Supporting Information

Electrochemical DABCOylation enables challenging aromatic C–H amination

Griffin Stewart, Eva Maria Alvarez, Chris Rapala, Jonathan Sklar, Julia A. Kalow, Christian A. Malapit*

Department of Chemistry, Northwestern University, Technological Institute, Evanston, Illinois 60208, United States

*Correspondence to: christian.malapit@northwestern.edu

TABLE OF CONTENTS

MATERIALS AND METHODS

All reactions were carried out under an ambient atmosphere unless otherwise stated. High-resolution mass spectra were obtained using a 1200 HPLC System (Agilent Technologies) with Direct loop injection (no Column), coupled to an Agilent 6230 time-of-flight (TOF) mass spectrometer with electrospray ionization (Agilent Technologies Inc.), utilizing a Dual ESI source. Concentration under reduced pressure was performed by rotary evaporation at 25–40 °C at an appropriate pressure. Purified compounds were further dried under vacuum (measured 0.200 mBar). Yields refer to purified and spectroscopically pure compounds, unless otherwise stated.

Solvents

99.5% 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) was purchased from Oakwood Chemical. Certified ACS grade acetonitrile (MeCN) and technical grade tetrahydrofuran (THF) were purchased from Fisher Scientific. All deuterated solvents were purchased from Cambridge Isotope Laboratories. Inc. (CIL).

Chromatography

Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F_{254} plates and visualized under UV light. Chromatography was performed in handmade columns fabricated from culture tubes or on a Biotage Selekt with a UV-Vis detector.

Electrosynthesis

Graphite electrodes were purchased from IKA for Electrasyn. Platinum mesh was purchased from Goodfellow Cambridge Ltd. with the following specification: Nominal aperature: 0.25 mm, thickness: 0.12 mm, wire diameter: 0.06mm, wires/inch: 82 × 82, open area: 65%, platinum mesh electrodes were fabricated by cutting a 1 × 1 cm square of this mesh and looping it tightly on a 22 or 24-gauge platinum wire between 11.5 and 14 cm long.

Between reactions electrodes were cleaned in the following ways. Graphite electrodes were left in an aq. HCl bath (~2M) for at least two hours. Then they were sonicated in DI water for 10 minutes, rinsed three times with deionized water, sonicated in acetone for 10 minutes, rinsed with acetone twice, and dried with an air stream. Platinum electrodes were rinsed with DI water three times, then acetone three times, and dried with an air stream.

Spectroscopy and Instruments

NMR spectra were recorded on Bruker Avance III HD 500 spectrometer operating at 500 MHz, 471 MHz, 202 MHz, and 126 MHz, for ^{1}H, ^{19}F, ^{31}P and ^{13}C acquisitions, respectively. Chemical shifts are reported in ppm against tetramethylsilane with the solvent residual peak as the internal standard. For ^{1}H NMR: $CDCl_3$, δ 7.26; CD_3CN, δ 1.96; DMSO-d_6, δ 2.50. For ^{13}C NMR: $CDCl_3$, δ 77.16; CD_3CN, δ 53.84; DMSO-d_6, δ 39.52. Data is reported as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m =

multiplet, bs = broad singlet; coupling constants are reported in Hz.

Starting materials

All substrates were used as received from commercial suppliers, unless otherwise stated. [2,2,2]-diazabicyclooctane (DABCO) and methyl methanesulfonate (MeOMs) were purchased from TCI. $Ir(ppy)_3$ was purchased from Ambeed or Sigma Aldrich. Triethyl phosphite was purchased from Sigma Aldrich. Lithium hexafluorophosphate was purchased from Oakwood chemical.

Safety and General considerations:

Graphite electrodes used for high current density reactions, especially with the DABCOnium amine as limiting reagent, tend to get pitted, flaked, and bent after multiple use. Such damage does not impair the electrode's effectiveness in the electrochemical reaction.

Lithium hexafluorophosphate undergoes hydrolysis in air, releasing HF vapor, which is highly hazardous. All weighing of $LiPF_6$ was done inside a fume hood, and the salt was stored in a well-sealed bottle inside a desiccator. When stored in a desiccator, a 25 g bottle of $LiPF_6$ remains dry enough for synthetic use for at least 2 months.

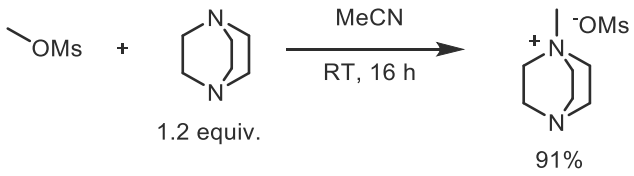
***N*-alkyl DABCOnium mesylate salts** range from highly hygroscopic to deliquescent. Care should be taken to weigh these salts quickly to minimize the time the salt is open to air. These amine salts were stored in a desiccator. When stored in a desiccator, they remain dry enough for synthetic use for at least 1 month.

Potassium cyanide is a colorless and highly toxic crystalline salt. The use of potassium cyanide should only be undertaken in a well-ventilated fume hood. All procedures for cyanide reactions were performed inside a fume hood with the sash as low as possible. A bleach solution (125 mL of bleach per 0.5 g of cyanide compound used, diluted with 250 mL of water) was prepared. After use of potassium cyanide, glassware was rinsed with acetone and immersed in the bleach bath for at least 24 hours to quench the cyanide. All surfaces in contact with potassium cyanide were carefully rinsed with acetone and aqueous bleach solution. All cyanide waste was collected in a cyanide waste bottle and quenched with bleach. The quenched cyanide waste was collected in a cyanide waste bottle, which was left in the fume hood for collection. Bleach baths were always stored in a fume hood and fresh bleach solution was prepared after each quench. The KCN reaction mixes revealed a pH of ~11-12. This somewhat basic pH should limit the amount of HCN produced. Regardless, these reaction liquids were never handled uncovered outside of a fumehood as a precaution.

EXPERIMENTAL DATA

Preparation of starting materials

_N_-methyl DABCOnium mesylate (4a)



To a 100 mL round-bottom flask, was added DABCO (6.48 g, 1.2 equiv.), 50mL MeCN and a magnetic stir bar. The flask was placed in a room-temperature water bath, and strong stirring was turned on. The flask was capped with a rubber septum, and methyl mesylate (4.0 mL, 47 mmol, 1.0 equiv.) was added dropwise via syringe over 15 min. After stirring at room temperature for 16 h, MeCN was removed using reduced pressure, and the resulting solid was washed with boiling acetone (3×30 mL). Excess acetone was removed with reduced pressure, affording the title compound as a white solid (91% yield, 9.51 g, 42.8 mmol).

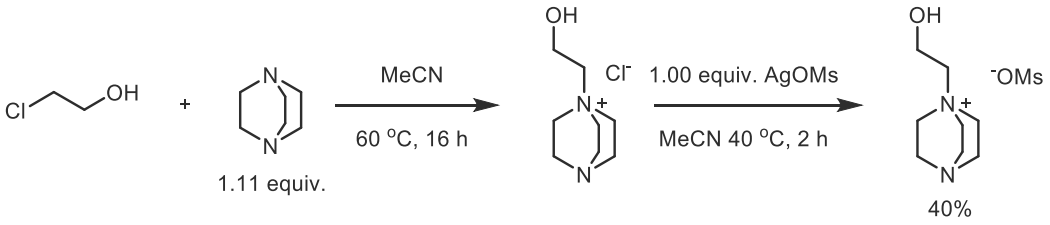
NMR Spectroscopy:

^{1}H NMR (500 MHz, DMSO-d_6, δ): 3.27 (t, J = 7.6 Hz, 6H), 3.01 (t, J = 7.6 Hz, 6H), 2.96 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6, δ): 53.2 (m), 50.8 (m), 44.7, 39.8.

HRMS-ESI(m/z) calc'd for $C_7H_{15}N_2$ $[M\text{-}OMs]^+$ 127.1235; found 127.1235; deviation +3.68 ppm.

***N*-(2-hydroxyethyl) DABCOnium mesylate (4x)**



To a 100 mL round-bottom flask was added a magnetic stir bar, 2-chloroethanol (1.00 mL, 14.9 mmol), MeCN (50 mL), and DABCO (1.85 g, 1.11 equiv.). The mixture was capped with a rubber septum, placed in an oil bath, heated to 60ºC, and stirred overnight. After this was complete, AgOMs (3.00 g, 1.0 equiv.) was added, and the mixture was stirred at 40ºC for 2 h. The mixture was then filtered through filter paper, followed by a filtration through a Whatman syringe filter (0.2 µm). MeCN was removed with reduced pressure, and the resulting solid was washed with DCM (3×20 mL). Residual DCM was removed with reduced pressure. The resulting solid was stored in a vial in a desiccator under fluorescent lighting for 1 week. After 1 week, the solid was redissolved in minimal MeCN and filtered once more through a Whatman syringe filter to remove formed black flecks. MeCN was removed under reduced pressure and the product was dried under vacuum, resulting in the title compound as an off-white solid (1.50 g, 5.94 mmol, 40%).

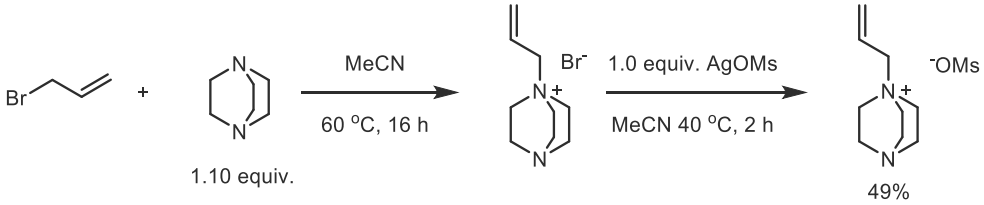
NMR Spectroscopy:

^{1}H NMR (500 MHz, Methanol-*d*$_4$, δ): 4.02 (dq, *J* = 7.6, 2.7 Hz, 2H), 3.50 (t, *J* = 7.6 Hz, 6H), 3.43-3.38 (m, 2H), 3.21 (t, *J* = 7.6 Hz, 6H), 2.88 (s, 1H), 2.70 (s, 3H).

^{13}C NMR (126 MHz, Methanol-*d*$_4$, δ): 67.5 (m), 56.0, 54.5(m), 46.1, 39.5.

HRMS-ESI(m/z) calc'd for $C_8H_{17}ON_2$ $[M\text{-}OMs]^+$ 157.1341; found 157.1330; deviation -3.31 ppm.

***N*-allyl DABCOnium mesylate (4y)**



To a 100 mL round-bottom flask was added a magnetic stir bar, allyl bromide (3.00 g, 24.8 mmol), MeCN (50 mL), and DABCO (3.06 g, 1.10 equiv.). The mixture was capped with a rubber septum, placed in an oil bath, heated to 60°C, and stirred overnight. After this was complete, AgOMs (5.00 g, 1.00 equiv.) was added, and the mixture was stirred at 40°C for 2 h. The mixture was then filtered through filter paper, followed by a filtration through a Whatman syringe filter (0.2 µm). MeCN was removed with reduced pressure, and the resulting solid was washed with warm THF (3×20 mL). Residual THF was removed with reduced pressure. The resulting solid was stored in a vial in a desiccator under fluorescent lighting for 1 week. After 1 week, the solid was redissolved in minimal MeCN and filtered once more through a Whatman syringe filter to remove formed black flecks. MeCN was removed under reduced pressure and the product was dried under vacuum, resulting in the title compound as a pink solid (2.99 g,12.0 mmol, 49%).

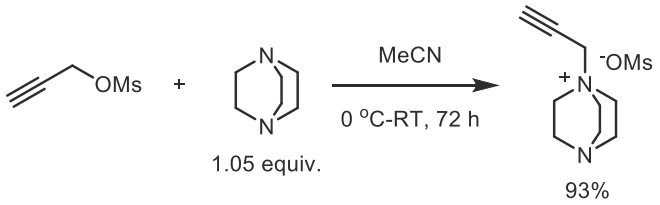
NMR Spectroscopy:

^{1}H NMR (500 MHz, DMSO-d_6, δ): 6.01 (ddt, *J* = 15.9, 10.9, 7.3 Hz, 1H), 5.64-5.57 (m, 2H), 3.91 (d, *J* = 7.3 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 6H), 3.03 (t, *J* = 7.5 Hz, 6H) 2.32 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6, δ): 127.2, 125.5, 65.2, 51.5, 44.7, 39.8.

HRMS-ESI(m/z) calc'd for $C_9H_{17}N_2$ $[M\text{-}OMs]^+$ 153.1392; found 153.1391; deviation +3.01 ppm.

***N*-propargyl DABCOnium mesylate (4z)**



To a 50 mL round-bottom flask was added a magnetic stir bar, DABCO (791 mg, 1.05 equiv.) and MeCN (12 mL). The mixture was capped with a rubber septum and placed in an ice-water bath. To the mixture 2-propynyl methanesulfonate (710 μL, 6.71 mmol) was added dropwise, and the mixture was stirred for 72 hours and allowed to come to room temperature ambiently. After this was complete, MeCN was removed with reduced pressure, and the resulting solid was washed with warm THF (5×15 mL). Residual THF was removed with reduced pressure and the product was dried under vacuum, resulting in the title compound as an off-white solid (1.53 g, 6.21 mmol, 93%).

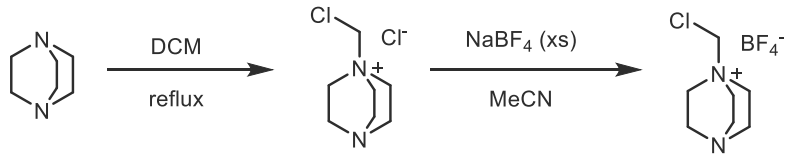
NMR Spectroscopy:

^{1}H NMR (500 MHz, DMSO-d_6, δ): 4.31 (d, J = 2.6 Hz, 2H), 4.13 (t, J = 2.5 Hz, 1H), 3.34 (t, J = 7.4 Hz, 6H), 3.06 (t, J = 7.5 Hz, 6H) 2.31 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6, δ): 84.2, 71.8, 52.7, 51.6, 44.6, 39.8.

HRMS-ESI(m/z) calc'd for $C_9H_{15}N_2$ $[M\text{-}OMs]^+$ 151.1235; found 151.1236; deviation +3.99 ppm.

***N*-methylene chloride DABCOnium tetrafluoroborate (4aa)**



N-methylene chloride DABCOnium Tetrafluoroborate was prepared according to a previously reported method.[1]

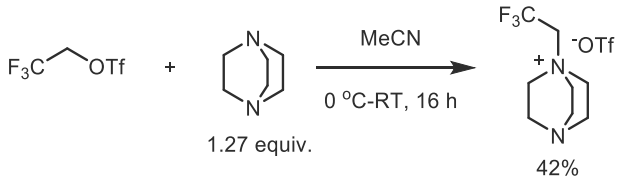
NMR Spectroscopy:

^{1}H NMR (500 MHz, DMSO-d_6, δ): 5.26 (s, 2H), 3.36 (t, J = 7.5 Hz, 6H), 3.09 (t, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, DMSO-d_6, δ): 67.8 (m), 50.9 (m), 44.6 (m).

^{19}F NMR (476MHz, DMSO-d_6, δ): -148.2 (d, J = 25.6 Hz).

***N*-(2,2,2-trifluoroethyl) DABCOnium triflate (4ab)**



To a 50 mL round-bottom flask was added a magnetic stir bar, DABCO (1.32 g, 1.27 equiv.) and MeCN (15 mL). The mixture was capped with a rubber septum and placed in an ice-water bath. To the mixture 2,2,2-trifluoroethyl trifluoromethanesulfonate (1.33 mL, 9.23 mmol) was added dropwise, and the mixture was stirred and allowed to come to room temperature overnight. After this was complete, MeCN was removed with reduced pressure, and the resulting solid was washed with warm THF (5×15 mL). Residual THF was removed with reduced pressure and the product was dried under vacuum, resulting in the title compound as a pale yellow solid (1.33 g, 3.85 mmol, 42%).

NMR Spectroscopy:

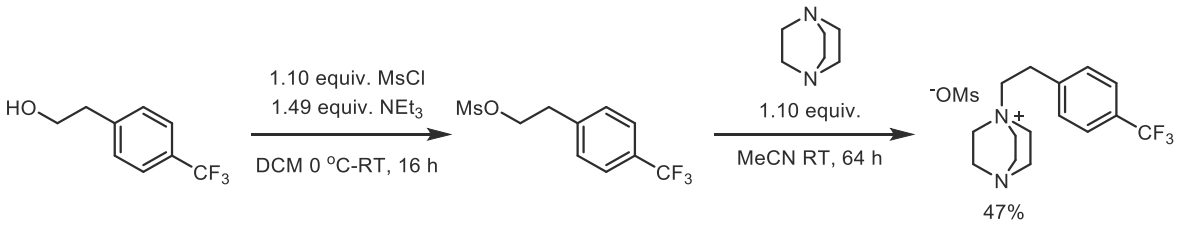
^{1}H NMR (500 MHz, DMSO-d_6, δ): 4.57 (q, *J* = 9.3 Hz, 2H), 3.53 (t, *J* = 7.3 Hz, 6H), 3.14 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, DMSO-d_6, δ): 122.2 (q, *J* = 279.6 Hz), 120.7 (q, *J* = 322.2 Hz), 59.8 (q, *J* = 32.4 Hz), 53.3, 44.4.

^{19}F NMR (476MHz, DMSO-d_6, δ): -59.6 (t, *J* = 9.4 Hz), -77.8 (s).

HRMS-ESI(m/z) calc'd for $C_8H_{14}F_3N_2$ $[M\text{-}OTf]^+$ 195.1109; found 195.1145; deviation +21.5 ppm.

***N*-(2-(4-trifluoromethylphenyl)ethyl) DABCOnium mesylate (4ac)**



To a 100 mL round-bottom flask was added a magnetic stir bar, 4-(trifluoromethyl)phenethyl alcohol (913 μL, 6.02 mmol), DCM (30 mL), and triethylamine (1.25 mL, 1.49 equiv.). The mixture was capped with a rubber septum and placed in an ice bath. To the mixture MsCl (511 μL, 1.10 equiv.) was added dropwise, and the mixture was stirred and allowed to come to room temperature overnight. The reaction mixture was added to a separatory funnel and washed with dilute aq. HCl (0.2M, 2×30 mL). After this was complete, the DCM added to a 100mL round bottom flask and removed with reduced pressure, and the resulting oil was redissolved in MeCN (14 mL). To the mixture was added a magnetic stir bar and DABCO (740 mg, 1.10 equiv.), and the mixture was stirred at room temperature for 64 hours. After this was complete, MeCN was removed under reduced pressure. The crude solid was washed with THF (3×15 mL). Residual THF was removed with reduced pressure, and the product was dried under vacuum, resulting in the title compound as an off-white solid (1.07 g, 2.81 mmol, 47%).

NMR Spectroscopy:

^{1}H NMR (500 MHz, DMSO-*d*$_6$, δ): 7.74 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 3.52-3.45 (m, 2H), 3.38 (t, *J* = 7.5 Hz, 6H), 3.19-3.12 (m, 2H), 3.07 (t, *J* = 7.5 Hz, 6H) 2.31 (s, 3H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$, δ): 141.6, 130.0, 127.7 (q, *J* = 31.8 Hz), 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.0 Hz), 63.1, 51.7, 44.7, 39.8, 27.1.

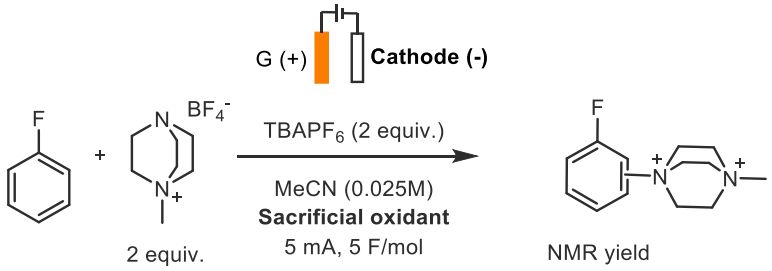
^{19}F NMR (476MHz, DMSO-*d*$_6$, δ): -60.9 (s).

HRMS-ESI(m/z) calc'd for $C_{15}H_{20}F_3N_2$ $[M\text{-}OMs]^+$ 285.1579; found 285.1581; deviation +2.74 ppm.

Optimization of electrochemical anodic DABCOylation

The components of the reaction were optimized sequentially in the order they appear in this section. Optimal condition is highlighted in each table in green. Electrochemical parameters (current and F/mol) were individually optimized to each substrate. HFIP in high loadings gave superior yield to other tested sacrificial oxidants. Lithium electrolytes gave broadly better yield than other cations, while PF_6 electrolytes gave generally better selectivity, with $LiPF_6$ being the ideal electrolyte. Graphite gave far superior yields to other carbon electrodes, while platinum proved the most consistent counter electrode for hydrogen evolution (triplicate reactions with Ni and Ni foam shown). Between OMs and BF_4 as counterions to the alkylated DABCO, OMs gave better selectivity.

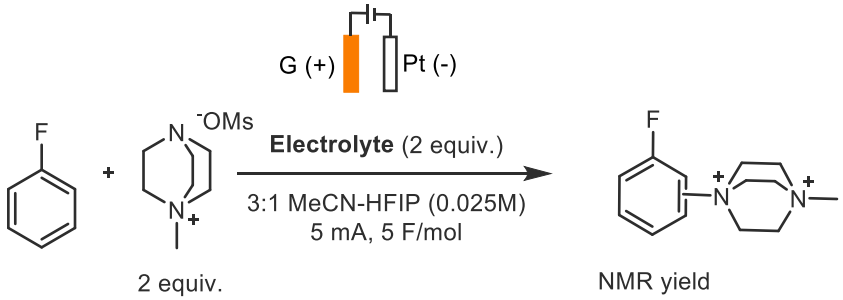
Optimization of sacrificial oxidant



Sac. Ox.	Equiv.	Cathode	Yield (%)	Selectivity (p:o+m)
HFIP	1	Pt	29	10.2:1
HFIP	10	Pt	50	7.4:1
HFIP	10	Graph	14	only p
HFIP	25v%	Pt	85	4.4:1
C6F6	1	Graph	18	only p
C6F6	4.3	Graph	55	7.2:1
C6F6	4.3	Pt	48	5.2:1
nonafluoro-tBuOH	0.75	Pt	60	5.6:1
Acetone	14	Graph	trace	NA
MeNO2	19	Graph	11	only p
AcOH	18	Pt	10	only p
Terephthalonitrile	8	Graph	trace	NA

Table S1: Optimization of sacrificial oxidant. Cathode was varied to be appropriate for the sacrificial oxidant.

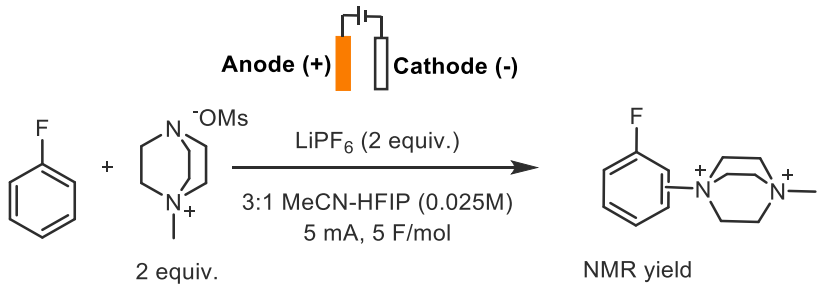
Optimization of electrolyte



Electrolyte	Yield (%)	Selectivity (p:o+m)
$LiPF_6$	91	12:1
$TBAPF_6$	75	7.8:1
$TBAClO_4$	73	8.4:1
$TBABF_4$	71	4.7:1
$LiBF_4$	83	2.8:1
$TMAPF_6$	62	10.1:1
$LiClO_4$*$3H_2O$	92	9.5:1
TBACl	0	NA
TBAI	0	NA

Table S2: Optimization of electrolyte.

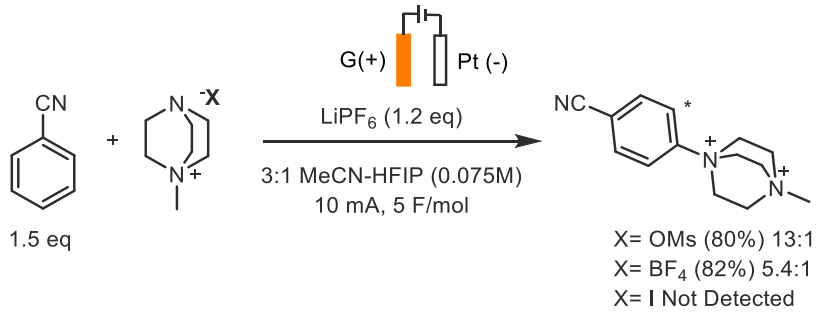
Optimization of electrodes



Anode	Cathode	Yield (%)	Selectivity (p:o+m)
Graphite	Pt Mesh	91	12:1
Graphite Felt	Pt Mesh	48	6:1
RVC	Pt Mesh	3	only p
Graphite	Ni	62	10.2:1
Graphite	Ni	80	9.7:1
Graphite	Ni	40	9.1:1
Graphite	Ni Foam	84	13.2:1
Graphite	Ni Foam	79	11.6:1
Graphite	Ni Foam	trace	NA

Table S3: Optimization of reaction electrodes, showing the inconsistency of nickel electrodes.

Amine counterions



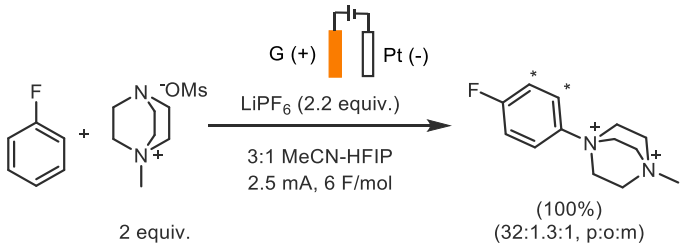
General procedure for aryl-DABCOnium salts and aryl piperazine products

Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added arene (1.2-3.0 equiv. or 1.0 equiv.) (if solid), $LiPF_6$ (~1.2 equiv. or ~2.2 equiv.), and *N*-alkyl DABCOnium sulfonate salt (1.0 equiv. or 2.0-3.0 equiv.), in sequence. Quickly, MeCN (3 mL; *c* = 0.075 M) was added, followed by arene (1.2-3.0 equiv. or 1.0 equiv.) (if liquid), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters appropriate to the arene substrate. The yield of the aryl DABCOnium salt product was determined by ^1H NMR spectroscopy using mesitylene as internal standard.

Reduction procedure 1: The crude reaction mixture was added to a 20 mL scintillation vial, dried under reduced pressure, and washed with THF (3 × 5 mL) to remove unreacted organics. Excess THF was removed with reduced pressure or a nitrogen stream. MeCN (8 mL) and KCN (3.0 equiv.) were added to the crude, and it was stirred at 40 °C for 48 h. MeCN is removed with reduced pressure. Products were purified on silica gel chromatography and dried with a nitrogen stream followed by vacuum (measured 0.3 mbar).

Reduction procedure 2: The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3 × 15 mL) and then discarded. The DCM volume was reduced using reduced pressure or a nitrogen stream. The remainder of the DCM was wet loaded onto the column. Products were purified on silica gel chromatography and dried with a nitrogen stream followed by vacuum (measured 0.3 mbar).

Fluorobenzene DABCOnium salt (2a)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (98 mg, 2.2 equiv.), and *N*-Me DABCOnium mesylate salt (132 mg, 2.0 equiv.), in sequence. Quickly, MeCN (3 mL, c = 0.075 M) was added, followed by fluorobenzene (29 µL, 0.30 mmol), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 2.5 mA, 6 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (100%). Selectivity was determined by ^{19}F NMR.

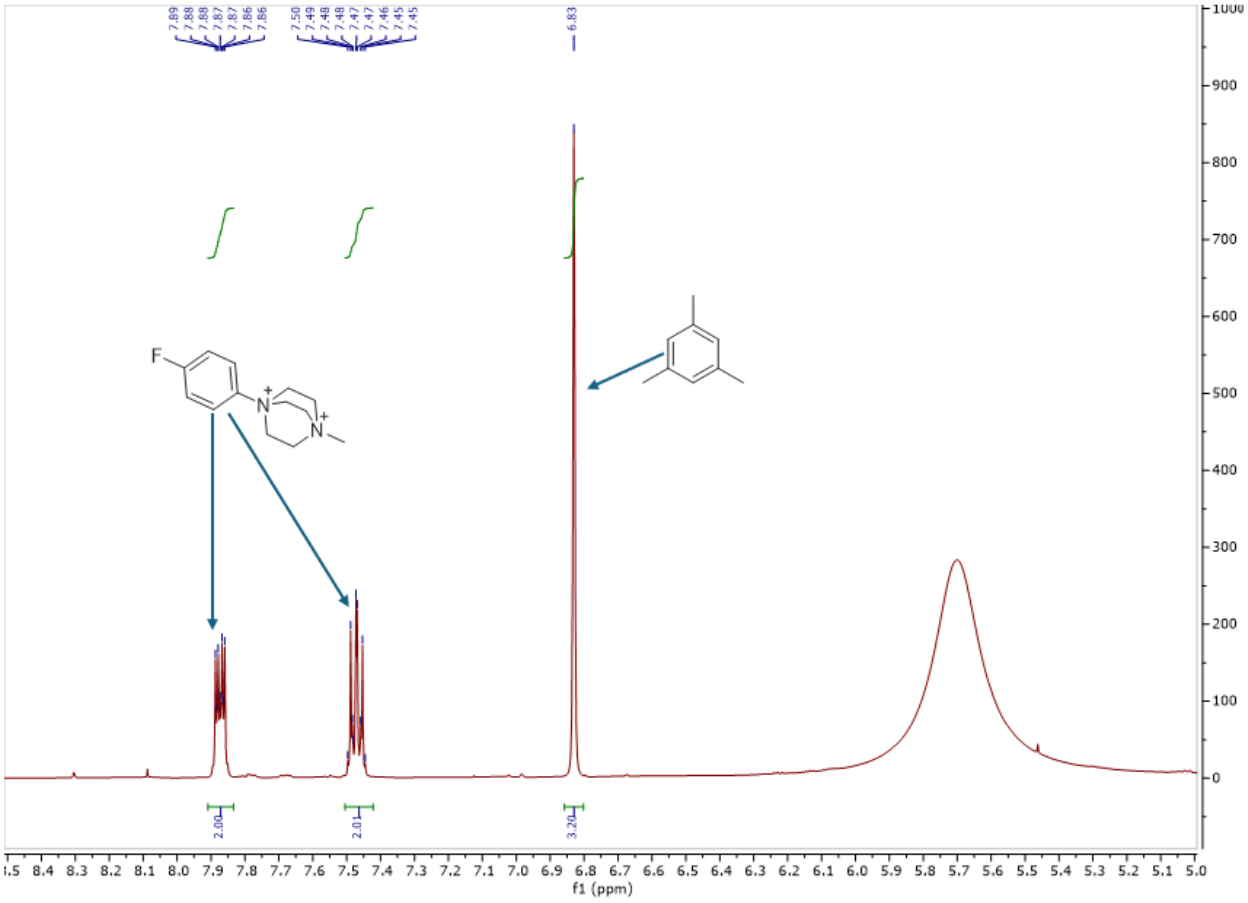


Figure S1: Crude ^{1}H-NMR showing the para regioisomer and the mesitylene internal standard.

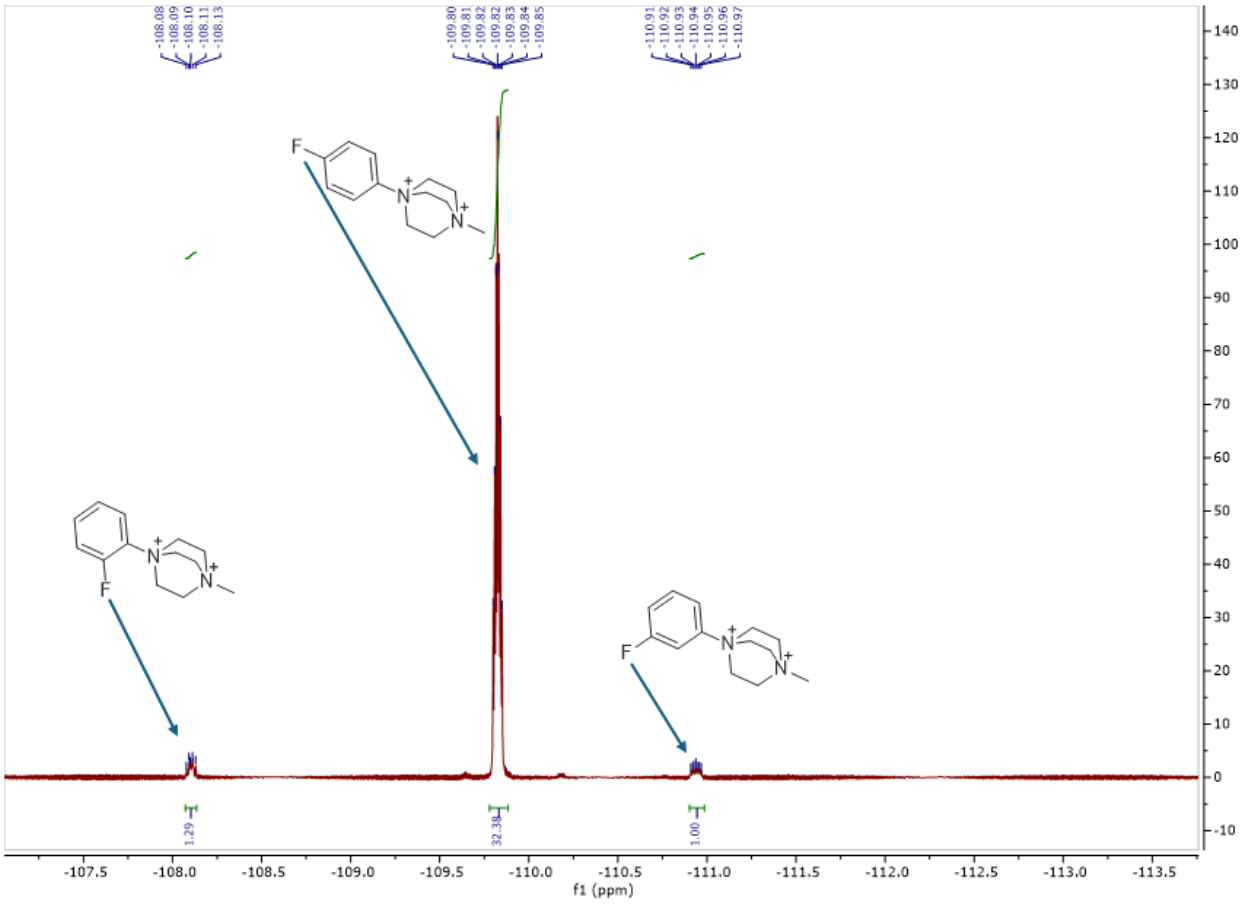
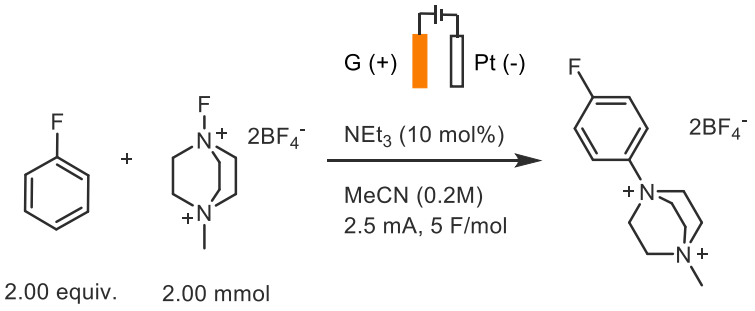


Figure S2: Crude ^{19}F NMR showing the product distribution of the DABCOnium salt.

Fluorobenzene DABCOnium salt (crystal)



Under ambient conditions, to a 10 mL ElectraSyn vial equipped with a magnetic stir bar were added, Selectfluor II (640 mg, 2.00 mmol) and fluorobenzene (0.377 mL, 2.00 equiv.) in sequence. 10 mL MeCN (*c* = 0.2 M) was added, followed by triethylamine (28 µL, 10 mol %). The ElectraSyn vial was equipped with two electrodes: graphite and platinum plate (10 mm × 10 mm × 0.1 mm) and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 2.5 mA, 5 F/mol. Once electrolysis was finished, the reaction crude was transferred to a 100 mL round bottom flask and MeCN was removed under reduced pressure. The solid residue was triturated

with 1:1 DCM:Et_2O (2 × 20 mL), and the washing solvent was decanted off after the solid settled. Excess DCM:Et_2O was removed with a nitrogen stream. Under stirring, acetone was added to the solid residue until solid stopped dissolving (~30 mL, some solid will never dissolve). The solution was filtered through celite, which was rinsed with acetone (2 × 4 mL). Under mild stirring, HCl gas was bubbled through the solution, forming a precipitate.[2] When precipitate stopped forming, the generator line for the HCl was removed and the solution was placed under a nitrogen stream. Upon drying, the resulting colorless crystals, corresponding to fluorobenzene DABCOnium tetrafluoroborate monohydrate, were submitted for single crystal X-ray crystallography. NOTE: It is key to remove the HCl line as soon as possible, since excessive acidity in the acetone can cause product degradation upon drying. Degradation can be seen visually as a brown tarry substance rather than a white or yellow powder or crystal. With the exception of the workup, this follows our previously reported method.[3]

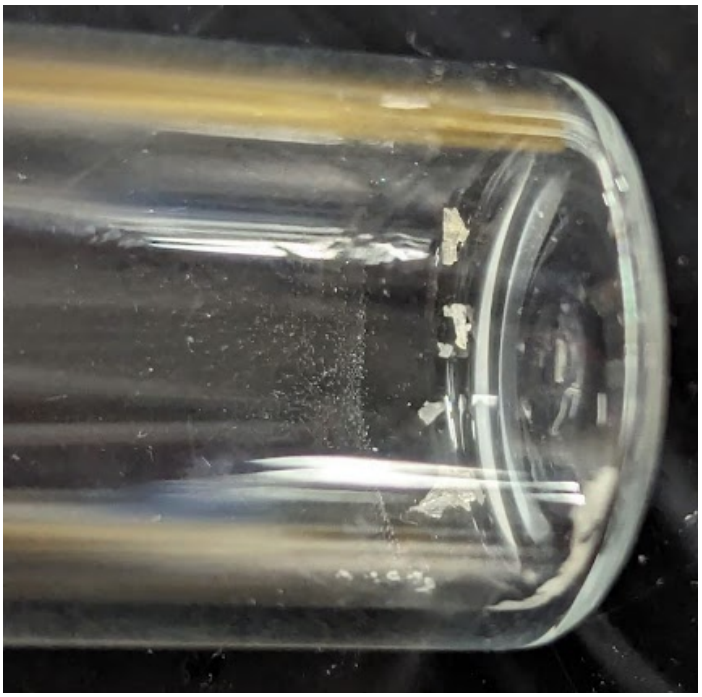
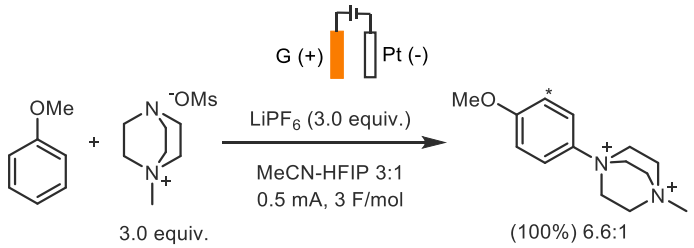


Figure S3: Image of crystals obtained via the above procedure.

Anisole DABCOnium salt (S1)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (45 mg, 3.0 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 3.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by anisole (11 µL, 0.10 mmol), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 0.5 mA, 3 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (100%). Selectivity was determined by ^{1}H NMR.

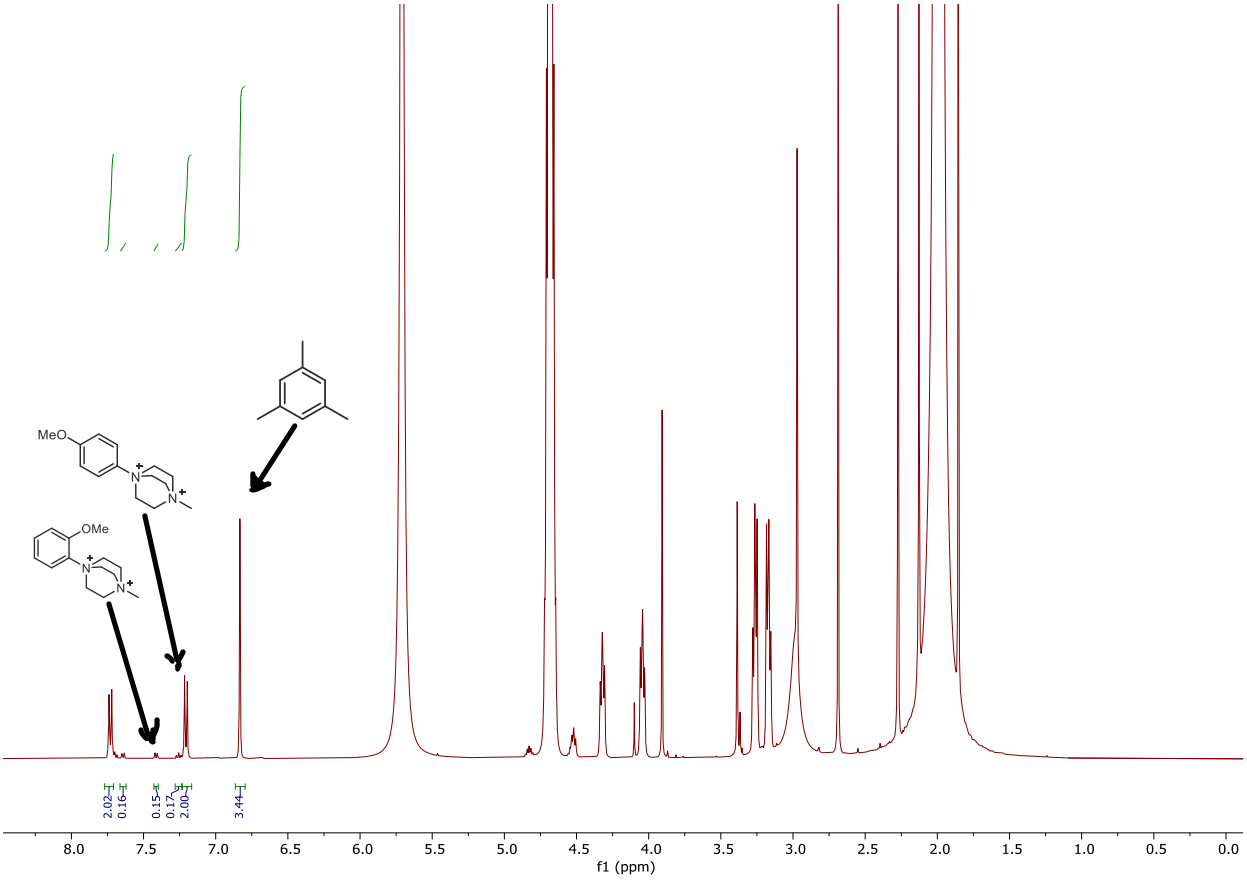
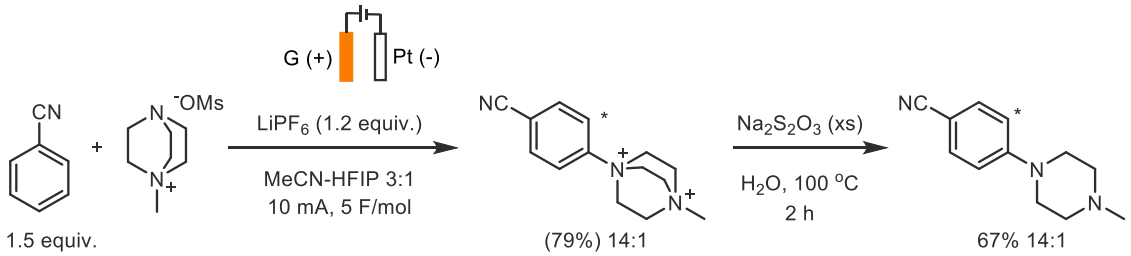


Figure S4: Crude ^{1}H NMR showing the para and ortho products and the mesitylene internal standard.

1-methyl-4-(4-cyanophenyl) piperazine (5b)



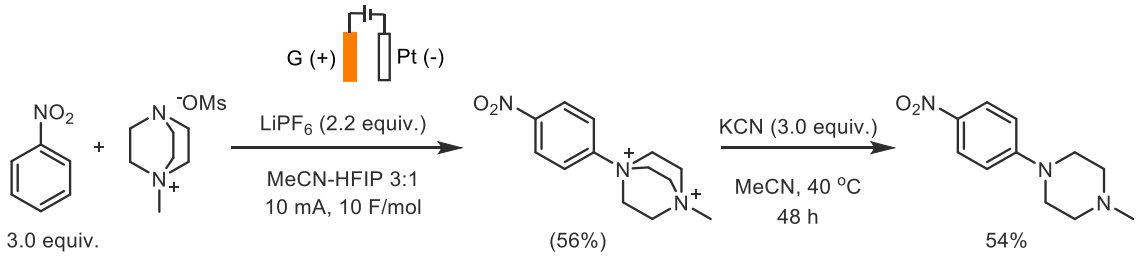
Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (55 mg, 1.2 equiv.), and *N*-Me DABCOnium mesylate salt (66 mg, 0.30 mmol, 1.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by benzonitrile (46 µL, 0.45 mmol, 1.5 equiv.) and 1mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (79%). 6% *N*-Me DABCOnium was also observed. The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid as a mixture of isomers (40.2 mg, 0.200 mmol, 67%). NMR data conforms to the literature.[4]

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.48 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.47-3.30 (m, 4H), 2.58 (t, *J* = 5.1 Hz, 4H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 153.4, 133.6, 120.1, 114.4, 100.5, 54.7, 47.1, 46.1.

