Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Hydrosilylation of Nitriles and Tertiary Amides to Amines using a Zinc Precursor

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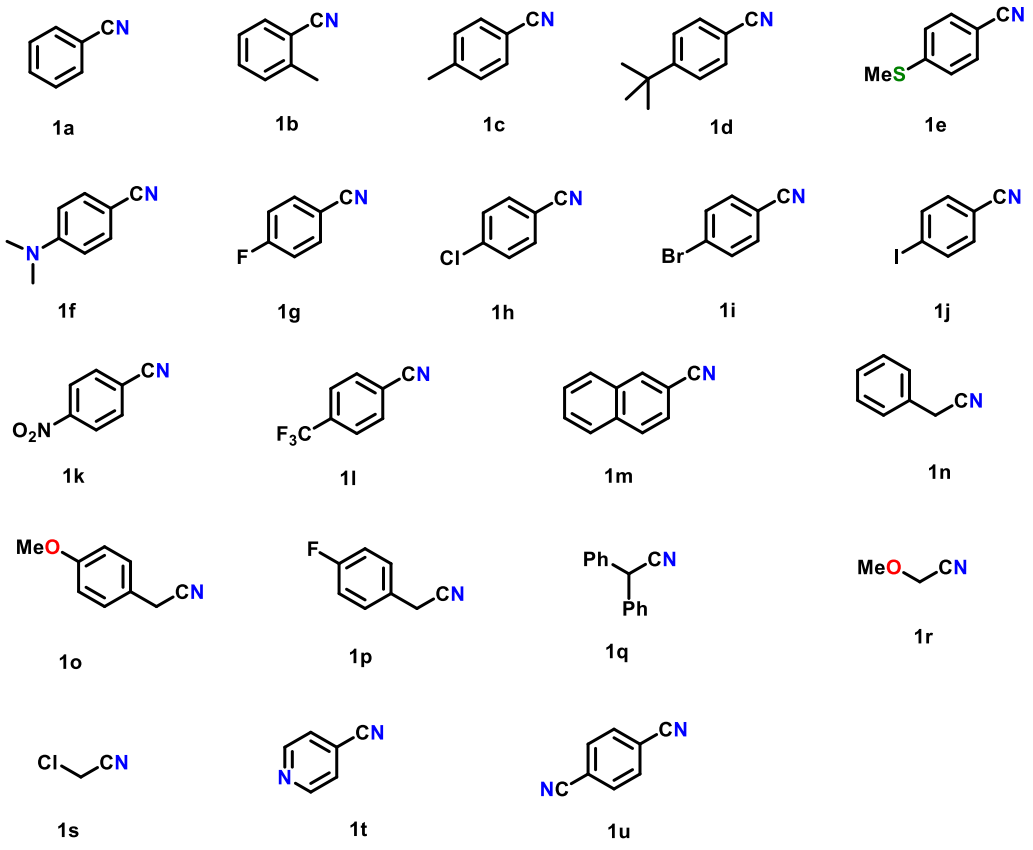
Experimental section

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled M. Braun glove box. Hydrocarbon solvents such as *n*-hexane, THF, and toluene were degassed using sodium metal and $LiAlH_4$ under a nitrogen atmosphere and stored inside the glove box. ^{1}H NMR (400 MHz and 600 MHz,),$^{13}C\{^{1}H\}$ (100 MHz and 150 MHz) spectra were recorded on the BRUKER ADVANCE III-400 and 600 MHz spectrometer. All nitriles and silanes were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals (India) Pvt. Ltd and stored in the glove box and used as received. NMR solvents D_2O, $CDCl_3$, and C_6D_6 were purchased from Merck, whereas $CDCl_3$ and C_6D_6 were distilled over molecular sieves, and stored inside the glove box.

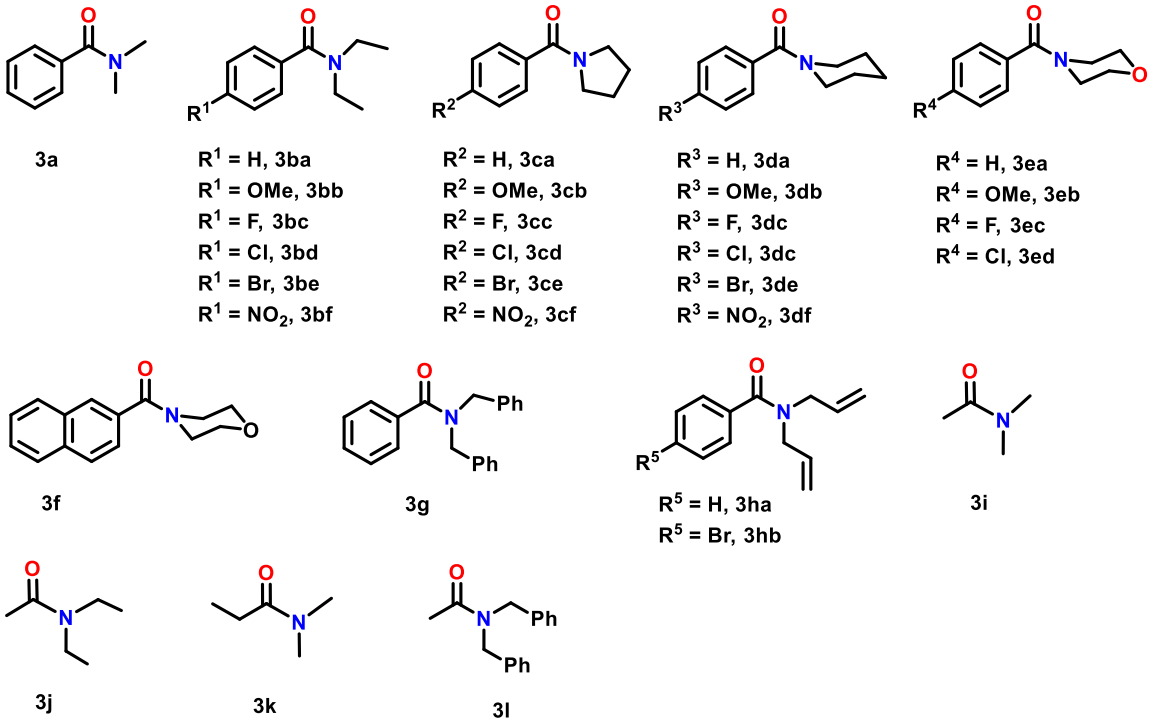
1. List of starting materials

1.1. List of nitriles



All nitriles (**1a-1u**) are commercially available.

1.2. List of tertiary amides

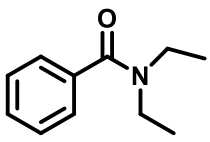


Compounds **3a, 3be, 3cd, 3da, 3dc, 3df, 3ea, 3i, 3j, 3k, and 3l** are commercially available and others are synthesized.

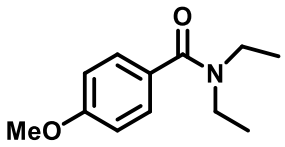
2. General procedure for synthesis of tertiary amides

The round bottom flask was loaded with benzoyl chloride or acetyl chloride (3.55 mmol), amine (3.55 mmol) and triethylamine (0.359 g, 3.55 mmol) in 5 ml of dichloromethane and stirred at room temperature for 12 hours. After that, 0.2 ml of 2N HCl was added to the reaction mixture and workup was done using dichloromethane and water. The organic layer was collected after drying over anhydrous sodium sulfate and evaporated using rotary evaporation, and the compound was purified by column chromatography using petroleum ether/ethyl acetate.

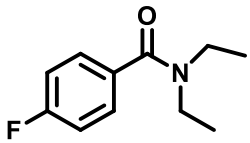
3. NMR data and spectra of tertiary amides



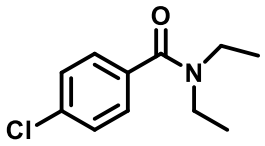
***N, N*-Diethylbenzamide (3ba).**[1] Following procedure **2**, the round bottom flask was loaded with benzoyl chloride (500 mg, 3.55 mmol), *N*, *N*-diethylamine (260.15 mg, 3.55 mmol), and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.5). Yield: 598.59 mg (95%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.39-7.35 (m, 5H, Ar-*H*), 3.54 (s, 2H, C*H*$_2$), 3.24 (s, 2H, C*H*$_2$), 1.24 (s, 3H, C*H*$_3$), 1.10 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 171.4, 137.3, 129.1, 128.4, 126.3, 43.3, 39.3, 14.2, 12.9.



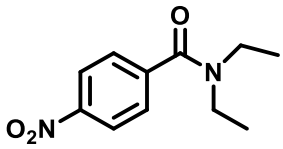
***N, N*-Diethyl-4-methoxybenzamide (3bb)**.[2] Following procedure **2**, the round bottom flask was loaded with 4-methoxybenzoyl chloride (605.59 mg, 3.55 mmol), *N*, *N*-diethylamine (260.15 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.3). Yield: 678.25 mg (92%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.36-7.33 (m, 2H, Ar-*H*), 6.92-6.88 (m, 2H, Ar-*H*), 3.81 (s, 3H, OC*H*$_3$), 3.42 (s, 4H, C*H*$_2$), 1.18 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 171.1, 160.2, 129.4, 128.1, 113.5, 55.2, 43.3, 39.5, 13.1.



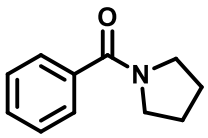
***N, N*-Diethyl-4-fluorobenzamide (3bc)**.[2] Following procedure **2**, the round bottom flask was loaded with 4-fluorobenzoyl chloride (562.88 mg, 3.55 mmol), *N*, *N*-diethylamine (260.15 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.2). Yield: 652.77 mg (94%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.37-7.34 (m, 2H, Ar-*H*), 7.07-7.03 (m, 2H, C*H*$_2$), 3.39 (s, 4H, C*H*$_2$), 1.15 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 170.5, 164.4, 161.9, 133.2, 133.2, 128.6, 128.5, 115.6, 115.4.



***N, N*-Diethyl-4-chlorobenzamide (3bd)**.[2] Following the procedure **2**, the round bottom flask was loaded with 4-chlorobenzoyl chloride (621.28 mg, 3.55 mmol), *N*, *N*-diethylamine (260.15 mg, 3.55 mmol) and triethylamine (359.22 g, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.2). Yield: 715.30 mg (95%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.37-7.29 (m, 4H, Ar-*H*), 3.45 (s, 2H, C*H*$_2$), 3.27 (s, 2H, C*H*$_2$), 1.16 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 170.4, 135.6, 135.3, 132.7, 129.5, 128.8, 128.0, 43.1, 39.5, 13.1.

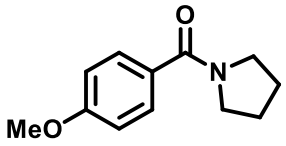


***N, N*-Diethyl-4-chlorobenzamide (3bf)**.[2] Following procedure **2**, the round bottom flask was loaded with 4-nitrobenzoyl chloride (658.73 g, 3.55 mmol), *N*, *N*-diethylamine (260.15 mg, 3.55 mmol), and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 60:40 as eluent (R_f = 0.2). Yield: 711.43 mg (90%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.27-8.24 (m, 2H, Ar-*H*), 7.55-7.53 (m, 2H, Ar-*H*), 3.55 (s, 2H, C*H*$_2$), 3.19 (s, 2H, C*H*$_2$), 1.26 (s, 3H, C*H*$_3$), 1.11 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 169.2, 148.2, 143.3, 127.5, 124.0, 43.4, 39.7, 14.3, 12.9.

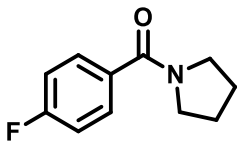


Phenyl(pyrrolidin-1yl)methanone (3ca).[3] Following procedure **2**, the round bottom flask was loaded with benzoyl chloride (500 mg, 3.55 mmol), pyrrolidine (252.44 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.7). Yield: 584.74 mg (94%, colourless liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.53-7.50 (m, 2H, Ar-

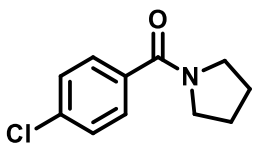
H), 7.41-7.39 (m, 3H, Ar-*H*), 3.67-63 (t, *J* = 8 Hz, 2H, C*H*$_2$), 3.44-3.41 (t, *J* = 6 Hz, 2H, C*H*$_2$), 1.99-1.93 (m, 2H, C*H*$_2$), 1.90-1.85 (m, 2H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 137.3, 129.8, 128.3, 127.1, 49.7, 46.2, 26.4, 24.5.



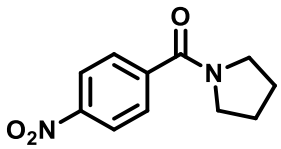
4-Methoxyphenyl(pyrrolidin-1yl)methanone (3cb).[3] Following the procedure **2**, the round bottom flask was loaded with 4-methoxybenzoyl chloride (605.59 mg, 3.55 mmol), pyrrolidine (252.47 mg, 6.83 mmol) and triethylamine (359.22 mg, 6.83 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.6). Yield: 670.37 mg (92%, colourless liquid). ^1H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.50-7.48 (m, 2H, Ar-*H*), 6.88-6.86 (m, 2H, Ar-*H*), 3.80 (s, 3H, OC*H*$_3$), 3.62-3.58 (t, *J* = 8 Hz, 2H, C*H*$_2$), 3.46-3.43 (t, *J* = 6 Hz, 2H, C*H*$_2$), 1.95-1.89 (m, 2H, C*H*$_2$), 1.87-1.80 (m, 2H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 169.5, 160.8, 129.5, 129.2, 113.4, 55.4, 49.9, 46.4, 26.6, 24.5.



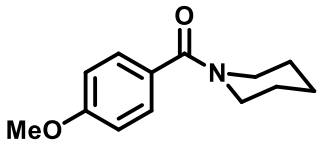
4-Fluorophenyl(pyrrolidin-1yl)methanone (3cc).[4] Following procedure **2**, the round bottom flask was loaded with 4-fluorobenzoyl chloride (562.88 mg, 3.55 mmol), pyrrolidine (252.47 mg, 6.83 mmol), and triethylamine (359.22 mg, 6.83 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.4). Yield: 644.77 mg (94%, colourless liquid). ^1H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.56-7.53 (m, 2H, Ar-*H*), 7.10-7.06 (m, 2H, Ar-*H*), 3.66-3.63 (t, *J* = 6 Hz, 2H, C*H*$_2$), 3.45-3.42 (t, *J* = 6 Hz, 2H, C*H*$_2$), 2.00-1.94 (m, 2H, C*H*$_2$), 1.92-1.85 (m, 2H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 164.8, 162.3, 133.3, 129.6, 129.5, 115.4, 115.2, 49.8, 46.4, 26.5, 24.5.



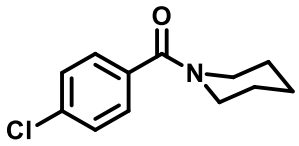
4-Chlorophenyl(pyrrolidin-1yl)methanone (3cd).[5] Following procedure **2**, the round bottom flask was loaded with 4-chlorobenzoyl chloride (621.28 mg, 3.55 mmol), pyrrolidine (252.47 mg, 6.83 mmol) and triethylamine (359.22 mg, 6.83 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.5). Yield: 744.327 mg (94%, colourless liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.44-7.42 (m, 2H, Ar-*H*), 7.34-7.31 (m, 2H, Ar-*H*), 3.61-3.57 (t, *J* = 8 Hz, 2H, C*H*$_2$), 3.38-3.35 (t, *J* = 6 Hz, 2H, C*H*$_2$), 1.95-1.88 (m, 2H, C*H*$_2$), 1.87-1.80 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



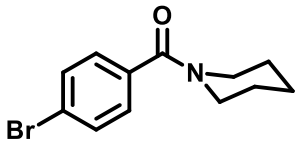
4-Nitrophenyl(pyrrolidin-1yl)methanone (3cf).[5] Following procedure **2**, the round bottom flask was loaded with 4-nitrobenzoyl chloride (658.73 g, 3.55 mmol), pyrrolidine (252.47 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 60:40 as eluent (R_f = 0.2). Yield: 687.99 mg (88%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.25-8.22 (m, 2H, Ar-*H*), 7.67-7.65 (m, 2H, Ar-*H*), 3.64 (s, 2H, C*H*$_2$), 3.43-3.37 (t, *J* = 6 Hz, 2H, C*H*$_2$), 1.96 (s, 2H, C*H*$_2$), 1.92 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 167.5, 148.5, 143.1, 128.2, 123.8, 49.6, 46.5, 26.4, 24.4.



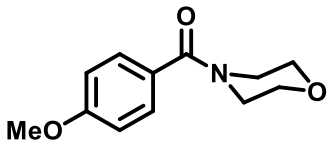
4-Methoxyphenyl(piperidin-1yl)methanone (3db).[6] Following procedure **2**, the round bottom flask was loaded with 4-methoxybenzoyl chloride (605.59 mg, 3.55 mmol), piperidine (302.28 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.4). Yield: 731.74 mg (94%, colourless). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.38-7.36 (m, 2H, Ar-*H*), 6.91-6.89 (m, 2H, Ar-*H*), 3.82 (s, 2H, OC*H*$_3$) 3.64 (s, 2H, C*H*$_2$), 3.44 (s, 2H, C*H*$_2$), 1.67-158 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 170.3, 160.5, 128.8, 128.5, 113.6, 55.3, 49.0, 43.3, 26.1, 24.6.



4-Chlorophenyl(piperidin-1yl)methanone (3dd).[6] Following procedure **2**, the round bottom flask was loaded with 4-chlorobenzoyl chloride (621.28 mg, 3.55 mmol), piperidine (302.28 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.7). Yield: 730.61 mg (92%, colourless). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.39-7.33 (m, 4H, Ar-*H*), 3.69 (s, 2H, CH_2), 3.34 (s, 2H, CH_2), 1.72-1.42 (m, 6H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 169.3, 135.4, 134.9, 128.7, 128.4, 53.5, 48.8, 43.3, 26.5, 24.6.

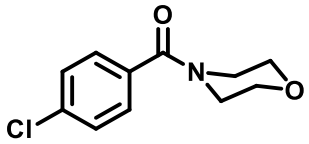


4-Bromophenyl(piperidin-1yl)methanone (3de).[7] Following procedure **2**, the round bottom flask was loaded with 4-bromobenzoyl chloride (779.08 mg, 3.55 mmol), piperidine (302.28 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 70:30 as eluent (R_f = 0.5). Yield: 875.78 mg (92%, brownish solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.55-7.52 (m, 2H, Ar-*H*), 7.29-7.26 (m, 2H, Ar-*H*), 3.69 (s, 2H, CH_2), 3.32 (s, 2H, CH_2), 1.72-1.52 (m, 6H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 169.4, 135.4, 131.7, 128.7, 123.7, 48.9, 43.3, 26.6, 25.7, 24.6.

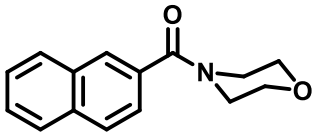


4-Methoxyphenyl(morphlino)methanone (3eb).[8] Following procedure **2**, the round bottom flask was loaded with 4-methoxybenzoyl chloride (605.59 mg, 3.55 mmol), morpholine (309.27 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 60:40 as eluent (R_f = 0.3). Yield: 722.62 mg (92%, colourless liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.40-

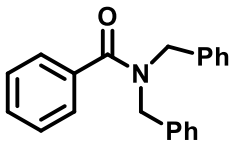
7.38 (m, 2H, Ar-*H*), 6.93-6.91 (m, 2H, Ar-*H*), 3.83 (s, 3H, OCH_3), 3.70-3.64 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 170.5, 161.0, 129.3, 127.3, 113.8, 67.0, 55.4, 43.6.



4-chlorophenyl(morphlino)methanone (3eb).[9] Following procedure **2**, the round bottom flask was loaded with 4-chlorobenzoyl chloride (621.28 mg, 3.55 mmol), morpholine (309.27 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 80:20 as eluent (R_f = 0.3). Yield: 729.01 mg (91%, colourless liquid). ^1H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.41-7.34 (m, 4H, Ar-*H*), 3.71-3.46 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 169.5, 136.1, 133.7, 128.8, 66.9, 48.3.

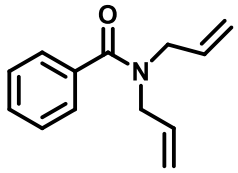


Morpholino(naphthalen-2-yl)methanone (3f).[9] Following procedure **2**, the round bottom flask was loaded with 2-naphthoyl chloride (676.73 mg, 3.55 mmol), morpholine (309.27 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 80:20 as eluent (R_f = 0.4). Yield: 770.90 mg (90%, colourless solid). ^1H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.92-7.85 (m, 2H, Ar-*H*), 7.55-7.48 (m, 2H, Ar-*H*), 3.80-3.51 (m, 8H, CH_2. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 170.7, 135.9, 133.8, 132.8, 128.5, 127.9, 127.2, 126.9, 125.6, 124.3, 67.0, 53.5.

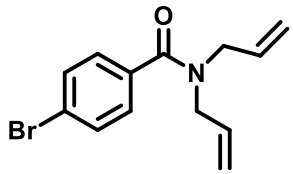


***N, N*-Dibenzylbenzamide (3g)**.[3] Following procedure **2**, the round bottom flask was loaded with benzoyl chloride (500 mg, 3.55 mmol), dibenzylamine (700.34 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 80:20 as eluent (R_f = 0.6). Yield: 962.93 mg

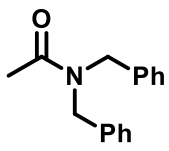
(90%, colourless solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.52-7.13 (m, 15H, Ar-*H*), 4.71 (s, 2H, C*H*$_2$), 4.41 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 172.4, 136.3, 129.8, 129.0, 128.9, 128.7, 128.5, 127.8, 127.2, 126.8, 51.6, 47.0.



***N, N*-Diallylbenzamide (3ha)**.[10] Following procedure **2**, the round bottom flask was loaded with benzoyl chloride (500 mg, 3.55 mmol), diallylamine (344.91 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 80:20 as eluent (R_f = 0.6). Yield: 657.34 mg (92%, colourless liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.44-7.36 (m, 5H, Ar-*H*), 5.88 (s, 1H, alkene-C*H*), 5.73 (s, 1H, alkene-C*H*), 5.25-5.17 (m, 4H, alkene-C*H*), 4.14 (s, 2H, C*H*$_2$), 3.83 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 171.8, 136.4, 129.7, 128.4, 126.7, 117.7, 50.8, 47.0.



***N, N*-Diallyl-4-bromobenzamide (3hb)**.[10] Following procedure **2**, the round bottom flask was loaded with 4-bromobenzoyl chloride (779.08 mg, 3.55 mmol), diallylamine (344.91 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 80:20 as eluent (R_f = 0.2). Yield: 875.25 mg (88%, brownish liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.54-7.51 (m, 2H, Ar-*H*), 7.34-7.28 (m, 2H, Ar-*H*), 5.86 (s, 1H, alkene-C*H*), 5.72 (s, 1H, alkene-C*H*), 5.26-4.92 (m, 4H, alkene-C*H*), 4.12 (s, 2H, C*H*$_2$), 3.82 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 170.8, 135.1, 131.7, 128.4, 124.1, 117.9, 50.8, 47.3.



***N, N*-Dibenzylacetamide (3i)**.[11] Following procedure **2**, the round bottom flask was loaded with acetyl chloride (278.67 mg, 3.55 mmol), dibenzylamine (700.34 mg, 3.55 mmol) and triethylamine (359.22 mg, 3.55 mmol) in 5ml of dichloromethane and product was isolated by column chromatography using petroleum ether/ethylacetate = 80:20 as eluent (R_f = 0.7). Yield: 722.14 mg (88%, colourless solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.39-7.14 (m, 10H, Ar-*H*), 4.60 (s, 2H, C*H*$_2$), 4.43 (s, 2H, C*H*$_2$), 2.21(s, 2H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_c (ppm) 137.4, 136.5, 129.1, 128.7, 128.4, 127.7, 127.5, 126.5, 50.8, 48.0, 21.8.

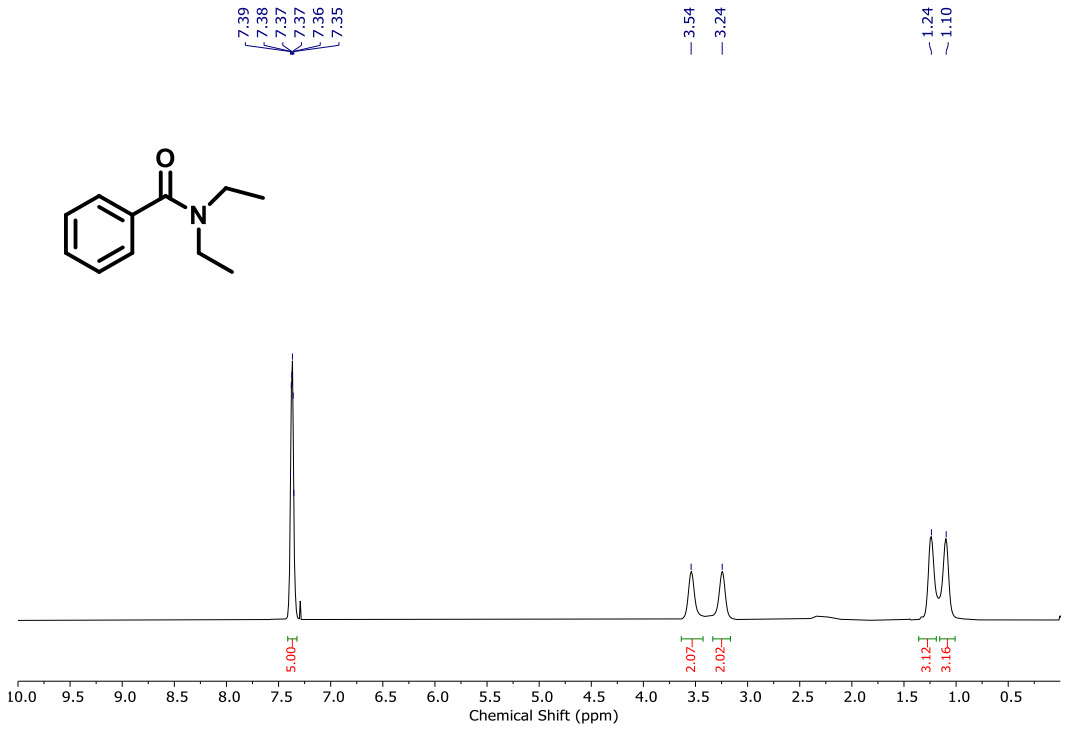


Figure S1: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3ba**.

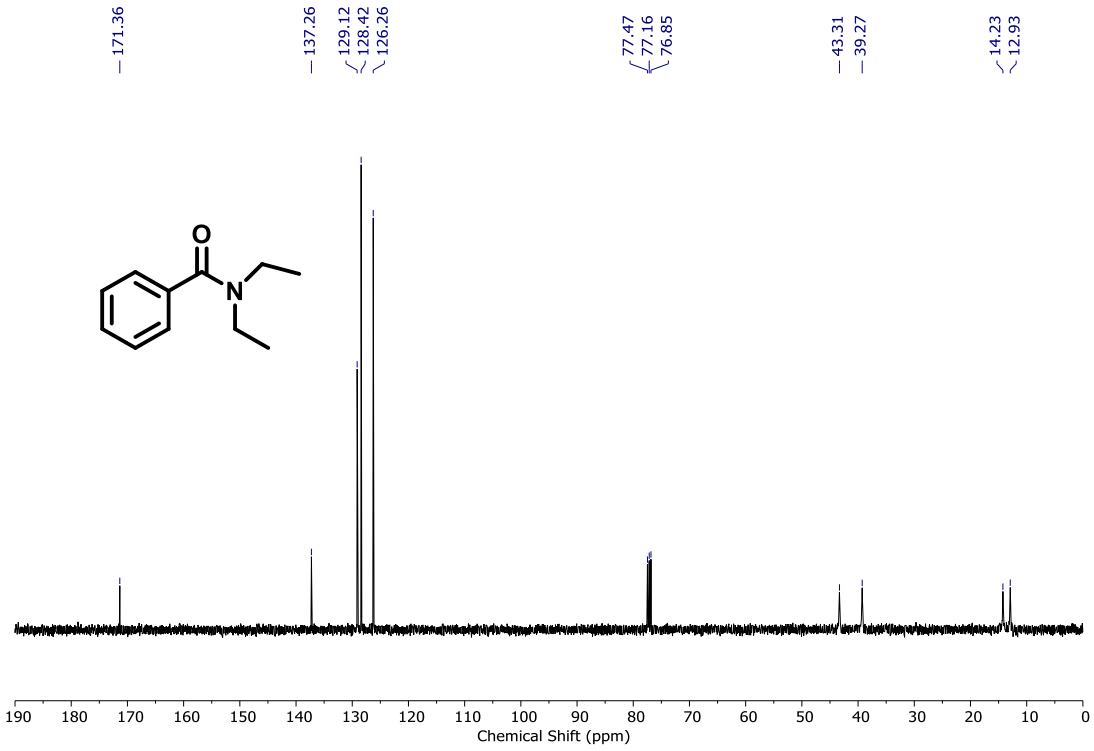


Figure S2: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3ba**.

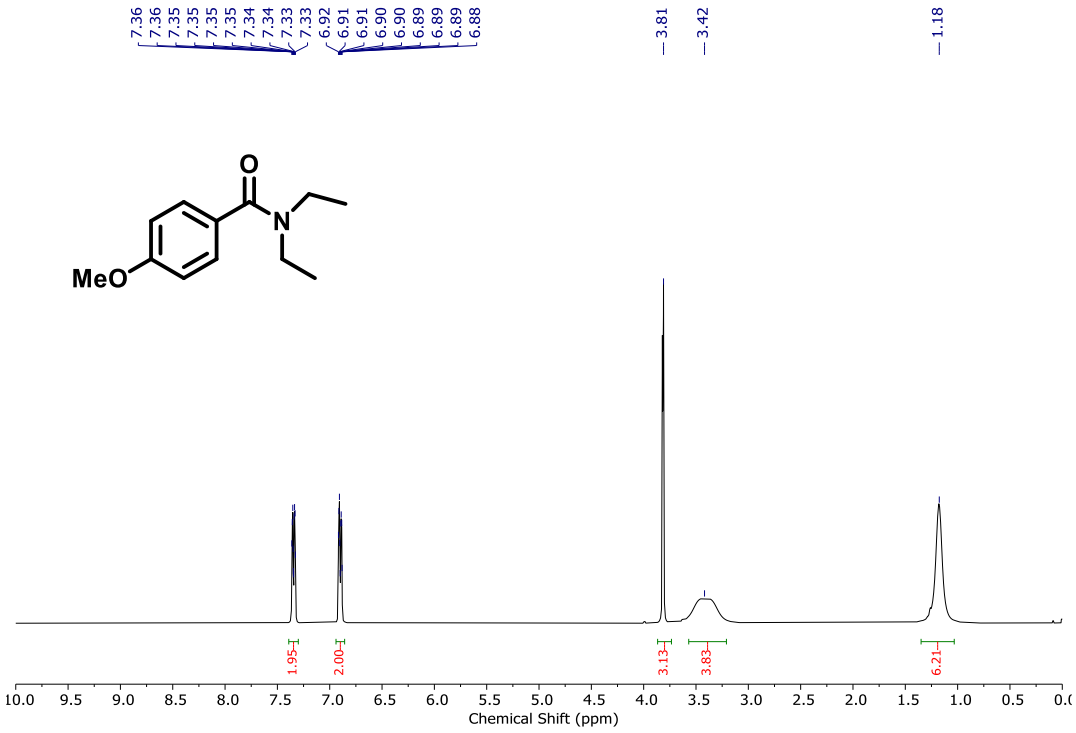


Figure S3: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3bb**.

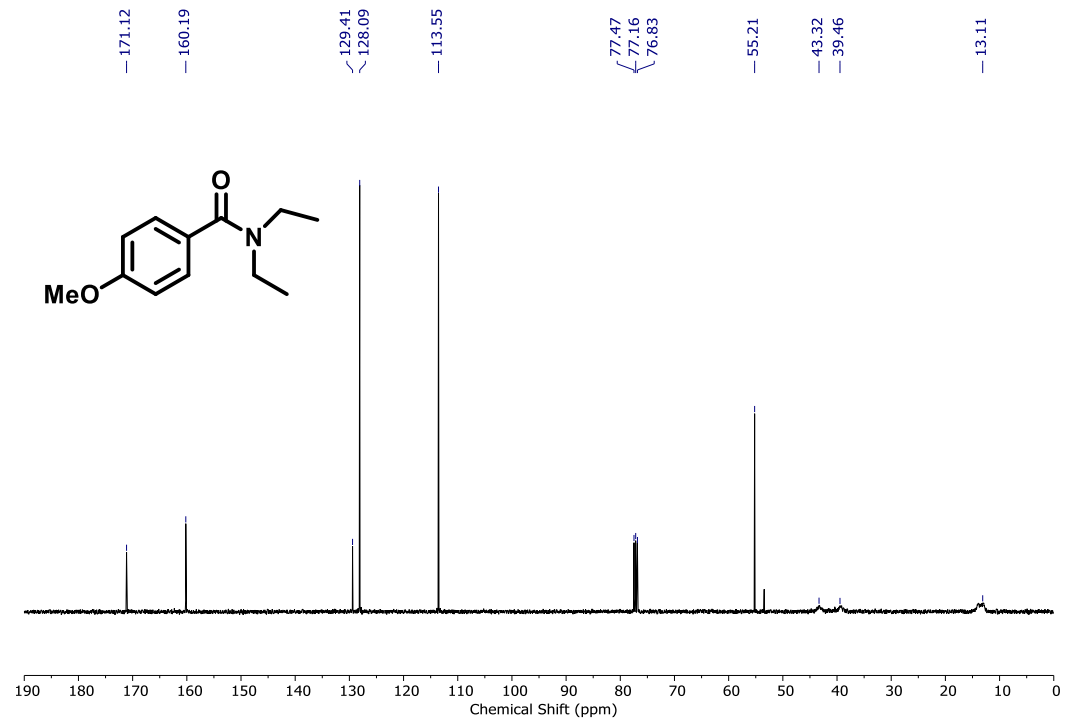


Figure S4: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3bb**.

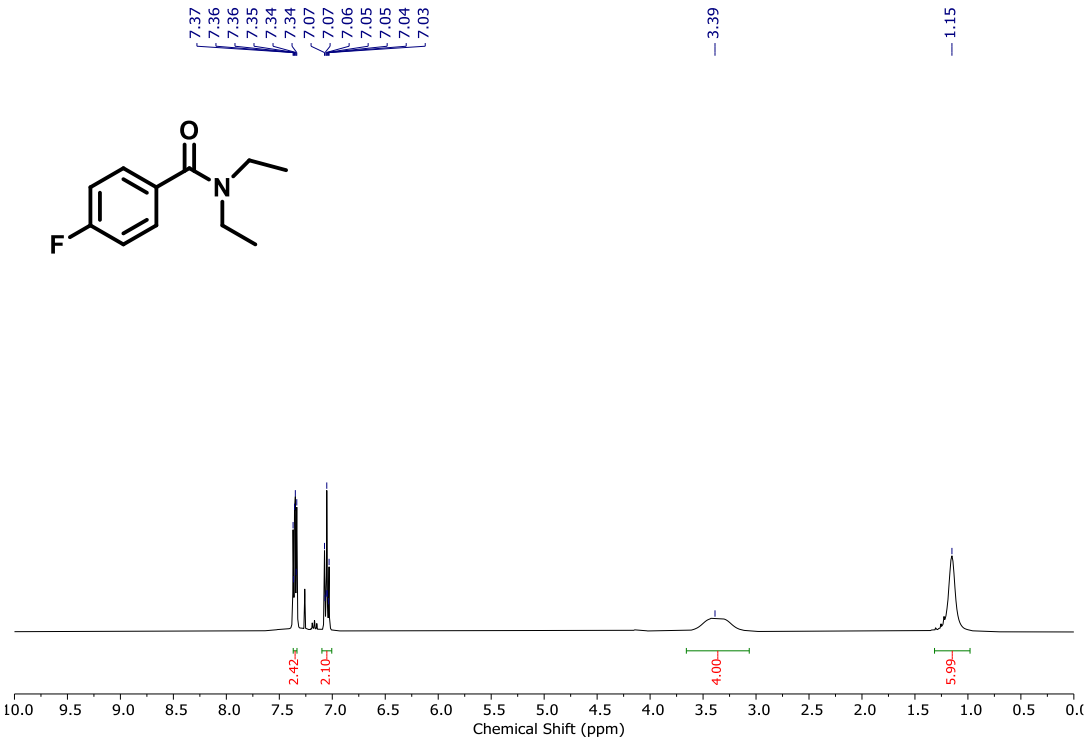


Figure S5: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3bc**.

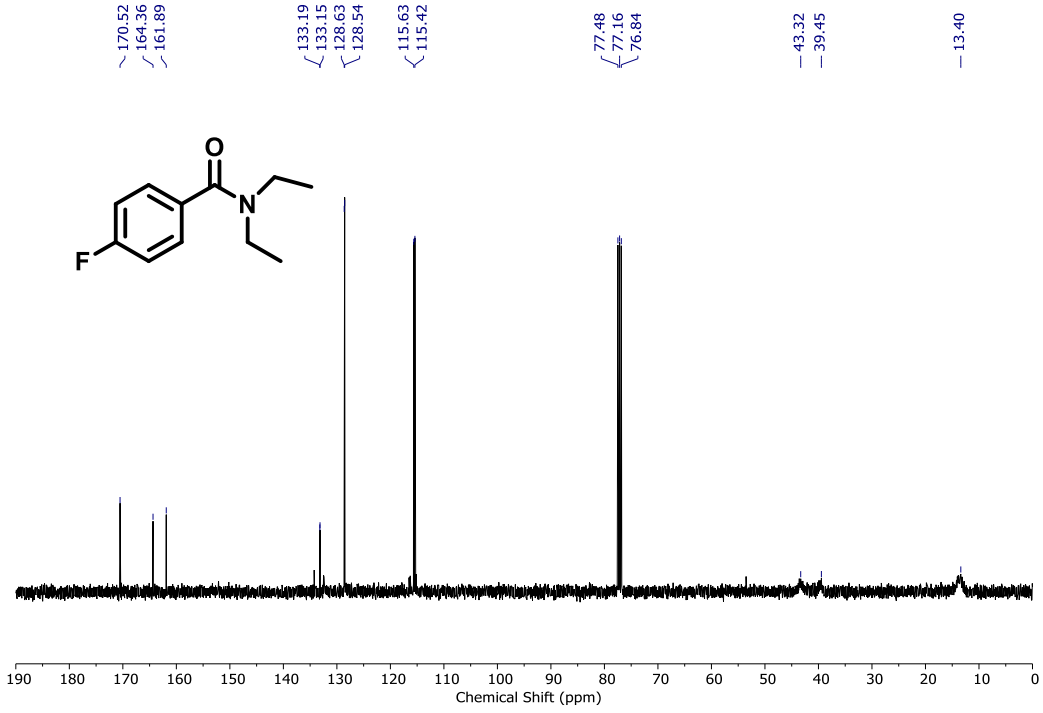


Figure S6: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3bc**.

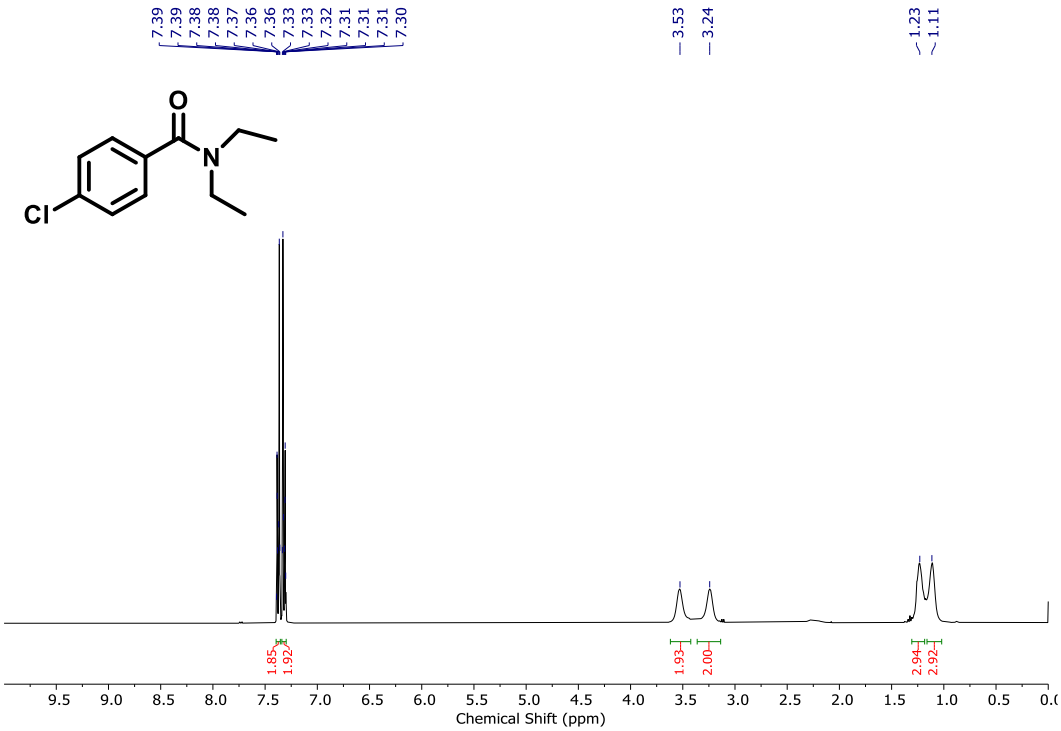


Figure S7: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3bd**.

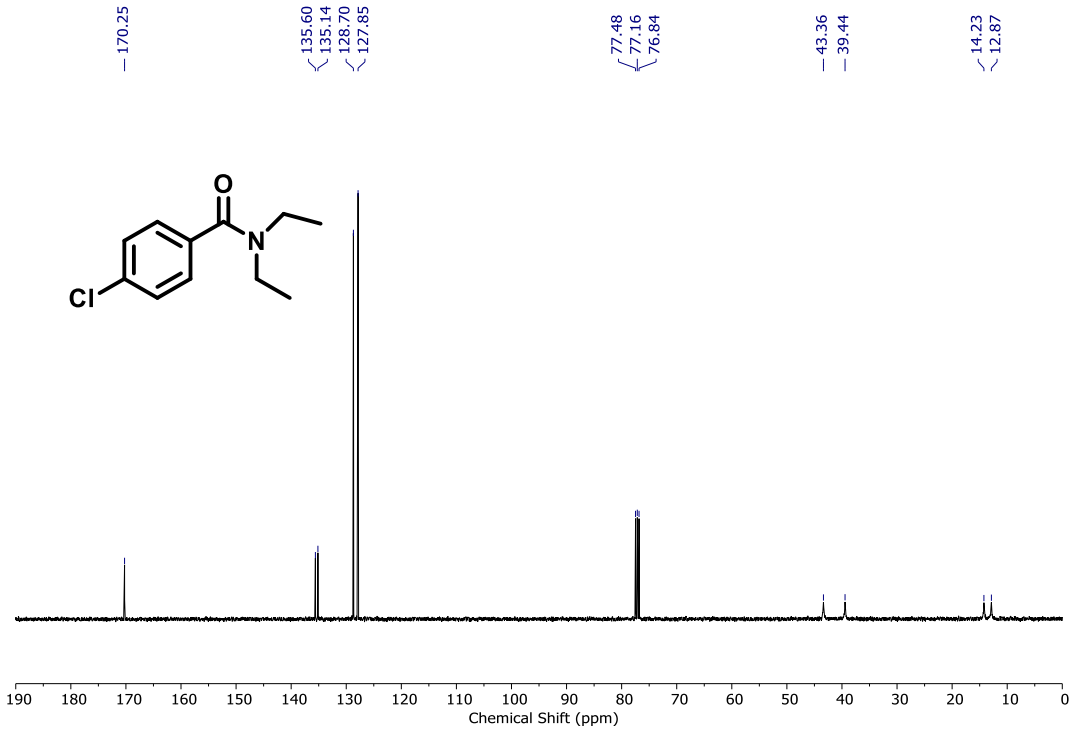


Figure S8: ^{13}C{^{1}H} (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3bd**.

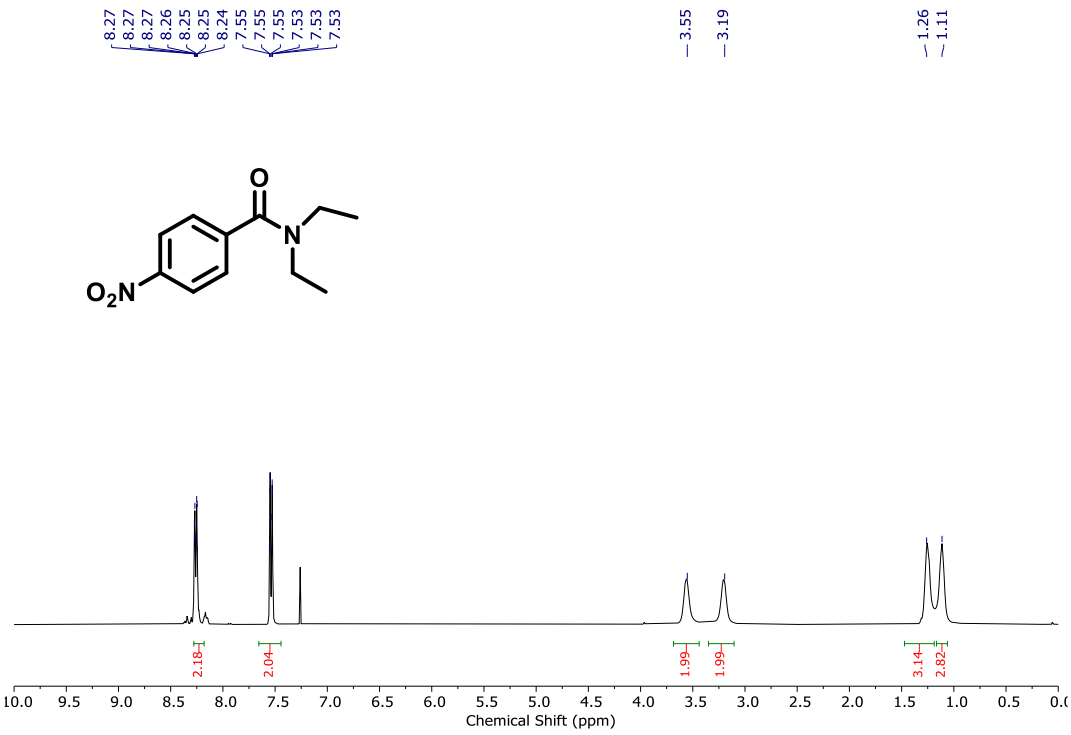


Figure S9: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3bf**.

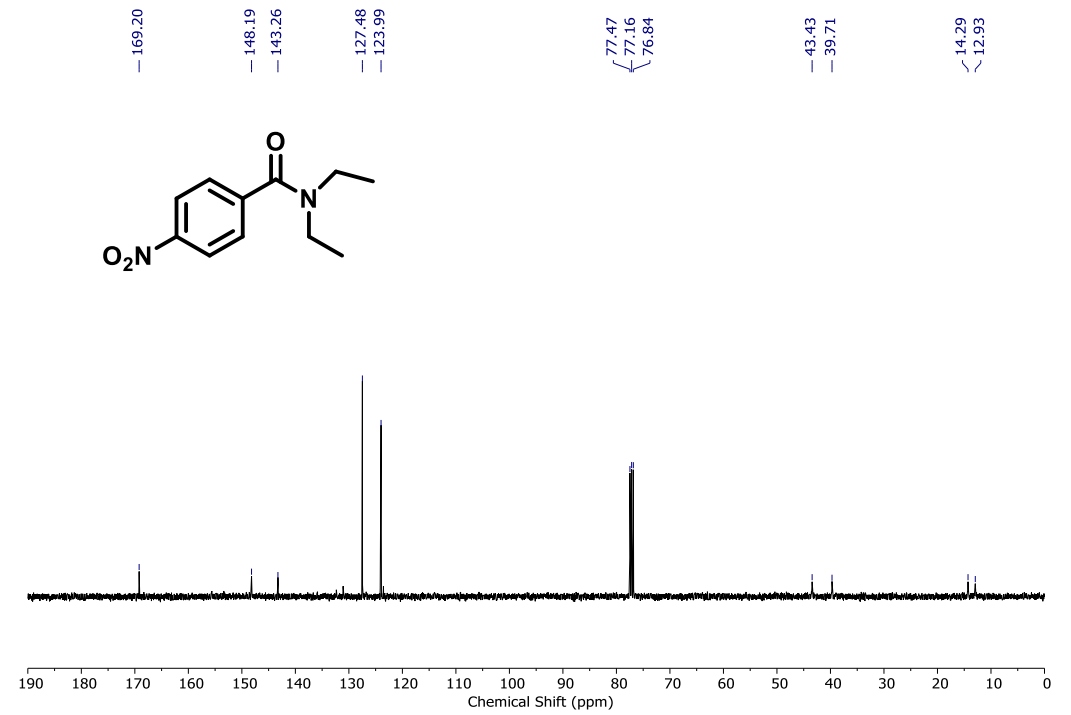


Figure S10: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3bf**.

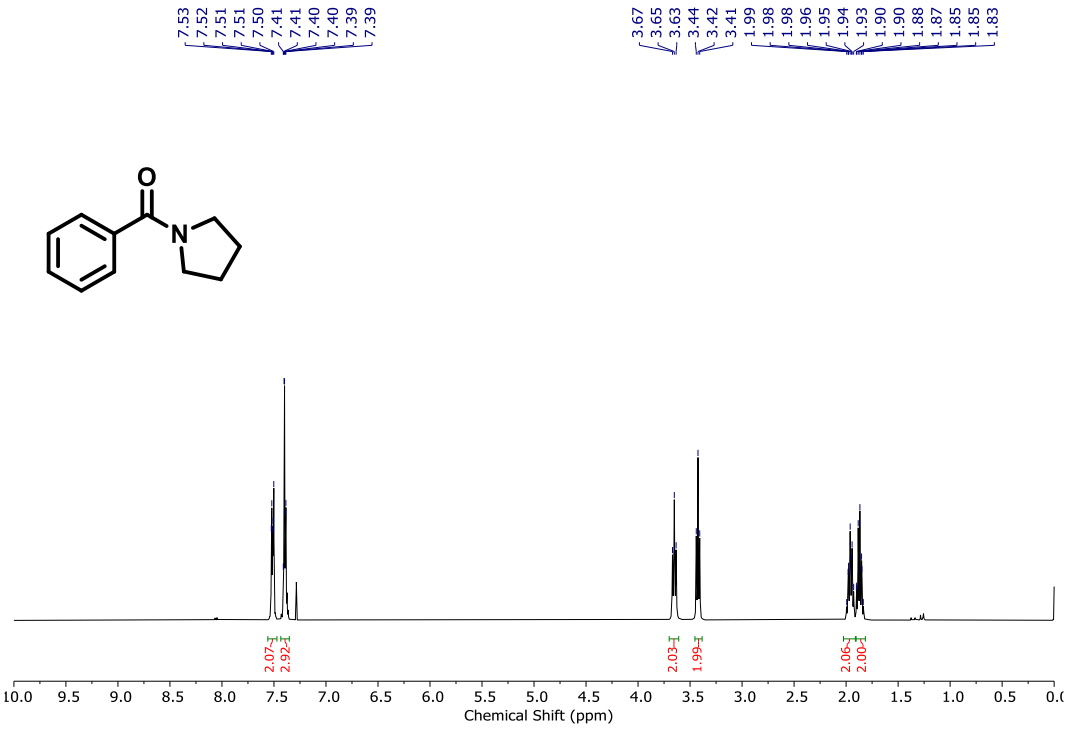


Figure S11: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3ca**.

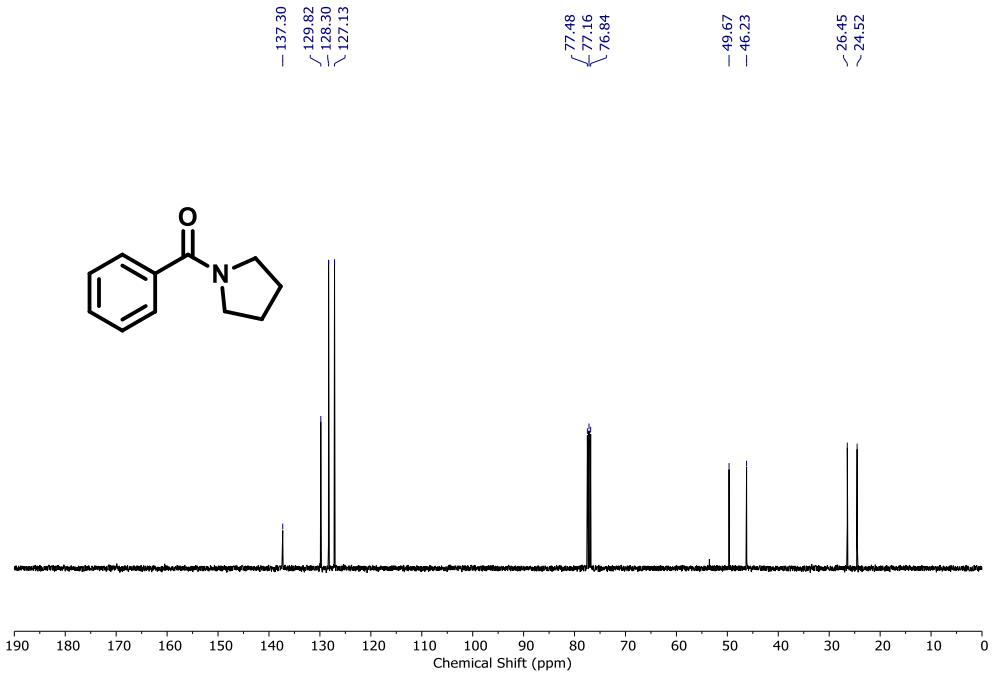


Figure S12: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3ca**.

