Electronic Supplementary Information

for

Gold Catalysed Site-Selective Cross-Coupling of Tertiary α-Silylamines with 1-Iodoalkynes Under UVA LED Light

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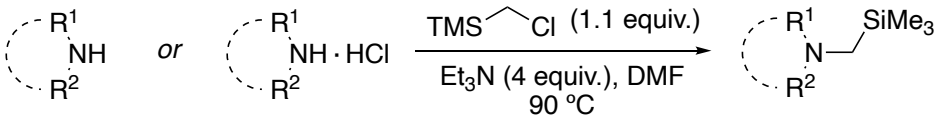
1. General Information

All reactions were performed in oven-dried glassware under a nitrogen atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Anhydrous solvent was freshly distilled and degassed through freeze-pump-thaw. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (petroleum ether:EtOAc as the eluent). Photoredox reactions were performed using a 365 nm LED (1.2 W) light source. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. Infrared spectra (IR) were taken on an IR spectrometer. High resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

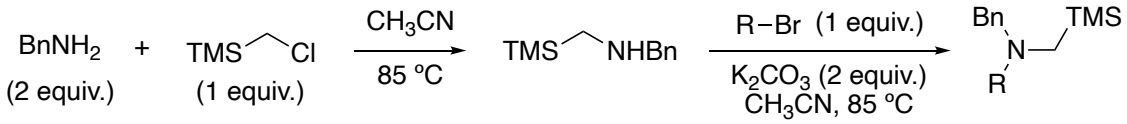
2. Experimental Procedures

2.1 General Procedure for the Preparation of α-Silylamines (1a–1h, 1k and 1v–1ε)



The secondary amine or its HCl salt (4.0 mmol, 1.0 equiv.) and triethylamine (16 mmol, 4.0 equiv.) was dissolved in DMF (2.5 mL) and (chloromethyl)trimethylsilane (541 mg, 4.4 mmol, 1.1 equiv.) was added to the mixture at room temperature under an atmosphere of nitrogen. The reaction mixture was allowed to stir at 90 °C for 17 h and, upon completion, cool to room temperature and diluted with Et_2O (40 mL). The organic layer was separated and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 20:1 or 10:1) to give the title compound in 36–98% yield.

2.2 General Procedure for the Preparation of α-Silylamines (1i, 1j, and 1l–1t)

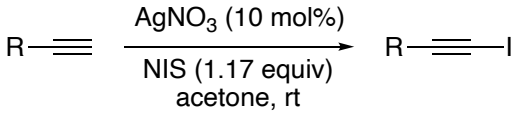


Benzylamine (942 mg, 8.8 mmol, 2.0 equiv.) and (chloromethyl)trimethylsilane (541 mg, 4.4 mmol, 1.0 equiv.) were dissolved in acetonitrile (13 mL) at room temperature and the resulting mixture was allowed to stir at 85 °C for 17 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting crude residue was filtered through a neutral Al_2O_3 pad with ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure to afford the crude product, which was subjected to next step without further purification.

To the solution of crude *N*-benzyl-1-(trimethylsilyl)methanamine in acetonitrile (44 mL) was added the respective bromide compound (4.4 mmol, 1 equiv.) and K_2CO_3 (1,214 mg, 8.8 mmol, 2 equiv.) at room temperature and the resulting reaction mixture was stirred at 85 °C for 17 h.

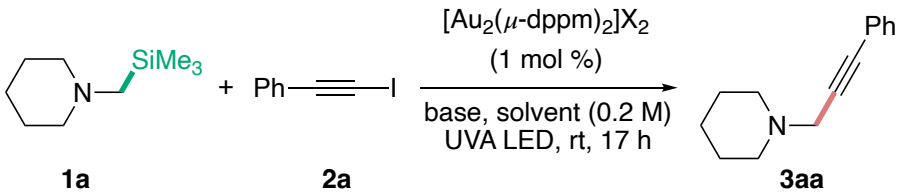
The reaction mixture was cooled to room temperature and filtered through a pad of celite pad with ethyl acetate (20 mL). The solvent of the resulting solution was removed under reduced pressure to give a crude residue, which was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 20:1 or 10:1) to afford the the title compound in 55–75% yield.

2.3 General Procedure for the Preparation of 1-Iodoalkynes (2a–o)[S7]



To a stirred solution of the terminal alkyne (2 mmol, 1 equiv.) in acetone (5 mL) was added NIS (2.3 mmol, 1.17 equiv.) and $AgNO_3$ (0.2 mmol, 10 mol %). The reaction mixture was stirred at room temperature for 2 h. On completion, the solvent was removed under reduced pressure and the residue was filtered through a pad of celite with petroleum ether (10 mL). Removal of the solvent under reduced pressure followed by purification by flash column chromatography on silica gel (petroleum ether as eluent) afforded the title compound in 37–99% yield.

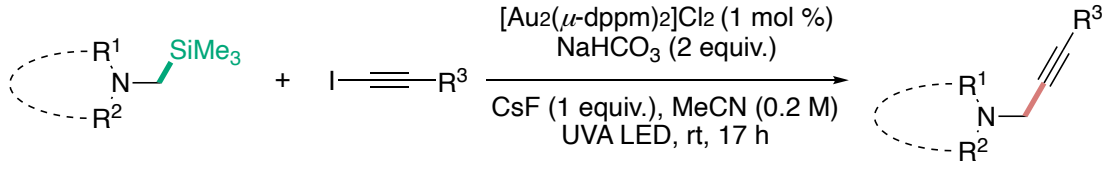
2.4 General Procedure for the Optimisation of the Gold(I,I)-Catalysed Cross-Coupling Reaction Conditions with 1a with 2a as the Model Substrates



A 10 mL screw cap reaction tube situated in a glovebox was charged with 1-((trimethylsilyl)methyl)piperidine (**1a**) (68 mg, 0.4 mmol, 2 equiv.) and (iodoethynyl)benzene (**2a**) (46 mg, 0.2 mmol, 1 equiv.). This was followed by the addition of various combinations of the base (0.4 mmol, 2 equiv.), additive (0.2 mmol, 1 equiv.) and $[Au_2(\mu\text{-dppm})_2]X_2$ (0.002 mmol, 1 mol %), and degassed acetonitrile (0.5 mL). The resulting reaction mixture was stirred

at 25 °C and irradiated with a UVA LED light source for 17 h. Upon completion, the solvent was removed under pressure and the ensuing crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:Et_2O = 25:1) to afford the propargyl amine product **3aa**.

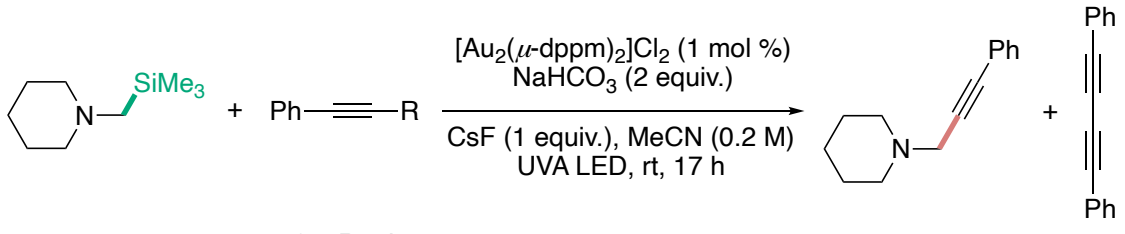
2.5 General Procedure for the Gold(I,I)-Catalysed Photoredox Cross-Coupling of 1-α-Silylamines (1) with Iodoalkynes (2)



1 **2** **3**

A 10 mL screw cap reaction tube situated in a glovebox was charged with α-silylamine **1** (0.4 mmol, 2 equiv.) and 1-iodoalkyne **2** (0.2 mmol, 1 equiv.). This was followed by the addition of $NaHCO_3$ (42 mg, 0.4 mmol, 2 equiv.), CsF (30 mg, 0.2 mmol, 1 equiv.), $[Au_2(\mu\text{-dppm})_2]Cl_2$ (2.4 mg, 0.002 mmol, 1 mol %) and degassed acetonitrile (0.5 mL). The resulting reaction mixture was stirred at 25 °C and irradiated with a UVA LED light source for 17 h. Upon completion, the solvent was removed under pressure and the ensuing crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:Et_2O = 25:1) to afford the propargyl amine product **3**.

2.6 General Procedure for the Control Experiments with 1a, 2a and 4

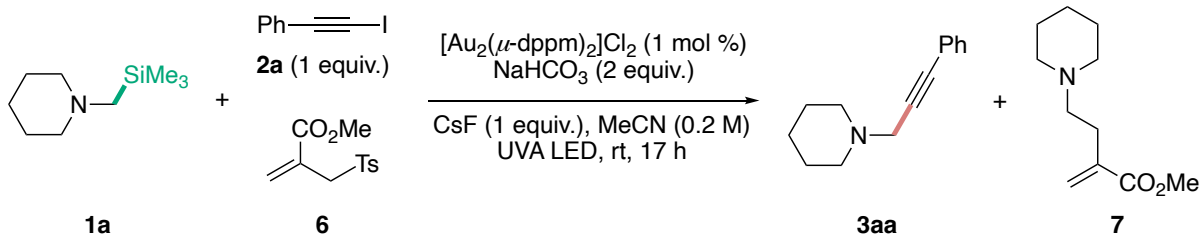


1a **2a**, R = I; **4**, R = H **3aa** **5**

A 10 mL screw cap reaction tube situated in a glovebox was charged with various combinations of 1-((trimethylsilyl)methyl)piperidine (**1a**) (68 mg, 0.4 mmol, 2 equiv.), (iodoethynyl)benzene

(**2a**) (46 mg, 0.2 mmol, 1 equiv.) and phenylacetylene (**4**) (20 mg, 0.2 mmol, 1 equiv.). This was followed by the addition of various combinations of $NaHCO_3$ (42 mg, 0.4 mmol, 2 equiv.), CsF (30 mg, 0.2 mmol, 1 equiv.), TEMPO (125 mg, 0.8 mmol, 4 equiv.), photocatalyst (0.002 or 0.02mmol, 1 or 10 mol %) and degassed acetonitrile (0.5 mL). The resulting reaction mixture was stirred at 25 or 50 °C and irradiated with a blue or UVA LED light source or no light source for 17 h. Upon completion, the solvent was removed under pressure and the ensuing crude reaction mixture was either subjected to ^{1}H NMR measurements or purified by flash column chromatography on silica gel (eluent: petroleum ether:Et_2O = 25:1) to afford the propargyl amine **3aa** and/or 1,3-diyne **5** and/or unidentifiable decomposition products.

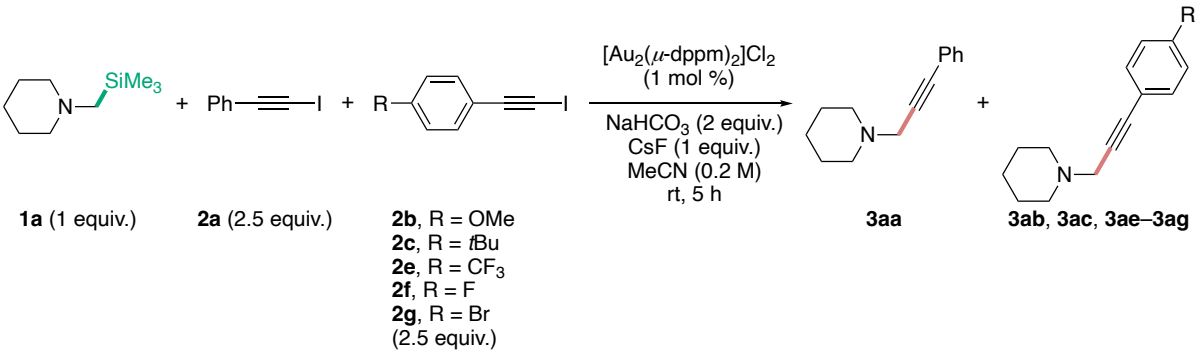
2.7 General Procedure for the Control Experiments with 1a, 2a and 4



1a **6** **3aa** **7**

A 10 mL screw cap reaction tube located in a glovebox was charged with $NaHCO_3$ (33.6 mg, 0.4 mmol, 2 equiv.), CsF (30 mg, 0.2 mmol, 1 equiv.) and $[Au_2(\mu\text{-dppm})_2]Cl_2$ (2.4 mg, 0.002 mmol, 1 mol %). This was followed by the addition of 1-((trimethylsilyl)methyl)piperidine (**1a**) (137 mg, 0.8 mmol, 4 equiv.), (iodoethynyl)benzene (**2a**) (46 mg, 0.2 mmol, 1 equiv.), methyl 2-(tosylmethyl)acrylate (**6**) (50.9 mg, 0.2 mmol, 1 equiv.) and degassed acetonitrile (2.5 mL). The reaction mixture was stirred at 25 °C and irradiated with a UVA LED light source for 17 h. Upon completion, the reaction mixture was filtered through celite to afford the crude residue, which was subjected to ^{1}H NMR and HRMS measurements.

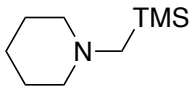
2.8 General Procedure for the Gold(I,I)-Catalysed Photoredox Competition Experiments of (Iodoethynyl)benzene with 1-Substituted-4-(iodoethynyl)benzene



A 10 mL screw cap reaction tube located in the glovebox was charged with Na_2CO_3 (42 mg, 0.4 mmol, 2 equiv.), CsF (30 mg, 0.2 mmol, 1 equiv.) and $[Au_2(\mu\text{-dppm})_2]Cl_2$ (2.4 mg, 0.002 mmol, 1 mol %). This was followed by the addition of 1-((trimethylsilyl)methyl)piperidine (**1a**) (34 mg, 0.2 mmol, 1 equiv.), (iodoethynyl)benzene (**2a**) (114 mg, 0.5 mmol, 2.5 equiv.), 1-substituted-4-(iodoethynyl)benzene (**2b**,**c** or **2e**–**g**) (0.5 mmol, 2.5 equiv.) and degassed MeCN (2.5 mL). The reaction was stirred at 25 °C under irradiation of a UVA LED light source for 5 h. Upon completion, the resulting mixture was filtered through celite and afforded the crude products, which was sent to ^{1}H NMR without further purification.

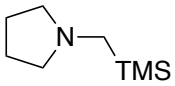
3. Spectroscopic Data

1-((Trimethylsilyl)methyl)piperidine (1a)[S1]



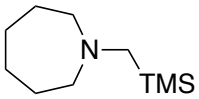
Colourless oil (3.52 g, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.31 (t, *J* = 5.4 Hz, 4H), 1.88 (s, 2H), 1.55 (p, *J* = 5.6 Hz, 4H), 1.37 (q, *J* = 6.2 Hz, 2H), 0.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 59.6, 52.8, 27.4, 24.9, 0.0.

1-((Trimethylsilyl)methyl)pyrrolidine (1b)[S2]



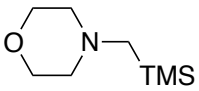
Colourless oil (950 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.51–2.43 (m, 4H), 2.00 (s, 2H), 1.75 (q, *J* = 3.6 Hz, 4H), 0.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 59.4, 59.4, 49.1, 25.1, 0.0.

1-((Trimethylsilyl)methyl)azepane (1c)[S3]



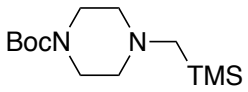
Colourless oil (910 mg, 98% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 2.60–2.56 (m, 4H), 2.05 (s, 2H), 1.60 (d, *J* = 5.4 Hz, 4H), 1.58–1.53 (m, 4H), 0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 60.7, 51.8, 28.9, 28.3, 0.0.

4-((Trimethylsilyl)methyl)morpholine (1d)[S3]



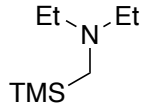
Pale yellow oil (1.2 g, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69–3.61 (m, 4H), 2.35 (dd, *J* = 5.7, 3.7 Hz, 4H), 1.87 (s, 2H), 0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.3, 58.6, 52.5, 0.0.

***tert*-Butyl 4-((trimethylsilyl)methyl)piperazine-1-carboxylate (1e)[S3]**



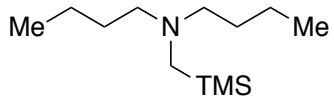
Yellow solid (700 mg, 86% yield); m.p. 100–102 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.39–3.34 (m, 4H), 2.28 (t, *J* = 5.1 Hz, 4H), 1.87 (s, 2H), 1.42 (s, 9H), 0.02 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 156.0, 80.6, 57.8, 52.1, 29.6, 0.0.

***N*-Ethyl-*N*-((trimethylsilyl)methyl)ethanamine (1f)[S4]**



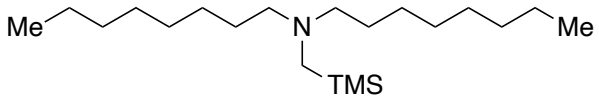
Yellow oil (236 mg, 37% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.45 (q, *J* = 7.1 Hz, 4H), 1.91 (d, *J* = 1.2 Hz, 2H), 0.97 (td, *J* = 7.1, 1.1 Hz, 6H), 0.04 (d, *J* = 1.2 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 51.5, 45.9, 12.8, 0.0.

***N*-Butyl-*N*-((trimethylsilyl)methyl)butan-1-amine (1g)[S3]**



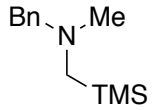
Pale yellow oil (577 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.29 (t, *J* = 7.4 Hz, 4H), 1.86 (s, 2H), 1.29 (dq, *J* = 37.7, 7.3 Hz, 9H), 0.87 (t, *J* = 7.2 Hz, 6H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 58.5, 47.2, 30.4, 21.9, 15.4, 0.0.

***N*-Octyl-*N*-((trimethylsilyl)methyl)octan-1-amine (1h)[S3]**



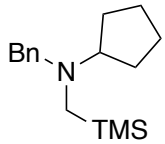
Yellow oil (680 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.35–2.27 (m, 4H), 1.90 (s, 2H), 1.44–1.35 (m, 4H), 1.27 (s, 20H), 0.91–0.84 (m, 6H), 0.04 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 58.8, 47.2, 33.1, 30.9, 30.6, 28.8, 28.1, 23.9, 15.3, 0.0.

***N*-Benzyl-*N*-methyl-1-(trimethylsilyl)methanamine (1i)[S5]**



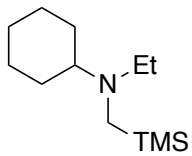
Colourless oil (1.0 g, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27–7.20 (m, 4H), 7.15 (ddd, *J* = 6.1, 4.8, 2.5 Hz, 1H), 3.36 (s, 2H), 2.12 (s, 3H), 1.84 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.1, 130.2, 129.4, 128.1, 67.6, 51.0, 47.4, 0.0.

***N*-Benzyl-*N*-((trimethylsilyl)methyl)cyclopentanamine (1j)**



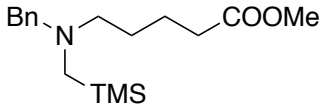
Colourless oil (210 mg, 40% yield); IR (neat, cm^{-1}): 2950,2867, 2790, 1452, 1363, 1246, 835, 733; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.34–7.31 (m, 2H), 7.25 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.19–7.16 (m, 1H), 3.49 (s, 2H), 3.11–3.04 (m, 1H), 1.92 (s, 2H), 1.62–1.50 (m, 4H), 1.45–1.35 (m, 4H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 142.7, 129.7, 129.4, 127.8, 65.5, 60.3, 43.1, 28.3, 25.9, 0.0; HRMS (ESI) calcd. for $C_{16}H_{28}NSi$ (M^+ + H): 262.1991, found: 262.19995.

***N*-Ethyl-*N*-((trimethylsilyl)methyl)cyclohexanamine (1k)[S3]**



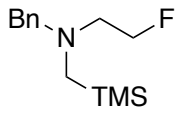
Pale yellow oil (760 mg, 71% yield); IR (neat, cm^{-1}): 2927, 2853, 1701, 1419, 1245, 1172, 853, 843, 761, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.43 (q, *J* = 7.1 Hz, 3H), 1.95 (s, 2H), 1.82–1.66 (m, 5H), 1.64–1.56 (m, 1H), 1.23–1.12 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 62.3, 42.3, 29.7, 28.0, 27.7, 0.0; HRMS (ESI) calcd. for $C_{12}H_{28}NSi$ (M^+ + H): 214.1991, found: 214.1961.

Methyl 4-(benzyl((trimethylsilyl)methyl)amino)butanoate (1l)[S3]



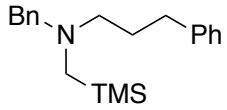
Colorless oil (385 mg, 57% yield); IR (neat, cm^{-1}): 2949, 2786, 1737, 1246, 1166, 1120, 837, 736; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.29–7.22 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 1H), 3.59 (s, 3H), 3.42 (s, 2H), 2.26 (t, *J* = 7.1 Hz, 2H), 2.20 (t, *J* = 7.5 Hz, 2H), 1.88 (s, 2H), 1.55 (p, *J* = 7.5 Hz, 2H), 1.42 (ddd, *J* = 11.1, 5.7, 3.4 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 175.4, 141.6, 130.0, 129.3, 127.9, 63.4, 57.9, 52.6, 47.2, 35.2, 27.8, 23.9, 0.0; HRMS (ESI) calcd. for $C_{17}H_{30}NO_2Si$ (M^+ + H): 308.20459, found: 308.20407.

***N*-Benzyl-2-fluoro-*N*-((trimethylsilyl)methyl)ethan-1-amine (1m)**



Colorless oil (320 mg, 64% yield); IR (neat, cm^{-1}): 2952, 2897, 2786, 1247, 1027, 836, 736; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.29–7.23 (m, 4H), 7.19–7.14 (m, 1H), 4.45 (td, *J* = 5.3, 1.4 Hz, 1H), 4.37 (td, *J* = 5.3, 1.4 Hz, 1H), 3.52 (d, *J* = 1.9 Hz, 2H), 2.65 (td, *J* = 5.3, 1.6 Hz, 1H), 2.61 (td, *J* = 5.3, 1.6 Hz, 1H), 2.01 (d, *J* = 1.9 Hz, 2H), 0.00 (d, *J* = 2.0 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.3, 130.1, 129.6, 128.3, 128.0, 84.2 (d, $J_{C\text{-}F}$ = 166 Hz), 64.1, 58.1 (d, $J_{C\text{-}F}$ = 20.1 Hz), 51.9, 48.2, 0.0; HRMS (ESI) calcd. for $C_{13}H_{23}FNSi$ (M^+ + H): 240.15838, found: 240.15728.

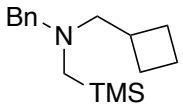
***N*-Benzyl-3-phenyl-*N*-((trimethylsilyl)methyl)propan-1-amine (1n)**



Colorless oil (610 mg, 63% yield); IR (neat, cm^{-1}): 2945, 2786, 1601, 1452, 1246, 1028, 837, 735; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.29 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.25 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.23–7.17 (m, 3H), 7.13–7.10 (m, 1H), 7.10–7.07 (m, 2H), 3.46 (s, 2H), 2.56–2.51

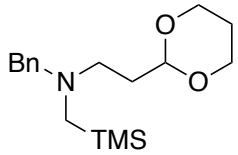
(m, 2H), 2.36–2.32 (m, 2H), 1.91 (s, 2H), 1.73 (dtd, J = 9.9, 7.8, 6.2 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 144.0, 141.7, 130.0, 129.6, 129.5, 129.3, 127.9, 126.8, 63.5, 58.1, 47.2, 34.9, 30.4, 0.0; HRMS (ESI) calcd. for $C_{20}H_{30}NSi$ (M^+ + H): 312.21475, found: 312.21386.

***N*-Benzyl-1-cyclobutyl-*N*-((trimethylsilyl)methyl)methanamine (1o)**



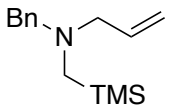
Colourless oil (450 mg, 74% yield); IR (neat, cm^{-1}): 2951, 2782, 1450, 1246, 1207, 837, 735; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.21 (m, 4H), 7.21–7.14 (m, 1H), 3.40 (s, 2H), 2.53–2.43 (m, 1H), 2.30 (d, J = 7.2 Hz, 2H), 1.96 (dddd, J = 11.4, 7.5, 5.6, 2.8 Hz, 2H), 1.86 (s, 2H), 1.83–1.65 (m, 2H), 1.62–1.51 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 142.0, 129.9, 129.3, 127.8, 65.0, 63.7, 47.6, 35.4, 28.5, 20.1, 0.0; HRMS (ESI) calcd. for $C_{16}H_{28}NSi$ (M^+ + H): 262.1991, found: 262.1982.

***N*-Benzyl-2-(1,3-dioxan-2-yl)-*N*-((trimethylsilyl)methyl)ethan-1-amine (1p)**



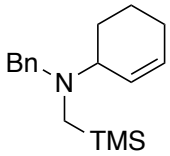
Colorless oil (580 mg, 70% yield); IR (neat, cm^{-1}): 2952, 2847, 1596, 1377, 1245, 1090, 1008, 839, 738; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30–7.21 (m, 4H), 7.20–7.13 (m, 1H), 4.54 (t, J = 5.3 Hz, 1H), 3.99 (ddt, J = 10.5, 5.0, 1.4 Hz, 2H), 3.71–3.60 (m, 2H), 3.43 (s, 2H), 2.39 (t, J = 7.1 Hz, 2H), 2.07–1.92 (m, 1H), 1.88 (s, 2H), 1.71 (td, J = 7.1, 5.3 Hz, 2H), 1.24 (dtt, J = 13.4, 2.6, 1.4 Hz, 1H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.7, 130.0, 129.4, 128.0, 102.4, 68.1, 63.4, 53.3, 47.4, 34.3, 27.2, 0.0; HRMS (ESI) calcd. for $C_{17}H_{30}NO_2Si$ (M^+ + H): 308.20459, found: 308.20269.

***N*-Benzyl-*N*-((trimethylsilyl)methyl)prop-2-en-1-amine (1q)**



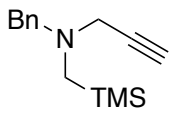
Colorless oil (240 mg, 51% yield); IR (neat, cm^{-1}): 3065, 2953, 2782, 1494, 1417, 1364, 1247, 917, 836, 736, 697; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (dddt, J = 13.0, 7.8, 6.2, 1.2 Hz, 4H), 7.21 – 7.14 (m, 1H), 5.88 – 5.73 (m, 1H), 5.17 – 5.02 (m, 2H), 3.45 (s, 2H), 2.92 (dt, J = 6.3, 1.3 Hz, 2H), 1.91 (d, J = 1.2 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.5, 137.8, 130.0, 129.4, 128.0, 118.2, 63.0, 61.4, 46.8; 0.0; HRMS (ESI) calcd. for $C_{14}H_{24}NSi$ (M^+ + H): 234.1678, found: 234.1668.

***N*-Benzyl-*N*-((trimethylsilyl)methyl)cyclohex-2-en-1-amine (1r)**



Colourless oil (510 mg, 93% yield); IR (neat, cm^{-1}): 3022, 2929, 1601, 1245, 1207, 836, 724; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.30 (m, 2H), 7.25 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.19–7.13 (m, 1H), 5.79–5.71 (m, 1H), 5.62 (dt, *J* = 10.2, 1.9 Hz, 1H), 3.67 (d, *J* = 14.2 Hz, 1H), 3.41 (d, *J* = 14.1 Hz, 1H), 3.30–3.19 (m, 1H), 2.03–1.87 (m, 4H), 1.81–1.68 (m, 2H), 1.43 (tt, *J* = 7.0, 1.8 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 142.8, 132.6, 131.0, 129.8, 129.5, 127.9, 58.8, 58.8, 42.4, 26.9, 23.9, 23.3, 0.0; HRMS (ESI) calcd. for $C_{17}H_{28}NSi$ (M^+ + H): 274.1991, found: 274.19835.

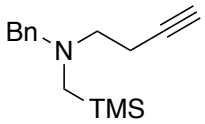
***N*-Benzyl-*N*-((trimethylsilyl)methyl)prop-2-yn-1-amine (1s)**



Colorless oil (280 mg, 61% yield); IR (neat, cm^{-1}): 3304, 2953, 2771, 1248, 844, 738, 697; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30–7.18 (m, 4H), 7.18–7.12 (m, 1H), 3.49 (s, 2H), 3.18 (d, *J* = 2.3 Hz, 2H), 2.15 (t, *J* = 2.3 Hz, 1H), 2.02 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz,

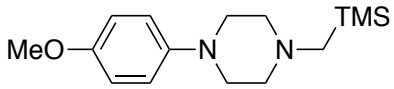
$CDCl_3$) δ (ppm) 130.4, 129.7, 128.5, 74.7, 62.3, 46.9, 46.4, 0.0; HRMS (ESI) calcd. for $C_{14}H_{22}NSi$ (M^+ + H): 232.15215, found: 232.14973.

***N*-Benzyl-*N*-((trimethylsilyl)methyl)but-3-yn-1-amine (1t)**



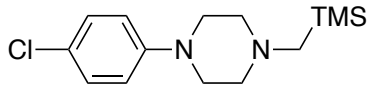
Colorless oil (290 mg, 59% yield); IR (neat, cm^{-1}): 3309, 2930, 2793, 1586, 1304, 1247, 837, 736; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.21 (m, 4H), 7.20–7.14 (m, 1H), 3.47 (s, 2H), 2.59–2.52 (m, 2H), 2.26 (td, J = 7.5, 2.7 Hz, 2H), 1.93 (s, 2H), 1.87–1.84 (m, 1H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.3, 130.0, 129.5, 128.2, 84.6, 70.2, 63.2, 57.0, 47.0, 17.9, 0.0; HRMS (ESI) calcd. for $C_{15}H_{24}NSi$ (M^+ + H): 246.1678, found: 246.1650.

1-(4-Methoxyphenyl)-4-((trimethylsilyl)methyl)piperazine (1u)[S3]



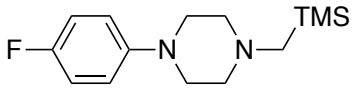
White oil (400 mg, 36% yield); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.92–6.86 (m, 2H), 6.86–6.81 (m, 2H), 3.76 (s, 3H), 3.12–3.02 (m, 4H), 2.60–2.53 (m, 4H), 1.98 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 154.7, 147.0, 119.1, 115.5, 58.2, 56.7, 51.9, 51.9, 0.0.

1-(4-Chlorophenyl)-4-((trimethylsilyl)methyl)piperazine (1v)[S3]



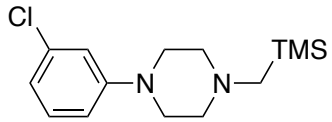
White solid (1.02 g, 90% yield); m.p. 78–80 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.19 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.20–3.08 (m, 4H), 2.58–2.51 (m, 4H), 1.97 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 151.1, 130.0, 125.3, 118.2, 57.9, 51.9, 50.4, 0.0.

1-(4-Fluorophenyl)-4-((trimethylsilyl)methyl)piperazine (1w)[S3]



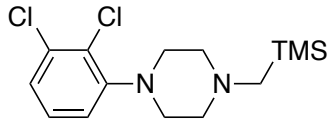
White solid (890 mg, 84% yield); m.p. 96–98 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.99–6.91 (m, 2H), 6.89–6.81 (m, 2H), 3.14–3.05 (m, 4H), 2.62–2.49 (m, 4H), 1.98 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.2 (d, $J_{C\text{-}F}$ = 238.5 Hz), 149.2 (d, $J_{C\text{-}F}$ = 2.3 Hz), 118.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 116.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 58.1, 51.9, 51.4, 0.0

1-(3-Chlorophenyl)-4-((trimethylsilyl)methyl)piperazine (1x)[S3]



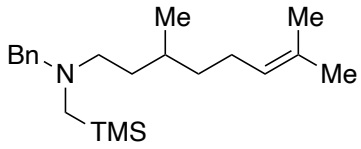
White oil (950 mg, 82% yield); m.p. 45–47 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15 (td, *J* = 8.1, 3.5 Hz, 1H), 6.91–6.84 (m, 1H), 6.78 (td, *J* = 8.5, 8.1, 2.5 Hz, 2H), 3.18 (q, *J* = 5.0, 4.3 Hz, 4H), 2.54 (q, *J* = 4.9, 4.4 Hz, 4H), 1.97 (d, *J* = 3.3 Hz, 2H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 136.0, 131.1, 120.1, 116.7, 114.8, 57.8, 51.9, 49.9, 0.0.

1-(2,3-Dichlorophenyl)-4-((trimethylsilyl)methyl)piperazine (1y)[S3]



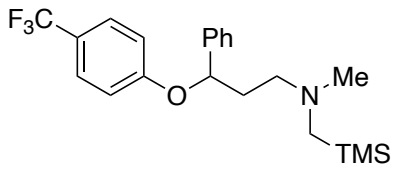
White solid (1.14 g, 90% yield); m.p. 80–81 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16–7.08 (m, 2H), 6.92 (dd, *J* = 6.4, 3.1 Hz, 1H), 3.10–2.98 (m, 4H), 2.66–2.51 (m, 4H), 1.98 (d, *J* = 1.4 Hz, 2H), 0.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 152.5, 135.1, 128.6, 128.5, 125.4, 119.6, 58.1, 52.6, 51.9, 0.0.

***N*-Benzyl-3,7-dimethyl-*N*-((trimethylsilyl)methyl)oct-6-en-1-amine (1z)**



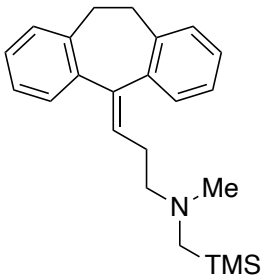
Colourless oil (270 mg, 44% yield); IR (neat, cm^{-1}): 3278, 2912, 1599, 1247, 1028, 837, 736; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30–7.21 (m, 5H), 7.21–7.14 (m, 1H), 5.03 (ddq, *J* = 8.6, 5.7, 1.4 Hz, 1H), 3.51–3.33 (m, 3H), 2.28 (ddd, *J* = 8.0, 6.4, 1.1 Hz, 2H), 1.93–1.82 (m, 5H), 1.63 (q, *J* = 1.3 Hz, 3H), 1.56–1.52 (m, 3H), 1.49–1.33 (m, 2H), 1.28–1.16 (m, 2H), 1.05 (dddd, *J* = 13.4, 9.4, 7.6, 6.0 Hz, 1H), 0.75 (d, *J* = 6.5 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.9, 132.2, 130.0, 129.3, 129.2, 127.8, 127.8, 126.2, 63.5, 56.5, 51.7, 47.3, 38.5, 35.5, 31.8, 27.0, 26.8, 21.0, 18.9, 0.0; HRMS (ESI) calcd. for $C_{21}H_{38}NSi$ ($M^+ + H$): 332.27735, found: 332.27562.

***N*-Methyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)-*N*-((trimethylsilyl)methyl)propan-1-amine (1*α*)[S3]**



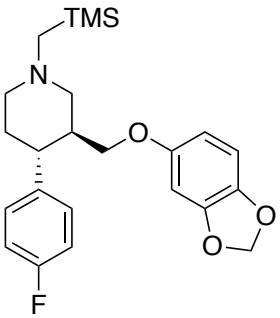
Yellow oil (550 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41–7.34 (m, 2H), 7.34–7.23 (m, 4H), 7.23–7.16 (m, 1H), 6.91–6.84 (m, 2H), 5.28 (dd, *J* = 8.2, 4.8 Hz, 1H), 2.50–2.41 (m, 1H), 2.35 (ddd, *J* = 12.2, 7.9, 5.4 Hz, 1H), 2.19 (s, 3H), 2.17–2.07 (m, 1H), 1.98–1.87 (m, 1H), 1.84 (d, *J* = 5.1 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.1, 142.7, 130.0, 129.0, 128.0 (q, J_{C-F} = 3.8 Hz), 127.2, 124.4, 124.1, 123.8, 117.1, 79.8, 59.0, 51.1, 47.4, 38.1, 0.0.

3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)-*N*-methyl-*N*-((trimethylsilyl)-methyl)propan-1-amine (1*β*)[S3]



Yellow oil (1.27 g, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28–7.20 (m, 1H), 7.14–7.02 (m, 6H), 6.98–6.90 (m, 1H), 5.84 (t, *J* = 7.3 Hz, 1H), 3.45–3.14 (m, 2H), 2.79 (d, *J* = 81.2 Hz, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.25 (t, *J* = 6.7 Hz, 2H), 2.11 (s, 3H), 1.86–1.72 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 144.4, 142.6, 141.3, 140.5, 138.2, 131.1, 130.9, 129.8, 129.5, 129.2, 128.5, 128.1, 127.2, 126.9, 62.6, 50.8, 47.3, 35.0, 33.3, 28.8, 0.0;

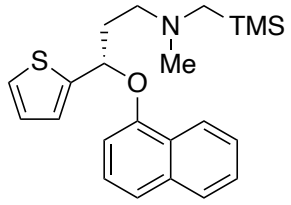
(3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-((trimethylsilyl)-methyl)piperidine (1*γ*)[S3]



Pale yellow oil (330 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21–7.14 (m, 2H), 7.03–6.93 (m, 2H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 2.5 Hz, 1H), 6.14 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.87 (s, 2H), 3.58 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.44 (dd, *J* = 9.4, 7.5 Hz, 1H), 3.25 (ddd, *J* = 11.3, 3.7, 1.7 Hz, 1H), 3.02–2.93 (m, 1H), 2.40 (td, *J* = 11.7, 4.1 Hz, 1H), 2.25 (dtd, *J* = 11.0, 7.6, 3.7 Hz, 1H), 2.10–1.71 (m, 6H), 0.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.5 (d, *J* = 244.1 Hz), 155.5, 149.2, 142.6, 141.0 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 7.7 Hz), 116.4 (d, *J*

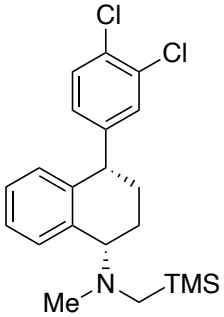
= 21.0 Hz), 108.9, 106.6, 102.1, 99.0, 70.8, 62.6, 59.1, 52.2, 44.8, 43.3, 35.9, 0.0; HRMS (ESI) calcd. for $C_{23}H_{31}FNO_3Si$ (M^+ + H): 416.20574, found: 416.20579.

(*S*)-*N*-Methyl-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)-*N*-((trimethylsilyl)methyl)-propan-1-amine (1*δ*)[S3]



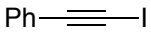
Pale yellow oil (470 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.37–8.30 (m, 1H), 7.76–7.68 (m, 1H), 7.48–7.40 (m, 2H), 7.37–7.30 (m, 1H), 7.23 (dd, *J* = 8.3, 7.7 Hz, 1H), 7.17–7.12 (m, 1H), 7.01 (ddd, *J* = 3.5, 1.3, 0.6 Hz, 1H), 6.90–6.81 (m, 2H), 5.76 (dd, *J* = 7.4, 5.5 Hz, 1H), 2.57–2.32 (m, 4H), 2.20 (s, 3H), 2.18–2.09 (m, 1H), 1.88–1.82 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 154.9, 146.8, 135.9, 128.7, 127.7, 127.5, 127.5, 127.0, 126.4, 125.9, 125.8, 123.5, 121.8, 108.3, 75.9, 59.2, 51.1, 47.4, 38.3, 0.0.

(1*S*,4*S*)-4-(3,4-Dichlorophenyl)-*N*-methyl-*N*-((trimethylsilyl)methyl)-1,2,3,4-tetrahydro-naphthalen-1-amine (1*ε*)[S3]



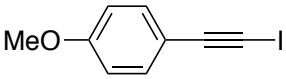
Colorless oil (250 mg, 36% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.37–7.25 (m, 2H), 7.21–7.11 (m, 2H), 6.96–6.85 (m, 2H), 4.16 (dd, *J* = 5.8, 3.4 Hz, 1H), 3.85 (t, *J* = 7.9 Hz, 1H), 2.29 (s, 3H), 2.23–1.97 (m, 4H), 1.82–1.66 (m, 2H), 0.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.0, 141.2, 139.3, 133.4, 132.2, 131.3, 131.2, 131.1, 130.0, 129.5, 128.2, 128.0, 65.7, 46.0, 45.0, 42.1, 31.4, 15.4, 0.0.

(Iodoethynyl)benzene (2a)[S6]



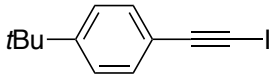
Yellow oil (355 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50–7.43 (m, 2H), 7.37–7.28 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 132.4, 128.9, 128.3, 123.4, 94.2, 6.4.

1-(Iodoethynyl)-4-methoxybenzene (2b)[S6]



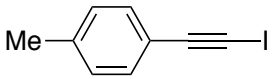
Pale yellow solid (320 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.28 (m, 2H), 6.76–6.73 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 160.0, 133.8, 133.6, 113.9, 113.8, 94.0, 75.8, 55.3, 3.7.

1-(*tert*-Butyl)-4-(iodoethynyl)benzene (2c)[S8]



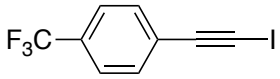
White solid (400 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41–7.28 (m, 4H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 152.1, 132.1, 125.2, 120.4, 94.2, 34.8, 31.2, 4.9.

1-(Iodoethynyl)-4-methylbenzene (2d)[S6]



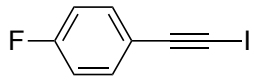
Yellow oil (324 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (d, J = 8.1 Hz, 1H), 7.24–7.10 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 139.0, 132.2, 129.0, 120.4, 94.3, 21.5, 4.9.

1-(Iodoethynyl)-4-(trifluoromethyl)benzene (2e)[S6]



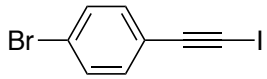
White solid (586 mg, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61–7.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 132.6, 130.5 (q, J_{C-F} = 32.7 Hz), 127.1 (d, J_{C-F} = 1.6 Hz), 125.2 (q, J_{C-F} = 3.8 Hz), 122.5, 92.9, 10.2.

1-Fluoro-4-(iodoethynyl)benzene (2f)[S8]



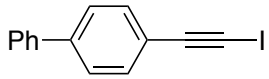
Pale yellow oil (423 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45–7.38 (m, 2H), 7.04–6.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 164.0, 161.5, 134.3 (d, J_{C-F} = 8.5 Hz), 119.5 (d, J_{C-F} = 3.0 Hz), 115.6 (d, J_{C-F} = 22.2 Hz), 93.0, 6.0 (d, J_{C-F} = 2.0 Hz).

1-Bromo-4-(iodoethynyl)benzene (2g)[S7]



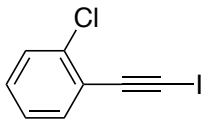
White solid (440 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47–7.42 (m, 2H), 7.31–7.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 133.7, 131.5, 123.2, 122.3, 93.1, 8.0.

4-(Iodoethynyl)-1,1'-biphenyl (2h)[S8]



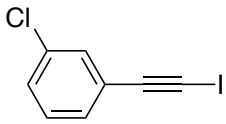
White solid (559 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61–7.48 (m, 6H), 7.48–7.41 (m, 2H), 7.39–7.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.5, 140.2, 132.7, 128.9, 127.7, 127.0, 126.9, 122.3, 94.0, 6.7.

1-Chloro-2-(iodoethynyl)benzene (2i)[S8]



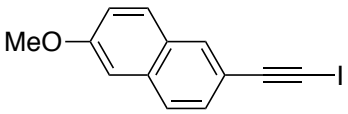
Yellow oil (373 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.35 (m, 1H), 7.32–7.25 (m, 1H), 7.20–7.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 136.7, 134.2, 129.8, 129.2, 126.4, 123.2, 90.9, 12.4.

1-Chloro-3-(iodoethynyl)benzene (2j)[S7]



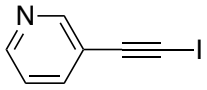
Yellow oil (378 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33–7.31 (m, 1H), 7.23–7.18 (m, 2H), 7.15 (dd, J = 7.4, 0.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 134.1, 132.3, 130.5, 129.5, 129.2, 125.0, 92.8, 8.6.

2-(Iodoethynyl)-6-methoxynaphthalene (2k)[S6]



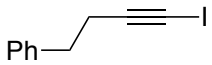
Pale yellow solid (345 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98–7.84 (m, 1H), 7.73–7.64 (m, 2H), 7.47 (ddd, J = 22.6, 8.4, 1.7 Hz, 1H), 7.16 (ddd, J = 8.9, 3.5, 2.6 Hz, 1H), 7.10 (dd, J = 5.8, 2.5 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.6, 134.4, 132.4, 132.1, 129.4, 129.3, 128.2, 126.8, 119.5, 118.3, 117.0, 105.8, 94.7, 55.4, 5.2.

3-(Iodoethynyl)pyridine (2l)[S8]



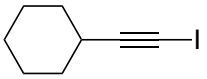
White solid (201 mg, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.60 (dd, J = 2.1, 0.9 Hz, 1H), 8.46 (dd, J = 4.9, 1.7 Hz, 1H), 7.64 (dt, J = 7.9, 1.9 Hz, 1H), 7.22–7.14 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.0, 148.9, 139.3, 123.0, 120.6, 90.7, 11.8.

(4-Iodobut-3-yn-1-yl)benzene (2m)[S6]



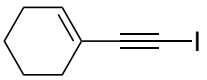
Colourless oil (450g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.24–7.18 (m, 2H), 7.16–7.08 (m, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.55 (td, *J* = 7.6, 0.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 140.3, 128.5, 128.4, 126.4, 93.9, 35.0, 23.1, -6.0.

(Iodoethynyl)cyclohexane (2n)[S9]



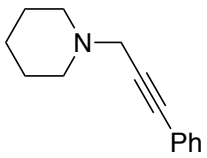
Colourless oil (173 mg, 37% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.53 (tt, *J* = 9.2, 3.8 Hz, 1H), 1.73 (dddd, *J* = 35.4, 15.6, 6.3, 3.4 Hz, 4H), 1.45 (tdd, *J* = 12.7, 9.1, 4.6 Hz, 3H), 1.33–1.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 99.1, 32.6, 31.3, 25.8, 24.9, -7.3.

1-(Iodoethynyl)cyclohex-1-ene (2o)[S7]



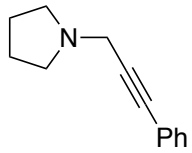
Yellow oil (255 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.12 (dt, J = 4.2, 2.1 Hz, 1H), 2.15–2.03 (m, 4H), 1.68–1.48 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 135.2, 119.4, 94.3, 27.1, 23.6, 20.3, 19.5.

1-(3-Phenylprop-2-yn-1-yl)piperidine (3aa)[S10]



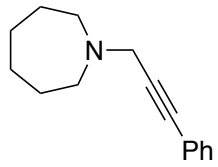
Yellow oil (32 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.24–7.17 (m, 2H), 7.09–7.01 (m, 3H), 3.25 (s, 2H), 2.35 (t, *J* = 5.3 Hz, 4H), 1.42 (p, *J* = 5.7 Hz, 4H), 1.23 (q, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.7, 128.2, 127.9, 123.3, 85.0 (d, $J_{C\text{-}C}$ = 6.9 Hz), 77.4, 77.0, 76.7, 53.4, 48.5, 25.9, 23.9.

1-(3-Phenylprop-2-yn-1-yl)pyrrolidine (3ba)[S10]



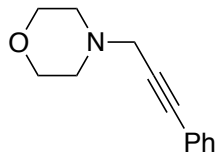
Yellow oil (15 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46–7.39 (m, 2H), 7.32–7.26 (m, 3H), 3.63 (s, 2H), 2.73–2.66 (m, 4H), 1.88–1.78 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.7, 128.2, 128.0, 123.3, 85.4, 84.4, 52.7, 43.8, 23.8.

1-(3-Phenylprop-2-yn-1-yl)azepane (3ca)[S10]



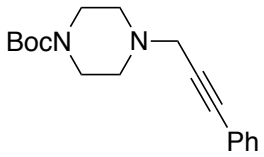
Yellow oil (24 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.31 (m, 2H), 7.27–7.15 (m, 3H), 3.51 (s, 2H), 2.75–2.65 (m, 4H), 1.71–1.59 (m, 4H), 1.55 (ddt, *J* = 6.0, 4.3, 2.6 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 132.8, 129.3, 129.0, 124.5, 87.0, 85.4, 56.5, 50.0, 29.3, 27.9.

4-(3-Phenylprop-2-yn-1-yl)morpholine (3da)[S10]



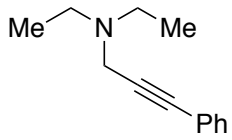
Yellow oil (19 mg, 47% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45–7.41 (m, 2H), 7.30 (dt, *J* = 4.9, 1.8 Hz, 3H), 3.80–3.74 (m, 4H), 3.51 (s, 2H), 2.68–2.60 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.7, 128.3, 128.2, 123.0, 85.6, 84.0, 66.9, 52.4, 48.1.

***tert*-Butyl 4-(3-phenylprop-2-yn-1-yl)piperazine-1-carboxylate (3ea)**



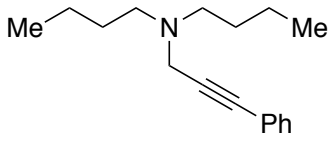
Yellow oil (27 mg, 45% yield); IR (neat, cm^{-1}): 2932, 2851, 2795, 1624, 1600, 1473, 1438, 1259, 1106, 1028, 855, 735; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39–7.31 (m, 2H), 7.25–7.18 (m, 3H), 3.47 (s, 2H), 3.43 (t, *J* = 5.1 Hz, 4H), 2.52 (t, *J* = 5.1 Hz, 4H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 155.9, 132.9, 129.4, 129.4, 124.1, 86.8, 85.2, 80.9, 57.7, 53.0, 49.0, 29.6; HRMS (ESI) calcd. for $C_{18}H_{25}N_2O_2$ (M^+ + H): 301.19162, found: 301.19549.

***N*,*N*-Diethyl-3-phenylprop-2-yn-1-amine (3fa)[S11]**



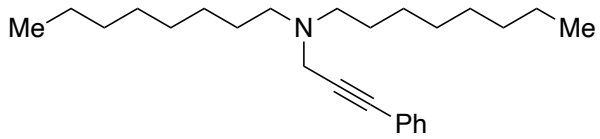
Yellow oil (26 mg, 69% yield); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 – 7.40 (m, 2H), 7.29 (q, J = 2.8 Hz, 3H), 3.64 (s, 2H), 2.63 (q, J = 7.2 Hz, 4H), 1.12 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.7, 128.2, 127.9, 123.4, 85.0, 84.4, 47.3, 41.4, 12.6.

***N*-Butyl-*N*-(3-phenylprop-2-yn-1-yl)butan-1-amine (3ga)[S11]**



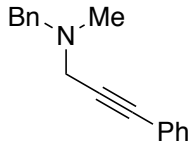
Yellow oil (29 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44–7.41 (m, 2H), 7.29 (dd, *J* = 5.0, 2.0 Hz, 3H), 3.62 (s, 2H), 2.56–2.49 (m, 4H), 1.53–1.44 (m, 4H), 1.40–1.31 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.7, 128.2, 127.8, 123.5, 84.9, 84.8, 53.7, 42.7, 29.8, 20.7, 14.1.

***N*-Octyl-*N*-(3-phenylprop-2-yn-1-yl)octan-1-amine (3ha)[S12]**



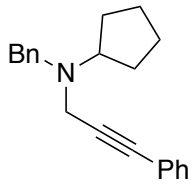
Yellow oil (61 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46–7.39 (m, 2H), 7.32–7.27 (m, 3H), 3.62 (s, 2H), 2.56–2.48 (m, 4H), 1.50 (t, *J* = 7.5 Hz, 4H), 1.31 (dp, *J* = 15.1, 5.4, 5.0 Hz, 20H), 0.92–0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.7, 128.2, 127.8, 123.5, 85.0, 84.8, 54.0, 42.7, 31.9, 29.6, 29.3, 27.6, 22.7, 14.1.

***N*-Benzyl-*N*-methyl-3-phenylprop-2-yn-1-amine (3ia)[S10]**



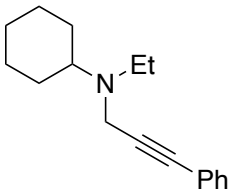
Yellow oil (34 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42–7.37 (m, 2H), 7.32–7.15 (m, 8H), 3.57 (s, 2H), 3.44 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.4, 131.7, 129.3, 128.3, 128.3, 128.0, 127.3, 123.3, 85.8, 84.4, 60.3, 45.7, 42.0.

***N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)cyclopentanamine (3ja)**



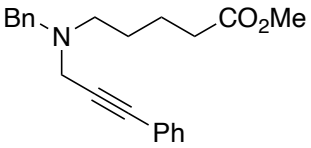
Yellow oil (44 mg, 76% yield); IR (neat, cm^{-1}): 2951, 2865, 2811, 1489, 1323, 1069, 1028, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46–7.41 (m, 2H), 7.38 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.31–7.25 (m, 5H), 7.25–7.19 (m, 1H), 3.73 (s, 2H), 3.47 (d, *J* = 1.0 Hz, 2H), 3.14–3.03 (m, 1H), 2.04–1.93 (m, 2H), 1.71 (tt, *J* = 8.7, 4.3 Hz, 2H), 1.63–1.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 140.5, 133.1, 130.7, 129.6, 129.2, 128.3, 124.9, 86.8, 86.2, 64.9, 57.3, 42.1, 32.8, 25.4; HRMS (ESI) calcd. for $C_{21}H_{24}N$ (M^+ + H): 290.19087, found: 290.18989.

_N_-Ethyl-_N_-(3-phenylprop-2-yn-1-yl)cyclohexanamine (3ka)



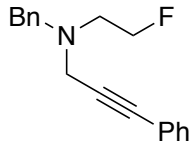
Yellow oil (42 mg, 87% yield); IR (neat, cm^{-1}): 2925, 2852, 1489, 1449, 1322, 1096, 753, 690; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39–7.33 (m, 2H), 7.23 (dd, J = 5.0, 1.9 Hz, 3H), 3.62 (s, 2H), 2.69 (qd, J = 7.2, 1.1 Hz, 2H), 2.52 (td, J = 7.1, 3.3 Hz, 1H), 1.98–1.88 (m, 2H), 1.82–1.68 (m, 2H), 1.62–1.53 (m, 1H), 1.28–1.16 (m, 4H), 1.07 (td, J = 7.2, 1.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.6, 128.2, 127.8, 123.6, 86.7, 84.3, 60.5, 43.8, 39.1, 30.3, 26.3, 25.9, 13.5; HRMS (ESI) calcd. for $C_{17}H_{24}N$ (M^+ + H): 242.19087, found: 242.18977.

Methyl 5-(benzyl(3-phenylprop-2-yn-1-yl)amino)pentanoate (3la)



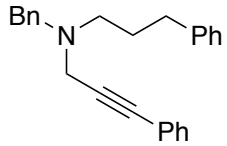
Yellow oil (39 mg, 58% yield); IR (neat, cm^{-1}): 2945, 2819, 1735, 1436, 1166, 1120, 755; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41–7.35 (m, 2H), 7.32–7.27 (m, 2H), 7.27–7.20 (m, 5H), 7.17 (ddd, J = 7.3, 4.3, 1.5 Hz, 1H), 3.61 (s, 2H), 3.58 (s, 3H), 3.44 (s, 2H), 2.55 (t, J = 7.1 Hz, 2H), 2.26 (t, J = 7.4 Hz, 2H), 1.69–1.58 (m, 2H), 1.58–1.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.1, 138.9, 131.8, 129.1, 128.3, 128.0, 127.1, 123.4, 85.6, 84.4, 58.1, 53.0, 51.5, 42.2, 33.9, 27.0, 22.8; HRMS (ESI) calcd. for $C_{22}H_{26}NO_2$ (M^+ + H): 336.19636, found: 336.19600.

***N*-Benzyl-*N*-(2-fluoroethyl)-3-phenylprop-2-yn-1-amine (3ma)**



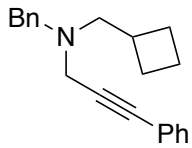
Yellow oil (30 mg, 56% yield); IR (neat, cm^{-1}): 3028, 2824, 1598, 1489, 1323, 1027, 755, 736; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 (dtd, *J* = 6.8, 3.8, 1.5 Hz, 2H), 7.32–7.26 (m, 2H), 7.22 (dddd, *J* = 7.6, 6.2, 3.8, 2.3 Hz, 5H), 7.19–7.13 (m, 1H), 4.55 (td, *J* = 5.2, 1.3 Hz, 1H), 4.43 (td, *J* = 5.1, 1.3 Hz, 1H), 3.69 (d, *J* = 1.2 Hz, 2H), 3.51 (d, *J* = 1.2 Hz, 2H), 2.89 (td, *J* = 5.2, 1.3 Hz, 1H), 2.83 (td, *J* = 5.2, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.4, 131.8, 129.2, 128.4, 128.3, 128.1, 127.3, 123.2, 85.8, 84.2, 83.6, 81.9, 77.2, 58.5, 53.3 (d, $J_{C\text{-}F}$ = 20.3 Hz), 43.3, 43.3; HRMS (ESI) calcd. for $C_{18}H_{19}FN$ (M^+ + H): 268.15015, found: 268.14916.

***N*-Benzyl-3-phenyl-*N*-(3-phenylpropyl)prop-2-yn-1-amine (3na)**



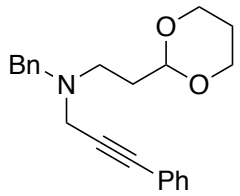
Colorless oil (59 mg, 87% yield); IR (neat, cm^{-1}): 3025, 2929, 2822, 1489, 1321, 1027, 736; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42–7.38 (m, 2H), 7.37–7.33 (m, 2H), 7.31–7.19 (m, 8H), 7.18–7.10 (m, 3H), 3.66 (s, 2H), 3.49 (s, 2H), 2.64 (dt, *J* = 12.4, 7.2 Hz, 4H), 1.85 (dtd, *J* = 9.2, 7.6, 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 142.4, 139.0, 131.8, 129.2, 128.5, 128.3, 128.3, 128.0, 127.1, 125.7, 123.4, 85.6, 84.5, 58.0, 53.0, 42.2, 33.6, 29.4; HRMS (ESI) calcd. for $C_{25}H_{26}N$ (M^+ + H): 340.20652, found: 340.20574.

***N*-Benzyl-*N*-(cyclobutylmethyl)-3-phenylprop-2-yn-1-amine (3oa)**



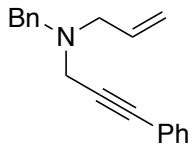
Yellow oil (50 mg, 86% yield); IR (neat, cm^{-1}): 2936, 2823, 1593, 1489, 1322, 1235, 1137, 1008, 814, 755; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46–7.40 (m, 2H), 7.37–7.32 (m, 2H), 7.31–7.24 (m, 5H), 7.24–7.18 (m, 1H), 3.63 (d, *J* = 1.3 Hz, 2H), 3.45 (d, *J* = 1.3 Hz, 2H), 2.63–2.50 (m, 3H), 2.05 (dtt, *J* = 9.6, 6.0, 1.9 Hz, 2H), 1.92–1.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 139.2, 131.8, 129.2, 128.3, 128.3, 127.9, 127.0, 123.5, 85.6, 84.8, 59.9, 58.2, 42.6, 34.3, 27.3, 18.8; HRMS (ESI) calcd. for $C_{21}H_{24}N$ (M^+ + H): 290.19087, found: 290.19005.

***N*-(2-(1,3-Dioxan-2-yl)ethyl)-*N*-benzyl-3-phenylprop-2-yn-1-amine (3pa)**



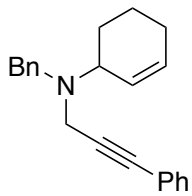
Yellow oil (48 mg, 72% yield); IR (neat, cm^{-1}): 2959, 2844, 1489, 1376, 1238, 1138, 1005, 891, 755; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.44–7.40 (m, 2H), 7.35–7.31 (m, 2H), 7.30–7.24 (m, 5H), 7.23–7.19 (m, 1H), 4.61 (t, *J* = 5.2 Hz, 1H), 4.04 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.70 (dddd, *J* = 12.0, 10.5, 2.6, 1.6 Hz, 2H), 3.66 (s, 2H), 3.48 (s, 2H), 2.73–2.66 (m, 2H), 2.08–1.98 (m, 1H), 1.82 (ddd, *J* = 8.0, 6.8, 5.3 Hz, 2H), 1.28 (ddt, *J* = 13.4, 2.6, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.9, 131.8, 129.2, 128.3, 128.0, 127.1, 123.4, 101.0, 85.5, 84.5, 66.9, 58.0, 48.6, 42.3, 33.5, 25.9; HRMS (ESI) calcd. for $C_{22}H_{26}NO_2$ (M^+ + H): 336.19636, found: 336.19553.

***N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (3qa)[S14]**



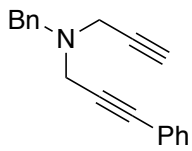
Colorless oil (41 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44–7.40 (m, 2H), 7.37–7.32 (m, 2H), 7.30–7.24 (m, 5H), 7.24–7.18 (m, 1H), 5.88 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.26 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.14 (ddt, *J* = 10.1, 2.2, 1.2 Hz, 1H), 3.67 (s, 2H), 3.48 (s, 2H), 3.21 (dt, *J* = 6.5, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.7, 135.7, 131.8, 129.2, 128.3, 128.3, 128.0, 127.1, 123.4, 118.0, 85.7, 84.5, 57.5, 56.9, 42.2.

***N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)cyclohex-2-en-1-amine (3ra)**



Pale yellow oil (43 mg, 71% yield); IR (neat, cm^{-1}): 3023, 2927, 1489, 1246, 1143, 1119, 852, 754; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42–7.37 (m, 4H), 7.31–7.25 (m, 5H), 7.24–7.20 (m, 1H), 5.87–5.79 (m, 2H), 3.88 (d, *J* = 13.6 Hz, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.53 (d, *J* = 5.2 Hz, 3H), 2.04–1.91 (m, 3H), 1.89–1.78 (m, 1H), 1.73–1.64 (m, 1H), 1.58–1.52 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 139.9, 131.6, 130.4, 130.3, 128.9, 128.2, 127.9, 126.9, 123.6, 87.2, 57.9, 53.3, 40.2, 25.3, 25.0, 21.4; HRMS (ESI) calcd. for $C_{22}H_{24}N$ (M^+ + H): 302.19087, found: 302.18999.

