Electronic Supplementary Information

for

Copper Catalyzed *N*-Formylation of *α*-Silyl-Substituted Tertiary *N*-Alkylamines by Air

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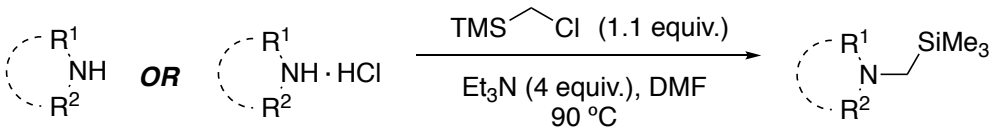
1. General Information

All reactions were performed in oven-dried glassware. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate and visualized with UV light (254 nm) or stained with a $KMnO_4$ solution. Flash chromatography was performed using silica gel and gradient solvent system (petroleum ether:EtOAc as the eluent). ^{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 data was collected on a FTIR spectrometer. High-resolution mass spectra (ESI) were obtained using LC/HRMS TOF spectrometer fitted with an analytical electrospray source using NaI mass calibration. Mass spectral data are reported in units of mass to charge (*m/s*).

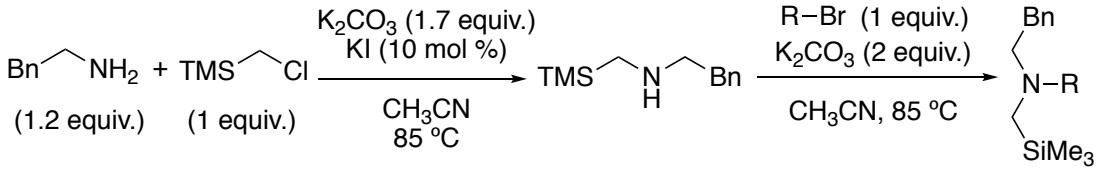
2. Experimental Procedures

2.1 General Procedure for the Preparation of *α*-Silylamines (1a–g, 1m–z)



To a solution of the secondary amine or its HCl salt (4 mmol, 1 equiv.) in TEA (16 mmol, 2.2 mL) and DMF (2.5 mL), (chloromethyl)trimethylsilane (4 mmol, 0.56 mL) was added dropwise into a 25 mL round bottom flask with a magnetic stirrer bar under a nitrogen atmosphere. The reaction was heated to 90 °C and was stirred for 16 h. Upon completion of the reaction, the organic layer was extracted with EtOAc (3 x 25 mL), then washed with brine (15 mL) and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure and the crude reaction residue was purified by flash column chromatography on neutral aluminum oxide (eluent: petroleum ether:EtOAc = 20:1–10:1) to give the *α*-silylamine derivative in 36–98% yield.

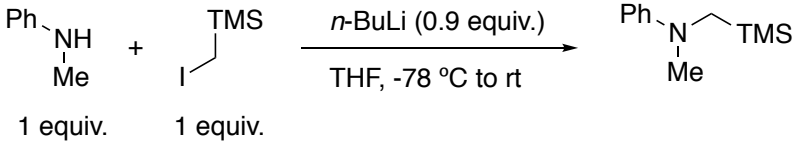
2.2 General Procedure for the Preparation of *α*-Silylamines (1h–k)



2-Phenethylamine (4.8 mmol, 0.6 mL) and (chloromethyl)trimethylsilane (4 mmol, 0.56 mL) were dissolved in CH_3CN (6 mL) at room temperature, followed by the addition of K_2CO_3 (6.8 mmol, 940 mg) and KI (0.4 mmol, 66 mg). The resulting solution was allowed to stir at 85 °C for 17 h. The reaction was cooled to room temperature and filtered through a neutral Al_2O_3 pad with EtOAc (30 mL). The filtrate was concentrated under reduced pressure to afford the crude product as a yellow oil (610 mg, 74% yield), which was subjected to next step without any further purification.

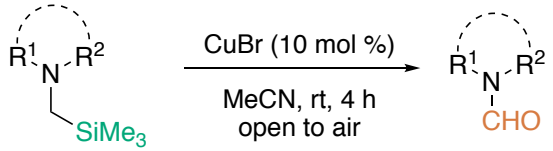
To the solution of crude 2-phenyl-*N*-((trimethylsilyl)methyl)ethan-1-amine (2 mmol, 415 mg) in CH_3CN (5 mL) was added respective bromide compound (2 mmol) and K_2CO_3 (4 mmol, 553 mg) at room temperature and the resulting mixture was stirred at 85 °C for 17 h. Upon completion, the crude mixture was filtered through a pad of celite pad with EtOAc (20 mL). The resulting filtrate was dried under vacuum to give the crude mixture, which was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 20:1 or 10:1) to afford the the title compounds in 55–75% yield.

2.3 Procedure for the Preparation of *N*-Methyl-*N*-((trimethylsilyl)methyl)aniline (1l)



To a solution of *N*-methylaniline (5 mmol, 536 mg) in THF (30 mL) was added *n*-BuLi (4.5 mmol) at −78 °C. After stirred for 1 h, (iodomethyl)trimethylsilane (5 mmol, 1.07 g) was added dropwise to the solutions and the resulting solutions were stirred for 5 h at room temperature. Then the solutions were quenched by aq. NH_4Cl and extraced with EA. The organic layers were dried and concentrated in *vacuo* to afford residues, which were subjected to neutral aluminum oxide (eluent: petroleum ether:EtOAc = 50:1) to give title compound as a yellow oil in 54% yield (522 mg).

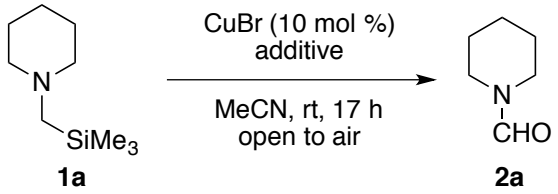
2.4 General Procedure for the Preparation of *N*-Formyl amines (2)



All *N*-formyl amines were synthesized using these conditions unless otherwise specified. CuBr (2.9 mg, 0.02 mmol, 0.1 equiv.) was added to a 10 mL reaction tube containing a magnetic stirrer. The *α*-silylamine (0.2 mmol, 1 equiv.) and acetonitrile (0.5 mL) was then added. The reaction was left to open to air and stirred at 25 °C for 4 h. *Work up for* ***2a–g, 2l–***

***n** and **2u**:* upon completion of the reaction, the crude mixture was subjected to a silica pad twice and neutral aluminum oxide pad once with EtOAc, the solvent was evaporated under reduced pressure each time, which led to corresponding *N*-formyl amine products **2a**–**g**, **2l**–**n** and **2u** in 62–94% yield. *Work up for **2h**–**k**, **2o**–**t** and **2v**–**z**:* upon completion of the reaction, the solvents were removed under reduced pressure and the crude reaction residue was purified by flash column chromatography on chromatography on silica gel (eluent: petroleum ether:EtOAc = 8:1–4:1) to afford the the title compound in 68–88% yield.

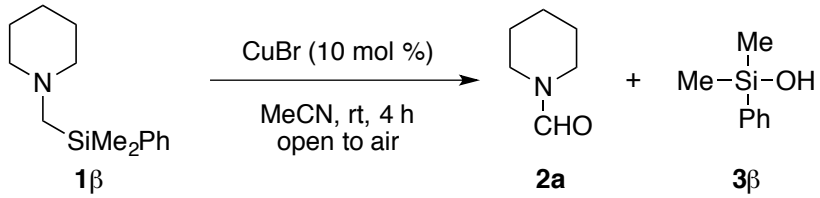
2.5 General Procedure for the Control Experiments with Additives



1a **2a**

All control experiments were conducted at 0.2 mmol scale with given additives. CuBr (2.9 mg, 0.02 mmol, 0.1 equiv.) was added to a 10 mL reaction tube containing a magnetic stirrer. 1-((Trimethylsilyl)methyl)piperidine (**1a**) (0.2 mmol, 34 mg, 1 equiv.), additive and acetonitrile (0.5 mL) was then added. The reaction was left to open to air and stirred at 25 °C for 17 h. Upon completion, the reaction mixture was dried under reduced pressure to give the crude product as oil, which was subjected to ^{1}H NMR analysis to determine the crude product yield without further purification.

2.5.1 General Procedure for the Isolation of Dimethyl(phenyl)silanol (3*β*)

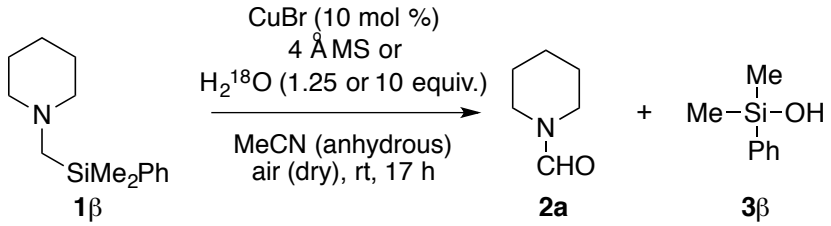


1β **2a** **3**β

CuBr (2.9 mg, 0.02 mmol, 0.1 equiv.) was added to a 10 mL reaction tube containing a magnetic stirrer. 1-((Dimethyl(phenyl)silyl)methyl)piperidine (**1*β***) (0.2 mmol, 46 mg, 1 equiv.) and acetonitrile (0.5 mL) was then added. The reaction was left to open to air and

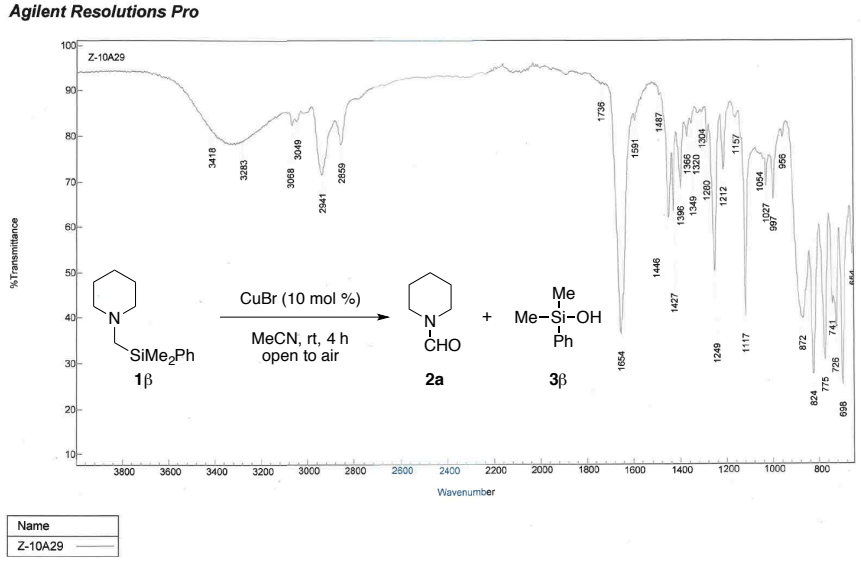
stirred at 25 °C for 4 h. The resulting mixture was dried under vacuum to give the crude mixture, which was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1) to afford the dimethyl(phenyl)silanol (***3β***) as a colorless oil (25 mg, 82% yield).

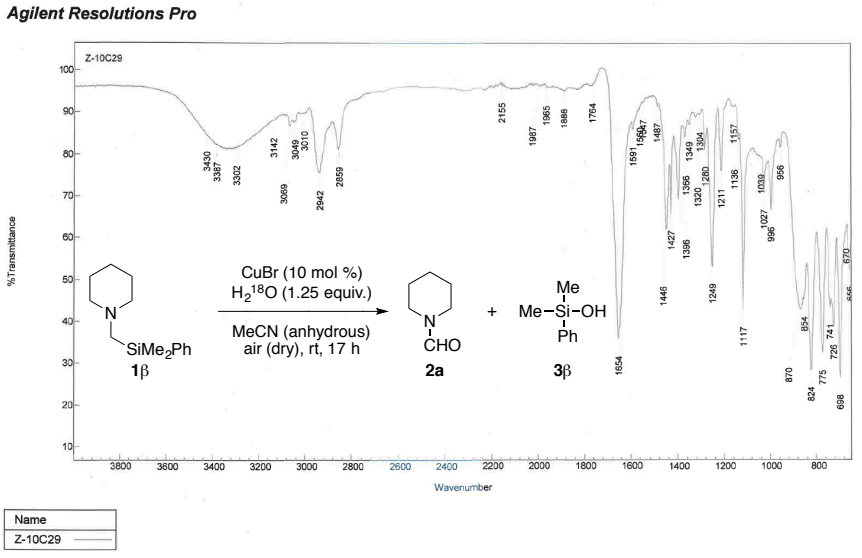
2.5.2 General Procedure for the Control Experiments with 4 Å MS or $H_2{}^{18}O$

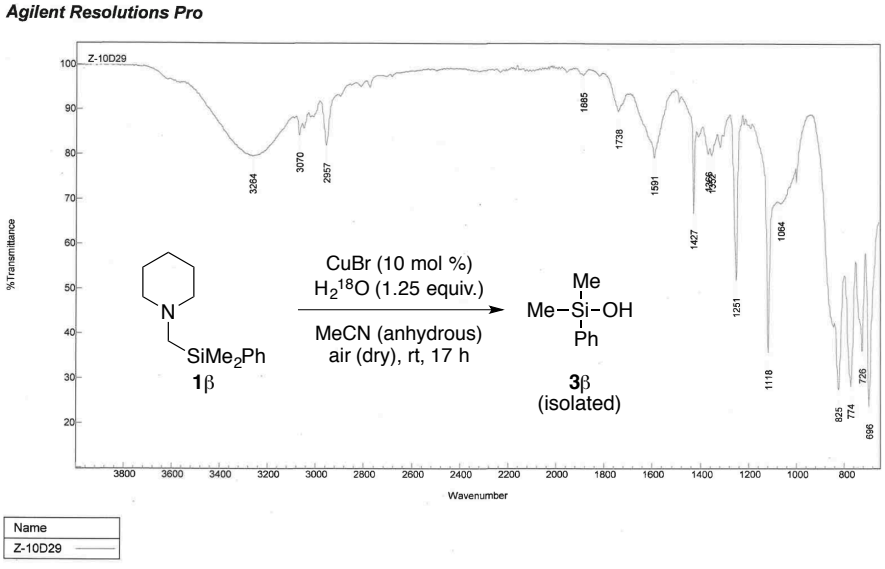


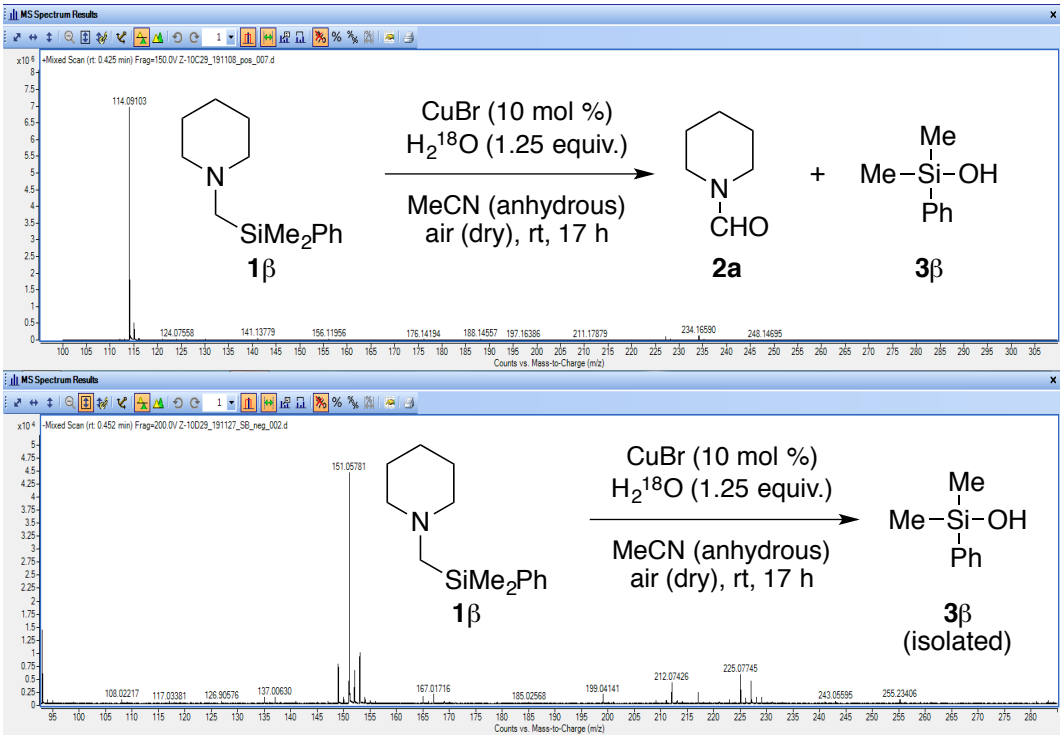
CuBr (2.9 mg, 0.02 mmol, 0.1 equiv.) was added to a 10 mL reaction tube containing a magnetic stirrer. 1-((Dimethyl(phenyl)silyl)methyl)piperidine (***1β***) (0.2 mmol, 46 mg, 1 equiv.), 4 Å MS (20 mg) or $H_2{}^{18}O$ (0.25 mmol, 5 mg, 1.25 equiv. or 2 mmol, 40 mg, 10 equiv.) and anhydrous acetonitrile (0.5 mL) was then added. The reaction was subjected to air dried through concentrated H_2SO_4 prior to use and stirred at 25 °C for 17 h. Upon completion, the reaction mixture was dried under reduced pressure to give the crude product as oil, which was subjected to ^1H NMR analysis to determine the crude product yield without further purification. The resulting mixture obtained for the reaction with 1.25 equiv. of $H_2{}^{18}O$ was also subjected to a neutral aluminum oxide pad once with ethyl acetate, the solvent was evaporated under reduced pressure to furnish the crude product, which was subject to HRMS (ESI) and IR analysis without further purification. IR (neat, cm^{-1}): 3387, 2942, 2859, 1654, 1446, 1249, 1117, 870, 824; HRMS (ESI) calcd. for **2a**: $C_6H_{12}NO$ (M^+ + H): 114.09189, found: 114.09103; HRMS (ESI) calcd. for ***3β***: $C_8H_{11}OSi$ (M^+ – H): 151.05781, found: 151.05793. The control experiment with $H_2{}^{18}O$ indicated no ^{18}O incorporation in the *N*-formylation product.

Figure S1. IR and HRMS Spectra of Control Experiments with $H_2{}^{18}O$

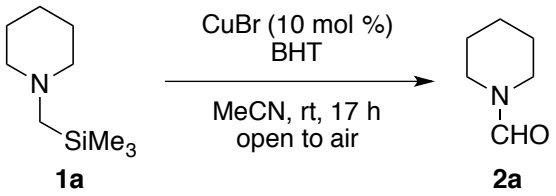








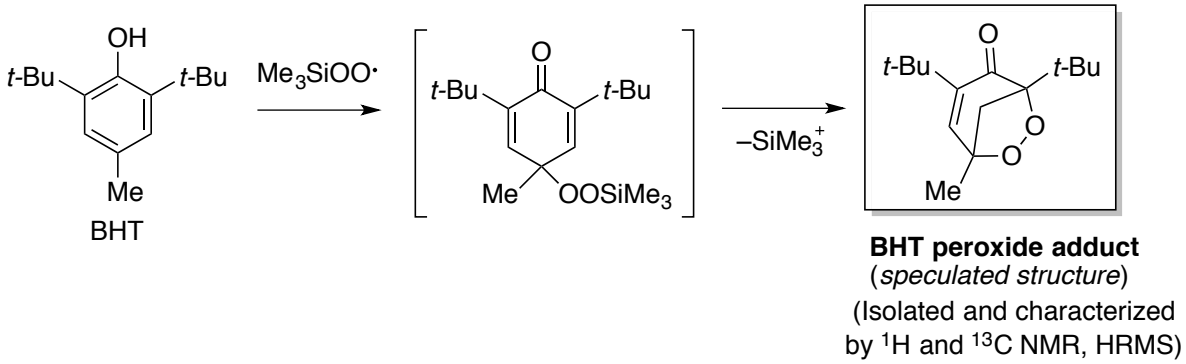
2.5.3 General Procedure for the Control Experiments with BHT



CuBr (2.9 mg, 0.02 mmol, 0.1 equiv.) was added to a 10 mL reaction tube containing a magnetic stirrer. 1-((Trimethylsilyl)methyl)piperidine (**1a**) (0.2 mmol, 34 mg, 1 equiv.), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 22 mg, 0.1 mmol) and acetonitrile (0.5 mL) was then added. The reaction was left to open to air and stirred at 25 °C for 17 h. The resulting mixture was dried under vacuum to give the crude mixture, which was subjected to ^{1}H NMR analysis to determine the crude yield of **2a** as 17%. Then the crude NMR sample was dried under vacuo and purified by flash column chromatography on neutral aluminum oxide (eluent: petroleum ether:EtOAc = 15:1) to afford the BHT-peroxide adduct as a yellow oil (12 mg, 48% yield); IR (neat, cm^{-1}): 2957, 2871, 1719, 1687, 1611, 1364, 1339, 1120, 1055; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 3.00 – 3.00 (m, 1H), 2.99 (s, 1H), 2.08 (s, 3H), 1.20 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 203.9, 170.5, 129.2, 91.4, 45.1, 37.5,

31.4, 29.7, 28.2, 24.4; HRMS (ESI) calcd. for $C_{15}H_{25}O_3$ (M^+ + H): 253.18039, found: 253.17831.

Figure S2. Proposed BHT Peroxide Adduct



BHT peroxide adduct
(*speculated structure*)
(Isolated and characterized by ^1H and ^{13}C NMR, HRMS)

Figure S3. HRMS Spectra for the BHT Peroxide Adduct

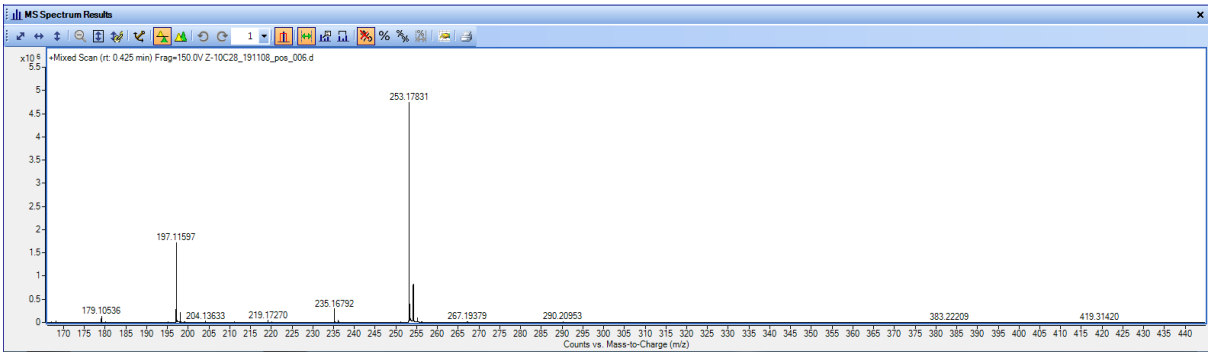
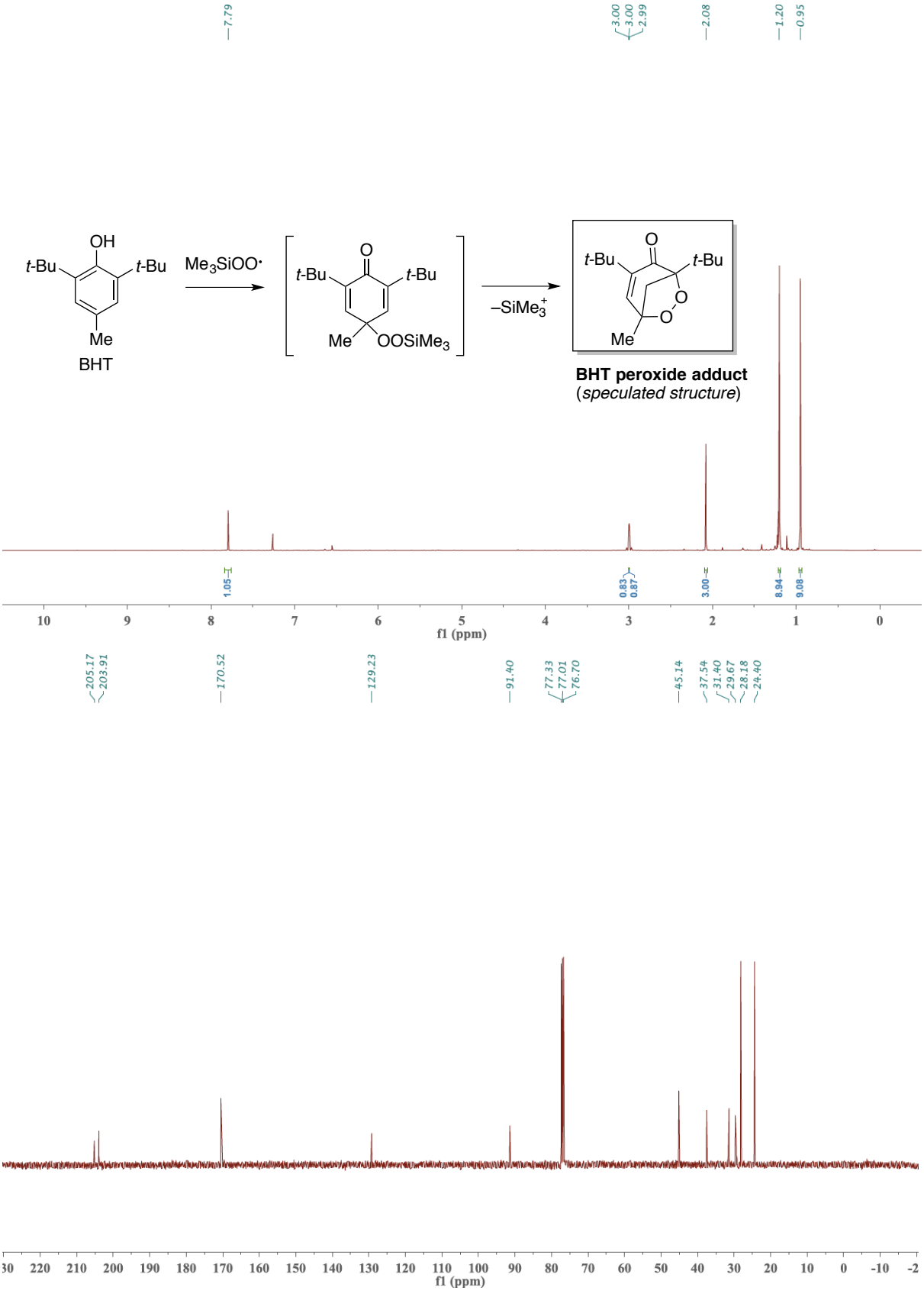
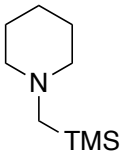


Figure S4. ^{1}H and ^{13}C NMR Spectra of the Speculated BHT Peroxide Adduct



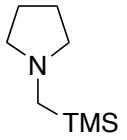
3. Spectroscopic Data

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



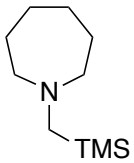
Colorless oil (562 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (t, J = 5.4 Hz, 4H), 1.88 (s, 2H), 1.55 (p, J = 5.6 Hz, 4H), 1.37 (q, J = 6.2 Hz, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.6, 52.8, 27.4, 24.9, 0.0.

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



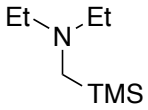
Colorless oil (378 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51–2.43 (m, 4H), 2.00 (s, 2H), 1.75 (q, J = 3.6 Hz, 4H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.4, 59.4, 49.1, 25.1, 0.0.

1-((Trimethylsilyl)methyl)azepane (1c)



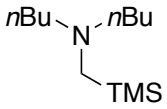
Colorless oil (726 mg, 98% yield); IR (neat, cm^{-1}): 2924, 2784, 1450, 1246, 835, 760, 690; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.60–2.56 (m, 4H), 2.05 (s, 2H), 1.60 (d, J = 5.4 Hz, 4H), 1.58–1.53 (m, 4H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.7, 51.8, 28.9, 28.3, 0.0; HRMS (ESI) calcd. for $C_{10}H_{24}NSi$ (M^{+} + H): 186.1678, found: 186.1665.

***N*-Ethyl-*N*-((trimethylsilyl)methyl)ethanamine (1d)[S3]**



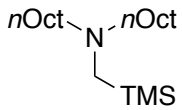
Yellow oil (357 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (q, *J* = 7.1 Hz, 4H), 1.91 (d, *J* = 1.2 Hz, 2H), 0.97 (td, *J* = 7.1, 1.1 Hz, 6H), 0.04 (d, *J* = 1.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 45.9, 12.8, 0.0.

***N*-Butyl-*N*-((trimethylsilyl)methyl)butan-1-amine (1e)**



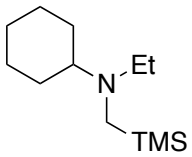
Pale yellow oil (577 mg, 67% yield); IR (neat, cm^{-1}): 2955, 2862, 2787, 1458, 1376, 1247, 1088, 836; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (t, *J* = 7.4 Hz, 4H), 1.86 (s, 2H), 1.29 (dq, *J* = 37.7, 7.3 Hz, 9H), 0.87 (t, *J* = 7.2 Hz, 6H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.5, 47.2, 30.4, 21.9, 15.4, 0.0; HRMS (ESI) calcd. for $C_{12}H_{30}NSi$ (M^+ + H): 216.21475, found: 216.21328.

***N*-Octyl-*N*-((trimethylsilyl)methyl)octan-1-amine (1f)**



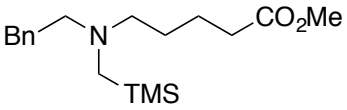
Yellow oil (680 mg, 52% yield); IR (neat, cm^{-1}): 2930, 2838, 1470, 1238, 836; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35–2.27 (m, 4H), 1.90 (s, 2H), 1.44–1.35 (m, 4H), 1.27 (s, 20H), 0.91–0.84 (m, 6H), 0.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.8, 47.2, 33.1, 30.9, 30.6, 28.8, 28.1, 23.9, 15.3, 0.0; HRMS (ESI) calcd. for $C_{20}H_{46}NSi$ (M^+ + H): 328.33995, found: 328.33957.

***N*-Ethyl-*N*-((trimethylsilyl)methyl)cyclohexanamine (1g)**



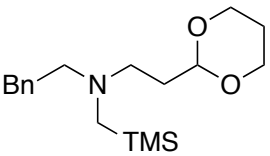
Pale yellow oil (606 mg, 71% yield); IR (neat, cm^{-1}): 2927, 2853, 1701, 1419, 1245, 1172, 853, 843, 761, 691; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (q, *J* = 7.1 Hz, 3H), 1.95 (s, 2H), 1.82–1.66 (m, 5H), 1.64–1.56 (m, 1H), 1.23–1.12 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 5-(Phenethyl((trimethylsilyl)methyl)amino)pentanoate (1h)



Colorless oil (482 mg, 75% yield); IR (neat, cm^{-1}): 2949, 2790, 1737, 1436, 1246, 1146, 837, 698; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 2H), 7.13 (ddt, *J* = 7.0, 3.4, 1.5 Hz, 3H), 3.62 (s, 3H), 2.71–2.63 (m, 2H), 2.61–2.54 (m, 2H), 2.40 (dd, *J* = 8.3, 6.2 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.95 (s, 2H), 1.62–1.52 (m, 2H), 1.47–1.36 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 142.1, 130.0, 129.5, 127.0, 60.5, 58.2, 52.7, 47.1, 35.3, 34.4, 27.9, 24.1, 0.0; HRMS (ESI) calcd. for $C_{18}H_{32}NO_2Si$ (M^+ + H): 322.22024, found: 322.21890.

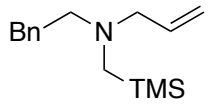
***N*-(2-(1,3-Dioxan-2-yl)ethyl)-2-phenyl-*N*-((trimethylsilyl)methyl)ethan-1-amine (1i)**



Colorless oil (353 mg, 55% yield); IR (neat, cm^{-1}): 2953, 2850, 1246, 1136, 838, 736; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 2H), 7.17–7.10 (m, 3H), 4.51 (t, *J* = 5.2 Hz, 1H), 4.04 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.74–3.62 (m, 2H), 2.71–2.65 (m, 2H), 2.60–2.54 (m,

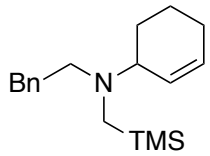
2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.11–1.96 (m, 1H), 1.95 (s, 2H), 1.73–1.65 (m, 2H), 1.27 (ddt, *J* = 13.4, 2.6, 1.3 Hz, 1H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 130.2, 129.6, 127.1, 102.4, 68.2, 60.6, 53.2, 47.3, 34.7, 34.3, 27.3, 0.0; HRMS (ESI) calcd. for $C_{18}H_{32}NO_2Si$ (M^+ + H): 322.22024, found: 322.21961.

***N*-Phenethyl-*N*-((trimethylsilyl)methyl)prop-2-en-1-amine (1j)**



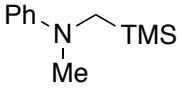
Colorless oil (302 mg, 61% yield); IR (neat, cm^{-1}): 2954, 2790, 1418, 1247, 1092, 853; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (ddd, *J* = 8.9, 6.3, 1.4 Hz, 2H), 7.15–7.08 (m, 3H), 5.80 (ddtd, *J* = 16.6, 10.1, 6.3, 1.4 Hz, 1H), 5.16–5.01 (m, 2H), 3.05 (dq, *J* = 6.3, 1.4 Hz, 2H), 2.73–2.55 (m, 4H), 1.97 (d, *J* = 1.3 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 137.6, 130.1, 129.5, 127.1, 118.1, 61.8, 60.3, 46.8, 34.5, 0.0; HRMS (ESI) calcd. for $C_{15}H_{26}NSi$ (M^+ + H): 248.18345, found: 248.18241.

***N*-Phenethyl-*N*-((trimethylsilyl)methyl)cyclohex-2-en-1-amine (1k)**



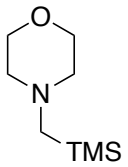
Colorless oil (357 mg, 62% yield); IR (neat, cm^{-1}): 2935, 1246, 852, 739, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.25–7.18 (m, 3H), 5.79 (ddq, *J* = 9.5, 3.4, 2.2, 1.7 Hz, 1H), 5.65–5.55 (m, 1H), 3.46–3.37 (m, 1H), 2.84–2.67 (m, 3H), 2.66–2.54 (m, 1H), 2.13 (d, *J* = 14.8 Hz, 1H), 2.04–1.95 (m, 3H), 1.87–1.78 (m, 2H), 1.63–1.49 (m, 1H), 1.49–1.36 (m, 1H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 132.7, 130.9, 130.3, 129.6, 127.1, 59.8, 56.8, 43.1, 37.3, 26.9, 24.3, 23.4, 0.0; HRMS (ESI) calcd. for $C_{18}H_{30}NSi$ (M^+ + H): 288.21475, found: 288.21340.

***N*-Methyl-*N*-((trimethylsilyl)methyl)aniline (1l)** [S18]



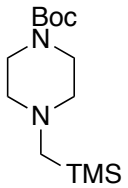
Pale yellow oil (522 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 2H), 6.71–6.60 (m, 3H), 2.93 (s, 3H), 2.86 (s, 2H), 0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.1, 116.3, 113.0, 105.9, 45.2, 41.4, 0.0.

4-((Trimethylsilyl)methyl)morpholine (1m)[S1]



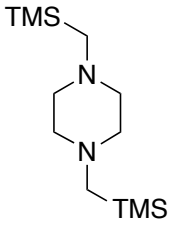
Pale yellow oil (534 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69–3.61 (m, 4H), 2.35 (dd, *J* = 5.7, 3.7 Hz, 4H), 1.87 (s, 2H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.3, 58.6, 52.5, 0.0.

***tert*-Butyl 4-((Trimethylsilyl)methyl)piperazine-1-carboxylate (1n)**



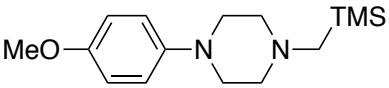
Yellow solid (937 mg, 86% yield); m.p. 100–102 ºC; IR (neat, cm^{-1}): 2953, 2786, 2738, 1686, 1421, 1244, 1164, 1126, 1007, 846, 762; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39–3.34 (m, 4H), 2.28 (t, *J* = 5.1 Hz, 4H), 1.87 (s, 2H), 1.42 (s, 9H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 80.6, 57.8, 52.1, 29.6, 0.0; HRMS (ESI) calcd. for $C_{13}H_{29}N_2O_2Si$ (M^+ + H): 273.19985, found: 273.19786.

1,4-Bis((trimethylsilyl)methyl)piperazine (1o)



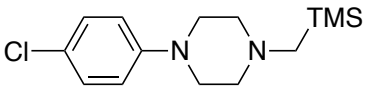
White solid (879 mg, 85% yield); IR (neat, cm^{-1}); 2940, 2787, 2734, 1247, 838; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (t, J = 5.2 Hz, 8H), 1.86 (s, 4H), 0.02 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.4, 51.9, 0.0; HRMS (ESI) calcd. for $C_{12}H_{31}N_2Si_2$ (M^+ + H): 259.20259, found: 259.20215.

