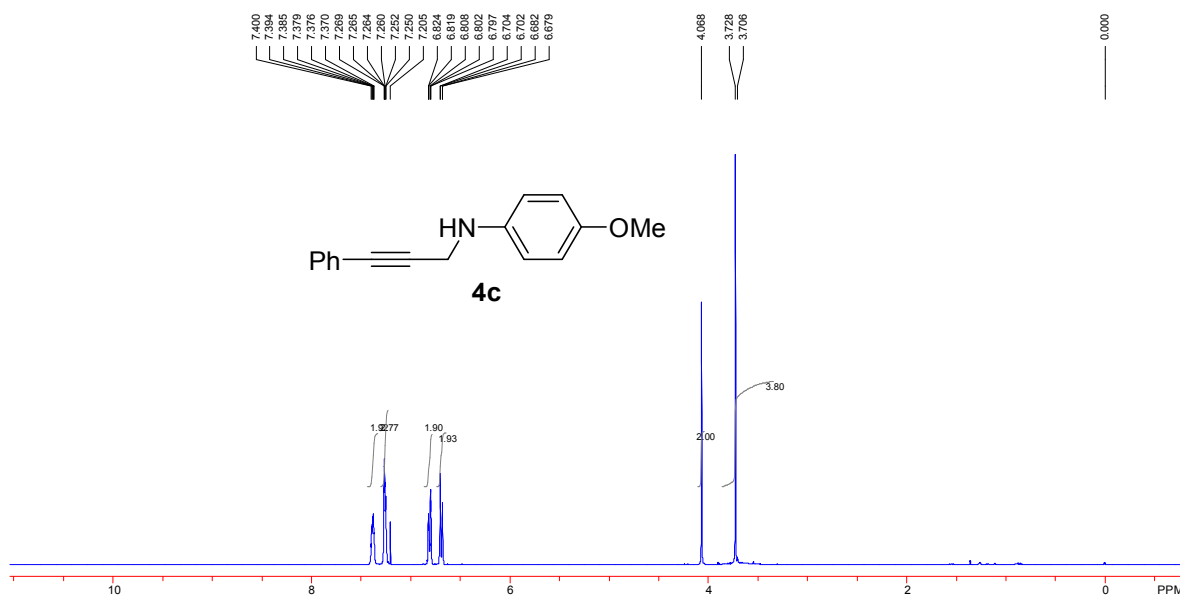


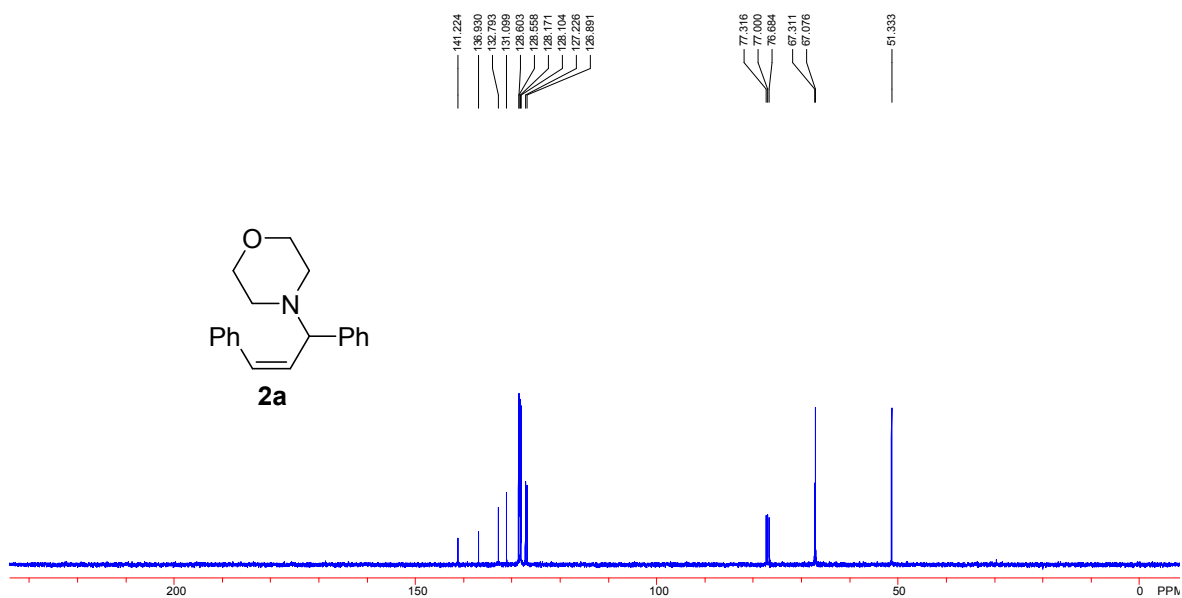
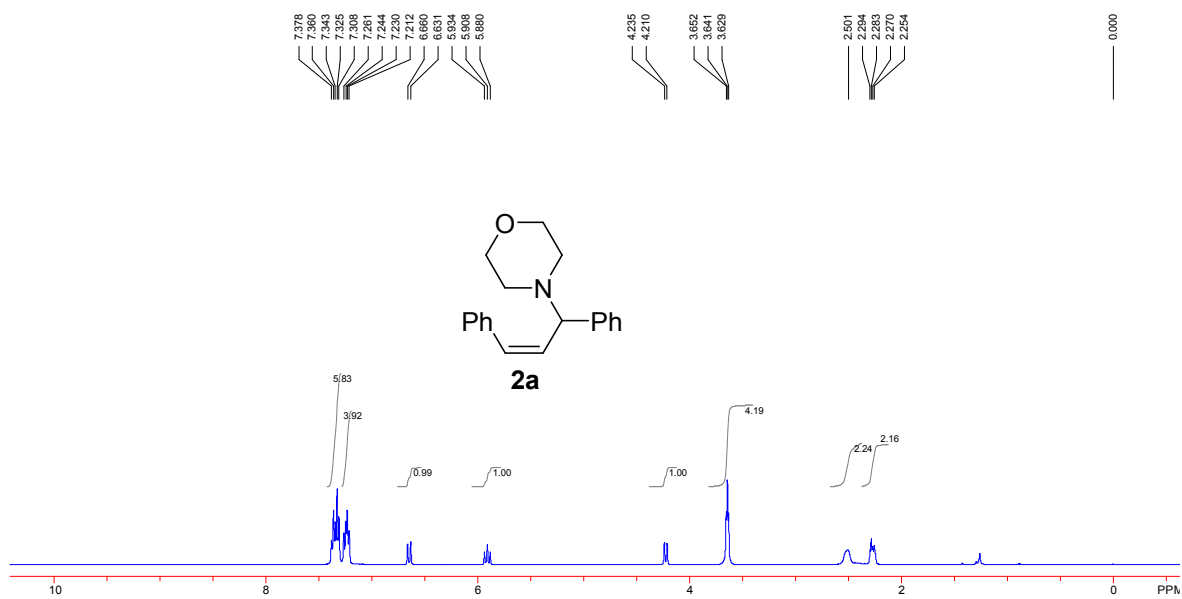


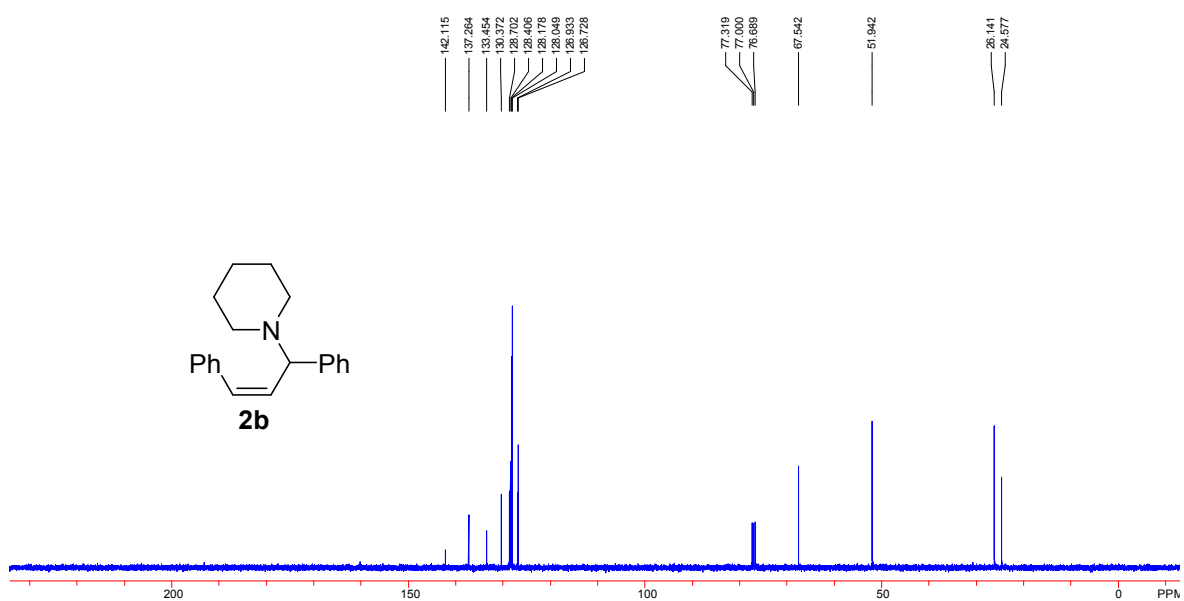
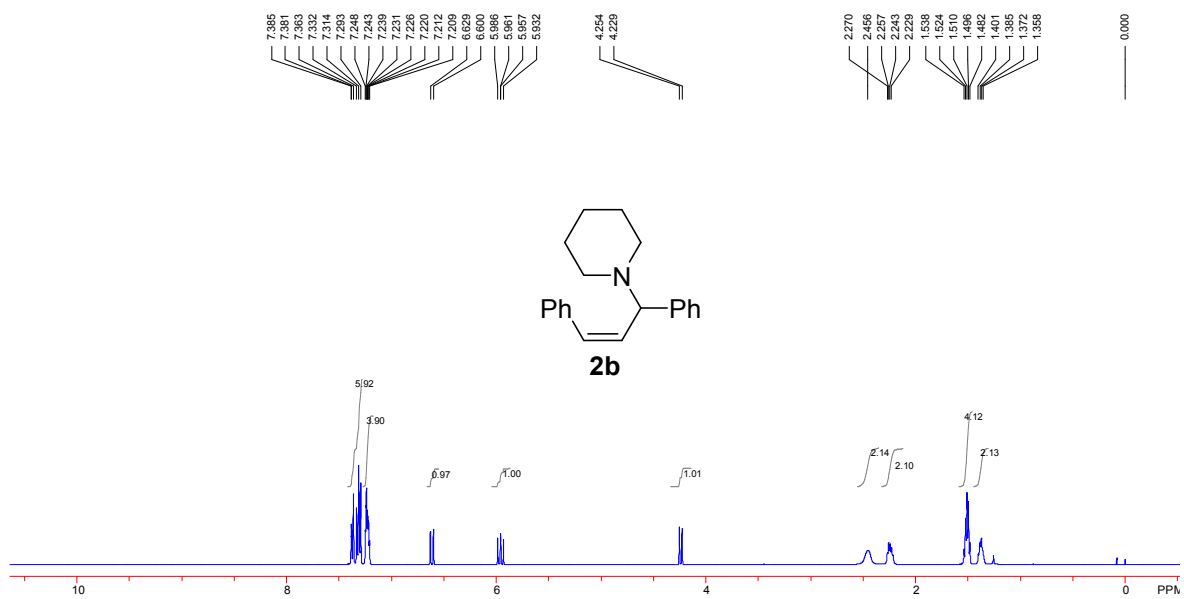


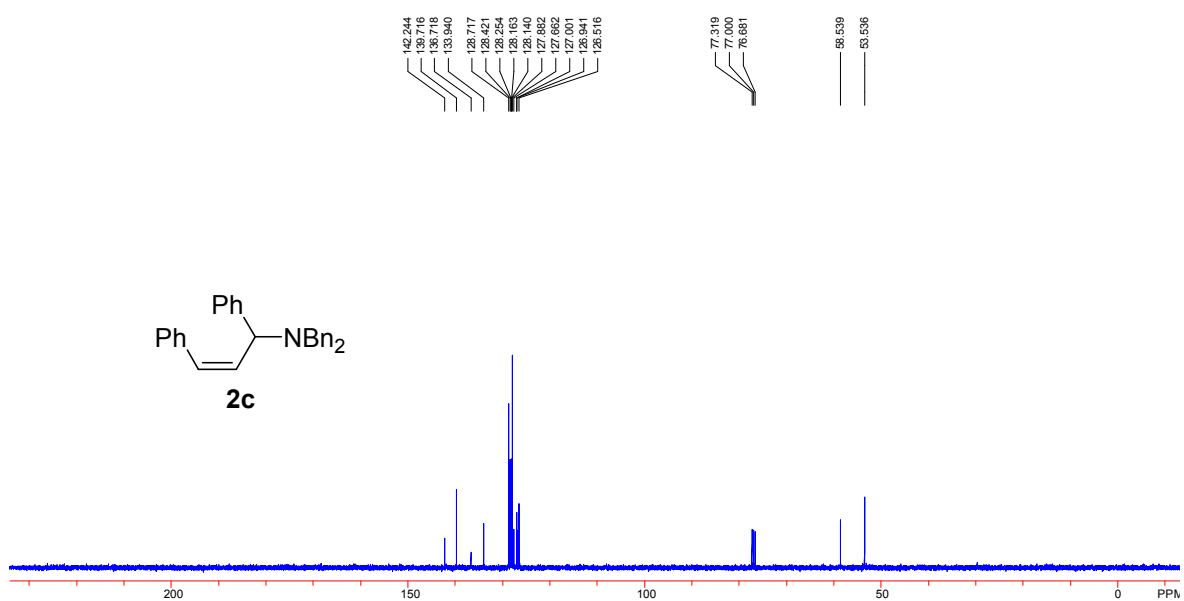
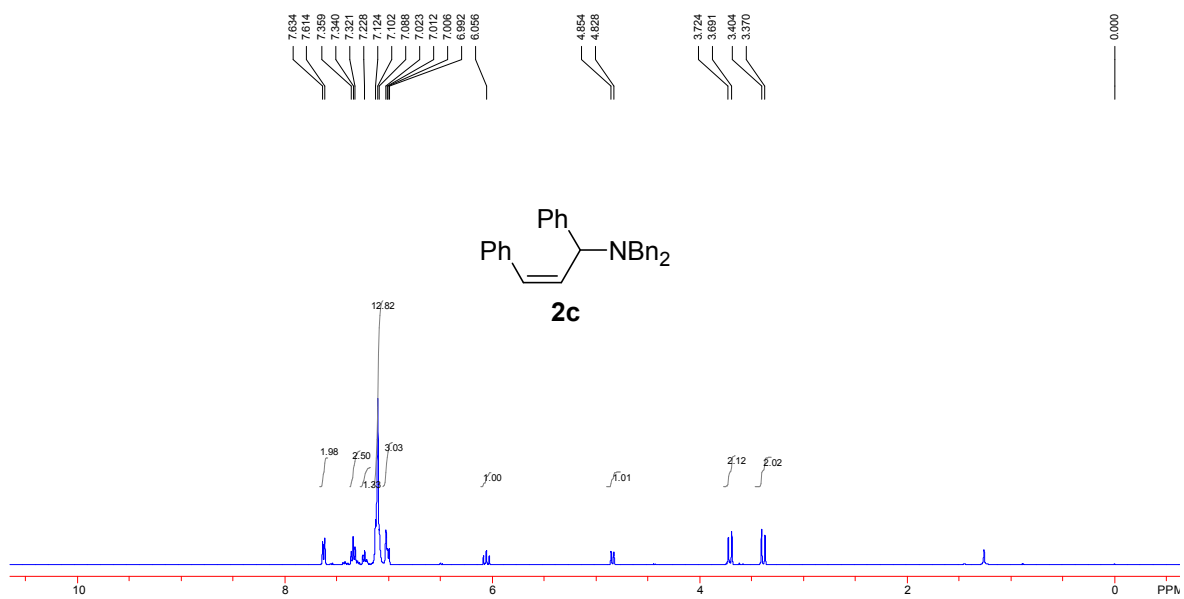


