Supporting Information

Aminomethylation of Aryl Halides using α-Silylamines Enabled by Ni/Photoredox Dual Catalysis

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Key to Abbreviated Terms:

4CzIPN: 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile
Bpy: 2,2′-Bipyridyl
dtbbpy: 4,4′-Di-*tert*-butyl-2,2′-dipyridyl
LED: Light-emitting diode
diOMebpy: 4,4′-Dimethoxy-2,2′-dipyridyl

General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactors described in our previous reports or the new reactor design outlined here.[1] NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-d_5 (δ 2.50) in DMSO-d_6, acetone-d_5 (δ 2.09) in acetone-d_6, and residual MeCN-d_2 (δ 1.94) in MeCN-d_3. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.30), DMSO-d_6 (δ 39.52), the carbonyl carbon of acetone (δ 205.87), or the nitrile carbon of MeCN-d_3 (δ 118.26), respectively ^{19}F NMR spectra were referenced to hexafluorobenzene (δ –164.9)[2] as an internal standard and are run with C-F/C-H decoupling. Reactions were monitored by HPLC, GC/MS, ^{1}H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain, Seebach's stain,[3] ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected. Optical rotations were recorded using a Jasco P-2000 polarimeter with concentration (c) is in g/100 mL.

Chemicals: Deuterated NMR solvents were either used as purchased (MeCN-d_3, acetone-d_6, DMSO-d_6) or stored over 4Å molecular sieves and/or K_2CO_3 ($CDCl_3$). Na_2SO_4, $MgSO_4$, CH_2Cl_2, $CHCl_3$, EtOAc, pentane, hexanes, MeOH, Et_2O, and toluene were used as purchased. Et_3N was purchased from commercial suppliers and distilled from CaH_2 prior to use. THF was purchased and dried *via* a solvent delivery system. DMF (99.8%, extra dry) was stored over 4 Å molecular sieves. The transition metal photocatalysts $Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ were prepared in-house by the procedure outlined in our previous publications.[1a,4] The organic photocatalyst 4CzIPN was prepared in-house by the procedure outlined in our previous

publication.[5] Bromo- or iodoarenes were either purchased from commercial suppliers or prepared in-house using the procedures outlined here. α-Silylamines were prepared according to the representative procedure outlined below from their corresponding chloromethylsilanes and amines

Photochemistry: Irradiation of reaction vessels was accomplished using blue LEDs. LEDs were configured as outlined in the *Photochemical Reactor Design* section of our previous articles[1b,c] or using a second generation reactor design outlined here. A fan was employed to ensure reactions remained at or near rt when using LEDs.

Information for LED-based Photoreactor Components:

- *Blue LEDs*: 39.4 inch strips, 470 nm blue light, 32918 mcd ft^{-1}
- *Power Supply*: 12V DC CPS series Power Supply - 15 Watt
- *Connectors*: LC2 Locking Male Connector CPS Adapter Cable
- *Clip Fan*: 2-Speed Clip Fan, 6-Inch
- Pyrex crystallizing dishes (125 X 65 mm)
- Aluminum foil
- Duct tape
- Polarized film[6]
- Recycling container

Photochemical Reactor Design

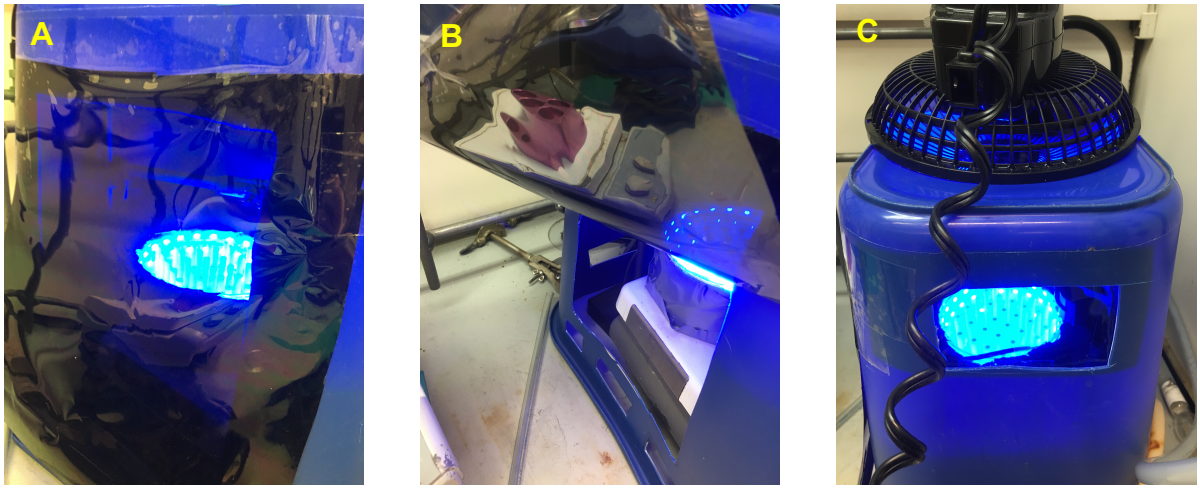
Protocol for Second Generation Reactor Setup

Remove the protective layer on the sticky side of the LED strip and carefully wrap the LED strips on the inside of a clean Pyrex dish.[7] Four bands of LEDs can fit into a 125 X 65 mm Pyrex crystallizing dish.[8] Once the LEDs are securely wrapped, place a layer of aluminum foil around the outside of the dish (including the bottom). Tape the connector wires as well as the foil with duct tape to secure both in place. For vial-scale reactions, cut a sample vial rack to the appropriate size using a saw and place it inside. Place the reactor on top of a 5 x 7 stirring place with a small ring stand underneath it.

Next, modifications to a standard office recycling bin (14.4 x 10.2 x 15 inches) are made. Using a box cutter or similar object, a circular hole is cut in the base of the bin that is smaller than the requisite clip fan such that the clip fan can rest on the top of the bin without falling (~7.5 inch diameter). Next, an additional rectangular hole ~9.5 × 6.5 inches) is cut into the center of the long side of the bin to serve as an entrance. Near the base of the bin, a total of six rectangular air vent holes (~1 × 4 inches) are cut just below the top of the bin (~2 inches). On a viewing port (~2 × 4 inches) is cut just above the base (~1.5 inches). A small square hole (~0.5 × 0.5 inches) is cut at the base of the bin behind the fan port to allow the bar of the ring stand bar to fit through. Polarized film is next cut to fit over the entrance and viewing port. For the viewing port, the film is placed inside and taped. For the entrance, the film is taped to the outside and a small segment of the cut-out piece of the bin is taped to the inside of the film to act as a weight. The bin is next inverted and placed over the

stirring plate, and the clip fan is placed atop the inverted bin. The reactor is now ready for use. Turn on the lights and fan (set it to its maximum setting). Allow 15 min to pass for temperature equilibration. Temperature should be monitored in real time using a temperature probe (or thermometer) to determine the ambient temperature within the reactor. Although typically used for vial-scale reactions, this reactor can be used for scale up. For larger vessels (e.g., round bottom flasks), simply lower the flask into the irradiation bay and use the ring stand bar for clamps to hold the flask.[9]

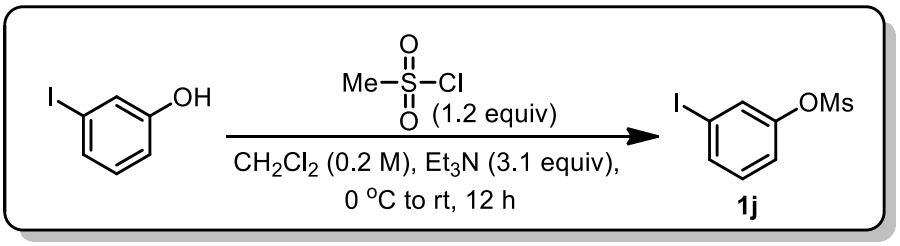
Additional Pictures:



A & B Entrance flap to photoreactor with polarized film; C Viewing port with polarized film

Synthesis of Iodoarenes

Mesylation of 3-Iodophenol



3-Iodophenyl Methanesulfonate (1j)[10]

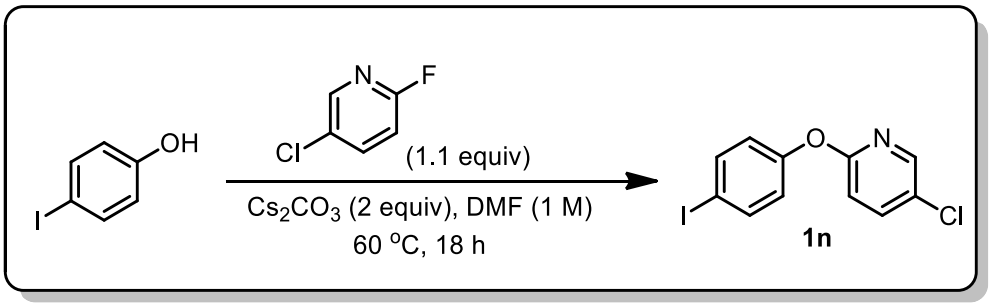
To a 100 mL round bottom flask equipped with a stir bar was added Et_3N (1.88 g, 2.59 mL, 18.6 mmol, 3.1 equiv), 3-iodophenol (1.32 g, 6 mmol, 1 equiv), and CH_2Cl_2 (30 mL). The reaction vessel was sealed with a rubber septum and placed under argon via an Ar inlet needle. The flask was cooled to 0 ºC *via* an ice-water bath. After cooling for 5 min, MsCl (0.825 g, 0.56 mL, 7.2 mmol, 1.2 equiv) was added dropwise *via* a syringe. The reaction mixture was allowed to stir at 0 ºC for 5 min, then warmed to rt. The solution was stirred at this temperature overnight. After this time, the reaction mixture was carefully quenched with 2 M HCl (50 mL) and transferred to a separatory funnel. CH_2Cl_2 (100 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with 2 M NaOH (2 × 100 mL), deionized H_2O (100 mL) and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure mesylate **1j** (1.56 g, 87%) as an off-white solid (mp = 61-62 °C).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.16 (s, 3H), 7.15 (t, J = 8.1 Hz, 1H), 7.28 (ddd, J = 8.4, 2.4, 1.1 Hz, 1H), 7.64 (t, J = 1.7 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.9 (CH_3), 94.1 (C), 121.8 (CH), 131.3 (CH), 131.5 (CH), 136.8 (CH), 149.3 (C).

Functionalization of 4-Iodophenol

S_NAr



5-Chloro-2-(4-iodophenoxy)pyridine (1n)[11]

To a 25 mL round bottom flask equipped with a stir bar was added Cs_2CO_3 (3.70 g, 11.7 mmol, 2 equiv), 4-iodophenol (1.28 g, 5.83 mmol, 1 equiv), and DMF (6 mL). The reaction vessel was sealed with a rubber septum and placed under argon via an Ar inlet needle. After stirring for 5 min, 5-chloro-2-fluoropyridine (0.843 g, 6.4 mmol, 1.1 equiv) was added in one portion to the flask via a syringe. The reaction mixture was heated to 60 °C in an oil bath and was stirred at this temperature overnight. After this time, the reaction mixture was diluted with deionized H_2O (7 mL) and Et_2O (7 mL) and transferred to a separatory funnel. Et_2O (30 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers were washed with 2 M NaOH (2 × 100 mL), deionized H_2O (100 mL) and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure pyridine **1n** (1.37 g, 71%) as a pale yellow oil.

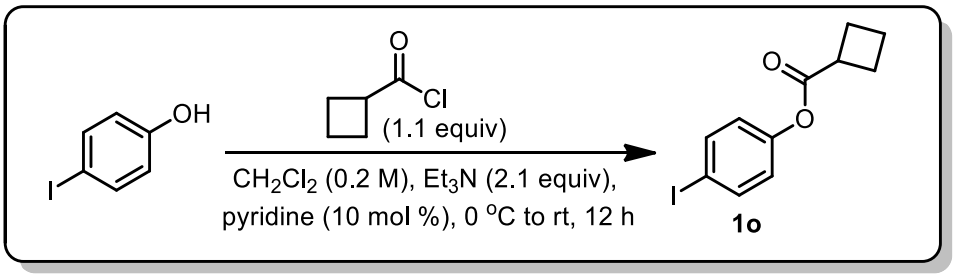
^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.88 - 6.90 (m, 2 H), 6.91 (d, J = 2.1 Hz, 1 H), 7.65 (dd, J = 8.7, 2.6 Hz, 1 H), 7.70 (d, J = 8.9 Hz, 2 H), 8.11 (d, J = 2.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 88.9 (C), 112.9 (CH), 123.6 (CH), 126.4 (C), 138.9 (CH), 139.6 (CH), 146.2 (CH), 153.9 (C), 161.7 (C).

FT-IR (cm^{-1}, neat, ATR) 3056 (vw), 1589 (m), 1454 (vs), 1369 (s), 1262 (vs), 1239 (vs), 1107 (s), 1007 (vs), 820 (vs), 498 (s).

HRMS (EI) calcd for $C_{11}H_7ClINO$ $[M]^+$: 330.9261, found: 330.9271.

Esterification



4-Iodophenyl Cyclobutanecarboxylate (1o)

To a 100 mL round bottom flask equipped with a stir bar was added Et_3N (1.06 g, 1.46 mL, 10.5 mmol, 2.1 equiv), 2-bromo-4-iodophenol (1.32 g, 5 mmol, 1 equiv), pyridine (0.040 g, 0.04 mL, 0.5 mmol, 0.1 equiv) and CH_2Cl_2 (25 mL). The reaction vessel was sealed with a rubber septum and placed under argon via an Ar inlet needle. The flask was cooled to 0 ºC *via* an ice-water bath. After cooling for 5 min, cyclobutanecarbonyl chloride (0.652 g, 0.63 mL, 5.5 mmol, 1.1 equiv) was added dropwise *via* a syringe. The reaction mixture was allowed to stir at 0 ºC for 5 min then warmed to rt. The solution was stirred at this temperature overnight. After this time, the reaction mixture was carefully quenched with 2 M HCl (50 mL) and transferred to a separatory funnel. Et_2O (100 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with 2 M NaOH (2 × 100 mL), deionized H_2O (100 mL), and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure ester **1o** (1.49 g, 99%) as a pale yellow oil that solidified to an off-white solid (mp = 40-41 °C).

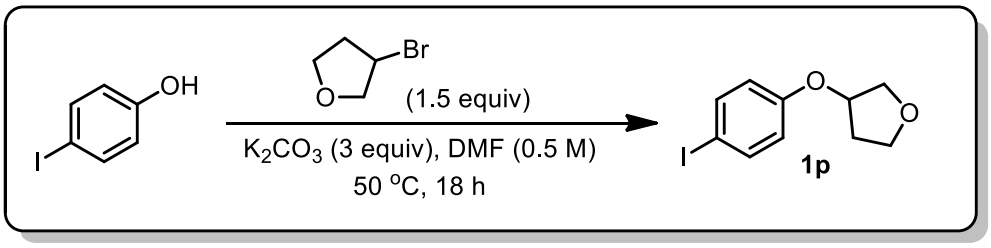
^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.90 - 2.11 (m, 2 H), 2.26 - 2.36 (m, 2 H), 2.37 - 2.47 (m, 2 H), 3.29 - 3.43 (m, 1 H), 6.86 (d, J = 9.0 Hz, 2 H), 7.68 (d, J = 9.2 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.6 (s, 6 C), 25.5 (s, 13 C), 38.3 (s, 5 C), 89.9 (s, 3 C), 124.0 (s, 12 C), 138.6 (s, 13 C), 150.9 (s, 2 C), 173.7 (s, 2 C).

FT-IR (cm^{-1}, neat, ATR) 2987 (w), 2947 (w), 1745 (vs), 1478 (s), 1343(m), 1197 (s), 1137 (vs), 1003 (s), 854 (m), 499 (vs).

HRMS (EI) calcd for $C_{11}H_{11}IO_2$ $[M]^+$: 301.9804, found: 301.9806.

Alkylation

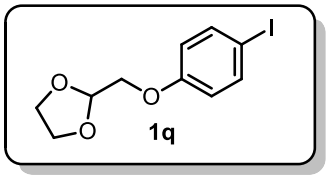


3-(4-Iodophenoxy)tetrahydrofuran (1p)[12]

To a 100 mL round bottom flask equipped with a stir bar was added K_2CO_3 (2.49 g, 18 mmol, 3 equiv), 4-iodophenol (1.32 g, 6 mmol, 1 equiv), and DMF (12 mL). The reaction vessel was sealed with a rubber septum and placed under argon via an Ar inlet needle. After stirring for 5 min, 3-bromotetrahydrofuran (1.36 g, 9 mmol, 1.5 equiv) was added in one portion to the flask via a syringe. The reaction mixture was heated to 60 °C in an oil bath and was stirred at this temperature overnight. After this time, the reaction mixture was diluted with deionized H_2O (7 mL) and Et_2O (7 mL) and transferred to a separatory funnel. Et_2O (50 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were washed with 2 M NaOH (2 × 100 mL), deionized H_2O (100 mL) and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure alkylated product **1p** (0.754 g, 43%) as a white solid (mp = 83-84 °C).[12]

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.07 - 2.15 (m, 1H), 2.15 - 2.24 (m, 1H), 3.84 - 3.92 (m, 1H), 3.92 - 4.01 (m, 3H), 4.83 - 4.89 (m, 1H), 6.64 (d, J = 8.9 Hz, 2H), 7.55 (d, J = 9.0 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 33.1 (CH_2), 67.4 (CH_2), 73.2 (CH_2), 77.7 (CH), 83.3 (C), 118.0 (CH), 138.6 (CH), 157.5 (C).
FT-IR (cm^{-1}, neat, ATR) 2972 (vw), 2852 (m), 1580 (m), 1481 (s), 1232 (vs), 1063 (s), 991 (m) 912 (vs), 826 (vs).
HRMS (EI) calcd for $C_{10}H_{11}IO_2$ $[M]^+$: 289.9804, found: 289.9794.

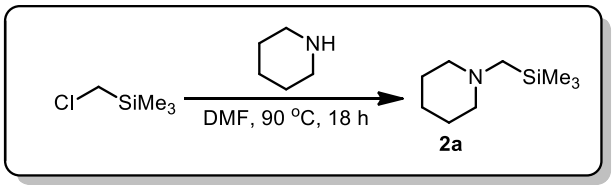
4-((4-Iodophenoxy)methyl)-1,3-dioxolane, 1q (1.16 g, 76%) was prepared according to the above alkylation procedure *with the following modifications*: *1)* 4-(bromomethyl)-1,3-dioxolane (1.09 g, 6.5 mmol, 1.3 equiv) was



used in place of 3-bromotetrahydrofuran; 2) Only 2.5 equiv of K_2CO_3 were used. The desired alkylated product **1q** was obtained as an off-white solid (mp = 70-71 ^oC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.92 - 3.96 (m, 2H), 3.98 (d, *J* = 4.0 Hz, 2H), 4.01 - 4.05 (m, 2H), 5.25 (t, *J* = 4.0 Hz, 1H), 6.70 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 65.5 (CH_2), 69.0 (CH_2), 83.6 (CH), 102.0 (C), 117.2 (CH), 138.4 (CH), 158.6 (C). **FT-IR** (cm^{-1}, neat, ATR) 2877 (m), 1586 (m), 1485 (vs), 1457 (s), 1252 (vs), 1145 (vs), 1092 (vs), 823 (vs), 618 (s), 501 (s). **HRMS** (ES+) calcd for $C_{10}H_{11}IO_3$ $[M]^+$: 305.9753, found: 305.9766.

Representative Synthesis of α-Silylamines

Preparation of 1-((trimethylsilyl)methyl)piperidine (1a)

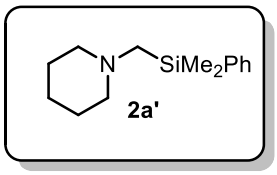


To a 100 mL round bottom flask equipped with a stir bar was added (chloromethyl)trimethylsilane (3.07 g, 25 mmol, 1 equiv) followed by DMF (25 mL) and piperidine (6.38 g, 7.41 mL, 75 mmol, 3.0 equiv). The mixture was placed under an argon atmosphere and was heated to 90 °C in an oil bath overnight. Reaction progress was assessed by GC/MS and/or NMR After this time, the reaction mixture was cooled to rt and was diluted with deionized H_2O (~50 mL). The solution was transferred to a separatory funnel and Et_2O[13] (75 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with deionized H_2O (2 ×100 mL) and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation affording the crude α-silylamine. Further purification was accomplished by vacuum distillation (bp 60-62 °C @ 1 mm Hg) giving pure **2a** as a clear colorless oil (2.45 g, 57%).[14]

^{1}H NMR 0.07 (br s, 9H), 1.31 - 1.46 (m, 2H), 1.52 - 1.67 (m, 4H), 1.92 (br s, 2H), 2.25 - 2.47 (m, 4H).

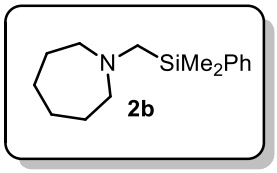
^{13}C NMR δ -0.8 (CH_3), 24.1 (CH_2), 26.5 (CH_2), 52.0 (CH_2), 58.7 (CH_2).

1-((Dimethyl(phenyl)silyl)methyl)piperidine, 2a′ (4.07 g, 70%) was prepared according to the representative procedure ***with the following modification:*** 1) ((chloromethyl)dimethylphenylsilane (4.73 g, 25 mmol) was used in place of (chloromethyl)trimethylsilane. Further purification was accomplished by vacuum distillation (bp 71-73 °C @ 0.1 mm Hg), giving pure **2a′** as a clear pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.36 (s, 6H), 1.29 - 1.42 (m, 2H), 1.47 - 1.62 (m, 4H), 2.16 (br s, 2H), 2.25 - 2.44 (m, 4H), 7.32 - 7.37 (m, 3H), 7.53 - 7.58 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -2.29 (CH_3), 24.06 (CH_2), 26.53 (CH_2), 50.88 (CH_2), 58.77 (CH_2), 127.93 (CH), 129.07 (CH), 133.85 (CH), 139.69 (C). **FT-IR** (cm^{-1}, neat,

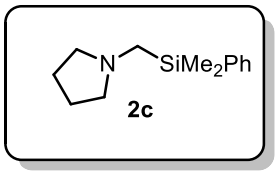


ATR) 2932 (m), 2774 (w), 1427 (w), 1247 (m), 1112 (m), 832 (vs), 723 (s), 697 (vs). **HRMS** (EI) calcd for $C_{14}H_{23}NSi$ $[M]^+$: 233.1600, found: 233.1605.

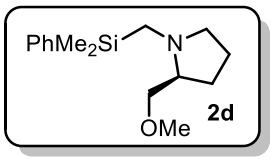
1-((Dimethyl(phenyl)silyl)methyl)azepane, 2b (3.54 g, 72%) was prepared according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (3.70 g, 20 mmol) was used in place of (chloromethyl)trimethylsilane; 2) Azepane (5.95 g, 7.21 mL, 60 mmol, 3 equiv) was used in place of piperidine. Further purification was accomplished by vacuum distillation (bp 83-85 °C @ 0.1 mm Hg) giving pure **2b** as a clear pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.37 (br s, 6H), 1.47 - 1.67 (m, 8H), 2.36 (br s, 2H), 2.55 - 2.74 (m, 4H), 7.32 - 7.38 (m, 3H), 7.53 - 7.59 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -2.4 (CH_3), 27.3 (CH_2), 28.1 (CH_2), 50.0 (CH_2), 59.7 (CH_2), 127.9 (CH), 129.0 (CH), 133.9 (CH), 139.7 (C). **FT-IR** (cm^{-1}, neat, ATR) 2925 (m), 2853 (w), 1450 (w), 1247 (m), 1113 (m), 831 (vs), 724 (s), 697 (vs). **HRMS** (EI) calcd for $C_{15}H_{25}NSi$ $[M]^+$: 247.1750, found: 247.1756.



1-((Dimethyl(phenyl)silyl)methyl)pyrrolidine, 2c (1.64 g, 50%) was prepared according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (2.77 g, 15 mmol) was used in place of (chloromethyl)trimethylsilane; 2) Pyrrolidine (3.20 g, 3.70 mL, 45 mmol, 3 equiv) was used in place of piperidine; 3) The reaction was conducted at 70 ^{o}C for 24 h. Further purification was accomplished by vacuum distillation (bp 60-62 °C @ 0.1 mm Hg) giving pure **2c** as a clear pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.40 (s, 6H), 1.69 - 1.82 (m, 4H), 2.31 (br s, 2H), 2.42 - 2.59 (m, 4H), 7.34 - 7.38 (m, 3H), 7.53 - 7.58 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -2.50 (CH_3), 24.14 (CH_2), 47.19 (CH_2), 58.43 (CH), 127.97 (CH), 129.16 (CH), 133.84 (CH), 139.28 (C). **FT-IR** (cm^{-1}, neat, ATR) 2957 (s), 2876 (w), 2774 (s), 1427 (w), 1247 (m), 1113 (m), 834 (vs), 725 (vs), 697 (vs). **HRMS** (EI) calcd for $C_{13}H_{21}NSi$ $[M]^+$: 219.1443, found: 219.1440.

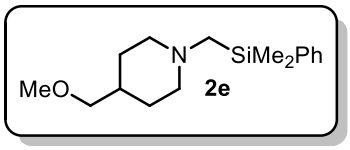


(*S*)-1-((Dimethyl(phenyl)silyl)methyl)-2-(methoxymethyl)pyrrolidine, 2d (1.73 g, 66%) was



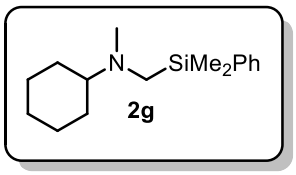
prepared according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (1.84 g, 10 mmol) was used in place of (chloromethyl)trimethylsilane; 2) (*S*)-2-(methoxymethyl)pyrrolidine (2.30 g, 20 mmol, 2 equiv) was used in place of piperidine. Further purification was accomplished by vacuum distillation (b.p. 90-92 °C @ 0.1 mmHg) giving pure **2d** as a clear colorless oil. $[\alpha]^{22}_{D}$ = -66.9 ($CHCl_3$, *c* = 0.50). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.29 - 0.40 (m, 6H), 1.50 - 1.61 (m, 1H), 1.61 - 1.76 (m, 2H), 1.81 - 1.92 (m, 1H), 1.94 - 2.15 (m, 2H), 2.32 - 2.49 (m, 1H), 2.66 - 2.78 (m, 1H), 2.90 - 3.06 (m, 1H), 3.20 - 3.29 (m, 1H), 3.33 (s, 3H), 3.35 - 3.49 (m, 1H), 7.33 - 7.38 (m, 3H), 7.53 - 7.59 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -2.5 (CH_3), -2.4 (CH_3), 23.5 (CH_2), 28.6 (CH_2), 46.0 (CH_2), 57.8 (CH_2), 59.3 (CH), 67.9 (CH), 76.5 (CH_3), 128.0 (CH), 129.2 (CH), 134.0 (CH), 139.4 (C). **FT-IR** (cm^{-1}, neat, ATR) 3069 (vw), 2957 (w), 2873 (w), 1458 (w), 1248 (m), 1112 (s), 833 (vs), 726 (s), 698 (vs). **HRMS** (EI) calcd for $C_{15}H_{25}NOSi$ $[M]^+$: 263.1705, found: 263.1724.

1-((Dimethyl(phenyl)silyl)methyl)-4-(methoxymethyl)piperidine, 2e (1.85 g, 53%) was



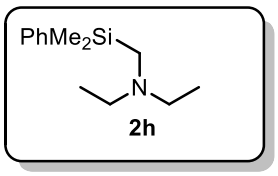
prepared according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (2.31 g, 12.5 mmol) was used in place of (chloromethyl)trimethylsilane; 2) 4-(methoxymethyl)piperidine (3.60 g, 27.9 mmol, 2.23 equiv) was used in place of piperidine. Further purification was accomplished by vacuum distillation (b.p. 101-103 °C @ 0.1 mmHg) giving pure **2e** as a clear pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.35 (s, 6H), 1.15 - 1.37 (m, 2H), 1.43 - 1.56 (m, 1H), 1.63 (d, *J* = 12.5 Hz, 2H), 1.83 - 1.98 (m, 2H), 2.16 (br. s., 2H), 2.77 - 2.93 (m, 2H), 3.19 (d, *J* = 6.7 Hz, 2H), 3.31 (s, 3H), 7.33 - 7.37 (m, 3H), 7.53 - 7.58 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -2.3 (CH_3), 29.8 (CH_2), 35.8 (CH), 50.4 (CH_2), 57.7 (CH_2), 59.1 (CH_3), 78.3 (CH_2), 128.0 (CH), 129.1 (CH), 133.9 (CH), 139.6 (C). **FT-IR** (cm^{-1}, neat, ATR) 2918 (w), 2850 (w), 1427 (vw), 1248 (w), 1111 (s), 833 (vs), 726 (s), 698 (s). **HRMS** (EI) calcd for $C_{16}H_{27}NOSi$ $[M]^+$: 277.1862, found: 277.1855.

***N*-((Dimethyl(phenyl)silyl)methyl)-*N*-methylcyclohexanamine, 2g** (1.92 g, 49%) was



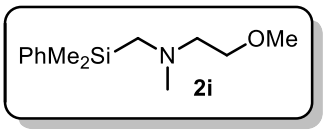
prepared according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (2.77 g, 15 mmol) was used in place of (chloromethyl)trimethylsilane; 2) *N*-methylcyclohexanamine (5.09 g, 5.86 mL, 45 mmol, 3 equiv) was used in place of piperidine. Further purification was accomplished by vacuum distillation (bp 90-92 °C @ 0.1 mm Hg) giving pure **2g** as a clear pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.38 (br s, 6H), 0.96 - 1.23 (m, 5H), 1.51 - 1.63 (m, 1H), 1.69 - 1.81 (m, 4H), 2.12 - 2.40 (m, 6H), 7.34 - 7.38 (m, 3H), 7.53 - 7.59 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 2.7 (CH_3), 26.2 (CH_2), 26.7 (CH_2), 28.2 (CH_2), 41.9 (CH_3), 44.2 (CH_2), 65.0 (CH), 128.0 (CH), 129.1 (CH), 133.9 (CH), 139.6 (C). **FT-IR** (cm^{-1}, neat, ATR) 2927 (m), 2853 (w), 1450 (w), 1247 (m), 1112 (m), 835 (vw), 808 (s), 697 (s). **HRMS** (EI) calcd for $C_{16}H_{27}NSi$ $[M]^+$: 261.1913, found: 261.1923.

***N*-((Dimethyl(phenyl)silyl)methyl)-*N*-ethylethanamine, 2h** (2.4 g, 54%) was prepared



according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (3.69 g, 20 mmol) was used in place of (chloromethyl)trimethylsilane; 2) Et_2NH (3.07 g, 3.4 mL, 42 mmol, 2.1 equiv) was used in place of piperidine; 3) DMSO was used in place of DMF as the solvent; 4) The reaction was conducted at 50 ^{o}C for 48 h. Further purification was accomplished by vacuum distillation (bp 54-56 °C @ 0.1 mm Hg) giving pure **2h** as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 0.34 (s, 6H), 0.95 (t, J = 7.2 Hz, 6H), 2.16 (s, 2H), 2.43 (q, J = 7.0 Hz, 4H), 7.32 - 7.37 (m, 3H), 7.53 - 7.60 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ -2.5 (CH_3), 11.8 (CH_3), 44.2 (CH_2), 50.5 (CH_2), 127.9 (CH), 129.1 (CH), 133.9 (CH), 139.6 (C).

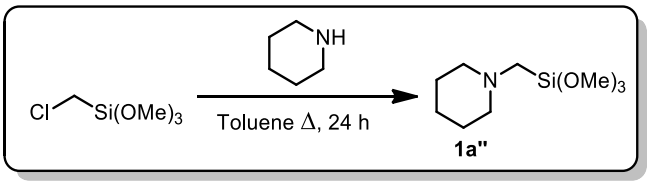
***N*-((dimethyl(phenyl)silyl)methyl)-2-methoxy-N-methylethanamine, 2i** (1.21 g, 51%) was



prepared according to the representative procedure ***with the following modification***s: 1) ((chloromethyl)dimethylphenylsilane (1.84 g, 10 mmol) was used in place of (chloromethyl)trimethylsilane; 2) 2-methoxy-N-methylethanamine (2.23 g, 2.7 mL, 25 mmol, 2.5 equiv) was used in place of piperidine. Further purification was accomplished by vacuum

distillation (b.p. 57-59 °C @ 0.1 mmHg) giving pure **2i** as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.37 (s, 6 H), 2.20 (s, 2 H), 2.25 (s, 3 H), 2.53 (t, *J* = 5.9 Hz, 2 H), 3.32 (s, 3 H), 3.44 (t, *J* = 5.9 Hz, 2 H), 7.33 - 7.39 (m, 3 H), 7.53 - 7.59 (m, 2 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -2.5 (CH_3), 47.2 (CH_3), 49.6 (CH_2), 59.0 (CH_3), 60.8 (CH_2), 71.1 (CH_2), 128.0 (CH), 129.2 (CH), 133.9 (CH), 139.2 (C). **FT-IR** (cm^{-1}, neat, ATR) 2953 (w), 2876 (w), 2811 (w), 2769 (w), 1427 (w), 1248 (m), 1112 (s), 834 (vs), 724 (s), 698 (s). **HRMS** (EI) calcd for $C_{13}H_{23}NOSi$ $[M]^+$: 237.1549, found: 237.1542.

Alternate Procedure for Preparation of 1-((Trimethoxysilyl)methyl)piperidine (1a'')[15]

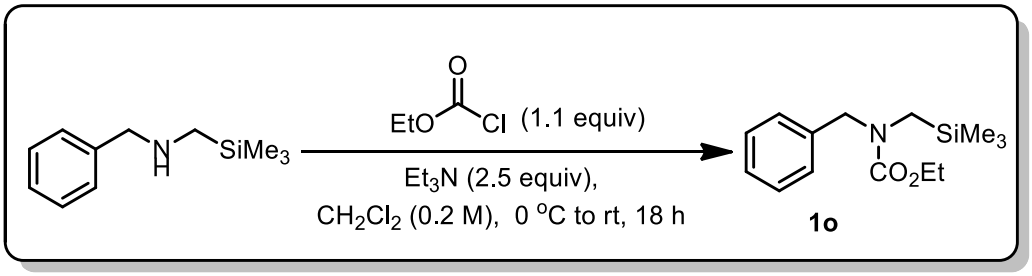


The following procedure is a modification of the procedure outlined by Strohmann.[15] To an oven-dried, 150 mL round bottom flask equipped with a stir bar was added (chloromethyl)trimethylsilane (3.41 g, 20 mmol, 1 equiv) followed by toluene (40 mL) and piperidine (4.26 g, 4.94 mL, 50 mmol, 2.5 equiv). The flask was equipped with a reflux condenser. The mixture was placed under an argon atmosphere and was heated to reflux in an oil bath overnight. Reaction progress was assessed by GC/MS and/or NMR After this time, the reaction mixture was cooled to rt, and the solvent was removed *in vacuo*. The resulting crude solid was suspended in pentane (~150 mL) and filtered. The filtrate was collected, and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by vacuum distillation (bp 45-47 °C @ 0.1 mm Hg), giving pure **1a″** as a clear colorless oil (2.91 g, 66%).

^{1}H NMR δ 1.31 - 1.40 (m, 2H), 1.51 - 1.61 (m, 4H), 1.99 (s, 2H), 2.30 - 2.48 (m, 4H), 3.59 (s, 9H).

^{13}C NMR δ 24.0 (CH_3), 26.5 (CH_2), 44.1 (CH_2), 50.9 (CH_3), 58.4 (CH_2).

Alternate Procedure for Preparation of Ethyl Benzyl((trimethylsilyl)methyl)carbamate (1f)



To a 50 mL round bottom flask equipped with a stir bar was added Et_3N (0.632 g, 0.87 mL, 6.25 mmol, 2.5 equiv), *N*-benzyl-1-(trimethylsilyl)methanamine (0.483 g, 2.5 mmol, 1 equiv), and CH_2Cl_2 (12.5 mL). The reaction vessel was sealed with a rubber septum and place under argon via an Ar inlet needle. The flask was cooled to 0 ºC *via* an ice-water bath. After cooling for 5 min, ethyl chloroformate (0.298 g, 0.26 mL, 2.75 mmol, 1.1 equiv) was added dropwise *via* a syringe. The reaction mixture was allowed to stir at 0 ºC for 5 min, then warmed to rt. The solution was stirred at this temperature overnight. After this time, the reaction mixture was carefully quenched with 2 M HCl (25 mL) and transferred to a separatory funnel. Et_2O (50 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with 2 M HCl (50 mL), saturated aq $NaHCO_3$ (100 mL), deionized H_2O (100 mL), and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation affording, the pure carbamate **1o** (0.520 g, 78%) as a clear pale yellow oil.[16]

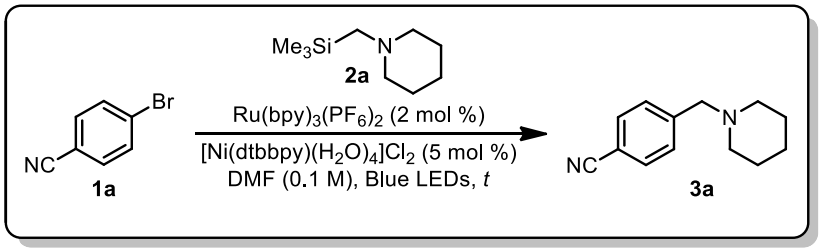
^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.04 (br s, 9H), 1.13 - 1.35 (m, 3H), 2.62 - 2.77 (m, 2H), 4.18 (br q, *J* = 6.80 Hz, 2H), 4.40 - 4.52 (m, 2H), 7.14 - 7.29 (m, 3H), 7.32 (t, *J* = 7.30 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ **-1.3 (CH_3), -1.2 (CH_3),** 15.0 (CH_3), **37.4 (CH_2), 38.5 (CH_2),** 52. 7 (CH_2), 61.5 (CH_2), 127.5 (CH), 128.1 (CH), 128.7 (CH), 138.0 (C), **156.5 (C), 157.2 (C)**.
FT-IR (cm^{-1}, neat, ATR) 2954 (w), 1692 (vs), 1452 (m), 1222 (s), 1102 (s), 840 (vs), 697 (s).
HRMS (EI) calcd for $C_{14}H_{23}NO_2Si$ $[M]^+$: 265.1498, found: 265.1509.

Optimization and Control Studies

Procedure for optimization and control studies:

To a 4 mL reaction vial equipped with a stir bar was added 4-bromobenzonitrile, **1a** (18.2 mg, 0.1 mmol, 1 equiv), the appropriate photocatalyst (0.002 mmol, 0.02 equiv), and the appropriate nickel complex (0.005 mmol, 0.05 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times *via* an inlet needle. The vial was then charged with α-silylamine **2a** (20.6 mg, 0.12 mmol, 1.2 equiv) in an appropriate anhydrous solvent (1 mL). After this, the cap was sealed with Parafilm,® and the vial was irradiated in the aforementioned LED reactor for 18 h. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. After 18 h, an aliquot of a solution of 4,4′-di-*tert*-butylbiphenyl in MeCN with a known concentration (20 mol % relative to the aryl halide) was added to each vial. Reaction progress was evaluated by GC-FID.

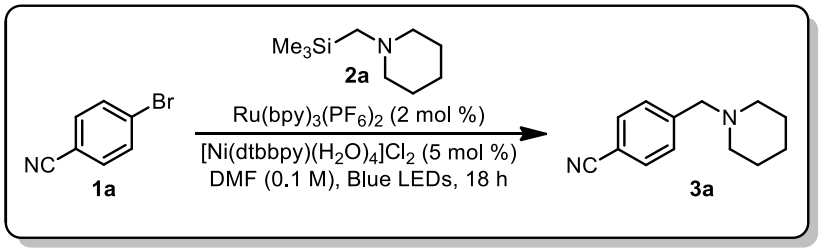
Table S1: Solvent Screen of Photoredox-Mediated Alkylation of Imines[a]



Entry	Ni Complex	Photocatalyst (mol %)	Solvent	Time (h)	% Conversion
1	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpz)_3(PF_6)_2$ (2 mol %)	DMF	18	12
2	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$[Ir\{dFCF_3ppy\}2(bpy)]PF_6$ (2 mol %)	DMF	18	88
3	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ir(ppy)_3$	DMF	18	85
4	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	MesAcr+ClO_4- (5 mol %)	DMF	18	0
5	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	4CzIPN (5 mol %)	DMF	18	89
6	$[Ni(bpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	DMF	18	75
7	$[Ni(diOMebpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	DMF	18	64
8	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	acetone	18	24
9	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	DMSO	18	37
10	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	MeCN	18	69
11	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	1,4-dioxane	18	0
12	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	DMF	18	82
13	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	$Ru(bpy)_3(PF_6)_2$ (2 mol %)	DMF	24	97

[a] Percent conversion was approximated based upon relative areas from the GC-FID trace of a given run. Conversion = 100 × (area of cross-coupled product **3a**)/(area of **3a** + area of **1a** + area of 4-chlorobenzonitrile)

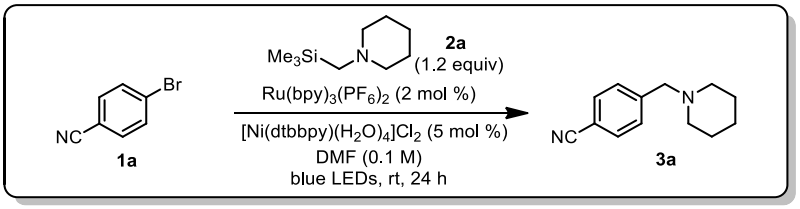
Table S2: Control Studies using α-Silylamine 2a



Entry	Deviation from procedure	% Conversion to 3a
1	*None*	82
2	*No $Ru(bpy)_3(PF_6)_2$*	0
3	*No $[Ni(dtbbpy)(H_2O)_4]Cl_2$*	0
4	*No light*	0
5	*No a-silylamine **2a***	0
6	*Air Atmosphere*	61

[a] Percent conversion was approximated based upon relative areas from the GC-FID trace of a given run. Conversion = 100 × (area of cross-coupled product **3a**)/(area of **3a** + area of **1a** + area of 4-chlorobenzonitrile)

General Procedure for Aminomethylation Using α-Silylamines



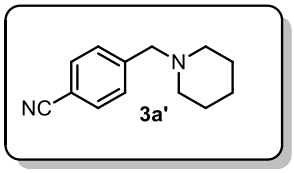
4-(Piperidin-1-ylmethyl)benzonitrile[17] (3a)

To an 8 mL reaction vial equipped with a stir bar were added $Ru(bpy)_3(PF_6)_2$ (8.6 mg, 0.01 mmol, 0.02 equiv), bromoarene **1a** (91.0 mg, 0.5 mmol, 1 equiv), and $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (11.8 mg, 0.025 mmol, 0.05 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle then. The vial was then charged with the α-silylamine **2a** (102.8 mg, 0.6 mmol, 1.2 equiv) in anhydrous DMF (5 mL) *via* a syringe. The cap was sealed with Parafilm®, and the now bright red solution was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 ^oC *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC and/or GC/MS. Once judged to be complete, the now dark red-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (20 mL) and 2 M NaOH (5 mL) and Et_2O (~20 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with deionized H_2O (2 × ~50 mL) followed by brine (~100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient CH_2Cl_2/MeOH)[18] to give the desired amine, **3a**, (59.9 mg, 60%) as a pale yellow oil.[19]

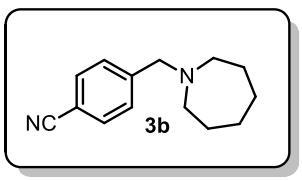
^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 - 1.50 (m, 2H), 1.53 - 1.63 (m, 4H), 2.27 - 2.47 (m, 4H), 3.52 (s, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.4 (CH_2), 26.1 (CH_2), 54.8 (CH_2), 63.4 (CH_2), 110.9 (C), 119.3 (C), 129.8 (CH), 132.3 (CH), 144.7 (C).

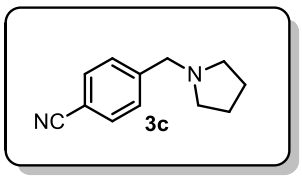
4-(Piperidin-1-ylmethyl)benzonitrile,[17] 3a′ (70.1 mg, 70%) was prepared according to the general procedure from α-silylamine **1a′** (140.1 mg, 0.6 mmol, 1.2 equiv). The desired amine **3a′** was isolated as a pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.50 (m, 2H), 1.53 - 1.63 (m, 4H), 2.27 - 2.47 (m, 4H), 3.52 (s, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.4 (CH_2), 26.1 (CH_2), 54.8 (CH_2), 63.4 (CH_2), 110.9 (C), 119.3 (C), 129.8 (CH), 132.3 (CH), 144.7 (C).



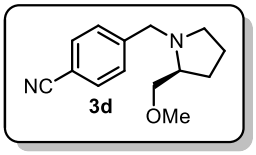
4-(Azepan-1-ylmethyl)benzonitrile, 3b (88.9 mg, 83%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv). The desired amine **3b** was isolated as clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.60 (s, 8H), 2.5 - 2.6 (m, 4H), 3.65 (s, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.1 (CH_2), 28.6 (CH_2), 55.9 (CH_2), 62.6 (CH_2), 110.6 (C), 119.3 (C), 129.3 (CH_2), 132.2 (CH_2), 146.4 (C). **FT-IR** (cm^{-1}, neat, ATR) 2924 (s), 2854 (m), 2227 (m), 1607 (m), 1455 (m), 1355 (m), 1082 (m), 836 (vs). **HRMS** (EI) calcd for $C_{14}H_{18}N_2$ $[M]^+$: 214.1470, found: 214.1467.



4-(Azepan-1-ylmethyl)benzonitrile,[20] 3c (66.2 mg, 71%) was prepared according to the general procedure from α-silylamine **2c** (131.6 mg, 0.6 mmol, 1.2 equiv). The desired amine **3c** was isolated as a as clear yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.69 - 1.87 (m, 4H), 2.40 - 2.59 (m, 4H), 3.66 (s, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.7 (CH_2), 54.4 (CH_2), 60.4 (CH_2), 110.9 (C), 119.3 (C), 129.6 (CH), 132.3 (CH), 145.4 (C).

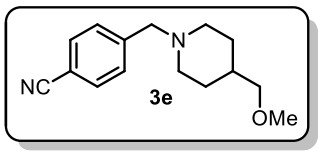


(*S*)-4-((2-(Methoxymethyl)pyrrolidin-1-yl)methyl)benzonitrile, 3d (62.6 mg, 54%) was prepared according to the general procedure from α-silylamine **2d** (158 mg, 0.6 mmol) ***with the following modification***s: 1) the reaction was run for 36 h. The desired amine **3d** was isolated as an clear pale yellow oil. $[\alpha]^{23}_D$ = -57.0 ($CHCl_3$, *c* = 0.50). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.56 - 1.68 (m, 1H), 1.67 -



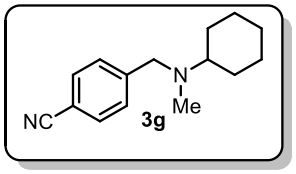
1.82 (m, 2H), 1.87 - 2.00 (m, 1H), 2.10 - 2.32 (m, 1H), 2.69 - 2.85 (m, 1H), 2.85 - 2.98 (m, 1H), 3.32 (s, 3H), 3.35 (dd, *J* = 9.5, 5.1 Hz, 1H), 3.40 - 3.57 (m, 2H), 4.21 (d, *J* = 13.9 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.0 (CH_2), 28.5 (CH_2), 54.9 (CH_2), 59.3 (CH_2), 59.4 (CH_2), 63.3 (CH), 76.7 (CH_3), 110.6 (C), 119.3 (C), 129.5 (CH), 132.2 (CH), 146.1 (C). **FT-IR** (cm^{-1}, neat, ATR) 2923 (m), 2874 (m), 2809 (m), 2227(m), 1608 (w), 1504 (w), 1458 (w), 1107 (vs), 819 (s), 548 (vs). **HRMS** (EI) calcd for $C_{14}H_{18}N_2O$ $[M]^+$: 230.1419, found: 230.1409.

4-((4-(Methoxymethyl)piperidin-1-yl)methyl)benzonitrile, 3e (50.2 mg, 41%) was prepared according to the general procedure from α-silylamine **2e** (166.4 mg, 0.6 mmol) ***with the following modification***s: 1) the reaction was run for 36 h. The desired amine **3e** was isolated as a clear colorless oil.



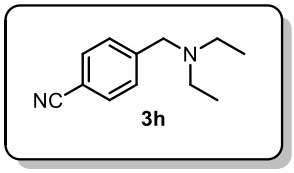
^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27 (qd, *J* = 12.4, 3.4 Hz, 2H), 1.58 (s, 1H), 1.69 (d, *J* = 13.6 Hz, 2H), 1.97 (td, *J* = 11.6, 2.1 Hz, 2H), 2.81 (d, *J* = 11.4 Hz, 2H), 3.21 (d, *J* = 6.6 Hz, 2H), 3.27 - 3.33 (m, 3H), 3.51 (s, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.4 (CH_2), 36.3 (CH), 53.8 (CH_2), 59.1 (CH_3), 63.1 (CH_2), 78.1 (CH_2), 110.9 (C), 119.3 (C), 129.7 (CH), 132.3 (CH), 145.0 (C). **FT-IR** (cm^{-1}, neat, ATR) 2920 (m), 2806 (m), 2227 (m), 1602 (w), 1341 (w), 1102 (vs), 979 (m), 818 (s), 547 (m). **HRMS** (EI+) calcd for $C_{15}H_{20}N_2O$ $[M]^+$: 244.1576, found: 244.1575.

4-((Cyclohexyl(methyl)amino)methyl)benzonitrile, 3g (88.1 mg, 77%) was prepared according to the general procedure from α-silylamine **2g** (137.0 mg, 0.6 mmol, 1.2 equiv). The desired amine **3g** was isolated as a clear, pale-yellow solid (mp = 45-46 ^{o}C).

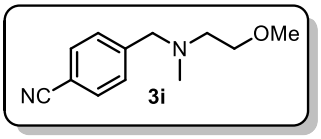


^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.04 - 1.15 (m, 1H), 1.17 - 1.32 (m, 4H), 1.59 - 1.67 (m, 1H), 1.76 - 1.88 (m, 4H), 2.17 (s, 3H), 2.36 - 2.46 (m, 1H), 3.61 (s, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 26.2 (CH_2), 26.6 (CH_2), 29.0 (CH_2), 38.0 (CH), 57.8 (CH_2), 63.1 (CH_3), 110.7 (C), 119.4 (C), 129.4 (CH), 132.3 (CH), 146.9 (C). **FT-IR** (cm^{-1}, neat, ATR) 2927 (vs), 2850 (s), 2230 (s), 1447 (m), 1376 (m), 1208 (m), 1059 (m), 847 (s), 815 (s). **HRMS** (ES+) calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1705, found: 229.1705.

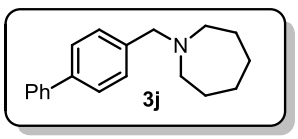
4-*N,N*-((Diethylamino)methyl)benzonitrile,[21] 3b (56.5 mg, 60%) was prepared according to the general procedure from α-silylamine **2h** (132.8 mg, 0.6 mmol, 1.2 equiv). The desired amine **3g** was isolated as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.04 (t, *J* = 7.0 Hz, 6H), 2.52 (q, *J* = 6.6 Hz, 4H), 3.61 (2H), 7.47 (d, *J* = 7.8 Hz, 2 H), 7.59 (d, *J* = 8.2 Hz, 2 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 12.1 (CH_3), 47.2 (CH_2), 57.6 (CH_2), 110.6 (C), 119.3 (C), 129.4 (CH), 132.2 (CH), 146.6 (C).