1-(4-Methoxyphenyl)-4-((trimethylsilyl)methyl)piperazine (1p)



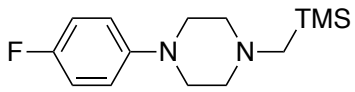
White oil (400 mg, 36% yield); IR (neat, cm^{-1}): 2953, 2833, 2744, 1511, 1443, 1245, 1038, 833; ^1H NMR (400 MHz, $CDCl_3$) δ 6.92–6.86 (m, 2H), 6.86–6.81 (m, 2H), 3.76 (s, 3H), 3.12–3.02 (m, 4H), 2.60–2.53 (m, 4H), 1.98 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 147.0, 119.1, 115.5, 58.2, 56.7, 51.9, 51.9, 0.0; HRMS (ESI) calcd. for $C_{15}H_{27}N_2OSi$ (M^+ + H): 279.18928, found: 279.18788.

1-(4-Chlorophenyl)-4-((trimethylsilyl)methyl)piperazine (1q)



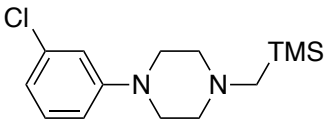
White solid (1.02 g, 90% yield); m.p. 78–80 ºC; IR (neat, cm^{-1}): 2953, 2740, 1686, 1502, 1244, 1126, 826; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 3.20–3.08 (m, 4H), 2.58–2.51 (m, 4H), 1.97 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 130.0, 125.3, 118.2, 57.9, 51.9, 50.4, 0.0; HRMS (ESI) calcd. for $C_{14}H_{24}ClN_2Si$ (M^+ + H): 283.13973, found: 283.13894.

1-(4-Fluorophenyl)-4-((trimethylsilyl)methyl)piperazine (1r)



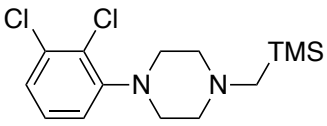
White solid (895 mg, 84% yield); m.p. 96–98 ºC; IR (neat, cm^{-1}): 2953, 2816, 2772, 1508, 1250, 851, 762; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99–6.91 (m, 2H), 6.89–6.81 (m, 2H), 3.14–3.05 (m, 4H), 2.62–2.49 (m, 4H), 1.98 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, $J_{C\text{-}F}$ = 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; HRMS (ESI) calcd. for $C_{14}H_{24}FN_2Si$ (M^+ + H): 267.16928, found: 267.16663.

1-(3-Chlorophenyl)-4-((trimethylsilyl)methyl)piperazine (1s)



White solid (928 mg, 82% yield); m.p. 45–47 ºC; IR (neat, cm^{-1}): 2948, 2817, 2748, 1594, 1247, 1130, 836, 746; ^1H NMR (400 MHz, $CDCl_3$) δ 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 (100 MHz, $CDCl_3$) δ 153.5, 136.0, 131.1, 120.1, 116.7, 114.8, 57.8, 51.9, 49.9, 0.0; HRMS (ESI) calcd. for $C_{14}H_{24}ClN_2Si$ (M^+ + H): 283.13973, found: 283.13894.

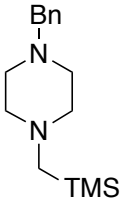
1-(2,3-Dichlorophenyl)-4-((trimethylsilyl)methyl)piperazine (1t)



White solid (1.14 g, 90% yield); m.p. 80–81 ºC; IR (neat, cm^{-1}): 2953, 2805, 1590, 1452, 1244, 837, 762; ^1H NMR (400 MHz, $CDCl_3$) δ 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

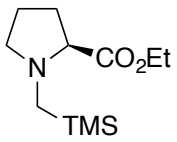
(100 MHz, $CDCl_3$) δ 152.5, 135.1, 128.6, 128.5, 125.4, 119.6, 58.1, 52.6, 51.9, 0.0; HRMS (ESI) calcd. for $C_{14}H_{23}Cl_2N_2Si$ (M^+ + H): 317.10077, found: 317.09981.

1-Benzyl-4-((trimethylsilyl)methyl)piperazine (1u)



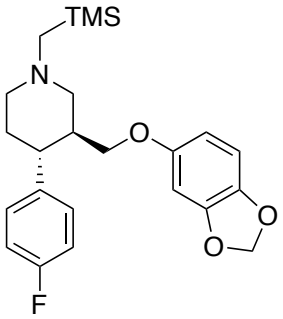
Colorless oil (745 mg, 71% yield); IR (neat, cm^{-1}): 2947, 2798, 1685, 1453, 1247, 854, 696; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 4H), 7.18 (dtd, *J* = 8.5, 4.9, 4.0, 2.3 Hz, 1H), 3.43 (d, *J* = 1.6 Hz, 2H), 2.39 (s, 8H), 1.87 (d, *J* = 1.5 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 130.3, 129.3, 128.1, 64.2, 58.1, 54.5, 51.9, 0.0; HRMS (ESI) calcd. for $C_{15}H_{27}N_2Si$ (M^+ + H): 263.19436, found: 263.19266.

Ethyl ((Trimethylsilyl)methyl)-*L*-prolinate (1v)



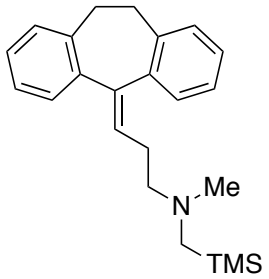
Pale yellow oil (477 mg, 52% yield); IR (neat, cm^{-1}): 2954, 1729, 1247, 1165, 827; ^1H NMR (400 MHz, $CDCl_3$) δ 4.23–4.08 (m, 2H), 3.14–2.98 (m, 2H), 2.38–2.24 (m, 2H), 2.13–2.02 (m, 1H), 1.96–1.72 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 71.5, 61.6, 57.5, 47.3, 30.4, 24.9, 15.7, 0.0; HRMS (ESI) calcd. for $C_{11}H_{24}NO_2Si$ (M^+ +H): 230.15764, found: 230.15731.

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



Pale yellow oil (1.20 g, 72% yield); IR (neat, cm^{-1}): 2892, 2737, 1605, 1486, 1222, 1180, 1038, 830; ^1H NMR (400 MHz, $CDCl_3$) δ 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 (100 MHz, $CDCl_3$) δ 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.

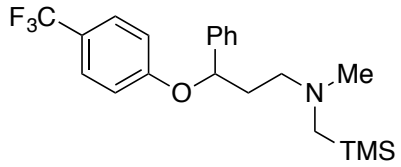
3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)-*N*-methyl-*N*-((trimethylsilyl)-methyl)propan-1-amine (1x)



Yellow oil (1.27 g, 91% yield); IR (neat, cm^{-1}): 2930, 2748, 1450, 1258, 836, 762; ^1H NMR (400 MHz, $CDCl_3$) δ 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*

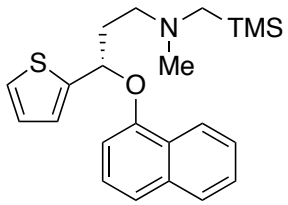
= 6.7 Hz, 2H), 2.11 (s, 3H), 1.86–1.72 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.6, 141.3, 140.5, 138.2, 131.1, 130.9, 129.8, 129.5, 129.2, 128.5, 128.1, 127.2, 126.9, 62.6, 50.8, 47.3, 35.0, 33.3, 28.8, 0.0; HRMS (ESI) calcd. for $C_{23}H_{32}NSi$ (M^+ + H): 350.2304, found: 350.2308.

_N_-Methyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)-_N_-((trimethylsilyl)methyl)propan-1-amine (1y)



Yellow oil (1.11 g, 70% yield); IR (neat, cm^{-1}): 2953, 2767, 1614, 1517, 1324, 1247, 1159, 1108, 1067, 832; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 (100 MHz, $CDCl_3$) δ 162.1, 142.7, 130.0, 129.0, 128.0 (q, $J_{C\text{-}F}$ = 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; HRMS (ESI) calcd. for $C_{21}H_{29}F_3NOSi$ (M^+ + H): 396.19705, found: 396.19731.

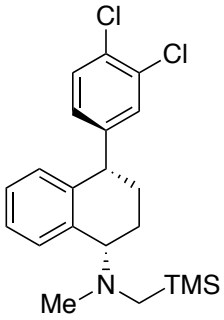
(_S_)-_N_-Methyl-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)-_N_-((trimethylsilyl)methyl)propan-1-amine (1z)



Pale yellow oil (936 mg, 61% yield); IR (neat, cm^{-1}): 2951, 2764, 1577, 1396, 1235, 1093, 838, 768; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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),

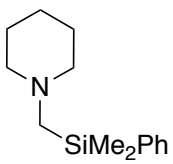
2.20 (s, 3H), 2.18–2.09 (m, 1H), 1.88–1.82 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 146.8, 135.9, 128.7, 127.7, 127.5, 127.5, 127.0, 126.4, 125.9, 125.8, 123.5, 121.8, 108.3, 75.9, 59.2, 51.1, 47.4, 38.3, 0.0; HRMS (ESI) calcd. for $C_{22}H_{30}NOSSi$ (M^+ + H): 384.18174, found: 384.18113.

(1*S*,4*S*)-4-(3,4-Dichlorophenyl)-*N*-methyl-*N*-((trimethylsilyl)methyl)-1,2,3,4-tetrahydro-naphthalen-1-amine (1α)



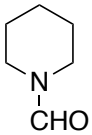
Colorless oil (565 mg, 36% yield); IR (neat, cm^{-1}): 2938, 2776, 1466, 1246, 1029, 851, 738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.37–7.25 (m, 2H), 7.21–7.11 (m, 2H), 6.96–6.85 (m, 2H), 4.16 (dd, *J* = 5.8, 3.4 Hz, 1H), 3.85 (t, *J* = 7.9 Hz, 1H), 2.29 (s, 3H), 2.23–1.97 (m, 4H), 1.82–1.66 (m, 2H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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; HRMS (ESI) calcd. for $C_{21}H_{28}Cl_2NSi$ (M^+ + H): 392.13681, found: 392.13564.

1-((Dimethyl(phenyl)silyl)methyl)piperidine (1β)[S4]



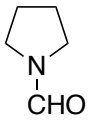
Pale yellow oil (905 mg, 97% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H), 7.37 (dt, *J* = 4.7, 1.8 Hz, 3H), 2.39–2.29 (m, 4H), 2.16 (s, 2H), 1.55 (p, *J* = 5.6 Hz, 4H), 1.38 (q, *J* = 5.8, 4.3 Hz, 2H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 134.1, 129.3, 128.1, 77.8, 77.5, 77.2, 59.0, 51.1, 26.8, 24.3, -2.1.

Piperidine-1-carbaldehyde (2a)[S5]



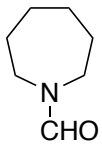
Pale yellow oil (20 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 3.54 – 3.39 (m, 2H), 3.35 – 3.23 (m, 2H), 1.70 – 1.63 (m, 2H), 1.54 (ddt, *J* = 16.8, 10.9, 5.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 46.8, 40.6, 26.6, 25.1, 24.7.

Pyrrolidine-1-carbaldehyde (2b)[S5]



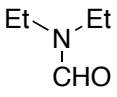
Colorless oil (18 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 3.48 (td, *J* = 5.6, 4.7, 2.1 Hz, 2H), 3.43–3.37 (m, 2H), 1.94–1.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 46.0, 43.1, 24.9, 24.2.

Asepane-1-carbaldehyde (2c)[S5]



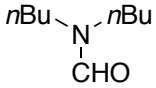
Colorless oil (20 mg, 80% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 3.47–3.41 (m, 2H), 3.39–3.33 (m, 2H), 1.72 (t, *J* = 5.8 Hz, 4H), 1.57 (h, *J* = 2.9, 2.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 46.7, 42.4, 29.2, 26.9, 25.9, 25.8.

***N*,*N*-Diethylformamide (2d)**[S6]



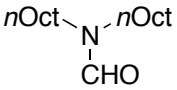
Yellow oil (19 mg, 94% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 3.53–3.46 (m, 2H), 3.46–3.38 (m, 2H), 1.90 (dt, *J* = 4.8, 2.3 Hz, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 45.0, 42.1, 23.9, 23.2.

***N,N*-Dibutylformamide (2e)**[S6]



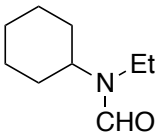
Brown oil (30 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.25 (dd, *J* = 8.5, 6.7 Hz, 2H), 3.16 (dd, *J* = 7.9, 6.4 Hz, 2H), 1.48 (tdd, *J* = 7.8, 5.4, 3.3 Hz, 4H), 1.27 (dtd, *J* = 16.5, 9.2, 8.4, 6.6 Hz, 6H), 0.90 (tt, *J* = 7.3, 2.1 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 47.1, 41.8, 30.7, 29.4, 20.1, 19.6, 13.8, 13.6.

***N,N*-Dioctylformamide (2f)**[S6]



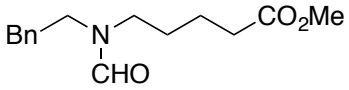
Light brown oil (47 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 3.33–3.16 (m, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.45 (qq, *J* = 10.1, 6.7, 4.6 Hz, 4H), 1.24–1.15 (m, 20H), 0.81 (td, *J* = 6.9, 2.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6,47.4, 42.1, 31.8, 31.7, 29.6, 29.5, 29.3, 28.7, 27.4, 27.0, 26.5, 22.6, 22.6, 14.1, 14.1.

***N*-Cyclohexyl-*N*-ethylformamide (2g)**[S6]



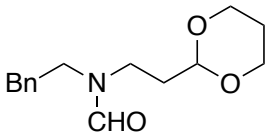
Yellow oil (29 mg, 93% yield); The presence of two rotamers (ratio 2.7:1) were observed in the NMR spectra; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 0.7H), 8.02 (s, 0.3H), 4.07–3.91 (m, 0.5H), 3.23 (q, *J* = 7.1 Hz, 2H), 3.19–3.12 (m, 1H), 1.82–1.56 (m, 6H), 1.44 (qd, *J* = 12.6, 3.6 Hz, 2H), 1.29–1.20 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 57.5, 35.2, 31.8, 29.8, 24.8, 24.2, 13.5.

Methyl 5-(*N*-phenethylformamido)pentanoate (2h)



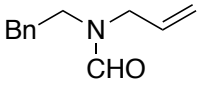
Colorless oil (41 mg, 78% yield); The presence of two rotamers (ratio 1:1) were observed in the NMR spectra; IR (neat, cm^{-1}): 2947, 2864, 1732, 1662, 1169, 701; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 90.2 Hz, 1H), 7.29–7.11 (m, 4H), 7.10–7.02 (m, 1H), 3.59 (s, 3H), 3.48–3.34 (m, 2H), 3.27 (t, *J* = 6.9 Hz, 1H), 3.04 (t, *J* = 6.5 Hz, 1H), 2.77 (dt, *J* = 14.2, 7.6 Hz, 2H), 2.26 (dt, *J* = 17.2, 6.9 Hz, 2H), 1.64–1.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.4, 162.8, 162.7, 138.7, 137.7, 128.8, 128.8, 128.7, 128.6, 126.8, 126.5, 77.3, 51.6, 51.6, 49.0, 47.7, 44.2, 41.8, 35.5, 33.7, 33.5, 33.4, 28.1, 26.7, 22.2, 21.8; HRMS (ESI) calcd. for $C_{15}H_{22}NO3$ (M^+ + H): 264.15998, found: 264.15949.

***N*-(2-(1,3-Dioxan-2-yl)ethyl)-*N*-phenethylformamide (2i)**



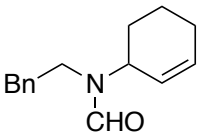
Pale yellow oil (40 mg, 75% yield); The presence of two rotamers (ratio 1.3:1) were observed in the NMR spectra; IR (neat, cm^{-1}): 2956, 2853, 1663, 1397, 1132, 701; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 0.5H), 7.72 (s, 0.4H), 7.26–7.18 (m, 2H), 7.18–7.11 (m, 2H), 7.09–7.04 (m, 1H), 4.48 (dt, *J* = 35.4, 5.0 Hz, 1H), 4.02 (dddd, *J* = 12.1, 8.5, 5.0, 1.4 Hz, 2H), 3.74–3.59 (m, 2H), 3.49–3.34 (m, 3H), 3.20 (t, *J* = 7.0 Hz, 1H), 2.82–2.70 (m, 2H), 2.08–1.88 (m, 1H), 1.85–1.65 (m, 2H), 1.27 (dtt, *J* = 13.5, 2.7, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 162.8, 138.7, 137.8, 128.8, 128.5, 126.8, 126.5, 100.3, 99.3, 66.9, 49.3, 44.0, 42.8, 37.8, 35.4, 33.8, 33.6, 33.0, 25.7, 25.7; HRMS (ESI) calcd. for $C_{15}H_{22}NO_3$ (M^+ + H): 264.15998, found: 264.15926.

***N*-Allyl-*N*-phenethylformamide (2j)**



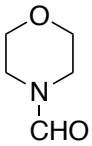
Colorless oil (28 mg, 73% yield); The presence of two rotamers (ratio 1:1) were observed in the NMR spectra; IR (neat, cm^{-1}): 3027, 2927, 2859, 1418, 1396, 1153, 924; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 0.5H), 7.77 (s, 0.5H), 7.23–7.15 (m, 2H), 7.15–7.08 (m, 2H), 7.05–7.01 (m, 1H), 5.71–5.53 (m, 1H), 5.15–5.02 (m, 2H), 3.87 (dt, *J* = 6.1, 1.5 Hz, 1H), 3.57 (dt, *J* = 5.8, 1.5 Hz, 1H), 3.45–3.38 (m, 1H), 3.34 (t, *J* = 7.1 Hz, 1H), 2.78–2.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 162.5, 138.8, 137.8, 133.3, 132.5, 128.8, 128.8, 128.7, 128.5, 126.8, 126.5, 118.5, 118.1, 50.6, 48.5, 44.7, 44.1, 35.3, 33.7; HRMS (ESI) calcd. for $C_{12}H_{16}NO$ (M^+ + H): 190.12319, found: 190.12038.

***N*-(Cyclohex-2-en-1-yl)-*N*-phenethylformamide (2k)**



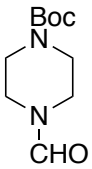
Colorless oil (32 mg, 69% yield); The presence of two rotamers (ratio 4:1) were observed in the NMR spectra; IR (neat, cm^{-1}): 3025, 2930, 2860, 1663, 1139, 699; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 0.7H), 7.89 (s, 0.2H), 7.24–7.02 (m, 5H), 5.83 (ddt, *J* = 10.0, 3.9, 2.7 Hz, 1H), 5.40–5.25 (m, 1H), 3.81 (tt, *J* = 5.6, 2.8 Hz, 1H), 3.53–3.08 (m, 2H), 2.92–2.68 (m, 2H), 2.03–1.83 (m, 2H), 1.77–1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.9, 139.2, 132.5, 131.6, 128.8, 128.8, 128.7, 128.5, 127.6, 127.0, 126.8, 126.4, 55.1, 49.3, 46.4, 44.4, 38.5, 34.8, 29.6, 27.5, 24.6, 24.5, 21.4, 20.4; HRMS (ESI) calcd. for $C_{15}H_{20}NO$ (M^+ + H): 230.15449, found: 230.15311.

Morpholine-4-carbaldehyde (2m)[S5]



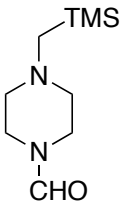
Colorless oil (24 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.65 (ddd, *J* = 14.2, 6.3, 4.2 Hz, 4H), 3.54 (dd, *J* = 5.9, 3.9 Hz, 2H), 3.40–3.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 67.2, 66.4, 45.8, 40.6.

***tert*-Butyl 4-formylpiperazine-1-carboxylate (2n)**[S8]



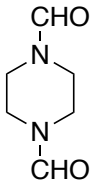
White solid (38 mg, 89% yield); m.p. 80–81 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 3.56–3.25 (m, 8H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 76.8, 45.4, 39.9, 28.3.

4-((Trimethylsilyl)methyl)piperazine-1-carbaldehyde ($2o_a$)



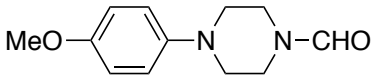
Yellow oil (25 mg, 62% yield); IR (neat, cm^{-1}): 2951, 2893, 2787, 2739, 1671, 1434, 1247, 1016, 839; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 3.55–3.48 (m, 2H), 3.37–3.30 (m, 2H), 2.35 (dt, *J* = 15.7, 5.2 Hz, 4H), 1.91 (s, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 58.5, 57.3, 52.1, 47.0, 41.4, 0.0; HRMS (ESI) calcd. for $C_9H_{21}N_2OSi$ (M^+ +H): 201.14233, found: 201.14133

Piperazine-1,4-dicarbaldehyde ($2o_b$)[S6]



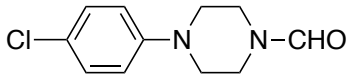
Yellow oil (24 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 2H), 3.63–3.52 (m, 4H), 3.43–3.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.8, 46.1, 45.0, 40.5, 39.5.

4-(4-Methoxyphenyl)piperazine-1-carbaldehyde (2p)[S9]



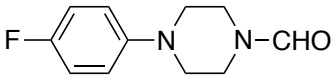
White solid (38 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 6.93–6.80 (m, 4H), 3.76 (s, 3H), 3.72–3.67 (m, 2H), 3.54–3.50 (m, 2H), 3.08–2.98 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 154.6, 145.3, 119.3, 114.6, 55.6, 51.9, 50.8, 45.8, 40.1.

4-(4-Chlorophenyl)piperazine-1-carbaldehyde (2q)[S9]



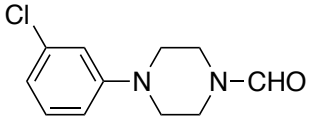
Yellow oil (36 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.23 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 3.73–3.66 (m, 2H), 3.55–3.49 (m, 2H), 3.19–3.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.6, 129.2, 125.9, 118.4, 50.5, 49.4, 45.4, 39.9.

4-(4-Fluorophenyl)piperazine-1-carbaldehyde (2r)[S10]



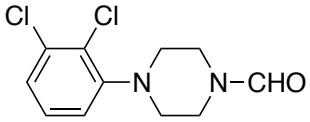
Brown oil (31 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 6.98 (t, J = 8.6 Hz, 2H), 6.92–6.86 (m, 2H), 3.74–3.68 (m, 2H), 3.56–3.50 (m, 2H), 3.08 (dt, J = 16.1, 5.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, $J_{C\text{-}F}$ = 172.6 Hz), 156.6, 147.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 119.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.3 Hz), 51.5, 50.4, 45.6, 40.0.

4-(3-Chlorophenyl)piperazine-1-carbaldehyde (2s)[S11]



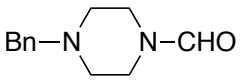
Colorless oil (31 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.91–6.85 (m, 2H), 6.79 (ddd, *J* = 8.4, 2.4, 1.0 Hz, 1H), 3.73–3.66 (m, 2H), 3.55–3.48 (m, 2H), 3.17 (ddd, *J* = 15.2, 6.2, 4.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 152.0, 135.1, 130.2, 120.5, 116.9, 114.9, 50.0, 48.9, 45.3, 39.8.

4-(2,3-Dichlorophenyl)piperazine-1-carbaldehyde (2t)[S12]



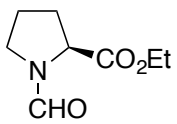
Light brown oil (36 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.21–7.12 (m, 2H), 6.91 (dd, *J* = 7.7, 1.8 Hz, 1H), 3.77–3.68 (m, 2H), 3.58–3.51 (m, 2H), 3.01 (dt, *J* = 16.5, 5.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 150.5, 134.2, 127.8, 127.6, 125.4, 118.9, 52.1, 50.9, 45.9, 40.2.

4-Bensylpiperazine-1-carbaldehyde (2u)[S5]



Yellow oil (37 mg, 90% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.26–7.23 (m, 4H), 7.20–7.18 (m, 1H), 3.52–3.46 (m, 2H), 3.45 (s, 2H), 3.29 (dd, *J* = 5.7, 4.5 Hz, 2H), 2.35 (dt, *J* = 15.4, 5.1 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 136.5, 128.0, 127.3, 126.3, 61.8, 52.3, 51.2, 44.6, 39.0.

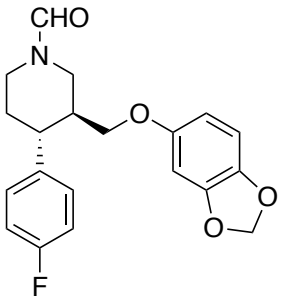
Ethyl formyl-*L*-prolinate (2v)[S13]



Pale yellow oil (25 mg, 72% yield); The presence of two rotamers (ratio 1:0.7) was observed

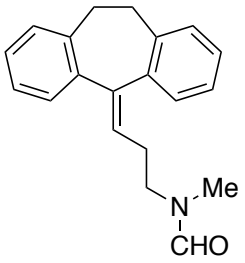
in the NMR spectra; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.19 (s, 1H), 4.38 (dd, *J* = 8.8, 4.2 Hz, 1H), 4.33 (ddd, *J* = 6.2, 4.5, 1.4 Hz, 1H), 4.21–4.07 (m, 4H), 3.65–3.45 (m, 4H), 2.26–2.07 (m, 3H), 2.00–1.81 (m, 5H), 1.21 (tdd, *J* = 7.2, 4.2, 1.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 171.6, 161.6, 160.7, 61.8, 61.3, 58.8, 56.5, 46.3, 43.9, 29.7, 29.4, 24.0, 22.8, 14.1, 14.1.

(3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine-1-carbaldehyde (2w)[S14,S15]



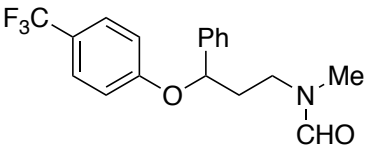
Colorless oil (56 mg, 78% yield); The presence of two rotamers (ratio 1:1) were observed in the NMR spectra; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.8 Hz, 1H), 7.16–7.09 (m, 2H), 6.99 (td, *J* = 8.6, 5.4 Hz, 2H), 6.63 (dd, *J* = 8.5, 3.7 Hz, 1H), 6.36 (t, *J* = 2.4 Hz, 1H), 6.14 (ddd, *J* = 8.5, 2.5, 1.5 Hz, 1H), 5.89 (d, *J* = 2.9 Hz, 2H), 4.77–4.53 (m, 1H), 3.97 (ddd, *J* = 13.4, 4.4, 1.7 Hz, 1H), 3.62 (ddd, *J* = 9.5, 5.3, 2.9 Hz, 1H), 3.54–3.43 (m, 1H), 3.31–3.08 (m, 1H), 2.92–2.65 (m, 2H), 2.14–1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.75 (d, $J_{C\text{-}F}$ = 244 Hz), 161.70 (d, $J_{C\text{-}F}$ = 243 Hz), 160.97, 160.88, 154.1, 153.9, 148.3, 148.2, 141.9, 138.32 (d, $J_{C\text{-}F}$ = 3 Hz), 138.2 (d, $J_{C\text{-}F}$ = 3 Hz), 128.8, 128.7, 128.6, 115.82 (d, $J_{C\text{-}F}$ = 8 Hz), 115.6 (d, $J_{C\text{-}F}$ = 8 Hz), 107.91, 107.86, 105.6, 105.5, 101.2, 101.1, 98.0, 97.9, 68.6, 68.4, 49.2, 46.2, 44.5, 44.1, 42.9, 41.5, 40.2, 34.6, 33.2.

***N*-(3-(10,11-Dihydro-5*H*-dibenso[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methylformamide (2x)**[S15]



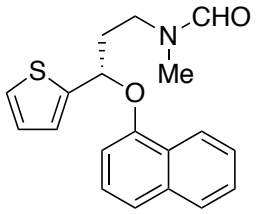
Colorless oil (42 mg, 72% yield); The presence of two rotamers (ratio 1:2) were observed in the NMR spectra; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.5 Hz, 1H), 7.18–7.04 (m, 6H), 7.02–6.93 (m, 2H), 5.70 (dt, *J* = 34.3, 7.5 Hz, 1H), 3.20 (q, *J* = 6.2, 5.0 Hz, 4H), 2.93–2.81 (m, 1H), 2.71 (s, 2H), 2.59 (s, 2H), 2.43–2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 146.2, 140.6, 139.5, 139.4, 137.1, 130.2, 130.0, 128.6, 128.4, 128.2, 128.1, 128.1, 127.9, 127.8, 127.6, 127.4, 127.2, 126.2, 126.1, 125.8, 49.4, 43.7, 34.4, 33.7, 32.0, 31.9, 29.3, 28.0.

***N*-Methyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)formamide (2y)**[S16]



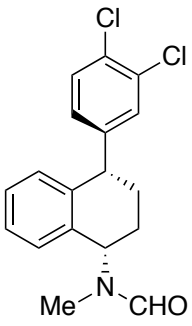
Colorless oil (49 mg, 72% yield); The presence of two rotamers (ratio 1:1.4) were observed in the NMR spectra; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 13.6 Hz, 1H), 7.46–7.40 (m, 2H), 7.39–7.27 (m, 5H), 6.92–6.84 (m, 2H), 5.16 (ddd, *J* = 24.7, 8.9, 4.1 Hz, 1H), 3.61–3.49 (m, 1H), 3.38 (ddd, *J* = 14.3, 7.4, 4.8 Hz, 1H), 2.92 (d, *J* = 14.9 Hz, 3H), 2.27–2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.6, 160.2, 159.9, 140.4, 139.9, 129.1, 128.9, 128.3, 128.1, 126.9 (q, $J_{C\text{-}F}$ = 4 Hz), 126.8 (q, $J_{C\text{-}F}$ = 4 Hz), 125.7, 125.6, 123.3 (d, $J_{C\text{-}F}$ = 32 Hz), 122.9 (d, $J_{C\text{-}F}$ = 6 Hz), 115.8, 115.7, 78.2, 77.2, 46.0, 41.6, 37.0, 35.9, 34.9, 29.6.

(*S*)-*N*-Methyl-*N*-(3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)formamide (2z)



Colorless oil (57 mg, 88% yield); The presence of two rotamers (ratio 1:1.6) were observed in the NMR spectra; IR (neat, cm^{-1}): 3052, 2924, 1664, 1394, 1234, 1093, 770; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 0.4H), 7.87 (s, 0.6H), 7.91 (d, *J* = 29.9 Hz, 1H), 7.75–7.67 (m, 1H), 7.46–7.37 (m, 2H), 7.35–7.30 (m, 1H), 7.22–7.11 (m, 2H), 6.99 (ddt, *J* = 16.2, 3.5, 1.0 Hz, 1H), 6.85 (td, *J* = 5.0, 3.5 Hz, 1H), 6.74 (td, *J* = 8.1, 0.9 Hz, 1H), 5.58 (ddd, *J* = 26.7, 8.1, 4.8 Hz, 1H), 3.62–3.33 (m, 2H), 2.87–2.78 (m, 3H), 2.50–2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.6, 153.0, 152.8, 144.4, 143.9, 127.7, 127.6, 126.8, 126.5, 126.4, 125.7, 125.7, 125.5, 125.3, 125.1, 125.0, 125.0, 122.0, 121.7, 121.2, 120.9, 107.0, 74.4, 73.1, 46.0, 41.6, 37.3, 36.1, 35.0, 29.7; HRMS (ESI) calcd. for $C_{19}H_{20}NO_2S$ (M^+ + H): 326.12148, found: 326.12160.

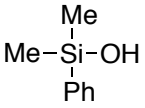
***N*-((1*S*,4*S*)-4-(3,4-Dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methylformamide (2α)**



Colorless oil (51 mg, 76% yield); The presence of two rotamers (ratio 1.7:1) were observed in the NMR spectra; IR (neat, cm^{-1}): 2937, 2863, 1661, 1466, 1029, 729; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 14.5 Hz, 1H), 7.34 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.31–7.16 (m, 3H), 7.16–7.04 (m, 1H), 6.97 (td, *J* = 8.8, 8.2, 1.5 Hz, 1H), 6.82 (dddd, *J* = 17.4, 8.3, 2.2, 0.6 Hz, 1H),

4.75 (dd, J = 10.4, 6.0 Hz, 1H), 4.21 (dt, J = 7.0, 3.5 Hz, 1H), 2.74 (d, J = 13.3 Hz, 3H), 2.34–2.23 (m, 1H), 2.09–1.88 (m, 2H), 1.77 (dddd, J = 12.3, 6.2, 3.2, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 163.3, 146.5, 138.3, 134.9, 132.5, 131.0, 130.8, 130.6, 130.6, 130.4, 130.2, 130.1, 128.2, 128.0, 127.9, 127.8, 127.6, 127.6, 127.3, 127.1, 57.6, 50.3, 43.1, 43.0, 30.6, 30.0, 29.8, 26.8, 23.4, 21.1; HRMS (ESI) calcd. for $C_{18}H_{18}Cl_2NO$ (M^+ + H): 334.07655, found: 334.07633.

Dimethyl(phenyl)silanol (3β)[S17]



Colorless oil (25 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 2H), 7.43–7.35 (m, 3H), 2.28 (s, 1H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.1, 129.6, 127.9, 0.0.