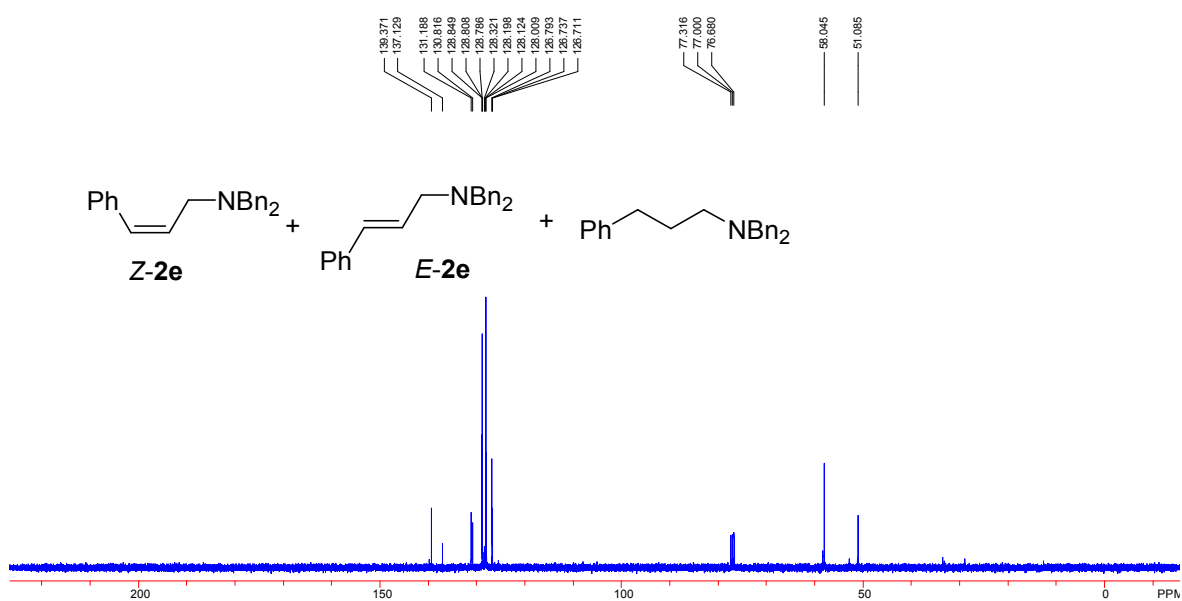
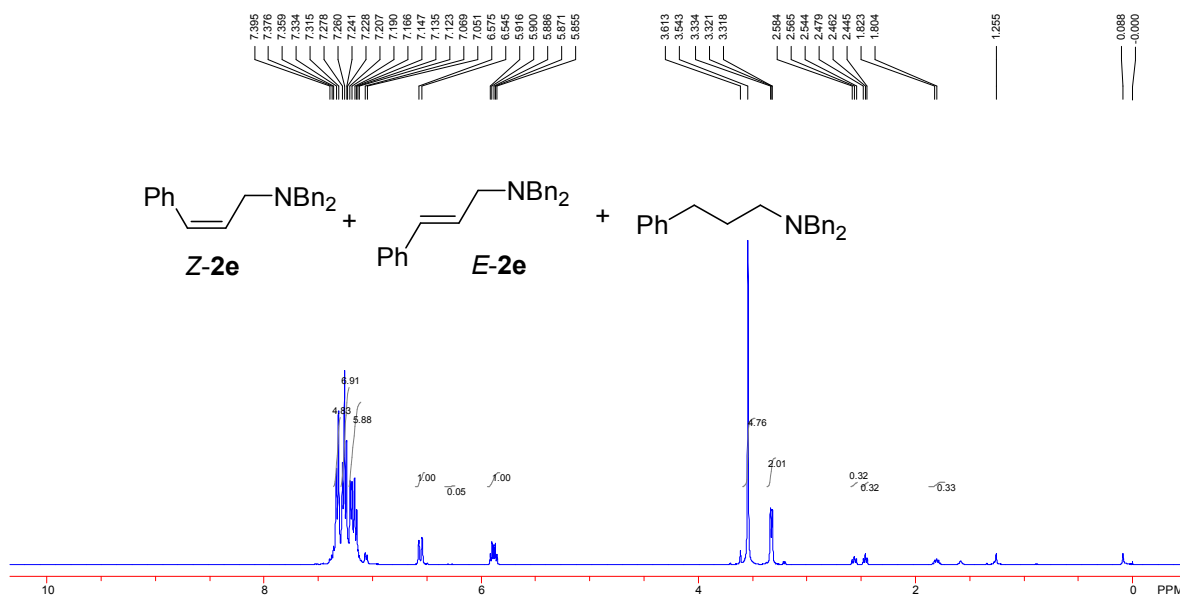


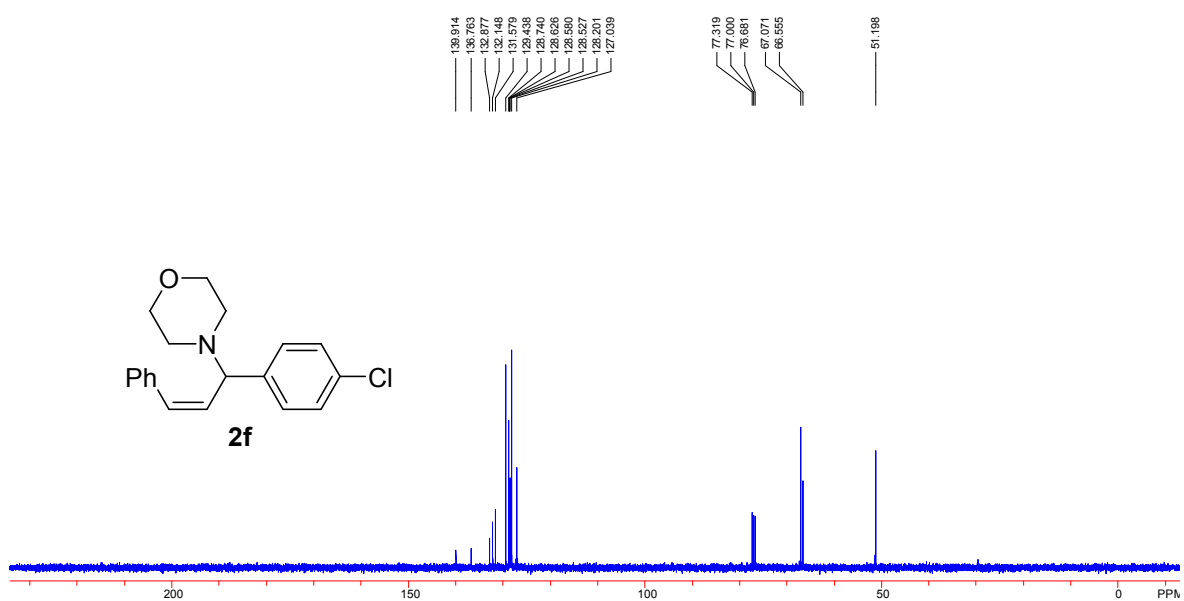
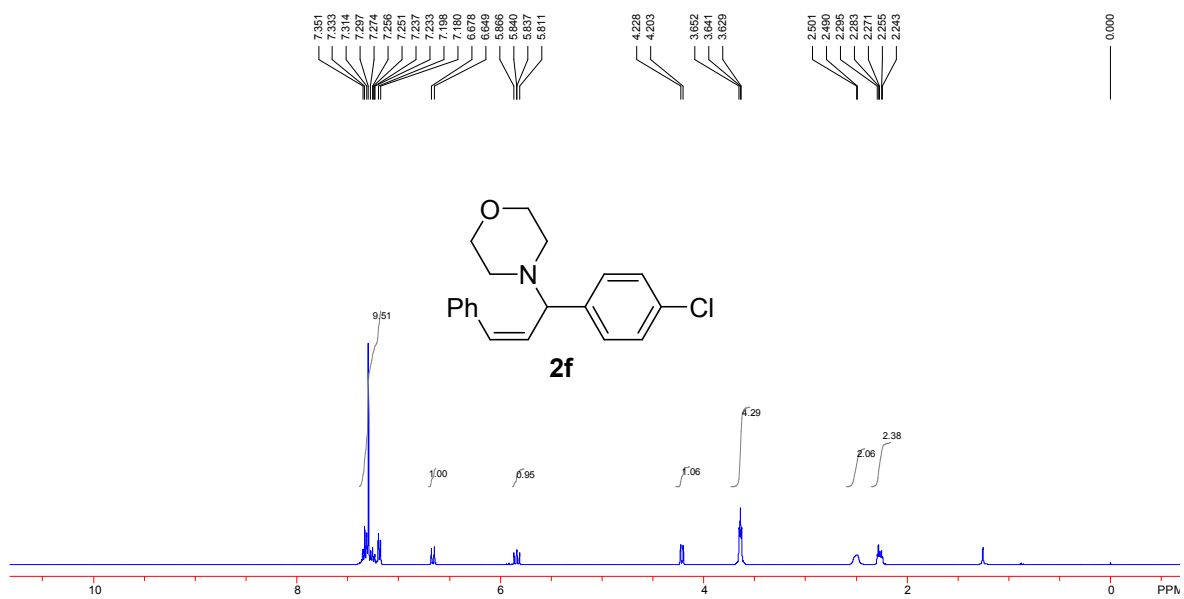


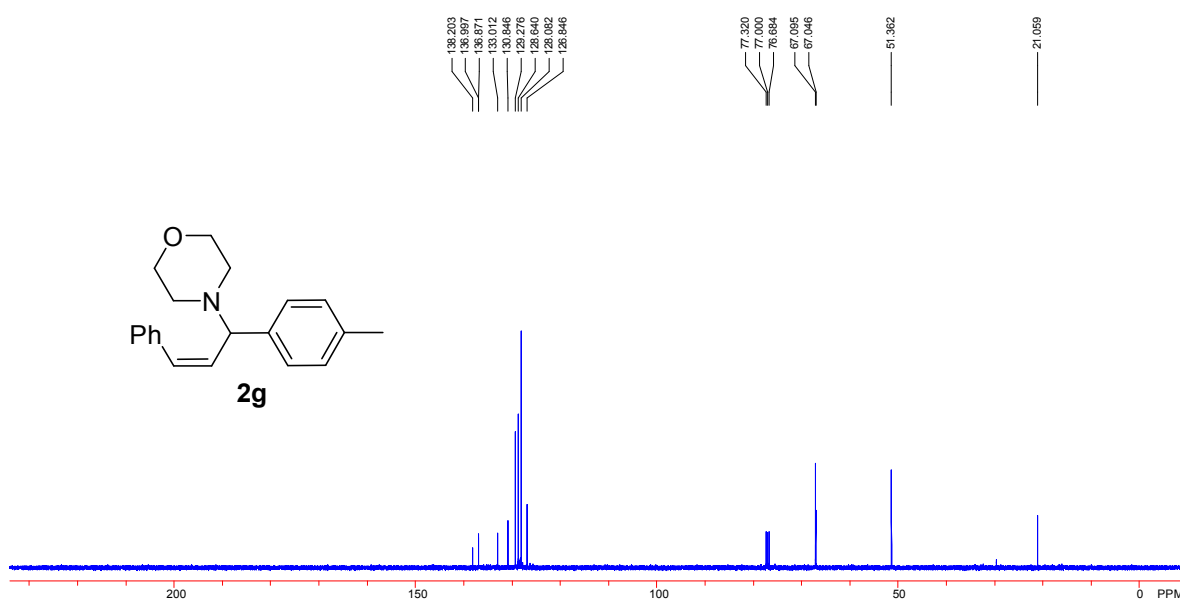
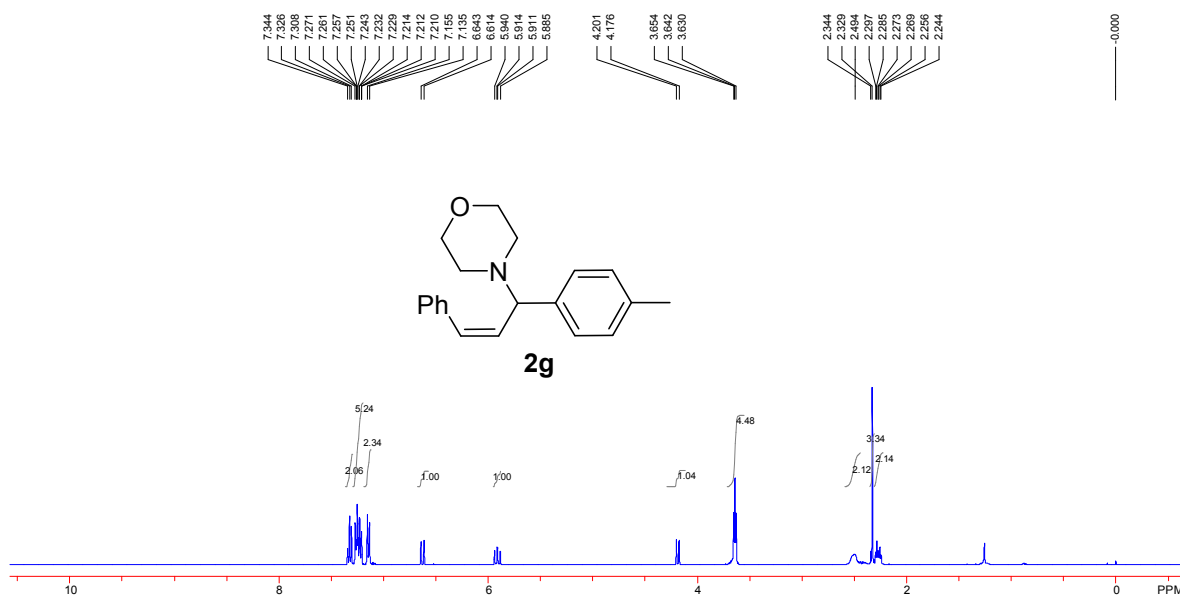


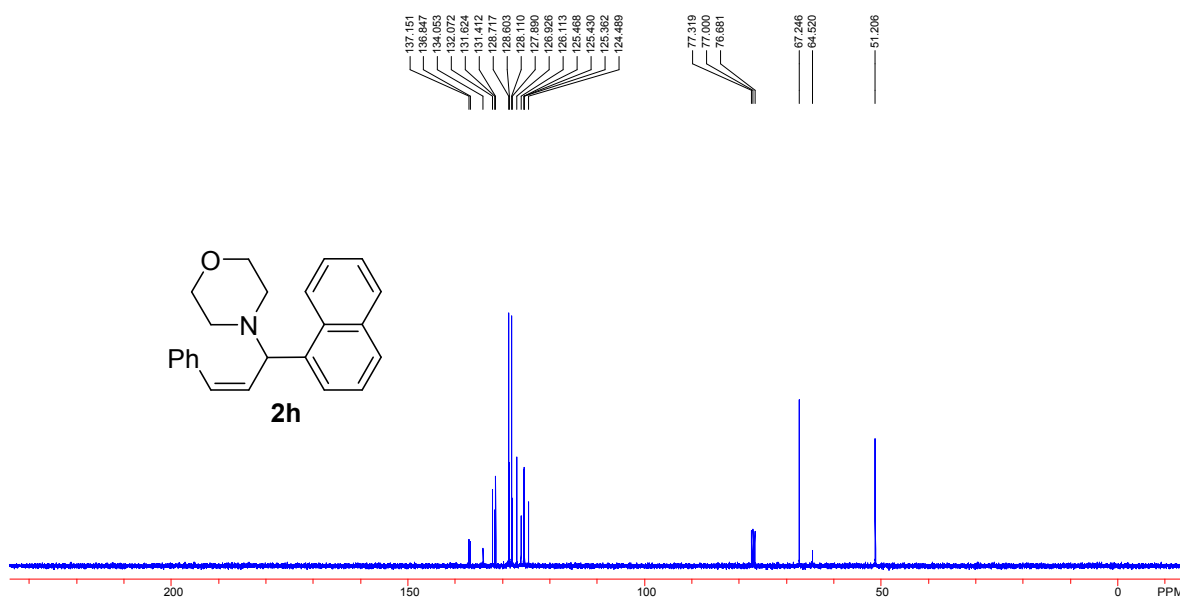
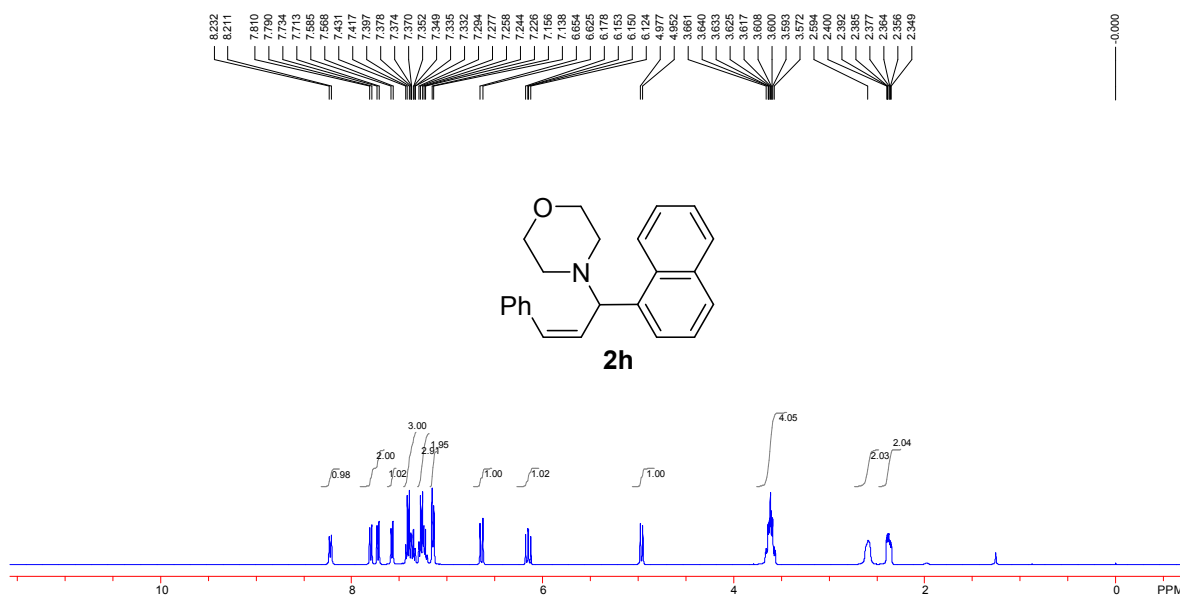