1-methyl-4-(4-nitrophenyl) piperazine (5c)



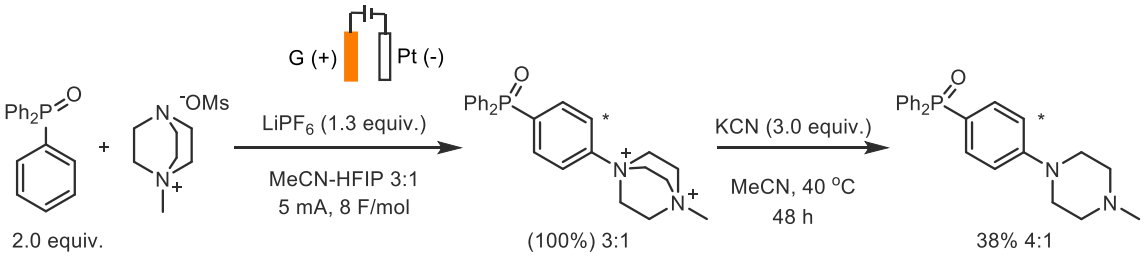
Under ambient conditions, to three 5 mL ElectraSyn vial equipped with a magnetic stir bar were added in parallel $LiPF_6$ (34 mg, 33 mg, 32 mg, 2.2 equiv., 2.2 equiv, 2.1 equiv), and *N*-Me DABCOnium mesylate salt (22 mg, 23 mg, 22 mg, 0.099 mmol, 0.10 mmol, 0.099 mmol, 1.0 equiv.) in sequence. Quickly, 3 mL MeCN (*c* = 0.025 M) was added followed by nitrobenzene (3×31 µL, 3.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 10 F/mol. The three reactions were combined and the average yield of DABCOnium product was determined by ^{1}H NMR, with mesitylene as internal standard (56%). 12% *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. Excess THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed under reduced pressure. The product was purified with silica gel chromatography (DCM->100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as a red-orange solid (36.0 mg, 0.163 mmol, 54%). NMR data conforms to the literature.[5]

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.12 (d, *J* = 9.4 Hz, 2H), 6.82 (d, *J* = 9.4 Hz, 2H), 3.46-3.41 (m, 4H), 2.57-2.53 (m, 4H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 155.0, 138.6, 126.1, 112.8, 54.7, 47.1, 46.2.

Triphenylphosphine oxide *N*-methyl piperazine (5d)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added triphenyl phosphine oxide (166 mg, 2.0 equiv.), $LiPF_6$ (60 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (66 mg, 0.30 mmol, 1 equiv.) in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 5 mA, 8 F/mol. The yield of DABCOnium products were determined by ^{31}P NMR with triethyl phosphite internal standard (100%). The crude reaction mixture was dried under reduced pressure and washed with DCM (3×5 mL) to remove unreacted organics. Excess THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-10-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as a mixture of isomers and appearing as a colorless solid (42.5 mg, 0.114 mmol, 38%).

NMR Spectroscopy:

***Para*-isomer**

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.67 (ddd, *J* = 11.9, 8.2, 1.4 Hz, 4H), 7.57-7.46 (m, 4H), 7.44 (dt, *J* = 7.0, 3.4 Hz, 4H), 6.92 (dd, *J* = 9.0, 2.4 Hz, 2H), 3.35-3.28 (m, 4H), 2.55 (t, *J* = 5.2 Hz, 4H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 153.3 (d, *J* = 2.5 Hz), 133.8, 133.5 (d, *J* = 11.1 Hz), 132.9, 132.1 (d, *J* = 9.8 Hz), 131.6 (d, *J* = 2.7 Hz), 128.4 (d, *J* = 12.0 Hz), 114.2, 54.8, 47.5, 46.1.

^{31}P NMR: (202 MHz, $CDCl_3$, δ): 29.1 (p, *J* = 11.8 Hz).

***Meta*-isomer**

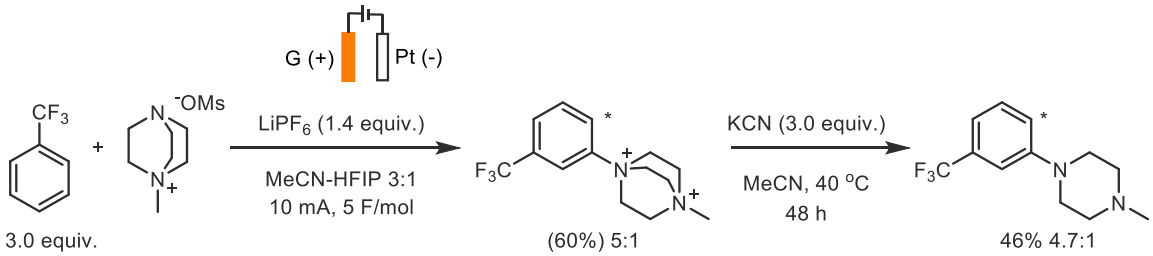
^{1}H NMR (500 MHz, $CDCl_3$, δ): Peaks for the meta isomer could not be clearly identified to due overlapping with the para isomer.

^{13}C NMR (126 MHz, $CDCl_3$, δ): 151.2 (d, *J* = 13.3 Hz), 132.1 (d, *J* = 10.0 Hz), 131.9 (d, *J* = 12.3 Hz), 129.1 (d, *J* = 14.3 Hz), 128.4 (d, *J* = 12.3 Hz), 122.7 (d, *J* = 10.9 Hz), 120.7, 119.8, 119.0 (d, *J* = 10.4 Hz), 118.9 (d, *J* = 3.0 Hz), 54.9, 48.5, 46.1.

^{31}P NMR: (202 MHz, $CDCl_3$, δ): 29.8 (m).

HRMS-ESI(m/z) calc'd for $C_{23}H_{26}N_2OP$ $[M+H]^+$ 377.1783; found 377.1809; deviation +5.24 ppm.

1-Methyl-4-(4-trifluoromethylphenyl) piperazine (5e)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (62 mg, 1.4 equiv.), and *N*-Me DABCOnium mesylate salt (66 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by trifluorotoluene (110 µL, 0.90 mmol, 3.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. Yield of DABCOnium product was determined by ^{19}F NMR with hexafluorobenzene internal standard (60%). *N*-Me DABCOnium was also observed (1:6.2 with DABCOnium products). The crude reaction mixture was dried under reduced pressure and washed with diethyl ether (1×5 mL) to remove unreacted organics. Excess ether was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->93-7 DCM-MeOH v/v) The eluent solvent was dried off to afford the title compound as a yellow oil in a mixture of isomers (33.5 mg, 0.137 mmol, 46%). NMR data conforms to the literature.[6,7]

NMR Spectroscopy:

***Meta*-isomer:**

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 7.08-7.03 (m, 2H), 3.29-3.21 (m, 4H), 2.62-2.54 (m, 4H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, δ): 151.5, 131.5 (q, *J* = 31.7 Hz), 129.7, 124.5 (q, *J* = 272.5 Hz), 118.8 (q, *J* = 1.4 Hz), 115.9 (q, *J* = 3.9 Hz), 112.3 (q, *J* = 3.9 Hz), 55.0, 48.7, 46.2.

^{19}F NMR (476 MHz, $CDCl_3$, δ): – 62.7 (s).

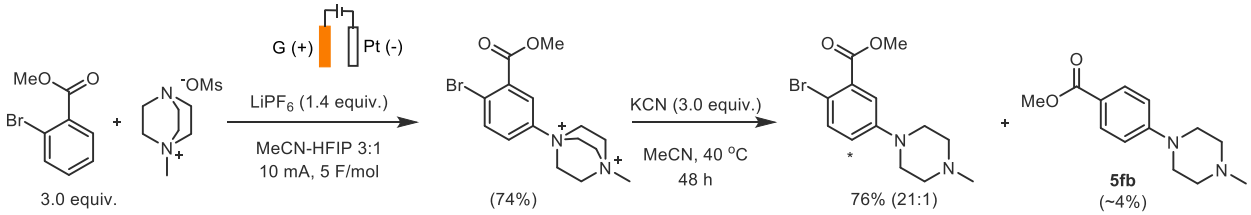
***Para*-isomer:**

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.47 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz. 2H), 3.32-3.27 (m, 4H), 2.35 (s, 3H) Note: one of the piperazine peaks for the para isomer is obscured by peaks of the meta isomer.

^{13}C NMR (150 MHz, $CDCl_3$, δ): 153.4, 126.5 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 270.8Hz), 120.6 (q, *J* = 32.7 Hz), 114.6, 54.9, 48.0, 46.2.

^{19}F NMR (476MHz, $CDCl_3$, δ): -61.4 (s).

Methyl-2-bromobenzoate *N*-methyl piperazine (5f)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (61 mg, 1.4 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by methyl-2-bromobenzoate (102 µL, 0.73 mmol, 2.4 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. Yield of DABCOnium product was determined by ^{1}H NMR with mesitylene internal standard (74%). 16% *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with 1-1 Et_2O-THF (3×5 mL) to remove unreacted organics. Excess Et_2O-THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The eluent solvent was dried off to afford the title compound as a yellow oil in a mixture of regioisomers (21:1) (70.9 mg, 0.228 mmol, 76%). Compound **5fb** was also observed as a minor product in the oil (1:18.6 with major isomer, ~4%). Regioselectivity was confirmed by COSY, HSQC, and HMBC.

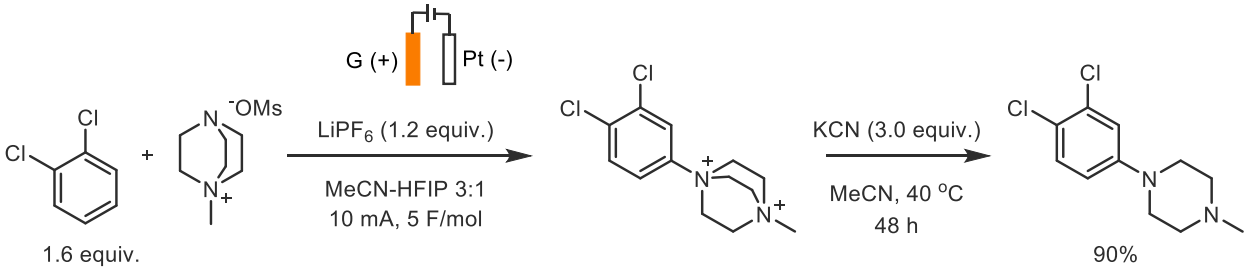
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.9 Hz, 1H), 7.27 (d, *J* = 3.1 Hz, 1H), 6.84 (dd, *J* = 8.9, 3.1 Hz), 3.89 (s, 3H), 3.19 (t, *J* = 5.1 Hz, 4H), 2.53 (t, *J* = 5.1 Hz, 4H) 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.1, 150.2, 134.7, 132.5, 119.9, 118.1, 110.2, 54.9, 52.5, 48.6, 46.2.

HRMS-ESI(m/z) calc'd for $C_{13}H_{18}BrO_2N_2$ $[M+H]^+$: 313.0546; found: 313.0558; deviation +3.81ppm.

1-methyl-4-(3,4-dichlorophenyl) piperazine (5g)



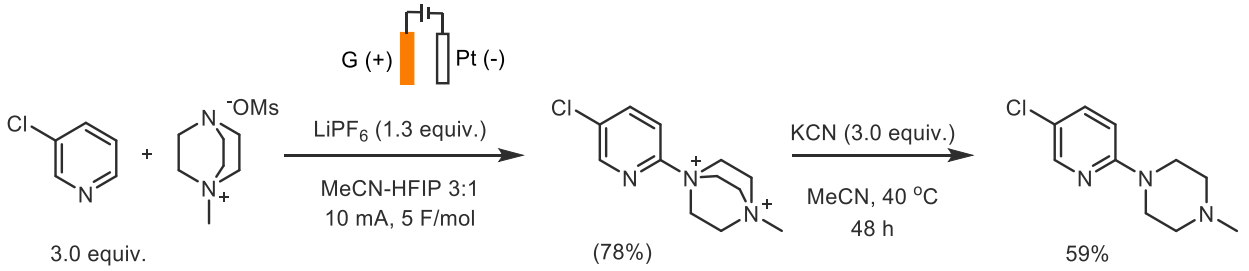
Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (57 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (63 mg, 0.28 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by o-dichlorobenzene (50 µL, 0.44 mmol, 1.6 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. Excess THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (59 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as a yellow oil (61.8 mg, 0.252 mmol, 90%). NMR data conforms to the literature.[8]

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.27 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 2.9 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.9 Hz, 1H), 3.21-3.16 (m, 4H), 2.59-2.53 (m, 4H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.8, 132.9, 130.5, 122.2, 117.3, 115.4, 54.9, 48.7, 46.2.

3-chloropyridine *N*-methyl piperazine (5h)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (59 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 3-chloropyridine (85 µL, 0.89 mmol, 3.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. Yield of DABCOnium product was determined by ^{1}H NMR with mesitylene internal standard (78%). 13% *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. Excess THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as a yellow solid (37.6 mg, 0.177 mmol, 59%).

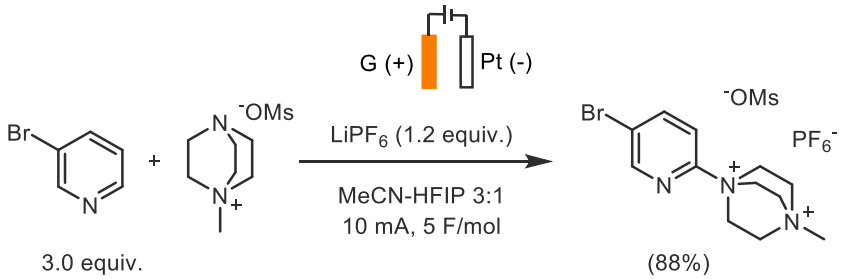
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.09 (d, *J* = 2.7 Hz, 1H), 7.39 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.56 (dd, *J* = 9.1, 0.7 Hz, 1H), 3.56-3.44 (m, 4H), 2.53-2.46 (m, 4H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 157.9, 146.4, 137.2, 120.3, 107.9, 54.9, 46.3, 45.4.

HRMS-ESI(m/z) calc'd for $C_{10}H_{15}ClN_3$ $[M+H]^+$ 212.0955; found 212.0956; deviation +0.56 ppm.

3-bromopyridine DABCOnium mesylate hexafluorophosphate salt (2i)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (57 mg, 1.2 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by, 3-bromopyridine (87 µL, 0.90 mmol, 3.0 equiv.) 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. The yield of product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (88%). Trace *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. THF residue was removed with a nitrogen stream. The solid residue was extracted with MeCN (2×5 mL), excluding particulates from the residue. This extract was dried down, yielding the title compound as a tan solid, with suspected electrolyte contamination. NMR analysis of the product showed the occupancy of mesylate as the anion to be 43% (0.87 mesylate anions per cation).

NMR Spectroscopy:

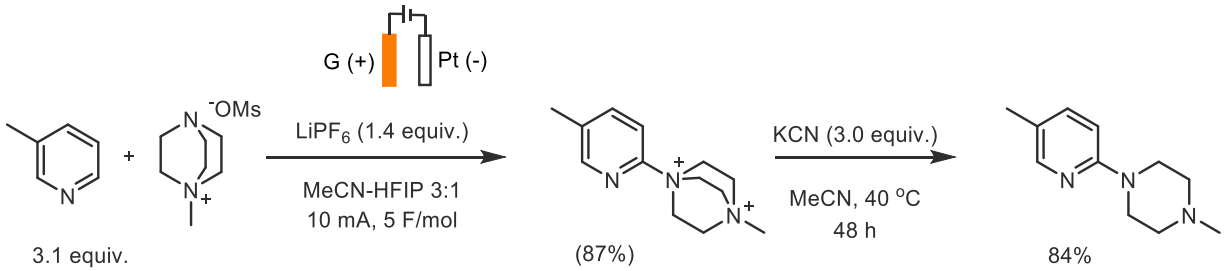
^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.93 (d, *J* = 2.4 Hz, 1H), 8.63 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 4.44 (t, *J* = 7.1 Hz, 6H), 4.07 (t, *J* = 7.3 Hz, 6H), 3.37 (s, 3H), 2.34 (s, 3H)

^{13}C NMR (126 MHz, DMSO-d_6, δ): 153.1, 149.7, 143.9, 123.2, 118.2, 52.8, 52.7, 51.7, 39.8

^{19}F NMR (476 MHz, DMSO-d_6, δ): -70.1 (d, *J* = 710.9 Hz)

HRMS-ESI(m/z) calc'd for $C_{13}H_{21}BrSO_3N_2$ $[M\text{-}PF_6]^+$ 378.0487; found 378.0493; deviation +2.26 ppm.

3-picoline *N*-methyl piperazine (5j)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (62 mg, 1.4 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 3-picoline (90 µL, 0.92 mmol, 3.1 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. Yield of DABCOnium product was determined by ^{1}H NMR with mesitylene internal standard (87%). 10% *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with 1-1 Et_2O-THF (3×5 mL) to remove unreacted organics. Excess Et_2O-THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-10-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as a yellow oil (48.4 mg, 0.253 mmol, 84%).

NMR Spectroscopy:

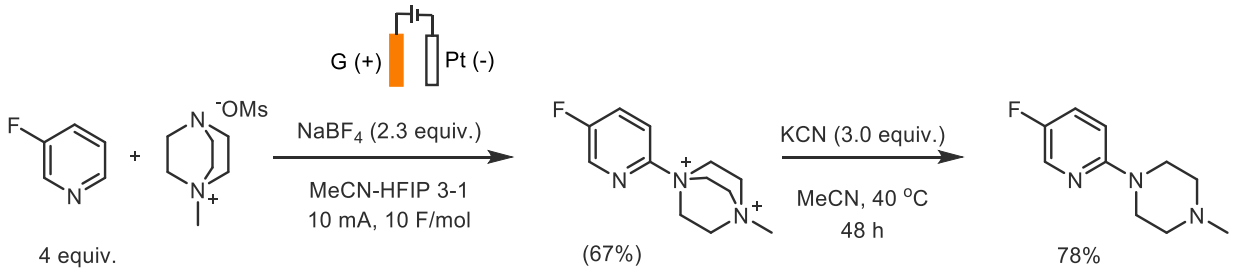
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.6 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.58 (d, *J* = 8.6 Hz, 1H), 3.49(t, *J* = 5.2 Hz, 4H), 2.54-2.48 (m, 4H), 2.33 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.2, 147.8, 138.5, 122.5, 107.1, 55.1, 46.3, 45.8, 17.4.

HRMS-ESI(m/z)

Calc'd for $C_{11}H_{18}N_3$ $[M+H]^+$: 192.1501. found: 192.1502; deviation: +3.62ppm.

3-fluoropyridine *N*-methyl piperazine (5k)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added dry $NaBF_4$ (75 mg, 2.3 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 3-fluoropyridine (104 µL, 1.20 mmol, 4.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 10 F/mol. Yield of DABCOnium product was determined by ^{1}H NMR with mesitylene internal standard (67%). Trace *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with 1-1 Et_2O-THF (3×5 mL) to remove unreacted organics. Excess Et_2O-THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-10-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as an orange oil with unknown inorganic contaminants (45.8 mg, 0.235 mmol, 78%). ^{19}F NMR revealed the product to have significant inorganic contamination from what appeared to be $BF_{4-x}R_x$ (1:5.6 with product) and a species related to HFIP (apparent dd, similar integration to the product). These species were not visible by ^{13}C or ^{1}H NMR. Attempting a water/DCM wash of the product resulted in all of the product migrating to water.

NMR Spectroscopy:

^{1}H NMR (500 MHz, C_6D_6): δ 8.12 (d, *J* = 3.1 Hz, 1H), 6.81 (ddd, *J* = 9.2, 7.6, 3.1 Hz, 1H), 5.98 (dd, *J* = 9.2, 3.3 Hz, 1H), 3.33 (t, *J* = 5.1 Hz, 4H), 2.19 (t, *J* = 5.1 Hz, 4H), 2.04 (s, 3H).

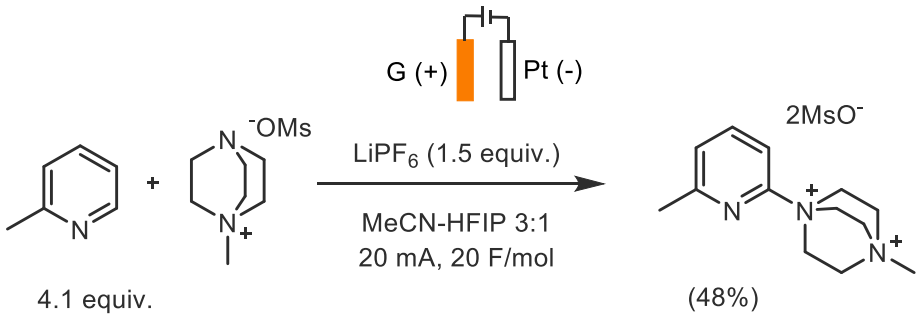
^{13}C NMR (126 MHz, C_6D_6): δ 156.5, 154.0 (d, *J* = 243.4 Hz), 135.0 (d, *J* = 23.9 Hz), 124.7 (d, *J* = 20.0 Hz), 107.5 (d, *J* = 3.6 Hz), 54.7, 45.6, 45.5.

^{19}F NMR (476 MHz, C_6D_6): δ -143.23 (dd, *J* = 7.8, 3.4 Hz).

HRMS-ESI(m/z)

Calc'd for $C_{10}H_{15}FN_3$ $[M+H]^+$: 196.1245. found: 196.1258; deviation: +6.51 ppm.

2-picoline DABCOnium mesylate salt (2l)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (68 mg, 1.5 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by 2-picoline (121 µL, 1.21 mmol, 4.1 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 20 mA, 20 F/mol. The yield of product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (48%). Trace *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with Et_2O (2×5 mL), then washed with THF (3×5 mL), then washed once more with Et_2O (4mL) to remove unreacted organics. Ether residue was removed with a nitrogen stream and reduced pressure. NMR analysis of the product showed the occupancy of mesylate as the anion to be 95% (1.9 mesylate anions per cation). A minor product appears to be present (~1:7 with shown product), but it could not be identified by NMR.

NMR Spectroscopy:

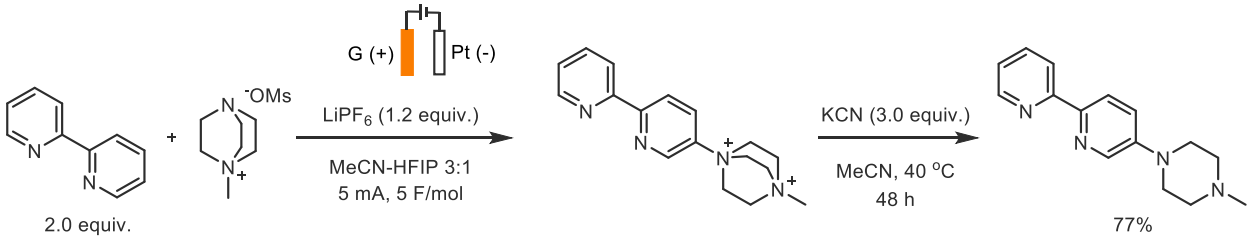
^{1}H NMR (500 MHz, DMSO-d_6): δ 8.19 (t, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.3, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 4.42 (t, *J* = 7.3 Hz, 6H), 4.08 (t, *J* = 7.3 Hz, 6H), 3.38 (s, 3H), 2.59 (s, 3H), 2.33 (s, 6H).

Note: the signal at 3.38 ppm appears under residual water.

^{13}C NMR (126 MHz, DMSO-d_6): δ 158.5, 153.6, 141.7, 126.7, 112.9, 52.8, 52.5, 51.7, 39.8, 23.7.

HRMS-ESI(m/z) Calc'd for $C_{13}H_{24}SO_3N_3$ [M-OMs]$^+$: 314.1538 . found: 314.1543; deviation: +2.79ppm.

Bipyridine *N*-methyl piperazine (5m)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, 2,2—bipyridine (95 mg, 2.0 equiv.), $LiPF_6$ (57 mg, 1.2 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 5 mA, 5 F/mol. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. Excess THF was removed with reduced pressure. MeCN (8 mL) and KCN (59 mg, 3.0 equiv.) were added to the crude, and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified via silica gel chromatography (DCM→100/5/0.5 DCM/MeOH/28% NH_4OH v/v/v). The eluent solvent was dried off to afford the title compound as an orange solid (58.5 mg, 0.230 mmol, 77%).

NMR Spectroscopy:

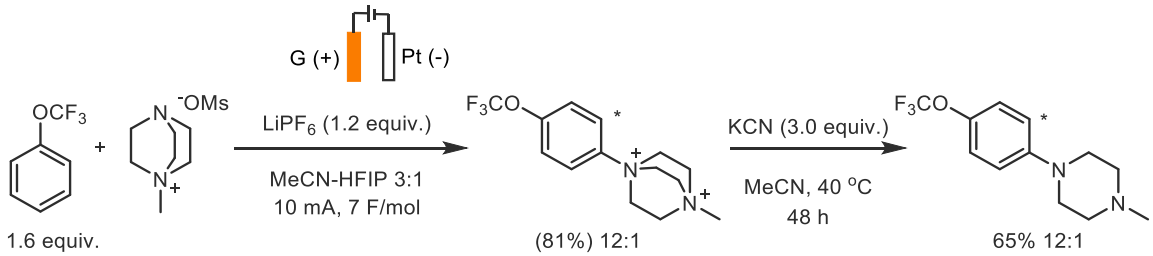
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.61 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.35 (d, *J* = 2.9 Hz, 1H), 8.29-8.24 (m, 2H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.29 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.21 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 3.36-3.19 (m, 4H), 2.59 (t, *J* = 5.1 Hz, 4H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 155.3, 148.0, 146.0, 145.8, 136.1, 135.7, 121.5, 121.4, 120.2, 119.0, 53.7, 47.0, 45.2.

R_f = 0.12 (DCM/NEt_3, 97:3 (v/v)).

HRMS-ESI(m/z) calc'd for $C_{15}H_{20}N_4^{2+}$ $[M+2H]^{2+}$ 128.0844. found 128.0838; deviation +2.31ppm.

1-methyl-4-(4-trifluoromethoxyphenyl) piperazine (5n)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (54 mg, 1.2 equiv.), and *N*-Me DABCOnium mesylate salt (65 mg, 0.29 mmol, 1 equiv.), in sequence. Quickly, 3mL MeCN (*c* = 0.075 M) was added followed by trifluoromethoxybenzene (60 µL, 0.45 mmol, 1.6 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 7 F/mol. Yield of DABCOnium product was determined by ^{1}H NMR with mesitylene internal standard (81%). Trace *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with diethyl ether (1×5 mL) to remove unreacted organics. Excess ether was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM→93-7 DCM-MeOH v/v) The eluent solvent was dried off to afford the title compound as a yellow solid in a mixture of isomers (50.5 mg, 0.194 mmol, 65%). NMR data conforms to the literature.[9]

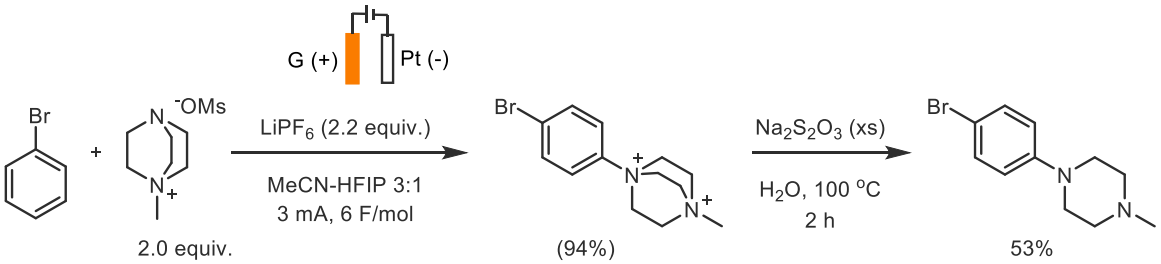
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.11 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 3.24-3.18 (m, 4H), 2.60 (t, *J* = 5.1 Hz, 4H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.0, 142.1 (q, *J* = 2.0 Hz), 122.0, 120.6 (q, *J* = 255.7 Hz), 116.7, 55.0, 49.1, 46.0.

^{19}F NMR (476 MHz, $CDCl_3$, δ): -58.3 (s).

1-methyl-4-(4-bromophenyl) piperazine (5o)



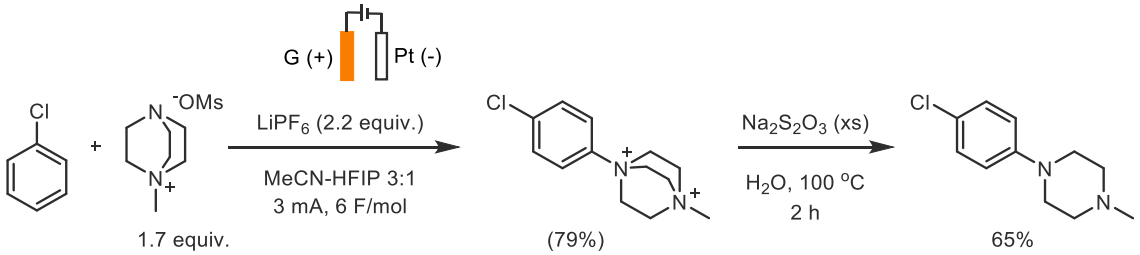
Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (104 mg, 2.3 equiv.), and *N*-Me DABCOnium mesylate salt (136 mg, 2.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by bromobenzene (31 µL, 0.30 mmol), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 6 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (94%). The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100ºC for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL), and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (40.6 mg, 0.159 mmol, 53%). NMR data conforms to the literature.[10]

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.33 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.33-3.10 (m, 4H), 2.59 (t, *J* = 5.1 Hz, 4H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.4, 132.0, 117.8, 112.0, 55.0, 49.0, 46.2.

1-methyl-4-(4-chlorophenyl)-piperazine (5p)



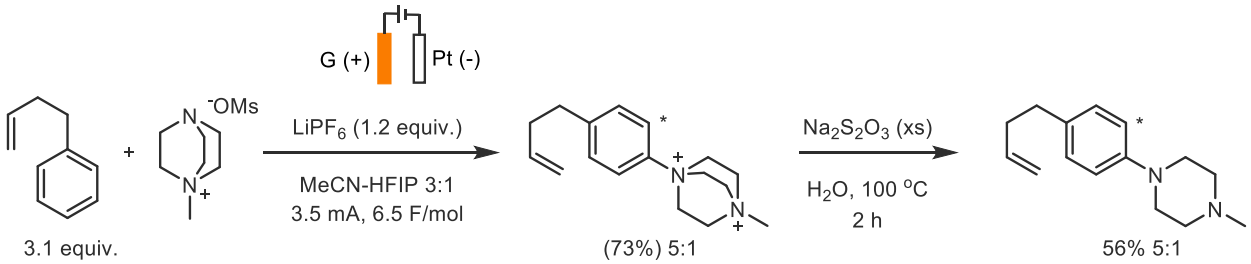
Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (101 mg, 2.2 equiv.), and *N*-Me DABCOnium mesylate salt (118 mg, 1.7 equiv.), in sequence. Quickly, 3mL MeCN (*c* = 0.075 M) was added, followed by chlorobenzene (30 µL, 0.30 mmol), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 6 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (79%). 12% chlorobenzene was also observed. The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified via silica gel chromatography (DCM→100/5/0.5 DCM/MeOH/28% NH_4OH v/v/v). The eluent solvent was dried off to yield the title compound as a yellow solid (41.1 mg, 0.195 mmol, 65%). NMR data conforms to the literature.[10]

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.20 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.19-3.14 (m, 4H), 2.56 (t, *J* = 5.1 Hz, 4H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.0, 129.1, 124.6, 117.4, 55.1, 49.3, 46.3.

4-phenyl-1-butene *N*-methyl piperazine (5q)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (55 mg, 1.2 equiv.), and *N*-Me DABCOnium mesylate salt (65 mg, 1.0 equiv., 0.29 mmol), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by 4-phenyl-1-butene (135 µL, 3.1 equiv.), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3.5 mA, 6.5 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (76%). 8% *N*-Me DABCOnium was also observed. The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (38.3 mg, 0.163 mmol, 56%).

NMR Spectroscopy:

***Para*-isomer:**

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.09 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.91-5.79 (m, 1H), 5.03 (dq, *J* =17.1, 1.7 Hz, 1H), 4.96 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 3.18 (t, *J* = 5.0 Hz, 4H), 2.65-2.61 (m, 2H), 2.59 (t, *J* = 5.0 Hz, 4H), 2.36 (s, 3H), 2.35-2.30 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 149.5, 138.5, 133.4, 129.2, 116.4, 114.9, 55.3, 49.5, 46.2, 35.8, 34.6.

***Meta*-isomer:**

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.18 (td, *J* = 7.4, 1.4 Hz, 1H), 6.79-6.73 (m, 2H), 6.71 (d, *J* = 7.5 Hz, 1H), 5.91-5.80 (m, 1H), 5.05 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.99-4.96 (m, 1H), 3.23-3.20 (m, 4H), 2.67 (t, *J* = 7.6 Hz, 2H).

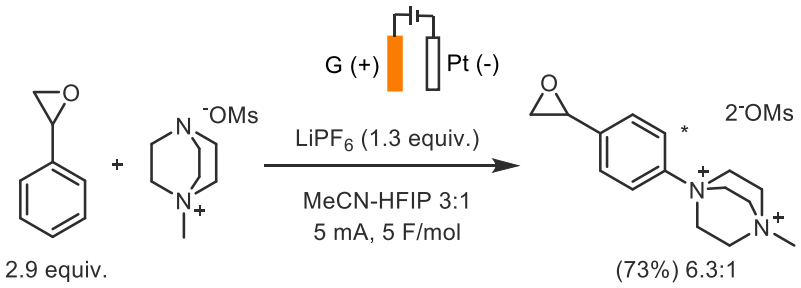
Note: some peaks for the meta isomer could not be positively identified, as they lay under the peaks for

the *para*-isomer.

^{13}C NMR (126 MHz, $CDCl_3$, δ): 151.5, 143.0, 138.4, 129.1, 120.1, 116.6, 114.9, 113.7, 53.6, 49.3, 46.2, 35.9, 35.7.

HRMS-ESI(m/z) calc'd for $C_{15}H_{23}N_2$ $[M+H]^+$ 231.1861; found 231.1877; deviation +9.11 ppm.

Styrene oxide DABCOnium mesylate salt (2r)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (60 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by styrene oxide (100 µL, 0.87 mmol, 2.9 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 5 mA, 5 F/mol. The yield of product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (73%). 8% *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL), followed by diethyl ether (1×5 mL) to remove unreacted organics. The was dried down, yielding the title compound as a mixture of isomers crude tan solid, with suspected electrolyte contamination. NMR analysis of the product showed the occupancy of mesylate as the anion to be 90% (1.8 mesylate anions per cation).

NMR Spectroscopy:

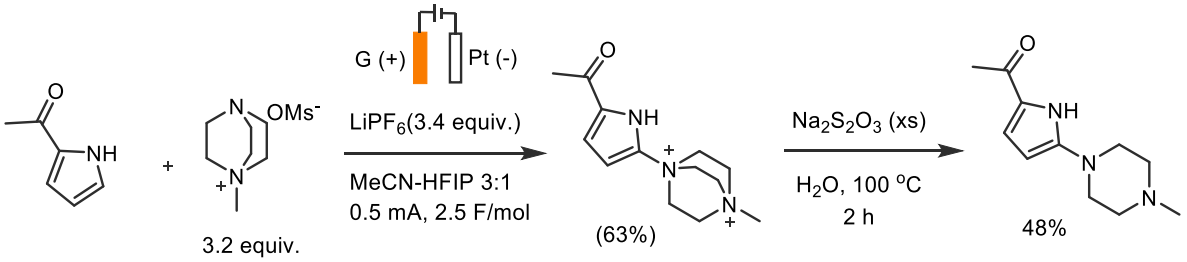
^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.01 (d, *J* = 9.1 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 4.45 (t, *J* = 7.5 Hz, 6H), 4.11-4.03 (m, 7H), 3.40 (s, 3H), 3.21 (dd, *J* = 5.4, 4.2 Hz, 1H), 2.92 (dd, *J* = 5.3, 2.5 Hz, 1H), 2.34 (s, 6H).

Note: One of the epoxide protons lies under one of the signals for the DABCOnium protons (4.11-4.03ppm). This was confirmed by COSY analysis.

^{13}C NMR (126 MHz, DMSO-d_6, δ): 144.1, 141.2, 127.7, 121.1, 54.1, 52.8, 51.6, 50.8, 50.5, 39.8.

HRMS-ESI(m/z) calc'd for $C_{16}H_{25}SO_4N_2$ $[M\text{-}OMs]^+$ 341.1535; found 341.1521; deviation -1.59ppm.

2-acetylpyrrole *N*-methyl piperazine (5s)



Under ambient conditions, to a 10 mL ElectraSyn vial equipped with a magnetic stir bar were added, 2-acetyl pyrrole (31 mg, 0.28 mmol, 1 equiv.), $LiPF_6$ (143mg, 3.4 equiv.), and *N*-Me DABCOnium mesylate salt (202 mg, 3.2 equiv.), in sequence. Quickly, 7.5 mL MeCN (*c* = 0.038 M) was added followed by 2.5mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 0.5 mA, 2.5 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (63%). 15% 2-acetyl pyrrole was also observed. The crude reaction mixture was added to a 30 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave an orange solid (27.7 mg, 0.134 mmol, 48%).

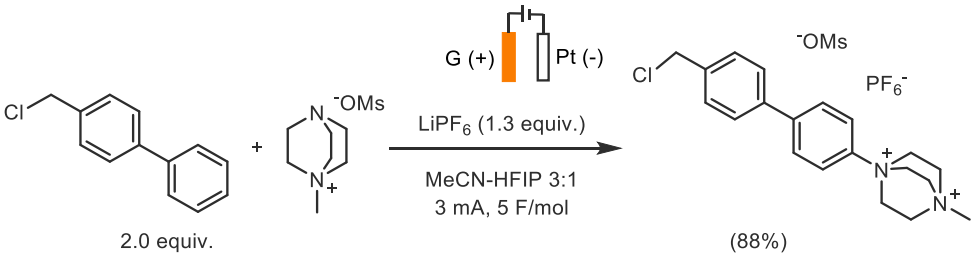
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.91 (br s, 1H), 6.86 (dd, *J* = 4.1, 1.7 Hz, 1H), 5.46 (dd, *J* = 4.1, 2.1 Hz, 1H), 3.26-3.16 (m, 4H), 2.53 (t, *J* = 5.1 Hz, 4H), 2.34 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 184.4, 149.0, 126.3, 120.3, 93.4, 54.3, 48.0, 46.3, 24.3.

HRMS-ESI(m/z) calc'd for $C_{11}H_{18}N_3O$ $[M+H]^+$:208.1450; found 208.1450; deviation +2.52ppm.

4-phenylbenzyl chloride DABCOnium mesylate hexafluorophosphate salt (2t)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, 4-phenylbenzyl chloride (124 mg, 2.0 equiv.), $LiPF_6$ (59 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 5 F/mol. The yield of the product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (88%). Trace *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. THF residue was removed with a nitrogen stream. The solid residue was extracted with MeCN (2×5 mL), excluding particulates from the residue. This extract was dried down, yielding the title compound as a tan solid, with suspected electrolyte contamination. A minor isomer appears to be present (1:12 with the para isomer). It could not be identified by NMR. NMR analysis of the product showed the occupancy of mesylate as the anion to be 60% (1.2 mesylate anions per cation).

NMR Spectroscopy:

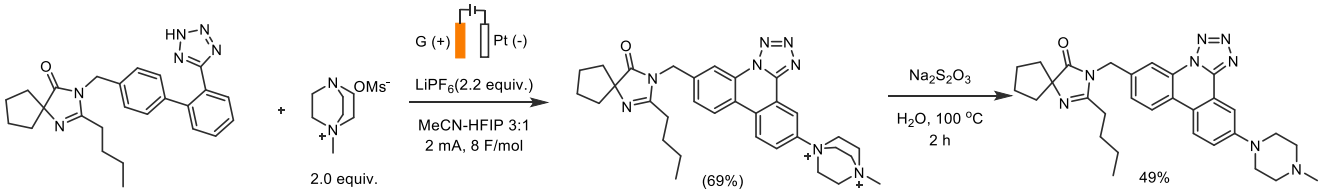
^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.10 (d, *J* = 9.3 Hz, 2H), 8.05 (d, *J* = 9.2 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 4.84 (s, 2H), 4.50 (t, *J* = 7.5 Hz, 6H), 4.08 (t, *J* = 7.5 Hz, 6H), 3.42 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6, δ): 143.5, 141.7, 138.0, 137.4, 129.5, 128.3, 127.2, 121.4, 53.9, 52.7, 51.4, 45.5, 39.6.

^{19}F NMR (476 MHz, DMSO-d_6, δ): -70.1 (d, *J* = 711.0 Hz).

HRMS-ESI(m/z) calc'd for $C_{21}H_{28}ClSO_3N_2$ $[M\text{-}PF_6]^+$ 423.1509; found 423.1523; deviation +4.15ppm.

Irbesartan cyclized *N*-methyl piperazine (5u)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, Irbesartan (127 mg, 0.296 mmol, 1 equiv.), $LiPF_6$ (98 mg, 2.2 equiv.), and *N*-Me DABCOnium mesylate salt (133 mg, 2.02 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 2 mA, 8 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (69%). The crude reaction mixture was added to a 30 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (77.0 mg, 0.146 mmol, 49%). Regioselectivity was confirmed by COSY, HSQC, and HMBC.

NMR Spectroscopy:

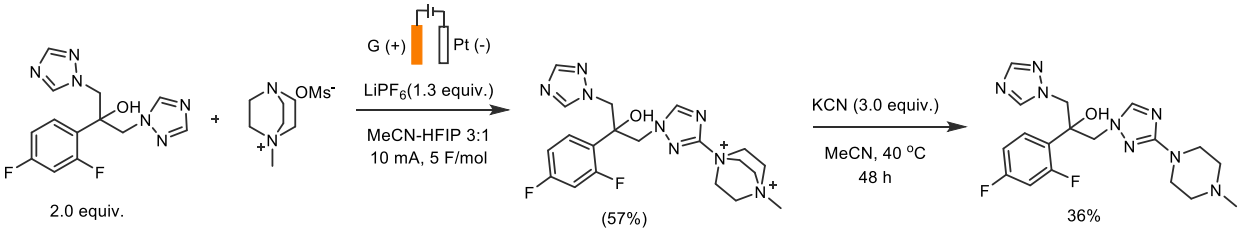
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.43 (d, *J* = 1.8 Hz, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 8.31 (d, *J* = 9.1 Hz, 1H), 8.10 (d, *J* = 2.7 Hz, 1H), 7.50-7.43 (m, 2H), 4.92 (s, 2H), 3.50 (t, *J* = 5.1 Hz, 4H), 2.65 (t, *J* = 5.1 Hz, 4H), 2.40 (s, 3H), 2.37 (t, *J* = 7.7 Hz, 2H), 2.11-1.93 (m, 6H), 1.91-1.85 (m, 2H), 1.68-1.53 (m, 2H), 1.33 (hextet, *J* = 7.4 Hz, 2H) 0.84 (t, *J* = 7.3 Hz, 3H).

Note: The signal at 1.68ppm is overlapping with residual water, so it integrates significantly larger than 2H.

^{13}C NMR (126 MHz, $CDCl_3$, δ): 186.8, 161.1, 151.3, 147.4, 137.3, 128.1, 126.3, 124.2, 124.0, 122.3, 120.5, 120.0, 119.8, 115.3, 108.9, 76.7, 54.7, 47.7, 46.1, 43.3, 37.5, 28.8, 27.7, 26.1, 22.3, 13.7.

HRMS-ESI(m/z) calc'd for $C_{30}H_{37}ON_8$ $[M+H]^+$ 525.3090; found 525.3113; deviation +4.38ppm.

Fluconazole *N*-methyl piperazine (5v)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added fluconazole (180 mg, 2.0 equiv.), $LiPF_6$ (58 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 5 F/mol. Yield of DABCOnium product was determined by ^{19}F NMR with hexafluorobenzene internal standard (57%). Trace *N*-Me DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with chloroform (2×4 mL) to remove excess organics. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->90-10 DCM-MeOH->85-15-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as a yellow-white solid (43.5 mg, 0.107 mmol, 36%). A small amount of PF_6 (~1 part in 60) and fluconazole (~1 part in 30) were observed as contaminants in ^{19}F NMR. Regioselectivity was confirmed by NOESY, HSQC, and HMBC.

NMR Spectroscopy:

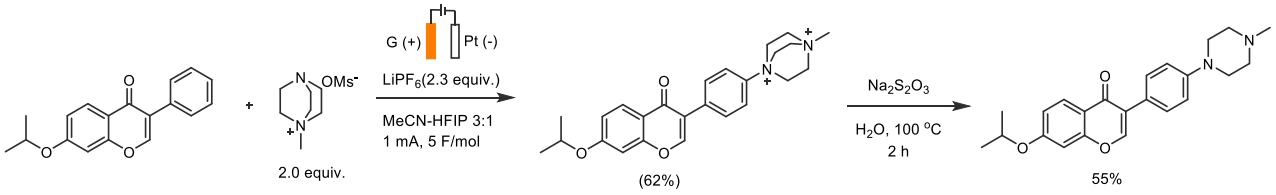
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.11 (s, 1H), 7.84 (s, 1H), 7.58 (s, 1H), 7.45 (td, *J* = 8.7, 6.0 Hz, 1H), 6.79 (m, 2H), 5.80 (s, 1H), 4.61 (d, *J* = 14.3 Hz, 1H), 4.57 (s, 2H), 4.16 (d, *J* = 14.2 Hz, 1H), 3.37 (m, 4H), 2.45 (t, *J* = 5.1 Hz, 4H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 166.4, 163.1 (dd, *J* = 251.4, 12.4 Hz), 158.6 (dd, *J* = 245.9, 11.8 Hz), 151.7, 144.8, 143.6, 130.2 (dd, *J* = 9.6, 5.6 Hz), 122.3 (dd, *J* = 13.2, 3.8 Hz), 112.1 (dd, *J* = 20.8, 3.3 Hz), 104.3 (dd, *J* = 27.5, 25.7 Hz), 75.5 (d, *J* = 5.0 Hz), 55.3 (d, *J* = 4.5 Hz), 54.3, 54.1 (d, *J* = 5.9 Hz), 46.3, 46.2.