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

Figure S5. ^{1}H and ^{13}C NMR Spectra of 1-((Trimethylsilyl)methyl)piperidine (**1a**)

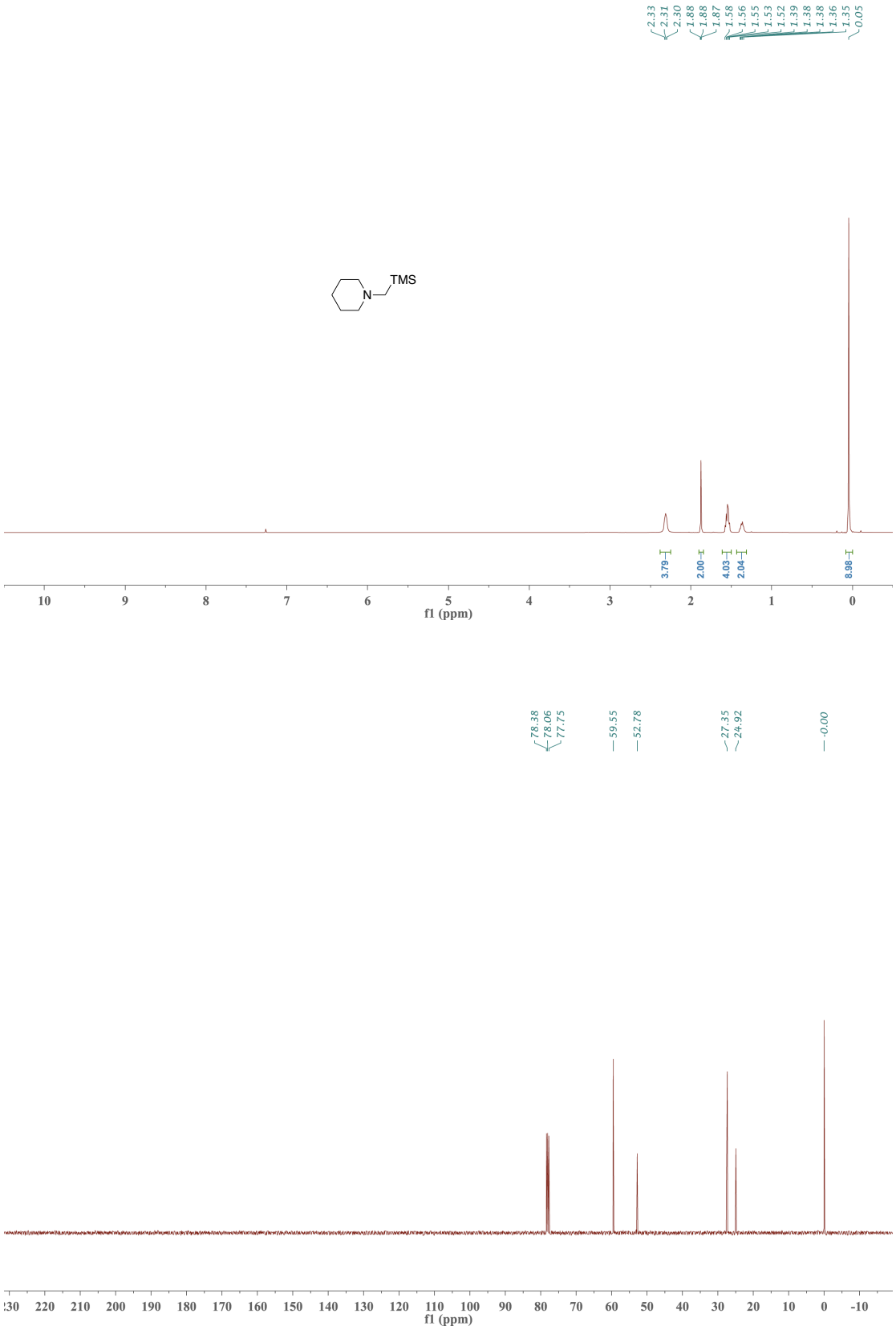


Figure S6. ^{1}H and ^{13}C NMR Spectra of 1-((Trimethylsilyl)methyl)pyrrolidine (**1b**)

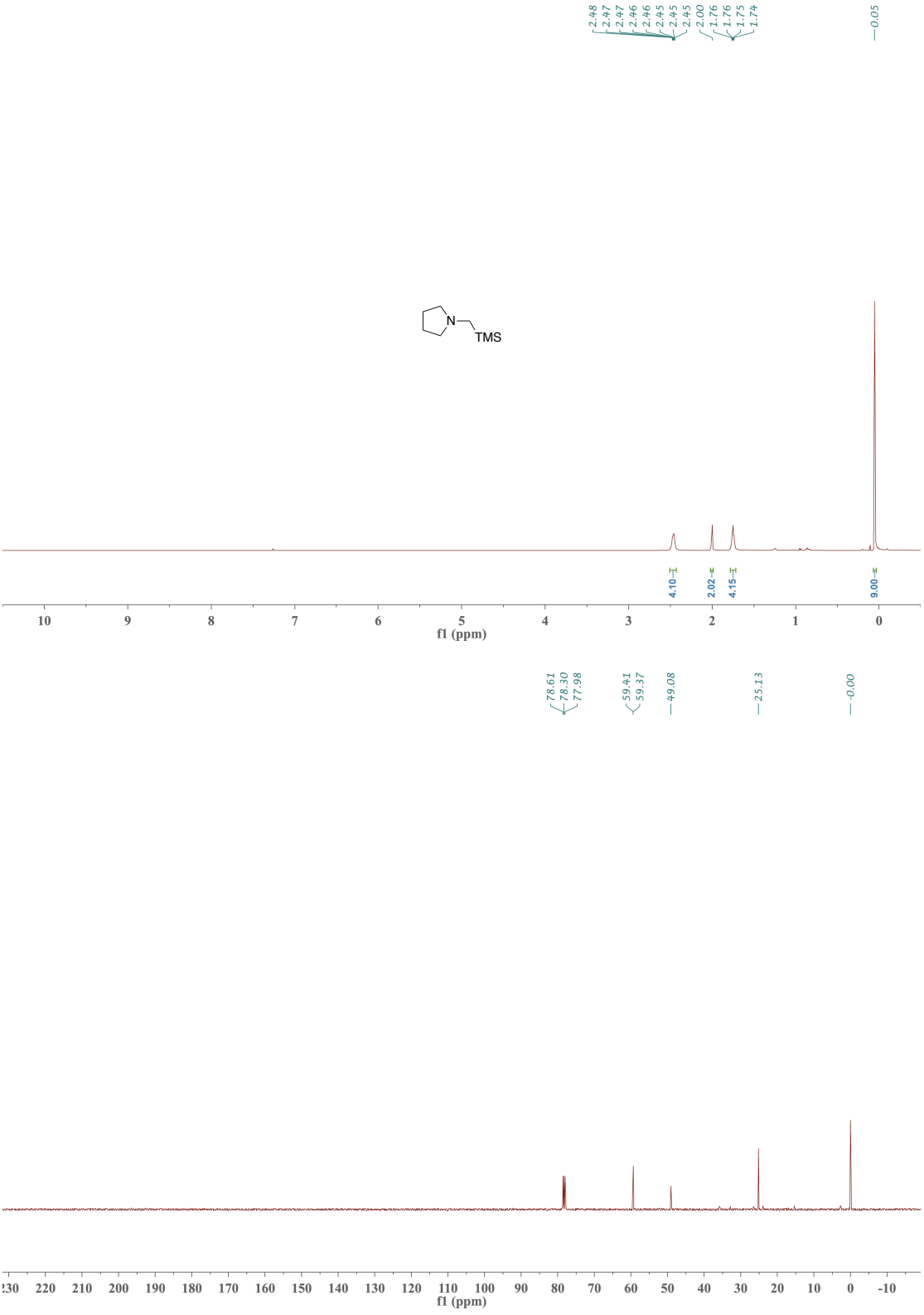


Figure S7. ^{1}H and ^{13}C NMR Spectra of 1-((Trimethylsilyl)methyl)azepane (**1c**)

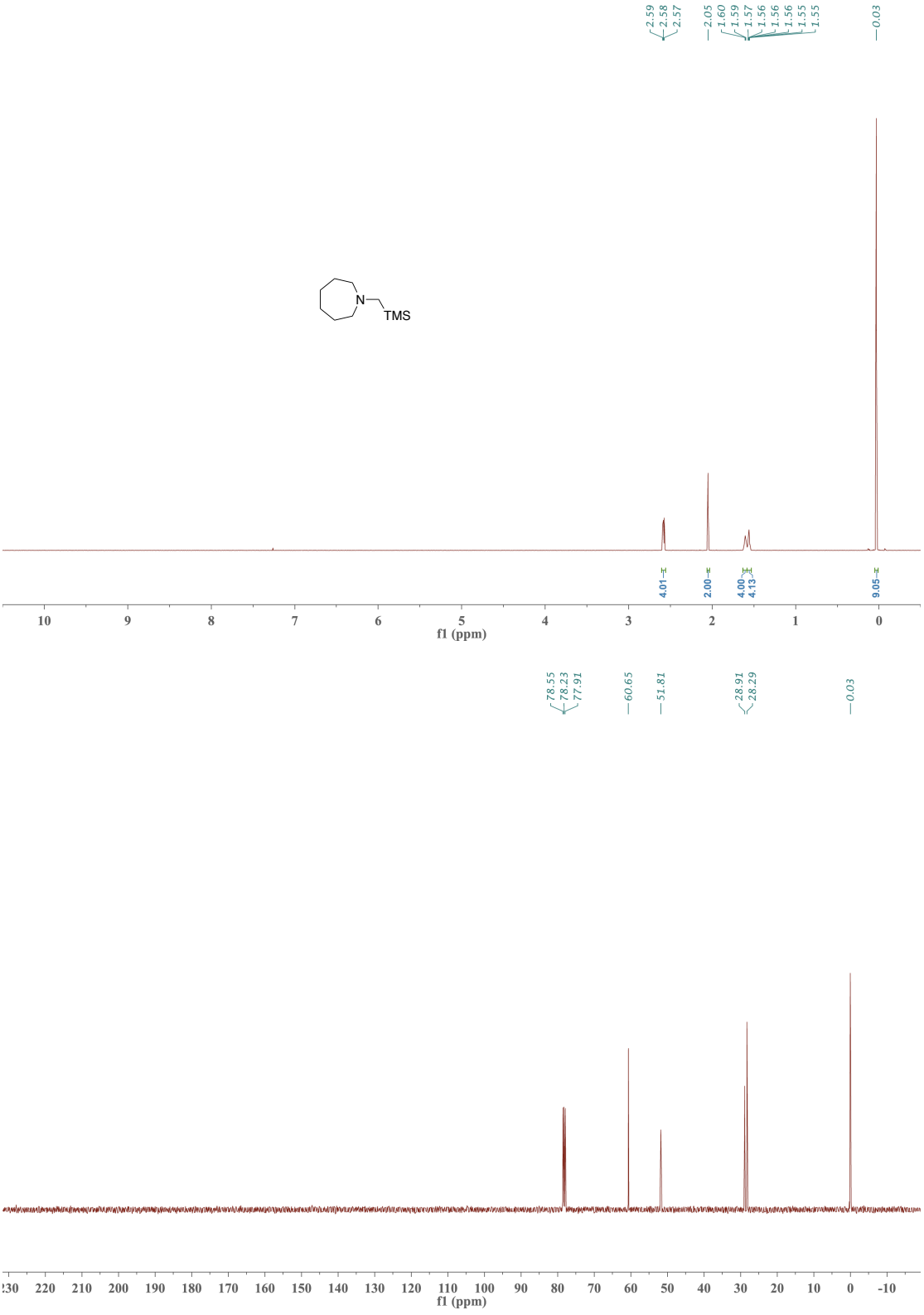


Figure S8. ^{1}H and ^{13}C NMR Spectra of *N*-Ethyl-*N*-((trimethylsilyl)methyl)ethanamine (**1d**)

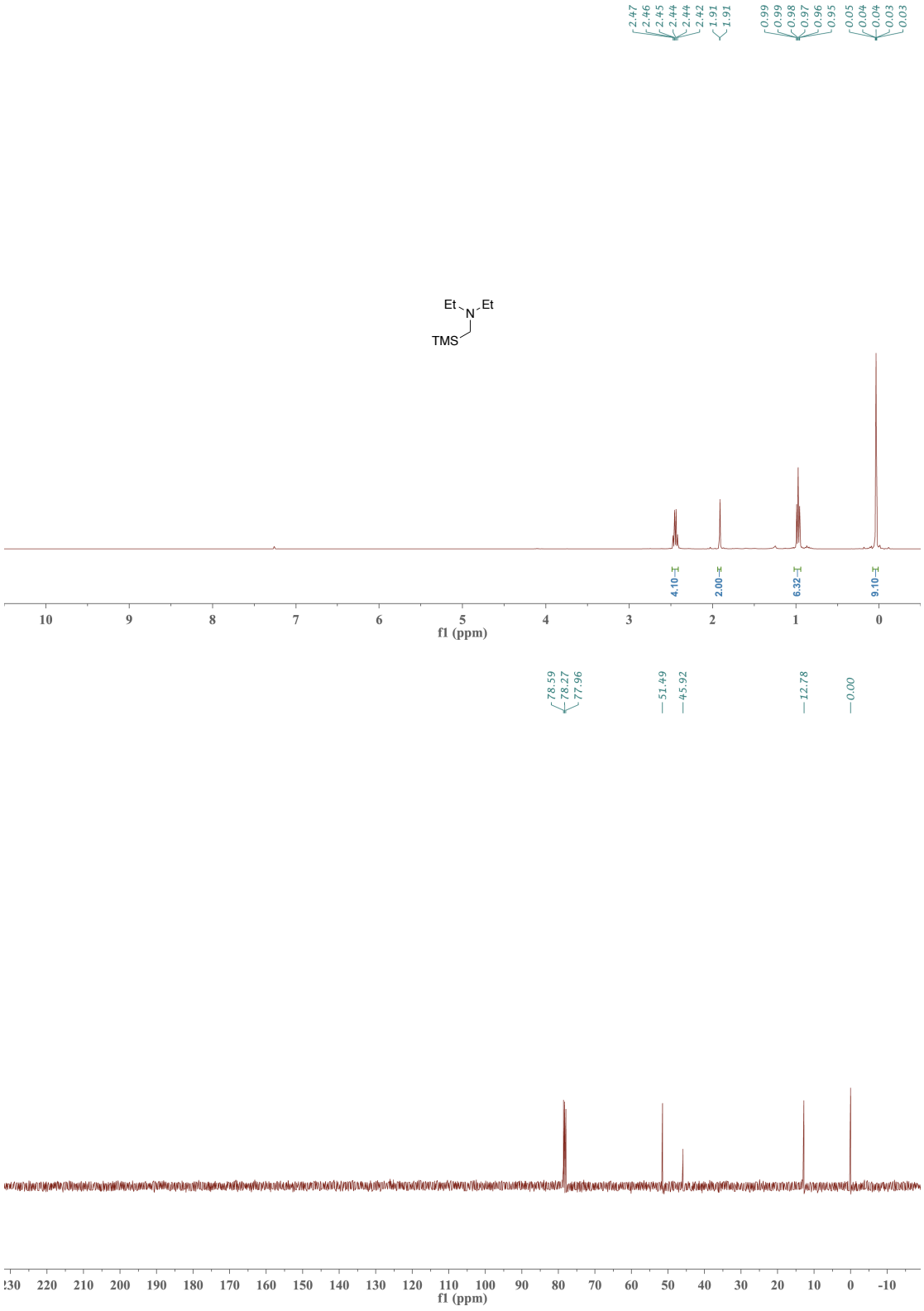


Figure S9. ^{1}H and ^{13}C NMR Spectra of *N*-Butyl-*N*-((trimethylsilyl)methyl)butan-1-amine (**1e**)

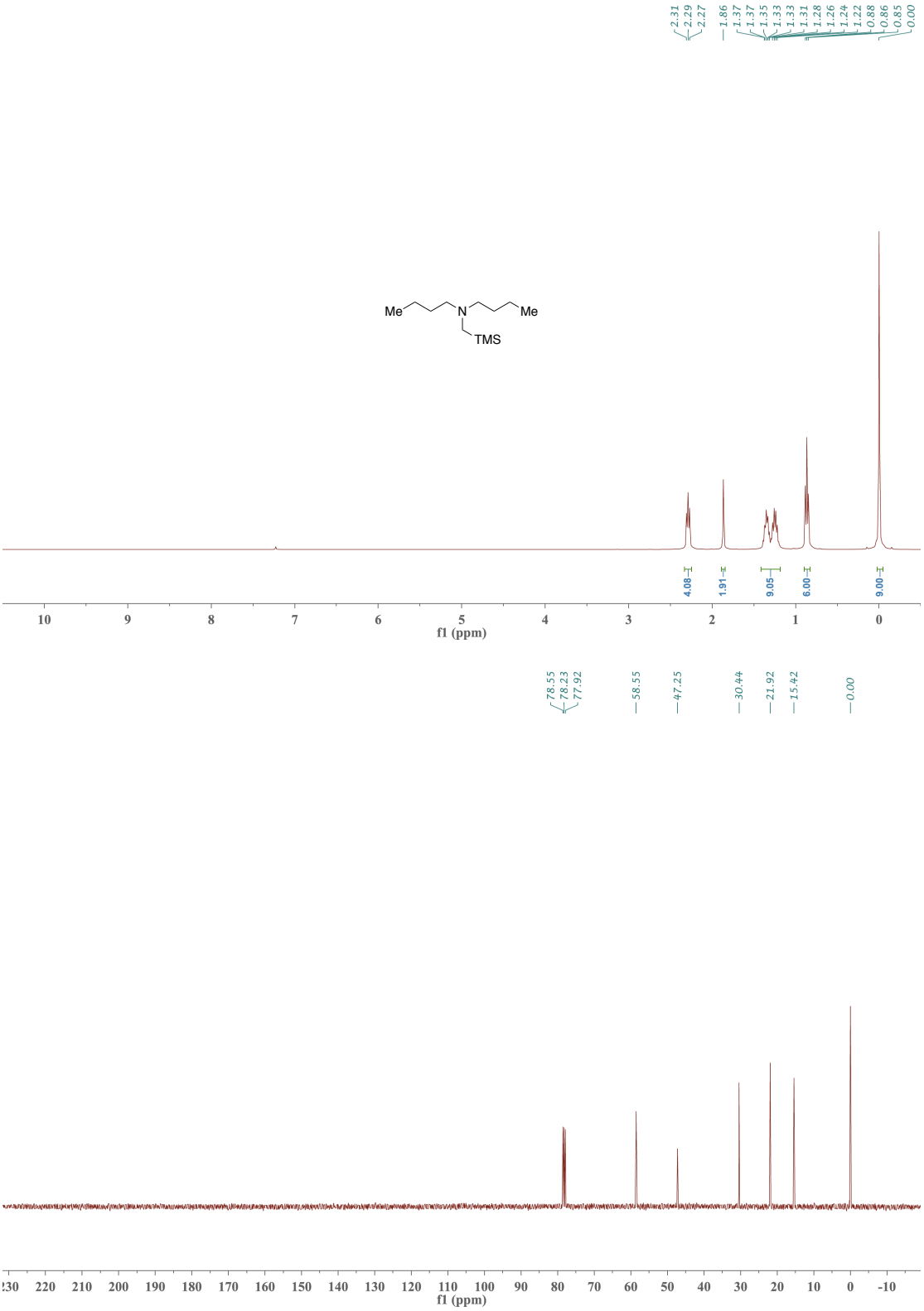


Figure S10. ^{1}H and ^{13}C NMR Spectra of *N*-Octyl-*N*-((trimethylsilyl)methyl)octan-1-amine (**1f**)

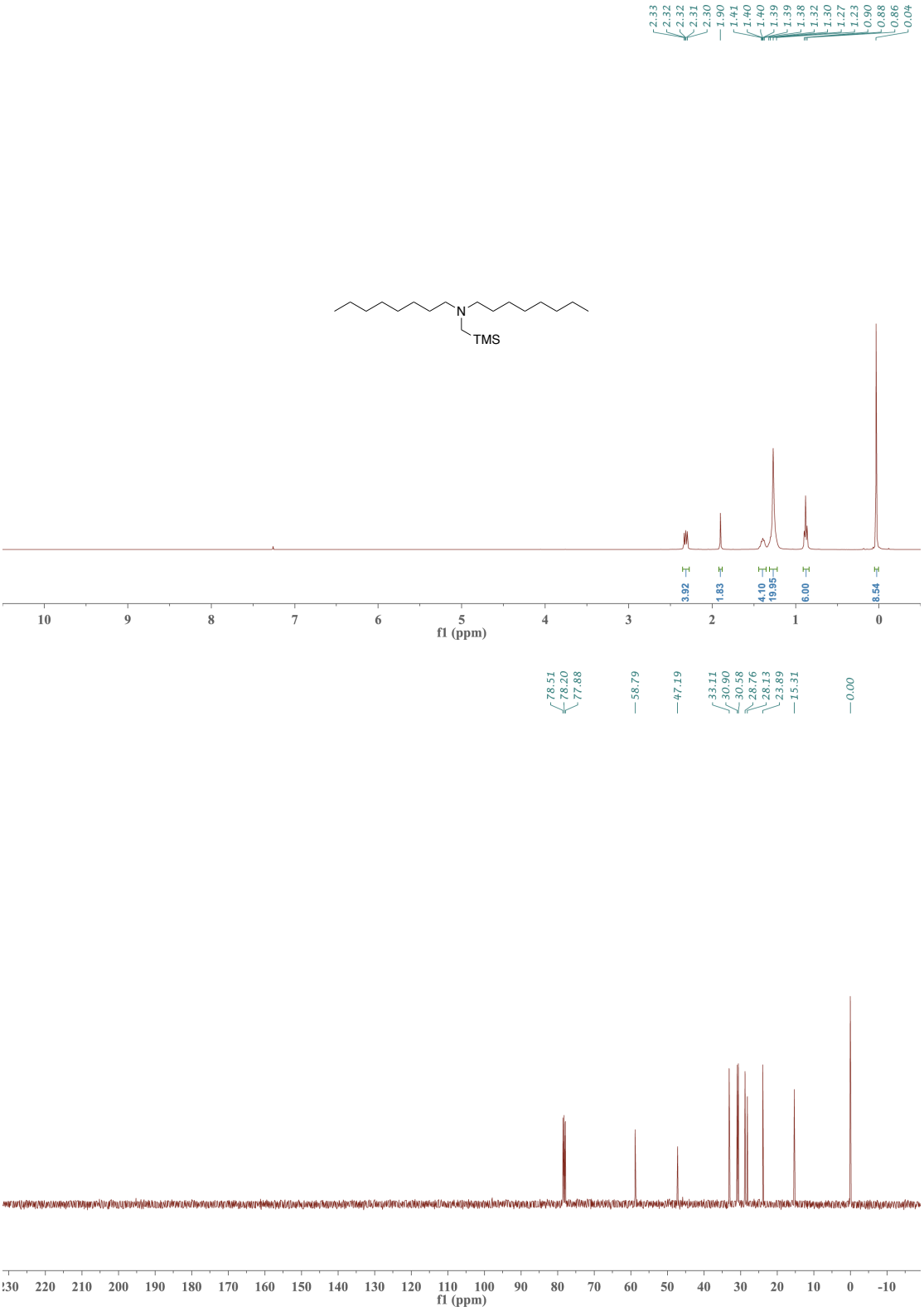
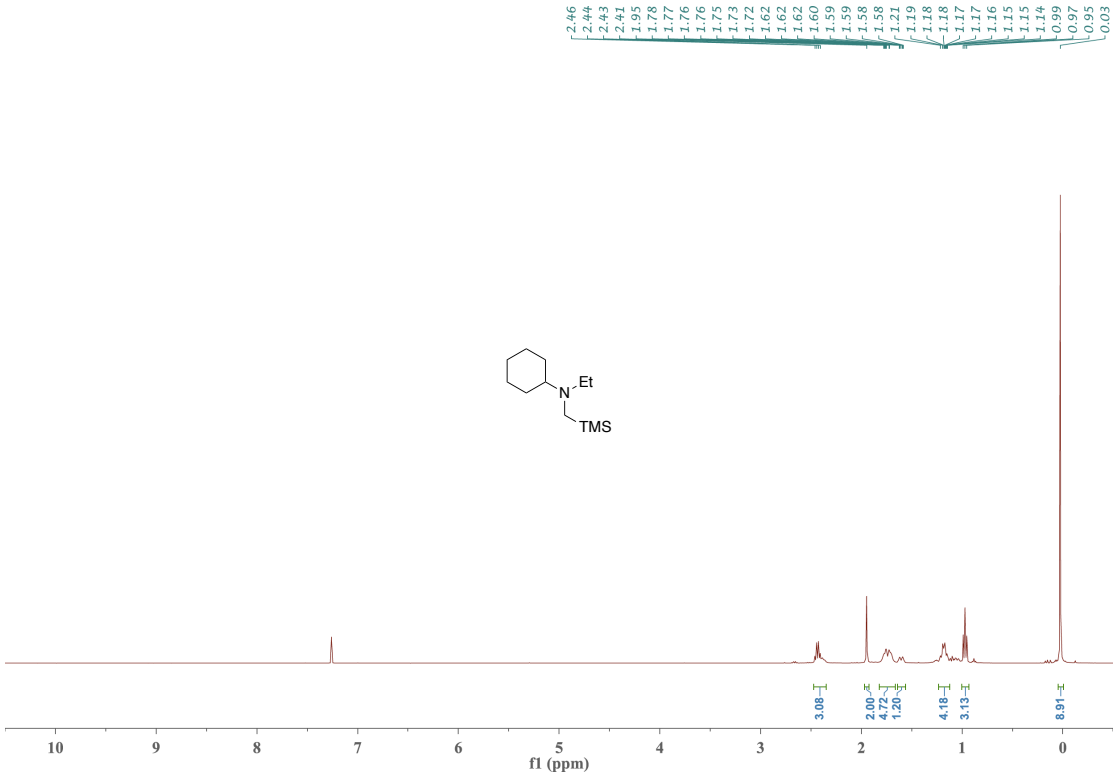


Figure S11. ^{1}H and ^{13}C NMR Spectra of *N*-Ethyl-*N*-((trimethylsilyl)methyl)cyclohexanamine (**1g**)



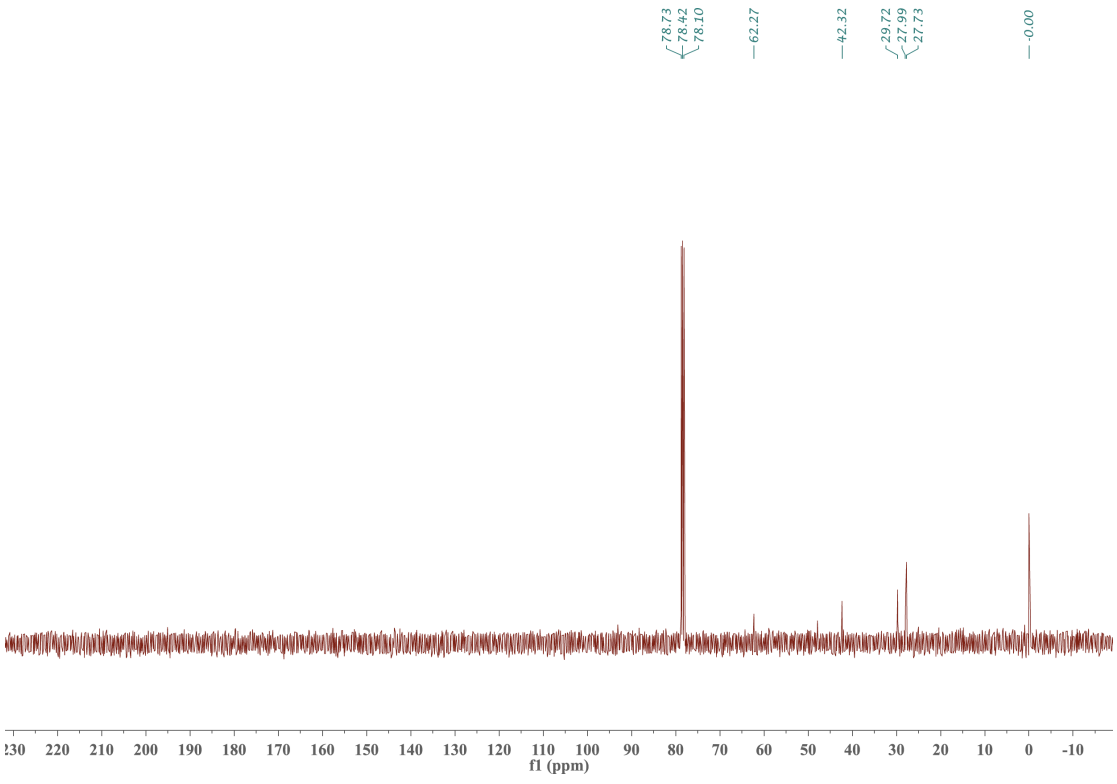


Figure S12. ^{1}H and ^{13}C NMR Spectra of Methyl 5-(Phenethyl((trimethylsilyl)methyl)amino)-pentanoate (**1h**)

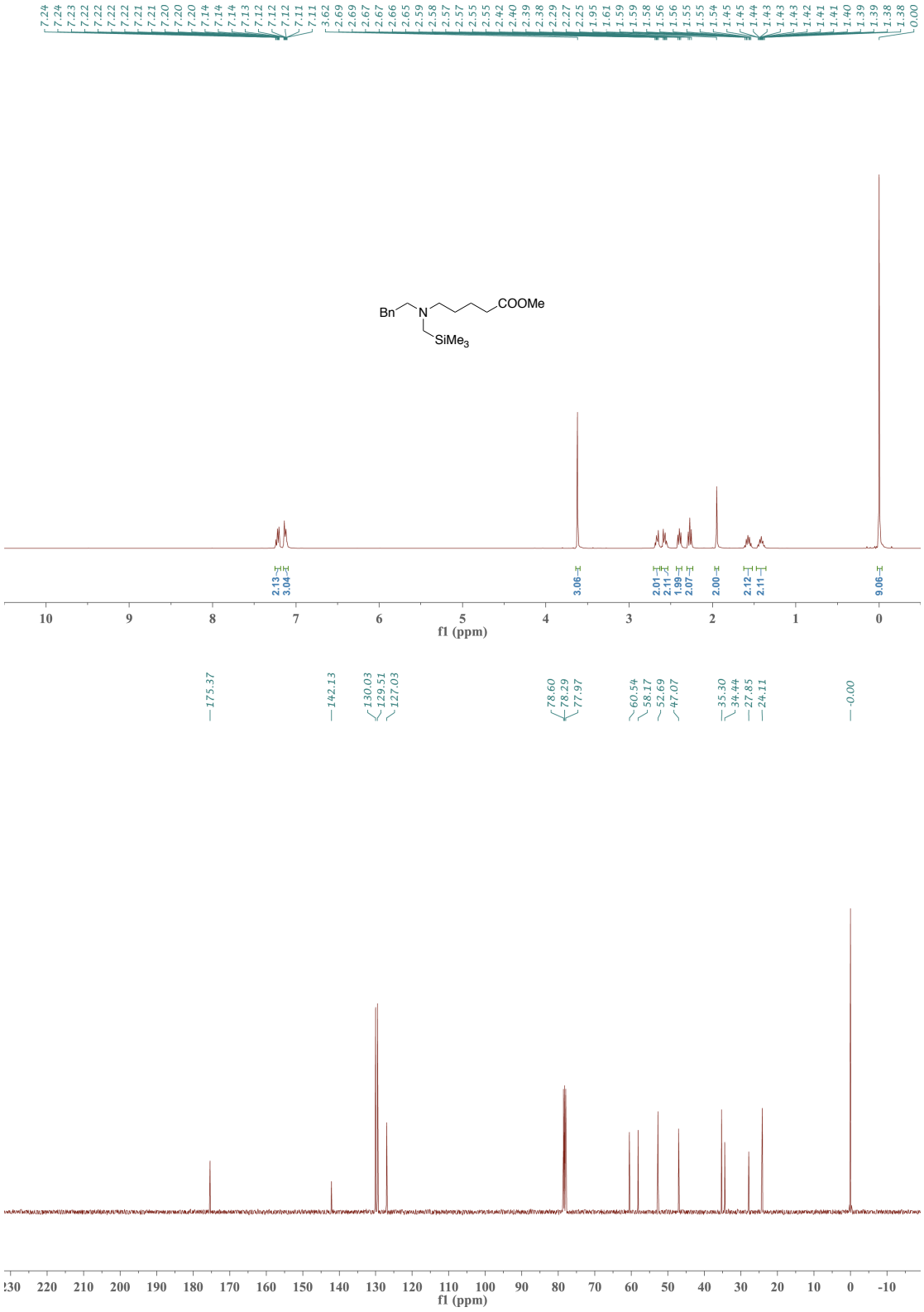


Figure S13. ^{1}H and ^{13}C NMR Spectra of *N*-(2-(1,3-Dioxan-2-yl)ethyl)-2-phenyl-*N*-((trimethylsilyl)methyl)ethan-1-amine (**1i**)

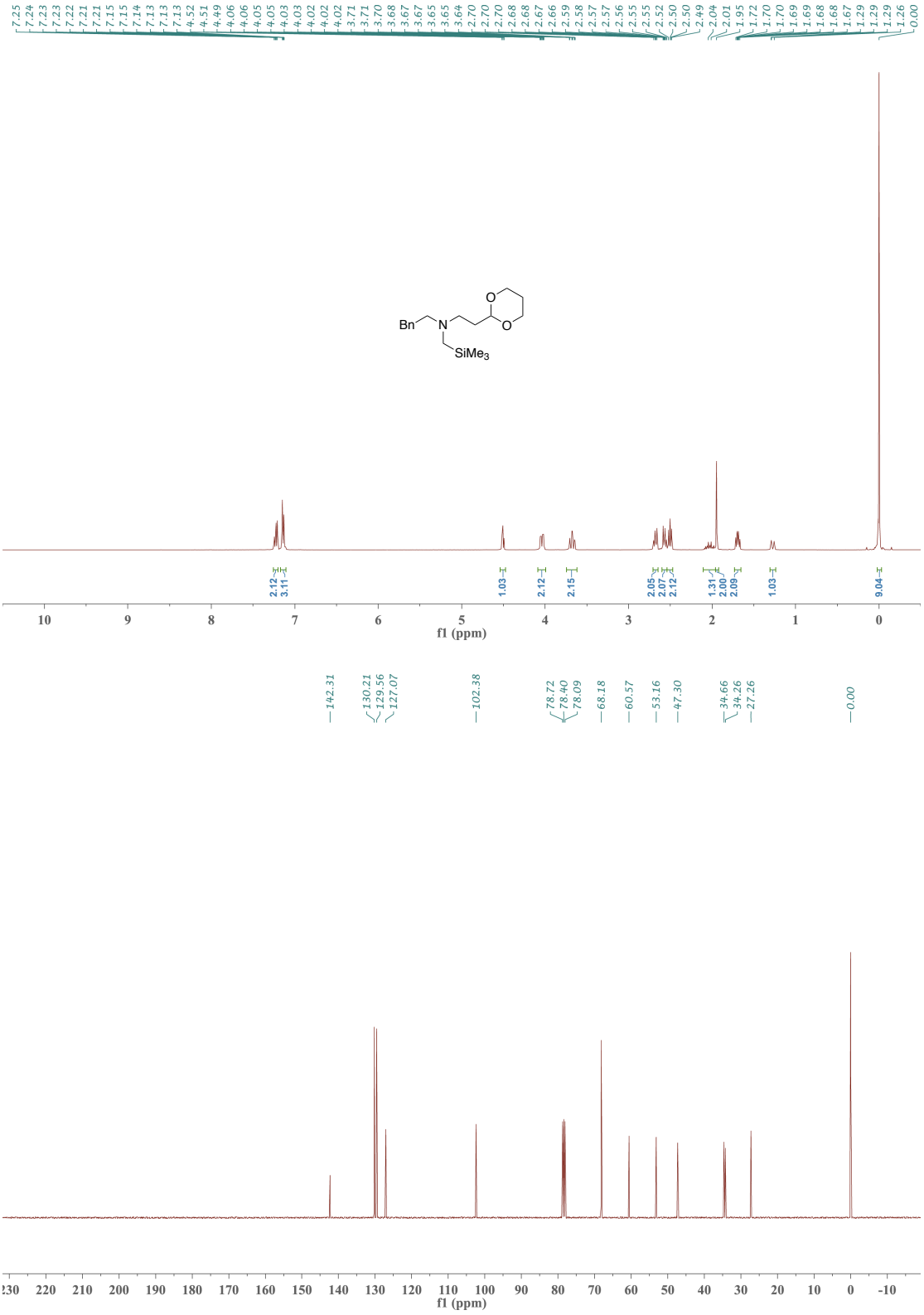


Figure S14. ^{1}H and ^{13}C NMR Spectra of *N*-Phenethyl-*N*-((trimethylsilyl)methyl)prop-2-en-1-amine (**1j**)

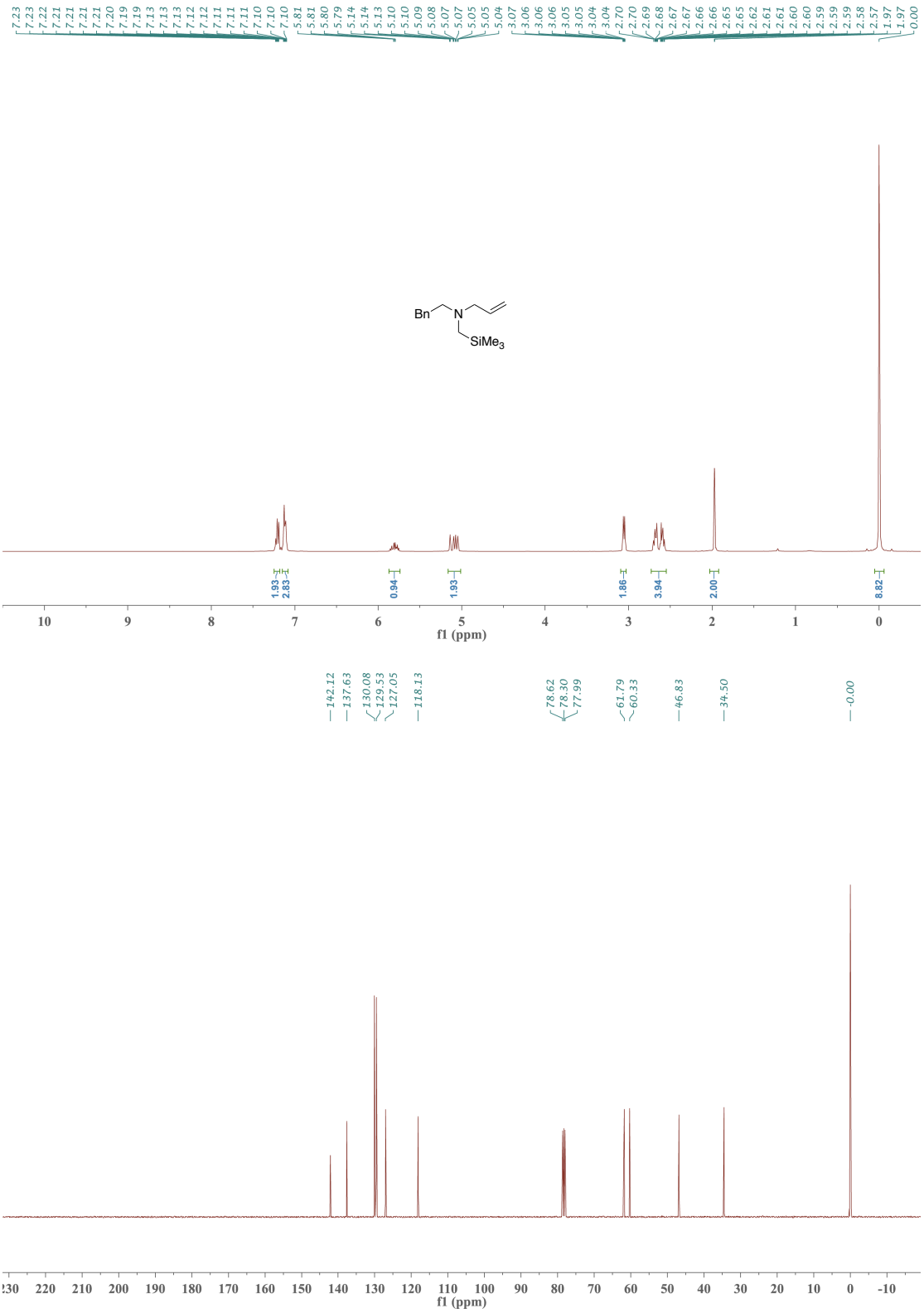


Figure S15. ^{1}H and ^{13}C NMR Spectra of *N*-Phenethyl-*N*-((trimethylsilyl)methyl)cyclohex-2-en-1-amine (**1k**)