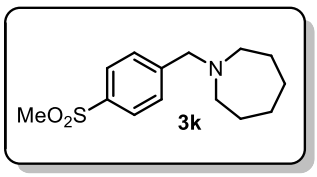
4-(((2-Methoxyethyl)(methyl)amino)methyl)benzonitrile, 3i (59.0 mg, 58%) was prepared according to the general procedure from α-silylamine **28** (142.4 mg, 0.6 mmol) ***with the following modification***s: 1) the reaction was run for 36 h. The desired amine **3e** was isolated as a clear pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 2.60 (t, *J* = 5.6 Hz, 2H), 3.33 (s, 3H), 3.50 (t, *J* = 5.6 Hz, 2H), 3.60 (s, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 43.0 (CH_3), 56.8 (CH_2), 59.1 (CH_3), 62.4 (CH_2), 70.9 (CH_2), 111.0 (C), 119.2 (C), 129.7 (CH), 132.3 (CH), 145.1 (C). **FT-IR** (cm^{-1}, neat, ATR) 2930 (w), 2811 (m), 2227 (m), 1608 (w), 1455 (m), 1364 (w), 1116 (vs), 819 (s), 548 (s). **HRMS** (EI+) calcd for $C_{10}H_{11}N_2$ $[M+CH_2OCH_3]^+$: 159.022, found: 159.0933.



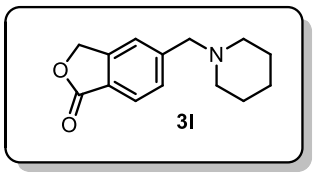
1-([1,1'-Biphenyl]-4-ylmethyl)azepane, 3j (82.0 mg, 62%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 4-bromo-1,1'-biphenyl **1b** (116.6 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a brown semisolid. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.63 - 1.73 (m, 4H), 1.76 - 1.96 (m, 4H), 2.83 - 3.14 (m, 4H), 3.99 (br s, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.56 - 7.63 (m, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 25.2 (CH_2), 27.1 (CH_2), 54.8 (CH_2), 61.5 (CH_2), 127.3 (CH), 127.7 (CH), 127.8 (CH), 129.0 (CH × 2), 131.0 (C), 140.5 (C), 141.8 (C). **FT-IR** (cm^{-1}, neat, ATR) 3050 (w), 2927 (m), 1487 (m), 762 (vs), 736 (vs), 697 (vs). **HRMS** (EI) calcd for $C_{19}H_{23}N$ $[M]^+$: 265.1830, found: 265.1831.



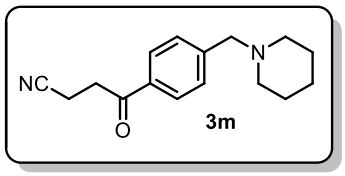
1-(4-(Methylsulfonyl)benzyl)azepane, 3k (75.1 mg, 58%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 1-bromo-4-(methylsulfonyl)benzene **1c** (117.5 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, light brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.58 - 1.71 (m, 8H), 2.62 - 2.72 (m, 4H), 3.05 (s, 3H), 3.78 (s, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.0 (CH_2), 27.4 (CH_2), 44.6 (CH_3), 55.6 (CH_2), 61.8 (CH_2), 127.5 (CH), 130.0 (CH), 139.4 (C), 145.2 (br, C). **FT-IR** (cm^{-1}, neat, ATR) 2925 (w), 2857 (vw), 1652 (w), 1297 (s), 1145 (vs), 1087 (m), 956 (m), 759 (s), 525 (s). **HRMS** (EI) calcd for $C_{14}H_{21}NO_2S$ $[M]^+$: 267.1293, found: 267.1288.



5-(Piperidin-1-ylmethyl)phthalide, 3l (58.1 mg, 50%) was prepared according to the general procedure from α-silylamine **2a′** (140.0 mg, 0.6 mmol, 1.2 equiv) and 5-bromophthalide **1d** (106.5 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a pale yellow solid (mp = 129-130 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.39 - 1.50 (m, 2H), 1.51 - 1.65 (m, 4H), 2.27 - 2.48 (m, 4H), 3.57 (s, 2H), 5.30 (s, 2H), 7.43 - 7.53 (m, 2H), 7.84 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.4 (CH_2), 26.1 (CH_2), 54.9 (CH_2), 63.7 (CH_2), 69.8 (CH_2), 122.5 (CH), 124.8 (C), 125.7 (CH), 130.2 (CH), 146.5 (C), 147.2 (C), 171.3 (C). **FT-IR** (cm^{-1}, neat, ATR) 2932 (w), 1748 (vs), 1437 (w), 1203 (w), 1043 (s), 999 (s), 767 (m). **HRMS** (EI) calcd for $C_{14}H_{17}NO_2$ $[M]^+$: 231.1259, found: 231.1251.

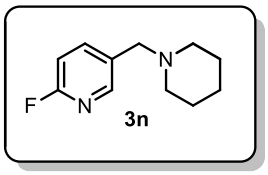


4-Oxo-4-(4-(piperidin-1-ylmethyl)phenyl)butanenitrile, 3m (68.2 mg, 53%) was prepared according to the general procedure from α-silylamine **2a′** (140.0 mg, 0.6 mmol, 1.2 equiv) and 4-(4-bromophenyl)-4-oxobutanenitrile **1e** (119.0 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.49 (m, 2H), 1.51 - 1.64 (m, 4H), 2.27 - 2.46 (m, 4 H), 2.77 (t, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 7.2 Hz, 2H), 3.52 (s, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 12.1 (CH_2), 24.5 (CH_2), 26.2 (CH_2), 34.5 (CH_2), 54.9 (CH_2), 63.6 (CH_2), 119.6 (C), 128.3 (CH), 129.6 (CH), 134.6 (C), 146.0 (C), 195.3 (C). **FT-IR** (cm^{-1}, neat,

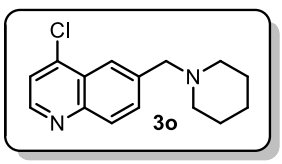


ATR) 2935 (w), 2247 (w), 1683 (vs), 1414 (m), 1213 (m), 914 (m), 728 (vs). **HRMS** (EI) calcd for $C_{16}H_{20}N_2O$ $[M]^+$: 256.1576, found: 256.1584.

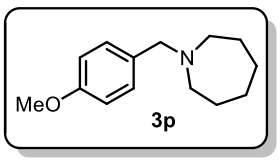
2-Fluoro-5-(piperidin-1-ylmethyl)pyridine,[22] 3n (46.8 mg, 48%) was prepared according to the general procedure from α-silylamine **2a′** (140.0 mg, 0.6 mmol, 1.2 equiv) and 5-bromo-2-fluoropyridine **1f** (88.0 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.37 - 1.48 (m, 2H), 1.50 - 1.61 (m, 4H), 2.35 (br s, 4H), 3.44 (s, 2H), 6.88 (dd, J = 8.3, 2.8 Hz, 1H), 7.77 (td, J = 8.1, 2.4 Hz, 1H), 8.09 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.5 (CH_2), 26.2 (CH_2), 54.7 (CH_2), 60.2 (CH_2), 109.3 (d, $J_{C\text{-}C\text{-}F}$ = 37.2 Hz, CH), 132.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.5 Hz, C), 142.2 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 8.2 Hz, CH), 148.0 (d, $J_{C\text{-}N\text{-}C\text{-}F}$ = 14.5 Hz, CH), 163.2 (d, $J_{C\text{-}F}$ = 237.1 Hz, CF). **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -74.03 (s, 1F).



4-Chloro-6-(piperidin-1-ylmethyl)quinoline, 3o (77.8 mg, 60%) was prepared according to the general procedure from α-silylamine **2a′** (140.0 mg, 0.6 mmol, 1.2 equiv) and 6-bromo-4-chloroquinoline **1g** (121.3 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.49 (m, 2H), 1.55 - 1.65 (m, 4H), 2.31 - 2.55 (m, 4H), 3.69 (s, 2H), 7.45 (d, J = 4.7 Hz, 1H), 7.82 (dd, J = 8.6, 1.8 Hz, 1H), 8.06 (d, J = 8.7 Hz, 1H), 8.09 (s, 1H), 8.72 (d, J = 4.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.5 (CH_2), 26.1 (CH_2), 54.8 (CH_2), 63.7 (CH_2), 121.5 (CH), 123.8 (CH), 126.5 (C), 129.9 (CH), 132.2 (CH), 138.7 (C), 142.6 (C), 148.9 (C), 149.7 (CH). **FT-IR** (cm^{-1}, neat, ATR) 2934 (m), 2796 (w), 266+ (m), 1497 (m), 1358 (m), 1112 (m), 842 (vs), 730 (vs), 677 (vs). **HRMS** (EI) calcd for $C_{15}H_{17}ClN_2$ $[M]^+$: 260.1080, found: 260.1071.

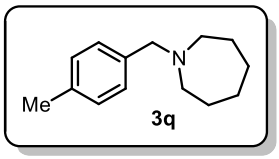


1-(4-Methoxybenzyl)azepane,[23] 3p (63.5 mg, 58%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 4-iodoanisole **1h** (117.0 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.51 - 1.68 (m, 8H), 2.52 - 2.66 (m, 4H), 3.58 (s, 2H), 3.80 (s, 3H), 6.85

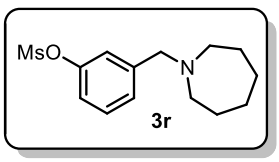


(d, J = 8.9 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.3 (CH_2), 28.4 (CH_2), 55.5 (CH_3), 55.7 (CH_2), 62.3 (CH_2), 113.7 (CH), 130.2 (CH), 132.2 (C), 158.7 (C).

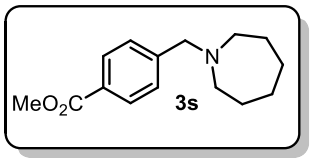
1-(4-Methylbenzyl)azepane, 3q (68.0 mg, 67%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 4-iodotoluene **1i** (109.0 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.53 - 1.68 (m, 8H), 2.34 (s, 3H), 2.53 - 2.66 (m, 4H), 3.61 (s, 2H), 7.12 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.4 (CH_3), 27.3 (CH_2), 28.5 (CH_2), 55.8 (CH_2), 62.7 (CH_2), 129.0 (CH), 129.1 (CH), 136.5 (C), 137.2 (C).



3-(Azepan-1-ylmethyl)phenyl Methanesulfonate, 3r (79.4 mg, 56%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 3-iodophenyl methanesulfonate **1j** (149.1 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.58 - 1.68 (m, 8H), 2.57 - 2.66 (m, 4H), 3.13 (s, 3H), 3.66 (s, 2H), 7.13 - 7.17 (m, 1H), 7.28 - 7.36 (m, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.2 (CH_2), 28.6 (CH_2), 37.6 (CH_3), 55.9 (CH_2), 62.4 (CH_2), 120.5 (CH), 122.2 (CH), 127.7 (CH), 129.8 (CH), 143.4 (C), 149.7 (C). **FT-IR** (cm^{-1}, neat, ATR) 2922 (w), 1667 (vw), 1584 (w), 1365 (s), 1176 (vs), 1120 (m) 966 (m), 817 (vs), 526 (vs). **HRMS** (ES+) calcd for $C_{14}H_{22}NO_3S$ $[M+H]^+$: 284.1320, found: 284.1311.

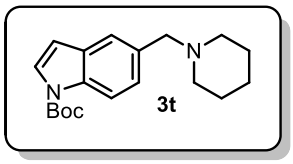


Methyl 4-(Azepan-1-ylmethyl)benzoate, 3s (64.2 mg, 52%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and methyl 4-iodobenzoate **1k** (131.0 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.58 - 1.66 (m, 8H), 2.56 - 2.64 (m, 4H), 3.68 (s, 2H), 3.90 (s, 3H), 7.42 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.3 (CH_2), 28.5 (CH_2), 52.2 (CH_3), 56.0 (CH_2), 62.7 (CH_2), 128.8 (CH), 128.9 (C), 129.8 (CH), 146.0 (C), 167.4 C). **FT-IR** (cm^{-1}, neat, ATR) 2924 (w), 2882 (vw), 1720 (vs), 1434

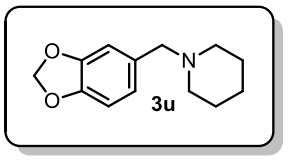


(m), 1273 (vs), 1106 (s), 757 (m). **HRMS** (ES+) calcd for $C_{15}H_{22}NO_2$ $[M+H]^+$: 248.1651, found: 248.1653.

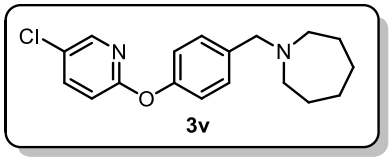
***tert*-Butyl 5-(piperidin-1-ylmethyl)-1*H*-indole-1-carboxylate, 3t** (86.2 mg, 55%) was prepared according to the general procedure from α-silylamine **2a′** (132.8 mg, 0.6 mmol, 1.2 equiv) and *tert*-butyl 5-iodo-1*H*-indole-1-carboxylate **1l** (171.6 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.37 - 1.48 (m, 2H), 1.55 - 1.63 (m, 4H), 1.67 (s, 9H), 2.28 - 2.53 (m, 4H), 3.59 (s, 2H), 6.54 (d, *J*=3.7 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.51 (s, 1H), 7.58 (d, *J* = 2.7 Hz, 1H), 7.98 - 8.13 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.5 (CH_2), 26.0 (CH_2), 28.4 (CH_3), 54.5 (CH_2), 64.0 (CH_2), 83.8 (C), 107.5 (CH), 114.9 (CH), 121.9 (CH), 126.1 (CH), 126.3 (CH), 130.8 (C), 132.3 (C), 134.6 (C), 150.0 (C). **FT-IR** (cm^{-1}, neat, ATR) 2931 (w), 1731 (s), 1471 (m), 1348 (m), 1257 (m), 1023 (m), 766 (m), 725 (vs). **HRMS** (EI) calcd for $C_{14}H_{18}N_2$ $[M-Boc+H]^+$: 214.1470, found: 214.1476.



1-(Benzo[*d*][1,3]dioxol-5-ylmethyl)piperidine,[24] 3u (54.9 mg, 50%) was prepared according to the general procedure from α-silylamine **2a′** (140.0 mg, 0.6 mmol, 1.2 equiv) and 5-iodobenzo[*d*][1,3]dioxole **1m** (124.0 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.36 - 1.49 (m, 2H), 1.48 - 1.63 (m, 4H), 2.25 - 2.47 (m, 4H), 3.39 (s, 2H), 5.93 (s, 2H), 6.74 (s, 2H), 6.86 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.6 (CH_2), 26.2 (CH_2), 54.6 (CH_2), 63.8 (CH_2), 101.1 (CH_2), 108.1 (CH), 109.9 (CH), 122.6 (CH), 132.5 (C), 146.8 (C), 147.8 (C).

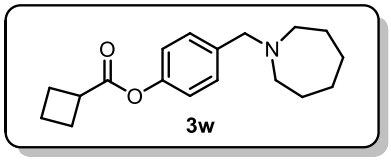


1-(4-((5-Chloropyridin-2-yl)oxy)benzyl)azepane, 3v (106.0 mg, 67%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 5-chloro-2-(4-iodophenoxy)pyridine **1n** (165.8 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.57 - 1.70 (m, 8H), 2.54 - 2.73 (m, 4H), 3.64 (s, 2H), 6.86 (dd, *J* = 8.9, 0.8 Hz, 1H),

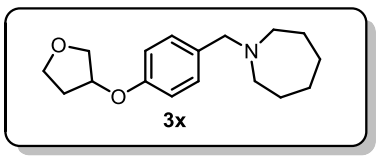


7.05 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.62 (dd, *J* = 8.9, 2.7 Hz, 1H), 8.13 (dd, *J* = 2.7, 0.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.3 (CH_2), 28.4 (CH_2), 55.9 (CH_2), 62.4 (CH_2), 112.7 CH), 120.9 (CH), 125.9 (C), 130.2 (CH), 137.0 (C), 139.4 (CH), 146.4 (CH), 152.9 (C), 162.5 (C). **FT-IR** (cm^{-1}, neat, ATR) 2922 (m), 2851 (w), 1583 (m), 1456 (vs), 1370 (s), 1266 (vs), 1241 (s), 1108 (m), 824 (m). **HRMS** (EI) calcd for $C_{18}H_{21}ClN_2O$ $[M]^+$: 316.1342, found: 316.1361.

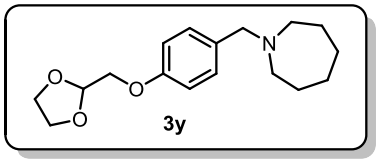
4-(Azepan-1-ylmethyl)phenyl cyclobutanecarboxylate, 3w (80.5 mg, 56%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 4-iodophenyl cyclobutanecarboxylate **1o** (151.1 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.58 - 1.68 (m, 8H), 1.93 - 2.10 (m, 2H), 2.27 - 2.36 (m, 2H), 2.38 - 2.48 (m, 2H), 2.61 - 2.67 (m, 4H), 3.32 - 3.41 (m, 1H), 3.65 (s, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 18.7 (CH_2), 25.6 (CH_2), 27.3 (CH_2), 28.1 (CH_2), 38.4 (C), 55.7 (CH_2), 62.2 (CH_2), 121.4 (CH), 130.0 (CH), 137.1 (C), 150.0 (C), 174.3 (C). **FT-IR** (cm^{-1}, neat, ATR) 2924 (m), 1752 (s), 1505 (m), 1352 (m), 1161 (s), 1133 (vs), 1017 (m), 853 (m). **HRMS** (ES+) calcd for $C_{18}H_{26}NO_2$ $[M+H]^+$: 288.1964, found: 288.1978.



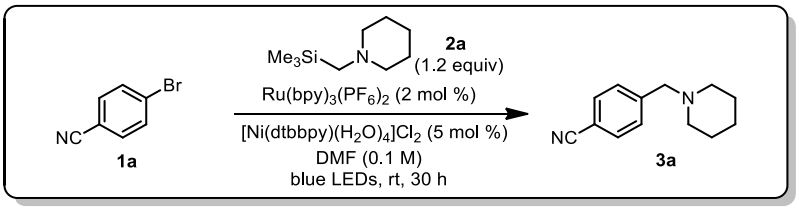
1-(4-((Tetrahydrofuran-3-yl)oxy)benzyl)azepane, 3x (74.1 mg, 54%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 3-(4-iodophenoxy)tetrahydrofuran **1p** (145.1 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.57 - 1.68 (m, 8H), 2.11 - 2.25 (m, 2H), 2.58 - 2.66 (m, 4H), 3.59 (s, 2H), 3.89 (td, *J* = 8.2, 4.6 Hz, 1H), 3.94 - 4.02 (m, 3H), 4.85 - 4.95 (m, 1H), 6.80 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.2 (CH_2), 28.0 (CH_2), 33.2 (CH_2), 55.5 (CH_2), 62.1 (CH_2), 67.4 (CH_2), 73.4 (CH_2), 77.5 (CH), 115.2 (CH), 130.4 (CH), 131.9 (C), 156.6 (C). **FT-IR** (cm^{-1}, neat, ATR) 2923 (m), 2854 (m), 1610 (w), 1507 (s), 1235 (vs), 1079 (s), 992 (m), 831 (s). **HRMS** (EI) calcd for $C_{17}H_{25}NO_2$ $[M]^+$: 275.1885, found: 277.1900.



1-(4-((1,3-Dioxolan-2-yl)methoxy)benzyl)azepane, 3y (84.7 mg, 60%) was prepared according to the general procedure from α-silylamine **2b** (148.5 mg, 0.6 mmol, 1.2 equiv) and 2-((4-iodophenoxy)methyl)-1,3-dioxolane **1q** (153.1 mg, 0.5 mmol, 1 equiv). The desired amine **3g** was isolated as a as a clear yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.57 - 1.67 (m, 8H), 2.60 (m, *J* = 5.5 Hz, 4 H), 3.58 (s, 2H), 3.94 - 3.98 (m, 2H), 4.02 (d, *J* = 4.0 Hz, 2H), 4.03 - 4.07 (m, 2H), 5.28 (t, *J* = 4.0 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 1.57 - 1.67 (m, 8H), 2.60 (m, *J* = 5.5 Hz, 4H), 3.58 (s, 2H), 3.93 - 3.98 (m, 2H), 4.00 - 4.09 (m, 4H), 5.28 (t, *J* = 4.0 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H). **FT-IR** (cm^{-1}, neat, ATR) 2922 (m), 2806 (m), 1611 (w), 1509 (s), 1455 (w), 1245 (s), 1147 (vs), 1049 (s), 831 (s). **HRMS** (EI) calcd for $C_{17}H_{25}NO_3$ $[M]^+$: 291.1834, found: 291.1819.



Representative Procedure for Large Scale Aminomethylation

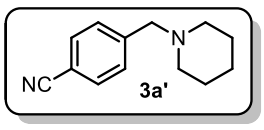


4-(Piperidin-1-ylmethyl)benzonitrile[17] (3a)

To an oven dried, 100 mL round bottom flask equipped with a stir bar were added $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.1 mmol, 0.02 equiv), bromoarene **1a** (0.910 g, 5 mmol, 1 equiv), and $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (0.118 g, 0.25 mmol, 0.05 equiv). The flask was sealed with a rubber septum and was evacuated and purged with argon three times *via* an inlet needle. The flask was then charged with anhydrous DMSO (50 mL) *via* a syringe. The now bright red solution was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 ^oC *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once complete (~30 h), the now dark red-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (100 mL) and 2 M NaOH (20 mL) and Et_2O (~100 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × ~50 mL). The combined organic layers were washed with deionized H_2O (2 × ~150 mL) followed by brine (~100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient CH_2Cl_2/MeOH)18 to give the desired amine **3a** (0.572 g, 57%) as a pale yellow oil.

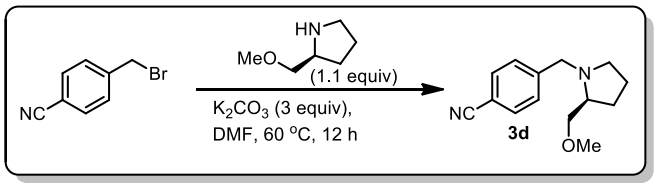
^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 - 1.50 (m, 2H), 1.53 - 1.63 (m, 4H), 2.27 - 2.47 (m, 4H), 3.52 (s, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.4 (CH_2), 26.1 (CH_2), 54.8 (CH_2), 63.4 (CH_2), 110.9 (C), 119.3 (C), 129.8 (CH), 132.3 (CH), 144.7 (C).

4-(Piperidin-1-ylmethyl)benzonitrile,[17] 3a′ (0.679 g, 68%) was prepared according to the general scale up procedure from **2a′** (1.40 g, 6 mmol). The desired amine **3a′** was isolated as a yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 -



1.50 (m, 2H), 1.53 - 1.63 (m, 4H), 2.27 - 2.47 (m, 4H), 3.52 (s, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.4 (CH_2), 26.1 (CH_2), 54.8 (CH_2), 63.4 (CH_2), 110.9 (C), 119.3 (C), 129.8 (CH), 132.3 (CH), 144.7 (C).

Synthesis of Authentic 3d for Comparison of Enantiopurity



(*S*)-4-((2-(methoxymethyl)pyrrolidin-1-yl)methyl)benzonitrile (3d)

To an 10 mL reaction vial equipped with a stir bar were added (*S*)-2-methoxymethyl)pyrrolidine (0.253 g, 2.2 mmol, 1.1 equiv), K_2CO_3 (0.829 g, 6.0 mmol, 3 equiv) and DMF (2 mL). After stirring at rt for five minute, 4-(bromomethyl)benzonitrile (0.392 g, 2.0 mmol, 1 equiv) was added in on portion to the vial. The vial was heated to 60 °C h via an oil bath. Reaction progress was monitored by GC/MS. Once judged to be complete (~12 h), the reaction mixture diluted with deionized H_2O (~3 mL) and Et_2O (~3 mL). The contents of the vial were transferred to a seperator funnel and diluted further with H_2O (~10 mL) and Et_2O (~10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with deionized H_2O (2 × ~25 mL) followed by brine (~50 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to give the desired amine, **3d**, (0.352 g, 76%) as a clear colorless oil. $[\alpha]^{23}_D$ = -59.4 ($CHCl_3$, *c* = 0.50).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.56 - 1.68 (m, 1H), 1.67 - 1.82 (m, 2H), 1.87 - 2.00 (m, 1H), 2.10 - 2.32 (m, 1H), 2.69 - 2.85 (m, 1H), 2.85 - 2.98 (m, 1H), 3.32 (s, 3H), 3.35 (dd, *J* = 9.5, 5.1 Hz, 1H), 3.40 - 3.57 (m, 2H), 4.21 (d, *J* = 13.9 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H).

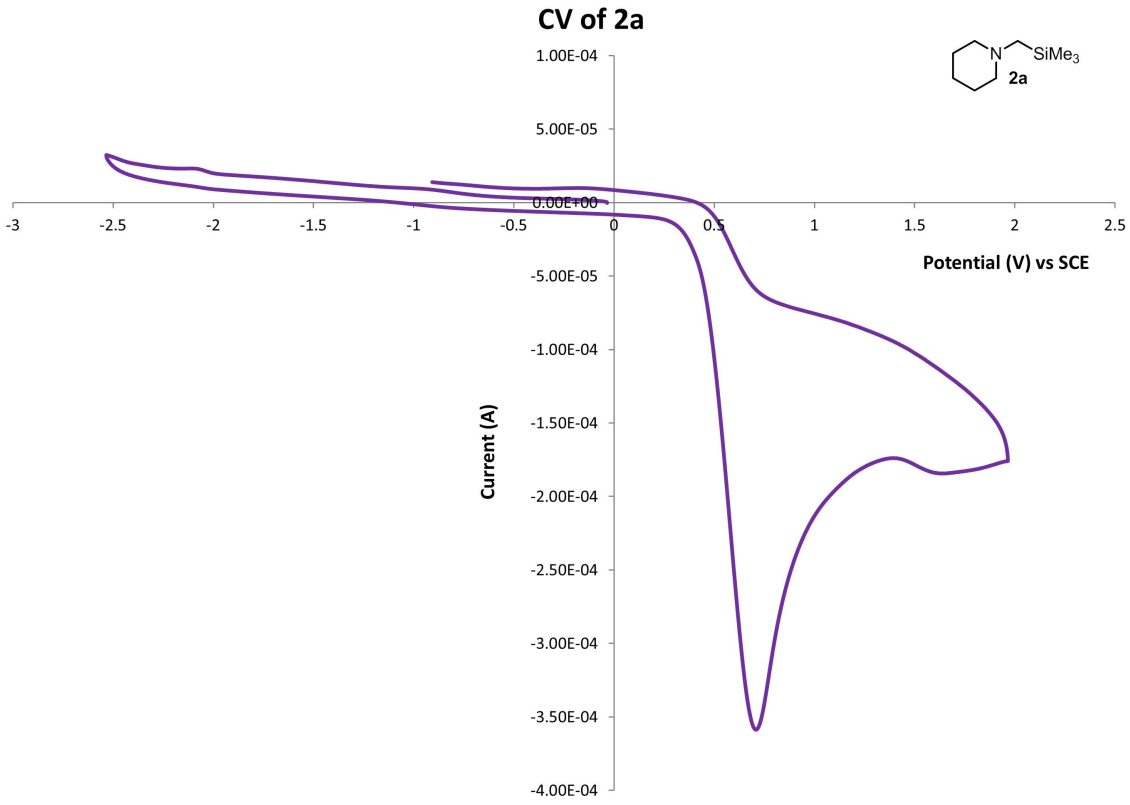
^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.0 (CH_2), 28.5 (CH_2), 54.9 (CH_2), 59.3 (CH_2), 59.4 (CH_2), 63.3 (CH), 76.7 (CH_3), 110.6 (C), 119.3 (C), 129.5 (CH), 132.2 (CH), 146.1 (C).

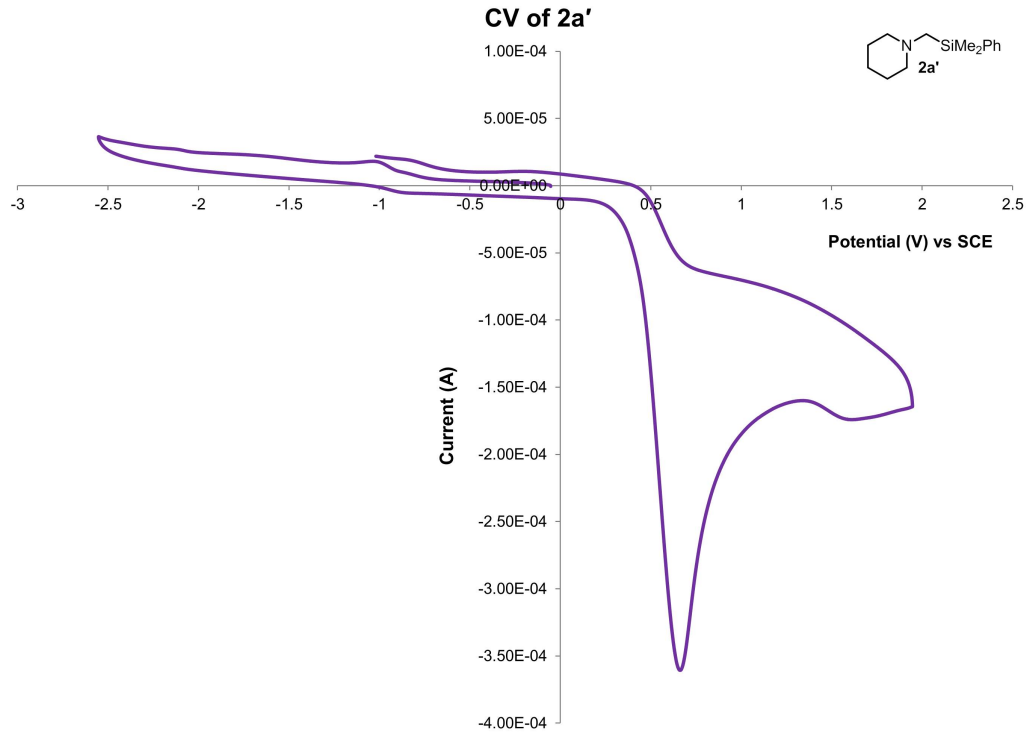
FT-IR (cm^{-1}, neat, ATR) 2923 (m), 2874 (m), 2809 (m), 2227(m), 1608 (w), 1504 (w), 1458 (w), 1107 (vs), 819 (s), 548 (vs).

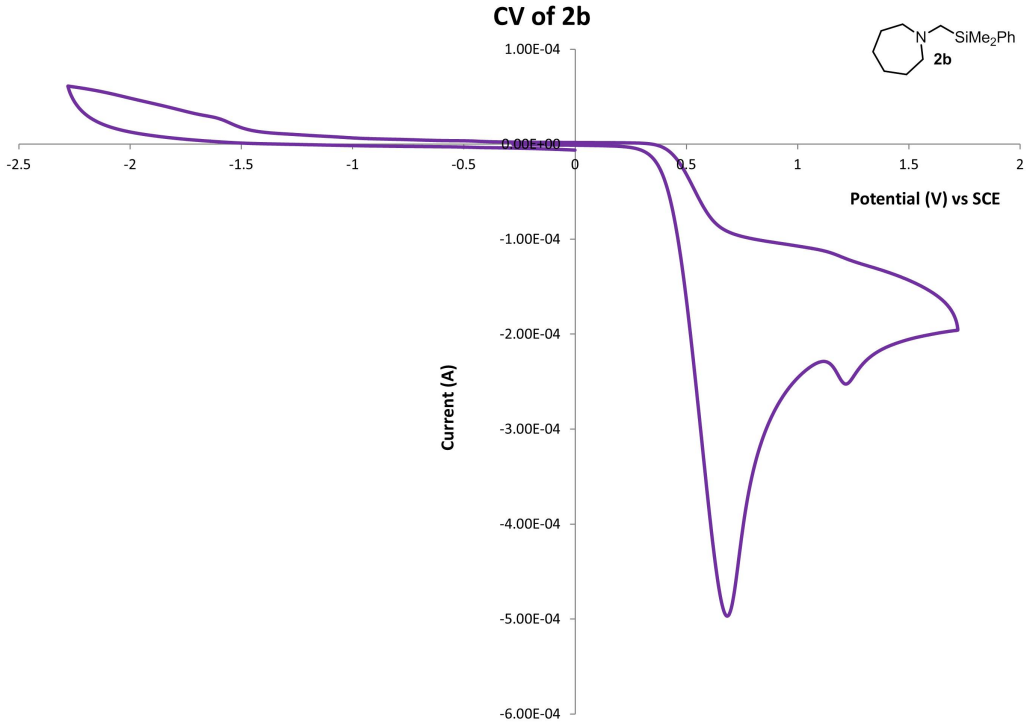
HRMS (EI) calcd for $C_{14}H_{18}N_2O$ $[M]^+$: 230.1419, found: 230.1409.

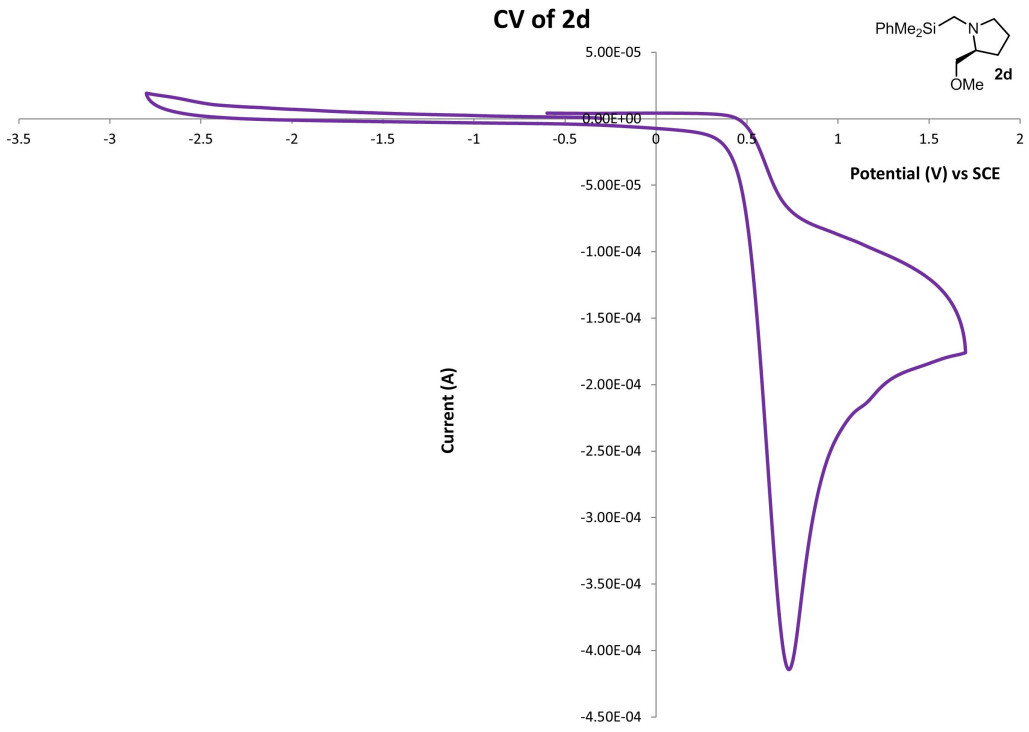
Cyclic Voltammogram of α-Silylamines & Aminomethylated Products

Voltammetric measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer using a standard three electrodes setup in dry and degassed MeCN (10 mL), with ferrocene as an internal reference ($E^0_{1/2}$ = + 0.40 V vs SCE) and Bu_4NPF_6 as the electrolyte (0.10 mmol). Cyclic voltammograms were recorded with a step potential of 0.001 V at a scan rate of 0.5 V/s.




CV of 2a′
1.00E-04
5.00E-05
0.00E+00
-5.00E-05
-1.00E-04
-1.50E-04
-2.00E-04
-2.50E-04
-3.00E-04
-3.50E-04
-4.00E-04
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
Potential (V) vs SCE
Current (A)
N
SiMe2Ph
2a'


CV of 2b
1.00E-04
0.00E+00
-1.00E-04
-2.00E-04
-3.00E-04
-4.00E-04
-5.00E-04
-6.00E-04
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE
Current (A)
N
SiMe2Ph
2b


CV of 2d
PhMe2Si
N
OMe
2d
5.00E-05
0.00E+00
-5.00E-05
-1.00E-04
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-3
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-2
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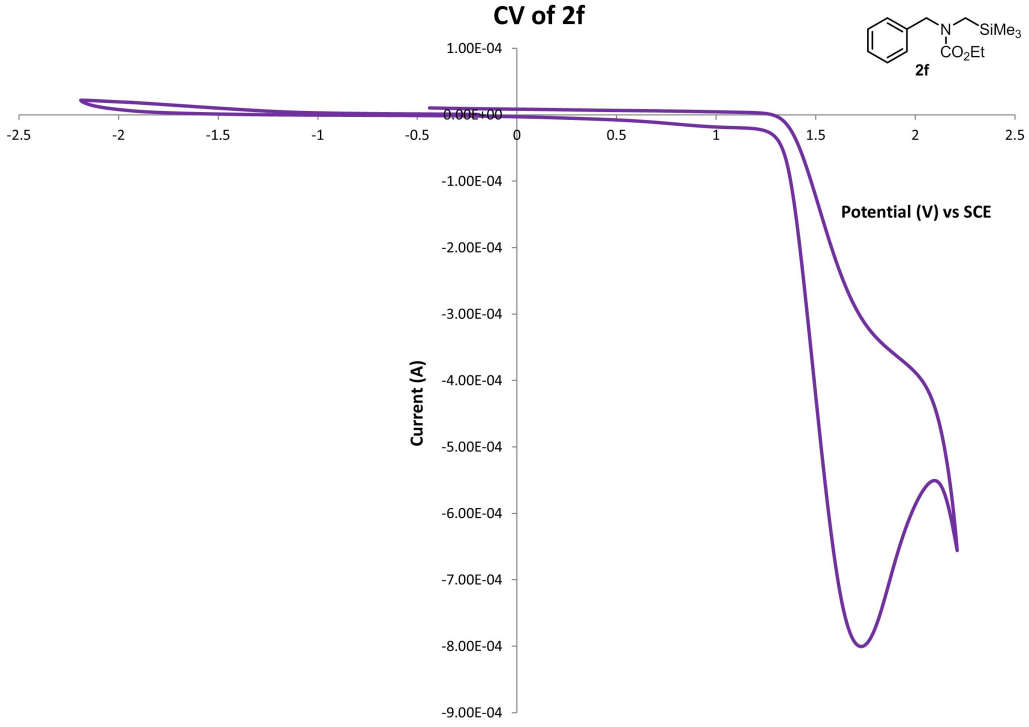
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE
Current (A)


CV of 2f
N
SiMe3
CO2Et
2f
1.00E-04
0.00E+00
-1.00E-04
-2.00E-04
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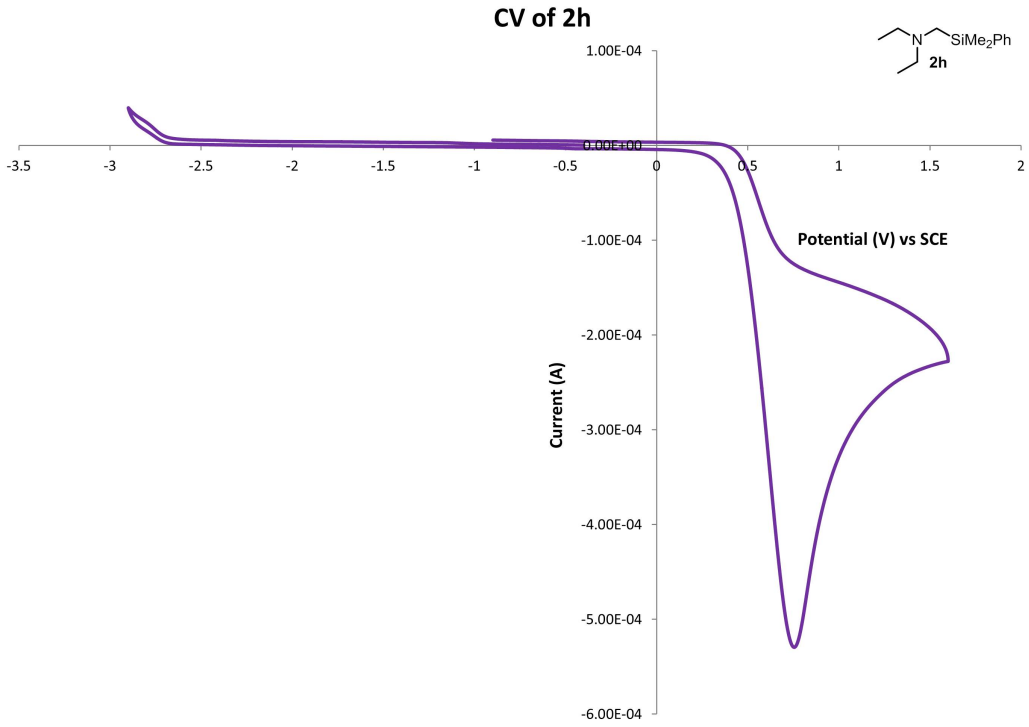
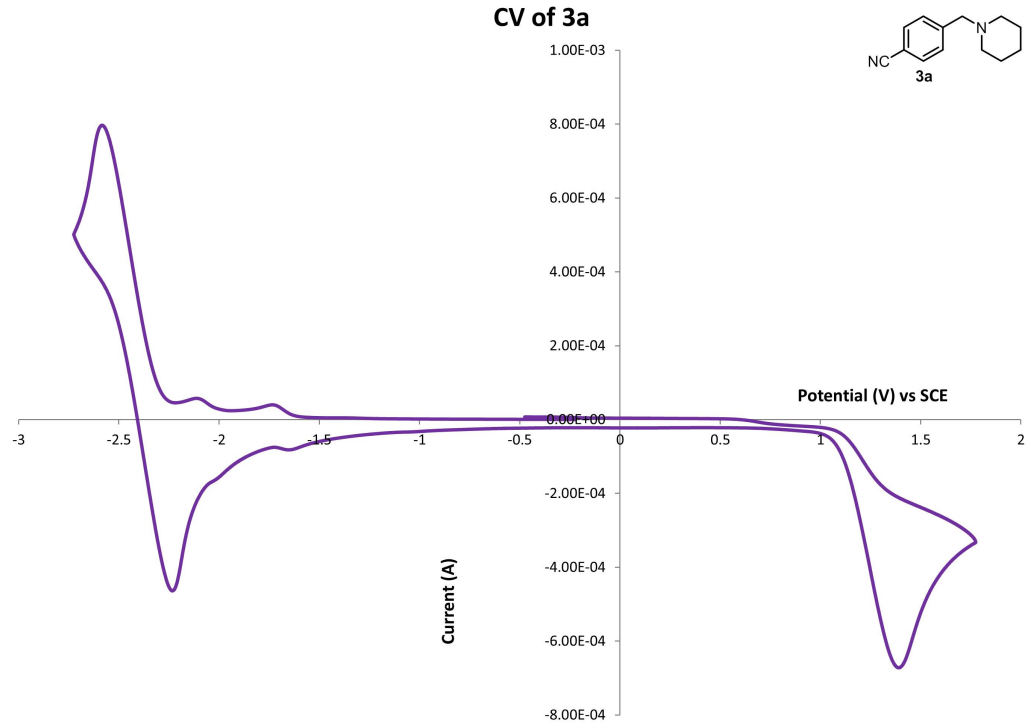
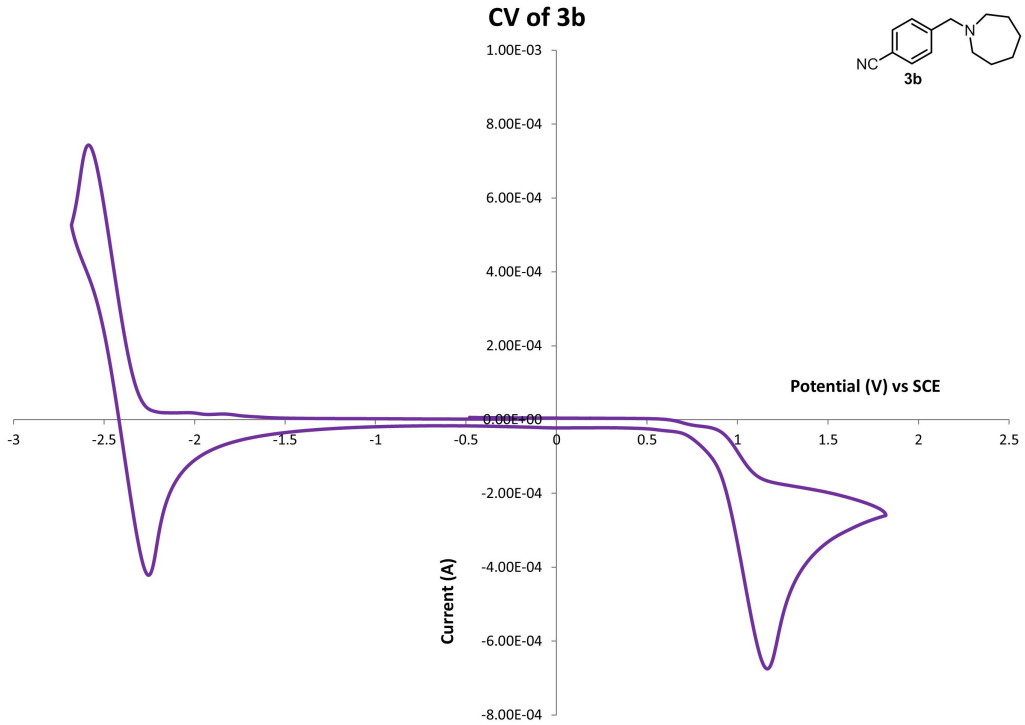
-4.00E-04
-5.00E-04
-6.00E-04
-7.00E-04
-8.00E-04
-9.00E-04
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
Potential (V) vs SCE
Current (A)


CV of 2h
SiMe2Ph
2h
1.00E-04
0.00E+00
-1.00E-04
-2.00E-04
-3.00E-04
-4.00E-04
-5.00E-04
-6.00E-04
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE
Current (A)


CV of 3a
N
NC
3a
1.00E-03
8.00E-04
6.00E-04
4.00E-04
2.00E-04
0.00E+00
-2.00E-04
-4.00E-04
-6.00E-04
-8.00E-04
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE
Current (A)


CV of 3b
NC
N
3b
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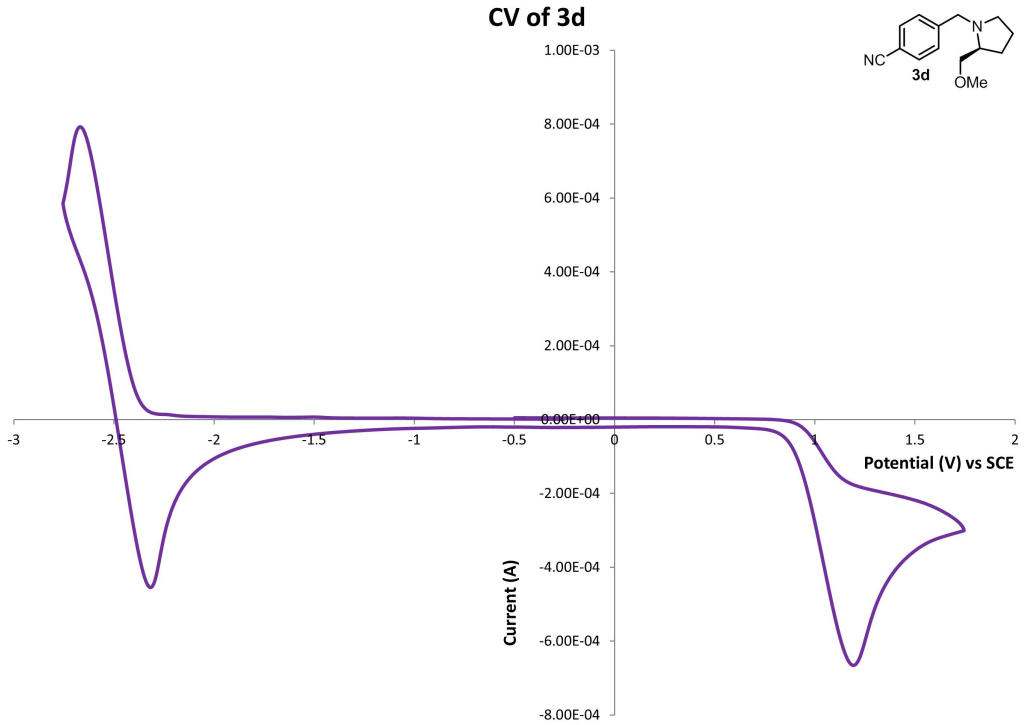
8.00E-04
6.00E-04
4.00E-04
2.00E-04
0.00E+00
-2.00E-04
-4.00E-04
-6.00E-04
-8.00E-04
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
Potential (V) vs SCE
Current (A)


CV of 3d
NC
N
3d
OMe
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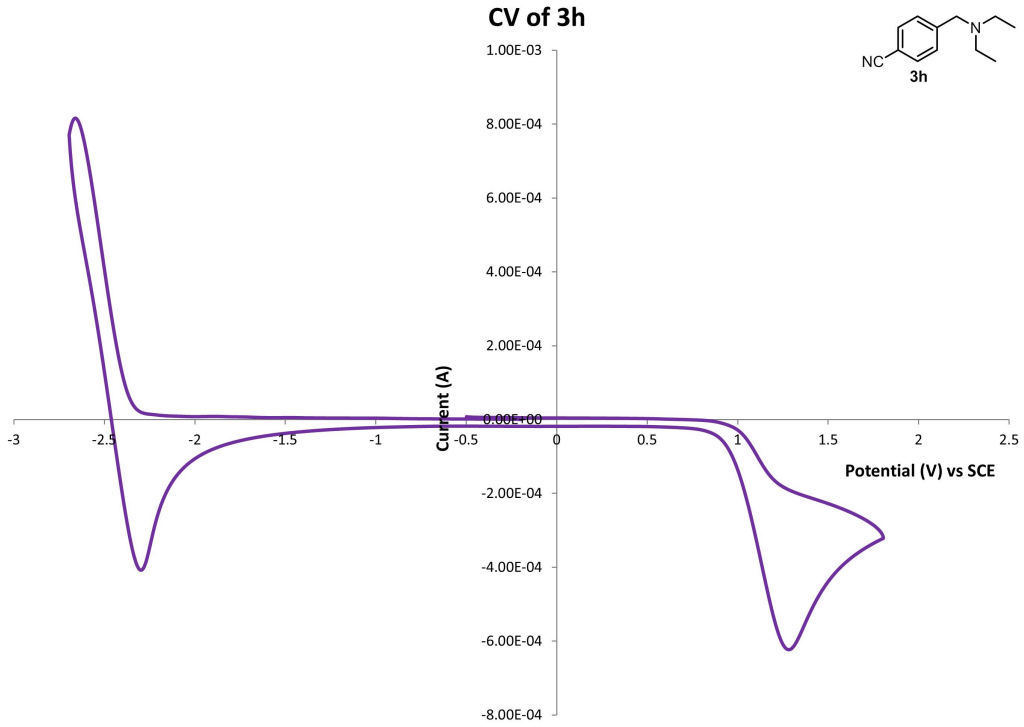
8.00E-04
6.00E-04
4.00E-04
2.00E-04
0.00E+00
-2.00E-04
-4.00E-04
-6.00E-04
-8.00E-04
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE
Current (A)


CV of 3h
NC
N
3h
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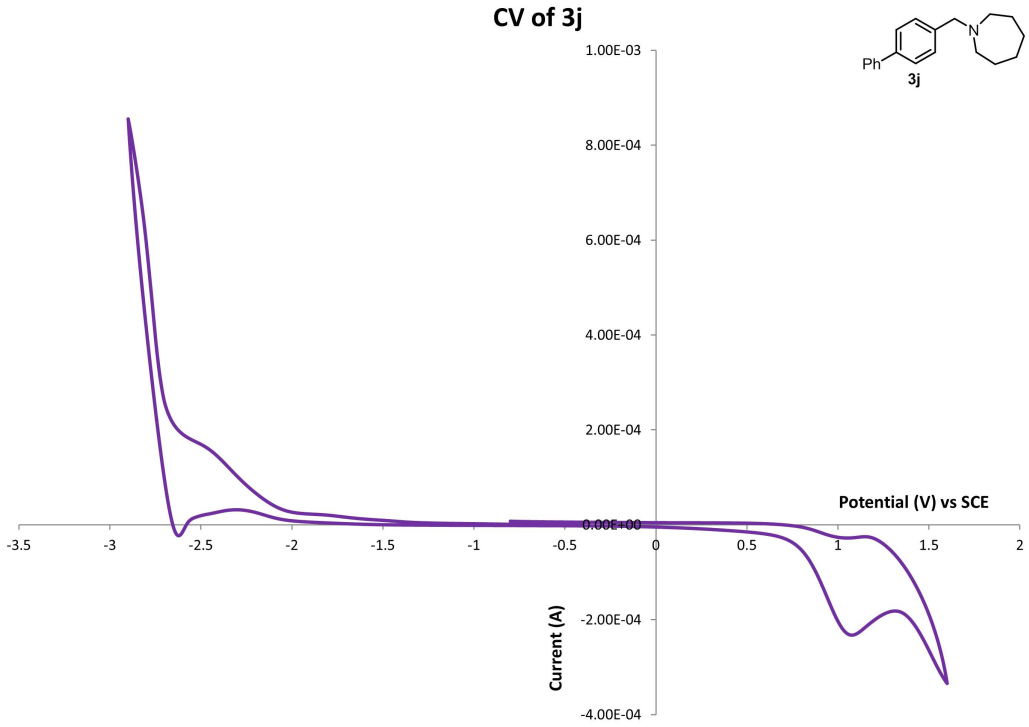
6.00E-04
4.00E-04
2.00E-04
0.00E+00
-2.00E-04
-4.00E-04
-6.00E-04
-8.00E-04
Current (A)
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
Potential (V) vs SCE


CV of 3j
Ph
N
3j
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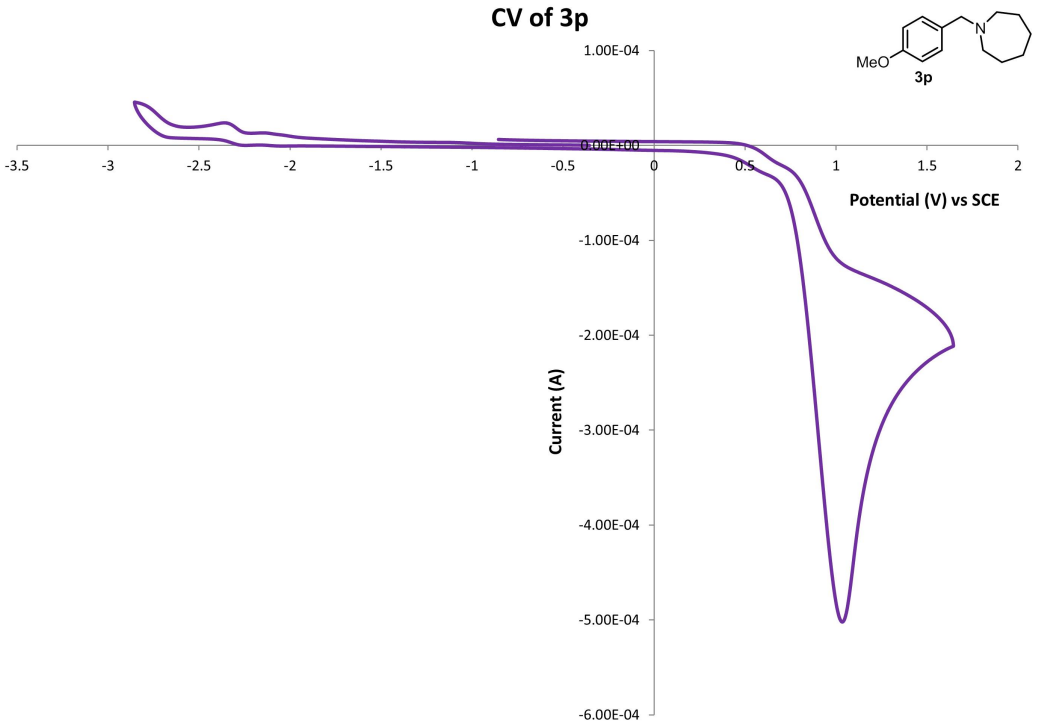
8.00E-04
6.00E-04
4.00E-04
2.00E-04
0.00E+00
-2.00E-04
-4.00E-04
Current (A)
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE


CV of 3p
MeO
N
3p
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0.00E+00
-1.00E-04
-2.00E-04
-3.00E-04
-4.00E-04
-5.00E-04
-6.00E-04
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V) vs SCE
Current (A)

References

1. For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764–767. (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**, *18*, 876–879.

2. Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun*. **2011**, *47*, 4721–4723.

3. Seebach, D.; Imwinkelried, R; Stucky, G. *Helv. Chim. Acta* **1987**, *70*, 448–464.

4. Tellis, J. C.; Primer, D. P.; Molander, G. A. *Science* **2014**, *345*, 433–436.

5. Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766–1770.

6. Example (type used in construction of this reactor) : https://www.amazon.com/gp/product/B01N1IUUIY?ref_=psdc_517834_t2_B00FQO48U8&pldnSite=1

7. Starting from the bottom upward affords the easiest approach.

8. If smaller lengths of LED strips are used, they can be linked together. Most LED strips are able to be cut (at specified locations) and powered by either end. The appropriate connector is required (male or female) for each end.

9. This design can accommodate up to a 250 mL round bottom flask. However, if desired, a larger reactor can be assembled by using larger variants of the necessary components and additional LEDs.

10. Asakawa, T.; Iinuma, M.; Wakasugi, Y.; Kuno, M.; Furuta, T.; Fujii, S.; Tanaka, K.; Kan, T. *Heterocycles* **2010**, *80*, 1125–1147.

11. In the event that residual 5-chloro-2-fluoropyridine remains, removal can be accomplished by heating the impure product to 50 ^{o}C under vacuum (< 1mm Hg).

12. In the event that any residual 3-bromotetrahydrofuran remains, removal can be accomplished by heating the impure product to 50 ^{o}C under vacuum (< 1 mm Hg).

13. Alternatively, for rather non-polar amines, pentane can be used. Comparable yields can be obtained so long as one extra extraction is utilized (four total extractions rather than the three listed for Et_2O).

14. In general, the peaks in ^{1}H NMR of α-silylamines appear broadened. We speculate that this may stem from an interaction between the deuterated solvent, $CDCl_3$, and the amine, although for some substrates this broadening can be resolved by increasing the relative concentration of the analyte in $CDCl_3$. See Lazareva, N. F.; Vakul'skaya, T. I.; Lazarev, I. M. *J. Phys. Org. Chem.* **2009**, *22*, 144–154.

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16. NMR spectra of this compound indicates significant rotameric character; rotameric carbons are given in bold.

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18. Alternatively, hexane/EtOAc (containing 1% Et_3N) may be used instead, although in some cases separation of the residual α-silylamine from the product is problematic with this solvent system.

19. Alternatively, EtOAc can be used for more polar products, albeit this can make remove of DMF more difficult during workup.

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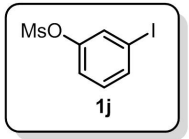
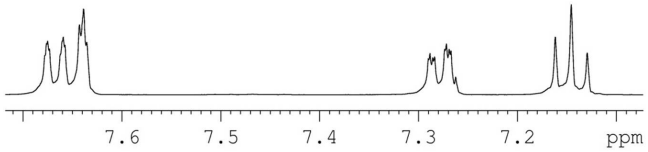
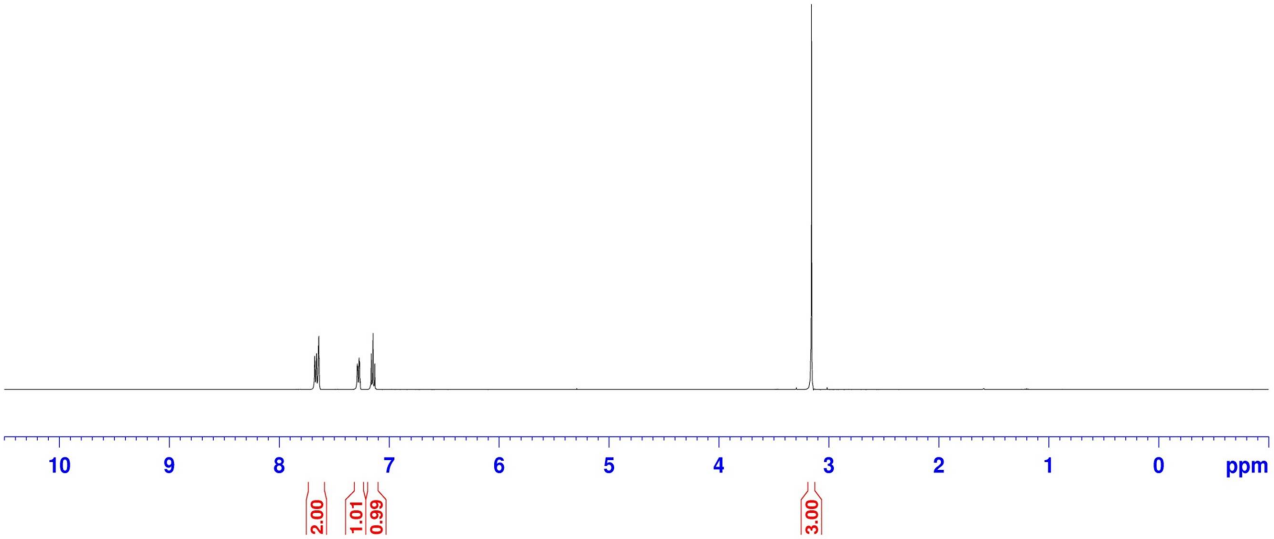
^{1}H NMR Spectra of Synthesized Compounds

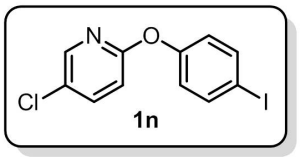
3–iodophenyl methanesulfonate
500 MHz, CDCl3



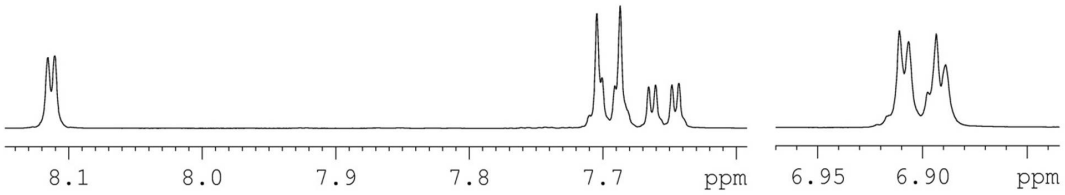


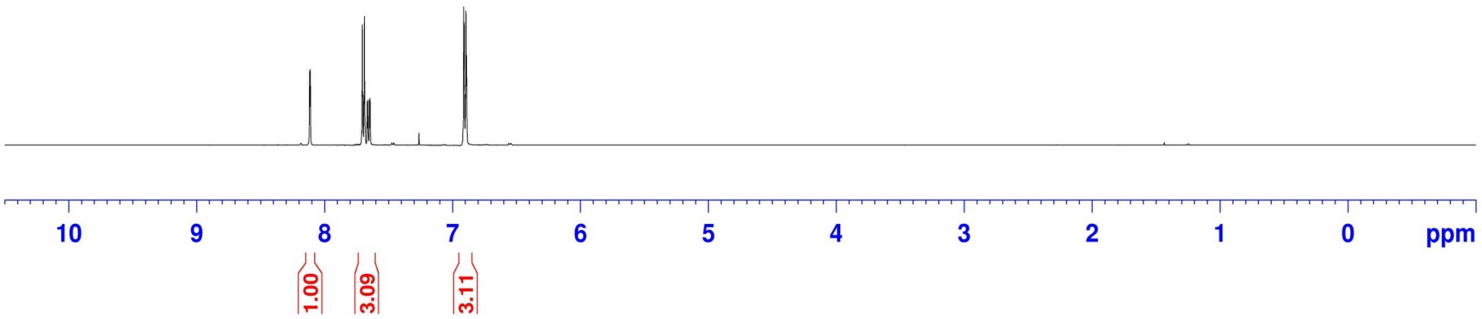


5–chloro–2–(4–iodophenoxy)pyridine
500 MHz, CDCl3

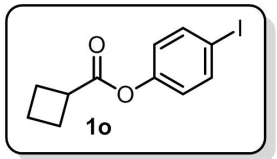


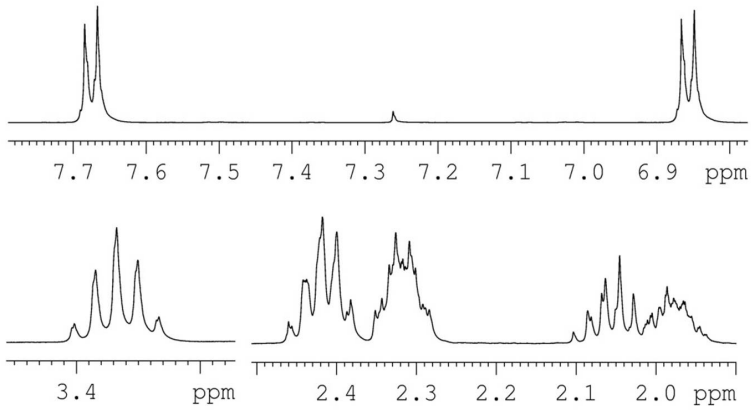
1n

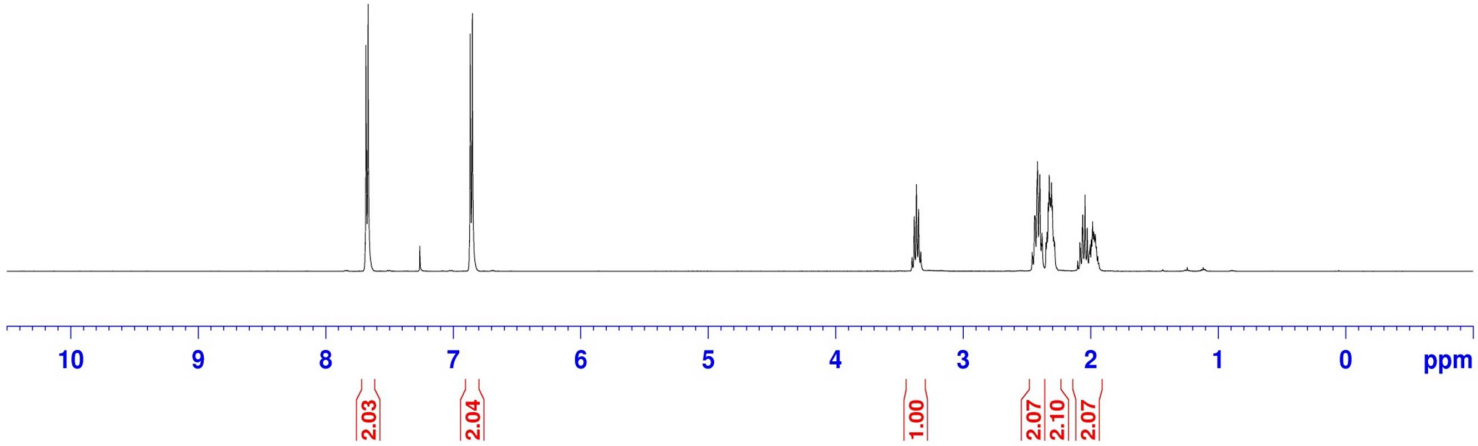




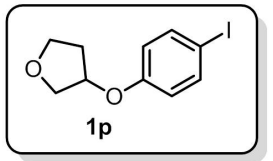
4–iodophenyl cyclobutanecarboxylate
500 MHz, CDCl3

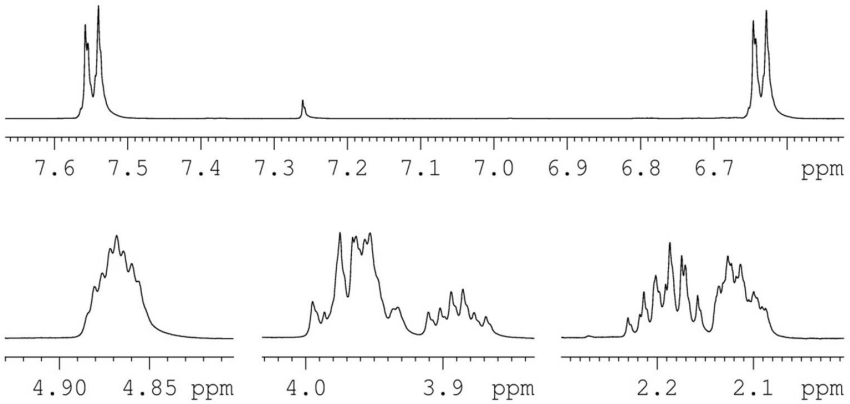


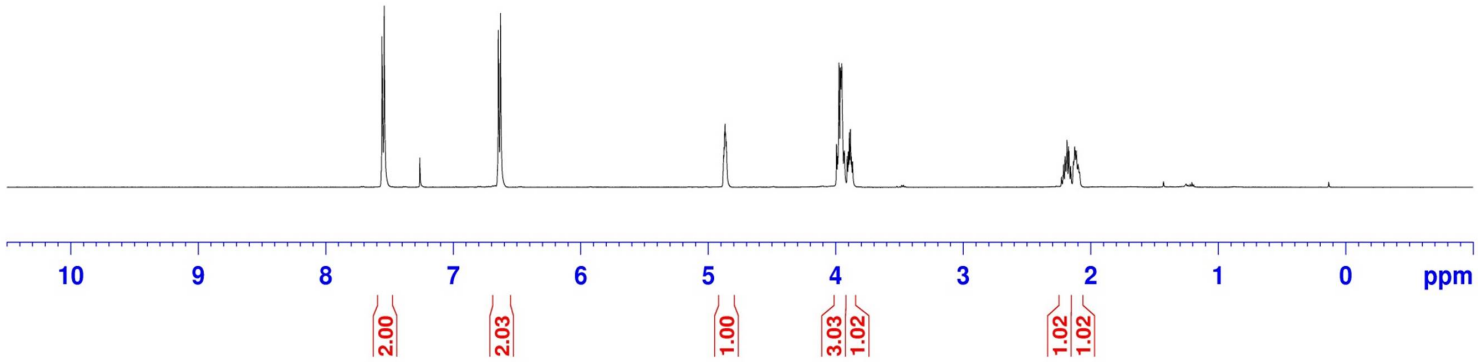




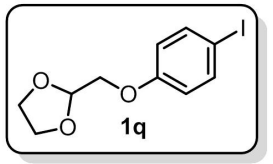
3–(4–iodophenoxy)tetrahydrofuran
500 MHz, CDCl3

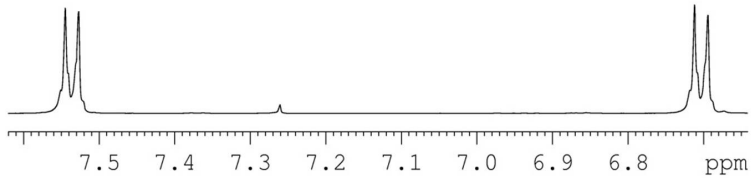


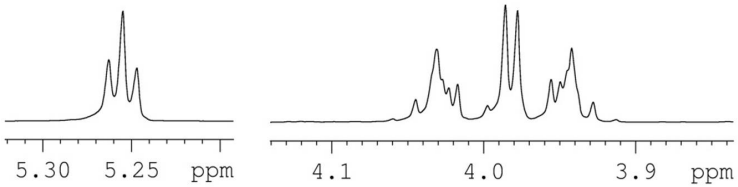


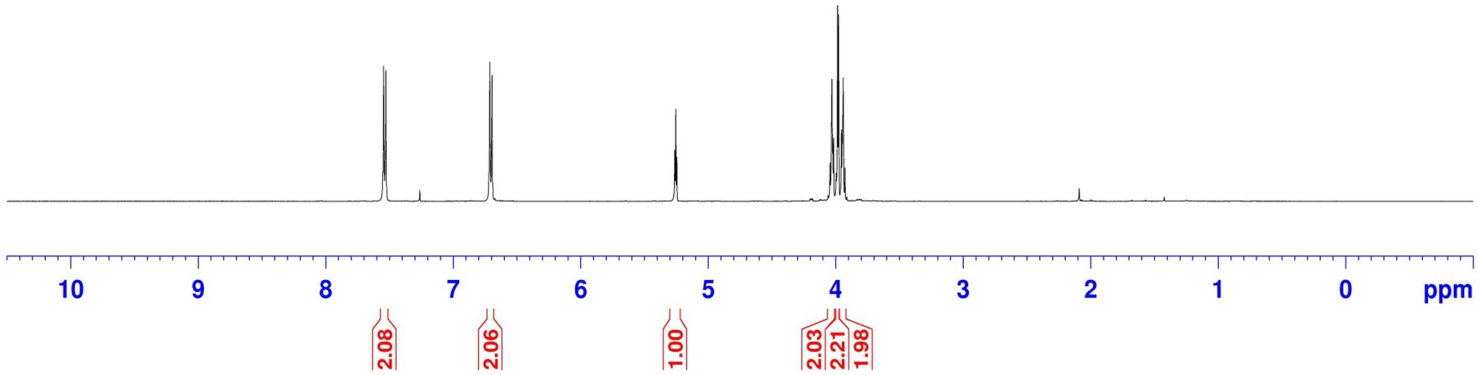


2–((4–iodophenoxy)methyl)–1,3–dioxolane
500 MHz, CDCl3

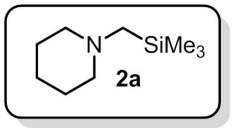


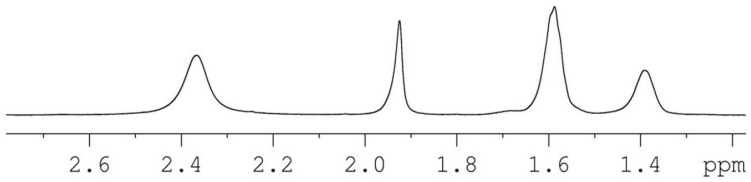


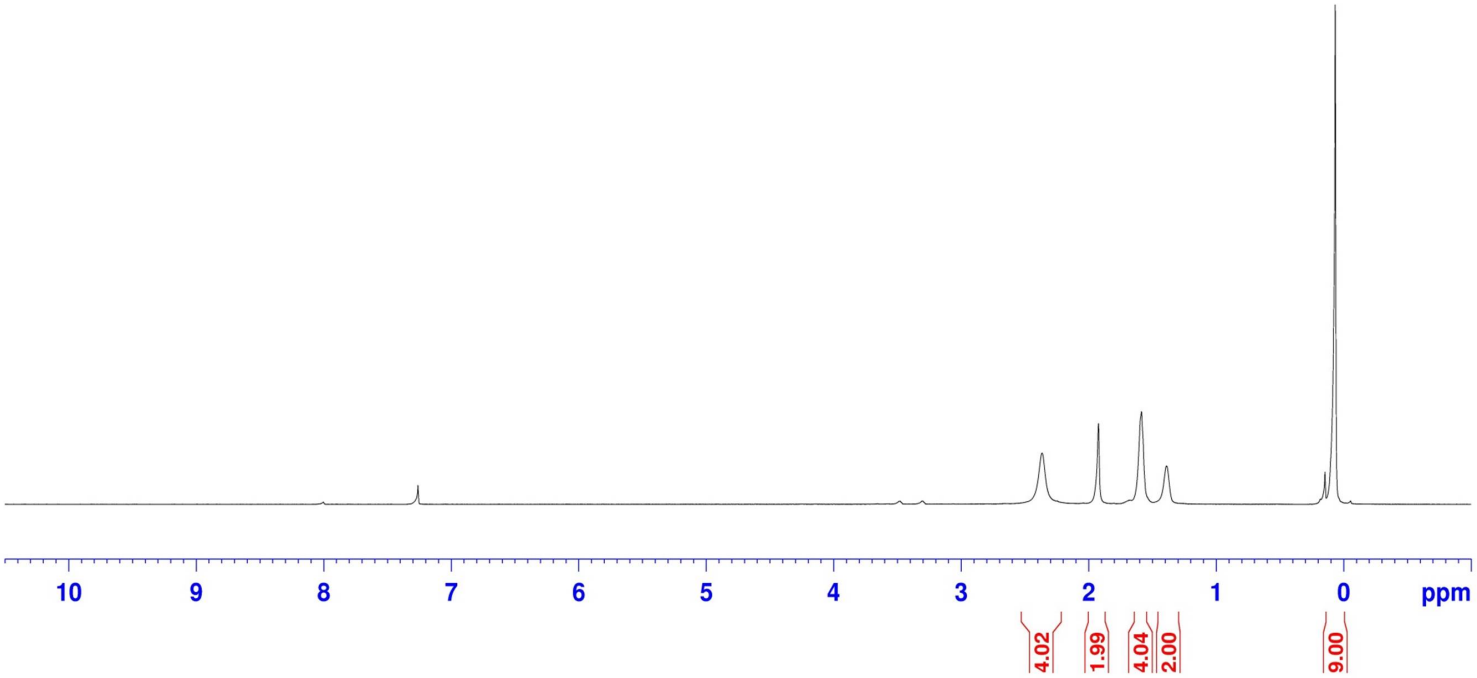




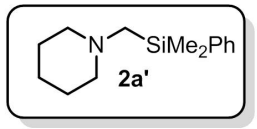
1–((trimethylsilyl)methyl)piperidine
500 MHz, CDCl3

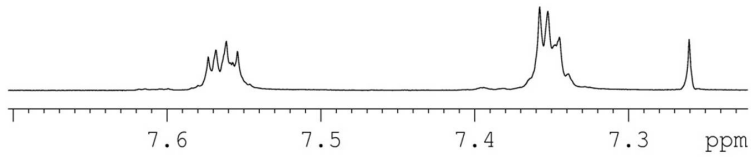


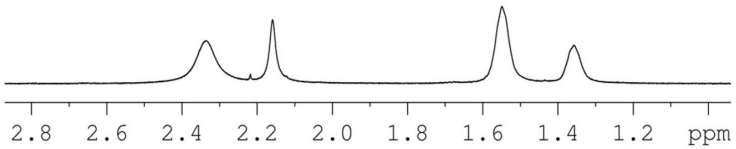


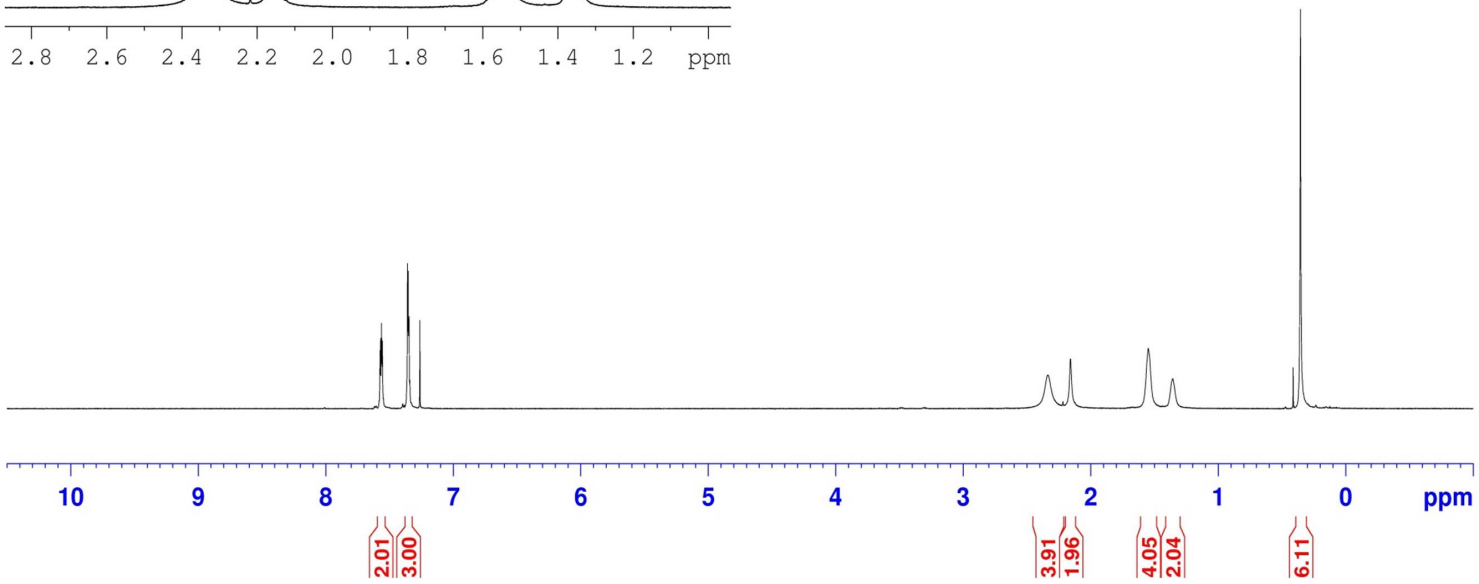


1–((dimethyl(phenyl)silyl)methyl)piperidine
500 MHz, CDCl3

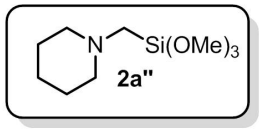


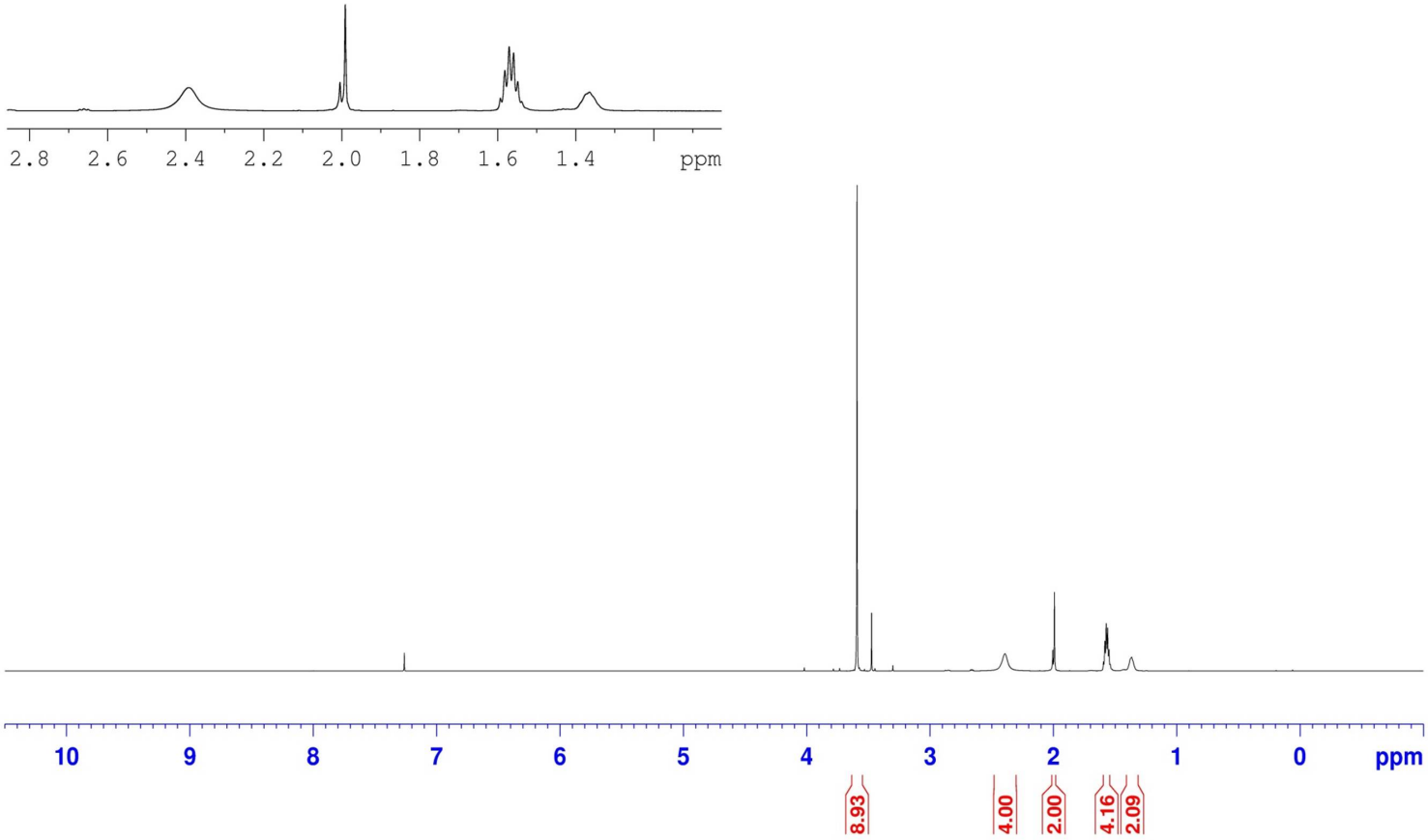




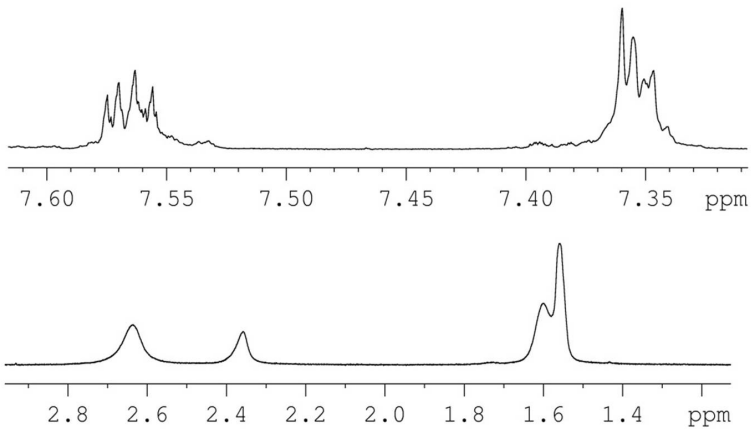


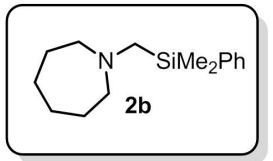
1–((trimethoxysilyl)methyl)piperidine
500 MHz, CDCl3

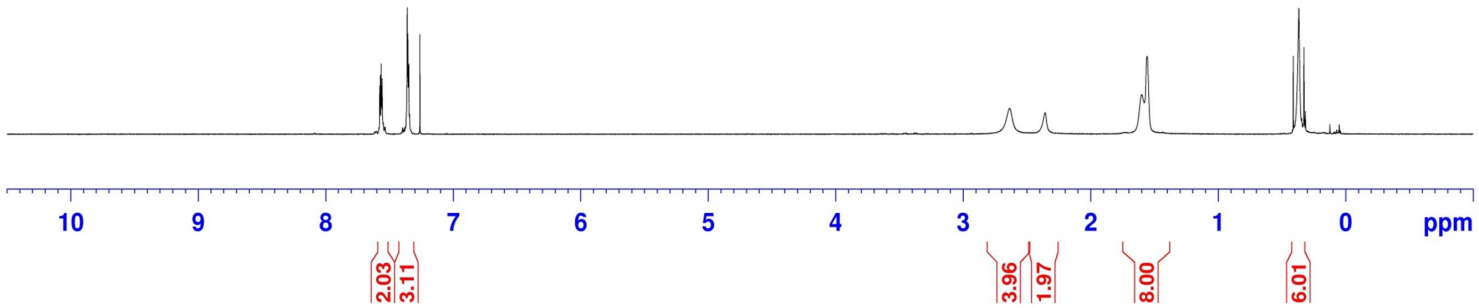




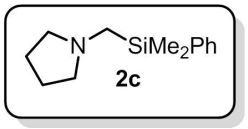
1–((dimethyl(phenyl)silyl)methyl)azepane
500 MHz, CDCl3

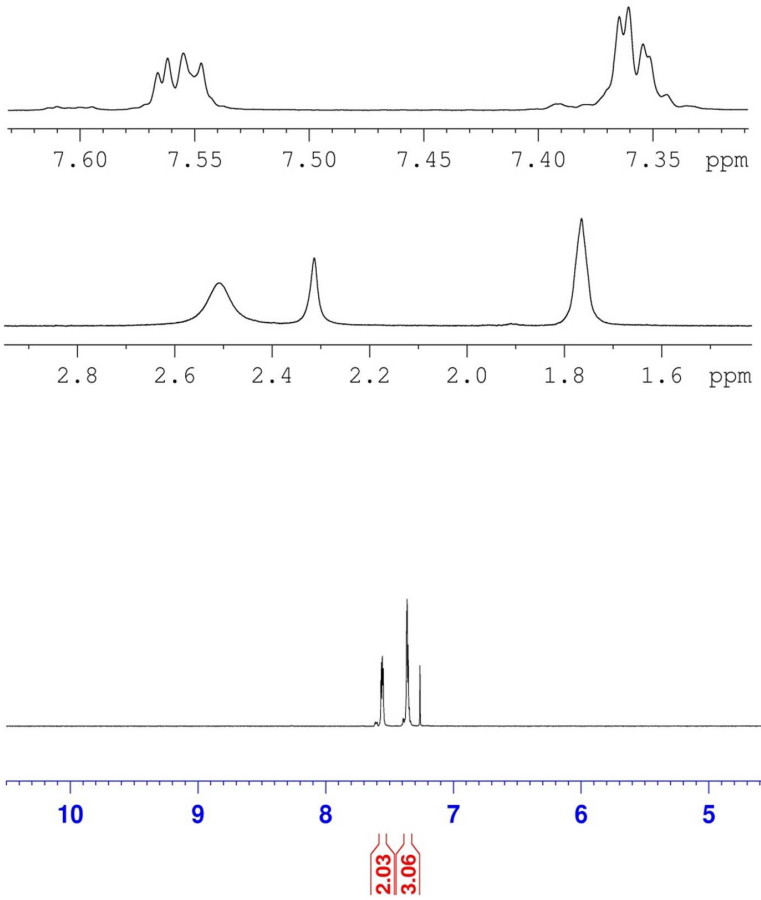




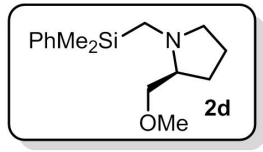


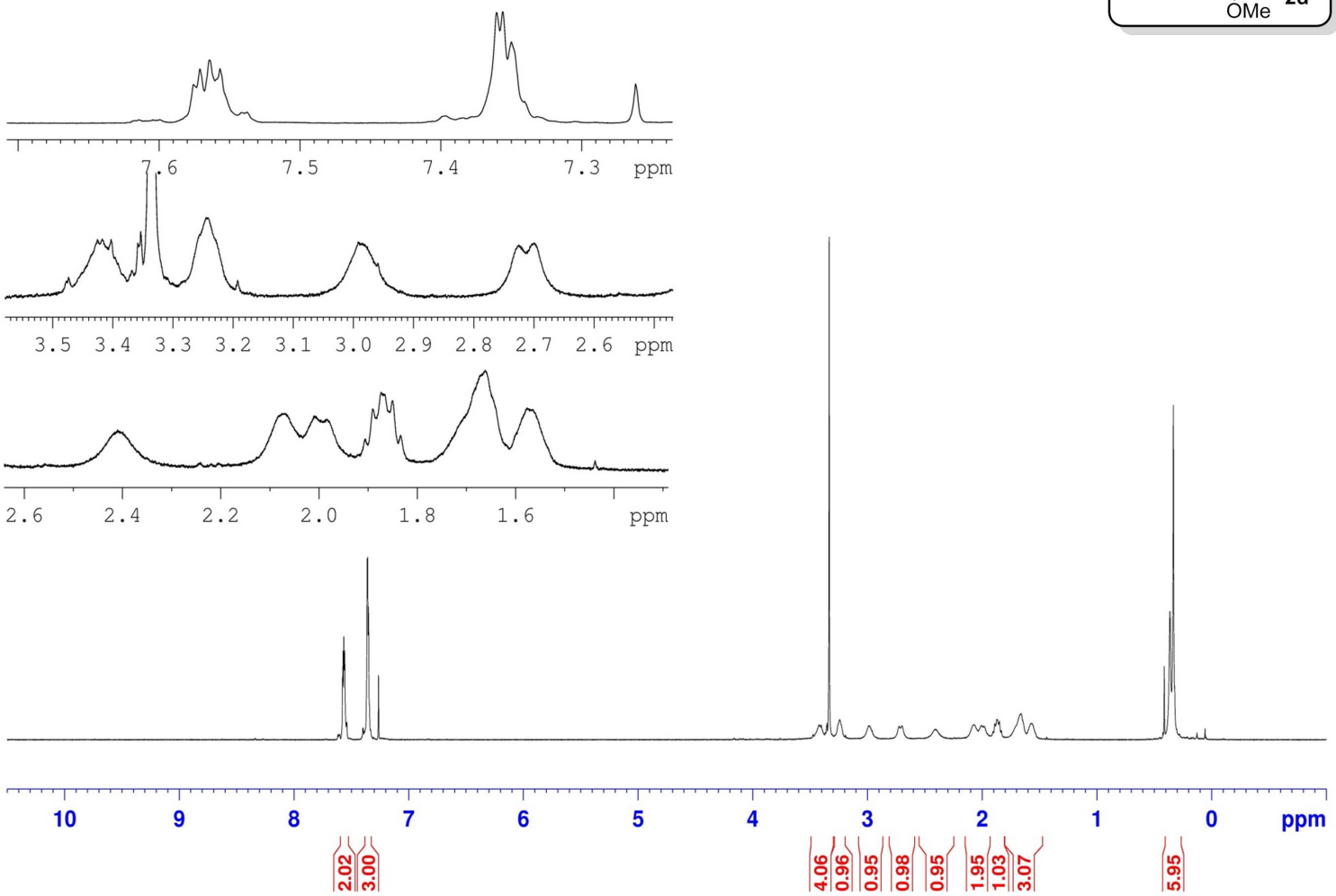
1–((dimethyl(phenyl)silyl)methyl)pyrrolidine
500 MHz, CDCl3



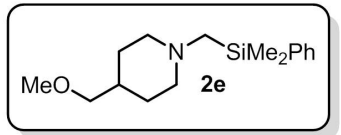


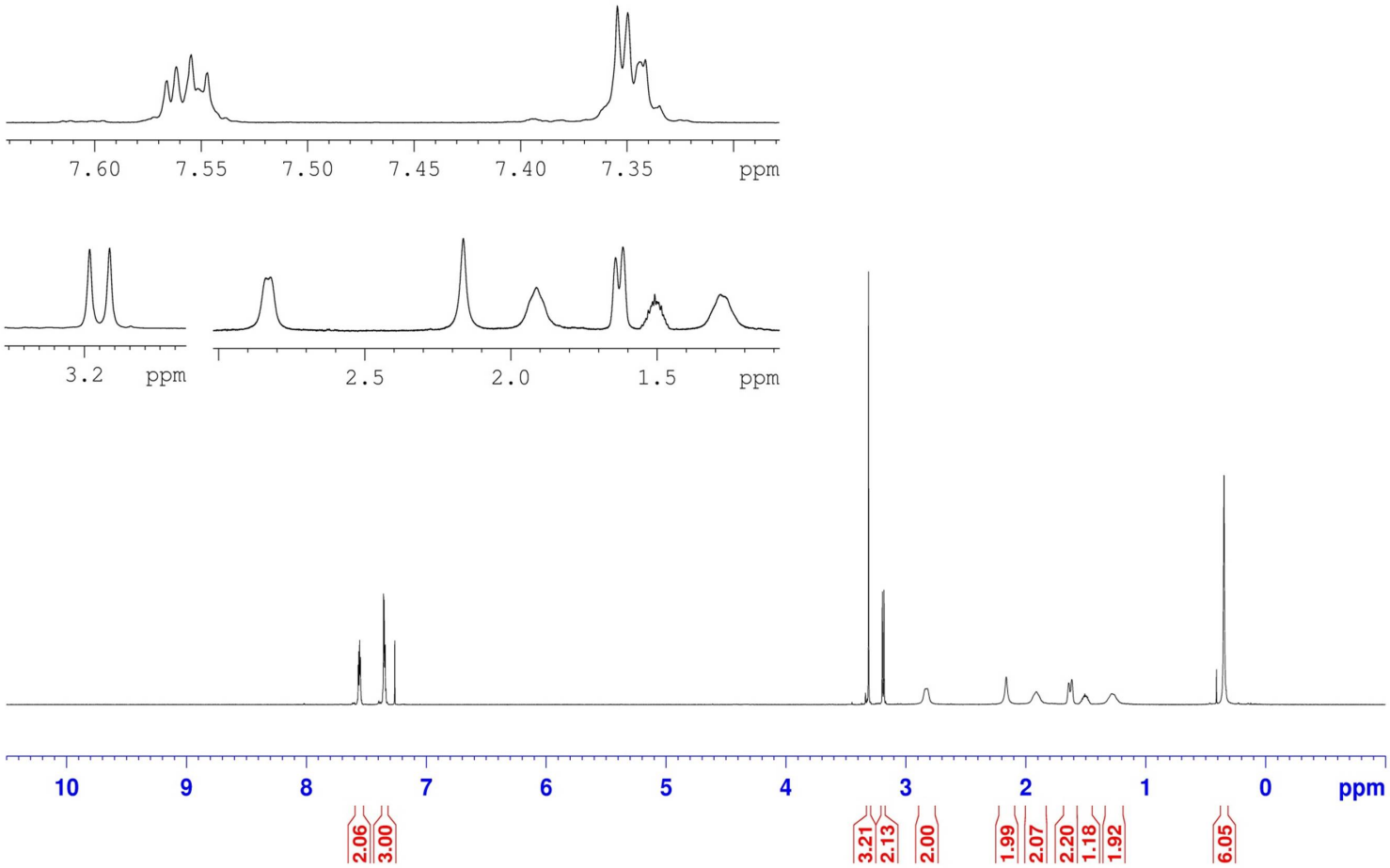
(S)−1−((dimethyl(phenyl)silyl)methyl)−2−(methoxymethyl)pyrrolidine
500 MHz, CDCl3



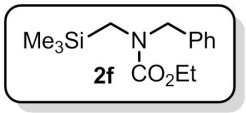


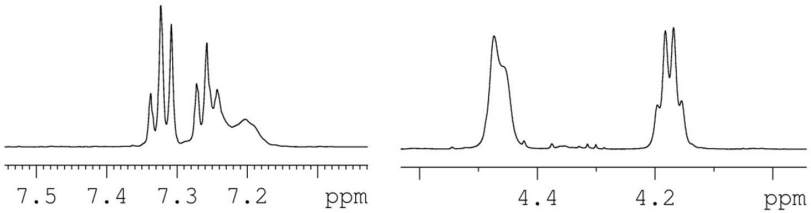
1–((dimethyl(phenyl)silyl)methyl)–4–(methoxymethyl)piperidine
500 MHz, CDCl3

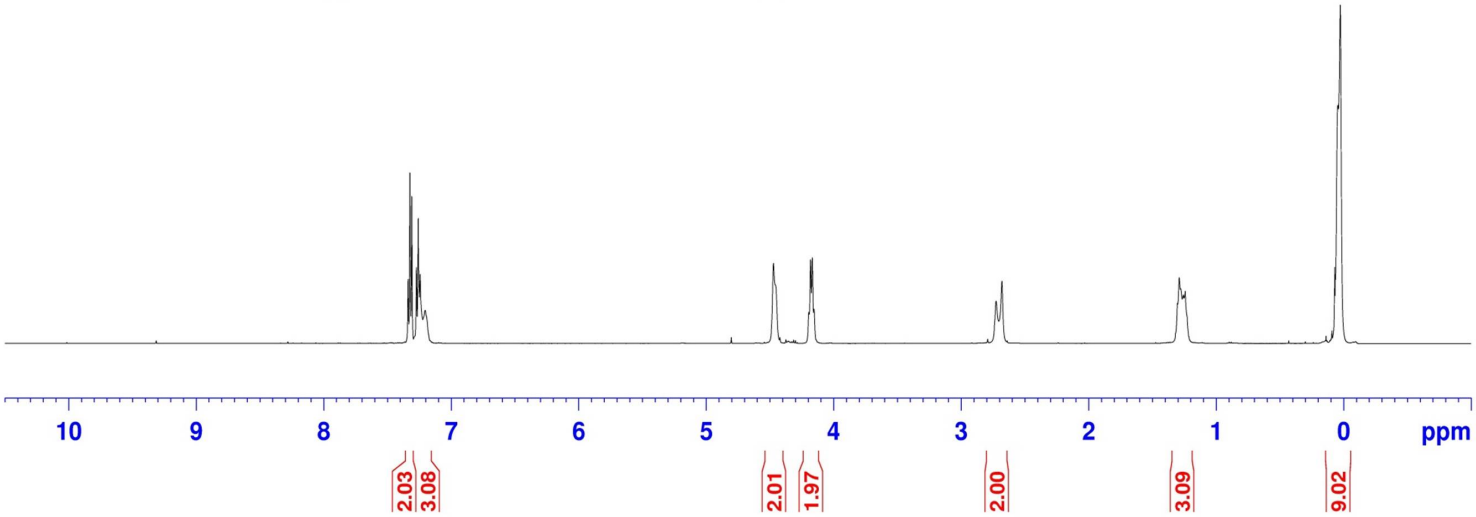




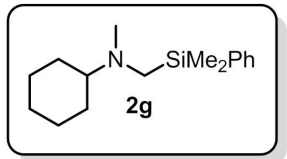
ethyl benzyl((trimethylsilyl)methyl)carbamate
500 MHz, CDCl3