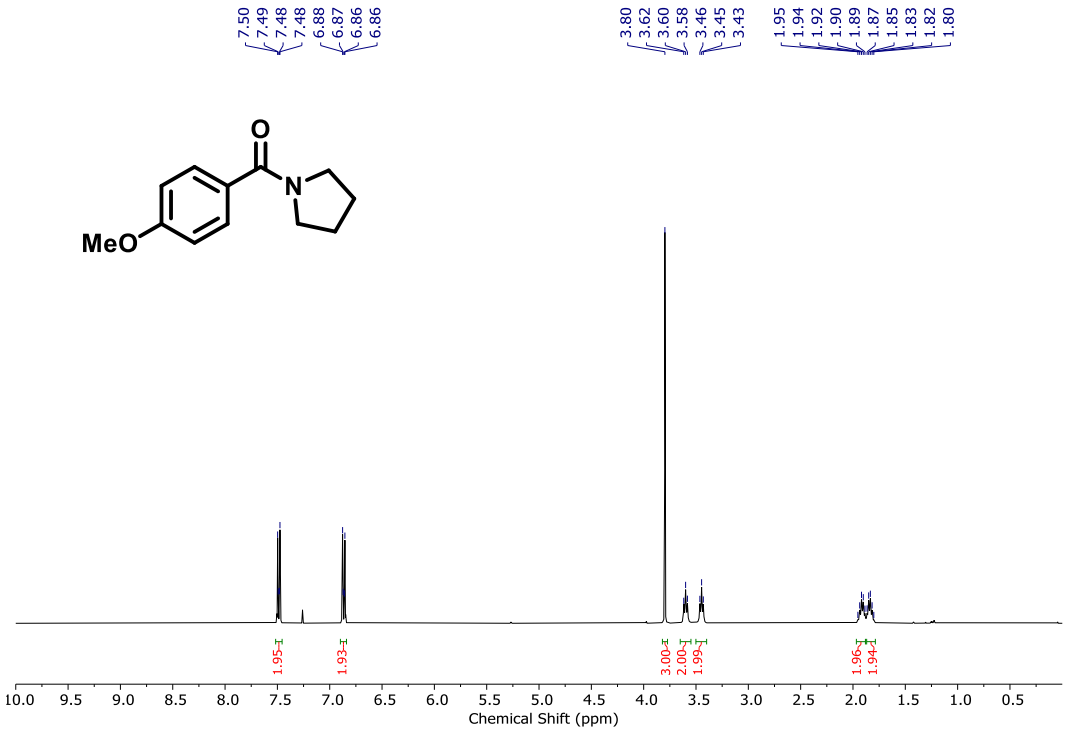


Figure S13: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3cb**.

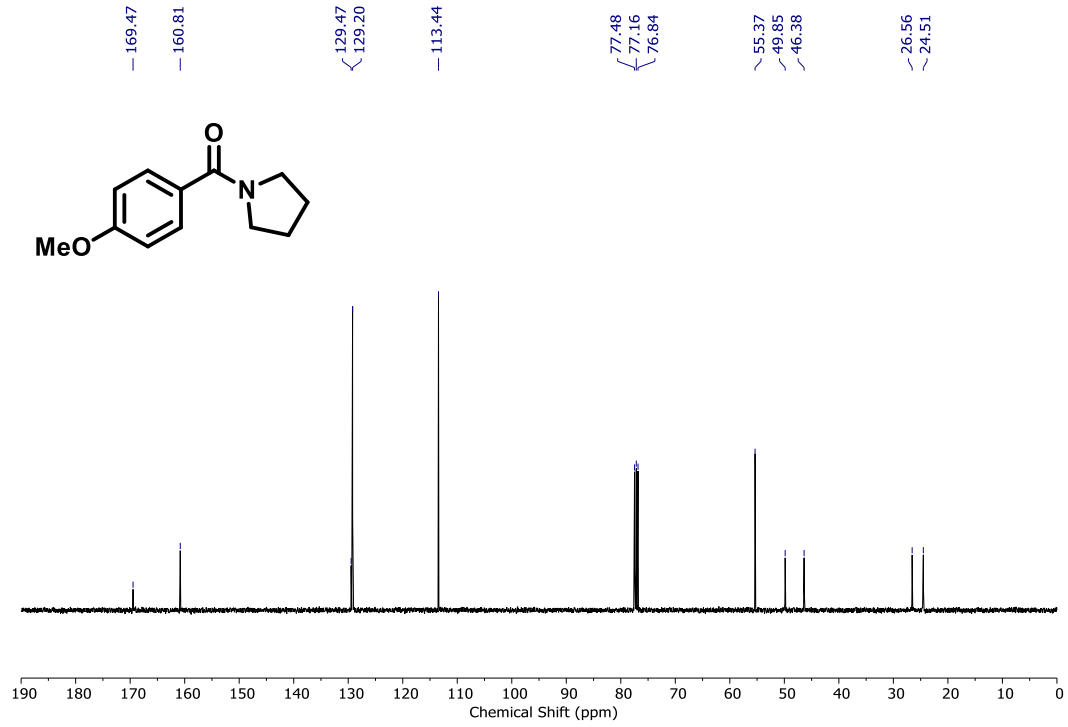


Figure S14: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3cb**.

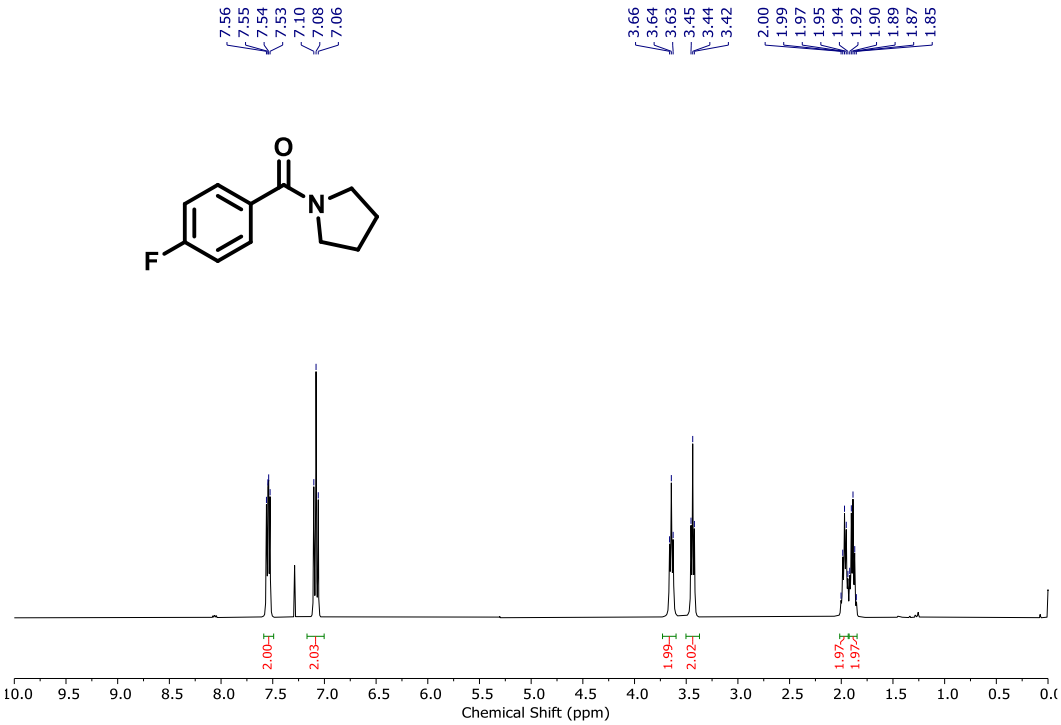


Figure S15: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3cc**.

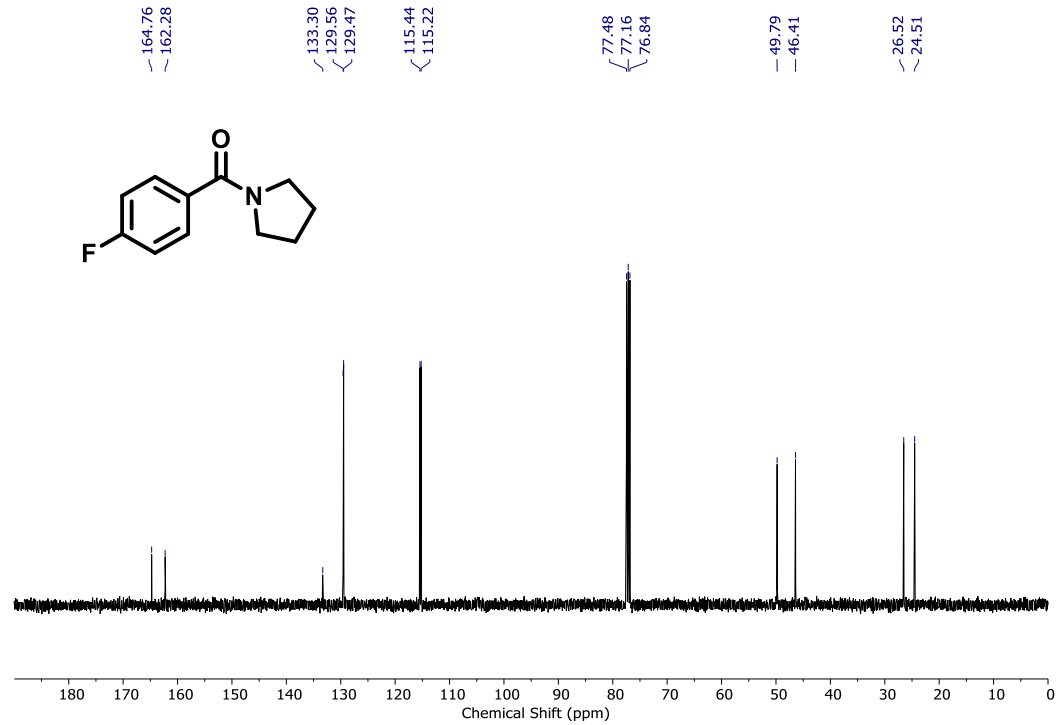


Figure S16: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3cc**.

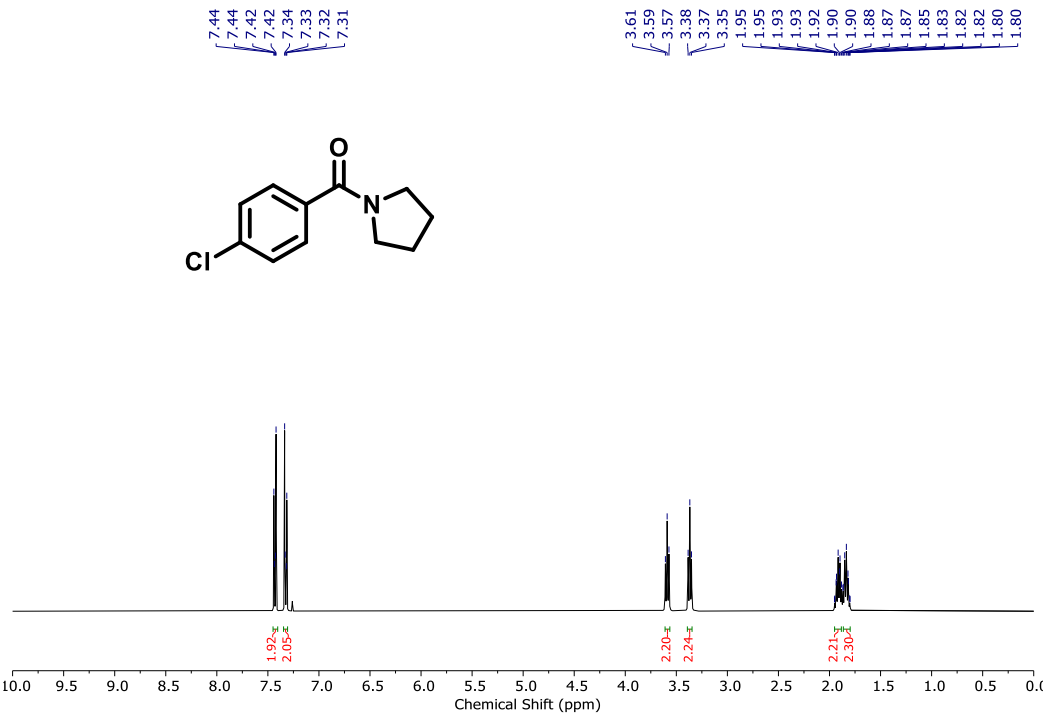


Figure S17: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3cd**.

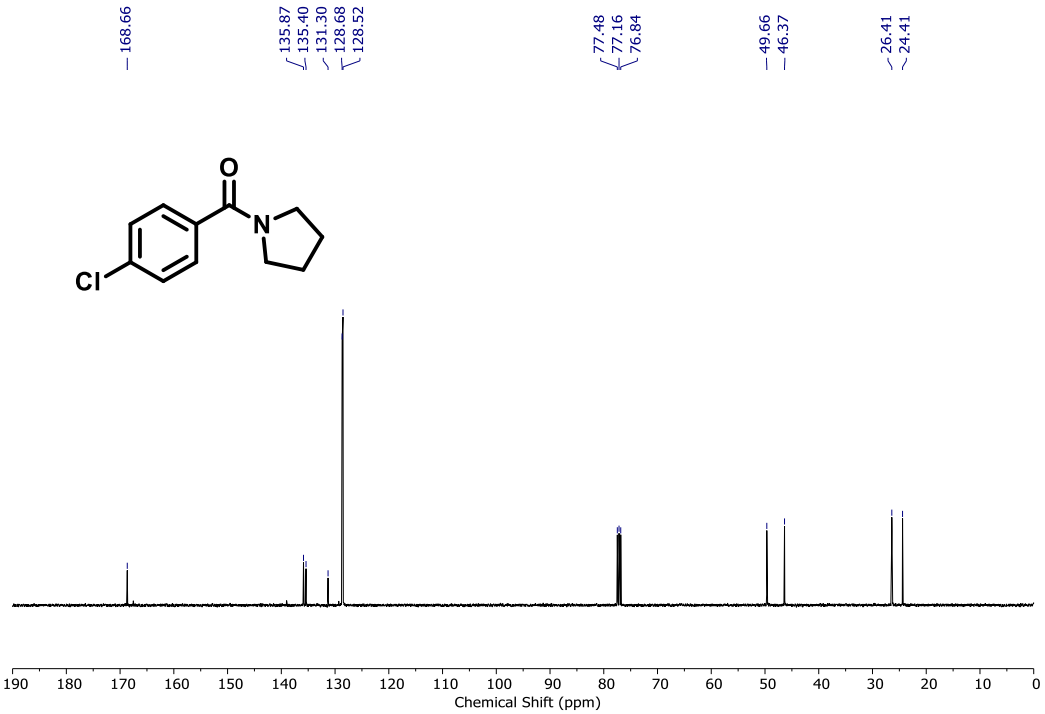


Figure S18: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3cd**.

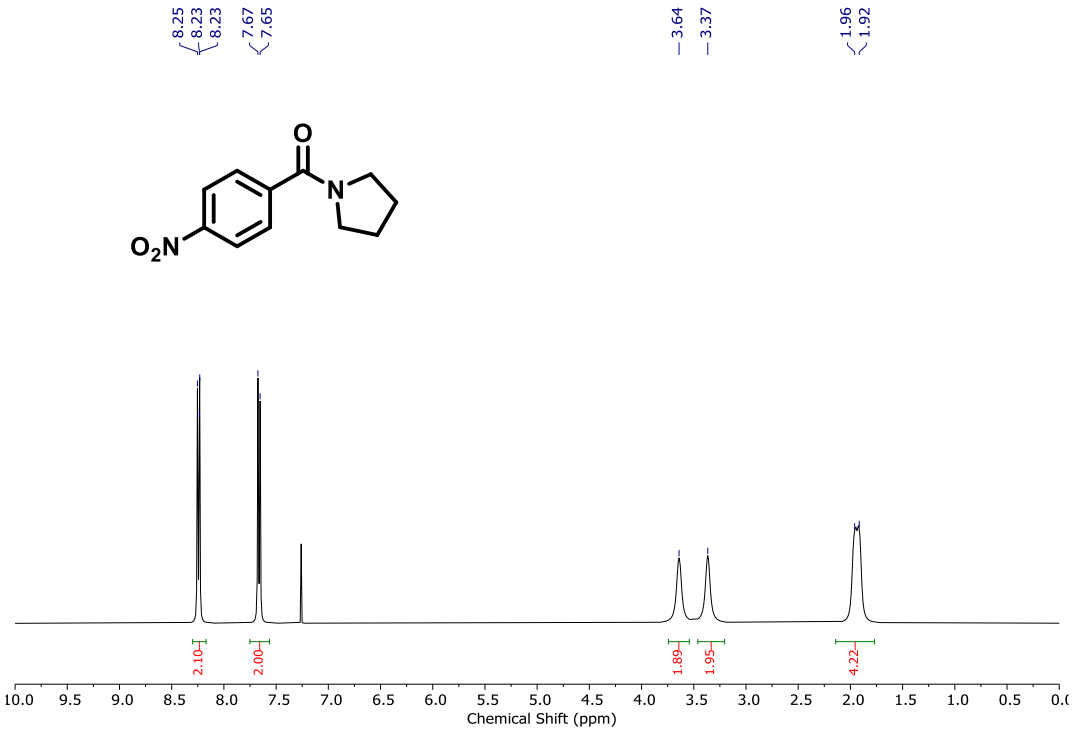


Figure S19: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3cf**.

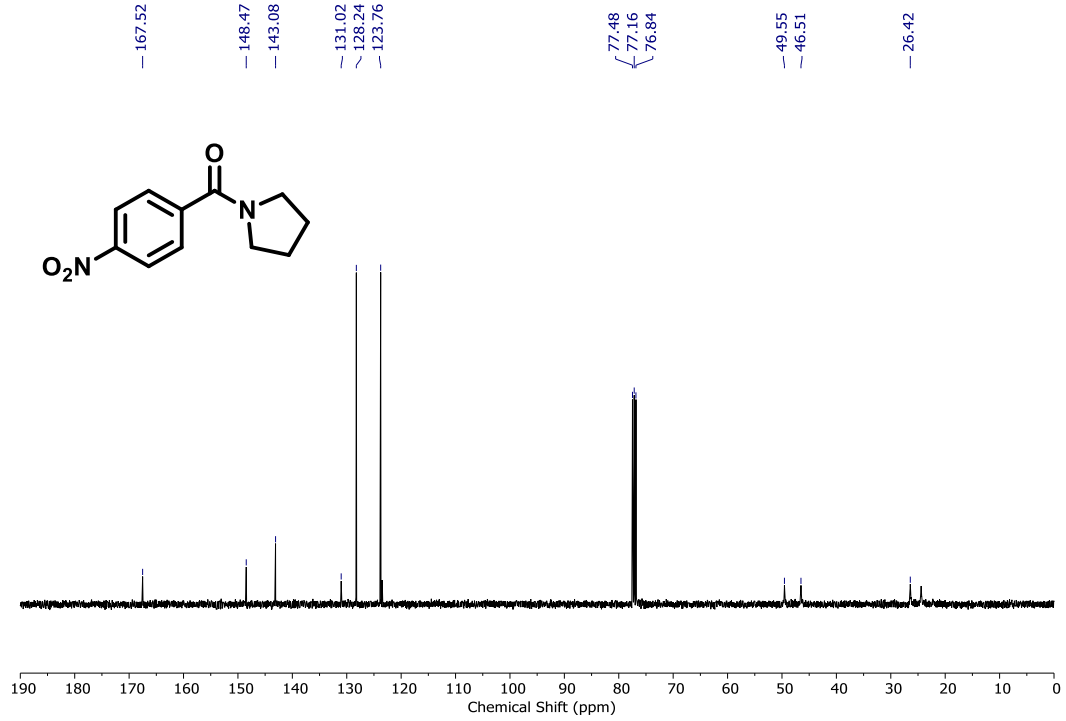


Figure S20: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3cf**.

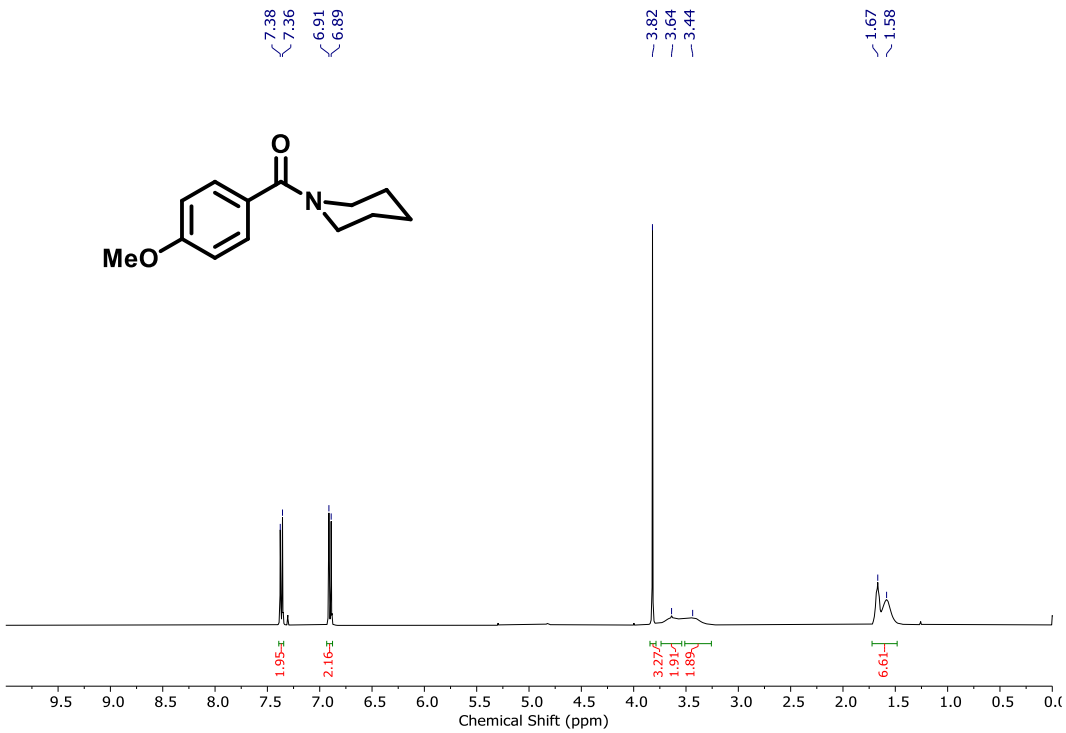


Figure S21: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3db**.

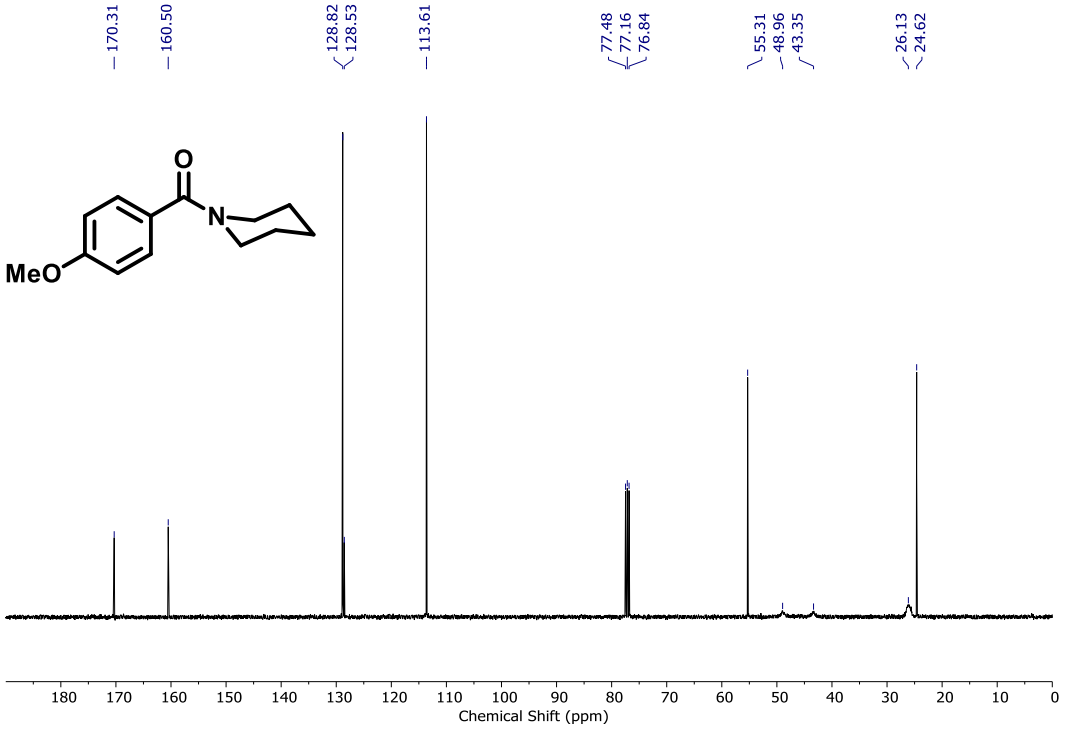


Figure S22: ^{13}C{^{1}H} (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3db**.

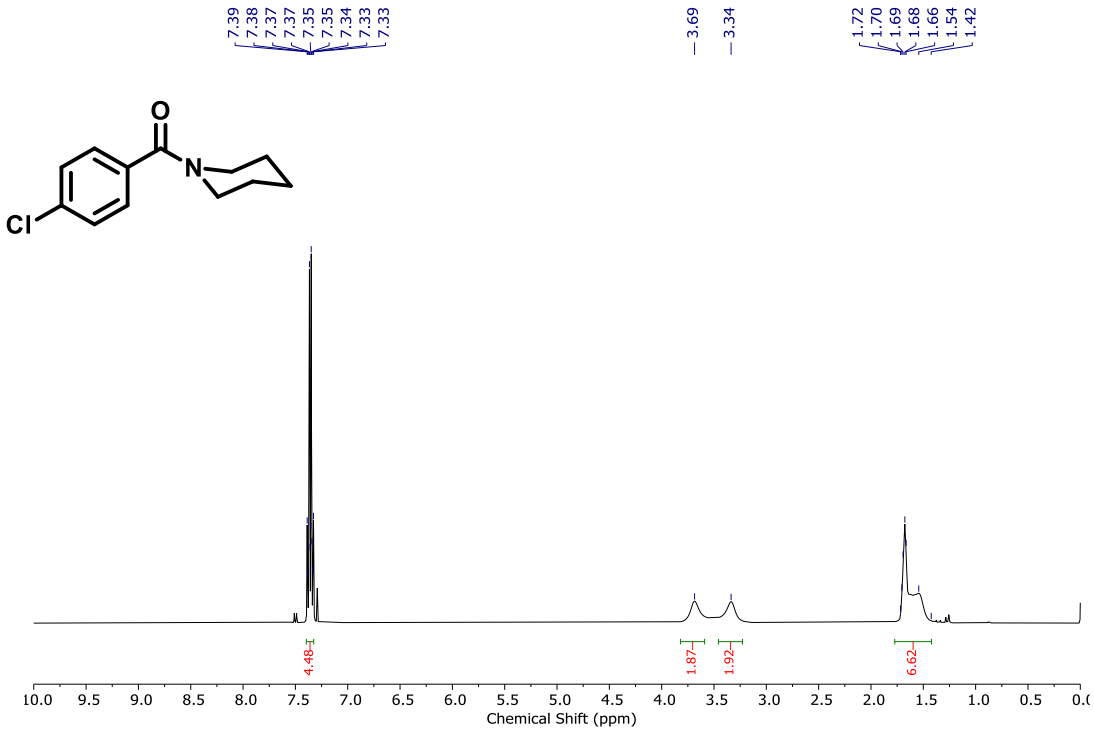


Figure S23: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3dd**.

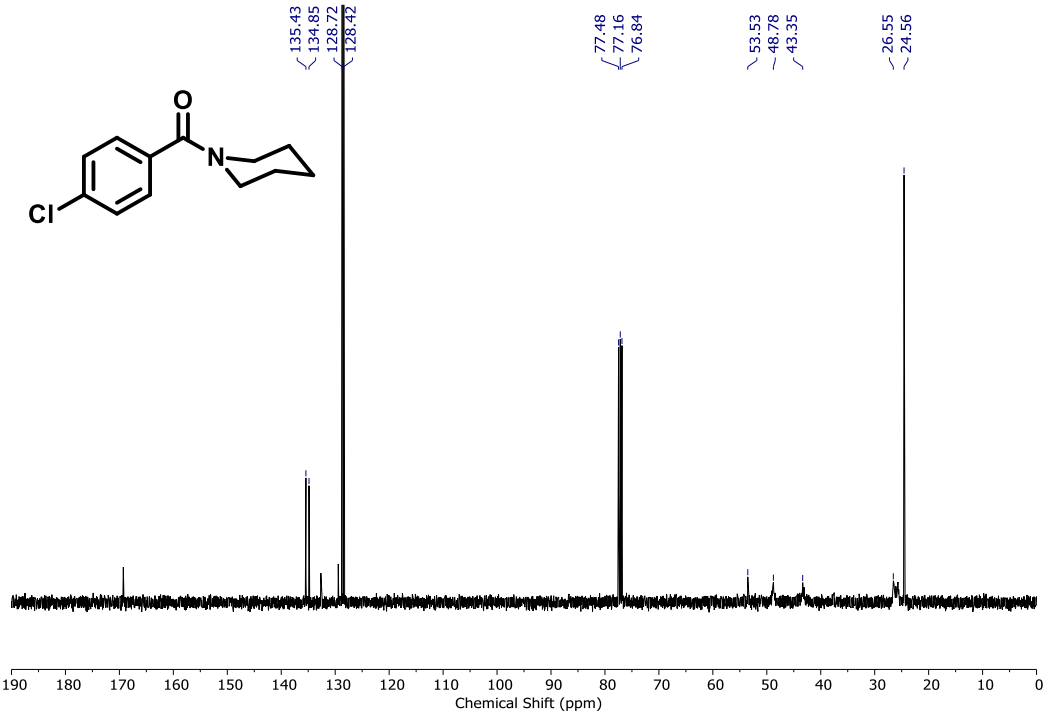


Figure S24: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3dd**.

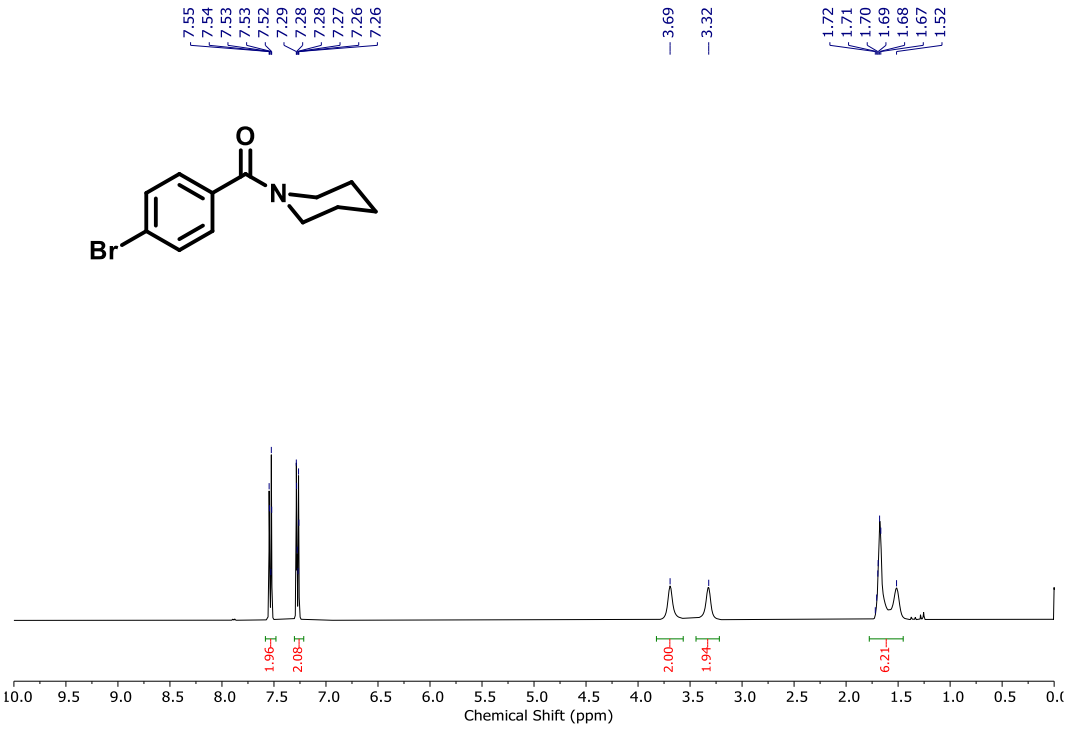


Figure S25: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3de**.

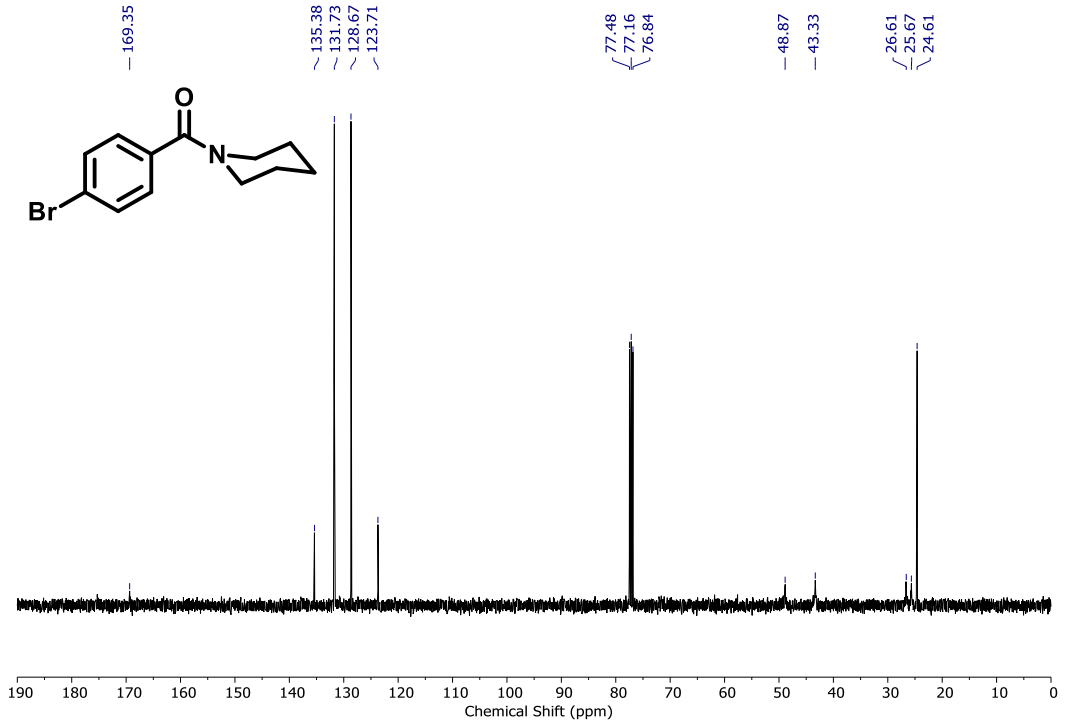


Figure S26: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3de**.

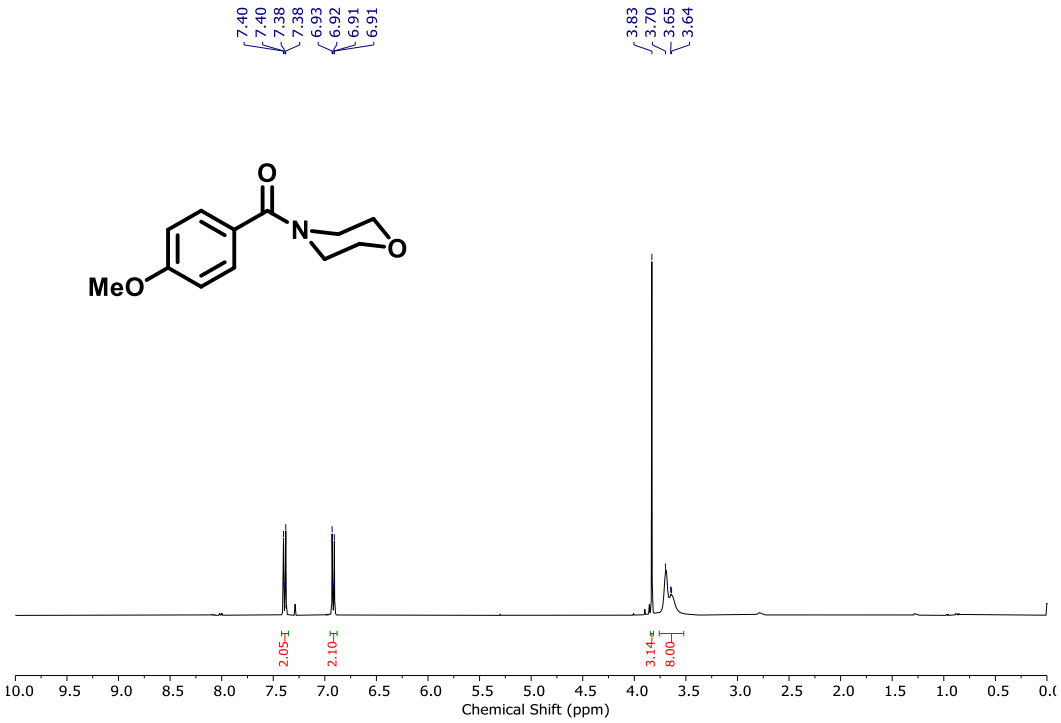


Figure S27: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3eb**.

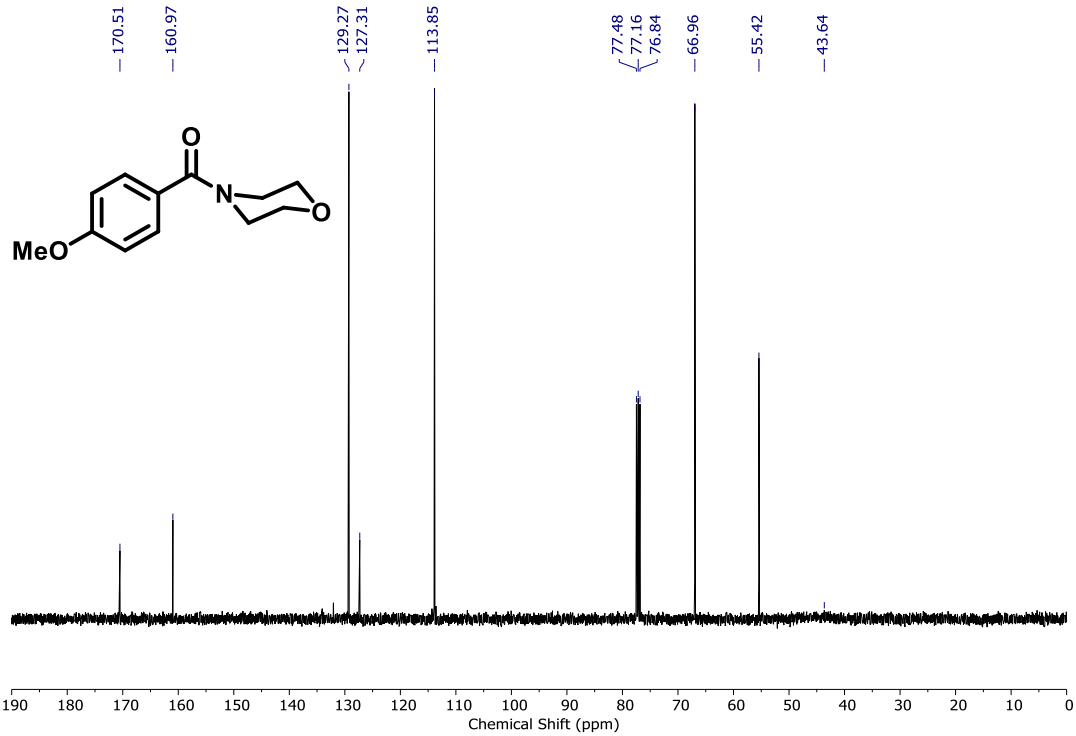


Figure S28: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3eb**.

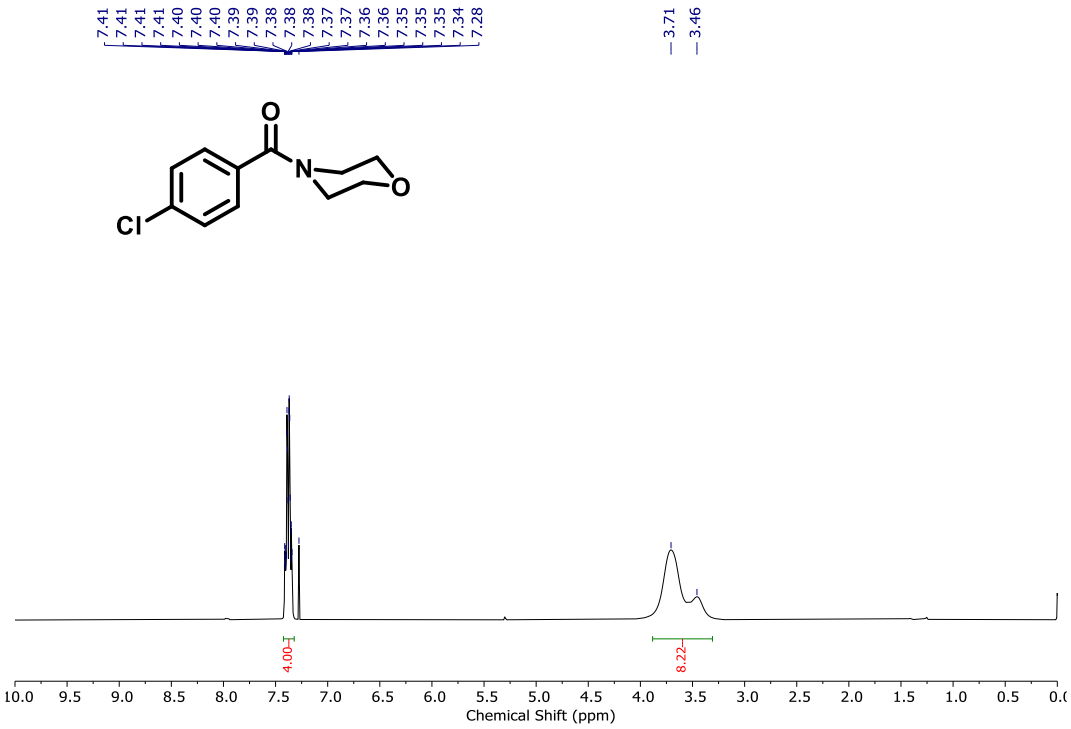


Figure S29: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3ed**.

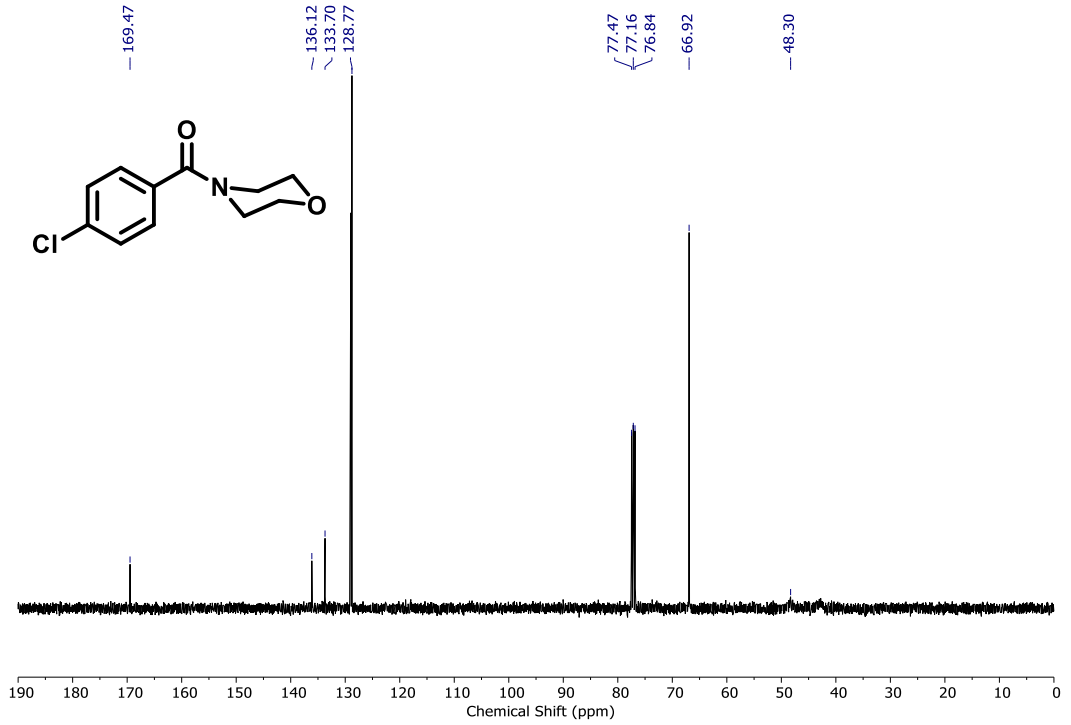


Figure S30: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra **3ed**.

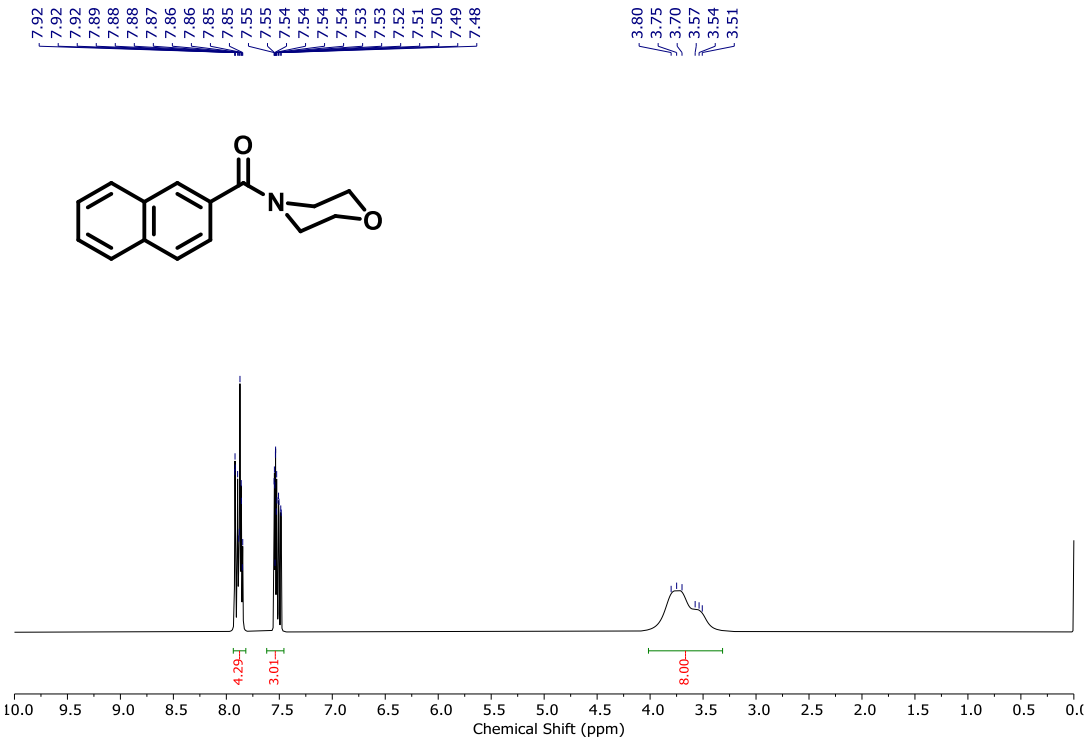


Figure S31: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3f**.

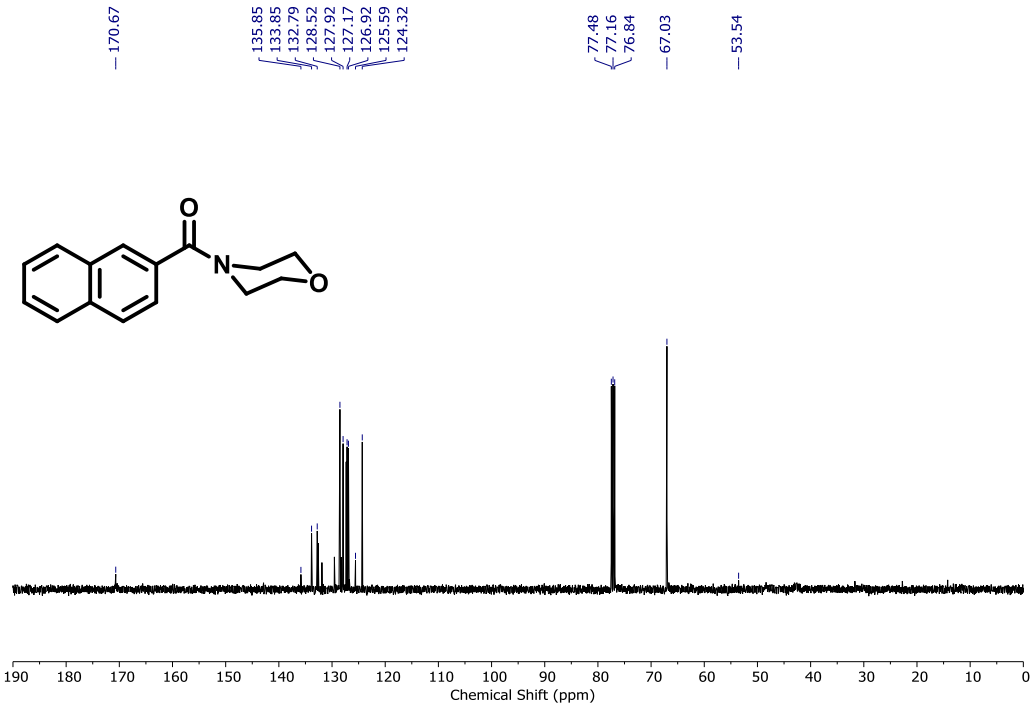


Figure S32: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3f**.

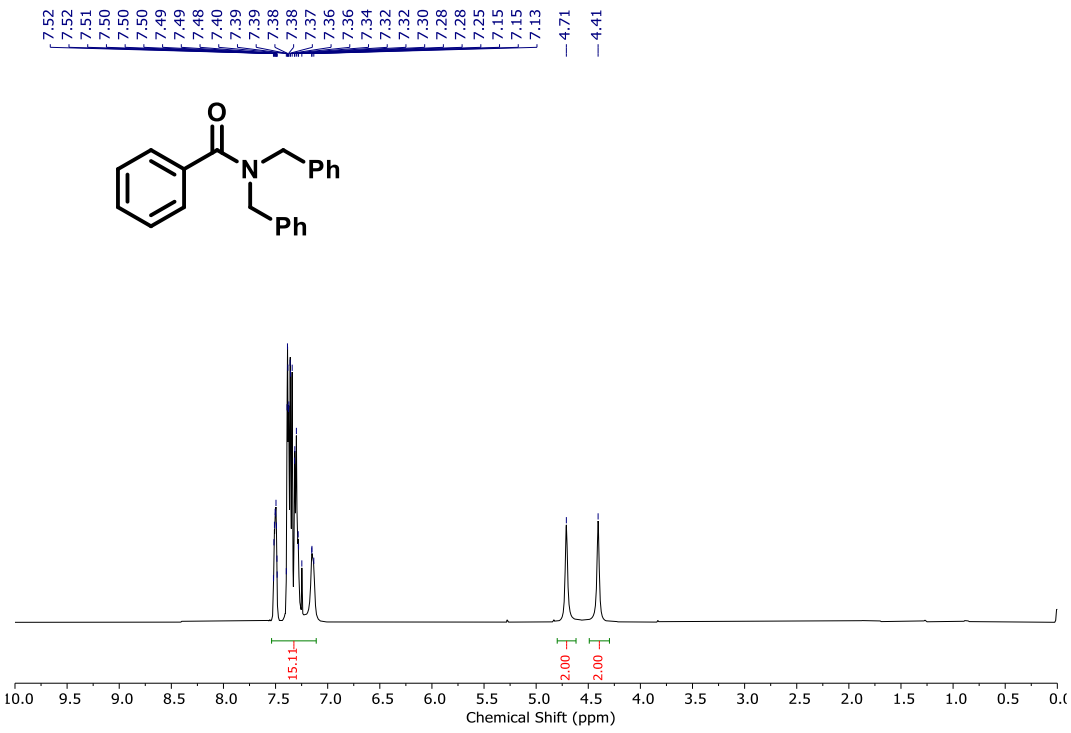


Figure S33: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3g**.

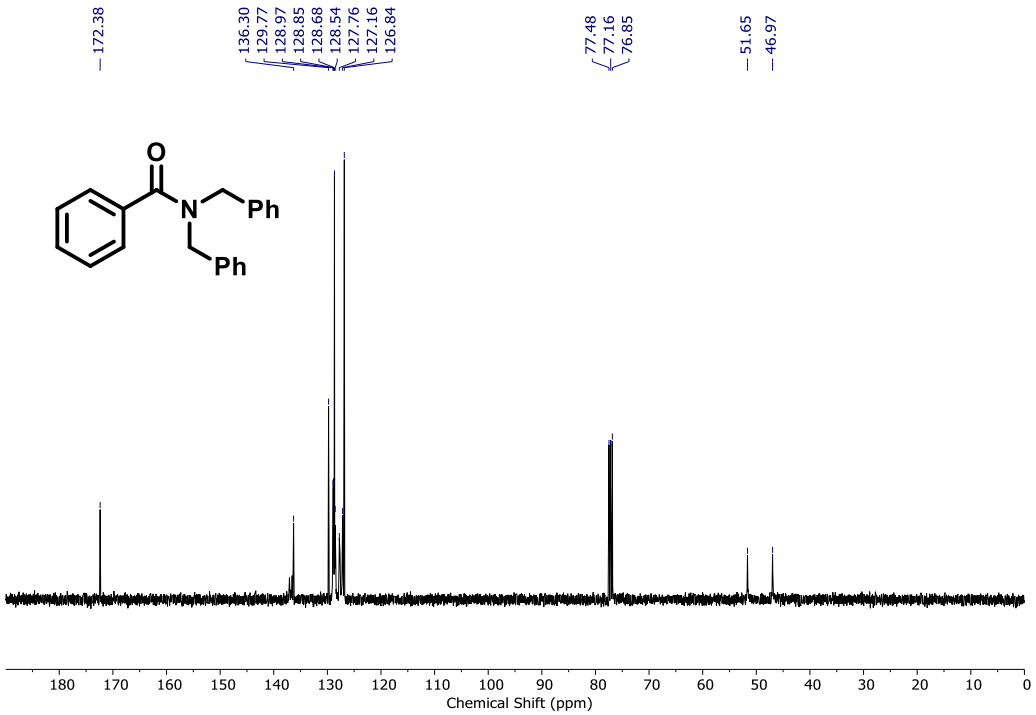


Figure S34: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3g**.

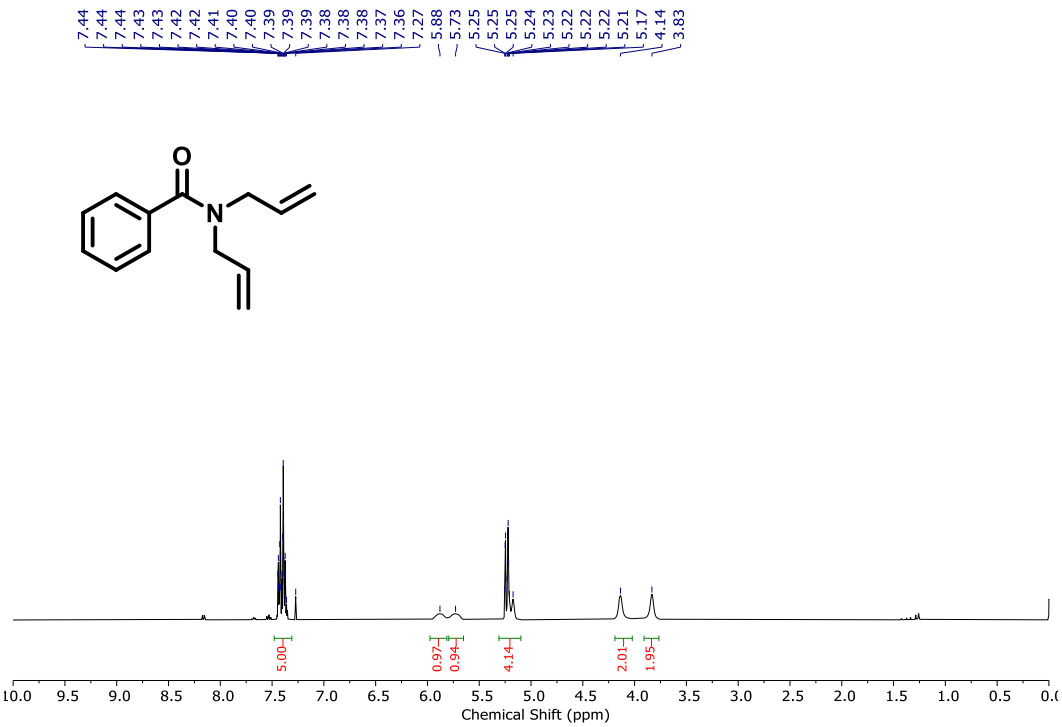


Figure S35: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3ha**.

