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Supporting Information

(118 pages including the cover page)

Hydrosilylative Reduction of Primary Amides to Primary Amines Catalyzed by a Terminal [Ni-OH] Complex

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Contents

1. Experimental Section

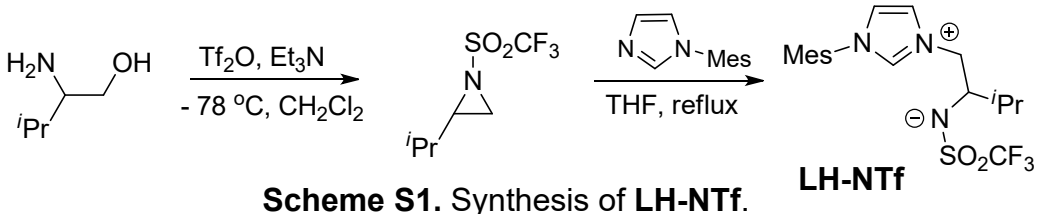
1.1. General procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk–vessel and vacuum line techniques. NMR spectra were obtained on JEOL JNM–LA 400MHz and 500MHz spectrometer. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. The chemical shift is given as dimensionless δ values and is frequency referenced relative to TMS for ^{1}H and ^{13}C NMR spectroscopy. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with petroleum ether, and dried in vacuum for at least 48 h prior to elemental analyses. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Vertex 70 Bruker spectrophotometer on nujol mull. ESI–MS were recorded on a Waters Micromass Quattro Micro triple–quadrupole mass spectrometer. The GC-MS experiments were performed by using an Agilent 7890 A GC and 5975C MS system.

Materials

Solvents were distilled under nitrogen and deoxygenated prior to use. The nickel salts ($Ni(acac)_2$, $Ni(COD)_2$, $Ni(Cp)_2$), $NiCl_2$, $Ni(OAc)_2.4H_2O$, $NiCl_2(dme)$, primary amides and chemicals were purchased from Sigma-Aldrich. The $LiAlD_4$ was purchased from BOC Sciences USA. The ligand **LH-NTf**[1], primary amides (in Table 1: **5**, **10**, **11**, **12**, **13**, **22**)[2], secondary and tertiary amides[3] and $PhSiD_3$[4] were prepared following the literature procedures. NMR spectra for synthesized compounds are consistent with literature reports.

1.2. Synthesis and characterization



LH-NTf

Scheme S1. Synthesis of **LH-NTf**.

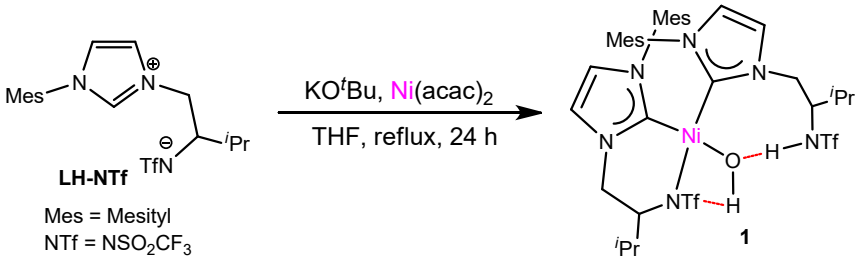
Synthesis of LH-NTf

^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ 8.89 (s, 1H, Im), 7.53 (s, 1H, Ph), 7.11 (s, 1H, Ph), 6.97 (s, 2H, Im), 4.36 (dd, *J* = 12.0 Hz, 1H, CH_2), 4.01 (dd, *J* = 12.0 Hz, 1H, CH_2), 3.35 (br t, 1H, CH), 2.33 (s, 3H, CH_3), 2.14 (s, 3H, CH_3) 2.01 (s, 3H, CH_3), 1.67 (m, 1H, CH), 0.95 (d, 6H, ^{i}pr). ^{13}C NMR (100 MHz, $CDCl_3$, 292 K): δ 141.2, 136.8, 135.3, 134.5, 130.9, 129.9, 129.6, 124.1, 122.9, 61.5, 55.5, 32.9, 21.2, 19.6, 18.7, 17.9, 17.5. (The CF_3 signal was not observed due to the low intensity). ^{19}F NMR (470 MHz, $CDCl_3$, 292 K): –76.8 ($NSO_2C\mathit{F}_3$). ESI–MS, *m/z*: 404.1623, (z=1), $[M+H]^+$.

Synthesis of 1

A suspension of 0.100 g (0.25 mmol) of **LH**, and 0.034 g (0.3 mmol) of KO^{t}Bu in 15 mL of THF was stirred for 1h at -78°C. $Ni(acac)_2$ 0.033 g (0.125 mmol) was added to the cooled reaction mixture and was allowed to attain room temperature then yellow colored solution was refluxed for 24 h. The volatiles were evaporated and crude solid was redissolved in 15 mL dichloromethane, and the yellow mixture was filtered through a small pad of celite. The yellow colored filtrate was evaporated to dryness and dissolved in minimum amount of dichloromethane. 15 mL of petroleum ether was added with stirring to induce precipitation. The obtained yellow solid was washed with petroleum ether and dried under vacuum. X–ray quality crystals were grown by layering petroleum ether over a saturated dichloromethane solution of **1** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 0.090 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ 7.26 (s, 1H, Ph), 7.25 (s, 1H, Ph), 7.09 (d, *J* = 1.5 Hz, 1H, Im), 7.04 (d, *J* = 1.4 Hz, 1H, Im), 7.00 (s,1H, Ph), 6.94 (s, 1H, Ph), 6.88 (d, *J* = 1.4 Hz, 1H, Im), 6.65 (d, *J* = 1.4 Hz, 1H, Im), 4.94 (t, *J* = 10.6 Hz, 1H CH_2), 3.78 (s, 1H, CH), 3.76 (d, *J* = 4.7 Hz, 1H, CH_2), 3.48 (td, *J* = 3.2 Hz, 9.9 Hz, 1H, CH), 3.03 (m, 1H, CH), 2.98 (dd, *J* = 3.5 Hz, 10.9 Hz, 1H, CH), 2.45 (d, *J* = 17.4 Hz, 6H, $^{ipr}CH_3$), 2.33 (s, 1H, CH), 2.25 (s, 3H, CH_3), 2.09 (s, 3H, CH_3),

1.40 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.06 (d, *J* = 5.6 Hz, 6H, $^{ipr}CH_3$), 1.03 (s, 1H, CH), 0.87 (d, *J* = 5.6 Hz, 6H, $^{ipr}CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 292 K): δ 157.9. 155.3, 140.6, 140.4, 140.1, 139.4, 134.9, 134.8, 134.3, 134.1, 133.9, 131.4, 130.5, 129.0, 128.5, 125.9, 124.9, 122.0, 121.5, 58.7, 58.3, 49.4, 48.8, 31.9, 29.8, 21.1, 20.9, 19.5, 18.9, 18.8, 18.2, 18.1, 14.9, 14.5, 14.1. (The CF_3 signal was not observed due to the low intensity). ^{19}F NMR (470 MHz, $CDCl_3$, 292 K): –76.4 ($NHSO_2CF_3$), -77.5 (NSO_2CF_3). Anal Calcd. for $Ni_1S_2F_6C_{36}N_6O_5H_{48}$: C, 49.04; H, 5.49; N, 9.53. Found: C, 49.31; H, 5.53; N, 9.51. ESI–MS, *m/z*: 863.2352, (z=1), [**1**−OH]$^+$. FT-IR (Nujol, cm^{-1}): $\nu_{(O-H)}$ = 3636, $\nu_{(N-H)}$ = 3096, 3124, 3155.

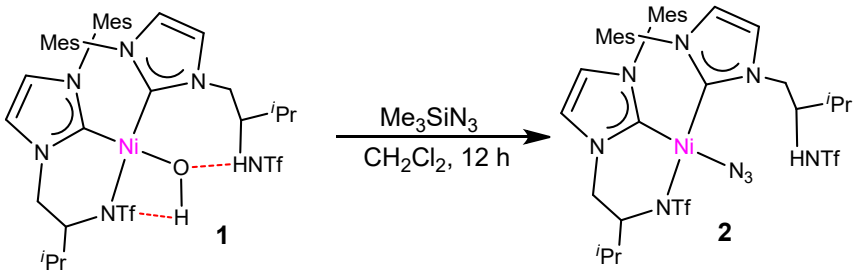


Scheme S2. Synthesis of **1**.

Synthesis of 2

0.080 g (0.09 mmol) **1** was dissolved in 10 mL dichloromethane and 0.118 mL (0.9 mmol) $TMSN_3$ was added and stirred for 12 h. The resulting pale yellow solution was passed through the pad of celite and the filtrate was concentrated under reduced pressure and petroleum ether was added to induce precipitation. The solid obtained was washed with 10 mL of petroleum ether and dried under vacuum. X–ray quality crystals were grown by layering petroleum ether over a saturated dichloromethane solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 0.070 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ 9.52 (br, 1H, $NHSO_2CF_3$), 7.21 – 7.18 (d, *J* = 9.1 Hz, 1H, Im), 7.05 – 6.98 (4H, Ph), 6.88 – 6.85 (d, *J* = 16.0 Hz, 2H, Im), 6.58 (s, 1H, Im), 5.51 (t, *J* = 12.4 Hz, 1H, CH_2), 4.26 (t, *J* = 12.4 Hz, 1H, CH_2), 3.90 (d, *J* = 12.4 Hz, 1H, CH), 3.69 (br d, *J* = 9.6 Hz, 2H, CH), 3.47 (br s, 1H, CH), 3.11 (br d, *J* = 11.0 Hz, 1H, CH), 2.63 (d, *J* = 13.3, 1H, CH), 2.45 (s, 6H, $2CH_3$), 2.37 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 0.86 (d, *J* = 5.04 Hz, 12H, $^{ipr}CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 292 K): δ 165.6. 160.3, 140.3, 140.2, 140.1, 140.0, 134.9, 134.8, 134.7, 133.9,

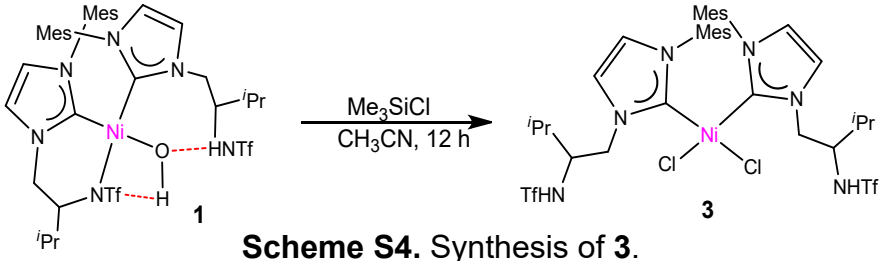
131.3, 130.7, 128.6, 128.5, 126.2, 124.3, 117.8, 59.3, 58.5, 49.6, 46.8, 31.7, 31.5, 22.7, 21.1, 20.3, 19.2, 18.9, 18.5, 18.2, 17.1, 15.1, 14.2. (The CF_3 signal was not observed due to the low intensity). ^{19}F NMR (470 MHz, $CDCl_3$, 292 K): –75.5 ($NHSO_2CF_3$), -77.9 (NSO_2CF_3). Anal Calcd. for $Ni_1S_2F_6N_9O_4C_{36}H_{47}$: C, 47.72; H, 5.23; N, 13.92 Found: C, 47.74; H, 5.27; N, 13.95. ESI–MS *m/z*: 863.2736, (z=1), [**2**-N_3]$^+$. FT-IR (Nujol, cm^{-1}): $\nu_{(N3)}$ = 2062, $\nu_{(N-H)}$ = 3133.



Scheme S3. Synthesis of **2**.

Synthesis of 3

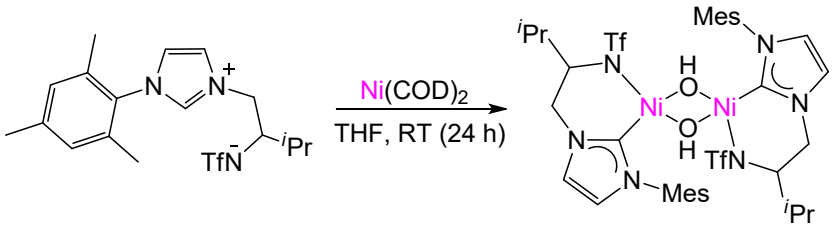
0.080 g (0.09 mmol) **1** was dissolved in 10 mL acetonitrile and 0.114 mL (0.9 mmol) $(CH_3)_3SiCl$ (TMSCl) was added and stirred for 12 h. The resulting pale yellow solution was passed through the pad of celite and the filtrate was concentrated under reduced pressure and petroleum ether was added to induce precipitation. The solid obtained was washed with 10 mL of petroleum ether and dried under vacuum. X–ray quality crystals were grown by layering petroleum ether over a saturated dichloromethane solution of **3** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 0.059 g (70%).^{1}H NMR (400 MHz, CD_3CN, 292 K): δ 8.31 (br, 2H, $NHSO_2CF_3$), 7.35 – 7.16 (br, m, 8H Ph, Im), 6.94 (s, 2H), 5.40 (t, *J* = 10.9 Hz, 2H, CH), 3.89 (br, s, 2H, CH), 3.12 (d, *J* = 12.8 Hz, 2H, CH_2), 2.44 – 2.40 (br d, 12H, $2^{ipr}CH_3$), 1.41 (s, 6H, $2CH_3$), 0.97 (br, s, 12H, $4CH_3$). ^{13}C NMR (100 MHz, CD_3CN, 292 K): δ 156.3,140.2, 138.5, 135.2, 135.1, 13.7, 130.4, 126.9, 123.0, 58.4, 46.5, 32.2, 21..0, 19.3, 18.2, 18.1, 15.6. (The CF_3 signal was not observed due to the low intensity).^{19}F NMR (470 MHz, CD_3CN, 292 K): –78.59 ($NHSO_2CF_3$). Anal Calcd. for $Ni_1S_2F_6N_6O_4C_{36}H_{48}Cl_2$: C, 46.24; H, 5.18; N, 8.99. Found: C, 46.19; H, 5 22; N, 9.04. ESI–MS, *m/z*: 899.2114, (z=1), [**3**+Cl]$^+$.



Scheme S4. Synthesis of **3**.

Synthesis of 4

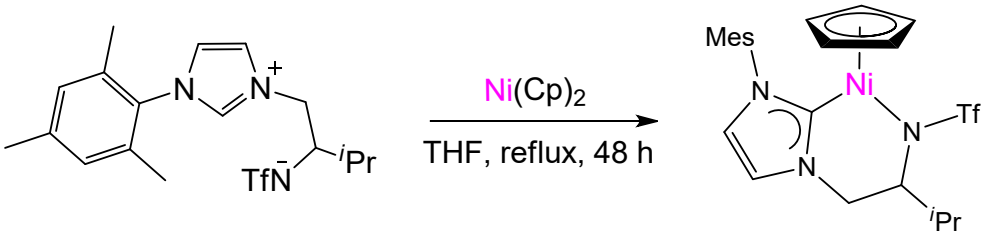
A suspension of 0.100 g (0.25 mmol) of **LH-NTf**, and 0.069 g (0.25 mmol) of $Ni(COD)_2$ in 15 mL of THF was stirred for 1h at -78°C. The mixture was allowed to attain room temperature and then stirred for 24h. Slowly the color of the solution changed to dark red. The red mixture was filtered through a small pad of celite. The filtrate was evaporated to dryness and dissolved in minimum amount of dichloromethane. 10 mL of petroleum ether was added with stirring to induce precipitation. The obtained red solid was washed with petroleum ether and dried under vacuum. Red colored crystals suitable for X-ray diffraction were grown by slow diffusion of petroleum ether into a saturated dichloromethane solution of **4**. Yield: 0.161 g (68%). ^{1}H NMR (400 MHz, CD_3CN, 292 K): δ 7.59 (br, s, 1H, Im), 7.31 (br, s, 1H, Im), 7.05 (br, s, 4H, Ph), 6.63 (br, s, 2H, Im), 4.41 (br, s, 1H), 4.25 (br, s, 2H), 3.95 (br, s, 1H), 3.71 (br, s, 1H), 3.34 (br, s, 2H), 2.55 (s, 1H), 2.44 - 2.01 (m, 1H, $6CH_3$), 1.25 (br, d, *J* = 21.9 Hz, 6H, $2CH_3$), 0.97 (s, 6H, $2CH_3$), -6.13 (s, OH). ^{13}C NMR (100 MHz, CD_3CN, 292 K): δ 162.3, 136.5, 129.8, 129.4, 129.2, 124.5, 124.2, 124.1. 122.9, 61.1, 54.6, 32.7, 20.2, 18.5, 17.8, 16.9, 16.6. (The CF_3 signal was not observed due to the low intensity). ^{19}F NMR (470 MHz, CD_3CN, 292 K): –77.49 (NSO_2CF_3). Anal Calcd. for $Ni_2S_2F_6C_{36}N_6O_6H_{48}$: C, 45.28; H, 5.07; N, 8.80. Found: C, 45.31; H, 5.10; N, 8.83. ESI–MS, *m/z*: = 519.1158, (z=1) for $[LNTfNiOH+CH_3CN+H]^+$.



Scheme S5. Synthesis of **4**.

Synthesis of 5

A suspension of 0.100 g (0.25 mmol) of **LH-NTf**, and 0.048 g (0.25 mmol) of $Ni(CP)_2$ in 15 mL of THF was dissolved. The green colored reaction mixture was refluxed for 48 h. Slowly the color of the solution changed to dark red. The red mixture was filtered through a small pad of celite. The filtrate was evaporated to dryness and dissolved in minimum amount of dichloromethane. 10 mL of petroleum ether was added with stirring to induce precipitation. The obtained red solid was washed with petroleum ether and dried under vacuum. Red colored crystals suitable for X-ray diffraction were grown by slow diffusion of petroleum ether into a saturated dichloromethane solution of **3**. Yield: 0.102 g (78%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 7.09 (s, 1H, Ph), 7.03 (s, 1H, Ph), 6.91 (s, 1H, Im), 6.66 (s, 1H, Im), 4.82 (s, 5H, Cp), 4.36 (d, *J* = 13.2 Hz, 1H, CH_2), 4.13 (d, *J* = 13.1 Hz, 1H, CH_2), 3.44 – 3.40 (q, *J* = 6.3, 1H, CH), 2.95 (br s, 1H, CH), 2.33 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.06 (s, 6H, ^{i}pr). ^{13}C NMR (100 MHz, $CDCl_3$, 292 K): δ 159.3, 139.8, 136.7, 136.3, 134.6, 129.5, 129.0, 124.4, 122.9, 92.4, 59.2, 52.4, 32.8, 21.2, 20.6, 19.2, 18.2, 17.7. (The CF_3 signal was not observed due to the low intensity). ^{19}F NMR (470 MHz, $CDCl_3$, 292 K): –75.06 (NSO_2CF_3). Anal Calcd. for $Ni_1S_1F_3C_{23}N_3O_2H_{28}$: C, 52.56; H, 5.37; N, 7.99. Found: C, 52.52; H, 5.39; N, 8.12. ESI–MS, *m/z*: 526.1287, (z=1), [**5**+H]$^+$.

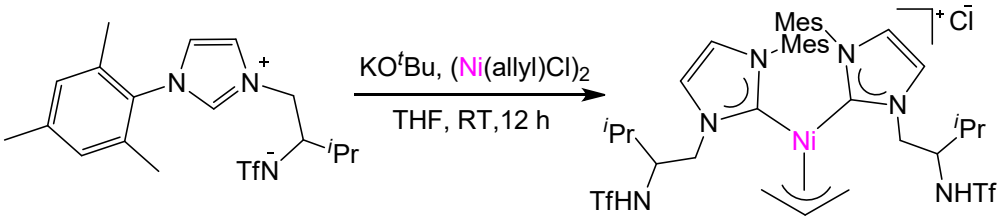


Scheme S6. Synthesis of **5**.

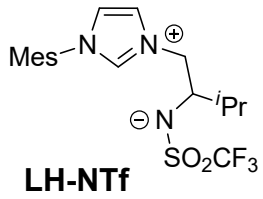
Synthesis of 6

$Ni(COD)_2$ 0.068 g (0.25 mmol) was suspended in 0.5 mL of 1, 5-cyclooctadiene. 0.019 g (0.25 mmol) of allyl chloride was then added dropwise. The resulting slurry was stirred for 5 minutes, resulted into the formation of a blood red allylnickel(II) chloride dimer. In another Schlenk flask suspension of 0.1 g (0.25 mmol) of **LH-NTf**, and 0.043 g (0.38 mmol) of KO^{t}Bu in 15 mL of THF was stirred for 3 h at -20°C. The light yellow colored

solution was slowly added to the a blood red allyl nickel(II) chloride dimer and stirred for 9 h at room temperature Slowly the color of the solution changed from dark red to yellow. The volatiles were evaporated and crude solid was redissolved in 15 mL acetonitrile, and the yellow mixture was filtered through a small pad of celite. The yellow colored filtrate was evaporated to dryness and dissolved in minimum amount of acetonitrile. 15 mL of petroleum ether was added with stirring to induce precipitation. The obtained light-yellow solid was washed with petroleum ether and dried under vacuum. Yield: 0.103 g (88%). ^{1}H NMR (500 MHz, CD_3CN, 292 K): δ 7.57 (d, *J* = 1.7 Hz, 1H, Im), 7.47 (d, *J* = 1.8 Hz, 1H, Im), 7.07 (s, 1H, Ph), 7.03 (s, 1H, Ph), 7.00 (s, 1H, Ph), 6.97 (s, 1H, Ph), 6.81 (d, *J* = 1.8 Hz, 1H, Im), 6.74 (d, *J* = 1.7 Hz, 1H, Im), 4.91 (m, 1H, allyl-CH), 3.66 - 3.63 (br, m, 4H, CH_2), 3.46 (dd, *J* =2.1 Hz,13.3 Hz, 1H, CH), 3.38 (br, d, *J* = 7.7 Hz, 1H, CH), 3.22 (dd, *J* =2.1 Hz, 11.2 Hz, 1H, CH), 3.13 (br, d, *J* = 10.7 Hz, 1H, CH), 2.98 (dd, *J* =2.4 Hz, 12.3 Hz, 2H, CH), 2.82 (dd, *J* =2.4 Hz, 11.4 Hz, 1H, CH), 2.33 – 2.29 (d, 6H $2^{ipr}CH_3$), 2.01 (d, J = 12.6 Hz, 1H, CH), 1.96 (br, s, 6H, $2CH_3$), 1.54 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 0.78 (d, *J* = 7.0 Hz, 3H, CH_3), 0.74 (d, *J* = 7.0 Hz, 3H, CH_3), 0.68 (d, *J* = 7.0 Hz, 3H, CH_3), 0.62 (d, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CD_3CN,, 292 K): δ 178.4, 178.1, 139.1, 138.9, 136.9, 136.9, 136.3, 136.1, 135.8, 135.6, 135.4, 129.7, 129.6, 129.5, 60.9, 60.7, 60.4, 59.1, 53.1, 52.3, 34.1, 33.7, 20.4, 18.7, 18.6, 17.0, 19.98, 16.96, 16.6,16.5. (The CF_3 signal was not observed due to the low intensity). ^{19}F NMR (470 MHz, CD_3CN, 292 K): –69.30, -70.81 ($NHSO_2CF_3$). Anal Calcd. for $Ni_1S_2F_6C_{39}N_6O_4H_{53}Cl$: C, 49.77; H, 5.68; N, 8.93 Found: C, 49.74; H, 5.67; N, 8.90. ESI–MS, *m/z*: 905.2853, (z=1), [**6**]$^{+}$.



Scheme S7. Synthesis of **6**.



LH-NTf

Figure S1. ^{1}H NMR spectrum of **LH-NTf** in $CDCl_3$.

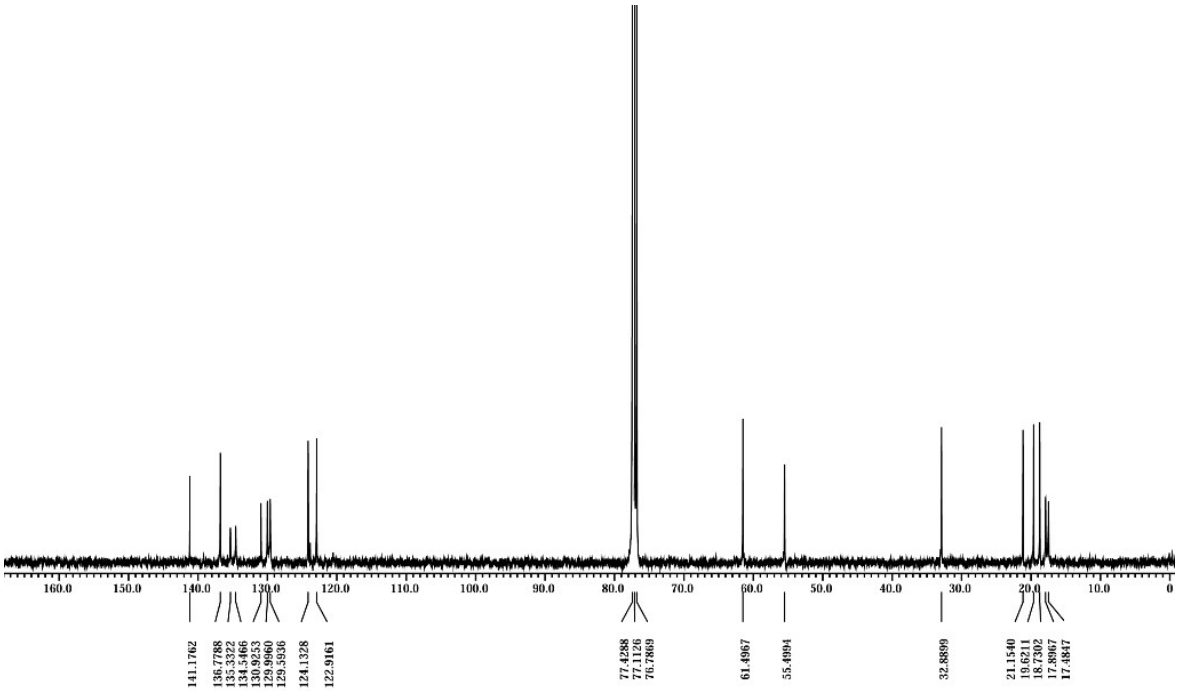


Figure S2. ^{13}C NMR spectrum of **LH-NTf** in $CDCl_3$.

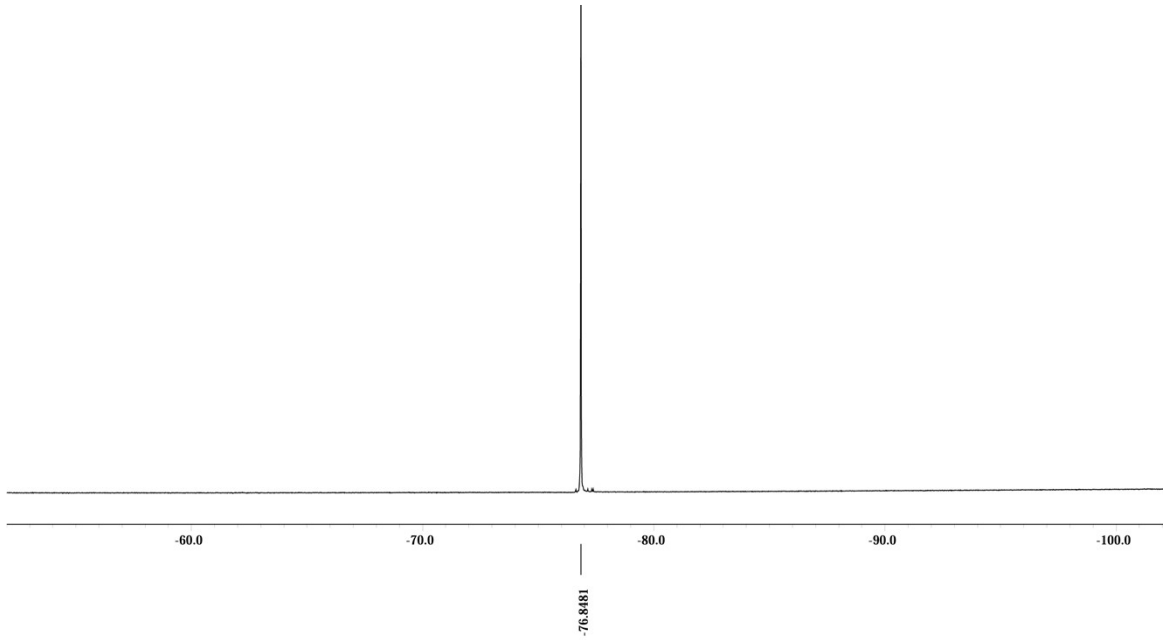


Figure S3. ^{19}F NMR spectrum of **LH-NTf** in $CDCl_3$.

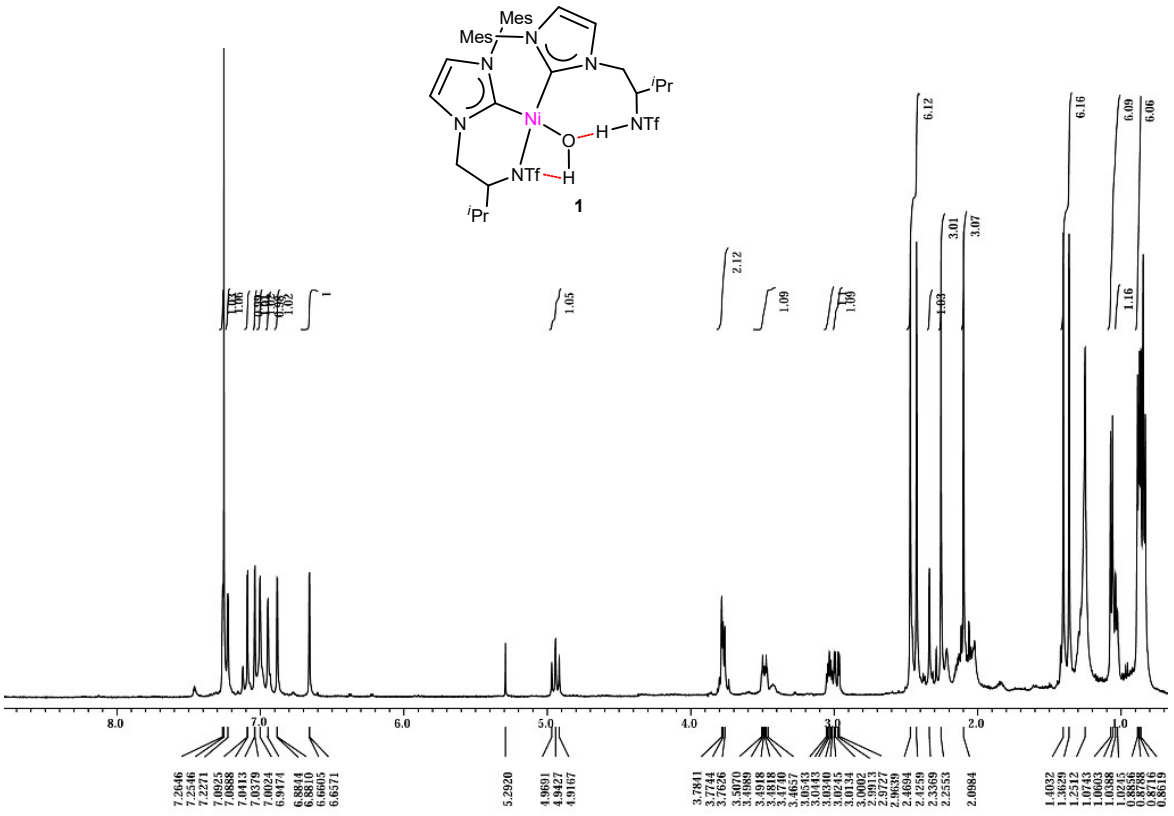


Figure S4. ^{1}H NMR spectrum of **1** in $CDCl_3$.

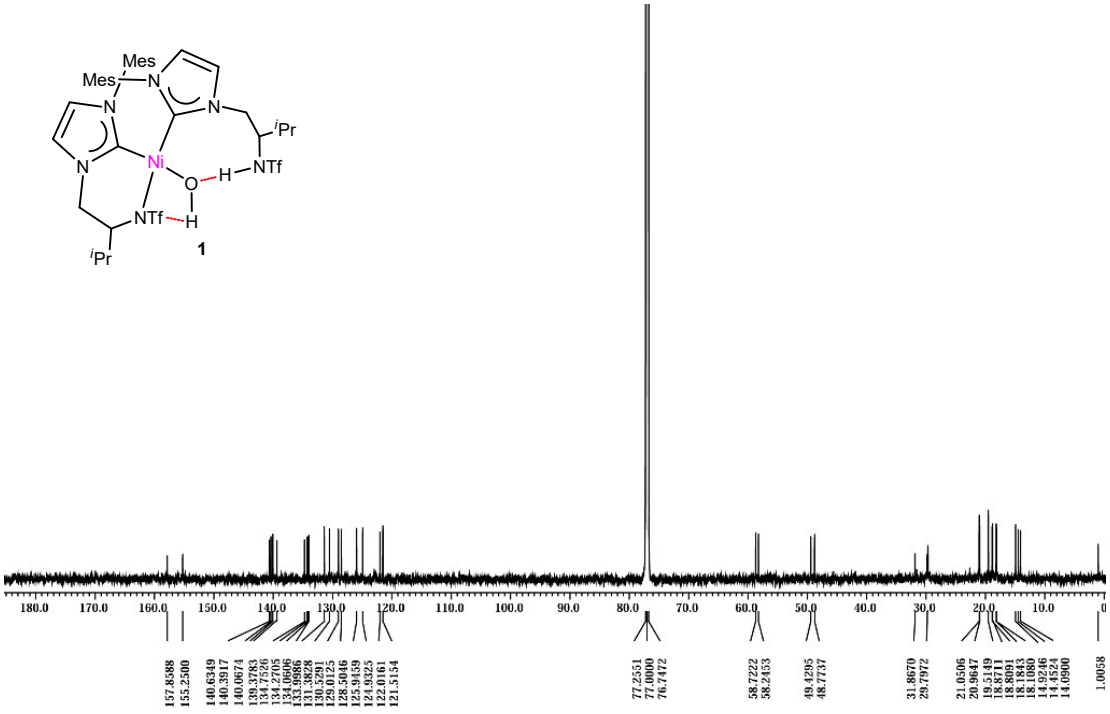


Figure S5. ^{13}C NMR spectrum of **1** in $CDCl_3$.

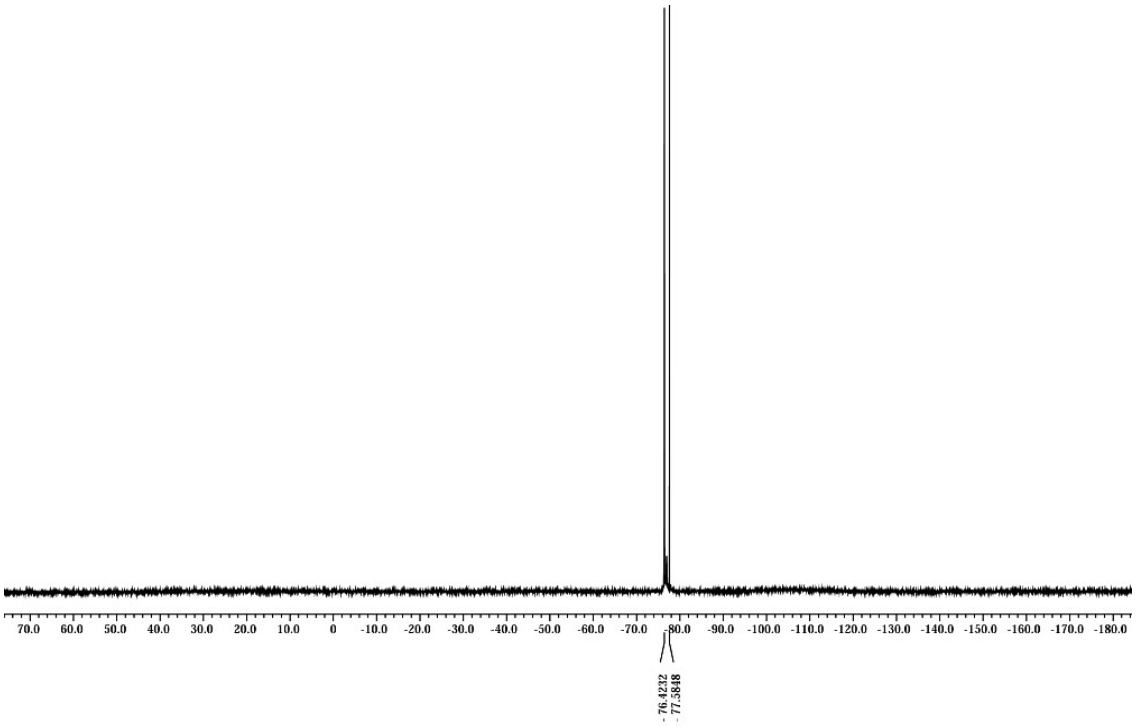


Figure S6. ^{19}F NMR spectrum of **1** in $CDCl_3$.

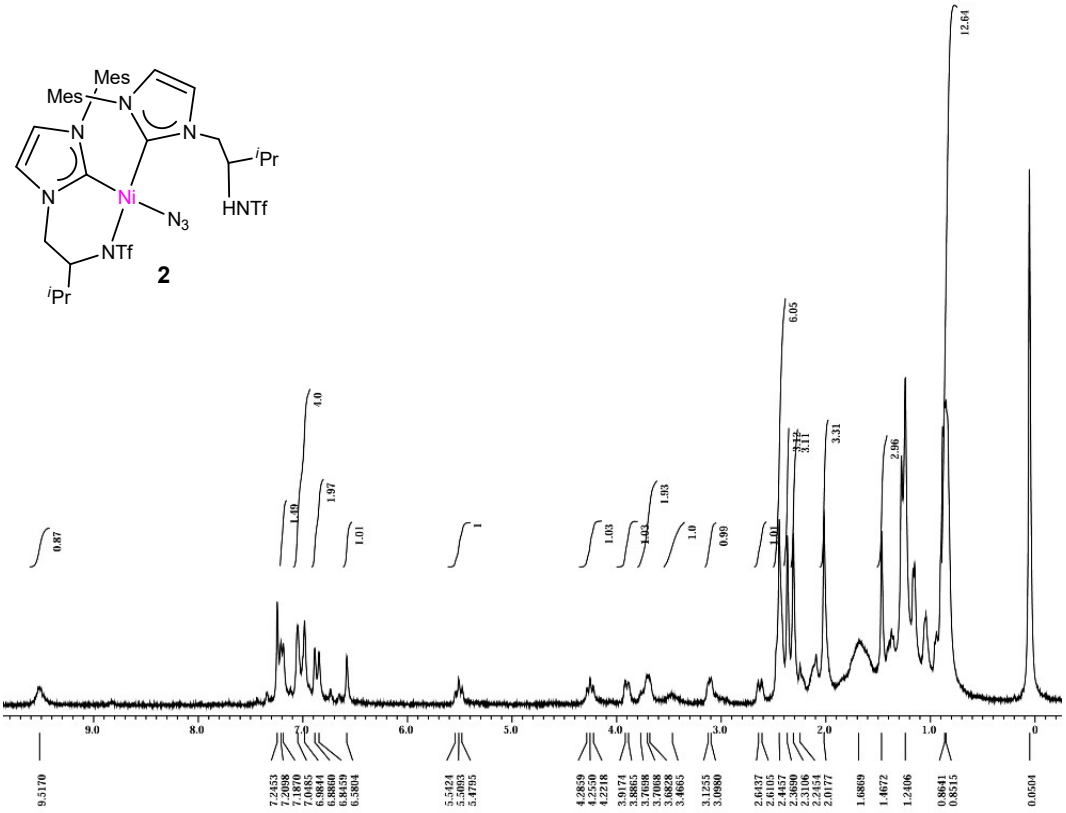


Figure S7. ^{1}H NMR spectrum of **2** in $CDCl_3$.

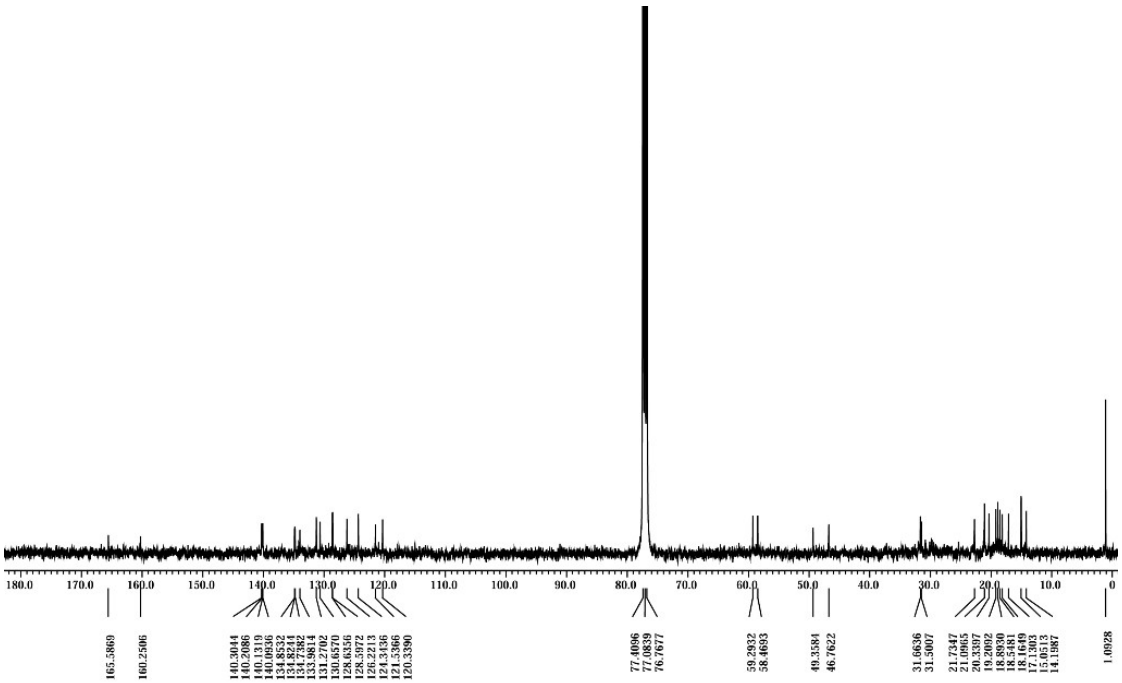


Figure S8. ^{13}C NMR spectrum of **2** in $CDCl_3$.

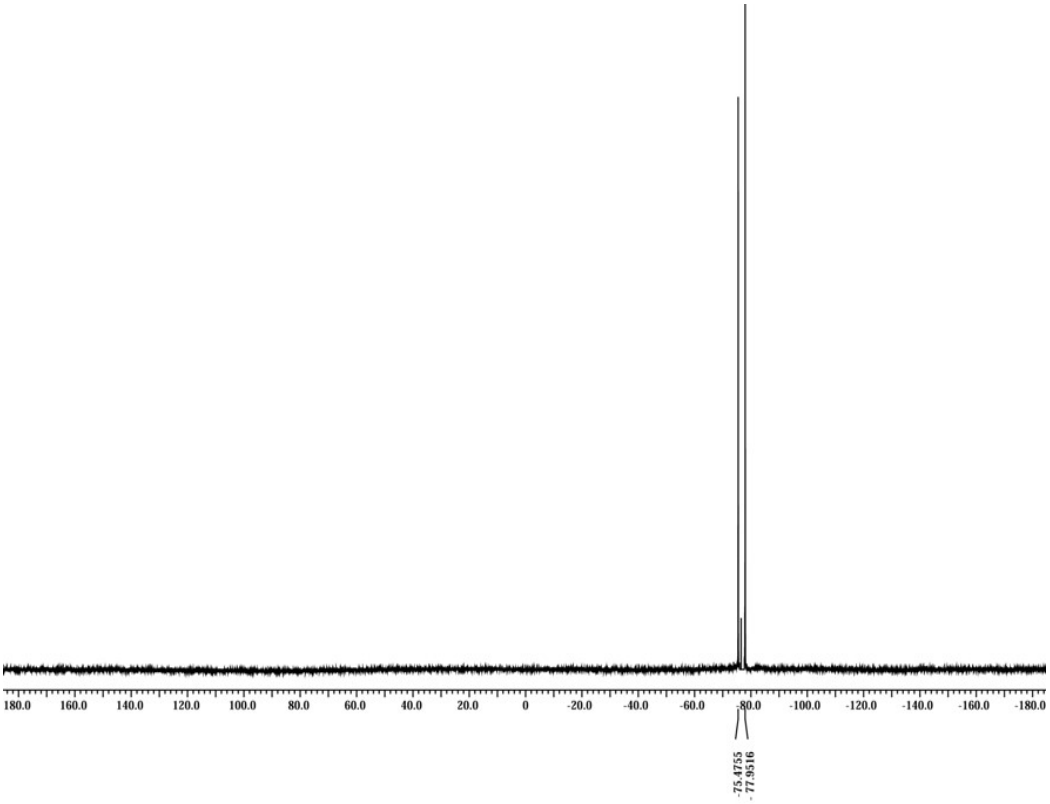


Figure S9. ^{19}F NMR spectrum of **2** in $CDCl_3$.

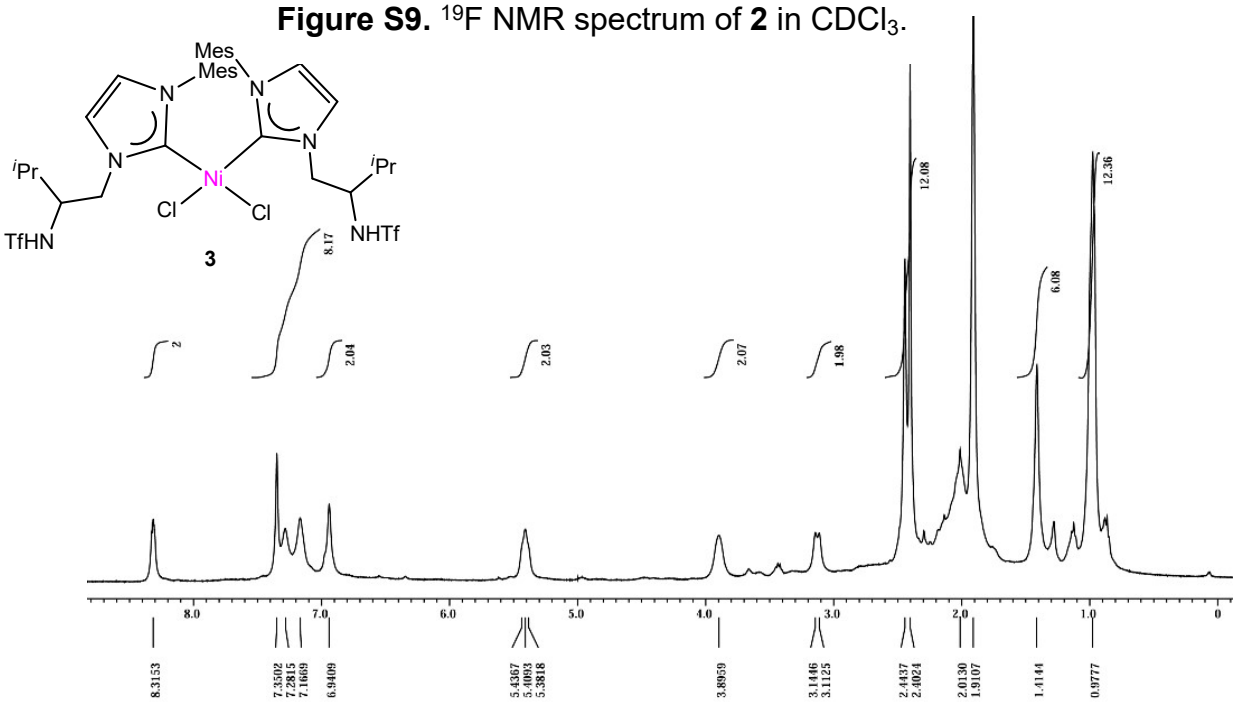


Figure S10. ^{1}H NMR spectrum of **3** in CD_3CN.

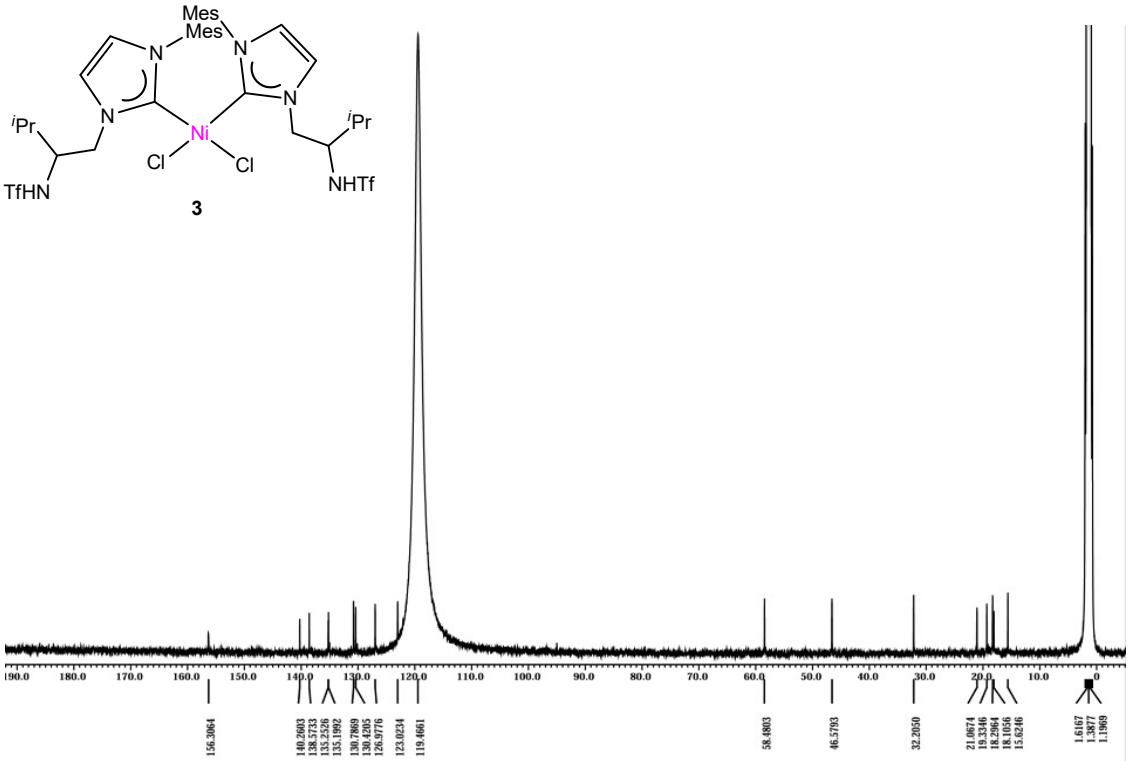


Figure S11. ^{13}C NMR spectrum of **3** in

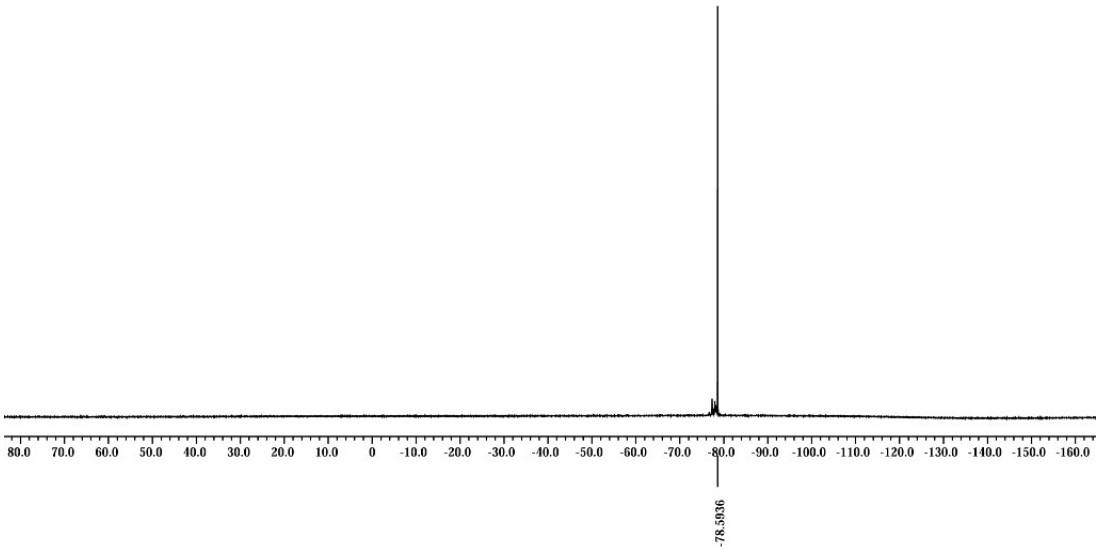


Figure S12. ^{19}F NMR spectrum of **3** in CD_3CN.

