Supporting Online Material

# Charge Transfer Directed Radical Substitution Enables *para*-Selective C–H Functionalization

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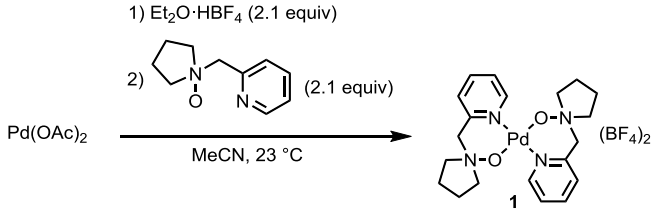
## Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 μm particle size using a forced flow of eluent at 0.3–0.5 bar pressure.[32] All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Acetonitrile and acetonitrile-$d_3$ were dried over $P_2O_5$ and vacuum-distilled. MeOH was degassed at –30 ºC under dynamic vacuum ($10^{-4}$ Torr) for one hour and stored over 3Å sieves. All chemicals were used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for $^1$H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for $^1$H and $^{13}$C acquisitions, respectively, or Varian Mercury 400 spectrometer operating at 375 MHz and 101 MHz for $^{19}$F and $^{13}$C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($^1$H: $CDCl_3$, δ 7.26; $(CD_3)_2SO$, δ 2.50; $(CD_3)_2CO$, δ 2.05; $CD_3CN$, δ 1.94), ($^{13}$C: $CDCl_3$, δ 77.16; $(CD_3)_2SO$, δ 39.52; $(CD_3)_2CO$, δ 29.84; $CD_3CN$, δ 1.32),[33] or added 3-nitrofluorobenzene (–112.0 ppm) for $^{19}$F spectra. Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained using an Agilent ESI-TOF (6210) mass spectrometer or a Bruker q-TOF Maxis Impact mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds, unless otherwise noted.

# Experimental Data

## Procedure for preparation of complex 1

**Palladium complex 1**



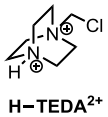

A flame-dried, 250 mL 2-neck flask under nitrogen was charged with $Pd(OAc)_2$ (5.00 g, 22.3 mmol, 1.00 equiv), and the flask was evacuated and refilled with $N_2$. Through a septum was added dry acetonitrile (50 mL, Aldrich Sure/Seal™), followed by $Et_2O{\cdot}HBF_4$ (6.4 mL, 47. mmol, 2.1 equiv). The resulting suspension was stirred at 23 °C for 30 min, after which 1-(pyridine-2-ylmethyl)pyrrolidine 1-oxide (8.334 g, 46.77 mmol, 2.10 equiv) was added as a solution in dry acetonitrile (40 mL, Aldrich Sure/Seal™). The resulting mixture was stirred for 1 hr, after which the reaction mixture was diluted with 100 mL acetonitrile to dissolve the precipitated product, and the solution was filtered through celite and then concentrated by rotary evaporation. The resulting brown solid was triturated with dichloromethane (40 mL) with sonication. The product was collected by filtration on a glass frit, then washed with dichloromethane (40 mL) followed by tetrahydrofuran (40 mL), then allowed to dry on the frit with applied suction to yield 10.61 g of a yellow powder (16.66 mmol, 75%).

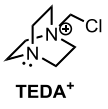
NMR Spectroscopy: $^1$H NMR (600 MHz, DMSO, 23 °C, δ): 8.50 (dd, $J$ = 5.8, 1.2 Hz, 2H), 8.30 (ddd, $J$ = 7.7, 7.7, 1.5 Hz, 2H), 7.86 (ddd, $J$ = 7.5, 5.8, 1.4 Hz, 2H), 7.79 (dd, $J$ = 7.8, 1.2 Hz, 2H), 5.35 (s, 4H), 3.56–3.46 (m, 4H), 3.45–3.36 (m, 4H), 2.26–2.15 (m, 4H), 2.10–1.99 (m, 4H). $^{13}$C NMR (125 MHz, DMSO, 23 °C, δ): 149.2, 148.2, 142.0, 128.2, 126.5, 70.1, 67.2, 21.3.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{20}H_{28}N_4O_2Pd$ $[M]^{2+}$, 231.0622; found, 231.0632.

Anal. Calcd for $C_{20}H_{28}B_2F_8N_4O_2Pd$: C, 37.74; H, 4.43; N, 8.80. Found: C, 37.83; H, 4.14; N, 9.04.

## General considerations for aromatic C–H TEDAylation reactions

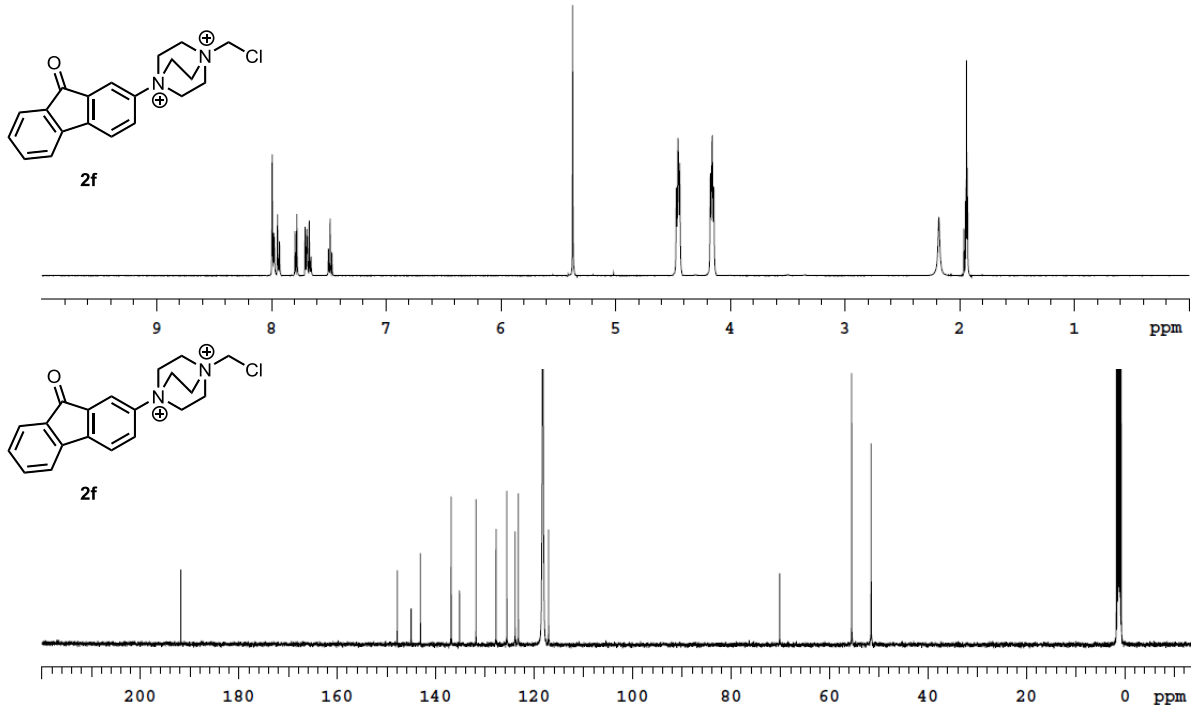



The Aryl–TEDA products are doubly cationic compounds, and similar cationic compounds are formed as byproducts of the reaction, including H–$TEDA^{2+}$ and $TEDA^+$. Therefore, it is difficult to isolate the Aryl–TEDA products from the reaction mixture. We have found that performing the reaction with an excess (at least five equivalents) of the arene substrate minimizes formation of H–$TEDA^{2+}$ and $TEDA^+$ byproducts. Upon reaction completion, evaporation of the solvent, followed by trituration of the residue with $CH_2Cl_2$/methanol mixtures to remove the excess arene, and the palladium and ruthenium catalysts, results in material that is sufficiently clean for characterization, albeit still contaminated to varying degrees with H–

$TEDA^{2+}$ and $TEDA^{+}$. Therefore, we have performed the Ar–TEDA formation reactions twice for each of the Ar–TEDA products **2a-g**: once utilizing the arene as limiting reagent (with yield determined by NMR integration relative to an internal standard), and once with excess arene (for characterization purposes). For Ar–TEDA compounds synthesized through the use of excess arene, yields of Ar–TEDA, $H–TEDA^{2+}$, and $TEDA^{+}$ are calculated relative to Selectfluor, and were determined via NMR analysis of a known amount of the mixture by integrating against an internal standard.

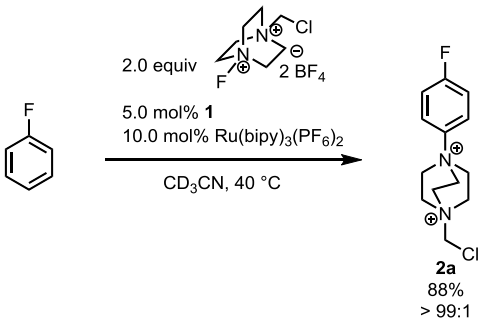
The Ar–TEDA products may be isolated from $H–TEDA^{2+}$, and $TEDA^{+}$ by repeated recrystallization. The Ar–TEDA product derived from fluorenone (**2f**) was isolated in this way and characterized as a pure compound.



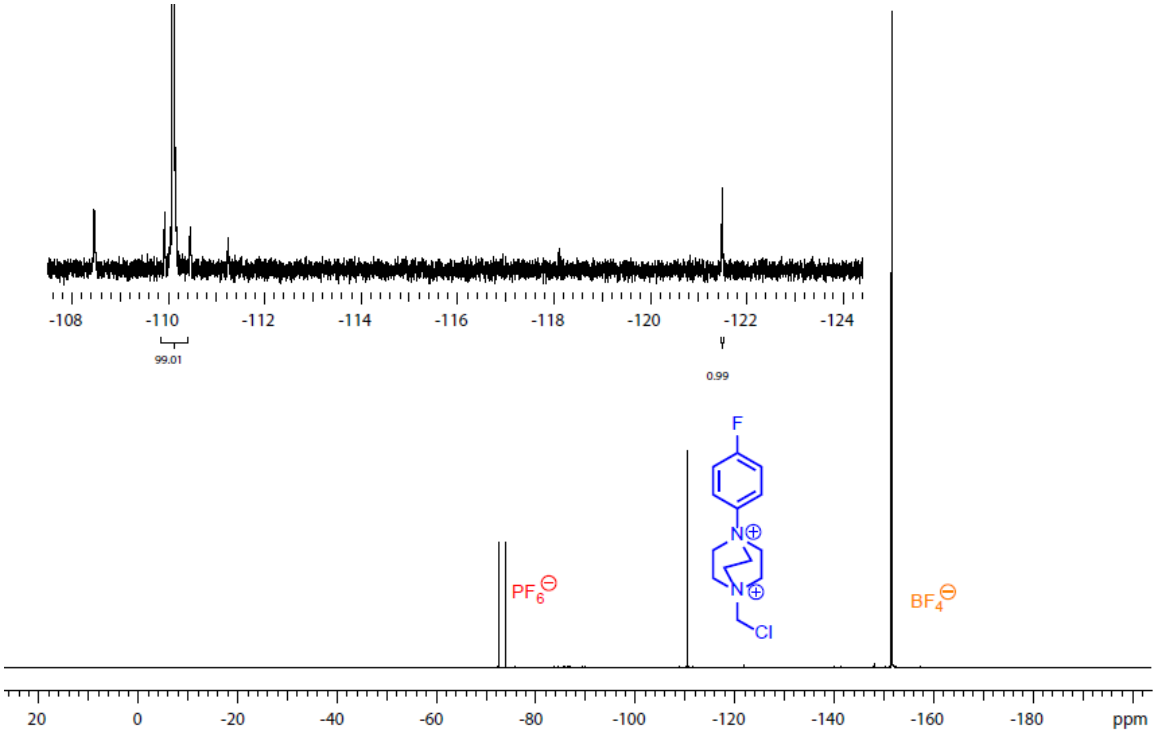

**Supplementary Figure S1.** $^{1}H$ and $^{13}C$ NMR of pure Ar–TEDA **2f** ($CD_3CN$, 23 °C)

## Procedure for aromatic C–H TEDAylation reactions (1 equiv arene)

### 1-(Chloromethyl)-4-(4-fluorophenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2a)



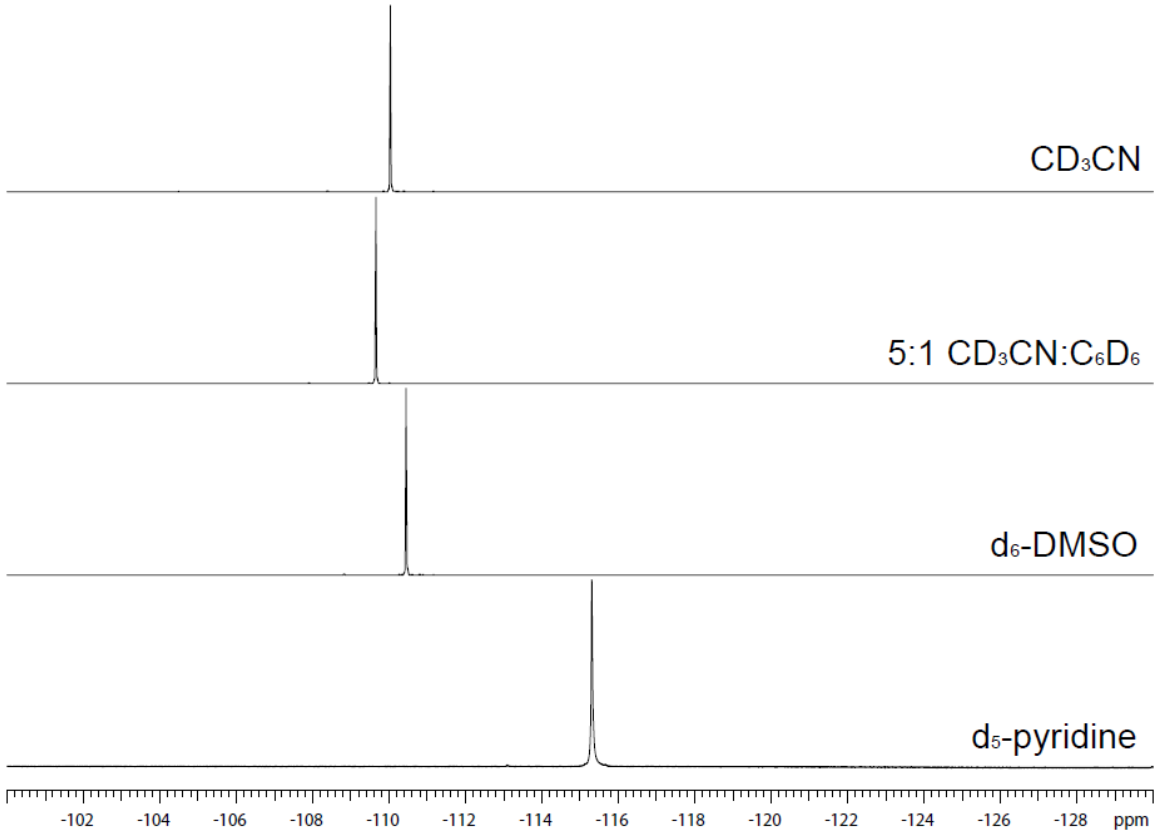
A 4 mL vial was charged with Selectfluor (70.9 mg, 0.200 mmol, 2.00 equiv), **1** (3.2 mg, 5.0 µmol, 5.0 mol%), and $Ru(bipy)_3(PF_6)_2$ (8.6 mg, 10 µmol, 10. mol%), and 0.50 mL $CD_3CN$, and finally fluorobenzene (9.4 µL, 0.10 mmol, 1.0 equiv). The vial was sealed and the mixture stirred at 40 °C for 36 h. The reaction mixture was diluted with 0.25 mL $CD_3CN$ and filtered through a 0.22 µm PVDF syringe filter, and an additional 0.25 mL $CD_3CN$ was washed through the filter to elute any remaining soluble material. The solution was analyzed by $^{19}F$ NMR:




**Supplementary Figure S2.** $^{19}F$ NMR evaluation of positional selectivity ($CD_3CN$, 23 °C)

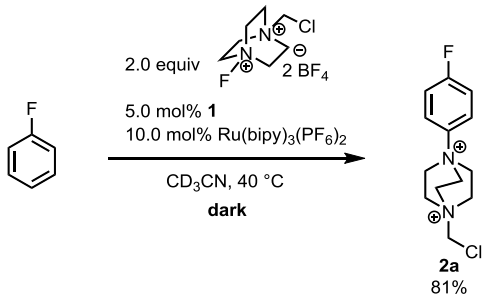
Only one significant aryl fluoride peak was observed in $^{19}F$ NMR, corresponding to the title compound. After 24 scans with a relaxation delay of 20 s, another peak in the aromatic region was observed at –121.5 ppm, at a ratio of 0.99:99.1 relative to the peak corresponding to **2a**. The ratio between the Ar–F signal and the rms noise over a 100 Hz range was measured to be 1286 (command 'dsnmax(100)' in VNMR), implying that any other products have a maximum concentration of 0.08% of the title compound. Given that the next largest peak in the aromatic region had an intensity of below 1% of the signal of **2a**, and given the magnitude of the noise level, we conclude that the positional selectivity of the TEDAylation reaction of fluorobenzene is >99:1 in favor of *para* substitution.

The product mixture of the reaction to form **2a** was analyzed by $^{19}F$ NMR in several different solvents in order to rule out coincidental overlap with any peaks corresponding to constitutional isomers of **2a**. The analysis was carried out by evaporating the acetonitrile solvent from the reaction mixtures and dissolving the residue in 5:1 $CD_3CN$:$C_6D_6$, $d_6$-DMSO, and $d_5$-pyridine, respectively. In each of these cases, only one aryl fluoride signal was observed by $^{19}F$ NMR:



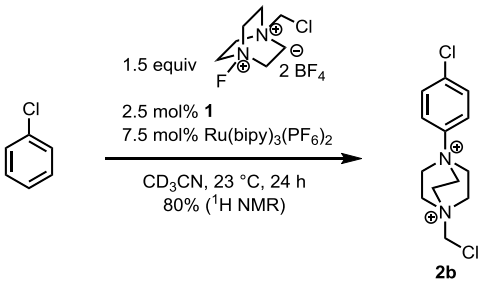

**Supplementary Figure S3.** $^{19}$F NMR evaluation of positional selectivity in different solvents (23 °C)

**Formation of 2a in the absence of light**



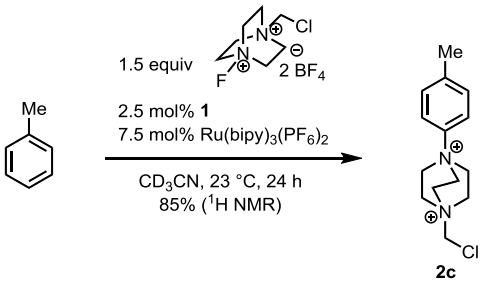

A 4 mL vial, completely covered with aluminum foil, was charged with Selectfluor (70.9 mg, 0.200 mmol, 2.00 equiv), **1** (3.2 mg, 5.0 µmol, 5.0 mol%), and $Ru(bipy)_3(PF_6)_2$ (8.6 mg, 10 µmol, 10. mol%), and 0.50 mL $CD_3CN$, and finally fluorobenzene (9.4 µL, 0.10 mmol, 1.0 equiv). The vial was sealed and the mixture stirred in the dark at 40 °C for 24 h, after which 2.0 µL of 3-fluoronitrobenzene was added as an internal standard. The reaction mixture was diluted with 0.50 mL $CD_3CN$, and passed through a 0.22 µm PVDF syringe filter. The resulting solution was analyzed by $^{19}$F NMR, and comparison of the Ar–F peak of the product (–110 ppm) with that of the internal standard (–112 ppm) revealed a yield of 81% of **2a**.

**1-(Chloromethyl)-4-(4-chlorophenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2b)**



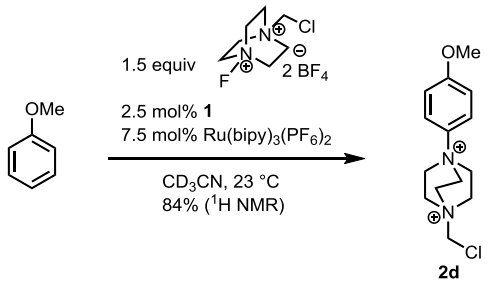

Palladium complex **1** (10.3 mg, 16.2 μmol) and $Ru(bipy)_3(PF_6)_2$ (41.9 mg, 48.8 μmol) were dissolved in $d_3$-acetonitrile (3.25 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (52.2 mg, 0.147 mmol, 1.50 equiv). The stock solution (491. μL) containing **1** (2.45 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (7.37 μmol, 7.50 mol%) was added, followed by chlorobenzene (10.0 μL 98.2 μmol, 1.00 equiv, c = 0.20 M) via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (3.0 mL). The yield of **2b** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2b** at 7.78–7.81 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 80% yield of **2b**.

**1-(Chloromethyl)-4-(4-methylphenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2c)**



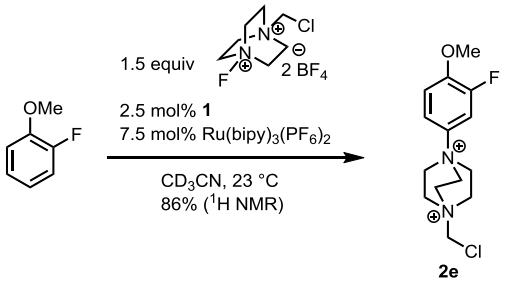

Palladium complex **1** (10.3 mg, 16.2 μmol) and $Ru(bipy)_3(PF_6)_2$ (41.9 mg, 48.8 μmol) were dissolved in $d_3$-acetonitrile (3.25 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (49.9 mg, 0.141 mmol, 1.50 equiv). The stock solution (469. μL) containing **1** (2.34 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (7.04 μmol, 7.50 mol%) was added, followed by toluene (10.0 μL, 93.9 μmol, 1.00 equiv, c = 0.20 M) via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (3.0 mL). The yield of **2c** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2c** at 7.67–7.65 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 85% yield of **2c**.

**1-(Chloromethyl)-4-(4-methoxyphenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2d)**



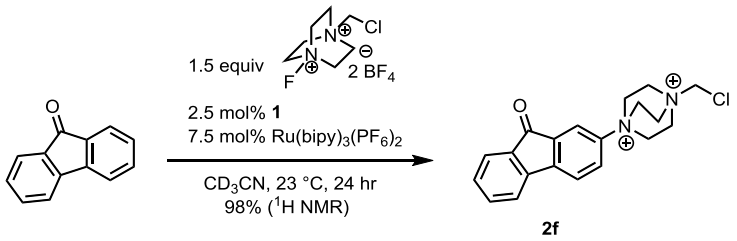

Palladium complex **1** (10.3 mg, 16.2 μmol) and $Ru(bipy)_3(PF_6)_2$ (41.9 mg, 48.8 μmol) were dissolved in $d_3$-acetonitrile (3.25 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (48.9 mg, 0.138 mmol, 1.50 equiv). The stock solution (460. μL, c = 0.200 M) containing **1** (2.34 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (7.04 μmol, 7.50 mol%) was added, followed by anisole (10.0 μL, 92.0 μmol, 1.00 equiv) via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (3.0 mL). The yield of **2d** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2c** at 7.72–7.69 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 84% yield of **2d**.

**1-(Chloromethyl)-4-(3-fluoro-4-methoxyphenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2e)**



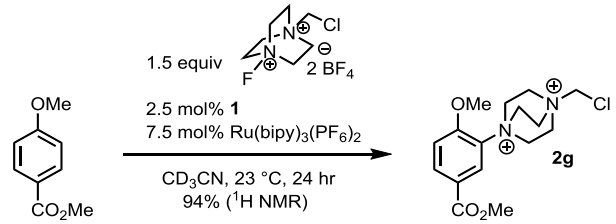

Palladium complex **1** (11.3 mg, 17.8 μmol) and $Ru(bipy)_3(PF_6)_2$ (45.9 mg, 53.4 μmol) were dissolved in $d_3$-acetonitrile (3.56 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (47.3 mg, 0.134 mmol, 1.50 equiv). The stock solution (445. μL, c = 0.200 M) containing **1** (2.23 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (6.68 μmol, 7.50 mol%) was added, followed by 2-fluoroanisole (10.0 μL, 89.0 μmol, 1.00 equiv) via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (2.5 mL). The yield of **2e** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2e** at 7.34 ppm (aromatic C–H, 1H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 86% yield of **2e**.

**1-(Chloromethyl)-4-(fluorenon-2-yl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2f)**




Palladium complex **1** (11.3 mg, 17.8 μmol) and $Ru(bipy)_3(PF_6)_2$ (45.9 mg, 53.4 μmol) were dissolved in $d_3$-acetonitrile (3.56 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (47.3 mg, 0.134 mmol, 1.50 equiv) and fluorenone (16.0 mg, 89.0 μmol, 1.00 equiv). The stock solution (445. μL, c = 0.200 M) containing **1** (2.23 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (6.68 μmol, 7.50 mol%) was added via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (2.0 mL). The yield of **2f** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2f** at 7.94–7.93 ppm (aromatic C–H, 1H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 98% yield of **2f**.

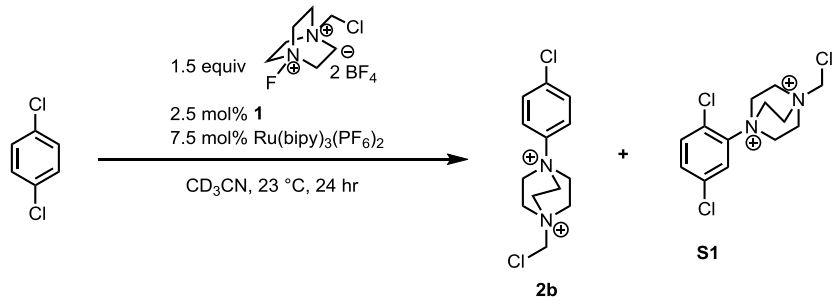
**1-(Chloromethyl)-4-(2-methoxy-5-(methoxycarbonyl)phenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2g)**




Palladium complex **1** (10.3 mg, 16.2 μmol) and $Ru(bipy)_3(PF_6)_2$ (41.9 mg, 48.8 μmol) were dissolved in $d_3$-acetonitrile (3.25 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (53.1 mg, 0.150 mmol, 1.50 equiv) and methyl 4-methoxybenzoate (16.6 mg, 100. μmol, 1.00 equiv). The stock solution (500. μL, c = 0.200 M) containing **1** (2.50 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (7.50 μmol, 7.50 mol%) was added via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (3.0 mL).

The yield of **2g** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2g** at 7.46 ppm (aromatic C–H, 1H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed a 94% yield of **2g**.

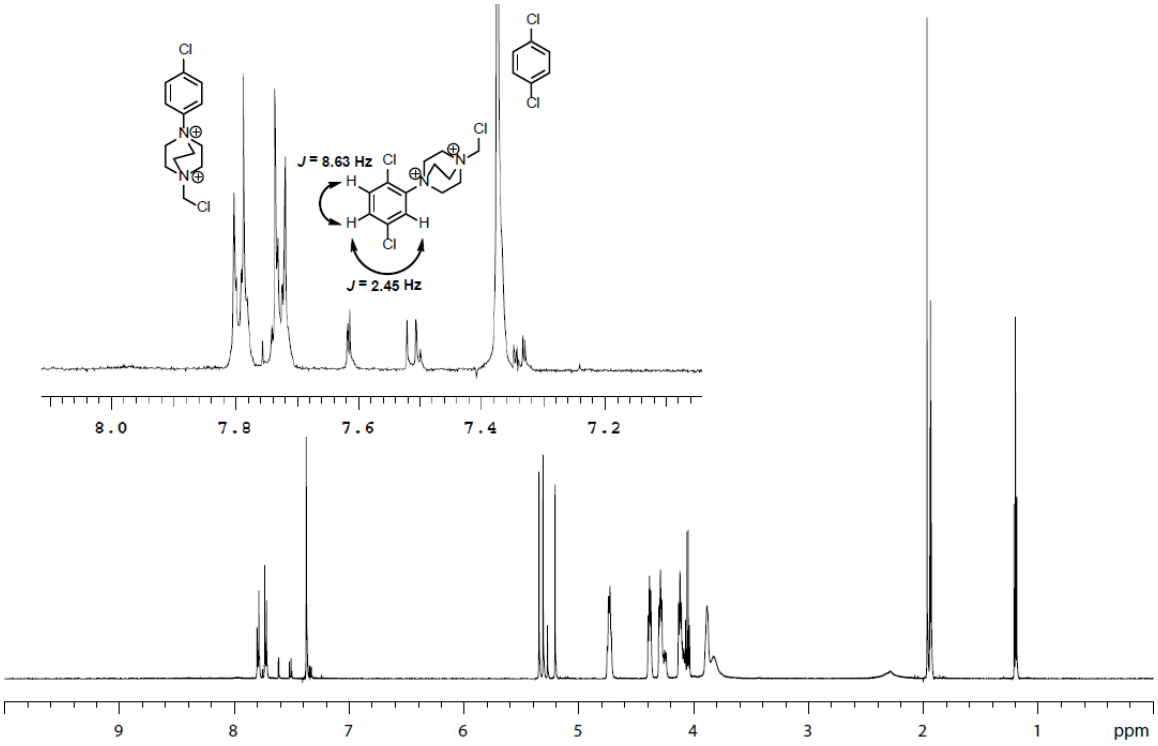
**1-(Chloromethyl)-4-(4-chlorophenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2b) from 1,4-dichlorobenzene**




Palladium complex **1** (11.3 mg, 17.8 μmol) and $Ru(bipy)_3(PF_6)_2$ (45.9 mg, 53.4 μmol) were dissolved in $d_3$-acetonitrile (3.56 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (47.3 mg, 0.134 mmol, 1.50 equiv) and 1,4-dichlorobenzene (13.1 mg, 89.0 μmol, 1.00 equiv). The stock solution (445 μL, c = 0.200 M) containing **1** (2.23 μmol, 2.50 mol%) and $Ru(bipy)_3(PF_6)_2$ (6.68 μmol, 7.50 mol%) was added via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (2.0 mL).

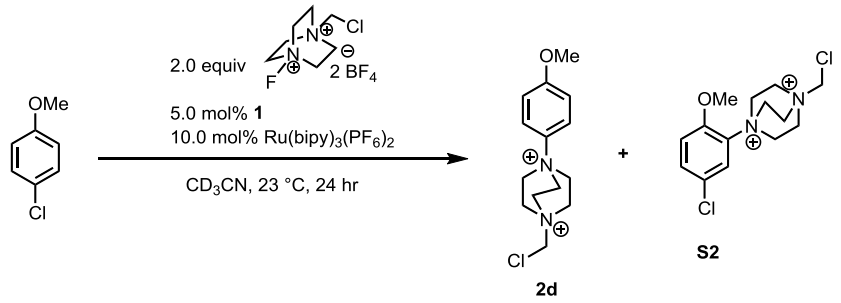
The yield of **2b** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2b** at 7.74–7.72 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 48% yield of **2b**.

Another compound, consistent with structure **S1**, was observed in 11% yield:



**Supplementary Figure S4.** $^1$H NMR of product mixture of TEDAylation of 1,4-dichlorobenzene ($CD_3CN$, 23 °C)

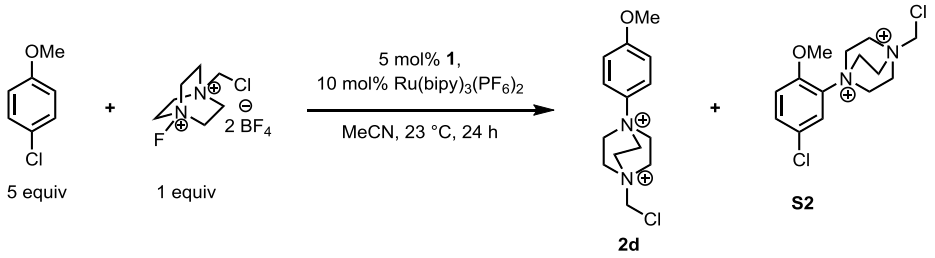
**1-(Chloromethyl)-4-(4-methoxyphenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2d) from 4-chloroanisole**



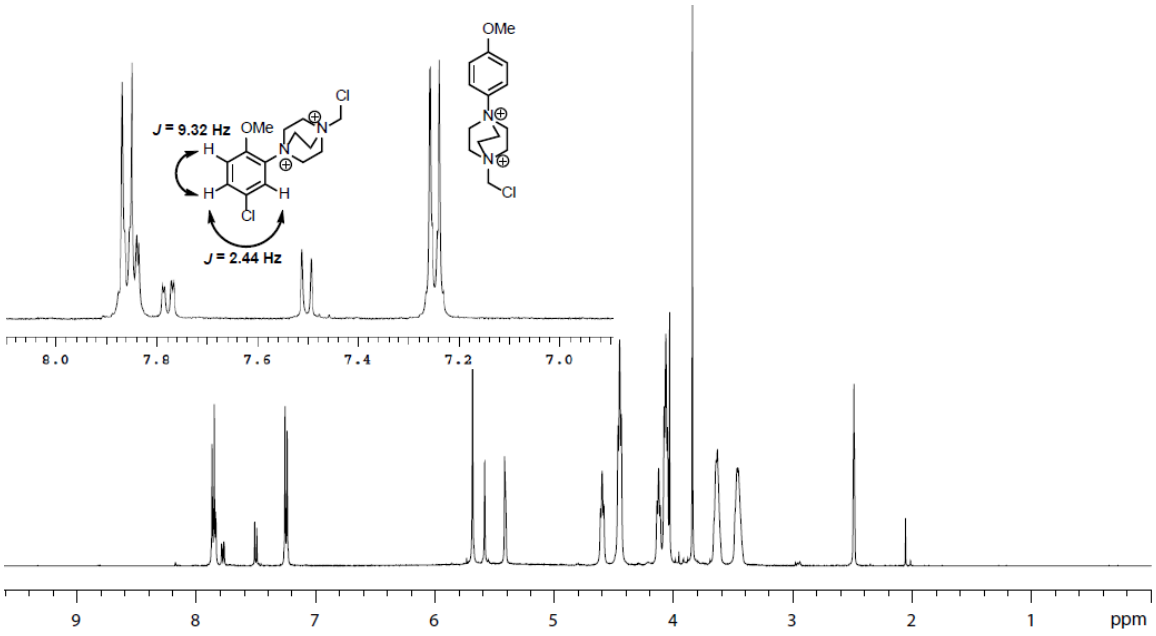

A stock solution was prepared, containing **1** (11.4 mg, 15.0 μmol) and $Ru(bipy)_3(PF_6)_2$ (25.8 mg, 30.0 μmol) were dissolved in $d_3$-acetonitrile (1.50 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (35.4 mg, 0.100 mmol, 2.0 equiv) and 4-chloroanisole (6.1 μL, 0.050 mmol, 1.0 equiv). The stock solution (250 μL, c = 0.20 M) containing **1** (2.5 μmol, 5.0 mol%) and $Ru(bipy)_3(PF_6)_2$ (5.00 μmol, 10.0 mol%) was added via syringe. After stirring at 23 °C for 48 h, the reaction mixture was diluted with $d_3$-acetonitrile (0.50 mL).

The yield of **2d** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2d** at 7.21–7.17 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 26% yield of **2d**.

The above reaction was repeated with 5 equivalents of 4-chloroanisole in order to isolate the Ar–TEDA products from other products.

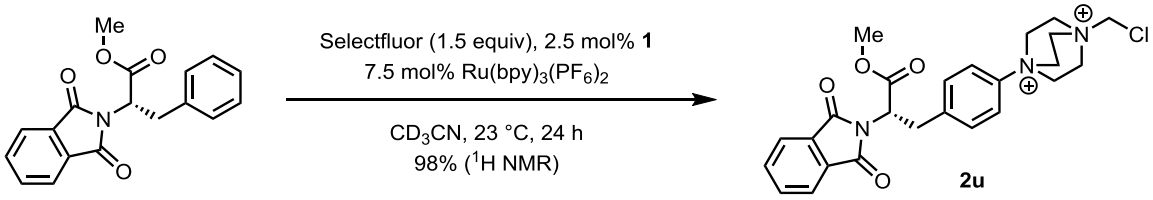



To a 20 mL vial were weighed **1** (31.8 mg, 50.0 μmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 0.100 mmol, 10.0 mol%), and Selectfluor (354. mg, 1.00 mmol, 1.00 equiv). Acetonitrile was added (5.0 mL, c = 0.20 M), followed by 4-chloroanisole (612. μL, 5.00 mmol, 5.00 equiv). The mixture was stirred for 24 hours at room temperature, after which the mixture was diluted with 10 mL acetonitrile, then filtered through celite. The filtrate was concentrated, and the residue was triturated with 20 mL of 9:1 dichloromethane:methanol. The solid was collected by filtration, then washed with 10 mL 9:1 dichloromethane:methanol, then dichloromethane (3 × 10 mL). The solid was dried in vacuo to yield 316. mg of a tan solid. $^1$H NMR analysis revealed **2c** as the dominant Ar–TEDA product, along with ca. 29% of **S2**:



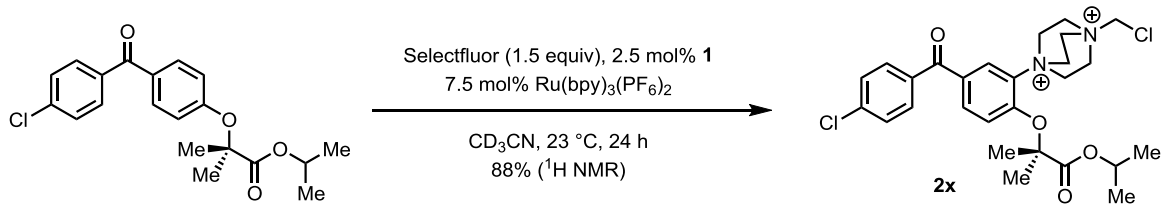

**Supplementary Figure S5.** $^1$H NMR spectrum of TEDAylation reaction mixture of 4-chloroanisole ($CD_3CN$, 23 °C)

**(*S*)-1-(Chloromethyl)-4-(4-(2-(1,3-dioxoisoindolin-2-yl)-3-methoxy-3-oxopropyl)phenyl)-1,4-diazabicyclo[2.2.2]octane-1,4-diium (2u)**



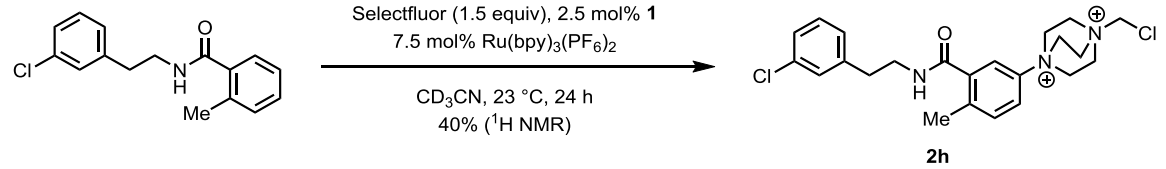

Palladium complex **1** (3.5 mg, 5.5 µmol) and $Ru(bipy)_3(PF_6)_2$ (14.2 mg, 16.5 µmol) were dissolved in $d_3$-acetonitrile (1.10 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (53.1 mg, 0.150 mmol, 1.50 equiv) and methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanoate (30.9 mg, 0.100 mmol, 1.00 equiv). The stock solution (1.0 mL, c = 0.20 M) containing **1** (2.5 µmol, 2.5 mol%) and $Ru(bipy)_3(PF_6)_2$ (7.50 µmol, 7.50 mol%) was added via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (2.0 mL). The yield of **2u** was determined via $^1$H NMR spectroscopy using *N,N*-dimethylformamide (5.0 µL, 64. µmol) as an internal standard. Comparison of the integral of the peak of **2u** at 4.28–4.30 ppm (alkyl C–H, 6H) with that of the peak of *N,N*-dimethylformamide at 2.89 ppm ($CH_3$, 3H) revealed an 98% yield of **2u**.

**1-(5-(4-Chlorobenzoyl)-2-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-4-(chloromethyl)-1,4-diazabicyclo[2.2.2]octane-1,4-diium (2x)**




Palladium complex **1** (3.5 mg, 5.5 μmol) and $Ru(bipy)_3(PF_6)_2$ (14.2 mg, 16.5 μmol) were dissolved in $d_3$-acetonitrile (1.10 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (53.1 mg, 0.150 mmol, 1.50 equiv) and fenofibrate (36.1 mg, 0.100 mmol, 1.00 equiv). The stock solution (1.0 mL, c = 0.20 M) containing **1** (2.5 μmol, 2.5 mol%) and $Ru(bipy)_3(PF_6)_2$ (7.50 μmol, 7.50 mol%) was added via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (2.0 mL). The yield of **2x** was determined via $^1$H NMR spectroscopy using *N,N*-dimethylformamide (5.0 μL, 64. μmol) as an internal standard. Comparison of the integral of the peak of **2x** at 4.61–4.64 ppm (alkyl C–H, 6H) with that of the peak of *N,N*-dimethylformamide at 2.89 ppm ($CH_3$, 3H) revealed an 88% yield of **2x**.

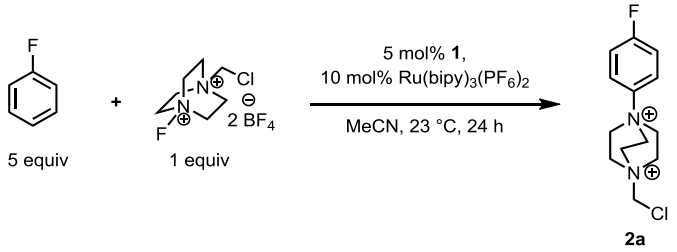
**1-(Chloromethyl)-4-(3-((3-chlorophenethyl)carbamoyl)-4-methylphenyl)-1,4-diazabicyclo[2.2.2]octane-1,4-diium (2h)**




Palladium complex **1** (7.2 mg, 11. μmol) and $Ru(bipy)_3(PF_6)_2$ (29.0 mg, 33.8 μmol) were dissolved in $d_3$-acetonitrile (2.25 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (26.6 mg, 75.0 μmol, 1.50 equiv) and *N*-(3-chlorophenethyl)-2-methylbenzamide (13.7 mg, 50.0 μmol, 1.00 equiv). The stock solution (0.25 mL, c = 0.20 M) containing **1** (1.2 μmol, 2.5 mol%) and $Ru(bipy)_3(PF_6)_2$ (3.75 μmol, 7.50 mol%) was added via syringe. After stirring at 23 °C for 24 h, the reaction mixture was diluted with $d_3$-acetonitrile (2.0 mL). The yield of **2h** was determined via $^1$H NMR spectroscopy using *N,N*-dimethylformamide (2.0 μL, 26. μmol) as an internal standard. Comparison of the integral of the peak of **2h** at 7.66 ppm (aromatic C–H, 1H) with that of the peak of *N,N*-dimethylformamide at 2.89 ppm (CH, 1H) revealed an 40% yield of **2h**.

## Procedure for aromatic C–H TEDAylation reactions (excess arene)

### 1-(Chloromethyl)-4-(4-fluorophenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2a)

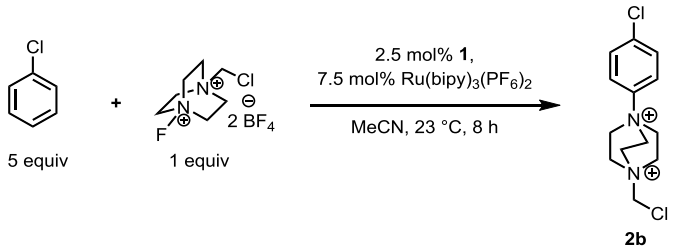



To a 20 mL vial were added palladium complex **1** (31.8 mg, 50.0 μmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 100. μmol, 10.0 mol%), Selectfluor (354. mg, 1.00 mmol, 1.00 equiv), and fluorobenzene (0.530 mL, 5.00 mmol, 5.00 equiv), and acetonitrile (2.5 mL, c = 0.20 M). The reaction mixture was stirred at 40 °C for 48 h. The reaction mixture was diluted with acetonitrile, filtered through celite, and the filtrate was concentrated *in vacuo*. The residue was triturated with 20 mL methanol:dichloromethane. The solid was collected by filtration on a glass frit, washed with 10 mL 1:9 methanol:dichloromethane, followed by 3 × 10 mL dichloromethane, then dried *in vacuo* to afford 341. mg of a tan powder. For yield determination, an NMR sample in $d_3$-acetonitrile was prepared containing 10.0 mg of the product mixture and 5.0 μL of ethyl acetate (51. μmol) as internal standard. Comparison of the integral of the peak of **2a** at 4.45–4.37 ppm (3 × $CH_2$, 6H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.60 mmol of Ar–TEDA (60% yield). Also present was 0.18 mmol H–TEDA$^{2+}$ (18%), measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.91–7.84 (m, 2H), 7.49–7.42 (m, 2H), 5.36 (s, 2H), 4.45–4.37 (m, 6H), 4.18–4.11 (m, 6H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 163.4 (d, $J$ = 252.4 Hz), 140.7 (s), 123.8 (d, $J$ = 9.6 Hz), 118.9 (d, $J$ = 24.0 Hz), 70.1 (s), 55.6 (s), 51.6 (s). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –110.0.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{13}H_{17}ClFN_2$ $[M–H]^+$, 255.1059; found, 255.1061.

### 1-(Chloromethyl)-4-(4-chlorophenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2b)



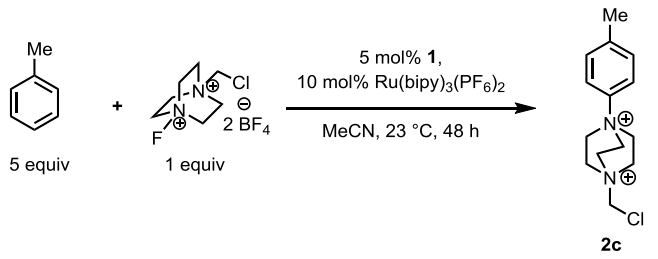

A 50 mL round-bottom flask was charged with palladium complex **1** (31.8 mg, 50.0 μmol. 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 0.100 mmol, 10.0 mol%), and Selectfluor (354. mg, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added, followed by chlorobenzene (509 μL, 5.00 mmol, 5.00 equiv) via syringe. After stirring at 23 °C for 19 h, the reaction mixture was filtered through celite and

concentrated *in vacuo*. The residue was triturated with a solvent mixture of dichloromethane/methanol (9/1 (v/v), 10 mL) and dichloromethane (5 × 10 mL) at 23 °C to afford 463 mg of the title compound as a light yellow solid. For yield determination, an NMR sample in *d*3-acetonitrile was prepared containing 20.0 mg of the product mixture and 3.0 µL of ethyl acetate (31. µmol) as internal standard. Comparison of the integral of the peak of **2b** at 7.79–7.77 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.80 mmol of Ar–TEDA (80% yield). Also present was 0.14 mmol H–$TEDA^{2+}$ (14%), measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.79–7.82 (m, 2H), 7.70–7.73 (m, 2H), 5.36 (s, 2H), 4.40–4.43 (m, 6H), 4.13–4.15 (m, 6H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 142.9, 137.9, 131.6, 122.9, 69.7, 55.1, 51.2.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{13}H_{18}Cl_2N_2^{2+}$ $[M]^{2+}$, 136.0418; found, 136.0419.

**1-(Chloromethyl)-4-(4-methyl-phenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2c)**

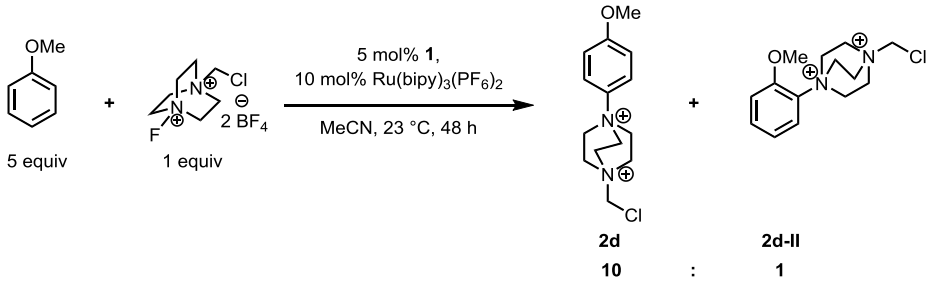



To a 20 mL vial were added palladium complex **1** (31.8 mg, 50.0 µmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 100. µmol, 10.0 mol%), Selectfluor (354. mg, 1.00 mmol, 1.0 equiv), and toluene (0.530 mL, 5.00 mmol, 5.00 equiv), and acetonitrile (2.5 mL, c = 0.20 M). The reaction mixture was stirred at 23 °C for 48 h. The reaction mixture was concentrated *in vacuo*, then triturated with $CH_2Cl_2$ to afford 324 mg of a tan powder. For yield determindation, an NMR sample in $d_3$-acetonitrile was prepared containing 10.0 mg of the product mixture and 5.0 µL of ethyl acetate (51. µmol) as internal standard. Comparison of the integral of the peak of **2c** at 4.37–4.32 ppm (3 × $CH_2$, 6H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.59 mmol of Ar–TEDA (59% yield). Also present was 0.18 mmol H–$TEDA^{2+}$ (18%), measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.67–7.63 (m, 2H), 7.54–7.00 (m, 2H), 5.33 (s, 2H), 4.37–4.32 (m, 6H), 4.11–4.07 (m, 6H), 2.44 (s, 3H). $^{13}$C NMR (125 MHz, DMSO, 23 °C, δ): 142.1, 141.4, 131.0, 120.3, 68.2, 53.94, 50.4, 20.3.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_{20}ClN_2^+$ $[M–H]^+$, 251.1310; found, 251.1312.

**1-(Chloromethyl)-4-(4-methyl-phenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2d)**

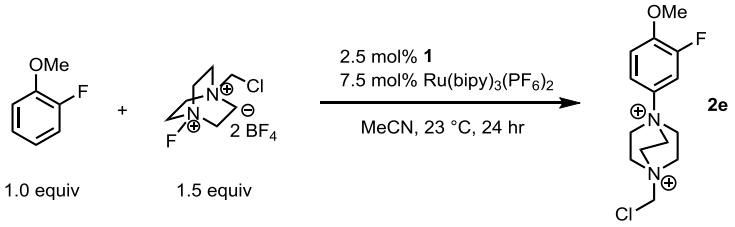



To a 20 mL vial were added palladium complex **1** (31.8 mg, 50.0 µmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 100. µmol, 10.0 mol%), Selectfluor (354. mg, 1.00 mmol, 1.0 equiv), and anisole (0.544 mL, 5.00 mmol, 5.0 equiv), and acetonitrile (2.5 mL, c = 0.20 M). The reaction mixture was stirred at 23 °C for 48 h. The reaction mixture was concentrated *in vacuo*, then triturated with $CH_2Cl_2$ to afford 324. mg of a tan powder. For yield determination, an NMR sample in $d_3$-acetonitrile was prepared containing 10.0 mg of the product mixture and 5.0 µL of ethyl acetate (51. µmol) as internal standard. Comparison of the integral of the peak of **2d** at 4.36–4.31 ppm (3 × $CH_2$, 6H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.43 mmol of **2d** (43% yield). An additional compound was observed in 4.3% yield, assignable to **2d-II**; (upon reduction, *N*-(2-methoxyphenyl)piperazine (**3e-II**) is observed in small amounts, see page S43). Also present was 0.31 mmol H–TEDA$^{2+}$ (31%), measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.72–7.67 (m, 2H), 7.21–7.17 (m, 2H), 5.33 (s, 2H), 4.36–4.31 (m, 6H), 4.20–4.15 (m, 6H), 3.88 (s, 3H). $^{13}$C NMR (125 MHz, DMSO, 23 °C, δ): 160.5, 137.0, 122.1, 115.5, 68.2, 54.1, 50.4, 43.4.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_{20}ClN_2O^+$ $[M–H]^+$, 267.1259; found, 267.1263.

**1-(Chloromethyl)-4-(3-fluoro-4-methoxyphenyl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2e)**




A 50 mL round-bottom flask was charged with palladium complex **1** (31.8 mg, 50.0 µmol. 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 0.100 mmol, 10.0 mol%), and Selectfluor (531. mg, 1.50 mmol, 1.50 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added, followed by 2-fluoroanisole (112 µL, 1.00 mmol, 1.00 equiv) via syringe. After stirring at 23 °C for 24 h, the reaction mixture was filtered through celite and concentrated *in vacuo*. The residue was triturated with a solvent mixture of dichloromethane/methanol (9/1 (v/v), 10 mL) and dichloromethane (5 × 10 mL) at 23 °C to afford 573 mg of a orange solid. The solid was triturated with a solvent mixture of dichloromethane/methanol (9/1 (v/v), 10 mL) and dichloromethane (5 × 10 mL) at 23 °C to afford 562 mg of the title compound as a light orange solid. For

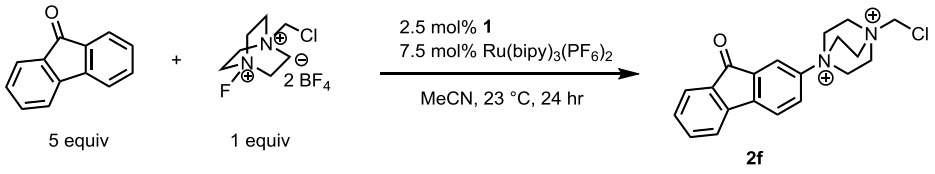
yield determination, an NMR sample in *d*3-acetonitrile was prepared containing 20.0 mg of the product mixture and 3.0 μL of ethyl acetate ($3.1 \times 10^{-5}$ mol) as internal standard. Comparison of the integral of the peak of **2e** at 7.34 ppm (aromatic C–H, 1H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.76 mmol of Ar–TEDA (76% yield). Also present was 0.42 mmol H–$TEDA^{2+}$ (42%) measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

See page S89 for structural assignment data.

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.67 (dd, *J* = 12.2, 3.3 Hz, 1H), 7.59 (ddd, *J* = 9.3, 3.3, 1.6 Hz, 1H), 7.34 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.36 (s, 2H), 4.36–4.38 (m, 6H), 4.11–4.13 (m, 6H), 3.96 (s, 3H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 152.0 (d, *J* = 249.4 Hz), 150.3 (d, *J* = 9.7 Hz), 135.9 (d, *J* = 7.8 Hz), 117.5 (d, *J* = 3.8 Hz), 114.9 (d, *J* = 2.8 Hz), 110.0 (d, *J* = 25.0 Hz), 69.5, 55.1, 51.0, 50.4. $^{19}$F NMR (475 MHz, $CD_3CN$, 23 °C, δ): –130.2.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_{20}ClFN_2O^{2+}$ $[M]^{2+}$, 143.0619; found, 143.0626.

**1-(Chloromethyl)-4-(fluorenon-2-yl)-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (2f)**




A 50 mL round-bottom flask was charged with palladium complex **1** (31.8 mg, 50.0 μmol. 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 0.100 mmol, 10.0 mol%), Selectfluor (354. mg, 1.00 mmol, 1.00 equiv), and 9*H*-fluoren-9-one (901 mg, 5.00 mmol, 5.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. After stirring at 23 °C for 16 h, the reaction mixture was filtered through celite and concentrated *in vacuo*. The residue was triturated with a solvent mixture of dichloromethane/methanol (9/1 (v/v), 10 mL) and dichloromethane (5 × 10 mL) at 23 °C to afford 559. mg of a yellow solid. The solid was triturated with a solvent mixture of dichloromethane/methanol (9/1 (v/v), 10 mL) and dichloromethane (5 × 10 mL) at 23 °C to afford 468. mg of a bright yellow solid. The solid was triturated with a solvent mixture of dichloromethane/methanol (9/1 (v/v), 10 mL) and dichloromethane (5 × 10 mL) at 23 °C to afford 453. mg of the title compound as a bright yellow solid. For yield determination, an NMR sample in $d_3$-acetonitrile was prepared containing 20.0 mg of the product mixture and 3.0 μL of ethyl acetate ($3.1 \times 10^{-5}$ mol) as internal standard. Comparison of the integral of the peak of **2f** at 5.36 ppm ($CH_2Cl$, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.77 mmol of Ar–TEDA (77% yield). Also present was 0.069 mmol H–$TEDA^{2+}$ (7%), measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

The product mixture of **2f** obtained above (50 mg) was further purified through repeated recrystallization by vapor diffusion of diethyl ether into an acetonitrile solution. Pure product **2f** (15 mg) was obtained as yellow crystals and characterized.

See page S94 for structural assignment data.

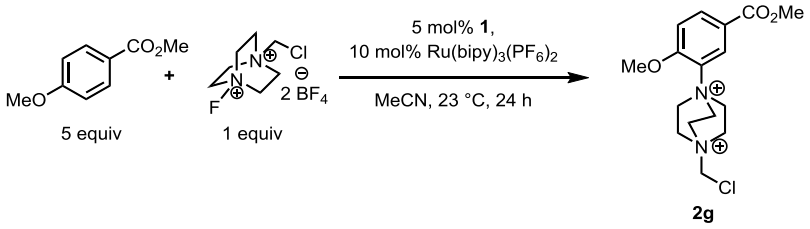
Note: Compound **2f** exhibits concentration-dependent chemical shifts. The chemical shifts listed below

were recorded from a sample of 12 mg **2f** in 7.5 mL $CD_3CN$.

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 8.00–7.97 (m, 2H), 7.95–7.92 (m, 1H), 7.80–7.77 (m, 1H), 7.71–7.65 (m, 2H), 7.51–7.47 (m, 1H), 5.38 (s, 2H), 4.45–4.47 (m, 6H), 4.15–4.18 (m, 6H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 191.7, 147.7, 145.0, 143.0, 136.8, 136.7, 135.0, 131.7, 127.7, 125.4, 123.8, 123.1, 116.9, 70.0, 55.4, 51.5.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{20}H_{21}ClN_2O^{2+}$ $[M]^{2+}$, 170.0666; found, 170.0672.

**1-(Chloromethyl)-4-(5-methoxy-2-(methoxycarbonyl)phenyl)$^{2+}$ (2g)**

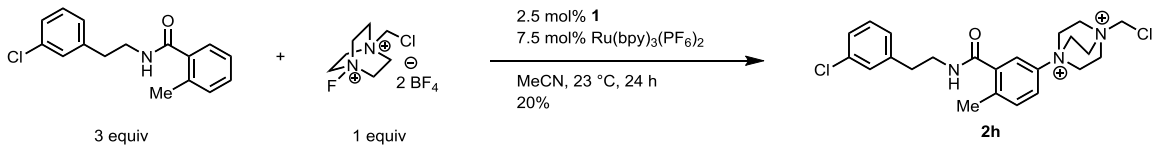



To a 20 mL vial were added palladium complex **1** (19.0 mg, 25.0 μmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (43.0 mg, 5.00 μmol, 10.0 mol%), Selectfluor (177. mg, 0.500 mmol, 1.00 equiv), and methyl 4-methoxybenzoate (416 mg, 2.50 mmol, 5.00 equiv), and acetonitrile (2.5 mL, c = 0.20 M). The reaction mixture was stirred at 23 °C for 48 h. The reaction mixture was concentrated *in vacuo*, then triturated with $CH_2Cl_2$ to afford 191. mg of a tan powder. $^1$H NMR shows ca. 35% contamination by H–TEDA$^{2+}$.

NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 8.27 (dd, *J* = 8.9, 1.8 Hz, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 5.33 (s, 2H), 4.62–4.54 (m, 6H), 4.15–4.09 (m, 6H), 4.14 (s, 3H), 3.92 (s, 3H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 165., 156.51, 135.4, 130.8, 124.7, 124.3, 116.6, 70.4, 58.4, 53.7, 51.6, 45.1.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{16}H_{22}ClN_2O_3^+$ $[M–H]^+$, 325.1313; found, 325.1315.

**1-(Chloromethyl)-4-(3-((3-chlorophenethyl)carbamoyl)-4-methylphenyl)-1,4-diazabicyclo[2.2.2]octane-1,4-diium (2h)**



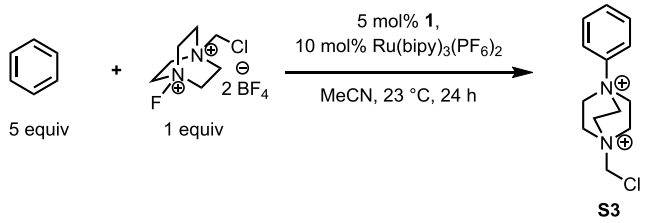

A 4 mL vial was charged with palladium complex **1** (3.2 mg, 5.0 μmol. 2.5 mol%), $Ru(bpy)_3(PF_6)_2$ (12.9 mg, 15.0 μmol, 7.50 mol%), Selectfluor (70.9 mg, 0.200 mmol, 1.00 equiv), and *N*-(3-chlorophenethyl)-2-methylbenzamide (164. mg, 0.600 mmol, 3.00 equiv). Acetonitrile (1.0 mL, c = 0.20 M) was added via syringe, and the reaction mixture was stirred at 23 °C for 24 h. The reaction mixture was concentrated *in vacuo* to afford a red heterogeneous solid mixture. The solid was triturated with dichloromethane to afford 62 mg of the title compound as a light yellow solid (20% yield). Also present was ca. 49% contamination by H–TEDA$^{2+}$, measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.71 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.67 (d, *J* =

2.9 Hz, 1H), 7.53 (d, $J$ = 8.8 Hz, 1H), 7.30–7.33 (m, 2H), 7.23–7.25 (m, 2H), 6.99 (bs, 1H), 5.36 (s, 2H), 4.38–4.40 (m, 6H), 4.12–4.15 (m, 6H), 3.61–3.64 (m, 2H), 2.91 (t, $J$ = 6.9 Hz, 2H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 168.2, 142.9, 142.0, 141.3, 140.1, 134.6, 134.1, 131.0, 129.9, 128.6, 127.3, 121.9, 120.0, 70.1, 55.4, 51.6, 41.4, 35.8, 19.3.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{23}H_{29}Cl_2N_3O^{2+}$ [M]2+, 216.5838; found, 216.5846.

**1-(Chloromethyl)-4-phenyl-1,4-diazabicyclo[2.2.2]octane$^{2+}$ (S3)**



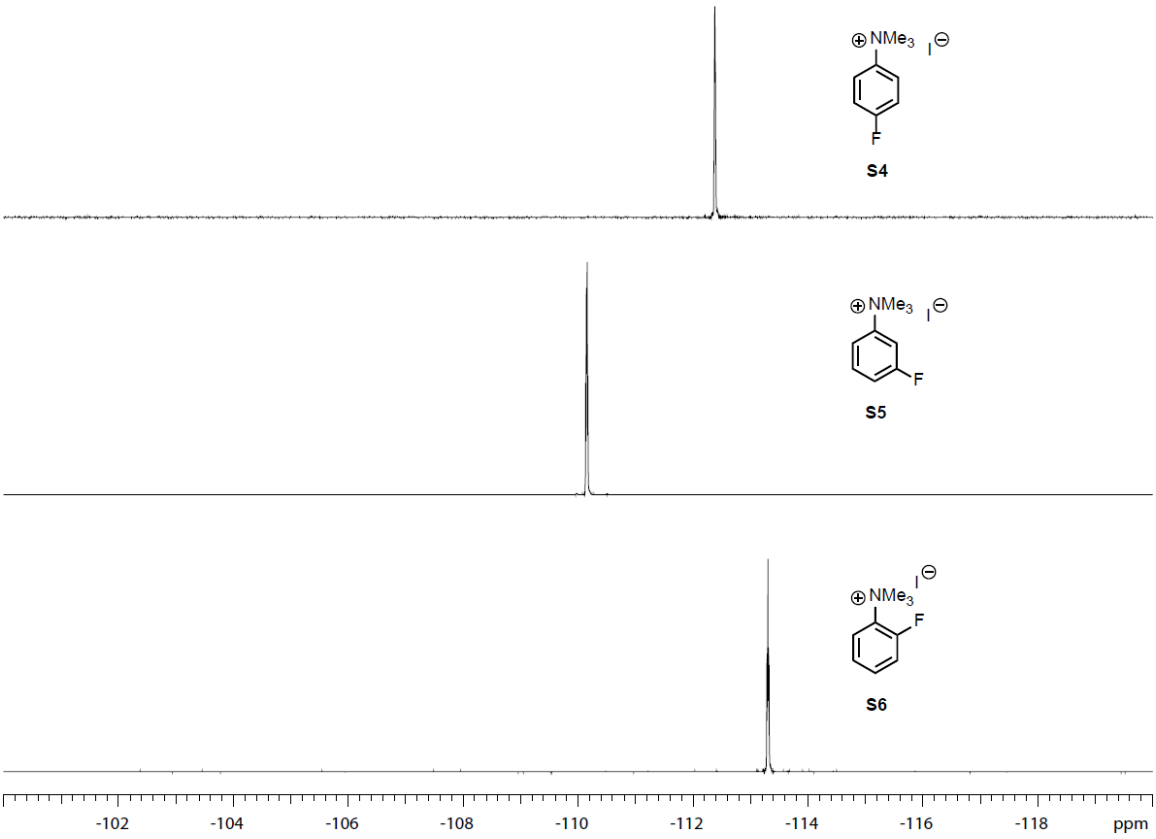

To a 20 mL vial were added palladium complex **1** (31.8 mg, 50.0 μmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 100. μmol, 10.0 mol%), Selectfluor (354. mg, 1.00 mmol, 1.00 equiv), and benzene (0.446 mL, 5.00 mmol, 5.0 equiv), and acetonitrile (2.5 mL, c = 0.20 M). The reaction mixture was stirred at 23 °C for 48 h. The reaction mixture was concentrated *in vacuo*, then triturated with $CH_2Cl_2$ to afford 360 mg of a tan powder. For yield determination, an NMR sample in $d_3$-acetonitrile was prepared containing 10.0 mg of the product mixture and 5.0 μL of ethyl acetate (51. μmol) as internal standard. Comparison of the integral of the peak of **S1** at 4.41–4.36 ppm (3 × $CH_2$, 6H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed the bulk mixture to contain 0.67 mmol of Ar–TEDA (67% yield). Also present was 0.15 mmol H–TEDA$^{2+}$ (15%), measured by integration of the peak at 3.85–3.81 ppm (3 × $CH_2$, 6H).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.82–7.77 (m, 2H); 7.75–7.69 (m, 3H), 5.35 (s, 2H), 4.41–4.36 (m, 6H), 4.41–4.09 (m, 6H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 144.4, 131.3, 130.8, 120.7, 68.2, 53.9, 50.4

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{13}H_{18}ClN_2^+$ $[M–H]^+$, 237.1153; found, 237.1154.

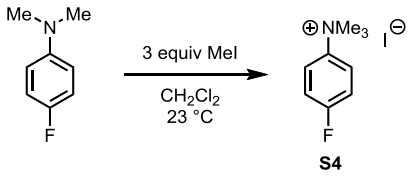
## Fluoro-*N*,*N*,*N*-trimethylanilinium cations

We have synthesized *ortho*-, *meta*-, and *para*-fluoro-*N*,*N*,*N*-trimethylanilinium iodide to ascertain the likelihood of the $^{19}$F NMR signal overlap of the different constitutional isomers of fluoroaryl trialkylammonium salts. We found the $^{19}$F chemical shifts in $CD_3CN$ of the *para*, *meta*, and *ortho* isomers to be –112.4 ppm, –110.2 ppm, and –113.3 ppm, respectively:




**Supplementary Figure S6.** $^{19}$F NMR chemical shifts of **S4**, **S5**, and **S6** ($CD_3CN$, 23 °C)

**4-Fluoro-*N*,*N*,*N*-trimethylanilinium iodide (S4)**

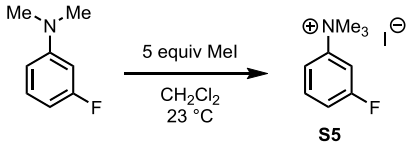



In a 20 mL vial, *N,N*-dimethylaniline (696. mg, 5.00 mmol, 1.00 equiv) was dissolved in $CH_2Cl_2$ (5.0 mL), and iodomethane (0.93 mL, 15. mmol, 3.0 equiv) was added dropwise via syringe. The mixture was stirred at room temperature for 4 hours, over which time a white precipitate formed. The precipitate was collected by filtration, then washed with dichloromethane (3 × 5 mL) to afford 767. mg of 4-fluoro-*N*,*N*,*N*-trimethylanilinium iodide as a white powder (2.73 mmol, 55%).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.89–7.84 (m, 2H), 7.39–7.34 (m, 2H), 3.58 (s, 9H). $^{13}$C NMR (125 MHz, DMSO, 23 °C, δ): 161.8 (d, $J$ = 248.6 Hz), 143.3 (d, $J$ = 3.1 Hz), 123.3 (d, $J$ = 9.3 Hz), 116.6 (d, $J$ = 23.5 Hz), 56.7 (s). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –112.4.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_9H_{13}NF$ $[M]^+$, 154.1027; found, 154.1023.

**3-Fluoro-*N*,*N*,*N*-trimethylanilinium iodide (S5)**



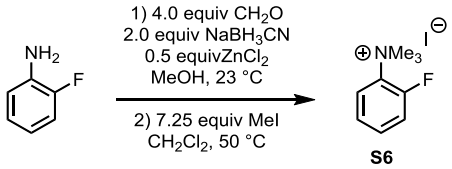

**S5**

In a 20 mL vial, *N,N*-dimethylaniline (500 mg, 3.59 mmol, 1.0 equiv) was dissolved in $CH_2Cl_2$ (5.0 mL), and iodomethane (1.12 mL, 18.0 mmol, 5.0 equiv) was added dropwise via syringe. The mixture was stirred at room temperature for 48 hours, over which time a white precipitate formed. The precipitate was collected by filtration, then washed with dichloromethane (3 × 5 mL) to afford 754 mg of 4-fluoro-*N*,*N*,*N*-trimethylanilinium iodide as a white powder (2.68 mmol, 75%).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.80–7.73 (m, 2H), 7.68–7.63 (ddd, $J$ = 6.47 Hz, 8.50 Hz, 14.7 Hz, 1H), 7.39–7.34 (ddd, $J$ = 0.83 Hz, 2.33 Hz, 7.86 Hz, 1H), 3.67 (s, 9H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 161.8 (d, $J$ = 246.4 Hz), 148.3 (d, $J$ = 9.1 Hz), 131.8 (d, $J$ = 9.0 Hz), 117.1 (d, $J$ = 21.0 Hz), 116.9 (d, $J$ = 3.8 Hz), 109.2 (d, $J$ = 27.4 Hz), 56.5 (s). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –110.2.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_9H_{13}NF$ $[M]^+$, 154.1027; found, 154.1020.

**2-Fluoro-*N*,*N*,*N*-trimethylanilinium iodide (S6)**




**S6**

In a round bottom flask were added 3-fluoroaniline (1.50 mL, 15.6 mmol, 1.00 equiv), methanol (50 mL), and 37% aqueous formaldehyde (5.0 mL, 62 mmol, 4.0 equiv). To this mixture was added a solution of sodium cyanoborohydride (2.010 g, 32.01 mmol, 2.00 equiv) and zinc chloride (1.090 g, 8.00 mmol, 0.500 equiv) in 50 mL methanol. The mixture was stirred for 12 hours at room temperature, after which time 50 mL 0.16 M NaOH was added, and the methanol was removed by rotary evaporation. The aqueous mixture was then extracted with dichloromethane (4 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to give a brown oil. The residue was redissolved in 15 mL dichloromethane and added to a pressure vessel, along with 7.00 mL of iodomethane (112. mmol, 7.25 equiv). The vessel was sealed and heated to 50 °C for 12 hours, over which time a white precipitate formed. The precipitate was collected by filtration, washed with dichloromethane (5 × 20 mL), and dried in vacuo to afford 2.27 g of 2-fluoro-*N*,*N*,*N*-trimethylanilinium iodide as a white powder (8.08 mmol, 52%).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.85–7.79 (dd, $J$ = 8.6, 1.4 Hz, 1H), 7.69–7.64 (dddd, $J$ = 8.3, 7.5, 4.7, 1.5 Hz, 1H), 7.50–7.55 (ddd, $J$ = 14.3, 8.3, 1.5 Hz, 1H), 7.45–7.41 (ddd, $J$ = 7.5, 1.4, 0.80 Hz, 1H), 3.68 (s, 9H). $^{13}$C NMR (125 MHz, DMSO, 23 °C, δ): 154.1 (d, $J$ = 251.2 Hz), 132.9 (d, $J$ = 6.4), 132.9 (d, $J$ = 9.6 Hz), 125.8 (d, 3.6 Hz), 122.9 (s), 118.8 (d, $J$ = 22.3), 56.1 (d, $J$ = 5.5 Hz). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –113.3.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_9H_{13}NF$ $[M]^+$, 154.1027; found, 154.1027.

