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Tandem Catalysis Enabled Highly Chemoselective Deoxygenative Alkynylation and Alkylation of Tertiary Amides: A Versatile Entry to Functionalized α-Substituted Amines

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Contents

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Experimental Procedures

General Methods: Melting points were determined on a Büchi M560 Automatic Melting Point apparatus and are uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. NMR spectra were recorded on a Bruker AV 400 or AC 500 spectrometer at 25 ºC in the solvents indicated. Chemical shifts (δ) are reported in ppm and respectively referenced to internal standard Me_4Si and solvent signals (Me_4Si, 0 ppm for ^1H NMR and $CDCl_3$, 77.0 ppm for ^{13}C NMR, some carbons are missing because of overlap). Mass spectra were recorded on a Bruker Dalton ESquire 3000 plus LC-MS apparatus (ESI direct injection). HRMS spectra were recorded on a 7.0T FT-MS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography eluting (unless otherwise stated) with EtOAc/*n*-hexane mixture. Toluene was distilled over sodium benzophenone ketyl under N_2.

Table 1. The structures of amides used

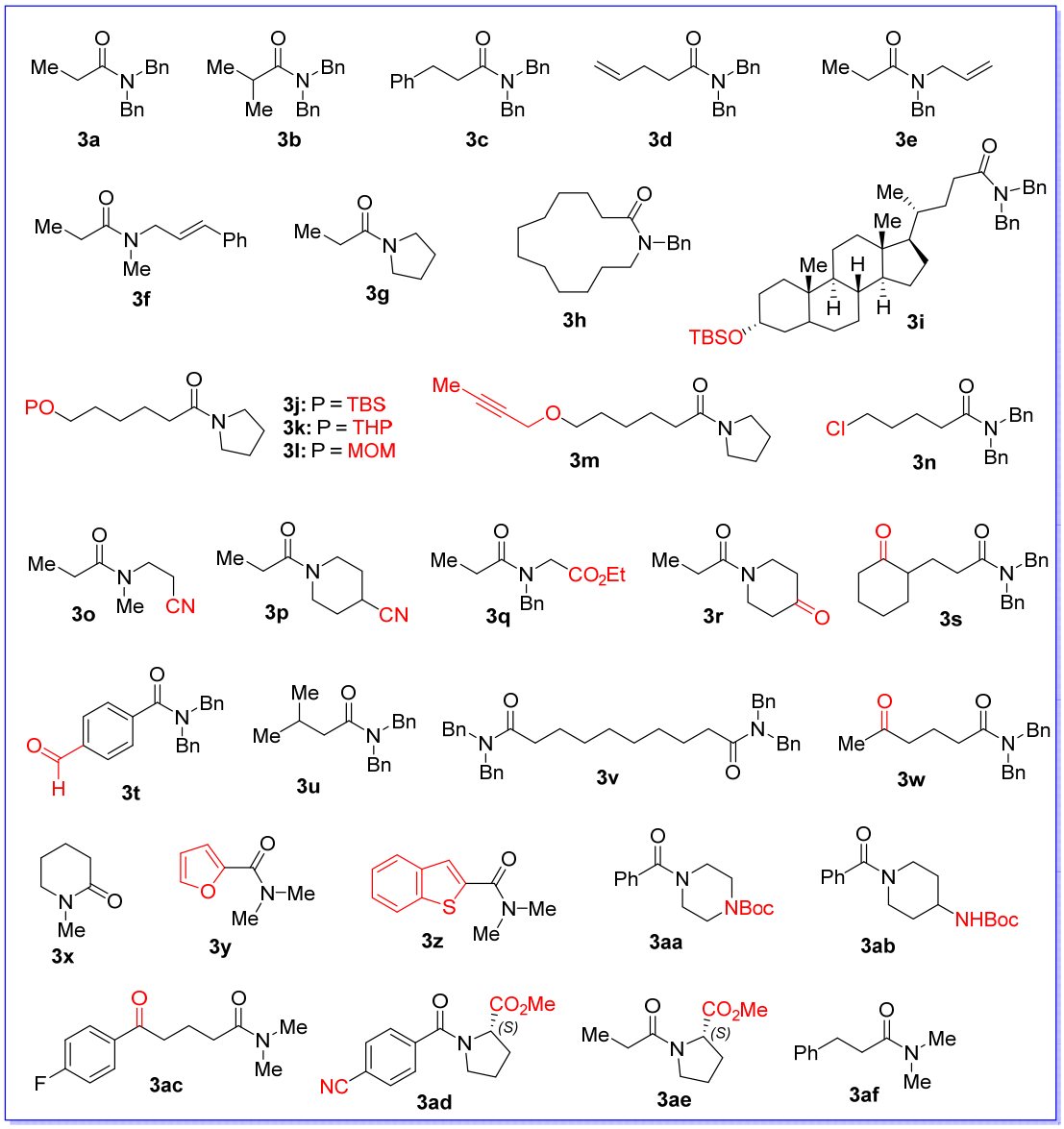
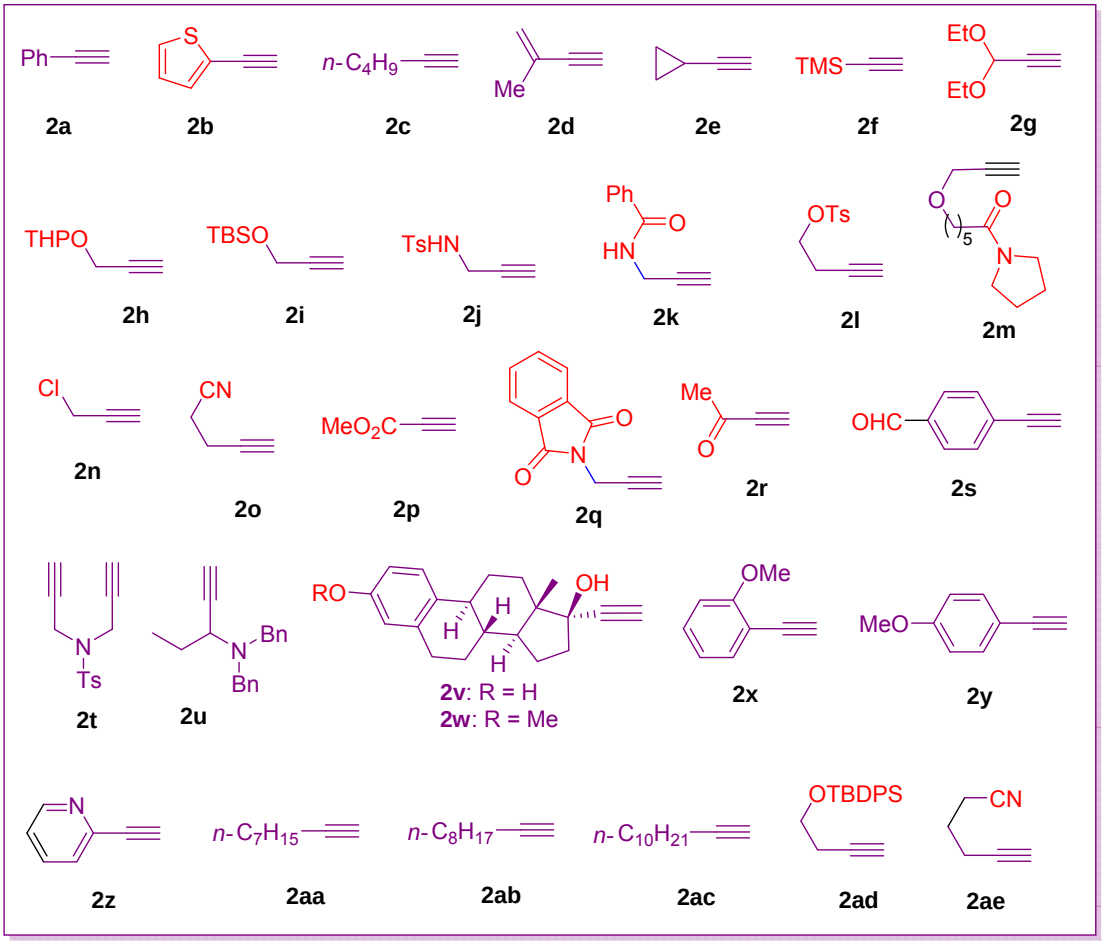


Table 2. The structures of alkynes used



General procedure A: The catalytic reductive alkynylation of amides.

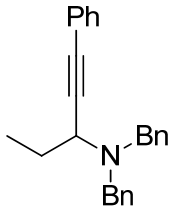
In a glove box charged with an atmosphere of nitrogen, $IrCl(CO)(PPh_3)_2$ (8 mg, 0.01 mmol, 1.0 mol%) was added to a dried 10-mL round-bottom flask equipped with a magnetic stirring bar. The flask was then removed from the glove box. A solution of a *tert*-amide (1.0 mmol, 1.0 equiv) in toluene (5 mL), and 1,1,3,3-tetramethyldisiloxane (0.36 mL, 2.0 mmol, 2.0 equiv or 1.2 equiv for amides without α-hydrogen) were successively added to the flask at room temperature. After being stirred for 30 min, the resulting mixture and a terminal alkyne (1.2 mmol, 1.2 equiv) were sequentially added to a suspension of CuBr (7 mg, 0.05 mmol, 5 mol %) in toluene (3 mL) in a 25-mL round-bottom flask under argon. The reaction mixture was stirred for 12 h at room temperature. The resulting mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (FC) on silica gel to afford the corresponding propargylic amine **3**.

General procedure B: the catalytic reductive alkylation of amides

To a dried 10-mL round-bottom flask containing $IrCl(CO)(PPh_3)_2$ (8 mg, 1.0 mol %, weighted in a glove box) were added a toluene (5 mL) solution of *tert*-amide (1.0 mmol) and TMDS (2.0 mmol or 1.2 mmol for amides without α-hydrogen) at room temperature. After being stirred for 10 min or 30 min (for amides without α-hydrogen), the resulting solution and an alkyne (1.2 mmol) were added to a suspension of CuBr (7 mg, 0.05 mmol, 5 mol%) in toluene (3 mL). After being stirred for 12 hours at room temperature, the mixture was filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was dissolved in MeOH (5 mL). 10% Pd/C (50 mg) was added, and the mixture was stirred under hydrogen atmosphere (1 atm) for 5 hours. The resulting mixture was filtered, the filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the corresponding α-alkylated amine **4**.

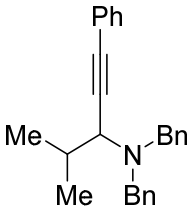
Preparation and Characterization of Alkynylated and Alkylated Products

N,N-Dibenzyl-1-phenylpent-1-yn-3-amine (1a)



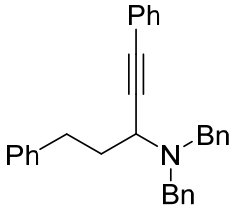
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1a** (298 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 3061, 3027, 2963, 2932, 1489, 1455, 1259, 1070, 801, 755, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, J = 7.4 Hz, 3H), 1.71-1.85 (m, 2H), 3.50 (d, J = 13.8 Hz, 2H), 3.51 (t, J = 7.6 Hz, 1H), 3.88 (d, J = 13.8 Hz, 2H), 7.19-7.50 (m, 15H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 27.0, 54.0, 55.0, 85.2, 88.0, 123.6, 126.8, 127.0, 127.8, 128.2, 128.3, 128.6, 128.8, 129.0, 131.8, 132.0, 139.9 ppm; MS (ESI) *m/z* 362 ($M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{25}H_{25}NNa]^+$ ($M + Na^+$): 362.1879; found: 362.1881.

N,N-Dibenzyl-4-methyl-1-phenylpent-1-yn-3-amine (1b)



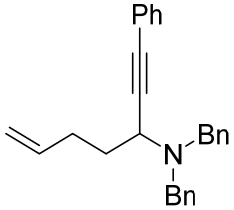
Following general procedure A, the reaction of *tert*-amide **3b** (267 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1b** (297 mg, yield: 84%) as a colorless oil. IR (film) ν_{max}: 2955, 2805, 1601, 1458, 1453, 1069, 1024, 752, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, J = 4.3 Hz, 3H), 1.04 (d, J = 4.3 Hz, 3H), 1.96-2.05 (m, 1H), 3.12 (d, J = 10.4 Hz, 1H), 3.47 (d, J = 13.9 Hz, 2H), 3.88 (d, J = 13.9 Hz, 2H), 7.21-7.24 (m, 2H), 7.29-7.35 (m, 7H), 7.42-7.44 (m, 4H), 7.50-7.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 21.0, 30.8, 55.1, 59.7, 86.0, 87.4, 123.7, 126.8, 127.8, 128.2, 128.3, 128.9, 131.8, 139.8 ppm; MS (ESI) *m/z* 354 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{26}H_{28}N]^+$ ($M + H^+$): 354.2216; found: 354.2215.

N,N-Dibenzyl-1,5-diphenylpent-1-yn-3-amine (1c)



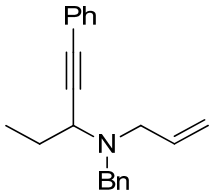
Following general procedure A, the reaction of *tert*-amide **3c** (329 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1c** (386 mg, yield: 93%) as a colorless oil. IR (film) ν_{max}: 2832, 1600, 1489, 1453, 1070, 1028, 755, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.97-2.16 (m, 2H), 2.64-2.85 (m, 2H), 3.52 (d, J = 13.7 Hz, 2H), 3.67 (t, J = 7.5 Hz, 1H), 3.92 (d, J = 13.7 Hz, 2H), 7.05-7.07 (m, 2H), 7.12-7.25 (m, 5H), 7.29-7.34(m, 7H), 7.40-7.42 (m, 4H), 7.49-7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.7, 35.7, 52.1, 55.2, 85.6, 87.7, 123.5, 125.7, 126.9, 127.9, 128.2, 128.3, .128.4, 128.8, 128.9, 131.8, 139.7, 141.9 ppm; MS (ESI) *m/z* 416 (M + H^+); HRMS (ESI) *m/z* calcd for $[C_{31}H_{30}N]^+$ (M + H^+): 416.2373; found: 416.2381.

_N,N_-Dibenzyl-1-phenylhept-6-en-1-yn-3-amine (1d)



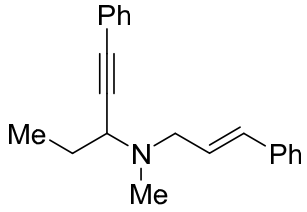
Following general procedure A, the reaction of *tert*-amide **3d** (279 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1d** (329 mg, yield: 90%) as a colorless oil. IR (film) ν_{max}: 3061, 3027, 2938, 2832, 1599, 1489, 1453, 1119, 912, 755, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.75-1.94 (m, 2H), 2.10-2.27 (m, 2H), 3.50 (d, J = 13.7 Hz, 2H), 3.64 (t, J = 7.6 Hz, 1H), 3.89 (d, J = 13.7 Hz, 2H), 4.85-4.95 (m, 2H), 5.66-5.76 (m, 1H), 7.21-7.24 (m, 2H), 7.29-7.34 (m, 7H), 7.40-7.42(m, 4H), 7.49-7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.6, 33.1, 51.9, 55.1, 85.4, 87.7, 114.8, 123.5, 126.9, 127.9, 128.2, 128.3, 128.9, 131.8, 138.0, 139.7 ppm; MS (ESI) *m/z* 366 (M + H^+); HRMS (ESI) *m/z* calcd for $[C_{27}H_{28}N]^+$ (M + H^+): 366.2216; found: 366.2217.

_N_-Allyl-_N_-benzyl-1-phenylpent-1-yn-3-amine (1e)



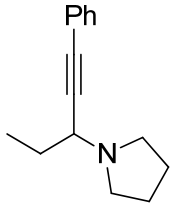
Following general procedure A, the reaction of *tert*-amide **3e** (203 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1e** (263 mg, yield: 91%) as a colorless oil. IR (film) ν_{max}: 3062, 2964, 2932, 2811, 1489, 1452, 1070, 917, 741, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, J = 7.4 Hz, 3H), 1.71-1.78 (m, 2H), 3.04 (dd, J = 14.3, 8.0 Hz, 1H), 3.28-3.33 (m, 1H), 3.46 (d, J = 14.0 Hz, 1H), 3.58 (t, J = 7.7 Hz, 1H), 3.91 (d, J = 14.0 Hz, 1H), 5.10-5.13 (m, 1H), 5.24-5.29 (m, 1H), 5.82-5.92 (m, 1H), 7.21-7.24 (m, 1H), 7.26-7.33 (m, 5H), 7.38-7.39 (m, 2H), 7.44-7.48 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 27.1, 54.0, 54.9, 85.1, 88.2, 116.9, 123.6, 126.7, 127.8, 128.1, 128.2, 128.7, 131.8, 136.9, 140.1 ppm; MS (ESI) *m/z* 240 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{21}H_{24}N]^+$ ($M + H^+$): 290.1903; found: 290.1904.

_N_-Cinnamyl-_N_-methyl-1-phenylpent-1-yn-3-amine (1f)



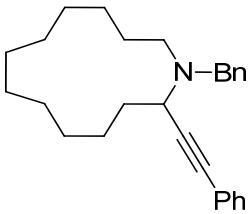
Following general procedure A, the reaction of *tert*-amide **3f** (203 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 40), propargylic amine **1f** (246 mg, yield: 85%) as a pale yellow oil. IR (film) ν_{max}: 2940, 2216, 1708, 1607, 1220, 1017, 759, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.07 (t, J = 7.4 Hz, 3H), 1.72-1.80 (m, 2H), 2.33 (s, 3H), 3.23-3.28 (m, 1H), 3.33-3.38 (m, 1H), 3.58 (t, J = 6.8 Hz, 1H), 6.24-6.32 (m, 1H), 6.57 (d, J = 15.8 Hz, 1H), 7.21-7.46 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 27.1, 37.7, 57.6, 58.0, 86.0, 87.3, 123.5, 126.3, 127.3, 127.8, 128.2, 128.5, 131.7, 132.4, 137.2 ppm; MS (ESI) *m/z* 290 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{21}H_{24}N]^+$ ($M + H^+$): 290.1903; found: 290.1901.

1-(1-Phenylpent-1-yn-3-yl)pyrrolidine (1g)



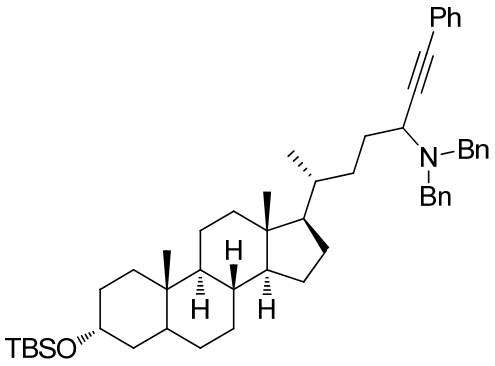
Following general procedure A, the reaction of *tert*-amide **3g** (127 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 40), propargylamine 1**g** (177 mg, yield: 83%) as a colorless oil. IR (film) ν_{max}: 2964, 2933, 2873, 1488, 1360, 1136, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, J = 7.4 Hz, 3H), 1.69-1.84 (m, 6H), 2.66-2.79 (m, 4H), 3.58 (dd, J = 9.2, 5.6 Hz, 1H), 7.26-7.30 (m, 3H), 7.41-7.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 23.5, 28.2, 49.8, 56.9, 85.2, 88.2, 123.5, 127.7, 128.2, 131.7 ppm; MS (ESI) *m/z* 214 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{15}H_{20}N]^+$ ($M + H^+$): 214.1590; found: 214.1582.

1-Benzyl-2-(phenylethynyl)azacyclotridecane (1h)



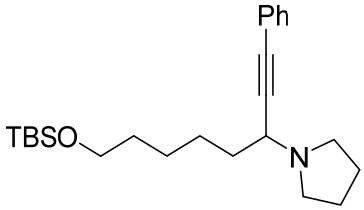
Following general procedure A, the reaction of *tert*-amide **3h** (287 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 200), propargylamine **1h** (328 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 2965, 2854, 1489, 1070, 754, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.27-1.64 (m, 19H), 1.83-1.91 (m, 1H), 2.50-2.62 (m, 2H), 3.36 (d, J = 13.6 Hz, 1H), 3.92 (d, J = 13.6 Hz, 1H), 3.64 (dd, d, J = 3.6, 3.1 Hz, 1H), 7.20-7.32 (m, 6H), 7.37-7.39 (m, 2H), 7.43-7.46 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 25.4, 25.5, 25.6, 26.3, 26.4, 26.6, 26.7, 33.3, 49.8, 52.0, 55.6, 84.5, 88.8, 123.7, 126.7, 127.7, 128.0, 128.2, 129.1, 131.7, 140.3 ppm; MS (ESI) m/z 374 ($M + H^+$); HRMS (ESI) m/z calcd for $[C_{27}H_{36}N]^+$ ($M + H^+$): 374.2842; found: 374.2837.

(6R)-*N*,*N*-Dibenzyl-6-((3R,8R,9S,10S,13R,14S,17R)-3-((tert-butyldimethylsilyl) oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-1-phenylhept-1-yn-3-amine (1i)



Following general procedure A, the reaction of lithocholic acid-derived amide **3i** (335 mg, 0.5 mmol) with phenylacetylene (**2a**) (0.065 mL, 0.6 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylic amine **1i** (325 mg, yield: 86%) as an inseparable diastereomeric mixture (*dr* = 1: 1, determined by ^{1}H NMR). White solid; Mp: 74-76 ^{o}C; IR (film) ν_{max}: 2936, 2862, 1597, 1450, 1373, 1248, 1079, 867, 835, 749, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, data of the two diastereomers): δ 0.05-0.06 (m, 6H), 0.59 (d, J = 5.8 Hz, 3H), 0.85-0.89 (m, 15H), 1.00-1.14 (m, 6H), 1.18-1.28 (m, 4H), 1.35-1.48 (m, 9H), 1.52-1.67 (m, 3H), 1.73-1.93 (m, 6H), 3.45-3.60 (m, 4H), 3.88 (d, J = 13.7 Hz, 2H), 7.21-7.51 (m, 15H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, data of the two diastereomers): δ −4.6, 12.0, 18.3, 18.7, 20.8, 23.4, 24.3, 26.0, 26.5, 27.4, 28.2, 28.3, 30.5, 31.1, 32.6, 32.7, 34.6, 35.5, 35.6, 35.9, 37.0, 40.2, 40.3, 42.4, 42.6, 42.7, 52.8, 52.9, 55.0, 55.1, 56.2, 56.3, 56.4, 72.9, 85.2, 88.2, 88.3, 123.7, 126.7, 126.8, 127.8, 128.1, 128.2, 128.3, 128.7, 128.8, 128.9, 131.8, 139.9, 140.0 ppm; MS (ESI) m/z 756 (M + H$^+$); HRMS (ESI) m/z calcd for $[C_{52}H_{74}NOSi]^+$ (M + H$^+$): 756.5534; found: 756.5545.

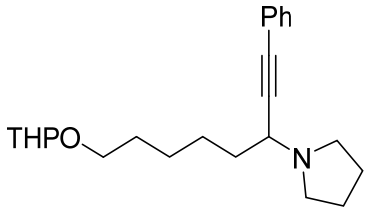
1-(8-((*Tert*-butyldimethylsilyl)oxy)-1-phenyloct-1-yn-3-yl)pyrrolidine (1j)



Following general procedure A, the reaction of *tert*-amide **3j** (299 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30), propargylamine **1j** (350 mg, yield: 91%) as a colorless oil. IR (film) ν_{max}: 2965, 2857, 2807, 1488, 1254, 1101, 835, 755, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 6H), 0.89 (s, 9H), 1.37-1.46 (m, 2H), 1.49-1.60 (m, 4H), 1.70-1.81 (m, 6H), 2.67-

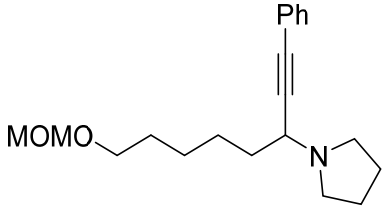
2.77 (m, 4H), 3.61 (t, J = 6.5 Hz, 2H), 3.67 (dd, J = 8.3, 6.5 Hz, 1H), 7.26-7.30 (m, 3H), 7.40-7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.3, 18.3, 23.5, 25.6, 26.0, 26.5, 32.8, 35.1, 49.7, 55.1, 63.1, 85.2, 88.3, 123.5, 127.8, 128.2, 131.7 ppm; MS (ESI) *m/z* 386 (M + H^+); HRMS (ESI) *m/z* calcd for $[C_{24}H_{40}NOSi]^+$ (M + H^+): 386.2874; found: 386.2870.

1-(1-Phenyl-8-((tetrahydro-2*H*-pyran-2-yl)oxy)oct-1-yn-3-yl)pyrrolidine (1k)



Following general procedure A, the reaction of *tert*-amide **3k** (269 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30), propargylamine **1k** (295 mg, yield: 83%) as a colorless oil. IR (film) ν_{max}: 2965, 2867, 2806, 1488, 1354, 1134, 1119, 1033, 755, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42-1.83 (m, 18H), 2.67-2.77 (m, 4H), 3.37-3.50 (m, 2H), 3.65-3.89 (m, 3H), 4.56-4.58 (m, 1H), 7.26-7.29 (m, 3H), 7.41-7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 23.5, 25.5, 26.1, 26.5, 29.7, 30.7, 35.0, 49.7, 55.0, 62.2, 67.5, 85.2, 88.3, 98.7, 98.8, 123.5, 127.8, 128.2, 131.7 ppm; MS (ESI) *m/z* 356 (M + H^+); HRMS (ESI) *m/z* calcd for $[C_{23}H_{34}NO_2]^+$ (M + H^+): 356.2584; found: 356.2583.

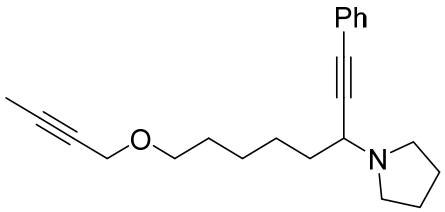
1-(8-(Methoxymethoxy)-1-phenyloct-1-yn-3-yl)pyrrolidine (1l)



Following general procedure A, the reaction of *tert*-amide **3l** (229 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30), propargylamine **1l** (252 mg, yield: 80%) as a colorless oil. IR (film) ν_{max}: 2965, 2874, 2818, 1439, 1131, 1101, 994, 755, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41-1.47 (m, 2H), 1.60-1.67 (m, 4H), 1.71-1.82 (m, 6H), 2.67-2.77 (m, 4H), 3.35 (s, 3H), 3.53 (t, J = 6.6 Hz, 2H), 3.67 (dd, J = 8.4, 6.3 Hz, 1H), 4.61 (s, 2H), 7.27-7.30 (m, 3H), 7.41-7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.5, 26.0, 26.5, 29.6,

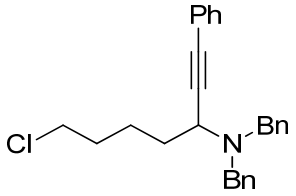
35.0, 49.7, 55.0, 67.7, 85.2, 88.2, 96.4, 123.4, 127.8, 128.2, 131.7 ppm; MS (ESI) *m/z* 316 (M + H^+); HRMS (ESI) *m/z* calcd for $[C_{20}H_{30}NO_2]^+$ (M + H^+): 316.2271; found: 316.2272.

1-(8-(But-2-yn-1-yloxy)-1-phenyloct-1-yn-3-yl)pyrrolidine (1m)



Following general procedure A, the reaction of *tert*-amide **3m** (237 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30), propargylamine **1m** (262 mg, yield: 81%) as a colorless oil. IR (film) ν_{max}: 2936, 2856, 1639, 1485, 1440, 1351, 1251, 1136, 1095, 755, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.39-1.46 (m, 2H), 1.48-1.67 (m, 4H), 1.70-1.85 (m, 9H), 2.68-2.77 (m, 4H), 3.48 (t, *J* = 6.6 Hz, 2H), 3.67 (dd, *J* = 8.6, 6.1 Hz, 1H), 4.07 (dd, *J* = 4.5, 2.2 Hz, 2H), 7.27-7.30 (m, 3H), 7.41-7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.5, 25.9, 26.5, 29.6, 34.9, 49.7, 55.0, 58.5, 70.0, 75.4, 82.0, 85.2, 123.4, 127.8, 128.2, 131.7 ppm; MS (ESI) *m/z* 324 (M + H^+); HRMS (ESI) *m/z* calcd for $[C_{22}H_{30}NO]^+$ (M + H^+): 324.2322; found: 324.2323.

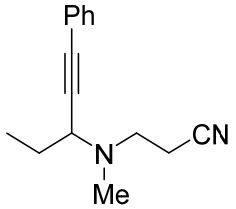
***N,N*-Dibenzyl-7-chloro-1-phenylhept-1-yn-3-amine (1n)**



Following general procedure A, the reaction of *tert*-amide **3n** (315 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 90), propargylamine **1n** (337 mg, yield: 84%) as a colorless oil. IR (film) ν_{max}: 2942, 2832, 1598, 1489, 1322, 1070, 755, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.52-1.87 (m, 6H), 3.45-3.50 (m, 4H), 3.60 (t, *J* = 7.5 Hz, 1H), 3.88 (d, *J* = 13.7 Hz, 2H), 7.22-7.25 (m, 2H), 7.29-7.35 (m, 7H), 7.40-7.42 (m, 4H), 7.49-7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.7, 32.0, 33.0, 44.9, 51.9, 55.0, 85.5, 87.6, 123.4, 126.9, 127.9, 128.2, 128.3, 128.9, 131.8, 139.7 ppm; MS (ESI) *m/z* 402 (M + H^+); HRMS (ESI)

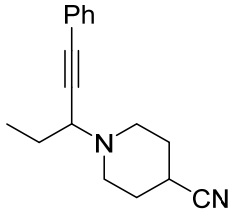
m/z calcd for $[C_{27}H_{29}ClN]^+$ (M + H^+): 402.1983; found: 402.1990.

3-(Methyl(1-phenylpent-1-yn-3-yl)amino)propanenitrile (1o)



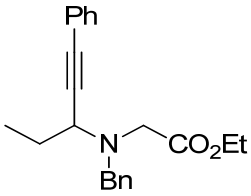
Following general procedure A, the reaction of *tert*-amide **3o** (140 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1o** (192 mg, yield: 85%) as a colorless oil. IR (film) ν_{max}: 2955, 2873, 2249, 1488, 1339, 1070, 1028, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, J = 7.4 Hz, 3H), 1.69-1.77 (m, 2H), 2.35 (s, 3H), 2.52 (t, J = 6.9 Hz, 2H), 2.73-2.80 (m, 1H), 2.84-2.91 (m, 1H), 3.47 (t, J = 7.6 Hz, 1H), 7.29-7.30 (m, 3H), 7.40-7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 17.0, 27.2, 37.8, 50.2, 58.7, 85.8, 86.7, 118.8, 123.0, 128.0, 128.2, 131.7 ppm; MS (ESI) *m/z* 249 (M+Na^+); HRMS (ESI) *m/z* calcd for $[C_{15}H_{18}N_2Na]^+$ (M + Na^+): 249.1362; found: 249.1356.

1-(1-Phenylpent-1-yn-3-yl)piperidine-4-carbonitrile (1p)



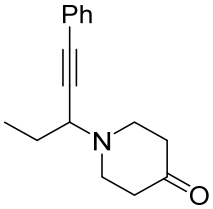
Following general procedure A, the reaction of *tert*-amide **3p** (166 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 60), propargylamine **1p** (194 mg, yield: 77%) as a colorless oil. IR (film) ν_{max}: 2964, 2243, 1488, 1257, 1100, 757, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, J = 7.4 Hz, 3H), 1.68-1.78 (m, 2H), 1.84-2.03 (m, 4H), 2.39-2.43 (m, 1H), 2.59-2.65 (m, 2H), 2.72-2.77 (m, 1H), 2.87-2.93 (m, 1H), 3.41 (dd, J = 8.0, 7.0 Hz, 1H), 7.28-7.30 (m, 3H), 7.42-7.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 26.3, 26.4, 29.0, 29.1, 46.8, 59.7, 86.1, 86.8, 121.7, 123.1, 127.9, 128.2, 131.7 ppm; MS (ESI) *m/z* 214 (M+H^+); HRMS (ESI) *m/z* calcd for $[C_{17}H_{21}N_2]^+$ (M + H^+): 253.1699; found: 253.1693.

Ethyl 2-(benzyl(1-phenylpent-1-yn-3-yl)amino)acetate (1q)



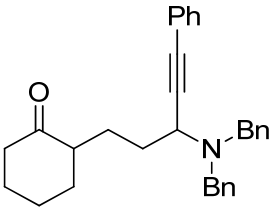
Following general procedure A, the reaction of *tert*-amide **3q** (249 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1q** (268 mg, yield: 80%) as a colorless oil. IR (film) ν_{max}: 2967, 2934, 1749, 1489, 1159, 1029, 755, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, J = 7.4 Hz, 3H), 1.24 (t, J = 7.4 Hz, 3H), 1.67-1.82 (m, 2H), 3.32 (d, J = 16.8 Hz, 2H), 3.43 (d, J = 16.8 Hz, 2H), 3.60-3.67 (m, 2H), 3.95 (d, J = 13.6 Hz, 2H), 4.13 (dt, J = 7.1, 1.0 Hz, 2H), 7.22-7.33 (m, 6H), 7.44-7.46 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 14.2, 27.3, 52.3, 55.6, 56.4, 60.4, 85.4, 87.5, 123.3, 127.1, 127.9, 128.2, 129.0, 131.8, 139.0, 171.7 ppm; MS (ESI) *m/z* 358 ($M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{25}NNaO_2]^+$ ($M + Na^+$):358.1778; found: 358.1782.

1-(1-Phenylpent-1-yn-3-yl)piperidin-4-one (1r)



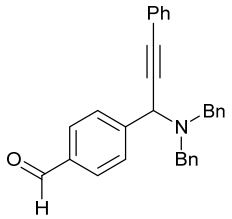
Following general procedure A, the reaction of *tert*-amide **3r** (155 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1r** (181 mg, yield: 75%) as a colorless oil. IR (film) ν_{max}: 2965, 2813, 1721, 1596, 1338, 1209, 757, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.10 (t, J = 7.4 Hz, 3H), 1.75-1.83 (m, 2H), 2.43-2.56 (m, 4H), 2.79-2.85 (m, 2H), 2.98-3.04 (m, 2H), 3.59 (t, J = 7.6 Hz, 1H), 7.27-7.31 (m, 3H), 7.39-7.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 27.0, 41.5, 49.3, 59.0, 86.1, 86.6, 123.0, 128.0, 128.2, 131.7, 209.0 ppm; MS (ESI) *m/z* 264 ($M+Na^+$); HRMS (ESI) *m/z* calcd for $[C_{16}H_{19}NNaO]^+$ ($M + Na^+$): 264.1359; found: 264.1356.

2-(3-(Dibenzylamino)-5-phenylpent-4-yn-1-yl)cyclohexanone (1s)



Following general procedure A, the reaction of *tert*-amide **3s** (349 mg, 1.0 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1s** (396 mg, yield: 91%) as an inseparable diastereomeric mixture (*dr* = 1: 3, determined by ^{1}H NMR). A colorless oil; IR (film) ν_{max}: 2927, 2853, 1601, 1460, 1133, 1050, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, data of the two diastereomers): δ 1.26-1.42 (m, 2H), 1.51-1.67 (m, 2H), 1.71-1.88 (m, 3H), 1.91-2.21 (m, 5H), 2.30-2.35 (m, 1H), 3.46 (d, J = 13.6 Hz, 2H), 3.56 (t, J = 7.5 Hz, 1H), 3.88 (d, J = 13.6 Hz, 2H), 7.22-7.50 (m, 15H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, data of the two diastereomers): δ 24.9, 25.8, 26.2, 27.9, 28.1, 30.8, 31.2, 33.6, 34.3, 42.0, 42.1, 49.7, 49.8, 51.8, 51.9, 54.9, 85.4, 87.8, 123.5, 127.9, 128.2, 128.3, 128.9, 129.0, 131.8, 139.7, 139.8, 212.9, 213.0 ppm; MS (ESI) *m/z* 436 (M + H$^+$); HRMS (ESI) *m/z* calcd for $[C_{31}H_{34}NO]^+$ (M + H$^+$): 436.2635; found: 436.2637.

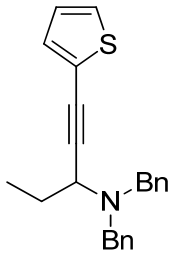
4-(1-(Dibenzylamino)-3-phenylprop-2-yn-1-yl)benzaldehyde (1t)



To a dried 10 mL round-bottom flask containing $IrCl(CO)(PPh_3)_2$ (5.5 mg, 0.5 mol%, weighted in a glove box) were added a toluene (5 mL) solution, *N,N*-dibenzyl-4-formylbenzamide (**3t**) (460.6 mg, 1.4 mmol) and TMDS (296 μL, 1.68 mmol) at rt. After being stirred for 5 min, the resulting solution and phenylacetylene (**2a**) (184 μL, 1.68 mmol) were added to a suspension of CuBr (5 mol%) in toluene (3 mL). The mixture was stirred for 3 h at rt and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:50) to afford the corresponding propargylic amine **1t** (430.0 mg, yield: 74%) as a light yellow oil. IR (film) ν_{max}: 2924, 2851, 2228, 1735, 1605, 1494, 1384, 1261, 1094, 801, 755, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.92–7.84 (m, 4H), 7.69–7.61 (m, 2H), 7.43–7.38 (m, 7H), 7.33 (d, J = 7.4 Hz, 4H), 7.24 (d, J = 6.3 Hz, 2H), 4.96 (s, 1H), 3.77

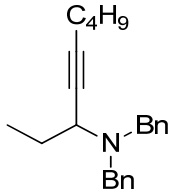
(d, J = 13.4 Hz, 2H), 3.56 (d, J = 13.4 Hz, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.9, 146.4, 139.0, 135.8, 132.0, 129.6, 128.9, 128.9, 128.7, 128.5, 128.5, 128.4, 128.3, 127.2, 122.8, 89.4, 83.5, 56.1, 54.9.ppm; HRMS-ESI calcd for $[C_{30}H_{25}NNaO]^+$ ($M+Na^+$): 438.1828; found: 438.1835.

_N_,_N_-dibenzyl-1-(thiophen-2-yl)pent-1-yn-3-amine (1u)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 2-ethynylthiophene (**2b**) (129.6 mg, 0.12 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1u** (310 mg, yield: 90%) as a colorless oil. IR (film) ν_{max}: 3027, 2964, 2932, 1493, 1453, 745, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, J = 7.4 Hz, 3H), 1.71-1.84 (m, 2H), 3.46 (d, J = 13.8 Hz, 2H), 3.52 (t, J = 7.7 Hz, 1H), 3.87 (d, J = 13.8 Hz, 2H), 6.97-6.99 (m, 1H), 7.21-7.24 (m, 4H), 7.29-7.32 (m, 4H), 7.40-7.42 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 26.9, 54.3, 55.0 (2C), 78.2, 92.2, 123.6, 126.3, 126.8, 128.2, 128.8, 131.5, 139.8 ppm; MS (ESI) *m/z* 346 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{23}H_{24}NS]^+$ ($M + H^+$): 346.1624; found: 346.1623.

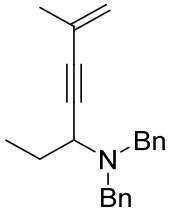
_N_,_N_-Dibenzylnon-4-yn-3-amine (1v)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with hex-1-yne (**2c**) (98.5 mg, 0.14 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1v** (271 mg, yield: 85%) as a colorless oil. IR (film) ν_{max}: 2931, 2872, 1494, 1453, 744, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, J = 7.5 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 1.45-1.72 (m, 6H), 2.28 (dt, J = 2.0, 6.8 Hz, 2H), 3.26 (tt, J = 2.0, 7.5 Hz, 1H), 3.38 (d, J = 13.8 Hz, 2H), 3.78 (d, J = 13.8 Hz, 2H), 7.18-7.40 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 13.6, 18.4, 22.0, 27.3, 31.4, 53.7,

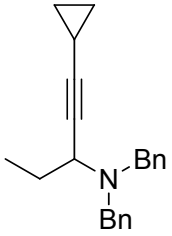
54.9, 77.9, 85.0, 126.7, 128.1, 128.8, 140.2 ppm; MS (ESI) *m/z* 320 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{23}H_{30}N]^+$ ($M + H^+$): 320.2373; found: 320.2370.

_N,N_-dibenzyl-6-methylhept-6-en-4-yn-3-amine (1w)



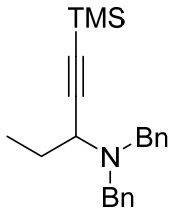
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 2-methylbut-1-en-3-yne (**2d**) (79 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1w** (332 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 3058, 3026, 2965, 2830, 1610, 1495, 1450, 1367, 1283, 1127, 1072, 1024, 896, 745, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.4 Hz, 3H), 1.63-1.77 (m ,2H), 1.96 (s, 3H), 3.38-3.42 (m, 3H), 3.82 (d, J = 13.6 Hz, 2H), 5.22 (br. s, 1H), 5.32 (br. s, 1H), 7.19-7.24 (m, 2H), 7.28-7.31 (m, 4H), 7.38-7.40 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 24.1, 27.0, 54.0, 54.9, 86.5, 87.0, 120.9, 126.8, 127.0, 128.2 (4C), 128.8, 139.9 ppm; MS (ESI) *m/z* 304 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{26}N]^+$ ($M + H^+$): 304.2060; found: 304.2059.

_N,N_-Dibenzyl-1-cyclopropylpent-1-yn-3-amine (1x)



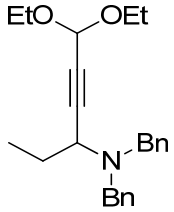
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with ethynylcyclopropane (**2e**) (79.2 mg, 0.10 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1x** (248 mg, yield: 82%) as a colorless oil. IR (film) ν_{max}: 3026, 2963, 2932, 1494, 1453, 1027, 745, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.67-0.71 (m, 2H), 0.77-0.85 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H), 1.26-1.34 (m, 1H), 1.53-1.70 (m, 2H), 3.22 (dt, J = 1.4, 7.5 Hz, 1H), 3.36 (d, J = 13.8 Hz, 2H), 3.77 (d, J = 13.8 Hz, 2H), 7.18-7.23 (m, 2H), 7.26-7.30 (m, 4H), 7.37-7.39 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.5, 8.6, 11.2, 27.2, 53.6, 54.8, 73.1, 88.4, 126.7, 128.1, 128.8, 140.1 ppm; MS (ESI) *m/z* 304 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{26}N]^+$ ($M + H^+$): 304.2060; found: 304.2060.

***N*,*N*-Dibenzyl-1-(trimethylsilyl)pent-1-yn-3-amine (1y)**



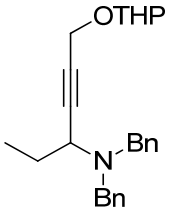
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with ethynyltrimethylsilane (**2f**) (117.7 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1y** (268 mg, yield: 80%) as a colorless oil. IR (film) ν_{max}: 3027, 2962, 2934, 2158, 1453, 1249, 842, 745, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, 9H), 0.92 (t, J = 7.4 Hz, 3H), 1.60-1.73 (m, 2H), 3.28 (t, J = 7.7 Hz, 1H), 3.37 (d, J = 13.8 Hz, 2H), 3.79 (d, J = 13.8 Hz, 2H), 7.21-7.23 (m, 2H), 7.27-7.31 (m, 4H), 7.37-7.39 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.4, 11.1, 26.8, 54.2, 54.8, 89.1, 104.5, 126.8, 128.2, 128.8, 140.0 ppm; MS (ESI) *m/z* 336 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{30}NSi]^+$ ($M + H^+$): 336.2142; found: 336.2139.

***N*,*N*-Dibenzyl-6,6-diethoxyhex-4-yn-3-amine (1z)**



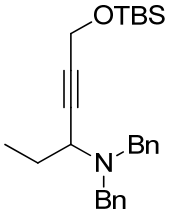
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 3,3-diethoxyprop-1-yne (**2g**) (153.6 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1z** (329 mg, yield: 90%) as a colorless oil. IR (film) ν_{max}: 2950, 1450, 1300, 1150, 1065, 705, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.3 Hz, 3H), 1.28 (t, J = 7.1 Hz, 6H), 1.64-1.78 (m, 2H), 3.36 (dt, J = 1.3, 7.6 Hz, 1H), 3.40 (d, J = 13.9 Hz, 2H), 3.61-3.72 (m, 2H), 3.77-3.86 (m, 4H), 5.39 (d, J = 1.3 Hz, 1H), 7.20-7.39 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 15.2, 26.7, 53.4, 54.9, 60.8, 80.5, 83.8, 91.5, 126.9, 128.2, 128.7, 139.7 ppm; MS (ESI) *m/z* 366 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{24}H_{32}NO_2]^+$ ($M + H^+$): 366.2428; found: 366.2428.

***N*,*N*-Dibenzyl-6-((tetrahydro-2*H*-pyran-2-yl)oxy)hex-4-yn-3-amine (1aa)**



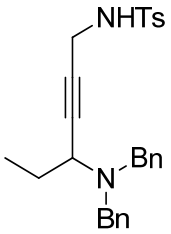
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 2-(prop-2-yn-1-yloxy)tetrahydro-2H-pyran (**2h**) (168.2 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1aa** (332 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 2939, 1492, 1453, 1360, 1123, 1024, 902, 745, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.4 Hz, 3H), 1.53-1.92 (m, 8H), 3.33 (t, J = 7.6 Hz, 1H), 3.39 (d, J = 13.9 Hz, 2H), 3.54-3.59 (m, 1H), 3.81 (d, J = 13.9 Hz, 2H), 3.88-3.93 (m, 1H), 4.39 (s, 2H), 4.94 (t, J = 3.4 Hz, 1H), 7.19-7.39 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 19.2, 25.4, 26.9, 30.4, 53.6, 54.4, 54.9, 62.2, 80.6, 84.2, 96.5, 126.8, 128.2, 128.7, 139.9 ppm; MS (ESI) *m/z* 378 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{25}H_{32}NO_2]^+$ ($M + H^+$): 378.2428; found: 378.2427.

_N,N_-Dibenzyl-6-((*tert*-butyldimethylsilyl)oxy)hex-4-yn-3-amine (1ab)



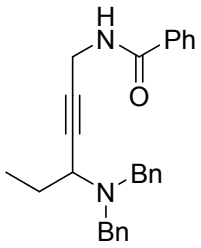
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (**2i**) (204.1mg, 0.14 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ab** (362 mg, yield: 89%) as a colorless oil. IR (film) ν_{max}: 2955, 2930, 2853, 1636, 1447, 1367, 1123, 1085, 838, 774, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 6H), 0.93 (t, J = 7.4 Hz, 3H), 0.96 (s, 9H), 1.61-1.76 (m, 2H), 3.31 (t, J = 7.9 Hz, 1H), 3.41 (d, J = 13.9 Hz, 2H), 3.80 (d, J = 13.9 Hz, 2H), 4.42 (d, J = 1.7 Hz, 2H), 7.19-7.39 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.9 (2C), 11.2, 18.3, 25.9, 26.9, 51.9, 53.5, 54.9, 83.0, 83.6, 126.8, 128.2, 128.7, 139.9 ppm; MS (ESI) *m/z* 408 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{26}H_{38}NOSi]^+$ ($M + H^+$): 408.2717; found: 408.2715.

_N_-(4-(Dibenzylamino)hex-2-yn-1-yl)-4-methylbenzenesulfonamide (1ac)



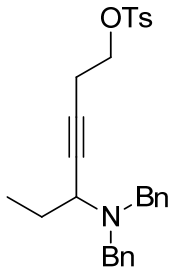
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2j**) (250.8 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ac** (401 mg, yield: 90%) as a white solid. Mp: 86-88 ºC; IR (film) ν_{max}: 3276, 2965, 1601, 1453, 1325, 1159, 1069, 697, 665, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, J = 7.3 Hz, 3H), 1.31-1.45 (m, 1H), 1.50-1.59 (m, 1H), 2.29 (s, 3H), 3.07 (t, J = 7.5 Hz, 1H), 3.16 (d, J = 13.9 Hz, 2H), 3.63 (d, J = 13.9 Hz, 2H), 3.96 (dt, J = 1.6, 6.0 Hz, 2H), 4.73 (br.s, 1H), 7.20-7.32 (m, 12H), 7.79-7.81 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 21.4, 26.6, 33.3, 53.3, 54.7, 79.0, 83.1, 126.9, 127.3, 128.2, 128.6, 129.7, 137.0, 139.6, 143.6 ppm; MS (ESI) *m/z* 447 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{27}H_{31}N_2O_2S]^+$ ($M + H^+$): 447.2101; found: 447.2102.

_N_-(4-(Dibenzylamino)hex-2-yn-1-yl)benzamide (1ad)



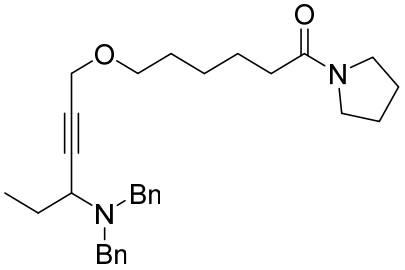
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with *N*-(prop-2-yn-1-yl)benzamide (**2k**) (191 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30), propargylamine **1ad** (356 mg, yield: 90%) as a white solid, Mp: 92-94 ºC; IR (film) ν_{max}: 3311, 3058, 3023, 2968, 2930, 1639, 1537, 1488, 1450, 1290, 1075, 970, 742, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.4 Hz, 3H), 1.61-1.77 (m, 2H), 3.32 (dt, J = 7.7, 1.8 Hz, 1H), 3.39 (d, J = 13.8 Hz, 2H), 3.80 (d, J = 13.8 Hz, 2H), 4.36 (dd, J = 5.1, 1.8 Hz, 2H), 6.31 (s, 1H), 7.19-7.54 (m, 13H), 7.80-7.82 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 26.8, 30.2, 53.5, 54.8, 80.3, 82.1, 126.8, 127.0, 128.2, 128.6, 128.7, 131.7, 134.1, 139.7, 167.0 ppm; MS (ESI) *m/z* 397 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{27}H_{29}N_2O]^+$ ($M + H^+$): 397.2274; found: 397.2278.

5-(Dibenzylamino)hept-3-yn-1-yl 4-methylbenzenesulfonate (1ae)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with but-3-yn-1-yl 4-methylbenzenesulfonate (**2l**) (268.9 mg, 0.21 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ae** (401 mg, yield: 87%) as a colorless oil; IR (film) ν_{max}: 2965, 1597, 1492, 1453, 1364, 1175, 1095, 976, 902, 752, 694, 662, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.4 Hz, 3H), 1.50-1.71 (m, 2H), 2.41 (s, 3H), 2.66 (dt, J = 1.8, 6.9 Hz, 2H), 3.20 (t, J = 7.6 Hz, 1H), 3.30 (d, J = 13.9 Hz, 2H), 3.73 (d, J = 13.9 Hz, 2H), 4.16 (dt, J = 1.1, 6.9 Hz, 2H), 7.20-7.37 (m, 12H), 7.81-7.83 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 19.8, 21.6, 26.9, 53.5, 54.8 (2C), 68.2, 78.9, 80.6, 126.8, 127.9, 128.2, 128.7, 129.9, 133.1, 139.9, 144.9 ppm; MS (ESI) *m/z* 462 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{28}H_{32}NO_3S]^+$ ($M + H^+$): 462.2097; found: 462.2098.

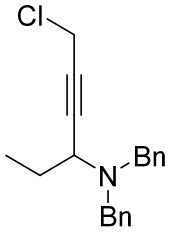
6-((4-(Dibenzylamino)hex-2-yn-1-yl)oxy)-1-(pyrrolidin-1-yl)hexan-1-one (1af)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 6-(prop-2-yn-1-yloxy)-1-(pyrrolidin-1-yl)hexan-1-one (**2m**) (268 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 40), propargylamine **1af** (368 mg, yield: 80%) as a colorless oil; IR (film) ν_{max}: 2936, 2869, 1642, 1428, 1348, 1095, 742, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.4 Hz, 3H), 1.42-1.50 (m, 2H), 1.63-1.75 (m, 6H), 1.80-1.86 (m, 2H), 1.89-1.94 (m, 2H), 2.27 (t, J = 7.6 Hz, 3H), 3.31-3.46 (m, 7H), 3.59 (t, J = 6.5 Hz, 2H), 3.81 (d, J = 13.8 Hz, 2H), 4.25 (d, J = 1.6 Hz, 2H), 7.20-7.39 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 24.4, 24.7, 26.1, 26.2, 26.9,

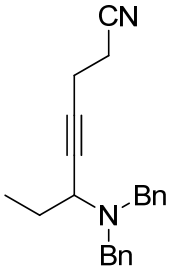
29.5, 34.7, 45.5, 53.6, 54.9, 58.4, 69.7, 80.9, 84.3, 126.8, 128.2, 128.7, 139.8, 171.5 ppm; MS (ESI) *m/z* 461 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{30}H_{41}N_2O_2]^+$ ($M + H^+$): 461.3163; found: 461.3167.