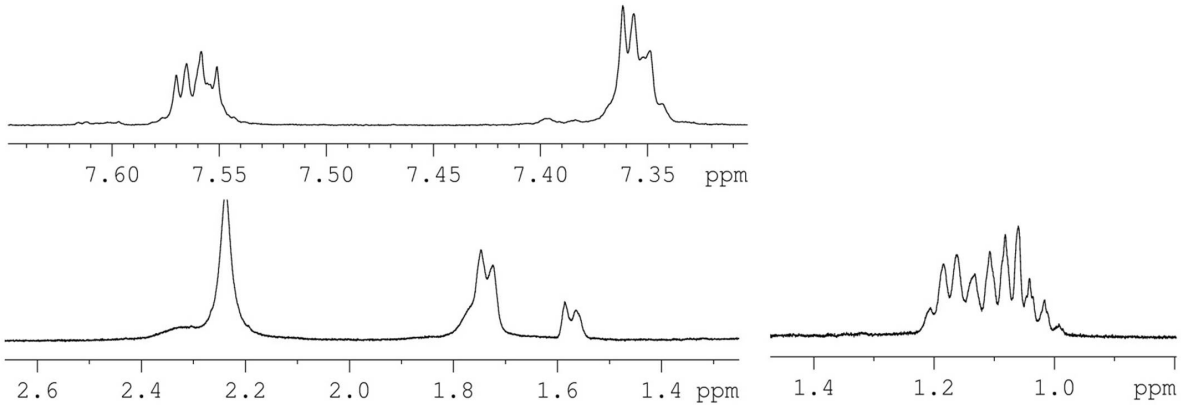


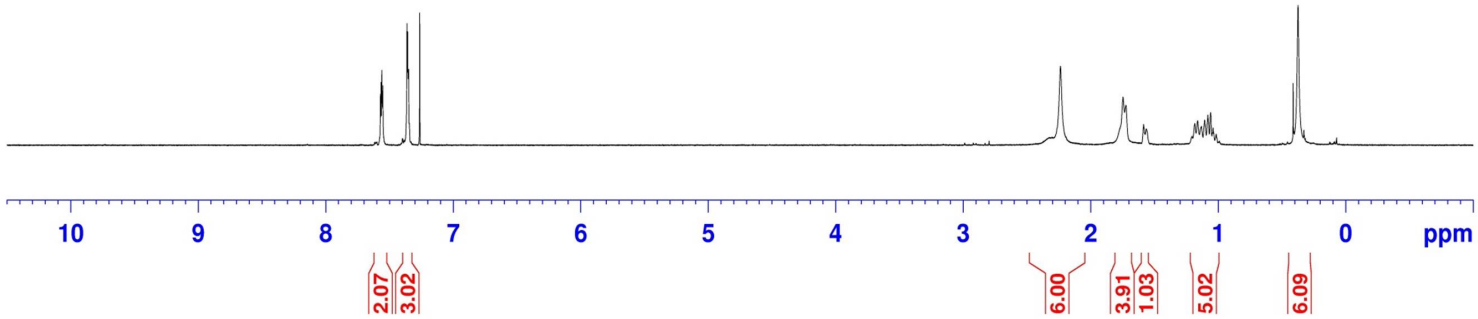




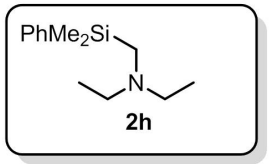
N–((dimethyl(phenyl)silyl)methyl)–N–methylcyclohexanamine
500 MHz, CDCl3

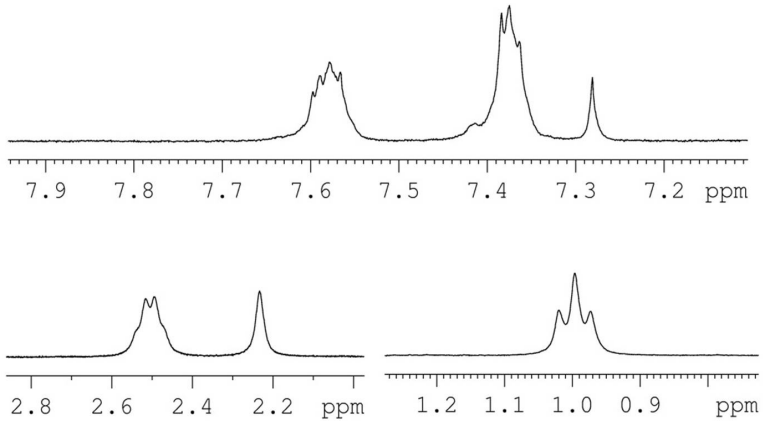


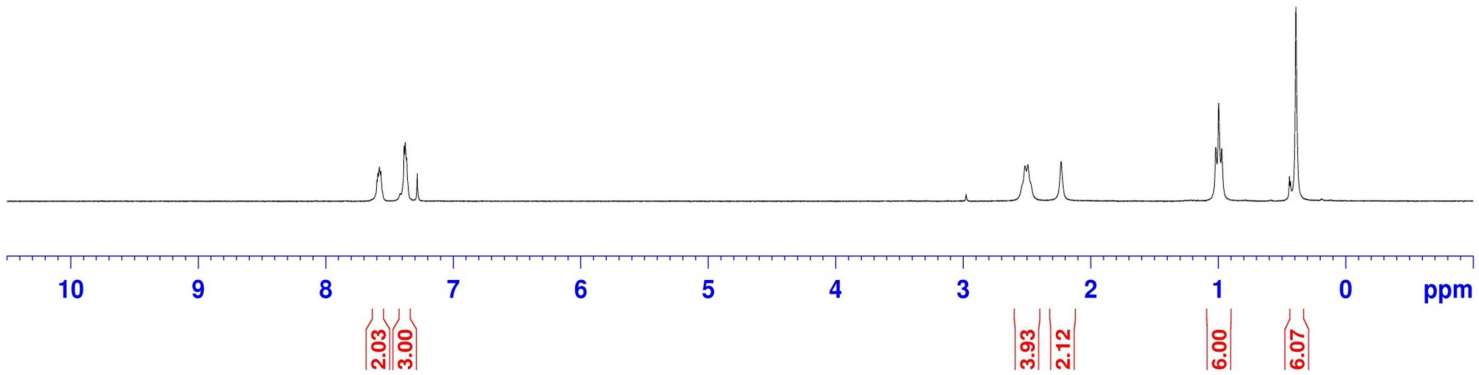




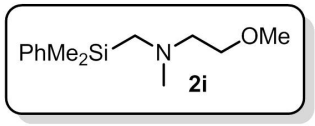
N–((dimethyl(phenyl)silyl)methyl)–N–ethylethanamine
300 MHz, CDCl3

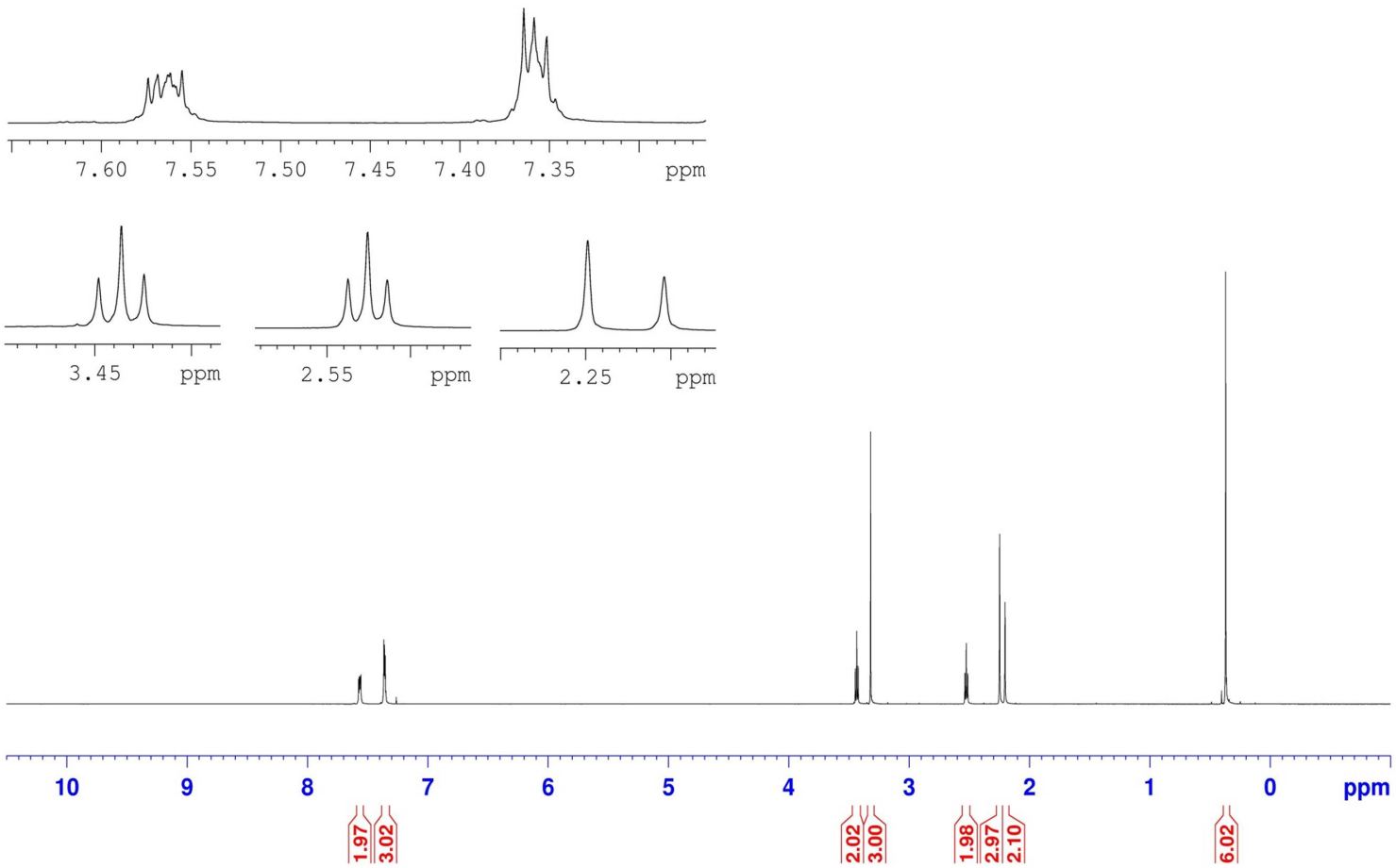




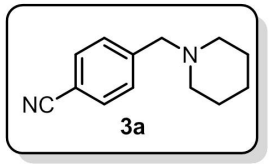


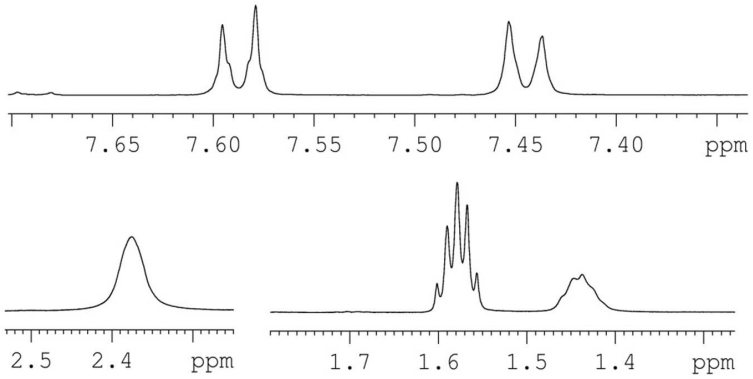
N–((dimethyl(phenyl)silyl)methyl)–2–methoxy–N–methylethanamine
500 MHz, CDCl3

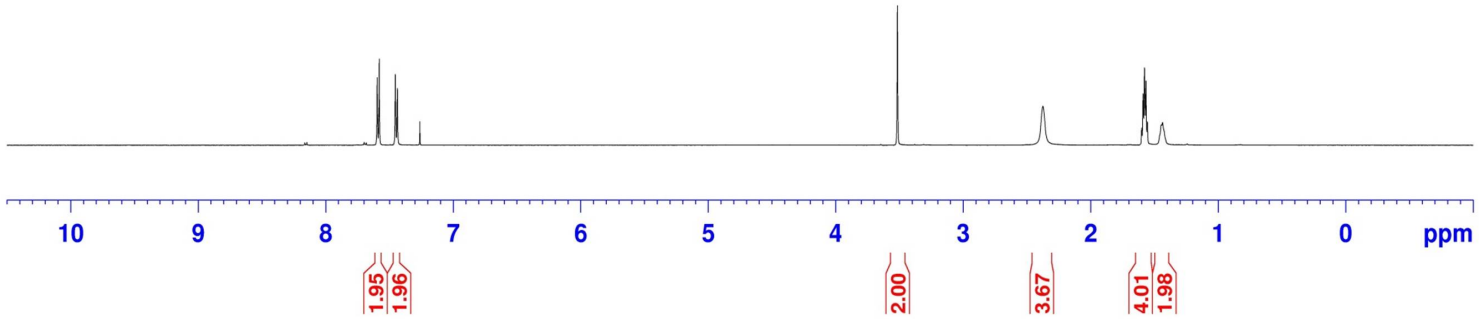




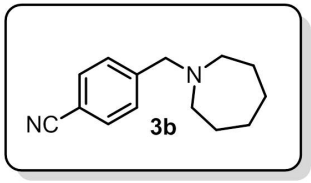
4–(piperidin–1–ylmethyl)benzonitrile
500 MHz, CDCl3

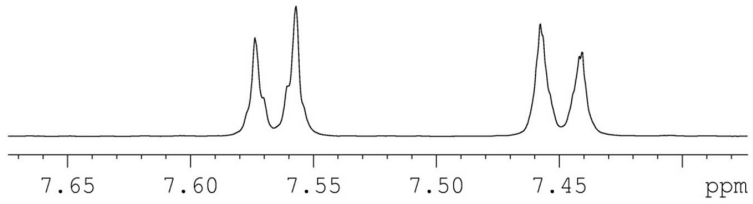


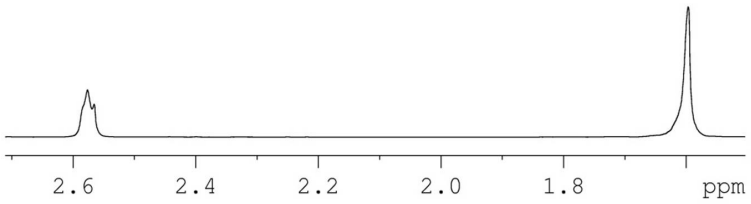


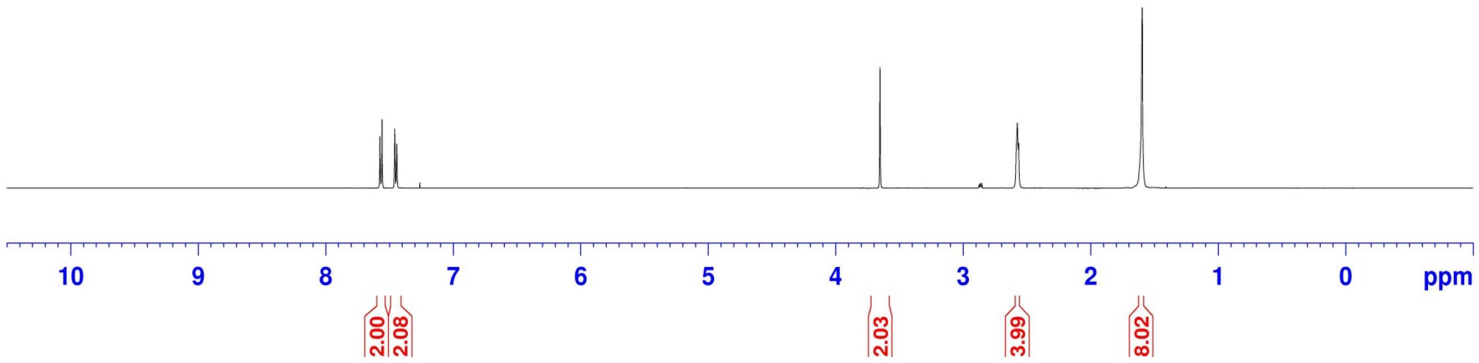


4–(azepan–1–ylmethyl)benzonitrile
500 MHz, CDCl3

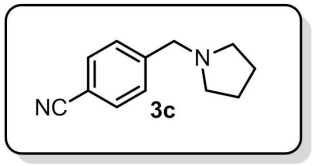


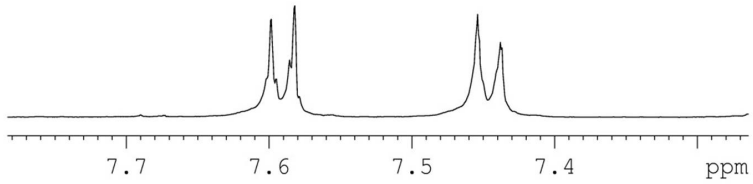


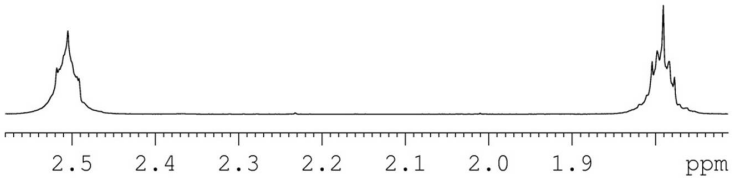


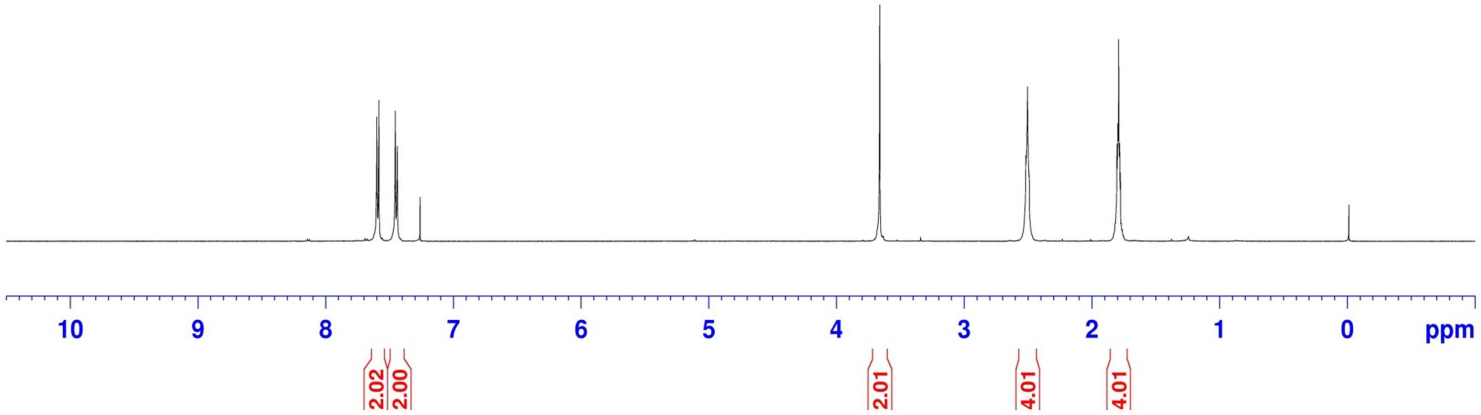


4–(pyrrolidin–1–ylmethyl)benzonitrile
500 MHz, CDCl3

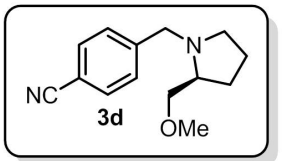


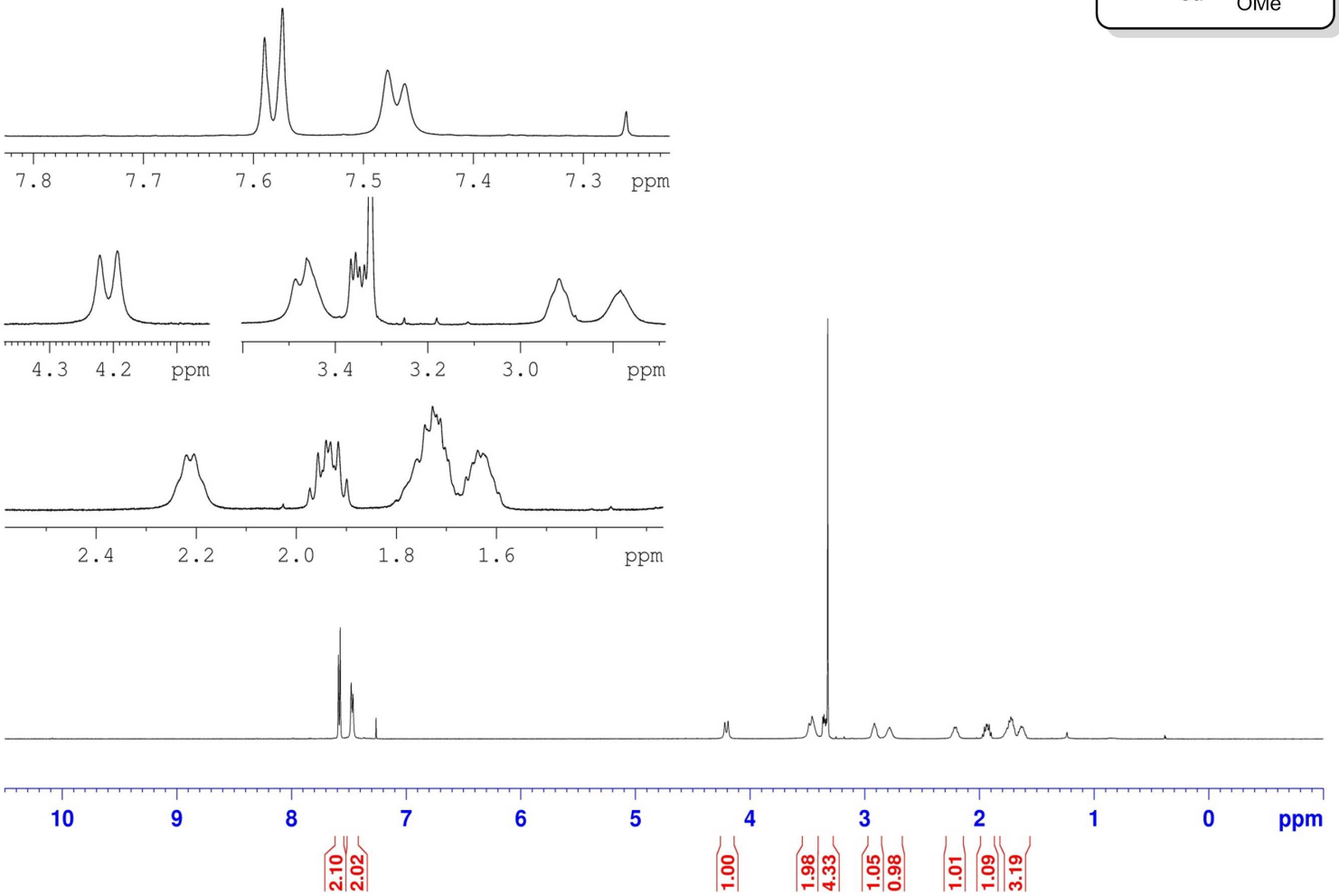




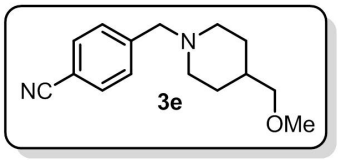


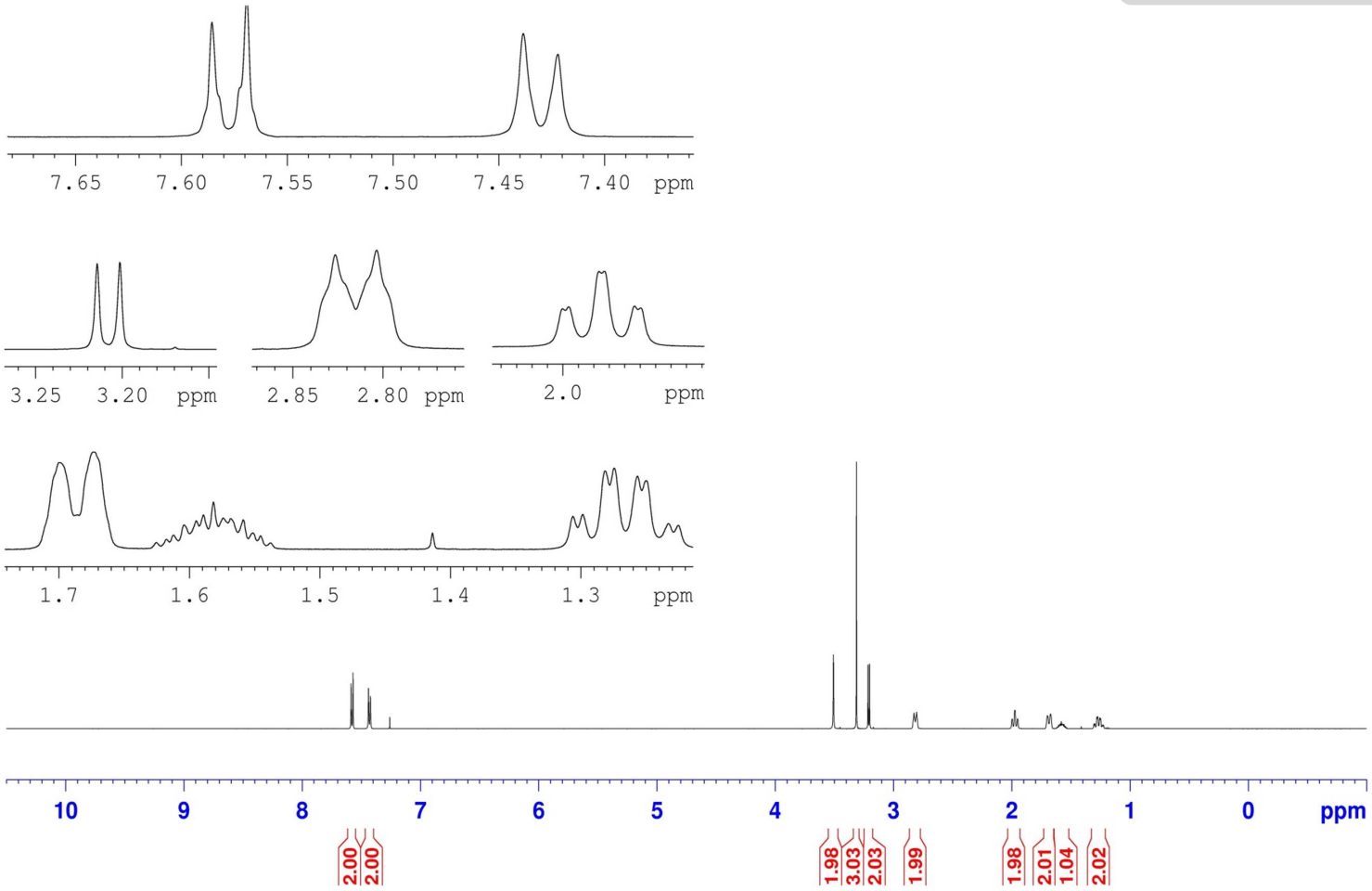
(S)−4−((2−(methoxymethyl)pyrrolidin−1−yl)methyl)benzonitrile
500 MHz, CDCl3



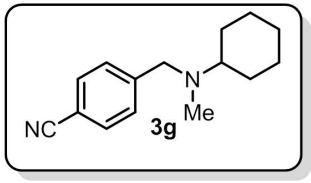


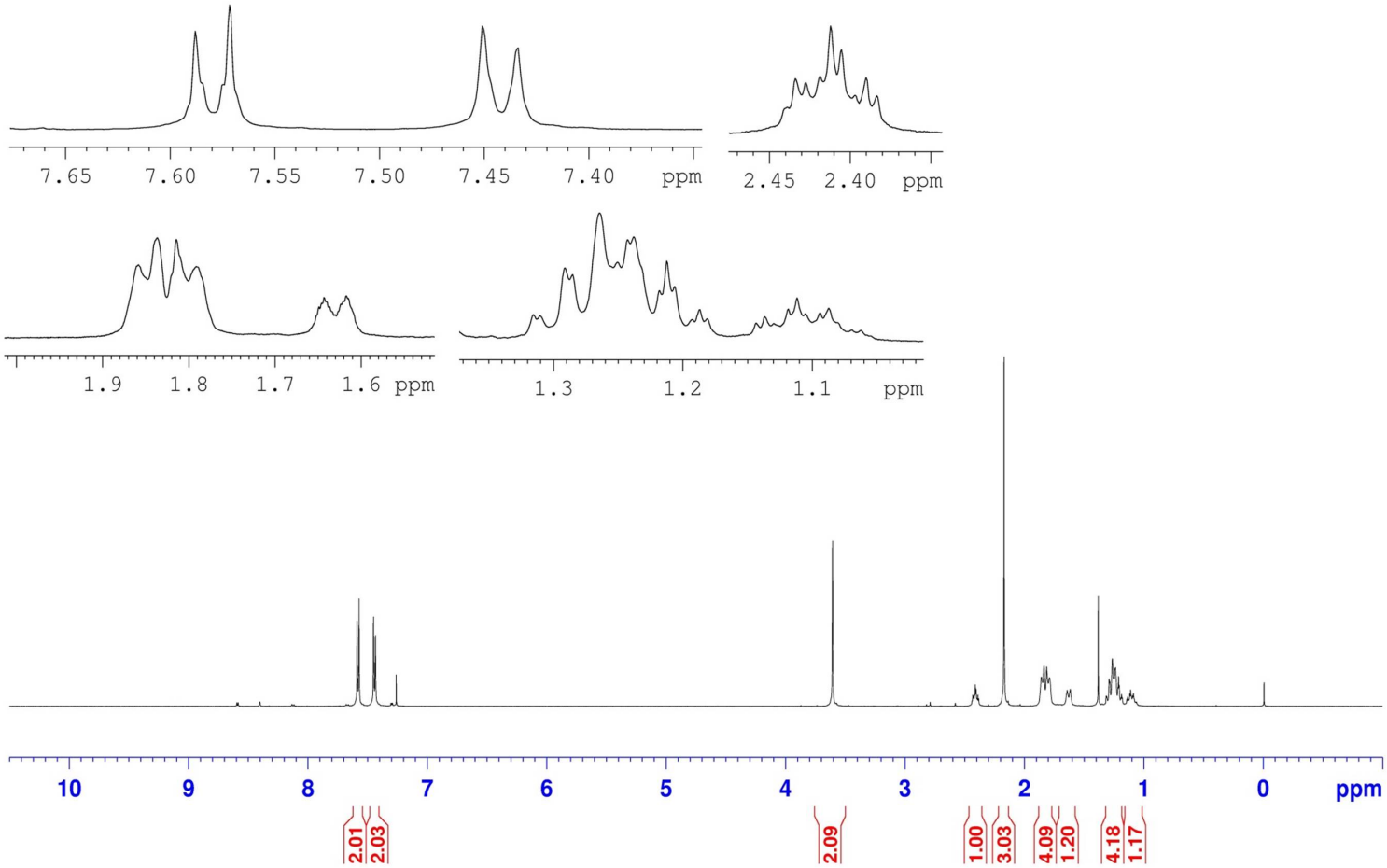
4–((4–(methoxymethyl)piperidin–1–yl)methyl)benzonitrile
500 MHz, CDCl3



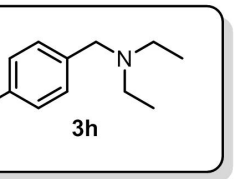


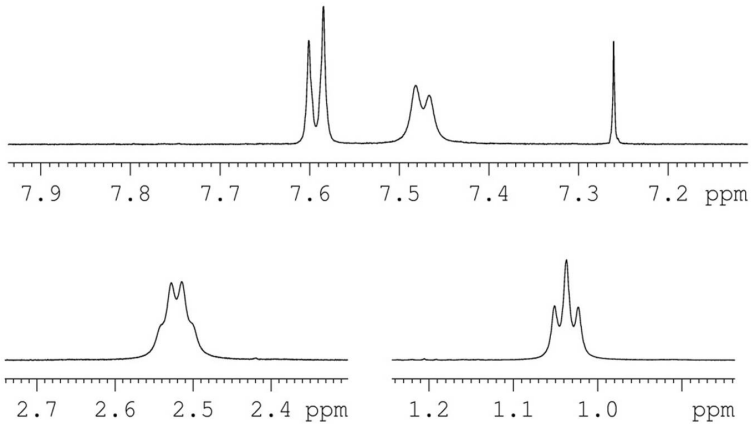
4–((cyclohexyl(methyl)amino)methyl)benzonitrile
500 MHz, CDCl3

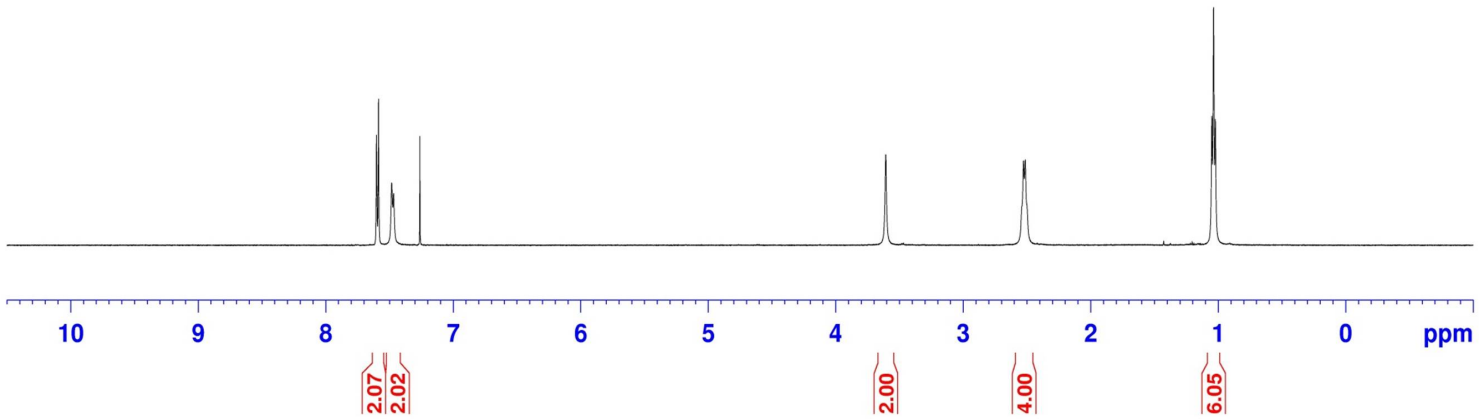




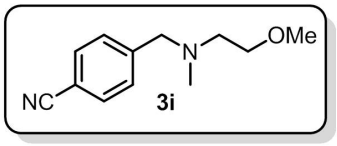
4–((diethylamino)methyl)benzonitrile
500 MHz, CDCl3

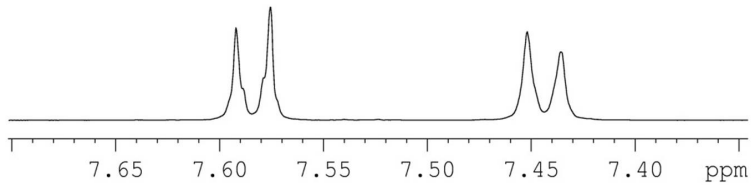


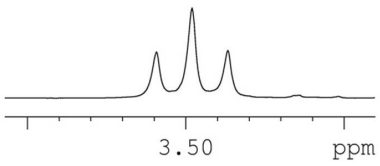


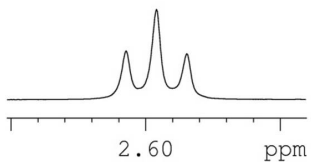


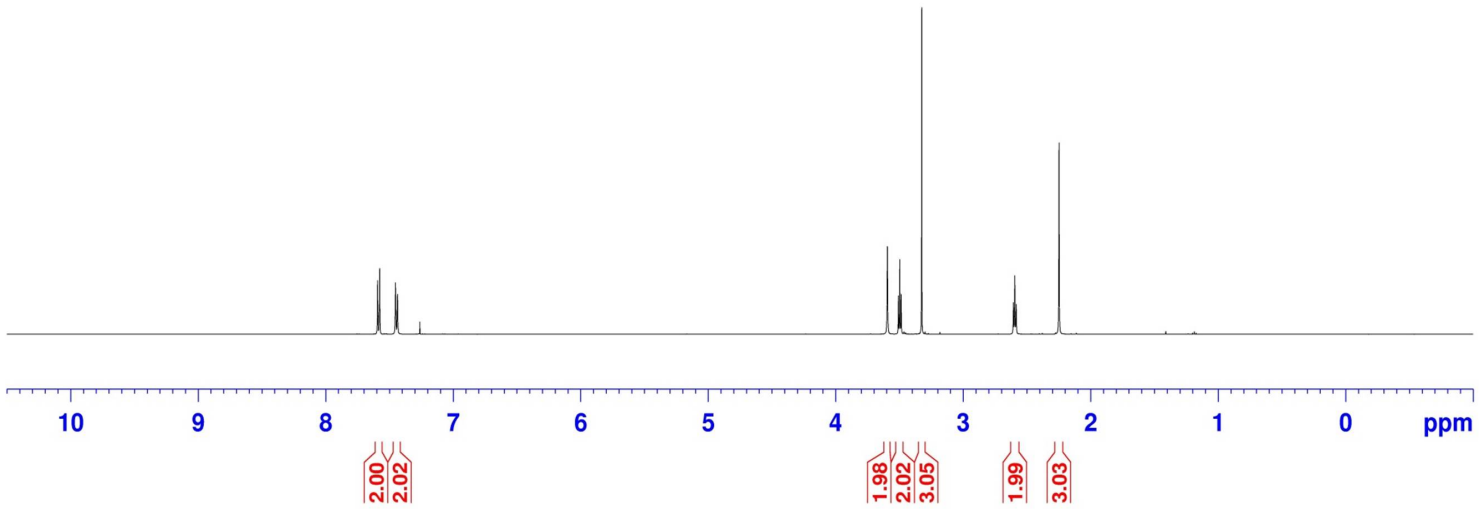
4–(((2–methoxyethyl)(methyl)amino)methyl)benzonitrile
500 MHz, CDCl3



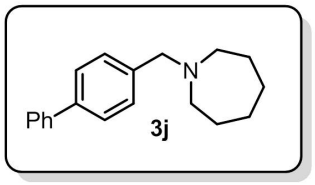


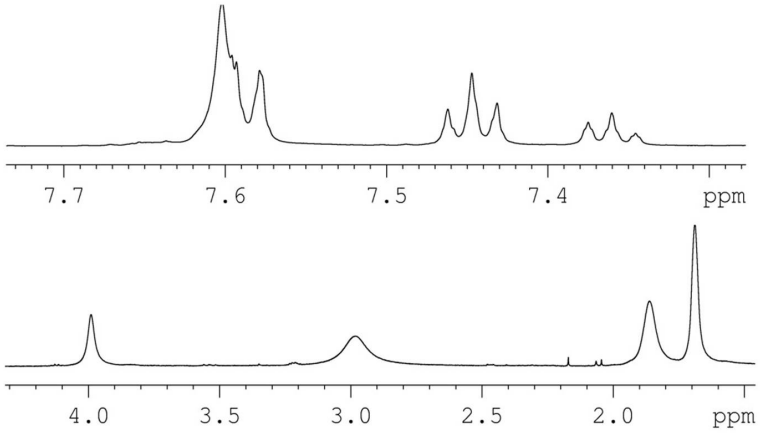


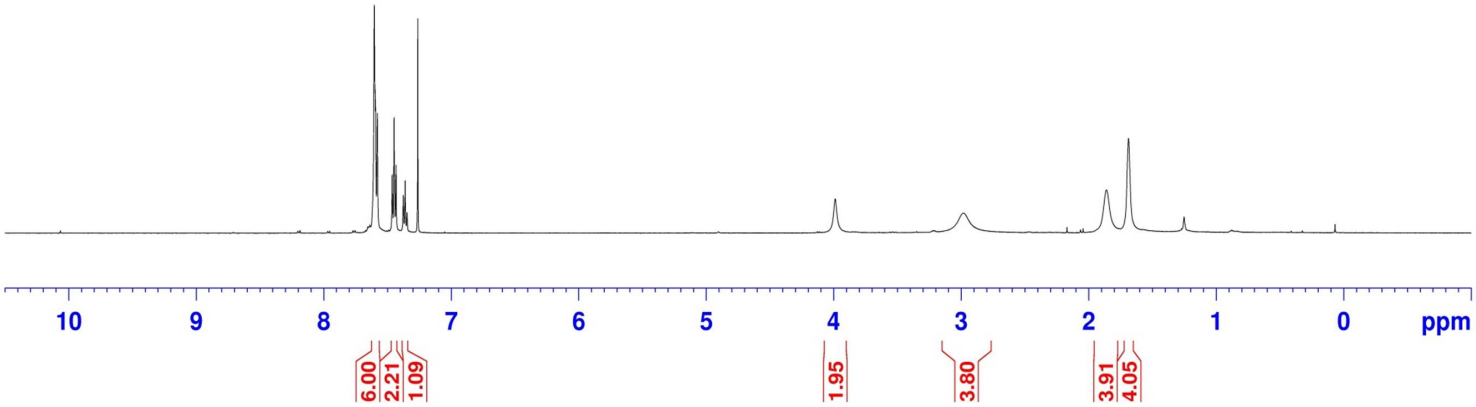




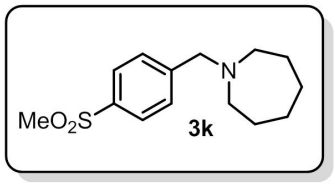
1–([1,1'–biphenyl]–4–ylmethyl)piperidine
500 MHz, CDCl3

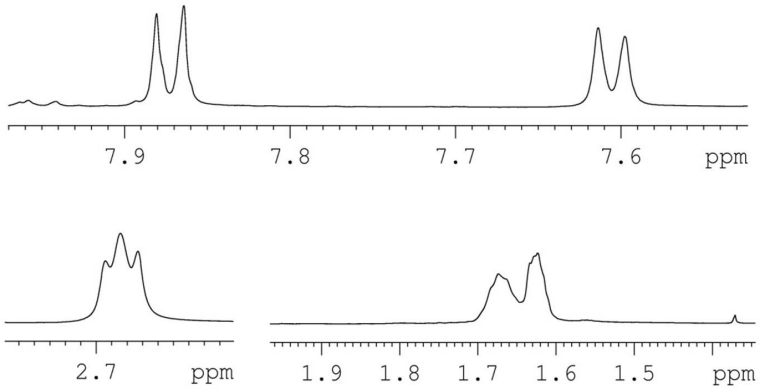


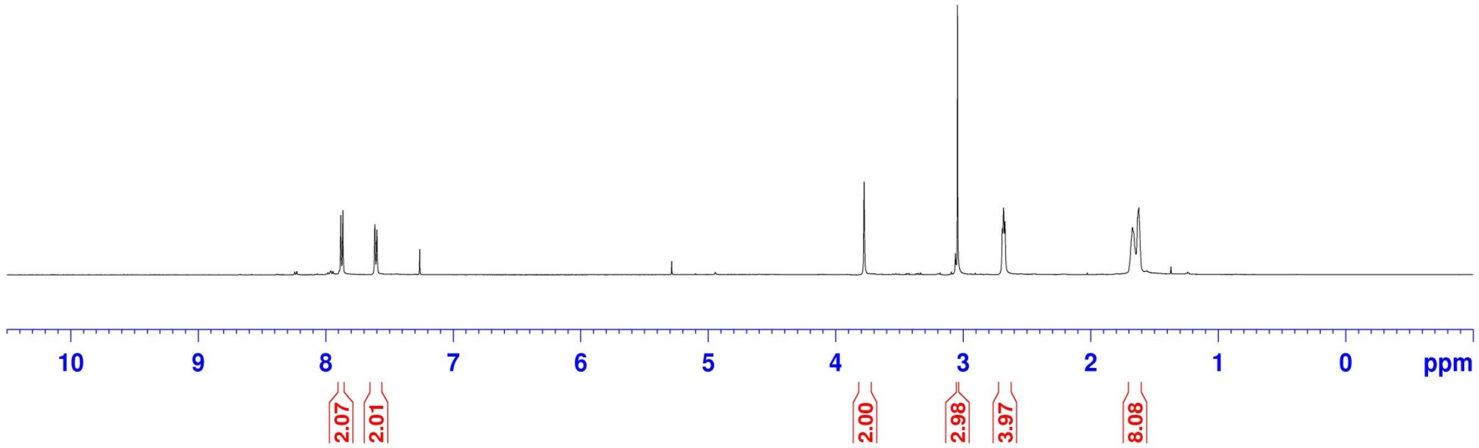




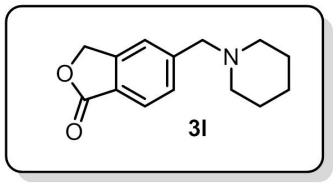
1–(4–(methylsulfonyl)benzyl)piperidine
500 MHz, CDCl3

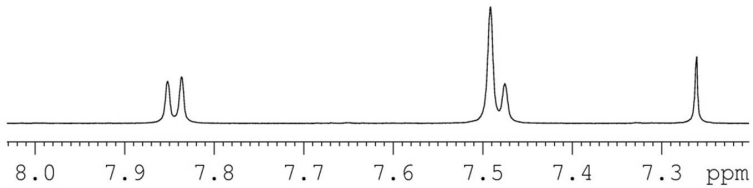


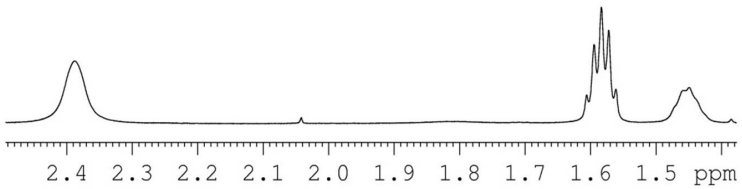


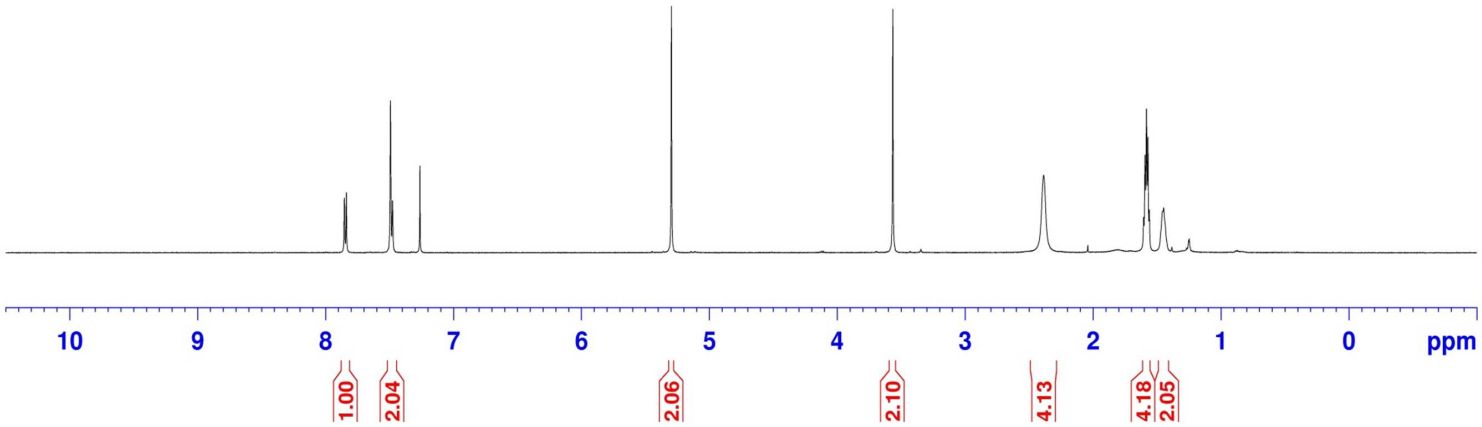


5–(piperidin–1–ylmethyl)phthalide
500 MHz, CDCl3

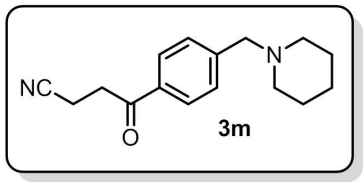


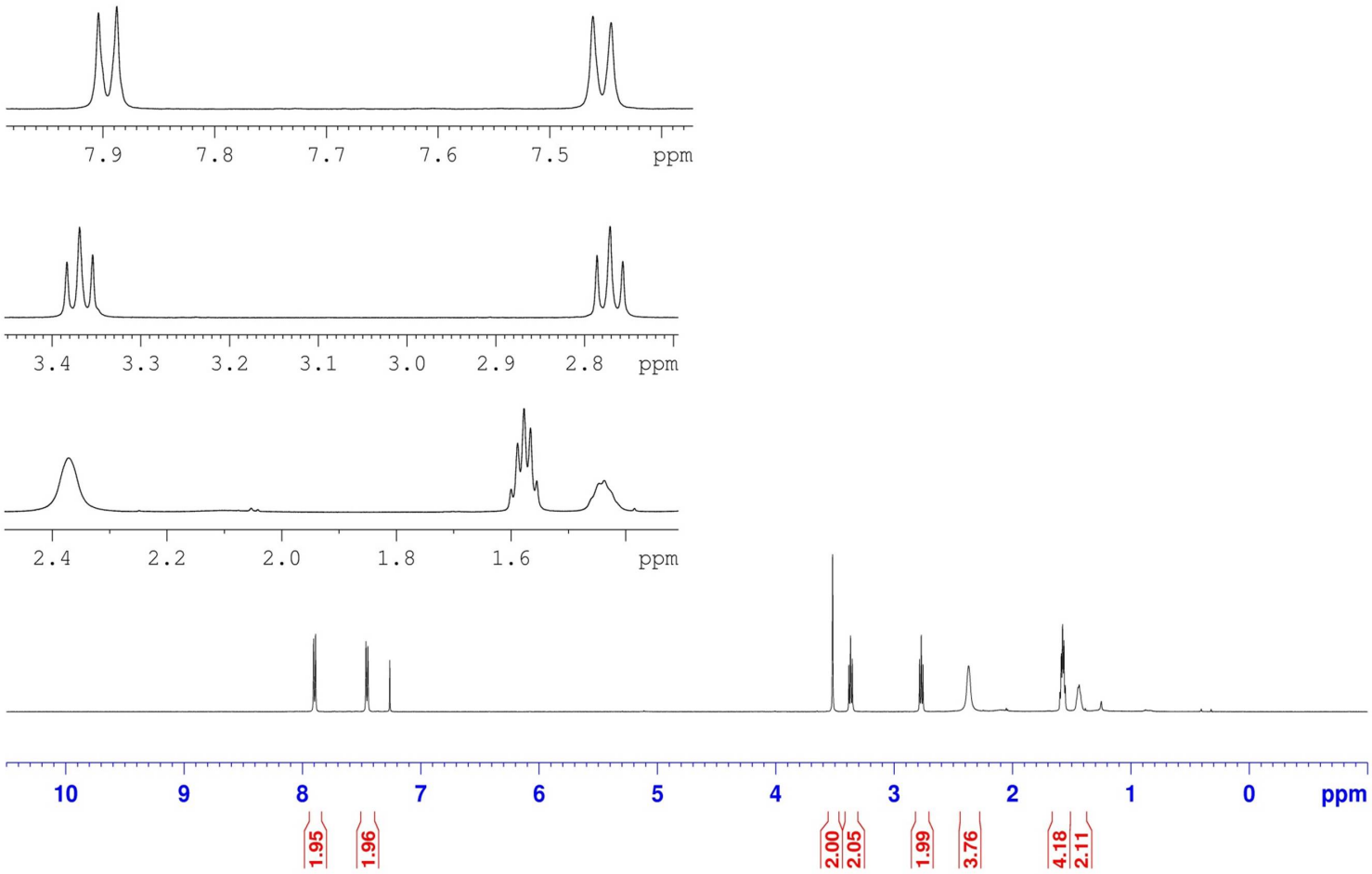




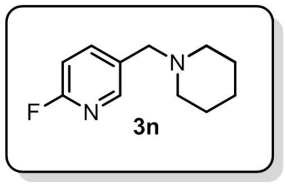


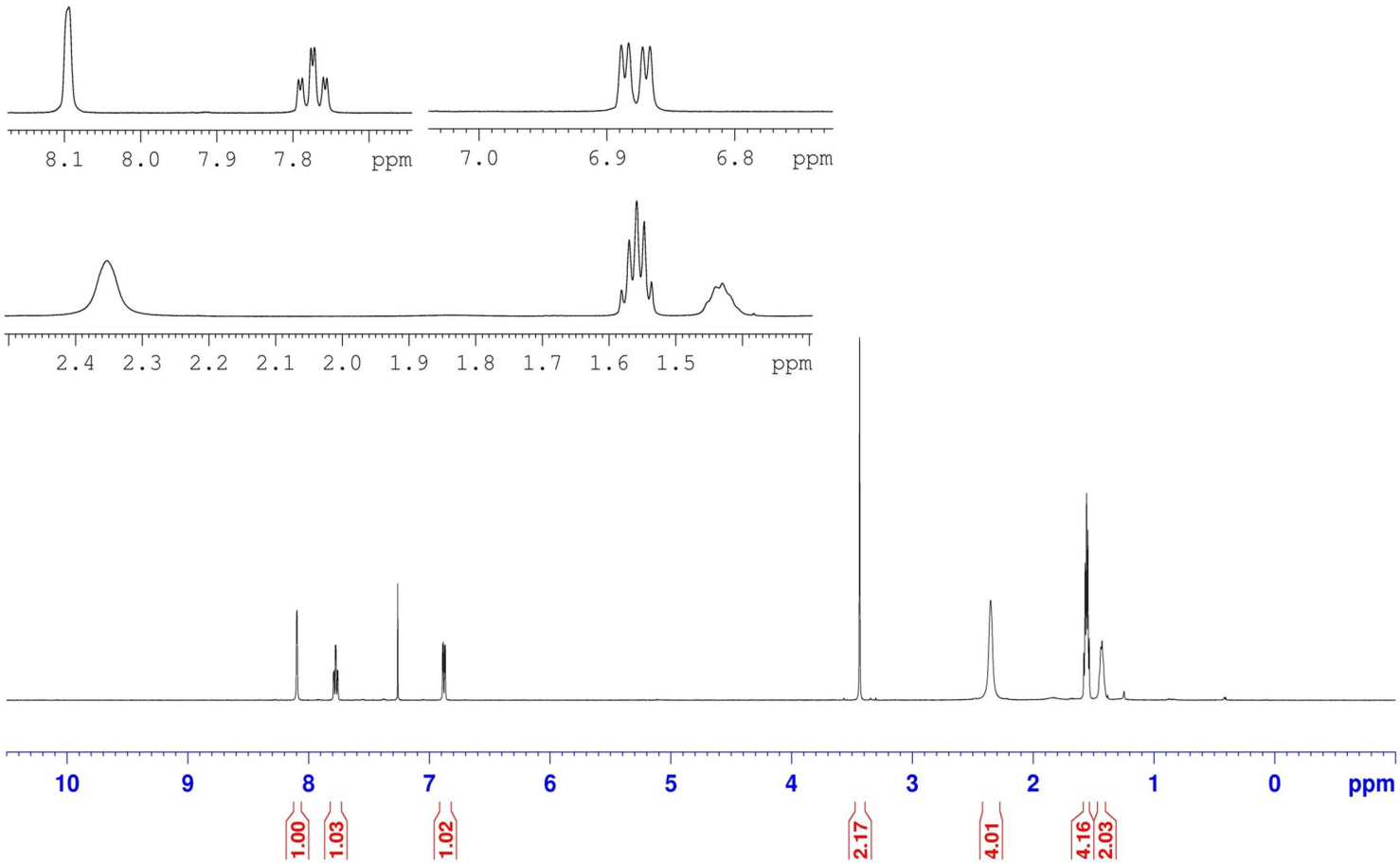
4–oxo–4–(4–(piperidin–1–ylmethyl)phenyl)butanenitrile
500 MHz, CDCl3