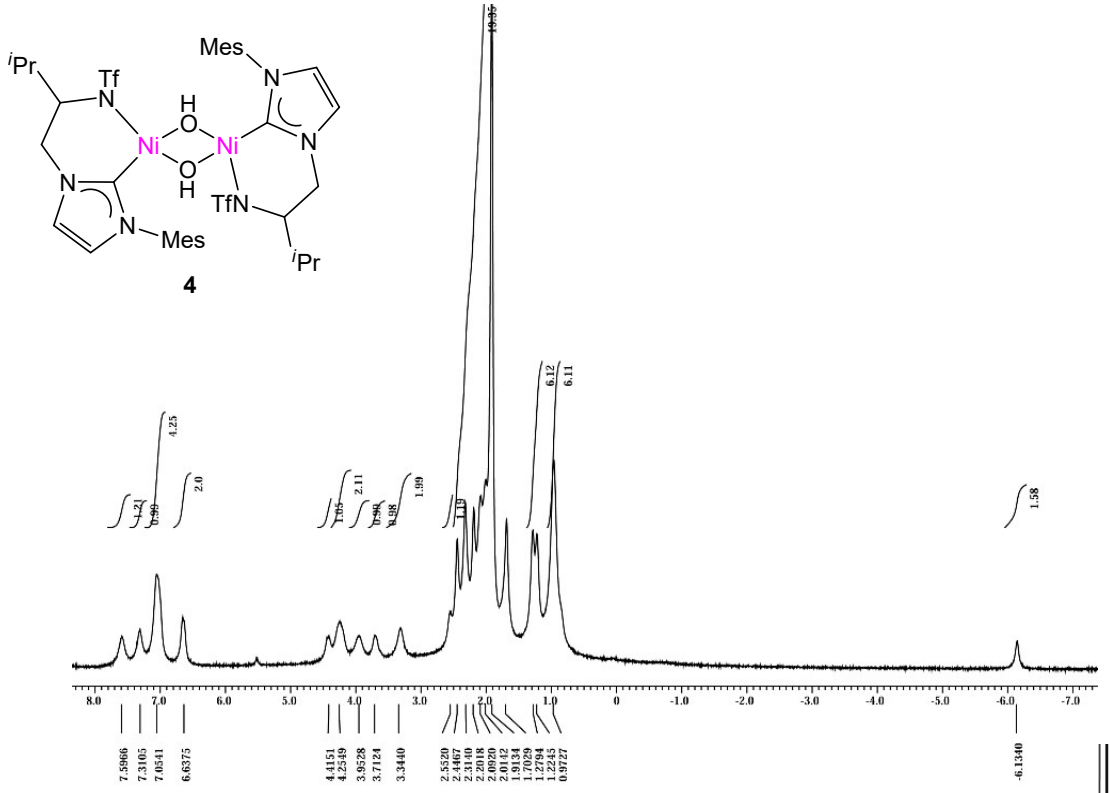


Figure S13. ^{1}H NMR spectrum of **4** in CD_3CN.

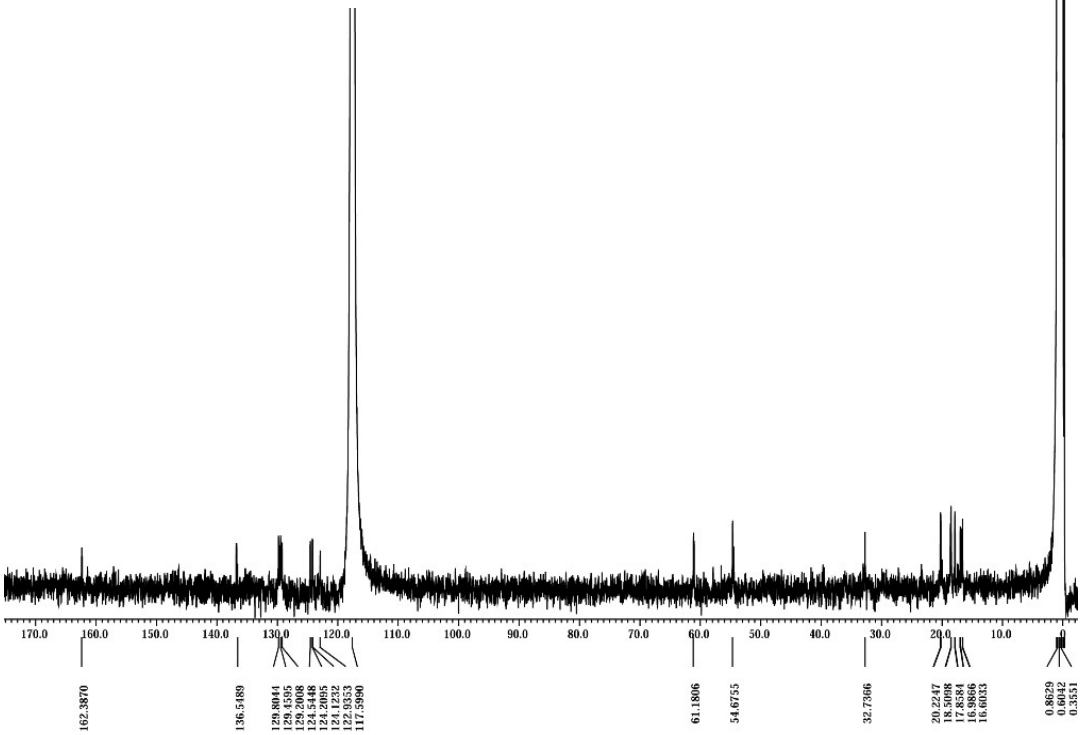


Figure S14. ^{13}C NMR spectrum of **4** in CD_3CN.

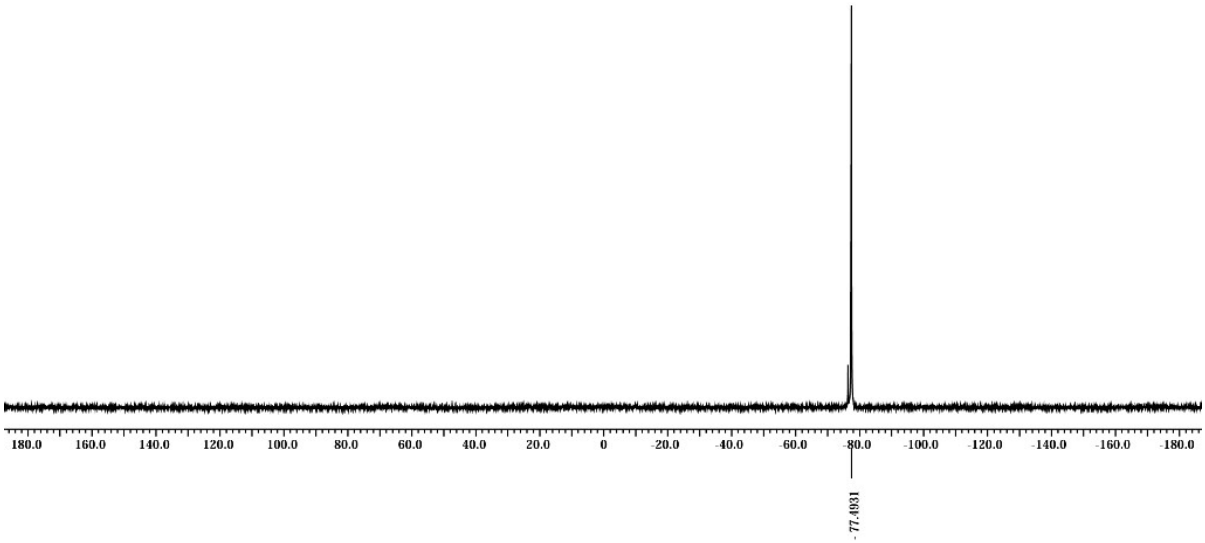


Figure S15. ^{19}F NMR spectrum of **4** in CD_3CN.

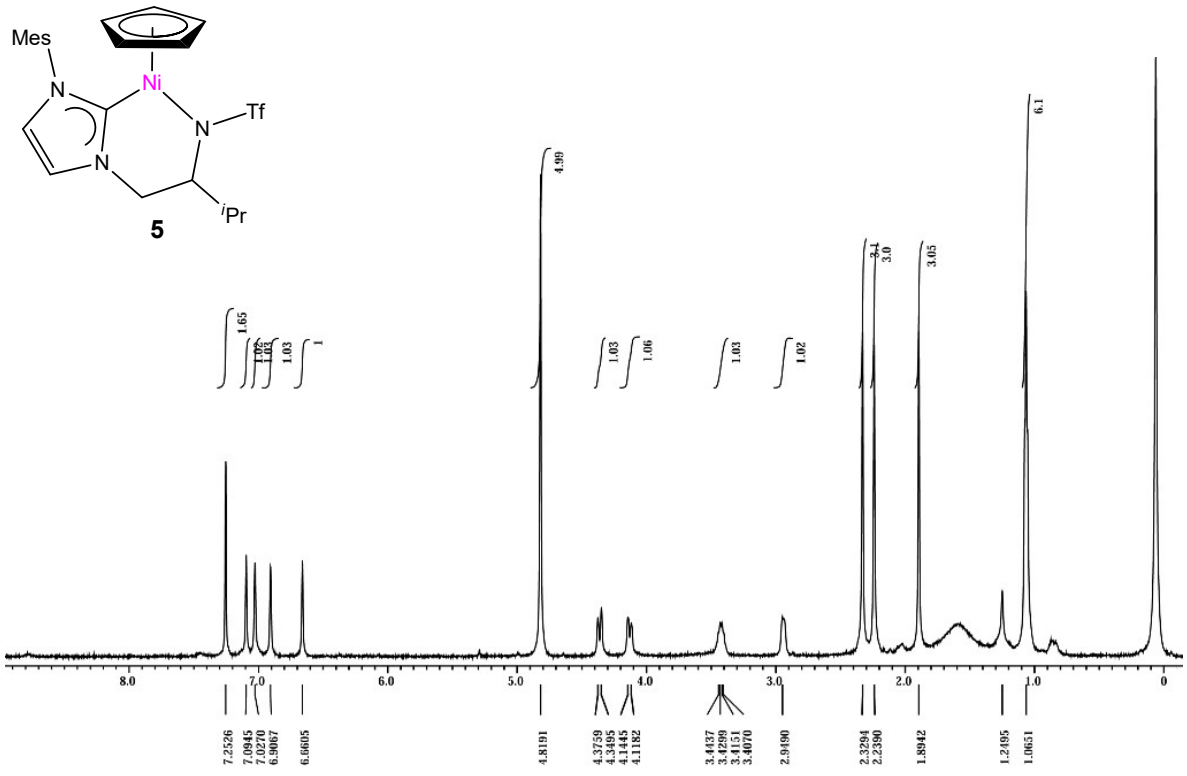


Figure S16. ^{1}H NMR spectrum of **5** in $CDCl_3$.

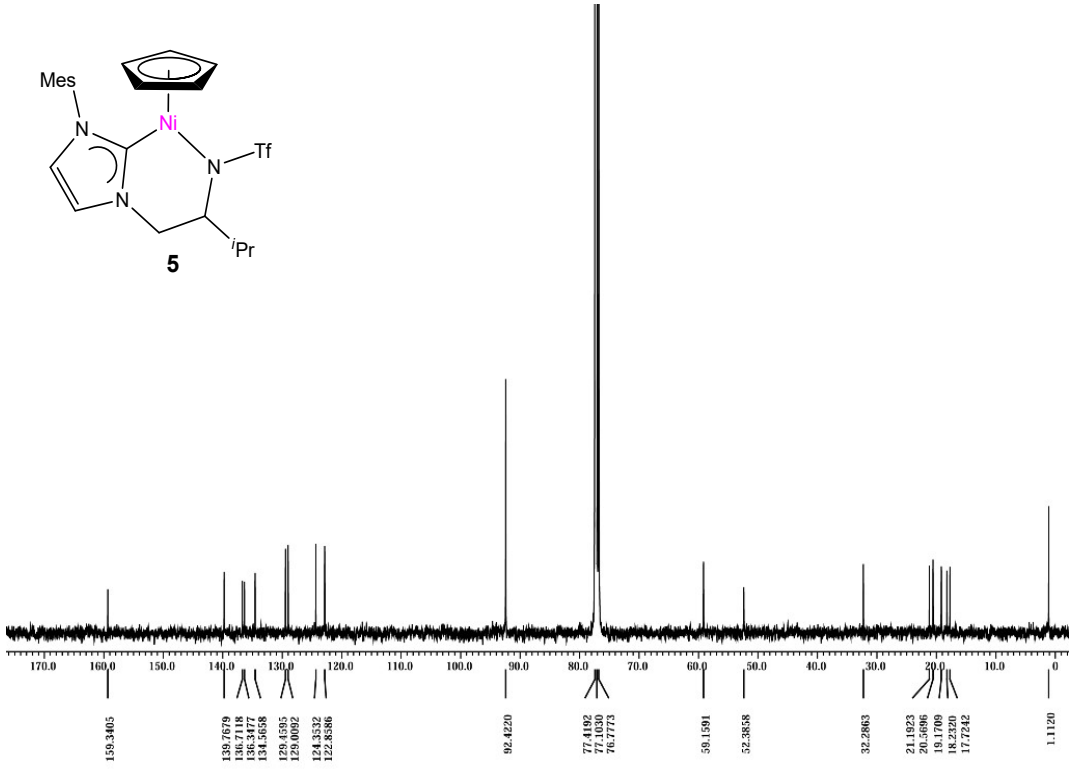


Figure S17. ^{13}C NMR spectrum of **5** in $CDCl_3$.

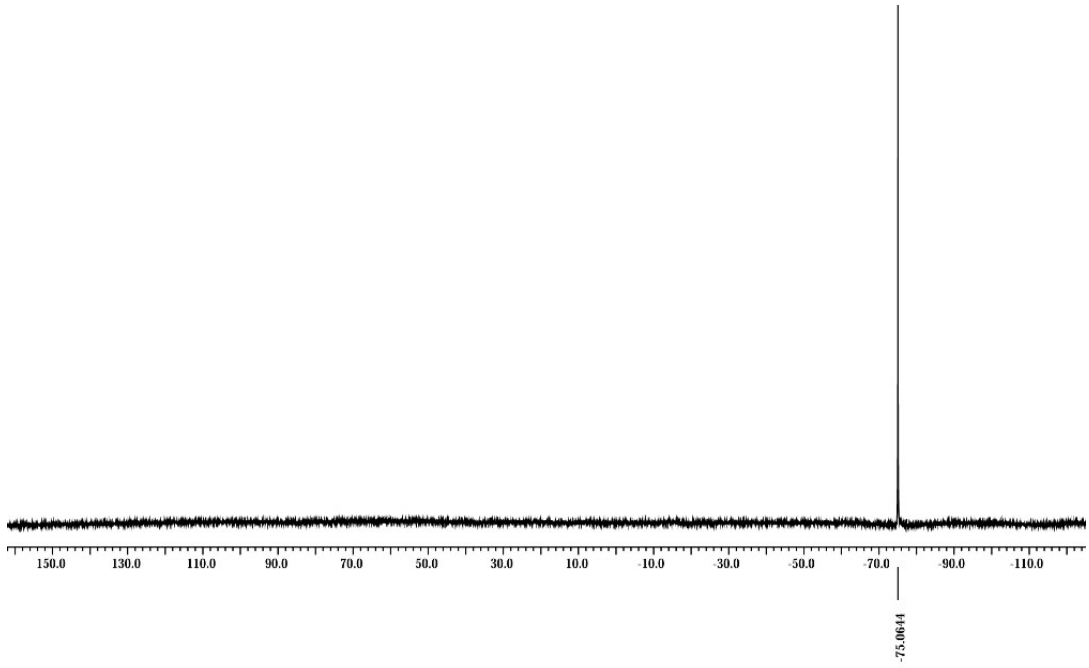


Figure S18. ^{19}F NMR spectrum of **5** in $CDCl_3$.

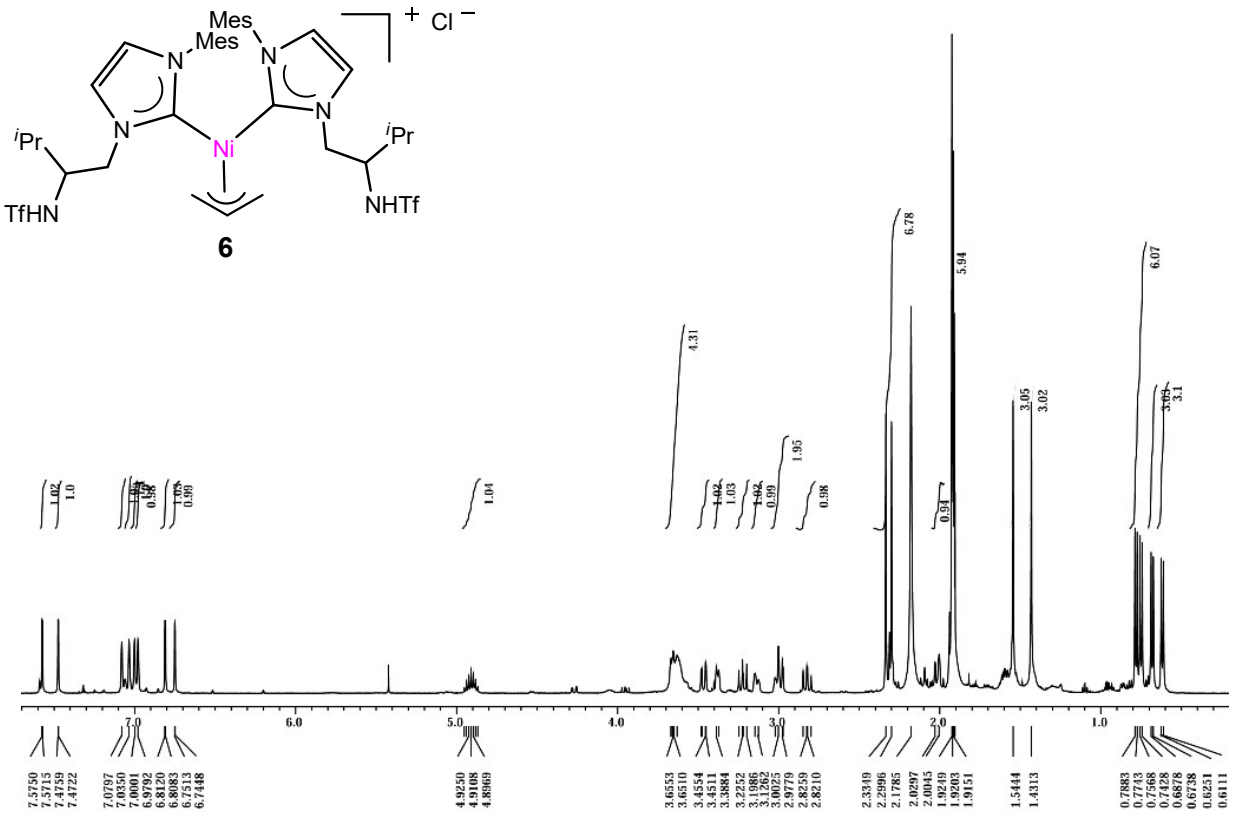


Figure S19. ^{1}H NMR spectrum of **6** in CD_3CN

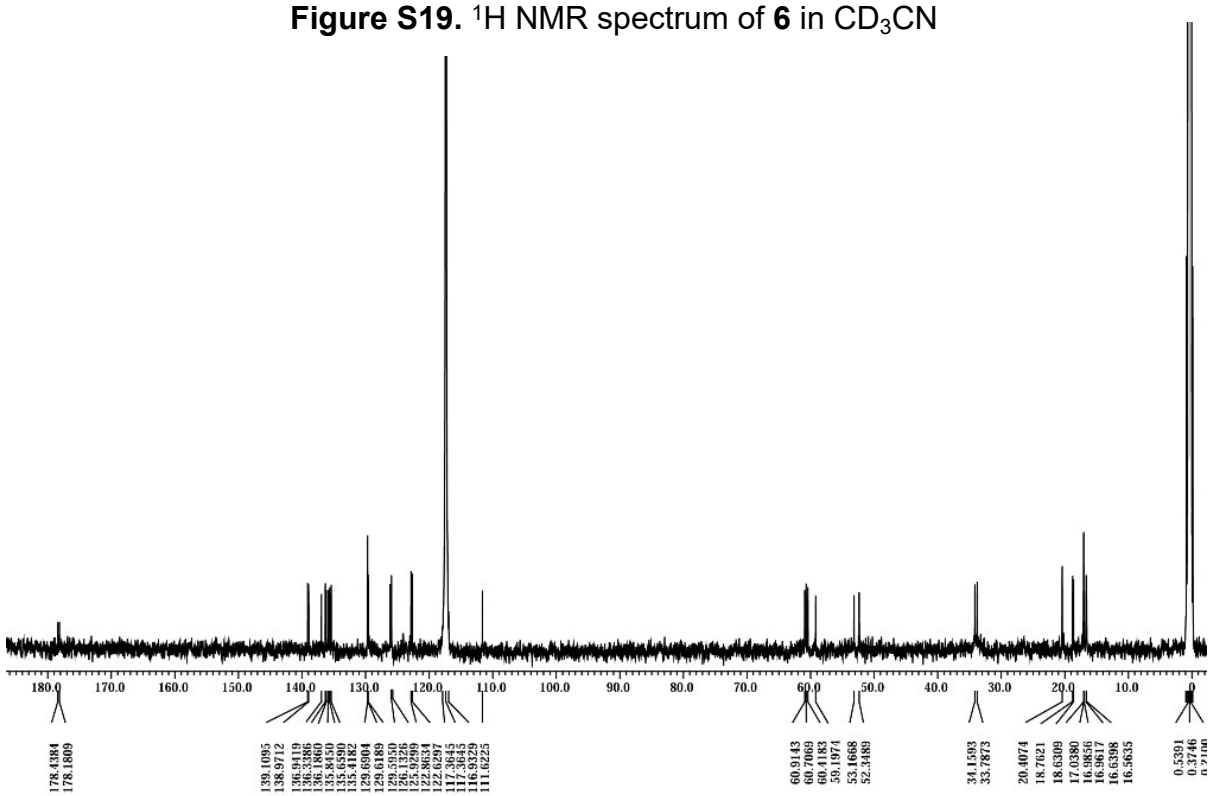


Figure S20. ^{13}C NMR spectrum of **6** in CD_3CN.

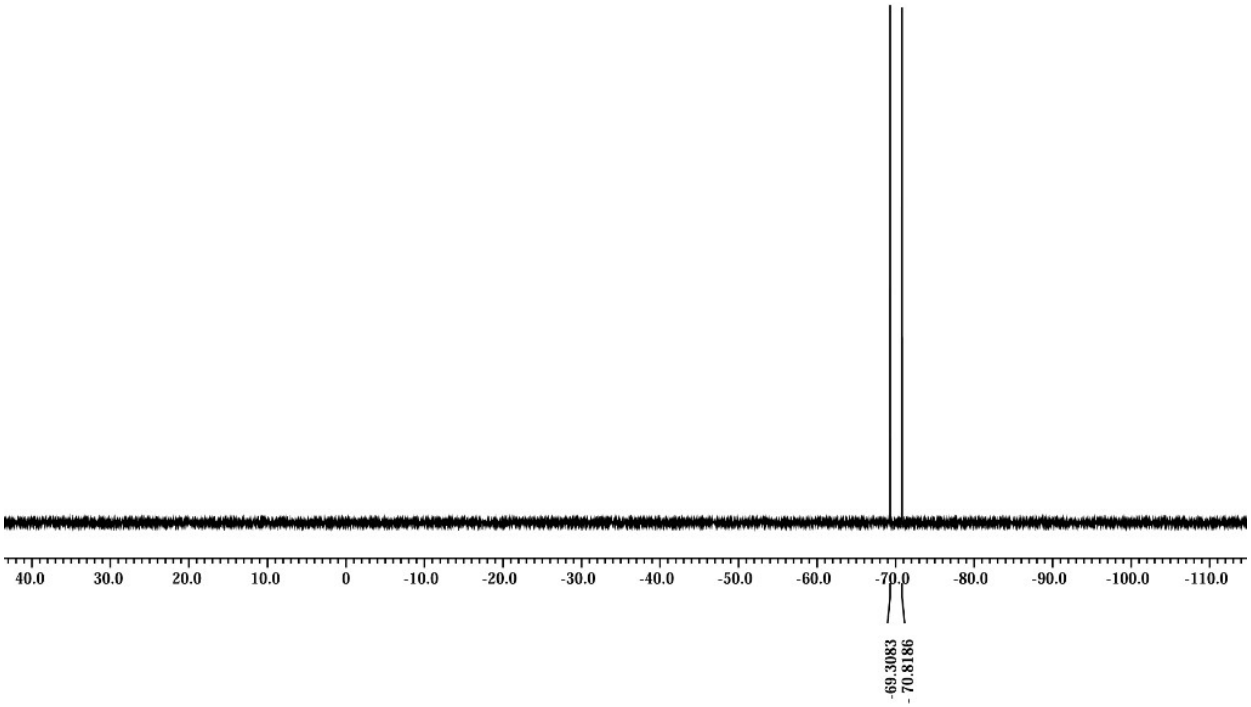


Figure S21. ^{19}F NMR spectrum of **6** in CD_3CN.

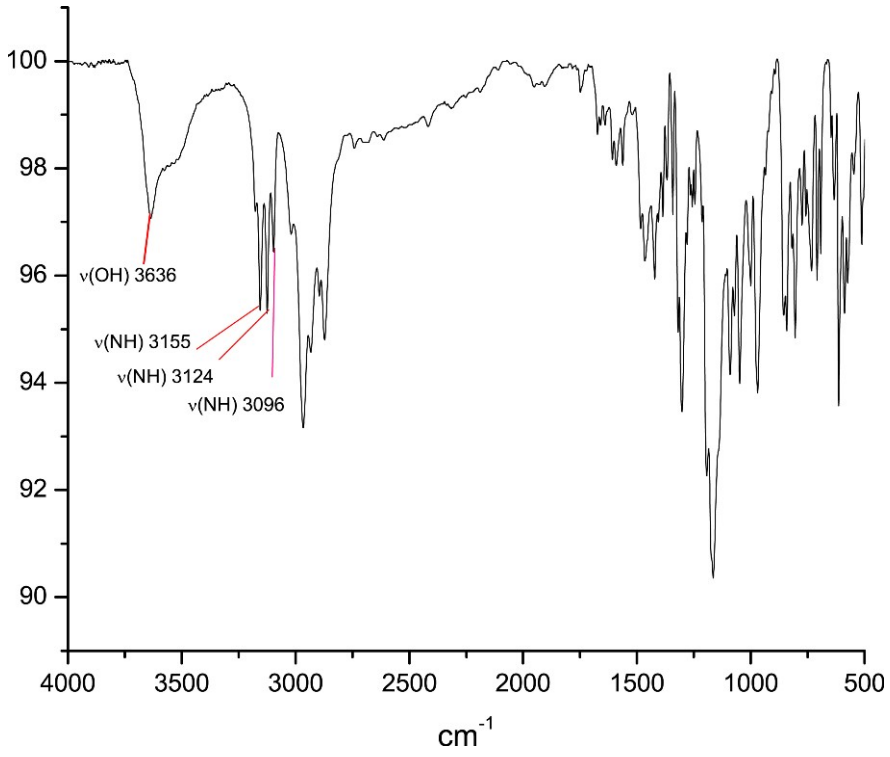


Figure S22. FT-IR spectrum of complex **1** in Nujol.

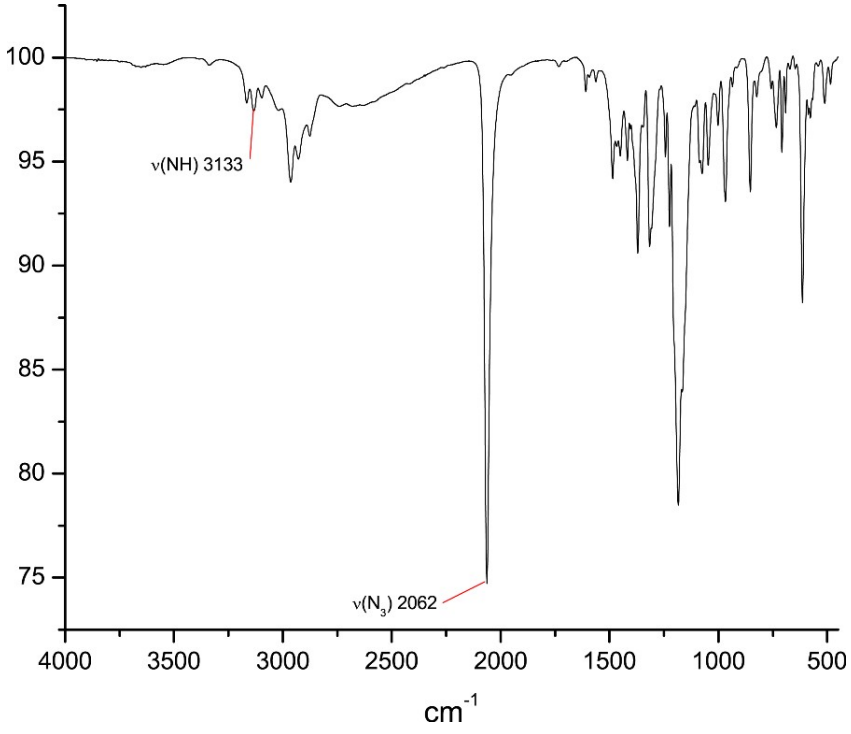


Figure S23. FT-IR spectrum of complex **2** in Nujol.

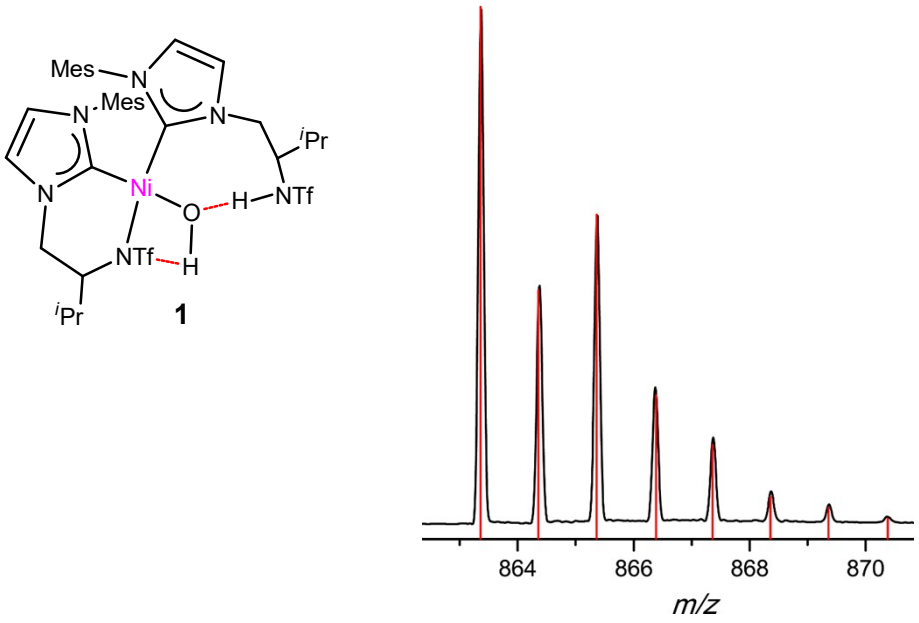


Figure S24. Experimental (black) and simulated (red) ESI-MS for [**1**-OH]$^+$ at *m/z* = 863.2352 (z=1).

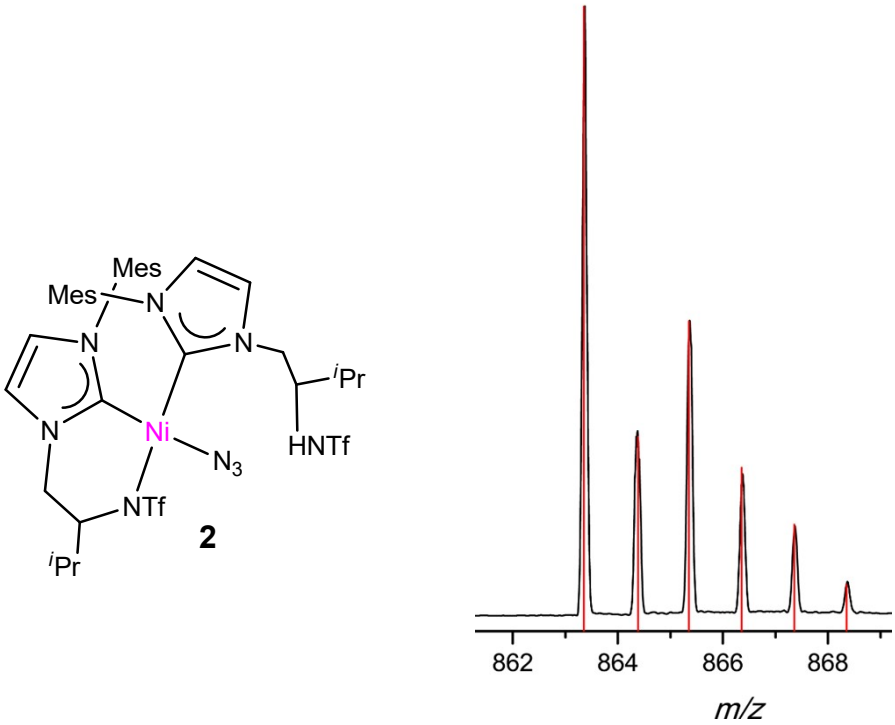


Figure S25. Experimental (black) and simulated (red) ESI-MS for [**2**-N_3]$^+$ at *m/z* = 863.2736 (z=1).

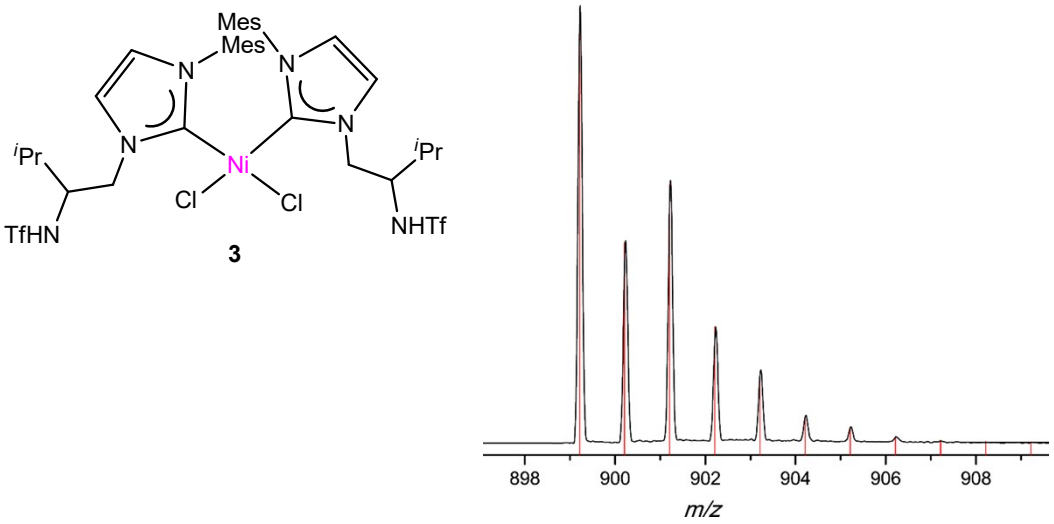


Figure S26. Experimental (black) and simulated (red) ESI-MS for [**3**-Cl]$^+$ at *m/z* = 899.2114 (z=1).

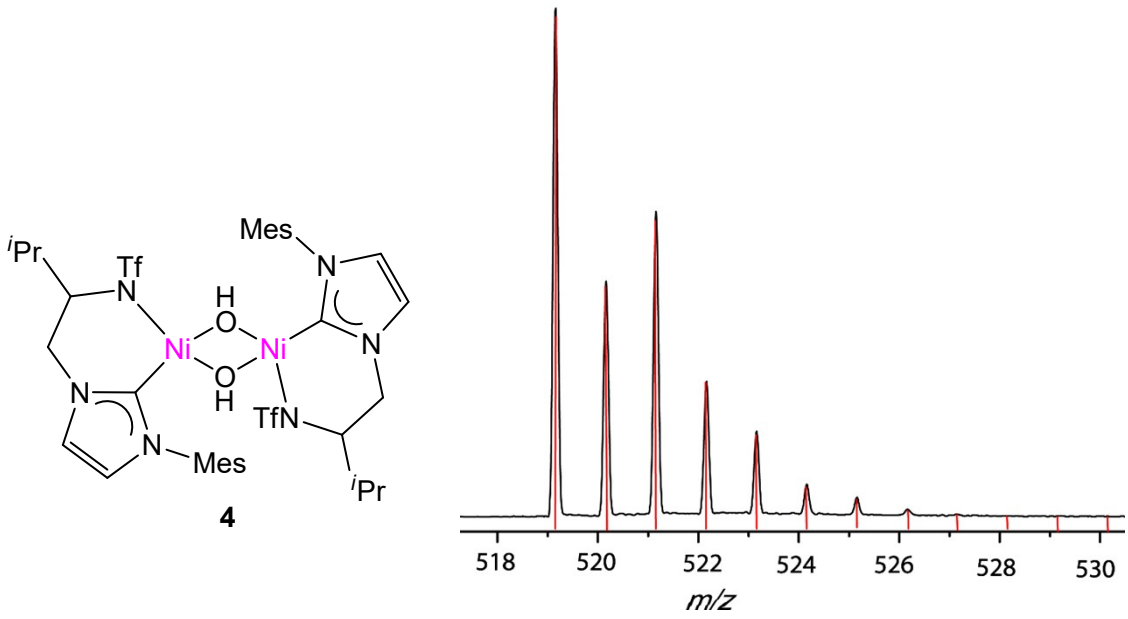


Figure S27. Experimental (black) and simulated (red) ESI-MS for [(LNTf)Ni(OH)+CH_3CN+H]$^+$ at *m/z* = 519.1158 (z=1).

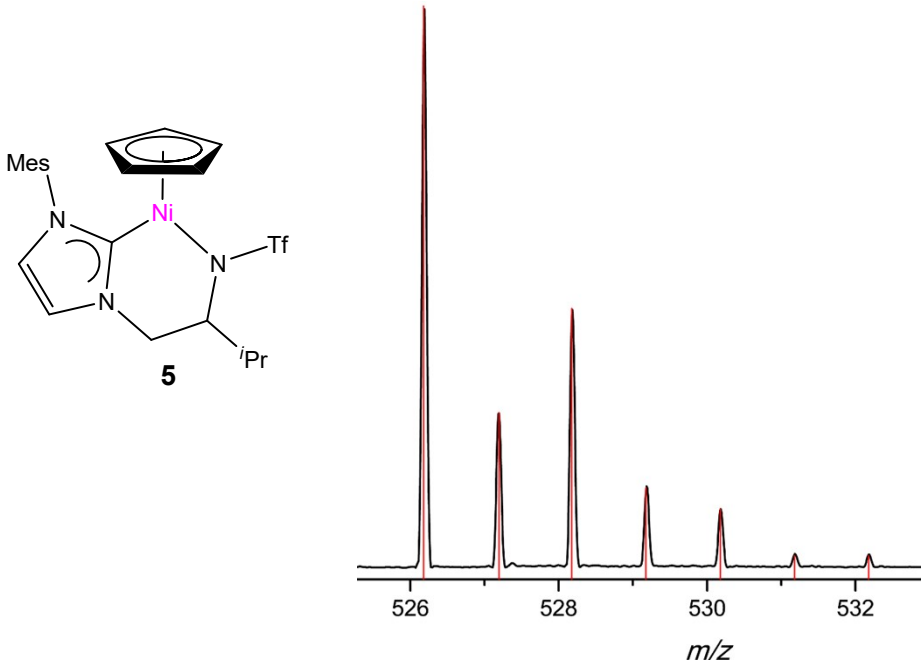


Figure S28. Experimental (black) and simulated (red) ESI-MS for [**5**+H]$^+$ at *m/z* = 526.1287 (z=1).

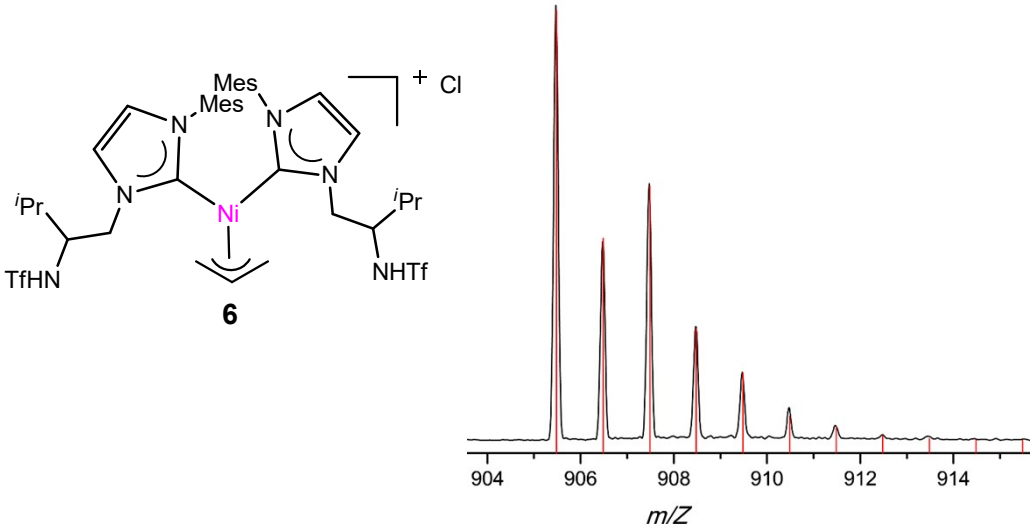


Figure S29. Experimental (black) and simulated (red) ESI-MS for [**6**-H]$^+$ at *m/z* = 905.2853 (z=1).

2. X–Ray Data Collection and Refinements

Single–crystal X–ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low–temperature attachment. All data were collected at 100(2) K using graphite–monochromated Mo–Kα radiation ($\lambda\alpha$ = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[5] and the data were corrected for absorption using the SADABS program.[6] The structures were solved and refined with the SHELX suite of programs.[7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of ligands were included into geometrically calculated positions in the final stages of the refinement and were refined according to 'riding model'. The hydrogen atoms of OH and NHTf groups of **1** - **4** were located from difference Fourier map and the bond lengths and bond angles were constrained geometrically. SQUEEZE option in PLATON program was used to remove the disordered water and solvent molecules from the overall intensity data of compounds wherever necessary.[8] Diamond 3.1e software was used to produce the diagrams.[9] CCDC numbers **1952208**, **1952209**, **1952210**, **1952211**, **1952212** contain the supplementary crystallographic data for compounds, **1** - **5**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

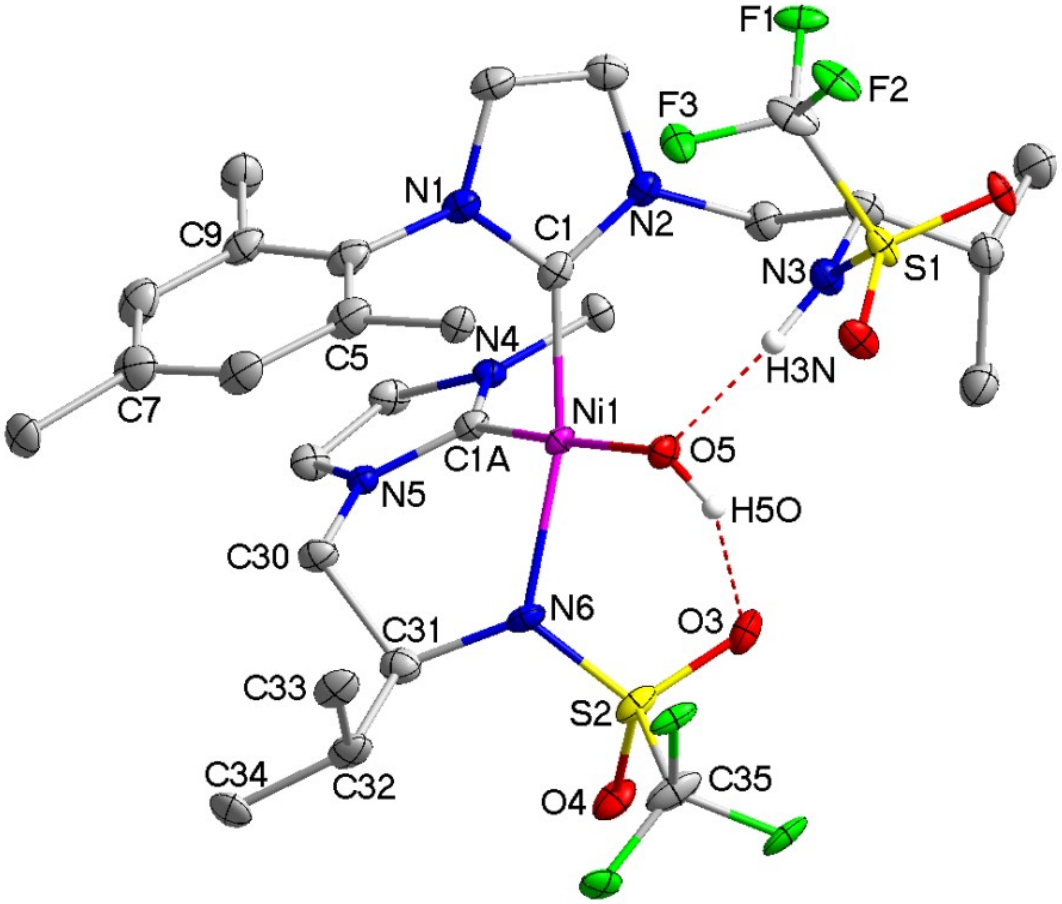


Figure S30. Molecular structure of **1** with important atoms labeled. All hydrogens are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ni1–C1 1.865(4), Ni1–C1A 1.851(4), Ni1–N6 1.976(3), Ni1–O5 1.931(3), N3–S1 1.533(4), N6–S2 1.558(3), O5…(H)–N3 2.627, O3…(H)–O5 2.902. C1–Ni1–O5 89.37(14), C1A–Ni1–C1 89.53(16), C1A–Ni1–O5 175.28(16), C1A–Ni1–N6 88.64(15), N6–Ni1–O5 93.50(13), N6–Ni1–C1 166.35(16), N3–H...O5 170.84, O5–H...O3 138.72.

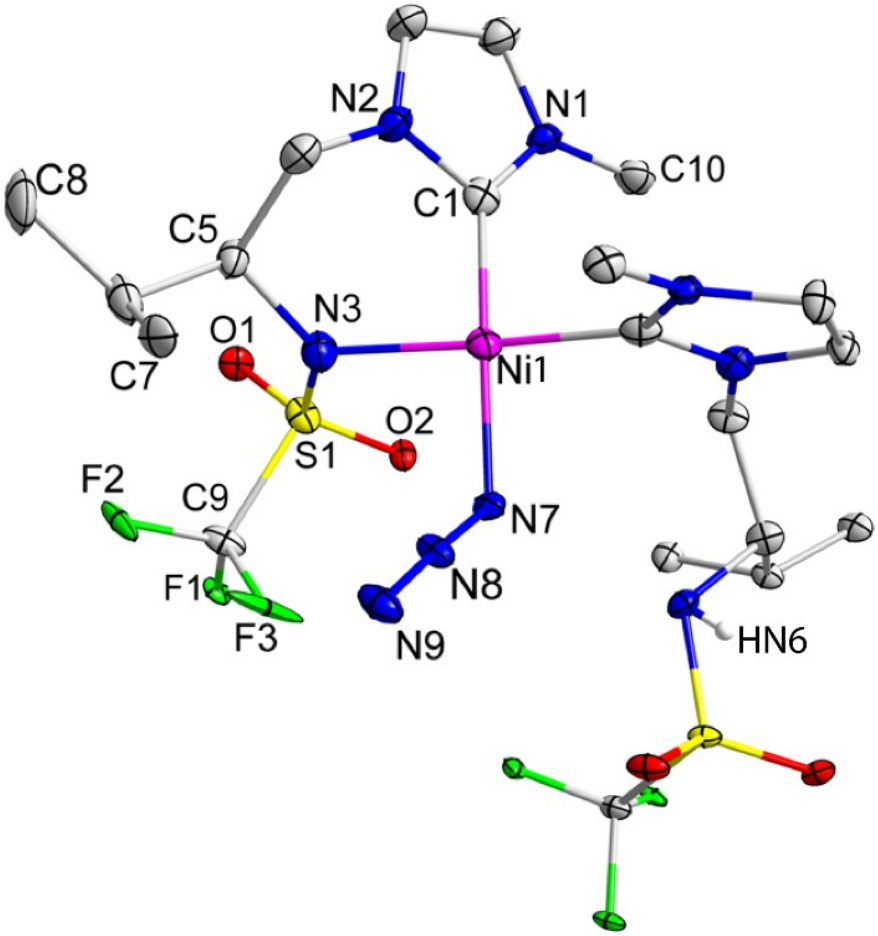


Figure S31. Molecular structure of **2** with important atoms labeled. Except for N–H, all other hydrogens and mesityl groups are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ni1–C1 1.87(5), Ni1–C19 1.873(5), Ni1–N7 1.920(5), Ni1–N3 1.973(4), N7–N8 1.190(6), N8–N9 1.155(7), C5–N3 1.483(7), S1–N3 1.563(4). C1–Ni1–C19 93.4(2), C1–Ni–N7 176.9(2), C19–Ni1–N7 86.4(2), C1–Ni1 N3 86.9(2), N7–Ni1–N3 93.7(2), N3–Ni1–C19 172.(2), N7–N8–N9 176.6(6).

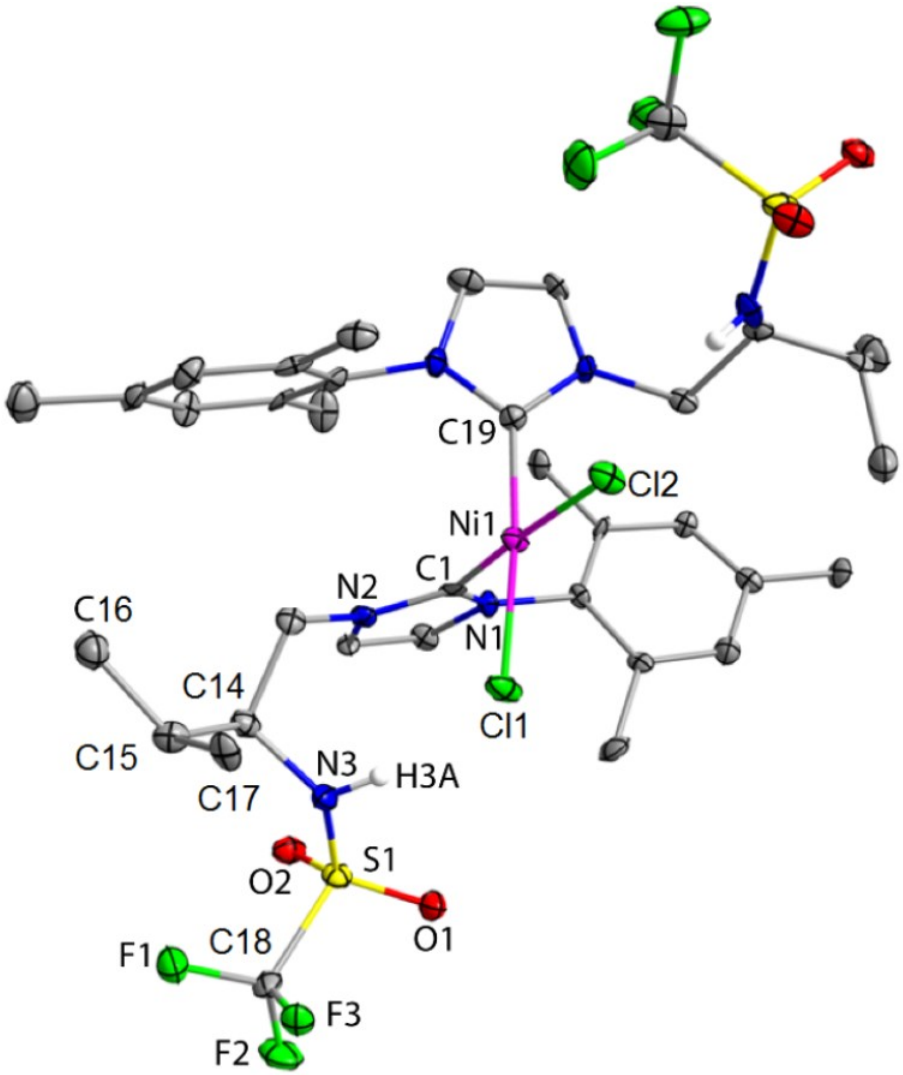


Figure S32. Molecular structure of **3** with important atoms labeled. Except for N–H, all other hydrogens are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ni1–C1 1.880(6), Ni1–C19 1.878(6), Ni1–Cl1 2.221(19), Ni1–Cl2 2.224(19), N3–S1 1.571(6). C1–Ni1–C19 90.6(2), C19–Ni1–Cl1 174.29(19), C1–Ni1–Cl1 91.39(19), Cl1–Ni1–Cl2 87.88(7), C1–Ni1–Cl2 176.24(19), C19–Ni1–Cl2 90.48(18).