_N,N_-dibenzyl-6-chlorohex-4-yn-3-amine (1ag)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 3-chloroprop-1-yne (**2n**) (88.8 mg, 90 μL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ag** (267 mg, yield: 86%) as a colorless oil; IR (film) ν_{max}: 2965, 1494, 1453, 1260, 1130, 745, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.4 Hz, 3H), 1.61-1.76 (m, 2H), 3.32-3.37 (m, 1H), 3.39 (d, J = 13.8 Hz, 2H), 3.81 (d, J = 13.8 Hz, 2H), 4.25 (d, J = 1.9 Hz, 2H), 7.20-7.23 (m, 2H), 7.28-7.31 (m, 4H), 7.37-7.40 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 26.7, 30.9, 53.6, 54.9, 79.8, 85.4, 126.9, 128.4, 128.8, 139.7 ppm; MS (ESI) *m/z* 312 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{20}H_{23}ClN]^+$ ($M + H^+$): 312.1514; found: 312.1512.

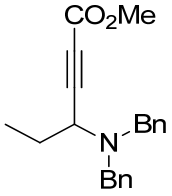
6-(Dibenzylamino)oct-4-ynenitrile (1ah)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with pent-4-ynenitrile (**2o**) (94.8 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ah** (256 mg, yield: 81%) as a colorless oil; IR (film) ν_{max}: 3027, 2965, 2932, 2205, 1494, 1453, 1154, 740, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.4 Hz, 3H), 1.59-1.75 (m, 2H), 2.56-2.66 (m, 4H), 3.29 (t, J = 7.7 Hz, 1H), 3.40 (d, J = 13.8 Hz, 2H), 3.81 (d, J = 13.8 Hz, 2H), 7.19-7.23 (m, 2H), 7.28-7.31 (m, 4H), 7.38-7.40 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 16.2, 18.3, 27.0, 53.5, 54.8, 80.5, 81.3, 118.5, 126.9, 128.2, 128.8, 139.9 ppm; MS (ESI) *m/z* 317

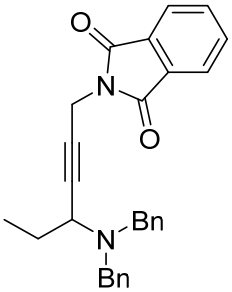
(M+H$^+$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{25}N_2]^+$ (M + H$^+$): 317.2012; found: 317.2014.

Methyl 4-(dibenzylamino)hex-2-ynoate (1ai)



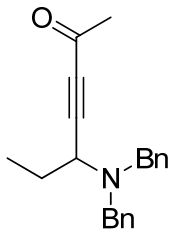
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with methyl propiolate (**2p**) (100.8 mg, 0.11 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ai** (260 mg, yield: 81%) as a colorless oil; IR (film) ν_{max}: 3028, 2967, 2223, 1710, 1453, 1250, 1072, 741, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, J = 7.4 Hz, 3H), 1.69-1.82 (m, 2H), 3.41 (d, J = 13.8 Hz, 2H), 3.43 (t, J = 7.8 Hz, 1H), 3.82 (s, 3H), 3.86 (d, J = 13.8 Hz, 2H), 7.21-7.25 (m, 2H), 7.29-7.32 (m, 4H), 7.37-7.39 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 26.2, 52.7, 53.4, 54.9, 77.1, 87.1, 127.1, 128.3, 128.7, 139.1, 154.1 ppm; MS (ESI) *m/z* 322 (M+H$^+$); HRMS (ESI) *m/z* calcd for $[C_{21}H_{24}NO_2]^+$ (M + H$^+$): 322.1802; found: 322.1798.

2-(4-(Dibenzylamino)hex-2-yn-1-yl)isoindoline-1,3-dione (1aj)



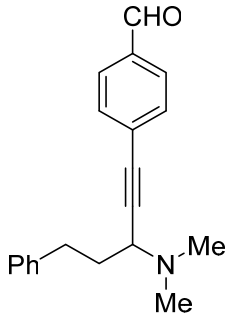
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (**2q**) (222 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50), propargylamine **1aj** (363 mg, yield: 86%) as a white solid. Mp: 76-79 ^{o}C; IR (film) ν_{max}: 1770, 1716, 1418, 1389, 1341, 1120, 1072, 944, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.3 Hz, 3H), 1.57-1.71 (m, 2H), 3.26 (t, J = 7.7 Hz, 1H), 3.35 (d, J = 13.8 Hz, 2H), 3.76 (d, J = 13.8 Hz, 2H), 4.06 (d, J = 1.8 Hz, 2H), 7.17-7.35 (m, 10H), 7.73-7.75 (m, 2H), 7.89-7.92 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 26.7, 27.5, 53.5, 54.8, 78.3, 81.6, 123.5, 126.7, 128.1, 128.7, 132.1, 134.1, 139.8, 167.1 ppm; MS (ESI) *m/z* 423 (M+H$^+$); HRMS (ESI) *m/z* calcd for $[C_{28}H_{27}N_2O_2]^+$ (M + H$^+$): 423.2067; found: 423.2067.

5-(Dibenzylamino)hept-3-yn-2-one (1ak)



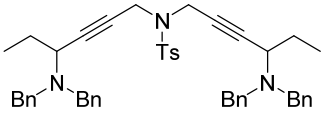
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with but-3-yn-2-one (**2r**) (81.6 mg, 0.09 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1ak** (262 mg, yield: 86%) as a pale yellow solid. Mp: 40-42 ^{o}C; IR (film) ν_{max}: 3028, 2967, 2223, 1710, 1453, 1250, 1072, 741, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, J = 7.4 Hz, 3H), 1.68-1.82 (m, 2H), 2.41 (s, 3H), 3.40 (d, J = 13.8 Hz, 2H), 3.47 (t, J = 7.7 Hz, 1H), 3.85 (d, J = 13.8 Hz, 2H), 7.21-7.25 (m, 2H), 7.29-7.32 (m, 4H), 7.36-7.38 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 26.3, 33.2, 53.6, 55.0, 85.4, 91.4, 127.2, 128.4, 128.8, 139.1, 184.5 ppm; MS (ESI) *m/z* 306 (M+H$^+$); HRMS (ESI) *m/z* calcd for $[C_{21}H_{24}NO]^+$ (M + H$^+$): 306.1852; found: 306.1851.

4-(3-(Dimethylamino)-5-phenylpent-1-yn-1-yl)benzaldehyde (1al)



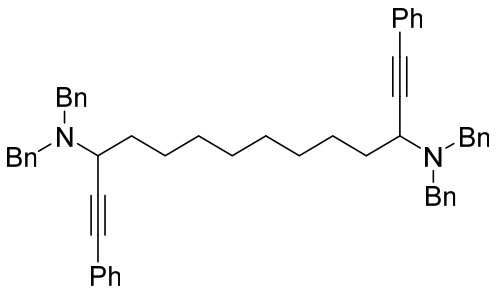
Following general procedure A, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 4-ethynylbenzaldehyde (**2s**) (157 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 5), propargylic amine **1al** (241 mg, yield: 83%) as a yellow solid. Mp: 95-97°C; IR (film): 3026, 2946, 2859, 2823, 2779, 2728, 1702, 1600, 1206, 1164, 829, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06-1.99 (m, 2H), 2.33 (s, 6H), 2.90-2.75 (m, 2H), 3.53 (t, J = 7.6 Hz, 1H), 7.25-7.17 (m, 3H), 7.31-7.27 (m, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.83-7.79 (m, 2H), 9.99 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.6, 35.2, 41.4, 57.3, 85.6, 91.4, 125.9, 128.3, 128.5, 129.4, 129.6, 132.2, 135.2, 141.4, 191.3 ppm; HRMS (ESI) calcd for $C_{20}H_{22}NO$ [M+H$^+$]: 292.1696, found: 292.1697.

***N,N*-Bis(4-(dibenzylamino)hex-2-yn-1-yl)-4-methylbenzenesulfonamide (1am)**



Following general procedure A (except that only 0.6 equiv of bisalkyne **2t** was used), the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with 4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide (**2t**) (148 mg, 0.6 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 150), propargylamine **1am** (314 mg, yield: 87%) as an inseparable diastereomeric mixture (*dr* = 1: 1, determined by ^{1}H NMR). Colorless oil; IR (film) ν_{max}: 2908, 1639, 1450, 1354, 1165, 749, 697, 659 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, data of the two diastereomers): δ 0.77 (t, J = 7.3 Hz, 6H), 1.37-1.57 (m, 4H), 2.12 (s, 3H), 3.08 (t, J = 7.6 Hz, 2H), 3.16 (d, J = 13.8 Hz, 4H), 3.61 (d, J = 13.8 Hz, 4H), 4.29 (br.s, 4H), 7.10-7.24 (m, 22H), 7.64-7.66 (m, 2H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ 11.4, 21.5, 27.2, 37.0, 54.0, 55.3, 77.4, 84.7, 127.3, 128.2, 128.6, 129.1, 130.2, 135.9, 140.1, 144.4 ppm; HRMS (ESI) *m/z* calcd for $[C_{47}H_{52}N_3O_2S]^+$ (M + H$^+$): 722.3775; found: 722.3782.

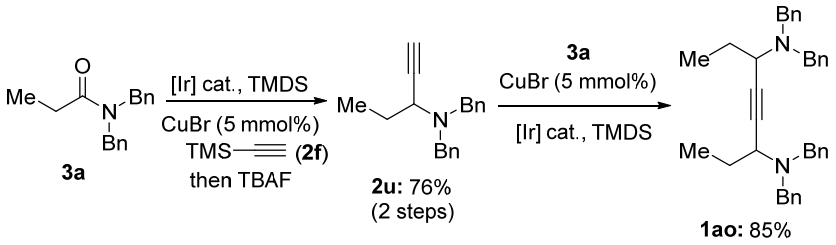
***N*^{3},*N*^{3},*N*^{12},*N*^{12}-Tetrabenzyl-1,14-diphenyltetradeca-1,13-diyne-3,12-diamine (1an)**



Following general procedure A (except that double amounts of Vaska's complex, TMDS, and alkyne **2a** were used), the reaction of *tert*-amide **3v** (280 mg, 0.5 mmol) with phenylacetylene (**2a**) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 100), propargylamine **1an** (344 mg, yield: 94%) as an inseparable diastereomeric mixture (*dr* = 1: 1, determined by ^{1}H NMR). White solid, Mp: 91-93 ^{o}C; IR (film) ν_{max}: 3026, 2927, 2850, 1601, 1495, 1447, 1133, 1075, 752, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, data of the two diastereomers): δ 1.06-1.09 (m, 8H), 1.29-1.40 (m, 4H), 1.57-1.76 (m, 4H), 3.39 (d, J = 13.7 Hz, 4H), 3.51 (t, J = 7.6 Hz, 2H), 3.80 (d, J = 13.7 Hz, 4H), 7.12-7.15 (m, 4H), 7.20-7.26 (m, 14H), 7.32-7.34 (m, 8H), 7.41-7.43 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, data of the two diastereomers): δ 26.3, 29.1, 29.5, 33.8, 52.1, 55.0, 85.2, 88.2, 123.6, 126.8, 127.8, 128.2, 128.3, 128.4, 131.8, 139.9 ppm; MS

(ESI) *m/z* 733 (M+H$^+$); HRMS (ESI) *m/z* calcd for $[C_{54}H_{57}N_2]^+$ (M + H$^+$): 733.4516; found: 733.4522.

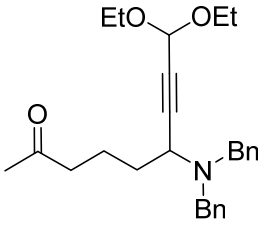
N^3,*N*^{3},*N*^{6}, *N*^{6}-Tetrabenzyloct-4-yne-3,6-diamine (1ao)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with ethynyltrimethylsilane (**2f**) (1.2 mmol, 1.2 equiv) gave, a crude propargylamine, which was dissolved in dichloromethane. Then TBAF (1.2 mmol, 1.2 equiv) was added. After the reaction was complete, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C and extracted with DCM (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the known product **2u**[1] (200 mg, yield: 76%) as a colorless oil.

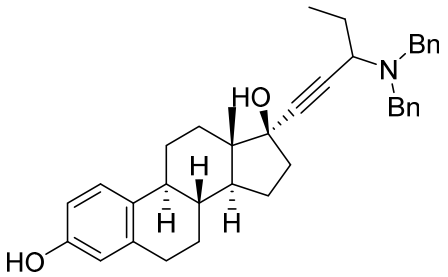
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with *N,N*-dibenzylpent-1-yn-3-amine (**2u**) (315 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 150), propargylamine **1ao** (425 mg, yield: 85%) as an inseparable diastereomeric mixture (*dr* = 1: 1, determined by ^{1}H NMR). White solid, Mp: 101-103 ^{o}C; IR (film) ν_{max}: 3026, 2962, 2930, 2805, 1597, 1495, 1450, 1130, 1069, 1027, 963, 742, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, data of the two diastereomers): δ 1.00 (t, *J* = 7.4 Hz, 6H), 1.68-1.82 (m, 4H), 3.41 (t, *J* = 7.3 Hz, 2H), 3.49 (d, *J* = 13.8 Hz, 4H), 3.88 (d, *J* = 13.8 Hz, 4H), 7.22-7.44 (m, 20H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, data of the two diastereomers): δ 11.3, 27.5, 53.7, 55.1, 82.6, 126.8, 128.2, 128.8, 140.0 ppm; MS (ESI) m/z 501 (M + H$^+$); HRMS (ESI) m/z calcd for $[C_{36}H_{41}N_2]^+$ (M + H$^+$): 501.3264; found: 501.3268.

6-(Dibenzylamino)-9,9-diethoxynon-7-yn-2-one (1ap)



Following general procedure A, the reaction of keto amide **3w** (309 mg, 1.0 mmol) with 3,3-diethoxyprop-1-yne (**2g**) (153.6 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 5), keto propargylamine **1ap** (358 mg, yield: 85%) as a colorless oil; IR (film) ν_{max}: 2976, 2931, 2884, 1716, 1454, 1356, 1134, 1052, 749, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39-7.34 (m, 4H), 7.32-7.27 (m, 4H), 7.24-7.20 (m, 2H), 5.38 (s, 1H), 3.87-3.76 (m, 4H), 3.68-3.61 (m, 2H), 3.45 (t, J = 7.1 Hz, 1H), 3.38 (d, J = 13.6 Hz, 2H), 2.25-2.12 (m, 2H), 2.01 (s, 3H), 1.82-1.67 (m, 2H), 1.65-1.55 (m, 2H), 1.28 (dt, J = 2.1, 7.1 Hz, 6H) ppm; ^{13}C-NMR (CDCl3, 125 MHz) δ 208.3, 139.3, 128.8 (2C), 128.2 (2C), 126.9, 91.4, 83.2, 80.7, 60.7, 54.8, 50.8, 42.5, 32.5, 29.7, 20.1, 15.1 ppm; HRMS (ESI) calcd for $[C_{27}H_{36}NO_3]^+$ $(M+H)^+$: 422.2690; found: 422.2695.

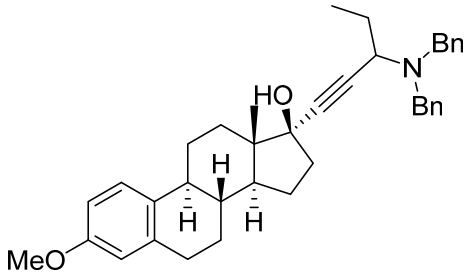
(8*R*,9*S*,13*S*,14*S*,17*S*)-17-(3-(Dibenzylamino)pent-1-yn-1-yl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene-3,17-diol (1aq)



Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with ethinylestradiol (**2v**) (355 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 20), propargylic amine **1aq** (341 mg, yield: 64%) as an inseparable diastereomeric mixture (*dr* = 1: 1.4, determined by ^1H NMR), white solid. Mp: 99-102 °C; IR (film) ν_{max}: 3385, 2927, 1604, 1498, 1447, 1383, 1248, 1197, 1175, 1130, 1072, 742, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, data of the two diastereomers): δ 0.92-0.96 (m, 6H), 1.34-1.56 (m, 4H), 1.61-2.14 (m, 10H), 2.20-2.25 (m, 1H), 2.33-2.40 (m, 2H), 2.82-2.86 (m, 2H), 3.35-3.39 (m, 1H), 3.42 (d, *J* = 13.7 Hz, 2H), 3.83 (d, *J* = 13.7 Hz, 2H), 6.56 (s, 1H), 6.62-6.65 (m, 1H), 7.16-7.23 (m, 3H), 7.27-7.32 (m, 4H), 7.36-7.37 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, data of the two diastereomers): δ 11.2, 12.9, 22.8, 26.5,

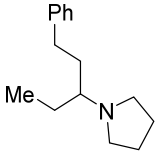
26.9, 27.0, 27.4, 29.6, 33.0, 33.1, 39.5, 39.7, 43.9, 44.0, 47.2, 49.8, 53.5, 53.6, 55.1, 80.2, 84.3, 84.4, 88.5, 112.8, 115.3, 126.5, 126.9, 128.2, 128.7, 132.5, 138.2, 139.7, 153.5 ppm; MS (ESI) *m/z* 534 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{37}H_{44}NO_2]^+$ ($M + H^+$): 534.3367; found: 534.3369.

(8*R*,9*S*,13*S*,14*S*,17*S*)-17-(3-(Dibenzylamino)pent-1-yn-1-yl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (1ar)



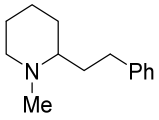
Following general procedure A, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with (8*R*,9*S*,13*S*,14*S*,17*R*)-17-ethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (**2w**) (372 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 20), propargylic amine **1ar** (470 mg, yield: 86%) as an inseparable diastereomeric mixture (*dr* = 1: 1.3, determined by ^{1}H NMR), colorless foam. IR (film) ν_{max}: 3420, 2927, 1626, 1455, 1194, 1136, 1075, 742, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, data of the two diastereomers): δ 0.92 (s, 3H), 0.95 (t, J = 7.4 Hz, 3H), 1.34-1.54 (m, 4H), 1.61-2.12 (m, 9H), 2.23-2.27 (m, 1H), 2.31-2.42 (m, 2H), 2.85-2.94 (m, 2H), 3.35-3.39 (m, 1H), 3.41 (d, J = 13.7 Hz, 2H), 3.78 (s, 3H), 3.84 (d, J = 13.7 Hz, 2H), 6.64 (s, 1H), 6.71-6.74 (m, 1H), 7.20-7.31 (m, 7H), 7.36-7.38 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, data of the two diastereomers): δ 11.2, 11.3, 12.8, 22.8, 26.5, 26.9, 27.0, 27.5, 29.8, 33.0, 33.1, 39.5, 39.6, 43.9, 44.0, 47.2, 49.7, 49.8, 53.5 (2C), 55.1, 55.2, 80.1 (2C), 84.2, 84.3, 88.6, 111.5, 113.8, 126.4, 126.9, 128.2, 128.7, 132.5 (2C), 137.9, 139.7, 157.5 ppm; MS (ESI) *m/z* 548 ($M+H^+$); HRMS (ESI) *m/z* calcd for $[C_{38}H_{46}NO_2]^+$ ($M + H^+$): 548.3523; found: 548.3528.

1-(1-Phenylpentan-3-yl)pyrrolidine (4a)



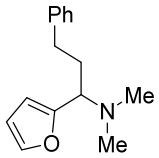
Following general procedure B, the reaction of the reaction of *tert*-amide **3g** (127 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4a** (165 mg, yield: 76%) as a colorless oil. IR (film) ν_{max}: 2963, 2873, 2781, 1603, 1495, 1454, 1379, 745, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.23-7.15 (m, 3H), 2.83-2.69 (m, 5H), 2.67-2.57 (m, 1H), 2.42-2.32 (m, 1H), 1.95-1.80 (m, 6H), 1.77-1.68 (m, 1H), 1.67-1.56 (m, 1H), 0.98 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 128.4, 128.3, 125.9, 64.5, 51.2, 32.4, 31.8, 23.6, 23.5, 10.1 ppm; HRMS (ESI) calcd for $[C_{15}H_{24}N]^+$ $(M+H)^+$: 218.1903; found: 218.1874.

1-Methyl-2-phenethylpiperidine (4b)



Following general procedure B, the reaction of *tert*-amide **3x** (113 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4b** (144 mg, yield: 71%) as a colorless oil. IR (film) ν_{max}: 2933, 2854, 2776, 1603, 1495, 1453, 1374, 1030, 770, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.24-7.17 (m, 3H), 2.96-2.86 (m, 1H), 2.75 (ddd, J = 5.3, 11.5, 14.0 Hz, 1H), 2.59 (ddd, J = 5.3, 11.5, 14.0 Hz, 1H), 2.32 (s, 3H), 2.20-2.10 (m, 1H), 2.06-1.88 (m, 2H), 1.84-1.72 (m, 3H), 1.68-1.59 (m, 2H), 1.53-1.40 (m, 1H), 1.38-1.24 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.4, 128.3, 125.7, 63.4, 57.1, 42.8, 34.6, 31.3, 30.4, 25.6, 24.3 ppm; HRMS (ESI) calcd for $[C_{14}H_{22}N]^+$ $(M+H)^+$: 204.1747; found: 204.1729.

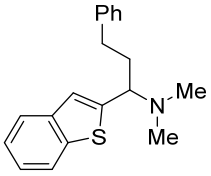
1-(Furan-2-yl)-*N*,*N*-dimethyl-3-phenylpropan-1-amine (4c)



Following general procedure B, the reaction of *tert*-amide **3y** (139 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (213 μL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 20) the title product **4c** (188 mg, yield: 82%) as colorless oil. IR (film): 3025, 2931, 2858, 2820, 2777, 1496, 1454, 1158, 1026, 873, 789, 699, 602 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 1H), 7.34-7.27 (m,

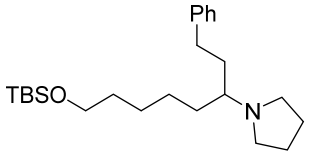
2H), 7.24-7.17 (m, 3H), 6.38 (dd, J = 1.8, 3.2 Hz, 1H), 6.19 (d, J = 3.2 Hz, 1H), 3.56 (t, J = 7.5 Hz, 1H), 2.61 (dd, J = 7.6, 8.3 Hz, 2H), 2.24 (s, 6H), 2.20-2.12 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 142.0, 141.7, 128.5, 128.3, 125.8, 109.7, 108.2, 61.7, 41.6, 32.9, 32.8 ppm; HRMS (ESI) calcd for $[C_{15}H_{20}NO]^+$ $(M+H)^+$: 230.1539; found: 230.1537.

1-(Benzo[*b*]thiophen-2-yl)-*N*,*N*-dimethyl-3-phenylpropan-1-amine (4d)



Following general procedure B, the reaction of *tert*-amide **3z** (205 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (213 μL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30) the title product **4d** (254 mg, yield: 86%) as a colorless oil. IR (film): 3059, 3025, 2928, 2857, 2822, 2778, 1602, 1495, 1455, 1434, 1355, 745, 726, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.36-7.23 (m, 4H), 7.20-7.13 (m, 3H), 7.11 (s, 1H), 3.70 (dd, J = 5.2, 9.2 Hz, 1H), 2.66-2.54 (m, 2H), 2.33-2.23 (m, 7H), 2.16-2.05 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 141.8, 139.6, 139.4, 128.5, 128.4, 125.9, 124.1, 124.0, 123.2, 122.8, 122.3, 65.2, 42.1, 36.1, 32.9 ppm; HRMS (ESI) calcd for $[C_{19}H_{22}NS]^+$ $(M+H)^+$: 296.1467; found: 296.1473.

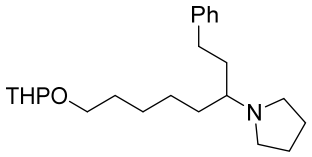
1-(8-((*Tert*-butyldimethylsilyl)oxy)-1-phenyloctan-3-yl)pyrrolidine (4e)



Following general procedure B, the reaction of *tert*-amide **3j** (299 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4e** (315 mg, yield: 81%) as a colorless oil. IR (film) ν_{max}: 3025, 2930, 2856, 2784, 1495, 1471, 1461, 1386, 1360, 1254, 1101, 835, 775, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.25-7.16 (m, 3H), 3.65 (t, J = 6.6 Hz, 2H), 2.79-2.58 (m, 6H), 2.41-2.29 (m, 1H), 1.95-1.74 (m, 6H), 1.70-1.49 (m, 4H), 1.48-1.32 (m, 4H), 0.94 (s, 9H), 0.09 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 128.3 (4C), 125.7, 63.2, 62.7, 50.8, 33.3, 32.9, 31.9,

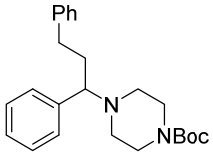
31.1, 26.3, 26.0, 25.7, 23.5, 18.4, −5.2 ppm; HRMS (ESI) calcd for $[C_{24}H_{44}NOSi]^+$ $(M+H)^+$: 390.3187; found: 390.3178.

1-(1-Phenyl-8-((tetrahydro-2*H*-pyran-2-yl)oxy)octan-3-yl)pyrrolidine (4f)



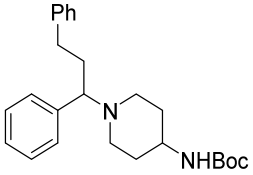
Following general procedure B, the reaction of *tert*-amide **3k** (269 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30) the title product **4f** (305 mg, yield: 85%) as a colorless oil. IR (film) ν_{max}: 2937, 2866, 2786, 1673, 1454, 1352, 1200, 1135, 1077, 1037, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.21-7.13 (m, 3H), 4.59-4.54 (m, 1H), 3.90-3.82 (m, 1H), 3.78-3.70 (m, 1H), 3.52-3.45 (m, 1H), 3.42-3.35 (m, 1H), 3.73-3.56 (m, 6H), 3.36-3.28 (m, 1H), 1.90-1.30 (m, 22H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 128.3, 125.7, 98.8, 67.6, 62.6, 62.3, 50.8, 33.2, 31.9, 31.0, 30.8, 29.7, 26.7, 25.7, 25.5, 23.5, 19.7 ppm; HRMS (ESI) calcd for $[C_{23}H_{38}NO_2]^+$ $(M+H)^+$: 360.2897; found: 360.2904.

***Tert*-butyl 4-(1,3-diphenylpropyl)piperazine-1-carboxylate (4g)**



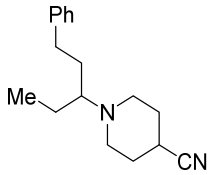
Following general procedure B, the reaction of *tert*-amide **3aa** (290 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (213 μL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 5) the title product **4g** (277 mg, yield: 73%) as a colorless oil. IR (film) ν_{max}: 2974, 2930, 2859, 2811, 1697, 1453, 1421, 1365, 1246, 1172, 1130, 764, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, J = 7.4 Hz, 2H), 7.19-7.10 (m, 5H), 7.06 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.3 Hz, 1H), 3.35-3.23 (m, 5H), 2.43-2.36 (m, 2H), 2.30-2.10 (m, 5H), 2.00-1.90 (m, 1H), 1.32 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 142.2, 139.4, 128.7, 128.4, 128.3, 128.2, 127.3, 125.8, 79.4, 69.1, 49.9, 34.2, 32.6, 28.5 ppm; HRMS (ESI) calcd for $[C_{24}H_{32}N_2O_2Na]^+$ $(M+Na)^+$: 403.2356; found: 403.2363.

***Tert*-butyl (1-(1,3-diphenylpropyl)piperidin-4-yl)carbamate (4h)**



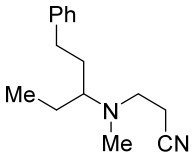
Following general procedure B, the reaction of *tert*-amide **3ab** (304 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (213 μL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 5) the title product **4h** (272 mg, yield: 69%) as a white solid. Mp: 147~149 ºC; IR (film) ν_{max}: 3347, 3025, 2974, 2930, 2800, 2753, 1712, 1495, 1452, 1389, 1365, 1286, 1235, 1172, 1045, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.13 (m, 10H), 4.52 (br. s, 1H), 3.48-3.31 (m, 2H), 2.88 (d, d, J = 10.7 Hz,1H), 2.80 (d, J = 11.5 Hz,1H), 2.59-2.45 (m, 2H), 2.33-2.20 (m, 1H), 2.18-2.05 (m, 2H), 2.02-1.83 (m, 3H), 1.47 (s, 9H), 1.41-1.35 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.3, 139.6, 128.7, 128.4, 128.3, 128.1, 127.2, 125.8, 79.1, 69.0, 50.2, 48.0, 47.7, 34.5, 33.1, 33.0, 32.7, 28.5 ppm; HRMS (ESI) calcd for $[C_{25}H_{35}N_2O_2]^+$ $(M+H)^+$: 395.2693; found: 395.2697.

1-(1-Phenylpentan-3-yl)piperidine-4-carbonitrile (4i)



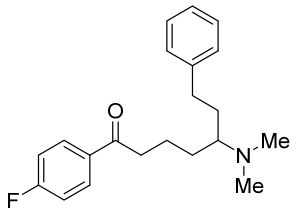
Following general procedure B, the reaction of *tert*-amide **3p** (166 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30) the title product **4i** (205 mg, yield: 80%) as a colorless oil. IR (film) ν_{max}: 2927, 2873, 2806, 2238, 1602, 1494, 1450, 752, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22-7.12 (m, 5H), 2.77-2.59 (m, 4H), 2.41-2.37 (m, 1H), 2.13-2.09 (m, 1H), 1.96-1.76 (m, 4H), 1.74-1.65 (m, 2H), 1,64-1.46 (m, 2H), 1.31-1.24 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 128.3 (2C), 128.2 (2C), 125.6, 122.0, 65.3, 46.7, 46.4, 33.2, 31.6, 29.4 (2C), 26.8, 22.1, 11.8 ppm; HRMS (ESI) calcd for $[C_{17}H_{25}N_2]^+$ $(M+H)^+$: 257.2012; found: 257.2014.

3-(Methyl(1-phenylpentan-3-yl)amino)propanenitrile (4j)



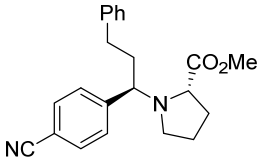
Following general procedure B, the reaction of *tert*-amide **3o** (140 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 10) the title product **4j** (202 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 2930, 2859, 2801, 2247, 1602, 1495, 1454, 1364, 1029, 749, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, J = 7.5 Hz, 2H), 7.21-7.13 (m, 3H), 2.76-2.58 (m, 4H), 2.40-2.27 (m, 3H), 2.23 (s, 3H), 1.70-1.56 (m, 2H), 1.51-1.41 (m, 1H), 1.35-1.25 (m, 1H), 0.89 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 128.5, 128.4, 125.7, 119.3, 64.7, 49.8, 36.1, 33.3, 32.1, 22.6, 17.7, 11.9 ppm; HRMS (ESI) calcd for $[C_{15}H_{23}N_2]^+$ $(M+H)^+$: 231.1856; found: 231.1857.

5-(Dimethylamino)-1-(4-fluorophenyl)-7-phenylheptan-1-one (4k)



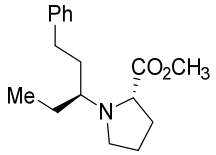
Following general procedure B, the reaction of *tert*-amide **3ac** (237 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4k** (212 mg, yield: 65%) as a colorless oil. IR (film) ν_{max}: 3062, 3025, 2928, 2857, 2819, 2774, 1686, 1598, 1505, 1454, 1230, 1155, 835, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06-7.93 (m, 2H), 7.32-7.27 (m, 2H), 7.25-7.10 (m, 5H), 2.95 (t, J = 7.1 Hz, 2H), 2.67 (t, J = 8.0 Hz, 2H), 2.48-2.39 (m, 1H), 2.27 (s, 6H), 1.88-1.73 (m, 3H), 1.66-1.54 (m, 2H), 1.47-1.37 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 166.8, 164.3, 142.6, 133.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.5 (d, $J_{C\text{-}F}$ = 9.3 Hz), 128.3 (d, $J_{C\text{-}F}$ = 7.1 Hz), 125.6, 115.5 (d, $J_{C\text{-}F}$ = 21.6 Hz), 62.9, 40.2, 38.4, 33.2, 31.2, 28.6, 21.8 ppm; HRMS (ESI) calcd for $[C_{21}H_{26}FNNaO]^+$ $(M+Na)^+$: 350.1891; found: 350.1897.

Methyl ((*R*)-1-(4-cyanophenyl)-3-phenylpropyl)-L-prolinate (4l)



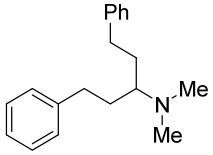
Following general procedure B, the reaction of *tert*-amide **3ad** (361.0 mg, 1.4 mmol) with ethynylbenzene (**2a**) (172 μL, 1.2 mmol) and TMDS (296 μL, 1.2 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 5) the title product **4l** (381.0 mg, yield: 78%, dr = 14: 1) as a light yellow oil. $[\alpha]^{25}_{D}$ −80.5 (*c* 1.0, $CHCl_3$); IR (film) ν_{max}: 2956, 2924, 2852, 2228, 1734, 1653, 1456, 1383, 1196, 1091, 801, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66-7.61 (m, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 7.19-7.16 (m, 1H), 7.06-7.00 (m, 2H), 3.67-3.63 (m, 1H), 3.52 (dd, J = 9.2, 3.0 Hz, 1H), 3.48 (s, 3H), 3.08-3.01 (m, 1H), 2.54-2.46 (m, 1H), 2.37-2.21 (m, 3H), 2.09-1.99 (m, 2H), 1.95-1.78 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 147.7, 141.3, 132.0, 129.5, 128.4, 128.2, 126.0, 118.8, 111.2, 66.9, 62.9, 51.4 (2C), 35.9, 32.1, 30.0, 23.3 ppm; HRMS-ESI calcd for $[C_{22}H_{24}N_2NaO_2]^+$ $(M+Na^+)$: 371.1730; found: 371.1721.

Methyl ((*S*)-1-phenylpentan-3-yl)-L-prolinate (4m)



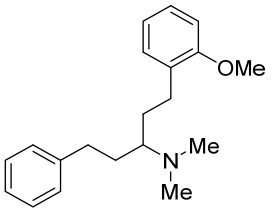
Following general procedure B, the reaction of *tert*-amide **3ae** (185 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30) the title product **4m** (206 mg, yield: 75%, dr = 10.7: 1, determined by ^1H NMR) as a colorless oil. $[\alpha]^{25}_{D}$ −39.8 (*c* 1.0, $CHCl_3$); IR (film) ν_{max}: 2950, 2872, 1732, 1495, 1454, 1434, 1276, 1193, 1167, 747, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.23-7.17 (m, 3H), 3.69 (s, 3H), 3.56 (dd, J = 8.5, 3.7 Hz, 1H), 3.07-7.17 (m, 3H), 2.75-2.56 (m, 4H), 2.08-1.91 (m, 3H), 1.84-1.63 (m, 3H), 1.59-1.48 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 142.8, 128.3 (4C), 125.6, 61.7, 60.9, 51.5, 48.1, 32.9, 32.3, 30.1, 24.5, 24.0, 10.9 ppm; HRMS (ESI) calcd for $[C_{17}H_{26}NO_2]^+$ $(M+H)^+$: 276.1958; found: 276.1959.

***N*,*N*-Dimethyl-1,5-diphenylpentan-3-amine (4n)**



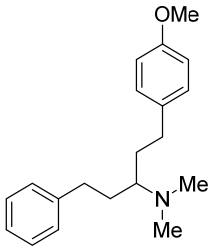
Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4n** (245 mg, yield: 92%) as a colorless oil. IR (film) ν_{max}: 3025, 2930, 2857, 2816, 2773, 1602, 1495, 1453, 748, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.19-7.13 (m, 4H), 7.10-7.03 (m, 6H), 2.52 (t, J = 8.0 Hz, 4H), 2.32-2.24 (m, 1H), 2.13 (s, 6H), 1.75-1.65 (m, 2H), 1.53-1.43 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 128.3, 128.2, 125.6, 62.4, 40.2, 33.3, 31.2 ppm; HRMS (ESI) calcd for $[C_{19}H_{26}N]^+$ $(M+H)^+$: 268.2060, found: 268.2060.

1-(2-Methoxyphenyl)-*N*,*N*-dimethyl-5-phenylpentan-3-amine (4o)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 1-ethynyl-2-methoxybenzene (**2x**) (158 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4o** (261 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 2928, 2855, 2773, 1601, 1493, 1454, 1241, 1048, 751, 698 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 7.36-7.17 (m, 7H), 6.99-6.86 (m, 2H), 3.84 (s, 3H), 3.04-2.94 (m, 1H), 2.86-2.69 (m, 4H), 2.60 (s, 6H), 2.16-1.97 (m, 2H), 1.93-1.76 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 142.1, 130.9, 129.9, 129.4 (2C), 129.3 (2C), 128.6, 127.0, 121.4, 111.5, 65.5, 55.9, 40.0 (2C), 32.9, 31.8, 29.7, 28.1 ppm; HRMS (ESI) calcd for $[C_{20}H_{28}NO]^+$ $(M+H)^+$: 298.2165; found: 298.2163.

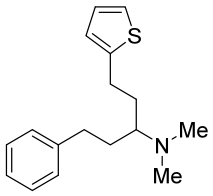
1-(4-Methoxyphenyl)-*N*,*N*-dimethyl-5-phenylpentan-3-amine (4p)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 1-ethynyl-4-methoxybenzene (**2y**) (158 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol)

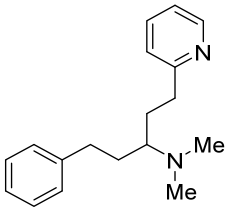
gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4p** (252 mg, yield: 85%) as a colorless oil. IR (film) ν_{max}: 3025, 2930, 2856, 2773, 1611, 1511, 1454, 1299, 1245, 1176, 1038, 822, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.25-7.18 (m, 3H), 7.15-7.07 (m, 2H), 6.90-6.82 (m, 2H), 3.82 (s, 3H), 2.67 (t, J = 8.0 Hz, 2H), 2.64-2.56 (m, 2H), 2.48-2.40 (m, 1H), 2.29 (s, 3H), 1.91-1.77 (m, 2H), 1.69-1.55 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.6, 134.6, 129.2 (2C), 128.4 (2C), 128.3 (2C), 125.7, 113.7, 62.5, 55.2, 40.2 (2C), 33.3, 32.3, 31.4, 31.3 ppm; HRMS (ESI) calcd for $[C_{20}H_{28}NO]^+$ $(M+H)^+$: 298.2165; found: 298.2163.

_N,N_-Dimethyl-1-phenyl-5-(thiophen-2-yl)pentan-3-amine (4q)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 2-ethynylthiophene (**2b**) (130 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4q** (248 mg, yield: 91%) as a colorless oil. IR (film) ν_{max}: 3025, 2928, 2856, 2818, 2773, 1452, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.19-7.13 (m, 3H), 7.11-7.07 (m, 1H), 6.90 (dd, J = 5.0, 3.5 Hz, 1H), 6.77-6.73 (m, 1H), 2.85 (t, J = 7.8 Hz, 2H), 2.67-2.56 (m, 2H), 2.45-2.37 (m, 1H), 2.24 (s, 6H), 1.90-1.76 (m, 2H), 1.72-1.62 (m, 1H), 1.60-1.49 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 142.7, 128.4, 128.2, 126.6, 125.7, 124.0, 122.8, 62.2, 40.2, 33.3, 31.6, 30.9, 27.3 ppm; HRMS (ESI) calcd for $[C_{17}H_{24}NS]^+$ $(M+H)^+$: 274.1624; found: 274.1622.

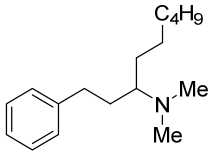
_N,N_-dimethyl-1-phenyl-5-(pyridin-2-yl)pentan-3-amine (4r)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 2-ethynylpyridine (**2z**) (124 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4r** (222 mg, yield: 83%) as a

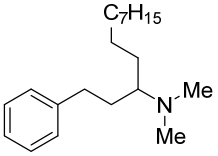
colorless oil. IR (film) ν_{max}: 2927, 2856, 2774, 1678, 1590, 1568, 1495, 1454, 1152, 1048, 749, 699 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.51 (d, J = 4.68 Hz, 1H), 7.66 (t, J = 7.62 Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.15 (m, 5H), 2.95-2.80 (m, 2H), 2.77-2.63 (m, 3H), 2.40 (s, 6H), 2.10-1.81 (m, 3H), 1.77-1.65 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 150.4, 143.6, 137.9, 129.8 (2C), 129.7 (2C), 127.2, 124.4, 122.6, 64.7, 40.6 (2C), 36.2, 33.9, 32.1, 30.0 ppm; HRMS (ESI) calcd for $[C_{18}H_{24}N_2Na]^+$ $(M+Na)^+$: 291.1832; found: 291.1839.

_N,N_-Dimethyl-1-phenylnonan-3-amine (4s)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with hex-1-yne (**2c**) (98 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30) the title product **4s** (212 mg, yield: 86%) as a colorless oil. IR (film) ν_{max}: 3084, 2926, 2855, 2818, 1495, 1454, 1377, 1044, 749, 698 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 7.34-7.26 (m, 4H), 7.24-7.19 (m, 1H), 2.82-2.71 (m, 3H), 2.48 (s, 6H), 2.01-1.91 (m, 1H), 1.79-1.64 (m, 2H), 1.52-1.27 (m, 10H), 0.92 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 131.8 (2C), 131.7 (2C), 129.3, 67.6, 42.5 (2C), 35.9, 34.7, 34.6, 32.3, 31.9, 29.8, 25.7, 16.7 ppm; HRMS (ESI) calcd for $[C_{17}H_{30}N]^+$ $(M+H)^+$: 248.2373; found: 248.2378.

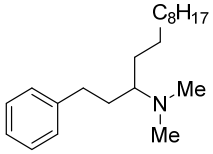
_N,N_-dimethyl-1-phenyldodecan-3-amine (4t)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with non-1-yne (**2aa**) (149 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4t** (240 mg, yield: 83%) as a colorless oil. IR (film) ν_{max}: 2925, 2854, 2817, 2775, 1495, 1454, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 7.28-7.19 (m, 3H), 2.78-2.63 (m, 2H), 2.44-2.35 (m, 1H), 2.29 (s, 6H), 1.87-1.74 (m, 1H), 1.69-1.49 (m, 2H), 1.39-1.28 (m, 15H), 0.95 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.3 (2C), 128.2 (2C), 125.5,

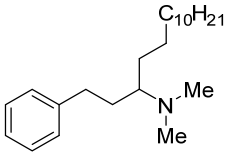
63.4, 40.4 (2C), 33.3, 31.9, 31.8, 30.0, 29.6 (2C), 29.3, 28.9, 27.2, 22.7, 14.1 ppm; HRMS (ESI) calcd for $[C_{20}H_{36}N]^+$ $(M+H)^+$: 290.2842; found: 290.2844.

***N*,*N*-Dimethyl-1-phenyltridecan-3-amine (4u)**



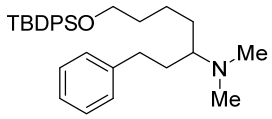
Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with dec-1-yne (**2ab**) (165 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4u** (254 mg, yield: 84%) as a colorless oil. IR (film) ν_{max}: 3026, 2925, 2854, 1454, 1030, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H), 7.27-7.19 (m, 3H), 2.75-2.63 (m, 2H), 2.43-2.34 (m, 1H), 2.29 (s, 6H), 1.86-1.73 (m, 1H), 1.68-1.58 (m, 1H), 1.42-1.22 (m, 18H), 0.94 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.3 (2C), 128.2 (2C), 125.6, 63.4, 40.4 (2C), 33.4, 31.9, 31.8, 30.0, 29.6 (3C), 29.3, 28.9, 27.2, 22.7, 14.1 ppm; HRMS (ESI) calcd for $[C_{21}H_{38}N]^+$ $(M+H)^+$: 304.2999; found: 304.3003.

***N*,*N*-dimethyl-1-phenylpentadecan-3-amine (4v)**



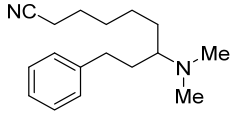
Following the general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with dodec-1-yne (**2ac**) (199 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4v** (291 mg, yield: 88%) as a colorless oil. IR (film) ν_{max}: 2924, 2853, 2775, 1682, 1604, 1495, 1376, 1259, 1030, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.25-7.17 (m, 3H), 2.75-2.59 (m, 2H), 2.43-2.32 (m, 1H), 2.28 (s, 6H), 1.84-1.72 (m, 1H), 1.66-1.57 (m, 1H), 1.34-1.27 (m, 22H), 0.92 (t. J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.3 (4C), 125.6, 63.5, 40.4 (2C), 33.4, 31.9, 31.8, 30.0, 29.7 (5C), 29.3, 29.0, 27.2, 22.7, 14.1 ppm; HRMS (ESI) calcd for $[C_{23}H_{42}N]^+$ $(M+H)^+$: 332.3312; found: 332.3310.

7-((*Tert*-butyldiphenylsilyl)oxy)-*N*,*N*-dimethyl-1-phenylheptan-3-amine (4w)



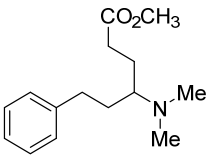
Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with (but-3-yn-1-yloxy)(*tert*-butyl)diphenylsilane (**3ad**) (370 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4w** (421 mg, yield: 89%) as a colorless oil. IR (film) ν_{max}: 3069, 2930, 2857, 2818, 2773, 1427, 1111, 822, 739, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71-7.63 (m, 4H), 7.42-7.32 (m, 6H), 7.28-7.22 (m, 2H), 7.20-7.12 (m, 3H), 3.67 (t, J = 6.4 Hz, 2H), 2.72-2.58 (m, 2H), 2.41-2.32 (m, 1H), 2.24 (s, 6H), 1.80-1.70 (m, 1H), 1.63-1.47 (m, 4H), 1.45-1.32 (m, 2H), 1.30-1.21 (m, 1H), 1.06 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 135.7, 134.2, 129.6, 128.5, 128.4, 127.7, 125.8, 63.9, 63.5, 40.4, 33.4, 32.9, 31.9, 28.8, 27.0, 23.5, 19.3 ppm; HRMS (ESI) calcd for $[C_{31}H_{44}NOS]^+$ $(M+H)^+$: 474.3187; found: 474.3186.

7-(Dimethylamino)-9-phenylnonanenitrile (4x)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with hex-5-ynenitrile (**2ae**) (111 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 50) the title product **4x** (219 mg, yield: 85%) as a colorless oil. IR (film) ν_{max}: 2931, 2857, 2818, 2773, 2243, 1454, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.16 (m, 3H), 2.74-2.62 (m, 2H), 2.58-2.48 (m, 1H), 2.36 (s, 6H), 2.33 (t, J = 7.0 Hz, 2H), 1.93-1.80 (m, 1H), 1.70-1.55 (m, 4H), 1.49-1.33 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 128.3, 128.2, 125.9, 119.6, 63.5, 40.0, 33.0, 31.0, 29.0, 28.6, 26.0, 25.0, 16.9 ppm; HRMS (ESI) calcd for $[C_{17}H_{27}N_2]^+$ $(M+H)^+$: 259.2169, found: 259.2170.

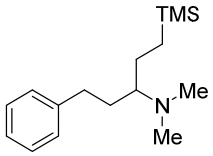
Methyl 4-(dimethylamino)-6-phenylhexanoate (4y)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with methyl propiolate (**2p**) (100 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after

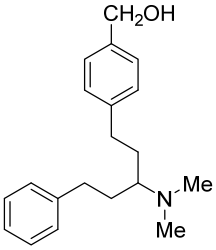
FC (eluent: EtOAc/*n*-hexane = 1: 20) the title product **4y** (189 mg, yield: 76%) as a colorless oil. IR (film) ν_{max}: 3025, 2934, 2858, 2821, 2776, 1737, 1453, 1275, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.6 Hz, 2H), 7.20-7.15 (m, 3H), 3.65 (s, 3H), 2.72-2.57 (m, 2H), 2.47-2.40 (m, 1H), 2.37 (t, J = 7.6 Hz, 2H), 2.26 (s, 6H), 1.88-1.77 (m, 2H), 1.75-1.67 (m, 1H), 1.56-1.47 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 142.1, 128.3, 128.2, 125.8, 62.8, 51.4, 40.0, 33.2, 31.4, 30.5, 24.9 ppm; HRMS (ESI) calcd for $[C_{15}H_{24}NO_2]^+$ $(M+H)^+$: 250.1802; found: 250.1801.

_N_,_N_-dimethyl-1-phenyl-5-(trimethylsilyl)pentan-3-amine (4z)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with ethynyltrimethylsilane (**2f**) (118 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 30) the title product **4z** (171 mg, yield: 65%) as a colorless oil. IR (film) ν_{max}: 3026, 2951, 2923, 2857, 2776, 1495, 1454, 1247, 862, 836, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.26-7.18 (m, 3H), 2.73-2.62 (m, 2H), 2.29 (s, 6H), 1.84-1.72 (m, 1H), 1.70-1.59 (m, 1H), 1.59-1.47 (m, 1H), 1.37-1.27 (m, 2H), 0.55-0.47 (m, 2H), 0.02 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 128.3 (4C), 125.6, 66.2, 40.5 (2C), 33.5, 31.1, 22.9, 13.5, −1.9 (3C) ppm; HRMS (ESI) calcd for $[C_{16}H_{30}NSi]^+$ $(M+H)^+$: 264.2142; found: 264.2144.

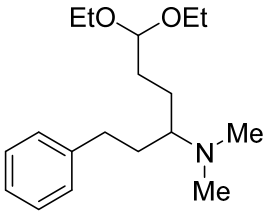
(4-(3-(Dimethylamino)-5-phenylpentyl)phenyl)methanol (4aa)



Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 4-ethynylbenzaldehyde (**2s**) (156 mg, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 10) the title product **4aa** (226 mg, yield: 74%) as a colorless oil. IR (film) ν_{max}: 3388, 3022, 2929, 2857, 2351, 1453, 1030, 749, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.20 (m, 4H), 7.19-7.08 (m, 5H), 4.59 (s, 2H), 3.91-3.19 (s, br, 1H), 2.66-2.54 (m, 4H), 2.44-2.34 (m, 1H), 2.22 (s, 6H), 1.86-1.74 (m,

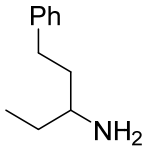
2H), 1.64-1.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 141.6, 138.6, 128.3, 128.2, 128.1, 127.0, 125.6, 64.7, 62.6, 40.1, 33.1, 32.8, 31.3, 31.2; HRMS (ESI) calcd for $[C_{20}H_{28}NO]^+$ $(M+H)^+$: 298.2165; found: 298.2163.

6,6-Diethoxy-*N*,*N*-dimethyl-1-phenylhexan-3-amine (4ab)



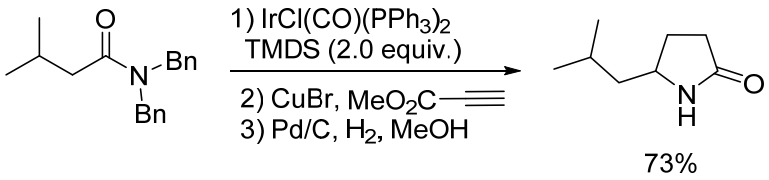
Following general procedure B, the reaction of *tert*-amide **3af** (177 mg, 1.0 mmol) with 3,3-diethoxyprop-1-yne **2g** (153.6 mg, 0.17 mL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 10) the title product **4ab** (249 mg, yield: 85%) as a colorless oil. IR (film) ν_{max}: 2972, 2930, 2868, 1454, 1373, 1129, 1064, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.11 (m, 2H), 7.10-7.00 (m, 3H), 4.34 (t, J = 5.5 Hz, 1H), 3.57-3.46 (m, 2H), 3.40-3.31 (m, 2H), 2.52 (t, J = 8.1 Hz, 2H), 2.27-2.18 (m, 1H), 2.11 (S, 6H), 1.71-1.59 (m, 1H), 1.57-1.37 (m, 4H), 1.28-1.19 (m, 1H), 1.08 (t, J = 7.2 Hz, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 142.7, 128.2 (2C), 128.1 (2C), 125.5, 102.9, 62.9, 60.8, 60.7, 40.2 (2C), 33.2, 31.4, 30.9, 23.8, 15.2 (2C) ppm; HRMS (ESI) calcd for $[C_{18}H_{32}NO_2]^+$ $(M+H)^+$: 294.2428; found: 294.2421.