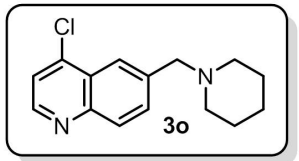


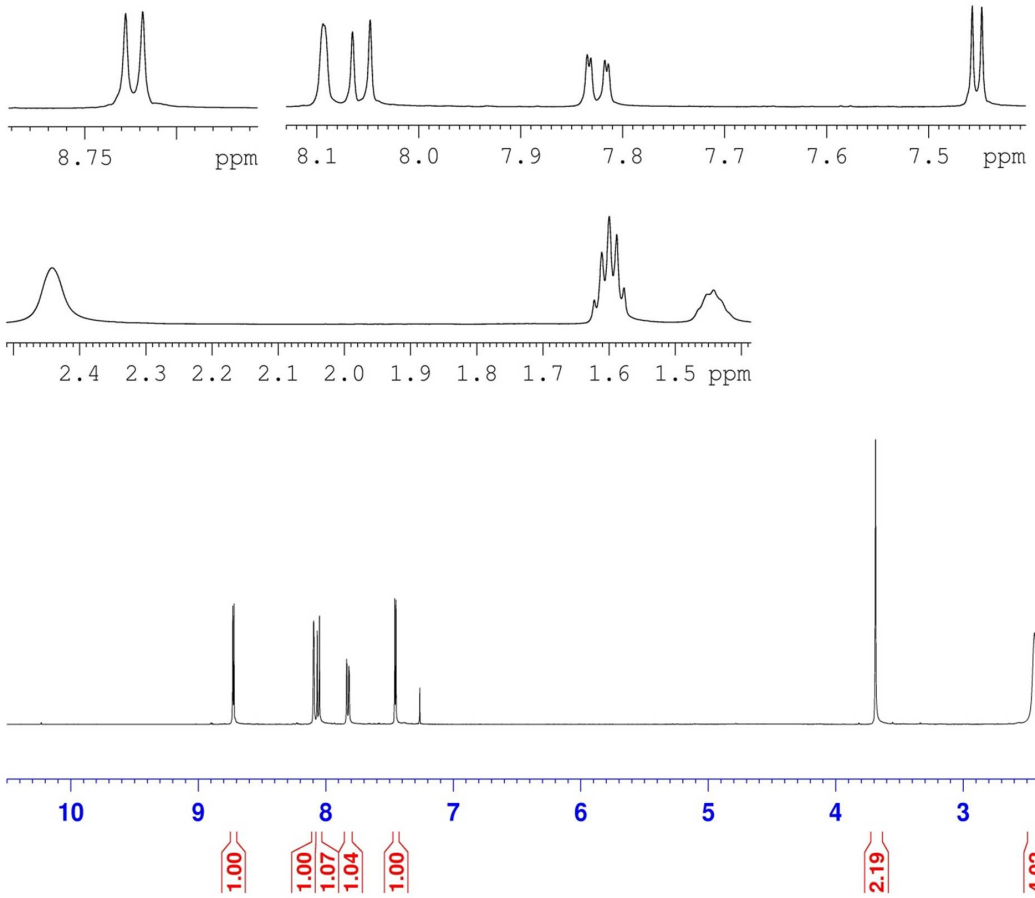
2–fluoro–5–(piperidin–1–ylmethyl)pyridine
500 MHz, CDCl3



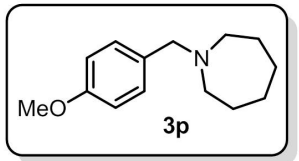


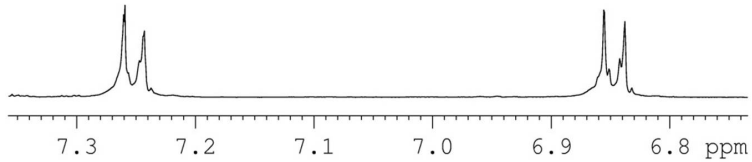
4–chloro–6–(piperidin–1–ylmethyl)quinoline
500 MHz, CDCl3

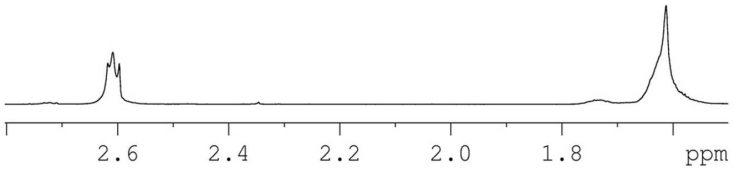


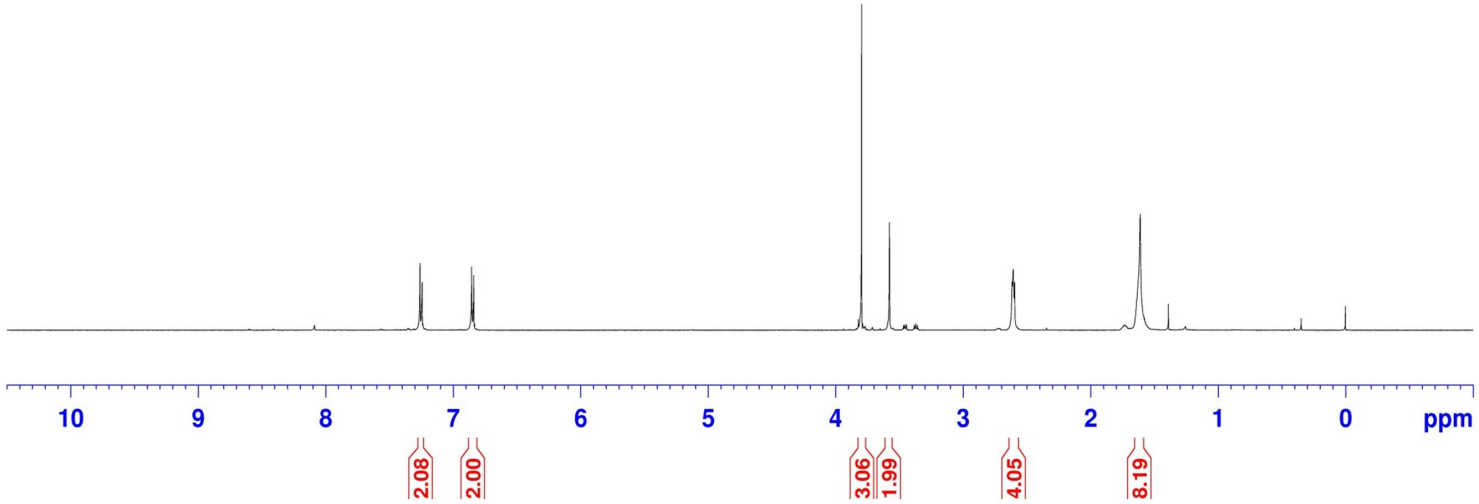


1–(4–methoxybenzyl)azepane
500 MHz, CDCl3

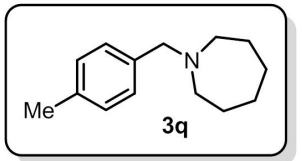


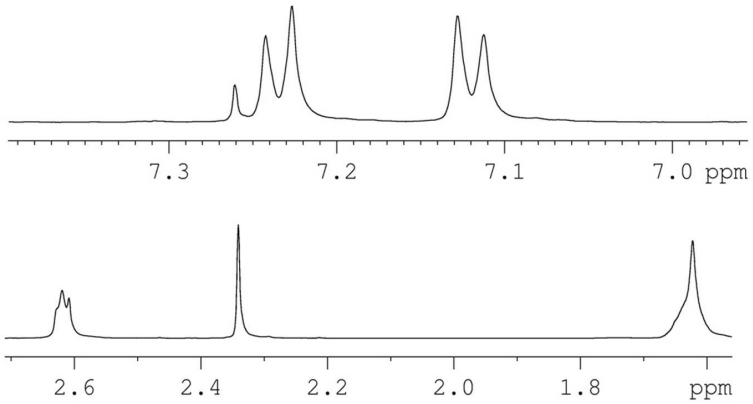


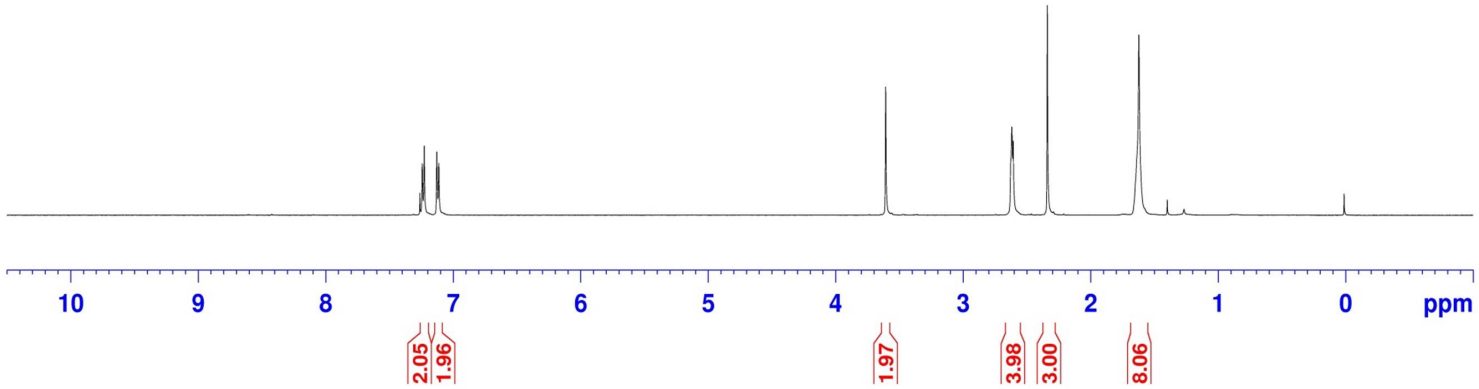




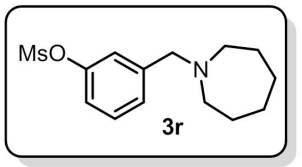
1–(4–methylbenzyl)azepane
500 MHz, CDCl3

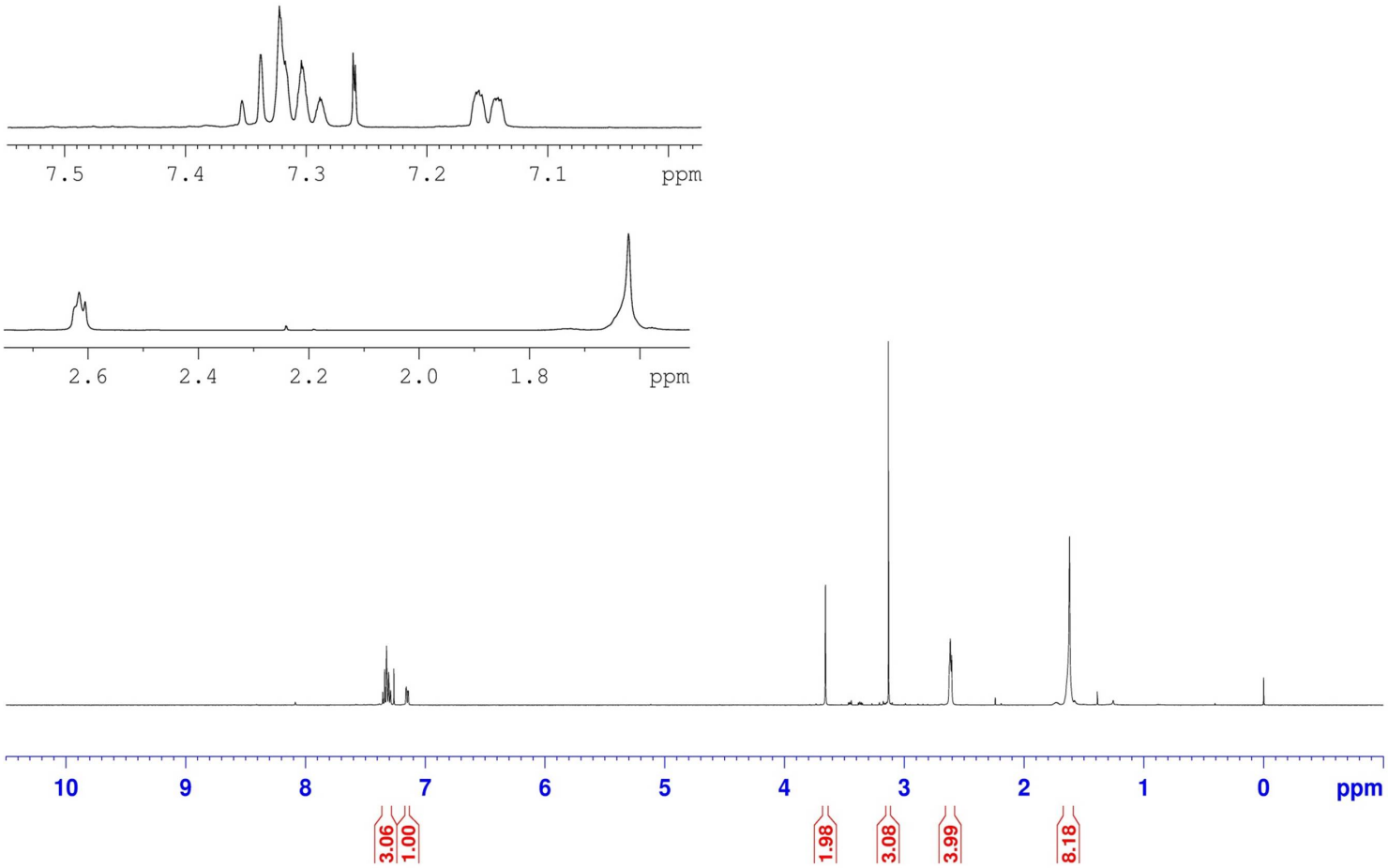




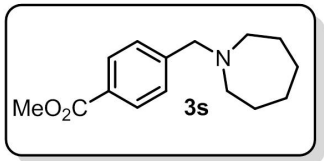


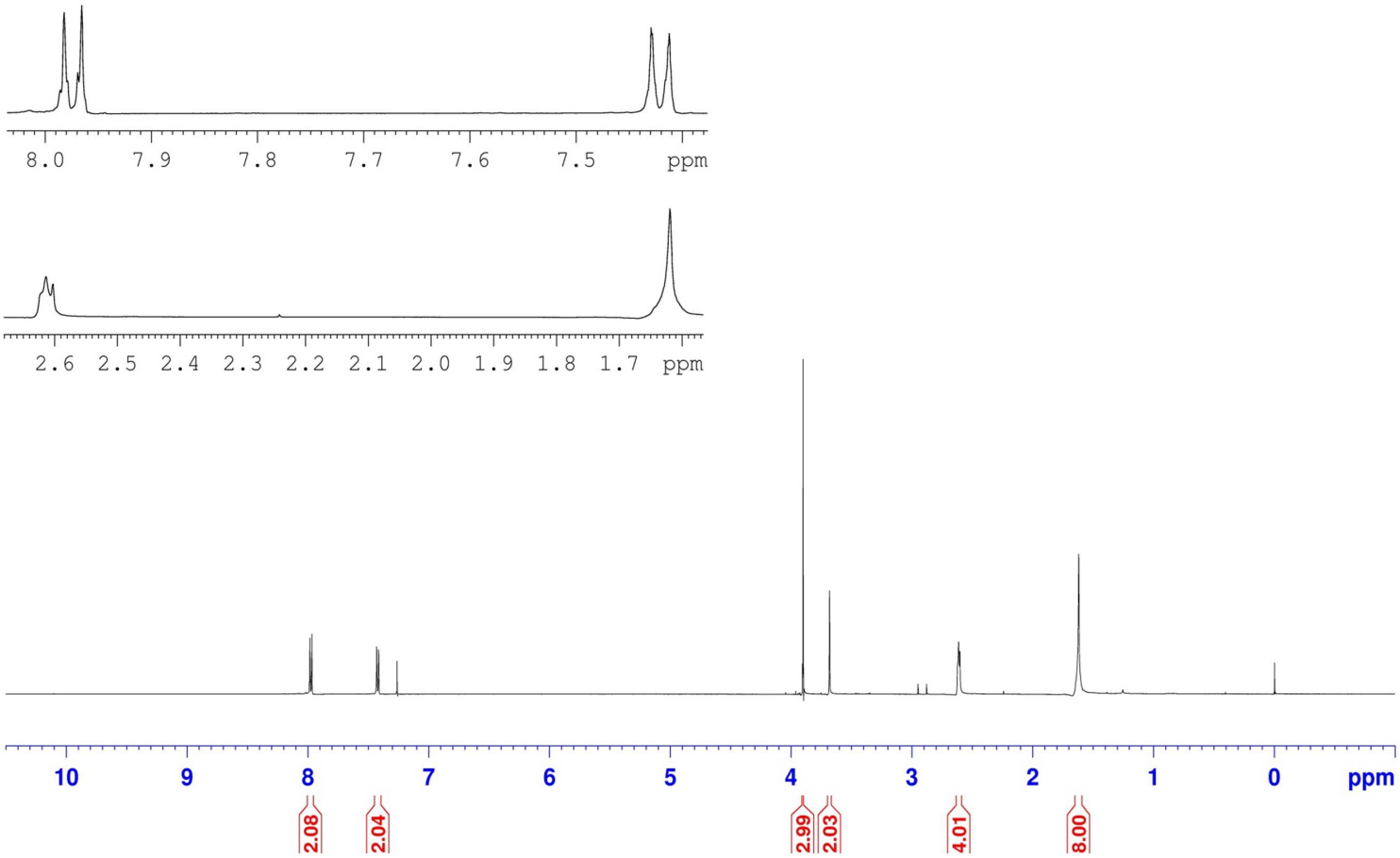
3–(azepan–1–ylmethyl)phenyl methanesulfonate
500 MHz, CDCl3



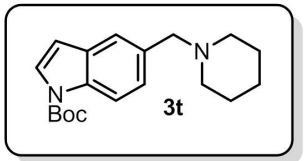


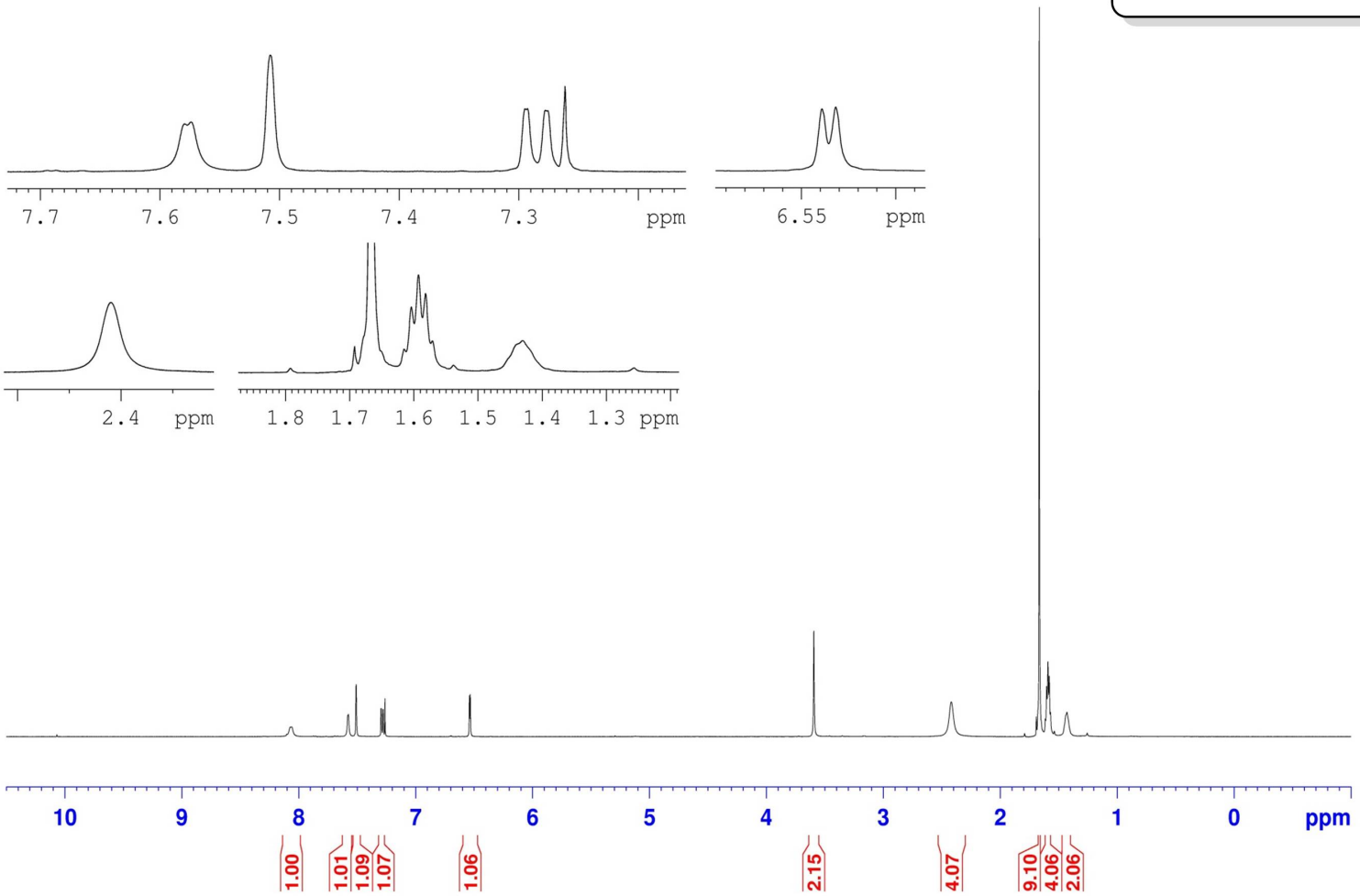
methyl 4–(azepan–1–ylmethyl)benzoate
500 MHz, CDCl3



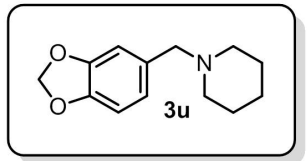


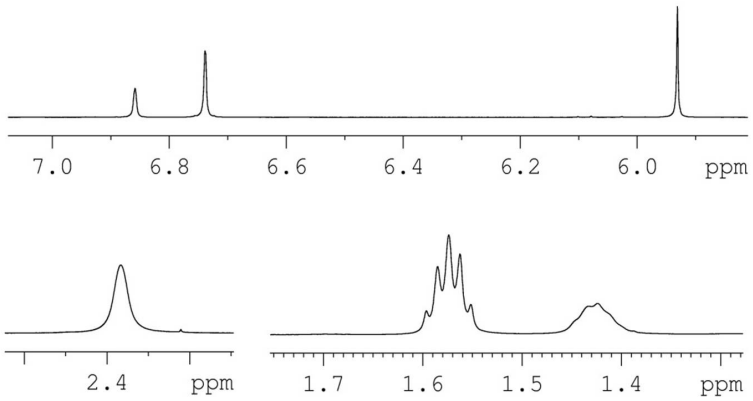
tert-butyl 5-(piperidin-1-ylmethyl)-1H-indole-1-carboxylate
500 MHz, CDCl3

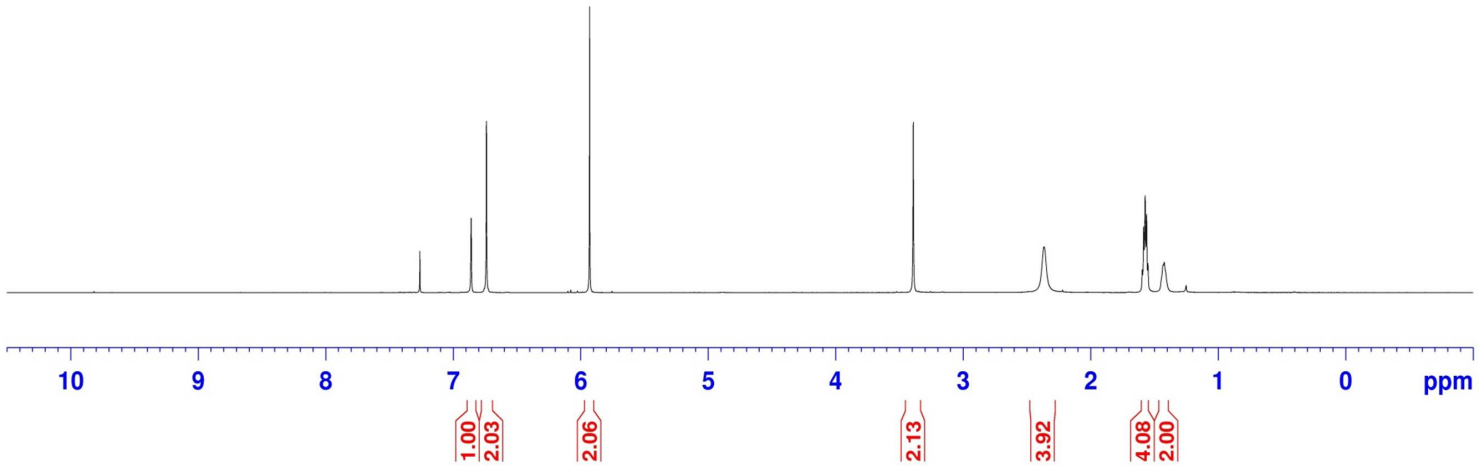




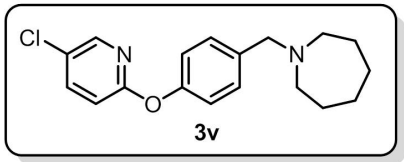
1−(benzo[d][1,3]dioxol−5−ylmethyl)piperidine
500 MHz, CDCl3

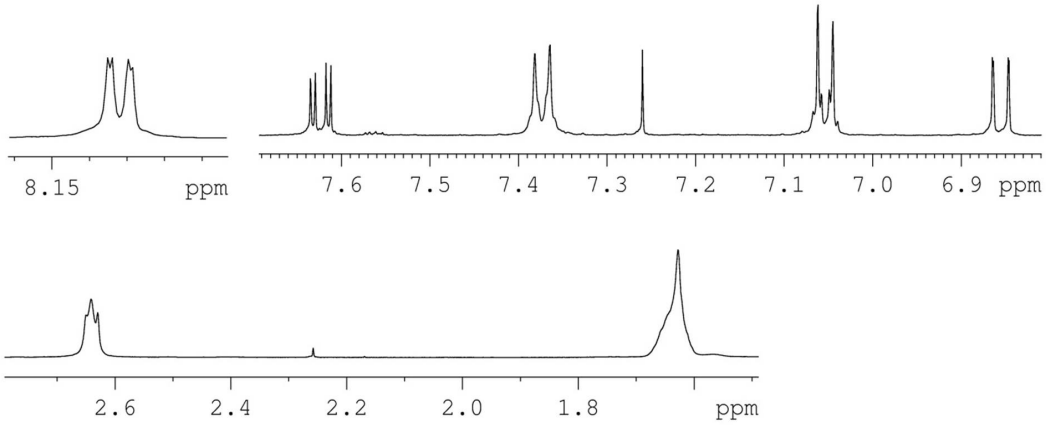


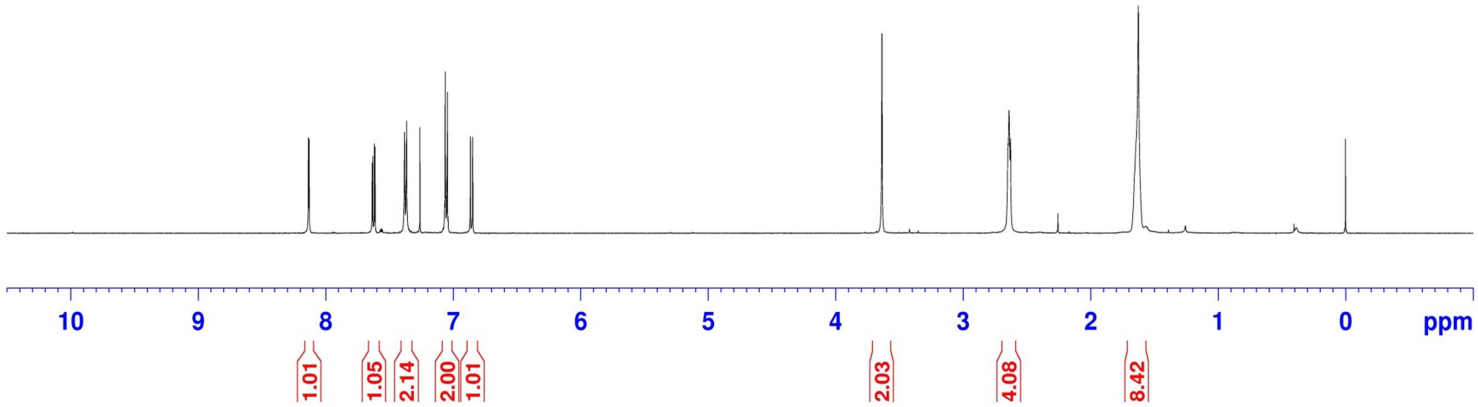




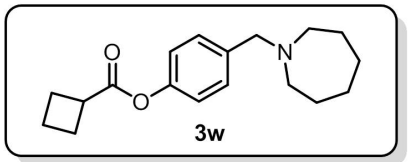
1–(4–((5–chloropyridin–2–yl)oxy)benzyl)azepane
500 MHz, CDCl3

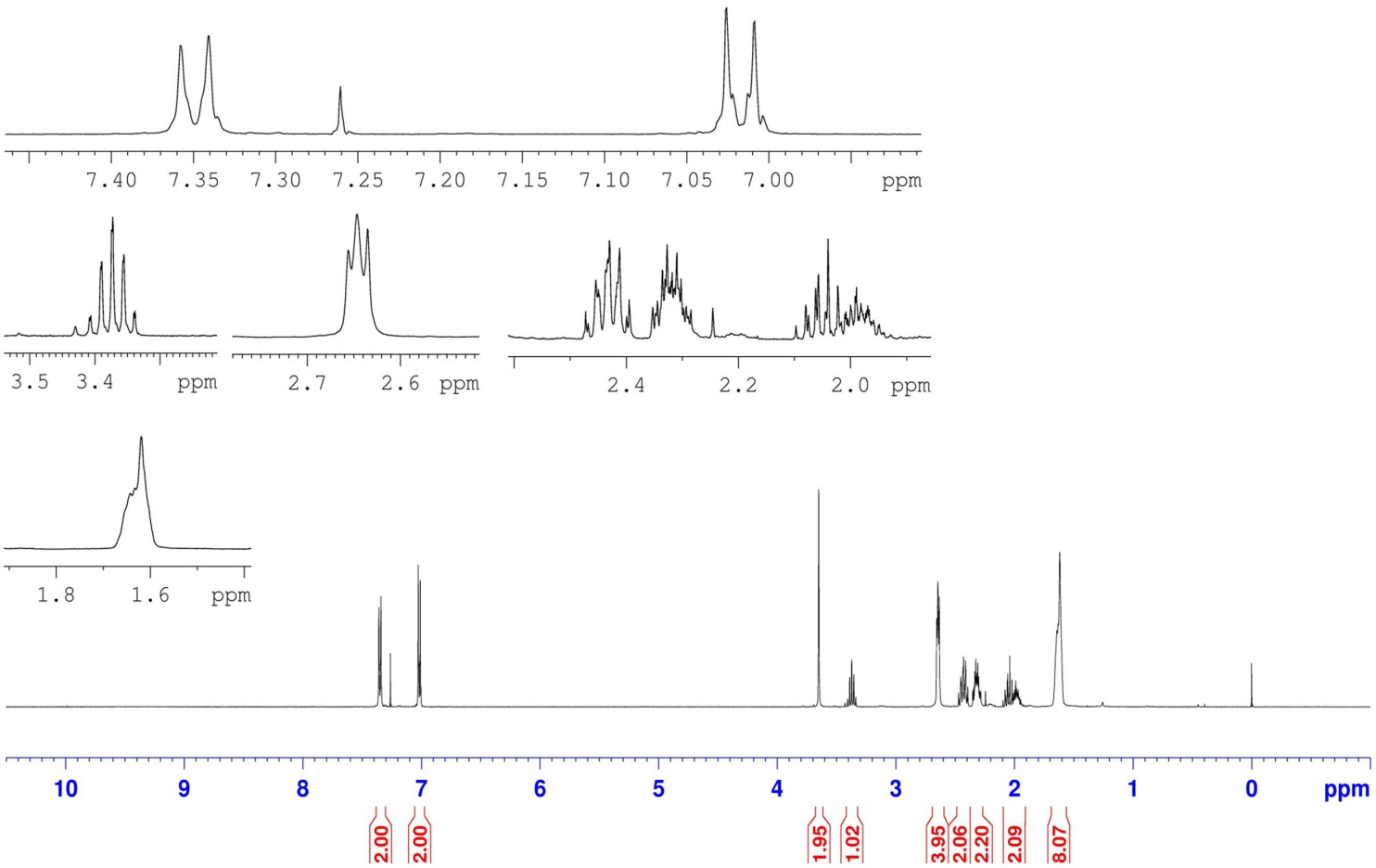




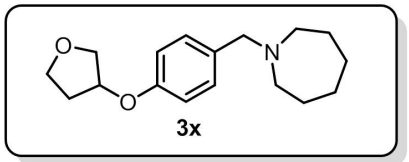


4–(azepan–1–ylmethyl)phenyl cyclobutanecarboxylate
500 MHz, CDCl3





1–(4–((tetrahydrofuran–3–yl)oxy)benzyl)azepane
500 MHz, CDCl3



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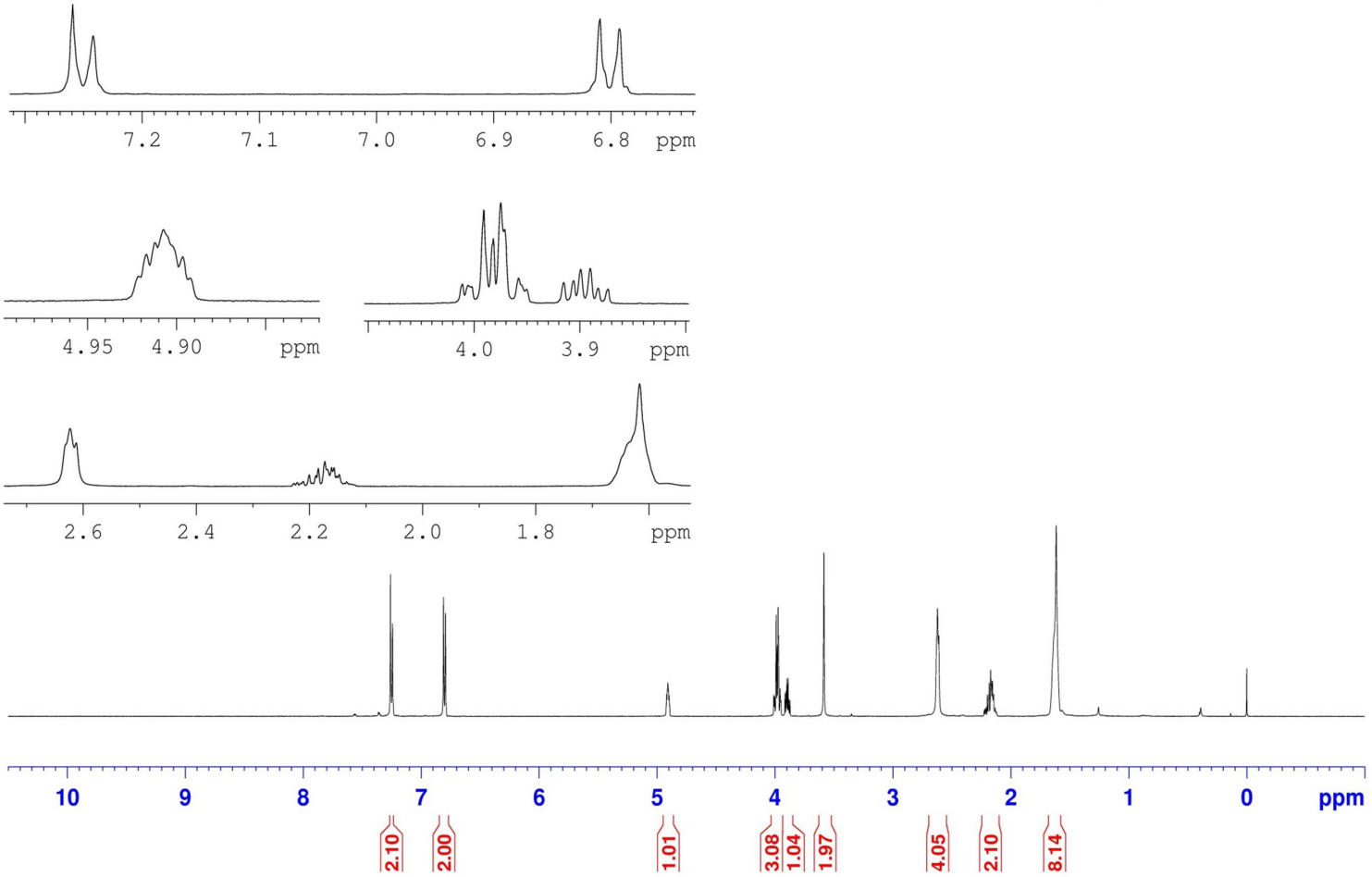
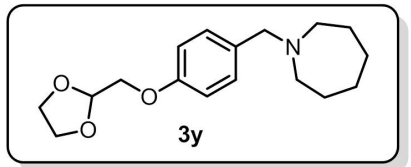
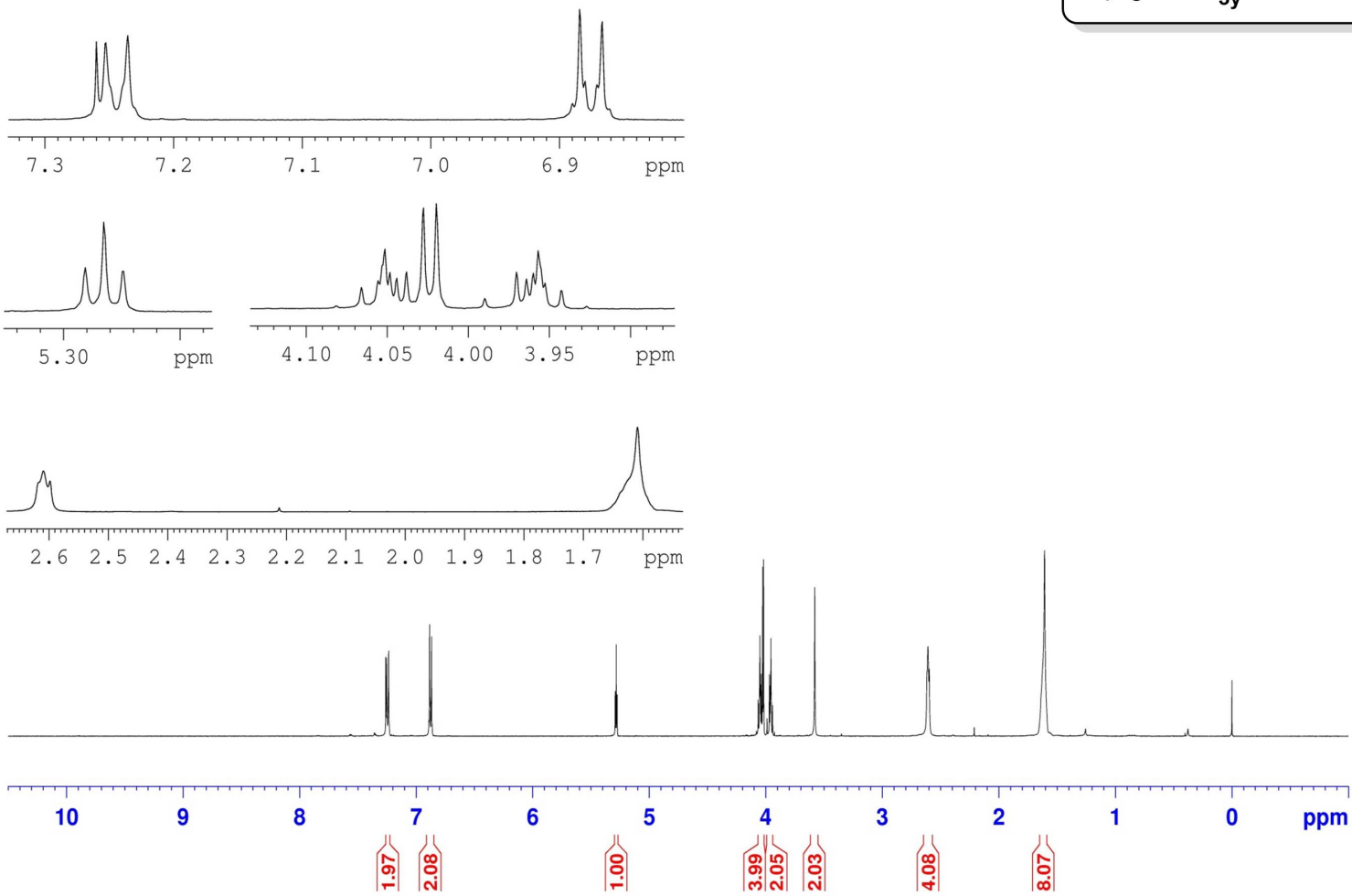


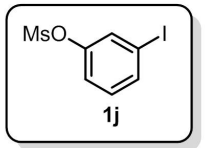
1–(4–((1,3–dioxolan–2–yl)methoxy)benzyl)azepane
500 MHz, CDCl3

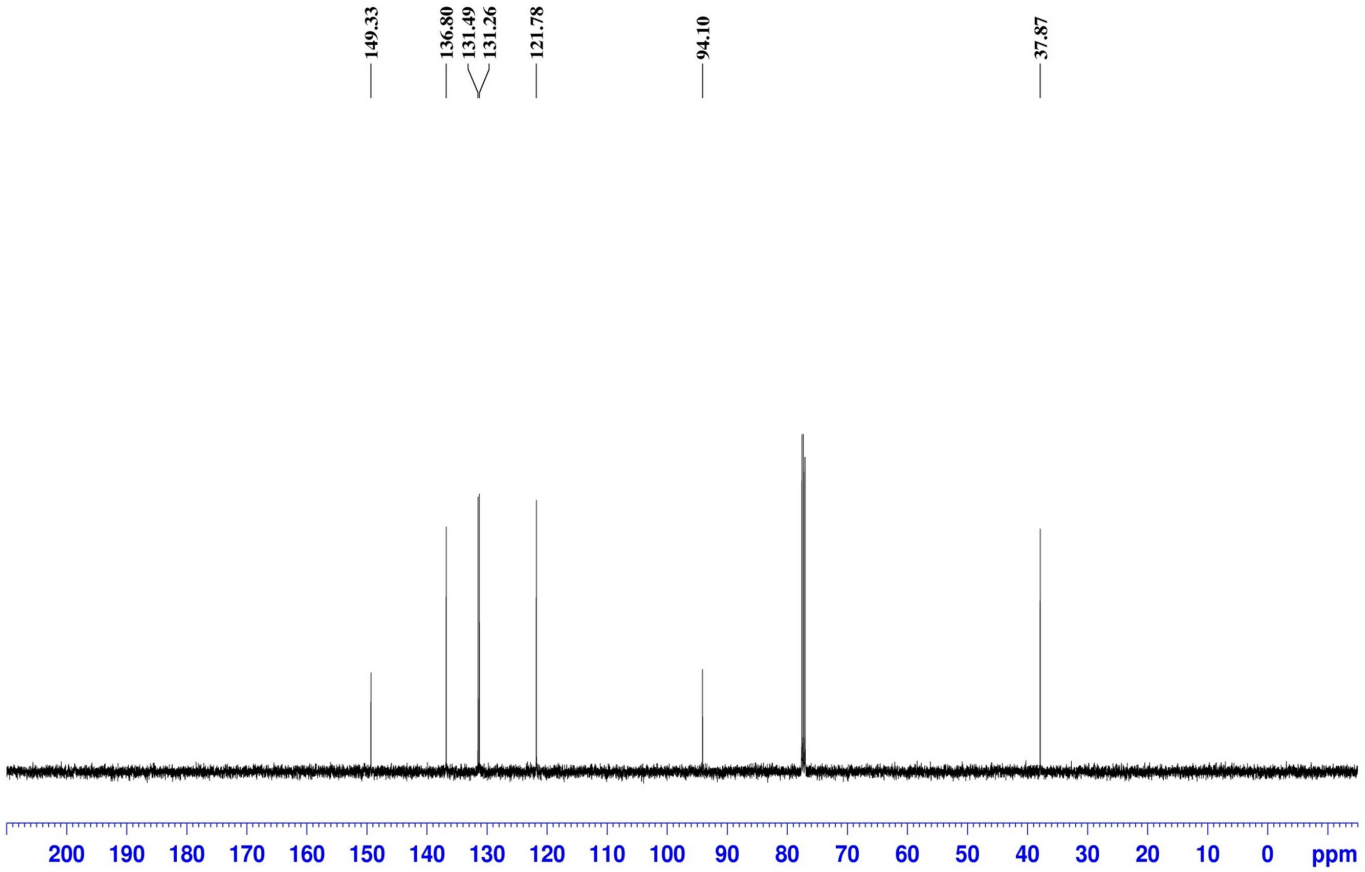




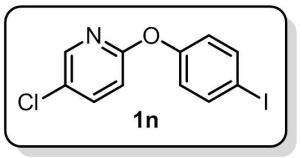
^{13}C NMR Spectra of Synthesized Compounds

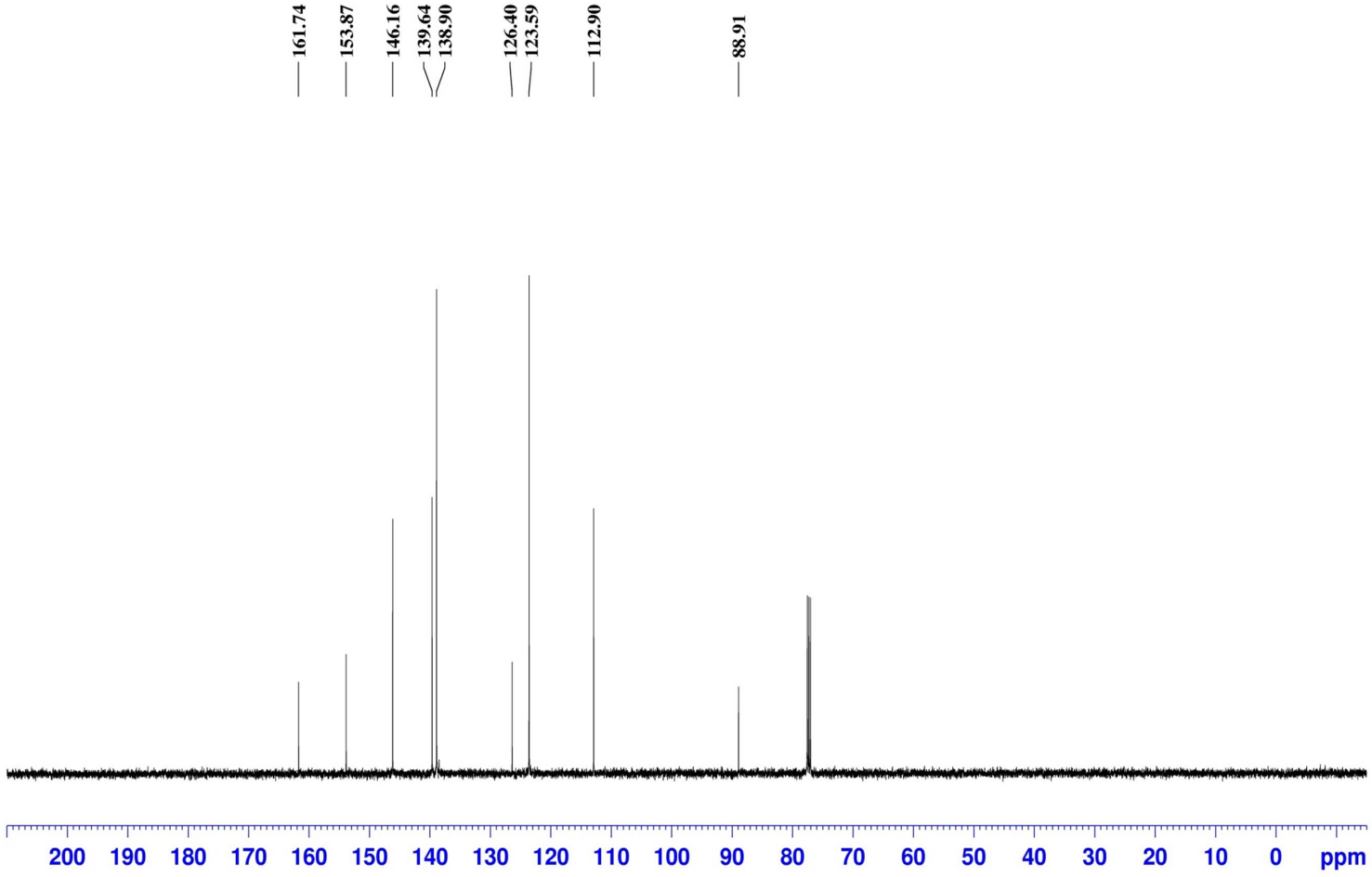
3–iodophenyl methanesulfonate
125 MHz, CDCl3