^{19}F NMR (476 MHz, $CDCl_3$, δ): -108.9 (p, *J* = 7.7 Hz), -109.8 (q, *J* = 9.6 Hz).

HRMS-ESI(m/z) calc'd for $C_{18}H_{23}F_2ON_8$ $[M+H]^+$ 405.1963; found 405.1969; deviation +2.79 ppm.

Ipriflavone *N*-methyl piperazine (5w)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, Ipriflavone (84 mg, 0.30 mmol, 1 equiv.), $LiPF_6$ (103 mg, 2.3 equiv.), and *N*-Me DABCOnium mesylate salt (133 mg, 2.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 1 mA, 5 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (62%). The crude reaction mixture was added to a 30 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100^{o}C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (62.2 mg, 0.164 mmol, 55%).

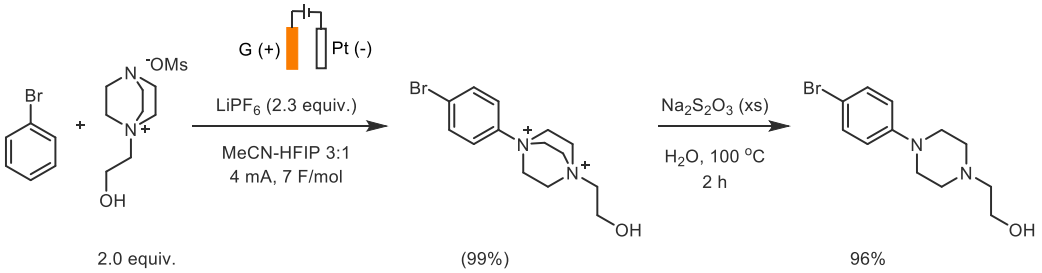
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.18 (d, *J* = 8.9 Hz, 1H), 7.90 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.94 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 4.66 (septet, *J* = 6.0 Hz, 1H), 3.26 (t, *J* = 5.0 Hz, 4H), 2.64 (t, *J* = 5.0 Hz, 4H), 2.39 (s, 3H), 1.40 (d, *J* = 6.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 176.1, 162.5, 158.1, 152.0, 151.0, 129.8, 127.9, 125.0, 123.1, 118.2, 115.9, 115.6, 101.7, 70.9, 55.1, 48.7, 46.1, 22.0.

HRMS-ESI(m/z) calc'd for $C_{23}H_{27}O_3N_2$ $[M+H]^+$ 379.2022; found 379.2029; deviation +1.85 ppm.

1-(2-hydroxyethyl)-4-(4-bromophenyl) piperazine (5x)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (104 mg, 2.3 equiv.), and *N*-(2-hydroxyethyl) DABCOnium mesylate salt (153 mg, 2.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by bromobenzene (31 µL, 0.30 mmol), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 4 mA, 7 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (99%). The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6M, 2mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave an off-white solid (82.2 mg, 0.288 mmol, 96%).

NMR Spectroscopy:

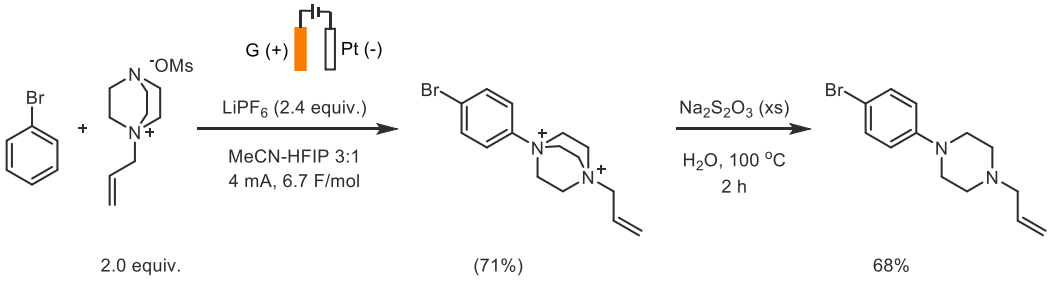
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.66 (q, *J* = 5.1 Hz, 2H), 3.20-3.14 (m, 4H), 2.67 (t, *J* = 5.1 Hz, 4H), 2.61 (t, *J* = 5.4 Hz, 2H).

Note: The signal at 2.67 ppm appears to integrate to 5H. This could be due to the alcohol proton overlapping, which is otherwise unaccounted for in the spectrum.

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.4, 132.0, 117.8, 112.1, 59.4, 57.9, 52.9, 49.3.

HRMS-ESI(m/z) calc'd for $C_{12}H_{18}BrON_2$ $[M+H]^+$ 285.0602; found 285.0625; deviation +8.1ppm.

1-allyl-4-(4-bromophenyl) piperazine (5y)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (104 mg, 2.3 equiv.), and *N*-allyl DABCOnium mesylate salt (159 mg, 2.1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by bromobenzene (31 µL, 0.30 mmol), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 4 mA, 6.7 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (71%). Trace bromobenzene was also observed. The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (57.8 mg, 0.206 mmol, 68%).

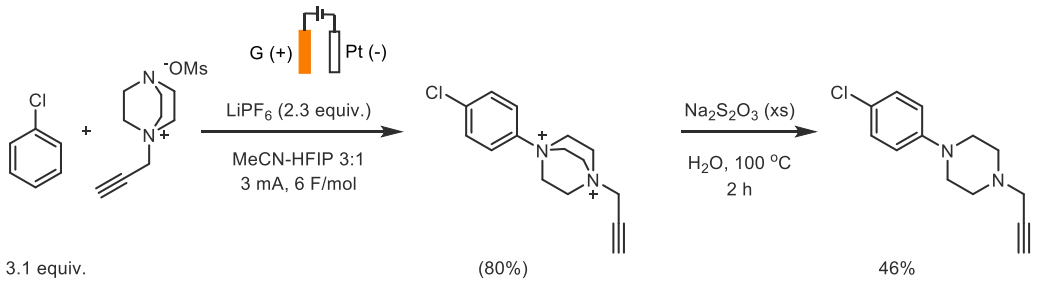
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.33 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 5.89 (ddt, *J* = 16.8, 10.2, 6.6 Hz), 5.27-5.14 (m, 2H), 3.19-3.16 (m, 4H), 3.05 (dt, *J* = 6.7, 1.3Hz, 2H), 2.61-2.58 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.4, 134.8, 132.0, 118.5, 117.7, 111.8, 61.8, 53.0, 49.1

HRMS-ESI(m/z) calc'd for $C_{13}H_{18}BrN_2$ $[M+H]^+$ 281.0653; found 281.0668; deviation +5.3ppm.

1-propargyl-4-(4-chlorophenyl) piperazine (5z)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (66 mg, 2.3 equiv.), and *N*-propargyl DABCOnium mesylate salt (47 mg, 1.0 equiv., 0.19 mmol), in sequence. Quickly, 3 mL MeCN (*c* = 0.050 M) was added, followed by chlorobenzene (60 µL, 3.1 equiv.), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 6 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (80%). 11% *N*-propargyl DABCOnium was also observed. The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (20.7 mg, 0.0882 mmol, 46%).

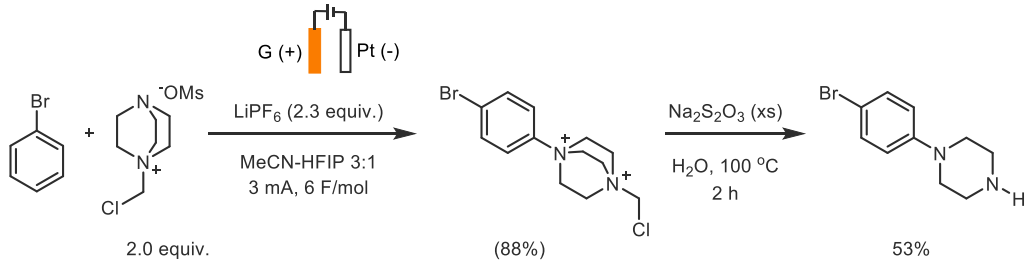
NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.20 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.37 (d, *J* = 2.5 Hz, 2H), 3.20 (t, *J* = 5.1 Hz, 4H), 2.73 (t, *J* = 5.1 Hz, 4H), 2.28 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.0, 129.1, 124.8, 117.5, 78.6, 73.6, 51.9, 49.3, 47.0.

HRMS-ESI(m/z) calc'd for $C_{13}H_{16}ClN_2$ $[M+H]^+$ 235.1002; found 235.0100; deviation – 0.87 ppm.

1-(4-bromophenyl) piperazine (5aa)



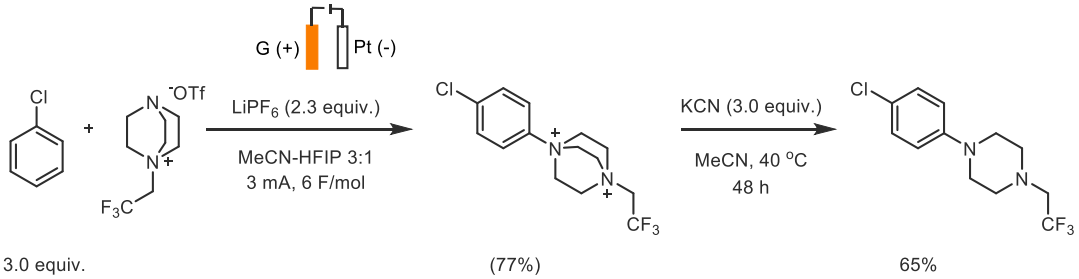
Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added, $LiPF_6$ (104 mg, 2.3 equiv.), and *N*-methylenechloride DABCOnium tetrafluoroborate salt (147 mg, 2.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added, followed by bromobenzene (31 µL, 0.30 mmol, 1 equiv.), and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 6 F/mol. The yield of the aryl DABCOnium salt product was determined by ^{1}H NMR spectroscopy using mesitylene as internal standard (88%). The crude reaction mixture was added to a 15 mL pressure-safe microwave reactor tube, along with a magnetic stir bar, 3 mL water, and 3 mL saturated $Na_2S_2O_3$ solution. The tube was sealed and stirred at 100°C for 2 h. After cooling to room temperature, the contents of the tube were added to a separatory funnel, along with NaOH solution (6 M, 2 mL) and saturated NaCl solution (20 mL). The tube was washed with water (5 mL) and DCM (15 mL) and those washings were also added to the funnel. The aqueous layer was extracted with DCM (3×15 mL) and then discarded. The DCM volume was reduced using reduced pressure. The product was purified using silica gel chromatography (100% DCM→100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v). The column eluent was removed with a nitrogen stream and the product was dried under vacuum to leave a yellow solid (42.8 mg, 0.177 mmol, 59%). NMR data conforms to the literature.[11]

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.33 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.19-3.14 (m, 4H), 3.03 (s, 1H), 2.71-2.63 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 150.5, 131.8, 117.6, 111.7, 51.3, 49.0.

1-(2,2,2-trifluoroethyl)-4-(4-chlorophenyl) piperazine (5ab)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (64 mg, 2.1 equiv.), and *N*-CH_2CF_3 DABCOnium triflate salt (68 mg, 0.20 mmol, 1.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.050 M) was added followed by chlorobenzene (60 µL, 3.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 6 F/mol. The yield of product was quantified by ^{1}H NMR with mesitylene as internal standard (77%). 12% *N*-(2,2,2,-trifluoroethyl) DABCOnium was also observed. The crude reaction mixture was dried under reduced pressure and washed with diethyl ether (2×4 mL) to remove unreacted organics. Excess ether was removed with a nitrogen stream. MeCN (8 mL) and KCN (59 mg, 3.0 equiv.) were added to the crude and it was stirred at 40°C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->DCM/MeOH 95/5 v/v). The eluent solvent was dried off to afford the title compound as a white solid (36.2 mg, 0.130 mmol, 65%).

NMR Spectroscopy:

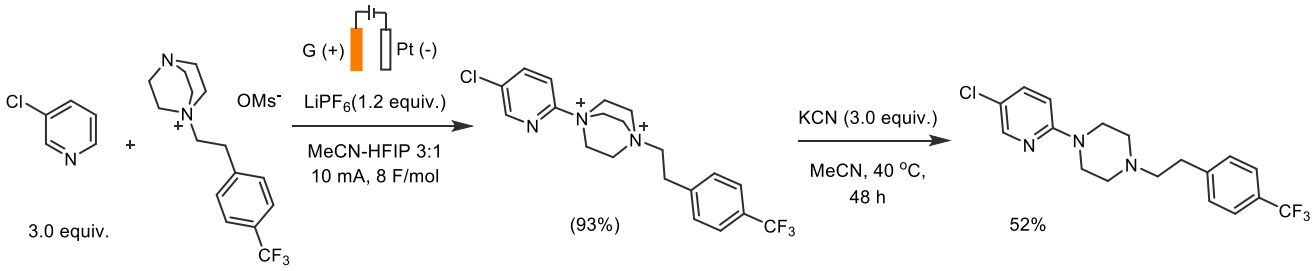
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.20 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 3.20-3.14 (m, 4H), 3.03 (q, *J* = 9.5 Hz, 2H), 2.85-2.79 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 149.9, 129.1, 125.5 (q, *J* = 280.0 Hz), 125.0, 117.6, 58.6 (q, *J* = 30.6 Hz), 53.6, 49.4.

^{19}F NMR (476 MHz, $CDCl_3$, δ): -69.0 (t, *J* = 9.5 Hz).

HRMS-ESI(m/z) calc'd for $C_{12}H_{15}ClF_3N_2$ $[M+H]^+$ 279.0876; found 279.0874; deviation -0.60ppm.

3-Chloropyridine *N*-2-(4-trifluoromethylphenyl)ethyl piperazine (5ac)



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (55 mg, 1.2 equiv.), and *N*-Et$PhCF_3$ DABCOnium mesylate salt (113 mg, 0.297 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 3-chloropyridine (85 µL, 0.89 mmol, 3.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 8 F/mol. Yield of DABCOnium product was determined by ^{1}H NMR with mesitylene internal standard (93%). The crude reaction mixture was dried under reduced pressure and washed with THF (3×5 mL) to remove unreacted organics. Excess THF was removed with a nitrogen stream. MeCN (8 mL) and KCN (60 mg, 3.0 equiv.) were added to the crude and it was stirred at 40^{o}C for 48 h. MeCN was removed with reduced pressure. The product was purified with silica gel chromatography (DCM->100-5-0.5 DCM-MeOH-28% NH_4OH v/v/v) The eluent solvent was dried off to afford the title compound as an off-white solid (59.5 mg, 0.156 mmol, 52%).

NMR Spectroscopy:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.12, (dd, *J* = 2.7, 0.7 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.42 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 1H), 3.57-3.51 (m, 4H), 2.93-2.87 (m, 2H), 2.69-2.64 (m, 2H), 2.62 (t, *J* = 5.1 Hz, 4H).

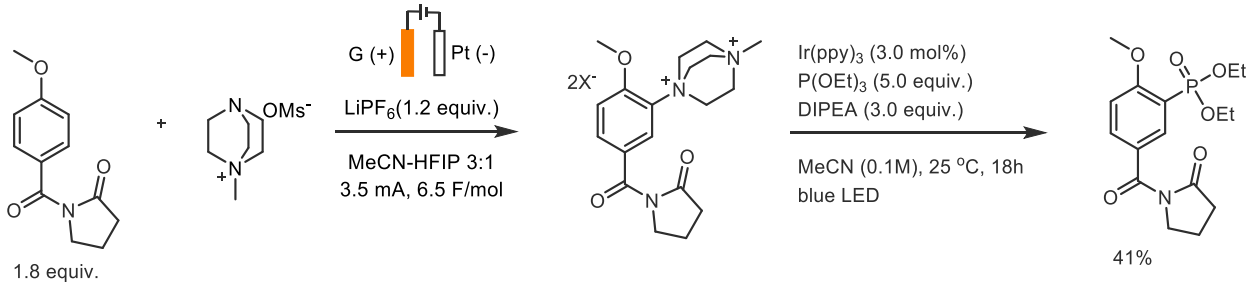
^{13}C NMR (126 MHz, $CDCl_3$, δ): 157.9, 146.4, 144.5, 137.3, 129.2, 128.7 (q, *J* = 32.3 Hz), 125.5 (q, *J* = 3.8 Hz), 123.4, 120.4, 107.9, 60.0, 53.0, 45.5, 33.5.

^{19}F NMR (476 MHz, $CDCl_3$, δ): -62.4 (s).

HRMS-ESI(m/z) calc'd for $C_{18}H_{20}ClF_3N_3$ $[M+H]^+$ 370.1298; found 370.1331; deviation +9.67 ppm.

Photoredox diversifications

Aniracetam phosphonate ester (6)



In duplicate, under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added aniracetam (132 mg, 1.8 equiv.), $LiPF_6$ (60 mg, 1.2 equiv.), and *N*-Me DABCOnium mesylate salt (75 mg, 0.34 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixtures were electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3.5 mA, 6.5 F/mol. The reaction mixtures were combined, and the solvent was evaporated off with a nitrogen stream. The solid residue was washed with THF (4×5mL) then diethyl ether (2×5mL), leaving aniracetam DABCOnium salt with electrolyte contamination as a tan solid. qNMR (shown below) was performed, with 10.0 mg of the tan solid with 5.0 uL of mesitylene, revealing 10.0mg of solid to contain 0.0126mmol of aniracetam DABCOnium salt (~73% mass purity, assuming X= one mesylate, one PF_6).

Under ambient conditions, a 5 mL scintillation vial with septum cap was equipped with a magnetic stir bar followed by addition of aniracetam-DABCOnium salt (0.12 g, 0.14 mmol, 1.0 equiv.) and $Ir(ppy)_3$ (4.0 mg, 3.0 mol%). Subsequently, 1.5 mL of anhydrous MeCN (0.1 M) was added trough the septum cap followed by DIPEA (75 µL, 0.45 mmol, 3.0 equiv.), and triethyl phosphite (0.13 mL, 0.75 mmol, 5.0 equiv.). The vial was flushed with N_2 for 1 min. The cap was sealed with parafilm. Subsequently, the vial was placed in between two blue LEDs and left stirring for 18 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with (100% DCM→ DCM/methanol/28% aqueous ammonium hydroxide (95/4.5/0.5) (v/v/v) to afford the title compound **6** as a light-yellow oil (21.2 mg, 0.060 mmol, 41%) in the presence of DIPEA in 1:1 mixture.

NMR Spectroscopy:

^{1}H NMR: (500MHz, CD_3CN, δ): 7.94 (dd, *J* = 15.2, 2.3 Hz, 1H), 7.82 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.10 (dd, *J* = 8.7, 6.4 Hz, 1H), 4.16 – 4.00 (m, 4H), 3.93 (s, 3H), 3.85 (t, *J* = 7.1 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.08 (p, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 6H).

^{31}P NMR: (202 MHz, CD_3CN, δ): 15.30 (tt, *J* = 15.0, 7.6 Hz).

^{13}C NMR: (126 MHz, CD_3CN, δ): 176.2, 169.9 (d, J = 1.8 Hz), 164.7 (d, J = 3.1 Hz), 137.0 (d, J = 7.8

Hz), 136.8 (d, J = 2.0 Hz), 128.0 (d, J = 14.3 Hz), 116.8 (d, J = 187.9 Hz), 111.8 (d, J = 9.2 Hz), 63.4 (d, J = 5.8 Hz), 56.9 (d, J = 3.3 Hz), 47.5, 33.9, 17.3, 16.7 (d, J = 6.4 Hz).

HRMS-ESI(m/z) calc'd for $C_{16}H_{22}OP_4N$ $[M+H]^+$ 356.12575; found 356.12619; deviation +1.22 ppm

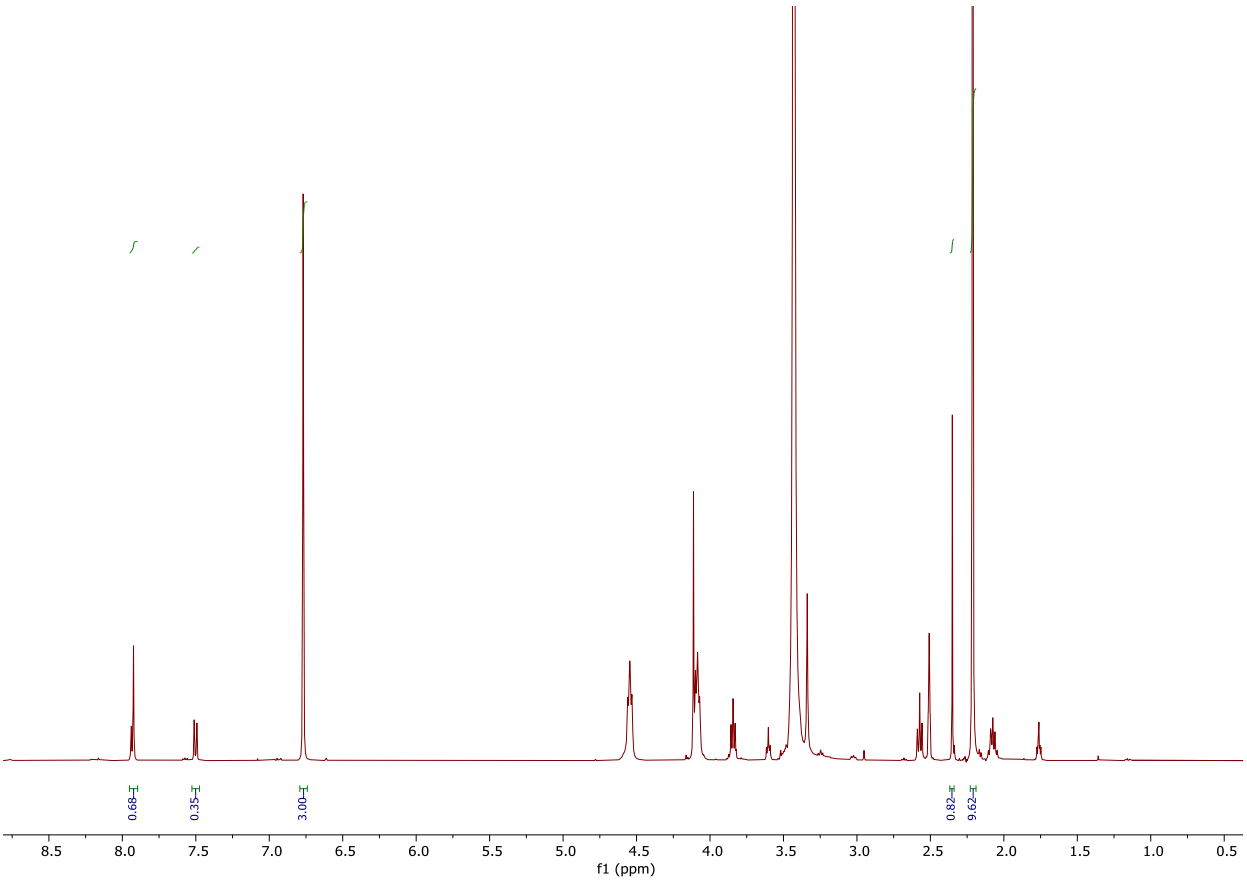
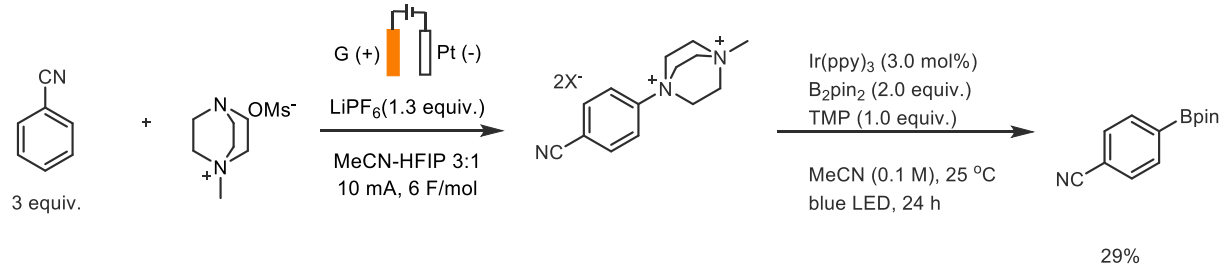


Figure S5: qNMR of aniracetam DABCOnium salt with mesitylene internal standard.

Benzonitrile 4-boronic acid pinacol ester (7)



In duplicate, under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (60 mg, 1.3 equiv.), and *N*-Me DABCOnium mesylate salt (67 mg, 0.30 mmol, 1 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.075 M) was added followed by benzonitrile (90 µL, 3 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixtures were electrolyzed under high stirring (1500 rpm), using electrolysis parameters 10 mA, 6 F/mol. The reaction mixtures were combined, and the solvent was evaporated off with a nitrogen stream. The solid residue was washed with THF (4×5 mL) then diethyl ether (2×5 mL), leaving benzonitrile DABCOnium salt with electrolyte contamination as a tan solid. qNMR (shown below) was performed, with 9.9 mg of the tan solid with 3.0 uL of mesitylene, revealing 9.9 mg of solid to contain 0.0146 mmol of benzonitrile DABCOnium salt (~69% mass purity, assuming X= one mesylate, one PF_6).

Under ambient conditions, a 5 mL scintillation vial with septum cap was equipped with a magnetic stir bar followed by addition of cyanobenzene-DABCOnium salt (31.0 mg, 0.050 mmol, 1.00 equiv.), $Ir(ppy)_3$ (0.80 mg, 2.4 mol%) and B_2pin_2 (25.4 mg, 0.100 mmol, 2.00 equiv.). Subsequently, 0.5 mL of anhydrous MeCN (0.1 M) was added trough the septum cap followed by 2,2,6,6-tetramethyl-piperidine (9 µL, 0.05 mmol, 1.0 equiv.). The vial was flushed with N_2 for 2 min and the cap was sealed with parafilm. Subsequently, the vial was placed in between two blue LEDs and left stirring for 24 h. Next, 5 µL of mesitylene was added in the reaction mixture and an aliquot of the reaction mixture was dissolved in $CDCl_3$, and a ^{1}H-NMR was submitted to quantify the borylation product **7** formed (29%).

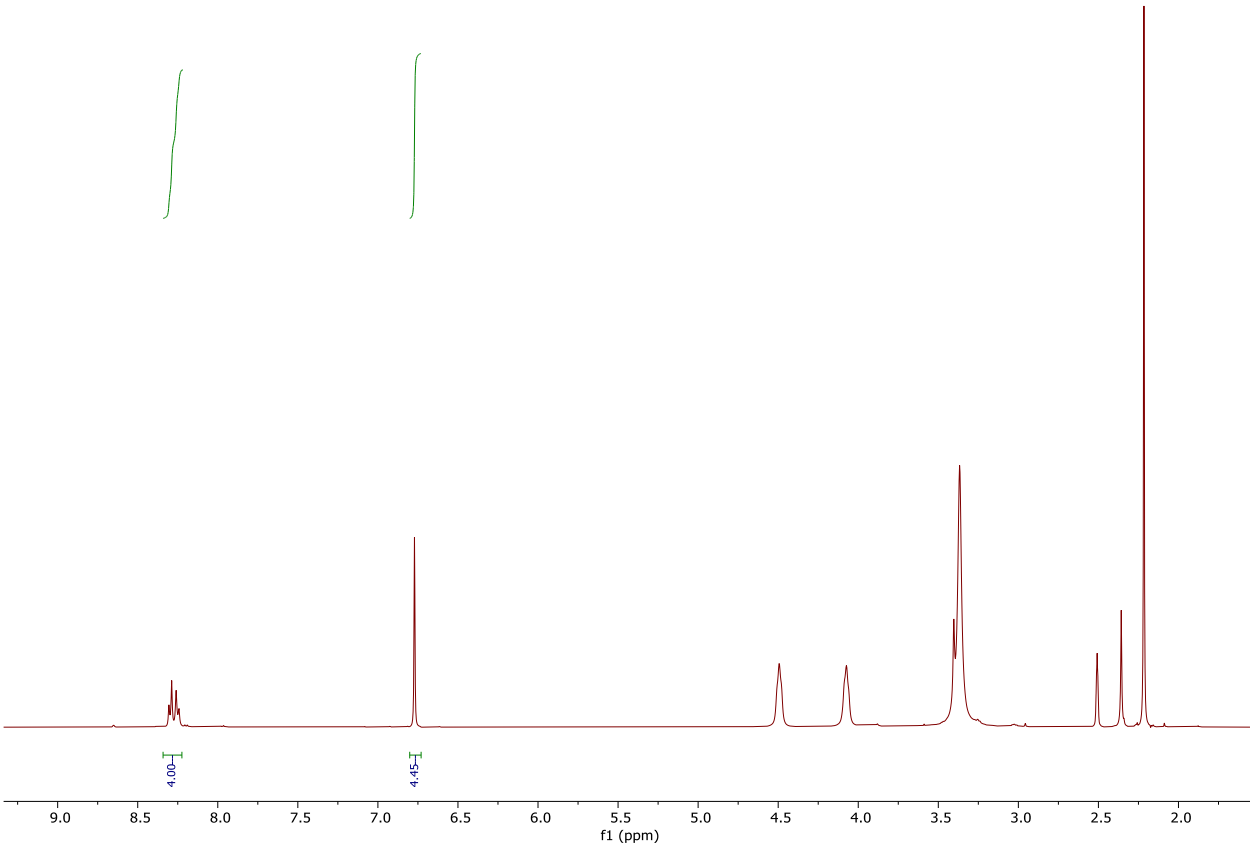


Figure S6: qNMR of Benzonitrile DABCOnium salt with mesitylene internal standard.

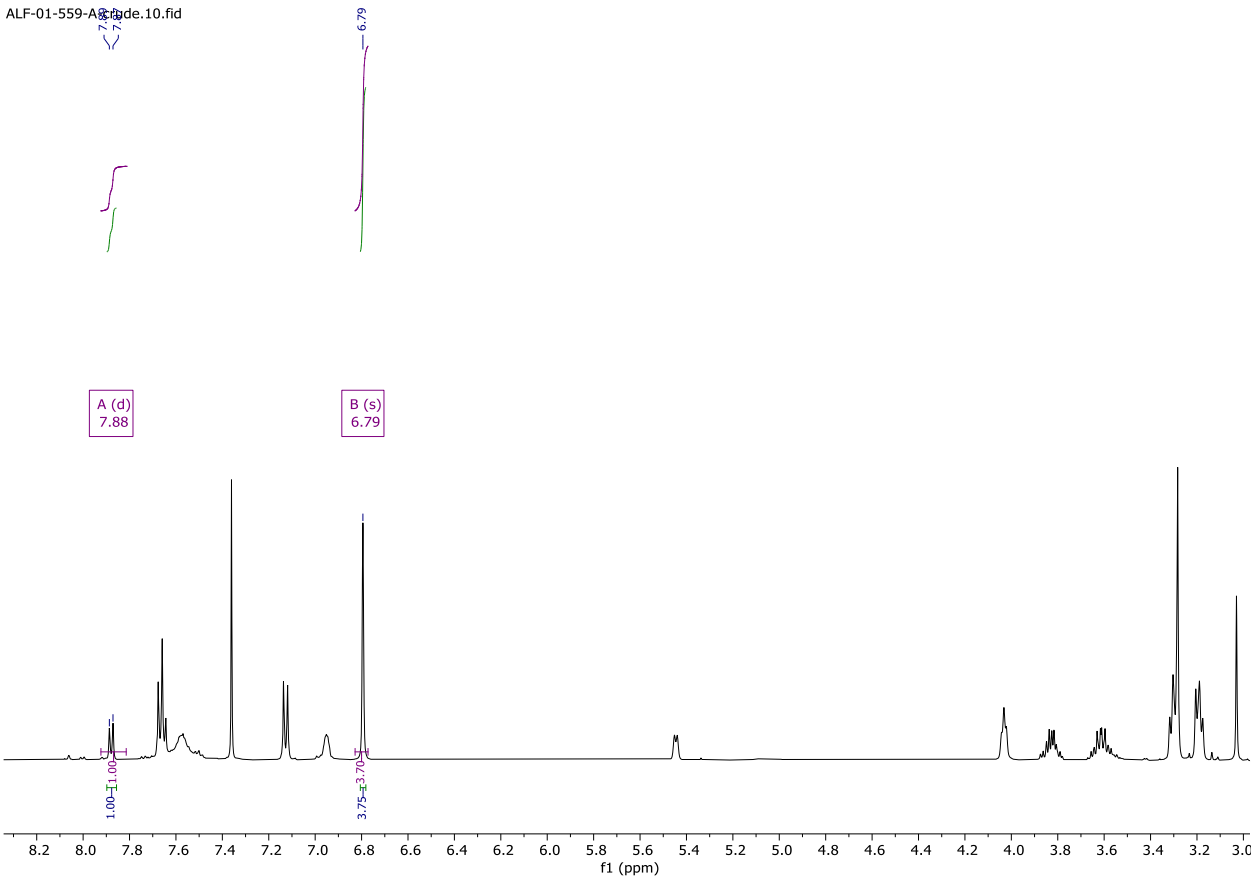
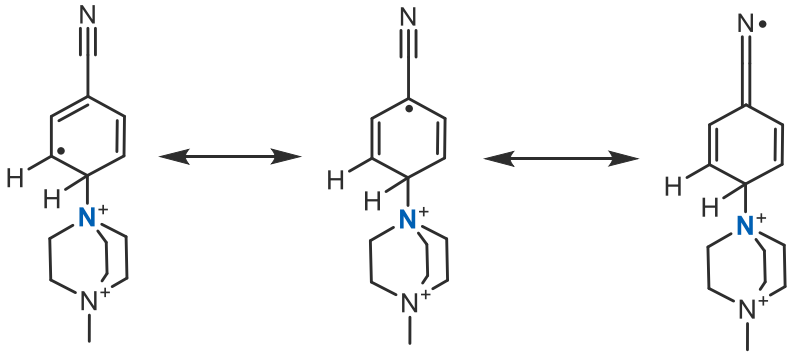


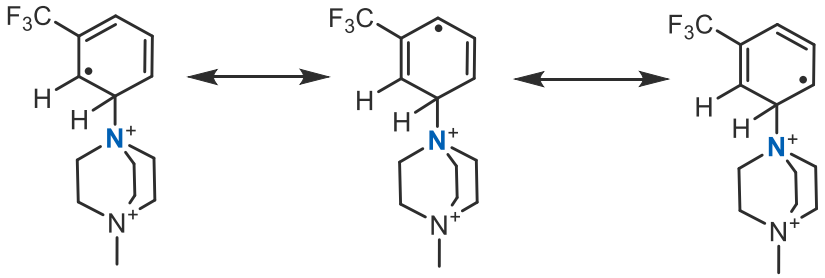
Figure S7: Crude NMR of benzonitrile DABCOnium salt borylation.

***Para*-selectivity in electron poor arenes**

Para-selectivity was observed for π-withdrawing groups (**5b-d)**, defying traditional E_AS trends but confirming observations made by Ritter and coworkers.[12] This can be rationalized as follows: the oxidation from intermediate II to intermediate III is likely anodic and irreversible in this system, meaning that intermediate II should be considered for regioselectivity. With π-withdrawing groups, the radical in II can be delocalized into the substituent with a para-addition, unlike with a meta-addition. This radical delocalizing effect is unique to π-withdrawing groups however, so other substrates aminate according to arene electronics and sterics. Ritter and coworkers explained their observed regioselectivity with benzonitrile similarly.

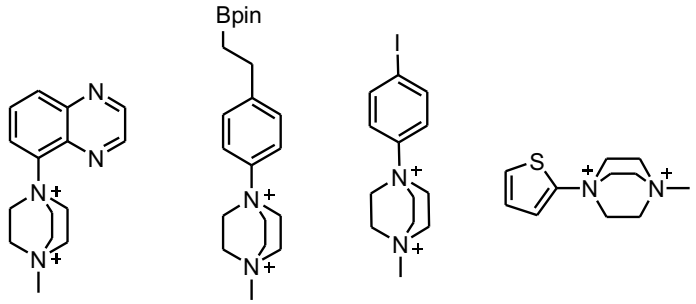


Para addition makes more delocalized radical



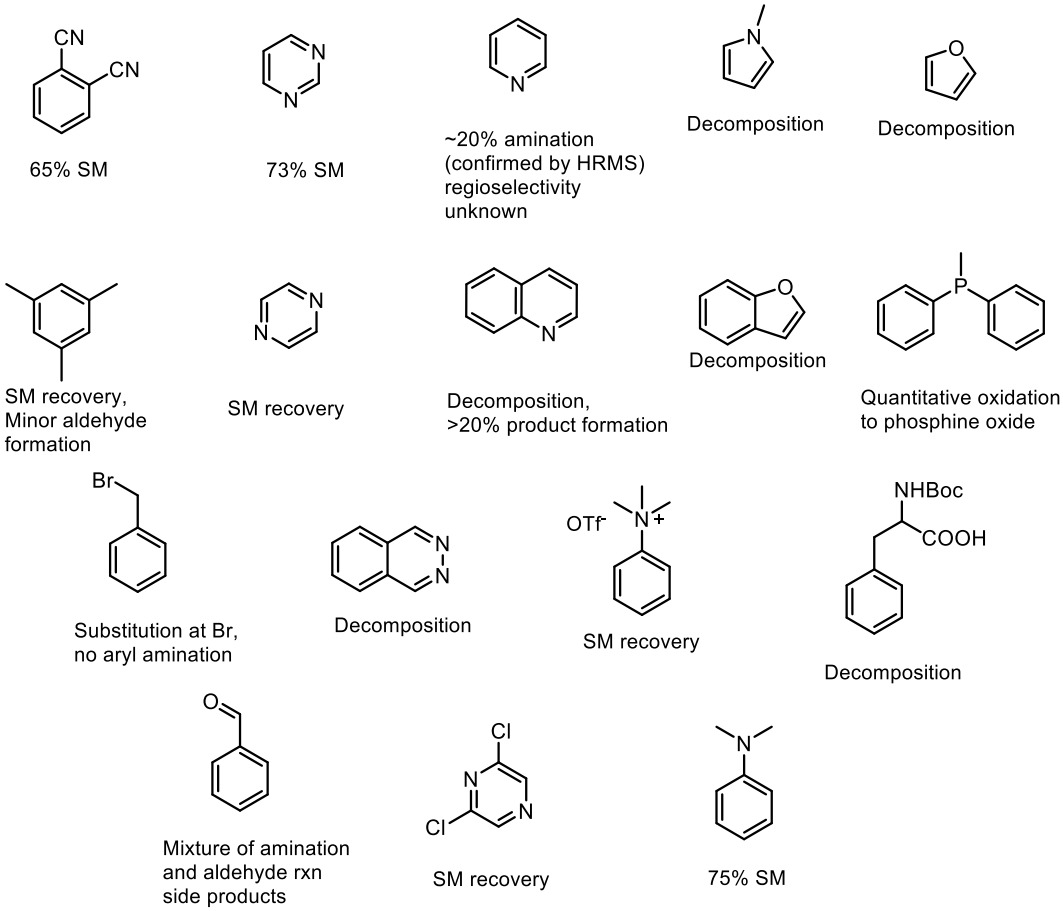
Radical unable to be further delocalized,
selectivity determined by electronics

Successful substrates with difficulties in isolation (^{1}H NMR yields of electrochemical step)



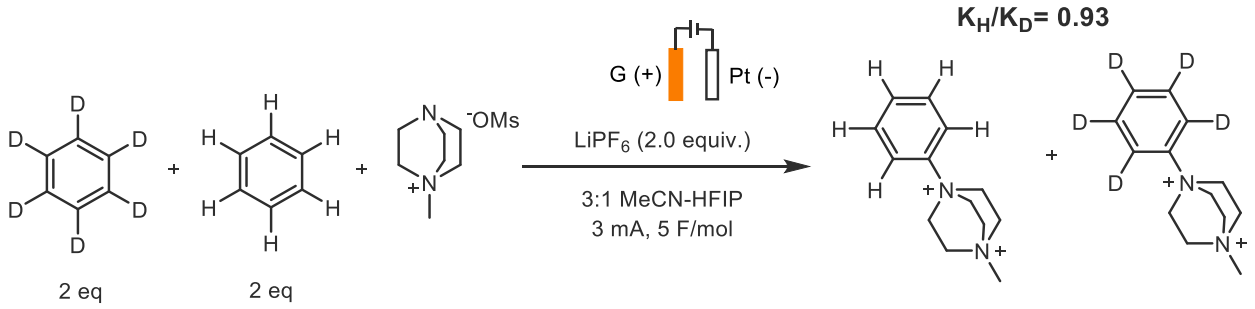
(50%) (79%) unable to convert to piperazine (71%) (51%) rapidly oxidizes when isolated as piperazine

Examples of unsuccessful substrates due to poor conversion or decomposition of substrates



Mechanistic investigations

Intermolecular KIE experiment:



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (32 mg, 2.0 equiv.), and *N*-Me DABCOnium mesylate salt (22 mg, 0.10 mmol, 1.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.025 M) was added followed by benzene (18 µL, 2.0 equiv.), benzene-d_6 (18 uL, 2.0 equiv.) and 1 mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 5 F/mol. The crude reaction mixture was filtered and analyzed by proton NMR to determine the KIE (K_H/K_D=0.93). Remaining starting amine was observed in trace amounts.

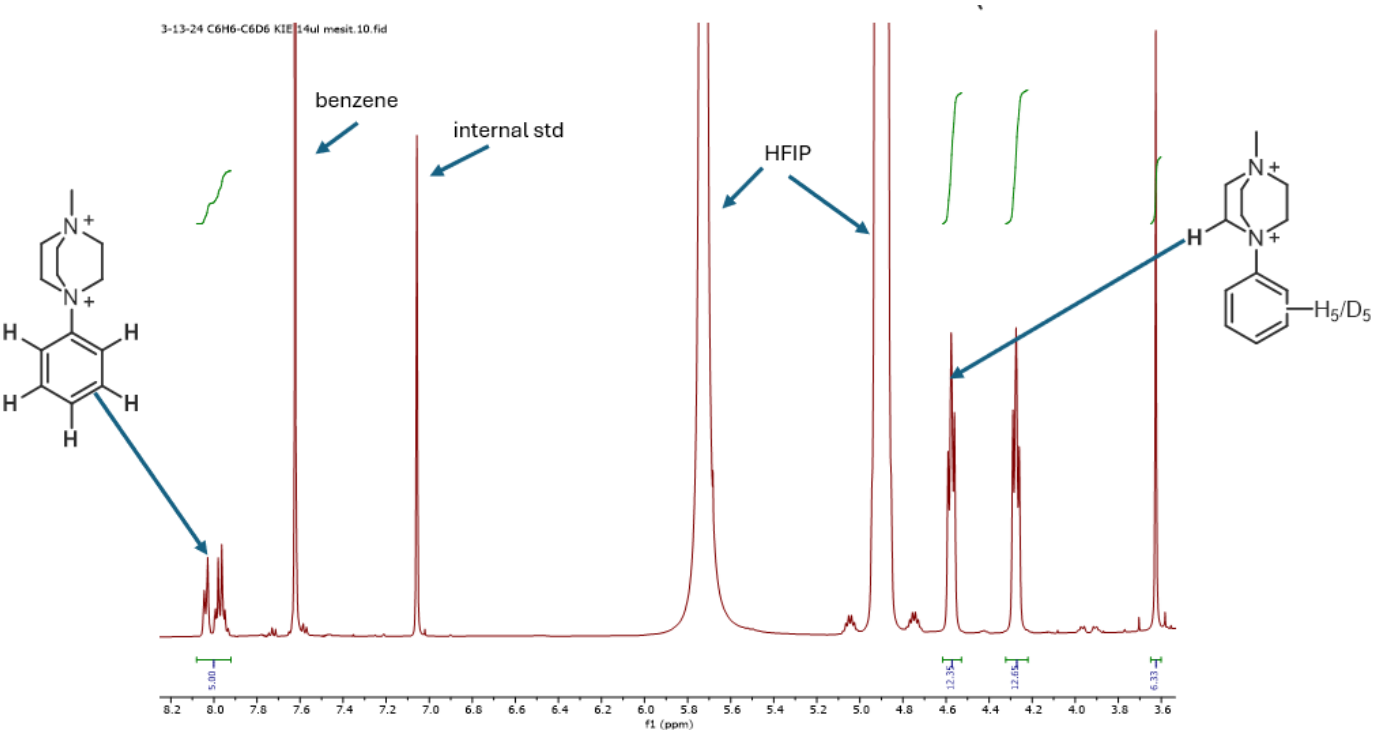
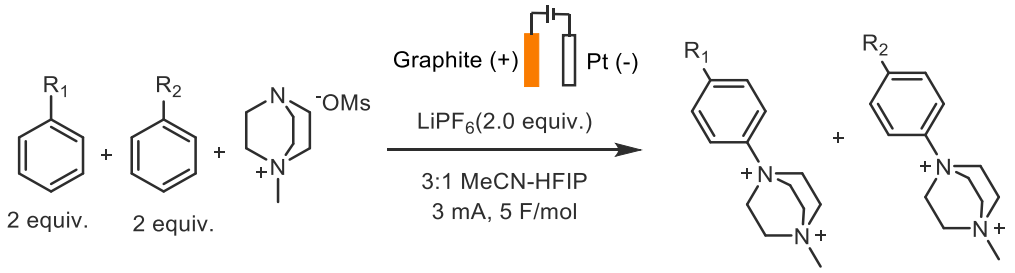


Figure S8: Crude ^{1}H NMR of intermolecular KIE experiment.