## Aromatic TEDAylation trials with 1.05 equivalents of Selectfluor

For the aromatic TEDAylation reaction, we have generally used 1.5–2.0 equivalents of Selectfluor, as we have found that the excess is required to push most substrates to completion. To probe the tolerance of the reaction to a reduction in the loading of Selectfluor, we have attempted the TEDAylation of toluene and anisole with 1.05 equivalents of Selectfluor, and compared the results to the standard conditions with 1.5 equivalents of Selectfluor. We have found only minor diminution of yield for these substrates with the reduced loading of Selectfluor:

| Substrate | Selectfluor Loading | Yield |
|---|---|---|
| anisole | 1.05 equivalents | 85% |
| | 1.50 equivalents | 89% |
| toluene | 1.05 equivalents | 83% |
| | 1.50 equivalents | 92% |

**Toluene substrate, 1.05 equivalents Selectfluor**

Palladium complex **1** (13.4 mg, 21.1 μmol) and $Ru(bipy)_3(PF_6)_2$ (36.1 mg, 42.0 μmol) were dissolved in $d_3$-acetonitrile (2.1 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (37.2 mg, 0.105 mmol, 1.05 equiv), followed by 0.50 mL of the stock solution containing **1** (5.0 μmol, 5.0 mol%) and $Ru(bipy)_3(PF_6)_2$ (10. μmol, 10. mol%). Finally, 10.7 μL toluene (0.10 mmol, 1.0 equiv) was added, and the solution was stirred at 23 °C for 48 h. The reaction mixture was diluted with $d_3$-acetonitrile (0.25 mL), passed through a 0.2 μm PVDF syringe filter, and analyzed by $^1$H NMR.

The yield of **2c** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2c** at 7.67–7.65 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 85% yield of **2c**.

**Toluene substrate, 1.50 equivalents Selectfluor**

Palladium complex **1** (13.4 mg, 21.1 μmol) and $Ru(bipy)_3(PF_6)_2$ (36.1 mg, 42.0 μmol) were dissolved in $d_3$-acetonitrile (2.1 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (53.1 mg, 0.150 mmol, 1.50 equiv), followed by 0.50 mL of the stock solution containing **1** (5.0 μmol, 5.0 mol%) and $Ru(bipy)_3(PF_6)_2$ (10. μmol, 10. mol%). Finally, 10.7 μL toluene (0.10 mmol, 1.0 equiv) was added, and the solution was stirred at 23 °C for 48 h. The reaction mixture was diluted with $d_3$-acetonitrile (0.25 mL), passed through a 0.2 μm PVDF syringe filter, and analyzed by $^1$H NMR.

The yield of **2c** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2c** at 7.67–7.65 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 89% yield of **2c**.

**Anisole substrate, 1.05 equivalents Selectfluor**

Palladium complex **1** (13.4 mg, 21.1 μmol) and $Ru(bipy)_3(PF_6)_2$ (36.1 mg, 42.0 μmol) were dissolved in

$d_3$-acetonitrile (2.1 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (37.2 mg, 0.105 mmol, 1.05 equiv), followed by 0.50 mL of the stock solution containing **1** (5.0 μmol, 5.0 mol%) and $Ru(bipy)_3(PF_6)_2$ (10. μmol, 10. mol%). Finally, 10.9 μL anisole (0.10 mmol, 1.0 equiv) was added, and the solution was stirred at 23 °C for 48 h. The reaction mixture was diluted with $d_3$-acetonitrile (0.25 mL), passed through a 0.2 μm PVDF syringe filter, and analyzed by $^1$H NMR.

The yield of **2d** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2c** at 7.72–7.69 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 83% yield of **2d**.

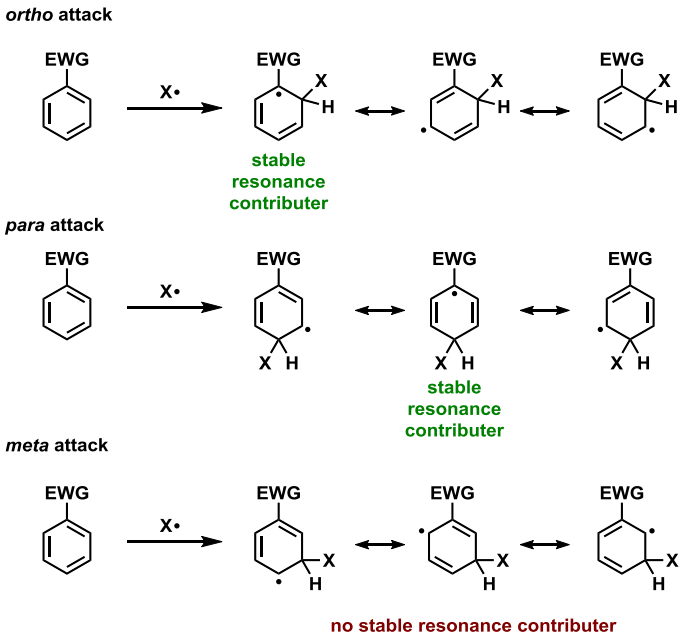
**Anisole substrate, 1.50 equivalents Selectfluor**

Palladium complex **1** (13.4 mg, 21.1 μmol) and $Ru(bipy)_3(PF_6)_2$ (36.1 mg, 42.0 μmol) were dissolved in $d_3$-acetonitrile (2.1 mL) to afford a stock solution. A 4 mL vial was charged with Selectfluor (53.1 mg, 0.150 mmol, 1.50 equiv), followed by 0.50 mL of the stock solution containing **1** (5.0 μmol, 5.0 mol%) and $Ru(bipy)_3(PF_6)_2$ (10. μmol, 10. mol%). Finally, 10.9 μL anisole (0.10 mmol, 1.0 equiv) was added, and the solution was stirred at 23 °C for 48 h. The reaction mixture was diluted with $d_3$-acetonitrile (0.25 mL), passed through a 0.2 μm PVDF syringe filter, and analyzed by $^1$H NMR.

The yield of **2d** was determined via $^1$H NMR spectroscopy using ethyl acetate (5.0 μL, 51. μmol) as an internal standard. Comparison of the integral of the peak of **2c** at 7.72–7.69 ppm (aromatic C–H, 2H) with that of the peak of ethyl acetate at 1.20 ppm ($CH_3$, 3H) revealed an 92% yield of **2d**.

## Selectivity of TEDAylation with Resonance Electron-withdrawing Substituents

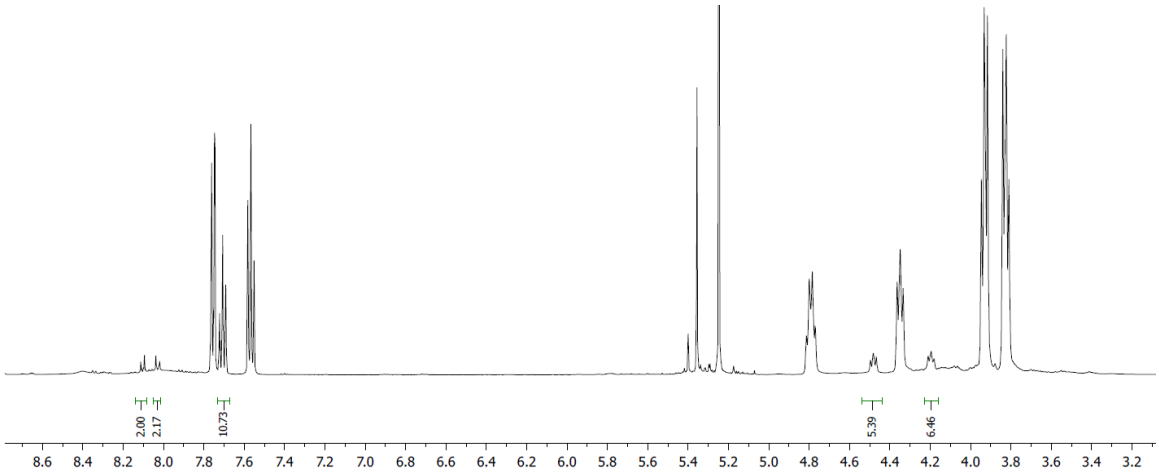
Radicals are stabilized both by electron-donating and electron-withdrawing substituents. Therefore, in radical aromatic substitution of arenes bearing electron-withdrawing groups, intermediates resulting from radical attack at the *ortho* and *para* positions are more stable than the one arising from attack at the *meta* position, because the *ortho* and *para* addition isomers provide opportunity for resonance stabilization of the radical. Therefore, by Hammond's postulate, the rate of attack in the *ortho* and *para* position is more rapid. This stands in contrast to electrophilic aromatic substitution, in which resonance electron-withdrawing substituents direct electrophilic attack to the *meta* position.




We have found that upon reaction with $TEDA^{2+\cdot}$, benzonitrile yields the *para* substituted Ar–TEDA isomer in ca. 10% conversion. No other isomer is observable. This result can be understood by considering the resonance stabilization effect described above. For arenes substituted with electron-donating groups, attack at the *ortho* and *para* positions are favored by resonance considerations, while attack at the *para* position is further favored by charge transfer in the transition state of addition. In the case of arenes bearing resonance electron-withdrawing groups, we rationalize that attack is constrained to the *ortho* and *para* positions by resonance stabilization considerations. Thus, attack occurs at the *para* position, even though the *meta* position may be capable of greater charge-transfer stabilization.

**TEDAylation of benzonitrile**

In a 4 mL vial, palladium complex **1** (3.2 mg, 5.0 μmol, 5.0 mol%), $Ru(bipy)_3(PF_6)_2$ (8.6 mg, 10. μmol, 10.0 mol%), and Selectfluor (70.9 mg, 0.200 mmol, 2.00 equiv) were dissolved in $d_3$-acetonitrile (0.50 mL). Finally, 10.2 μL benzonitrile (0.100 mmol, 1.00 equiv) was added, and the solution was stirred at 40 °C for 48 h. The reaction mixture was diluted with $d_3$-acetonitrile (0.25 mL), passed through a 0.2 μm PVDF syringe filter, and analyzed by $^1$H NMR:



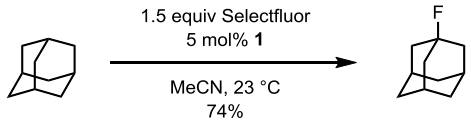

**Supplementary Figure S7.** $^{1}$H NMR of reaction mixture of TEDAylation of benzonitrile ($CD_3CN$, 23 °C)

## Evidence for TEDA$^{2+\cdot}$ radical dication as the C–N bond forming species

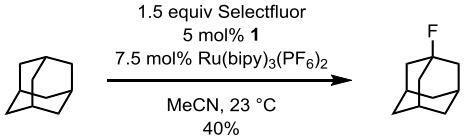
Lectka has reported that treatment of adamantane with Selectfluor in the presence of various radical initiators leads to C–H fluorination.[22,23] It was proposed that such reactions proceed through the intermediacy of TEDA$^{2+\cdot}$, which abstracts a hydrogen atom from the substrate. We have observed aliphatic C–H fluorination in the presence of Selectfluor and **1**, which is consistent with the formation of TEDA$^{2+\cdot}$ through the action of **1** on Selectfluor. We propose that the yield is diminished in the presence of $Ru(bipy)_3(PF_6)_2$ due to oxidation by $Ru^{III}$ of the alkyl radical generated upon hydrogen atom abstraction, leading to non-fluorinated products.

We have furthermore observed the formation of **2a** from fluorobenzene via copper catalysis, under conditions similar to those reported by Baran.[24] This finding indicates that neither **1** or $Ru(bipy)_3(PF_6)_2$ is uniquely effective catalyst for Ar–TEDA formation, and is consistent with the free TEDA$^{2+\cdot}$ radical as the C–N bond forming species.

**Observation of aliphatic C–H fluorination under TEDAylation conditions**

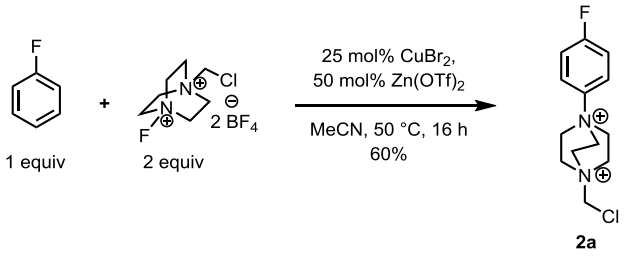



To a 4 mL vial were added adamantane (13.6 mg, 0.100 mmol, 1.00 equiv), Selectfluor (53.2 mg, 0.150 mmol, 1.50 equiv), **1** (3.2 mg, 5.0 μmol, 5.0 mol%), and $CD_3CN$ (0.70 mL). The reaction was stirred for 16 hours at room temperature, after which 2.0 μL of 3-fluoronitrobenzene was added as an internal standard, and the solution was analyzed by $^{19}$F NMR. 1-Fluoroadamantane was observed in 74% yield.



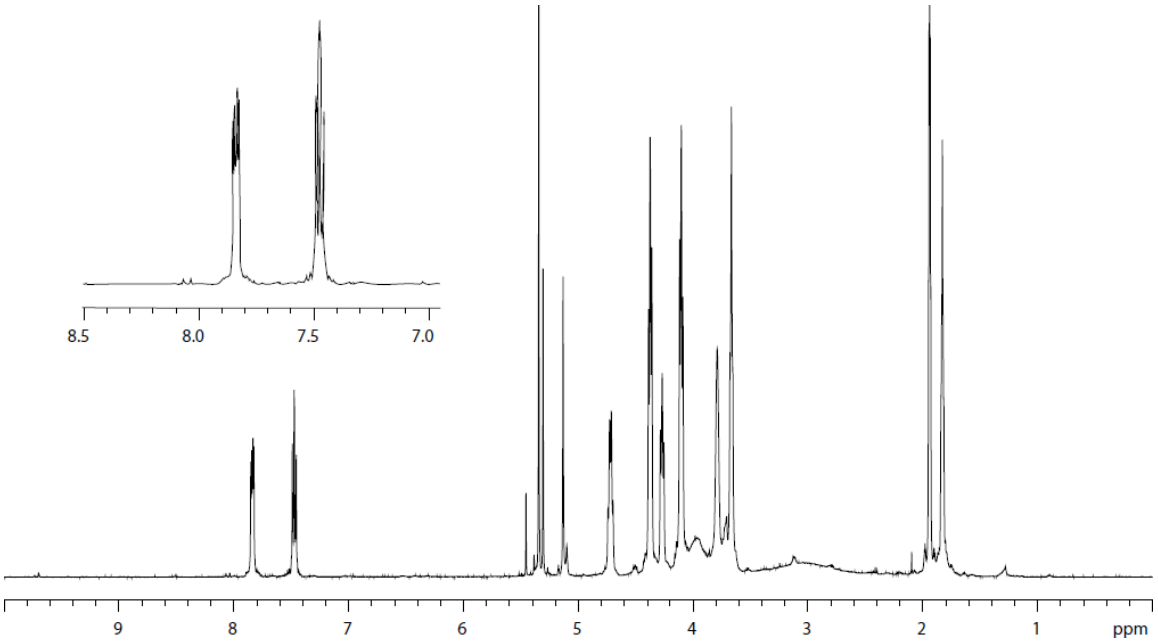
To a 4 mL vial were added adamantane (13.6 mg, 0.100 mmol, 1.00 equiv), Selectfluor (53.2 mg, 0.150 mmol, 1.50 equiv), **1** (3.2 mg, 5.0 µmol, 5.0 mol%), $Ru(bipy)_3(PF_6)_2$ (6.4 mg, 7.5 µmol, 7.5 mol%) and $CD_3CN$ (0.70 mL). The reaction was stirred for 16 hours at room temperature, after which 2.0 µL of 3-fluoronitrobenzene was added as an internal standard, and the solution was analyzed by $^{19}F$ NMR. 1-Fluoroadamantane was observed in 40% yield.

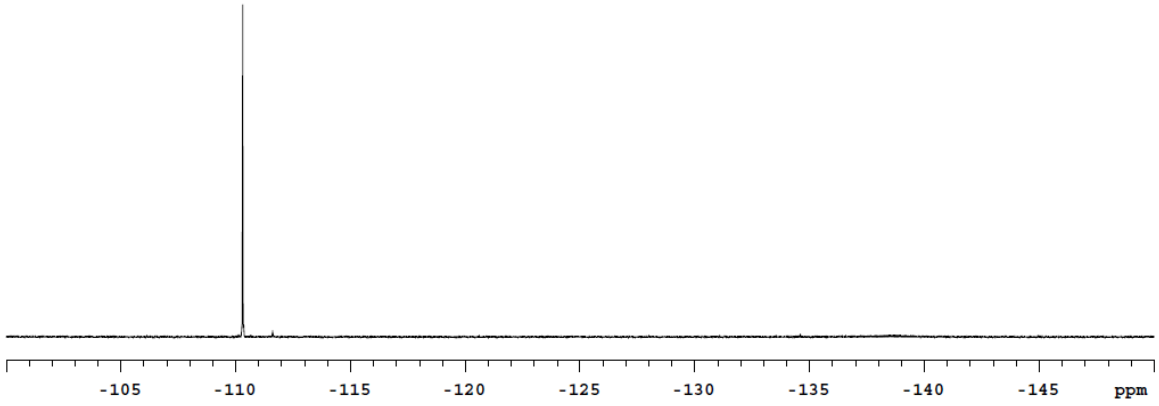
**Observation of Aryl–TEDA formation under copper catalysis**




To a 4 mL vial were added cupric bromide (7.3 mg, 33. µmol, 25 mol%), zinc triflate (23.6 mg, 64.9 µmol, 50.0 mol%), and Selectfluor-$PF_6$ (135. mg, 0.286 mmol, 2.00 equiv). Acetonitrile-$d_3$ (1.0 mL) was then added, followed by fluorobenzene (12.0 µL, 0.128 mmol, 1.00 equiv). The reaction mixture was stirred for 16 hours at 50 °C. The mixture was allowed to cool to room temperature, 2.0 µL of 3-fluoronitrobenzene was added as internal standard. The mixture was filtered through a PVDF syringe filter to remove insoluble materials, and the filtrate was analyzed by $^{1}H$ and $^{19}F$ NMR. Compound **2a** was observed in 60% yield, along with ca. 32% of 4-fluorobromobenzene.

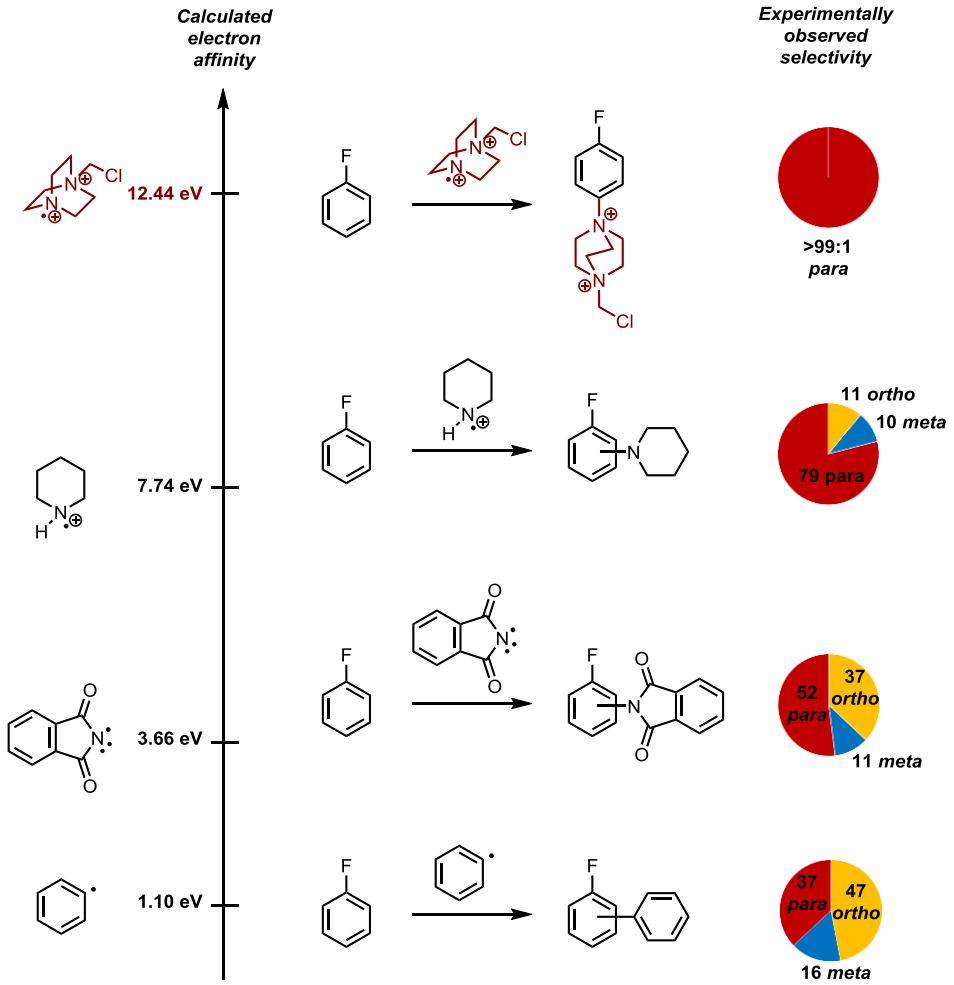
The NMR sample was concentrated by rotary evaporation, and the residue was triturated with dichloromethane (3 × 1 mL), then tetrahydrofuran (2 × 2 mL) to yield a tan powder. Analysis by $^{1}H$ and $^{19}F$ NMR shows **2a** is the only Ar–TEDA product formed in significant amounts:






**Supplementary Figure S8**. $^{1}H$ and $^{19}F$ NMR of **2a** synthesized via copper catalysis ($CD_3CN$, 23 °C)

## Positional Selectivity as a Function of Electron Affinity: A Discussion



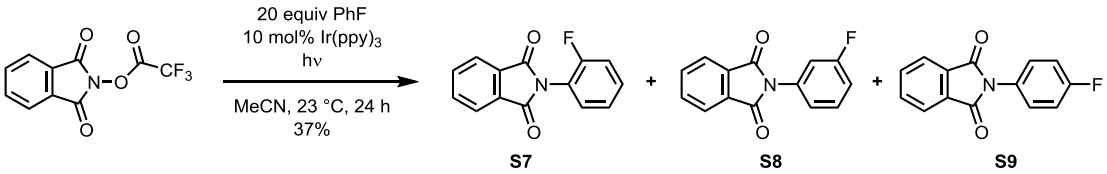

We argue in this work that the electron affinity of a radical has a strong effect on the positional selectivity exhibited by the radical in aromatic substitution, with higher electron affinity leading to higher selectivity for the *para* position of monosubstituted arenes. To illustrate this trend, we compare the selectivity of

several radicals across a range of electron affinities in their aromatic substitution with fluorobenzene. It should be noted that electron affinity is not the only factor influencing positional selectivity. Different radicals with similar electron affinities may yield differing positional selectivity due to the influence of other factors, such as differing degrees of steric hinderance. Furthermore, the same radical may exhibit somewhat differing positional selectivities with the same substrate under varying experimental conditions.[29] Thus, to illustrate the general trend, we have chosen four radicals with widely varying electron affinities, so that the influence of confounding factors is minimized:

- Phenyl radical: data taken from the work of Li *et al*[26]
- Phthalimidyl radical: aromatic substitution carried out based on conditions reported by Sanford *et al*[27]
- Piperidine aminium radical: aromatic substitution carried out based on conditions reported by Minsci *et al*[28-30]
- $TEDA^{2+\cdot}$: the subject of this work

Full experimental procedures and characterization of products for the reactions of phthalimidyl radical and piperidine aminium radical are found in the sections below.

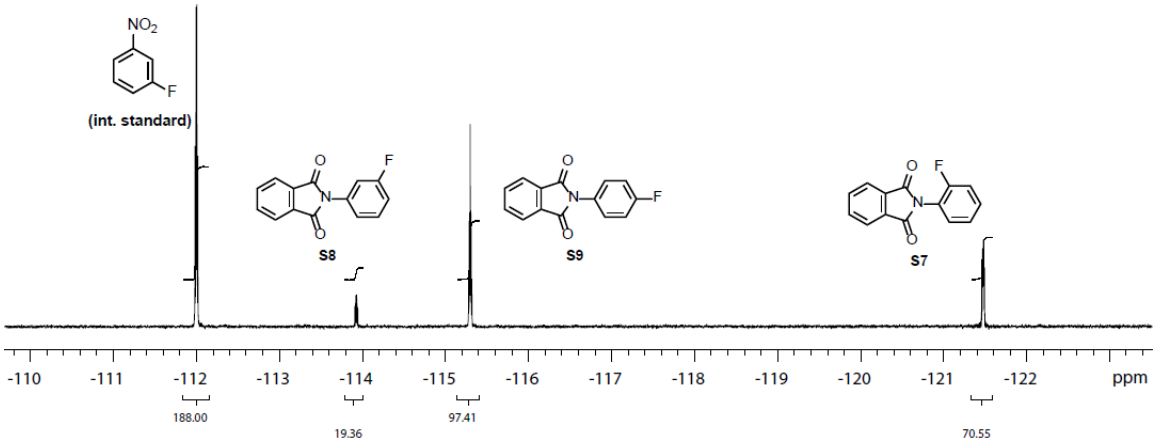
## Aromatic substitution of fluorobenzene by phthalimidyl radical




In an $N_2$-filled glovebox, into a 4 mL vial were weighed N-trifluoroacetoxy phthalimide (13.0 mg, 50.2 μmol, 1.00 equiv) and tris(2-phenylpyridyl)iridium(III) (3.3 mg, 5.0 μmol, 10. mol%). Acetonitrile (1.0 mL) was then added, followed by fluorobenzene (94. μL, 1.0 mmol, 20 equiv). The vial was sealed, removed from the glovebox, and stirred magnetically for 24 hours at room temperature under irradiation by a 60 W desk lamp. The volatile components were removed by rotary evaporation. The residue was taken up in $CD_3CN$, and 2.0 μL (18.8 μmol) of 3-fluoronitrobenzene was added as internal standard. The mixture was filtered through a PVDF syringe filter to remove all insoluble materials, and the filtrate was analyzed by $^{19}F$ NMR. The following amounts of **S7**, **S8**, and **S9** were observed:

| | |
|---|---|
| N-(2-fluorophenyl)phthalimide (**S7**) | 7.1 μmol |
| N-(3-fluorophenyl)phthalimide (**S8**) | 1.9 μmol |
| N-(4-fluorophenyl)phthalimide (**S9**) | 9.7 μmol |

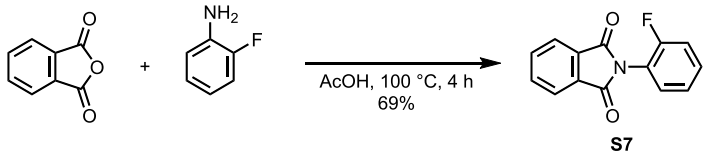
The total yield is thus 18.7 μmol (37%), and the *ortho*:*meta*:*para* ratio is 37:11:52.




**Supplementary Figure S9.** $^{19}$F NMR analysis of product mixture of phthalimidyl radical substitution ($CD_3CN$, 23 °C)

## Synthesis of authentic samples of S7, S8, and S9

### *N*-(2-Fluorophenyl)-phthalimide (S7)

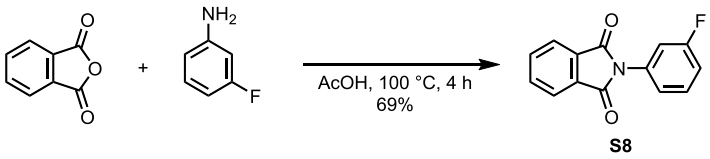



To a 20 mL vial were added phthalic anhydride (296. mg, 2.00 mmol, 1.00 equiv), acetic acid (5.0 mL), and 2-fluoroaniline (193. µL, 2.00 mmol, 1.00 equiv). The vial was sealed and magnetically stirred for 4 hr at 100 °C. The reaction mixture was allowed to come to room temperature, and 10 mL water was added to precipitate the product. The precipitate was collected by filtration, washed with water (4 × 10 mL), and dried *in vacuo* to yield 334. mg (1.38 mmol, 69%) of the title compound as a colorless powder.

NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.97–7.93 (m, 2H), 7.90–7.86 (m, 2H), 7.57–7.51 (m, 1H), 7.49–7.44 (m, 1H), 7.39–7.32 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 166.4 (s), 157.8 (d, $J$ = 252.7 Hz), 134.4 (s), 131.8 (s), 130.7 (d, $J$ = 8.0 Hz), 129.8 (d, $J$ = 0.9 Hz), 124.6 (d, $J$ = 4.0 Hz), 123.8 (s), 119.3 (d, $J$ = 13.2 Hz), 116.7 (d, $J$ = 19.5 Hz). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –113.9.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_9FNO_2$ $[M+H]^+$, 242.0612; found, 242.0613.

### *N*-(3-Fluorophenyl)-phthalimide (S8)



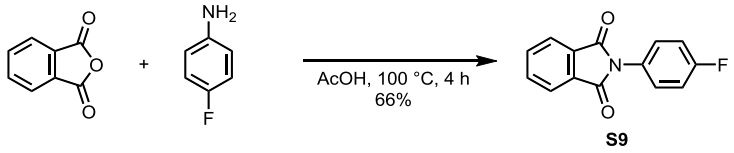

To a 20 mL vial were added phthalic anhydride (296. mg, 2.00 mmol, 1.00 equiv), acetic acid (5.0 mL),

and 3-fluoroaniline (192. µL, 2.00 mmol, 1.00 equiv). The vial was sealed and magnetically stirred for 2 hr at 100 °C. The reaction mixture was allowed to come to room temperature, and 10 mL water was added to precipitate the product. The precipitate was collected by filtration, washed with water (4 × 10 mL), and dried *in vacuo* to yield 334. mg (1.38 mmol, 69%) of the title compound as a colorless powder.

NMR Spectroscopy: $^{1}$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.96–7.92 (m, 2H), 7.89–7.85 (m, 2H), 7.55 (ddd, $J$ = 14.7, 8.3, 6.4 Hz, 1H), 7.32 (ddd, $J$ = 8.0, 1.9, 0.9 Hz, 1H), 7.28–7.24 (m, 1H), 7.21 (ddd, $J$ = 8.7, 2.6, 0.9 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 166.8 (s), 162.6 (d, $J$ = 246.7 Hz), 134.6 (s), 133.0 (d, $J$ = 10.3 Hz), 131.5 (s), 130.2 (d, $J$ = 9.0 Hz), 123.9 (s), 122.0 (d, $J$ = 3.5 Hz), 115.0 (d, $J$ = 21.1 Hz), 113.9 (d, $J$ = 24.7 Hz). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –121.5.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_9FNO_2$ $[M+H]^+$, 242.0612; found, 242.0611.

***N*-(4-Fluorophenyl)-phthalimide (S9)**



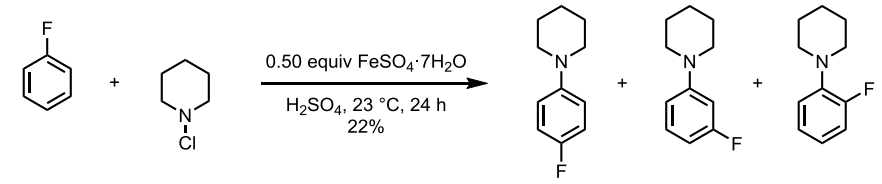

**S9**

To a 20 mL vial were added phthalic anhydride (296. mg, 2.00 mmol, 1.00 equiv), acetic acid (5.0 mL), and 4-fluoroaniline (190. µL, 2.00 mmol, 1.00 equiv). The vial was sealed and magnetically stirred for 2 hr at 100 °C. The reaction mixture was allowed to come to room temperature, and 10 mL water was added to precipitate the product. The precipitate was collected by filtration, washed with water (4 × 10 mL), and dried *in vacuo* to yield 319. mg (1.32 mmol, 66%) of the title compound as a tan powder.

NMR Spectroscopy: $^{1}$H NMR (500 MHz, $CD_3CN$, 23 °C, δ): 7.94–7.90 (m, 2H), 7.88–7.84 (m, 2H), 7.48–7.43 (m, 2H), 7.30–7.25 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 167.1 (s), 161.8 (d, $J$ = 247.6 Hz), 134.4 (s), 131.5 (s), 128.3 (d, $J$ = 8.7 Hz), 127.5 (d, $J$ = 3.2 Hz), 123.7 (s), 116.1 (d, $J$ = 22.5 Hz). $^{19}$F NMR (470 MHz, $CD_3CN$, 23 °C, δ): –115.3.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_9FNO_2$ $[M+H]^+$, 242.0612; found, 242.0615.

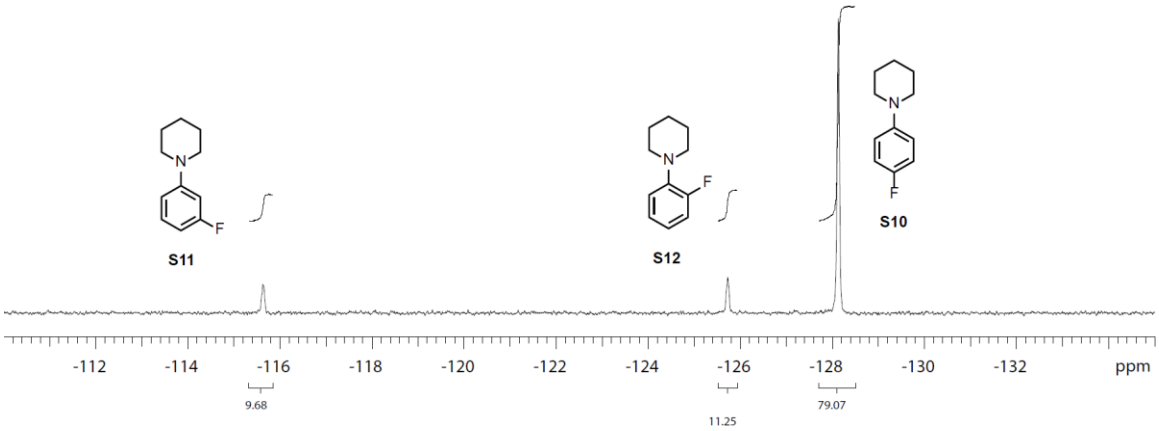
## Aromatic substitution of fluorobenzene by piperidine aminium radical




2.0 equiv 1.0 equiv **S10** **S11** **S12**

To 2.00 g of concentrated sulfuric acid in a 20 mL vial at 0 °C were added 188. µL of fluorobenzene (2.00 mmol, 2.00 equiv), 120. mg of N-chloropiperidine (1.00 mmol, 1.00 equiv), and finally 139. mg of pulverized ferrous sulfate heptahydrate (0.500 mmol, 0.500 equiv). The mixture rapidly turned brown upon addition of ferrous sulfate heptahydrate, and was stirred at 0 °C for 2 hours, after which significant beige precipitate was observed. The reaction mixture was poured onto ice and filtered through a glass frit.

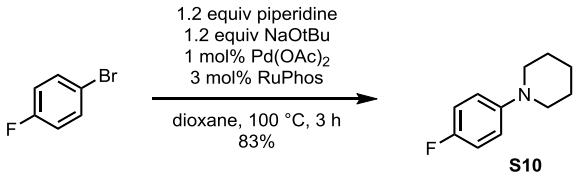
The acidic filtrate was extracted with diethyl ether (2 × 10 mL), then brought to pH 14 with 6 M NaOH. The basic mixture was extracted with dichloromethane (5 × 20 mL), until no more UV-active compound was observed in the organic extract. The combined organic layers were dried over $Na_2SO_4$ and concentrated to yield 39.1 mg of a brown oil (0.218 mmol, 22%). $^{19}F$ NMR analysis revealed an *o*:*m*:*p* ratio of 11:10:79.




**Supplementary Figure S10.** $^{19}F$ NMR analysis of product mixture of piperidine aminium radical substitution ($CDCl_3$, 23 °C)

## Synthesis of authentic samples of S10, S11, and S12

### 1-(4-Fluorophenyl)piperidine (S10)



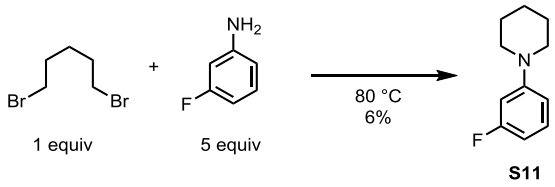

To a flame-dried 50 mL Schlenk flask were added 22.5 mg palladium acetate (22.5 mg, 0.100 mmol, 1.00 mol%), 140. mg RuPhos (0.300 mmol, 3.00 mol%), and 1.153 g of sodium tert-butoxide (12.00 mmol, 1.20 equiv). The flask was sealed with a septum, then evacuated and refilled with $N_2$ three times. Anhydrous dioxane (10.0 mL) was added via syringe through the septum, followed by 1.75 g 4-fluorobromobenzene (10.0 mmol, 1.00 equiv) and 1.19 mL piperidine (12.0 mmol, 1.20 equiv). The mixture was degassed via $N_2$ sparge for 10 minutes, then heated at 100 °C for 3 hours. The reaction mixture was diluted with ethyl acetate to 50 mL, and filtered through celite to remove the precipitated palladium metal. The filtrate was washed with water (3 × 50 mL) and brine (2 × 50 mL), dried over $NaSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel (hexanes → 19:1 hexanes:EtOAc) to yield 1.48 g of the title compound as a brown oil (8.28 mmol, 83%).

NMR Spectroscopy: $^1H$ NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.94–7.90 (m, 2H), 7.88–7.84 (m, 2H), 7.48–7.43 (m, 2H), 7.30–7.25 (m, 2H). $^{13}C$ NMR (125 MHz, $CDCl_3$, 23 °C, δ): 167.1 (s), 161.8 (d, $J$ = 247.6 Hz), 134.4 (s), 131.5 (s), 128.3 (d, $J$ = 8.7 Hz), 127.5 (d, $J$ = 3.2 Hz), 123.7 (s), 116.1 (d, $J$ = 22.5 Hz). $^{19}F$

NMR (470 MHz, $CDCl_3$, 23 °C, δ): –128.1.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{11}H_{15}FN$ [M+H]+, 180.1183; found, 180.1182.

**1-(3-Fluorophenyl)piperidine (S11)**




**S11**

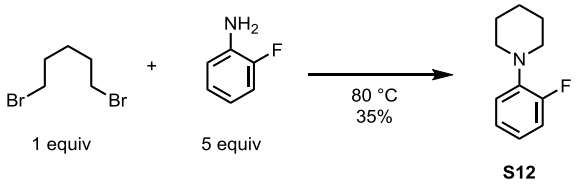
To a 20 mL vial were added 0.55 mL 1,5-dibromopentane (4.0 mmol, 1.0 equiv) and 1.92 mL 3-fluoroaniline (20.0 mmol, 5.0 equiv). The vial was sealed, and the mixture was heated with stirring at 80 °C for 4 hours, after which the mixture was allowed to come to room temperature, and 10 mL of 6 M NaOH was added. The mixture was then extracted with diethyl ether (3 × 10 mL), and the combined organic layers were concentrated. To the residue was added 10 mL $Ac_2O$, and the mixture was stirred for 30 minutes at room temperature. To the mixture was added 20 mL of 1 M HCl and 10 mL water. The mixture was extracted with dichloromethane (2 × 20 mL), then basified to pH 14 with 6 M NaOH. The basic mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over $Na_2SO_4$, and concentrated to give a brown oil. The brown oil was distilled with a Hickmann still to give 126. mg of a colorless oil.

To remove the remaining 3-fluoroacetanilide impurity, the oil was dissolved in 20 mL diethyl ether, and extracted with (3 × 10 mL) 0.1 HCl. The combined acidic aqueous layers were basified to pH 14 with 6 M NaOH, then extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated to yield 40.0 mg of the title compound as a colorless liquid (0.223 mmol, 6%).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.20–7.14 (m, 1H), 6.71–6.68 (m, 1H), 6.64–6.59 (m, 1H), 6.52–6.47 (m, 1H), 3.20–3.16 (m, 4H), 1.74–1.68 (m, 4H), 1.63–1.58 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 163.9 (d, $J$ = 242.6 Hz), 153.6 (d, 10.9 Hz), 129.9 (d, $J$ = 10.1 Hz), 111.4 (d, $J$ = 2.2 Hz), 105.1 (d, $J$ = 21.6 Hz), 102.8 (d, $J$ = 24.8 Hz), 50.0 (s), 25.5 (s), 24.2 (s). $^{19}$F NMR (470 MHz, $CDCl_3$, 23 °C, δ): –115.6.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{11}H_{15}FN$ $[M+H]^+$, 180.1183; found, 180.1183.

**1-(2-Fluorophenyl)piperidine (S12)**




**S12**

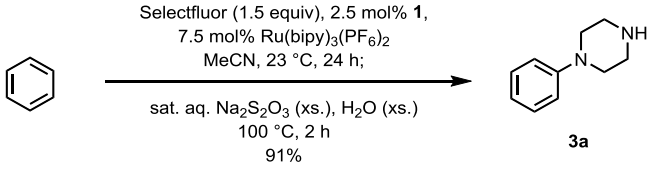
To a 20 mL vial were added 2.20 mL 1,5-dibromopentane (16.2 mmol, 1.00 equiv) and 7.80 mL 3-fluoroaniline (80.8 mmol, 5.00 equiv). The vial was sealed, and the mixture was heated with stirring at 80 °C for 24 hours, after which the mixture was allowed to come to room temperature, and 20 mL of 1 M

NaOH was added. The mixture was then extracted with dichloromethane (3 × 20 mL), and the combined organic layers were dried over $Na_2SO_4$, then concentrated. To the residue was added 50 mL $Ac_2O$, and the mixture was stirred for 2 hours at room temperature. To the solution was added 50 mL of 1 M HCl and ice. The mixture was extracted with dichloromethane (5 × 25 mL), then basified to pH 14 with 6 M NaOH. The basic mixture was extracted with dichloromethane (5 × 25 mL). The combined organic layers were dried over $Na_2SO_4$, and concentrated to give 994. mg of the title compound as a yellow oil (5.55 mmol, 35%).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.09–6.97 (m, 3H), 6.95–6.90 (m, 1H), 3.07–3.04 (m, 4H), 1.81–1.76 (m, 4H), 1.64–1.58 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 155.8 (d, $J$ = 245.6 Hz), 141.3 (d, $J$ = 8.4 Hz), 124.2 (d, $J$ = 3.6 Hz), 121.9 (d, $J$ = 7.9 Hz), 119.1 (d, $J$ = 3.2 Hz), 115.8 (d, $J$ = 21.1 Hz), 52.0 (s), 26.1 (s), 24.2 (s). $^{19}$F NMR (470 MHz, $CDCl_3$, 23 °C, δ): –125.7.

## Procedures for the preparation of aryl piperazines

### 1-Phenylpiperazine (3a)



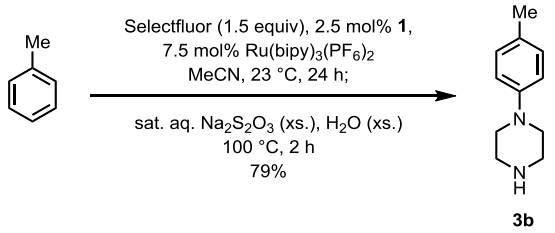

A 100 mL pressure tube was charged with palladium complex **1** (17.8 mg, 28.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (72.1 mg, 83.9 μmol, 7.50 mol%), and Selectfluor (595. mg, 1.68 mmol, 1.50 equiv). Acetonitrile (5.6 mL, c = 0.20 M) was added, followed by benzene (100. μL, 1.12 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (11 mL) and water (11 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) and ethylenediamine (1.5 mL) were added and the organic layer was washed with 6 M aqueous sodium hydroxide (5 mL). The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (2 × 10 mL). Ethylenediamine (6.5 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (190. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (95.5/4.0/0.5 (v/v/v)) to afford 163. mg of the title compound as a yellow oil (91% yield).

$R_f$ = 0.32 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.27 (dd, $J$ = 9.0, 7.8 Hz, 2H), 6.94 (d, $J$ = 7.8 Hz, 2H), 6.86 (t, $J$ = 7.8 Hz, 1H), 3.14–3.16 (m, 4H), 3.03–3.05 (m, 4H), 1.65 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 151.9, 129.2, 119.9, 116.3, 50.5, 46.3.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{10}H_{15}N_2$ $[M+H]^+$, 163.1230; found, 163.1238.

**1-(*p*-Tolyl)piperazine (3b)**




**3b**

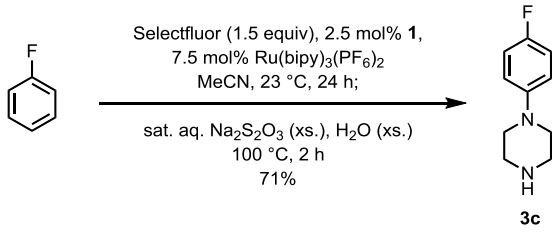
A 100 mL pressure tube was charged with palladium complex **1** (13.6 mg, 21.4 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (55.2 mg, 64.2 μmol, 7.50 mol%), and Selectfluor (455. mg, 1.28 mmol, 1.50 equiv). Acetonitrile (4.3 mL, c = 0.20 M) was added, followed by toluene (91.1 μL, 0.856 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (8.6 mL) and water (8.6 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) and ethylenediamine (1.5 mL) were added and the organic layer was washed with 6 M aqueous sodium hydroxide (5 mL). The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (2 × 15 mL). Ethylenediamine (5.0 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (8 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (143. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (97.5/2.0/0.5 (v/v/v)) to afford 119. mg of the title compound as a yellow oil (79% yield).

$R_f$ = 0.35 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.07–7.09 (m, 2H), 6.84–6.86 (m, 2H), 3.07–3.10 (m, 4H), 3.01–3.04 (m, 4H), 2.28 (s, 3H), 1.68 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 149.7, 129.7, 129.3, 116.5, 50.9, 46.1, 20.5.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{11}H_{17}N_2$ $[M+H]^+$, 177.1386; found, 177.1387.

**1-(4-Fluorophenyl)piperazine (3c)**




**3c**

A 100 mL pressure tube was charged with palladium complex **1** (17.0 mg, 26.6 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (68.7 mg, 80.0 μmol, 7.50 mol%), and Selectfluor (566. mg, 1.60 mmol, 1.50 equiv). Acetonitrile (11 mL, c = 0.10 M) was added, followed by fluorobenzene (100. μL, 1.06 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (21

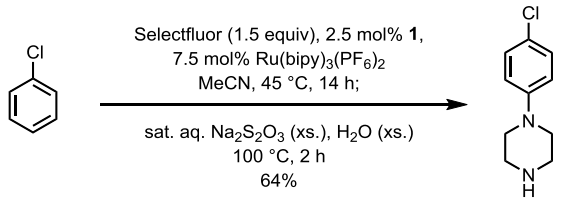
mL) and water (21 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (30 mL) and ethylenediamine (1.5 mL) were added and the organic layer was washed with 6 M aqueous sodium hydroxide (5 mL). The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (2 × 15 mL). Ethylenediamine (6.5 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (160. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (91.5/8.0/0.5 (v/v/v)) to afford 136. mg of the title compound as a yellow oil (71% yield).

$R_f$ = 0.14 (dichloromethane/methanol/28% aqueous ammonium hydroxide 91.5:8.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 6.94–6.96 (m, 2H), 6.85–6.87 (m, 2H), 3.03–3.07 (m, 8H), 2.45 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 157.3 (d, $J$ = 238.8 Hz), 148.5 (d, $J$ = 2.8 Hz), 118.0 (d, $J$ = 7.7 Hz), 115.6 (d, $J$ = 22.0 Hz), 51.4 (s), 46.1 (s). $^{19}$F NMR (500 MHz, $CDCl_3$, 23 °C, δ): –127.4.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{10}H_{14}FN_2$ $[M+H]^+$, 181.1136; found, 181.1128.

**1-(4-Chlorophenyl)piperazine (3d)**




**3d**

A 100 mL pressure tube was charged with palladium complex **1** (15.6 mg, 24.6 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (63.3 mg, 73.7 μmol, 7.50 mol%), and Selectfluor (522 mg, 1.47 mmol, 1.50 equiv). Acetonitrile (4.9 mL, c = 0.20 M) was added, followed by chlorobenzene (100. μL, 0.982 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 45 °C for 14 h. Saturated aqueous sodium thiosulfate (9.8 mL) and water (9.8 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL), ethylenediamine (0.5 mL), and 6 M aqueous sodium hydroxide (5 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (3 × 10 mL). Ethylenediamine (5.0 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (4 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (180. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (94.5/5.0/0.5 (v/v/v)) to afford a yellow solid (171. mg). The residue was further

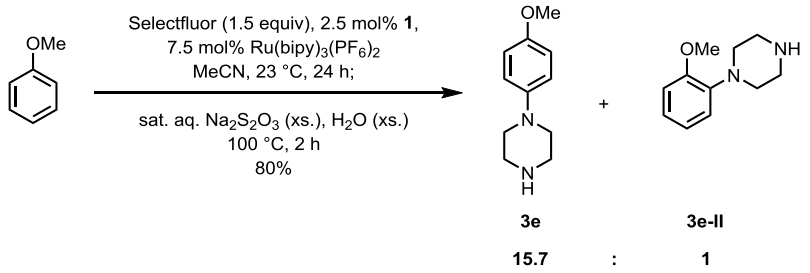
purified by preparatory HPLC with a solvent mixture of water/acetonitrile/trifluoroacetic acid (89.9/10.0/0.1 to 49.9/50.0/0.1 (v/v/v)) to afford 125. mg of the title compound as a bright yellow solid (64% yield).

$R_f$ = 0.26 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.18–7.21 (m, 2H), 6.81–6.84 (m, 2H), 3.08–3.10 (m, 4H), 3.00–3.02 (m, 4H), 1.62 (s, 1H). $^{13}$C NMR (500 MHz, $CDCl_3$, 23 °C, δ): 150.6, 129.0, 124.6, 117.4, 50.5, 46.2.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{10}H_{14}ClN_2$ $[M+H]^+$, 197.0846; found, 197.0846.

**1-(4-Methoxyphenyl)piperazine (3e)**



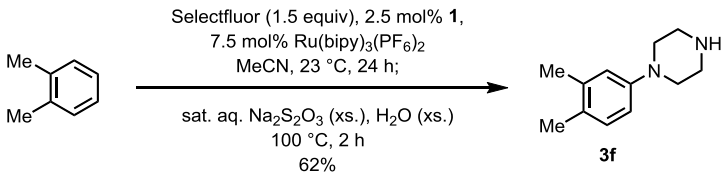

A 100 mL pressure tube was charged with palladium complex **1** (14.6 mg, 23.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (59.3 mg, 69.0 μmol, 7.50 mol%), and Selectfluor (489. mg, 1.38 mmol, 1.50 equiv). Acetonitrile (4.6 mL, c = 0.20 M) was added, followed by anisole (100. μL, 0.920 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (9.2 mL) and water (9.2 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (25 mL) and ethylenediamine (3.0 mL) were added and the organic layer was washed with 6 M aqueous sodium hydroxide (5 mL). The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (2 × 15 mL). Ethylenediamine (6.5 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (170. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (93.0/6.5/0.5 (v/v/v)) to afford 152. mg of the title compound as a light yellow solid (80% yield), containing 1-(2-methoxyphenyl)piperazine (6%). For characterization, 35. mg of the mixture was further purified by preparatory HPLC with a solvent mixture of water/acetonitrile/trifluoroacetic acid (89.9/10.0/0.1 to 69.9/30.0/0.1 (v/v/v)) to afford 23. mg of the title compound as an off-white solid.

$R_f$ = 0.46 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 6.86–6.89 (m, 2H), 6.81–6.84 (m, 2H), 3.74 (s, 3H), 3.03 (s, 8H), 2.74 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 153.9, 146.1, 118.4, 114.5, 55.6, 51.7, 46.1.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{11}H_{17}N_2O$ $[M+H]^+$, 193.1335; found, 193.1332.

**1-(3,4-Dimethylphenyl)piperazine (3f)**



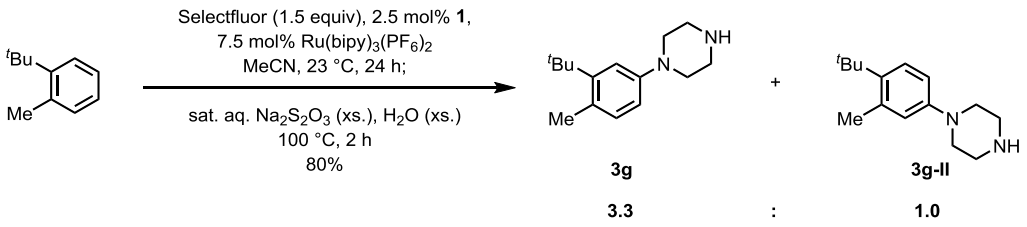

A 100 mL pressure tube was charged with palladium complex **1** (13.2 mg, 20.7 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (53.4 mg, 62.1 μmol, 7.50 mol%), and Selectfluor (440. mg, 1.24 mmol, 1.50 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added, followed by *o*-xylene (100. μL, 1.00 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (8.3 mL) and water (8.3 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, ethylenediamine (5.0 mL) and water (15 mL) were added, and the mixture was stirred for 1 h further. The reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (3 × 10 mL). Ethylenediamine (2.0 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (6 mL). The basic aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (117. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (97.5/2.0/0.5 (v/v/v)) to afford 97.0 mg of the title compound as a yellow solid (62% yield).

$R_f$ = 0.32 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.03 (d, $J$ = 8.2 Hz, 1H), 6.76 (d, $J$ = 2.6 Hz, 1H), 6.69 (dd, $J$ = 8.2, 2.6 Hz, 1H), 3.09 (m, 4H), 3.03 (m, 4H), 2.24 (s, 3H), 2.19 (s, 3H), 1.72 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 150.3, 137.2, 130.2, 128.2, 118.2, 114.0, 51.2, 46.4, 20.3, 18.9.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{12}H_{19}N_2$ $[M+H]^+$, 191.1543; found, 191.1538.

**1-(3-(*tert*-Butyl)-4-methylphenyl)piperazine (3g), 1-(4-(*tert*-Butyl)-3-methylphenyl)piperazine (3g-II)**




A 100 mL pressure tube was charged with palladium complex **1** (7.16 mg, 11.2 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (29.0 mg, 33.8 μmol, 7.50 mol%), and Selectfluor (239. mg, 0.675 mmol, 1.50 equiv).

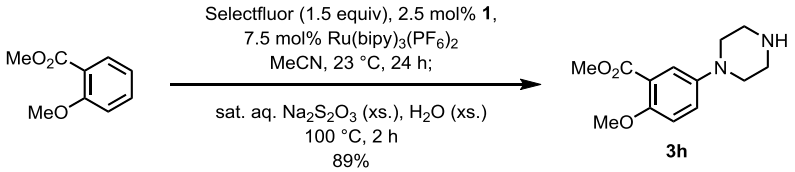
Acetonitrile (2.2 mL, c = 0.20 M) was added, followed by 1-(*tert*-butyl)-2-methylbenzene (75.0 µL, 0.450 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (4.5 mL) and water (4.5 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL), ethylenediamine (0.5 mL), water (5 mL) and 6 M aqueous sodium hydroxide (0.5 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (3 × 10 mL). Ethylenediamine (2.0 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (91.4 mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (96.5/3.0/0.5 (v/v/v)) to afford 83.5 mg of the title compounds (**3g**:**3g-II** = 3.3 : 1.0, see page S143–S145 for structural assignment) as a yellow oil (80% yield).

$R_f$ = 0.25 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): **3g** 7.01–7.03 (m, 2H), 6.68 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.09–3.13 (m, 4H), 3.01–3.06 (m, 4H), 2.46 (s, 3H), 1.88 (s, 1H), 1.40 (s, 9H). **3g-II** 7.26 (d, *J* = 8.7 Hz, 1H), 6.67–6.72 (m, 2H), 3.09–3.13 (m, 4H), 3.01–3.06 (m, 4H), 2.51 (s, 3H), 1.38 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 150.0, 149.6, 148.6, 139.5, 137.1, 133.4, 128.0, 126.9, 120.6, 115.6, 113.6, 113.0, 51.3, 50.4, 46.4, 46.3, 36.2, 35.2, 31.2, 30.8, 23.6, 22.5.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{15}H_{25}N_2$ $[M+H]^+$, 233.2012; found, 233.2022.

**Methyl 2-methoxy-5-(piperazin-1-yl)benzoate (3h)**




A 100 mL pressure tube was charged with palladium complex **1** (11.1 mg, 17.4 µmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (44.9 mg, 52.2 µmol, 7.50 mol%), and Selectfluor (370. mg, 1.04 mmol, 1.50 equiv). Acetonitrile (3.5 mL, c = 0.20 M) was added, followed by methyl 2-methoxybenzoate (100. µL, 0.700 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (7.0 mL) and water (7.0 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) and ethylenediamine (0.3 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 10% aqueous glacial acetic acid (2 × 15 mL). The combined acidic aqueous layers were basified with ethylenediamine (4.0 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (175. mg). The residue was purified by chromatography on silica

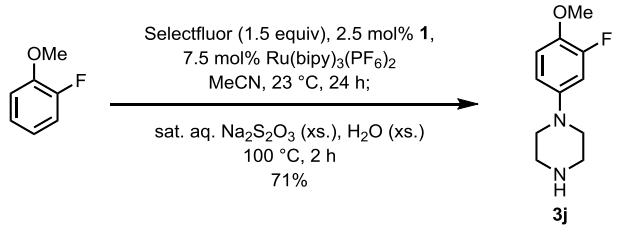
gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (96.5/3.0/0.5 (v/v/v)) to afford 155. mg of the title compound as a yellow oil (89% yield).

$R_f$ = 0.16 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (125 MHz, $CDCl_3$, 23 °C, δ): 7.35 (d, *J* = 3.0 Hz, 1H), 7.03 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.98–3.03 (m, 8H), 1.67 (s, 1H). $^{13}$C NMR (500 MHz, $CDCl_3$, 23 °C, δ): 166.9, 153.2, 145.6, 122.1, 120.3, 119.8, 113.5, 56.6, 52.1, 51.5, 46.2.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{13}H_{18}N_2O_3Na$ $[M+Na]^+$, 273.1210; found, 273.1207.

**1-(3-Fluoro-4-methoxyphenyl)piperazine (3j)**



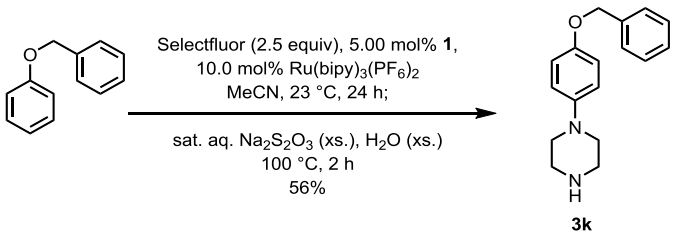

A 100 mL pressure tube was charged with palladium complex **1** (15.9 mg, 25.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (64.5 mg, 75.0 μmol, 7.50 mol%), Selectfluor (531.5 mg, 1.500 mmol, 1.50 equiv), and 2-fluoroanisole (112 μL, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 1 h. After cooling to 23 °C, the reaction mixture was filtered through celite, and the filter cake was extracted with 5 × 15 mL acetonitrile and 2 × 15 mL water. The acetonitrile was removed from the filtrate by rotary evaporation. To the remaining aqueous mixture 0.50 mL ethylene diamine was added, and the aqueous mixture was basified to pH 14 with 6 M NaOH, then transferred to a separatory funnel. The aqueous layer was extracted with dichloromethane (5 × 15 mL). The combined organic layers were extracted with 1 M HCl (5 × 15 mL). To the combined acidic aqueous layers was added ethylene diamine (0.5 mL), and the mixture was basified to pH 14 with 6 M NaOH. The basic aqueous layer was extracted with dichloromethane (5 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil. The residue was purified by chromatography on silica gel eluting with dichloromethane/methanol 9:1 (v/v) to afford 150. mg of the title compound as a brown oil (71% yield).

$R_f$ = 0.28 (dichloromethane/methanol 9:1 (v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 6.86 (dd, *J* = 9.1, 9.1 Hz, 1H), 6.69 (dd, *J* = 14.0, 2.8 Hz, 1H), 6.59 (m, 1H), 3.81 (s, 4H), 3.63 (br, 1H), 3.05 (s, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 152.8 (d, *J* = 243.7 Hz), 146.3 (d, *J* = 7.8 Hz), 141.3 (d, *J* = 10.6 Hz), 114.6 (d, *J* = 2.9 Hz), 111.6 (d, *J* = 3.5 Hz), 105.7 (d, *J* = 21.1 Hz), 56.9 (s), 50.5 (s), 45.5 (s).

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{11}H_{16}FN_2O$ $[M+H]^+$, 211.1247; found, 211.1245.

**1-(4-(Benzyloxy)phenyl)piperazine (3k)**




**3k**

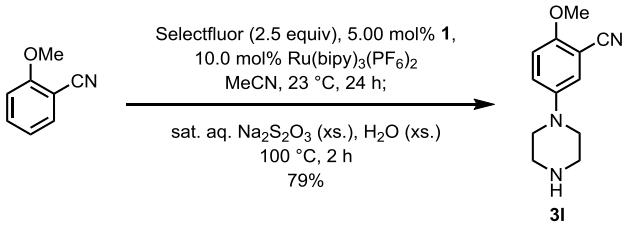
A 100 mL pressure tube was charged with palladium complex **1** (31.8 mg, 50.0 μmol. 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 100. μmol, 10.0 mol%), Selectfluor (886. mg, 2.50 mmol, 2.50 equiv), and benzyl phenyl ether (184. mg, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, 0.5 mL ethylene diamine was added and the reaction mixture was basified to pH 14 with 6 M NaOH, then filtered through celite. The filter cake was extracted with acetonitrile (5 × 15 mL). The acetonitrile was removed from the filtrate by rotary evaporation. The remaining aqueous mixture was transferred to a separatory funnel and extracted with dichloromethane (5 × 15 mL). The combined organic layers were extracted with 1 M HCl (5 × 15 mL). To the combined acidic aqueous layers was added ethylene diamine (0.5 mL), and the mixture was basified to pH 14 with 6 M NaOH. The basic aqueous layer was extracted with dichloromethane (5 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil. The residue was purified by chromatography on silica gel eluting with dichloromethane/methanol 19:1 ⟶ 9:1 (v/v) to afford 151. mg of the title compound as an off-white powder (56% yield).

$R_f$ = 0.35 (dichloromethane/methanol 9:1 (v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.44–7.41 (m, 2H), 7.40–7.33 (m, 2H), 7.34–7.30 (m, 1H), 6.94–6.88 (m, 4H), 5.02 (s, 2H), 3.07 (s, 8H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 153.1, 146.2, 137.3, 128.5, 127.8, 127.5, 118.3, 115.6, 70.5, 51.4, 46.0.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$, 269.1648; found, 269.1635.

**2-Methoxy-5-(piperazin-1-yl)benzonitrile (3l)**




**3l**

A 100 mL pressure tube was charged with palladium complex **1** (31.8 mg, 50.0 μmol. 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (86.0 mg, 100. μmol, 10.0 mol%), Selectfluor (886. mg, 2.50 mmol, 2.50 equiv), and 2-methoxybenzonitrile (122. μL, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10

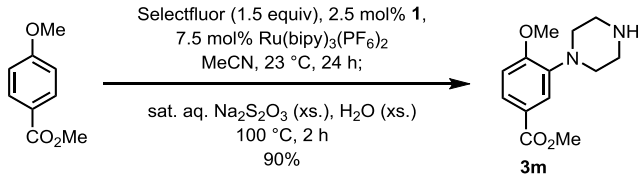
mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, 0.5 mL ethylene diamine was added and the reaction mixture was basified to pH 14 with 6 M NaOH, then filtered through celite. The filter cake was extracted with acetonitrile (5 × 15 mL). The acetonitrile was removed from the filtrate by rotary evaporation. The remaining aqueous mixture was transferred to a separatory funnel and extracted with dichloromethane (5 × 15 mL), then 9:1 dichloromethane/methanol (v/v) (3 × 15 mL). The combined organic layers were extracted with 1 M HCl (5 × 15 mL). To the combined acidic aqueous layers was added ethylene diamine (0.5 mL), and the mixture was basified to pH 14 with 6 M NaOH. The basic aqueous layer was extracted with 9:1 dichloromethane/methanol (v/v) (6 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil. The residue was purified by chromatography on silica gel eluting with dichloromethane/methanol 9:1 (v/v) to afford 190. mg of the title compound as a brown oil (79% yield).

$R_f$ = 0.31 (dichloromethane/methanol 9:1 (v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.12 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.07 (d, *J* = 3.1 Hz, 1H), 6.88 (d, *J* = 9.1 Hz, 1H), 3.86 (s, 4H), 3.04 (s, 4H), 2.56 (br, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 155.2, 145.8, 123.2, 121.1, 116.7, 112.3, 101.7, 56.2, 50.9, 40.8.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{12}H_{16}N_3O$ $[M+H]^+$, 218.1293; found, 218.1300.

**Methyl 4-methoxy-3-(piperazin-1-yl)benzoate (3m)**



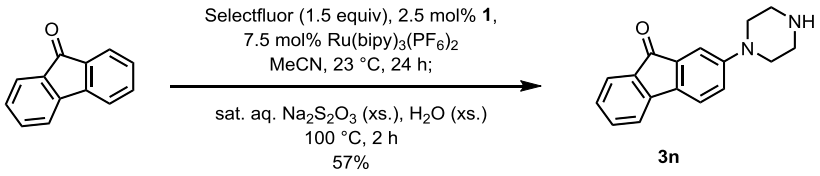

A 100 mL pressure tube was charged with palladium complex **1** (15.9 mg, 25.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (64.5 mg, 75.0 μmol, 7.50 mol%), Selectfluor (531. mg, 1.50 mmol, 1.50 equiv), and methyl 4-methoxybenzoate (166. mg, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, ethylenediamine (1.5 mL) and water (15 mL) were added, and the mixture was stirred for 1 h further. The reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 10% aqueous glacial acetic acid (2 × 15 mL). The combined acidic aqueous layers were basified with ethylenediamine (4.5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (252. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (91.5/8.0/0.5 (v/v/v)) to afford 226. mg of the title compound as a yellow solid (90% yield).

$R_f$ = 0.16 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.74 (dd, $J$ = 8.1, 2.1 Hz, 1H), 7.61 (d, $J$ = 2.4 Hz, 1H), 6.88 (d, $J$ = 8.4 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.09–3.11 (m, 8H), 1.67 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 167.1, 156.2, 141.3, 125.6, 122.9, 119.7, 110.5, 55.8, 52.0, 51.6, 46.0.

Mass Spectrometry: HRMS-FIA (m/z) calcd for $C_{13}H_{18}N_2O_3Na$ $[M+Na]^+$, 273.1210; found, 273.1215.

**2-(Piperazin-1-yl)-9*H*-fluoren-9-one (3n)**



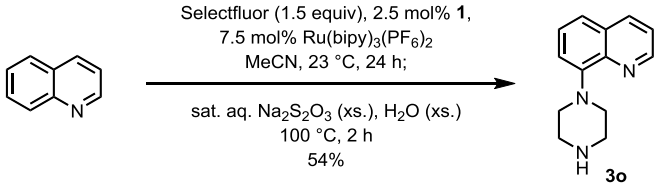

A 100 mL pressure tube was charged with palladium complex **1** (8.83 mg, 13.9 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (35.8 mg, 41.6 μmol, 7.50 mol%), Selectfluor (295. mg, 0.832 mmol, 1.50 equiv), and fluorenone (100. mg, 0.555 mmol, 1.00 equiv). Acetonitrile (2.8 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (5.5 mL) and water (5.5 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) and ethylenediamine (0.3 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were extracted with 10% aqueous glacial acetic acid (3 × 15 mL). Ethylenediamine (3.0 mL) was added to the combined acidic aqueous layers, followed by basification with saturated aqueous sodium carbonate (5 mL). The basic aqueous layer was extracted with dichloromethane (4 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (102. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (96.0/3.5/0.5 (v/v/v)) to afford 83.1 mg of the title compound as a yellow solid (57% yield).

$R_f$ = 0.34 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.57 (d, $J$ = 7.3 Hz, 1H), 7.40 (td, $J$ = 7.4, 1.1 Hz, 1H), 7.34–7.36 (m, 2H), 7.23 (d, $J$ = 2.4 Hz, 1H), 7.15 (td, $J$ = 7.4, 1.1 Hz, 1H), 6.93 (dd, $J$ = 8.2, 2.4 Hz, 1H), 3.19–3.21 (m, 4H), 3.02–3.04 (m, 4H), 1.74 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 194.6, 152.9, 145.4, 135.7, 135.1, 134.9, 134.4, 127.6, 124.3, 121.2, 120.5, 119.5, 111.9, 50.1, 46.1.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$, 265.1335; found, 265.1341.

**8-(Piperazin-1-yl)quinoline (3o)**



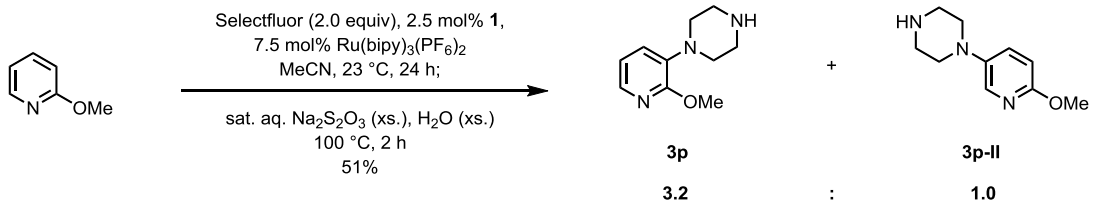
A 100 mL pressure tube was charged with palladium complex **1** (13.5 mg, 21.2 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (54.6 mg, 63.5 μmol, 7.50 mol%), and Selectfluor (450. mg, 1.27 mmol, 1.50 equiv). Acetonitrile (4.2 mL, c = 0.20 M) was added, followed by quinoline (100. μL, 84.6 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (8.5 mL) and water (8.5 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) and ethylenediamine (2.5 mL) were added and the organic layer was washed with 6 M aqueous sodium hydroxide (5 mL). The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (2 × 15 mL). Ethylenediamine (5.0 mL) was added to the combined acidic aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (137. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (91.5/8.0/0.5 (v/v/v)) to afford 98.2 mg of the title compound as a yellow oil (54% yield).

$R_f$ = 0.18 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 8.86 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.42–7.44 (m, 2H), 7.34 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.12 (dd, *J* = 6.5, 2.4 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 149.8, 148.3, 142.8, 136.6, 129.7, 126.8, 121.8, 120.9, 116.1, 53.2, 46.2.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{13}H_{16}N_3$ $[M+H]^+$, 214.1339; found, 214.1328.

**1-(2-Methoxypyridin-3-yl)piperazine (3p), 1-(6-methoxypyridin-3-yl)piperazine (3p-II)**




A 100 mL pressure tube was charged with palladium complex **1** (15.1 mg, 23.8 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (61.3 mg, 71.3 μmol, 7.50 mol%), and Selectfluor (674. mg, 1.90 mmol, 2.00 equiv). Acetonitrile (4.8 mL, c = 0.20 M) was added, followed by 2-methoxypyridine (100. μL, 0.951 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (9.5 mL) and water (9.5 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (15 mL) and ethylenediamine (2.5 mL) were added and the organic layer was washed with 6 M aqueous sodium hydroxide (5 mL). Volume of the aqueous layer was reduced by half and then the aqueous layer was extracted with dichloromethane (2 × 15 mL) and then mixture of dichloromethane/methanol (9.0/1.0 (v/v), 3 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (3 × 15 mL). Ethylenediamine (5.0 mL) was added to the combined acidic

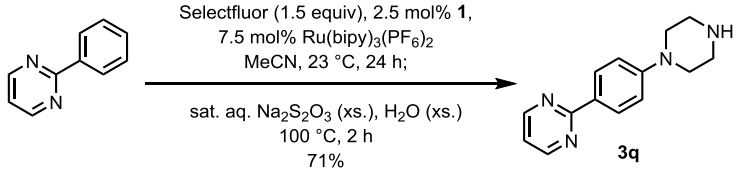
aqueous layers, followed by basification with 6 M aqueous sodium hydroxide (5 mL). The basic aqueous layer was extracted with dichloromethane (2 × 15 mL) and then mixture of dichloromethane/methanol (9.0/1.0 (v/v), 3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (120. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (96.0/3.5/0.5 (v/v/v)) to afford 94.5 mg of the title compounds (**3p**:**3p-II** = 3.2:1.0, see page S163–S164 for structural assignment) as a yellow oil (51% yield).

$R_f$ = 0.16 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): **3p** 7.76 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.80 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.95 (s, 3H), 2.98–3.02 (m, 8H), 2.19 (s, 1H). **3p-II** 7.74 (d, *J* = 3.0 Hz, 1H), 7.24 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.64 (d, *J* = 8.9 Hz, 1H), 3.84 (s, 3H), 2.98-3.02 (m, 8H), 2.19 (s, 1H). $^{13}$C NMR (500 MHz, $CDCl_3$, 23 °C, δ): **3p** 156.9, 139.0, 136.6, 124.7, 117.1, 53.4, 51.3, 46.1. **3p-II** 158.9, 142.9, 134.6, 129.8, 110.7, 53.4, 51.6, 46.1.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{10}H_{16}N_3O$ $[M+H]^+$, 194.1293; found, 194.1295.