1-phenylpentan-3-amine (4ac)



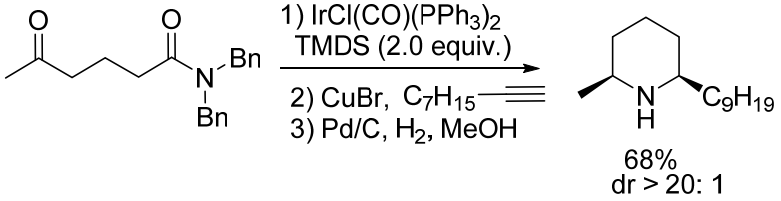
Following general procedure B, the reaction of *tert*-amide **3a** (253 mg, 1.0 mmol) with ethynylbenzene (**2a**) (131 μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: MeOH/CH_2Cl_2 = 1: 20) the title product **4ac** (142 mg, yield: 87%) as a colorless oil. IR (film) ν_{max}: 3429, 2955, 2927, 1569, 1456, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.22-7.14 (m, 3H), 2.78-2.70 (m, 1H), 2.69-2.58 (m, 2H), 1.81-1.69 (m, 1H), 1.61-1.45 (m, 2H), 1.37 (br s, 2H), 1.34-1.26 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 142.4, 128.3 (4C), 125.6, 52.2, 39.3, 32.6, 30.7, 10.2 ppm; HRMS (ESI) calcd for $[C_{11}H_{18}N]^+$ $(M+H)^+$: 164.1434; found: 164.1425.

5-Isobutylpyrrolidin-2-one (6)



Following general procedure B, the reaction of *tert*-amide **3u** (281 mg, 1.0 mmol) with methyl propiolate (**2p**) (107μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 5) the title product **6** (103 mg, yield: 73%) as a white solid. Mp: 70~72 ºC (lit.[2] 65~66 ºC); IR (film) ν_{max}: 3189, 2957, 2355, 1699, 1461, 1288, 1074, 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 1H), 3.72-3.68 (m, 2H), 2.33-2.20 (m, 3H), 1.70-1.59 (m, 2H), 1.49-1.40 (m, 1H), 1.34-1.25 (m, 1H), 0.91 (d, J = 6.5 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 52.7, 45.9, 30.2, 27.8, 25.2, 22.9, 22.4 ppm; HRMS (ESI) calcd for $[C_8H_{16}NO]^+$ $(M+H)^+$: 142.1226; found: 142.1221.

Isosolenopsin (8)



Following general procedure B, the reaction of *tert*-amide **3w** (309 mg, 1.0 mmol) with non-1-yne (**2aa**) (197μL, 1.2 mmol) and TMDS (355 μL, 2.0 mmol) gave, after FC (eluent: $MeOH/CH_2Cl_2$ = 1: 10) isosolenopsin (**8**) (153 mg, yield: 68%) as a colorless oil, which was converted to isosolenopsin hydrochloride salt as a white solid. Analytical data are in full agreement with those previously published.[3] Mp: 172~173 ºC (lit.[3a] 174-175 ºC); IR (film) ν_{max}: 3429, 2931, 2849, 2525, 1464, 1132, 1076 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (br s, 1H), 9.06 (br s, 1H), 3.13-2.96 (m, 1H), 2.96-2.90 (m, 1H), 2.22-2.09 (m, 1H), 2.00-1.79 (m, 5H), 1.65-1.55 (m, 3H), 1.43-1.21 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.6, 54.5, 33.2, 31.8, 30.7, 29.5, 29.4, 29.3, 29.2, 27.4, 25.6, 22.9, 22.6, 19.4, 14.0 ppm; HRMS (ESI) calcd for $[C_{15}H_{32}N]^+$ $(M+H)^+$: 226.2529; found: 226.2523.

Reference:

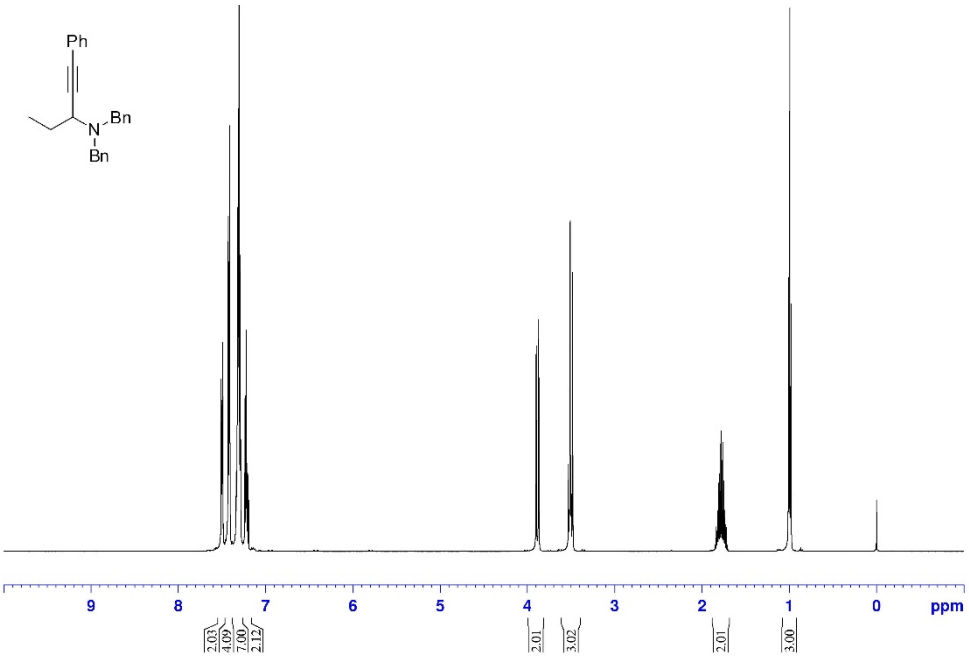
[1] D. P. Chauhan, S. J. Varma, A. Vijeta, P. Banerjee and P. Talukdar, *Chem. Commun.*, 2014, **50**, 323.

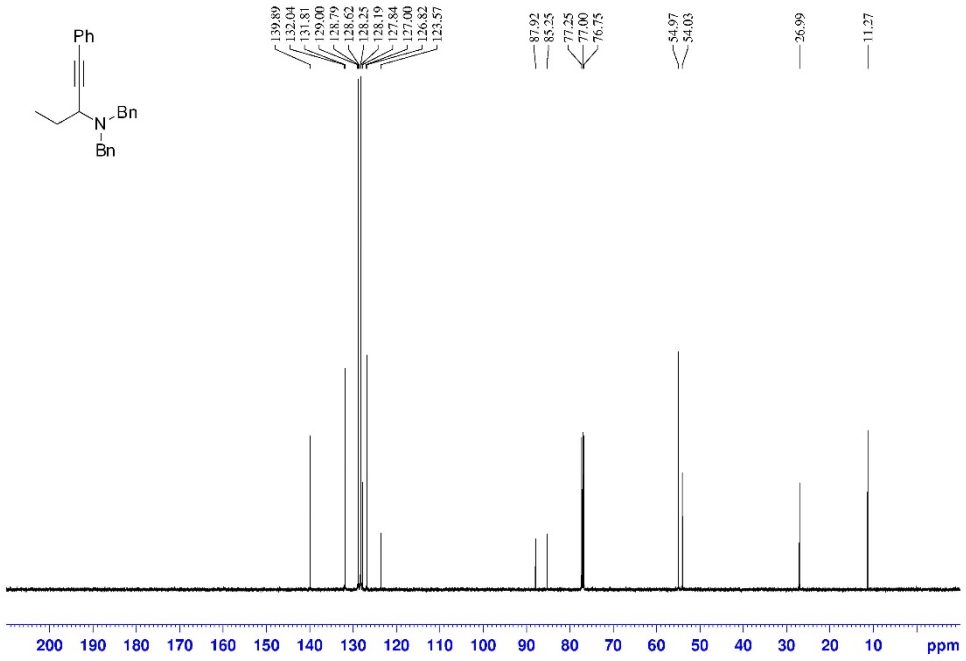
[2] J. Sperry, E. B. J. Harris and M. A. Brimble, *Org. Lett*., 2010, **12**, 420.

[3] a) N. Gouault, M. L. Roch, G. de Campos Pinto, M. David, *Org. Biomol. Chem.*, 2012, **10**, 5541; b) R. C. Simon, C. S. Fuchs, H. Lechner, F. Zepeck and W. Kroutil, *Eur. J. Org. Chem.* 2013, 3397.

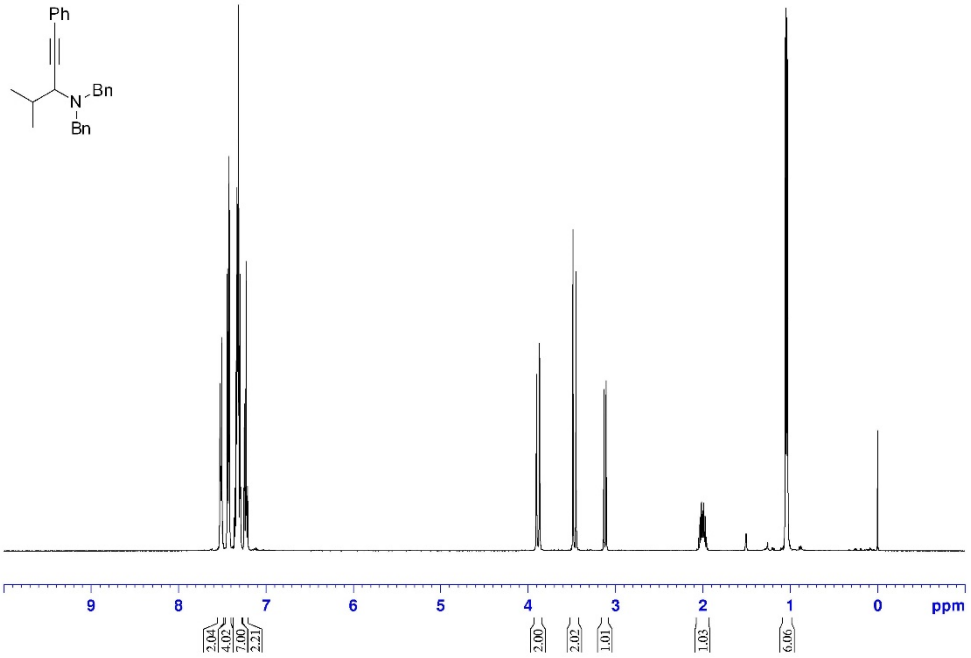
^{1}H and ^{13}C NMR Spectra of the Alkynylated and Alkylated Products

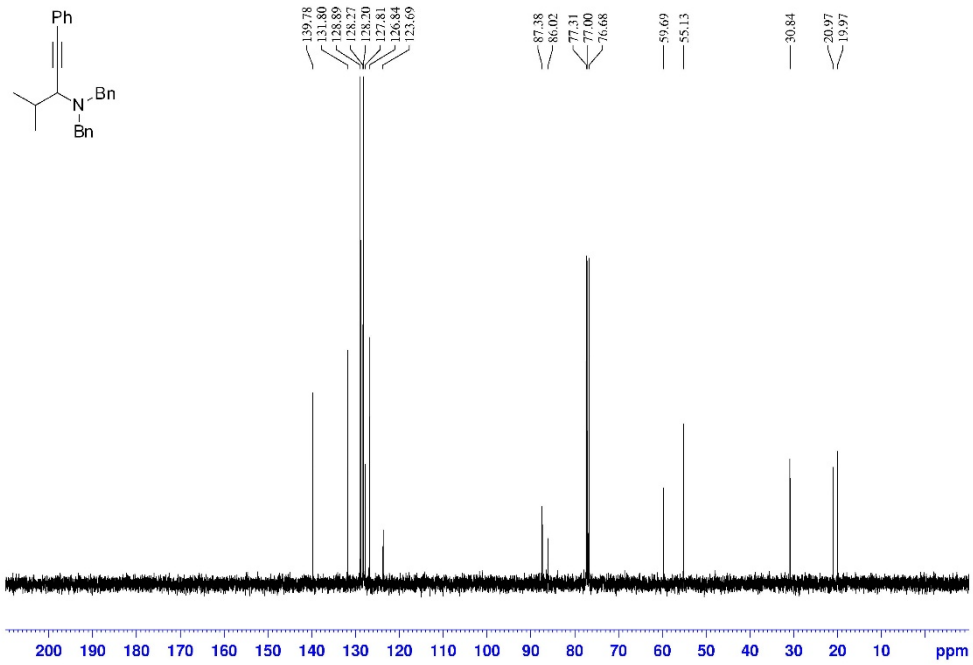
^{1}H NMR and ^{13}C NMR spectra of compound **1a**



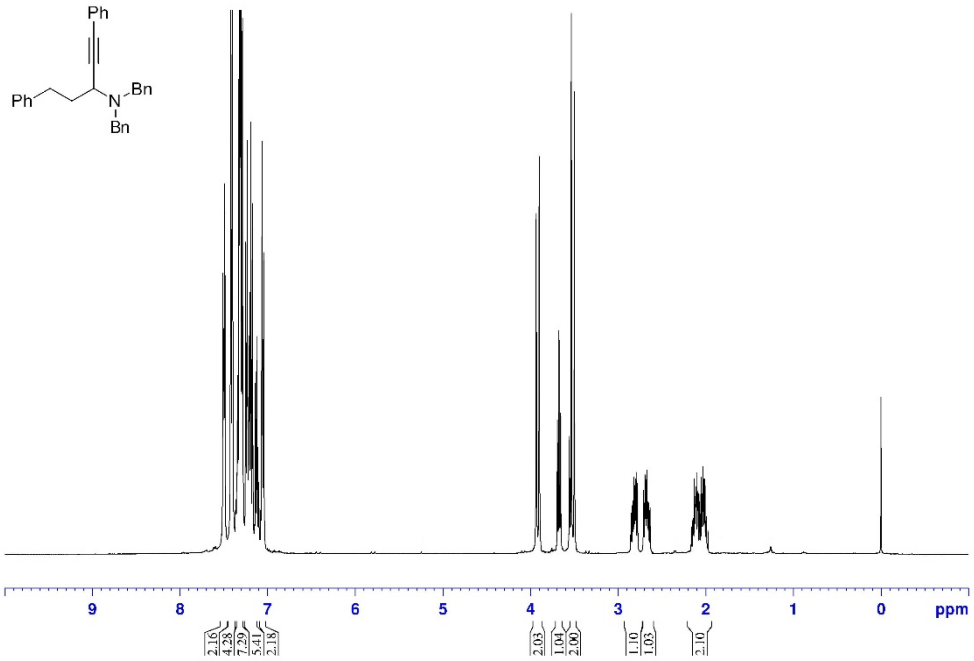


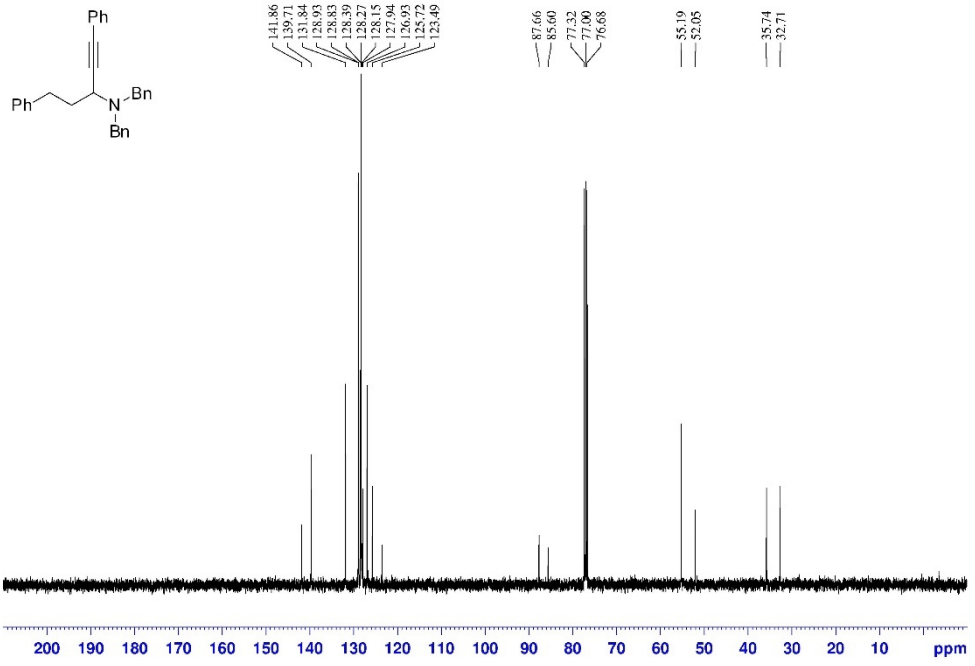
^{1}H NMR and ^{13}C NMR spectra of compound **1b**



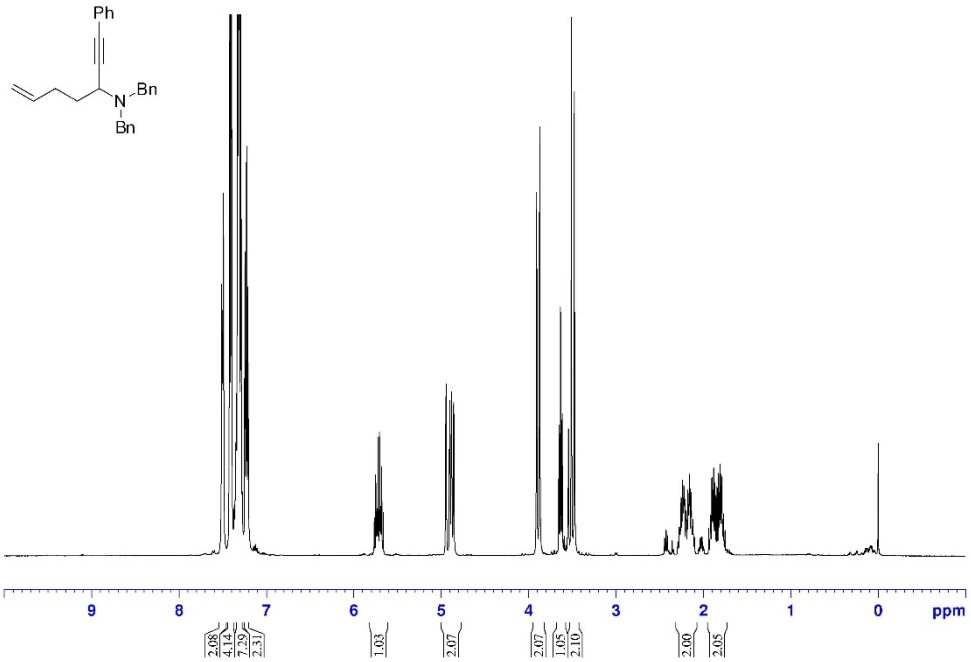


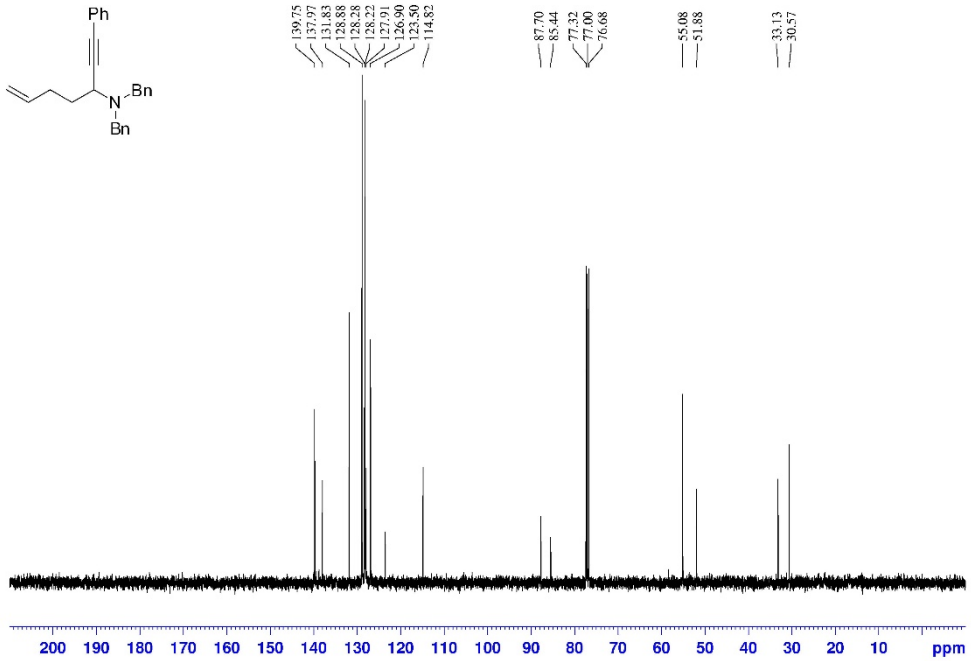
^{1}H NMR and ^{13}C NMR spectra of compound **1c**



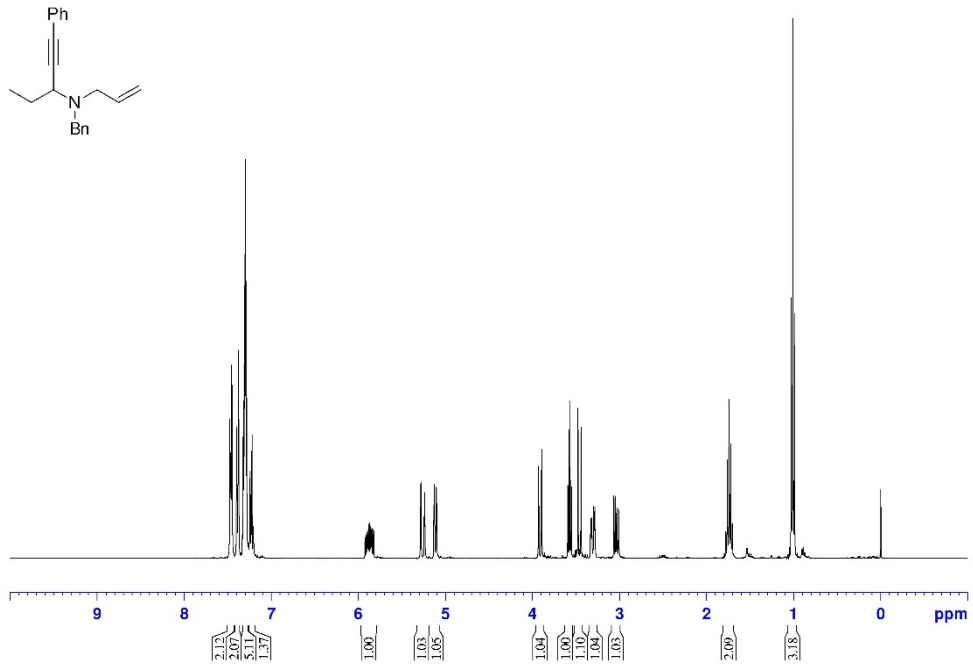


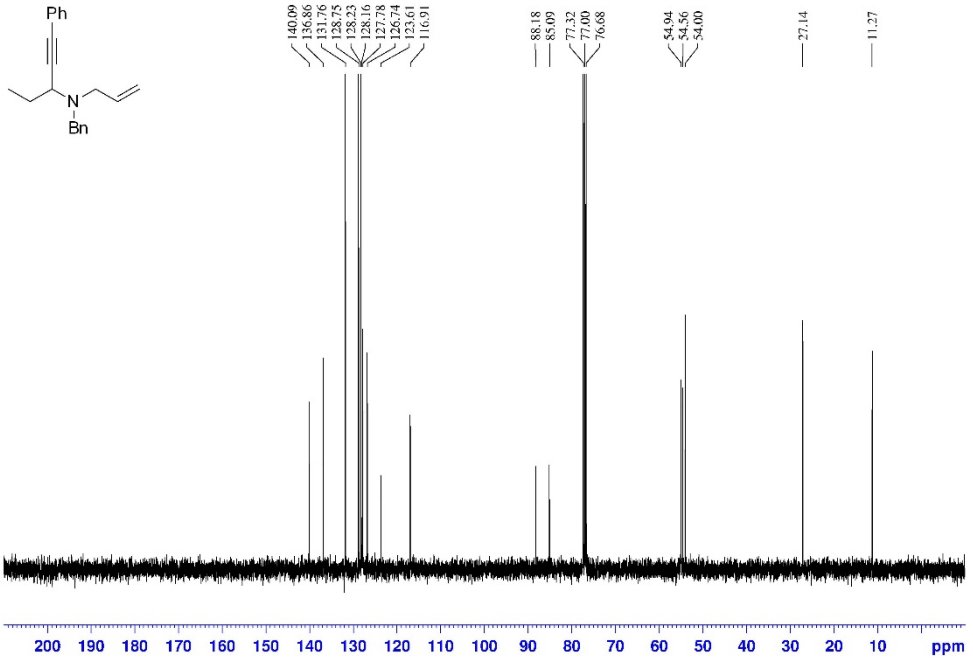
^{1}H NMR and ^{13}C NMR spectra of compound **1d**



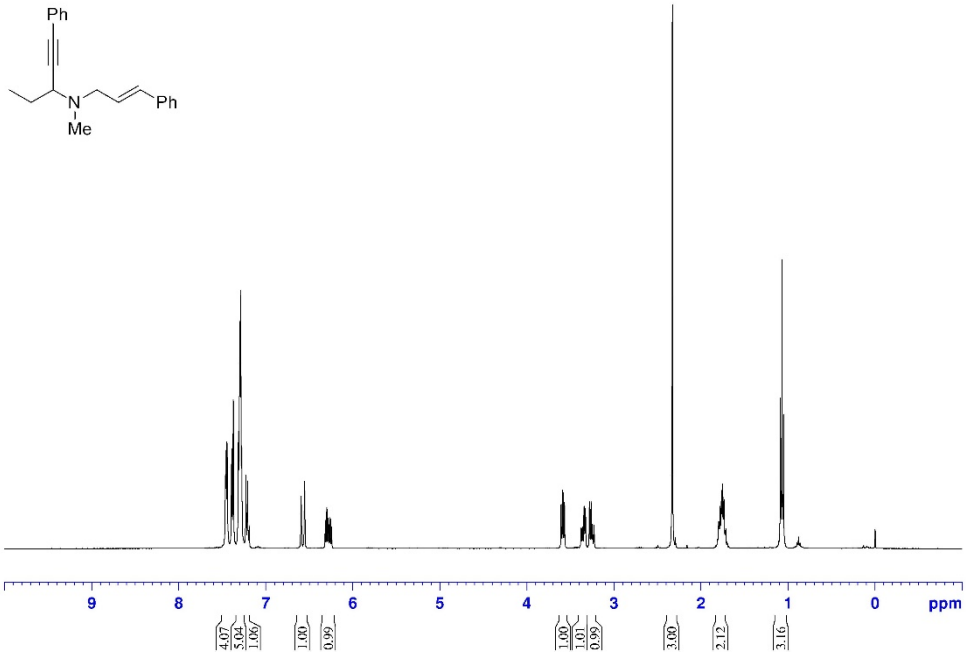


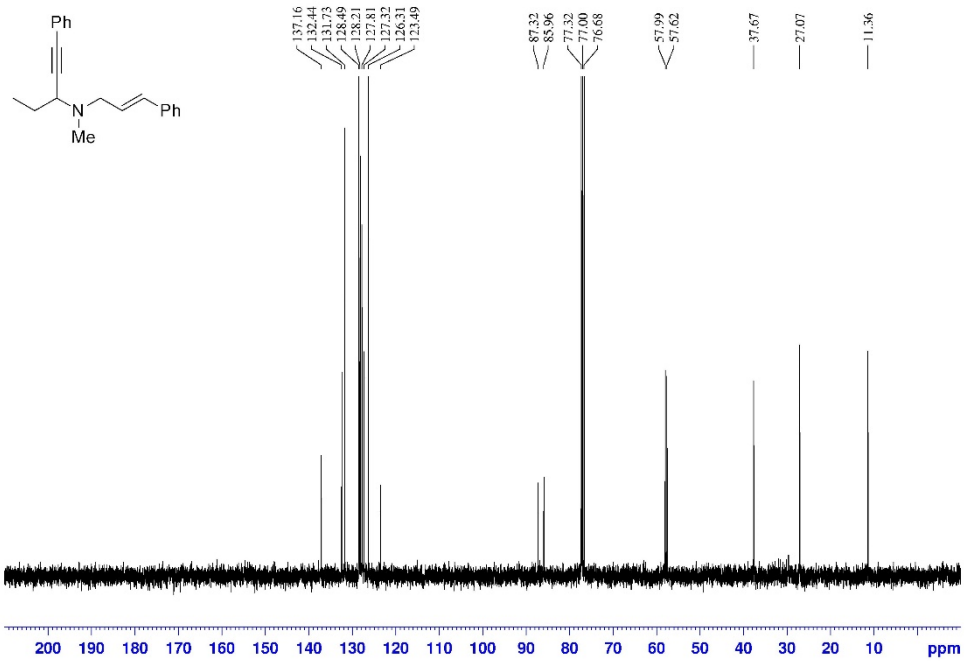
^{1}H NMR and ^{13}C NMR spectra of compound **1e**



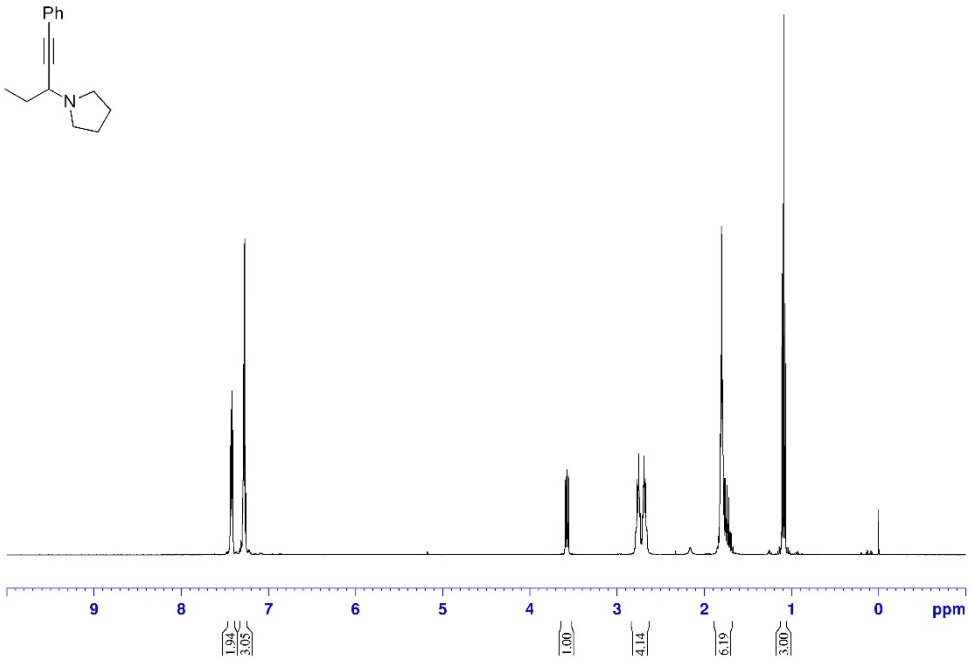


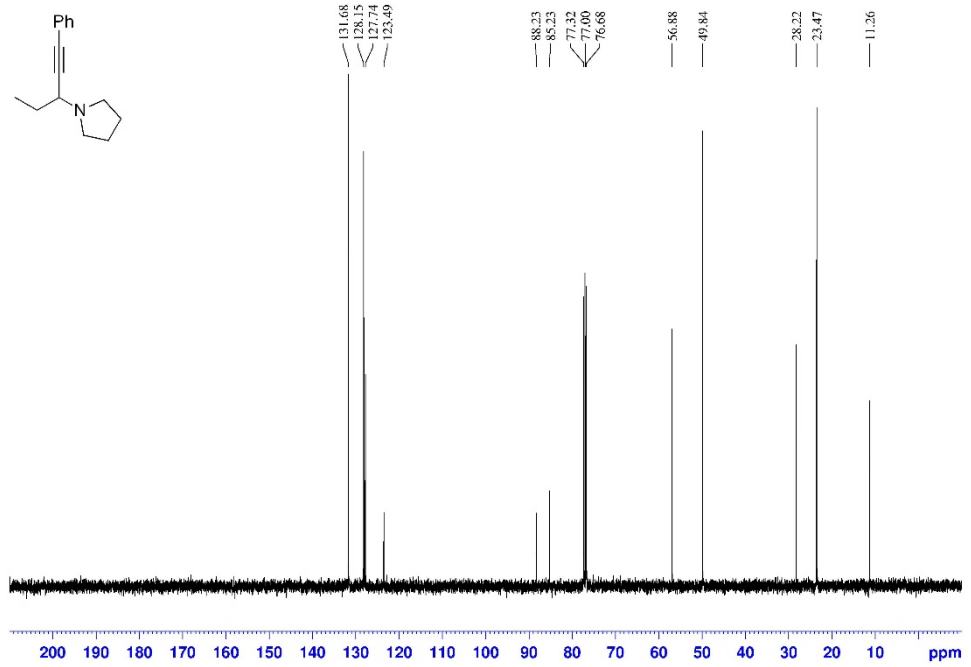
^{1}H NMR and ^{13}C NMR spectra of compound **1f**



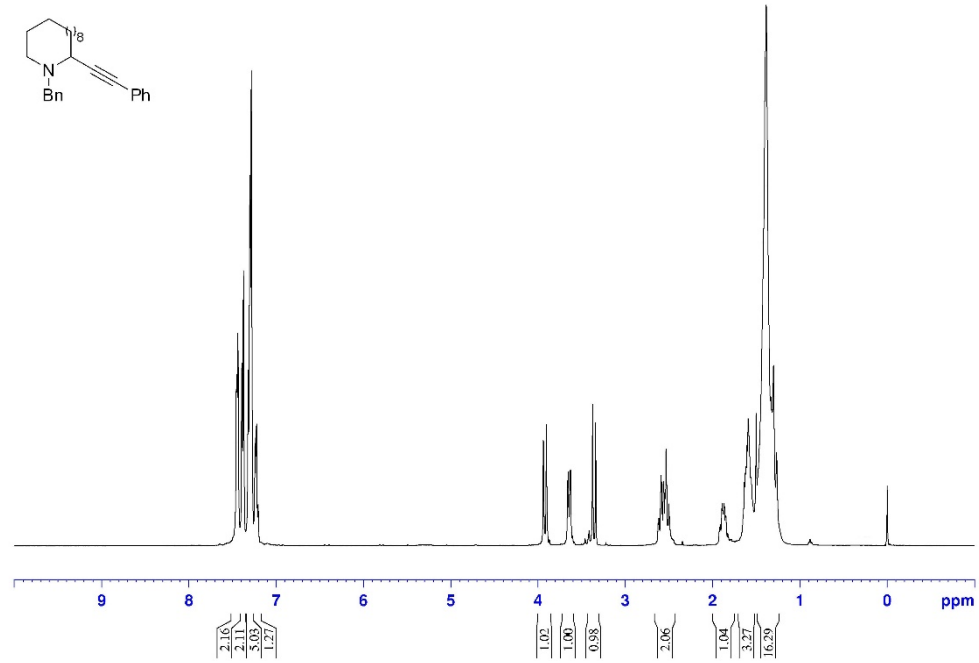


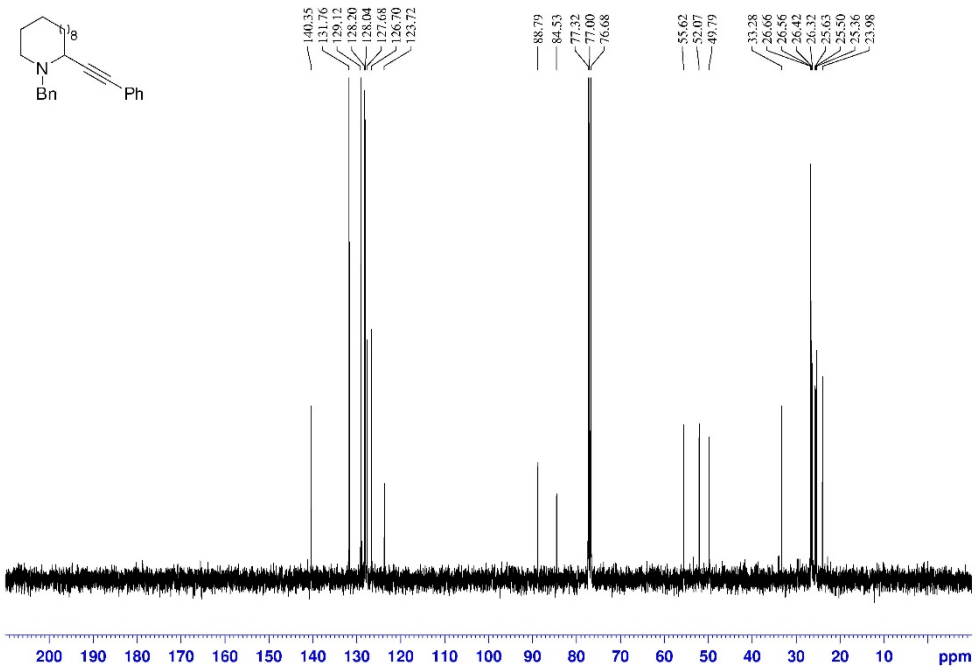
^{1}H NMR and ^{13}C NMR spectra of compound **1g**



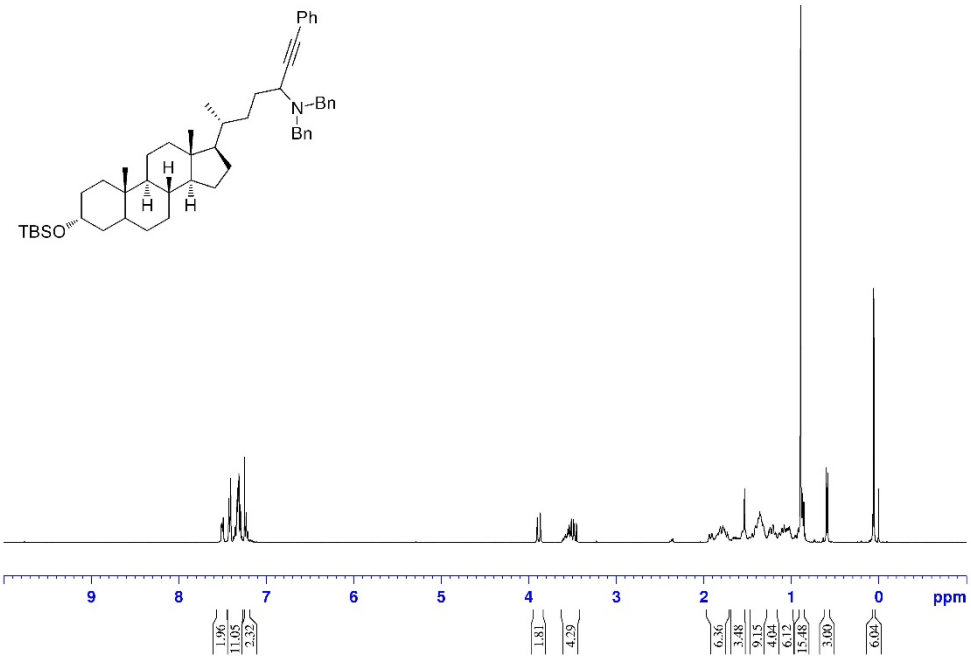


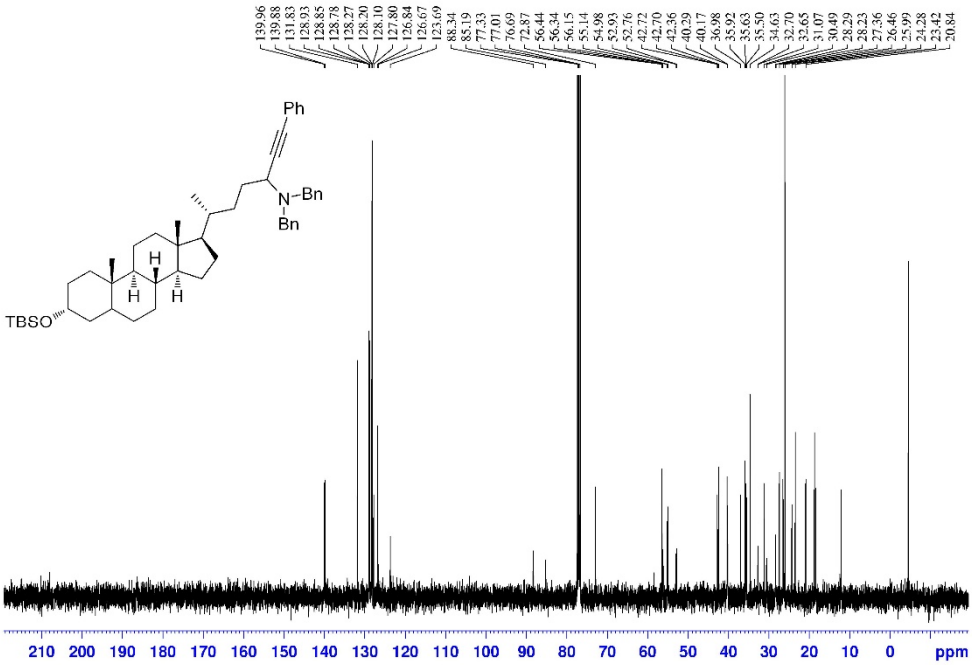
^{1}H NMR and ^{13}C NMR spectra of compound **1h**



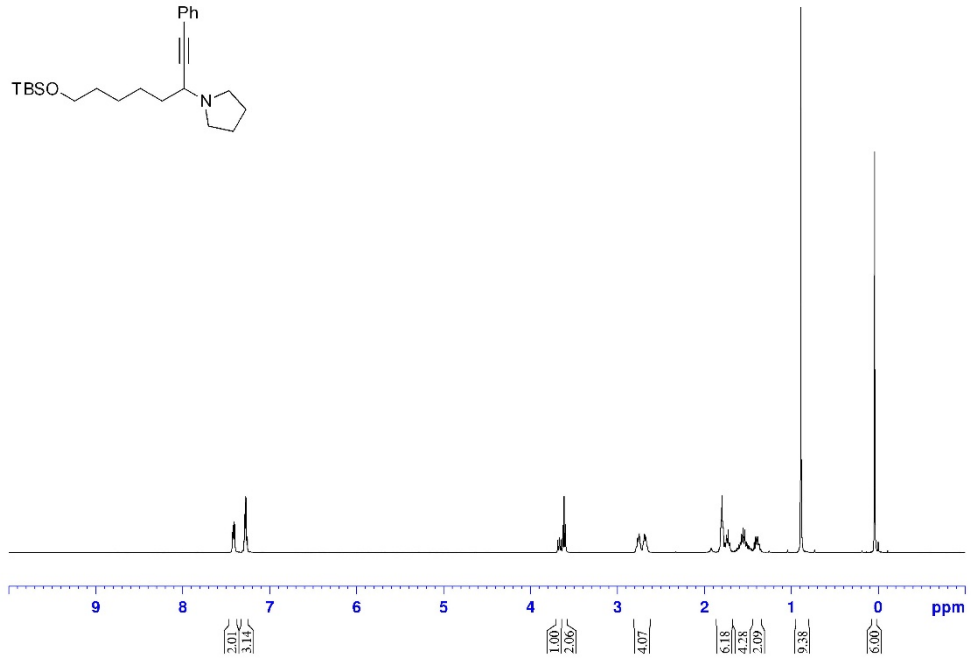


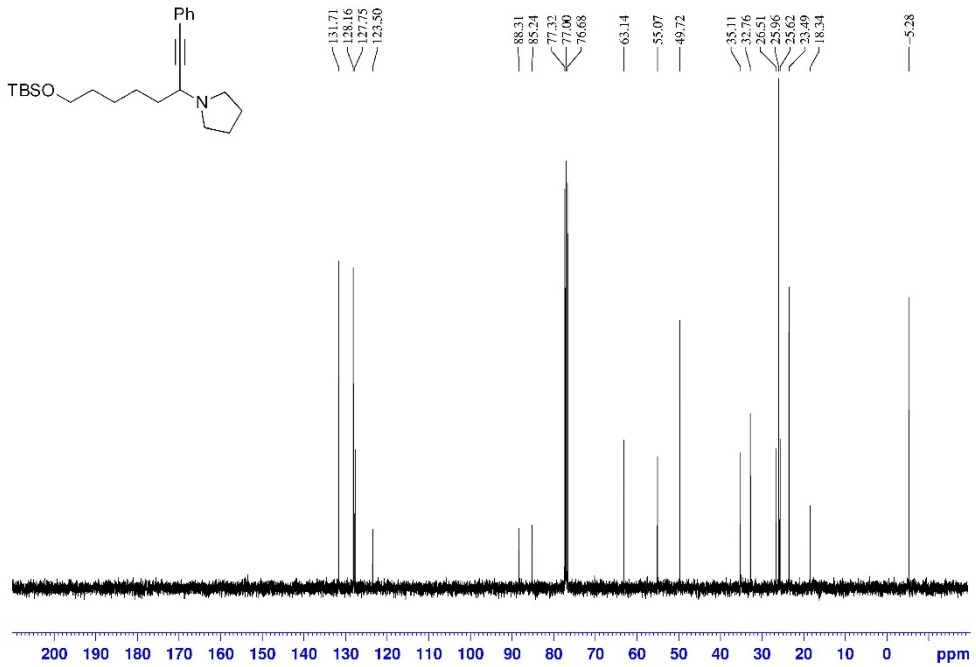
^{1}H NMR and ^{13}C NMR spectra of compound **1i**



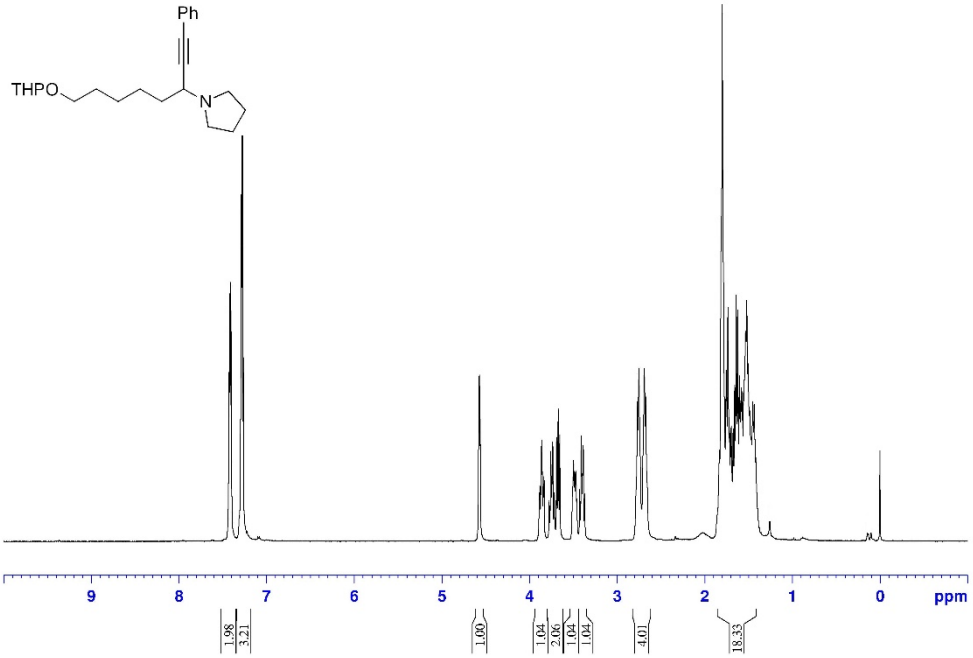


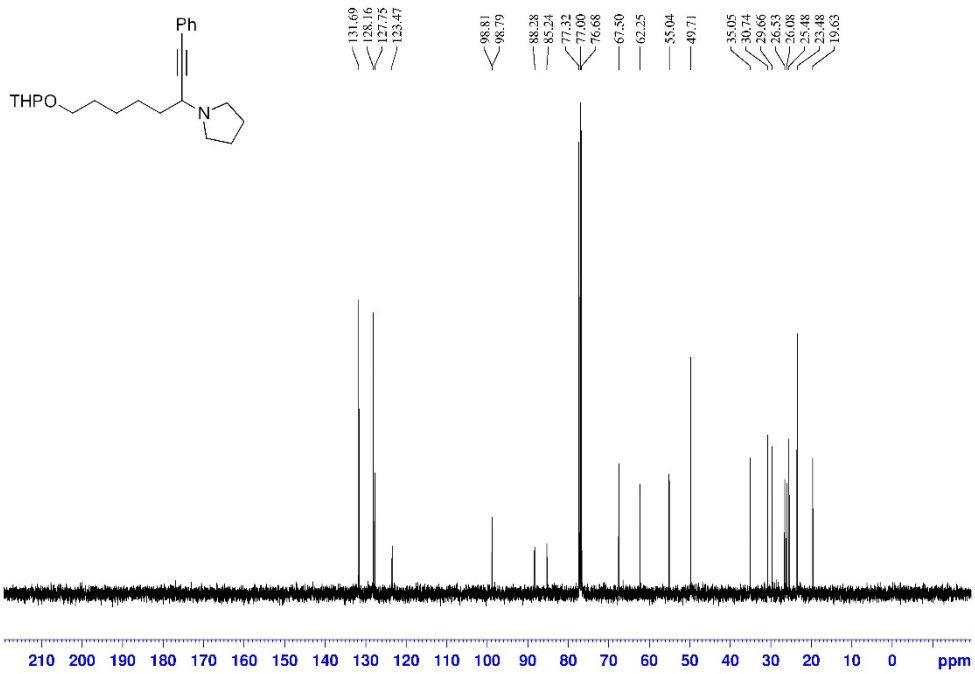
^{1}H NMR and ^{13}C NMR spectra of compound **1j**



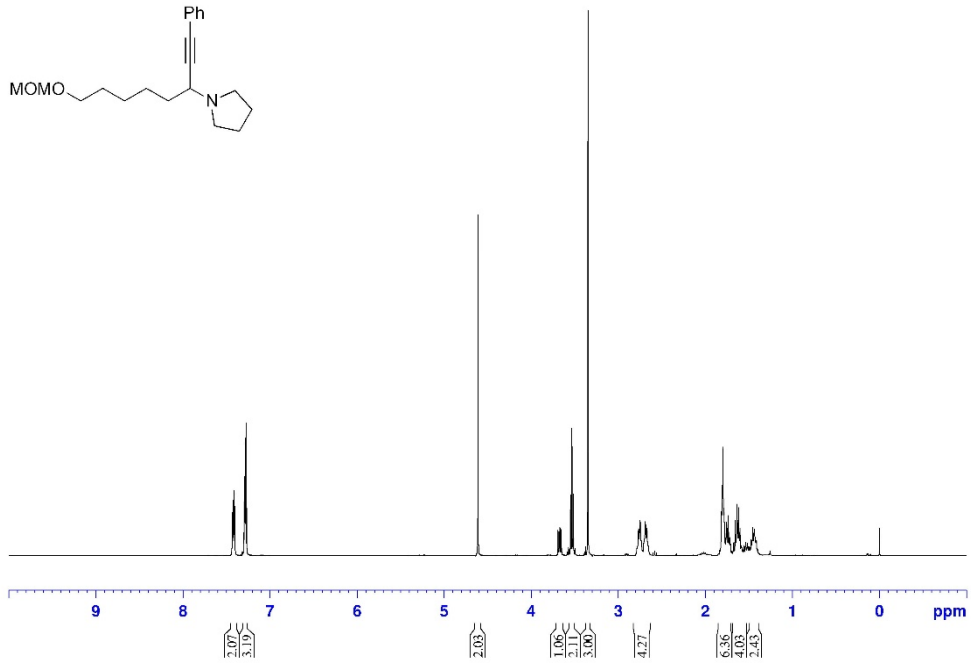


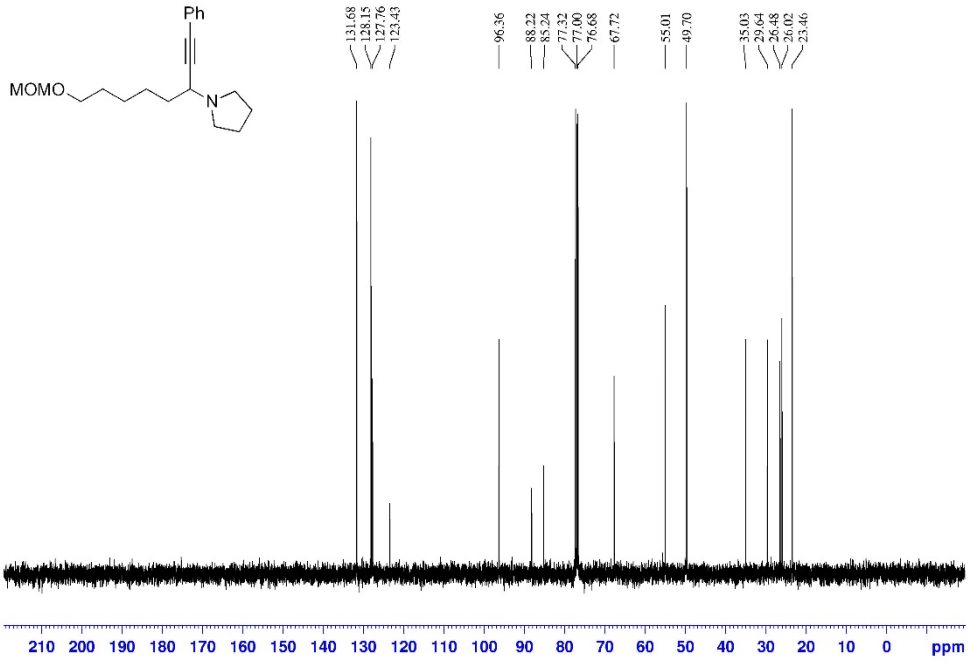
^{1}H NMR and ^{13}C NMR spectra of compound **1k**