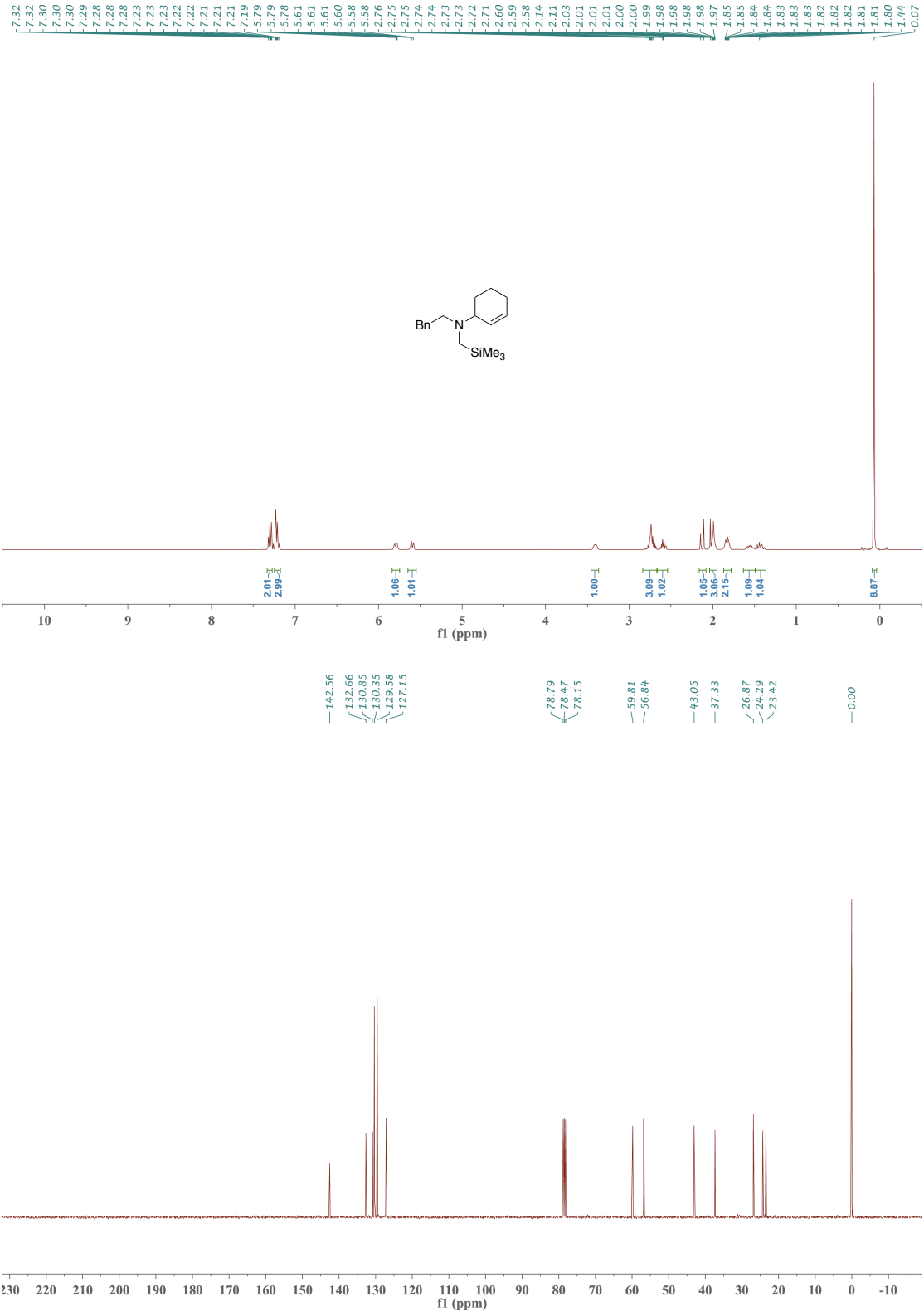


Figure S16. ^{1}H and ^{13}C NMR Spectra of *N*-Methyl-*N*-((trimethylsilyl)methyl)aniline **(1l)**

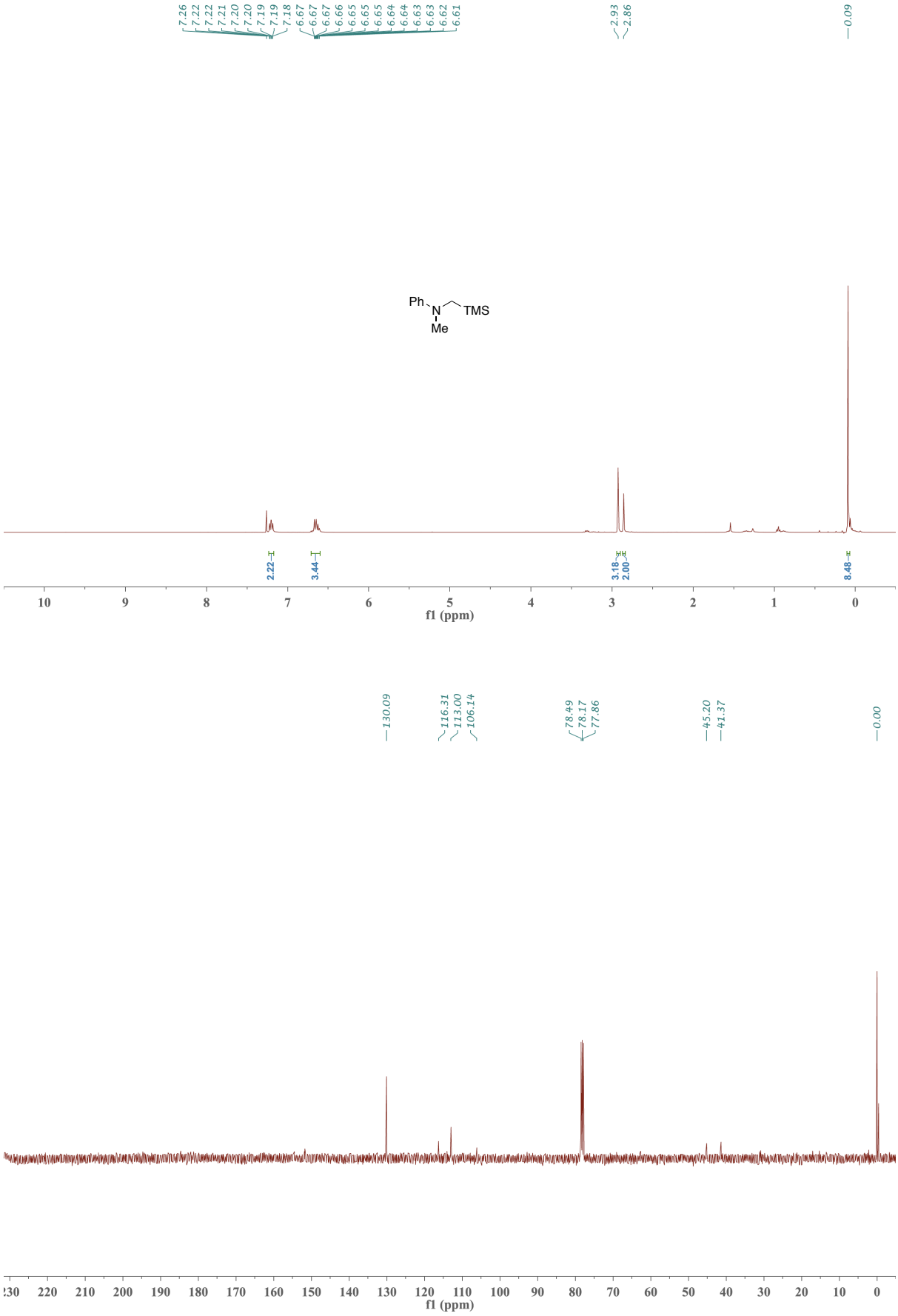


Figure S17. ^{1}H and ^{13}C NMR Spectra of 4-((Trimethylsilyl)methyl)morpholine (**1m**)

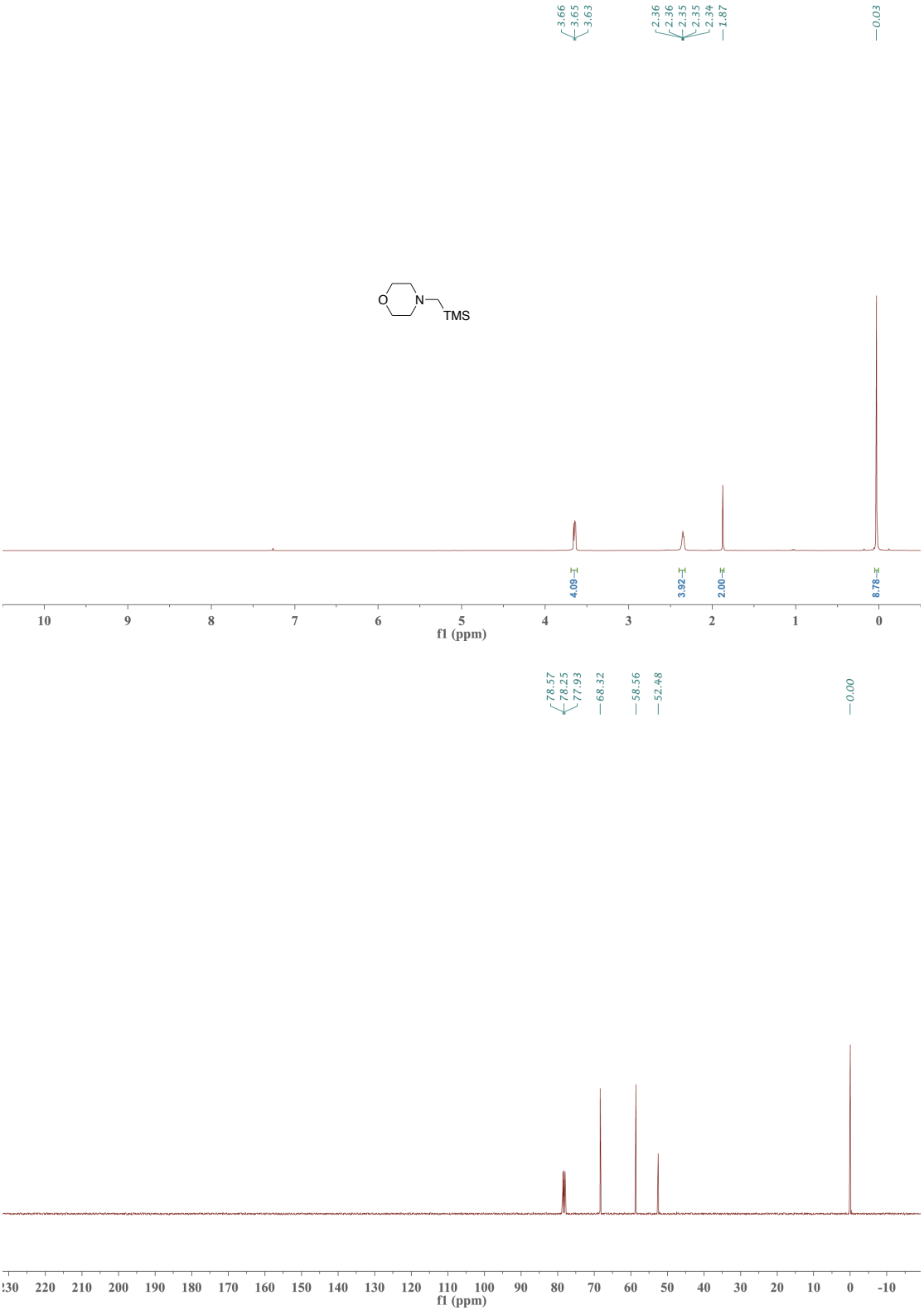


Figure S18. ^{1}H and ^{13}C NMR Spectra of *tert*-Butyl 4-((Trimethylsilyl)methyl)piperazine-1-carboxylate (**1n**)

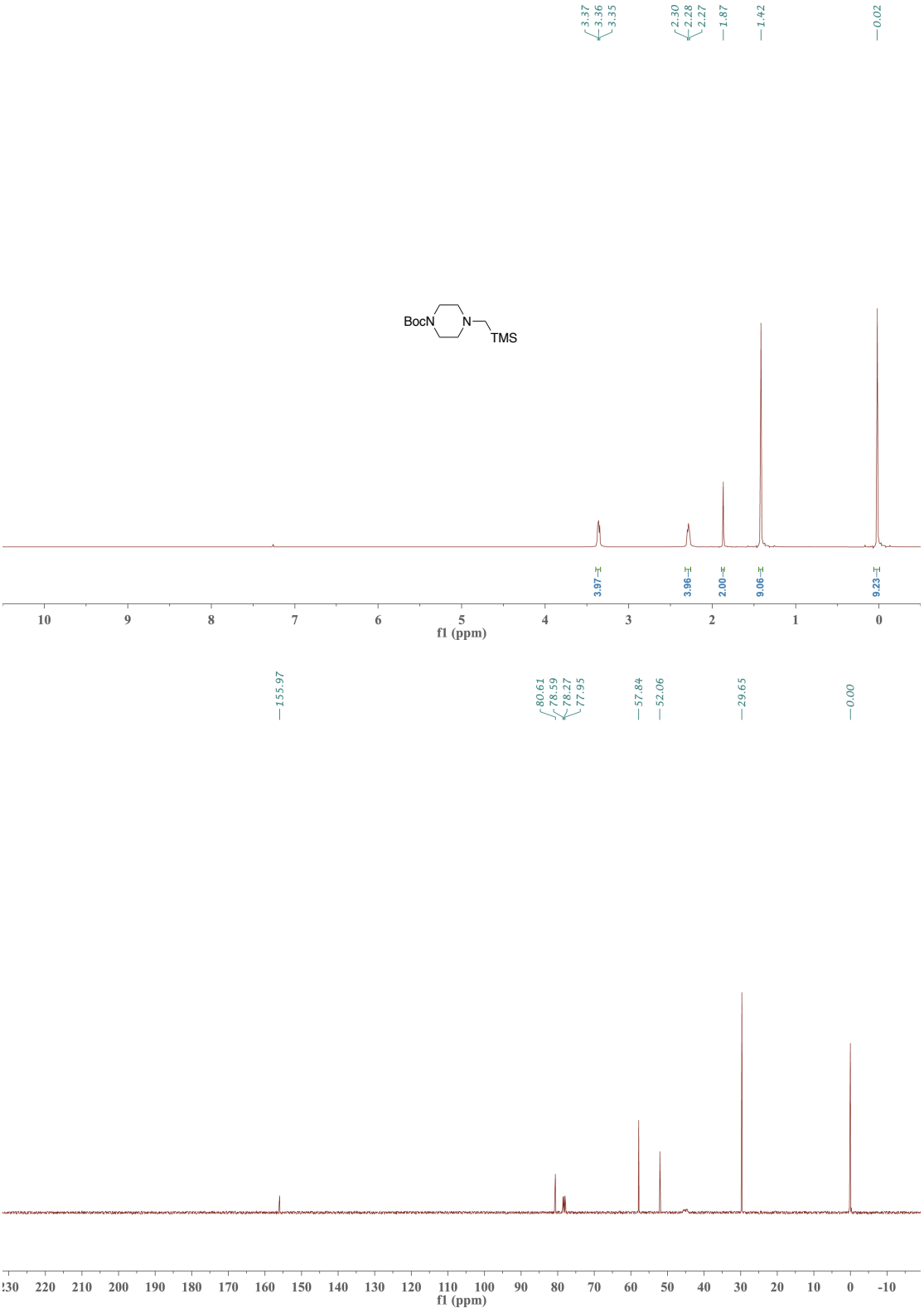


Figure S19. ^{1}H and ^{13}C NMR Spectra of 1,4-Bis((trimethylsilyl)methyl)piperazine (**1o**)

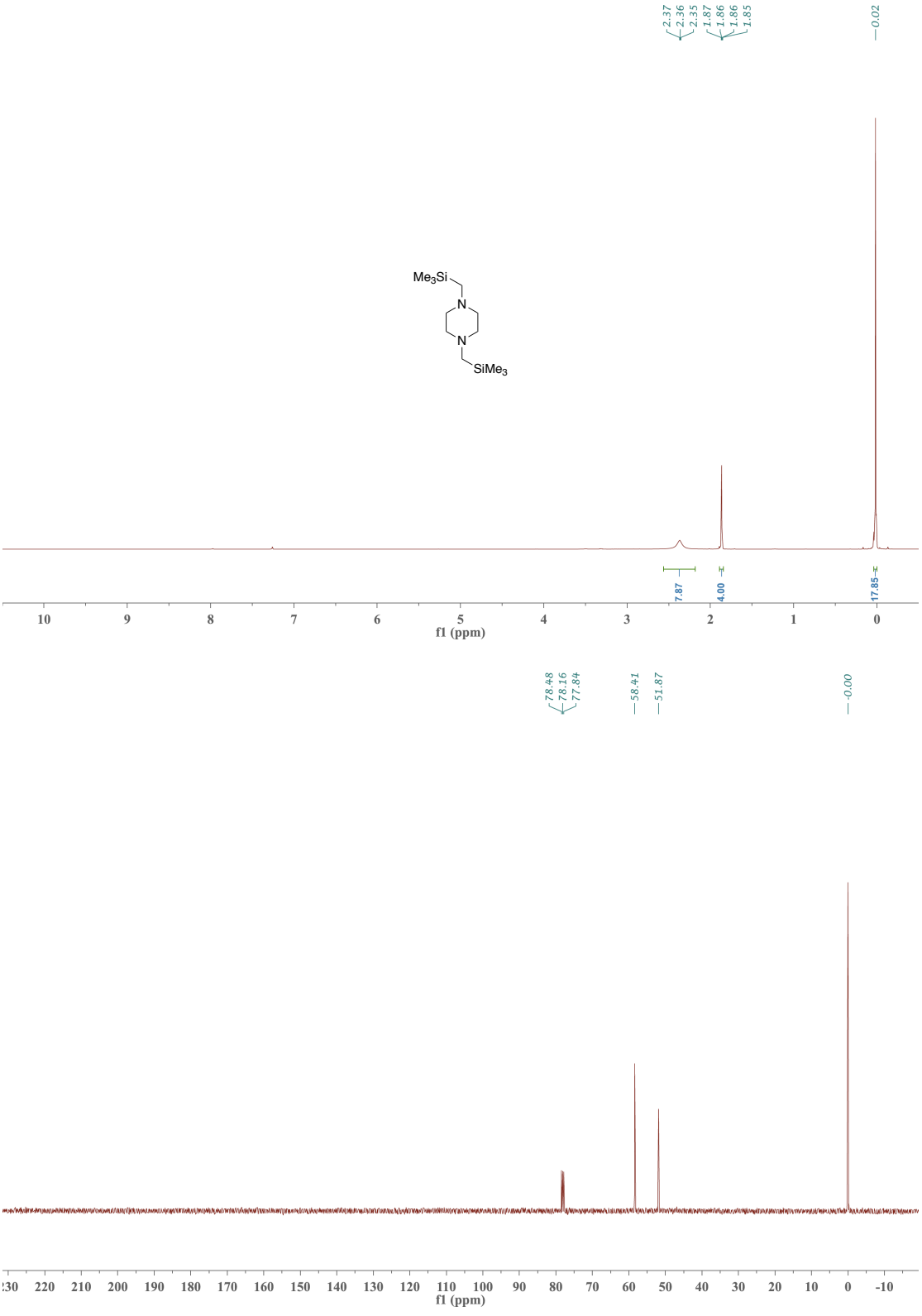
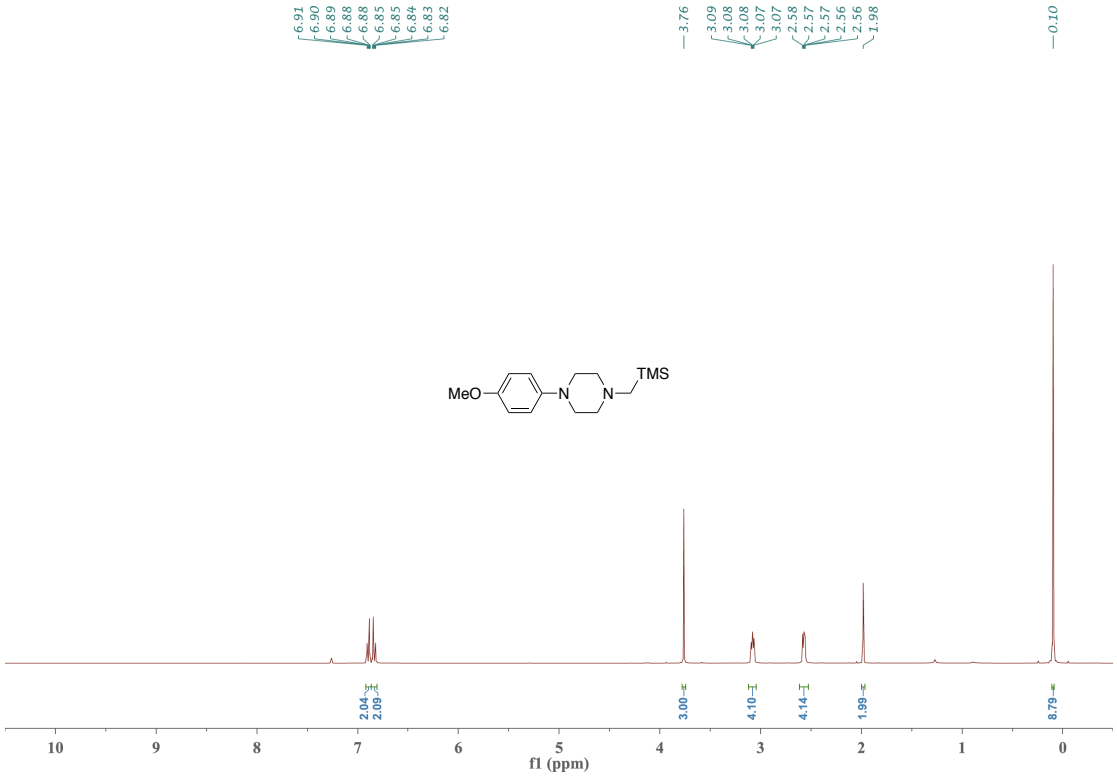


Figure S20. ^{1}H and ^{13}C NMR Spectra of 1-(4-Methoxyphenyl)-4-((trimethylsilyl)methyl)-piperazine (**1p**)



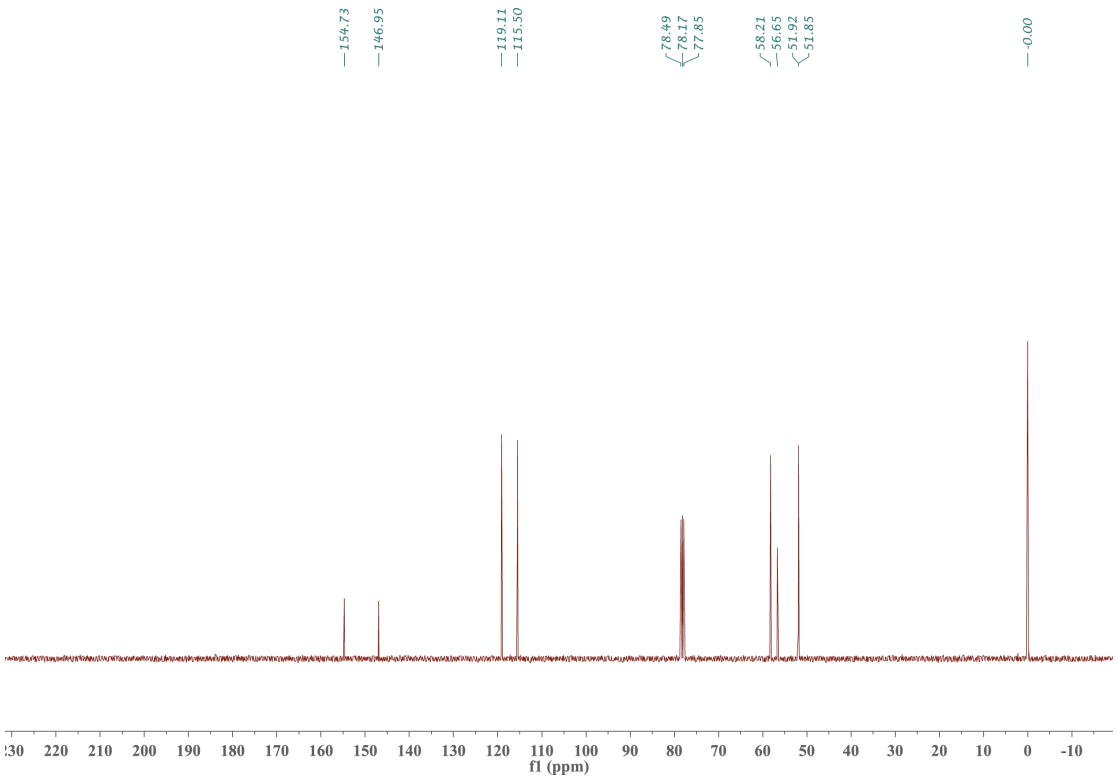


Figure S21. ^{1}H and ^{13}C NMR Spectra of 1-(4-Chlorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1q**)

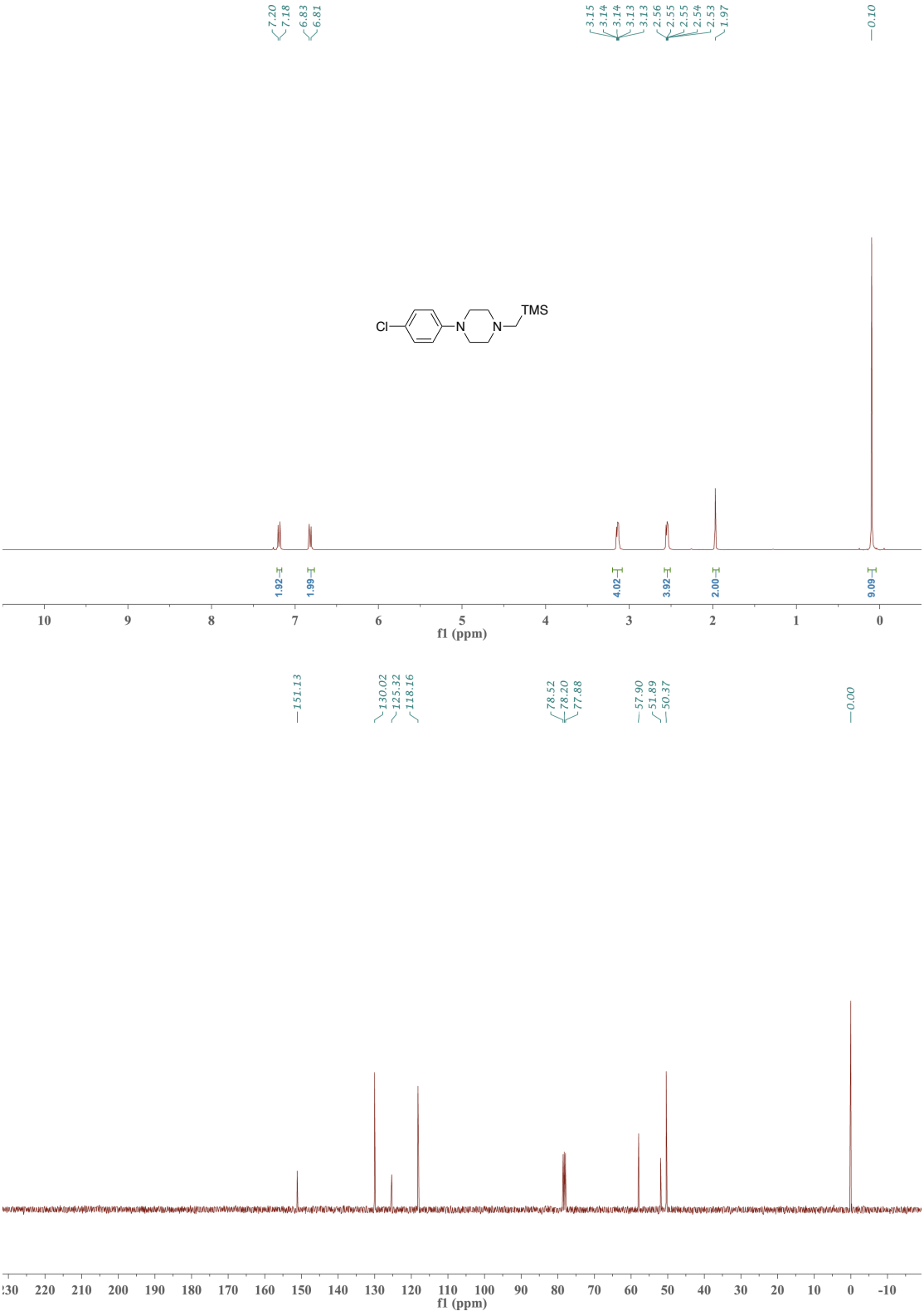


Figure S22. ^{1}H and ^{13}C NMR Spectra of 1-(4-Fluorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1r**)

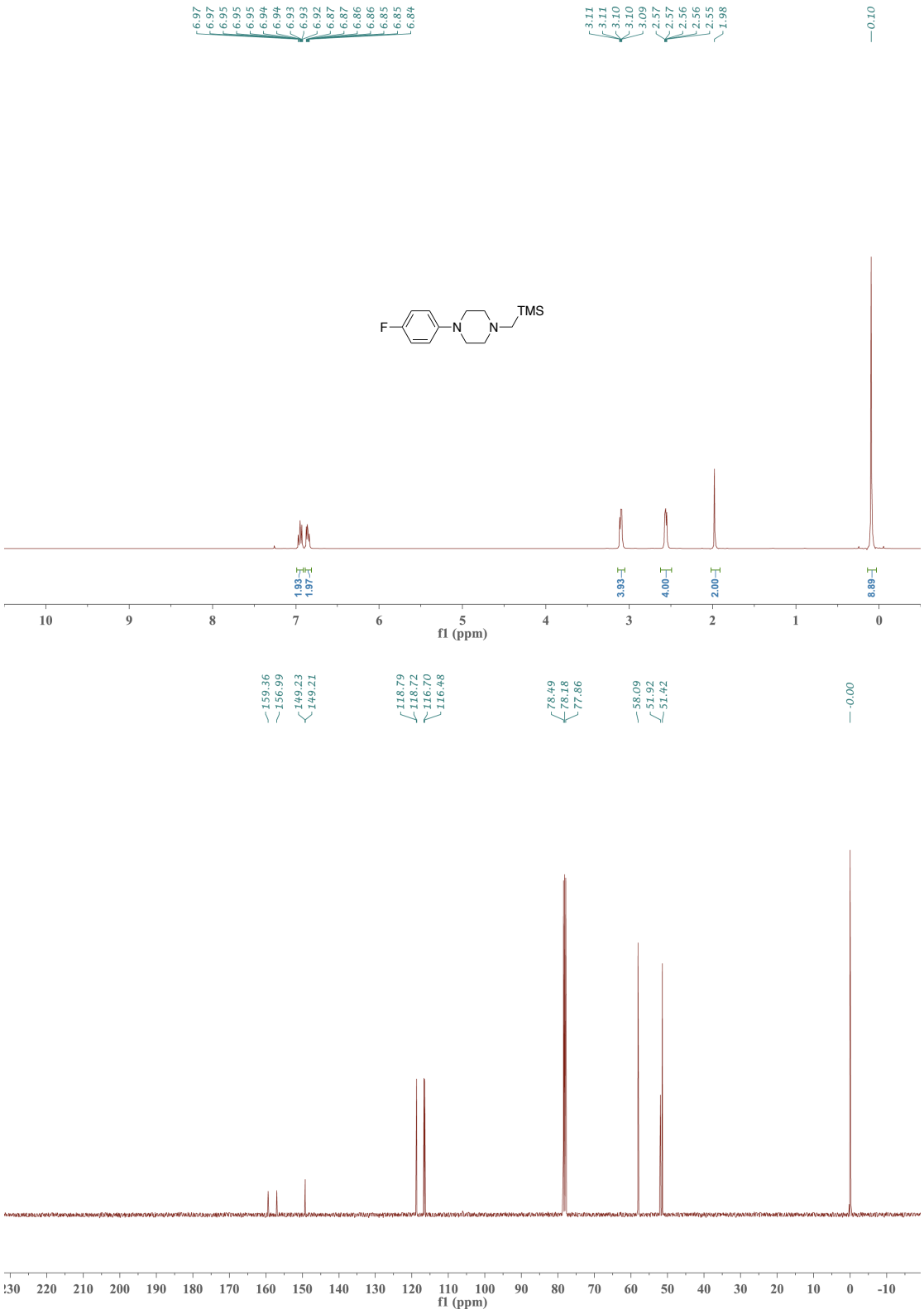
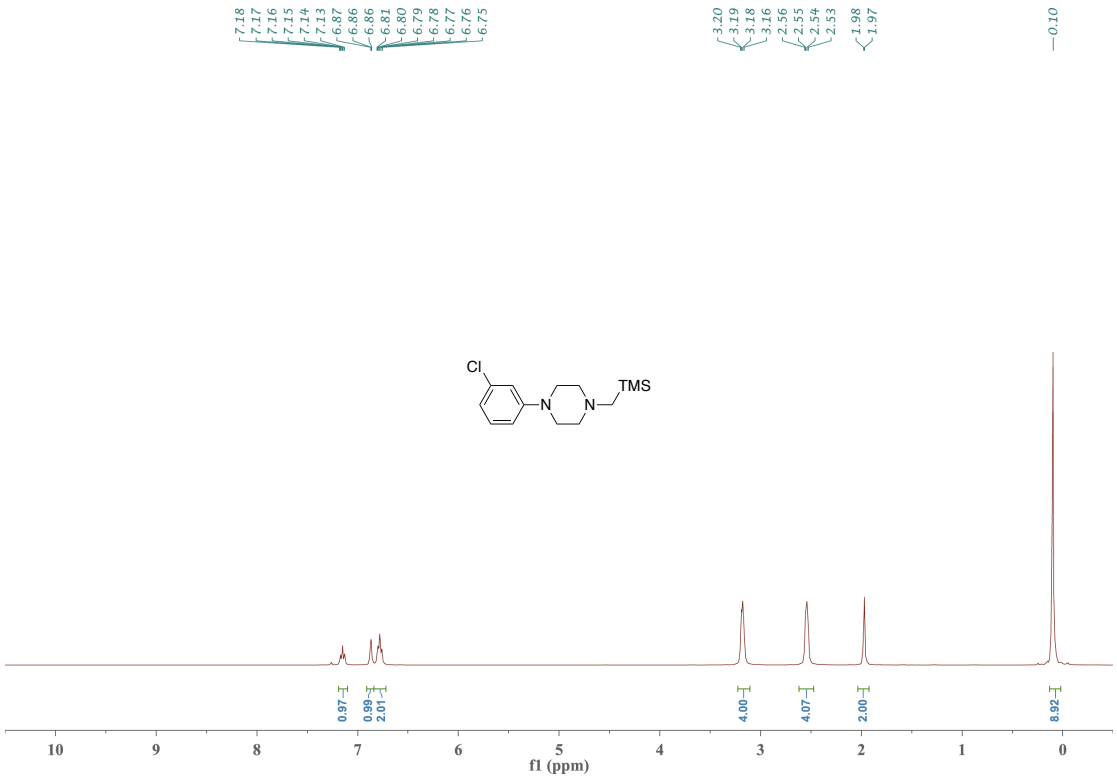


Figure S23. ^{1}H and ^{13}C NMR Spectra of 1-(3-Chlorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1s**)



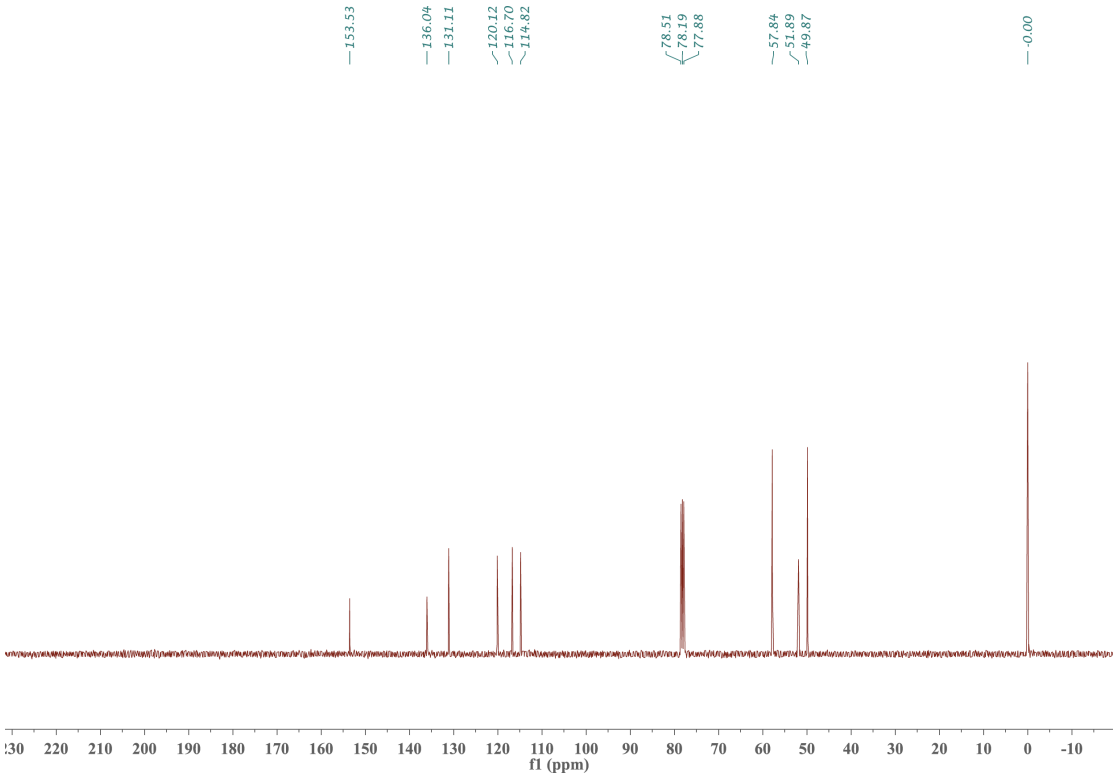


Figure S24. ^{1}H and ^{13}C NMR Spectra of 1-(2,3-Dichlorophenyl)-4-((trimethylsilyl)methyl)-piperazine (**1t**)