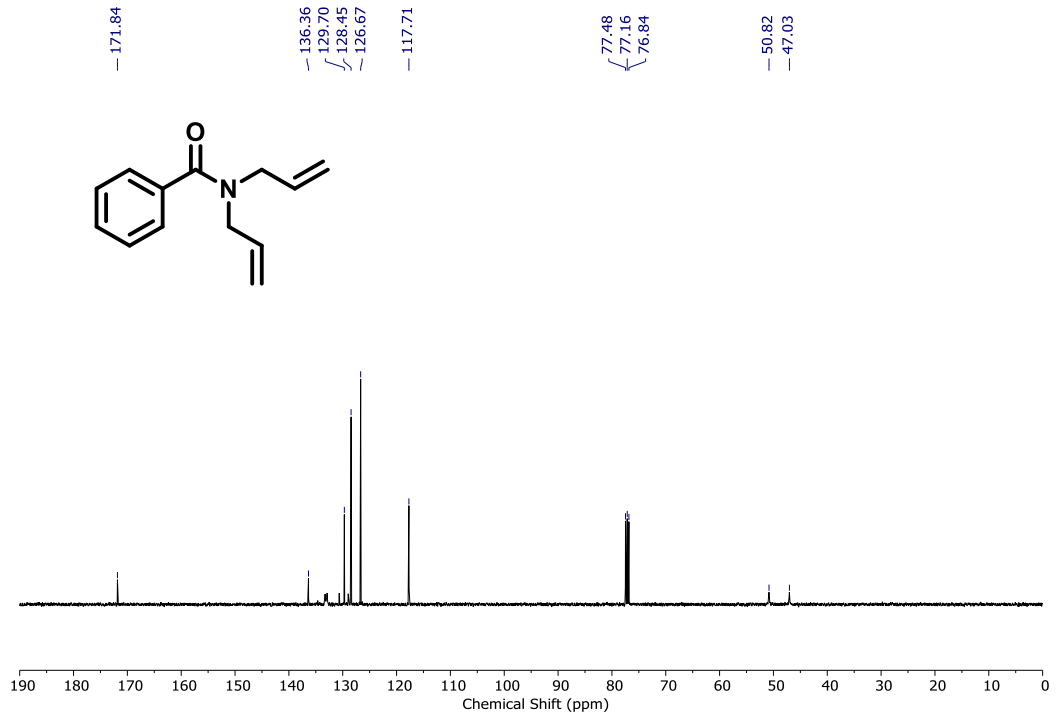


Figure S36: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3ha**.

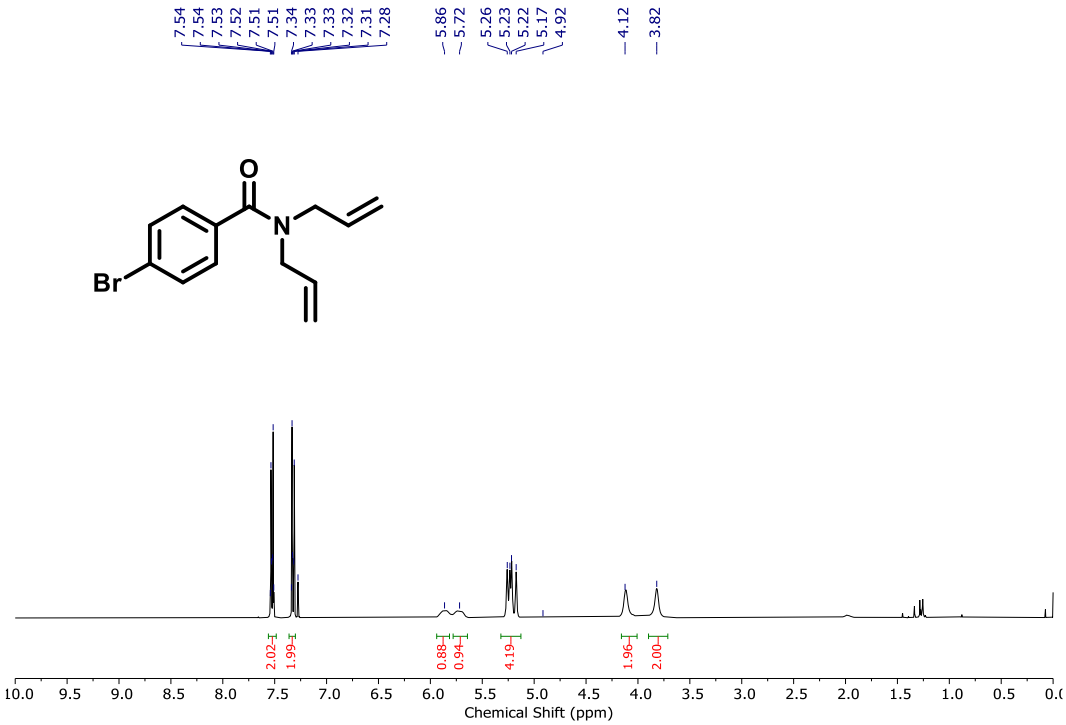


Figure S37: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3hb**.

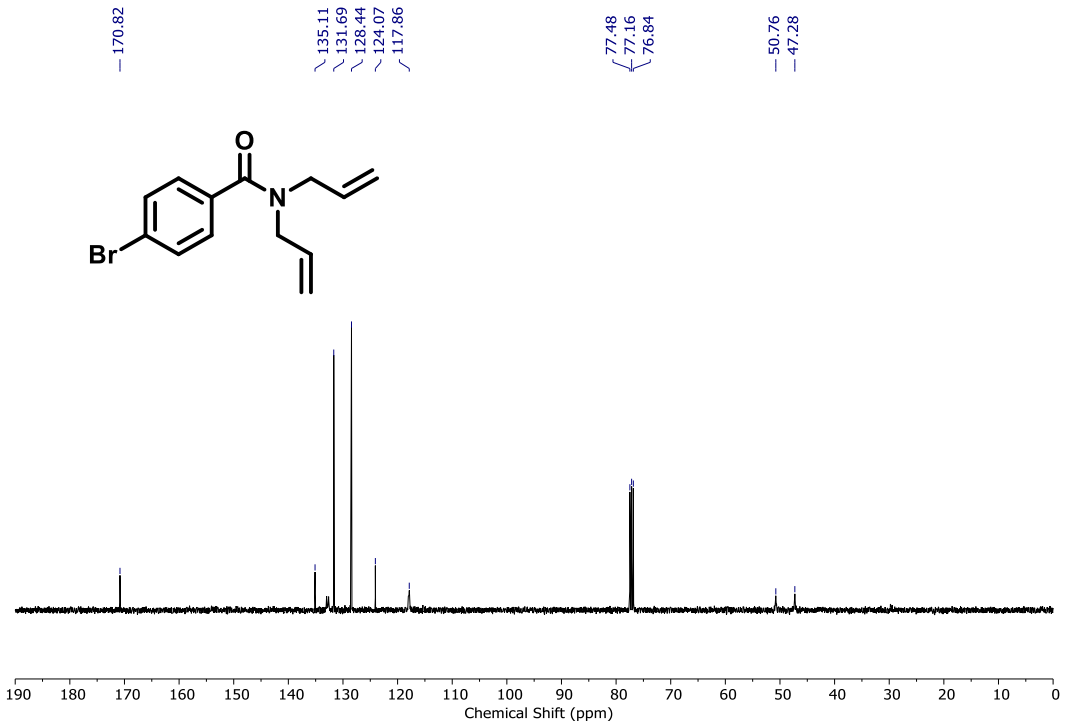


Figure S38: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3hb**.

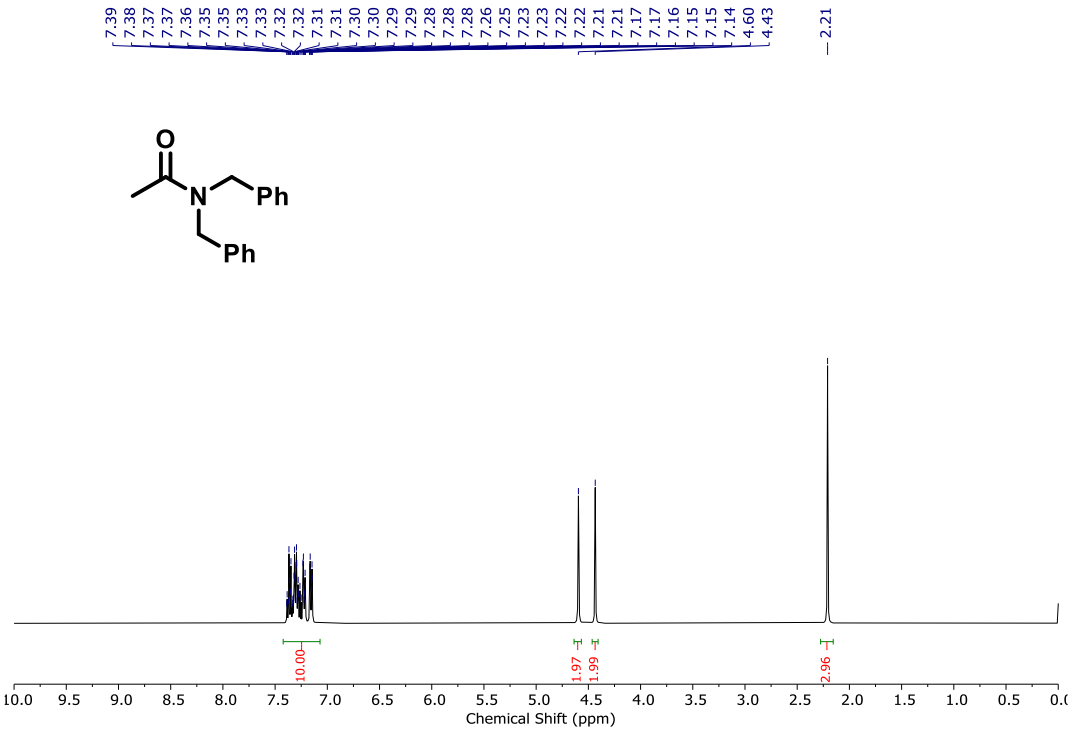


Figure S39: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of **3i**.

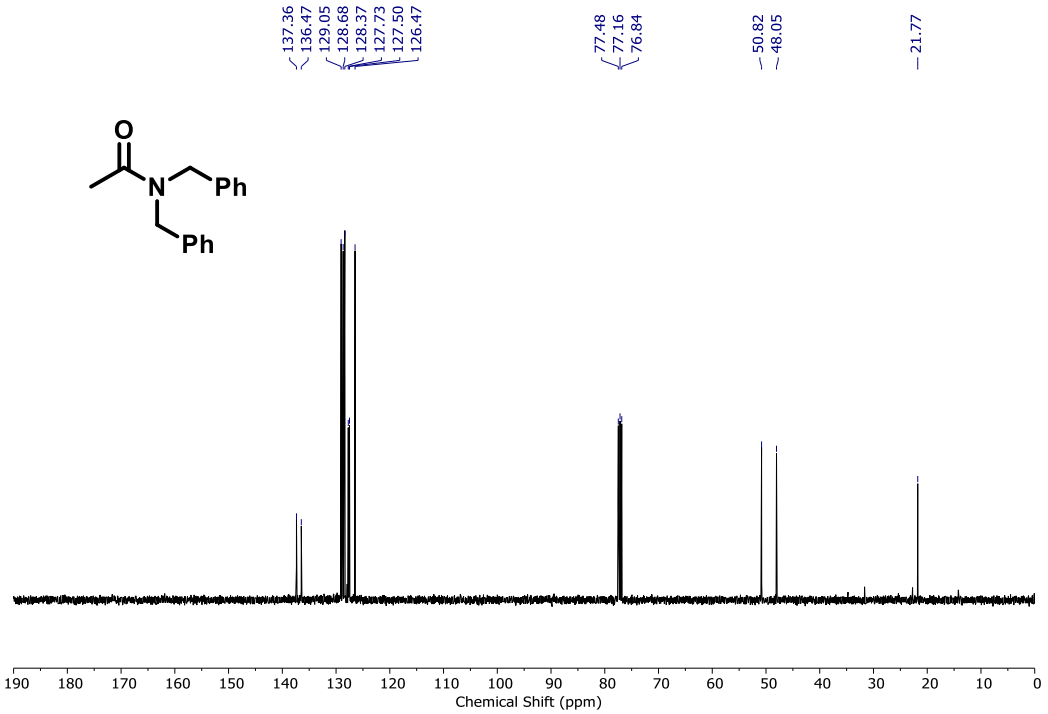
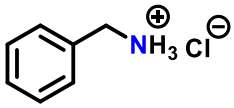


Figure S40: ^{13}C{^{1}H} (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **3i**.

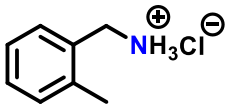
4. General procedure of hydrosilylation of nitriles

The Schlenk tube was placed inside the glove box and loaded with $[Zn(HMDS)_2]_2$ (9.65, 5 mol%), respective nitriles (0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) and kept in an oil bath at 60 °C for 12 hours. The reaction was then quenched by adding 0.2 mL of 2 N HCl to the Schlenk tube and worked up with water and dichloromethane. Following that, the water layer was collected and evaporated the water through rotatory evaporation to obtain the product.

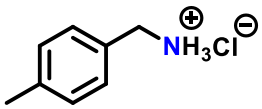
5. NMR data of ammonium salts



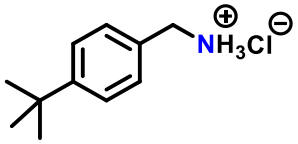
Phenylmethanaminium chloride (2a).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), benzonitrile (51.52 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2a** as a white solid (64.62 mg, 90%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.46-7.45 (m, 5H, Ar-*H*), 4.16 (s, 2H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 131.6, 128.3, 127.9, 42.2.



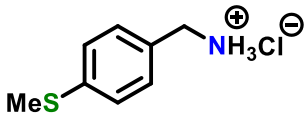
***o*-tolylmethanaminium chloride (2b)**.[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *o*-tolunitrile (58.57 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2b** as a white solid (69.36 mg, 88%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.34-7.25 (m, 4H, Ar-*H*), 4.17 (s, 2H, C*H*$_2$), 2.33 (s, 3H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 138.91, 132.60, 131.12, 130.81, 128.38, 42.19, 19.83.



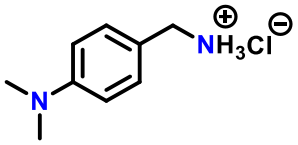
***p*-tolylmethanaminium chloride (2c)**.[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *p*-tolunitrile (58.57 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2c** as a white solid (70.93 mg, 88%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.34-7.27 (m, 4H, Ar-*H*), 4.11 (s, 2H, C*H*$_2$), 2.32 (s, 3H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 139.6, 129.8, 129.6, 128.9, 42.9, 20.3.



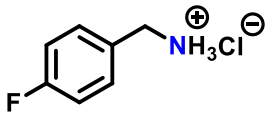
4-*t*-buylphenylmethanaminium chloride (2d).[13] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-*tert*-butylbenzonitrile (79.61 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2d** as a white solid (86.87 mg, 87%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.43-7.41 (m, 2H, Ar-*H*), 7.27-7.26 (m, 2H, Ar-*H*), 4.00 (s, 2H, CH_2), 1.16 (s, 9H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 152.9, 129.7, 128.7, 126.2, 42.6, 34.0, 30.4.



(4-(methylthio)phenyl)methanaminium chloride (2e).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-(methylthio)benzonitrile (74.65 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2e** as a white solid (83.52 mg, 88%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.38-7.33 (m, 4H, Ar-*H*), 4.12 (s, 2H, CH_2), 2.48 (s, 3H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 139.2, 129.6, 129.4, 126.5, 125.9, 42.7, 14.3.

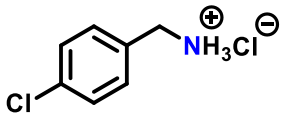


(4-(dimethylamino)phenyl)methanaminium chloride (2f).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-(dimethylamino)benzonitrile (73.09 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2f** as a white solid (84.01 mg, 90%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.68-7.64 (m, 4H, Ar-*H*), 4.25 (s, 2H, CH_2), 3.29 (s, 6H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 144.9, 137.5, 133.5, 123.8, 48.9, 44.7.

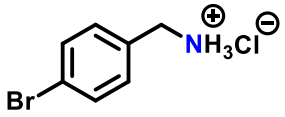


4-fluorophenylmethanaminium chloride (2g).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-fluorobenzonitrile (60.55 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2g** as a white solid (67.87 mg, 84%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.48-7.46 (m, 2H, Ar-

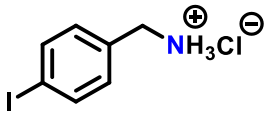
H), 7.22-7.19 (m, 2H, Ar-*H*), 4.18 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D$_2$O): δ_c (ppm) 131.1, 116.1, 115.9, 42.5.



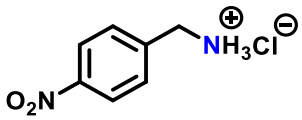
4-chlorophenylmethanaminium chloride (2h).[12] Following procedure **4**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), 4-chlorobenzonitrile (68.78 mg, 0.5 mmol) and PhSiH$_3$ (108.22 mg, 1 mmol) afforded **2h** as a white solid (73.00 mg, 82%). ^{1}H NMR (400 MHz, D$_2$O): δ_H (ppm) 7.45-7.38 (m, 4H, Ar-*H*), 4.14 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D$_2$O): δ_c (ppm) 138.4, 134.4, 131.1, 130.4, 129.1, 127.1, 126.6, 42.3.



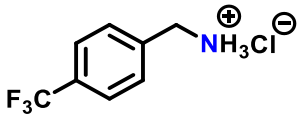
4-bromophenylmethanaminium chloride (2i).[12] Following procedure **4**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), 4-bromobenzonitrile (91.01 mg, 0.5 mmol) and PhSiH$_3$ (108.22 mg, 1 mmol) afforded **2i** as a dark yellow solid (94.56 mg, 85%). ^{1}H NMR (400 MHz, D$_2$O): δ_H (ppm) 7.60-7.58 (m, 2H, Ar-*H*), 7.33-7.31 (m, 2H, Ar-*H*), 4.12 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D$_2$O): δ_c (ppm) 146.3, 132.1, 131.7, 130.7, 122.7, 42.5.



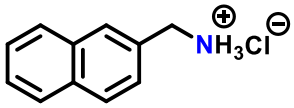
4-iodophenylmethanaminium chloride (2j).[12] Following procedure **4**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), 4-iodobenzonitrile (114.51 mg, 0.5 mmol) and PhSiH$_3$ (108.22 mg, 1 mmol) afforded **2j** as a white solid (113.19 mg, 84%). ^{1}H NMR (400 MHz, D$_2$O): δ_H (ppm) 7.82-7.80 (d, *J* = 8 Hz, 2H, Ar-*H*), 7.21-7.19 (d, *J* = 8 Hz, 2H, Ar-*H*), 4.11 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D$_2$O): δ_c (ppm) 137.9, 131.9, 130.4, 94.3, 42.3.



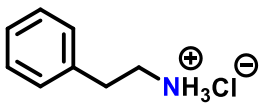
4-nitrophenylmethanaminium chloride (2k).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-nitrobenzonitrile (74.06 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2k** as a yellow solid (75.44 mg, 80%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 8.27-8.25 (d, J = 8 Hz, 2H, Ar-*H*), 7.66-7.64 (d, J = 8 Hz, 2H, Ar-*H*), 4.31 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 147.9, 139.8, 129.8, 124.2, 42.2.



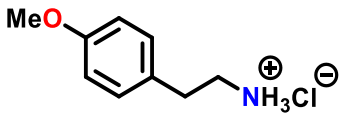
4-(trifluormethyl)phenylmethanaminium chloride (2l).[13] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-(trifluoromethyl)benzonitrile (85.56 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2l** as a colourless solid (89.93 mg, 85%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.79-7.78 (d, J = 8 Hz, 2H, Ar-*H*), 7.63-7.61 (d, J = 8 Hz, 2H, Ar-*H*), 4.27 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 136.6, 130.5, 129.2, 128.5, 126.0, 42.5.



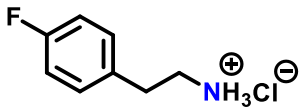
Naphthylmethanaminium chloride (2m).[13] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), naphthalene-2-carbonitrile (76.59 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2m** as a colourless solid (87.15 mg, 90%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.98-7.93 (m, 5H, Ar-*H*), 7.60-7.58 (m, 5H, Ar-*H*), 7.53-7.51 (m, 5H, Ar-*H*), 4.31 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 132.9, 132.8, 130.2, 128.9, 128.2, 127.9, 127.7, 127.1, 126.9, 125.9, 43.2.



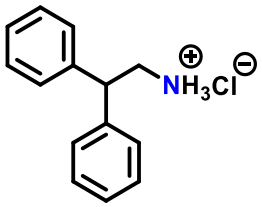
2-phenylethan-1-aminiumchloride (2n).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), benzylcyanide (58.57 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2n** as a colourless solid (67.78 mg, 86%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.44-7.41 (m, 2H, Ar-*H*), 7.37-7.33 (m, 3H, Ar-*H*), 3.30-3.27 (t, J = 6 Hz, 2H, CH_2), 3.02-2.99 (t, J = 6 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 136.6, 129.1, 128.9, 127.3, 40.6, 32.7.



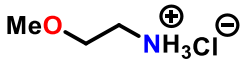
2-(4-methoxyphenyl)ethan-1-aminiumchloride (2o).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-methoxyphenylacetonitrile (73.58 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2o** as a colourless solid (82.57 mg, 88%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.25-7.23 (m, 2H, Ar-*H*), 6.98-6.95 (m, 2H, Ar-*H*), 3.79 (s, 3H, OCH_3), 3.23-3.19 (t, *J* = 8 Hz, 2H, CH_2), 2.93-2.89 (t, *J* = 8 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 159.4, 131.6, 130.6, 115.9, 56.8, 42.2, 33.3.



2-(4-fluorophenyl)ethan-1-aminiumchloride (2p).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-fluorophenylacetonitrile (67.57 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2p** as a colourless solid (79.15 mg, 89%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.32-7.28 (m, 2H, Ar-*H*), 7.13-7.09 (m, 2H, Ar-*H*), 3.26-3.23 (t, *J* = 8 Hz, 2H, CH_2), 2.98-2.94 (t, *J* = 8 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 132.7, 130.9, 130.8, 116.0, 115.8, 40.9, 32.3.

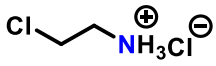


2,2-diphenylethanaminium chloride (2q).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), diphenylacetonitrile (96.62 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2q** as a colourless solid (93.49 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.40-7.39 (m, 8H, Ar-*H*), 7.34-7.30 (m, 2H, Ar-*H*), 4.36-4.32 (t, *J* = 8 Hz, 1H, CH_2), 3.72-3.70 (t, *J* = 8 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_c (ppm) 139.8, 129.0, 127.5, 127.4, 49.3, 42.8.

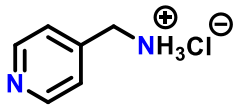


2-methoxyethan-1-aminium chloride (2r).[12] Following procedure **4**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), methoxyacetonitrile (35.54 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2r**

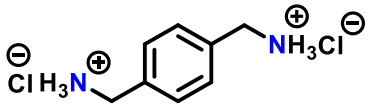
as a colourless solid (49.09 mg, 88%). ^{1}H NMR (600 MHz, D_2O): δ_H (ppm) 3.59-3.57 (t, *J* = 6 Hz, 2H, C*H*$_2$), 3.30 (s, 3H, OC*H*$_3$), 3.10-3.08 (t, *J* = 6 Hz, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (150 MHz, D_2O): δ_c (ppm) 67.7, 58.2, 38.8.



2-chloroethan-1-aminium chloride (2s).[12] Following procedure **4**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), chloroacetonitrile (37.75 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2s** as a colourless solid (52.19 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 3.85-3.83 (t, *J* = 6 Hz, 2H, C*H*$_2$), 3.39-3.37 (t, *J* = 6 Hz, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 42.3, 41.8.



Pyridine-4-ylmethanaminium chloride (2t).[14] Following procedure **4**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), 4-cyanopyridine (52.05 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2t** as a colourless solid (57.83 mg, 80%). ^{1}H NMR (600 MHz, D_2O): δ_H (ppm) 8.64-8.63 (m, 2H, Ar-*H*), 7.61-7.60 (m, 2H, Ar-*H*), 4.33 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (150 MHz, D_2O): δ_c (ppm) 148.1, 144.6, 124.0, 41.7.



1,4-phenylenedimethaminium chloride (2s).[15] Following procedure **4**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), 4-cyanopyridine (64.06 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2t** as a colourless solid (78.41 mg, 75%). ^{1}H NMR (600 MHz, D_2O): δ_H (ppm) 7.41 (s, 4H, Ar-*H*), 4.11 (s, 4H, C*H*$_2$). ^{13}C{^{1}H} NMR (150 MHz, D_2O): δ_c (ppm) 133.5, 129.5, 42.6.

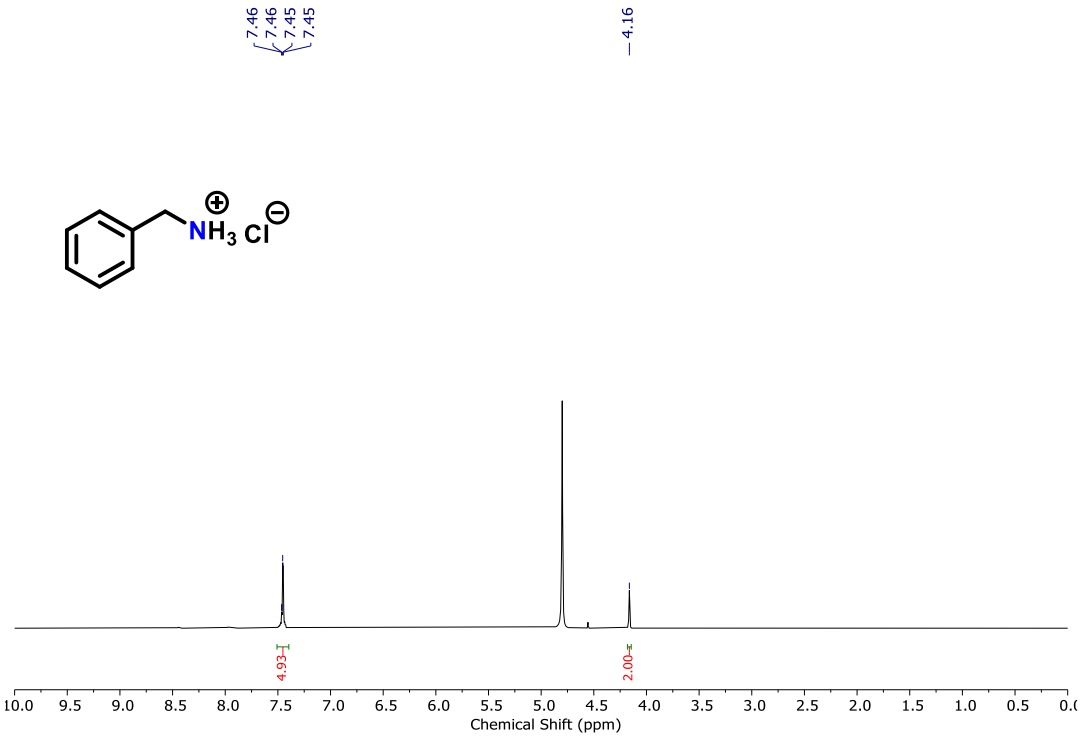


Figure S41: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2a**.

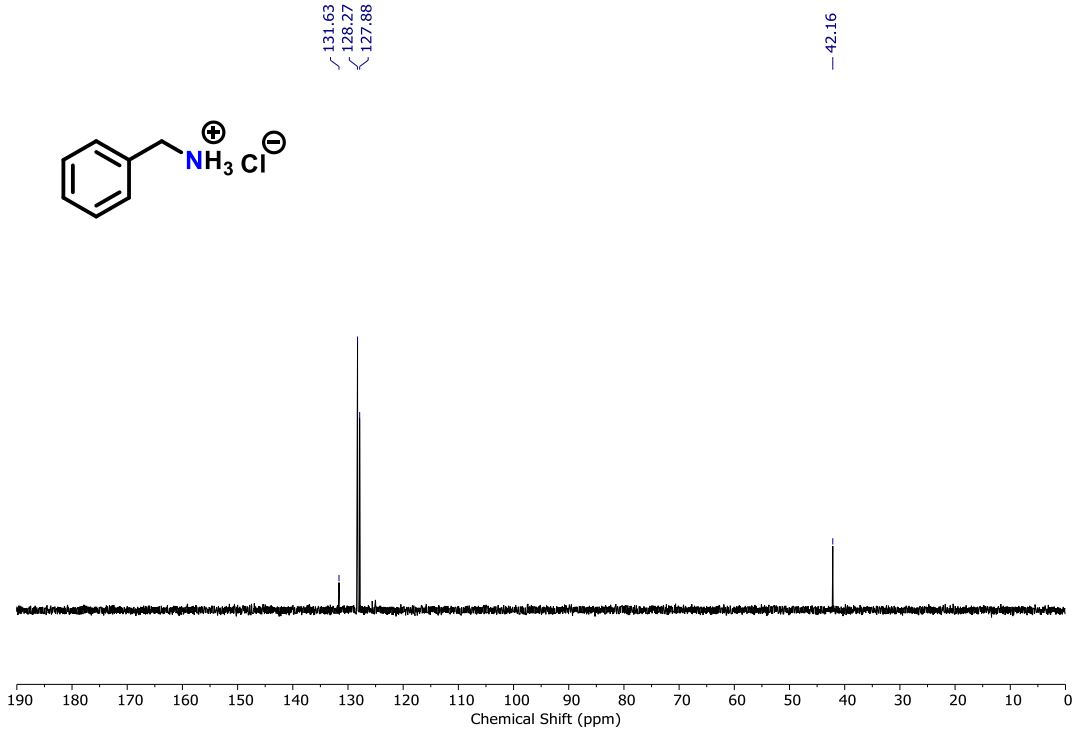


Figure S42: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2a**.

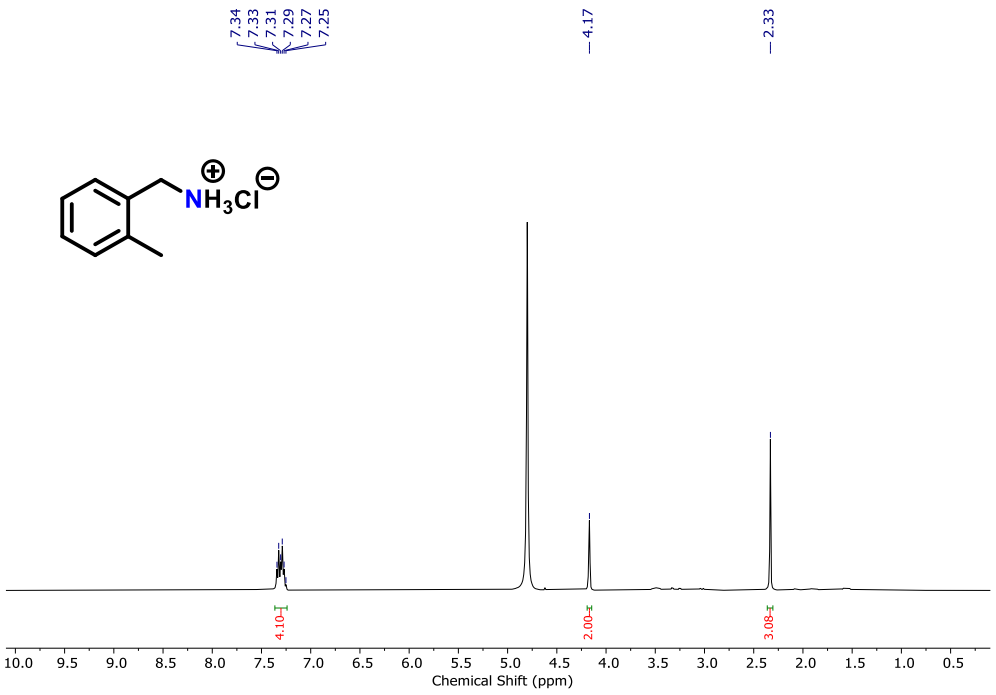


Figure S43: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2b**.

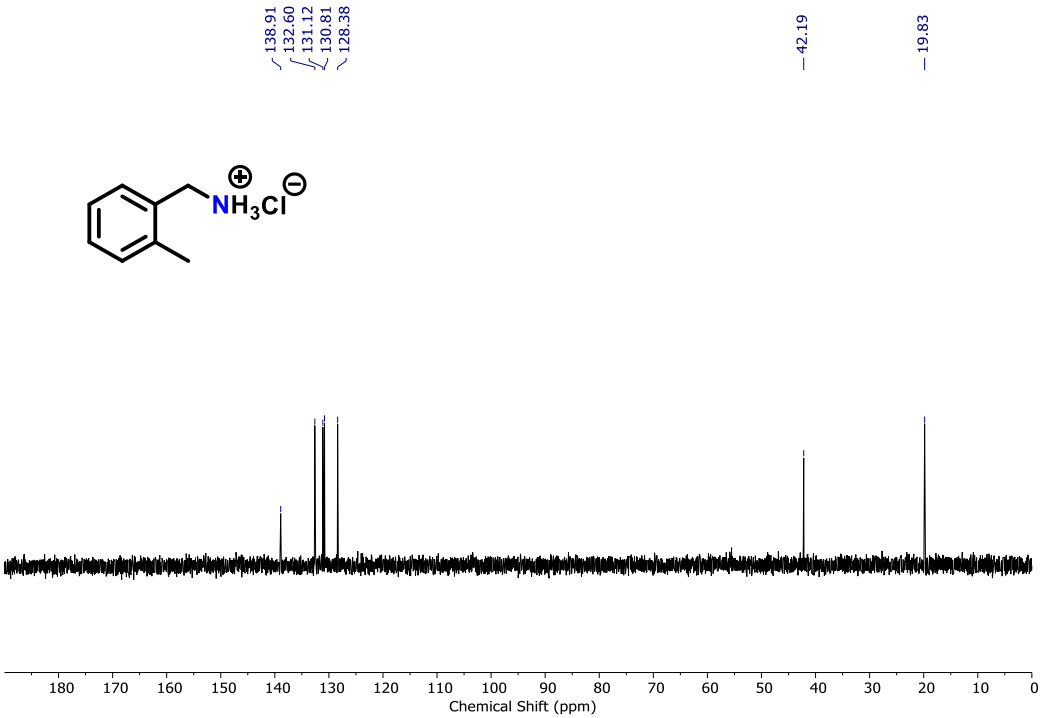


Figure S44: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2b**.

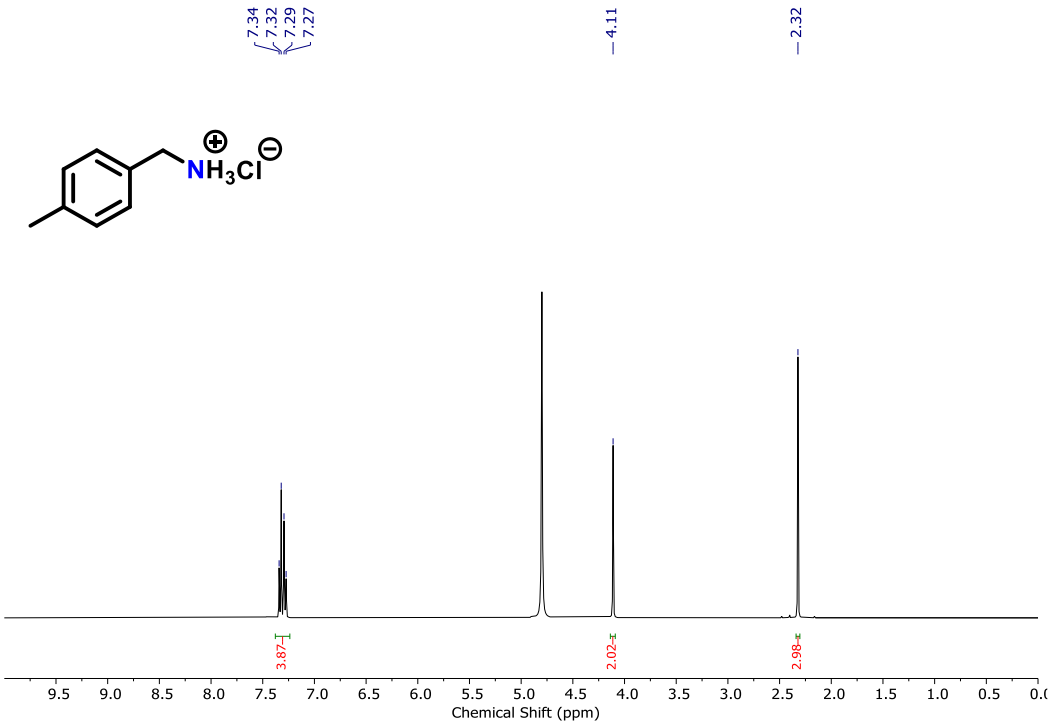


Figure S45: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2c**.

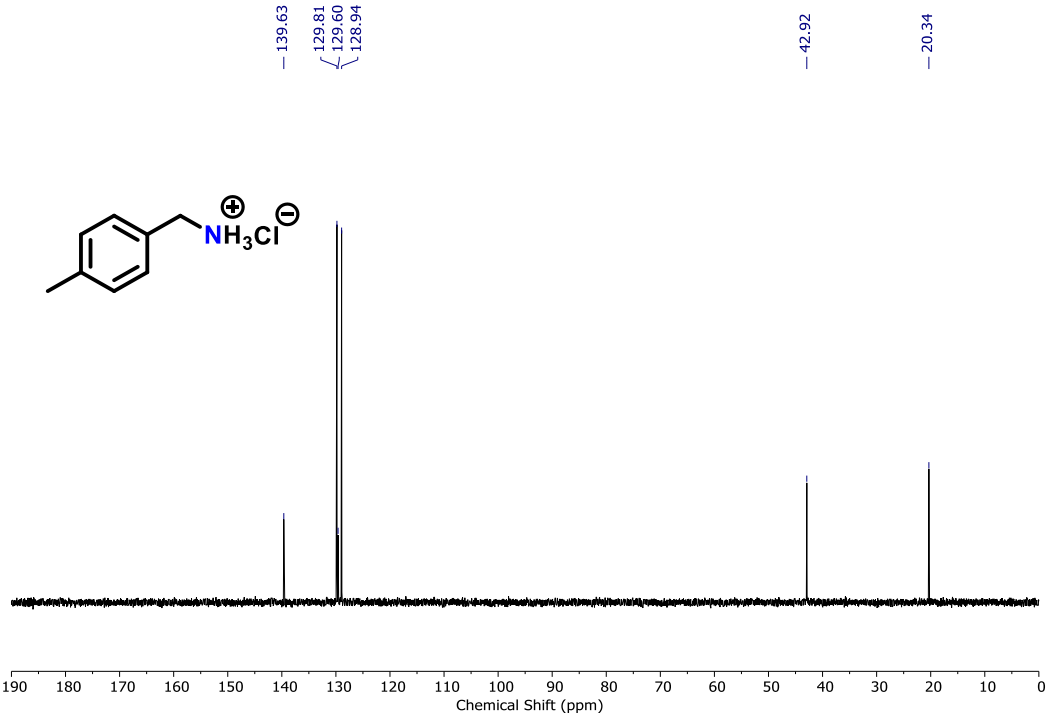


Figure S46: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2c**.

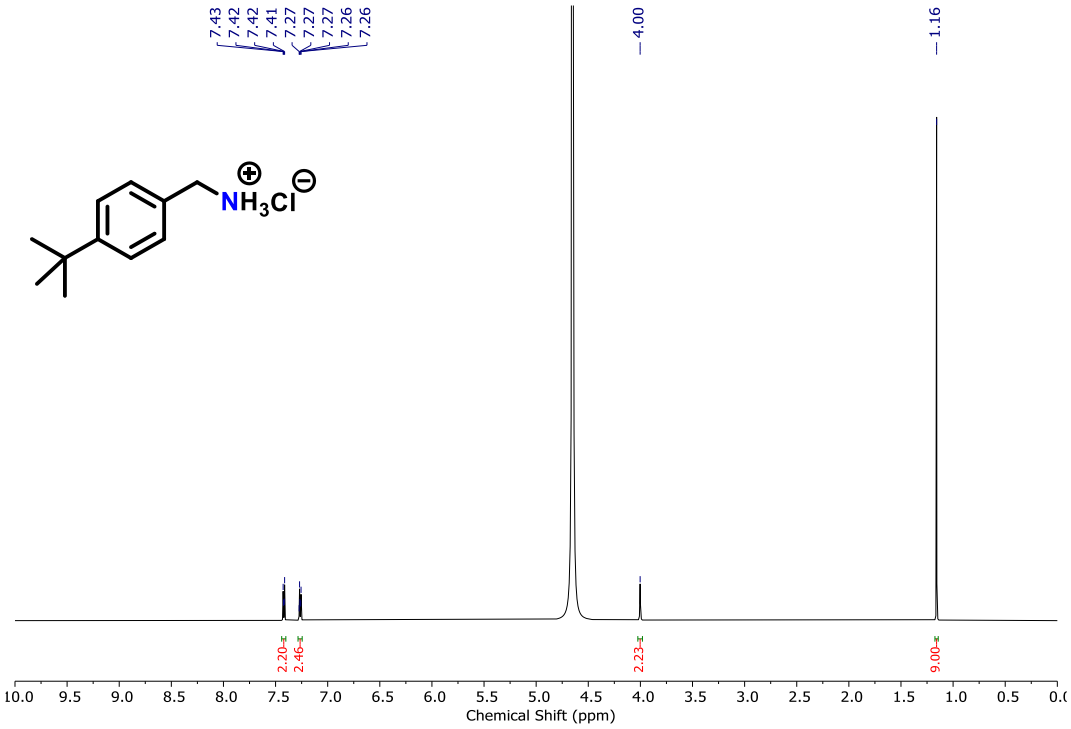


Figure S47: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2d**.

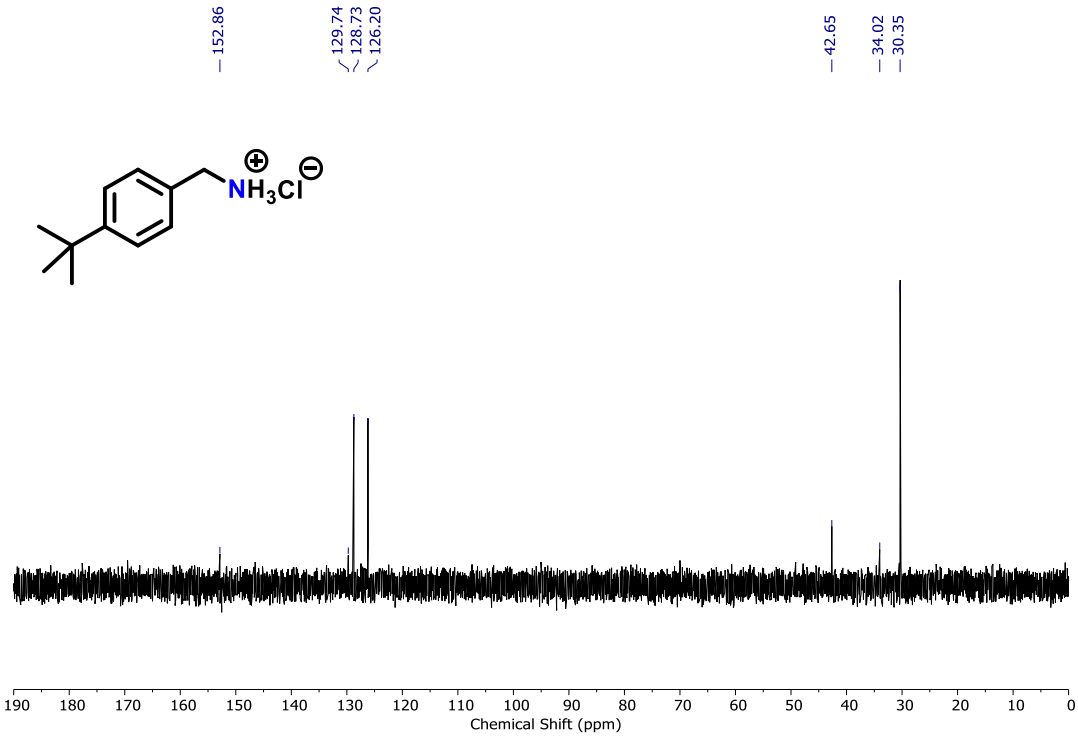


Figure S48: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2d**.

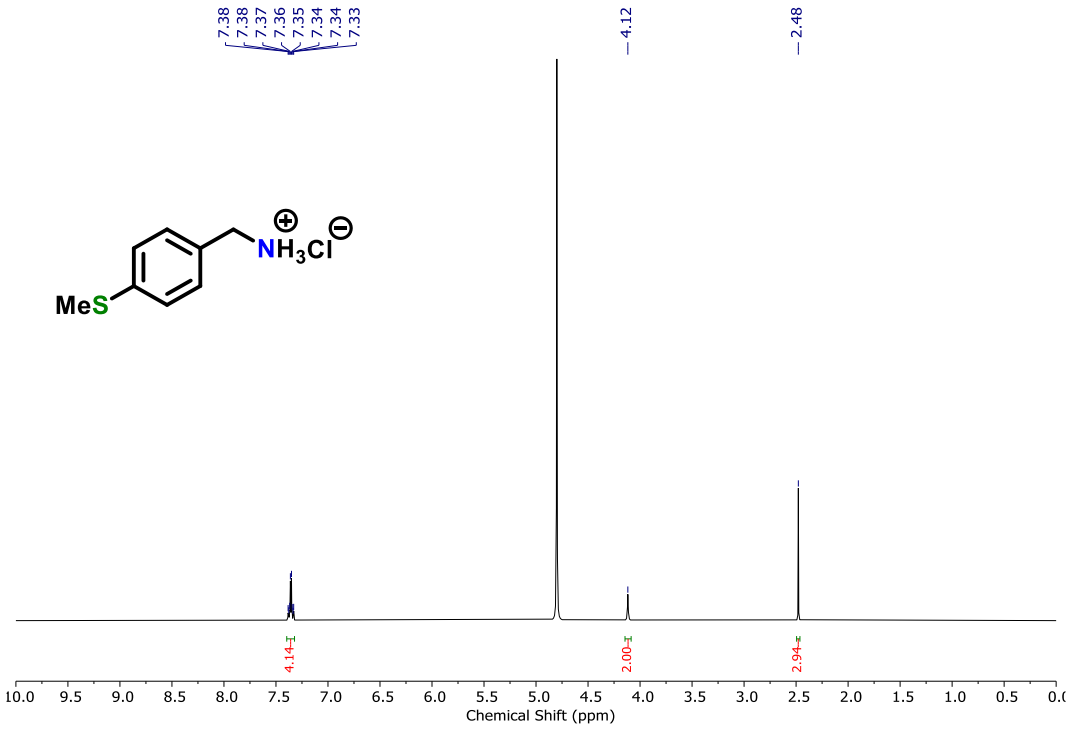


Figure S49: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2e**.

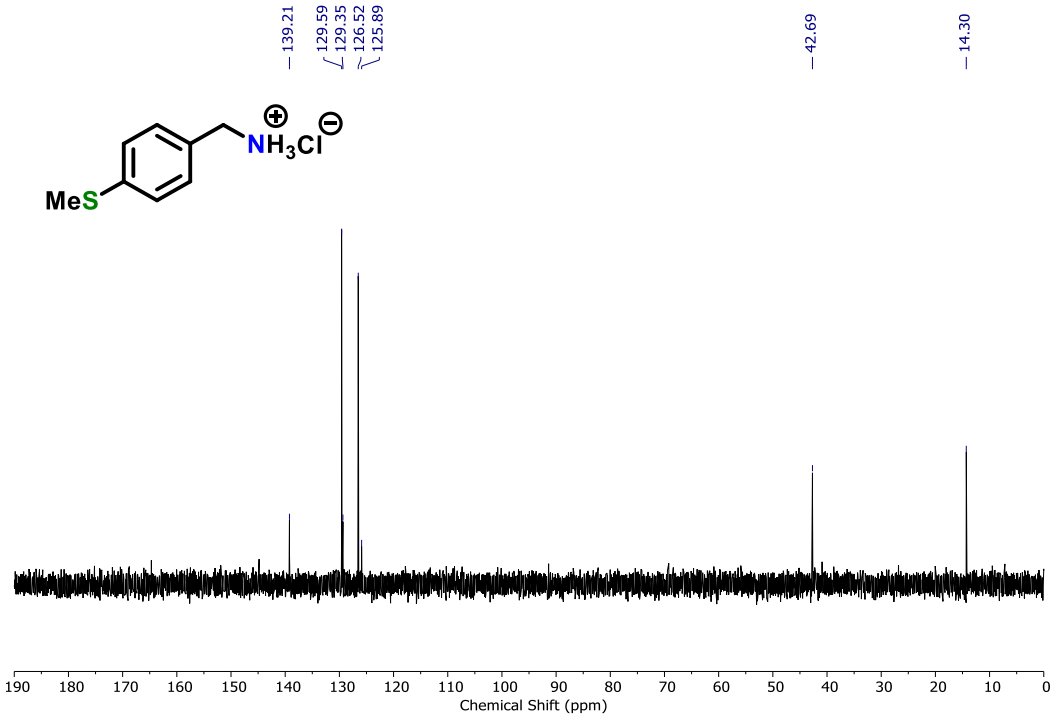


Figure S50: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2e**.

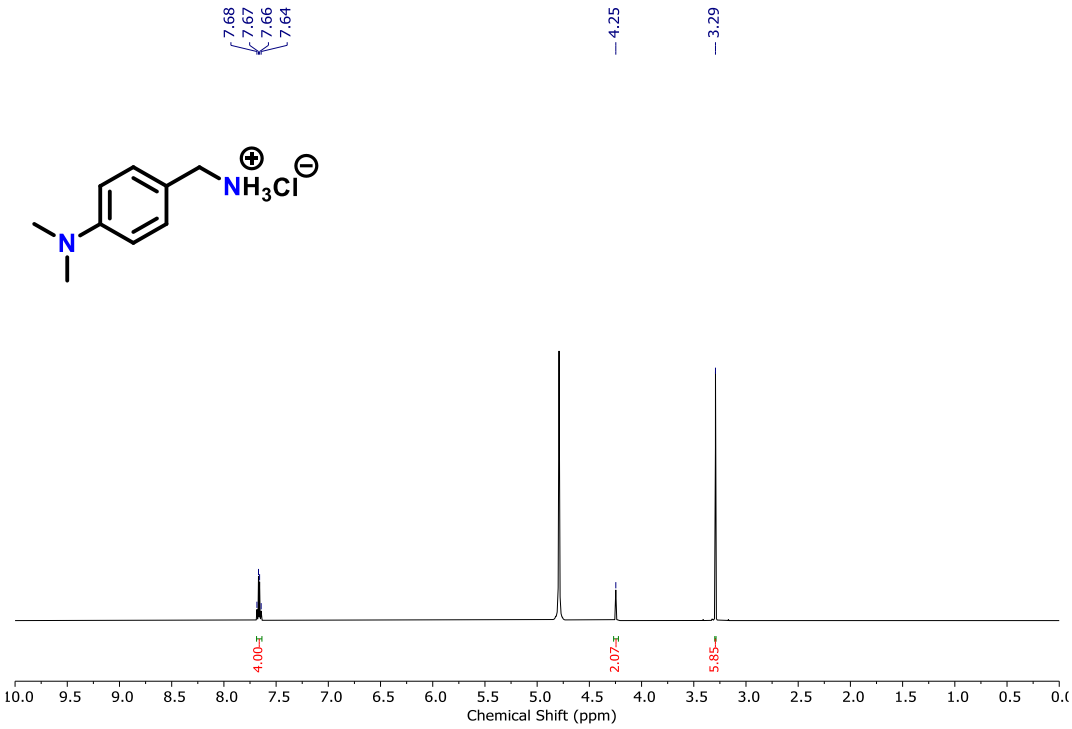


Figure S51: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2f**.

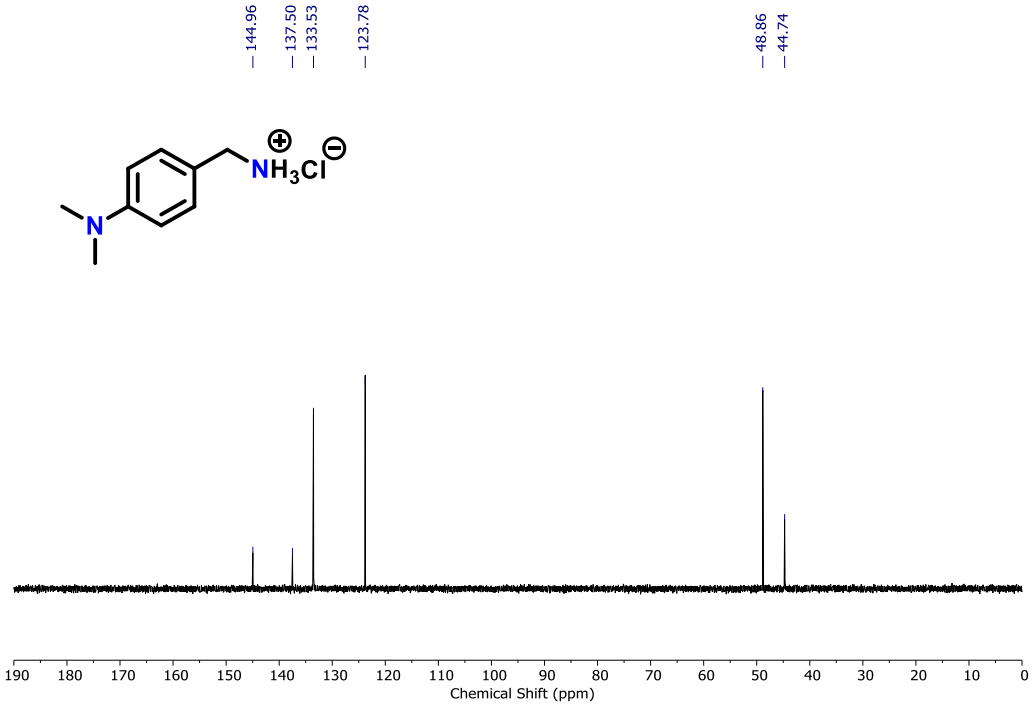


Figure S52: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2f**.