**2-(4-(Piperazin-1-yl)phenyl)pyrimidine (3q)**




A 100 mL pressure tube was charged with palladium complex **1** (15.9 mg, 25.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (64.5 mg, 75.0 μmol, 7.50 mol%), Selectfluor (531. mg, 1.50 mmol, 1.50 equiv), and 2-phenylpyrimidine (156. mg, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was basified with aqueous 6 M sodium hydroxide solution (10 mL) and ethylenediamine (0.5 mL), filtered through celite rinsing with acetonitrile (5 × 15 mL), and acetonitrile removed *in vacuo* to afford a brown aqueous solution. The aqueous layer was transferred to a separatory funnel and extracted with a solvent mixture of methanol/dichloromethane (1/9 (v/v), 5 × 15 mL). The combined organic layers were extracted with aqueous 1M hydrochloric acid solution (3 × 15 mL). The combined acidic aqueous layers were basified to pH 14 with aqueous 6M sodium hydroxide solution and ethylenediamine (0.5 mL). The basic aqueous layer was extracted with a solvent mixture of methanol/dichloromethane (1/9 (v/v), 5 × 15 mL). The organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil. The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol (9/1 (v/v)) to to afford 171. mg of the title compound as an off-white solid (71% yield).

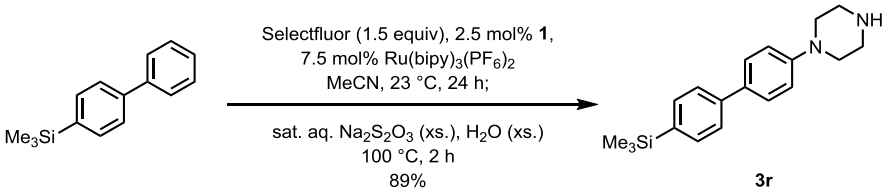
$R_f$ = 0.08 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, DMSO-$d_6$, 23 °C, δ): 8.77 (d, *J* = 5.0 Hz, 2H), 8.23 (d, *J* = 9.5

Hz, 2H), 7.27 (t, *J* = 4.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 3.21 (t, *J* = 5.0 Hz, 4H), 2.86 (t, *J* = 5.0 Hz, 4H). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 23 °C, δ): 163.5, 157.4, 153.0, 128.8, 126.7, 118.4, 114.1, 47.9, 45.2.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{14}H_{17}N_4$ $[M+H]^+$, 241.1448; found, 241.1457.

**1-(4'-(Trimethylsilyl)-[1,1'-biphenyl]-4-yl)piperazine (3r)**



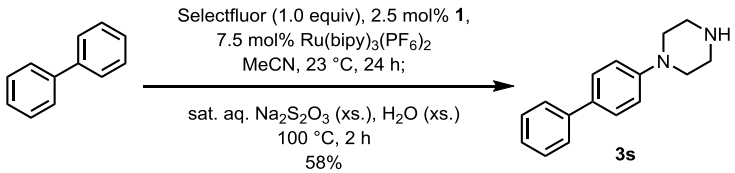

A 100 mL pressure tube was charged with palladium complex **1** (7.03 mg, 11.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (28.5 mg, 33.1 μmol, 7.50 mol%), Selectfluor (235. mg, 0.662 mmol, 1.50 equiv), and [1,1'-biphenyl]-4-yltrimethylsilane (100. mg, 0.442 mmol, 1.00 equiv). Acetonitrile (2.2 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, ethylenediamine (2.5 mL) and water (20 mL) were added, and the mixture was stirred for 1 h further. The reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (220. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (97.5/2.0/0.5 (v/v/v)) to afford 122. mg of the title compound as a yellow solid (89% yield).

$R_f$ = 0.31 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.56–7.60 (m, 4H), 7.53–7.55 (m, 2H), 6.99–7.02 (m, 2H), 3.21–3.23 (m, 4H), 3.06–3.08 (m, 4H), 2.16 (s, 1H), 0.31 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 151.2, 141.4, 138.2, 133.9, 132.3, 127.8, 125.9, 116.2, 50.2, 46.2, -0.9.

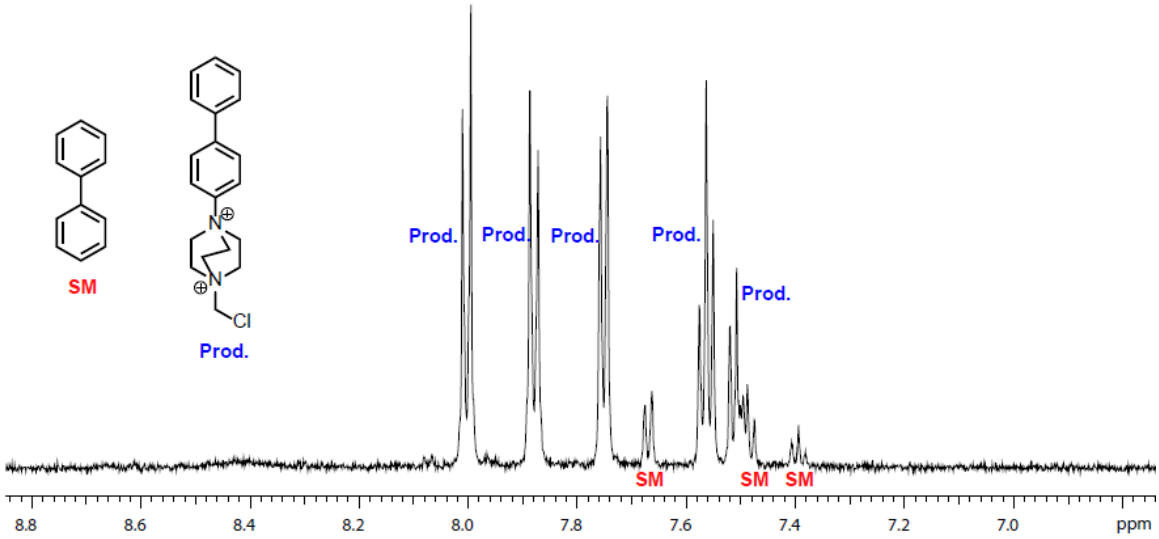
Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{19}H_{27}N_2Si$ $[M+H]^+$, 311.1938; found, 311.1950.

**1-([1,1'-Biphenyl]-4-yl)piperazine (3s)**




A 100 mL pressure tube was charged with palladium complex **1** (15.9 mg, 25.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (64.5 mg, 75.0 μmol, 7.50 mol%), Selectfluor (531. mg, 1.00 mmol, 1.00 equiv), and 1,1'-biphenyl (154. mg, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe.

The reaction mixture was stirred at 23 °C for 24 h. An aliquot was removed, concentrated, redissolved in $CD_3CN$, and analyzed by $^1H$ NMR, which showed a 9:1 mixture of biphenyl–TEDA:biphenyl, with no significant double TEDAylation product:




**Supplementary Figure S11.** $^1H$ NMR of biphenyl TEDAylation reaction mixture ($CD_3CN$, 23 °C)

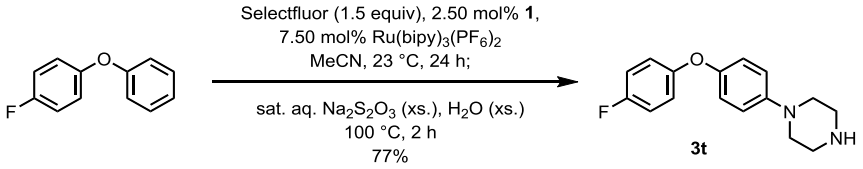
Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was basified with aqueous 6 M sodium hydroxide solution (10 mL) and ethylenediamine (0.5 mL), filtered through celite rinsing with acetonitrile (5 × 15 mL), and acetonitrile removed *in vacuo* to afford a brown aqueous solution. The aqueous layer was transferred to a separatory funnel and extracted with a solvent mixture of methanol/dichloromethane (1/9 (v/v), 5 × 15 mL). The combined organic layers were extracted with aqueous 1M hydrochloric acid solution (3 × 15 mL). The combined acidic aqueous layers were basified to pH 14 with aqueous 6M sodium hydroxide solution and ethylenediamine (0.5 mL). The basic aqueous layer was extracted with a solvent mixture of methanol/dichloromethane (1/9 (v/v), 5 × 15 mL). The organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil. The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol (9/1 (v/v)) to afford 138. mg of the title compound as an off-white solid (58% yield).

$R_f$ = 0.10 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1H$ NMR (600 MHz, $F_3CO_2D$, 23 °C, δ): 7.83 (m, 2H), 7.65 (m, 2H), 7.53 (m, 2H), 7.41 (m, 2H), 7.36 (m, 1H), 4.31 (s, 4H), 4.15 (s, 4H). $^{13}C$ NMR (125 MHz, $F_3CO_2D$, 23 °C, δ): 149.6, 141.4, 133.0, 132.2, 132.0, 130.1, 123.6, 55.9, 45.8.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{16}H_{19}N_2$ $[M+H]^+$, 239.1543; found, 239.1545.

**1-(3-Fluoro-4-methoxyphenyl)piperazine (3t)**



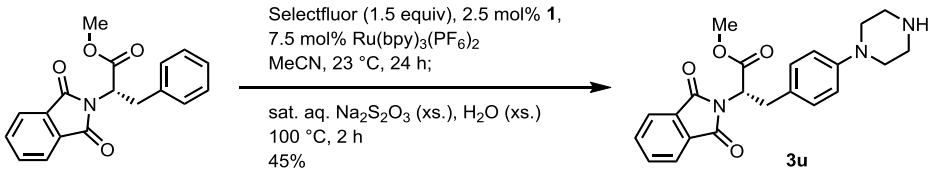

A 100 mL pressure tube was charged with palladium complex **1** (15.9 mg, 25.0 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (64.5 mg, 75.0 μmol, 7.50 mol%), Selectfluor (532. mg, 1.50 mmol, 1.50 equiv), and phenyl 4-fluorophenyl ether (188. mg, 1.00 mmol, 1.00 equiv). Acetonitrile (5.0 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (10 mL) and water (10 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was filtered through celite, and the filter cake was extracted with 5 × 15 mL acetonitrile and 2 × 15 mL water. The acetonitrile was removed from the filtrate by rotary evaporation. To the remaining aqueous mixture 0.50 mL ethylene diamine was added, and the aqueous mixture was basified to pH 14 with 6 M NaOH, then transferred to a separatory funnel. The aqueous layer was extracted with dichloromethane (7 × 30 mL). The combined organic layers were extracted with 1 M HCl (5 × 30 mL). To the combined acidic aqueous layers was added ethylene diamine (0.5 mL), and the mixture was basified to pH 14 with 6 M NaOH. The basic aqueous layer was extracted with dichloromethane (5 × 30 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red oil (220. mg). The residue was purified by chromatography on silica gel eluting with dichloromethane/methanol 19:1 → 9:1 (v/v) to afford 190. mg of the title compound as an off-white powder (77% yield).

$R_f$ = 0.35 (dichloromethane/methanol 9:1 (v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.00–6.95 (m, 2H), 6.94–6.88 (m, 6H), 3.74 (br, 1H), 3.19–3.12 (m, 4H), 3.12–3.06 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 158.3 (d, $J$ = 240.4 Hz), 154.1 (d, $J$ = 2.5 Hz), 156.6 (s), 147.9 (s), 119.8 (s), 119.2 (d, $J$ = 8.1 Hz), 117.9 (s), 116.0 (d, $J$ = 23.2 Hz), 50.6 (s), 45.7 (s).

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{16}H_{18}FN_2O$ $[M+H]^+$, 273.1398; found, 273.1397.

**Methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-(piperazin-1-yl)phenyl)propanoate (3u)**

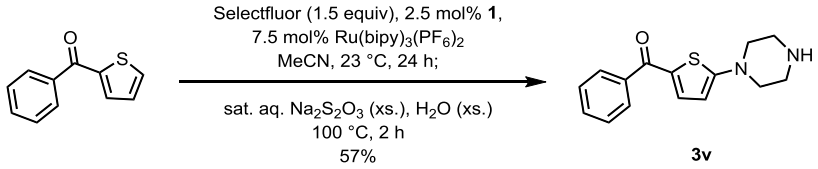



A 100 mL pressure tube was charged with palladium complex **1** (5.9 mg, 9.3 μmol. 2.5 mol%), $Ru(bpy)_3(PF_6)_2$ (24.0 mg, 27.9 μmol, 7.50 mol%), and Selectfluor (198 mg, 0.558 mmol, 1.50 equiv). Solution of methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanoate (115 mg, 0.372 mmol, 1.00 equiv) in dry acetonitrile (1.9 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at

23 °C for 24 h. Saturated aqueous sodium thiosulfate (3.8 mL) and water (3.8 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, water (5 mL) and saturated aqueous sodium carbonate (1 mL) were added, and the mixture was filtered over a glass frit with a filter paper. The filtrate was transferred to a separatory funnel. Dichloromethane (30 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (123 mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (93.7/6.0/0.3 (v/v/v)) to afford 66.3 mg of the title compound as a yellow solid (45% yield).

$R_f$ = 0.76 (dichloromethane/methanol/28% aqueous ammonium hydroxide 93.7:6.0:0.3 (v/v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.76–7.79 (m, 2H), 7.68–7.70 (m, 2H), 7.04–7.07 (m, 2H), 6.72–6.75 (m, 2H), 5.12 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.77 (s, 3H), 3.46–3.53 (m, 2H), 3.08–3.11 (m, 4H), 3.04–3.06 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 169.6, 167.6, 150.1, 134.2, 131.8, 129.7, 128.4, 123.6, 116.7, 53.5, 53.0, 49.4, 45.5, 33.8. Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{22}H_{23}N_3O_4$ [M+H]+, 394.1761; found, 394.1760.

**Phenyl(5-(piperazin-1-yl)thiophen-2-yl)methanone (3v)**




A 100 mL pressure tube was charged with palladium complex **1** (8.5 mg, 13. μmol. 2.5 mol%), $Ru(bipy)_3(PF_6)_2$ (34.2 mg, 40.0 μmol, 7.50 mol%), Selectfluor (282. mg, 0.800 mmol, 1.50 equiv), and phenyl(thiophen-2-yl)methanone (100. mg, 0.530 mmol, 1.00 equiv). Acetonitrile (2.6 mL, c = 0.20 M) was added via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (5.3 mL) and water (5.3 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL), ethylenediamine (0.5 mL) and saturated aqueous sodium carbonate (5 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were extracted with 1 M aqueous hydrochloric acid (3 × 10 mL). Ethylenediamine (6.0 mL) was added to the combined acidic aqueous layers, followed by basification with 3 M aqueous sodium hydroxide (6 mL). The basic aqueous layer was extracted with dichloromethane (4 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (126. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (95.5/4.0/0.5 (v/v/v)) to afford 82. mg of the title compound as a yellow solid (57% yield).

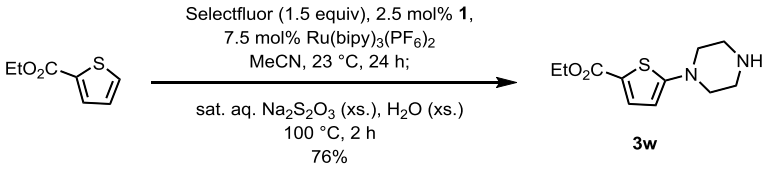
$R_f$ = 0.38 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 7.73 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz,

1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 4.3 Hz, 1H), 6.03 (d, *J* = 4.3 Hz, 1H), 3.30 (t, J = 4.9 Hz, 4H), 2.99 (t, *J* = 4.9 Hz, 4H), 2.00 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 186.7, 167.8, 139.0, 138.3, 131.1, 128.7, 128.3, 127.5, 104.4, 50.6, 45.2. Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{15}H_{16}N_2OS$ $[M+H]^+$, 273.1056; found, 273.1046.

Mass spectrometry: HRMS-FIA(m/z) calcd for $C_{15}H_{17}N_2OS$ $[M+H]^+$, 273.1056; found, 273.1044.

**Ethyl 5-(piperazin-1-yl)thiophene-2-carboxylate (3w)**



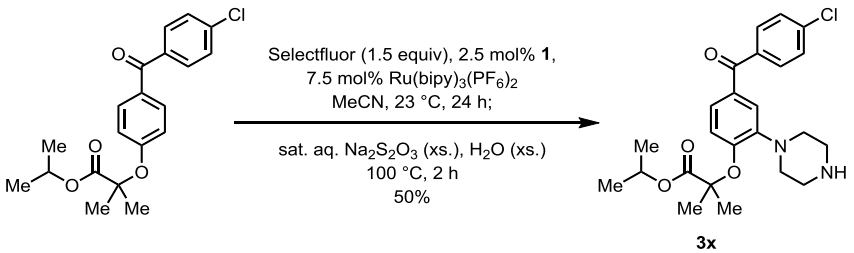

A 100 mL pressure tube was charged with palladium complex **1** (11.8 mg, 18.6 μmol. 2.50 mol%), $Ru(bipy)_3(PF_6)_2$ (47.9 mg, 55.7 μmol, 7.50 mol%), and Selectfluor (395. mg, 1.11 mmol, 1.50 equiv). Acetonitrile (3.7 mL, c = 0.20 M) was added, followed by ethyl thiophene-2-carboxylate (100. μL, 0.743 mmol, 1.00 equiv) via syringe. The reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (7.4 mL) and water (7.4 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, the reaction mixture was transferred to a separatory funnel. Dichloromethane (20 mL) and ethylenediamine (0.5 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layers were extracted with 10% aqueous glacial acetic acid (3 × 10 mL). The combined acidic aqueous layers were basified with ethylenediamine (4.5 mL). The basic aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (156. mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (95.5/4.0/0.5 (v/v/v)) to afford 135. mg of the title compound as a yellow solid (76% yield).

$R_f$ = 0.52 (dichloromethane/methanol/28% aqueous ammonium hydroxide 90.5:9.0:0.5 (v/v/v)).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.52 (d, *J* = 4.3 Hz, 1H), 6.00 (d, *J* = 4.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.19–3.20 (m, 4H), 2.98–2.99 (m, 4H), 2.17 (s, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 165.2, 162.9, 134.9, 116.9, 104.1, 60.5, 50.8, 45.2, 14.5.

Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{11}H_{17}N_2O_2S$ $[M+H]^+$, 241.1005; found, 241.0995.

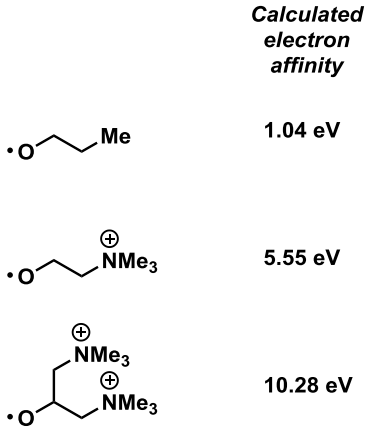
**Isopropyl 2-(4-(4-chlorobenzoyl)-2-(piperazin-1-yl)phenoxy)-2-methylpropanoate (3x)**



A 100 mL pressure tube was charged with palladium complex **1** (4.4 mg, 6.9 μmol. 2.5 mol%), $Ru(bpy)_3(PF_6)_2$ (17.9 mg, 20.8 μmol, 7.50 mol%), Selectfluor (147 mg, 0.416 mmol, 1.50 equiv), and fenofibrate (100 mg, 0.277 mmol, 1.00 equiv). Acetonitrile (1.4 mL, c = 0.20 M) was added via syringe, and the reaction mixture was stirred at 23 °C for 24 h. Saturated aqueous sodium thiosulfate (2.8 mL) and water (2.8 mL) were added, the pressure tube was sealed, and the reaction mixture was stirred at 100 °C for 2 h. After cooling to 23 °C, water (10 mL), saturated aqueous sodium carbonate (0.25 mL), and ethylenediamine (70 μL) were added, and the mixture was filtered over a glass frit with a filter paper. The filtrate was transferred to a separatory funnel. Dichloromethane (40 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a red solid (146 mg). The residue was purified by chromatography on silica gel eluting with a solvent mixture of dichloromethane/methanol/28% aqueous ammonium hydroxide (96.5/3.0/0.5 to 94.5/5.0/0.5 (v/v/v)) to afford 62 mg of the title compound as a yellow solid (50% yield).

$R_f$ = 0.11 (dichloromethane/methanol/28% aqueous ammonium hydroxide 95.5:4.0:0.5 (v/v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 7.69–7.71 (m, 2H), 7.51–7.53 (m, 2H), 7.37 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.02 (hept, *J* = 6.2 Hz, 1H), 3.01–3.06 (m, 8H), 2.68 (bs, 1H), 1.65 (s, 6H), 1.18 (d, *J* = 6.2 Hz, 6H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 195.0, 173.7, 153.4, 144.4, 138.6, 137.8, 132.2, 131.4, 129.4, 126.4, 121.1, 116.7, 80.8, 70.2, 51.7, 46.5, 25.6, 21.7. Mass Spectrometry: HRMS-FIA(m/z) calcd for $C_{24}H_{29}ClN_2O_4$ [M+H]+, 445.1889; found, 445.1888.

## Positively Charged Oxyl Radicals




**Supplementary Figure S12.** Positive charge increases electron affinity for alkoxyl radicals

To address the question of whether other radicals can be found with electron affinities comparable to $TEDA^{2+\bullet}$, we have calculated electron affinities for a series of alkoxyl radicals bearing 0, 1, and 2 proximal positive charges. We have found that electron affinities increase significantly with each additional positive charge. It is noteworthy that this trend holds despite the lack of a positive formal charge centered on the open-shell atom.

We rationalize these results in terms of electrostatic effects. When an electron is absorbed by $TEDA^{2+\bullet}$, the

Coulombic repulsion between the two proximal positive charges is alleviated, which leads to a large energetic benefit. For the oxyl radicals, Coulombic attraction is created instead, which is worth the same amount of energy, but with opposite sign.

Therefore, in principle, radicals centered on any atom could be made to have electron affinity comparable to $TEDA^{2+\bullet}$ through incorporation of proximal positive charges.

## DFT Calculations

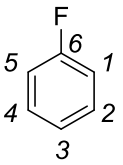
Density functional theory (DFT) calculations were performed using Gaussian09[34] on the Odyssey cluster at Harvard University. BS I includes 6-311G(d) on H and 6-31G(d,p) on all other nuclei.[35] All geometry optimizations were performed using the B3PW91 functional with the BS I basis set. Geometry optimization was carried out using the atomic coordinates from MM2 optimization in Chem3D as a starting point. Images were generated using Chem3D.

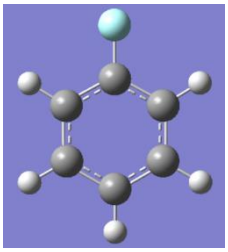
## Calculation and visualization of Fukui indices

Fukui indices were calculated in the following way: The neutral arene (with *N* electrons) was subjected to a geometry optimization, and total local atomic electron populations were determined by NBO analysis. NBO electron populations of the corresponding cationic arene (*N*–1 electrons) were calculated without geometry reoptimization. Fukui nucleophilicity indices were calculated for each atom by subtracting the atomic electron population in the cationic arene from the population in the neutral arene. A color gradient for the set of Fukui values was generated using the conditional formatting tool in Microsoft Excel 2013, with the maximum value assigned a shade of red (RGB code 255:00:00) and the smallest value assigned a shade of blue (RGB 0:112:192).

## Fluorobenzene

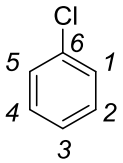
| Atom | No. | X | Y | Z | neutral pop. | cation pop. | f- | RGB color |
|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.259886 | 1.216343 | 0.000001 | 6.3189 | 6.2378 | 0.0811 | 36:96:165 |
| C | 2 | -1.134888 | 1.20758 | 0.000002 | 6.22836 | 6.17806 | 0.0503 | 0:112:192 |
| C | 3 | -1.83353 | 0 | -0.000003 | 6.26548 | 6.00175 | 0.26373 | 255:00:00 |
| C | 4 | -1.134888 | -1.20758 | -0.000001 | 6.22836 | 6.17806 | 0.0503 | 0:112:192 |
| C | 5 | 0.259886 | -1.216343 | 0.000004 | 6.3189 | 6.2378 | 0.0811 | 36:96:165 |
| C | 6 | 0.926134 | 0 | 0.000001 | 5.57659 | 5.38877 | 0.18782 | 164:40:69 |
| H | 7 | 2.284414 | 0 | -0.000003 | | | | |
| H | 8 | 0.823179 | 2.140225 | 0 | | | | |
| H | 9 | -1.672798 | 2.147473 | 0.000007 | | | | |
| H | 10 | -2.916086 | 0 | -0.000008 | | | | |
| H | 11 | -1.672798 | -2.147473 | -0.000004 | | | | |
| H | 12 | 0.823179 | -2.140225 | 0.000011 | | | | |

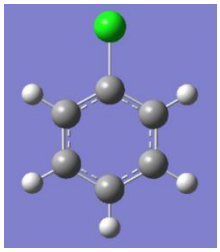


## Chlorobenzene

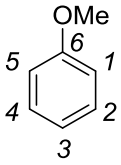
| Atom | No. | X | Y | Z | neutral pop. | cation pop. | f- | RGB color |
|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.179285 | -1.21559 | 0.000165 | 6.27732 | 6.2134 | 0.06392 | 30:99:170 |
| C | 2 | 1.573669 | -1.2065 | 0.000139 | 6.22736 | 6.1853 | 0.04206 | 0:112:192 |
| C | 3 | 2.27212 | 0 | -0.000004 | 6.24852 | 6.02219 | 0.22633 | 10.625 |
| C | 4 | 1.573669 | 1.2065 | 0.000105 | 6.22736 | 6.1853 | 0.04206 | 0:112:192 |
| C | 5 | 0.179285 | 1.21559 | 0.000197 | 6.27732 | 6.2134 | 0.06392 | 30:99:170 |
| C | 6 | -0.496734 | 0 | 0.000085 | 6.01645 | 5.87299 | 0.14346 | 140:51:87 |
| Cl | 7 | -2.266123 | 0 | -0.000282 | | | | |
| H | 8 | -0.368529 | -2.148194 | 0.000212 | | | | |
| H | 9 | 2.109408 | -2.147525 | 0.000224 | | | | |
| H | 10 | 3.354575 | 0 | -0.000209 | | | | |
| H | 11 | 2.109408 | 2.147525 | 0.000097 | | | | |
| H | 12 | -0.368529 | 2.148194 | 0.000342 | | | | |

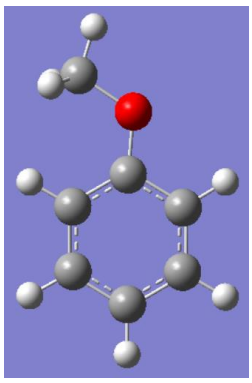


## Anisole

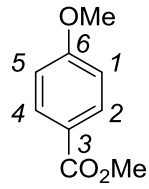
| Atom | No. | X | Y | Z | neutral pop. | cation pop. | f- | RGB code |
|---|---|---|---|---|---|---|---|---|
| C | 1 | -0.033836 | 1.060164 | 0.000014 | 6.33899 | 6.24884 | 0.09015 | 100:68:117 |
| C | 2 | 1.332708 | 1.351578 | 0.000002 | 6.22761 | 6.18489 | 0.04272 | 41:94:161 |
| C | 3 | 2.282523 | 0.334411 | -0.000005 | 6.28458 | 6.07066 | 0.21392 | 255:00:00 |
| C | 4 | 1.854924 | -0.996328 | -0.00001 | 6.23365 | 6.22391 | 0.00974 | 0:112:192 |
| C | 5 | 0.499813 | -1.302165 | -0.000013 | 6.29766 | 6.18131 | 0.11635 | 133:54:92 |
| C | 6 | -0.453266 | -0.274134 | 0.000006 | 5.671 | 5.56534 | 0.10566 | 119:60:102 |
| O | 7 | -1.757597 | -0.674453 | 0.000051 | | | | |
| C | 8 | -2.775555 | 0.326026 | -0.000034 | | | | |
| H | 9 | -0.75023 | 1.869366 | 0.000028 | | | | |
| H | 10 | 1.648206 | 2.388251 | 0.000004 | | | | |
| H | 11 | 3.339052 | 0.570766 | -0.000001 | | | | |
| H | 12 | 2.580826 | -1.80078 | -0.000015 | | | | |
| H | 13 | 0.156078 | -2.329145 | -0.000018 | | | | |
| H | 14 | -3.721506 | -0.212468 | -0.000184 | | | | |
| H | 15 | -2.717873 | 0.956111 | 0.892796 | | | | |
| H | 16 | -2.717645 | 0.956213 | -0.892776 | | | | |

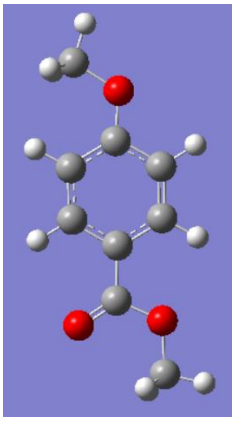


## Methyl 4-methoxybenzoate

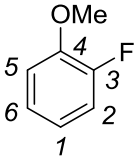
| Atom | No. | X | Y | Z | neutral pop | cation pop. | f- | RGB code |
|---|---|---|---|---|---|---|---|---|
| C | 1 | -1.601873 | 0.989296 | -0.002515 | 6.33589 | 6.24271 | 0.09318 | 116:61:105 |
| C | 2 | -0.227542 | 1.197998 | -0.003572 | 6.17724 | 6.1546 | 0.02264 | 30:99:170 |
| C | 3 | 0.668545 | 0.125151 | -0.003953 | 6.19724 | 5.99103 | 0.20621 | 255:00:00 |
| C | 4 | 0.157707 | -1.183531 | -0.004934 | 6.19285 | 6.195 | -0.00215 | 0:112:192 |
| C | 5 | -1.20764 | -1.404584 | -0.004408 | 6.29373 | 6.17326 | 0.12047 | 150:47:80 |
| C | 6 | -2.100704 | -0.320323 | -0.002287 | 5.64165 | 5.55312 | 0.08853 | 110:64:109 |
| O | 7 | -3.416329 | -0.641362 | 0.000343 | | | | |
| C | 8 | 2.122181 | 0.416199 | -0.00178 | | | | |
| O | 9 | 2.873255 | -0.703082 | 0.001834 | | | | |
| O | 10 | 2.603652 | 1.531646 | -0.002239 | | | | |
| C | 11 | 4.301648 | -0.5117 | 0.007744 | | | | |
| C | 12 | -4.383654 | 0.413925 | 0.008411 | | | | |
| H | 13 | -2.267946 | 1.839732 | -0.001523 | | | | |
| H | 14 | 0.162764 | 2.20751 | -0.003306 | | | | |
| H | 15 | 0.837023 | -2.024738 | -0.005716 | | | | |
| H | 16 | -1.611431 | -2.408873 | -0.004859 | | | | |
| H | 17 | 4.727268 | -1.512171 | 0.010726 | | | | |
| H | 18 | 4.619059 | 0.034312 | -0.881153 | | | | |
| H | 19 | 4.61118 | 0.036185 | 0.898343 | | | | |
| H | 20 | -5.354109 | -0.0776 | 0.011292 | | | | |
| H | 21 | -4.285845 | 1.033512 | 0.903987 | | | | |
| H | 22 | -4.294588 | 1.039928 | -0.88353 | | | | |

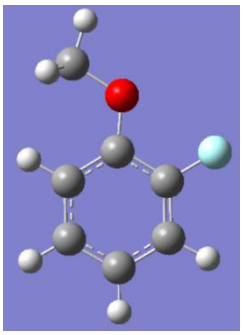


## 2-Fluoroanisole

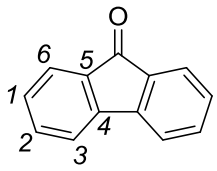
| Atom | No. | X | Y | Z | neutral pop. | cation pop. | f- | RGB code |
|---|---|---|---|---|---|---|---|---|
| C | 1 | 2.262553 | -0.684283 | 0.00009 | 6.2645 | 6.07427 | 0.19023 | 255:00:00 |
| C | 2 | 1.860767 | 0.654606 | 0.000099 | 6.30621 | 6.30142 | 0.00479 | 0:112:192 |
| C | 3 | 0.51384 | 0.954606 | -0.000018 | 5.61834 | 5.50098 | 0.11736 | 154:45:83 |
| C | 4 | -0.476755 | -0.039137 | -0.000116 | 5.73459 | 5.62397 | 0.11062 | 145:49:83 |
| C | 5 | -0.061865 | -1.373036 | -0.000126 | 6.32203 | 6.26755 | 0.05448 | 68:82:141 |
| C | 6 | 1.300232 | -1.687381 | -0.000036 | 6.24341 | 6.16008 | 0.08333 | 108:65:111 |
| O | 7 | -1.763375 | 0.39429 | -0.000224 | | | | |
| C | 8 | -2.800369 | -0.589598 | 0.000232 | | | | |
| F | 9 | 0.116766 | 2.251437 | -0.000008 | | | | |
| H | 10 | 3.316139 | -0.930699 | 0.000182 | | | | |
| H | 11 | 2.57862 | 1.464685 | 0.000207 | | | | |
| H | 12 | -0.792961 | -2.168943 | -0.000239 | | | | |
| H | 13 | 1.599854 | -2.727755 | -0.000069 | | | | |
| H | 14 | -3.734618 | -0.031988 | -0.000278 | | | | |
| H | 15 | -2.750507 | -1.219218 | -0.892868 | | | | |
| H | 16 | -2.750829 | -1.217995 | 0.894177 | | | | |

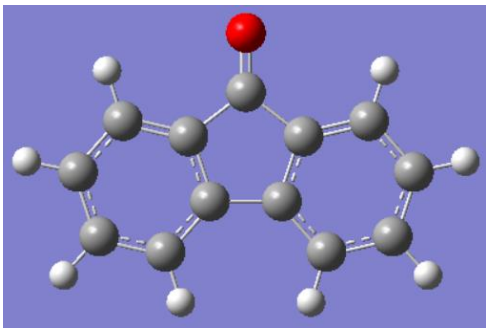


## Fluorenone

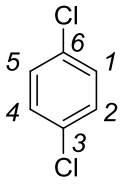
| Atom | No. | X | Y | Z | neutral pop | cation pop | f- | RGB color |
|---|---|---|---|---|---|---|---|---|
| C | 1 | -3.464482 | -0.066685 | 0.00001 | 6.24593 | 6.10276 | 0.14317 | 255:00:00 |
| C | 2 | -3.02693 | -1.392015 | 0.000004 | 6.20893 | 6.17721 | 0.03172 | 48:91:156 |
| C | 3 | -1.660952 | -1.708684 | -0.000006 | 6.23588 | 6.18207 | 0.05381 | 89:73:125 |
| C | 4 | -0.741884 | -0.668882 | -0.000007 | 6.01765 | 5.94323 | 0.07442 | 127:57:97 |
| C | 5 | -1.188548 | 0.666481 | -0.000003 | 6.12856 | 6.05053 | 0.07803 | 134:54:92 |
| C | 6 | -2.537913 | 0.98222 | 0.000004 | 6.19665 | 6.19085 | 0.0058 | 0:112:192 |
| C | 7 | 0.741884 | -0.668882 | -0.000007 | | | | |
| C | 8 | 1.188548 | 0.666481 | -0.000003 | | | | |
| C | 9 | 0 | 1.576164 | -0.000006 | | | | |
| C | 10 | 1.660952 | -1.708684 | -0.000007 | | | | |
| C | 11 | 3.02693 | -1.392015 | 0.000004 | | | | |
| C | 12 | 3.464482 | -0.066685 | 0.000011 | | | | |
| C | 13 | 2.537913 | 0.982221 | 0.000005 | | | | |
| O | 14 | 0 | 2.792501 | -0.000007 | | | | |
| H | 15 | -4.525551 | 0.148606 | 0.000021 | | | | |
| H | 16 | -3.756128 | -2.193077 | 0.000009 | | | | |
| H | 17 | -1.343091 | -2.743965 | -0.000011 | | | | |
| H | 18 | -2.863832 | 2.015329 | 0.000009 | | | | |
| H | 19 | 1.343091 | -2.743965 | -0.000012 | | | | |
| H | 20 | 3.756128 | -2.193077 | 0.000008 | | | | |
| H | 21 | 4.525551 | 0.148606 | 0.000022 | | | | |
| H | 22 | 2.863832 | 2.015329 | 0.00001 | | | | |

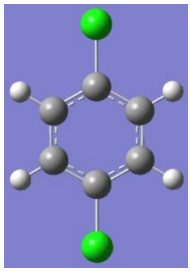


## 1,4-Dichlorobenzene

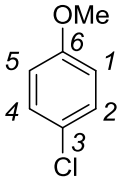
| Atom | No. | X | Y | Z | neutral pop. | cation pop. | f- | RGB code |
|---|---|---|---|---|---|---|---|---|
| C | 1 | -0.696474 | -1.213336 | -0.000036 | 6.25498 | 6.20651 | 0.04847 | 0:112:192 |
| C | 2 | 0.696474 | -1.213336 | 0 | 6.25498 | 6.20651 | 0.04847 | 0:112:192 |
| C | 3 | 1.37651 | 0 | 0.000038 | 6.02094 | 5.89246 | 0.12848 | 255:00:00 |
| C | 4 | 0.696474 | 1.213336 | 0.000047 | 6.25498 | 6.20651 | 0.04847 | 0:112:192 |
| C | 5 | -0.696474 | 1.213336 | 0.000014 | 6.25498 | 6.20651 | 0.04847 | 0:112:192 |
| C | 6 | -1.37651 | 0 | -0.000031 | 6.02094 | 5.89246 | 0.12848 | 255:00:00 |
| Cl | 7 | -3.13958 | 0 | -0.000085 | | | | |
| Cl | 8 | 3.13958 | 0 | 0.000071 | | | | |
| H | 9 | -1.239177 | -2.148648 | -0.000069 | | | | |
| H | 10 | 1.239177 | -2.148648 | -0.000002 | | | | |
| H | 11 | 1.239177 | 2.148648 | 0.000079 | | | | |
| H | 12 | -1.239177 | 2.148648 | 0.000022 | | | | |

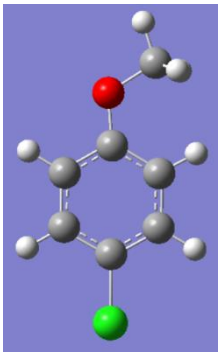


## 4-Chloroanisole

| Atom | No | X | Y | Z | neutral pop. | cation pop. | total f- | RGB color |
|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.797679 | -0.99734 | -0.00153 | 6.31747 | 6.23401 | 0.08346 | 138:52:88 |
| C | 2 | -0.59062 | -1.14466 | -0.00118 | 6.25568 | 6.21406 | 0.04162 | 50:91:155 |
| C | 3 | -1.40103 | -0.01937 | -0.00024 | 6.04578 | 5.90732 | 0.13846 | 255:00:00 |
| C | 4 | -0.85138 | 1.261271 | 0.000005 | 6.26128 | 6.2433 | 0.01798 | 0:112:192 |
| C | 5 | 0.528284 | 1.406969 | -0.00049 | 6.2745 | 6.17893 | 0.09557 | 164:40:69 |
| C | 6 | 1.364223 | 0.281188 | -0.00106 | 5.66925 | 5.56888 | 0.10037 | 174:36:61 |
| O | 7 | 2.700233 | 0.535292 | -0.00096 | | | | |
| Cl | 8 | -3.16102 | -0.20975 | 0.000878 | | | | |
| C | 9 | 3.603996 | -0.57207 | 0.002255 | | | | |
| H | 10 | 1.414708 | -1.88405 | -0.0022 | | | | |
| H | 11 | -1.0265 | -2.13458 | -0.00156 | | | | |
| H | 12 | -1.49132 | 2.133269 | 0.000755 | | | | |
| H | 13 | 0.977672 | 2.391617 | -0.00017 | | | | |
| H | 14 | 4.601996 | -0.13856 | 0.002292 | | | | |
| H | 15 | 3.47503 | -1.18804 | 0.897014 | | | | |
| H | 16 | 3.476992 | -1.19211 | -0.88994 | | | | |



## Electron affinity calculations

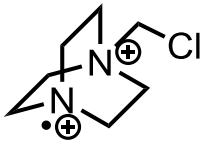
Adiabatic gas-phase electron affinities were calculated by performing independent geometry optimizations on the neutral amine (N electrons) and the corresponding aminium radical cation (N–1 electrons). The energy of the optimal geometry of the neutral species was subtracted from that of the cation to obtain the electron affinity. The computational methodology was validated by comparing computed and experimental electron affinities of amines for which experimental data is available: computed electron affinities of the dimethylamine radical cation and the piperazine radical cation were both within experimental error of the values measured by photoelectron spectroscopy.

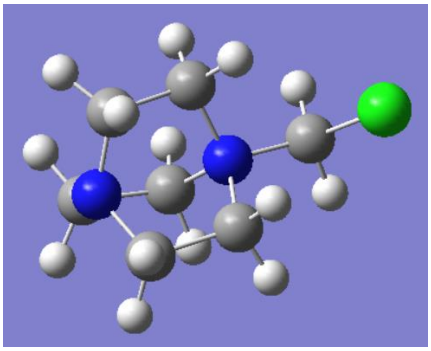
**$TEDA^{2+\cdot}$ aminium radical electron affinity**

| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| TEDA-radical | -844.269588 | 0.45723623 | 12.44186 |
| TEDA-amine | -844.7268242 | | |

**Aminium radical coordinates:**

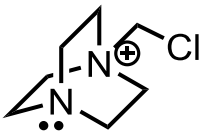
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -1.502796 | -1.053089 | 1.17534 |
| N | 2 | -2.081089 | -0.422573 | 0.001872 |
| C | 3 | -2.224674 | 1.020409 | 0.092382 |
| C | 4 | -0.018599 | -0.552881 | -1.192487 |
| C | 5 | -0.074436 | -0.385706 | 1.291968 |
| N | 6 | 0.213142 | 0.373179 | -0.000623 |
| C | 7 | -0.749673 | 1.55458 | -0.100918 |
| C | 8 | -1.560298 | -0.902954 | -1.265036 |
| C | 9 | 1.655183 | 0.933436 | -0.002893 |
| Cl | 10 | 2.870297 | -0.338254 | 0.000836 |
| H | 11 | -2.100747 | -0.8362 | 2.061814 |
| H | 12 | -1.436613 | -2.129349 | 1.023332 |
| H | 13 | -2.631327 | 1.293433 | 1.06508 |
| H | 14 | -2.875104 | 1.3901 | -0.70155 |
| H | 15 | 0.58468 | -1.44623 | -1.048307 |
| H | 16 | 0.3007 | -0.039896 | -2.09928 |
| H | 17 | -0.034077 | 0.329972 | 2.11247 |
| H | 18 | 0.691474 | -1.147074 | 1.429798 |
| H | 19 | -0.503325 | 2.276454 | 0.677428 |
| H | 20 | -0.617851 | 2.012672 | -1.08054 |
| H | 21 | -2.054477 | -0.390531 | -2.089246 |
| H | 22 | -1.704096 | -1.980554 | -1.353857 |
| H | 23 | 1.756835 | 1.543483 | 0.89278 |
| H | 24 | 1.756278 | 1.53703 | -0.903006 |

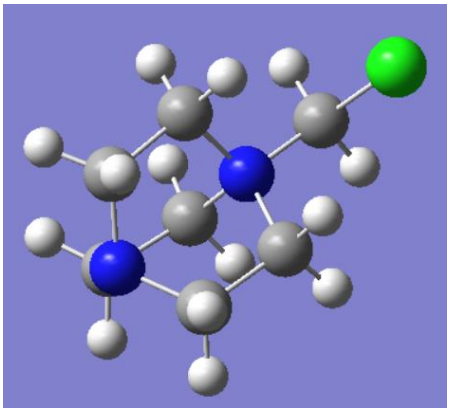


**Amine coordinates:**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -1.52039 | -0.97889 | 1.177463 |
| N | 2 | -2.20498 | -0.44473 | 0.001019 |
| C | 3 | -2.19114 | 1.01465 | 0.039047 |
| C | 4 | -0.03551 | -0.51737 | -1.21788 |
| C | 5 | -0.06416 | -0.42926 | 1.27014 |
| N | 6 | 0.22812 | 0.364061 | -6.1E-05 |
| C | 7 | -0.72967 | 1.554396 | -0.0538 |
| C | 8 | -1.54381 | -0.91583 | -1.21508 |
| C | 9 | 1.633869 | 0.914167 | -0.00103 |
| Cl | 10 | 2.889936 | -0.34304 | 0.000453 |
| H | 11 | -2.07823 | -0.705 | 2.073361 |
| H | 12 | -1.51093 | -2.06716 | 1.112894 |
| H | 13 | -2.65914 | 1.348855 | 0.965326 |
| H | 14 | -2.78159 | 1.403113 | -0.79108 |
| H | 15 | 0.626516 | -1.37658 | -1.13689 |
| H | 16 | 0.250636 | 0.062813 | -2.09572 |
| H | 17 | 0.074763 | 0.260884 | 2.103103 |
| H | 18 | 0.682059 | -1.21783 | 1.339754 |
| H | 19 | -0.47067 | 2.21366 | 0.774959 |
| H | 20 | -0.53251 | 2.072774 | -0.99243 |
| H | 21 | -2.05201 | -0.48833 | -2.07993 |
| H | 22 | -1.64019 | -1.99987 | -1.27725 |
| H | 23 | 1.752754 | 1.520072 | 0.893925 |
| H | 24 | 1.752484 | 1.517753 | -0.8976 |



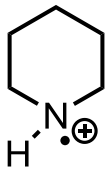
**Piperadine aminium radical electron affinity**

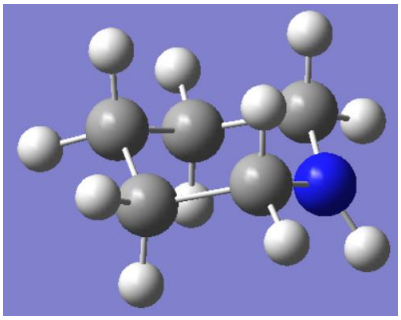
| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| piperidine-radical | -251.6866948 | 0.28432455 | 7.736755 |
| piperidine-amine | -251.9710194 | | |

The gas-phase adiabatic electron affinity of the piperazine aminium radical was measured by photoelectron spectroscopy to be 7.78±0.1 eV.[36] Therefore, the computed electron affinity is within experimental error.

**Aminium radical coordinates**

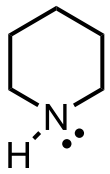
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -1.2674 | 0.722618 | -0.23782 |
| C | 2 | -1.23889 | -0.78513 | 0.236564 |
| N | 3 | 0.00005 | -1.35192 | -0.20833 |
| C | 4 | 1.23901 | -0.78503 | 0.236397 |
| C | 5 | 1.26733 | 0.722812 | -0.23765 |
| C | 6 | -0.00012 | 1.439559 | 0.224229 |
| H | 7 | -2.17206 | 1.160151 | 0.188847 |
| H | 8 | -1.36391 | 0.742646 | -1.32591 |
| H | 9 | -2.07727 | -1.34799 | -0.16937 |
| H | 10 | -1.26126 | -0.79989 | 1.330253 |
| H | 11 | 0.000001 | -1.93408 | -1.04411 |
| H | 12 | 2.077366 | -1.34771 | -0.16985 |
| H | 13 | 1.261626 | -0.80008 | 1.330083 |
| H | 14 | 2.171829 | 1.16041 | 0.189278 |
| H | 15 | 1.364063 | 0.743055 | -1.32572 |
| H | 16 | -0.00022 | 1.543908 | 1.31352 |
| H | 17 | -0.00016 | 2.454033 | -0.18903 |

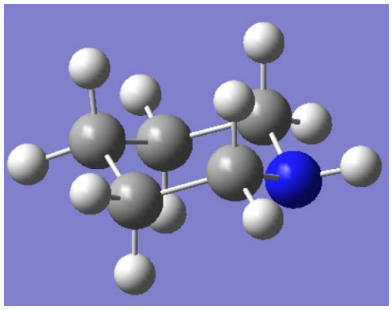


**Amine coordinates:**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -1.30906 | 0.629959 | -0.22682 |
| C | 2 | -1.16377 | -0.83228 | 0.206876 |
| N | 3 | 0.092106 | -1.37689 | -0.315 |
| C | 4 | 1.264356 | -0.66972 | 0.20663 |
| C | 5 | 1.213439 | 0.798713 | -0.22658 |
| C | 6 | -0.09743 | 1.454954 | 0.232918 |
| H | 7 | -2.23538 | 1.047365 | 0.178815 |
| H | 8 | -1.38159 | 0.662432 | -1.31864 |
| H | 9 | -1.99119 | -1.42774 | -0.18922 |
| H | 10 | -1.22068 | -0.88329 | 1.310862 |
| H | 11 | 0.158196 | -2.36509 | -0.09977 |
| H | 12 | 2.163568 | -1.14972 | -0.18989 |
| H | 13 | 1.327906 | -0.71324 | 1.310598 |
| H | 14 | 2.075799 | 1.335918 | 0.17951 |
| H | 15 | 1.281378 | 0.841131 | -1.31833 |
| H | 16 | -0.102 | 1.521478 | 1.327989 |
| H | 17 | -0.16598 | 2.479185 | -0.14513 |



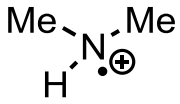
**Dimethylamine radical cation**

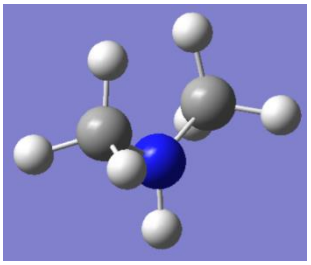
| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| dimethylamine-radical | -134.9054068 | 0.29774864 | 8.102038 |
| dimethylamine-amine | -135.2031554 | | |

The gas-phase adiabatic electron affinity of the piperazine aminium radical was measured by photoelectron spectroscopy to be 8.08±0.1 eV.[36] Therefore, the computed electron affinity is within experimental error.

**Aminium radical coordinates:**

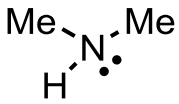
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | 1.279205 | 0.207143 | -0.0037 |
| N | 2 | 0.000034 | -0.444643 | -0.00405 |
| C | 3 | -1.278752 | 0.20804 | 0.002496 |
| H | 4 | 1.166922 | 1.278438 | -0.150269 |
| H | 5 | 1.91543 | -0.240072 | -0.777665 |
| H | 6 | 1.776845 | 0.007374 | 0.959843 |
| H | 7 | -0.000709 | -1.466021 | 0.007209 |
| H | 8 | -1.832183 | -0.084906 | -0.903177 |
| H | 9 | -1.867394 | -0.161104 | 0.854054 |
| H | 10 | -1.161861 | 1.287694 | 0.045576 |

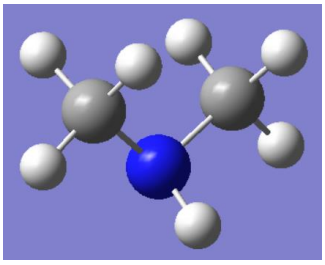


**Amine coordinates:**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | 1.215605 | -0.222816 | 0.020462 |
| N | 2 | 0 | 0.563444 | -0.147187 |
| C | 3 | -1.215605 | -0.222816 | 0.020462 |
| H | 4 | 1.280145 | -0.965613 | -0.780483 |
| H | 5 | 1.27918 | -0.76513 | 0.980323 |
| H | 6 | 2.088595 | 0.428644 | -0.063204 |
| H | 7 | 0 | 1.333879 | 0.511497 |
| H | 8 | -1.279179 | -0.765131 | 0.980323 |
| H | 9 | -2.088595 | 0.428644 | -0.063203 |
| H | 10 | -1.280146 | -0.965612 | -0.780484 |



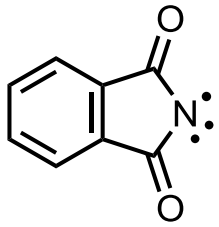



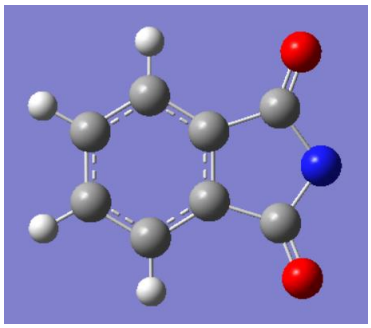
**Phthalimide radical**

| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| phthalimide-radical | -512.5232453 | 0.13462626 | 3.663315 |
| phthalimide-anion | -512.6578715 | | |

**Radical coordinates**

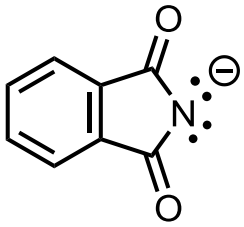
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | 2.519142 | 0.702378 | 0.000171 |
| C | 2 | 2.519141 | -0.70238 | 0.000186 |
| C | 3 | 1.326846 | -1.42438 | 0.009011 |
| C | 4 | 0.142758 | -0.69785 | 0.012201 |
| C | 5 | 0.142758 | 0.697852 | 0.012195 |
| C | 6 | 1.326847 | 1.424379 | 0.008988 |
| C | 7 | -1.27998 | -1.15123 | 0.01175 |
| N | 8 | -2.09713 | 0.000001 | 0.229165 |
| C | 9 | -1.27998 | 1.151234 | 0.011756 |
| O | 10 | -1.71191 | 2.269465 | -0.12492 |
| O | 11 | -1.71192 | -2.26946 | -0.12494 |
| H | 12 | 3.465318 | 1.2294 | -0.01006 |
| H | 13 | 3.465317 | -1.2294 | -0.01003 |
| H | 14 | 1.317325 | -2.50664 | 0.008664 |
| H | 15 | 1.317326 | 2.506639 | 0.008622 |

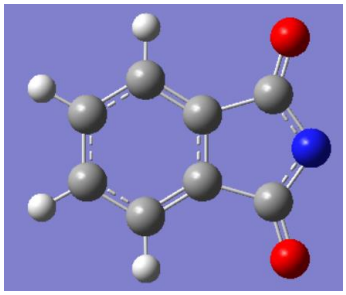




**Anion coordinates**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -2.53043 | 0.698872 | -0.000052 |
| C | 2 | -2.53041 | -0.69904 | 0.000581 |
| C | 3 | -1.32437 | -1.41527 | 0.000104 |
| C | 4 | -0.14256 | -0.69334 | -0.000595 |
| C | 5 | -0.14259 | 0.693361 | -0.00063 |
| C | 6 | -1.32443 | 1.415172 | -0.000413 |
| C | 7 | 1.326985 | -1.11371 | -0.000106 |
| N | 8 | 2.115615 | -4.7E-05 | 0.000547 |
| C | 9 | 1.32692 | 1.113913 | -0.000157 |
| O | 10 | 1.675405 | 2.293616 | 0.00047 |
| O | 11 | 1.675676 | -2.29351 | -0.000191 |
| H | 12 | -3.47668 | 1.231066 | -0.000013 |
| H | 13 | -3.47664 | -1.23125 | 0.001487 |
| H | 14 | -1.30962 | -2.49976 | 0.000585 |
| H | 15 | -1.30973 | 2.499652 | -0.000515 |



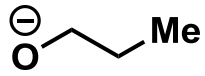


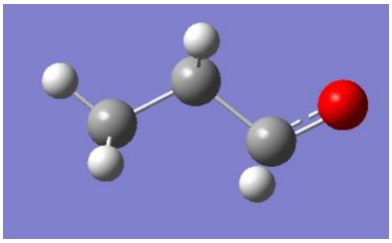
**Propyloxyl radical**

| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| oxyl-radical | -193.7386246 | 0.03826599 | 1.041255854 |
| oxyl-adiab | -193.7768906 | | |

**Oxide coordinates**

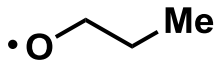
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | 0.763732 | -0.43796 | -0.00011 |
| C | 2 | -0.47058 | 0.544986 | -0.0001 |
| O | 3 | 1.937513 | 0.150841 | 0.000133 |
| C | 4 | -1.83673 | -0.15272 | 0.00009 |
| H | 5 | 0.534858 | -1.13448 | 0.889117 |
| H | 6 | 0.535038 | -1.13425 | -0.88954 |
| H | 7 | -0.37396 | 1.193723 | -0.88044 |
| H | 8 | -0.37382 | 1.193933 | 0.880077 |
| H | 9 | -2.68559 | 0.543467 | -0.0005 |
| H | 10 | -1.93777 | -0.79695 | 0.881912 |
| H | 11 | -1.93743 | -0.79803 | -0.88099 |

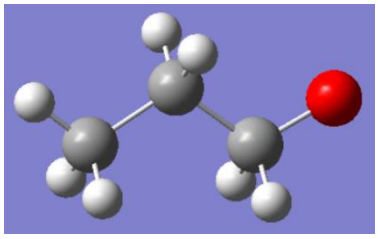


**Radical coordinates**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | 0.705869 | -0.42319 | 0.001047 |
| C | 2 | -0.47505 | 0.550545 | 0.000715 |
| O | 3 | 1.947649 | 0.143382 | -0.00068 |
| C | 4 | -1.82722 | -0.1683 | -0.00062 |
| H | 5 | 0.653282 | -1.11833 | 0.864516 |
| H | 6 | 0.654521 | -1.11517 | -0.86529 |
| H | 7 | -0.3879 | 1.198174 | -0.87669 |
| H | 8 | -0.38937 | 1.197086 | 0.879089 |
| H | 9 | -2.65307 | 0.545654 | -0.00146 |
| H | 10 | -1.94108 | -0.80444 | 0.88226 |
| H | 11 | -1.93921 | -0.80437 | -0.88381 |



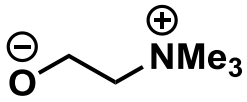



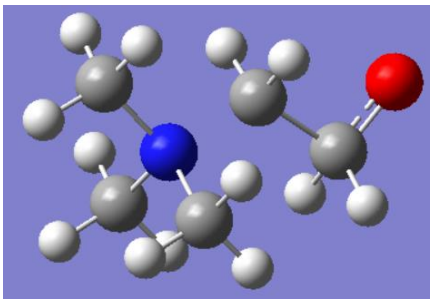
**2-(trimethylammonium)ethyl-oxyl radical**

| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| oxyl-ium-radical | -328.0938967 | 0.20405086 | 5.552427951 |
| oxyl-ium-adiab | -328.2979475 | | |

**Oxide coordinates**

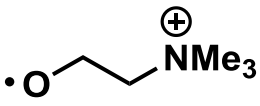
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -1.86801 | -0.435 | 0.000092 |
| C | 2 | -0.65391 | 0.552462 | -0.00081 |
| O | 3 | -2.88665 | 0.390796 | -0.00031 |
| N | 4 | 0.878361 | 0.023995 | -3.5E-05 |
| C | 5 | 1.814541 | 1.18381 | -0.00172 |
| C | 6 | 1.097568 | -0.80077 | 1.224285 |
| C | 7 | 1.097998 | -0.80456 | -1.2217 |
| H | 8 | -1.7524 | -1.12517 | -0.89084 |
| H | 9 | -1.75215 | -1.12366 | 0.892317 |
| H | 10 | -0.72042 | 1.171774 | 0.893078 |
| H | 11 | -0.72017 | 1.170197 | -0.8958 |
| H | 12 | 2.850333 | 0.834773 | 0.006975 |
| H | 13 | 1.633037 | 1.779764 | -0.89469 |
| H | 14 | 1.62184 | 1.790948 | 0.881286 |
| H | 15 | 2.121396 | -1.18021 | 1.235152 |
| H | 16 | 0.382097 | -1.61954 | 1.227742 |
| H | 17 | 0.923361 | -0.17734 | 2.099921 |
| H | 18 | 0.913328 | -0.18672 | -2.09913 |
| H | 19 | 2.125133 | -1.17488 | -1.23652 |
| H | 20 | 0.390134 | -1.62991 | -1.21771 |

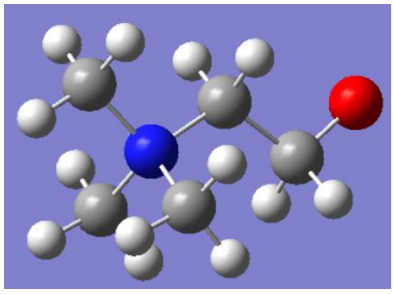


**Radical coordinates**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -1.76307 | -0.36881 | -6.9E-05 |
| C | 2 | -0.57413 | 0.615749 | -0.00826 |
| O | 3 | -2.93211 | 0.32905 | 0.000177 |
| N | 4 | 0.830879 | 0.019991 | -2.4E-05 |
| C | 5 | 1.820594 | 1.161259 | -0.02513 |
| C | 6 | 1.061778 | -0.79366 | 1.248917 |
| C | 7 | 1.055773 | -0.84322 | -1.21627 |
| H | 8 | -1.77203 | -1.0454 | -0.87245 |
| H | 9 | -1.76672 | -1.03902 | 0.87736 |
| H | 10 | -0.64592 | 1.25885 | 0.869294 |
| H | 11 | -0.64331 | 1.240845 | -0.89896 |
| H | 12 | 2.829461 | 0.752275 | -0.01506 |
| H | 13 | 1.664044 | 1.74477 | -0.93036 |
| H | 14 | 1.662635 | 1.785398 | 0.852353 |
| H | 15 | 2.095226 | -1.13588 | 1.257254 |
| H | 16 | 0.396794 | -1.65407 | 1.25459 |
| H | 17 | 0.872429 | -0.16701 | 2.118828 |
| H | 18 | 0.85082 | -0.25572 | -2.10966 |
| H | 19 | 2.092315 | -1.17604 | -1.22201 |
| H | 20 | 0.399284 | -1.70926 | -1.17759 |



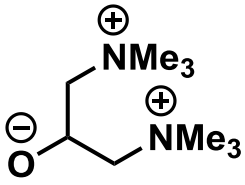



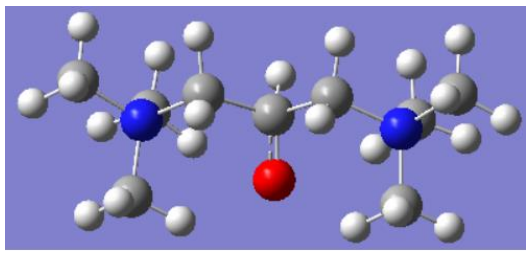
**2-(trimethylammonium)-1-(trimethylammoniummethyl)ethyl-oxyl radical**

| | B3LYP Energy (Hartrees) | EA (Hartrees) | EA (eV) |
|---|---|---|---|
| oxyl-diium-radical | -541.0113122 | 0.37791639 | 10.28348289 |
| oxyl-diium-adiab | -541.3892286 | | |

**Oxide coordinates**

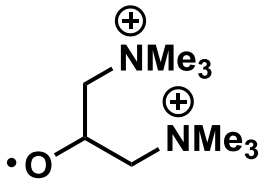
| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | 0.003972 | 0.082421 | 0.33451 |
| O | 2 | 0.001594 | -1.17519 | -0.06517 |
| C | 3 | 1.258936 | 0.88764 | -0.17453 |
| N | 4 | 2.535536 | 0.107476 | -0.02127 |
| C | 5 | 3.714939 | 1.054572 | -0.11223 |
| C | 6 | 2.593767 | -0.6241 | 1.299861 |
| C | 7 | 2.641502 | -0.90692 | -1.13822 |
| C | 8 | -1.25427 | 0.898854 | -0.15155 |
| N | 9 | -2.55073 | 0.111279 | -0.0254 |
| C | 10 | -3.70511 | 1.051243 | -0.11679 |
| C | 11 | -2.6426 | -0.90787 | -1.14078 |
| C | 12 | -2.60063 | -0.62004 | 1.302508 |
| H | 13 | -0.00151 | 0.227491 | 1.424172 |
| H | 14 | 1.184025 | 1.150219 | -1.22523 |
| H | 15 | 1.383749 | 1.83829 | 0.414384 |
| H | 16 | 4.635672 | 0.47366 | -0.09962 |
| H | 17 | 3.643194 | 1.610744 | -1.04393 |
| H | 18 | 3.688909 | 1.733993 | 0.733137 |
| H | 19 | 3.569584 | -1.1009 | 1.389718 |
| H | 20 | 1.792942 | -1.34699 | 1.292212 |
| H | 21 | 2.468739 | 0.106017 | 2.108177 |
| H | 22 | 2.736597 | -0.37066 | -2.08172 |
| H | 23 | 3.529742 | -1.51996 | -0.97034 |
| H | 24 | 1.718505 | -1.48611 | -1.10079 |
| H | 25 | -1.38436 | 1.824445 | 0.406385 |
| H | 26 | -1.18069 | 1.153561 | -1.23884 |
| H | 27 | -4.63524 | 0.469773 | -0.10575 |
| H | 28 | -3.69079 | 1.731341 | 0.730114 |
| H | 29 | -3.64083 | 1.610057 | -1.04619 |
| H | 30 | -3.52584 | -1.52244 | -0.96826 |
| H | 31 | -1.7115 | -1.49518 | -1.09734 |
| H | 32 | -2.73266 | -0.377 | -2.07892 |
| H | 33 | -2.46751 | 0.109132 | 2.105681 |
| H | 34 | -3.56259 | -1.09468 | 1.388782 |
| H | 35 | -1.78767 | -1.3494 | 1.295525 |

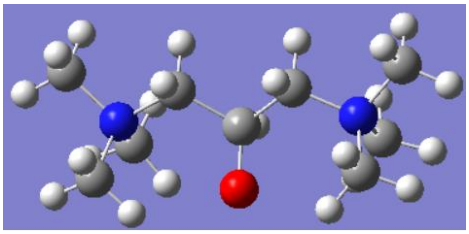


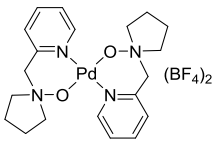
**Radical coordinates**

| Atom | No. | X | Y | Z |
|---|---|---|---|---|
| C | 1 | -0.0057 | -0.03555 | 0.177828 |
| O | 2 | -0.00119 | -1.36205 | -0.09346 |
| C | 3 | 1.26408 | 0.748281 | -0.31241 |
| N | 4 | 2.627074 | 0.12118 | -0.01488 |
| C | 5 | 3.681719 | 1.185113 | -0.25827 |
| C | 6 | 2.727635 | -0.34261 | 1.435245 |
| C | 7 | 2.921764 | -1.06837 | -0.93445 |
| C | 8 | -1.27162 | 0.744921 | -0.31466 |
| N | 9 | -2.61992 | 0.122391 | -0.00592 |
| C | 10 | -3.67365 | 1.179757 | -0.26033 |
| C | 11 | -2.91034 | -1.05432 | -0.92768 |
| C | 12 | -2.72158 | -0.34284 | 1.426886 |
| H | 13 | -0.00362 | -0.01253 | 1.288262 |
| H | 14 | 1.222717 | 0.86727 | -1.38614 |
| H | 15 | 1.262237 | 1.729523 | 0.148307 |
| H | 16 | 4.631522 | 0.741642 | -0.12027 |
| H | 17 | 3.56892 | 1.542206 | -1.26471 |
| H | 18 | 3.528728 | 1.99126 | 0.448004 |
| H | 19 | 3.740306 | -0.63678 | 1.620674 |
| H | 20 | 2.060791 | -1.1876 | 1.597292 |
| H | 21 | 2.462091 | 0.495955 | 2.094908 |
| H | 22 | 2.882601 | -0.70528 | -1.94496 |
| H | 23 | 3.88048 | -1.42501 | -0.69407 |
| H | 24 | 2.164008 | -1.82908 | -0.77142 |
| H | 25 | -1.27056 | 1.725545 | 0.143449 |
| H | 26 | -1.22763 | 0.864193 | -1.38953 |
| H | 27 | -4.65455 | 0.731339 | -0.12331 |
| H | 28 | -3.53634 | 1.990987 | 0.444053 |
| H | 29 | -3.57467 | 1.540283 | -1.28085 |
| H | 30 | -3.90544 | -1.44012 | -0.69204 |
| H | 31 | -2.1616 | -1.83909 | -0.76828 |
| H | 32 | -2.88715 | -0.71096 | -1.95797 |
| H | 33 | -2.46918 | 0.499853 | 2.091176 |
| H | 34 | -3.76013 | -0.6421 | 1.622159 |
| H | 35 | -2.06798 | -1.18634 | 1.595646 |



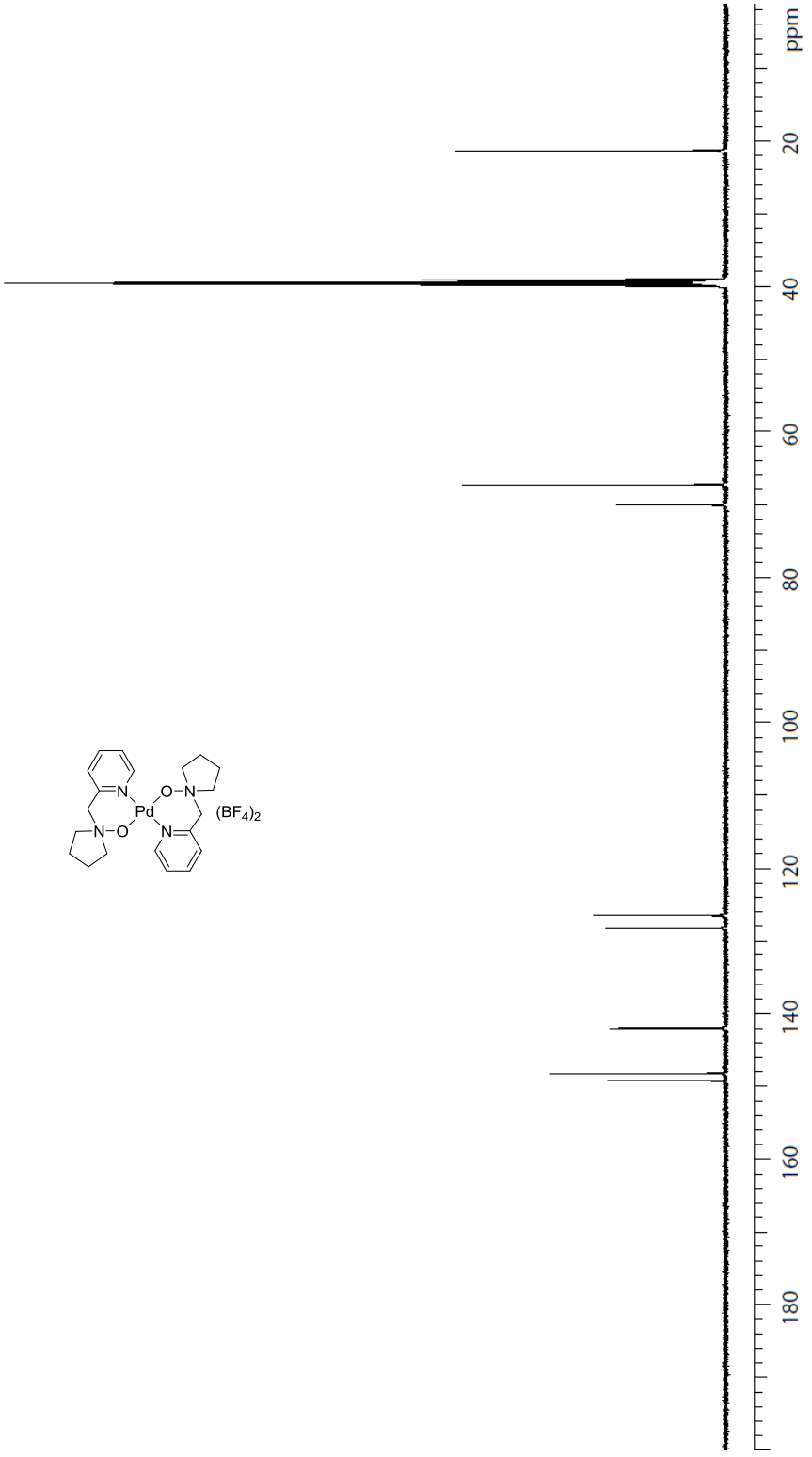
## Spectroscopic Data



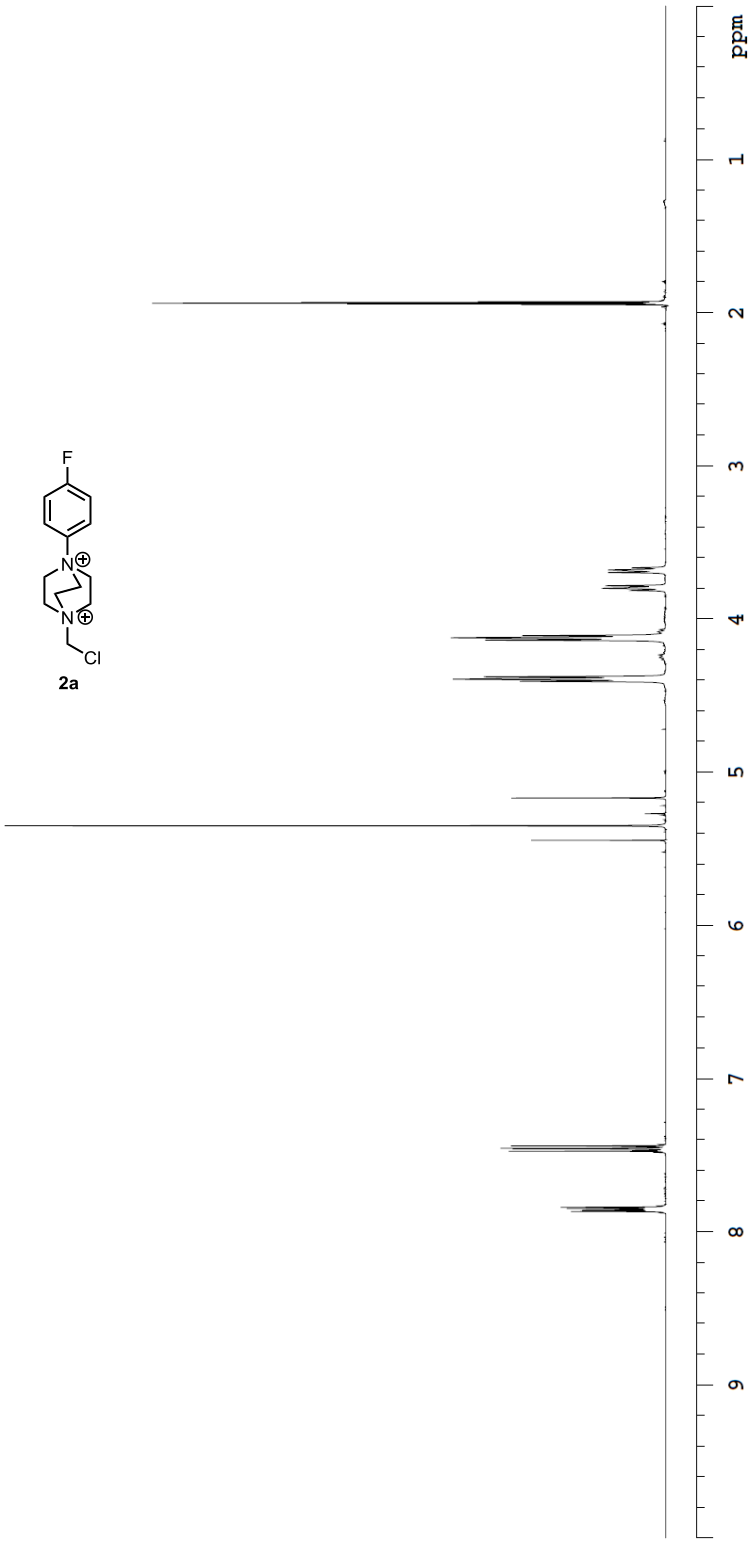




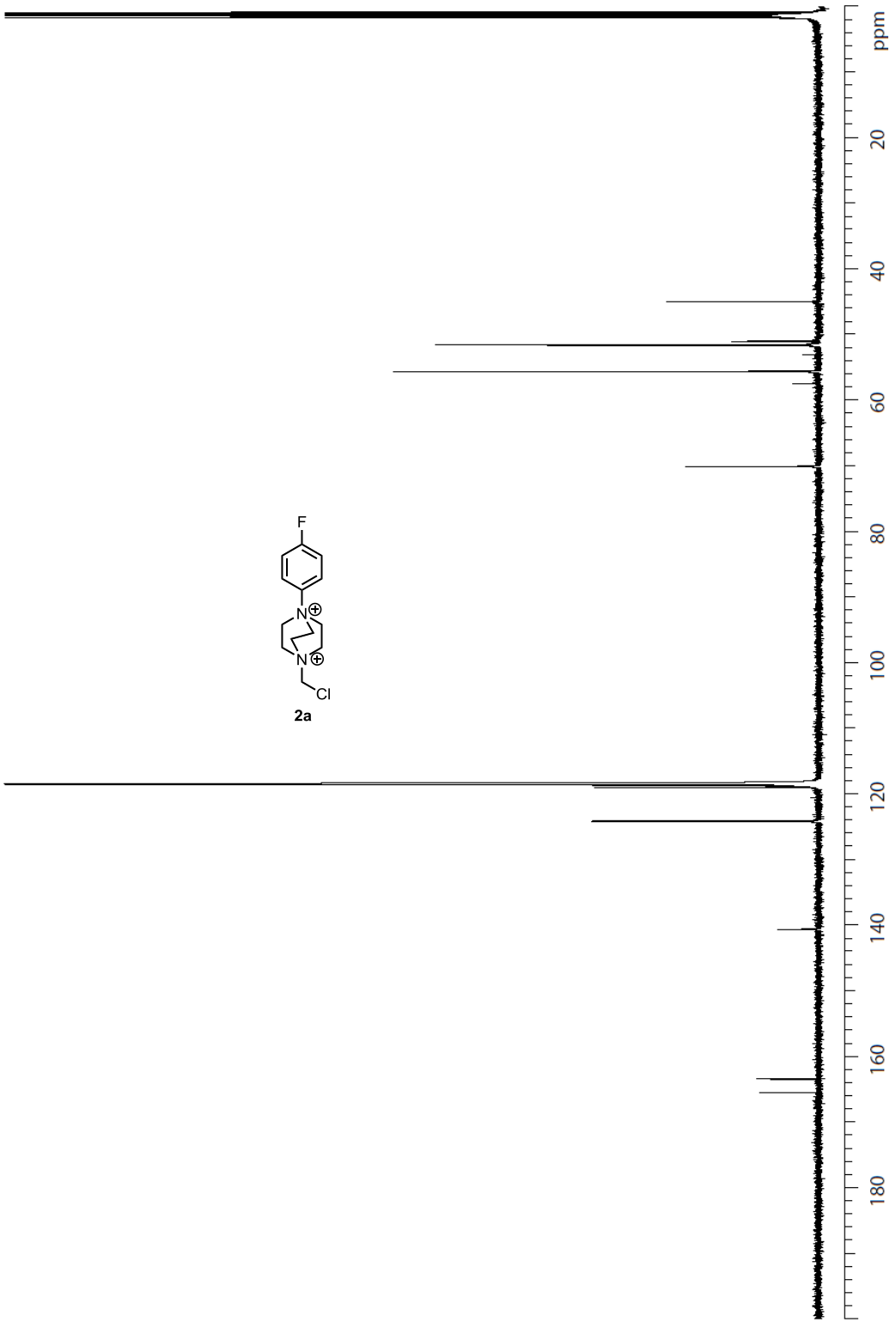
$^{1}$H NMR (DMSO, 23 ºC) of palladium complex **1**