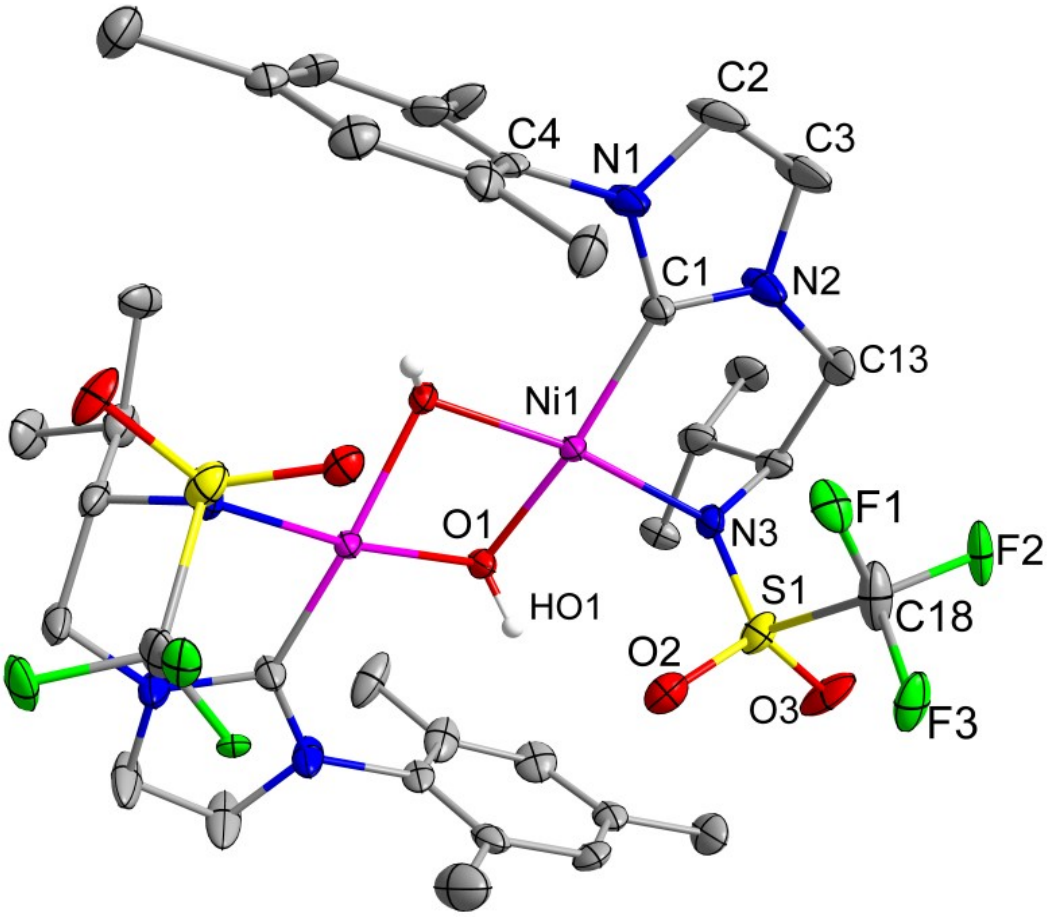


Figure S33. Molecular structure of **4** with important atoms labeled. Except for O–H, all other hydrogens are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ni1–C1 1.890(5), Ni1–N3 1.907(4), Ni1–O1 1.852(4), Ni1–O1' 1.902(4), Ni1–Ni1' 2.8301(13). C1–Ni1–N3 89.95(19), N3–Ni1–O1 93.49(17), O1–Ni1–C1 167.4(2), O1–Ni1'–C1' 99.30(19), Ni1–O1–Ni1' 41.78(11), O1–Ni1-O1' 77.62(19).

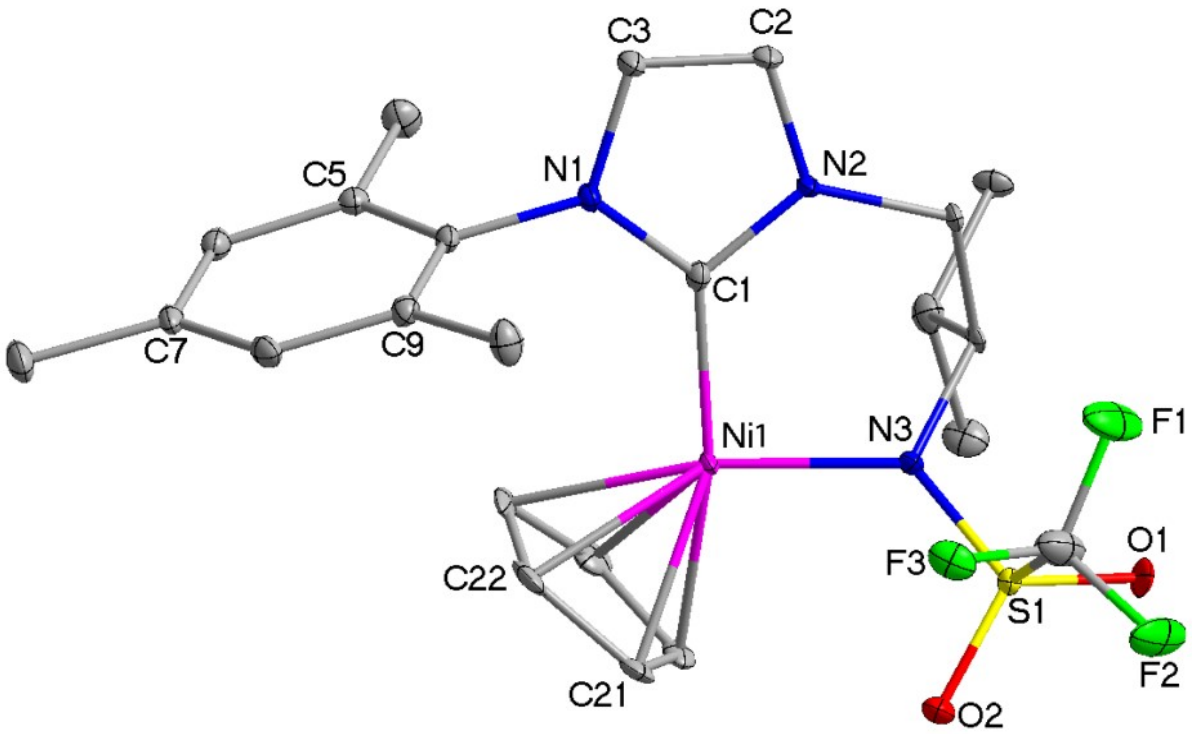


Figure S34. Molecular structure of **5** with important atoms labeled. All hydrogens are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ni1–C1 1.900(4), Ni1–N3 1.944(4), Ni1–C19 2.135(4), Ni1–C20 2.156(4), Ni1–C21 2.136(5), Ni1–C22 2.100(5), Ni1–C23 2.196(4), S1–C18 1.841(5). C1–Ni1–N3 93.62(17), C22–Ni1–N3 157.32(16), C1–Ni1–C22 102.50(18), C1–Ni1–C19 97.01(16), C1–Ni1–N3 112.12(18).

Table S1. Crystallographic data and pertinent refinement parameters for complexes **1**-**5**.

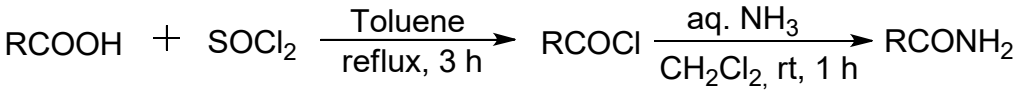
	1	**2**• Solvent	**3**•CH_2Cl_2	**4**•$2CH_2Cl_2$	**5**
Empirical formula	$C_{36}H_{48}F_6N_6NiO_5S_2$	$C_{36}H_{47}F_6N_9NiO_4S_2$	$C_{36}H_{48}Cl_2F_6N_6NiO_4S_2$	$C_{38}H_{52}Cl_4F_6N_6Ni_2O_6S_2$	$C_{23}H_{28}F_3N_3NiO_2S$
Formula Weight	881.63	905.64	1021.44	1126.16	526.23
Crystal System	Orthorhombic	Hexagonal	Monoclinic	Orthorhombic	Triclinic
Space Group	*P*212121	P65	*P*21	C 2 2 21	P1
a (Å)	11.9598(7)	23.6705(11)	11.504(5)	16.6591(10)	8.7211(9)
b (Å)	12.3574(7)	23.6705(11)	15.705(6)	16.9699(10)	10.2273(11)
c (Å)	28.0107(15)	16.1646(8)	13.626(5)	17.4164(9)	13.1114(15)
α (deg)	90	90	90	90	86.861(3)
β (deg)	90	90	101.704(7)	90	89.208(3)
γ (deg)	90	120	90	90	88.693(3)
V (Å^3)	4139.8(4)	7843.5(8)	2410.7(17)	4923.7(5)	1167.3(2)
Z	4	6	2	8	1
ρcalcd (g cm^{-3})	1.415	1.172	1.407	1.519	1.497
μ (mm^{-1})	0.644	1.711	0.776	0.644	0.970
F(000)	1840.0	2880	1056.0	2320	548
Reflections Collected	50886	95940	20779	21315	14603
Independent	10258	9299	11011	4823	8814
Observed [I >2σ (I)]	8063	7523	6711	3865	8469
No. of variables	524	562	559	299	606
GooF	1.042	1.028	1.035	1.004	1.027
Rint	0.0709	0.0867	0.0384	0.0711	0.0326
Flack	0.016(15)	0.015(6)	0.019(9)	0.016(10)	0.023(12)
Final R indices [I > 2σ(I)][a]	R1 = 0.0456 wR2 = 0.0890	R1 = 0.0449 wR2 = 0.1031	R1 = 0.0498 wR2 = 0.0962	R1 = 0.0453 wR2 = 0.0864	R1 = 0.0311 wR2 = 0.0785
R indices (all data)[a]	R1 = 0.0708 wR2 = 0.0964	R1 = 0.0652 wR2 = 0.1117	R1 = 0.0968 wR2 = 0.1235	R1 = 0.0676 wR2 = 0.0932	R1 = 0.0329 wR2 = 0.0808

[a]$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

3. Catalytic Studies

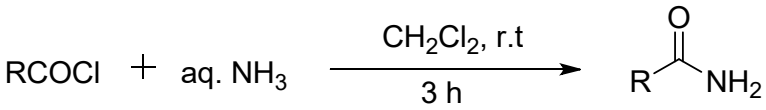
3.1.1. Synthesis of primary amides

Method A (For entries 5, 22 in Table 1)



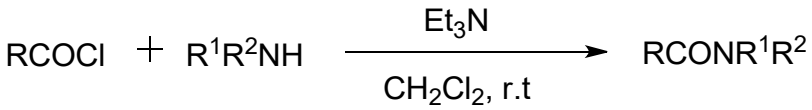
In a two necked round bottom flask carboxylic acid (5.0 mmol) was added to the 15 mL of toluene. To that reaction mixture, dropwise thionyl chloride (10 mmol) was added together with cat. amount of DMF and the reaction mixture was refluxed for 3 h. The excess of thionyl chloride was evaporated and the crude acid chloride was redissolved in dichloromethane. After that aq. ammonia was added below 10 ^{o}C and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was extracted with 1N HCl and saturated $NaHCO_3$ solution. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to get white solid in 90-95% yield.

Method B (For entries 11, 12, 13 in Table 1)



In a two necked round bottom flask acyl chloride (5.0 mmol) was added in 20 mL of dichloromethane solution. In the reaction mixture aq. ammonia (10.0 mmol) was added in one portion at room temperature, and stirred for 3 h. The reaction mixture was then diluted with dichloromethane (30 mL) and was transferred to a separating funnel, washed with 1N HCl (50 mL), and saturated solution of $NaHCO_3$ (50 mL). The organic layer was dried over brine solution and anhydrous Na_2SO_4. The combined fractions were concentrated under reduced pressure to get the desired compound in high yeilds.

3.1.2. Synthesis of tertiary and secondary amides



In a two necked round bottom flask amine (5.5 mmol) and Et_3N (6.25 mmol) was added in 20 mL of dichloromethane solution. In the reaction mixture acyl chloride (5.0 mmol) was added in one portion at room temperature, and stirred for 2 h. The reaction mixture was then diluted with dichloromethane (30 mL) and was transferred to a separating funnel, washed with 1N HCl (50 mL), and saturated solution of $NaHCO_3$ (50 mL). The organic layer was dried over brine solution and anhydrous Na_2SO_4 and filtered on a short silica gel column and washed with ethyl acetate/hexane (1:1). The combined fractions were concentrated under reduced pressure.

3.2.1. General procedure for hydrosilylative reduction of primary amides to primary amines

Amide (0.5 mmol) and $PhSiH_3$ (184 μL, 1.5 mmol) was sequentially added to a 3 mL dry toluene solution of the catalyst **1** (2 mol%, 0.025 mmol) and the closed reaction vessel was heated at 110 ºC for given the reaction time. After completion of reaction, the solution was cooled, diluted with 3 mL of EtOAc and was subjected to GC-MS analysis using mesitylene as internal standard to determine the conversion. Then 2 mL of 1M HCl solution in ether was added to isolate the corresponding amine salt. Precipitate was filtered and washed with ether to get pure amine salt. The isolated product was characterized by NMR spectroscopy.

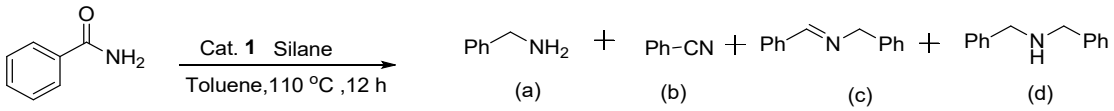
3.2.2. General procedure for hydrosilylative reduction of tertiary and secondary amides to corresponding amines

Amide (0.5 mmol) and $PhSiH_3$ (184 μL, 1.5 mmol) was sequentially added to a 3 mL dry toluene solution of the catalyst **1** (2 mol%, 0.025 mmol) and the closed reaction vessel was heated at 110 ºC for given reaction time. After completion of reaction, the solution was cooled, diluted with 3 mL of EtOAc and washed with 0.1M methanolic NaOH

solution (0.1 M, 2×10 mL). The organic phase was subjected to GC-MS analysis using mesitylene as internal standard to determine the conversion. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography using silica/neutral alumina (hexane/EtOAc). The isolated product was characterized by NMR spectroscopy. For entries 2 and 6 in Table S5 and for all entries except 2, 3, 8, 9, and 12 in Table S7, products were isolated as hydrochloride salts.

3.3. Optimization Table

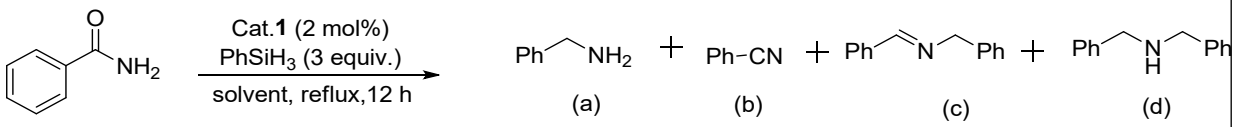
Table S2. Screening of silane and catalyst loading for reduction of primary amide catalyzed by **1** [a]



Entry	Catalyst loading (mol%)	Silane (x equiv.)	Conversion (%)	Product Distribution Ratio			
				(a)	(b)	(c)	(d)
1.	5	$PhSiH_3$ (4)	100	81	-	13	6
2.	5	Ph_2SiH_2 (4)	15	100	-	-	-
3.	5	Ph_3SiH (4)	0	-	-	-	-
4.	5	Et_3SiH (4)	0	-	-	-	-
5.	5	EtO_3SiH (4)	0	-	-	-	-
6.	5	$Ph(Me)_2SiH$ (4)	0	-	-	-	-
7.	5	TMDS (4)	7	100	-	-	-
8.	5	PMHS (4)	4	100	-	-	-
9.	5	$PhSiH_3$ (3)	100	50	-	50	-
10.	5	$PhSiH_3$ (2)	31	45	55	-	-
11.	5	$PhSiH_3$ (1)	3	100	-	-	-
12.	3	$PhSiH_3$ (4)	100	98	-	2	-
13.	3	$PhSiH_3$ (3)	100	46	7	44	3
14.	2	$PhSiH_3$ (4)	100	99	1	-	-
15.	2	$PhSiH_3$ (3)	100	98	1	1	-
16.	2	$PhSiH_3$ (2)	85	51	3	38	8
17.	0(Blank)	$PhSiH_3$ (4)	n.r	-	-	-	-

[a]Conversions are determined by GC–MS with mesitylene as internal standard.

Table S3. Solvent screening for reduction of primary amide catalyzed by **1**[a]



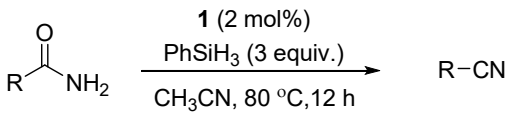
Entry	Solvent	Temperature (°C)	Conversion (%)	Product Distribution Ratio			
				(a)	(b)	(c)	(d)
1.	DCM	40	0	-	-	-	-
2.	THF	70	40	50	50	-	-
3.	Acetonitrile	80	100	-	100	-	-
4.	1, 4 dioxane	110	89	64	-	1	35
5.	DMSO	110	0	-	-	-	-
6.	DMF	70	0	-	-	-	-
7.	Dimethyl carbonate(DMC)	90	14	86	14	-	-
8.	1,1,2,2,Tetrachloroethane	110	23	39	31	30	-
9.	Benzene	90	90	94	-	6	-
10.	Toluene	110	100	98	1	1	-

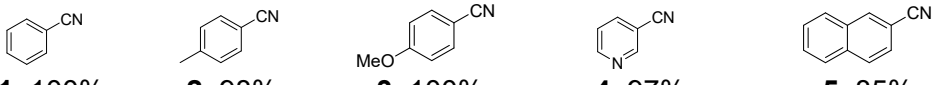
[a]Conversions are determined by GC–MS with mesitylene as internal standard.

3.4. Dehydration of primary amides to nitriles in CH_3CN

Amide (0.5 mmol) and $PhSiH_3$ (184 μL, 1.5 mmol) was sequentially added to a 3 mL dry acetonitrile solution of the catalyst **1** (2 mol%, 0.025 mmol) and the closed reaction vessel was heated at 80 ºC for given the reaction time. After completion of the reaction, the solution was cooled, diluted with 3 mL of EtOAc and subjected to GC-MS analysis using mesitylene as internal standard to determine the conversion.

Table S4. Solvent dependent dehydration of primary amide catalyzed by **1**.



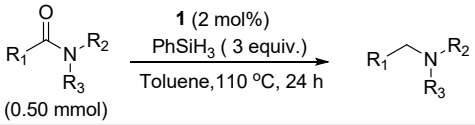


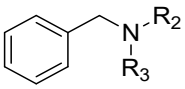
1, 100% **2**, 98% **3**, 100% **4**, 97% **5**, 85%

[a]Yields are determined by GC–MS using mesitylene as an internal standard.

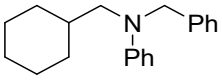
3.5.1 Hydrosilylative reduction of tertiary amide

Table S5. Tertiary amide reduction catalyzed by **1**.[a,b]

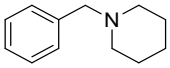




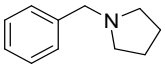
1, R_2, R_3 = CH_3 100% (95%)
2[c], R_2, R_3 = Et 88% (80%)
3, R_2, R_3 = Bn 99% (96%)
4, R_2 = CH_3, R_3 = Bn 80% (77%)
5, R_1 = CH_3, R_2, R_3= Bn 99% (95%)
6[c], R_2, R_3 = i-Pr 40%



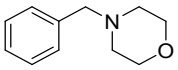
7, 68% (62%)



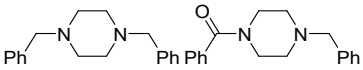
8, 95% (90%)



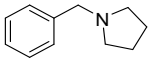
9, 94% (90%)



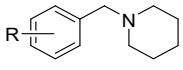
10, 96% (92%)



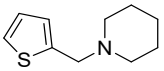
11, 100% (48:52)



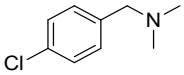
12, 52% (48%)



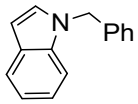
13 R = 4-OCH_3 95% (92%)
14 R = 4-CF_3 87% (82%)
15 R = 3,5-CF_3 83 (65%)
16 R = 4-OCH_3CO 97% (88%)



17, 70% (68%)



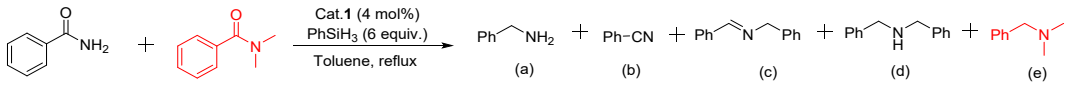
18[c], 52% (48%)



19, nr

[a]Conversions are determined by GC–MS using mesitylene as internal standard. [b]Isolated yields are given in parenthesis. [c]Isolated as hydrochloride salts.

Table S6. Competitive reaction between primary amide and tertiary amide catalyzed by **1**.[a]

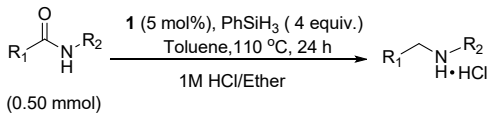


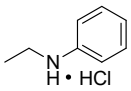
Entry	Time (h)	Primary Amide (%)	Tertiary Amide (%)	Product Distribution (%)				
				(a)	(b)	(c)	(d)	(e)
1.	0	100	100	0	0	0	0	0
2.	1	49.0	88.0	48.0	2.0	1	0	12.0
3.	3	0	82.0	96.0	0.4	3.0	0.6	18.0
4.	6	0	76.0	94.0	0	1	5.0	24.0

[a]Conversions are determined by GC–MS with mesitylene as internal standard. Data are averaged from three reactions.

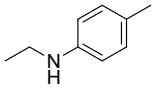
3.5.2 Hydrosilylative reduction of secondary amide

Table S7. Secondary amide reduction catalyzed by **1**.[a,b]

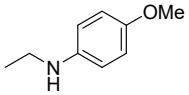




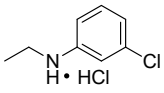
1, 100% (92%)



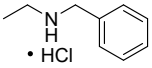
2[c], 95% (90%)



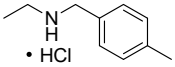
3[c], 98% (91%)



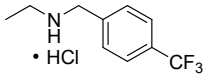
4, 87% (82%)



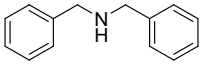
5, 100% (94%)



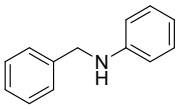
6, 98% (95%)



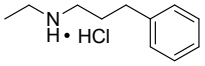
7, 93% (85%)



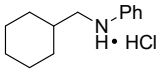
8[c], 52% (45%)



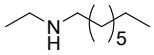
9[c], 50% (46%)



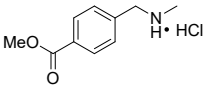
11, 83% (78%)



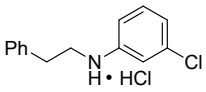
10, 98% (92%)



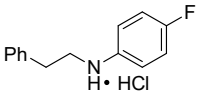
12, 88%



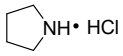
13[d], 96% (90%)



14[d], 87% (80%)



15[d], 85% (63%)



16, 100% (77%)

[a]Conversions are determined by GC–MS using mesitylene as internal standard. [b]Isolated yields are given in parenthesis. [c]Isolated as free amine after chromatography on neutral alumina. [d]36 h.

4. Mechanistic Studies

4.1. ^{1}H NMR of [Ni-H] species

In a screw cap NMR tube a 1:2 mixture of **1** and $PhSiH_3$ in $CDCl_3$ was heated for 2 h and then subjected to ^{1}H NMR analysis to observed the [Ni-H] species.

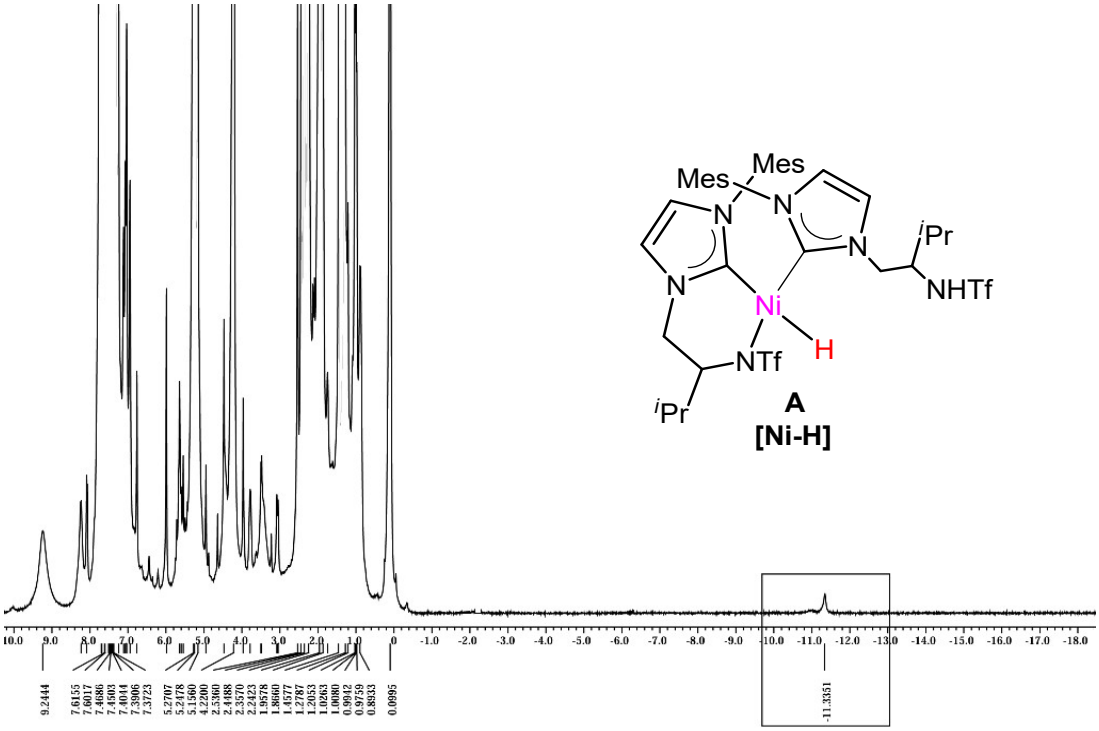
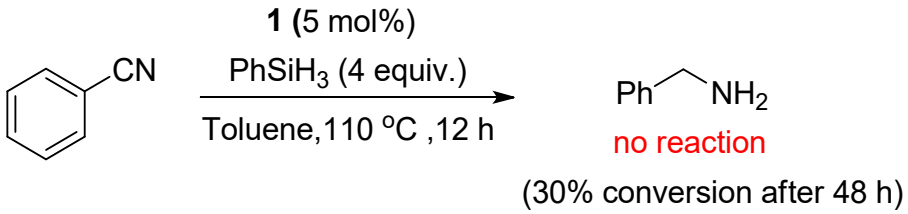


Figure S35. ^{1}H NMR for [**Ni-H**] species observed after reaction of **1** with $PhSiH_3$.

4.2. Attempted reduction of nitrile to primary amine



Scheme S8. Reduction of nitrile to primary amine under the catalytic condition.

4.3. Reaction profile studies

4.3.1. Primary amide reduction

Benzamide (0.5 mmol) and $PhSiH_3$ (184 uL, 1.5 mmol) was sequentially added to a 3 mL dry toluene solution of the catalyst **1** (2 mol%, 0.025 mmol) and the closed reaction vessel was placed on preheated (110 ºC) oil bath with stirring. After stipulated time intervals, 200 uL of aliquots were taken out with hypodermic needle and quenched with 800 uL of EtOAc. Samples were subjected to GC-MS analysis using mesitylene as internal standard to determine the conversion. Data are averaged from three reactions.

4.3.2. Reduction of 1:1 mixture of benzamide and benzonitrile

Benzamide (0.25 mmol), benzonitrile (0.25 mmol and $PhSiH_3$ (184 uL, 1.5 mmol) was sequentially added to a 3 mL dry toluene solution of the catalyst **1** (2 mol%, 0.025 mmol) and the closed reaction vessel was placed on preheated (110 ºC) oil bath with stirring. After stipulated time intervals, 200 uL of aliquots were taken out with hypodermic needle and quenched with 800 uL of EtOAc. Samples were subjected to GC-MS analysis using mesitylene as internal standard to determine the conversion. Data are averaged from three reactions.

4.3.3. Competitive reaction between 1:1 mixture of benzamide and N,N-dimethylbenzamide

Benzamide (0.5 mmol), N,N–dimethylbenzamide (0.5 mmol) and $PhSiH_3$ (369 uL, 3 mmol) was sequentially added to a 5 mL dry toluene solution of the catalyst **1** (4 mol%, 0.050 mmol) and the closed reaction vessel was placed on preheated (110 ºC) oil bath with stirring. After stipulated time intervals (1 h, 3 h and 6 h) 200 uL of aliquots were taken out with hypodermic needle and quenched with 800 uL of EtOAc. Samples were subjected to GC-MS analysis using mesitylene as internal standard to determine the conversions (Table S6).

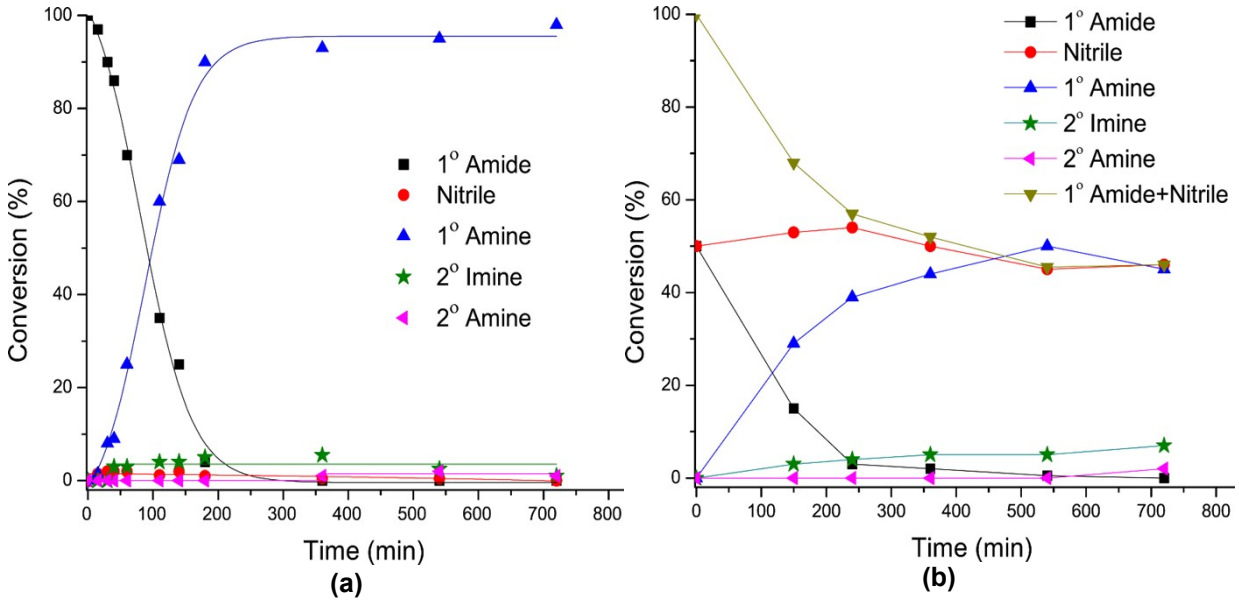
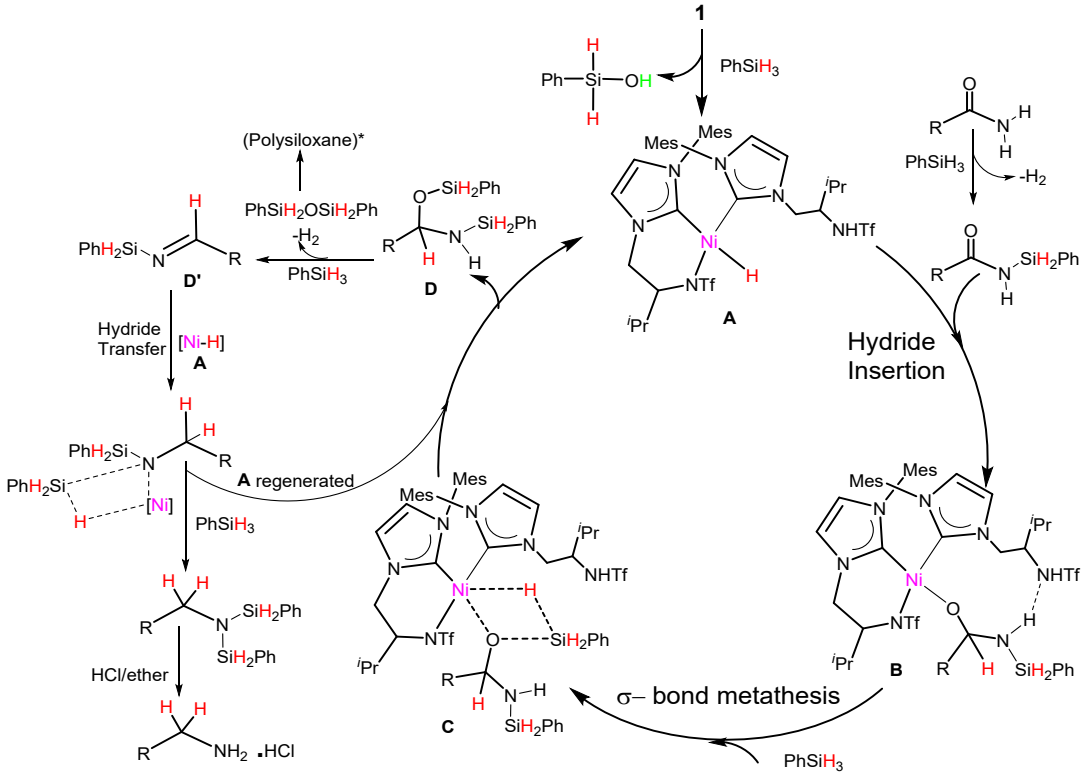
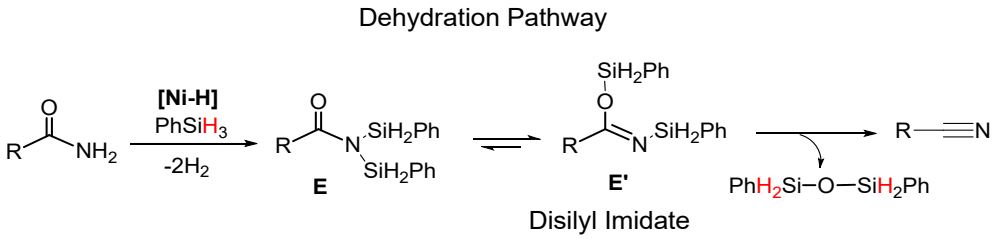


Figure S36. Reaction profiles for benzamide reduction in the absence (a), and in the presence of equimolar benzonitrile (b). Data are averaged from three reactions.



Scheme S9. Proposed reaction pathway.

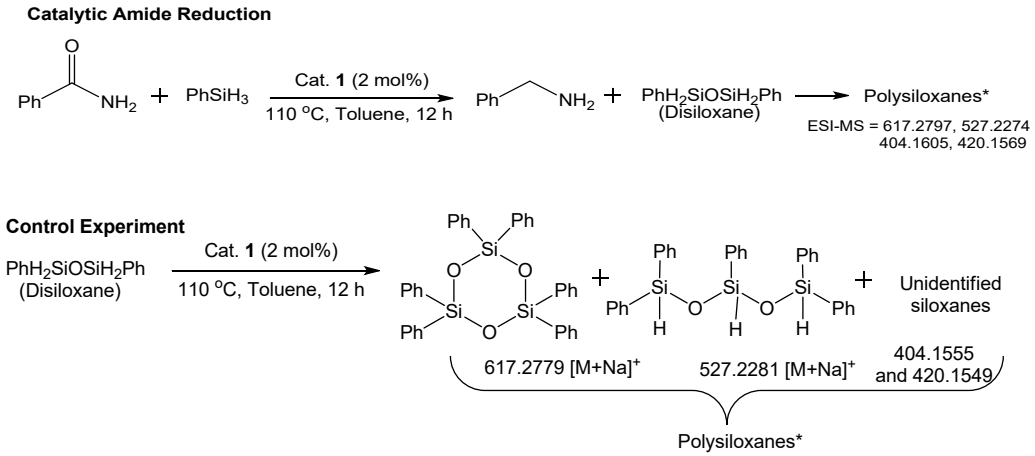
4.4. Silylative dehydration mechanism for primary amide



Scheme S10. Proposed reaction pathway for silylative dehydration.

4.5. Identification of side product (siloxanes)

To identify the side product siloxane, ESI-MS analysis of the reaction mixture obtained after the catalytic primary amide reduction was performed. In the ESI-MS spectrum, different mass distribution for polysiloxanes was observed instead of disiloxane. To confirm that polysiloxanes were obtained from the polymerization of disiloxane, a control experiment was performed (scheme 10). At first, the disiloxane ($PhH_2SiOSiH_2Ph$) was synthesized according to a literature procedure,[10] and then reacted with catalyst **1** under the standard catalytic conditions. The reaction mixture obtained after 12 h was subjected to ESI-MS analysis (Figure S36). The same mass distribution pattern was observed as that with primary amide reduction. This experiment suggests that the disiloxane was converted to polysiloxane.



Scheme S11. Control experiment to show the formation of polysiloxanes.

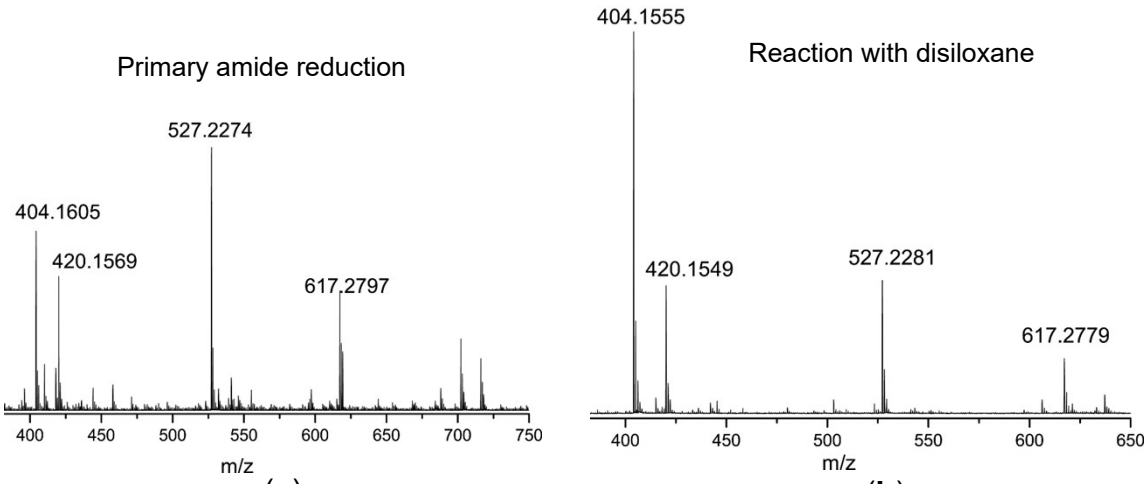
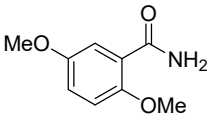
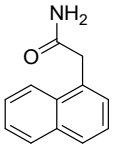


Figure S37. ESI-MS spectra of reaction mixture of (**a**) catalytic primary amide reduction (**b**) control experiment.

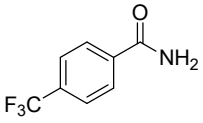
5. Spectral data of the primary amides



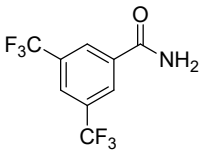
^{1}H ($CDCl_3$, 500 MHz): δ 7.77 (br, s, 1H), 7.68 (d, *J* = 2.9 Hz, 1H), 6.95 (dd, *J* =2.8 Hz, 8.9 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.11 (br, s, 1H), 3.85 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 153.8, 152.1, 121.3, 120.0, 115.6, 113.0, 56.4, 55.8.



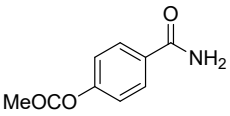
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.47 – 7.41 (m, 2H), 5.66 (s, 1H)), 5.31 (s, 1H), 4.03 (s, 2H).



^{1}H ($CDCl_3$, 500 MHz): δ 7.91 (d, *J* = 9.9 Hz, 2H), 7.71 (d, *J* = 12.9 Hz, 2H), 6.11 (br, s, 1H), 5.82 (br, s, 1H); ^{13}C NMR DMSO-D_6, 100 MHz): δ 169.3, 140.7, 133.7 (q, *J* = 31.6 Hz), 130.9, 127.8 (q, *J* = 3.74 Hz), 126.5 (q, *J* = 270.5 Hz).

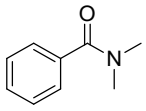


^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.51 (s. 2H), 8.47 (br. s. 1H), 8.21 (s, 1H) 7.86 (br. s. 1H). ^{13}C NMR (100 MHz, CD_3OD): δ 168.62, 137.63, 133.13 (q. *J* =33.75 Hz), 129.36, 126.16 (q. *J* =3.73 Hz), 124.59 (q. *J* = 272.01 Hz).

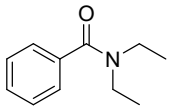


^{1}H ($CDCl_3$, 500 MHz): δ 7.97 (s, 2H), 7.79 (s, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.48, 166.4, 137.3, 132.77, 129.5, 127.3, 52.2.

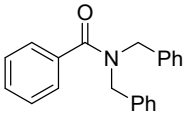
Spectral data of the tertiary amides



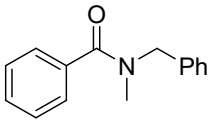
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 5H), 3.05 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 136.2, 129.4, 128.2, 126.9, 39.5, 35.2.



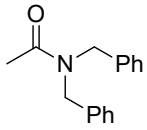
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37-7.32 (m, 5H), 3.50 (br, s, 2H), 3.25 (br, s, 2H), 1.24 (br, s, 3H), 1.09 (br, s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.4, 137.3, 129.1, 128.5, 128.4, 126.3, 43.3, 39.3, 14.2, 12.9.



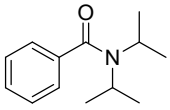
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51-7.49 (m, 2H), 7.40-7.34 (m, 7H), 7.30 (t, *J* = 7.1 Hz, 4H), 7.15 (br, d, *J* = 6.0 Hz, 2H), 4.71 (s, 2H), 4.40 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.2, 136.2, 129.60, 128.5, 128.4, 127.5, 127.0, 126.6, 51.4, 46.8.



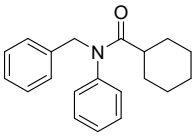
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50-7.48 (m, 2H), 7.44-7.36 (m, 6H), 7.32 (d, *J* = 5.7 Hz, 1H), 7.20 (m, 1H), 4.76 (s, 1H), 4.51 (s, 1H), 2.89 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ172.3, 171.6, 137.1, 136.7, 136.3, 131.5, 129.6, 129.0, 128.9, 128.8, 128.5, 128.2, 127.6, 127.0, 126.8, 55.1, 50.8, 37.0, 33.2.



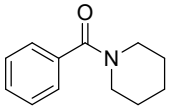
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.13 (m, 8H), 7.07-7.10 (m, 2H), 4.58 (s, 2H), 4.42 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 137.3, 136.4, 128.8, 128.6, 128.3, 127.7, 127.6, 126.4, 50.8, 48.0, 21.7.



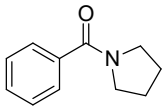
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.23 (m, 5H), 3.77 (s, 1H), 3.46 (s, 1H), 1.47 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.8, 129.8, 128.6, 128.4, 128.1, 125.5, 50.9, 45.8, 20.7.



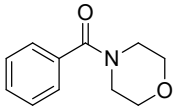
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.14 (m, 8H), 6.95-6.93 (m, 2H), 4.84 (s, 2H), 2.13 (t, *J* = 11.5 Hz, 1H), 1.72-1.51 (m, 7H), 1.24-1.13 (m, 1H), 0.98-0.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.3, 142.6, 137.9, 129.5, 128.7, 128.4, 128.3, 127.9, 127.2, 52.9, 41.7, 29.5, 25.7, 25.5.



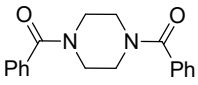
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (s, 5H), 3.69 (br, s, 2H), 3.31 (s, 2H), 1.65 (s, 4H), 1.49 (br, s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 136.5, 129.4, 128.3, 48.8, 43.2, 26.6, 25.7, 24.6.



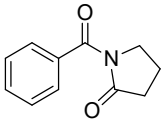
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 2H), 7.33-7.32 (m, 3H), 3.46 (br, s, 4H), 1.84 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.4, 136.9, 129.5, 127.9, 126.8, 49.1, 46.2, 25.2.



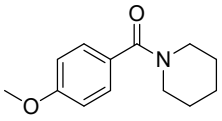
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41-7.37 (m, 5H), 3.70 (br, s, 6H), 3.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5, 135.4, 129.9, 128.6, 127.1, 66.9, 48.4, 42.6.



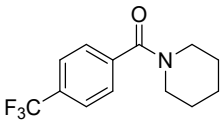
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (s, 10H), 3.72 (br, s, 4H), 3.51 (br, s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 135.1, 130.2, 128.7, 127.1, 47.9, 42.5.



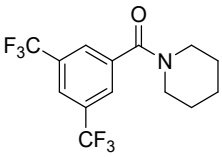
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.37 (m, 5H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 2.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.6, 170.8, 134.6, 132.0, 129.0, 127.8, 46.6, 33.4, 17.7.



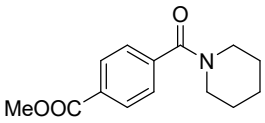
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (dd, *J* = 1.24 Hz, 8.5 Hz, 2H), 6.87 (dd, *J* = 1.24 Hz, 8.5 Hz, 2H), 3.78 (d, *J* = 1.8 Hz, 3H), 3.50 (br s, 4H); 1.64 (br s, 2H), 1.63 (br s, 4H);^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 160.5, 128.9, 128.6, 113.6, 55.4, 26.1, 24.7.



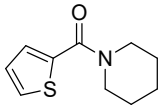
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.62 (m, 2H), 3.19 (m, 2H), 1.57 (m, 4H), 1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 140.1 (q, *J* = 1.3 Hz), 131.1 (q, *J* = 32.6 Hz), 127.1, 125.4 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.3 Hz), 48.5, 43.0, 26.4, 25.4, 24.3.



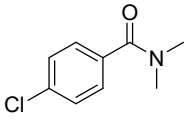
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91 (s, 1H), 7.85 (s, 2H), 3.73 (br, 2H), 3.32 (br s, 2H); 1.71 (br s, 4H), 1.56 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 138.4, 132.0 (q, *J* = 35.7 Hz), 128.9, 127.2, 124.0 (q, *J* = 275.4 Hz), 121.8 (q, *J* = 275.4 Hz), 113.6, 48.8, 43.5, 26.5, 25.5, 24.3.



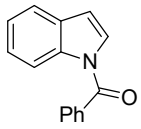
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, *J* = 9.9 Hz, 2H), 7.37 (d, *J* = 10.7 Hz, 2H), 3.87 (s, 3H), 3.48 (s, 2H), 2.34 (br s, 4H), 1.57-1.52 (m, 4H), 1.47 (br, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.1, 166.3, 140.7, 130.7, 129.6, 126.6, 52.2, 48.5, 43.0, 26.4, 25.4, 24.4.



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38 (dd, *J*= 1.2, 4.7 Hz, 1H), 7.22 (dd, *J* = 1.2, 3.6 Hz, 1H), 6.99 (dd, *J* = 3.6, 4.7 Hz, 1H), 3.62 (t, *J* = 5.5 Hz, 4H), 1.66-1.58 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.5, 137.7, 128.3, 128.1, 126.6, 26.2, 24.7.

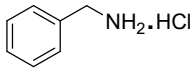


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.21 (m, 4H), 3.09 (s, 3H), 2.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.6, 135.1, 134.3, 128.6, 127.2, 38.1, 34.7.

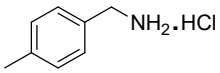


^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, *J* = 7.3 Hz, 1H), 7.74-7.72 (m, 2H), 7.62-7.57 (m, 2H), 7.54-7.50 (m, 2H), 7.38 (tt, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 7.33- 7.28 (m, 2H), 6.60 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8, 136.1, 134.6, 131.9, 130.8, 129.2, 128.6, 127.7, 125.0, 124.0, 116.4, 108.6.

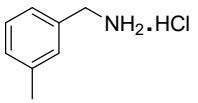
6. Spectral data of the isolated primary amine salts



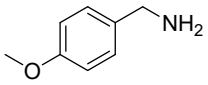
^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.60 (br, s, 3H), 7.47 (d, *J* = 6.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 3H), 3.93 (s, 2H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 134.6, 129.5, 129.0, 128.9, 42.6.



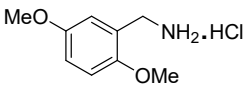
^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.50 (br, s, 3H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 2H), 3.89 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 138.2, 131.6, 129.6, 129.5, 42.4.



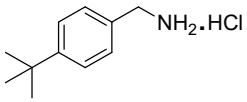
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.50 (br, s, 3H), 7.27-7.13 (br, m, 5H), 3.89 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 137.3, 133.7, 129.2, 128.6, 128.1, 125.7, 41.8, 20.6.



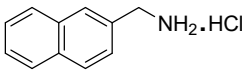
^{1}H NMR (D_2O, 500 MHz): δ 7.45 (s, 2H), 7.09 (s, 2H), 4.16 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (D_2O, 125 MHz): δ 157.3, 128.4, 123.0,112.4, 53.2, 48.4.



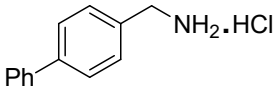
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.43 (br, s, 3H), 7.10-7.0 (m, 3H), 3.91 (d, *J* = 5.1, Hz, 2H), 3.75 (s, 3H), 7.69 (s, 3H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 152.7, 150.9, 128.6, 115.9, 114.0, 111.6, 55.7, 55.3, 41.2.



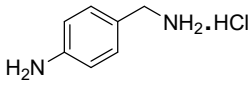
^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.48 (br, s, 3H), 7.36 (br, s, 4H), 3.88 (s, 2H), 1.22 (s, 9H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 151.4, 131.7, 129.3, 125.8, 42.3, 34.8, 31.6.



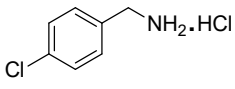
^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.50 (br, s, 3H), 8.05 – 7.79 (m, 4H), 7.54 (s, 1H), 7.45 (s, 2H), 4.06 (s, 2H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 133.0, 132.1, 129.2, 128.7, 128.4, 128.2, 128.1, 128.13, 127.0, 42.8.



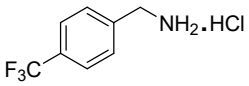
^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.52 (br, s, 3H), 7.67 – 7.62 (m, 4H), 7.55 (d, *J* =7.9 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H); 4.00 (d, *J* = 5.5 Hz, 2H) ^{13}C NMR (DMSO-D_6, 100 MHz): δ 140.7, 140.0, 133.8, 130.1, 129.5, 128.2, 127.3, 127.2, 42.3



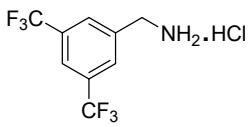
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.43 (br, s, 3H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 133.4, 132.6, 130.2, 122.4, 41.5.



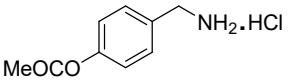
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.62 (br, s, 3H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 133.6, 133.5, 131.5, 128.9, 41.9.



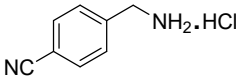
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.75 (br, s, 3H), 7.77-7.73 (m, 4H), 4.10 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 138.7, 129.7, 128.8 (q, *J* = 31.0 Hz) 125.2, 123.0, 41.5; ^{19}F NMR (470 MHz, DMSO-D_6, 292 K): –61.01 (CF_3).