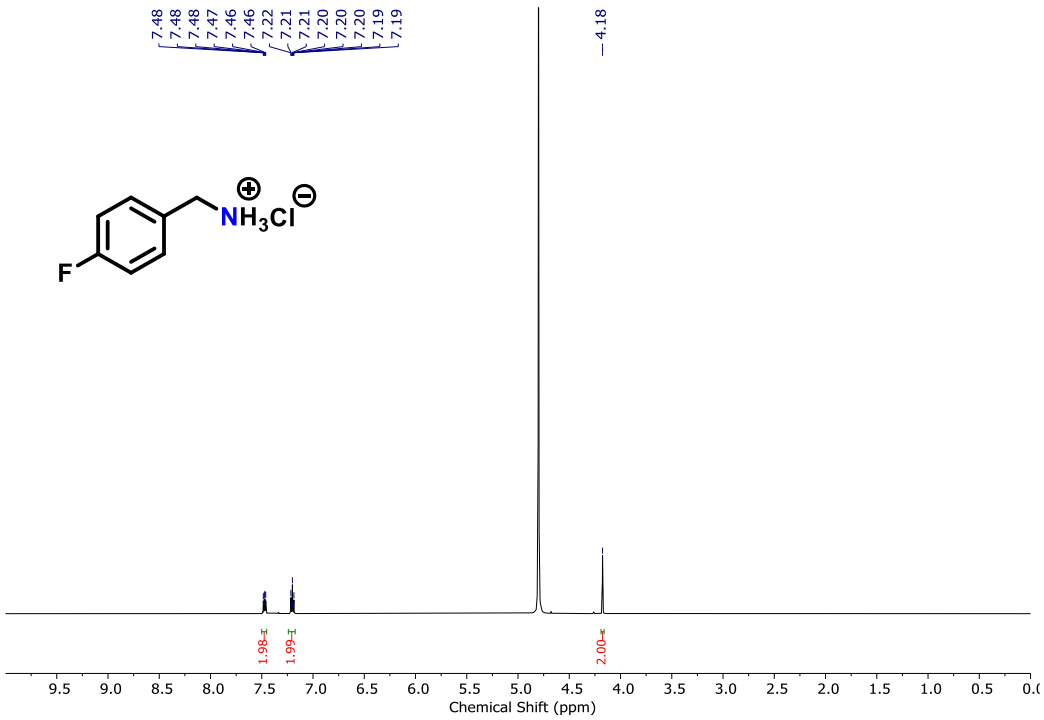


Figure S53: ^{1}H NMR (600 MHz, 25 ˚C, D_2O) spectra of **2g**.

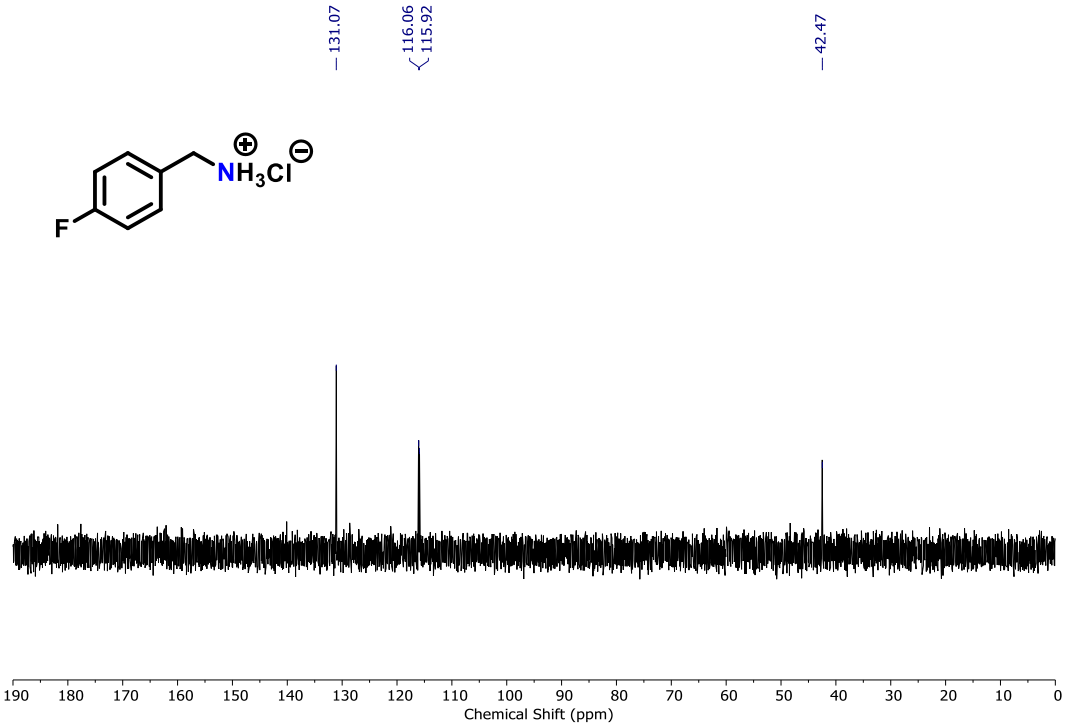


Figure S54: $^{13}C\{^{1}H\}$ (150 MHz, 25 ˚C, D_2O) NMR spectra of **2g**.

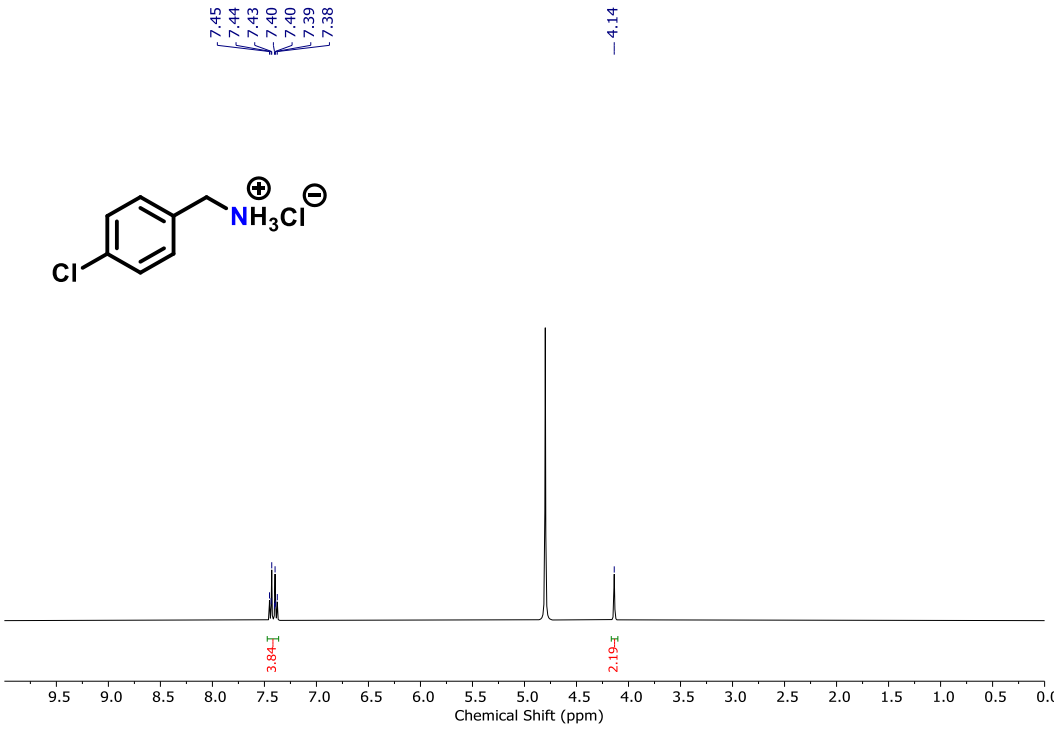


Figure S55: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2h**.

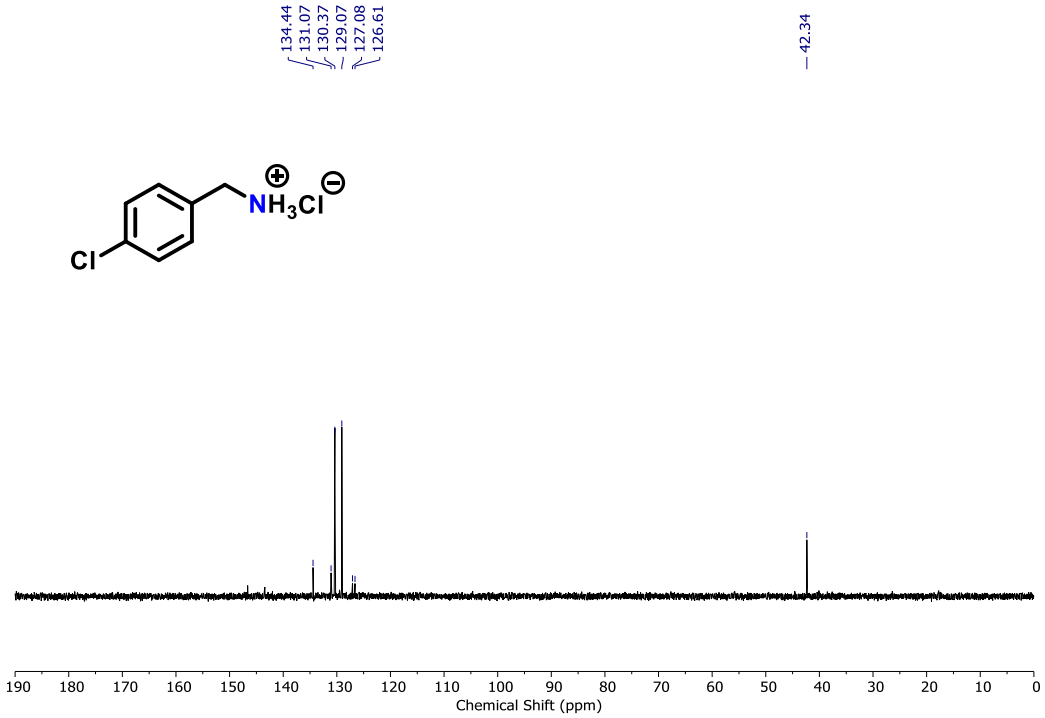


Figure S56: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **2h**.

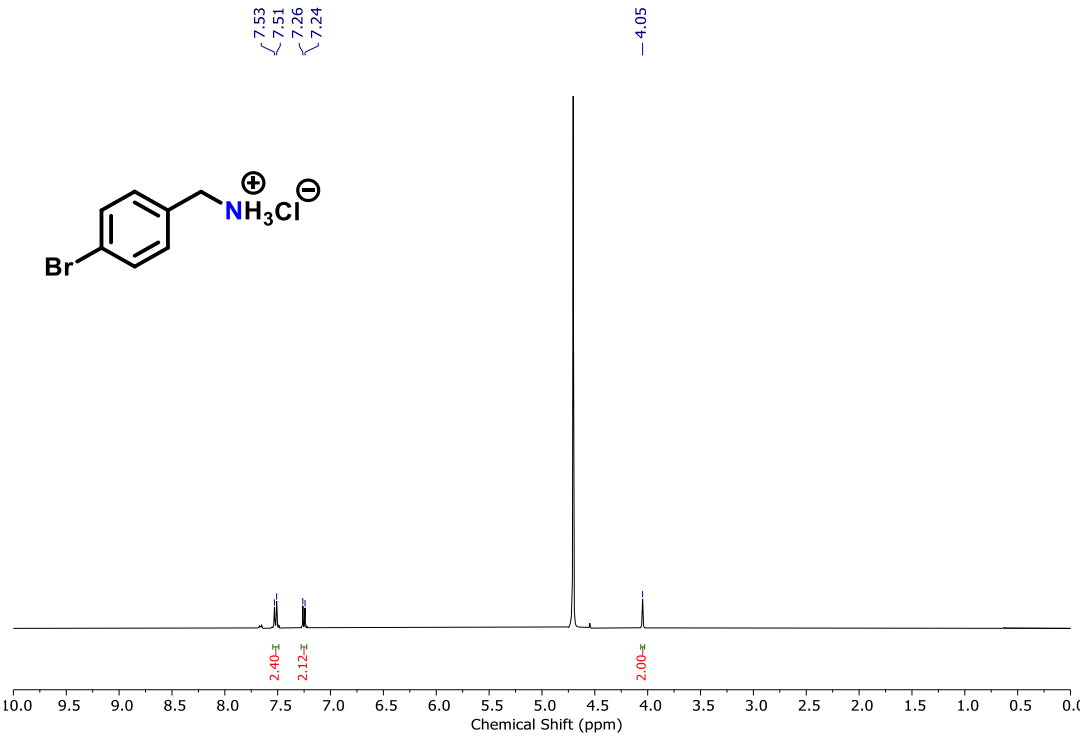


Figure S57: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2i**.

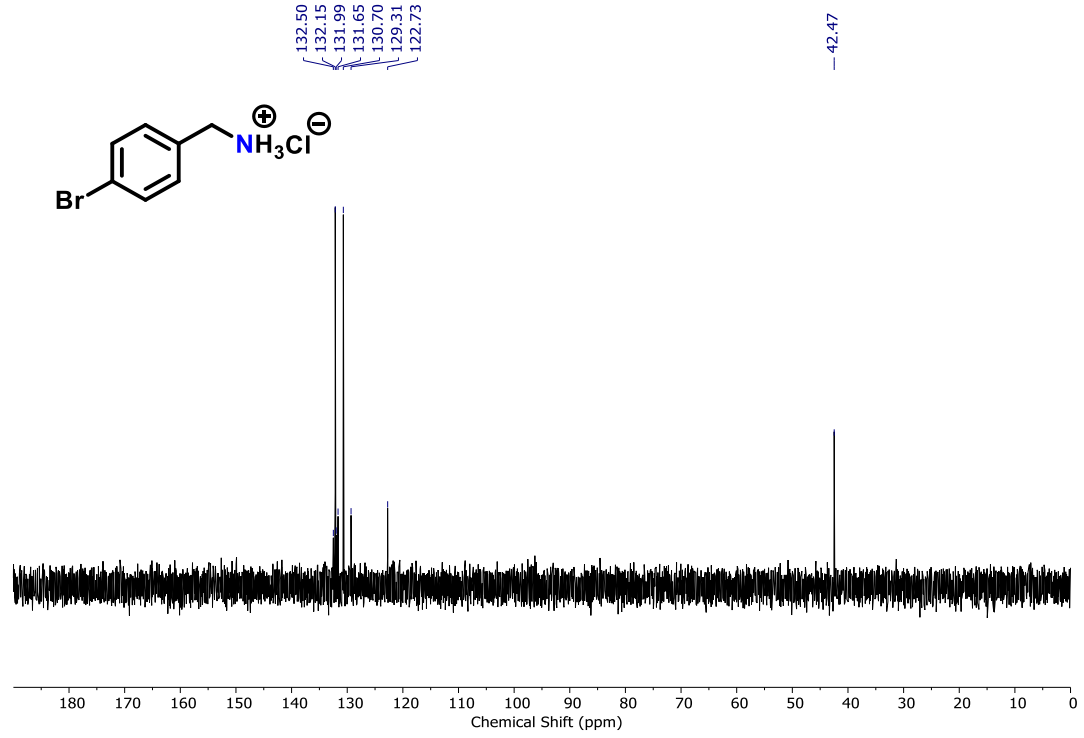


Figure S58: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2i**.

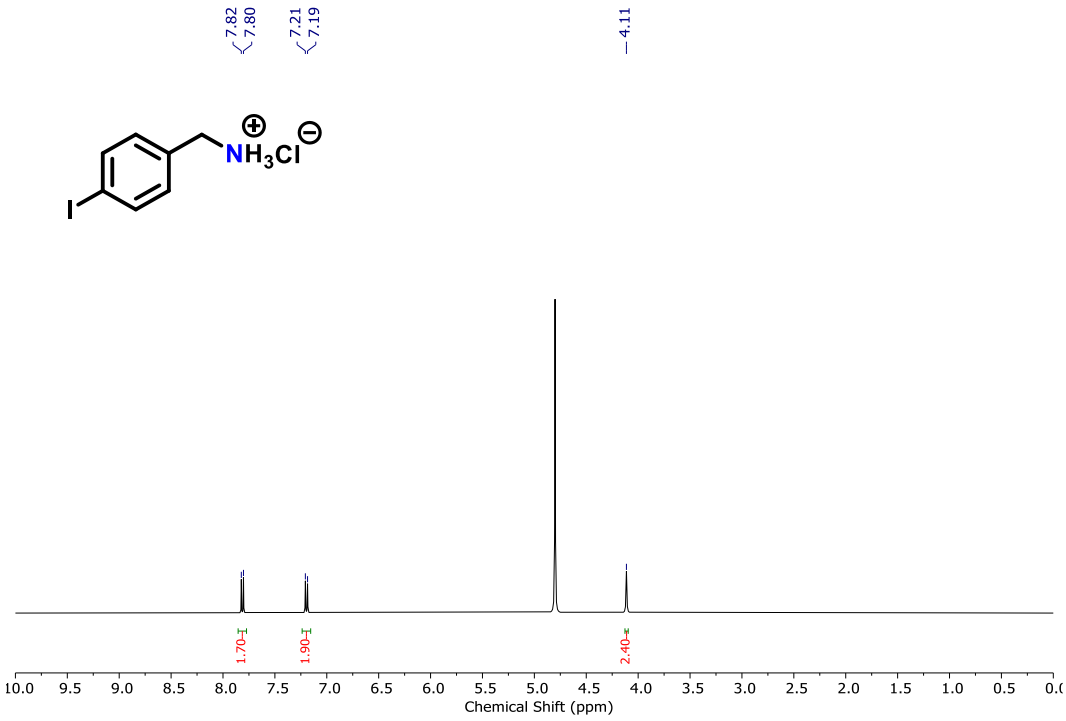


Figure S59: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2j**.

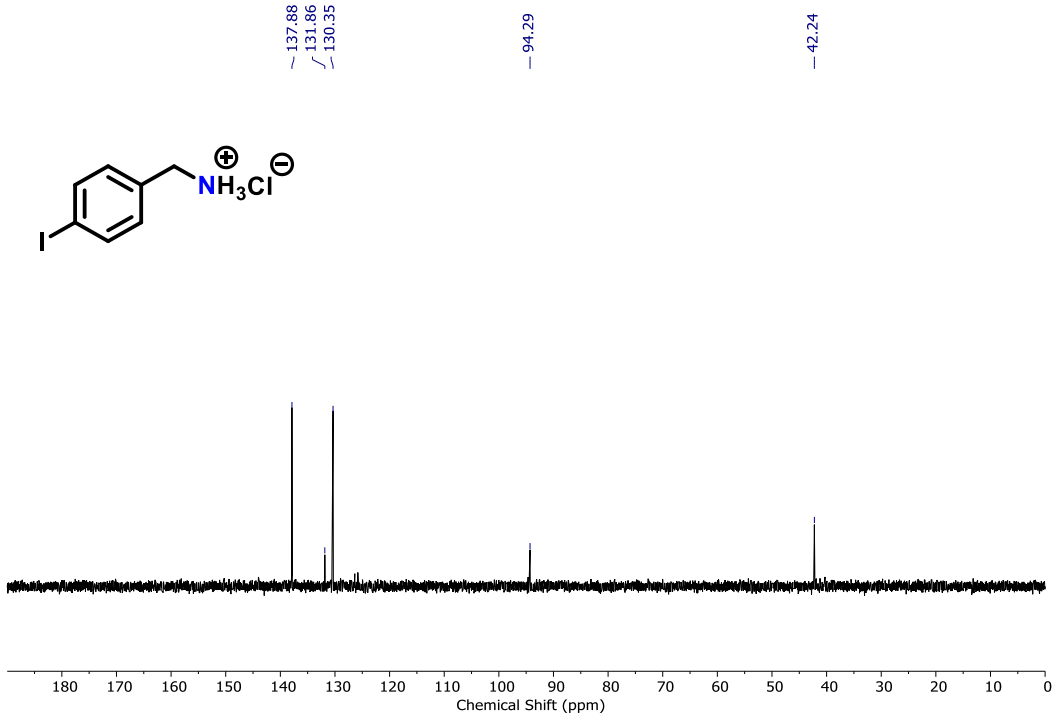


Figure S60: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2j**.

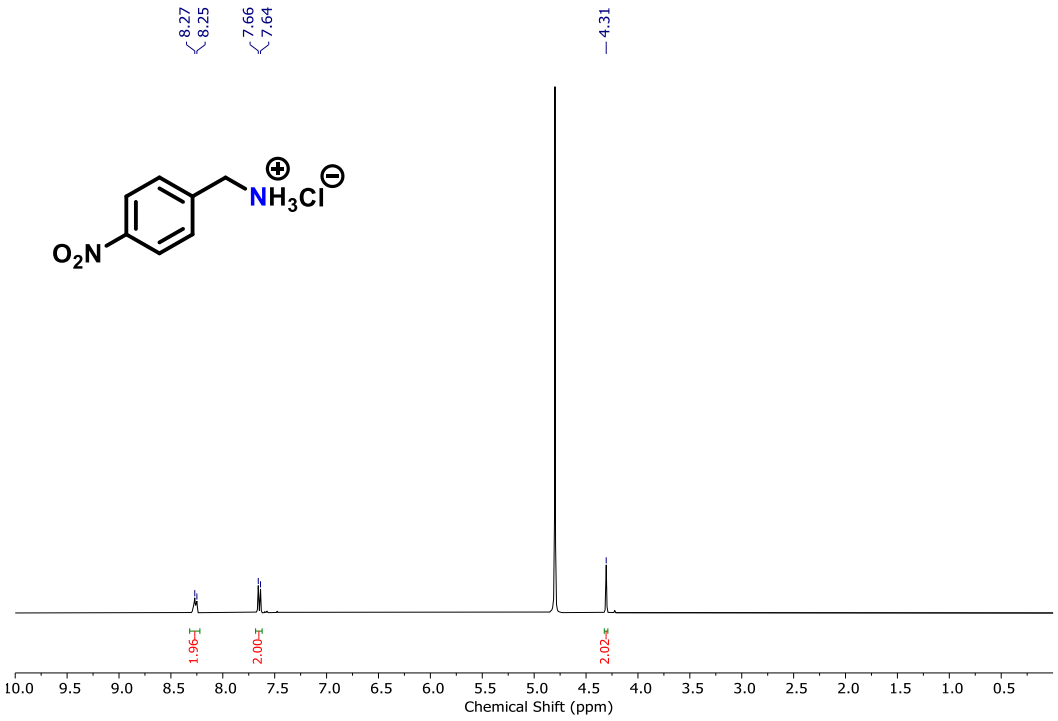


Figure S61: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2k**.

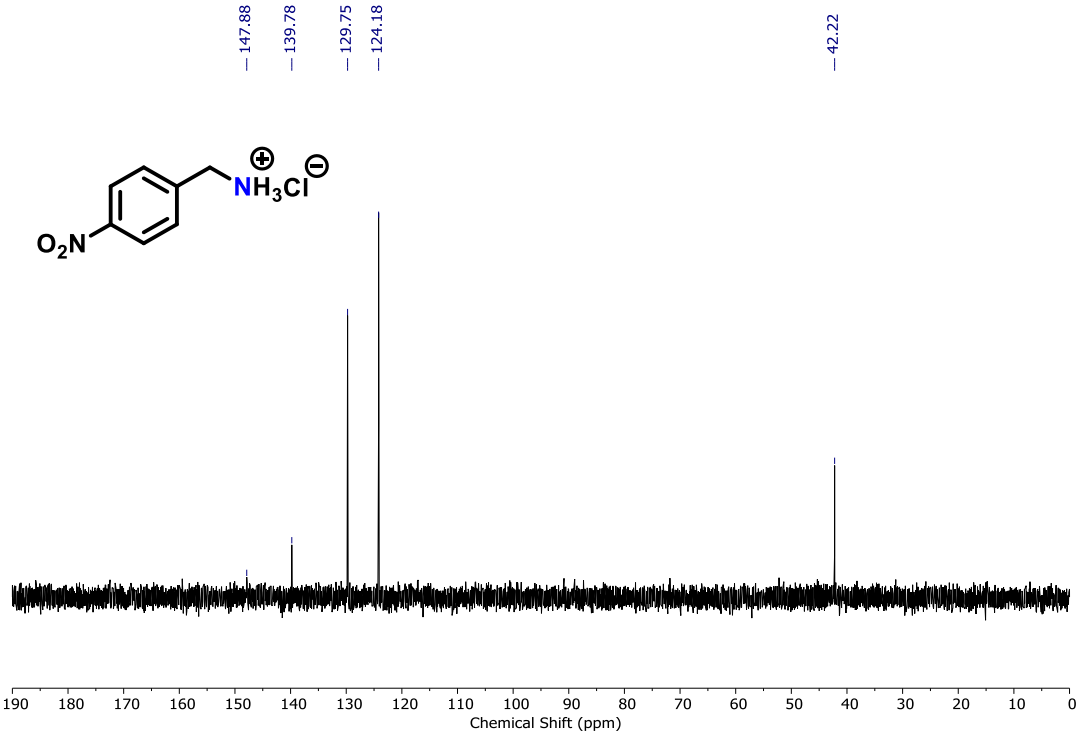


Figure S62: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **2k**.

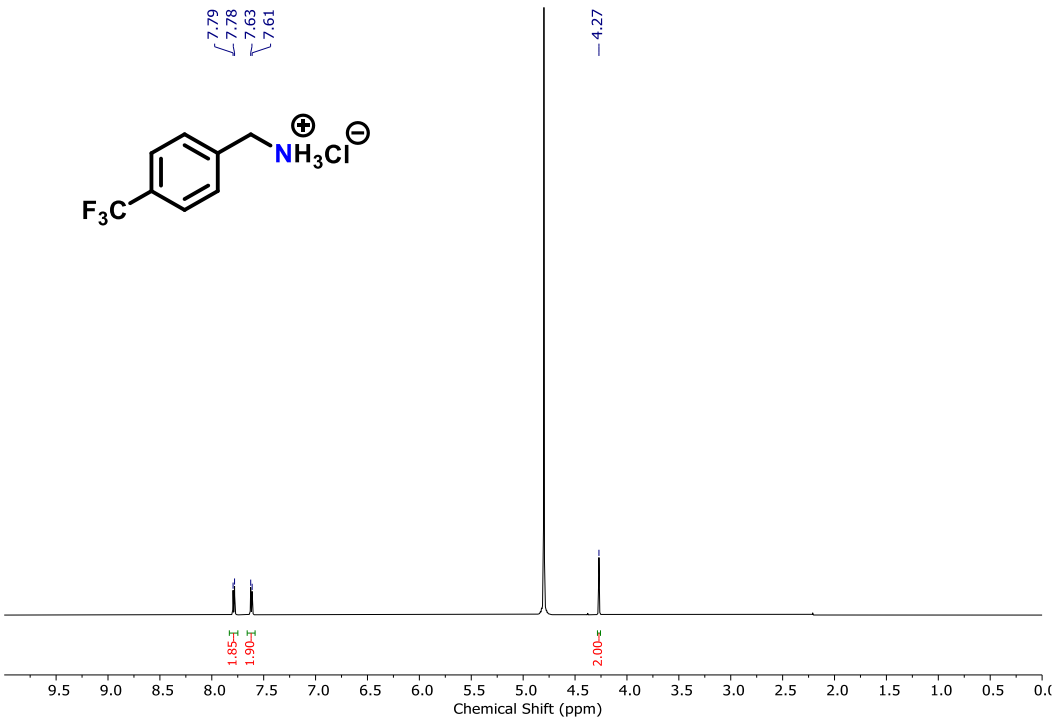


Figure S63: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2l**.

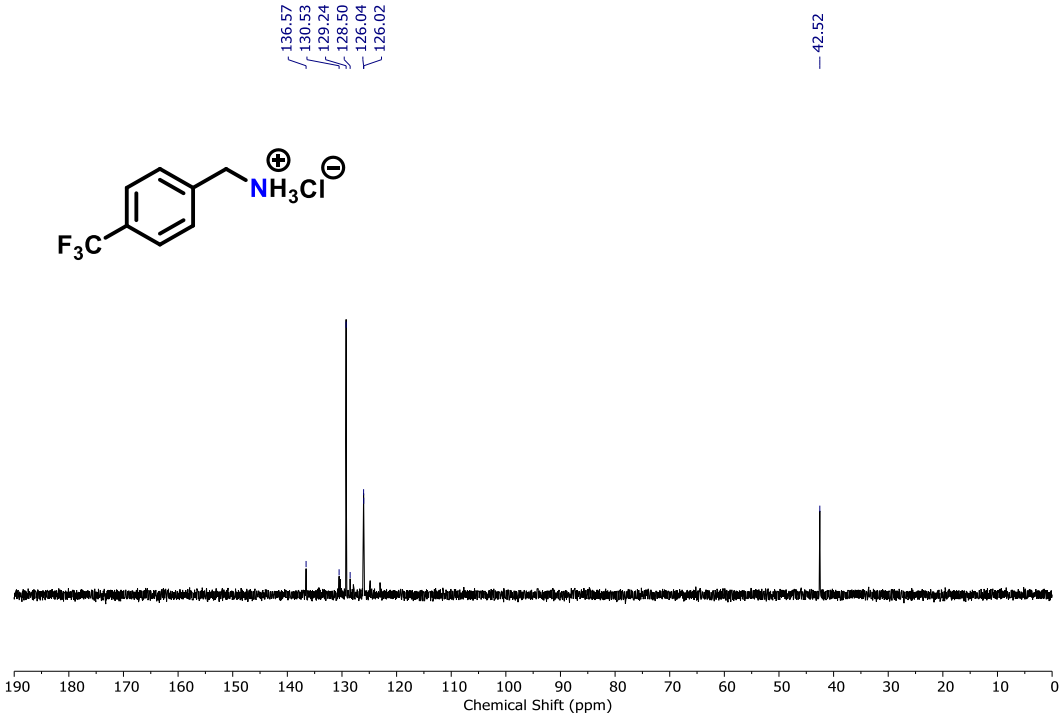


Figure S64: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2l**.

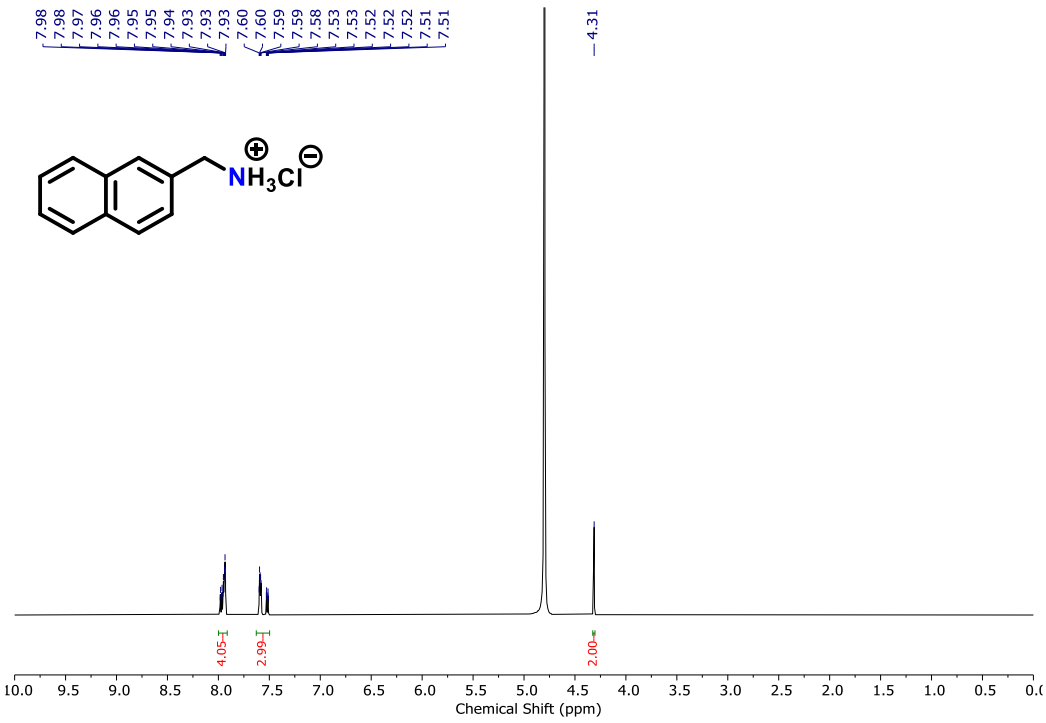


Figure S65: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2m**.

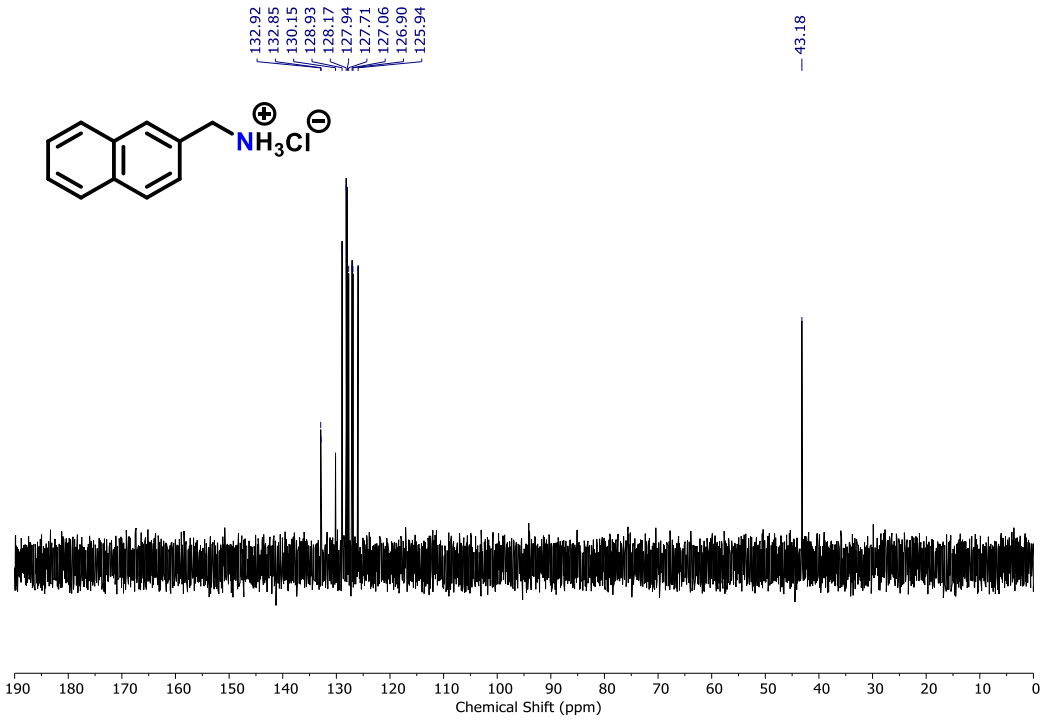


Figure S66: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2m**.

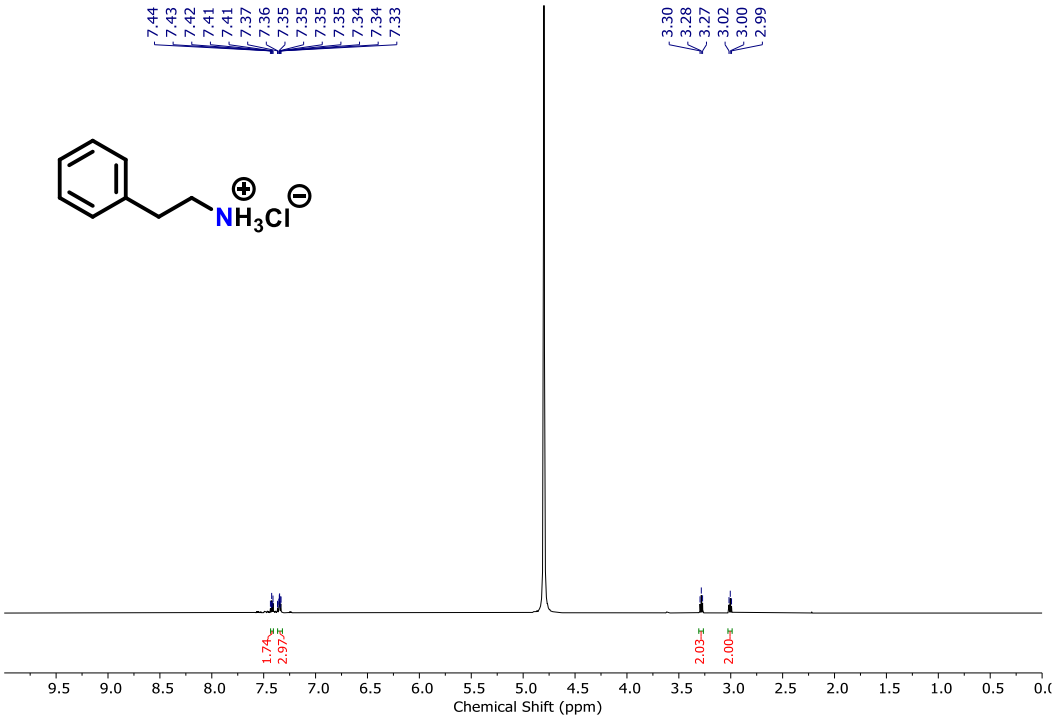


Figure S67: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2n**.

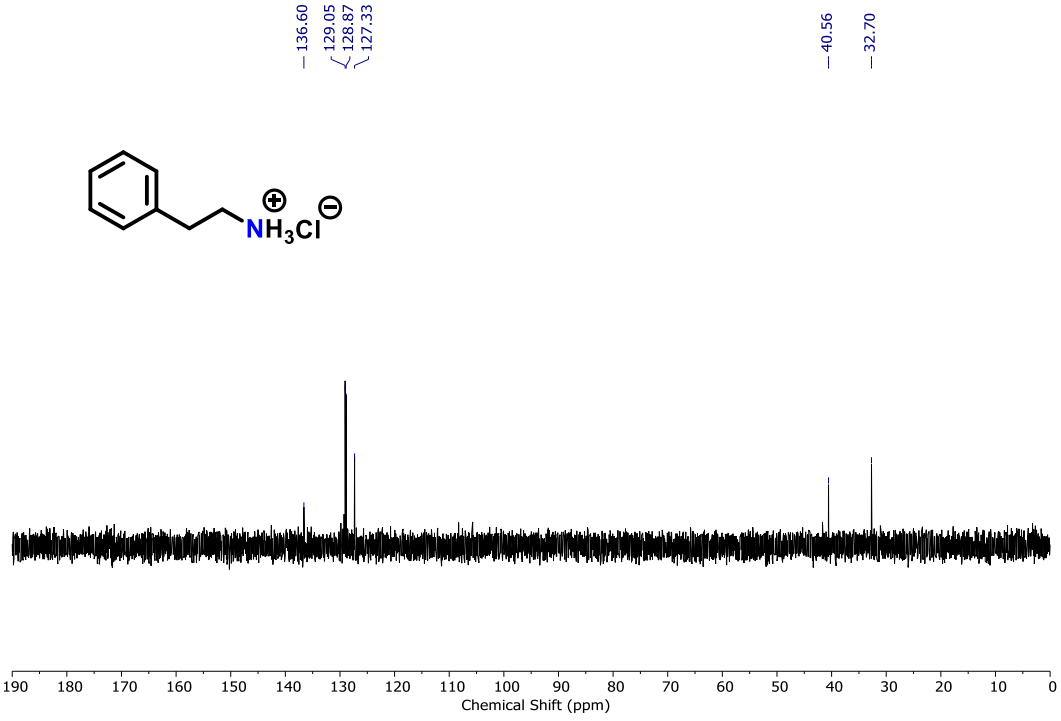


Figure S68: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **2n**.

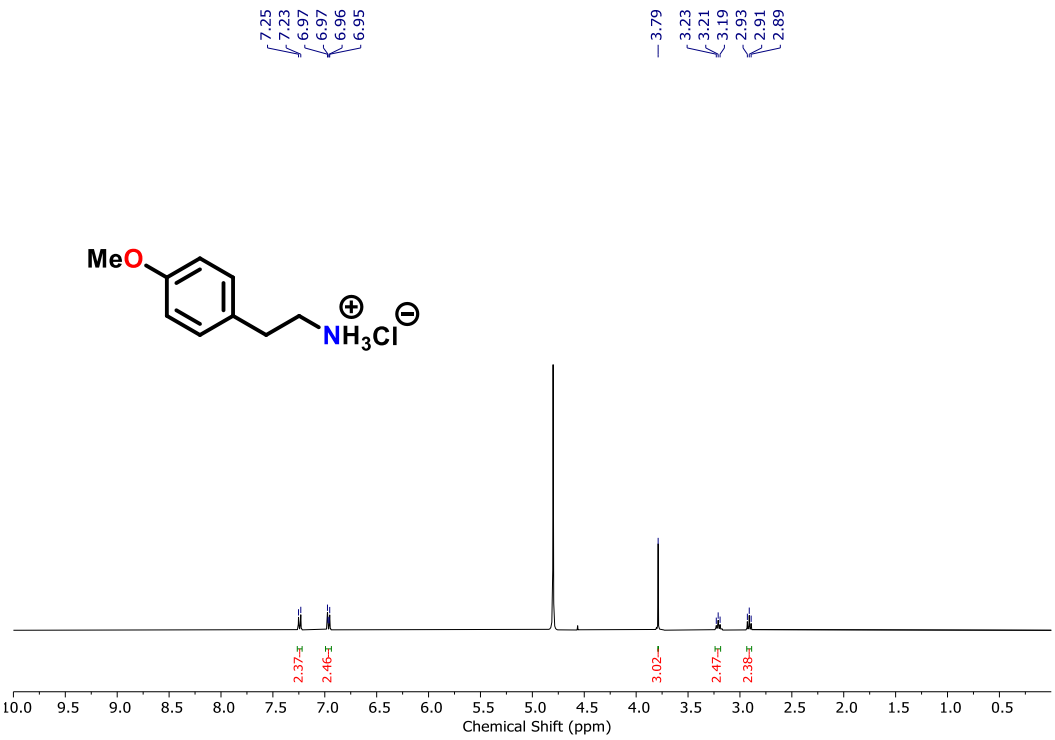


Figure S69: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2o**.

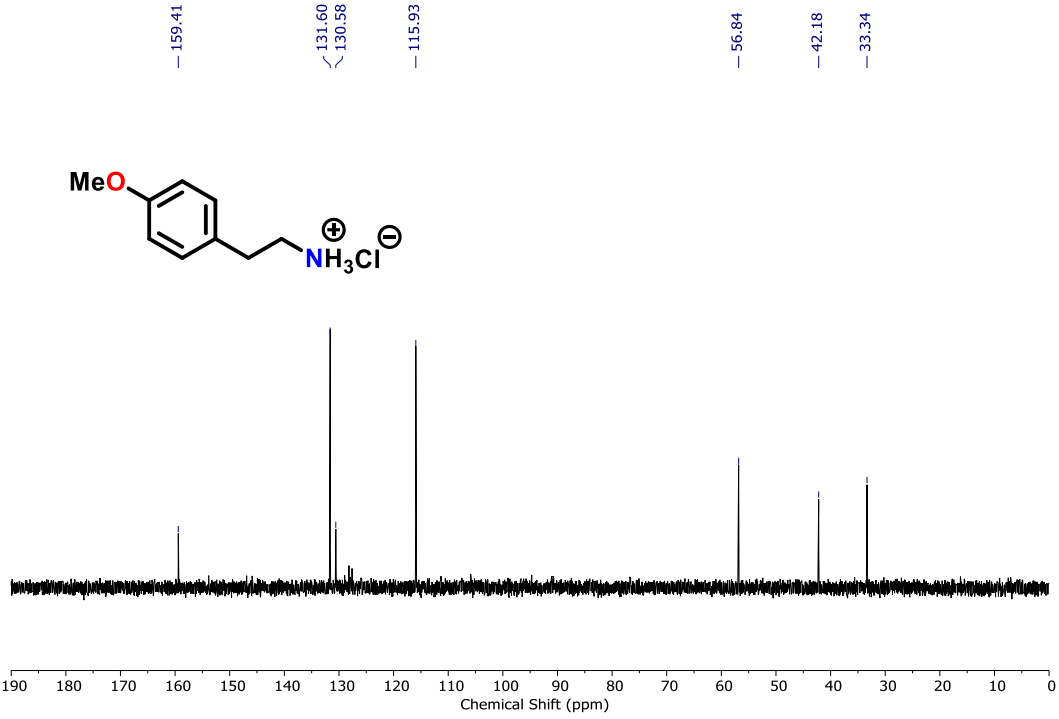


Figure S70: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **2o**.

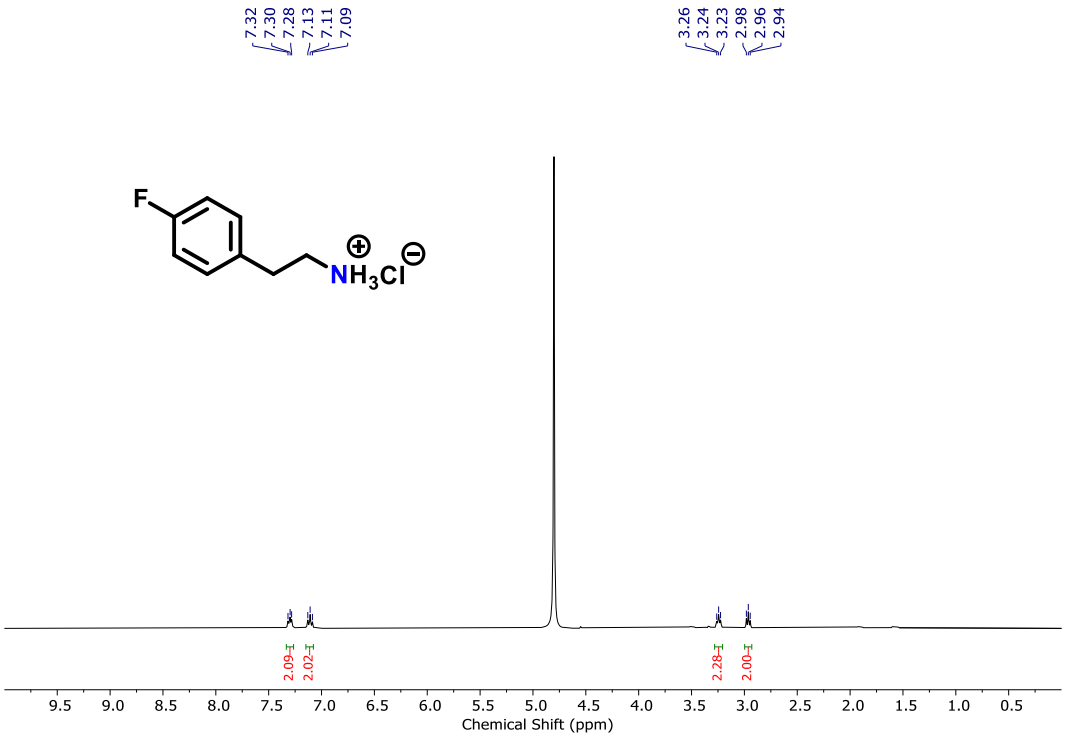


Figure S71: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2p**.

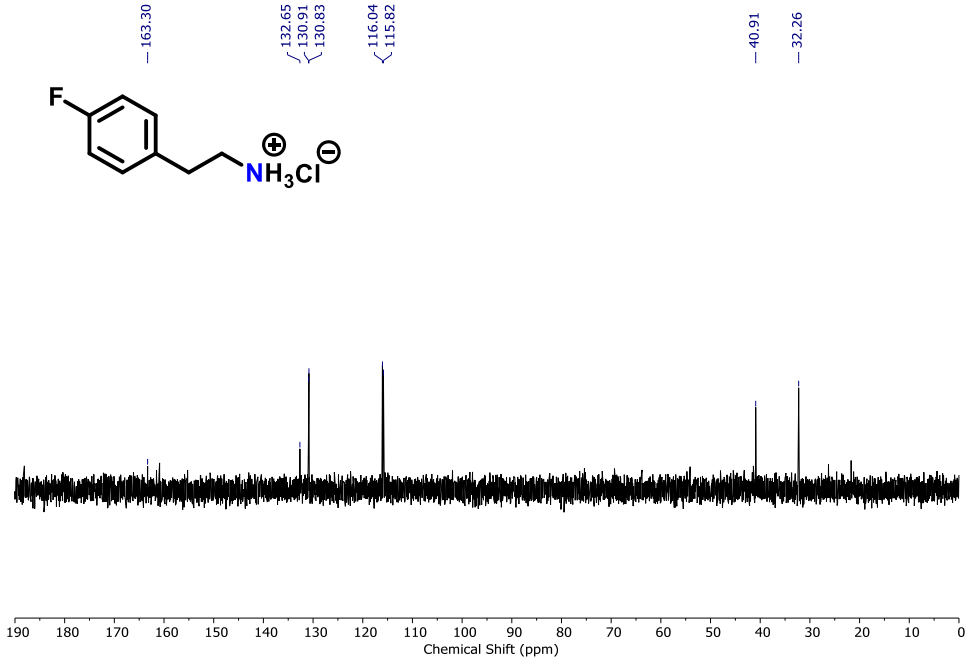


Figure S72: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2p**.

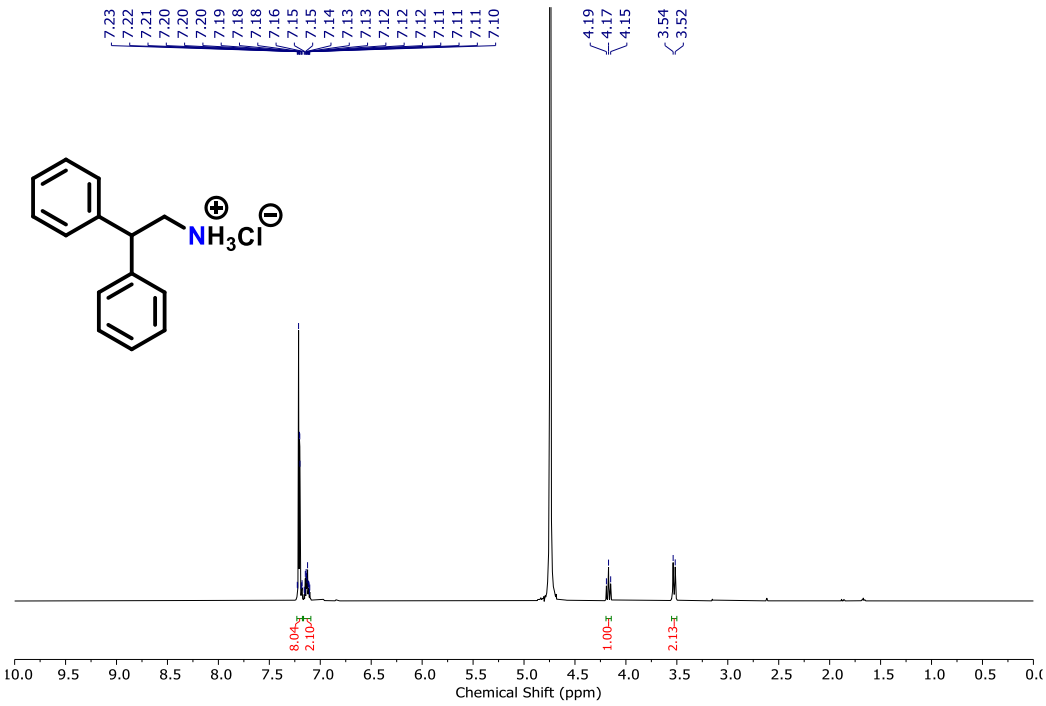


Figure S73: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2q**.

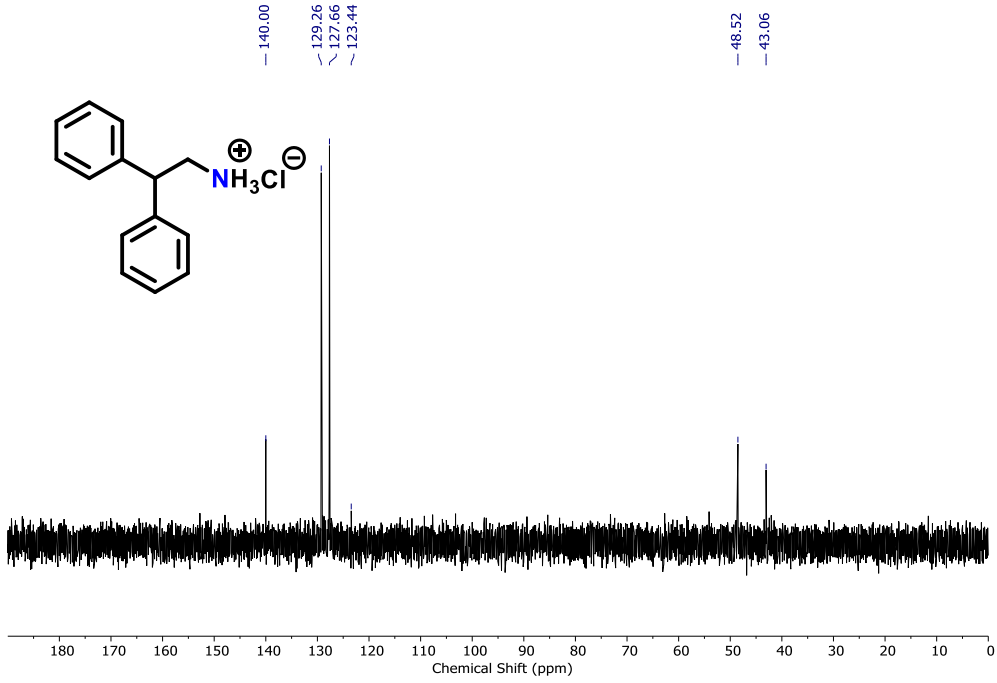


Figure S74: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2q**.

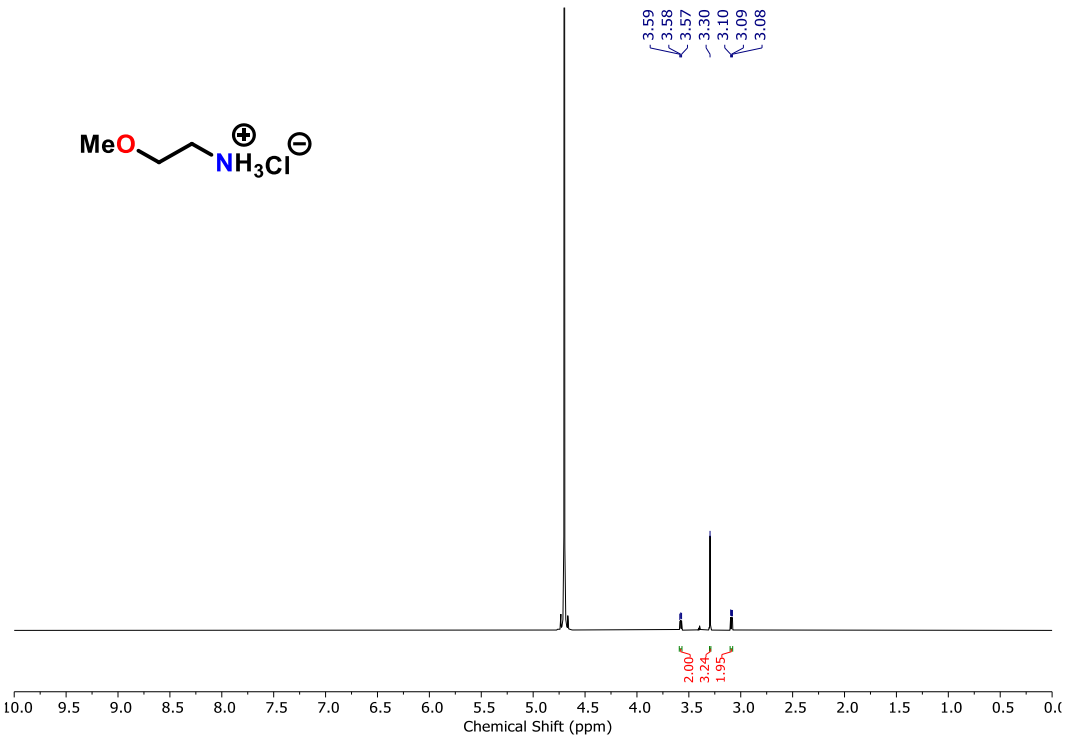


Figure S75: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2r**.