Intermolecular competition experiments:



Under ambient conditions, to a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added $LiPF_6$ (32 mg, 2.0 equiv.), and N-Me DABCOnium mesylate salt (22 mg, 0.10 mmol, 1.0 equiv.), in sequence. Quickly, 3 mL MeCN (*c* = 0.025 M) was added followed by arene-1 (2.0 equiv.), arene-2 (2.0 equiv.) and 1mL HFIP. The ElectraSyn vial was equipped with two electrodes: graphite and platinum wire electrode with mesh and sealed with an ElectraSyn septum-cap. The reaction mixture was electrolyzed under high stirring (1500 rpm), using electrolysis parameters 3 mA, 5 F/mol. Mesitylene (14 uL, 1.0 equiv.) was added to the crude reaction mixture. The mixture was filtered, and the yields of the para isomers for the two arenes were determined by proton NMR. Remaining starting amine was not detected or detected in trace amounts. Results of the competition experiments, along with the Hammett constants for the substituents are provided below.[13]

R_1	R_2	R_1-DABCOnium:R_2-DABCOnium	σ_p 1	σ_p 2
Me	H	2:1	-0.17	0
H	CN	1:ND	0	0.66
H	OCF_3	1:ND	0	0.35
H	Cl	1.9:1	0	0.23
H	F	5.6:1	0	0.06
Cl	OCF_3	13.2:1	0.23	0.35
Cl	F	2.5:1	0.23	0.06
OCF_3	CN	2.4:1	0.35	0.66

Table S4: Results of intermolecular competition experiments

Cyclic Voltammogram Studies

Cyclic voltammetry was conducted using EC-Lab and a BioLogic SP-50e potentiostat. Measurements were performed using a divided three-compartment cell (Voltammetry Cell, BASi). A platinum disk electrode (BASi, d=3mm) was used as a working electrode for reductive CVs. A glassy carbon disk electrode (BASi, d= 3mm) was used as working electrode for oxidative CVs. A platinum wire was used as counter electrode. The reference electrode was a leakless Ag/AgCl electrode (EDAQ). The reference was calibrated to ferrocene with a 3-5mM ferrocene in the corresponding solvent system. All CVs were taken at a scan rate of 150mV/s. All oxidative CVs were taken in solvent system **A** (0.1M $TBAClO_4$ in 3-1 MeCN-HFIP). Reductive CVs were taken in solvent system **A** or solvent system **B** (0.1M $TBAClO_4$ in MeCN). Concentration of the compounds of interest are noted on the voltammograms. The working electrode was polished with a synthetic rayon cloth (MicroCloth) after each measurement. Unless otherwise noted, all shown voltammograms are 2nd scans of three total taken for the material.

Solvent blanks

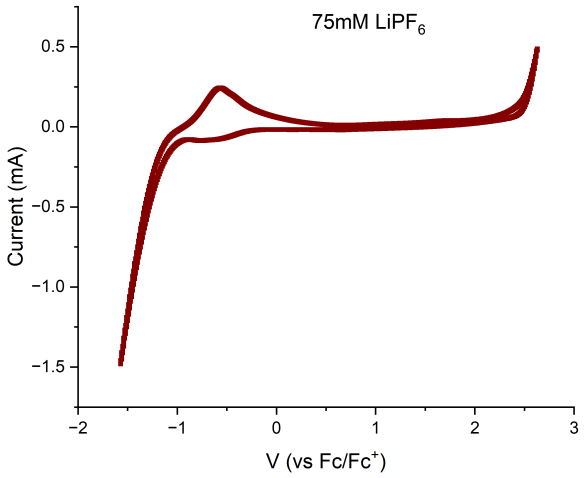


Figure S9. Solvent blank **A** with 75 mM $LiPF_6$ and a Pt working electrode.

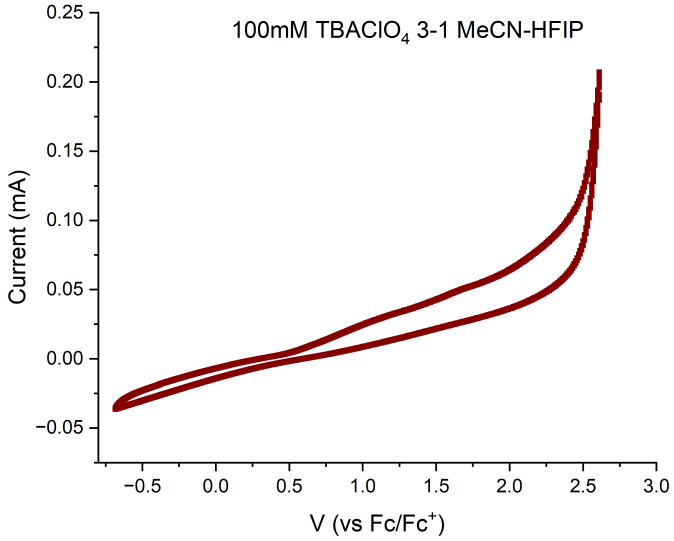


Figure S10. Oxidative solvent blank **A** with a glassy carbon working electrode.

N-alkyl DABCOnium Oxidation Profiles

Solvent system: **A**. Working electrode: glassy carbon.

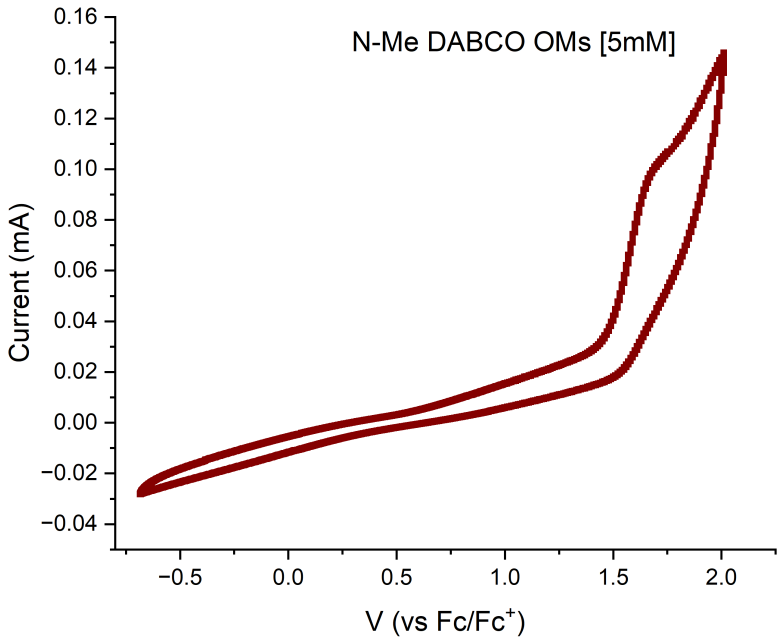


Figure S11. Oxidation profile of N-Me DABCOnium mesylate (**4a**).

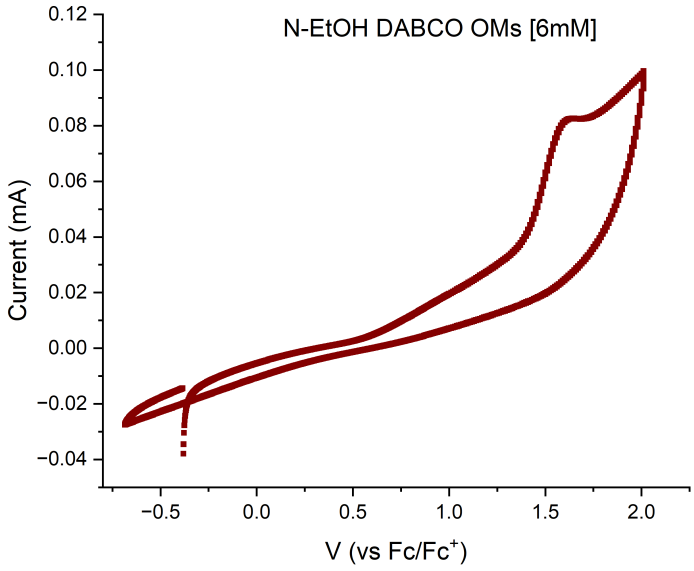


Figure S12. Oxidation profile of N-EtOH DABCO mesylate (1st scan) (**4b**).

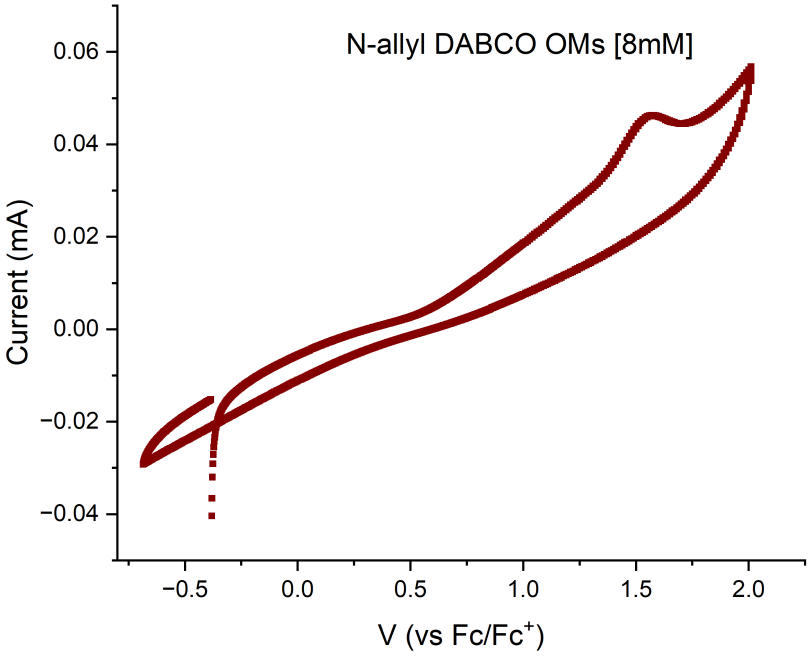


Figure S13. Oxidaiton profile of N-allyl DABCO mesylate (**4c**).

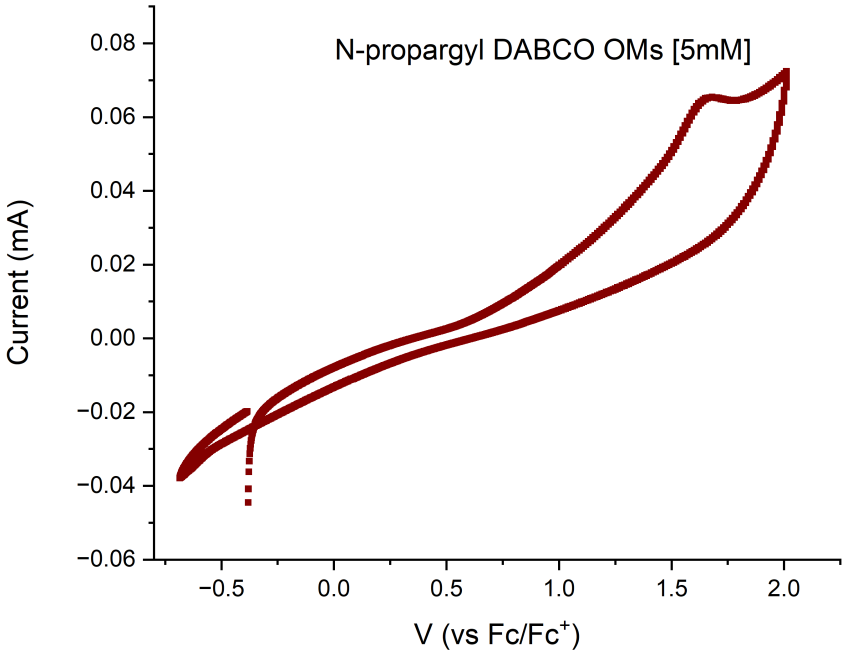


Figure S14. Oxidation profile of N-propargyl DABCO mesylate (1st scan) (**4d**).

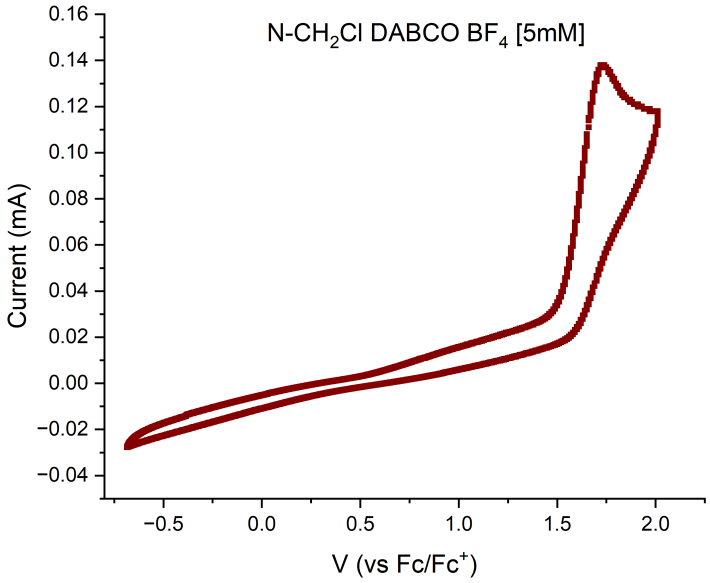


Figure S15. Oxidation profile of N-CH_2Cl DABCO BF_4 (**4e**)

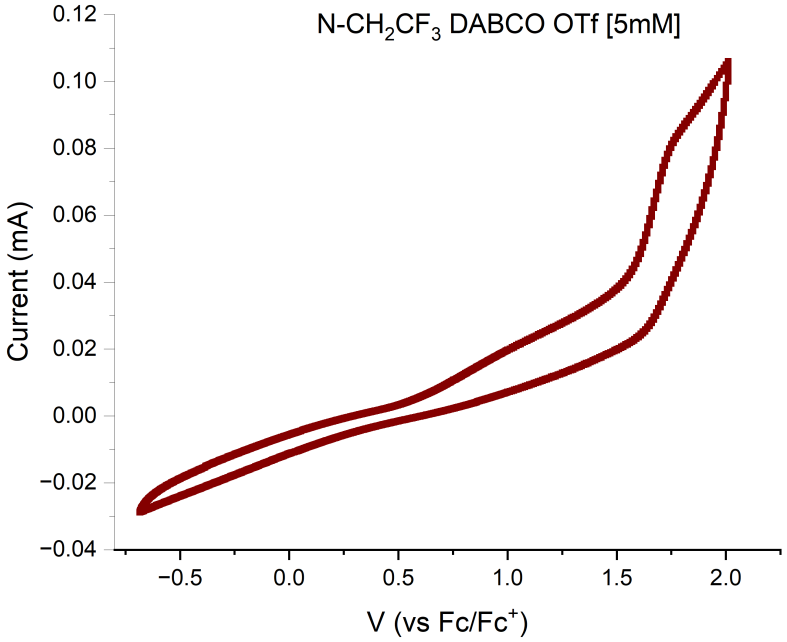


Figure S16. Oxidation profile of N-CH_2CF_3 DABCO triflate (**4f**).

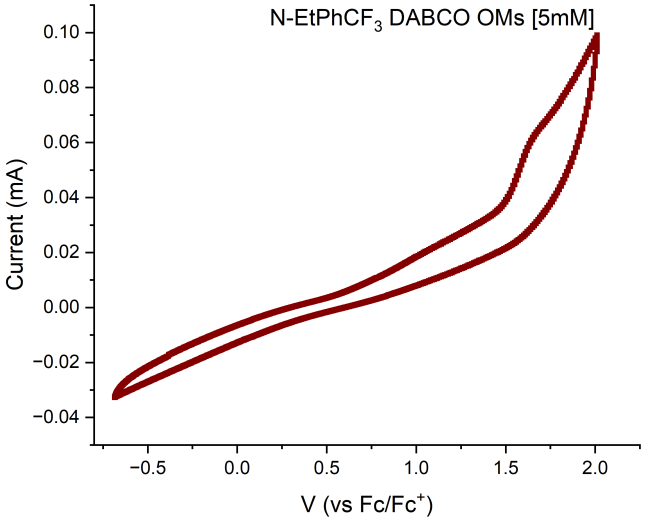


Figure S17. Oxidation profile of N-EtPhCF_3 mesylate (**4g**).

Arene/N-Me DABCO OMs titration studies

Solvent system: A. Working electrode: glassy carbon. Arenes were added as a 20V% solution in MeCN iteratively to the same vial.

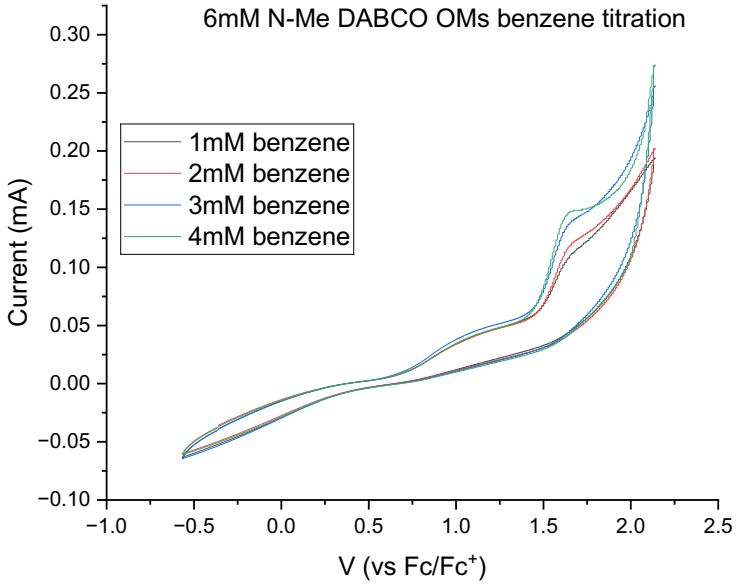


Figure S18. Oxidation profile of **4a** with various concentrations of benzene

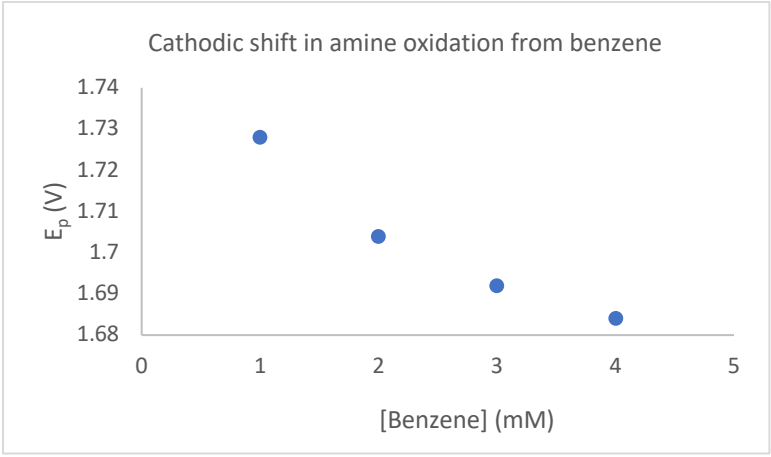


Figure S19: Shift in **4a** oxidation over benzene concentration. E_p was estimated by estimating the first derivative $((y_2-y_1)\div(x_2-x_1))$ for adjacent points in the forward scan of the CV. The local minimum of the first derivative in the oxidation range (onsetting ~1.5 V until scan reverse) was taken as an estimate of E_p

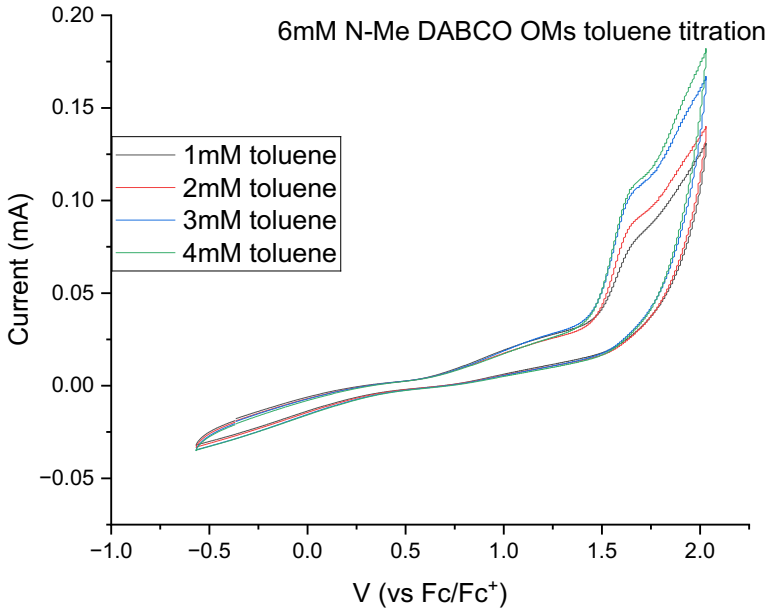


Figure S20: Oxidation profile of **4a** with various concentrations of toluene

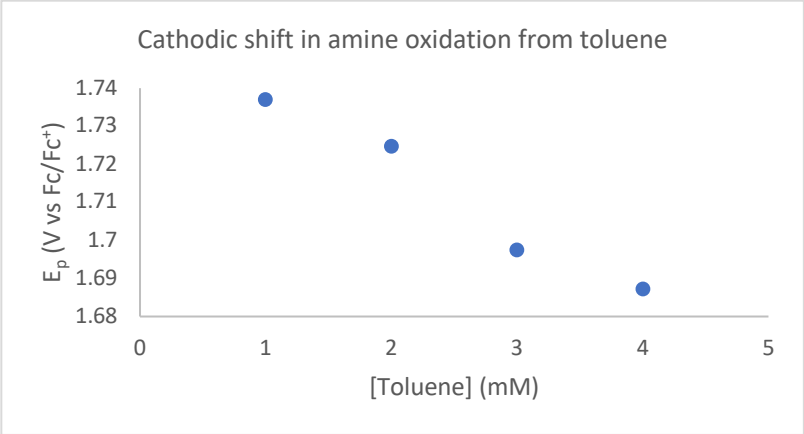


Figure S21: Shift in **4a** oxidation over toluene concentration. E_p was estimated by estimating the first derivative $((y_2-y_1)\div(x_2-x_1))$ for adjacent points in the forward scan of the CV. The local minimum of the first derivative in the oxidation range (onsetting ~1.5 V until scan reverse) was taken as an estimate of E_p

Aryl DABCOnium salt reduction profiles

Solvent system: **B**. Working electrode: Pt

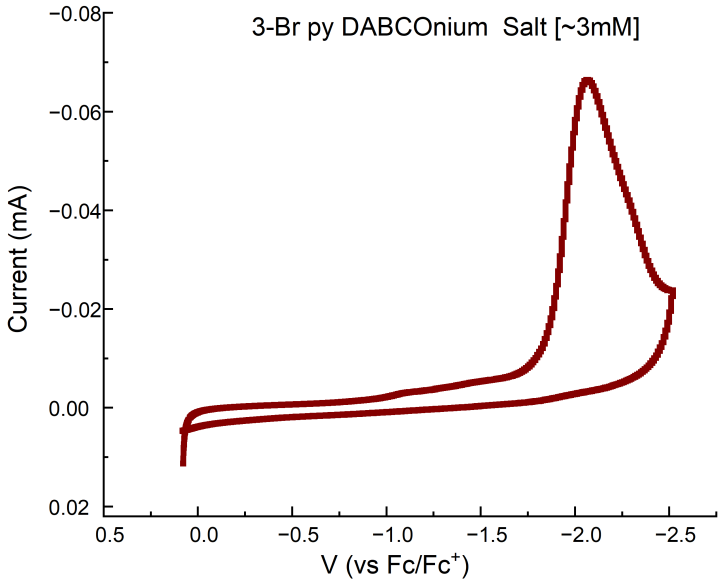


Figure S22. Reduction profile of 3-bromopyridine DABCOnium salt (1st scan) (**2g**).

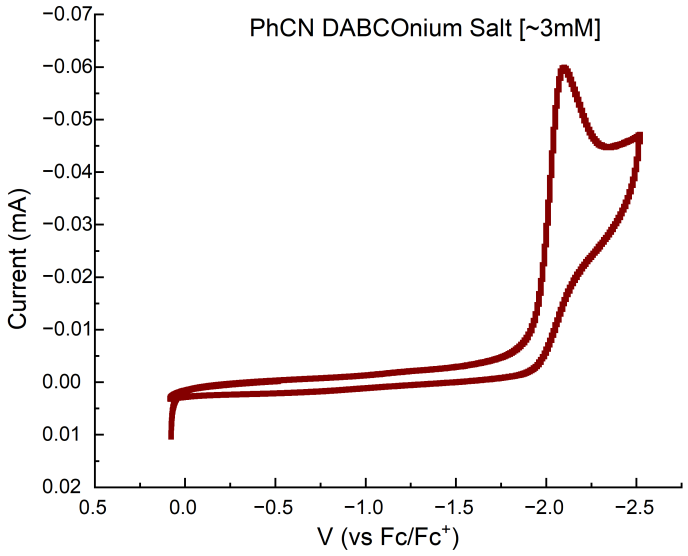


Figure S23. Reduction profile of PhCN DABCOnium salt (1st scan) (**2b**).

Spectroelectrochemistry

Potentials were controlled and currents measured using a NuVant EZstat Pro potentiostat. The spectroelectrochemcial cell (product number AKSTCKIT3) was purchased from Pine Research, consisting of a thin path quartz cuvette and a combined honeycomb working/flat counter electrode printed in gold on a ceramic substrate. A silver wire coated in silver chloride was inserted directly into the cell and used as a pseudoreference electrode. UV/vis spectra were collected with an Agilent Cary UV/vis Compact Peltier instrument measuring in the 1000-200 nm range. Because the honeycomb electrode has significant absorbance, samples were referenced relative to air.

Experiments were conducted under air, at a controlled temperature of 25 °C. The decision to run the experiments under air was made to align with the normal procedure in the electrosynthesis. Potentials were held in 120 second cycles, with the beginning of each UV/vis scan occurring after 80 seconds. Potentials were steadily increased in 0.2 V increments from 0.0 V to 2.8 V relative to the Ag/AgCl wire reference. Spectra showed very little change between 0.0 and 0.8 V and after 2.2 V spectra were dominated by solvent breakdown.

For all samples, the electrolyte/solvent combination was 0.1 M $TBAClO_4$ in LCMS-grade acetonitrile. When present, the concentration of **4a** was 5 mM and the concentration of the various arenes tested (benzene, benzonitrile, anisole) were 1 mM.

Spectroelectrochemical Data

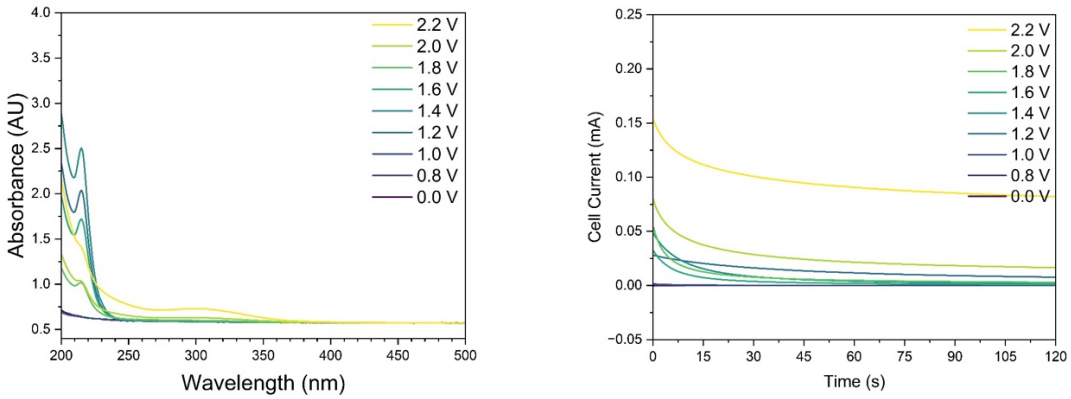


Figure S24. Spectroelectrochemical absorbance (left) and current data (right) for an acetonitrile/tetrabutylammonium perchlorate blank.

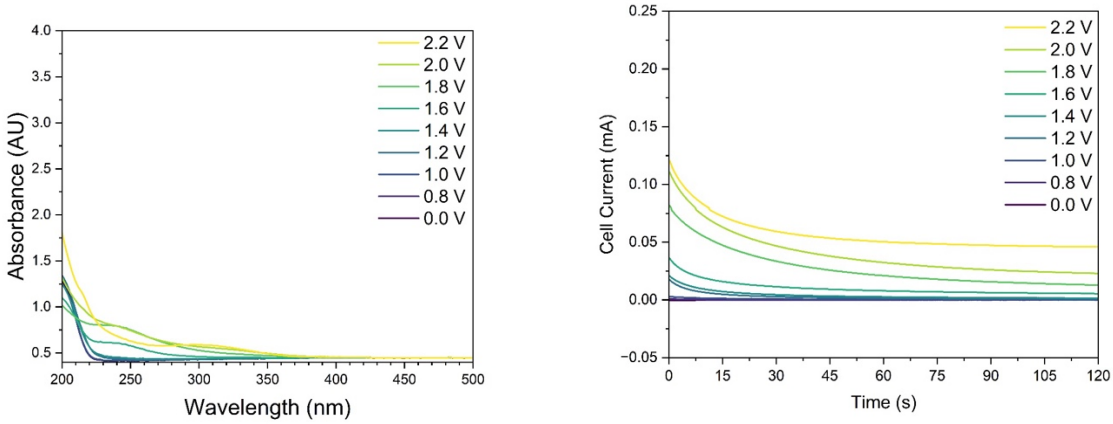


Figure S25. Spectroelectrochemical absorbance (left) and current data (right) for **4a**.

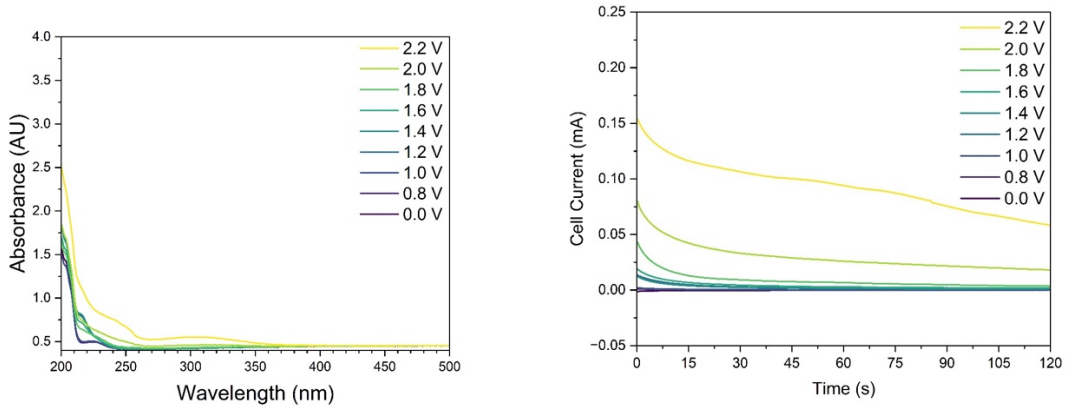


Figure S26. Spectroelectrochemical absorbance (left) and current data (right) for benzene.

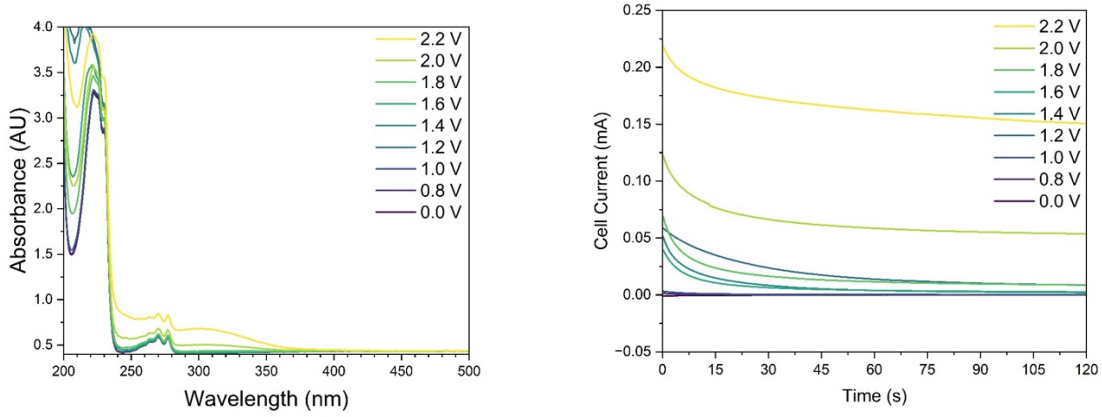


Figure S27. Spectroelectrochemical absorbance (left) and current data (right) for benzonitrile.

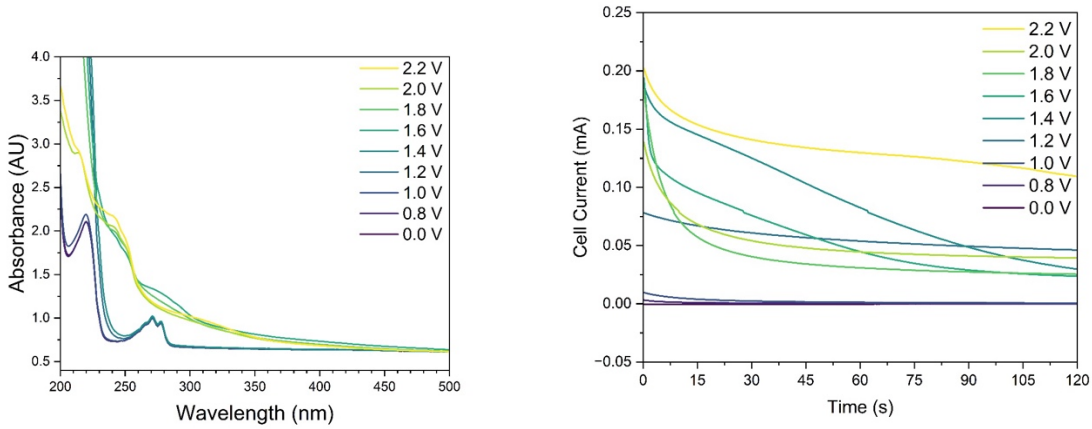


Figure S28. Spectroelectrochemical absorbance (left) and current data (right) for anisole.

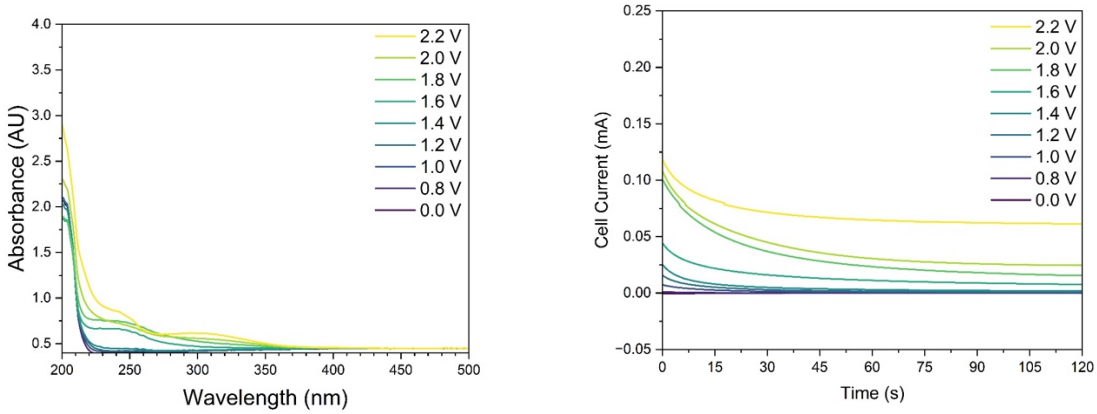


Figure S29. Spectroelectrochemical absorbance (left) and current data (right) for benzene with **4a**.

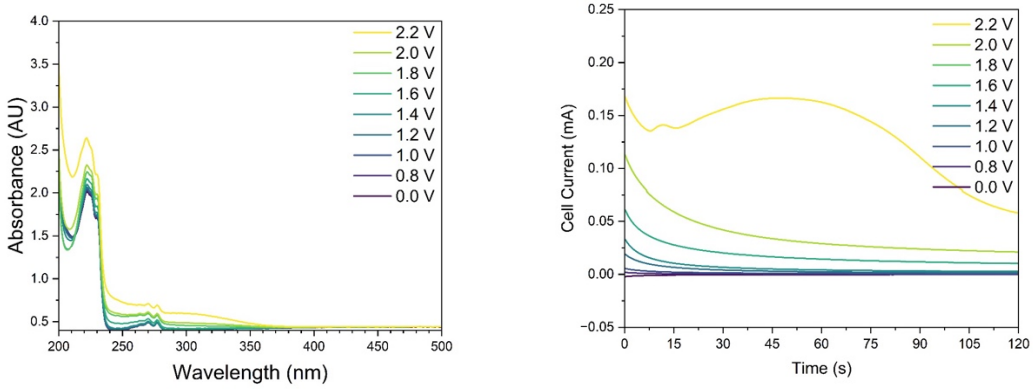


Figure S30. Spectroelectrochemical absorbance (left) and current data (right) for benzonitrile with **4a**.

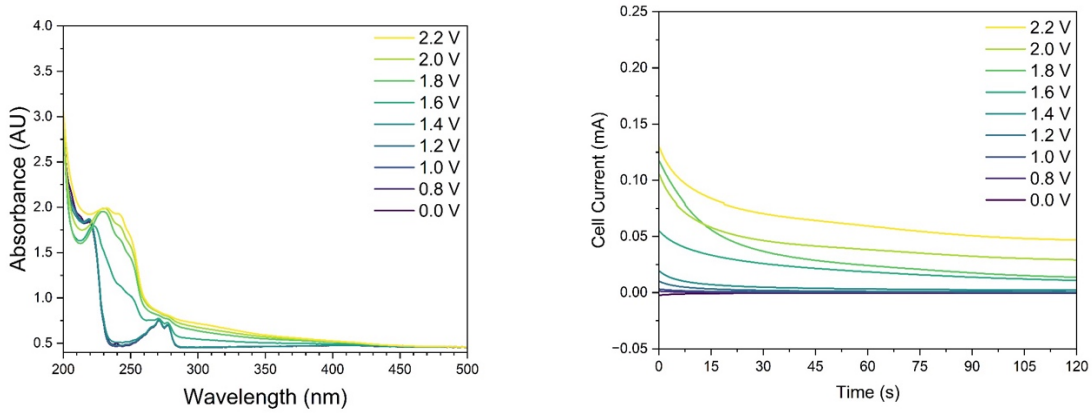


Figure S31. Spectroelectrochemical absorbance (left) and current data (right) for anisole with **4a**.

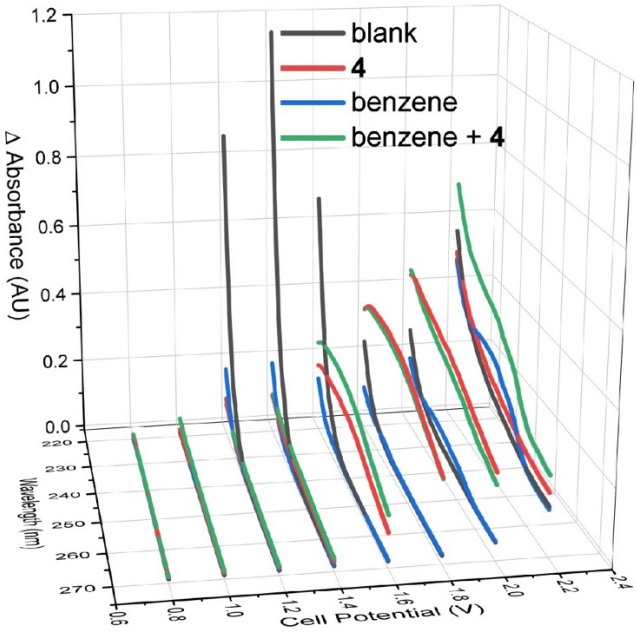


Figure S32. Spectroelectrochemical comparisons for benzene samples in the 220-270 nm region. For each oxidative voltage of each sample composition, the 0.0 V trace has been subtracted from the raw absorbance data.

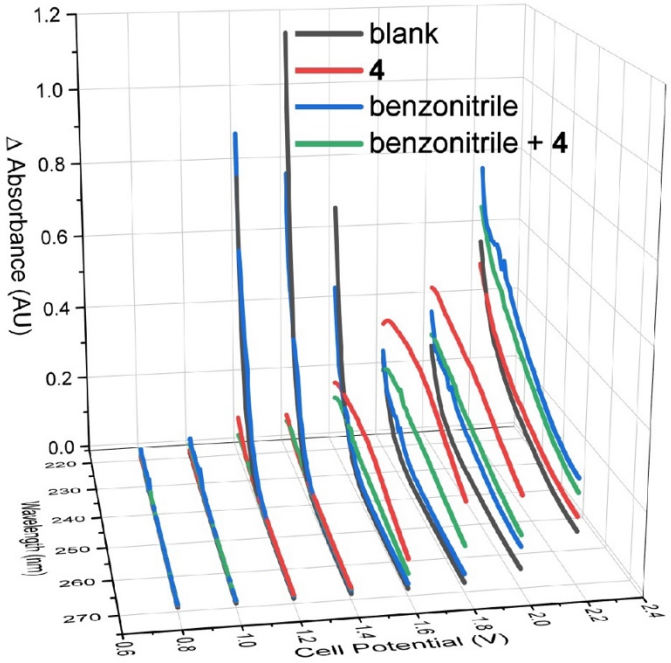


Figure S33. Spectroelectrochemical comparisons for benzonitrile samples in the 220-270 nm region. For each oxidative voltage of each sample composition, the 0.0 V trace has been subtracted from the raw absorbance data.

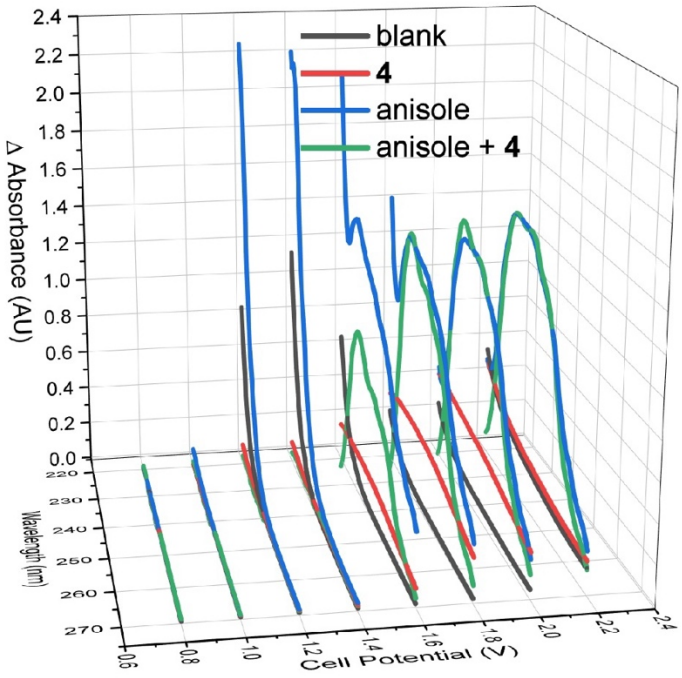


Figure S34. Spectroelectrochemical comparisons for anisole samples in the 220-270 nm region. For each oxidative voltage of each sample composition, the 0.0 V trace has been subtracted from the raw absorbance data.

Discussion of spectroelectrochemical results

Given our mechanistic proposal, we hypothesized that we might be able to observe transient charge transfer complexes of oxidized **4a** associating with arenes via spectroelectrochemsitry. We chose to study electron-neutral benzene, electron-poor benzonitrile, and electron-rich anisole for this purpose, expecting difficult-to-oxidize benzonitrile to yield the best results.

Directly observing a charge transfer complex, however, proved difficult. Analysis of the data was complicated by significant solvent oxidation, with an acetonitrile/0.1 M $TBAClO_4$ blank showing significant absorption bands growing in first at around 215 nm/1.2 V and then a broad peak around 300 nm/2.0 V. This overlaps both with the absorbance observed for **4a** and that of the tested arenes. Additionally, the hypothesized charge transfer species may be too short-lived to allow for detection by UV/vis at room temperature.

When a solution of **4a** is subjected to oxidative potential, the background peaks at 215 nm and 300 nm still appear. However, a new broad feature appears at about 240 nm/1.4 V. Correspondingly, the cell current in the intermediate potential region (after the background 215 nm/1.2V oxidation and before the 300 nm/2.0 V peak appears) is higher than for the solvent blank. This is consistent with the cyclic voltammetry studies of **4a**. Thus, we attribute the peak around 240 nm to the oxidation of **4a**.

On its own, benzene is oxidized with a broad UV feature appearing at 2.0 V. In solution with **4a**, the spectral profile is dominated by that of the oxidation of **4a** until 1.8 V, after which the oxidation of benzene competes with the oxidation of **4a** and solvent oxidation. Though the related electrosynthesis reaction produces aminated product, no clear evidence of product formation or charge transfer complex is visible.

Anisole is easily oxidized on its own, resulting in intense and broad features in the UV/vis spectrum. The presence of anisole appears to suppress background oxidation of **4a** through about 1.4 V, and the spectral behavior beyond that potential is dominated by the oxidation of anisole alone. Interestingly, there is the presence of a feature similar in appearance to an isosbestic point around 210 nm in the anisole + **4a** experiment. Perhaps, oxidized anisole is quickly consumed by neutral **4a**. Otherwise, the feature may have only coincidental resemblance to an isosbestic point. In either case, the data supports the notion that the reaction mechanism for anisole and electronically similar arenes occurs through a direct arene oxidation mechanism, since its oxidation features dominate the spectrum even at potentials where **4a** is otherwise observed to oxidize.

At the potentials tested, benzonitrile alone does not appear to oxidize significantly. However, the presence of benzonitrile suppresses the feature at 240 nm corresponding to the oxidation of **4a**, as is visible in the benzonitrile comparison plot in the 1.4-1.8 V region. This suggests benzonitrile reacts quickly with oxidized **4**. This may be attributable to the presence of a charge transfer complex with different/lessened absorbance, or simply the immediate formation of aminated product.