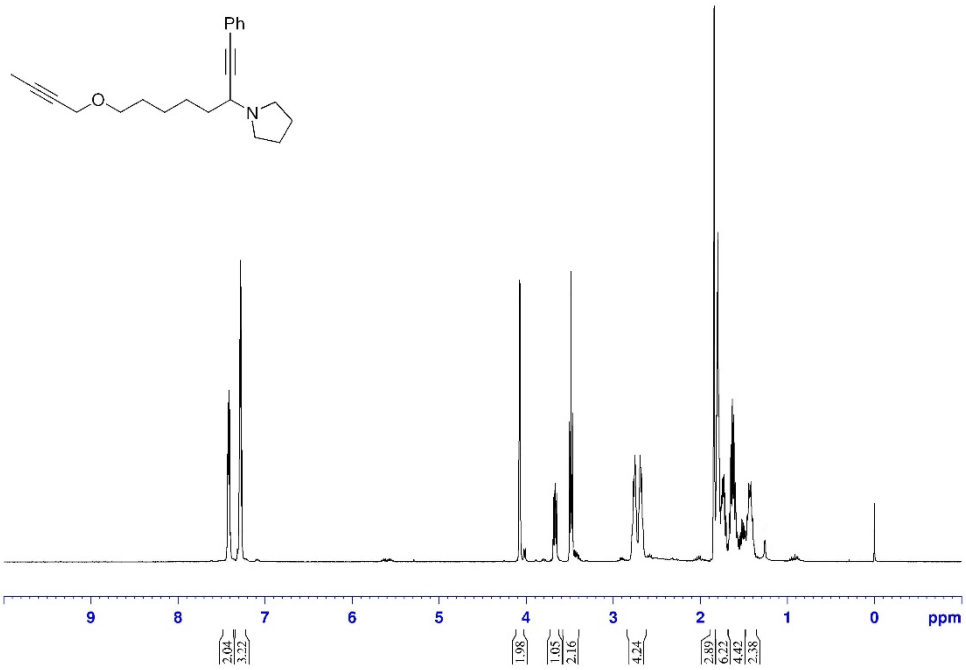


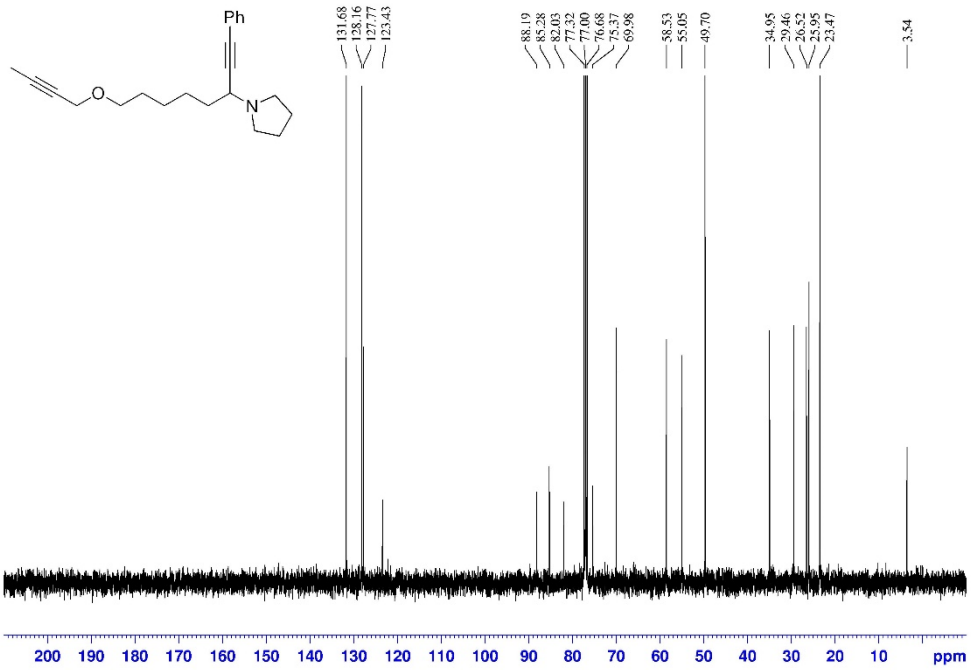
^{1}H NMR and ^{13}C NMR spectra of compound **1l**



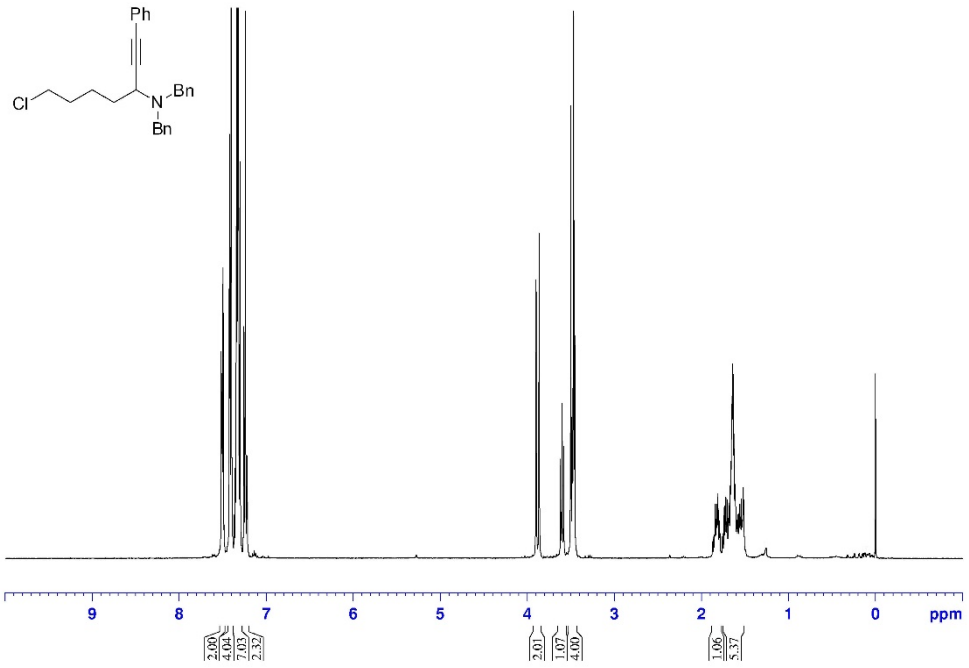


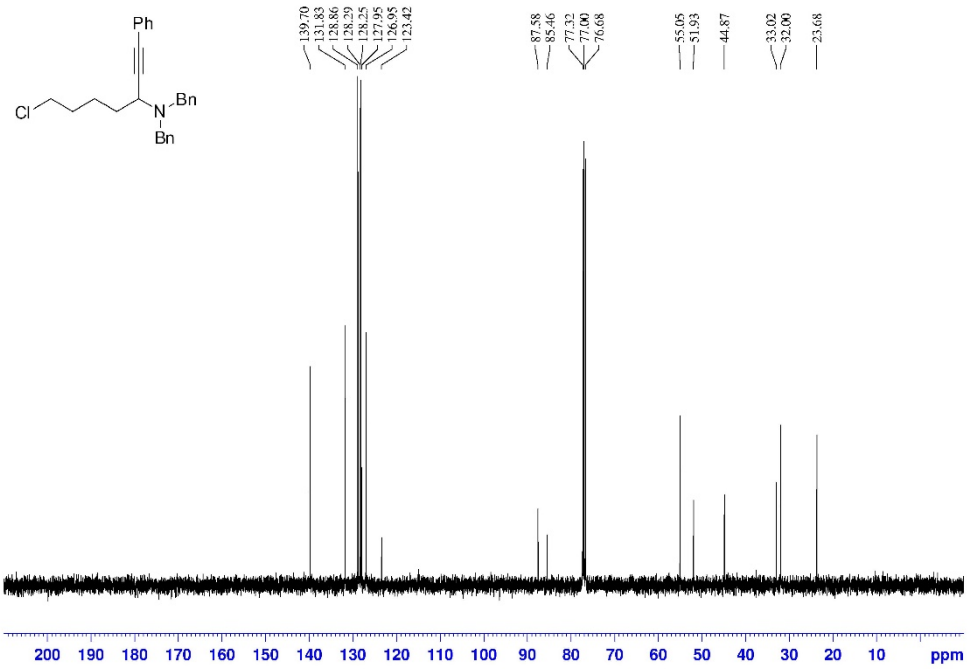
^{1}H NMR and ^{13}C NMR spectra of compound **1m**



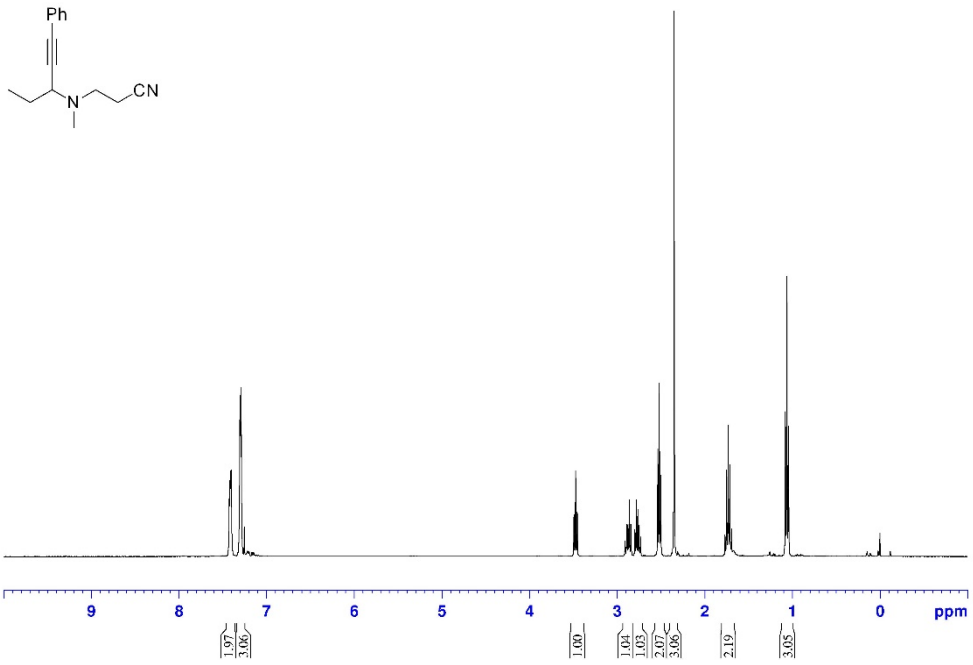


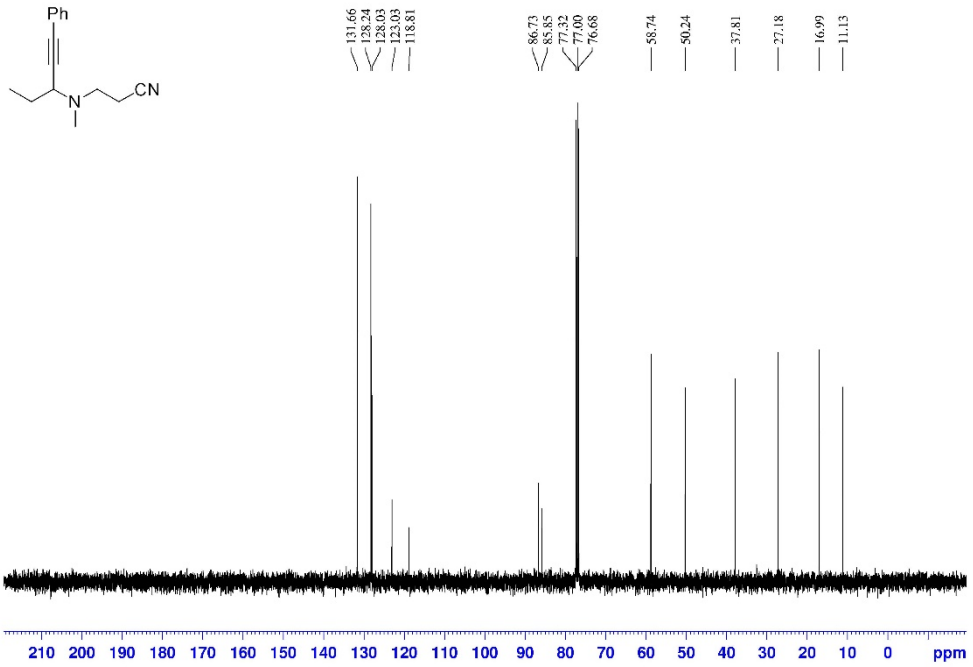
^{1}H NMR and ^{13}C NMR spectra of compound **1n**



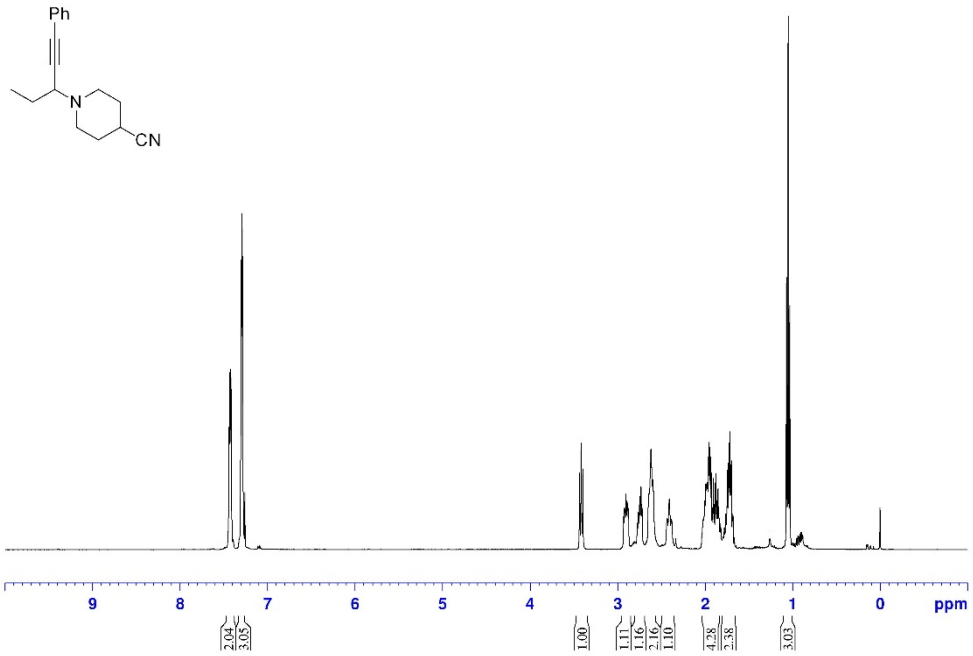


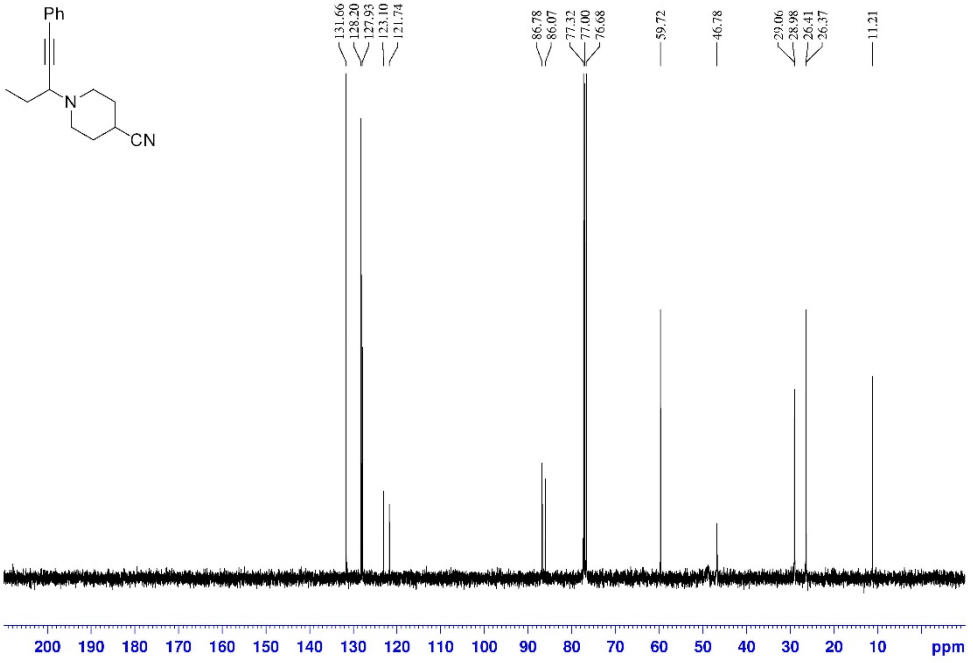
^{1}H NMR and ^{13}C NMR spectra of compound **1o**



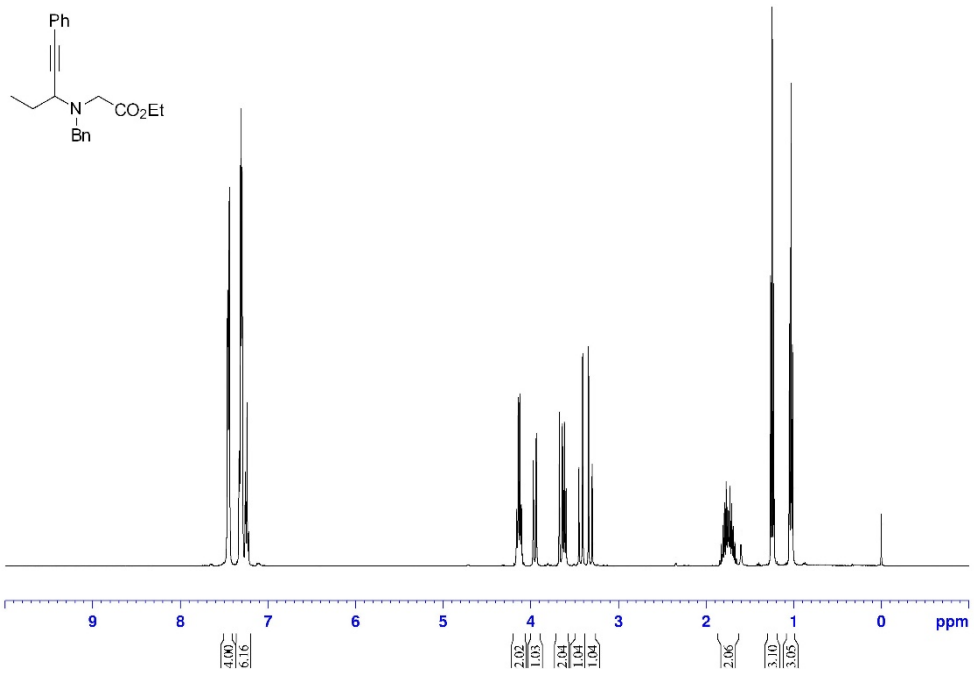


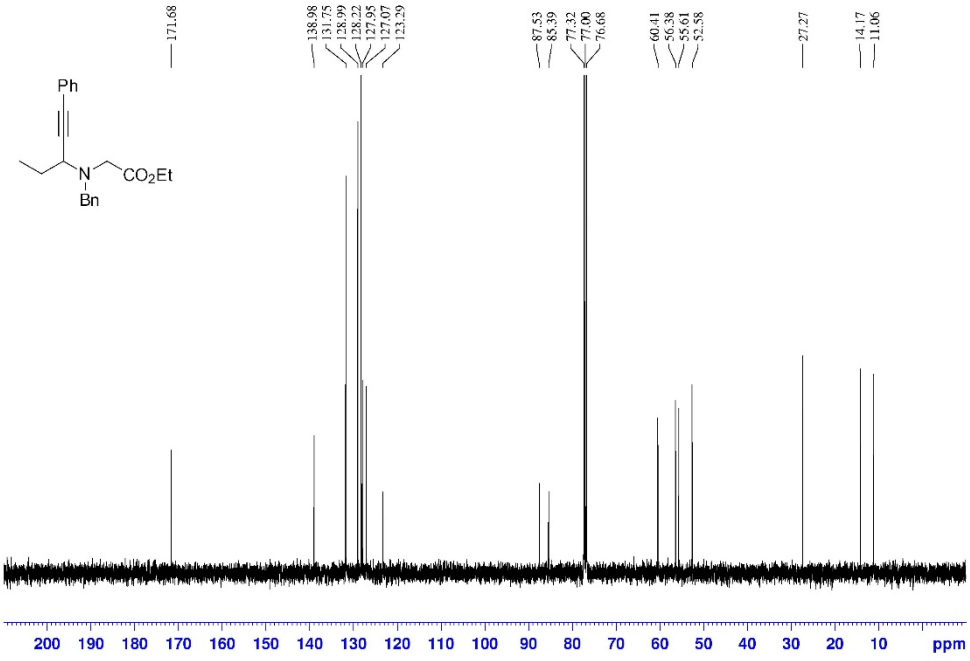
^{1}H NMR and ^{13}C NMR spectra of compound **1p**



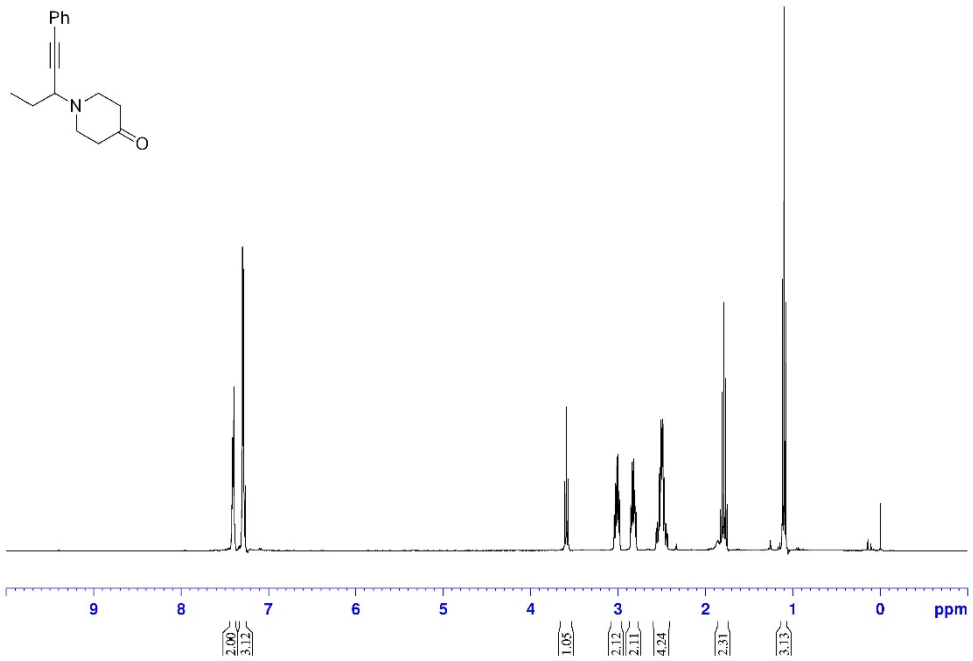


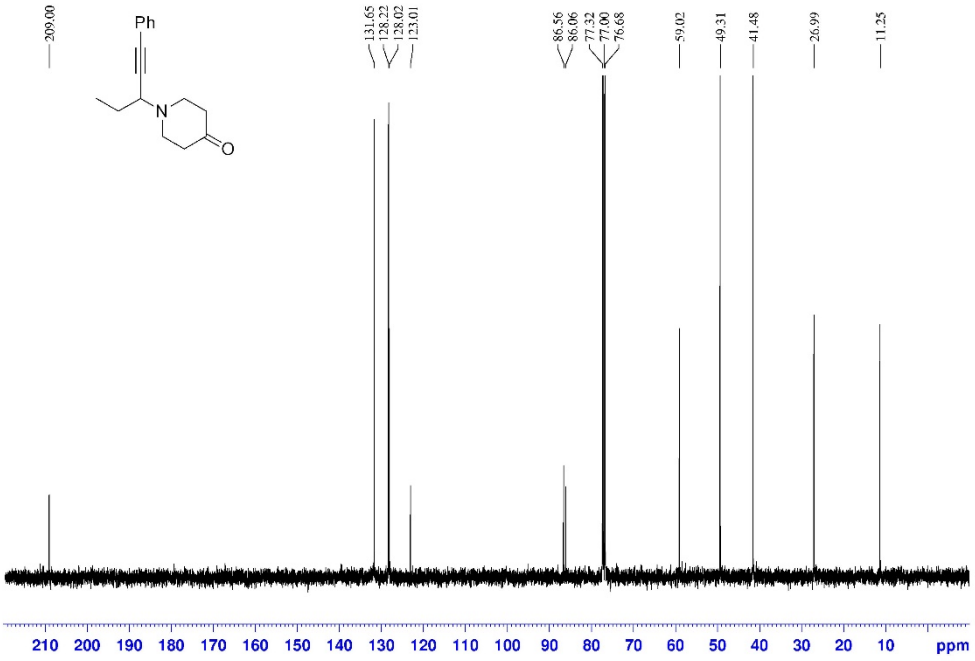
^{1}H NMR and ^{13}C NMR spectra of compound **1q**



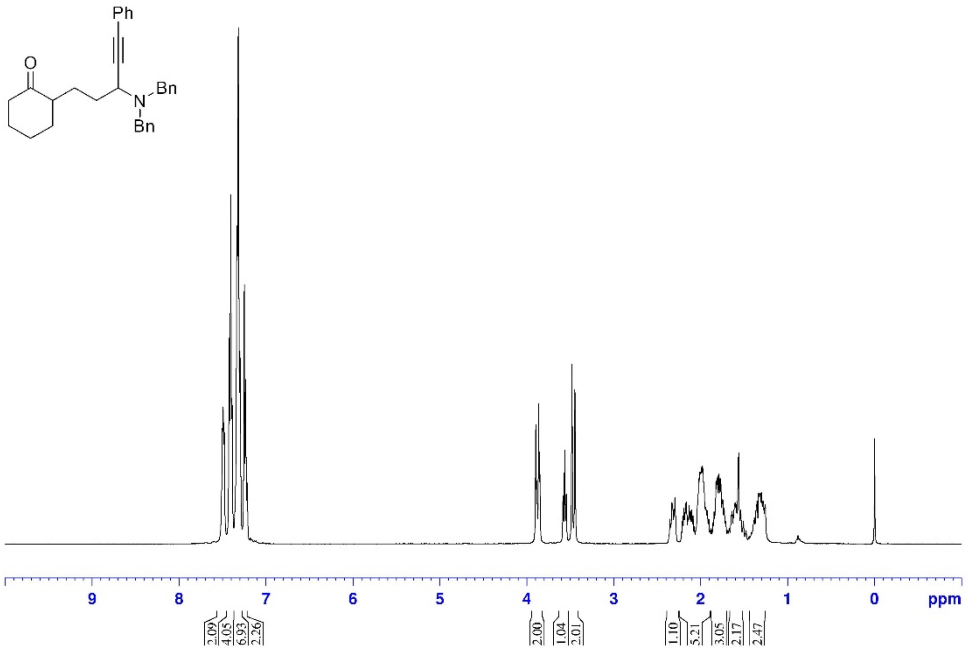


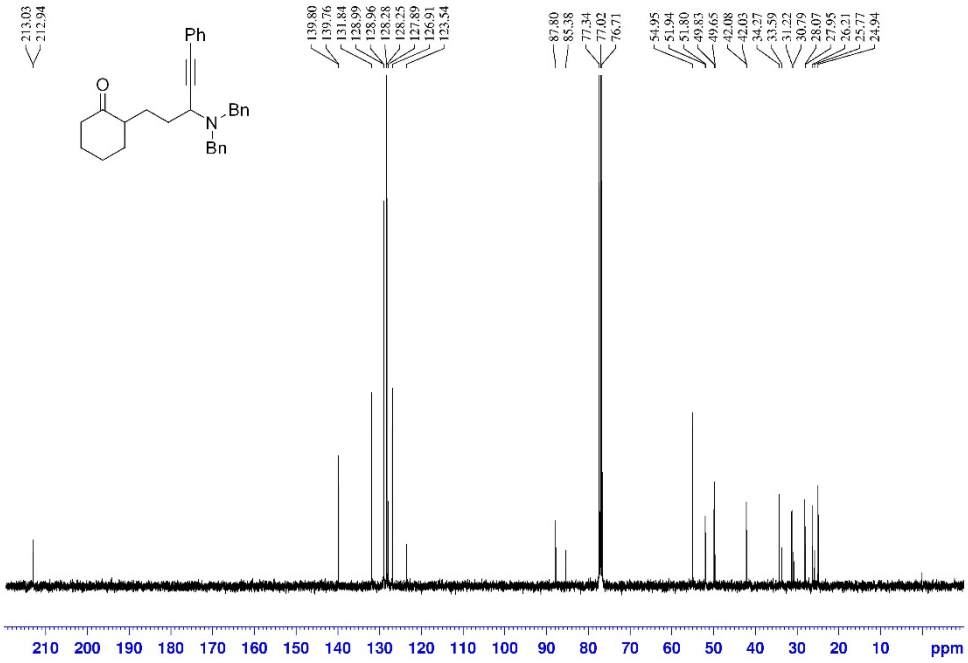
^{1}H NMR and ^{13}C NMR spectra of compound **1r**



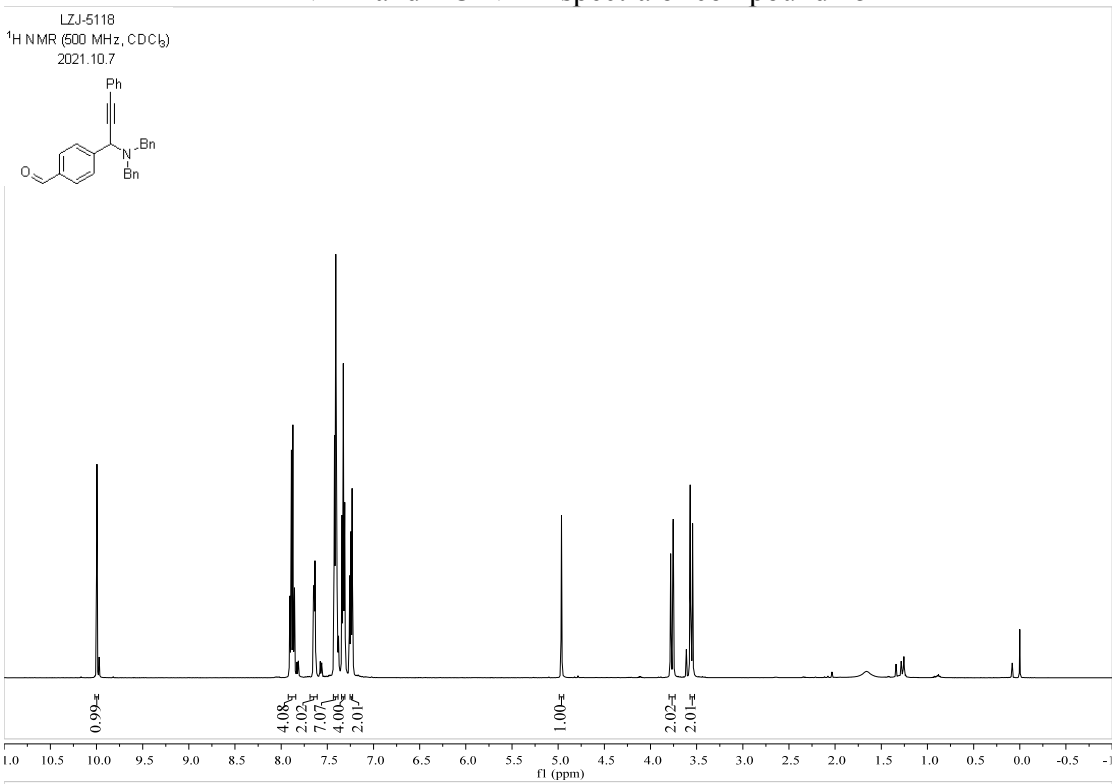


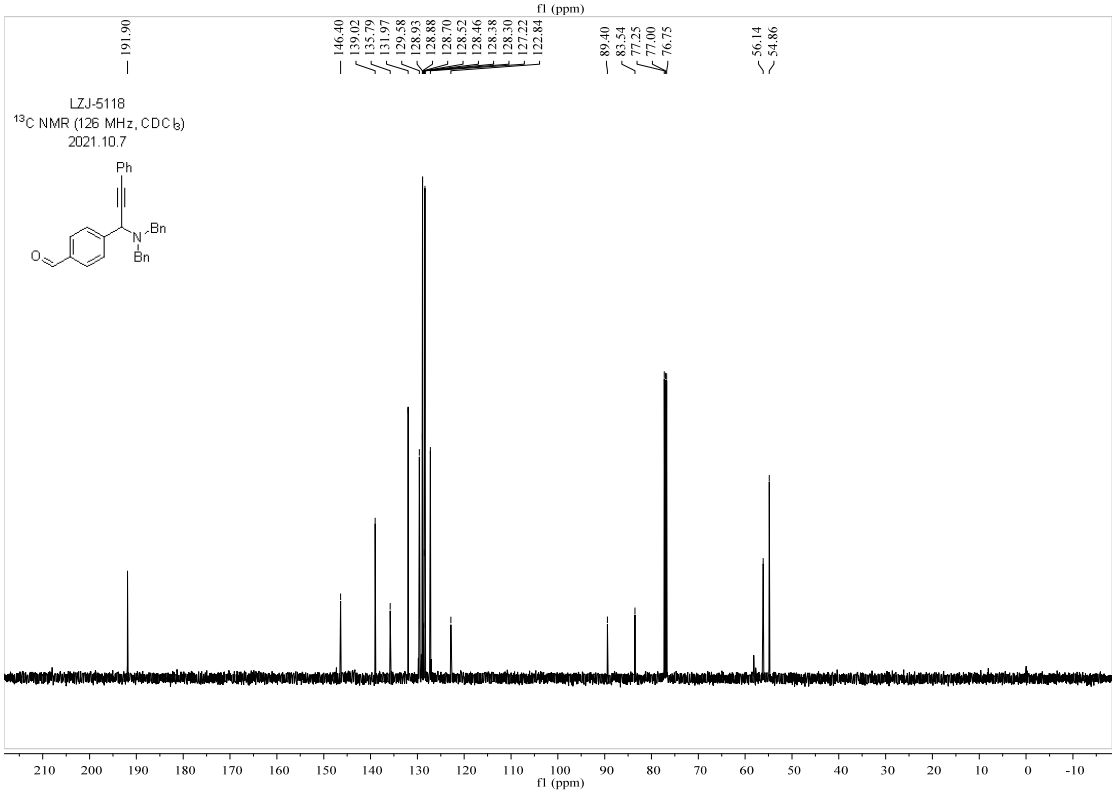
^{1}H NMR and ^{13}C NMR spectra of compound **1s**



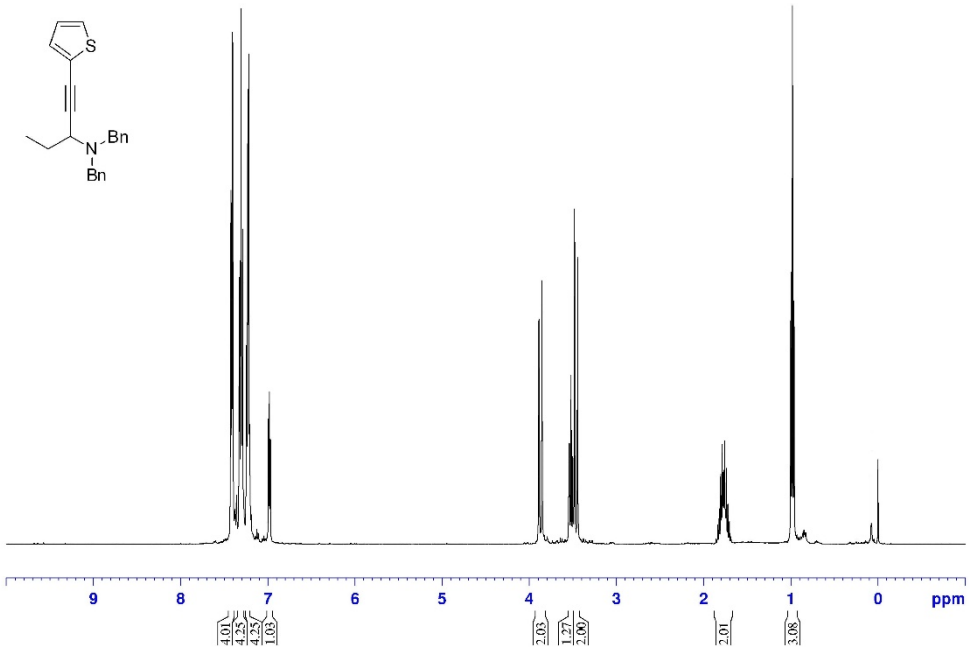


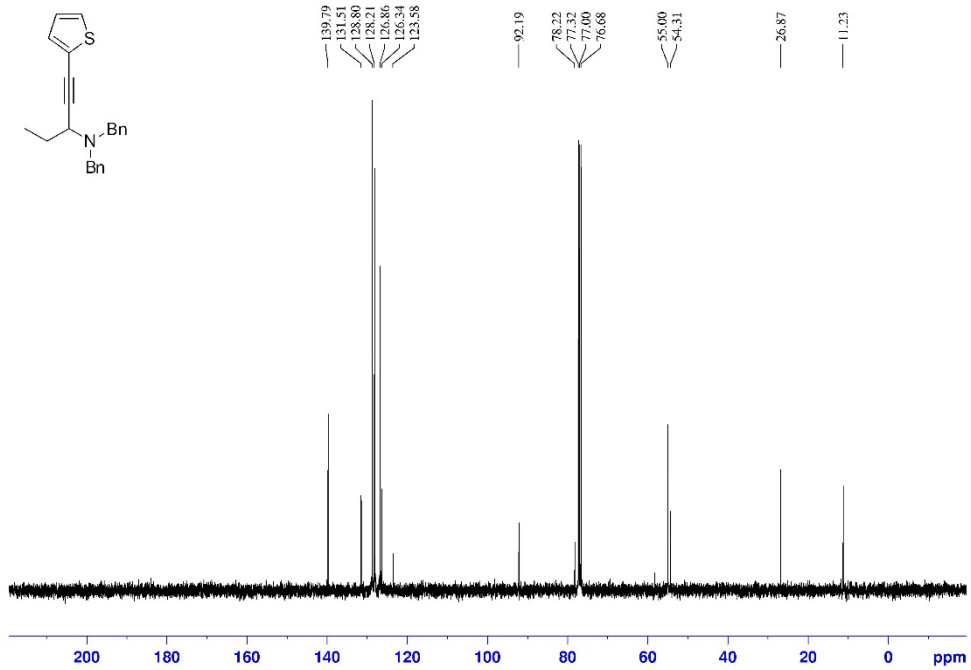
^{1}H NMR and ^{13}C NMR spectra of compound **1t**



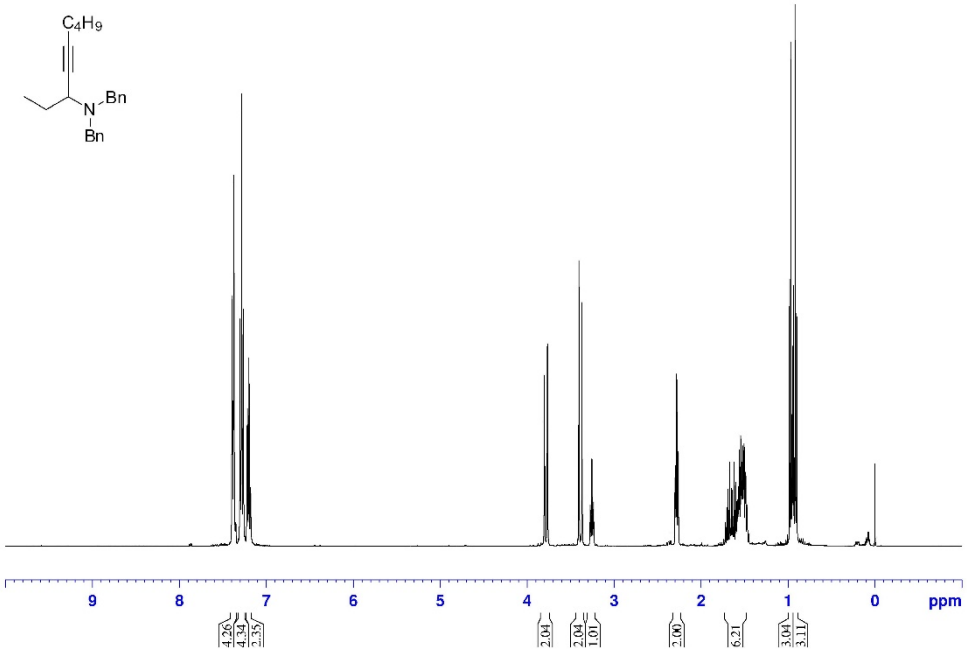


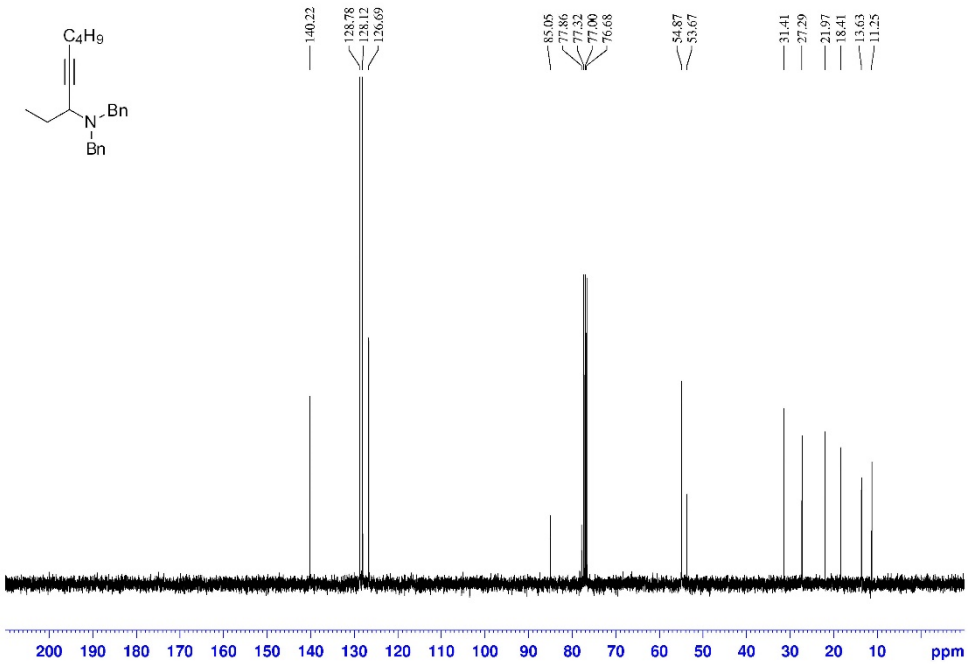
^{1}H NMR and ^{13}C NMR spectra of compound **1u**



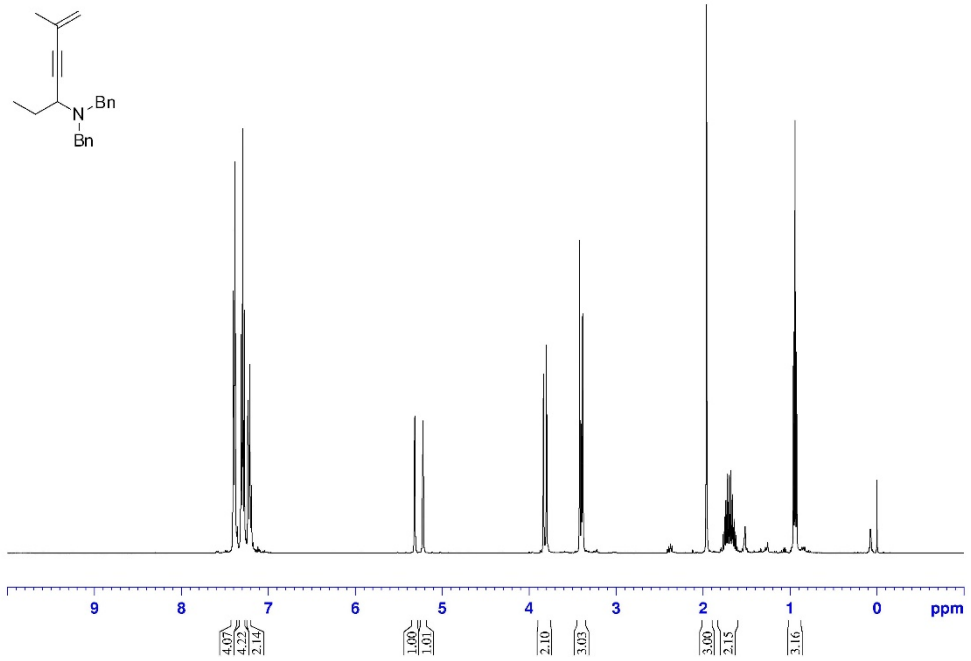


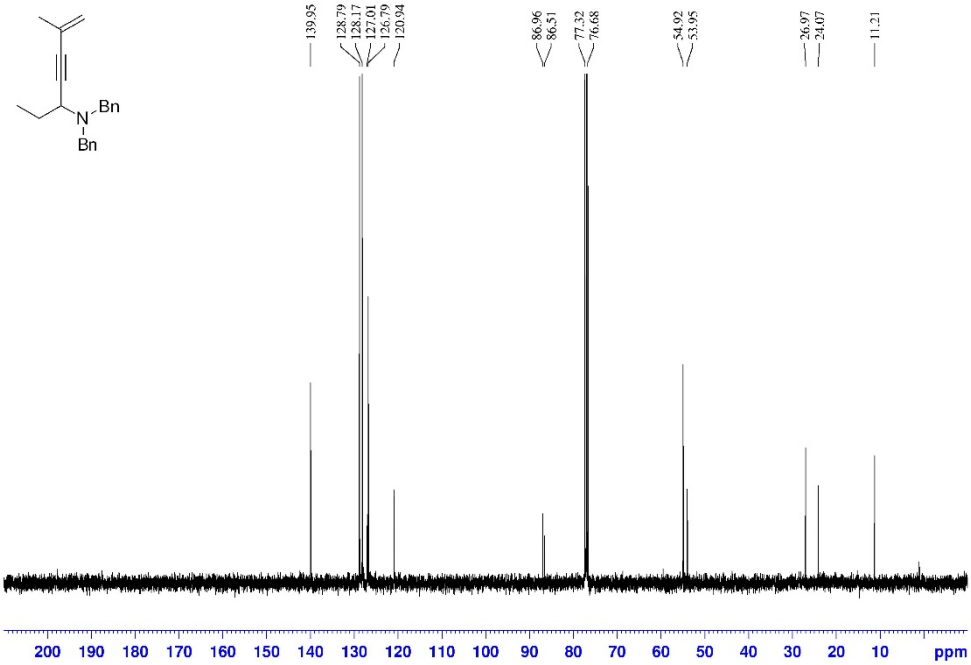
^{1}H NMR and ^{13}C NMR spectra of compound **1v**



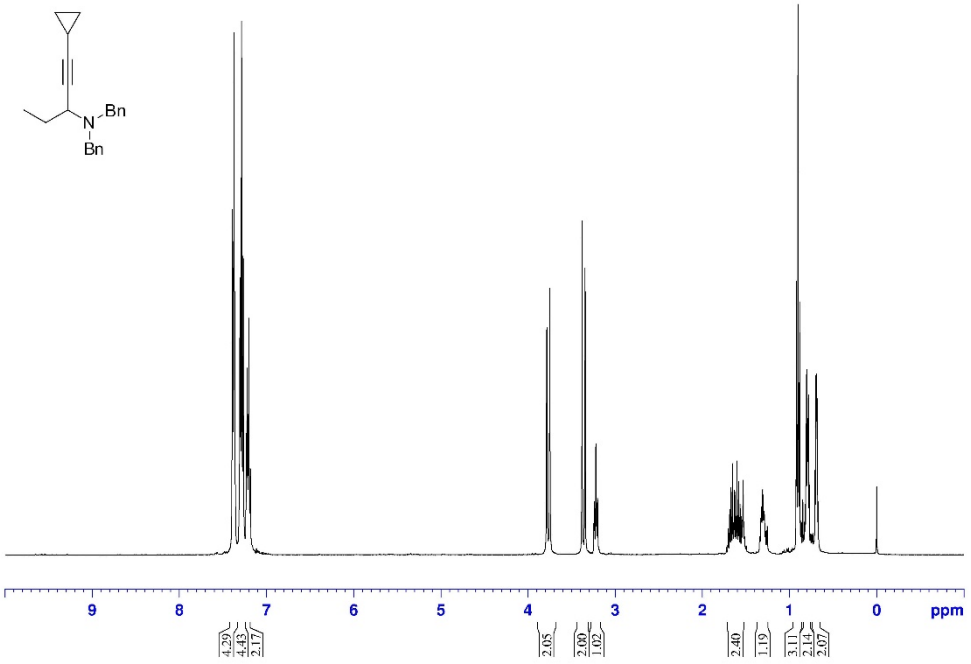


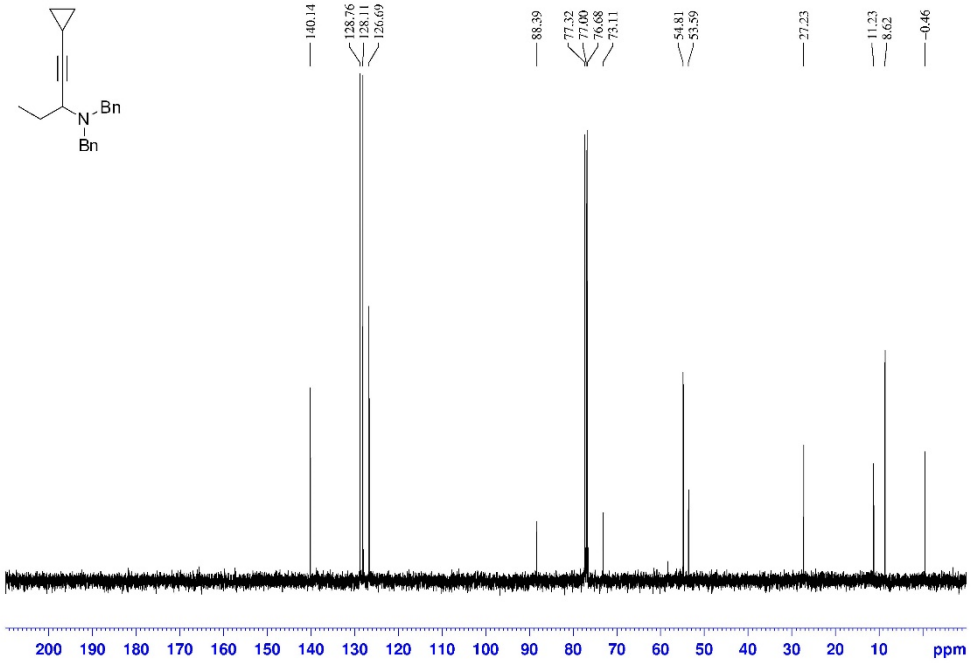
^{1}H NMR and ^{13}C NMR spectra of compound **1w**