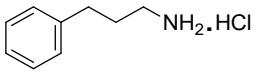
^{1}H (DMSO-D_6, 500 MHz): δ 8.75 (br, s, 3H), 8.31 (s, 2H), 8.10 (s, 1H), 4.23 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 137.4, 130.3, 130.1 (q, *J* = 33.3 Hz) 124.2. (q, *J* = 270.6 Hz) 121.9, 40.9; ^{19}F NMR (470 MHz, DMSO-D_6, 292 K): –61.23 (CF_3).



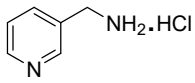
^{1}H (DMSO-D_6, 500 MHz): δ 8.73 (br, s, 3H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 4.07 (d, *J* = 4.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 165.6, 139.1, 129.1, 128.9, 51.9, 41.4



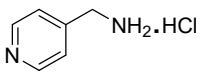
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.64 (br, s, 3H), 7.85 (s, 2H), 7.67 (s, 2H), 4.07 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 140.2, 132.9, 130.4, 119.1, 111.6, 42.3.



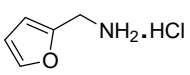
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.13 (br, s, 3H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.21-7.16 (m, 3H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 1.88-1.82 (m, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 140.8, 128.2, 128.1, 125.8, 38.1, 31.7, 28.5.



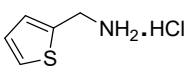
^{1}H NMR (CD_3OD, 400 MHz): δ 9.04 (s, 1H), 8.92 (d, *J* = 4.2 Hz, 1H), 8.73 (d, *J* = 7.9 Hz, 1H), (t, *J* = 6.1 Hz, 1H), 4.41 (s, 2H); ^{13}C NMR (CD_3OD, 100 MHz): δ 147.1, 142.9, 142.5, 133.6, 127.5, 39.6.



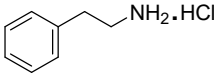
^{1}H NMR (DMSO-D_6, 500 MHz): δ 9.17 (br, s, 3H), 8.98 (d, *J* = 5.1 Hz, 2H), 8.21 (d, *J* = 5.7 Hz, 2H), 4.36 (br, s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 151.9, 141.8, 126.3, 41.0.



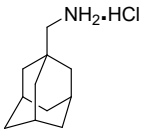
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.50 (br, s, 3H), 7.67 (s, 1H), 6.48 (d, *J* = 32.0 Hz, 2H), 3.99 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 147.7, 143.5, 110.9, 110.1, 34.9.



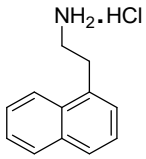
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.55 (br, s, 3H), 7.51 (s, 1H), 7.23 (s, 1H), 7.00 (s, 1H), 4.15 (s, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 134.8, 128.6, 126.8, 126.7, 36.2.



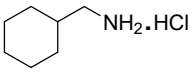
^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.21 (br, s, 3H), 7.26 – 7.19 (m, 5H), 2.94 (s, 2H), 2.86 (s, 2H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 136.8, 128.0, 127.9, 126.0, 39.8, 32.3.



^{1}H NMR (DMSO-D_6, 400 MHz): δ 7.92 (br, s, 3H), 2.45 (s, 2H), 1.89 (s, 3H), 2.55 (s, 3H), 1.62 – 1.45 (m, 12H,); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 50.4, 39.4, 36.6, 32.1, 27.8.

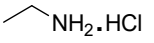


^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.30 (br, s, 3H), 8.15 (d, *J* = 9.9 Hz, 1H), 7.90 (d, *J* = 9.9 Hz, 1H), 7.79 (d, *J* = 9.9 Hz, 1H), 7.56-7.47 (m, 2H), 7.41-7.37 (m, 2H), 3.36 (d, *J* = 9.9 Hz, 2H), 3.05-3.00 (m, 2H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 134.0, 131.81, 129.2, 127.9, 127.4, 126.9, 126.3, 126.2, 124.0, 30.6.

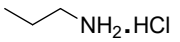


^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.03 (br, s, 3H), 2.44 (br, d, J = 22.6 Hz, 2H), 1.60 – 1.48 (m, 6H,) 1.02 (br, s, 3H), 0.78 (br, s, 2H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 44.8, 35.8, 30.3, 26.1, 25.5.

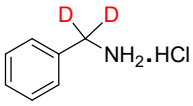
^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.05 (br, s, 3H), 2.66 (br, s, 2H), 1.49 (s, 2H), 1.20 (s, 6H), 0.81 (s, 3H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 38.3, 30.3, 26.5, 25.7, 21.5, 13.8.



^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.00 (br, s, 3H), 2.71 (br, s, 2H), 1.08 (s, 3H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 33.1, 11.6.

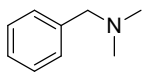


^{1}H NMR (DMSO-D_6, 500 MHz): δ 8.02 (br, s, 3H), 2.64 (s, 2H), 1.52 (s, 2H), 0.84 (s, 3H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 40.9 (merged in DMSO-D_6 confirmed by DEPT (135) NMR), 19.9, 10.6.

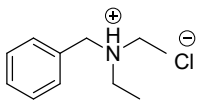


^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.56 (br, s, 3H), 7.47 (d, *J* = 6.7 Hz, 2H), 7.37 – 7.30 (m, 3H), 3.93 (s, 0.054H); ^{13}C NMR (DMSO-D_6, 100 MHz): δ 134.5, 129.5, 129.0, 128.9, 42.5 – 41.6 (quintet for CD_2); ESI-MS calcd. for $[M]^+$ M=$C_7H_8D_2N$: 110.09367, found: 110.0964.

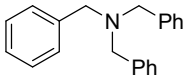
Spectral data for the isolated tertiary amines



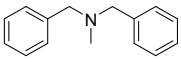
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 – 7.22 (m, 5H), 3.38 (s, 2H), 2.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 129.4, 128.3, 127.2, 64.2, 45.0.



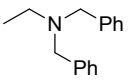
^{1}H NMR (D_2O, 400 MHz): δ 7.41 – 7.39 (m, 5H), 4.20 (s, 2H), 3.14 – 3.05 (m, 4H), 1.19 (t, *J* = 7.32 Hz, 6H); ^{13}C NMR (D_2O, 100 MHz): δ 130.8, 130.6, 130.0, 129.3, 55.9, 46.7, 8.1.



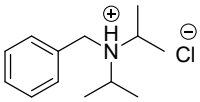
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, *J* = 6.7 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 3.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.7, 128.8, 128.3, 126.9, 58.0.



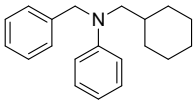
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.25 (m, 7H), 7.23 (t, *J* = 7.3 Hz, 3H), 3.51 (s, 4H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.4, 129.0, 128.3, 127.0, 61.9, 42.3.



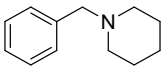
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.26 (m, 10H), 3.61 (s, 4H), 2.57 – 2.52 (q, 2H) 1.11 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.1, 128.9, 128.2, 126.8, 57.8, 47.2, 12.0.



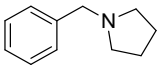
^{1}H NMR (D_2O, 400 MHz): δ 7.38 (s, 5H), 4.24 (s, 2H), 1.32 (d, *J* = 6.7 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (D_2O, 100 MHz): δ 130.7, 130.6, 129.6, 129.1, 54.3, 50.0, 17.8, 17.1.



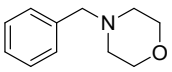
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 – 7.14 (m, 7H), 6.67 – 6.62 (m, 3H), 4.59 (s, 2H), 3.26 (d, *J* = 6.7 Hz, 2H), 1.83 – 1.66 (m, 6H), 1.26 – 1.17 (m, 3H), 1.00 – 0.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 138.9, 129.2, 128.6, 126.7, 126.6, 115.8, 112.3, 58.5, 55.4, 37.0, 31.5, 26.7, 26.2.



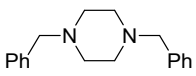
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 – 7.22 (m, 5H), 3.46 (s, 2H), 2.37 (t, *J* = 4.9 Hz, 4H) 1.57 (m, 4H) 1.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.7, 129.3, 128.2, 127.0, 126.9, 64.0, 54.6, 26.1, 24.5.



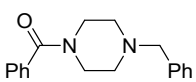
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.28 (m, 4H), 7.25 (t, *J* = 3.1 Hz, 1H), 3.61 (s, 2H), 2.50 (m, 4H), 1.77 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.3, 129.1, 128.3, 127.0, 60.8, 54.2, 23.5.



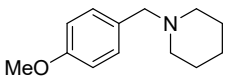
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 – 7.26 (m, 5H), 3.70 (t, *J* = 4.3 Hz, 4H), 3.49 (s, 2H) 2.43 (t, *J* = 4.3 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 129.3, 128.3, 127.2, 67.1, 63.6, 53.7.



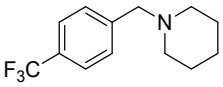
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 – 7.23 (m, 10H), 3.51 (s, 4H), 2.48 (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 129.3, 128.3, 127.0, 63.2, 53.2.



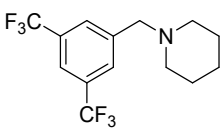
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 – 7.23 (s, 5H), 7.35-7.30 (m, 5H), 3.78 (br, s, 2H), 3.52 (s, 2H), 3.40 (br, s, 2H), 2.51 (br, s, 2H), 2.37 (br, s, 2H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 137.6, 135.9, 129.7, 129.2, 128.5, 128.4, 127.4, 127.1, 63.0, 53.5, 52.9, 47.8, 42.2.



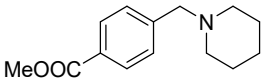
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 3.42 (s, 2H) 2.37 (br, s, 4H), 1.58 – 1.56 (m, 4H) 1.44-1.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 130.6, 130.2, 113.5, 63.2, 55.3, 54.3, 25.9, 24.4.



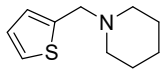
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 2H), 2.36 (br, m, 4H), 1.58 – 1.54 (m, 4H), 1.44 – 1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 140.1 (q, *J* = 1.3 Hz), 131.1 (q, *J* = 32.6 Hz), 127.1, 125.4 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.3 Hz), 63.3, 54.6, 26.0, 24.3.; ^{19}F NMR (470 MHz, $CDCl_3$, 292 K): –62.45 (CF_3).



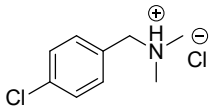
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, 1H), 7.85 (s, 2H), 3.73 (br, 2H), 3.32 (br s, 2H); 1.71 (br s, 4H), 1.56 (br s, 2H);^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 138.4, 132.0 (q, *J* = 35.7 Hz), 128.9, 127.2, 124.0 (q, *J* = 275.4 Hz), 121.8 (q, *J* = 275.4 Hz),113.6, 48.8, 43.5, 26.5, 25.5, 24.3; ^{19}F NMR (470 MHz, $CDCl_3$, 292 K): –62.66 (CF_3).



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, *J*= 7.7 Hz, 2H), 7.37 (d, *J*= 7.7 Hz, 2H), 3.87 (s, 3H), 3.48 (s, 2H), 2.34 (br s, 4H), 1.54 (m, 4H), 1.40 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.1, 144.2, 129.5, 129.0, 128.8, 63.5, 54.6, 52.0, 25.9, 24.3.

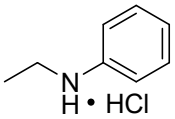


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21-7.19 (m, 1H), 6.94-6.88 (m, 2H), 3.69 (s, 2H), 2.41 (br m, 4H), 1.61-1.55 (m, 4H), 1.44-1.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.1, 126.4, 125.9, 124.7, 57.9, 54.2, 26.0, 24.4.

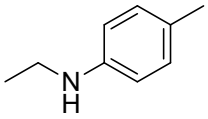


^{1}H NMR (DMSO-D_6, 500 MHz): δ 11.04 (br, s, 1H), 7.76 (d, *J* = 5.7, Hz, 1H), 7.42 (d, *J* = 6.3, Hz, 1H), 7.42 (t, *J* = 8.5 Hz, 2H), 4.27 (s, 2H), 2.57 (s, 6H); ^{13}C NMR (DMSO-D_6, 125 MHz): δ 135.1, 134.3, 128.6, 127.2, 38.1, 34.7.

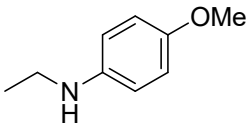
Spectral data for the isolated secondary amines



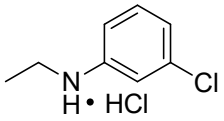
^{1}H NMR (D_2O, 500 MHz): δ 7.49 (d, *J* = 7.4 Hz, 3H), 7.38 (d, *J* = 7.1 Hz, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.4, 130.4, 130.0, 122.6, 47.4, 10.2.



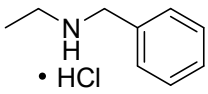
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.91 (d, *J* = 8.6 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 2H), 3.06 (q, *J* = 6.8 Hz, 2H), 2.16 (s, 3H), 1.77 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.9, 129.6, 126.6, 113.1, 39.0, 20.3, 14.8.



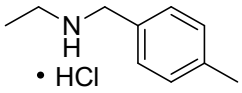
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.72-6.70 (m, 2H), 6.55-6.53 (m, 2H), 3.67 (s, 3H), 3.04 (q, J= 7.4 Hz, 2H), 1.17 (t, J= 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.4, 142.1, 114.9, 114.5, 55.8, 39.7, 14.8.



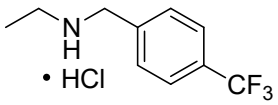
^{1}H NMR (CD_3OD, 500 MHz): δ 7.57 (s, 1H), 7.54 (d, *J* = 5.7 Hz, 2H), 7.44 (d, *J* = 5.7 Hz, 1H), 3.44 (q, *J* = 6.7 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz): δ 1.34 (t, *J* = 6.8 Hz, 3H); 137.8, 136.8, 132.8, 131.0, 124.2, 122.4, 48.4, 11.4.



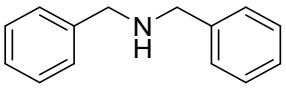
^{1}H NMR (D_2O, 500 MHz): δ 7.41 (s, 5H), 4.13 (s, 2H), 3.05 (q, *J* = 6.8 Hz, 2H), 1.21 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (D_2O, 125 MHz): δ 131.0, 129.7, 129.6, 129.3, 50.6, 42.5, 10.5.



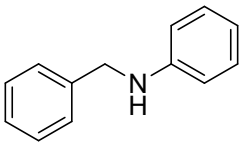
^{1}H NMR (D_2O, 500 MHz): δ 7.25 (q, *J* = 10.3 Hz, 4H), 4.07 (s, 2H), 3.01 (q, *J* = 6.9 Hz, 2H), 2.26 (s, 3H), 1.19 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (D_2O, 125 MHz): δ 140.1, 129.8, 129.7, 127.9, 50.4, 42.4, 20.3, 10.5.



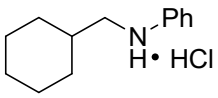
^{1}H NMR (CD_3OD, 500 MHz): δ 7.76 (d, *J* = 8 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 4.28 (s, 2H), 3.14 (q, *J* = 6.9 Hz, 2H), 1.34 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz): δ 137.0, 131.7, 127.0, 126.9, 51.2, 44.1, 11.4; ^{19}F NMR (470 MHz, CD_3OD, 292 K): -64.34 (CF_3).



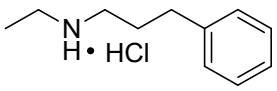
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 – 7.30 (m, 8H), 7.27 – 7.23 (m, 2H), 3.81 (s, 4H), 1.68 (br, s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.4, 128.5, 128.3, 127.1, 53.3.



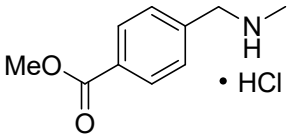
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 – 7.34 (m, 4H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 6.1 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.34 (s, 2H), 4.04 (br, s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.3, 139.5, 129.4, 128.8, 127.6, 127.3, 117.7, 112.7, 48.4.



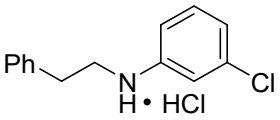
^{1}H NMR (D_2O, 500 MHz): δ 7.61-7.22 (m, 5H), 3.34-3.0 (m, 2H), 1.78-1.39 (m, 6H), 1.22-1.00 (m, 5H); ^{13}C NMR (D_2O, 125 MHz): δ 135.0, 130.4, 129.9, 122.4, 58.0, 34.2, 29.8, 25.5, 25.0.



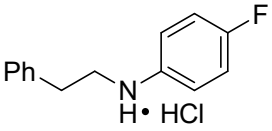
^{1}H NMR (CD_3OD, 500 MHz): δ 7.27-7.15 (m, 5H), 3.02 (d, *J* = 5.7 Hz, 2H), 2.97 (br, s, 2H), 2.70 (br, t, *J* = 6.8 Hz, 2H), 1.98 (br, s, 2H), 1.27 (t, *J* = 5.7 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz): δ 141.5, 129.5, 129.3, 127.3, 48.1, 44.2, 33.5, 29.0, 11.0.



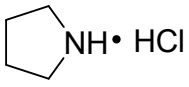
^{1}H NMR (D_2O, 500 MHz): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 4.20 (s, 2H), 3.84 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (D_2O, 125 MHz): δ 169.0, 136.1, 130.7, 130.2, 129.9, 52.8, 51.9, 32.4.



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (t, *J* = 6.9 Hz, 2H), 7.17 (m, 4H), 7.07 (td, *J* = 7.4, 1.1 Hz, 1H), 6.66 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.57 (td, *J* = 7.4, 1.7 Hz, 1H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.4, 138.8, 129.2, 128.7, 128.6, 127.8, 126.5, 119.5, 117.5, 111.6, 45.1, 35.3.



^{1}H NMR (D_2O, 500 MHz): δ 7.42-7.37 (m, 7H), 7.13 (t, *J* = 8.6 Hz, 2H), 4.18 (d, *J* = 3.4 Hz, 4H); ^{13}C NMR (D_2O, 125 MHz): δ 164.2, 132.2, 132.1, 129.9, 129.7, 129.3, 116.2, 116.1, 50.6, 49.9; ^{19}F NMR (470 MHz, D_2O, 292 K): -112.28.



^{1}H NMR (D_2O, 500 MHz): δ 3.18 (t. *J* = 6.8 Hz, 4H), 1.90 (m, 4H); ^{13}C NMR (D_2O, 125 MHz): δ 45.6, 23.7.