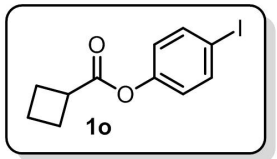


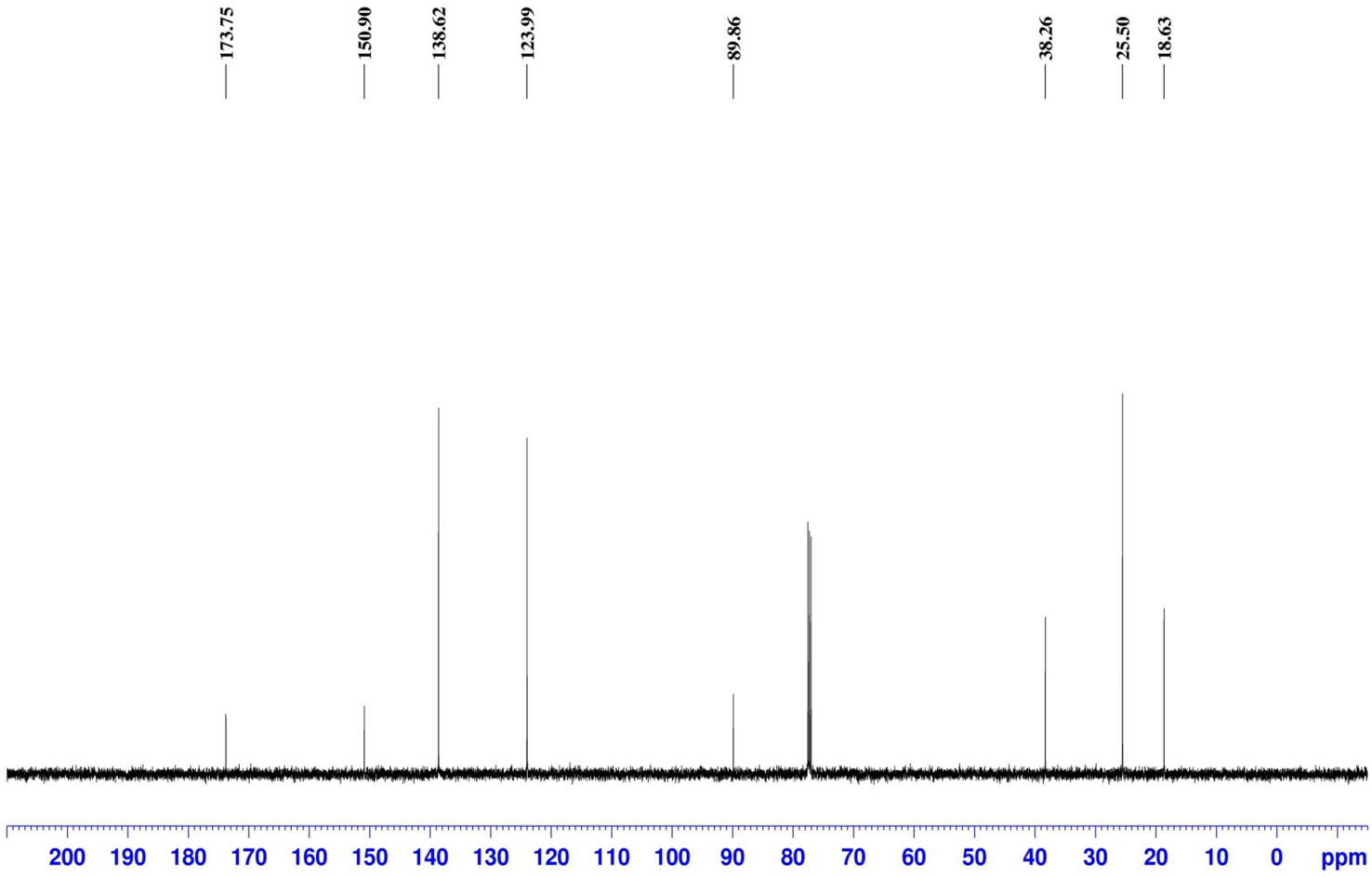
5–chloro–2–(4–iodophenoxy)pyridine
125 MHz, CDCl3



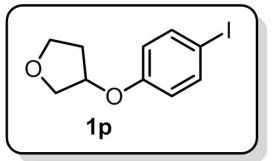


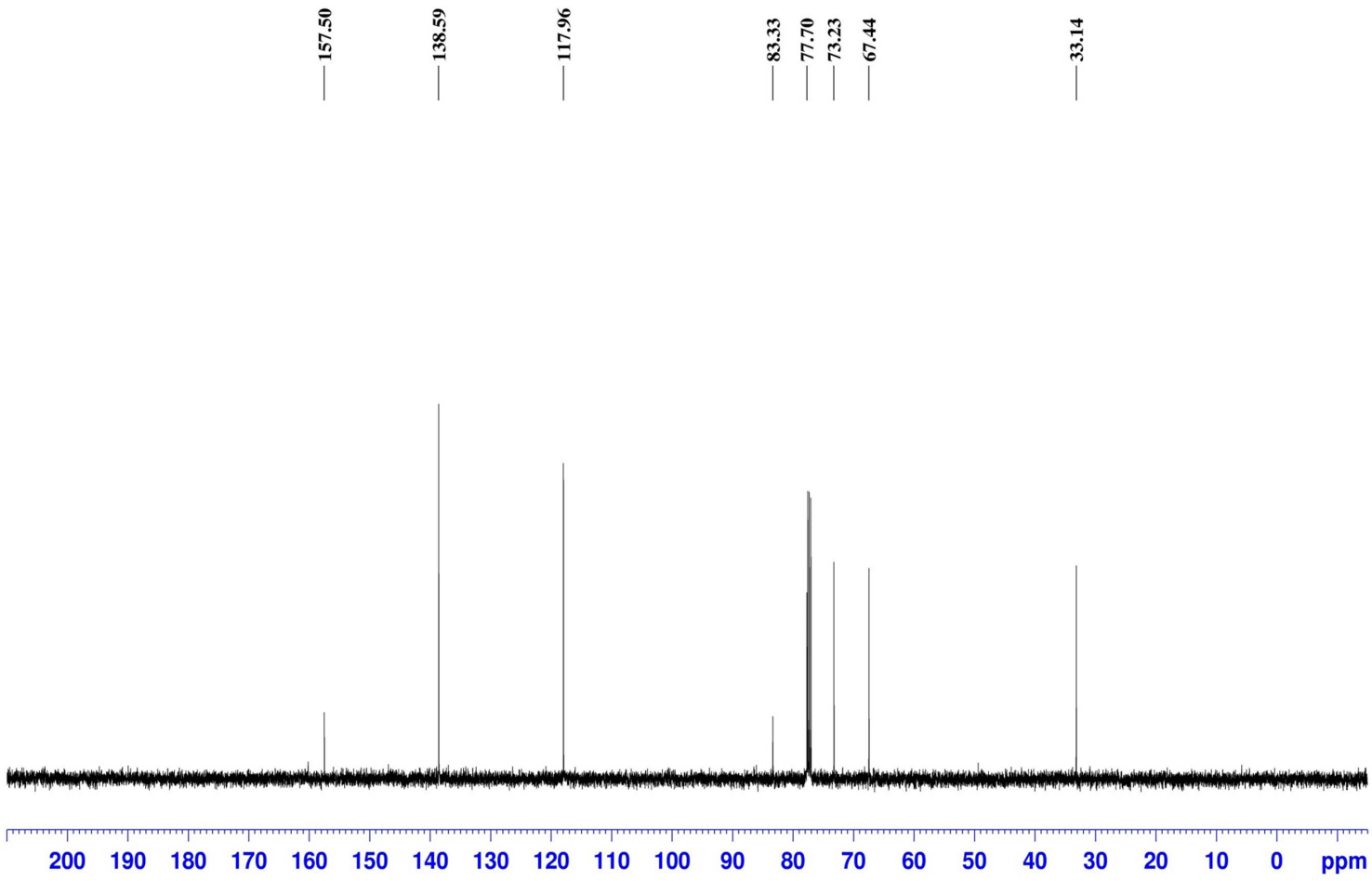
4–iodophenyl cyclobutanecarboxylate
125 MHz, CDCl3



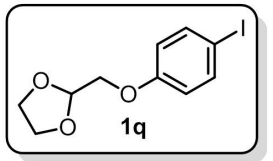


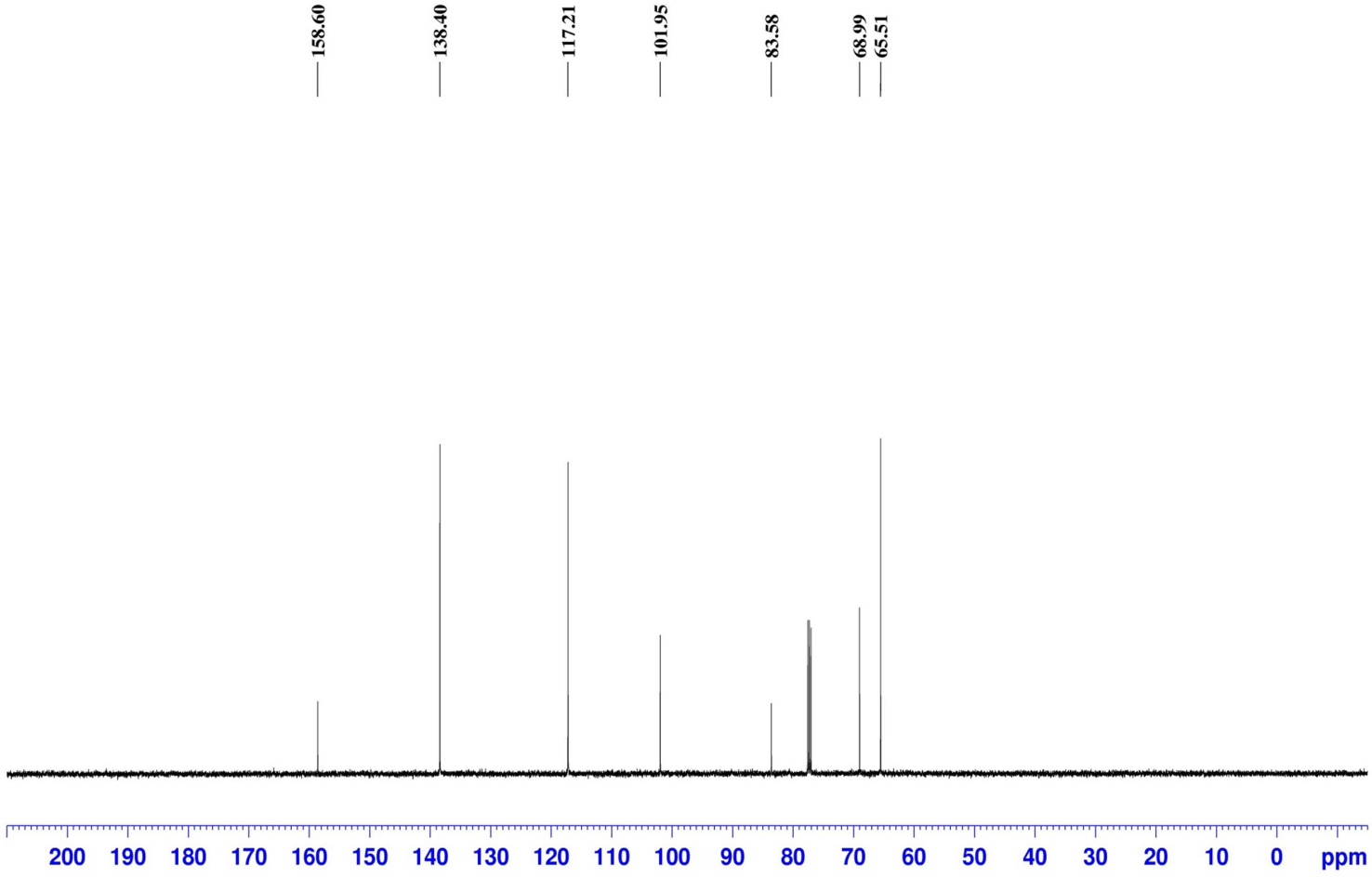
3–(4–iodophenoxy)tetrahydrofuran
125 MHz, CDCl3



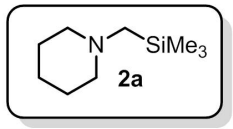


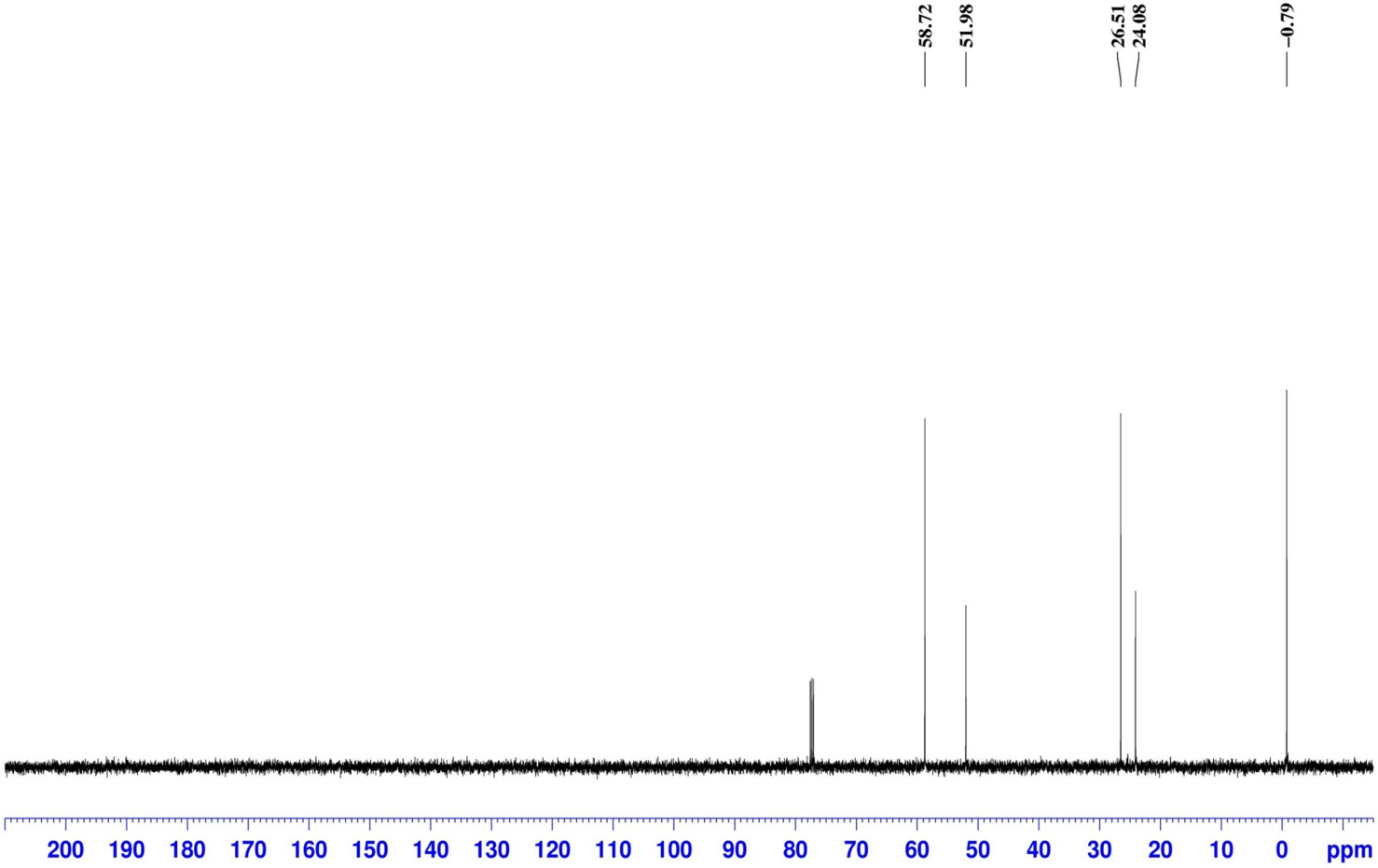
2–((4–iodophenoxy)methyl)–1,3–dioxolane
125 MHz, CDCl3



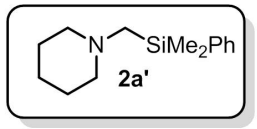


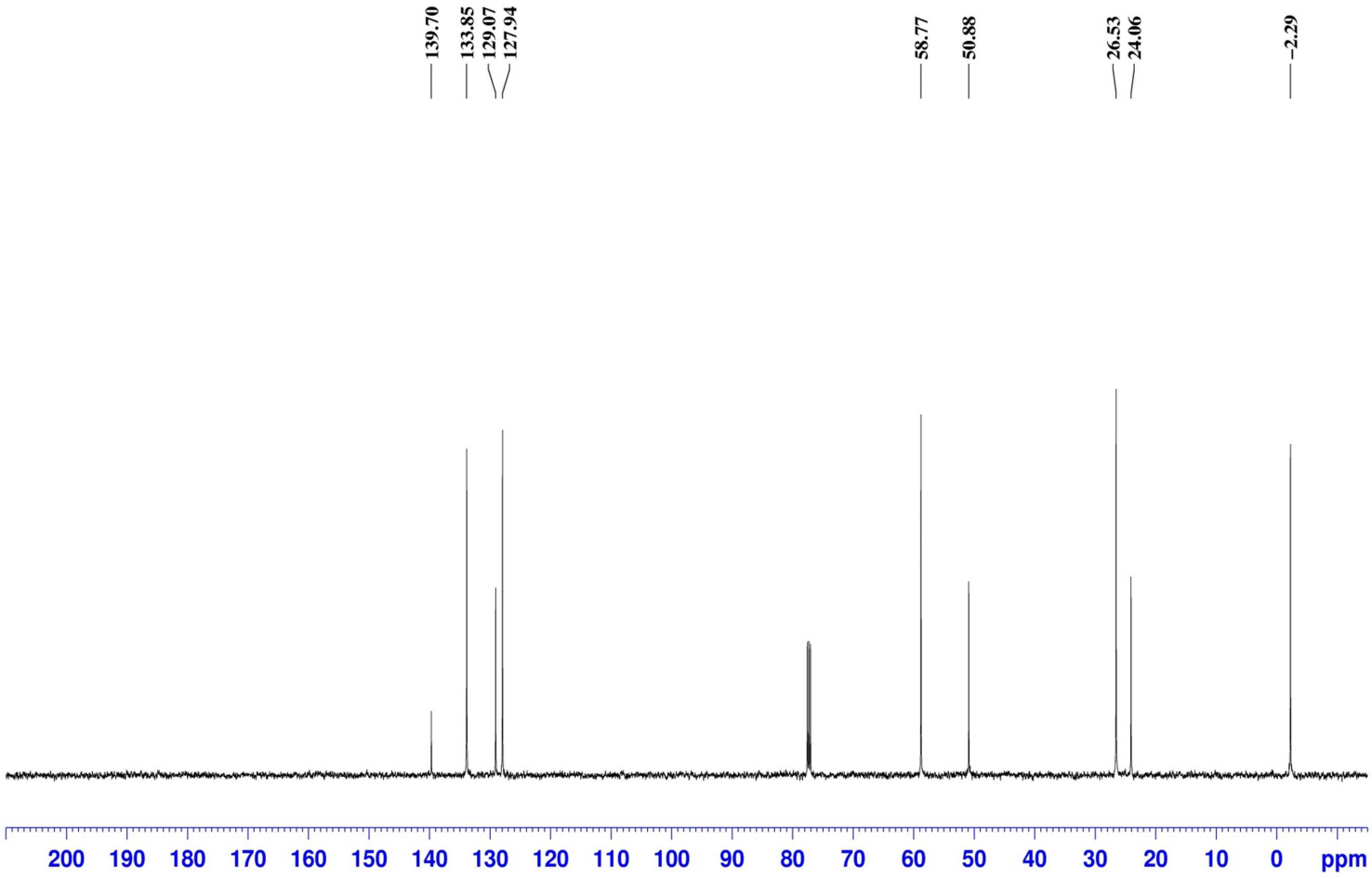
1–((trimethylsilyl)methyl)piperidine
125 MHz, CDCl3



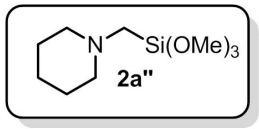


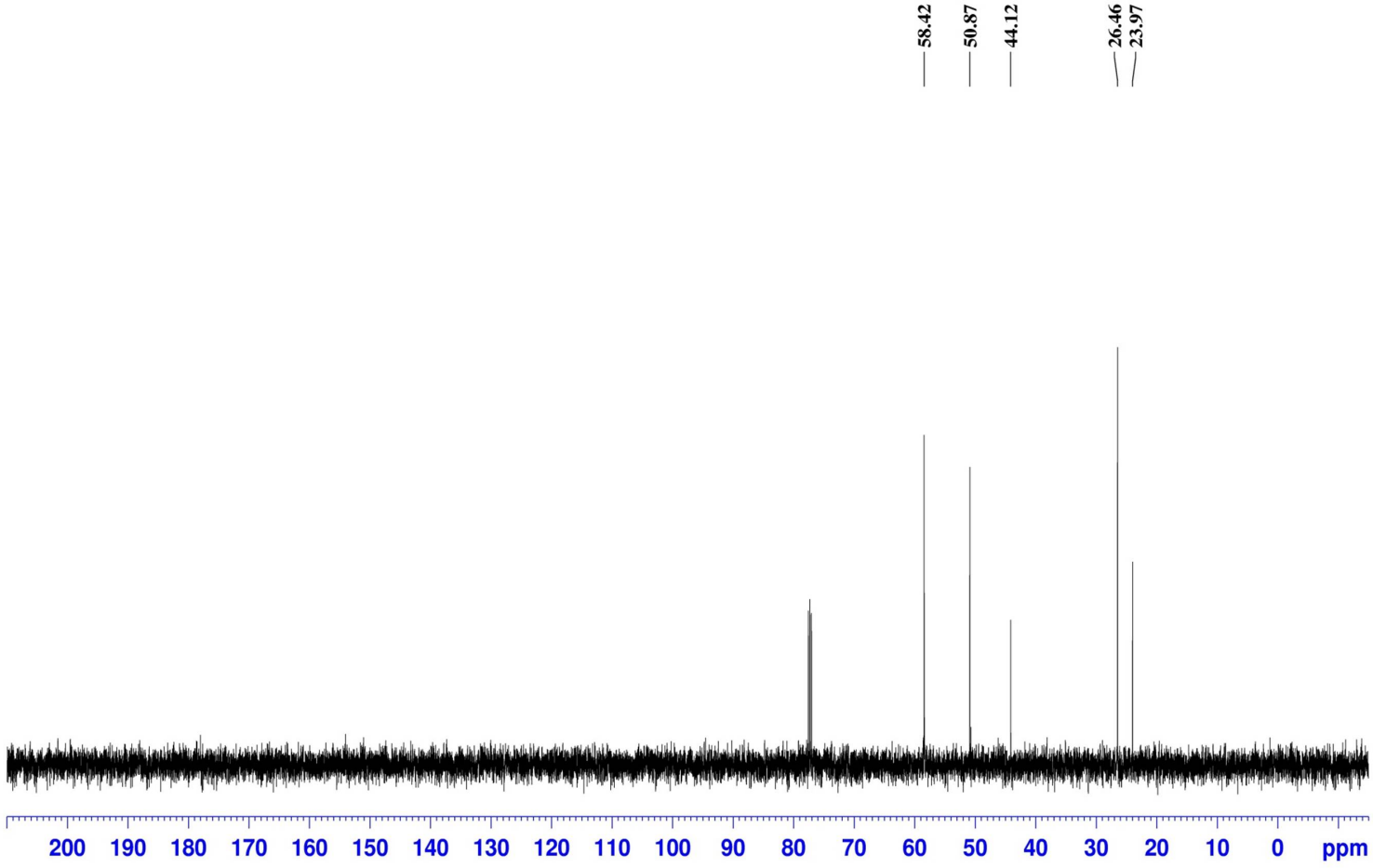
1–((dimethyl(phenyl)silyl)methyl)piperidine
125 MHz, CDCl3



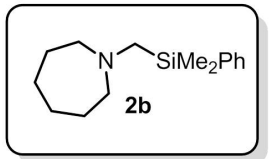


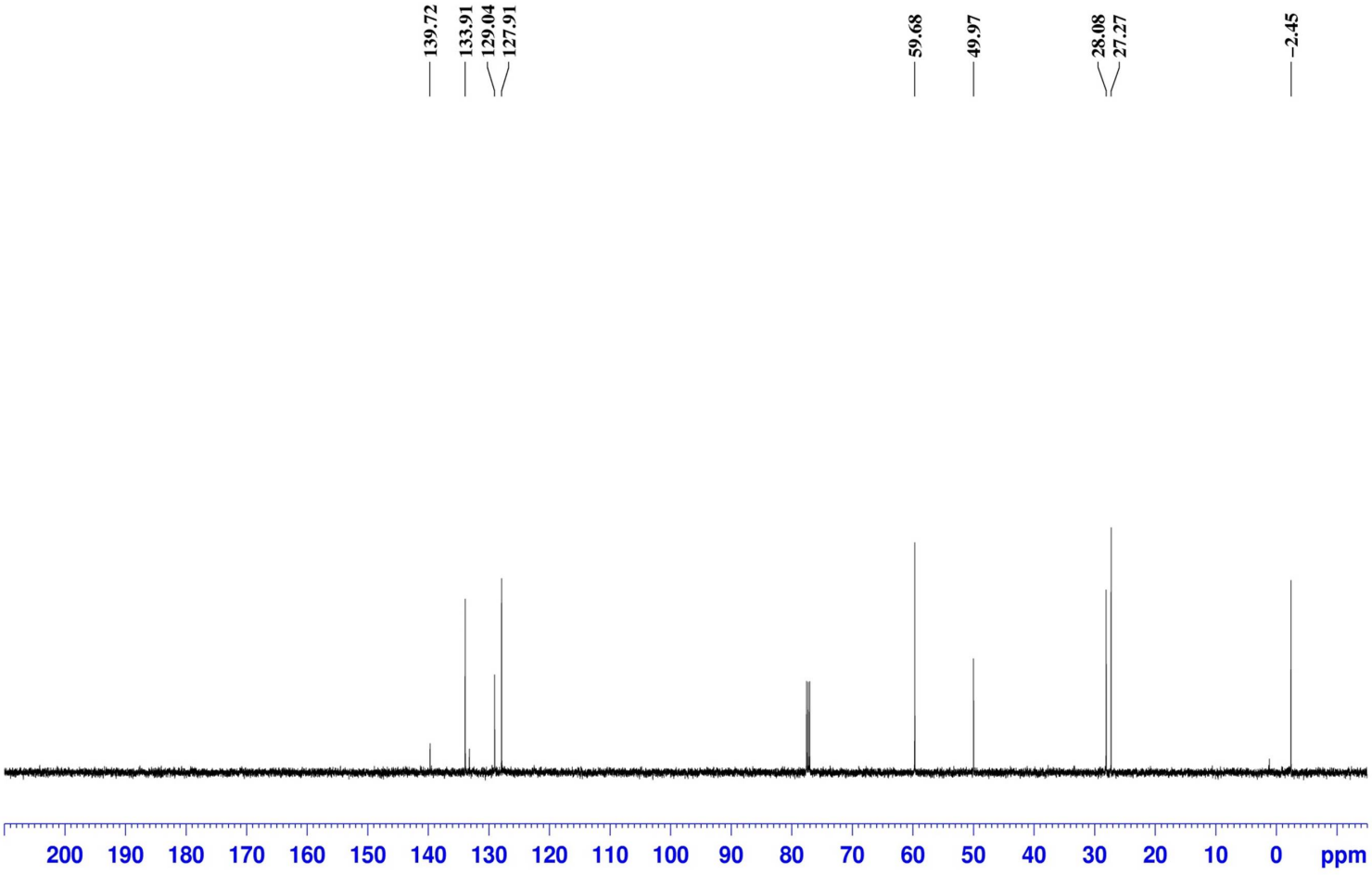
1–((trimethoxysilyl)methyl)piperidine
125 MHz, CDCl3



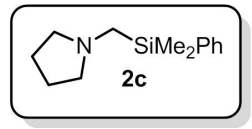


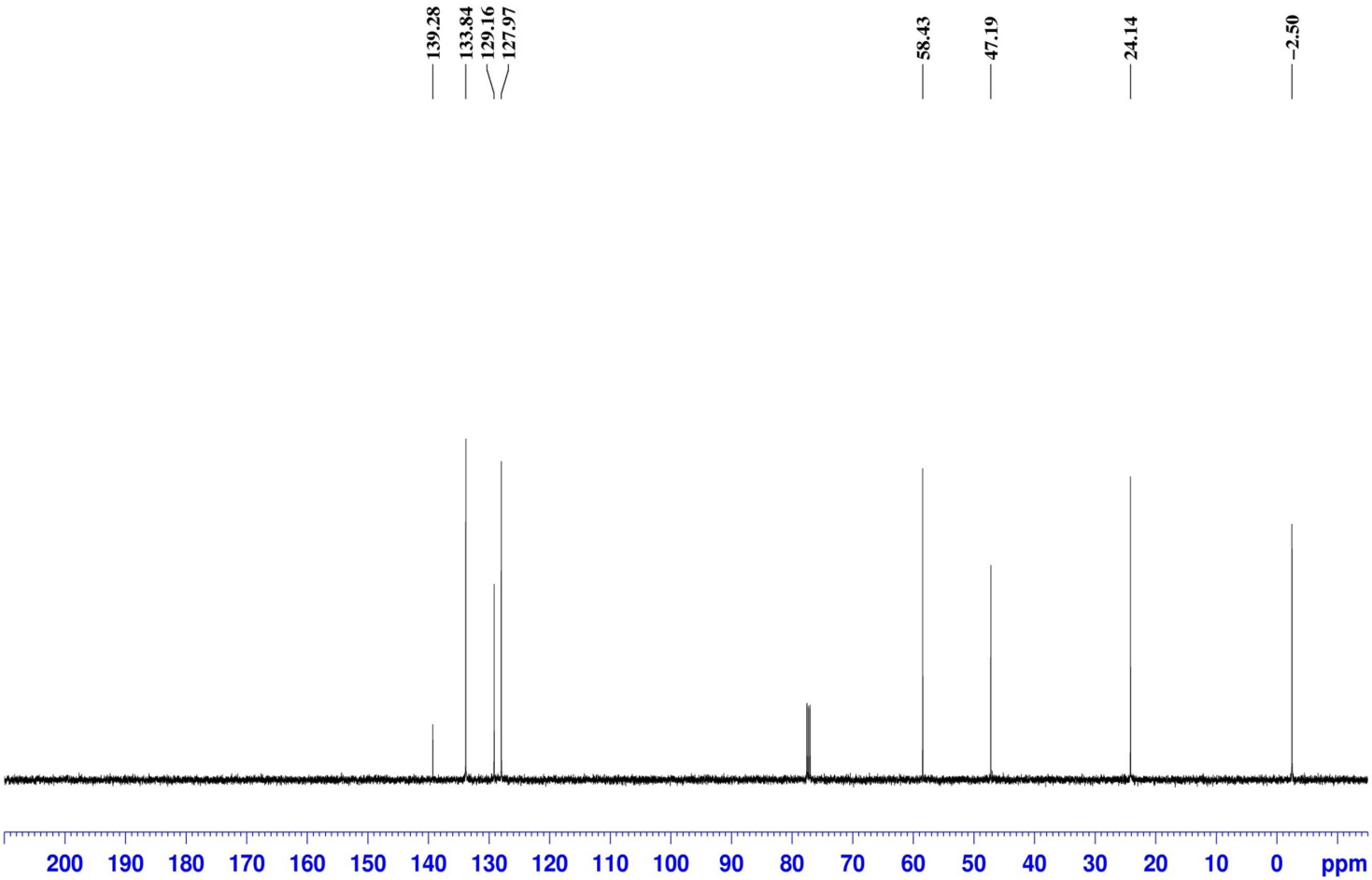
1–((dimethyl(phenyl)silyl)methyl)azepane
125 MHz, CDCl3



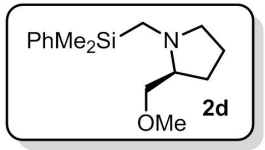


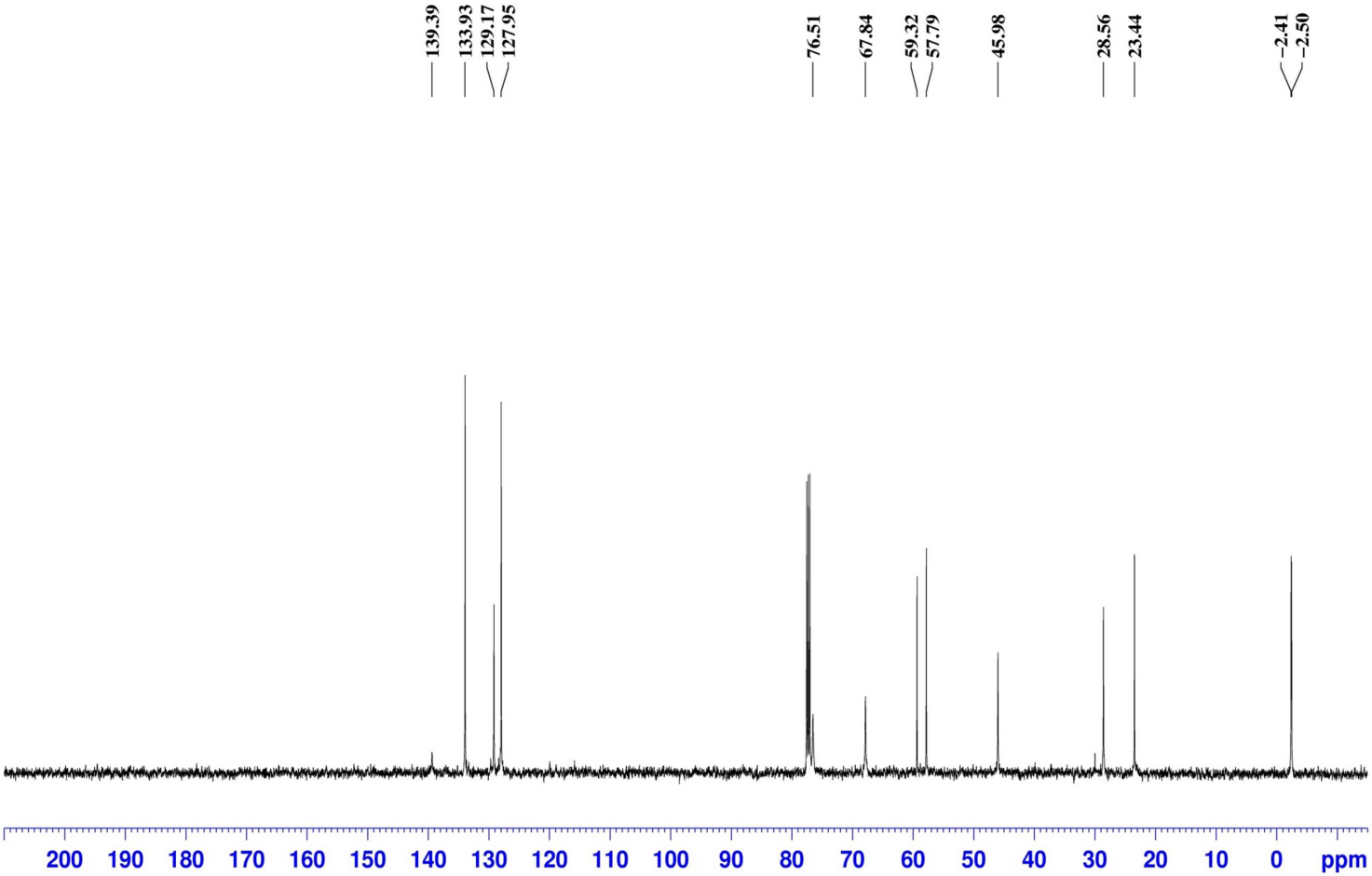
1–((dimethyl(phenyl)silyl)methyl)pyrrolidine
125 MHz, CDCl3



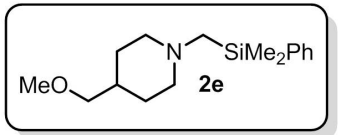


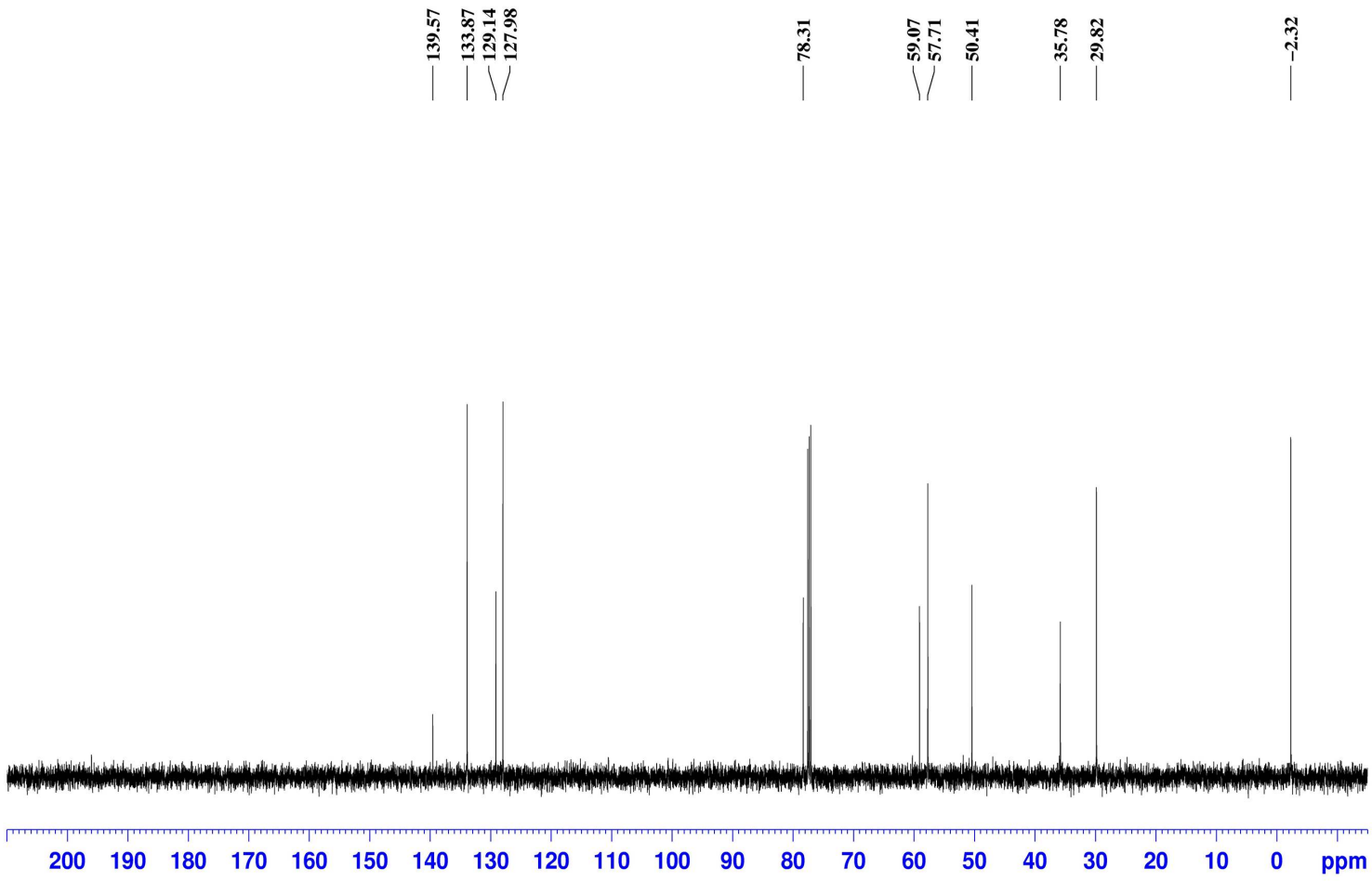
(S)−1−((dimethyl(phenyl)silyl)methyl)−2−(methoxymethyl)pyrrolidine
125 MHz, CDCl3



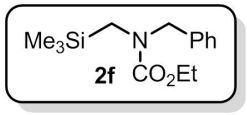


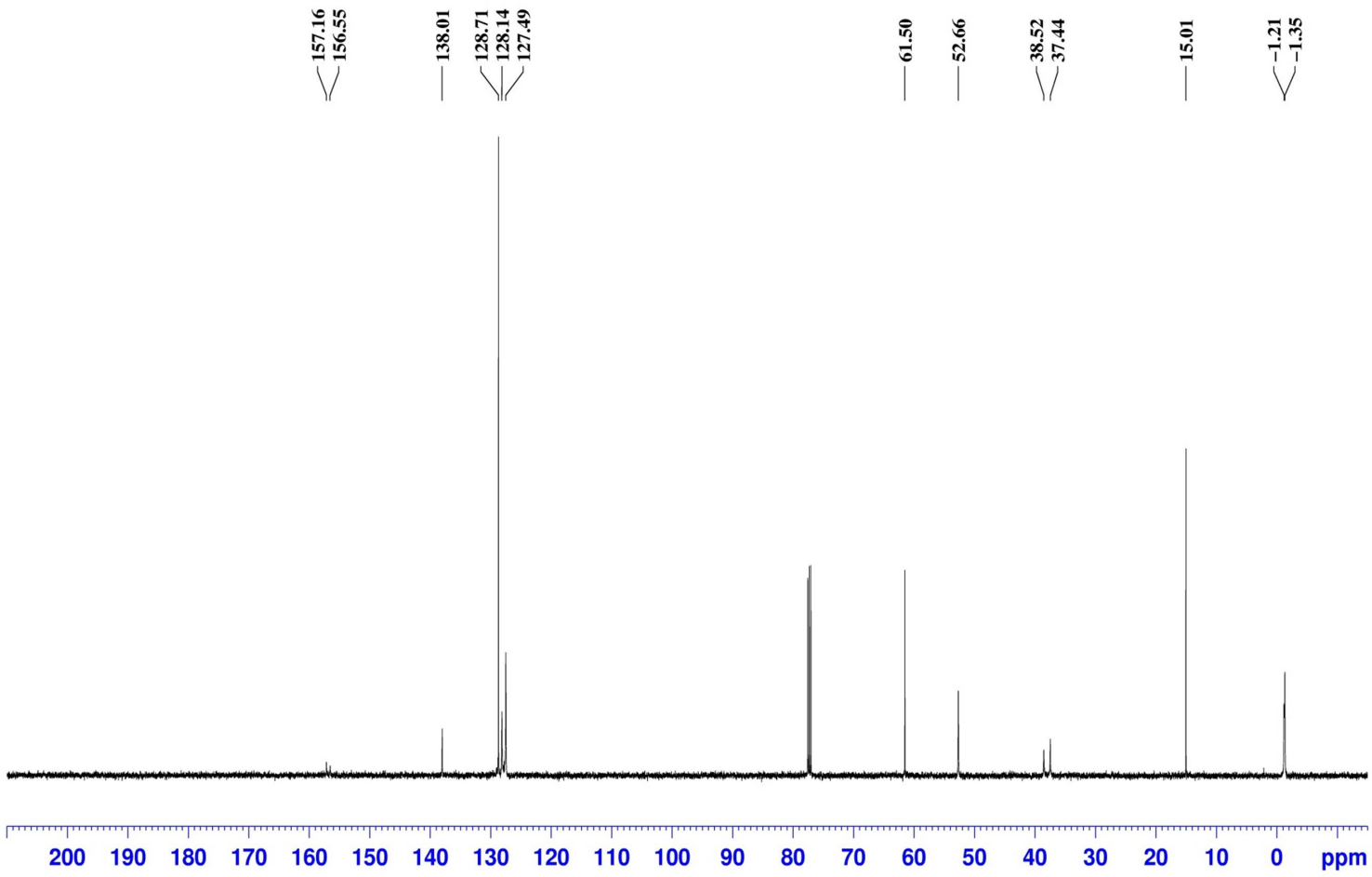
1−((dimethyl(phenyl)silyl)methyl)−4−(methoxymethyl)piperidine
125 MHz, CDCl3



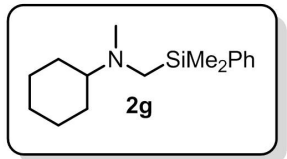


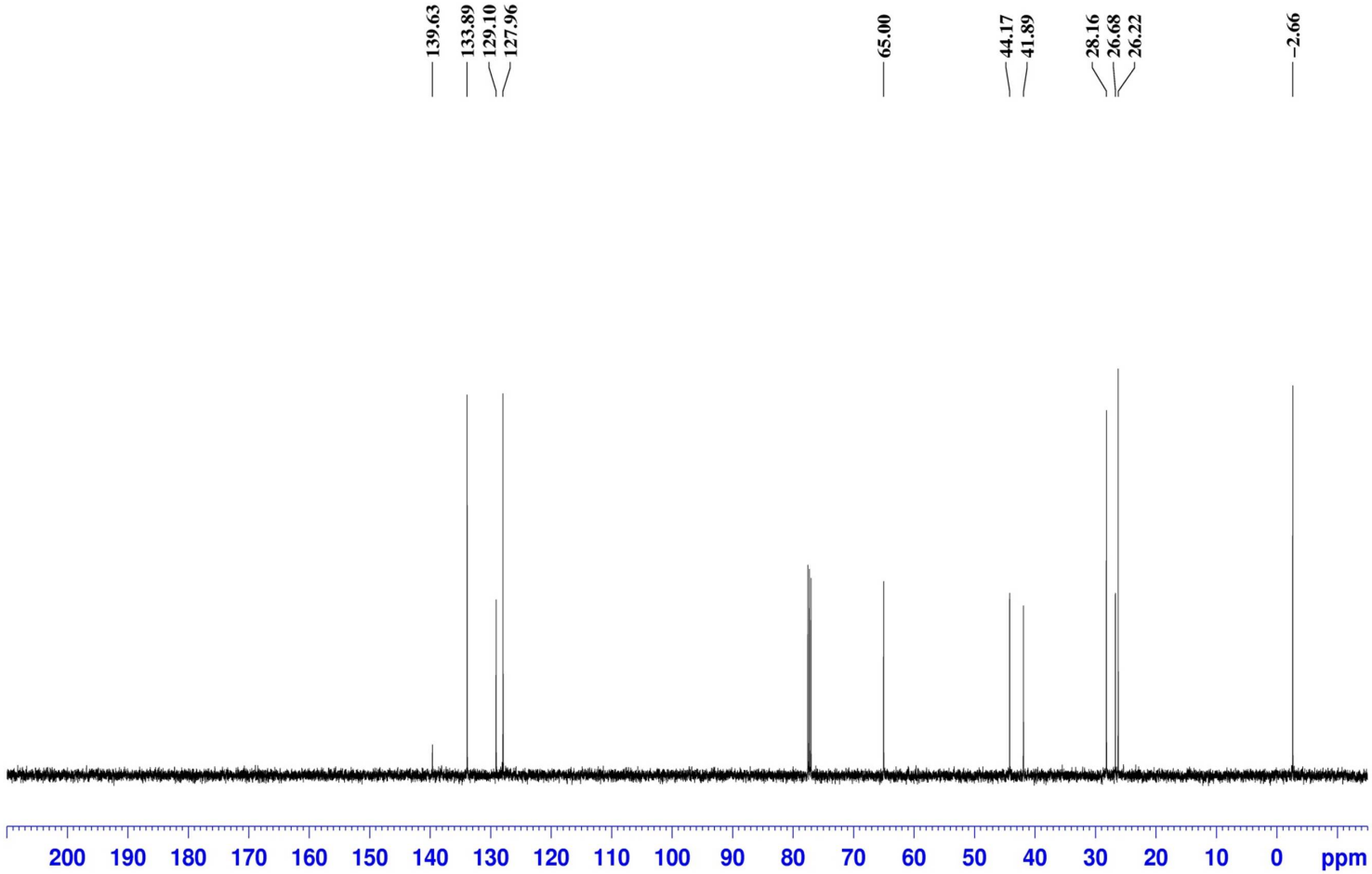
ethyl benzyl((trimethylsilyl)methyl)carbamate
125 MHz, CDCl3



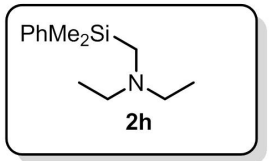


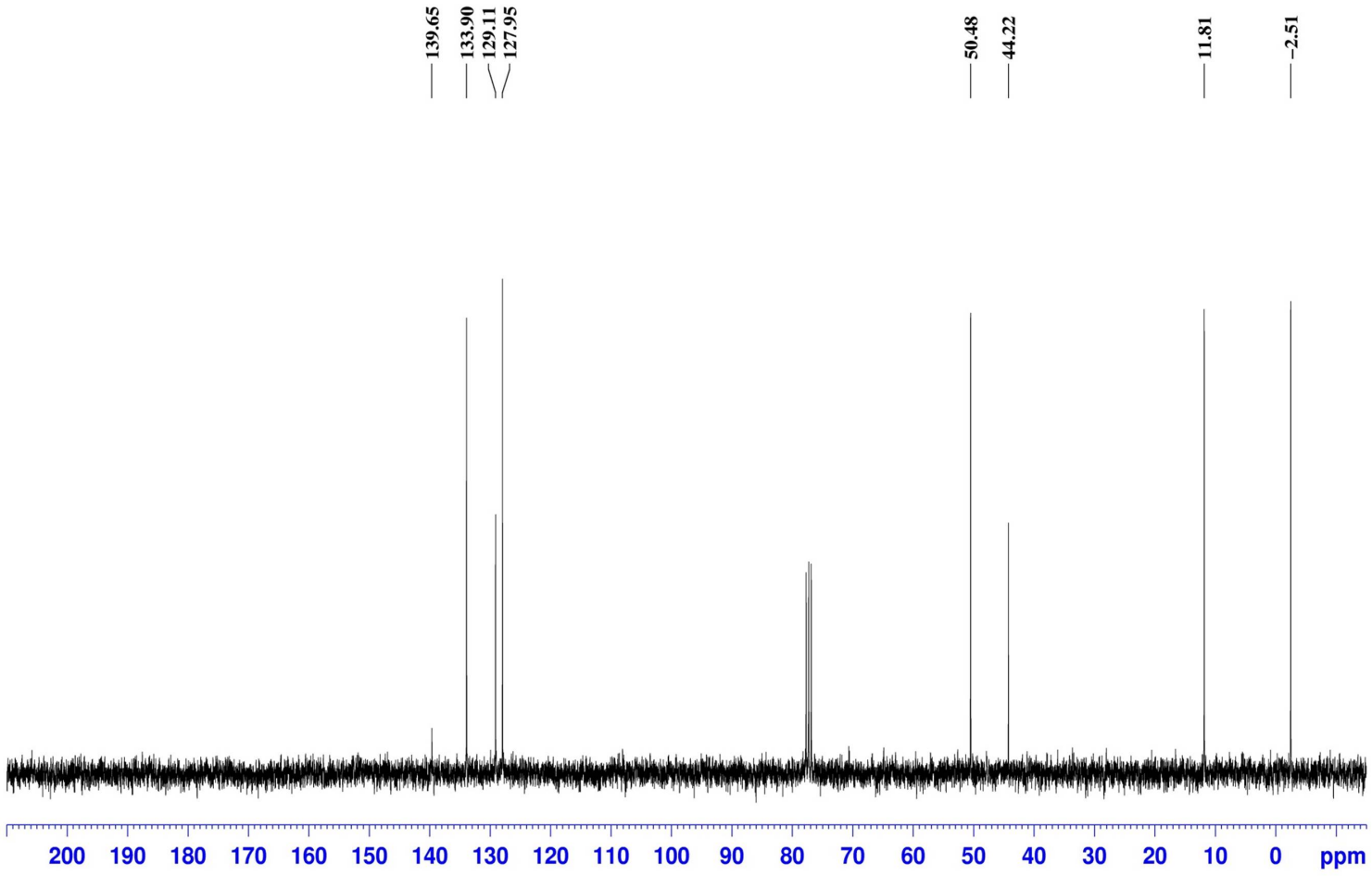
N–((dimethyl(phenyl)silyl)methyl)–N–methylcyclohexanamine
125 MHz, CDCl3