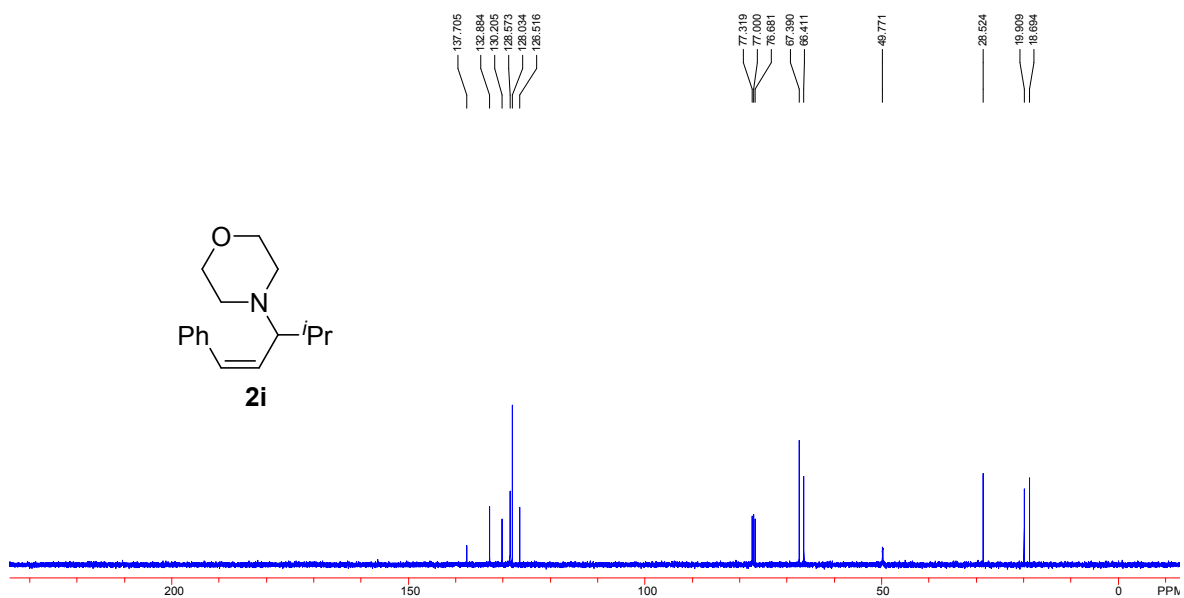
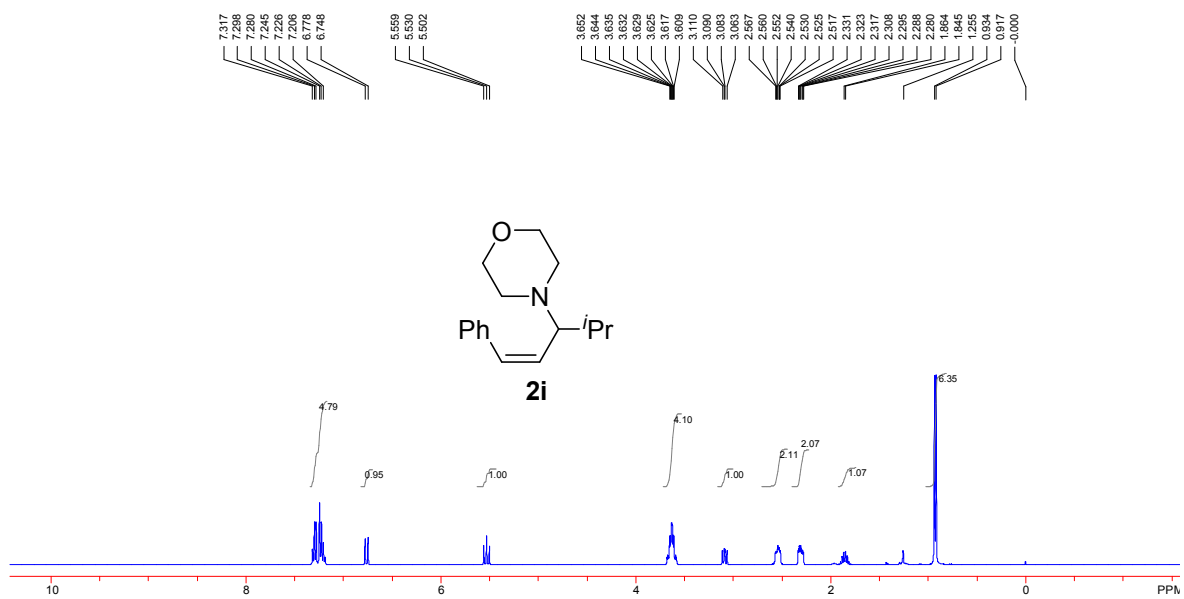


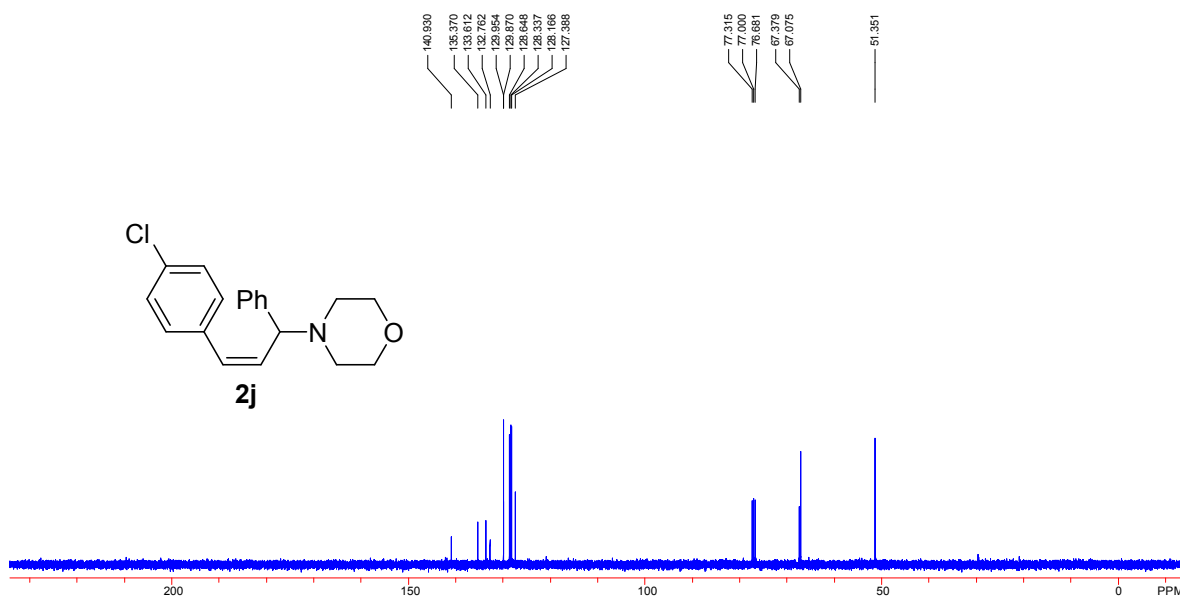
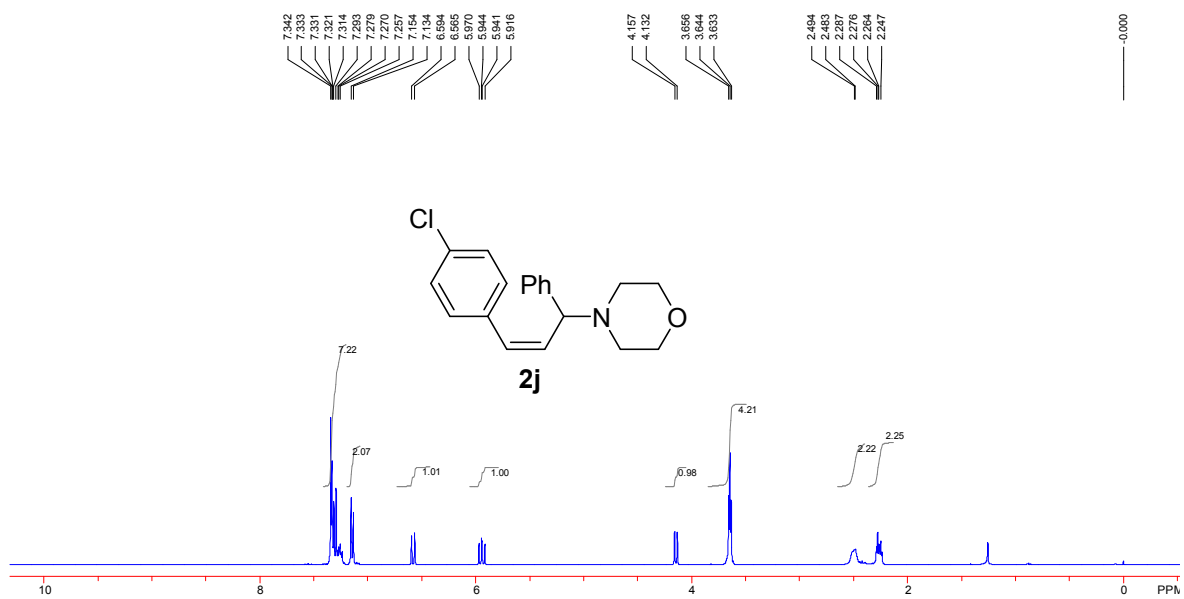


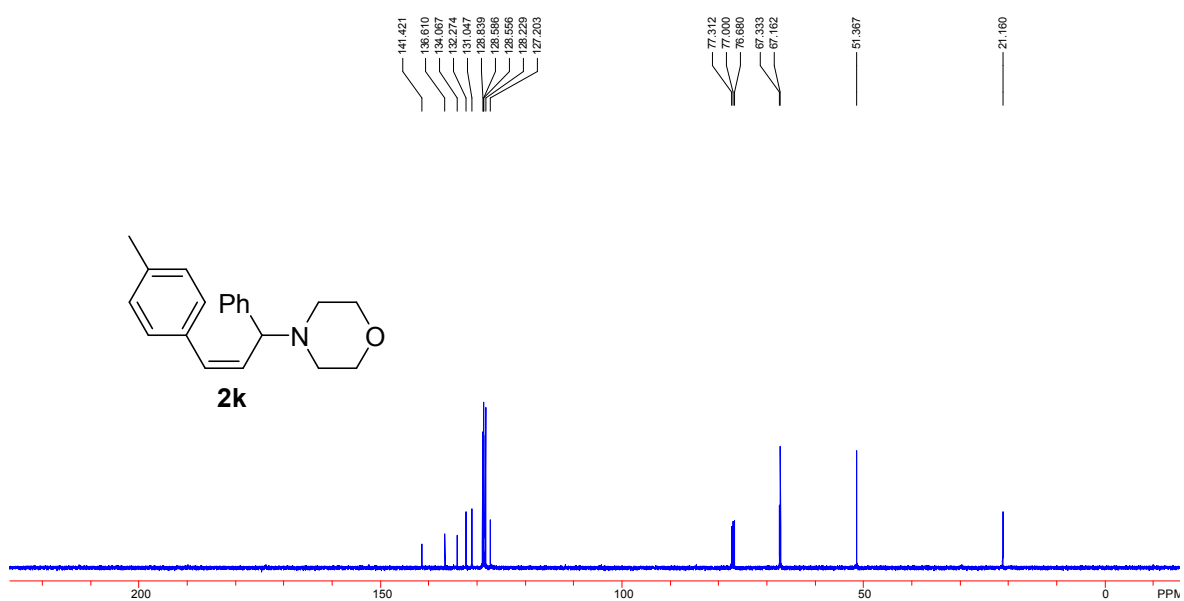
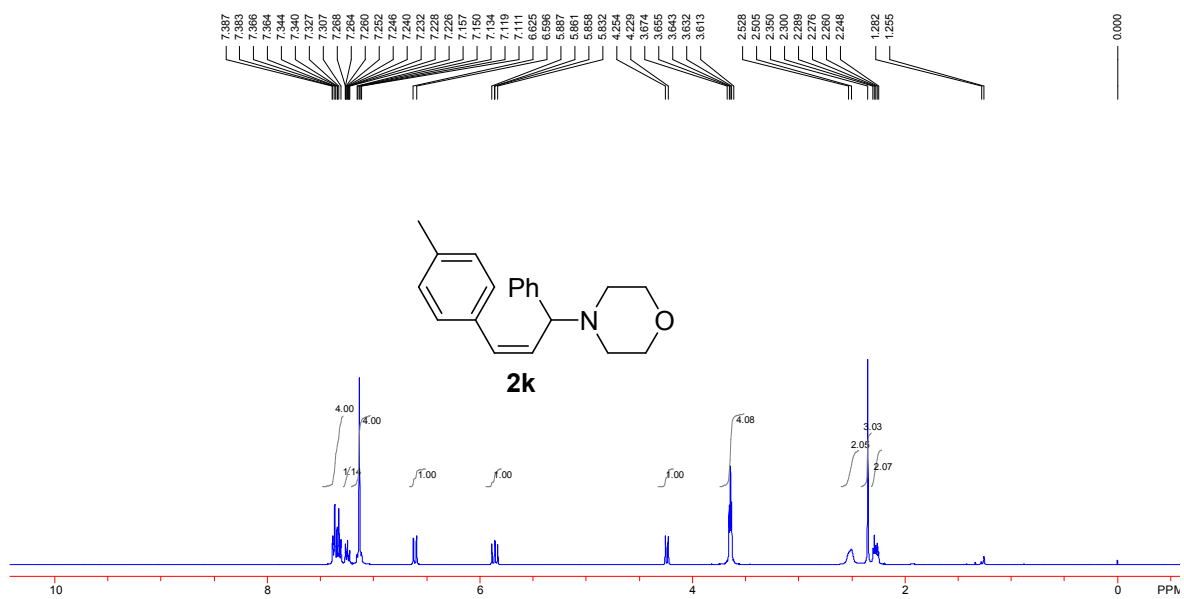


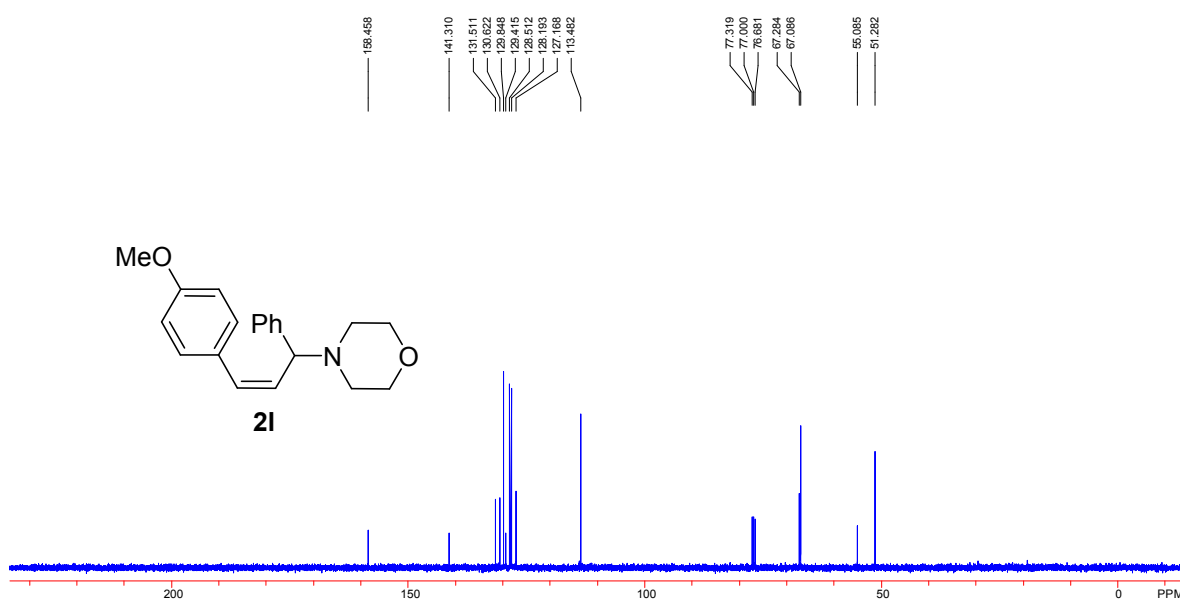
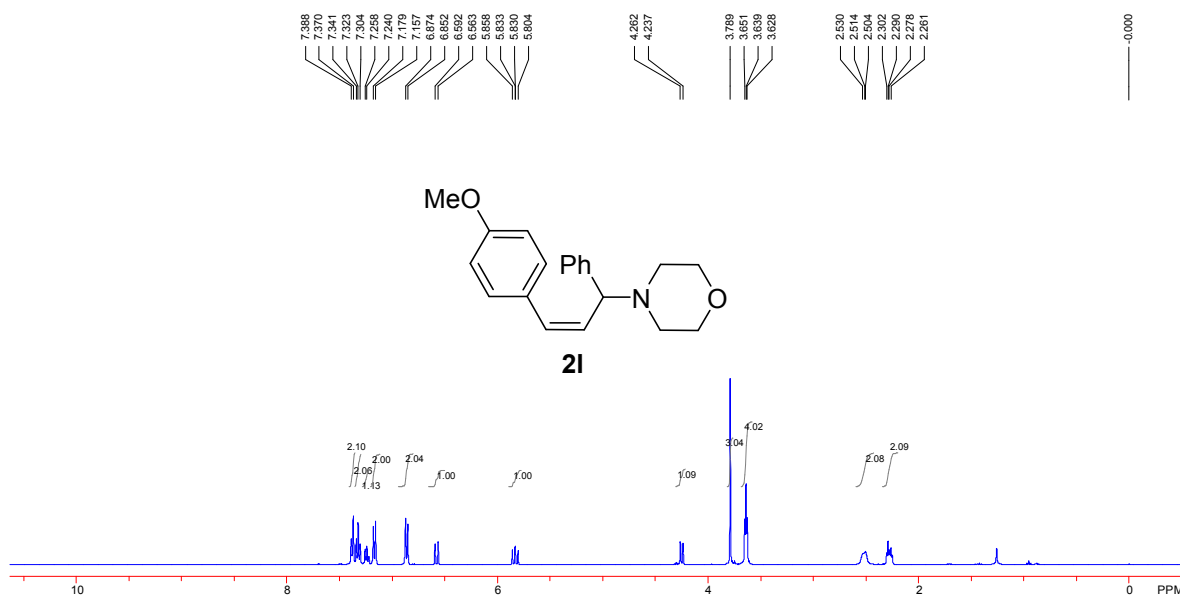