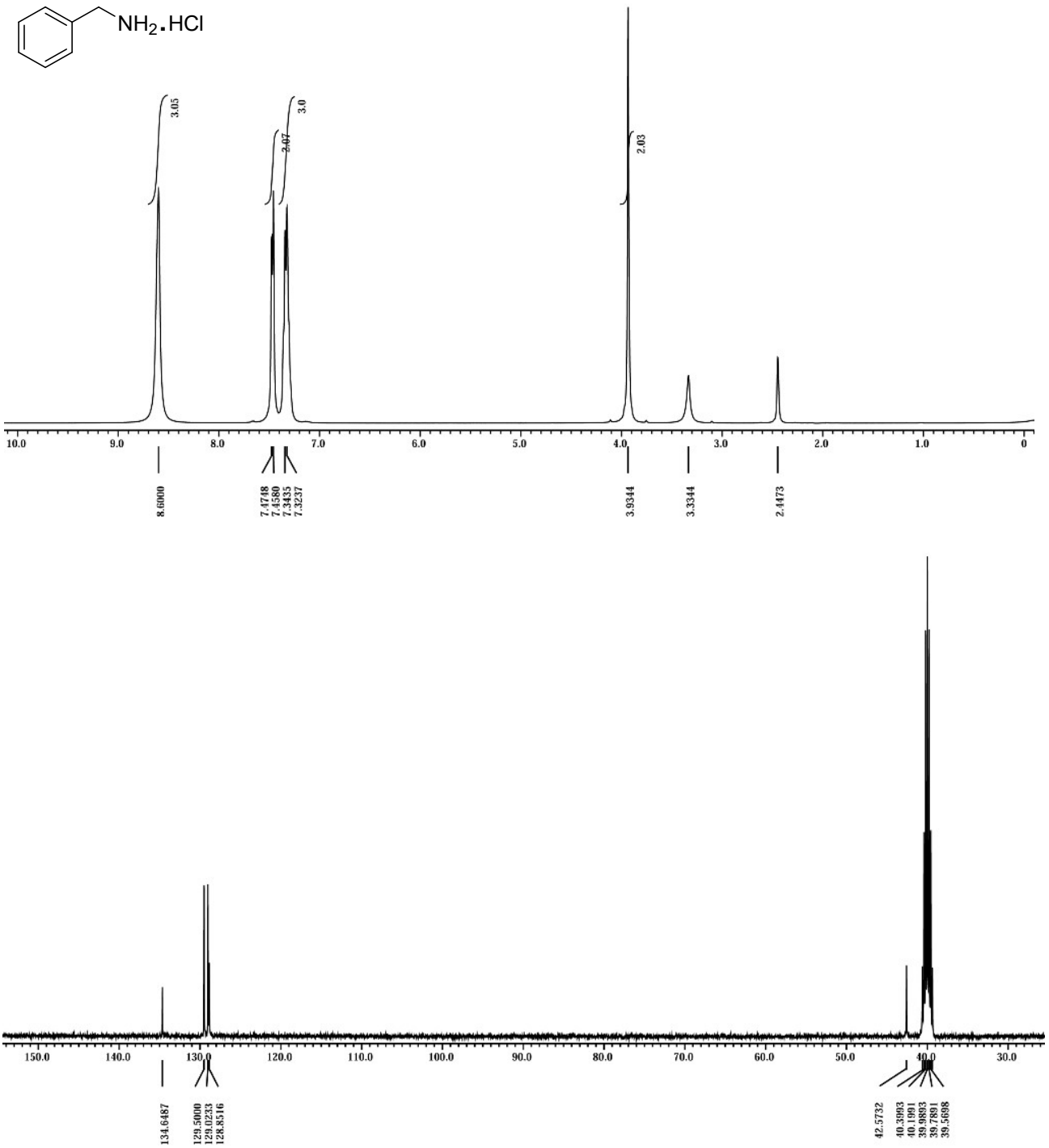


Figure S38. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

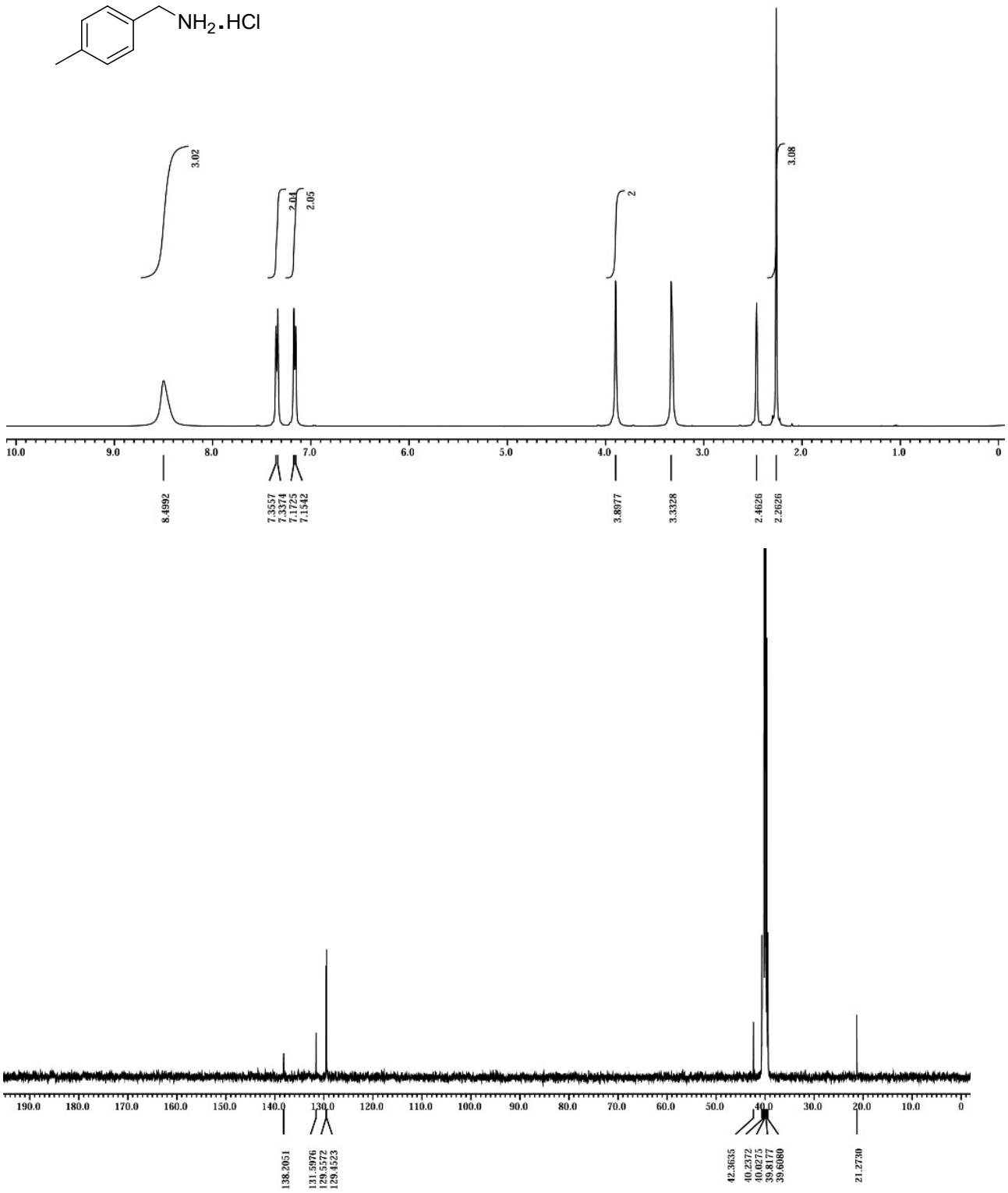


Figure S39. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

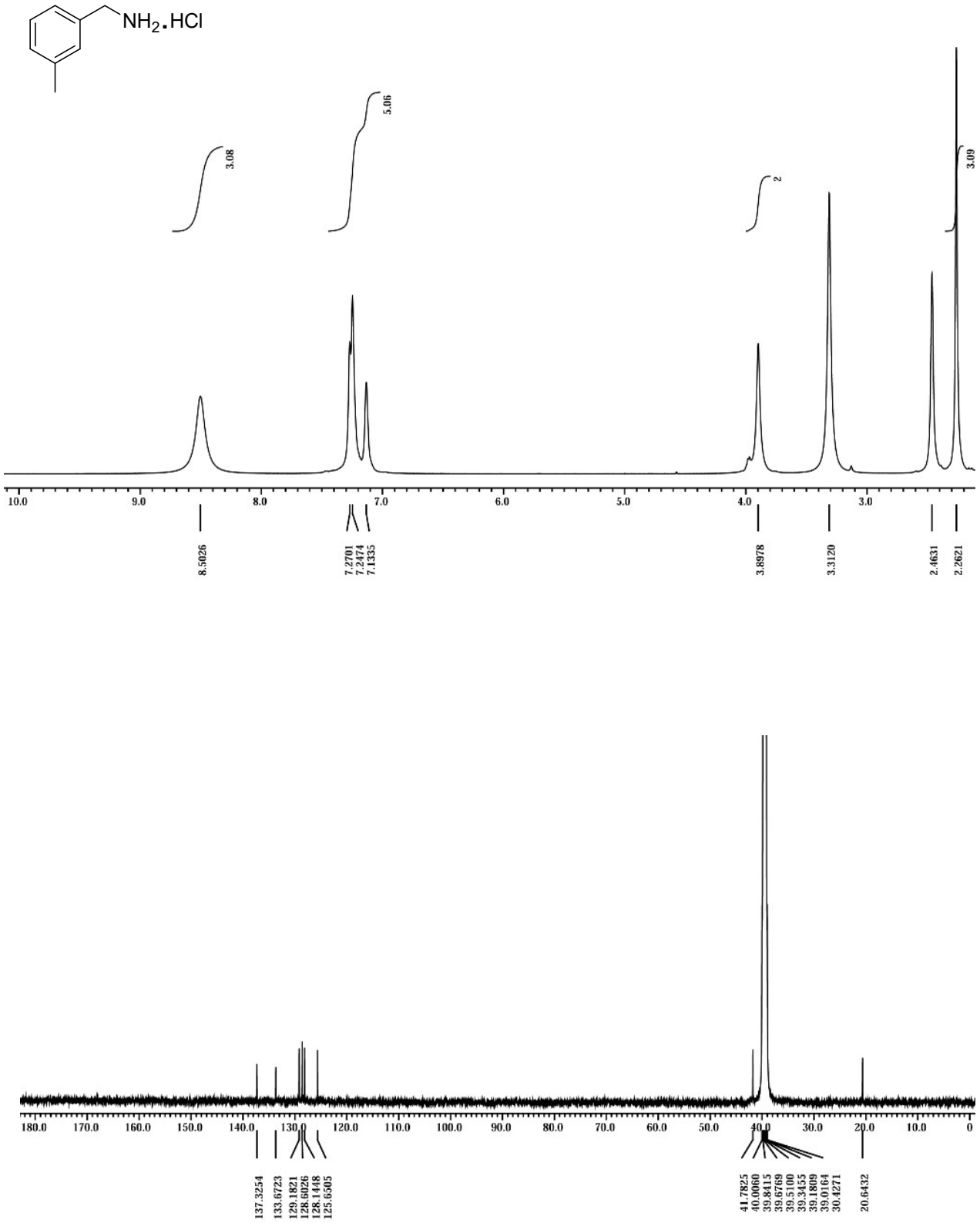


Figure S40. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

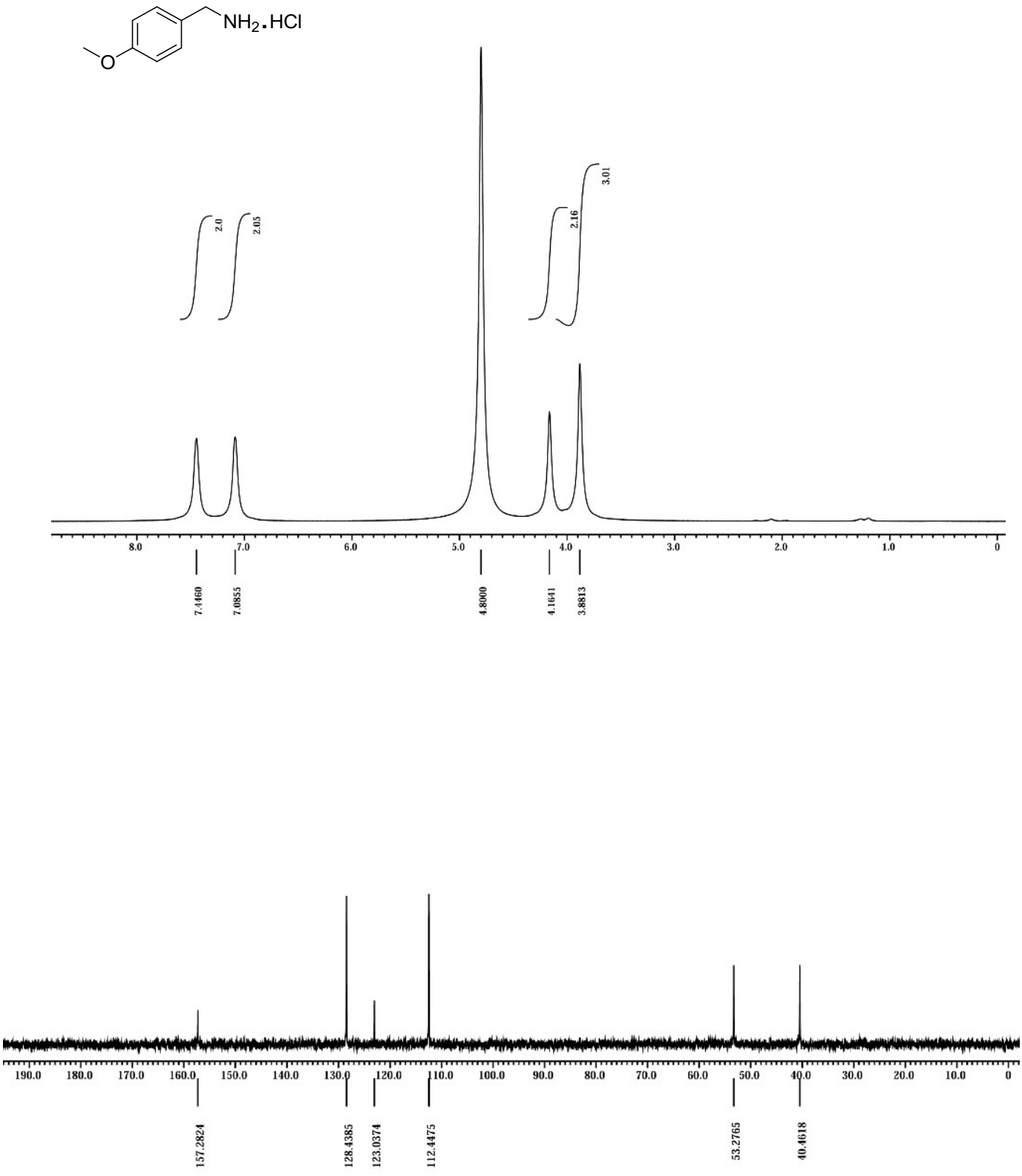


Figure S41. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

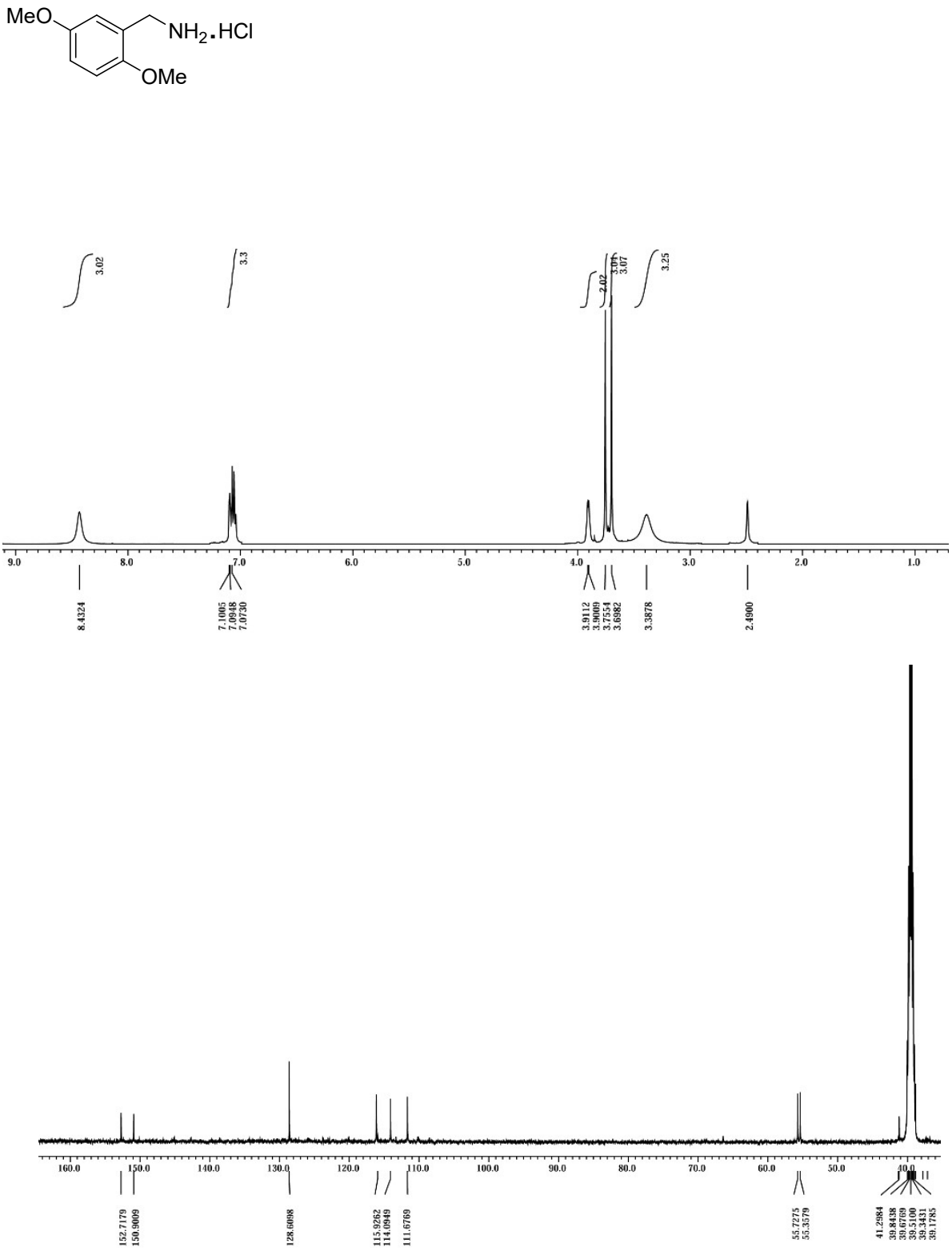


Figure S42. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

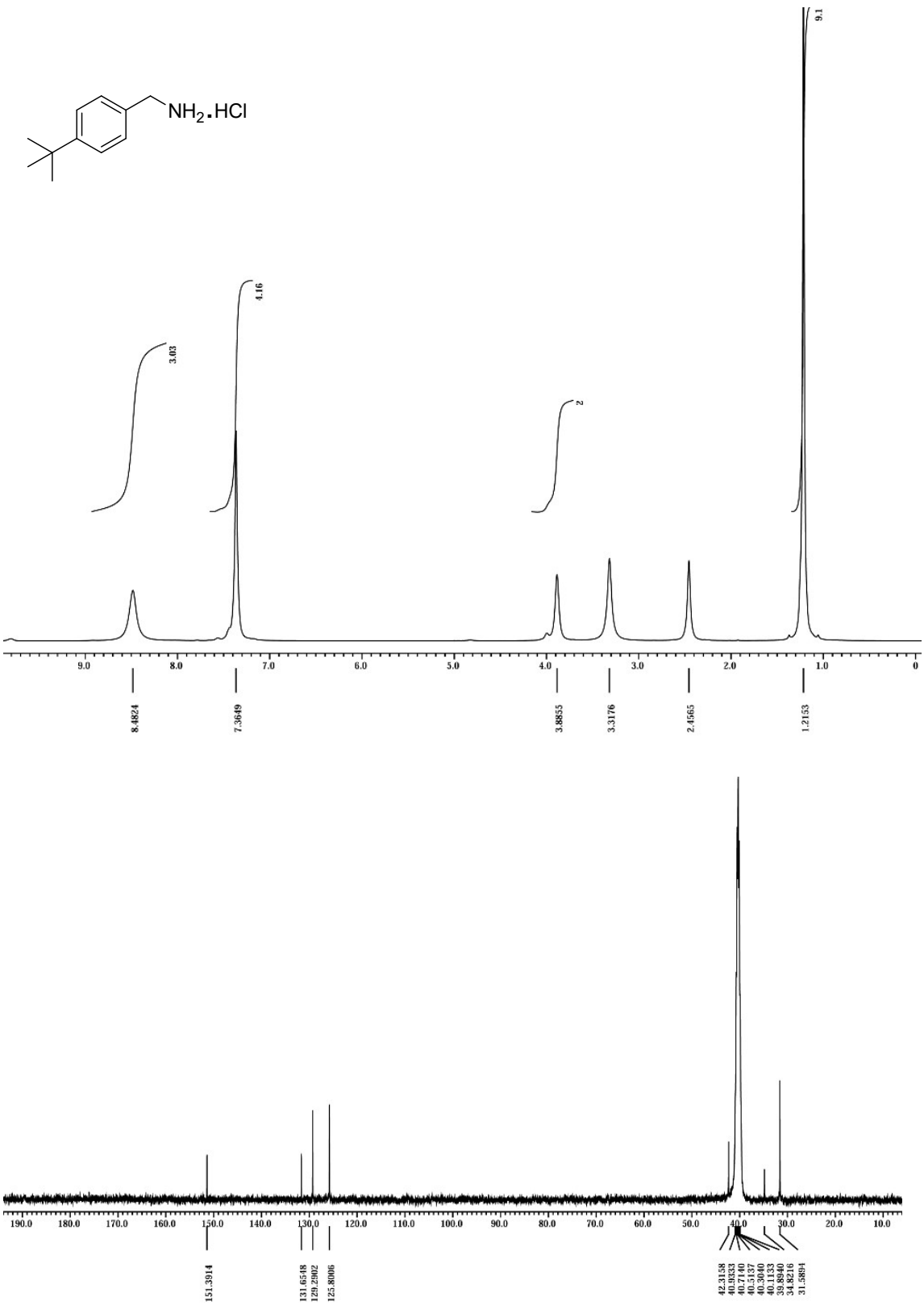


Figure S43. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

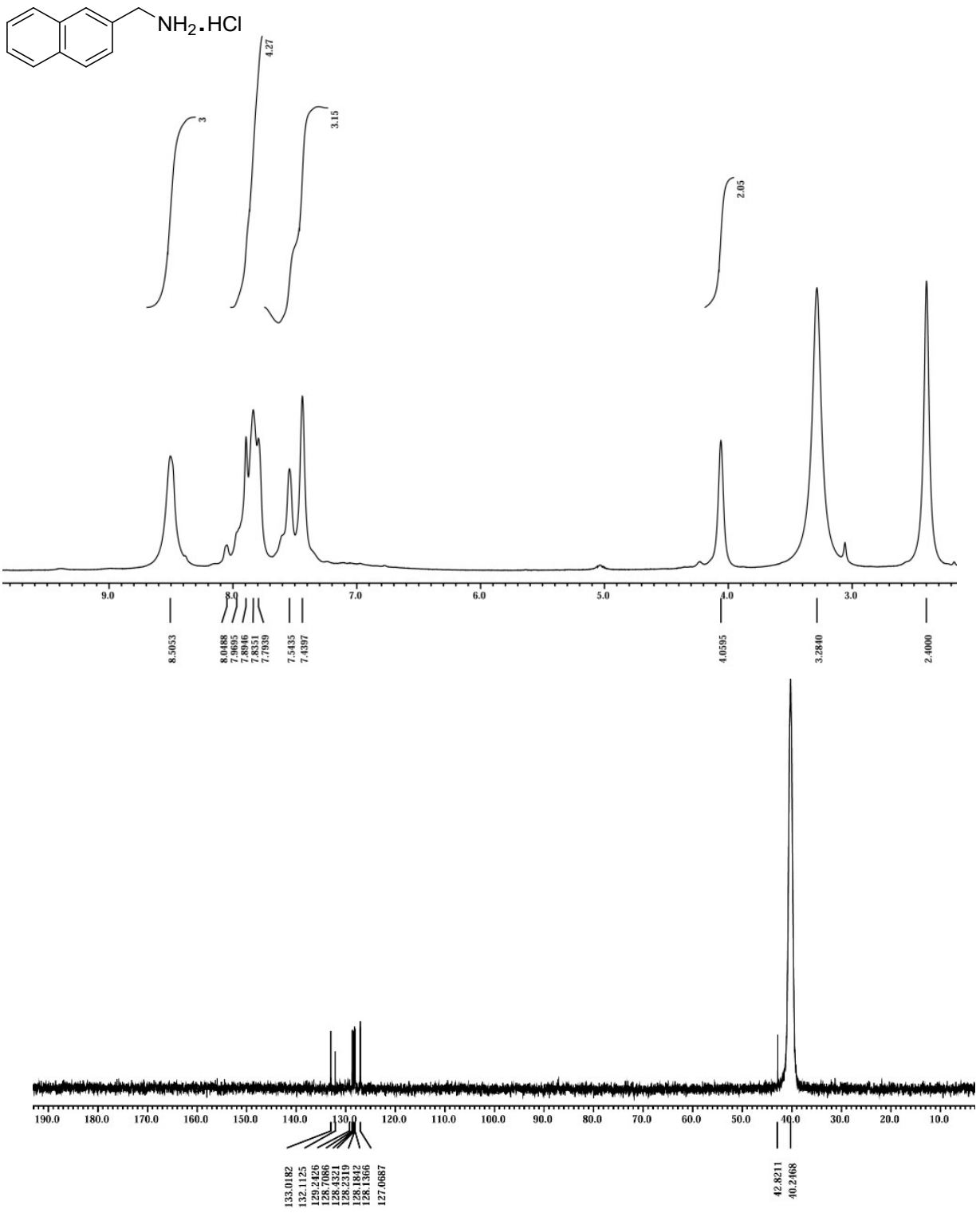


Figure S44. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

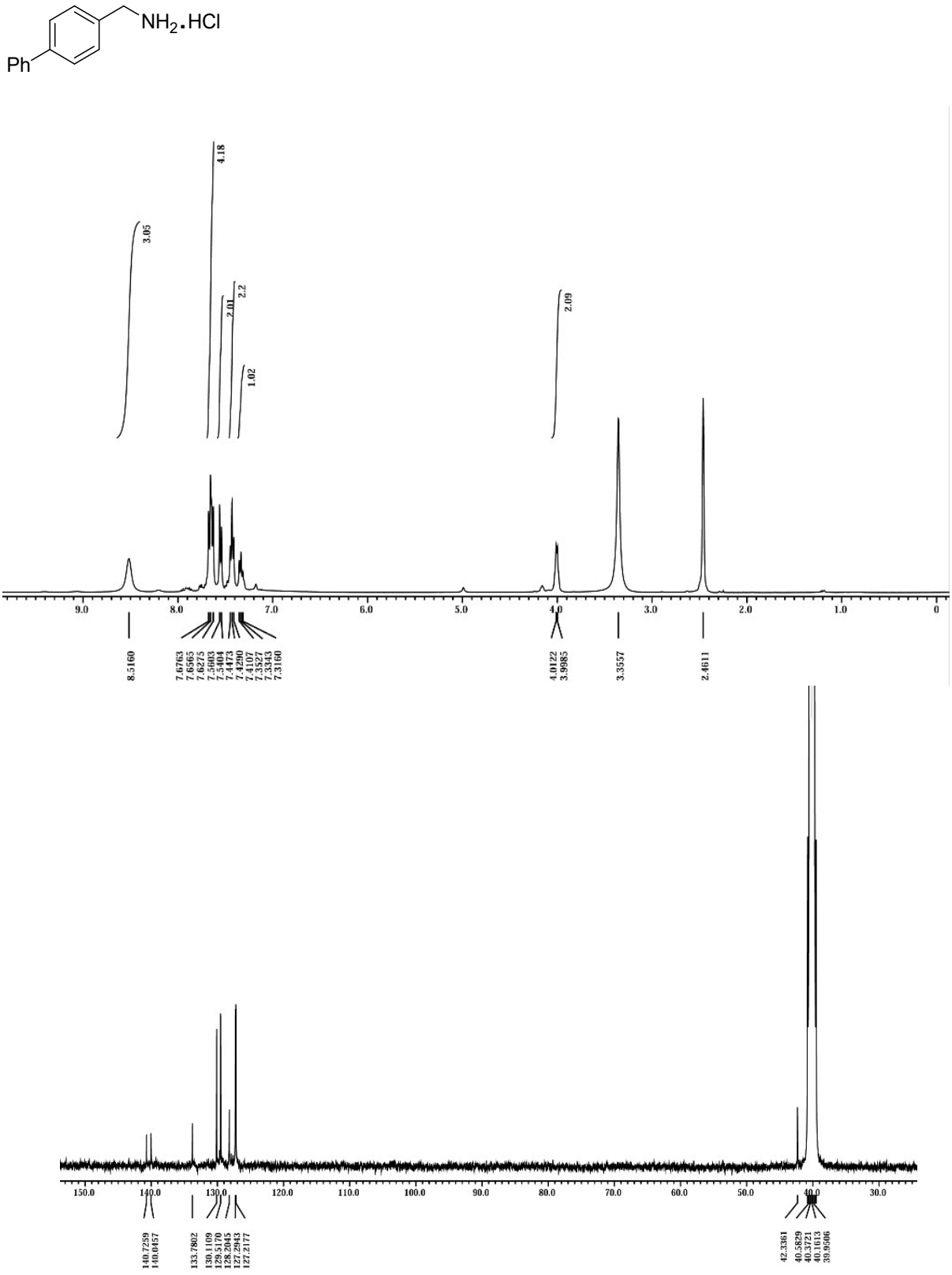


Figure S45. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-

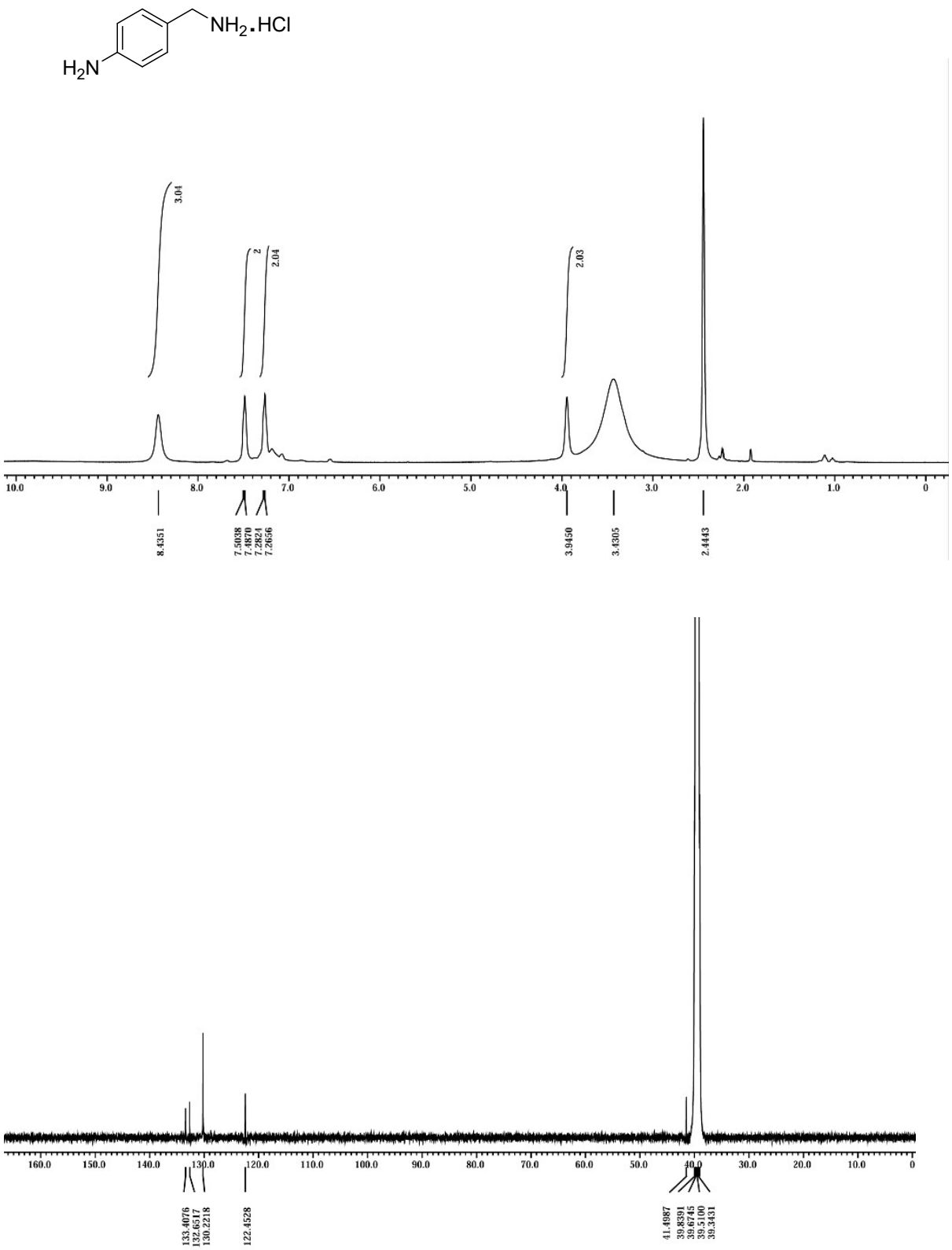


Figure S46. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-

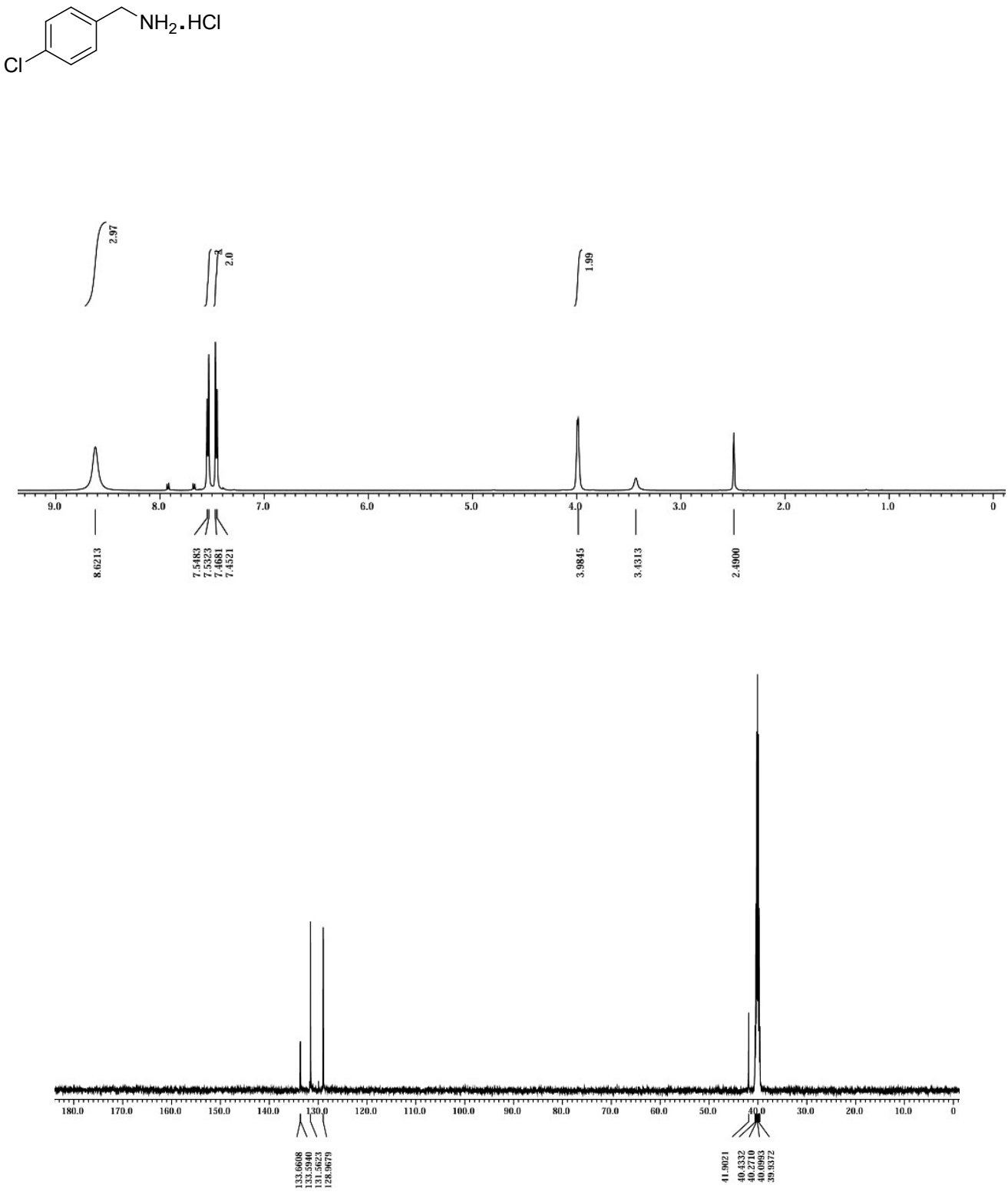


Figure S47. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

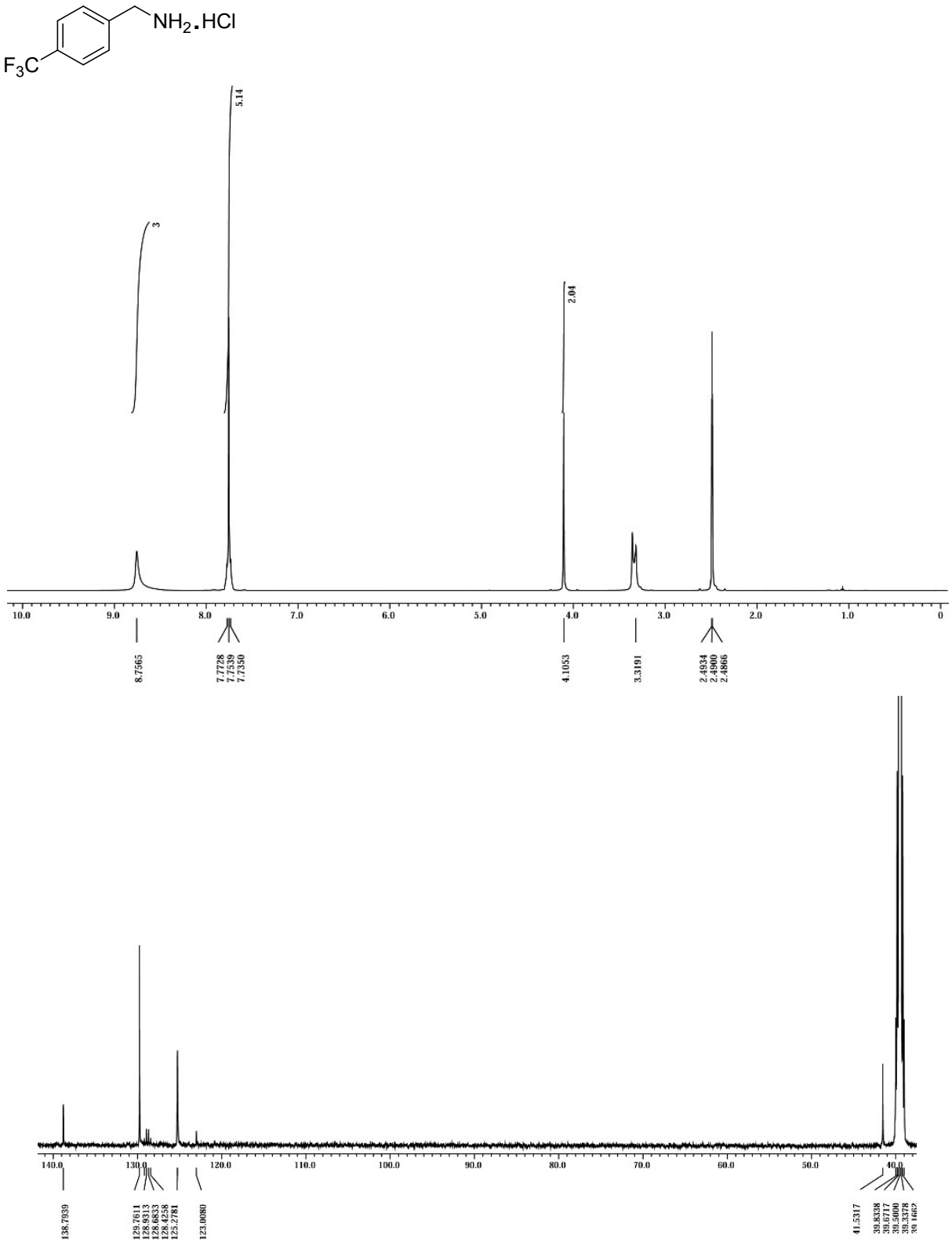


Figure S48. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

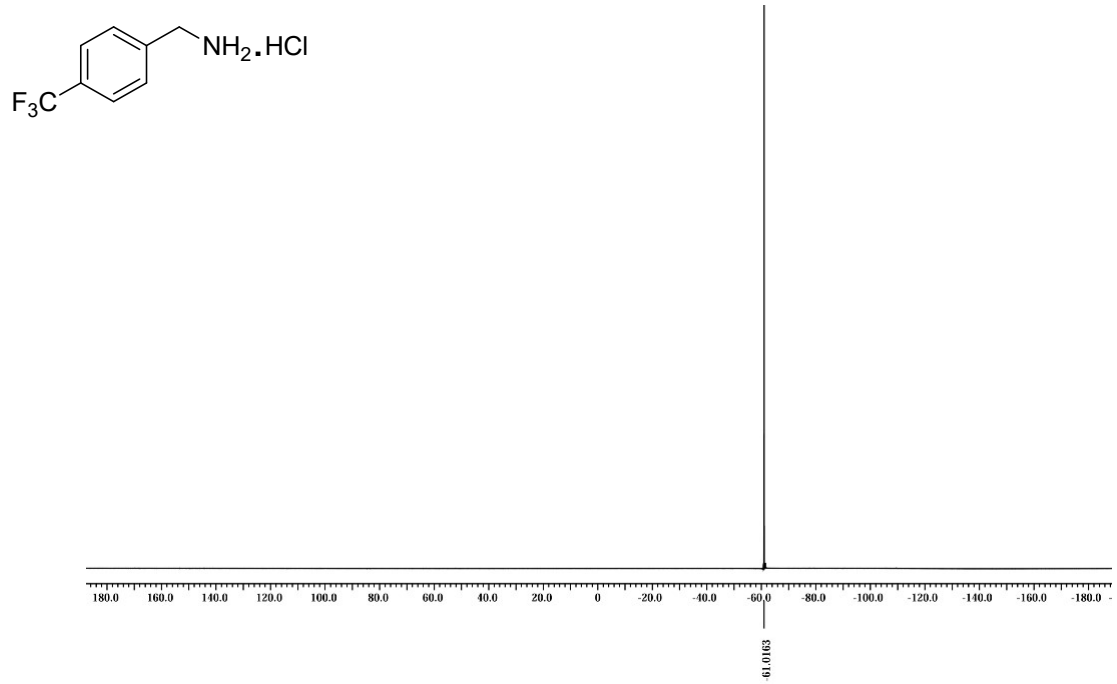


Figure S49. ^{19}F NMR spectrum in DMSO-D_6.

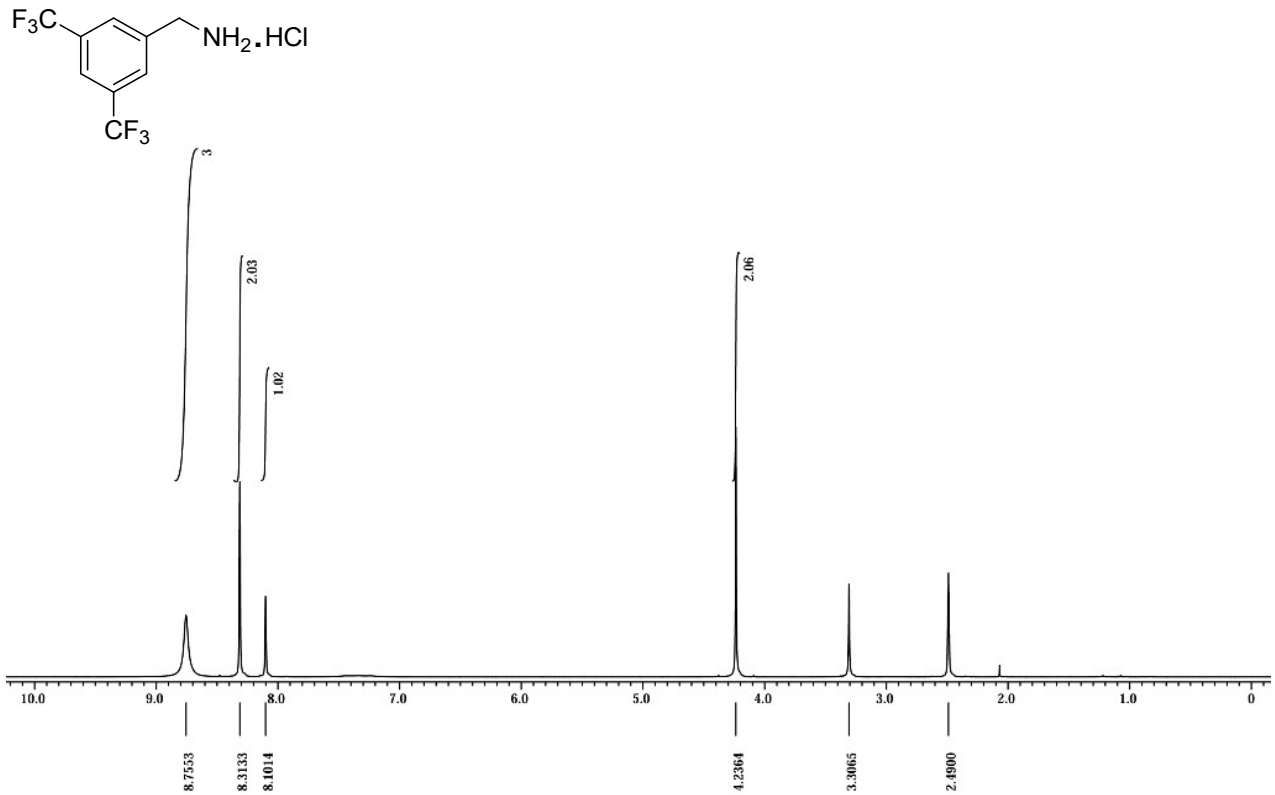


Figure S50. ^{1}H NMR spectrum in DMSO-D_6.

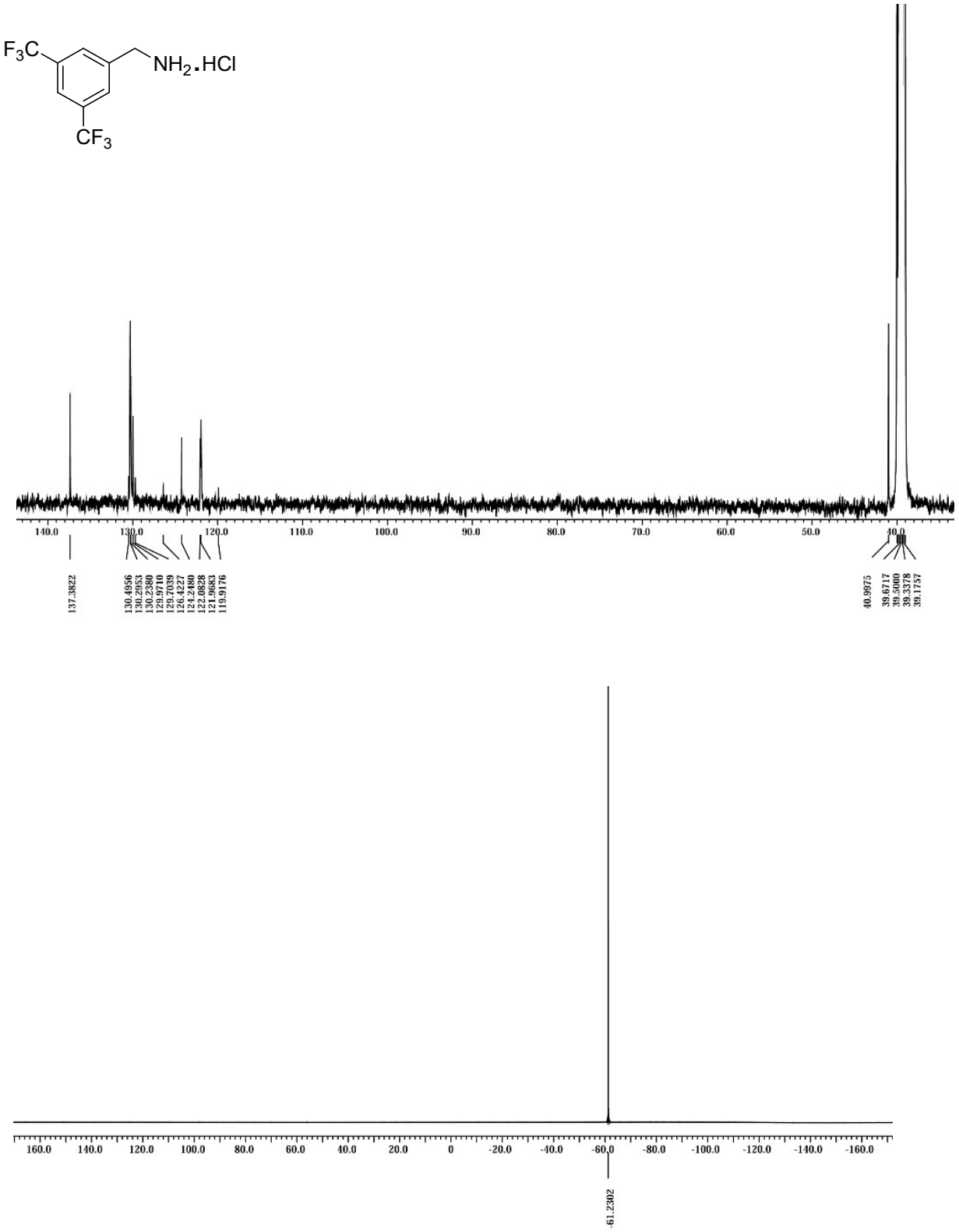


Figure S51. ^{13}C (top) ^{19}F (bottom) NMR spectra in DMSO-D_6.