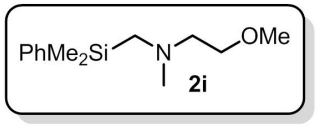


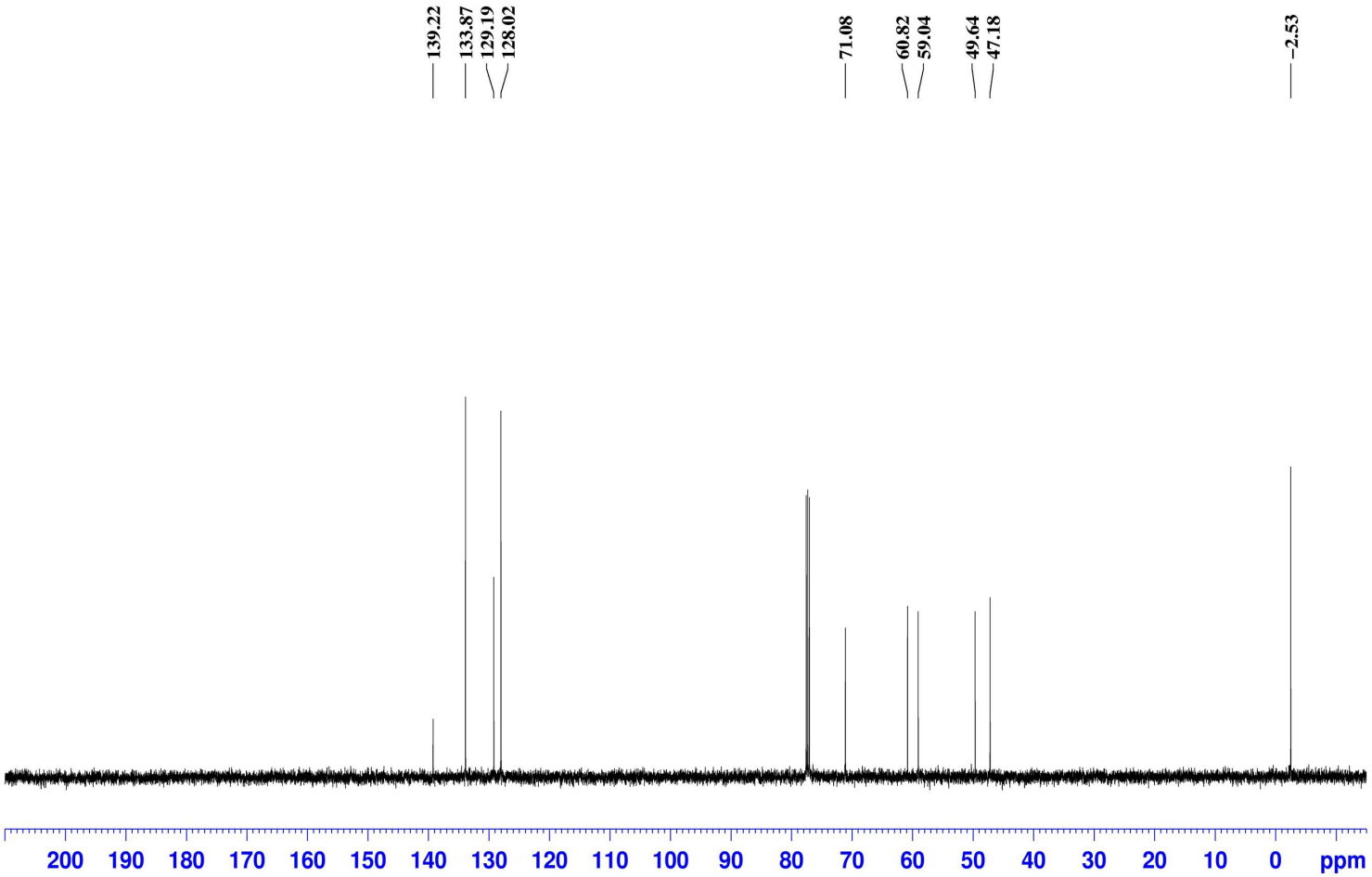
N–((dimethyl(phenyl)silyl)methyl)–N–ethylethanamine
75 MHz, CDCl3



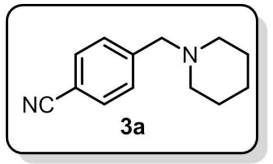


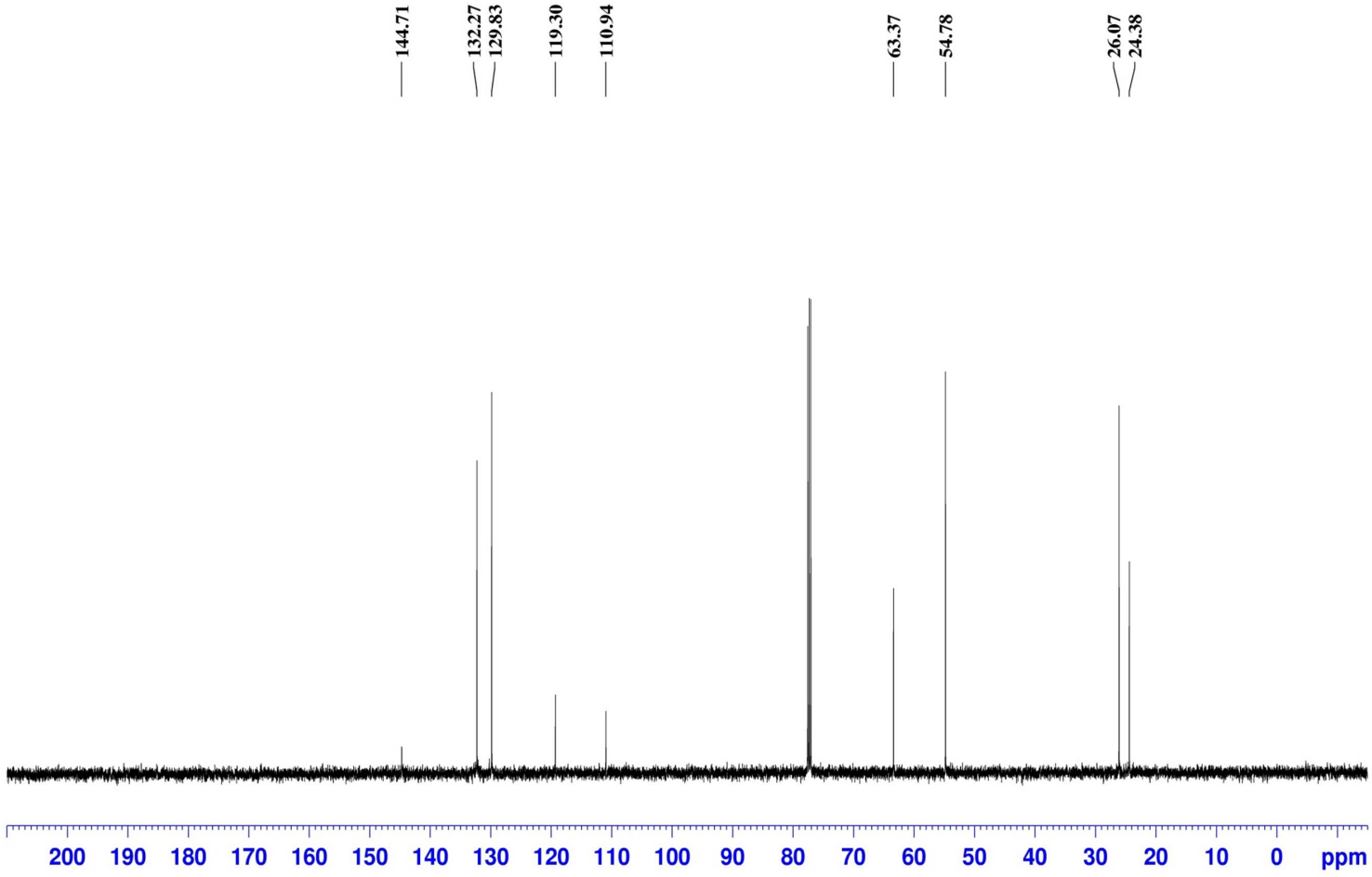
N–((dimethyl(phenyl)silyl)methyl)–2–methoxy–N–methylethanamine
125 MHz, CDCl3



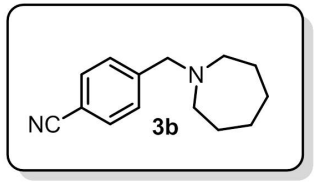


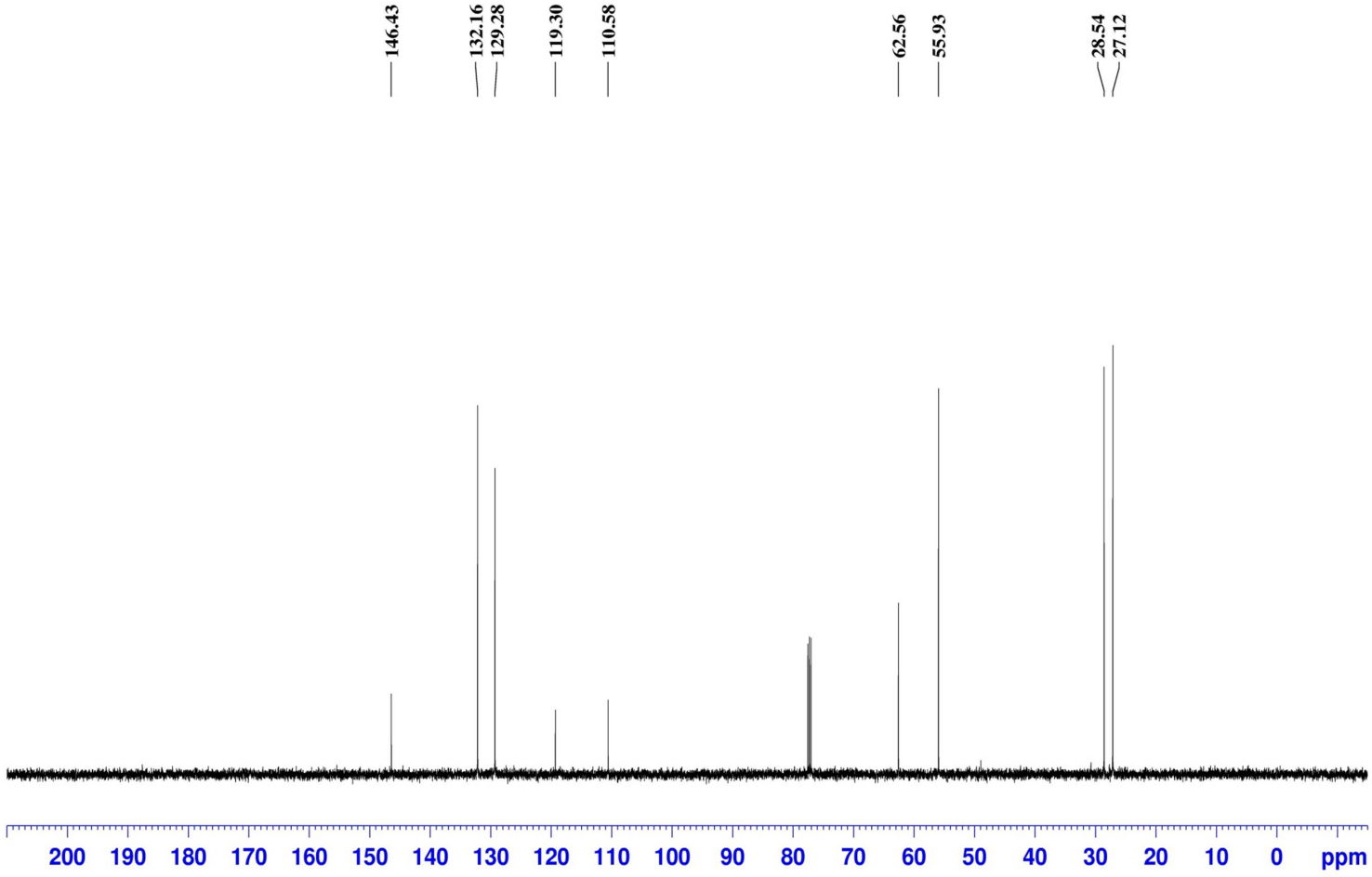
4–(piperidin–1–ylmethyl)benzonitrile
125 MHz, CDCl3



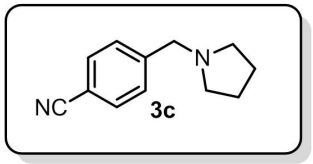


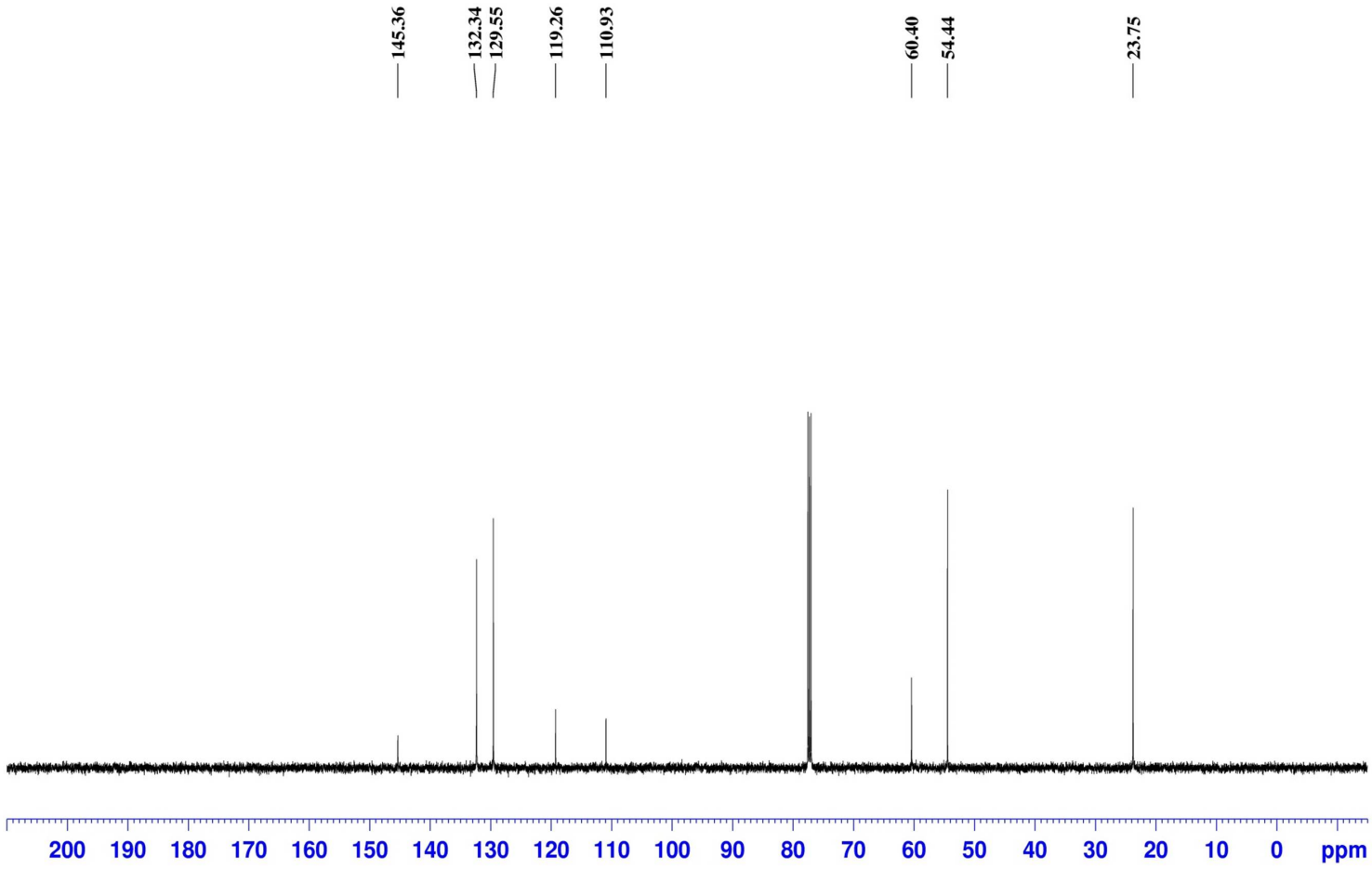
4–(azepan–1–ylmethyl)benzonitrile
125 MHz, CDCl3



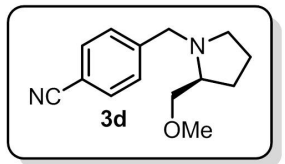


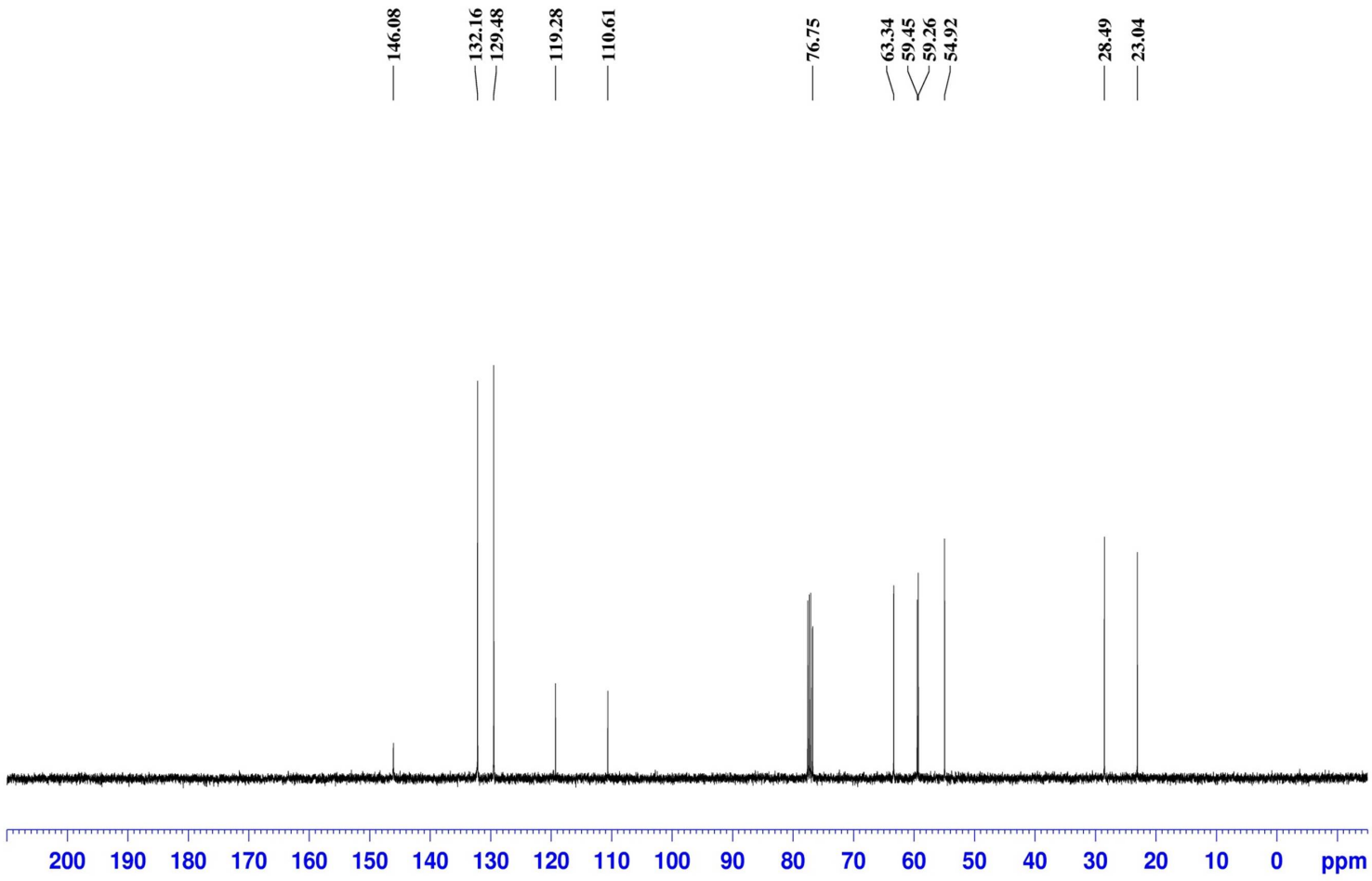
4–(pyrrolidin–1–ylmethyl)benzonitrile
125 MHz, CDCl3



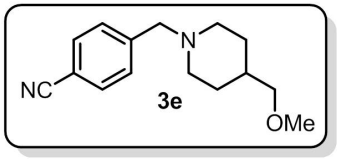


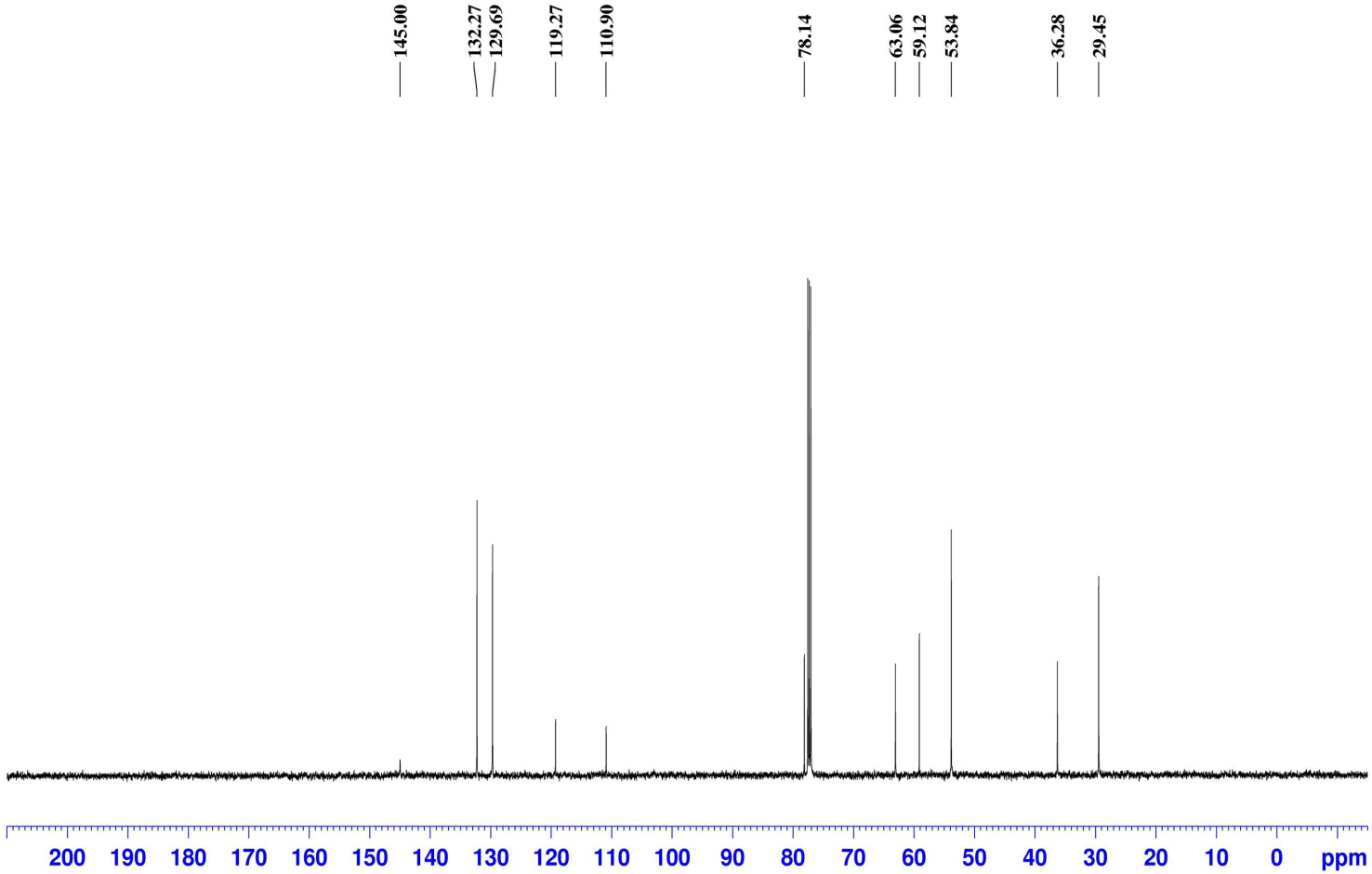
(S)−4−((2−(methoxymethyl)pyrrolidin−1−yl)methyl)benzonitrile
125 MHz, CDCl3



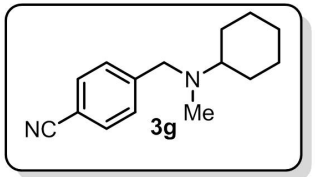


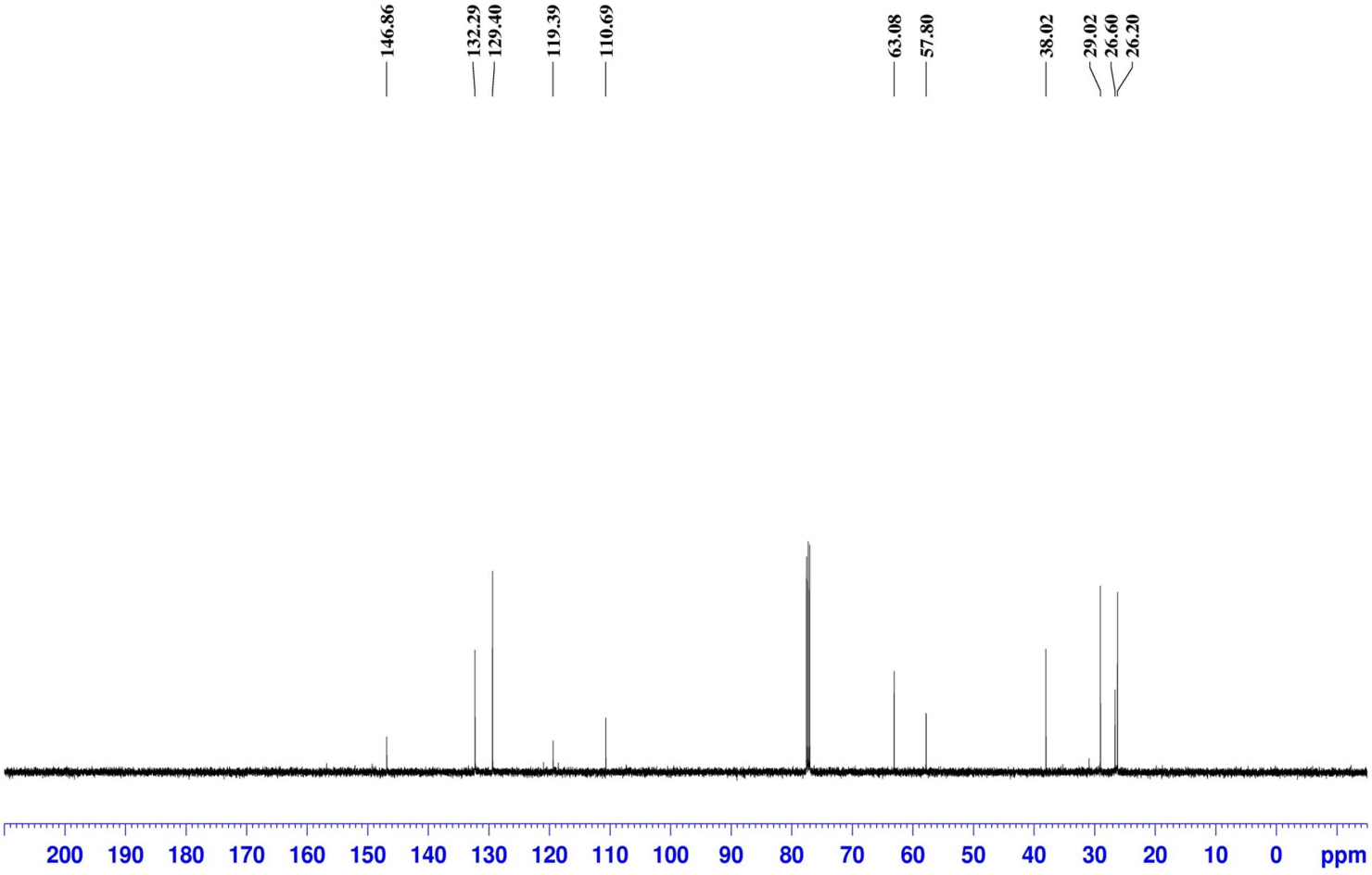
4–((4–(methoxymethyl)piperidin–1–yl)methyl)benzonitrile
125 MHz, CDCl3



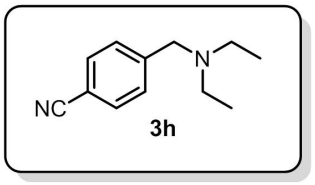


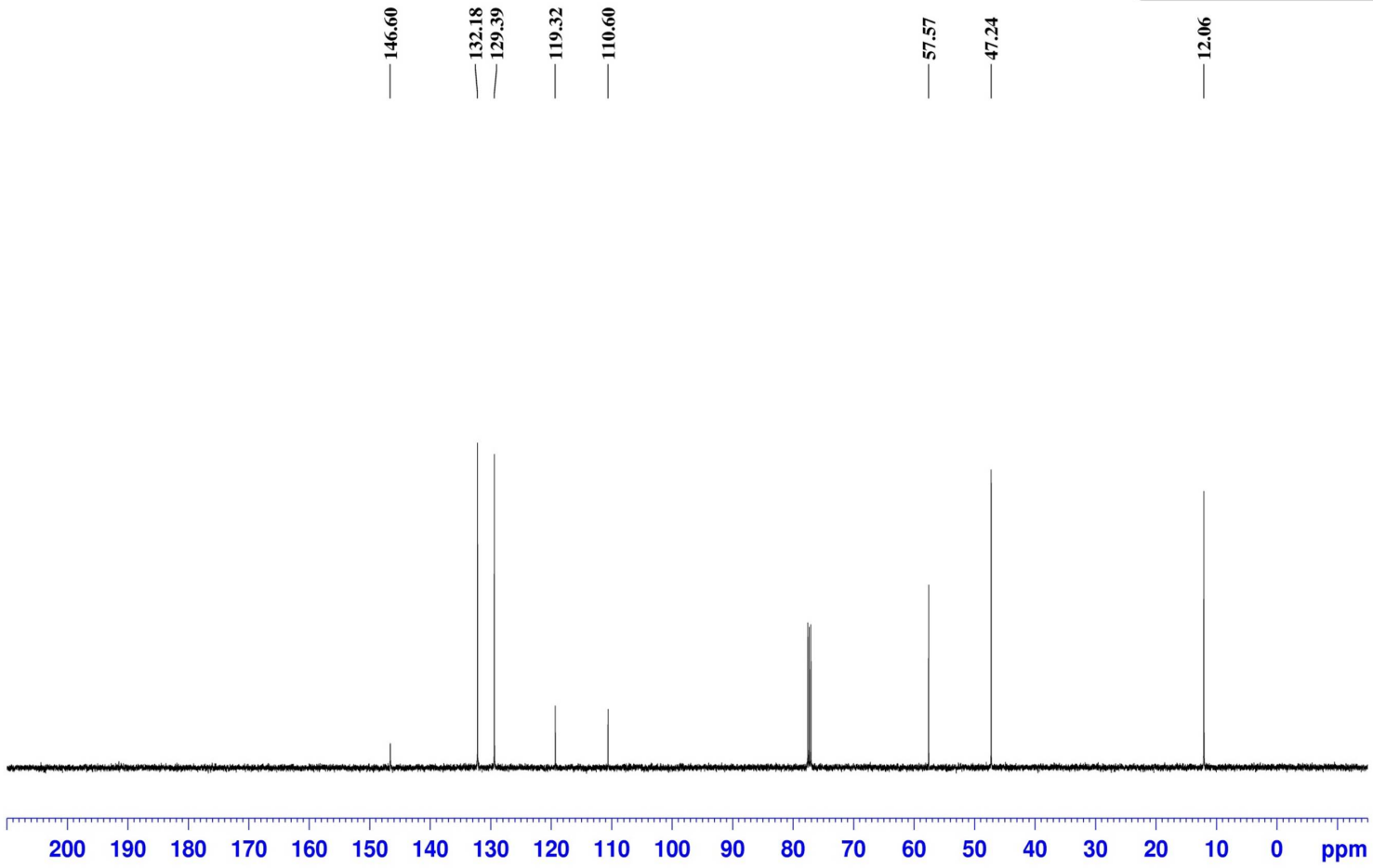
4–((cyclohexyl(methyl)amino)methyl)benzonitrile
125 MHz, CDCl3



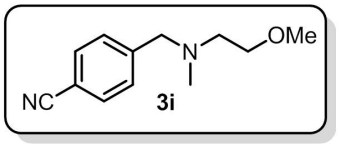


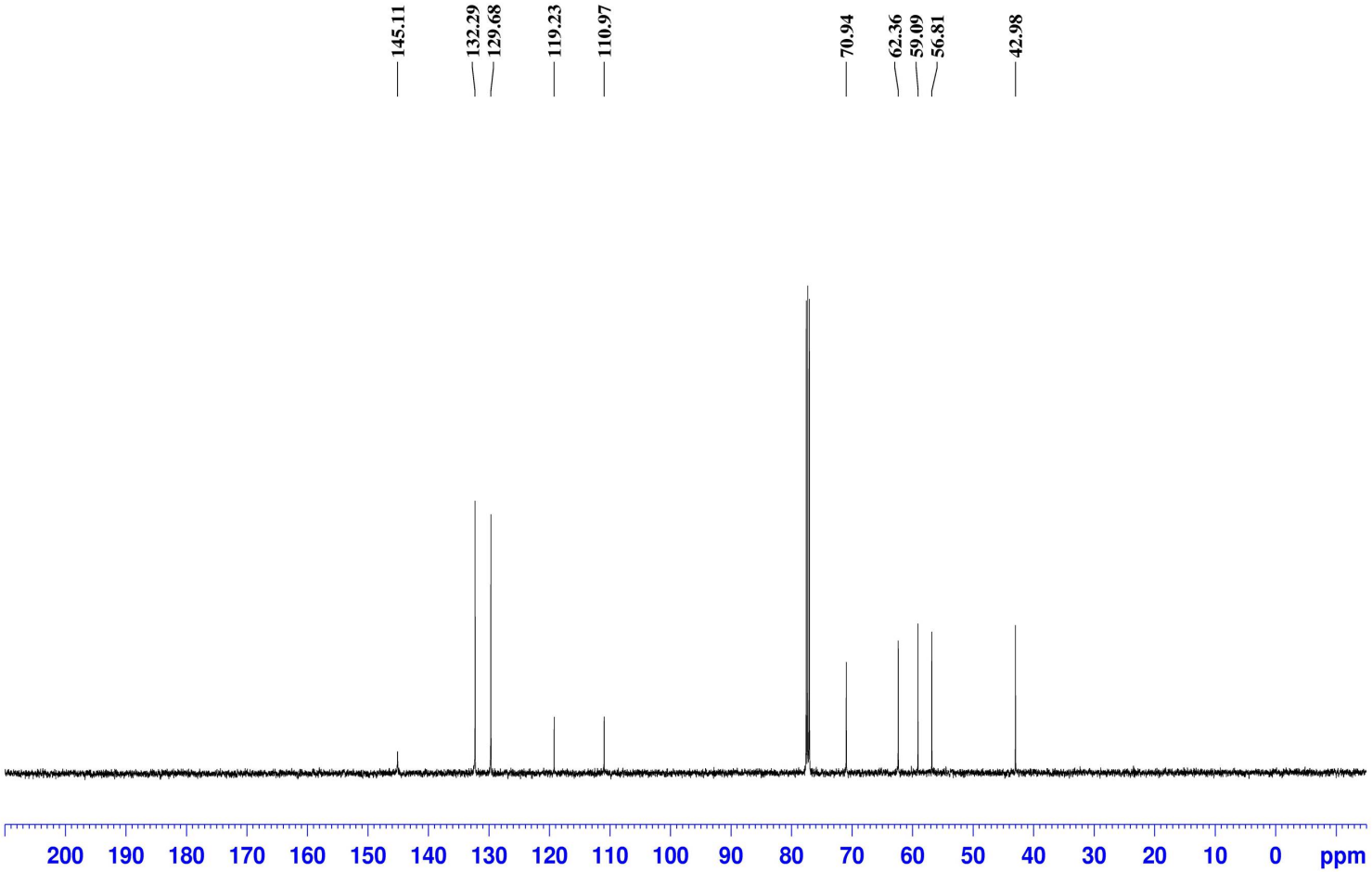
4–((diethylamino)methyl)benzonitrile
125 MHz, CDCl3



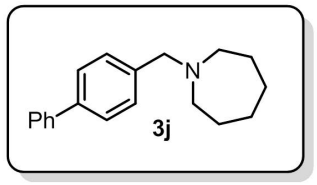


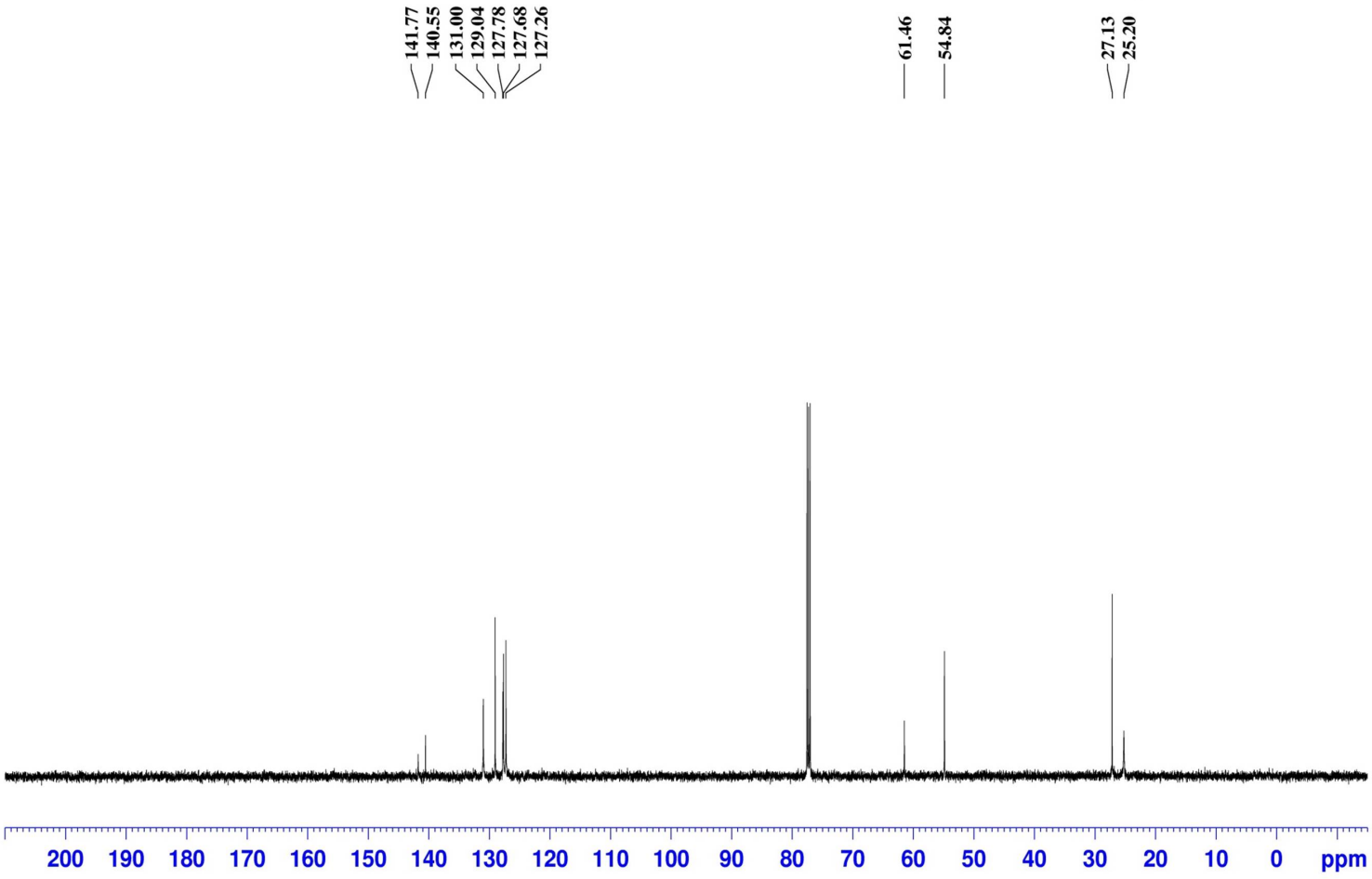
4–(((2–methoxyethyl)(methyl)amino)methyl)benzonitrile
125 MHz, CDCl3



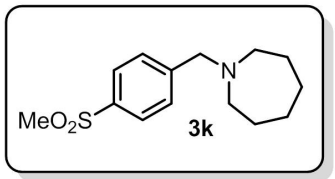


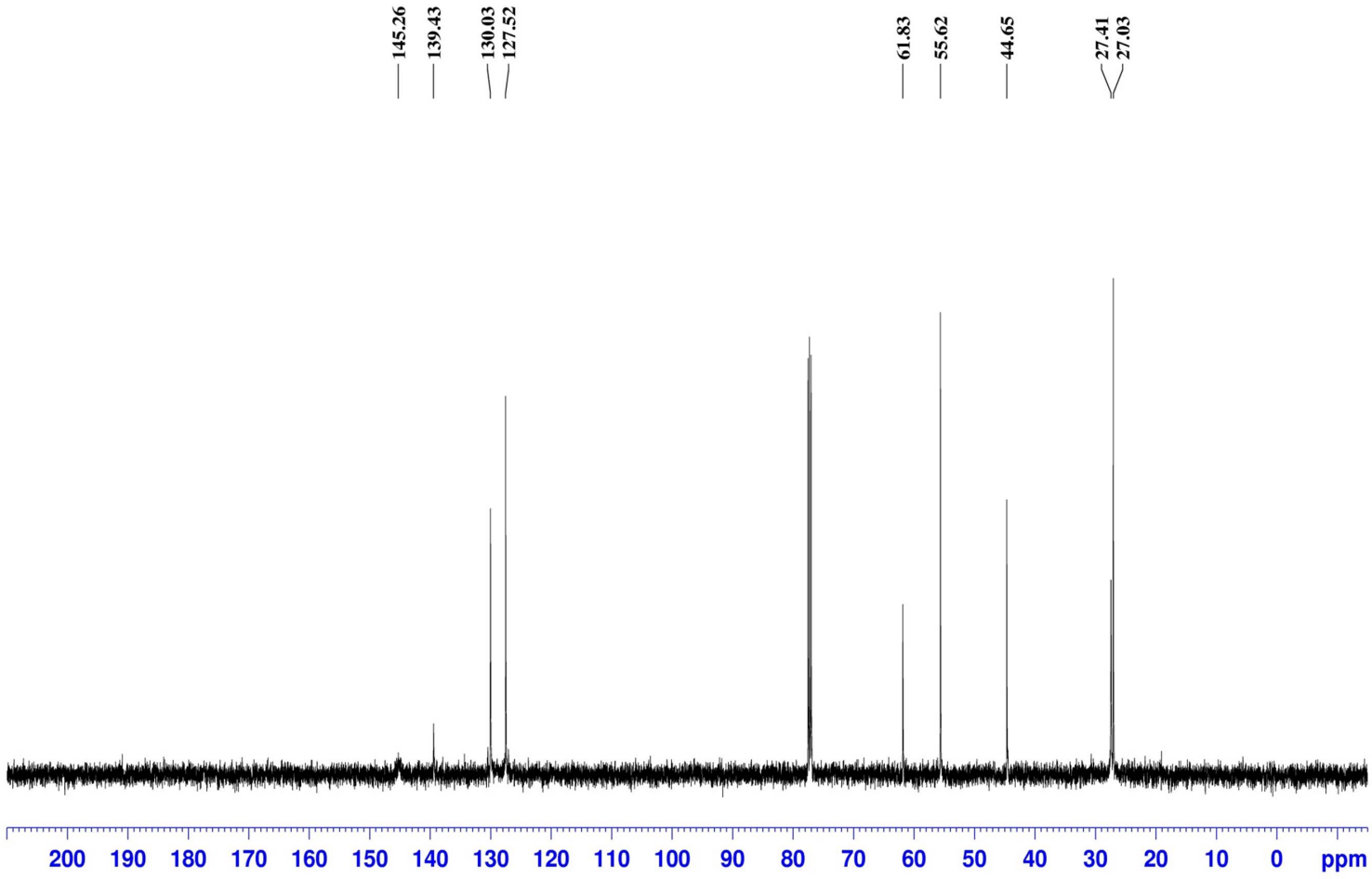
1–([1,1'–biphenyl]–4–ylmethyl)azepane
125 MHz, CDCl3



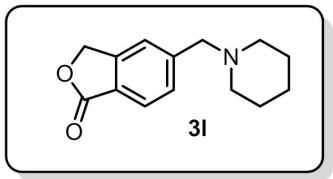


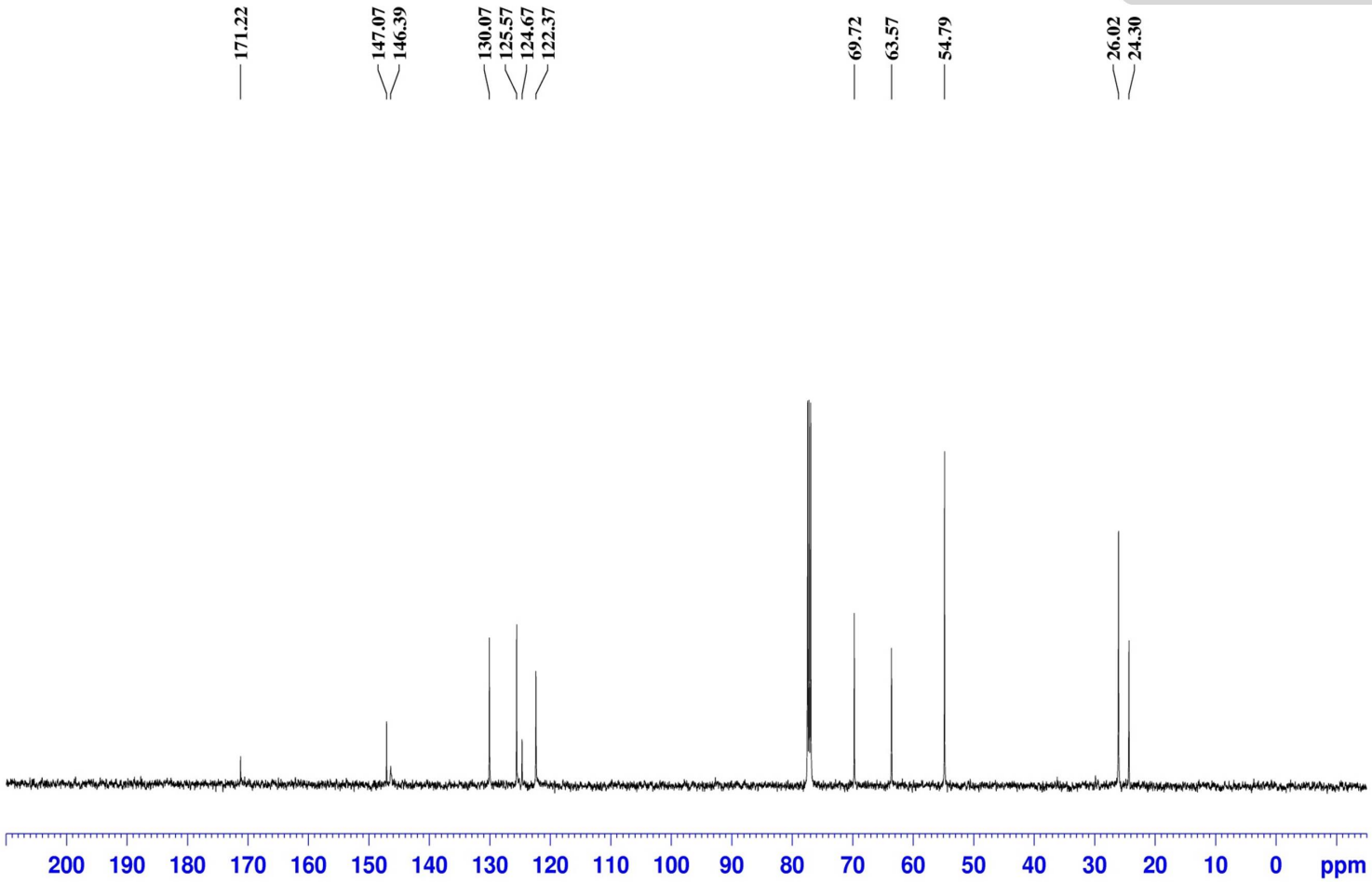
1–(4–(methylsulfonyl)benzyl)azepane
125 MHz, CDCl3