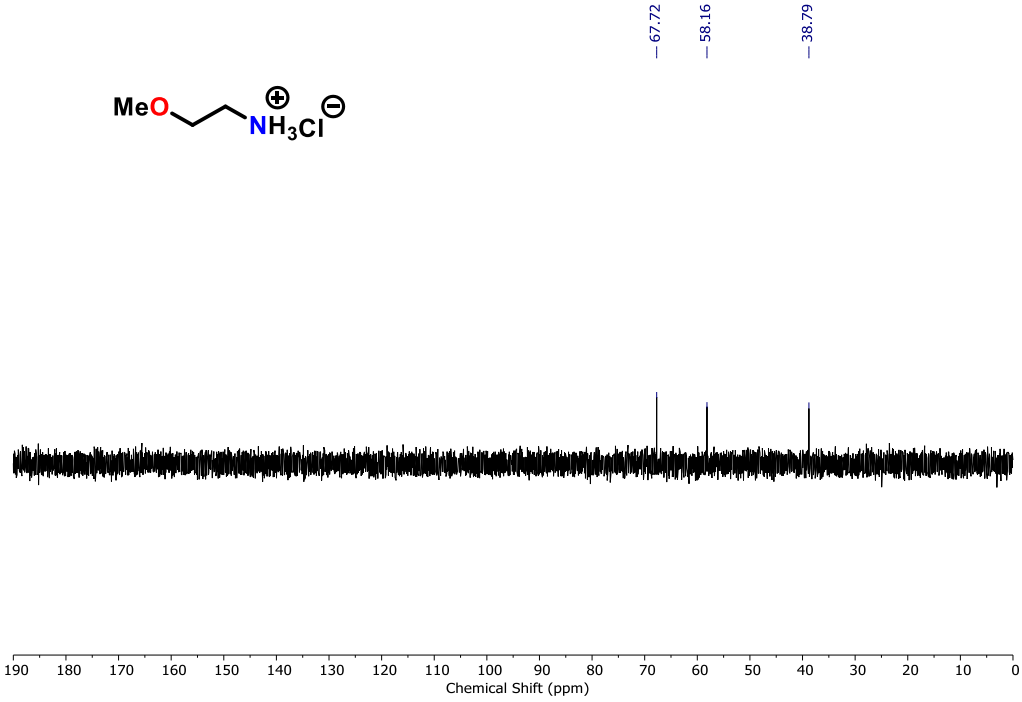


Figure S76: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2r**.

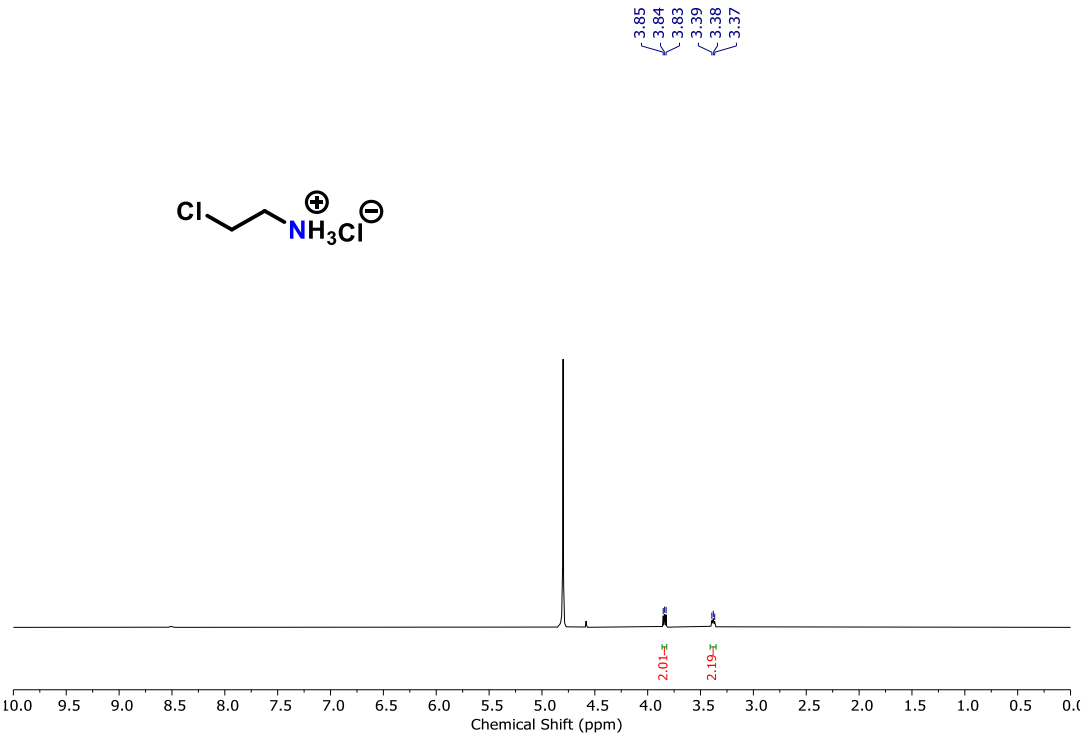


Figure S77: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **2s**.

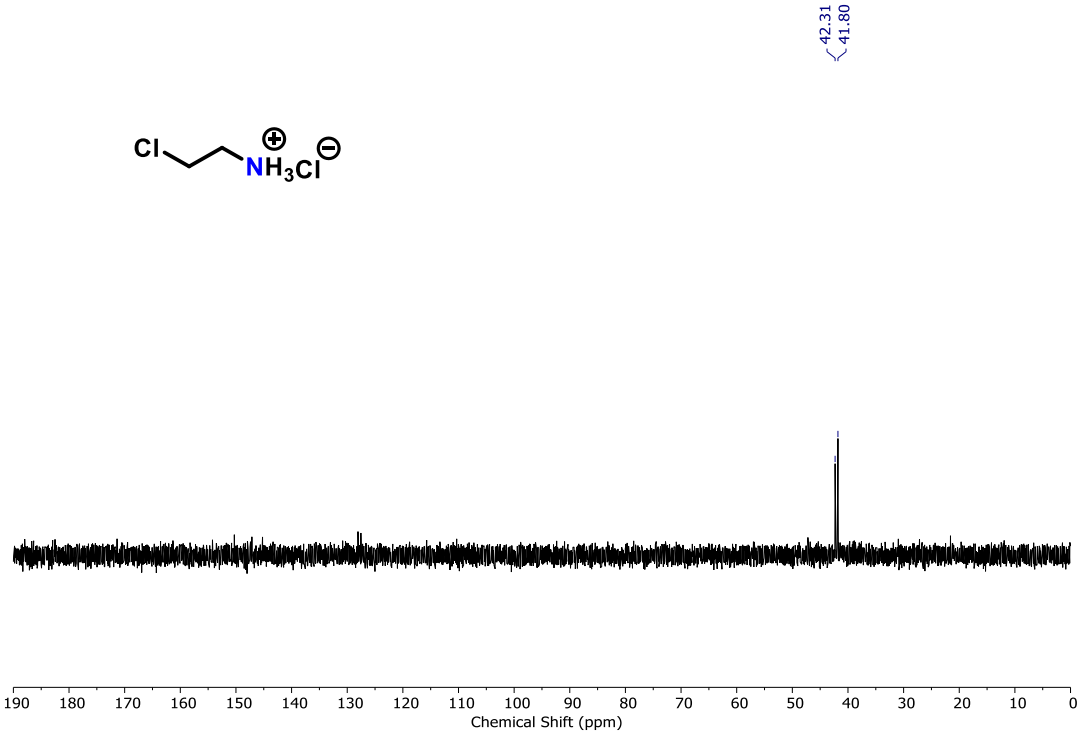


Figure S78: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **2s**.

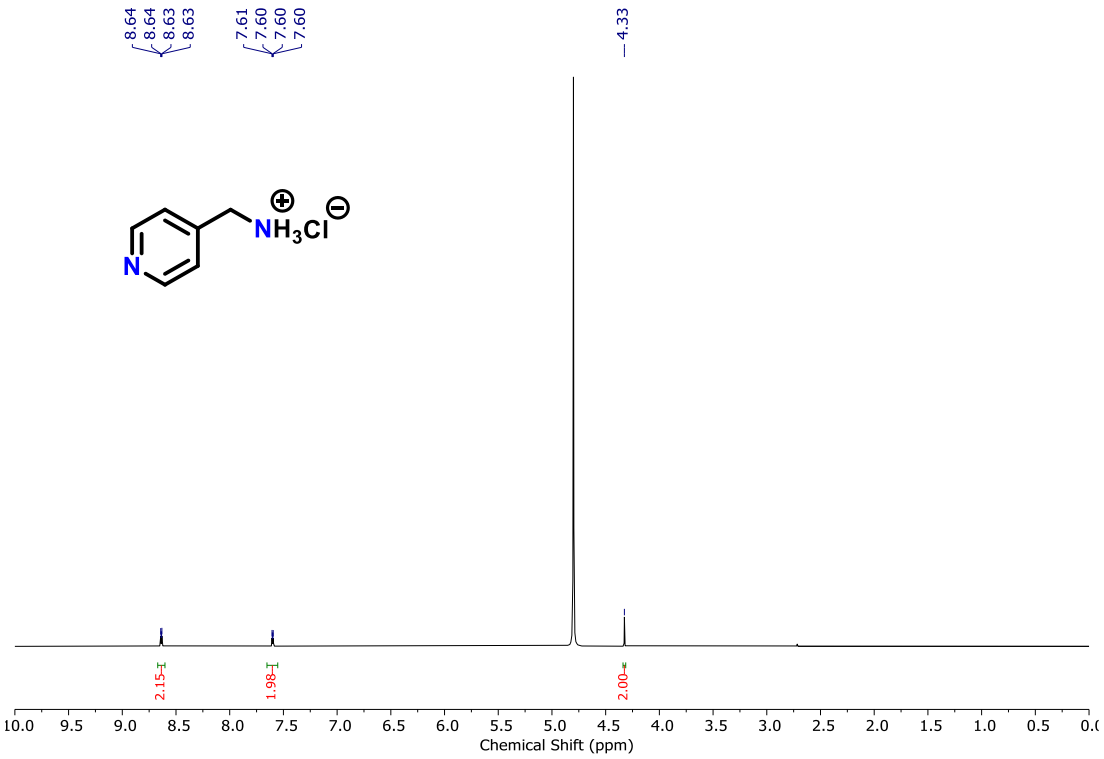


Figure S79: ^{1}H NMR (600 MHz, 25 ˚C, D_2O) spectra of **2t**.

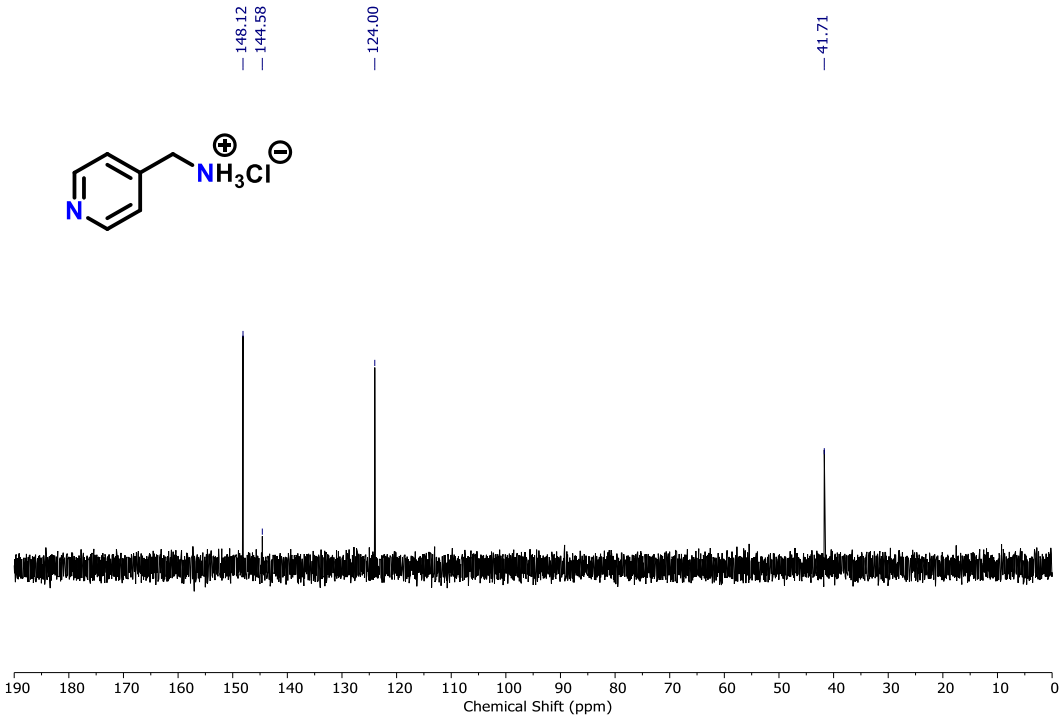


Figure S80: $^{13}C\{^{1}H\}$ (150 MHz, 25 ˚C, D_2O) NMR spectra of **2t**.

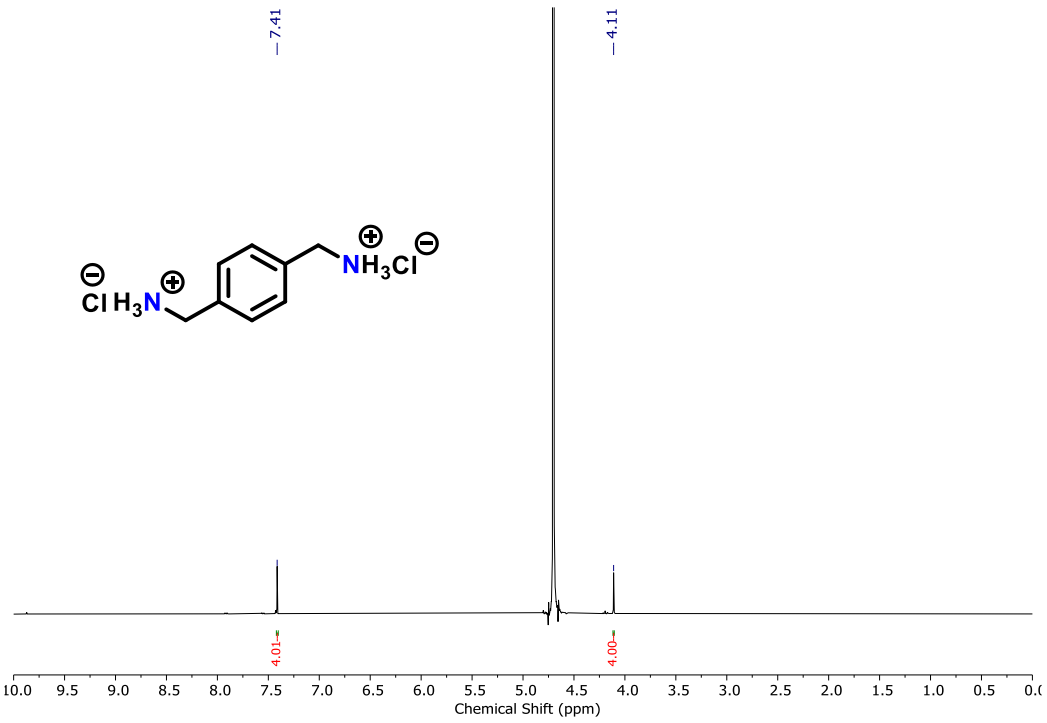


Figure S81: ^{1}H NMR (600 MHz, 25 ˚C, D_2O) spectra of **2u**.

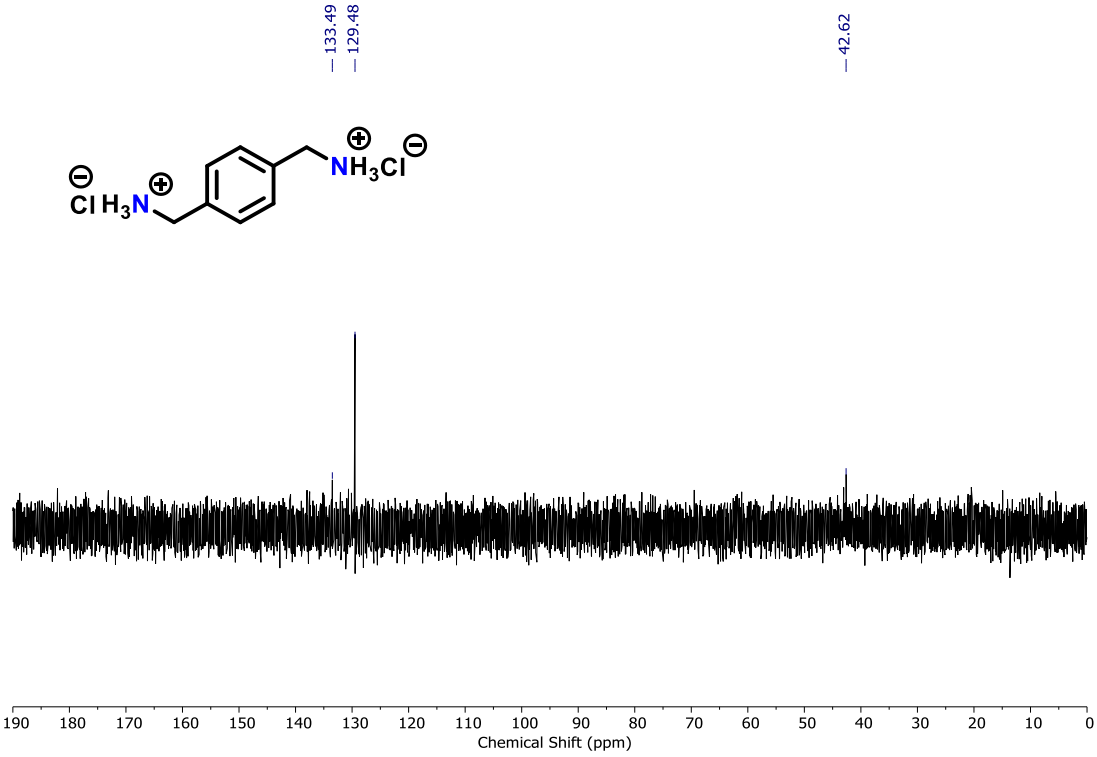
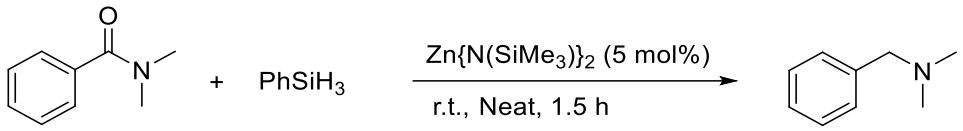


Figure S82: ^{13}C{^{1}H} (150 MHz, 25 ˚C, D_2O) NMR spectra of **2u**.

6. General procedure of hydrosilylation of tertiary amides.

The Schlenk tube was placed inside the glove box and loaded with [Zn(HMDS)$_2$] (9.65, 5 mol%), respective tertiary amides (0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) and kept in an oil bath at 60 °C for 12 hours. The reaction was then quenched by adding 0.2 mL of 2 N HCl to the Schlenk tube and worked up with water and dichloromethane. Following that, the water layer was collected and evaporated the water through rotatory evaporation to obtain the product.

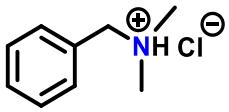
7. Optimization table for the Zn-catalyzed hydrosilylation of tertiary amides



Entry	Cat.	Cat. (mol %)	Silane	Temp. (˚C)	Time (h)	Isolated Yield (%)
1	-	-	$PhSiH_3$	90	12	-
2	Zn(HMDS)$_2$	5	$PhSiH_3$	60	1.5	92
3	Zn(HMDS)$_2$	5	$PhSiH_3$	r.t.	6	90
4	Zn(HMDS)$_2$	5	$PhSiH_3$	r.t.	1.5	90
5	Zn(HMDS)$_2$	5	$PhSiH_3$	r.t.	1	80
6	Zn(HMDS)$_2$	5	$PhMeSiH_2$	r.t.	1.5	75
7	Zn(HMDS)$_2$	5	Ph_2SiH_2	r.t.	1.5	72
8	Zn(HMDS)$_2$	5	Ph_3SiH	r.t.	1.5	50
9	$ZnCl_2$	5	$PhSiH_3$	r.t.	12	-
10	$ZnBr_2$	5	$PhSiH_3$	r.t.	12	-
11	ZnI_2	5	$PhSiH_3$	r.t.	12	-
12	Zn(HMDS)$_2$	5	Et_3SiH	r.t.	1.5	40

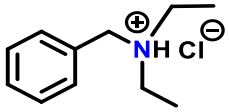
[a]Reaction conditions: Zn(HMDS)$_2$ (5 mol%), *N*, *N*-dimethylbenzamide (0.5 mmol) followed by $PhSiH_3$ (1 mmol) at room temperature under neat condition for 1.5h. [b]Isolated Yield.

8. NMR data of tertiary ammonium salts

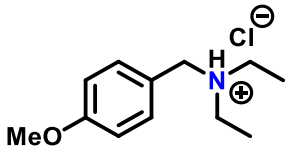


***N*,*N*-dimethyl-1-phenylmethanaminium chloride (4a)**.[16] Following procedure **6**, Zn(HMDS)$_2$ (9.65 mg, 5 mol%), *N*,*N*-dimethylbenzamide (74.59 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **2a** as a colourless solid (77.25 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm)

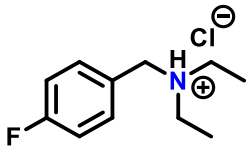
7.42-7.39 (m, 5H, Ar-*H*), 4.19 (s, 2H, CH_2), 2.73 (s, 2H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 130.8, 130.2, 129.3, 61.1, 42.1.



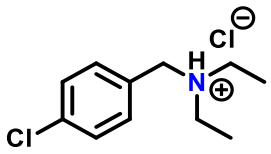
***N*-benzyl-*N*-ethyl-ethanaminium chloride (4ba)**.[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethylbenzamide (88.62 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4ba** as a colourless solid (84.88 mg, 85%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.40-7.35 (m, 5H, Ar-*H*), 4.19 (s, 2H, CH_2), 3.11-3.04 (m, 4H, CH_2), 1.20-1.16 (t, *J* = 8 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 130.8, 129.9, 129.3, 55.9, 46.7, 8.07.



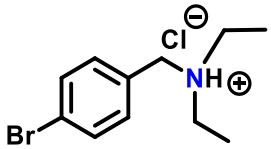
***N*-ethyl-*N*-(4-methoxybenzyl)ethanaminium chloride (4bb)**.[16] Followzwing procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethylbenzamide (103.63 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4bb** as a white solid (101.09 mg, 85%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.33-7.31 (t, 2H, Ar-*H*), 6.96-6.94 (t, 2H, Ar-*H*), 4.14 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.10-3.03 (m, 4H, CH_2), 1.21-1.17 (t, *J* = 8 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 159.9, 132.5, 121.6, 114.6, 55.4, 55.3, 46.5, 8.1.



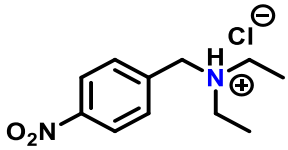
***N*-ethyl-*N*-(4-fluorobenzyl)ethanaminium chloride (4bc)**.[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethyl-4-fluorobenzamide (97.62 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4bb** as a white solid (97.96 mg, 90%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.41-7.37 (t, 2H, Ar-*H*), 7.12-7.08 (t, 2H, Ar-*H*), 4.19 (s, 2H, CH_2), 3.13-3.03 (m, 3H, CH_2), 1.20-1.17 (t, *J* = 8 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 164.5, 162.1, 133.1, 132.9, 125.3, 116.3, 116.0, 55.10, 46.6, 8.1.



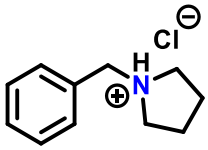
***N*-(4-chlorobenzyl)-*N*-ethylethanaminium chloride (4bd)**.[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethyl-4-chlorobenzamide (105.84 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4bd** as a white solid (103.03 mg, 88%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.38-7.32 (m, 4H, Ar-*H*), 4.17 (s, 2H, CH_2), 3.12-3.02 (m, 3H, CH_2), 1.20-1.16 (t, *J* = 8 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 135.5, 132.4, 129.3, 127.9, 55.1, 46.8, 8.1.



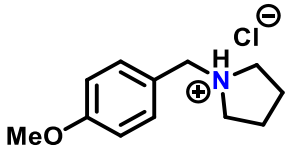
***N*-(4-bromobenzyl)-*N*-ethylethanaminium chloride (4be)**.[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethyl-4-bromobenzamide (105.84 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4be** as a white solid (119.80 mg, 86%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.40-7.38 (d, 2H, Ar-*H*), 7.26-7.23 (d, 2H, Ar-*H*), 4.10 (s, 2H, CH_2), 3.03-2.96 (m, 3H, CH_2), 1.15-1.11 (t, *J* = 8 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 132.7, 132.3, 128.4, 123.8, 55.1, 46.8, 8.3.



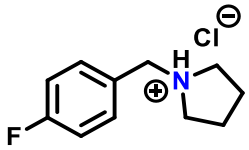
***N*-ethyl-*N*-(4-nitrobenzyl)ethanaminium chloride (4bf)**.[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethyl-4-nitrobenzamide (111.14 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4bf** as a yellow solid (97.90 mg, 80%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 8.16-8.13 (d, 2H, Ar-*H*), 7.61-7.59 (d, 2H, Ar-*H*), 4.32 (s, 2H, CH_2), 3.12-3.02 (m, 3H, CH_2), 1.21-1.17 (t, *J* = 8 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 148.3, 136.5, 132.0, 124.3, 54.9, 47.2, 8.1.



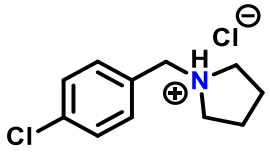
1-benzylpyrrolidin-1-ium chloride (4ca).[17] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), phenyl(pyrrolidin-1-yl)methanone (87.63 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4ca** as a colourless semisolid (83.05 mg, 84%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.39-7.35 (d, 5H, Ar-*H*), 4.21 (s, 2H, C*H*$_2$), 3.37-3.32 (m, 2H, C*H*$_2$), 3.07-3.00 (m, 2H, C*H*$_2$), 3.07-3.00 (m, 2H, C*H*$_2$), 2.03-1.99 (m, 2H, C*H*$_2$), 1.85-1.80 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 130.5, 130.2, 129.9, 129.3, 57.9, 53.6, 22.4.



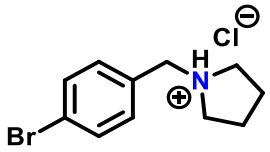
1-(4-methoxybenzyl)pyrrolidin-1-ium chloride (4cb).[17] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-methoxyphenyl(pyrrolidin-1-yl)methanone (102.63 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4cb** as a colourless semisolid (93.36 mg, 82%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.32-7.28 (m, 2H, Ar-*H*), 6.93-6.89 (m, 2H, Ar-*H*), 4.16 (s, 2H, C*H*$_2$), 3.70 (s, 3H, OC*H*$_3$), 3.36-3.30 (m, 2H, C*H*$_2$), 3.05-2.98 (m, 2H, C*H*$_2$), 2.05-1.96 (m, 2H, C*H*$_2$), 1.88-1.80 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 159.9, 131.9, 122.9, 114.6, 57.3, 55.4, 53.3, 22.3.



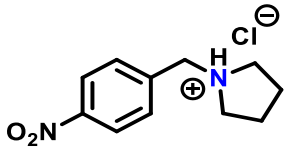
1-(4-fluorobenzyl)pyrrolidin-1-ium chloride (4cc).[18] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-fluorophenyl(pyrrolidin-1-yl)methanone (96.61 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4cc** as a colourless semisolid (86.28 mg, 80%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.40-7.36 (m, 2H, Ar-*H*), 7.11-7.06 (m, 2H, Ar-*H*), 4.22 (s, 2H, C*H*$_2$), 3.39-3.34 (m, 2H, C*H*$_2$), 3.07-3.00 (m, 2H, C*H*$_2$), 2.05-1.98 (m, 2H, C*H*$_2$), 1.87-1.81 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 164.5, 162.0, 132.4, 132.3, 126.5, 116.2, 115.9, 57.1, 53.5, 22.3.



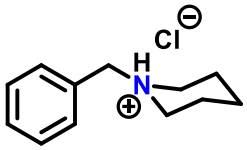
1-(4-chlorobenzyl)pyrrolidin-1-ium chloride (4cd).[7] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-chlorophenyl(pyrrolidin-1-yl)methanone (104.83 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4cd** as a colourless semisolid (95.17 mg, 82%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.37-7.32 (m, 5H, Ar-*H*), 4.22 (s, 2H, C*H*$_2$), 3.39-3.33 (m, 2H, C*H*$_2$), 3.07-3.01 (m, 2H, C*H*$_2$), 2.05-2.01 (m, 2H, C*H*$_2$), 1.87-1.82 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 135.3, 131.8, 129.3, 129.1, 57.1, 53.6, 22.4.



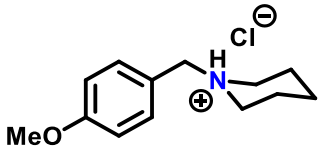
1-(4-bromobenzyl)pyrrolidin-1-ium chloride (4ce).[19] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-bromophenyl(pyrrolidin-1-yl)methanone (127.06 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4ce** as a colourless semisolid (110.64 mg, 80%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.47-7.45 (m, 2H, Ar-*H*), 7.25-7.23 (m, 2H, Ar-*H*), 4.18 (s, 2H, C*H*$_2$), 3.36-3.30 (m, 2H, C*H*$_2$), 3.04-2.97 (m, 2H, C*H*$_2$), 2.03-1.97 (m, 2H, C*H*$_2$), 1.87-1.79 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 132.3, 132.1, 129.5, 123.6, 57.2, 53.6, 22.4.



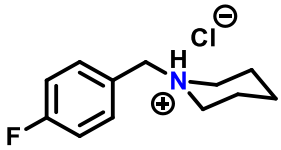
1-(4-nitrobenzyl)pyrrolidin-1-ium chloride (4cf).[19] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-nitrophenyl(pyrrolidin-1-yl)methanone (110.11 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4cf** as a yellow semisolid (94.65 mg, 78%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 8.23-8.20 (m, 2H, Ar-*H*), 7.65-7.63 (m, 2H, Ar-*H*), 4.42 (s, 2H, C*H*$_2$), 3.48-3.42 (m, 2H, C*H*$_2$), 3.15-3.08 (m, 2H, C*H*$_2$), 2.11-2.04 (m, 2H, C*H*$_2$), 1.92-1.86 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 148.4, 137.5, 131.4, 124.3, 56.9, 54.0, 22.4.



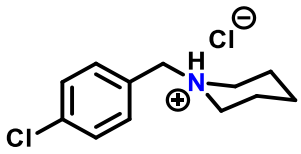
1-benzylpiperidin-1-ium chloride (4da).[17] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), phenyl(piperdin-1-yl)methanone (94.63 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4da** as a colourless solid (86.80 mg, 82%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.38-7.34 (m, 5H, Ar-*H*), 4.10 (s, 2H, C*H*$_2$), 3.32-3.27 (m, 2H, C*H*$_2$), 2.83-2.76 (m, 2H, C*H*$_2$), 1.78-1.72 (m, 2H, C*H*$_2$), 1.67-1.62 (m, 1H, C*H*), 1.58-1.46 (m, 2H, C*H*$_2$), 1.35-1.25 (m, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 131.2, 130.0, 129.2, 128.7, 60.5, 52.7, 22.6, 21.1.



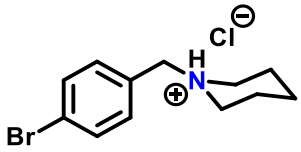
1-(4-methoxybenzyl)piperidin-1-ium chloride (4db).[17] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-methoxyphenyl(piperdin-1-yl)methanone (109.64 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4da** as a colourless solid (97.91 mg, 81%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.29-7.25 (m, 2H, Ar-*H*), 6.91-6.87 (m, 2H, Ar-*H*), 4.04 (s, 2H, C*H*$_2$), 3.69 (s, 2H, C*H*$_3$), 3.30-3.25 (m, 2H, C*H*$_2$), 2.79-2.72 (m, 2H, C*H*$_2$), 1.78-1.73 (m, 2H, C*H*$_2$), 1.67-1.62 (m, 1H, C*H*), 1.57-1.45 (m, 2H, C*H*$_2$), 1.33-1.26 (m, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 159.9, 132.8, 121.1, 114.5, 59.9, 55.4, 52.4, 22.7, 21.1.



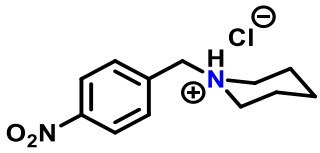
1-(4-fluorobenzyl)piperidin-1-ium chloride (4dc).[20] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-fluorophenyl(piperdin-1-yl)methanone (103.62 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4da** as a colourless solid (91.88 mg, 80%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.39-7.35 (m, 2H, Ar-*H*), 7.11-7.06 (m, 2H, Ar-*H*), 4.12 (s, 2H, C*H*$_2$), 3.34-3.29 (m, 2H, C*H*$_2$), 2.85-2.78 (m, 2H, C*H*$_2$), 1.82-1.75 (m, 2H, C*H*$_2$), 1.69-1.63 (m, 1H, C*H*), 1.60-1.48 (m, 2H, C*H*$_2$), 1.37-1.27 (m, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 164.6, 162.1, 133.4, 133.3, 124.7, 116.1, 115.9, 59.7, 52.6, 22.7, 21.1.



1-(4-chlorobenzyl)piperidin-1-ium chloride (4dd).[21] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-chlorophenyl(piperdin-1-yl)methanone (112.85 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4dd** as a colourless solid (101.83 mg, 82%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.39-7.32 (m, 4H, Ar-*H*), 4.13 (s, 2H, C*H*$_2$), 3.34-3.31 (m, 2H, C*H*$_2$), 2.86-2.76 (m, 2H, C*H*$_2$), 1.82-1.77 (m, 2H, C*H*$_2$), 1.70-1.65 (m, 1H, C*H*), 1.61-1.50 (m, 2H, C*H*$_2$), 1.37-1.30 (m, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 135.5, 132.7, 129.2, 127.3, 59.7, 52.7, 22.6, 21.1.

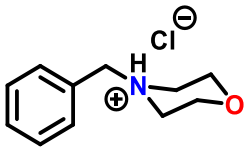


1-(4-bromobenzyl)piperidin-1-ium chloride (4de).[20] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-bromophenyl(piperdin-1-yl)methanone (134.07 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4de** as a colourless solid (116.25 mg, 80%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.51-7.48 (m, 2H, Ar-*H*), 7.25-7.22 (m, 2H, Ar-*H*), 4.09 (s, 2H, C*H*$_2$), 3.32-3.27 (m, 2H, C*H*$_2$), 2.83-2.76 (m, 2H, C*H*$_2$), 1.79-1.74 (m, 2H, C*H*$_2$), 1.67-1.62 (m, 1H, C*H*), 1.57-1.47 (m, 2H, C*H*$_2$), 1.35-1.28 (m, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 132.9, 132.2, 127.8, 123.8, 59.7, 52.8, 22.6, 21.0.

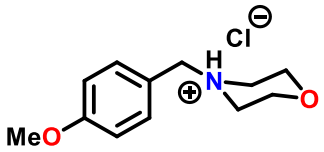


1-(4-nitrobenzyl)piperidin-1-ium chloride (4df).[21] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), 4-bromophenyl(piperdin-1-yl)methanone (117.07 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4df** as a yellow solid (96.27 mg, 75%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 8.14-8.12 (m, 2H, Ar-*H*), 7.60-7.58 (m, 2H, Ar-*H*), 4.27 (s, 2H, C*H*$_2$), 3.37-3.32 (m, 2H, C*H*$_2$), 2.92-2.85 (m, 2H, C*H*$_2$), 1.83-1.77 (m, 2H, C*H*$_2$), 1.70-1.62 (m, 1H, C*H*), 1.61-1.52 (m, 2H,

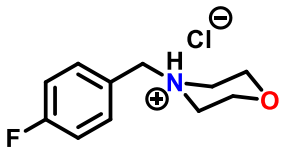
C*H*$_2$), 1.39-1.31 (m, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 148.4, 135.9, 132.4, 124.1, 59.2, 53.1, 22.7, 20.9.



4-benzylmorpholin-4-ium chloride (4ea).[22] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), morpholino(phenyl)methanone (95.61 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4ea** as a colourless solid (91.89 mg, 86%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.44-7.41 (m, 2H, Ar-*H*), 4.27 (s, 2H, C*H*$_2$), 4.02-3.98 (m, 2H, C*H*$_2$), 3.71-3.64 (m, 2H, C*H*$_2$), 3.36-3.32 (m, 2H, C*H*$_2$), 3.18-3.11 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 131.3, 130.4, 129.3, 127.9, 63.7, 60.9, 51.2.

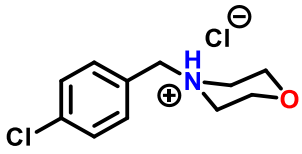


4-(4-methoxybenzyl)morpholin-4-ium chloride (4eb).[22] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), morpholino(4-methoxyphenyl)methanone (110.63 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4eb** as a colourless solid (107.24 mg, 88%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.35-7.33 (m, 2H, Ar-*H*), 6.94-6.92 (m, 2H, Ar-*H*), 4.19 (s, 2H, C*H*$_2$), 4.00-3.96 (m, 2H, C*H*$_2$), 3.72 (s, 3H, OC*H*$_3$), 3.70-3.63 (m, 2H, C*H*$_2$), 3.32-3.28 (m, 2H, C*H*$_2$), 3.13-3.06 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_c (ppm) 160.2, 132.9, 120.2, 114.6, 63.7, 60.3, 55.5, 51.0.

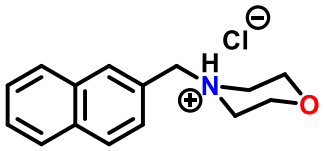


4-(4-fluorobenzyl)morpholin-4-ium chloride (4ec).[19] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), morpholino(4-fluorophenyl)methanone (104.61 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4eb** as a colourless solid (104.26 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 7.42-7.38 (m, 2H, Ar-*H*), 7.13-7.08 (m, 2H, Ar-*H*), 4.24 (s, 2H, C*H*$_2$), 3.99-3.95 (m, 2H,

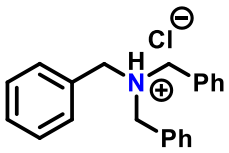
CH_2), 3.68-3.61 (m, 2H, CH_2), 3.33-3.29 (m, 2H, CH_2), 3.15-3.08 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 164.8, 162.3, 133.5, 133.4, 123.9, 116.3, 116.0, 63.6, 59.9, 51.1.



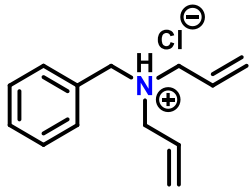
4-(4-chlorobenzyl)morpholin-4-ium chloride (4ed).[22] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), morpholino(4-chlorophenyl)methanone (112.83 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4eb** as a colourless solid (105.46 mg, 85%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.40-7.34 (m, 4H, Ar-*H*), 4.71 (s, 2H, CH_2), 4.00-3.96 (m, 2H, CH_2), 3.69-3.62 (m, 2H, CH_2), 3.33-3.30 (m, 2H, CH_2), 3.16-3.10 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 135.8, 132.8, 129.3, 126.4, 63.6, 59.9, 51.2.



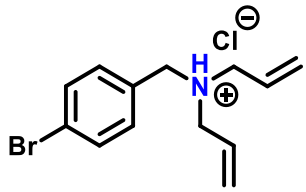
4-(naphthalene-2-ylmethyl)morpholin-4-ium chloride (4f).[23] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), morpholino(naphthalen-1-yl)methanone (120.64 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4f** as a colourless solid (110.78 mg, 85%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.77-7.70 (m, 4H, Ar-*H*), 7.44-7.40 (m, 2H, Ar-*H*), 7.30-7.26 (m, 1H, Ar-*H*), 4.19 (s, 2H, CH_2), 3.88-3.81 (m, 2H, CH_2), 3.60-3.53 (m, 2H, CH_2), 3.19-3.14 (m, 2H, CH_2), 3.03-2.96 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 133.3, 132.6, 131.4, 128.9, 128.2, 127.7, 127.6, 127.4, 127.1, 125.2, 63.5, 60.7, 51.1, 43.1.



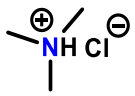
tribenzylammonium chloride (4g).[24] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-dibenzylbenzamide (150.69 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4g** as a colourless solid (113.35 mg, 70%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.44-7.33 (m, 15H, Ar-*H*), 4.15 (s, 6H, CH_2).$^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 131.3, 130.6, 129.6, 129.7, 129.3, 50.5.



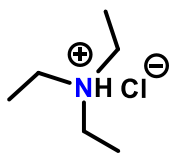
***N*-allyl-*N*-benzylprop-2-en-1-aminium chloride (4ha)**.[25] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diallylbenzamide (100.63 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4hb** as a colourless solid (91.73mg, 82%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.44-7.39 (m, 4H, Ar-*H*), 5.91-5.78 (m, 2H, C*H*), 5.55-5.47 (m, 4H, CH_2), 4.25 (s, 2H, CH_2), 3.69-3.67 (dd, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 130.9, 129.3, 126.7, 125.5, 108.1, 56.3, 54.4.



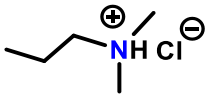
***N*-allyl-*N*-(4-bromobenzyl)prop-2-en-1-aminium chloride (4hb)**.[25] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diallyl-4-bromobenzamide (140.08 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4hb** as a brownish solid (121.05 mg, 80%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.55-7.53 (d, 2H, Ar-*H*), 7.28-7.26 (d, 2H, Ar-*H*), 5.88-5.78 (m, 2H, C*H*), 5.54-5.46 (m, 4H, CH_2), 4.18 (s, 2H, CH_2), 3.66-3.64 (dd, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 133.7, 132.4, 128.2, 126.9, 125.4, 123.9, 55.5, 54.5.



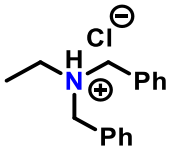
trimethylammonium chloride (4i).[26] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-dimethylformamide (36.54 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4i** as a colourless semisolid (42.05 mg, 88%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 2.81 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 44.7.



triethylammonium chloride (4j).[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-diethylacetamide (57.55 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4j** as a colourless semisolid (61.94 mg, 90%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 3.14-3.08 (q, *J* = 8 Hz, 6H, C*H*$_2$), 1.20-1.17 (t, *J* = 8 Hz, 9H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 46.7, 8.3.



***N,N*-dimethylpropan-1-aminium chloride (4k)**.[16] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-dimethylpropionamide (50.52 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4k** as a colourless semisolid (52.48 mg, 85%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 3.02-2.98 (t, *J* = 8 Hz, 2H, C*H*$_2$), 2.77 (s, 6H, C*H*$_2$), 1.68-1.59 (m, 2H, C*H*$_3$), 0.89-0.85 (t, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 59.3, 42.6, 17.6, 9.9.



***N,N*-dibenzylethanaminium chloride (4l)**.[27] Following procedure **6**, $Zn(HMDS)_2$ (9.65 mg, 5 mol%), *N*, *N*-dibenzylacetamide (119.66 mg, 0.5 mmol) and $PhSiH_3$ (108.22 mg, 1 mmol) afforded **4l** as a colourless semisolid (109.95 mg, 84%). ^1H NMR (400 MHz, D_2O): δ_H (ppm) 7.41-7.38 (m, 8H, Ar-*H*), 7.33-7.30 (m, 2H, Ar-*H*), 4.18 (s, 2H, C*H*$_2$), 4.13 (s, 2H, C*H*$_2$), 3.10-3.04 (q, *J* = 8 Hz, 6H, C*H*$_2$), 1.27-1.24 (t, *J* = 8 Hz, 3H, C*H*$_3$), 0.89-0.85 (t, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ_c (ppm) 130.9, 130.6, 130.1, 129.9, 129.7, 129.3, 129.2, 129.1,50.2, 50.5, 47.5, 8.1.

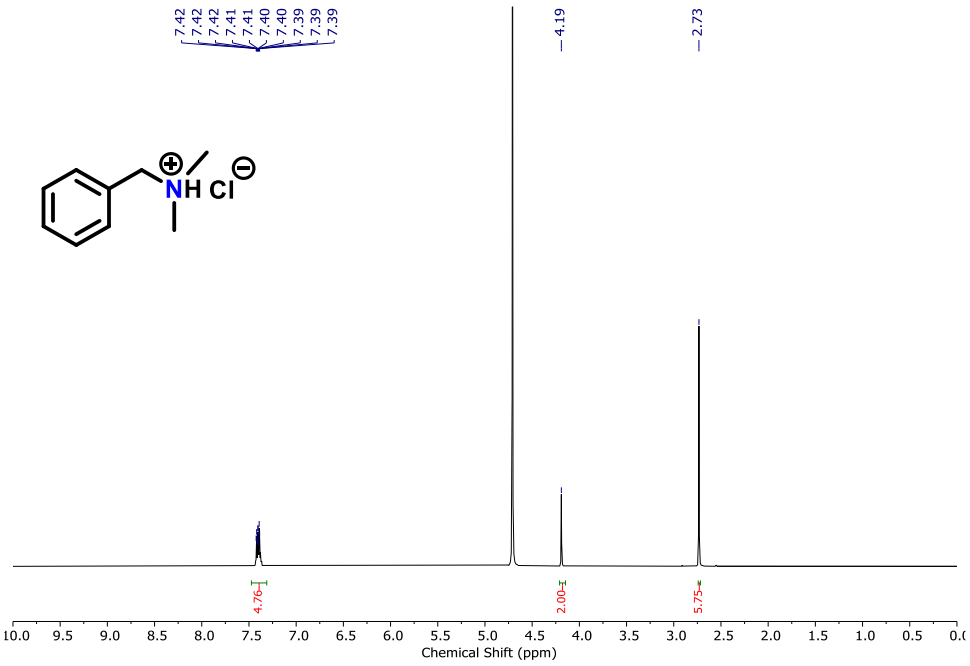


Figure S83: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4a**.

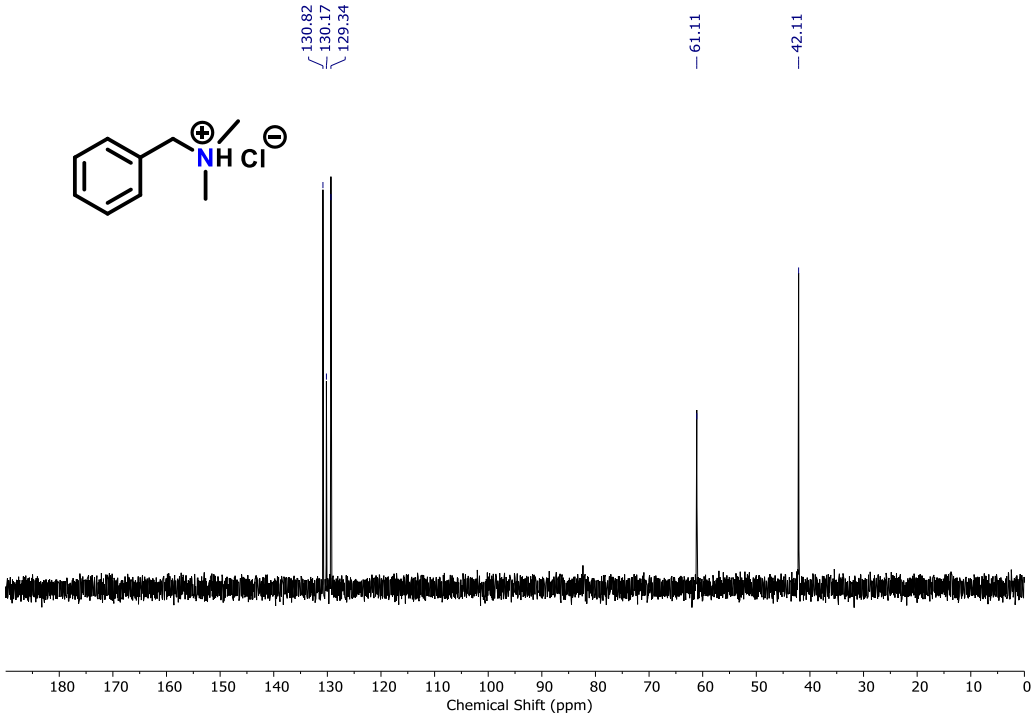


Figure S84: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4a**.

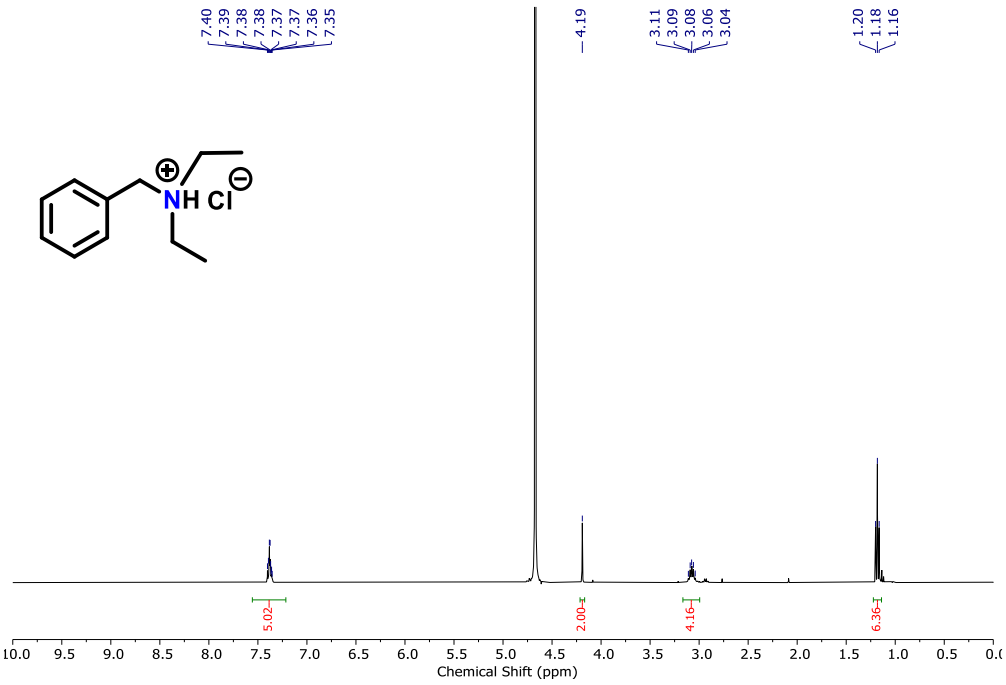


Figure S85: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ba**.

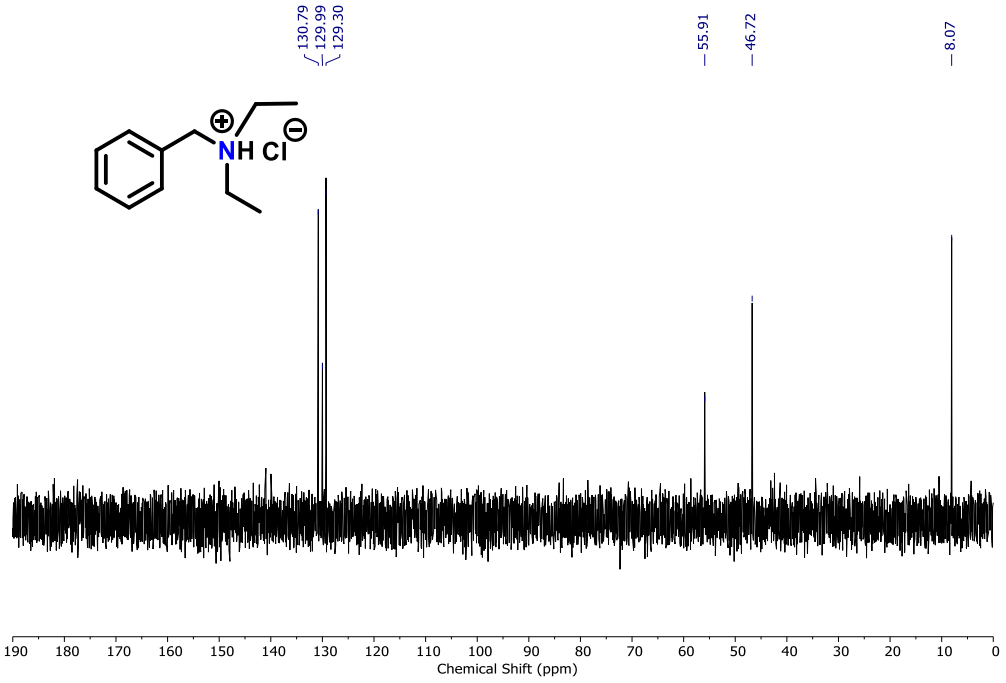


Figure S86: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ba**.

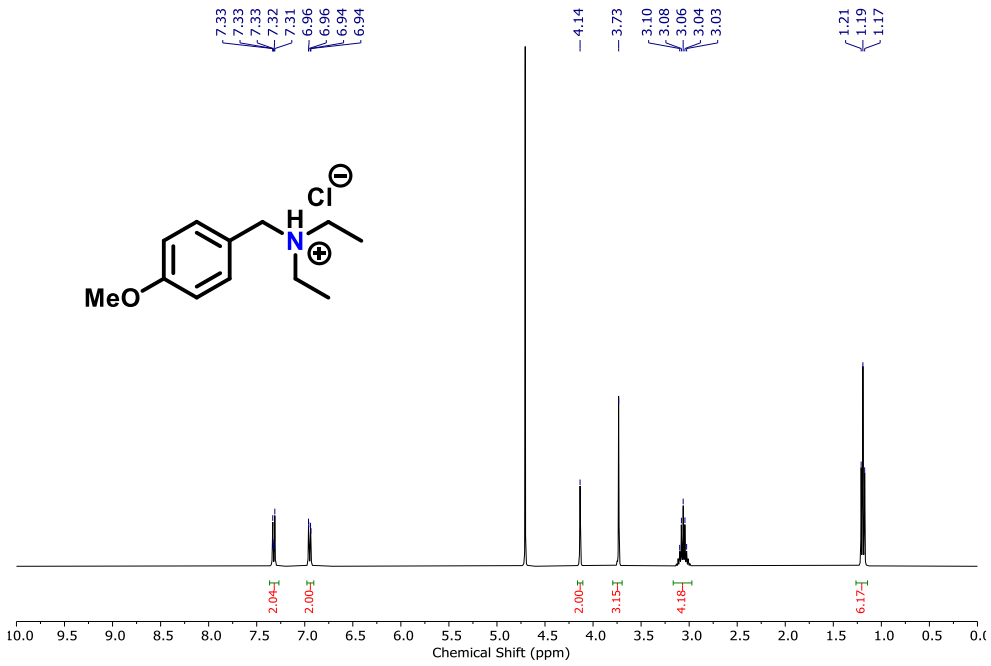


Figure S87: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4bb**.