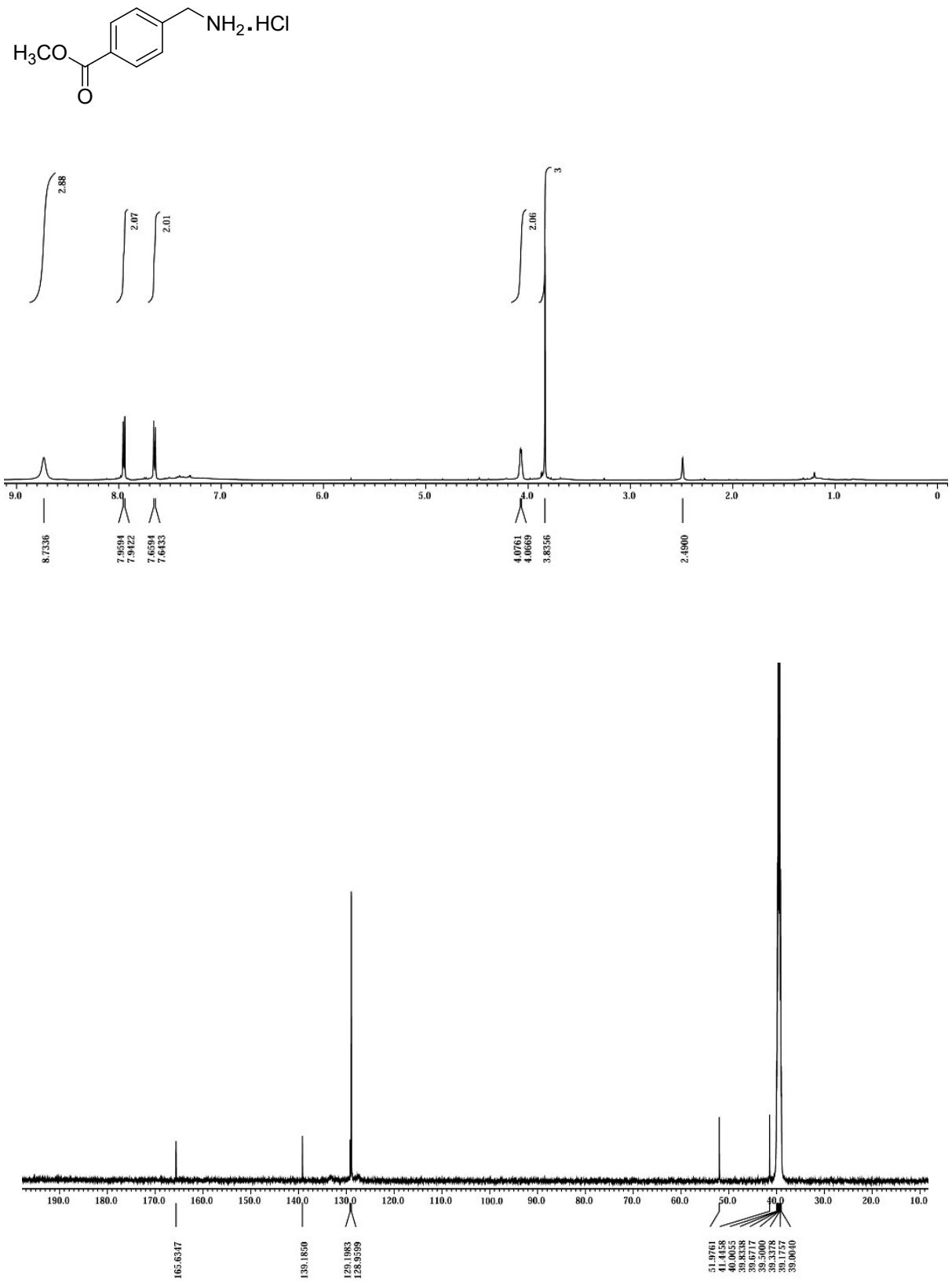


Figure S52. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

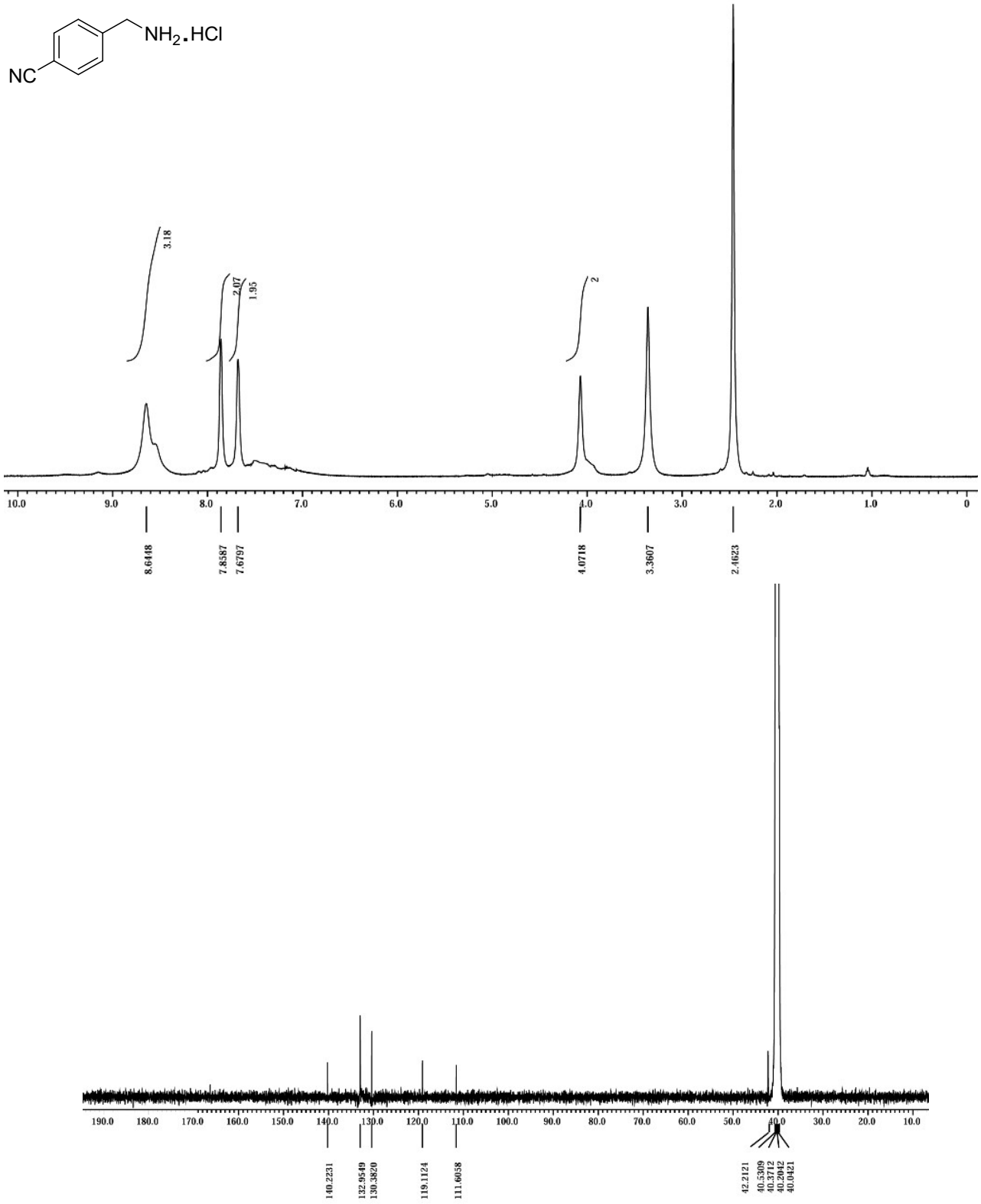


Figure S53. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-

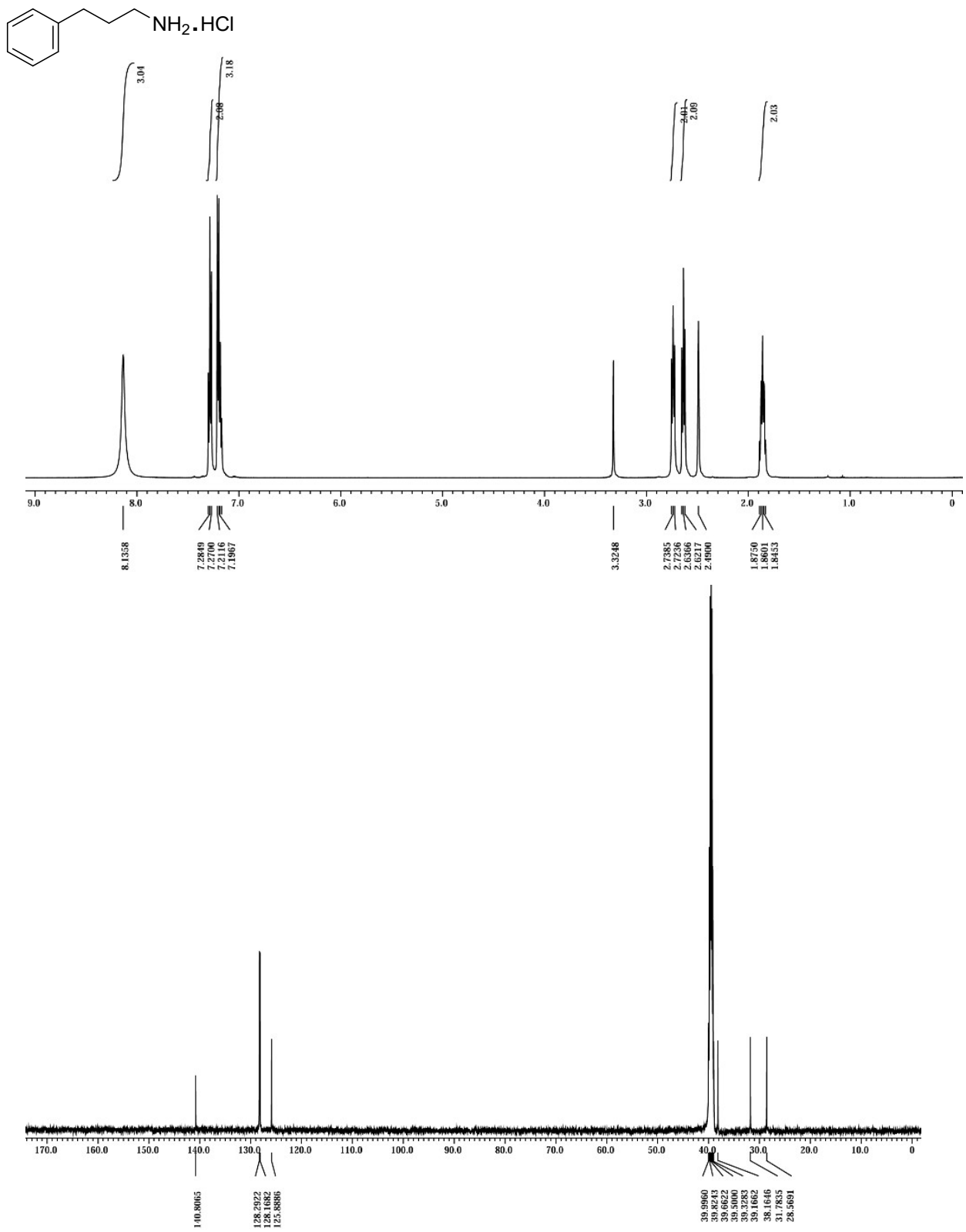


Figure S54. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

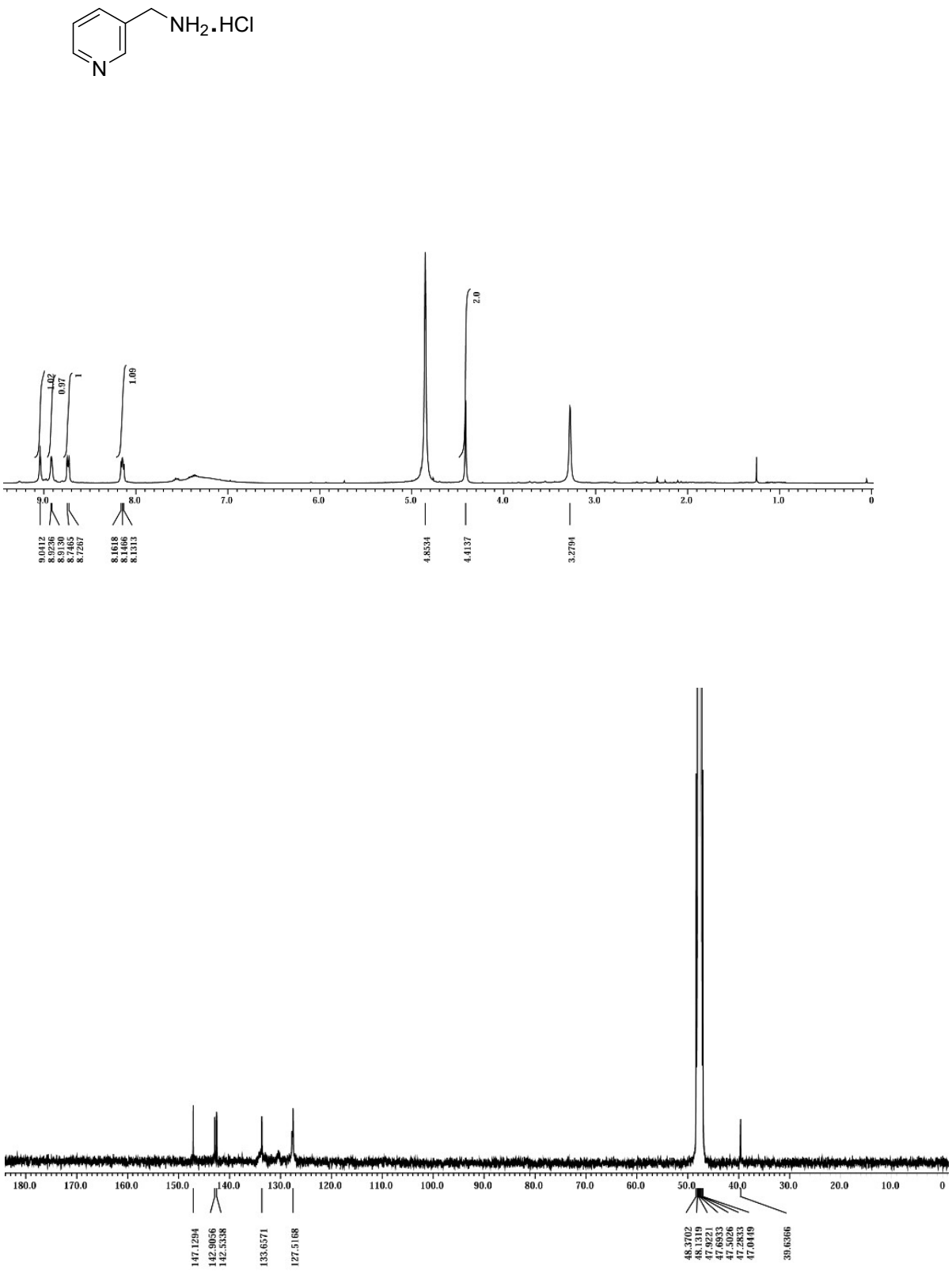


Figure S55. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

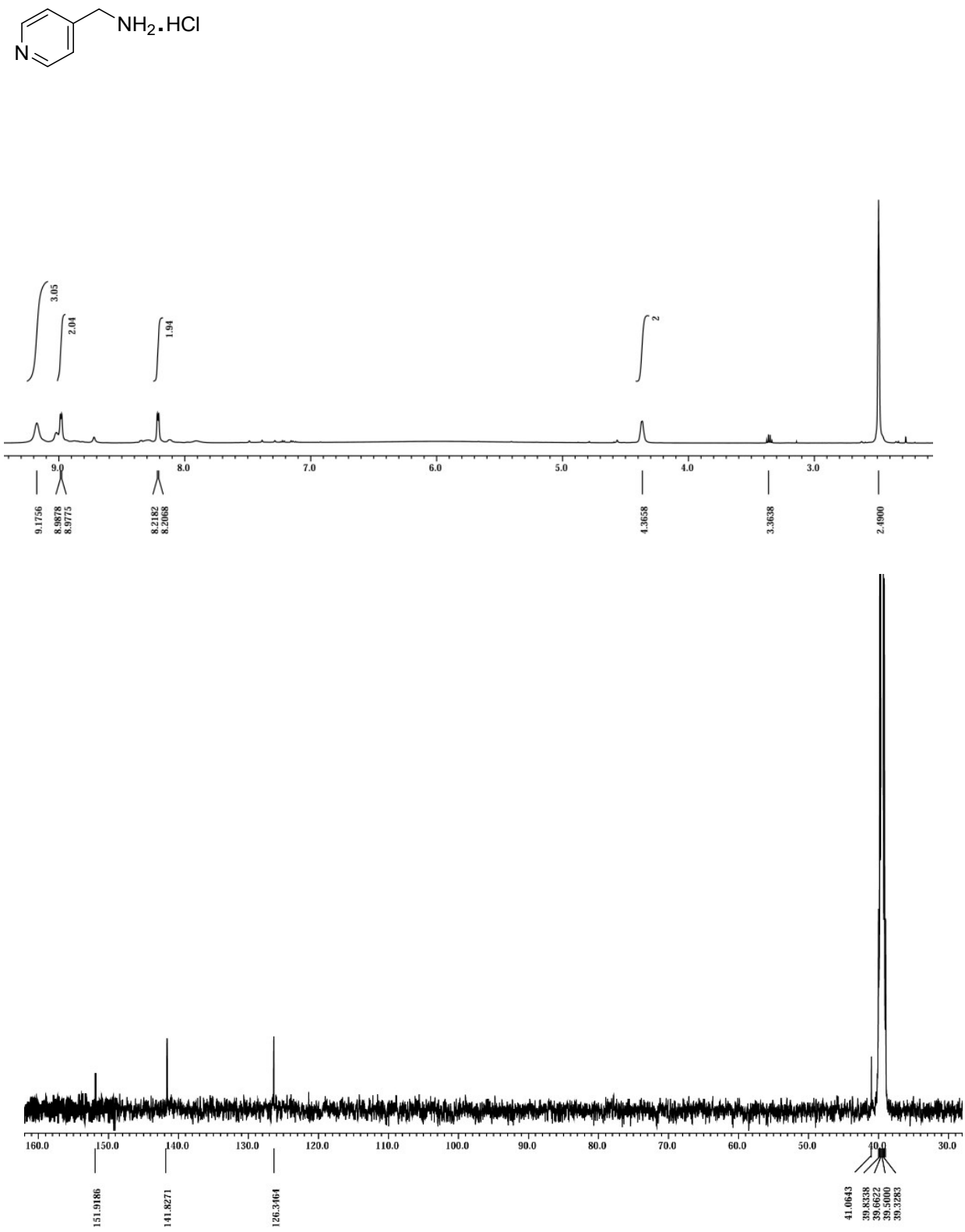


Figure S56. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

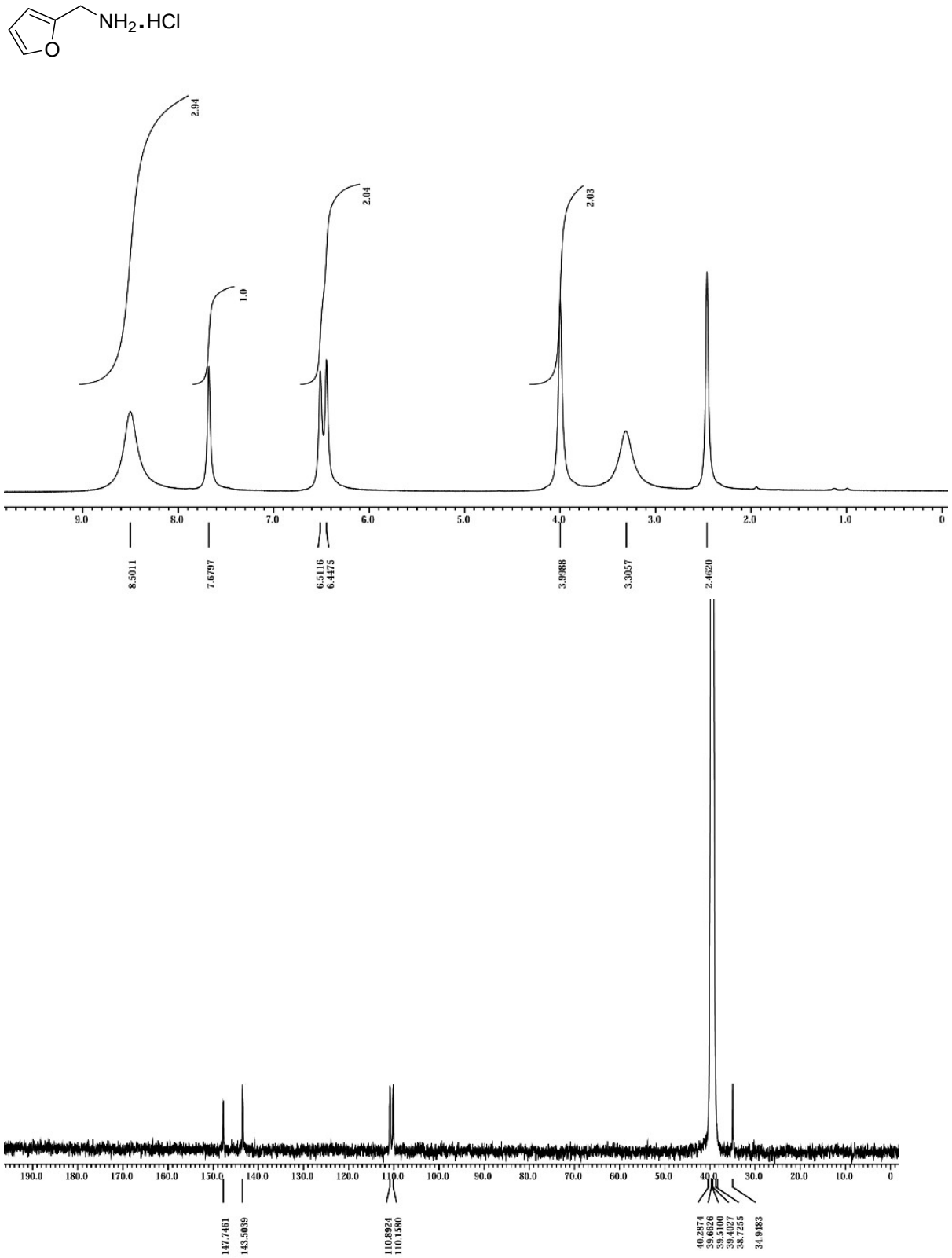


Figure S57. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

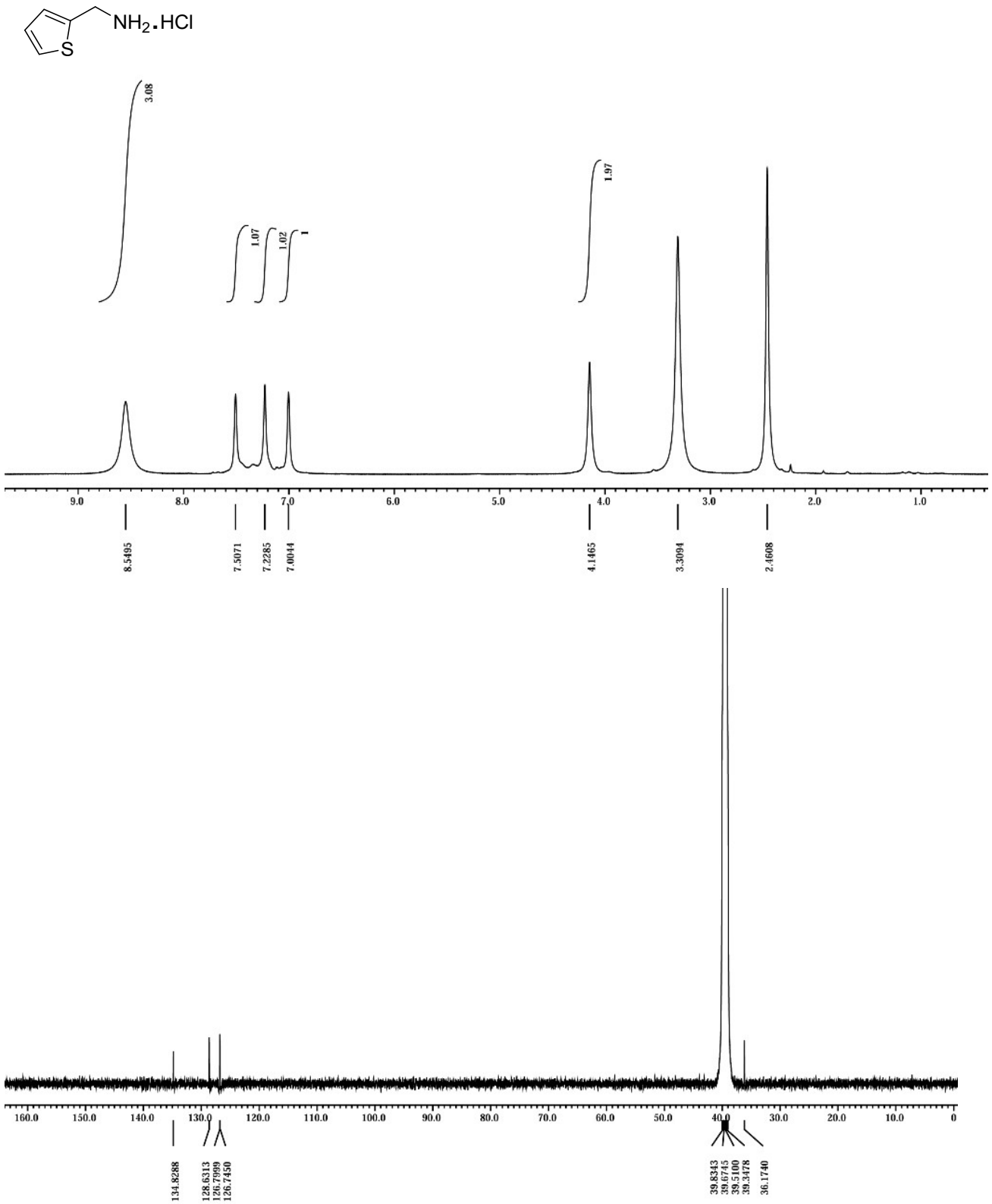


Figure S58. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

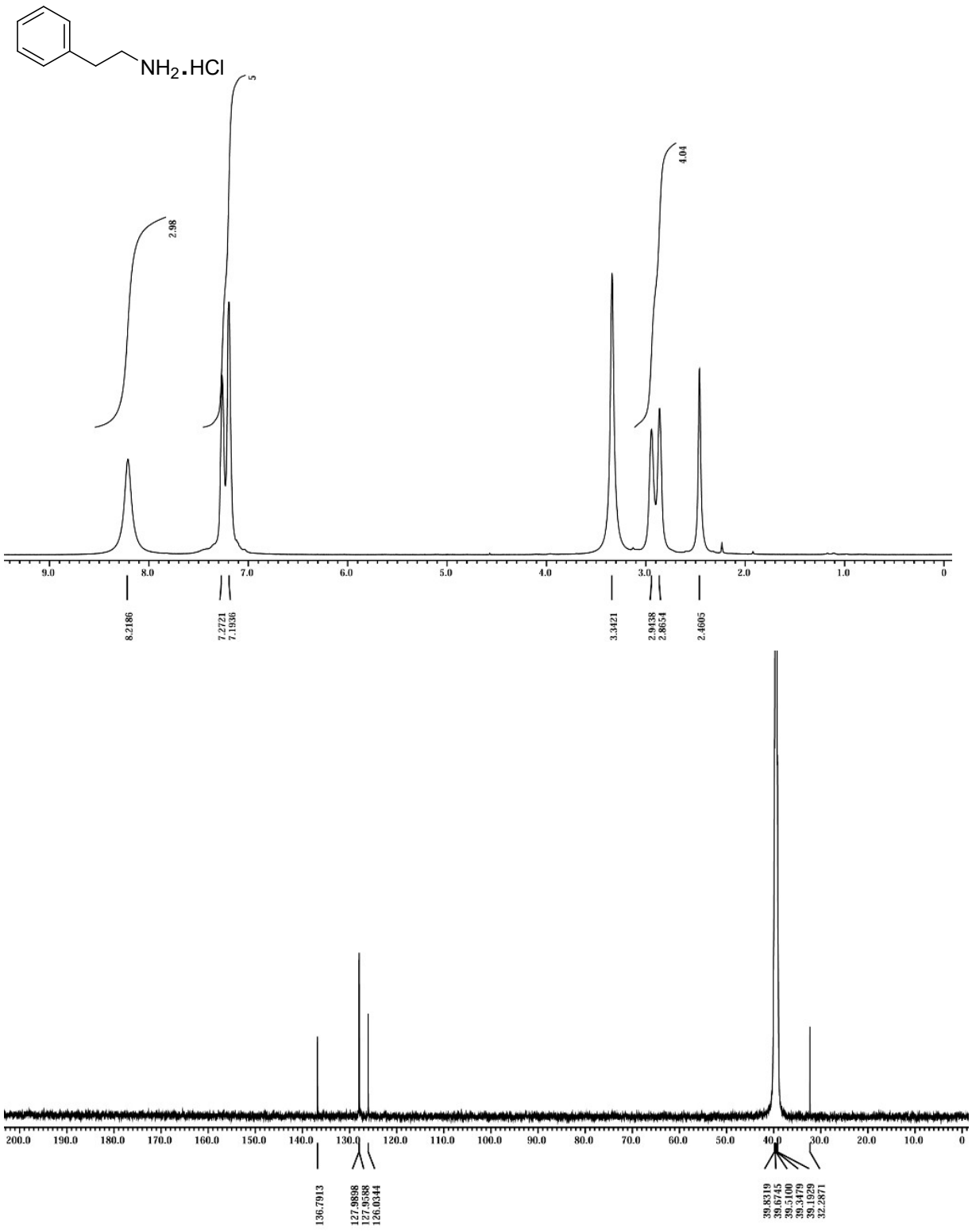


Figure S59. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

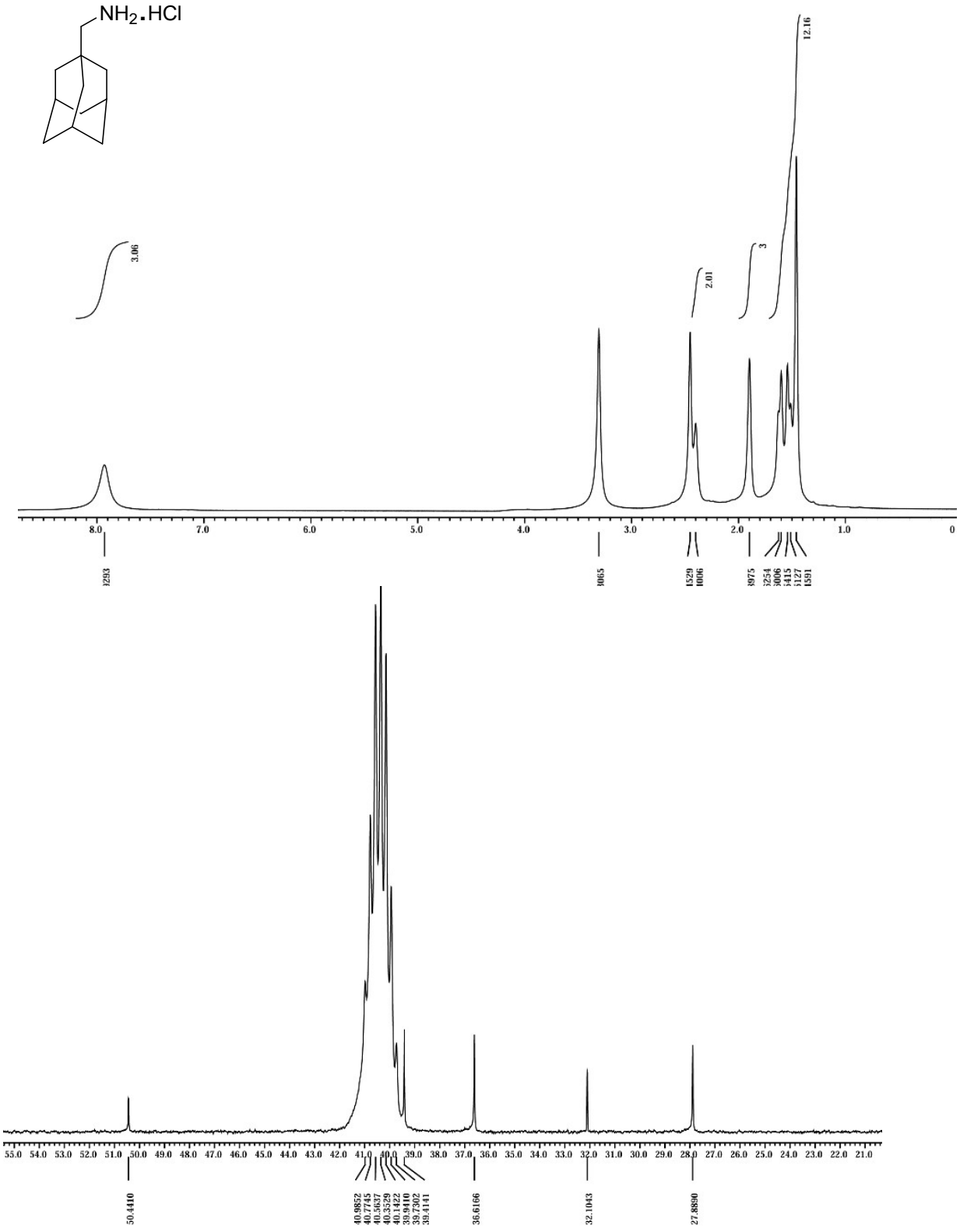


Figure S60. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

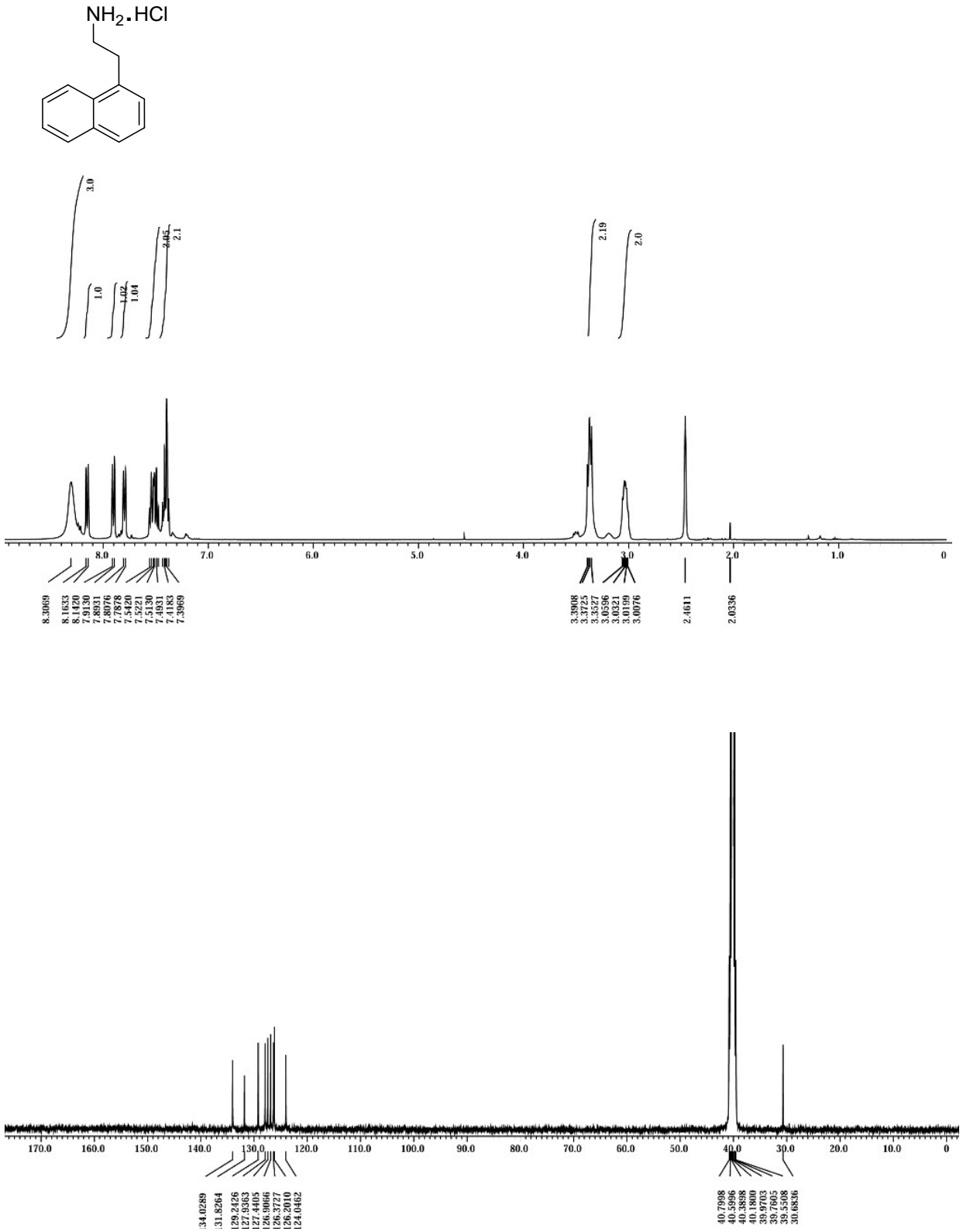


Figure S61. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

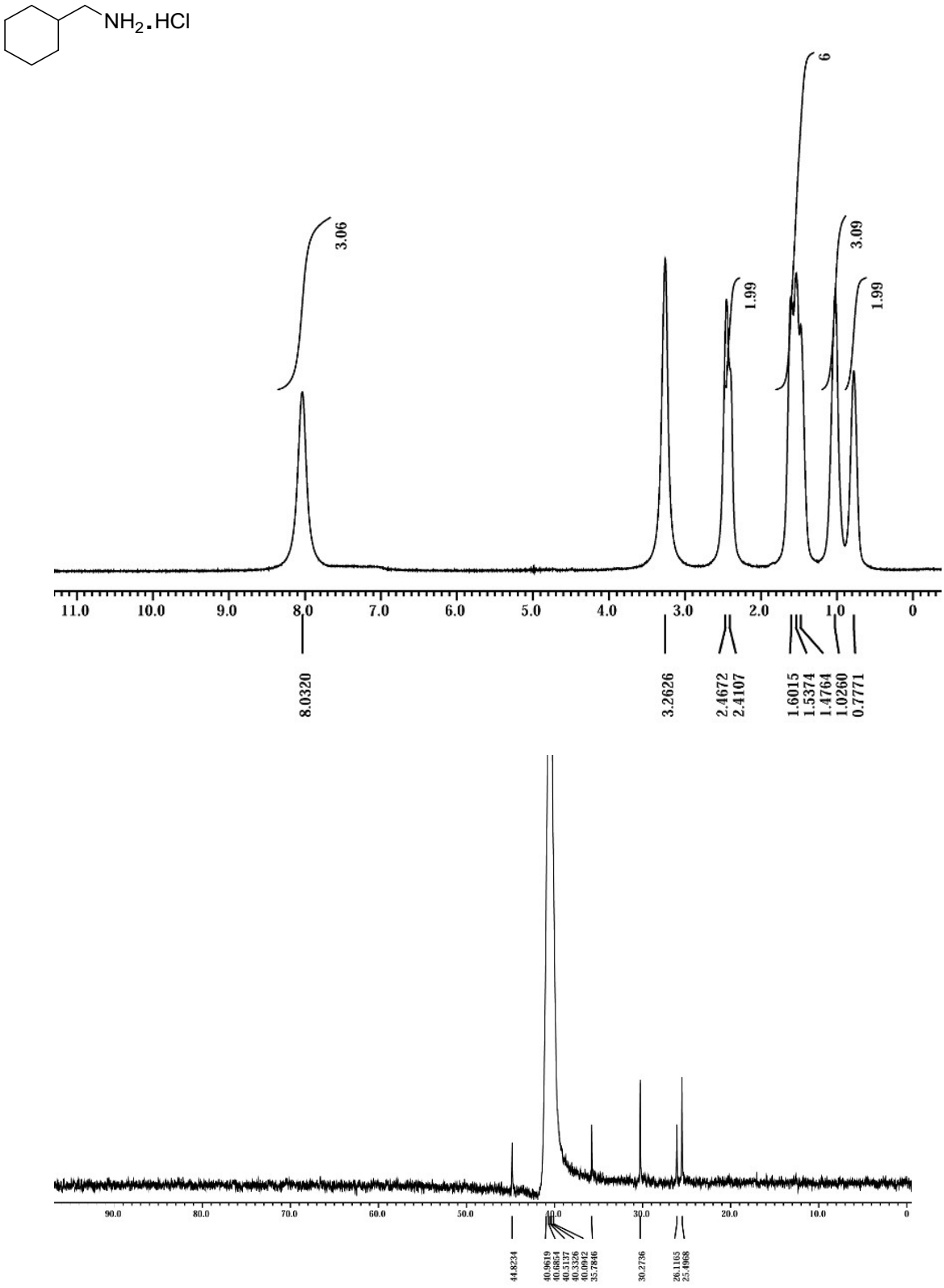


Figure S62. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

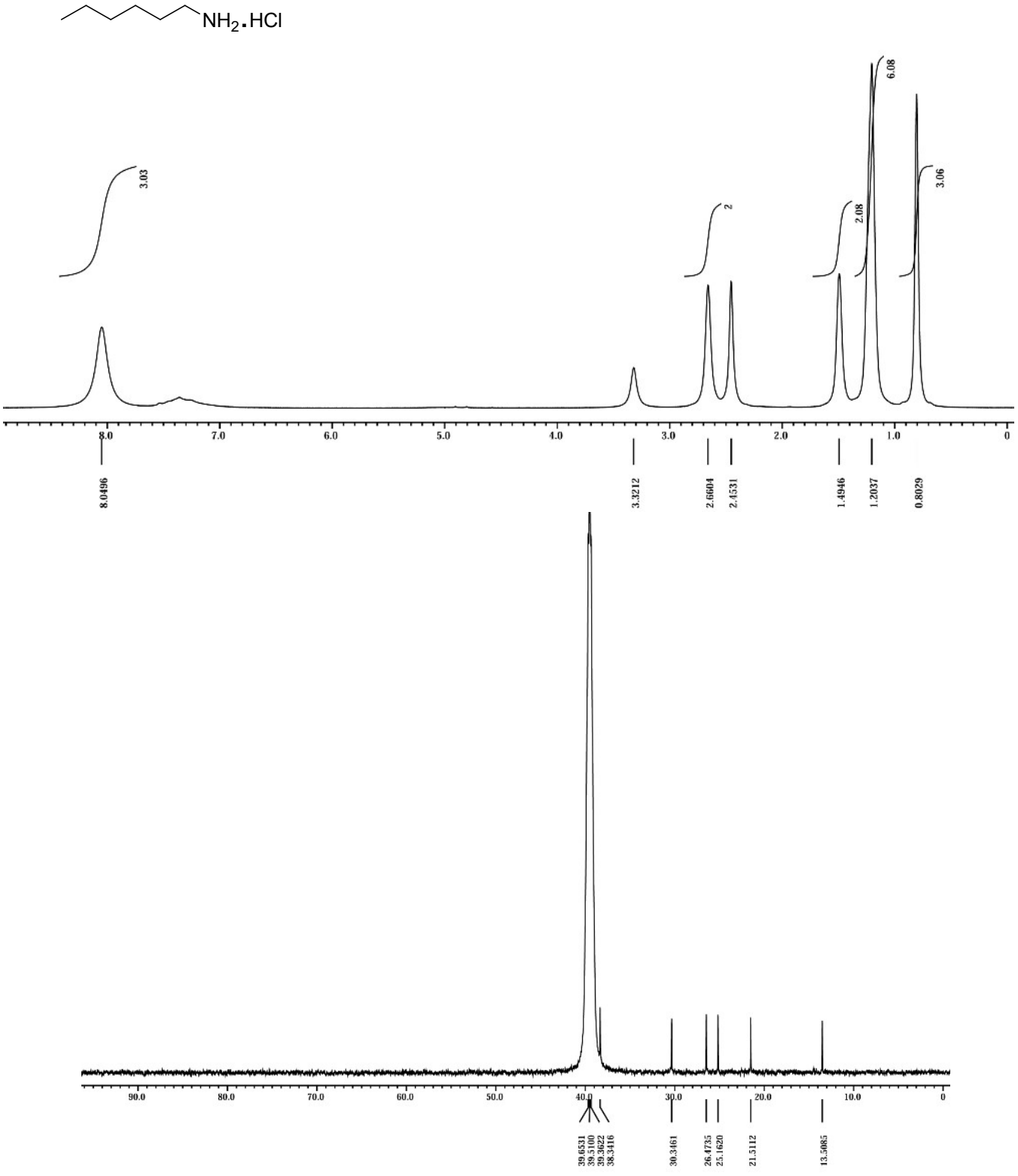


Figure S63. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

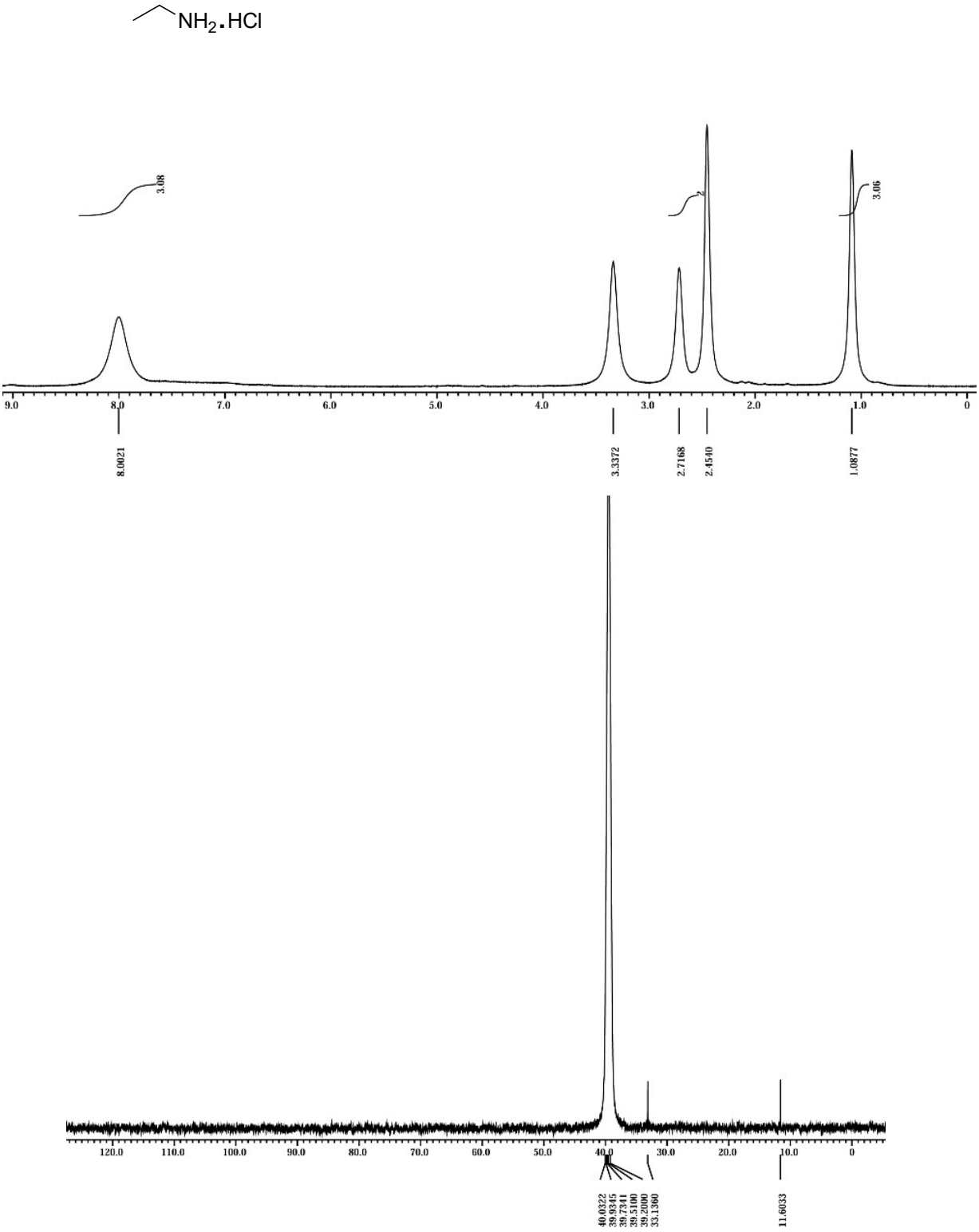


Figure S64. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

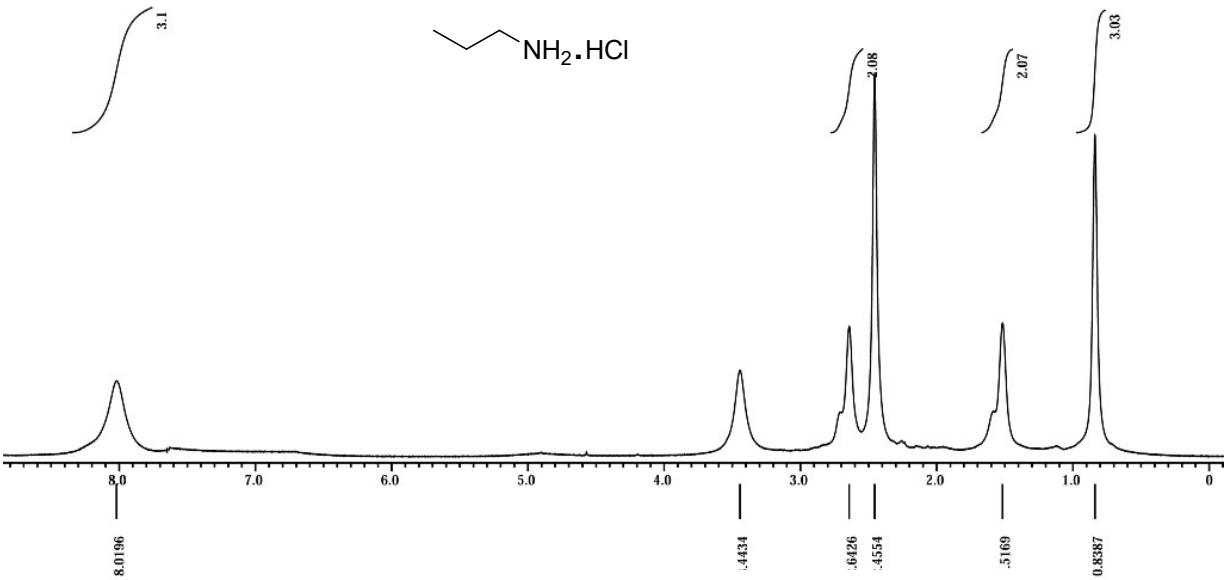


Figure S65. ^{1}H NMR spectrum in DMSO-D_6.

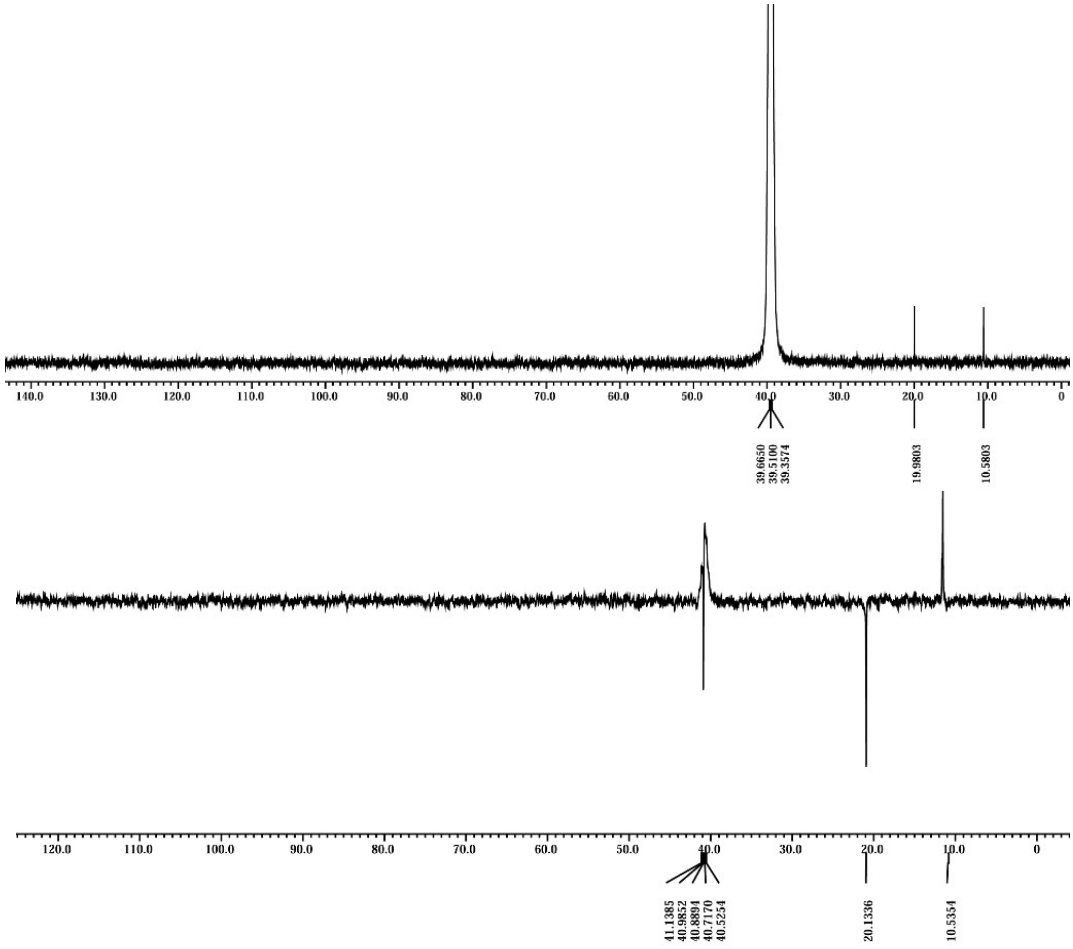


Figure S66. ^{13}C and DEPT(135) NMR spectra in DMSO-D_6.

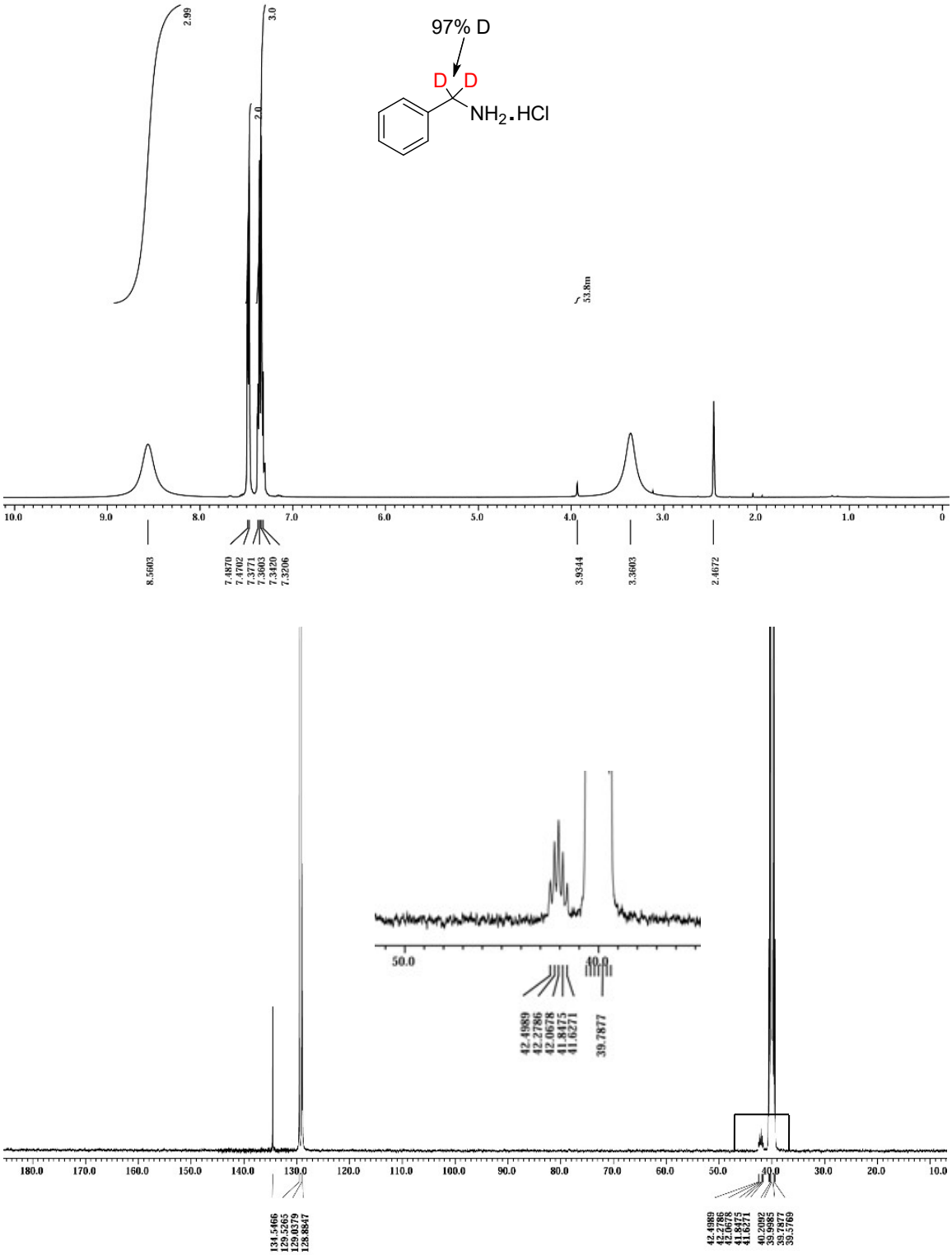


Figure S67. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

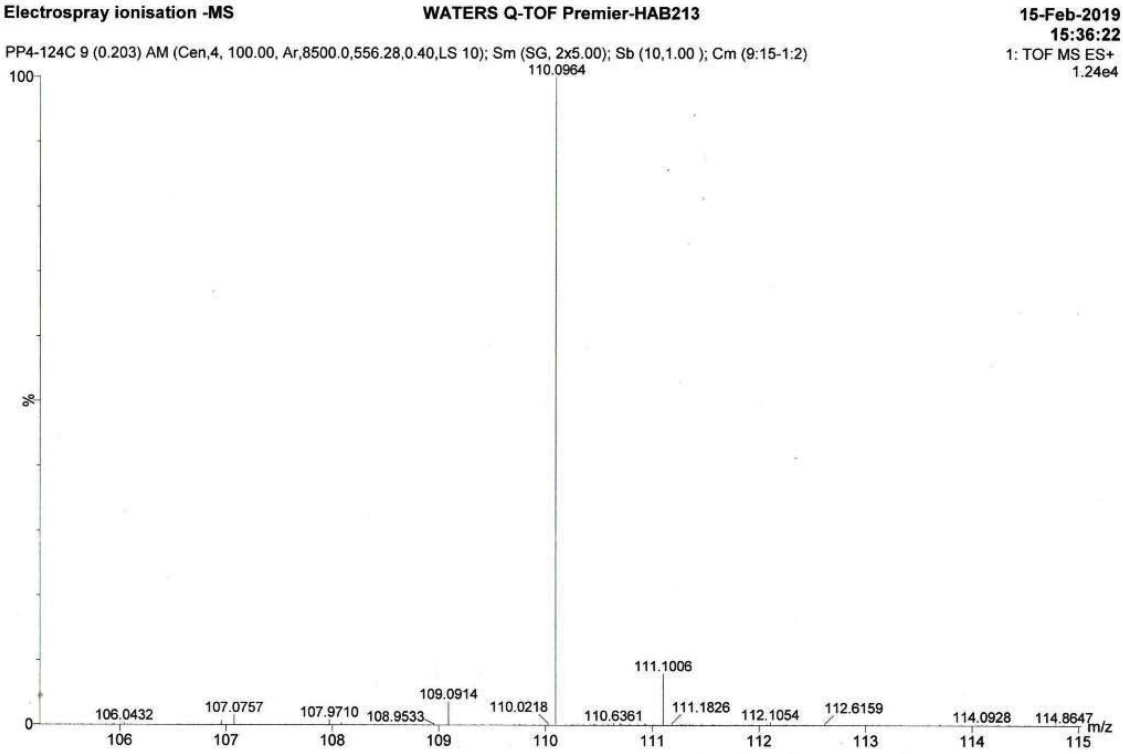


Figure S68. ESI-MS of $PhCD_2NH_2$..

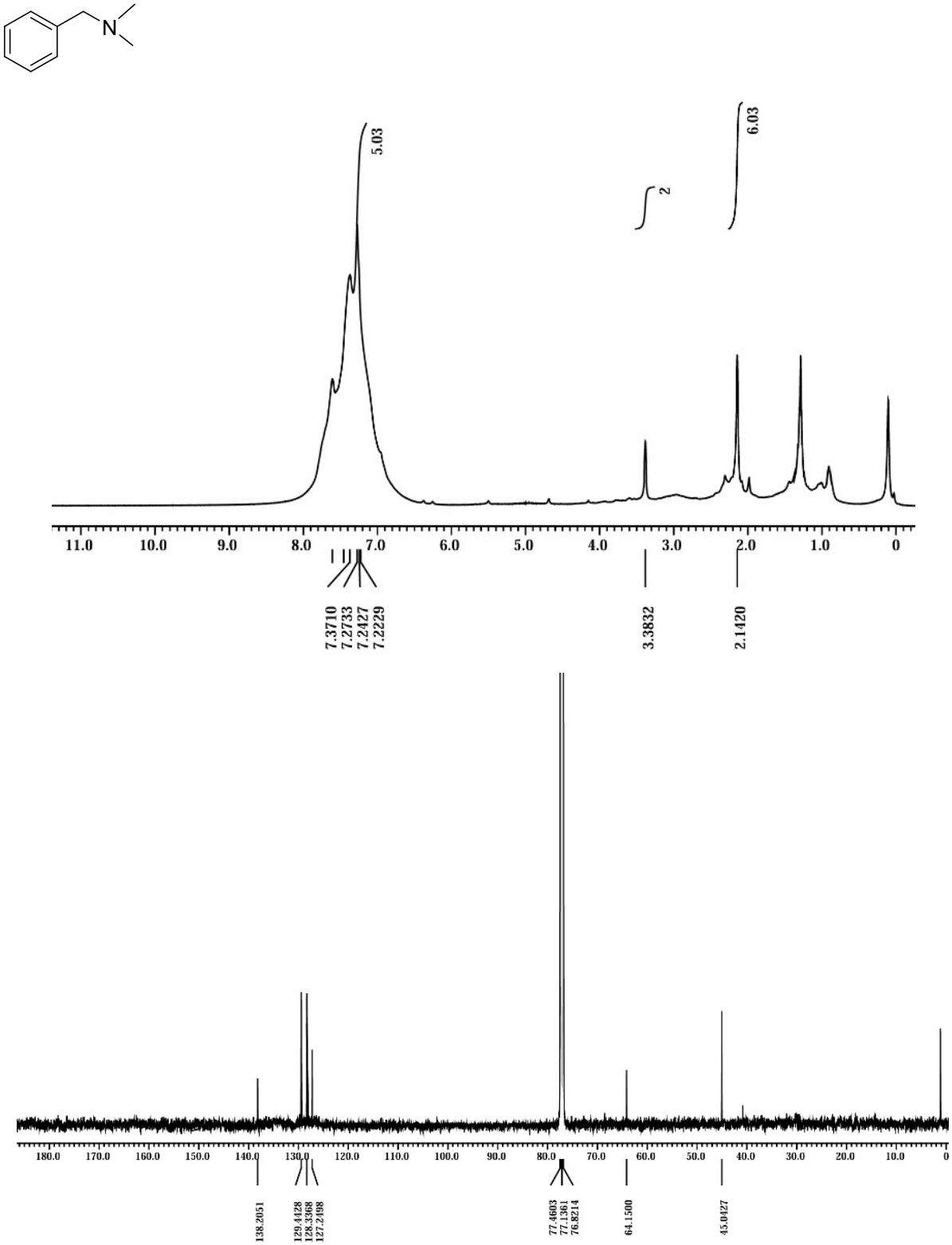


Figure S69. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

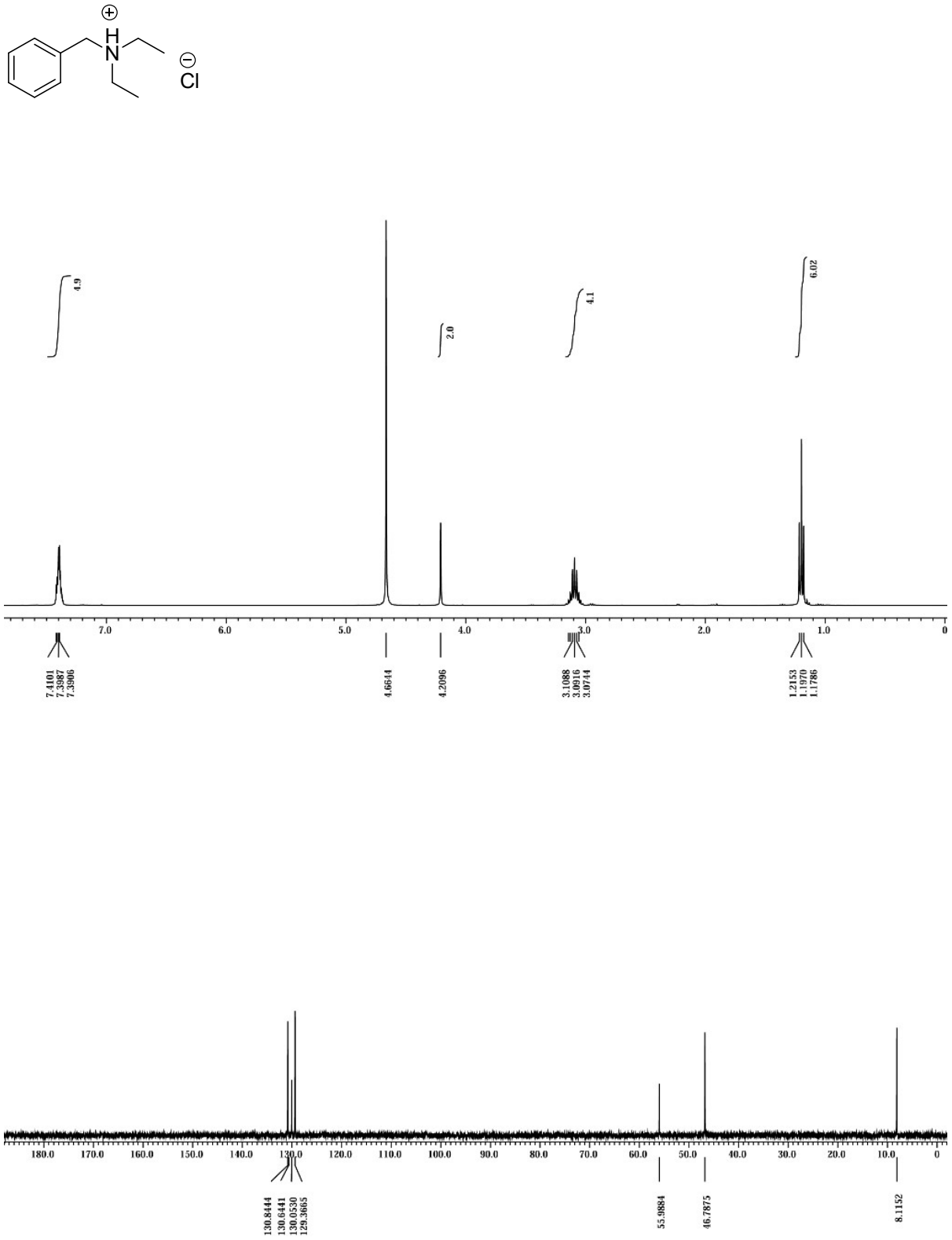


Figure S70. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

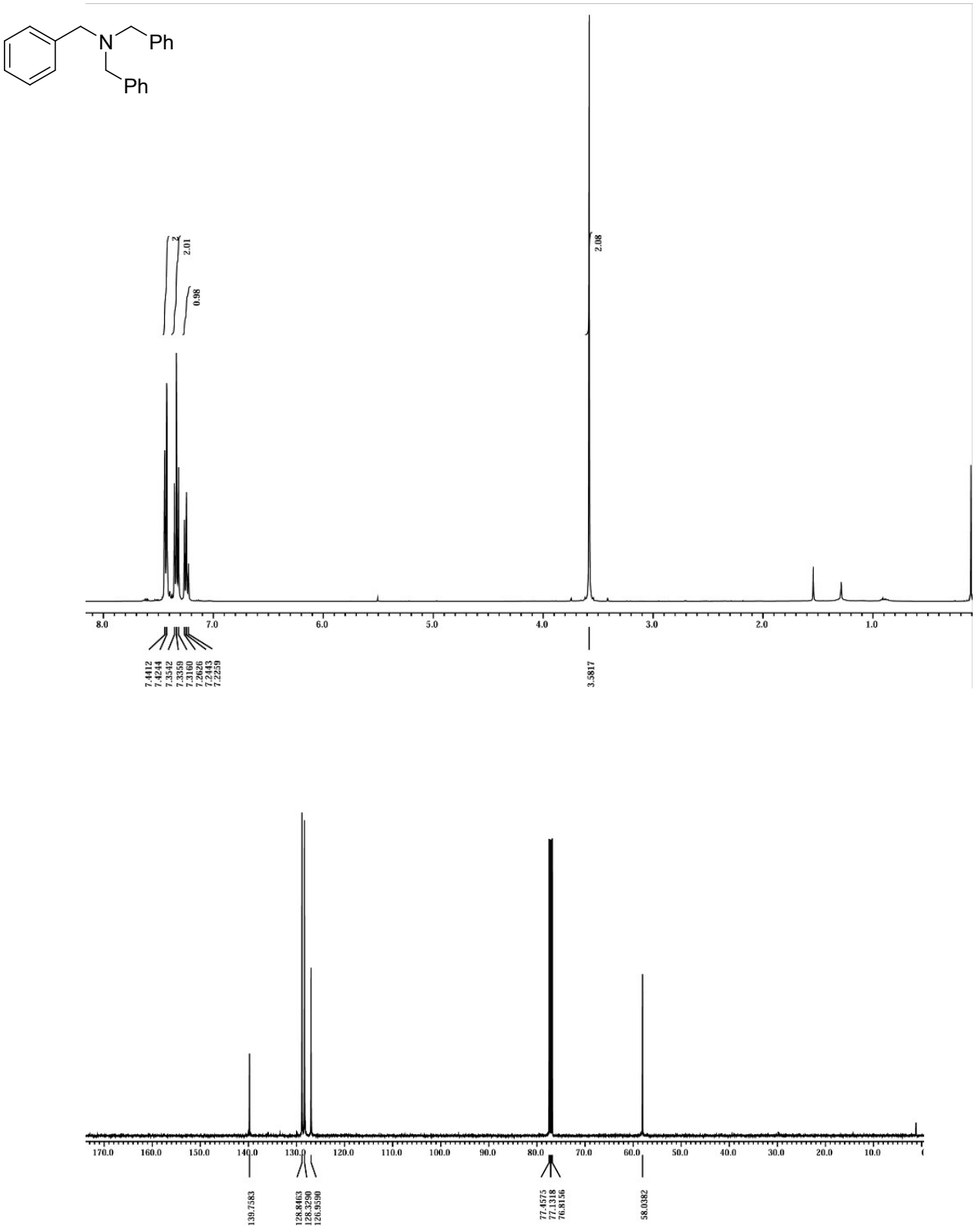


Figure S71. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

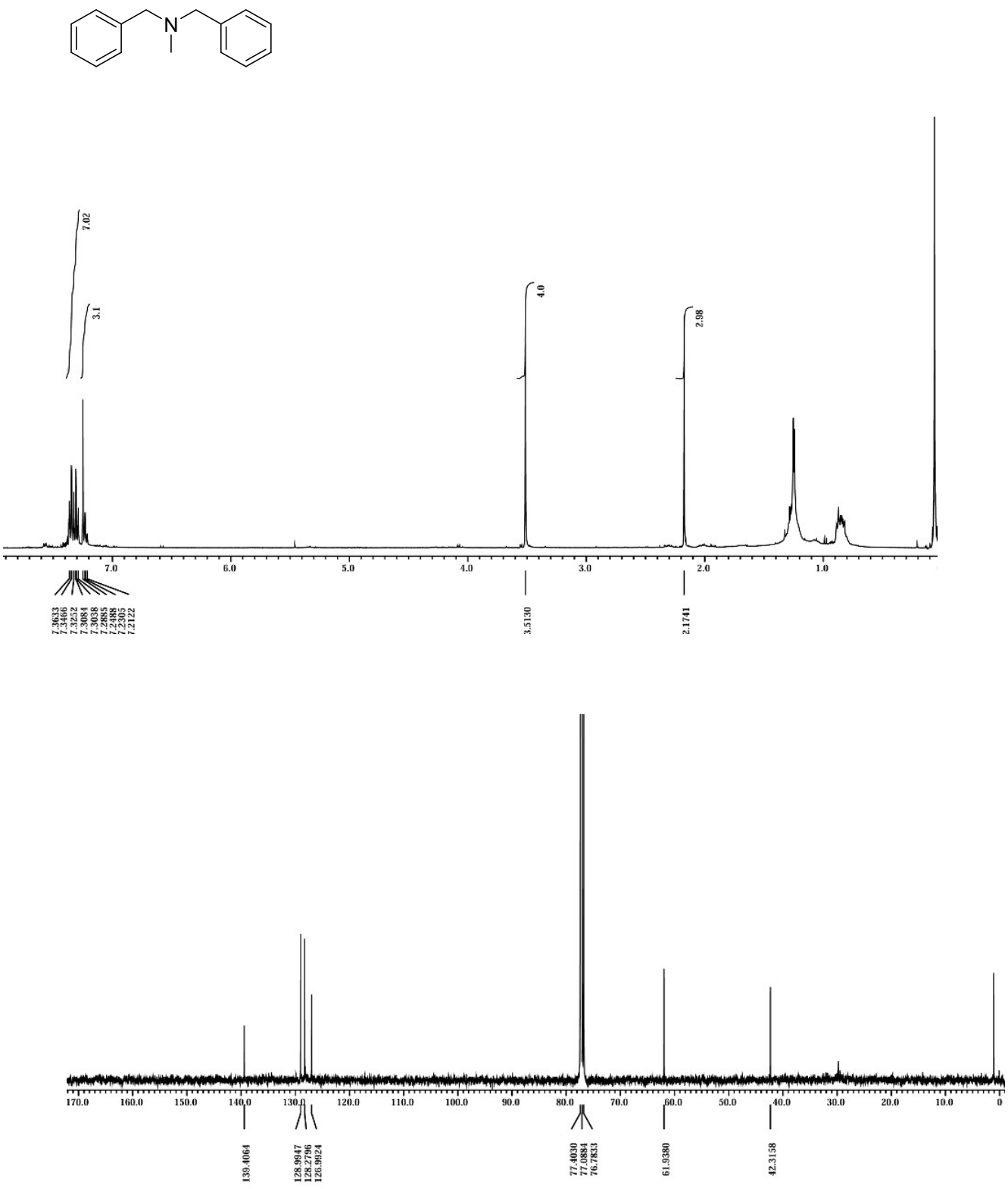


Figure S72. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

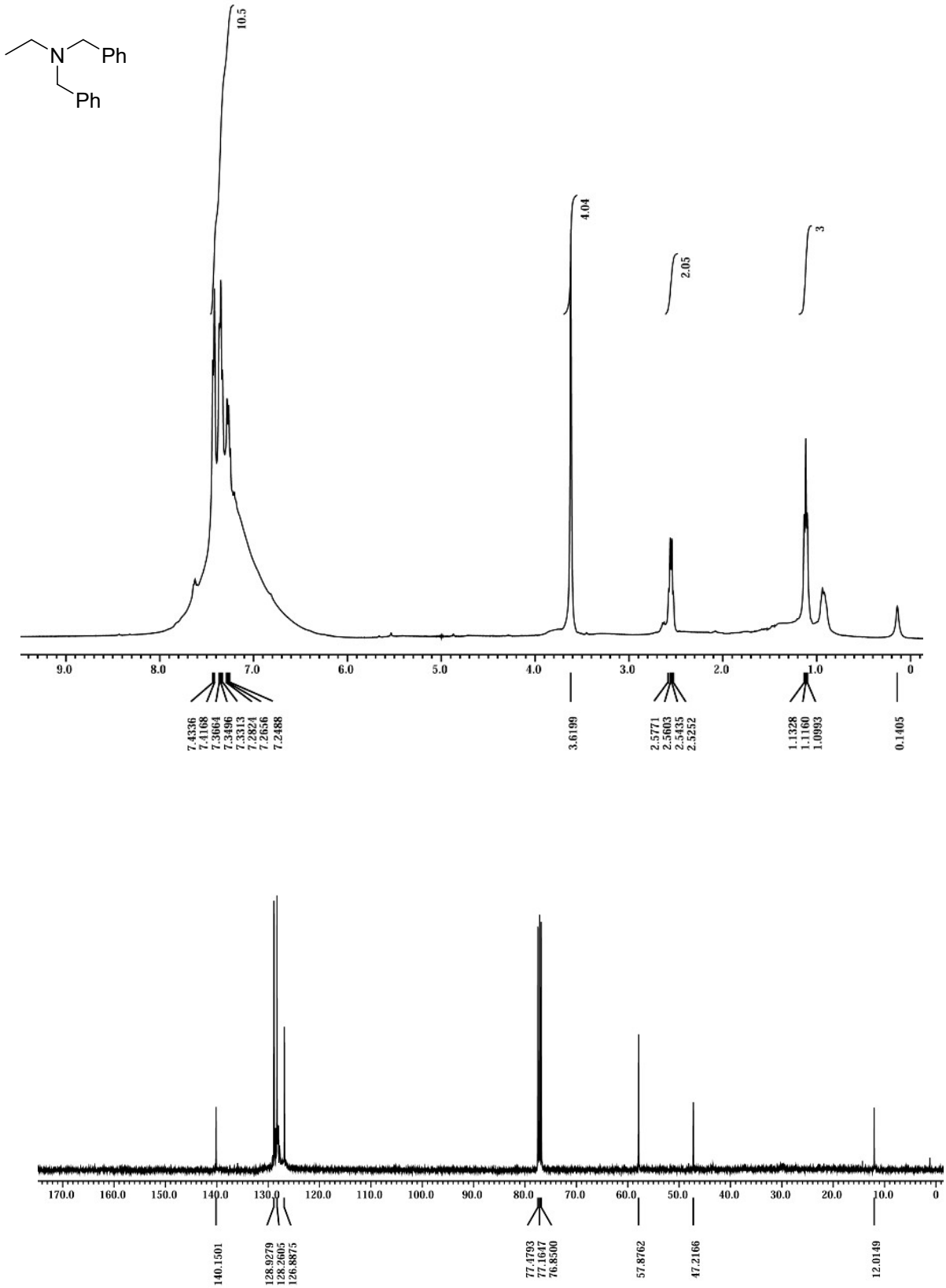


Figure S73. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

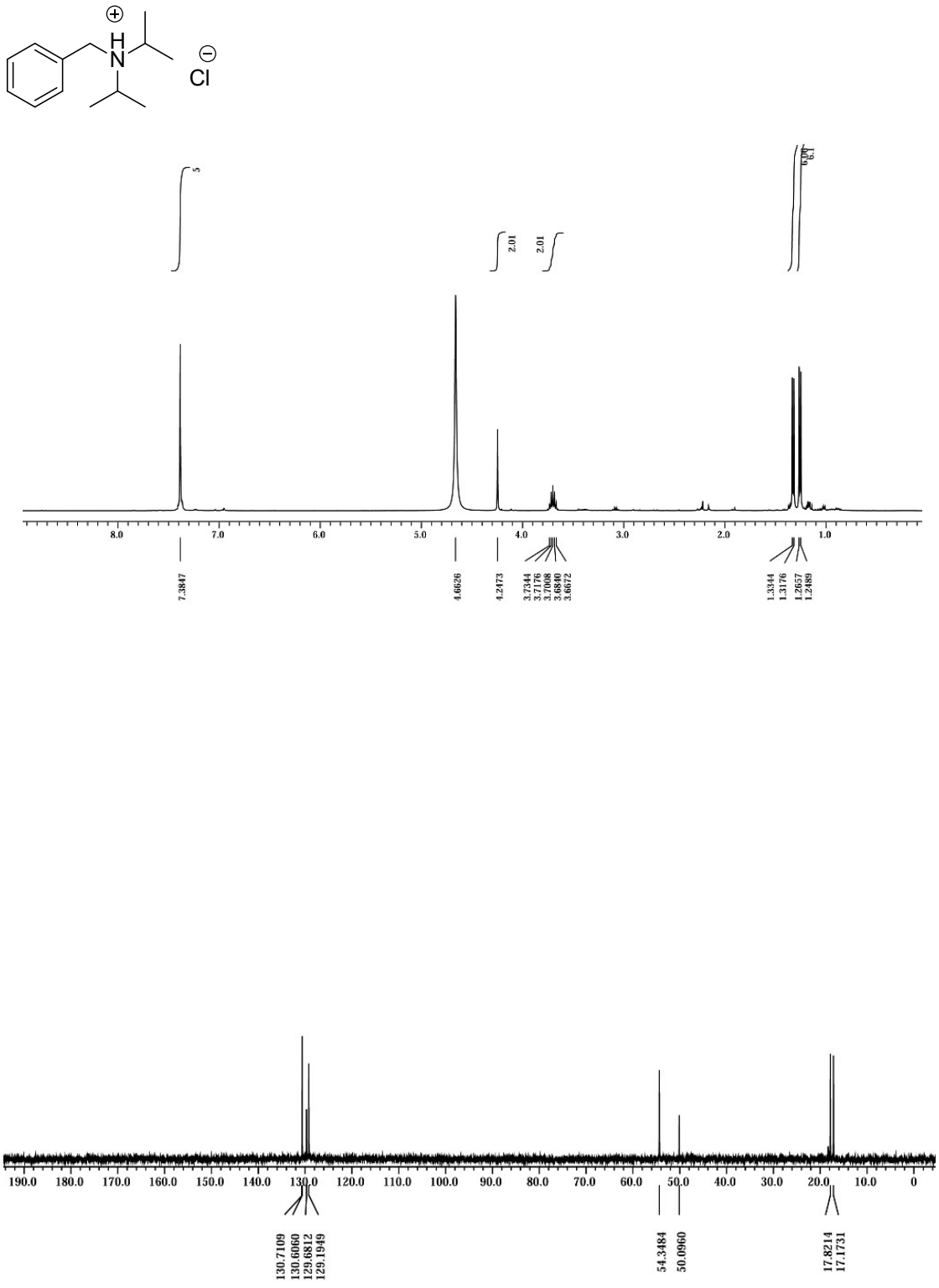


Figure S74. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

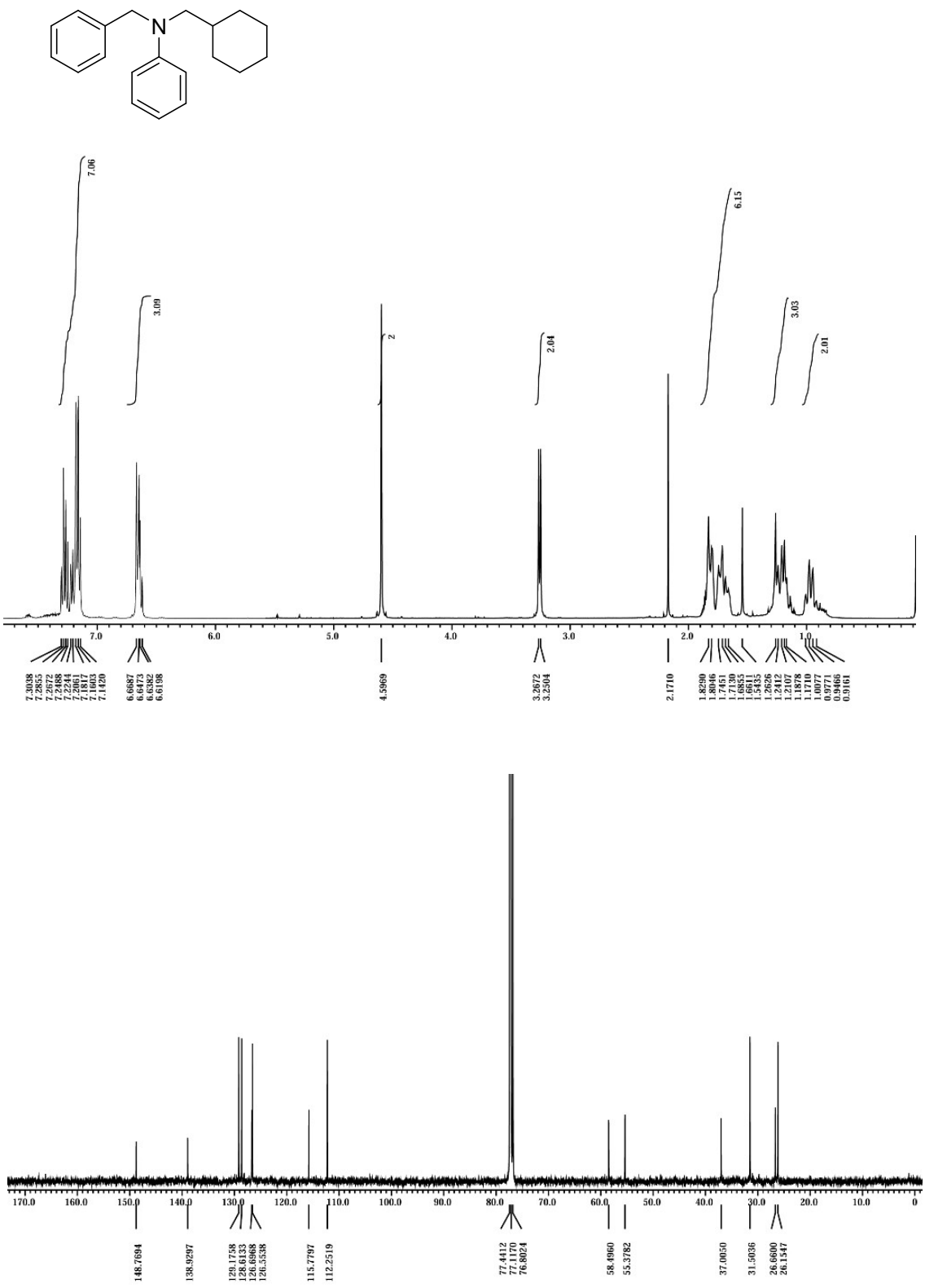


Figure S75. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

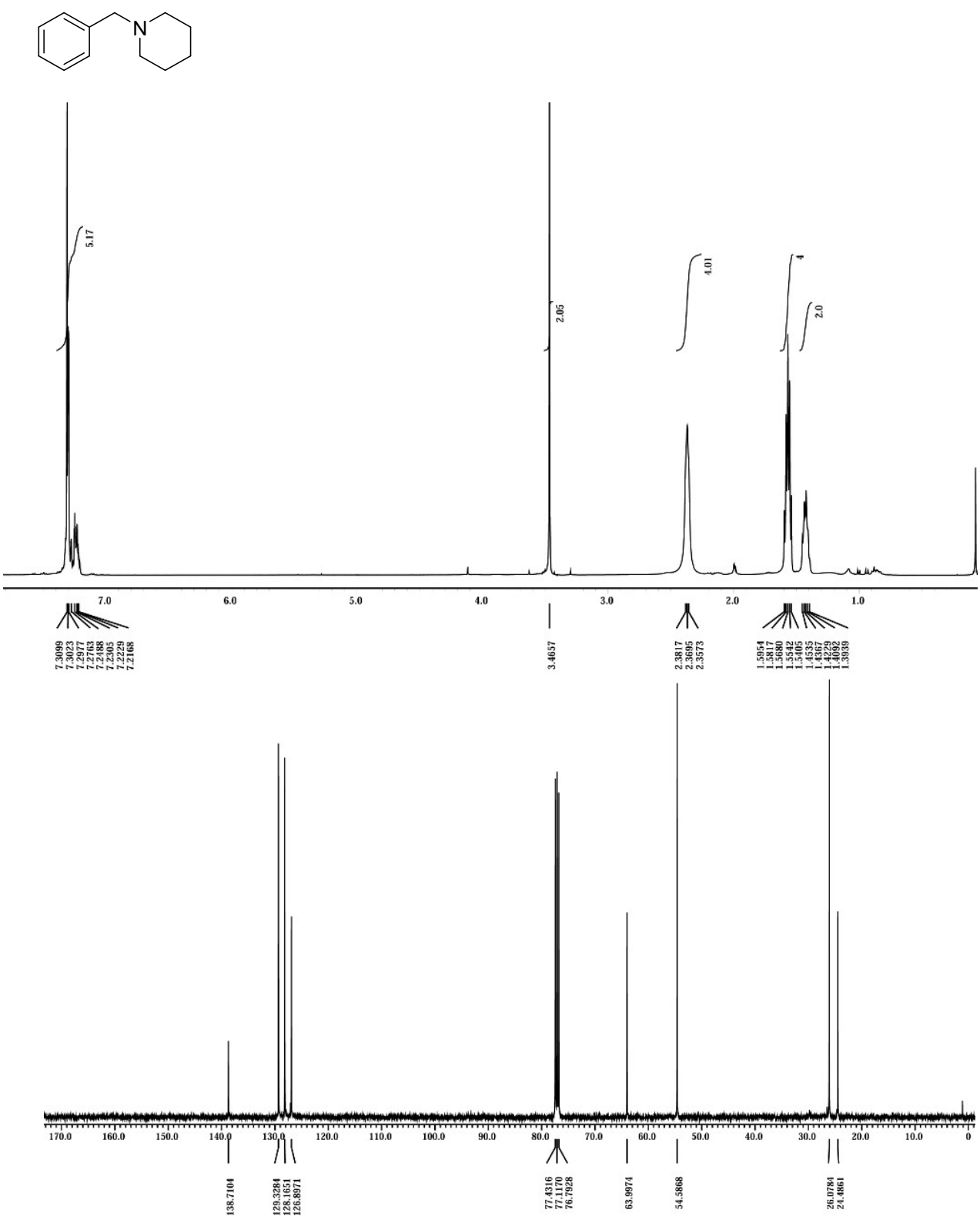
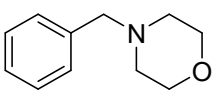
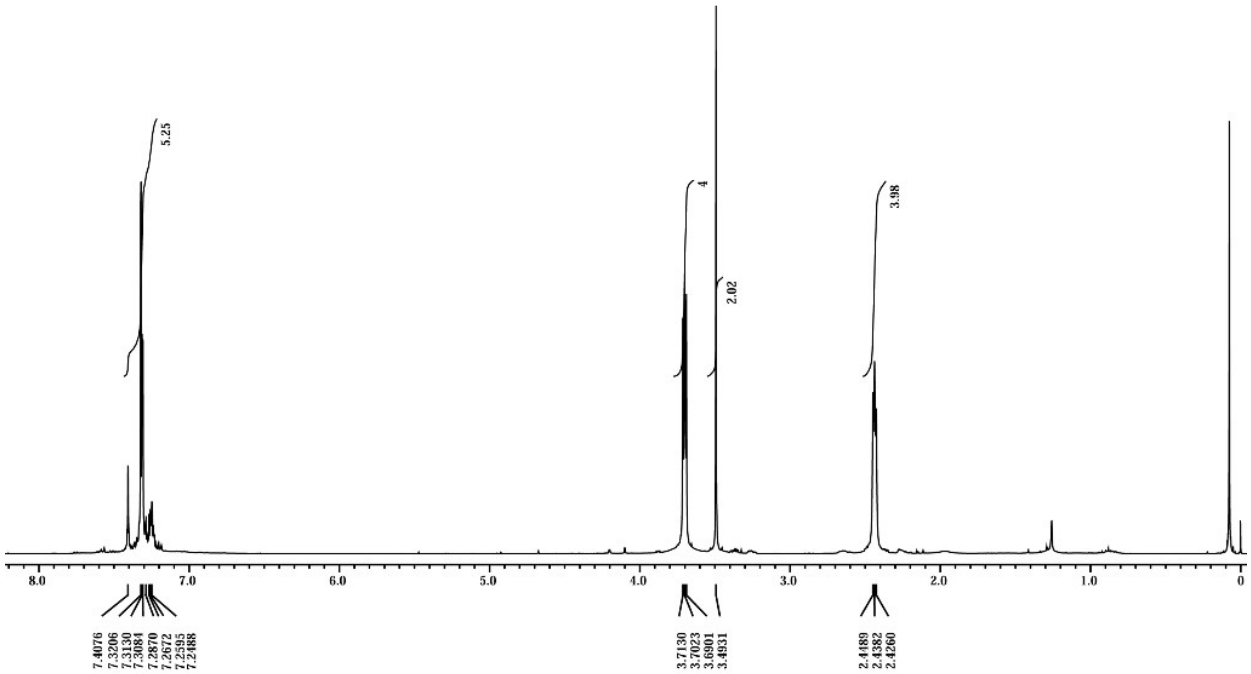


Figure S76. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.