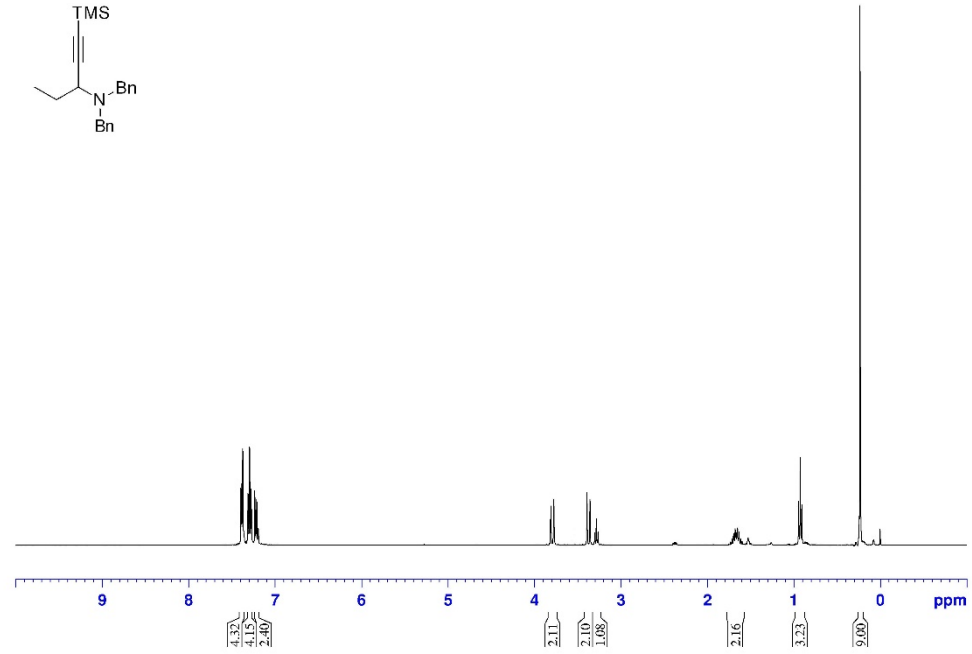


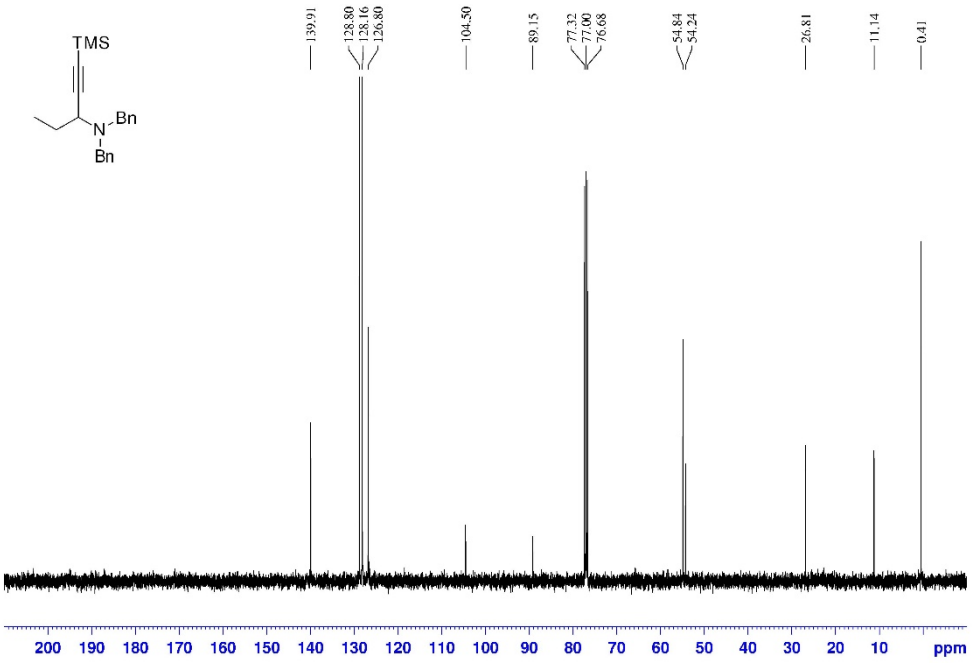
^{1}H NMR and ^{13}C NMR spectra of compound **1x**



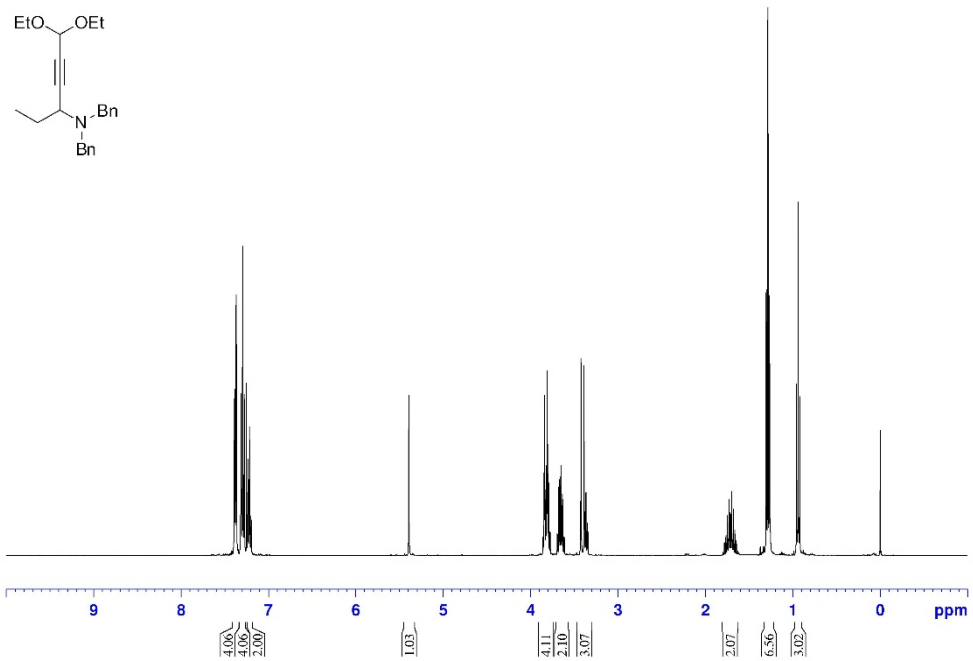


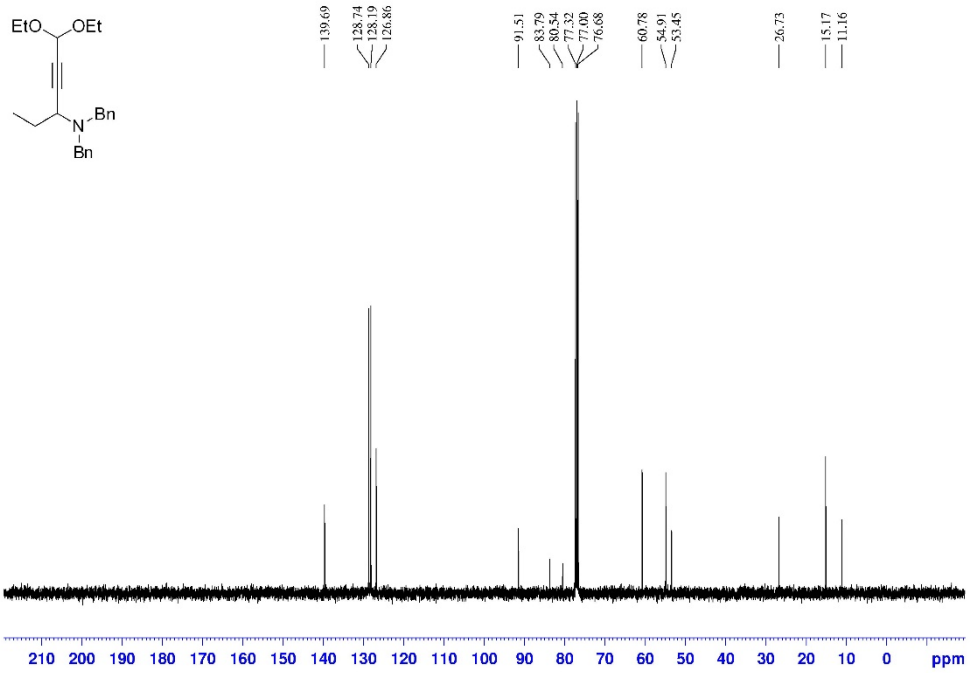
^{1}H NMR and ^{13}C NMR spectra of compound **1y**



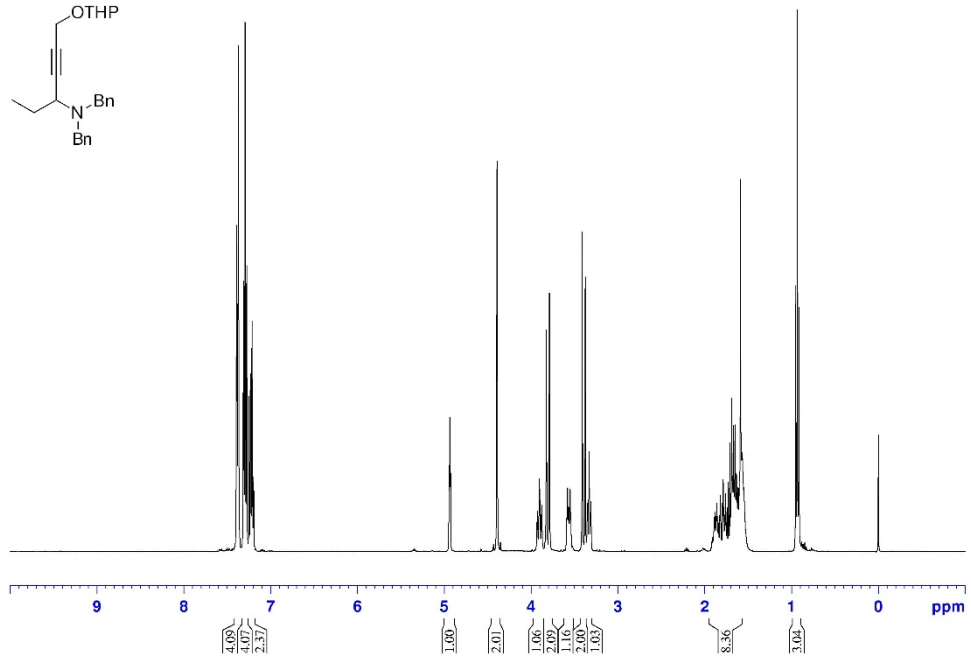


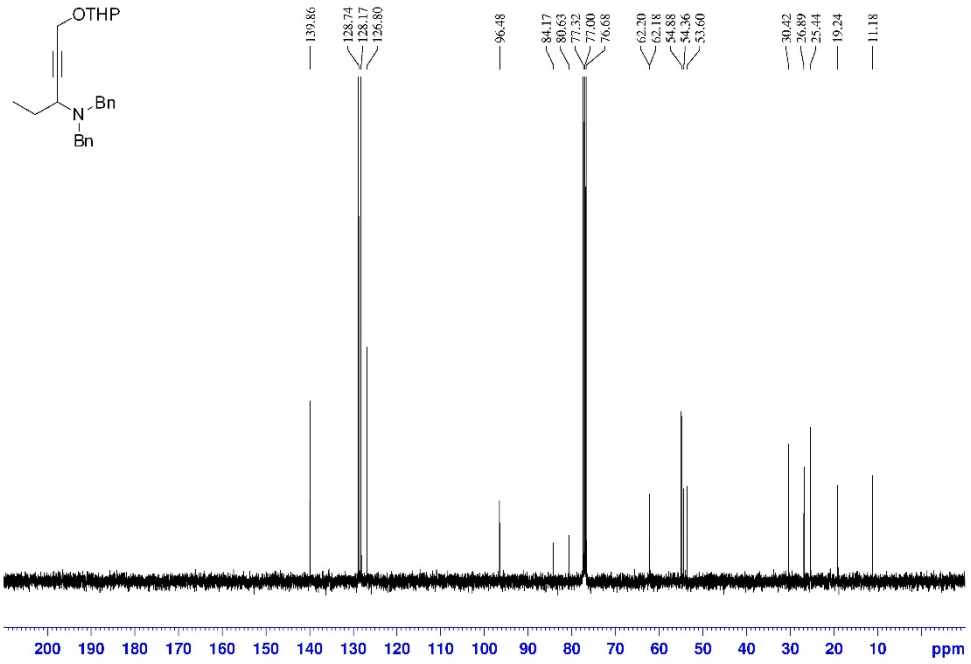
^{1}H NMR and ^{13}C NMR spectra of compound **1z**



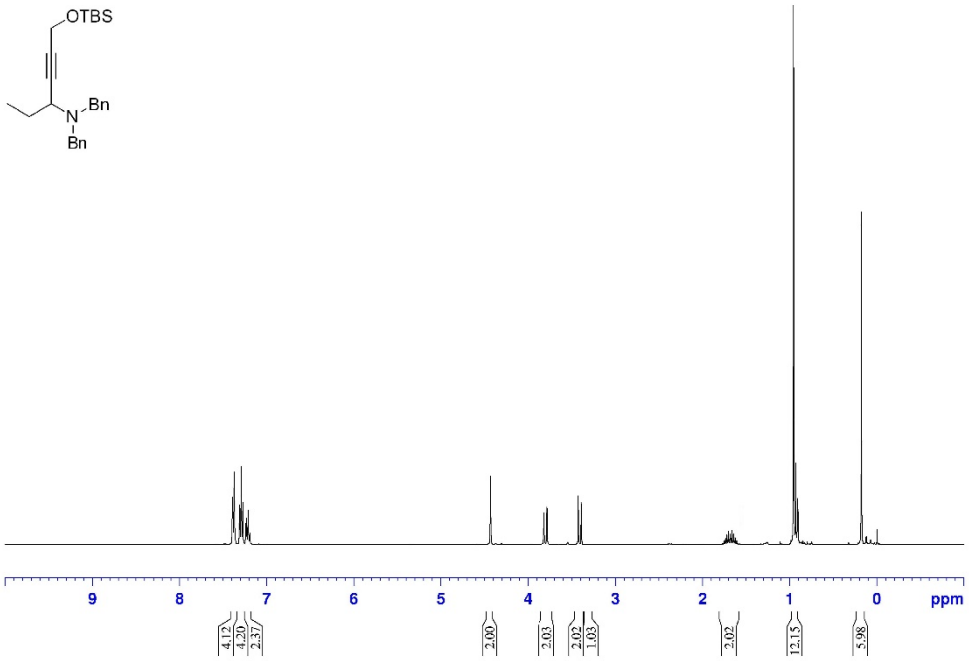


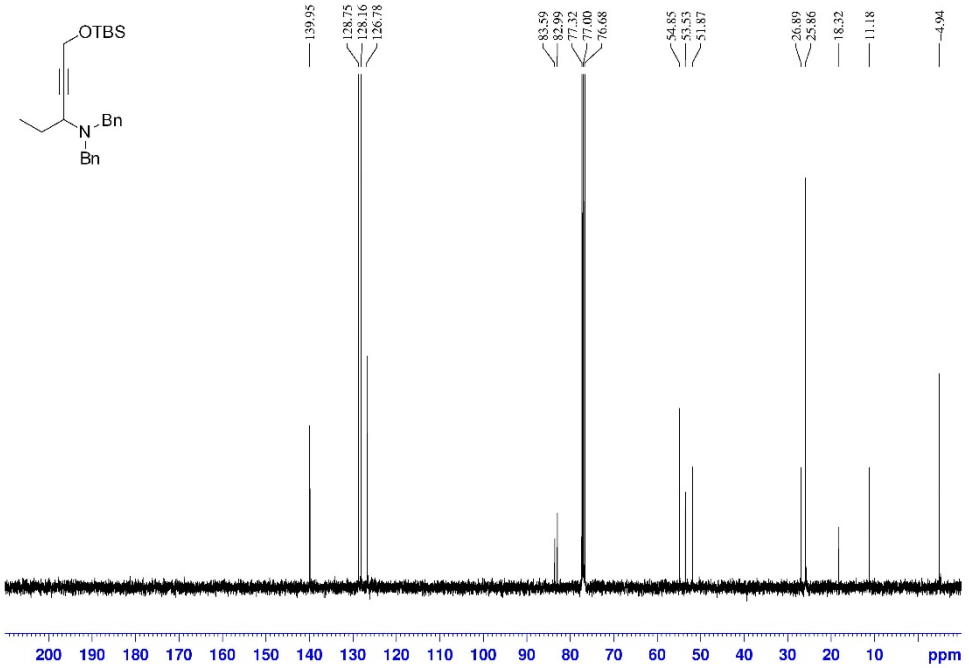
^{1}H NMR and ^{13}C NMR spectra of compound **1aa**



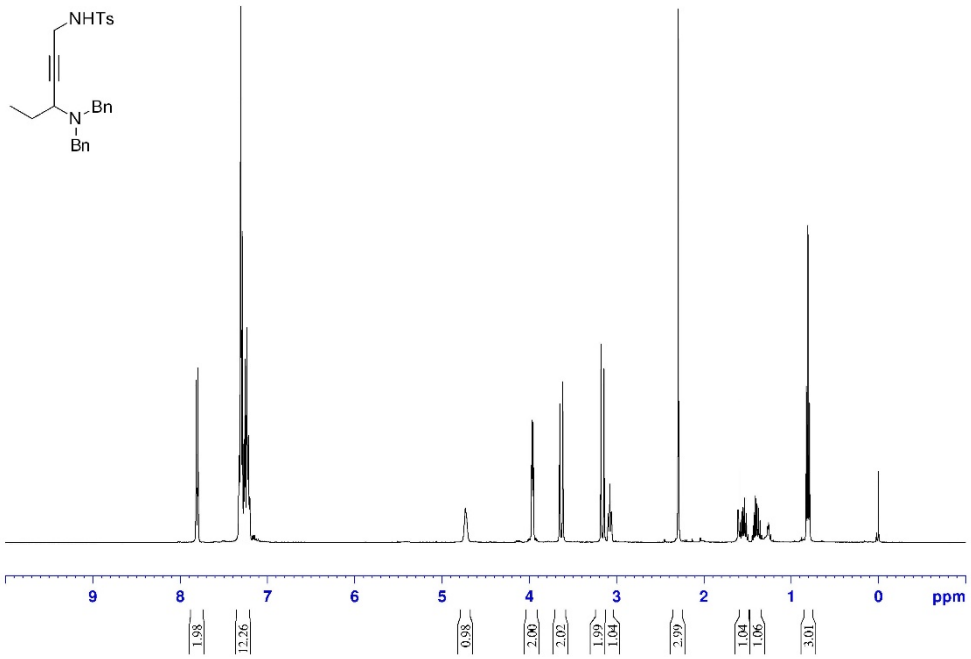


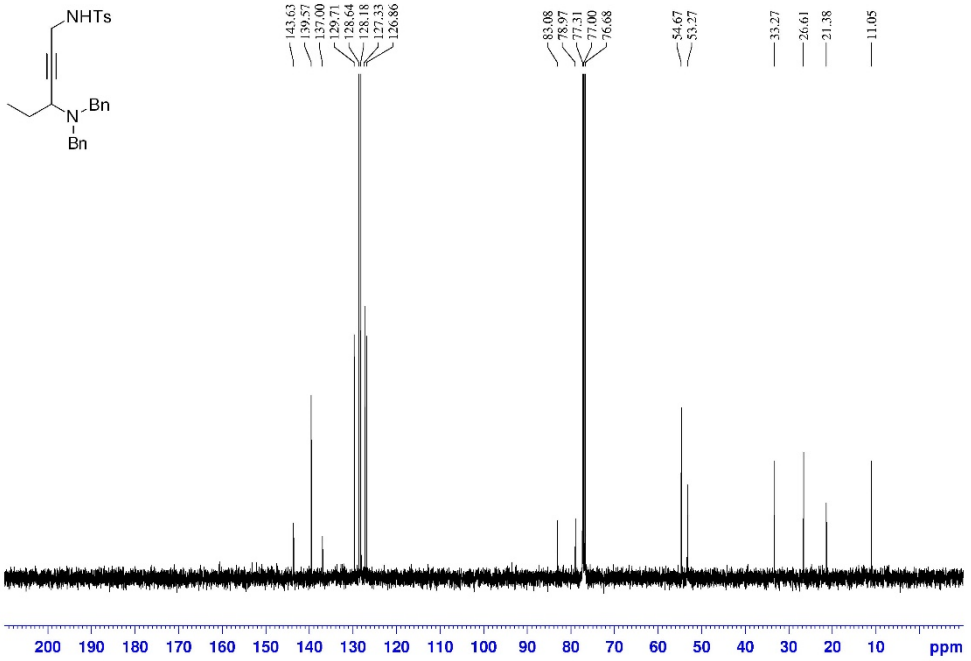
^{1}H NMR and ^{13}C NMR spectra of compound **1ab**



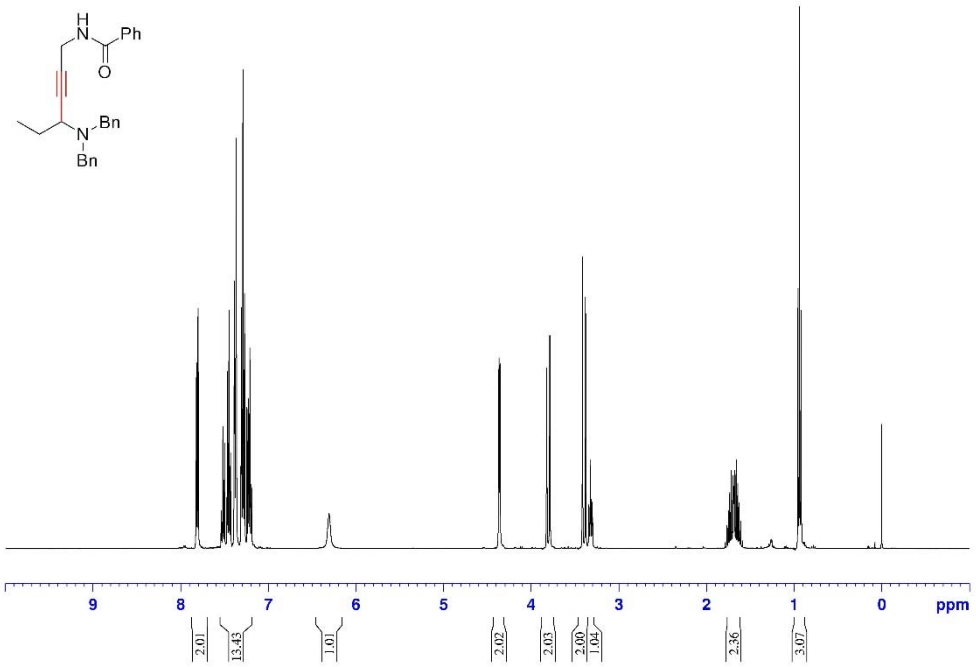


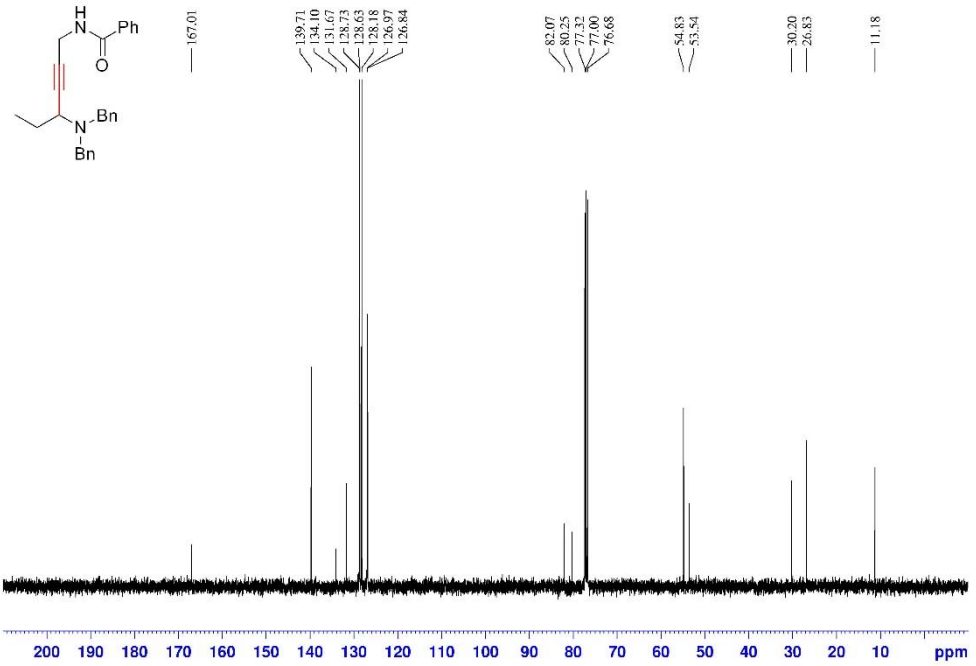
^{1}H NMR and ^{13}C NMR spectra of compound **1ac**



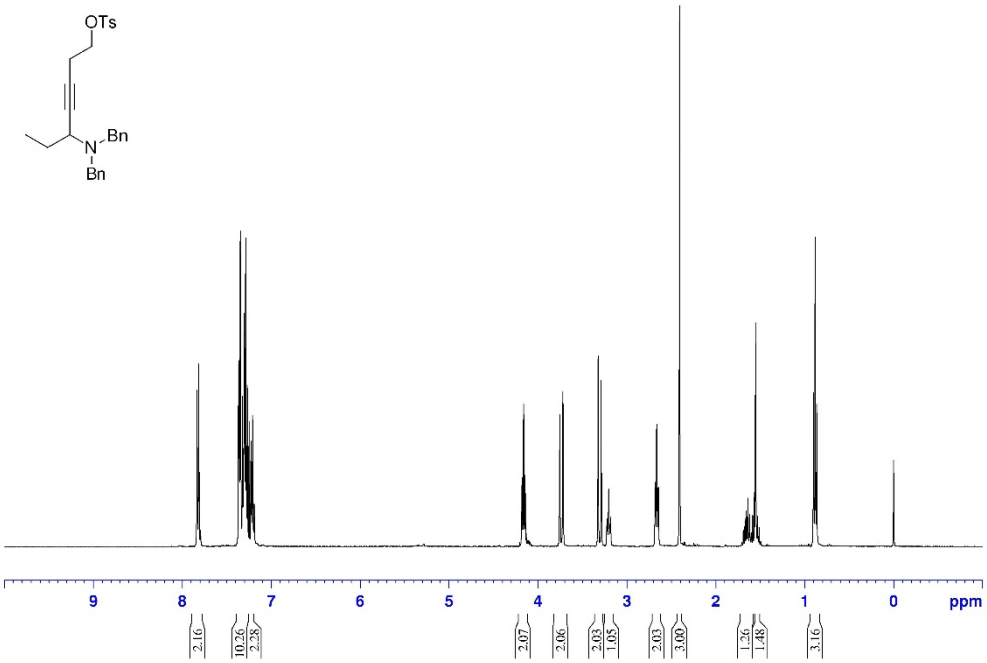


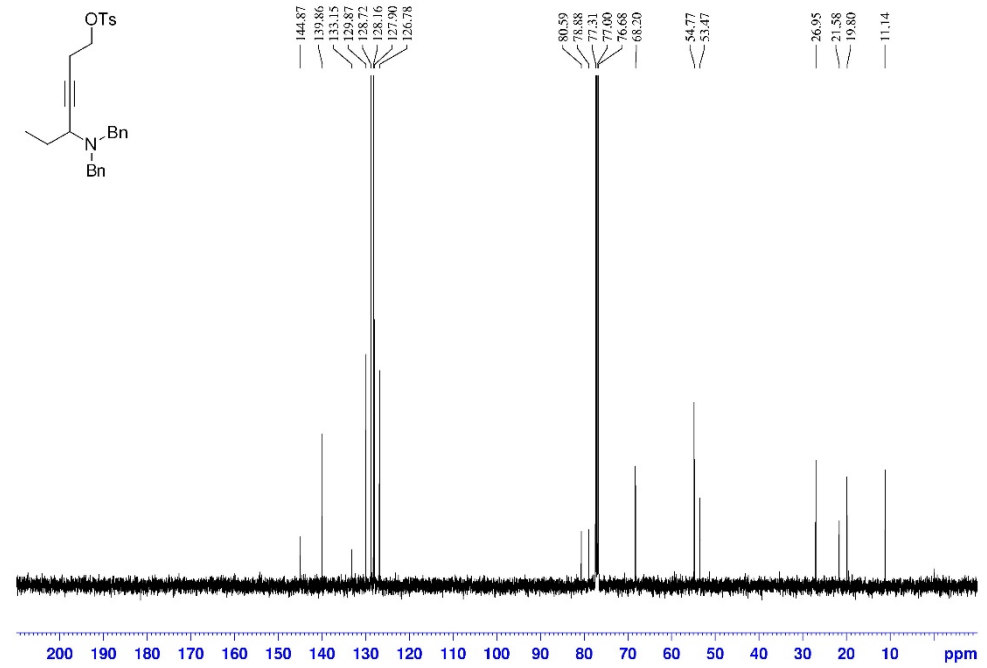
^{1}H NMR and ^{13}C NMR spectra of compound **1ad**



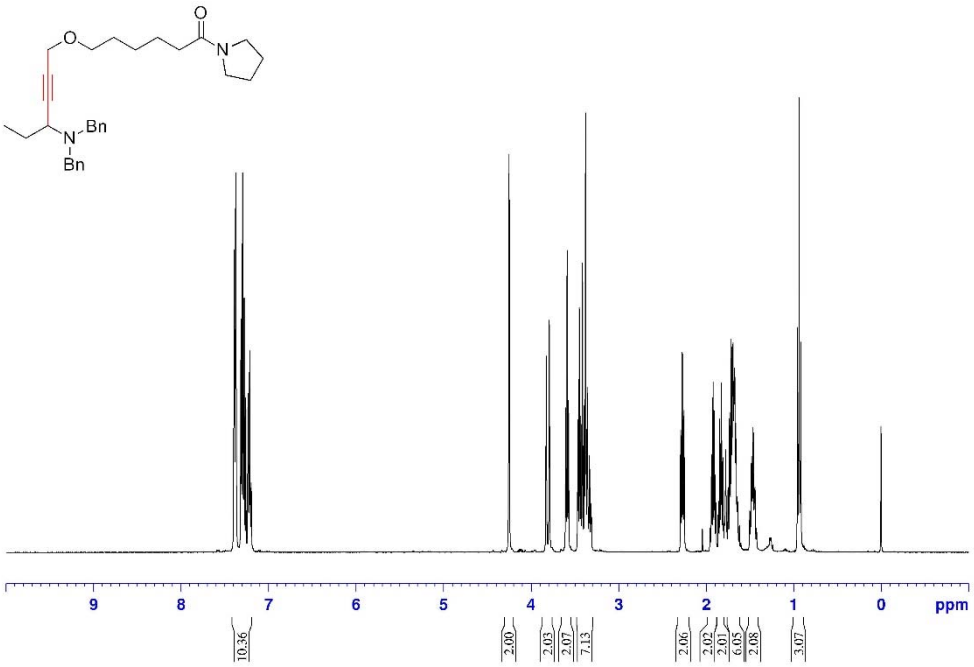


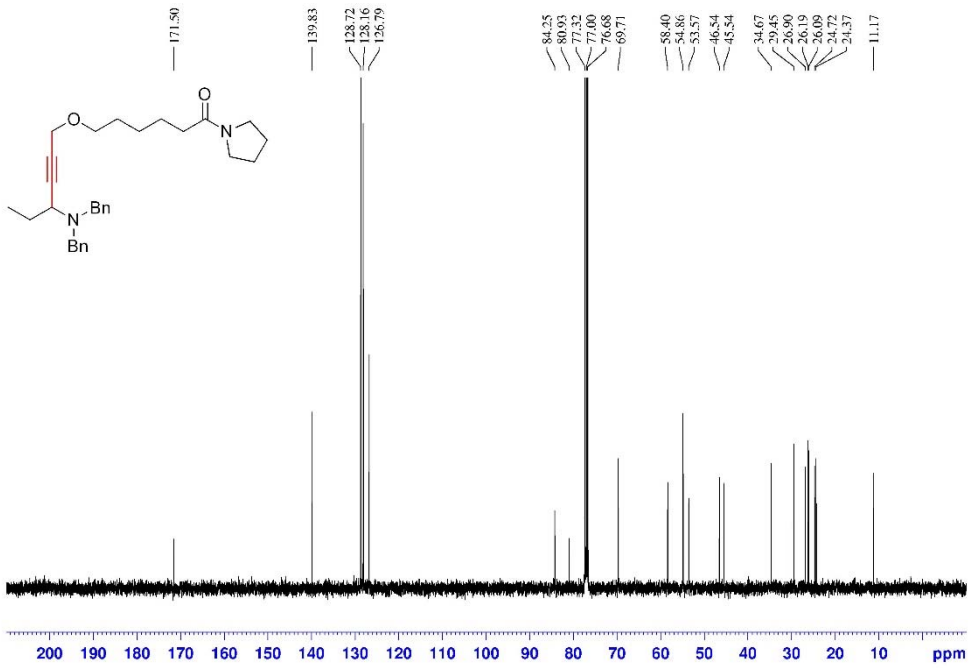
^{1}H NMR and ^{13}C NMR spectra of compound **1ae**



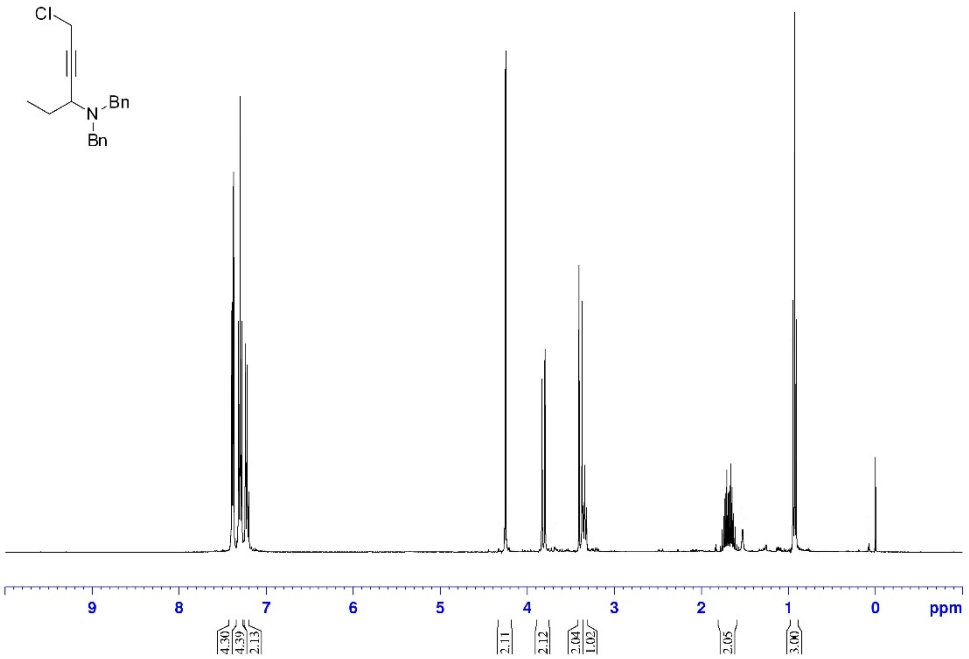


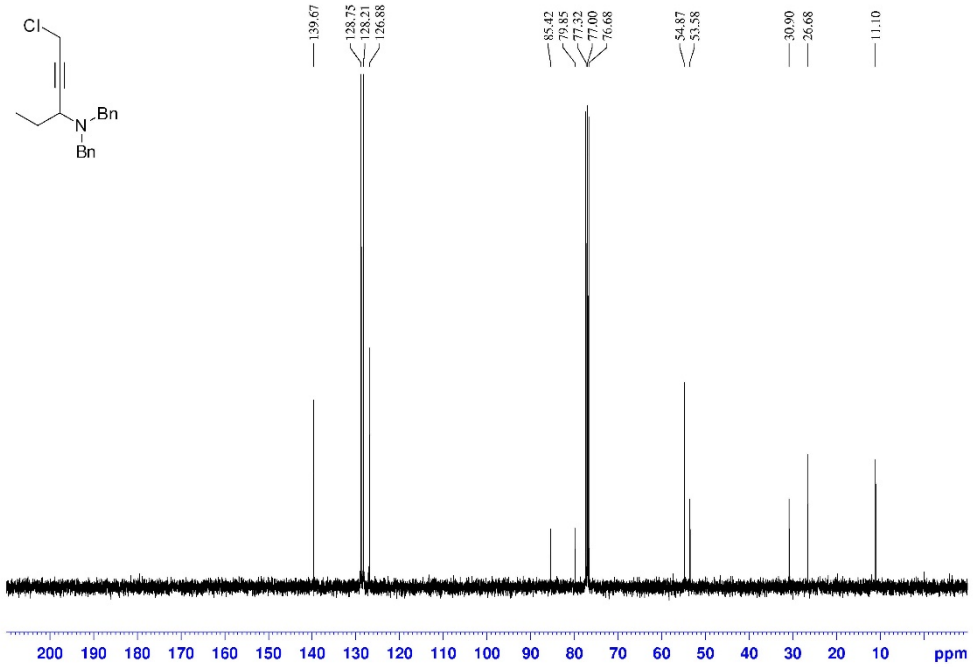
^{1}H NMR and ^{13}C NMR spectra of compound **1af**



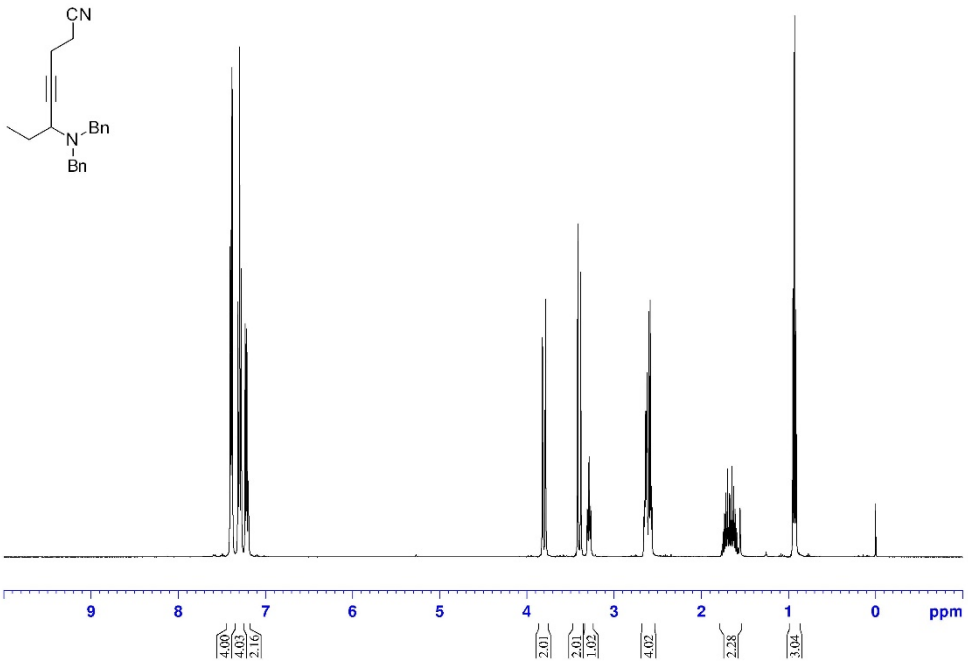


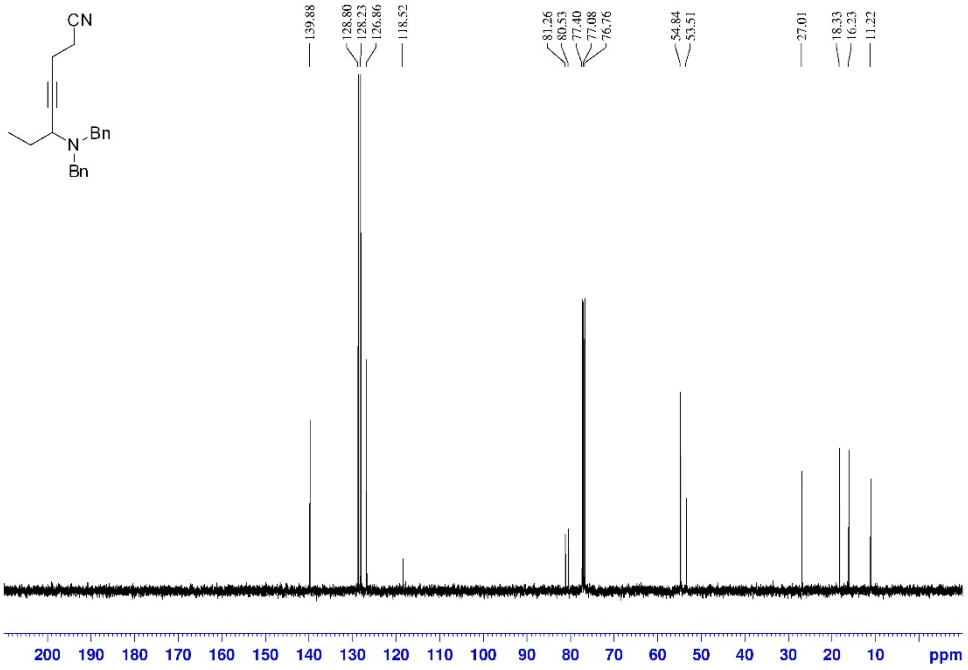
^{1}H NMR and ^{13}C NMR spectra of compound **1ag**



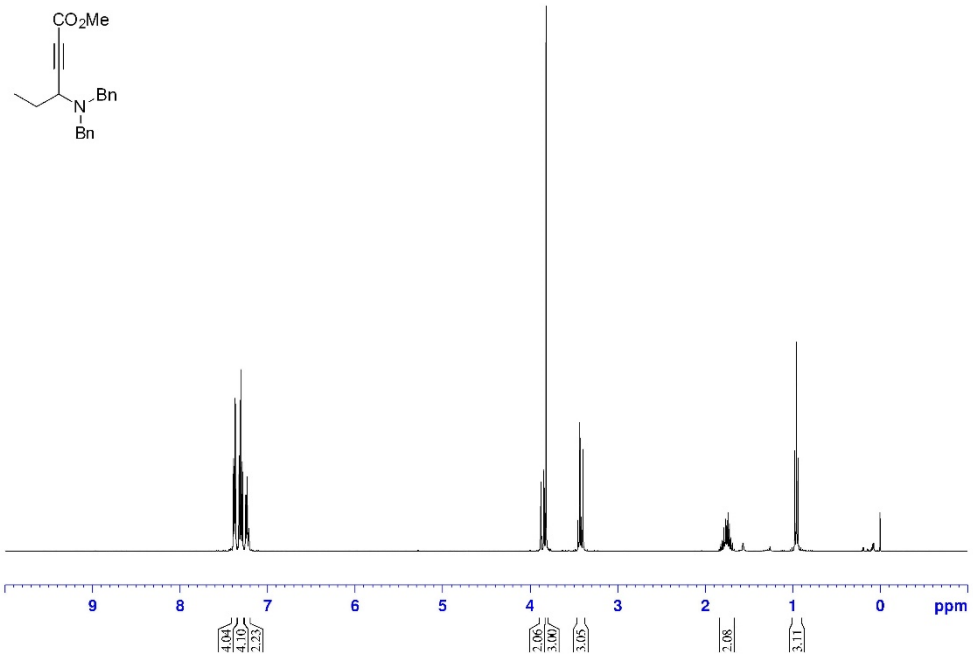


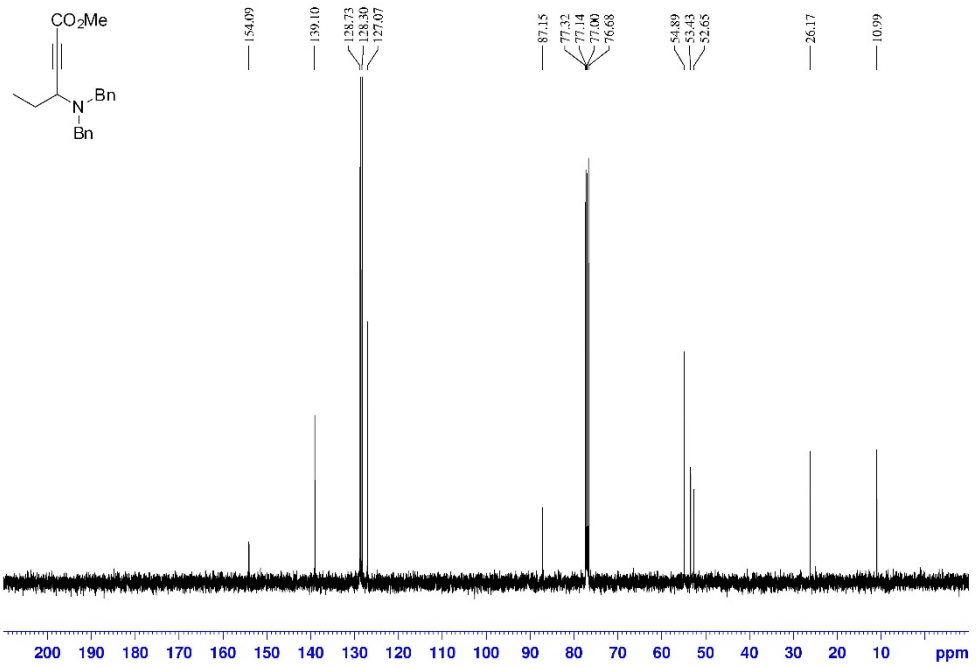
^{1}H NMR and ^{13}C NMR spectra of compound **1ah**



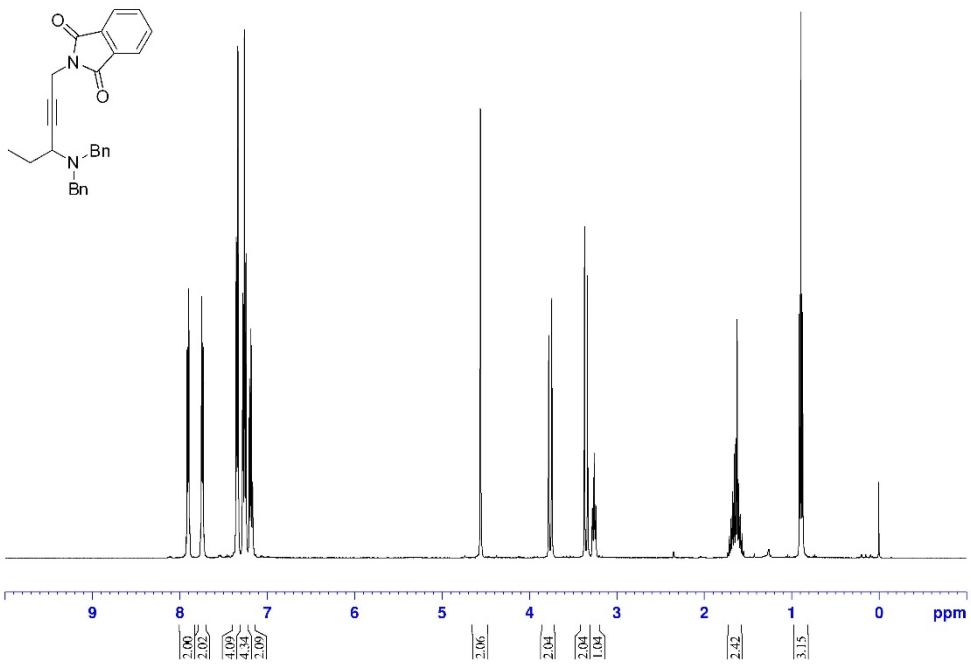


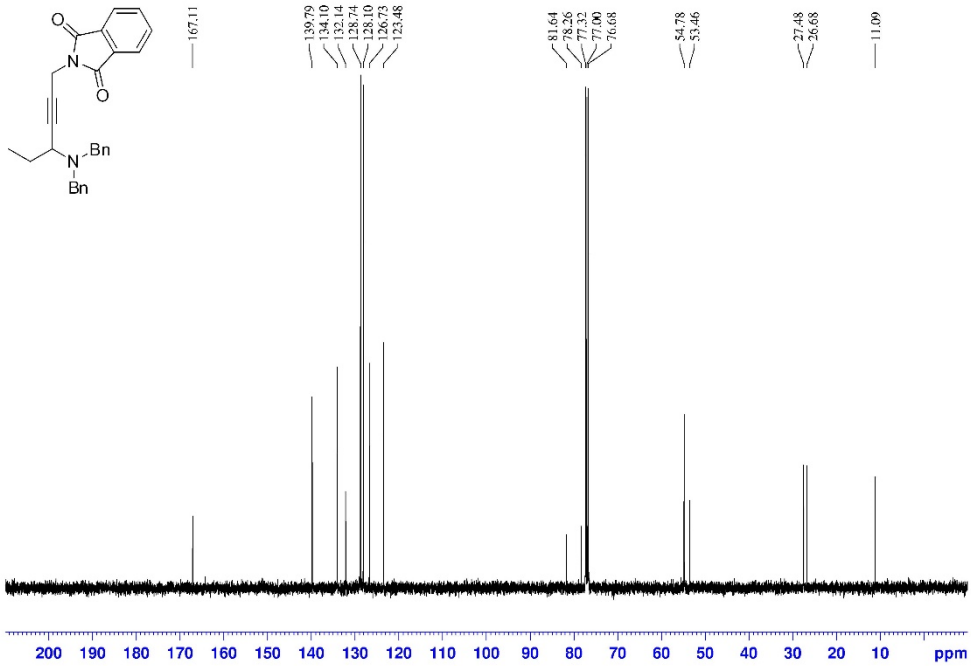
^{1}H NMR and ^{13}C NMR spectra of compound **1ai**



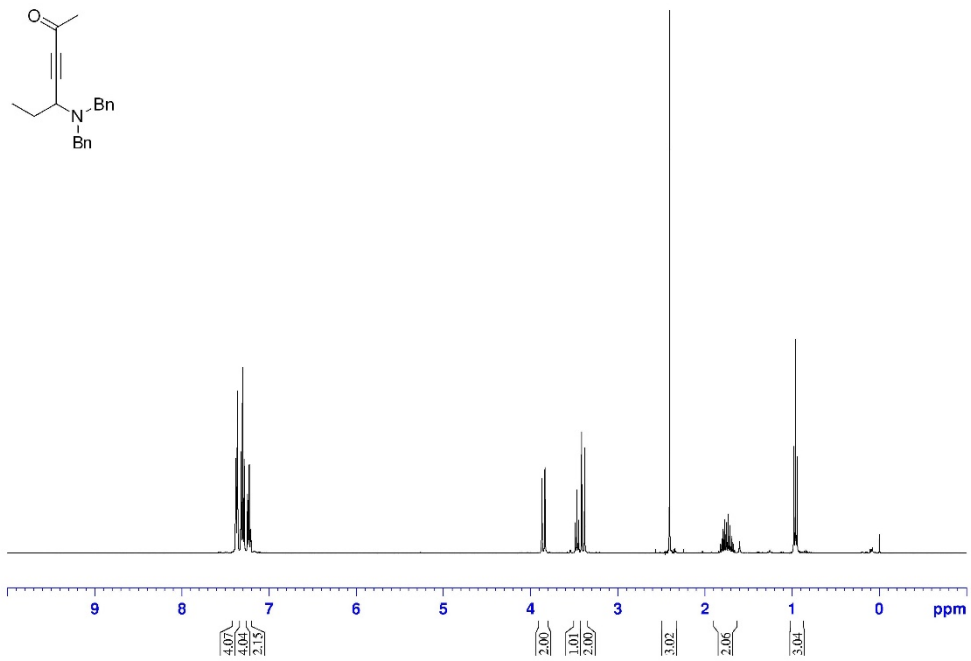


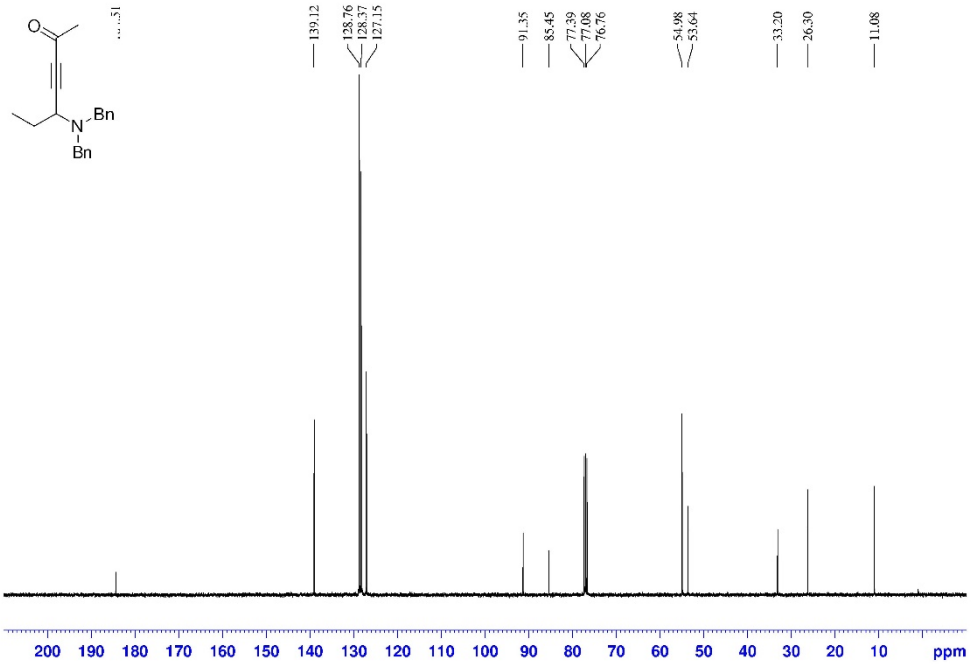
^{1}H NMR and ^{13}C NMR spectra of compound **1aj**