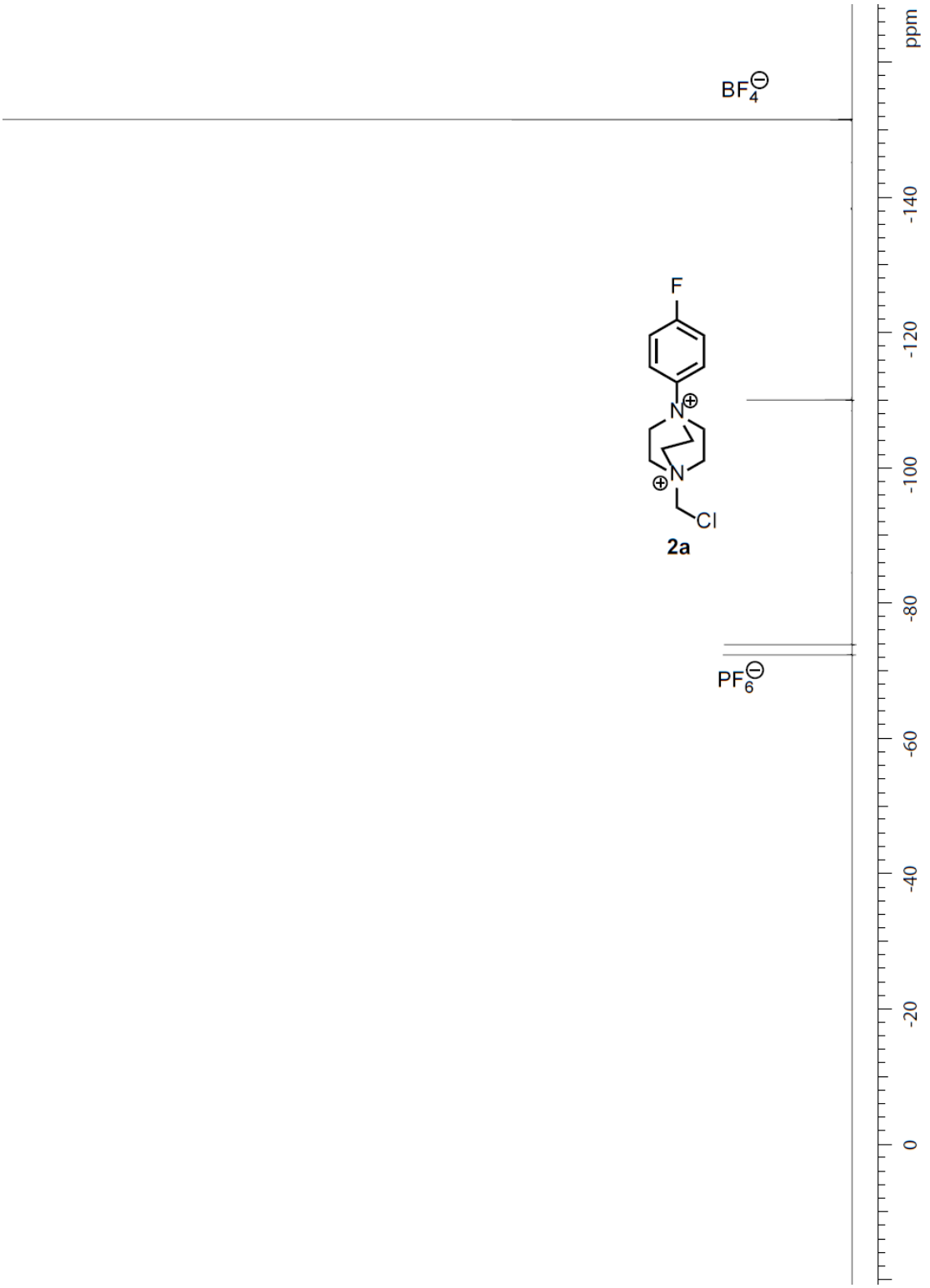

$^{13}$C NMR (DMSO, 23 ºC) of palladium complex **1**



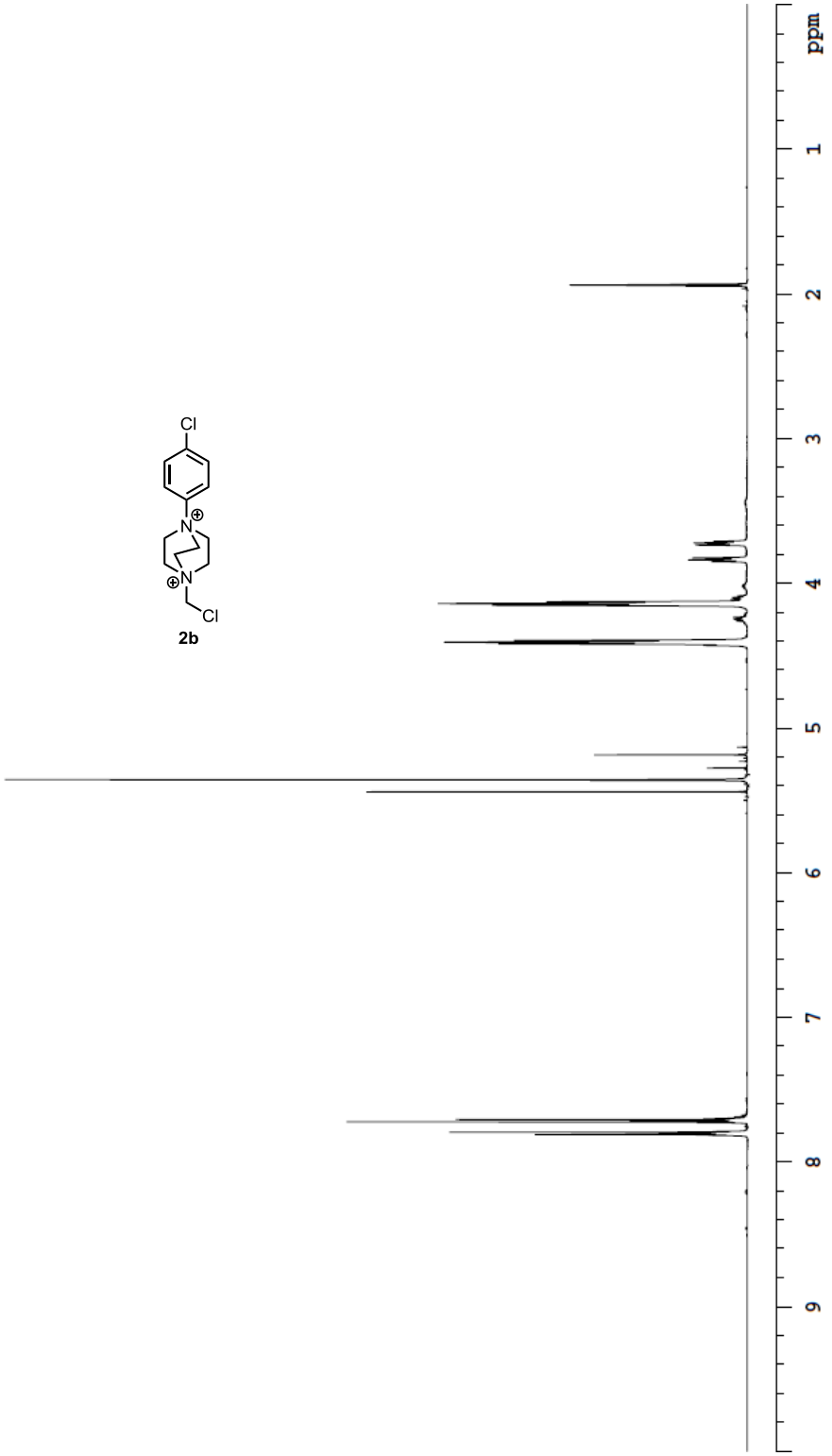

$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2a**



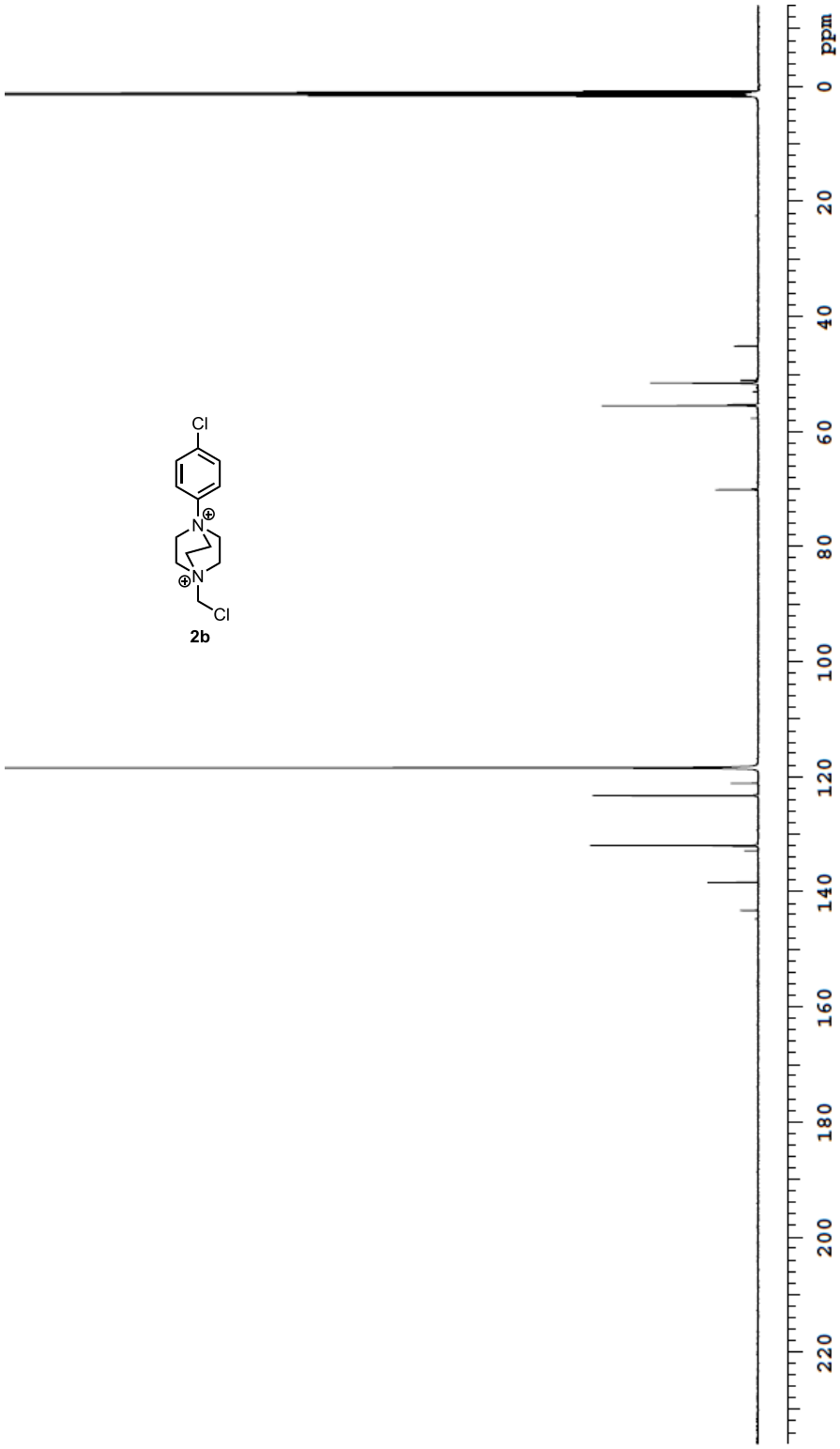

$^{13}$C NMR ($CD_3CN$, 23 ºC) of **2a**



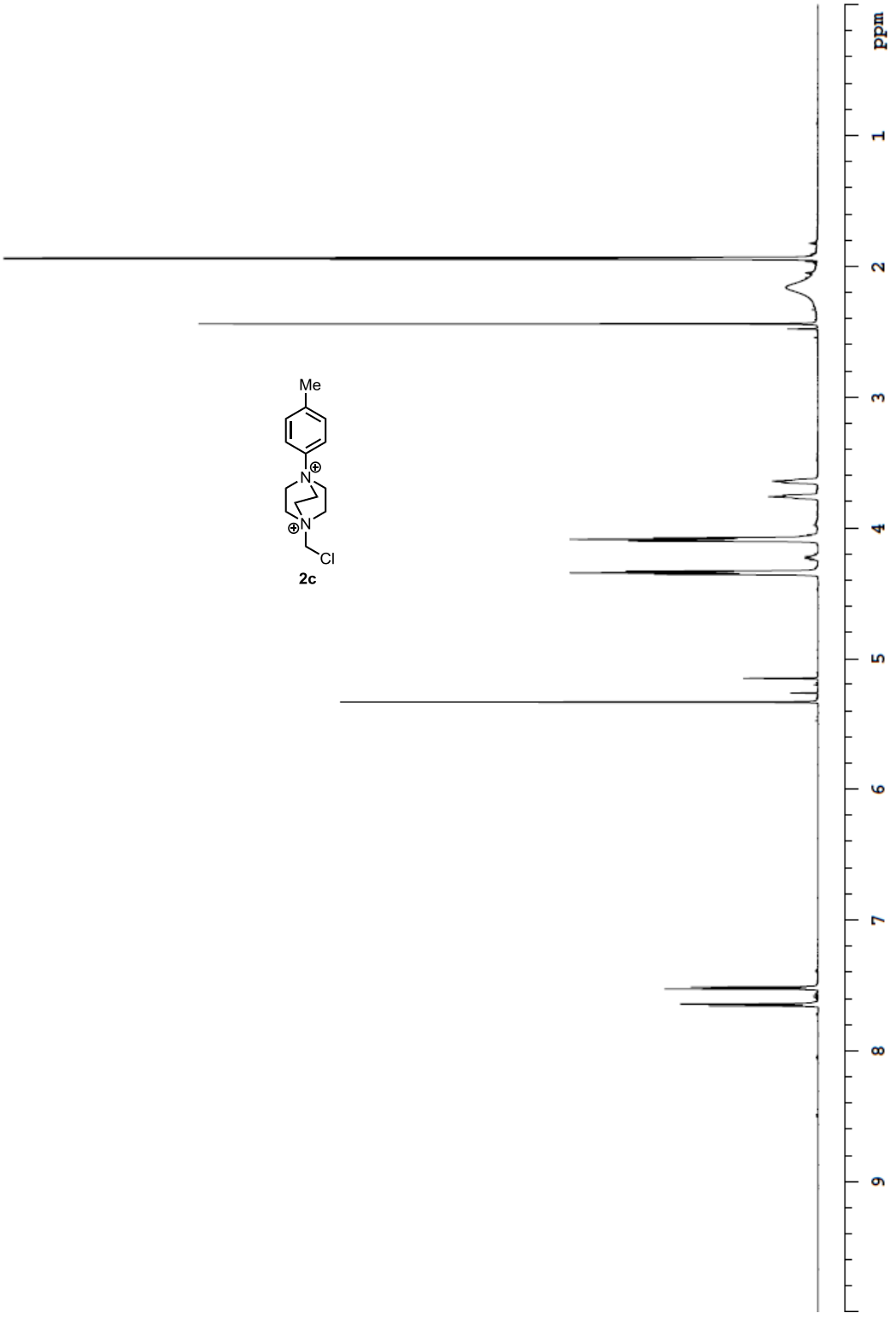

$^{19}$F NMR ($CD_3CN$, 23 ºC) of **2a**



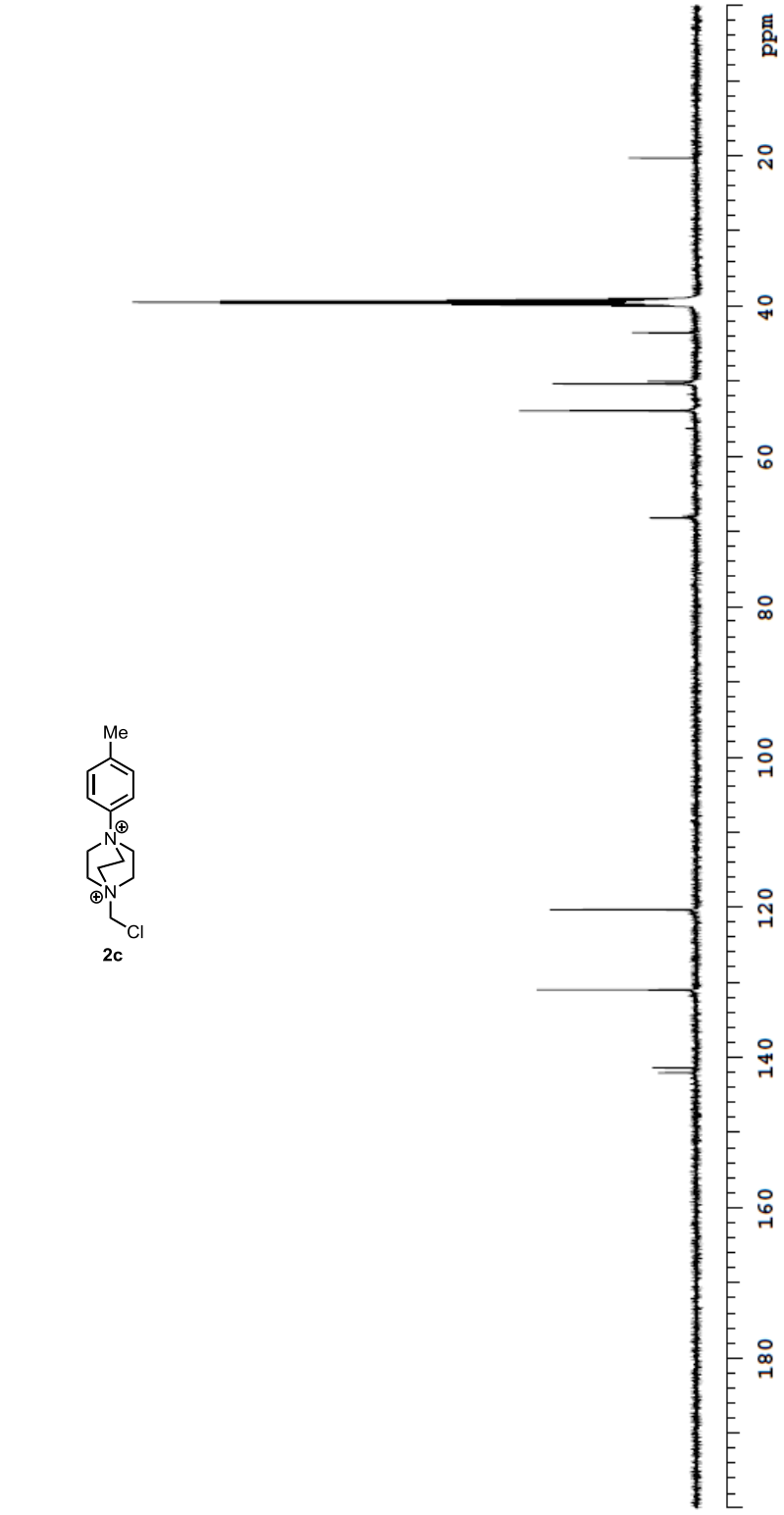

$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2b**



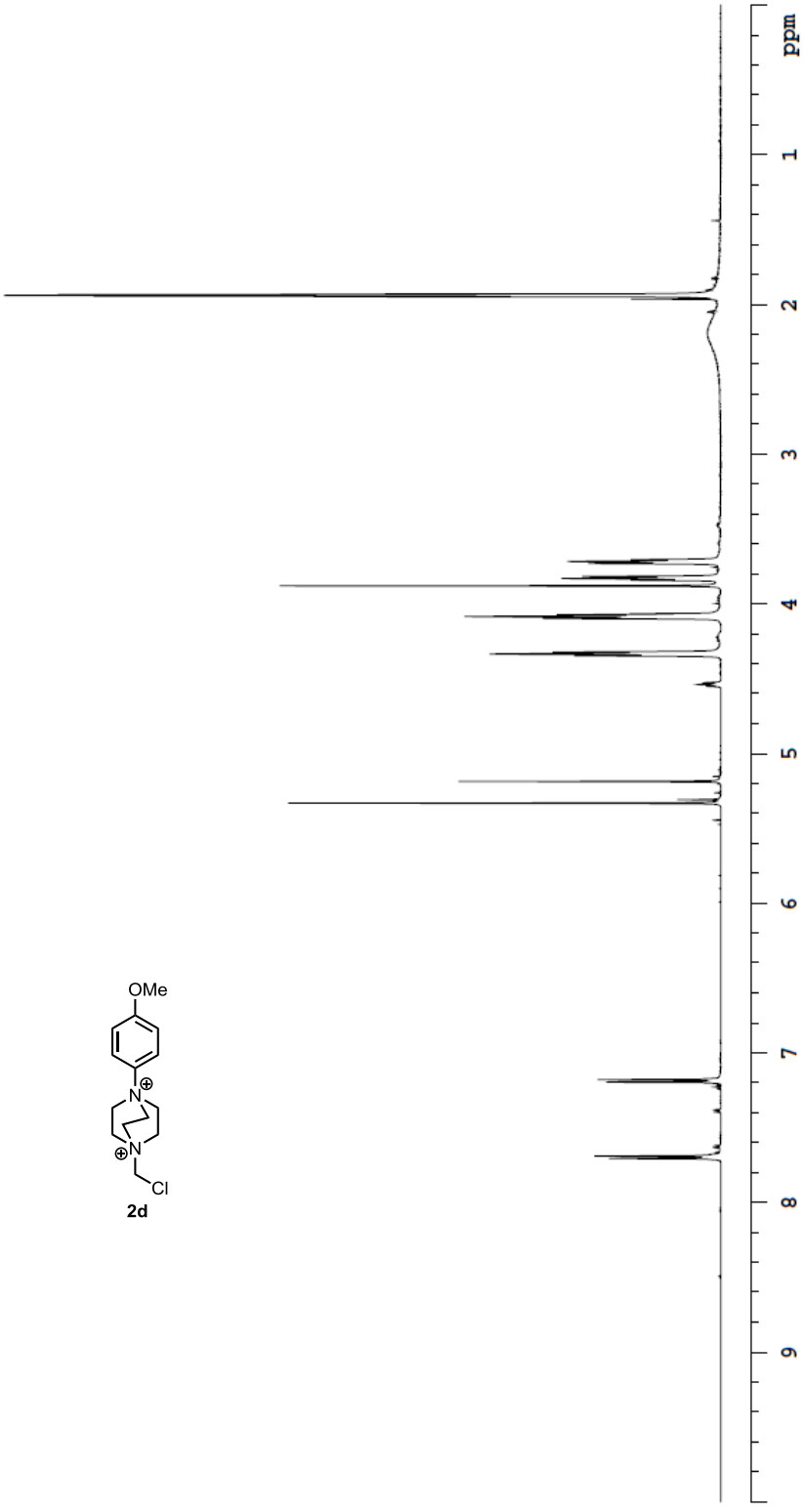

$^{13}C$ NMR ($CD_3CN$, 23 ºC) of **2b**




$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2c**

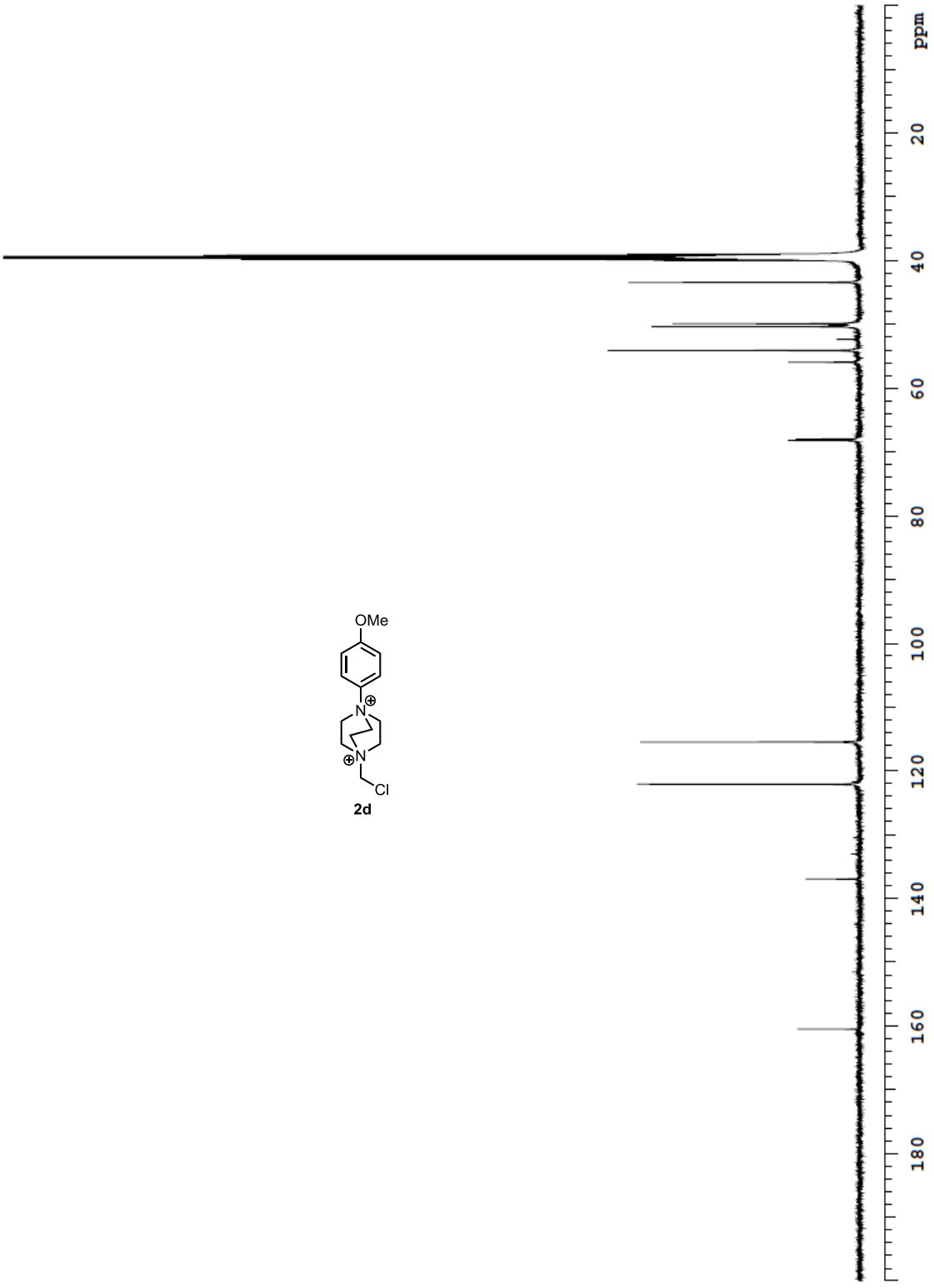



$^{13}$C NMR (DMSO, 23 ºC) of **2c**

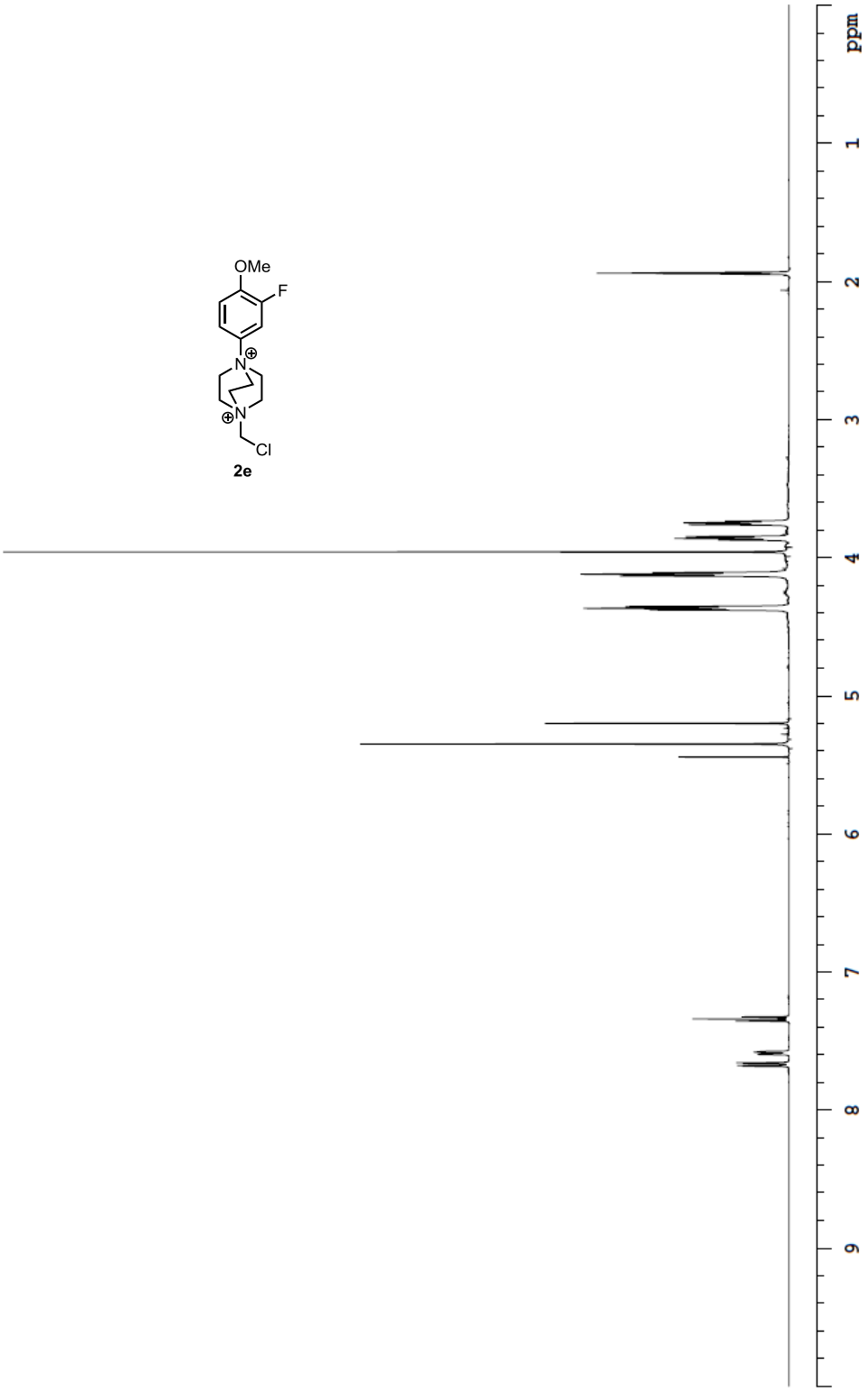



**2d**

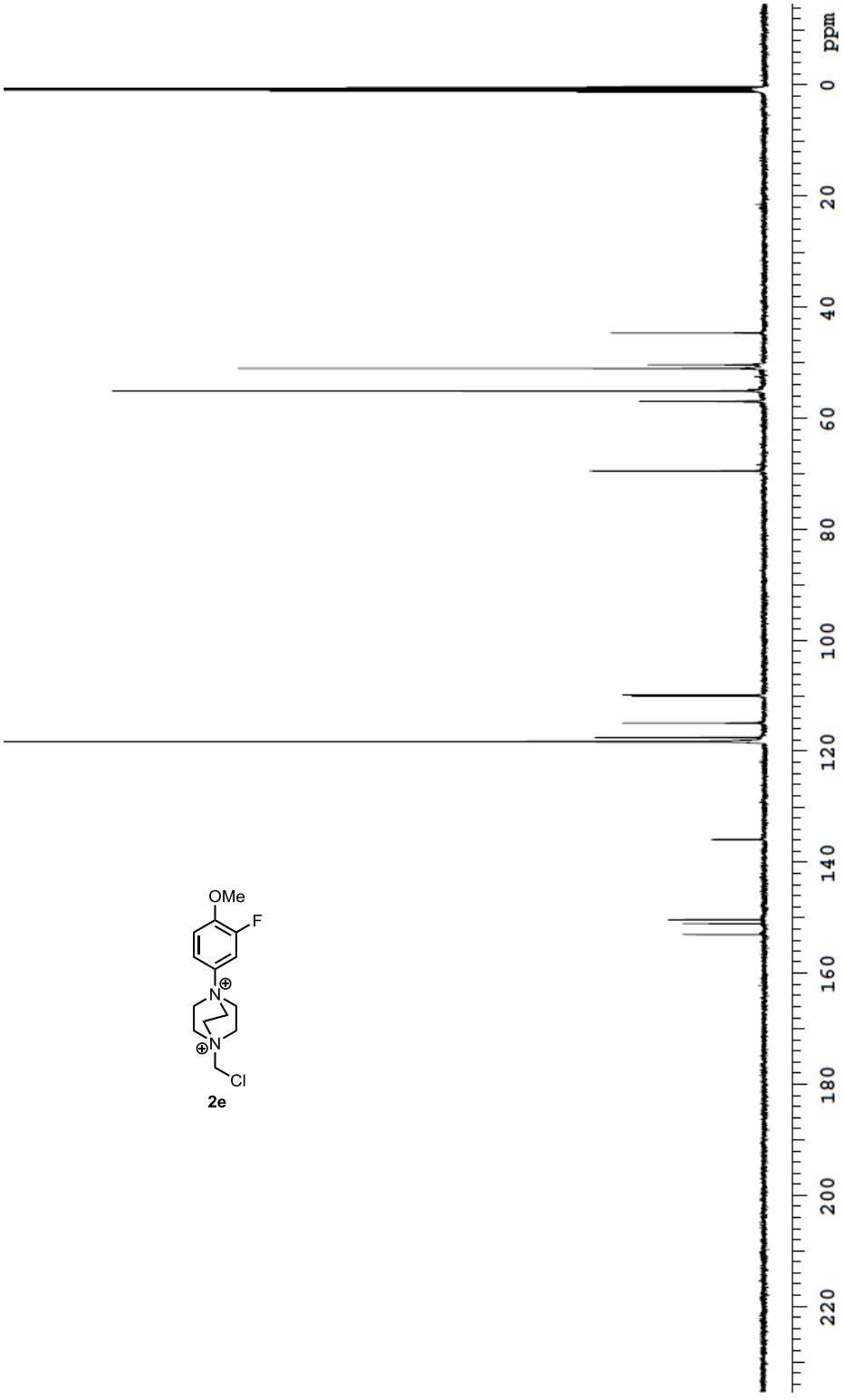
$^1$H NMR ($CD_3CN$, 23 ºC) of **2d**



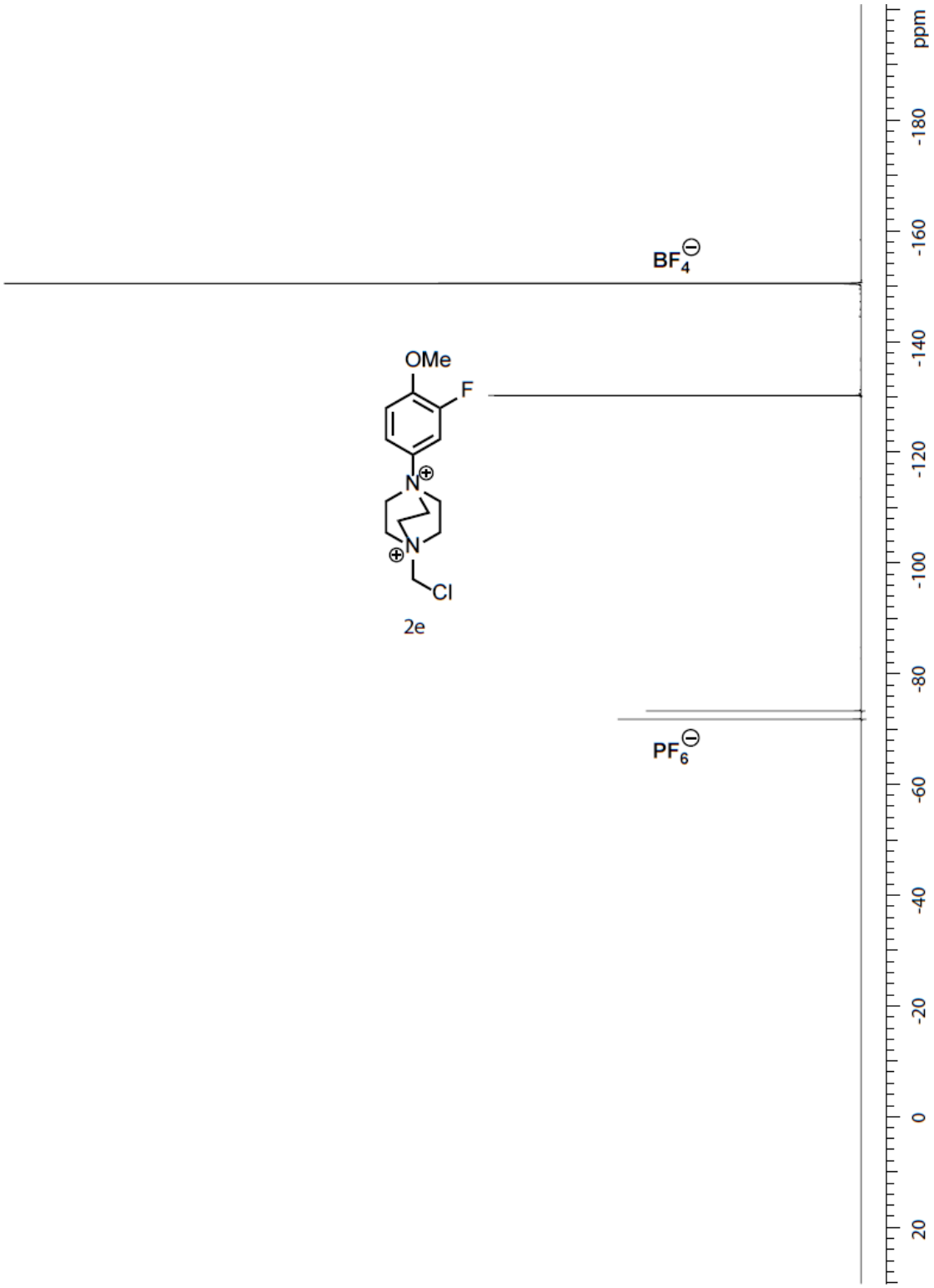

$^{13}$C NMR (DMSO, 23 ºC) of **2d**




$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2e**

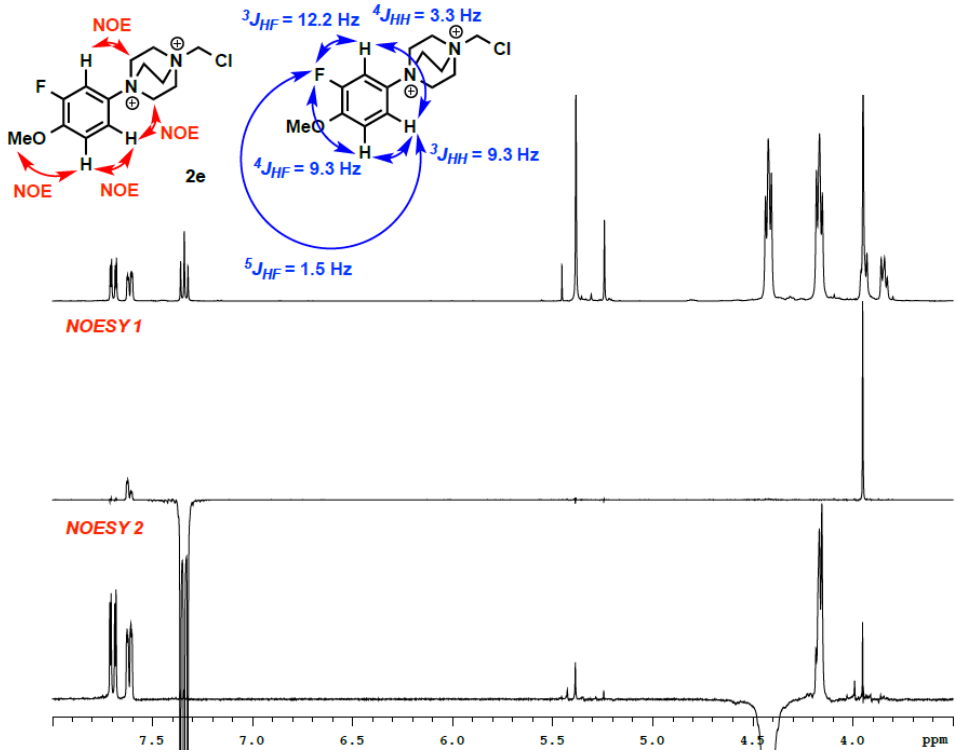


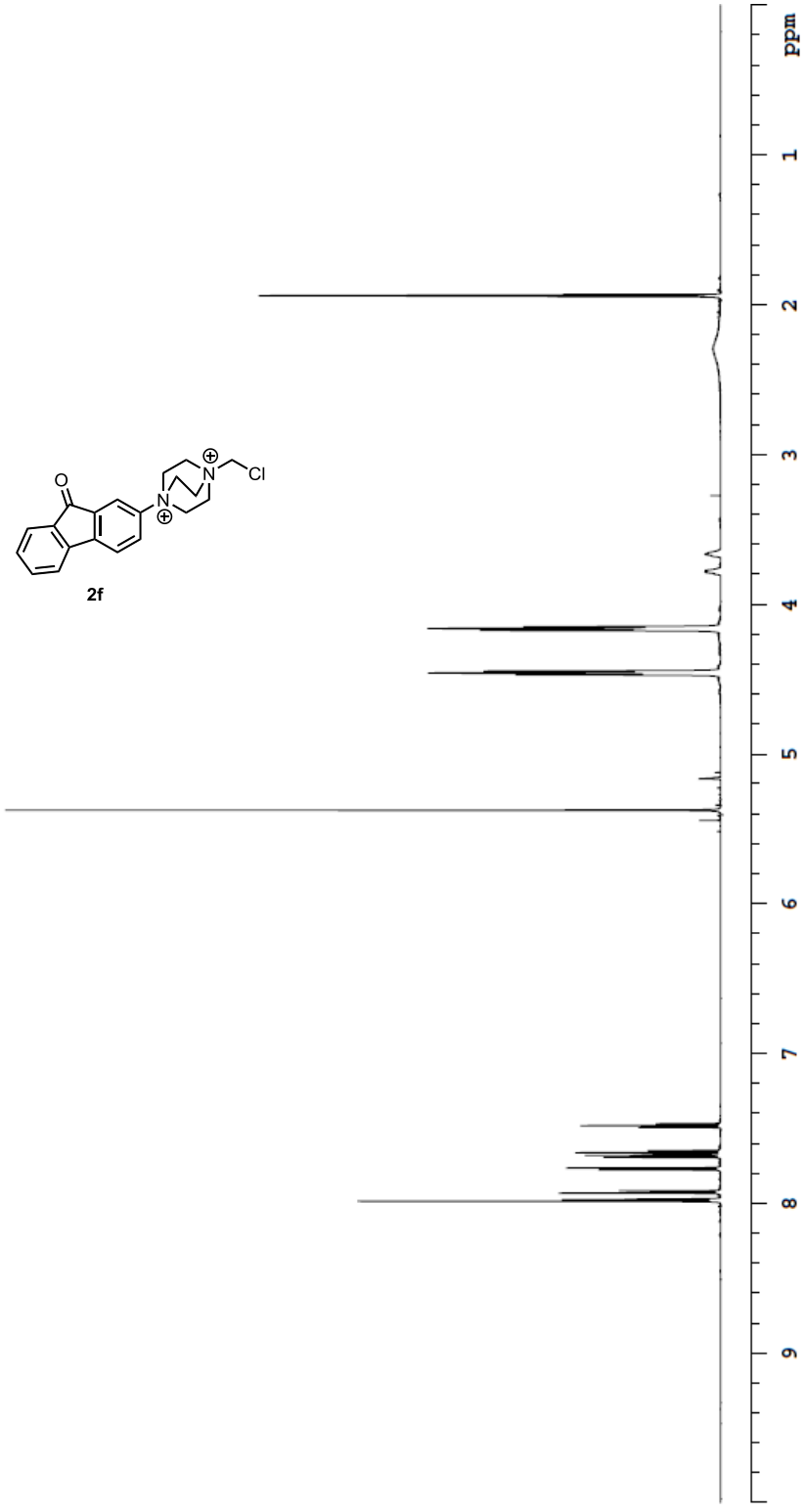

$^{13}$C NMR ($CD_3CN$, 23 ºC) of **2e**



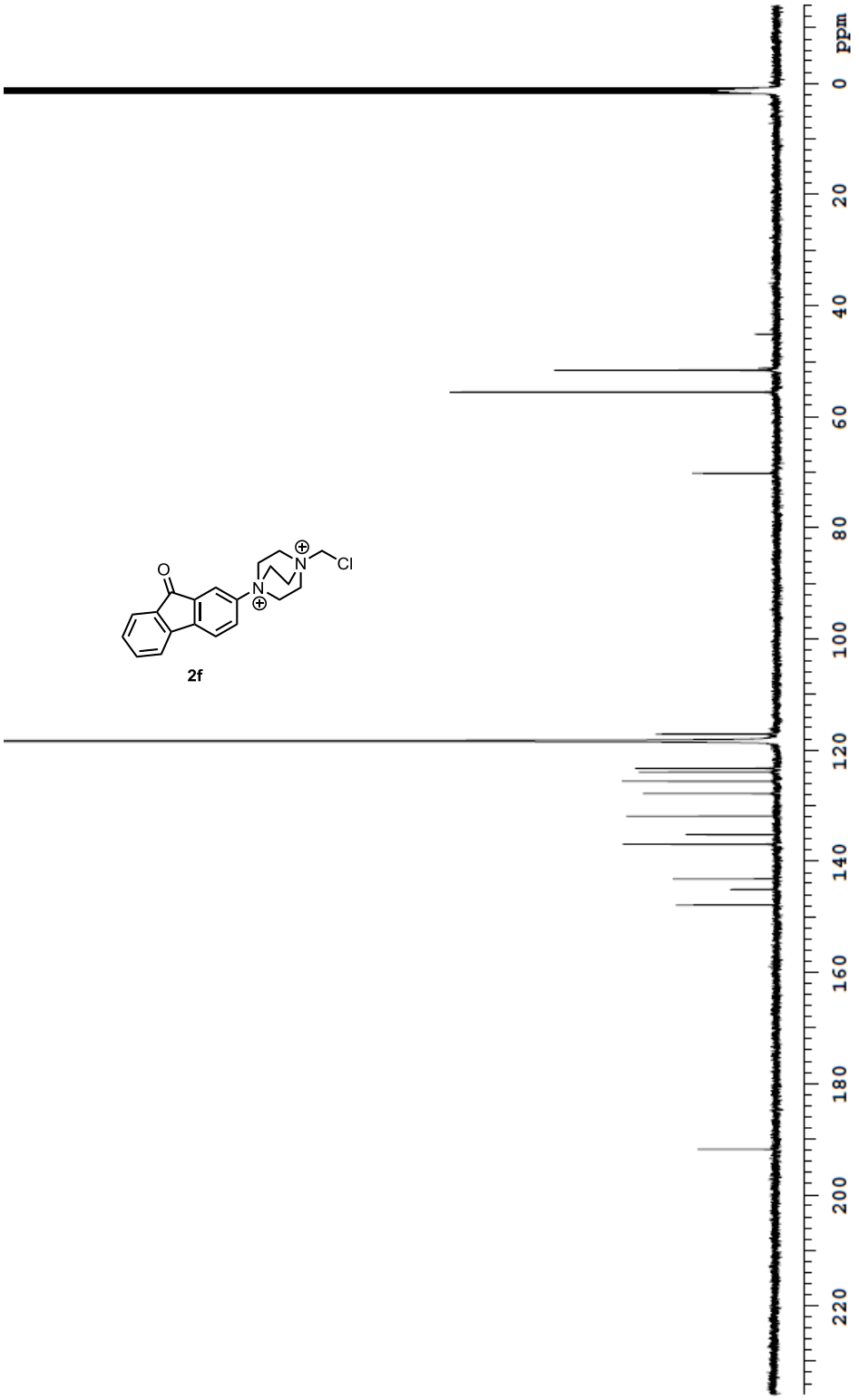

$^{19}$F NMR ($CD_3CN$, 23 ºC) of **2e**

1D NOESY analysis for structural assignment of **2e**

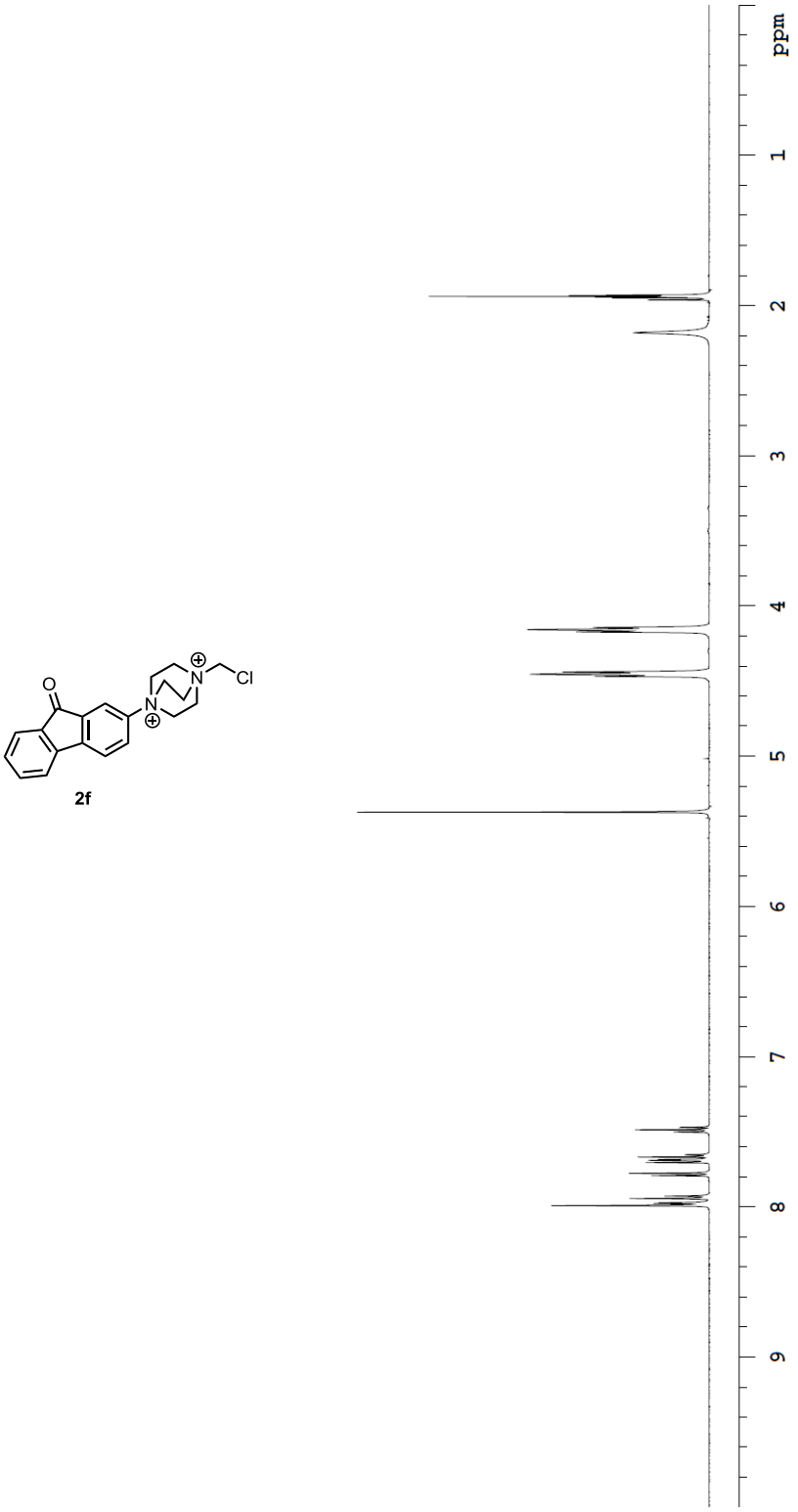




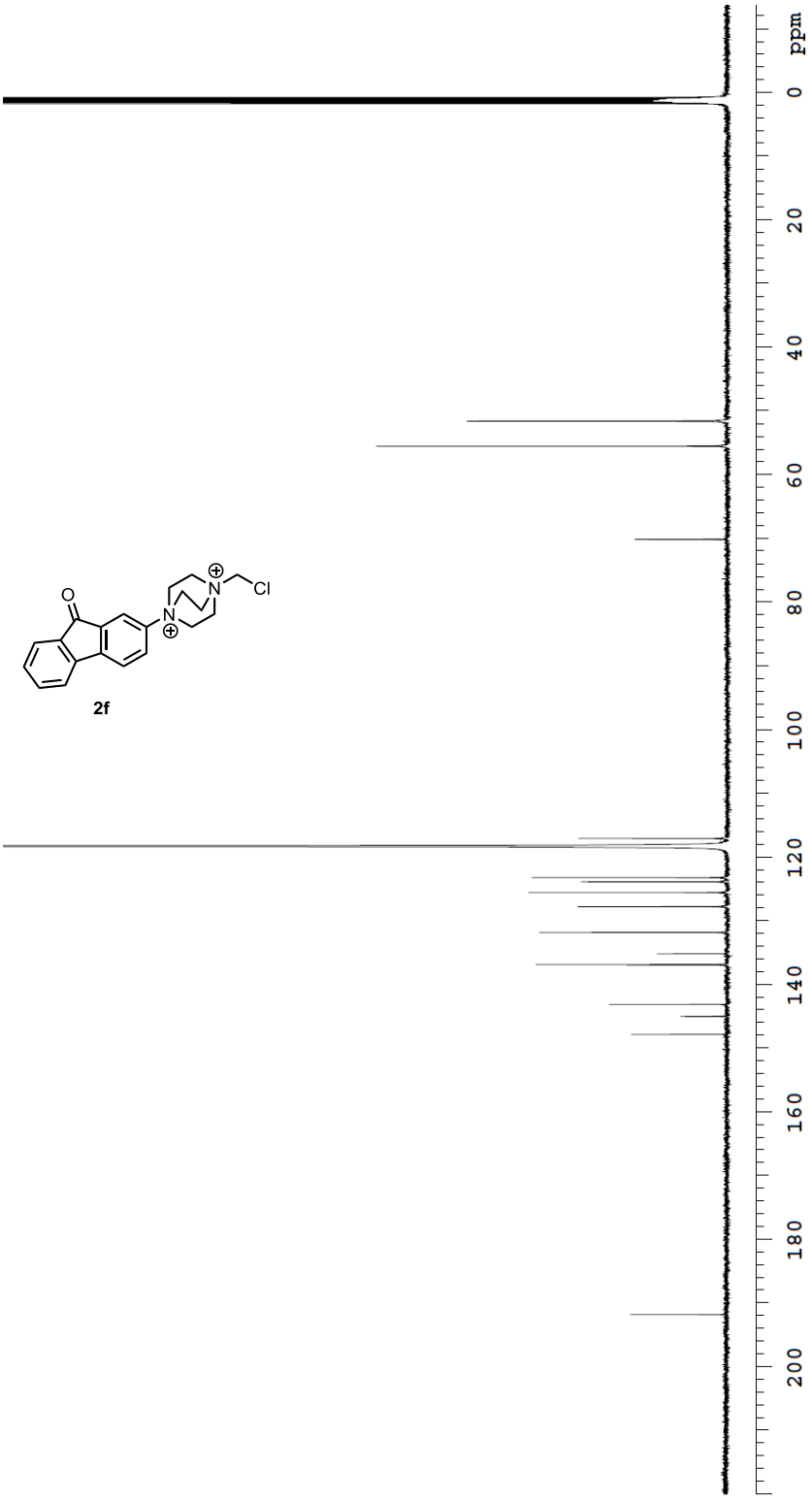

$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2f**




$^{13}$C NMR ($CD_3CN$, 23 ºC) of **2f**

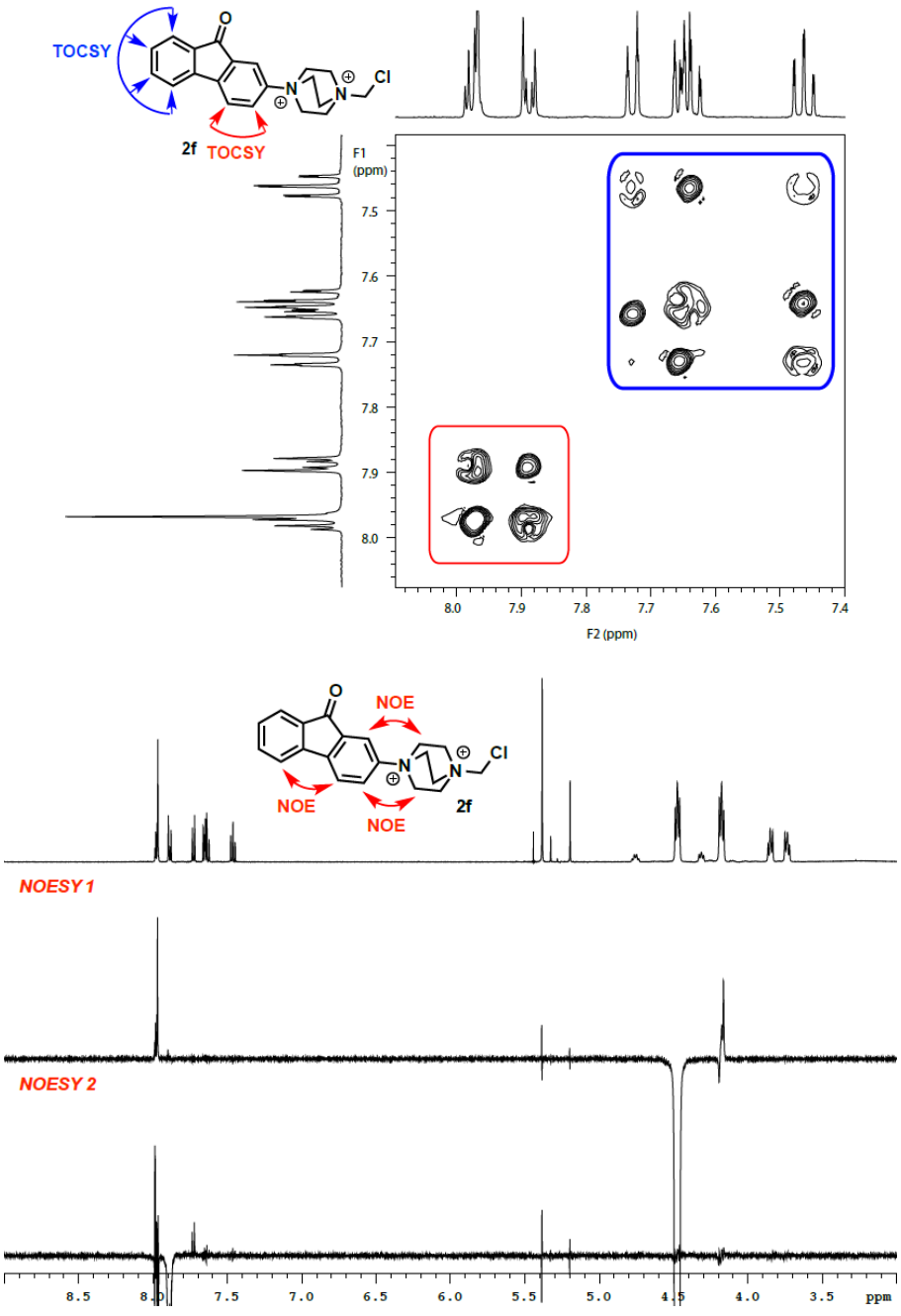


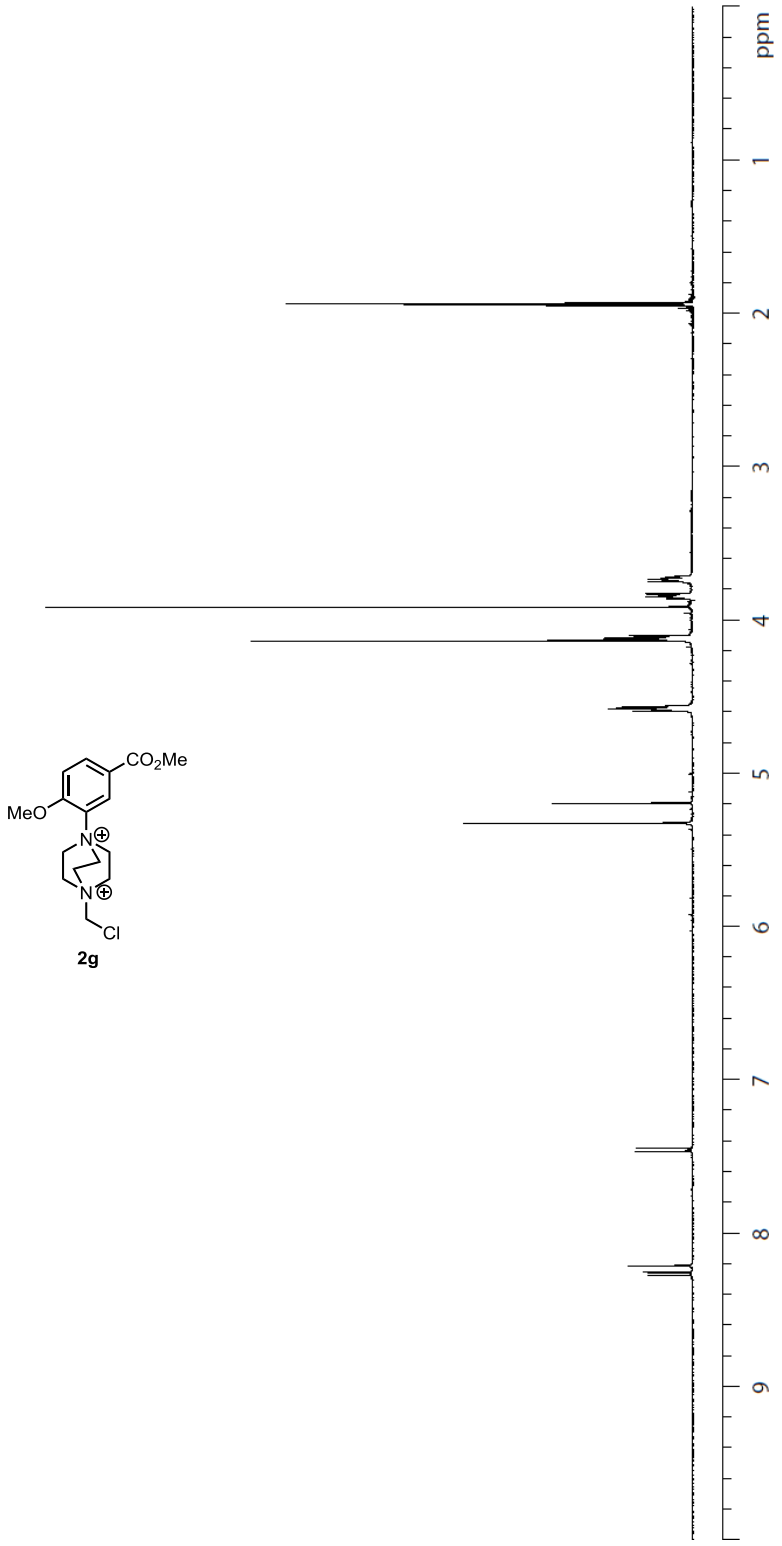

$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2f (recrystallized)**



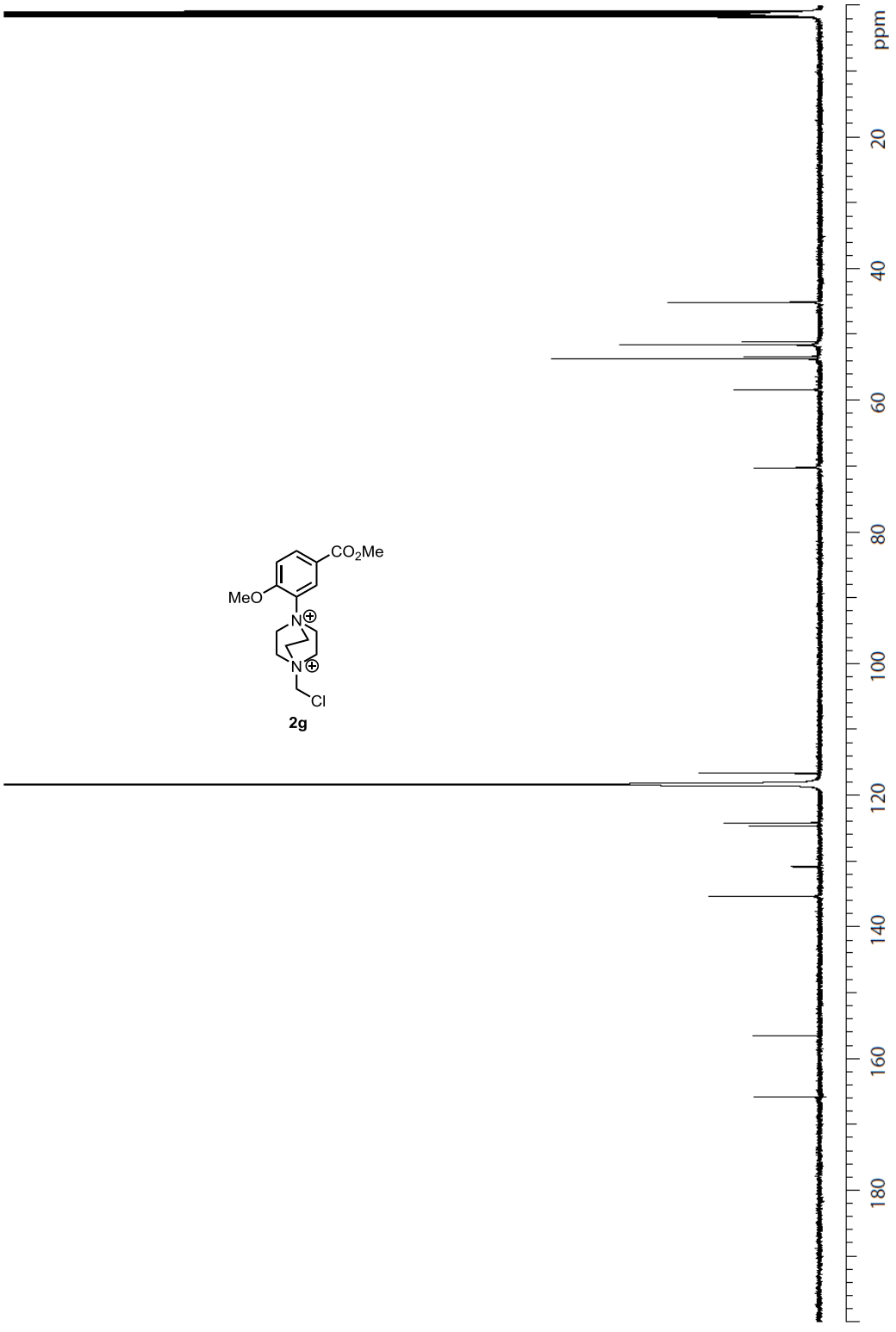