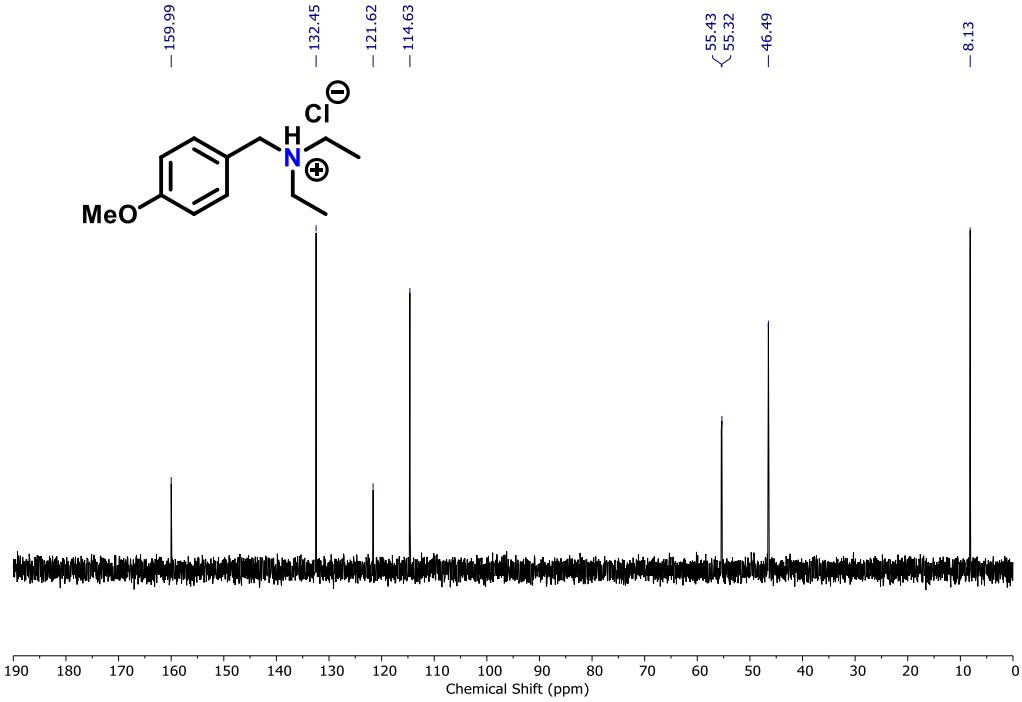


Figure S88: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4bb**.

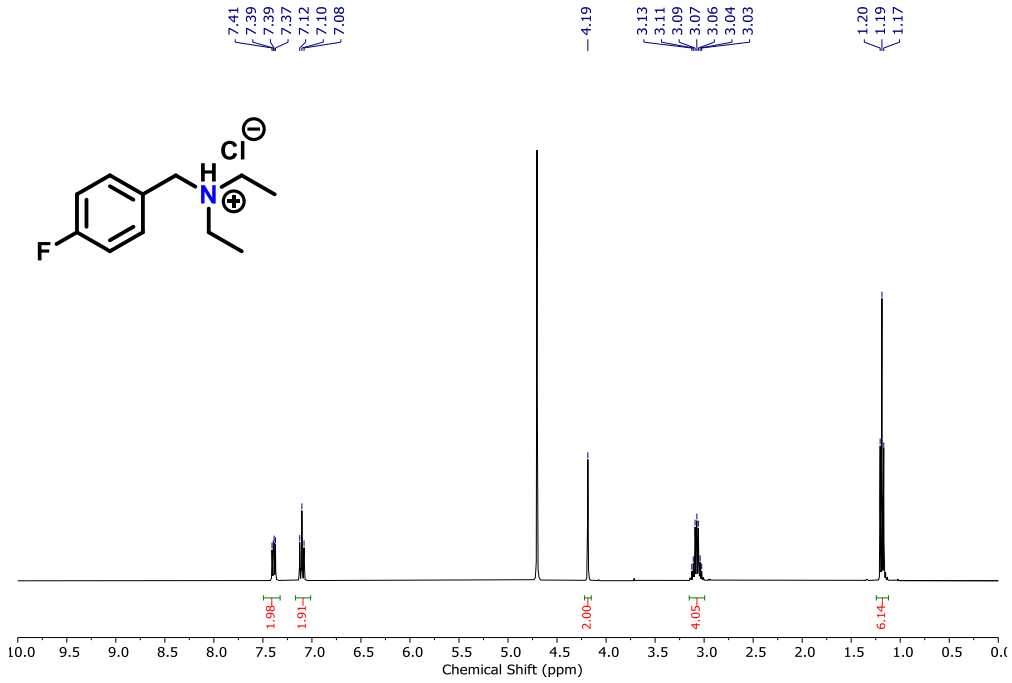


Figure S89: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4bc**.

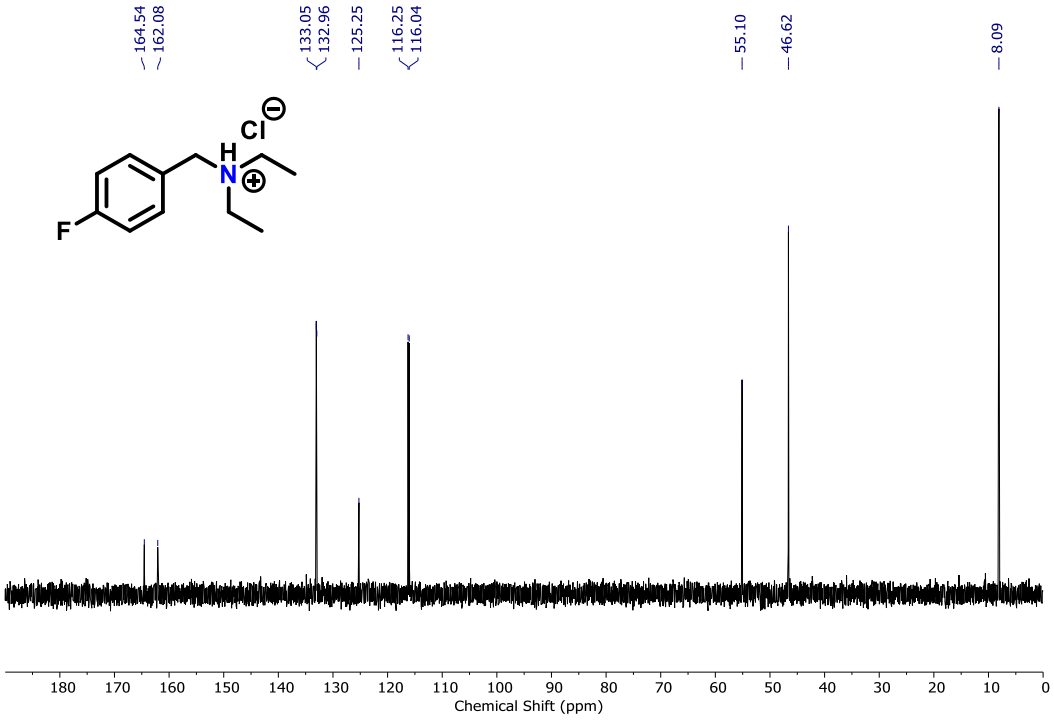


Figure S90: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4bc**.

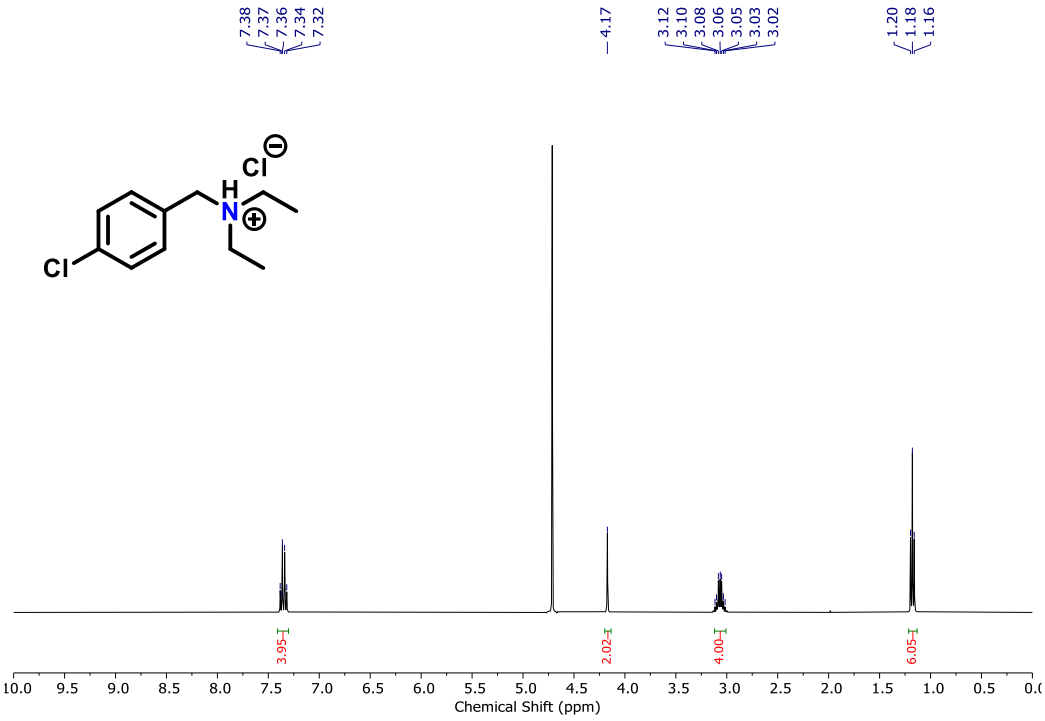


Figure S91: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4bd**.

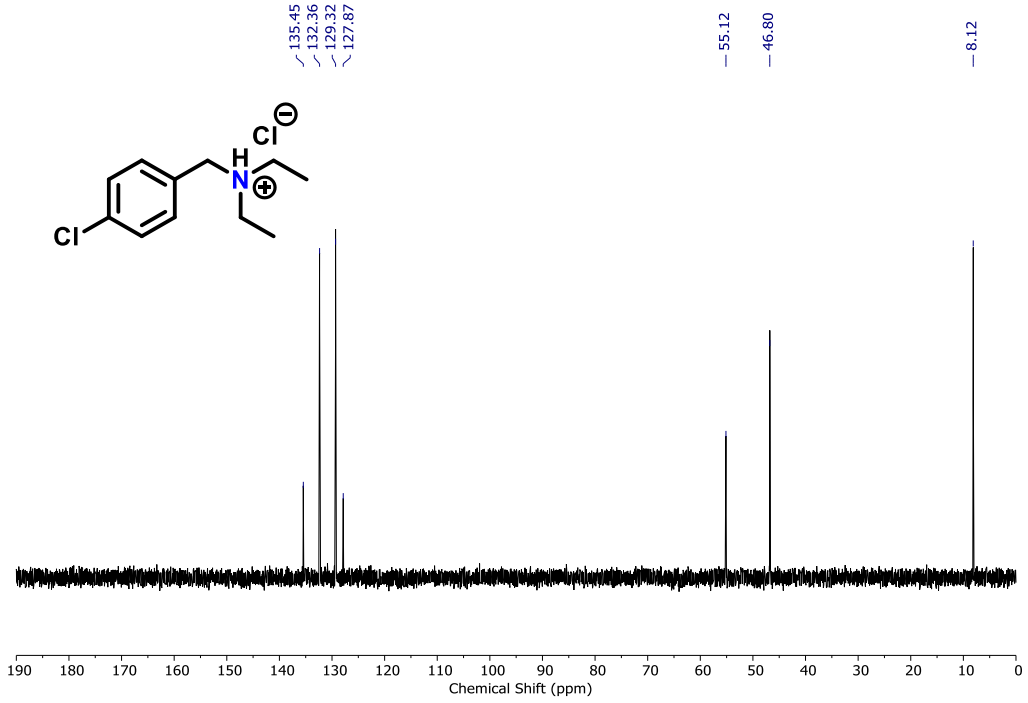


Figure S92: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4bd**.

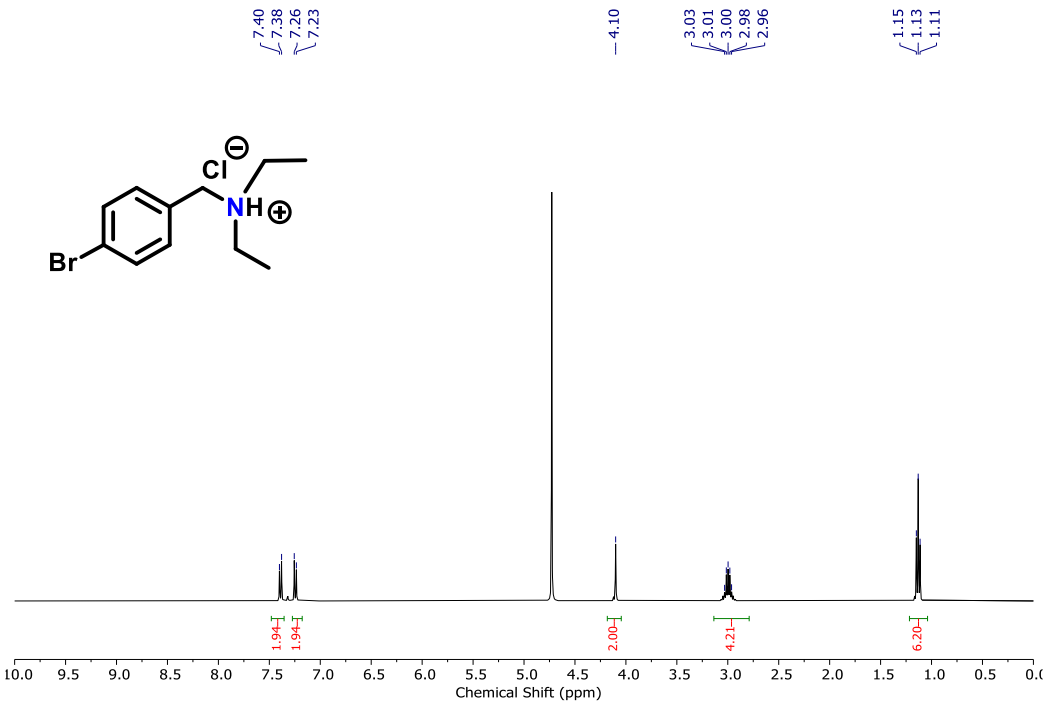


Figure S93: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4be**.

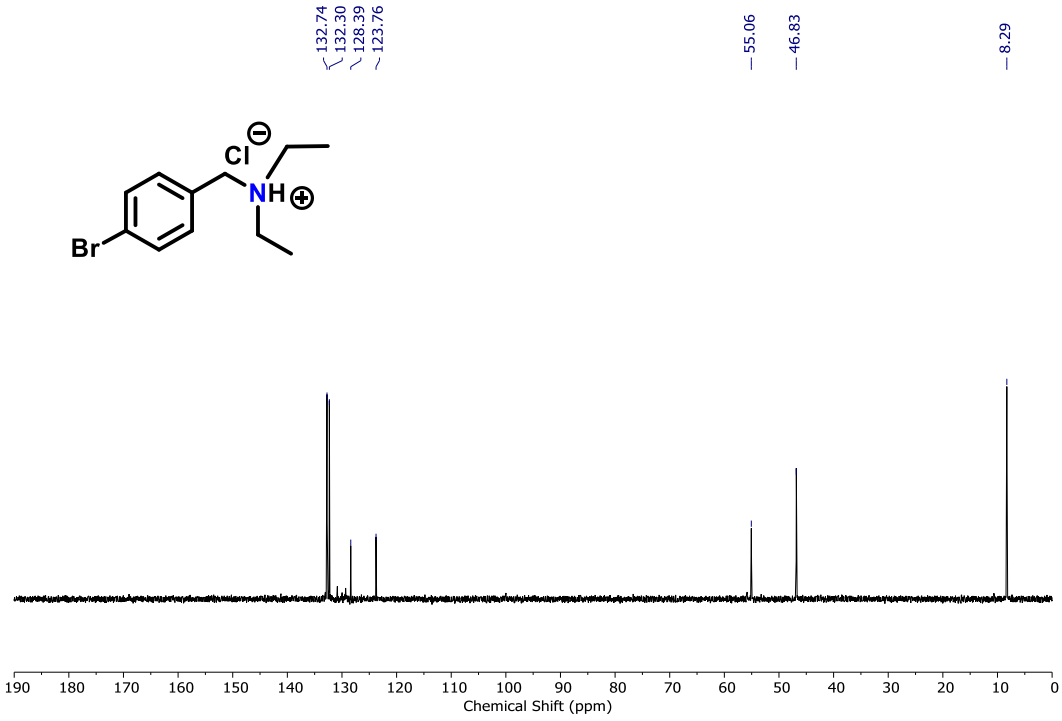


Figure S94: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4be**.

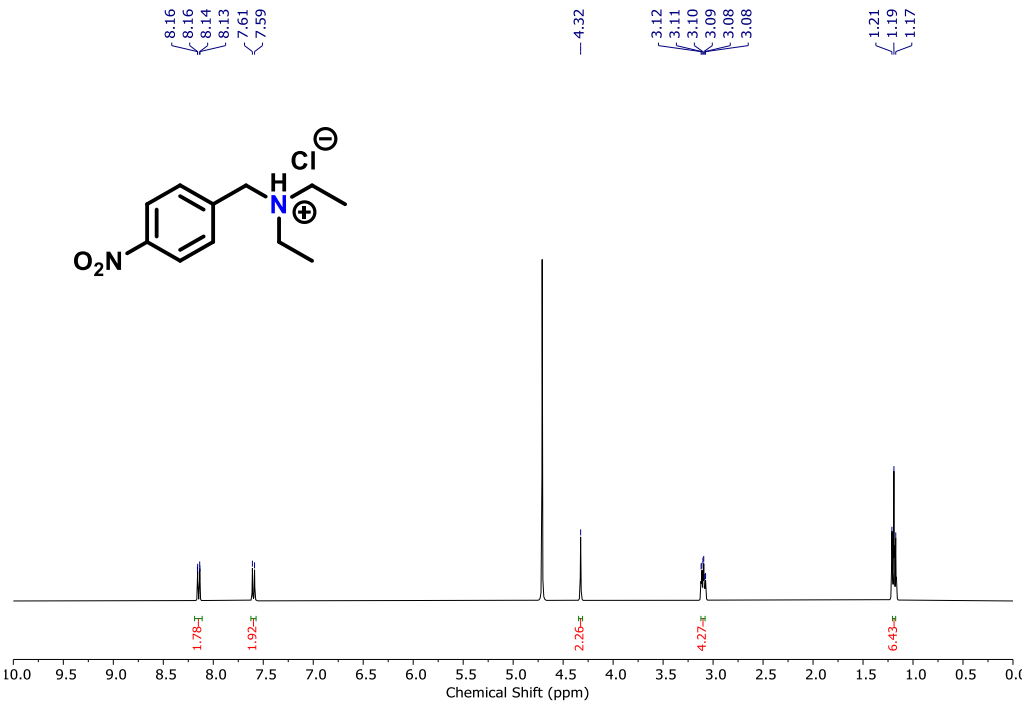


Figure S95: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4bf**.

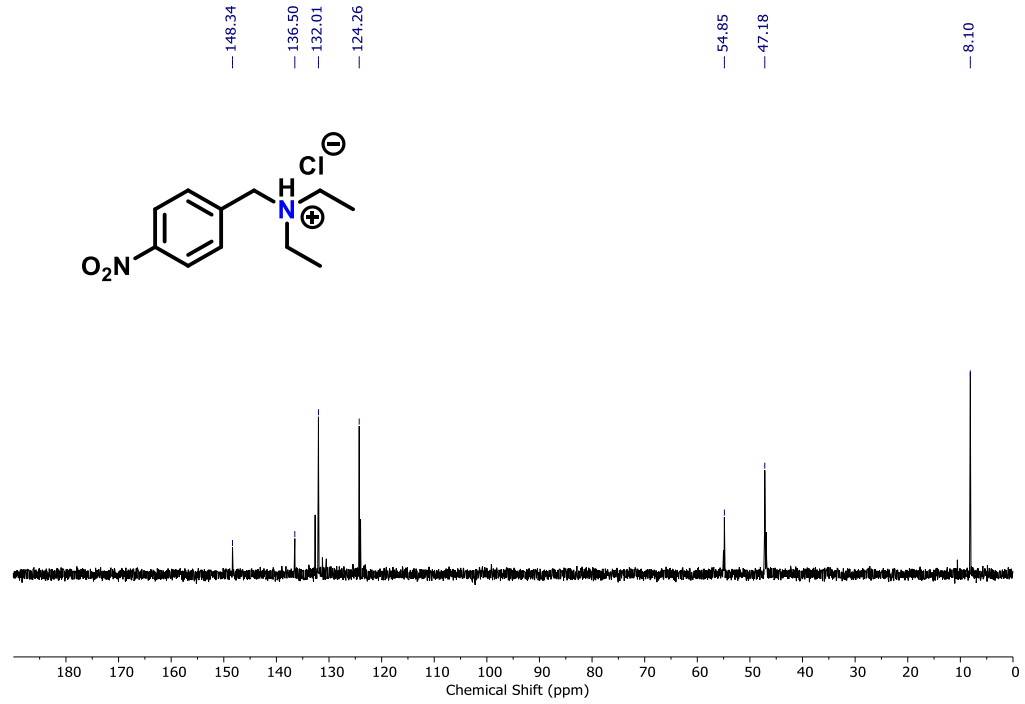


Figure S96: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4bf**.

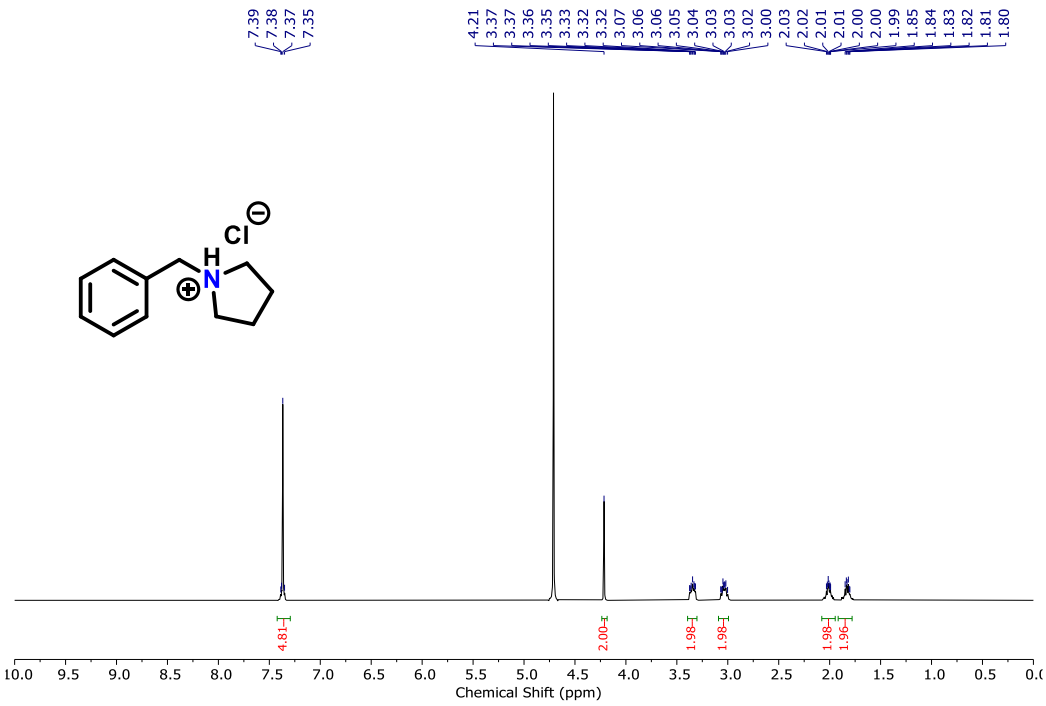


Figure S97: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ca**.

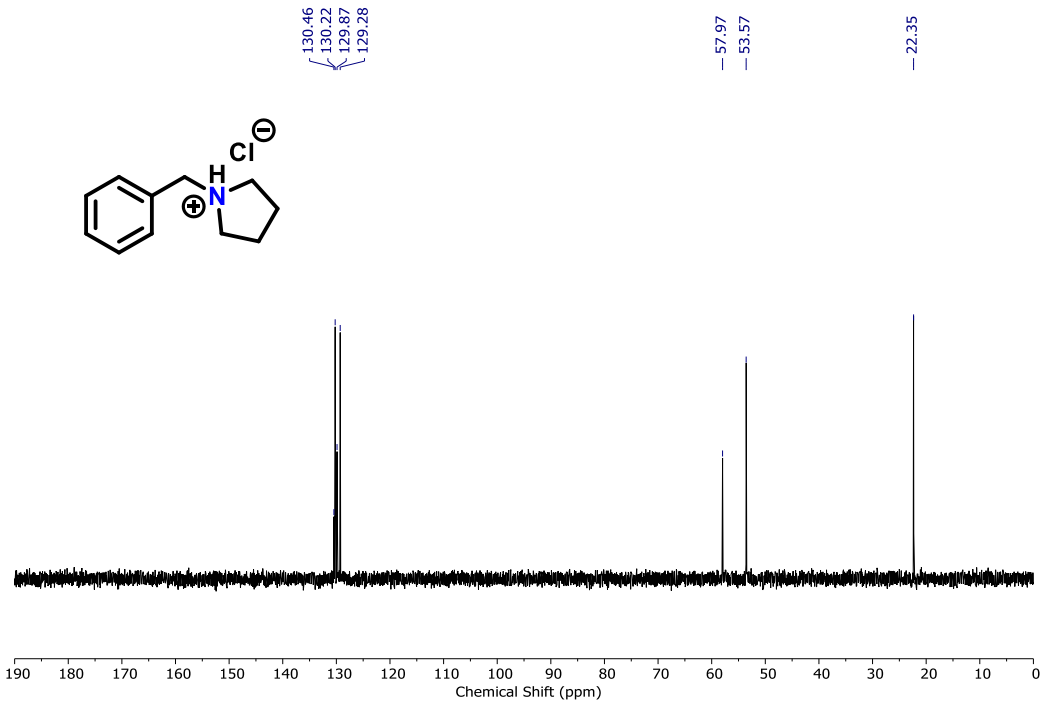


Figure S98: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ca**.

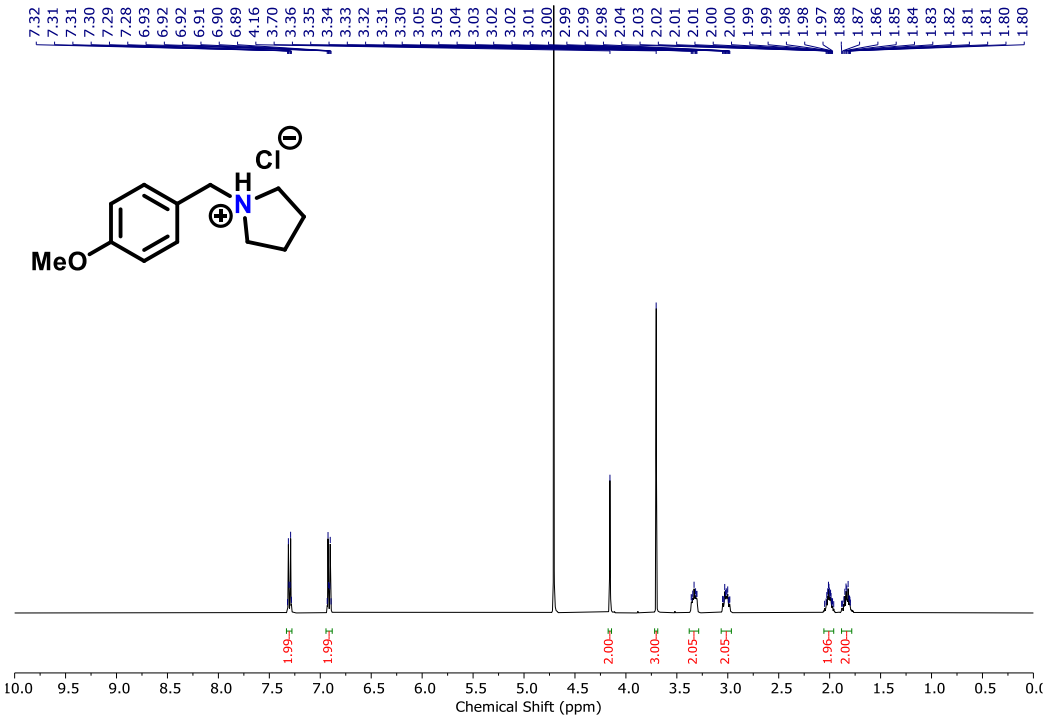


Figure S99: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4cb**.

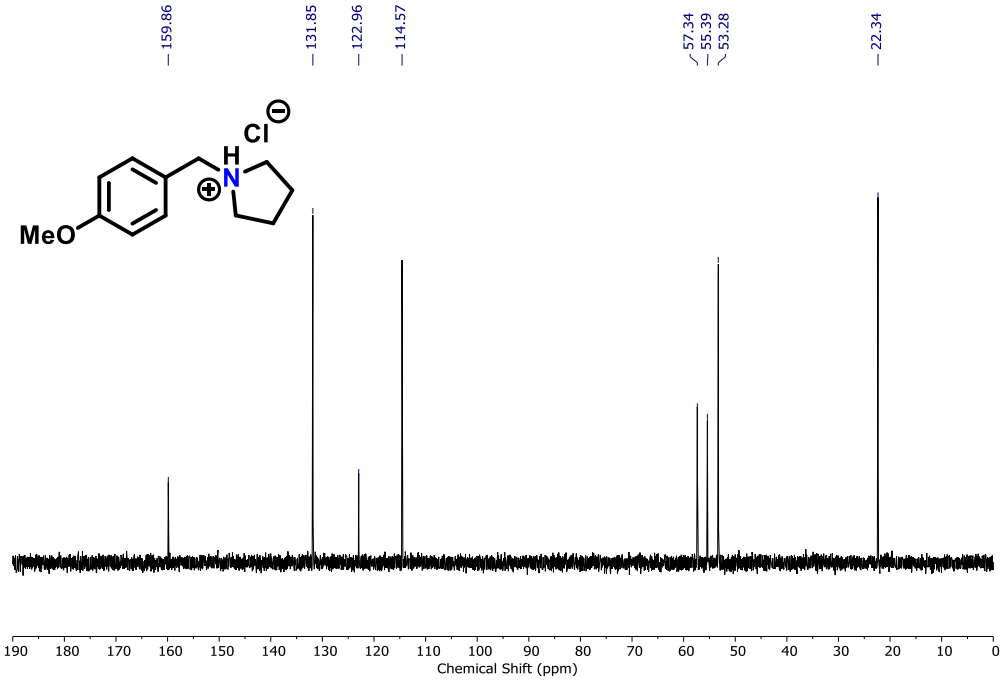


Figure S100: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4cb**.

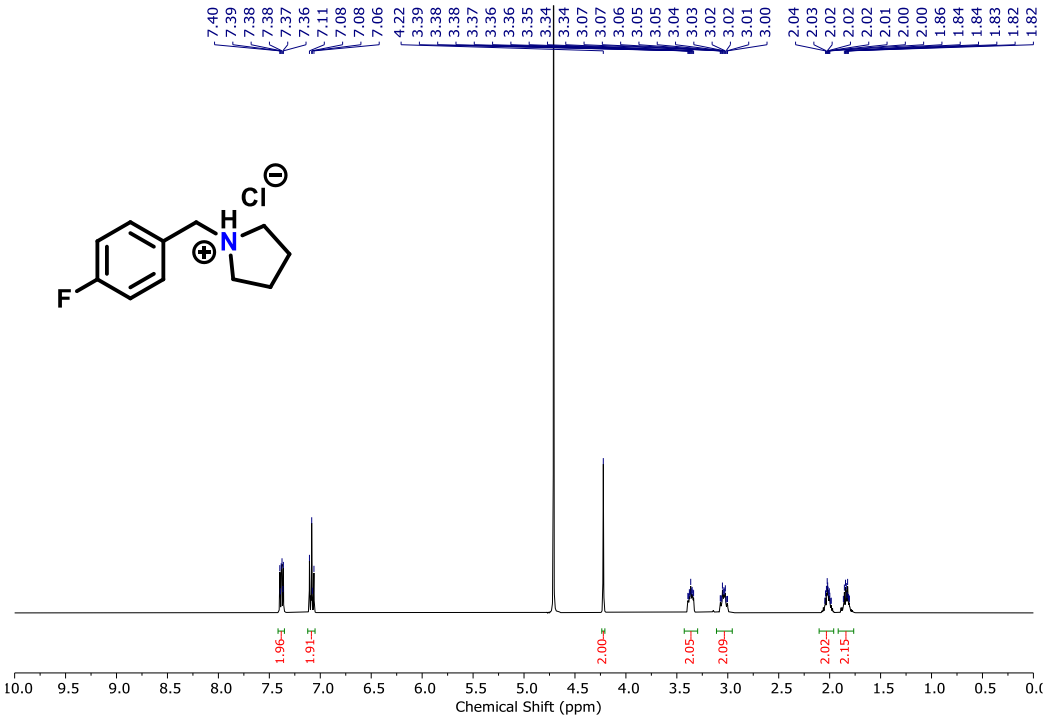


Figure S101: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4cc**.

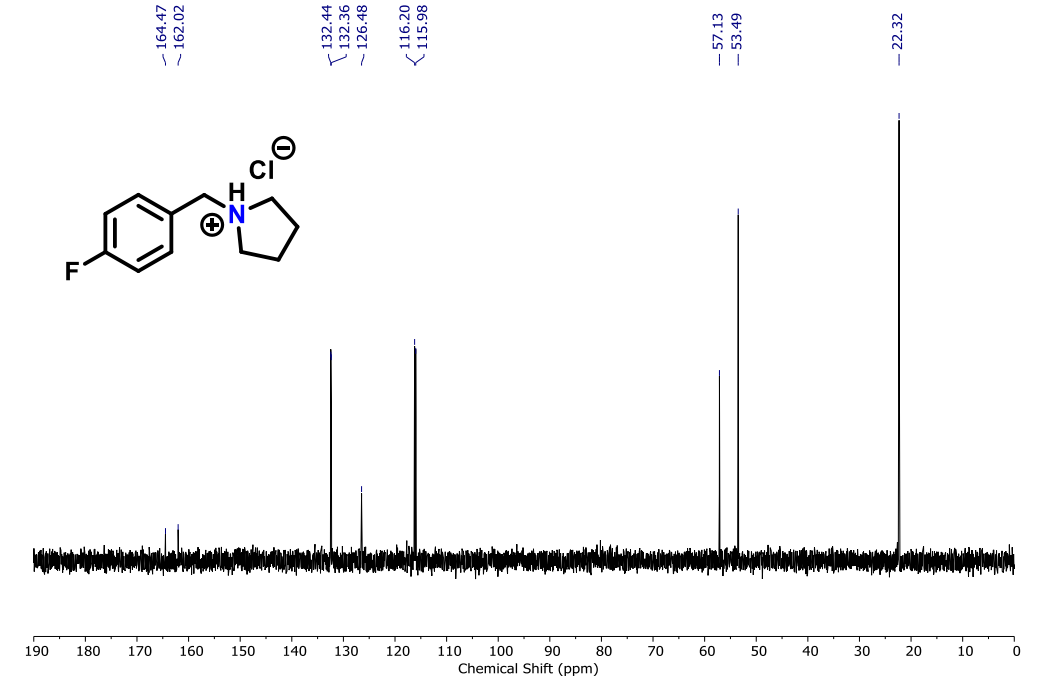


Figure S102: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4cc**.

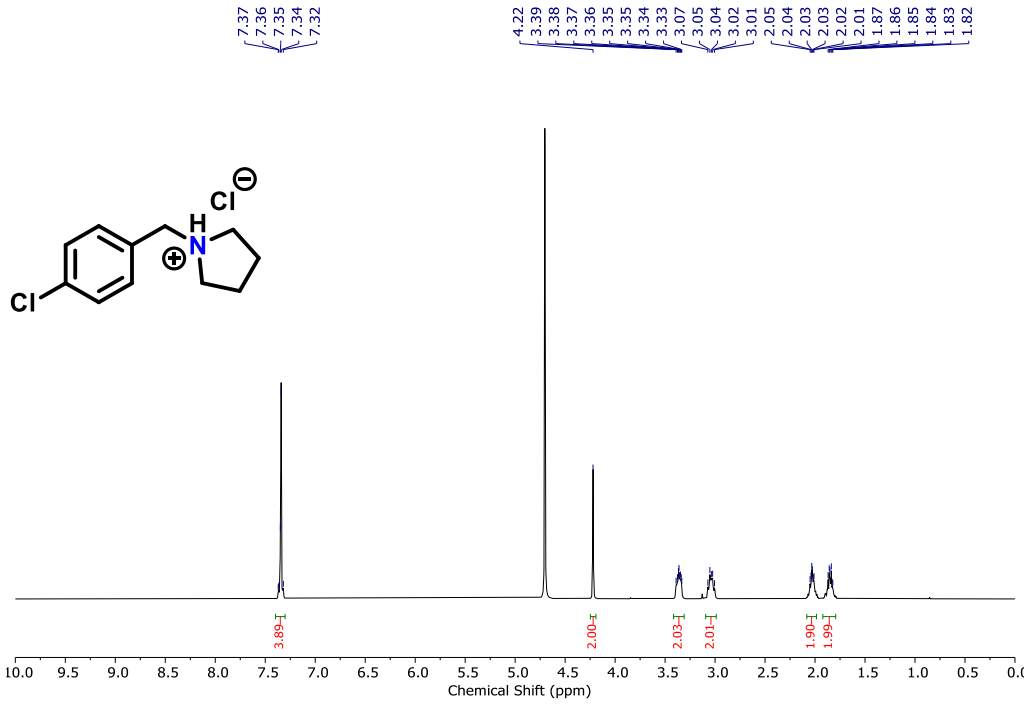


Figure S103: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4cd**.

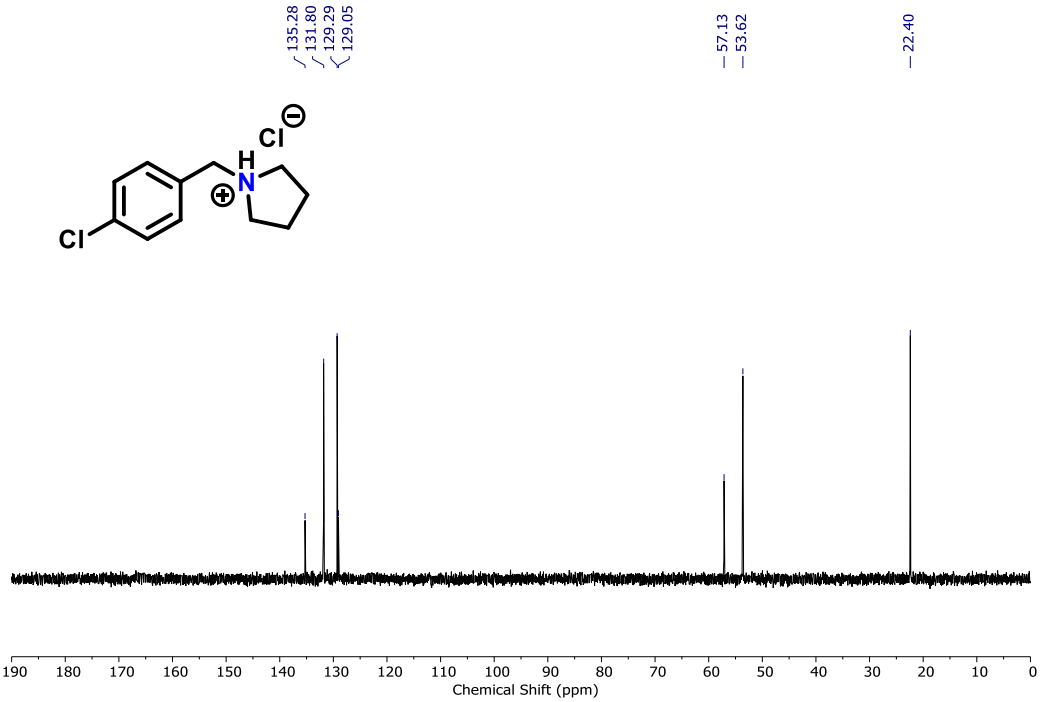


Figure S104: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4cd**.

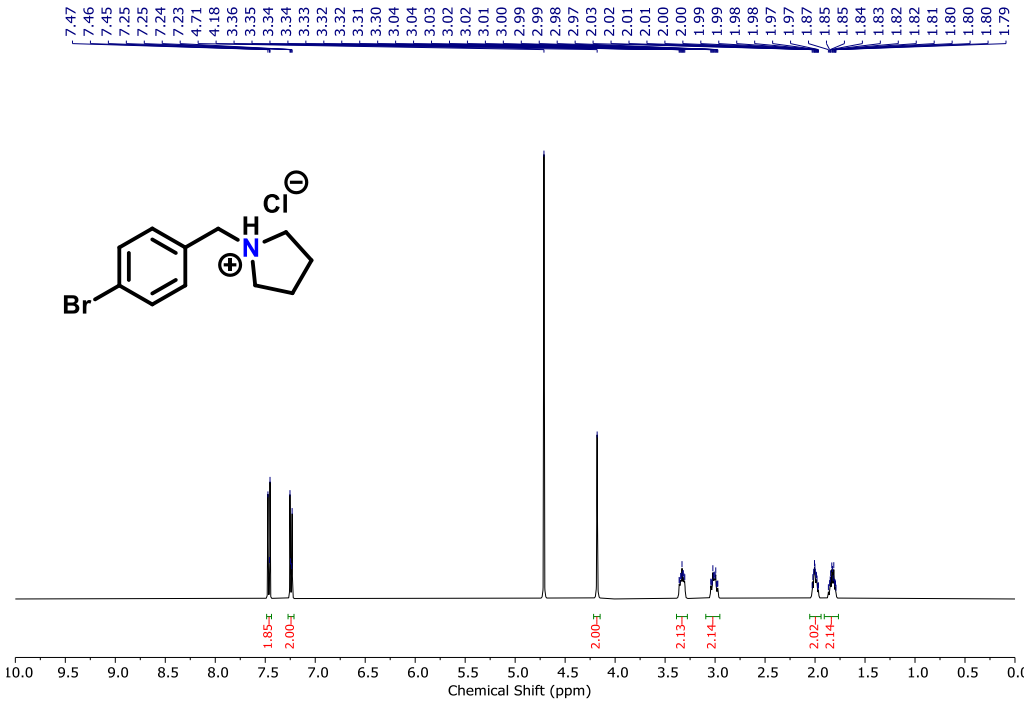


Figure S105: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ce**

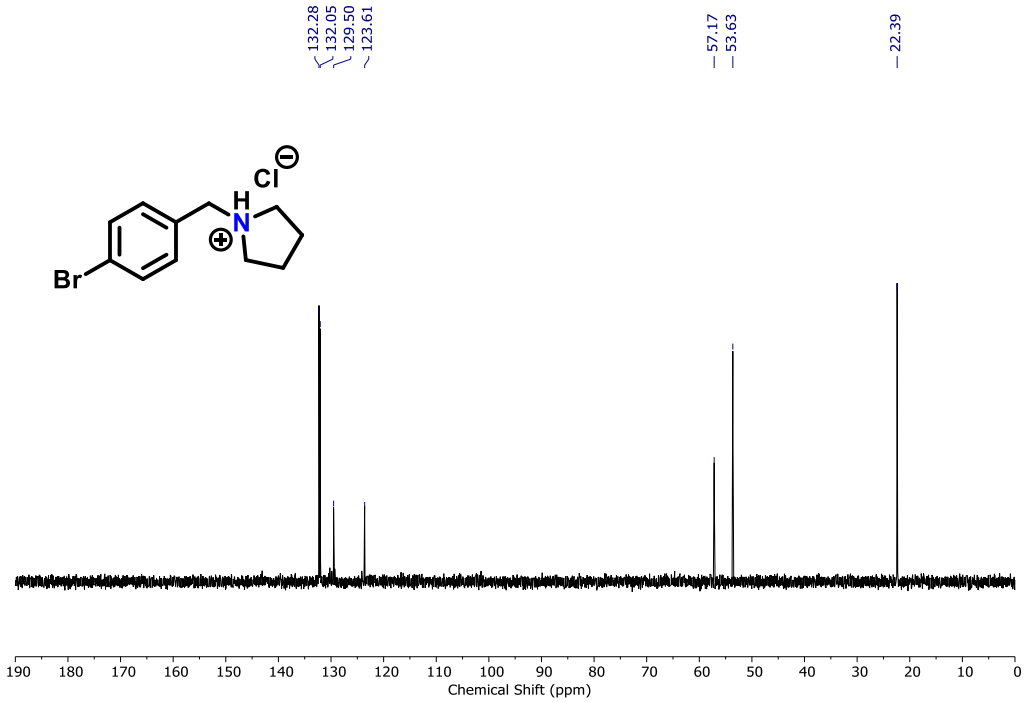


Figure S106: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ce**.

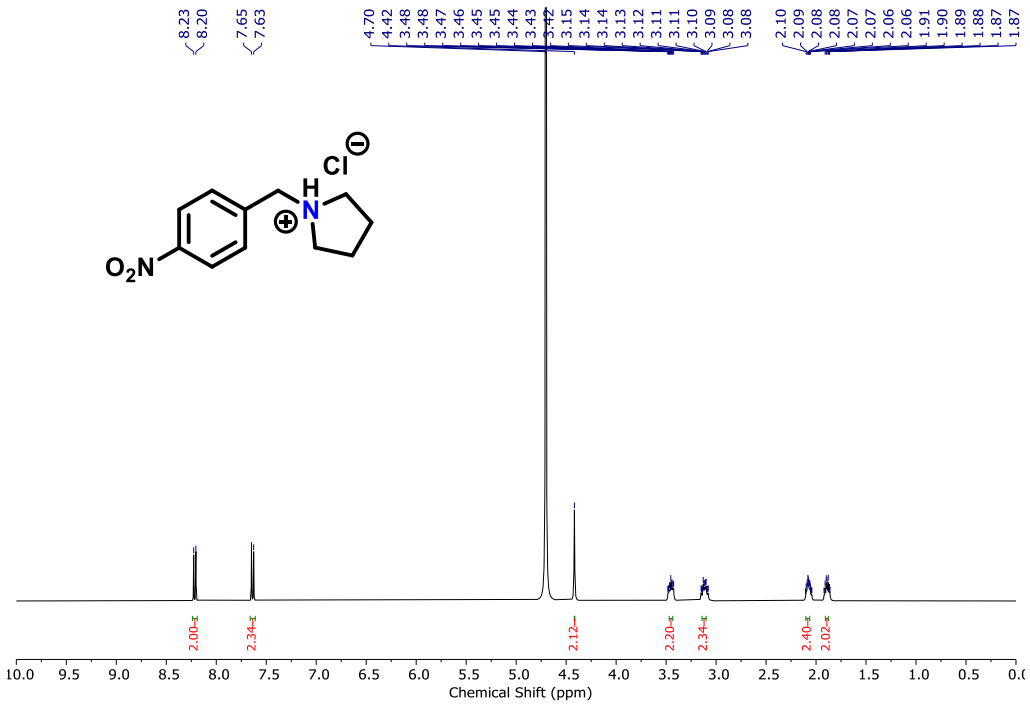


Figure S107: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4cf**.

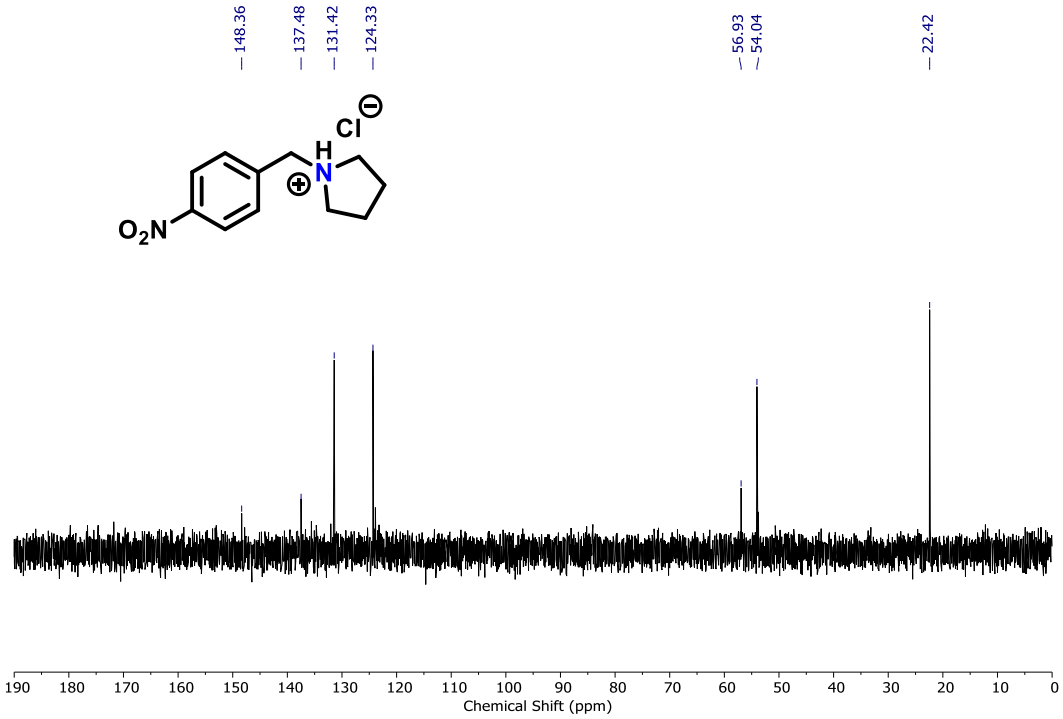


Figure S108: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4cf**.

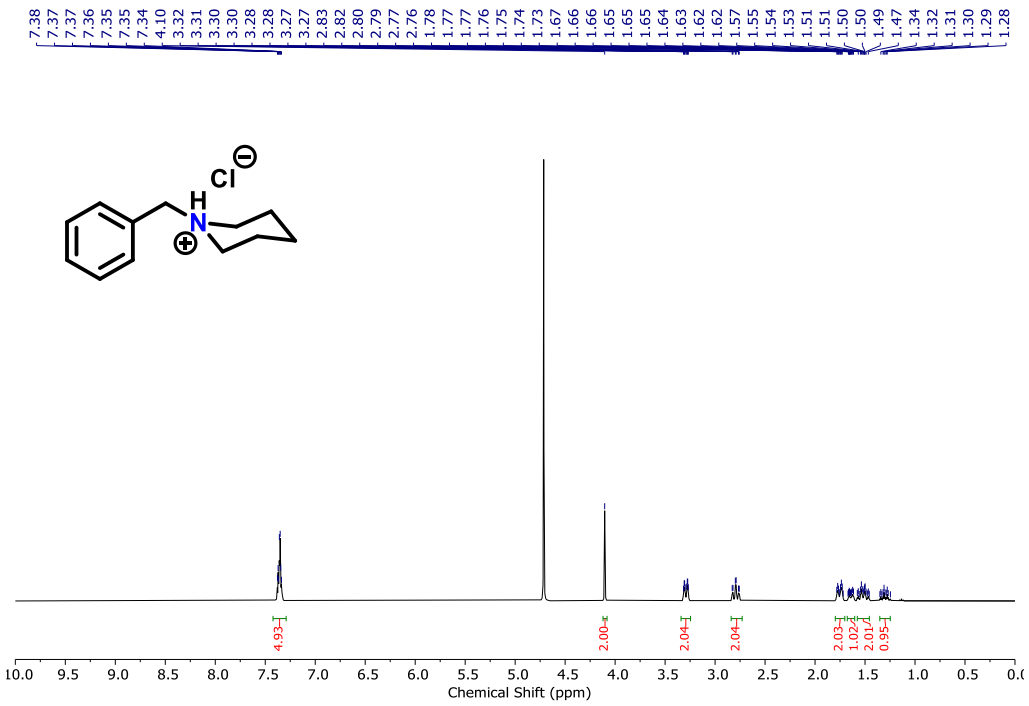


Figure S109: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4da**.

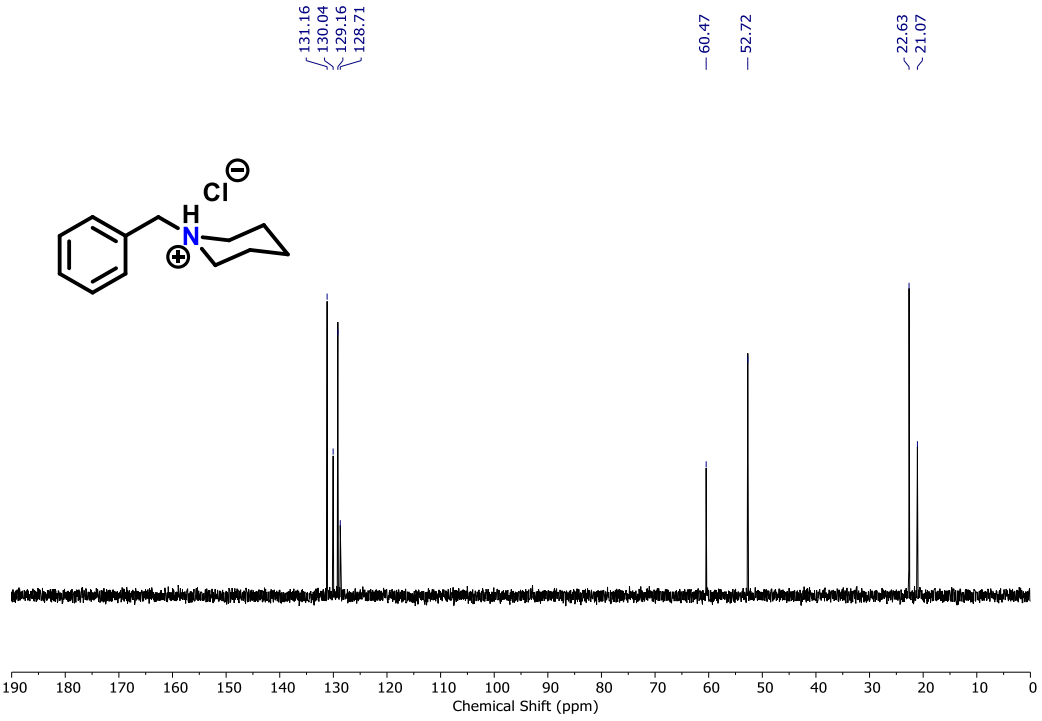


Figure S110: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4da**.