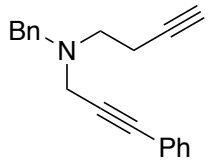
***N*-Benzyl-3-phenyl-*N*-(prop-2-yn-1-yl)prop-2-yn-1-amine (3sa)**



Yellow oil (29 mg, 56% yield); IR (neat, cm^{-1}): 3293, 2921, 2807, 1490, 1247, 839, 755, 740, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50–7.43 (m, 2H), 7.43–7.39 (m, 2H), 7.38–7.27

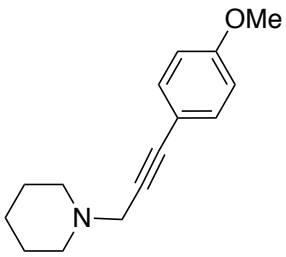
(m, 6H), 3.78 (s, 2H), 3.65 (s, 2H), 3.50 (d, J = 2.5 Hz, 2H), 2.30 (t, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 137.8, 131.8, 129.3, 128.4, 128.3, 128.1, 127.4, 123.1, 85.4, 84.5, 79.0, 73.3, 57.2, 42.8, 42.1; HRMS (ESI) calcd. for $C_{19}H_{18}N$ (M^+ + H): 260.14392, found: 260.14301.

***N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)but-3-yn-1-amine (3ta)**



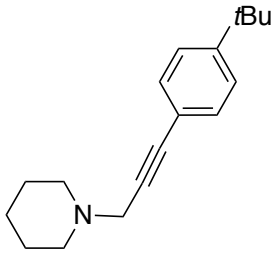
Colorless oil (41 mg, 75% yield); IR (neat, cm^{-1}): 2953, 2786, 2739, 1686, 1420, 1244, 1165, 1126, 1008, 838, 762, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43–7.38 (m, 2H), 7.37–7.31 (m, 3H), 7.29–7.24 (m, 5H), 7.23–7.18 (m, 1H), 3.69 (s, 2H), 3.52 (s, 2H), 2.80 (t, J = 7.4 Hz, 2H), 2.39 (td, J = 7.4, 2.7 Hz, 2H), 1.94 (t, J = 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.6, 131.8, 129.1, 128.4, 128.3, 128.1, 127.2, 123.2, 85.7, 84.2, 82.8, 69.1, 57.9, 52.3, 42.5, 17.9; HRMS (ESI) calcd. for $C_{19}H_{18}N$ (M^+ + H): 260.14392, found: 260.14211.

1-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)piperidine (3ab)[S11]



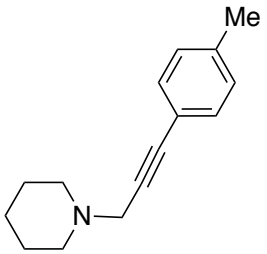
Yellow oil (31 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38–7.33 (m, 2H), 6.84–6.78 (m, 2H), 3.78 (s, 3H), 3.45 (s, 2H), 2.56 (t, J = 5.5 Hz, 4H), 1.64 (p, J = 5.6 Hz, 4H), 1.44 (q, J = 6.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.4, 133.1, 115.4, 113.8, 84.9, 83.3, 55.2, 53.4, 48.5, 25.9, 23.9.

1-(3-(4-(*tert*-Butyl)phenyl)prop-2-yn-1-yl)piperidine (3ac)[S16]



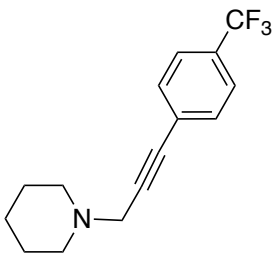
Yellow oil (42 mg, 83% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.39–7.35 (m, 2H), 7.33–7.29 (m, 2H), 3.47 (s, 2H), 2.57 (s, 4H), 1.68–1.59 (m, 4H), 1.44 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 151.2, 131.4, 125.2, 120.3, 85.0, 84.3, 77.2, 53.4, 48.5, 34.7, 31.2, 26.0, 24.0.

1-(3-(*p*-Tolyl)prop-2-yn-1-yl)piperidine (3ad)[S11,S13]



Pale yellow oil (22 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35–7.30 (m, 2H), 7.13–7.06 (m, 2H), 3.47 (s, 2H), 2.58 (t, J = 5.4 Hz, 4H), 2.33 (s, 3H), 1.64 (q, J = 5.6 Hz, 4H), 1.45 (tt, J = 8.6, 4.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.0, 131.6, 128.9, 120.2, 85.2, 84.1, 53.4, 48.5, 25.9, 23.9, 21.4.

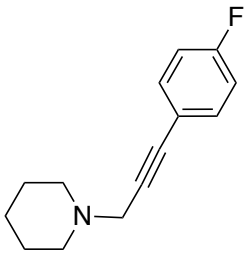
1-(3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-yl)piperidine (3ae)[S13]



Pale yellow oil (29 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 – 7.48 (m, 4H), 3.49 (s, 2H), 2.57 (t, J = 5.4 Hz, 4H), 1.65 (p, J = 5.6 Hz, 4H), 1.45 (dt, J = 6.6, 2.9 Hz, 2H);

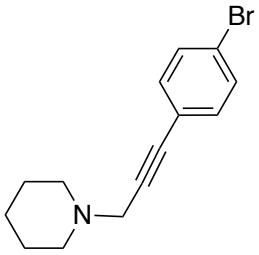
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.9, 129.8 (d, J_{C-F} = 33.0 Hz), 127.1, 125.1 (q, J_{C-F} = 3.9 Hz), 122.6, 87.8, 53.5, 48.4, 25.9, 23.9.

1-(3-(4-Fluorophenyl)prop-2-yn-1-yl)piperidine (3af)[S11,S13]



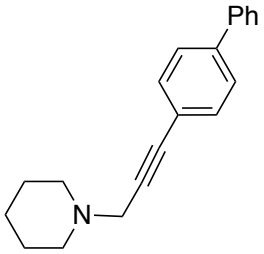
Pale yellow oil (27 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43–7.36 (m, 2H), 7.02–6.93 (m, 2H), 3.45 (s, 2H), 2.62–2.48 (m, 4H), 1.64 (p, J = 5.7 Hz, 4H), 1.50–1.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.31 (d, J_{C-F} = 248.9 Hz), 133.54 (d, J_{C-F} = 8.4 Hz), 115.44 (d, J_{C-F} = 22.0 Hz), 84.52, 84.05, 53.45, 48.37, 25.83, 23.86.

1-(3-(4-Bromophenyl)prop-2-yn-1-yl)piperidine (3ag)[S13]



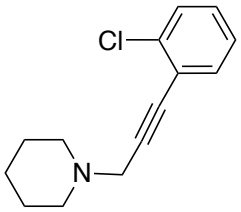
Yellow oil (41 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.32 (m, 2H), 7.25–7.18 (m, 2H), 3.38 (s, 2H), 2.49 (t, J = 5.4 Hz, 4H), 1.57 (p, J = 5.6 Hz, 4H), 1.38 (q, J = 6.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 133.1, 131.5, 122.2, 122.1, 86.3, 84.0, 53.5, 48.4, 25.9, 23.9.

1-(3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)piperidine (3ah)[S15]



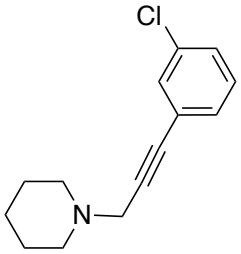
Yellow oil (25 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60–7.56 (m, 2H), 7.56–7.49 (m, 4H), 7.47–7.41 (m, 2H), 7.37–7.32 (m, 1H), 3.51 (s, 2H), 2.60 (t, *J* = 5.4 Hz, 4H), 1.67 (p, *J* = 5.7 Hz, 4H), 1.52–1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 140.8, 140.4, 132.1, 128.8, 127.6, 127.0, 126.9, 122.2, 85.6, 85.0, 53.4, 48.5, 25.9, 23.9.

1-(3-(2-Chlorophenyl)prop-2-yn-1-yl)piperidine (3ai)



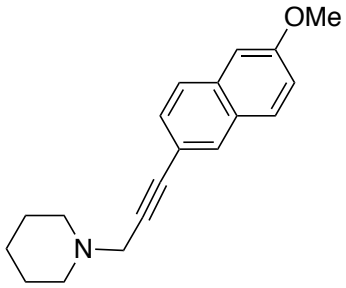
Yellow oil (26 mg, 56% yield); IR (neat, cm^{-1}): 2932, 2852, 2795, 1472, 1438, 1107, 1061, 1033, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48–7.43 (m, 1H), 7.40–7.35 (m, 1H), 7.19 (pd, *J* = 7.4, 1.8 Hz, 2H), 3.56 (s, 2H), 2.61 (t, *J* = 5.5 Hz, 4H), 1.64 (p, *J* = 5.7 Hz, 4H), 1.45 (td, *J* = 8.1, 7.4, 3.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 135.8, 133.4, 129.2, 128.9, 126.3, 123.2, 90.6, 82.0, 53.2, 48.5, 26.0, 23.9; HRMS (ESI) calcd. for $C_{14}H_{17}ClN$ (M^+ + H): 234.10495, found: 234.11657.

1-(3-(3-Chlorophenyl)prop-2-yn-1-yl)piperidine (3aj)[S11]



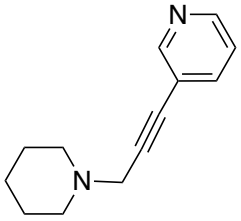
Yellow oil (25 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34 (t, *J* = 1.8 Hz, 1H), 7.28–7.05 (m, 3H), 3.40 (s, 2H), 2.48 (t, *J* = 5.4 Hz, 4H), 1.57 (p, *J* = 5.6 Hz, 4H), 1.38 (q, *J* = 6.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 134.0, 131.6, 129.8, 129.4, 128.2, 125.0, 86.5, 83.7, 53.5, 48.4, 25.9, 23.9.

1-(3-(6-Methoxynaphthalen-2-yl)prop-2-yn-1-yl)piperidine (3ak)



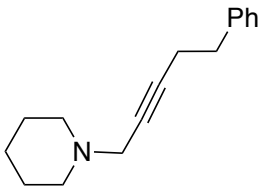
Yellow oil (28 mg, 50% yield); IR (neat, cm^{-1}): 2932, 2849, 1624, 1599, 1387, 1237, 1161, 1027, 855, 816; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (t, *J* = 1.1 Hz, 1H), 7.71–7.63 (m, 2H), 7.45 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 3.91 (s, 3H), 3.54 (s, 2H), 2.63 (s, 4H), 1.67 (p, *J* = 5.7 Hz, 4H), 1.47 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.2, 134.0, 131.3, 129.2, 129.2, 128.5, 126.7, 119.3, 118.2, 105.8, 85.6, 84.4, 77.2, 55.3, 53.4, 48.6, 29.7, 25.9, 23.9; HRMS (ESI) calcd. for $C_{19}H_{22}NO$ (M^+ + H): 280.17014, found: 280.16898.

3-(3-(Piperidin-1-yl)prop-1-yn-1-yl)pyridine (3al)[S15]



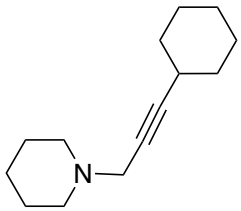
Yellow oil (22 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67–8.61 (m, 1H), 8.48 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.69 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.20 (ddd, *J* = 7.9, 4.9, 1.0 Hz, 1H), 3.47 (s, 2H), 2.55 (t, *J* = 5.4 Hz, 4H), 1.63 (p, *J* = 5.6 Hz, 4H), 1.49–1.38 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 152.4, 148.3, 138.6, 122.9, 120.4, 88.7, 81.7, 53.5, 48.4, 25.9, 23.9.

1-(5-Phenylpent-2-yn-1-yl)piperidine (3am)[S17]



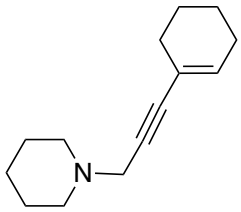
Colorless oil (21 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.17 (m, 2H), 7.14 (dt, *J* = 8.5, 2.8 Hz, 3H), 3.11 (t, *J* = 2.2 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.43 (tt, *J* = 7.6, 2.2 Hz, 3H), 2.39–2.28 (m, 4H), 1.52 (p, *J* = 5.6 Hz, 4H), 1.34 (dt, *J* = 12.4, 3.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 140.8, 128.5, 128.3, 126.2, 84.2, 76.1, 53.3, 48.1, 35.3, 25.9, 24.0, 20.9.

1-(3-Cyclohexylprop-2-yn-1-yl)piperidine (3an)



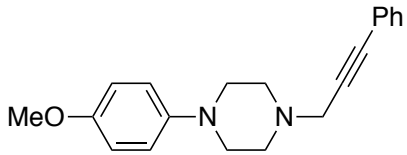
Colorless oil (30 mg, 75% yield); IR (neat, cm^{-1}): 2928, 2852, 2752, 1587, 1298, 1106, 764; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.23 (d, *J* = 2.1 Hz, 2H), 2.48 (t, *J* = 5.4 Hz, 4H), 2.37 (dddt, *J* = 7.2, 5.5, 3.5, 2.0 Hz, 1H), 1.77 (ddd, *J* = 12.1, 6.0, 3.3 Hz, 2H), 1.73–1.65 (m, 3H), 1.61 (p, *J* = 5.7 Hz, 5H), 1.46–1.35 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 89.6, 74.8, 53.1, 48.0, 36.7, 32.9, 29.7, 29.1, 25.9, 25.8, 24.9, 24.7, 24.0; HRMS (ESI) calcd. for $C_{14}H_{24}N$ (M^+ + H): 206.19087, found: 206.19093.

1-(3-(Cyclohex-1-en-1-yl)prop-2-yn-1-yl)piperidine (3ao)



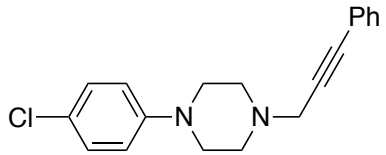
Yellow oil (24 m g, 59% yield); IR (neat, cm^{-1}): 2928, 2854, 2793, 1436, 1322, 1298, 1106, 1038, 917, 842; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.05 (dq, *J* = 3.8, 1.9 Hz, 1H), 3.35 (s, 2H), 2.56–2.41 (m, 4H), 2.08 (dtd, *J* = 17.2, 6.0, 2.6 Hz, 4H), 1.66–1.51 (m, 9H), 1.47–1.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 134.2, 120.6, 86.8, 82.0, 53.3, 48.4, 29.4, 25.9, 25.6, 24.0, 22.3, 21.5; HRMS (ESI) calcd. for $C_{14}H_{22}N$ (M^+ + H): 204.17522, found: 204.17332.

1-(4-Methoxyphenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (3ua)



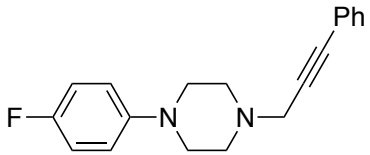
Yellow oil (51 mg, 84% yield); IR (neat, cm^{-1}): 2935, 2832, 2769, 1511, 1440, 1255, 1037, 821, 760; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46 (ddt, *J* = 5.5, 3.0, 1.5 Hz, 2H), 7.33–7.27 (m, 3H), 6.96–6.81 (m, 5H), 3.77 (s, 3H), 3.59 (s, 2H), 3.20–3.14 (m, 4H), 2.83 (dd, *J* = 6.2, 3.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 155.0, 146.8, 132.9, 129.4, 129.2, 124.2, 119.4, 119.1, 115.6, 115.5, 86.6, 85.5, 56.7, 53.4, 51.7, 48.9; HRMS (ESI) calcd. for $C_{20}H_{23}N_2O$ (M^+ + H): 307.18105, found: 307.17948.

1-(4-Chlorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (3va)



Yellow oil (30 mg, 48% yield); IR (neat, cm^{-1}): 2938, 2908, 2829, 1593, 1490, 1455, 1236, 1138, 997, 818, 756; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48–7.43 (m, 2H), 7.31 (dp, *J* = 4.0, 2.6, 2.2 Hz, 3H), 7.24–7.18 (m, 2H), 6.89–6.82 (m, 2H), 3.59 (s, 2H), 3.26–3.20 (m, 4H), 2.84–2.78 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 149.9, 131.7, 129.0, 128.3, 128.2, 124.6, 123.0, 117.3, 85.6, 84.1, 52.0, 49.2, 47.8; HRMS (ESI) calcd. for $C_{19}H_{20}ClN_2$ (M^+ + H): 311.1315, found: 311.1304.

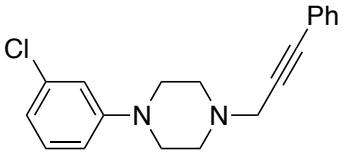
1-(4-Fluorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (3wa)



Yellow oil (33 mg, 56% yield); IR (neat, cm^{-1}): 2939, 2816, 2772, 1508, 1227, 1149, 1126, 816, 758; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48–7.42 (m, 2H), 7.31 (tt, *J* = 3.9, 2.5 Hz,

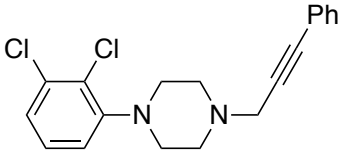
3H), 7.02–6.92 (m, 2H), 6.92–6.86 (m, 2H), 3.59 (s, 2H), 3.22–3.14 (m, 4H), 2.85–2.78 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.5, 157.2, 149.1 (d, J_{C-F} = 2.3 Hz), 132.9, 129.4 (d, J_{C-F} = 9.6 Hz), 124.2, 119.1 (d, J_{C-F} = 7.6 Hz), 116.7 (d, J_{C-F} = 22.0 Hz), 86.7, 85.4, 53.3, 51.3, 48.9; HRMS (ESI) calcd. for $C_{19}H_{20}FN_2$ (M^+ + H): 295.16105, found: 295.16063.

1-(3-Chlorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (3xa)



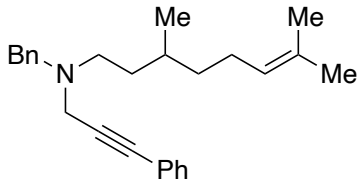
Yellow oil (32 mg, 51% yield); IR (neat, cm^{-1}): 2938, 2823, 1593, 1489, 1452, 1235, 1138, 1008, 813, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 (ddd, J = 6.9, 3.3, 1.5 Hz, 2H), 7.30 (dq, J = 6.1, 2.6, 2.0 Hz, 3H), 7.17 (td, J = 8.2, 1.3 Hz, 1H), 6.90 (q, J = 1.9 Hz, 1H), 6.81 (td, J = 7.3, 6.9, 1.5 Hz, 2H), 3.59 (d, J = 1.3 Hz, 2H), 3.29–3.23 (m, 4H), 2.83–2.76 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 152.3, 135.0, 131.8, 130.0, 128.3, 128.2, 123.0, 119.4, 115.9, 114.0, 85.7, 84.1, 51.9, 48.7, 47.8; HRMS (ESI) calcd. for $C_{19}H_{20}ClN_2$ (M^+ + H): 311.1315, found: 311.1306.

1-(2,3-Dichlorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (3ya)



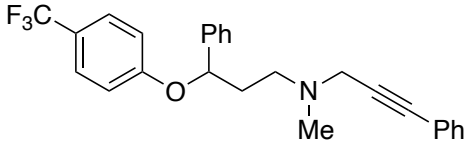
Yellow oil (39 mg, 56% yield); IR (neat, cm^{-1}): 2932, 2817, 1577, 1446, 1237, 1131, 951, 777, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42–7.36 (m, 2H), 7.27–7.21 (m, 3H), 7.12–7.04 (m, 2H), 6.90 (dd, J = 6.9, 2.8 Hz, 1H), 3.51 (s, 2H), 3.07 (t, J = 4.8 Hz, 4H), 2.77 (t, J = 4.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 151.2, 134.1, 131.8, 128.3, 128.2, 127.6, 127.5, 124.6, 123.1, 118.7, 85.4, 84.4, 52.4, 51.3, 47.8; HRMS (ESI) calcd. for $C_{19}H_{19}Cl_2N_2$ (M^+ + H): 345.09254, found: 345.09053.

***N*-Benzyl-3,7-dimethyl-*N*-(3-phenylprop-2-yn-1-yl)oct-6-en-1-amine (3za)**



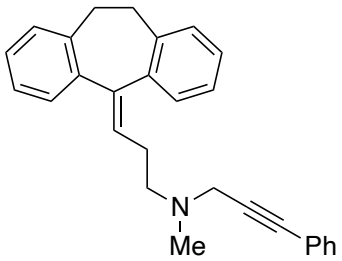
Pale yellow oil (37 mg, 51% yield); IR (neat, cm^{-1}): 3028, 2915, 2851, 1598, 1489, 1451, 1321, 1069, 1028, 754; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38–7.31 (m, 2H), 7.30–7.24 (m, 2H), 7.24–7.17 (m, 5H), 7.17–7.10 (m, 1H), 4.98 (tq, *J* = 7.1, 1.5 Hz, 1H), 3.63–3.51 (m, 2H), 3.40 (d, *J* = 1.2 Hz, 2H), 2.61–2.44 (m, 2H), 1.96–1.78 (m, 2H), 1.56 (d, *J* = 1.4 Hz, 3H), 1.54–1.37 (m, 5H), 1.30–1.17 (m, 2H), 1.12–1.00 (m, 1H), 0.78 (dd, *J* = 6.4, 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 139.0, 131.8, 131.1, 129.2, 128.3, 127.9, 127.0, 124.9, 123.5, 85.5, 84.6, 58.1, 51.6, 42.2, 37.2, 34.6, 30.7, 25.8, 25.5, 19.7, 17.7; HRMS (ESI) calcd. for $C_{26}H_{34}N$ (M^+ + H): 360.26912, found: 360.26794.

***N*-Methyl-3-phenyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)prop-2-yn-1-amine (3*α*a)**



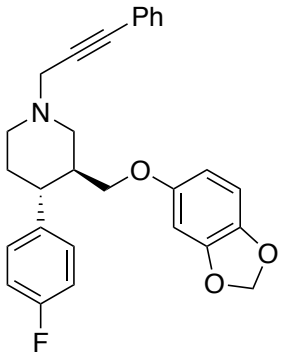
Yellow oil (59 mg, 70% yield); IR (neat, cm^{-1}): 2944, 2842, 1613, 1516, 1322, 1247, 1158, 1108, 1067, 833, 754; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36–7.32 (m, 1H), 7.32–7.25 (m, 6H), 7.24 (q, *J* = 1.7, 1.3 Hz, 1H), 7.23–7.14 (m, 6H), 6.86–6.80 (m, 2H), 5.24 (dd, *J* = 8.1, 5.0 Hz, 1H), 3.47 (s, 2H), 2.67–2.47 (m, 2H), 2.30 (s, 3H), 2.15 (dtd, *J* = 13.8, 7.8, 5.7 Hz, 1H), 1.93 (dddd, *J* = 14.2, 7.8, 6.8, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 160.7, 141.2, 131.7, 128.8, 128.2, 128.1, 127.8, 126.7 (q, J_{C-F} = 3.8 Hz), 125.9, 125.8, 123.2, 122.9, 122.5, 115.8, 85.4, 84.4, 78.4, 51.9, 46.7, 42.0, 36.7; HRMS (ESI) calcd. for $C_{26}H_{25}F_3NO$ (M^+ + H): 424.18882, found: 424.18905.

***N*-(3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (3*β*a)**



Yellow oil (37 mg, 49% yield); IR (neat, cm^{-1}): 3056, 3016, 2914, 2792, 1487, 1447, 1024, 753; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (ddt, *J* = 5.4, 2.9, 1.5 Hz, 2H), 7.34–7.28 (m, 4H), 7.22–7.10 (m, 6H), 7.07–7.01 (m, 1H), 5.91 (t, *J* = 7.3 Hz, 1H), 3.50 (s, 2H), 3.48–3.21 (m, 2H), 2.97 (s, 1H), 2.77 (s, 1H), 2.60 (s, 2H), 2.33 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 143.6, 141.3, 140.1, 139.3, 137.1, 131.7, 130.0, 129.3, 128.6, 128.2, 128.0, 128.0, 127.4, 127.0, 126.0, 125.8, 123.3, 85.3, 84.5, 55.7, 46.2, 42.0, 33.8, 32.1, 27.9; HRMS (ESI) calcd. for $C_{28}H_{28}N$ (M^+ + H): 378.22217, found: 378.22155.

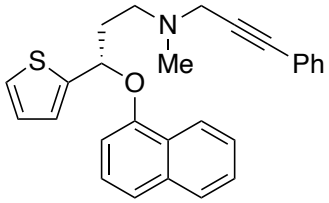
(3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-(3-phenylprop-2-yn-1-yl)piperidine (3*γ*a)



Yellow oil (73 mg, 82% yield); IR (neat, cm^{-1}): 2917, 2802, 1502, 1486, 1181, 1037, 830, 730; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53–7.44 (m, 2H), 7.36–7.29 (m, 3H), 7.23–7.14 (m, 2H), 7.04–6.95 (m, 2H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 2.5 Hz, 1H), 6.14 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.87 (s, 2H), 3.67–3.57 (m, 3H), 3.49 (dd, *J* = 9.4, 6.9 Hz, 1H), 3.33 (ddd, *J* = 10.7, 3.3, 1.7 Hz, 1H), 3.12 (ddd, *J* = 9.1, 3.9, 1.9 Hz, 1H), 2.57–2.21 (m, 4H), 2.01–1.83 (m,

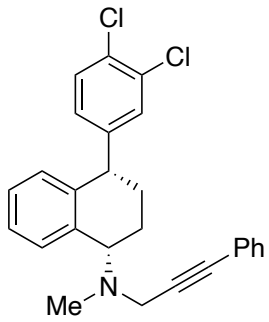
2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.5 (d, J_{C-F} = 244 Hz), 154.4, 148.2, 141.6, 139.6 (d, J_{C-F} = 3.1 Hz), 131.8, 128.8 (d, J_{C-F} = 7.7 Hz), 128.3, 128.1, 123.2, 115.5 (d, J_{C-F} = 21.0 Hz), 107.8, 105.6, 101.1, 98.0, 85.4, 84.7, 77.3, 69.5, 56.6, 53.1, 48.2, 43.8, 42.2, 34.4; HRMS (ESI) calcd. for $C_{28}H_{27}FNO_3$ (M^+ + H): 444.19751, found: 444.19645.

(*S*)-*N*-Methyl-*N*-(3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)-3-phenylprop-2-yn-1-amine (3*δ*a)



Yellow oil (56 mg, 68% yield); IR (neat, cm^{-1}): 2958, 2795, 1577, 1396, 1261, 1093, 1016, 788; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.28 (dq, *J* = 7.7, 0.8 Hz, 1H), 7.71–7.63 (m, 1H), 7.35 (dddd, *J* = 14.8, 8.3, 6.8, 1.5 Hz, 3H), 7.31–7.26 (m, 3H), 7.21–7.15 (m, 4H), 7.15–7.08 (m, 2H), 6.98 (dt, *J* = 3.6, 0.9 Hz, 1H), 6.84–6.76 (m, 2H), 5.71 (dd, *J* = 7.6, 5.5 Hz, 1H), 3.48 (s, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.40 (tt, *J* = 14.1, 6.8 Hz, 1H), 2.31 (s, 3H), 2.14 (dtd, *J* = 14.1, 7.1, 5.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 145.3, 134.6, 131.8, 128.2, 128.0, 127.5, 126.6, 126.3, 126.2, 125.8, 125.2, 124.7, 124.7, 123.2, 122.2, 120.6, 107.1, 85.5, 84.4, 74.6, 52.0, 46.7, 42.1, 37.0; HRMS (ESI) calcd. for $C_{27}H_{26}NOS$ (M^+ + H): 412.17351, found: 412.17164.

(1*S*,4*S*)-4-(3,4-Dichlorophenyl)-*N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-amine (3*za*)



Yellow oil (62 g, 74% yield); IR (neat, cm^{-1}): 2933, 2862, 1596, 1466, 1316, 1029, 755; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.39–7.33 (m, 2H), 7.23 (dp, *J* = 4.2, 1.4 Hz, 3H), 7.21–7.06 (m, 3H), 6.83 (dd, *J* = 8.2, 1.9 Hz, 2H), 4.05 (t, *J* = 5.8 Hz, 1H), 3.95 (dd, *J* = 8.2, 4.8 Hz, 1H), 3.57 (s, 2H), 2.36 (s, 3H), 2.12–1.96 (m, 2H), 1.85 (dtd, *J* = 17.2, 8.5, 3.5 Hz, 1H), 1.74 (tdd, *J* = 9.6, 4.7, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.9, 138.7, 138.5, 132.2, 131.7, 131.7, 130.8, 130.3, 130.1, 129.9, 129.3, 128.3, 128.2, 128.0, 127.2, 126.6, 123.4, 86.6, 84.9, 60.7, 44.1, 43.8, 37.9, 29.4, 19.1; HRMS (ESI) calcd. for $C_{26}H_{24}Cl_2N$ (M^+ + H): 420.12858, found: 420.12846.

4. ^{1}H and ^{13}C NMR Spectra

Figure S1. ^{1}H and ^{13}C NMR Spectra of 1-((Trimethylsilyl)methyl)piperidine (**1a**)

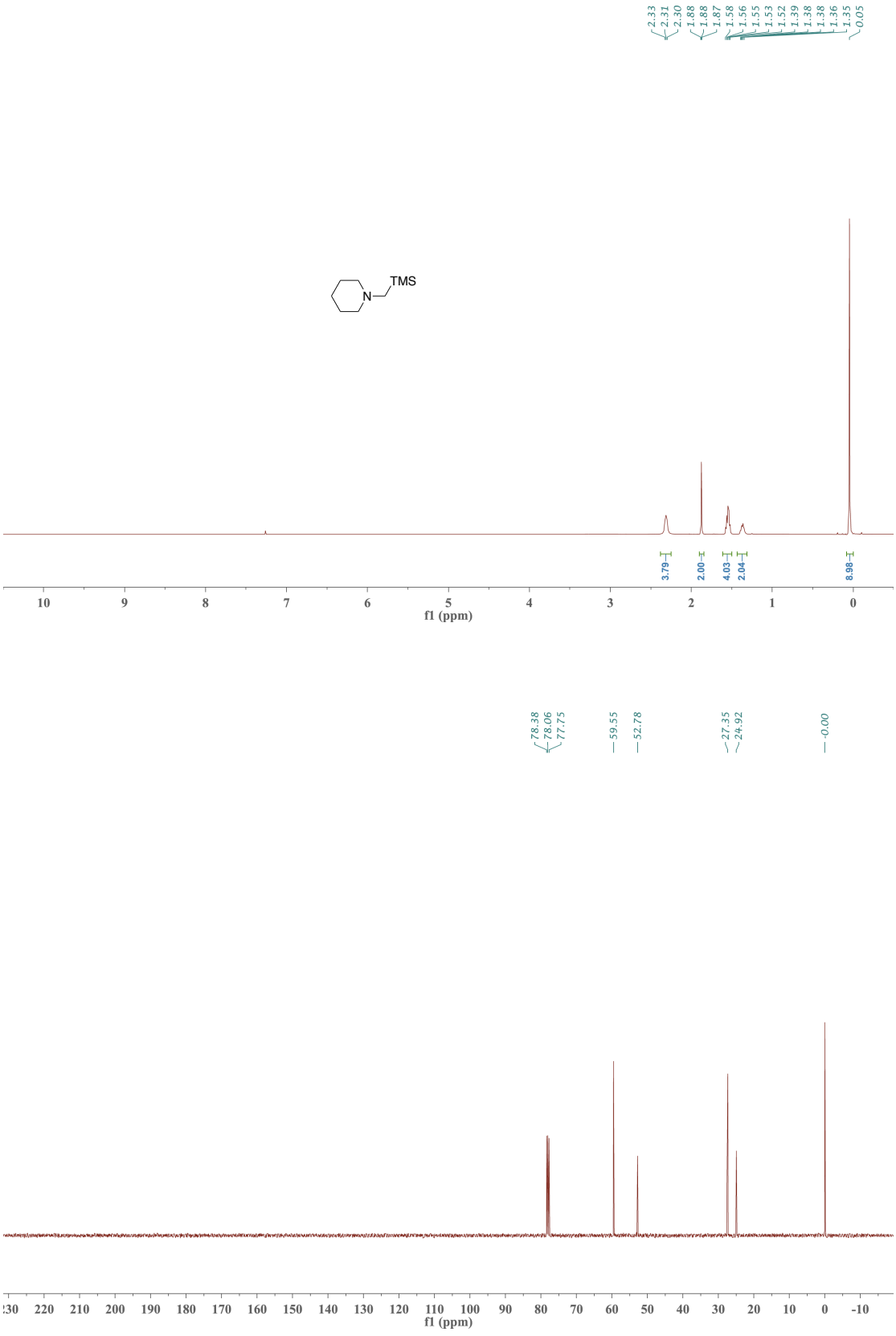


Figure S2. ^{1}H and ^{13}C NMR Spectra of 1-((Trimethylsilyl)methyl)pyrrolidine (**1b**)

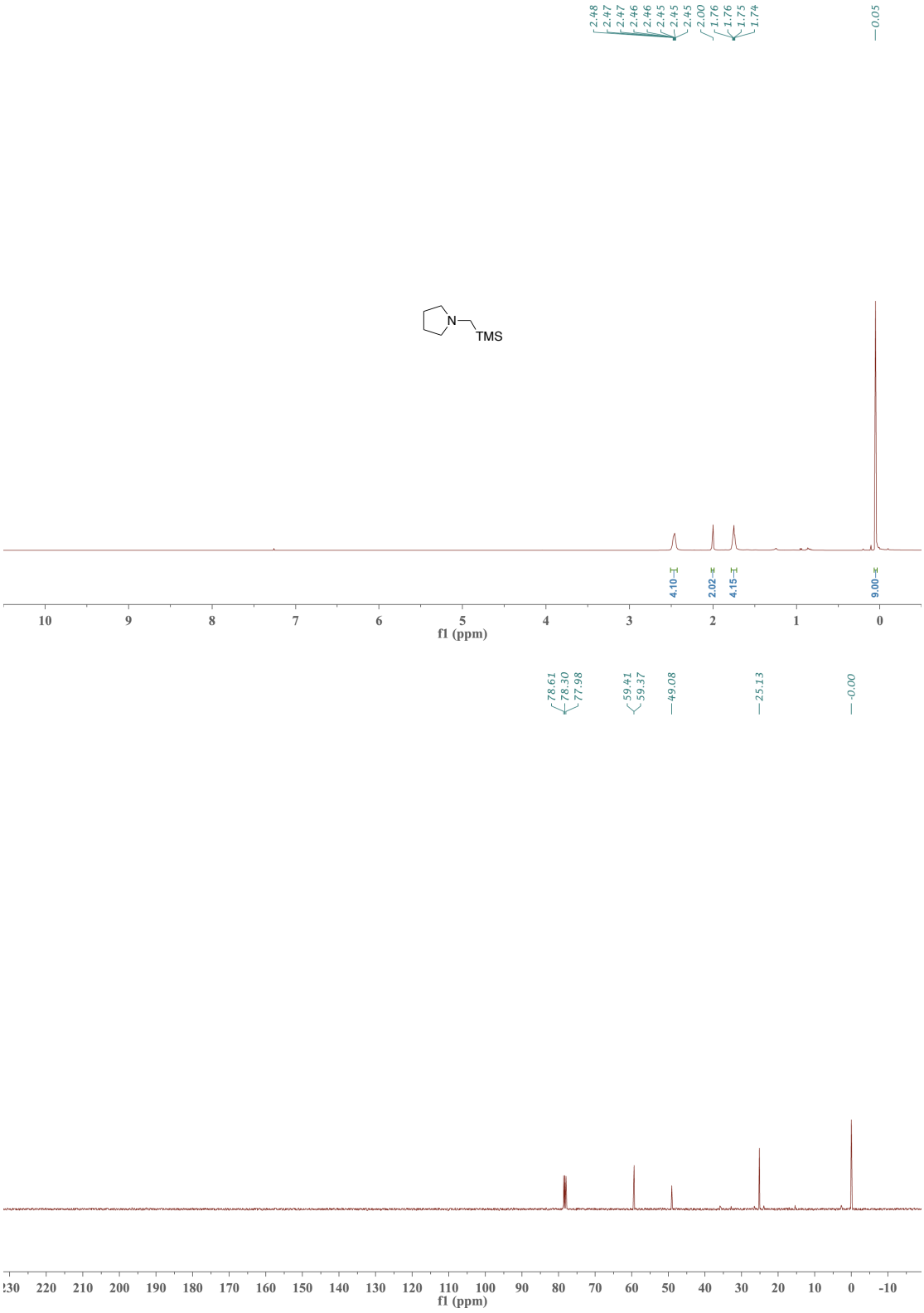


Figure S3. ^{1}H and ^{13}C NMR Spectra of 1-((Trimethylsilyl)methyl)azepane (**1c**)

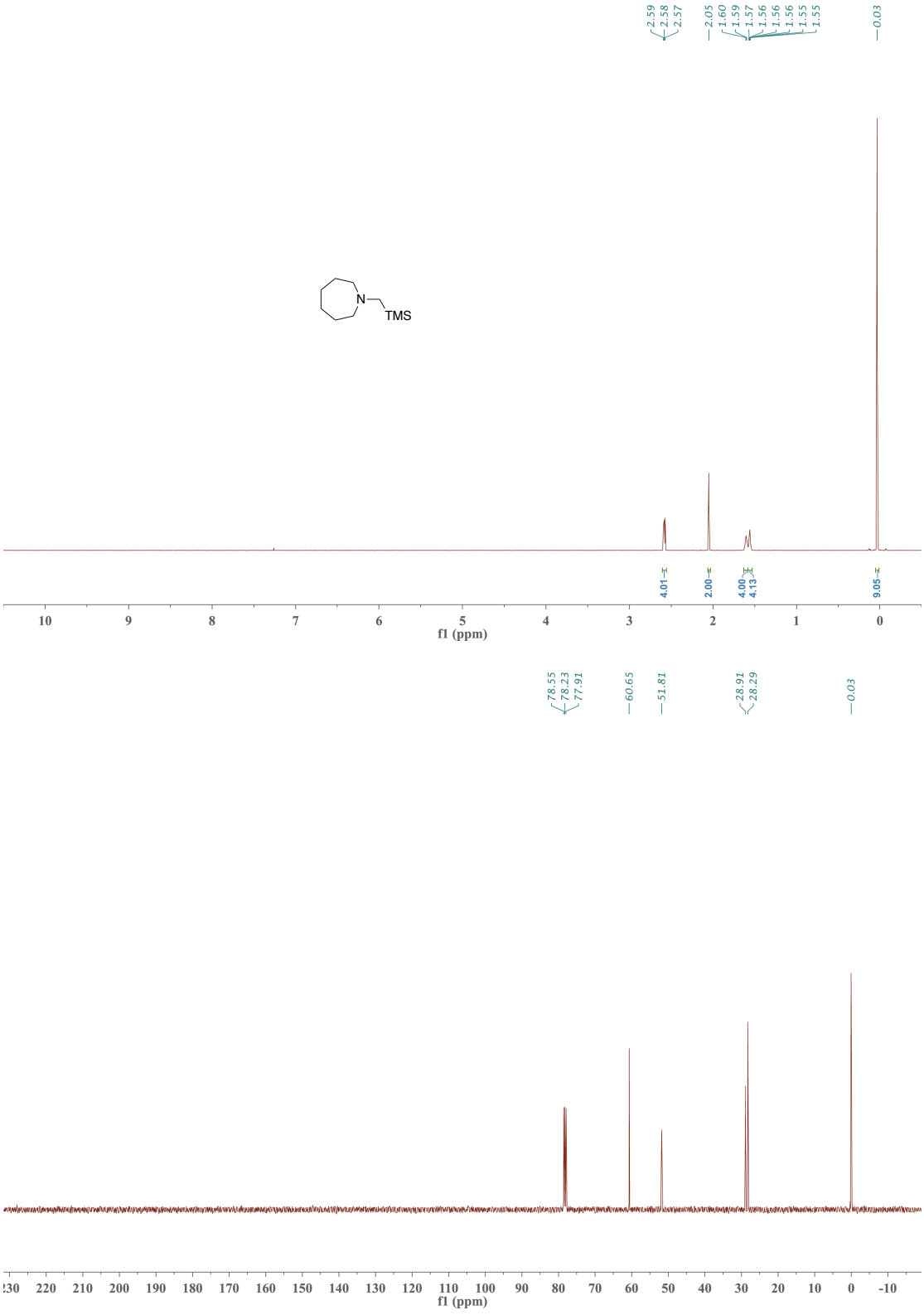


Figure S4. ^{1}H and ^{13}C NMR Spectra of 4-((Trimethylsilyl)methyl)morpholine (**1d**)

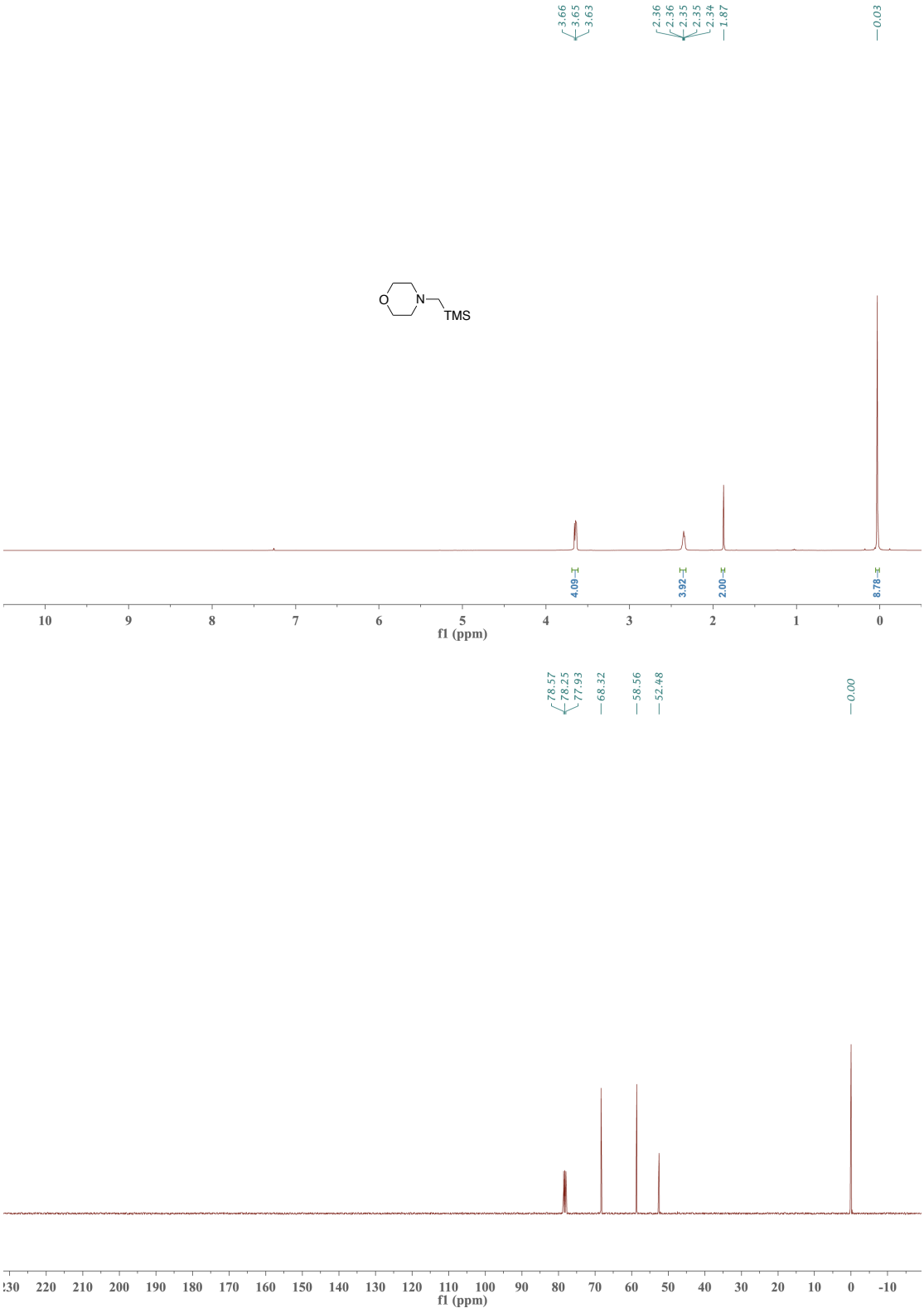


Figure S5. ^{1}H and ^{13}C NMR Spectra of *tert*-Butyl 4-((trimethylsilyl)methyl)piperazine-1-carboxylate (**1e**)

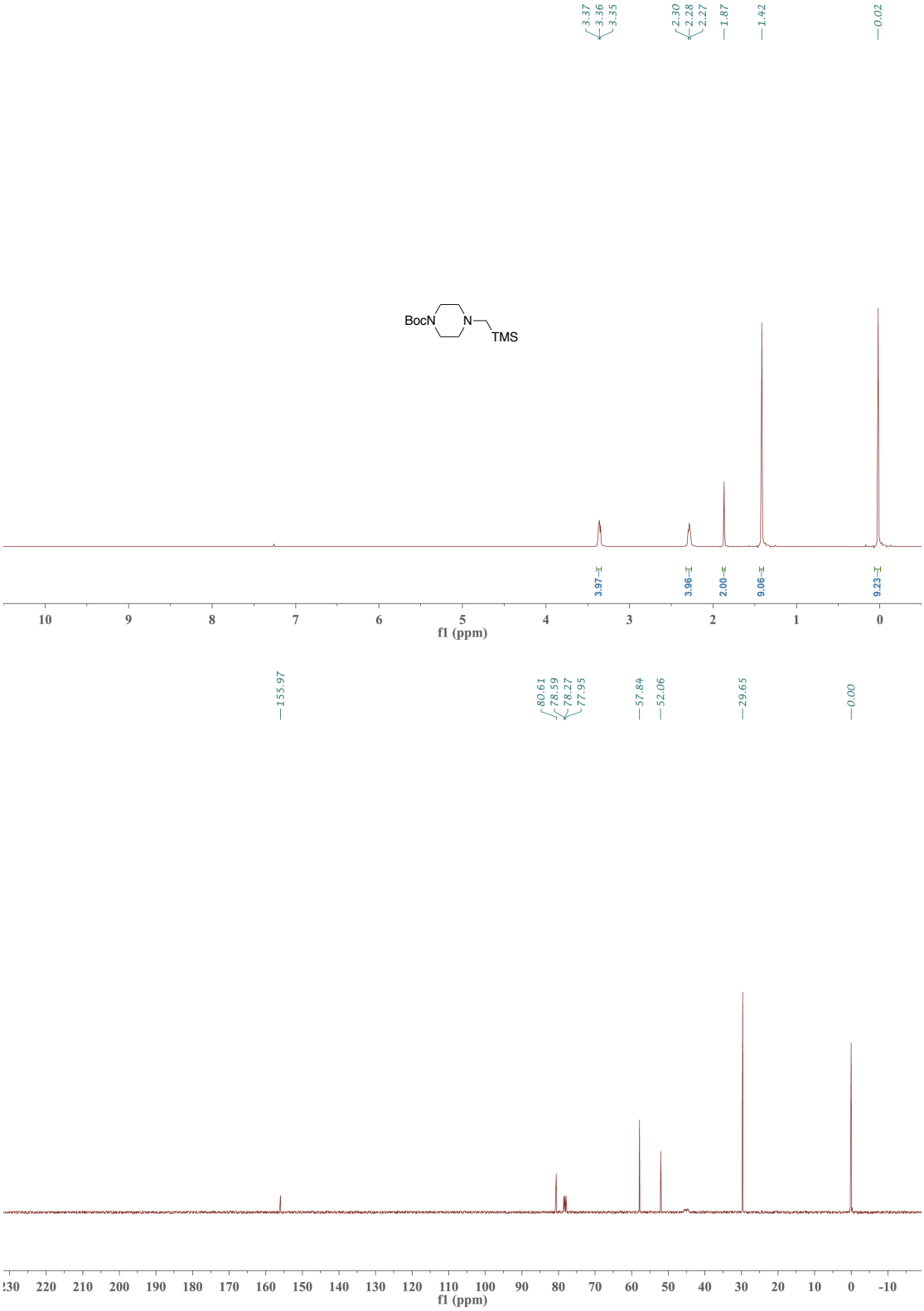


Figure S6. ^{1}H and ^{13}C NMR Spectra of *N*-Ethyl-*N*-((trimethylsilyl)methyl)ethanamine (**1f**)

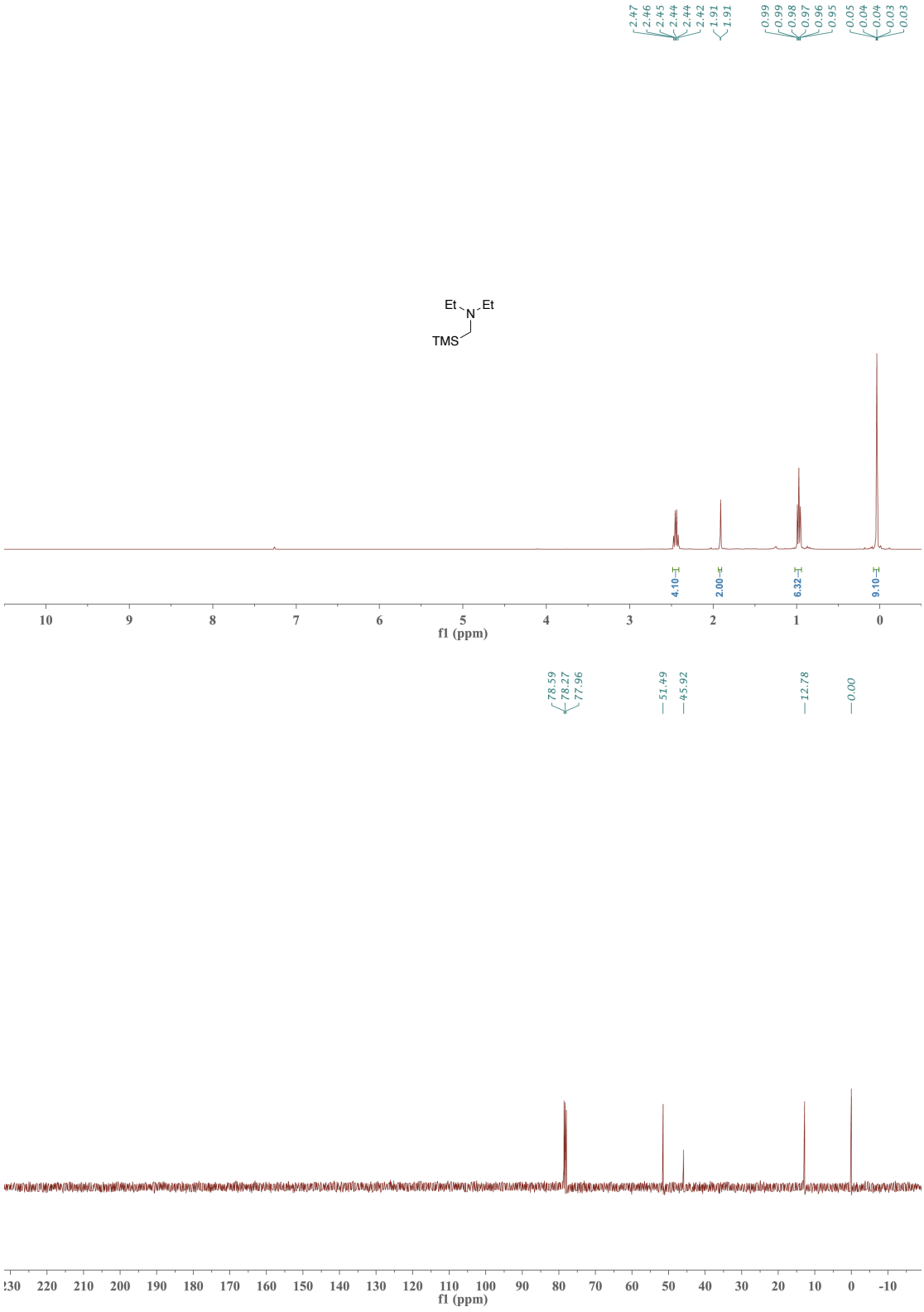


Figure S7. ^{1}H and ^{13}C NMR Spectra of *N*-Butyl-*N*-((trimethylsilyl)methyl)butan-1-amine (**1g**)

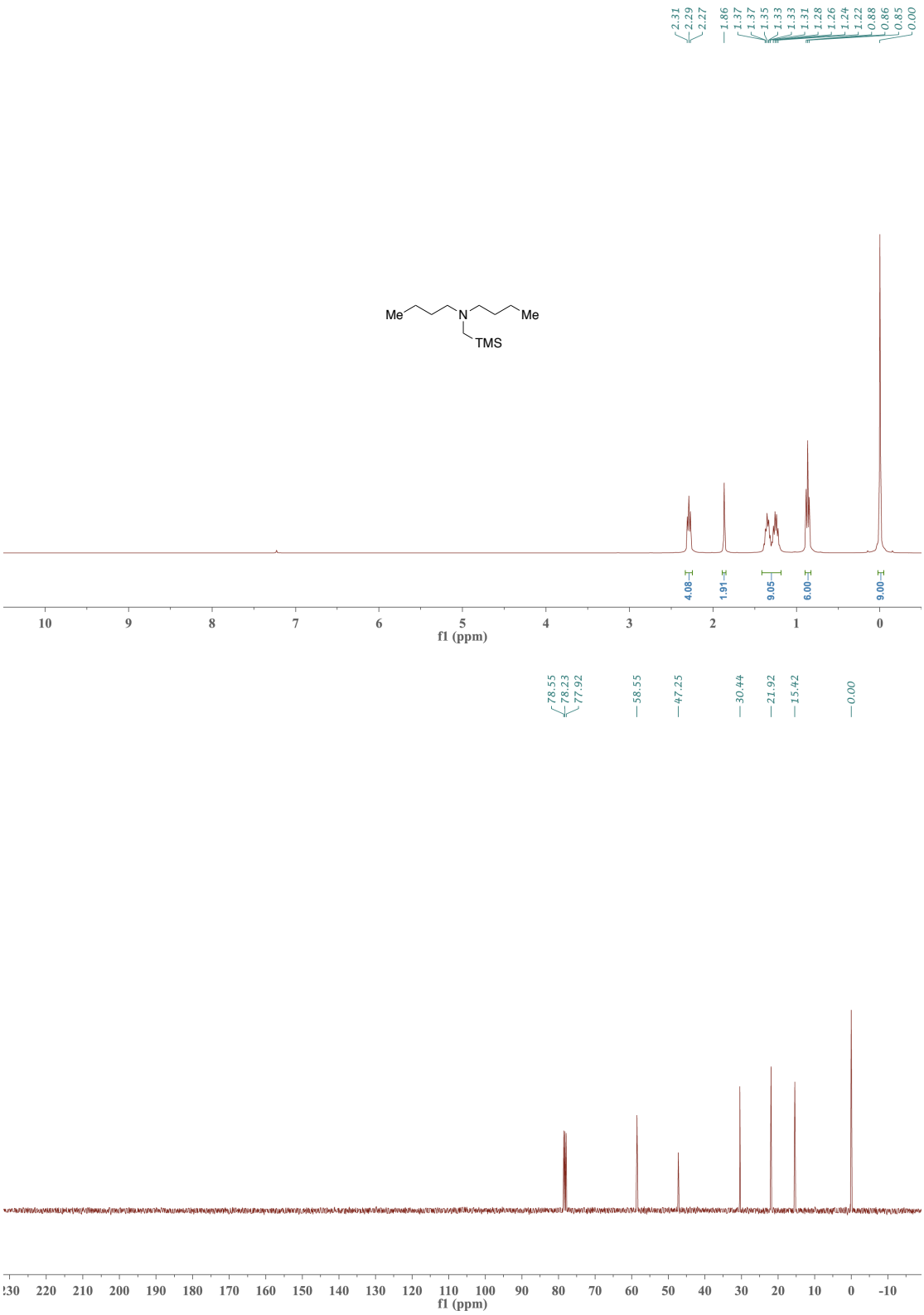


Figure S8. ^{1}H and ^{13}C NMR Spectra of *N*-Octyl-*N*-((trimethylsilyl)methyl)octan-1-amine (**1h**)

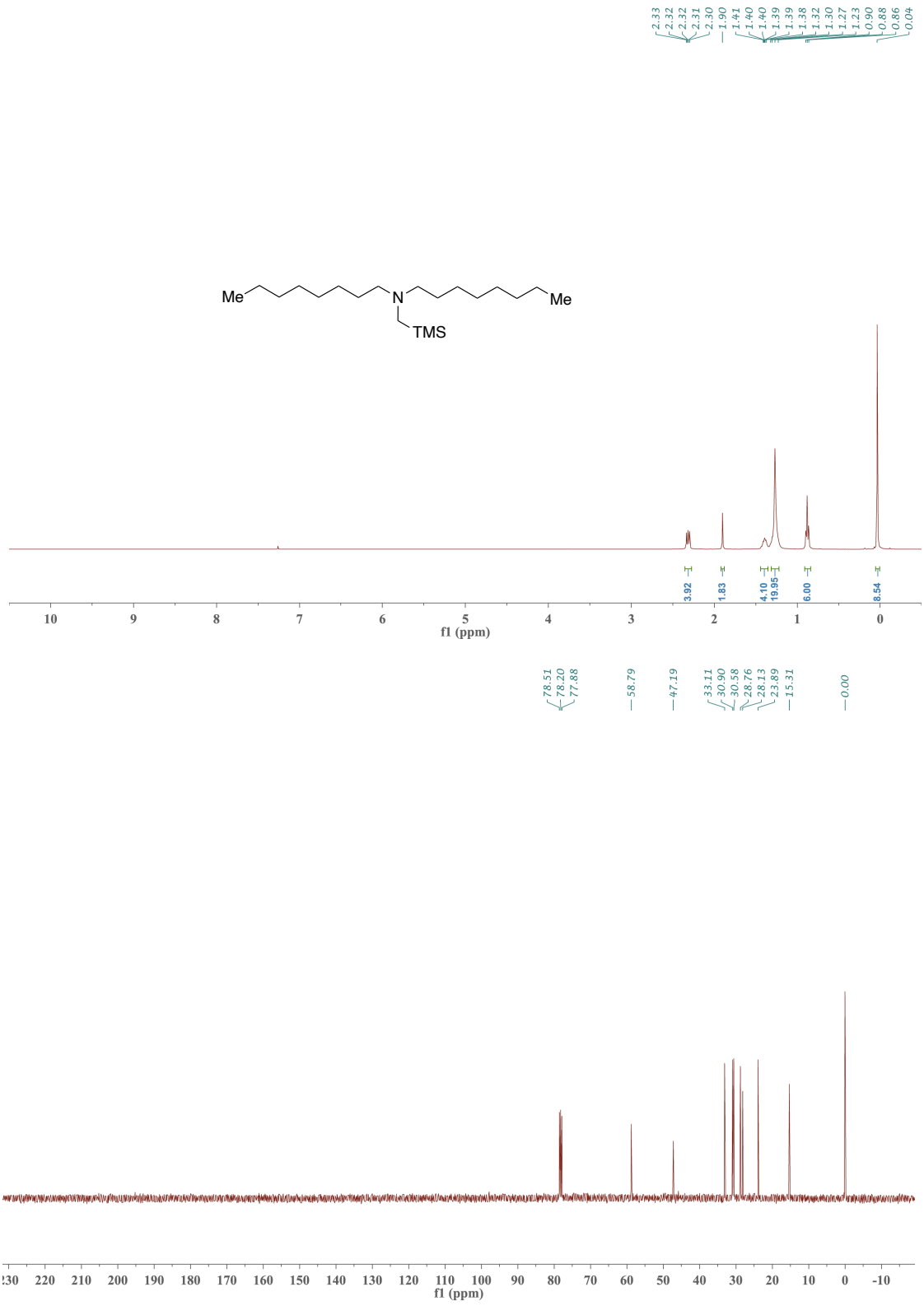
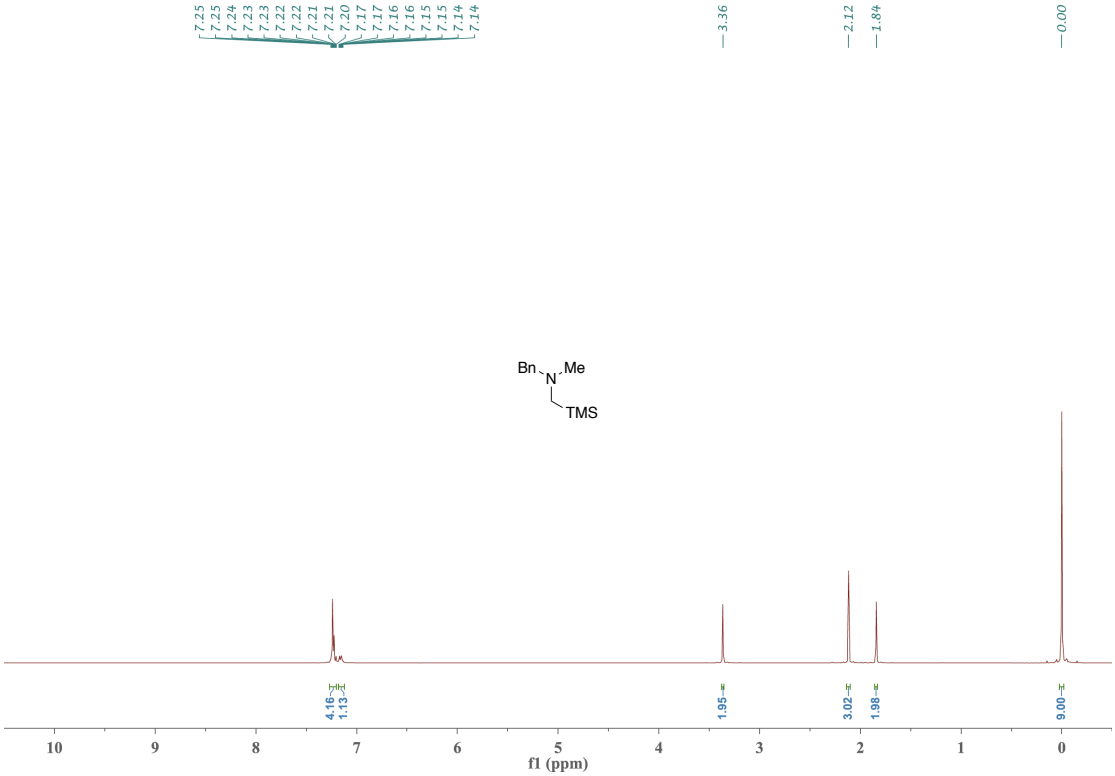