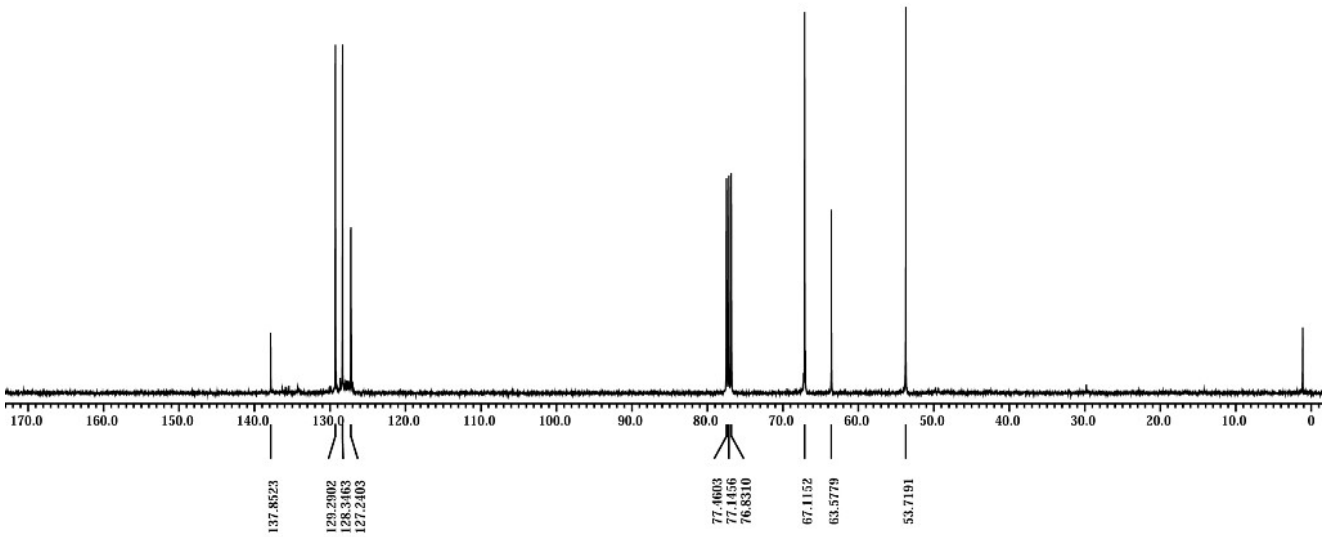


Figure S77. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

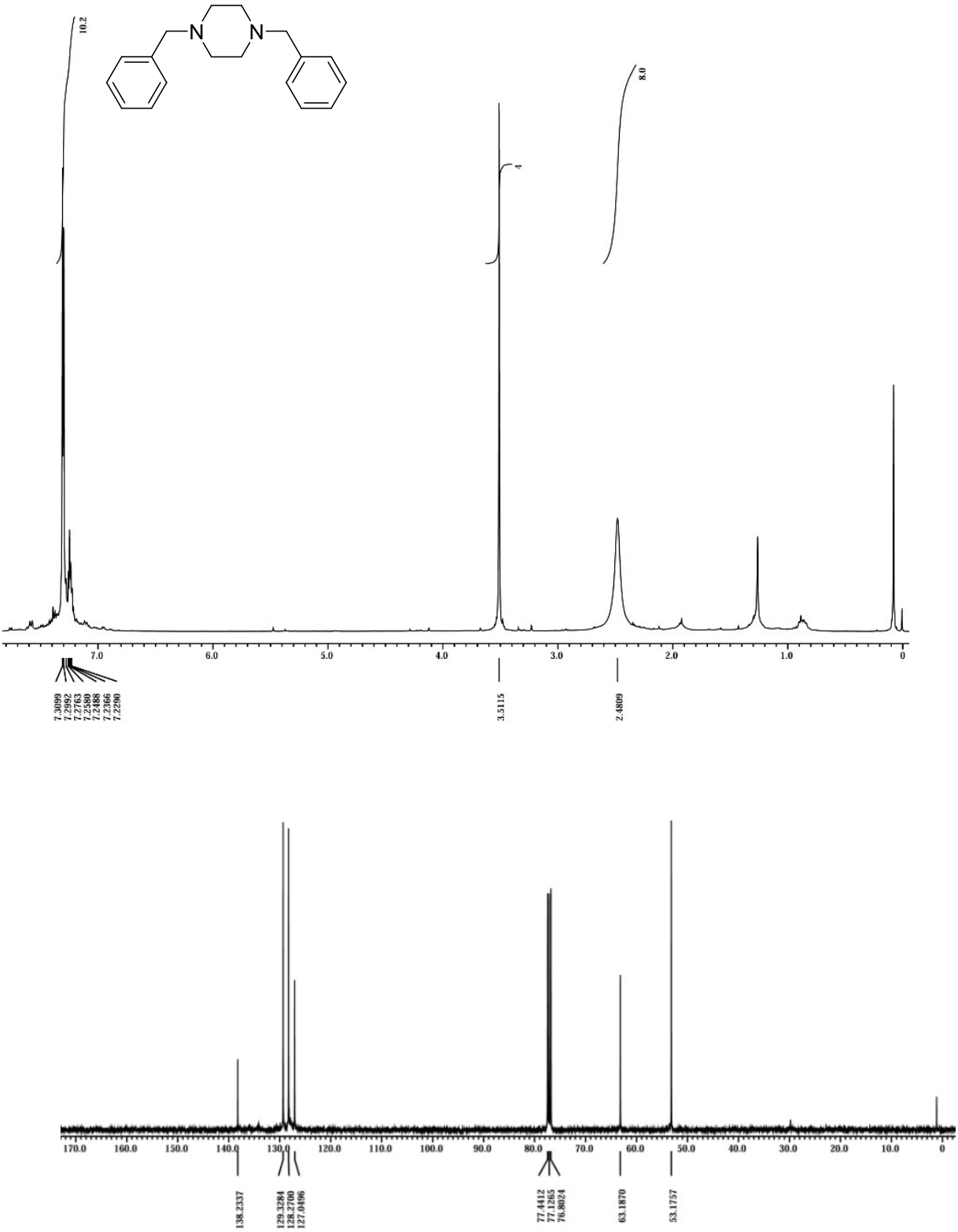


Figure S78. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

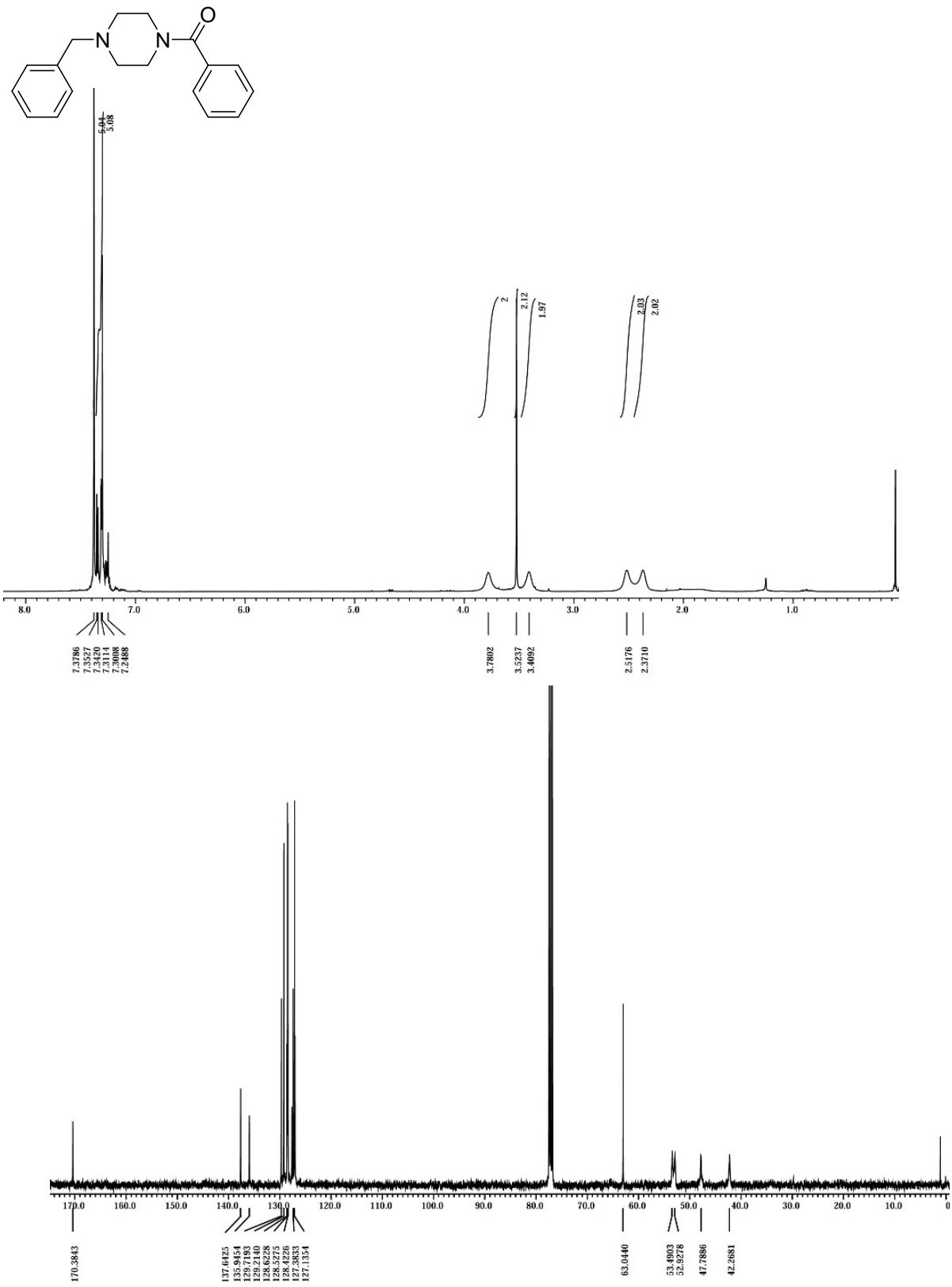


Figure S79. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

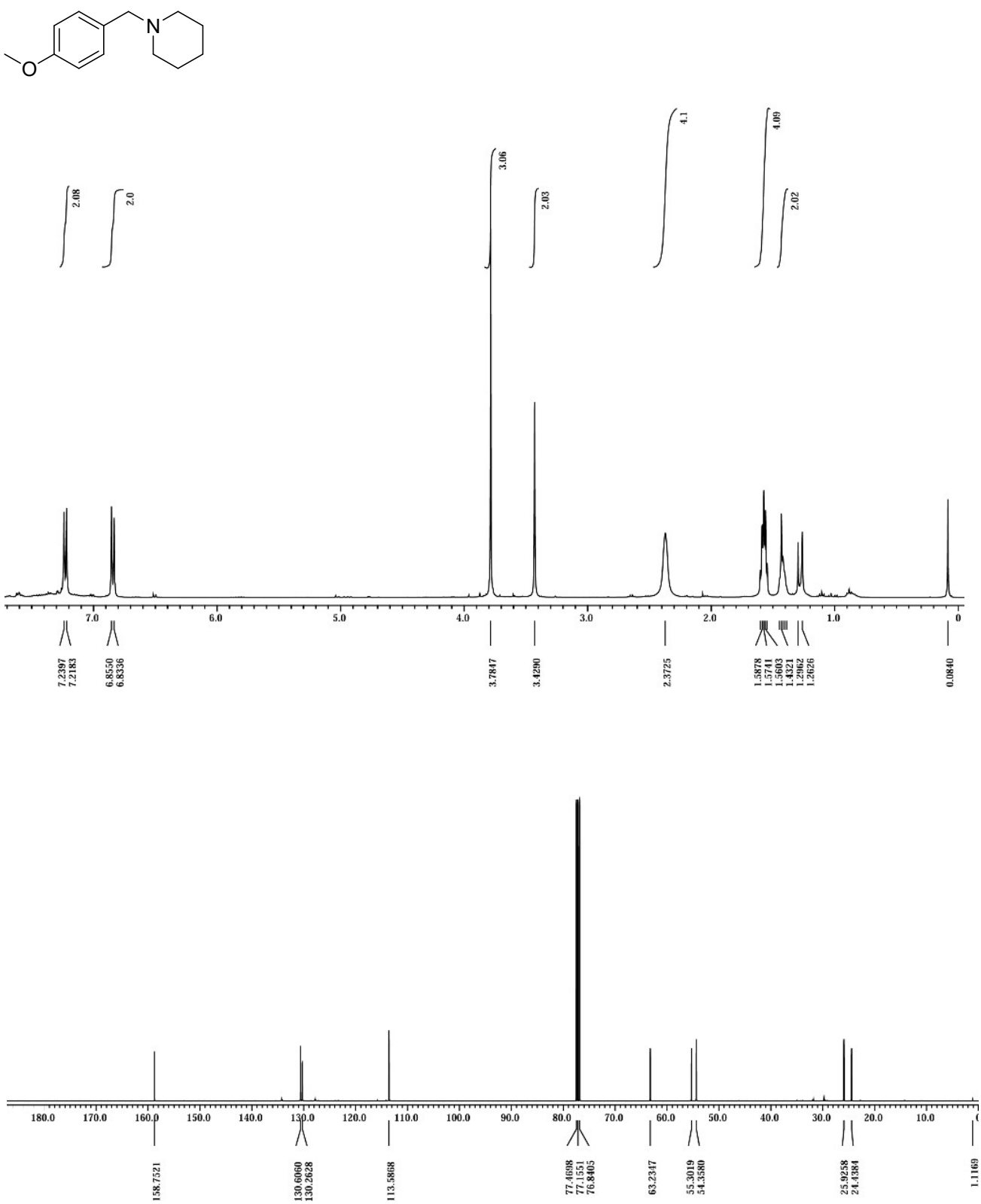


Figure S80. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

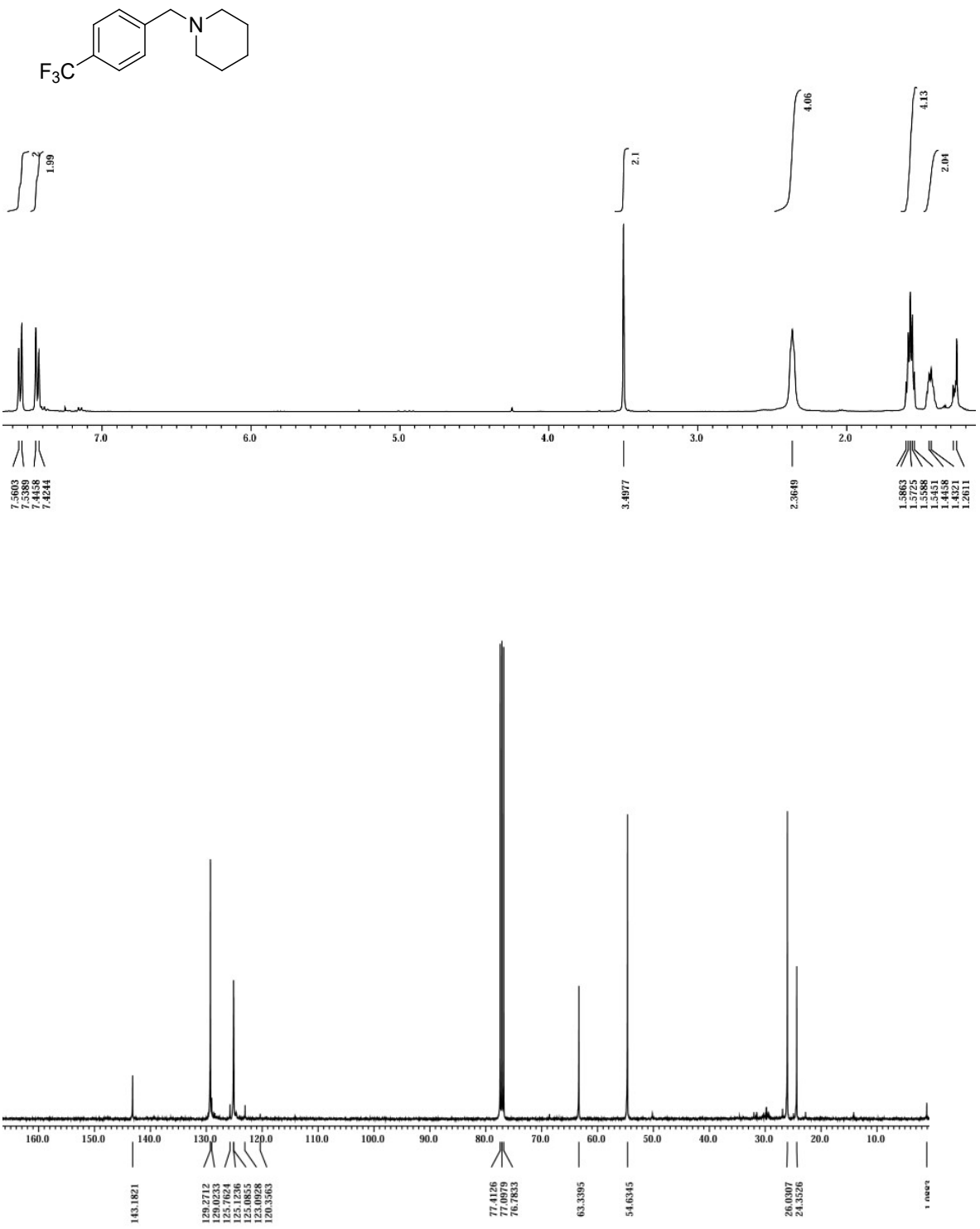


Figure S81. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

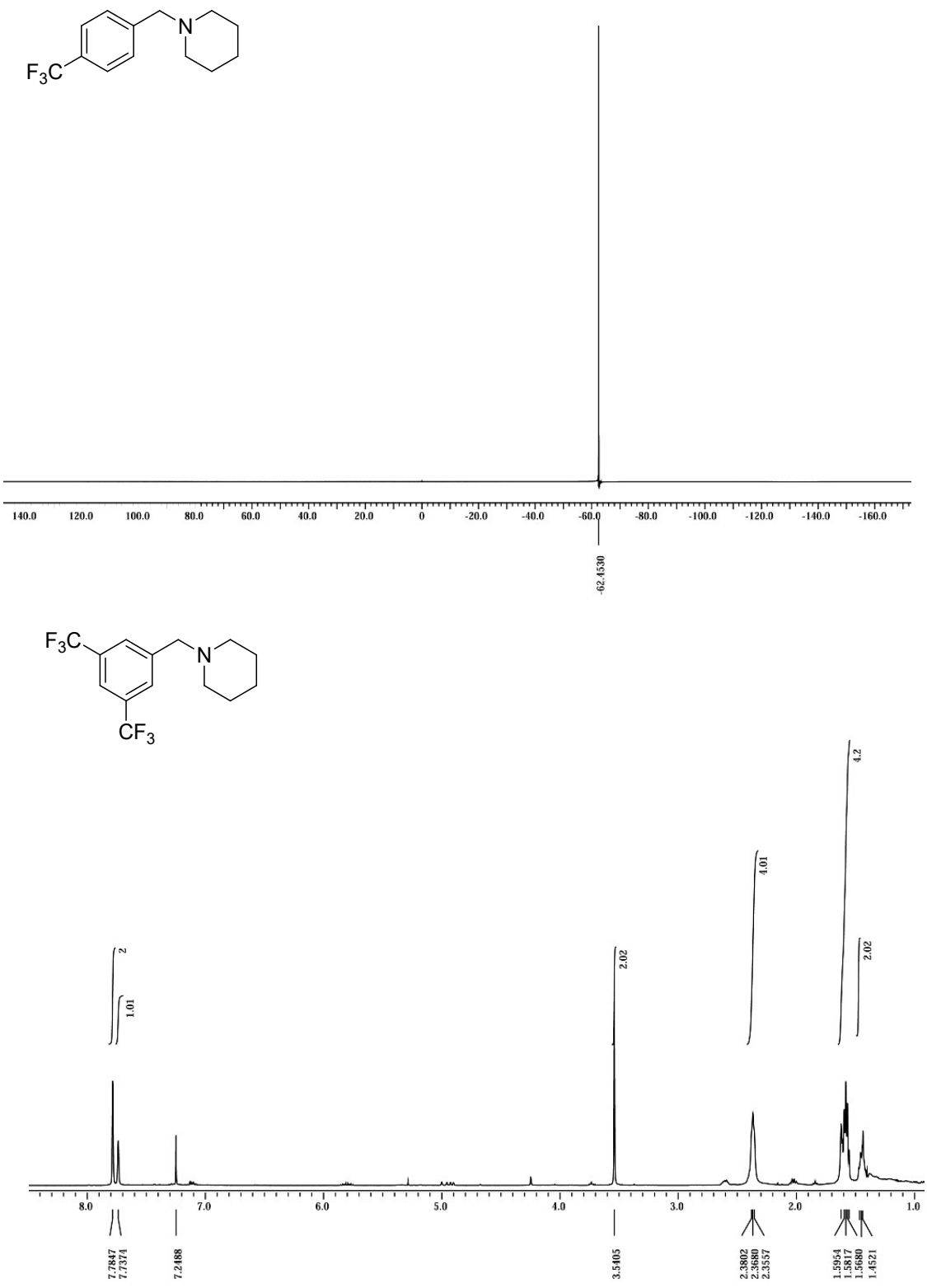


Figure S82. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

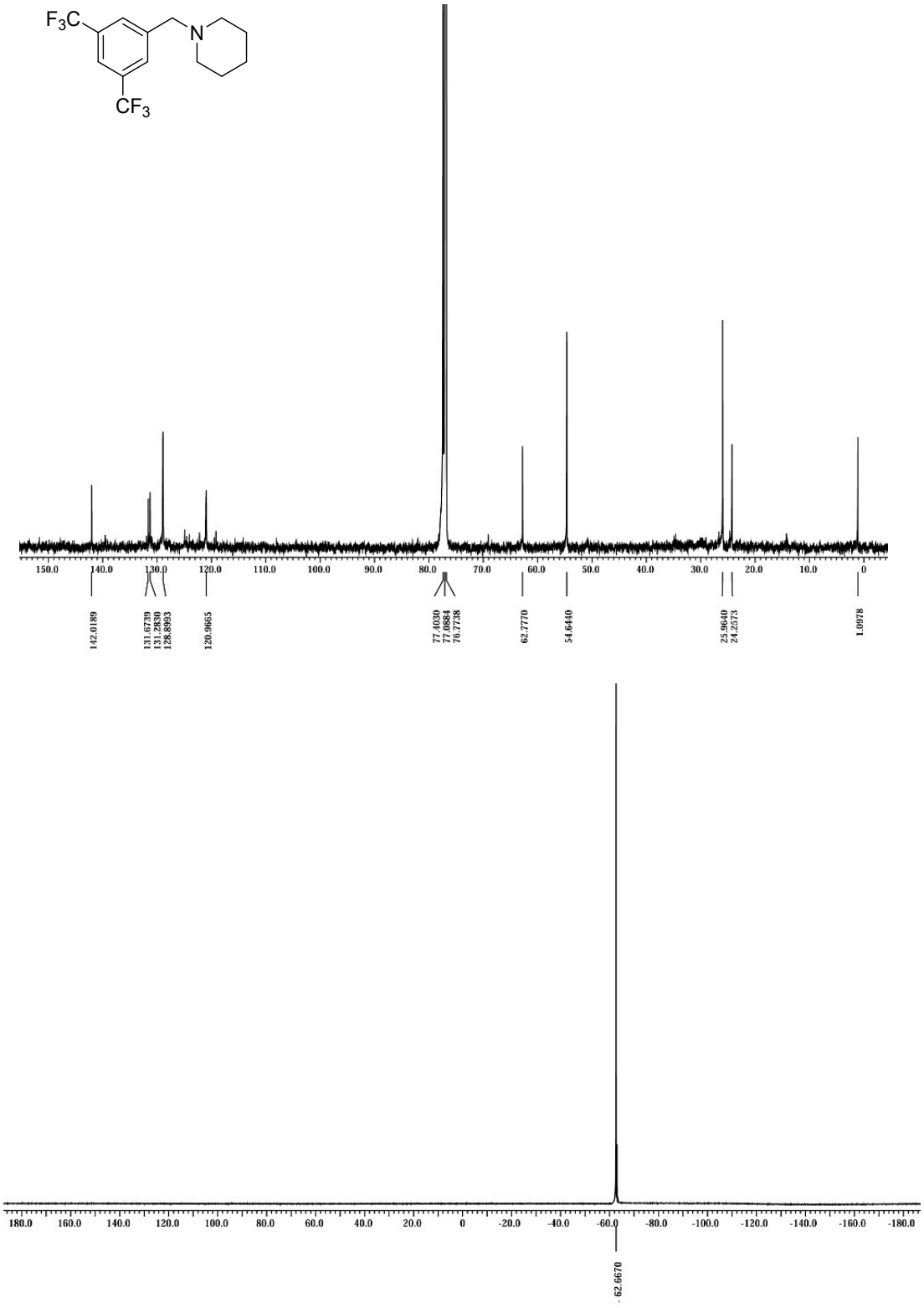


Figure S83. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

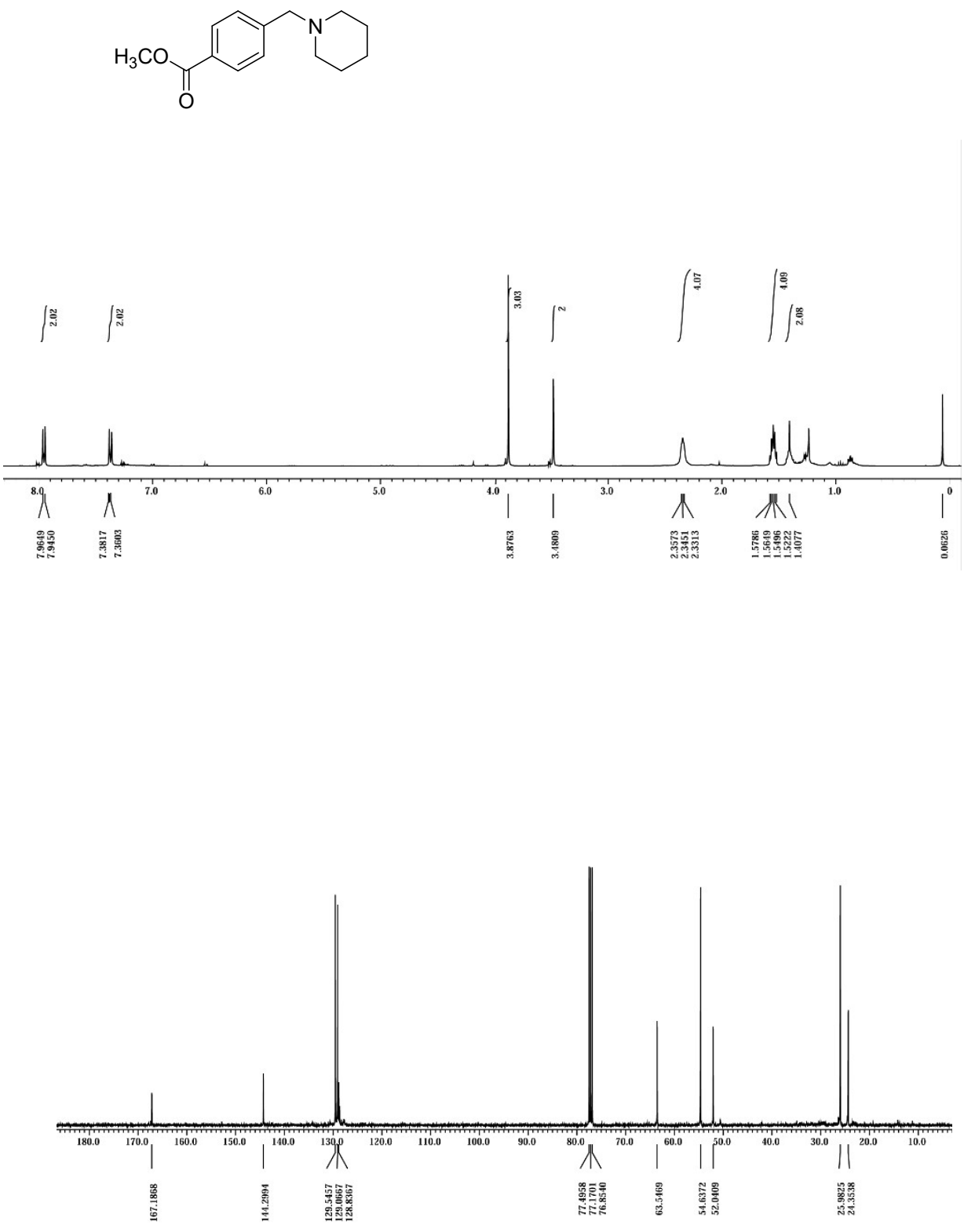


Figure S84. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

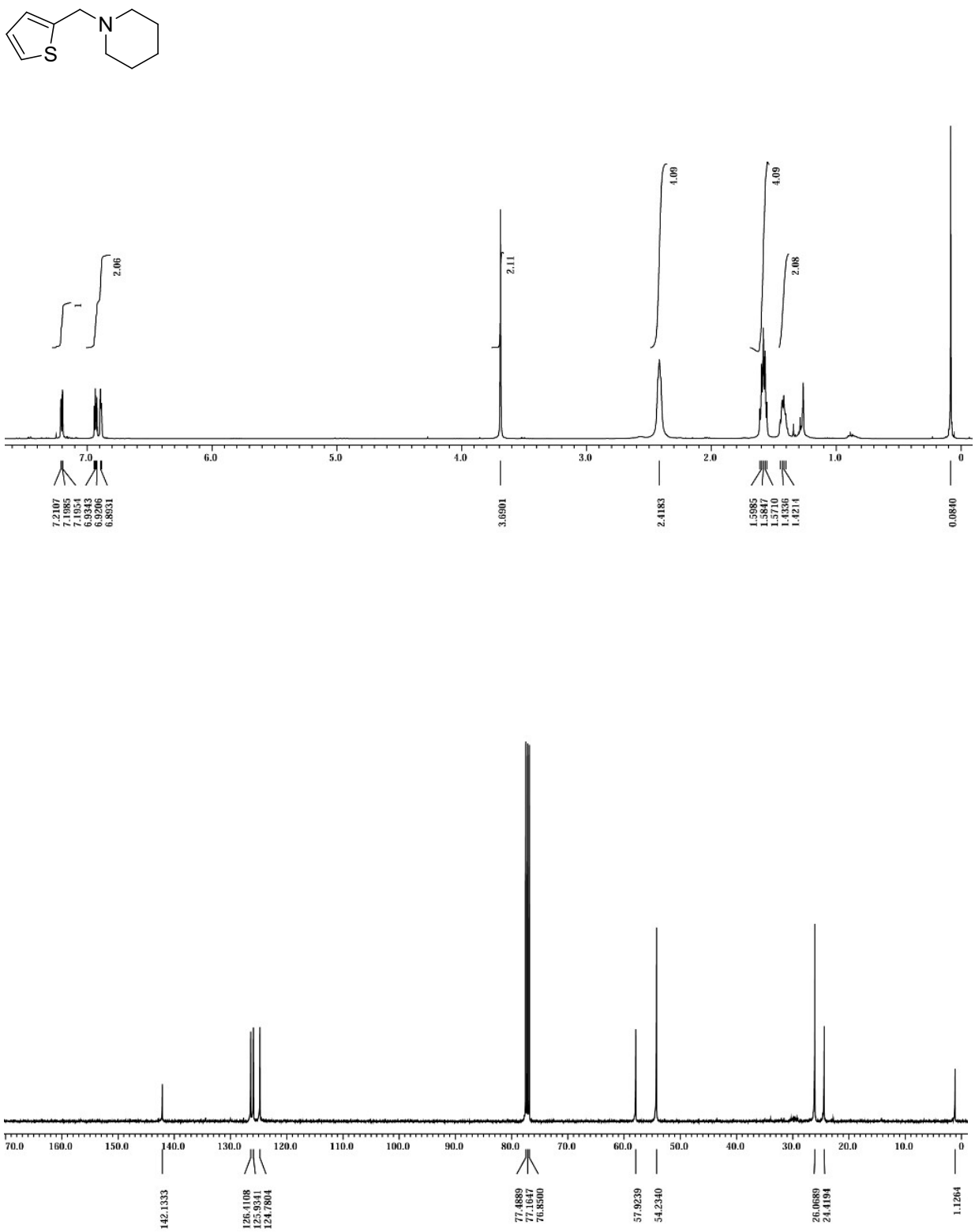


Figure S85. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

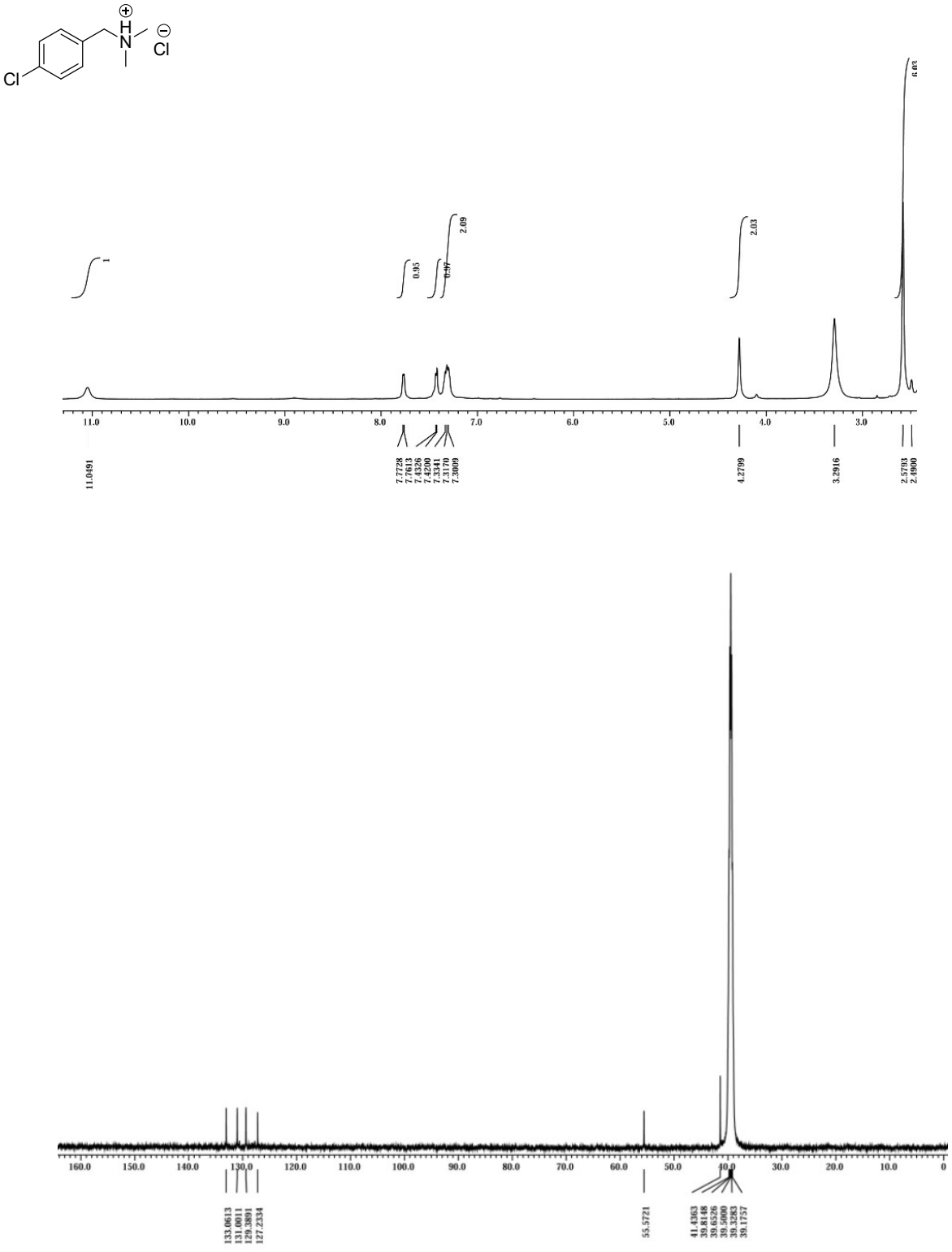


Figure S86. ^{1}H (top) ^{13}C (bottom) NMR spectra in DMSO-D_6.

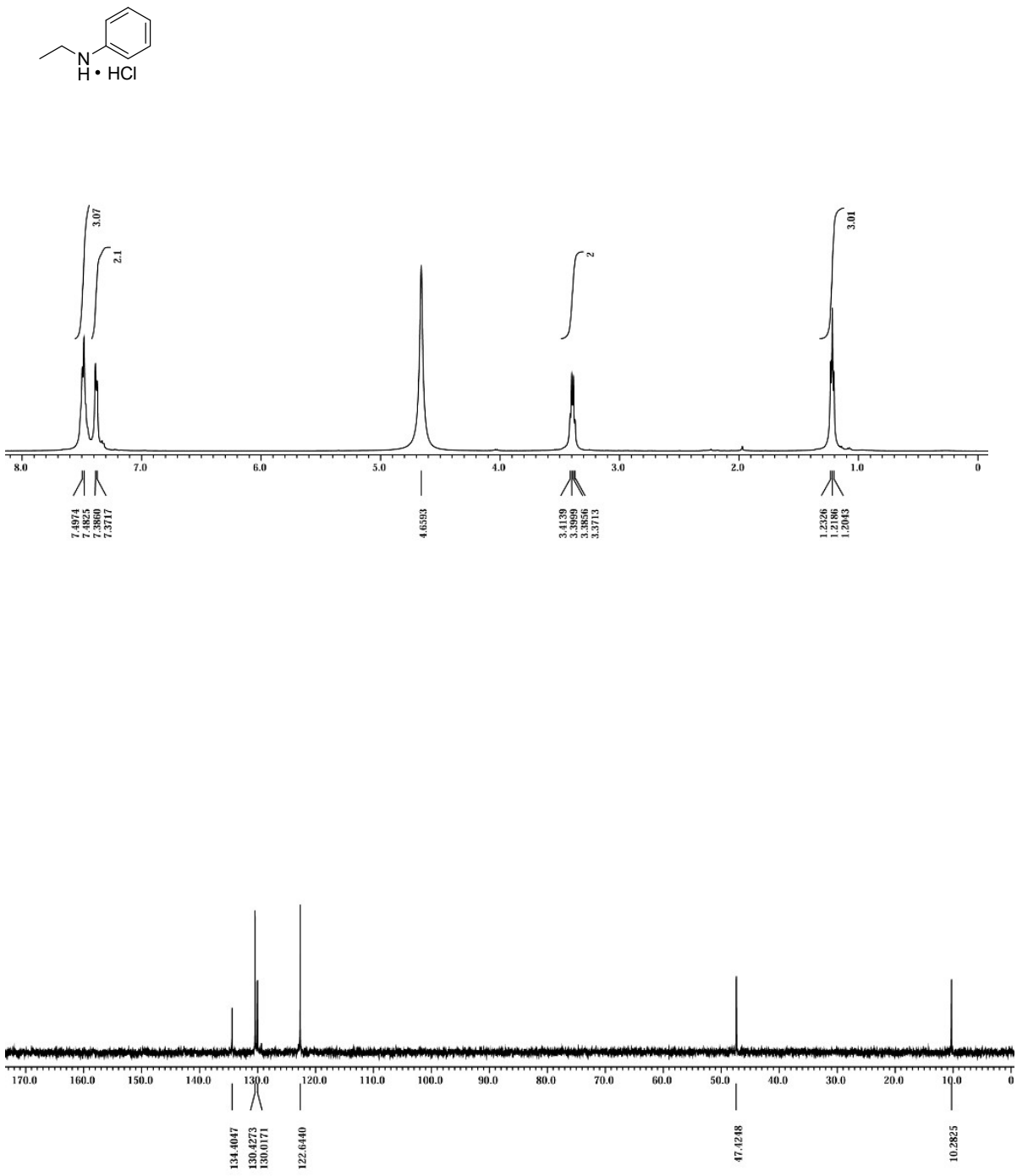


Figure S87. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

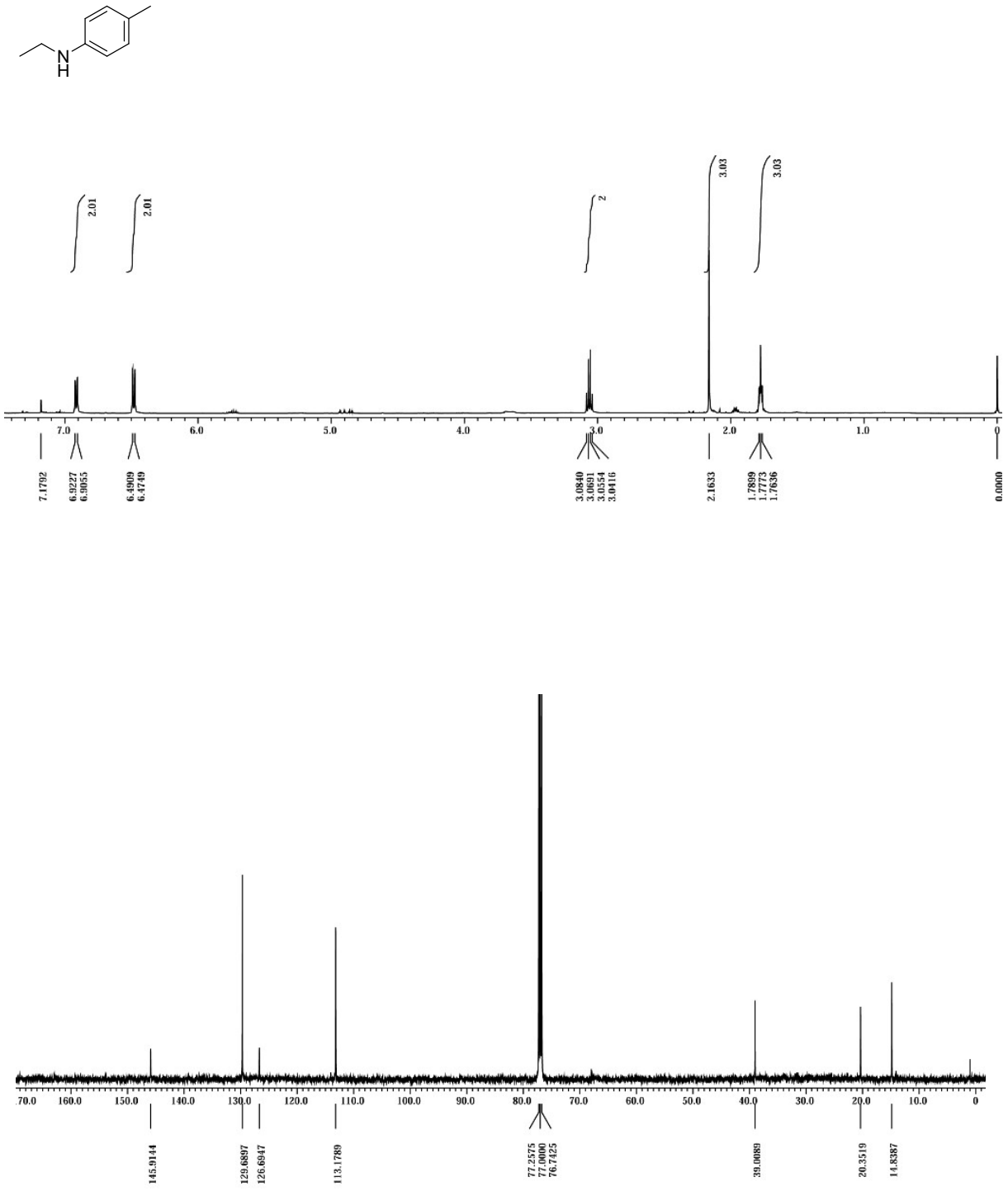


Figure S88. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

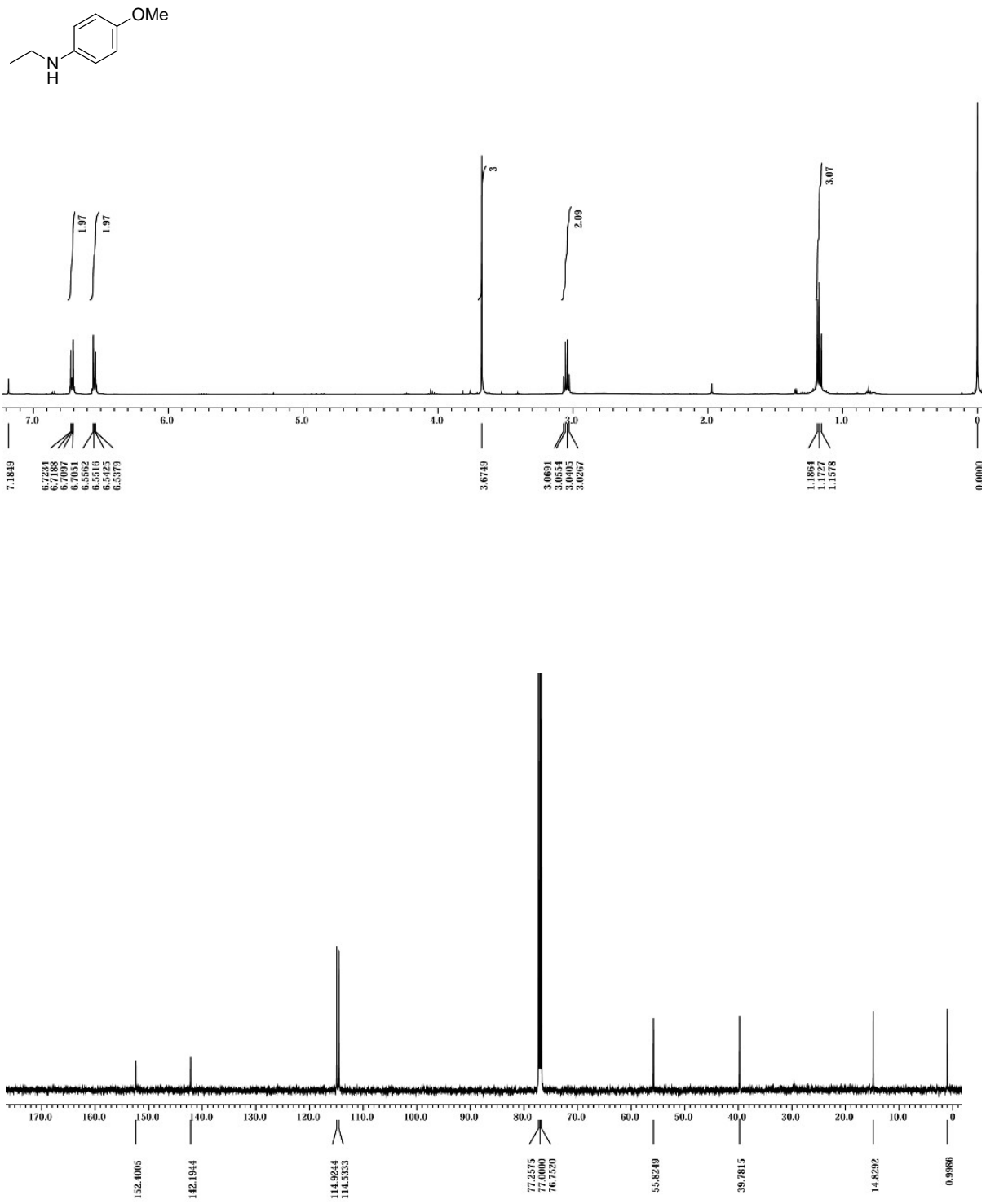


Figure S89. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

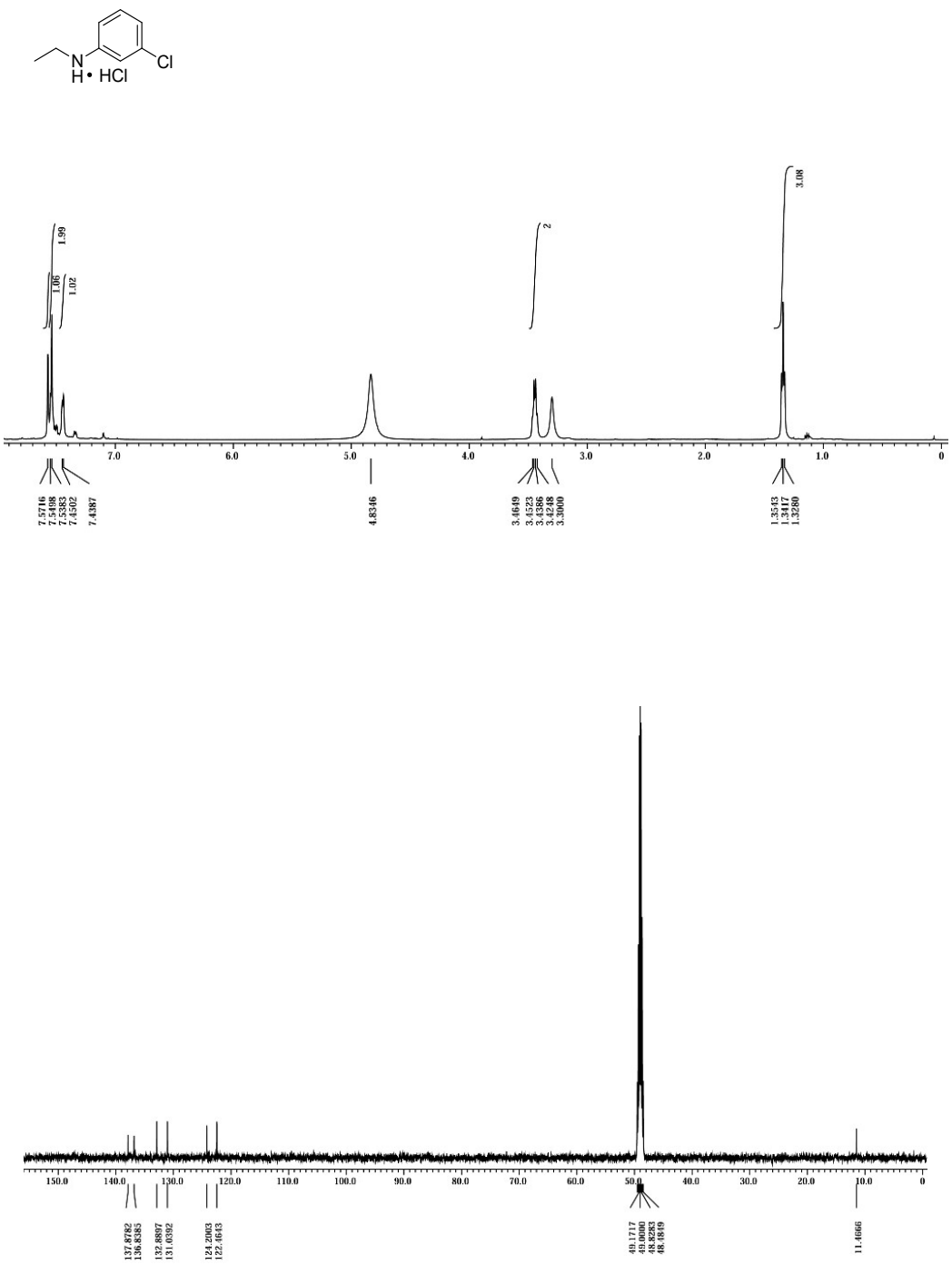


Figure S90. ^{1}H (top) ^{13}C (bottom) NMR spectra in CD_3OD.