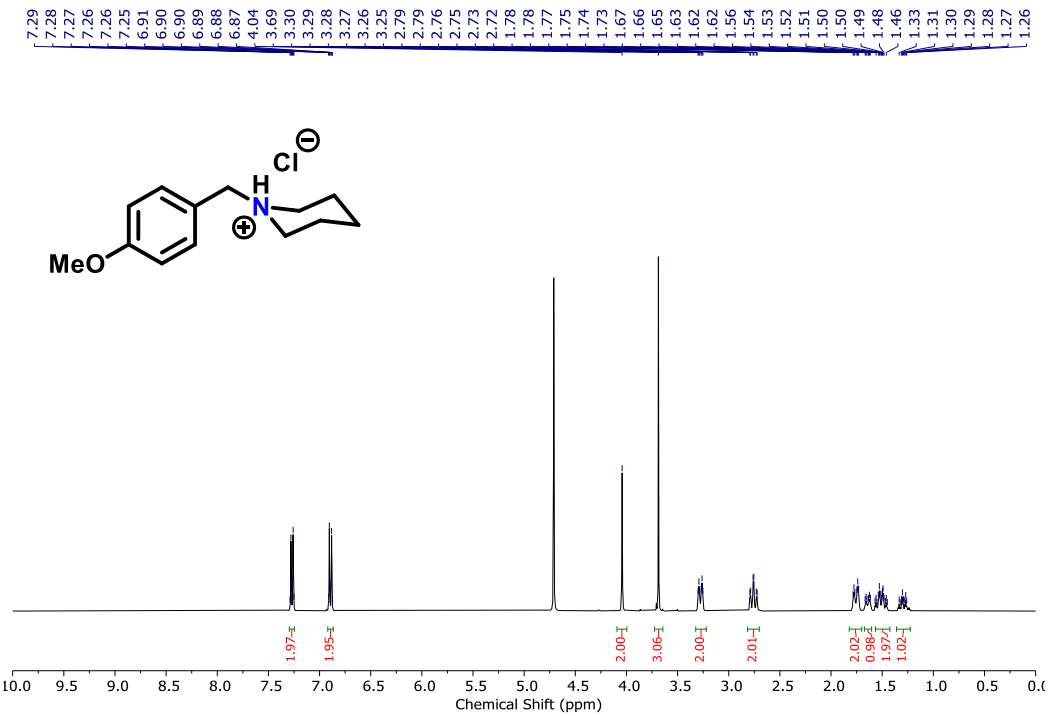


Figure S111: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4db**.

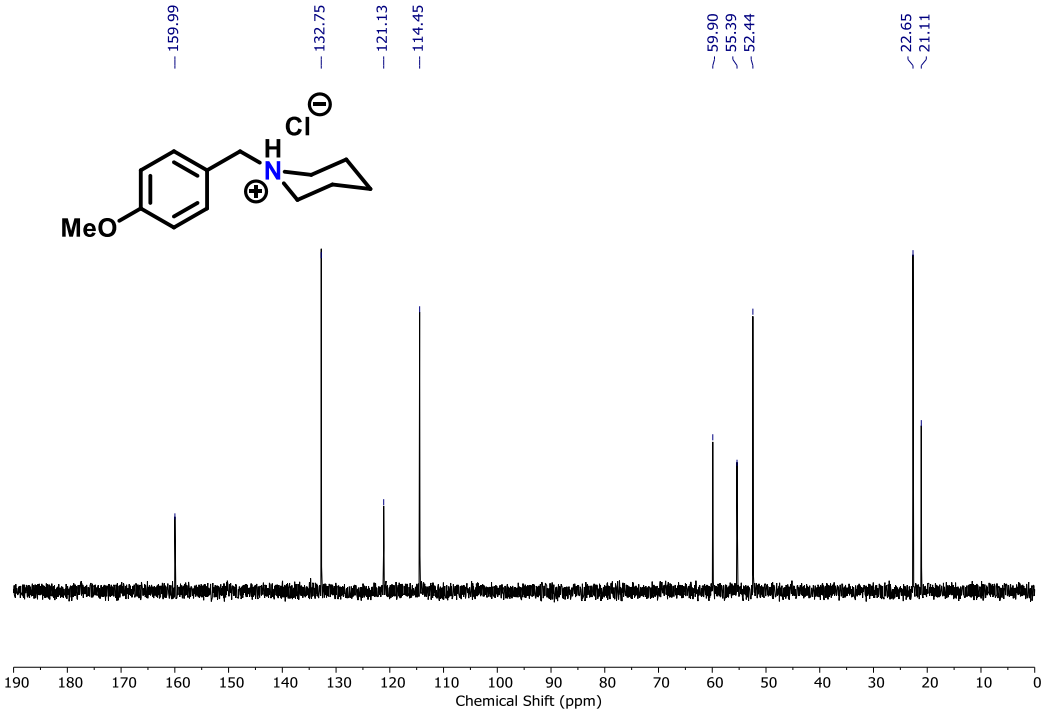


Figure S112: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4db**.

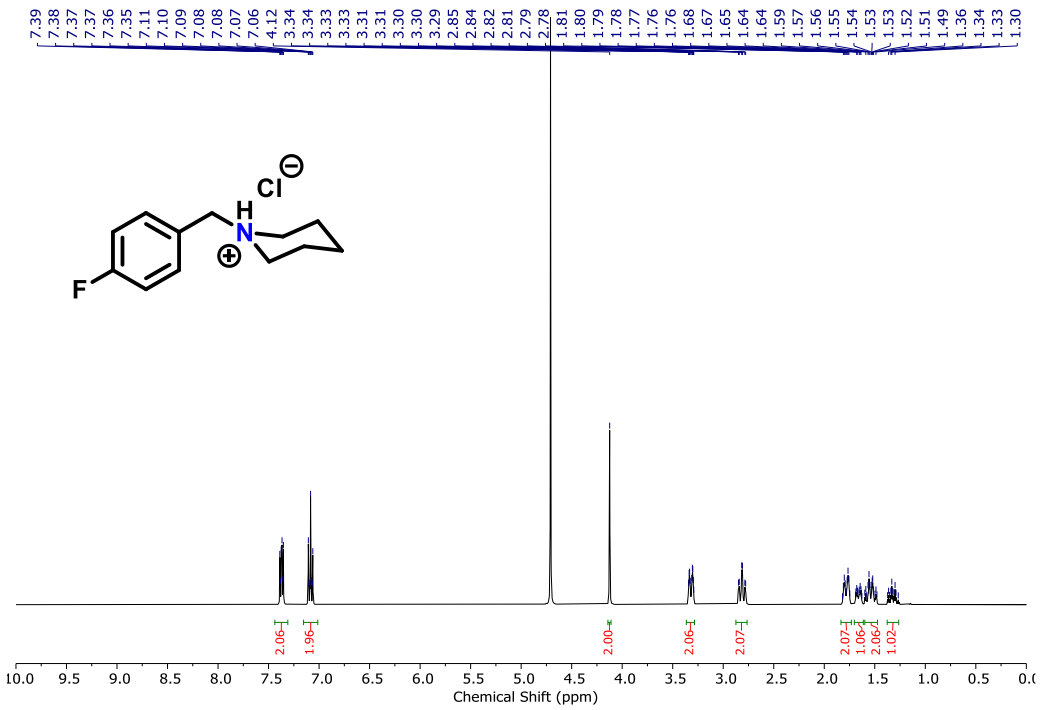


Figure S113: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4dc**.

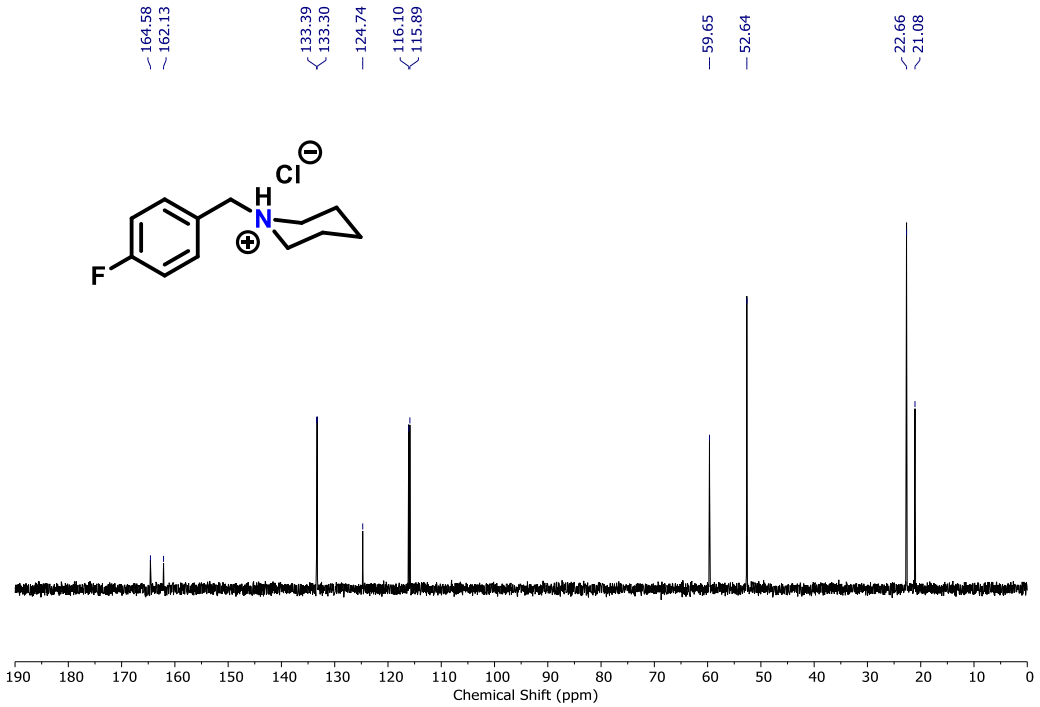


Figure S114: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4dc**.

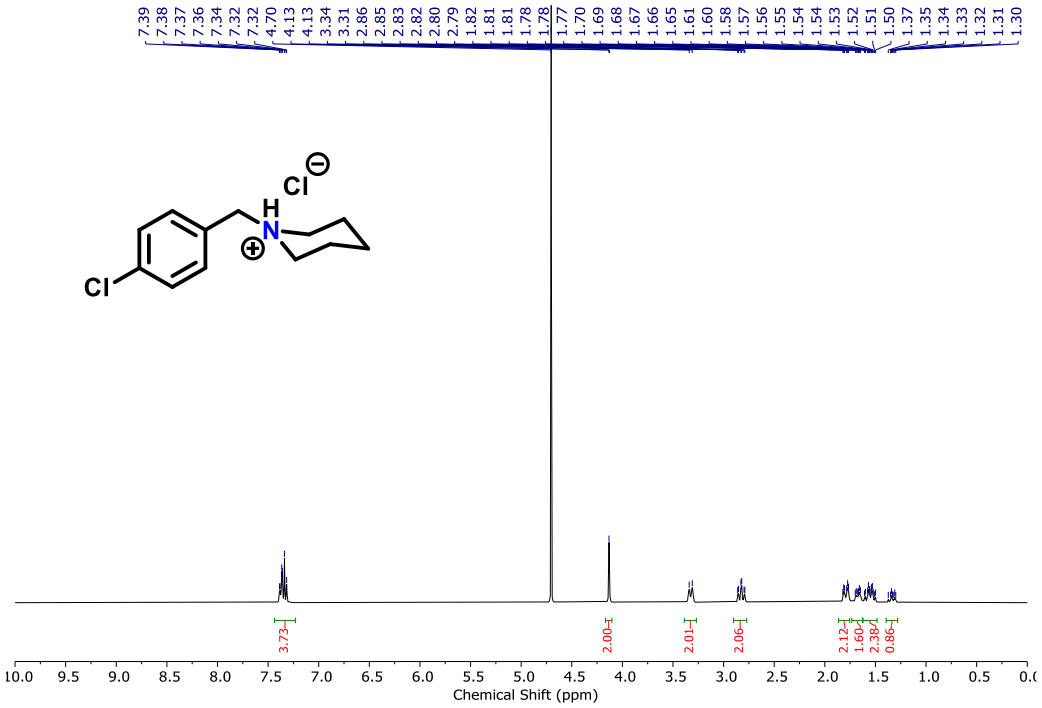


Figure S115: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4dd**.

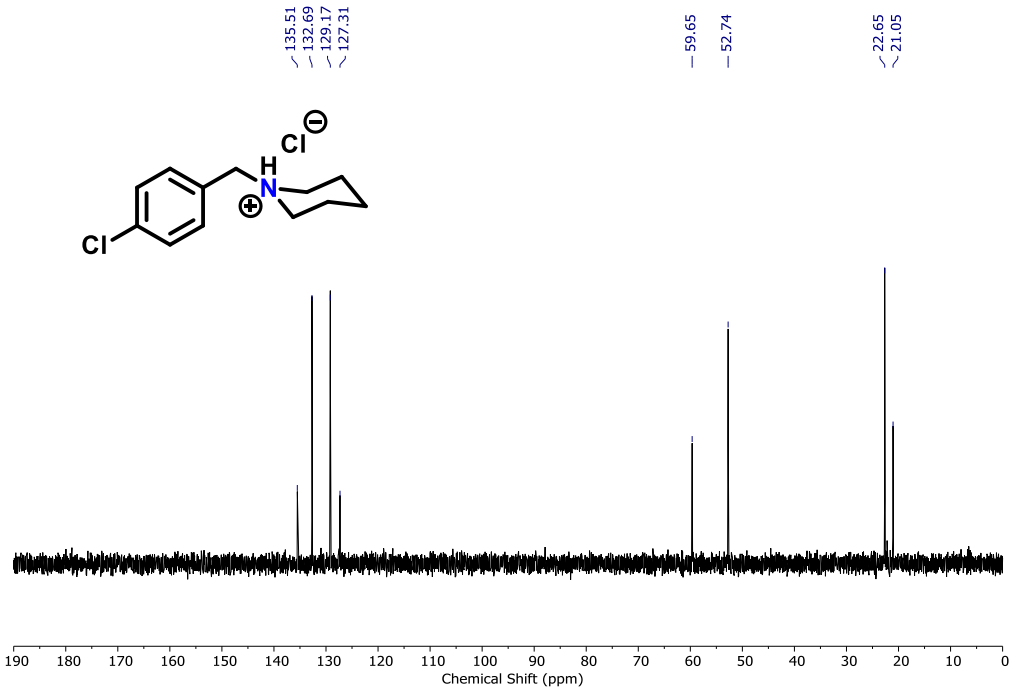


Figure S116: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4dd**.

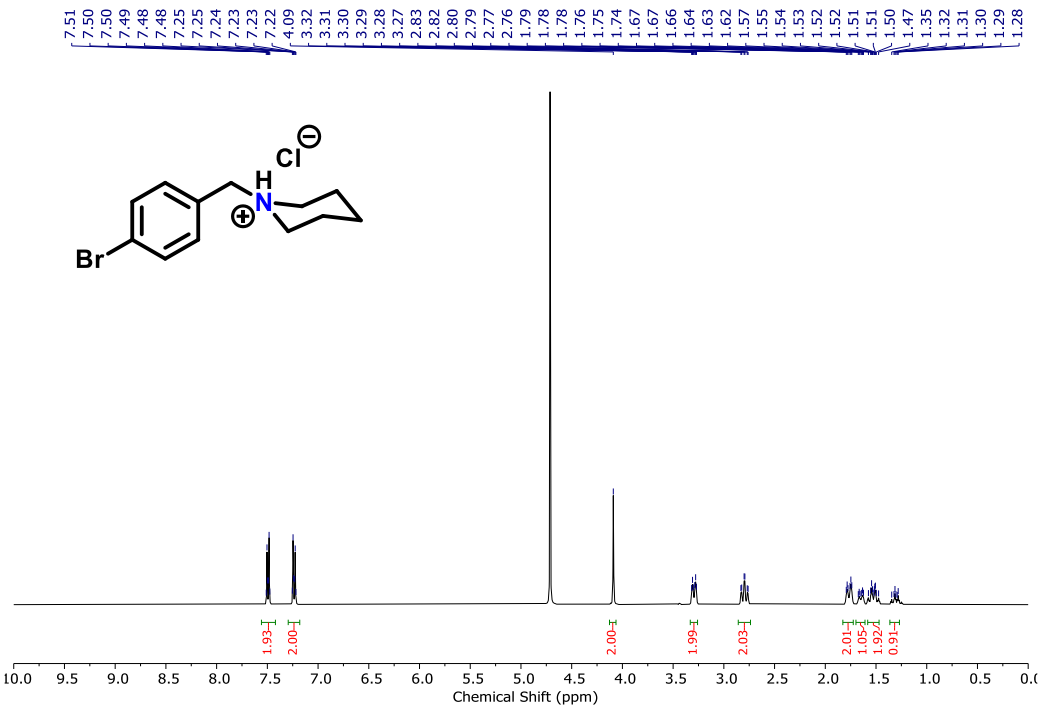


Figure S117: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4de**.

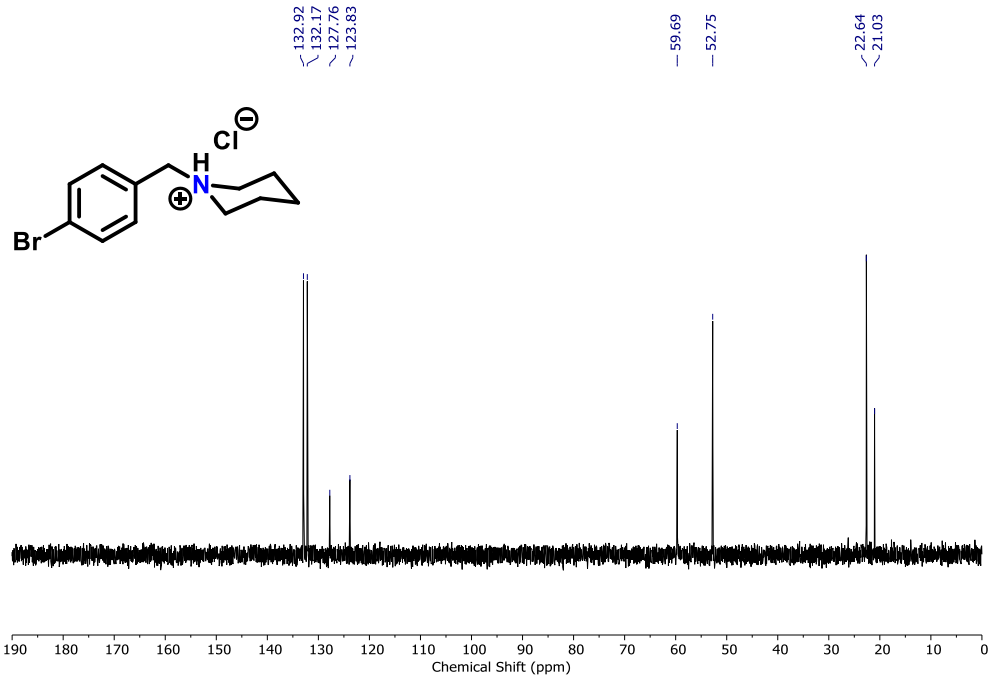


Figure S118: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4de**.

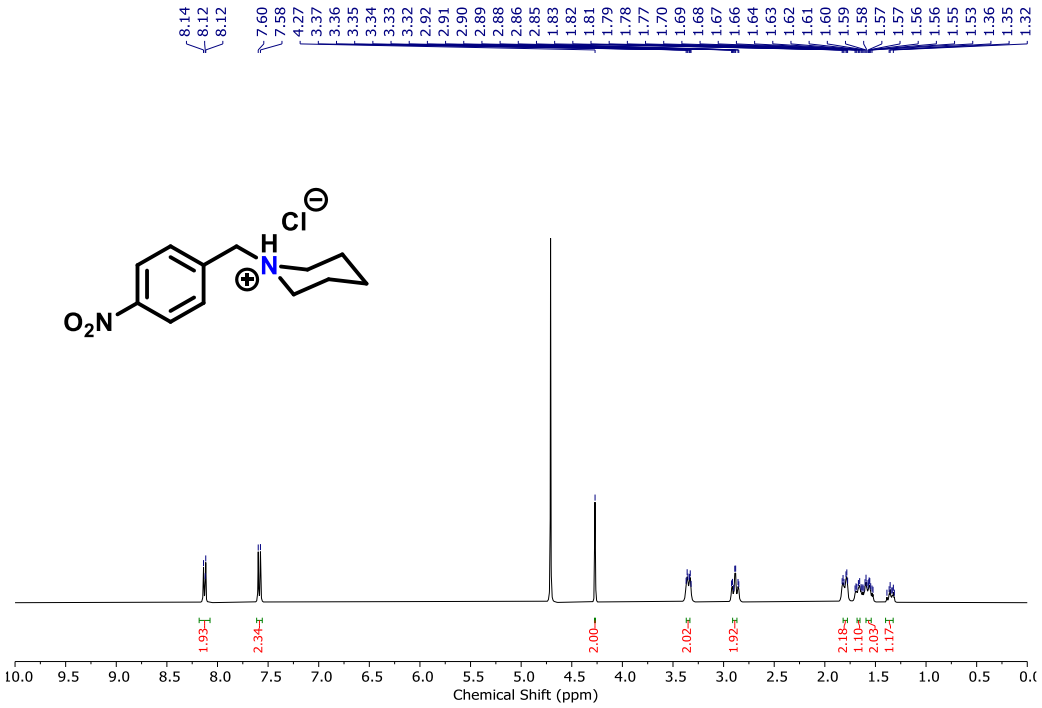


Figure S119: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4df**.

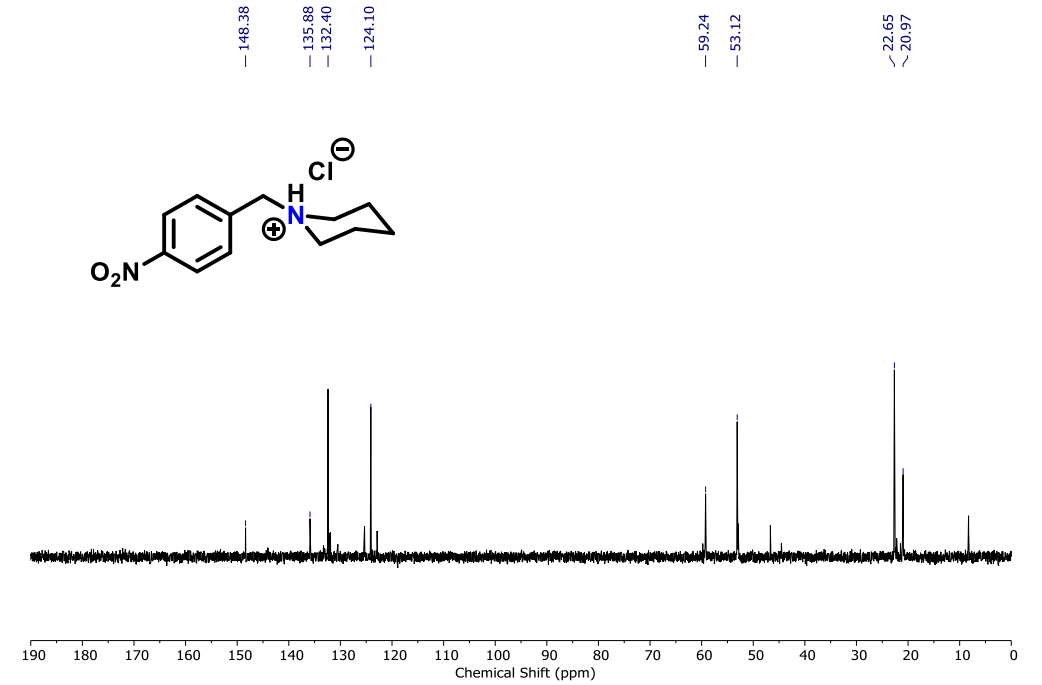


Figure S120: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4df**.

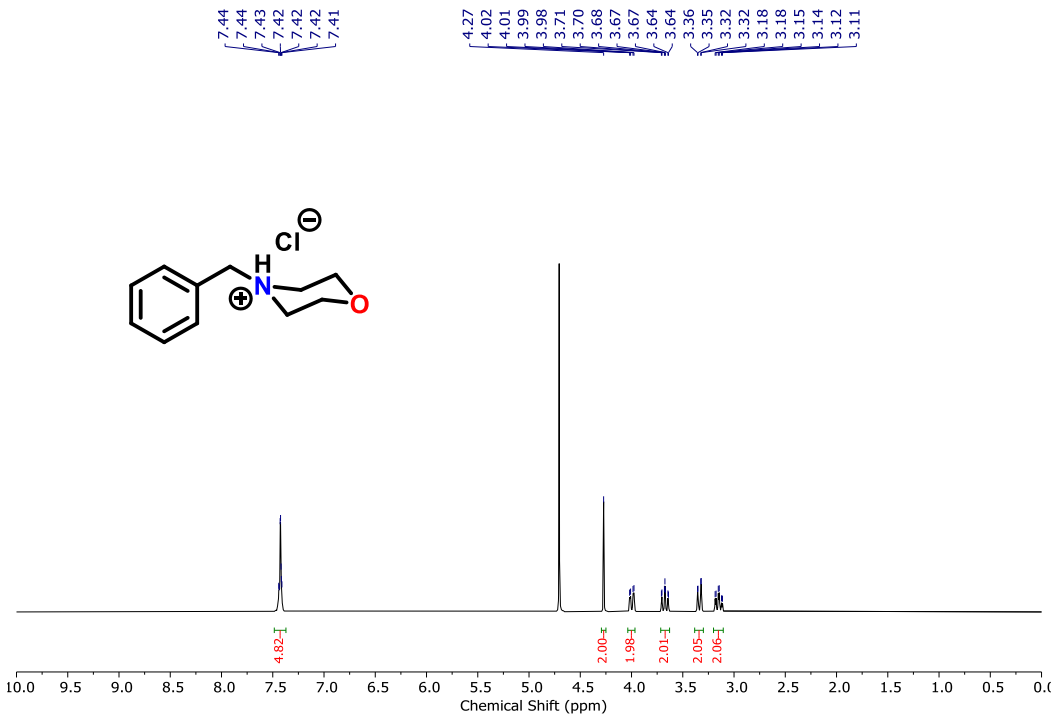


Figure S121: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ea**.

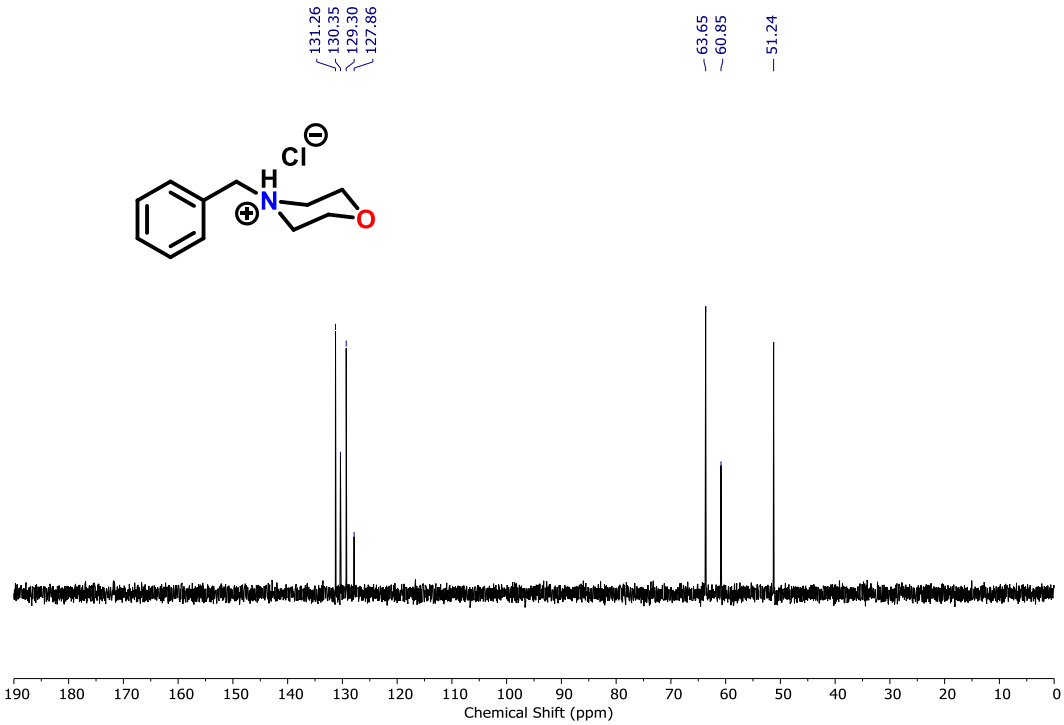


Figure S122: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ea**.

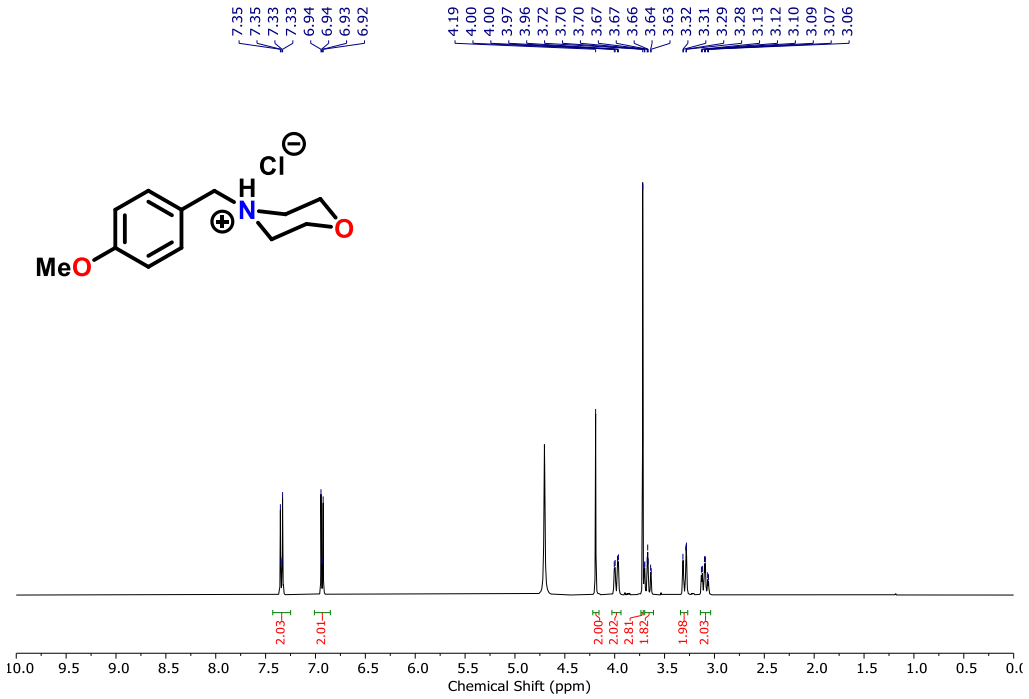


Figure S123: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4eb**.

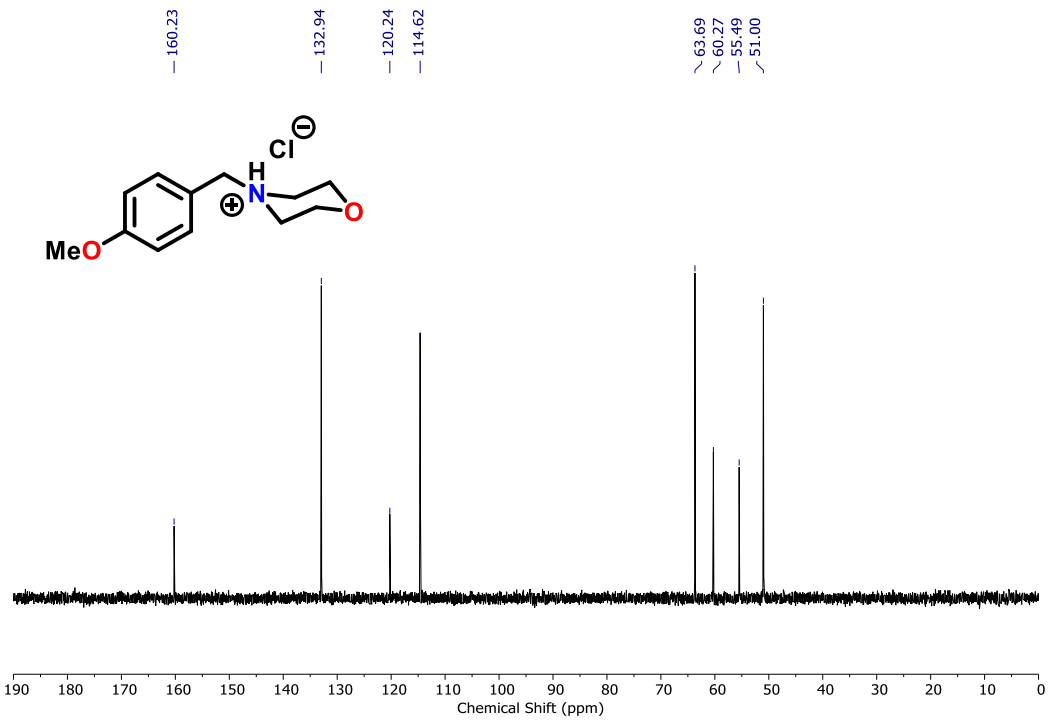


Figure S124: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4eb**.

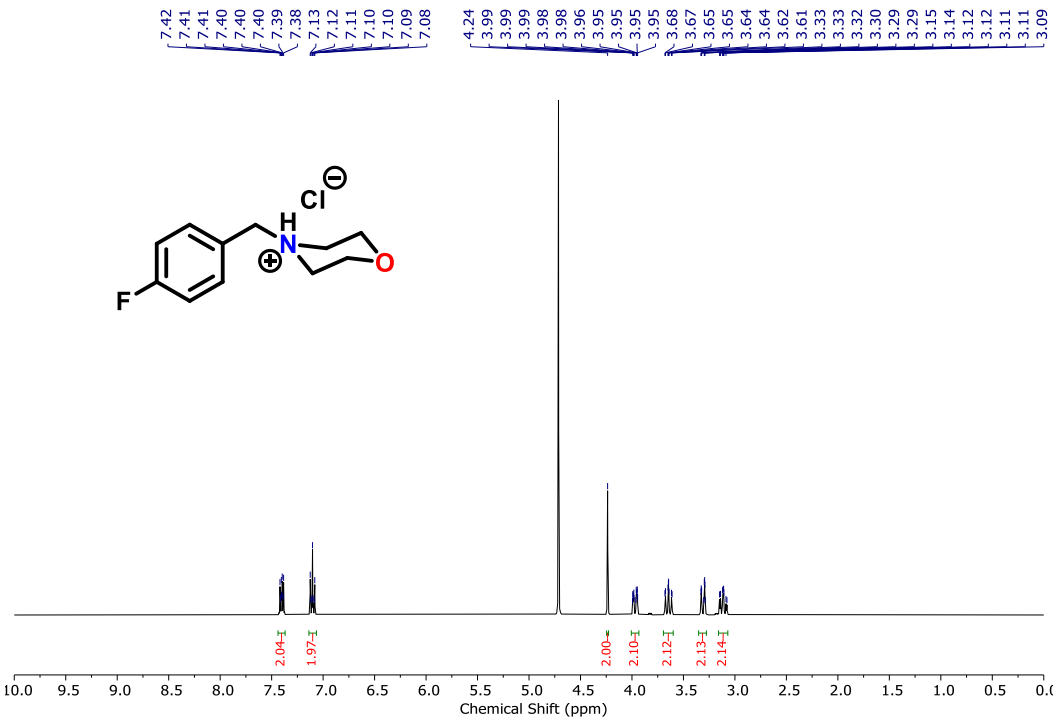


Figure S125: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ec**.

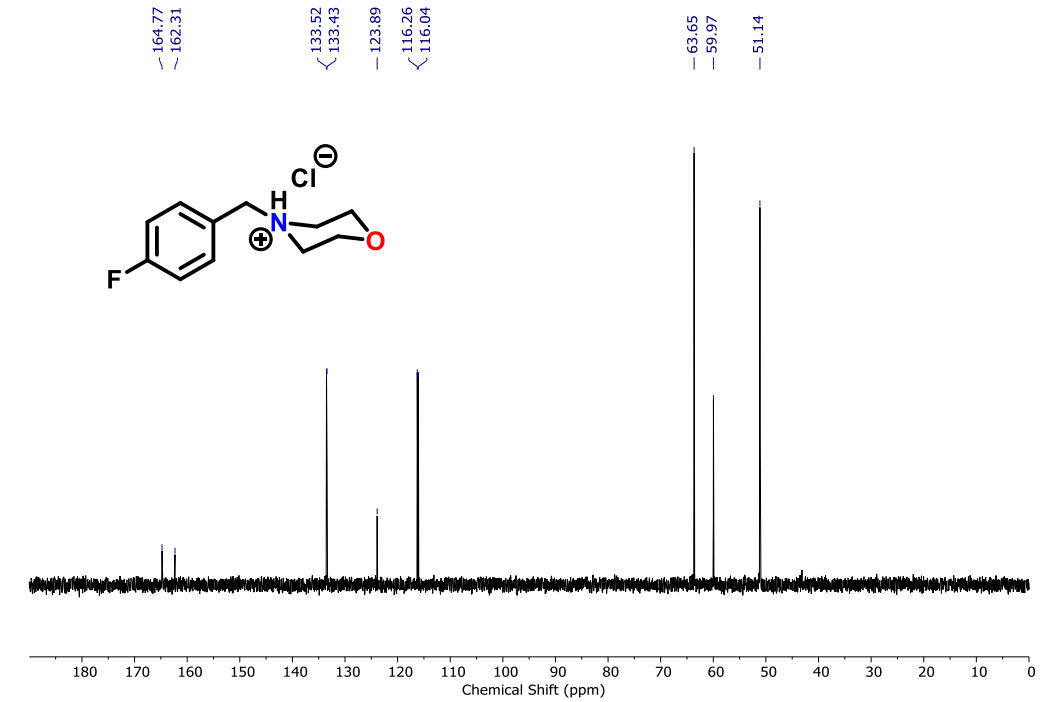


Figure S126: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ec**.

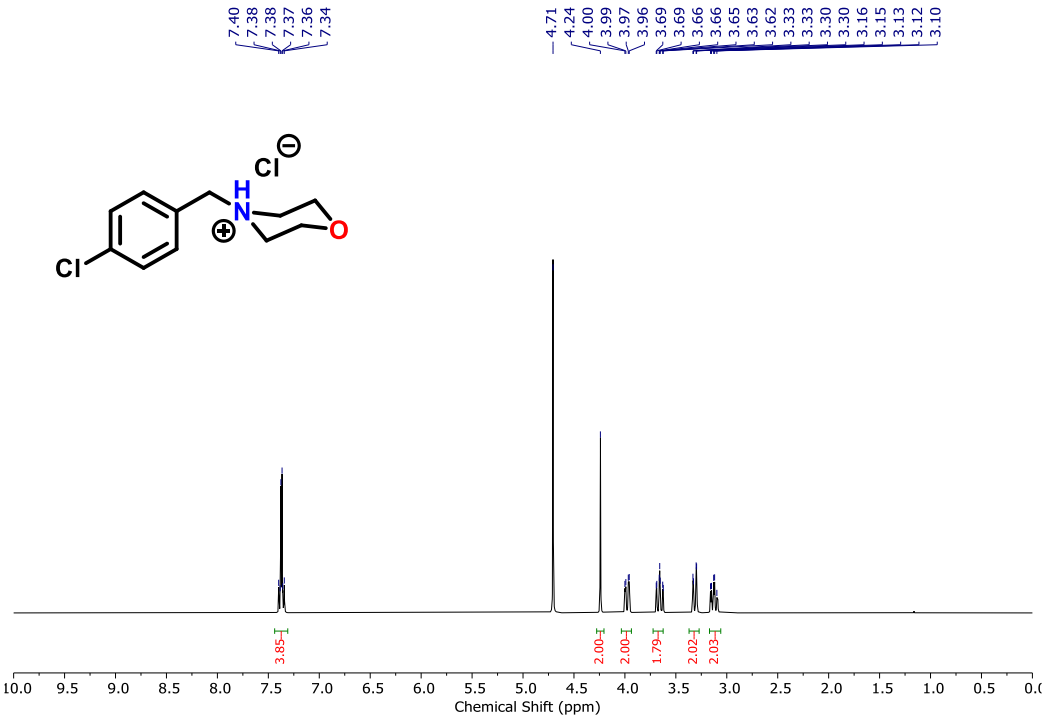


Figure S127: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ed**.

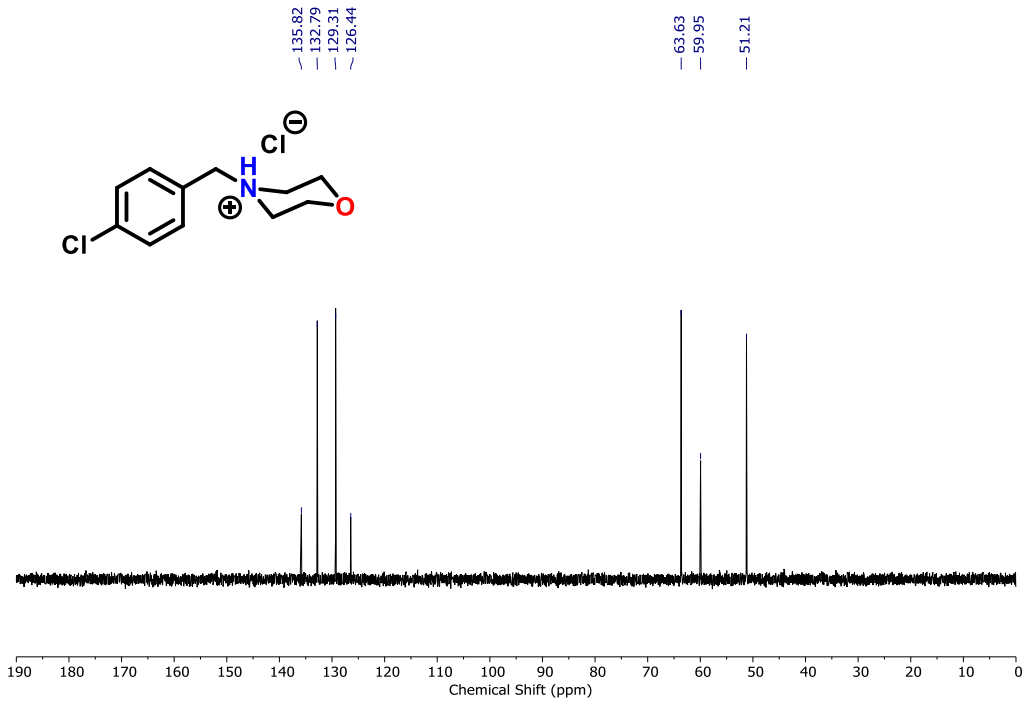


Figure S128: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ed**.

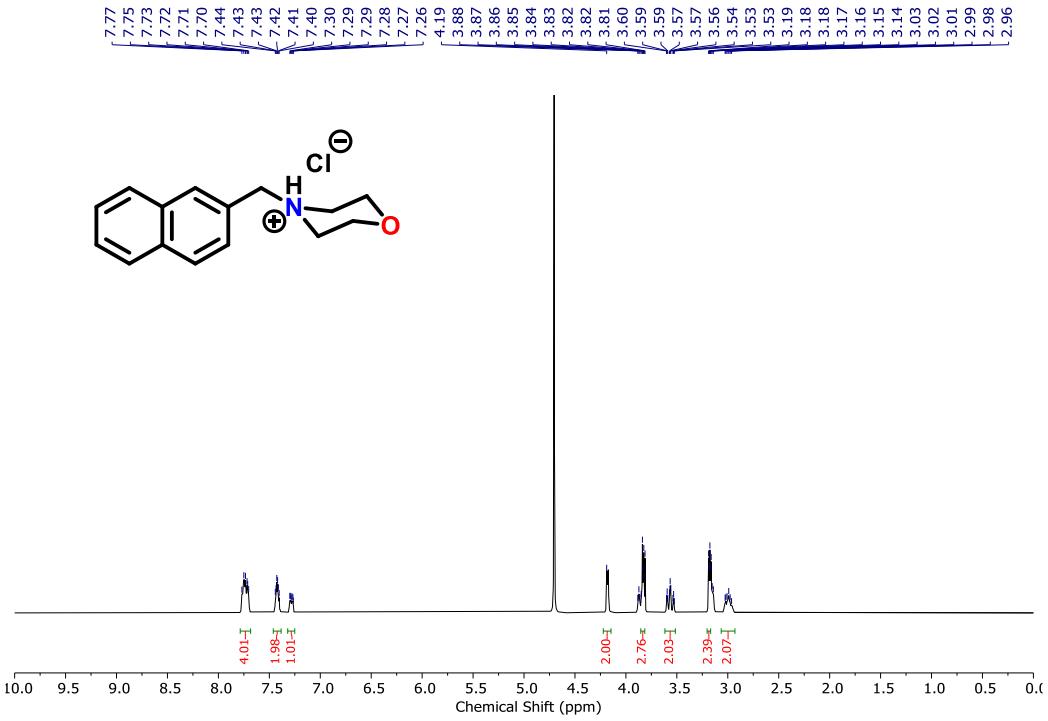


Figure S129: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4f**.

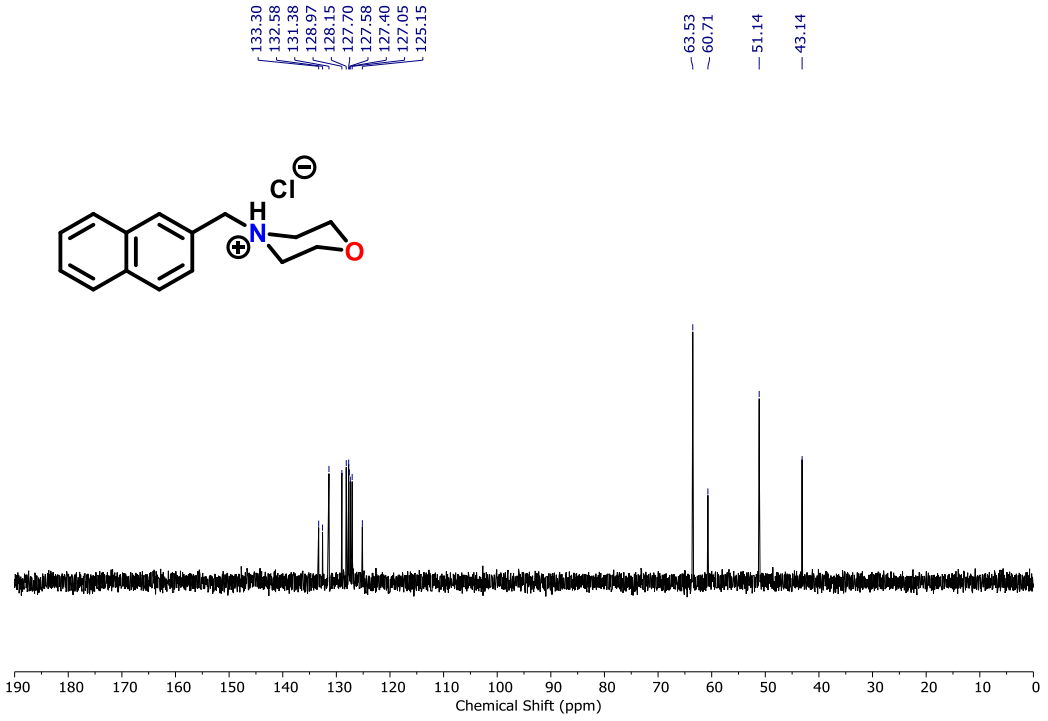


Figure S130: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4f**.

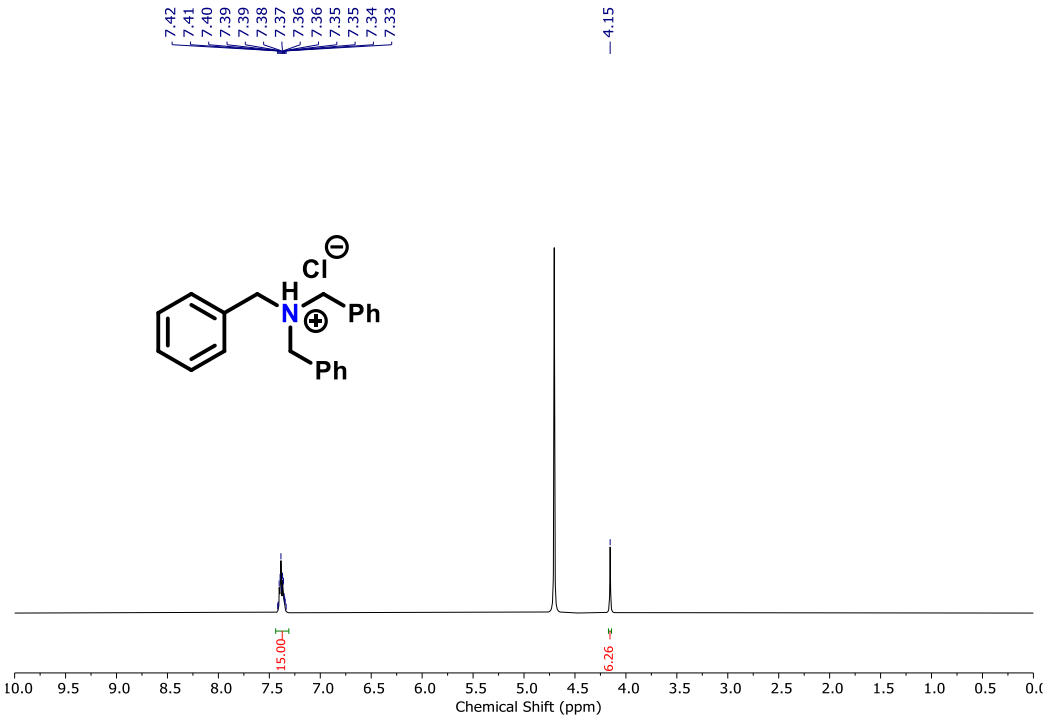


Figure S131: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4g**.

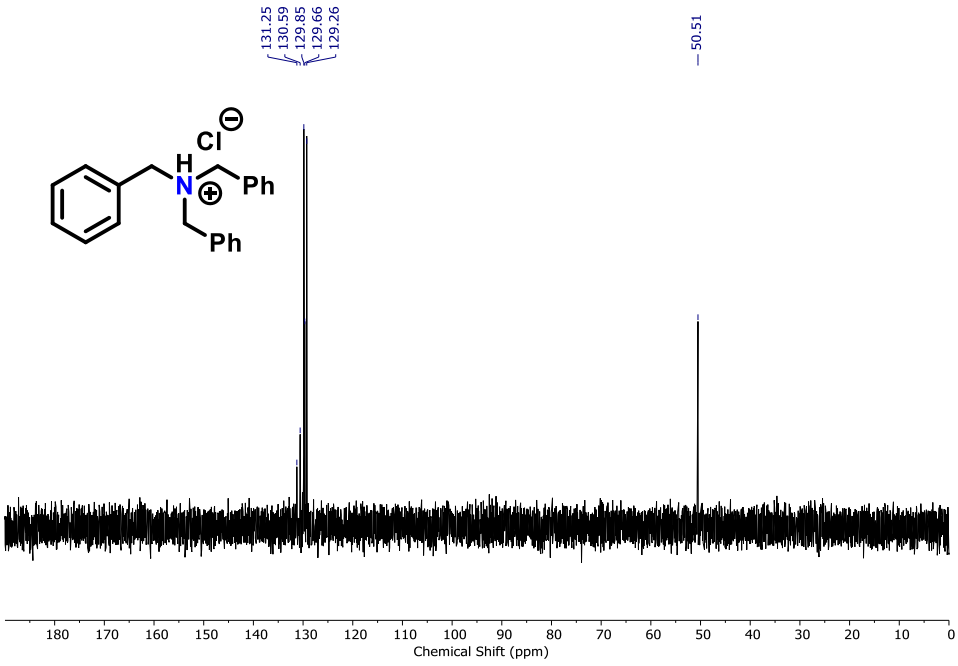


Figure S132: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4g**.

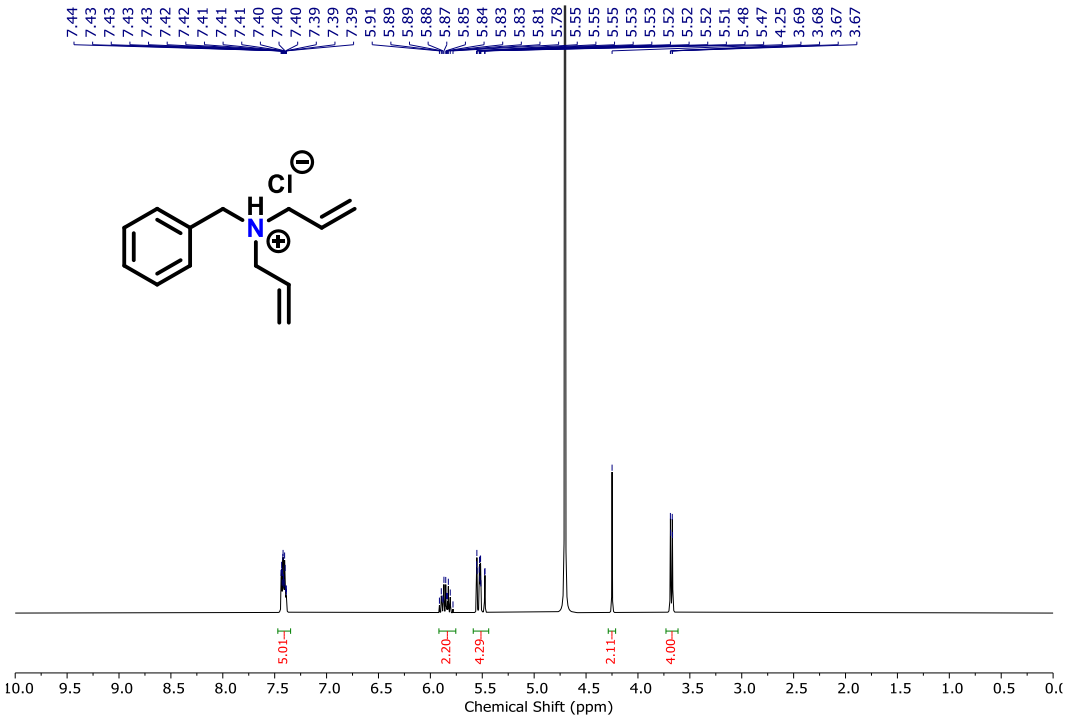


Figure S133: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4ha**.