Figure S9. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-methyl-1-(trimethylsilyl)methanamine (**1i**)



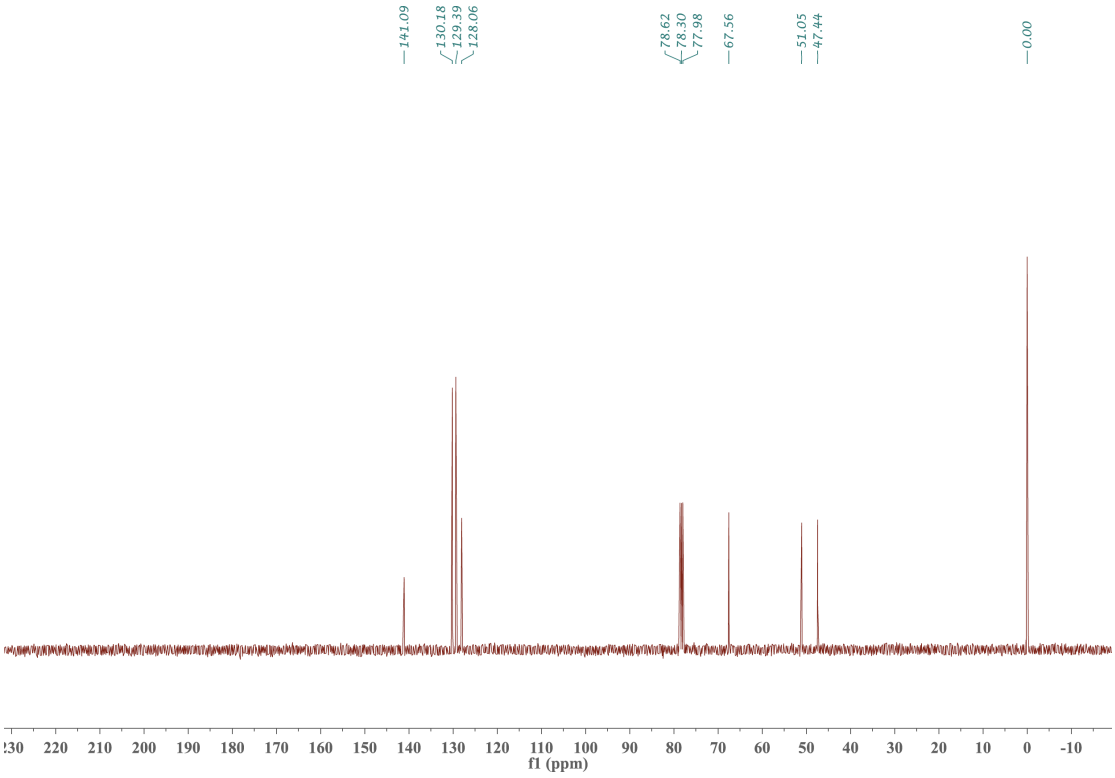


Figure S10. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-((trimethylsilyl)methyl)cyclopentanamine (**1j**)

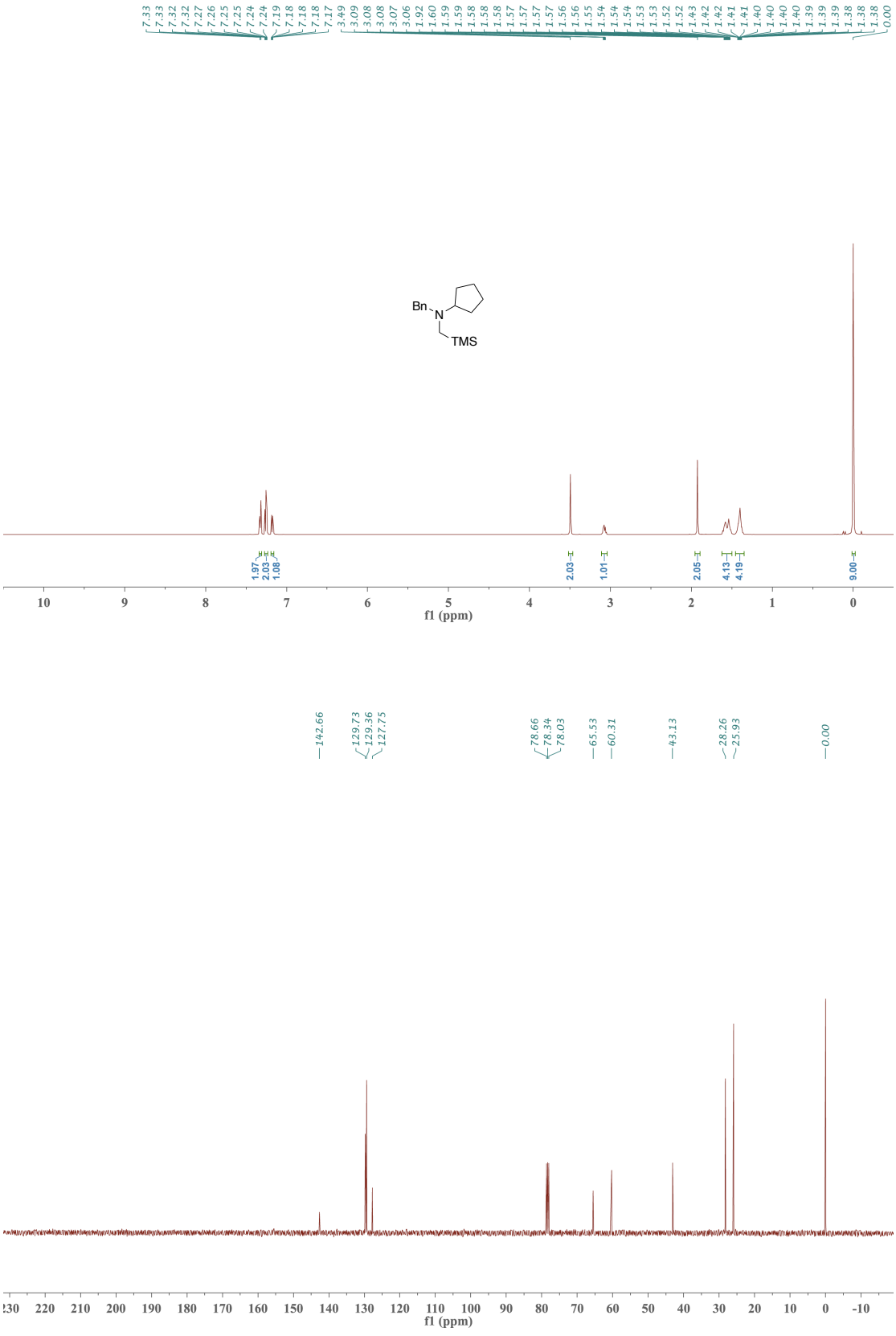


Figure S11. ^{1}H and ^{13}C NMR Spectra of *N*-ethyl-*N*-((Trimethylsilyl)methyl)cyclohexanamine (**1k**)

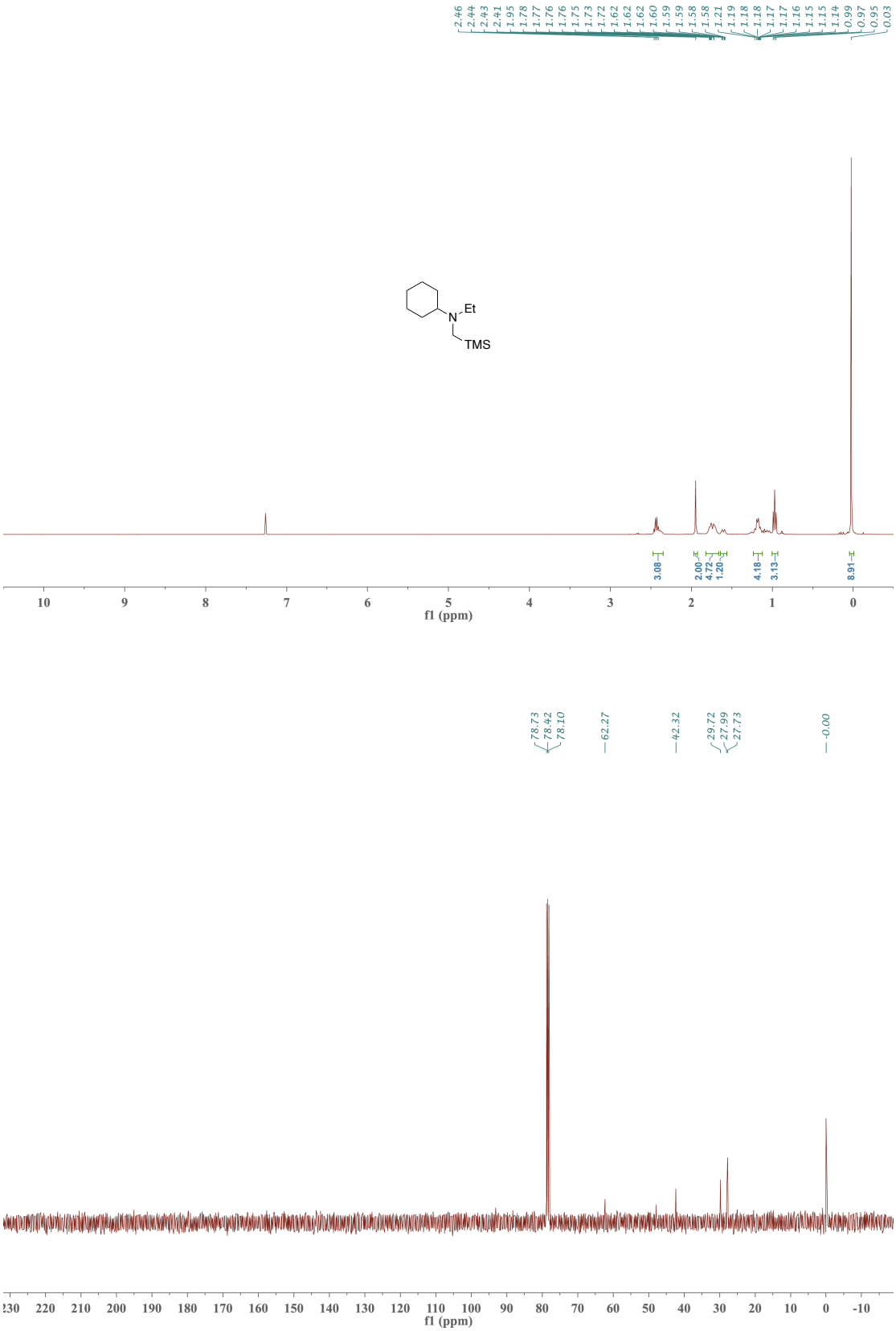


Figure S12. ^{1}H and ^{13}C NMR Spectra of Methyl 4-(benzyl((trimethylsilyl)methyl)amino)-butanoate (**1l**)

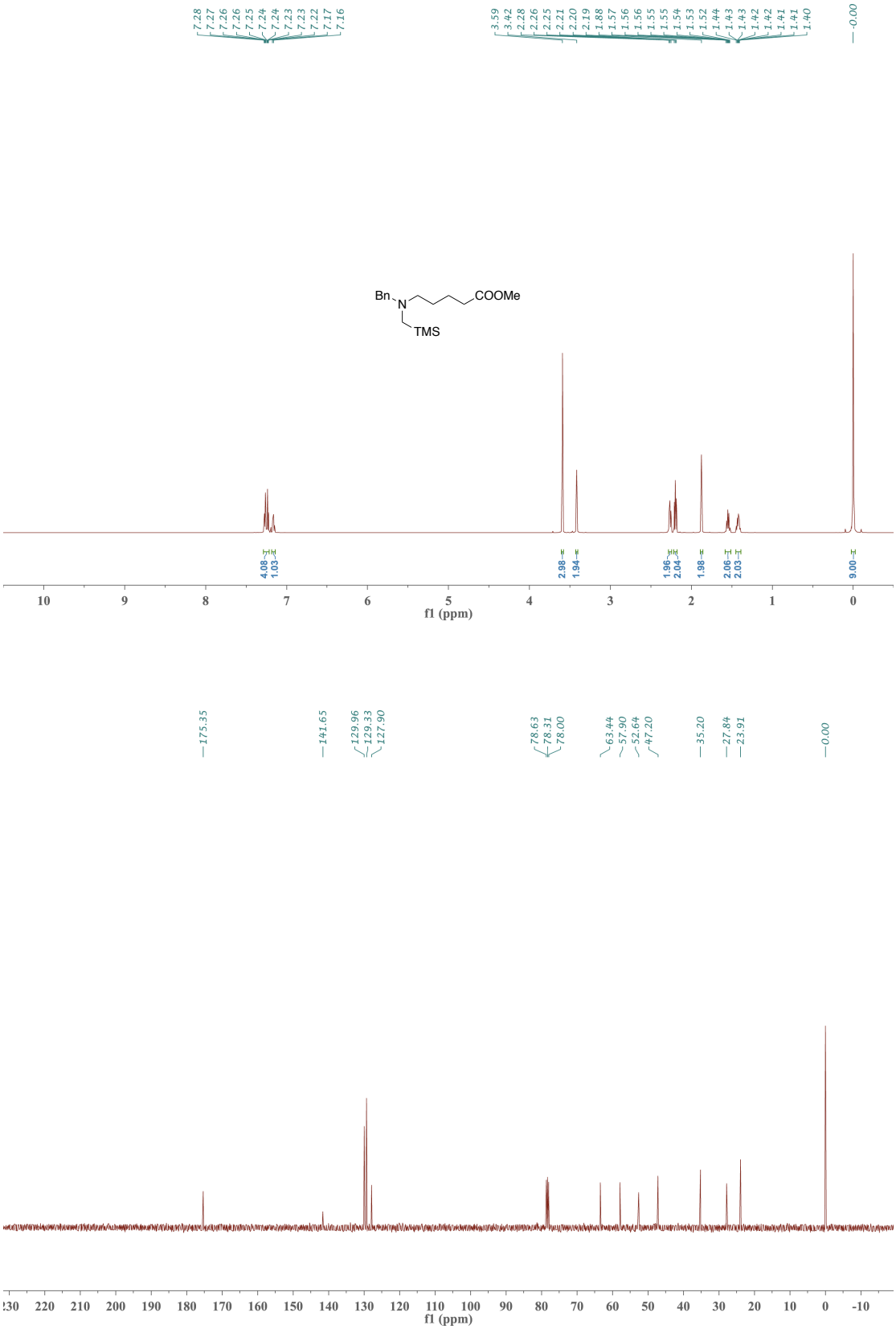


Figure S13. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-2-fluoro-*N*-((trimethylsilyl)methyl)ethan-1-amine (**1m**)

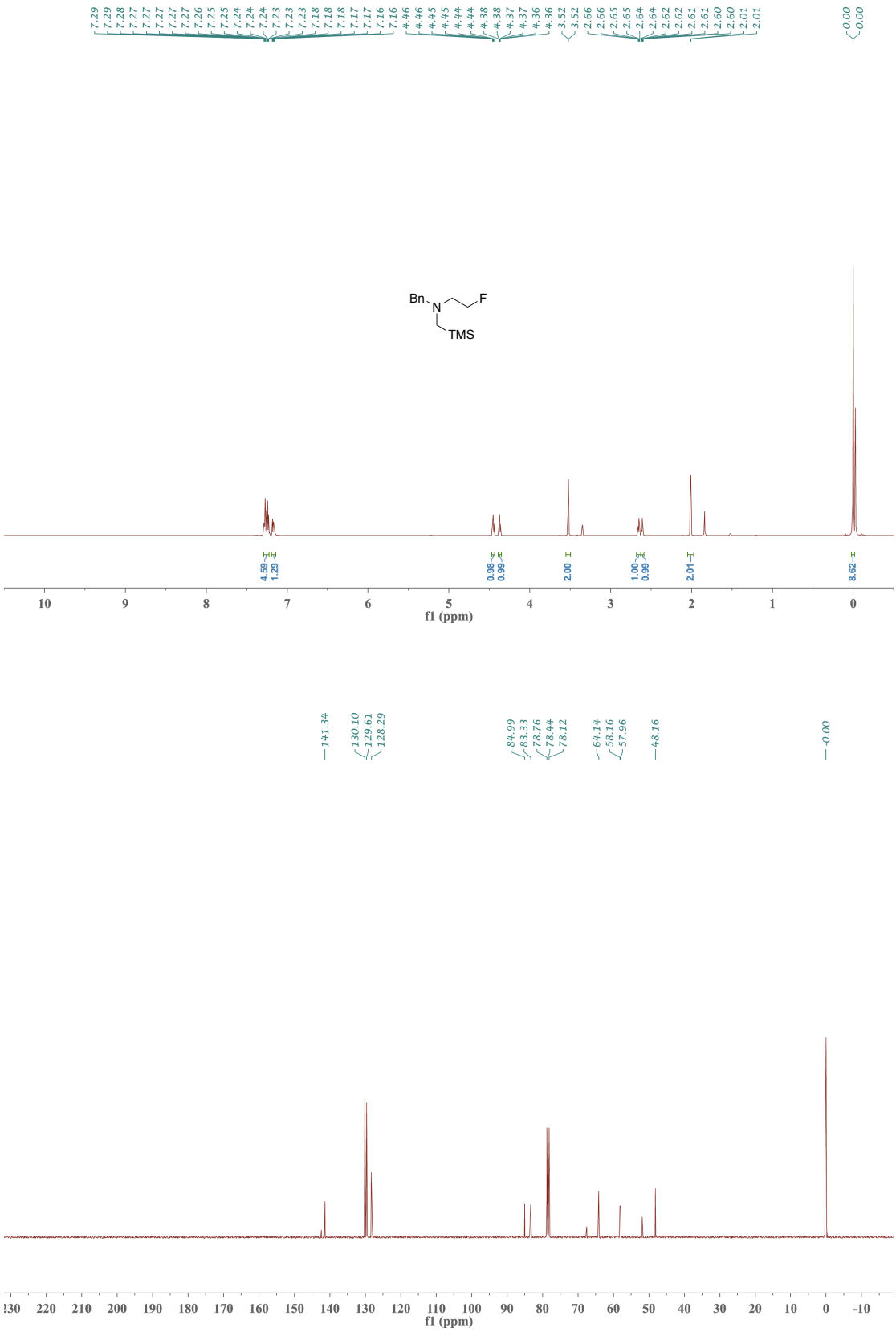


Figure S14. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-3-phenyl-*N*-((trimethylsilyl)methyl)-propan-1-amine (**1n**)

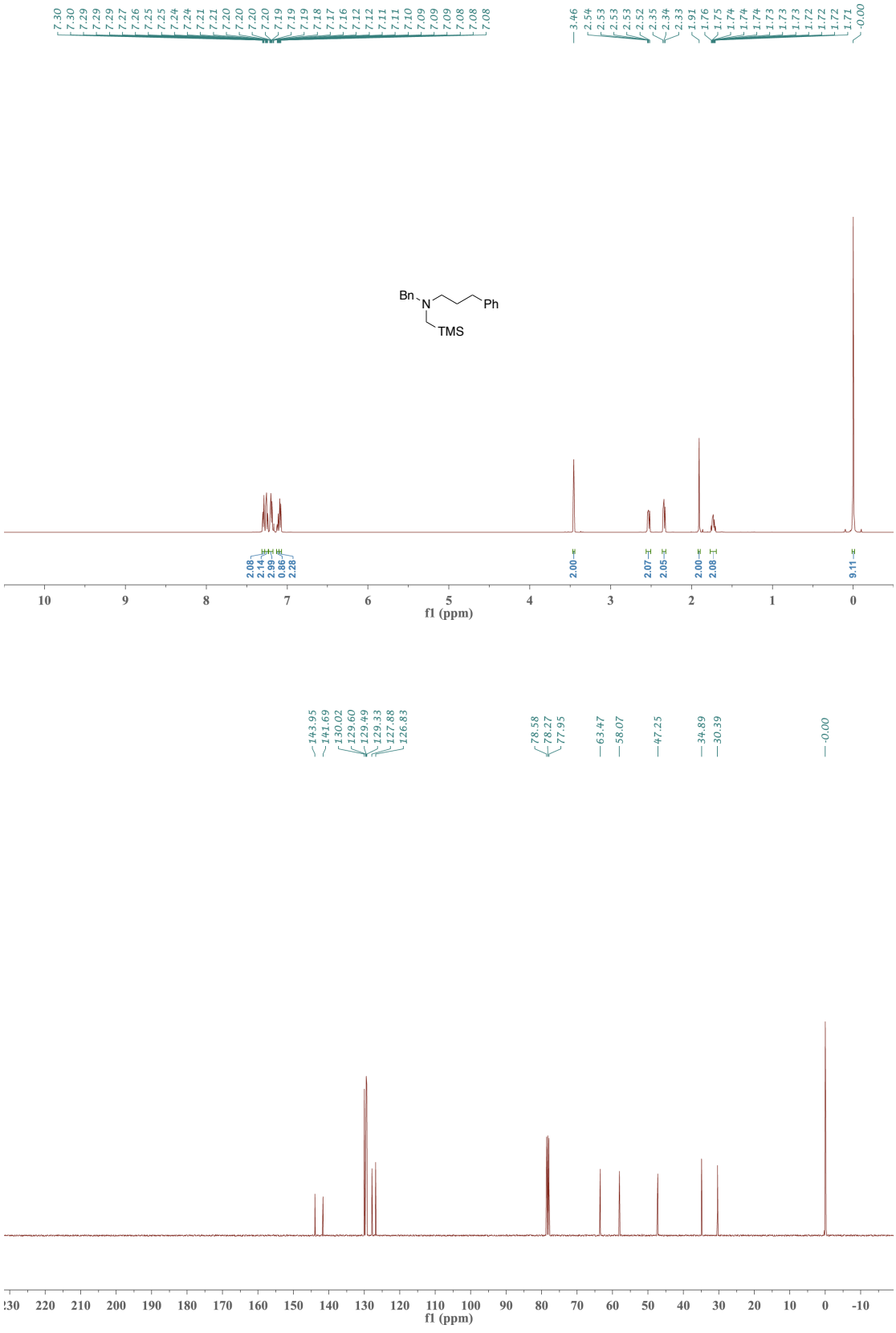


Figure S15. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-1-cyclobutyl-*N*-((trimethylsilyl)methyl)-methanamine (**1o**)

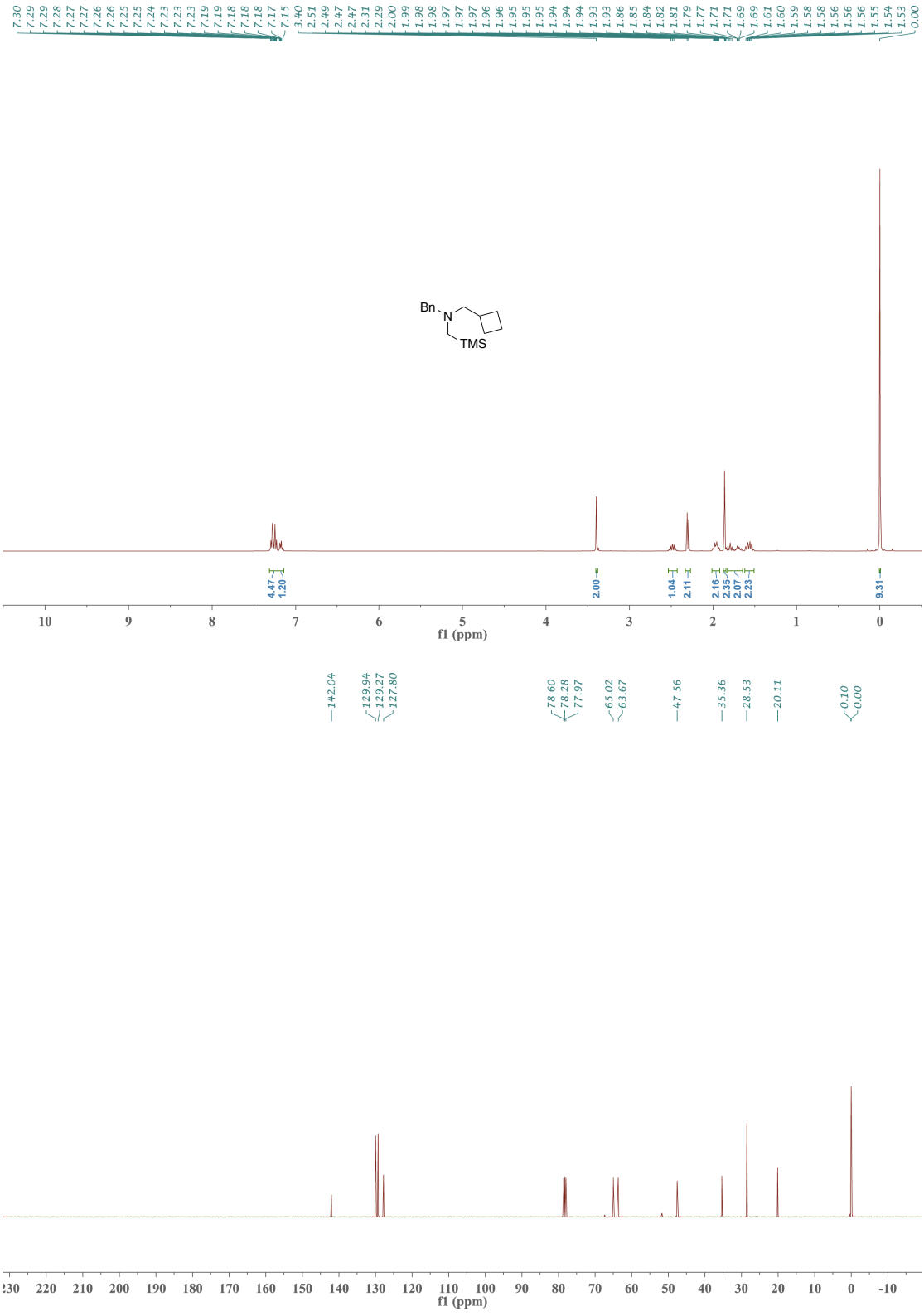


Figure S16. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-2-(1,3-dioxan-2-yl)-*N*-((trimethylsilyl)-methyl)ethan-1-amine (**1p**)

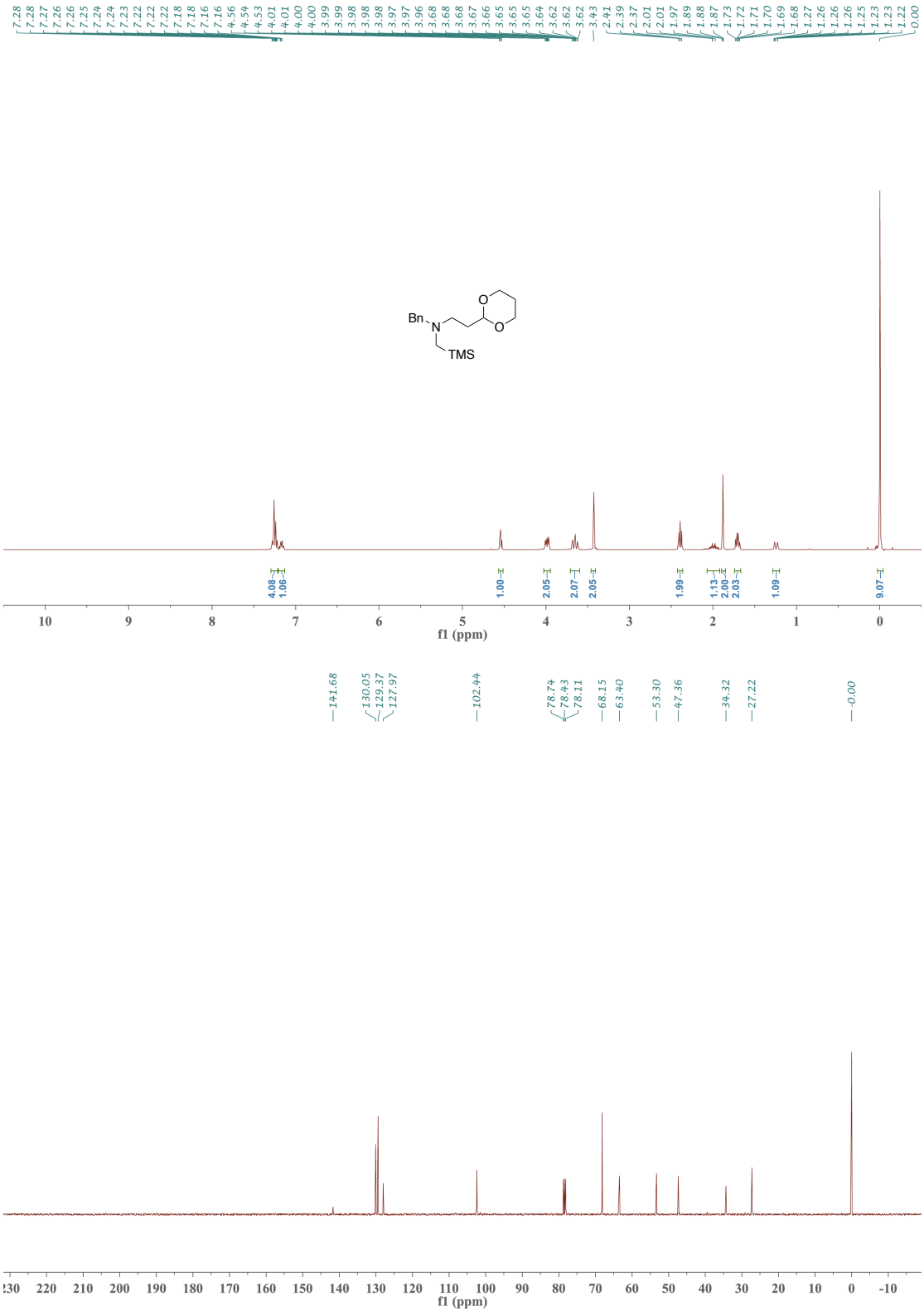
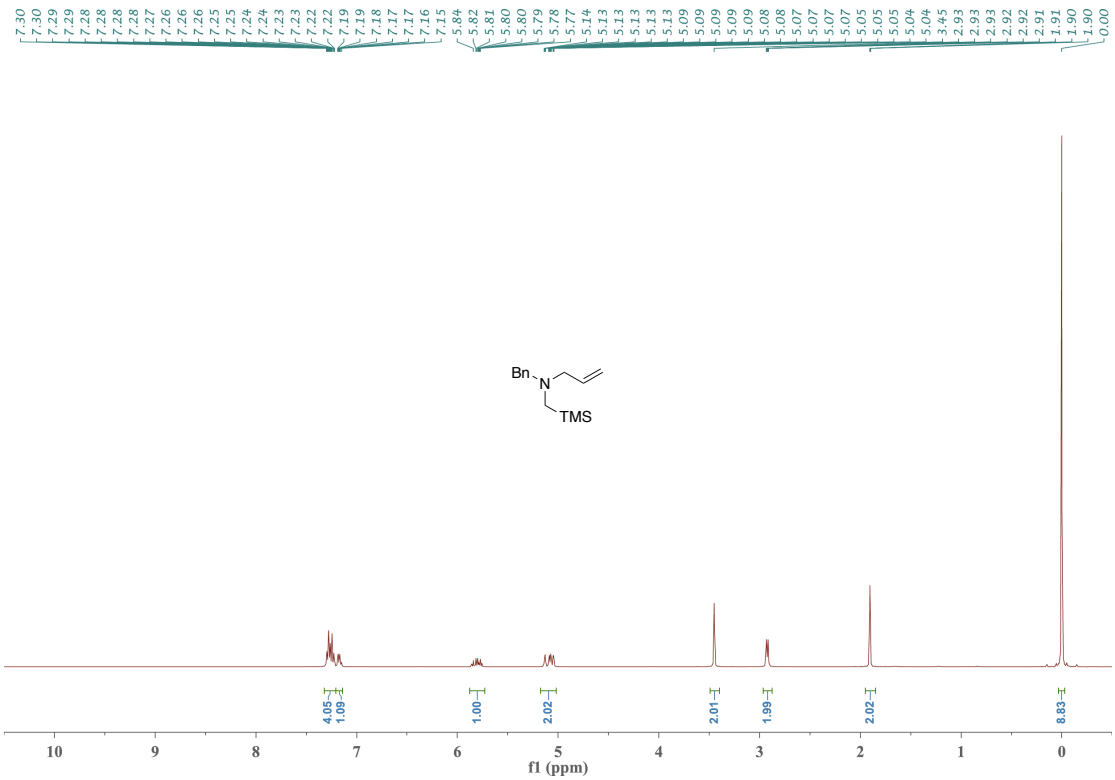


Figure S17. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-((trimethylsilyl)methyl)prop-2-en-1-amine (**1q**)



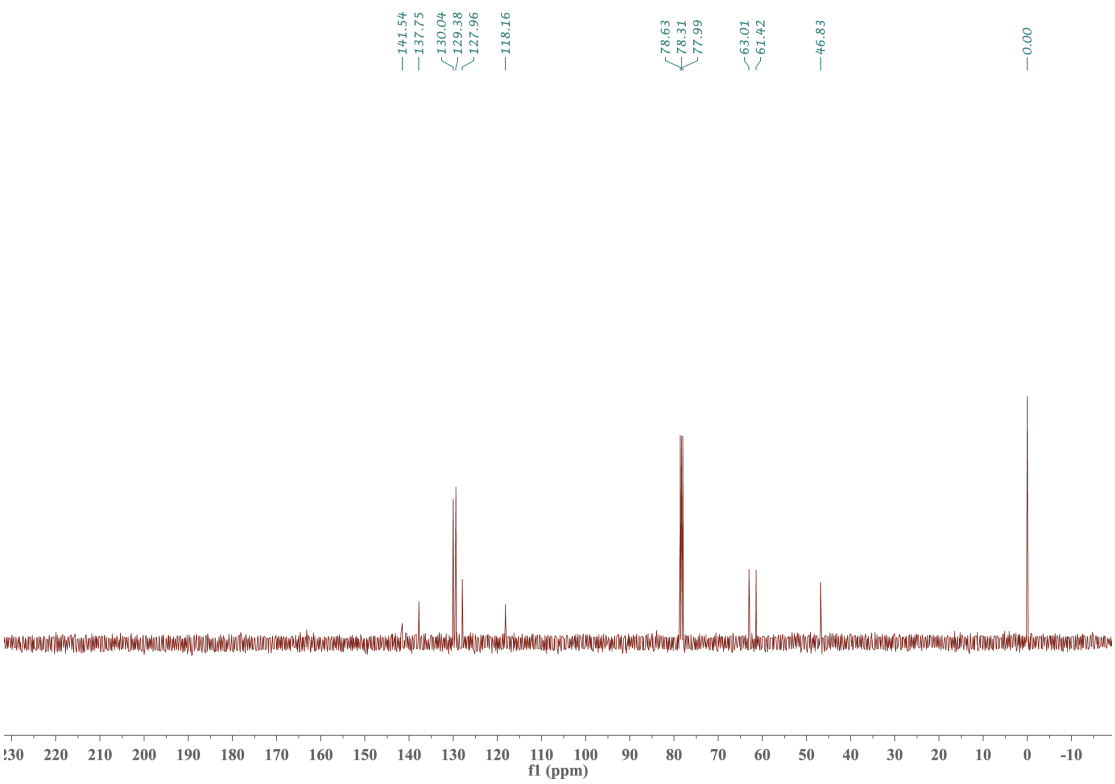


Figure S18. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-((trimethylsilyl)methyl)cyclohex-2-en-1-amine (**1r**)

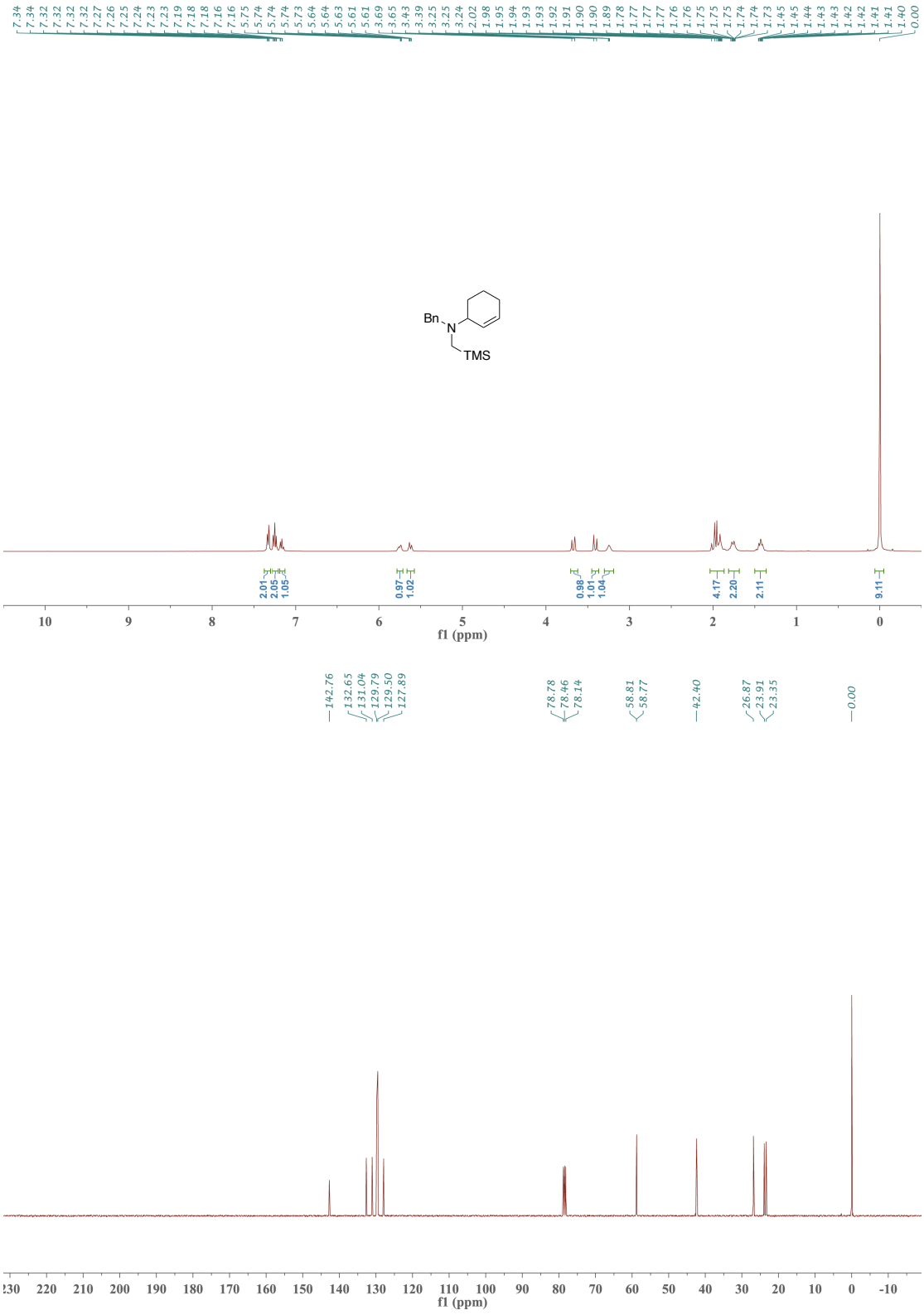


Figure S19. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-((trimethylsilyl)methyl)prop-2-yn-1-amine (**1s**)

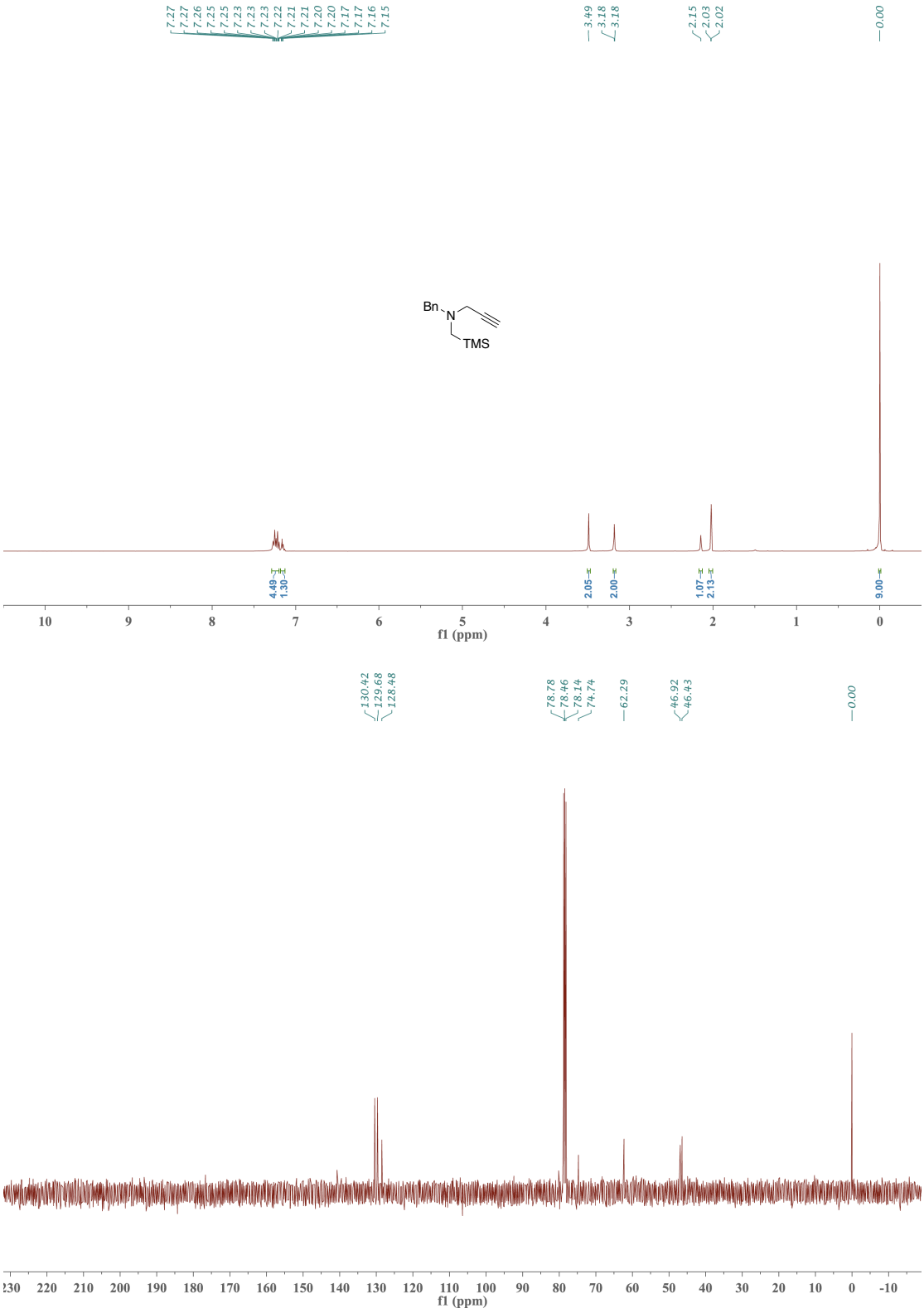


Figure S20. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-((trimethylsilyl)methyl)but-3-yn-1-amine (**1t**)

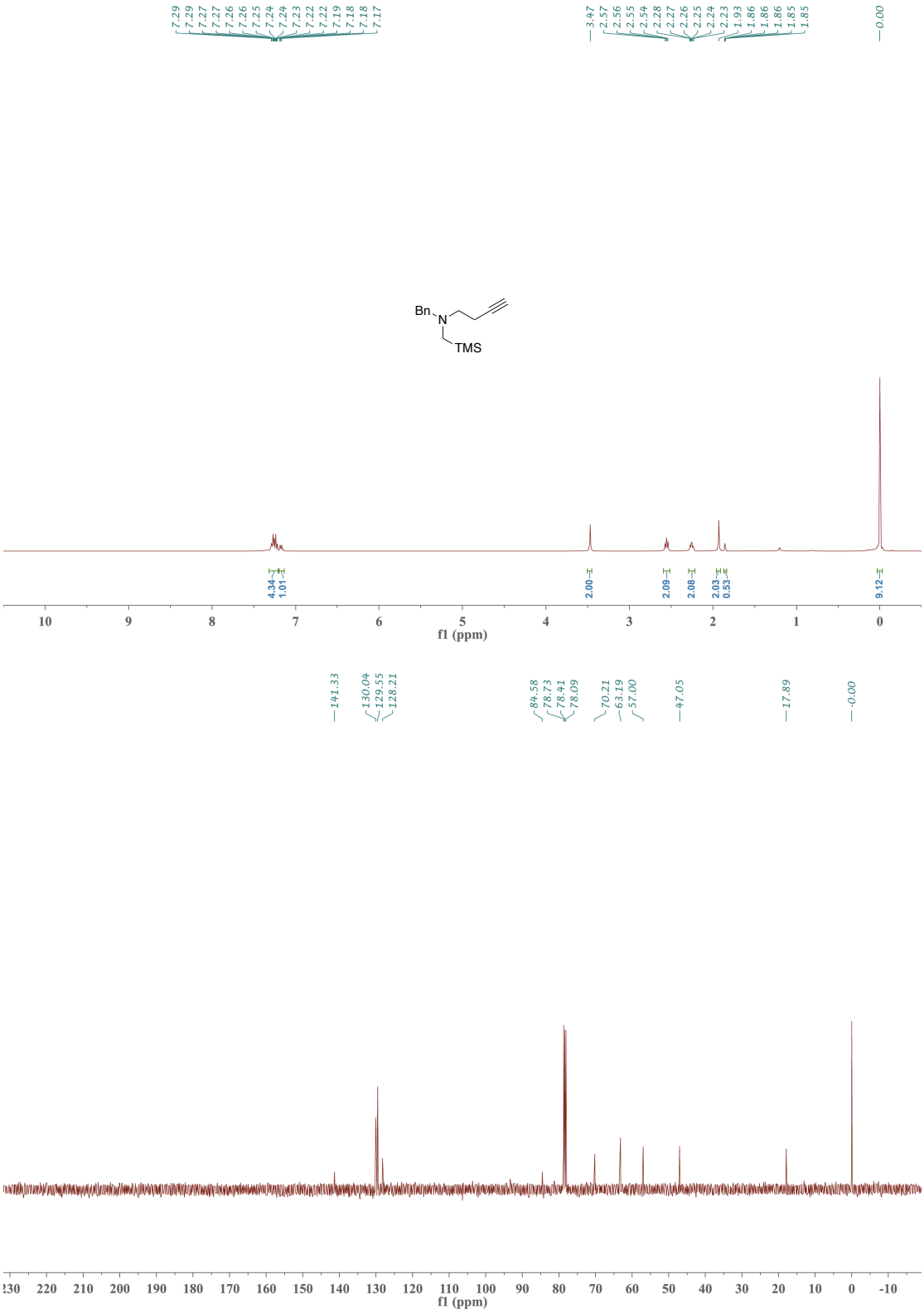


Figure S21. ^{1}H and ^{13}C NMR Spectra of 1-(4-Methoxyphenyl)-4-((trimethylsilyl)methyl)-piperazine (**1u**)

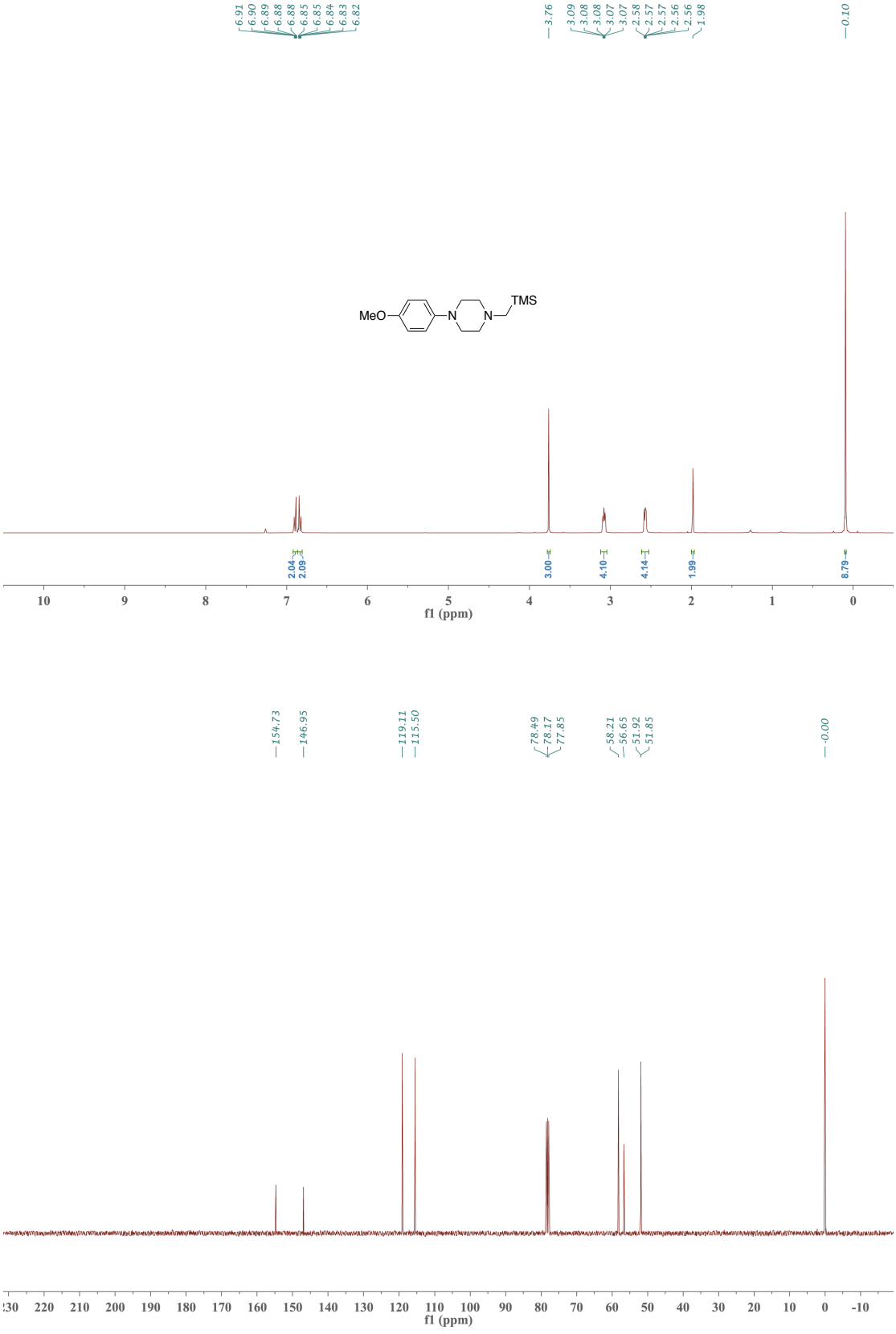


Figure S22. ^{1}H and ^{13}C NMR Spectra of 1-(4-Chlorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1v**)

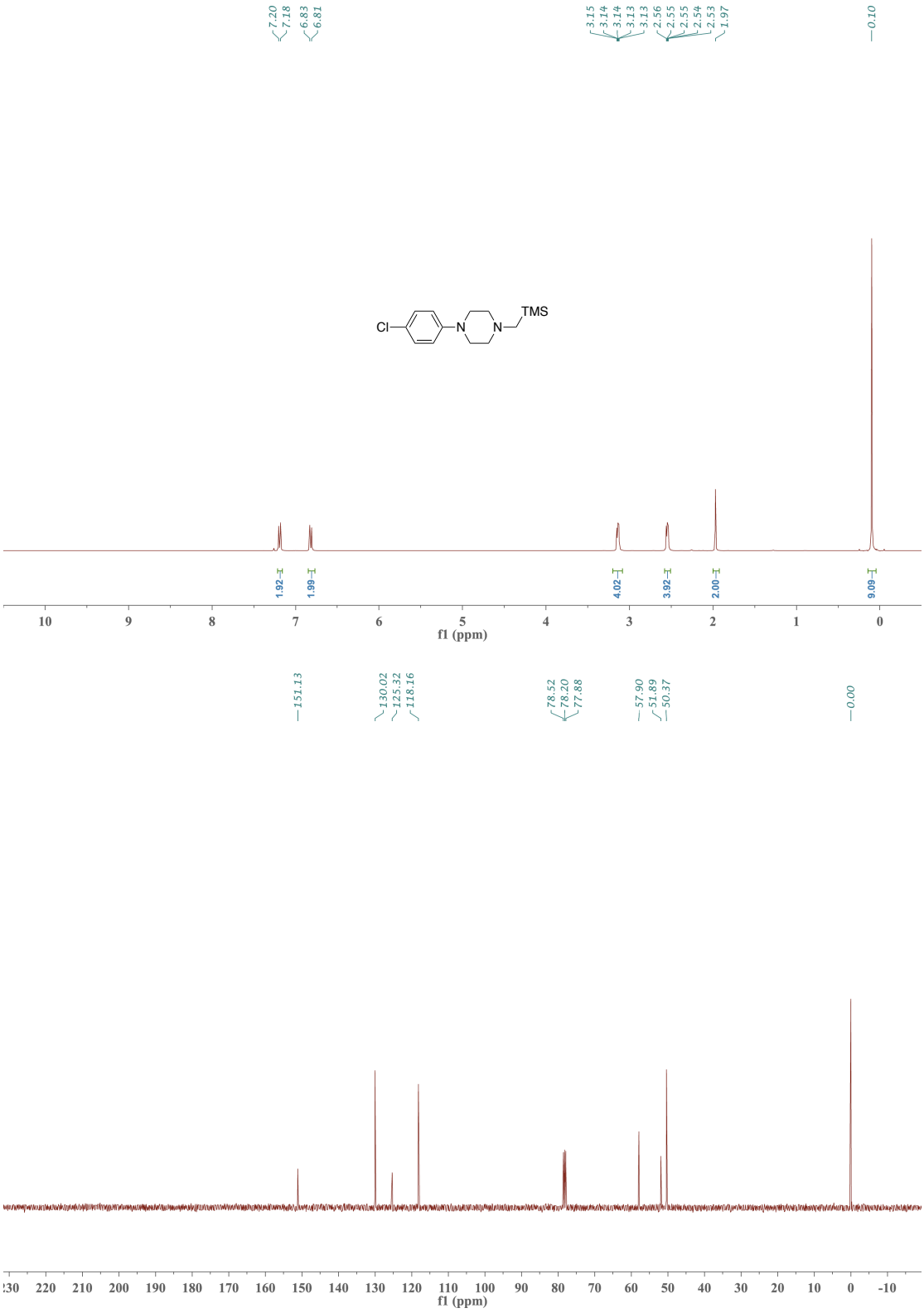


Figure S23. ^{1}H and ^{13}C NMR Spectra of 1-(4-Fluorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1w**)

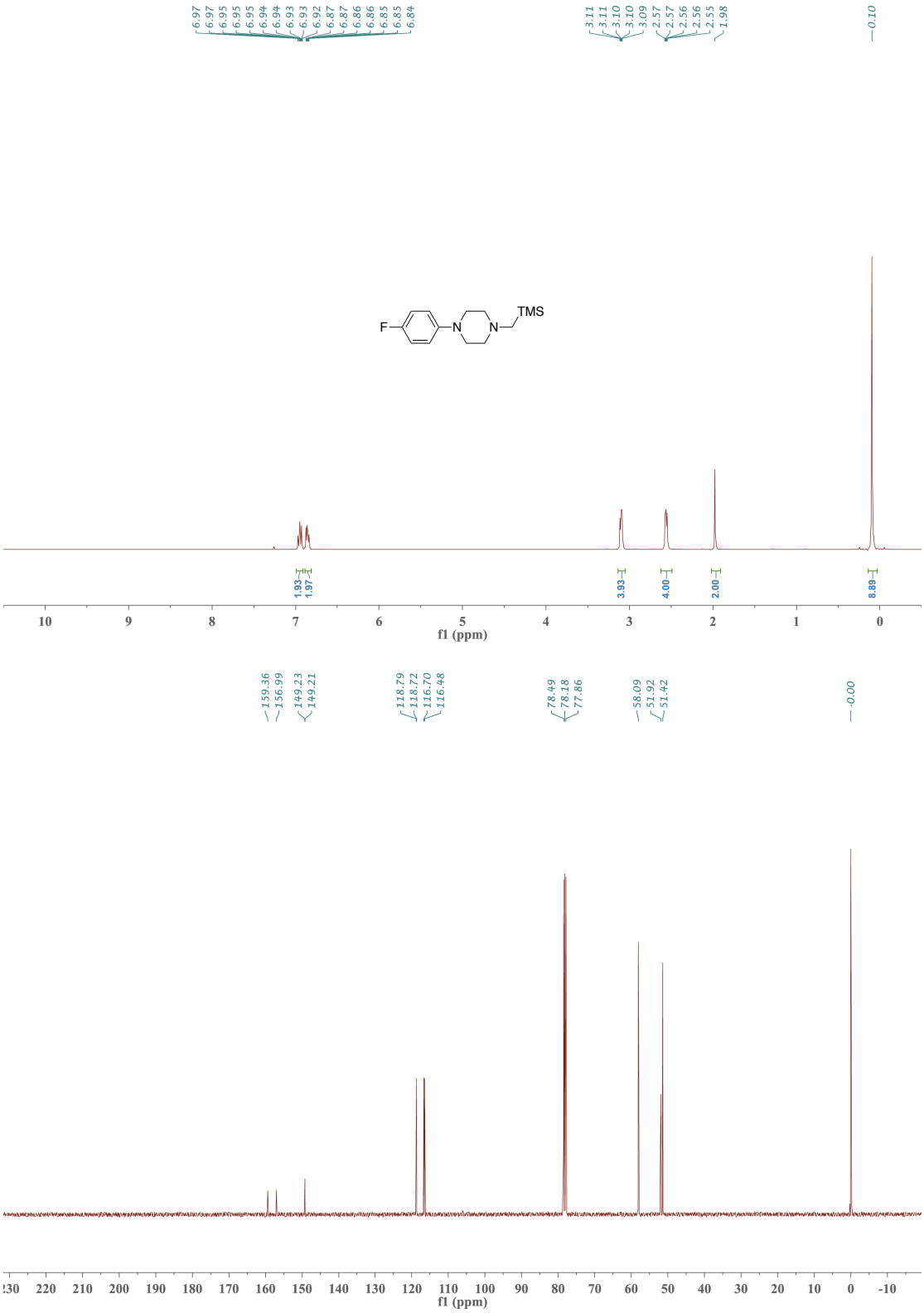


Figure S24. ^{1}H and ^{13}C NMR Spectra of 1-(3-Chlorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1x**)

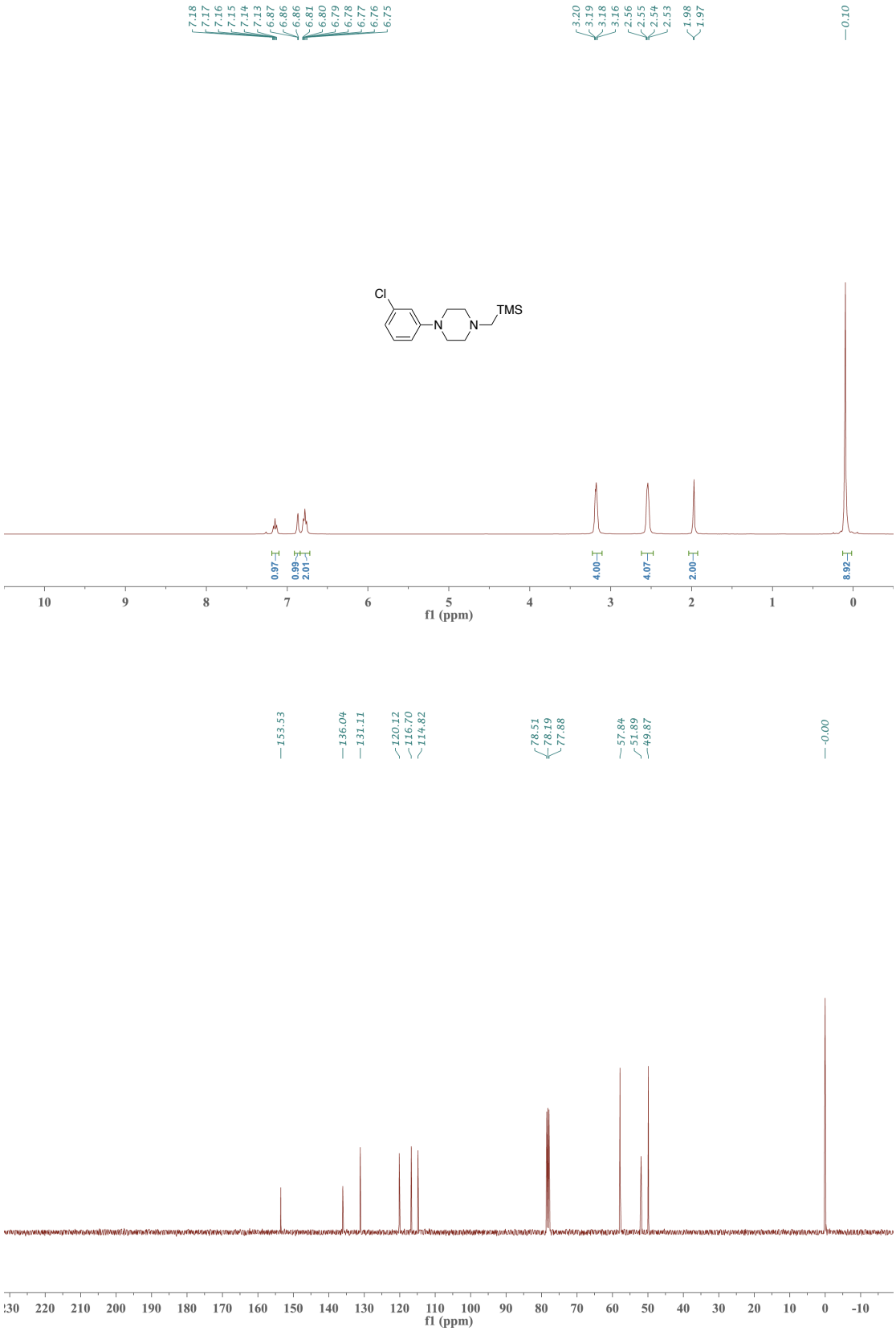


Figure S25. ^{1}H and ^{13}C NMR Spectra of 1-(2,3-Dichlorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1y**)