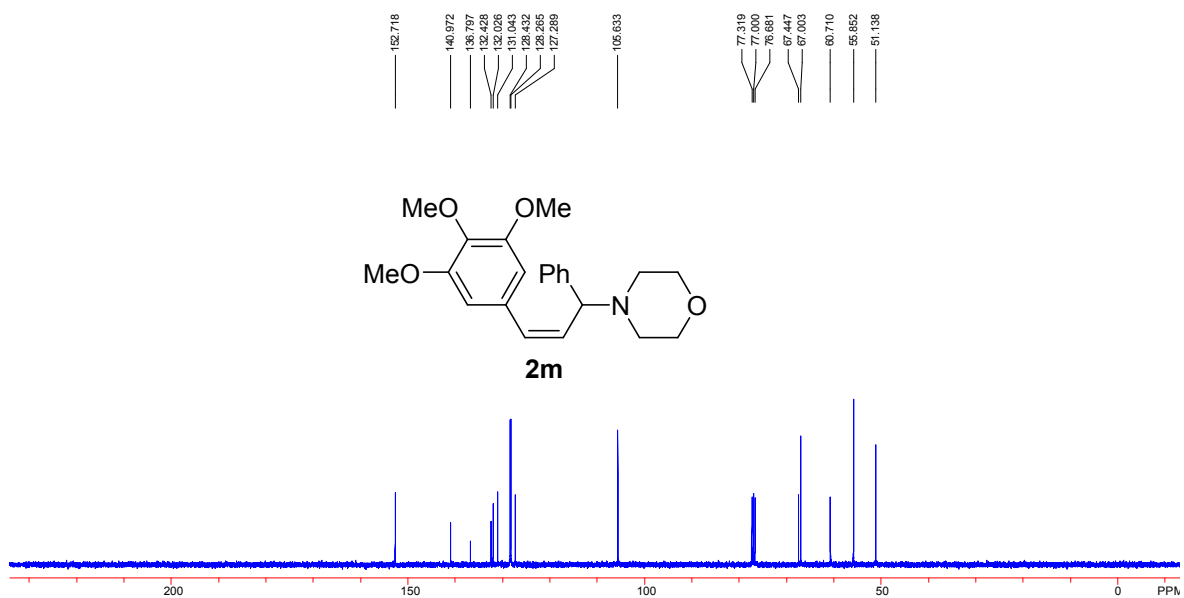
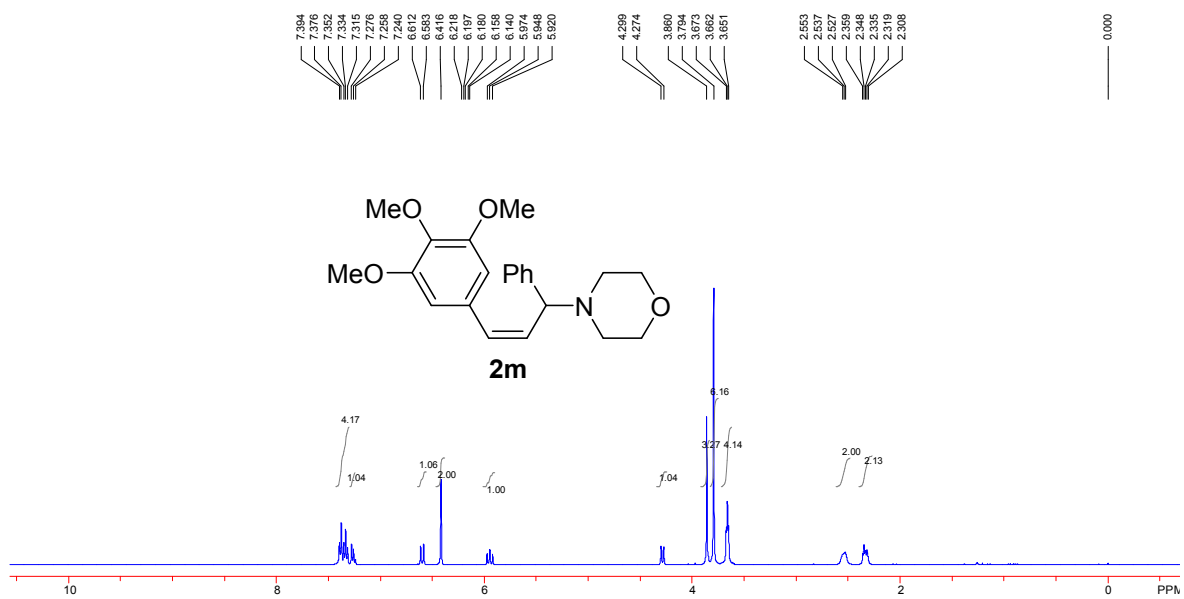


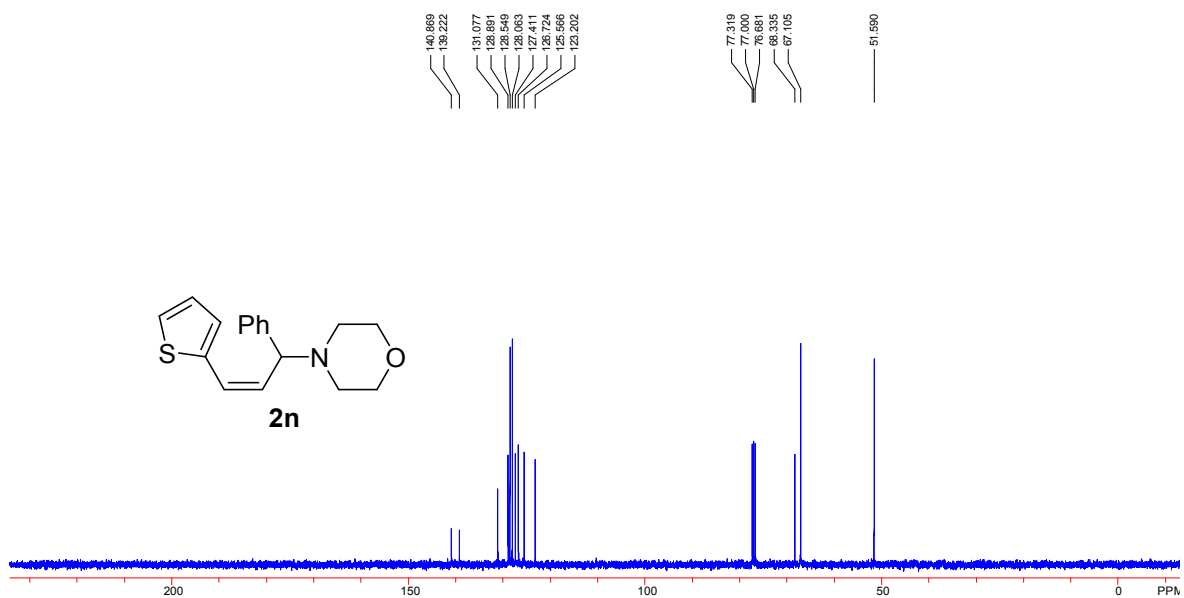
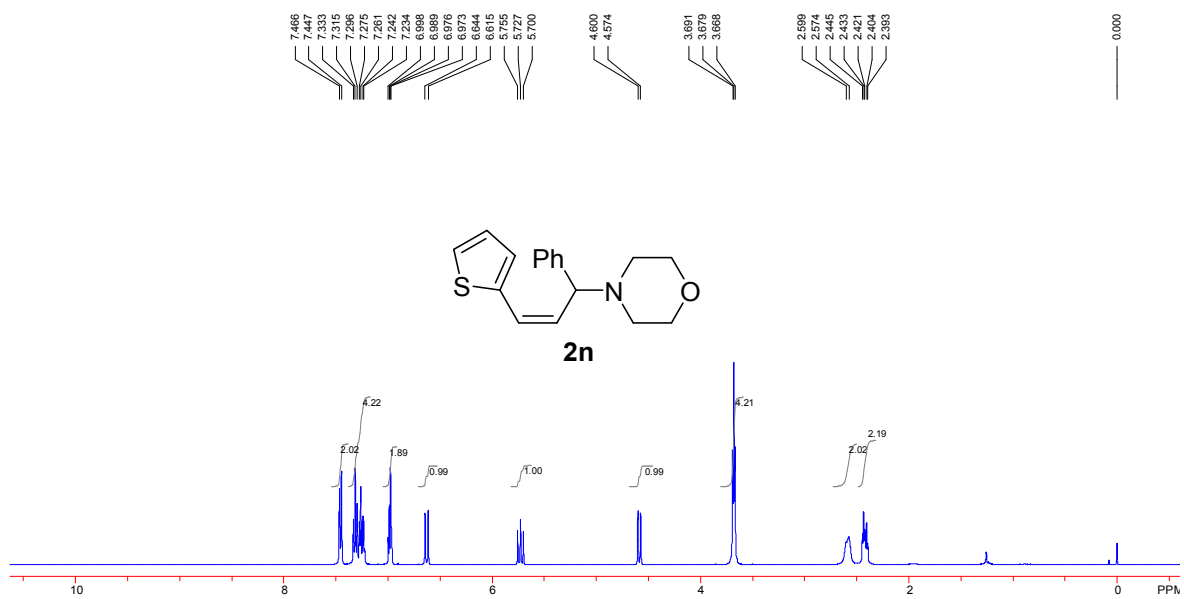


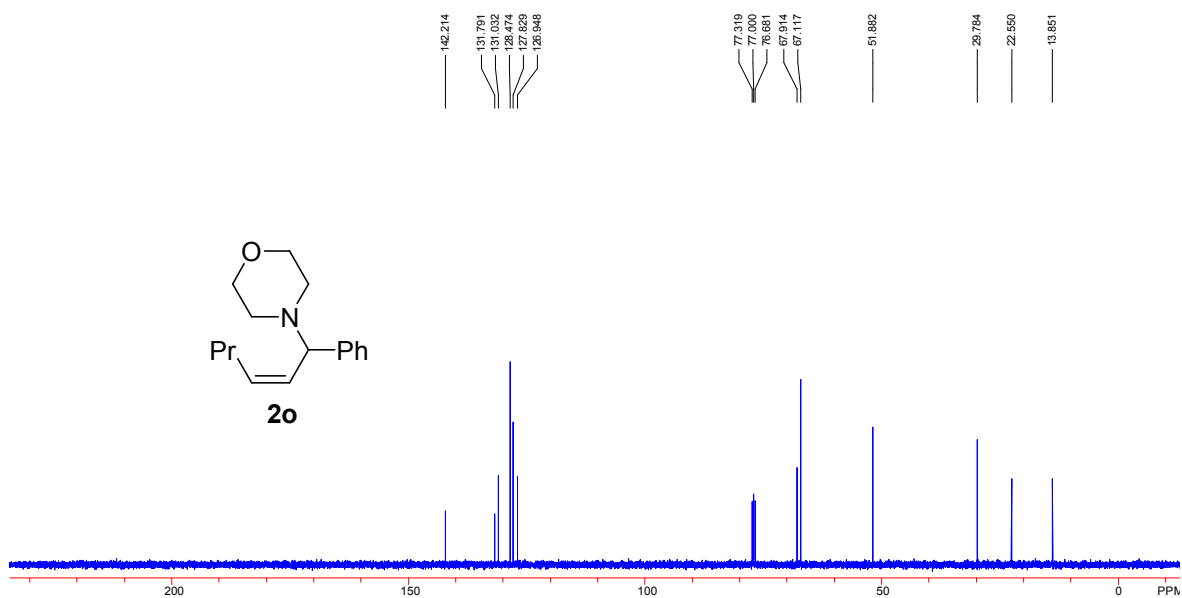
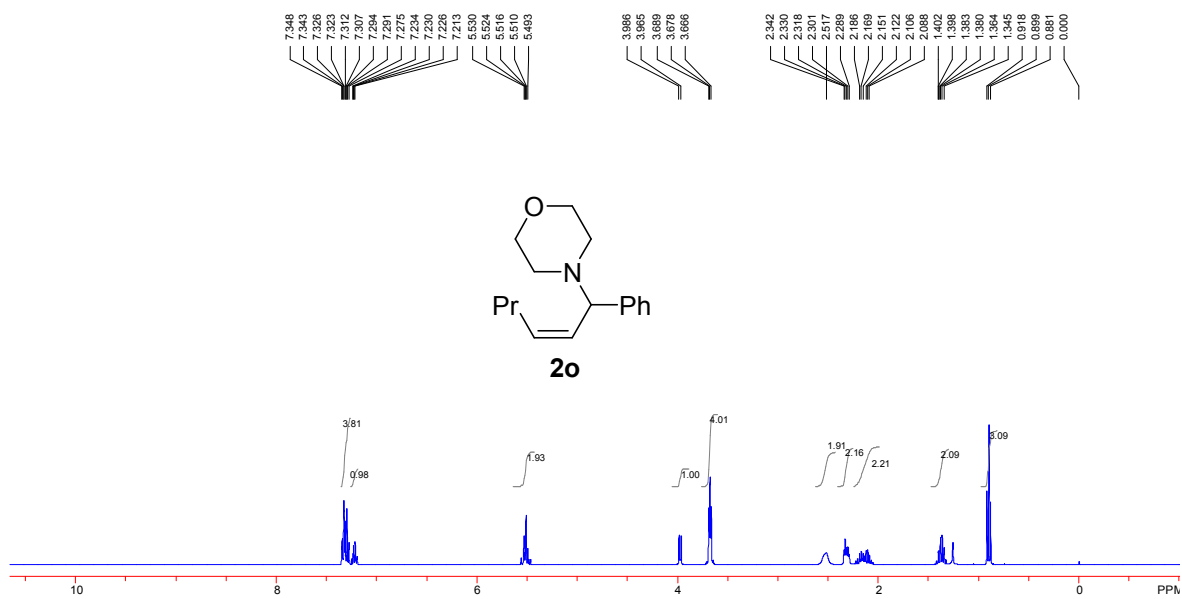


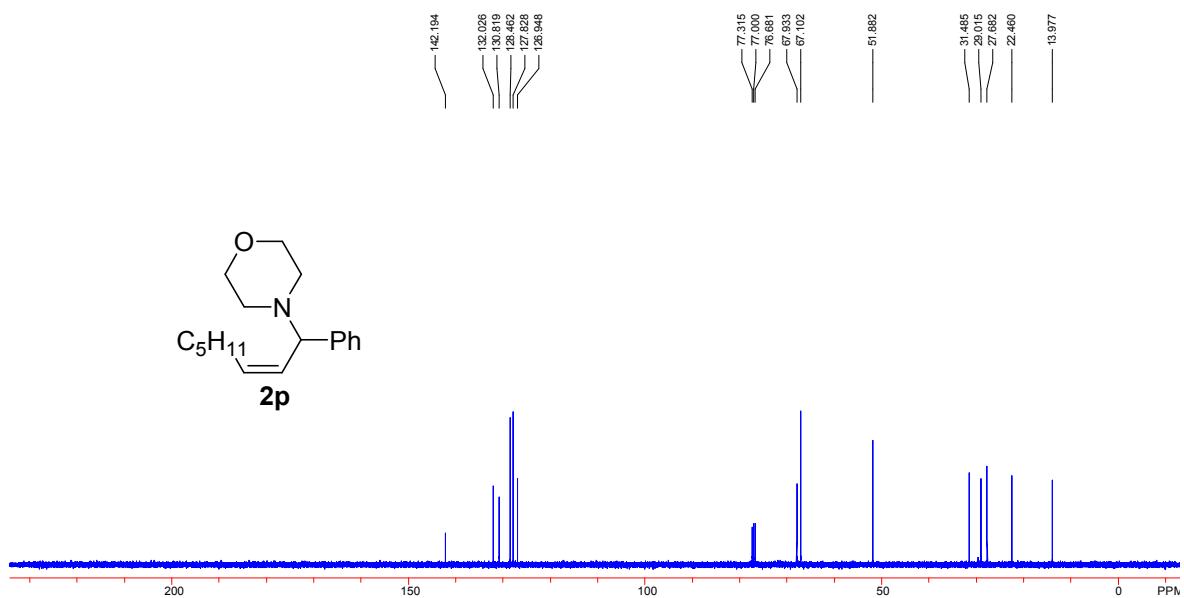
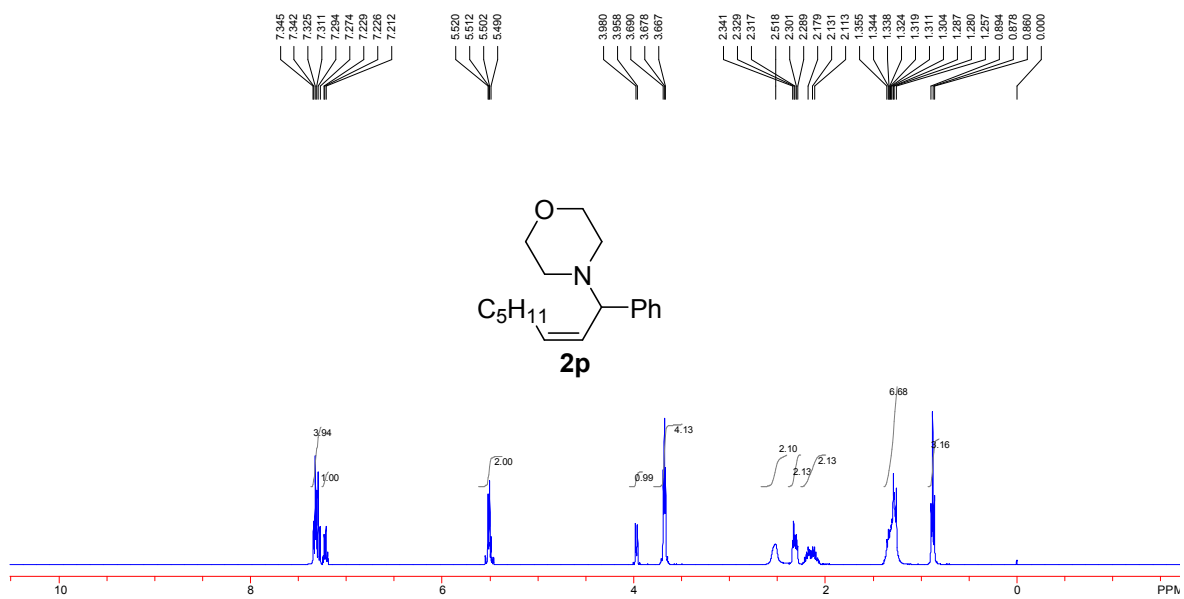