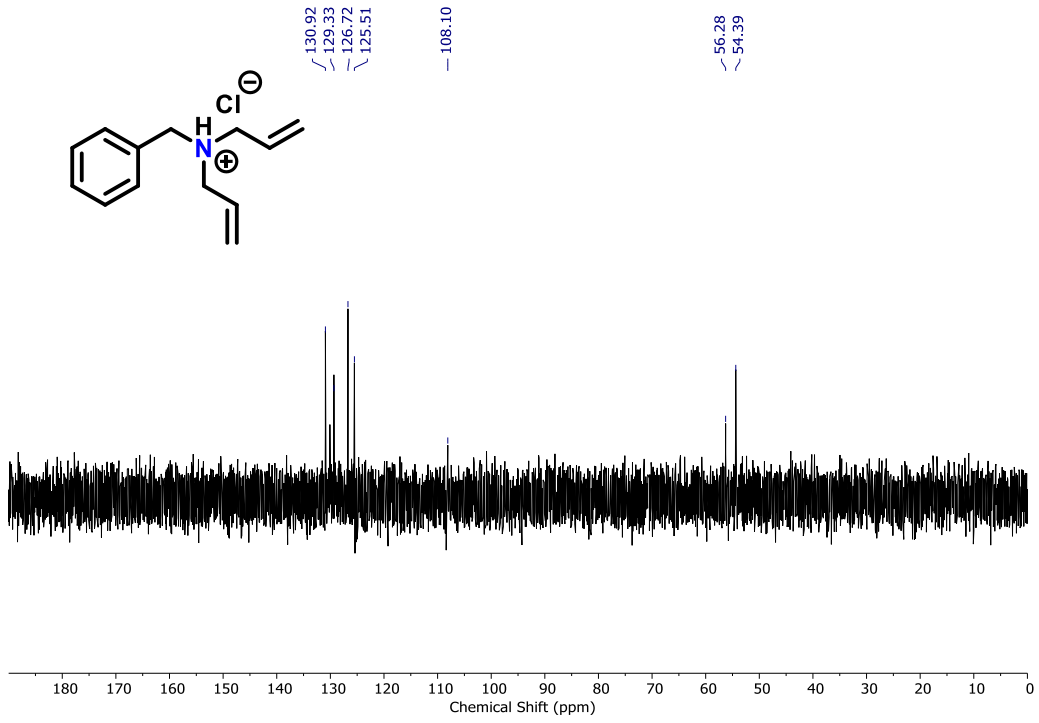


Figure S134: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4ha**.

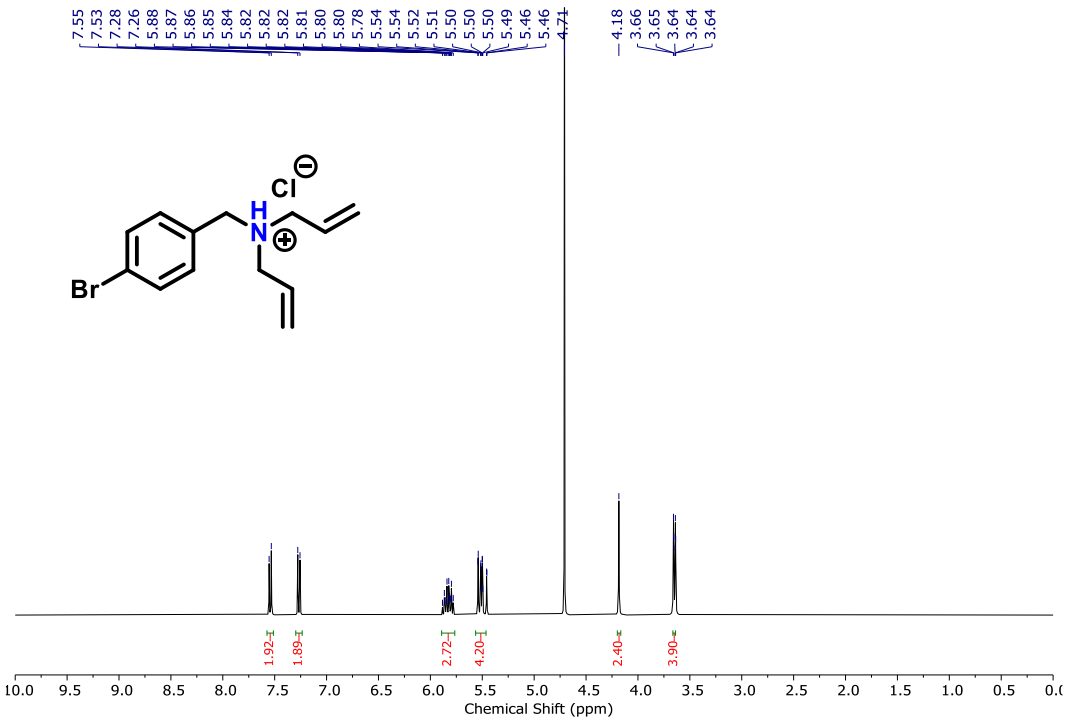


Figure S135: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4hb**.

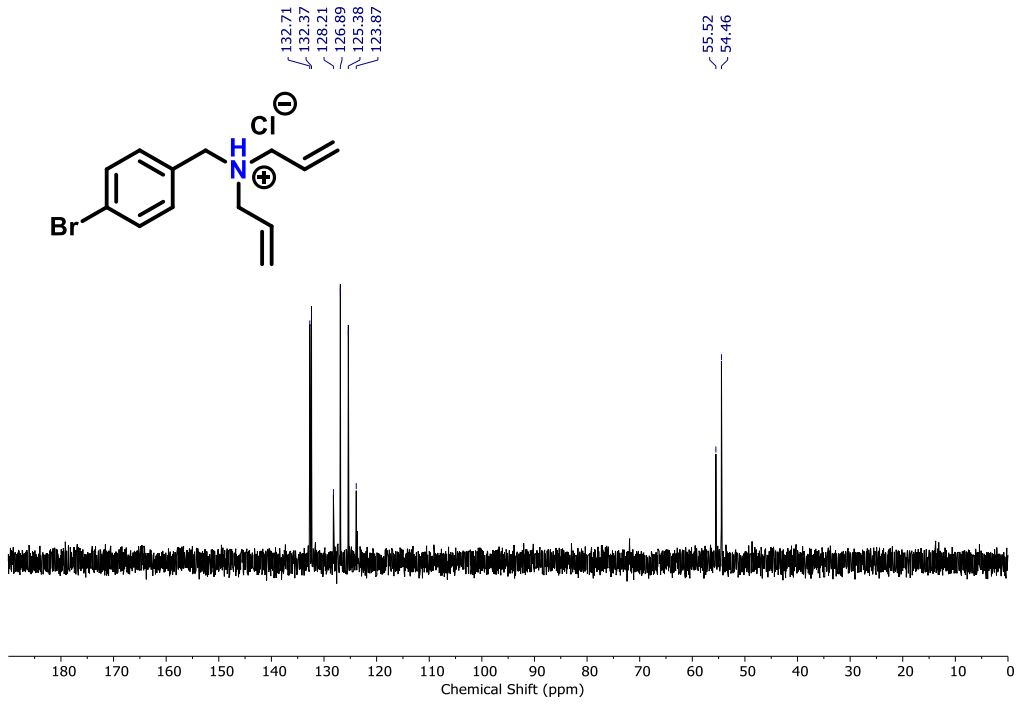


Figure S136: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4hb**.

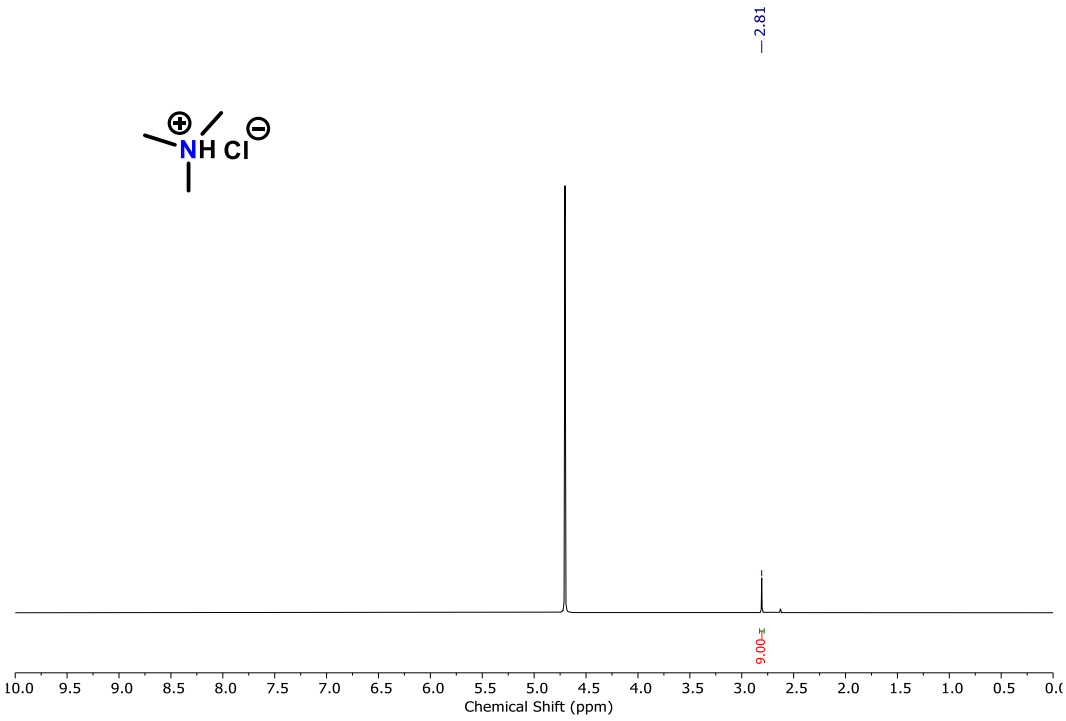


Figure S137: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4i**.

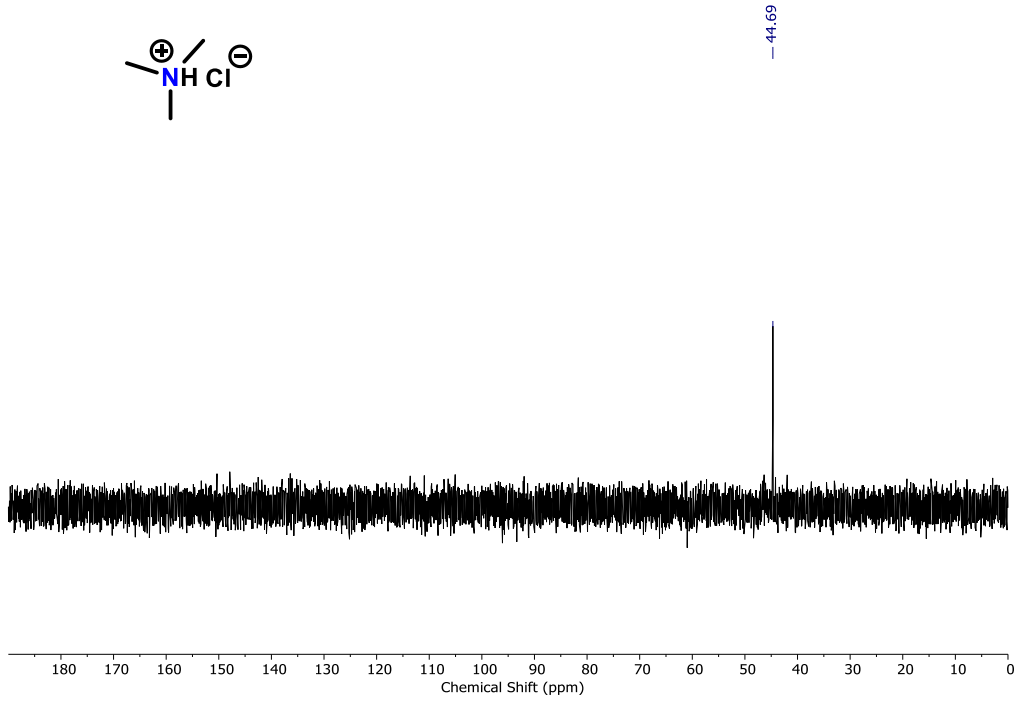


Figure S138: ^{13}C{^{1}H} (100 MHz, 25 ˚C, D_2O) NMR spectra of **4i**.

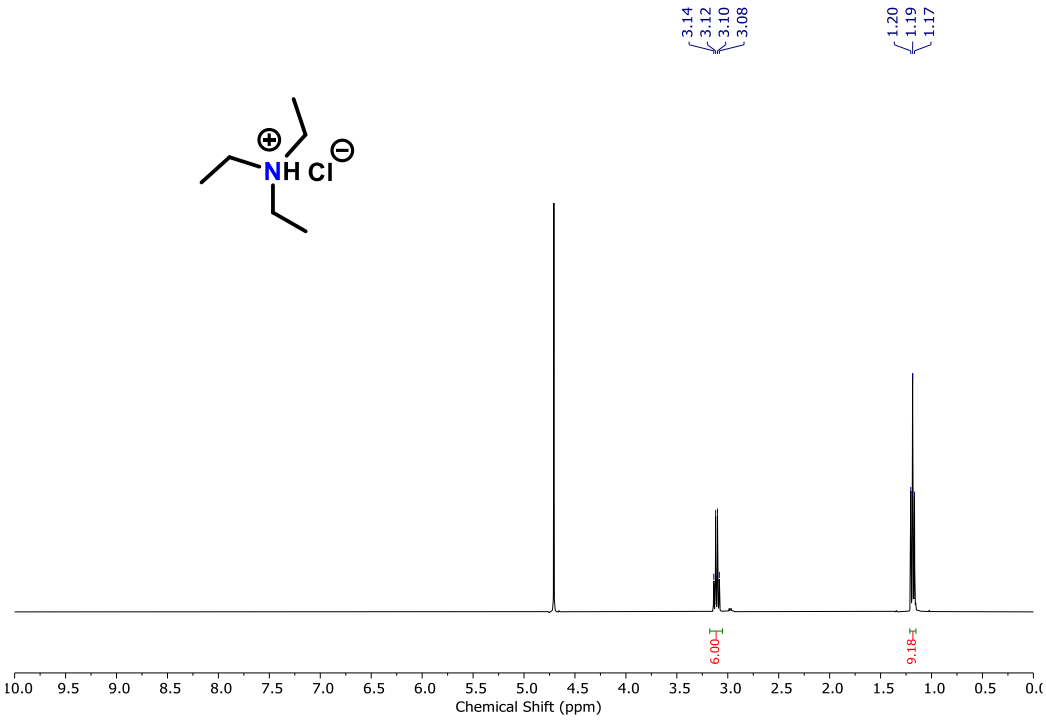


Figure S139: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4j**.

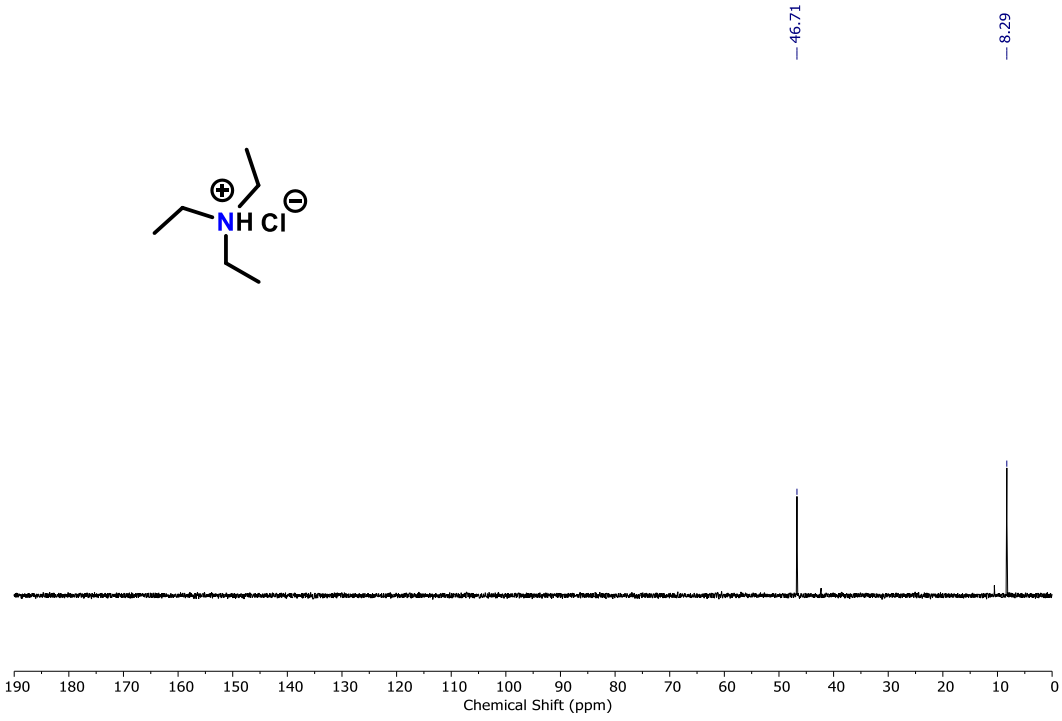


Figure S140: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4j**.

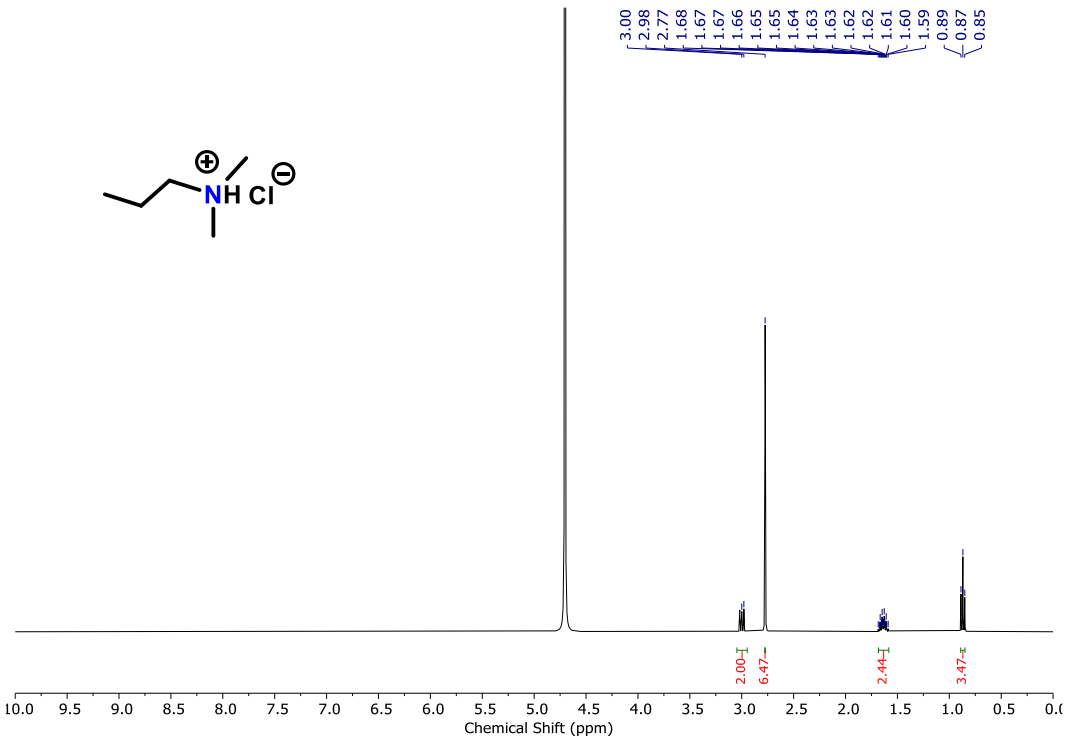


Figure S141: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4k**.

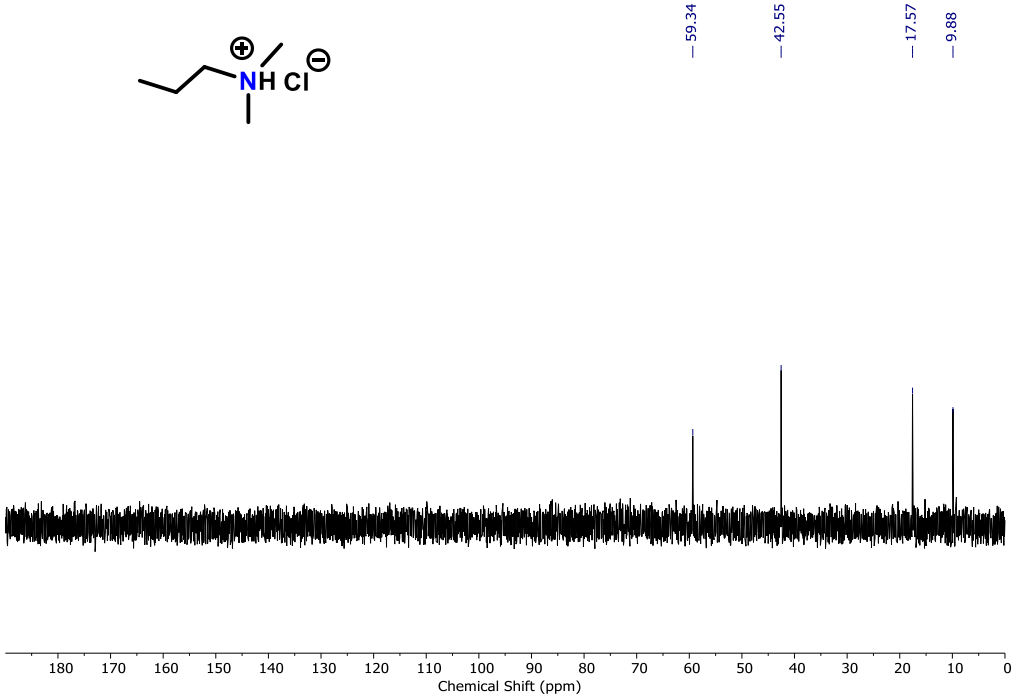


Figure S142: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4k**.

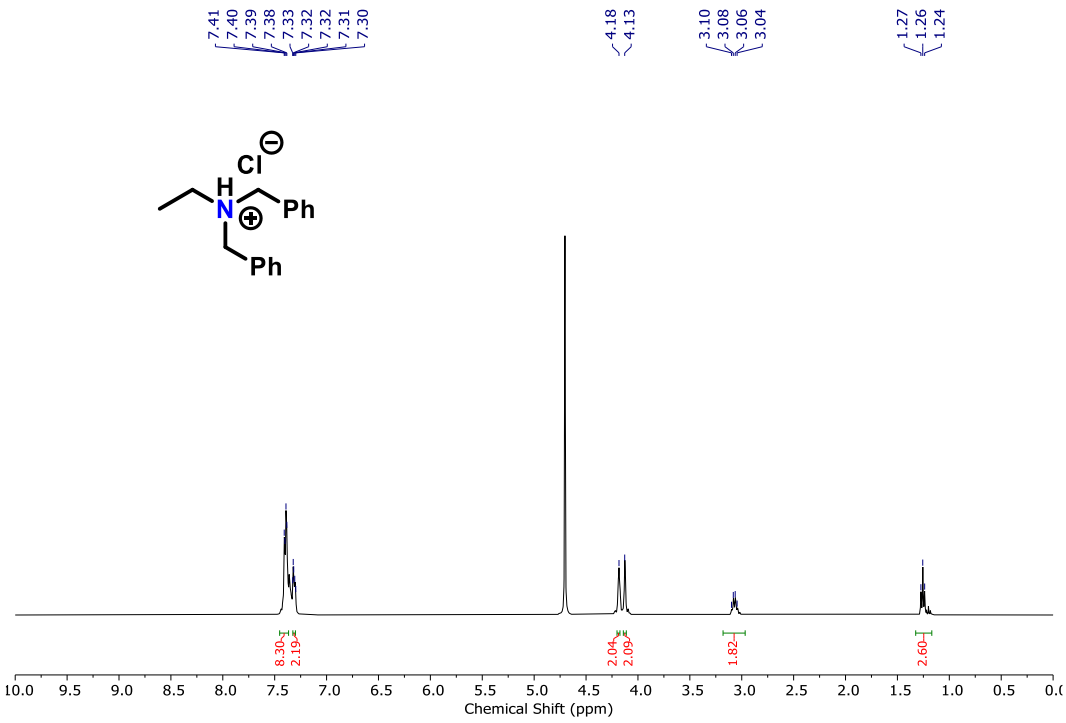


Figure S143: ^{1}H NMR (400 MHz, 25 ˚C, D_2O) spectra of **4l**.

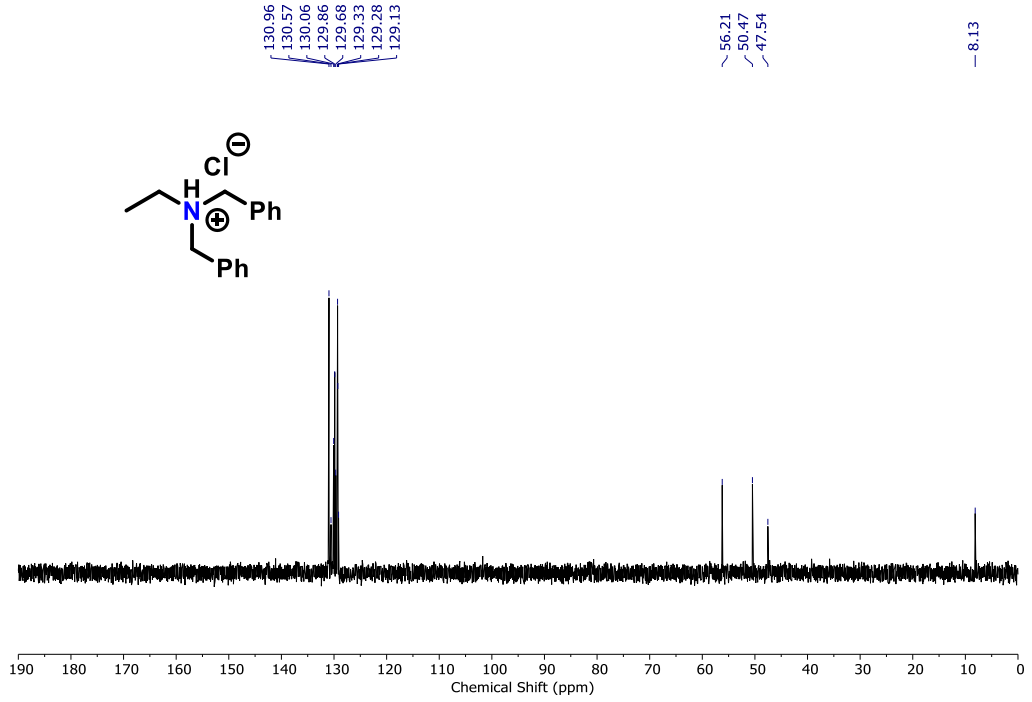


Figure S144: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, D_2O) NMR spectra of **4l**.

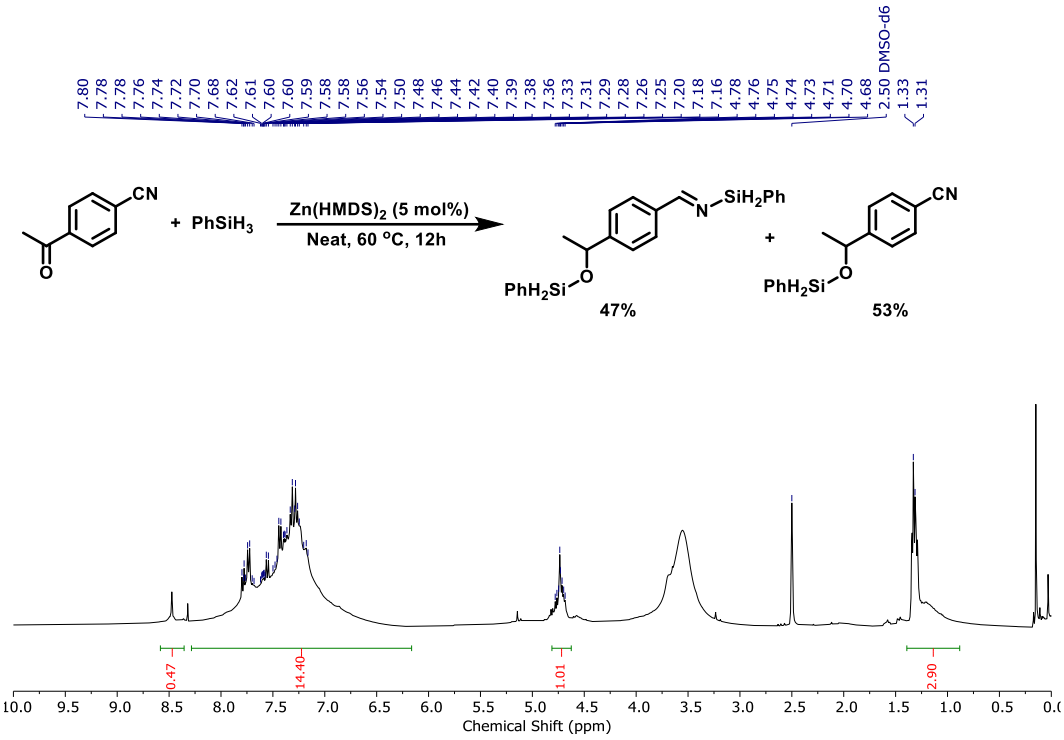


Figure S145: ^{1}H NMR (400 MHz, 25 ˚C, DMSO-d_6) spectra of hydrosilylation of 4-acetylbenzonitrile.

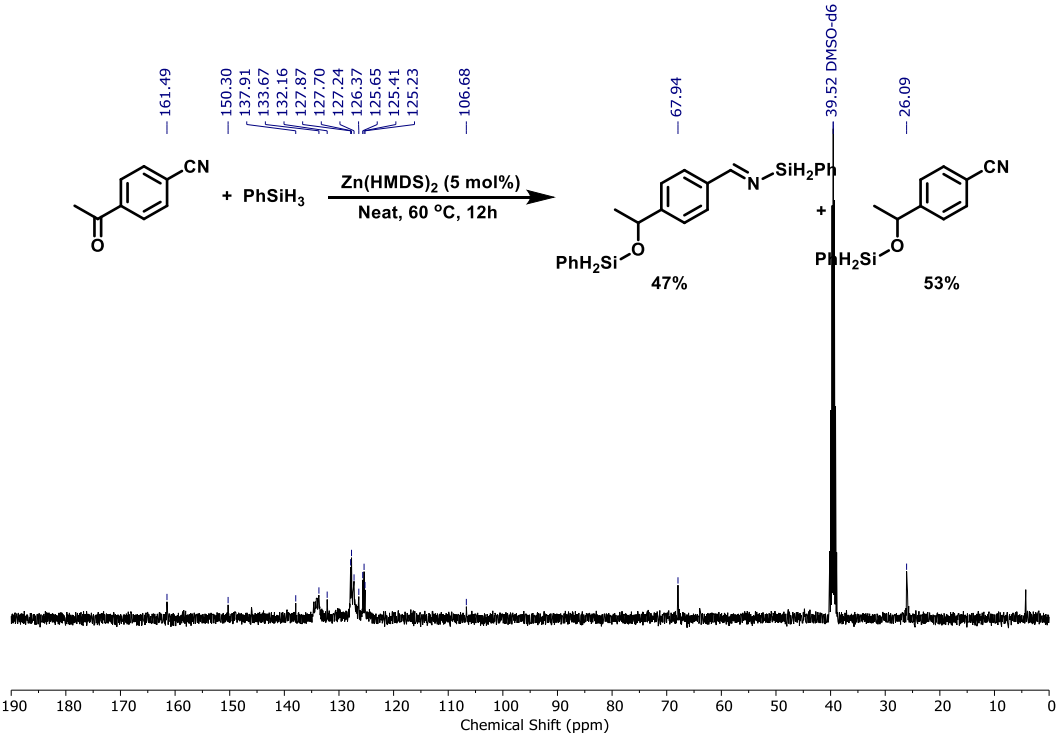


Figure S146: ^{13}C{^{1}H} (100 MHz, 25 ˚C, DMSO-d_6) NMR spectra of hydrosilylation of 4-acetylbenzonitrile.

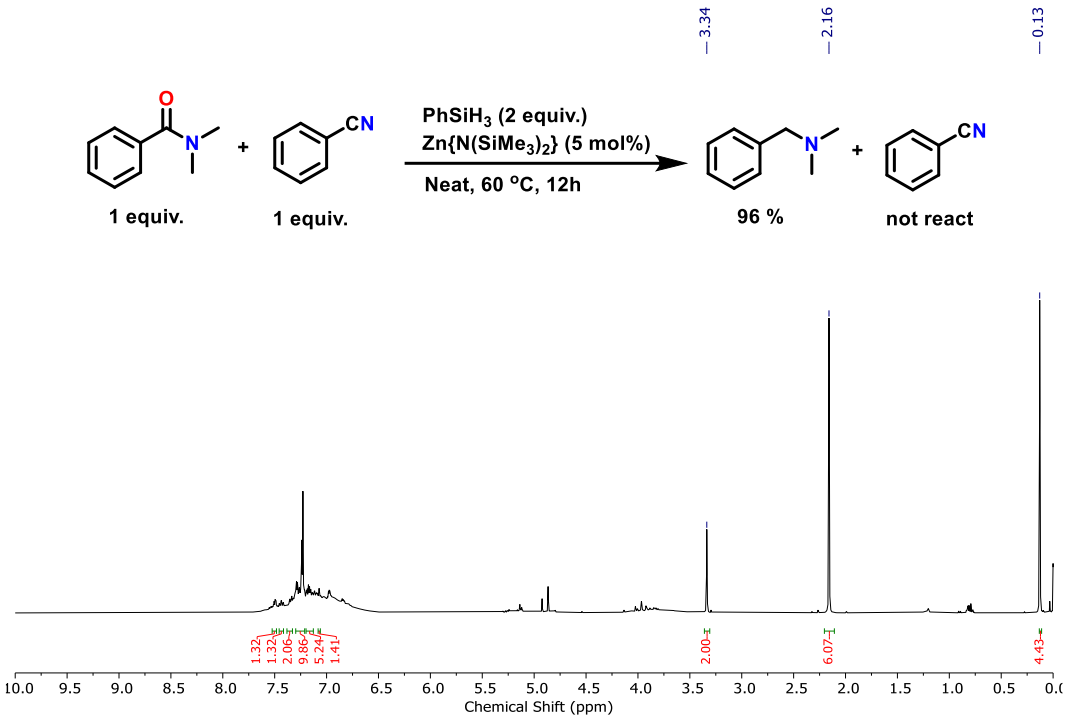


Figure S147: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of hydrosilylation of *N*,*N*-dimethylbenzamide in presence of benzonitrile.

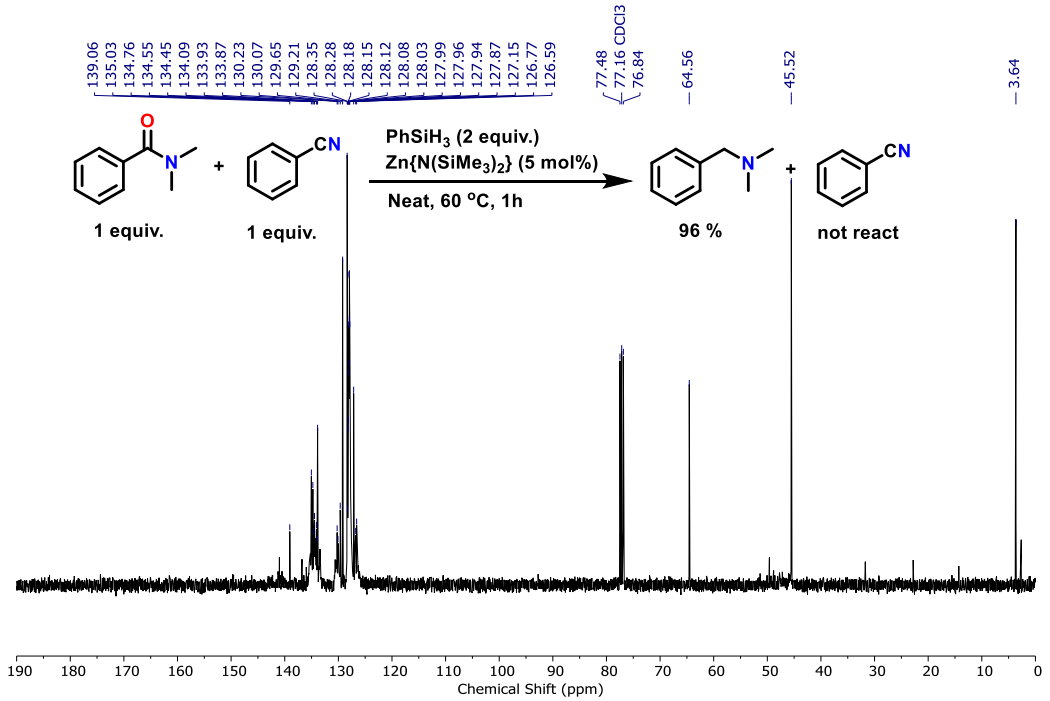


Figure S148: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of hydrosilylation of *N*,*N*-dimethylbenzamide in presence of benzonitrile.

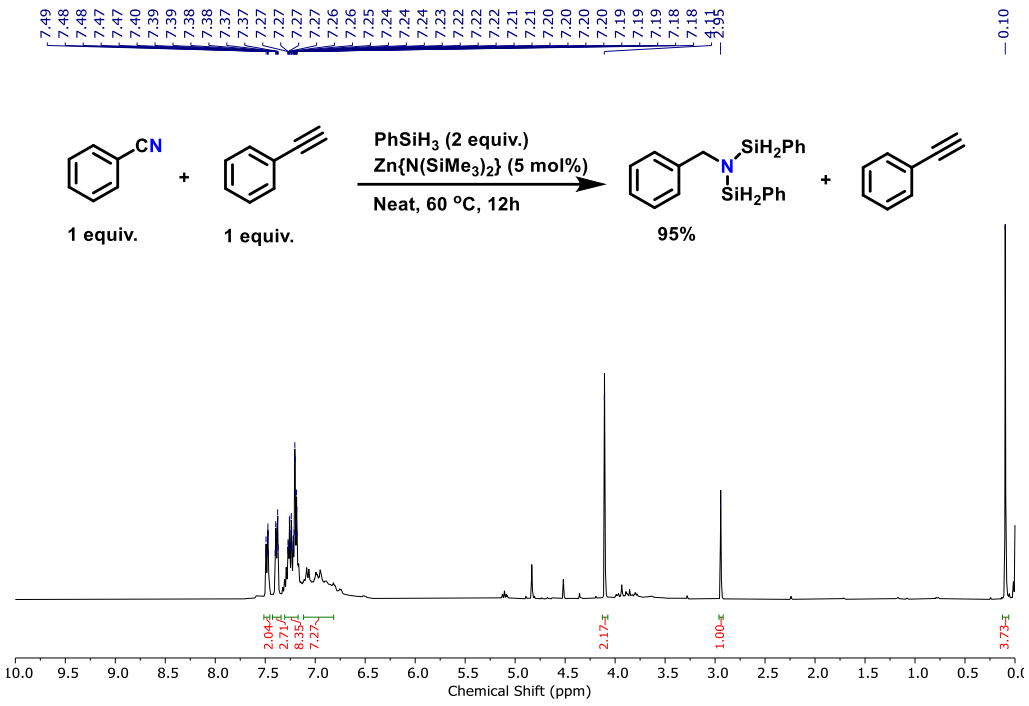


Figure S149: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of hydrosilylation of benzonitrile in presence of phenylacetylene.

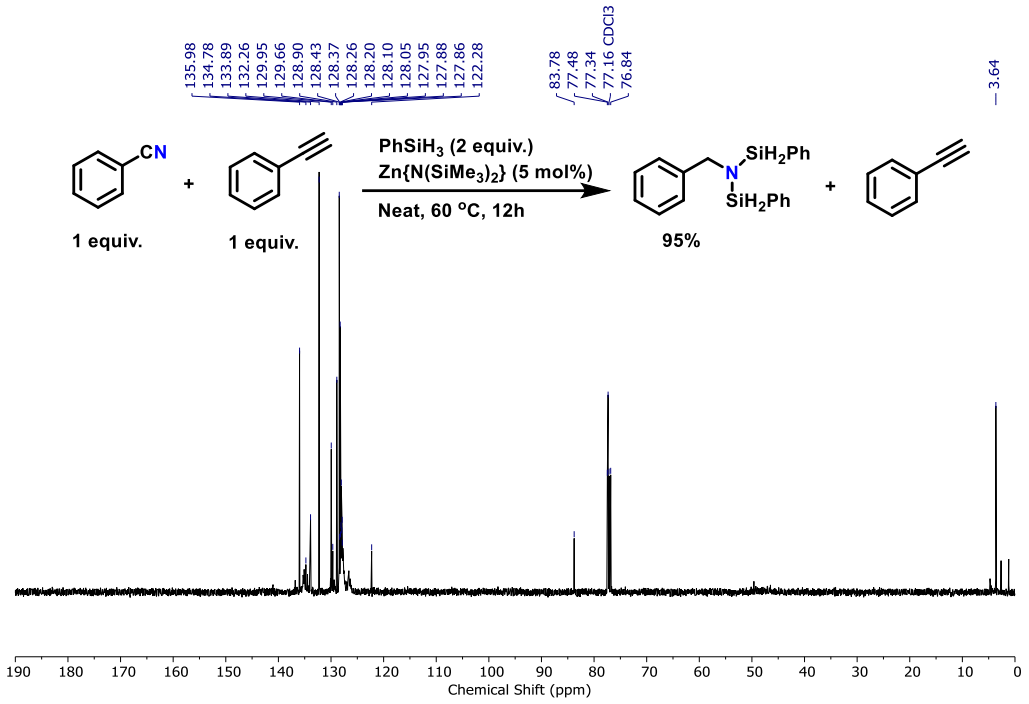


Figure S150: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, , $CDCl_3$) NMR spectra of hydrosilylation of benzonitrile in presence of phenylacetylene.

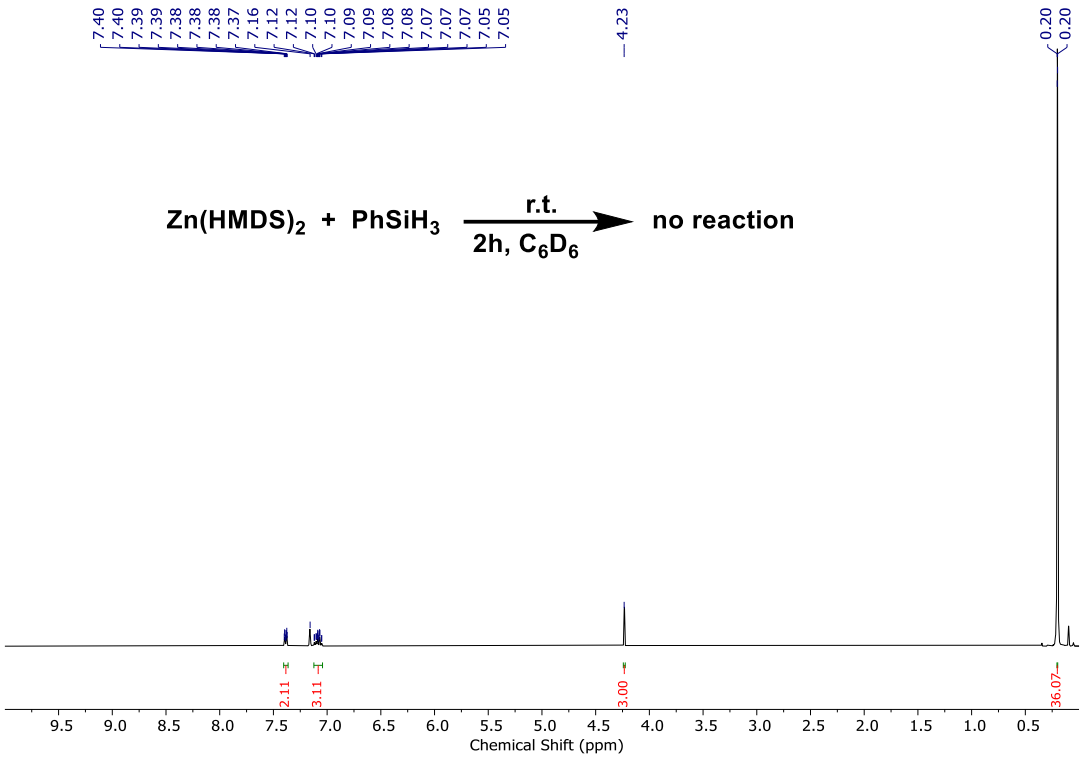


Figure S147: ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectra of 1:1 reaction of $Zn(HMDS)_2$ and phenylsilane.

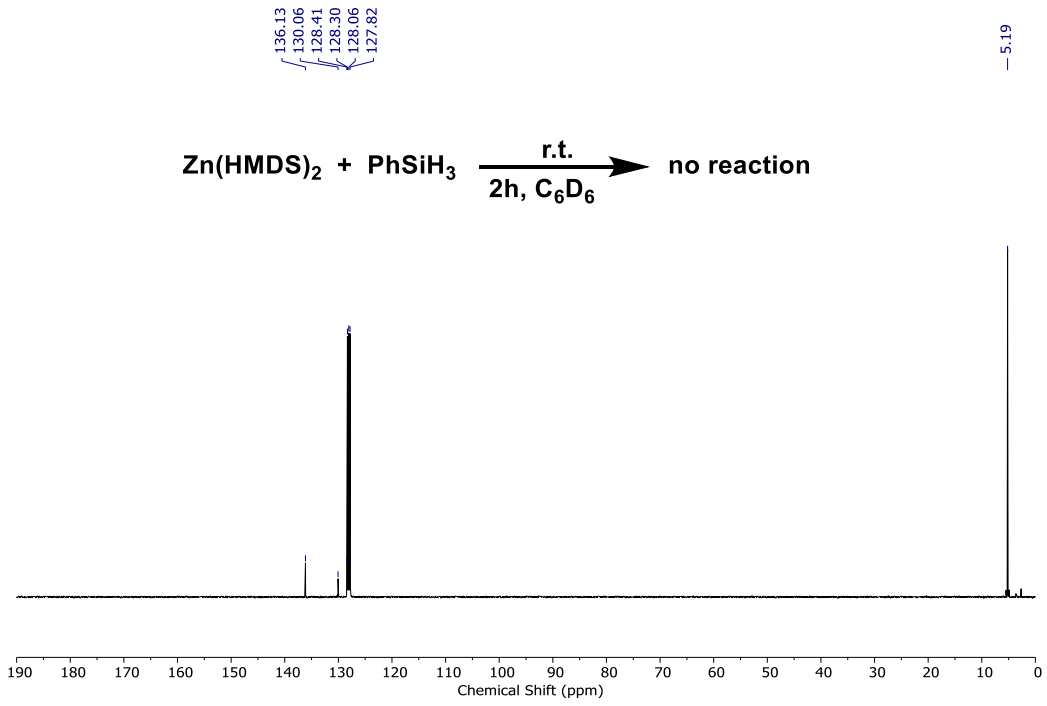
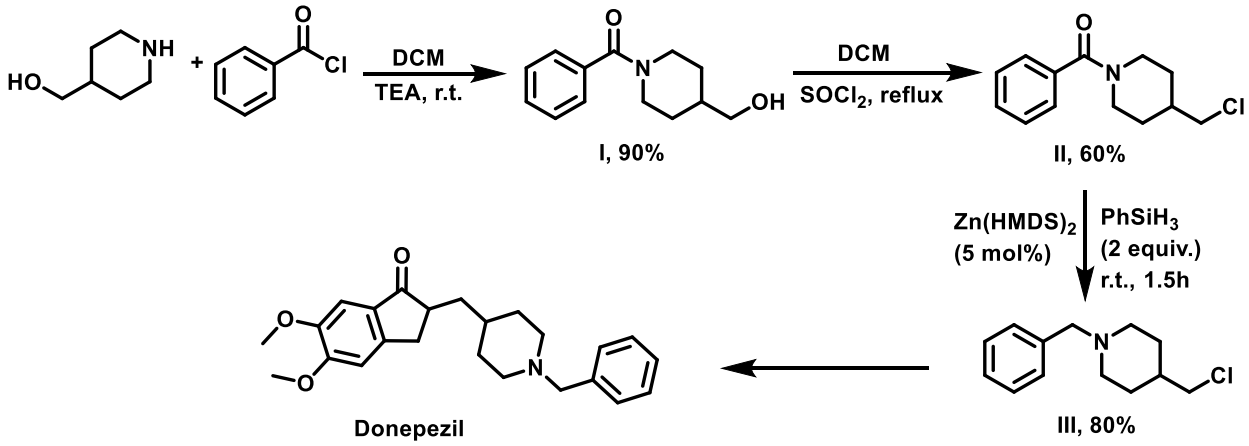


Figure S150: $^{13}C\{^{1}H\}$ (100 MHz, 25 ˚C, $CDCl_3$) NMR spectra of 1:1 reaction of $Zn(HMDS)_2$ and phenylsilane.

Synthesis of 1-benzyl-4-(chloromethyl)piperidine

Firstly, Piperdine-4-methanol (1 g, 8.68 mmol), triethylamine (0.88 g, 8.68 mmol) and benzoyl chloride (1.22 g, 8.68 mmol) were taken in round bottom flask containing dichloromethane solvent and stirred it for 12 hours at room temperature. After that, workup with water and dichloromethane and dichloromethane layer was collected for rotatory evaporation to obtain the product **I** (1.40g, 90%). In second step, product **I** (1.40 g, 6.40 mmol) was transfer in dichloromethane solvent containing thionyl chloride (1.52 g, 12.8 mmol) and reflux it for 48 hours. Then, worked up with water and dichloromethane and dichlormethane layer was collected for rotatory evaporation. After that, purify the crude compound with column chromatography using hexane/ethylacetate as eluent to obtain the product **II** (0.913, 60%). In third step, Schlenk tube was charged with product **II** (0.913, 3.84 mmol) and phenylsilane (0.83g, 7.68 mmol) under inert atmosphere and solvent-free condition and kept for stirring at room temperature for 1.5 hours. After that, reaction was quenched by 0.5 ml 0.1N HCl and worked up with water and dichloromethane and aqueous layer was collected. Then, neutralize the aqueous layer by 0.1N NaOH solution and worked up with dichloromethane. The dichloromethane layer was collected and evaporated the solvent using rotatory evaporation to obtain the product **III** (0.687 g, 80%).



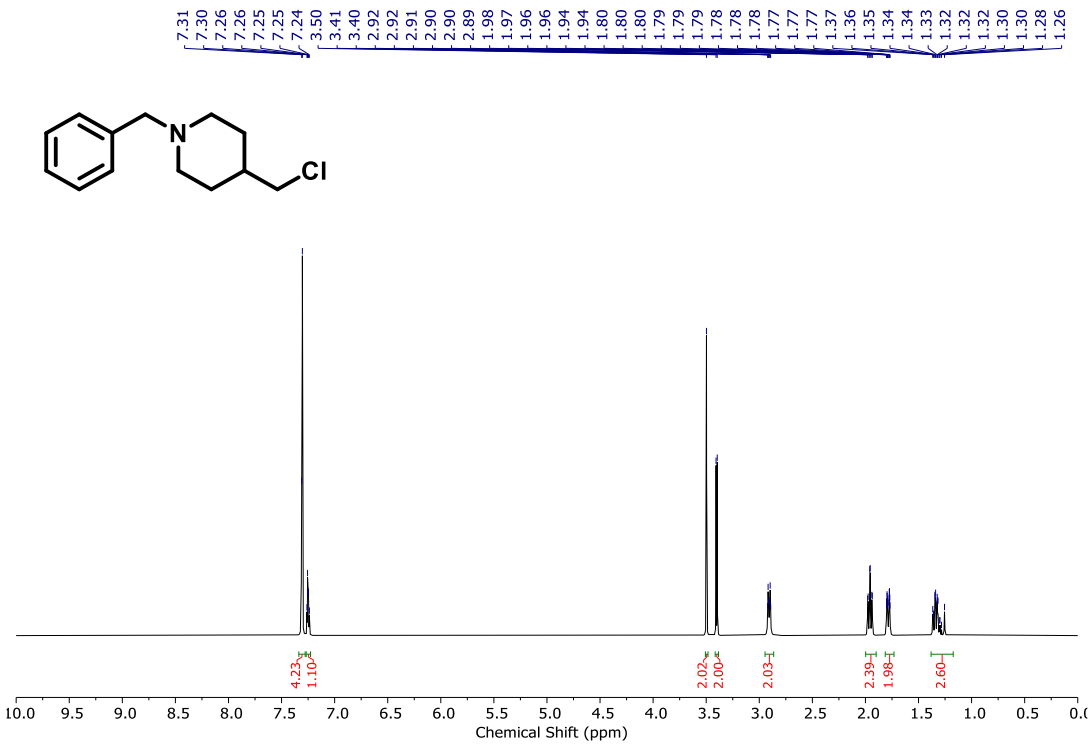


Figure 1: ^{1}H NMR (600 MHz, 25 ˚C, $CDCl_3$) spectra of **1-benzyl-4-(chloromethyl)piperidine**.

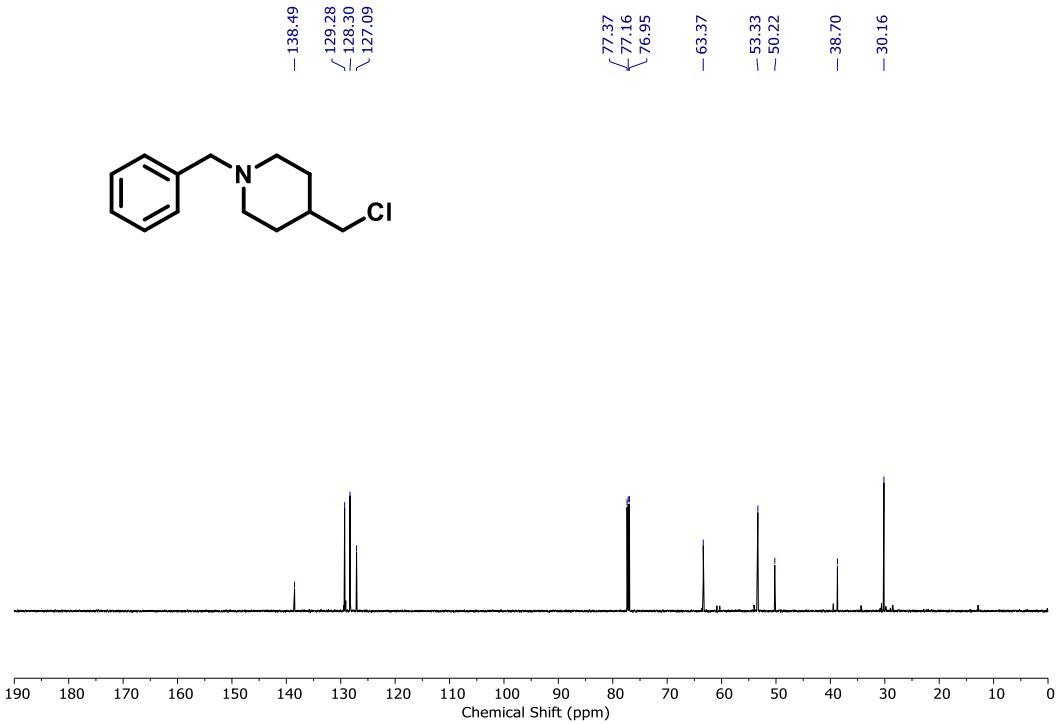


Figure S28: $^{13}C\{^{1}H\}$ (150 MHz, 25 ˚C, $CDCl_3$) NMR spectra of **1-benzyl-4-(chloromethyl)piperidine**.

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