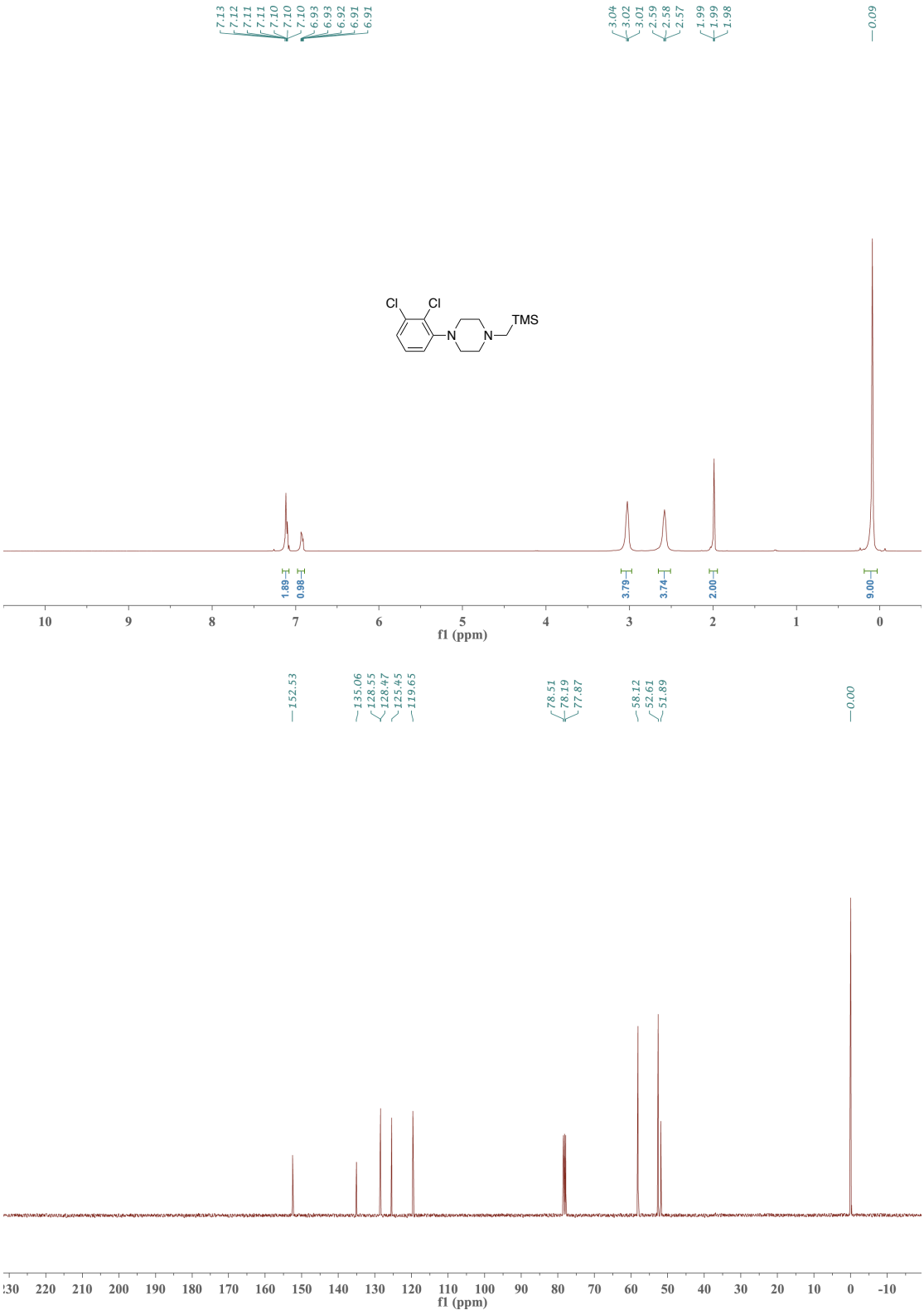


Figure S26. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-3,7-dimethyl-*N*-((trimethylsilyl)methyl)-oct-6-en-1-amine **(1z)**

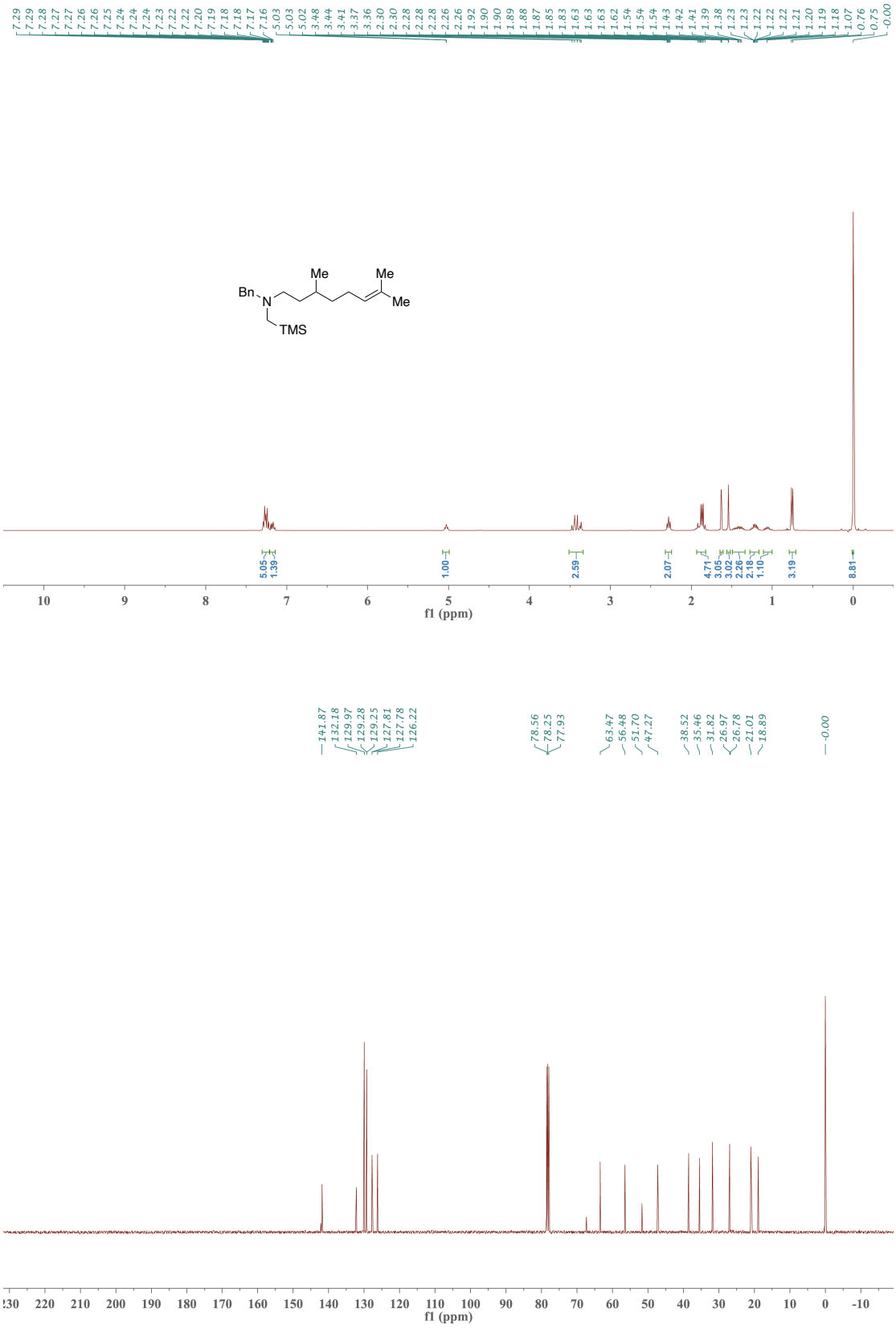


Figure S27. ^{1}H and ^{13}C NMR Spectra of *N*-Methyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)-*N*-((trimethylsilyl)methyl)propan-1-amine (**1α**)

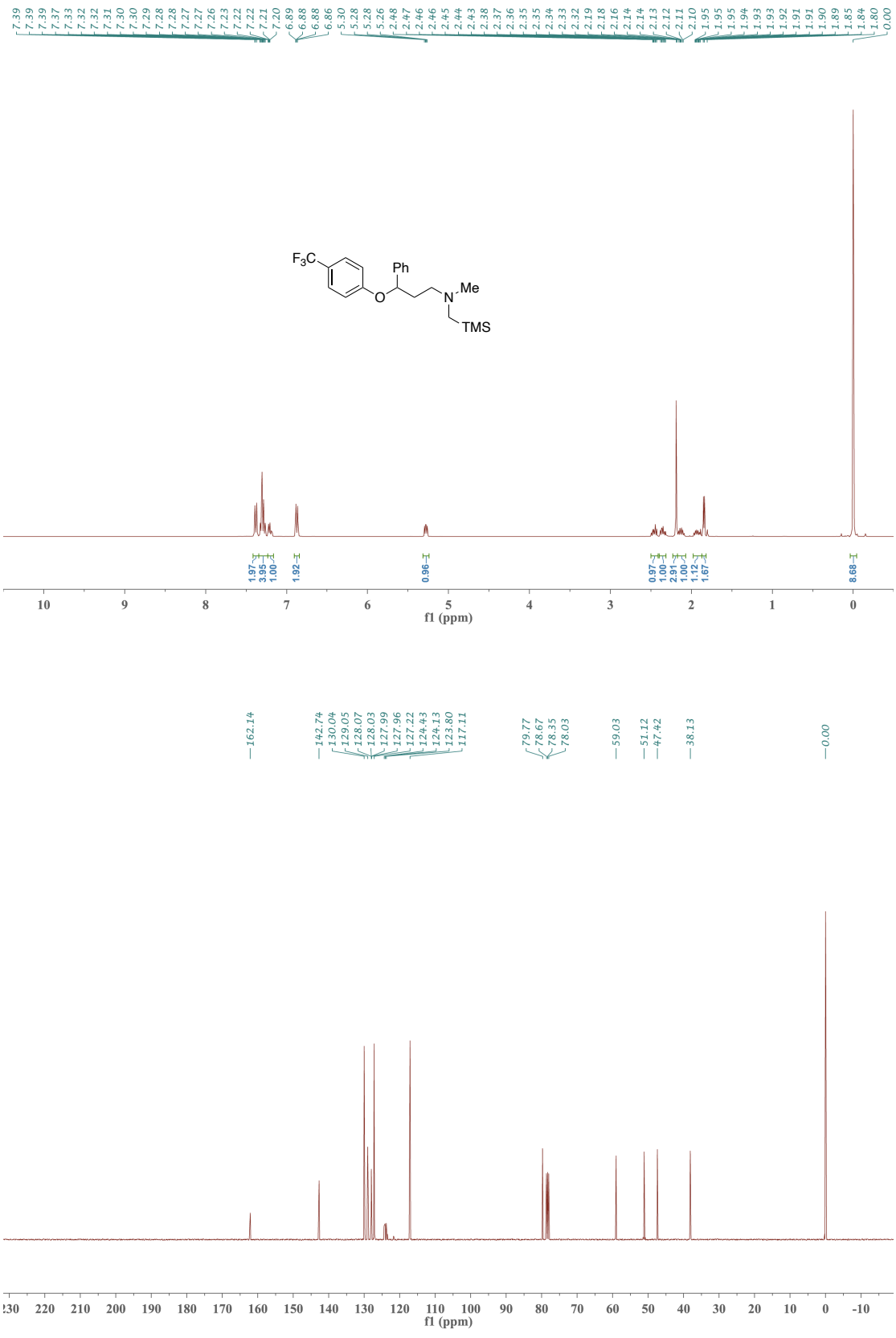
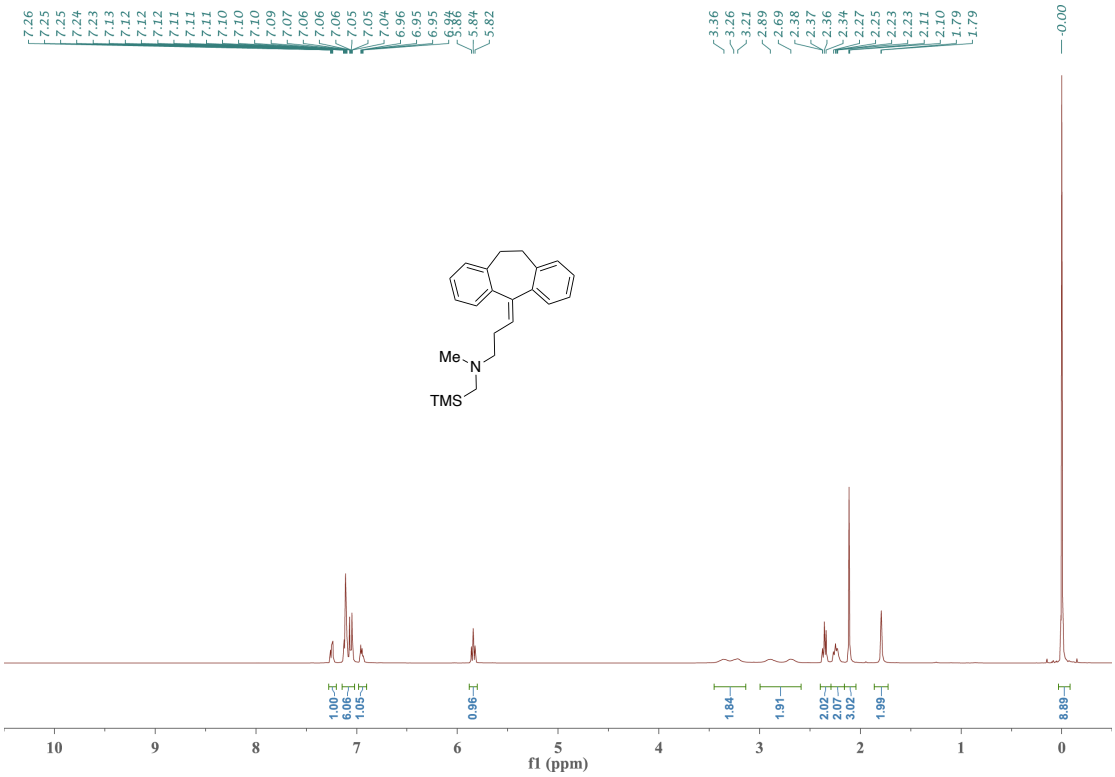


Figure S28. ^{1}H and ^{13}C NMR Spectra of 3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]-annulen-5-ylidene)-*N*-methyl-*N*-((trimethylsilyl)methyl)propan-1-amine (**1*β***)



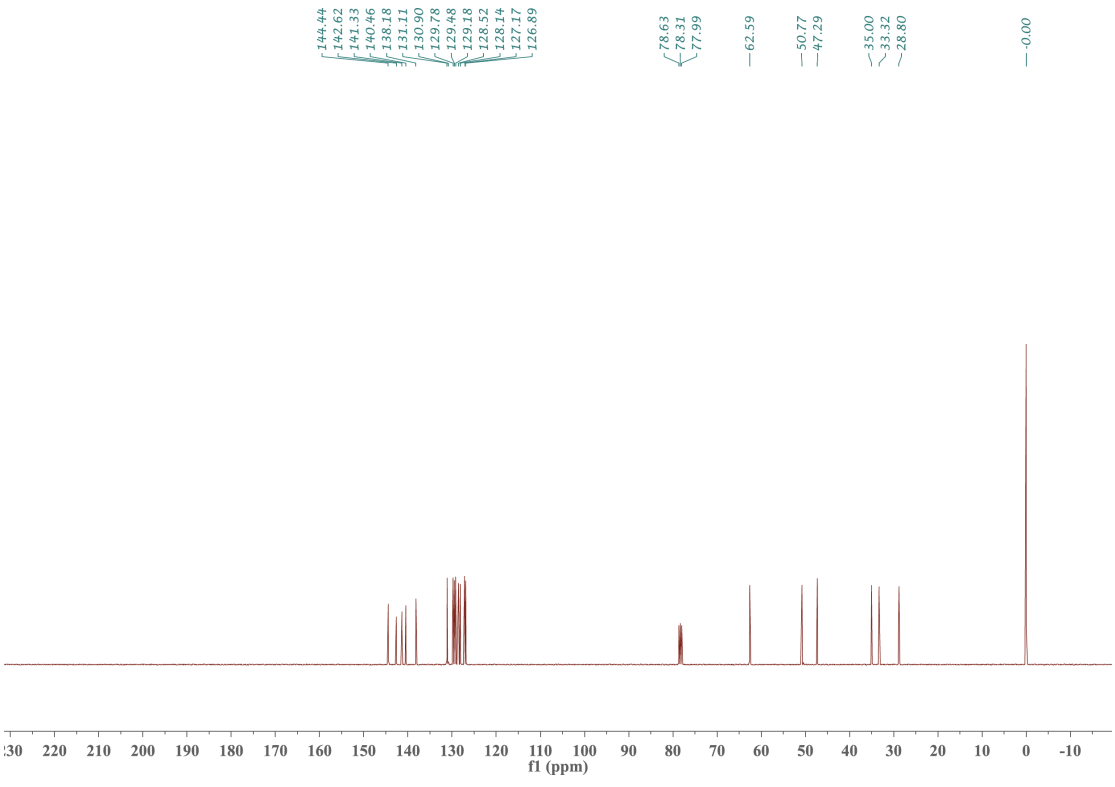


Figure S29. ^{1}H and ^{13}C NMR Spectra of (3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-((trimethylsilyl)methyl)piperidine (**1*γ***)

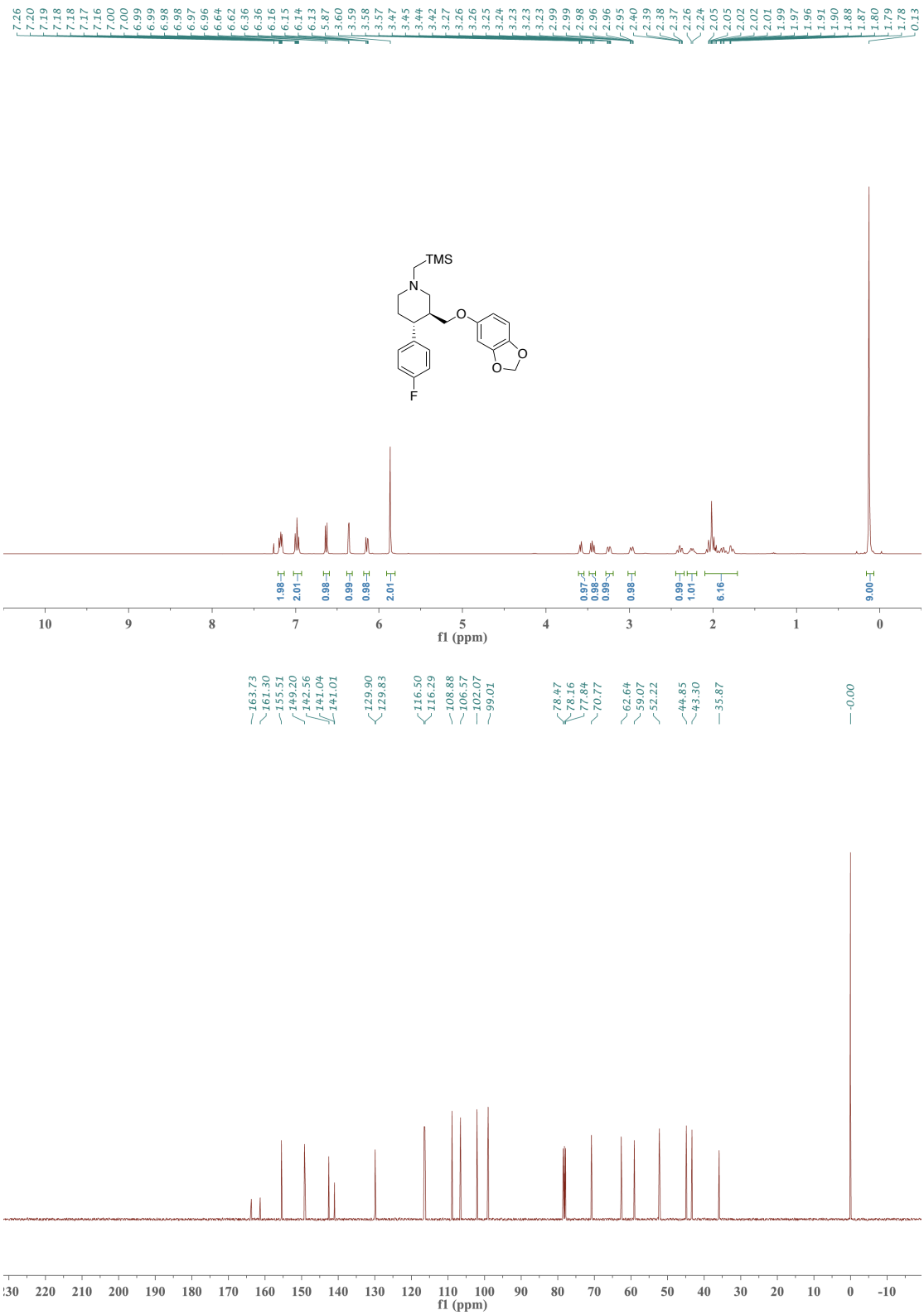


Figure S30. ^{1}H and ^{13}C NMR Spectra of (*S*)-*N*-Methyl-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)-*N*-((trimethylsilyl)methyl)propan-1-amine (**1*δ***)

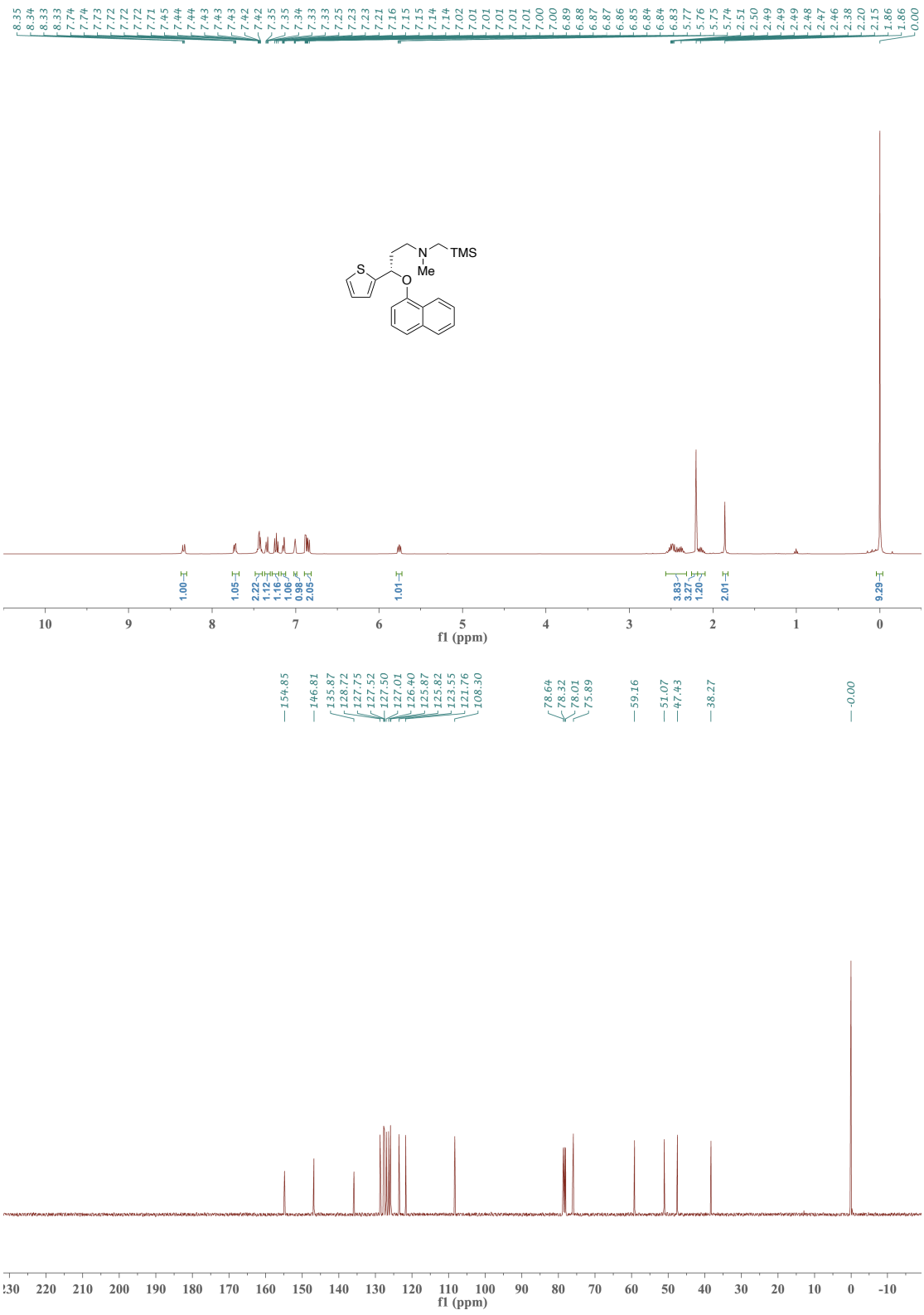


Figure S31. ^{1}H and ^{13}C NMR Spectra of (1*S*,4*S*)-4-(3,4-Dichlorophenyl)-*N*-methyl-*N*-((trimethylsilyl)methyl)-1,2,3,4-tetrahydronaphthalen-1-amine (**1*ε***)

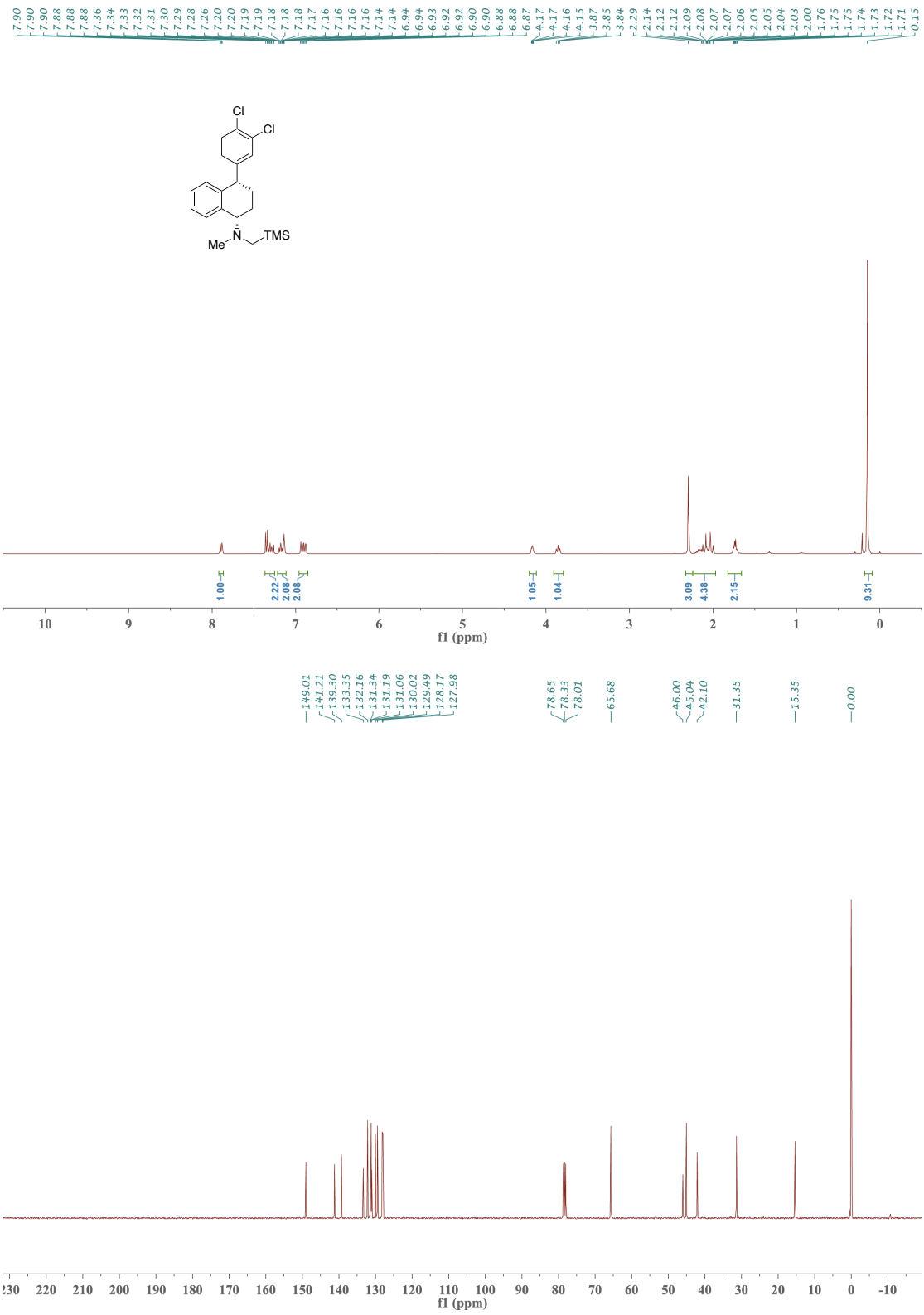


Figure S32. ^{1}H and ^{13}C NMR Spectra of (Iodoethynyl)benzene (**2a**)

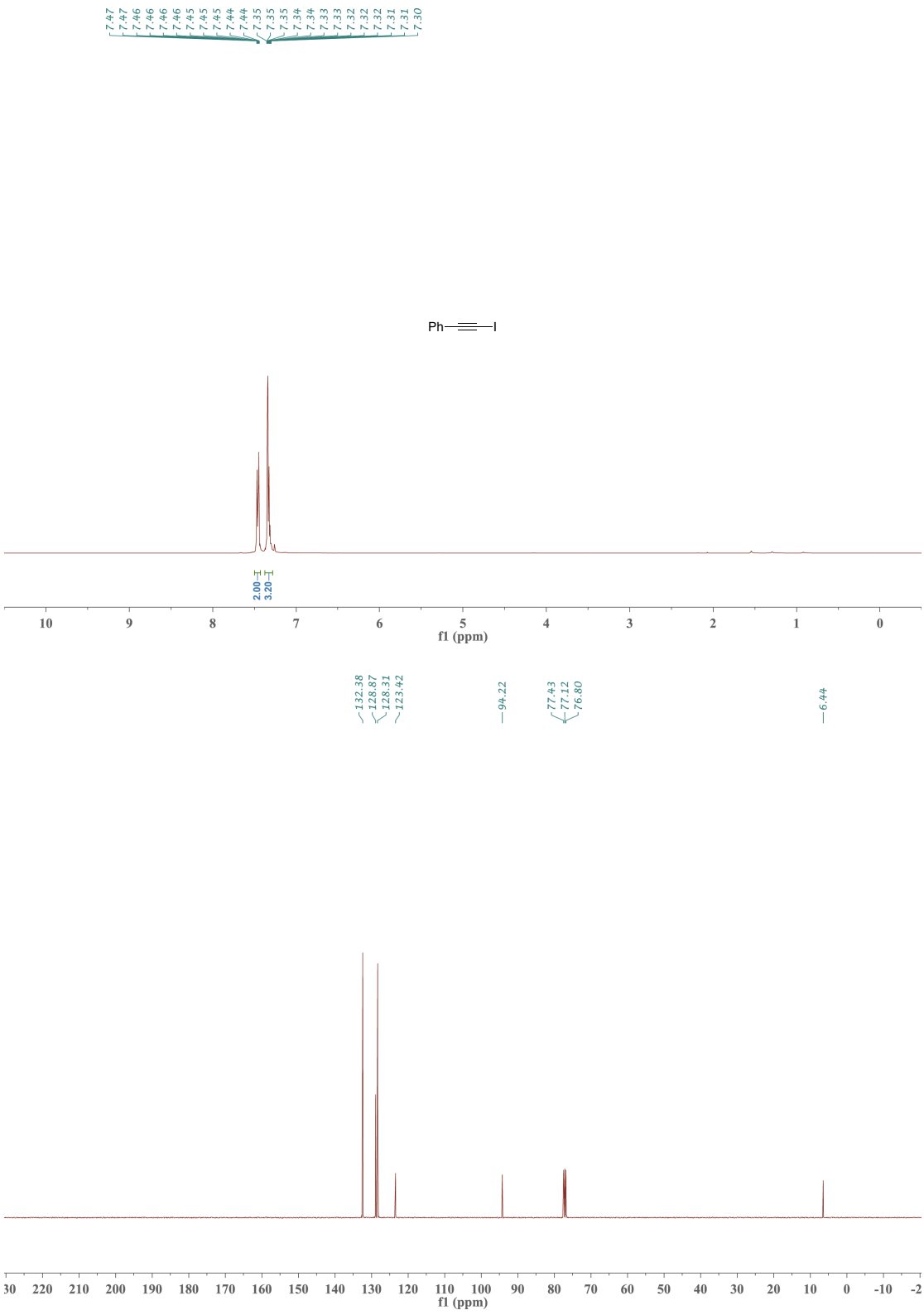


Figure S33. ^{1}H and ^{13}C NMR Spectra of 1-(Iodoethynyl)-4-methoxybenzene (**2b**)

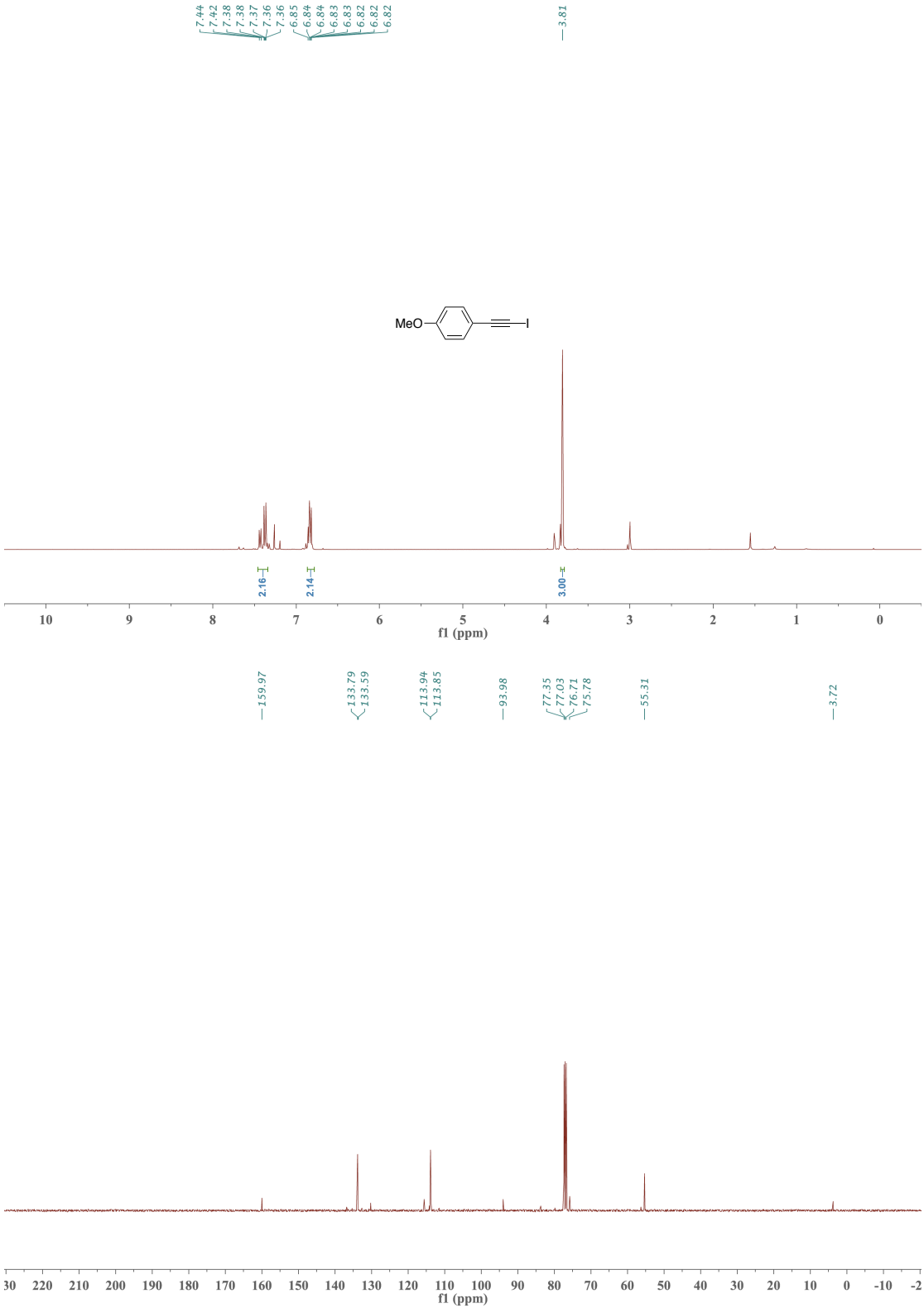


Figure S34. ^{1}H and ^{13}C NMR Spectra of 1-(*tert*-Butyl)-4-(iodoethynyl)benzene (**2c**)

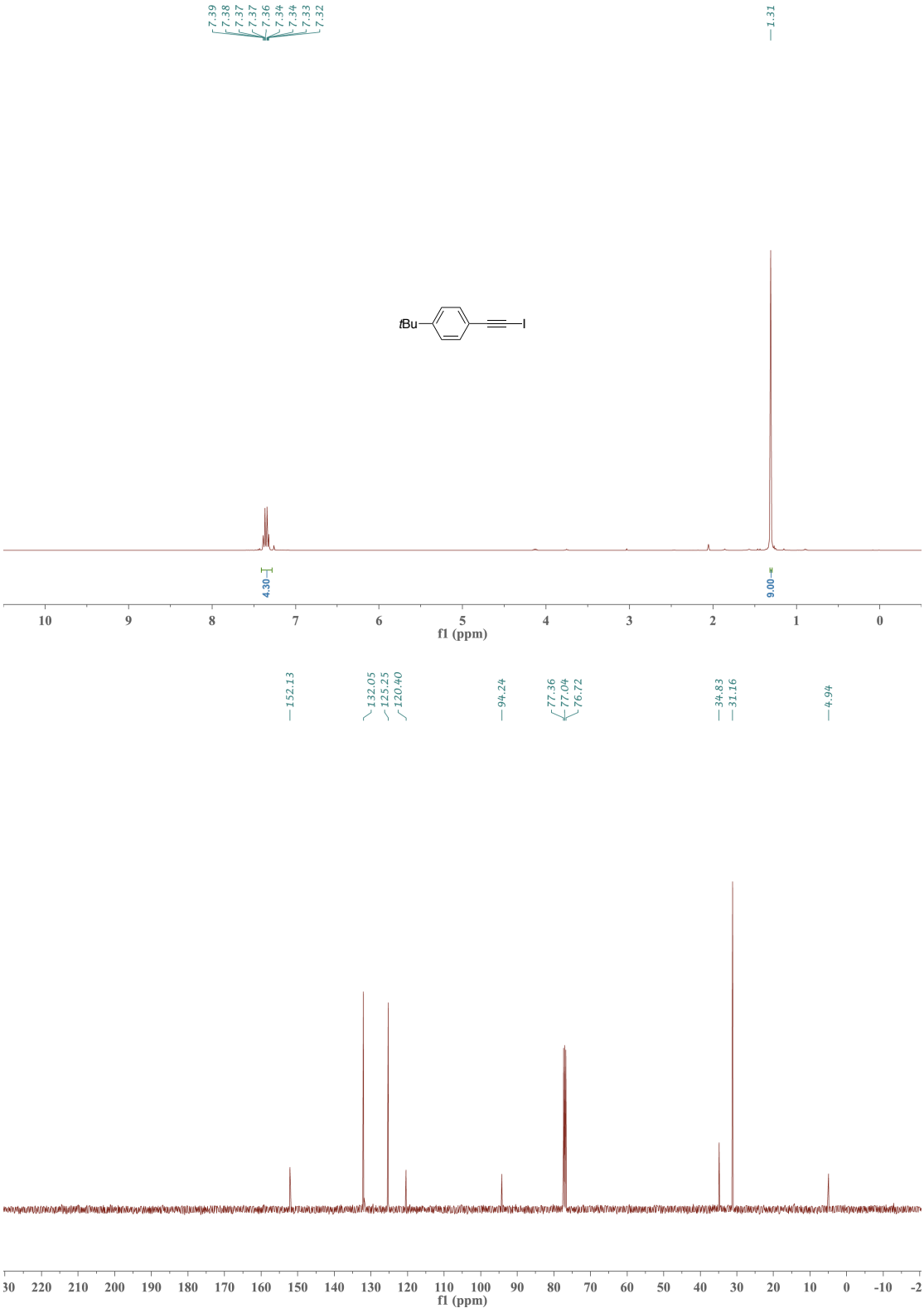


Figure S35. ^{1}H and ^{13}C NMR Spectra of 1-(Iodoethynyl)-4-methylbenzene (**2d**)

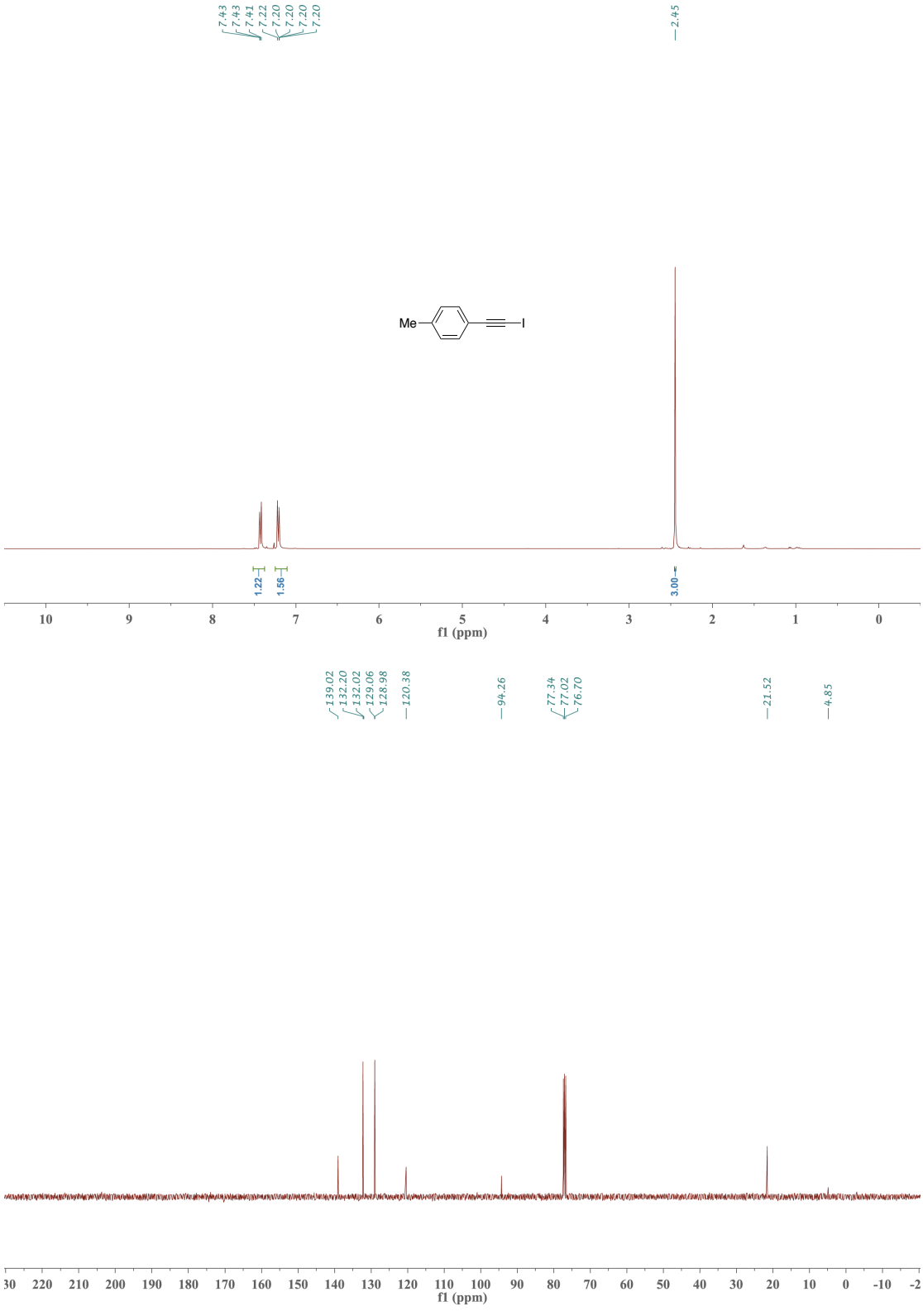


Figure S36. ^{1}H and ^{13}C NMR Spectra of 1-(Iodoethynyl)-4-(trifluoromethyl)benzene (**2e**)

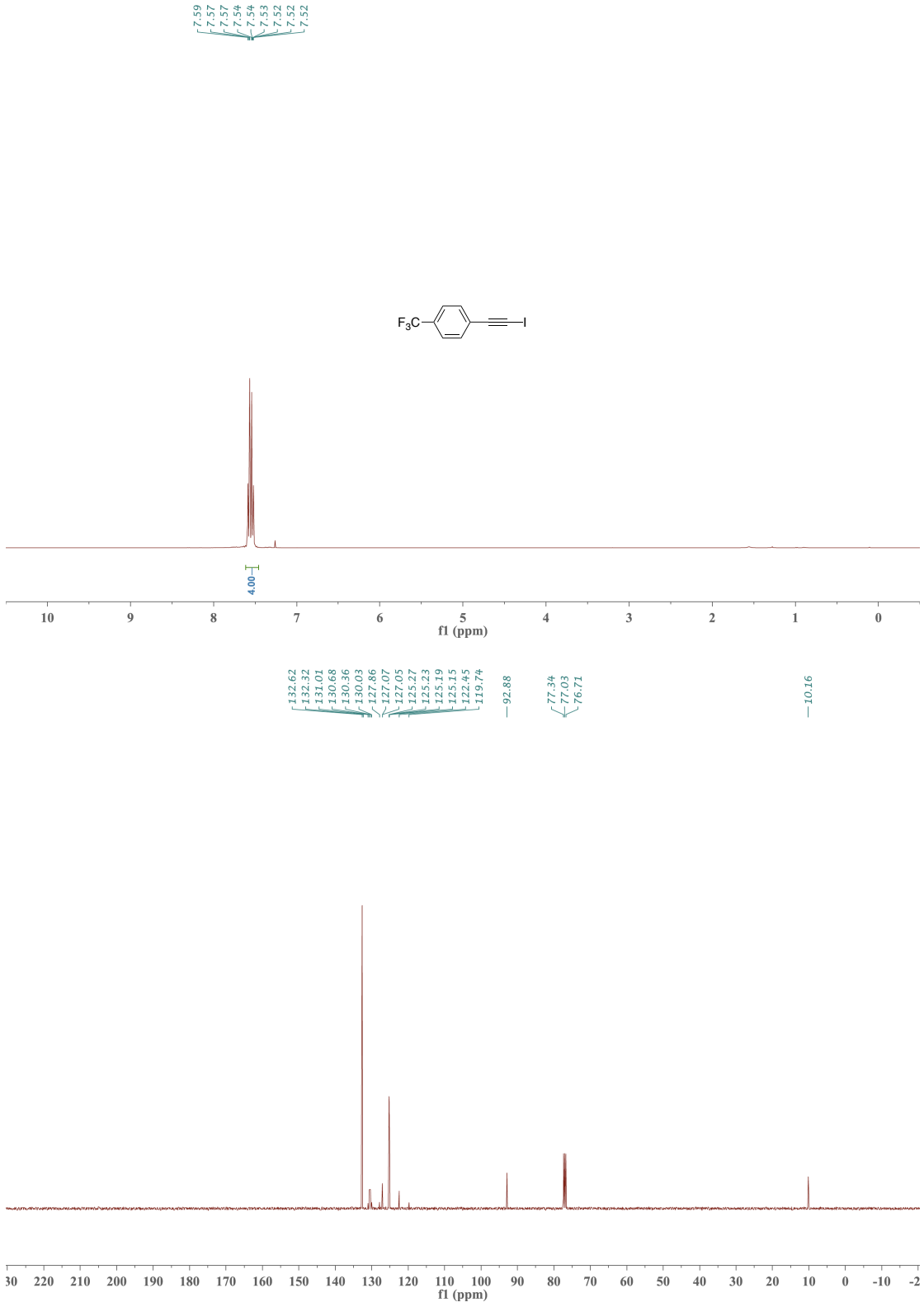


Figure S37. ^{1}H and ^{13}C NMR Spectra of 1-Fluoro-4-(iodoethynyl)benzene (**2f**)

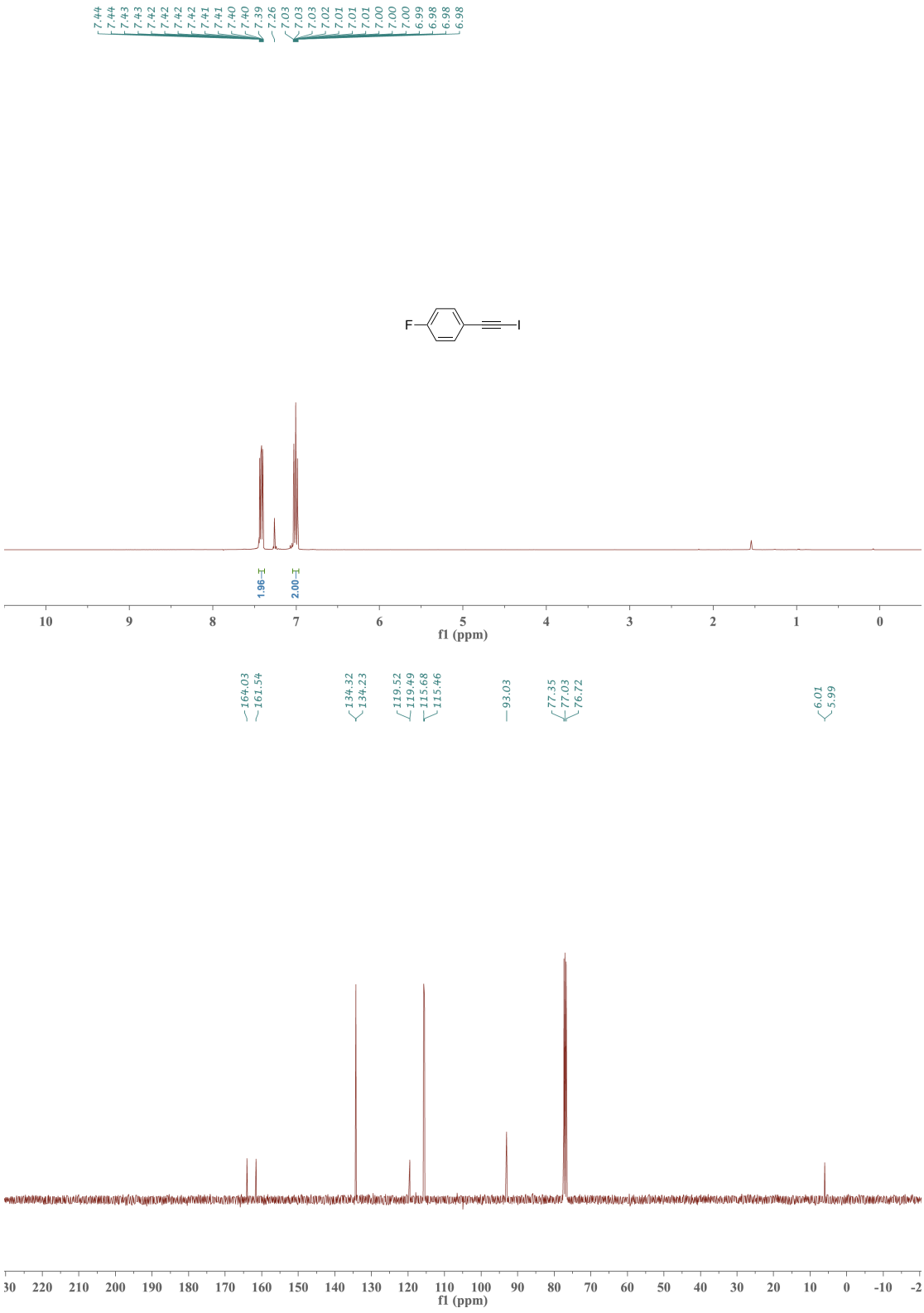


Figure S38. ^{1}H and ^{13}C NMR Spectra of 1-Bromo-4-(iodoethynyl)benzene (**2g**)

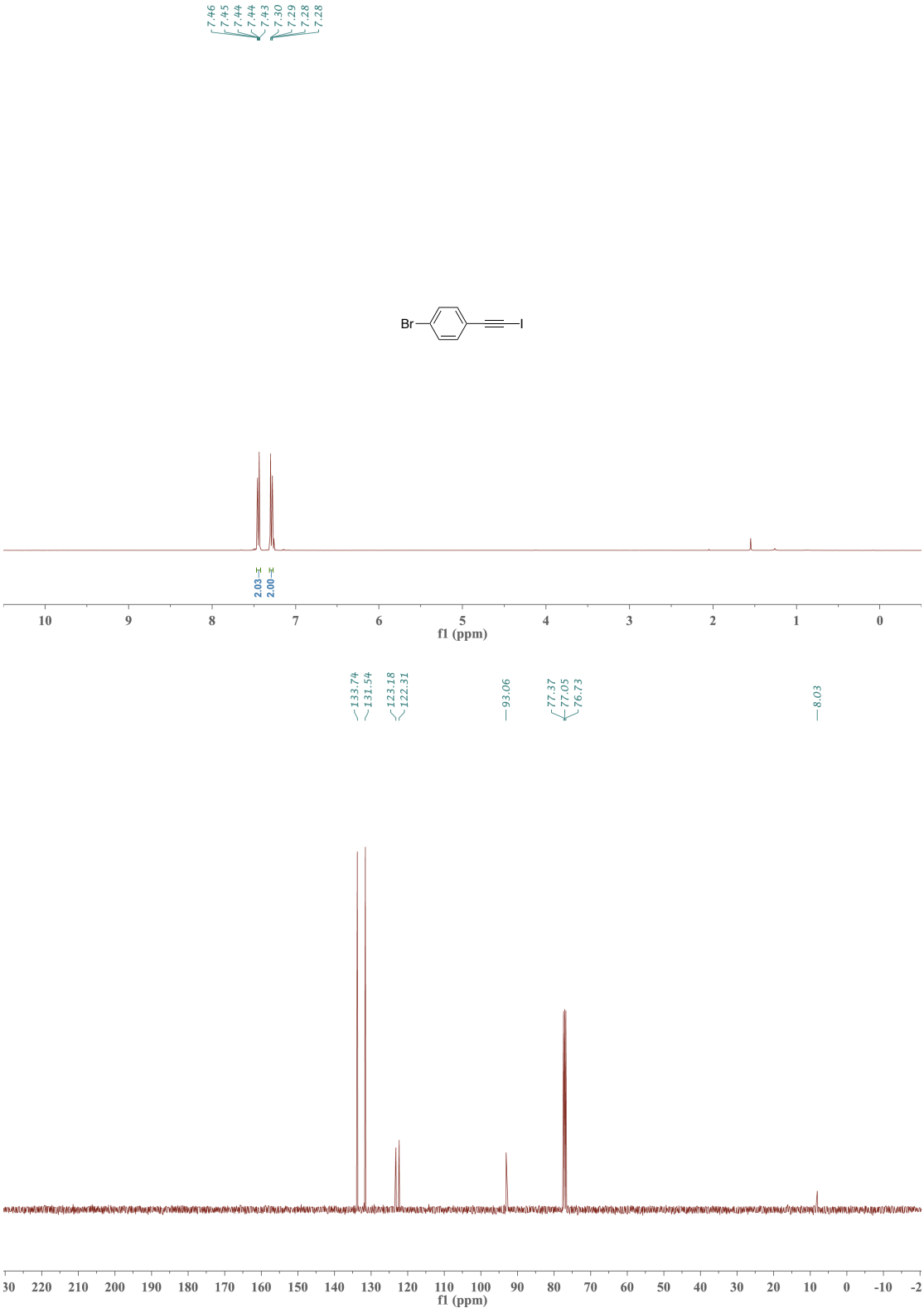


Figure S39. ^{1}H and ^{13}C NMR Spectra of 4-(Iodoethynyl)-1,1'-biphenyl (**2h**)

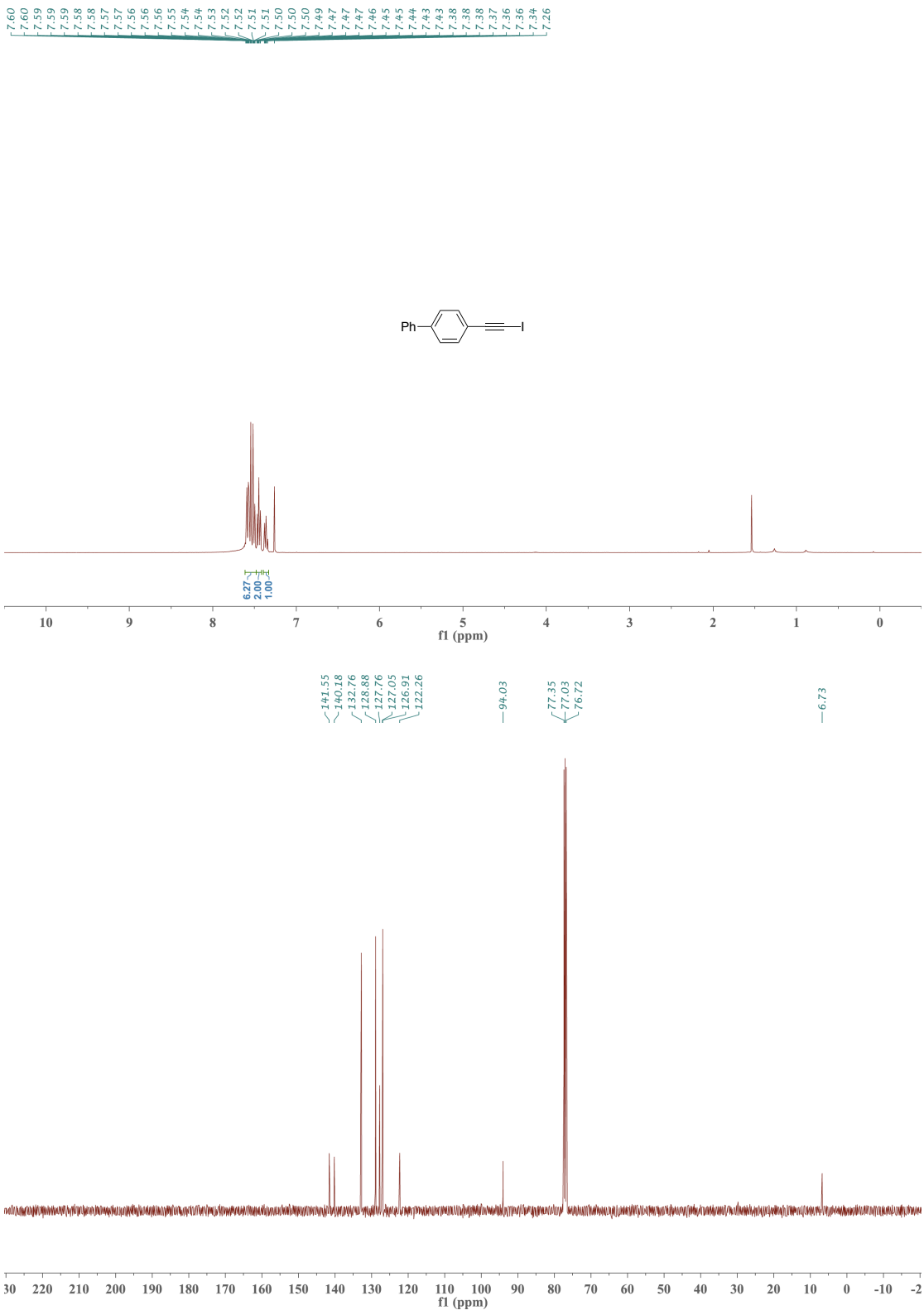


Figure S40. ^{1}H and ^{13}C NMR Spectra of 1-Chloro-2-(iodoethynyl)benzene (**2i**)