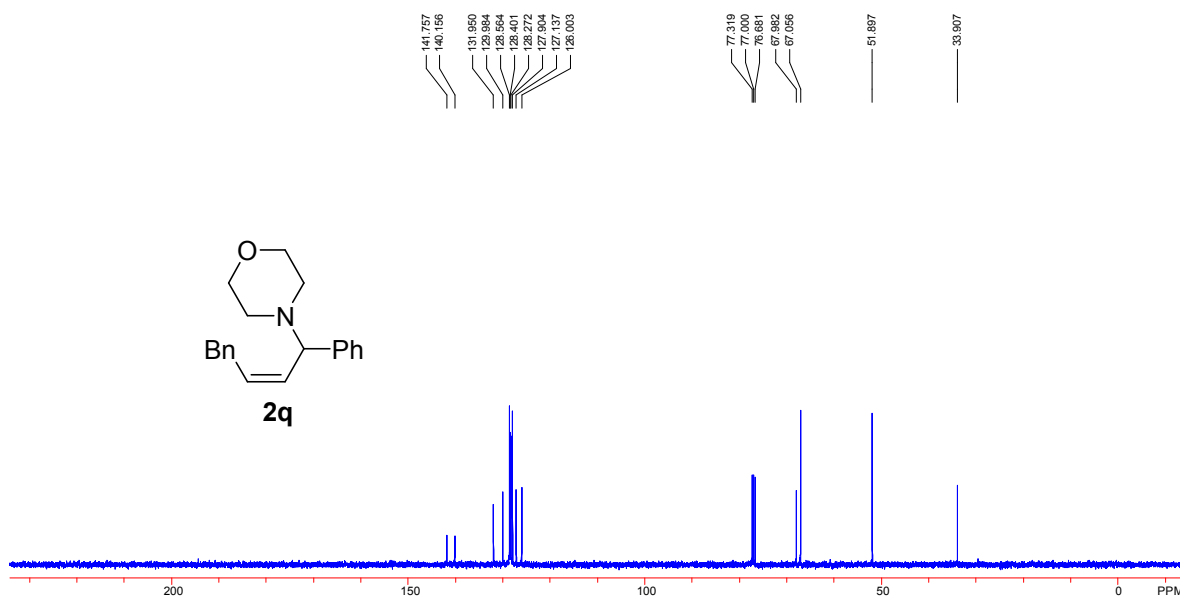
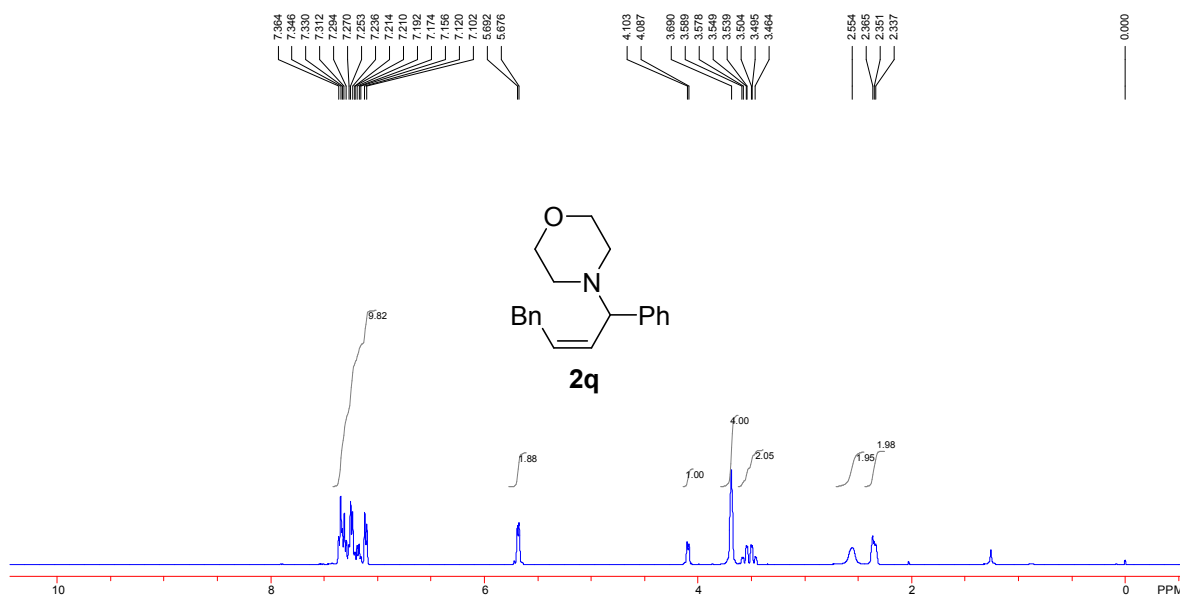


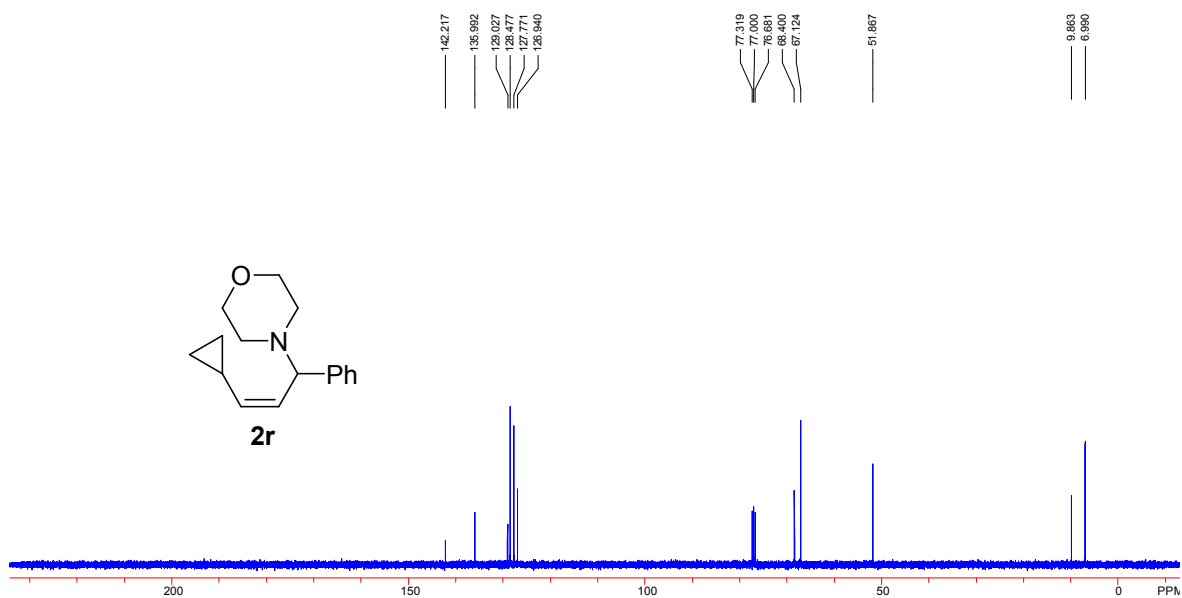
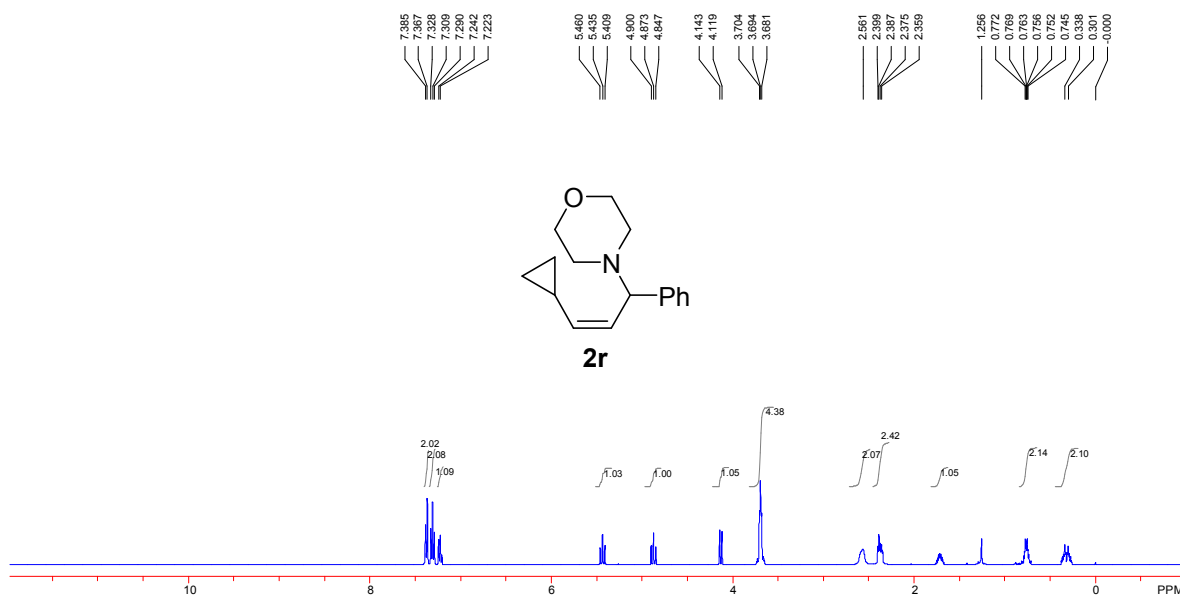


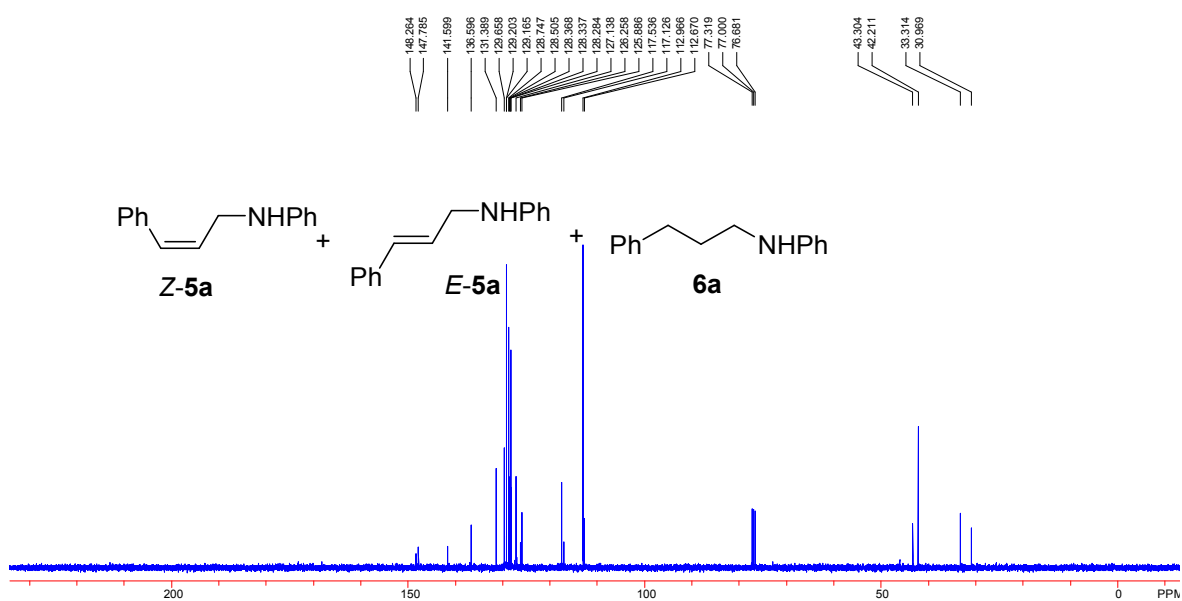
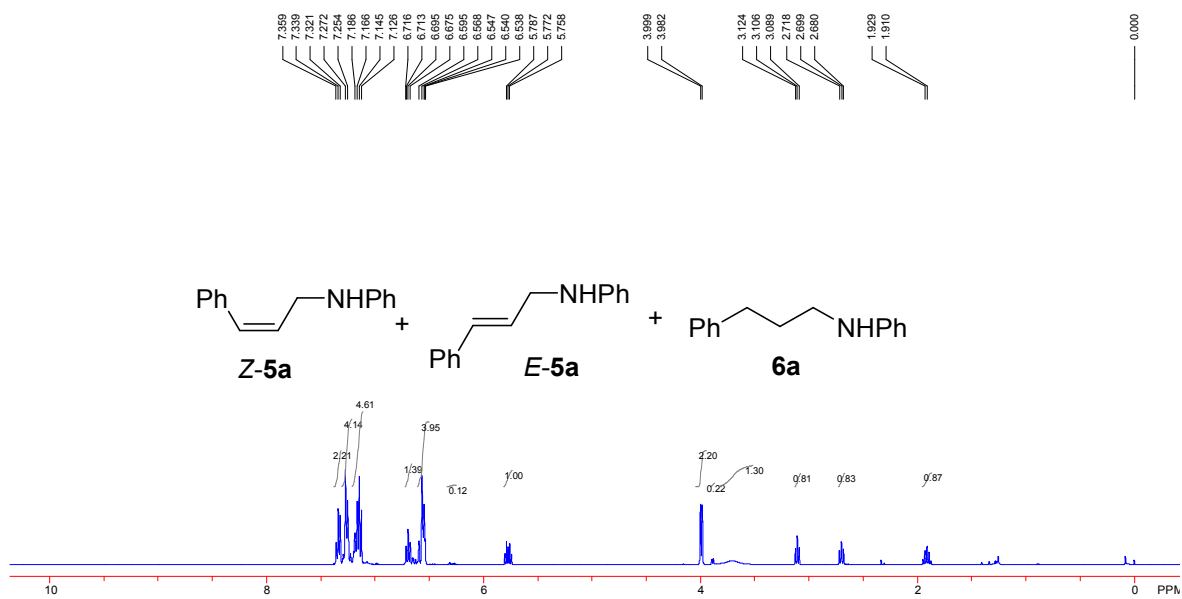


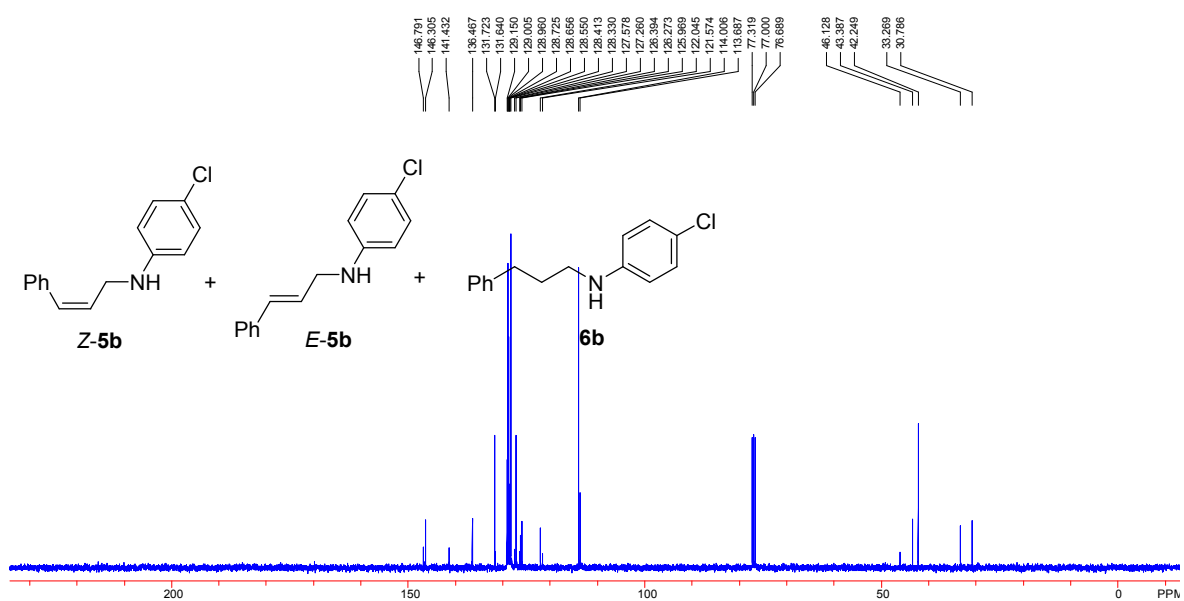
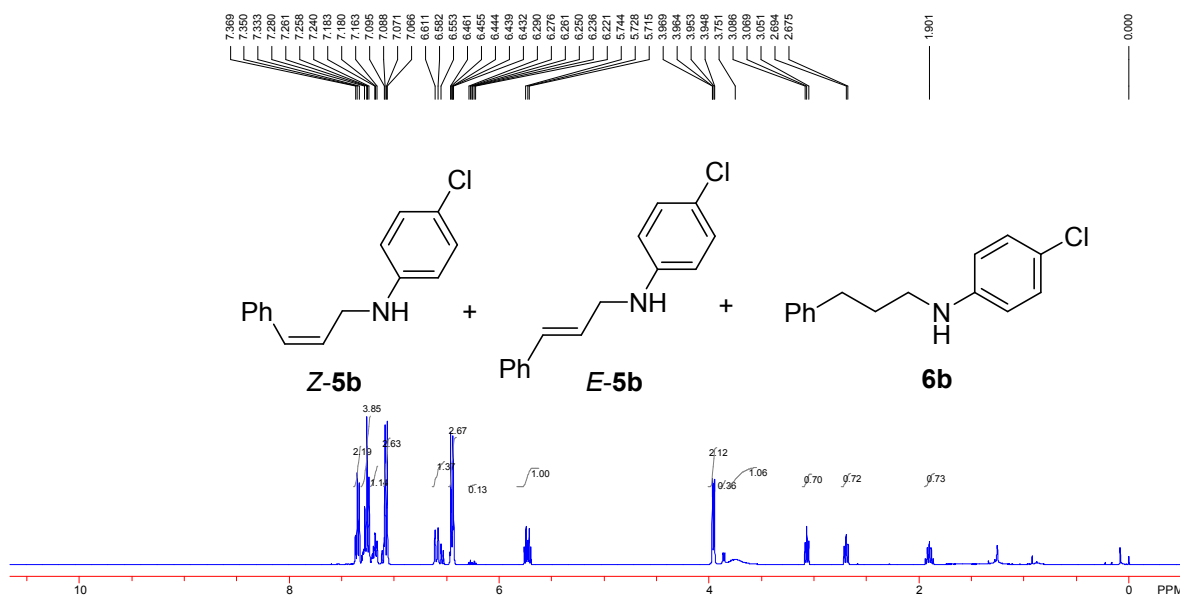