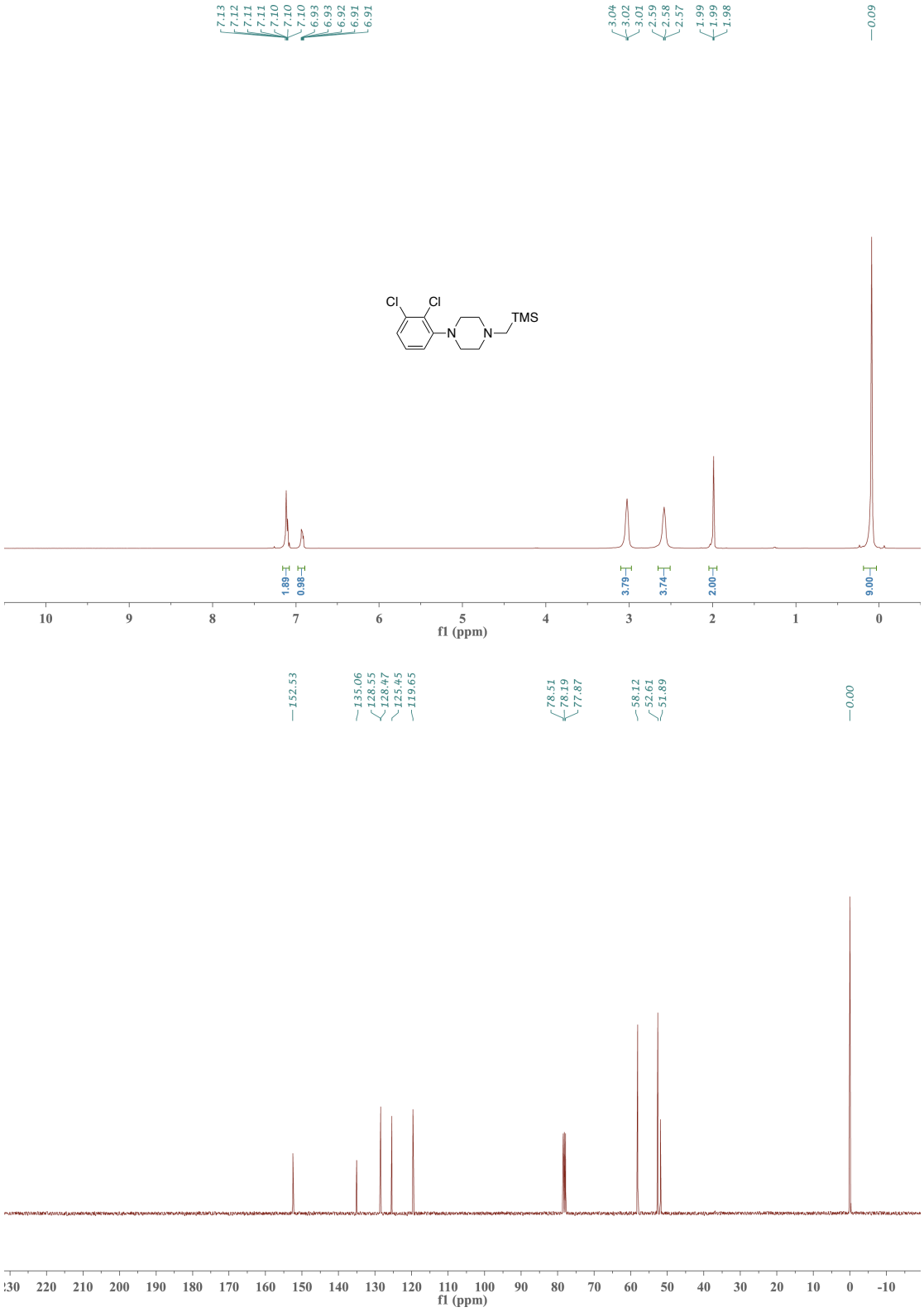


Figure S25. ^{1}H and ^{13}C NMR Spectra of 1-Benzyl-4-((trimethylsilyl)methyl)piperazine (**1u**)

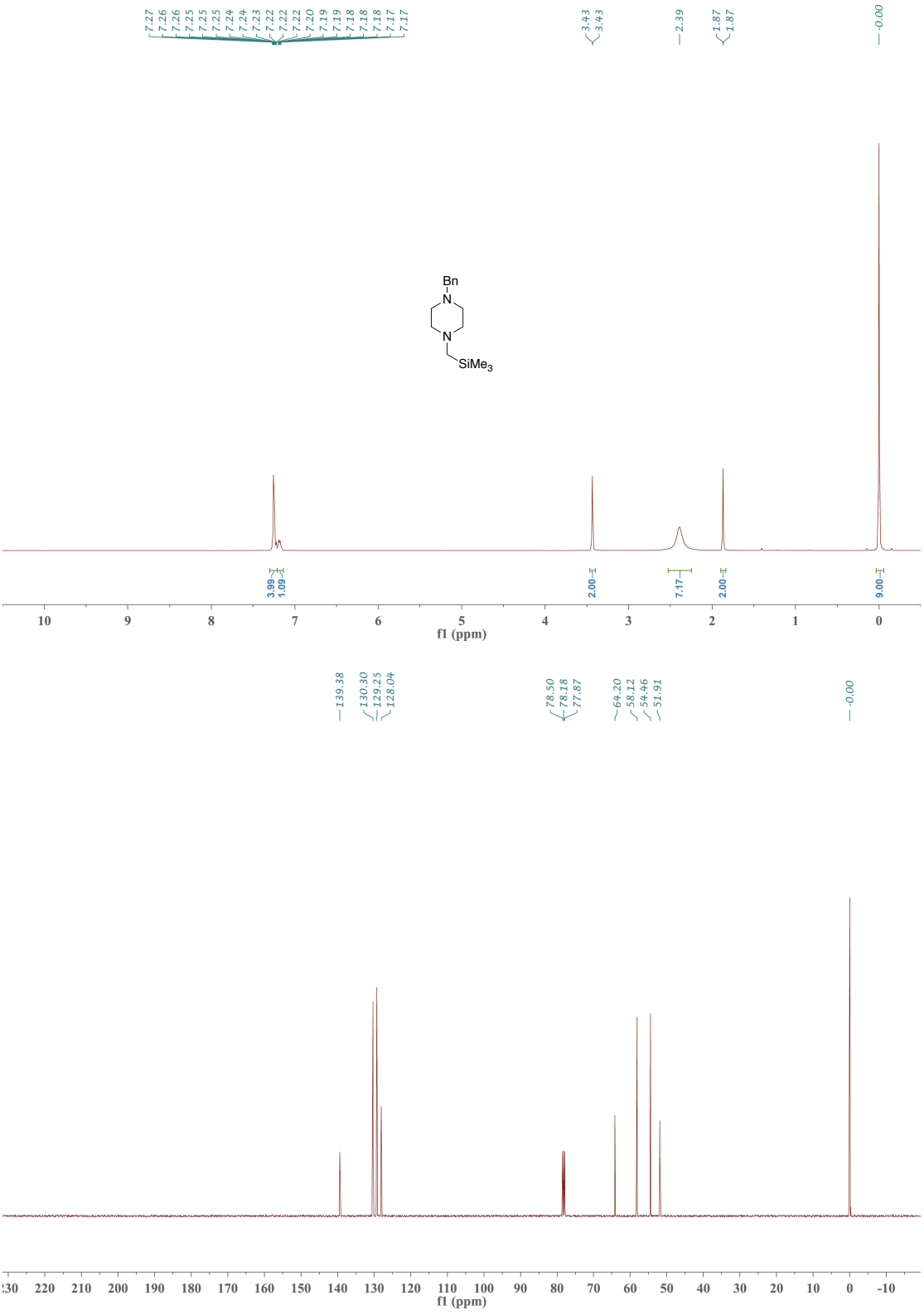


Figure S26. ^{1}H and ^{13}C NMR Spectra of Ethyl ((Trimethylsilyl)methyl)-*L*-prolinate (**1v**)

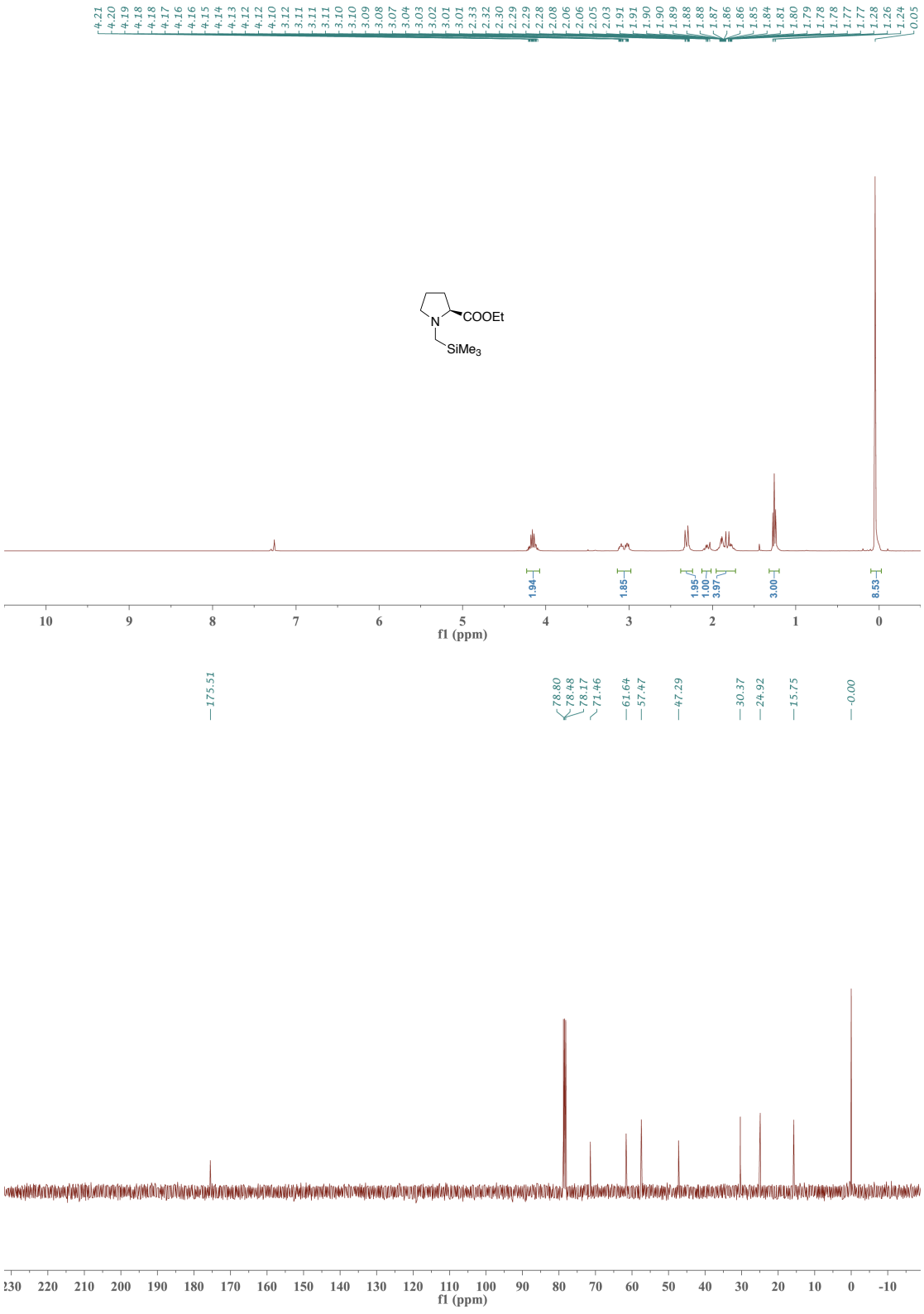


Figure S27. ^{1}H and ^{13}C NMR Spectra of (3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-((trimethylsilyl)methyl)piperidine (**1w**)

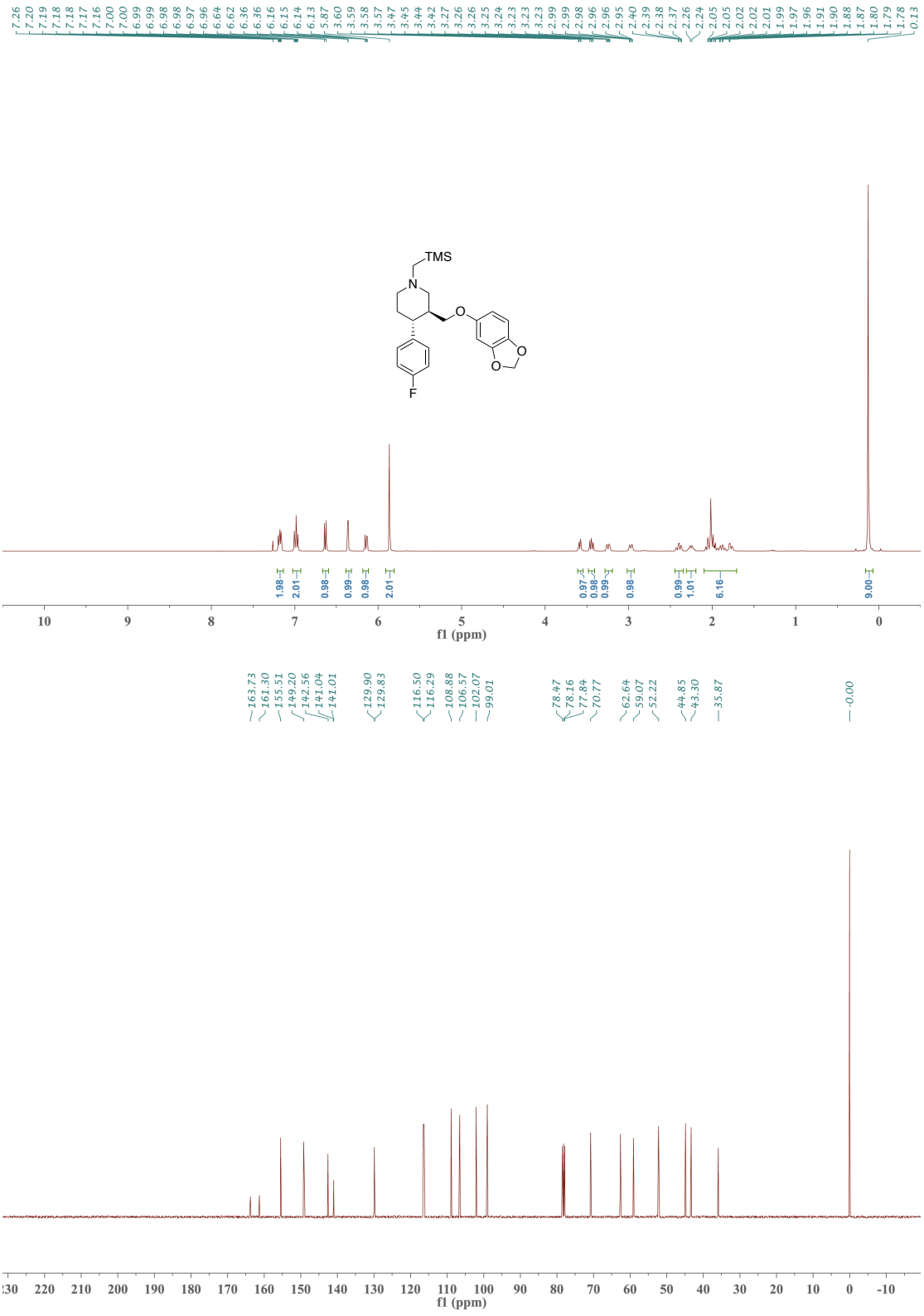
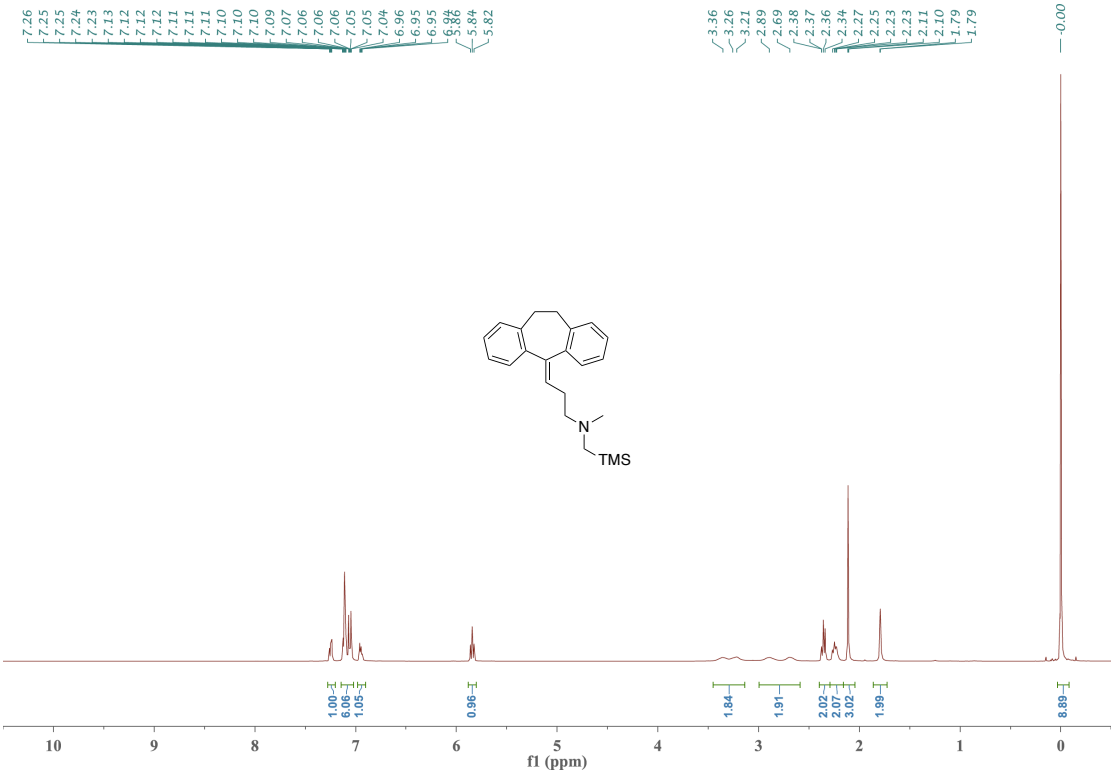


Figure S28. ^{1}H and ^{13}C NMR Spectra of 3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]-annulen-5-ylidene)-*N*-methyl-*N*-((trimethylsilyl)methyl)propan-1-amine (**1x**)



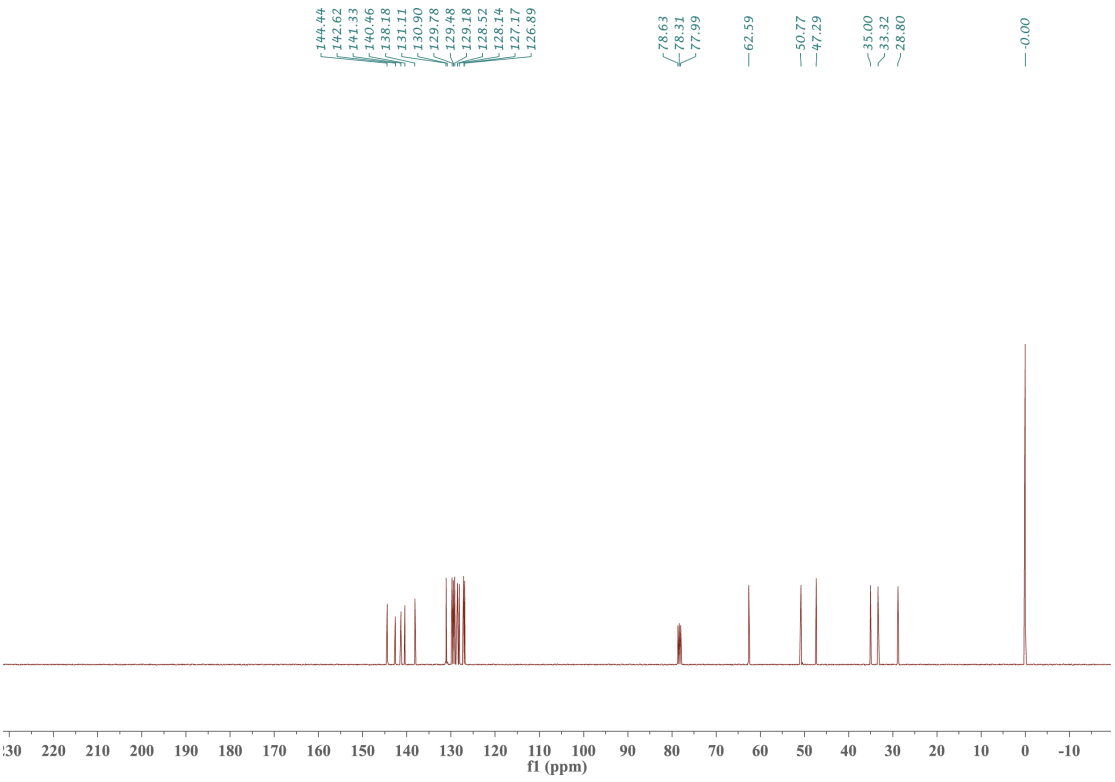
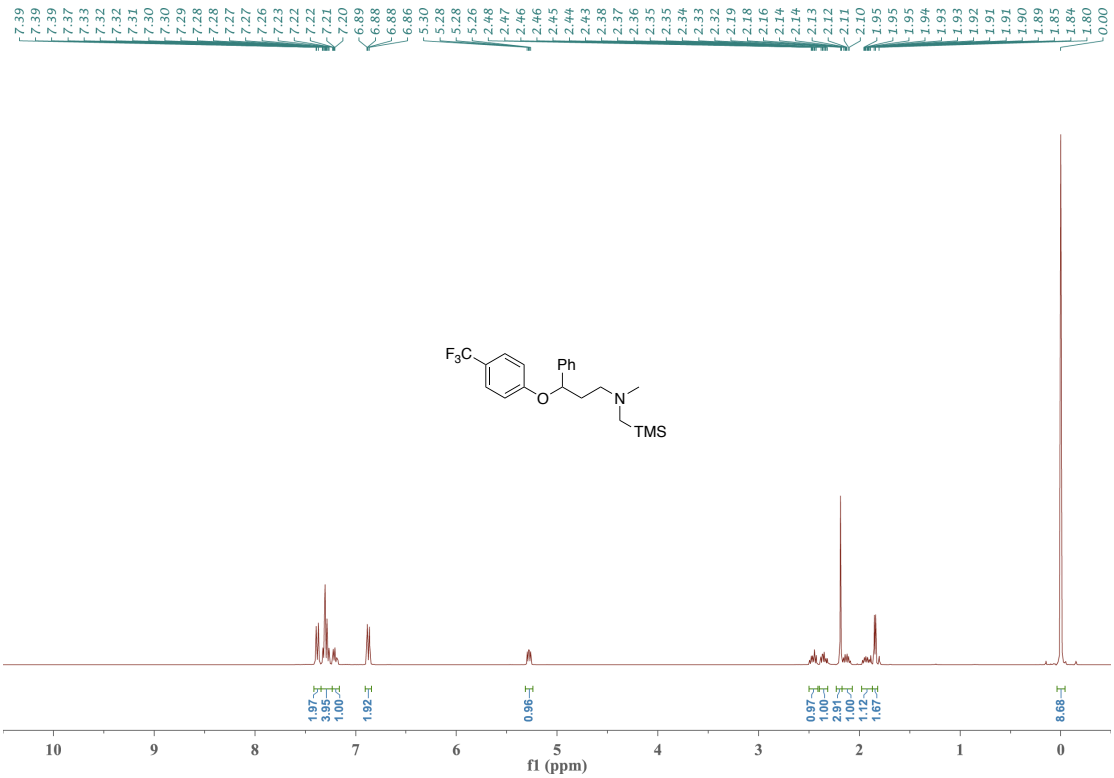


Figure S29. ^{1}H and ^{13}C NMR Spectra of *N*-Methyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)-*N*-((trimethylsilyl)methyl)propan-1-amine (**1y**)



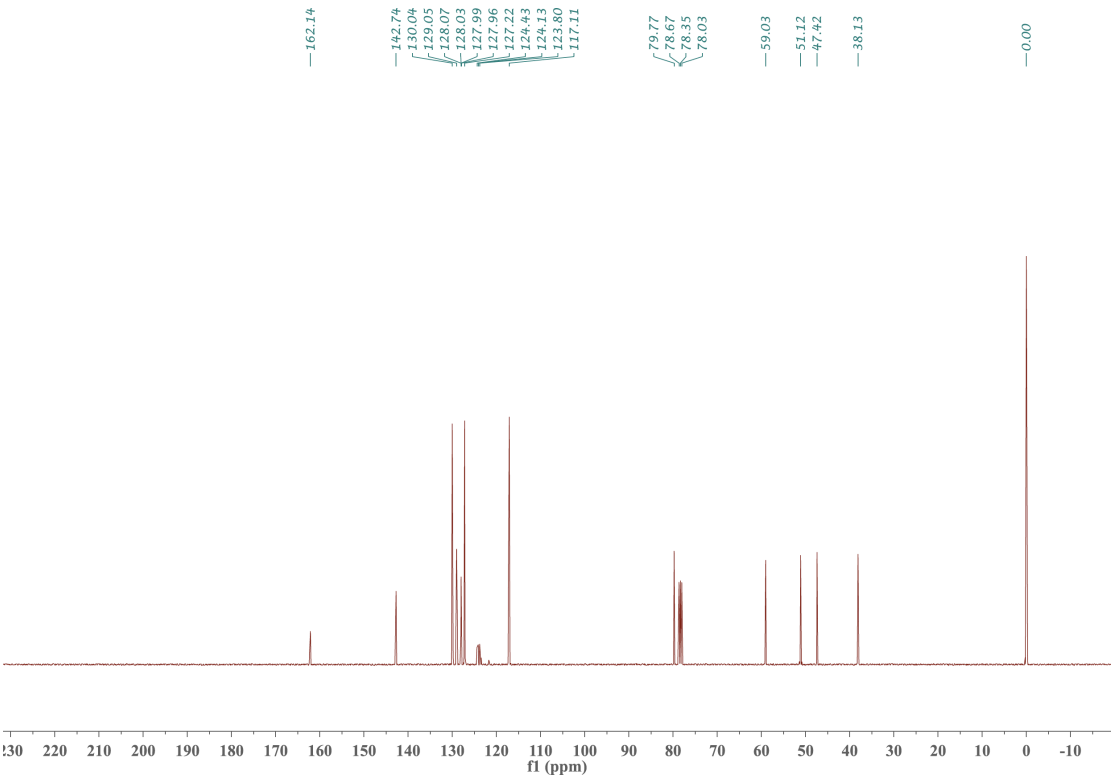


Figure S30. ^{1}H and ^{13}C NMR Spectra of (*S*)-*N*-Methyl-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)-*N*-((trimethylsilyl)methyl)propan-1-amine (**1z**)

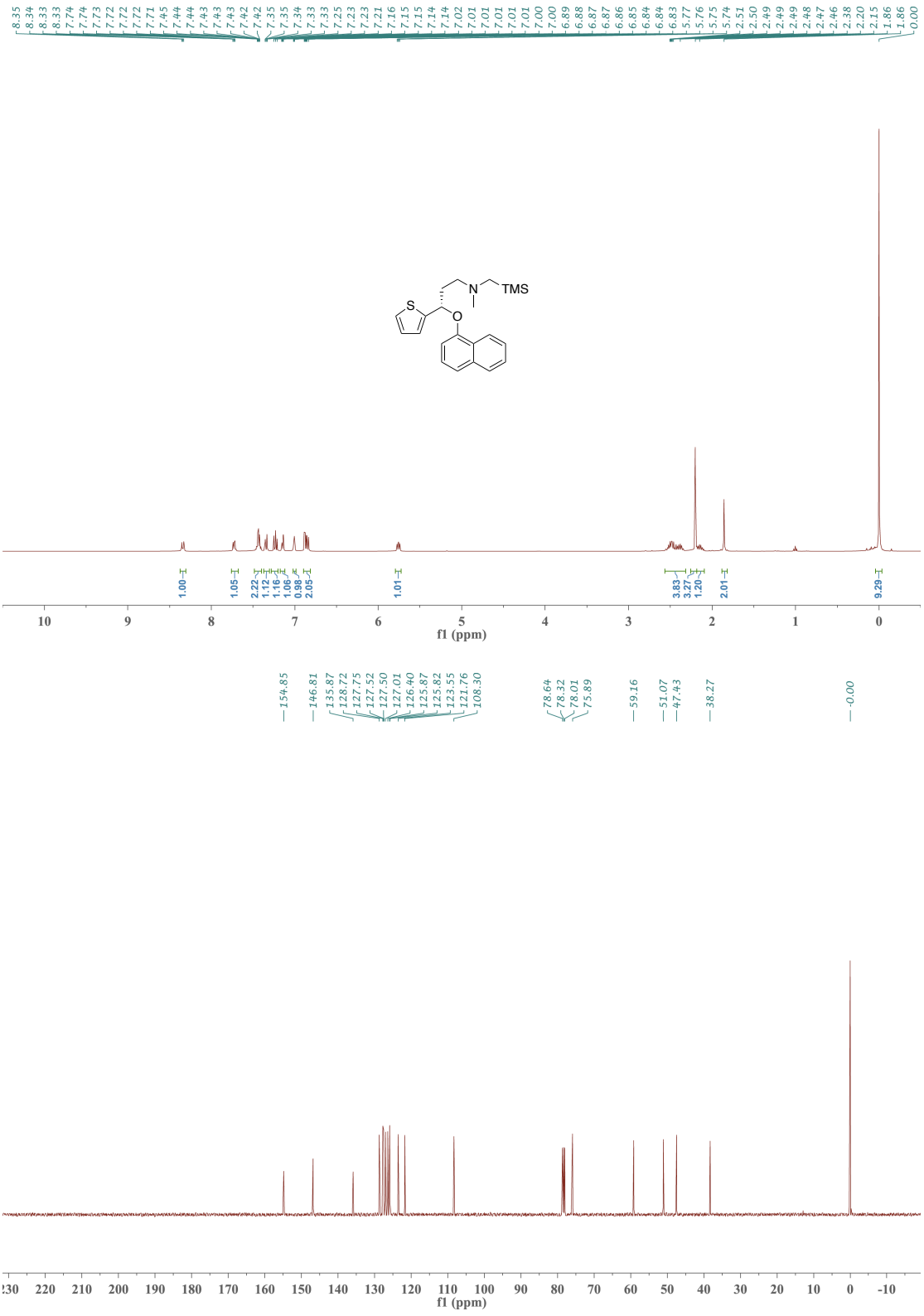


Figure S31. ^{1}H and ^{13}C NMR Spectra of (1*S*,4*S*)-4-(3,4-Dichlorophenyl)-*N*-methyl-*N*-((trimethylsilyl)methyl)-1,2,3,4-tetrahydronaphthalen-1-amine (**1α**)

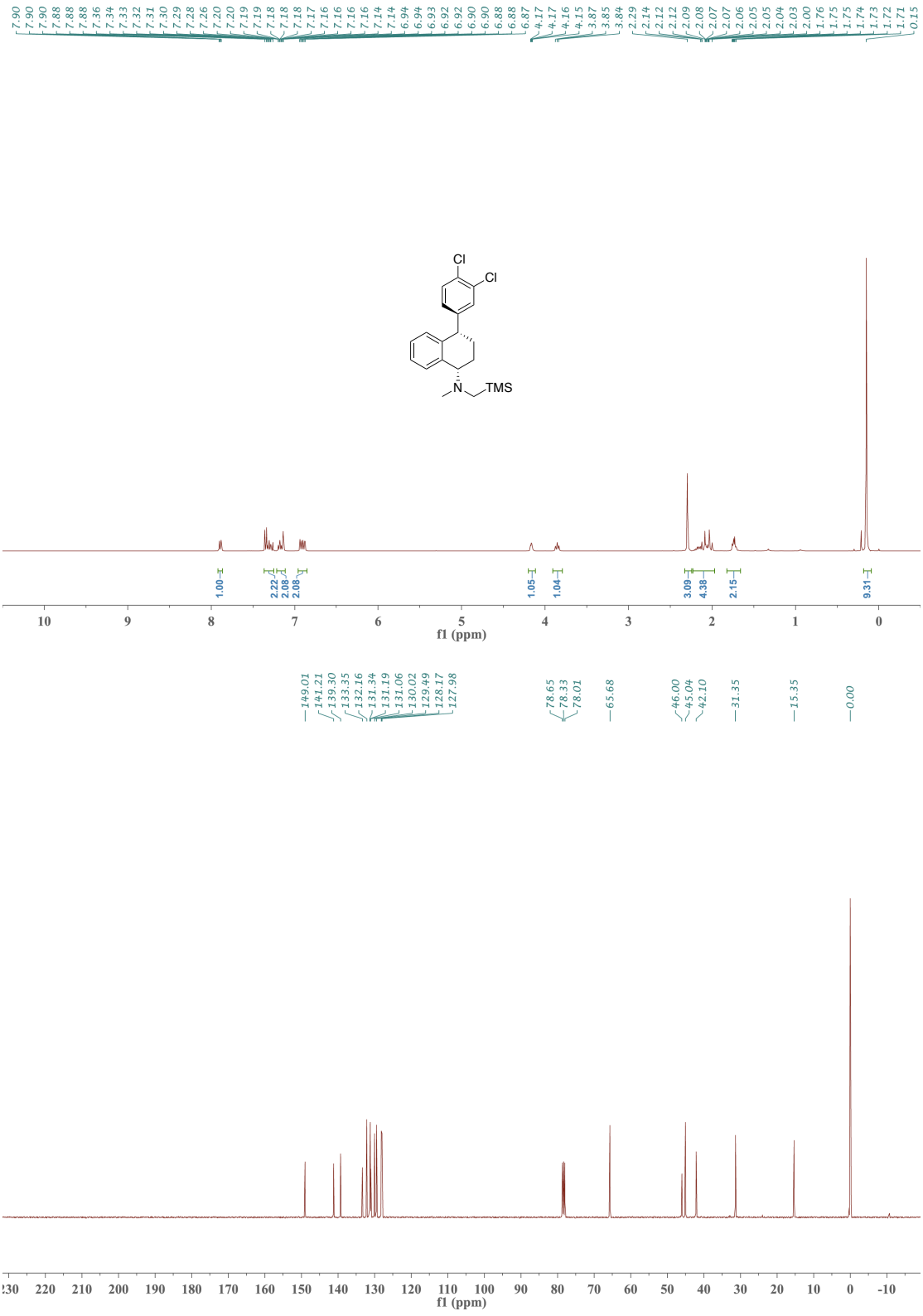


Figure S32. ^{1}H and ^{13}C NMR Spectra of 1-((Dimethyl(phenyl)silyl)methyl)piperidine (**1β**)