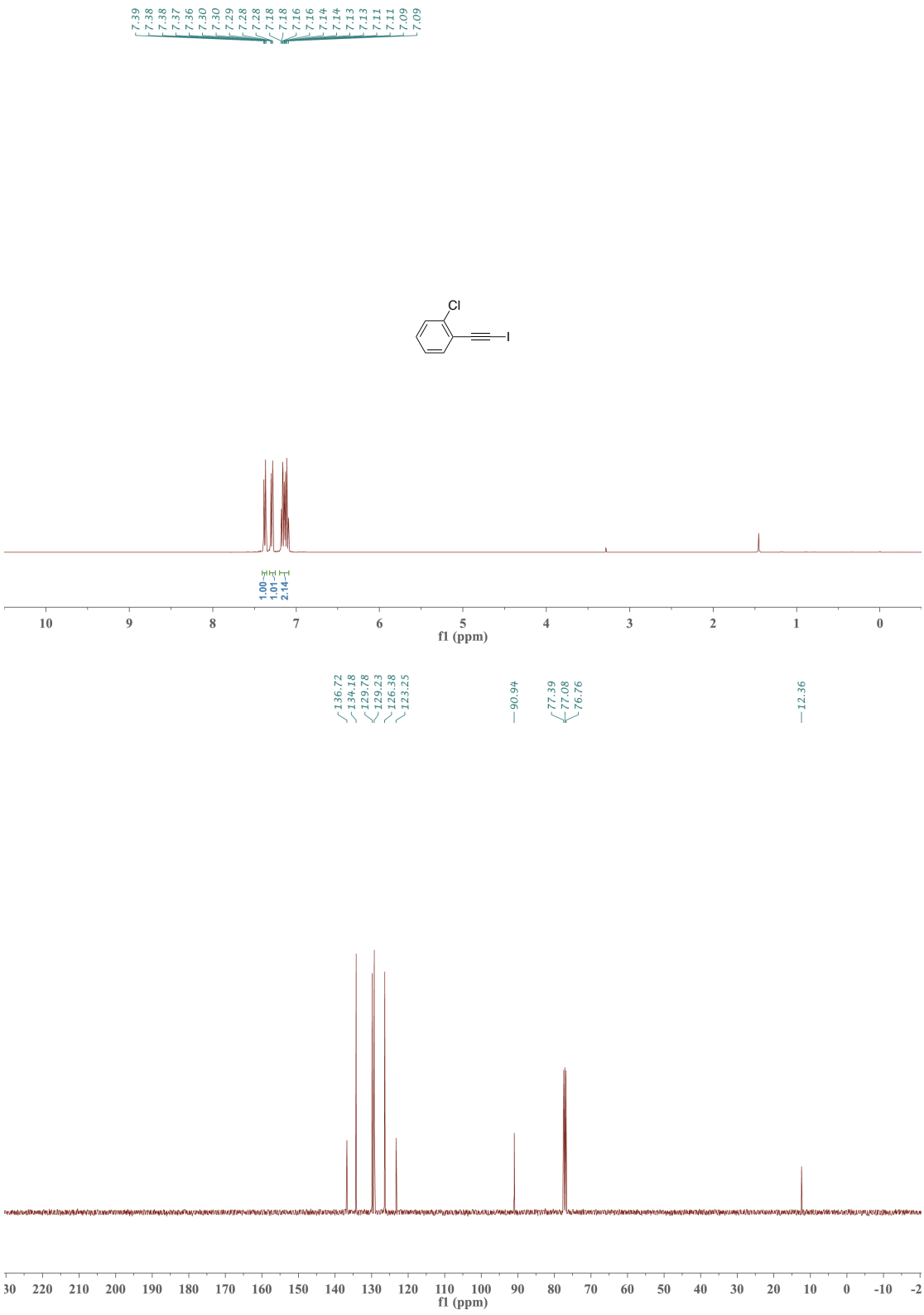


Figure S41. ^{1}H and ^{13}C NMR Spectra of 1-Chloro-3-(iodoethynyl)benzene (**2j**)

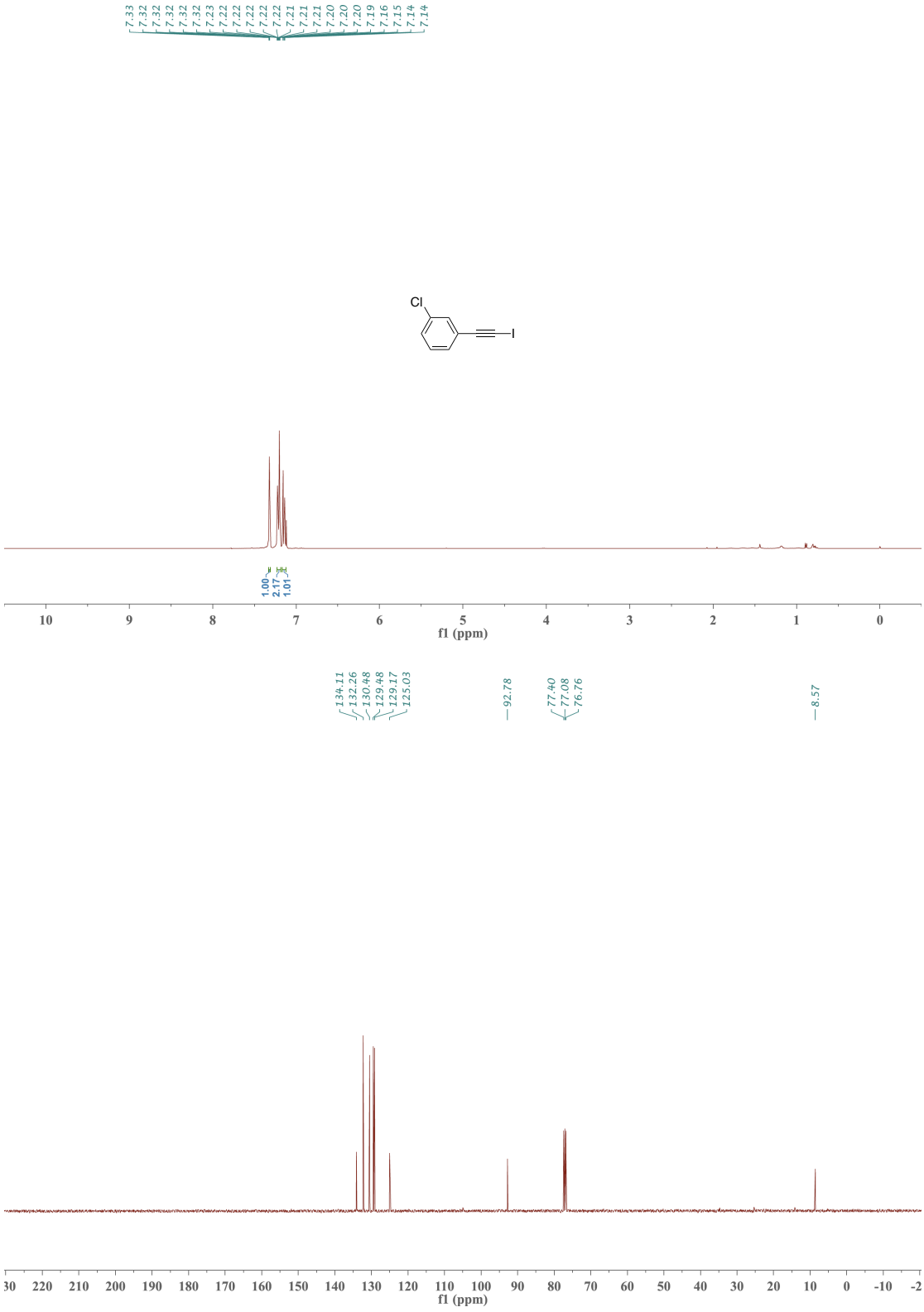


Figure S42. ^{1}H and ^{13}C NMR Spectra of 2-(Iodoethynyl)-6-methoxynaphthalene (**2k**)

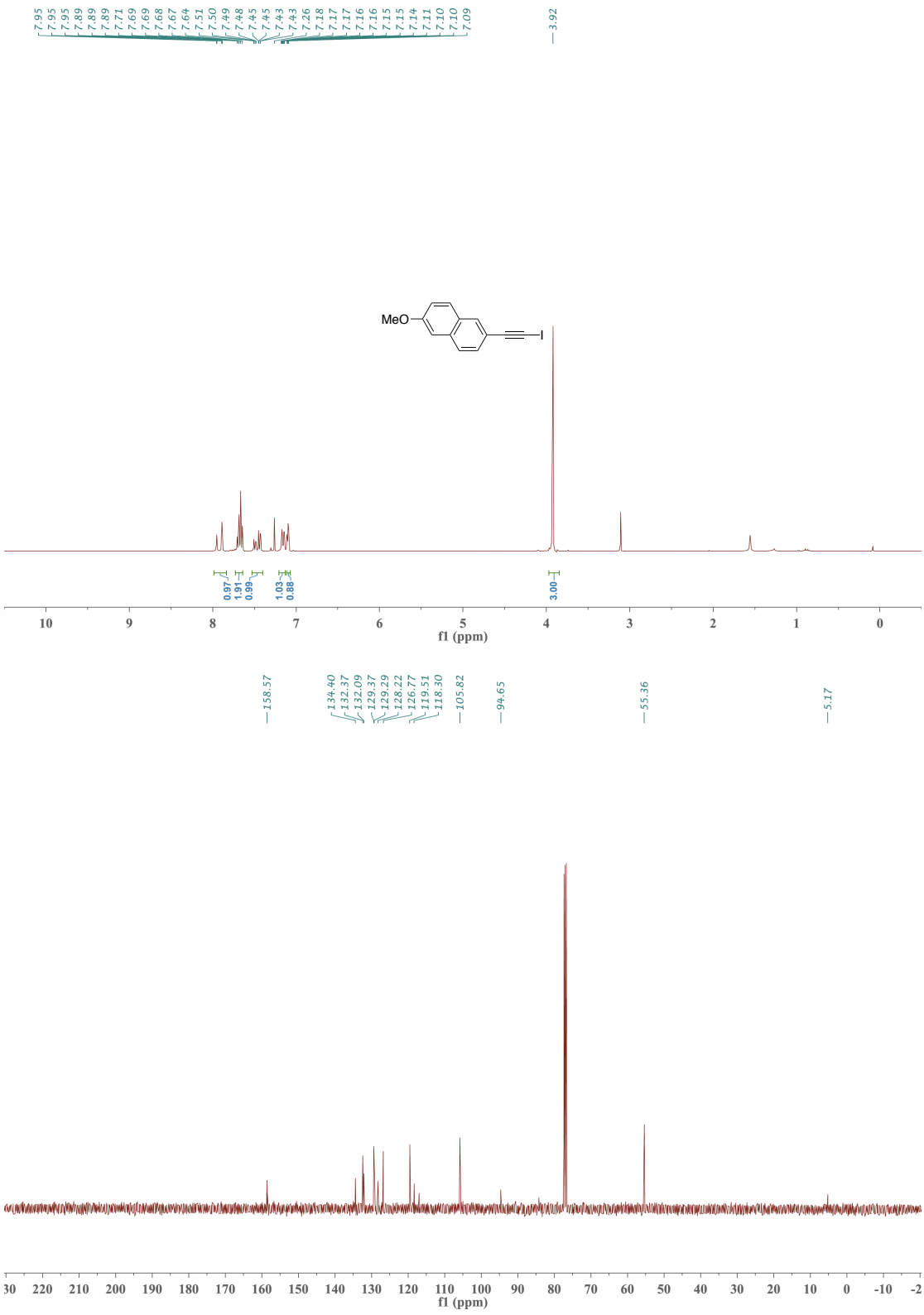


Figure S43. ^{1}H and ^{13}C NMR Spectra of 3-(Iodoethynyl)pyridine (**2l**)

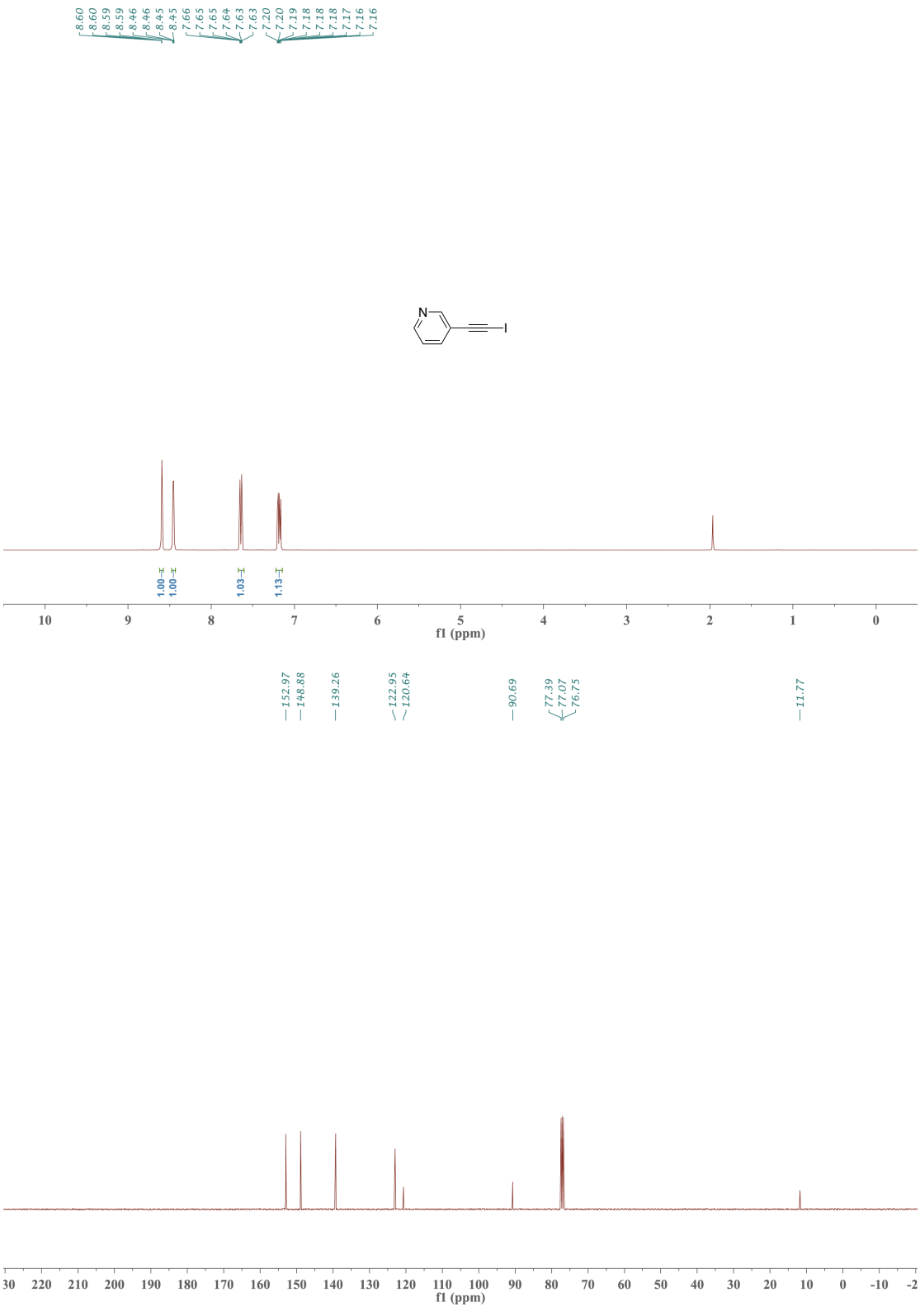


Figure S44. ^{1}H and ^{13}C NMR Spectra of (4-Iodobut-3-yn-1-yl)benzene (**2o**)

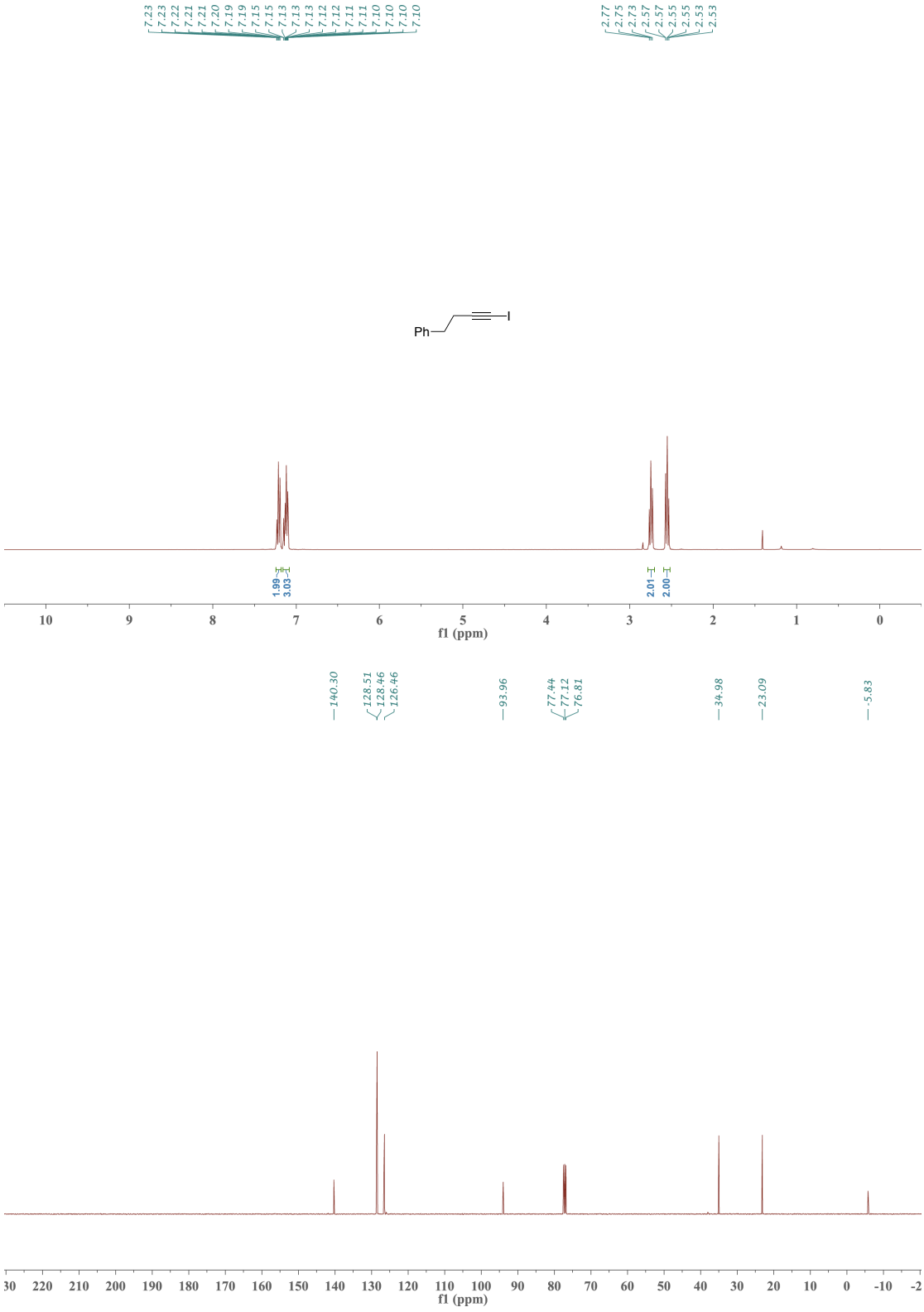


Figure S45. ^{1}H and ^{13}C NMR Spectra of (Iodoethynyl)cyclohexane (**2n**)

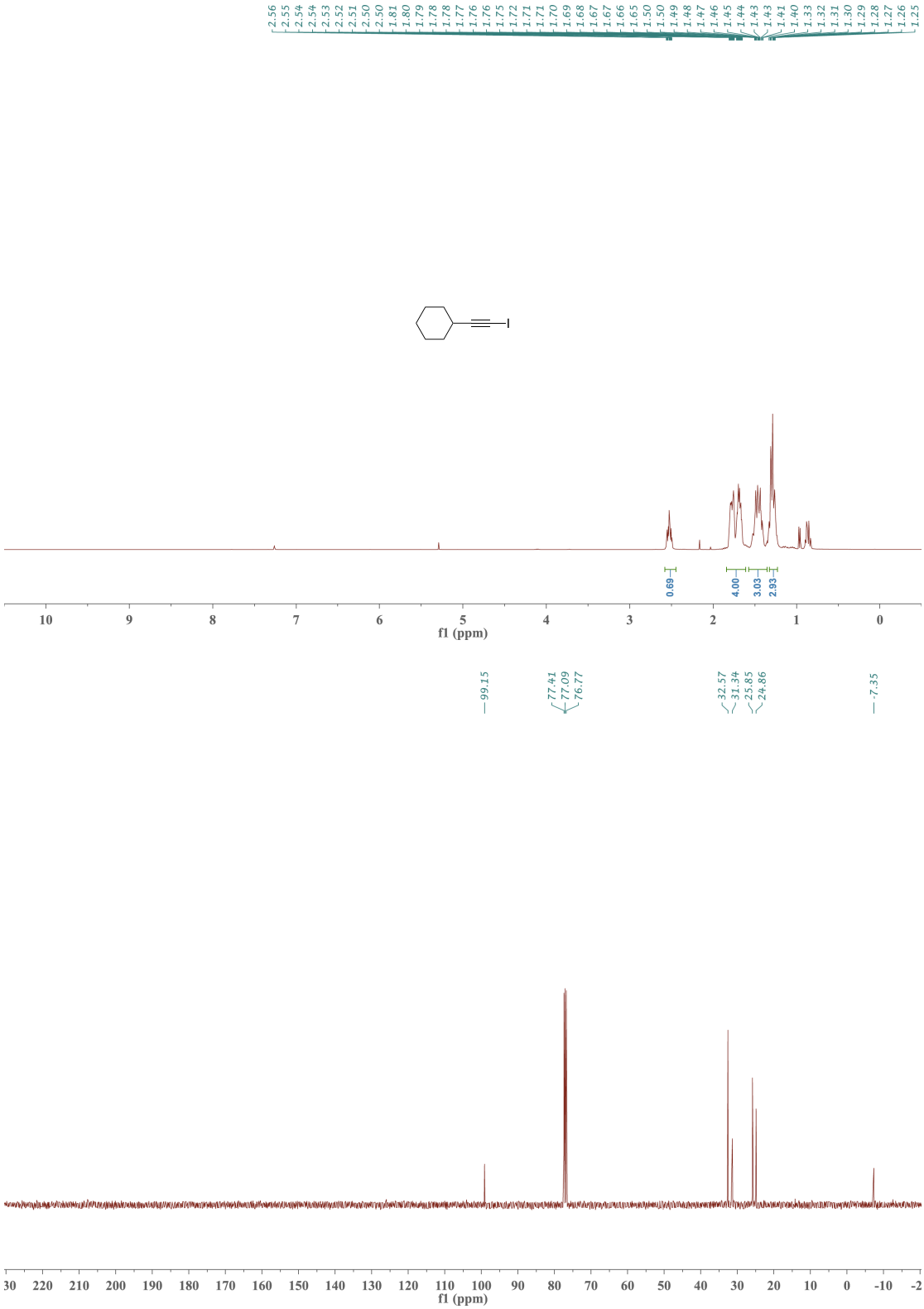


Figure S46. ^{1}H and ^{13}C NMR Spectra of 1-(Iodoethynyl)cyclohex-1-ene (**2o**)

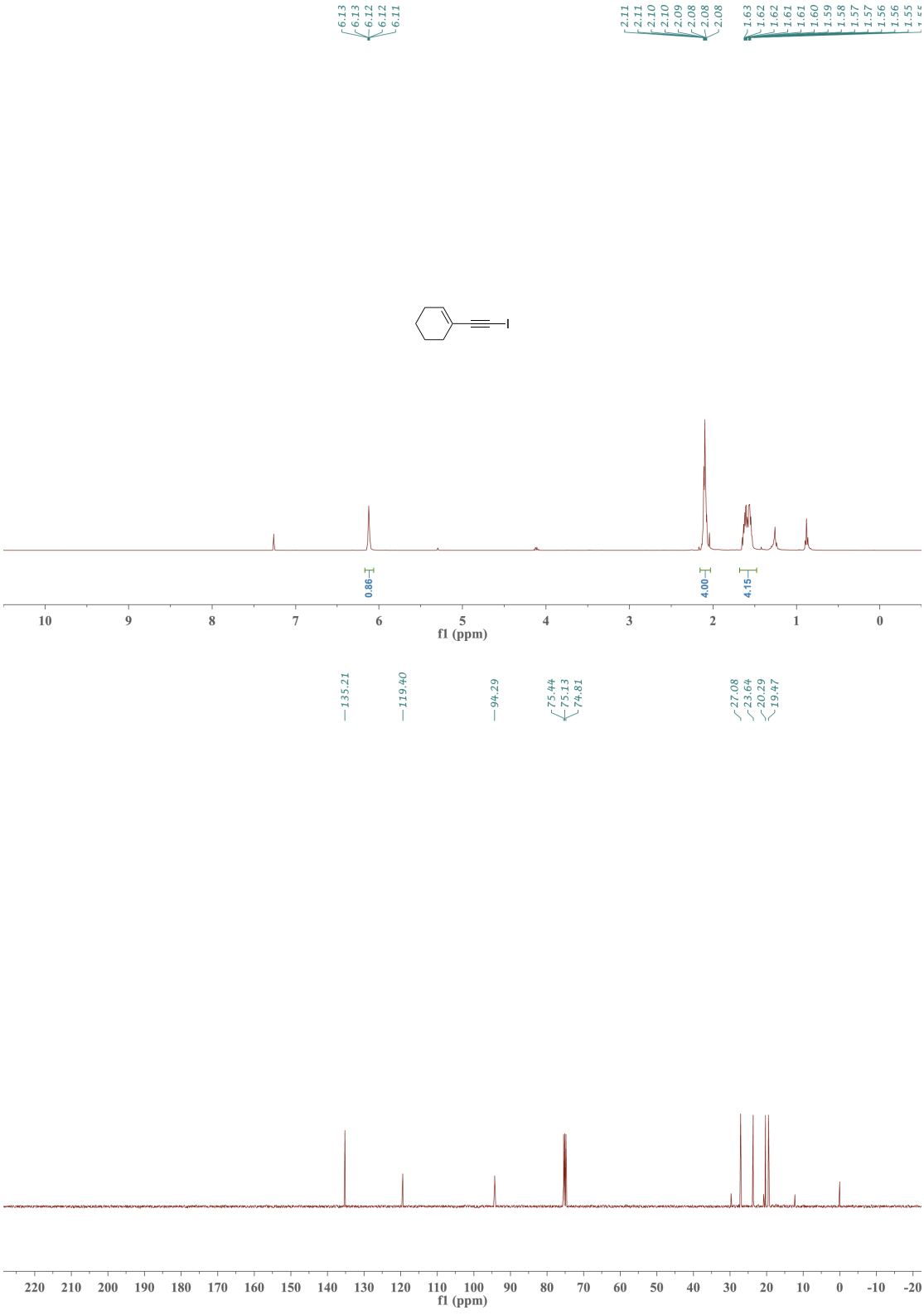


Figure S47. ^{1}H and ^{13}C NMR Spectra of 1-(3-Phenylprop-2-yn-1-yl)piperidine (**3aa**)

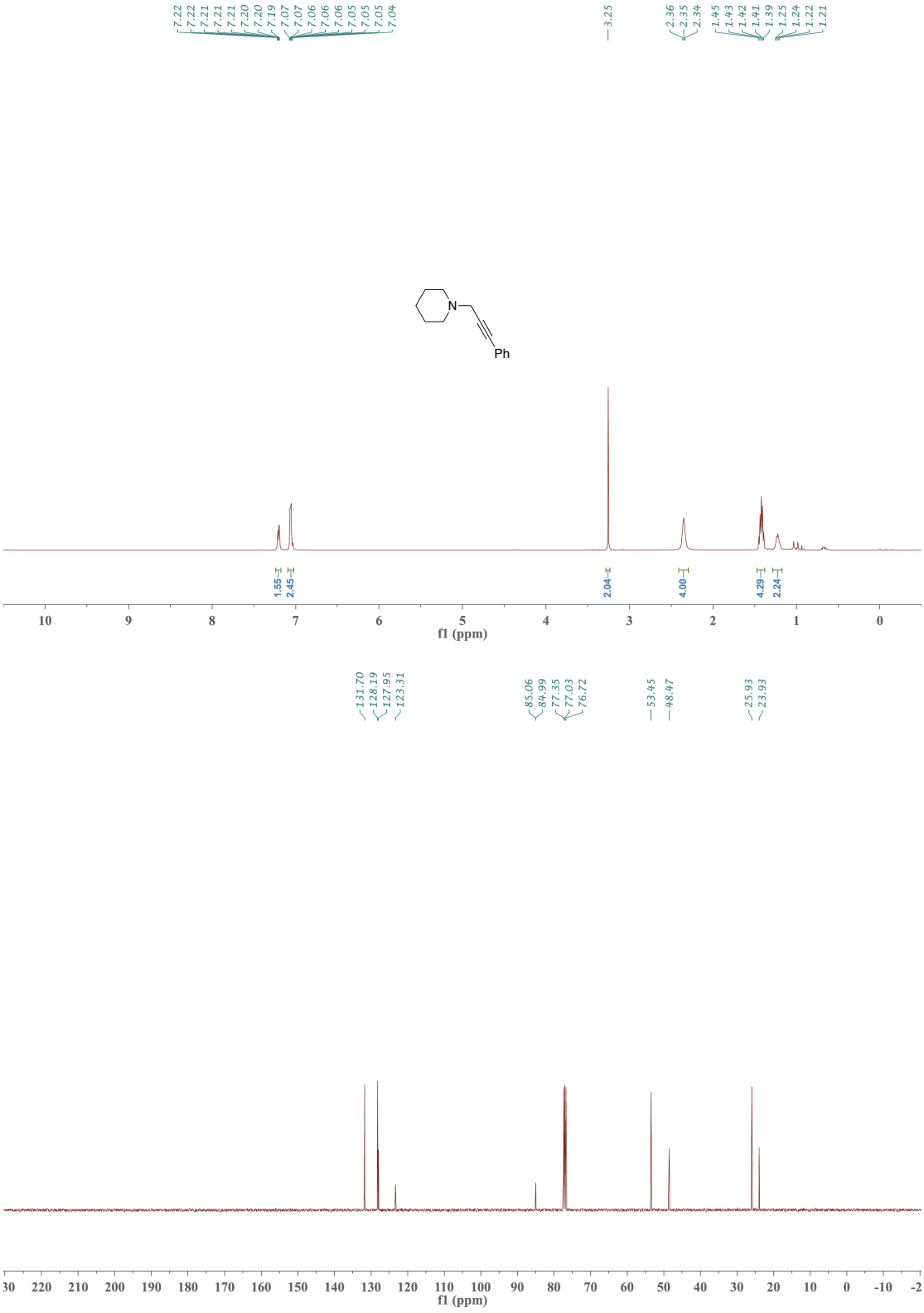


Figure S48. ^{1}H and ^{13}C NMR Spectra of 1-(3-Phenylprop-2-yn-1-yl)pyrrolidine (**3ba**)

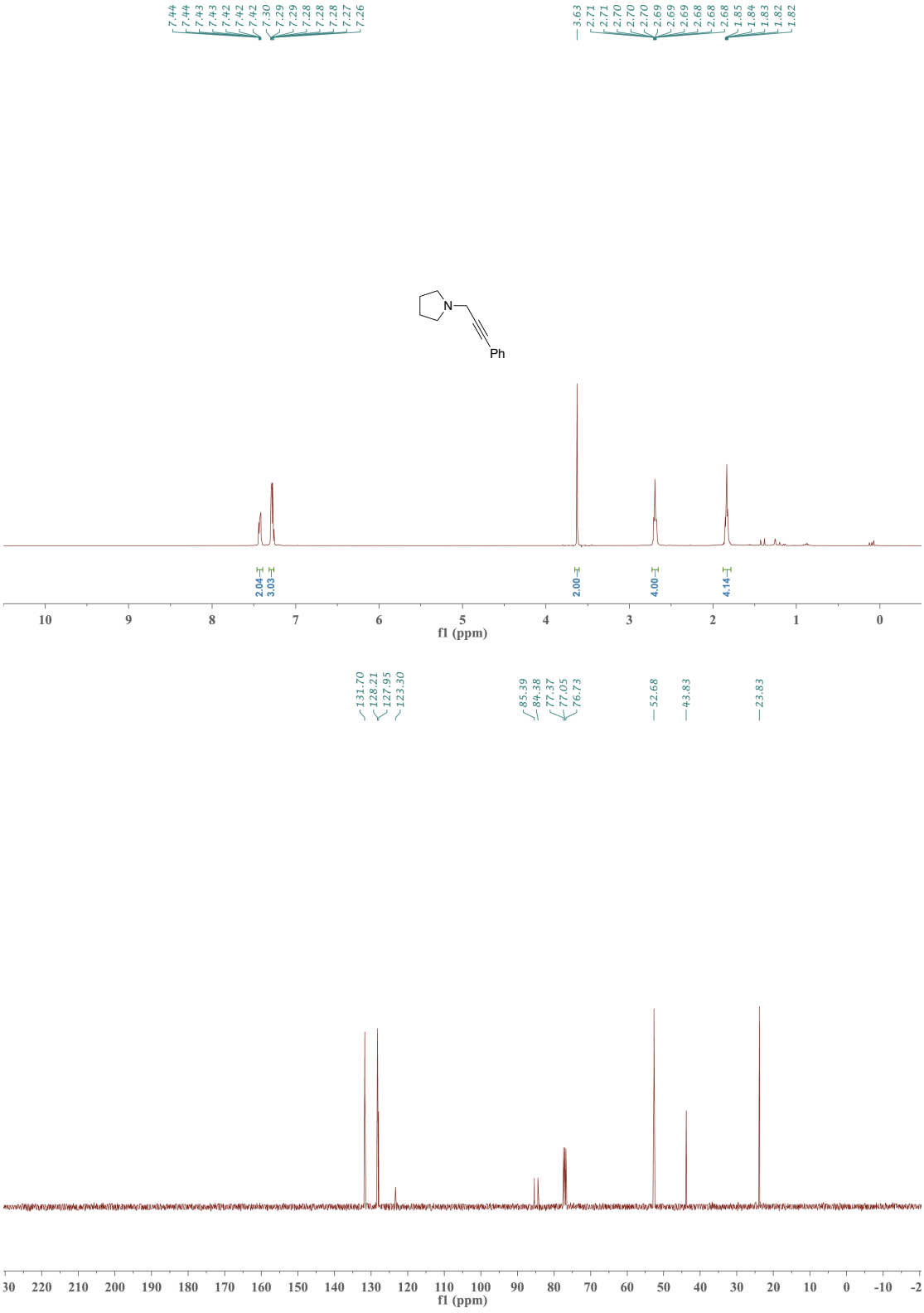


Figure S49. ^{1}H and ^{13}C NMR Spectra of 1-(3-Phenylprop-2-yn-1-yl)azepane (**3ca**)

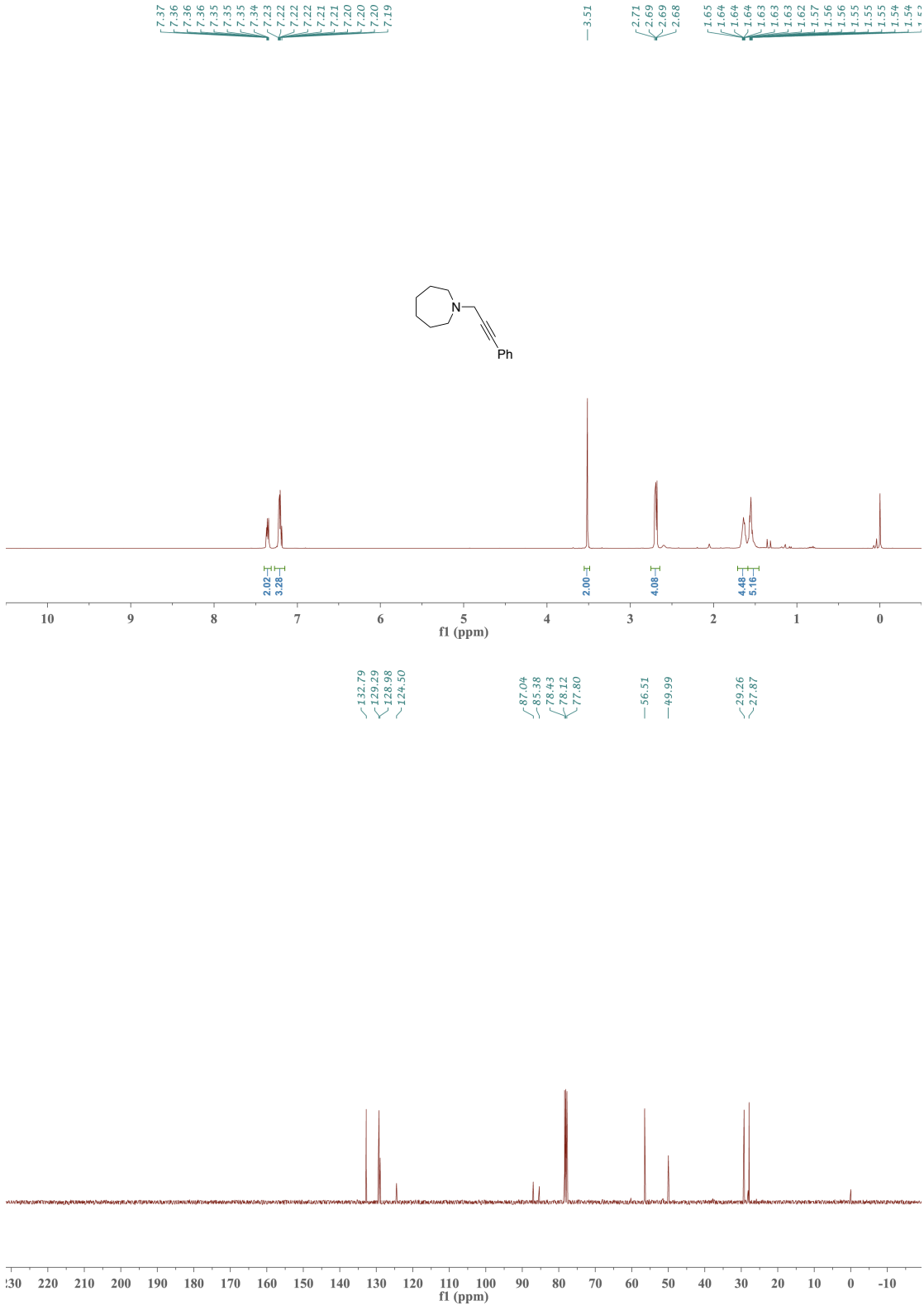


Figure S50. ^{1}H and ^{13}C NMR Spectra of 4-(3-Phenylprop-2-yn-1-yl)morpholine (**3da**)

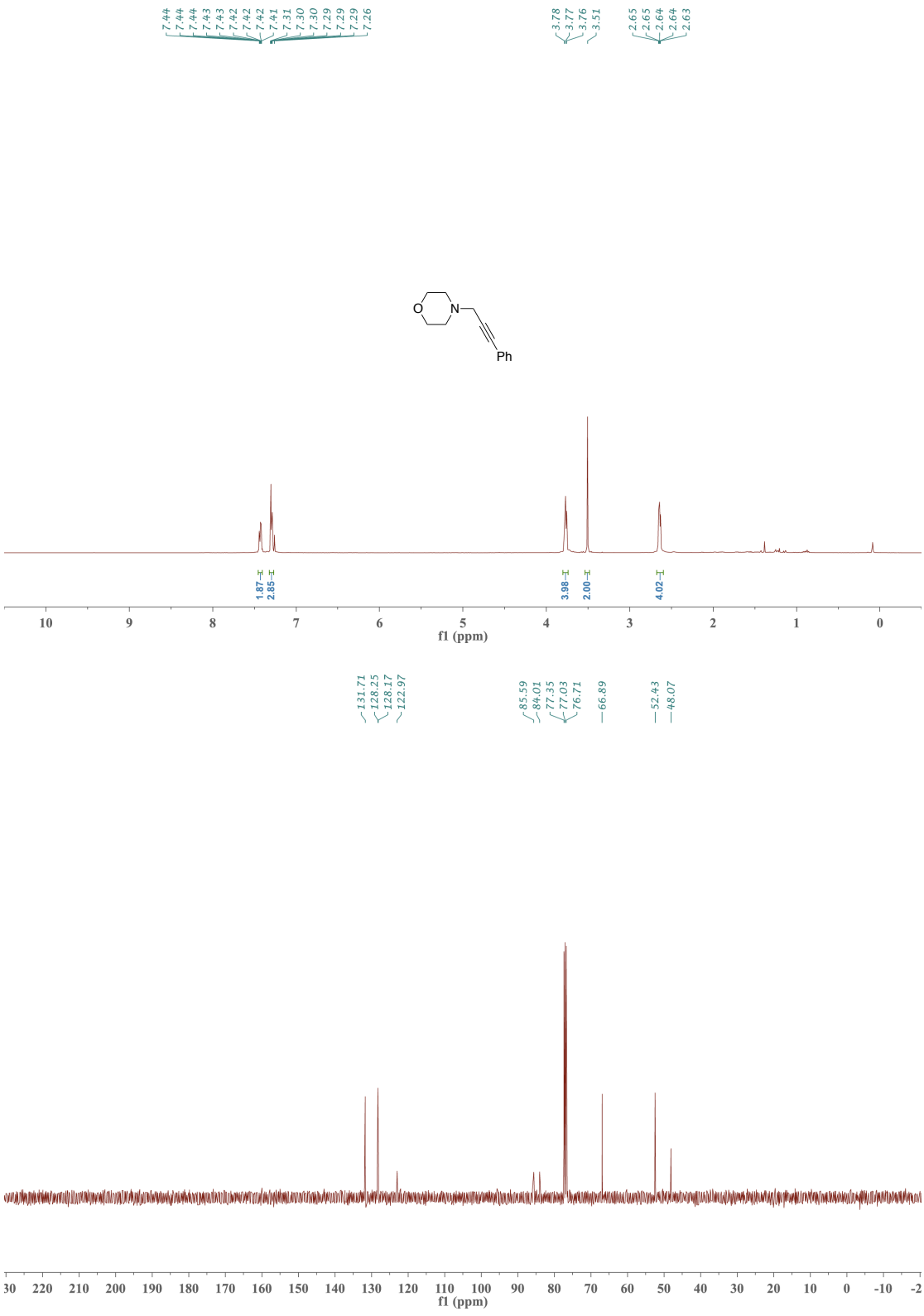


Figure S51. ^{1}H and ^{13}C NMR Spectra of *tert*-Butyl 4-(3-phenylprop-2-yn-1-yl)piperazine-1-carboxylate (**3ea**)

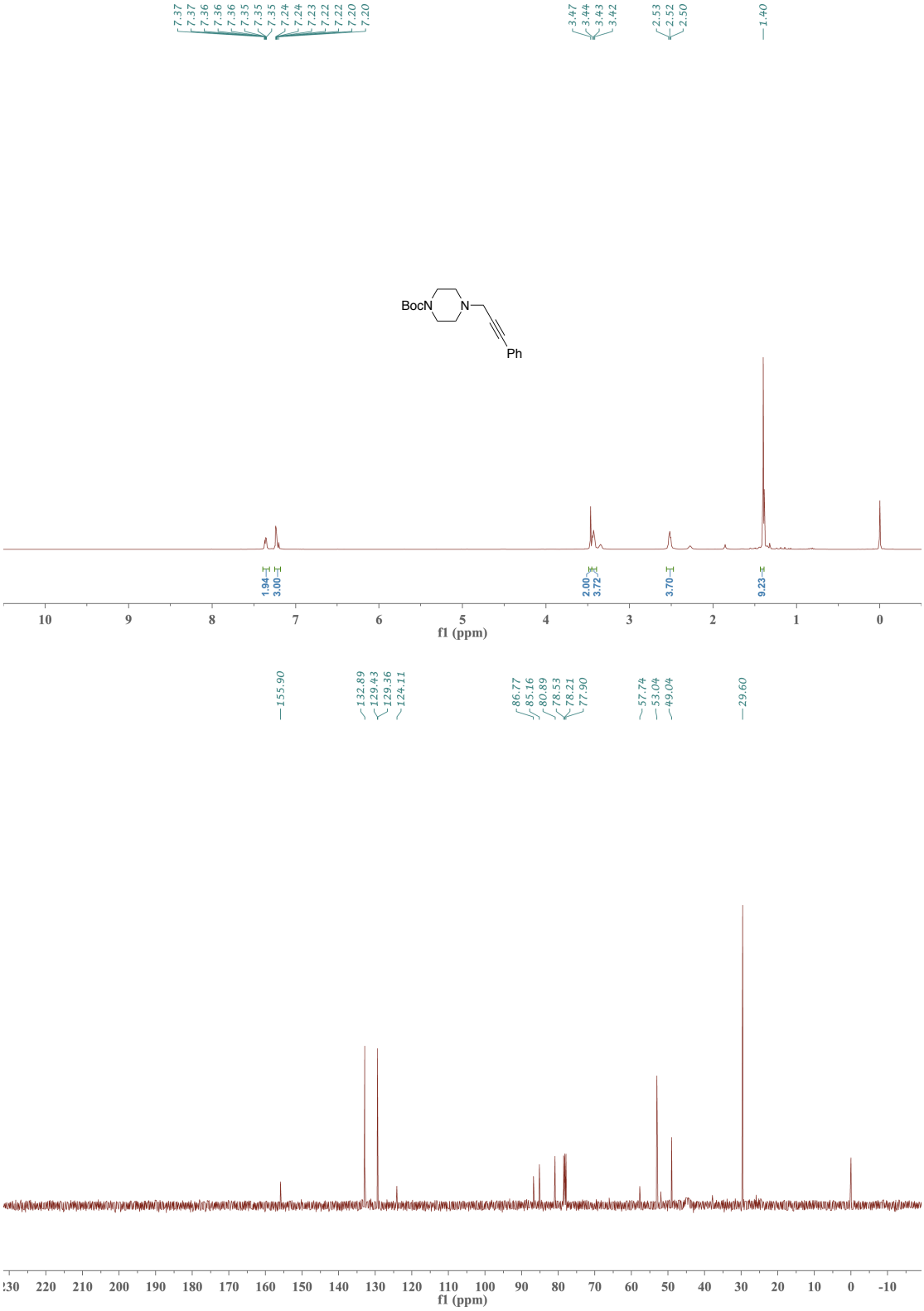


Figure S52. ^{1}H and ^{13}C NMR Spectra of *N*,*N*-Diethyl-3-phenylprop-2-yn-1-amine (**3fa**)

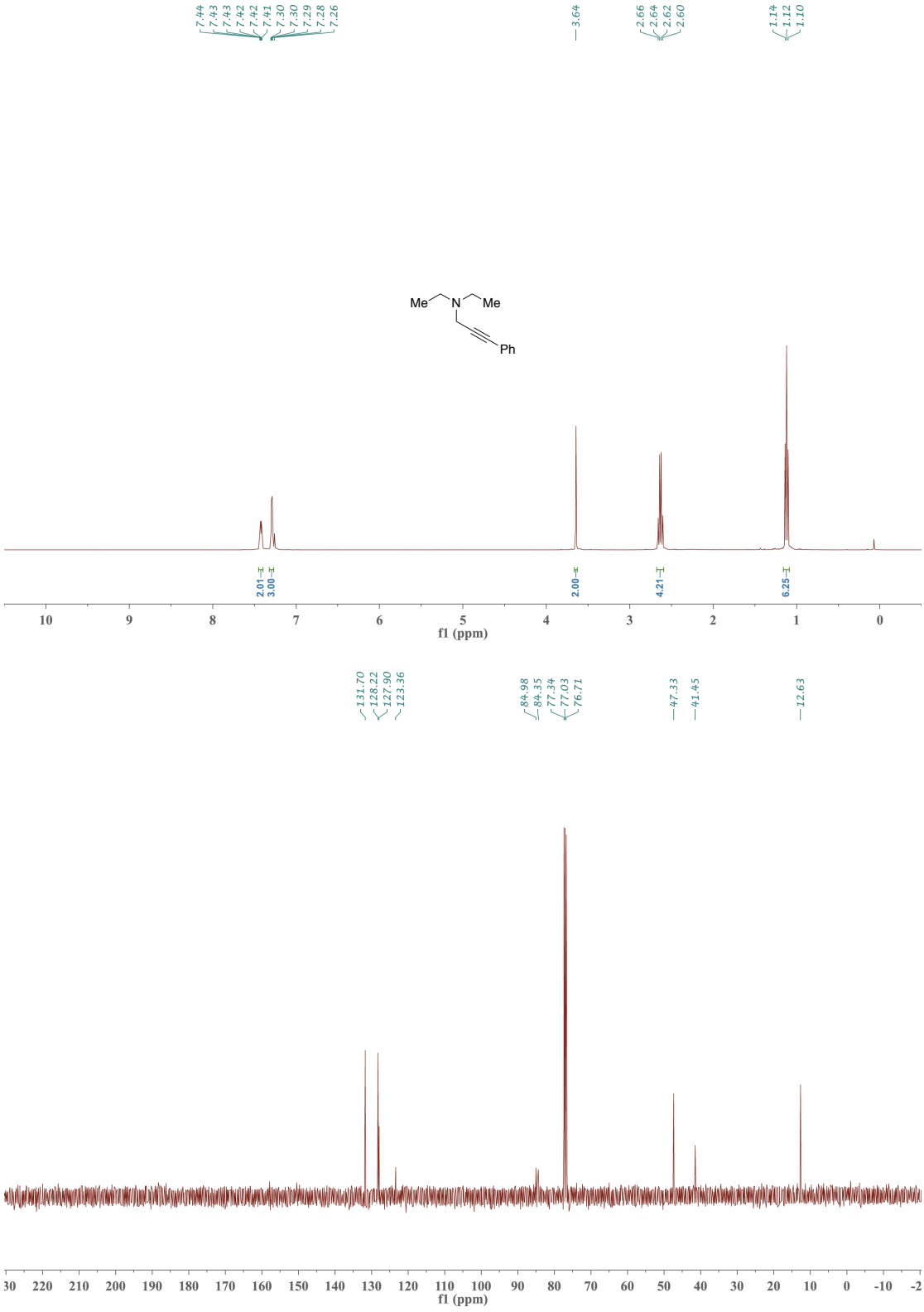


Figure S53. ^{1}H and ^{13}C NMR Spectra of *N*-Butyl-*N*-(3-phenylprop-2-yn-1-yl)butan-1-amine (**3ga**)

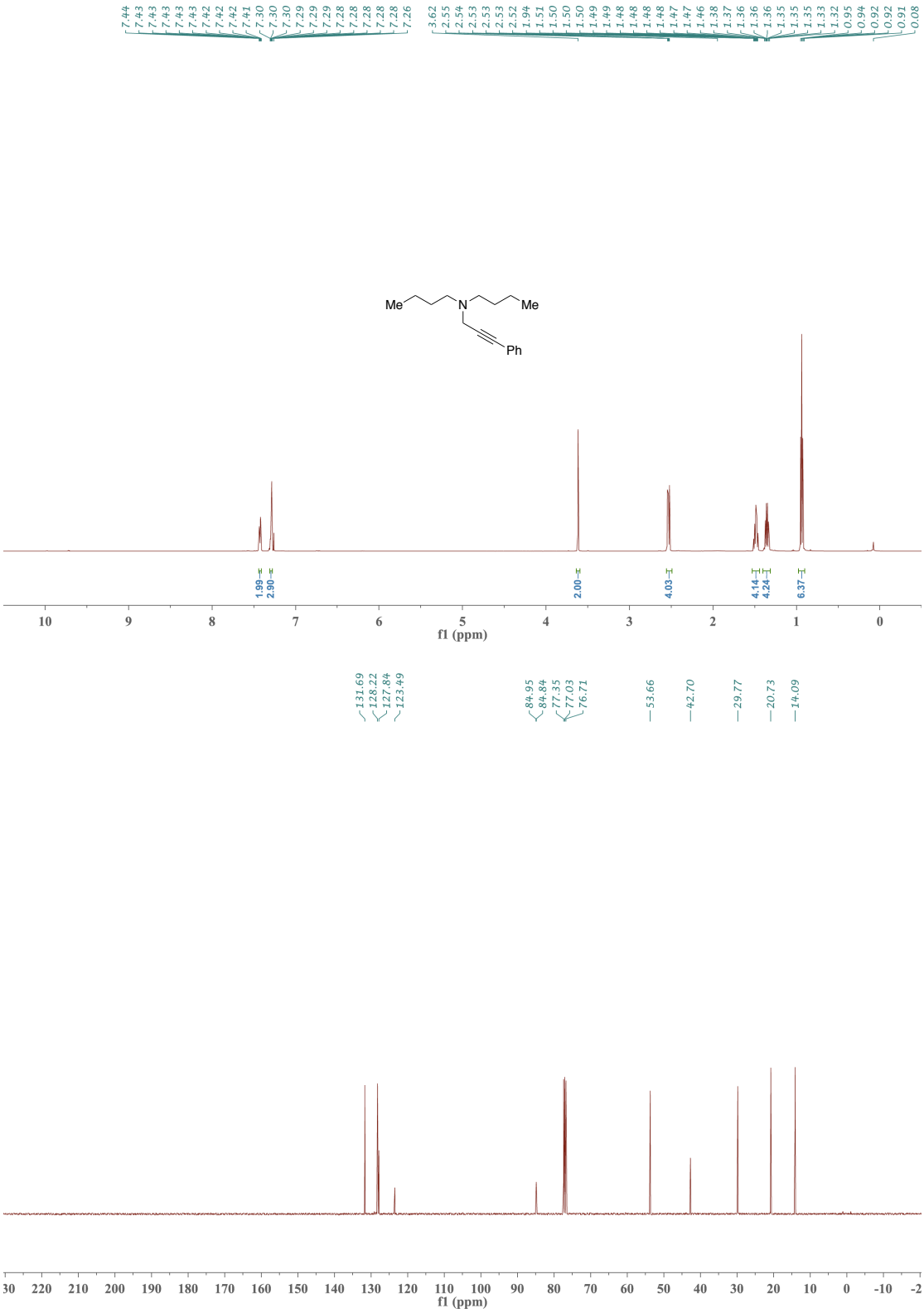


Figure S54. ^{1}H and ^{13}C NMR Spectra of *N*-Octyl-*N*-(3-phenylprop-2-yn-1-yl)octan-1-amine (**3ha**)

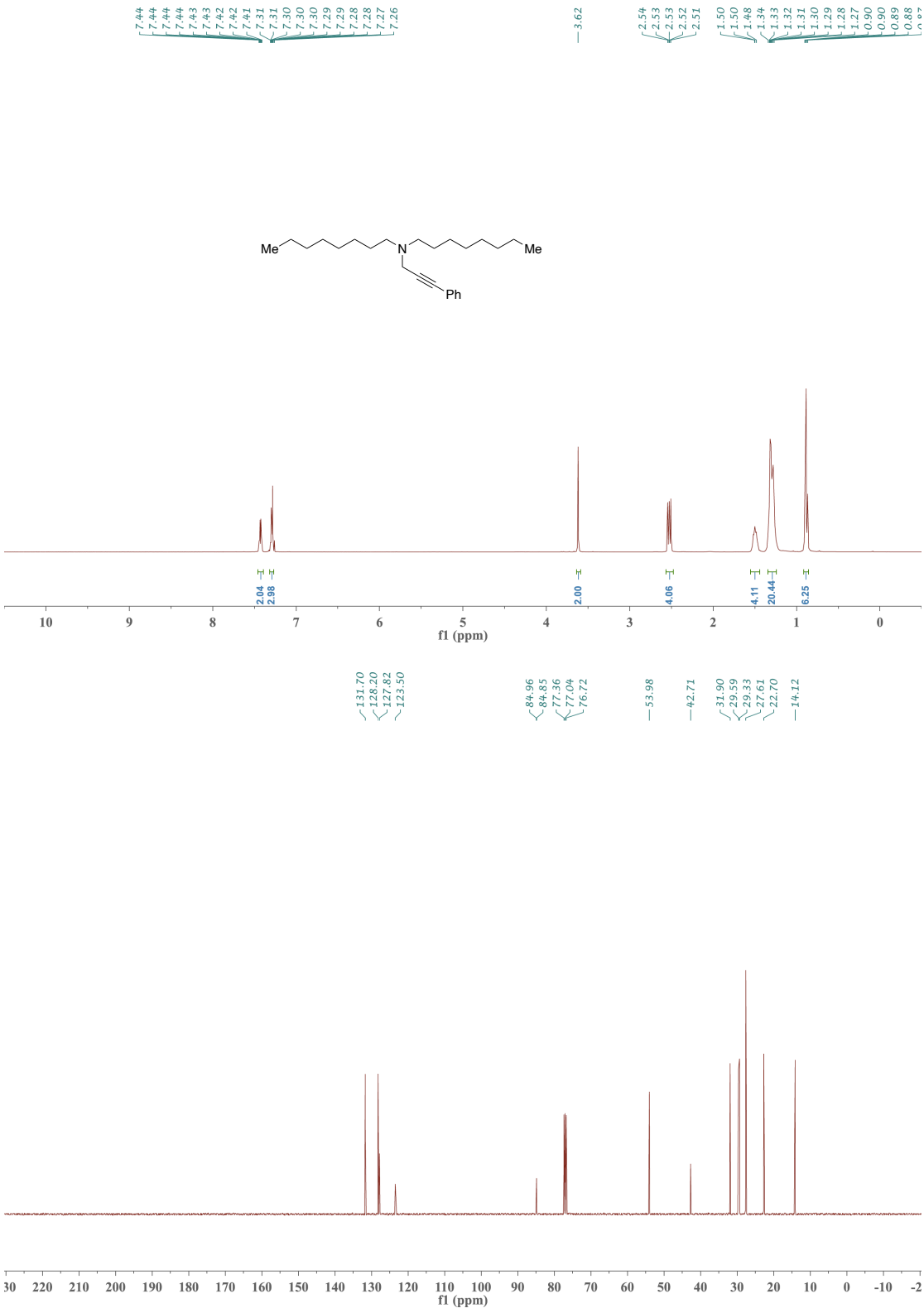


Figure S55. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-methyl-3-phenylprop-2-yn-1-amine (**3ia**)

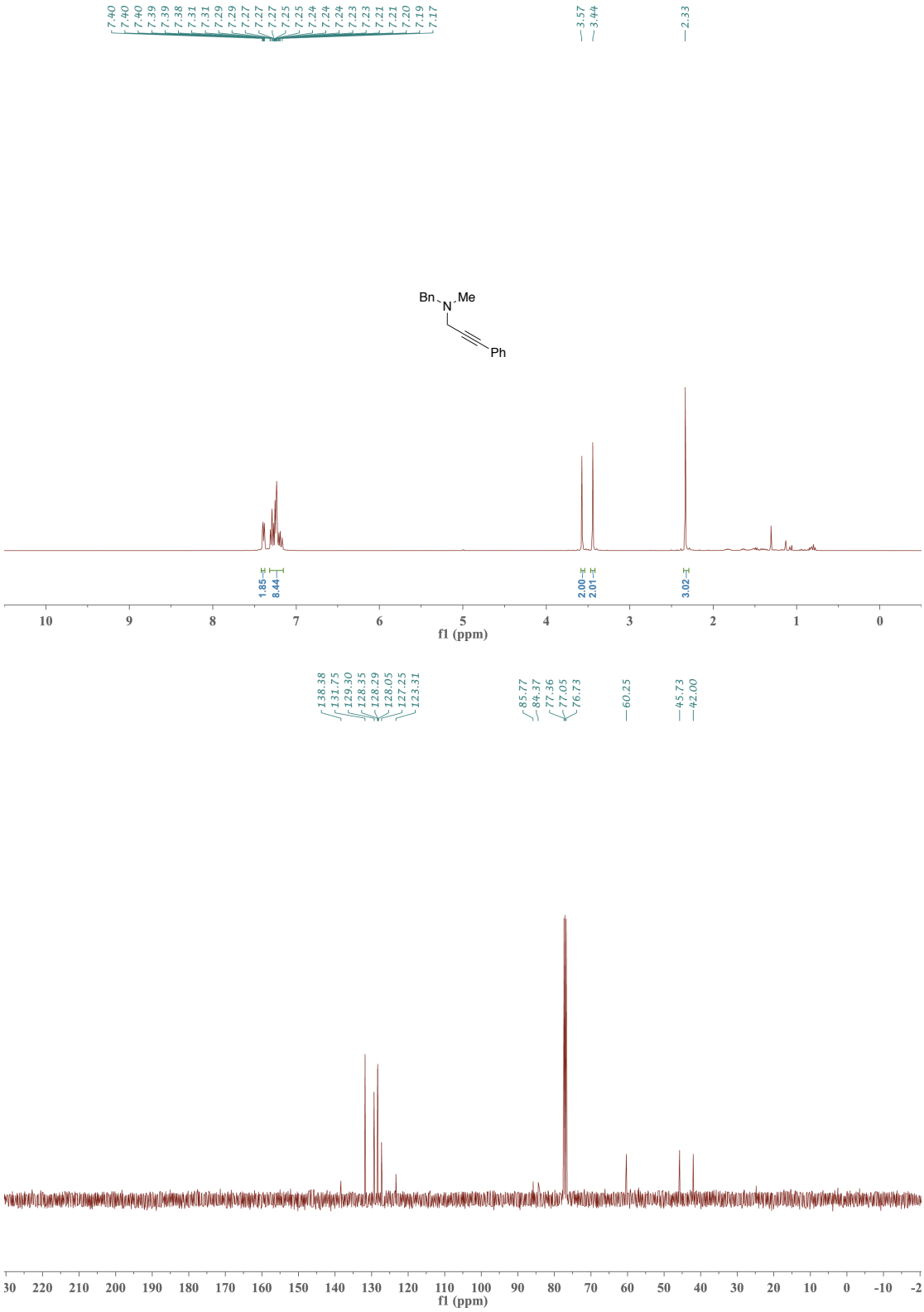


Figure S56. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)cyclopentanamine (**3ja**)