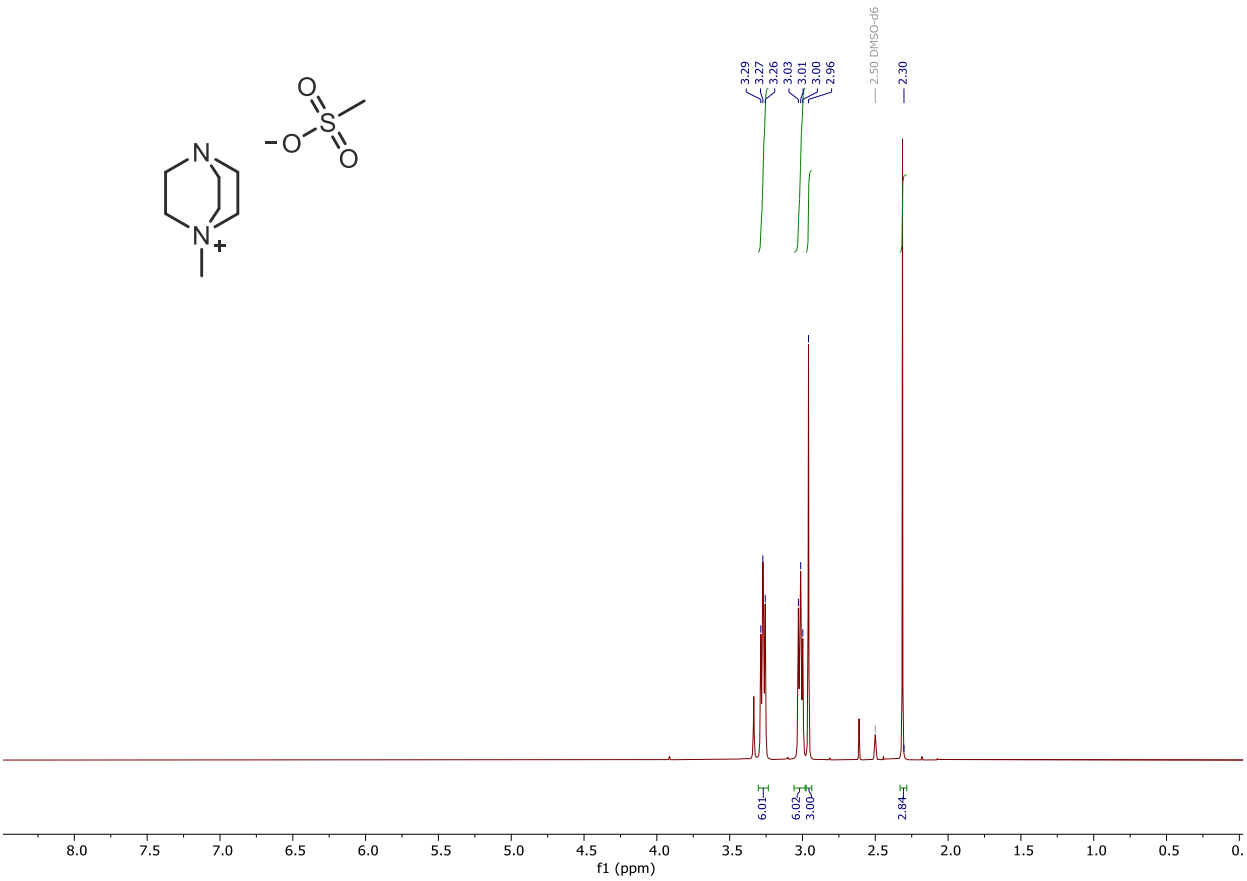
References

1. Wang, Y.-M., Wu, J., Hoong, C., Rauniyar, V., Toste, F. D. Enantioselective Halocyclization Using Reagents Tailored for Chiral Anion Phase-Transfer Catalysis. *J. Am. Chem. Soc.* **134**, 12928–12931 (2012).
2. Alvarez, E. M., Stewart, G., Ullah, M., Lalisse, R., Gutierrez, O. & Malapit, C. A. Site-Selective Electrochemical Arene C–H Amination. *J. Am. Chem. Soc.* **146**, 3591–3597 (2024).
3. Arnáiz, F. J. A Convenient Way to Generate Hydrogen Chloride in the Freshman Lab. *J. Chem. Educ.* **72**, 1139 (1995).
4. Tao, S.-K.; Chen, S.-Y.; Feng, M.-L.; Xu, J.-Q.; Yuan, M.-L.; Fu, H.-Y.; Li, R.-X.; Chen, H.; Zheng, X.-L.; Yu, X.-Q. Electrochemical Cross-Dehydrogenative Aromatization Protocol for the Synthesis of Aromatic Amines. *Org. Lett.* **24**, 1011–1016 (2022).
5. Nguyen, T.; Yoo, W.J.; Kobayashi, S. Chelating Bis(1,2,3-triazol-5-ylidene) Rhodium Complexes: Versatile Catalysts for Hydrosilylation Reactions. *Adv. Synth. Catal.* **358**, 452-458 (2016).
6. Abbenhuis, R. A. T. M.; Boersma, J.; Van Koten, G. Ruthenium-Complex-Catalyzed N-(Cyclo)Alkylation of Aromatic Amines with Diols. Selective Synthesis of *N* -(ω-Hydroxyalkyl)Anilines of Type PhNH(CH $_2$) $_n$ OH and of Some Bioactive Arylpiperazines. *J. Org. Chem.* **63**, 4282–4290 (1998).
7. Sengmany, S.; Daili, F.; Kribii, I.; Léonel, E. Electrogenerated Nickel Catalyst for C–N Cross-Coupling. *J. Org. Chem.* **88**, 675–683 (2023).
8. Rudbeck, H. C.; Johannsen, I.; Nielsen, O.; Ruhland, T.; Sommer, M. B.; Tanner, D.; Dancer, R. Gram-Scale Synthesis of *N* -Aryl- and *N* -Aryl- *N ′*-Methylpiperazines on a Novel, Water-Swellable, Oxethane-Linked Poly(Ethylene Glycol) High-Loading Resin. *Synthesis*.**19**, 3456–3462 (2005).
9. Wong, M. J.; Oftadeh, E.; Saunders, J. M.; Wood, A. B.; Lipshutz, B. H. Palladium-Catalyzed Aminations in Flow ... *on Water*. *ACS Catal.* **14**, 1545–1552 (2024).
10. Saito, Y.; Senzaki, T.; Nishizawa, K.; Kobayashi, S. Continuous-Flow Reductive *N* -Methylation with Highly Active Heterogeneous Pd Catalysts and Sequential-Flow Synthesis of *N* -Monomethyl Amines. *Green Chem.* **25**, 7524–7528 (2023).
11. Mills, L. R.; Graham, J. M.; Patel, P.; Rousseaux, S. A. L. Ni-Catalyzed Reductive Cyanation of Aryl Halides and Phenol Derivatives via Transnitrilation. *J. Am. Chem. Soc.* **141**, 19257–19262 (2019).
12. Boursalian, G. B., Ham, W. S., Mazzotti, A. R. & Ritter, T. Charge-transfer-directed radical substitution enables para-selective C–H functionalization. *Nat. Chem.* **8**, 810–815 (2016).
13. Hansch, Corwin.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **91**, 165–195 (1991).

NMR Spectra for synthesized compounds

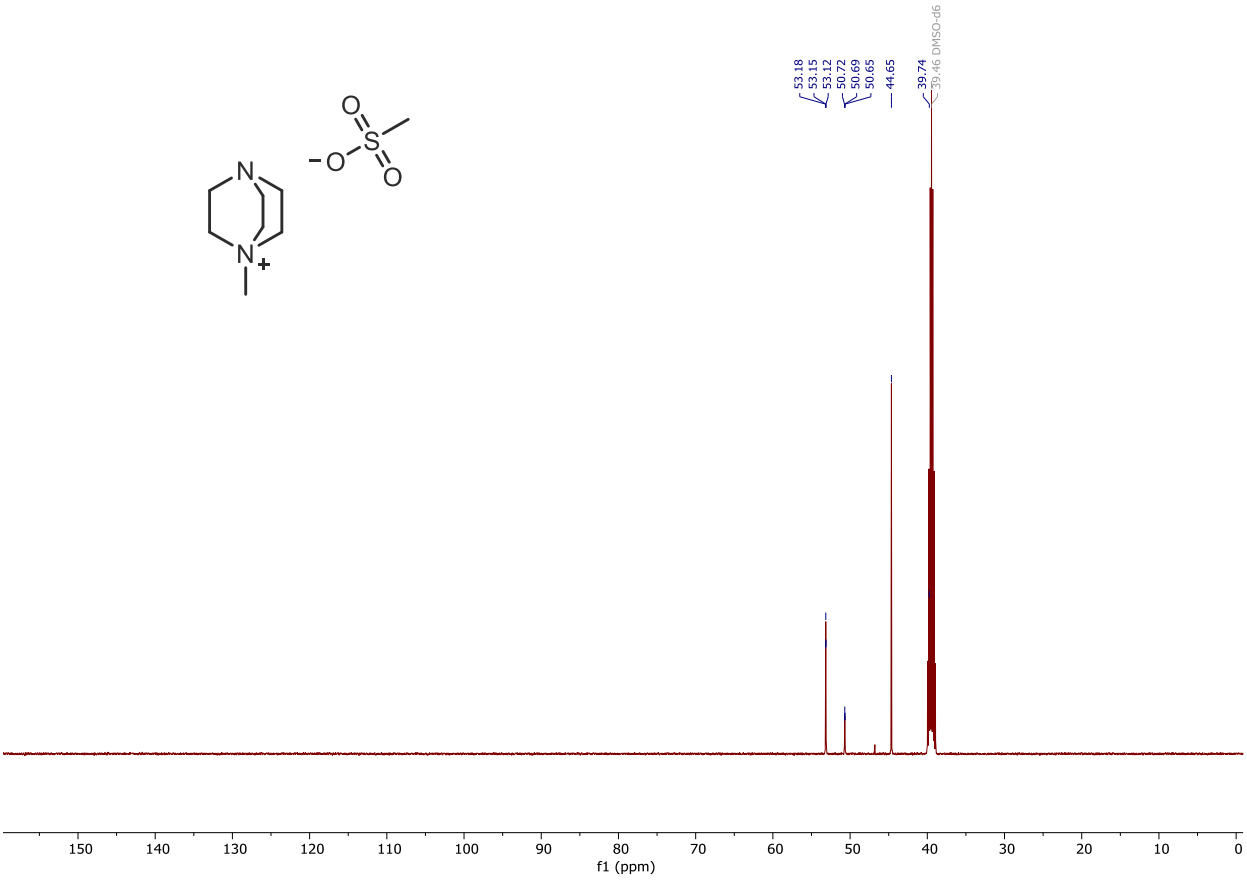
N-Me DABCOnium OMs (4a)

^{1}H NMR, DMSO-d_6

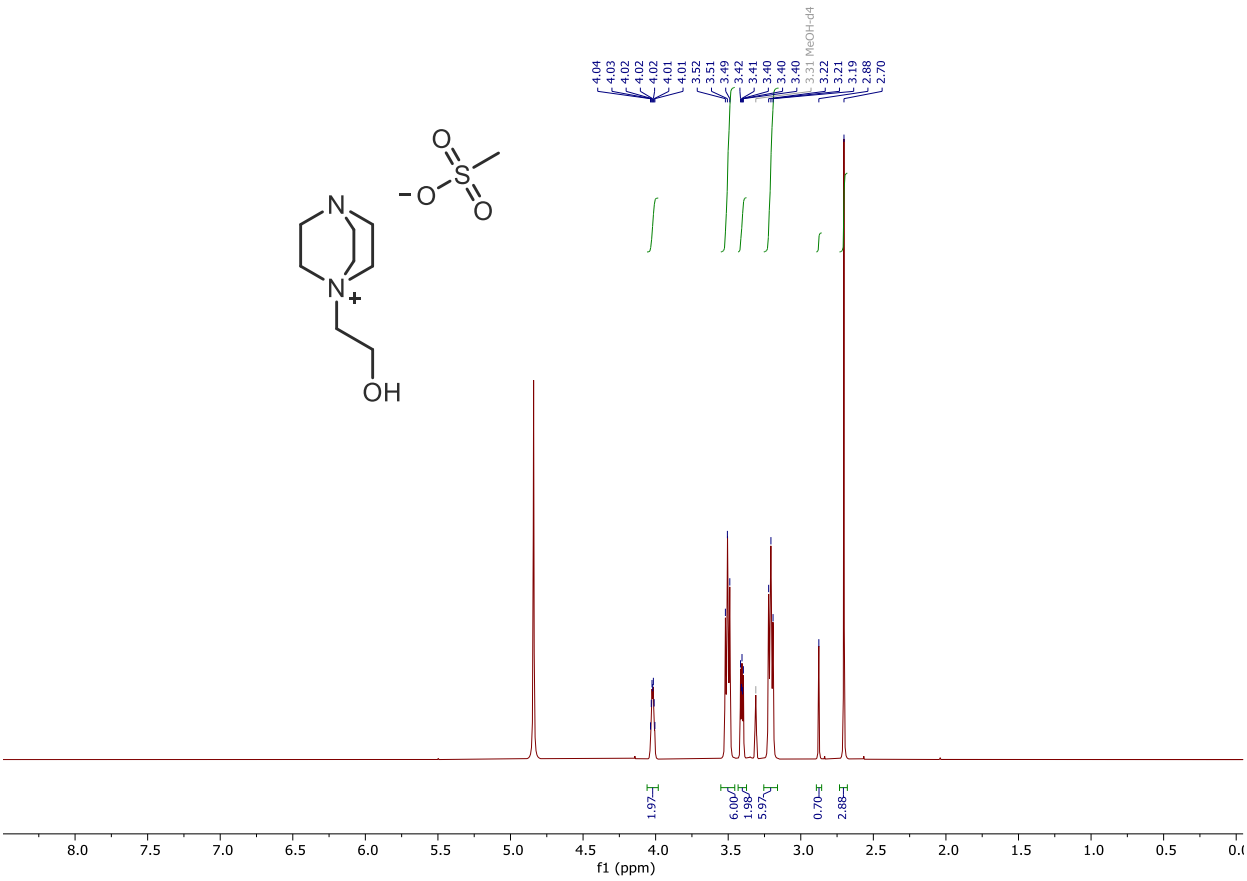


_N_-Me DABCOnium OMs (4a)

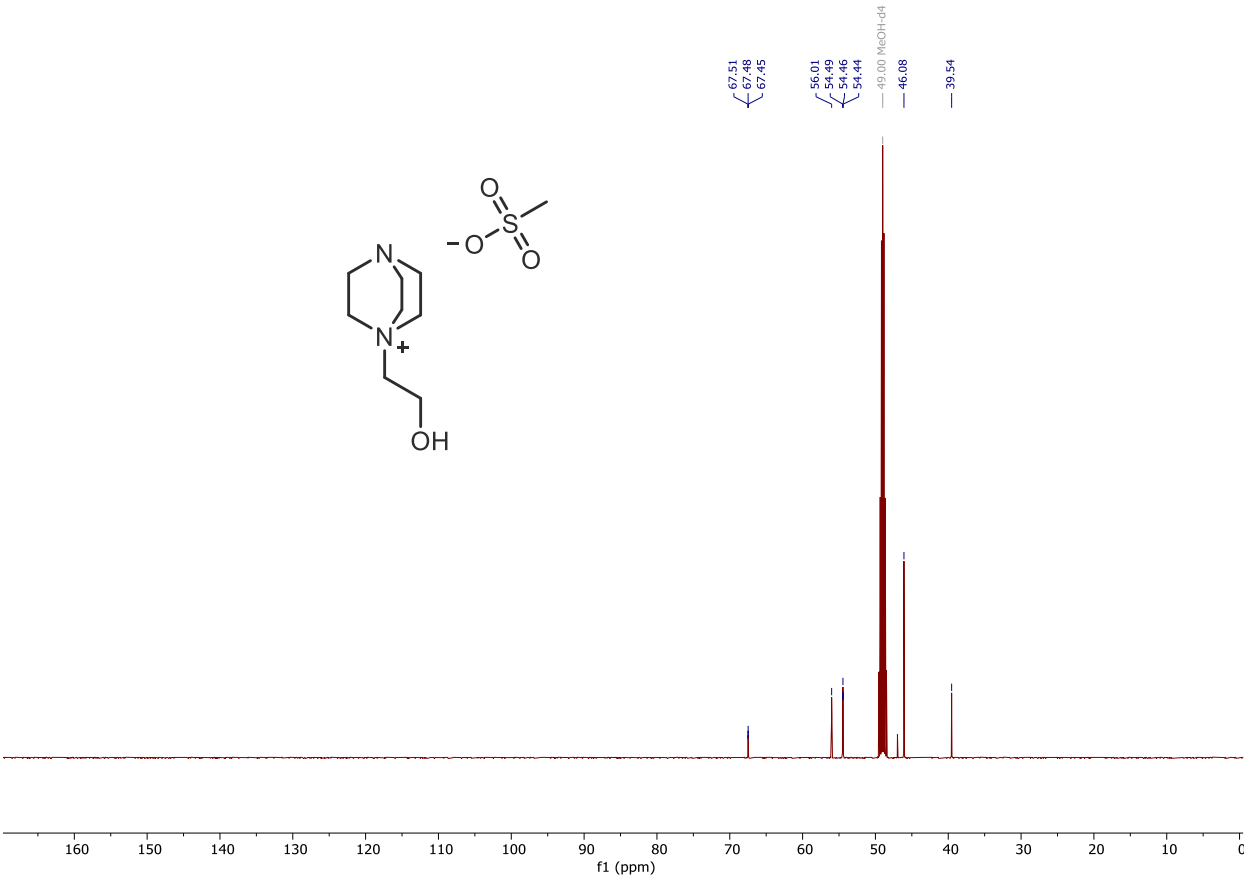
^{13}C NMR, DMSO-d_6



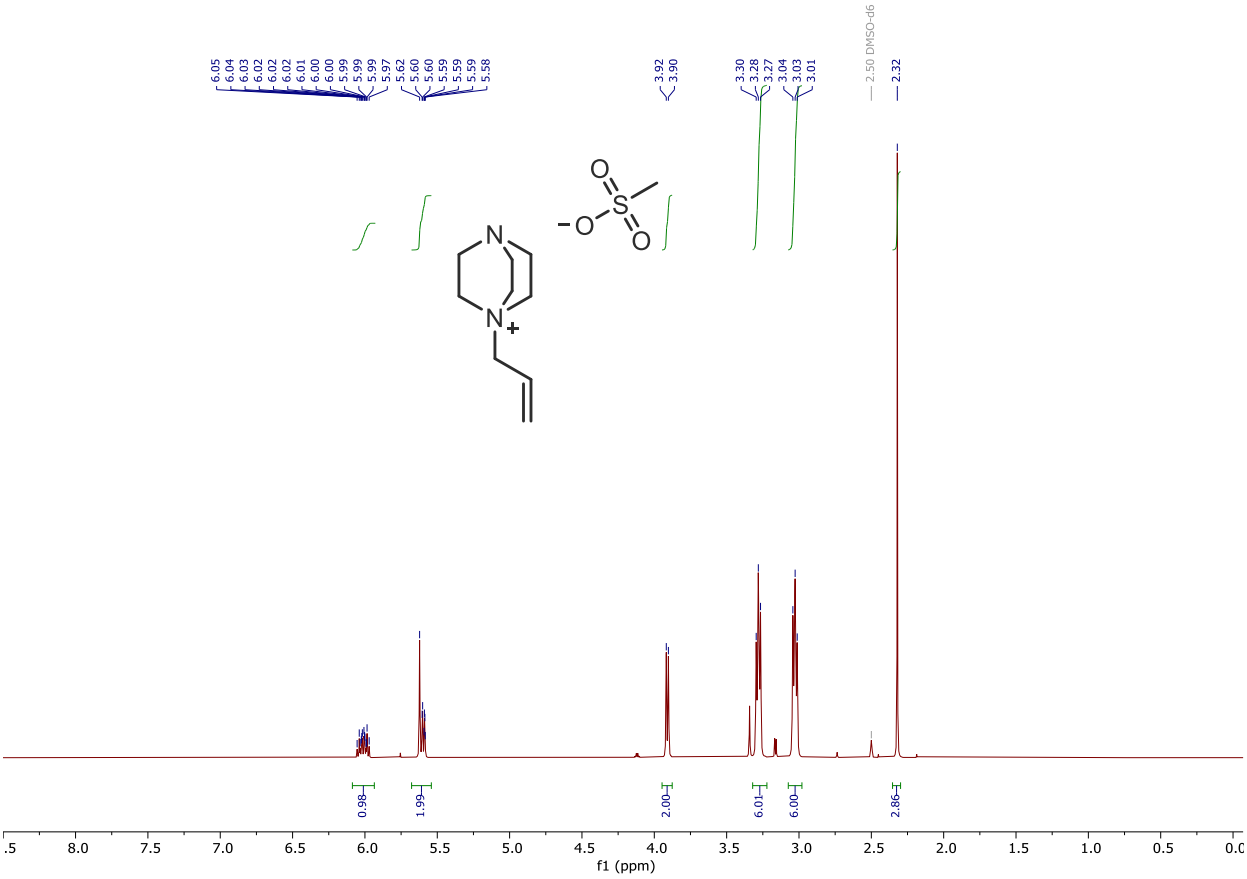
_N_-(2-hydroxyethyl) DABCOnium OMs (4w)
Methanol-d_4
1H NMR



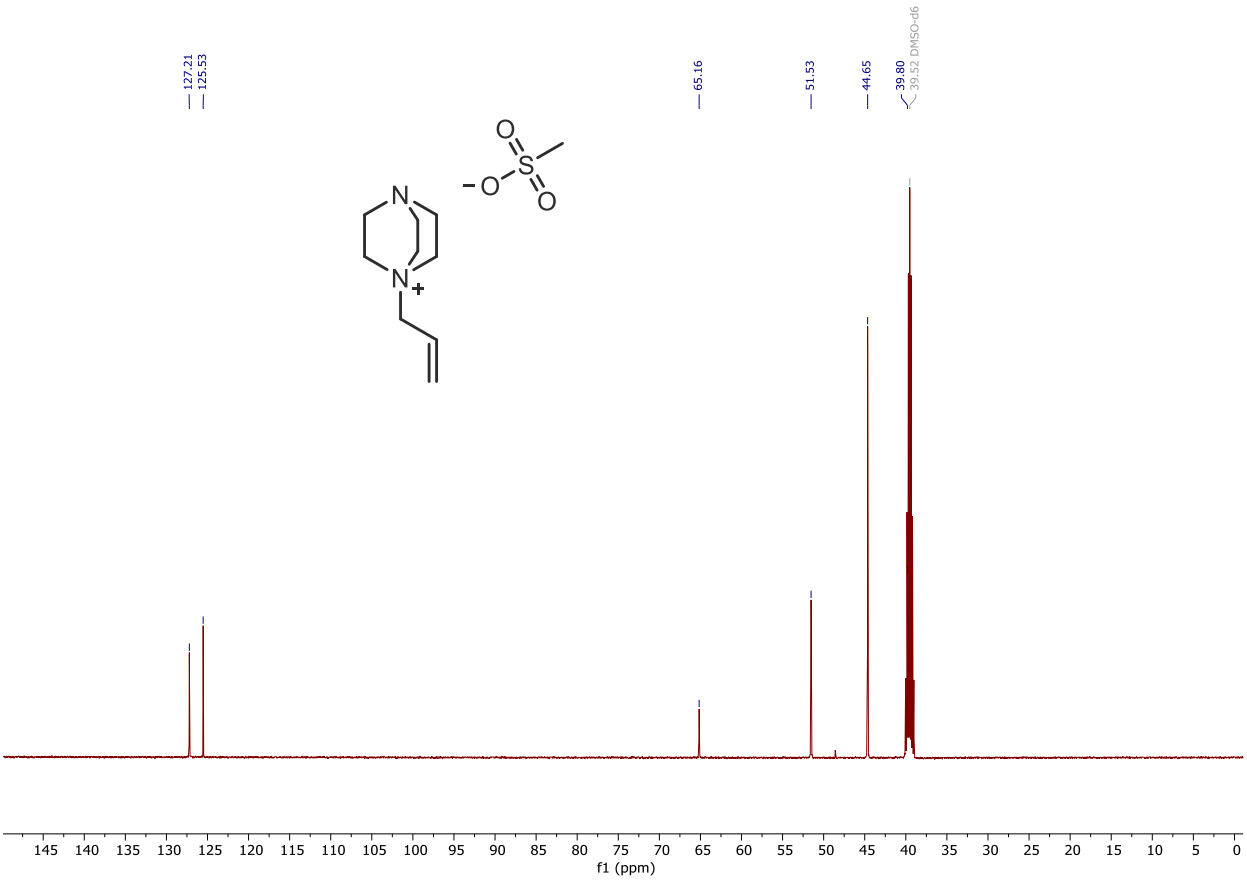
_N_-(2-hydroxyethyl) DABCOnium OMs (4w)
Methanol-d_4
13C NMR



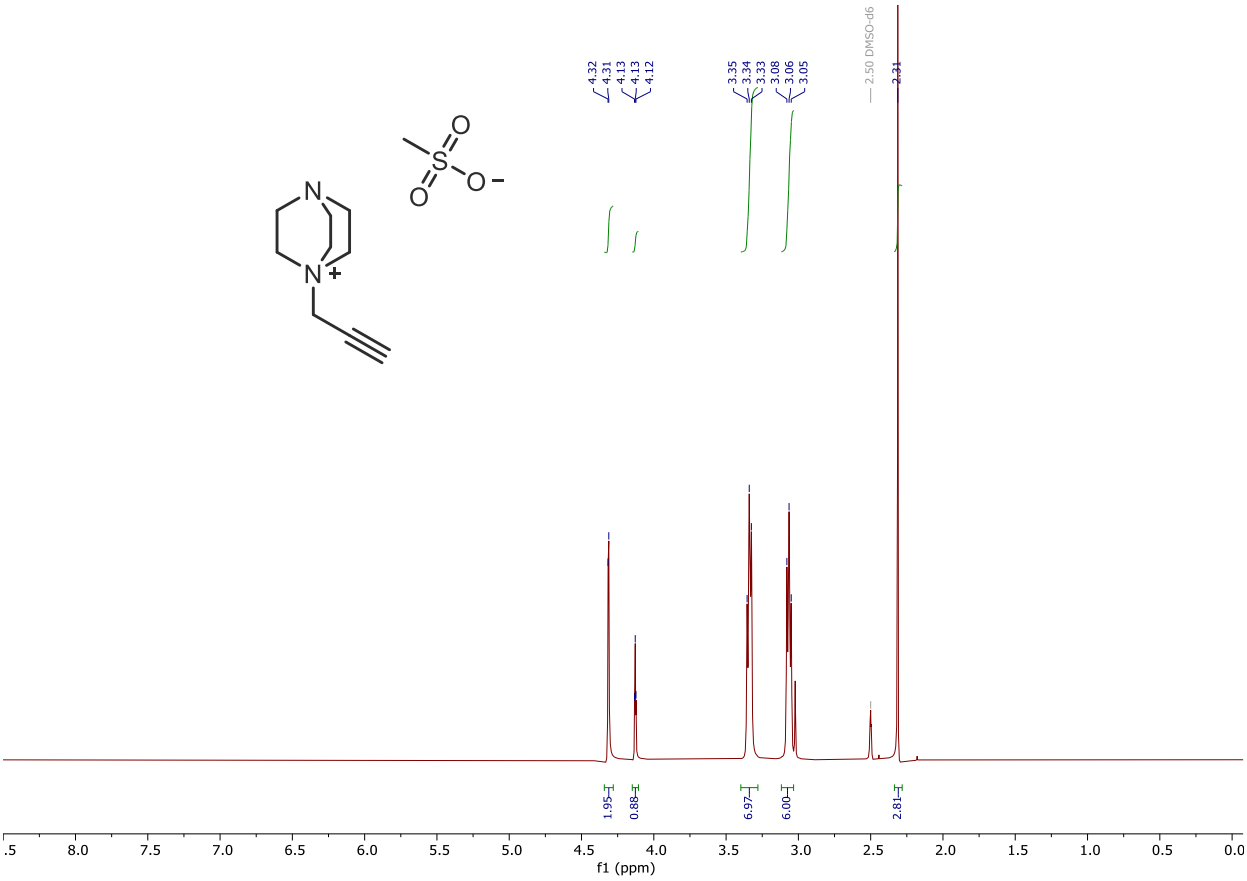
_N_-allyl DABCOnium OMs (4x)
DMSO-d_6
1H NMR



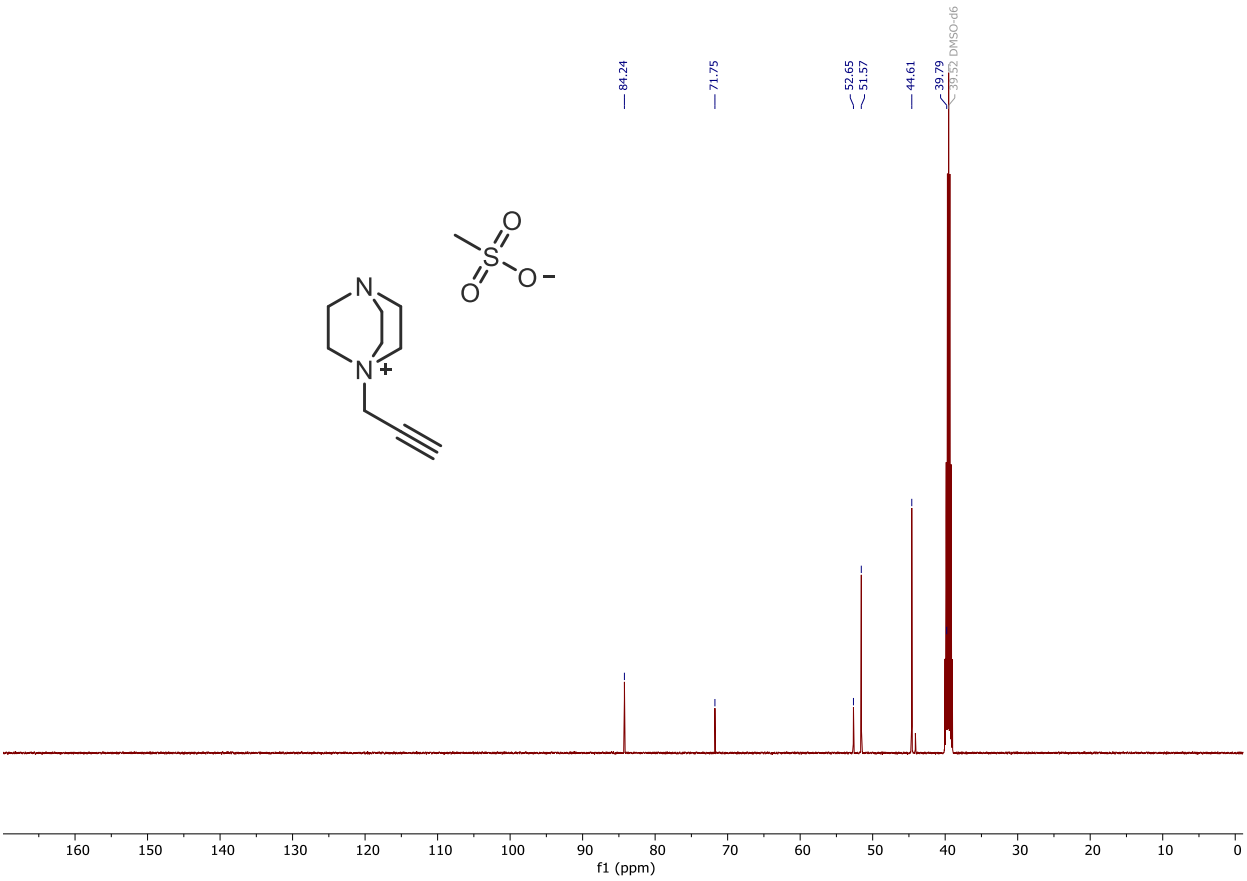
_N_-allyl DABCOnium OMs (4x)
DMSO-d_6
13C NMR



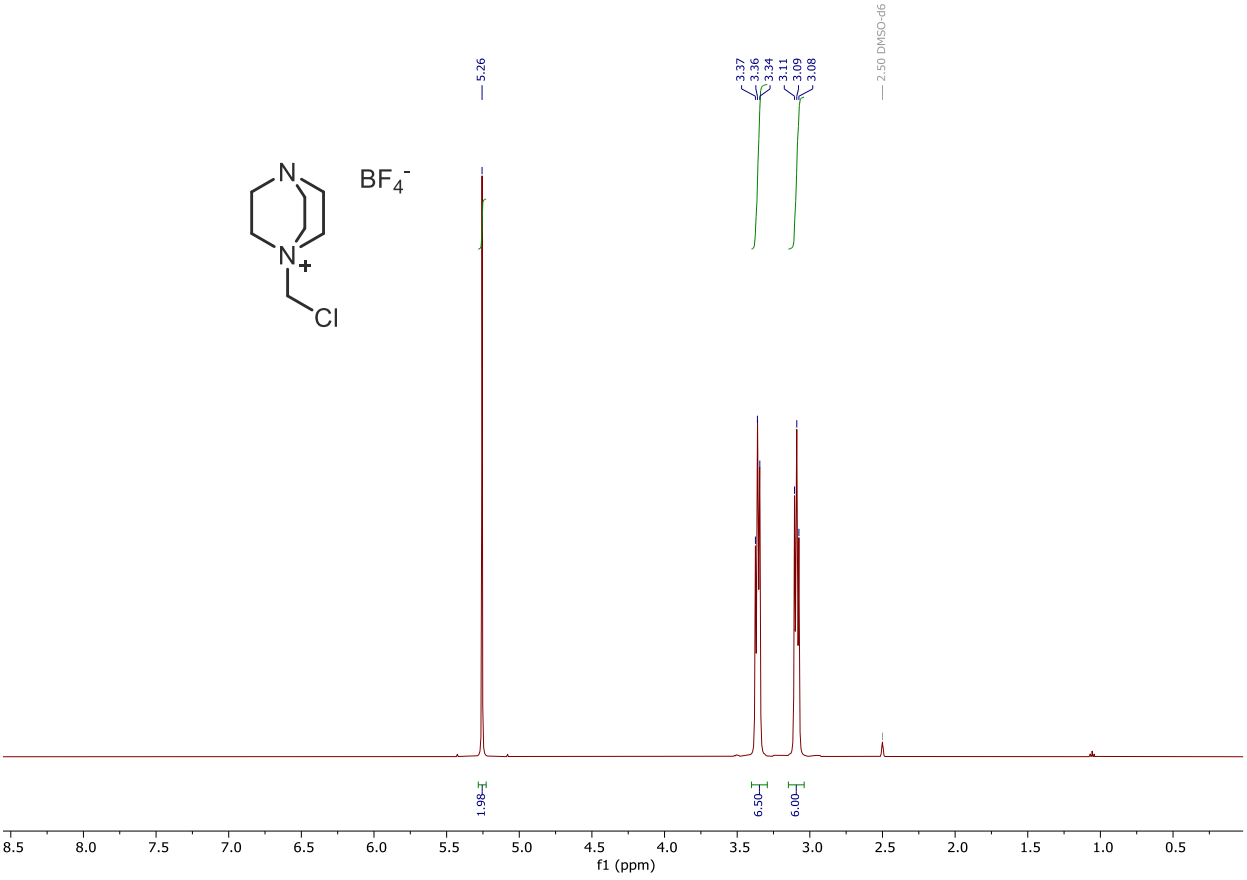
_N_-propargyl DABCOnium OMs (4y)
DMSO-d_6
1H NMR



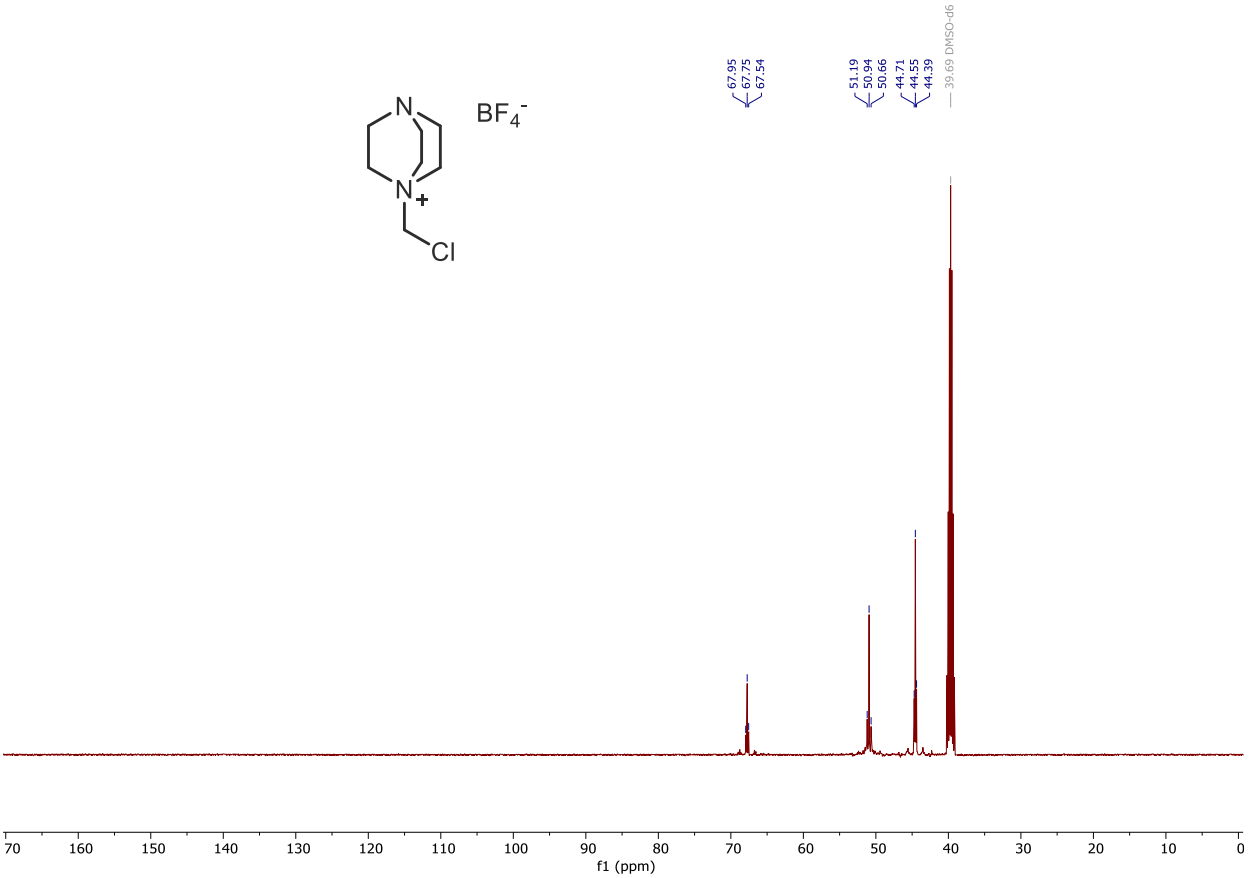
_N_-propargyl DABCOnium OMs (4y)
DMSO-d_6
13C NMR



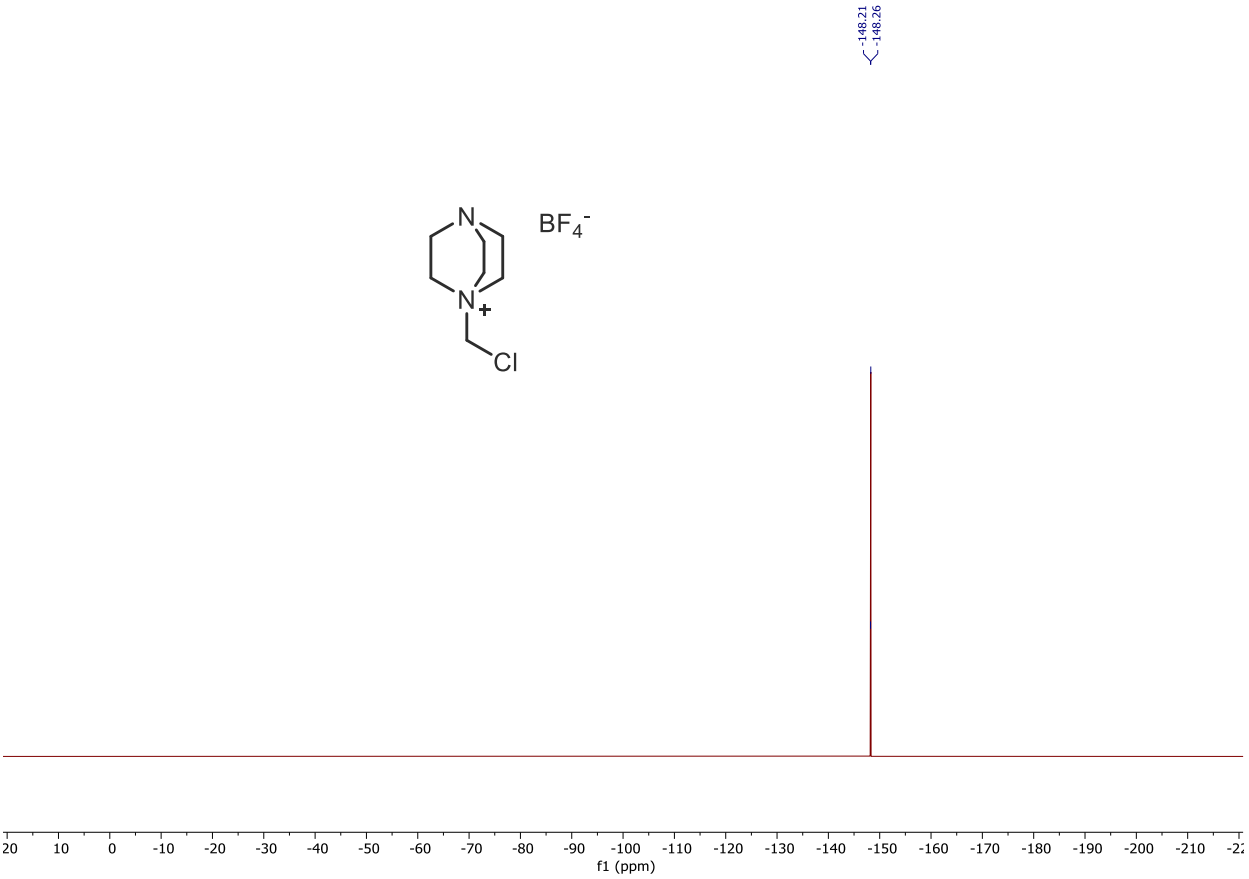
_N_-methylene chloride DABCOnium tetrafluoroborate (4z)
DMSO-d_6
1H NMR



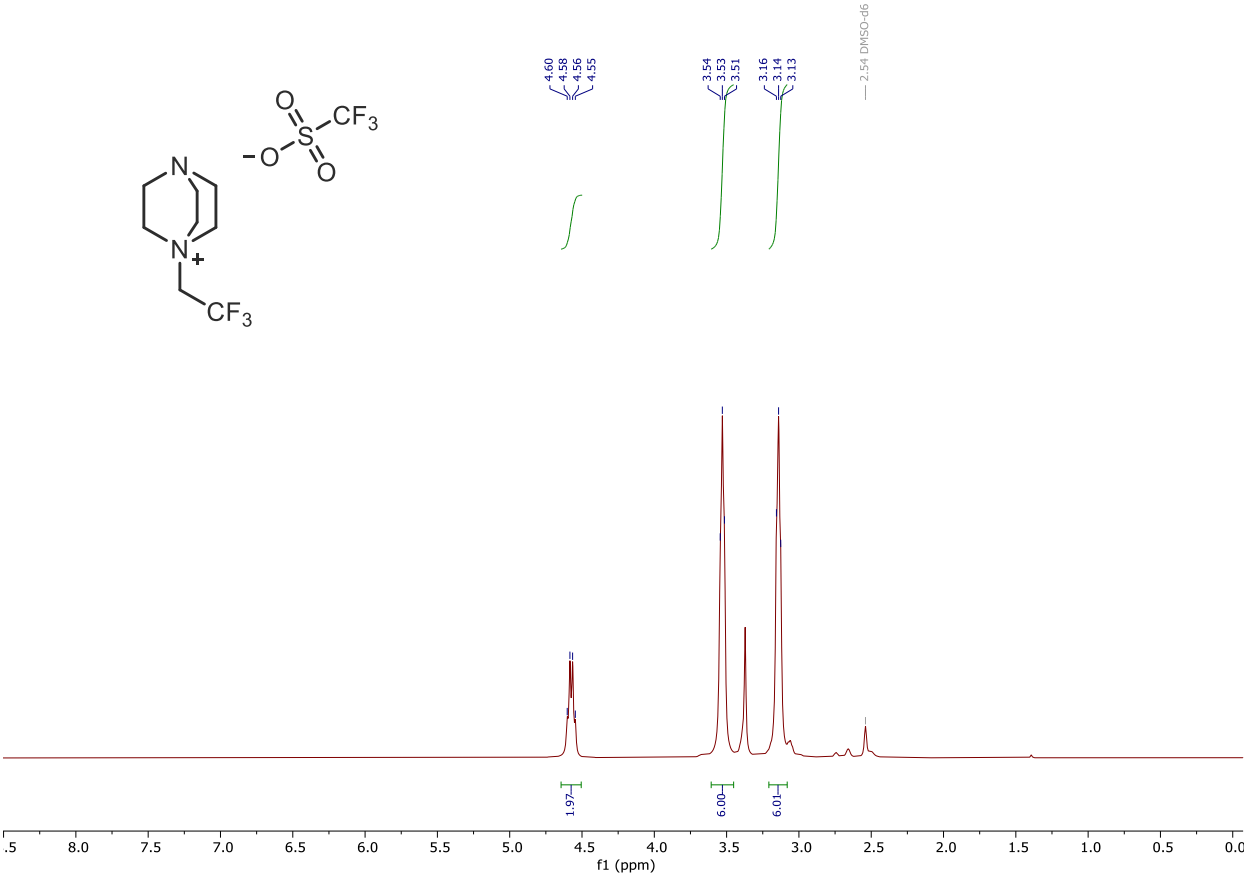
_N_-methylene chloride DABCOnium tetrafluoroborate (4z)
DMSO-d_6
13C NMR