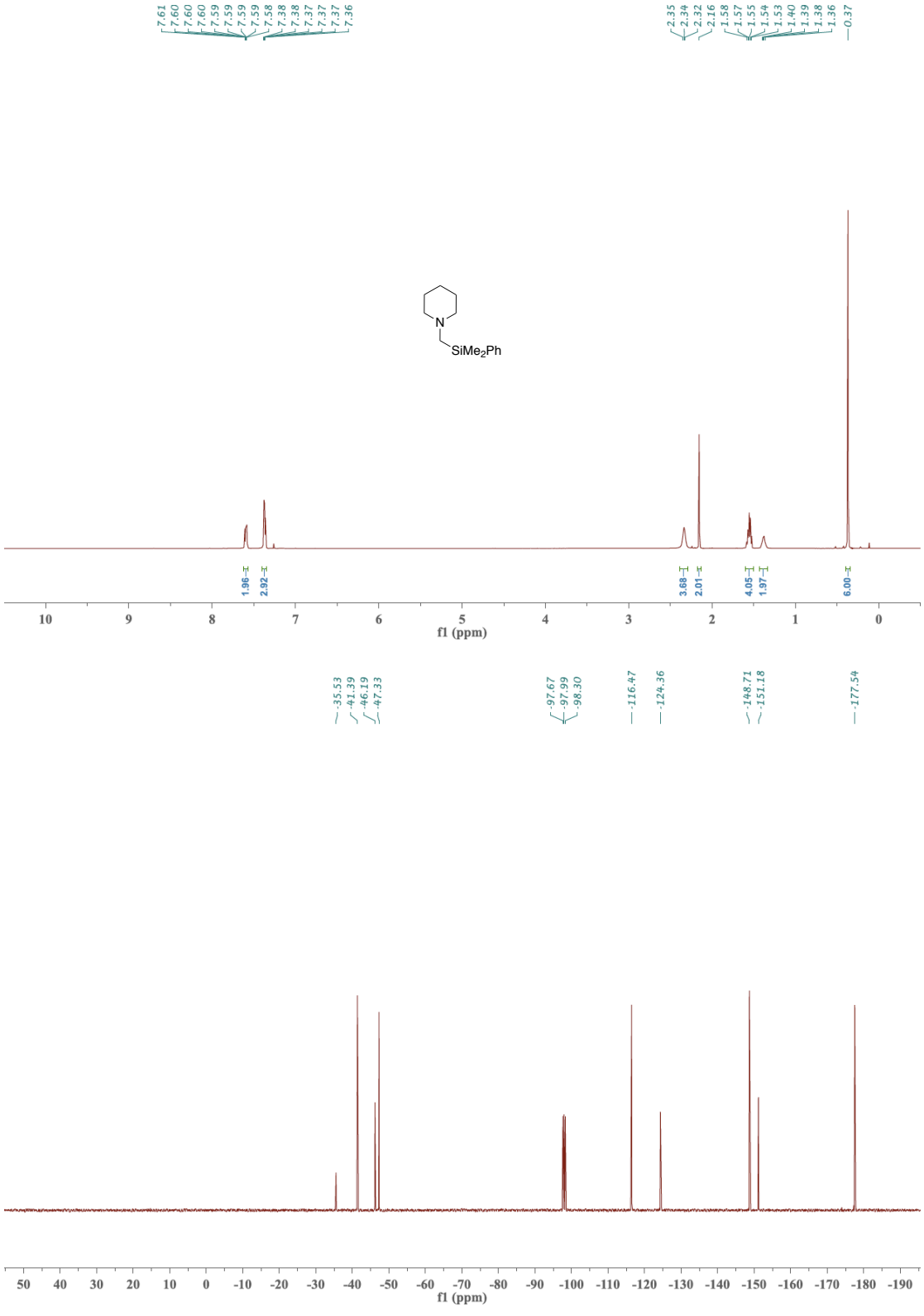


Figure S33. ^{1}H and ^{13}C NMR Spectra of Piperidine-1-carbaldehyde (**2a**)

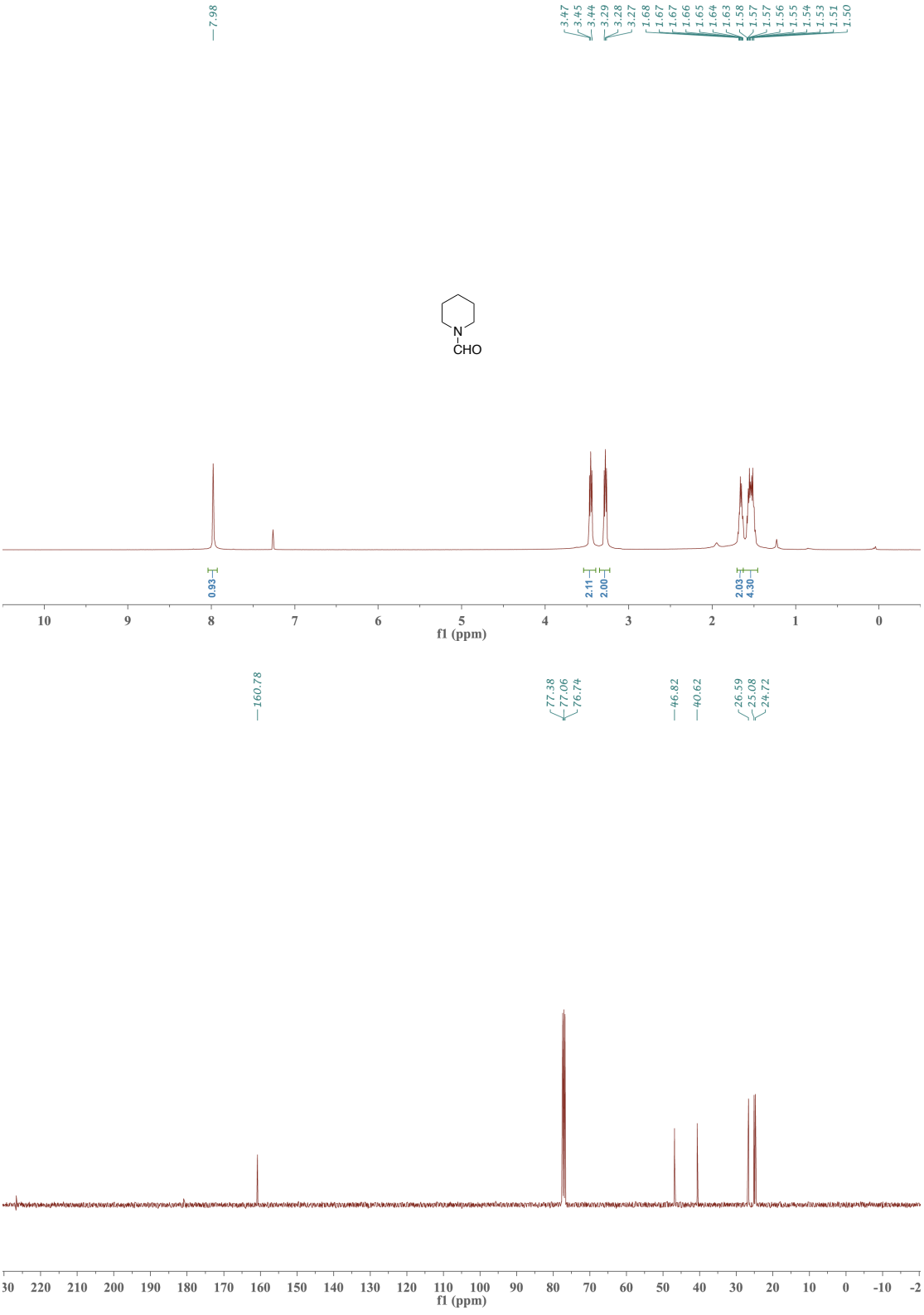


Figure S34. ^{1}H and ^{13}C NMR Spectra of Pyrrolidine-1-carbaldehyde (**2b**)

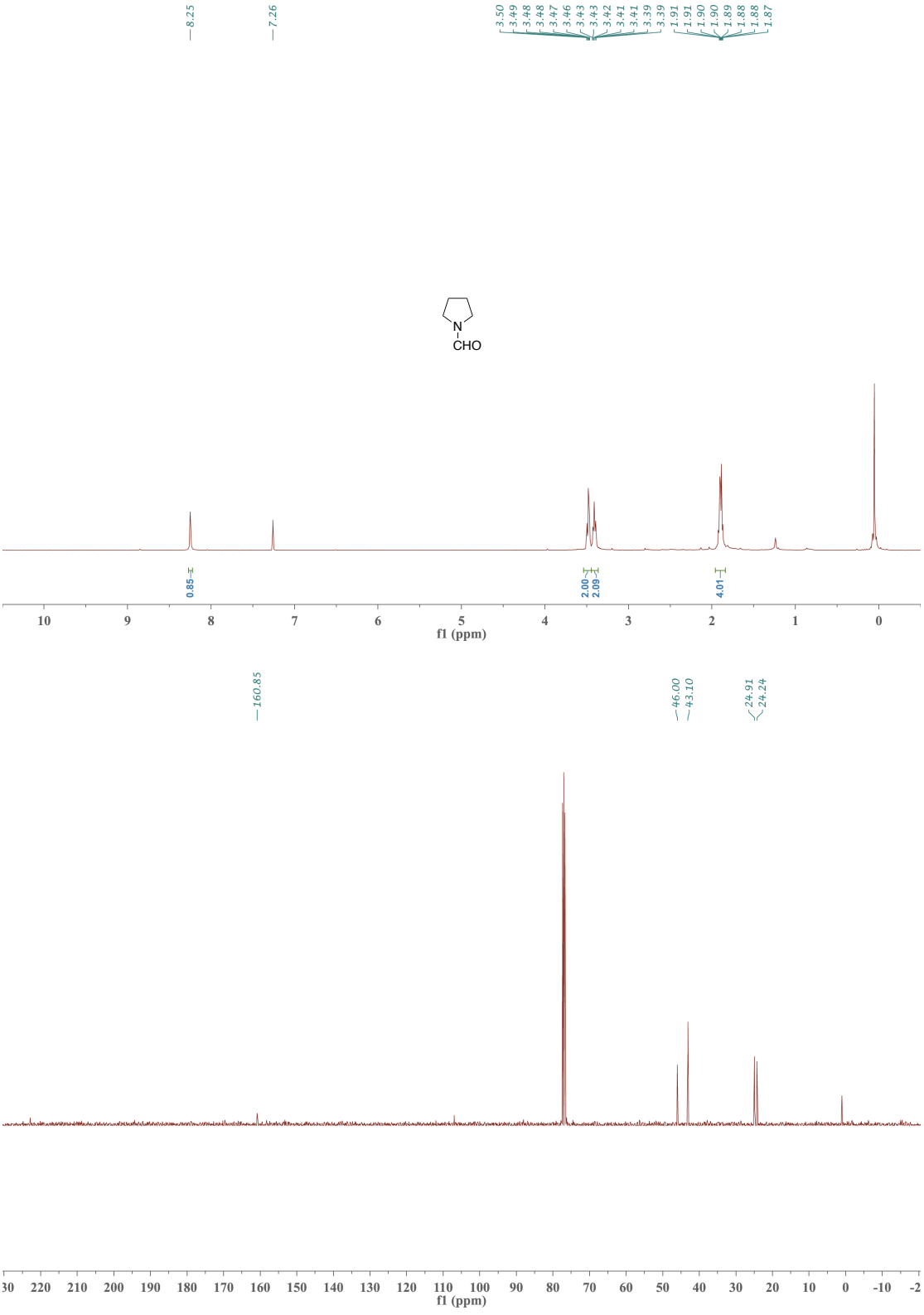


Figure S35. ^{1}H and ^{13}C NMR Spectra of Asepane-1-carbaldehyde (**2c**)

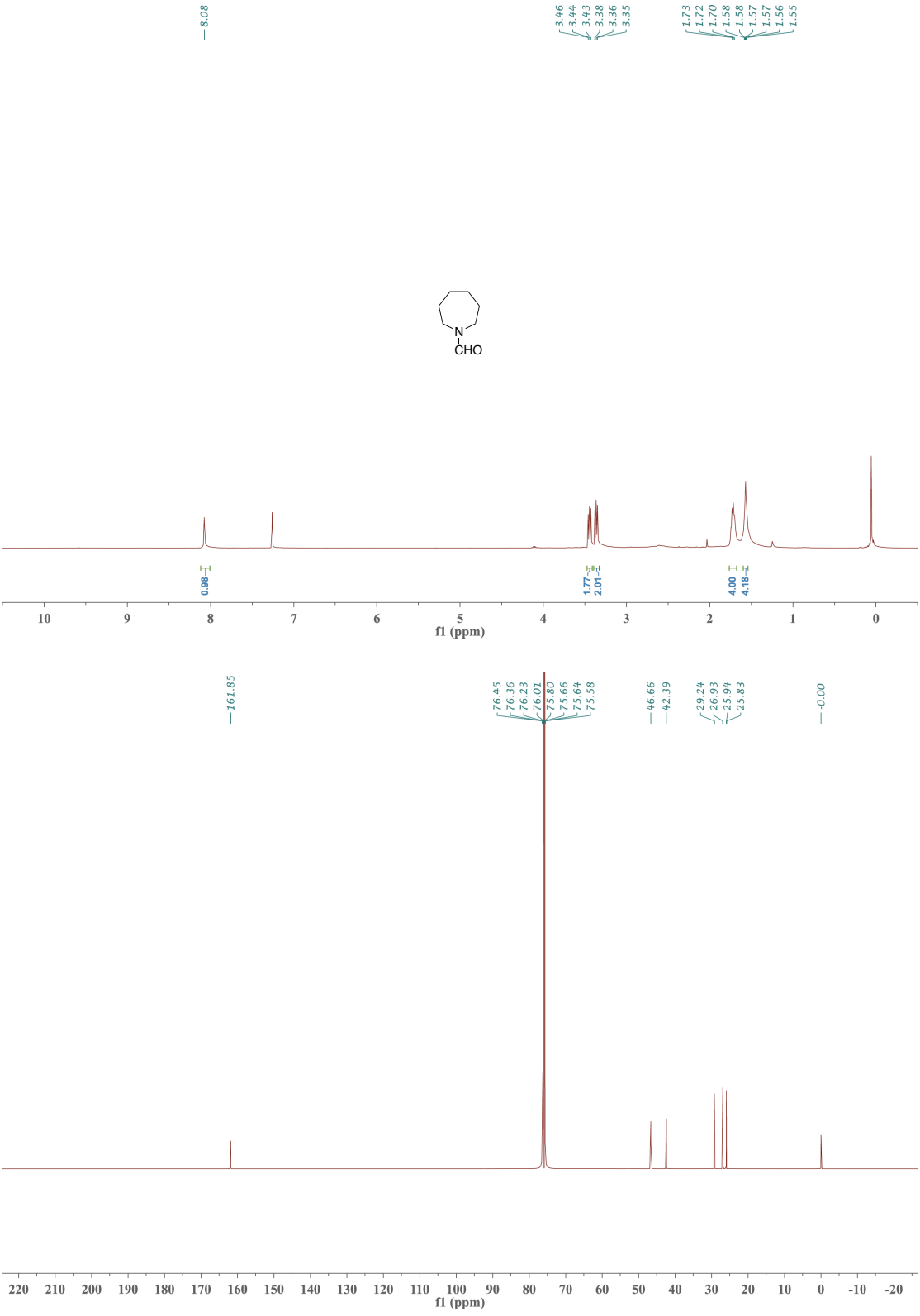


Figure S36. ^{1}H and ^{13}C NMR Spectra of *N*,*N*-Diethylformamide (**2d**)

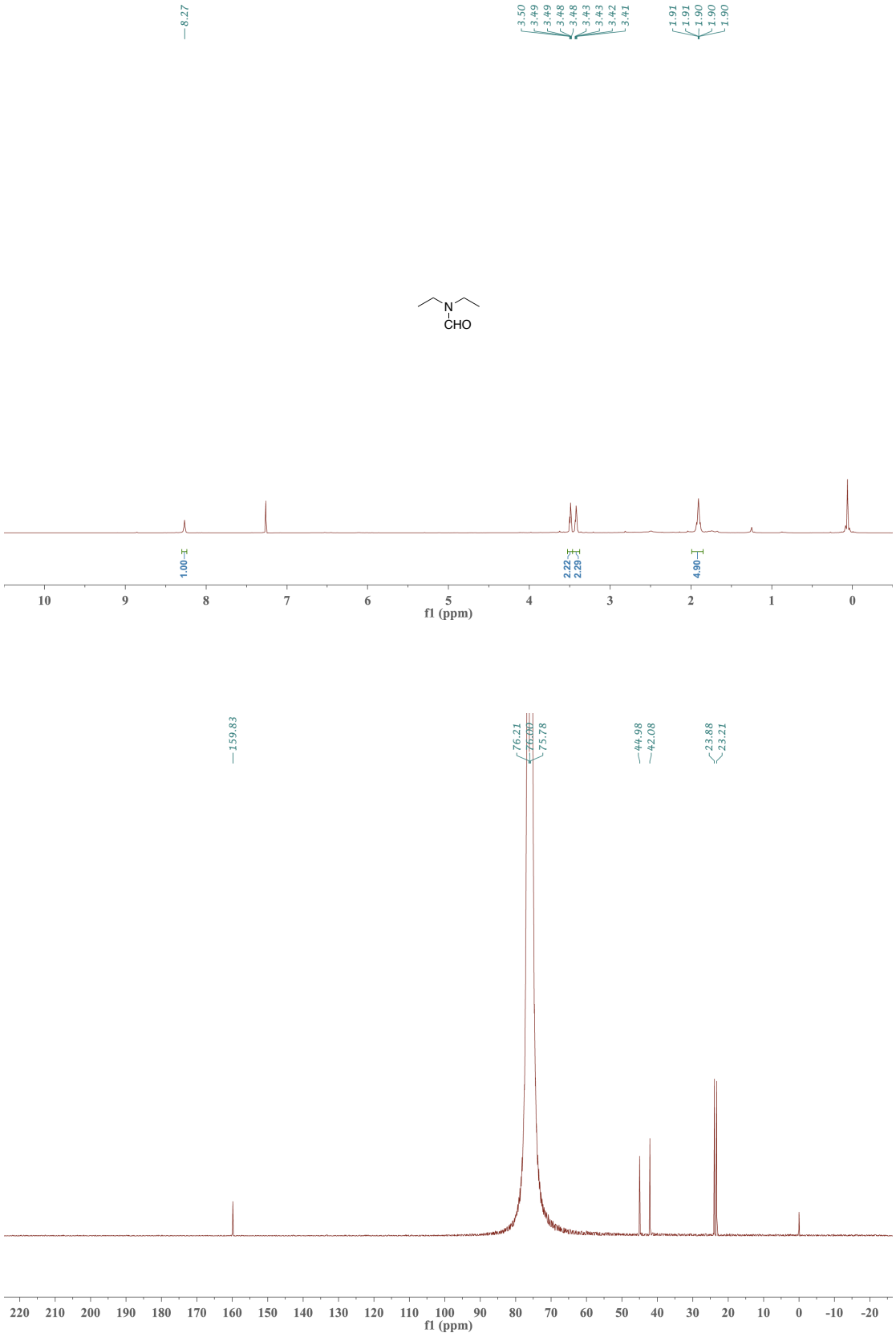


Figure S37. ^{1}H and ^{13}C NMR Spectra of *N,N*-Dibutylformamide (**2e**)

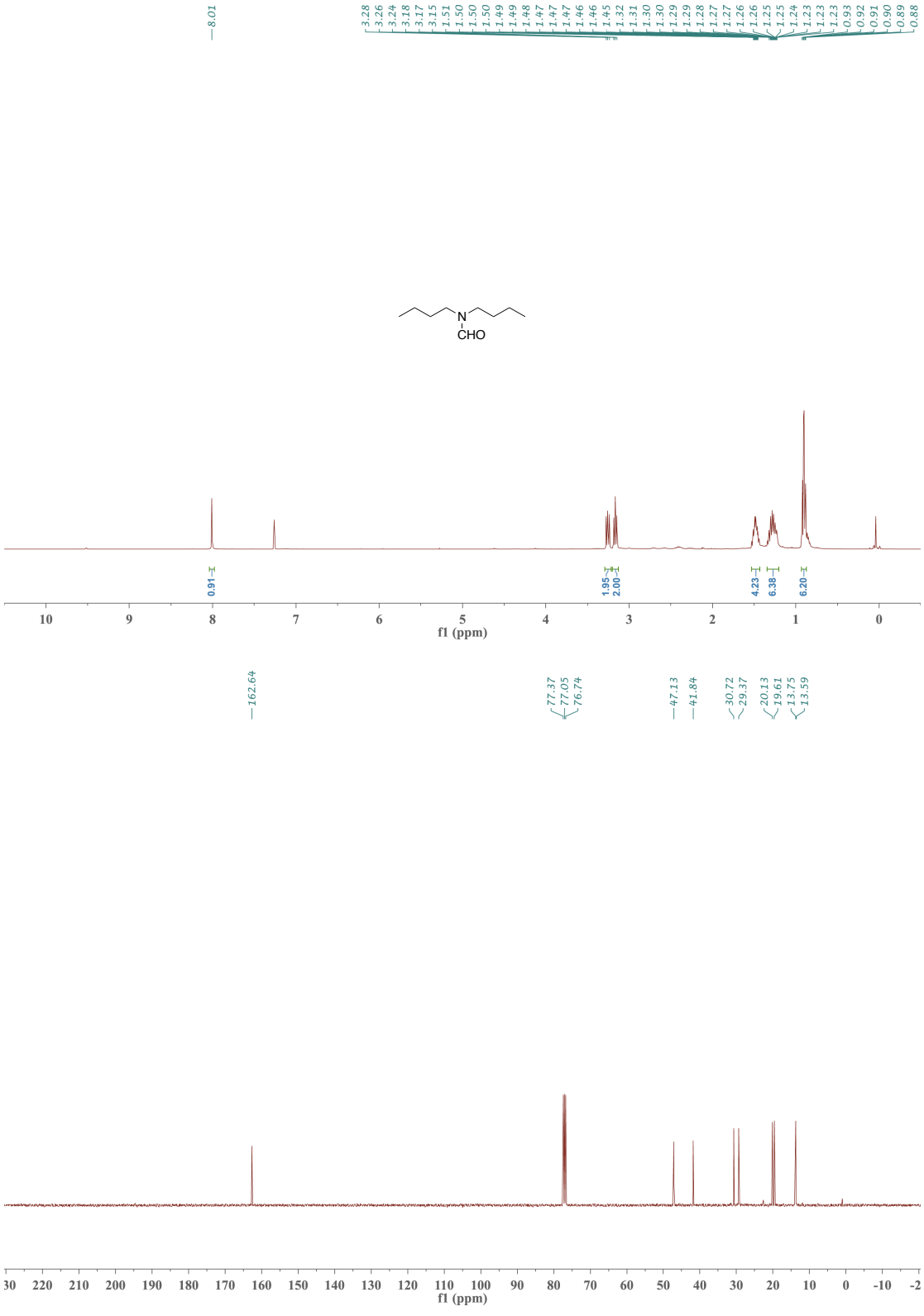


Figure S38. ^{1}H and ^{13}C NMR Spectra of *N,N*-Dioctylformamide (**2f**)

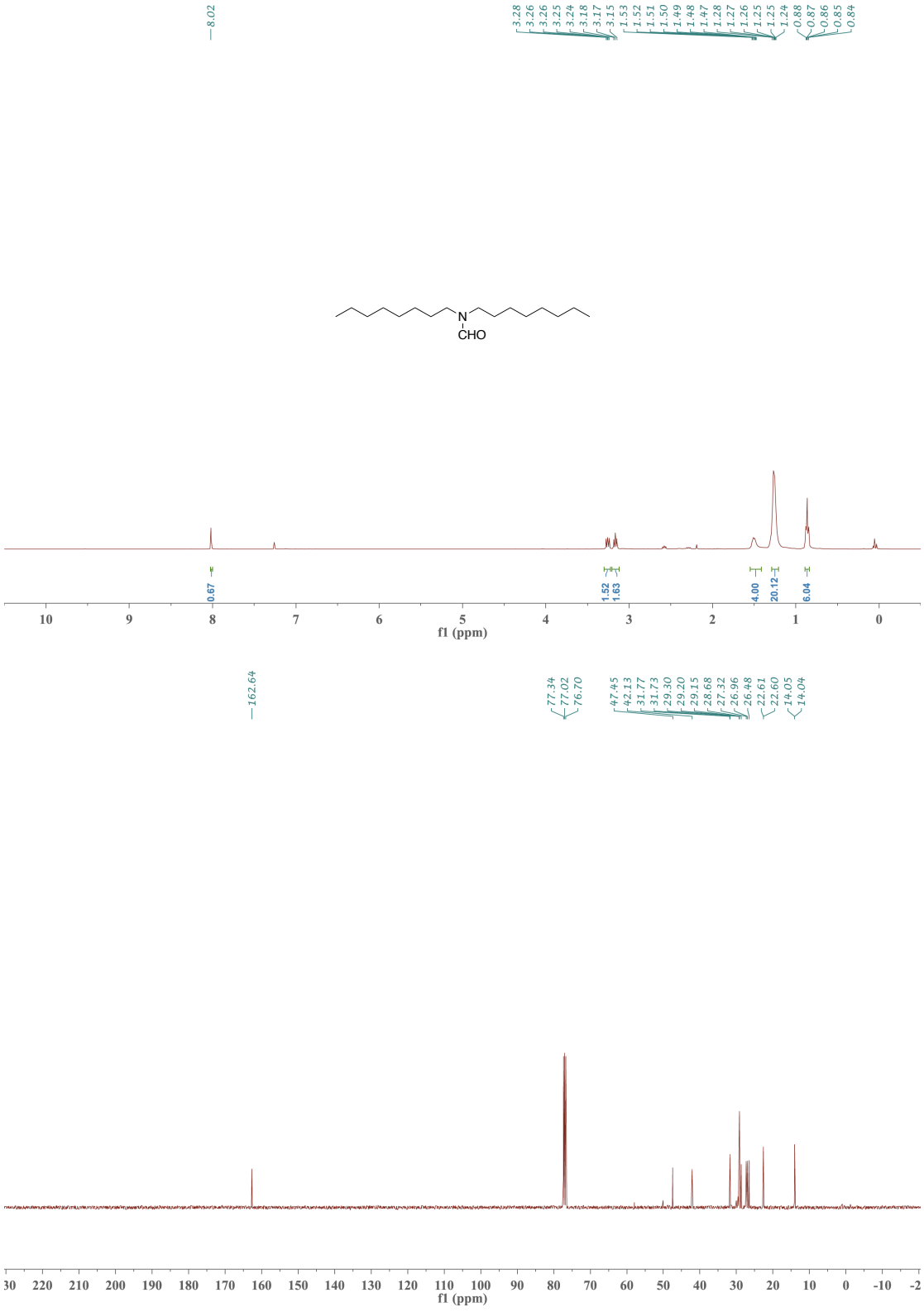


Figure S39. ^{1}H and ^{13}C NMR Spectra of *N*-Cyclohexyl-*N*-ethylformamide (**2g**)

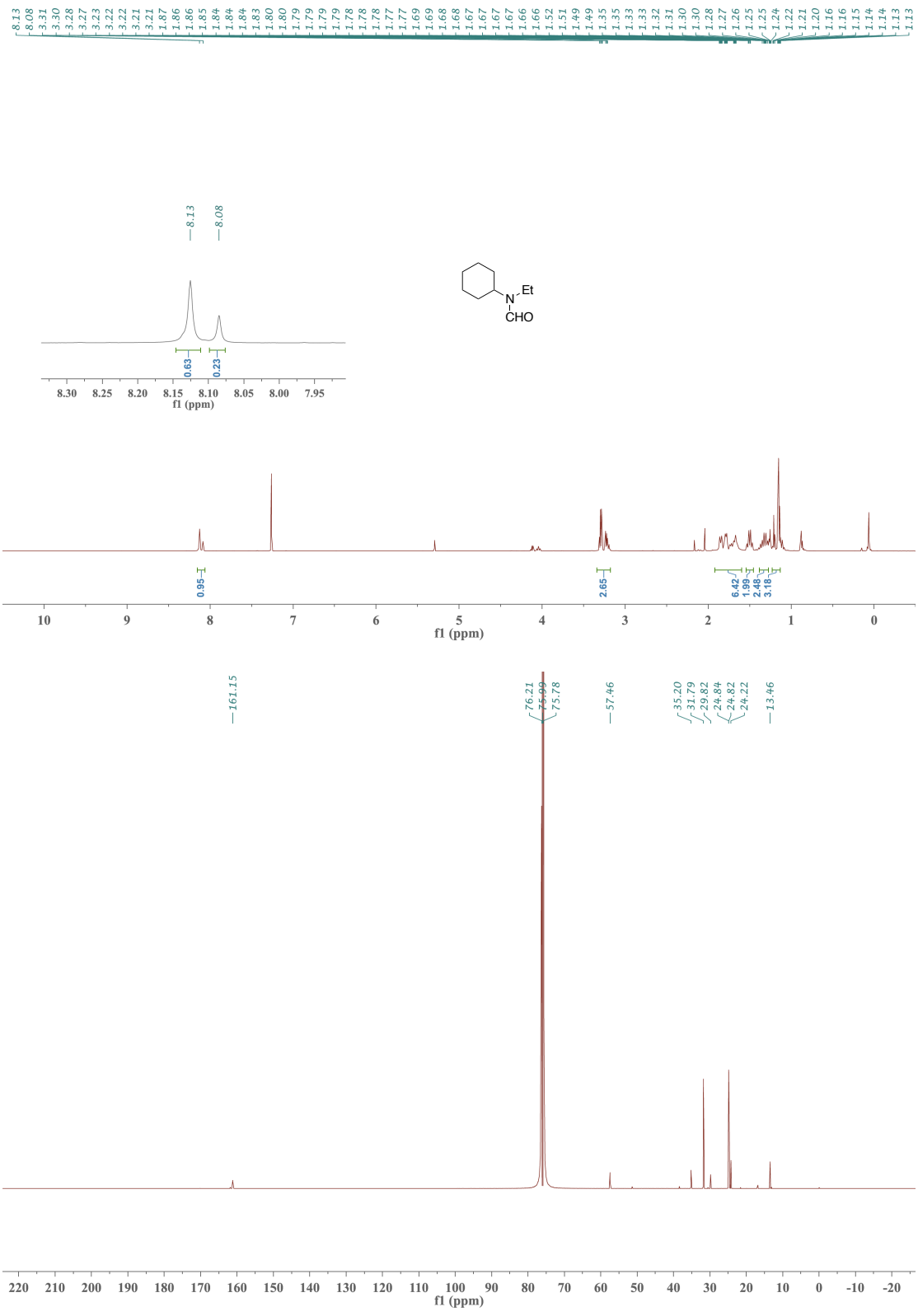


Figure S40. ^{1}H and ^{13}C NMR Spectra of Methyl 5-(*N*-Phenethylformamido)pentanoate **(2h)**

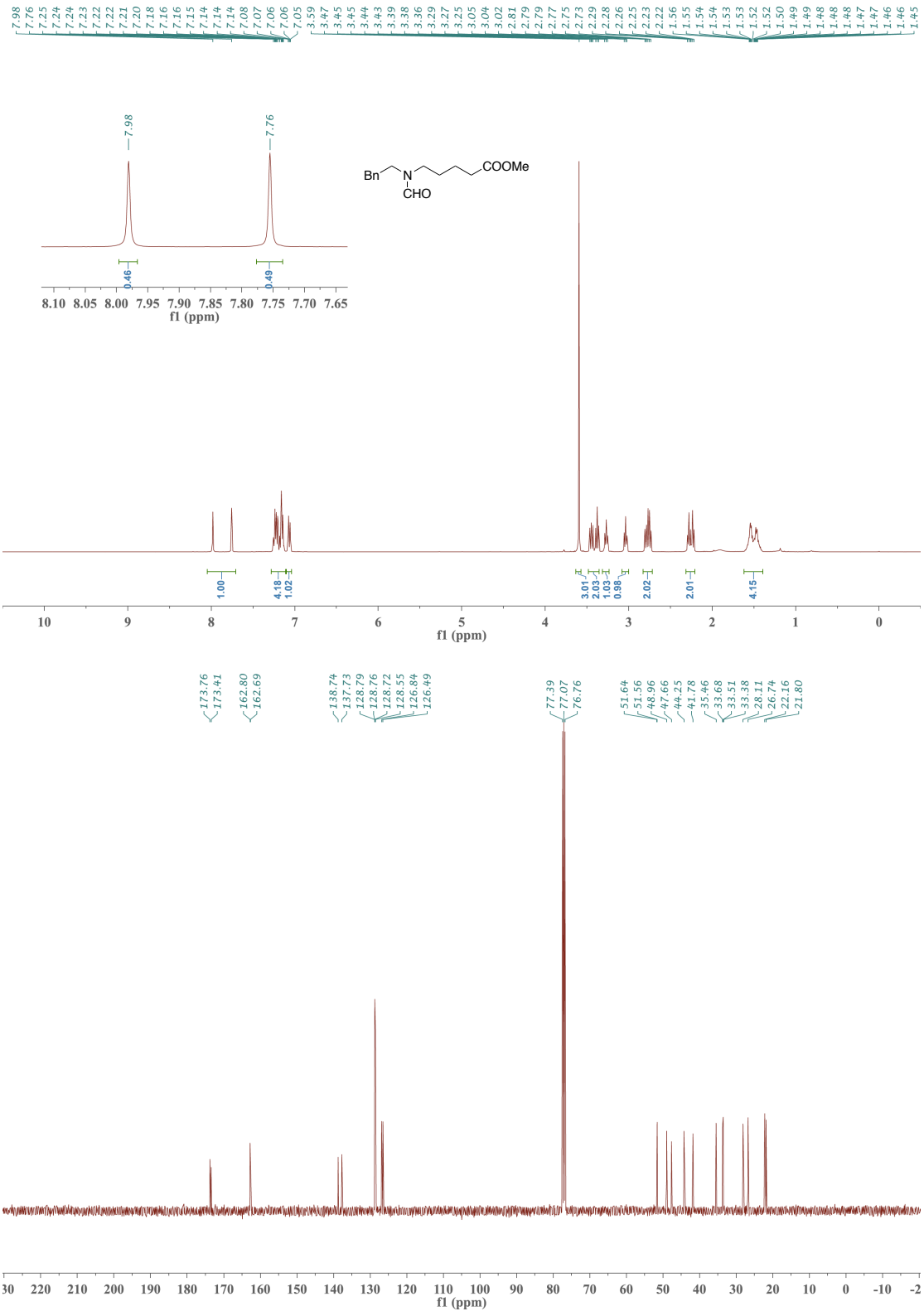


Figure S41. ^{1}H and ^{13}C NMR Spectra of *N*-(2-(1,3-Dioxan-2-yl)ethyl)-*N*-phenethyl-formamide (**2i**)

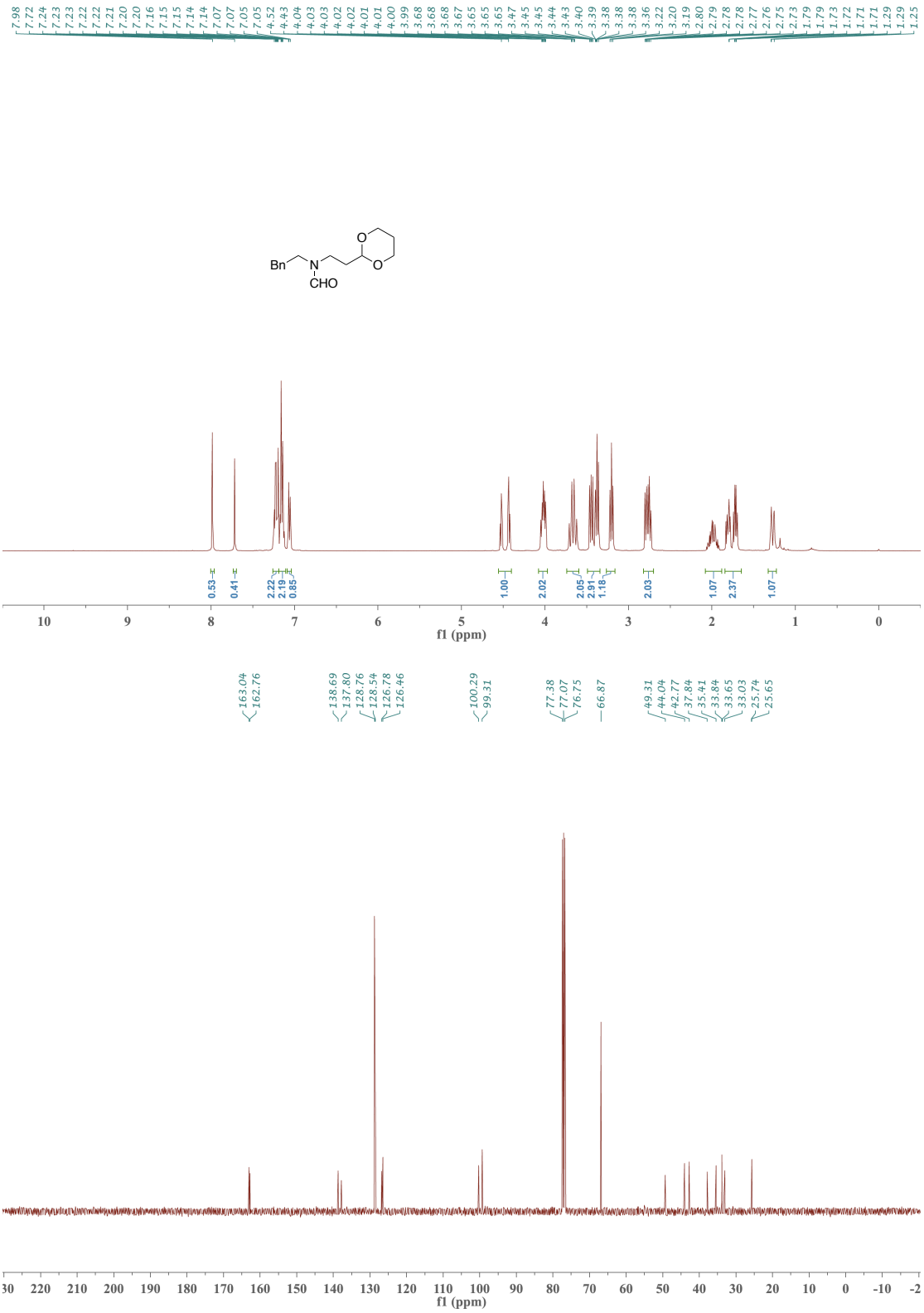


Figure S42. ^{1}H and ^{13}C NMR Spectra of *N*-Allyl-*N*-phenethylformamide (**2j**)