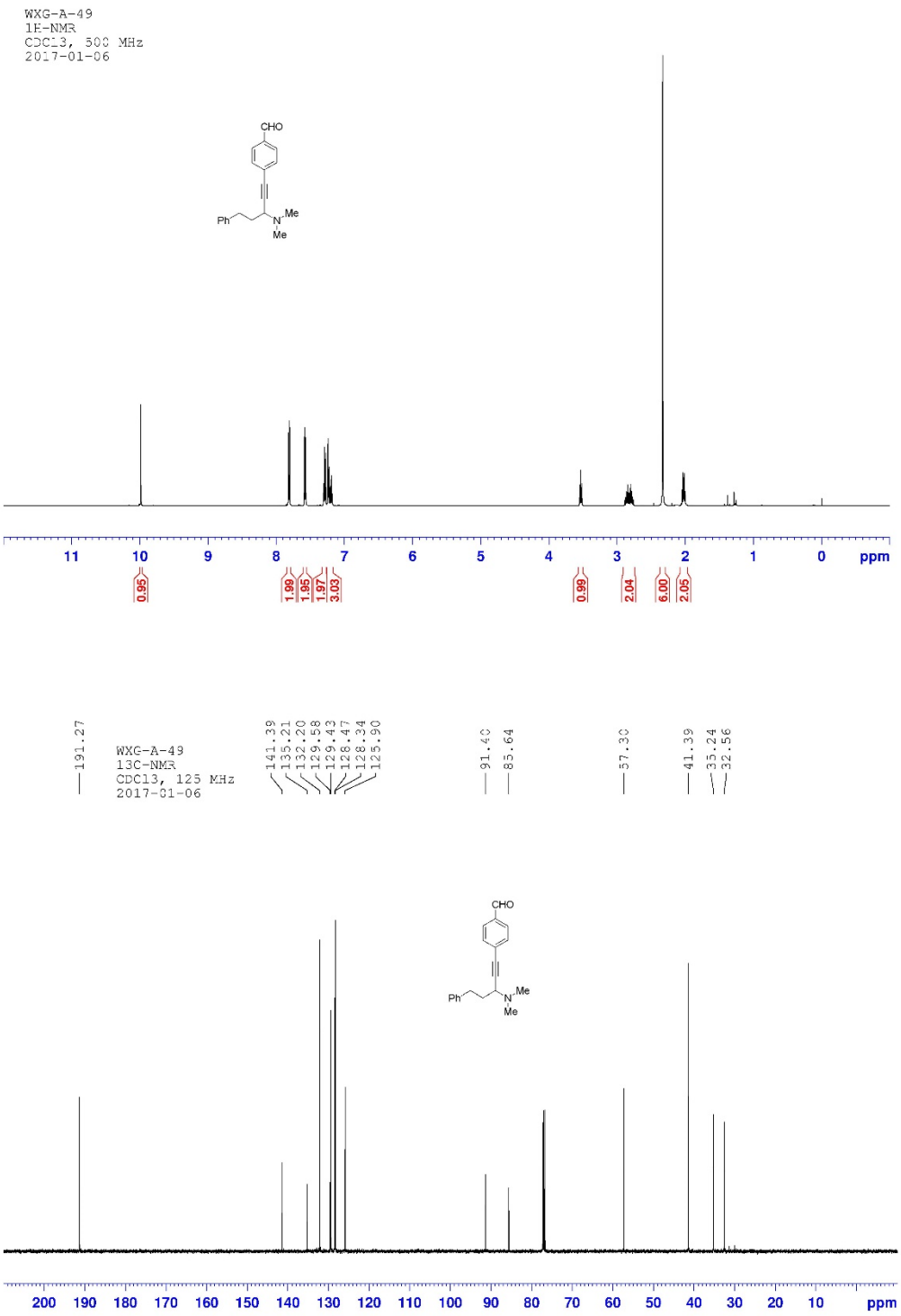


^{1}H NMR and ^{13}C NMR spectra of compound **1ak**

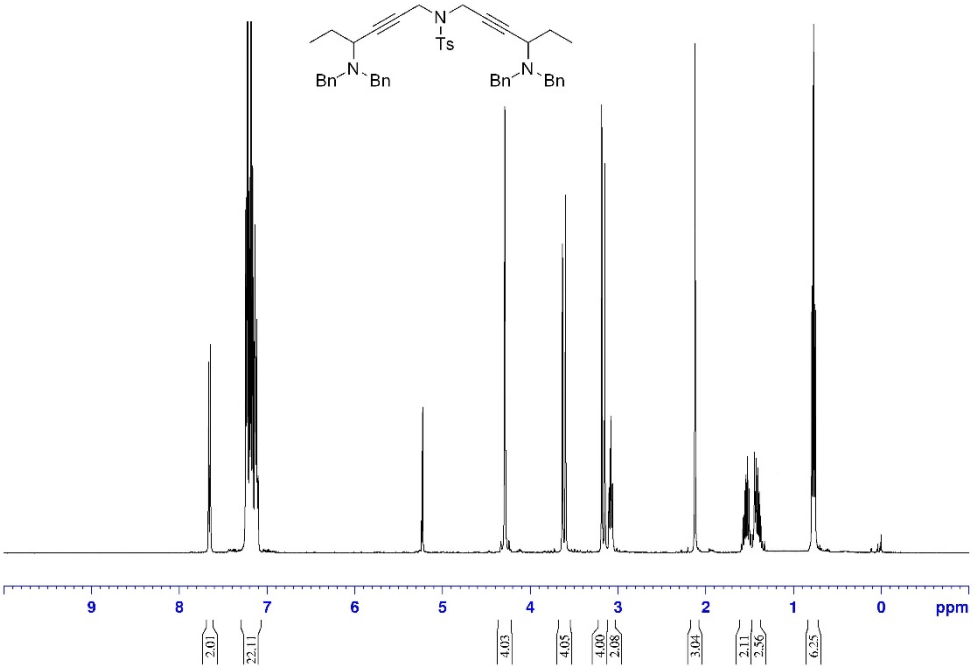


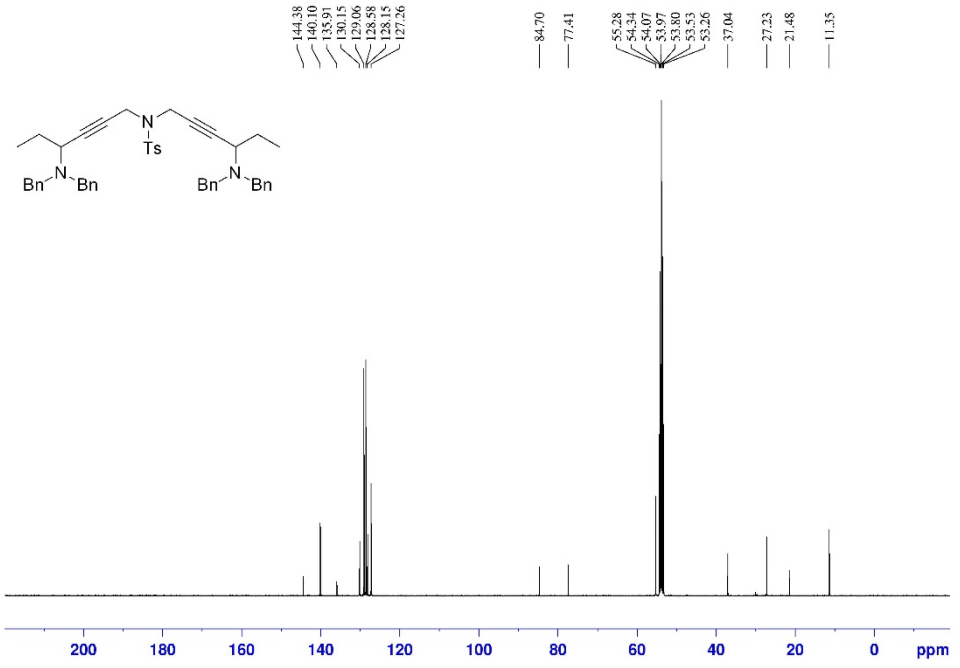


^{1}H NMR and ^{13}C NMR spectra of compound **1al**

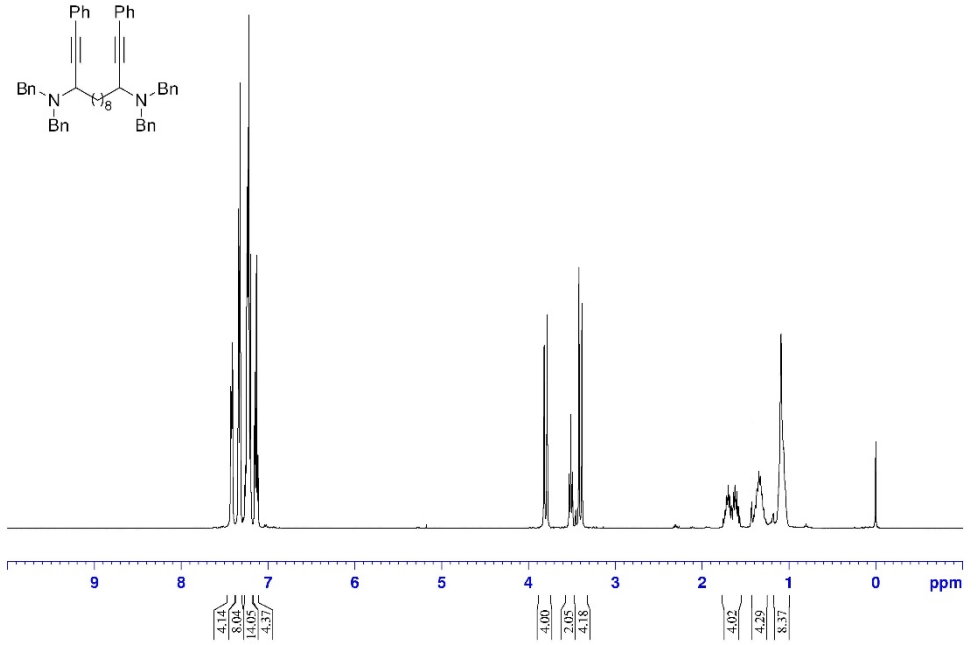


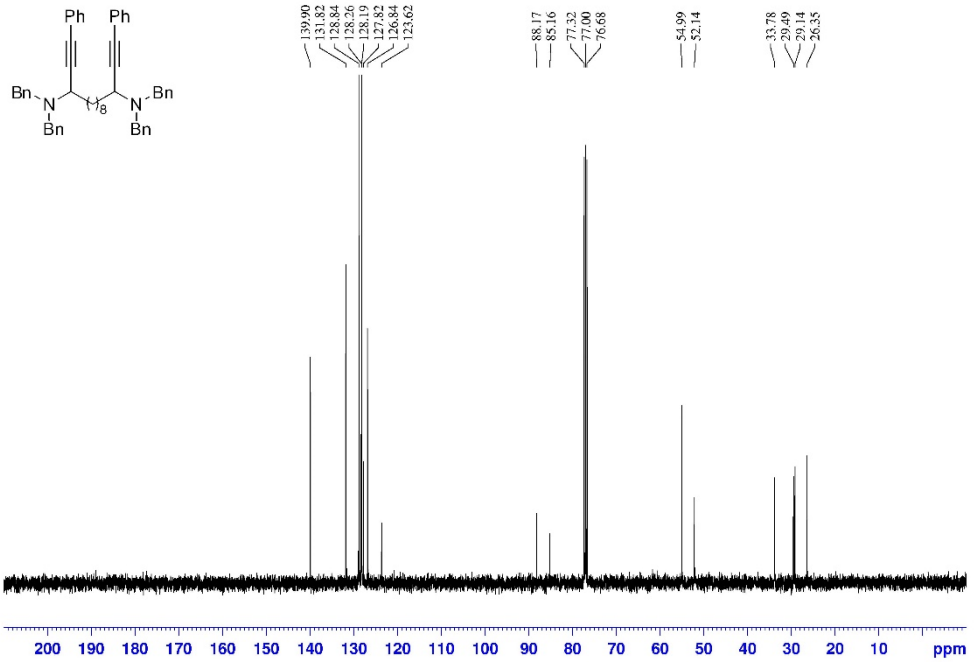
^{1}H NMR and ^{13}C NMR spectra of compound **1am**



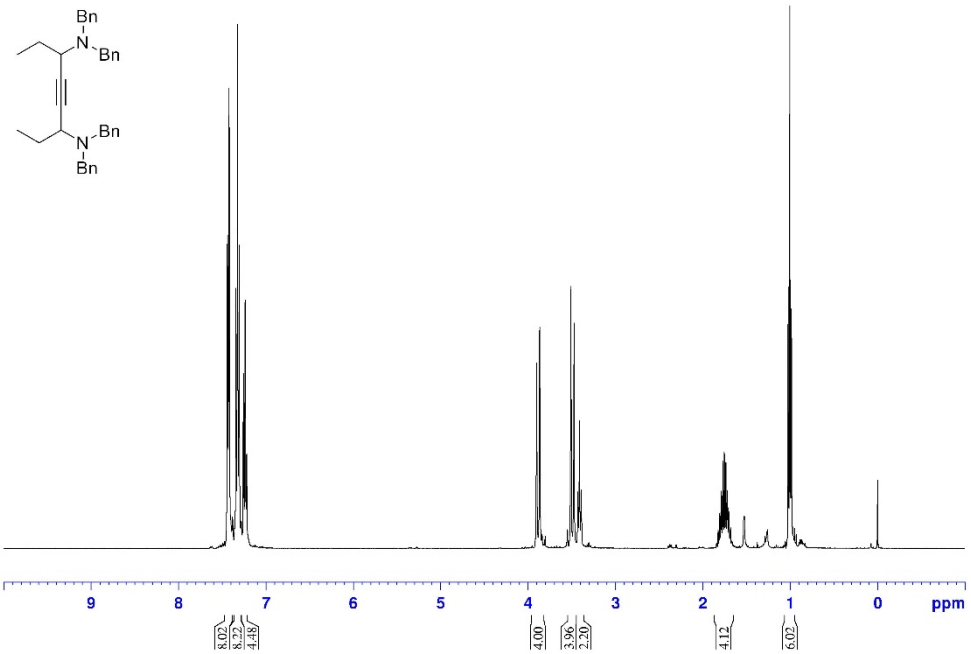


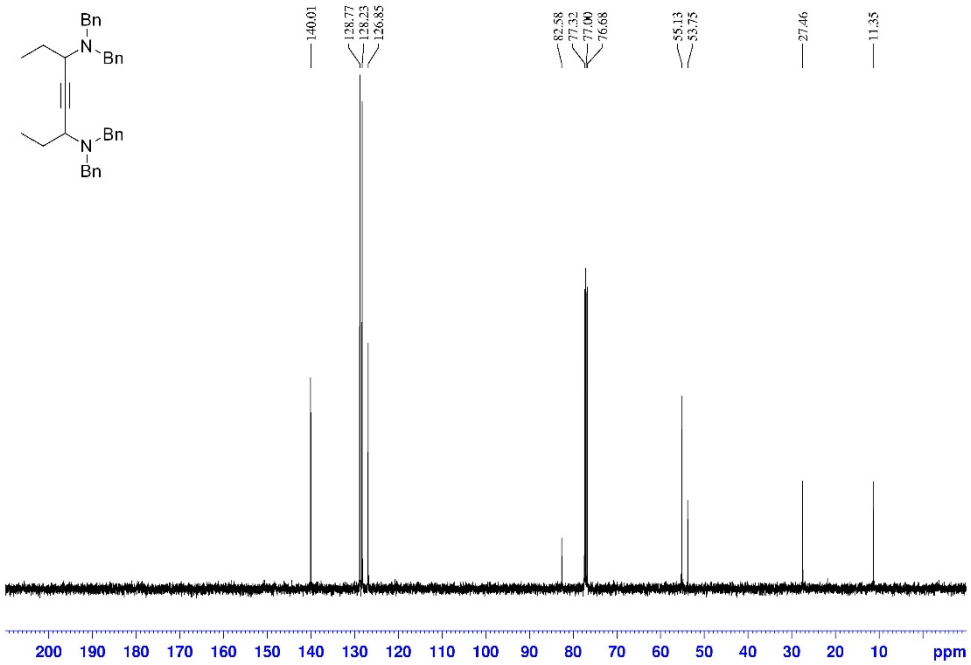
^{1}H NMR and ^{13}C NMR spectra of compound **1an**



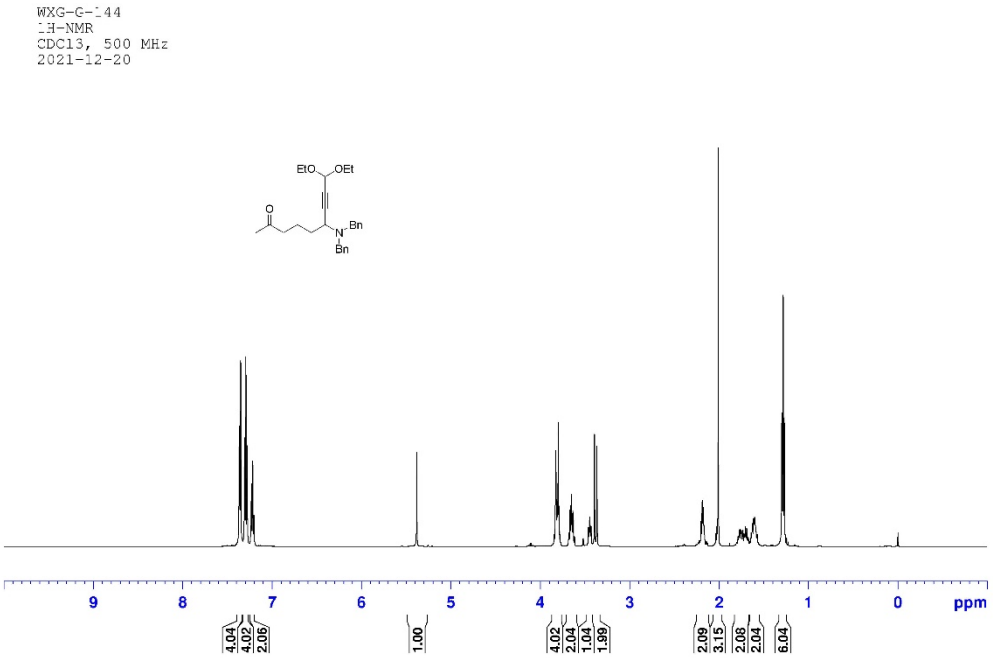


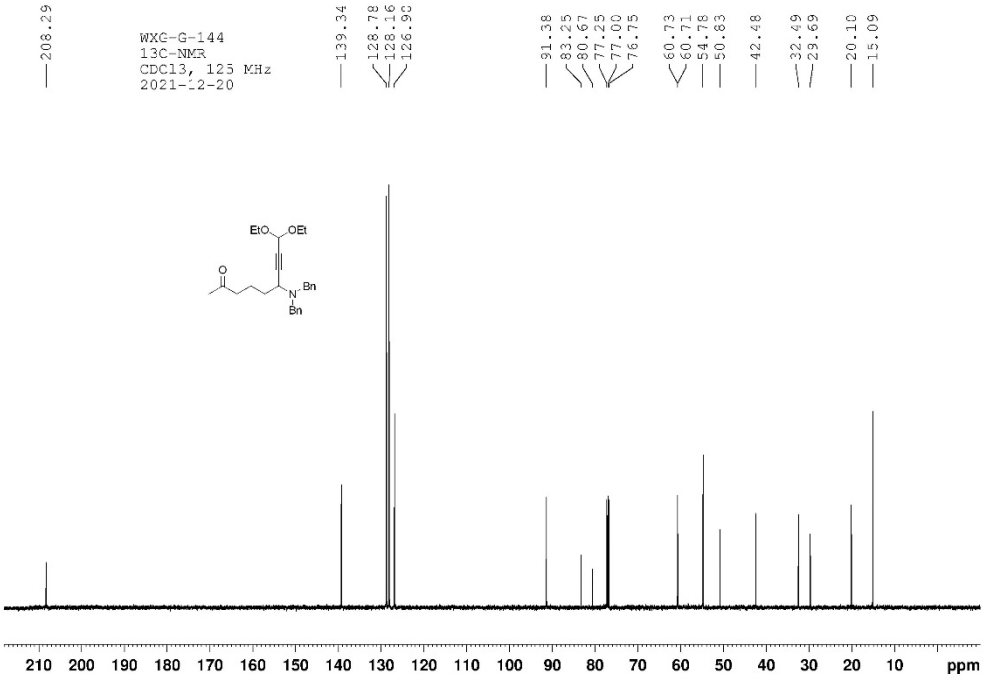
^{1}H NMR and ^{13}C NMR spectra of compound **1ao**



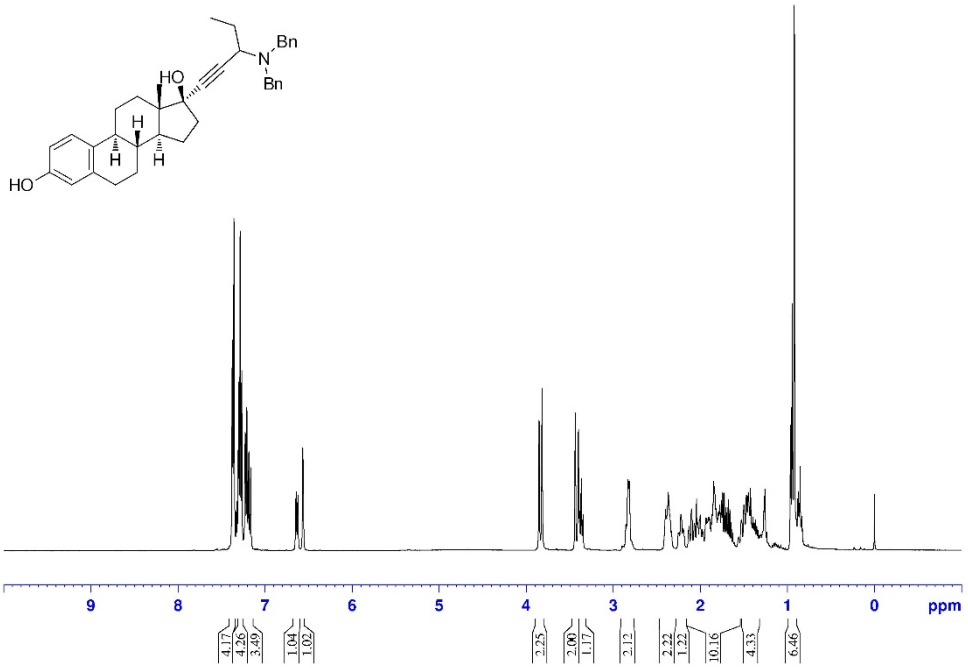


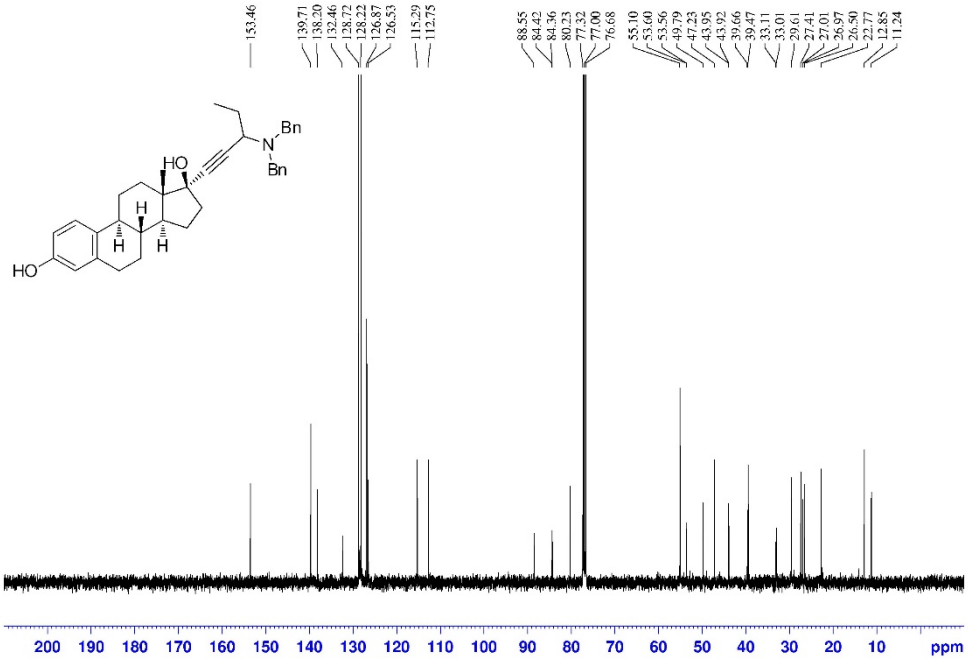
^{1}H NMR and ^{13}C NMR spectra of compound **1ap**



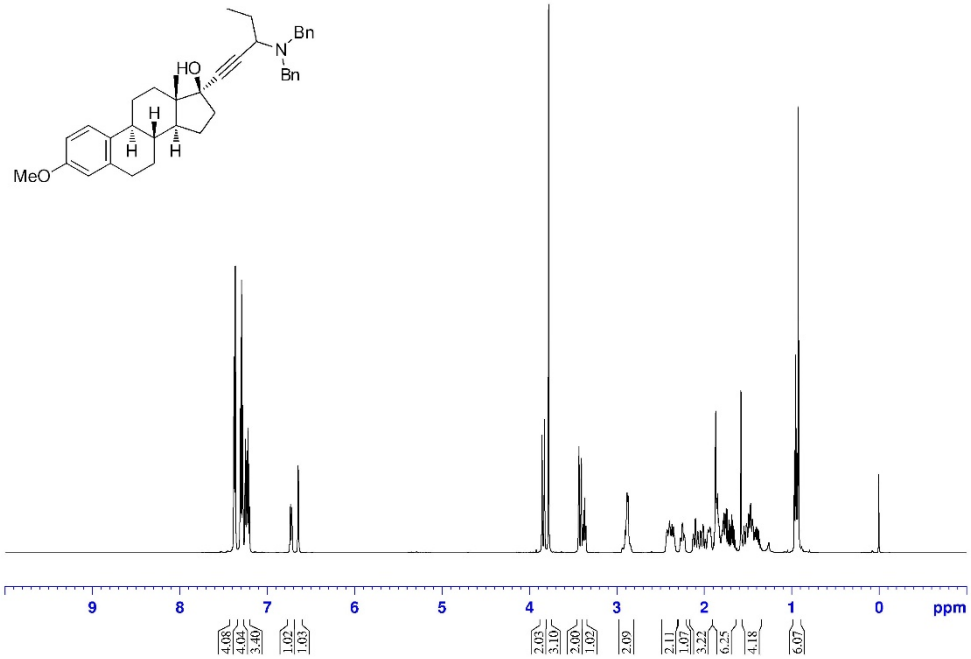


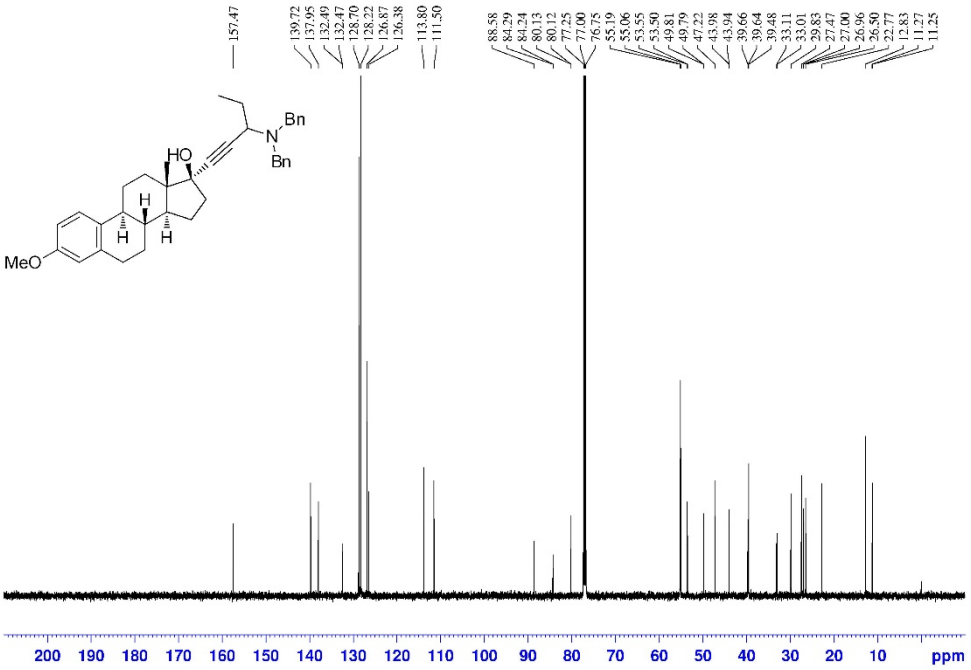
^{1}H NMR and ^{13}C NMR spectra of compound **1aq**



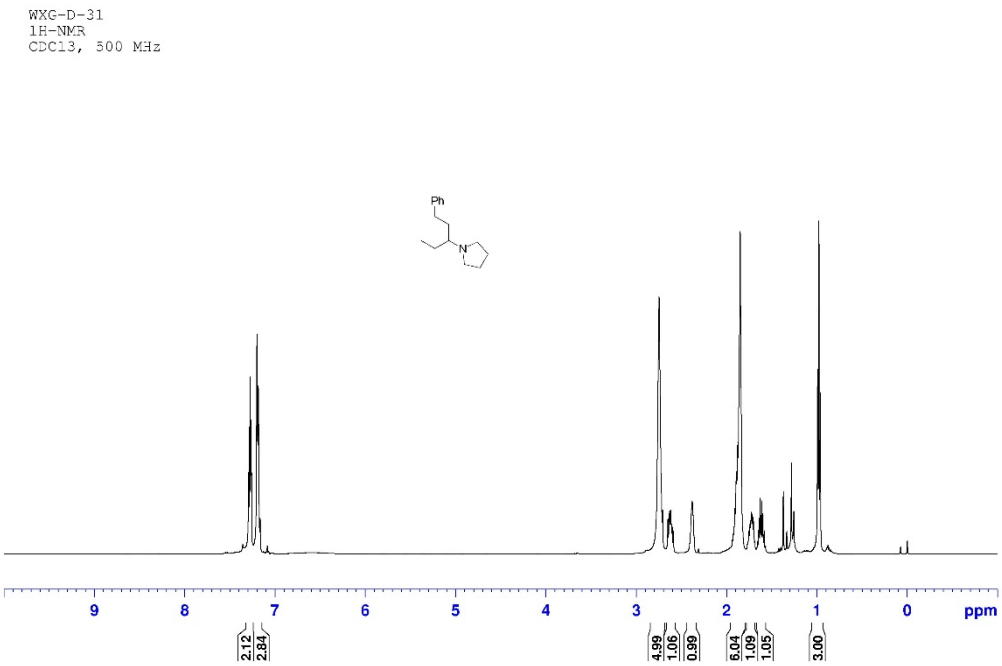


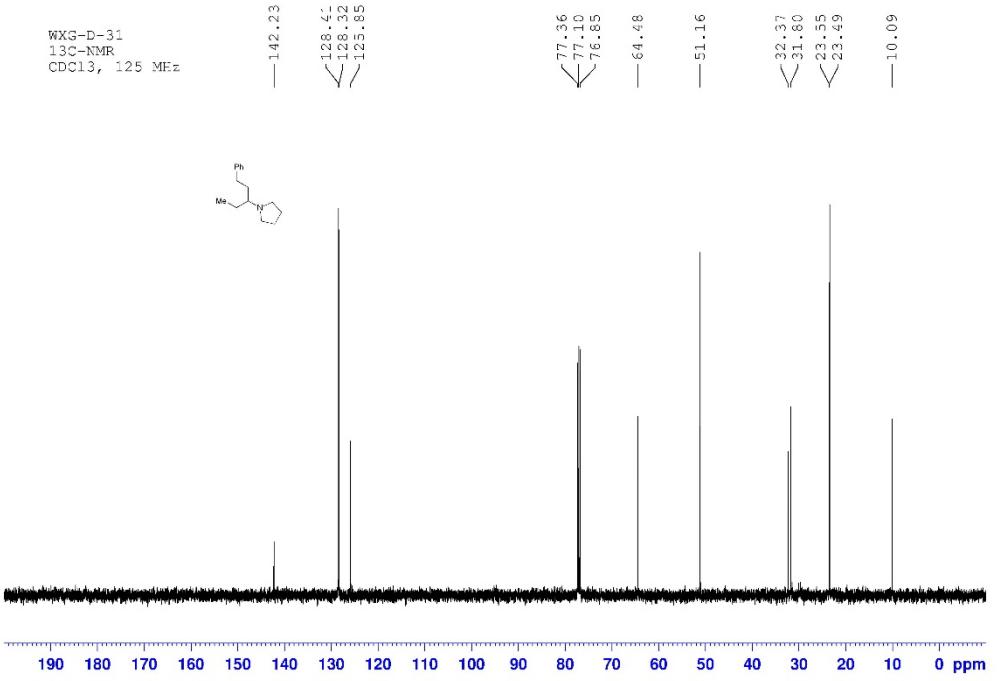
^{1}H NMR and ^{13}C NMR spectra of compound **1ar**



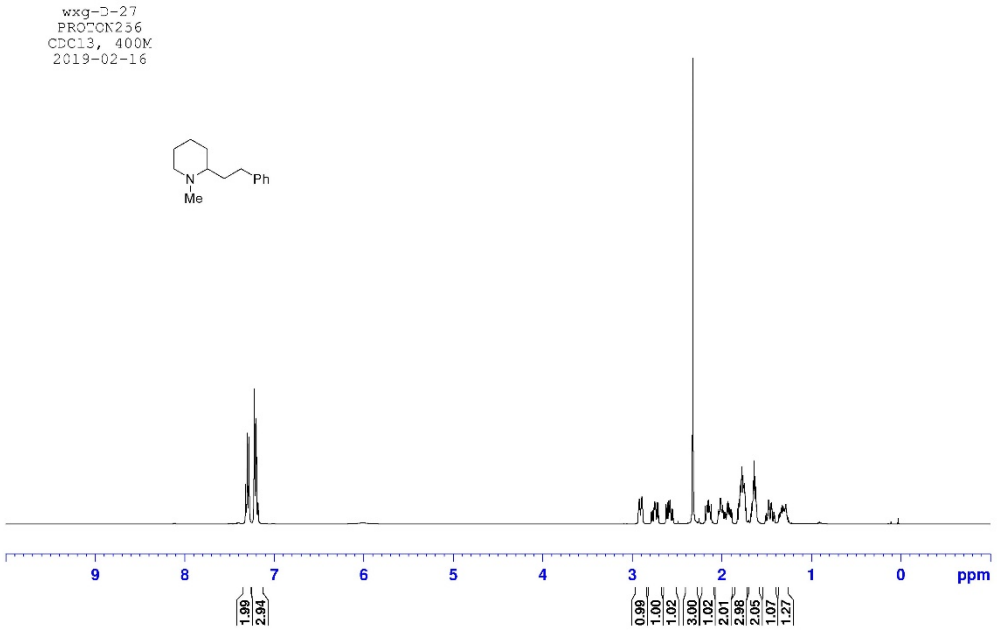


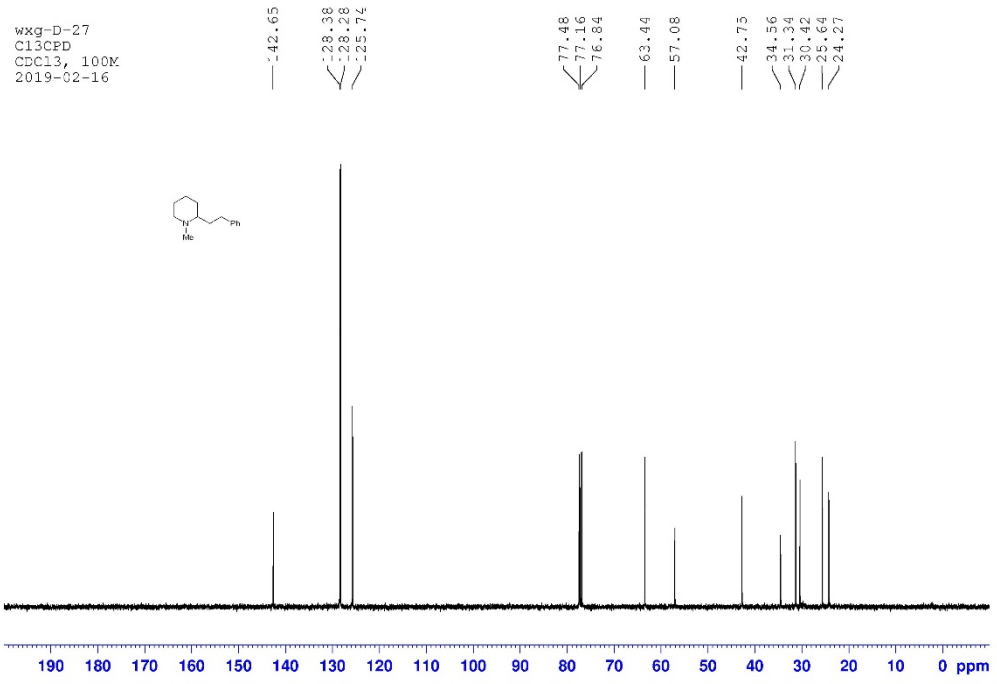
^{1}H and ^{13}C NMR Spectra of Compound **4a**



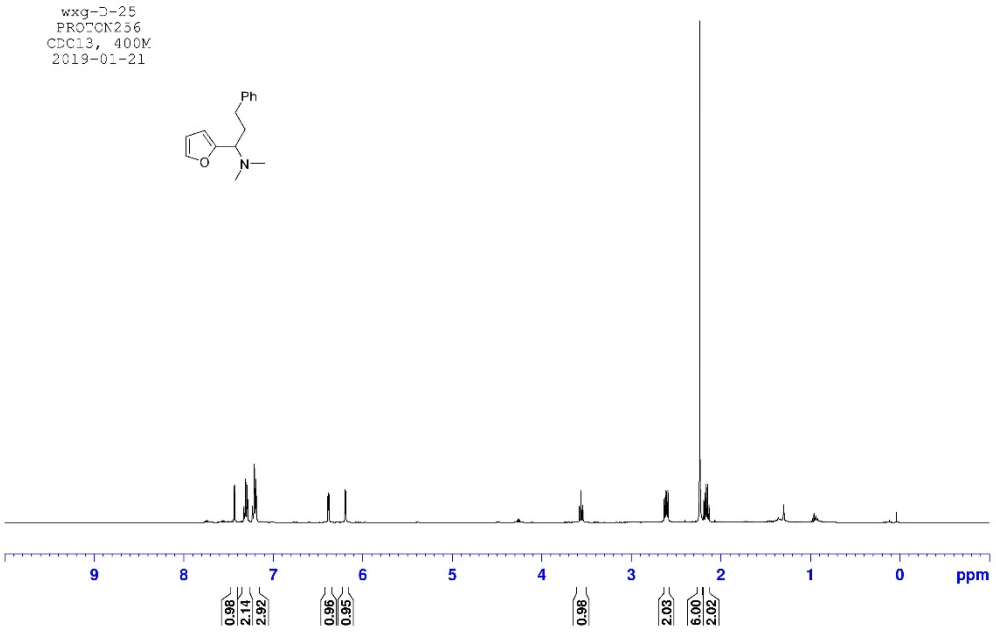


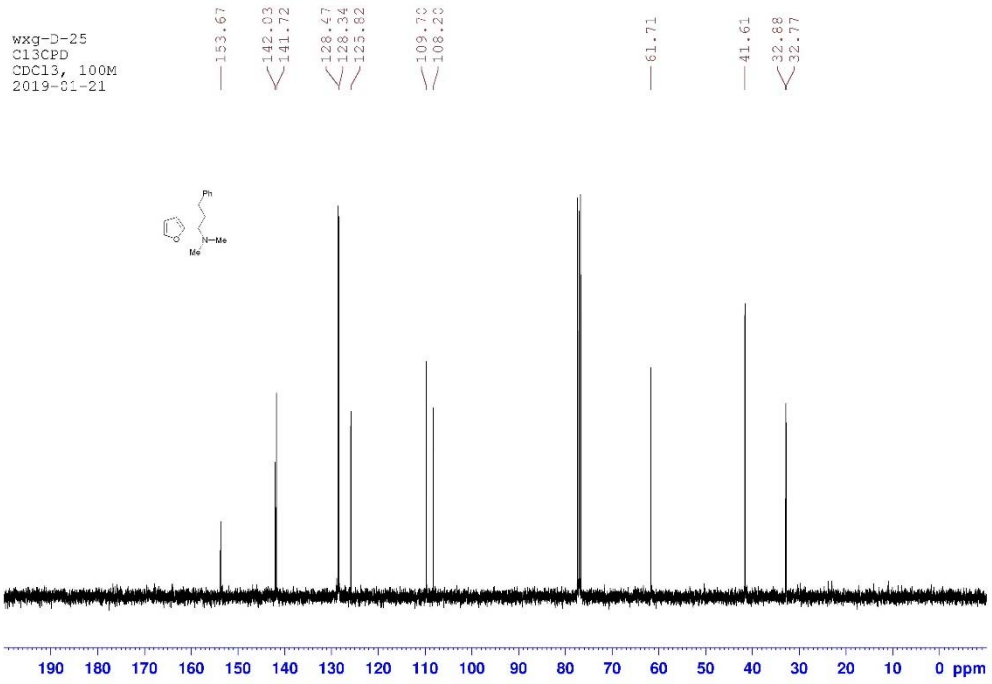
^{1}H and ^{13}C NMR Spectra of Compound **4b**



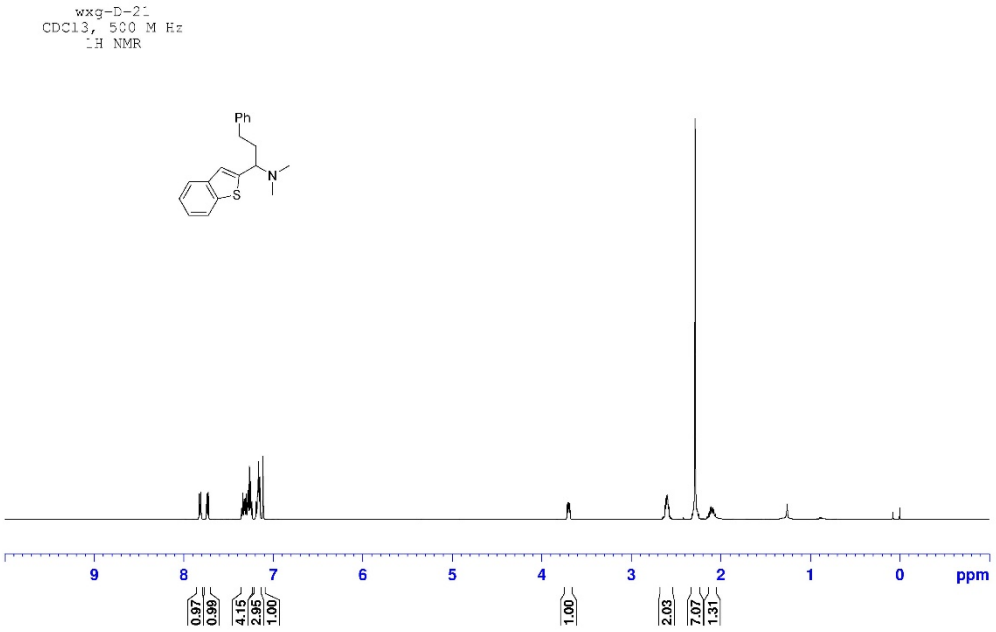


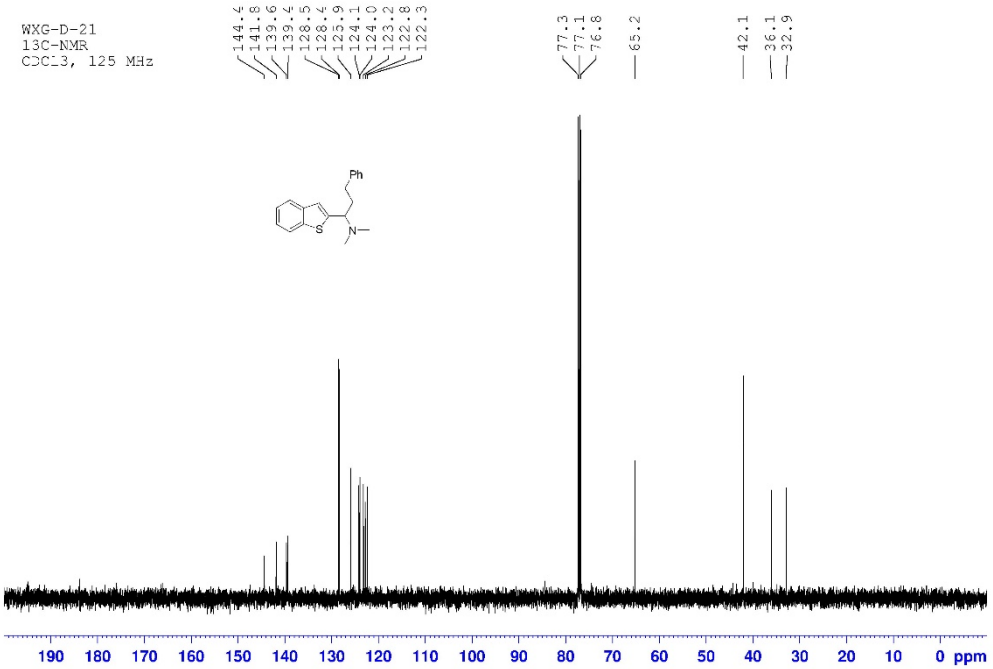
^{1}H and ^{13}C NMR Spectra of Compound **4c**



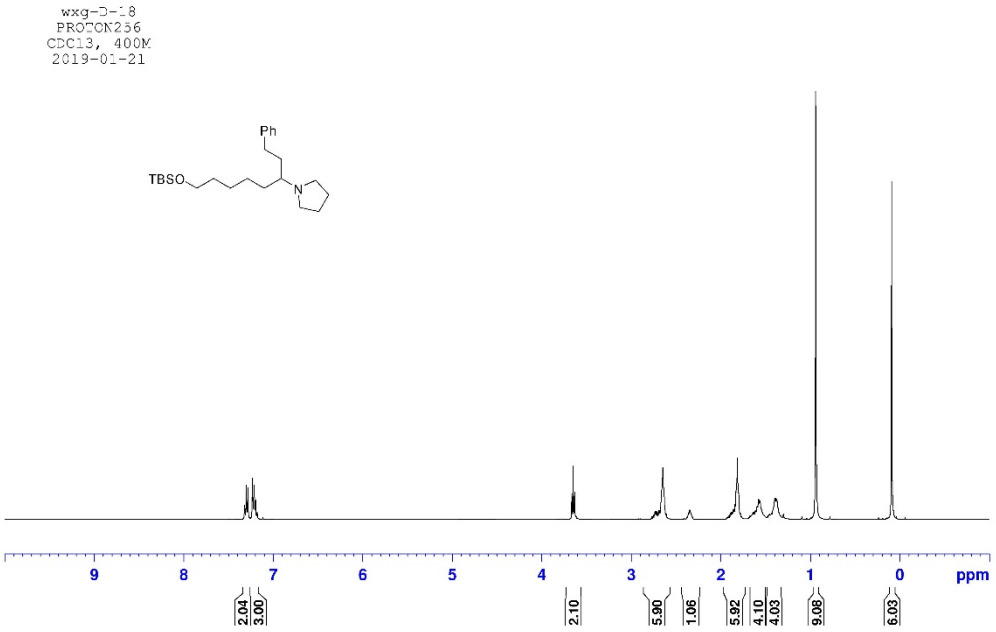


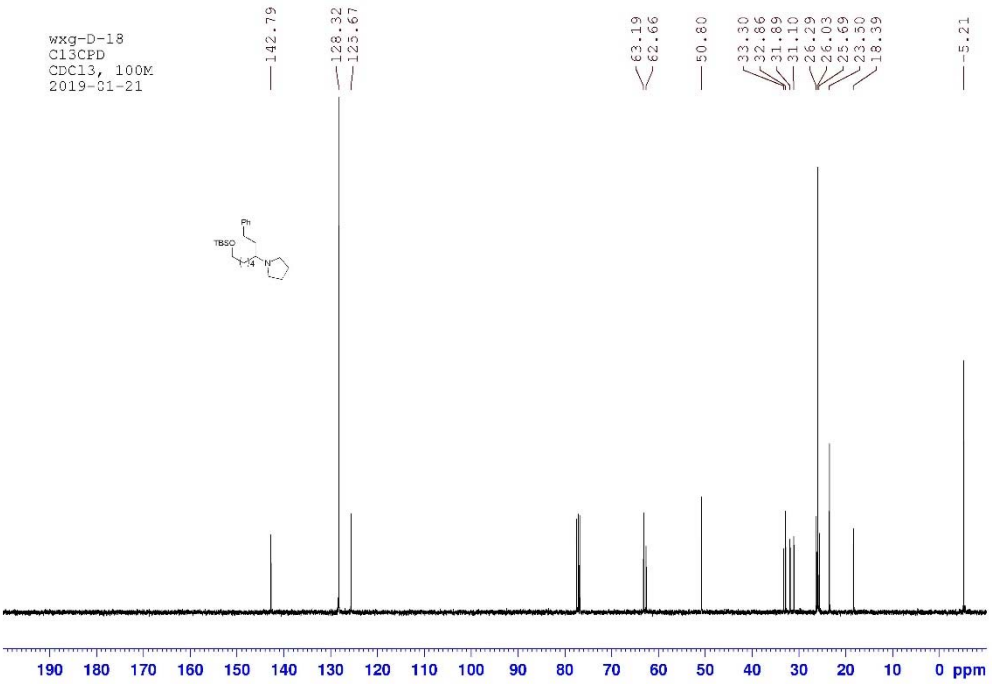
^{1}H and ^{13}C NMR Spectra of Compound **4d**