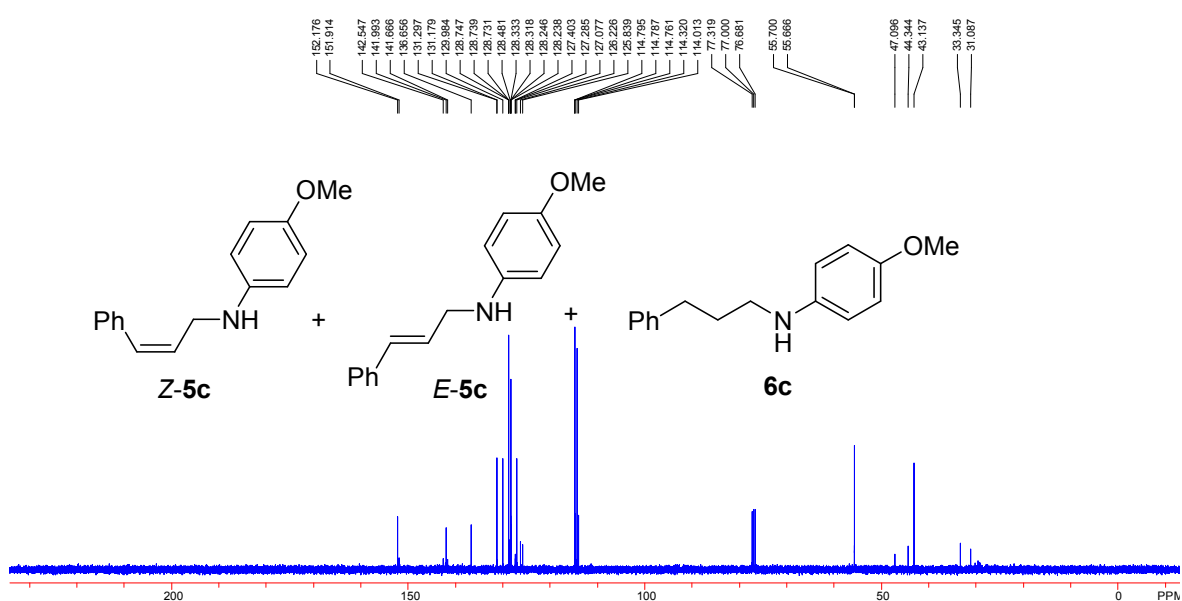
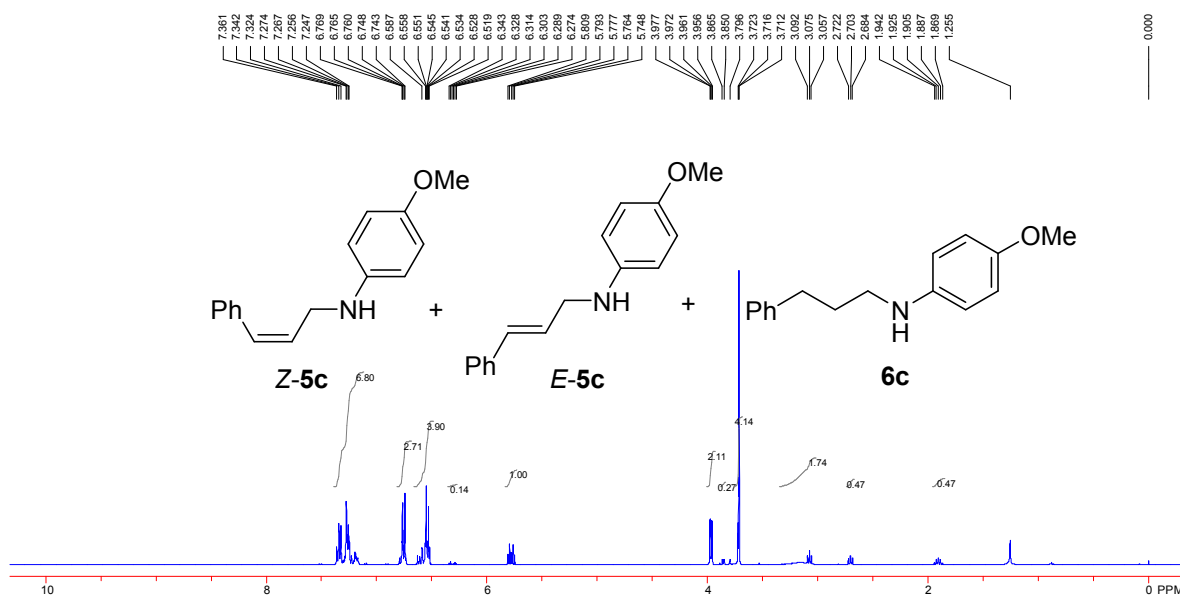


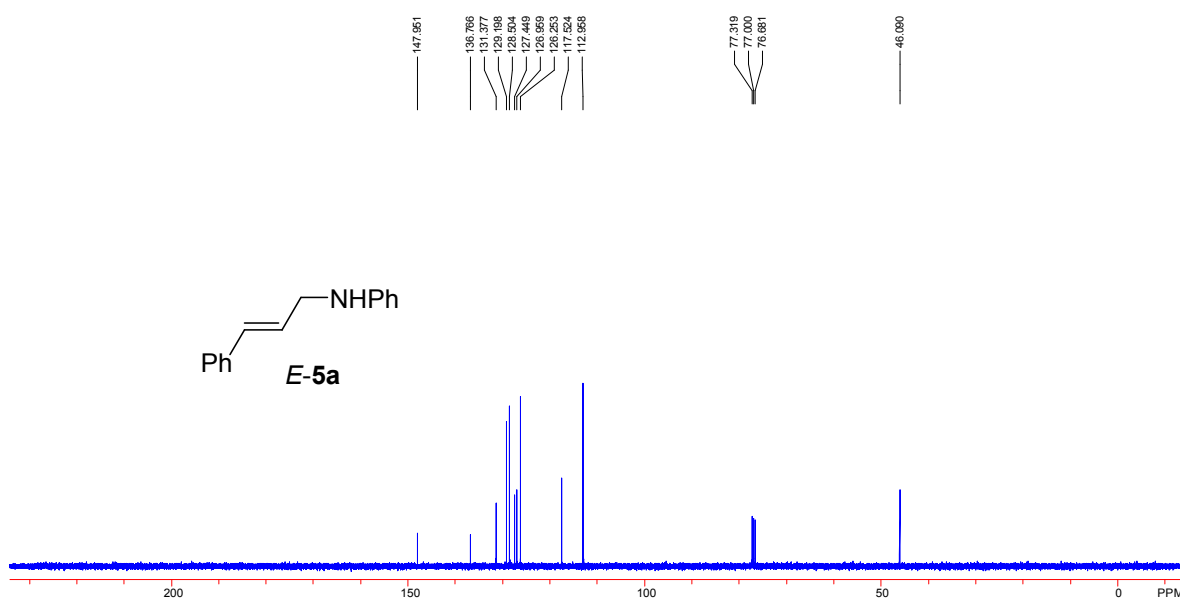
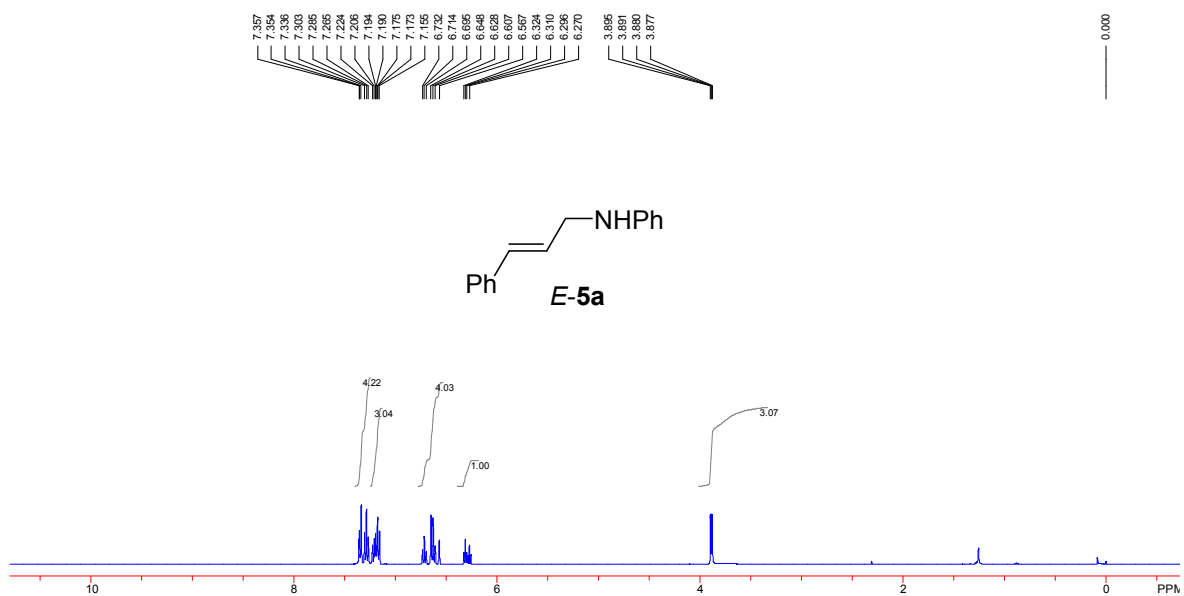


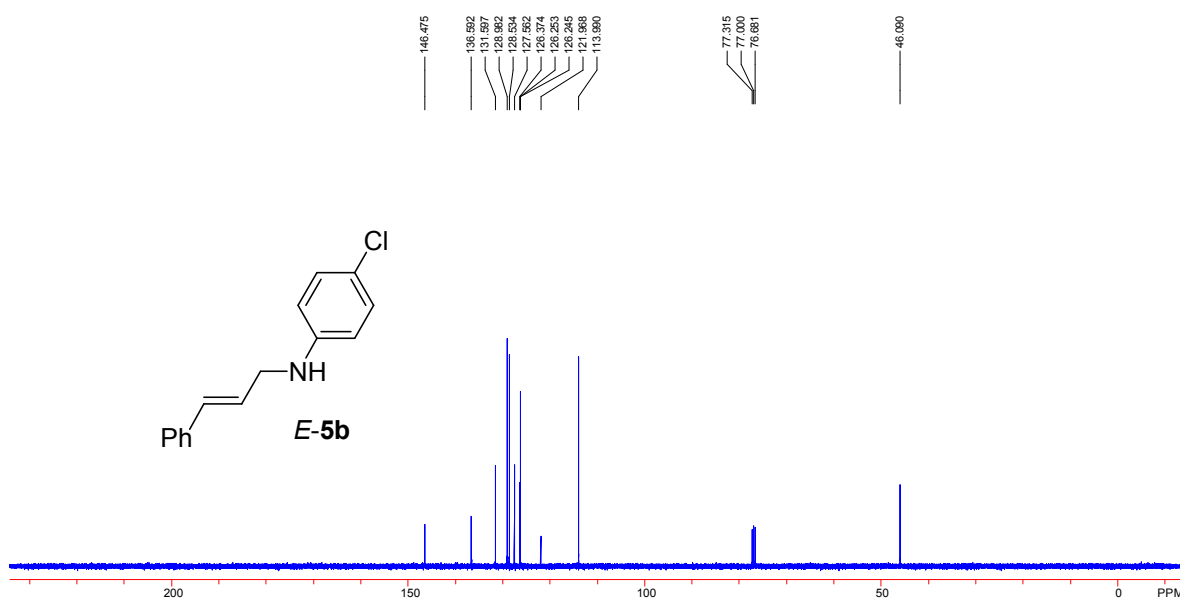
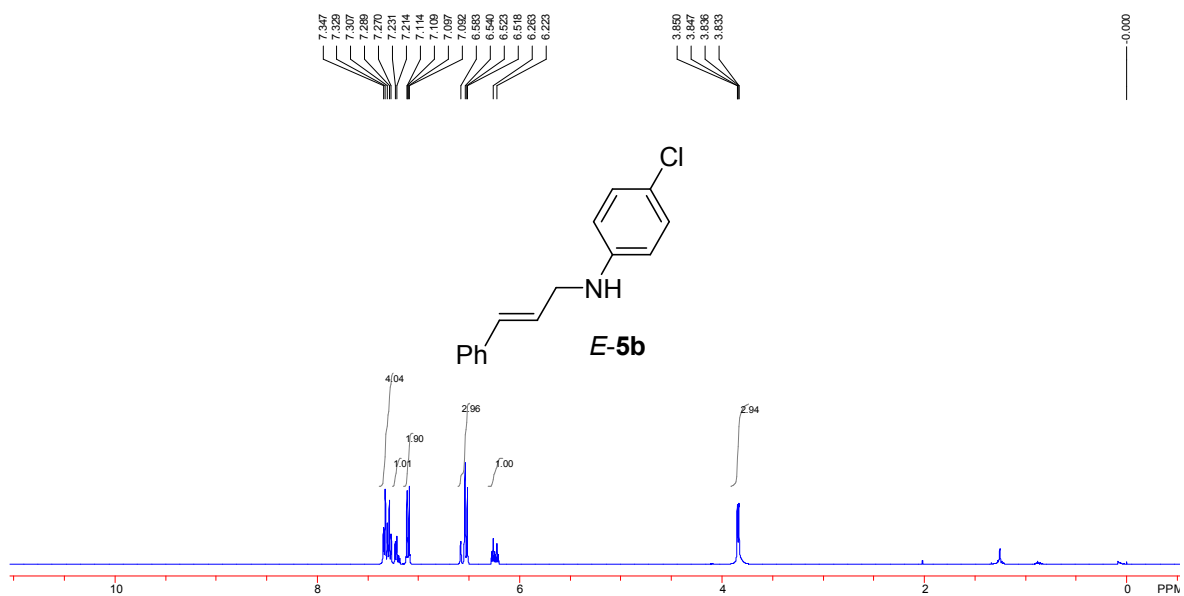


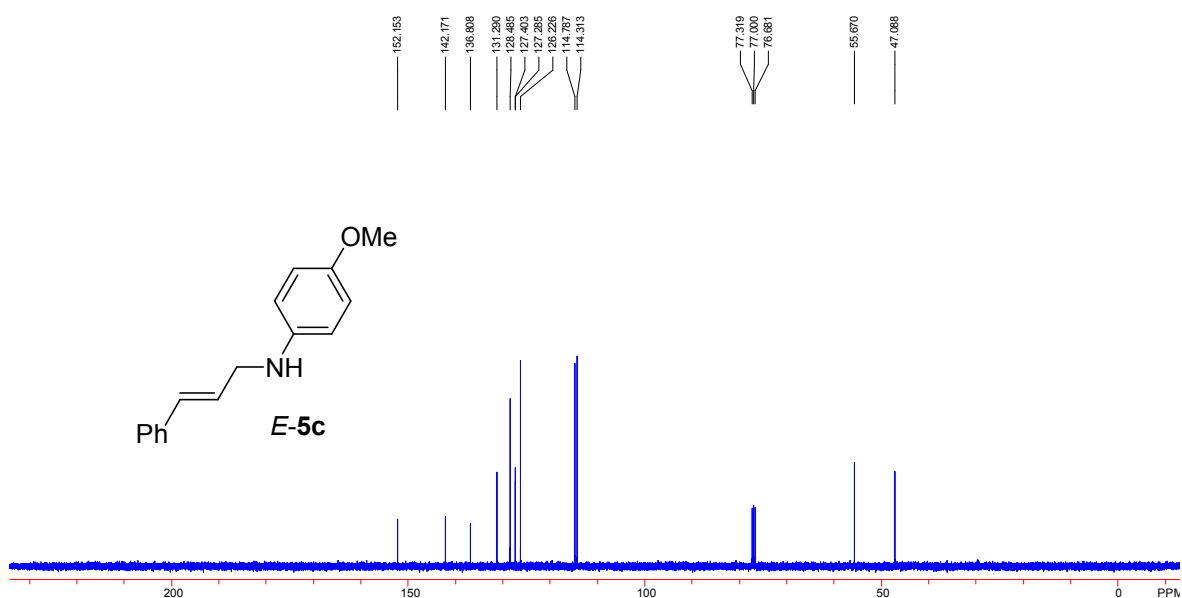
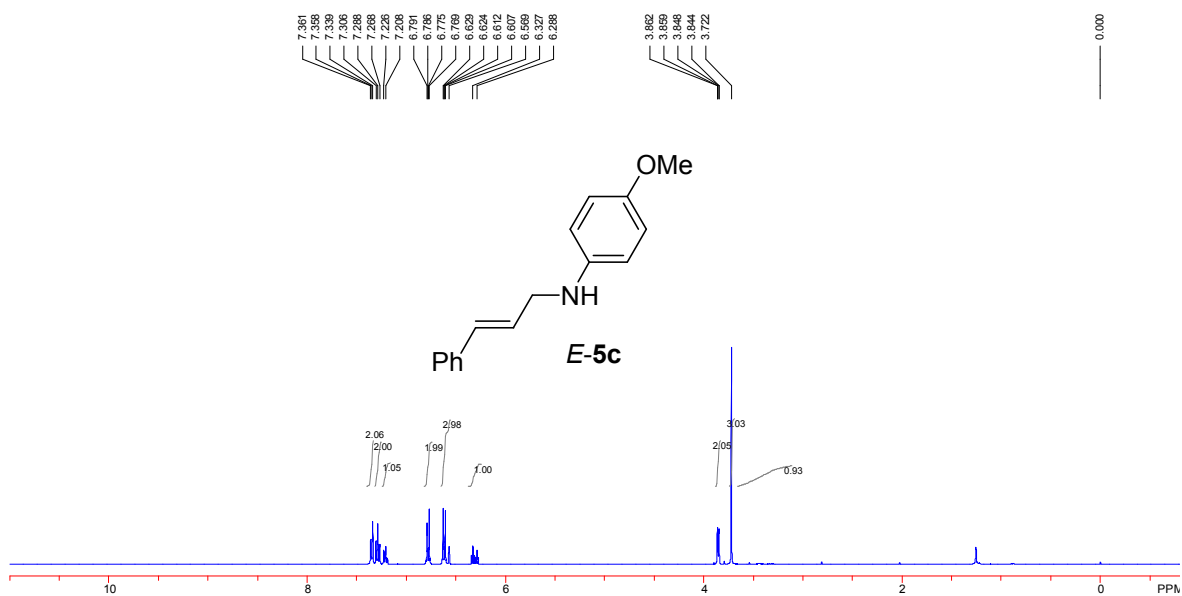