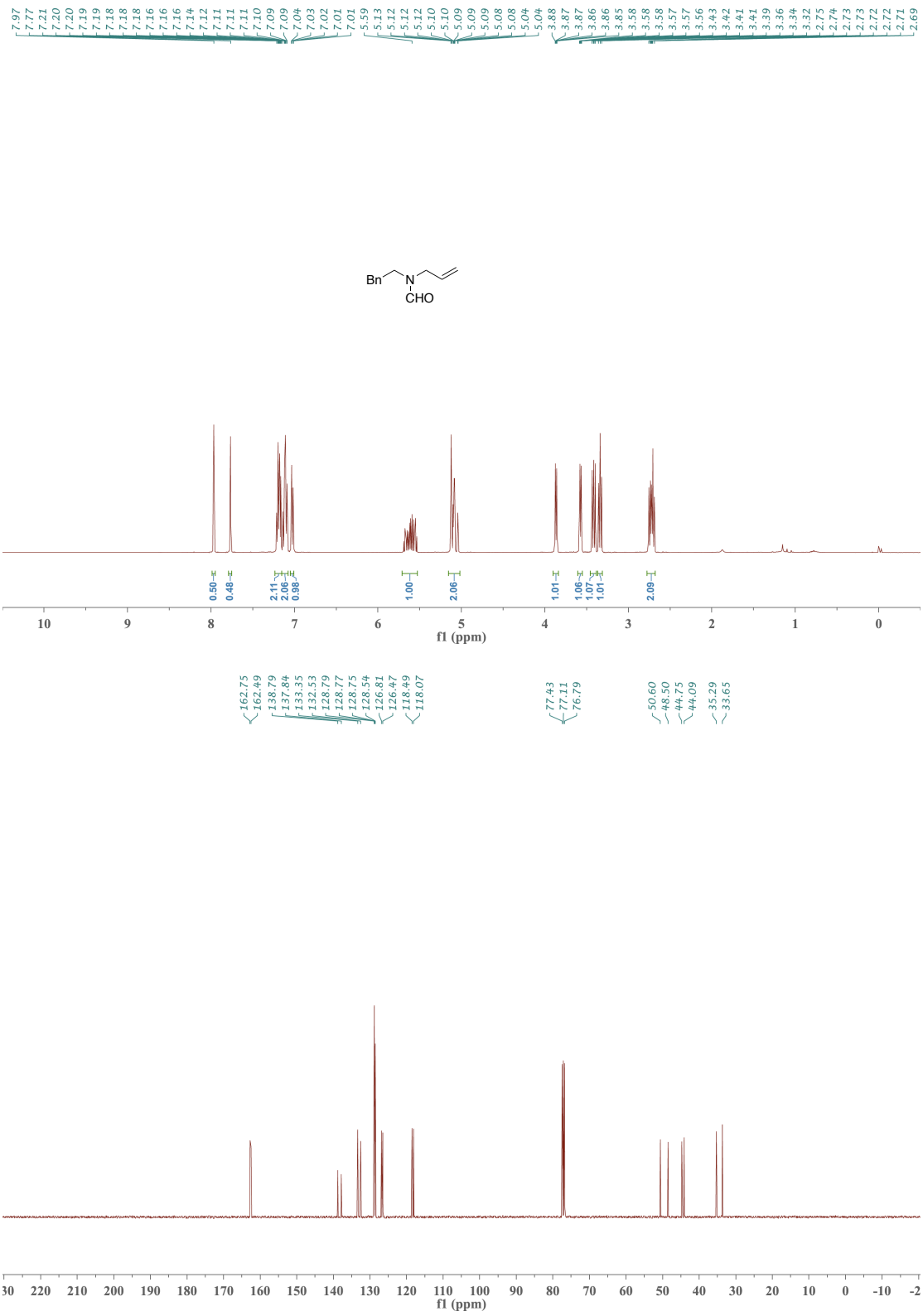


Figure S43. ^{1}H and ^{13}C NMR Spectra of *N*-(Cyclohex-2-en-1-yl)-*N*-phenethylformamide (**2k**)

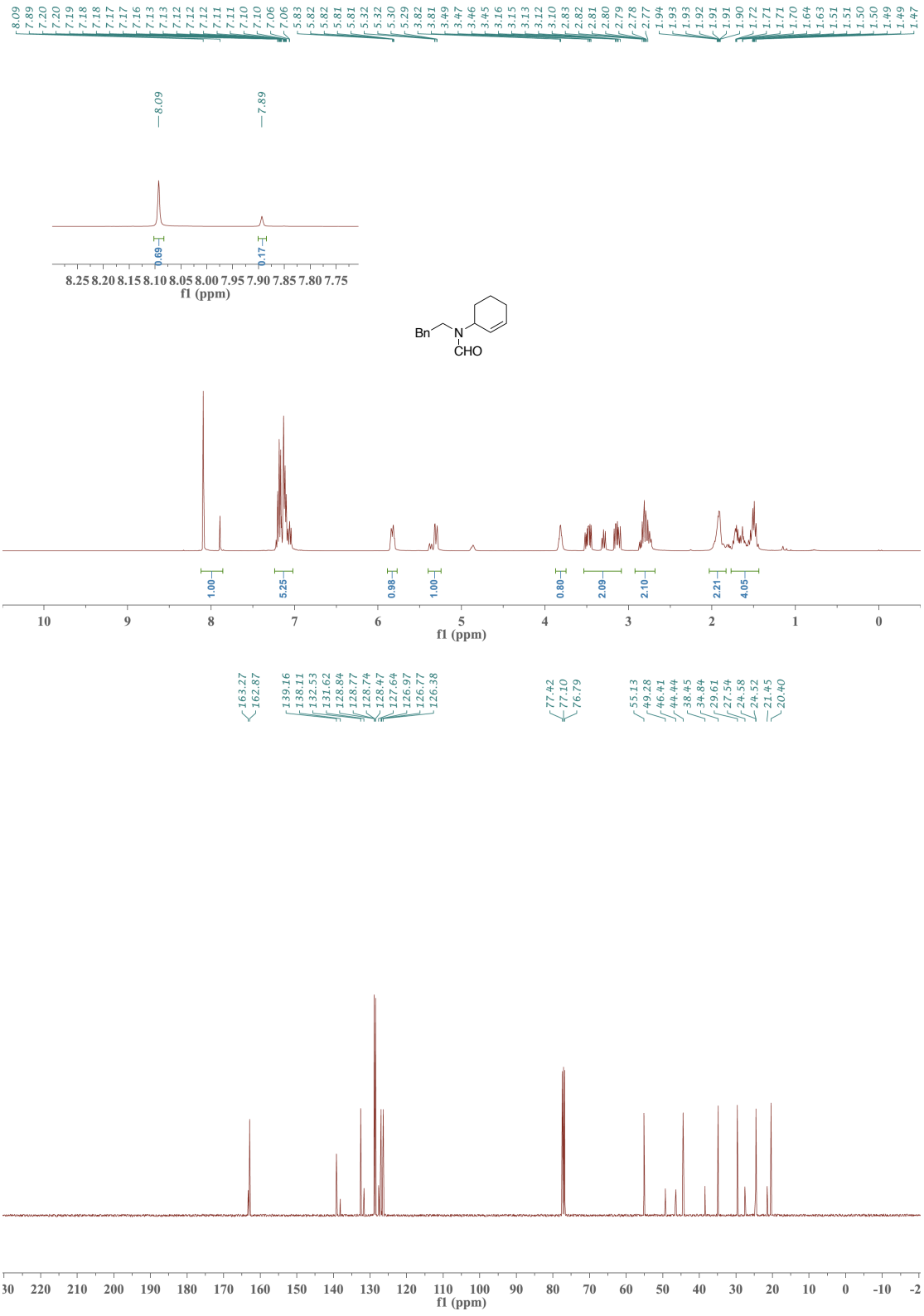


Figure S44. ^{1}H and ^{13}C NMR Spectra of Morpholine-4-carbaldehyde (**2m**)

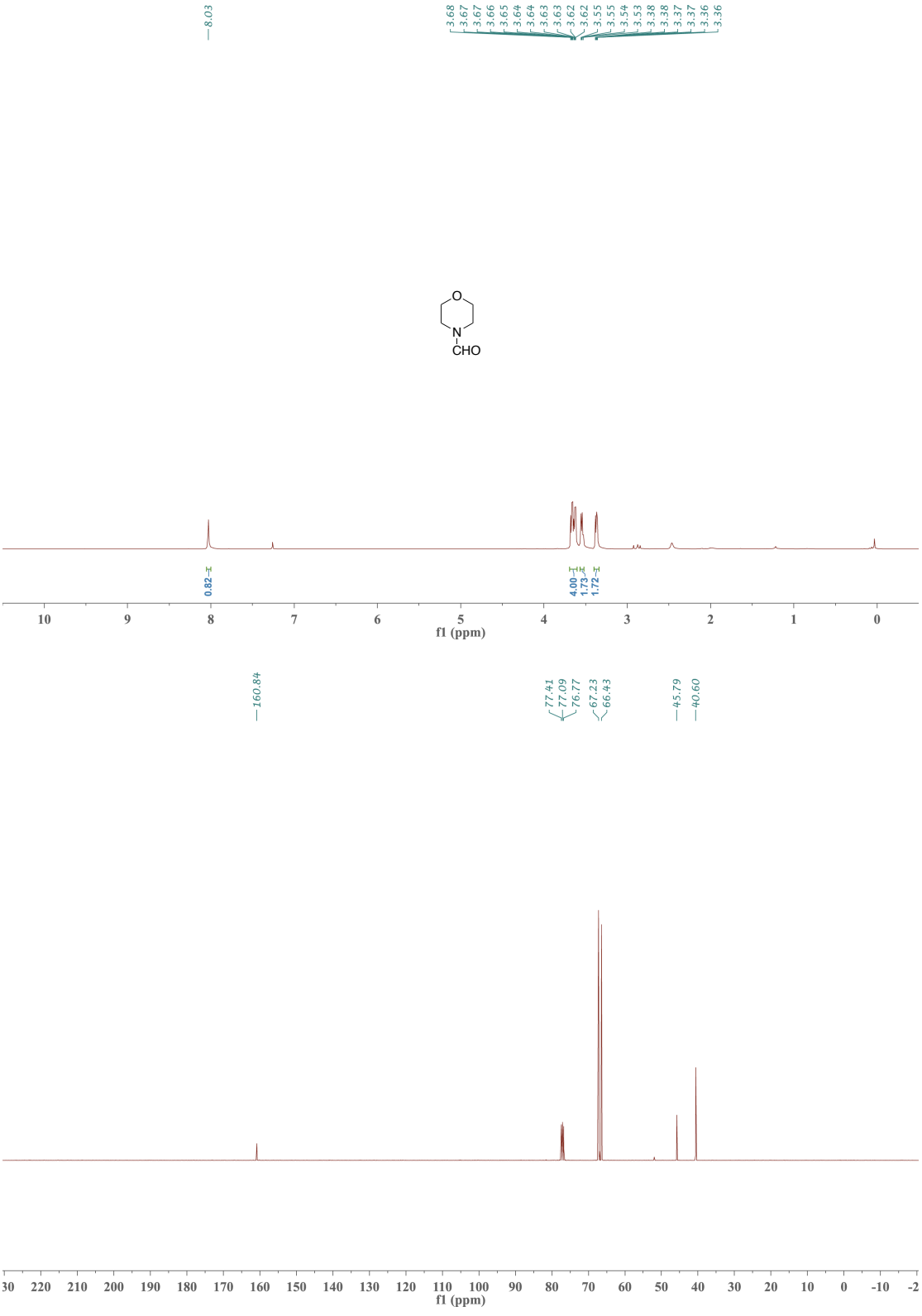


Figure S45. ^{1}H and ^{13}C NMR Spectra of *tert*-Butyl 4-Formylpiperazine-1-carboxylate (**2n**)

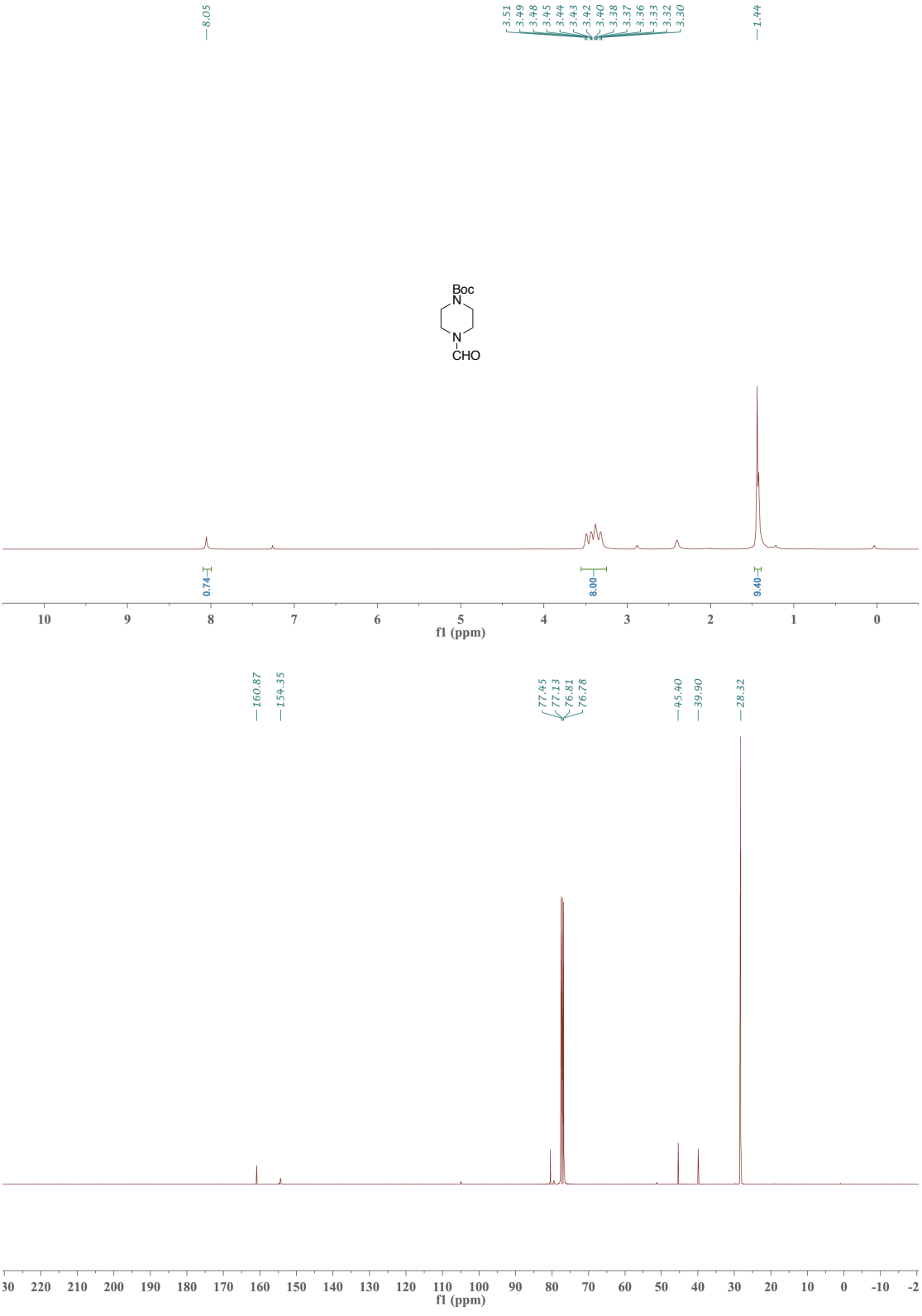


Figure S46. ^{1}H and ^{13}C NMR Spectra of 4-((Trimethylsilyl)methyl)piperazine-1-carbaldehyde (**2o$_a$**)

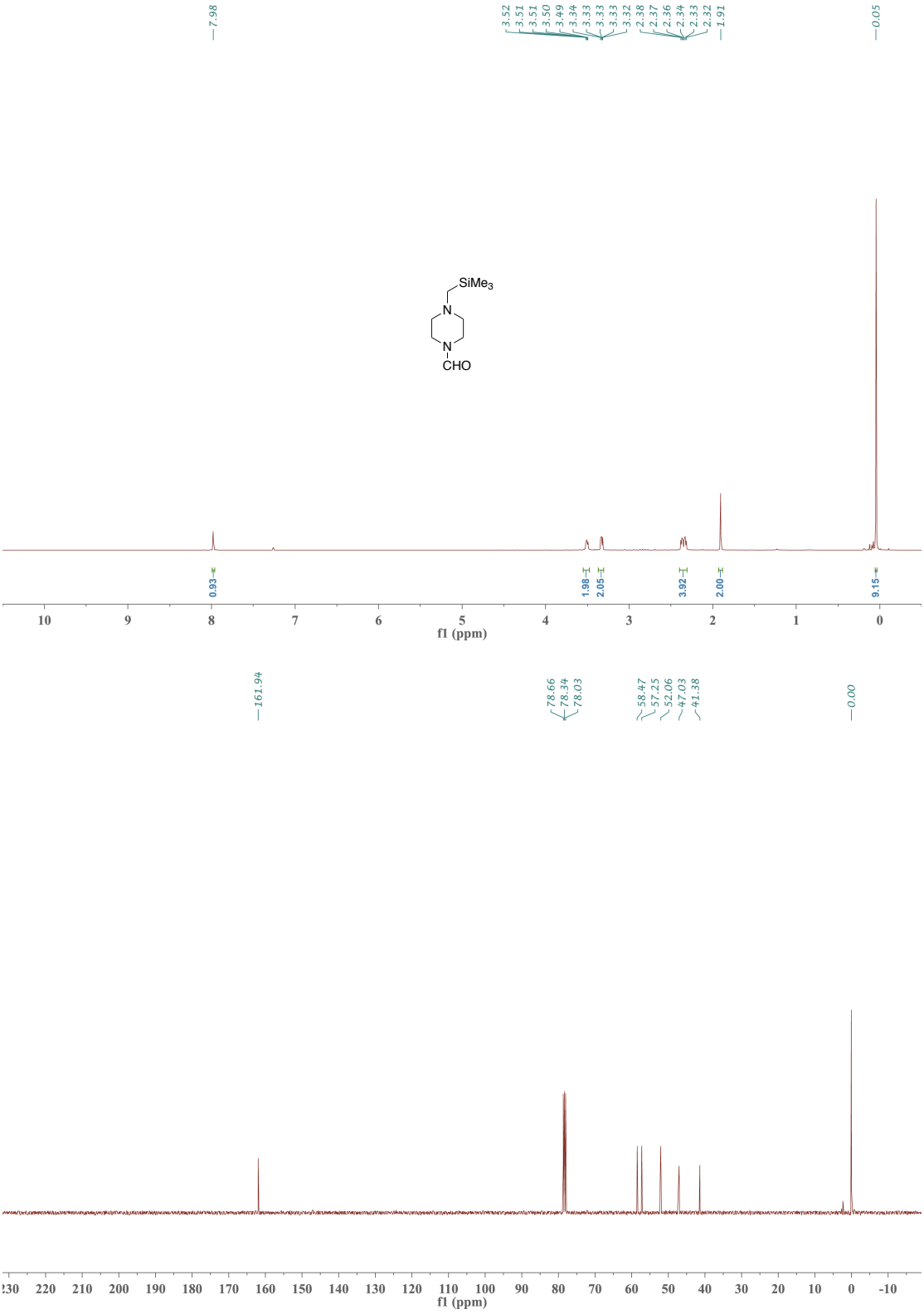


Figure S47. ^{1}H and ^{13}C NMR Spectra of Piperazine-1,4-dicarbaldehyde (**2o$_b$**)

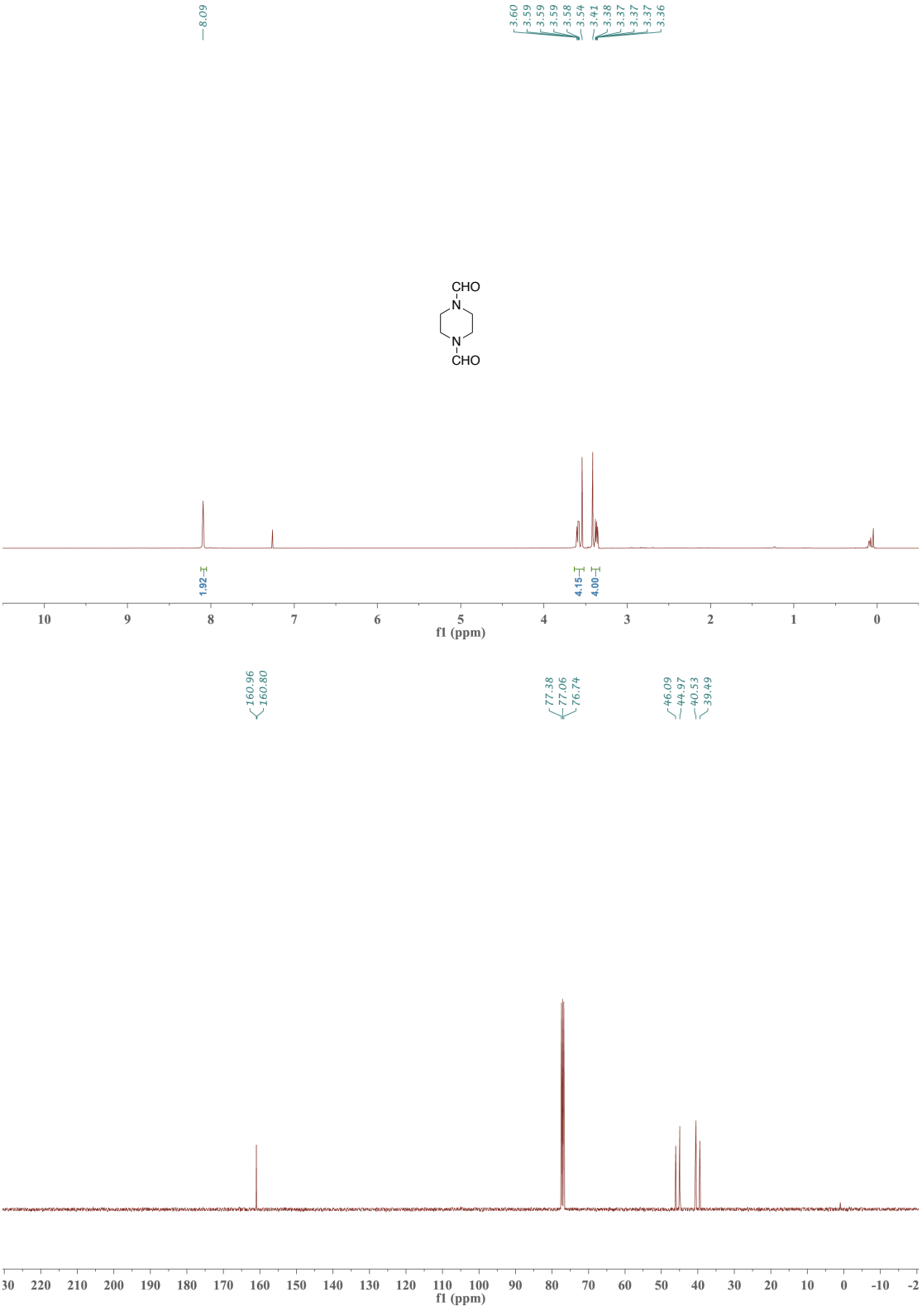


Figure S48. ^{1}H and ^{13}C NMR Spectra of 4-(4-Methoxyphenyl)piperazine-1-carbaldehyde (**2p**)

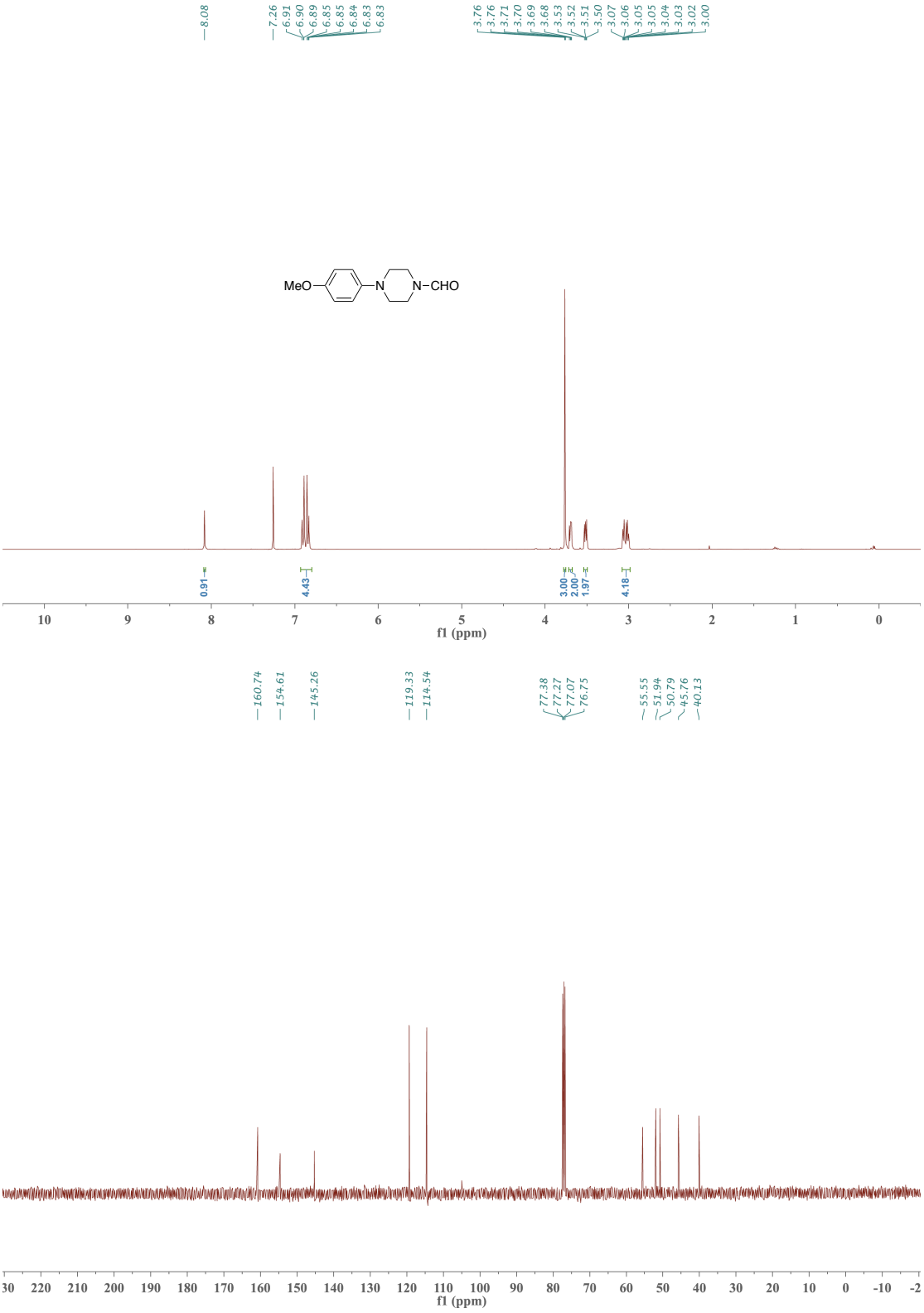


Figure S49. ^{1}H and ^{13}C NMR Spectra of 4-(4-Chlorophenyl)piperazine-1-carbaldehyde (**2q**)

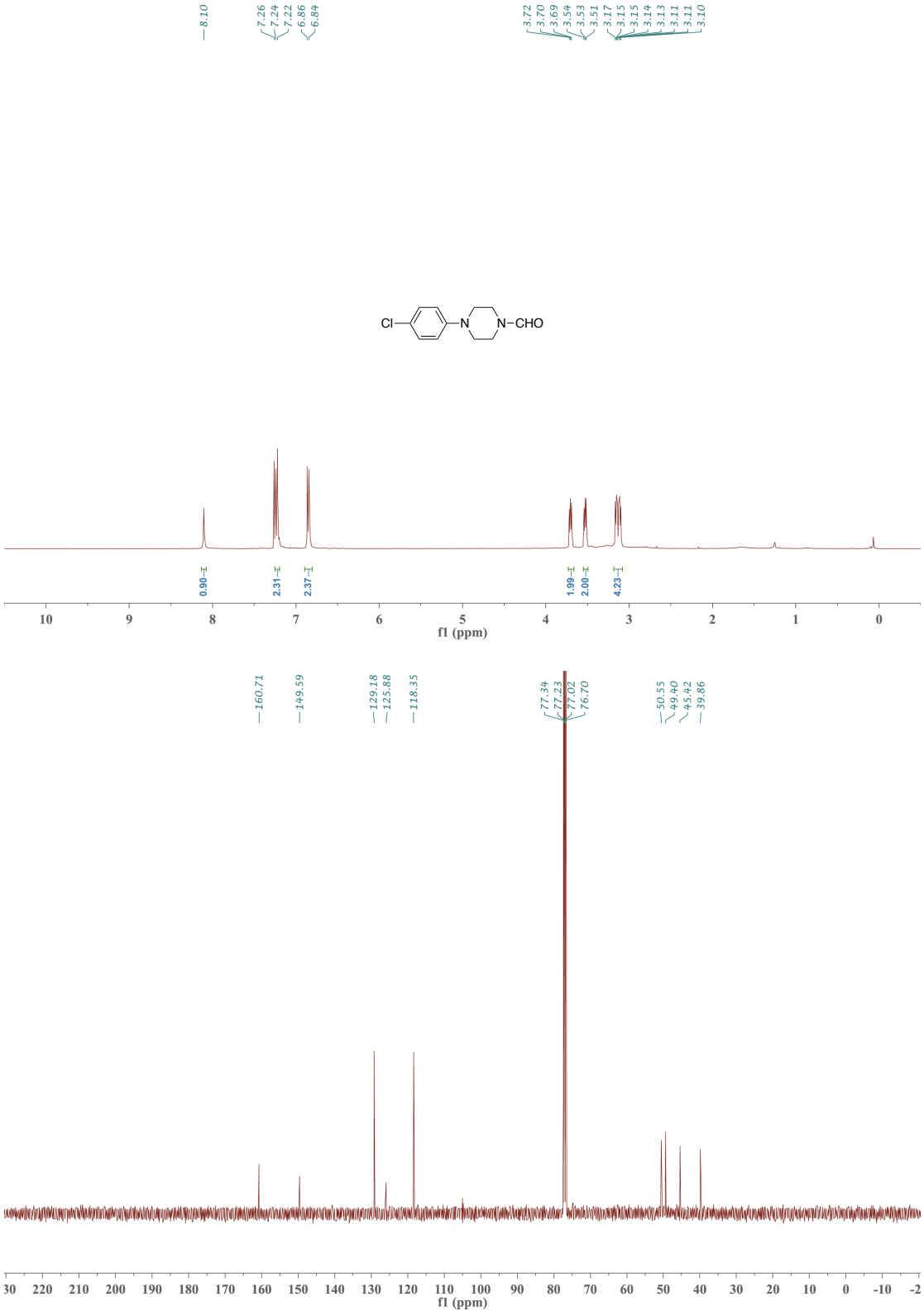


Figure S50. ^{1}H and ^{13}C NMR Spectra of 4-(4-Fluorophenyl)piperazine-1-carbaldehyde (**2r**)

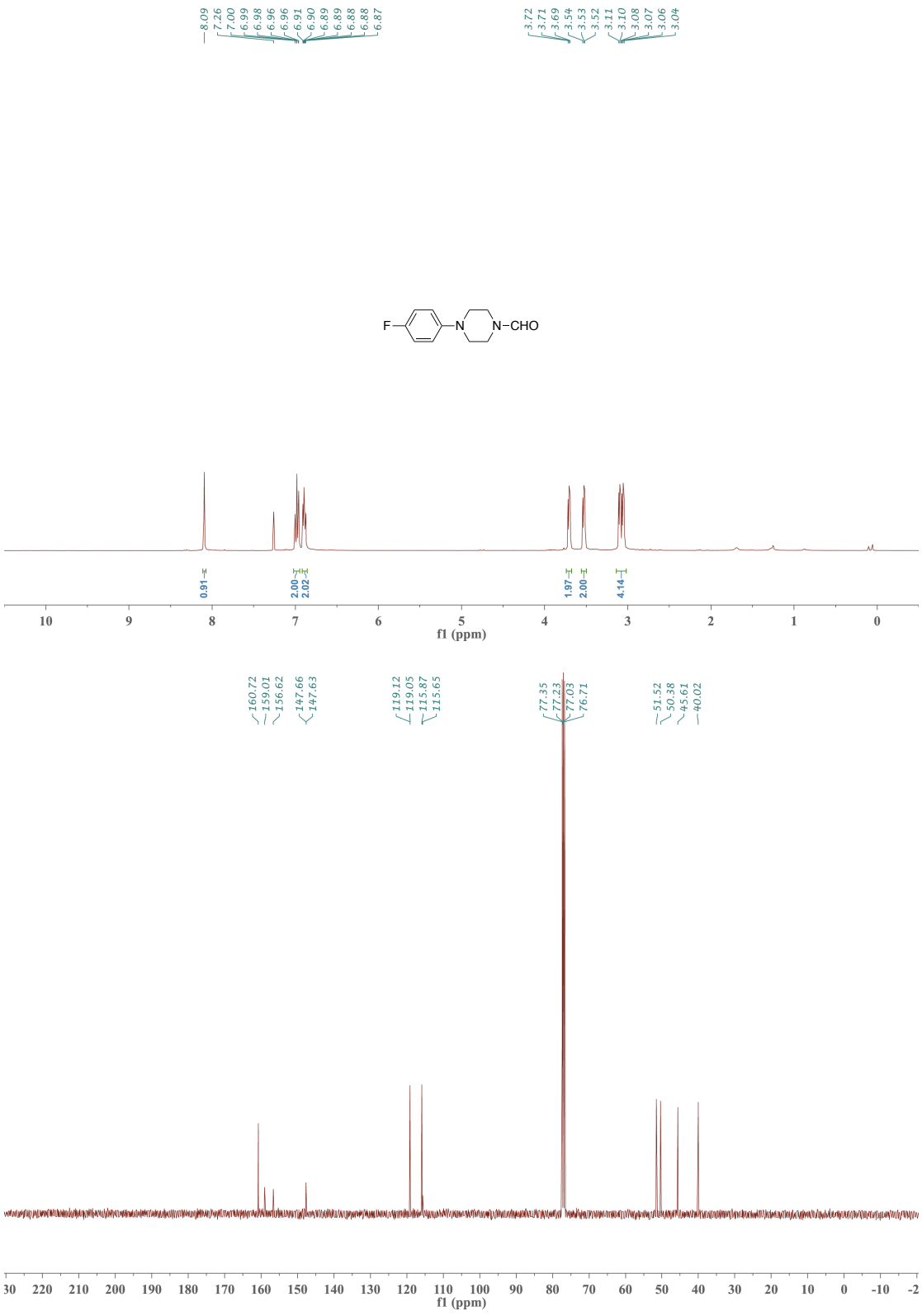


Figure S51. ^{1}H and ^{13}C NMR Spectra of 4-(3-Chlorophenyl)piperazine-1-carbaldehyde (**2s**)