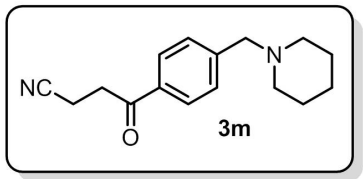


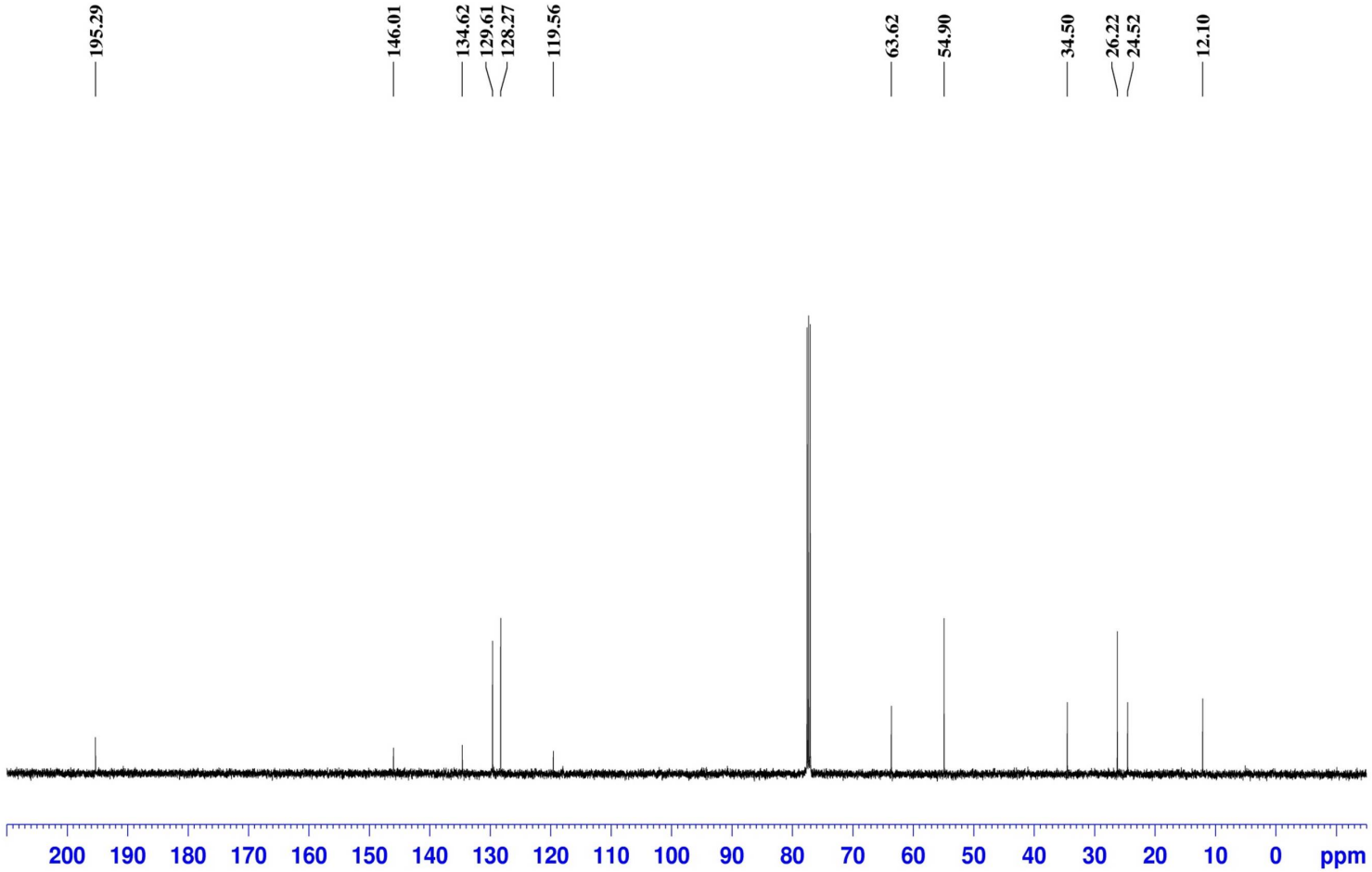
5–(piperidin–1–ylmethyl)pthalide
125 MHz, CDCl3



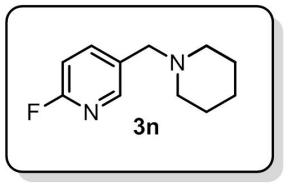


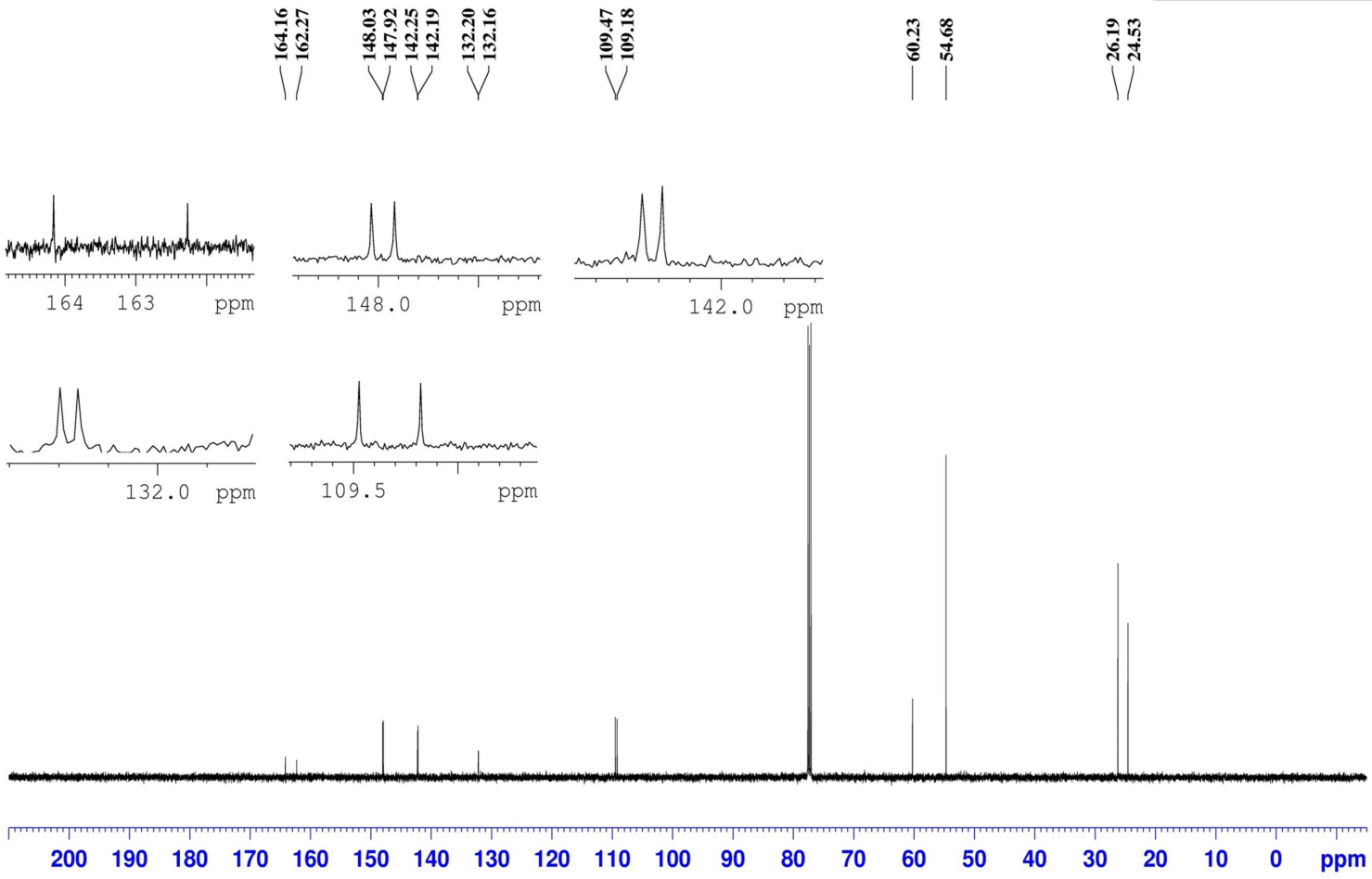
4–oxo–4–(4–(piperidin–1–ylmethyl)phenyl)butanenitrile
125 MHz, CDCl3



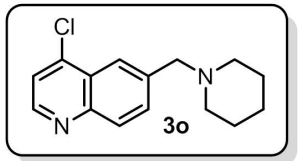


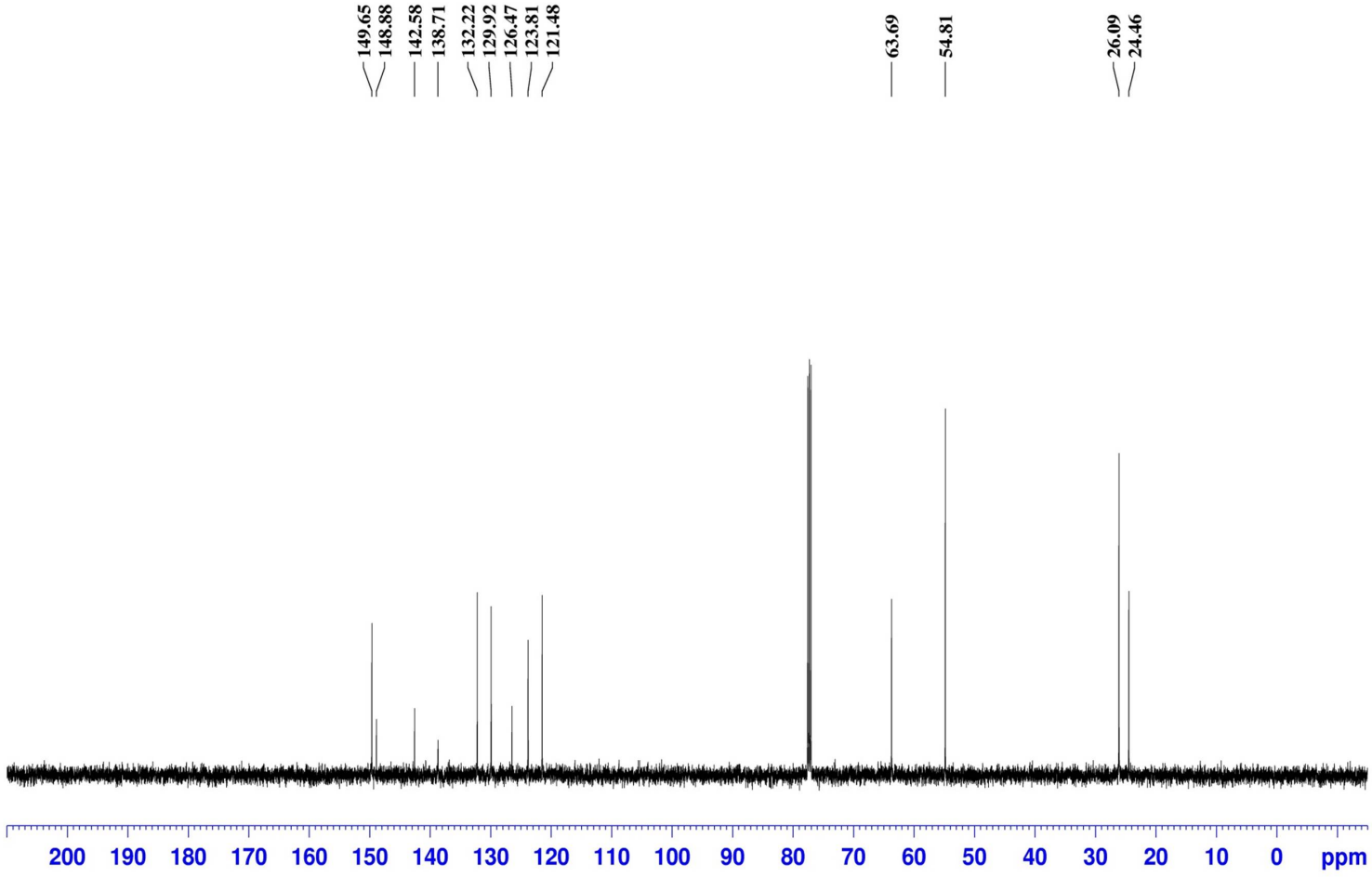
2–fluoro–5–(piperidin–1–ylmethyl)pyridine
125 MHz, CDCl3



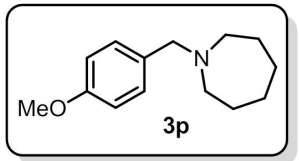


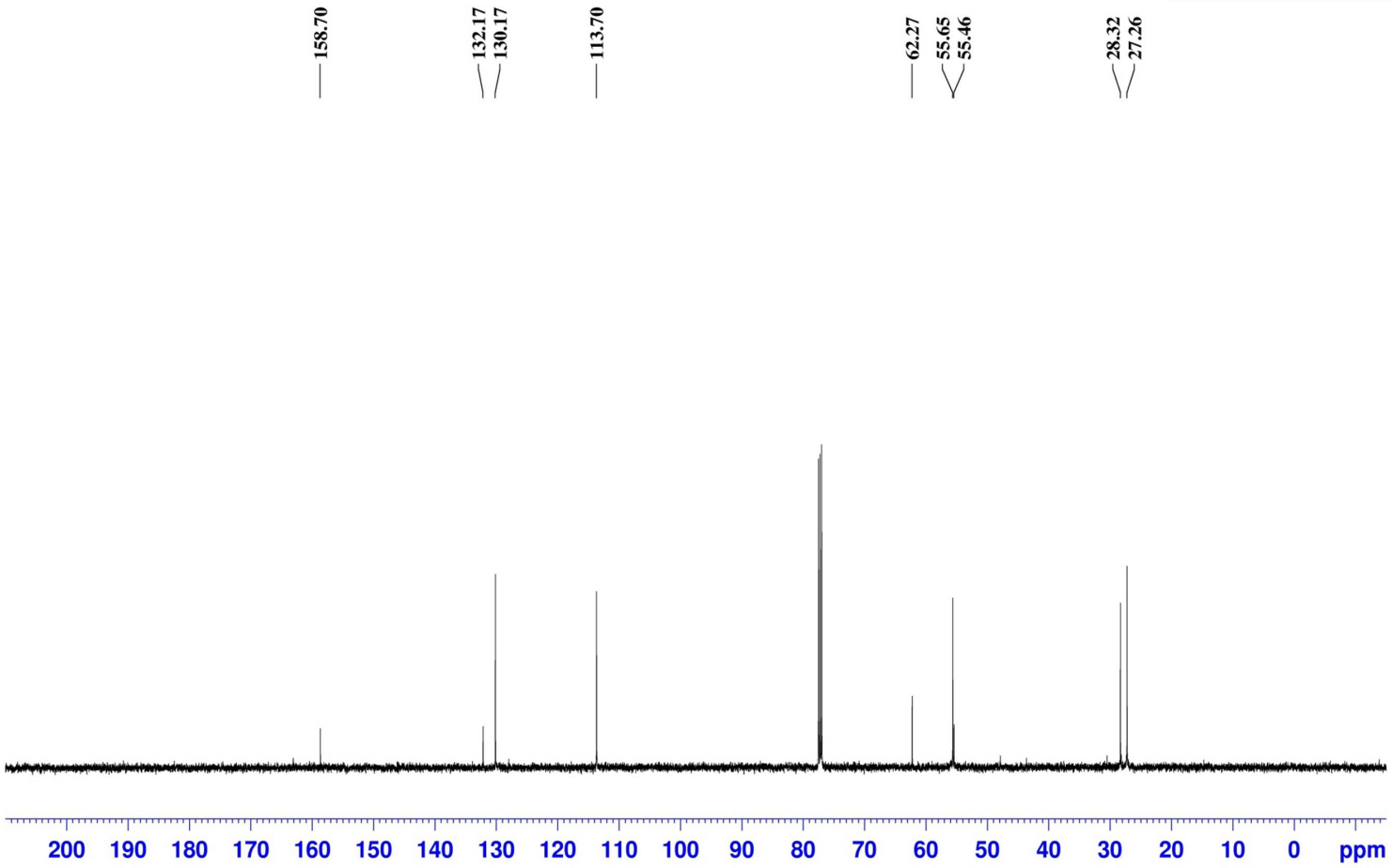
4–chloro–6–(piperidin–1–ylmethyl)quinoline
125 MHz, CDCl3



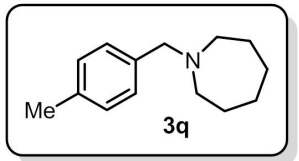


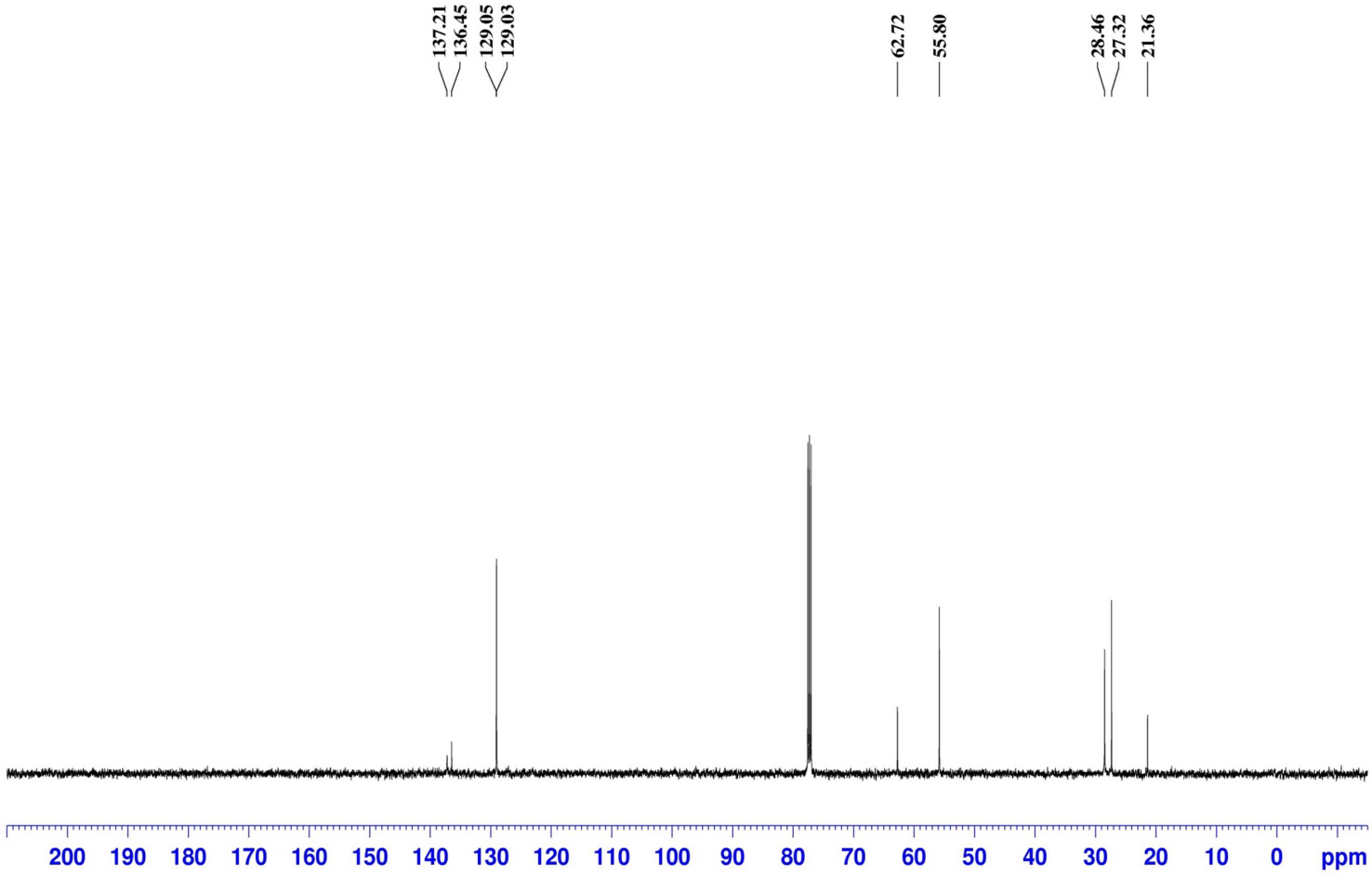
1–(4–methoxybenzyl)azepane
125 MHz, CDCl3



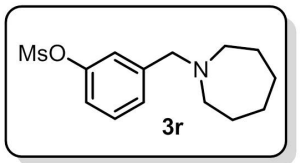


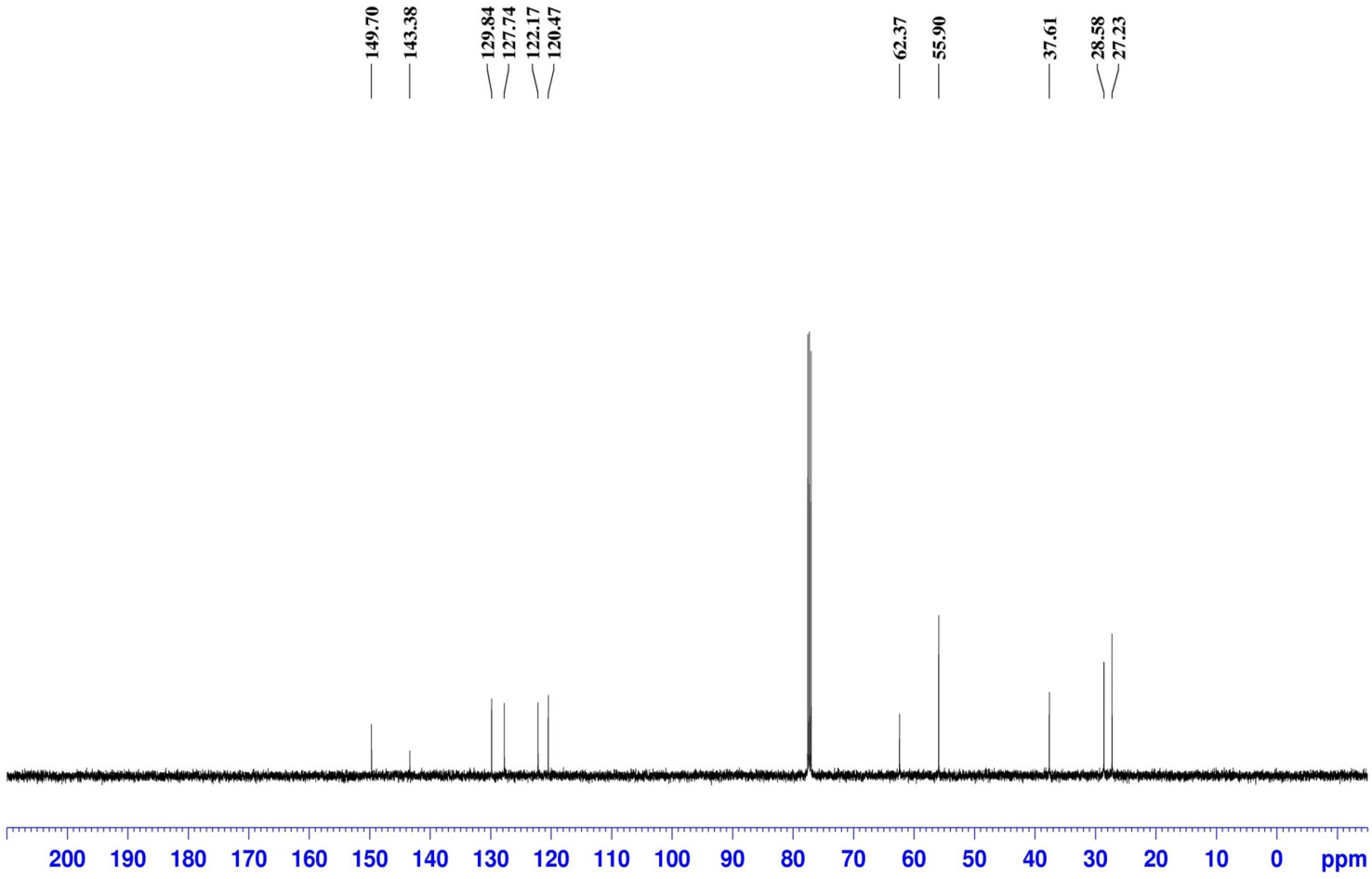
1–(4–methylbenzyl)azepane
125 MHz, CDCl3



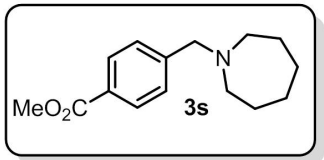


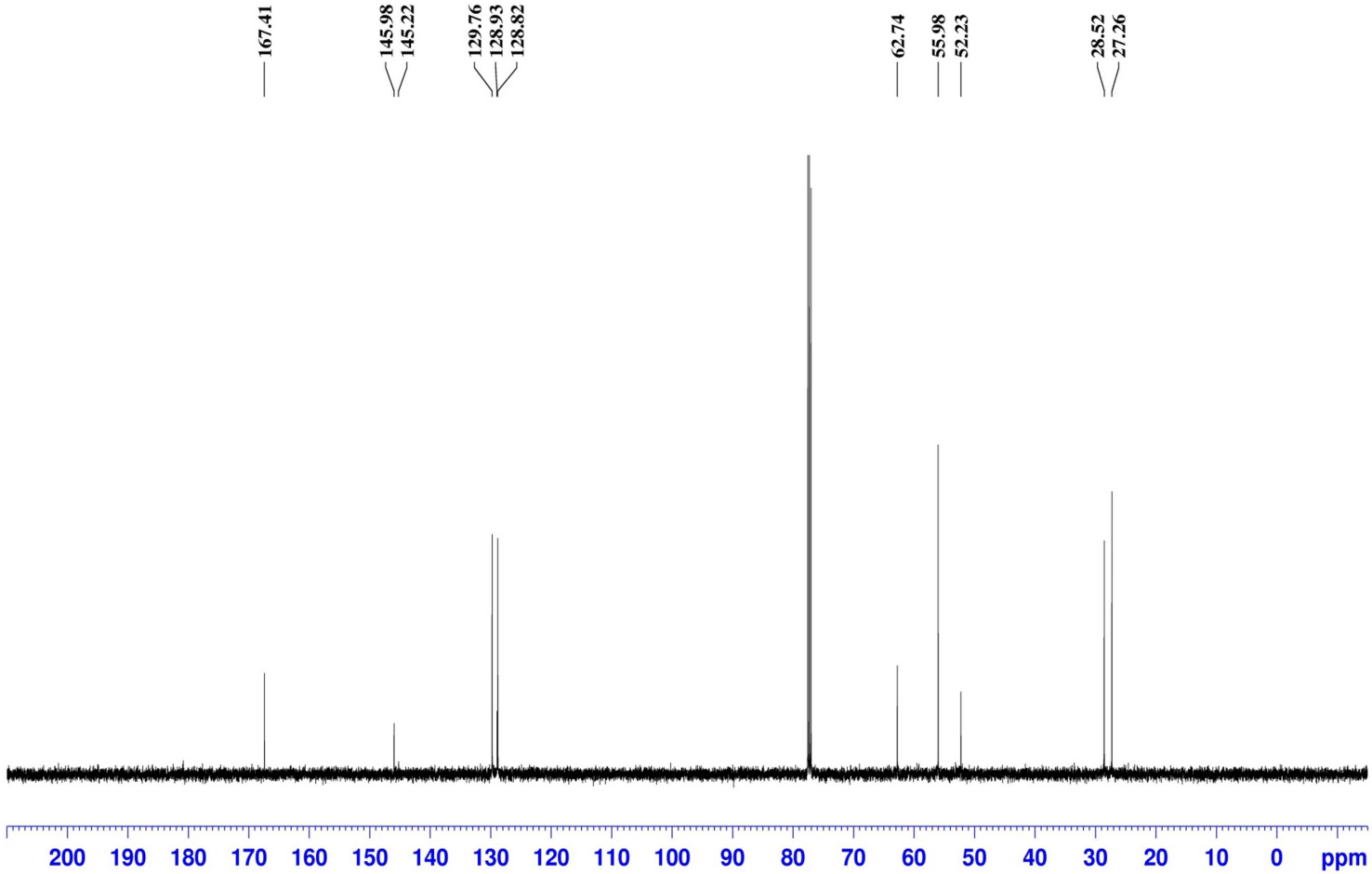
3–(azepan–1–ylmethyl)phenyl methanesulfonate
125 MHz, CDCl3



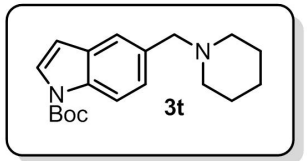


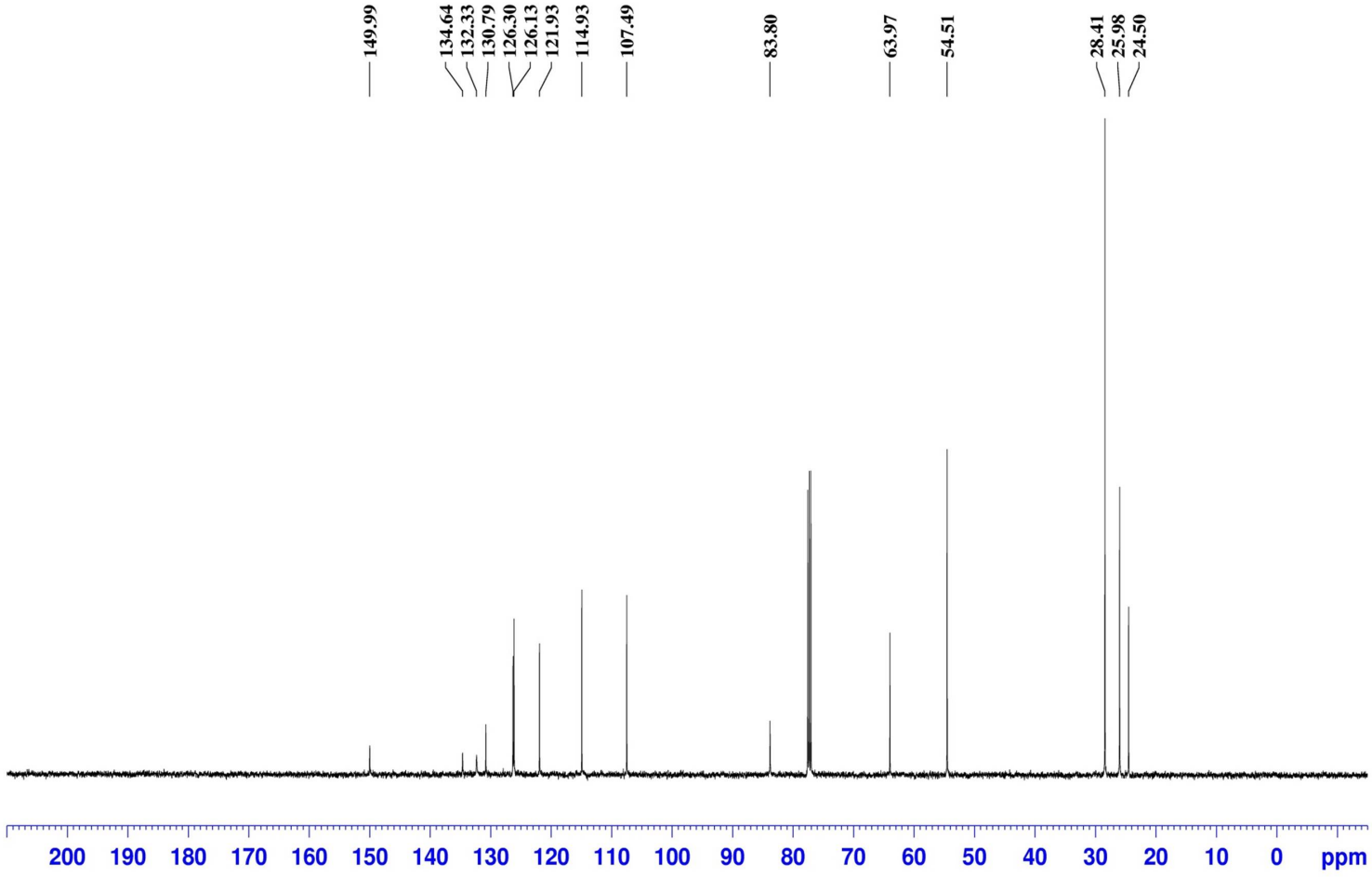
methyl 4–(azepan–1–ylmethyl)benzoate
125 MHz, CDCl3



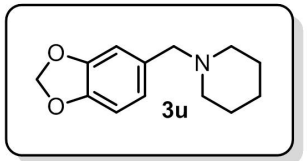


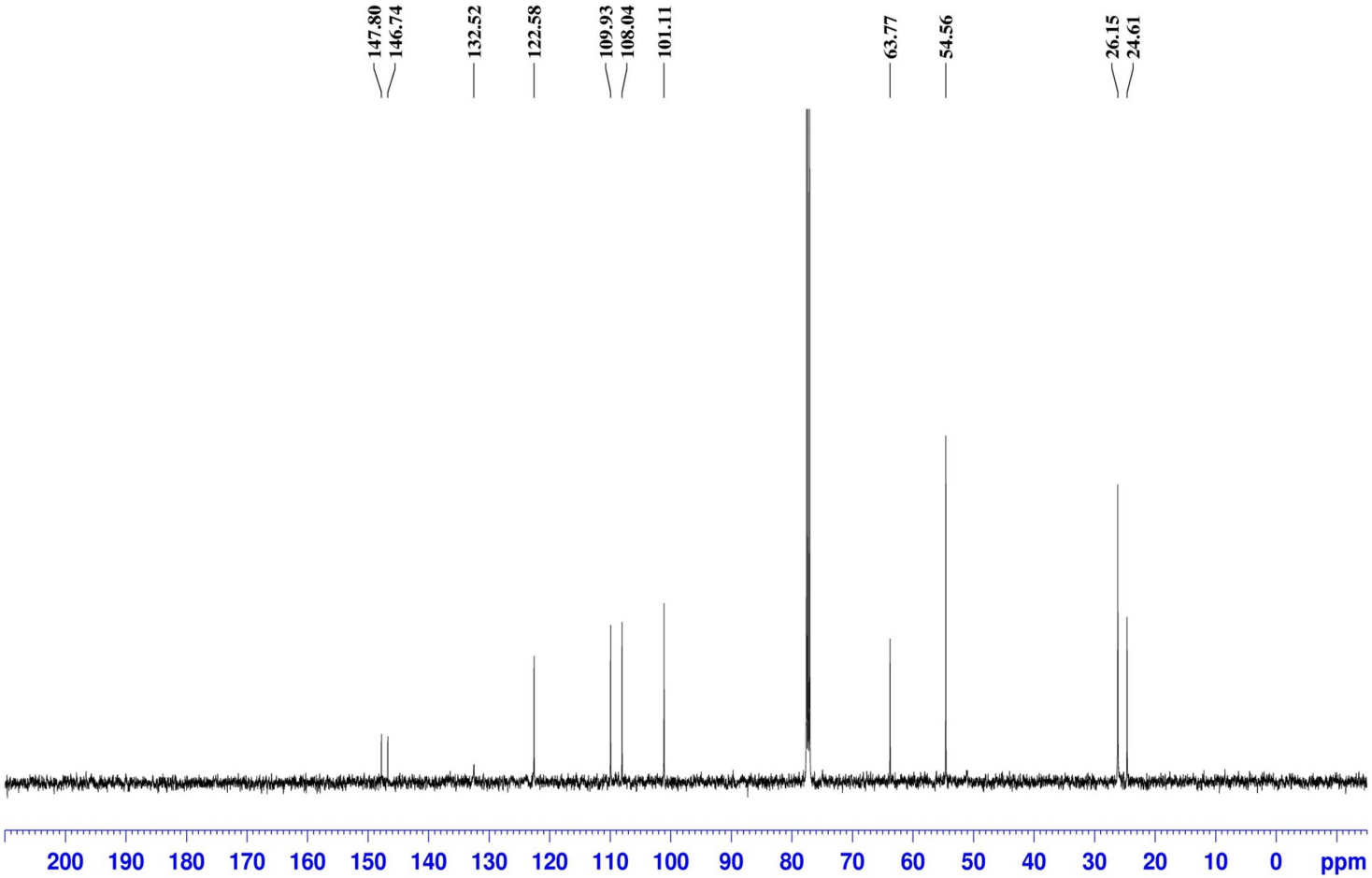
tert−butyl 5−(piperidin−1−ylmethyl)−1H−indole−1−carboxylate
125 MHz, CDCl3



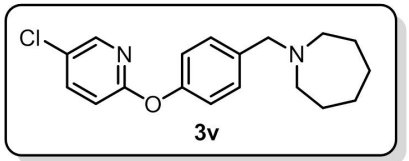


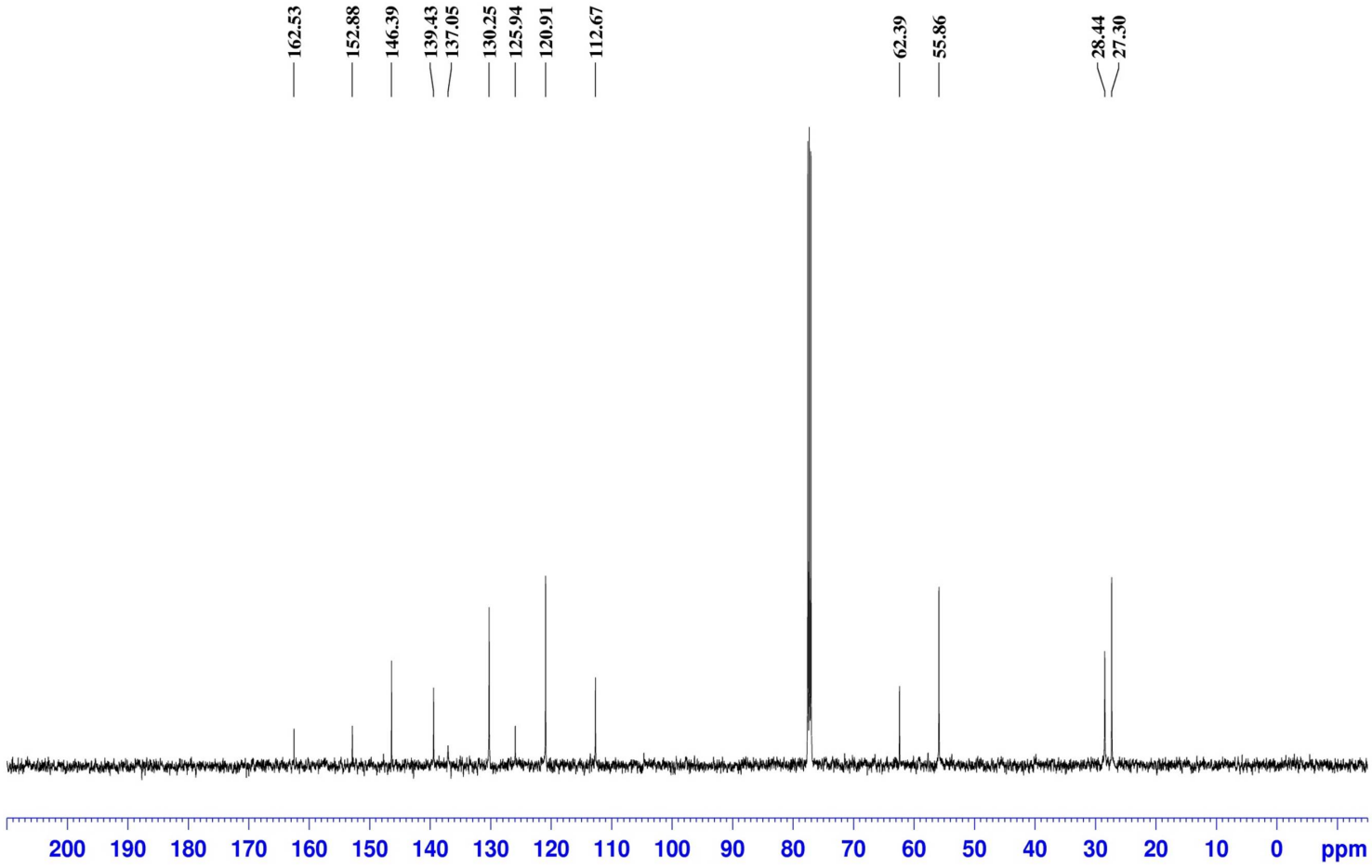
1–(benzo[d][1,3]dioxol–5–ylmethyl)piperidine
125 MHz, CDCl3



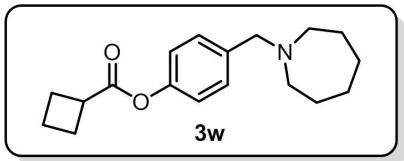


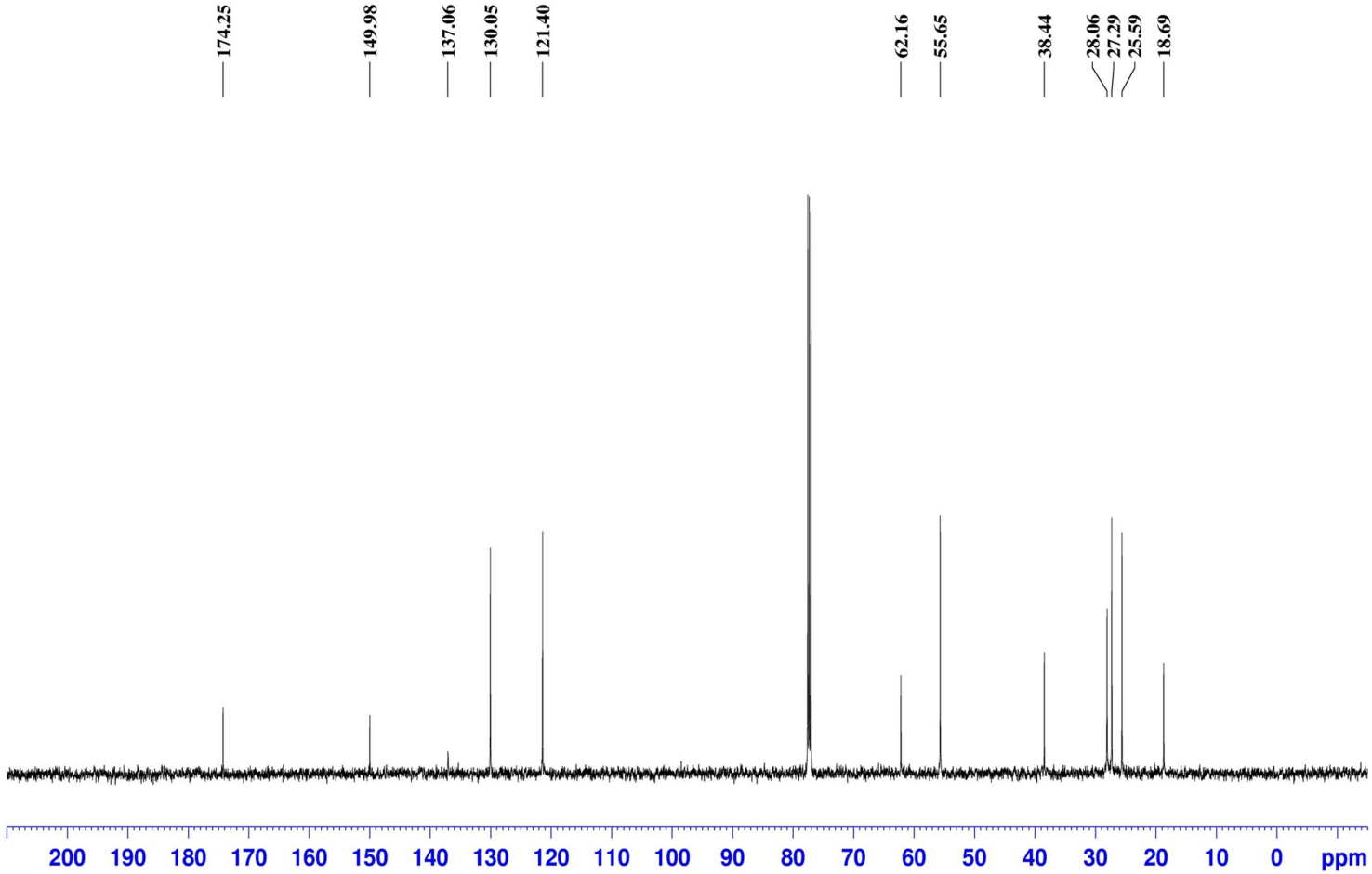
1-(4-((5-chloropyridin-2-yl)oxy)benzyl)azepane
125 MHz, CDCl3



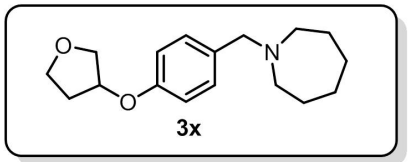


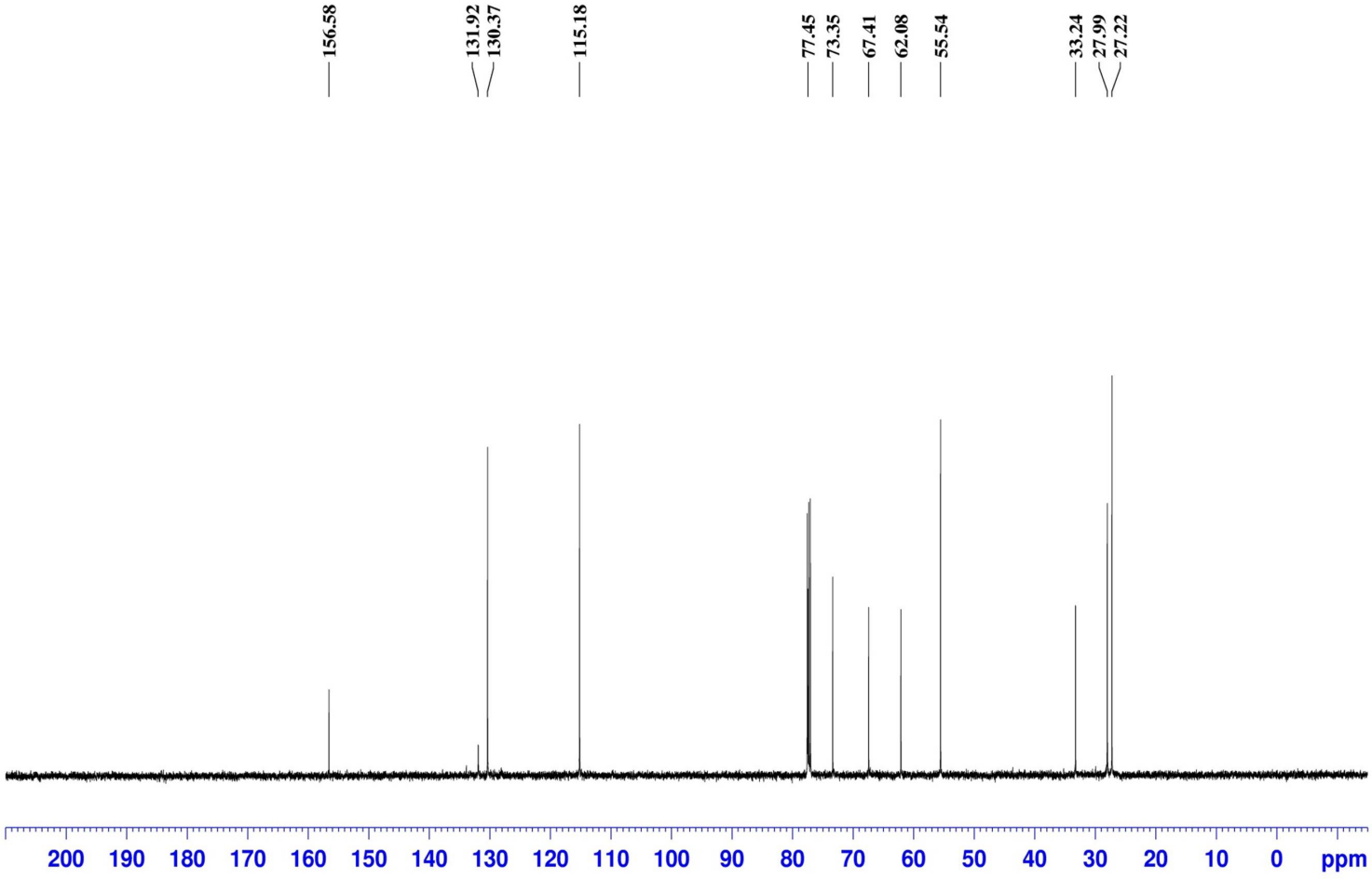
4–(azepan–1–ylmethyl)phenyl cyclobutanecarboxylate
125 MHz, CDCl3



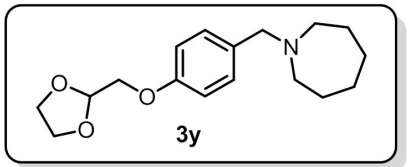


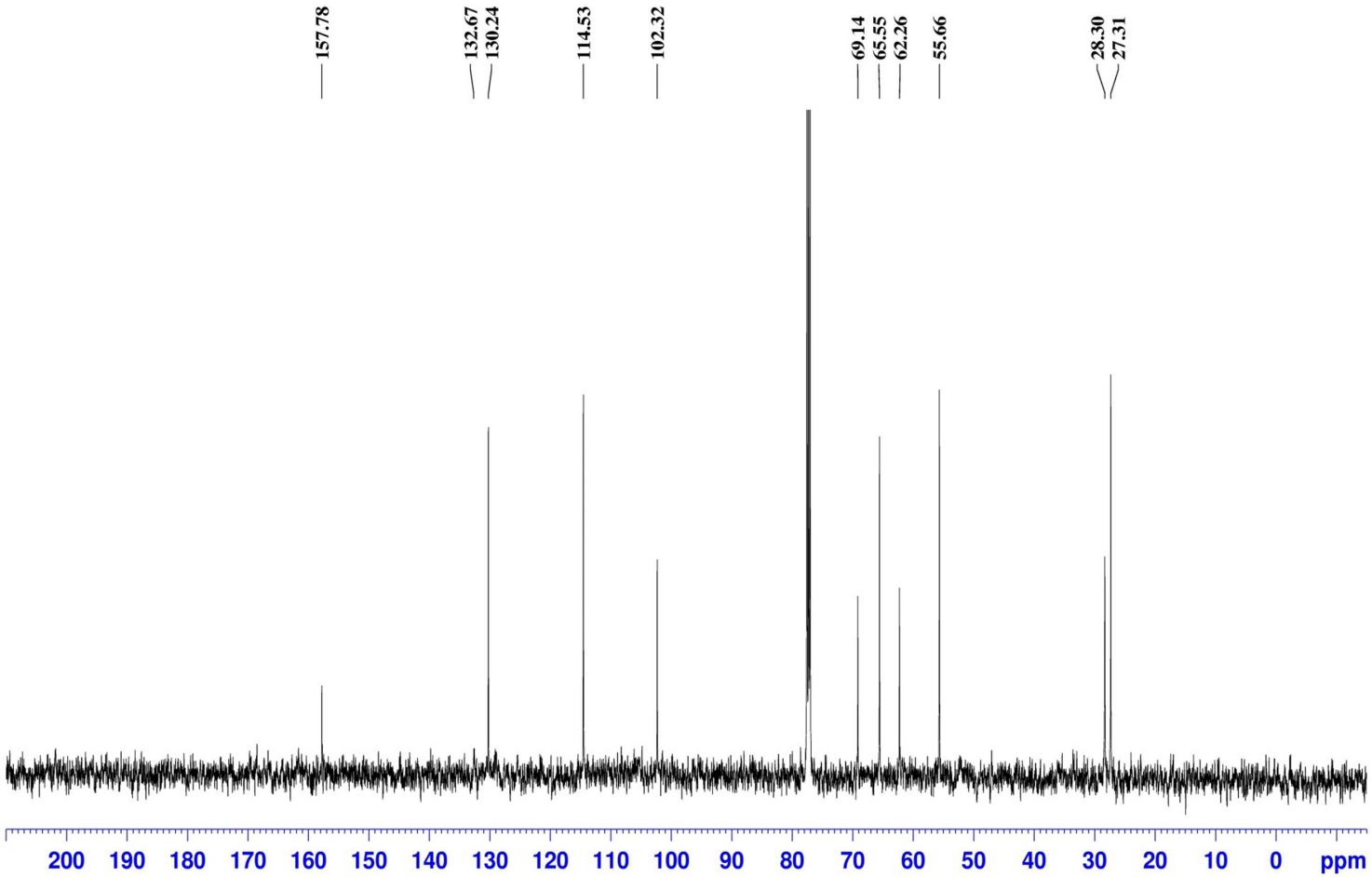
1–(4–((tetrahydrofuran–3–yl)oxy)benzyl)azepane
125 MHz, CDCl3





1–(4–((1,3–dioxolan–2–yl)methoxy)benzyl)azepane
125 MHz, CDCl3





^{19}F NMR Spectra of Synthesized Compounds

2–fluoro–5–(piperidin–1–ylmethyl)pyridine
282 MHz, CDCl3