$^{13}$C NMR ($CD_3CN$, 23 ºC) of **2f (recrystallized)**

TOCSY and 1D NOESY analysis for structural assignment of **2f**

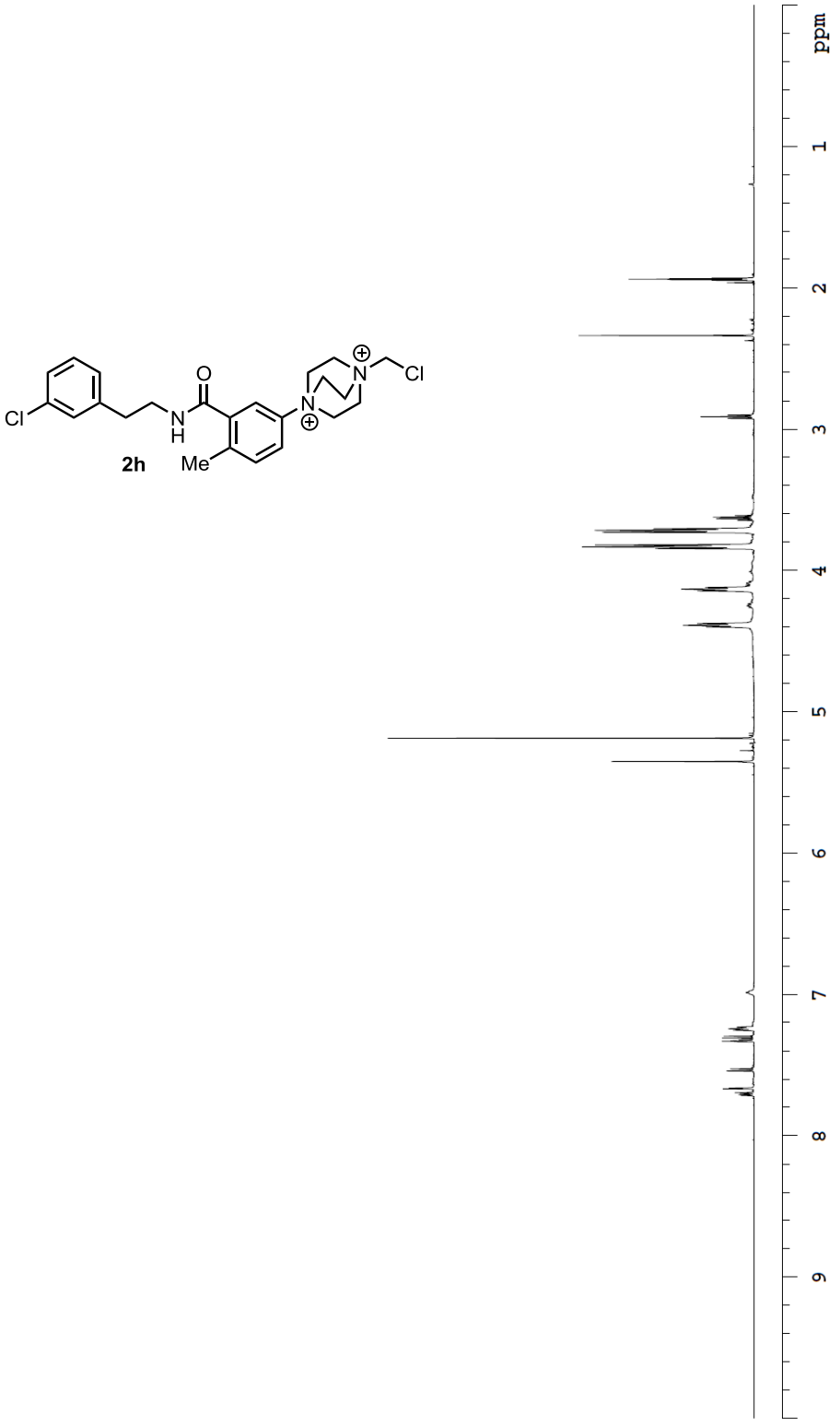




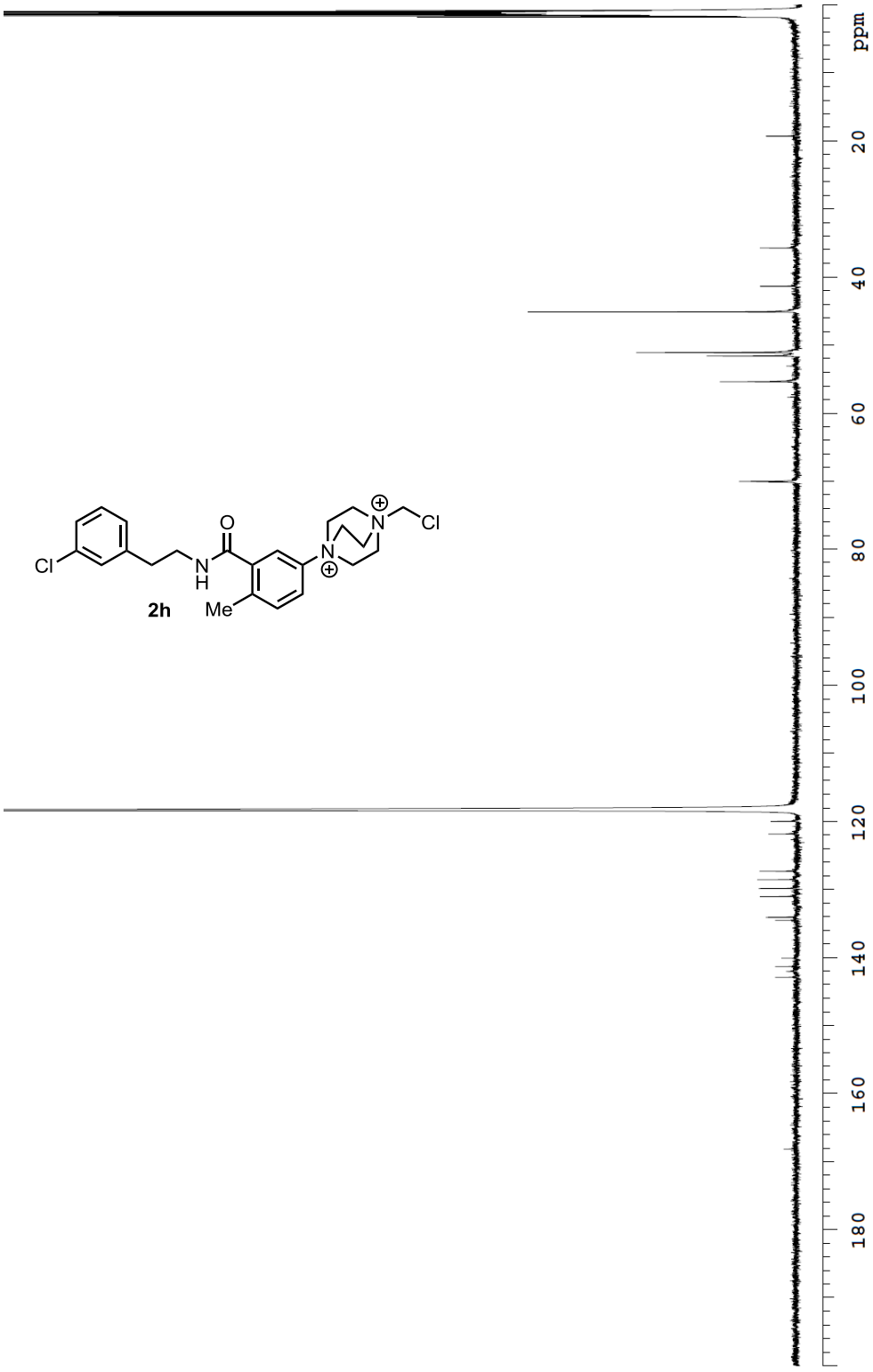

$^1$H NMR ($CD_3CN$, 23 ºC) of **2g**



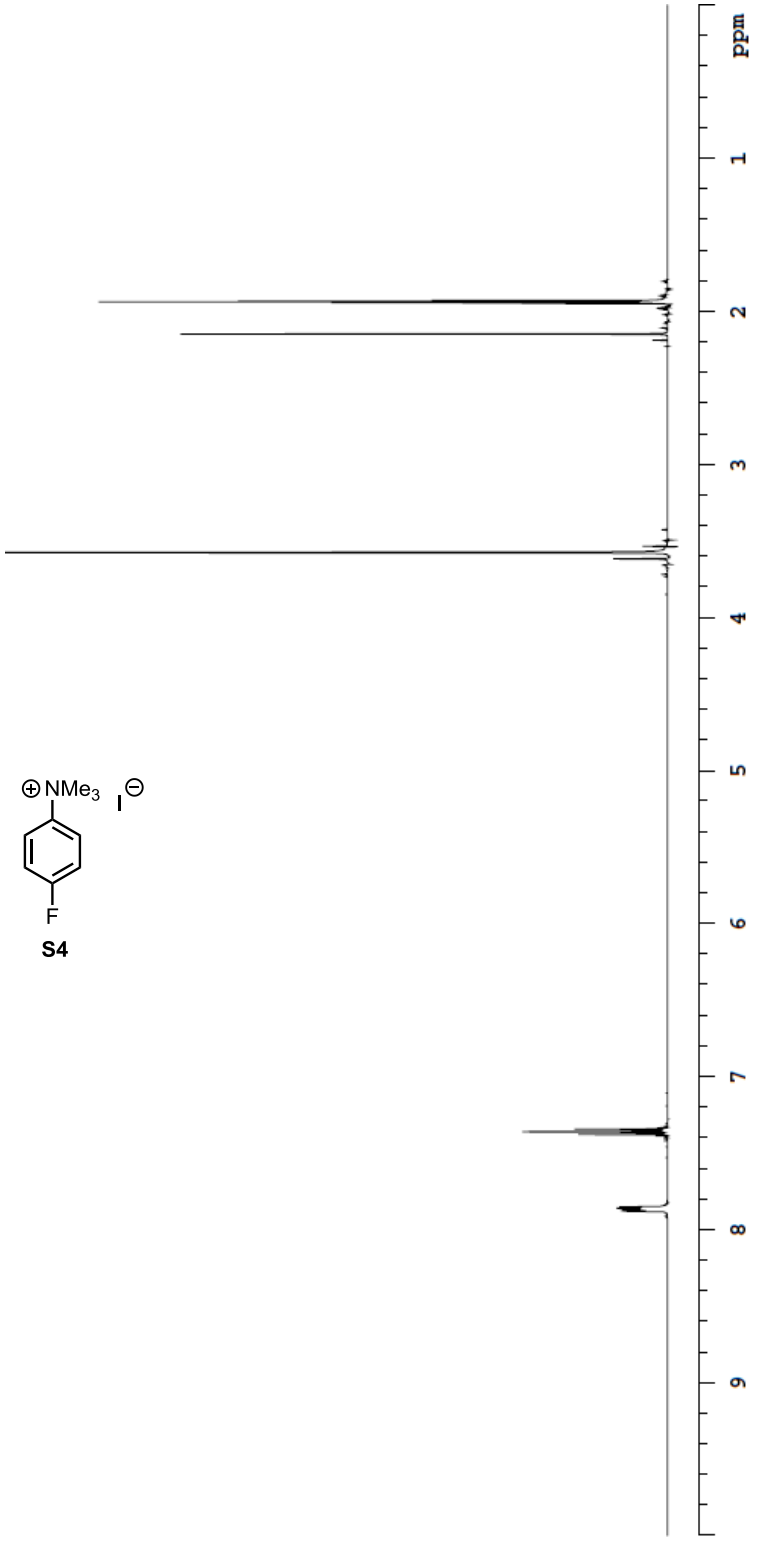

$^{13}$C NMR ($CD_3CN$, 23 ºC) of **2g**



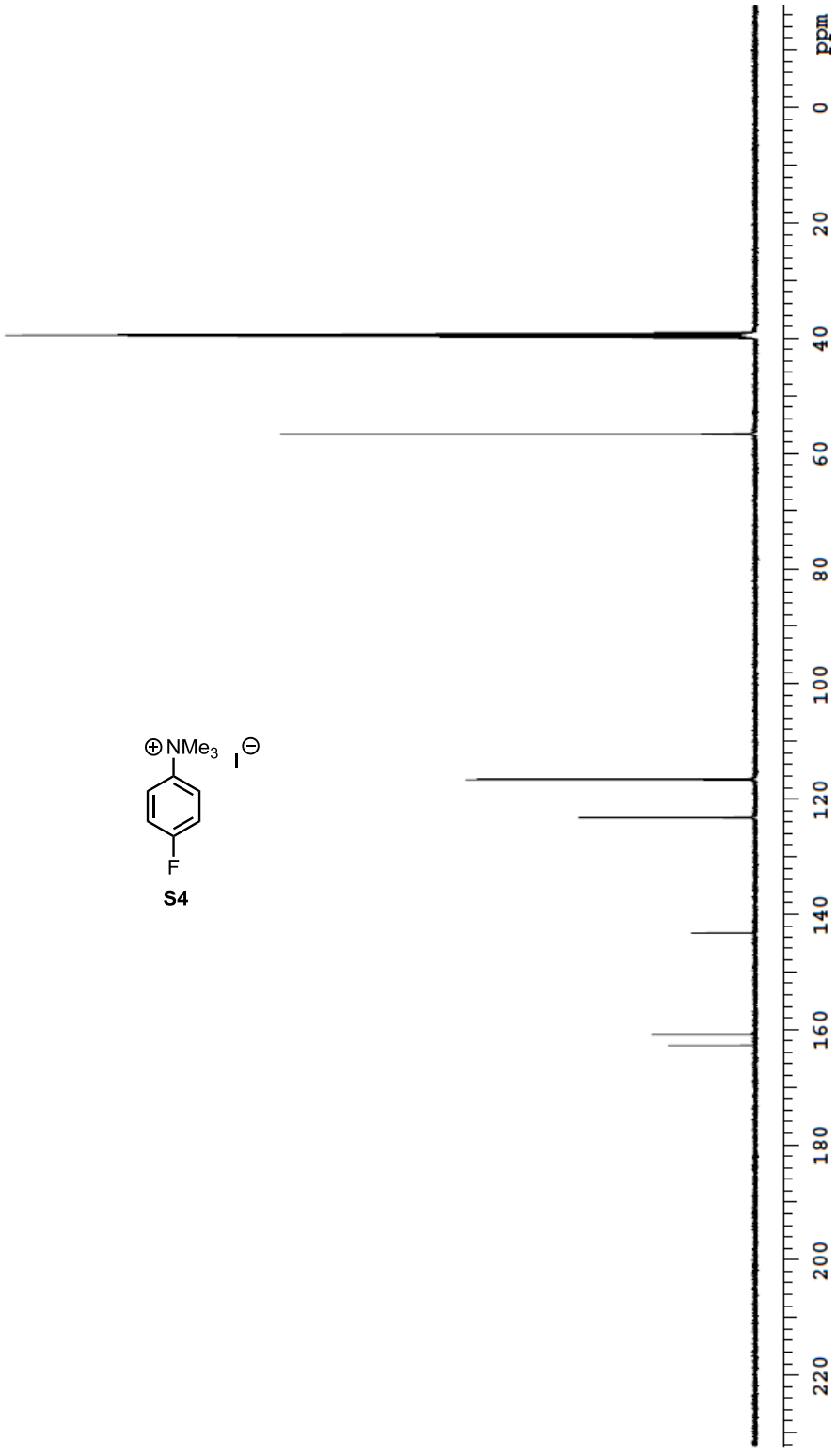

$^{1}$H NMR ($CD_3CN$, 23 ºC) of **2h**



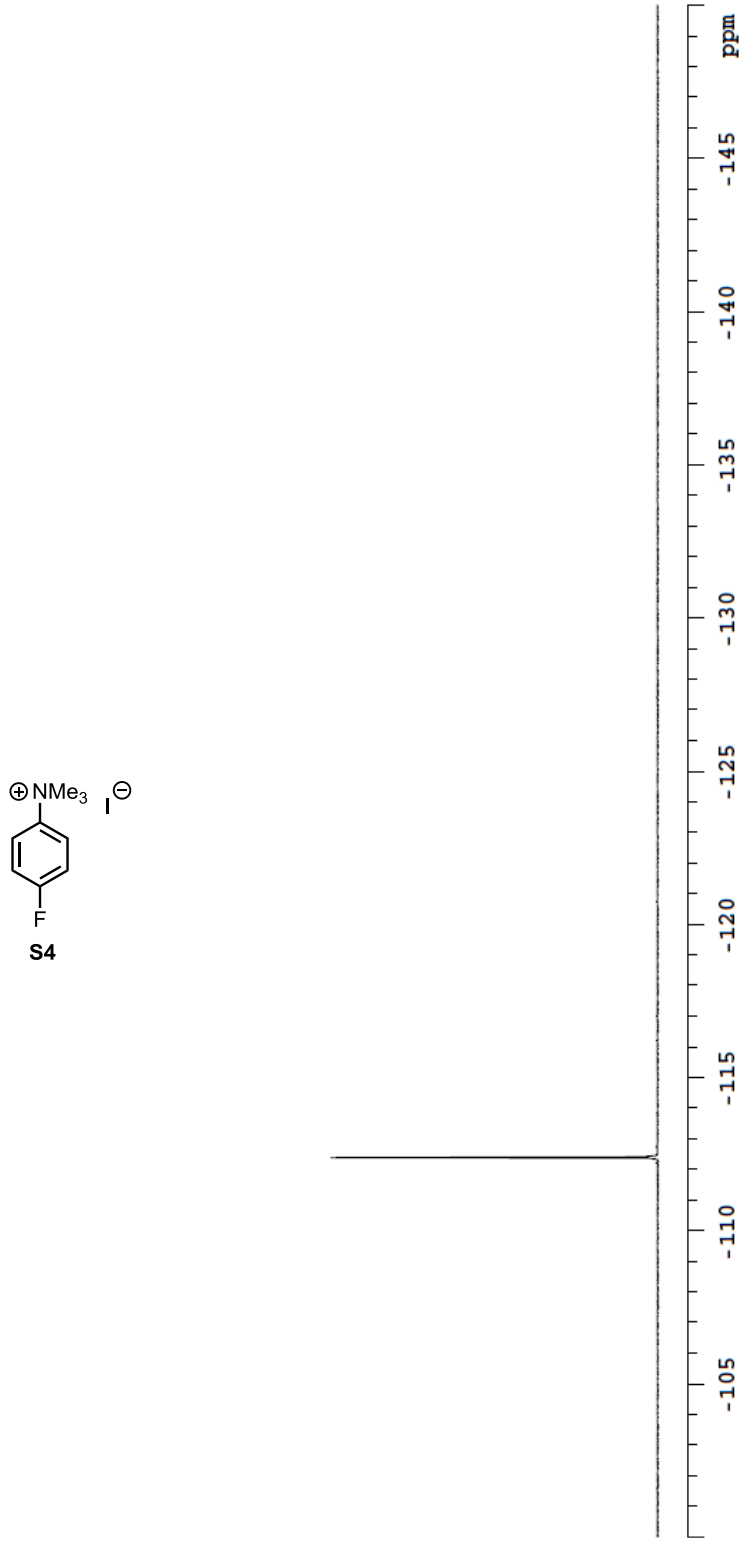

$^{13}$C NMR ($CD_3CN$, 23 ºC) of **2h**




$^{1}$H NMR ($CD_3CN$, 23 ºC) of **S4**




$^{13}$C NMR (DMSO, 23 ºC) of **S4**

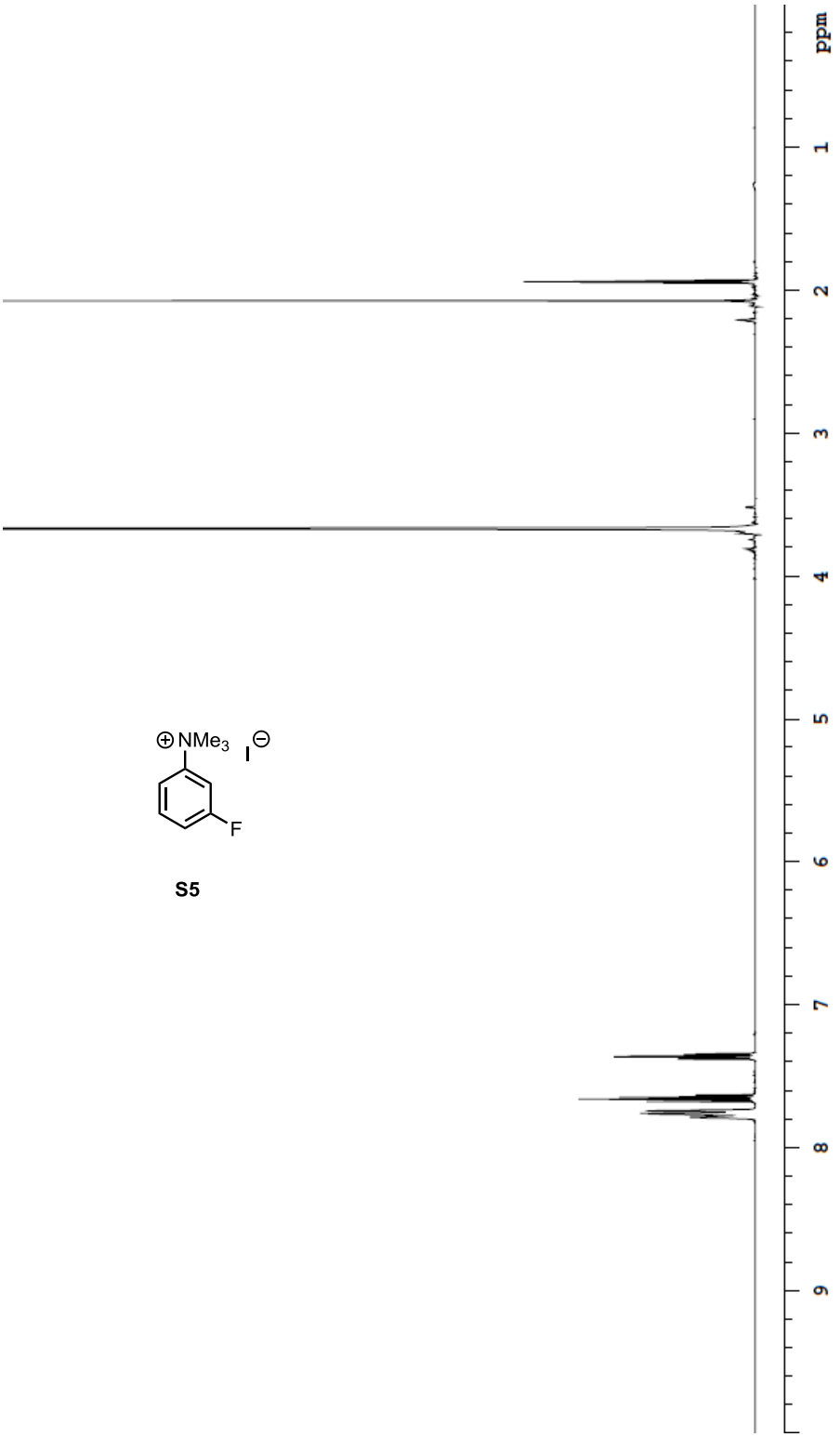






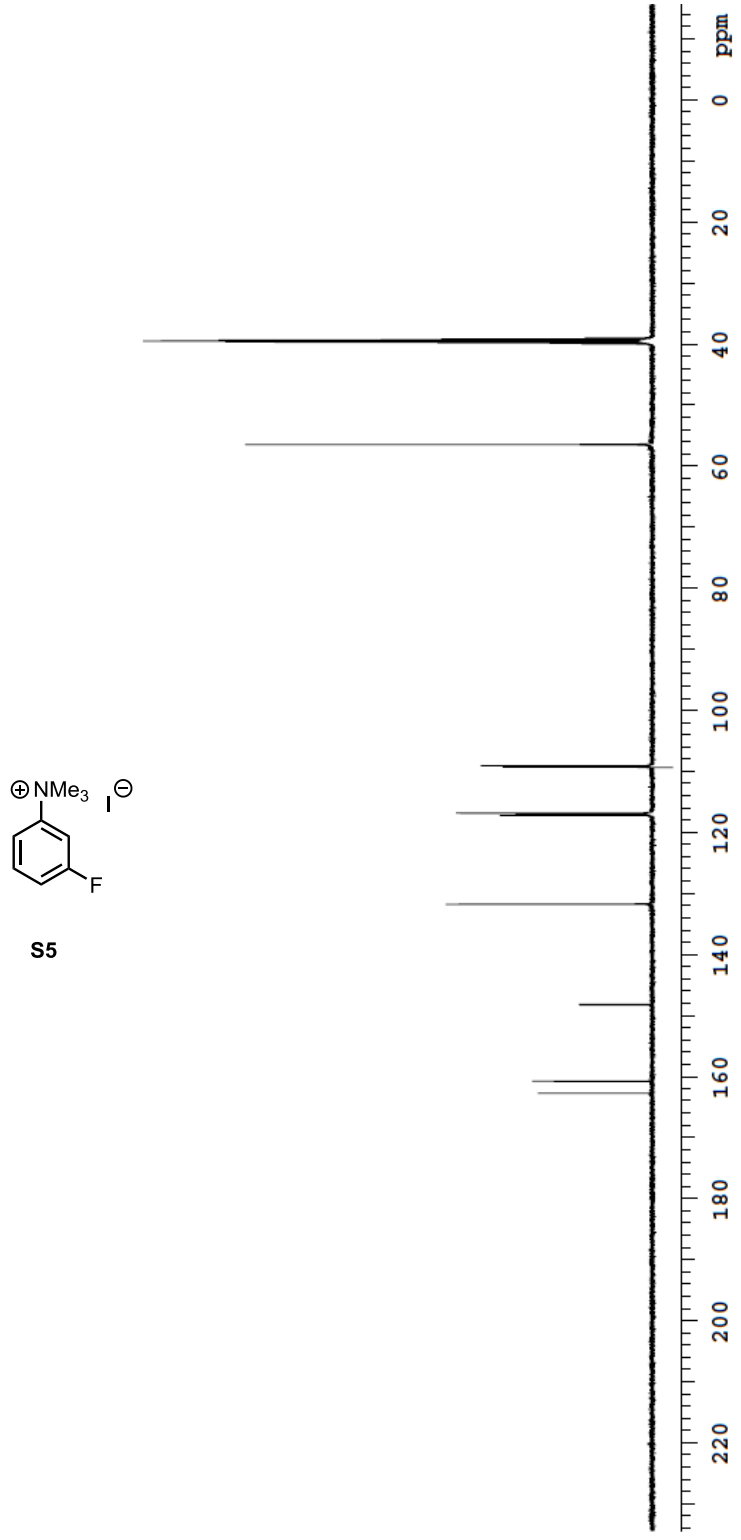
**S4**

$^{19}$F NMR ($CD_3CN$, 23 ºC) of **S4**

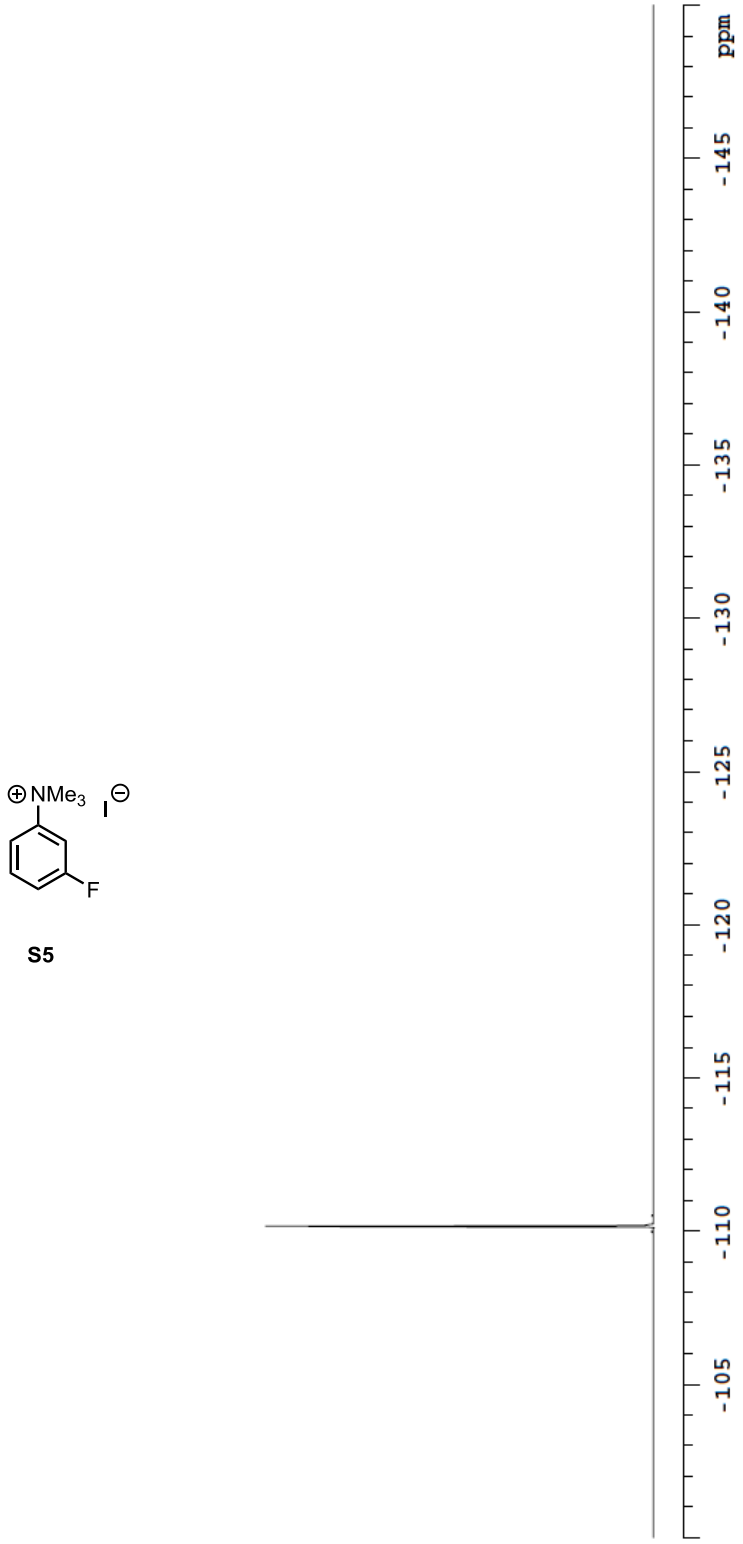



**S5**

$^1$H NMR ($CD_3CN$, 23 ºC) of **S5**




$^{13}$C NMR (DMSO, 23 ºC) of **S5**

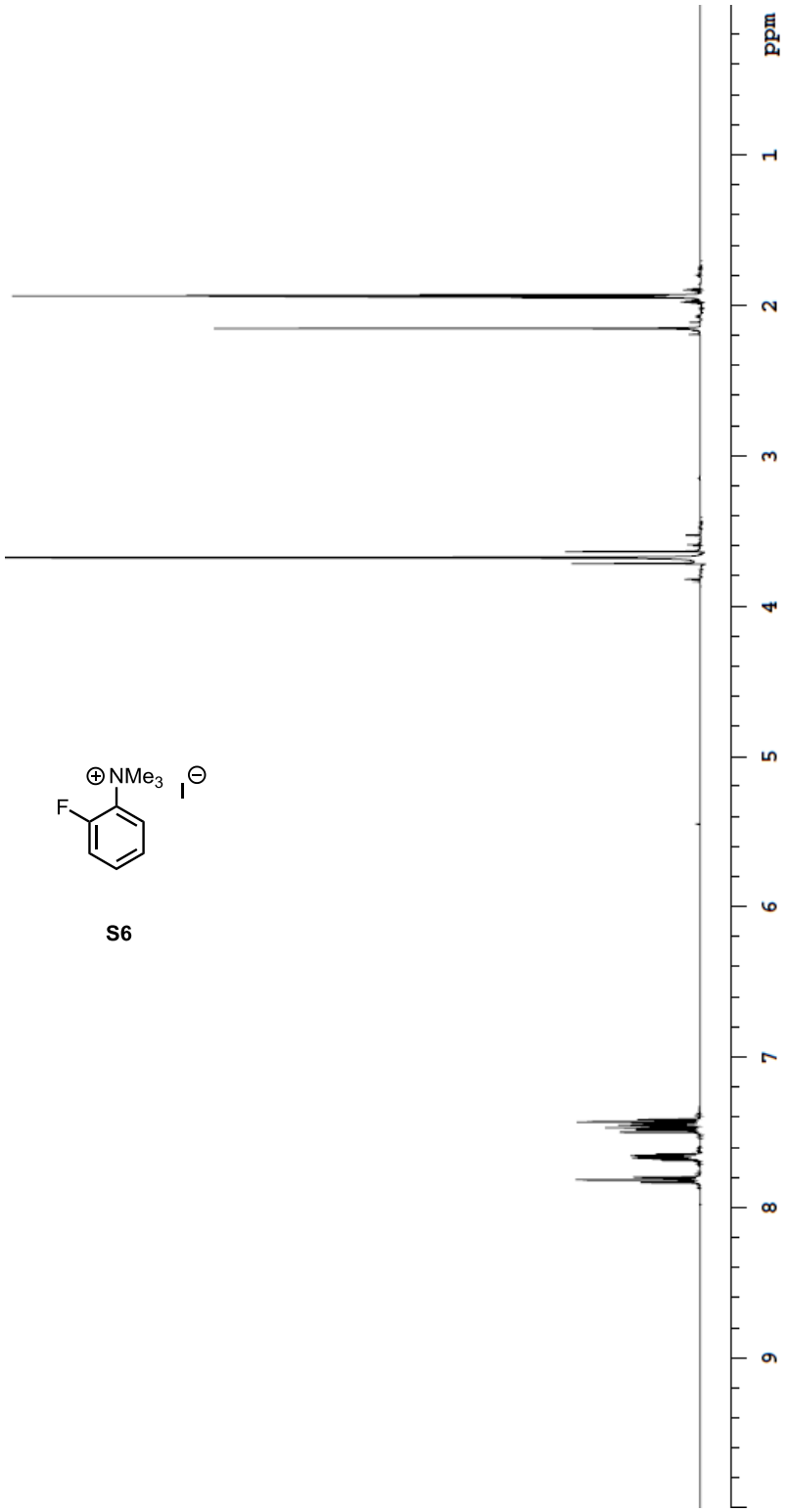






**S5**

$^{19}$F NMR ($CD_3CN$, 23 ºC) of **S5**

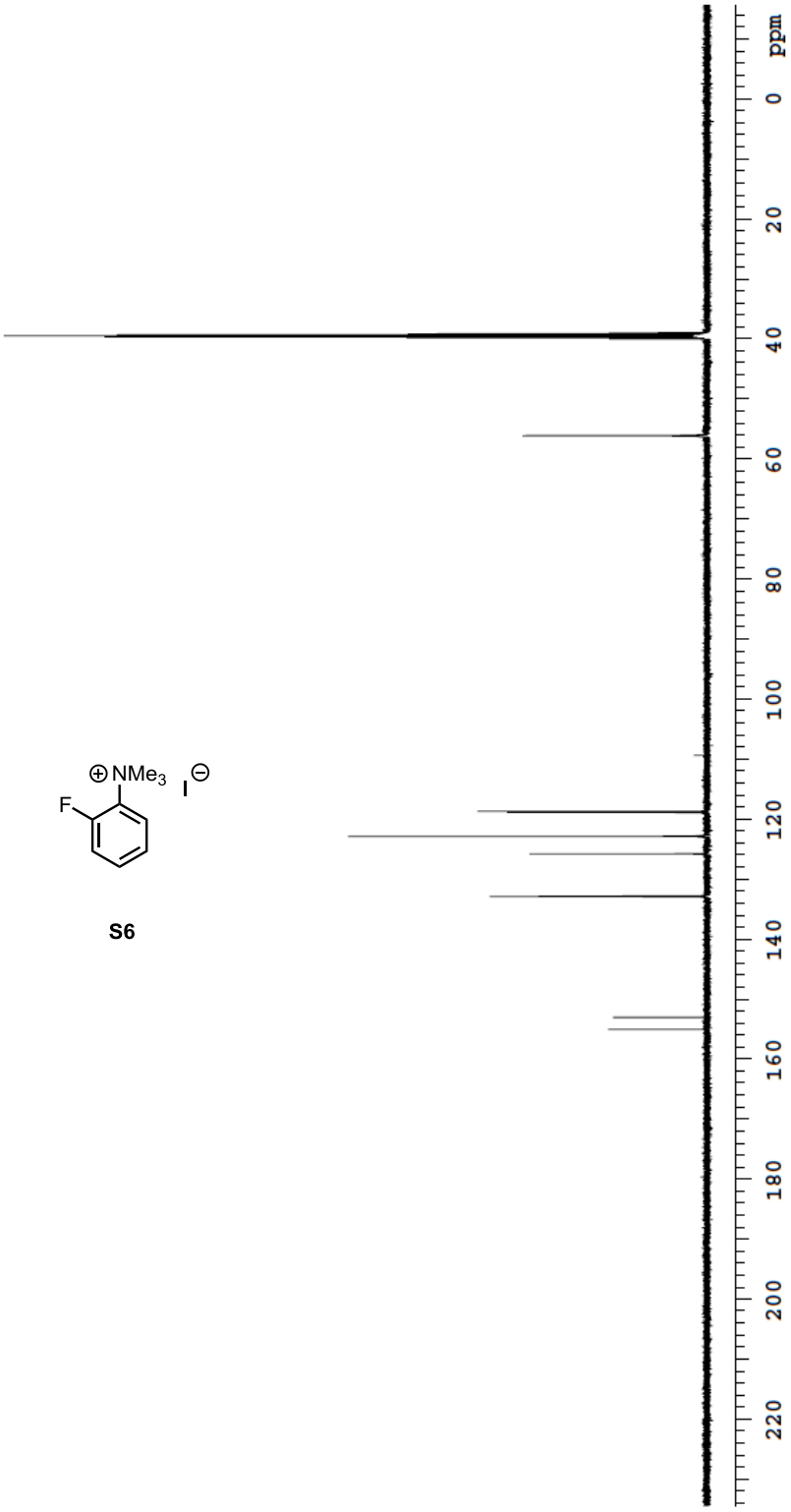




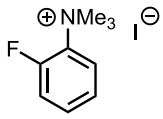


**S6**

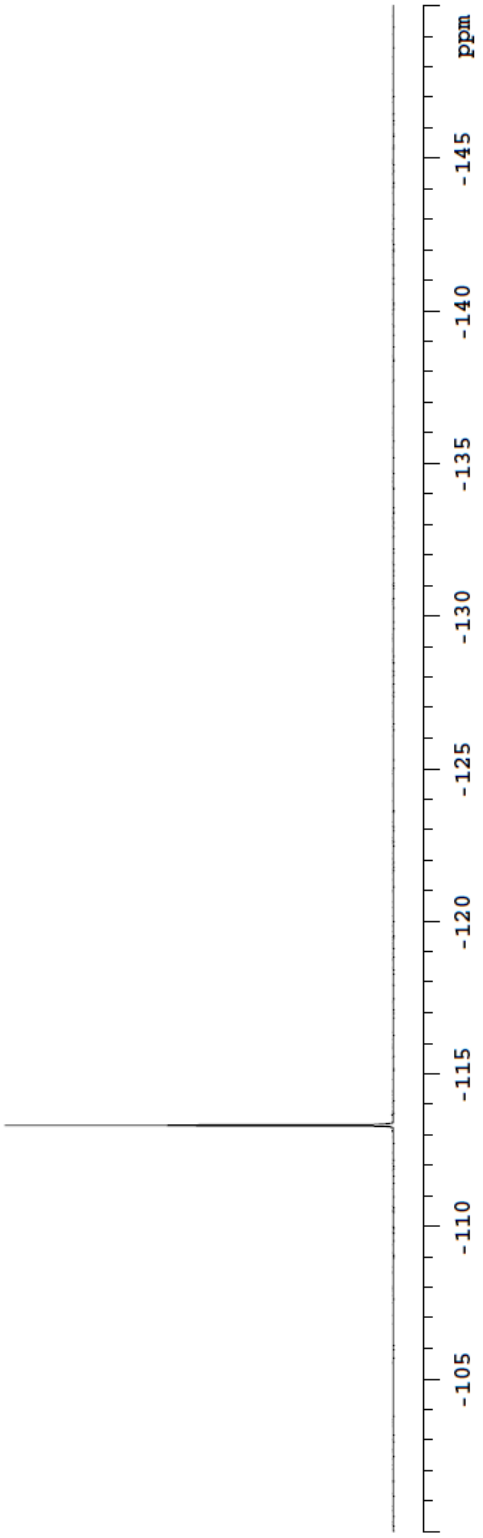
$^{1}$H NMR ($CD_3CN$, 23 ºC) of **S6**



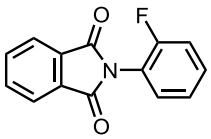

$^{13}$C NMR (DMSO, 23 ºC) of **S6**



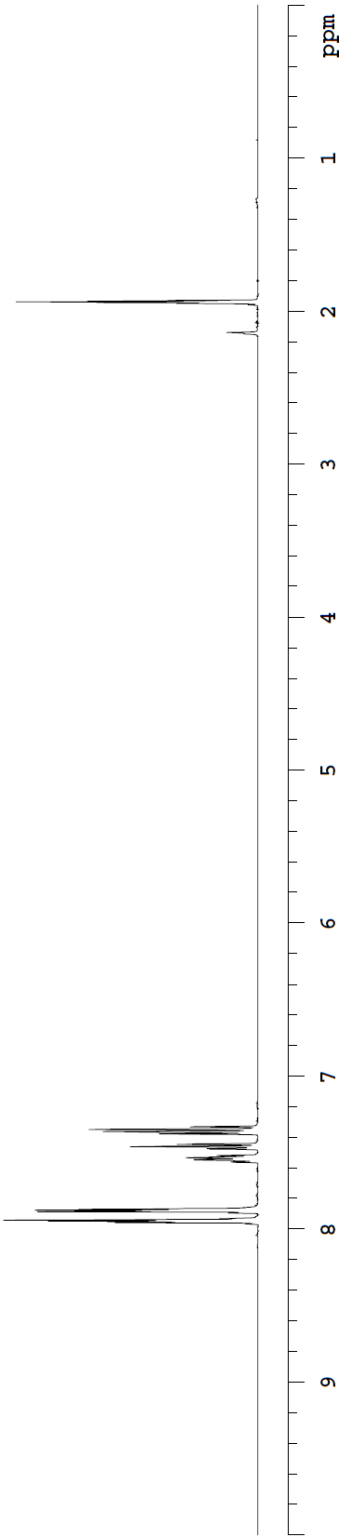

**S6**



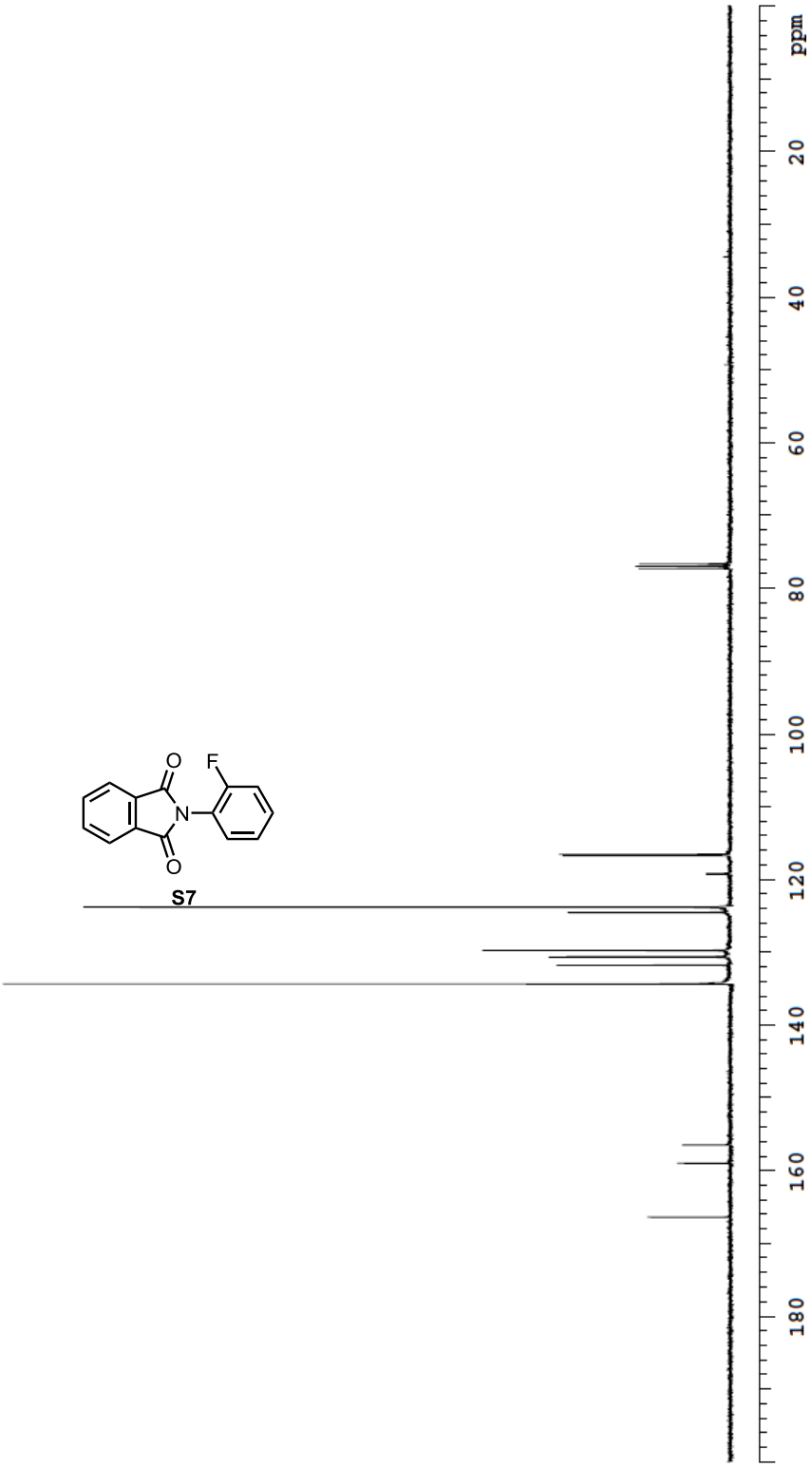

$^{19}$F NMR ($CD_3CN$, 23 ºC) of **S6**



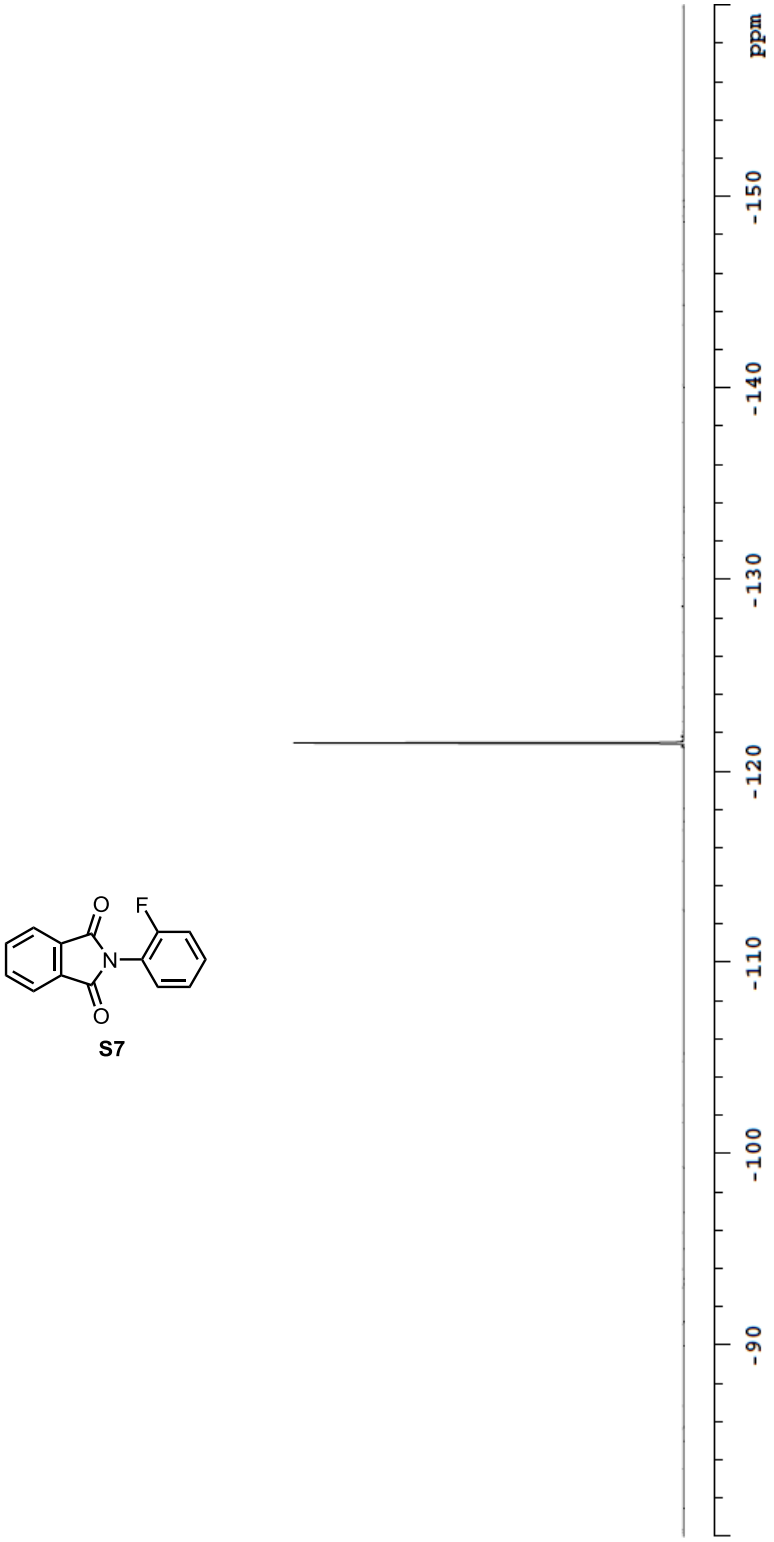

**S7**




$^{1}$H NMR ($CD_3CN$, 23 ºC) of **S7**

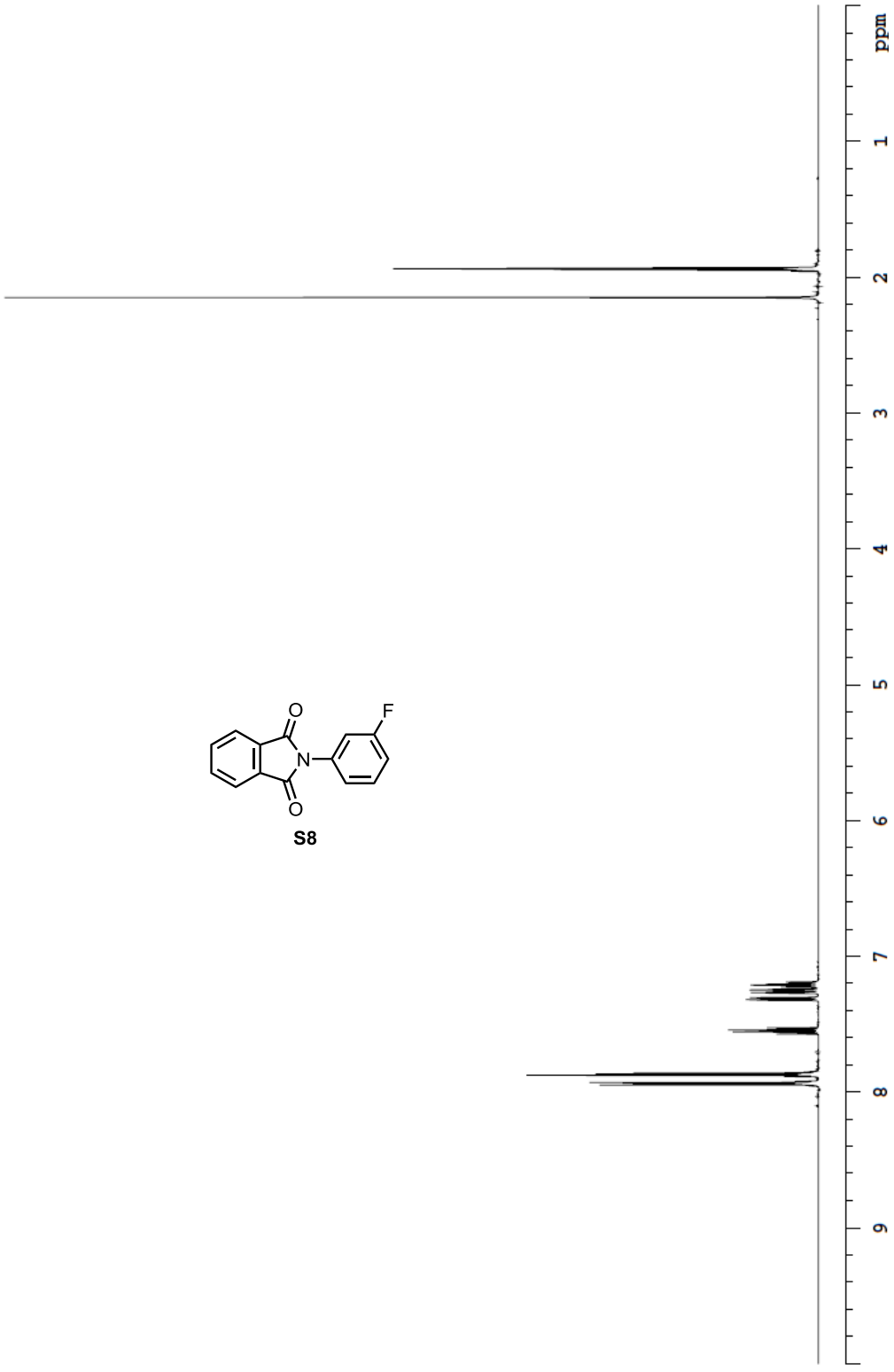



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S7**

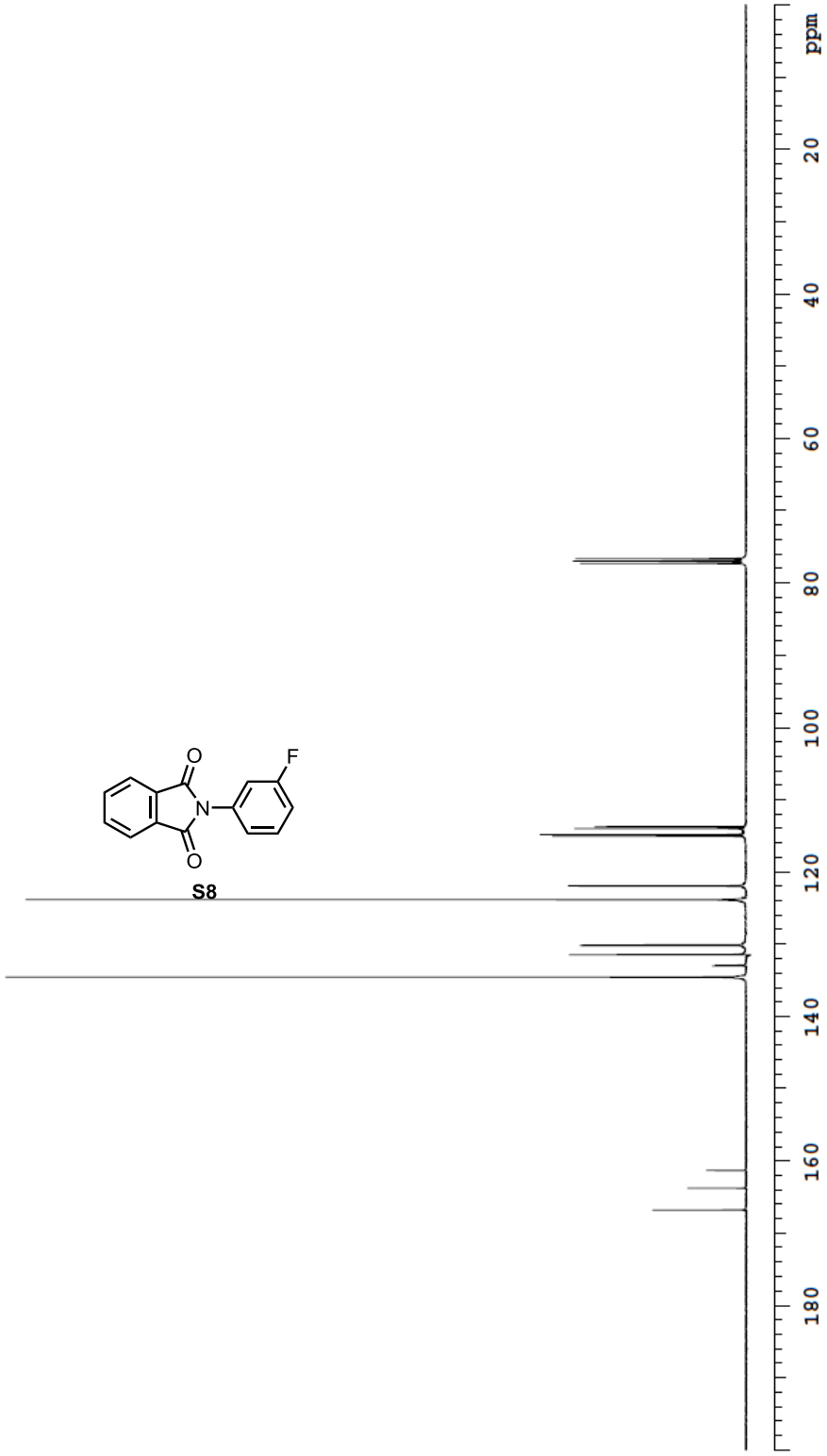



**S7**

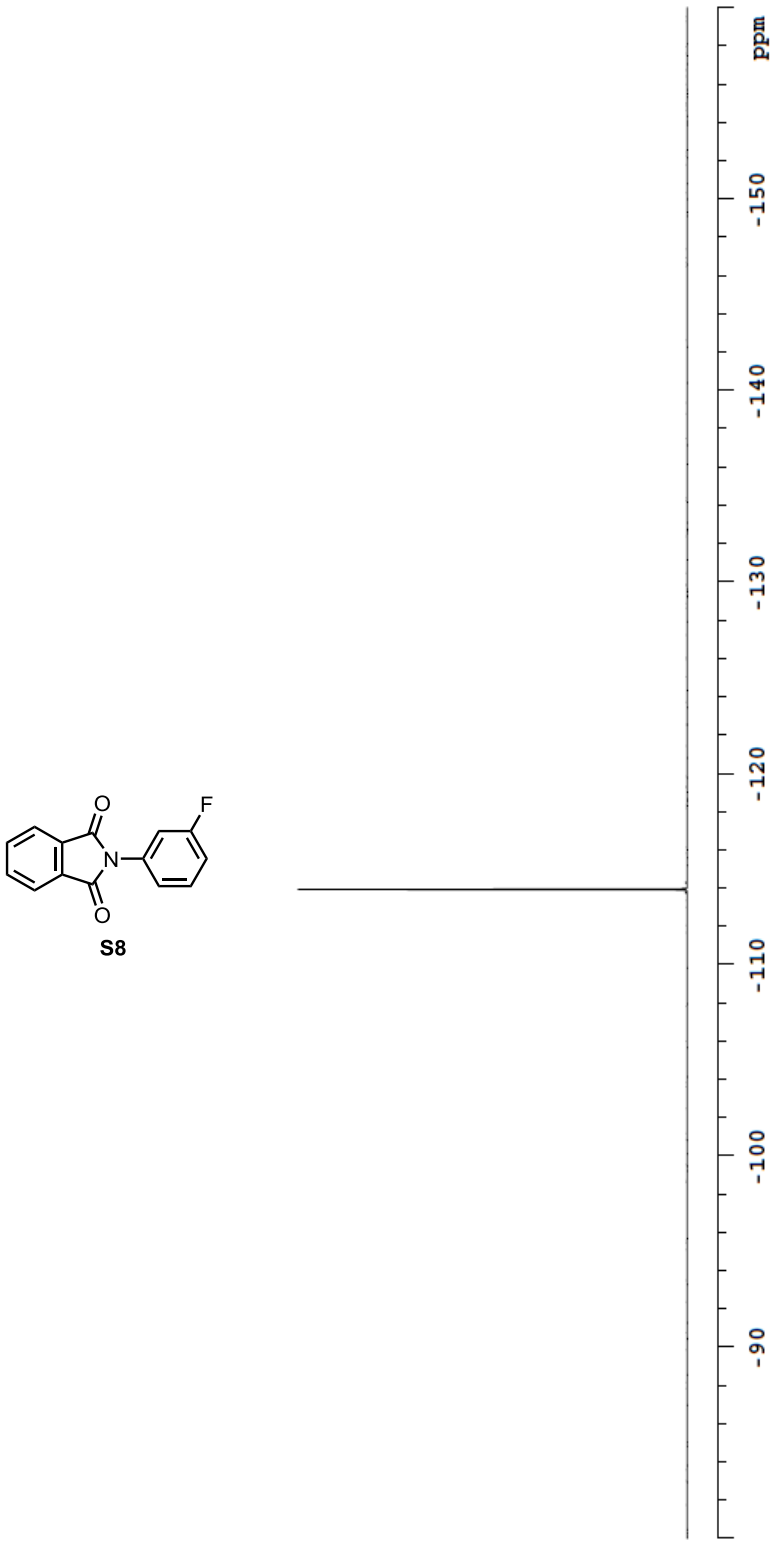
$^{19}$F NMR ($CD_3CN$, 23 ºC) of **S7**