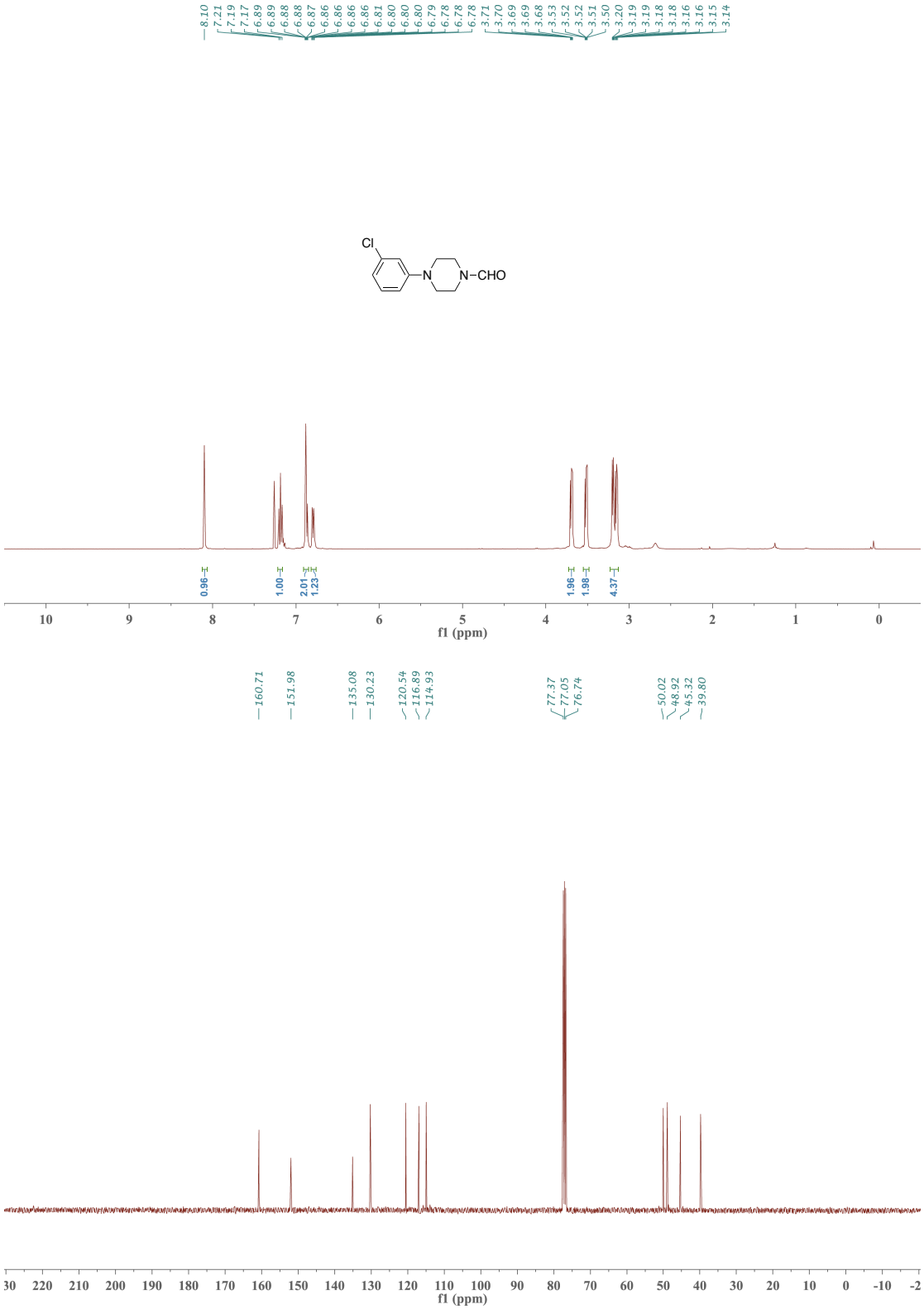


Figure S52. ^{1}H and ^{13}C NMR Spectra of 4-(2,3-Dichlorophenyl)piperazine-1-carbaldehyde (**2t**)

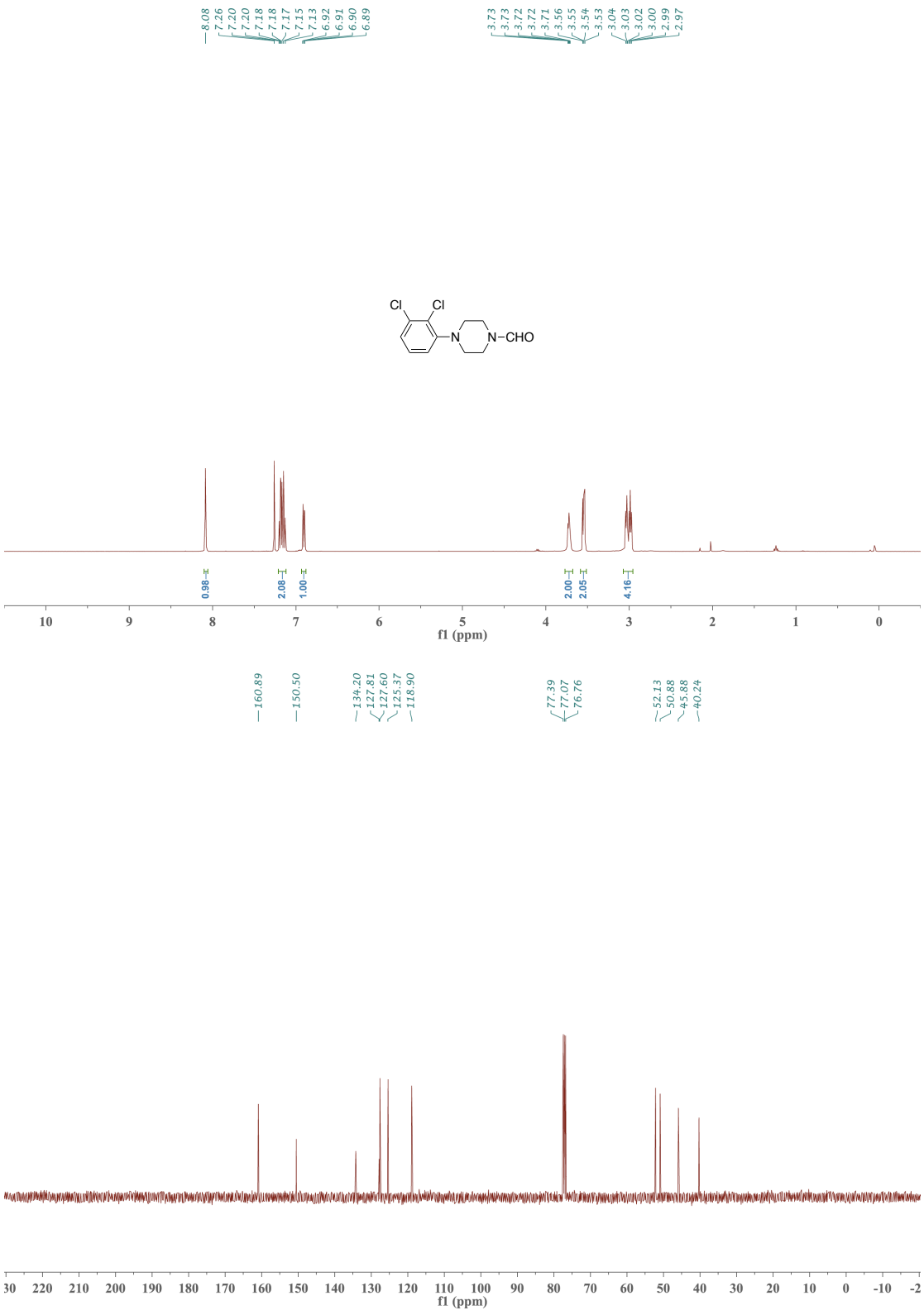


Figure S53. ^{1}H and ^{13}C NMR Spectra of 4-Bensylpiperazine-1-carbaldehyde (**2u**)

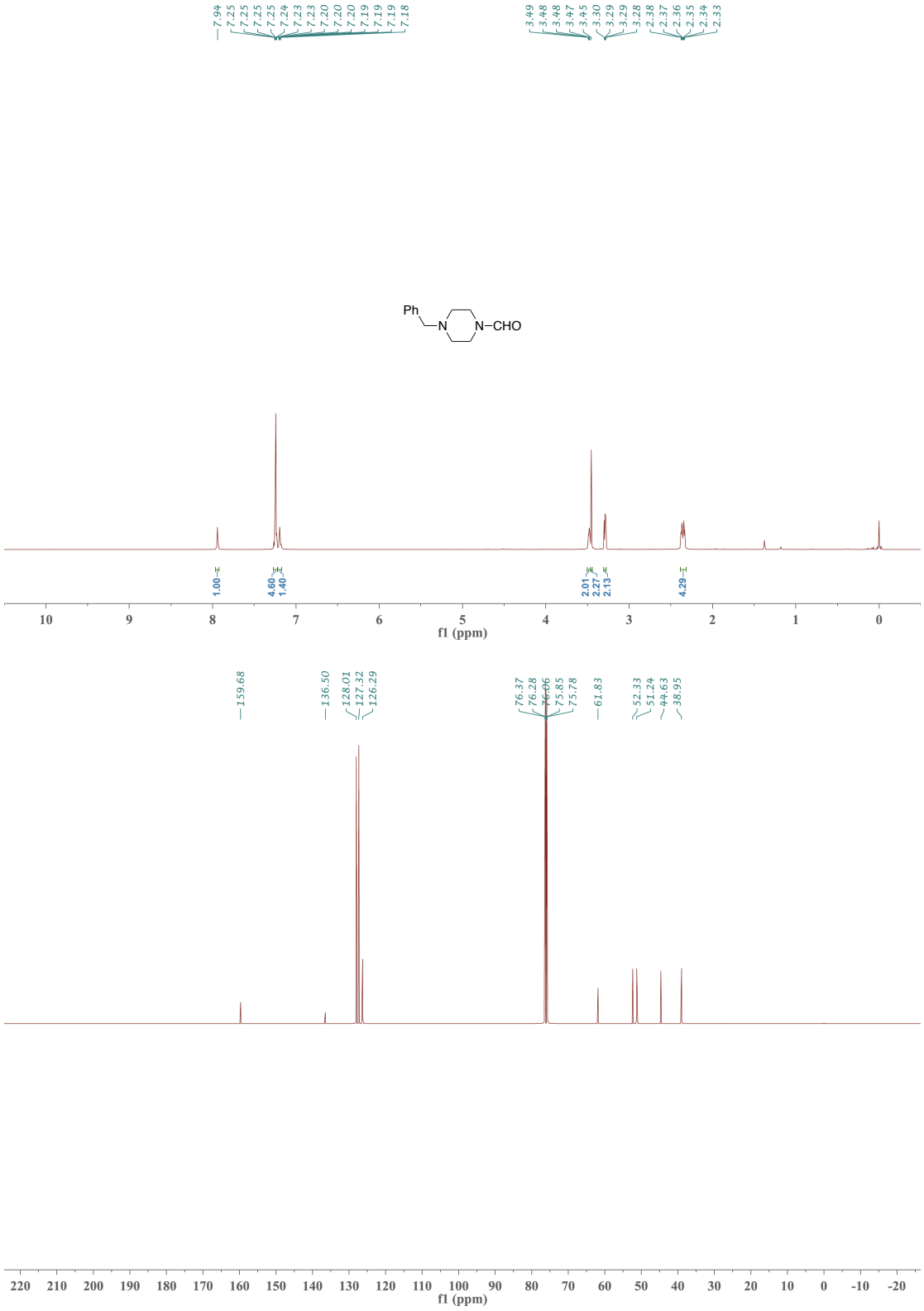


Figure S54. ^{1}H and ^{13}C NMR Spectra of Ethyl Formyl-*L*-prolinate (**2v**)

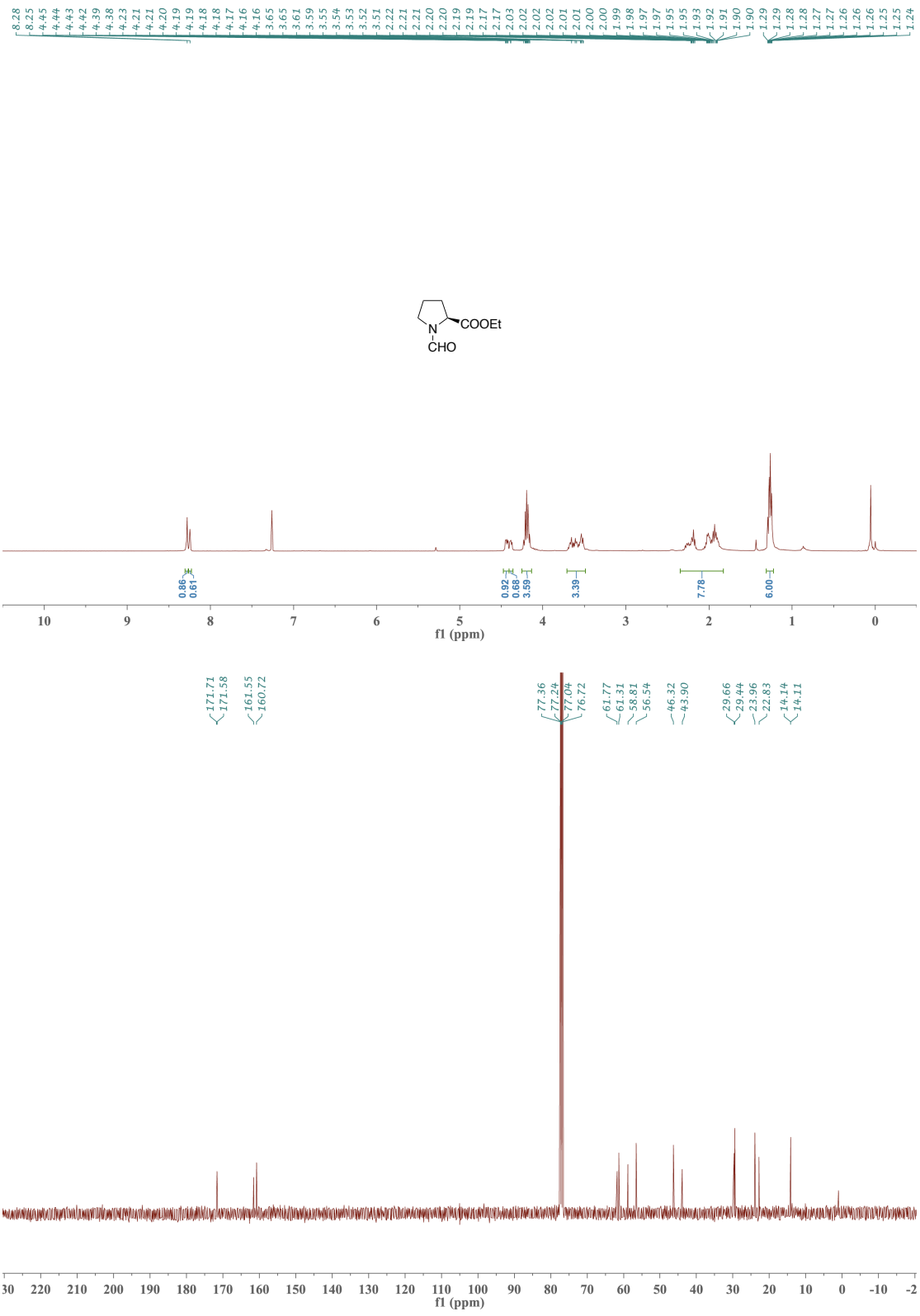


Figure S55. ^{1}H and ^{13}C NMR Spectra of (3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine-1-carbaldehyde (**2w**)

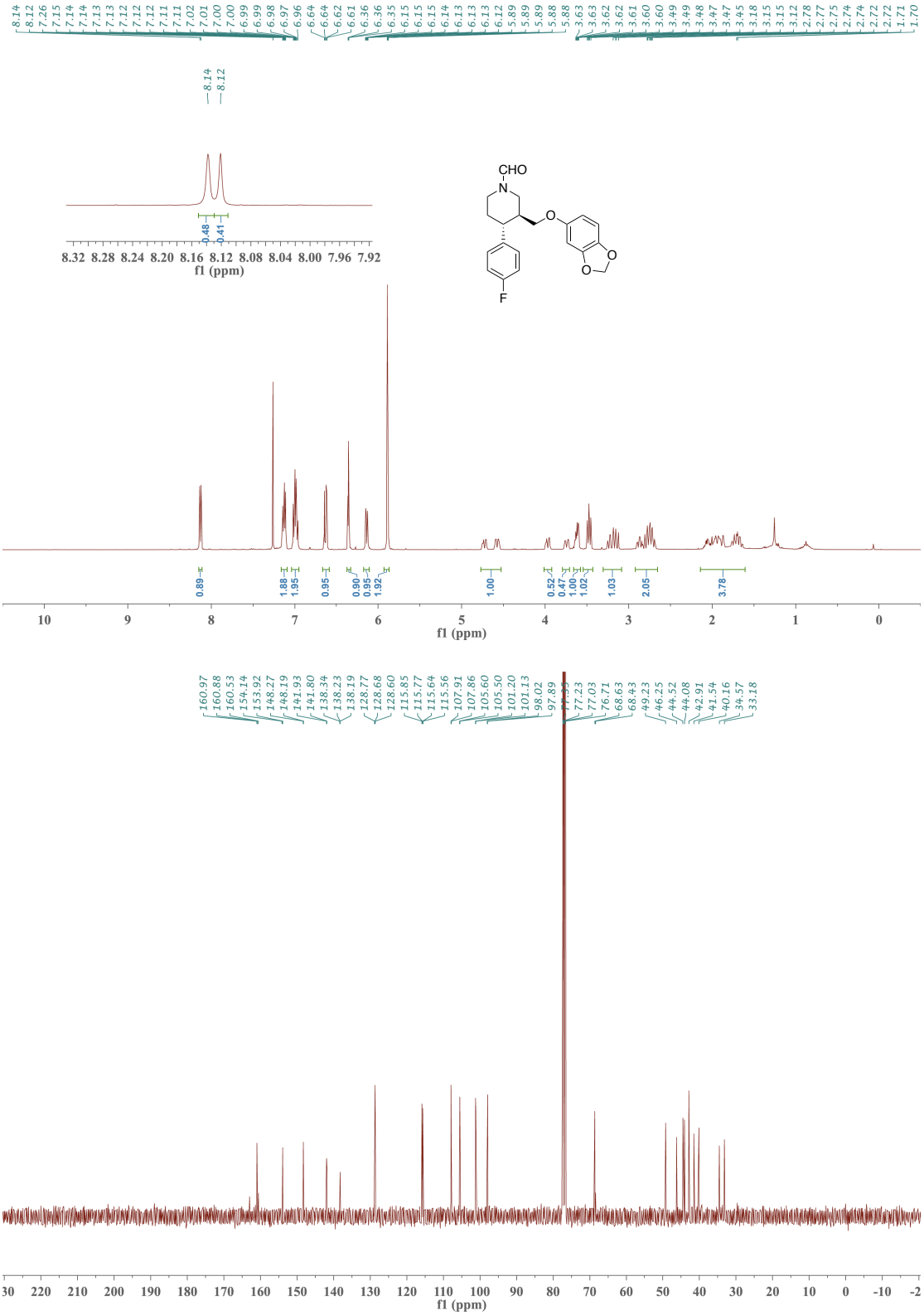


Figure S56. ^{1}H and ^{13}C NMR Spectra of *N*-(3-(10,11-Dihydro-5*H*-dibenso[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methylformamide (**2x**)

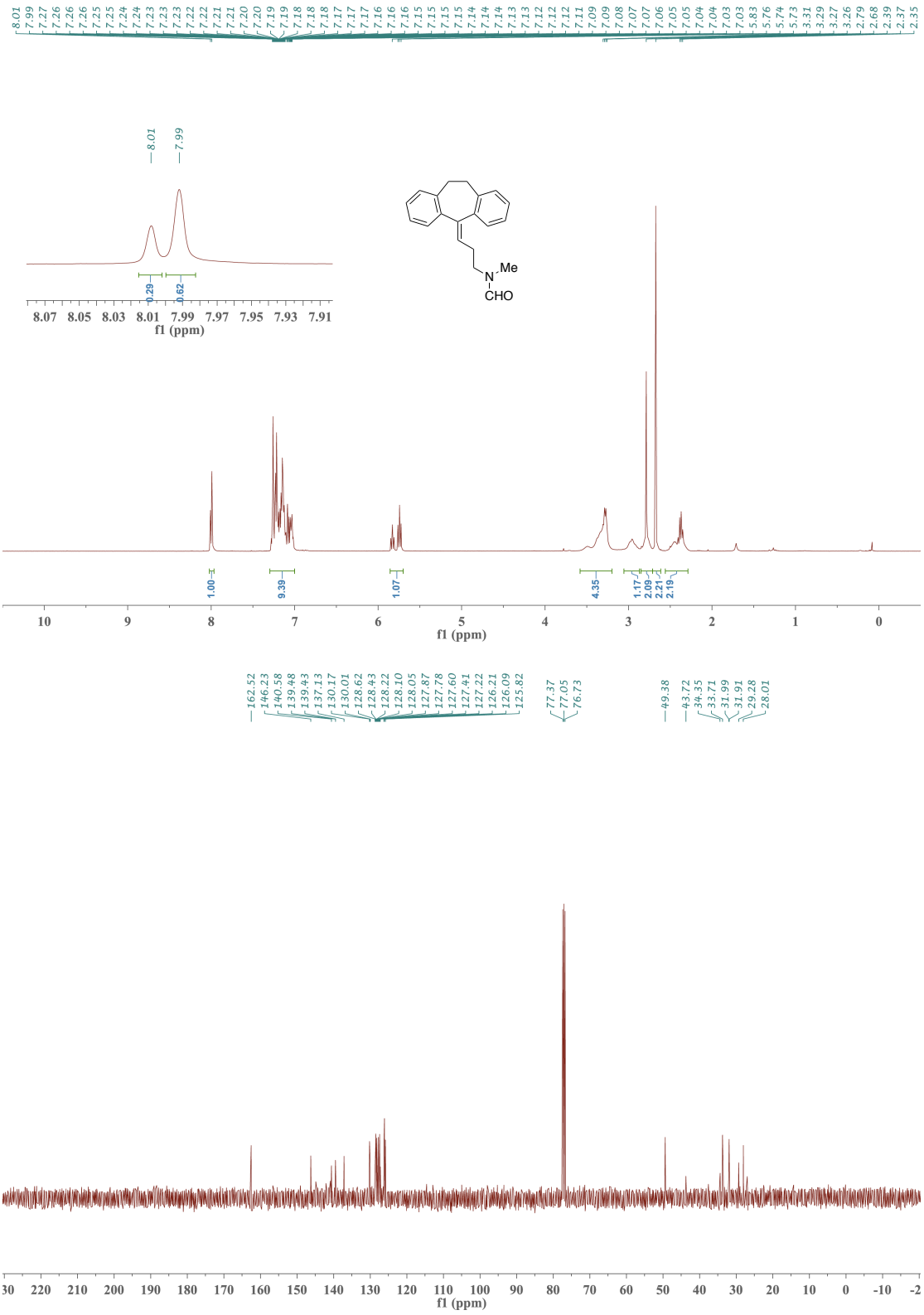


Figure S57. ^{1}H and ^{13}C NMR Spectra of *N*-Methyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)formamide (**2y**)

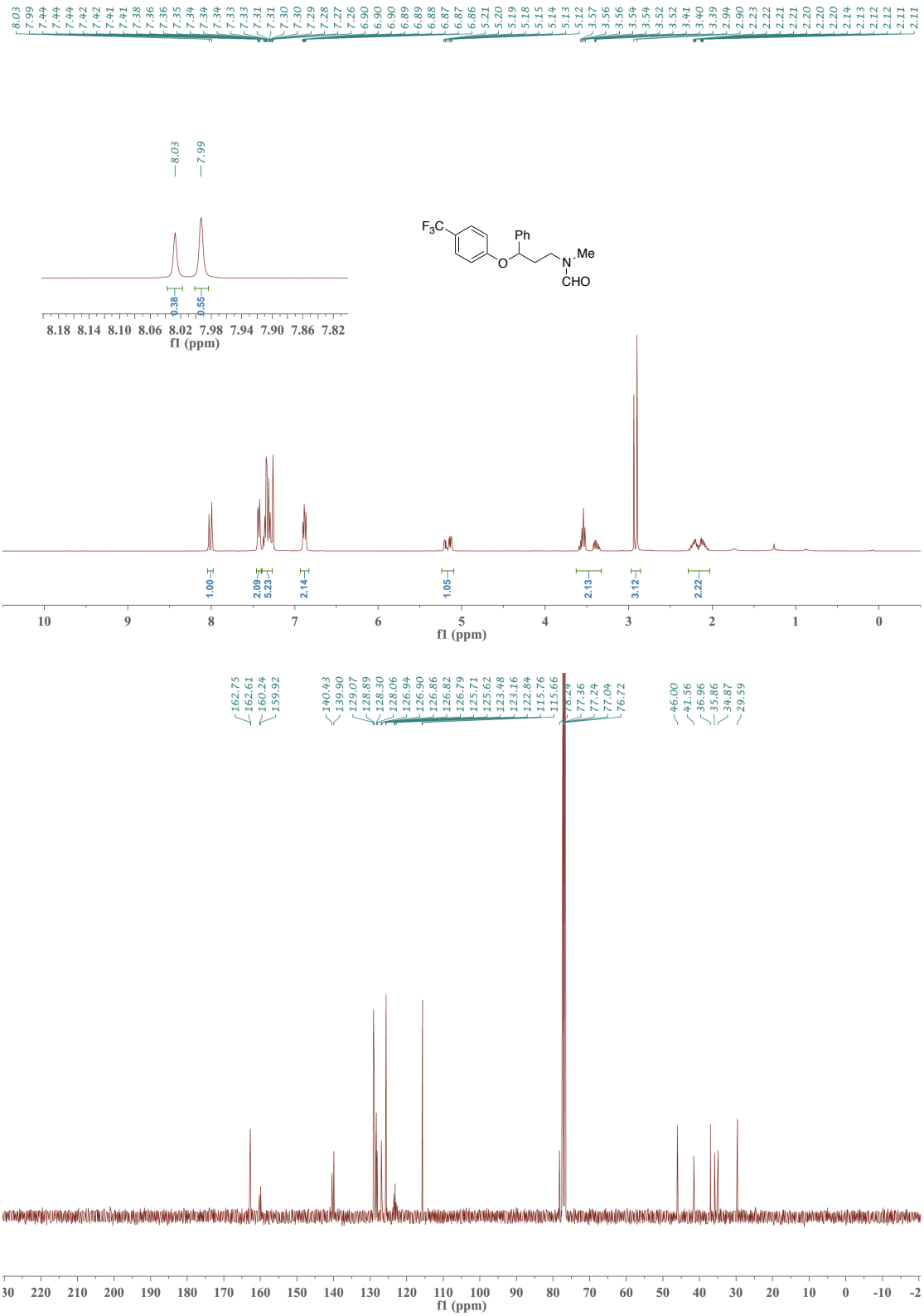


Figure S58. ^{1}H and ^{13}C NMR Spectra of (*S*)-*N*-Methyl-*N*-(3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)formamide (**2z**)

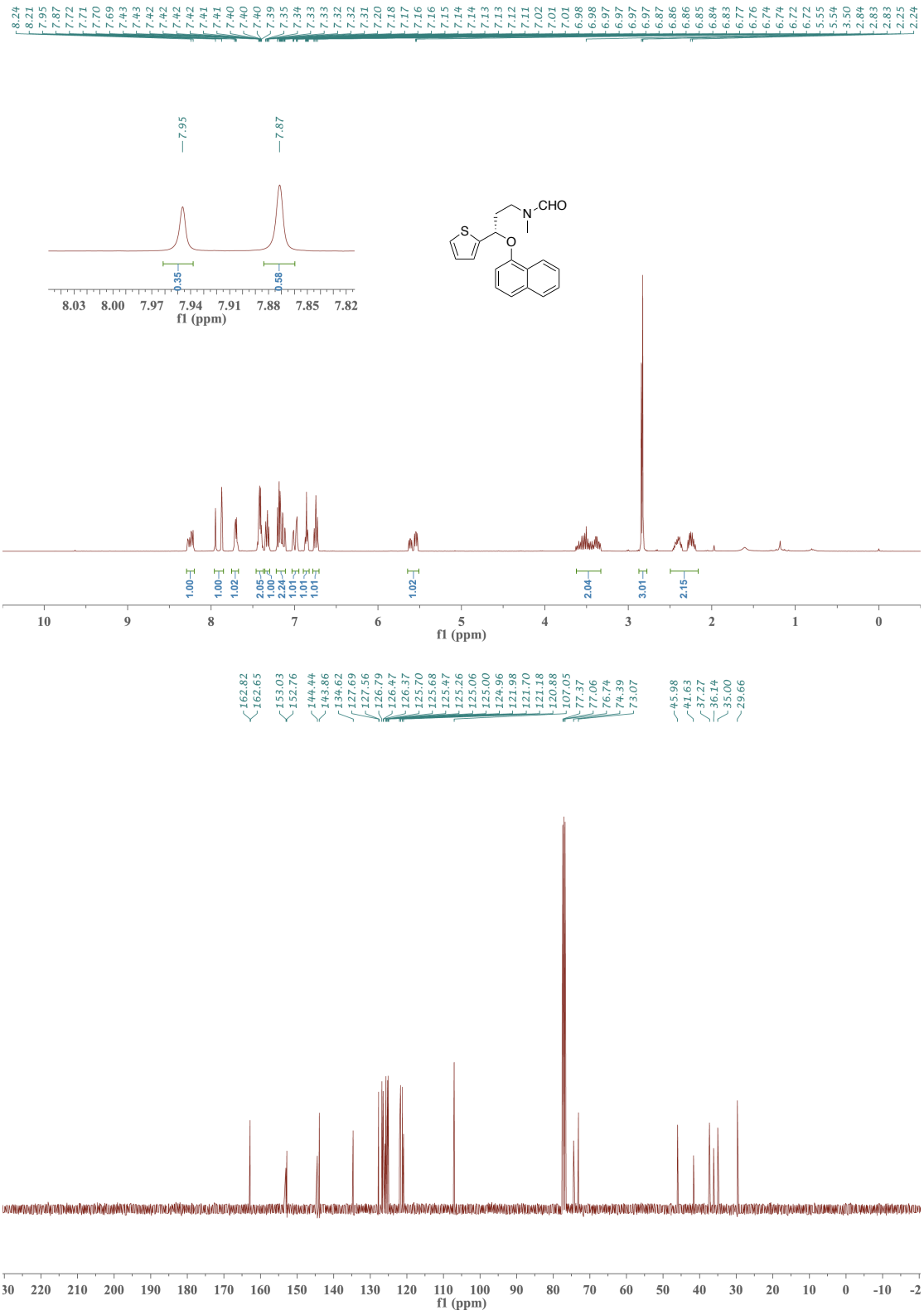


Figure S59. ^{1}H and ^{13}C NMR Spectra of *N*-((1*S*,4*S*)-4-(3,4-Dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methylformamide (**2α**)

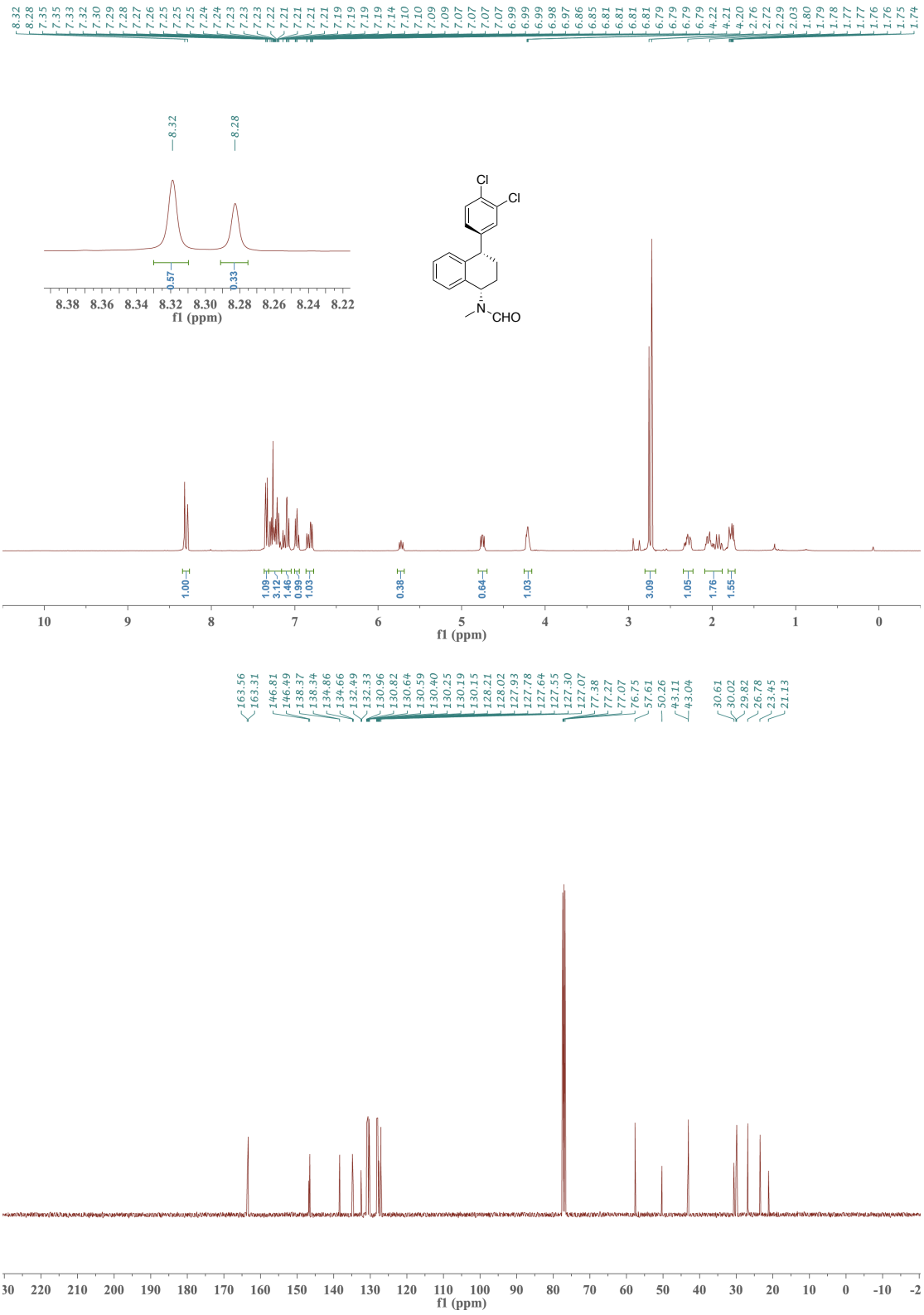
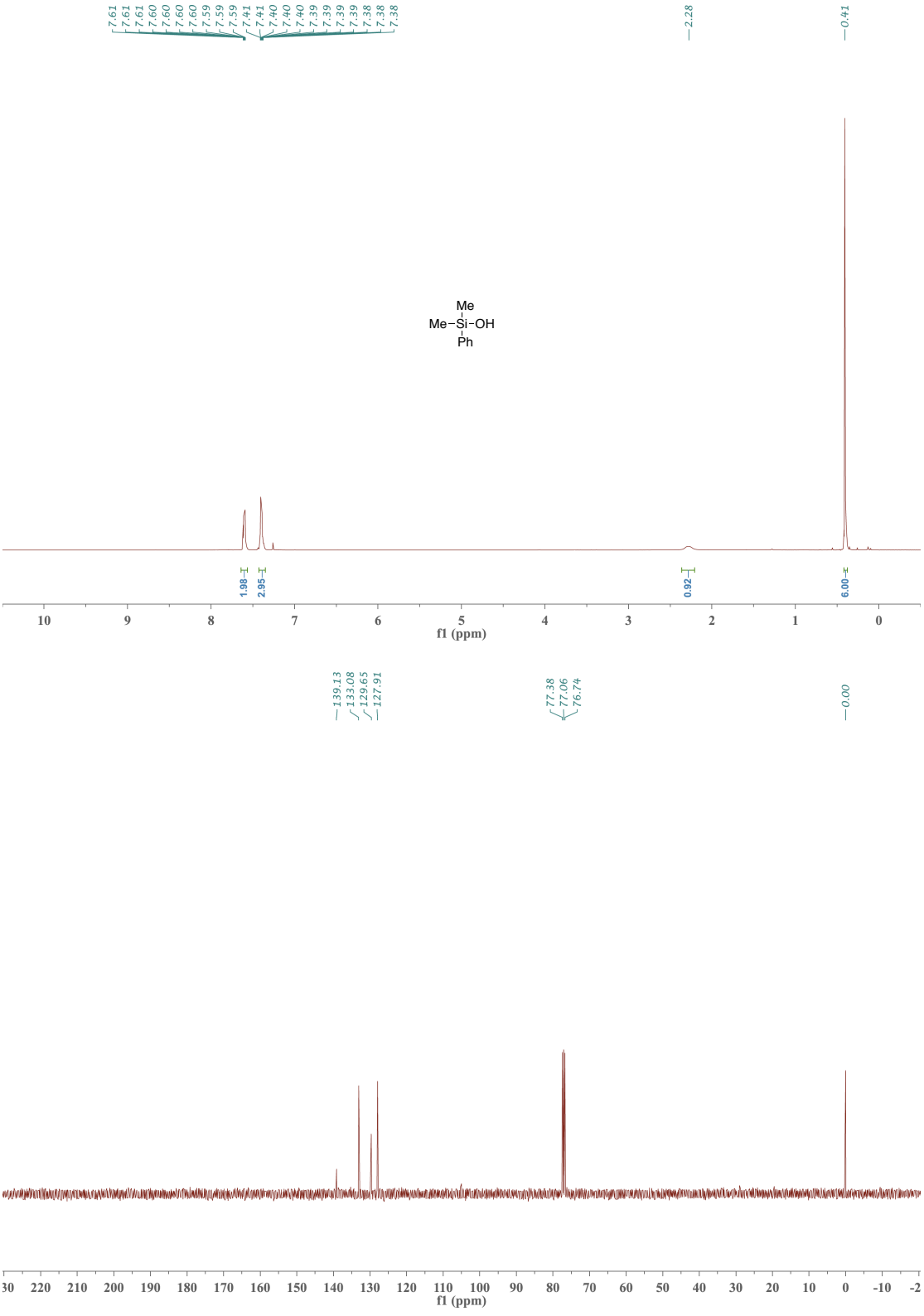


Figure S60. ^{1}H and ^{13}C NMR Spectra of Dimethyl(phenyl)silanol (***3β***)



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