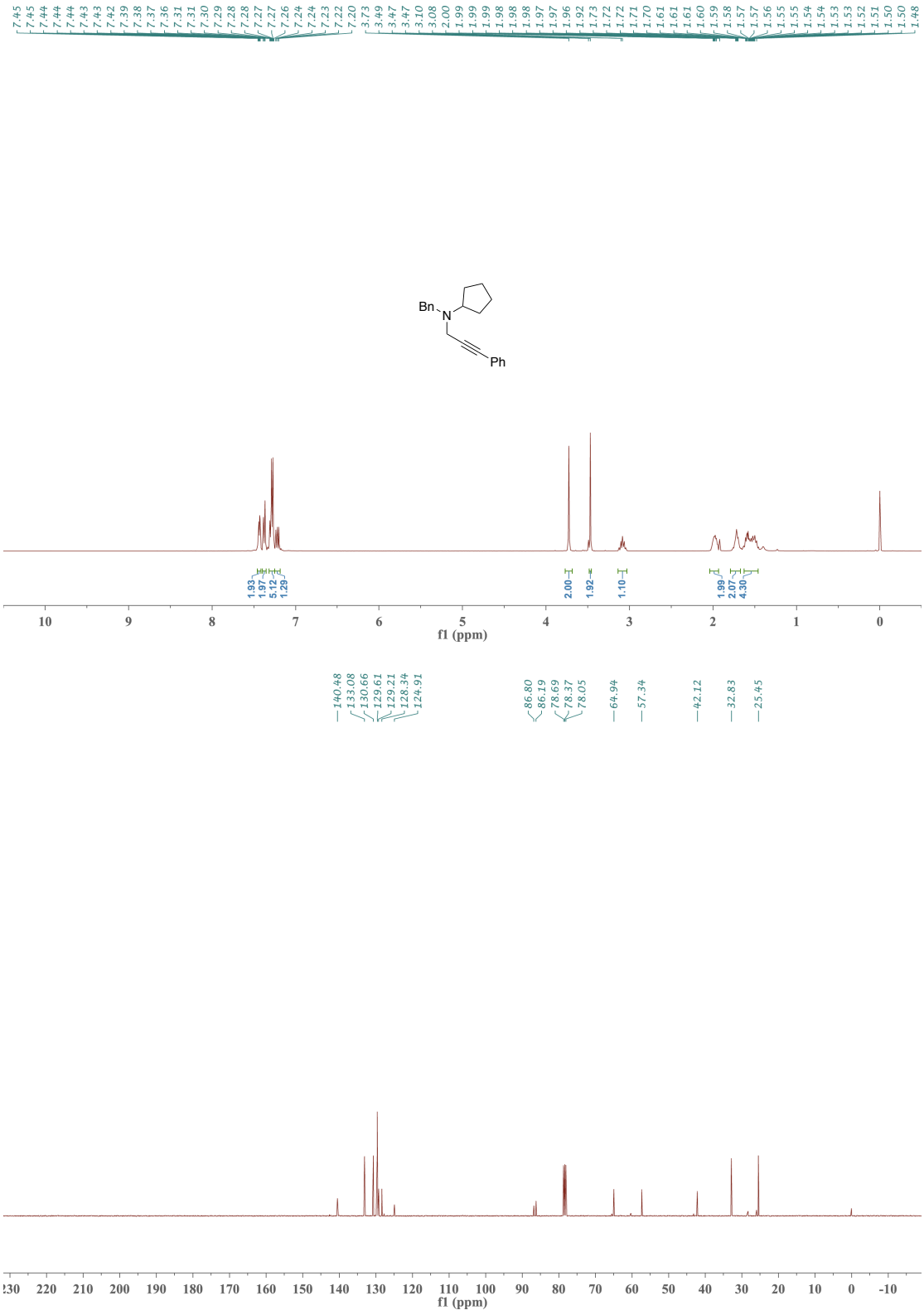


Figure S57. ^{1}H and ^{13}C NMR Spectra of *N*-Ethyl-*N*-(3-phenylprop-2-yn-1-yl)cyclohexanamine (**3ka**)

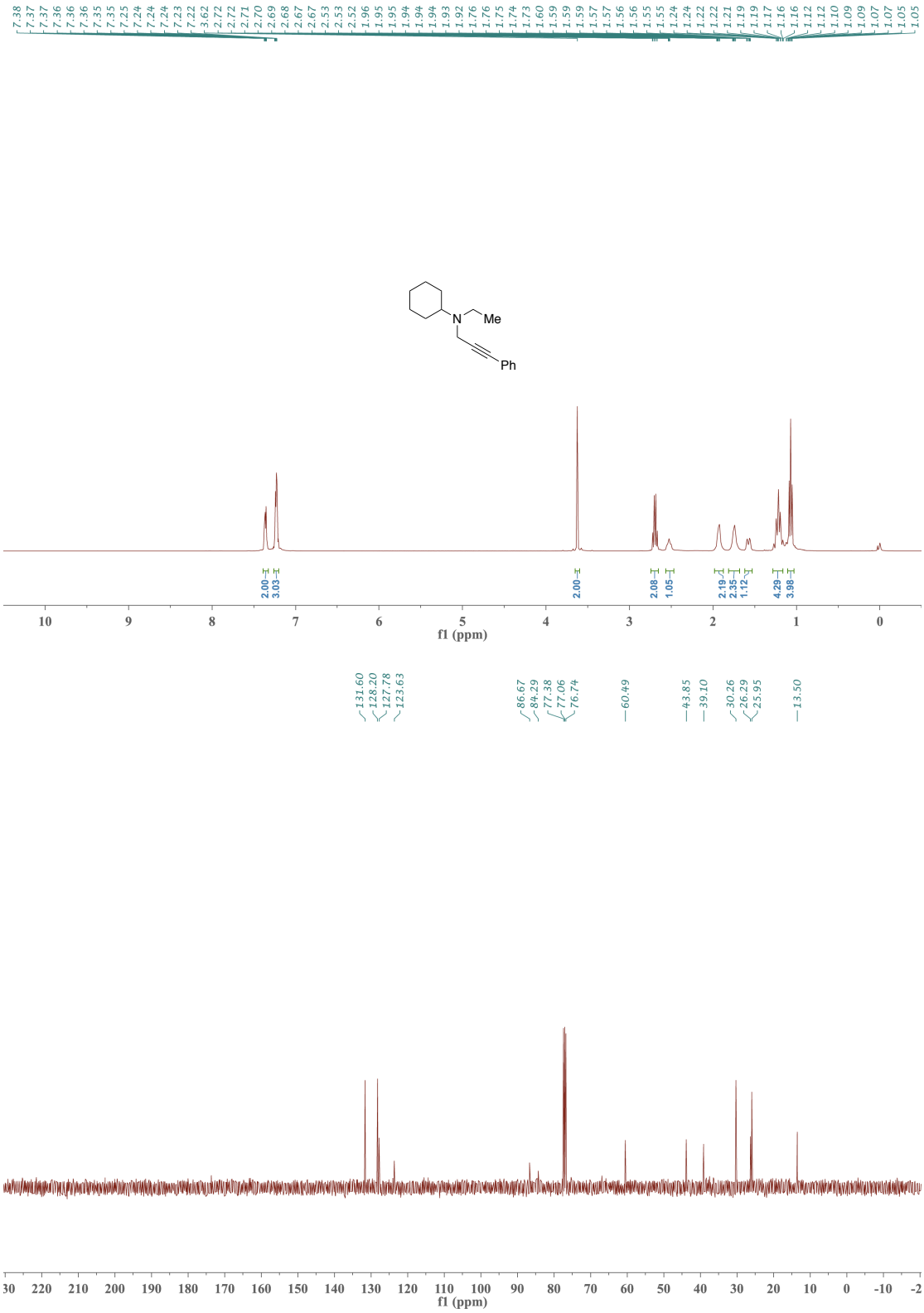


Figure S58. ^{1}H and ^{13}C NMR Spectra of Methyl 5-(Benzyl(3-phenylprop-2-yn-1-yl)amino)pentanoate (**3la**)

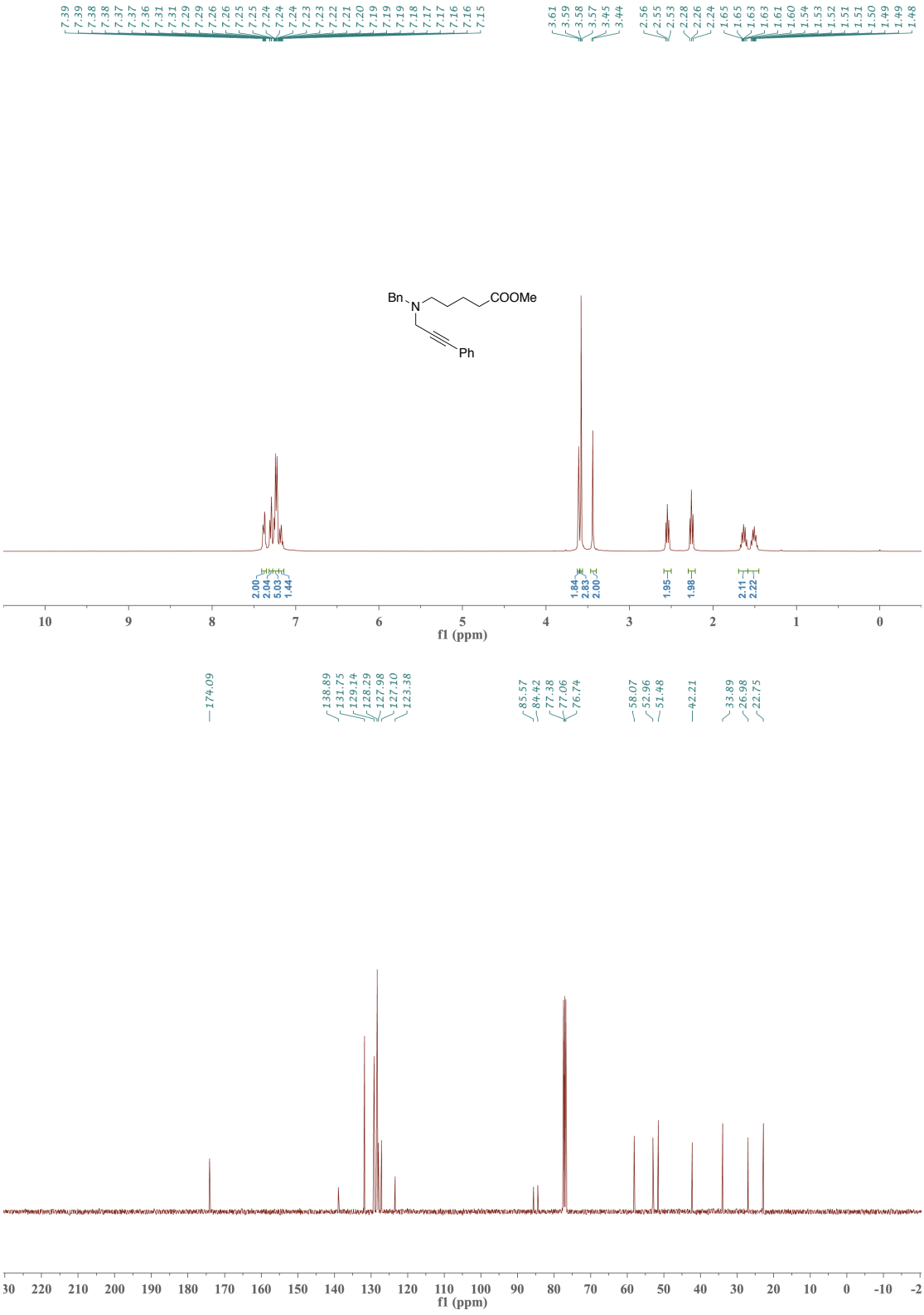


Figure S59. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-(2-fluoroethyl)-3-phenylprop-2-yn-1-amine (**3ma**)

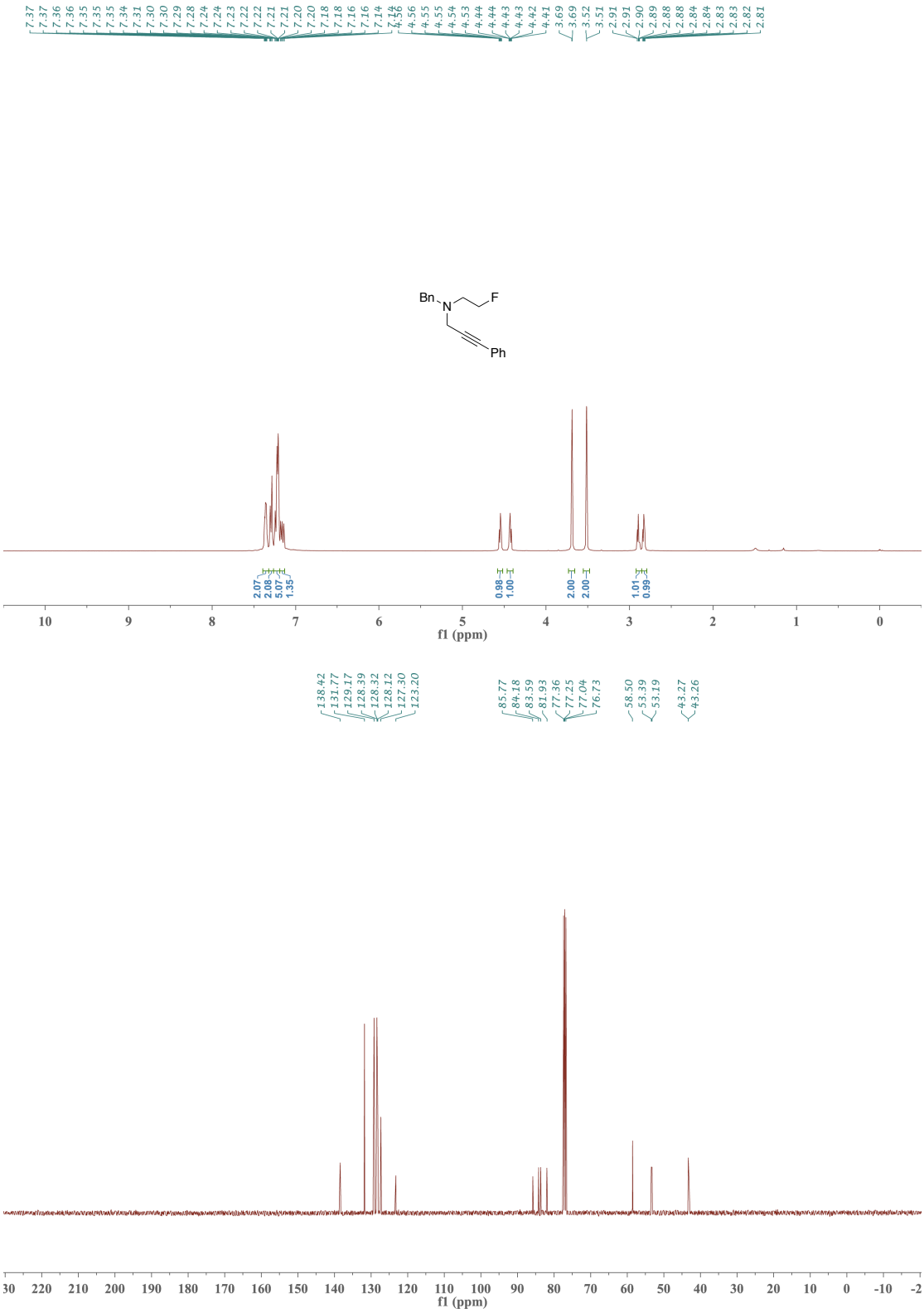


Figure S60. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-3-phenyl-*N*-(3-phenylpropyl)prop-2-yn-1-amine (**3na**)

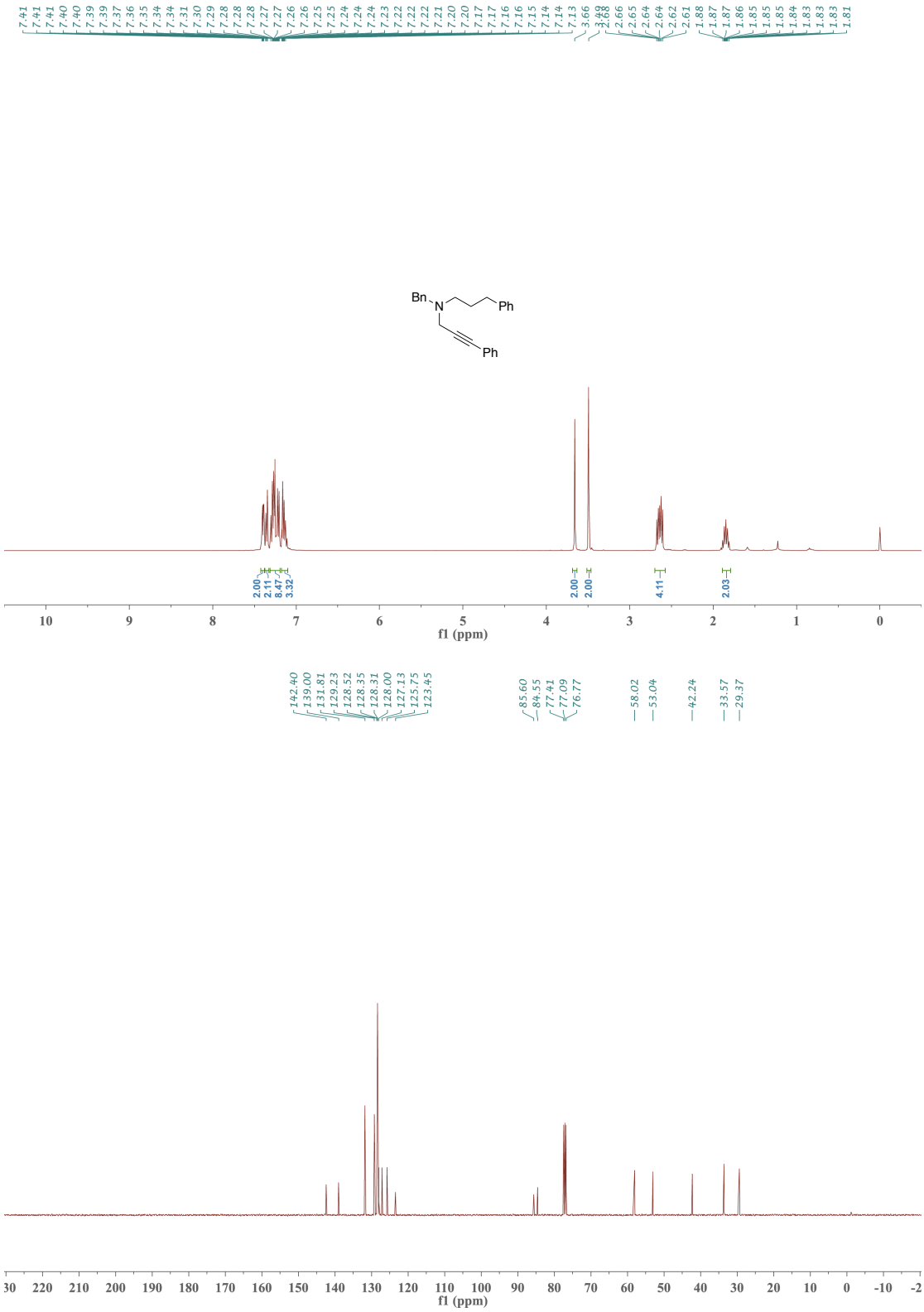


Figure S61. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-(cyclobutylmethyl)-3-phenylprop-2-yn-1-amine (**3oa**)

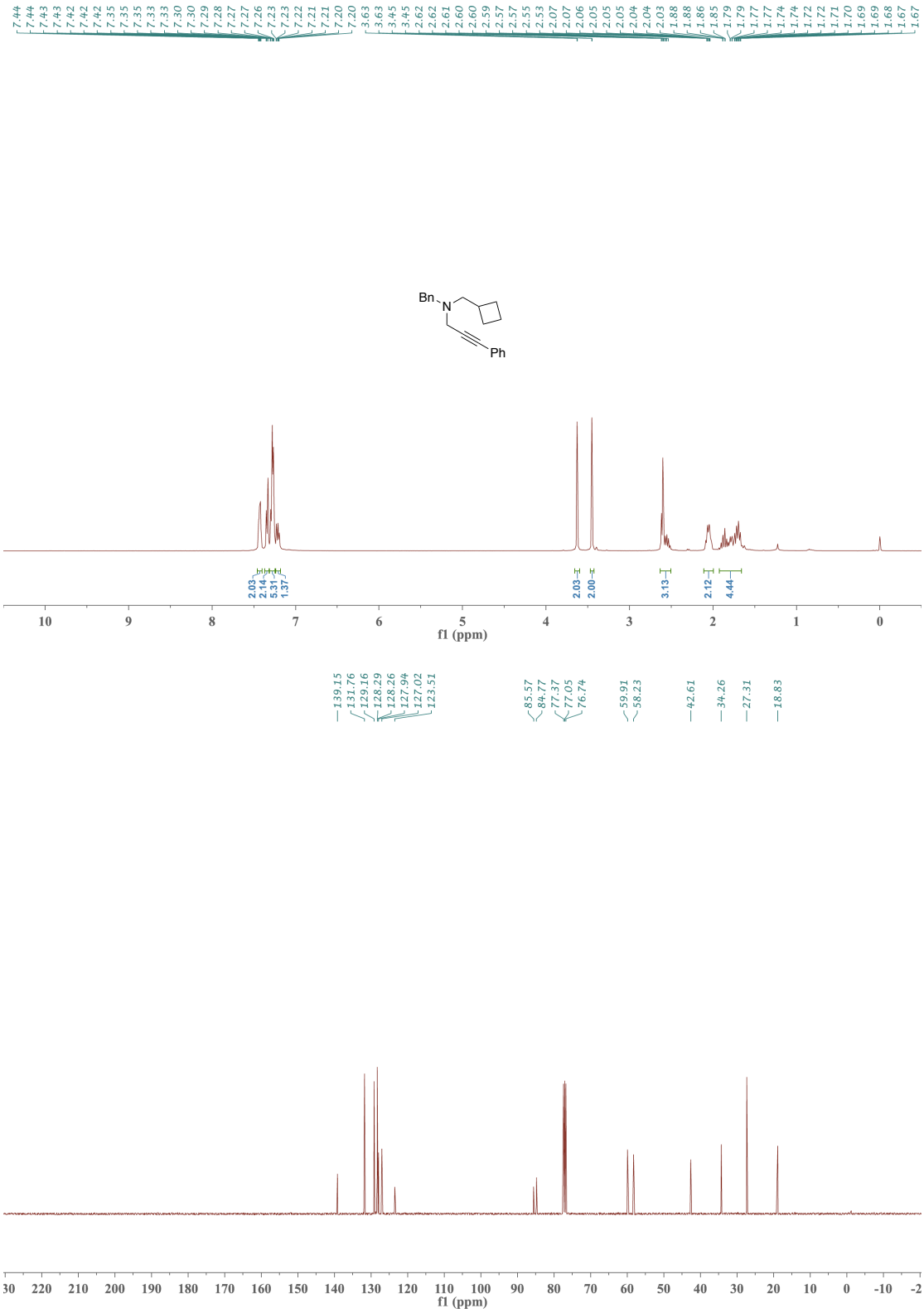


Figure S62. ^{1}H and ^{13}C NMR Spectra of *N*-(2-(1,3-Dioxan-2-yl)ethyl)-*N*-benzyl-3-phenylprop-2-yn-1-amine (**3pa**)

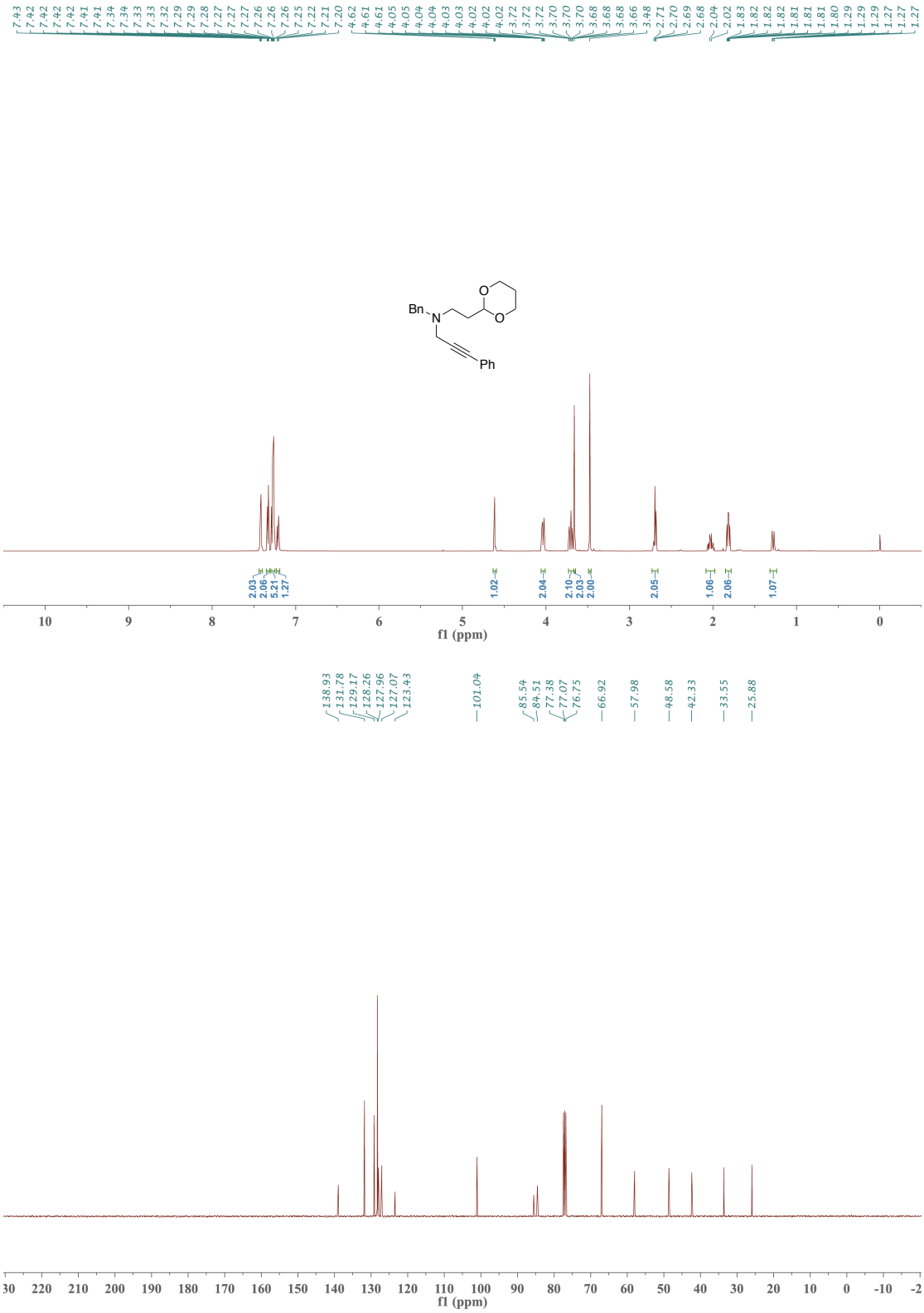


Figure S63. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (**3qa**)

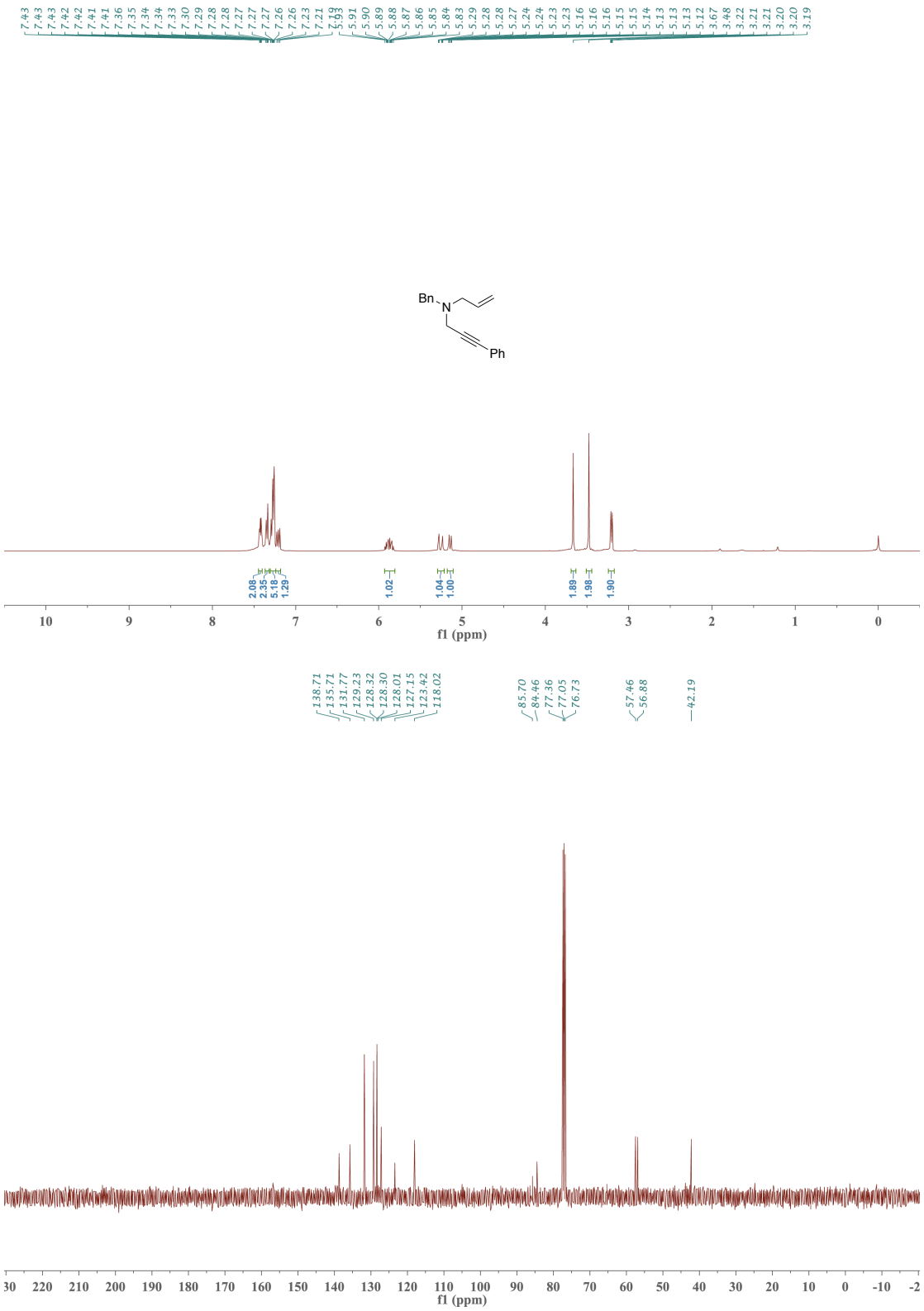


Figure S64. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)cyclohex-2-en-1-amine (**3ra**)

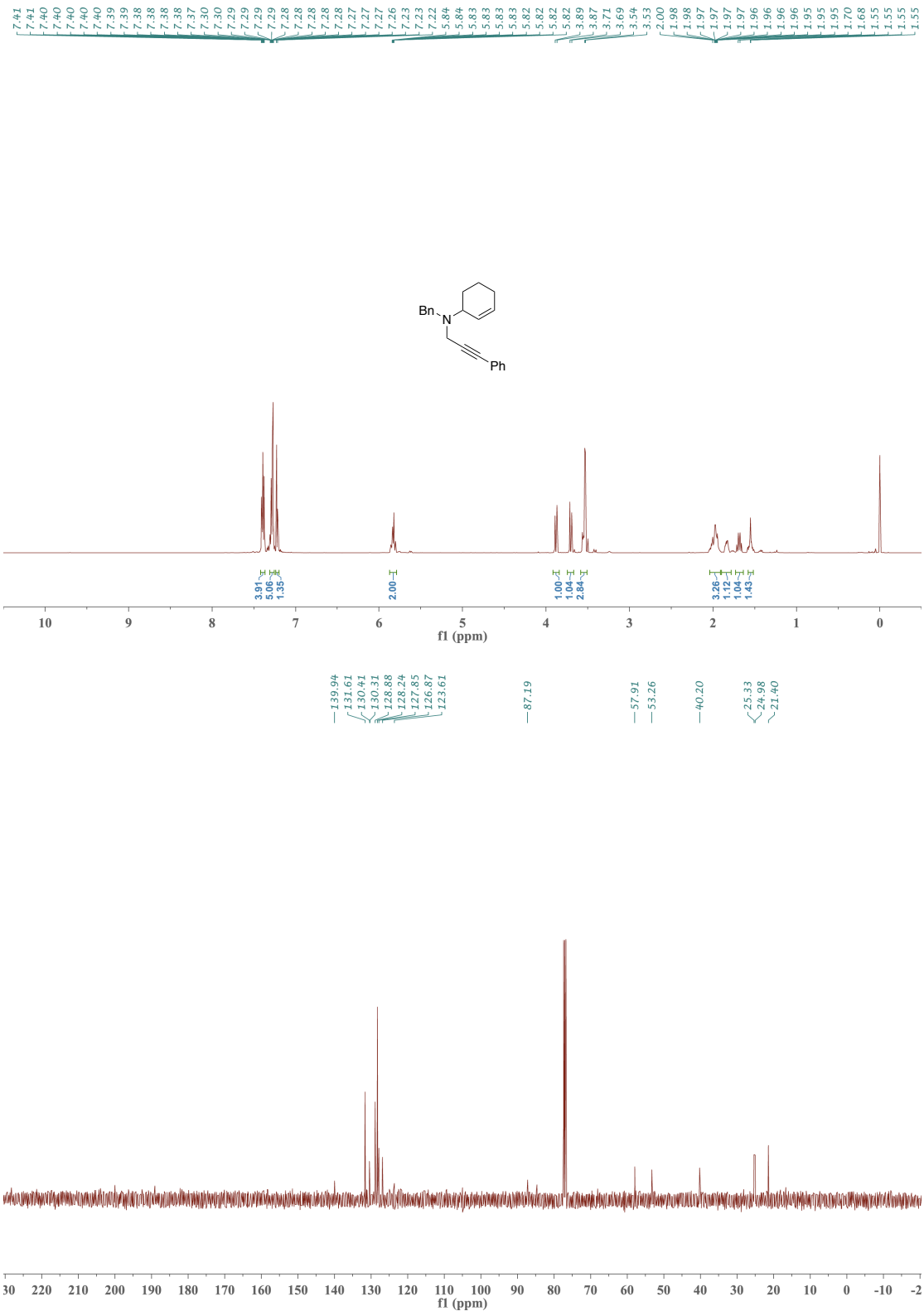


Figure S65. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-3-phenyl-*N*-(prop-2-yn-1-yl)prop-2-yn-1-amine (**3sa**)

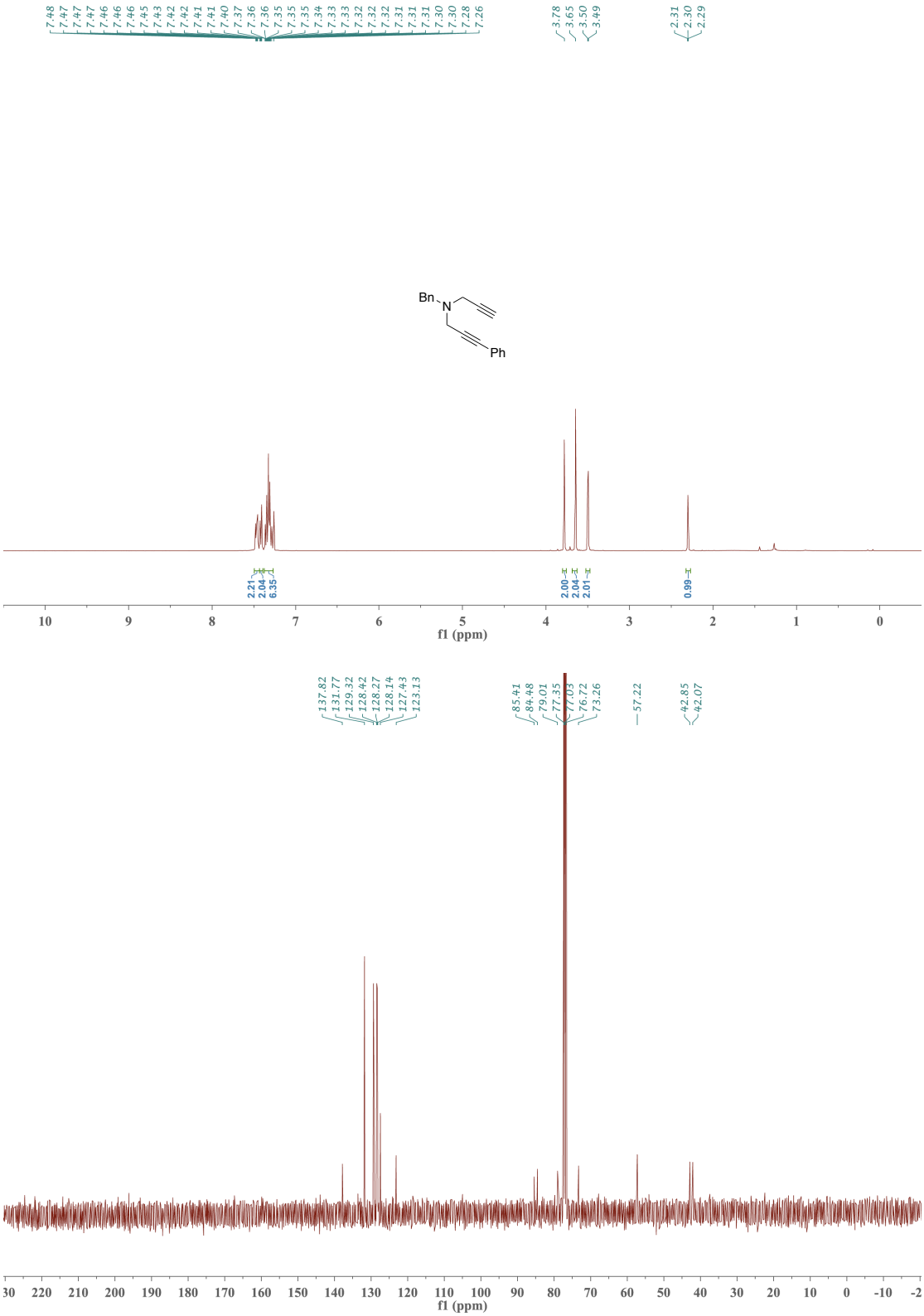


Figure S66. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-*N*-(3-phenylprop-2-yn-1-yl)but-3-yn-1-amine (**3ta**)

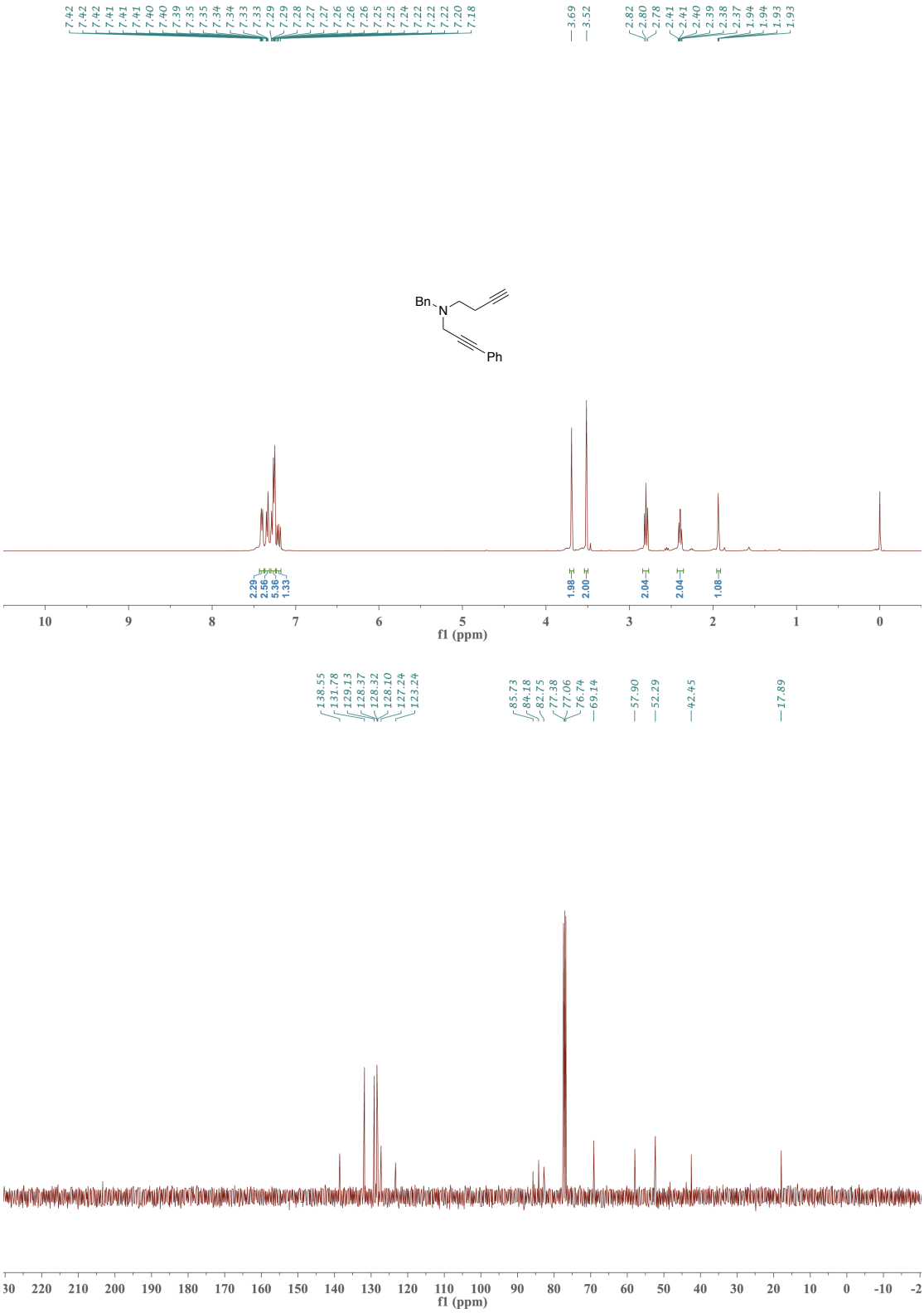


Figure S67. ^{1}H and ^{13}C NMR Spectra of 1-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)piperidine (**3ab**)

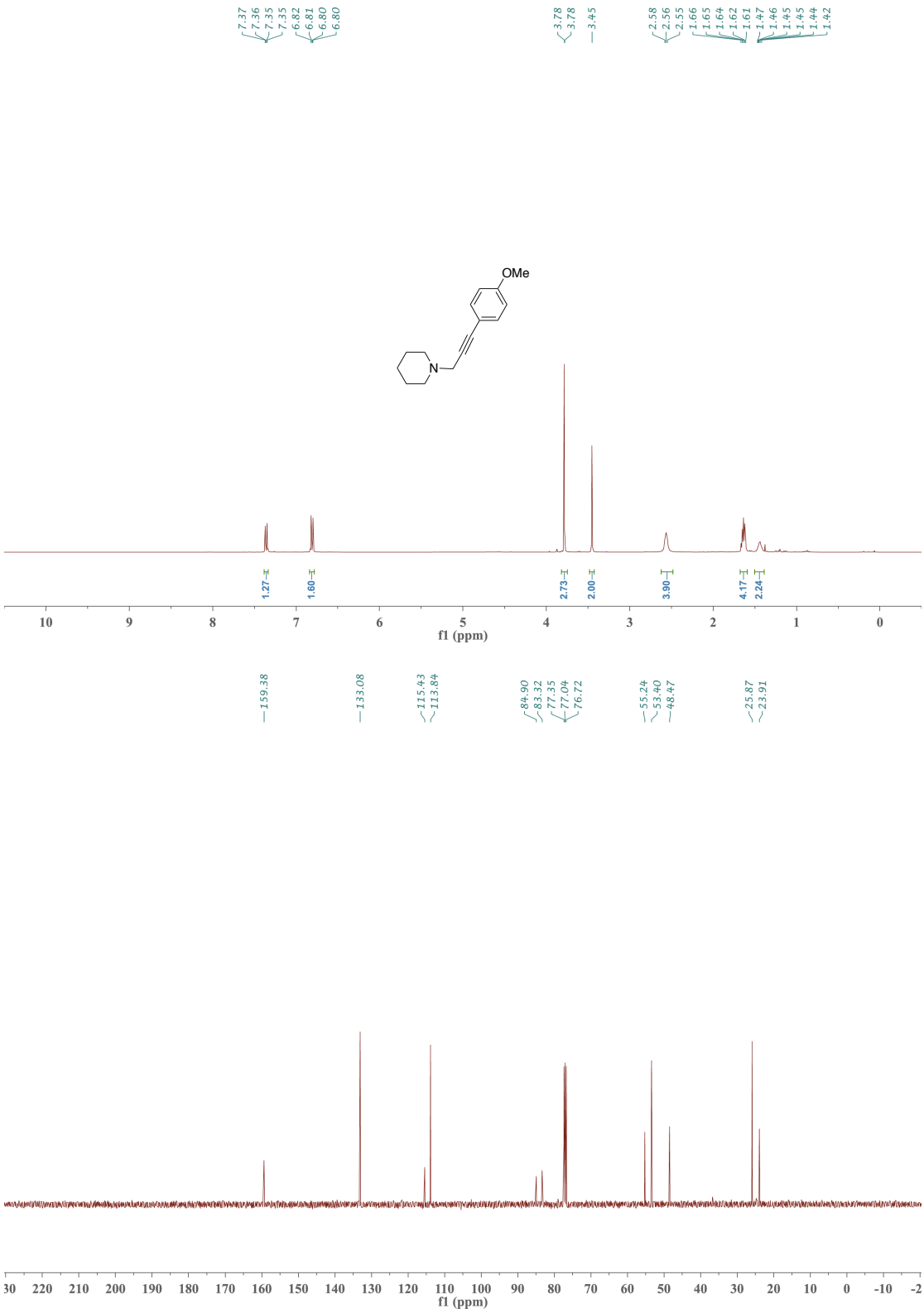


Figure S68. ^{1}H and ^{13}C NMR Spectra of 1-(3-(4-(*tert*-Butyl)phenyl)prop-2-yn-1-yl)piperidine (**3ac**)

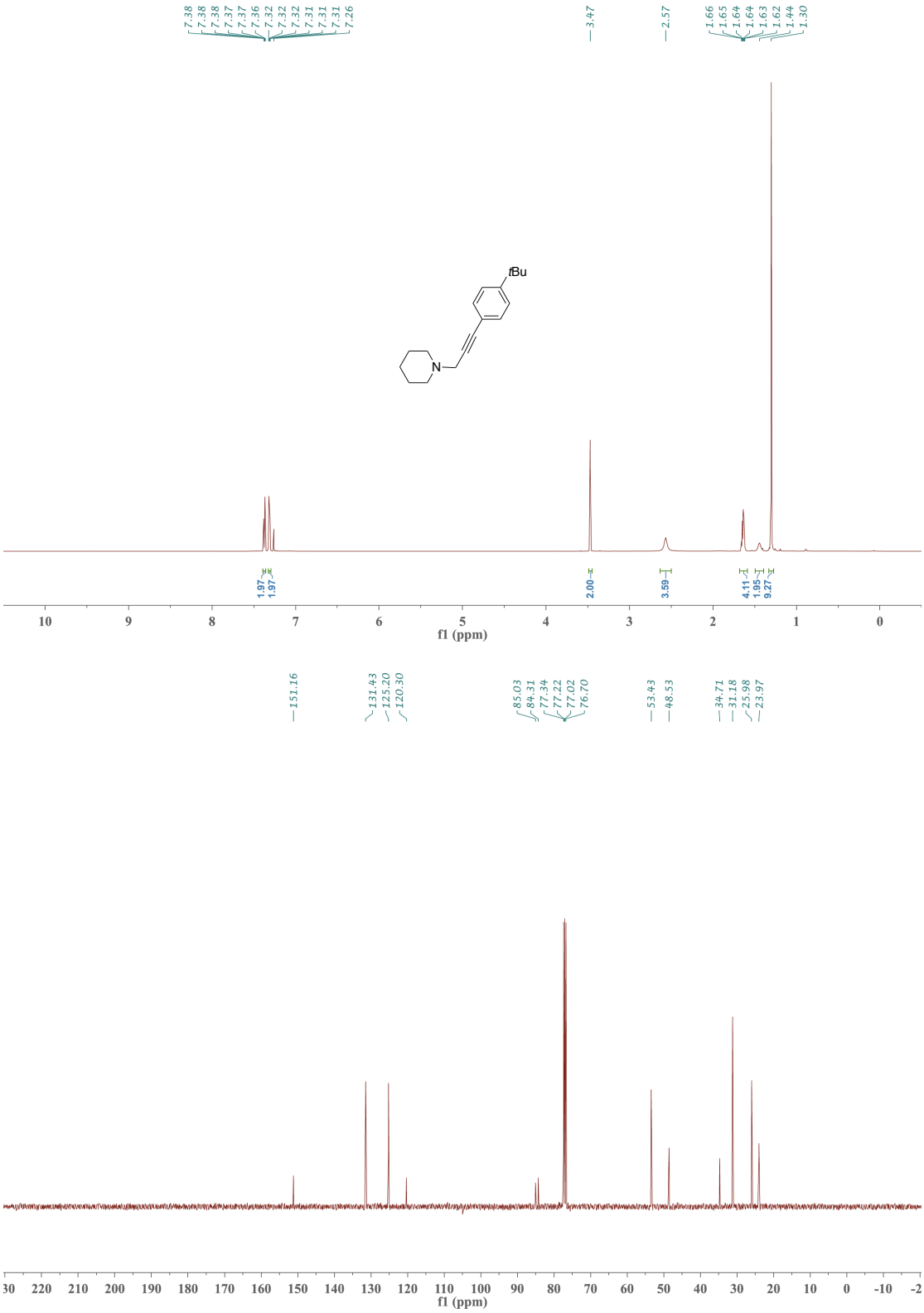


Figure S69. ^{1}H and ^{13}C NMR Spectra of 1-(3-(*p*-Tolyl)prop-2-yn-1-yl)piperidine (**3ad**)

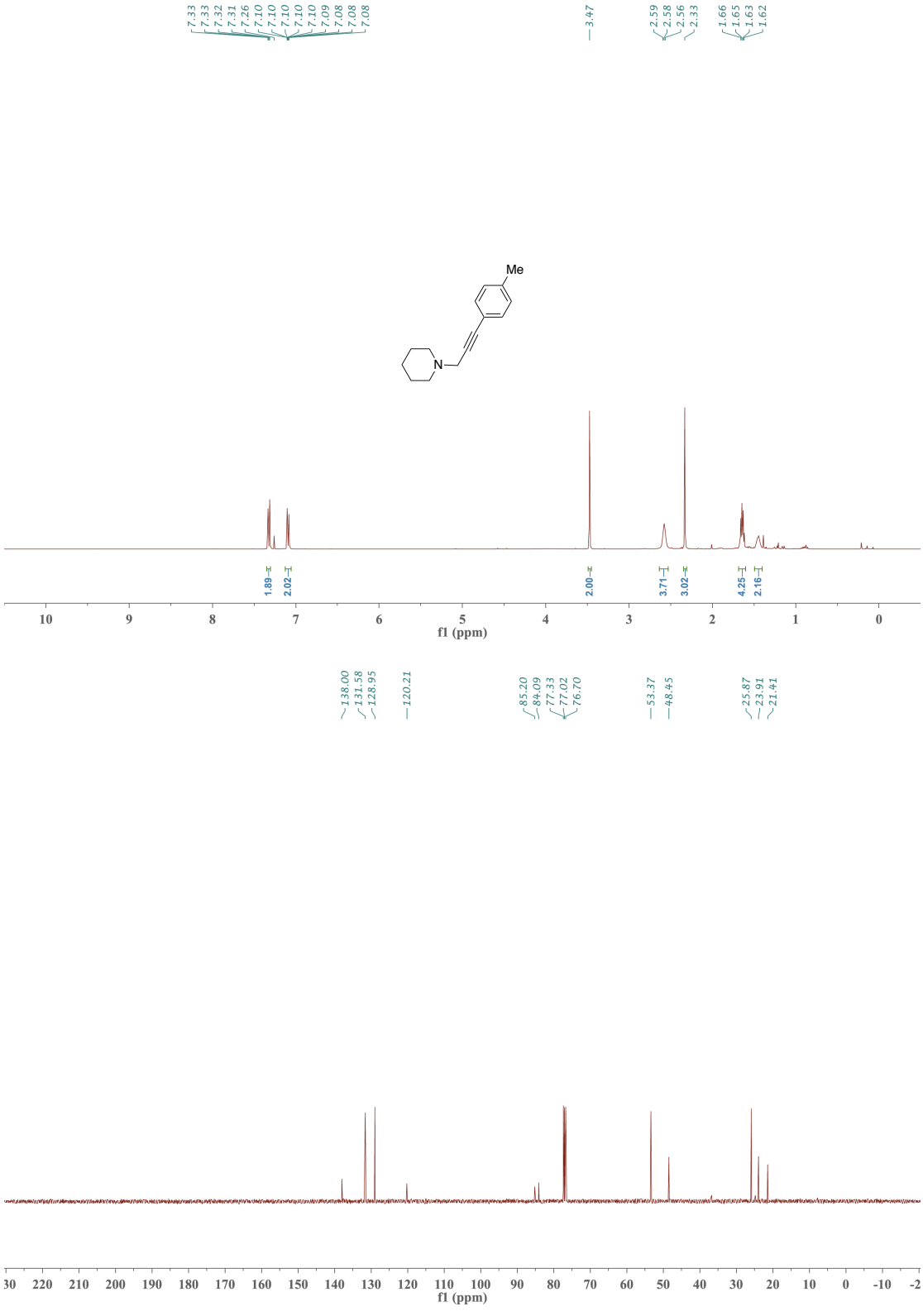


Figure S70. ^{1}H and ^{13}C NMR Spectra of 1-(3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-yl)piperidine (**3ae**)

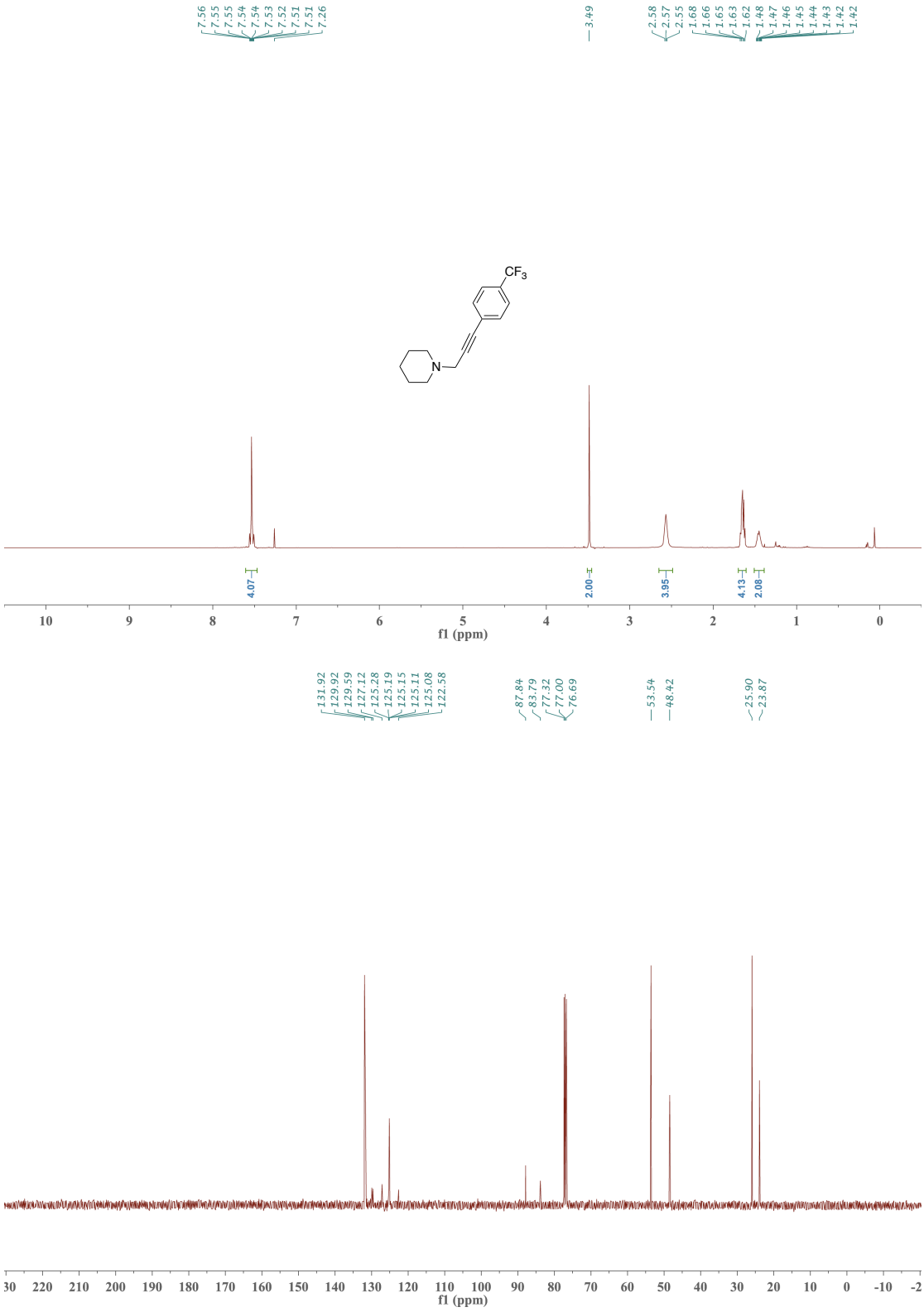


Figure S71. ^{1}H and ^{13}C NMR Spectra of 1-(3-(4-Fluorophenyl)prop-2-yn-1-yl)piperidine (**3af**)

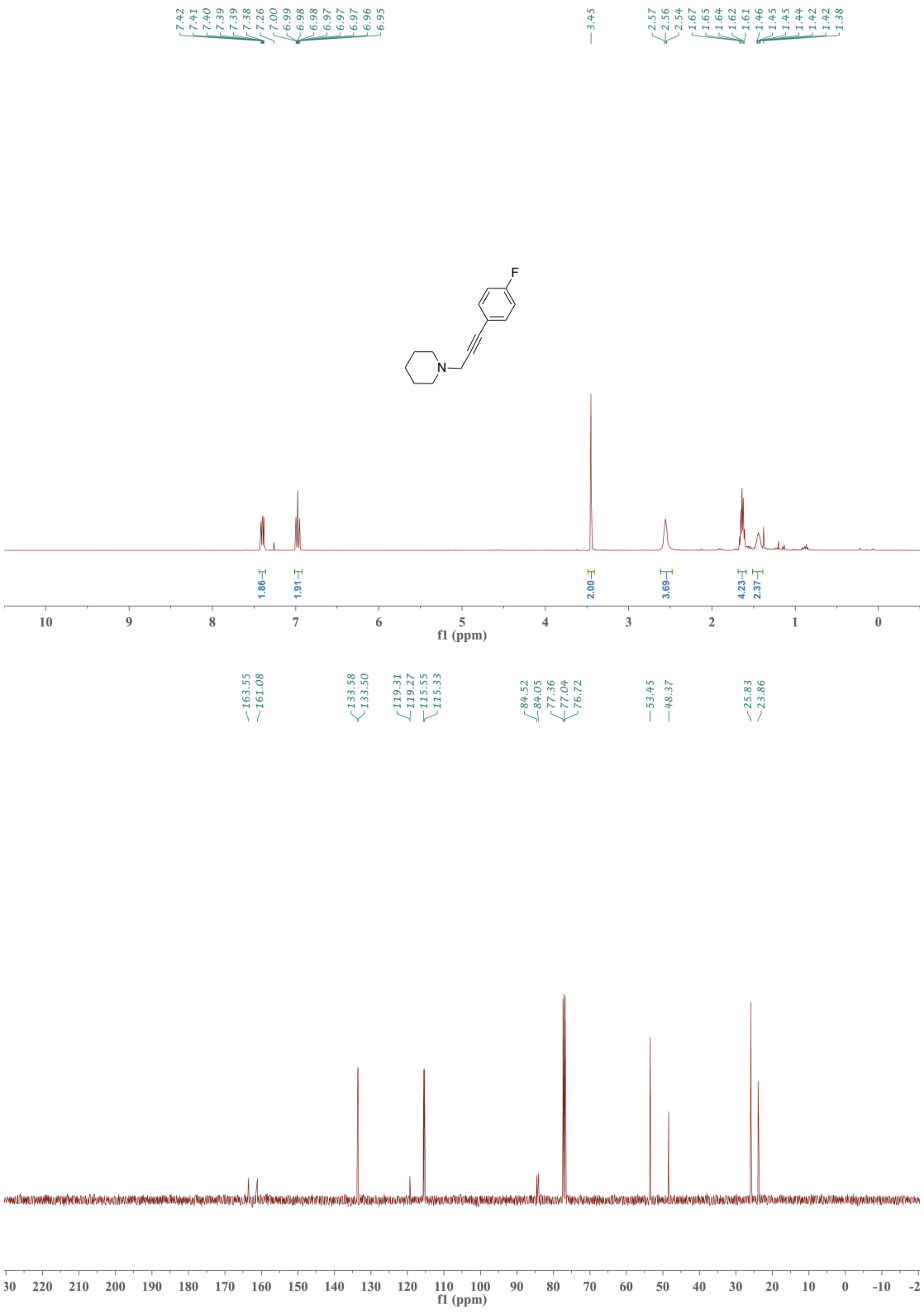


Figure S72. ^{1}H and ^{13}C NMR Spectra of 1-(3-(4-Bromophenyl)prop-2-yn-1-yl)piperidine (**3ag**)