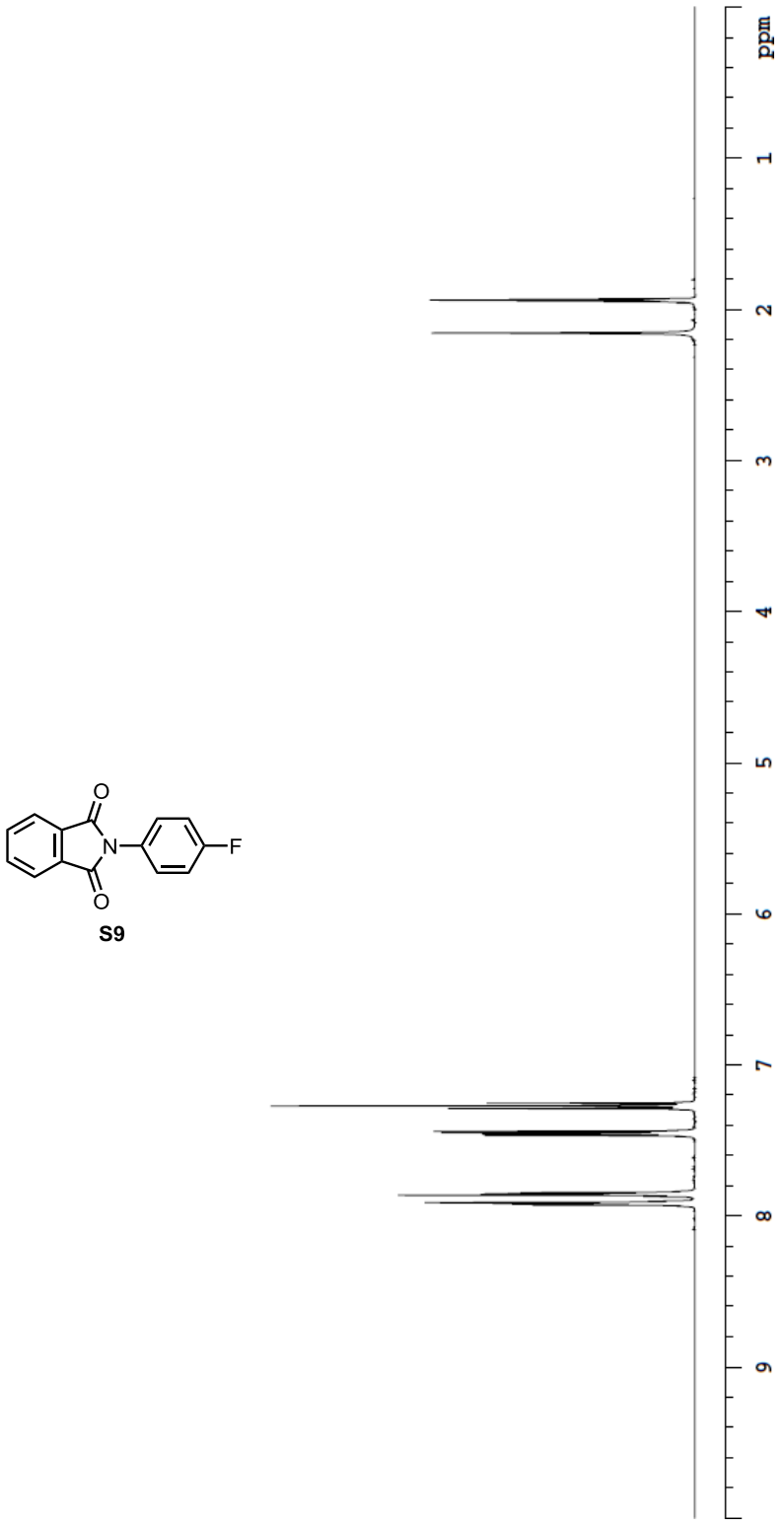

$^{1}$H NMR ($CD_3CN$, 23 ºC) of **S8**



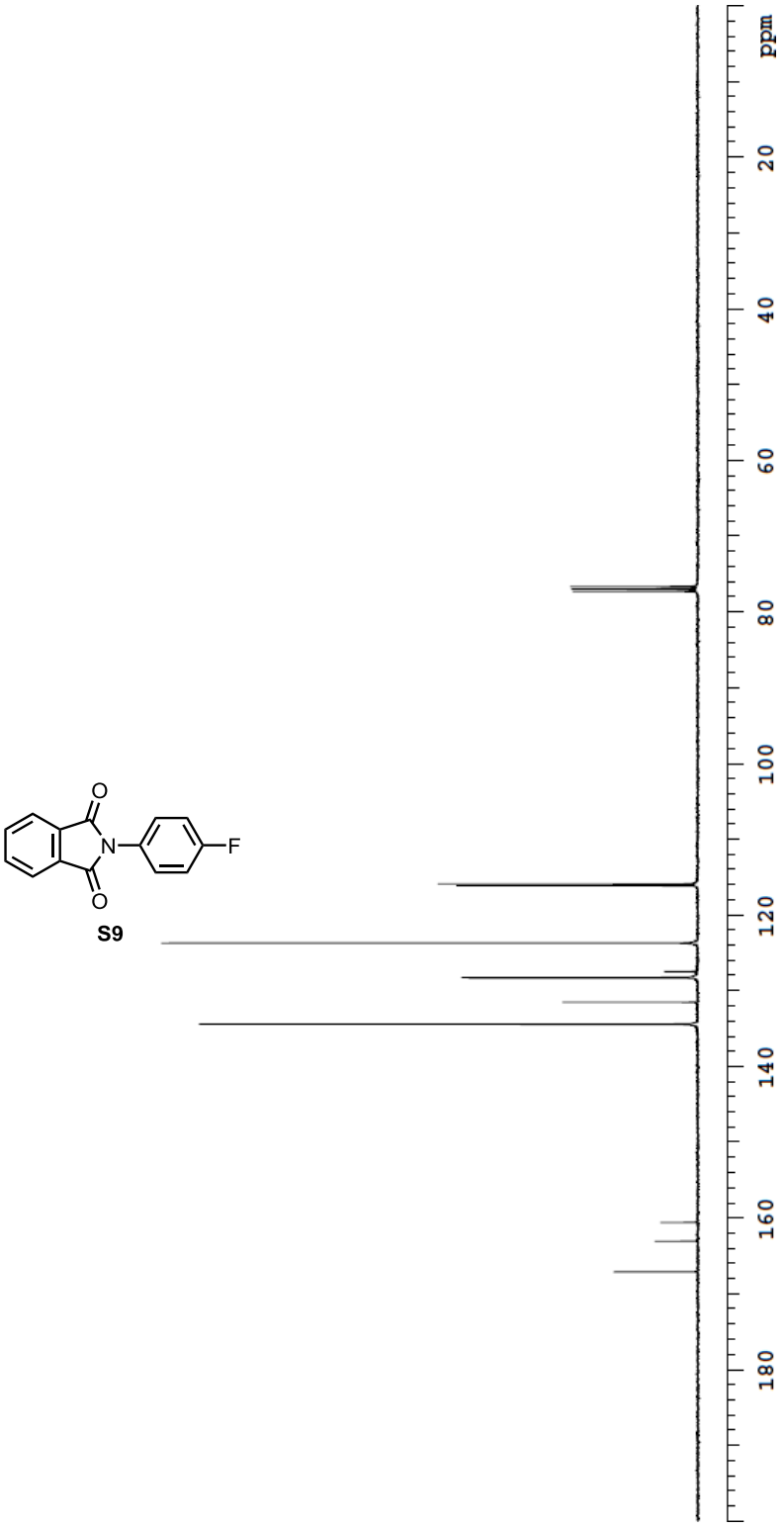

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S8**



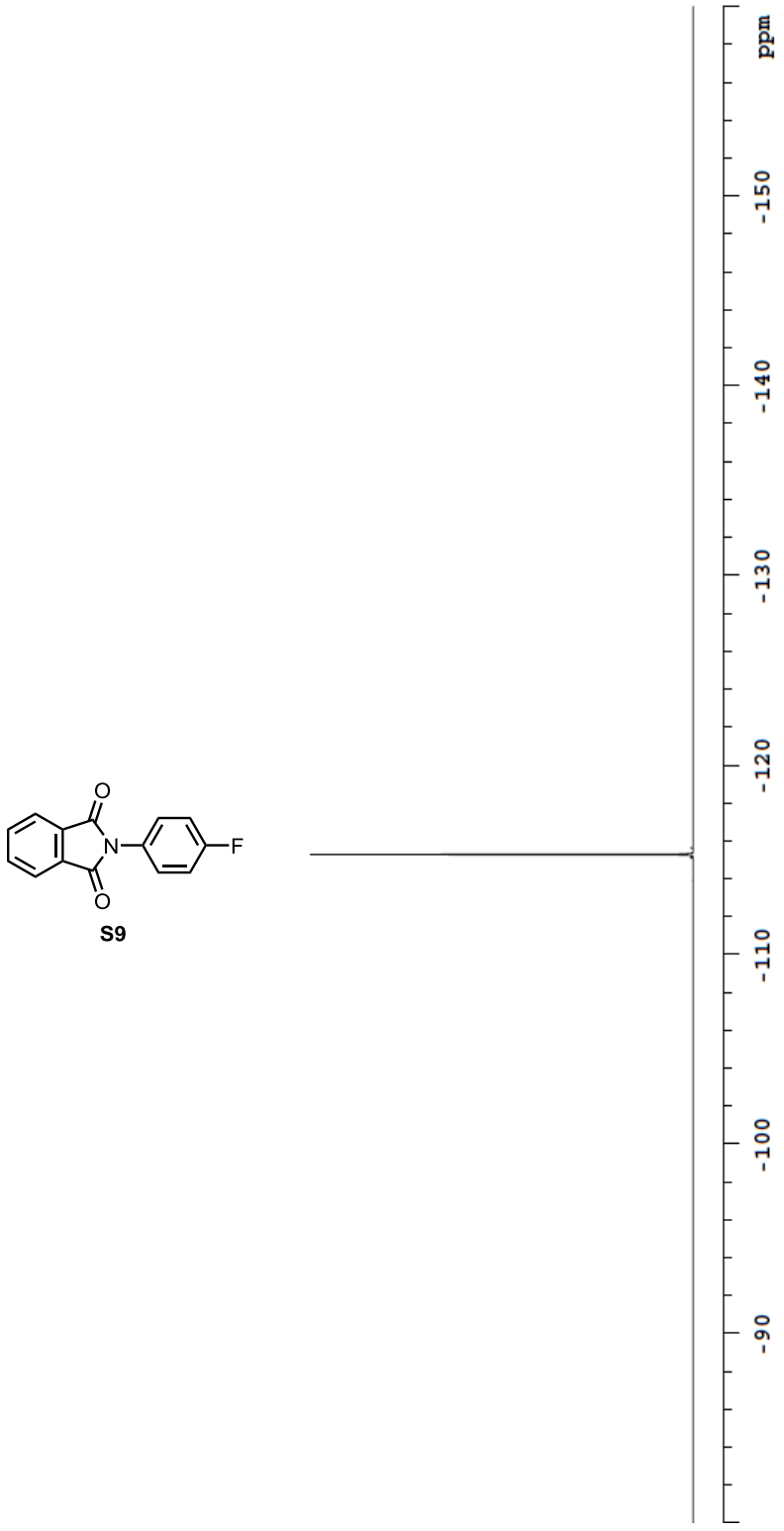

$^{19}$F NMR ($CD_3CN$, 23 ºC) of **S8**



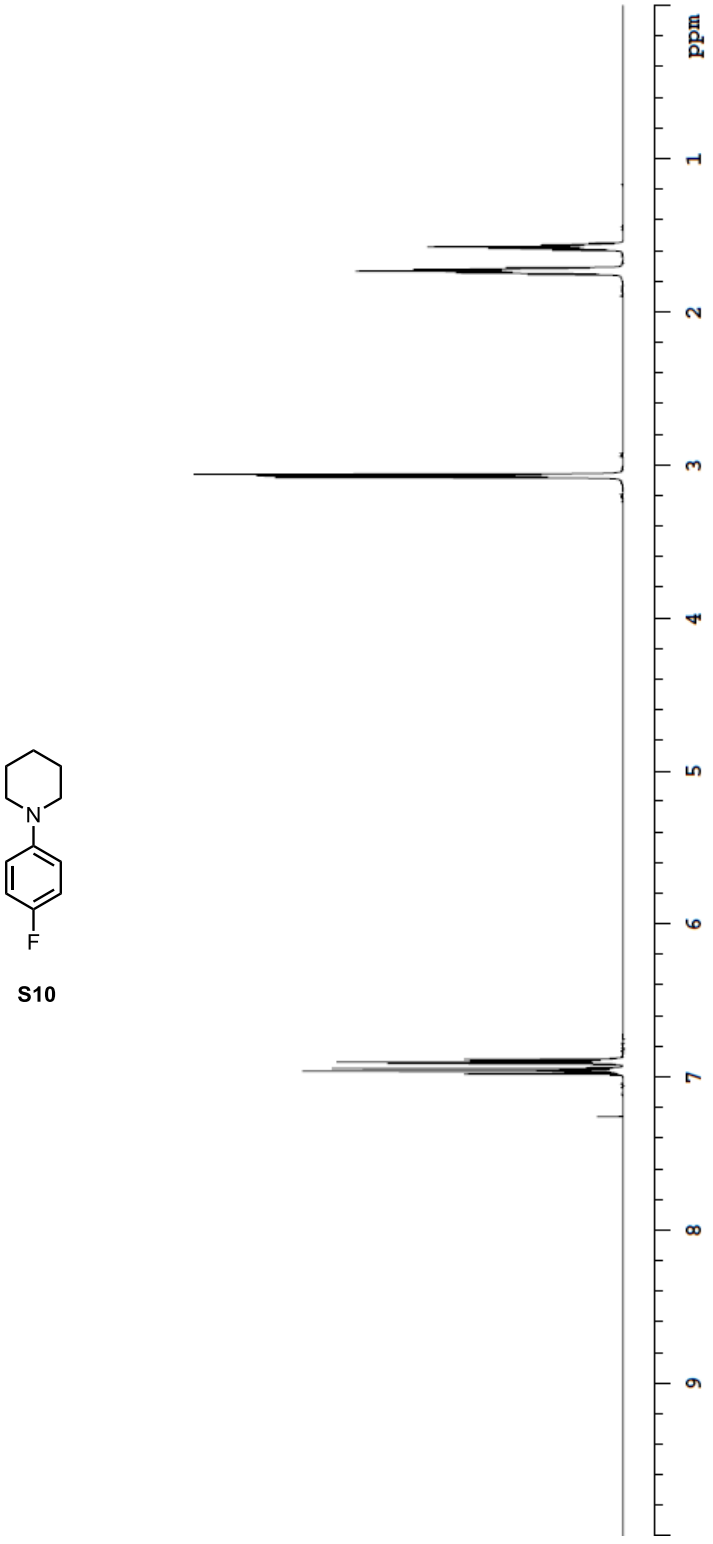

$^1$H NMR ($CD_3CN$, 23 ºC) of **S9**




$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S9**

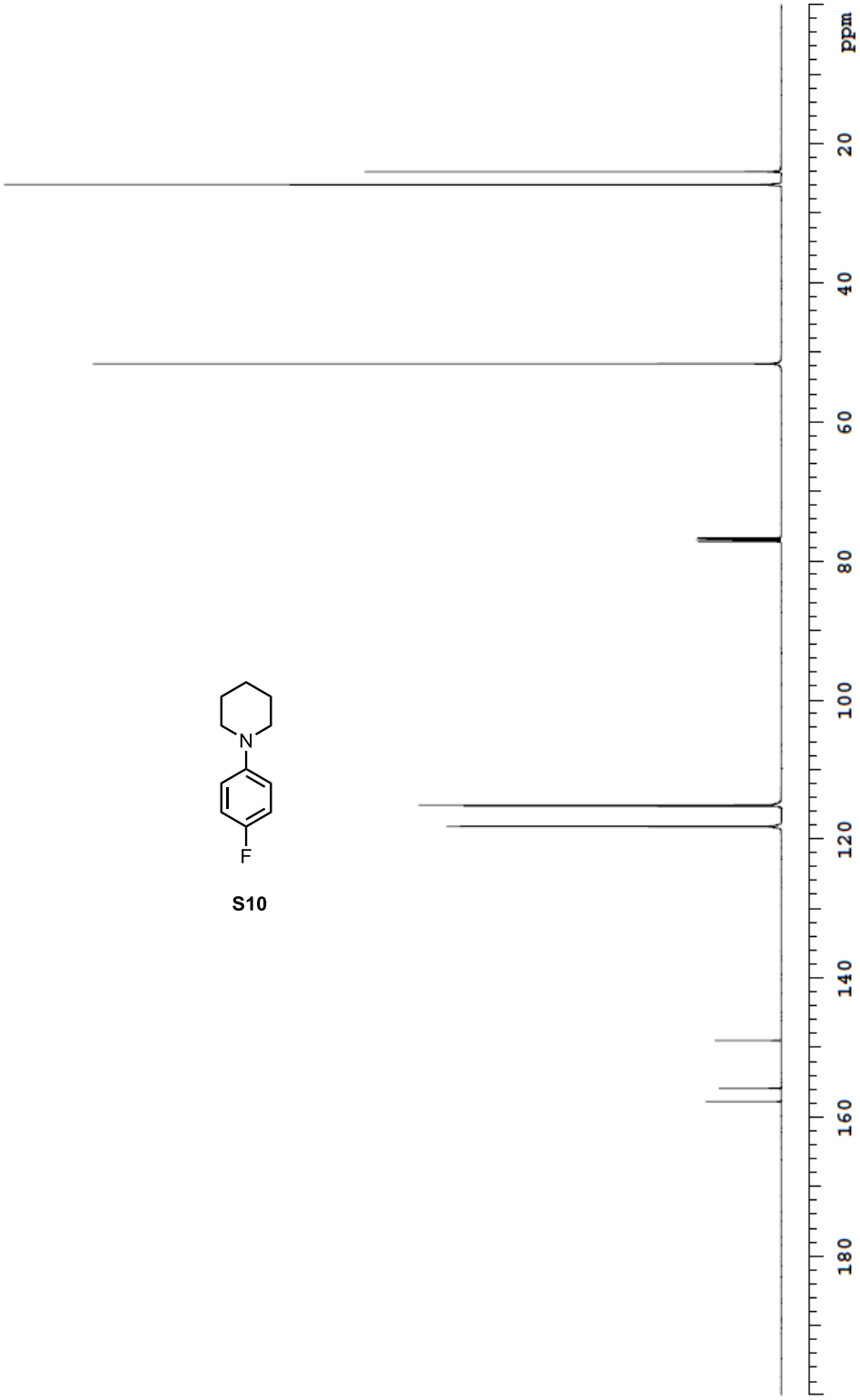



$^{19}$F NMR ($CD_3CN$, 23 ºC) of **S9**

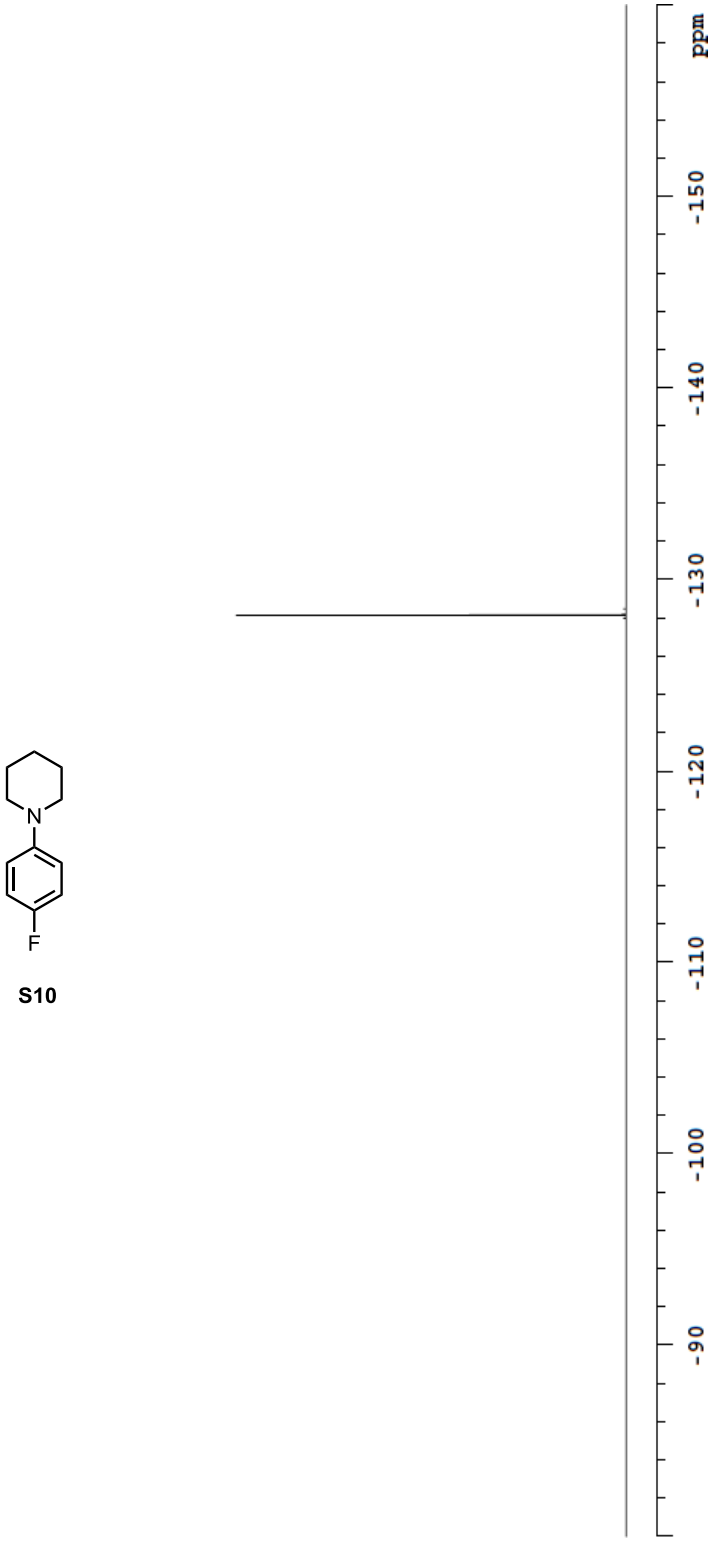



**S10**

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **S10**

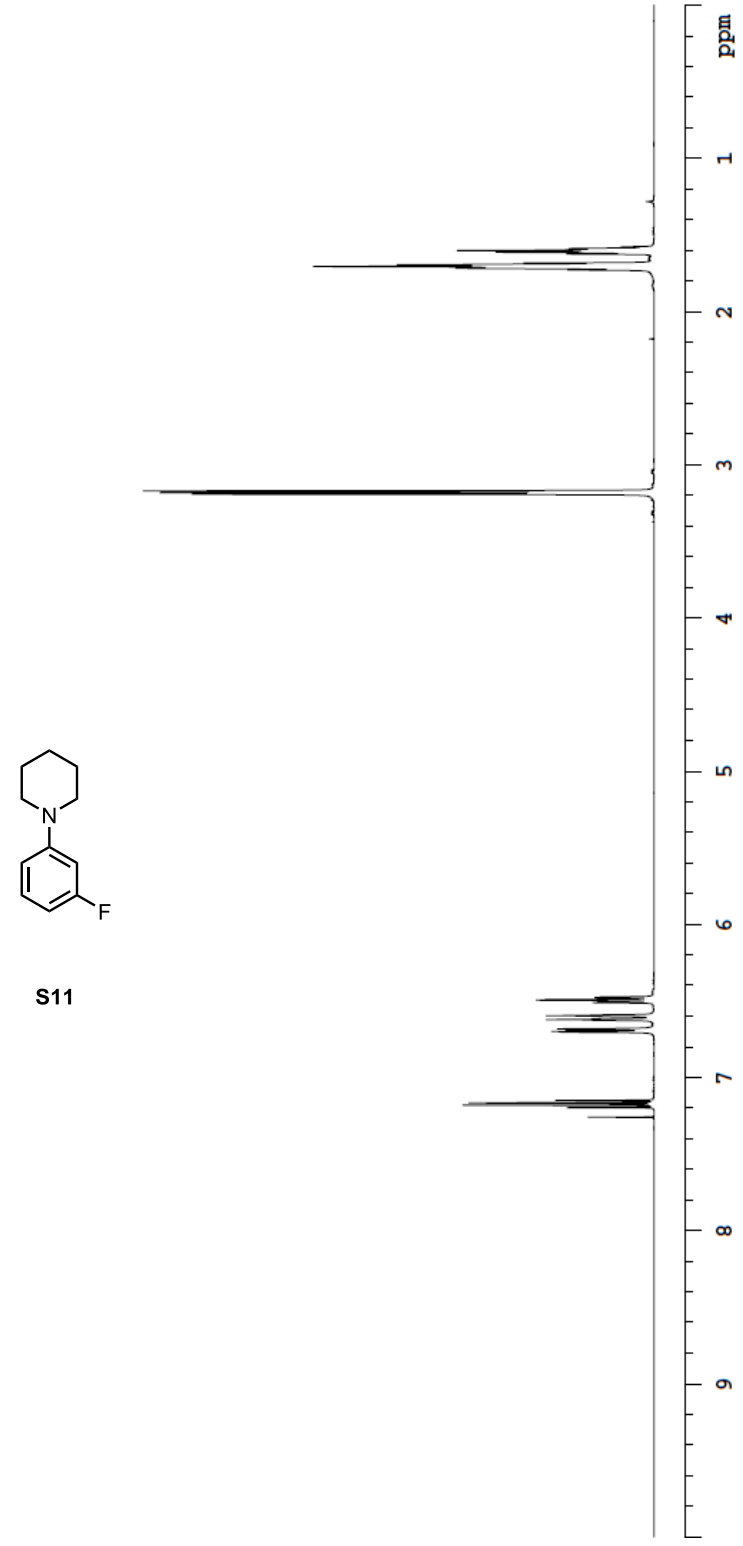



$^{13}$C NMR ($CDCl_3$, 23 ºC) of **S10**



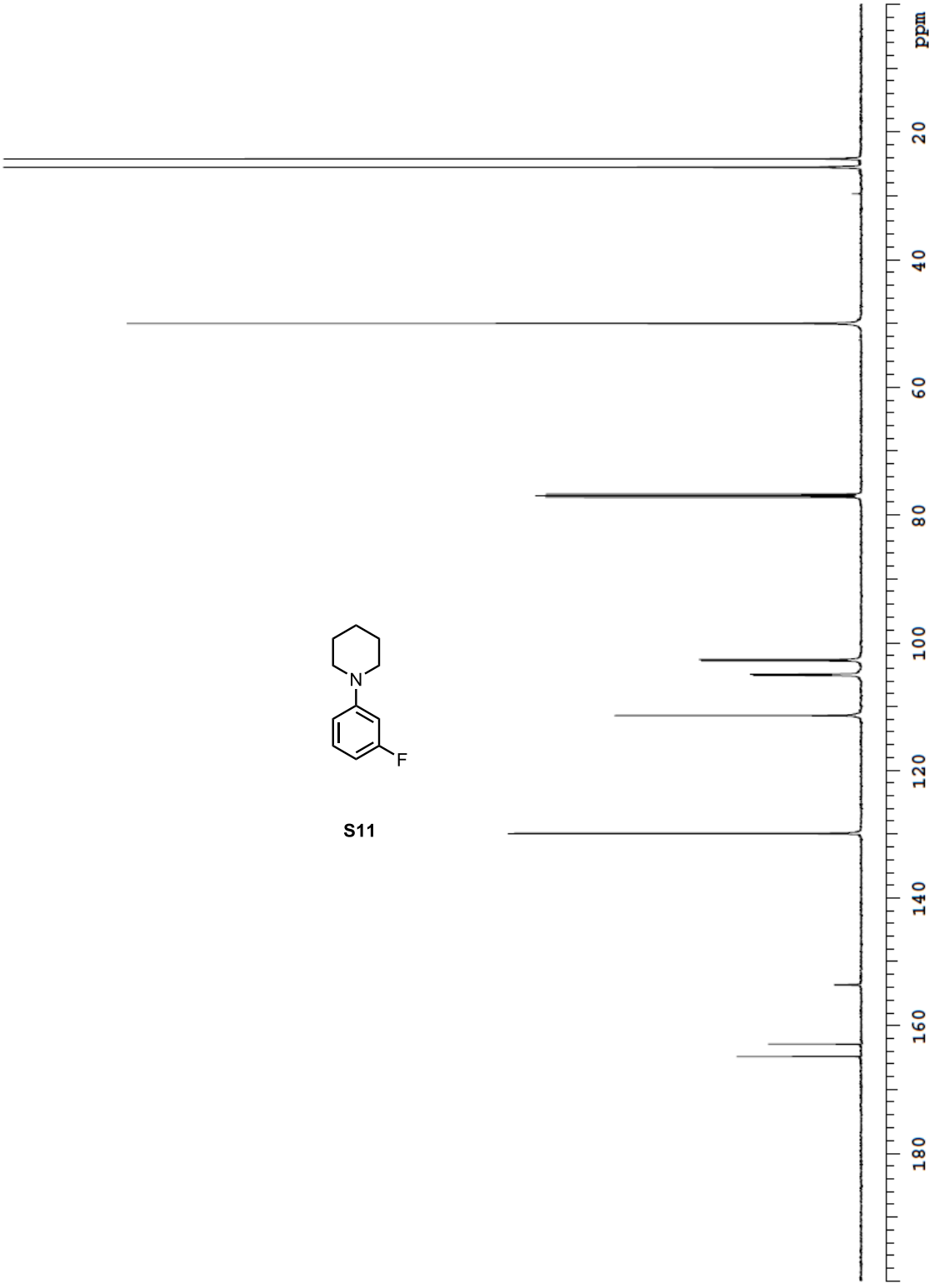

**S10**

$^{19}$F NMR ($CDCl_3$, 23 ºC) of **S10**



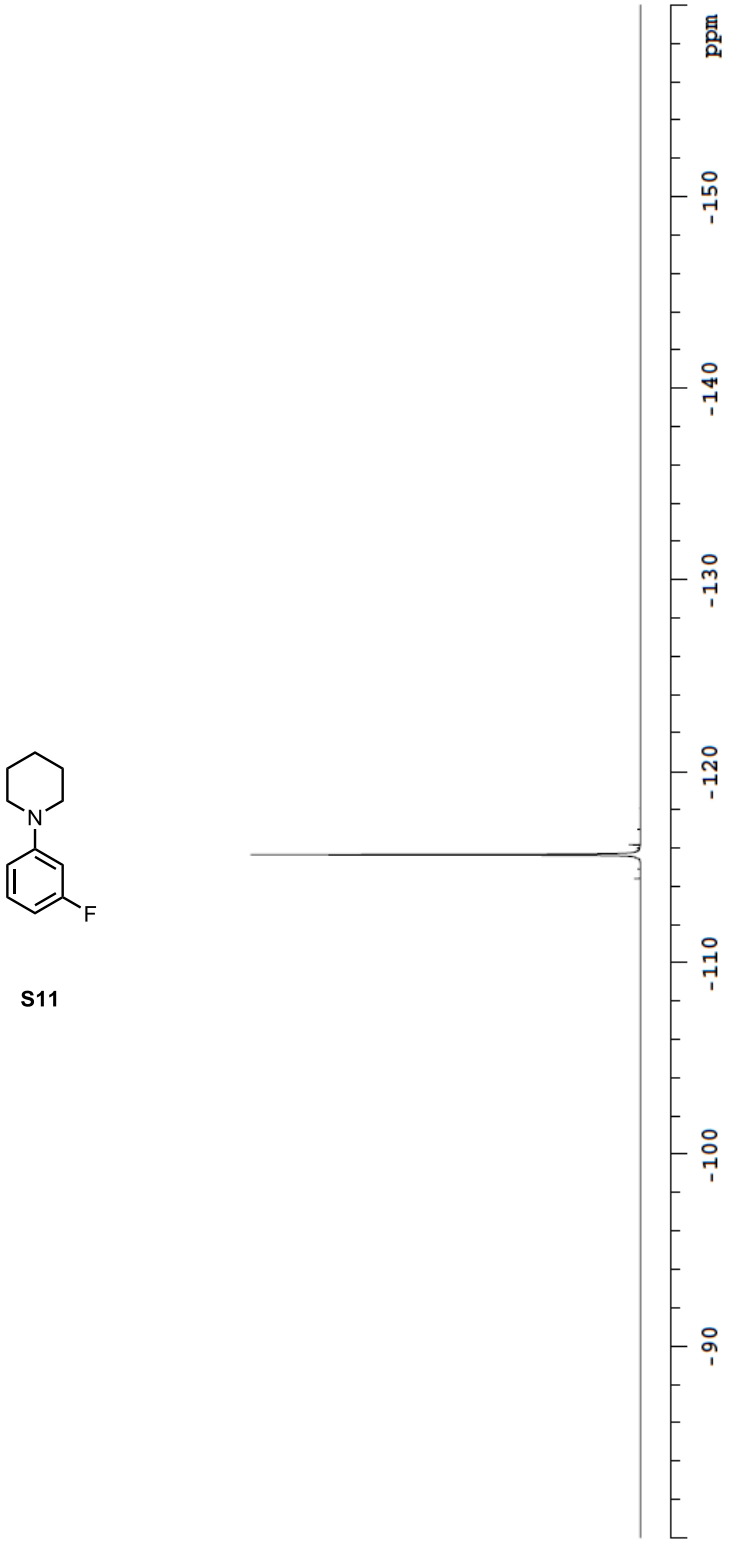

**S11**

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **S11**



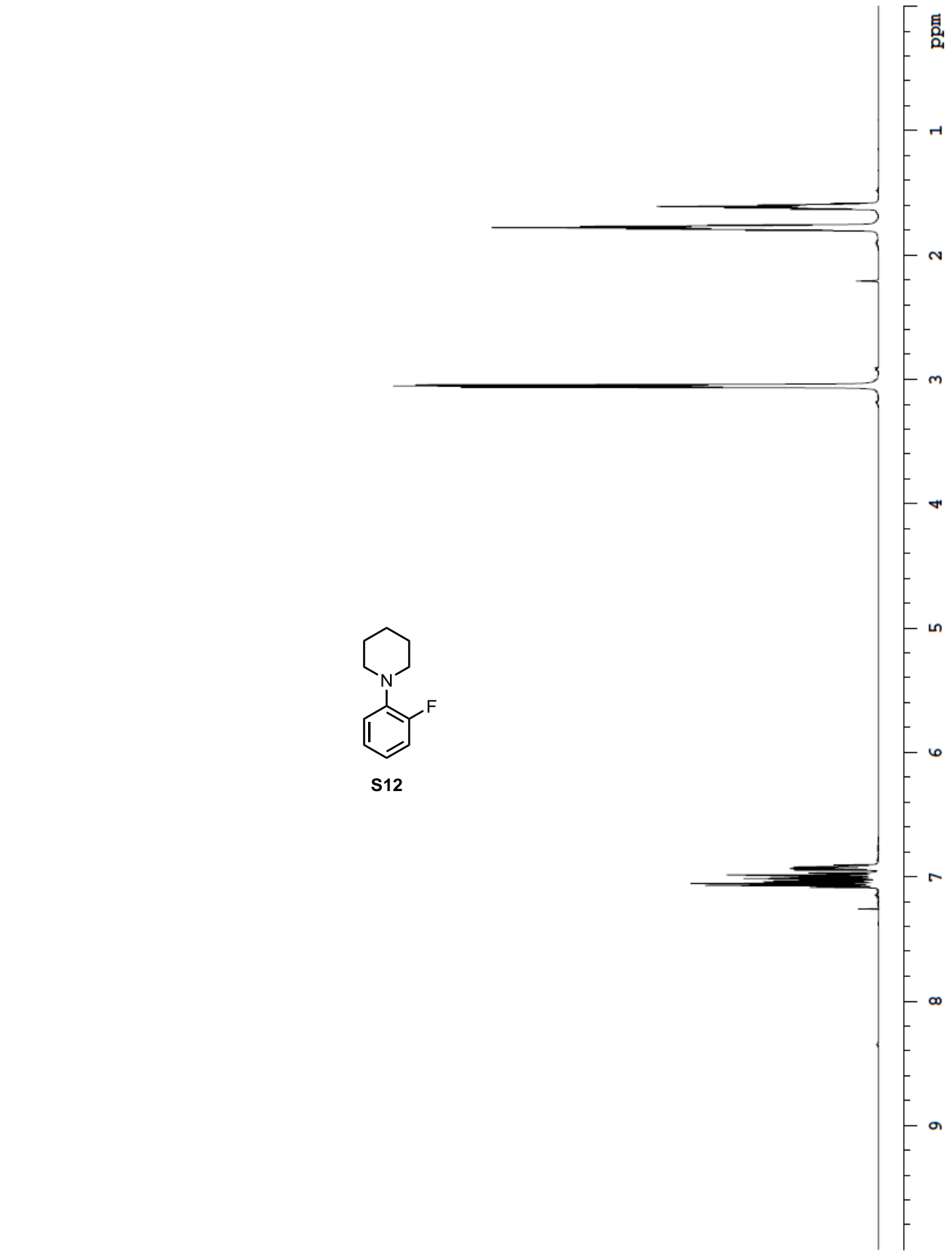

**S11**

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S11**

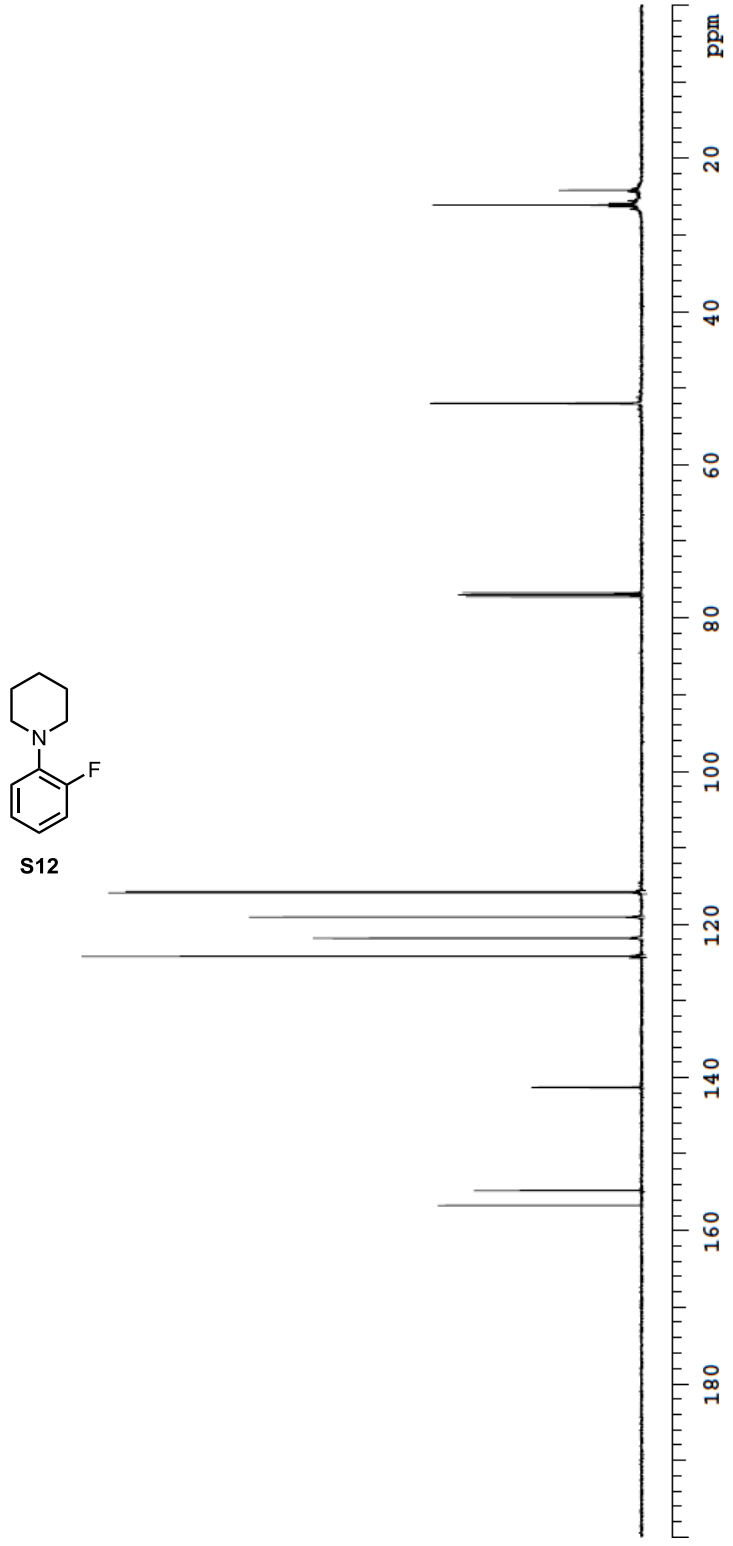



**S11**

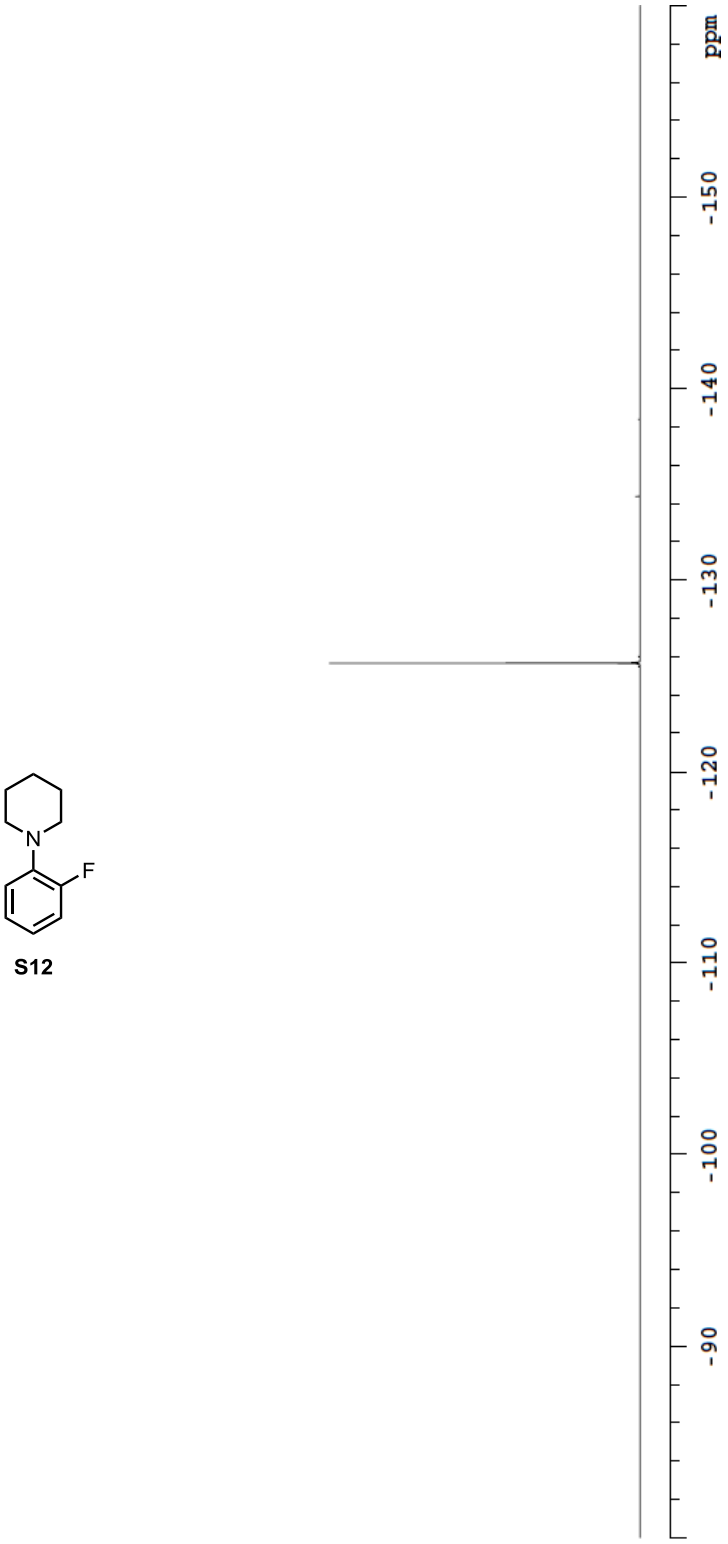
$^{19}$F NMR ($CDCl_3$, 23 ºC) of **S11**