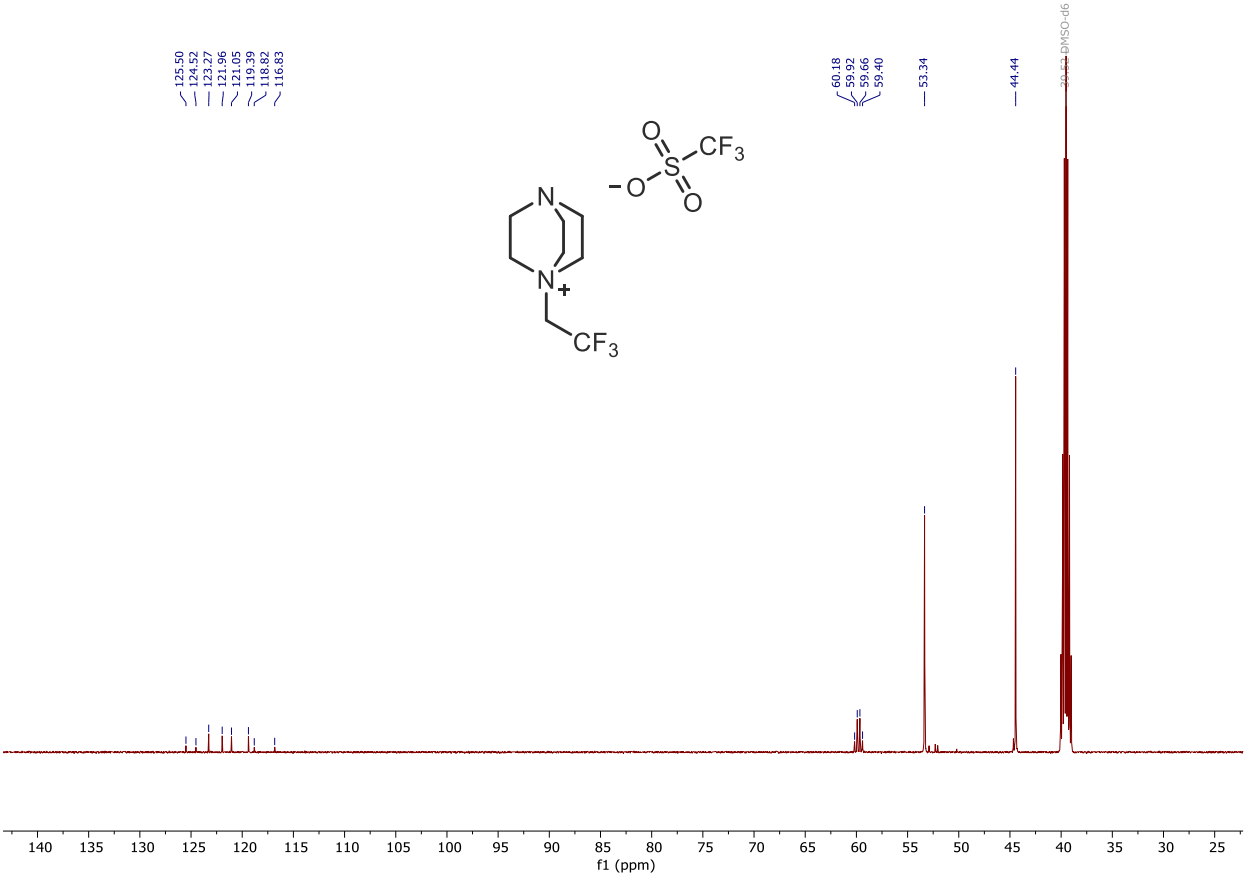
_N_-methylene chloride DABCOnium tetrafluoroborate (4z)
DMSO-d_6
19F NMR



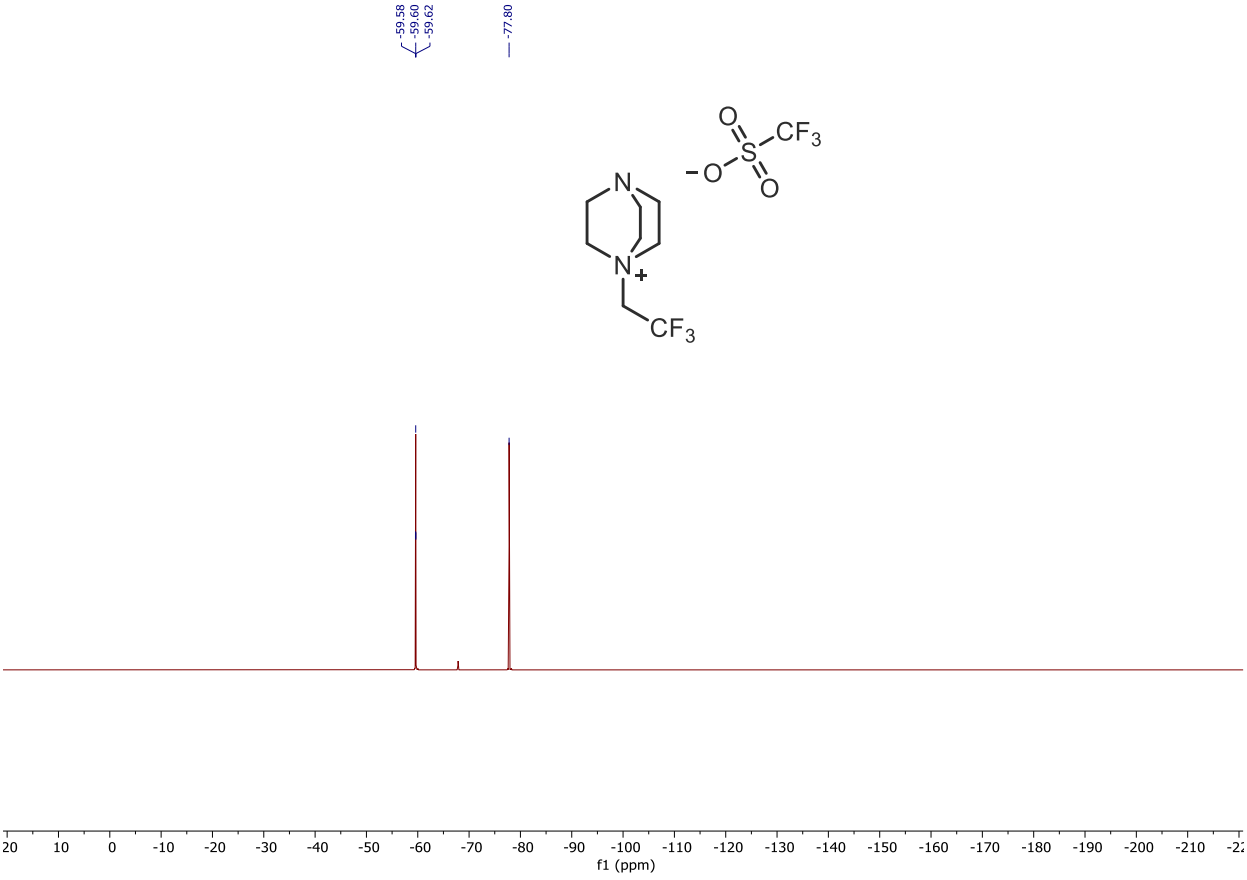
_N_-(2,2,2-trifluoroethyl) DABCOnium triflate (4aa)
DMSO-d_6
1H NMR



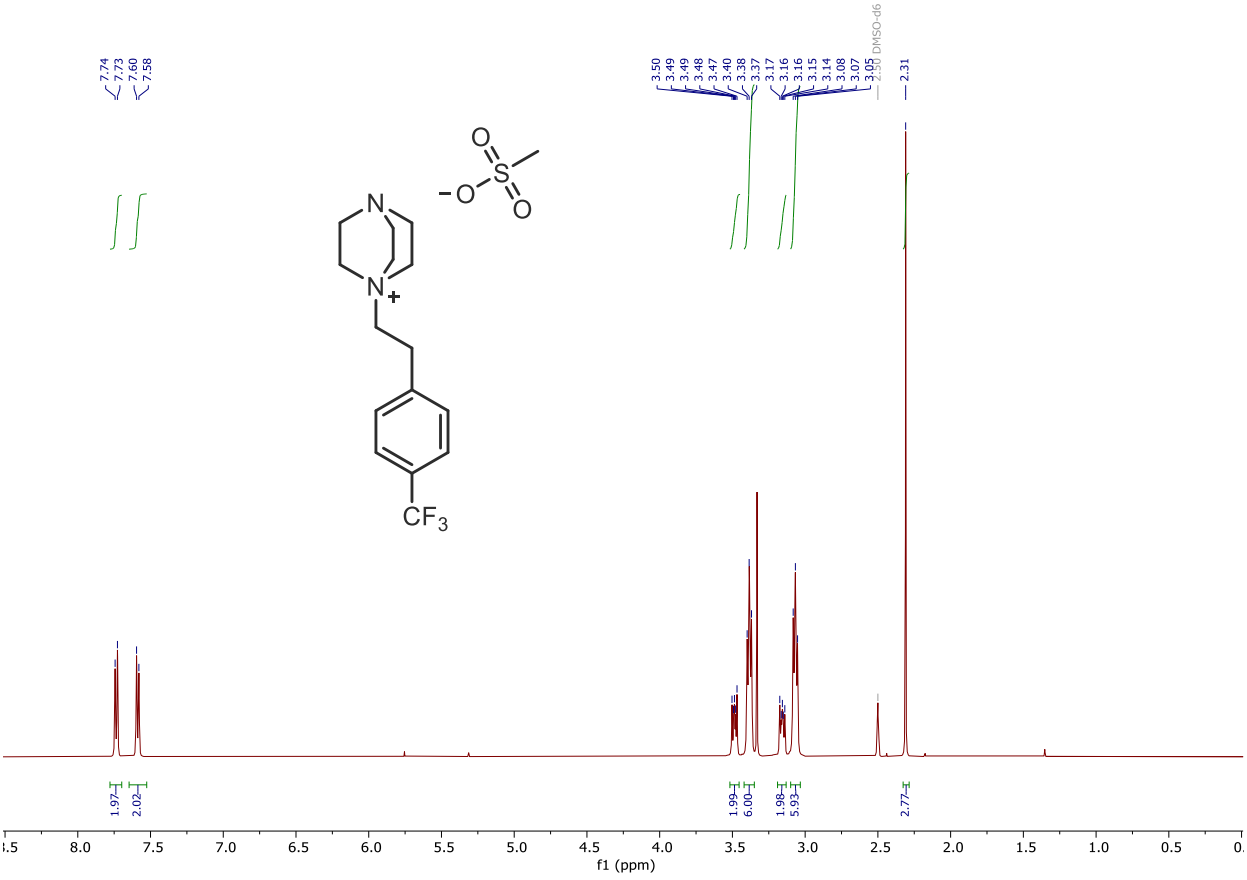
_N_-(2,2,2-trifluoroethyl) DABCOnium triflate (4aa)
DMSO-d_6
13C NMR



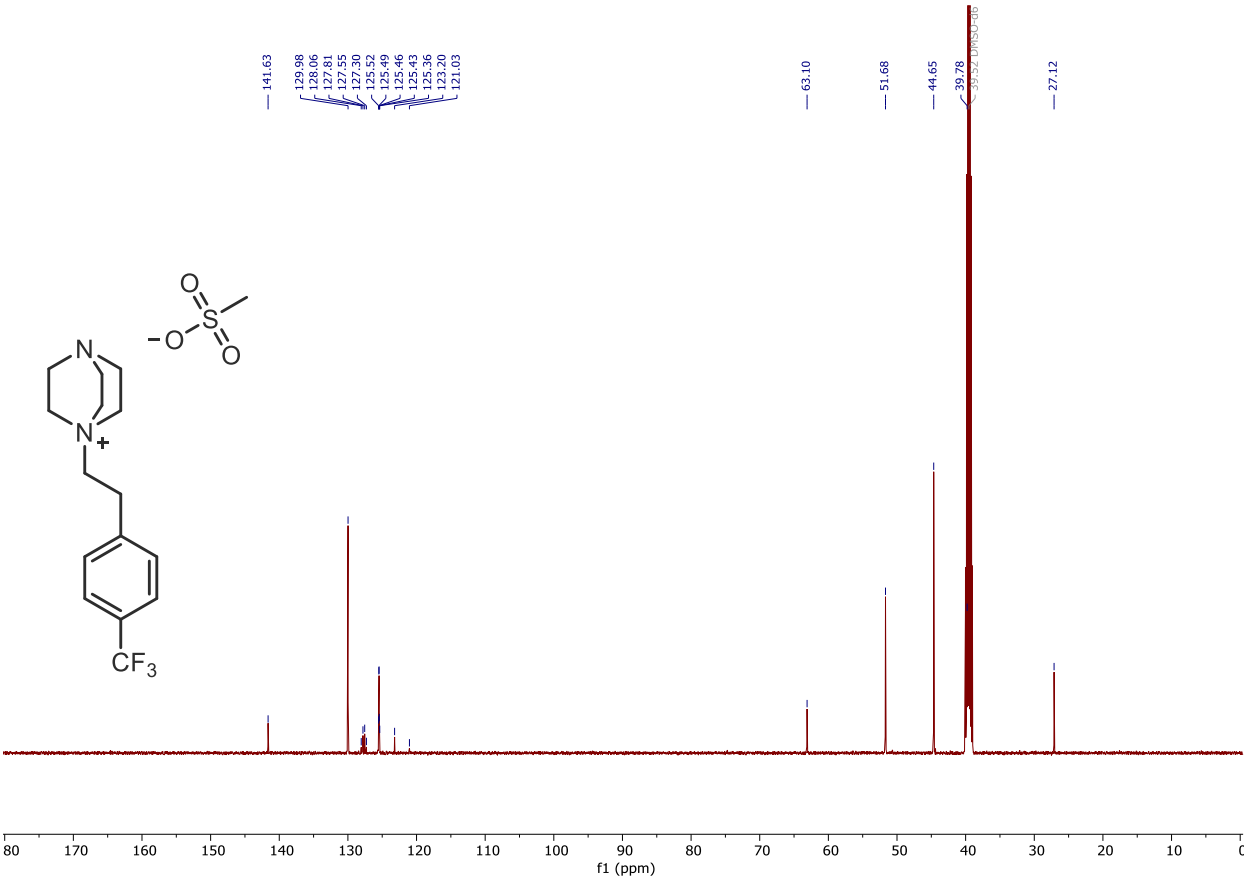
_N_-(2,2,2-trifluoroethyl) DABCOnium triflate (4aa)
DMSO-d_6
19F NMR



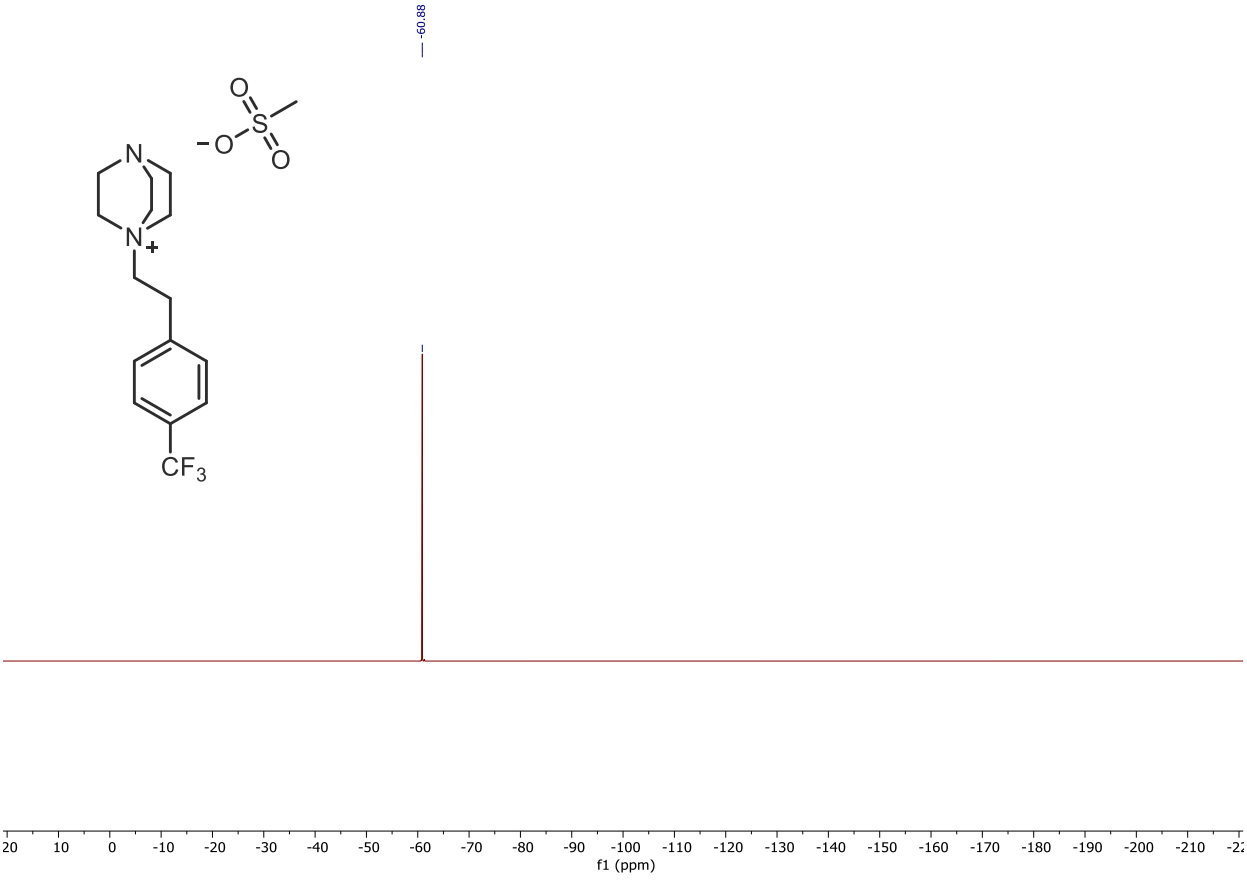
_N_-EtPhCF$_3$ DABCOnium OMs (4ab)
DMSO-d_6
1H NMR



_N_-EtPhCF$_3$ DABCOnium OMs (4ab)
DMSO-_d_$_6$
13C NMR



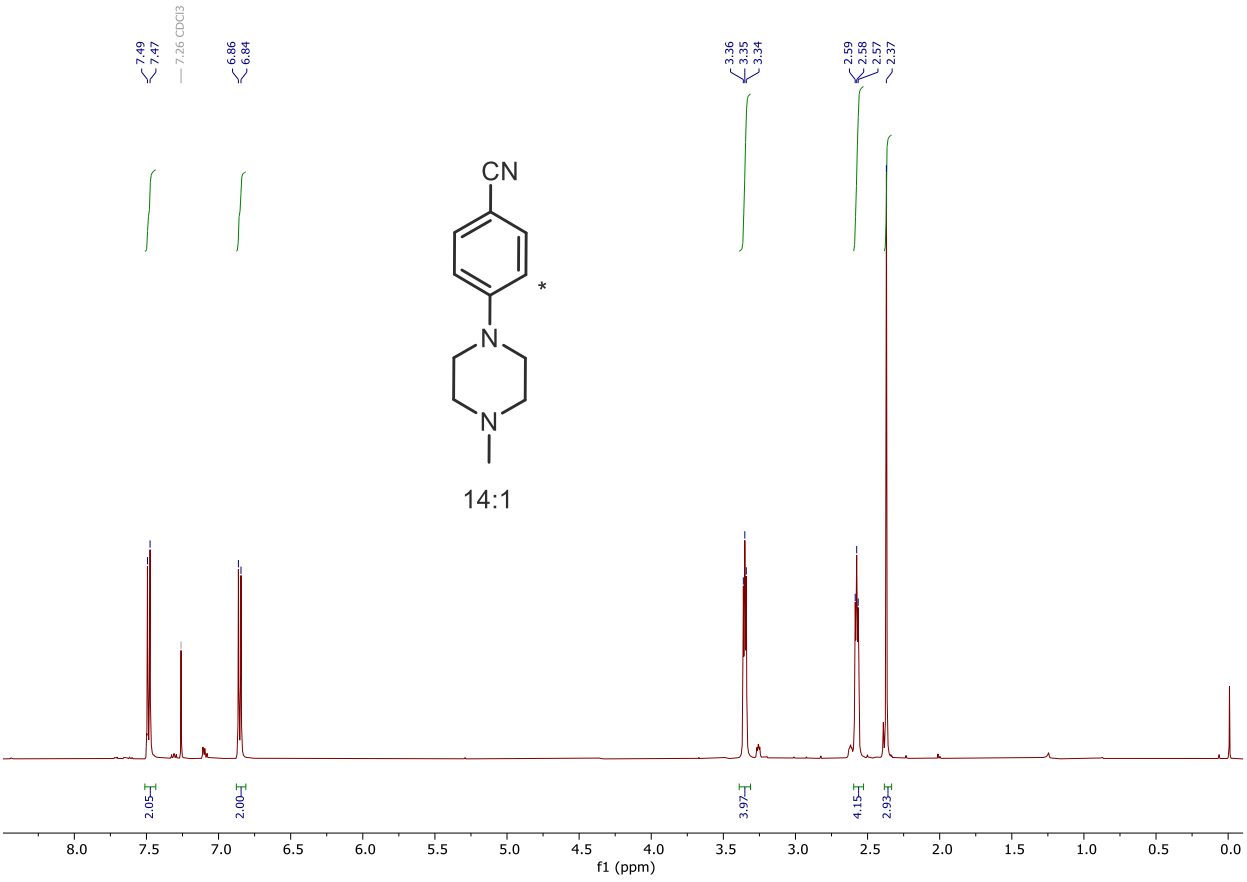
_N_-EtPhCF$_3$ DABCOnium OMs (4ab)
DMSO-d_6
19F NMR



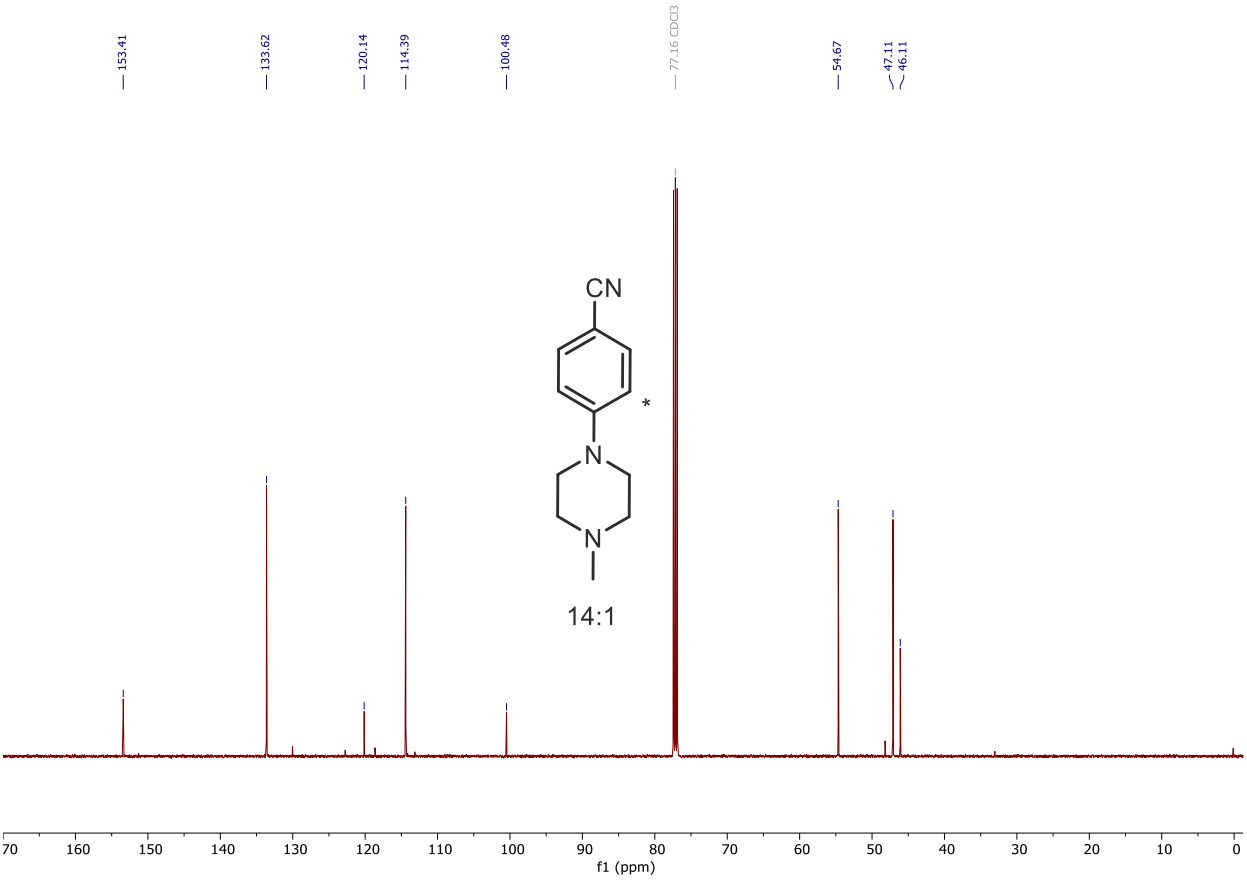
1-methyl-4-(4-cyanophenyl) piperazine (5b)

$CDCl_3$

1H NMR



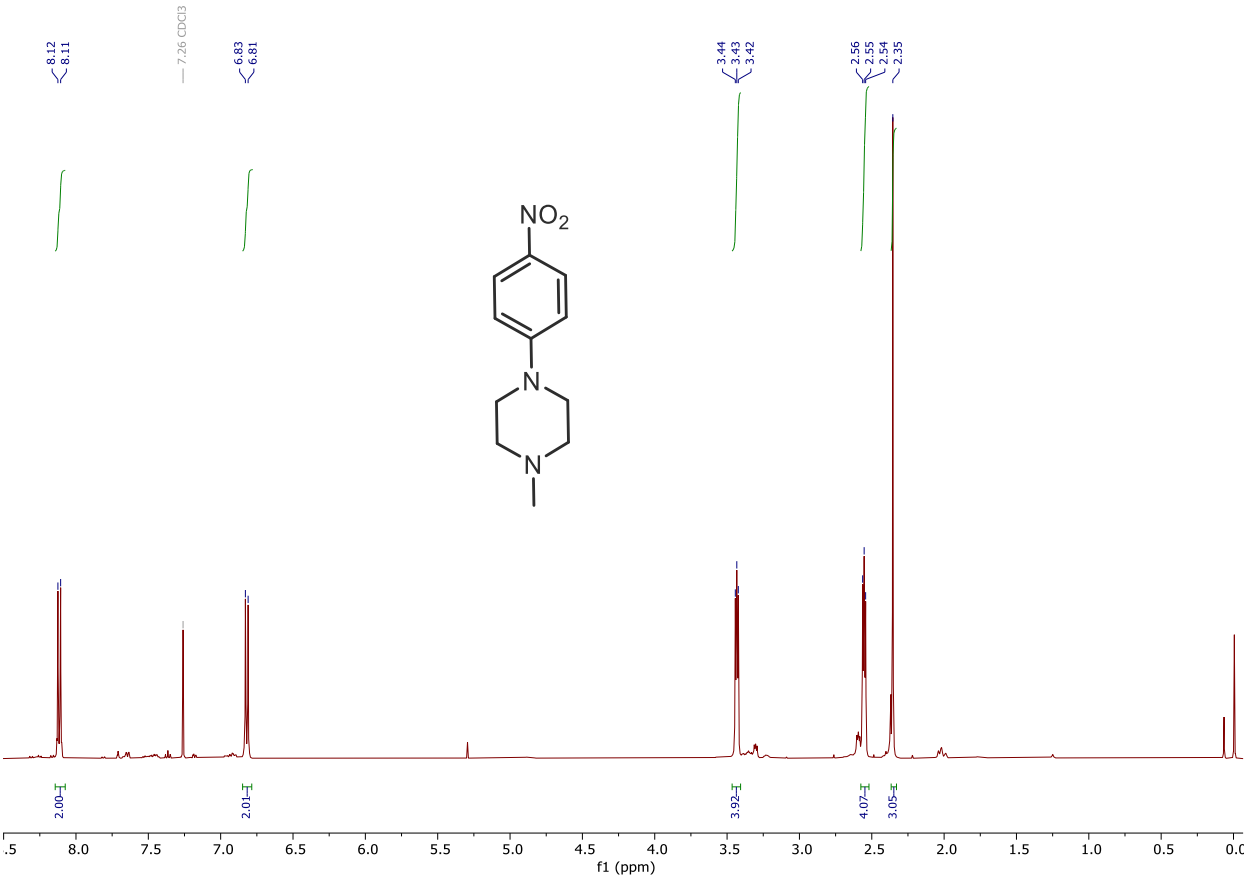
1-methyl-4-(4-cyanophenyl) piperazine (5b)
$CDCl_3$
13C NMR



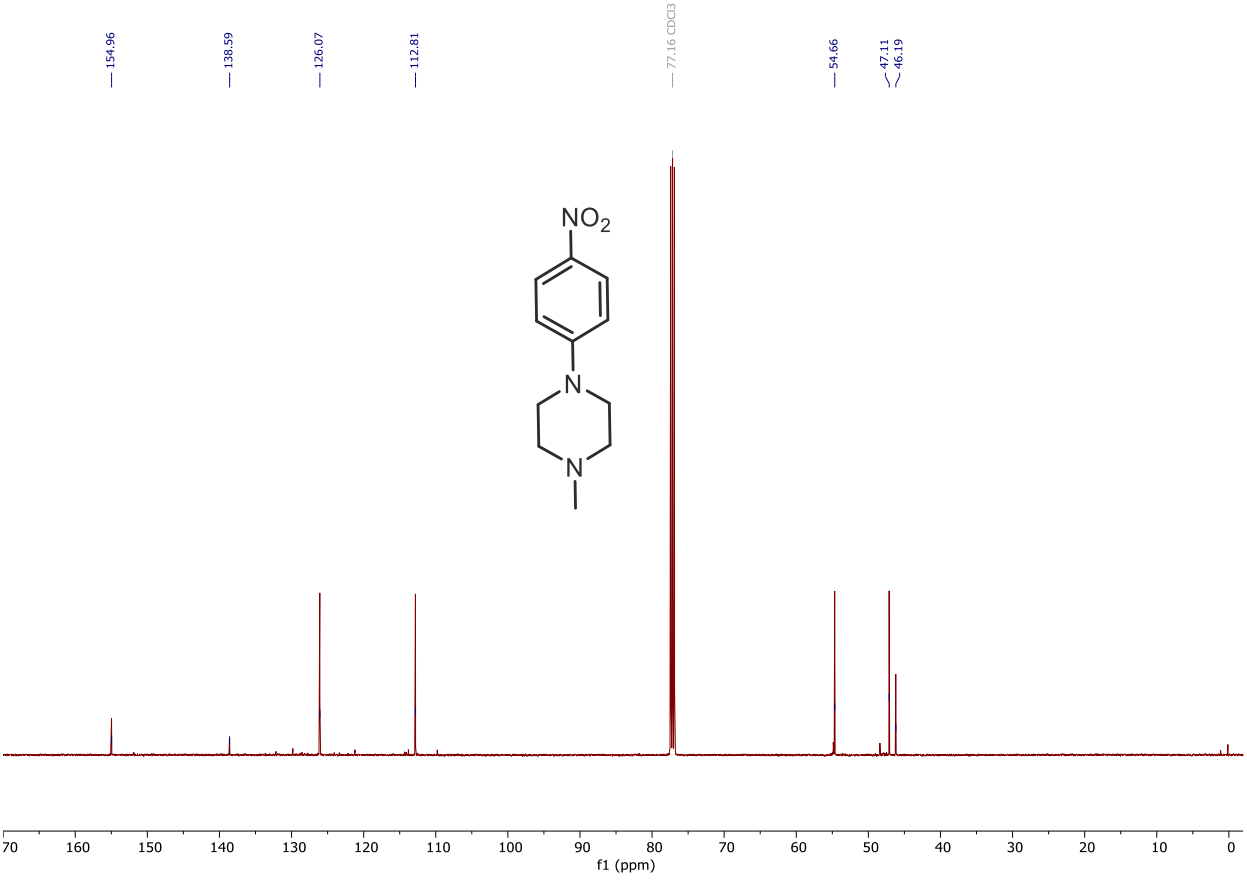
1-methyl-4-(4-nitrophenyl) piperazine (5c)

$CDCl_3$

1H NMR



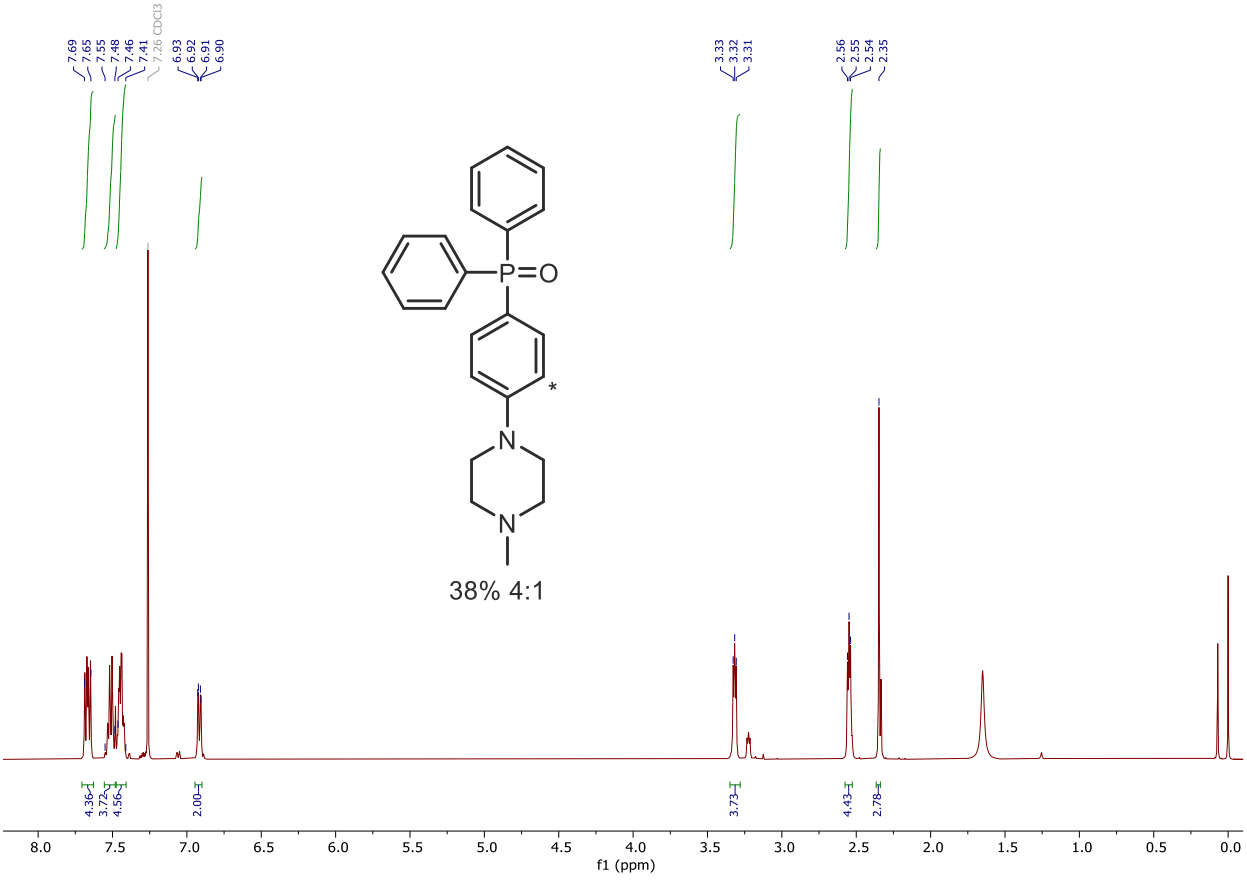
1-methyl-4-(4-nitrophenyl) piperazine (5c)
$CDCl_3$
13C NMR



Triphenyl phosphine oxide N-methyl piperazine (5d)

$CDCl_3$

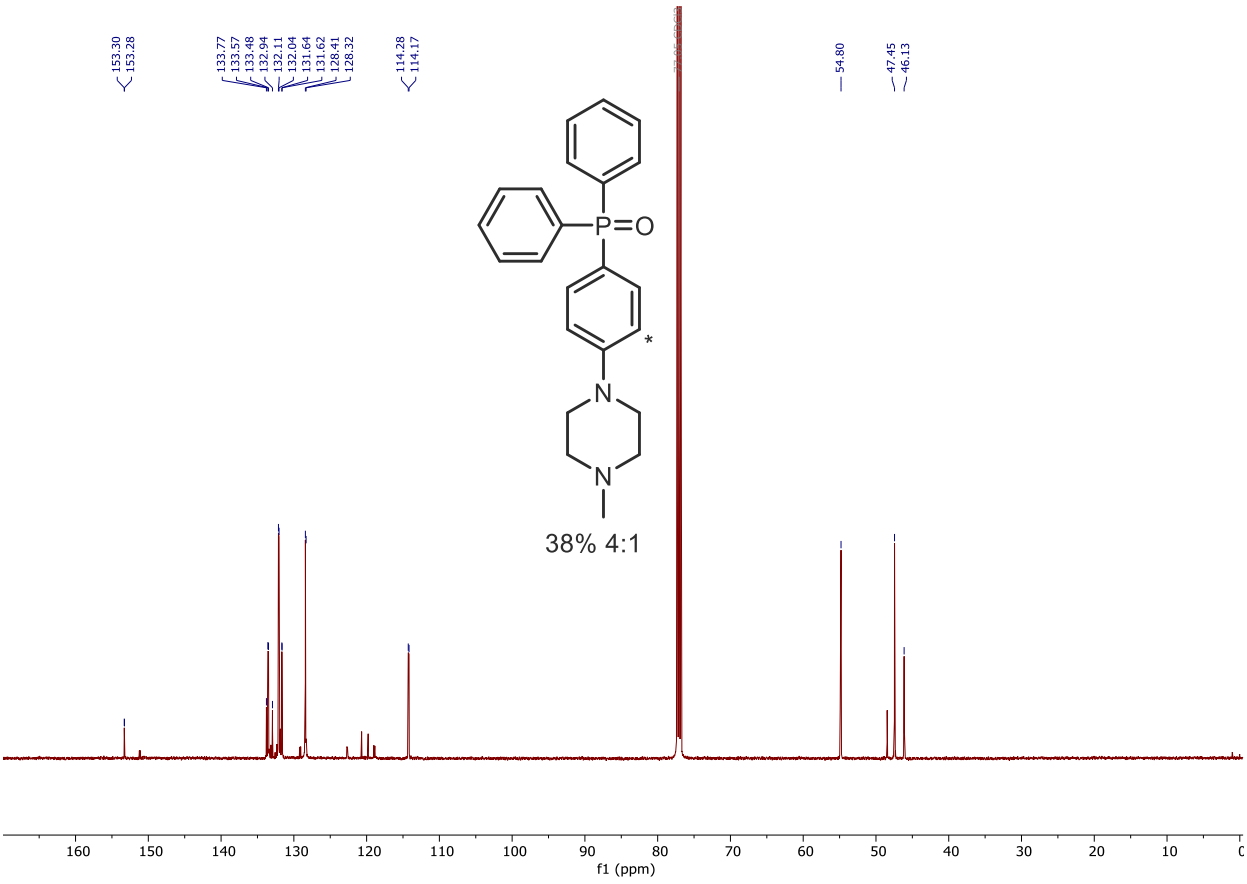
1H NMR



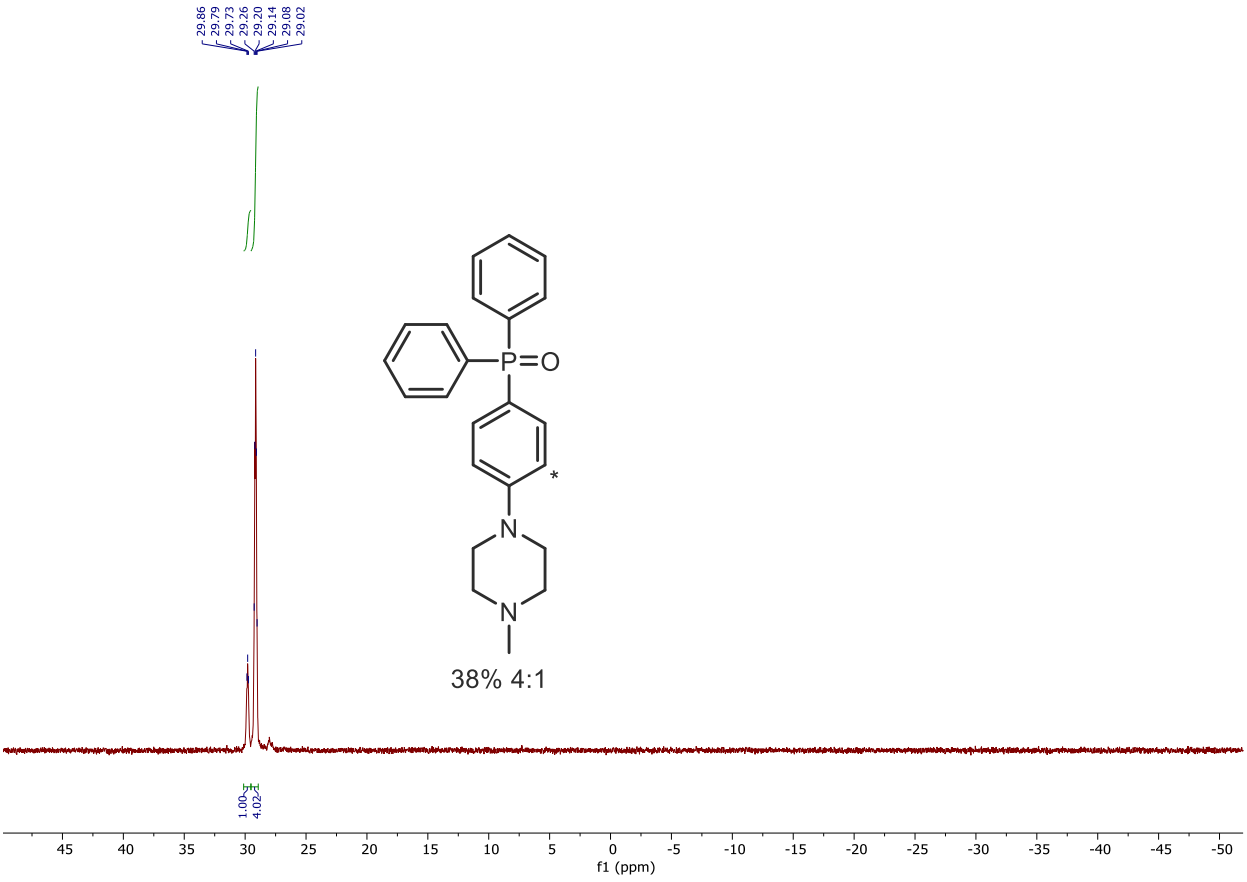
Triphenyl phosphine oxide N-methyl piperazine (5d)

$CDCl_3$

13C NMR



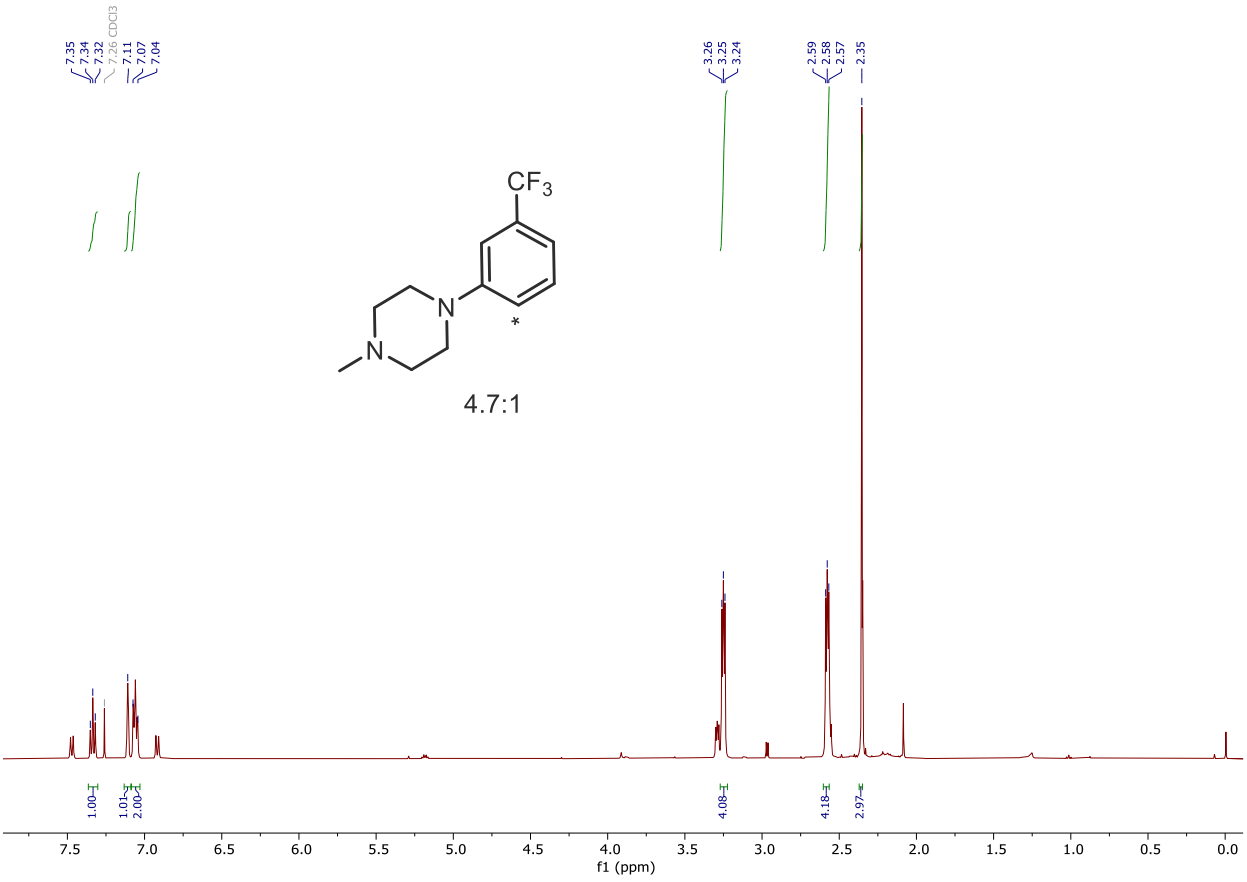
Triphenyl phosphine oxide N-methyl piperazine (5d)
$CDCl_3$
31P NMR



1-methyl-4-(3-trifluoromethylphenyl) piperazine (5e)