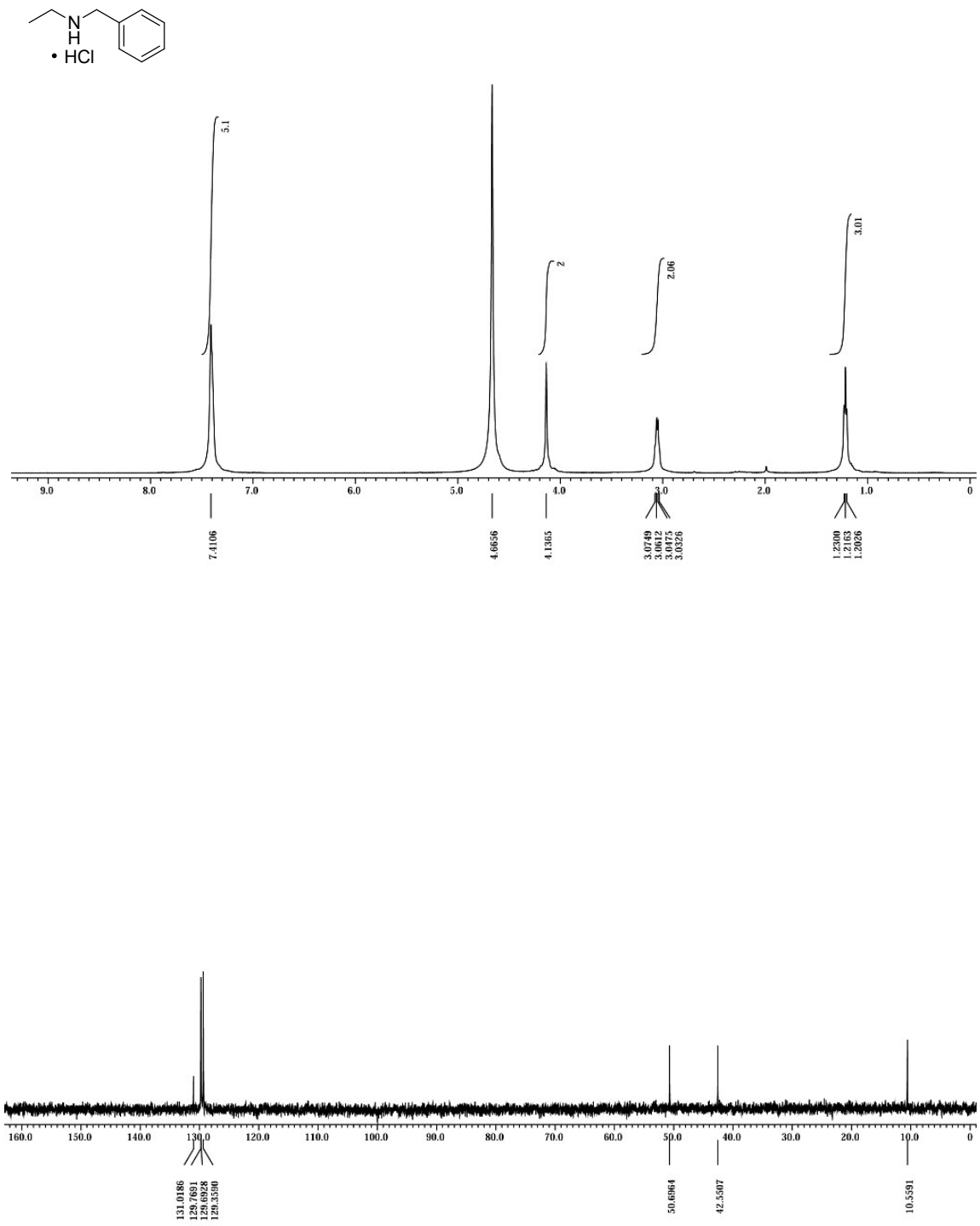


Figure S91. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

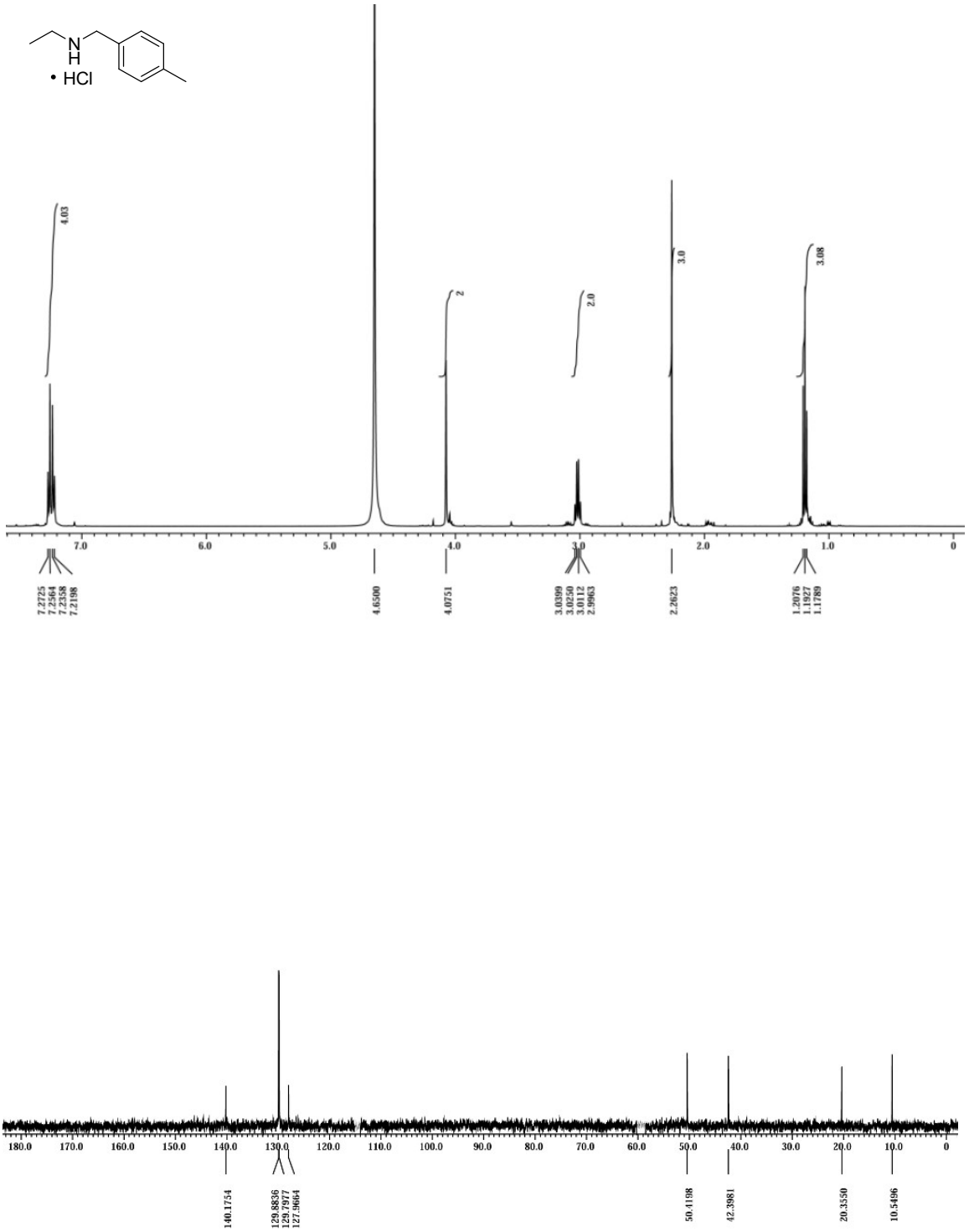


Figure S92. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

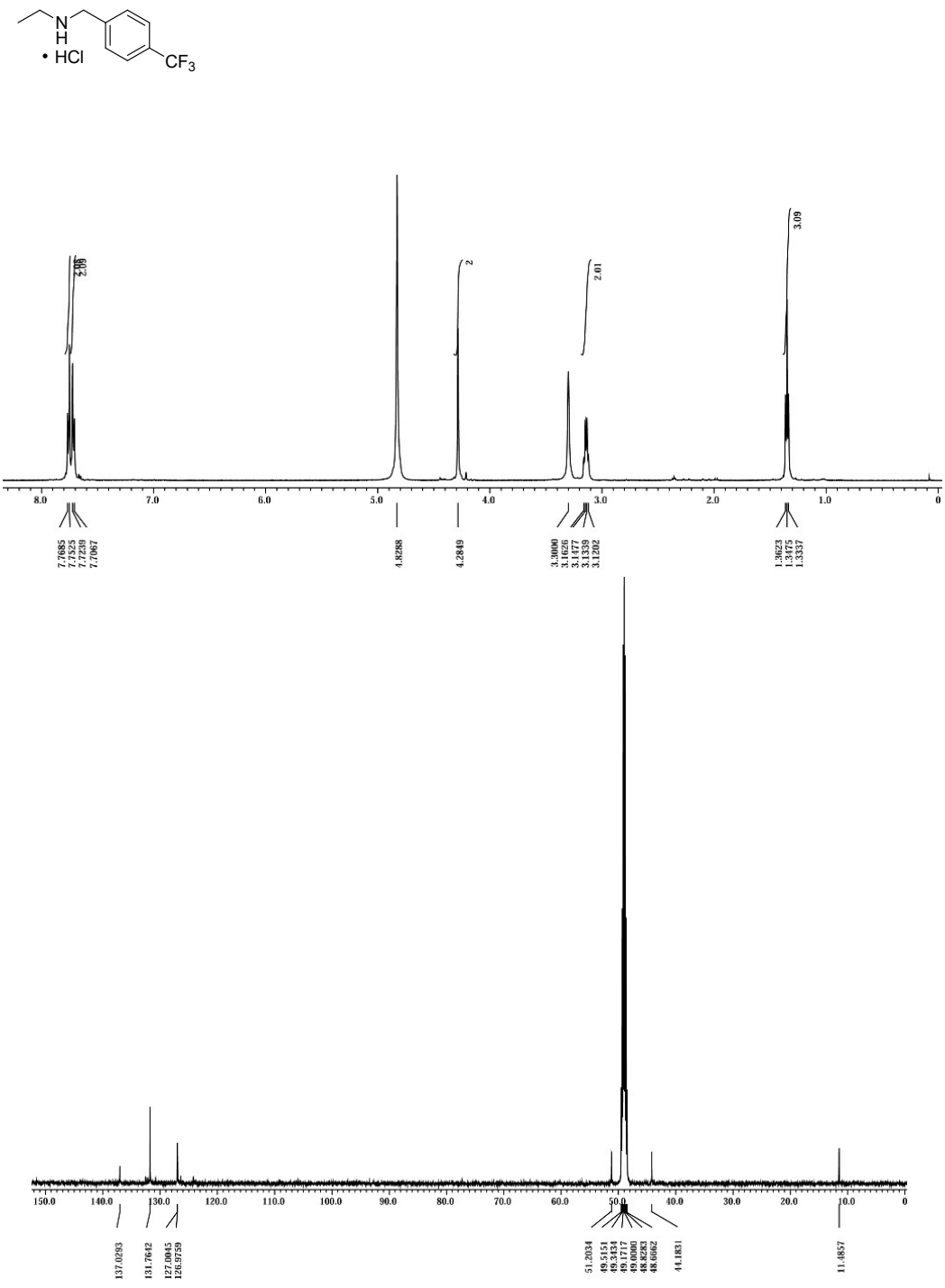


Figure S93. ^{1}H (top) ^{13}C (bottom) NMR spectra in

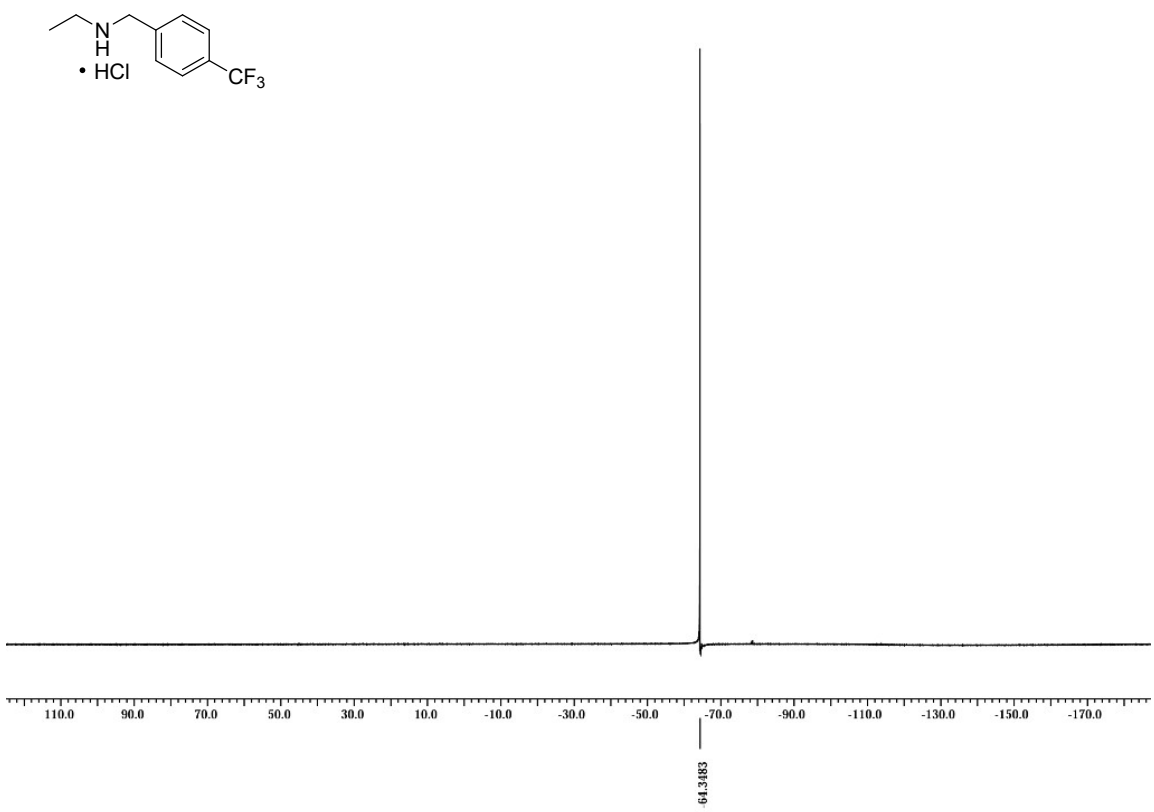


Figure S94. ^{19}F NMR spectrum in D_2O.

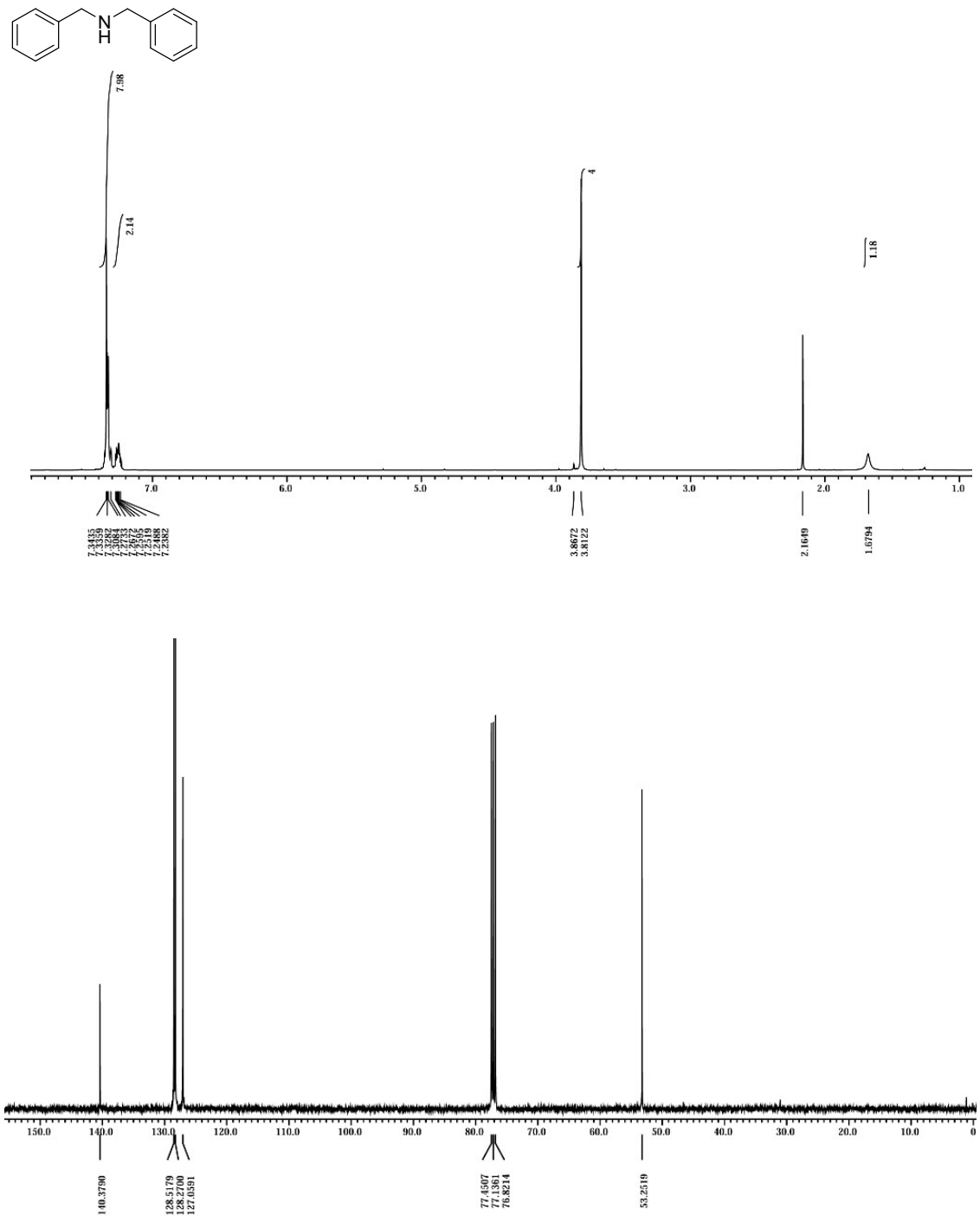


Figure S95. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

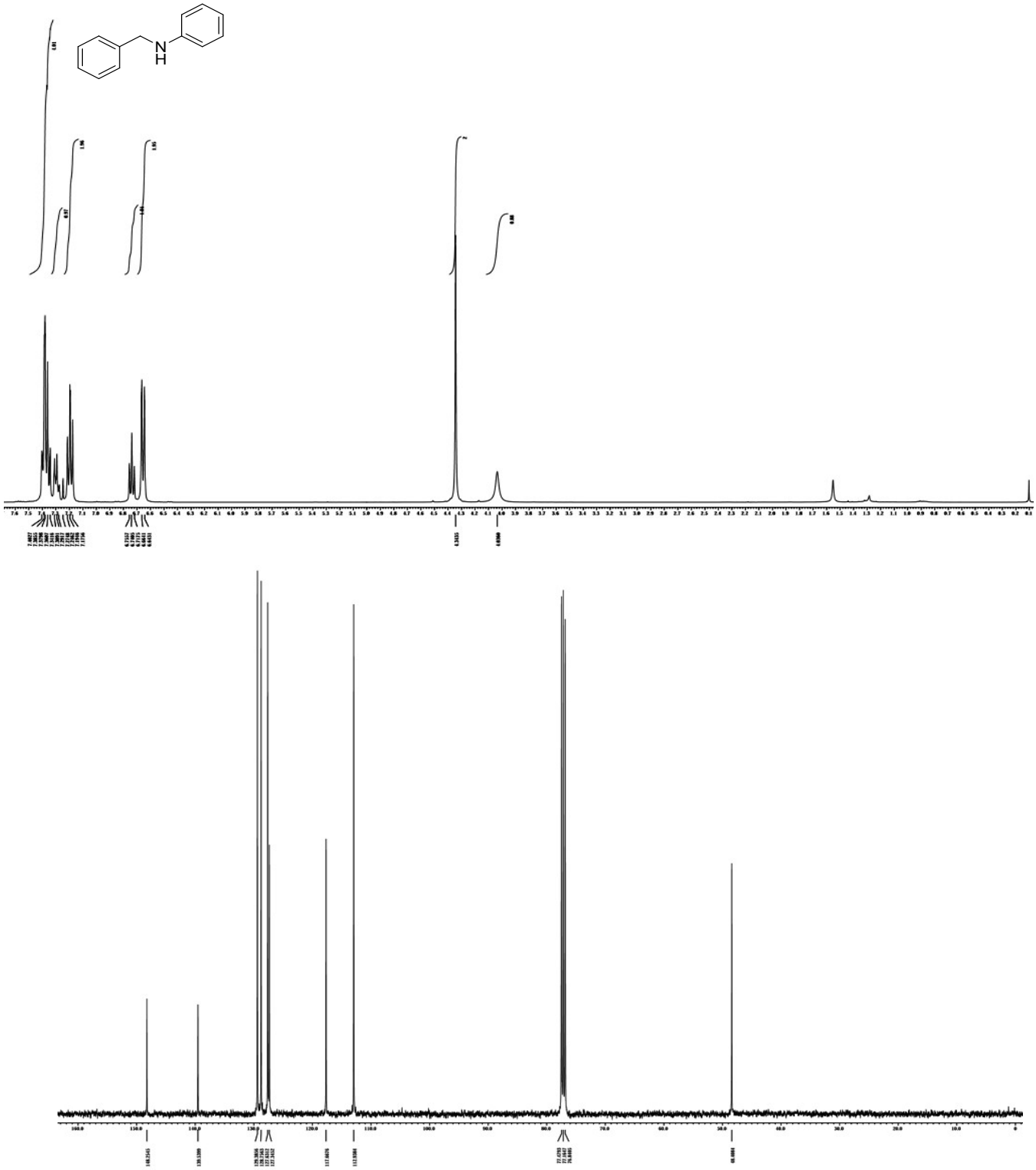


Figure S96. ^{1}H (top) ^{13}C (bottom) NMR spectra in $CDCl_3$.

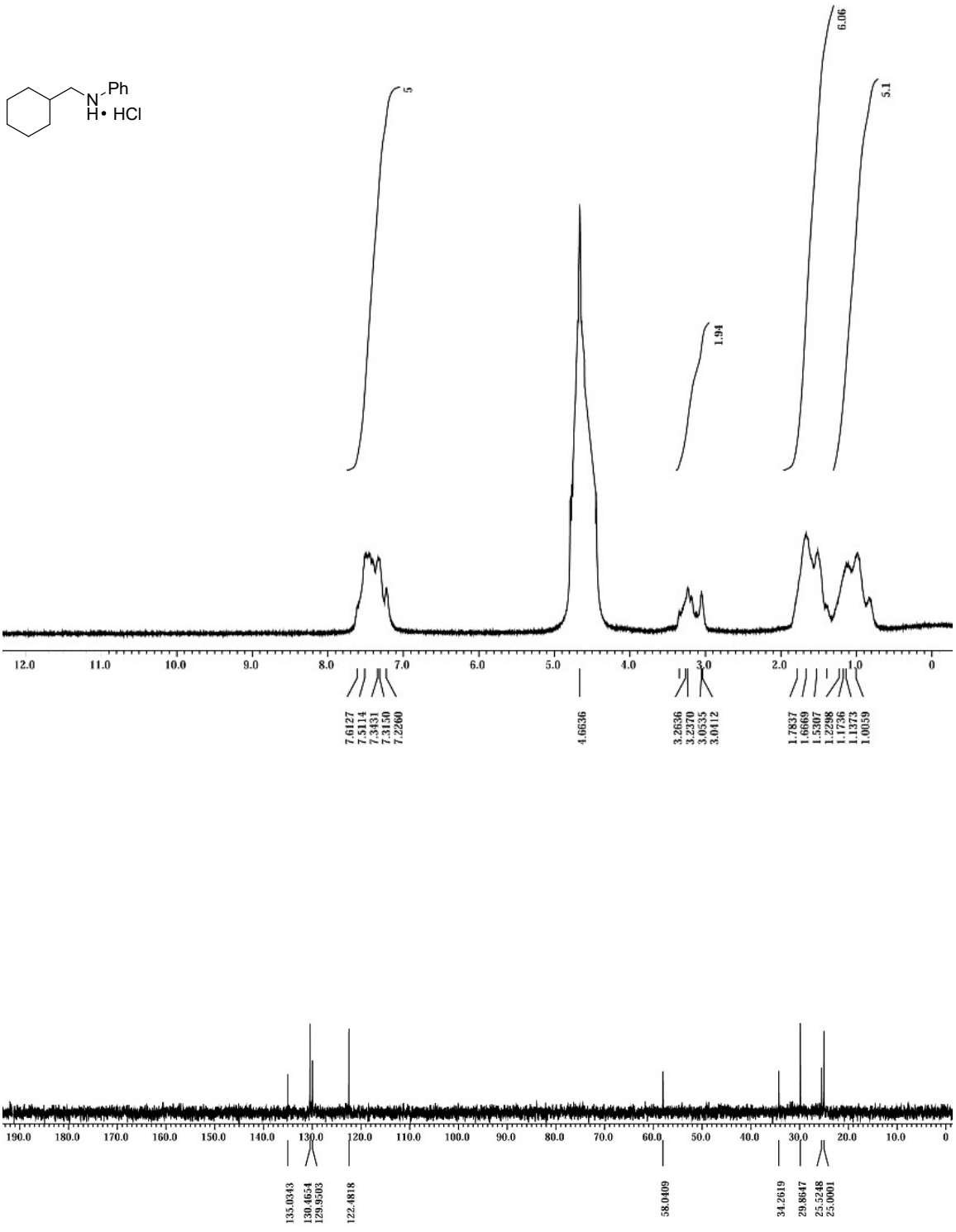


Figure S97. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

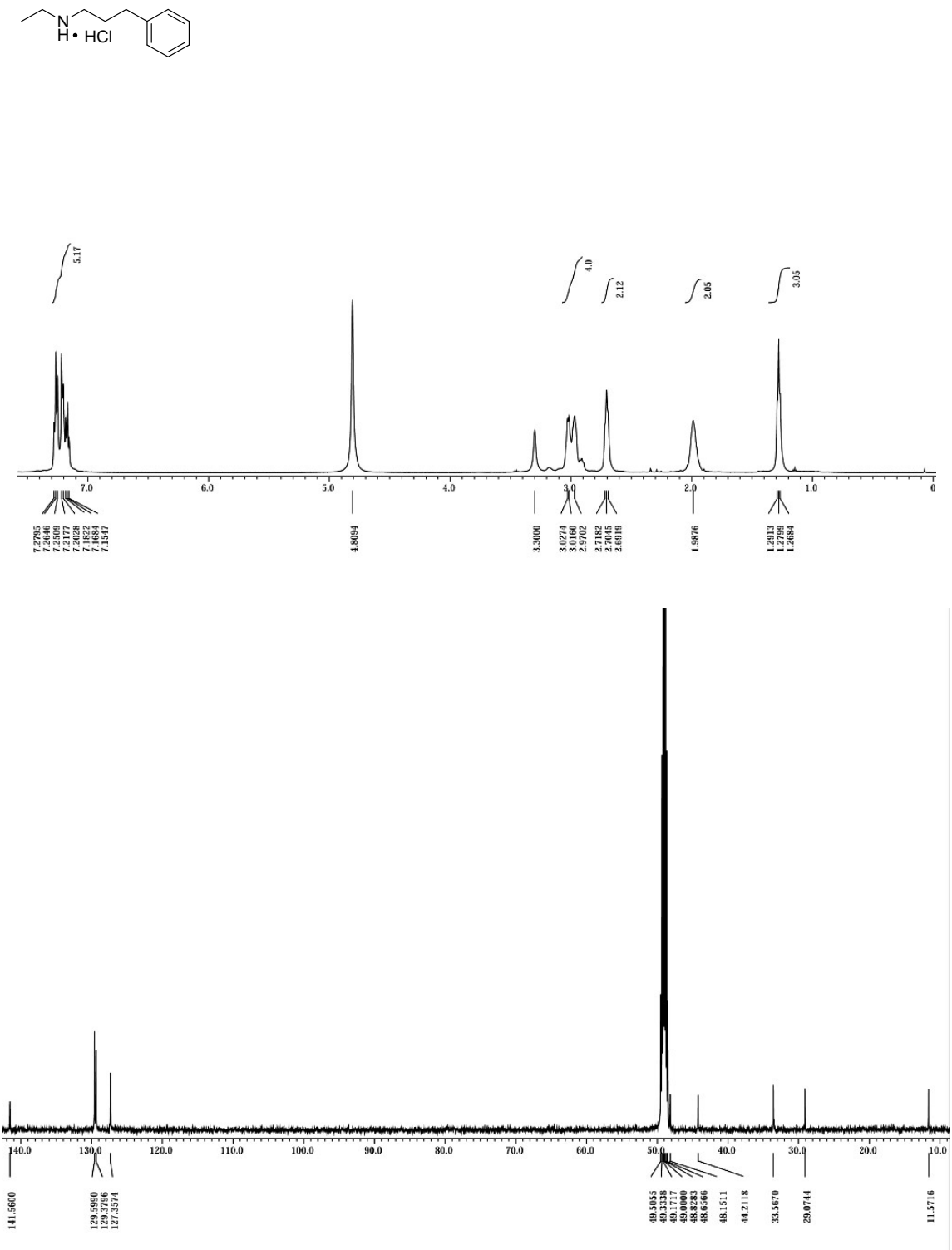


Figure S98. ^{1}H (top) ^{13}C (bottom) NMR spectra in

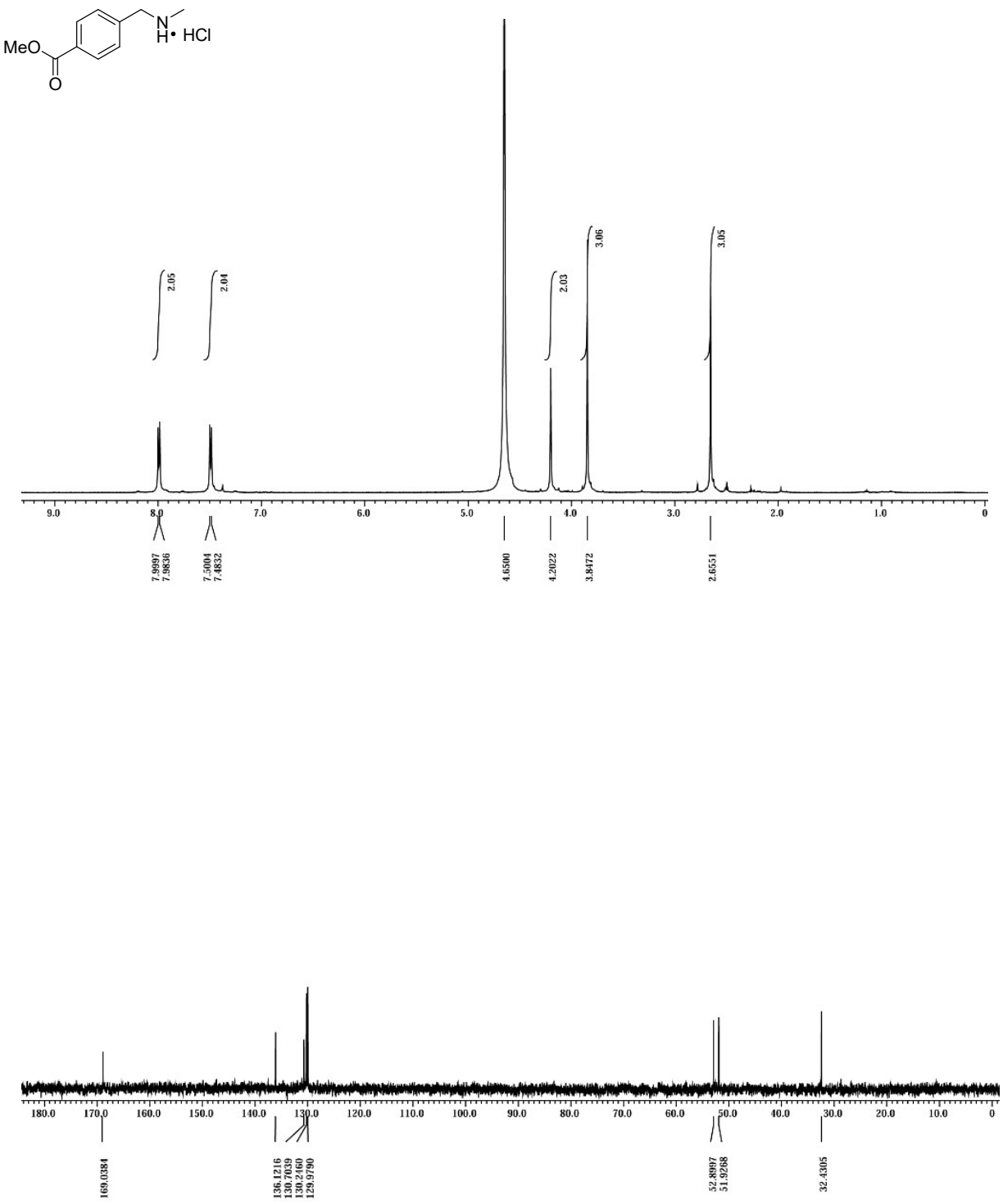


Figure S99. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

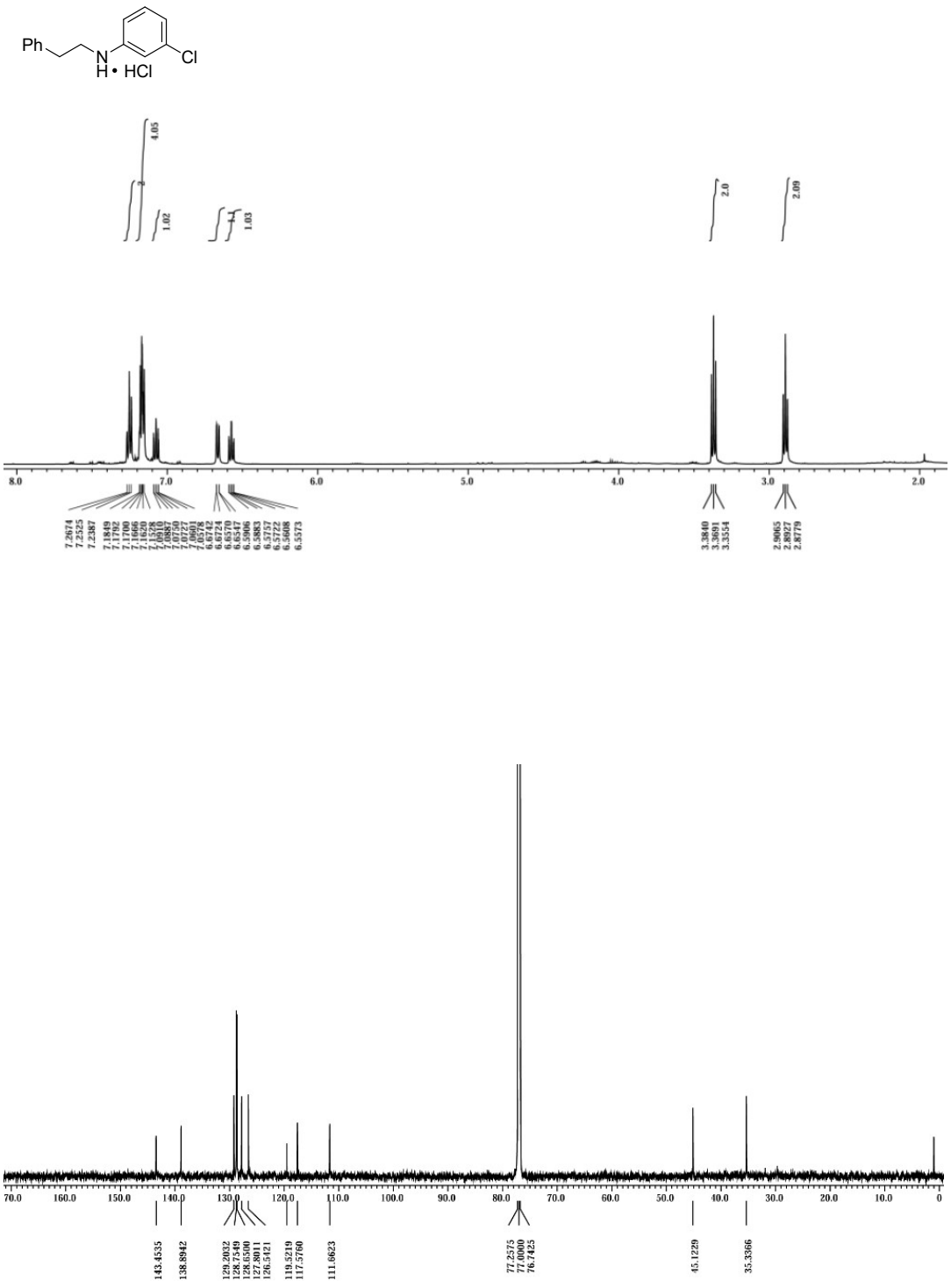


Figure S100. ^{1}H (top) ^{13}C (bottom) NMR spectra in

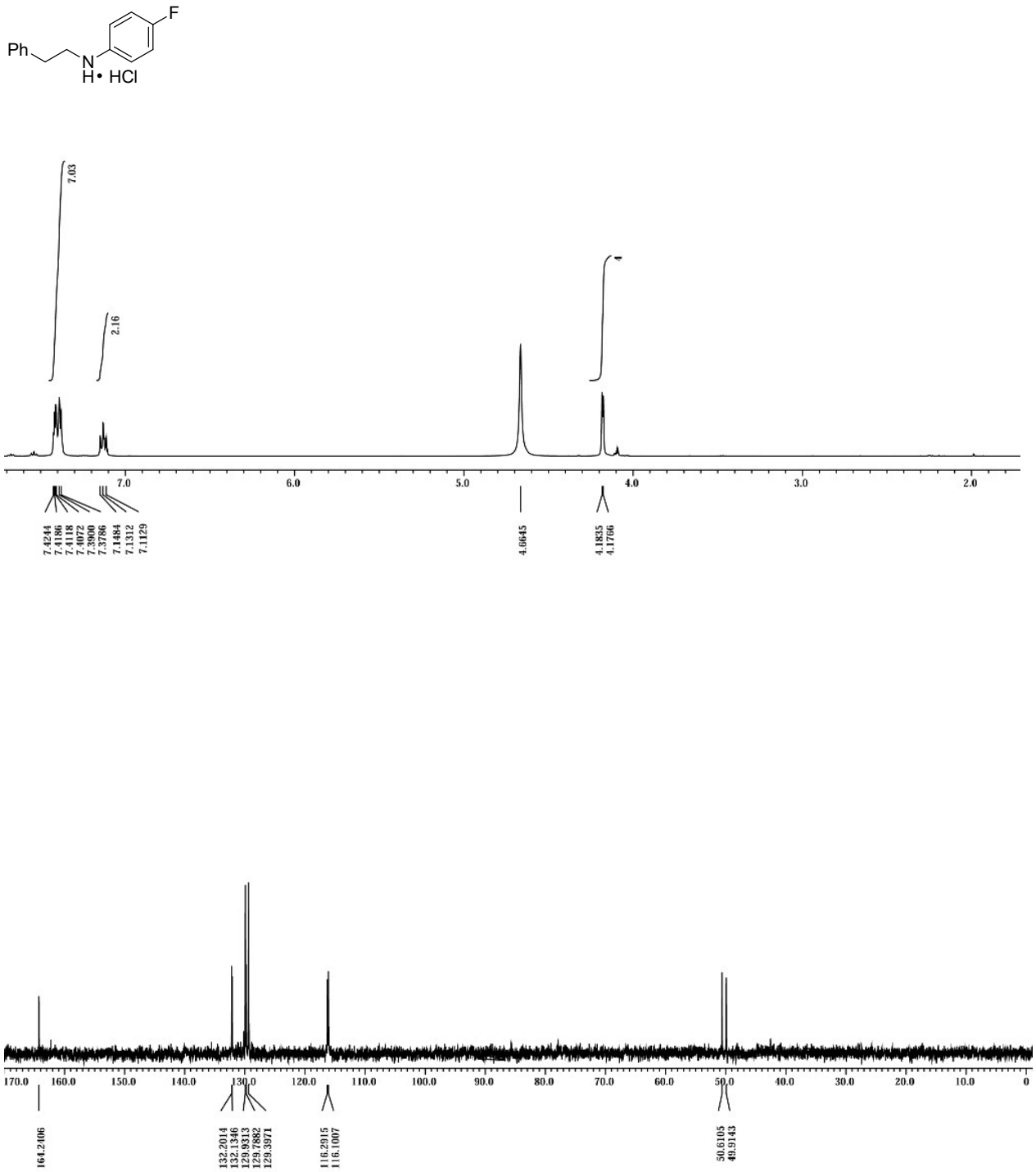


Figure S101. ^{1}H (top) ^{13}C (bottom) NMR spectra in D_2O.

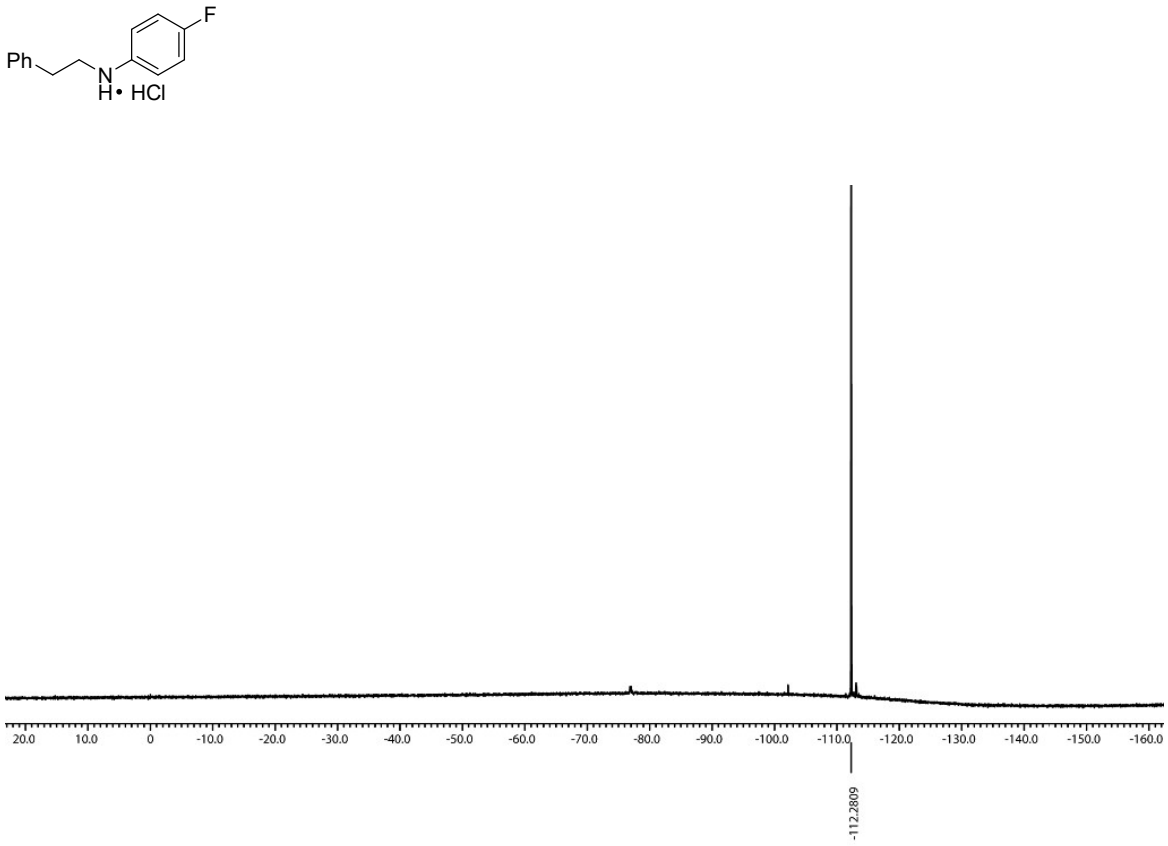


Figure S102. ^{19}F NMR spectrum in D_2O.

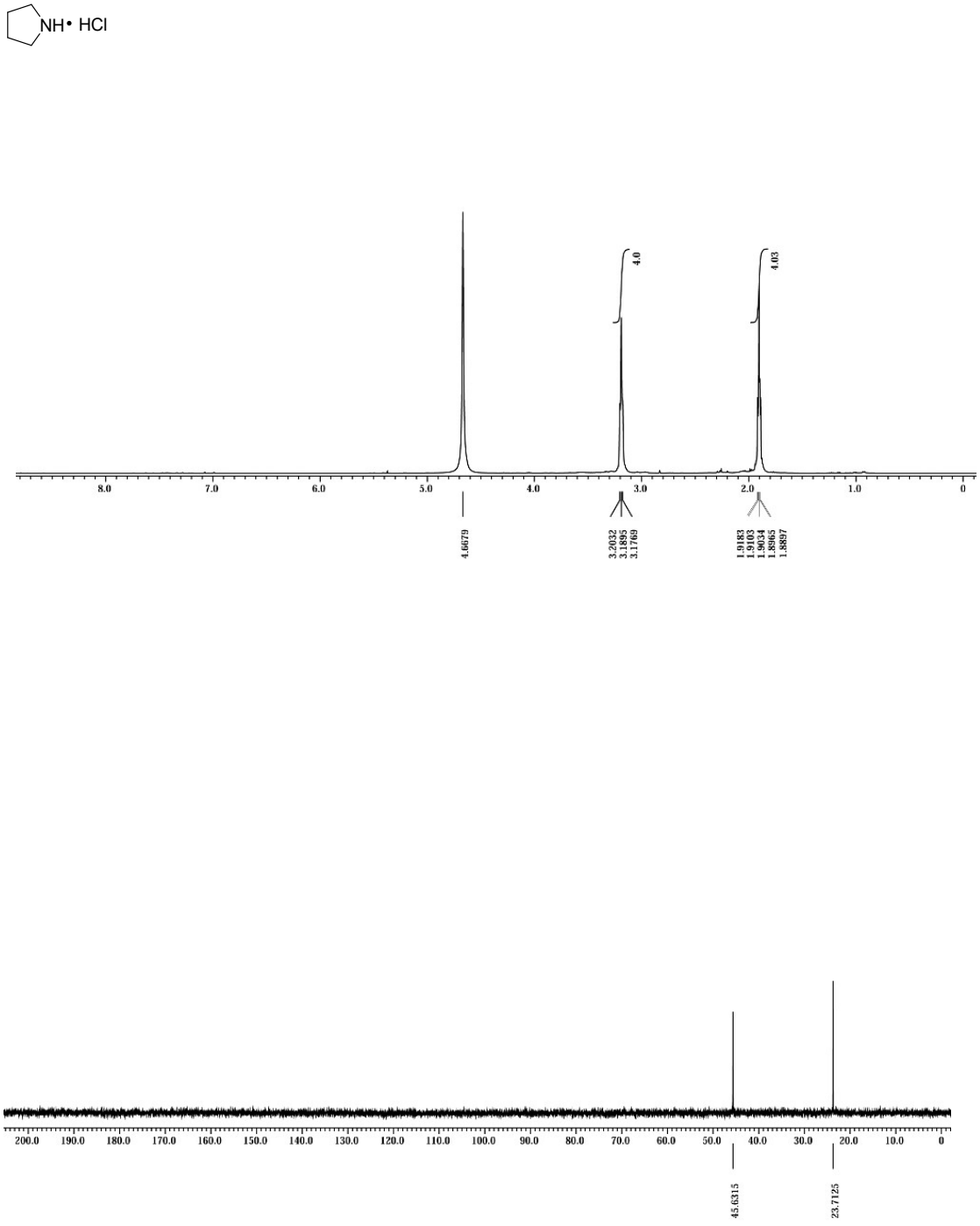


Figure S103. ^{1}H (top) ^{13}C (bottom) NMR spectra in

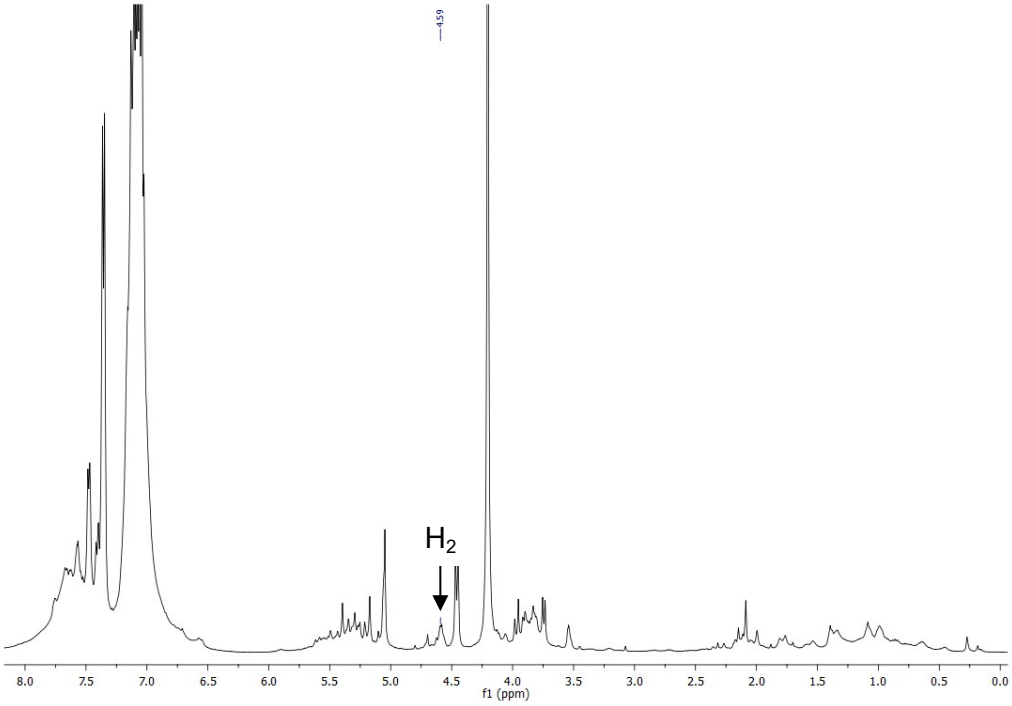


Figure S104. ^{1}H NMR spectrum for H_2 signal at δ 4.59 ppm in C_6D_6 after reaction of benzamide under the catalytic condition in J-Young NMR tube.

7. References

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