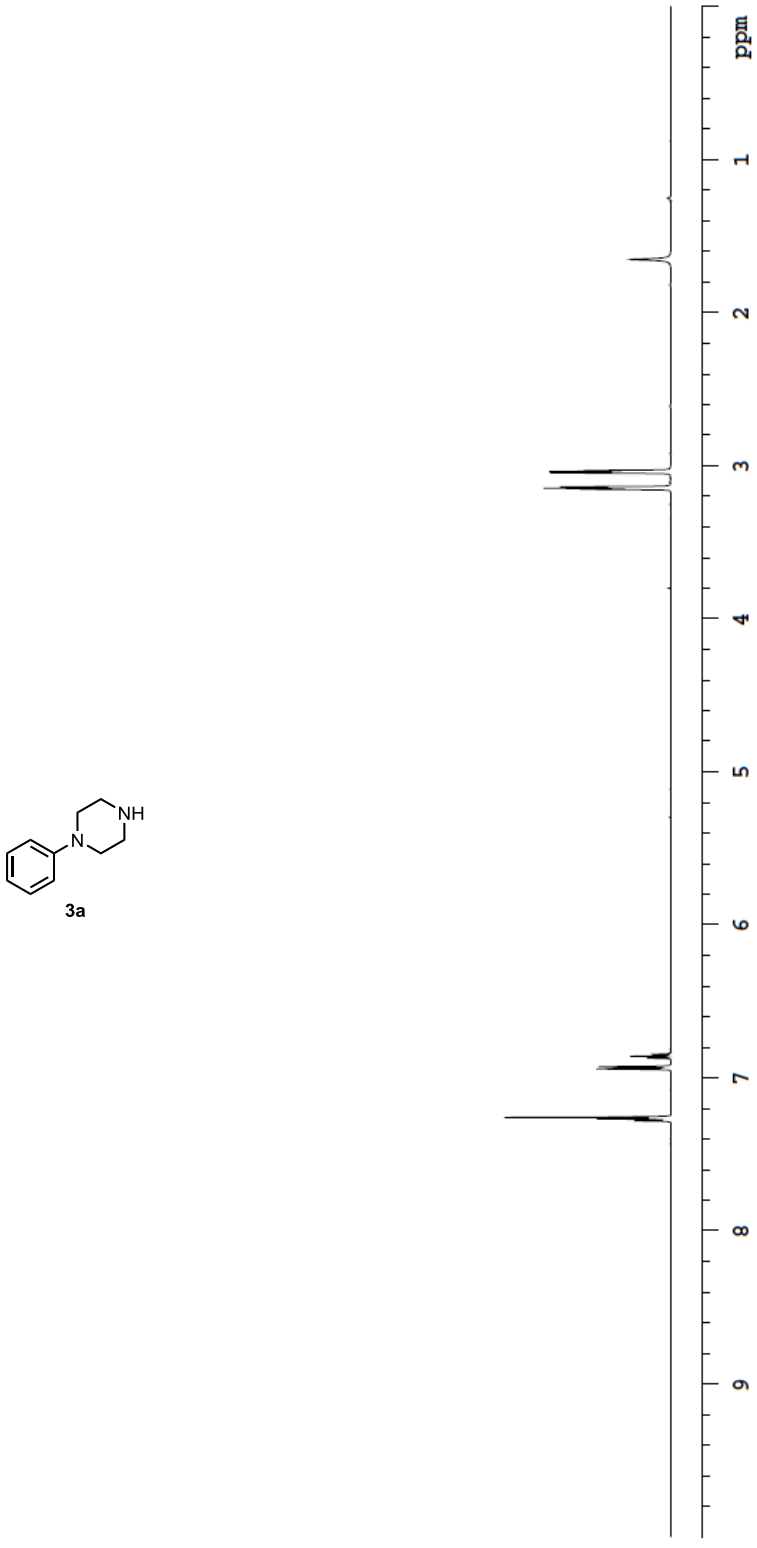

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **S12**



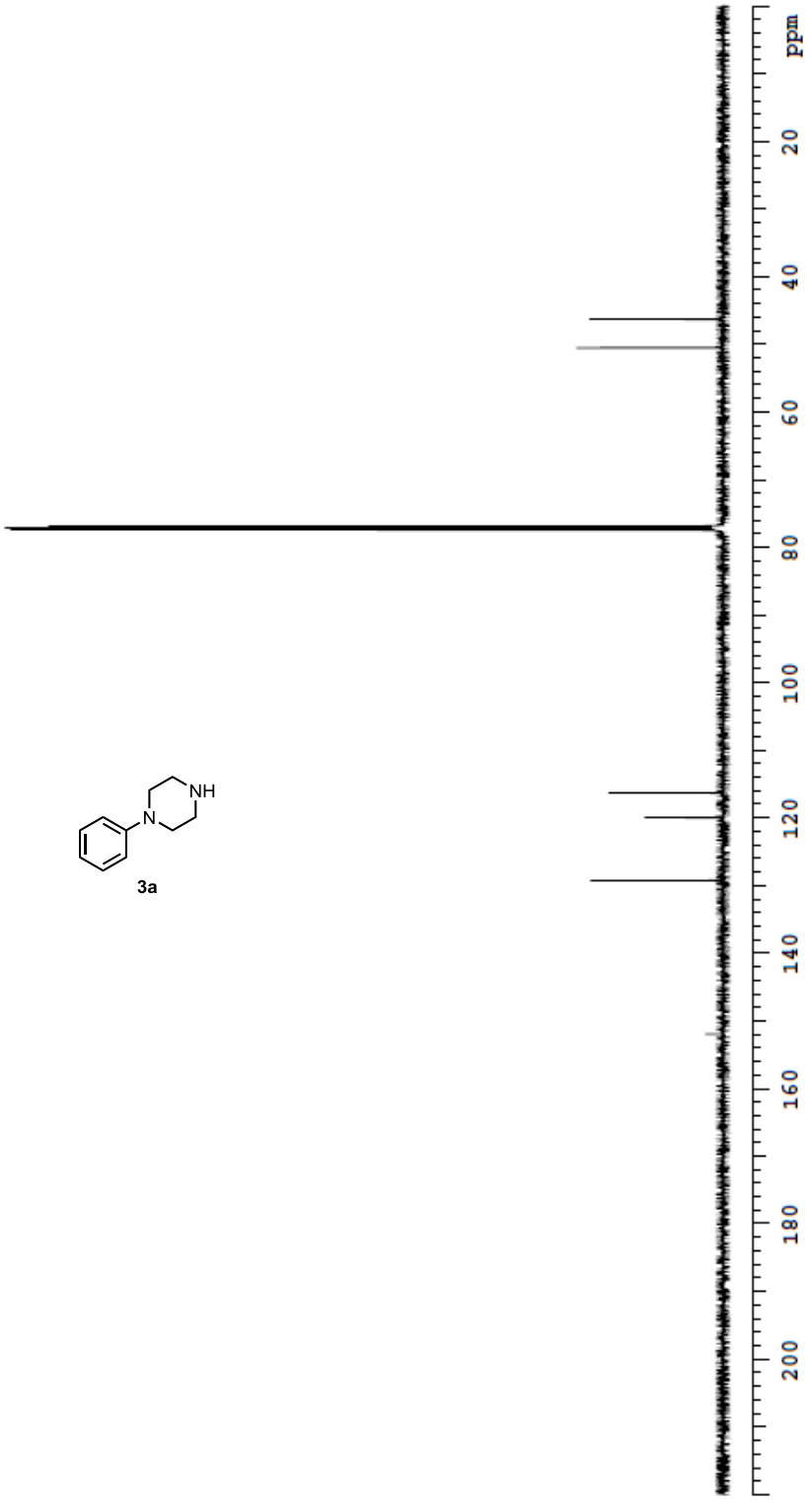

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S12**



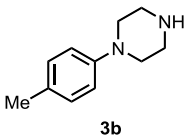

$^{19}$F NMR ($CDCl_3$, 23 ºC) of **S12**



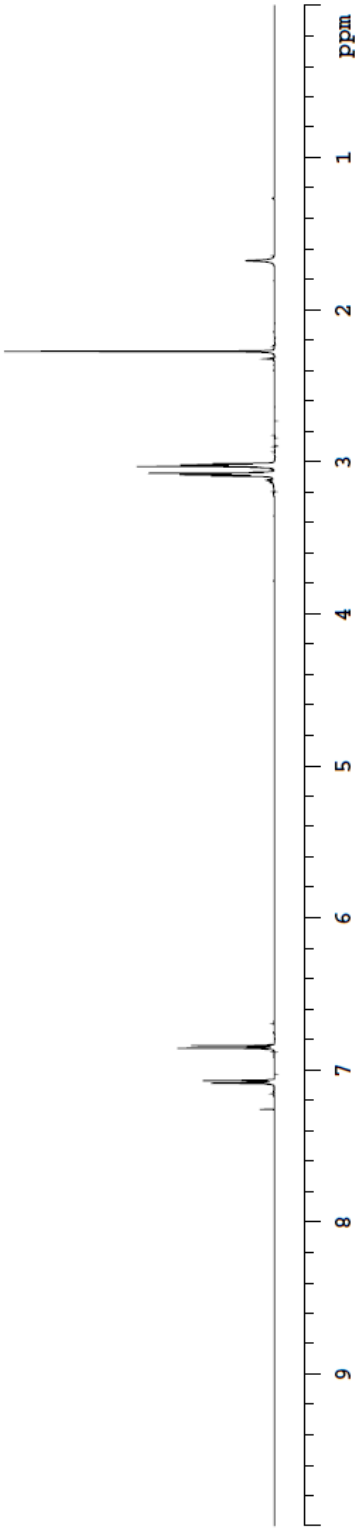

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3a**



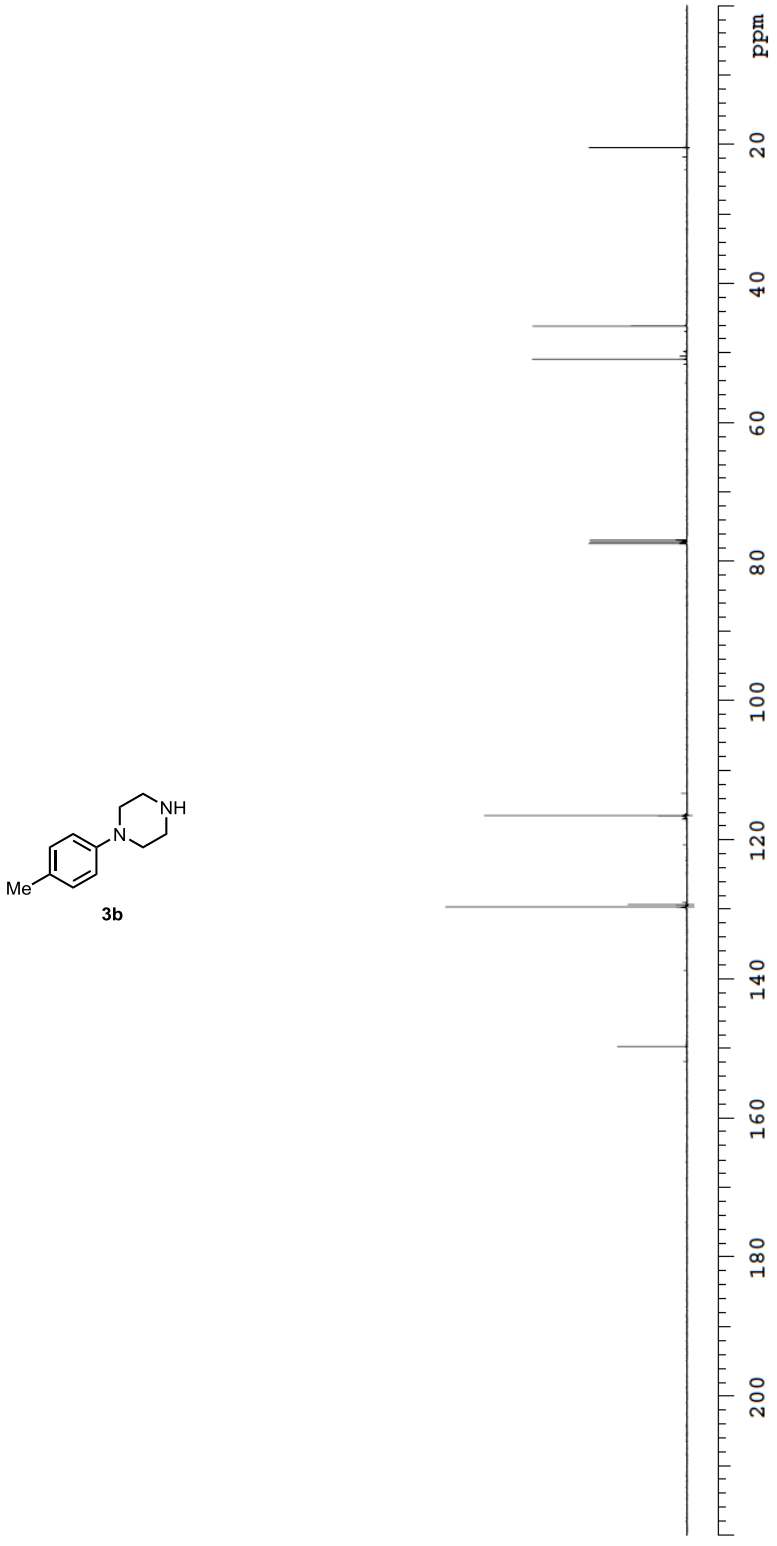

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3a**



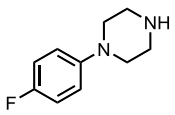

**3b**



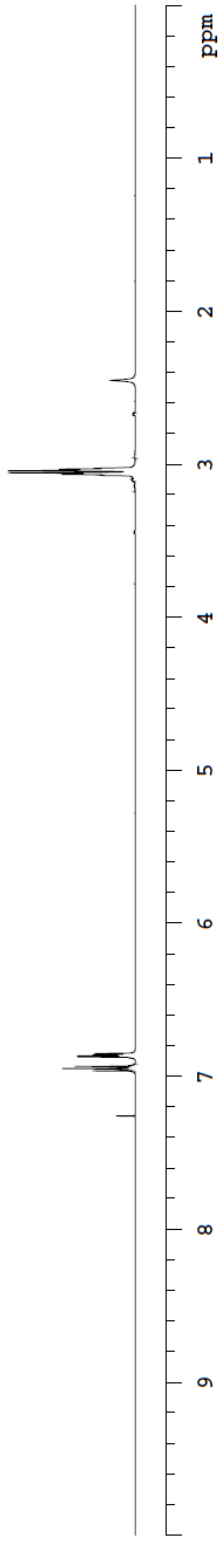

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3b**



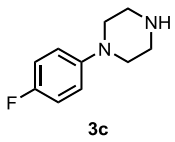

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3b**



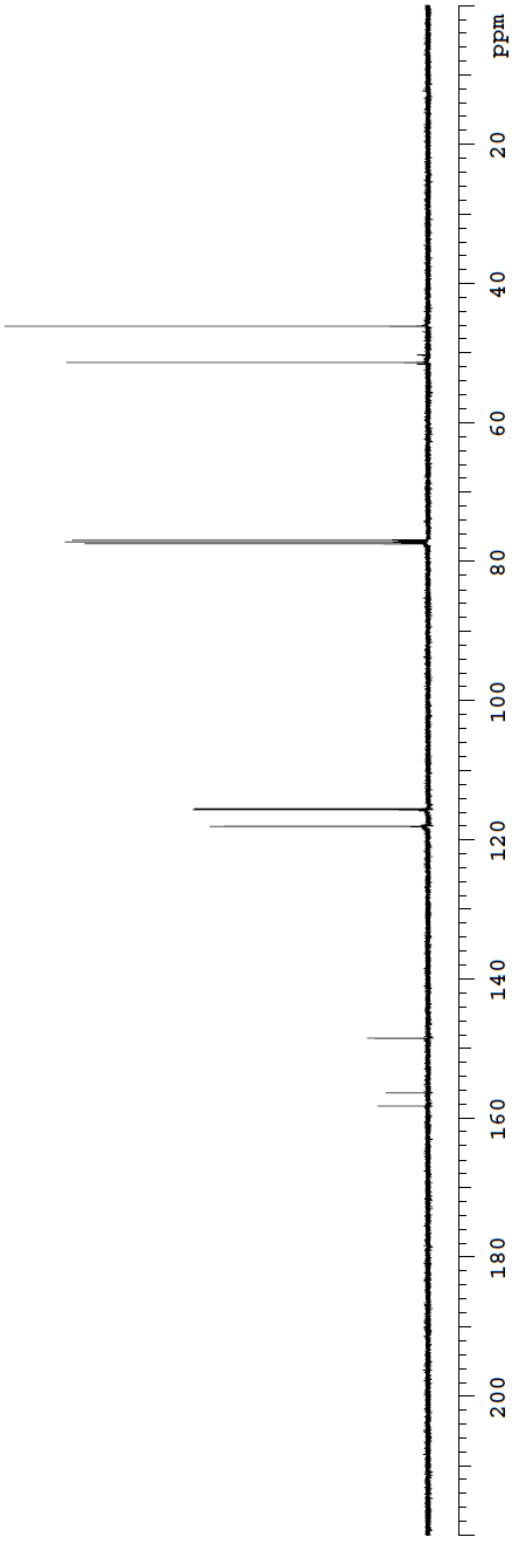

**3c**



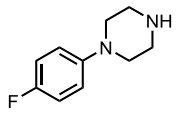

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3c**



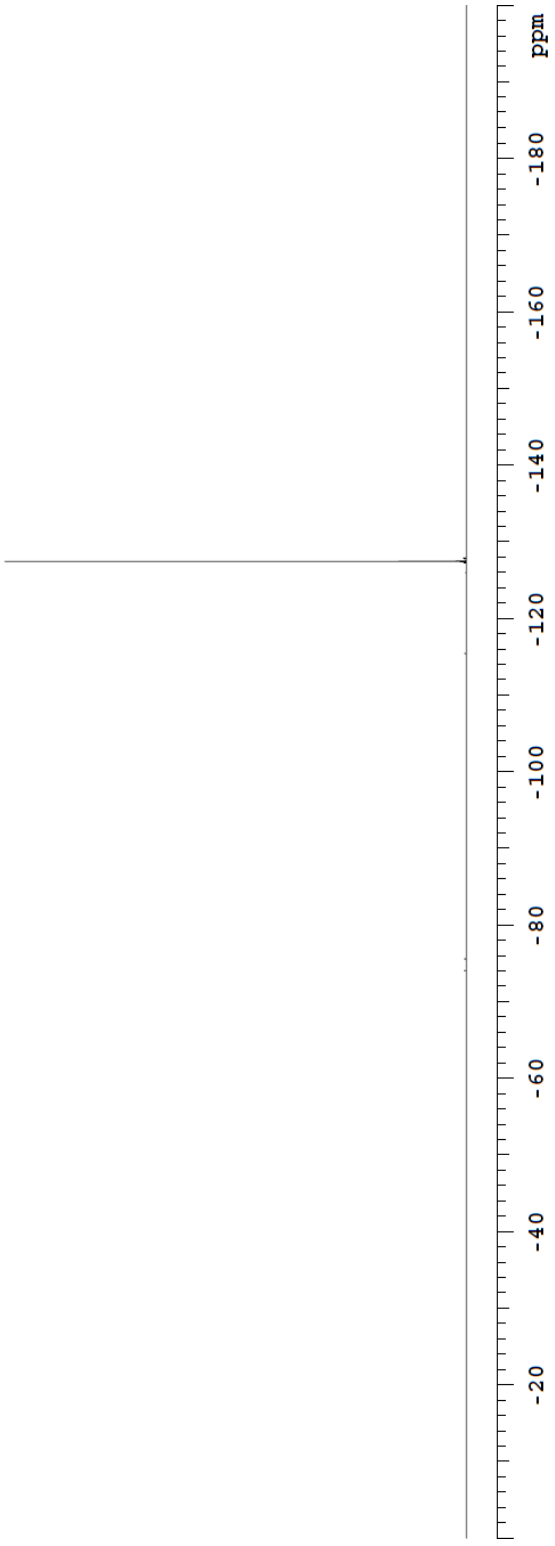

**3c**



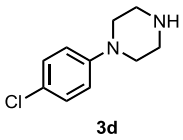

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3c**



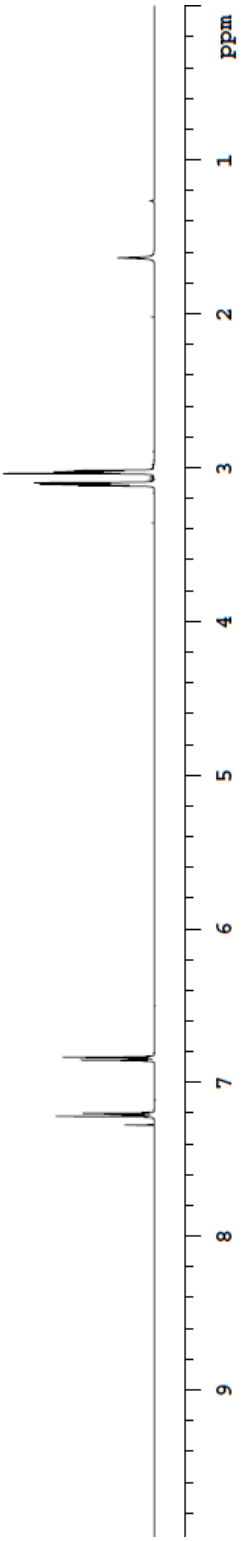

**3c**



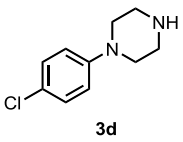

$^{19}F$ NMR ($CDCl_3$, 23 ºC) of **3c**



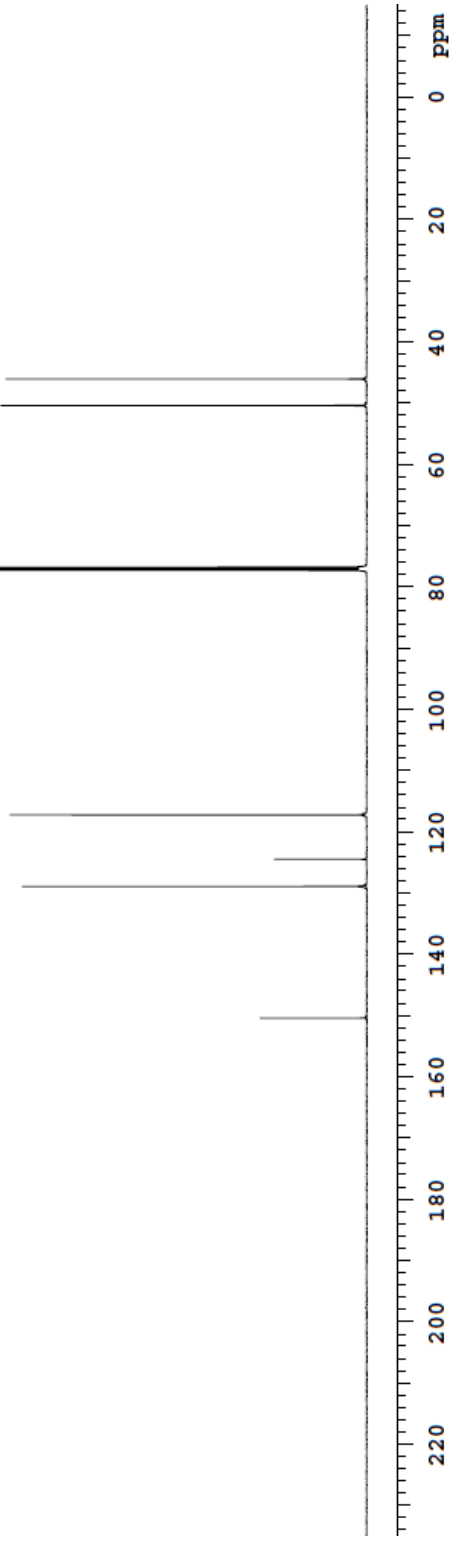

**3d**




$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3d**



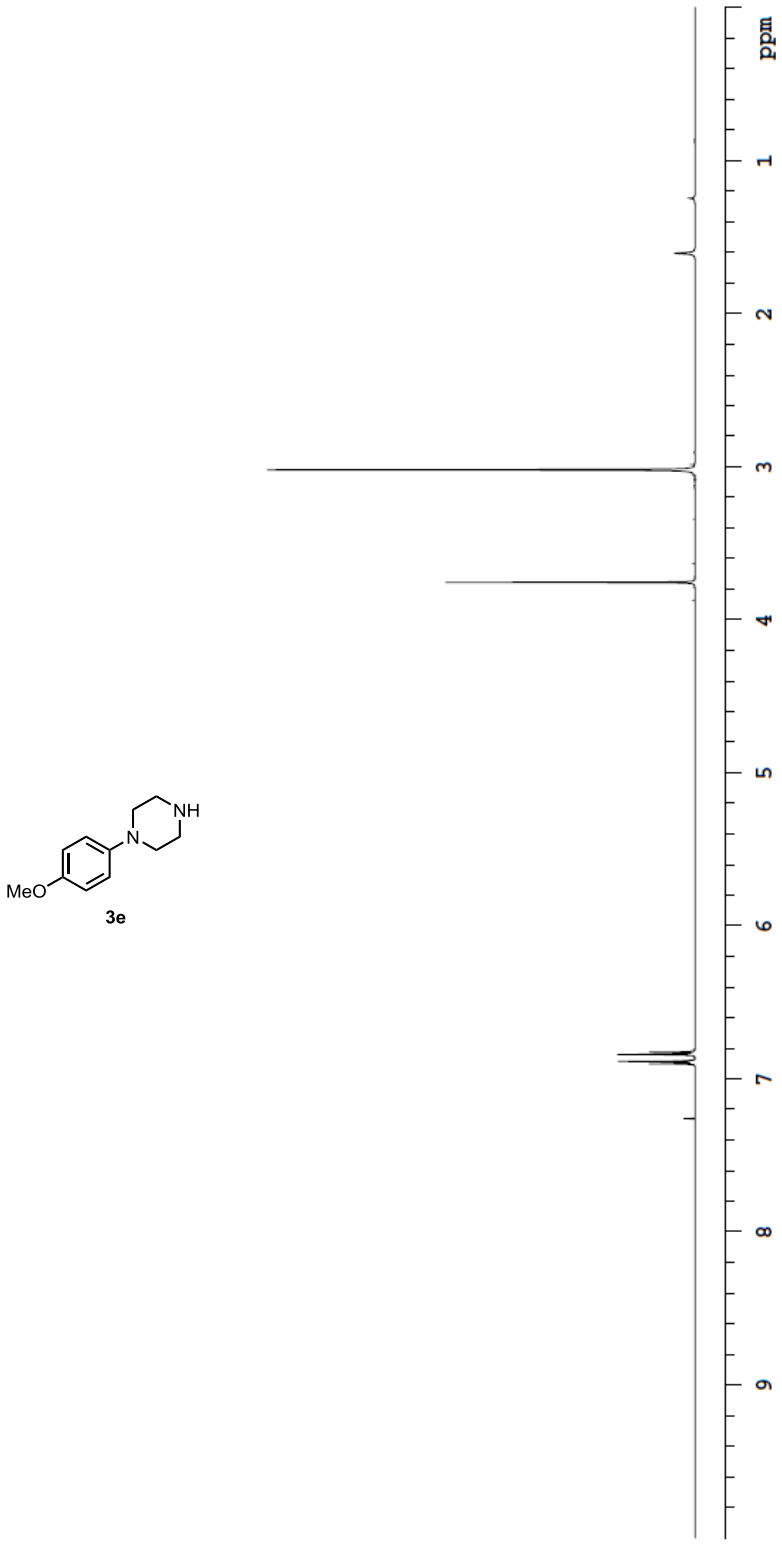

**3d**



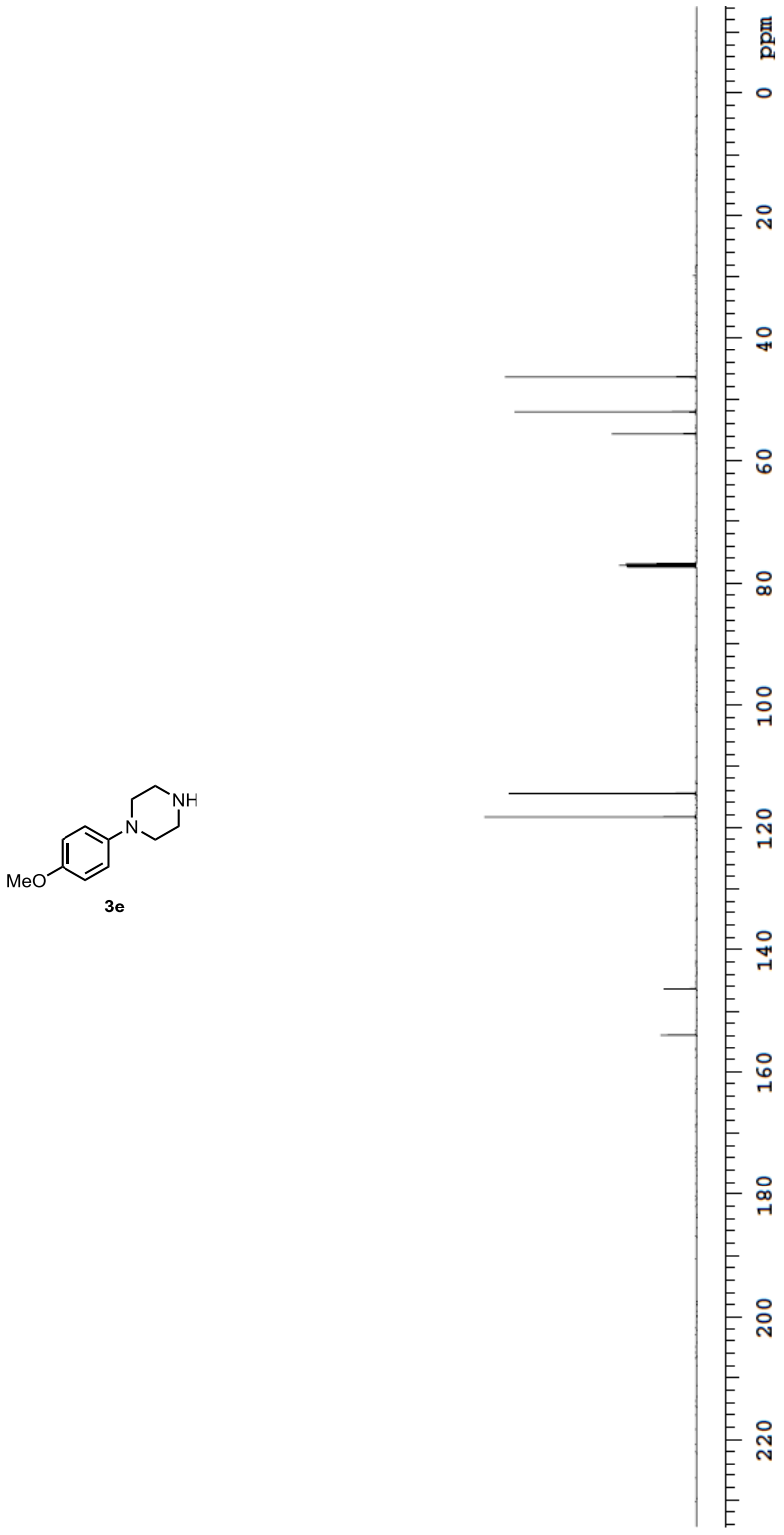

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3d**


$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3e** + **3e-II**

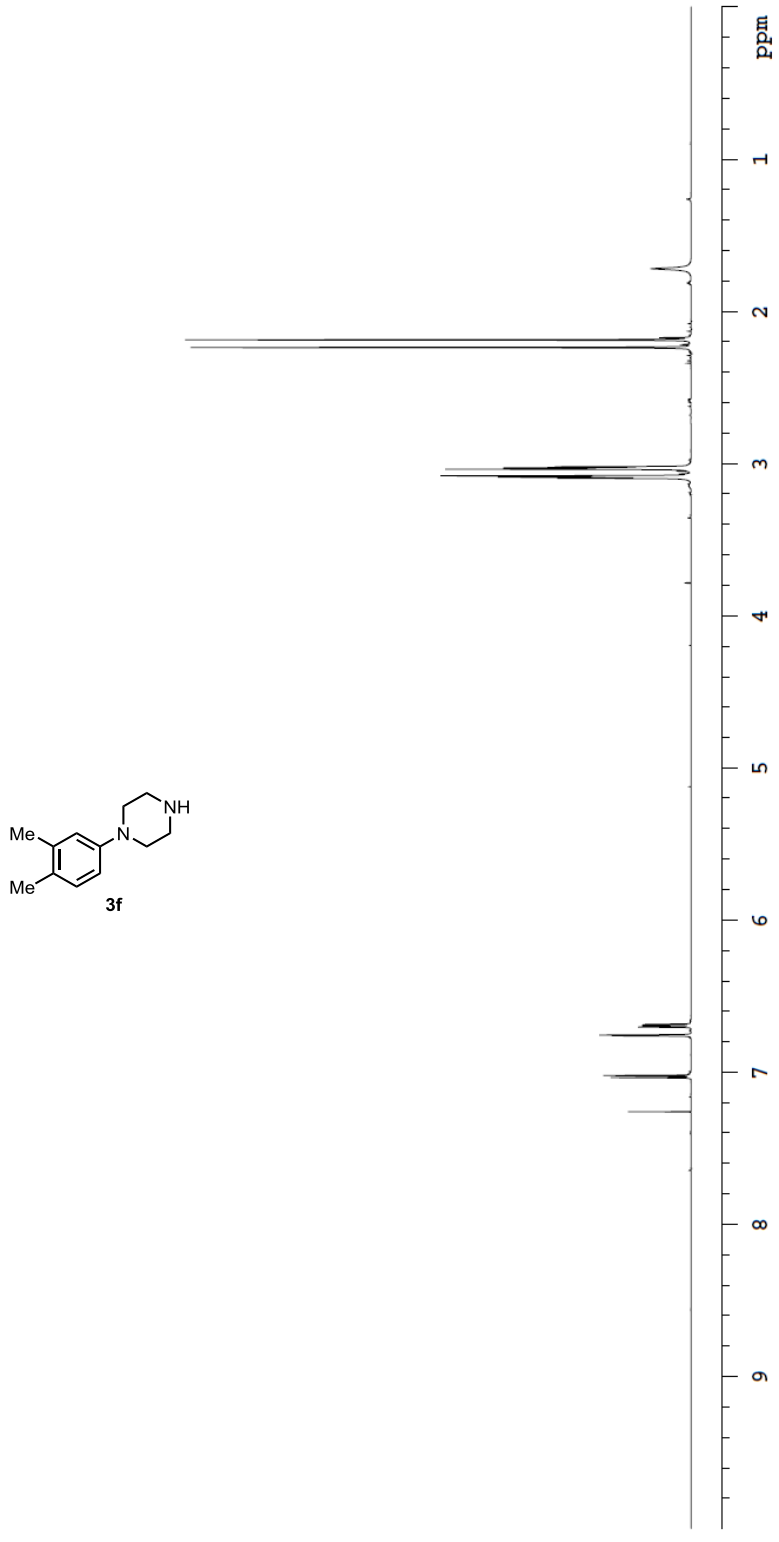

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3e** + **3e-II**



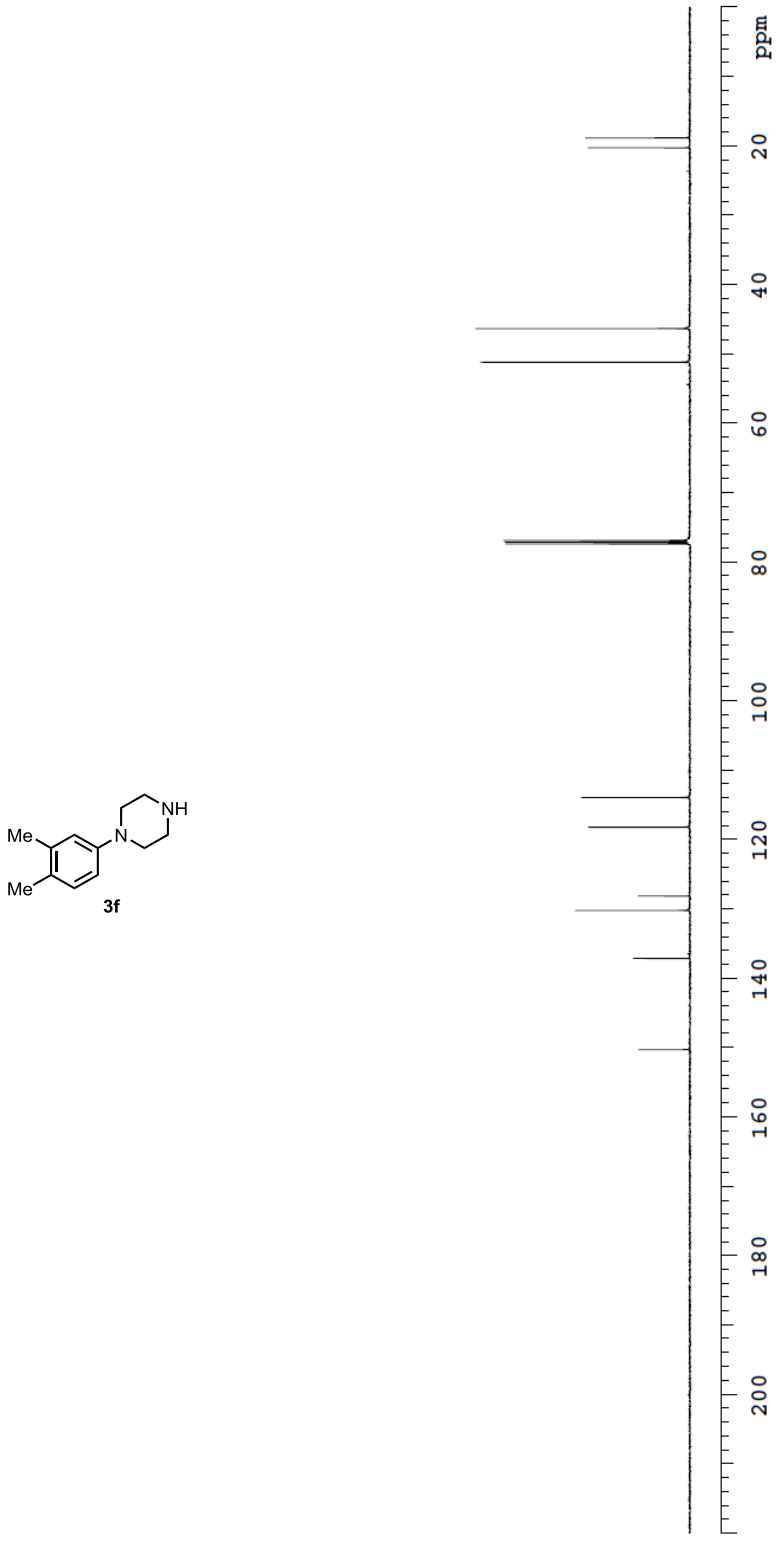

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3e**



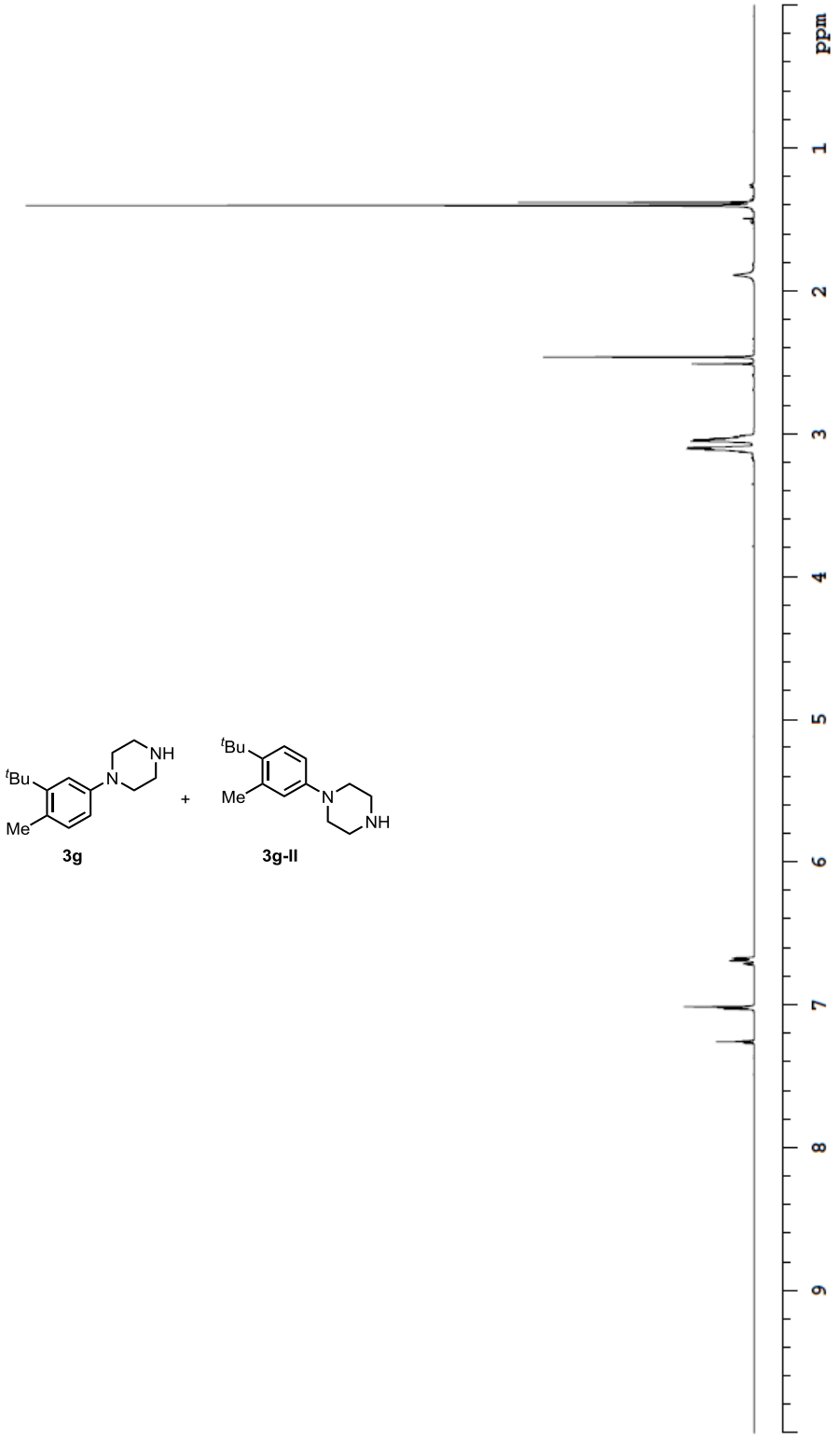

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3e**



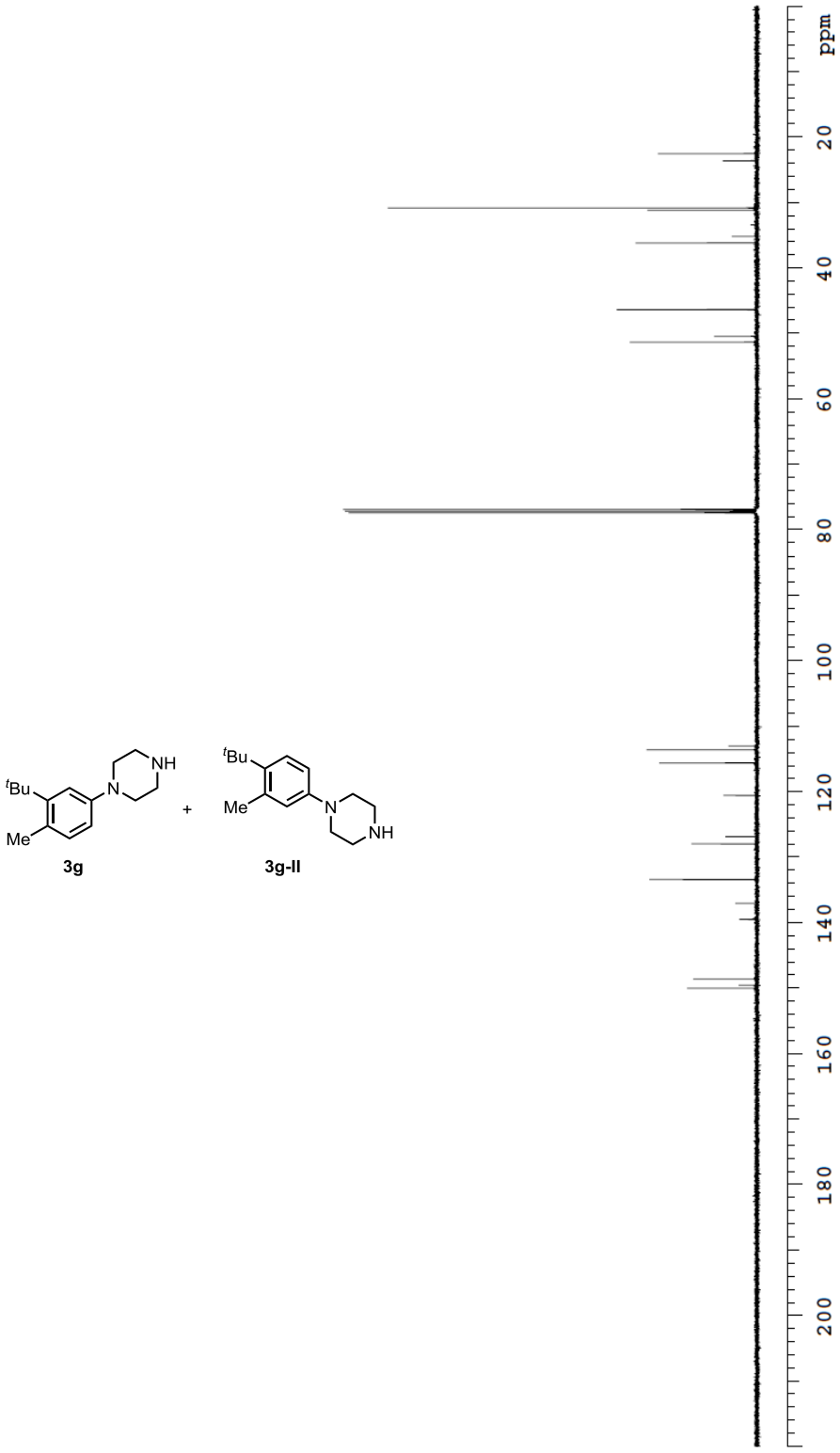

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3f**




$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3f**

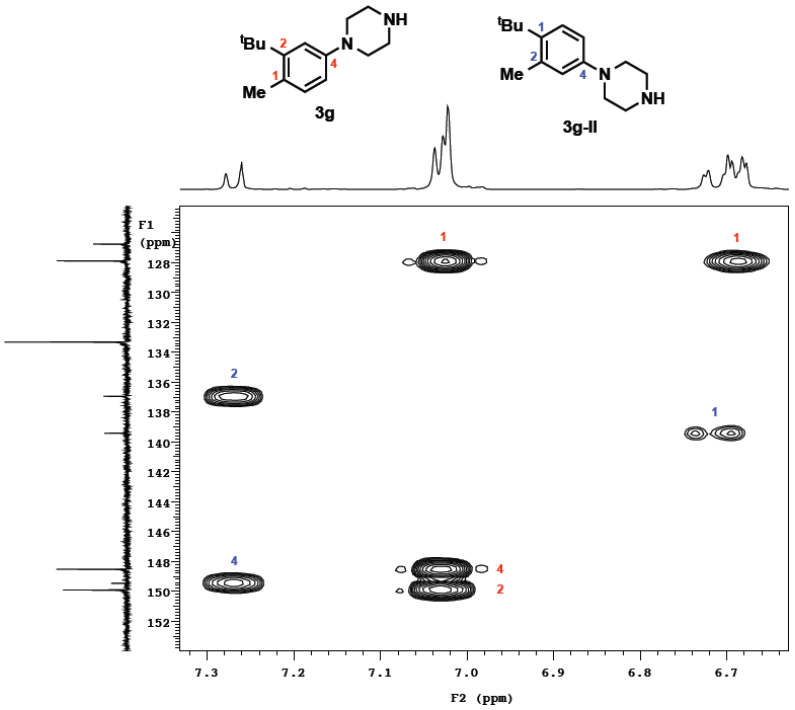


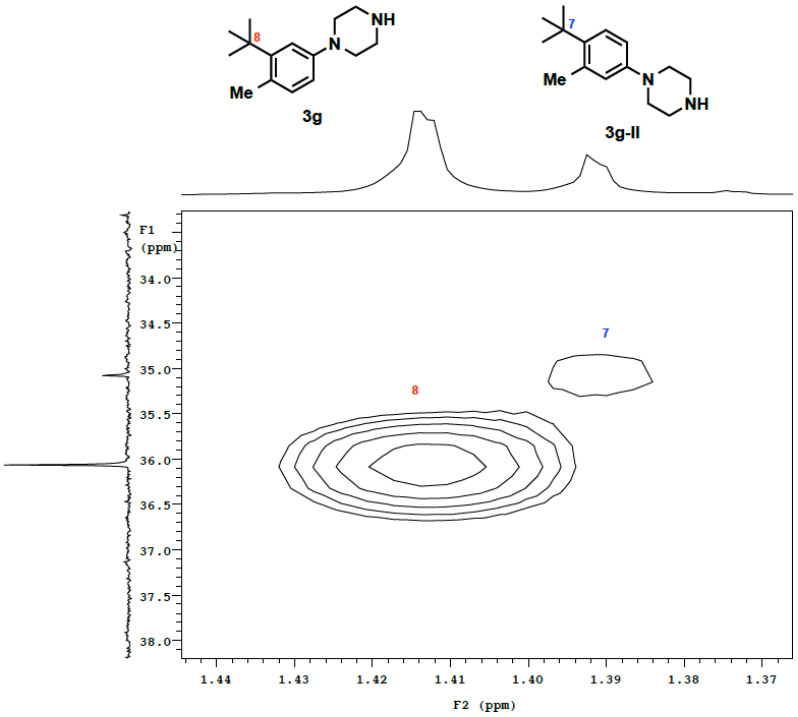

$^1$H NMR ($CDCl_3$, 23 ºC) of **3g** + **3g-II**



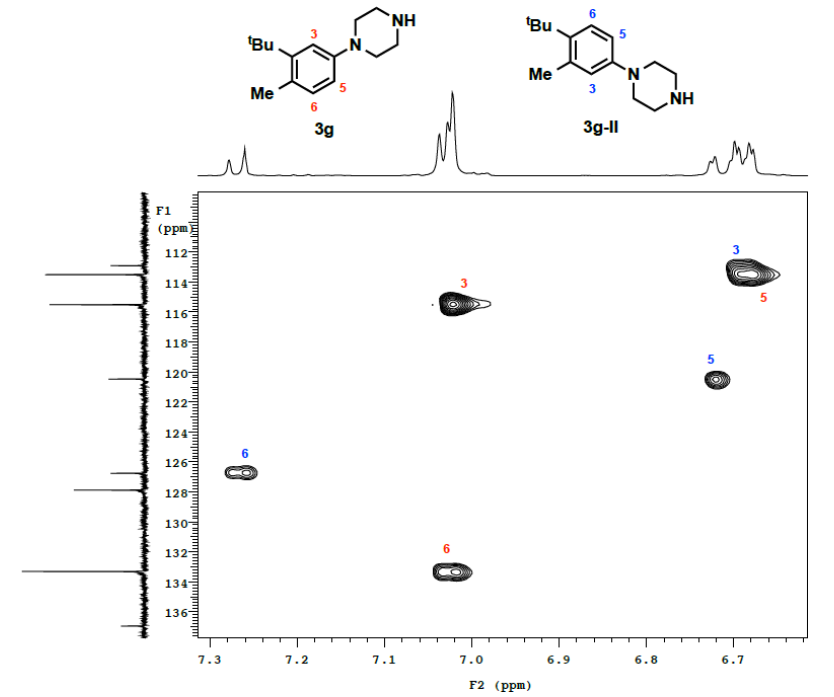

$^{13}$C NMR ($CDCl_3$, 23 ºC) of **3g** + **3g-II**

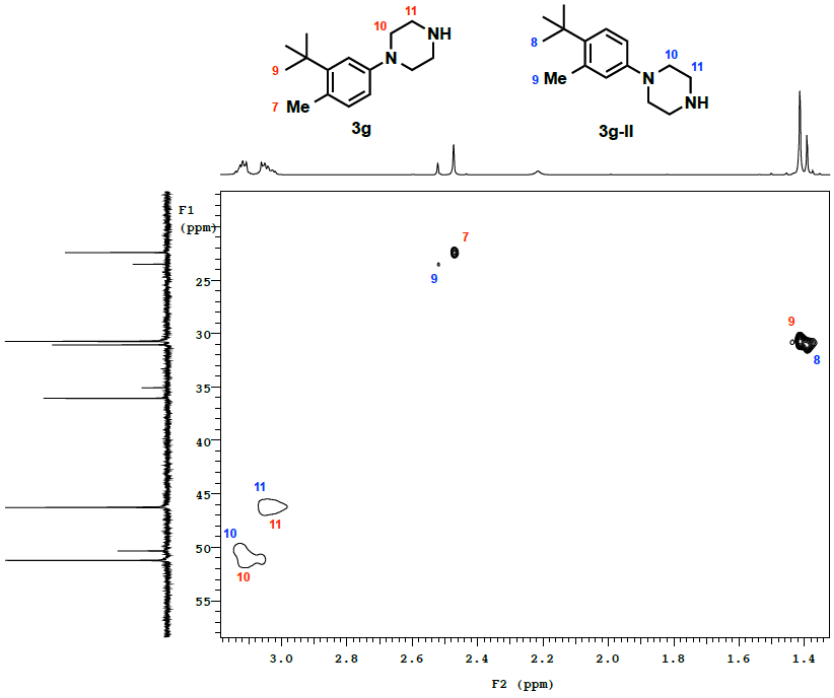
HMBC analysis of **3g** + **3g-II** for assignment of quaternary carbons



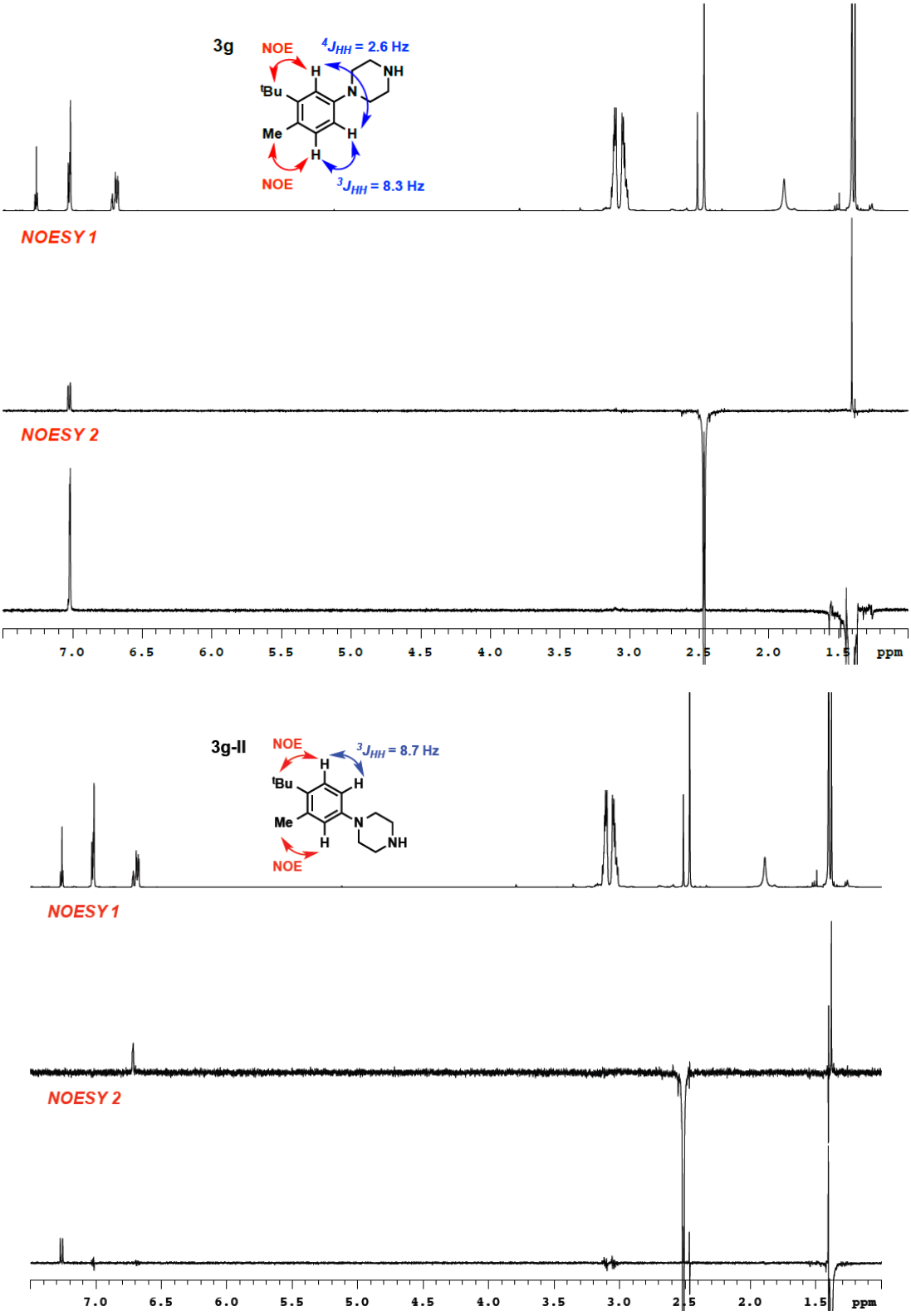



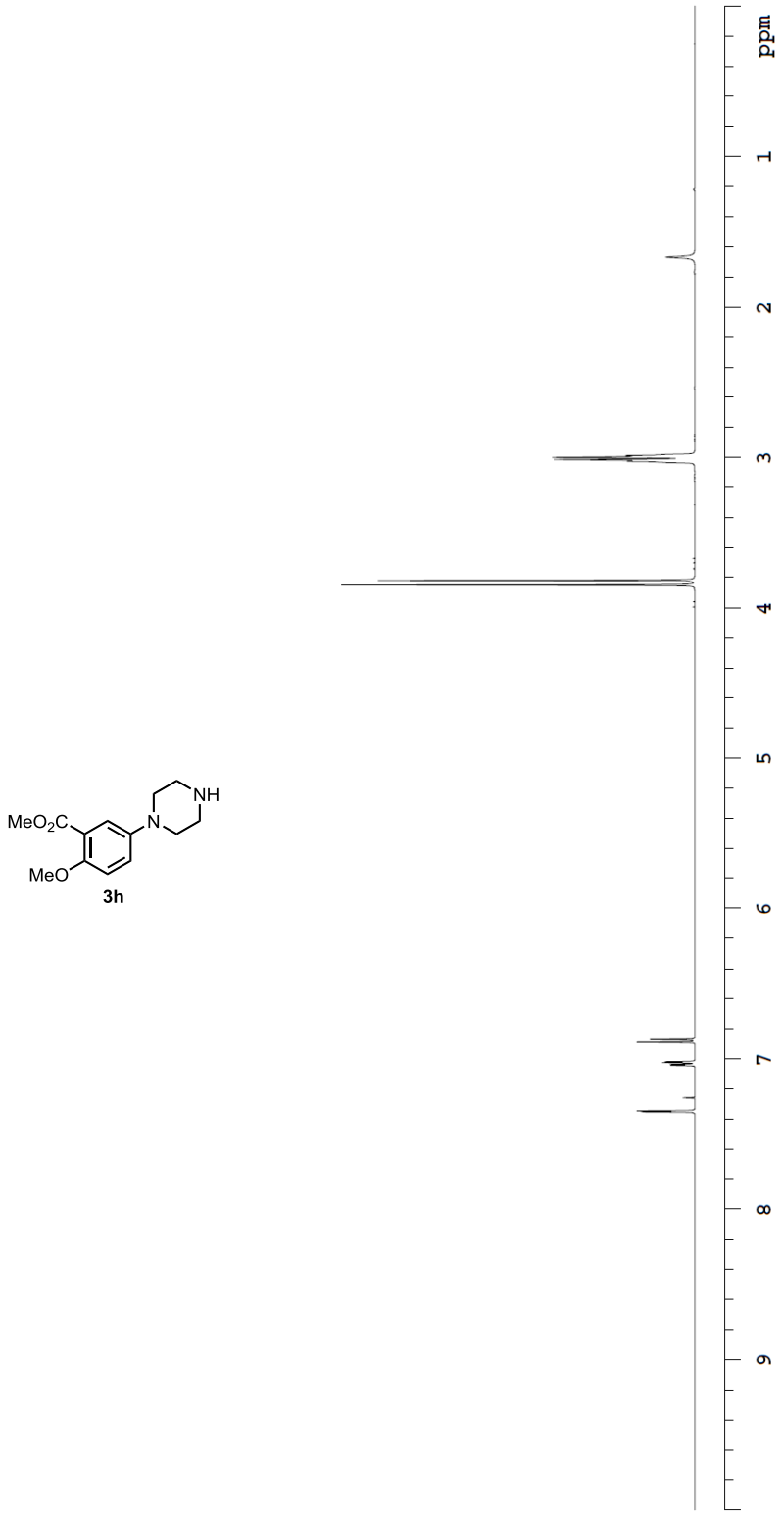
HSQC analysis of **3g** + **3g-II** for assignment of $^{13}C$ NMR signals



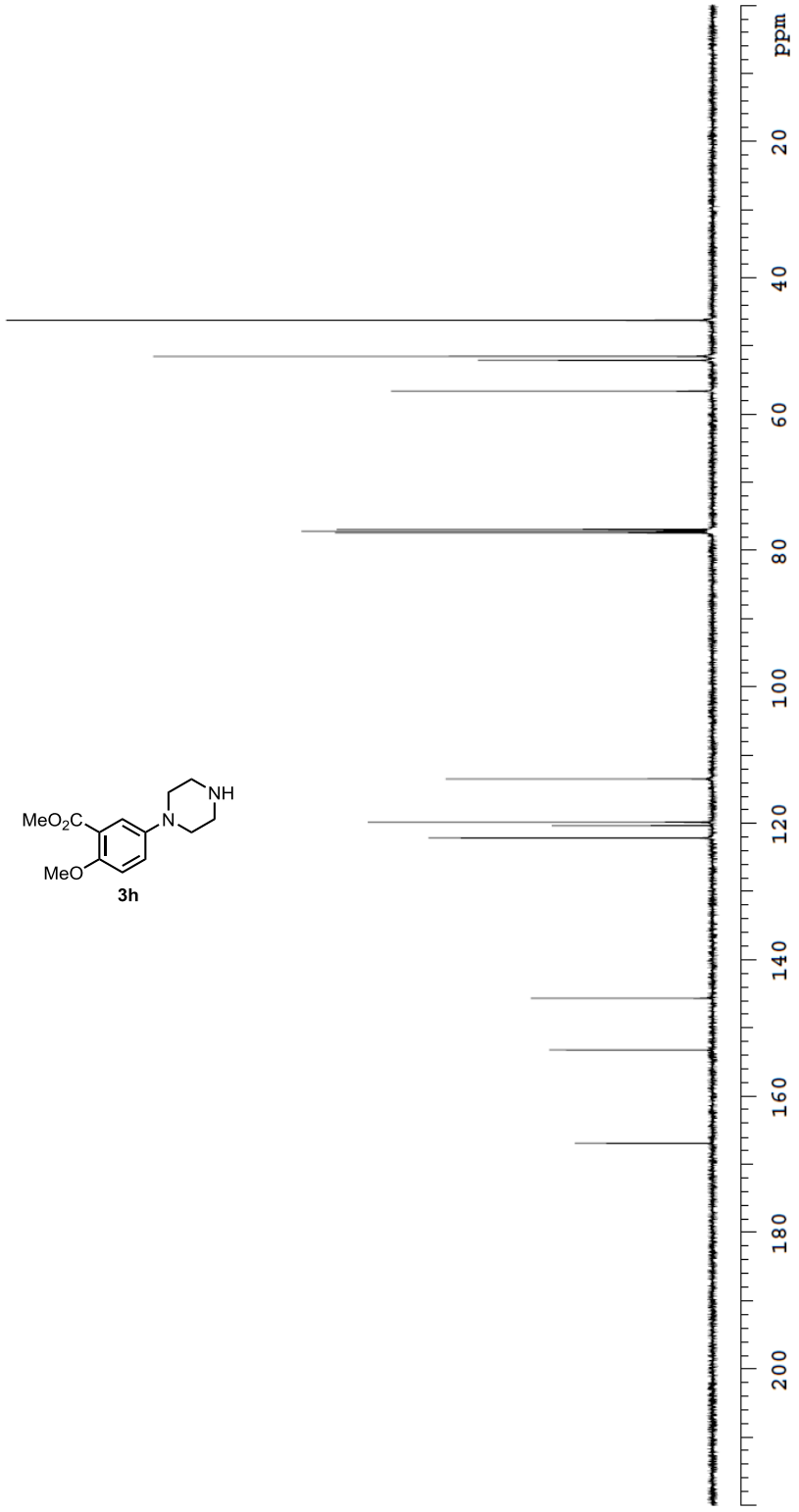



1D NOESY analysis for assignment of **3g** + **3g-II**

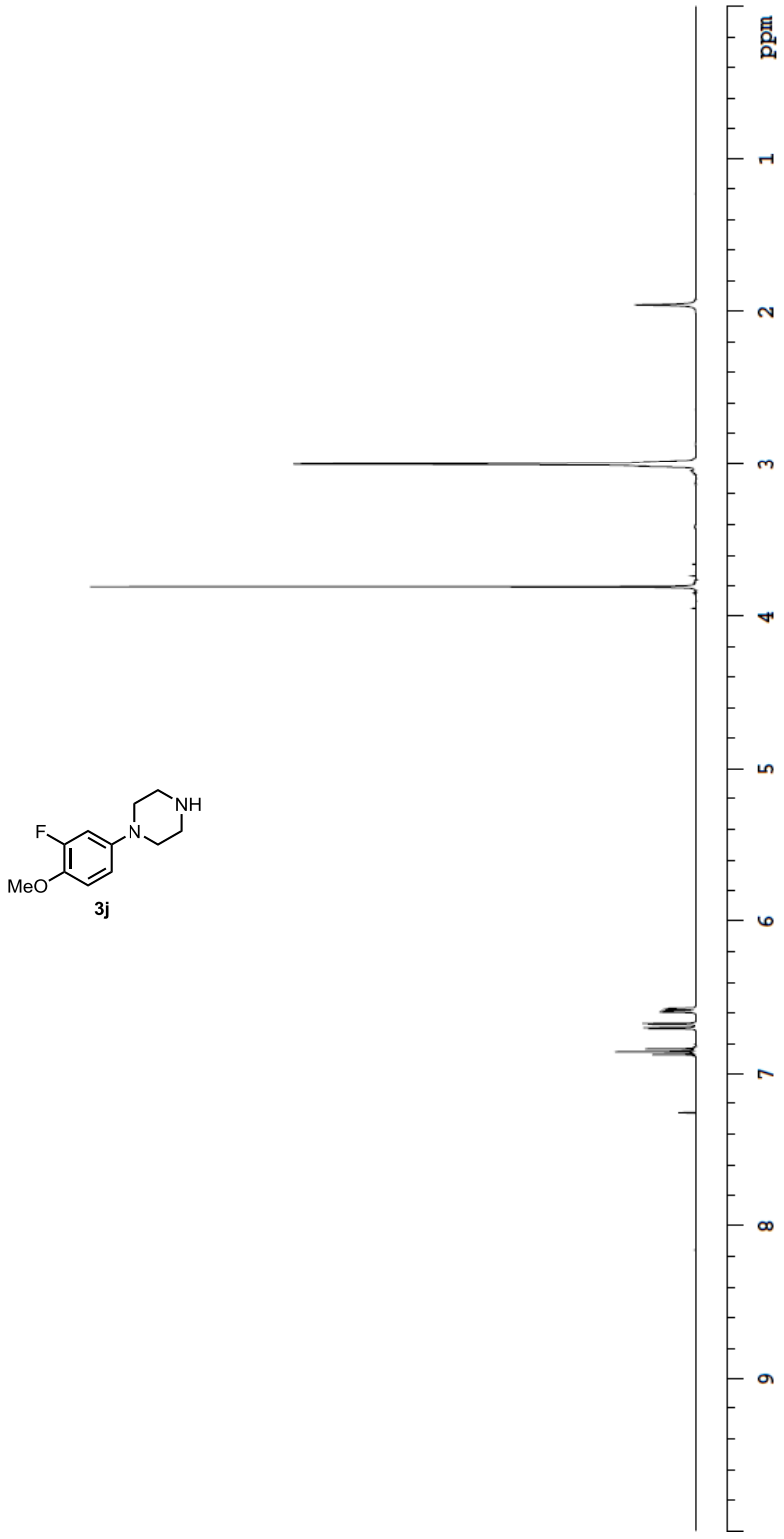




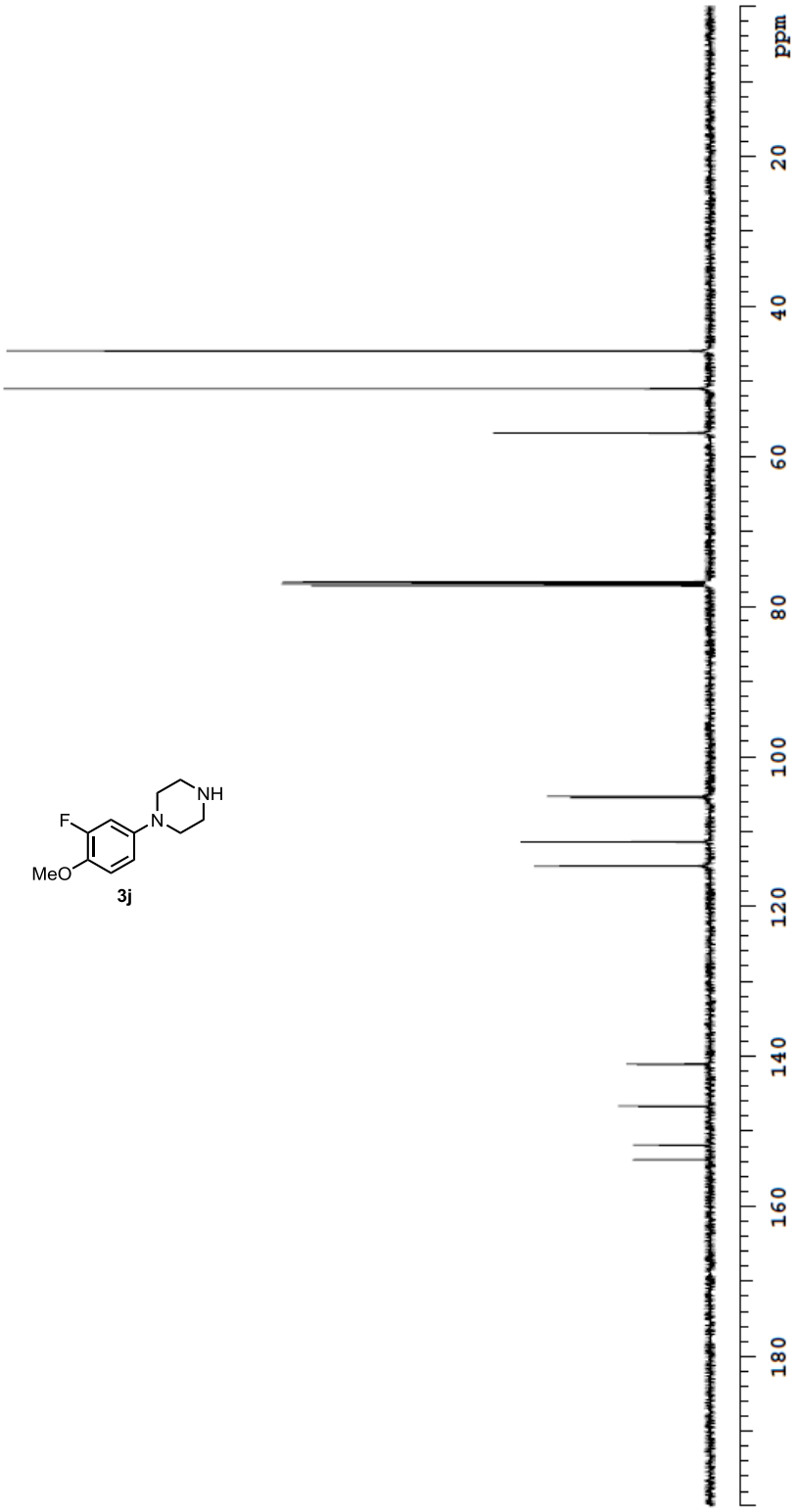

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3h**



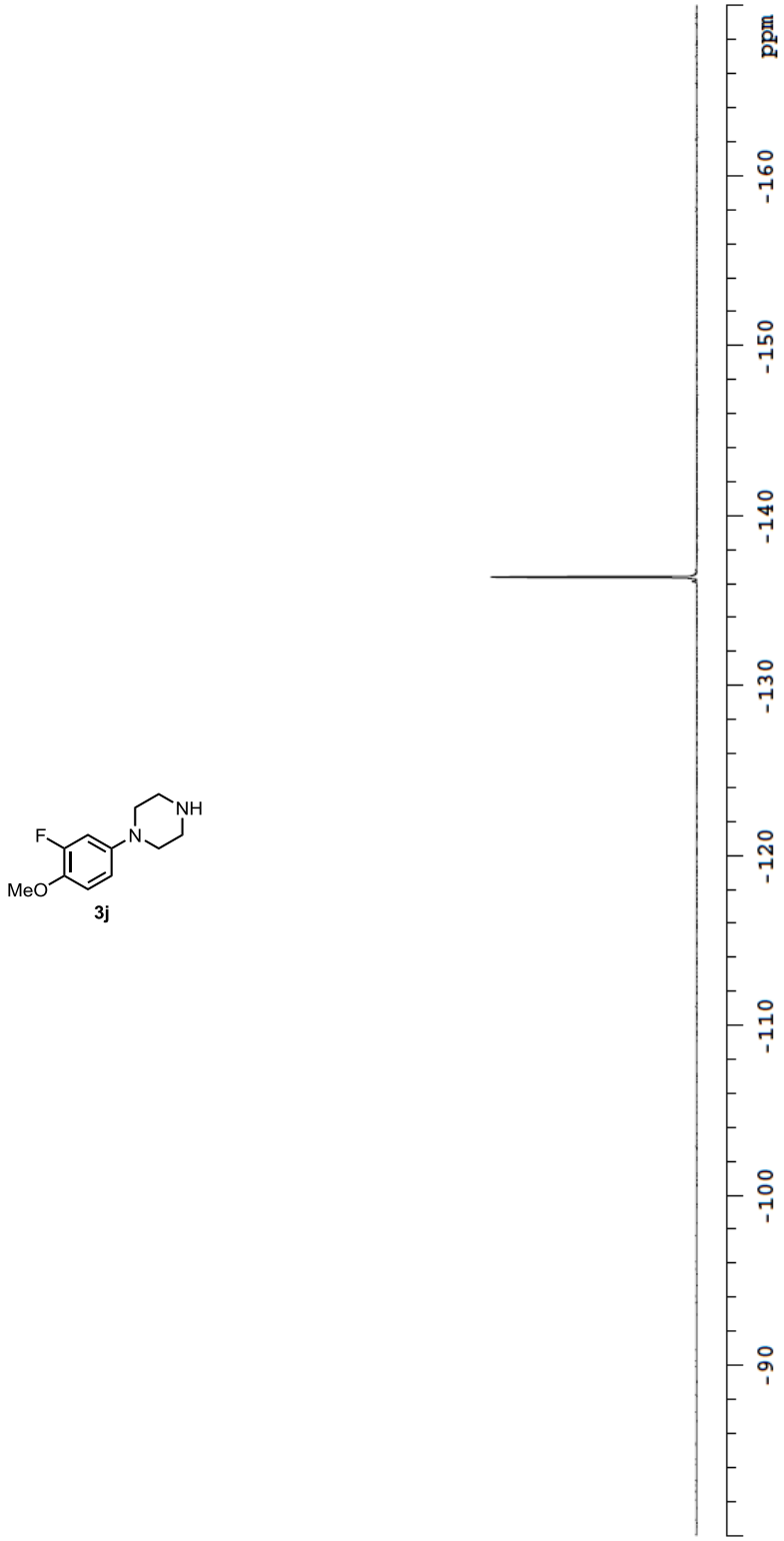

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3h**




$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3j**




$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3j**

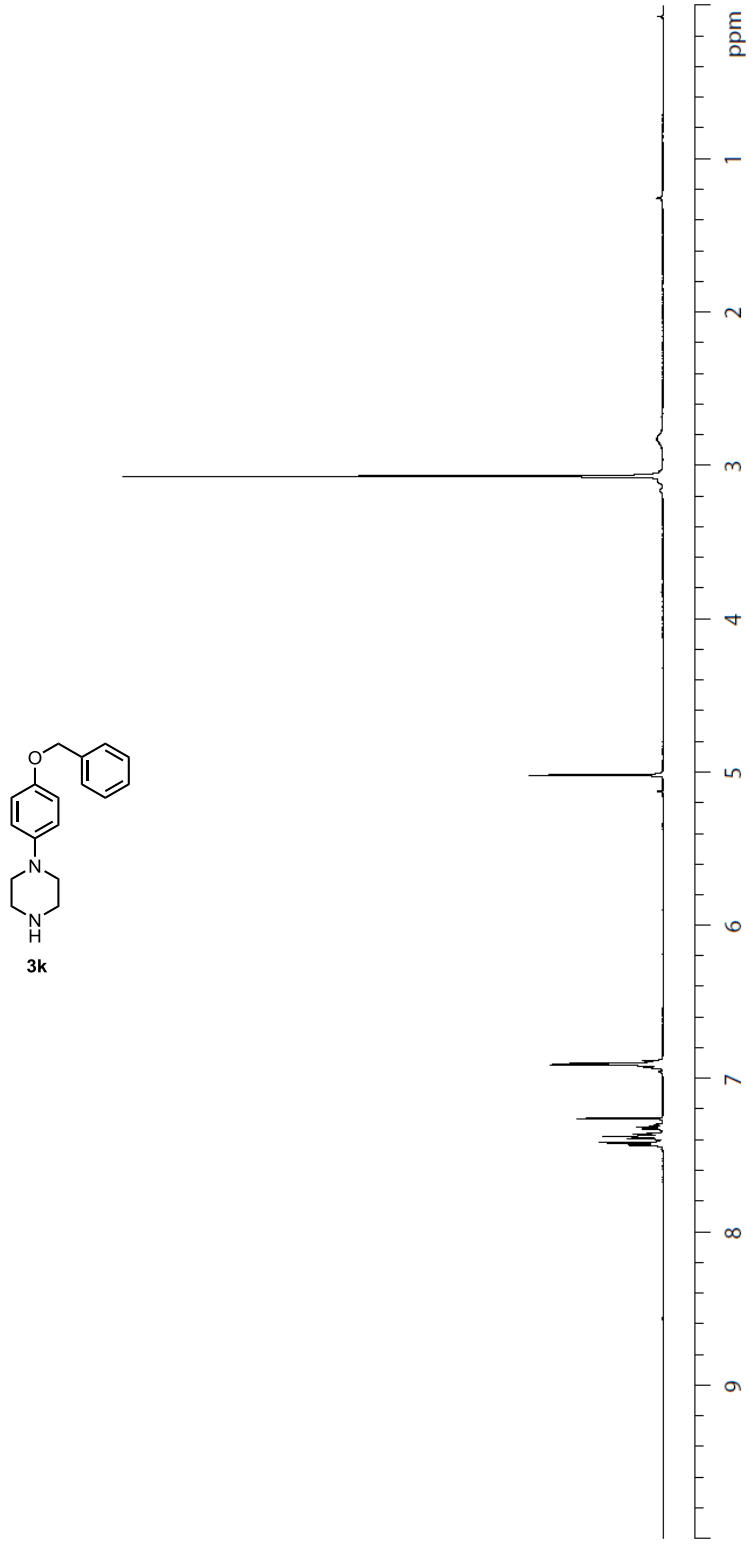




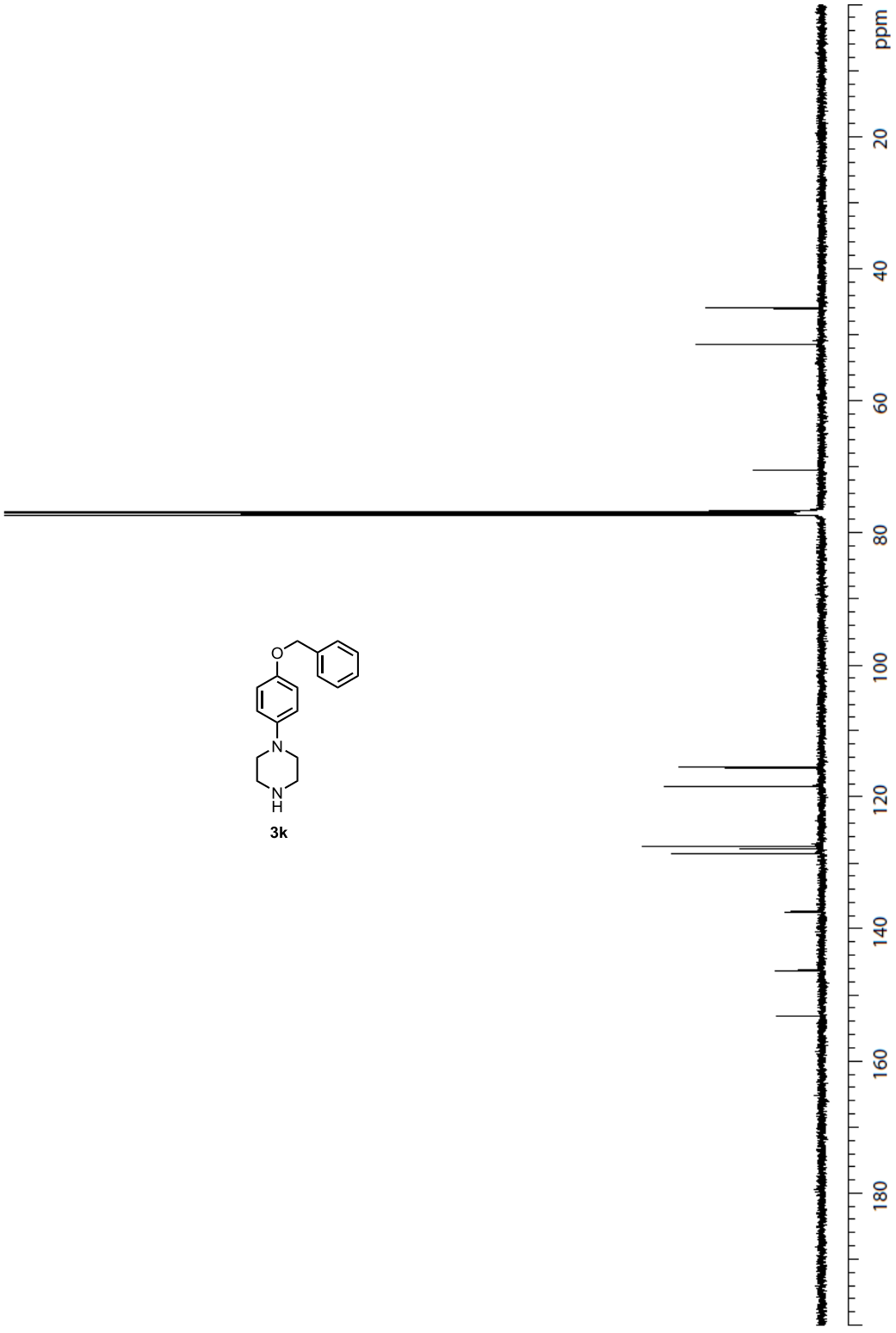


**3j**

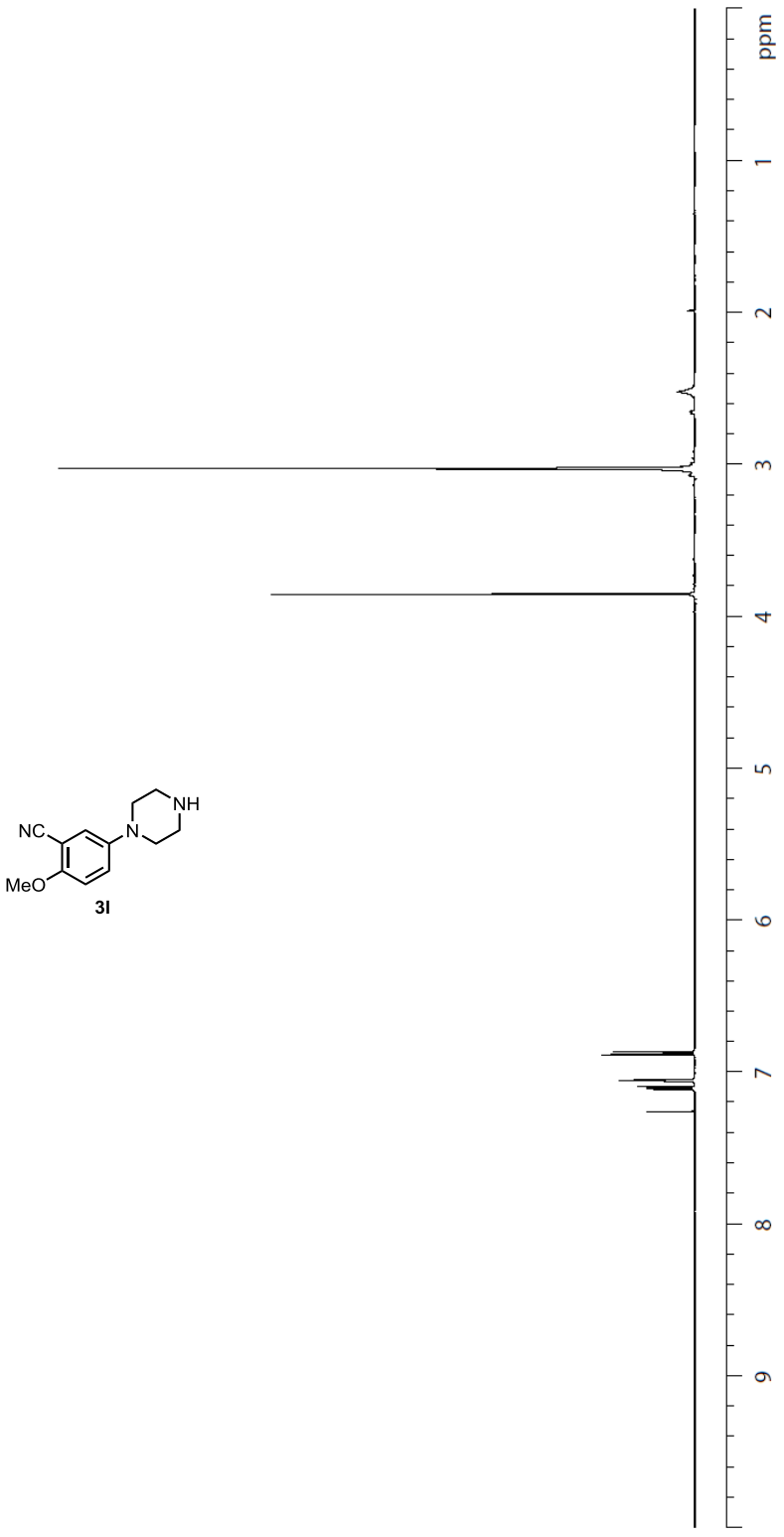
$^{19}$F NMR ($CDCl_3$, 23 ºC) of **3j**




$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3k**

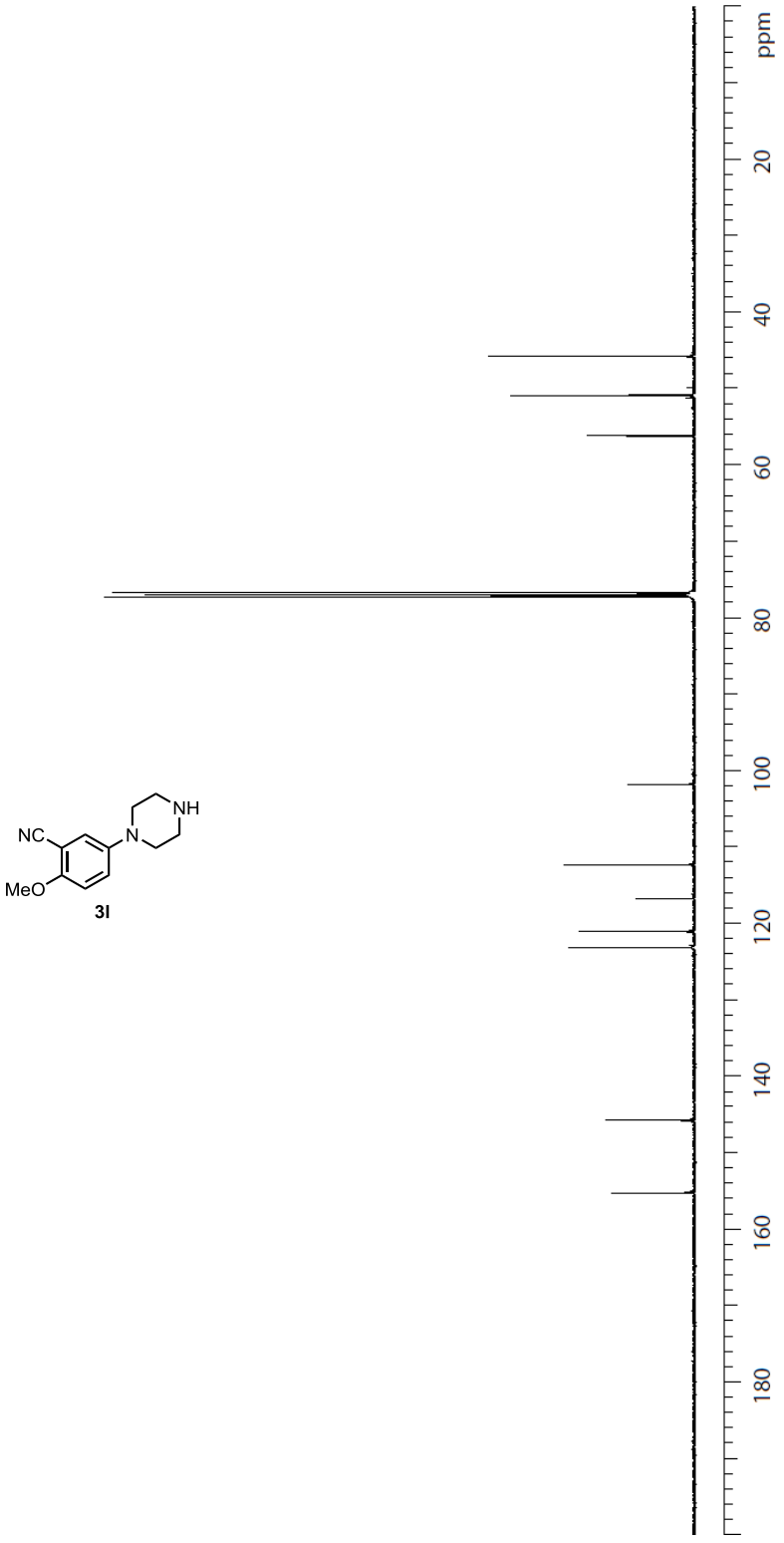



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3k**

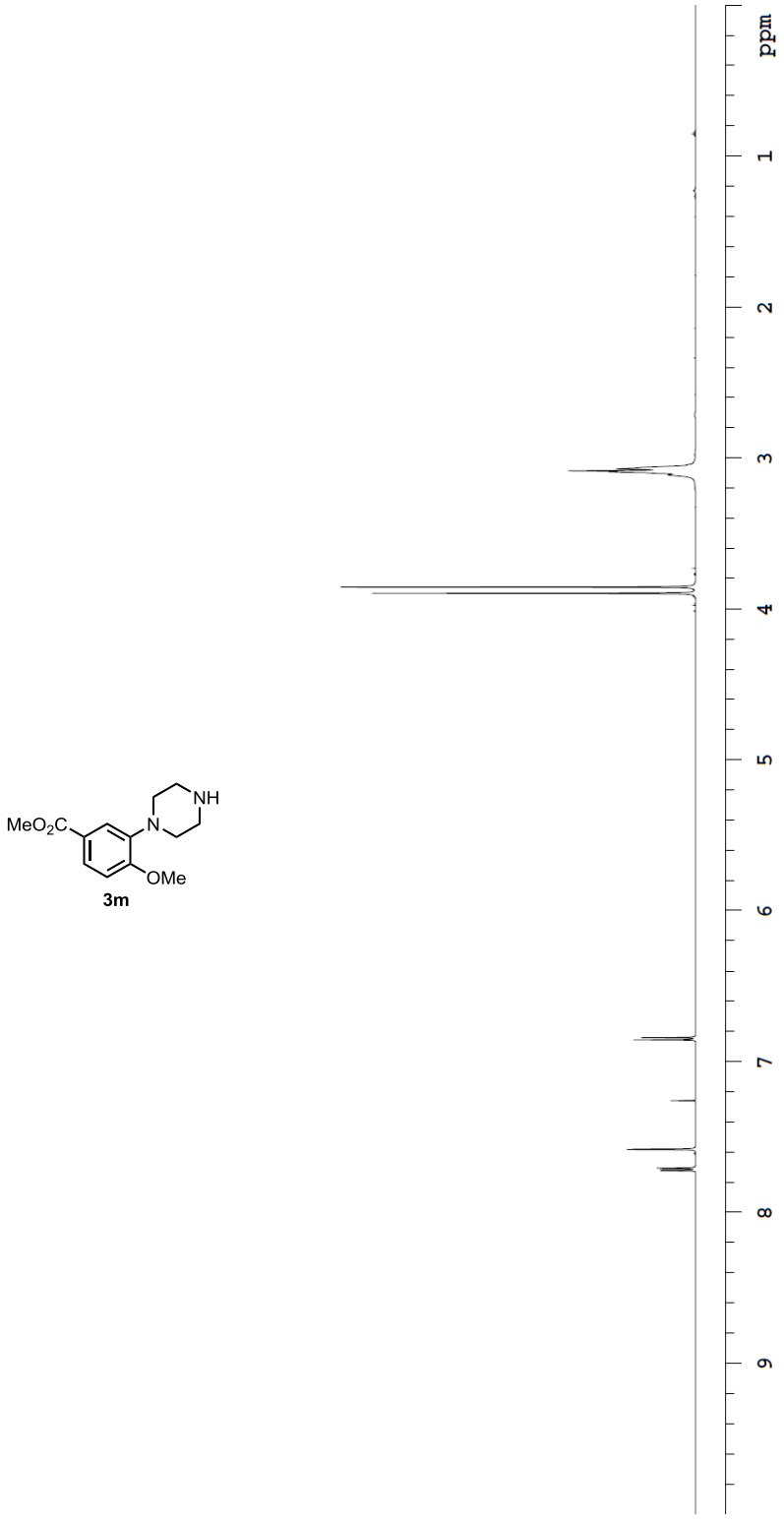



**3l**

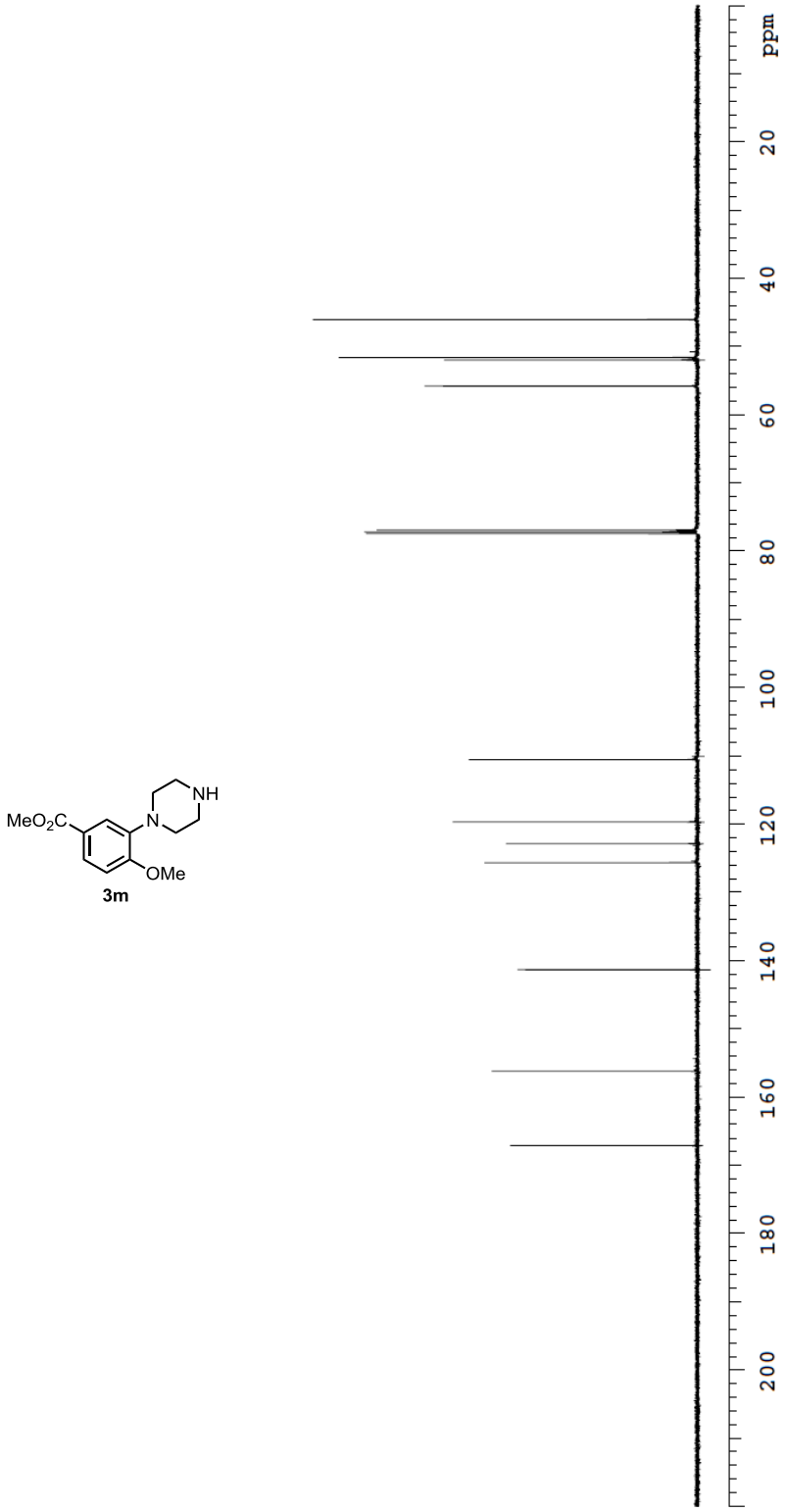
$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3l**