$CDCl_3$

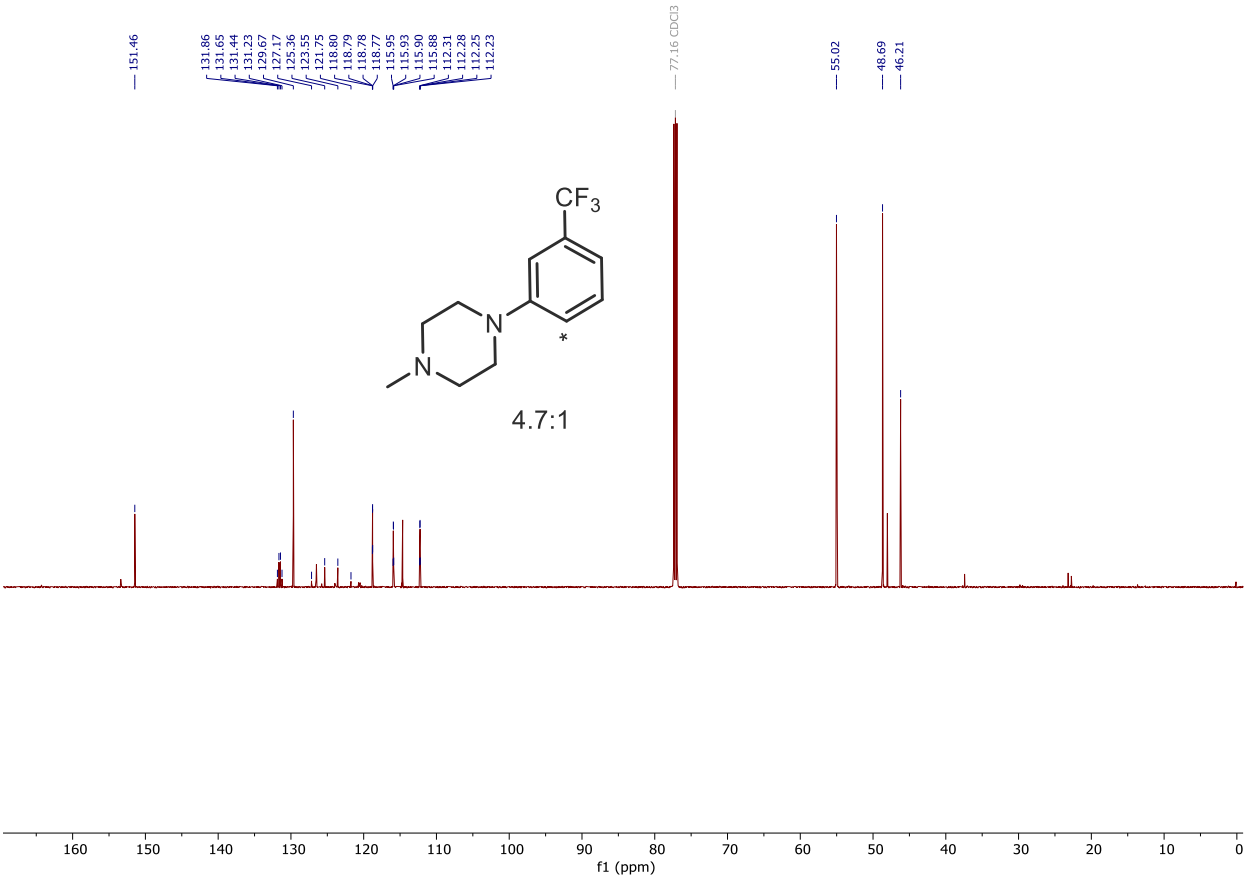
1H NMR



1-methyl-4-(3-trifluoromethylphenyl) piperazine (5e)

$CDCl_3$

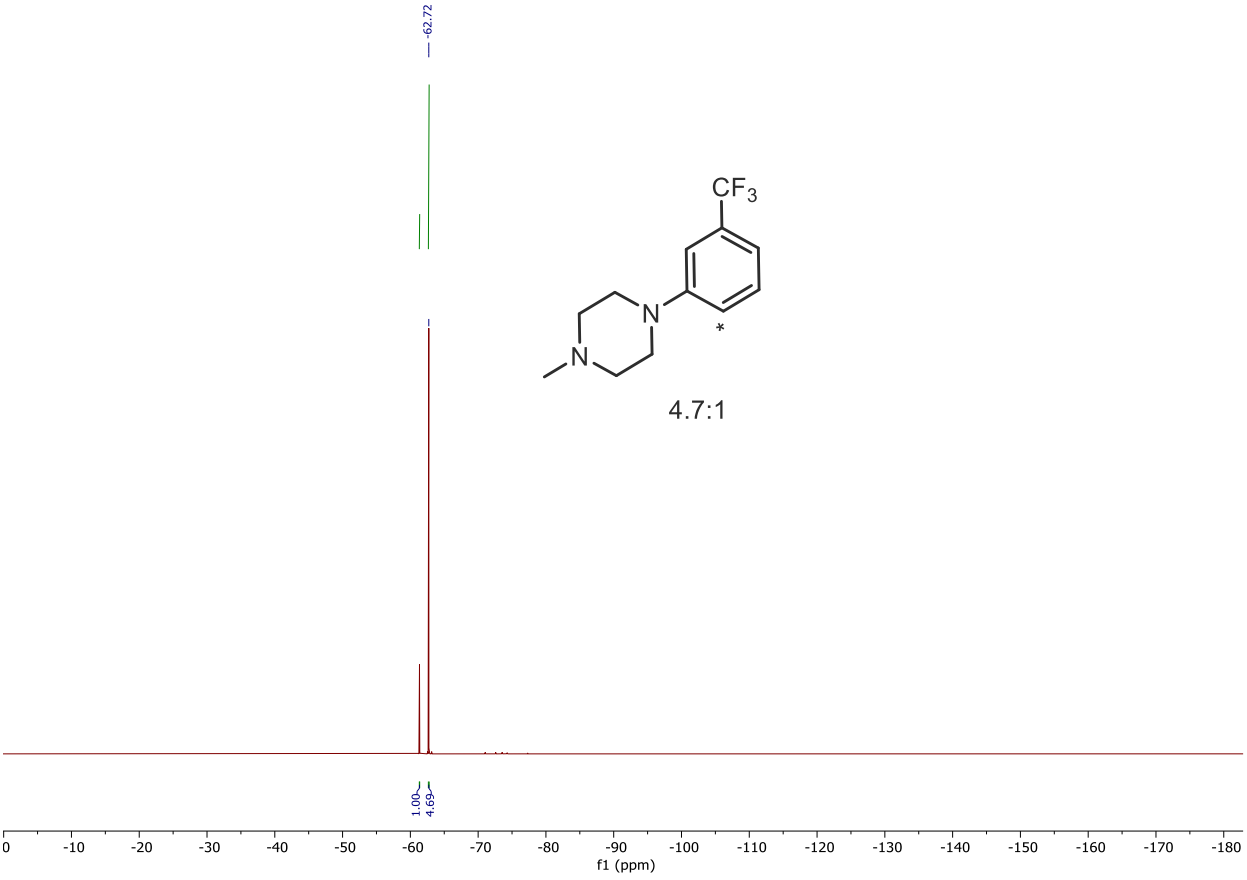
13C NMR



1-methyl-4-(3-trifluoromethylphenyl) piperazine (5e)

$CDCl_3$

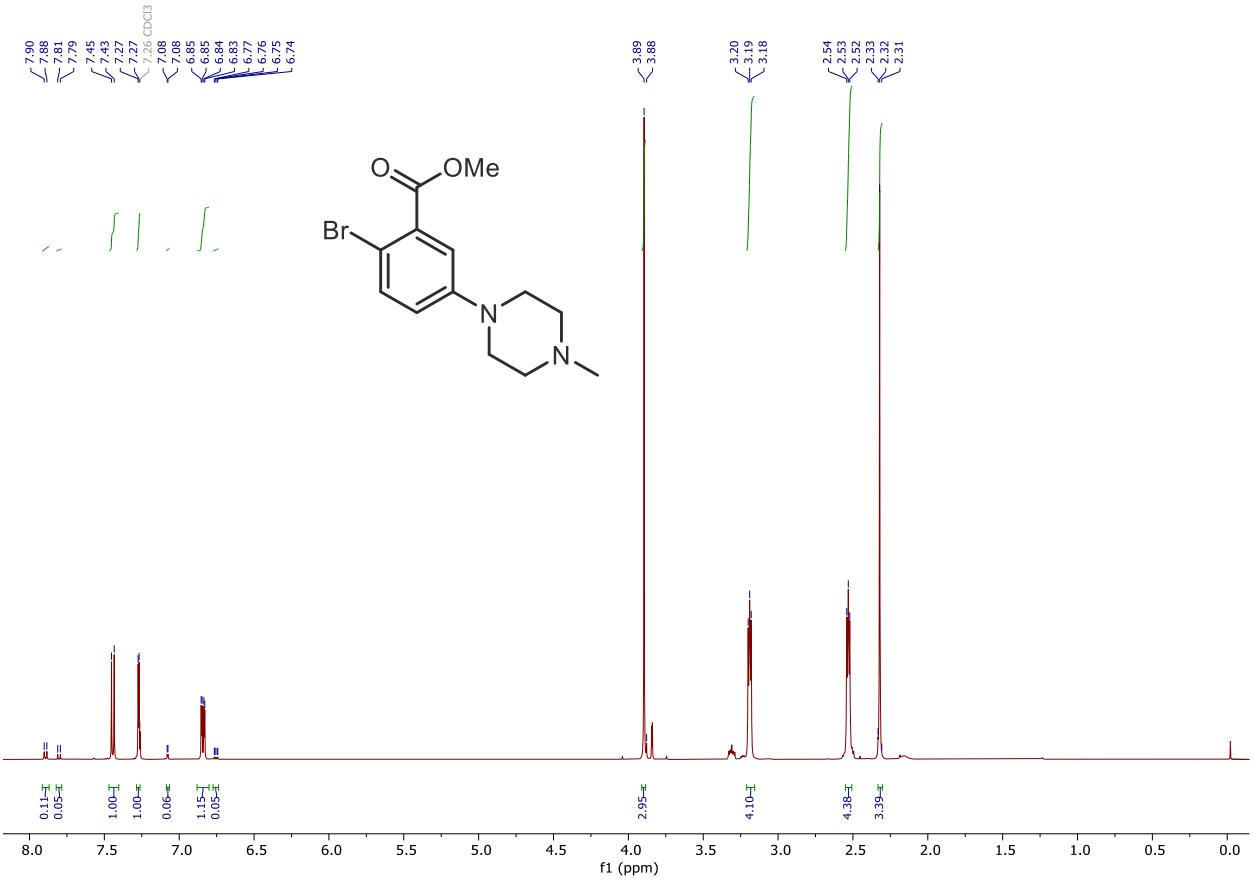
19F NMR



Methyl-2-bromobenzoate piperazine (5f)

$CDCl_3$

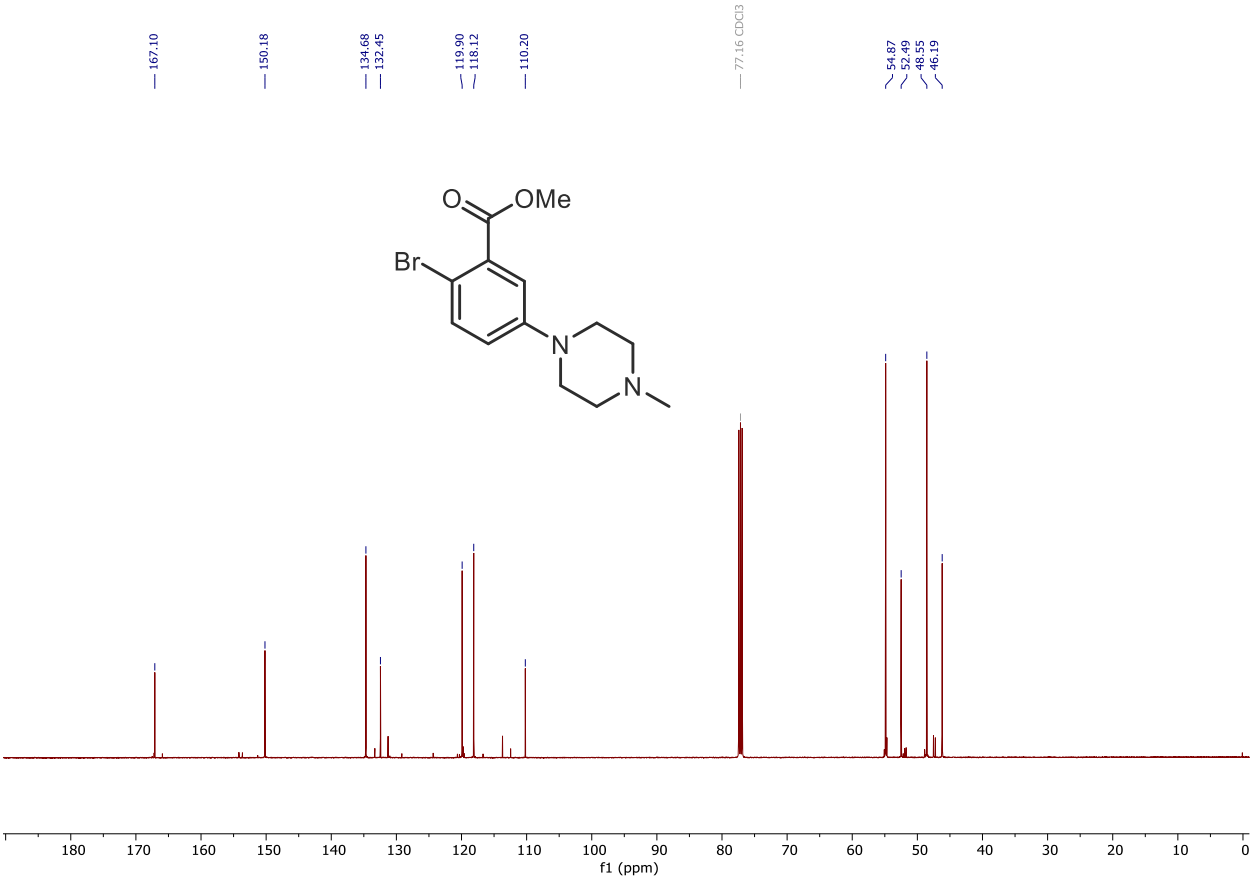
1H NMR



Methyl-2-bromobenzoate piperazine (5f)

$CDCl_3$

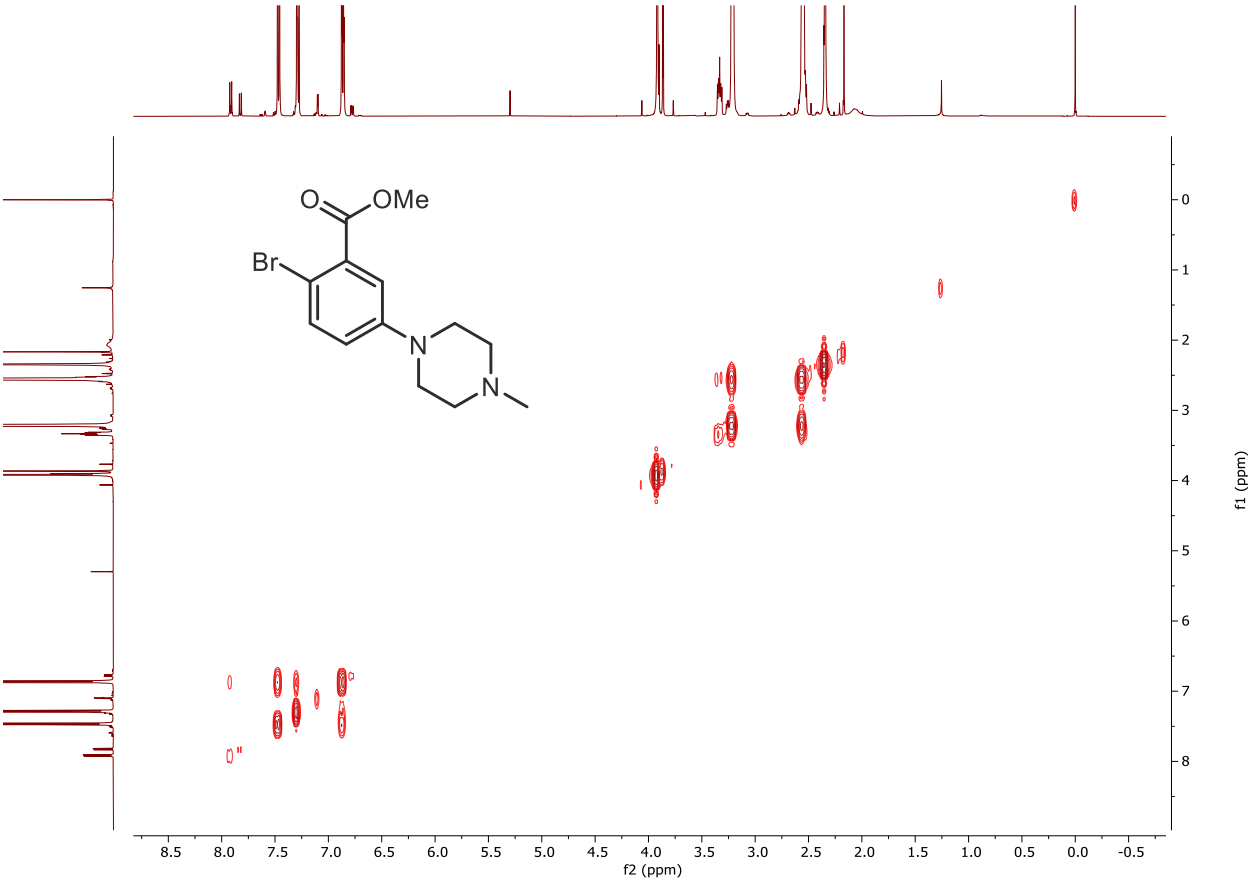
13C NMR



Methyl-2-bromobenzoate piperazine (5f)

$CDCl_3$

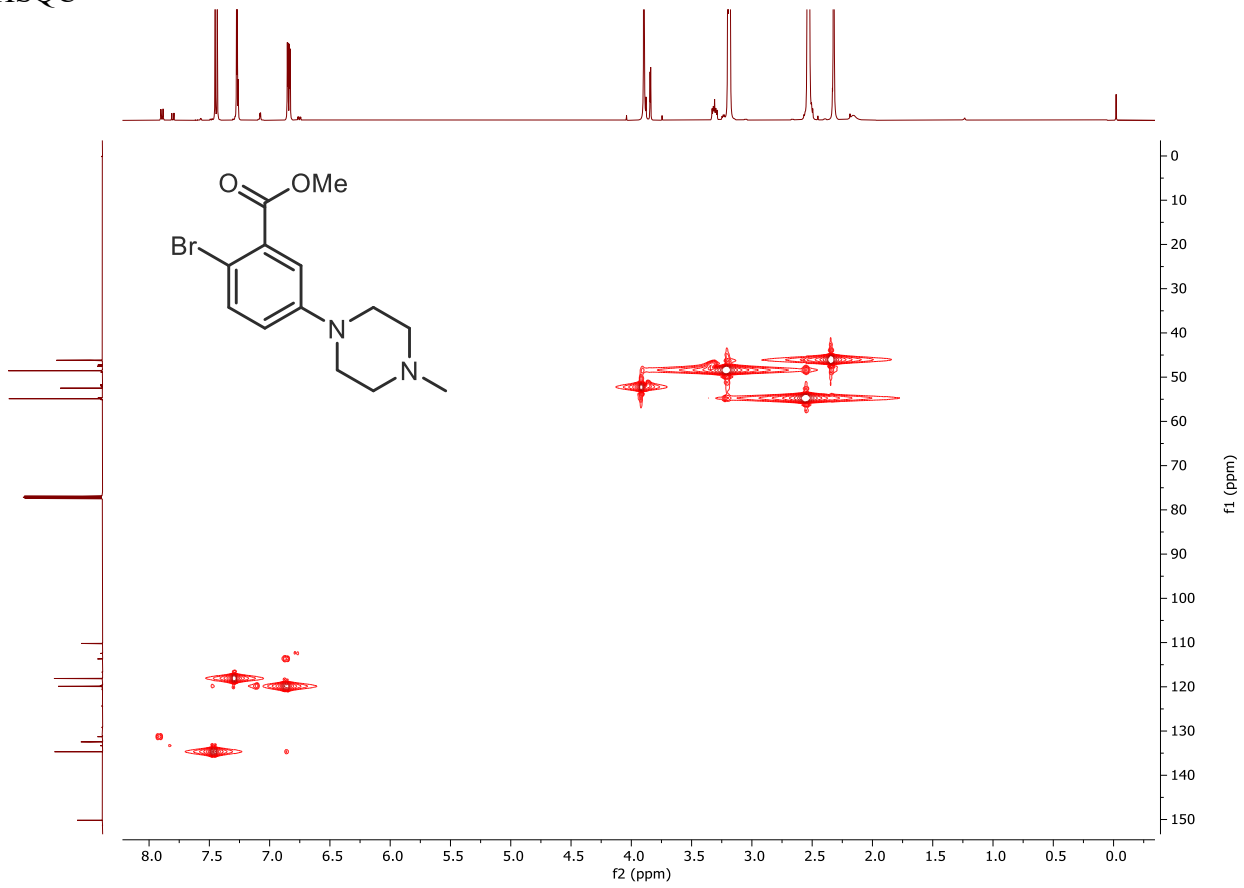
COSY



Methyl-2-bromobenzoate piperazine (5f)

$CDCl_3$

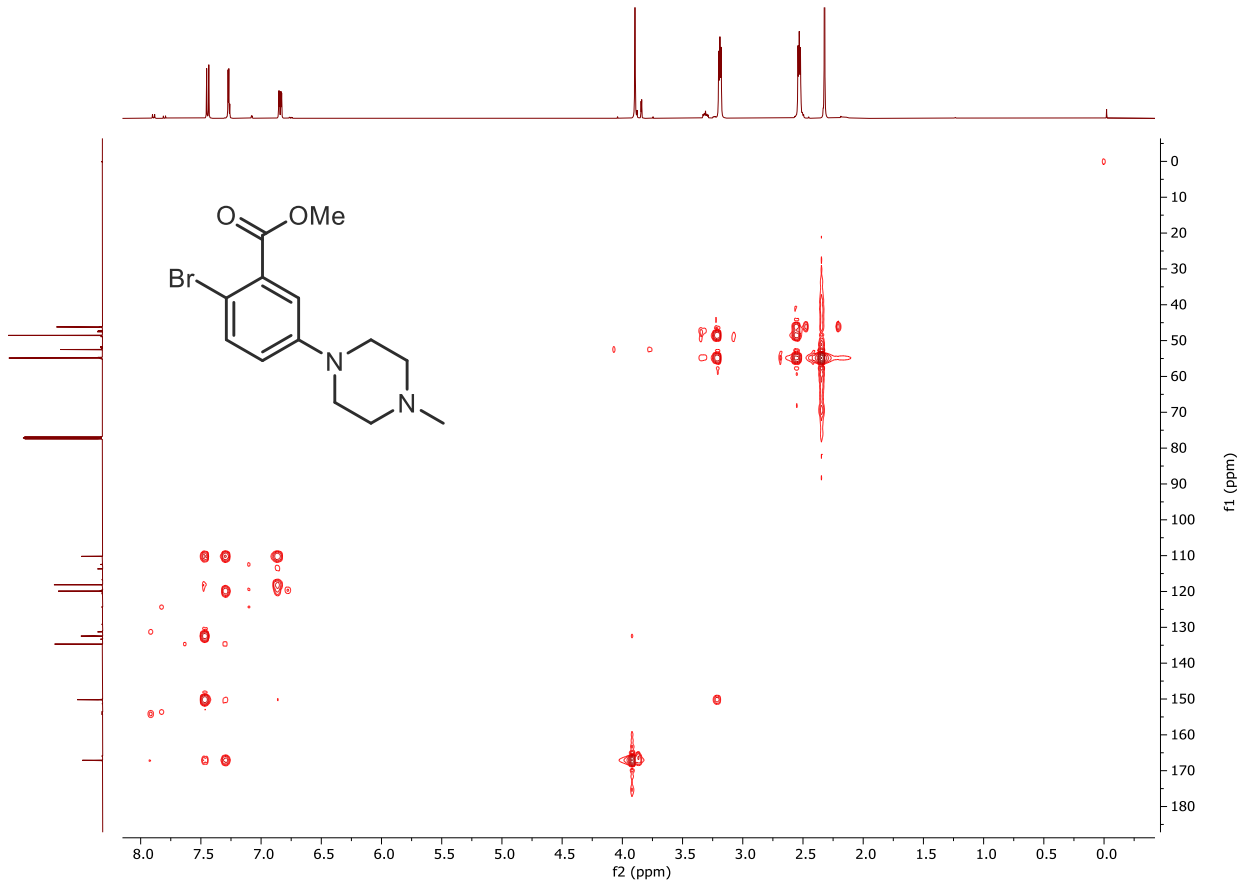
HSQC



Methyl-2-bromobenzoate piperazine (5f)

$CDCl_3$

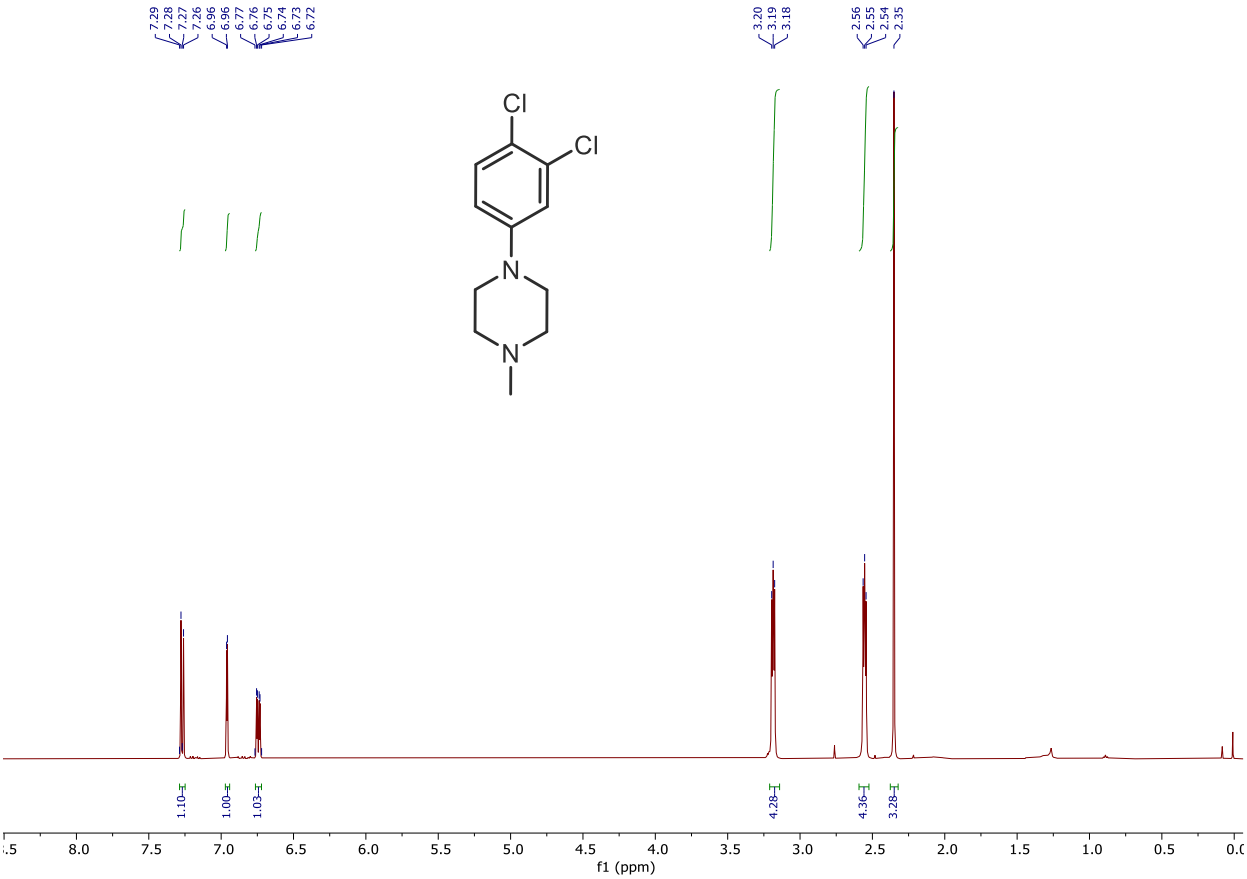
HMBC



1-methyl-4-(3,4-dichlorophenyl) piperazine (5g)

$CDCl_3$

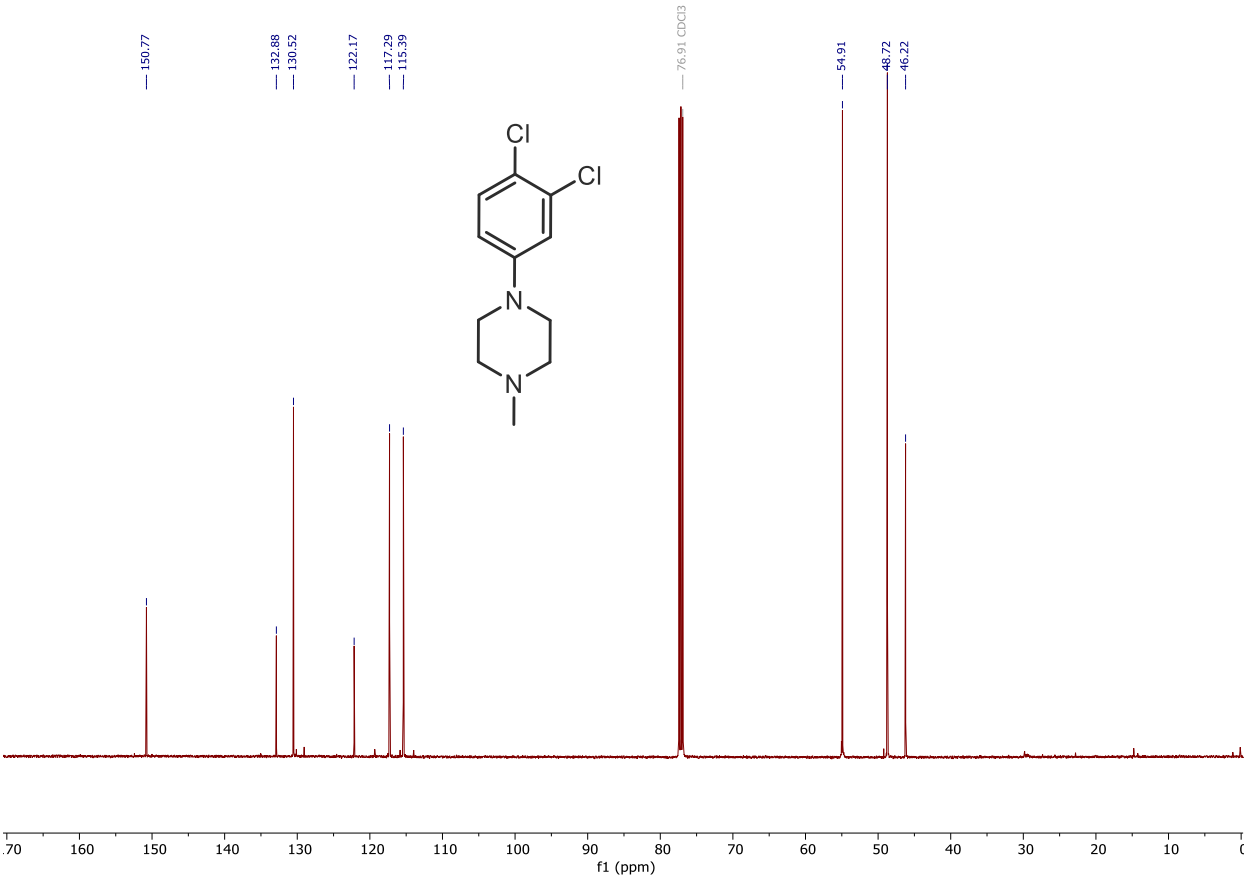
1H NMR



1-methyl-4-(3,4-dichlorophenyl) piperazine (5g)

$CDCl_3$

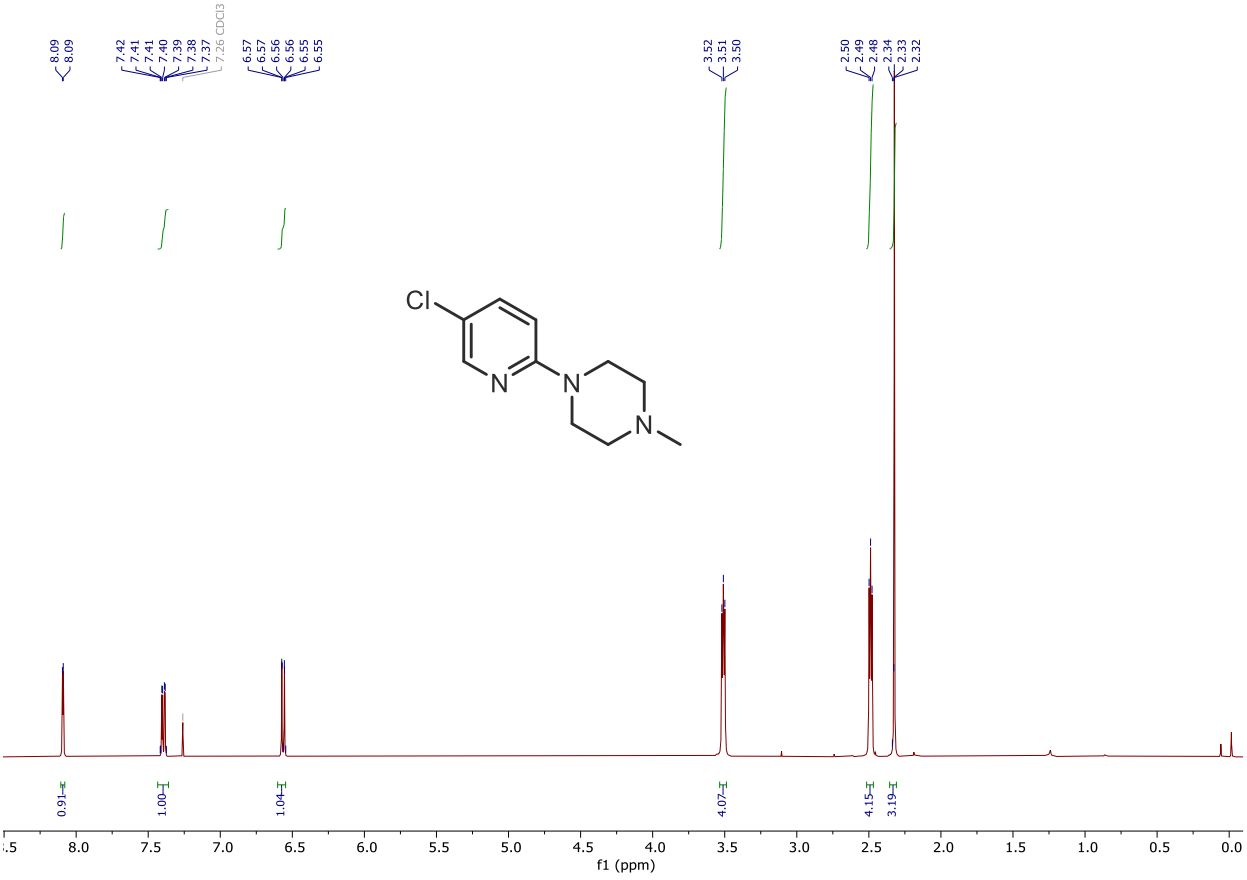
13C NMR



3-chloropyridine N-methyl piperazine (5h)

$CDCl_3$

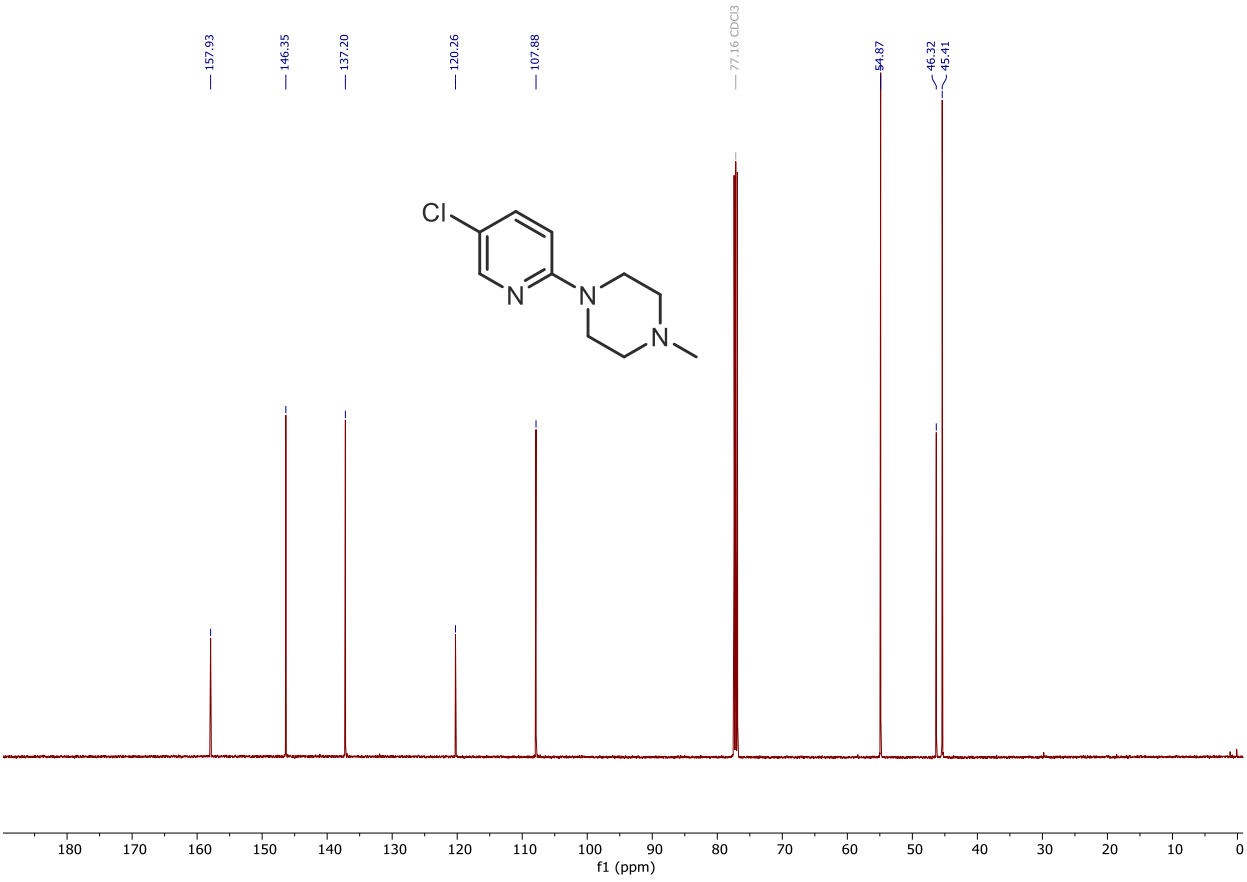
1H NMR



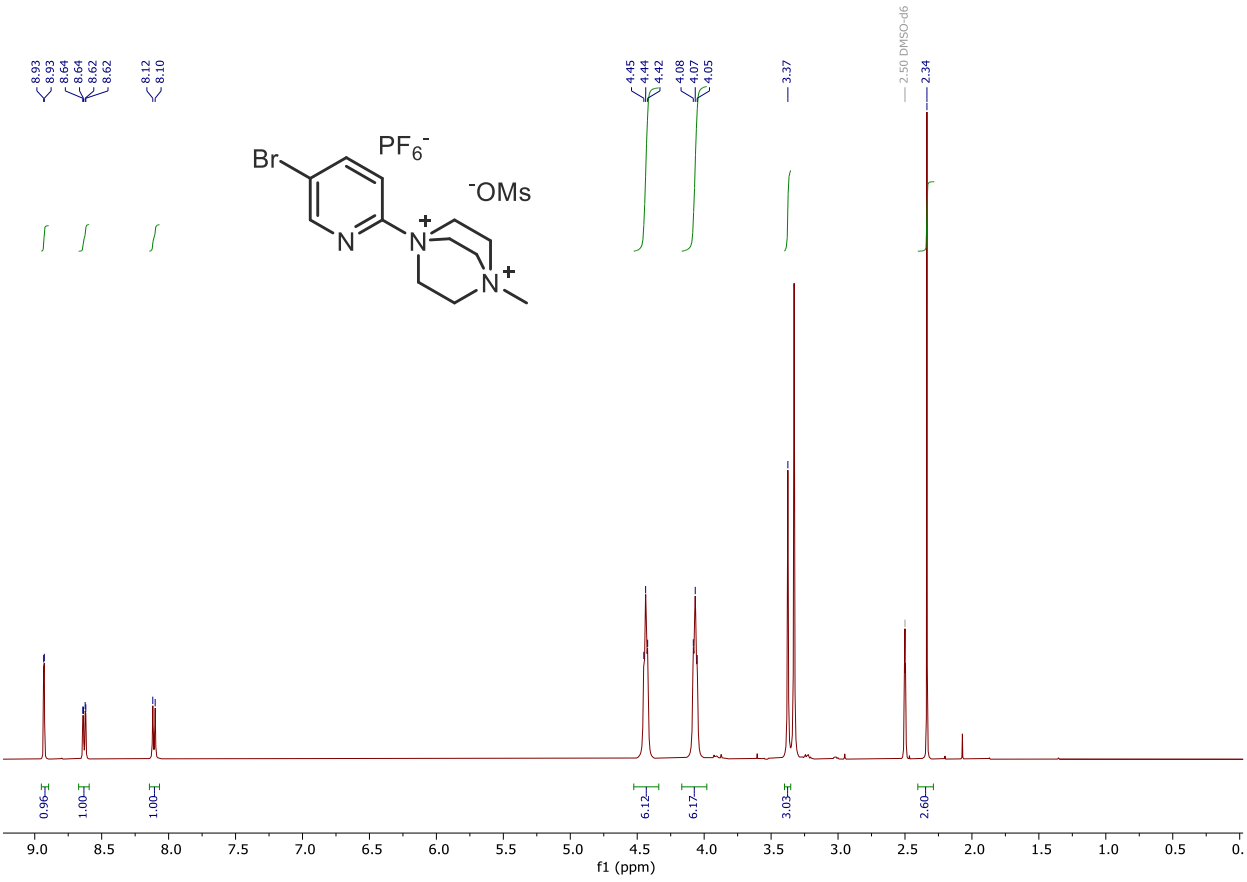
3-chloropyridine N-methyl piperazine (5h)

$CDCl_3$

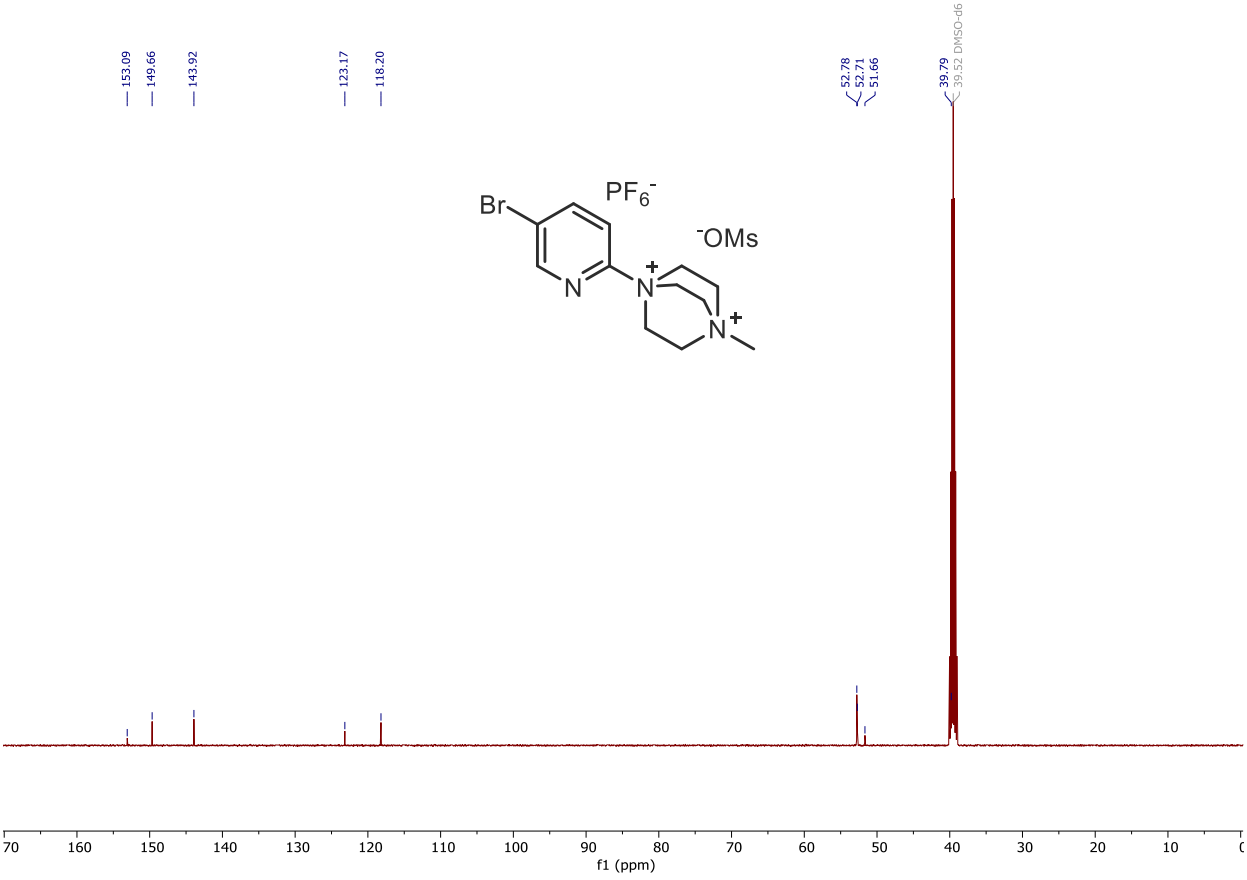
13C NMR



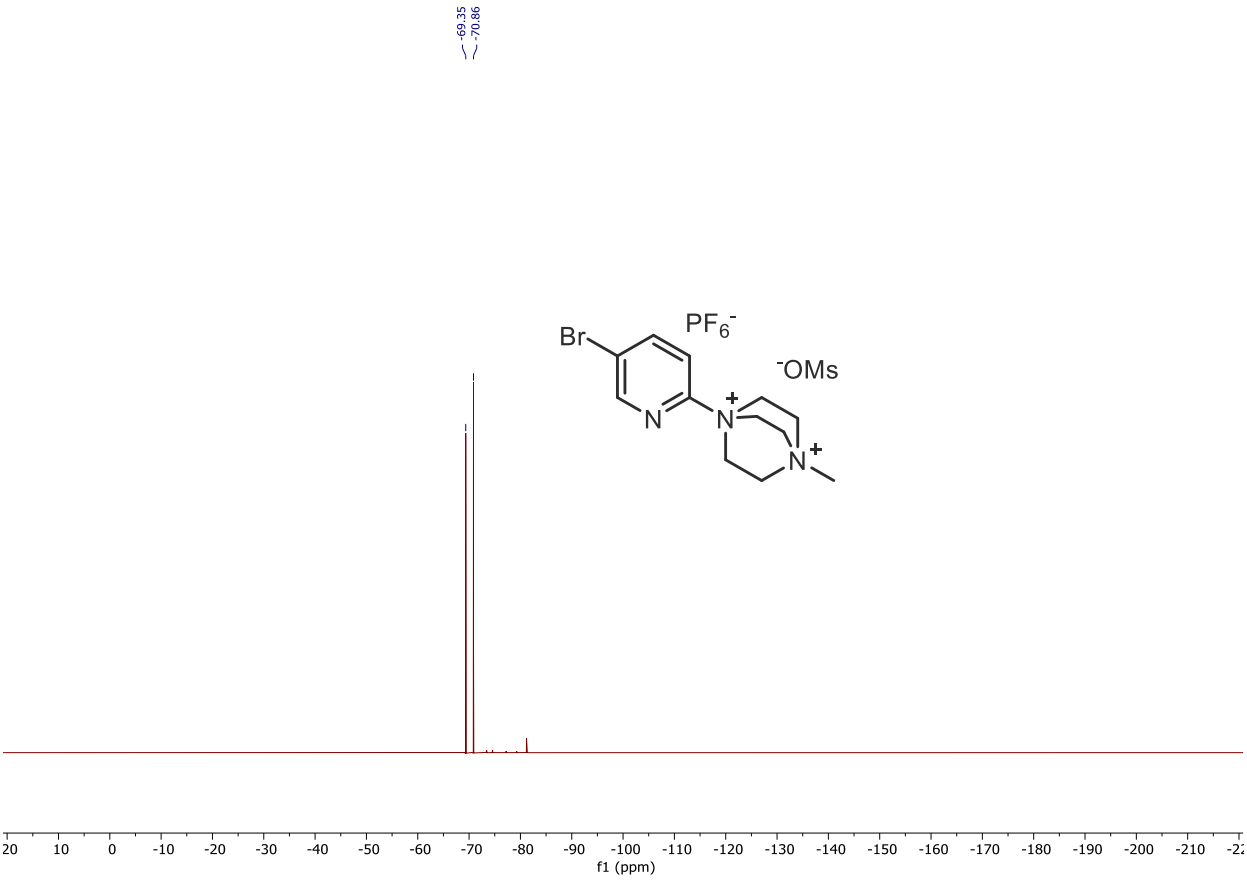
3-Br pyridine DABCOnium salt (2i)
DMSO-d_6
1H NMR