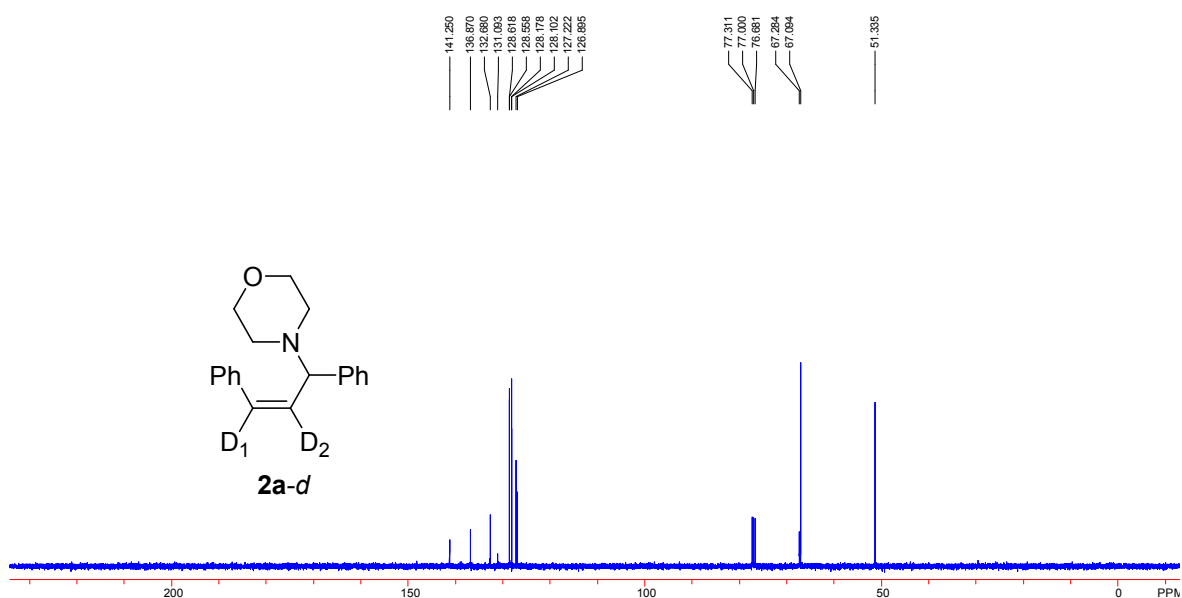
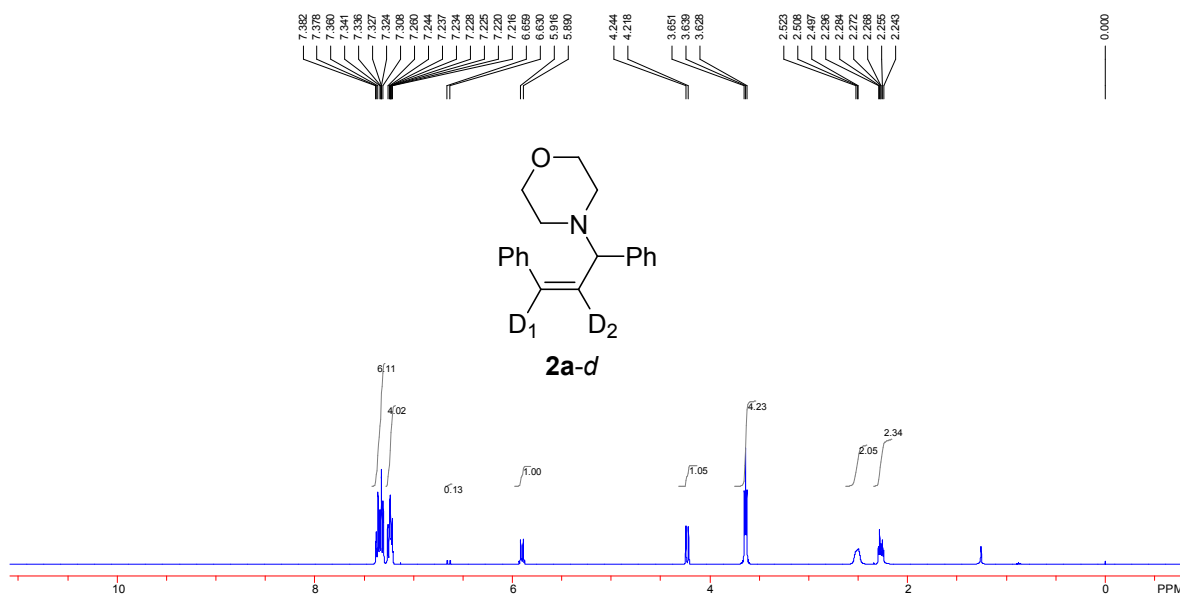


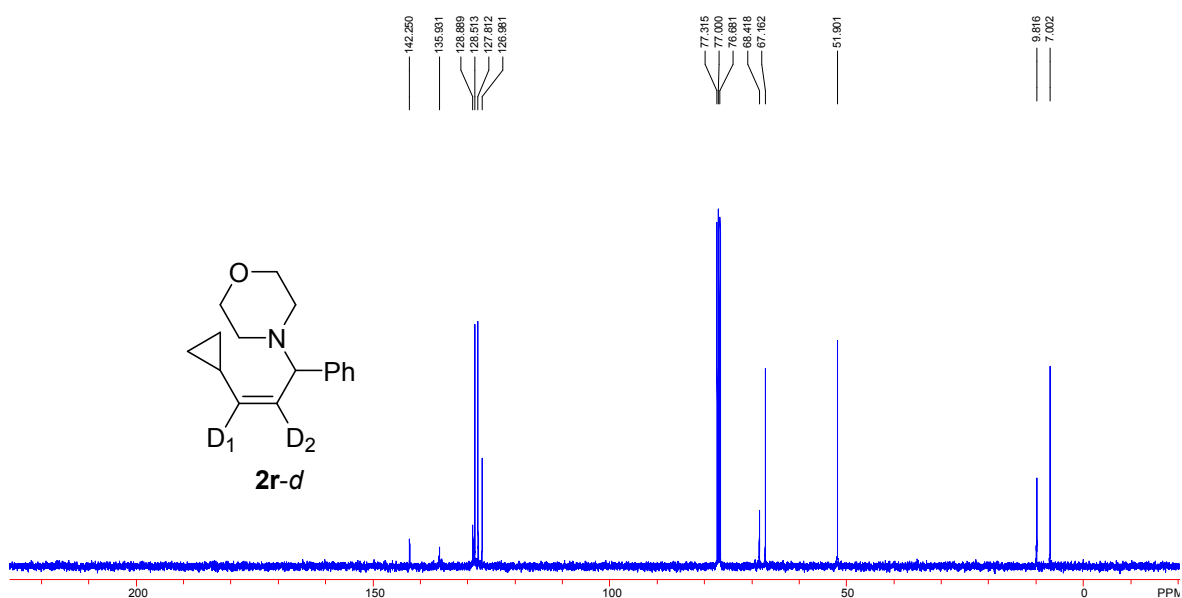
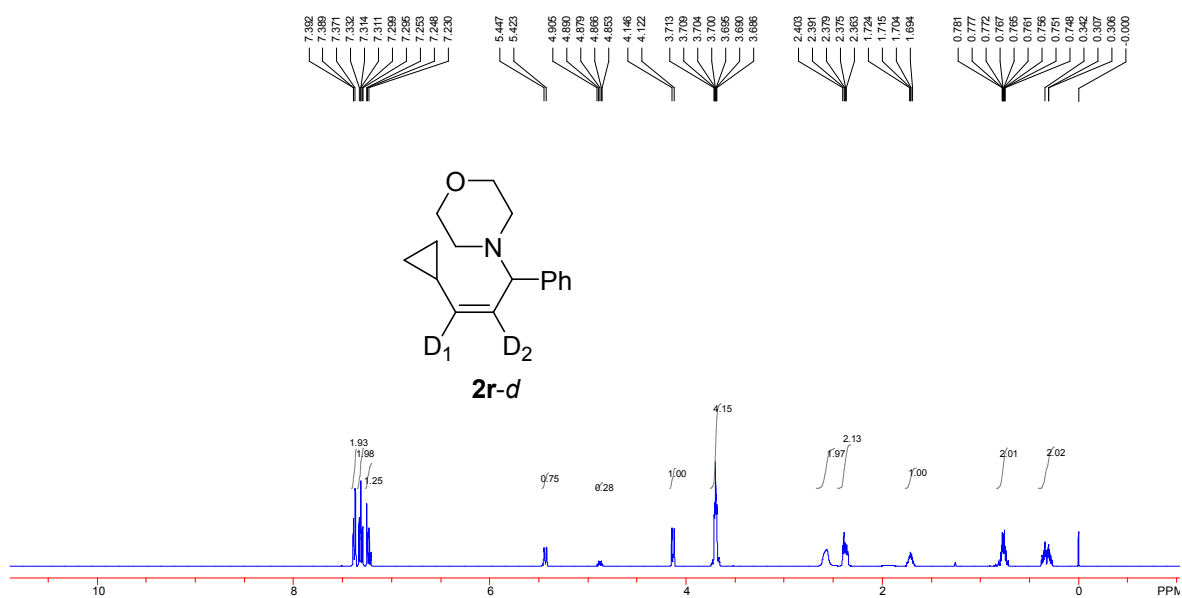


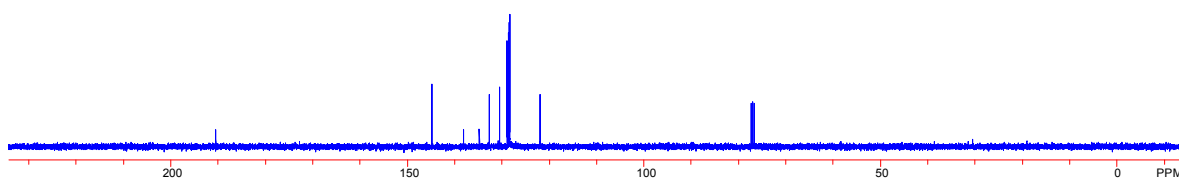
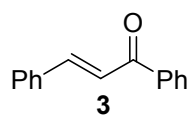
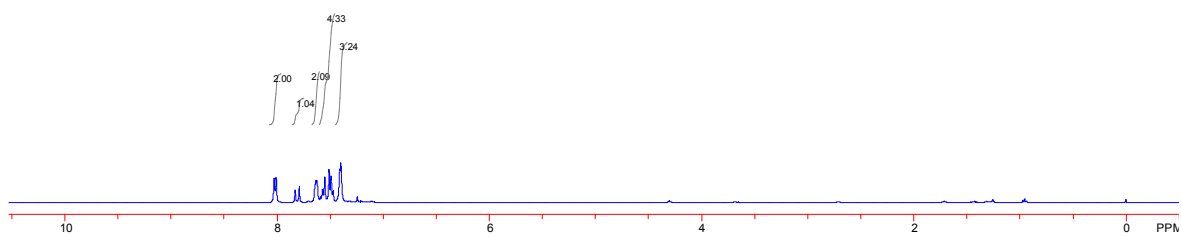
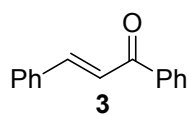
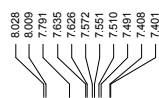


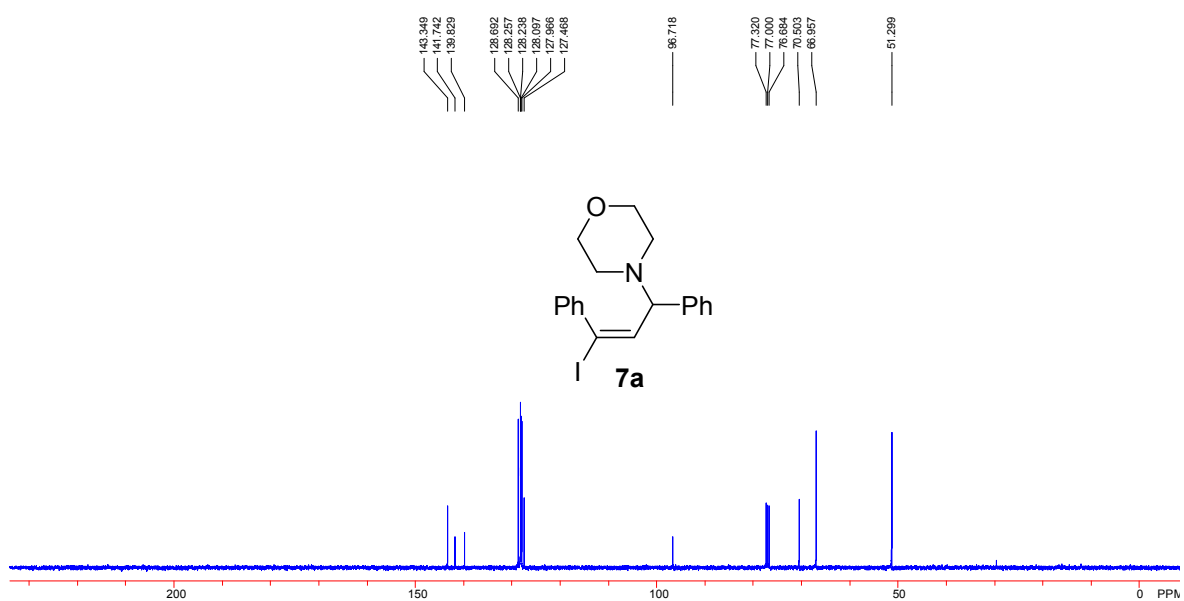
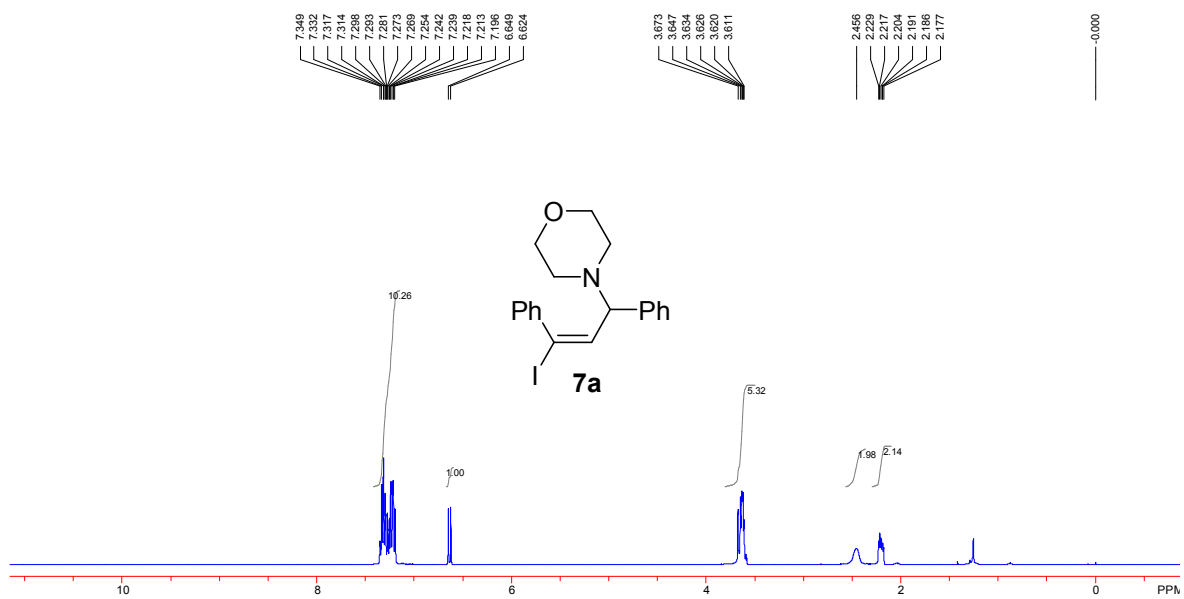


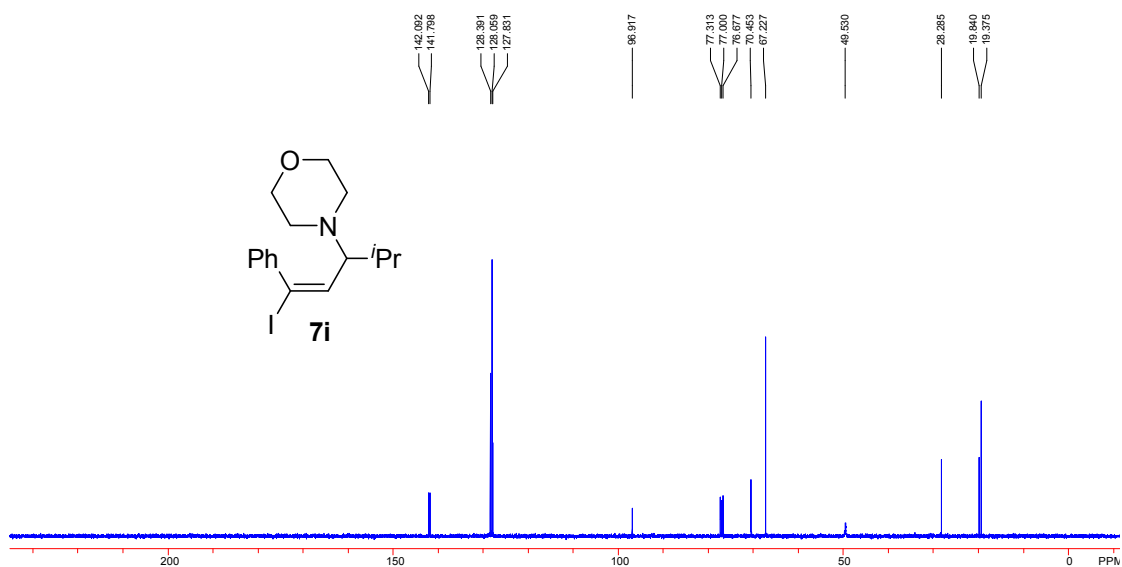
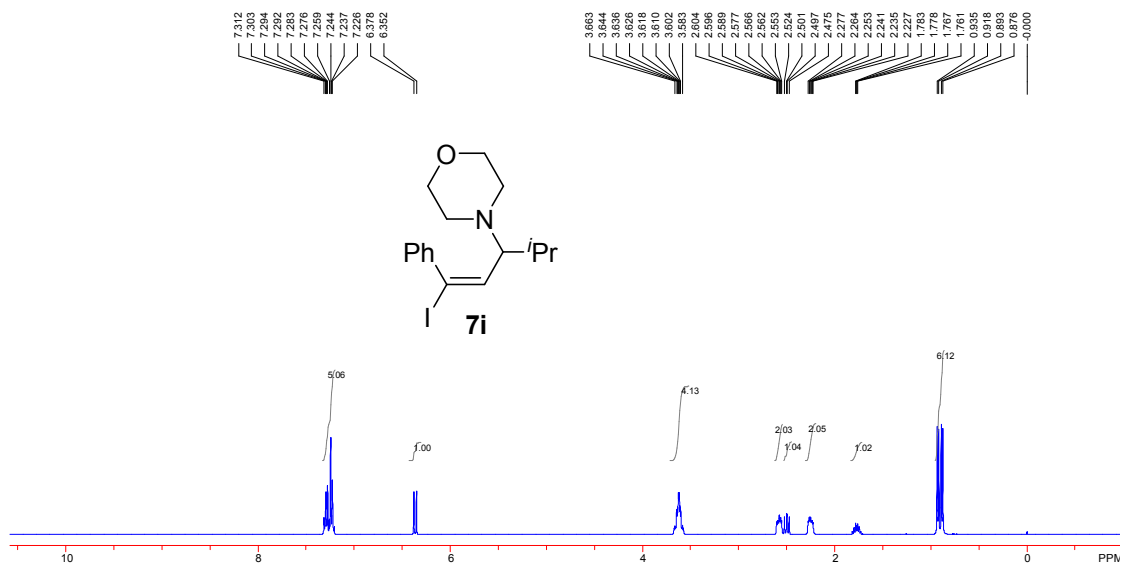