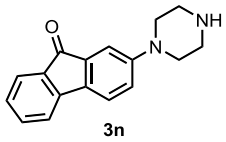

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3l**



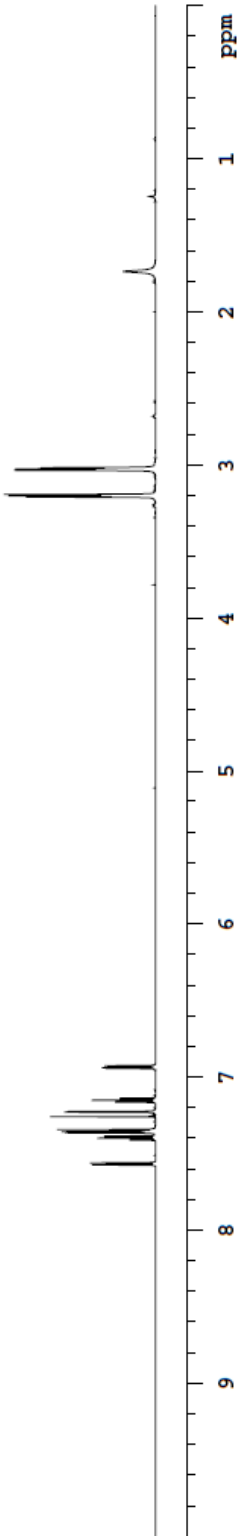

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3m**



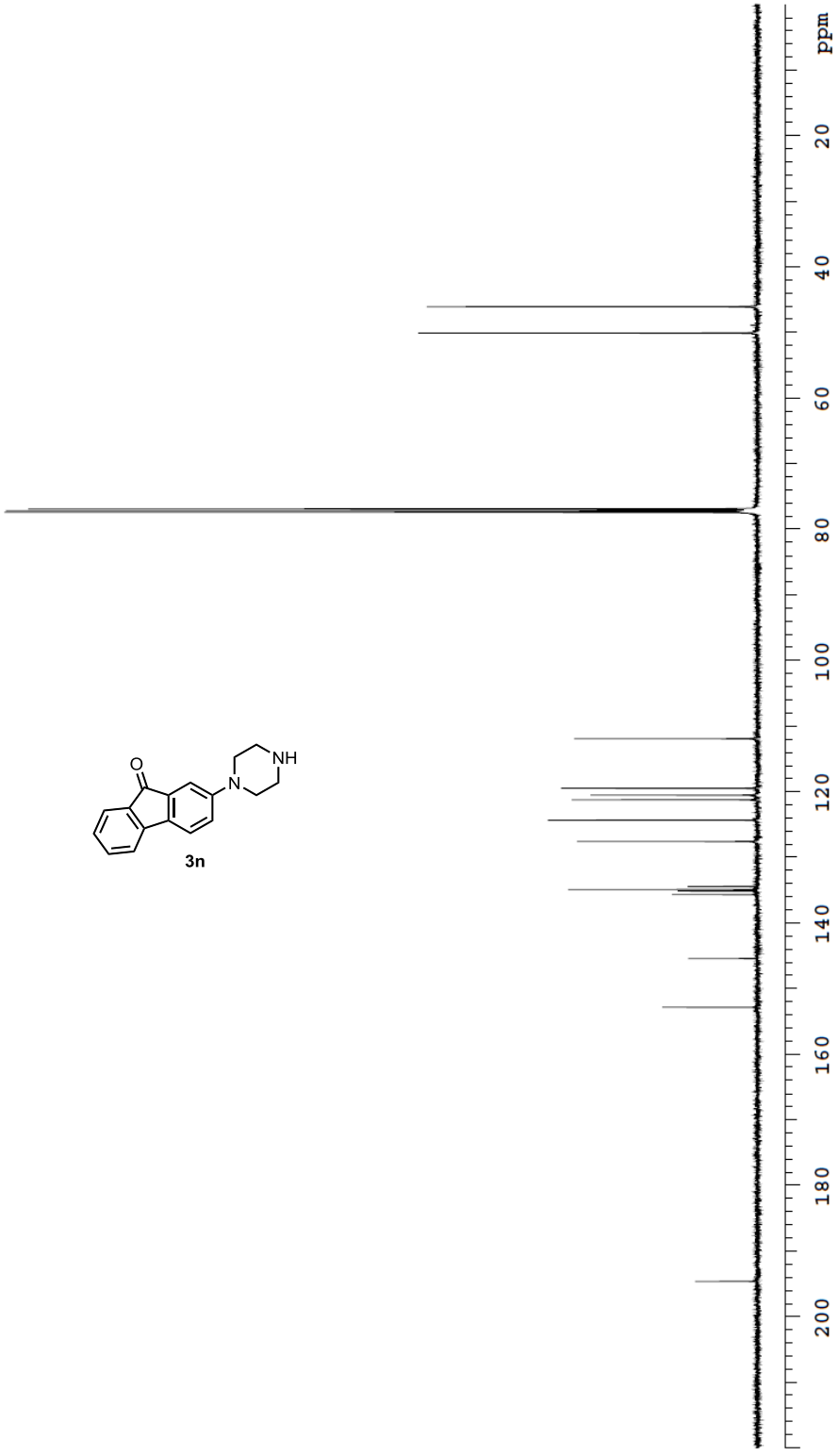

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3m**



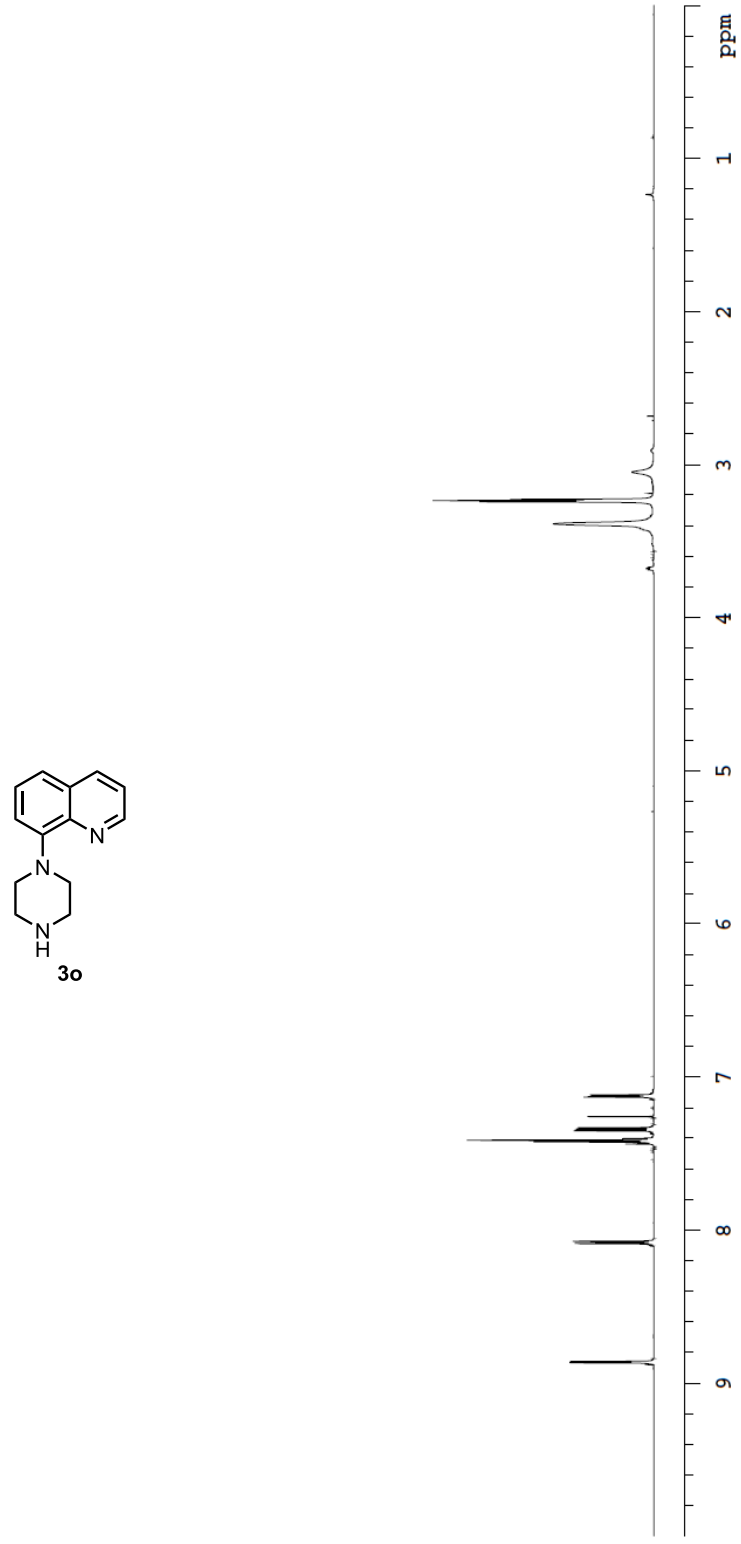

3n



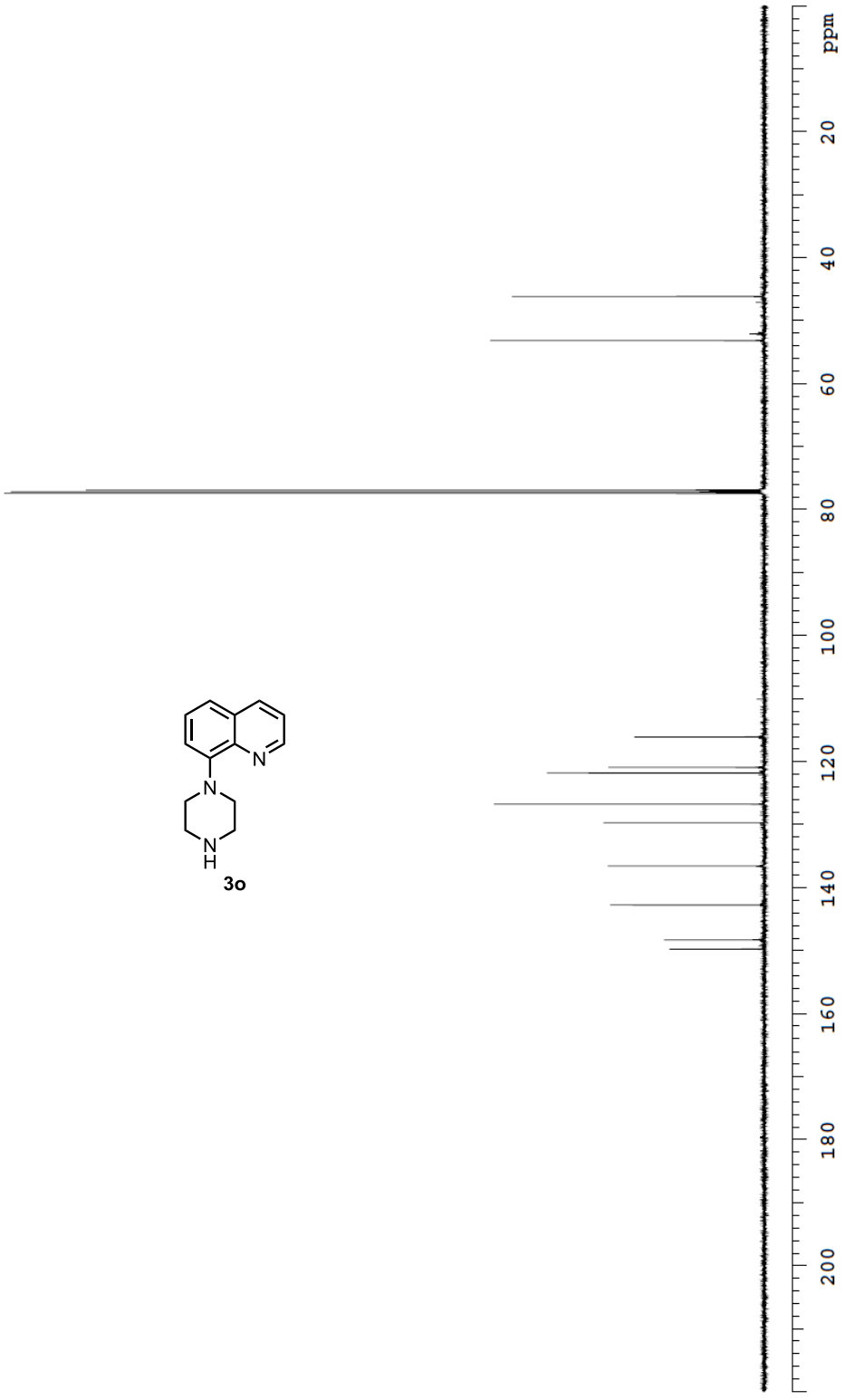

$^1$H NMR ($CDCl_3$, 23 ºC) of **3n**



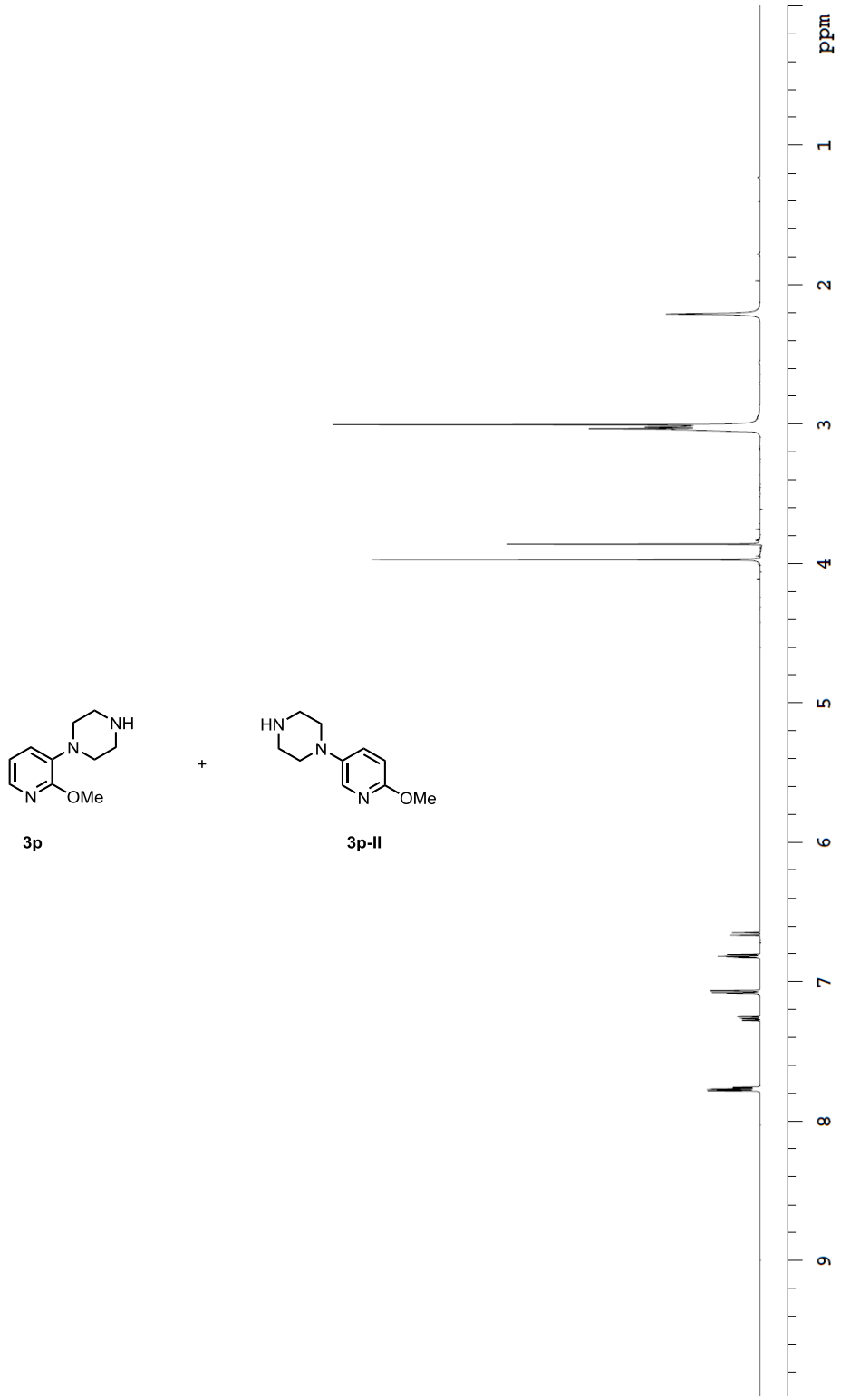

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3n**



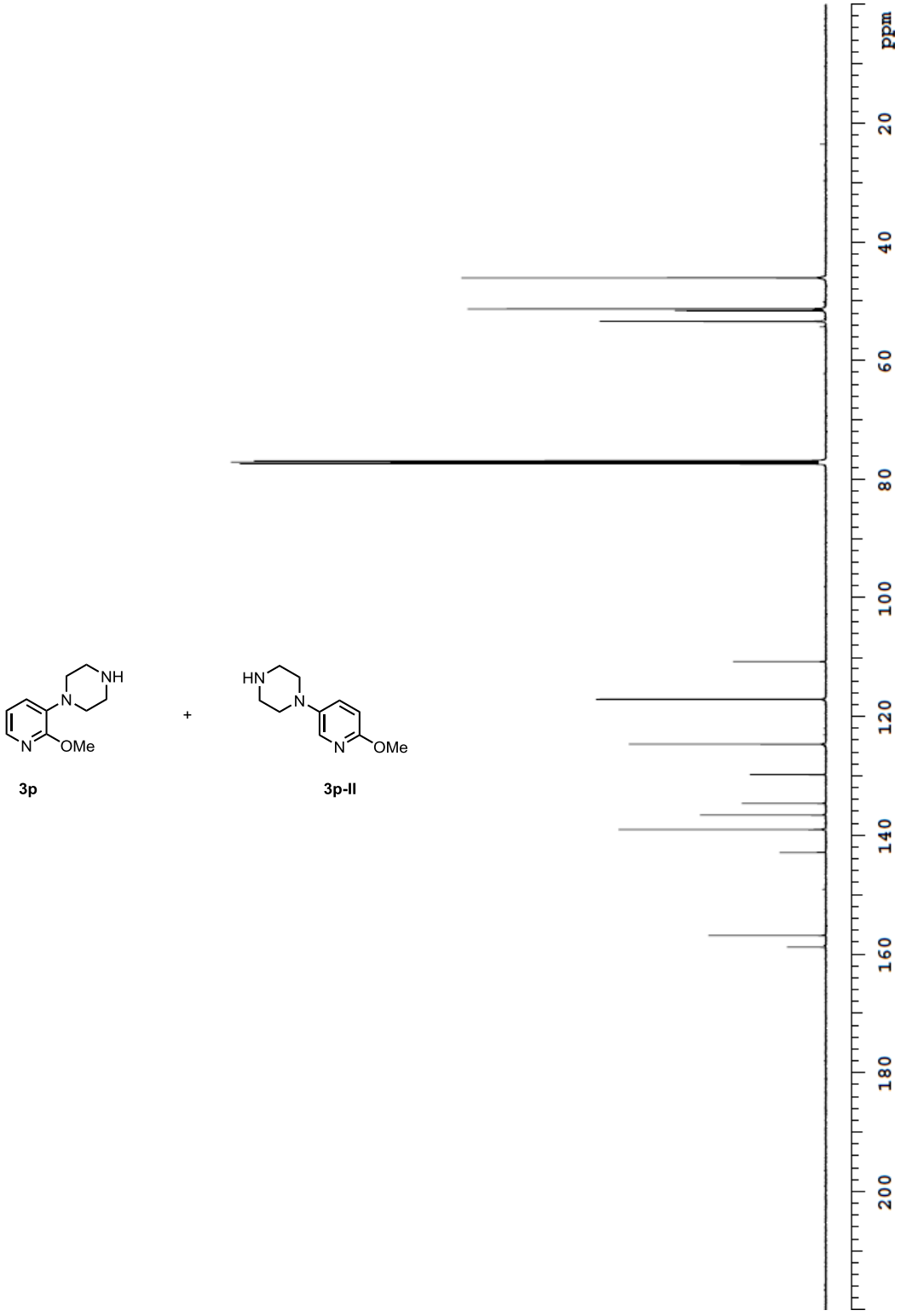

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3o**




$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3o**

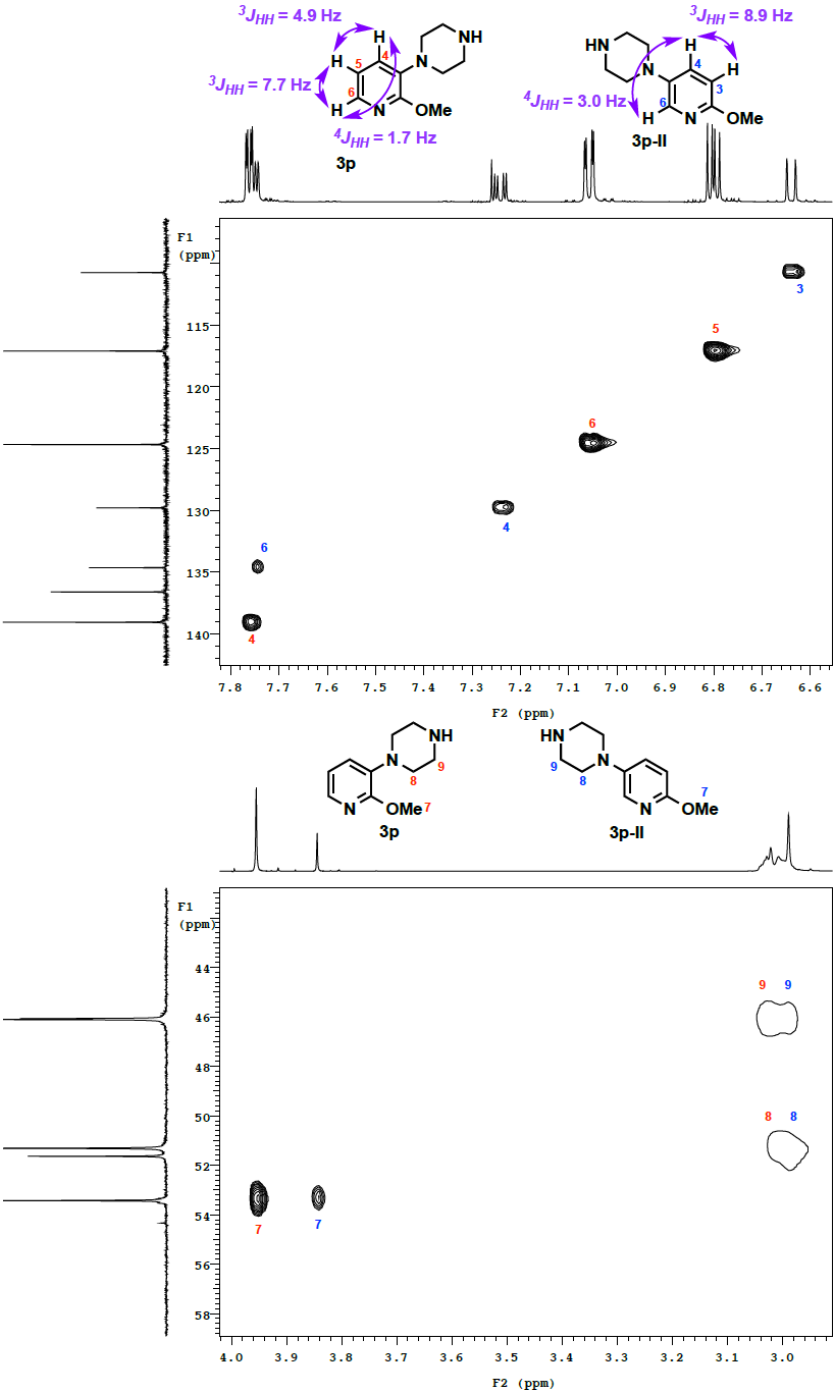



$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3p** + **3p-II**

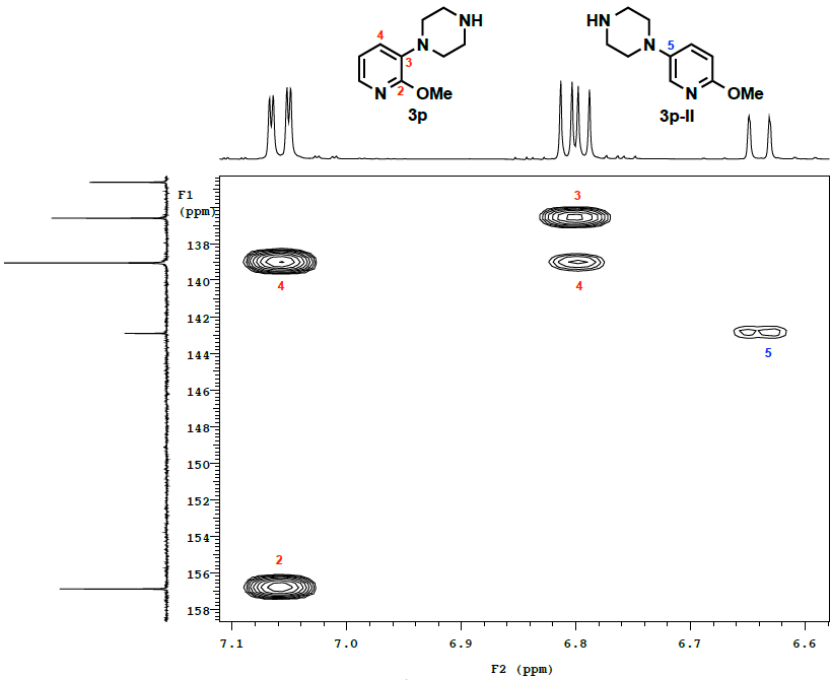


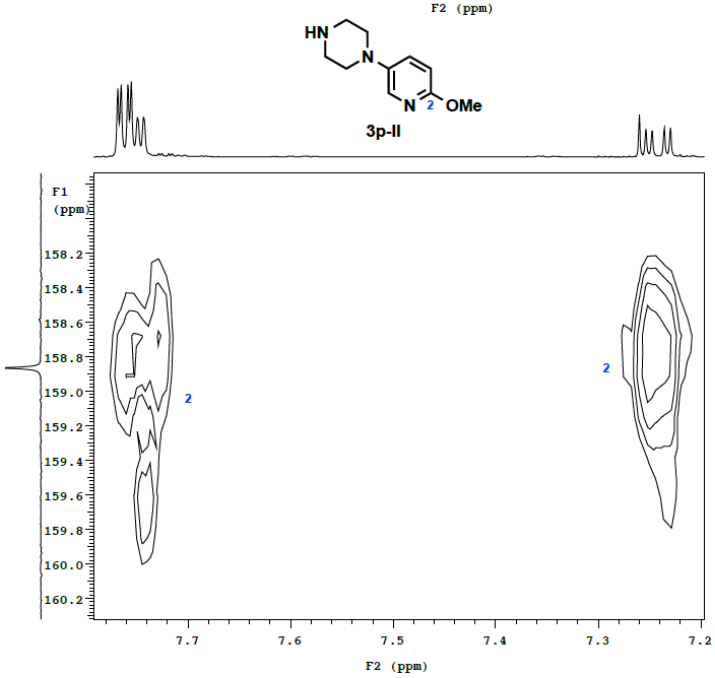

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3p** + **3p-II**

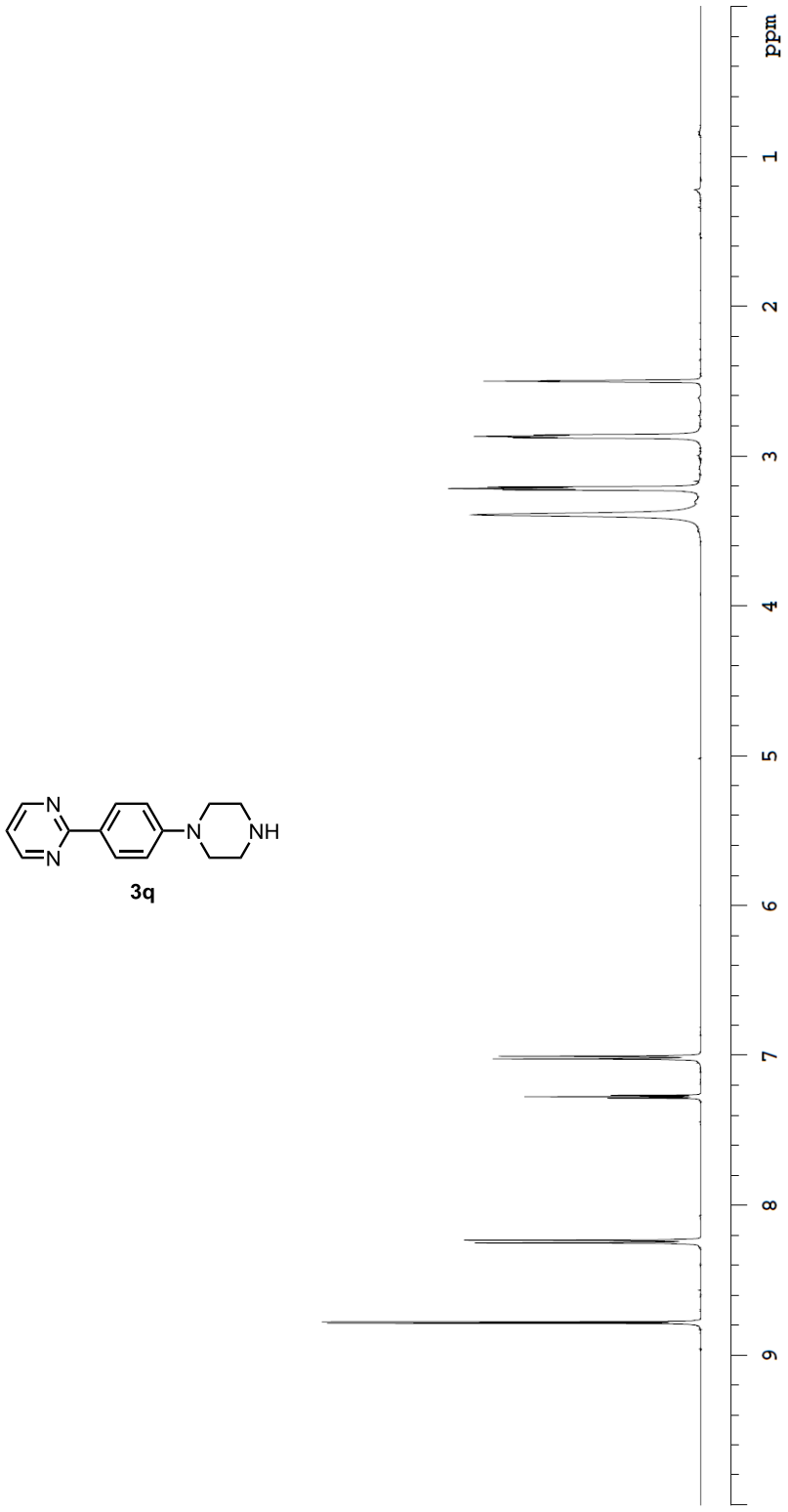
HSQC analysis of **3p** + **3p-II** for assignment of $^{13}C$ signals



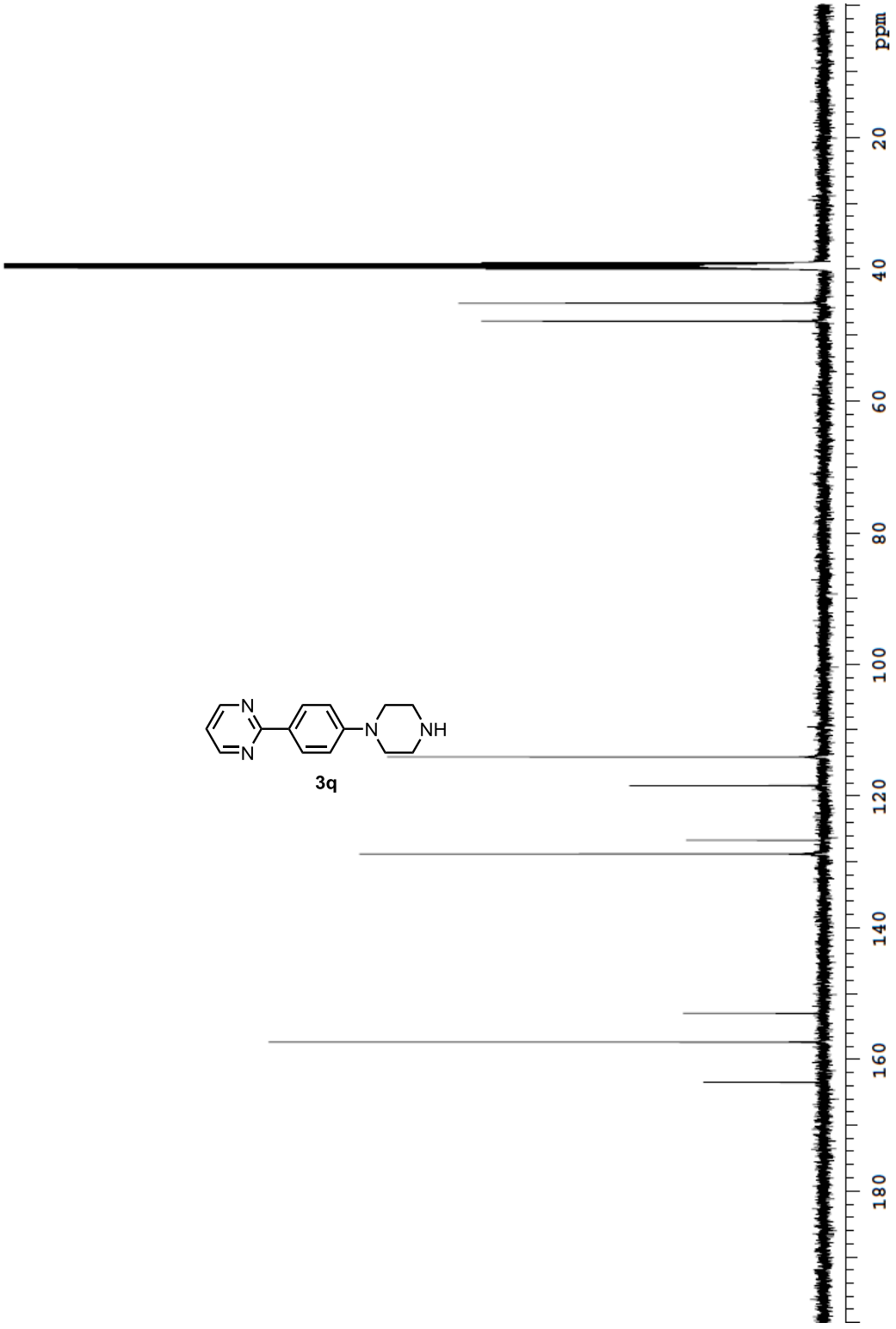
HMBC analysis of **3p** + **3p-II** for assignment of quaternary carbons



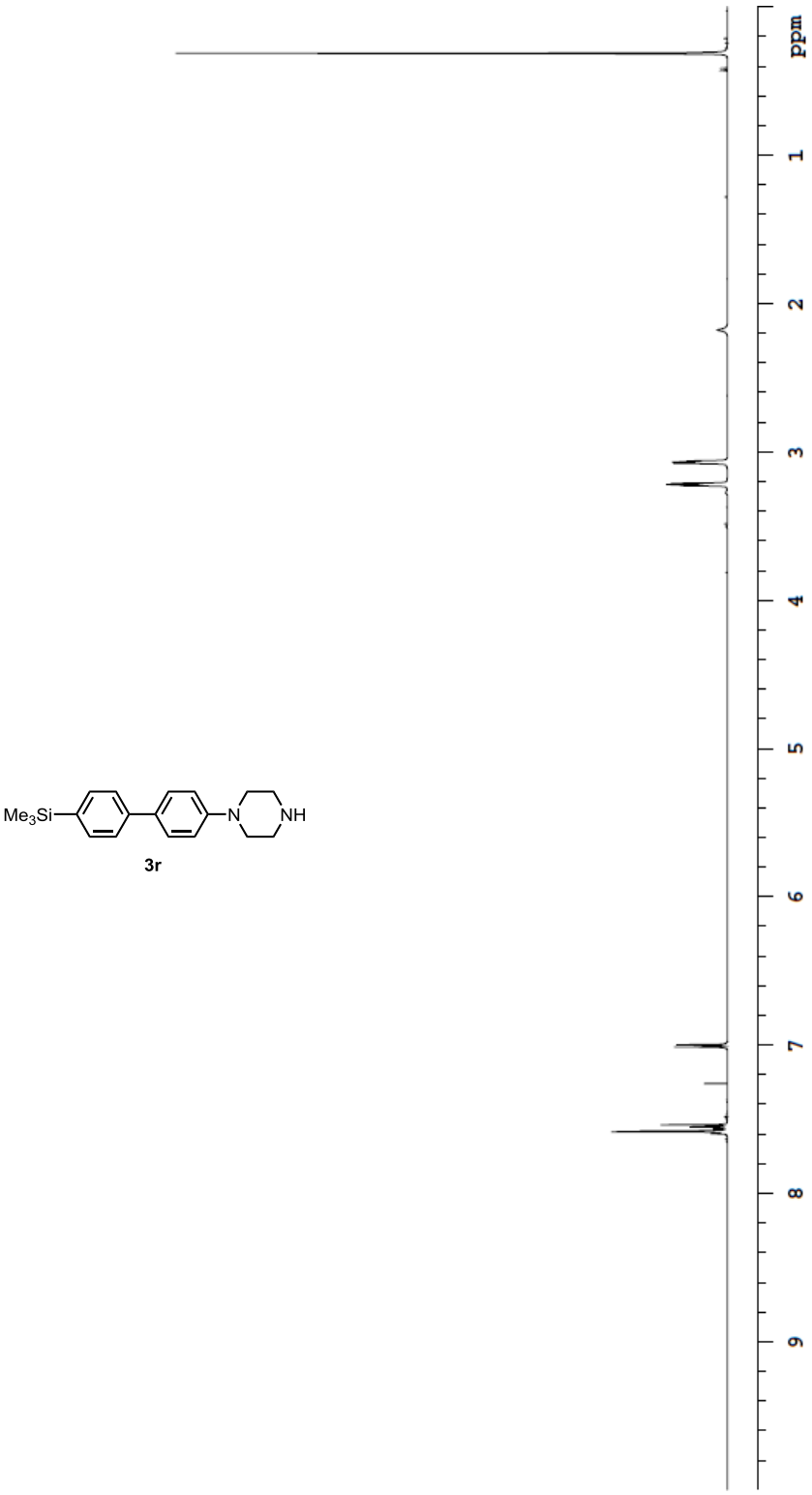





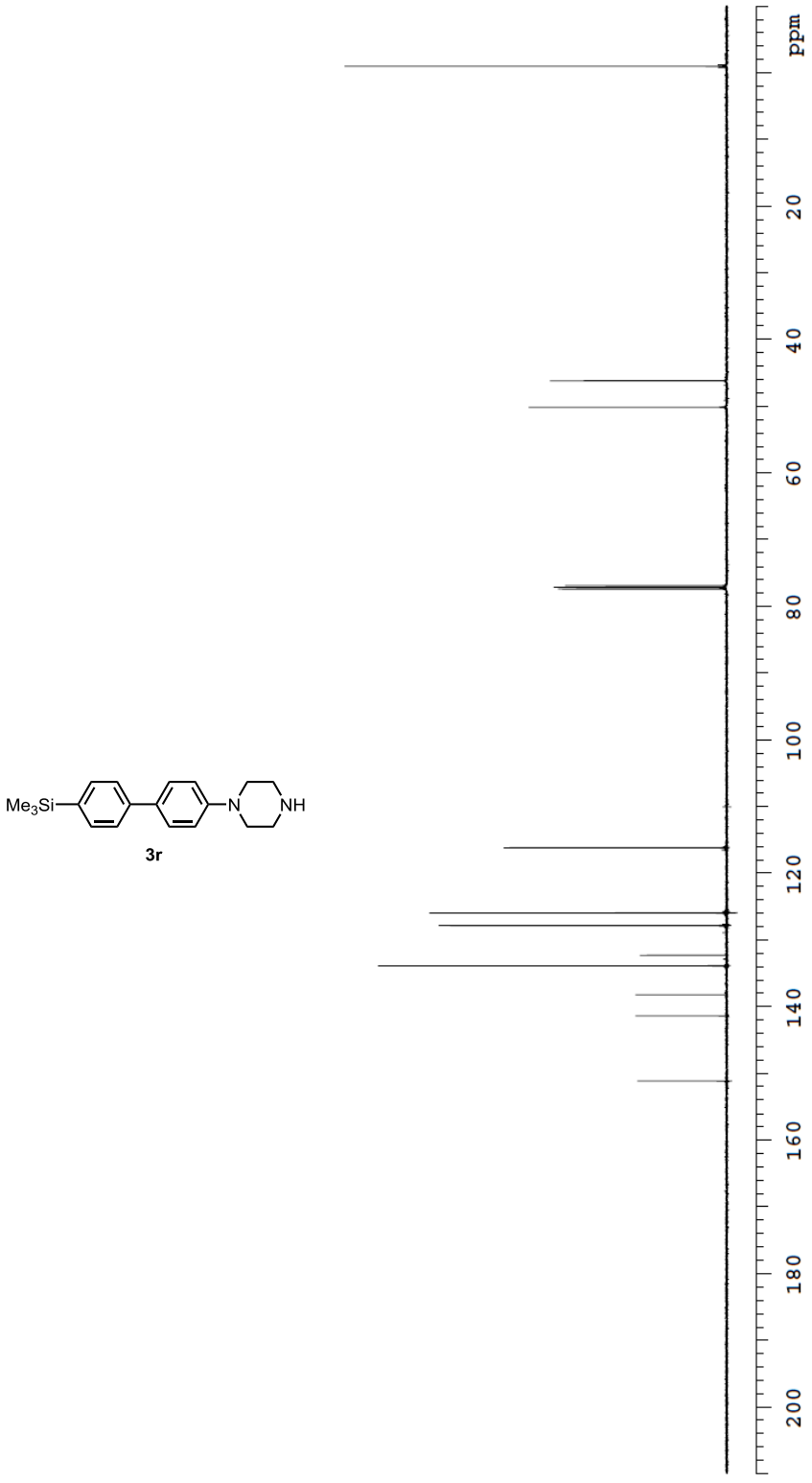

$^{1}$H NMR (DMSO, 23 ºC) of **3q**



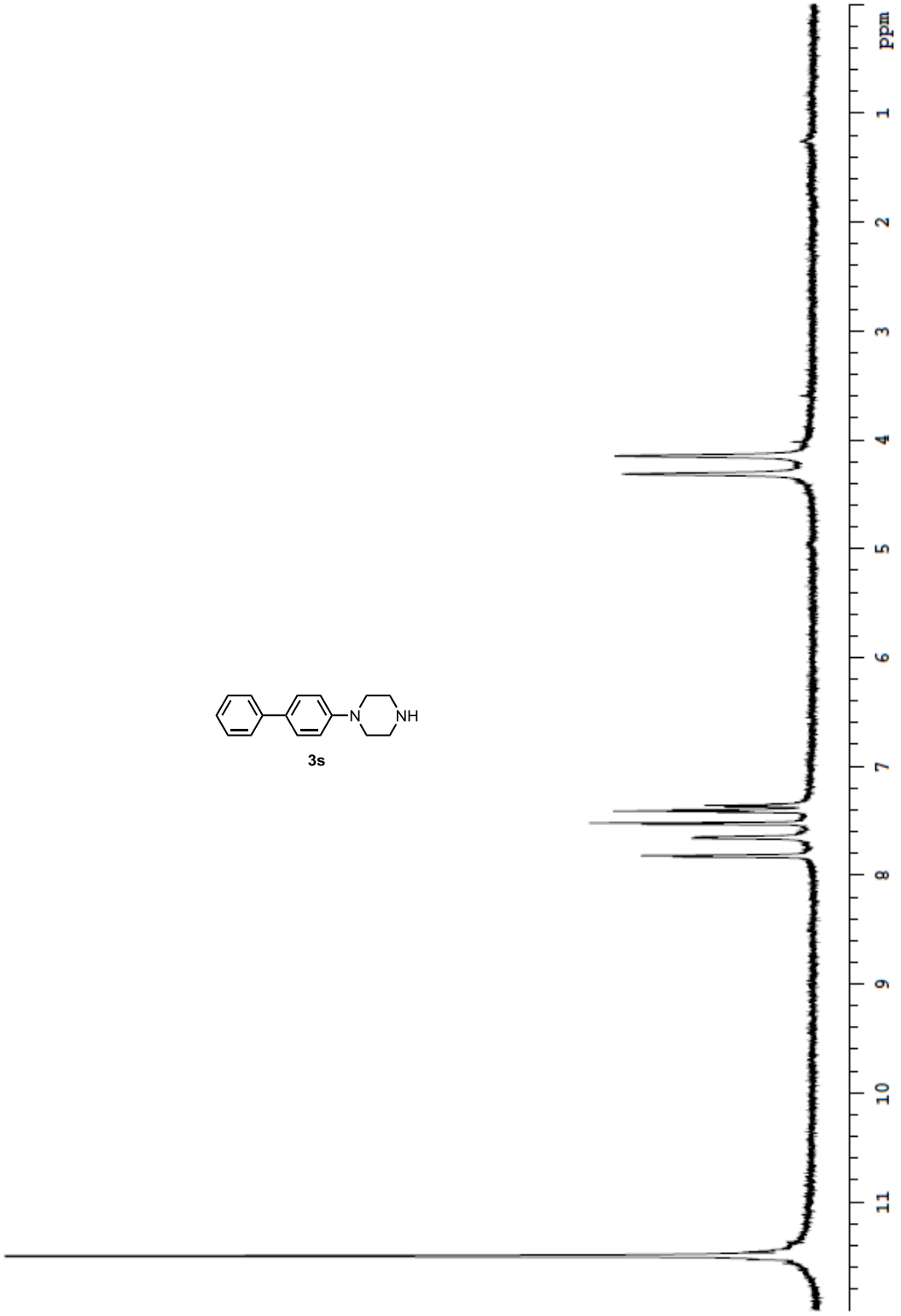

$^{13}$C NMR (DMSO, 23 ºC) of **3q**



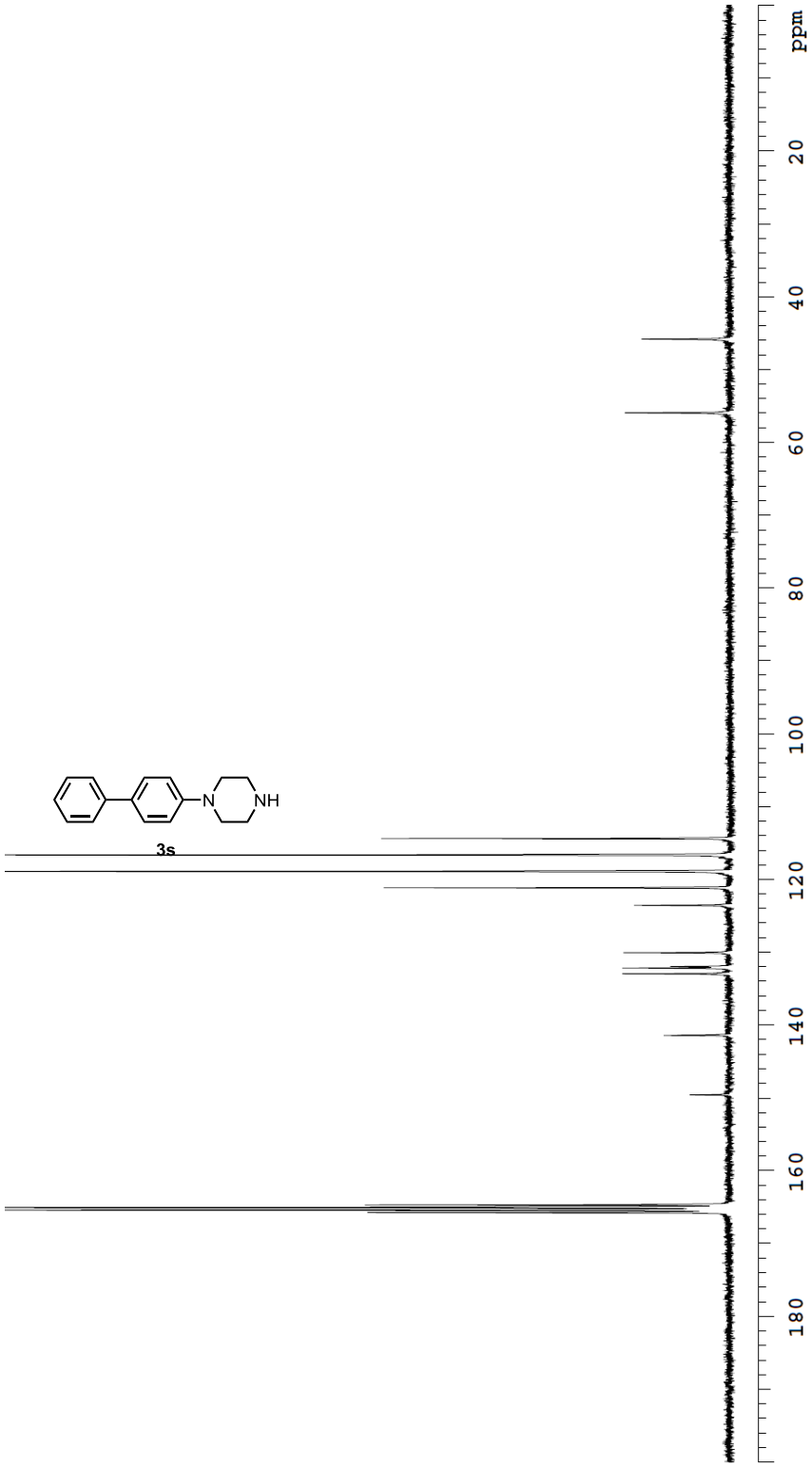

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3r**



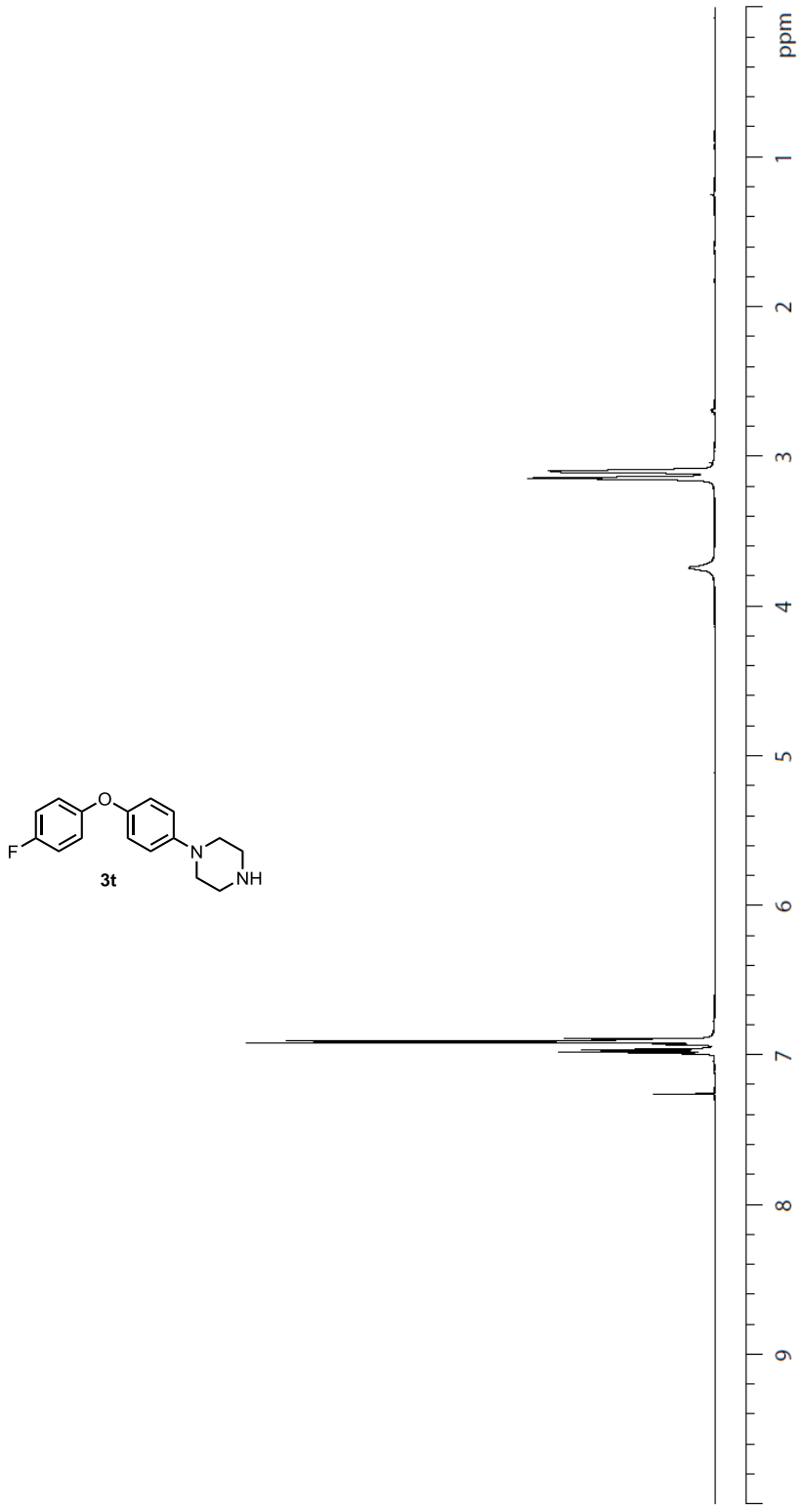

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3r**



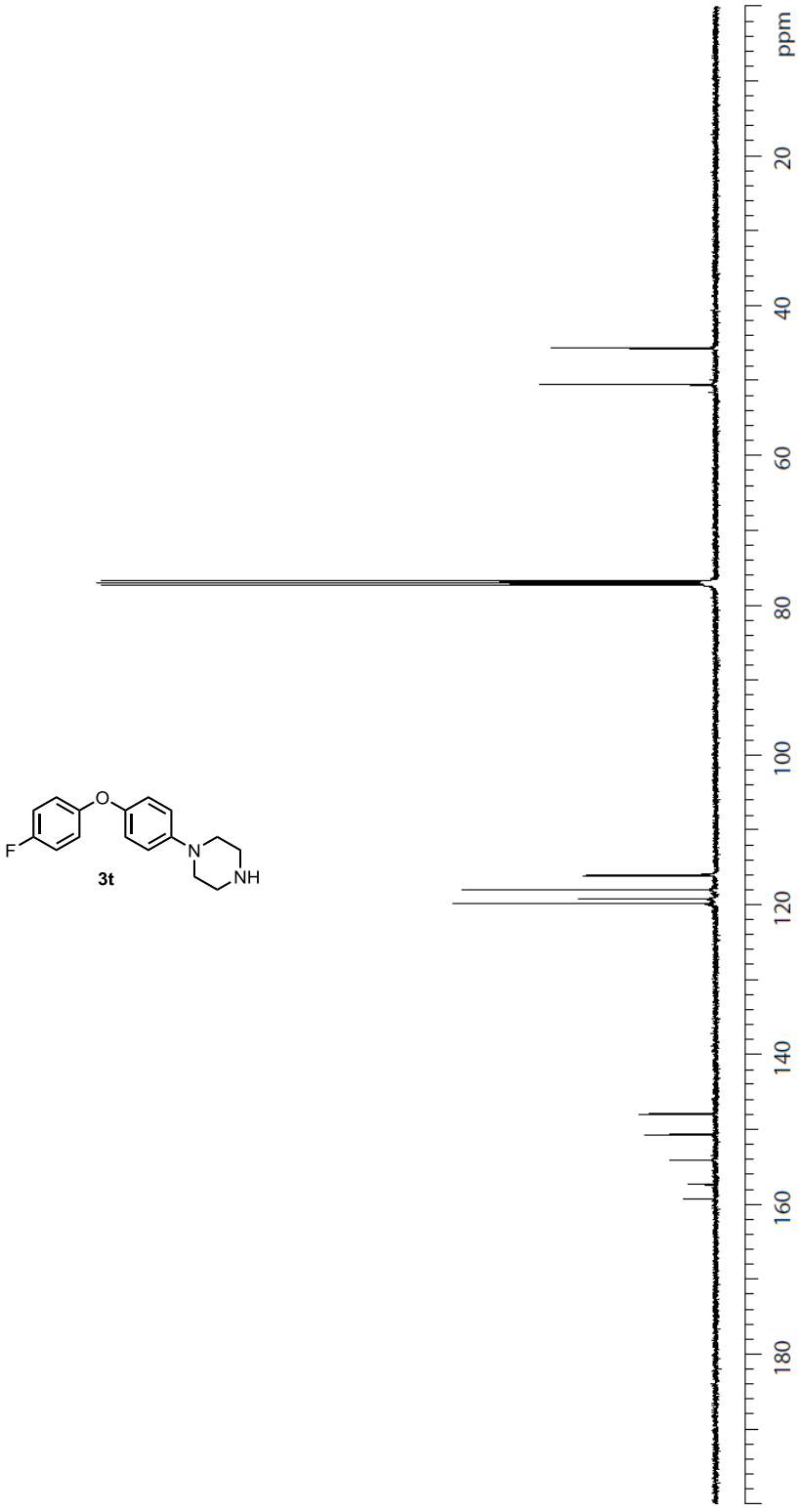

$^{1}$H NMR ($F_3CO_2D$, 23 ºC) of **3s**



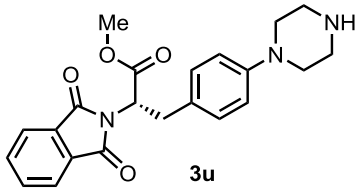

$^{13}$C NMR ($F_3CO_2D$, 23 ºC) of **3s**



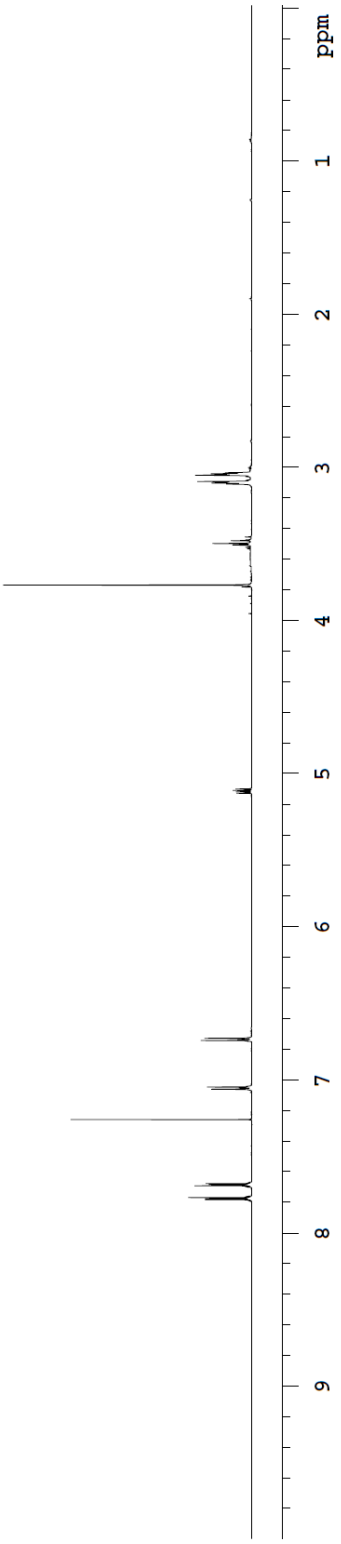

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3t**



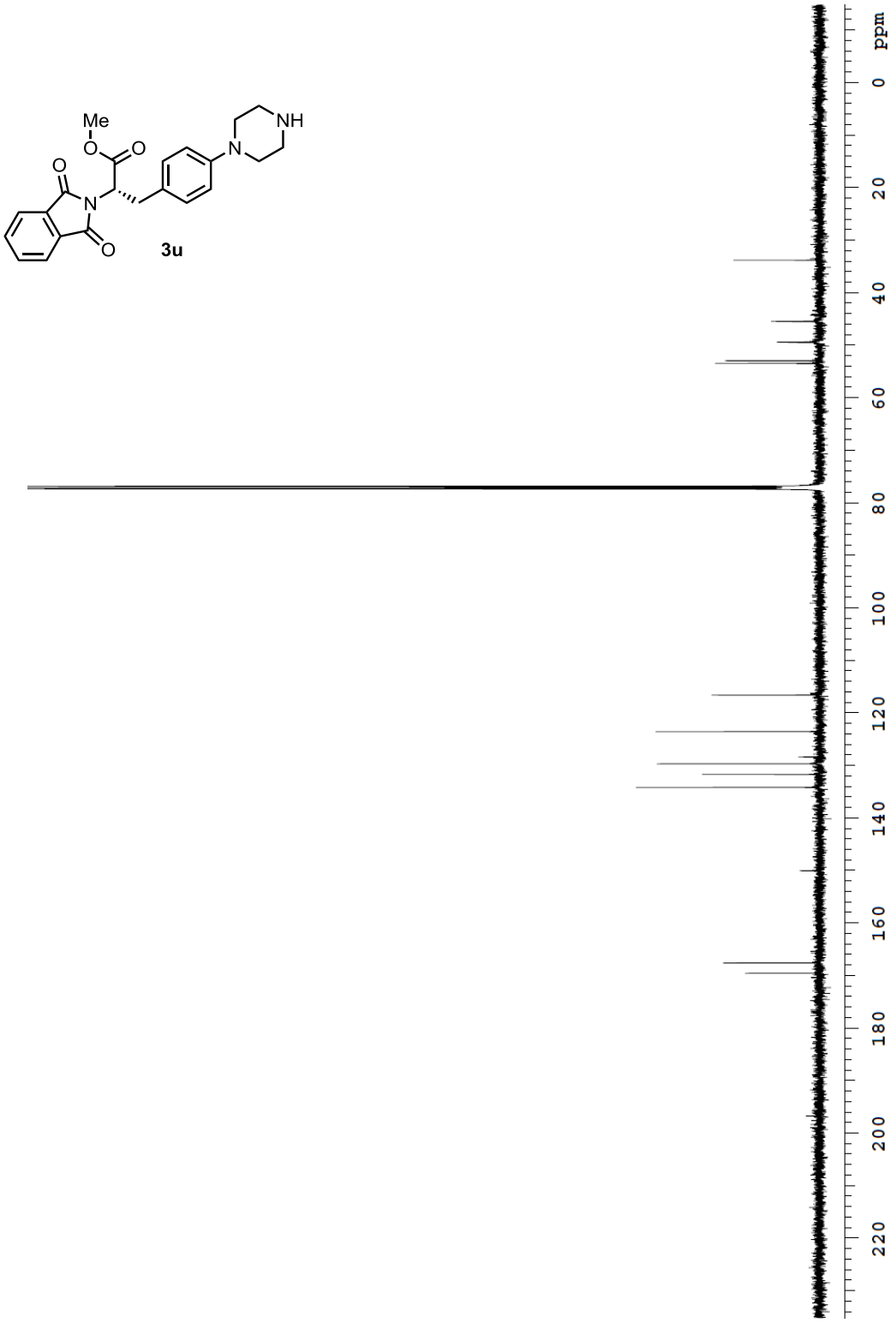

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3t**



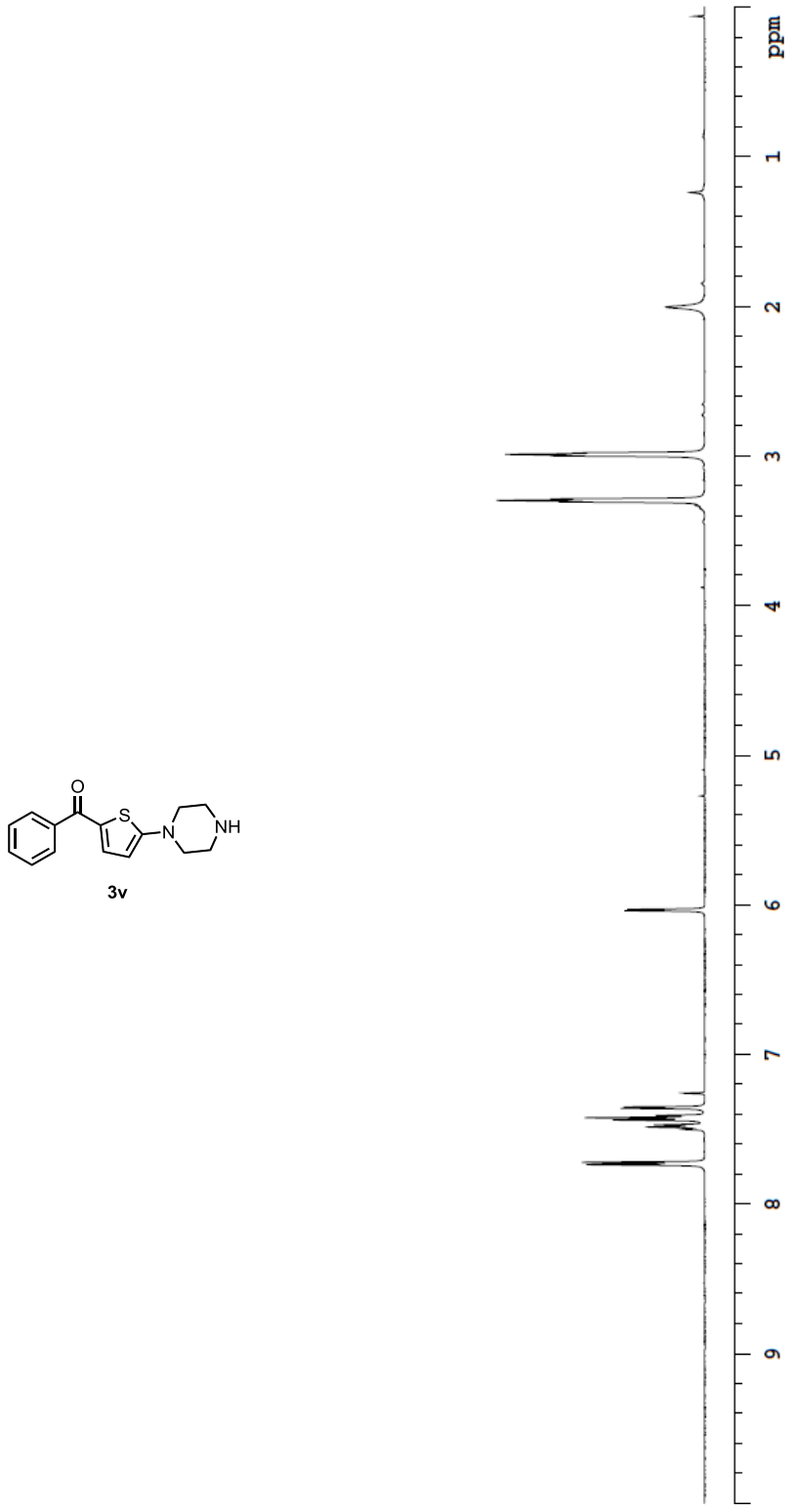

**3u**



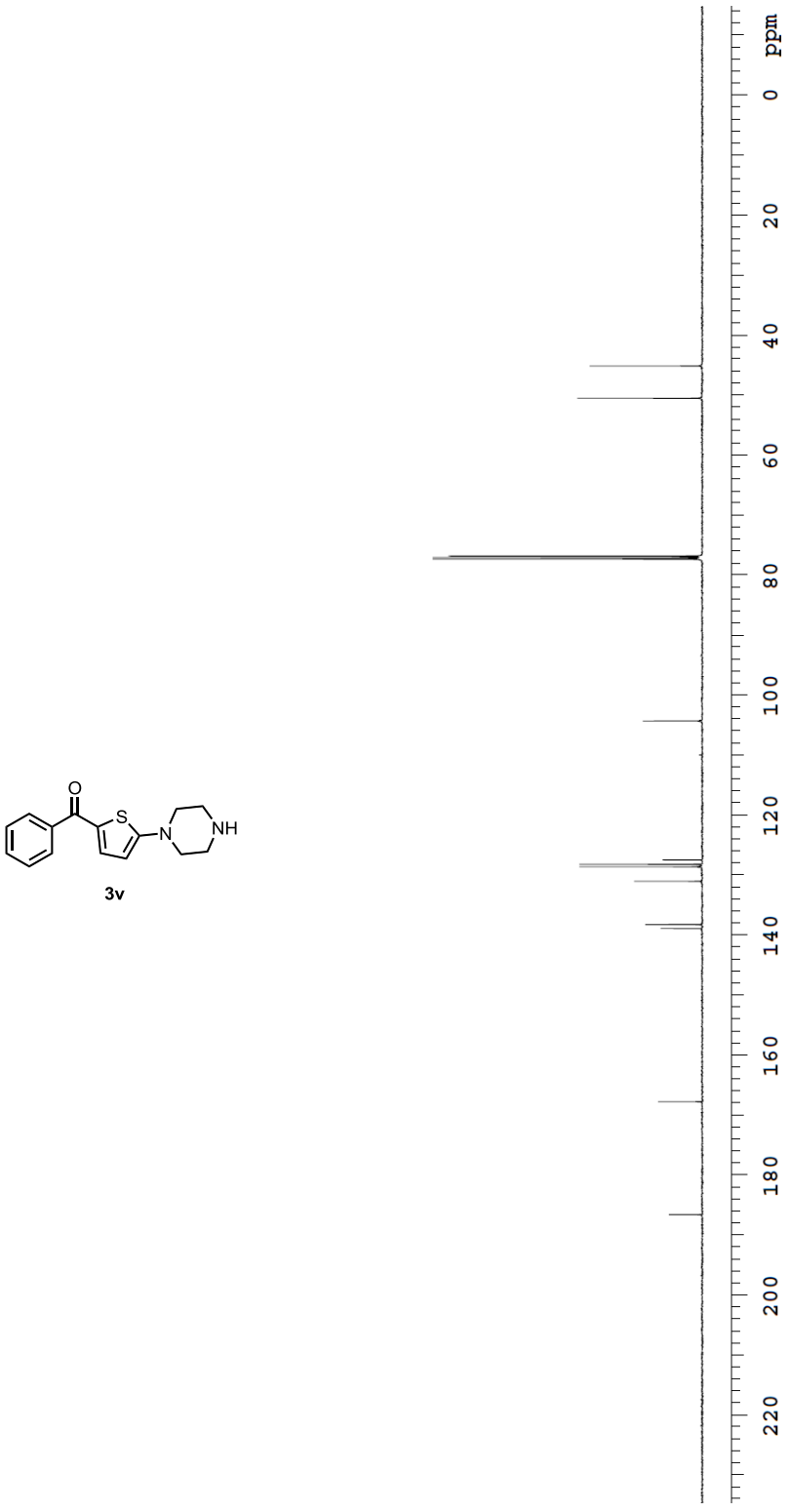

$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3u**



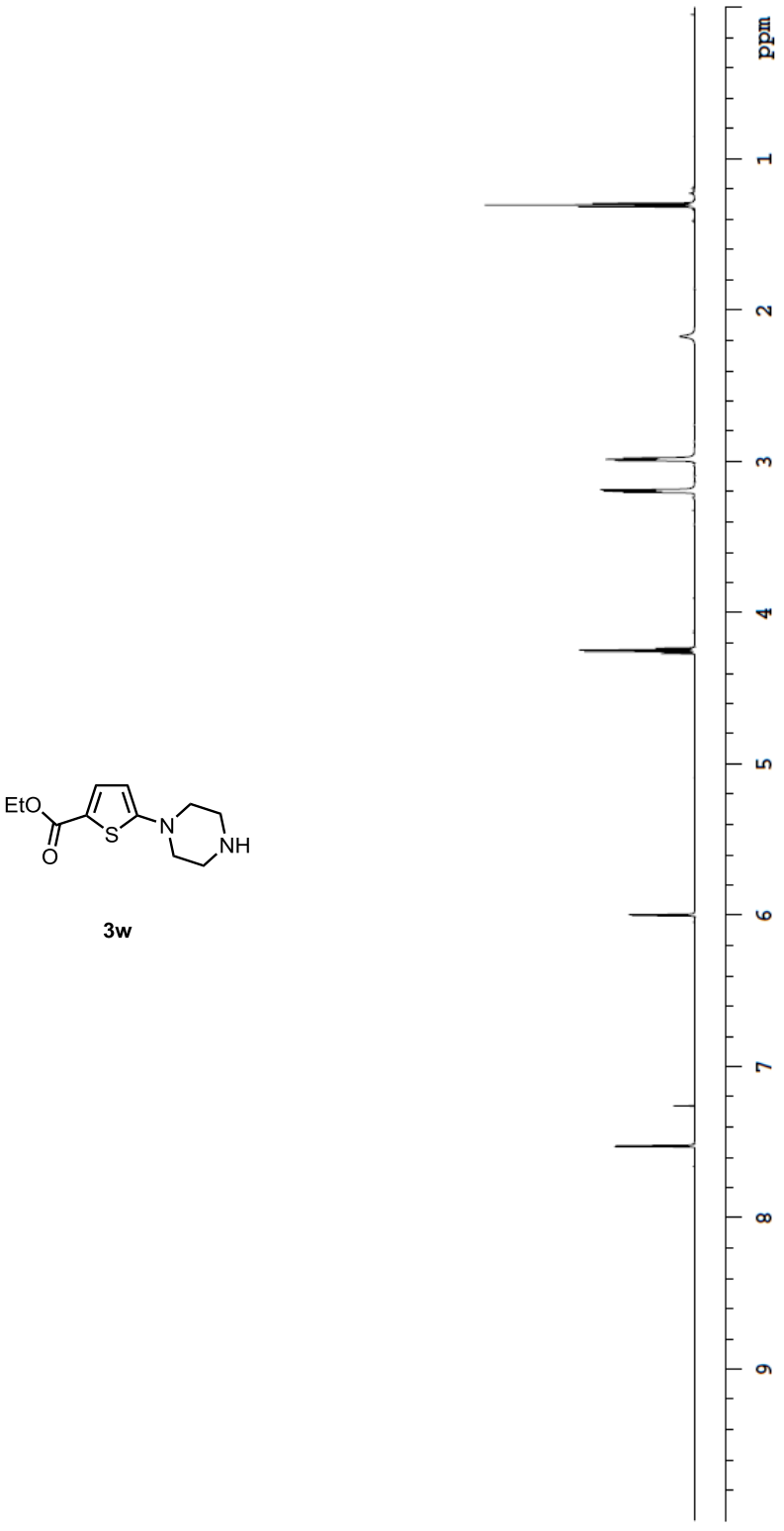

$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3u**




$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3v**

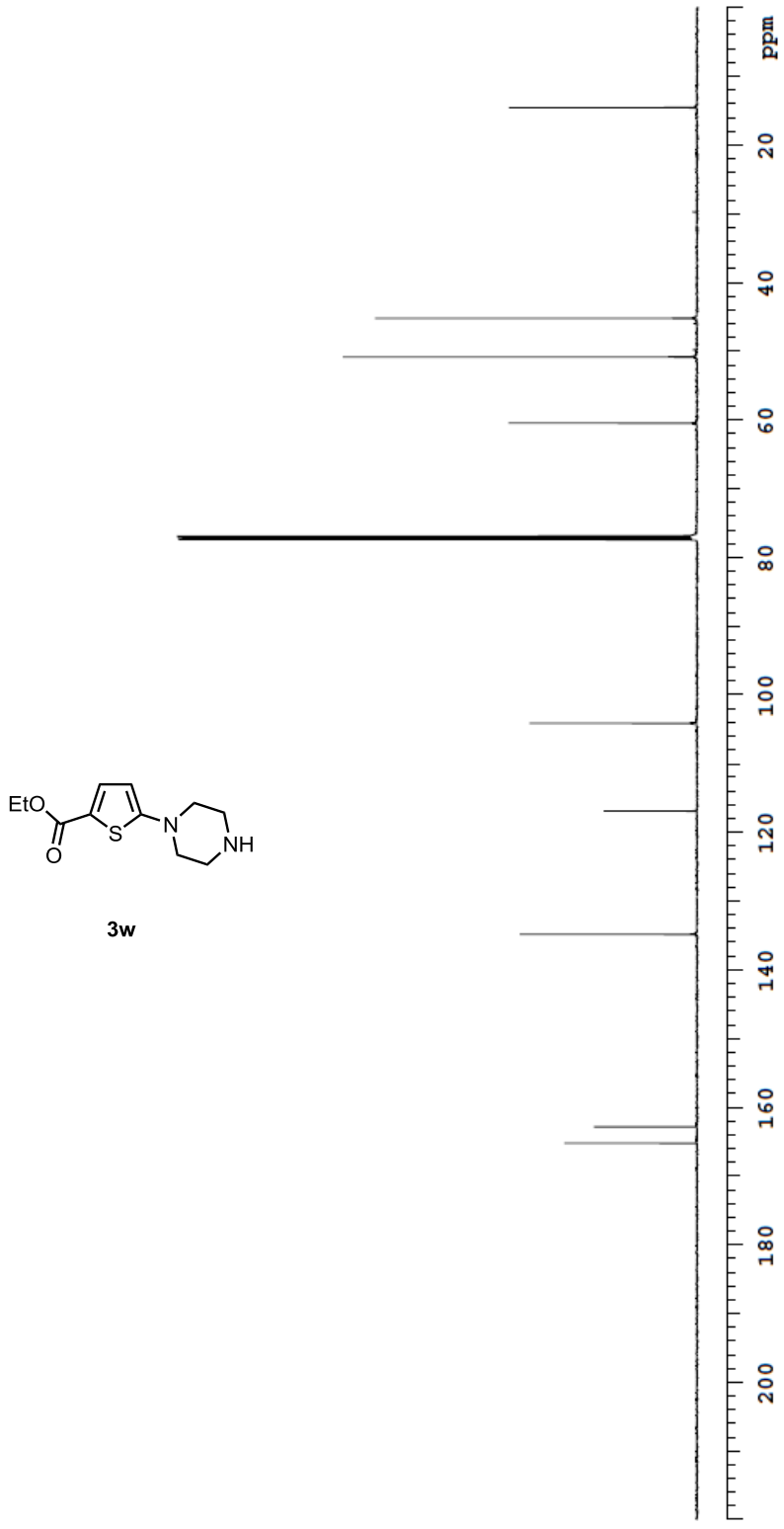



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3v**

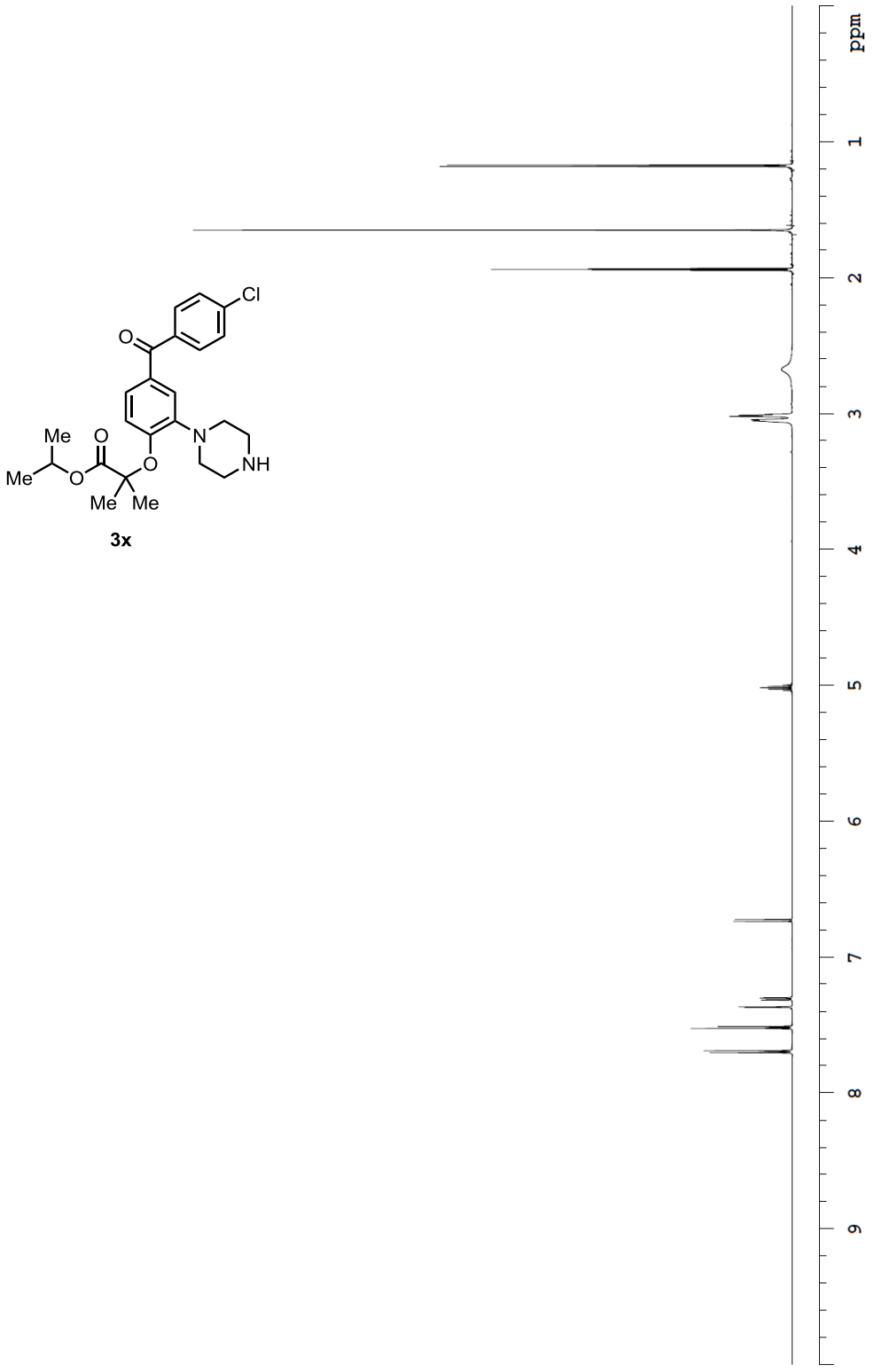



**3w**

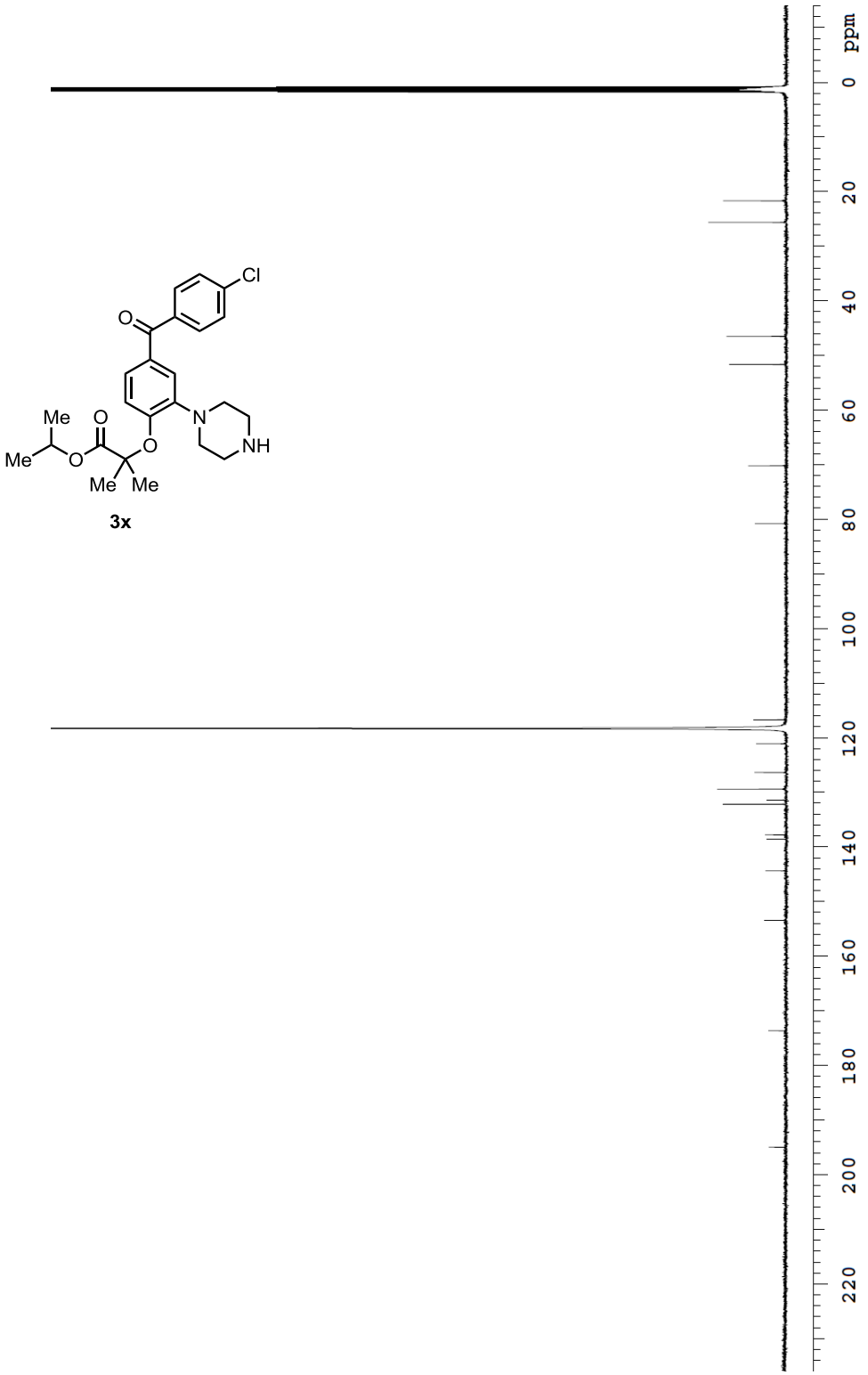
$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3w**




$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **3w**

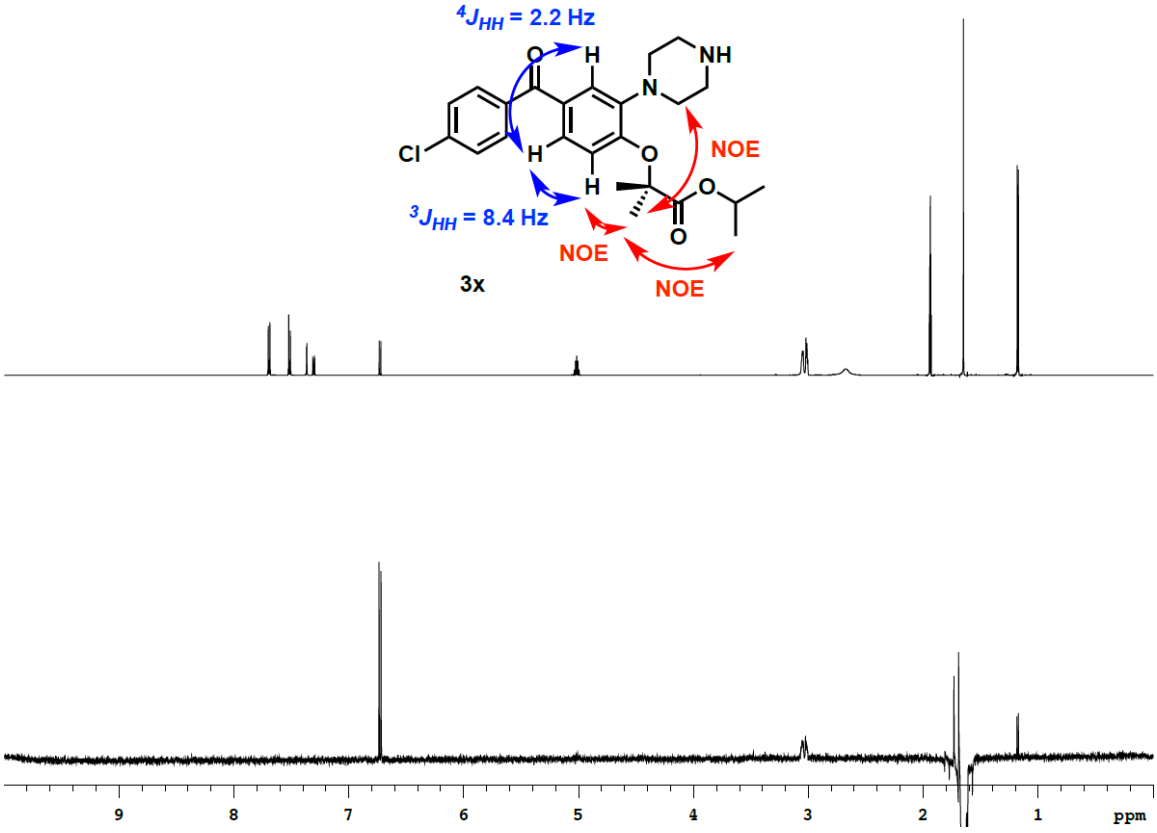



$^{1}$H NMR ($CDCl_3$, 23 ºC) of **3x**




$^{13}$C NMR ($CD_3CN$, 23 ºC) of **3x**

1D NOESY analysis for assignment of **3x**



**Additional References**

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