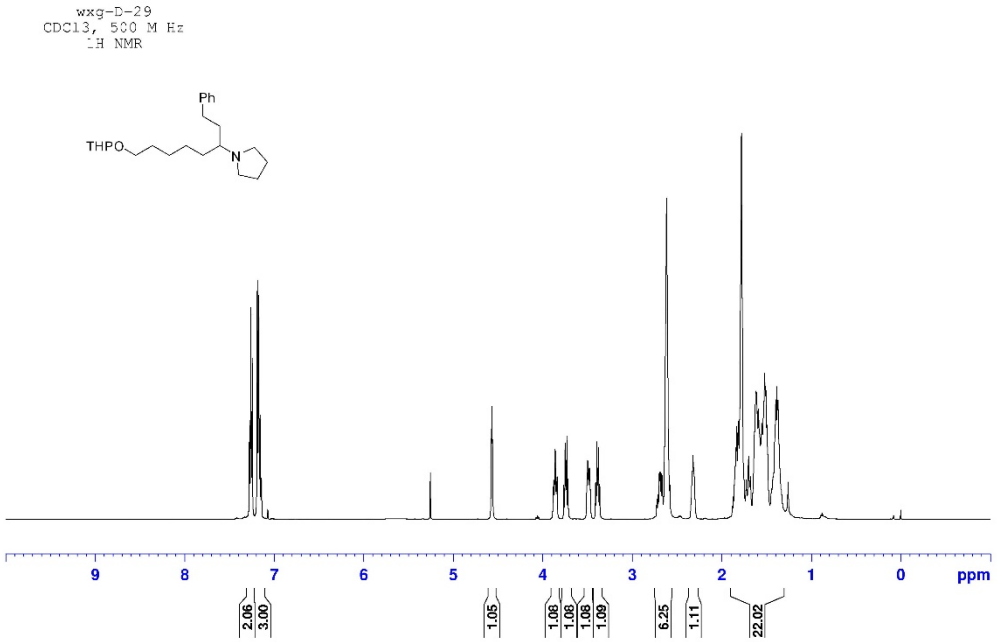


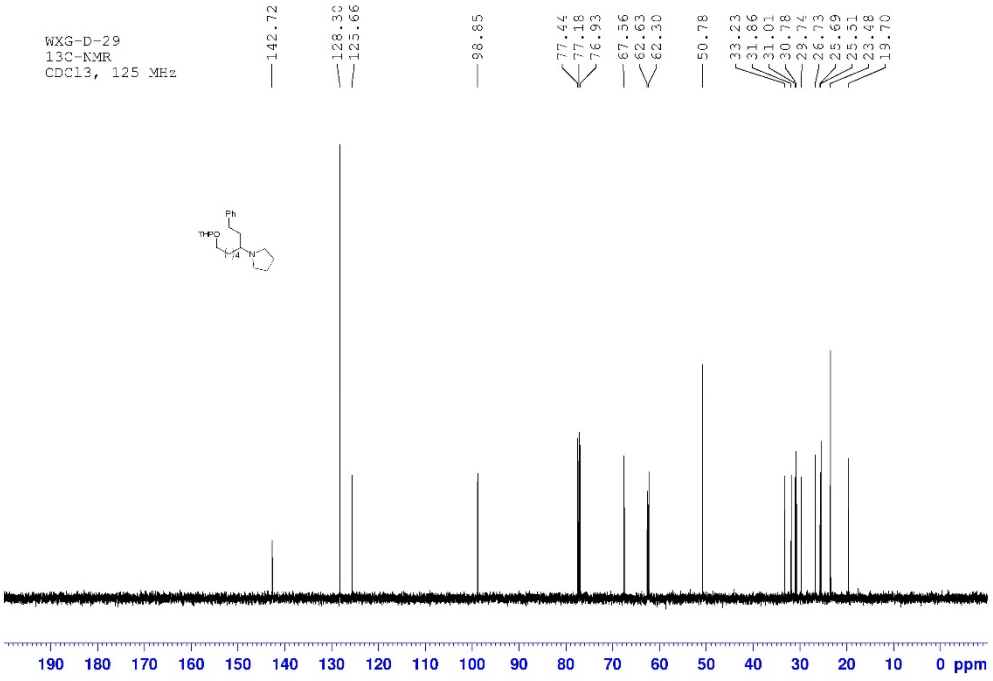
^{1}H and ^{13}C NMR Spectra of Compound **4e**



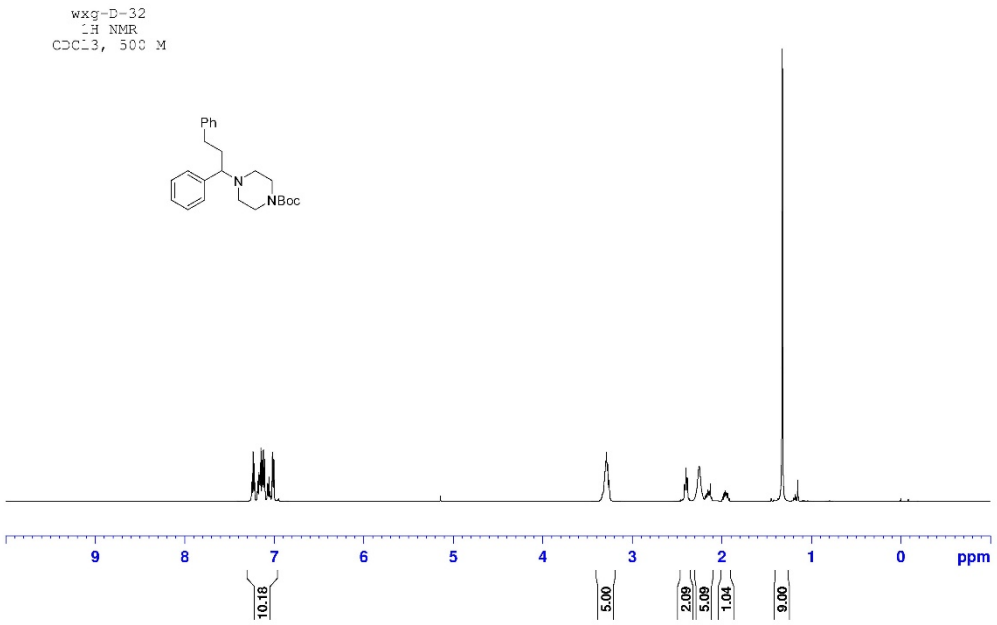


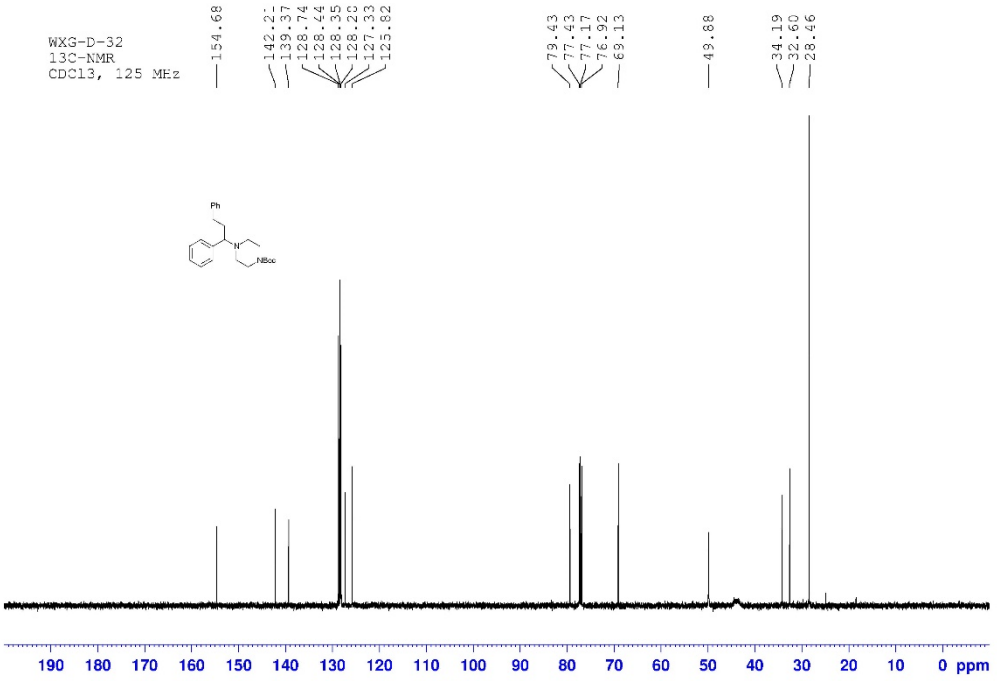
^{1}H and ^{13}C NMR Spectra of Compound **4f**



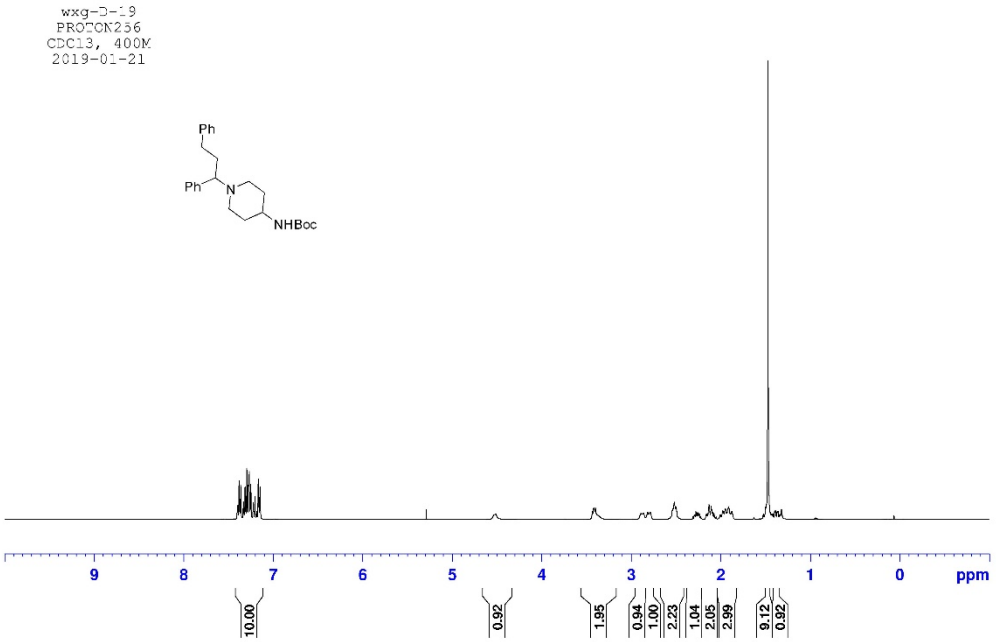


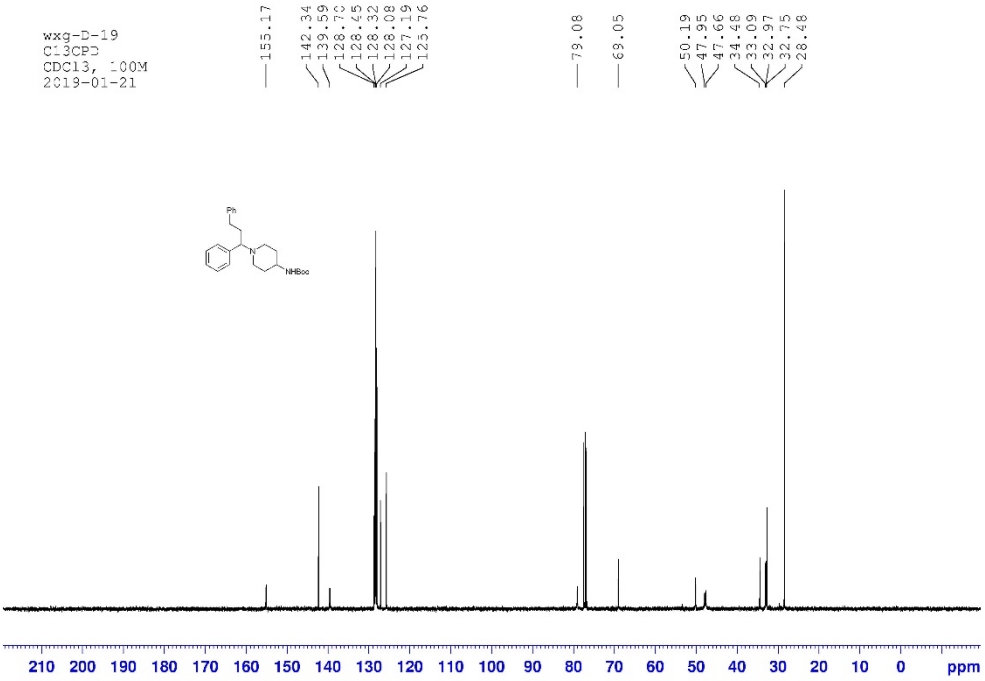
^{1}H and ^{13}C NMR Spectra of Compound **4g**



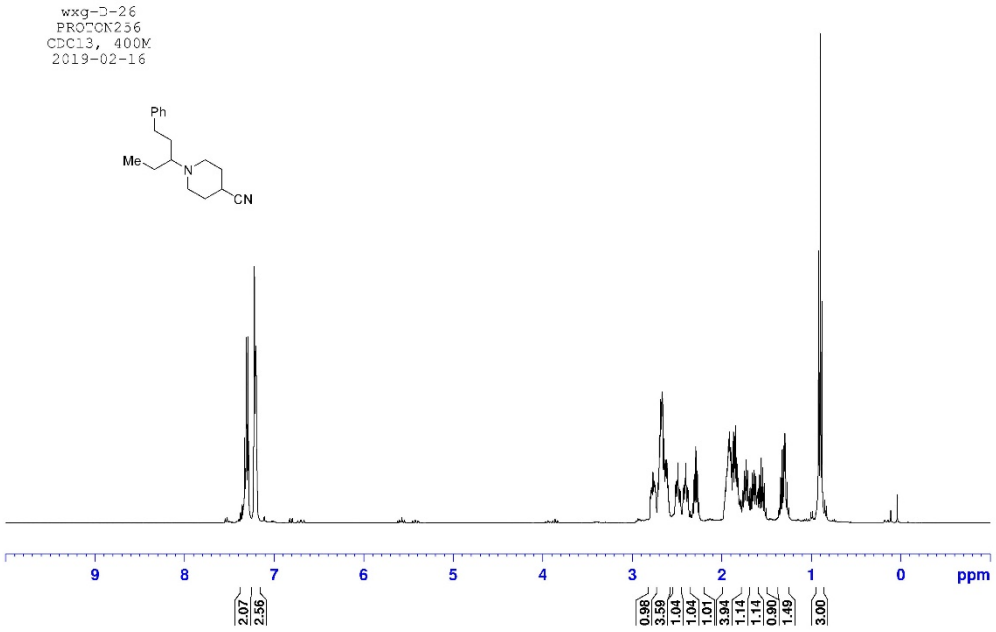


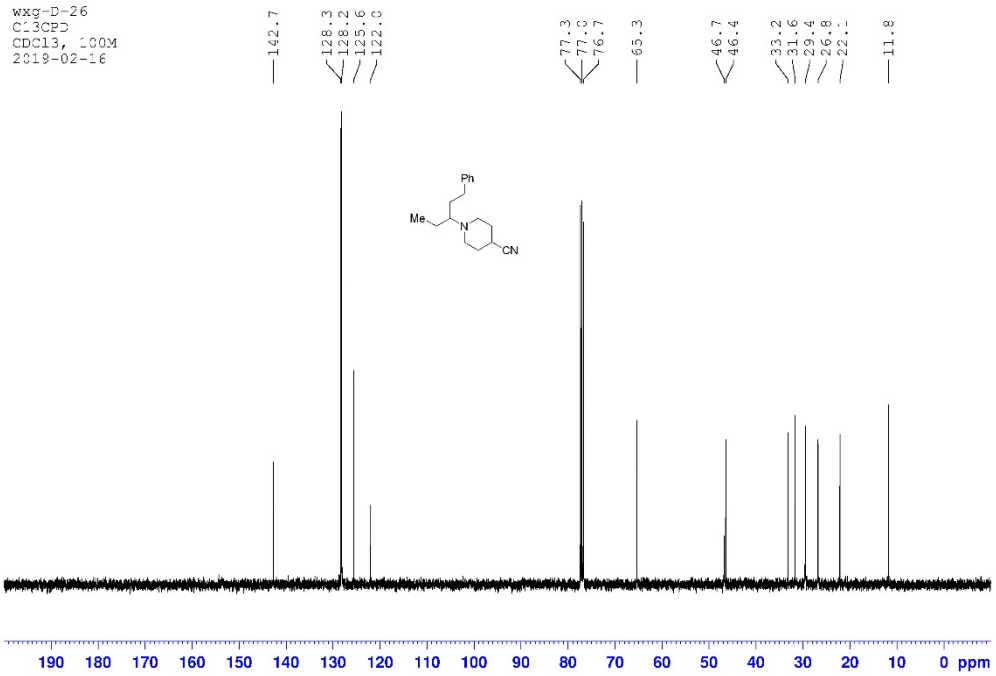
^{1}H and ^{13}C NMR Spectra of Compound **4h**



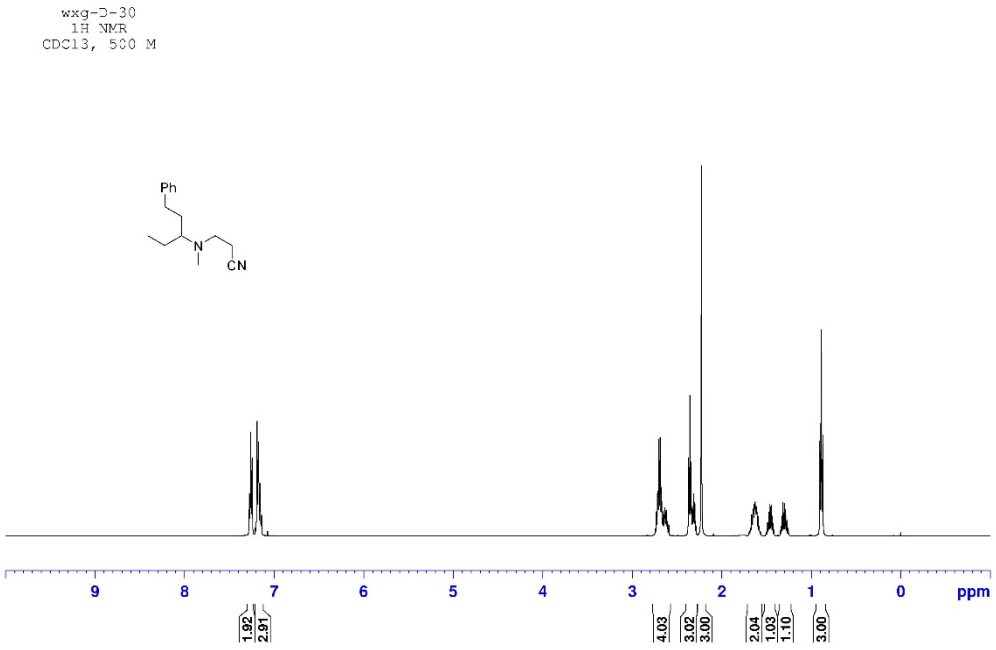


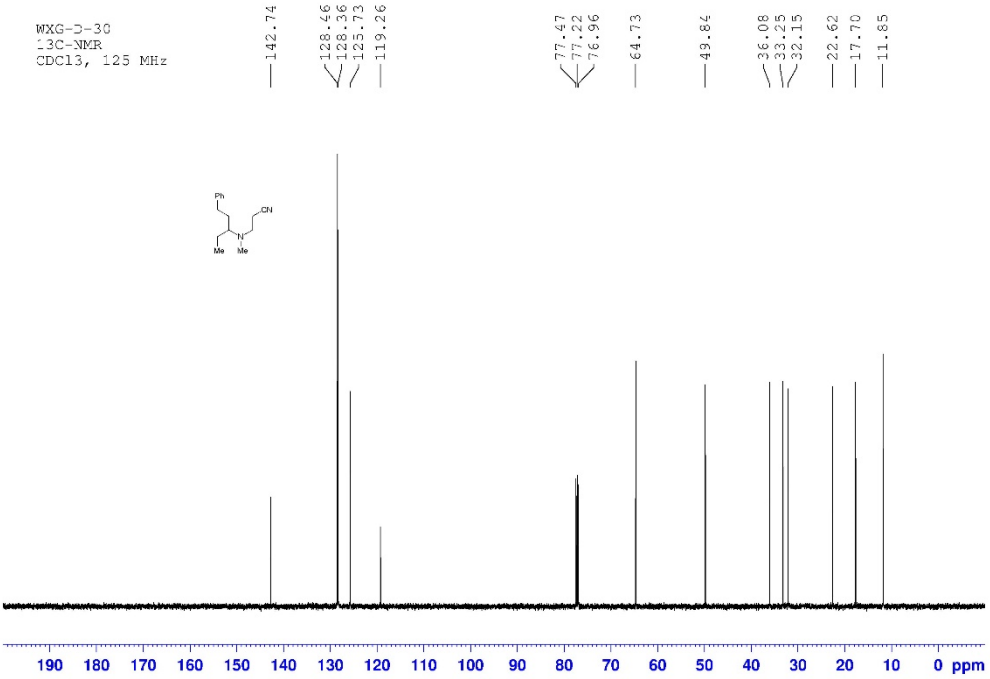
^{1}H and ^{13}C NMR Spectra of Compound **4i**



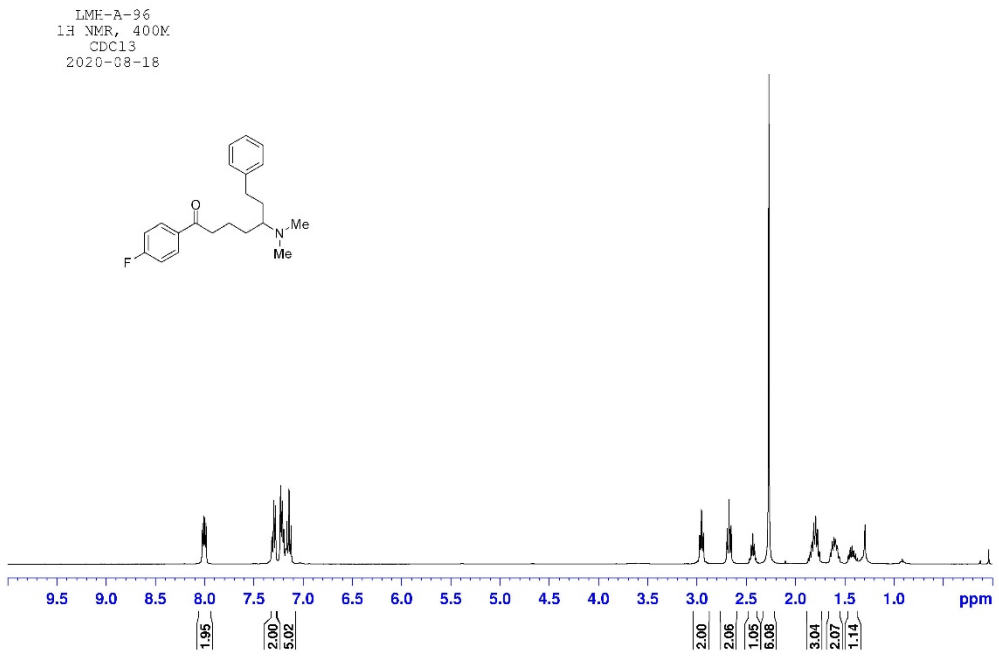


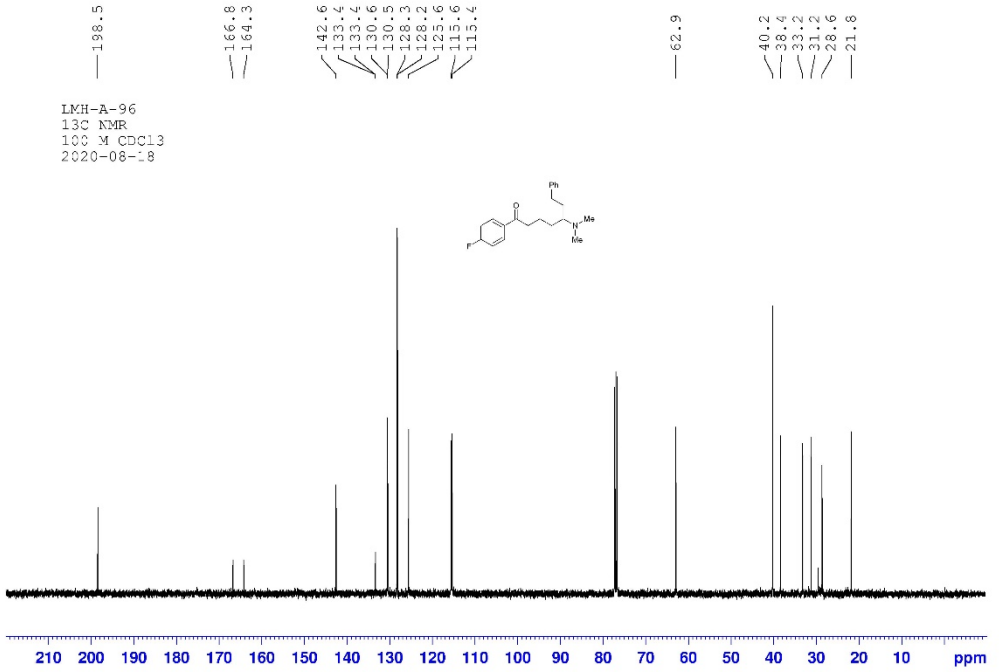
^{1}H and ^{13}C NMR Spectra of Compound **4j**



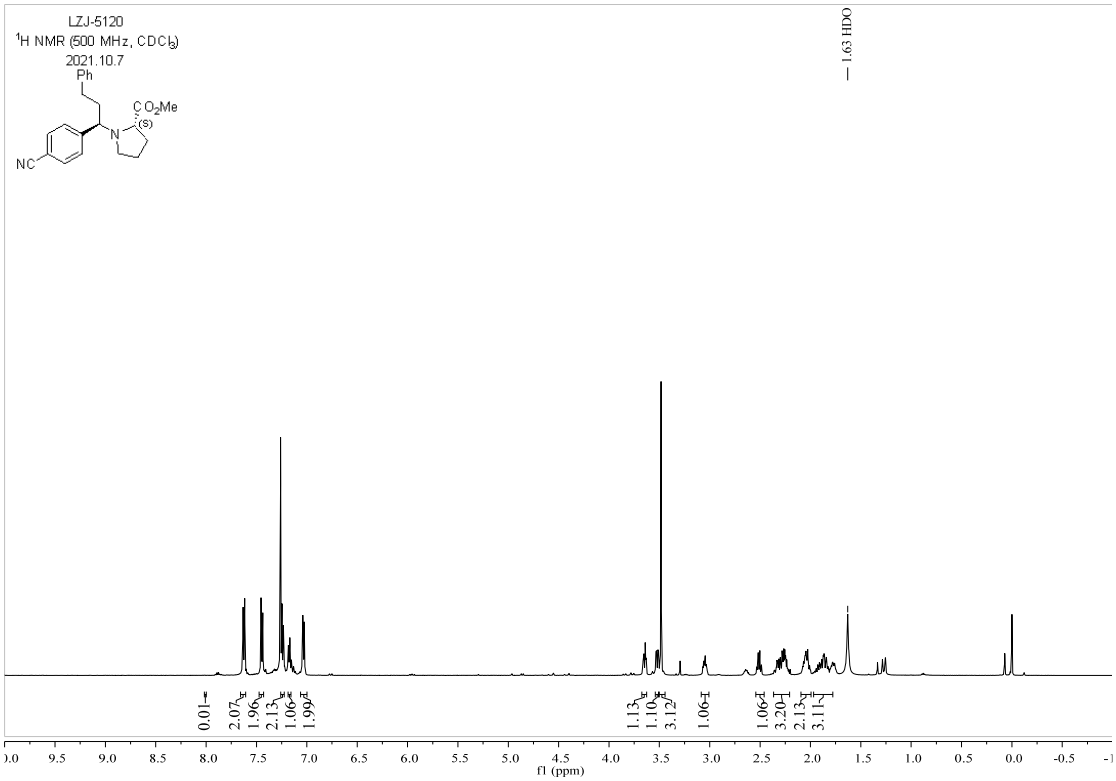


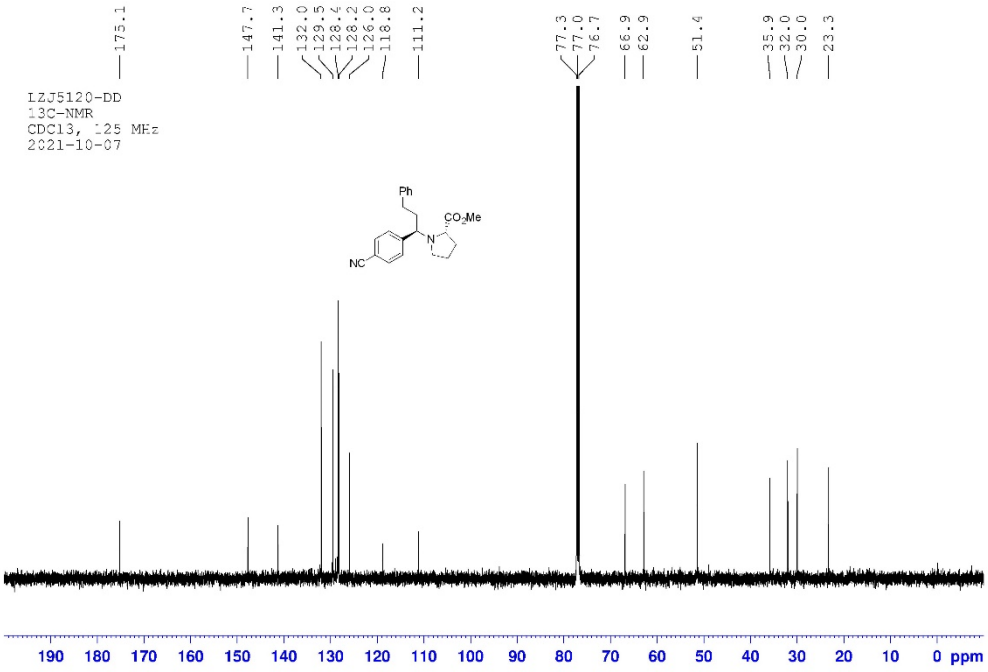
^{1}H and ^{13}C NMR Spectra of Compound **4k**



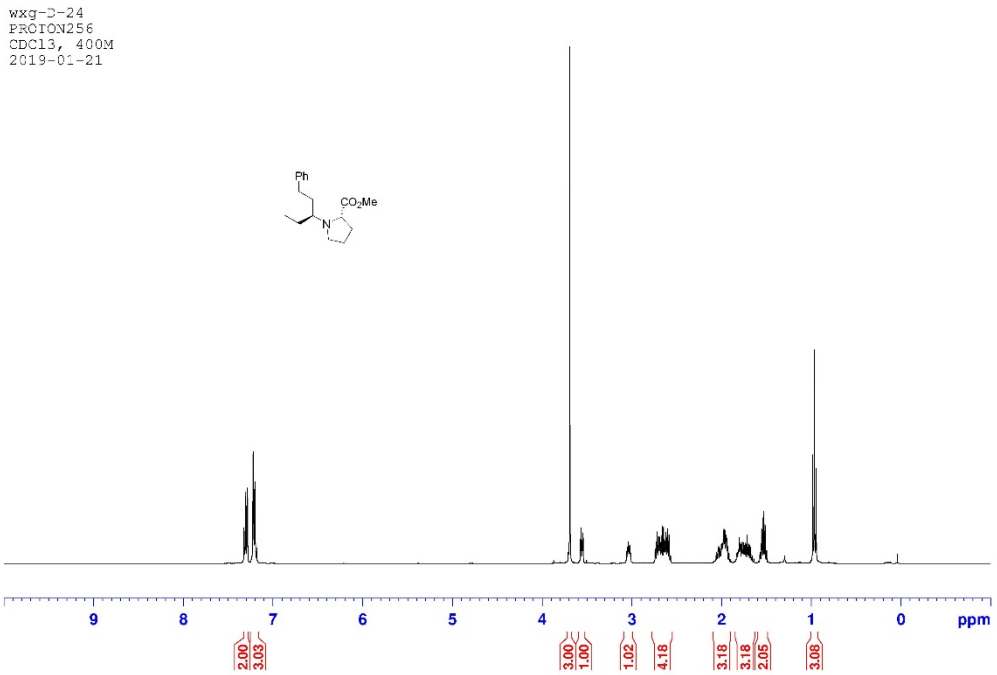


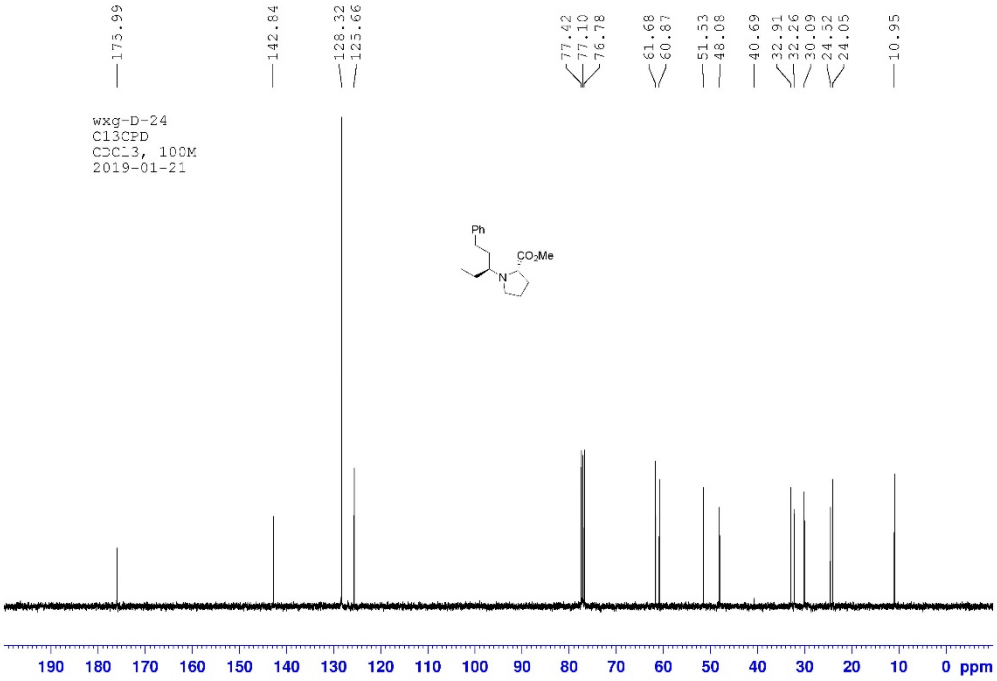
^{1}H and ^{13}C NMR Spectra of Compound **4l**



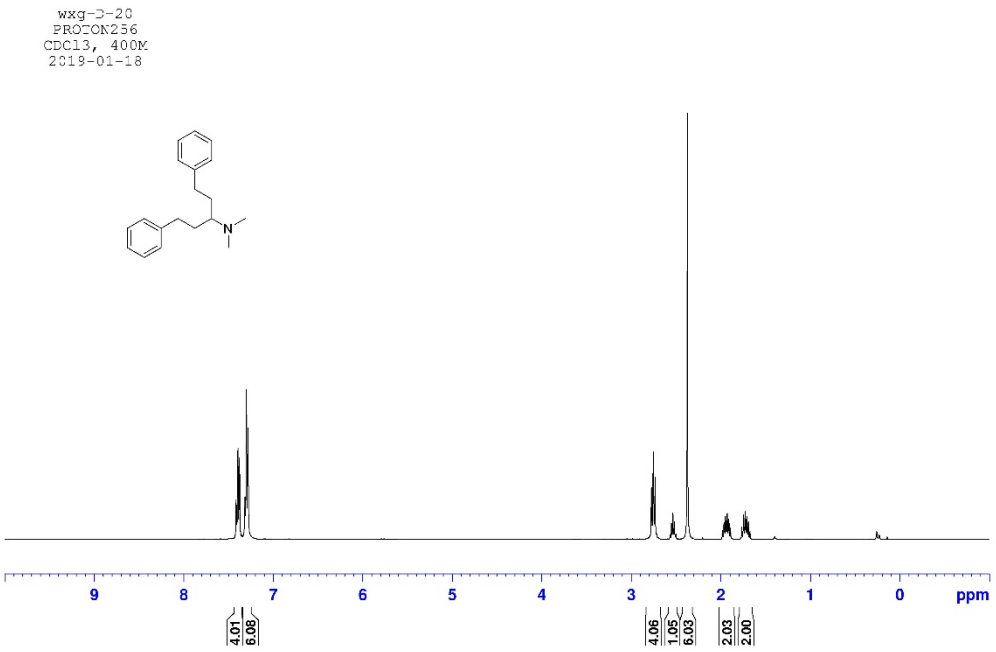


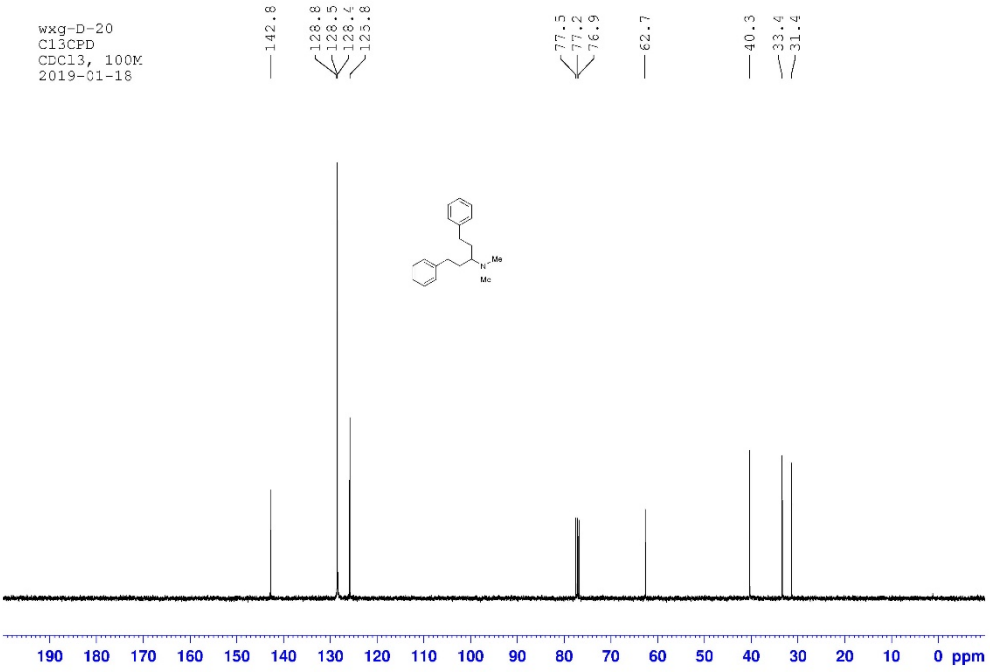
^{1}H and ^{13}C NMR Spectra of Compound **4m**



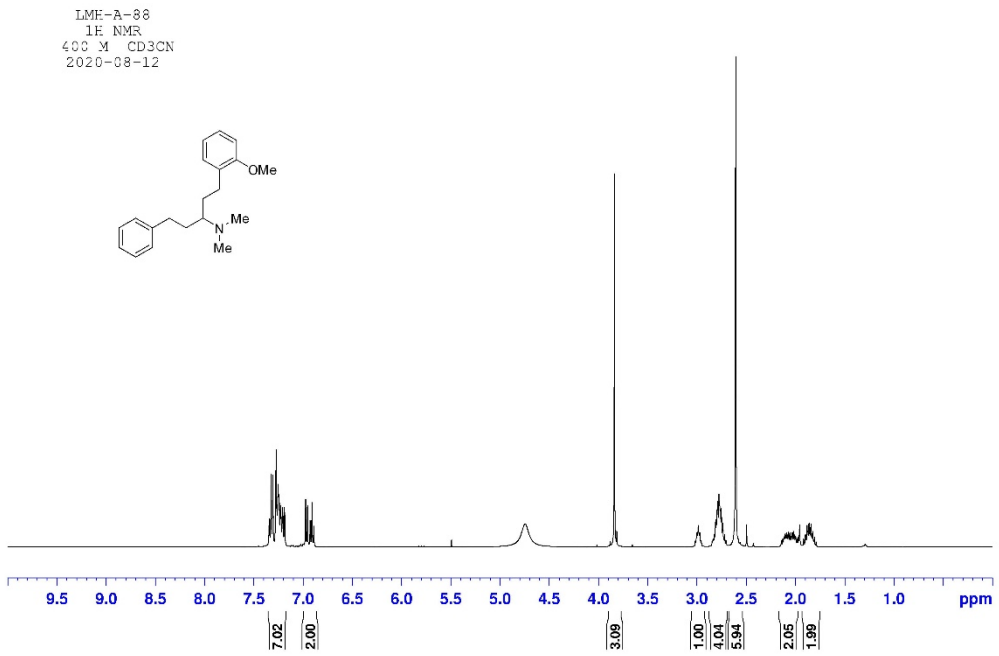


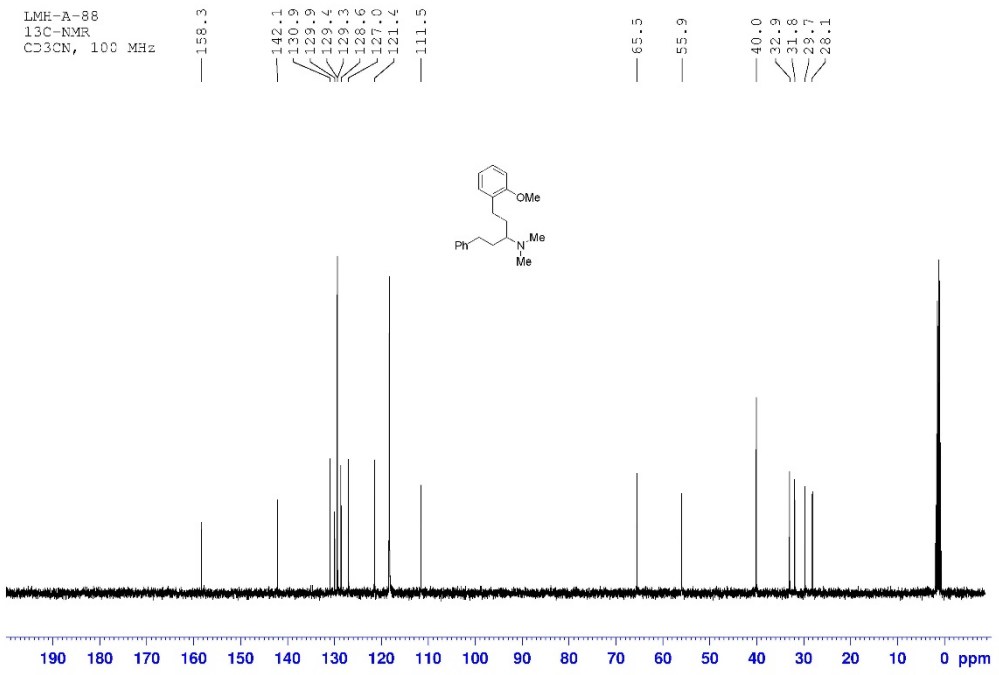
^{1}H and ^{13}C NMR Spectra of Compound **4n**



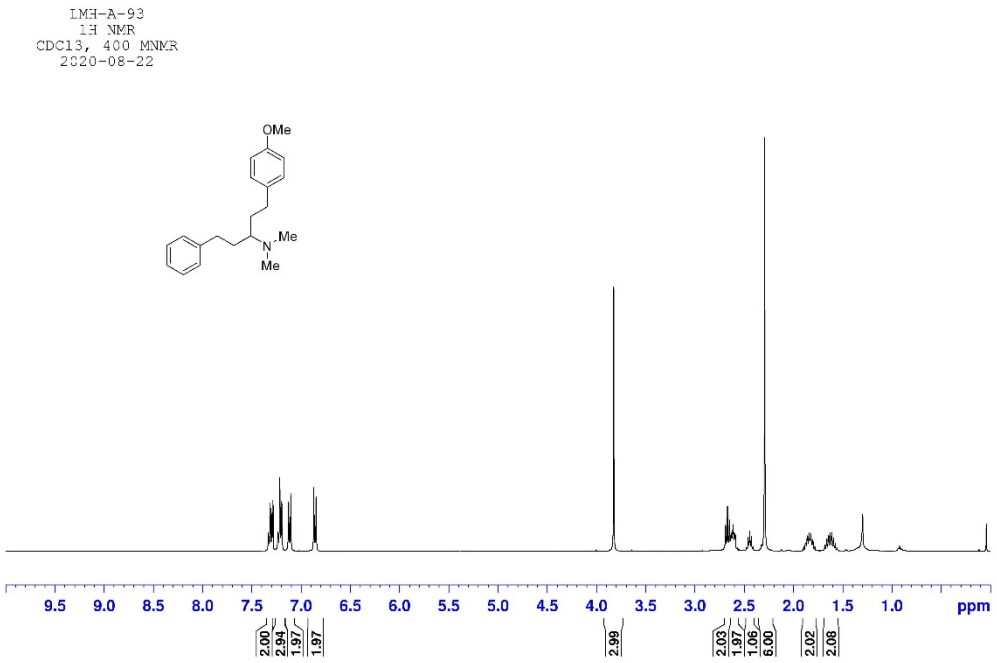


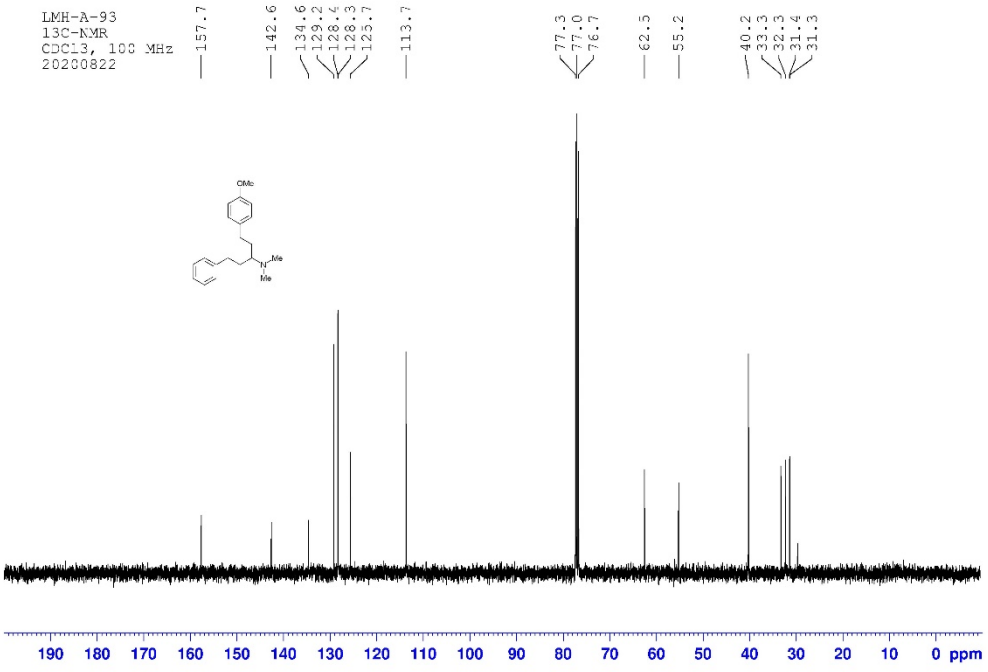
^{1}H and ^{13}C NMR Spectra of Compound **4o**



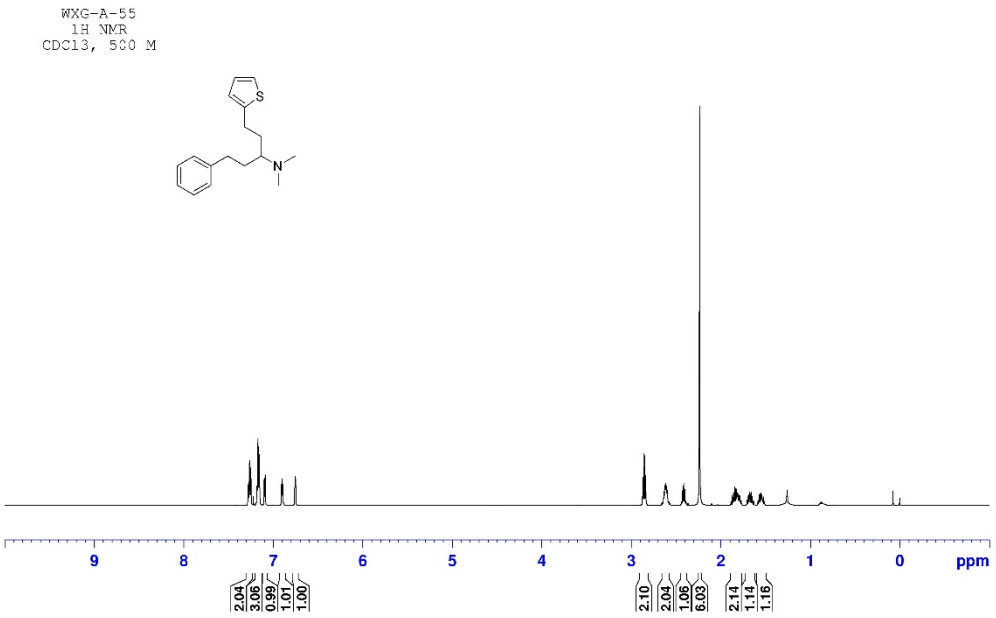


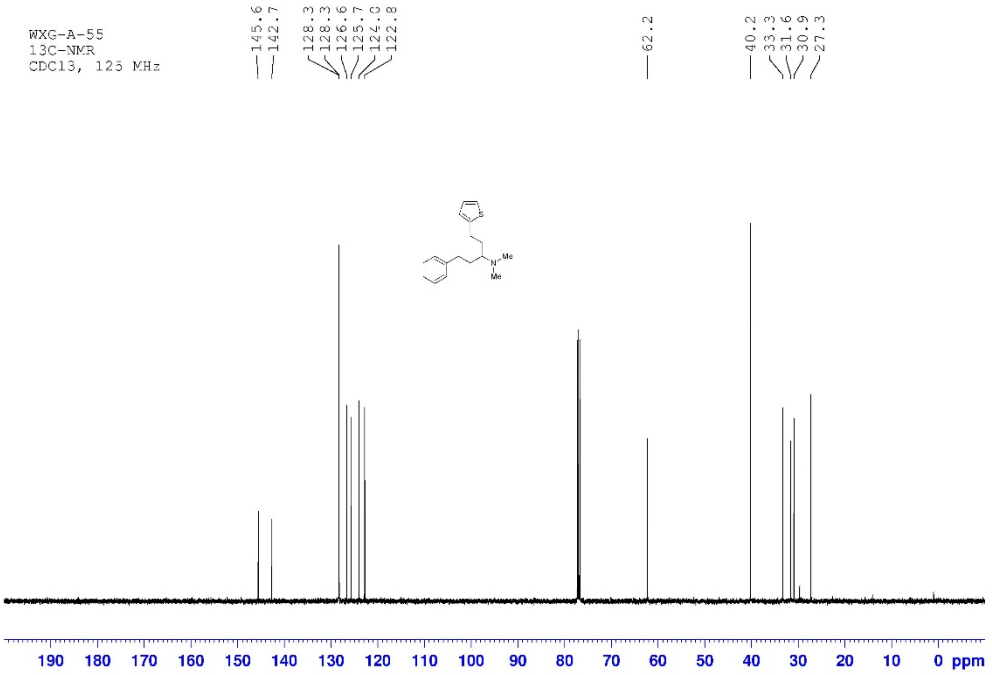
^{1}H and ^{13}C NMR Spectra of Compound **4p**



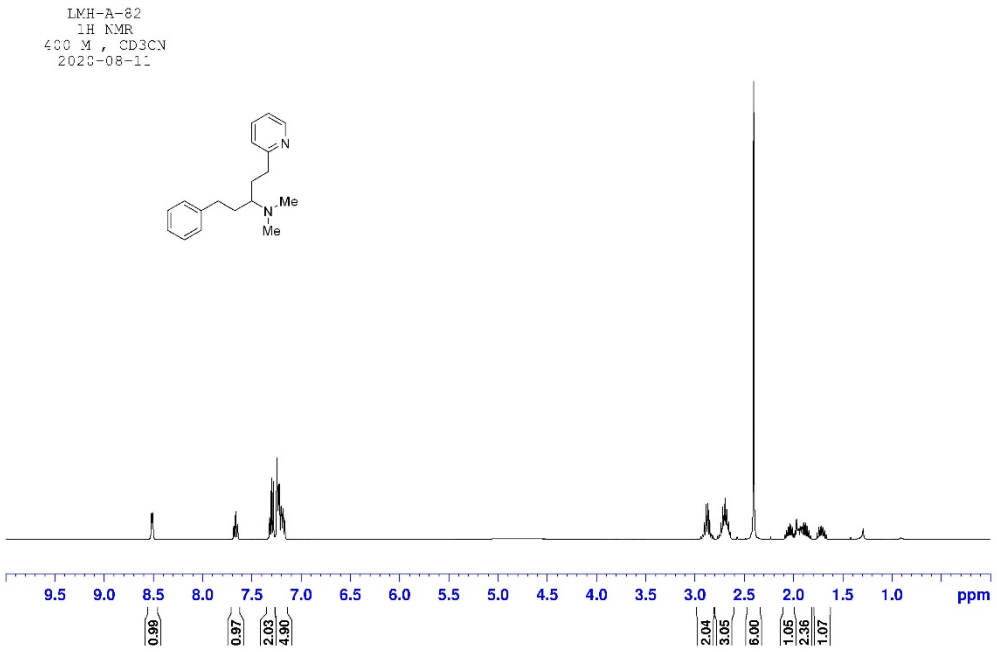


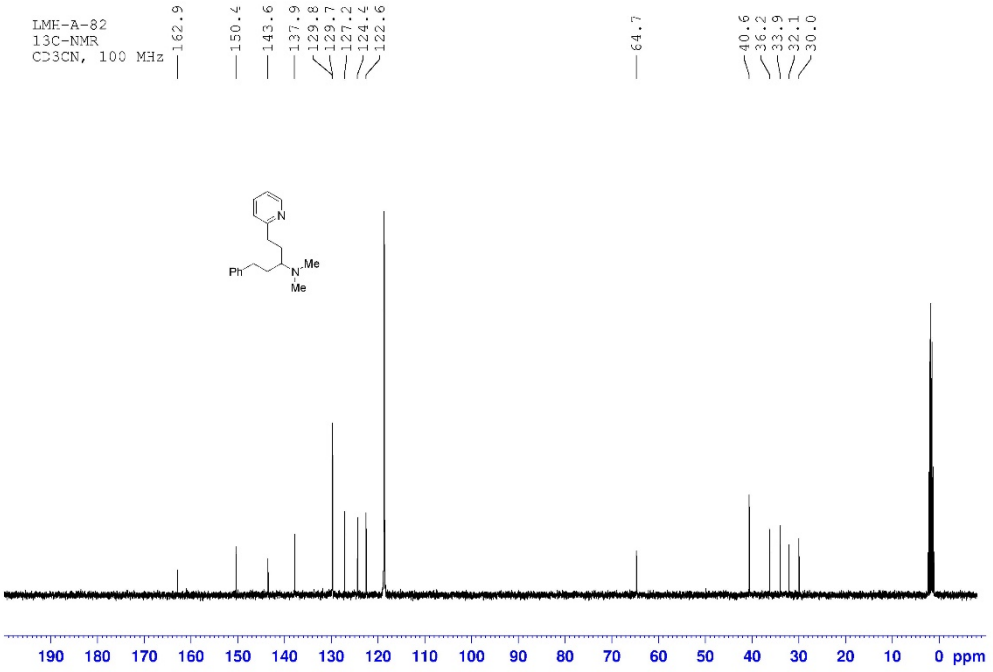
^{1}H and ^{13}C NMR Spectra of Compound **4q**