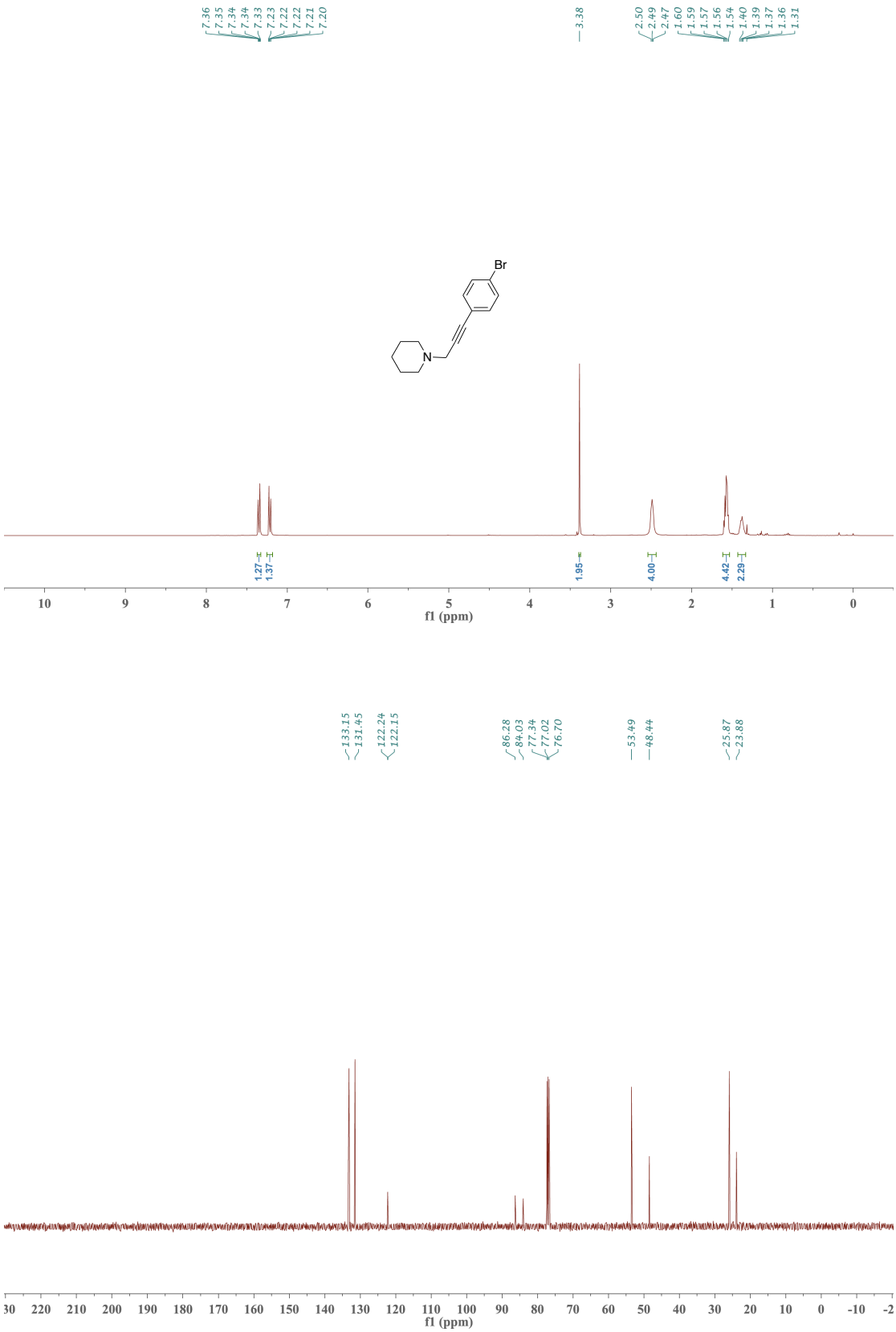


Figure S73. ^{1}H and ^{13}C NMR Spectra of 1-(3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)piperidine (**3ah**)

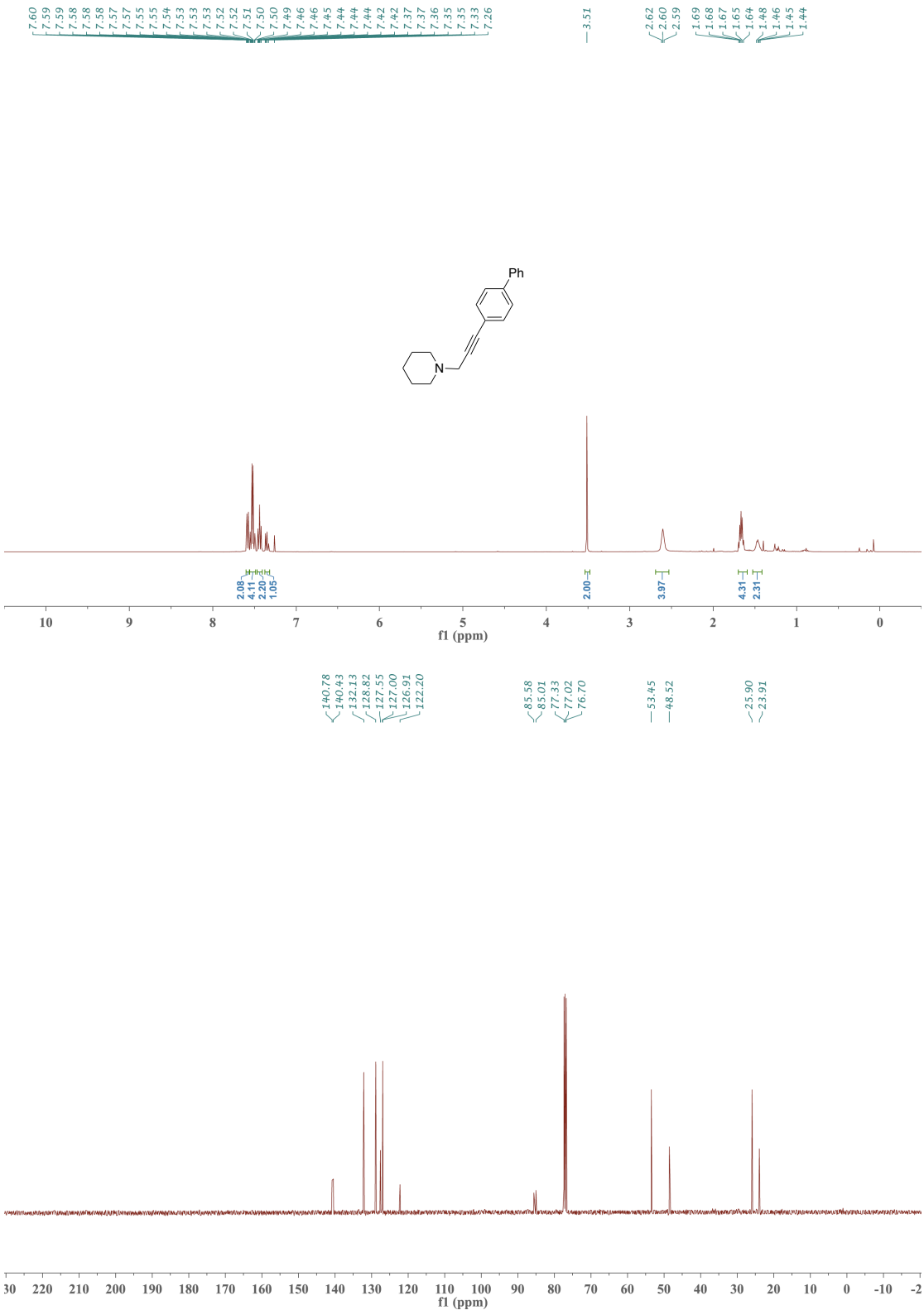


Figure S74. ^{1}H and ^{13}C NMR Spectra of 1-(3-(2-Chlorophenyl)prop-2-yn-1-yl)piperidine (**3ai**)

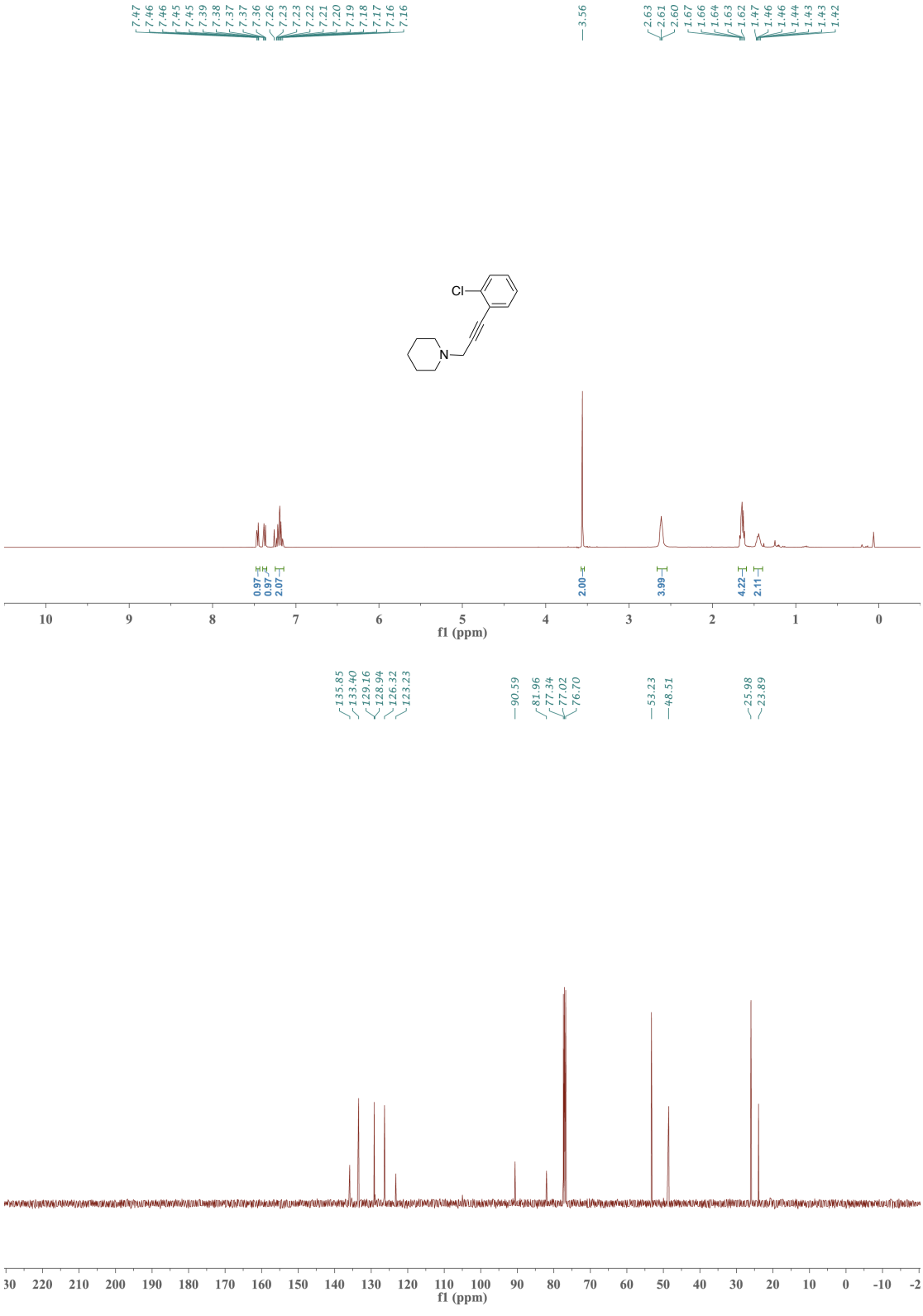


Figure S75. ^{1}H and ^{13}C NMR Spectra of 1-(3-(3-Chlorophenyl)prop-2-yn-1-yl)piperidine (**3aj**)

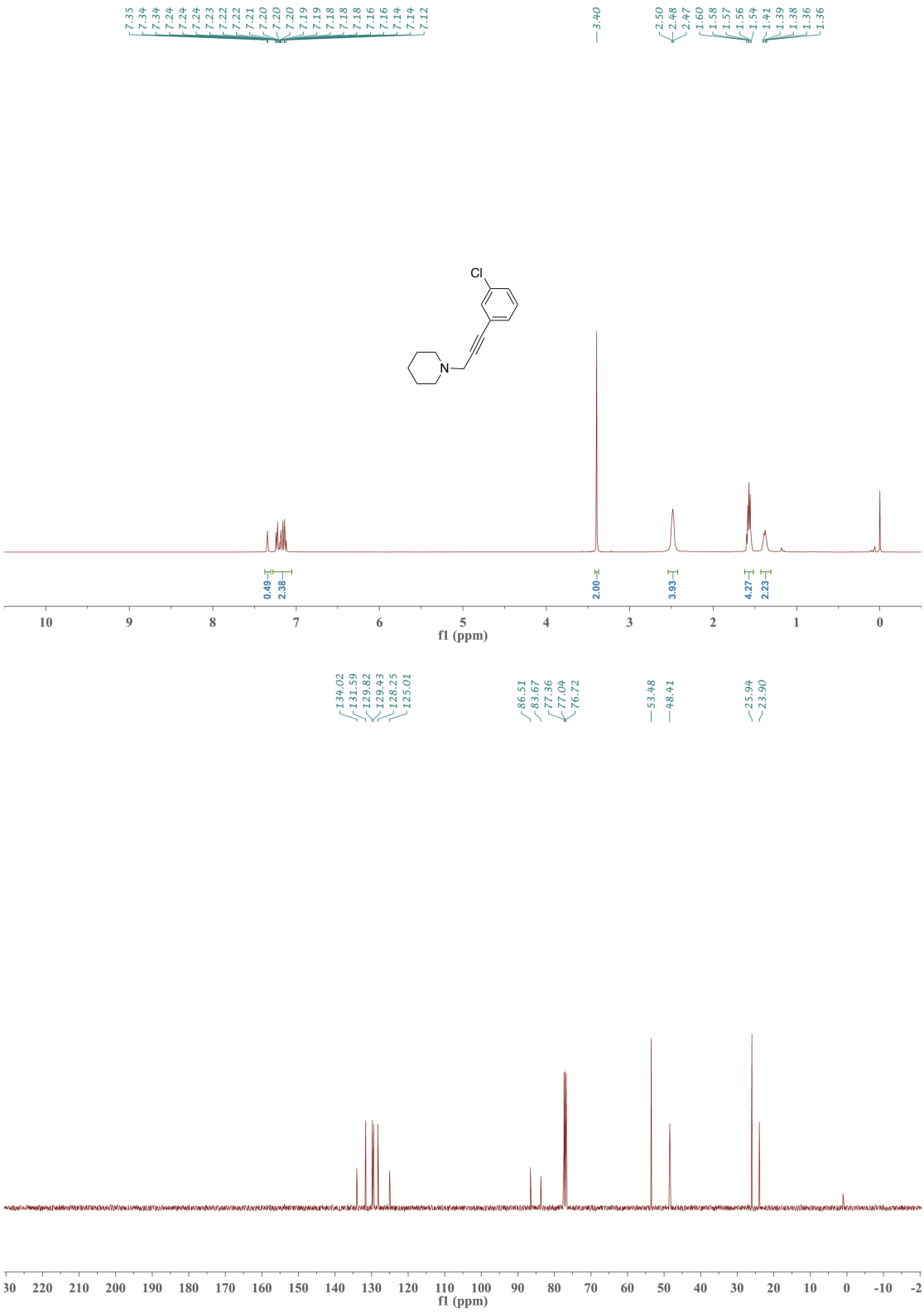


Figure S76. ^{1}H and ^{13}C NMR Spectra of 1-(3-(6-Methoxynaphthalen-2-yl)prop-2-yn-1-yl)piperidine (**3ak**)

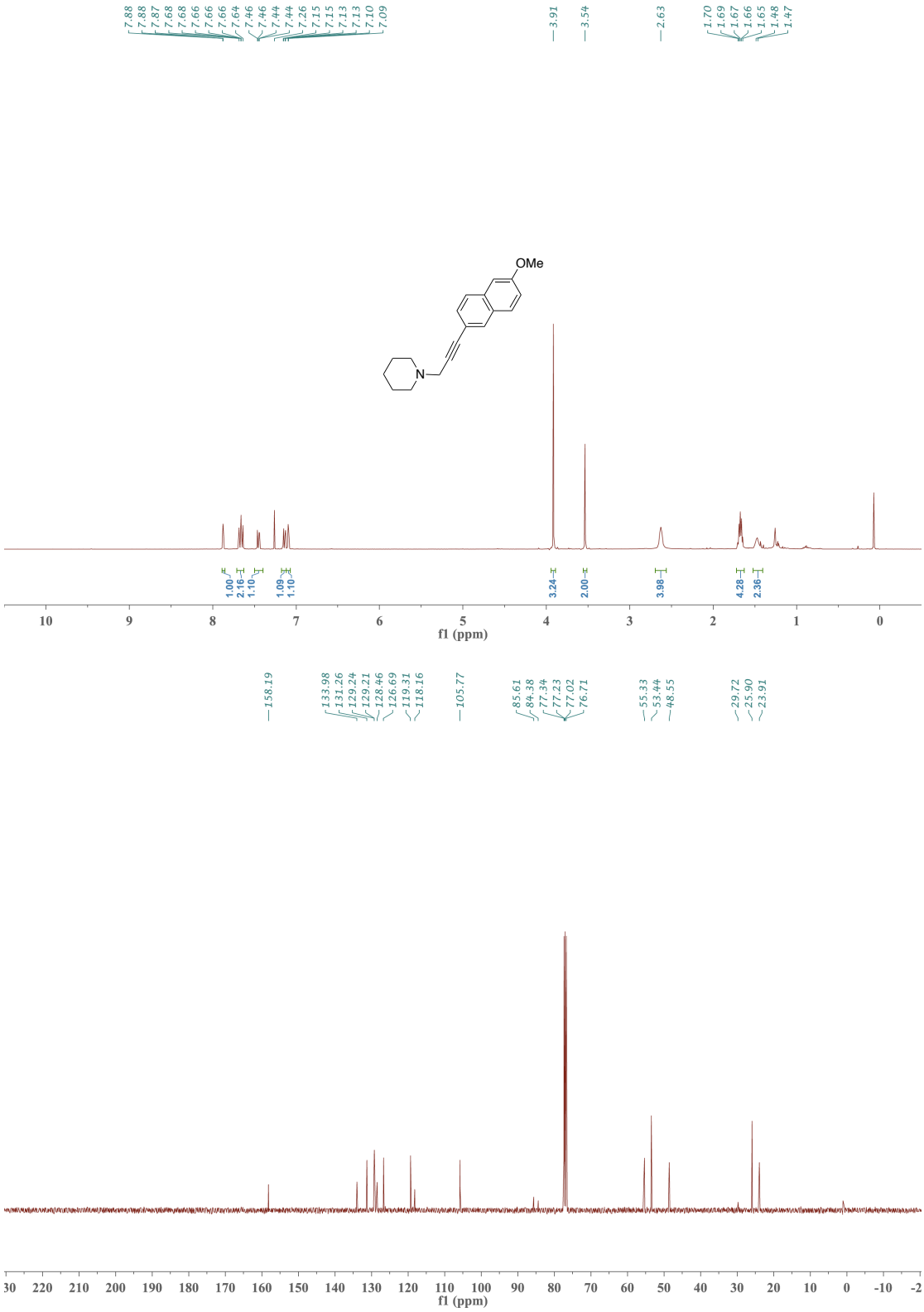


Figure S77. ^{1}H and ^{13}C NMR Spectra of 3-(3-(Piperidin-1-yl)prop-1-yn-1-yl)pyridine (**3al**)

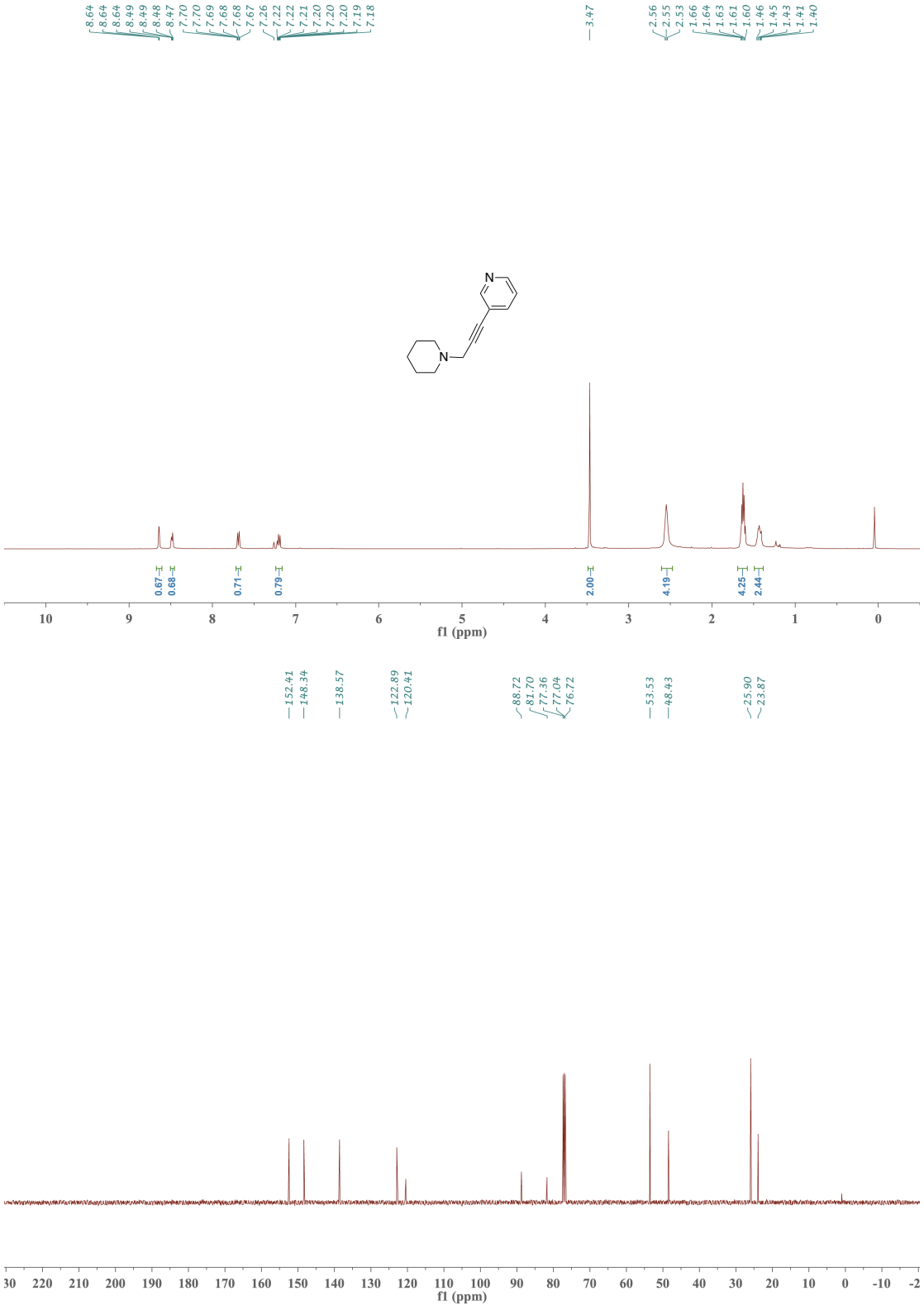


Figure S78. ^{1}H and ^{13}C NMR Spectra of 1-(5-Phenylpent-2-yn-1-yl)piperidine (**3am**)

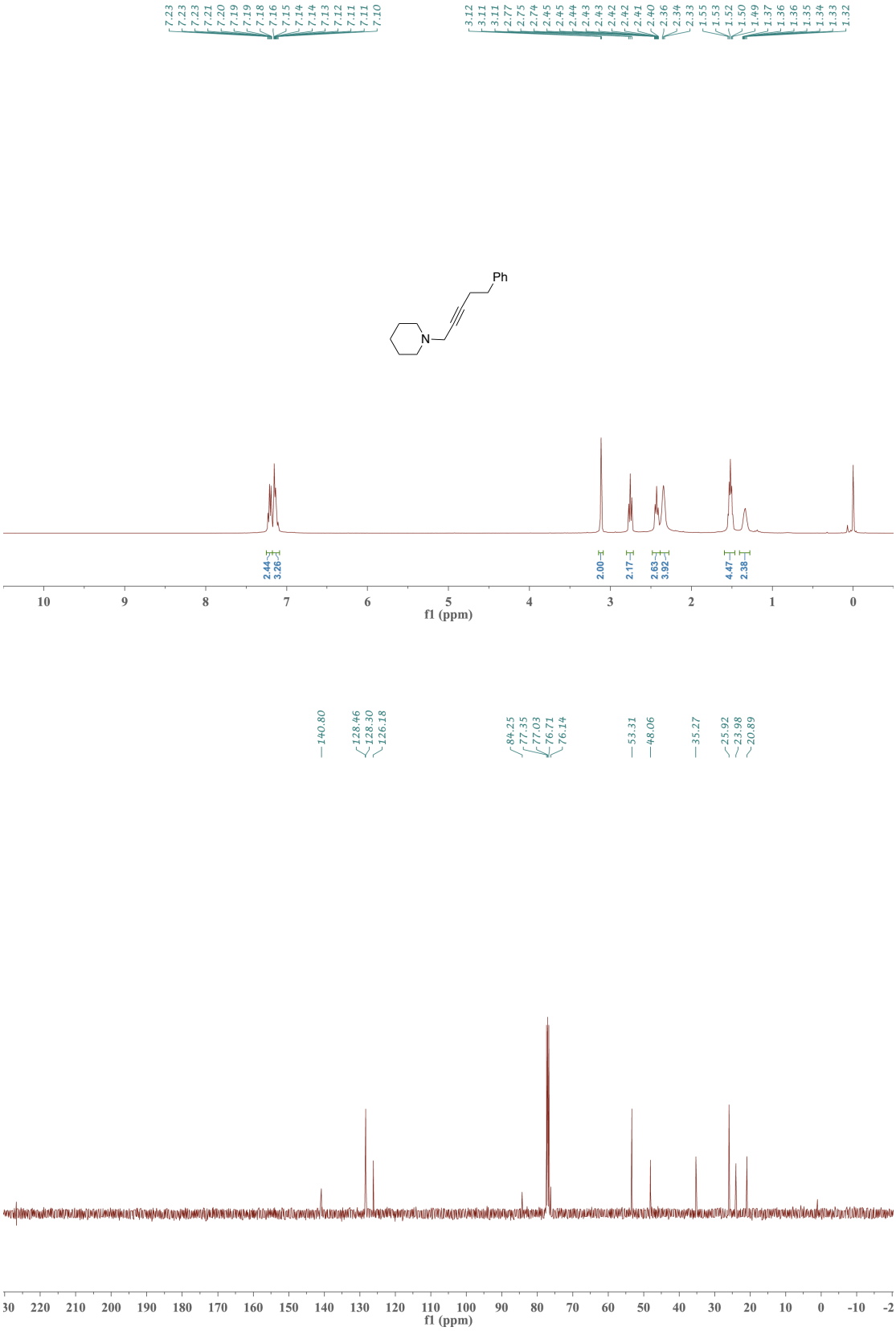


Figure S79. ^{1}H and ^{13}C NMR Spectra of 1-(3-Cyclohexylprop-2-yn-1-yl)piperidine (**3an**)

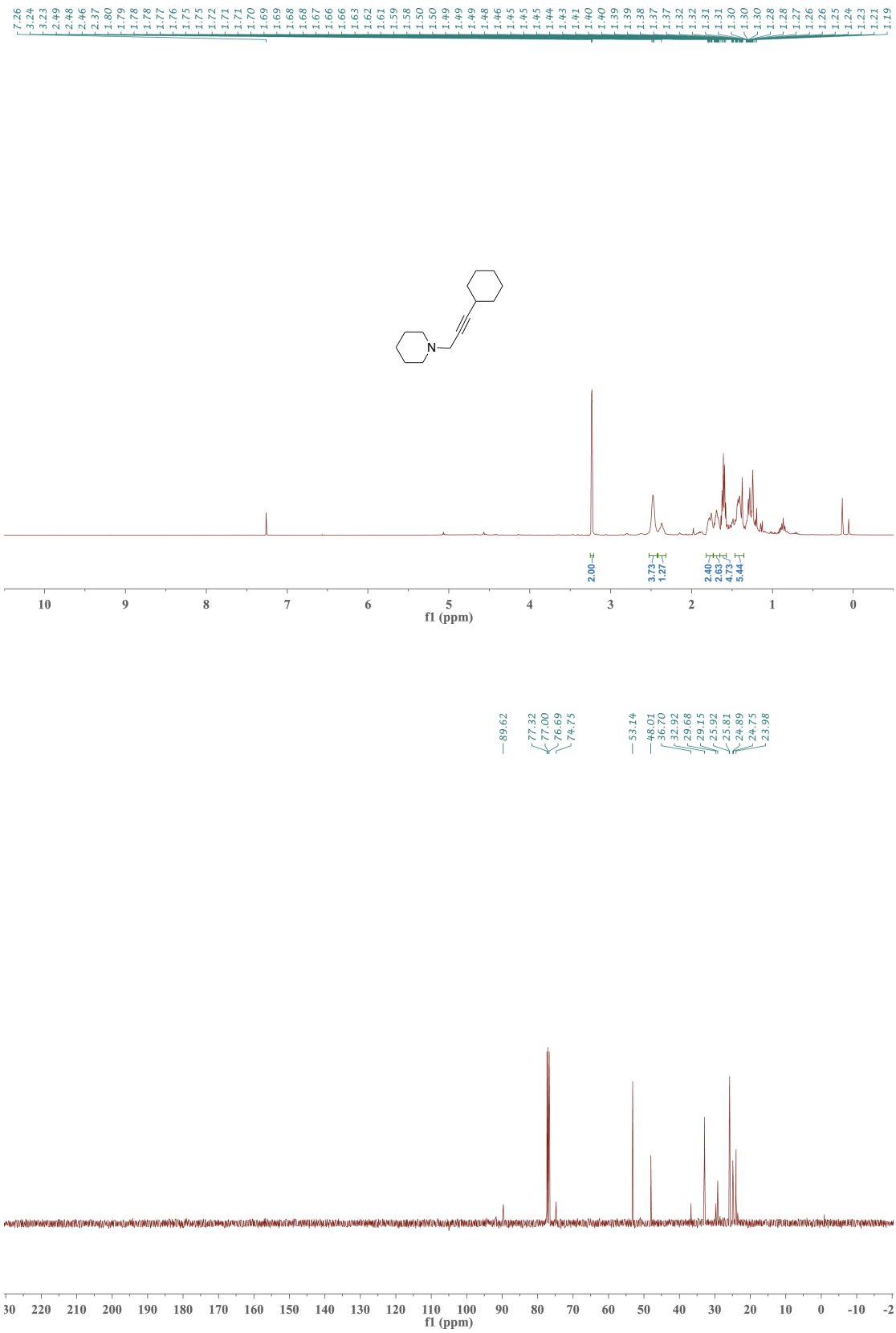


Figure S80. ^{1}H and ^{13}C NMR Spectra of 1-(3-(Cyclohex-1-en-1-yl)prop-2-yn-1-yl)piperidine (**3ao**)

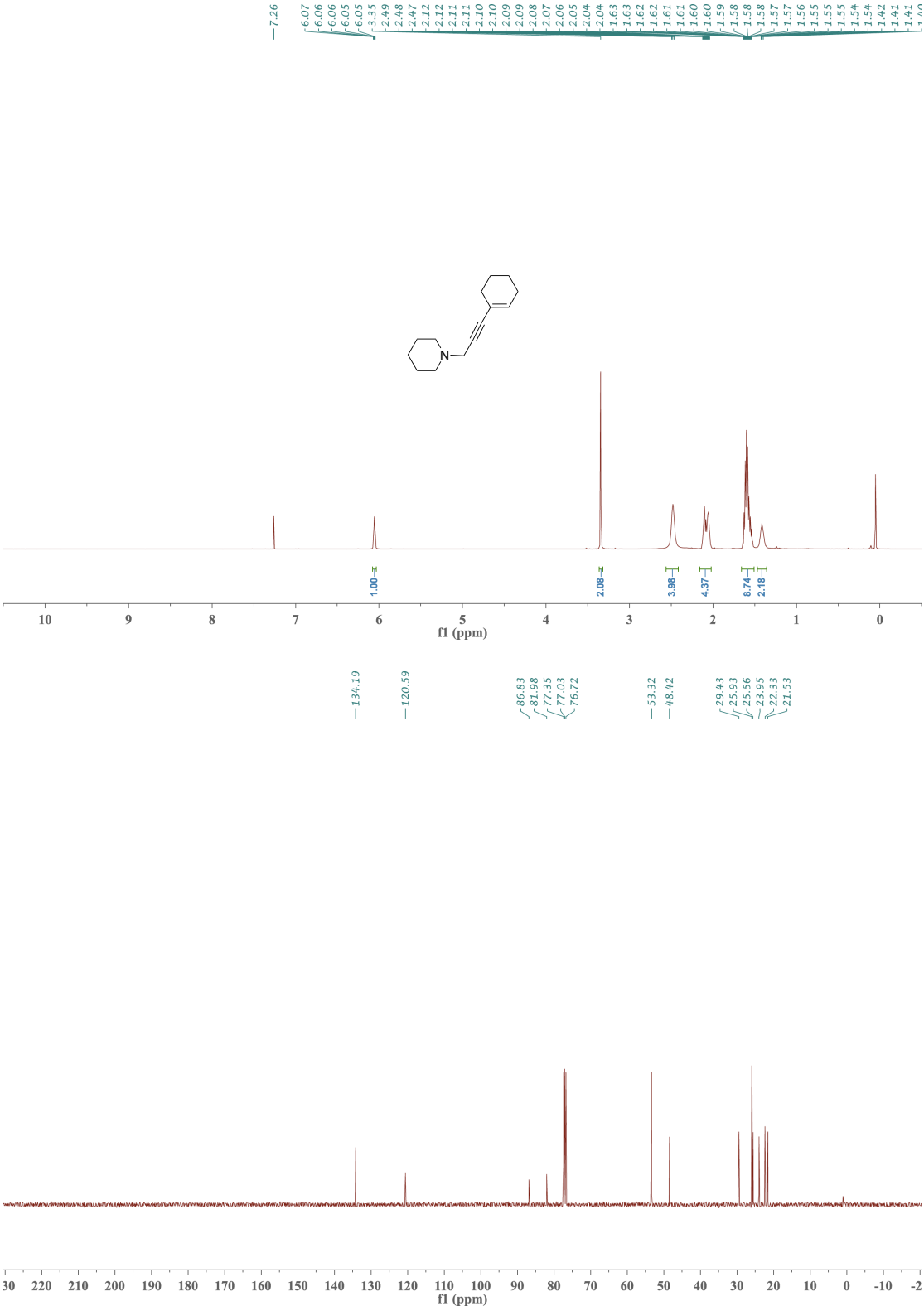


Figure S81. ^{1}H and ^{13}C NMR Spectra of 1-(4-Methoxyphenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (**3ua**)

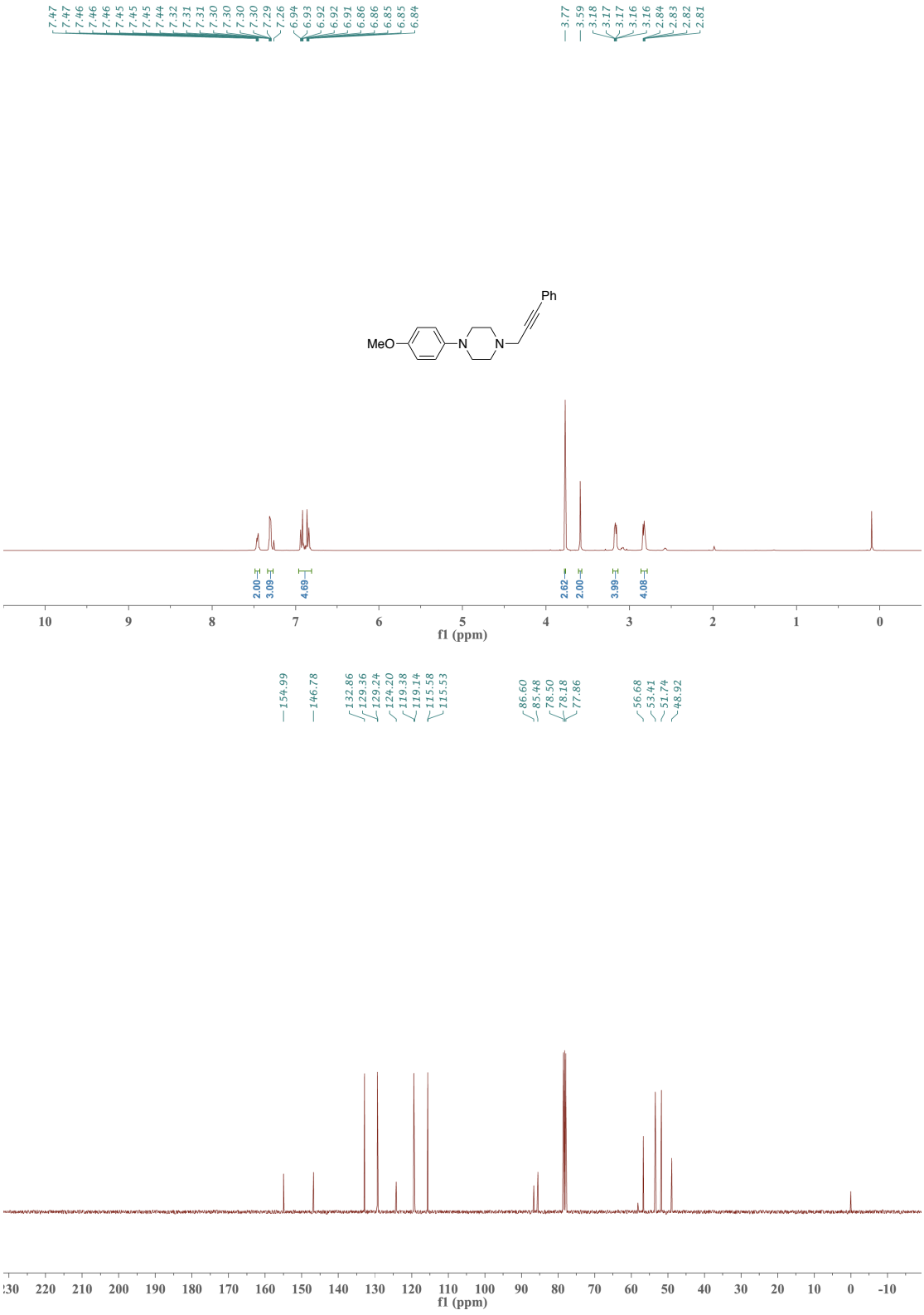


Figure S82. ^{1}H and ^{13}C NMR Spectra of 1-(4-Chlorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (**3va**)

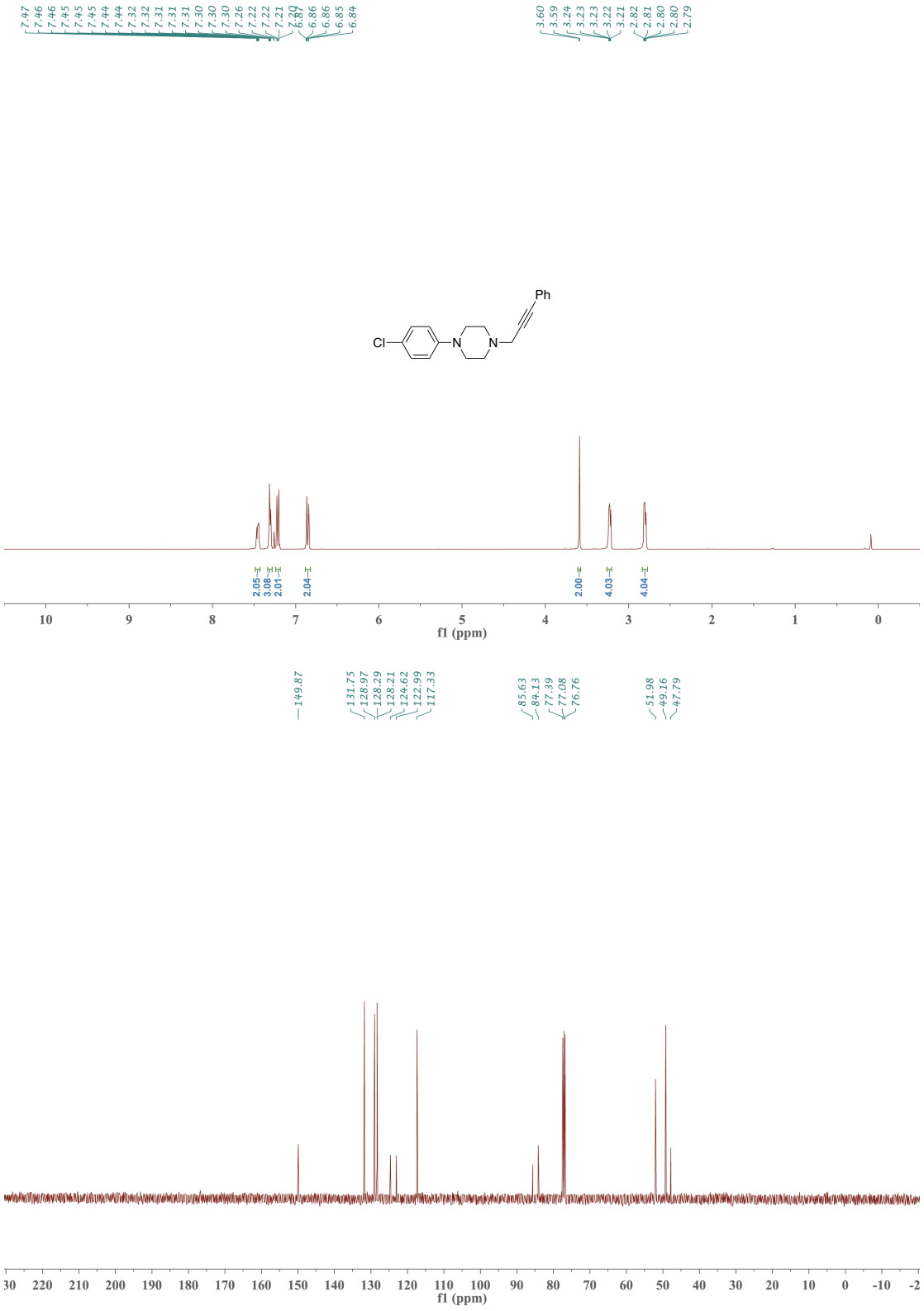


Figure S83. ^{1}H and ^{13}C NMR Spectra of 1-(4-Fluorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (**3wa**)

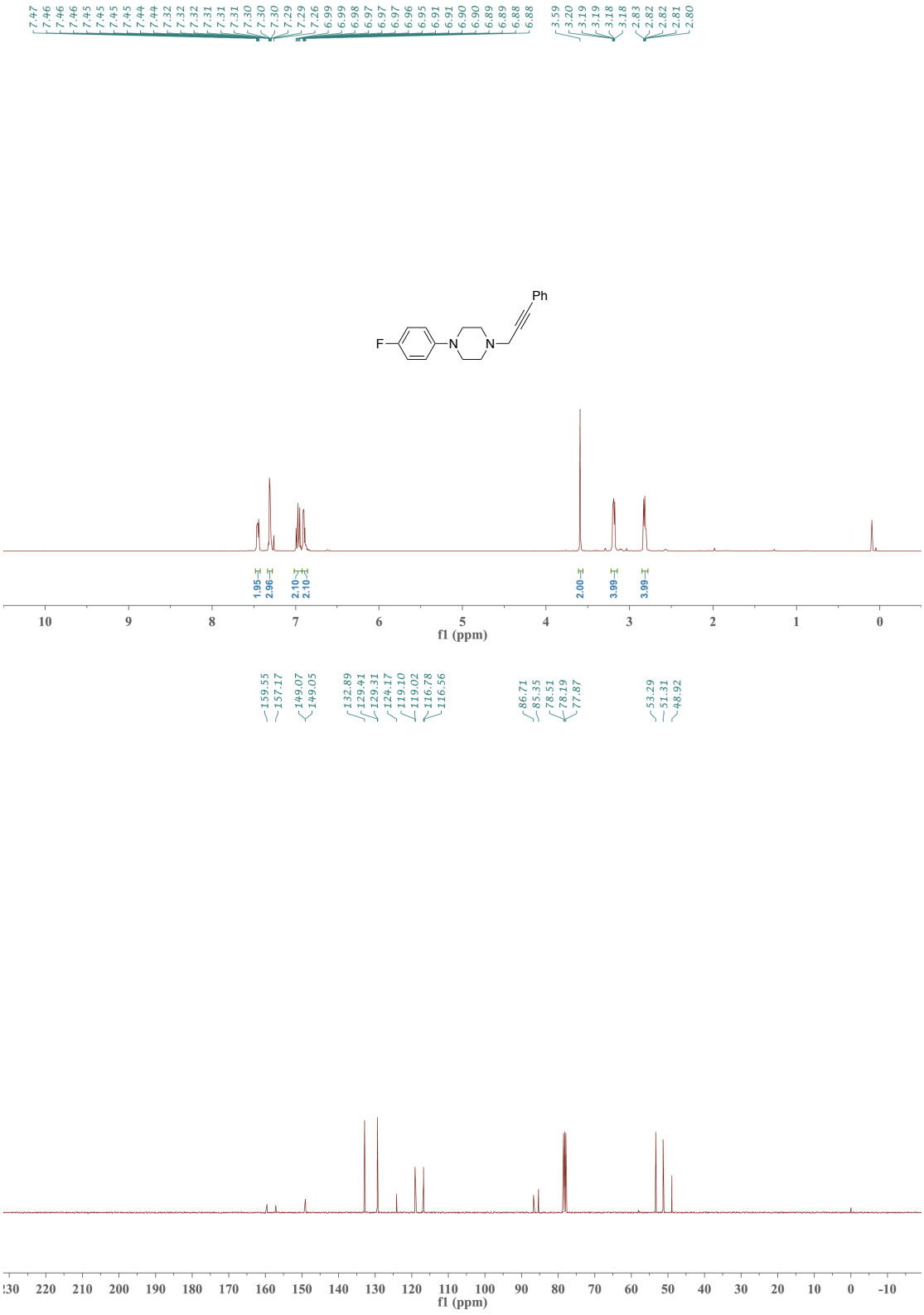


Figure S84. ^{1}H and ^{13}C NMR Spectra of 1-(3-Chlorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (**3xa**)

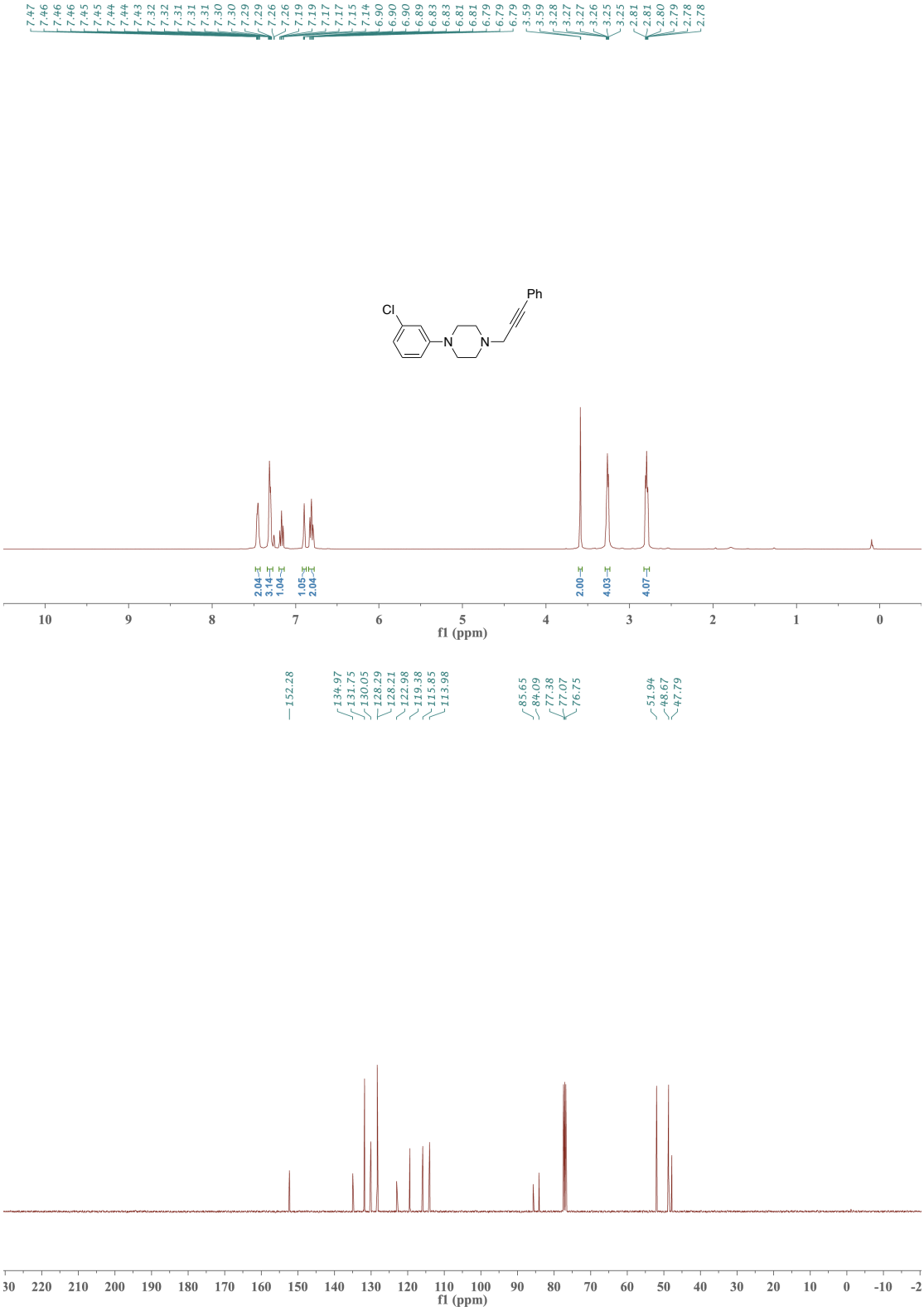


Figure S85. ^{1}H and ^{13}C NMR Spectra of 1-(2,3-Dichlorophenyl)-4-(3-phenylprop-2-yn-1-yl)piperazine (**3ya**)

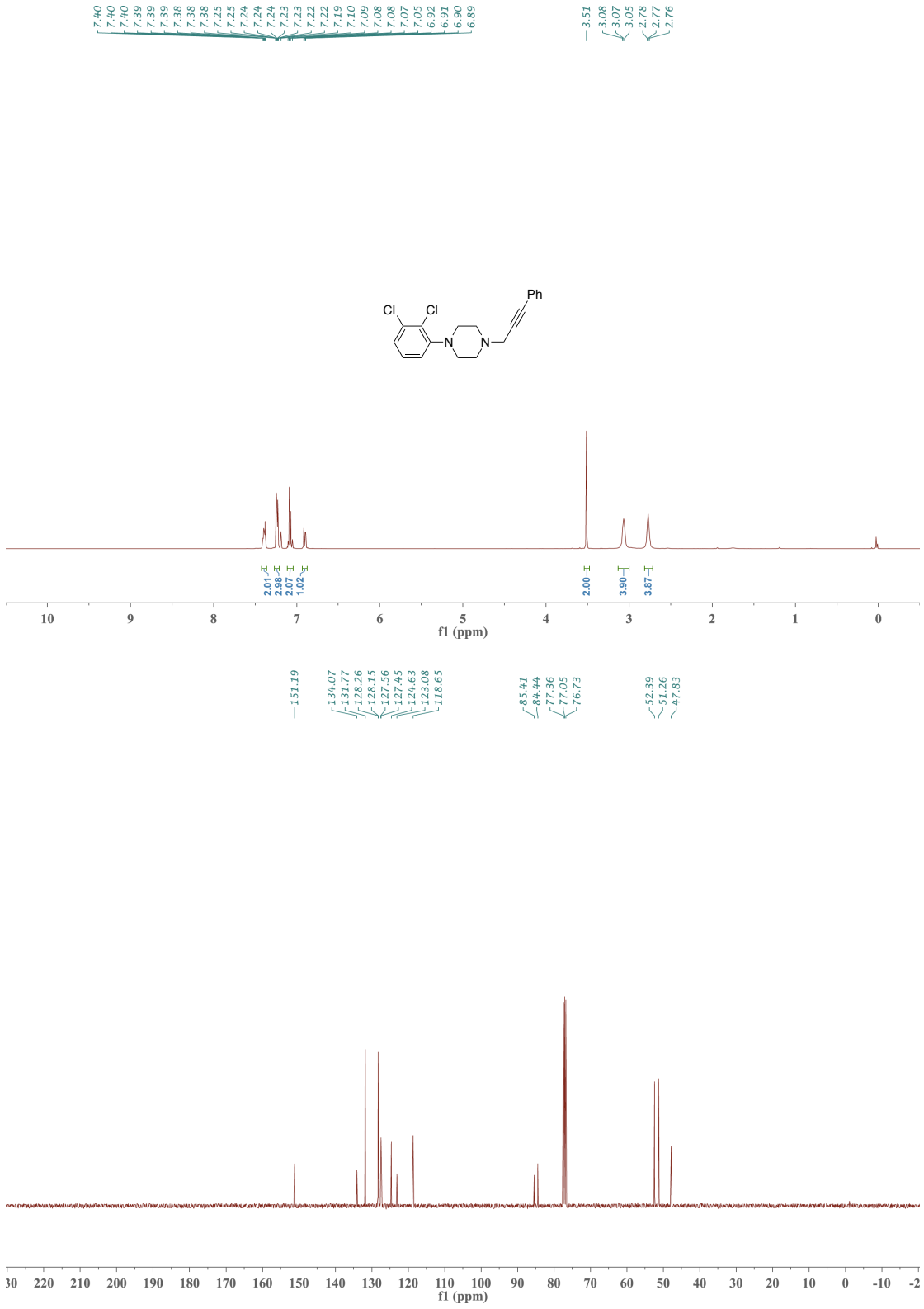


Figure S86. ^{1}H and ^{13}C NMR Spectra of *N*-Benzyl-3,7-dimethyl-*N*-(3-phenylprop-2-yn-1-yl)oct-6-en-1-amine (**3za**)

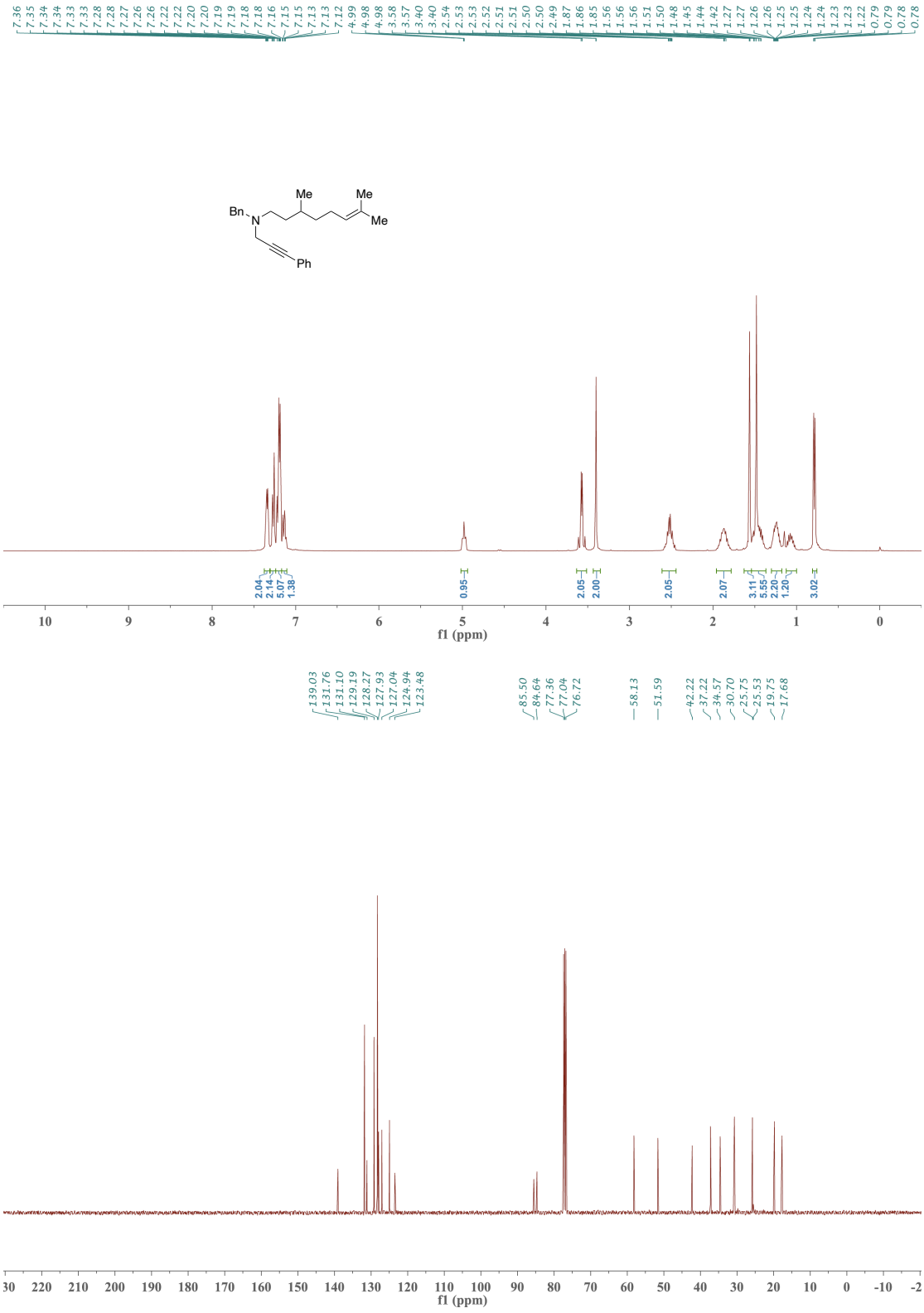


Figure S87. ^{1}H and ^{13}C NMR Spectra of *N*-Methyl-3-phenyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)prop-2-yn-1-amine (**3*ca***)

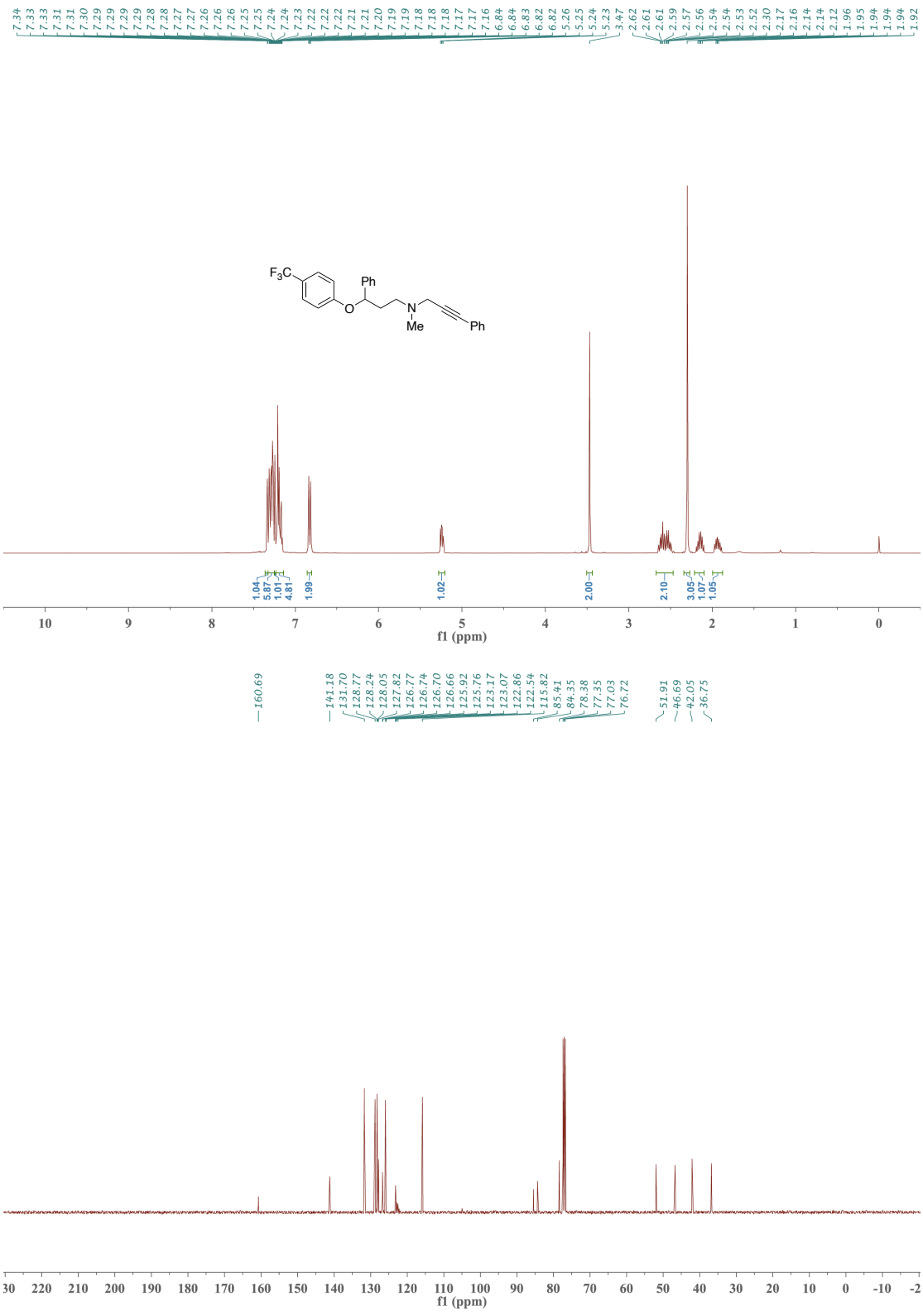


Figure S88. ^{1}H and ^{13}C NMR Spectra of *N*-(3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (**3*β*a**)