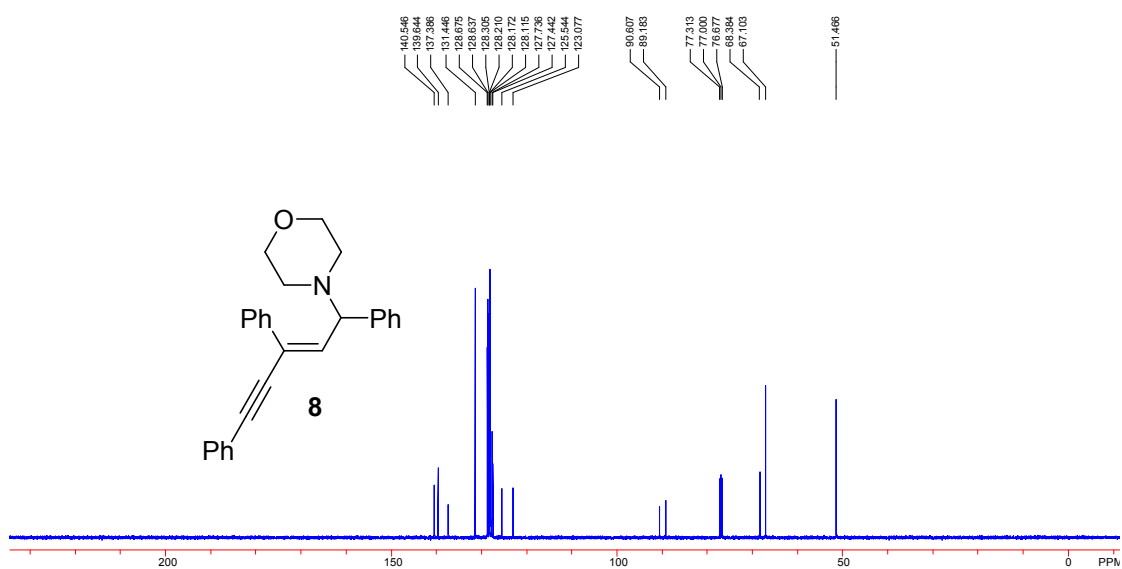


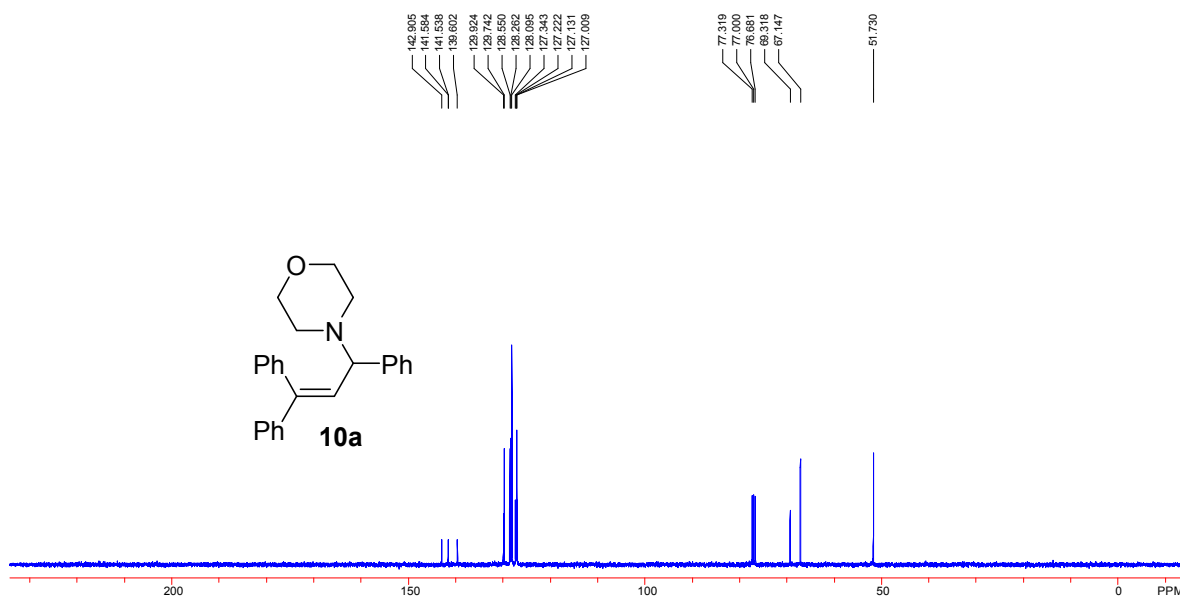
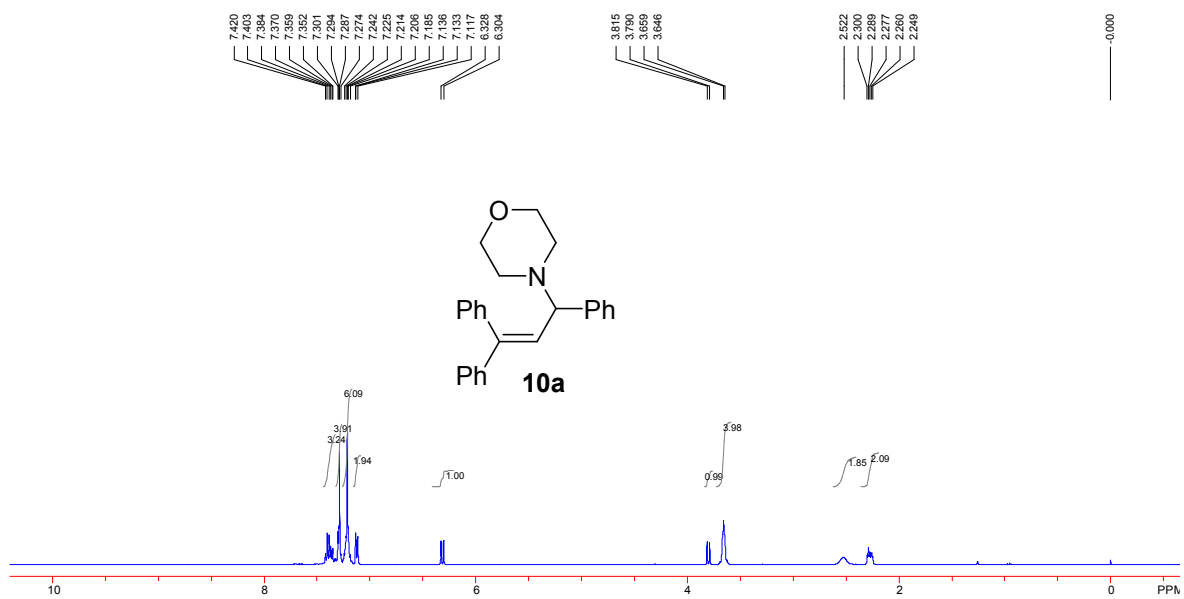


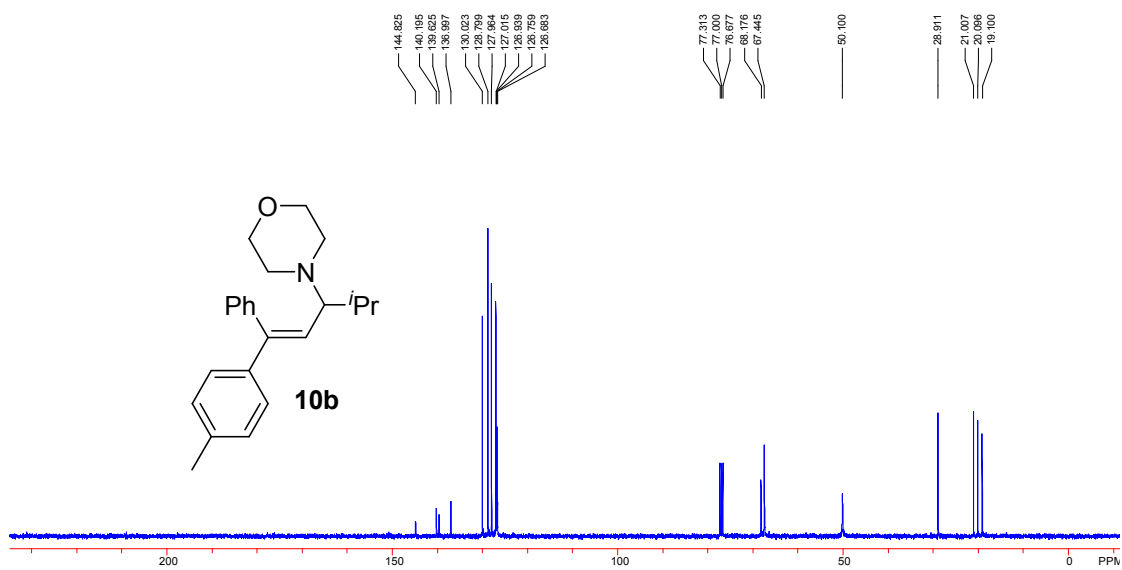
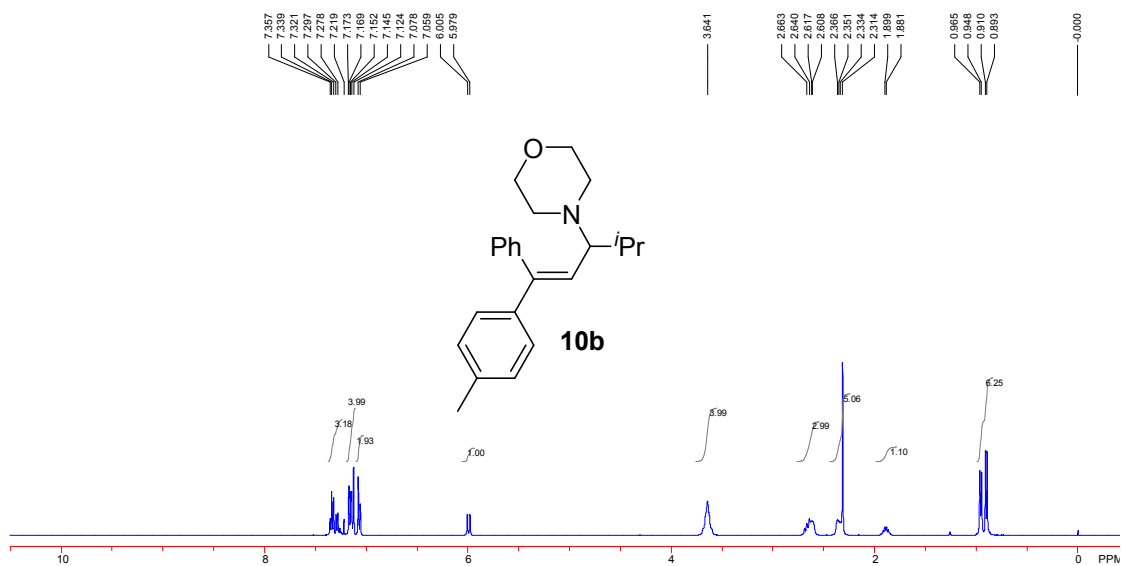


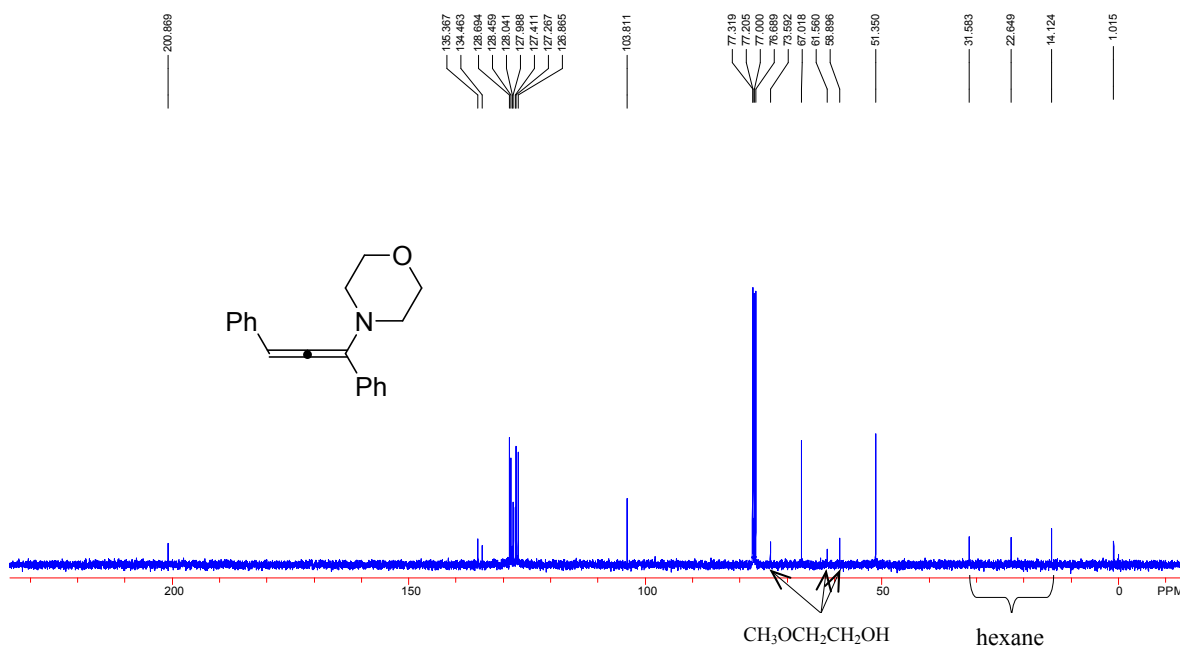
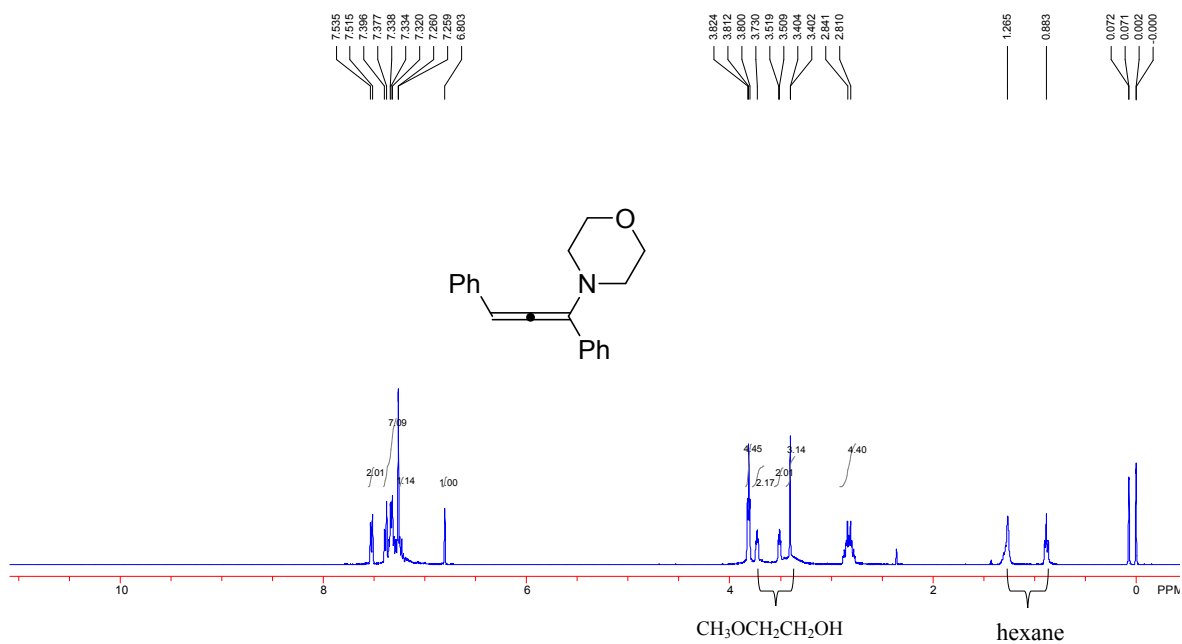












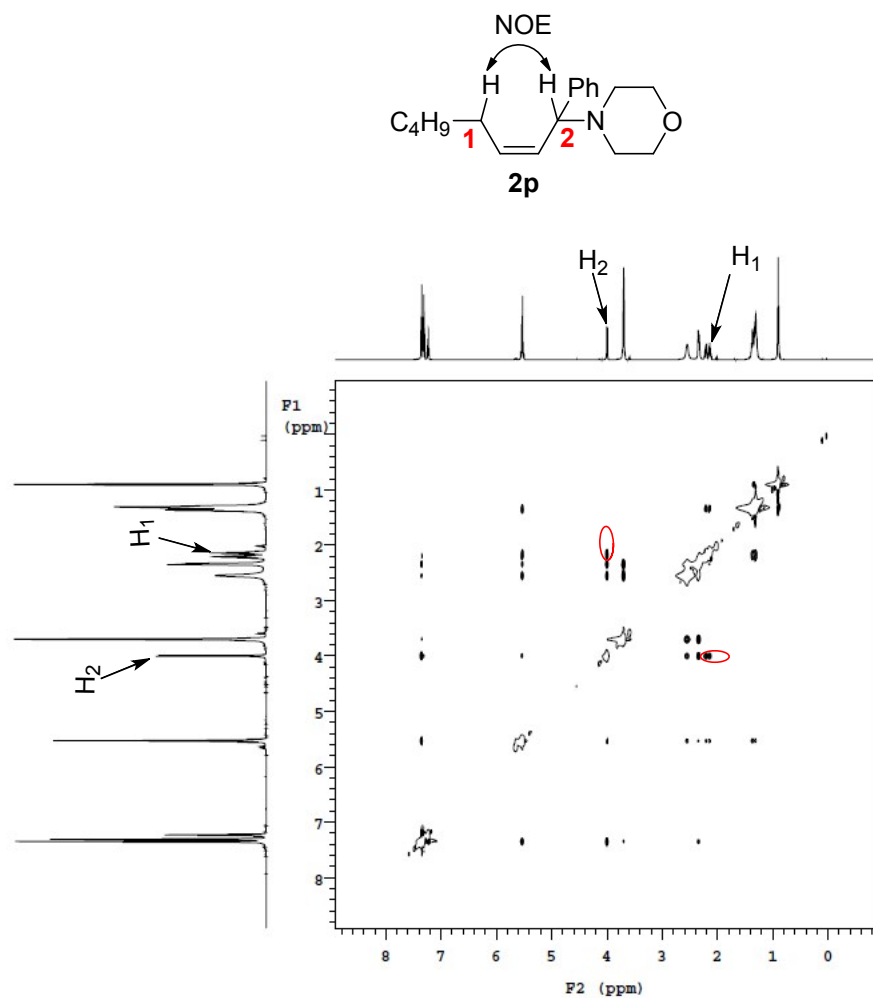


Figure S3. NOE spectra of compound **2p**