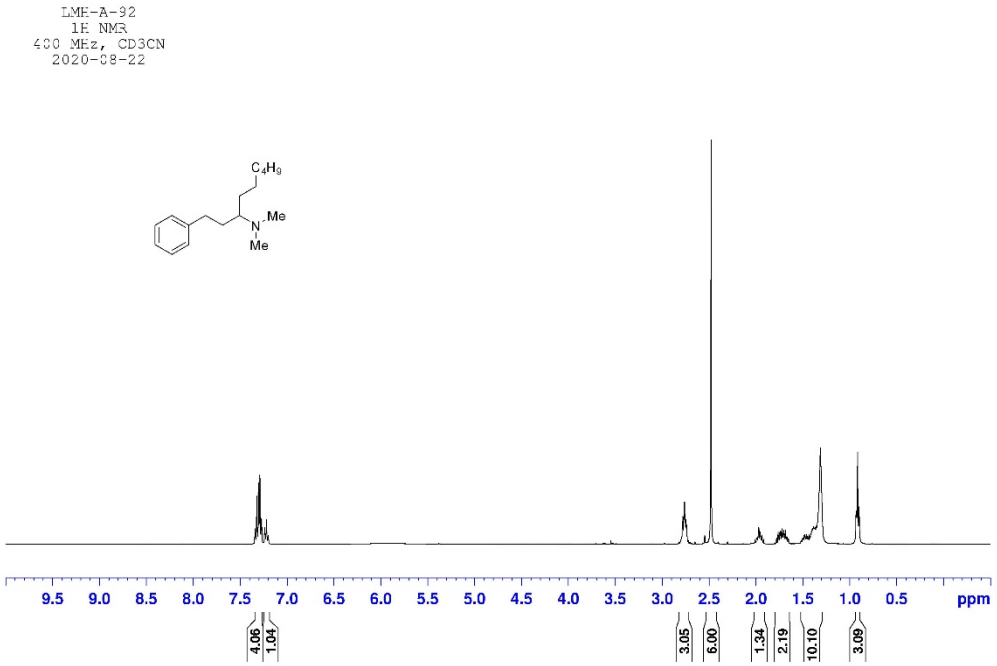


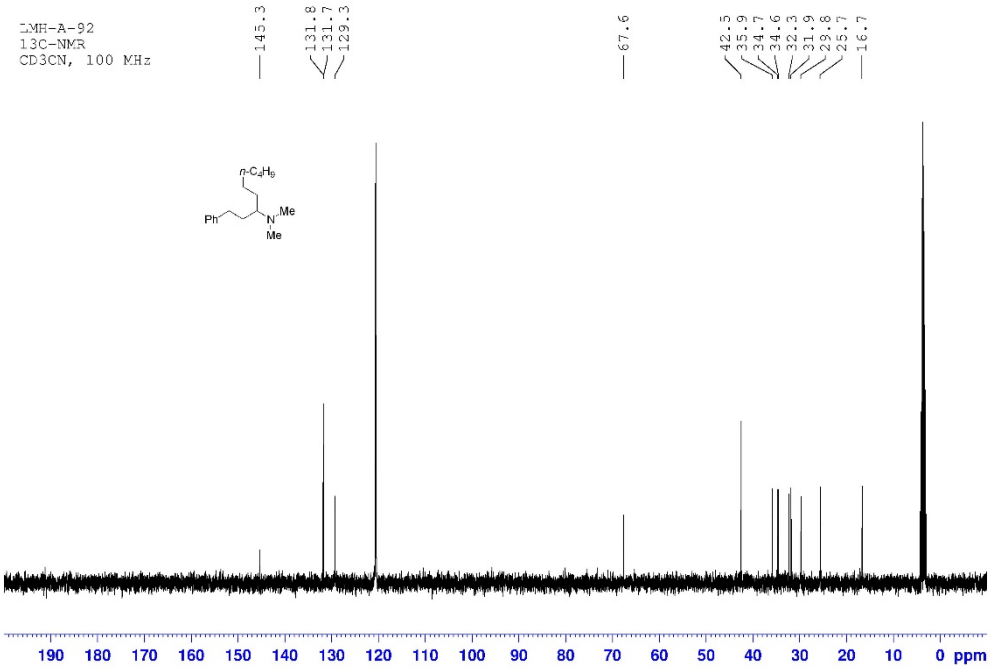
^{1}H and ^{13}C NMR Spectra of Compound **4r**



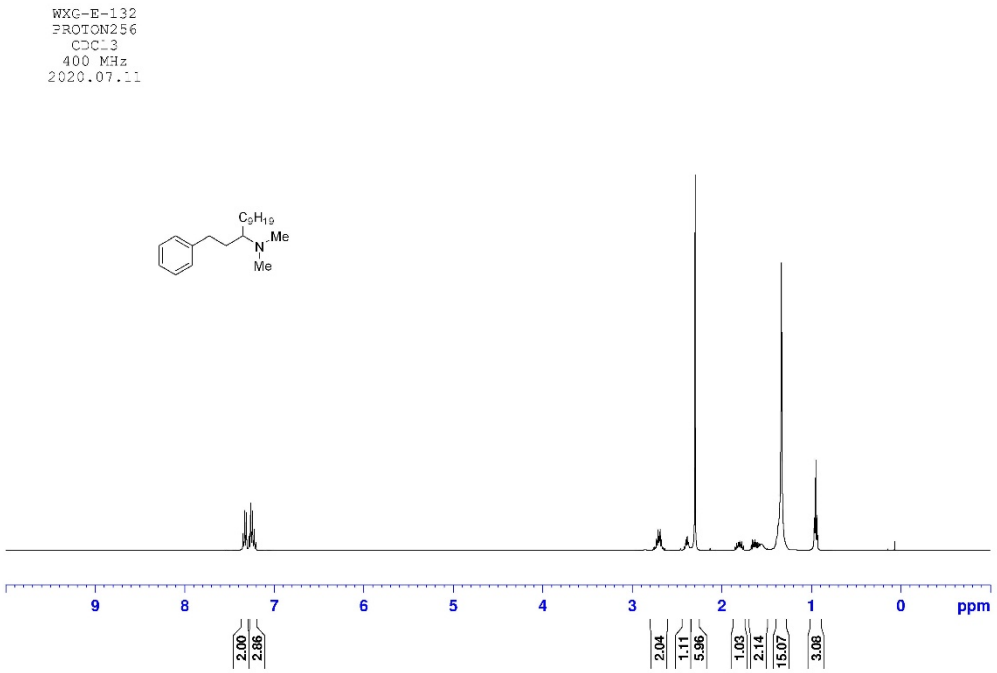


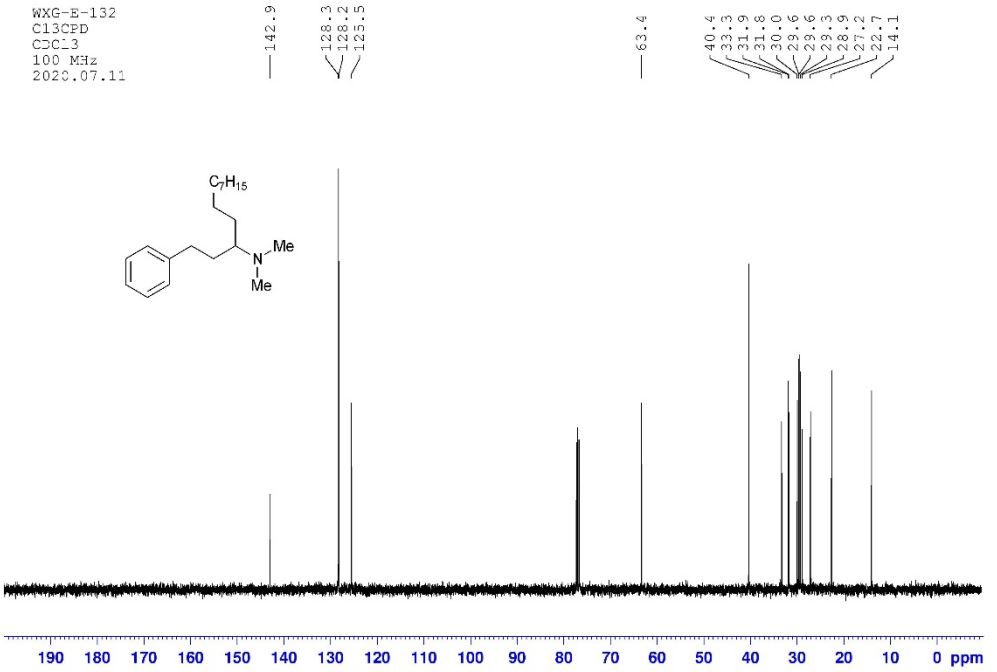
^{1}H and ^{13}C NMR Spectra of Compound **4s**



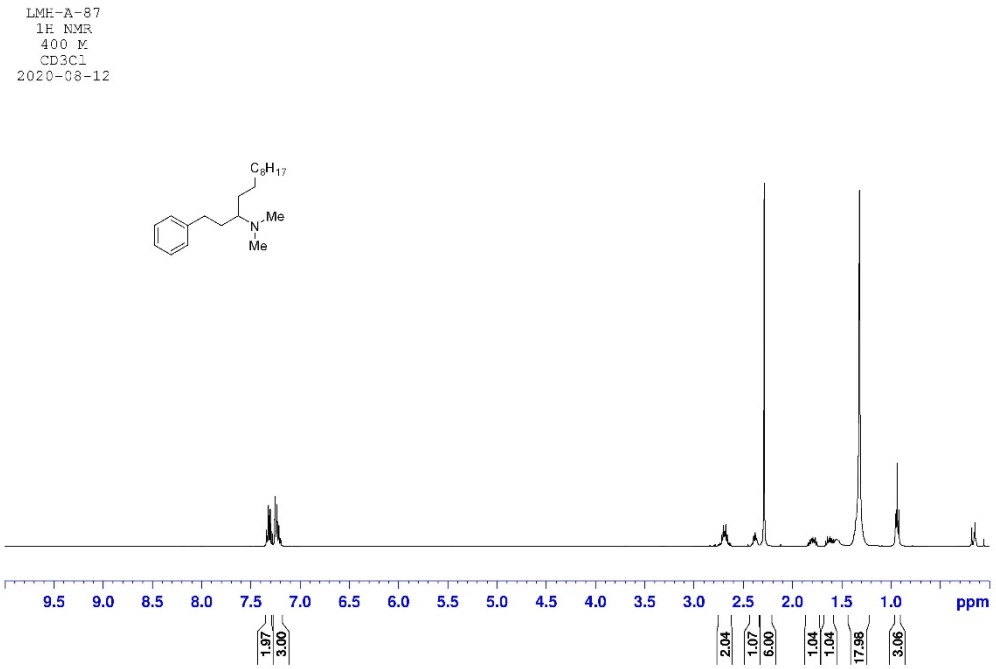


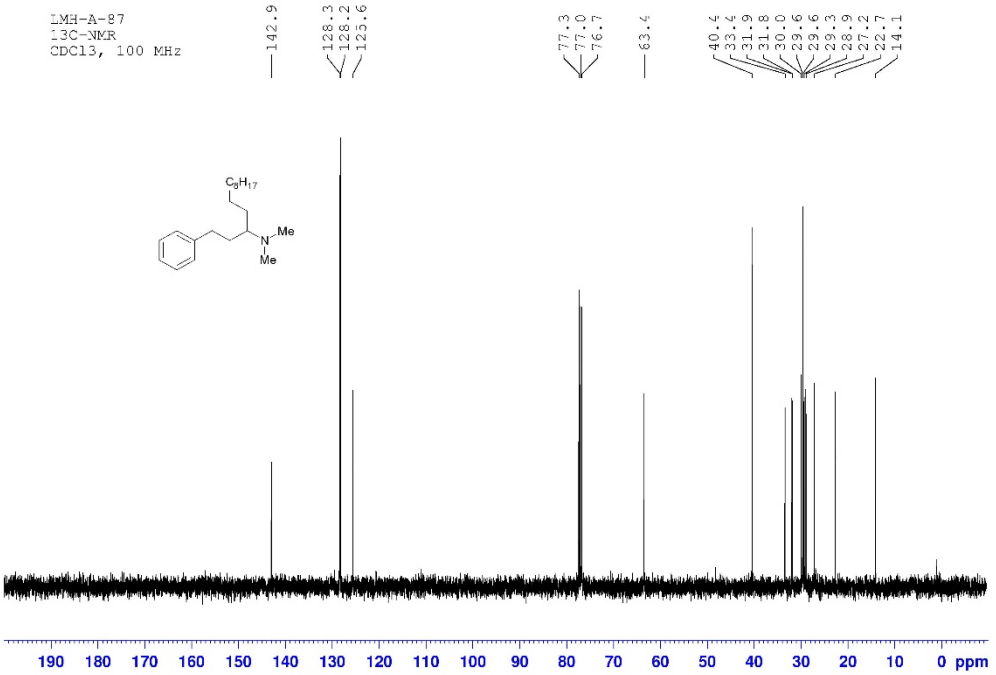
^{1}H and ^{13}C NMR Spectra of Compound **4t**



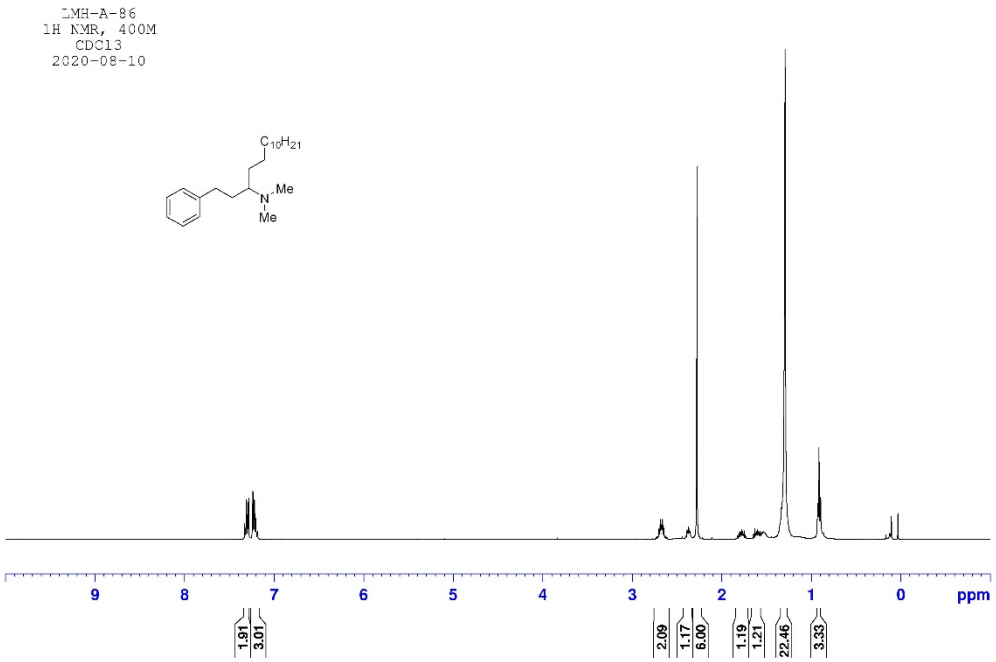


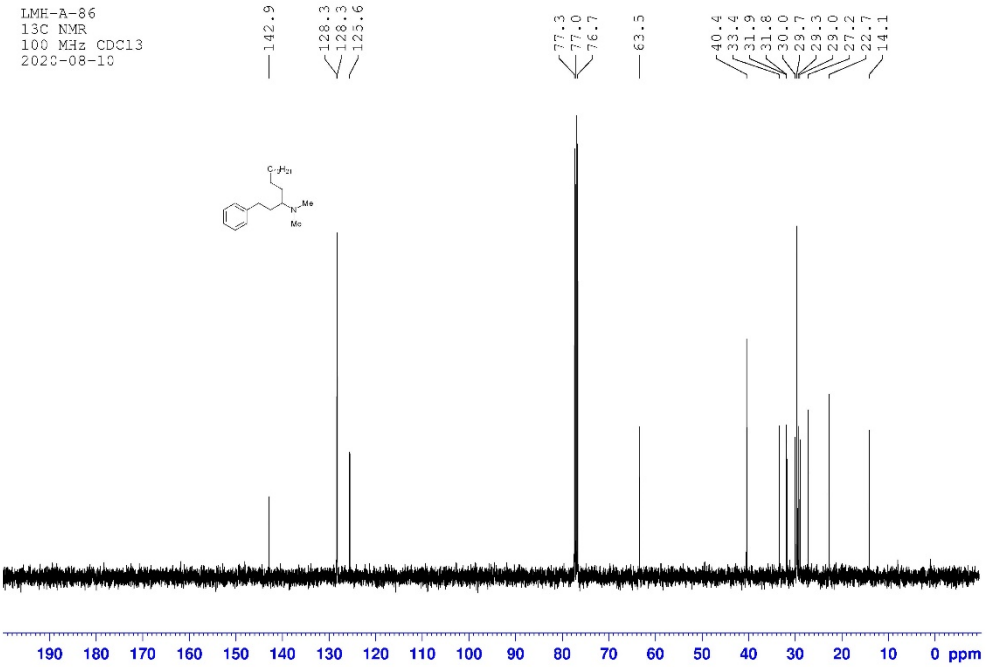
^{1}H and ^{13}C NMR Spectra of Compound **4u**



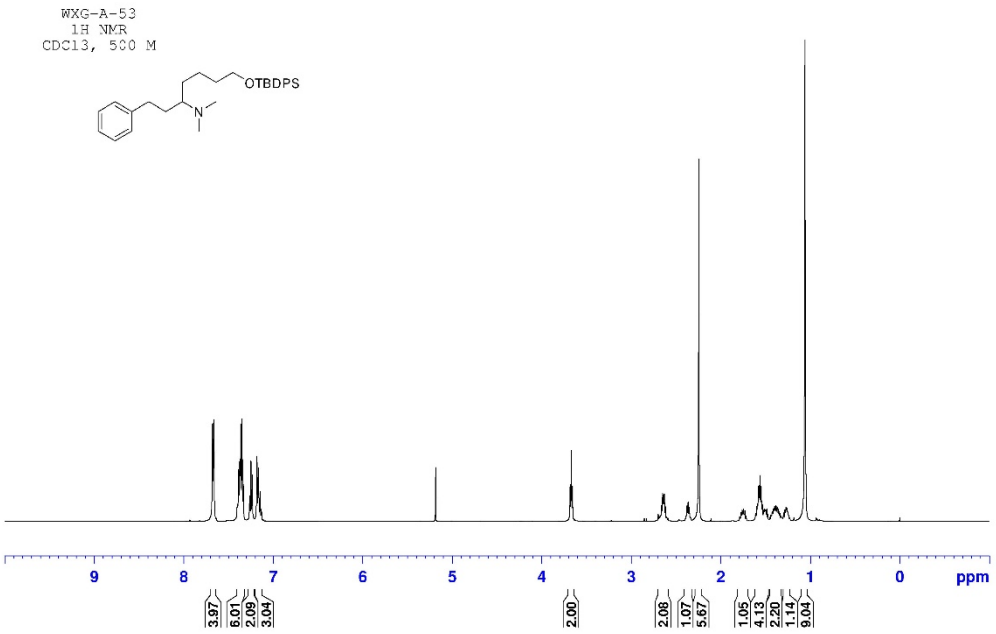


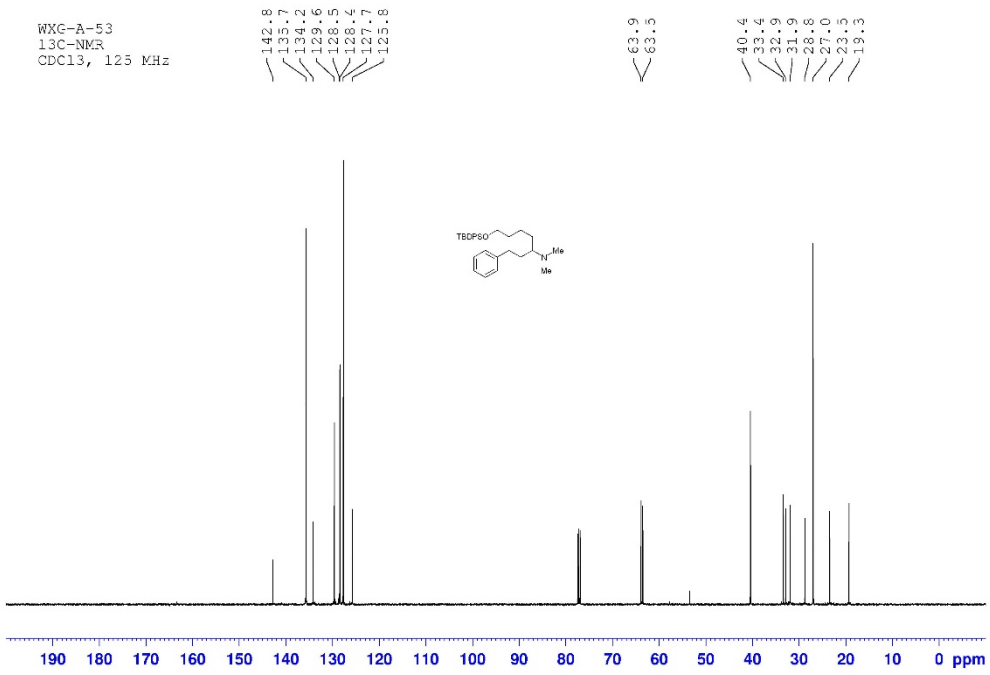
^{1}H and ^{13}C NMR Spectra of Compound **4v**



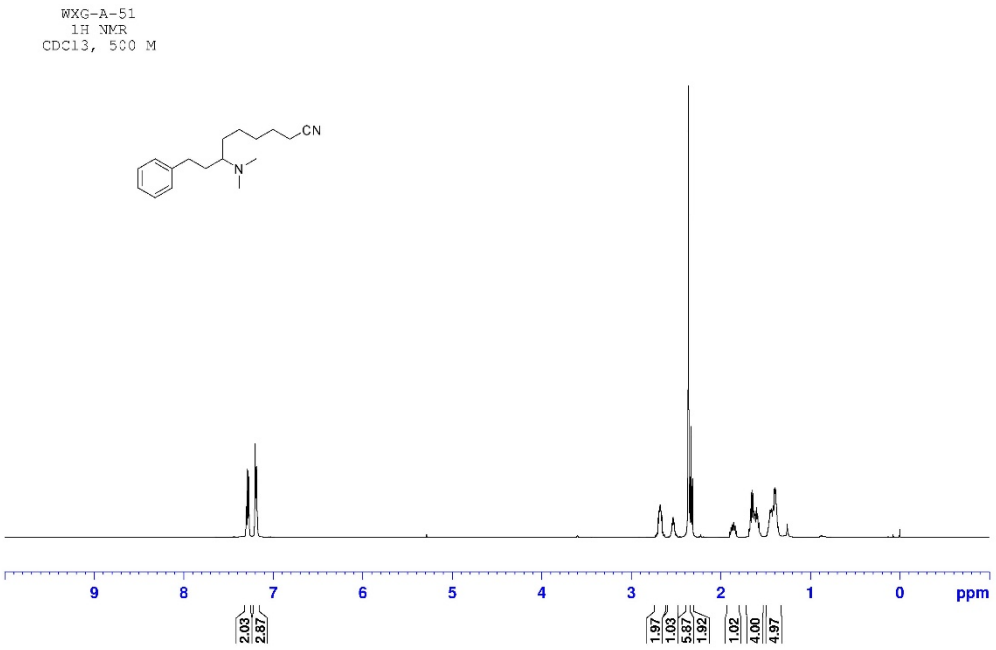


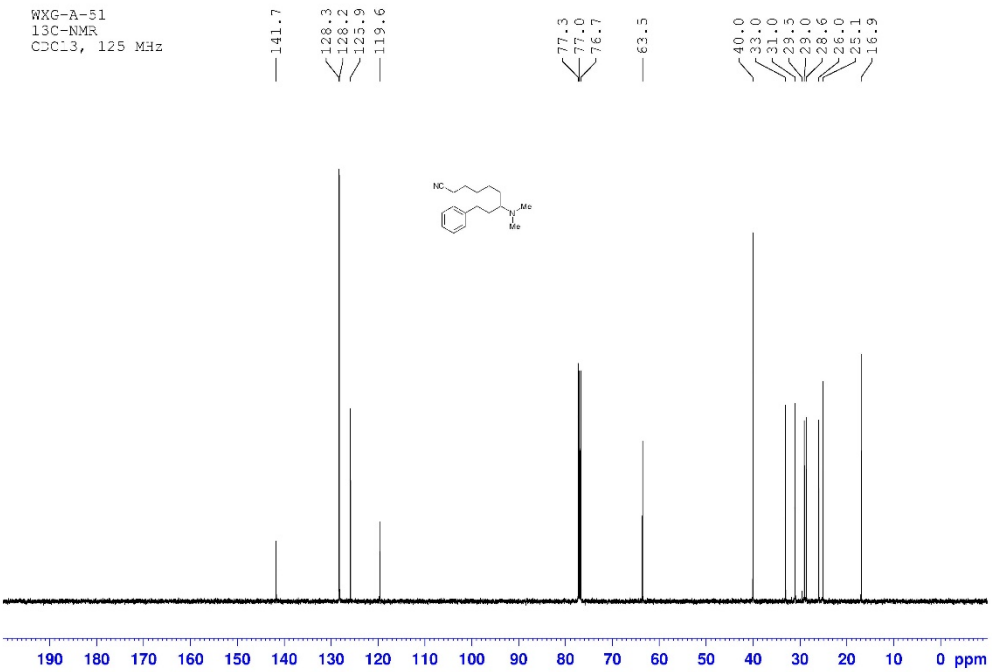
^{1}H and ^{13}C NMR Spectra of Compound **4w**



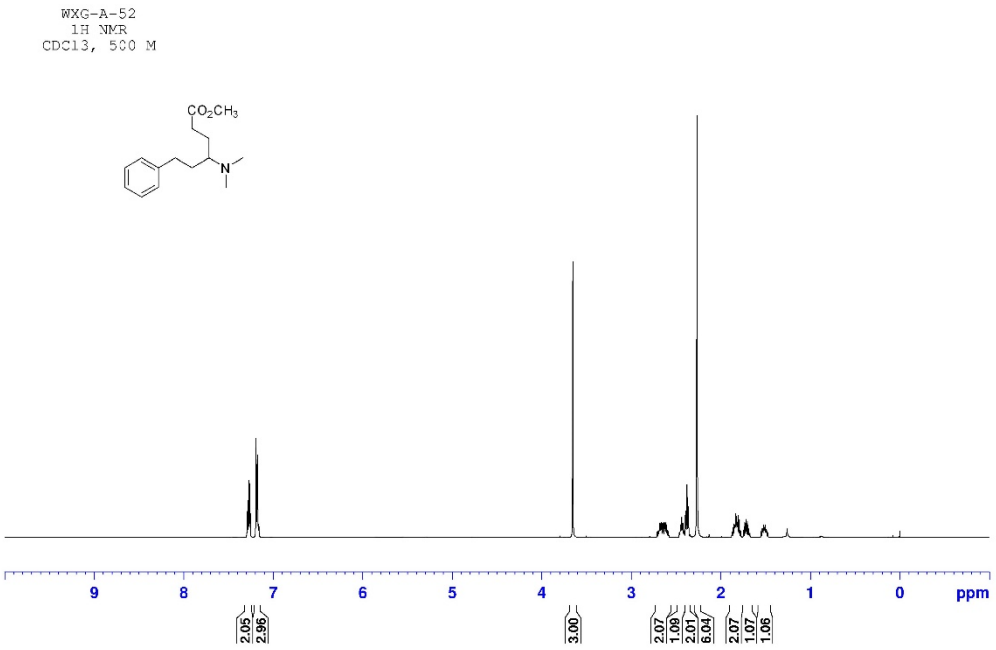


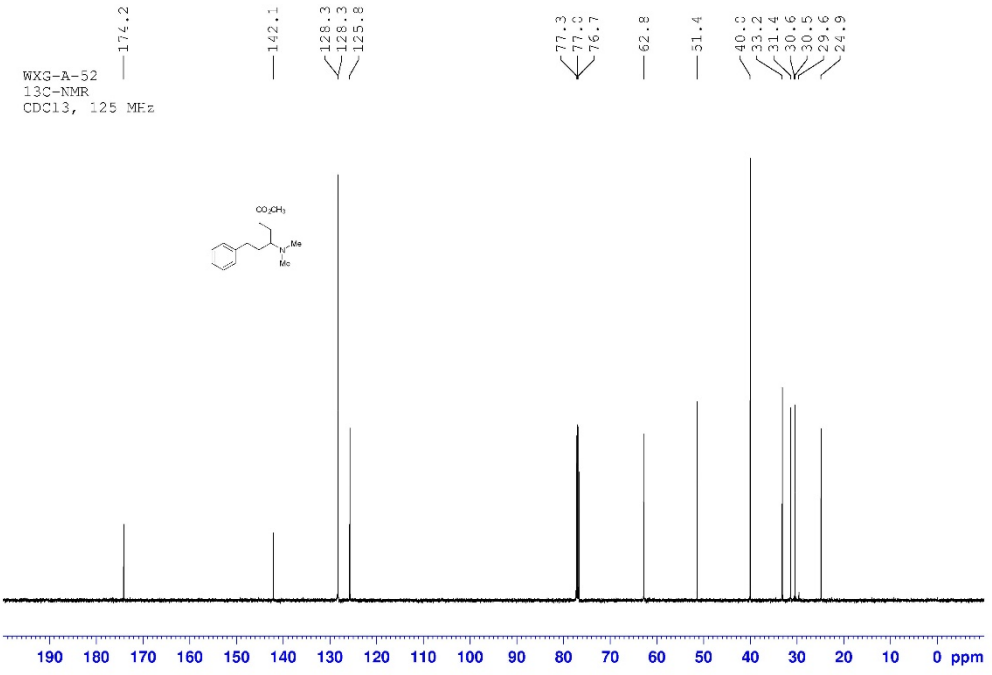
^{1}H and ^{13}C NMR Spectra of Compound **4x**



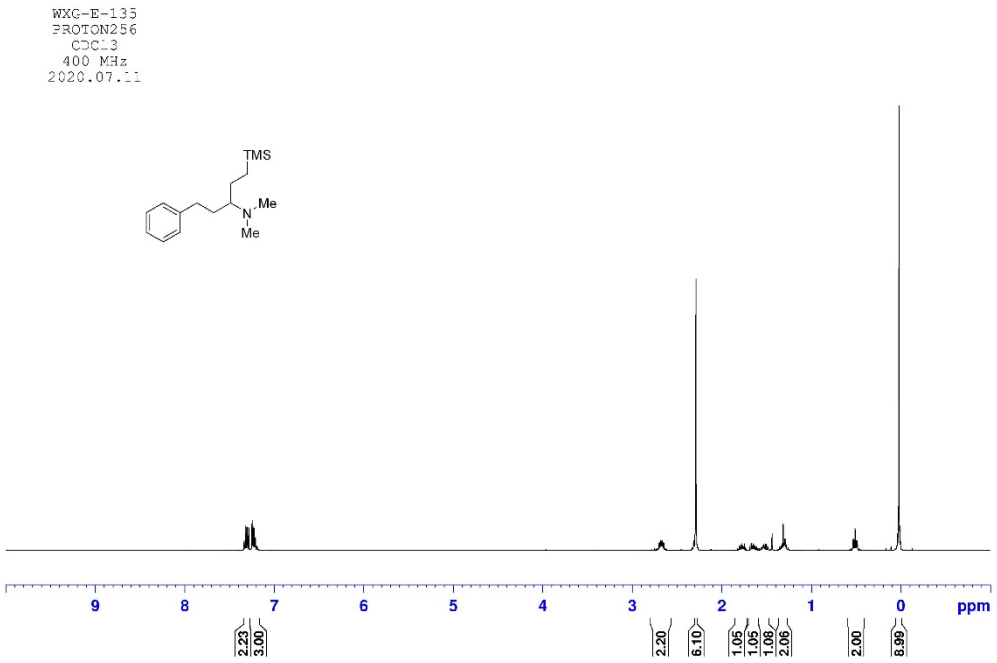


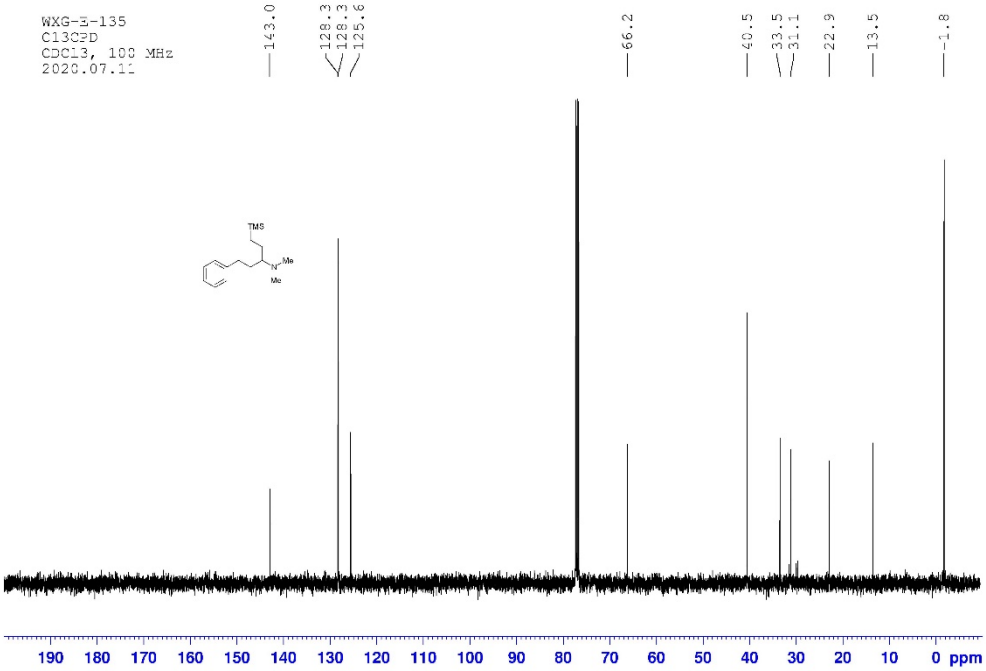
^{1}H and ^{13}C NMR Spectra of Compound **4y**



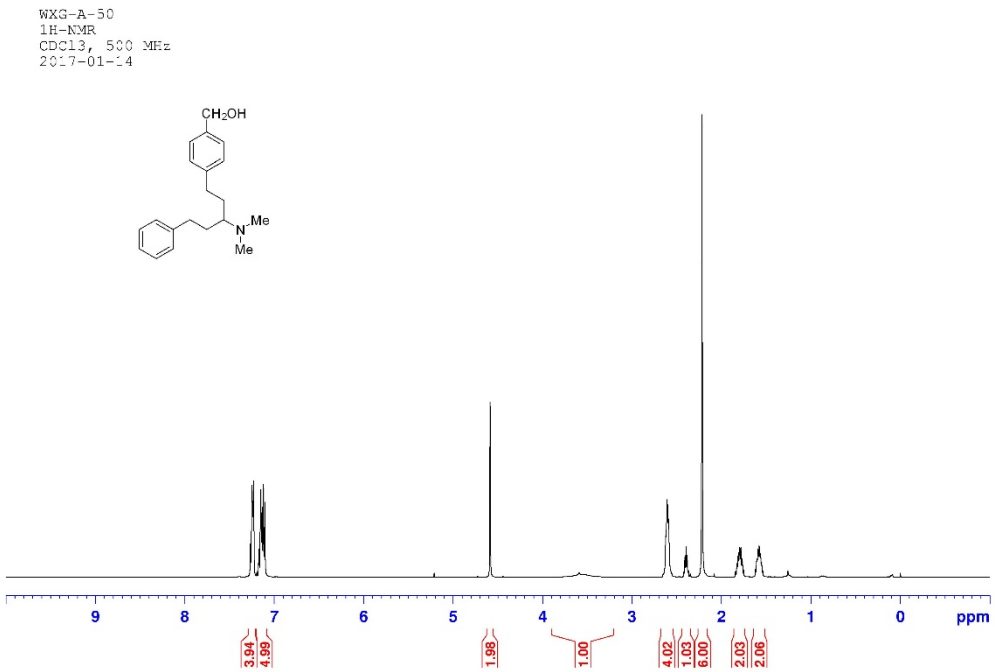


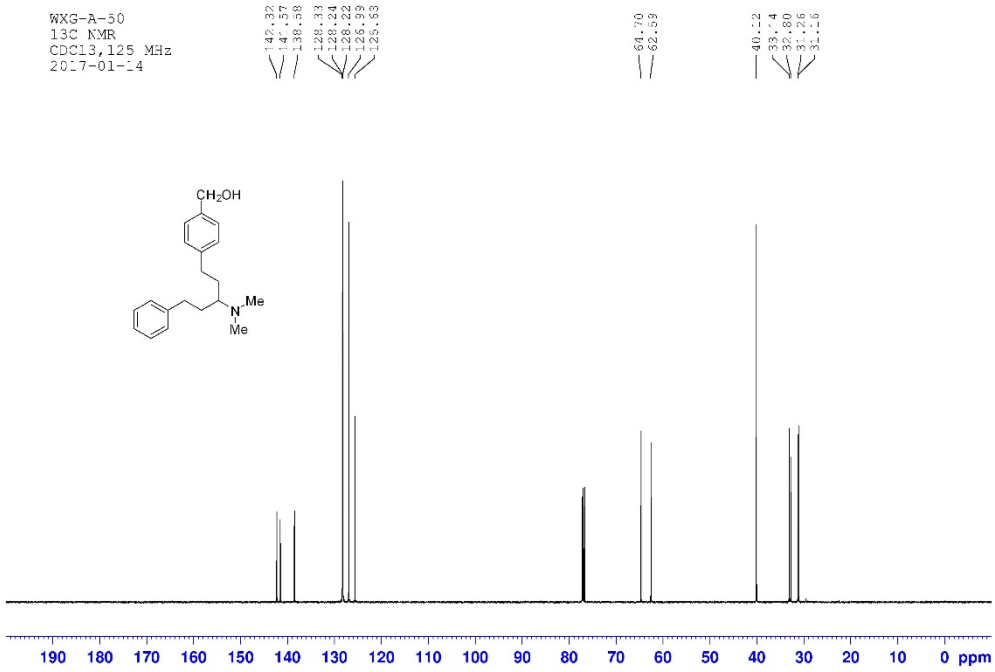
^{1}H and ^{13}C NMR Spectra of Compound **4z**



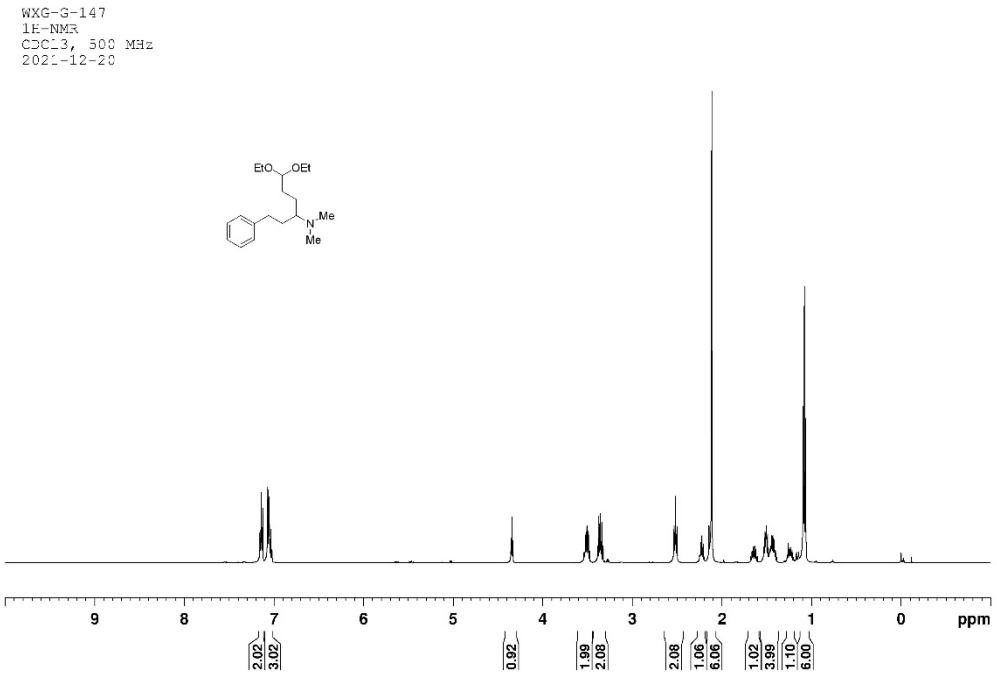


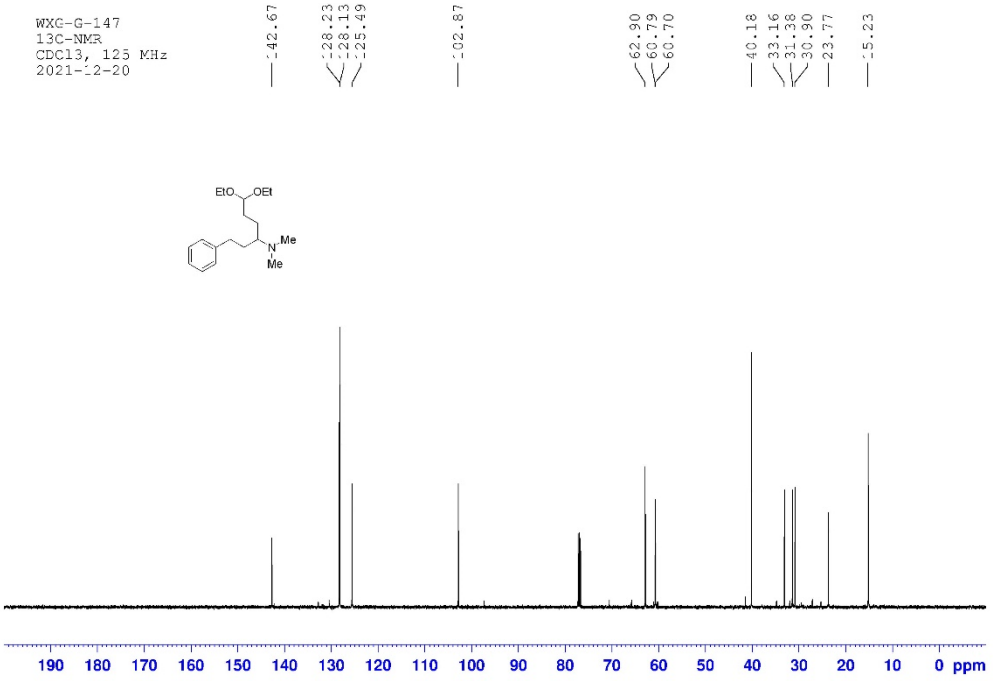
^{1}H and ^{13}C NMR Spectra of Compound **4aa**

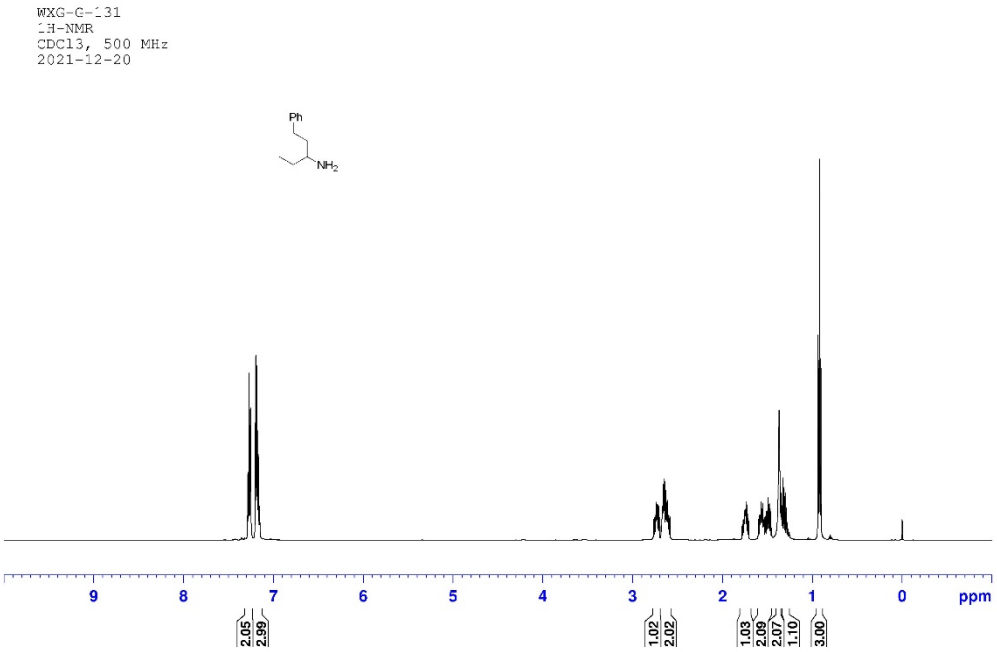


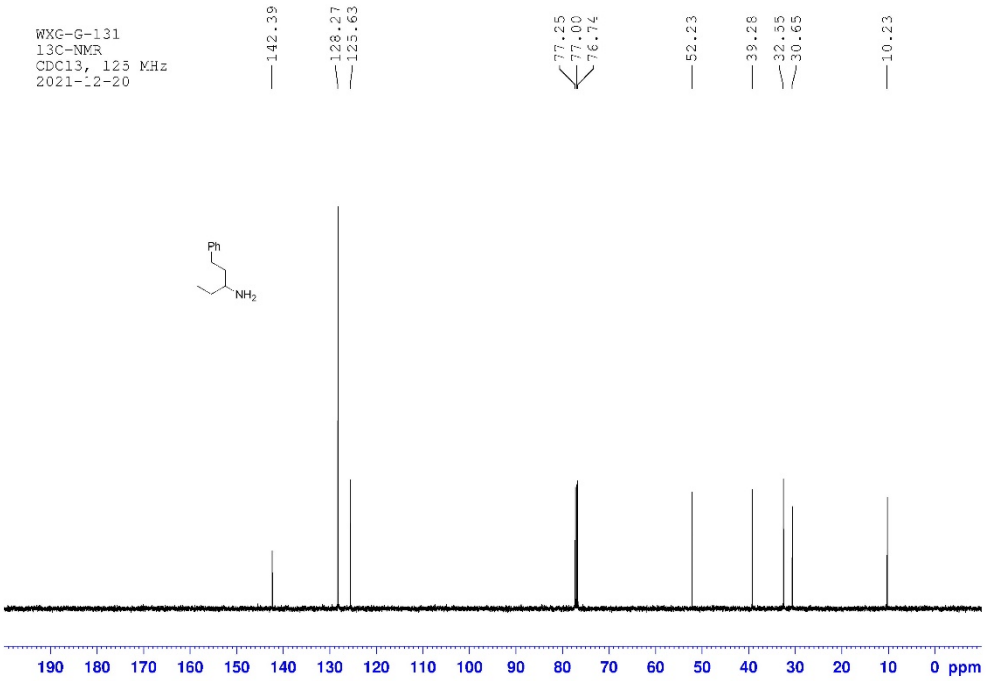


^{1}H and ^{13}C NMR Spectra of Compound **4ab**

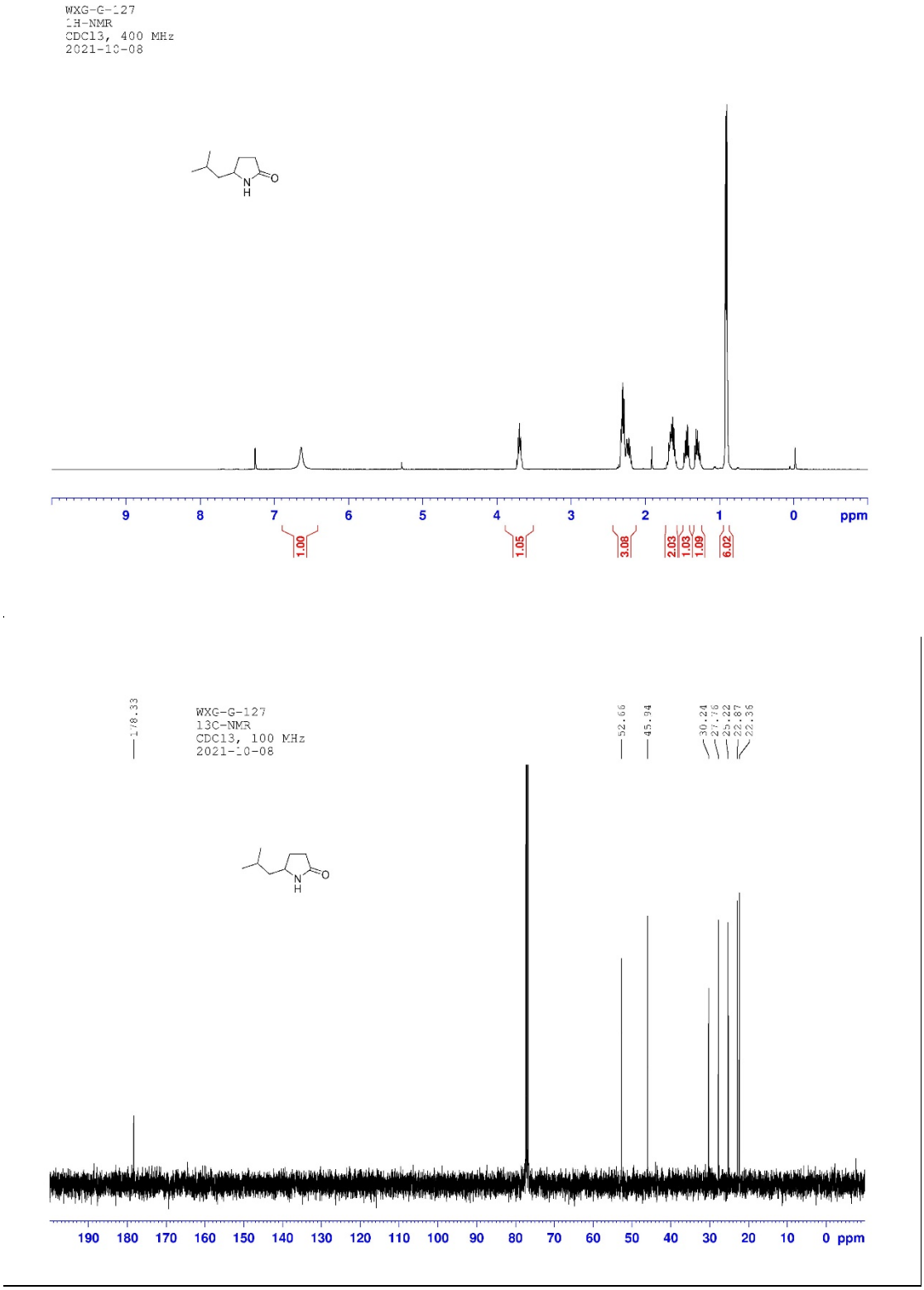





WXG-G-131
1H-NMR
CDCl3, 500 MHz
2021-12-20
Ph
NH2
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.99
1.02
2.02
1.03
2.06
2.07
1.10
3.00


WXG-G-131
13C-NMR
CDCl3, 125 MHz
2021-12-20
142.39
128.27
125.63
77.25
77.00
76.74
52.23
39.28
32.55
30.65
10.23
Ph
NH2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

^{1}H and ^{13}C NMR Spectra of Compound **(±)-6**



^{1}H and ^{13}C NMR Spectra of Compound **(±)**-isosolenopsin (**8**)