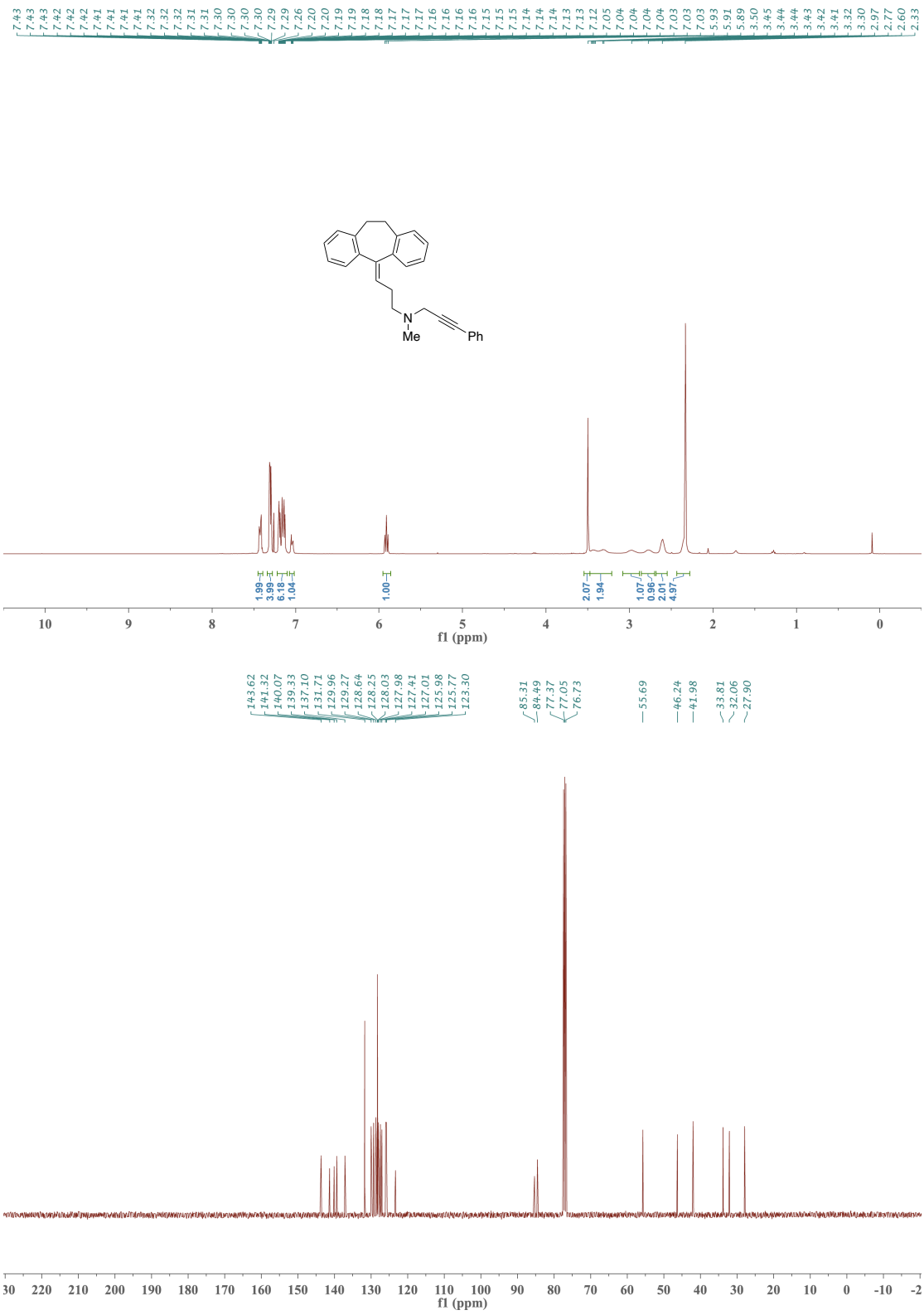


Figure S89. ^{1}H and ^{13}C NMR Spectra of (3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-(3-phenylprop-2-yn-1-yl)piperidine (**3γa**)

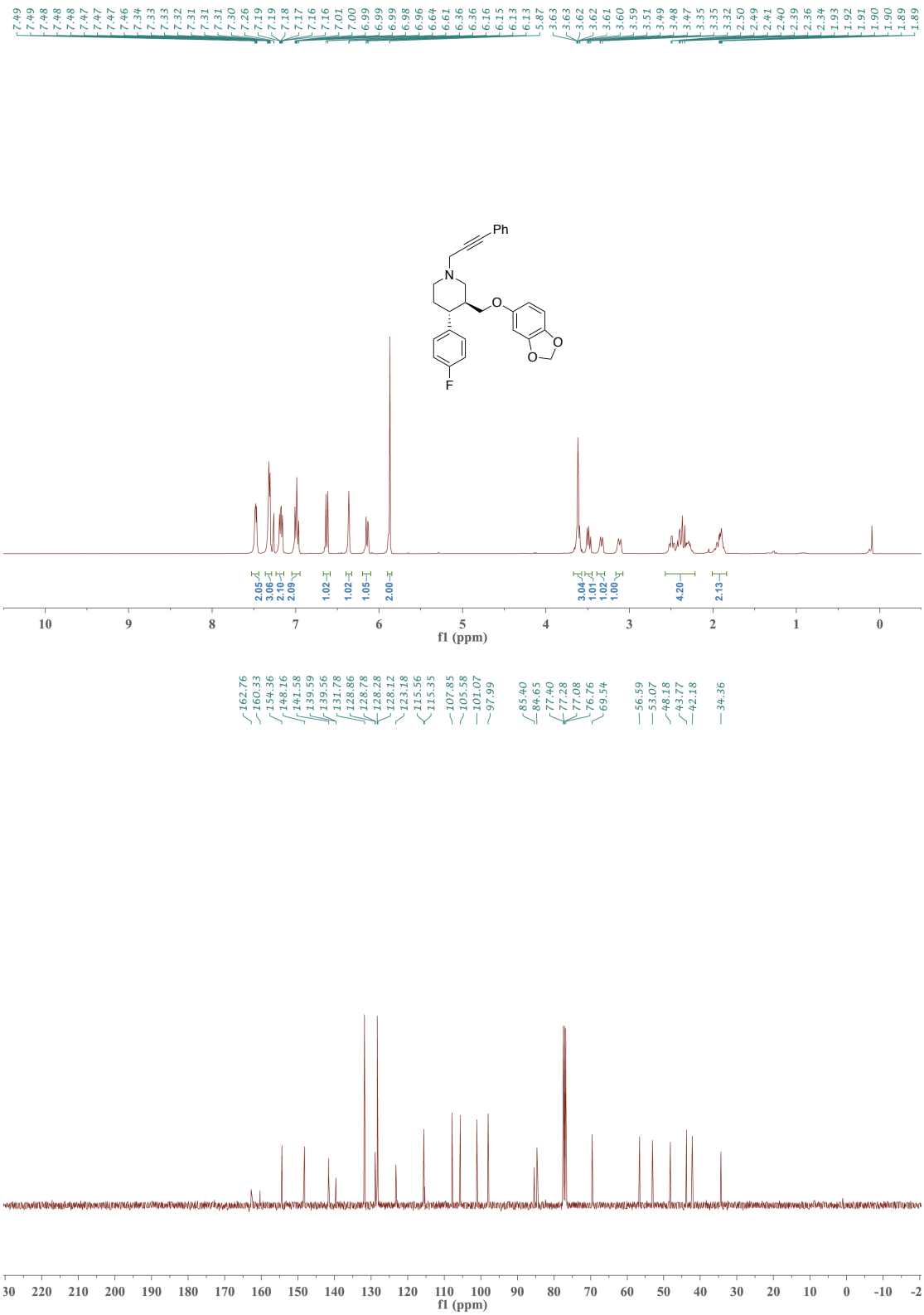


Figure S90. ^{1}H and ^{13}C NMR Spectra of (*S*)-*N*-Methyl-*N*-(3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)-3-phenylprop-2-yn-1-amine (**3δa**)

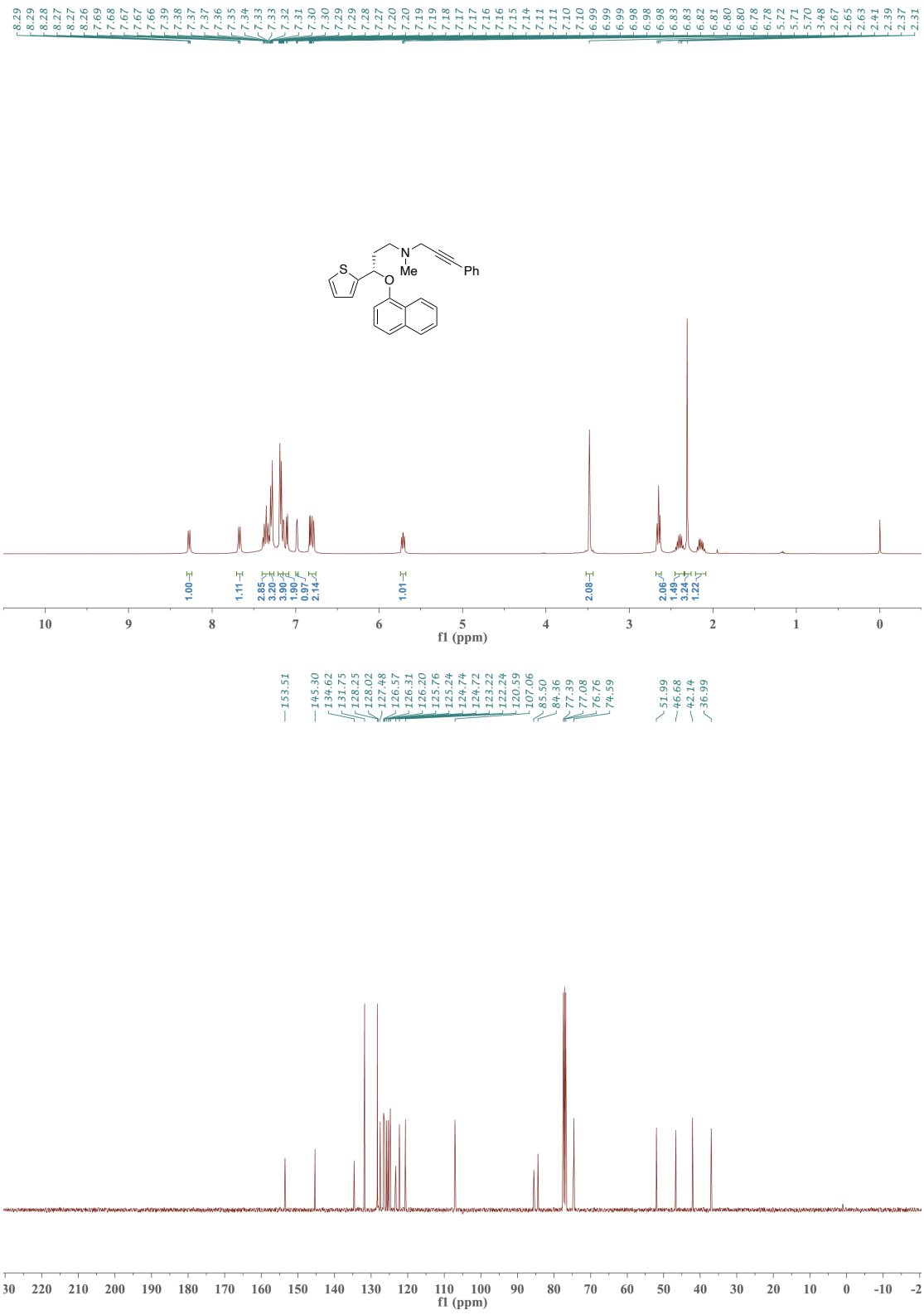
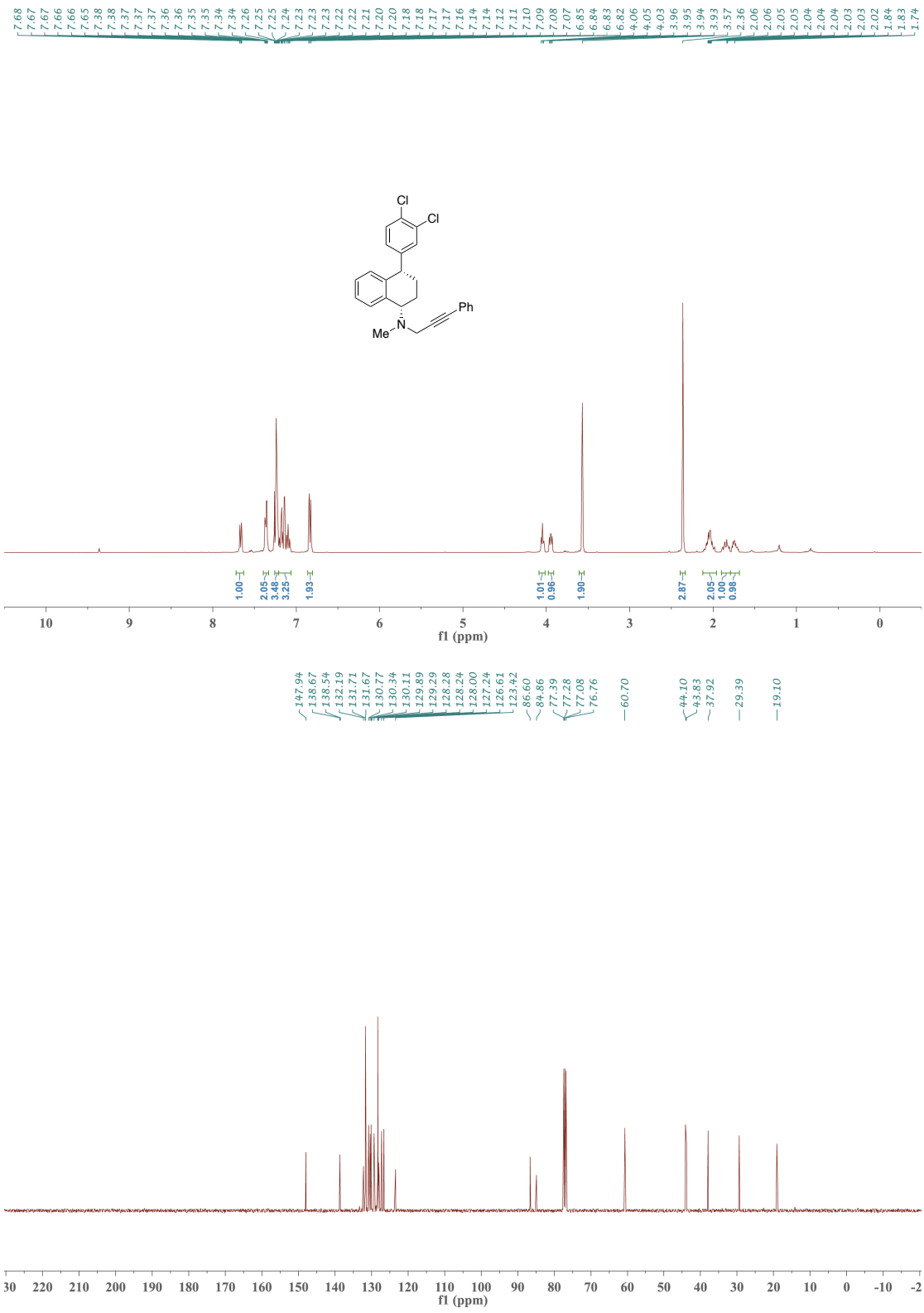


Figure S91. ^{1}H and ^{13}C NMR Spectra of (1*S*,4*S*)-4-(3,4-Dichlorophenyl)-*N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-amine (**3*ea***)



5. ^{1}H NMR and HRMS Spectra

Figure S92. ^{1}H NMR Spectrum for the Gold(I,I)-Catalysed Reaction of **2a**

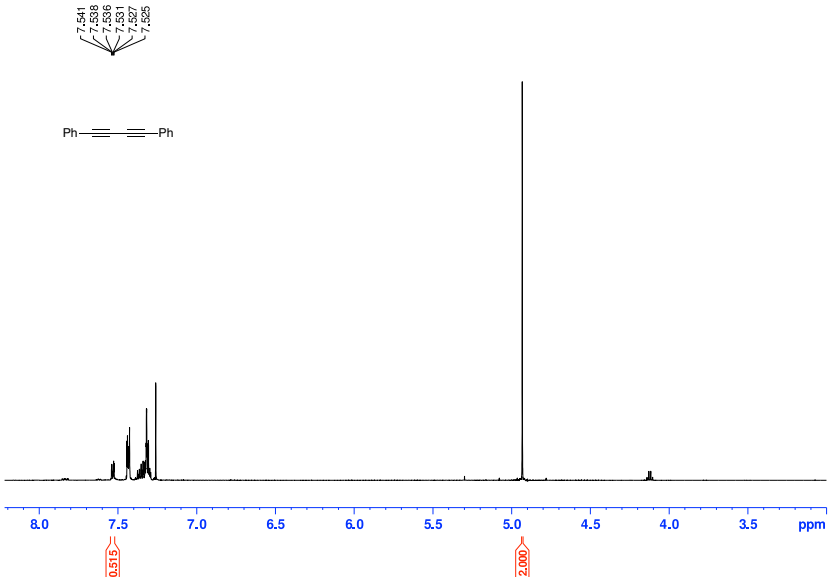
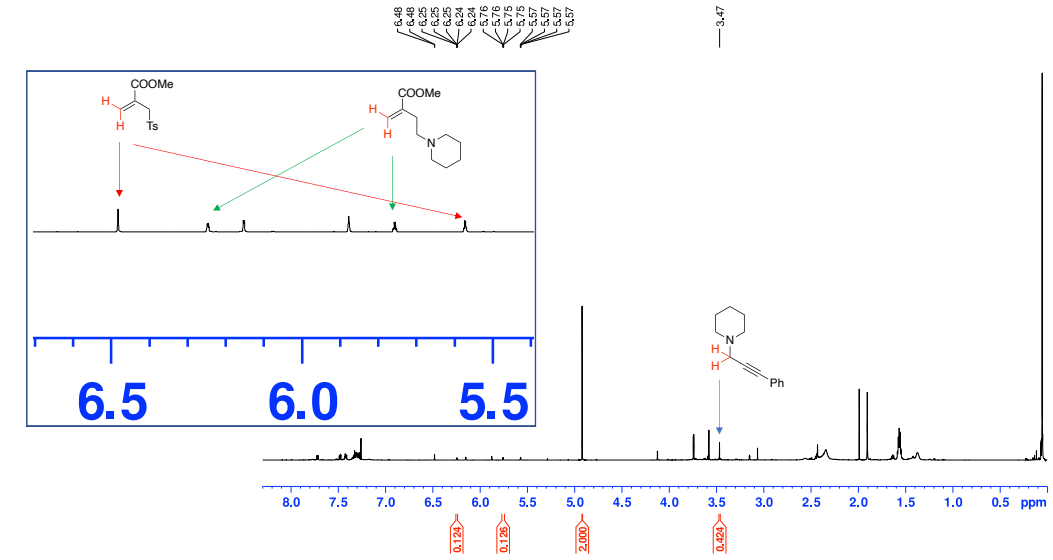
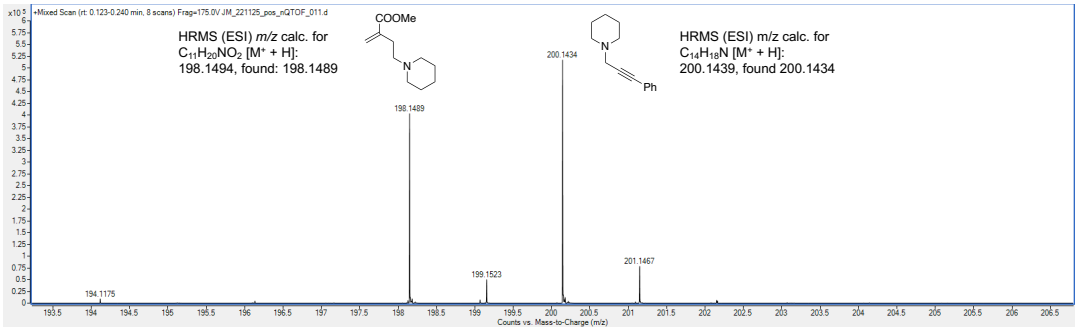


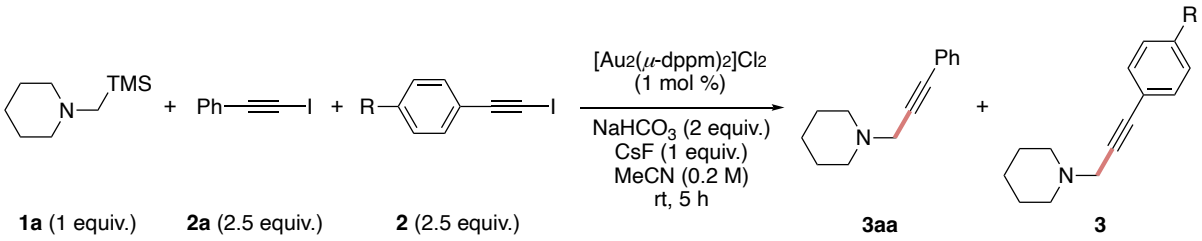
Figure S93. ^{1}H NMR and NMR Spectra for the Gold(I,I)-Catalysed α-Alkynylation of **1a** with **2a** and **6**

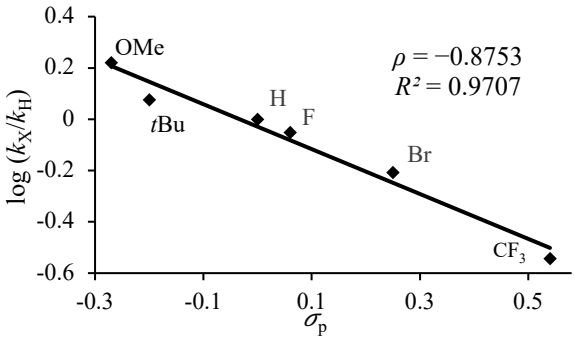




6. Hammett Plot

Figure S94. Linear Free-Energy Correlation of log k_X/k_H vs σ_P Plot for the α-Alkynylation of Tertiary α-Silylamines **1a** and *para*-Substituted Alkynyl Iodides **2a**–**2c** and **2e**–**2g**.[a]





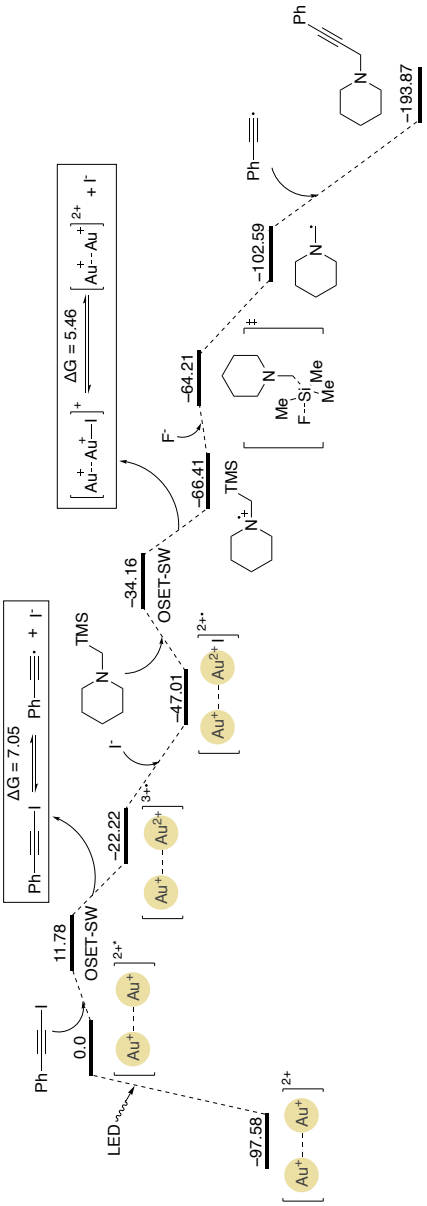
Entry	R	σ_P	log (k_X/k_H)[b]
1	OMe (**2b**)	−0.27	1.66
2	*t*Bu (**2c**)	−0.20	1.19
3	H (**2a**)	0	1
4	F (**2f**)	0.06	0.889
5	Br (**2g**)	0.25	0.621
6	CF_3 (**2e**)	0.54	0.286

[a] See Section 2.5 for the experimental procedure. [b] Measurements based on ^{1}H NMR measurements of the crude reaction mixture.

7. Computational Details

All density functional theory (DFT) and time dependent DFT (TD-DFT) calculations were performed using Gaussian 16 software package.[S18] Geometry optimizations and frequency analysis were calculated with ω-B97XD functional and a mixed basis set of SDD for Au and I and 6-31+G(d) for other atoms (denoted as Basis-set-1) in the presence of acetonitrile as modelled using SMD solvent model.[S19–S21] The level of theory used in the current study was previously benchmarked for the initial single electron transfer reaction.[S22] Single point energies were calculated using ω-B97XD functional with Def2TZVP basis set with SMD solvent model for higher-level electronic energy correction.[S23] Reported Gibbs free energies in solution at 298K were calculated using the direct method based on solution phase optimised geometries, including zero-point correction, thermal corrections and entropy calculated at ω-B97XD/Basis-set-1 and electronic energy calculated at ω-B97XD/Def2TZVP.[S24] The conversion from gas-phase standard state to solution-phase standard of 1 M (RTln(RT/P)) was added in the final Gibbs free energies.[S25] The activation free energy for the outer-sphere single electron transfer reaction was calculated using Marcus theory.[S26,S27]

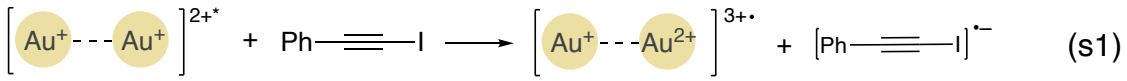
Figure S95. Energy Profile for the Photoredox Cycle. The Relative Gibbs Free Energies (ΔG, kcal/mol) were Obtained from ω-B97XD/Def2TZVP//ω-B97XD/Basis-set-1 in Acetonitrile at 25 °C.



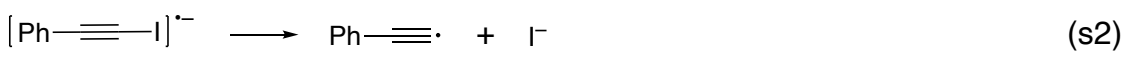
Marcus Theory Calculations for the Free Energy of Activation of Single Electron Transfer

We used the modified Marcus theory to estimate the barriers for the stepwise outer-sphere single electron transfer (OSET-SW). The DFT calculations were performed the ω-B97XD/Def2TZVP// ω-B97XD/Basis-set-1 acetonitrile at 25 °C.

The OSET-SW pathway is shown as:



(s1)



(s2)

The following equation was used to calculate the free energy of activation ($\Delta G^{\ddagger}_{\text{OSET-SW}}$):

$$\Delta G^{\ddagger}_{OSET-SW} = \Delta G^{\ddagger}_{0}\left(1+\frac{\Delta_r G^{\ominus}}{4\Delta G^{\ddagger}_{0}}\right)^2$$

Here, $\Delta_r G^{\ominus}$ = –22.22 kcal/mol is the reaction energy of eq. s1 obtained from DFT calculations. The intrinsic barrier is determined using $\Delta G^{\ddagger}_{0} = \lambda_0/4$, where λ_0 is the solvent reorganization energy that can be calculated using the numerical model.[S28,S29] For eq. (s1), the calculated λ_0 is 85.80 kJ/mol.

Leading to

$$\Delta G^{\ddagger}_{0} = \frac{\lambda_0}{4} = 21.45 \text{ kcal/mol}$$

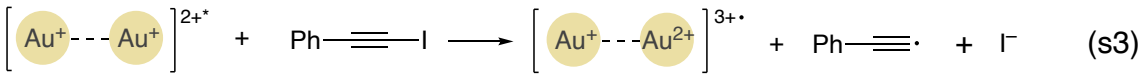
Thus,

$$\Delta G^{\ddagger}_{OSET-SW} = 21.45 \times \left(1+\frac{-22.22}{4\times 21.45}\right)^2 = 11.78 \text{ kcal/mol}$$

The dissociation of the radical anion (eq s2) is slightly endergonic (ΔG = 7.05 kcal mol^{-1}) and is expected to be fast. Therefore, the rate-determining step in the OSET-SW pathway is the outer-sphere electron transfer (eq. s1).

For comparison, the dissociative electron transfer (DET) process was considered as well.

The DET pathway is shown as:



(s3)

In the DET pathway (eq s3), the electron transfer occurs with simultaneous bond dissociation to form the PhCC• radical and the I^- anion in a polar solvent (MeCN) cage. Thus, the "sticky" model[12] is used to estimate the free energy of activation of the DET pathway:

$$\Delta G_{DET}^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\ominus} - D_p}{4\Delta G_0^{\ddagger}}\right)^2$$

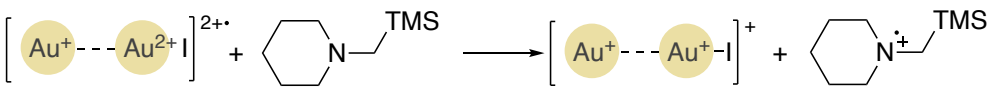
$$\Delta G_0^{\ddagger} = \frac{\left(\sqrt{D_{PhCC-I}} - \sqrt{D_p}\right)^2 + \lambda_0}{4}$$

Where $\Delta G_0^{\ddagger}$ is the intrinsic barrier; $\Delta_r G^{\ominus}$ = –15.18 kcal/mol is the DFT calculated reaction energy for eq. s3; D_p is the interaction energy between PCC• and I^- in the solvent cage, and the calculated interaction of 7.05 kcal/mol is used in our calculation; D_{PCC-I} is the PCC-I bond dissociation energy calculated using DFT (D_{PCC-I} = 70.09 kcal/mol); λ_0 is the solvent reorganization that is the same as that in the OSET-SW pathway.

$$\Delta G_0^{\ddagger} = \frac{\left(\sqrt{D_{PCC-I}} - \sqrt{D_p}\right)^2 + \lambda_0}{4} = 29.62\ kcal/mol$$

$$\Delta G_{DET}^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\ominus} - D_p}{4\Delta G_0^{\ddagger}}\right)^2 = 19.55\ kcal/mol$$

From the results above, it indicates the OSET-SW pathway is more favourable. For the second single electron transfer process, similar calculations were carried out for the following reaction via OSET-SW.



Based on the calculated solvent reorganization energy (85.83 kcal/mol) and reaction Gibbs free energy (–19.40 kcal/mol), the free energy of activation is 12.85 kcal/mol.

Table S1. Gaussian raw data (in a.u., otherwise indicated) and number of imaginary frequencies (NImag) for the species shown in Figure S93.

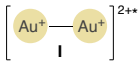
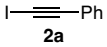
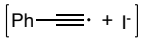
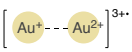
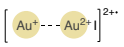
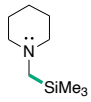
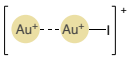
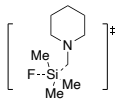
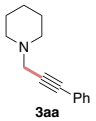
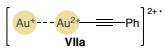
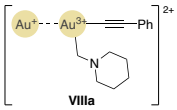
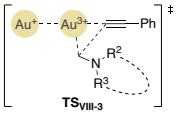
Species	NImag	Ee	E0	H	G	Ee(high)	G_corrected[a]
	0	-2034.724417	-2034.351869	-2034.324150	-2034.408613	-2035.008414	-2034.689602
 **I**	0	-2034.713657	-2034.197195	-2034.169793	-2034.253316	-2034.997447	-2034.534097
 **2a**	0	-319.113197	-319.011542	-319.002783	-319.045953	-605.580371	-605.510118
	0	-319.227177	-319.127065	-319.117689	-319.165140	-605.681808	-605.616762
 **IVa**	0	-307.599175	-307.500408	-307.493167	-307.530865	-307.693282	-307.621963
I^-	0	-11.614199	-11.614199	-11.611838	-11.631047	-297.969731	-297.983571
		-2034.497325	-2034.124208	-2034.096778	-2034.179698	-2034.783506	-2034.462870
	0	-2046.155635	-2045.782705	-2045.752493	-2045.845197	-2332.799387	-2332.485940
 **1a**	0	-699.760962	-699.470426	-699.454892	-699.511269	-699.925515	-699.672813
	0	-2046.353995	-2045.981713	-2045.951240	-2046.045639	-2332.993245	-2332.681880
 **Va**	0	-699.595994	-699.304315	-699.288757	-699.346184	-699.760609	-699.507790
F^-	0	-99.966694	-99.966694	-99.964334	-99.980853	-99.990166	-100.001316
	1	-799.561055	-799.268789	-799.251841	-799.312561	-799.757097	-799.505595
$F–SiMe_3$		-509.108523	-508.994355	-508.985068	-509.025087	-509.223977	-509.137532
 **VIa**	0	-290.481332	-290.306313	-290.298193	-290.337880	-290.575696	-290.429235
 **3aa**	0	-598.249425	-597.968018	-597.953584	-598.010673	-598.438411	-598.196649
 **VIIa**	0	-2342.375156	-2341.901998	-2341.866149	-2341.972585	-2342.756336	-2342.350756

Table S1. (continued).

Species	NImag	Ee	E0	H	G	Ee(high)	G_corrected[a]
 VIIIa	0	-2632.940374	-2632.285625	-2632.243285	-2632.362065	-2633.415101	-2632.833784
 TS_{VIII-3}	1	-2632.931405	-2632.278213	-2632.234985	-2632.357100	-2633.403268	-2632.825954

[a]After adding phase change correction term to the Gibbs free energy.

Cartesian coordinates for the optimised geometries shown in Figure 6 and Figure S93.

Au	0.000359	1.555095	-0.034279
Au	-0.000359	-1.555095	-0.034279
P	-2.335998	1.436305	0.207973
P	-2.335998	-1.652218	-0.275506
P	2.335998	-1.436305	0.207973
P	2.335998	1.652218	-0.275506
C	-3.056165	-0.006498	-0.671854
H	-4.141063	-0.033060	-0.512050
H	-2.874015	0.164574	-1.740026
C	3.056165	0.006498	-0.671854
H	2.874015	-0.164574	-1.740026
H	4.141063	0.033060	-0.512050
C	2.940234	2.700109	-1.637859
C	2.876878	-1.298463	1.942124
C	3.236602	2.257094	1.189198
C	-3.236602	-2.257094	1.189198
C	-3.279802	2.842744	-0.462124
C	3.279802	-2.842744	-0.462124
C	-2.940234	-2.700109	-1.637859
C	-2.876878	1.298463	1.942124
H	3.952071	-1.098639	1.993393
H	2.326963	-0.497278	2.443075
H	2.656004	-2.242097	2.451025
H	4.352415	-2.688532	-0.305138
H	2.964743	-3.758150	0.048111
H	3.075972	-2.946137	-1.531899
H	4.316092	2.172989	1.027026
H	2.974098	3.307798	1.347712
H	2.952473	1.689294	2.078263
H	4.031068	2.633837	-1.707727
H	2.491435	2.373147	-2.580150
H	2.649426	3.737692	-1.447472
H	-3.075972	2.946137	-1.531899
H	-4.352415	2.688532	-0.305138
H	-2.964743	3.758150	0.048111
H	-2.656004	2.242097	2.451025
H	-3.952071	1.098639	1.993393
H	-2.326963	0.497278	2.443075
H	-2.952473	-1.689294	2.078263
H	-4.316092	-2.172989	1.027026
H	-2.974098	-3.307798	1.347712
H	-2.649426	-3.737692	-1.447472
H	-4.031068	-2.633837	-1.707727
H	-2.491435	-2.373147	-2.580150

I

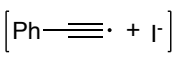
Au	0.004274	1.381790	-0.024345
Au	-0.004274	-1.381790	-0.024345
P	-2.354968	1.518622	0.109692
P	-2.354968	-1.566542	-0.228182

P	2.354968	-1.518622	0.109692
P	2.354968	1.566542	-0.228182
C	-3.112692	0.045170	-0.682179
H	-4.190127	0.020665	-0.478785
H	-2.974777	0.168529	-1.763698
C	3.112692	-0.045170	-0.682179
H	2.974777	-0.168529	-1.763698
H	4.190127	-0.020665	-0.478785
C	3.070055	2.698684	-1.471206
C	2.922480	-1.543321	1.841111
C	3.133163	2.060972	1.343944
C	-3.133163	-2.060972	1.343944
C	-3.263616	2.892597	-0.684812
C	3.263616	-2.892597	-0.684812
C	-3.070055	-2.698684	-1.471206
C	-2.922480	1.543321	1.841111
H	3.998114	-1.343427	1.886572
H	2.382243	-0.795904	2.427423
H	2.719709	-2.533407	2.261121
H	4.343142	-2.762325	-0.544699
H	2.948300	-3.837917	-0.233473
H	3.032871	-2.913746	-1.753863
H	4.220668	1.956854	1.267961
H	2.882269	3.106635	1.546505
H	2.762712	1.444755	2.166377
H	4.162594	2.609257	-1.478470
H	2.675853	2.450719	-2.460997
H	2.788171	3.725958	-1.222486
H	-3.032871	2.913746	-1.753863
H	-4.343142	2.762325	-0.544699
H	-2.948300	3.837917	-0.233473
H	-2.719709	2.533407	2.261121
H	-3.998114	1.343427	1.886572
H	-2.382243	0.795904	2.427423
H	-2.762712	-1.444755	2.166377
H	-4.220668	-1.956854	1.267961
H	-2.882269	-3.106635	1.546505
H	-2.788171	-3.725958	-1.222486
H	-4.162594	-2.609257	-1.478470
H	-2.675853	-2.450719	-2.460997

2a

C	0.000000	1.208196	-4.096525
C	0.000000	1.212963	-2.704684
C	0.000000	0.000000	-1.998577
C	-0.000000	-1.212963	-2.704684
C	-0.000000	-1.208196	-4.096525
C	0.000000	0.000000	-4.795043
H	0.000000	2.150572	-4.636945
H	0.000000	2.151861	-2.158506
H	-0.000000	-2.151861	-2.158506
H	-0.000000	-2.150572	-4.636945
H	0.000000	0.000000	-5.881525

C	0.000000	0.000000	-0.563327
C	0.000000	-0.000000	0.648511
I	0.000000	-0.000000	2.666746



C	1.560004	-4.351364	-0.000000
C	1.459054	-2.962440	-0.000000
C	0.199553	-2.338895	-0.000000
C	-0.952975	-3.143242	-0.000000
C	-0.845605	-4.531708	-0.000000
C	0.409647	-5.141349	-0.000000
H	2.541541	-4.817866	-0.000000
H	2.356852	-2.350446	-0.000000
H	-1.932008	-2.671966	-0.000000
H	-1.746577	-5.139398	-0.000000
H	0.490848	-6.224888	-0.000000
C	0.091910	-0.903439	-0.000000
C	-0.000000	0.322286	0.000000
I	-0.249815	3.009537	0.000000

IVa

C	0.000000	1.221752	-1.424234
C	-0.000000	1.231632	-0.044256
C	-0.000000	-0.000000	0.674396
C	-0.000000	-1.231632	-0.044256
C	-0.000000	-1.221752	-1.424234
C	0.000000	0.000000	-2.113877
H	0.000000	2.155647	-1.976897
H	-0.000000	2.164410	0.510488
H	-0.000000	-2.164410	0.510488
H	-0.000000	-2.155647	-1.976897
H	0.000000	0.000000	-3.199982
C	-0.000000	-0.000000	2.064241
C	-0.000000	-0.000000	3.334354

I^-

I	0.000000	0.000000	0.000000

Au	-0.000766	1.407432	-0.037247
Au	0.000766	-1.407432	-0.037247
P	-2.356983	1.461431	0.230698
P	-2.356983	-1.553505	-0.290020
P	2.356983	-1.461431	0.230698
P	2.356983	1.553505	-0.290020
C	-3.144399	0.062112	-0.642311
H	-4.216949	0.020616	-0.419152
H	-3.020205	0.252212	-1.715214
C	3.144399	-0.062112	-0.642311
H	3.020205	-0.252212	-1.715214
H	4.216949	-0.020616	-0.419152
C	2.842777	2.621734	-1.676366
C	2.861339	-1.375764	1.972524
C	3.172363	2.242576	1.179342
C	-3.172363	-2.242576	1.179342
C	-3.126466	2.951594	-0.461933

C	3.126466	-2.951594	-0.461933
C	-2.842777	-2.621734	-1.676366
C	-2.861339	1.375764	1.972524
H	3.948584	-1.269539	2.042705
H	2.371801	-0.529653	2.461122
H	2.549494	-2.298499	2.471191
H	4.210911	-2.903411	-0.317694
H	2.727830	-3.831645	0.051166
H	2.898338	-3.021894	-1.529037
H	4.256311	2.251572	1.026029
H	2.815769	3.266606	1.326780
H	2.929429	1.652155	2.065830
H	3.934571	2.643326	-1.758052
H	2.410806	2.238461	-2.604768
H	2.469237	3.634050	-1.496120
H	-2.898338	3.021894	-1.529037
H	-4.210911	2.903411	-0.317694
H	-2.727830	3.831645	0.051166
H	-2.549494	2.298499	2.471191
H	-3.948584	1.269539	2.042705
H	-2.371801	0.529653	2.461122
H	-2.929429	-1.652155	2.065830
H	-4.256311	-2.251572	1.026029
H	-2.815769	-3.266606	1.326780
H	-2.469237	-3.634050	-1.496120
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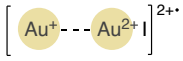
H	-2.410806	-2.238461	-2.604768



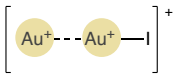
Au	-2.166745	0.000690	0.040501
Au	0.904893	-0.000207	-0.182211
P	-2.222070	-2.346620	0.043981
P	0.878790	-2.382212	-0.210022
P	0.881127	2.381731	-0.210975
P	-2.219521	2.348104	0.045025
C	-0.733793	-3.076663	-0.734971
H	-0.728062	-4.163671	-0.588632
H	-0.819520	-2.877668	-1.810280
C	-0.731297	3.077331	-0.734776
H	-0.817839	2.878577	-1.810060
H	-0.724808	4.164312	-0.588269
C	-3.588162	3.077248	-0.909346
C	1.276705	3.114950	1.405605
C	-2.363298	3.090131	1.701715
C	1.271912	-3.114552	1.407544
C	-3.590655	-3.073615	-0.912124
C	2.042267	3.142278	-1.386558
C	2.040318	-3.144957	-1.383800
C	-2.368436	-3.089693	1.699970
H	1.098637	4.194738	1.380085
H	0.669763	2.656688	2.189637
H	2.331827	2.923750	1.623544
H	3.068631	2.917301	-1.085422

H	1.866403	2.740338	-2.388331
H	1.893805	4.227146	-1.393952
H	-2.249934	4.177232	1.638946
H	-3.353439	2.849908	2.101514
H	-1.607723	2.676940	2.373827
H	-3.525414	4.170052	-0.878828
H	-3.536309	2.734773	-1.946709
H	-4.539150	2.754345	-0.475218
H	-3.537762	-2.730261	-1.949140
H	-3.528990	-4.166507	-0.882531
H	-4.541635	-2.750179	-0.478363
H	-3.358613	-2.848282	2.098972
H	-2.256723	-4.176919	1.636391
H	-1.612895	-2.678251	2.373179
H	0.664883	-2.654726	2.190598
H	1.092426	-4.194125	1.382894
H	2.327088	-2.924546	1.626284
H	3.066628	-2.921470	-1.081385
H	1.890198	-4.229600	-1.390945
H	1.866414	-2.743193	-2.385983
I	3.760002	-0.001409	0.259879

1a

C	-1.066671	0.959970	-0.454505
C	-2.553156	1.334822	-0.325702
C	-3.239826	0.461146	0.721799
C	-3.181279	-1.012456	0.280892
C	-1.913175	-1.293014	-0.543515
H	-0.727143	1.159280	-1.489388
H	-2.638458	2.397955	-0.075439
H	-2.731785	0.586914	1.686091
H	-3.204091	-1.665396	1.161318
H	-1.610873	-2.338344	-0.425215
H	-2.106376	-1.139982	-1.624246
H	-4.060804	-1.260604	-0.326126
H	-4.279405	0.776416	0.866766
H	-3.059514	1.196023	-1.289700
H	-0.466773	1.594727	0.208590
N	-0.815366	-0.440315	-0.093211
C	0.480111	-0.898636	-0.586402
H	0.600777	-1.950617	-0.290182
H	0.512459	-0.889867	-1.698260
Si	2.022919	-0.001455	0.080411
C	1.831275	0.284162	1.931230
H	2.740193	0.728730	2.357221
H	0.994542	0.960660	2.146028
H	1.640887	-0.660448	2.456815
C	2.355031	1.632114	-0.802327
H	3.348224	2.012746	-0.528683
H	2.339408	1.500493	-1.892093
H	1.620873	2.404759	-0.546189
C	3.475743	-1.155297	-0.253890
H	3.566095	-1.377029	-1.325521

H	4.420616	-0.701863	0.072488
H	3.359533	-2.108843	0.276968

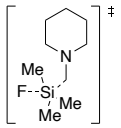


Au	-0.063649	-1.592914	-0.554530
Au	0.063068	1.594549	-0.551304
P	2.287488	-1.641534	-0.581388
P	2.408266	1.500149	-0.656367
P	-2.288173	1.642960	-0.576568
P	-2.408852	-1.498755	-0.657578
C	3.013152	-0.112330	-1.298936
H	4.105860	-0.152530	-1.208761
H	2.761118	-0.128956	-2.366407
C	-3.014291	0.115000	-1.296486
H	-2.762989	0.133667	-2.364111
H	-4.106932	0.155076	-1.205497
C	-3.177319	-2.691824	-1.801862
C	-3.087087	1.871877	1.043932
C	-3.266764	-1.778325	0.924652
C	3.266315	1.776034	0.926456
C	3.013381	-2.947315	-1.626899
C	-3.014872	2.950400	-1.619460
C	3.176850	2.695293	-1.798374
C	3.087496	-1.873515	1.038135
H	-4.172431	1.763854	0.948381
H	-2.701921	1.146527	1.764291
H	-2.850501	2.877082	1.406976
H	-4.107615	2.879918	-1.608687
H	-2.709414	3.926854	-1.231161
H	-2.650654	2.848576	-2.645840
H	-4.341309	-1.603139	0.809395
H	-3.096982	-2.815480	1.230756
H	-2.863583	-1.120519	1.698270
H	-4.262916	-2.550226	-1.824588
H	-2.767998	-2.554510	-2.806848
H	-2.949766	-3.707316	-1.463370
H	2.649640	-2.842953	-2.653191
H	4.106189	-2.877875	-1.615557
H	2.706880	-3.924322	-1.240812
H	2.851641	-2.879632	1.399134
H	4.172727	-1.764818	0.942071
H	2.702520	-1.150001	1.760438
H	2.860336	1.118793	1.699101
H	4.340450	1.597968	0.811930
H	3.099073	2.813407	1.233274
H	2.948677	3.710202	-1.458589
H	4.262513	2.554139	-1.820667
H	2.768186	2.559226	-2.803805
I	0.001753	-0.004080	3.247288

Va

C	1.396590	-1.276269	0.020548
C	2.906978	-1.145900	-0.152019

C	3.437290	0.169194	0.449671
C	2.365735	1.274829	0.420215
C	1.406882	1.099366	-0.749448
H	1.006975	-2.216212	-0.375633
H	3.376713	-2.012571	0.321168
H	3.754848	0.008180	1.484862
H	1.780355	1.267050	1.346907
H	0.652446	1.888558	-0.793609
H	1.945043	1.104336	-1.709765
H	2.823637	2.264562	0.339582
H	4.320890	0.488080	-0.112468
H	3.136225	-1.200238	-1.222133
H	1.126252	-1.220732	1.085585
N	0.720255	-0.182732	-0.663266
C	-0.572672	-0.335960	-1.195099
H	-0.734474	0.383755	-2.004497
H	-0.728354	-1.362254	-1.542644
Si	-1.989346	0.013444	0.126683
C	-1.758047	1.755781	0.768201
H	-2.554264	1.994244	1.485465
H	-0.798563	1.869550	1.287439
H	-1.803294	2.494882	-0.040502
C	-1.842639	-1.254077	1.495805
H	-2.735484	-1.208596	2.133290
H	-1.766235	-2.273374	1.098781
H	-0.971665	-1.064690	2.133849
C	-3.562703	-0.190229	-0.865709
H	-3.648516	-1.204990	-1.272533
H	-4.435903	-0.008512	-0.226218
H	-3.602057	0.519462	-1.700634
F^-			
F	0.000000	0.000000	0.000000



C	-1.724645	-1.201121	-0.340222
C	-3.244376	-1.071164	-0.326973
C	-3.696218	0.358841	-0.678754
C	-2.639785	1.400896	-0.266152
C	-1.836262	0.939093	0.942319
H	-1.395350	-2.218809	-0.117756
H	-3.654837	-1.797479	-1.034340
H	-3.878235	0.441384	-1.755335
H	-1.942996	1.586666	-1.091722
H	-1.096805	1.679877	1.253605
H	-2.493595	0.746272	1.803221
H	-3.107850	2.358961	-0.022218
H	-4.646064	0.567793	-0.175519
H	-3.605337	-1.354271	0.668434
H	-1.323190	-0.924985	-1.326115
N	-1.136049	-0.308118	0.651286
C	0.077593	-0.603829	1.267089
H	0.188362	-0.042244	2.199184

H	0.195894	-1.681456	1.418122
Si	1.700476	-0.088627	0.151505
C	1.351138	1.721663	-0.179175
H	2.183054	2.169920	-0.728127
H	0.437893	1.838758	-0.776177
H	1.215456	2.271326	0.760597
C	1.571880	-1.275323	-1.296461
H	2.572661	-1.519038	-1.665042
H	1.069931	-2.206764	-1.009327
H	1.010928	-0.827177	-2.125339
C	2.991679	-0.497866	1.447806
H	2.880716	0.153139	2.323839
H	2.885296	-1.536796	1.784567
H	3.997573	-0.364650	1.040589
F	3.949573	0.603337	-1.280230

$F\text{-}SiMe_3$

Si	0.000000	0.000000	0.005086
C	0.000000	1.790825	-0.519541
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H	0.000000	1.864439	-1.614786
H	-0.888735	2.315728	-0.148439
C	-1.550900	-0.895413	-0.519541
H	-1.561112	-1.927532	-0.148439
H	-2.449847	-0.388197	-0.148439
H	-1.614652	-0.932220	-1.614786
C	1.550900	-0.895413	-0.519541
H	1.614652	-0.932220	-1.614786
H	2.449847	-0.388197	-0.148439
H	1.561112	-1.927532	-0.148439
F	0.000000	0.000000	1.668392

VIa

C	-0.390665	1.295898	0.117043
C	1.124007	1.179481	0.324974
C	1.688971	0.049999	-0.535365
C	1.104199	-1.304123	-0.088037
C	-0.296713	-1.134550	0.523957
H	-0.859392	1.790312	0.983225
H	1.590028	2.139040	0.077500
H	1.430579	0.241204	-1.584990
H	1.056102	-1.988373	-0.942595
H	-0.895006	-2.038066	0.379972
H	-0.225706	-0.963902	1.610673
H	1.755161	-1.769714	0.661453
H	2.782672	0.029207	-0.476861
H	1.346414	0.980331	1.381121
H	-0.604459	1.907768	-0.768217
N	-0.995666	-0.018715	-0.098687
C	-2.361644	-0.075530	-0.254067
H	-2.788317	-1.056837	-0.446904
H	-2.827346	0.792984	-0.714594

3aa

C	-2.190039	0.501575	-0.931558

C	-3.439182	1.399219	-0.965348
C	-4.090968	1.473587	0.414203
C	-4.553321	0.069970	0.844891
C	-3.631597	-1.018121	0.268739
H	-2.068485	0.001425	-1.910668
H	-3.159672	2.394881	-1.326020
H	-3.365831	1.869237	1.135907
H	-4.568663	0.002658	1.938810
H	-3.615863	-1.889467	0.930860
H	-4.005539	-1.368624	-0.712219
H	-5.576634	-0.114805	0.496137
H	-4.939057	2.167361	0.402281
H	-4.168699	0.997079	-1.679920
H	-1.292741	1.107373	-0.762596
N	-2.269674	-0.499858	0.143481
C	-1.309204	-1.577601	-0.062915
H	-1.447590	-2.324113	0.727289
H	-1.477994	-2.092936	-1.028227
C	0.081226	-1.105561	-0.022708
C	1.229169	-0.719993	0.008791
C	2.589926	-0.259992	0.046322
C	3.374019	-0.270213	-1.118175
C	3.147787	0.205131	1.247690
C	4.691807	0.176984	-1.077720
H	2.945424	-0.629261	-2.049586
C	4.465854	0.652234	1.279627
H	2.543874	0.214118	2.150642
C	5.240566	0.639299	0.119104
H	5.291205	0.165191	-1.983778
H	4.888706	1.011346	2.213742
H	6.269012	0.988429	0.147332

VIIa

Au	-2.516543	0.023230	0.050228
Au	0.551998	-0.019715	-0.184648
P	-2.659862	-2.324159	0.117482
P	0.413055	-2.407149	-0.226413
P	0.486887	2.369145	-0.211322
P	-2.592065	2.373507	0.068836
C	-1.213821	-3.120128	-0.678003
H	-1.214631	-4.199610	-0.483877
H	-1.329211	-2.965515	-1.757936
C	-1.108930	3.126652	-0.697730
H	-1.205735	2.973493	-1.779655
H	-1.084020	4.206089	-0.504807
C	-3.972036	3.110154	-0.863563
C	0.937892	3.053394	1.412295
C	-2.728671	3.087366	1.739204
C	0.886796	-3.121826	1.377547
C	-4.079589	-3.042236	-0.768141
C	1.673663	3.091526	-1.383793
C	1.553143	-3.146763	-1.434179
C	-2.765406	-3.009267	1.801767

H	0.827375	4.142397	1.406755
H	0.311134	2.620674	2.195405
H	1.981485	2.793321	1.616108
H	2.686640	2.790016	-1.103100
H	1.459882	2.729637	-2.393503
H	1.597786	4.183571	-1.360198
H	-2.635118	4.177167	1.692662
H	-3.708455	2.823171	2.149223
H	-1.956354	2.677551	2.394275
H	-3.916017	4.202740	-0.817297
H	-3.926804	2.783193	-1.906240
H	-4.917409	2.774811	-0.426580
H	-4.053058	-2.732076	-1.816597
H	-4.047555	-4.135050	-0.706324
H	-5.005639	-2.678411	-0.313039
H	-3.728112	-2.719567	2.234331
H	-2.693562	-4.101260	1.770541
H	-1.967195	-2.603693	2.427892
H	0.289975	-2.685348	2.181748
H	0.750181	-4.207779	1.360757
H	1.941007	-2.889486	1.558855
H	2.579403	-2.871601	-1.174840
H	1.452190	-4.236908	-1.419165
H	1.323998	-2.769773	-2.434994
C	7.403347	-1.202356	0.189052
C	6.013323	-1.223722	0.112344
C	5.284677	-0.023330	0.131108
C	5.976410	1.195162	0.229007
C	7.366452	1.209193	0.305312
C	8.083648	0.012262	0.285344
H	7.957057	-2.137065	0.173151
H	5.483766	-2.169459	0.036739
H	5.418042	2.127110	0.244670
H	7.890997	2.157751	0.380431
H	9.168430	0.026090	0.344578
C	3.849991	-0.039300	0.046301
C	2.630504	-0.045791	-0.033803

VIIIa

Au	1.326211	0.777631	-1.501951
Au	-0.949779	-0.027204	0.626025
P	1.536369	-1.446928	-2.232656
P	-1.147930	-1.983140	-0.708659
P	-0.662278	1.972789	1.877249
P	1.021981	2.923812	-0.595484
C	0.492120	-2.600221	-1.243278
H	0.347046	-3.528288	-1.809763
H	1.051616	-2.840911	-0.333107
C	0.804584	2.868547	1.233837
H	1.689779	2.364694	1.639268
H	0.783390	3.892200	1.627854
C	2.408399	4.086738	-0.795023
C	-2.018625	3.178580	1.918930

C	-0.431894	3.797551	-1.259110
C	-2.119795	-1.830954	-2.233758
C	3.202932	-2.156115	-2.035490
C	-0.291211	1.652057	3.625024
C	-1.864443	-3.354791	0.235464
C	1.108848	-1.765365	-3.974899
H	-1.706623	4.024786	2.539900
H	-2.268993	3.540708	0.920088
H	-2.901707	2.709847	2.362938
H	-0.094046	2.599721	4.136564
H	-1.155039	1.161405	4.084209
H	0.579897	0.998001	3.706543
H	-0.602471	4.733557	-0.717729
H	-0.249368	4.015762	-2.316114
H	-1.316617	3.157573	-1.185964
H	2.166423	5.048678	-0.331533
H	3.305319	3.669013	-0.328216
H	2.600161	4.232839	-1.862337
H	3.906452	-1.599944	-2.662485
H	3.514637	-2.070845	-0.990407
H	3.201140	-3.209875	-2.333132
H	1.809871	-1.214883	-4.610053
H	1.184881	-2.835760	-4.191877
H	0.095549	-1.418117	-4.190728
H	-1.766784	-0.979993	-2.822704
H	-2.005622	-2.751075	-2.816020
H	-3.170784	-1.685263	-1.976365
H	-2.868259	-3.070163	0.561698
H	-1.920854	-4.249985	-0.392262
H	-1.241823	-3.556021	1.112048
C	5.700951	-1.024382	1.689630
C	4.375408	-0.690499	1.427913
C	3.330590	-1.380103	2.066837
C	3.641846	-2.405647	2.972914
C	4.970753	-2.733452	3.230919
C	6.003041	-2.046415	2.591076
H	6.500289	-0.486188	1.187494
H	4.137062	0.102202	0.722944
H	2.838813	-2.942746	3.470097
H	5.200248	-3.529907	3.933502
H	7.038394	-2.305953	2.793770
C	1.970686	-1.032936	1.766008
C	0.844115	-0.698923	1.430075
C	-4.124868	-0.407350	1.507497
C	-5.488135	-1.061470	1.784861
C	-5.870317	-2.022688	0.661118
C	-5.992456	-1.254029	-0.666874
C	-5.045802	-0.042951	-0.698369
H	-4.103099	0.601924	1.959799
H	-5.453024	-1.576374	2.751033
H	-5.104512	-2.802958	0.575151
H	-5.765653	-1.923077	-1.505159

H	-4.756189	0.182186	-1.729927
H	-5.550198	0.860764	-0.305712
H	-7.021174	-0.900406	-0.807253
H	-6.812522	-2.530751	0.895428
H	-6.262592	-0.288047	1.867236
H	-3.320243	-0.987948	1.978854
N	-3.834909	-0.330442	0.070403
C	-2.774233	0.612056	-0.213008
H	-2.619753	0.678498	-1.294683
H	-3.023870	1.618995	0.151903

TS_{VIII-3}

Au	3.328991	-0.298974	0.041808
Au	-0.162268	0.337421	0.207324
P	3.020932	-2.547066	0.636188
P	0.059820	-1.990800	-0.192005
P	0.617671	2.550293	0.618834
P	3.466210	1.978850	-0.506278
C	1.238305	-2.933101	0.868626
H	1.083142	-4.010157	0.728615
H	0.985225	-2.688298	1.907027
C	2.418741	2.959450	0.634557
H	2.790586	2.758351	1.646393
H	2.549296	4.029747	0.432035
C	5.100798	2.774366	-0.384585
C	-0.094874	3.731226	-0.581417
C	2.879142	2.366263	-2.187551
C	0.519847	-2.411929	-1.909137
C	3.780744	-3.055093	2.213015
C	0.062797	3.209535	2.228870
C	-1.492034	-2.914831	0.079978
C	3.634635	-3.766399	-0.572349
H	0.258671	4.747719	-0.378594
H	0.172741	3.450655	-1.603618
H	-1.184865	3.704119	-0.484213
H	0.371519	4.254005	2.344708
H	-1.028822	3.144448	2.280739
H	0.489453	2.610382	3.038812
H	2.831643	3.449971	-2.336510
H	3.572546	1.928748	-2.912560
H	1.888655	1.928136	-2.344760
H	5.027058	3.836063	-0.641667
H	5.482912	2.669918	0.635232
H	5.792473	2.279816	-1.073434
H	4.868238	-2.964783	2.131712
H	3.429658	-2.401568	3.016734
H	3.516757	-4.092918	2.441878
H	4.720627	-3.659343	-0.655679
H	3.393614	-4.781077	-0.239121
H	3.189594	-3.587962	-1.554415
H	1.475884	-1.945456	-2.167262
H	0.591309	-3.497020	-2.038375
H	-0.245994	-2.017659	-2.584405

H	-2.272321	-2.501410	-0.565906
H	-1.358532	-3.978081	-0.146076
H	-1.805020	-2.799413	1.122508
C	-6.269220	-1.394863	2.467930
C	-5.110985	-1.112179	1.749330
C	-4.626048	0.205475	1.669347
C	-5.328303	1.228503	2.329808
C	-6.486329	0.939277	3.046144
C	-6.961312	-0.371396	3.117346
H	-6.632770	-2.417542	2.521075
H	-4.571747	-1.909194	1.244230
H	-4.960515	2.249522	2.273716
H	-7.020085	1.740132	3.550685
H	-7.865440	-0.594276	3.677200
C	-3.440138	0.492159	0.913505
C	-2.426380	0.692278	0.235414
C	-4.927053	1.037064	-2.187909
C	-5.908059	0.244180	-3.038514
C	-5.868839	-1.254434	-2.687010
C	-4.460617	-1.687349	-2.235402
C	-3.379516	-0.818438	-2.868755
H	-4.968758	2.106758	-2.404852
H	-6.910242	0.654606	-2.883839
H	-6.583363	-1.468112	-1.884508
H	-4.370794	-1.606521	-1.145903
H	-2.379525	-1.139682	-2.568764
H	-3.441889	-0.849648	-3.962067
H	-4.266474	-2.732412	-2.495902
H	-6.181892	-1.837074	-3.560019
H	-5.661559	0.397405	-4.095822
H	-5.133946	0.894023	-1.117292
N	-3.551240	0.576720	-2.429856
C	-2.549599	1.256302	-1.955579
H	-1.543775	0.913076	-2.163592
H	-2.709427	2.292127	-1.681652

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