3-Br pyridine DABCOnium salt (2i)
DMSO-d_6
13C NMR



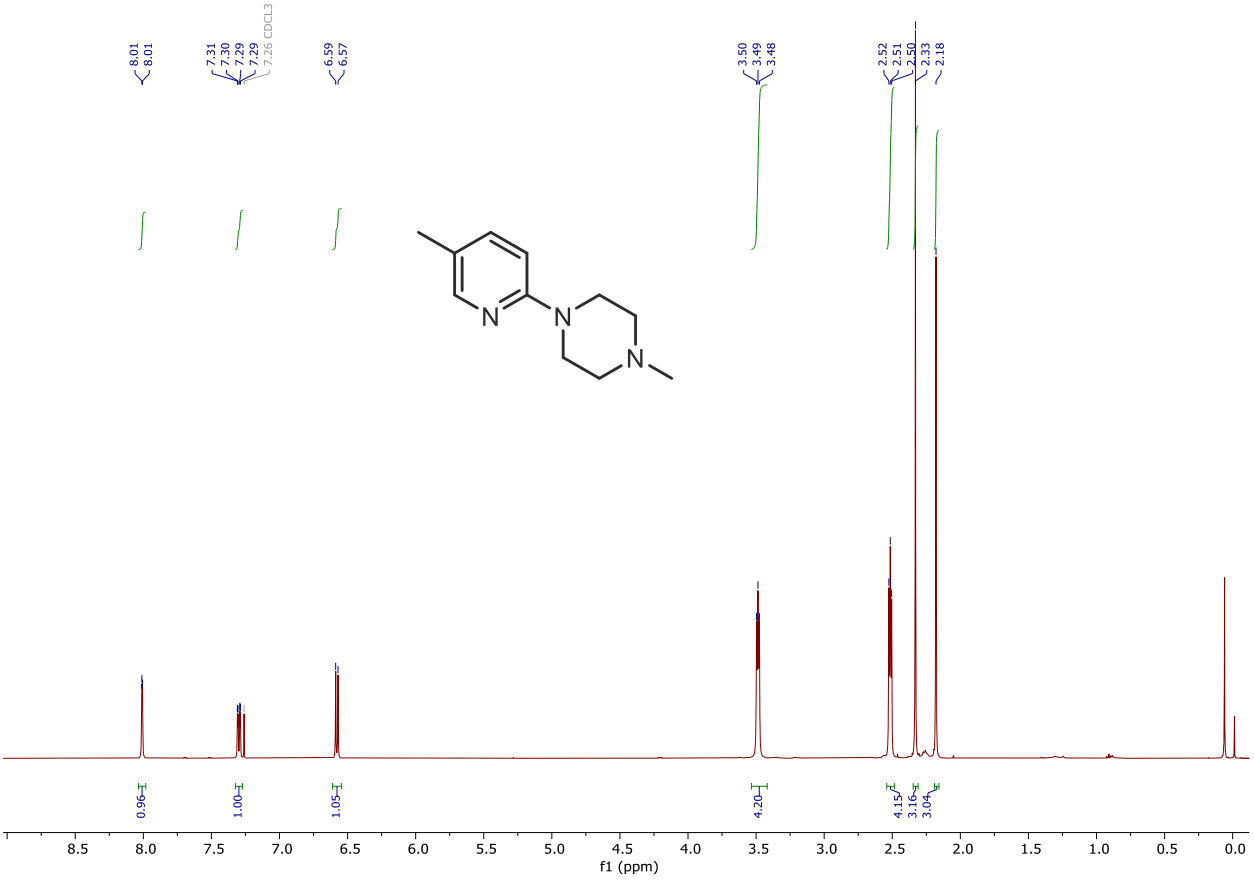
3-Br pyridine DABCOnium salt (2i)
DMSO-d_6
19F NMR



3-picoline N-methyl piperazine (5j)

$CDCl_3$

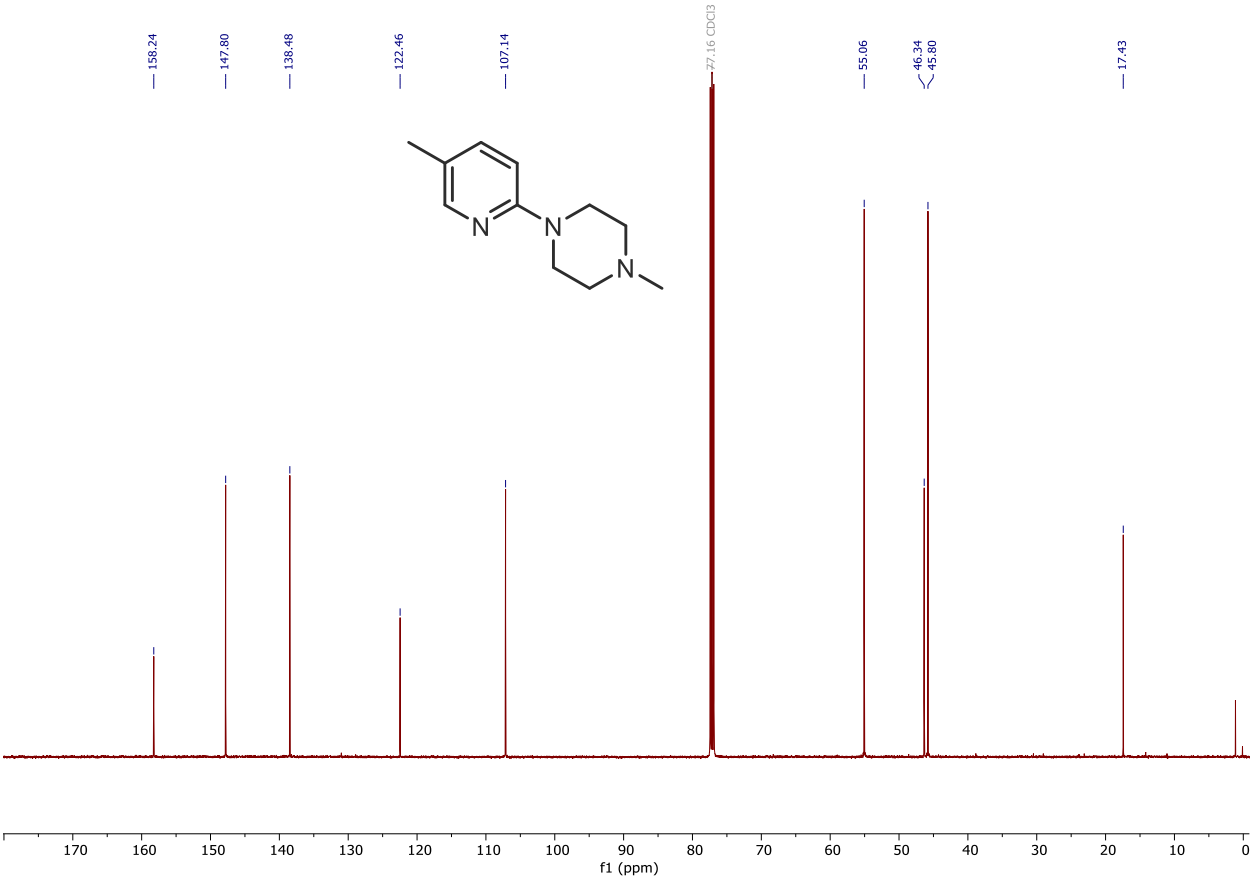
1H NMR



3-picoline N-methyl piperazine (5j)

$CDCl_3$

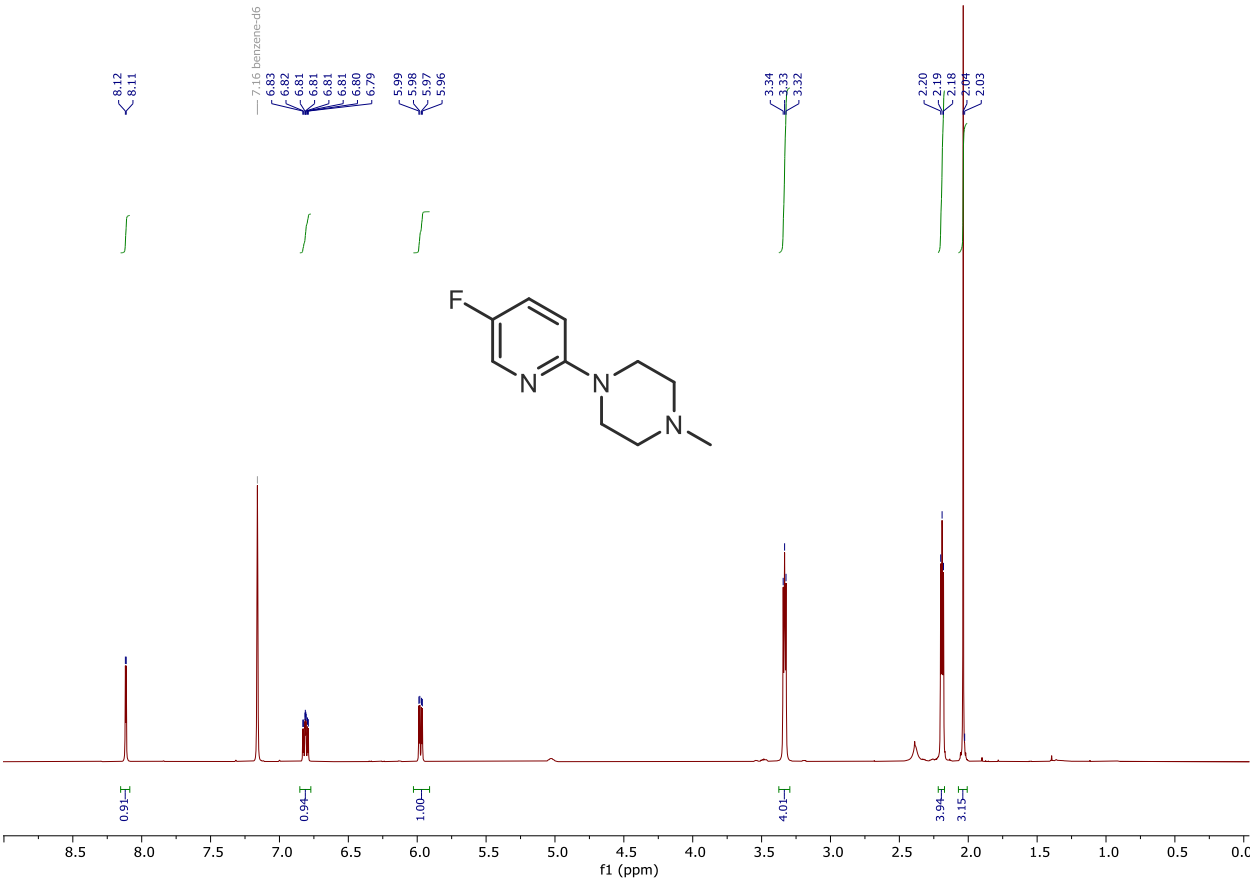
13C NMR



3-fluoropyridine N-methyl piperazine (5j)

C_6D_6

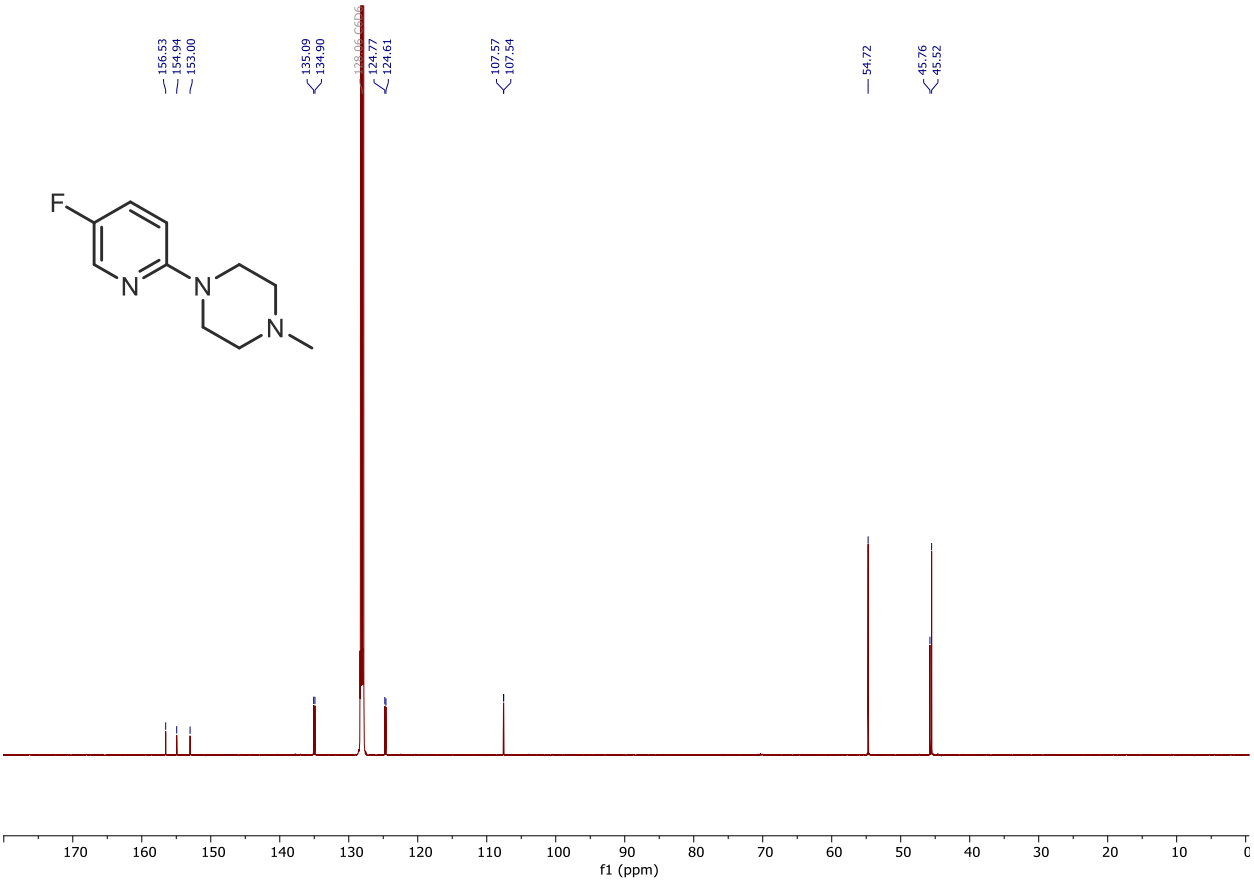
1H NMR



3-fluoropyridine N-methyl piperazine (5j)

C_6D_6

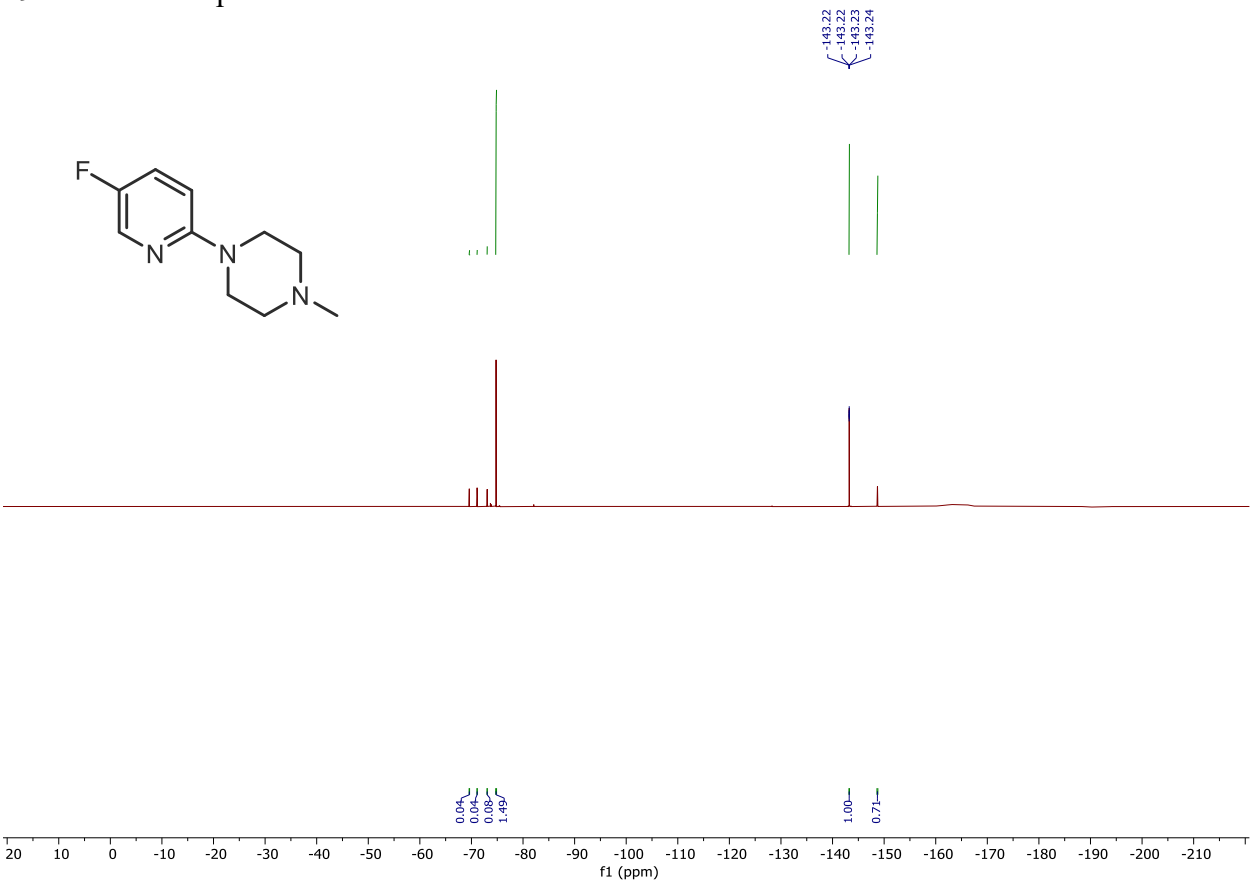
13C NMR



3-fluoropyridine N-methyl piperazine (5j)

C_6D_6

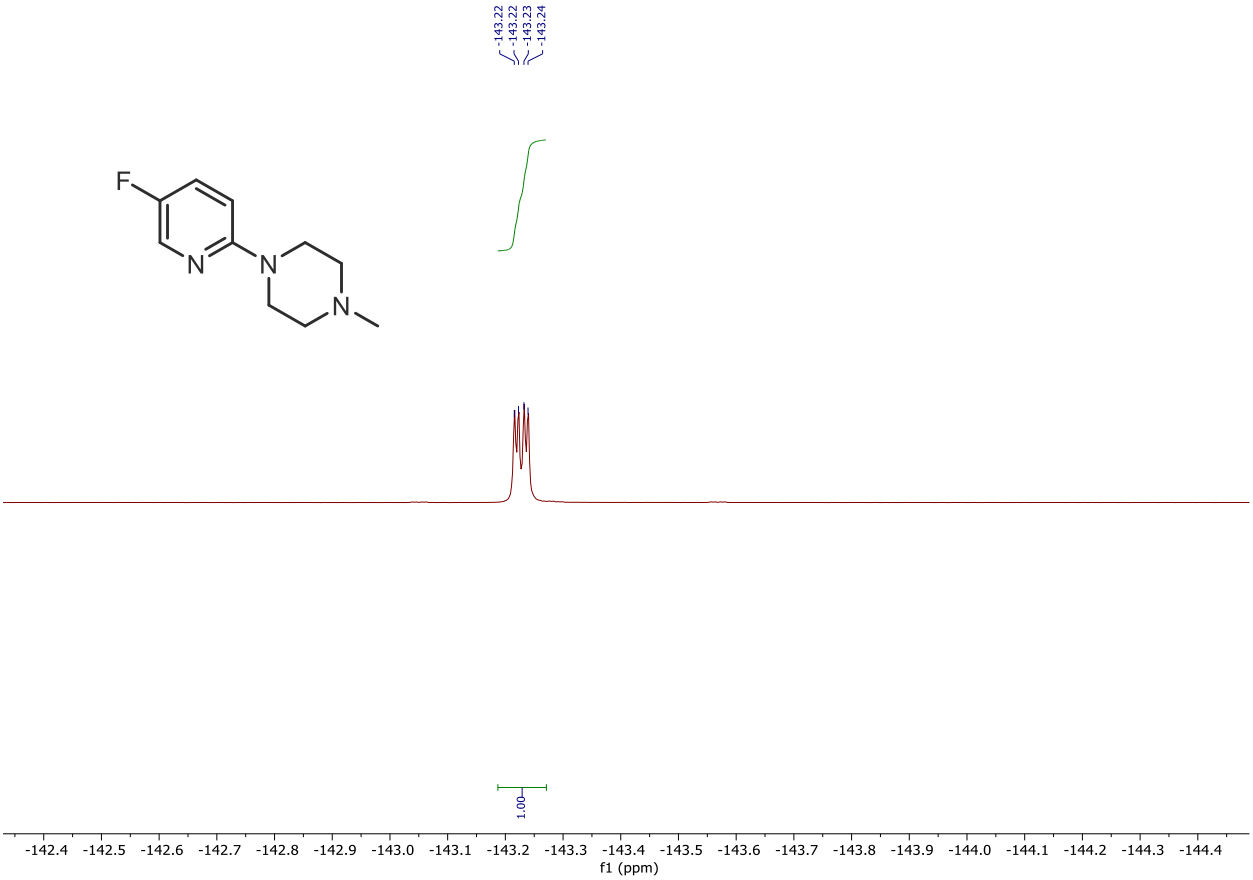
19F NMR-Full spectrum



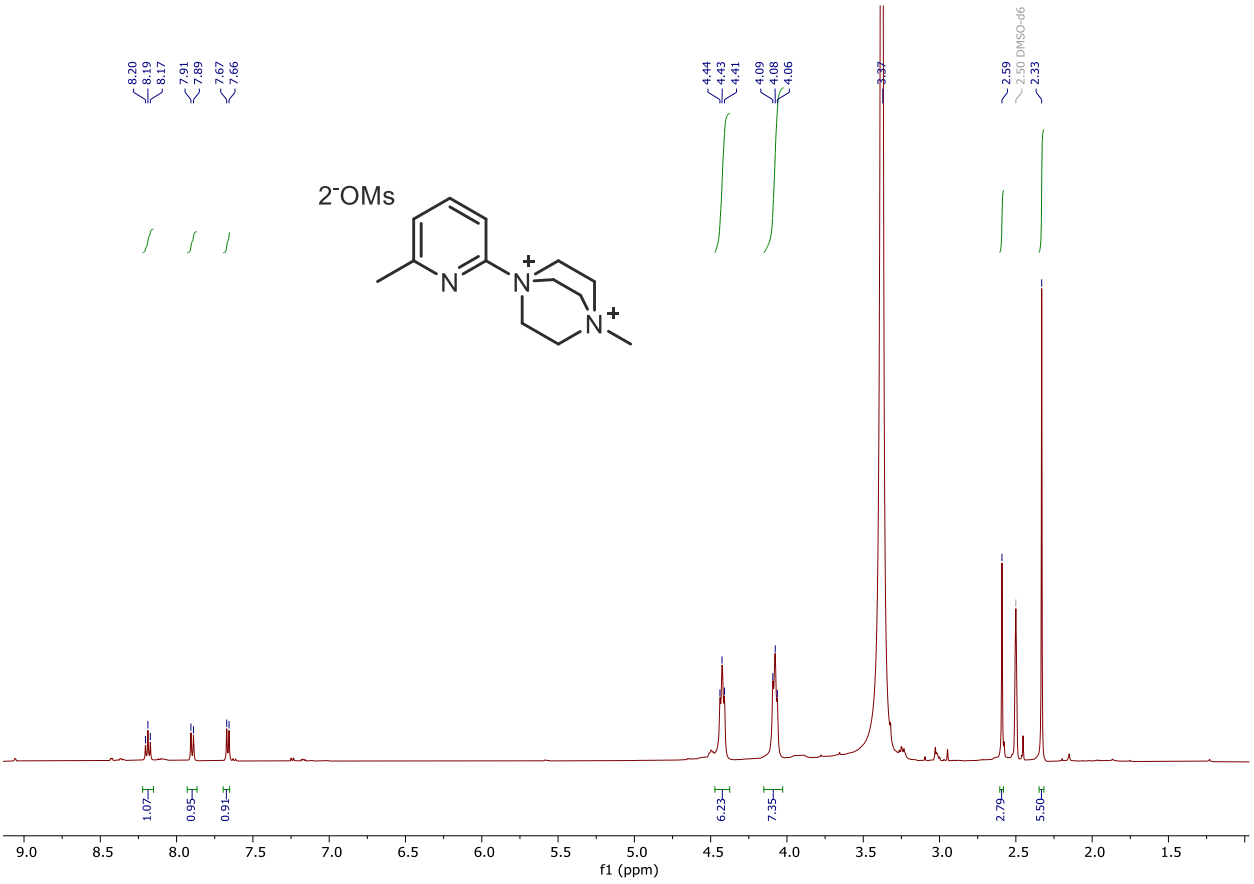
3-fluoropyridine N-methyl piperazine (5j)

C_6D_6

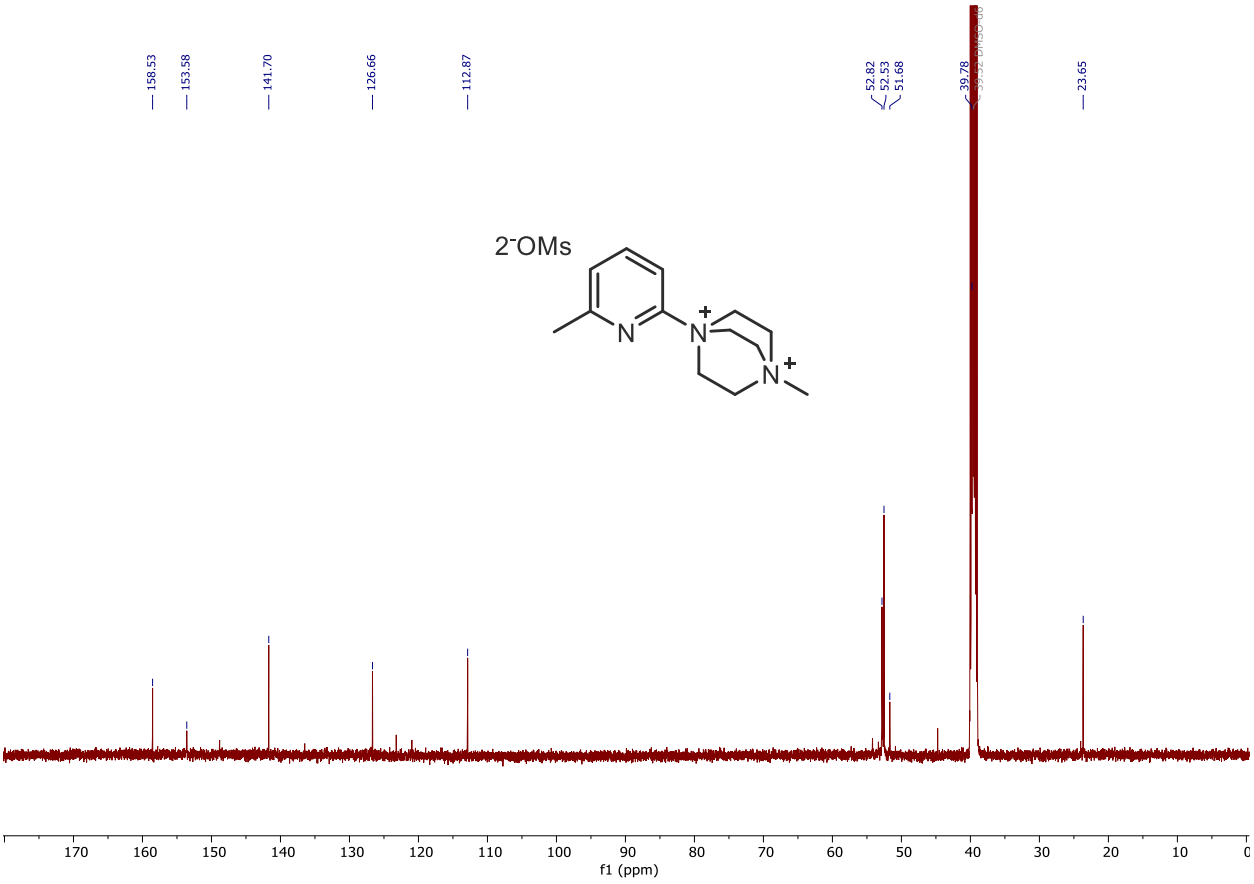
19F NMR-zoomed



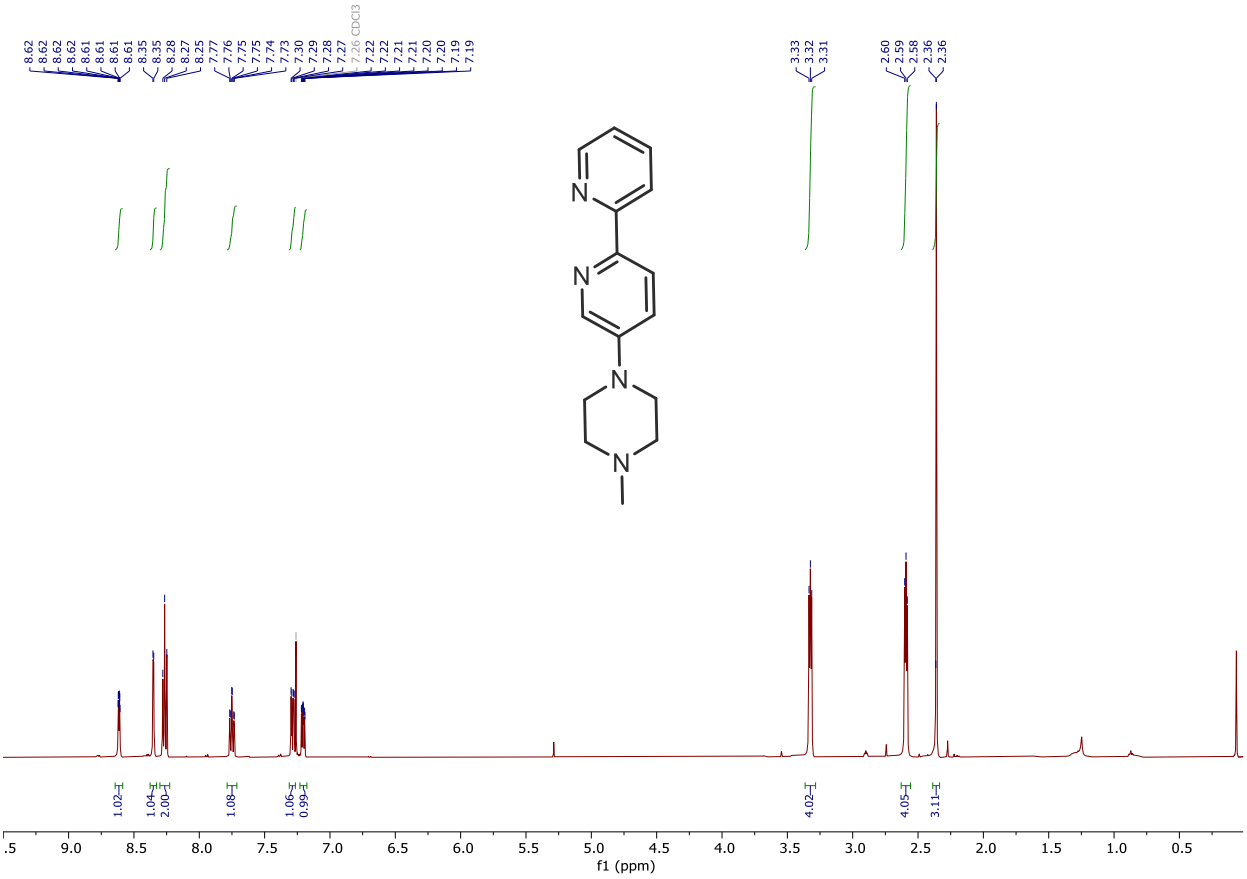
2-picoline DABCOnium salt (2l)
DMSO-d_6
1H NMR



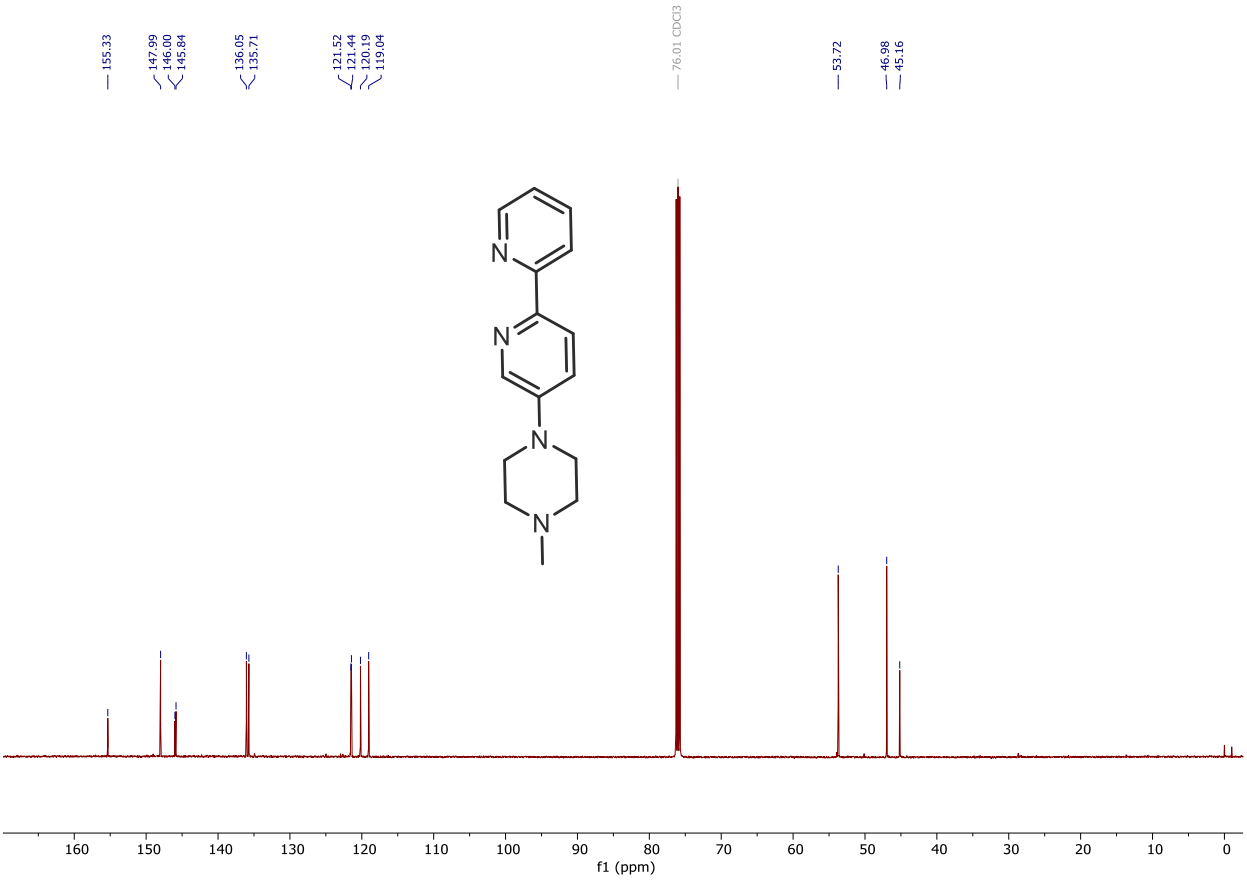
2-picoline DABCOnium salt (2l)
DMSO-d_6
13C NMR



Bipyridine N-methyl piperazine (5m)
$CDCl_3$
1H NMR



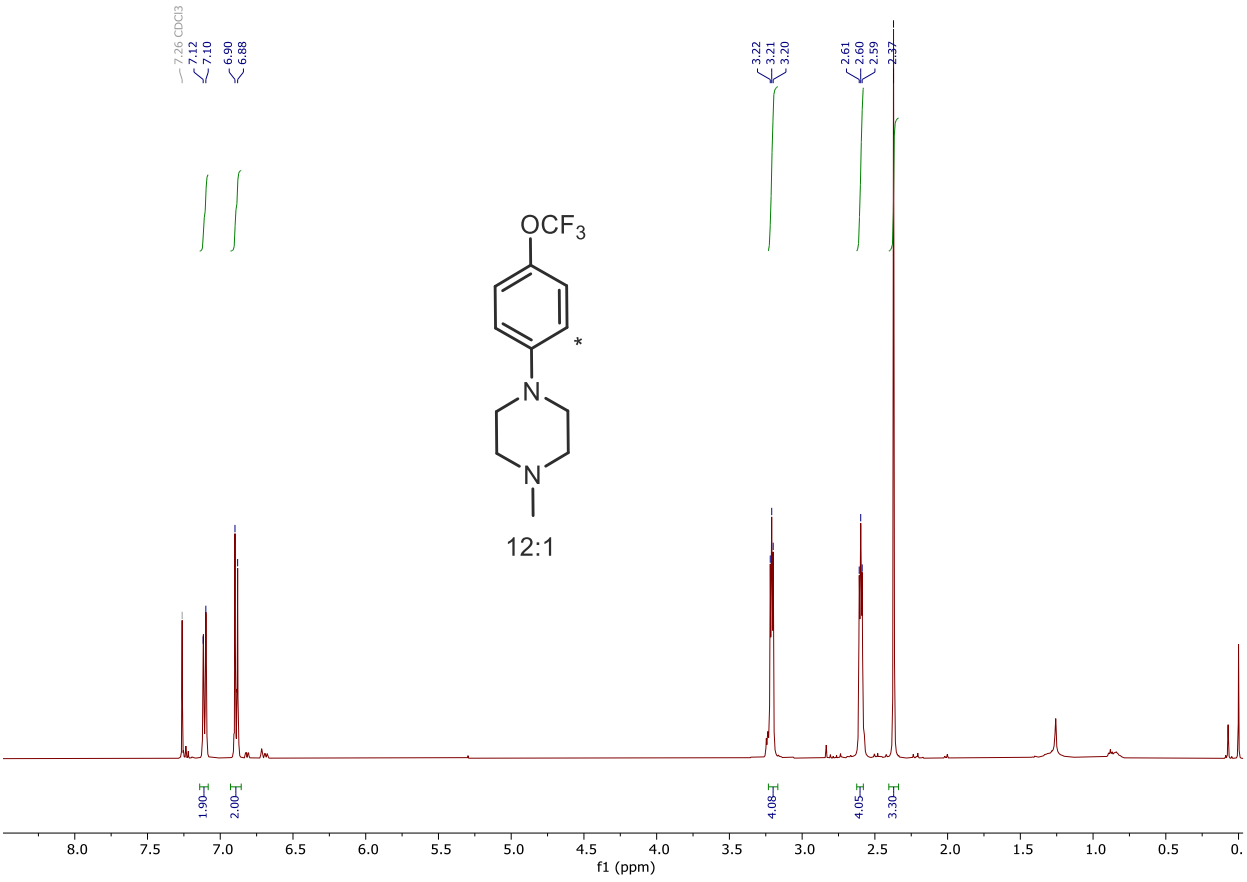
Bipyridine N-methyl piperazine (5m)
$CDCl_3$
13C NMR



1-methyl-4-(4-trifluoromethoxyphenyl) piperazine (5n)

$CDCl_3$

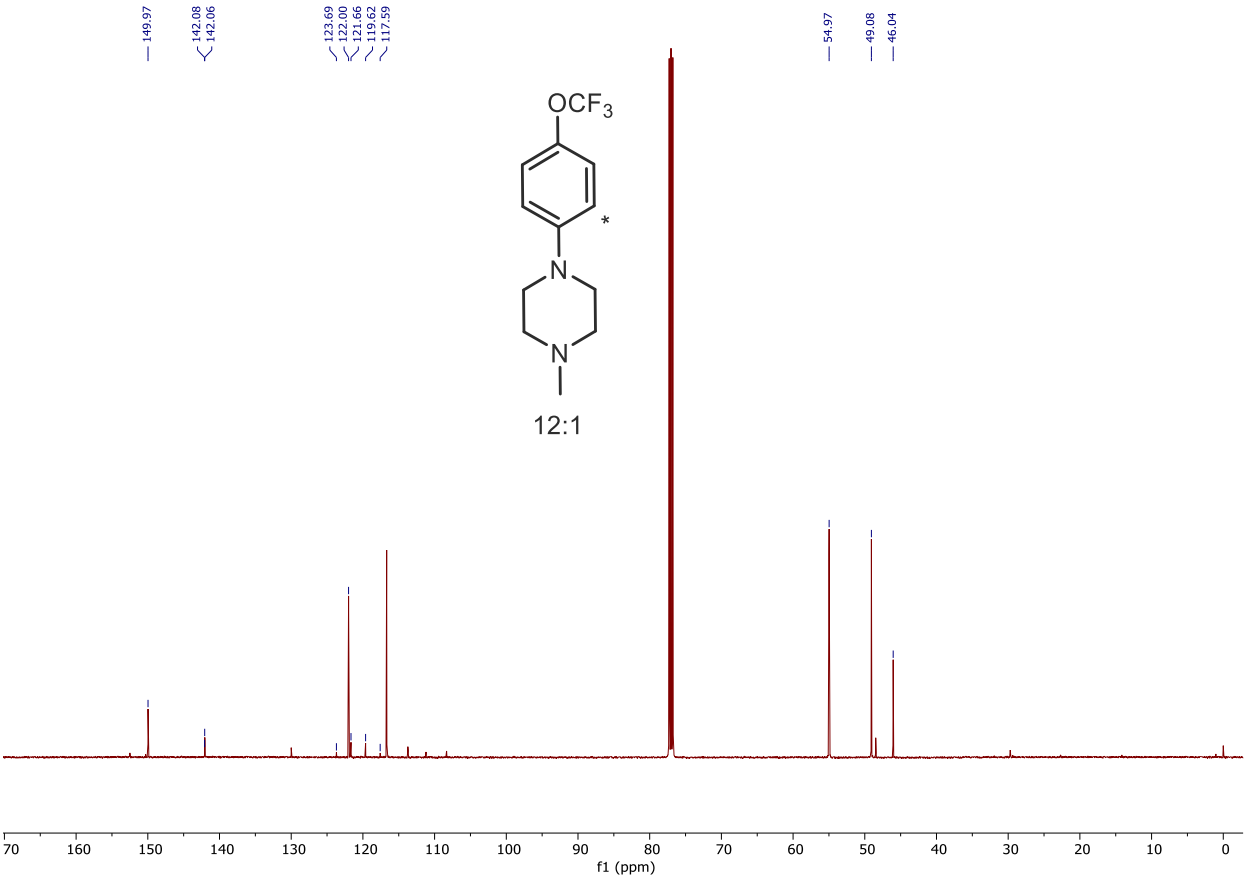
1H NMR



1-methyl-4-(4-trifluoromethoxyphenyl) piperazine (5n)

$CDCl_3$

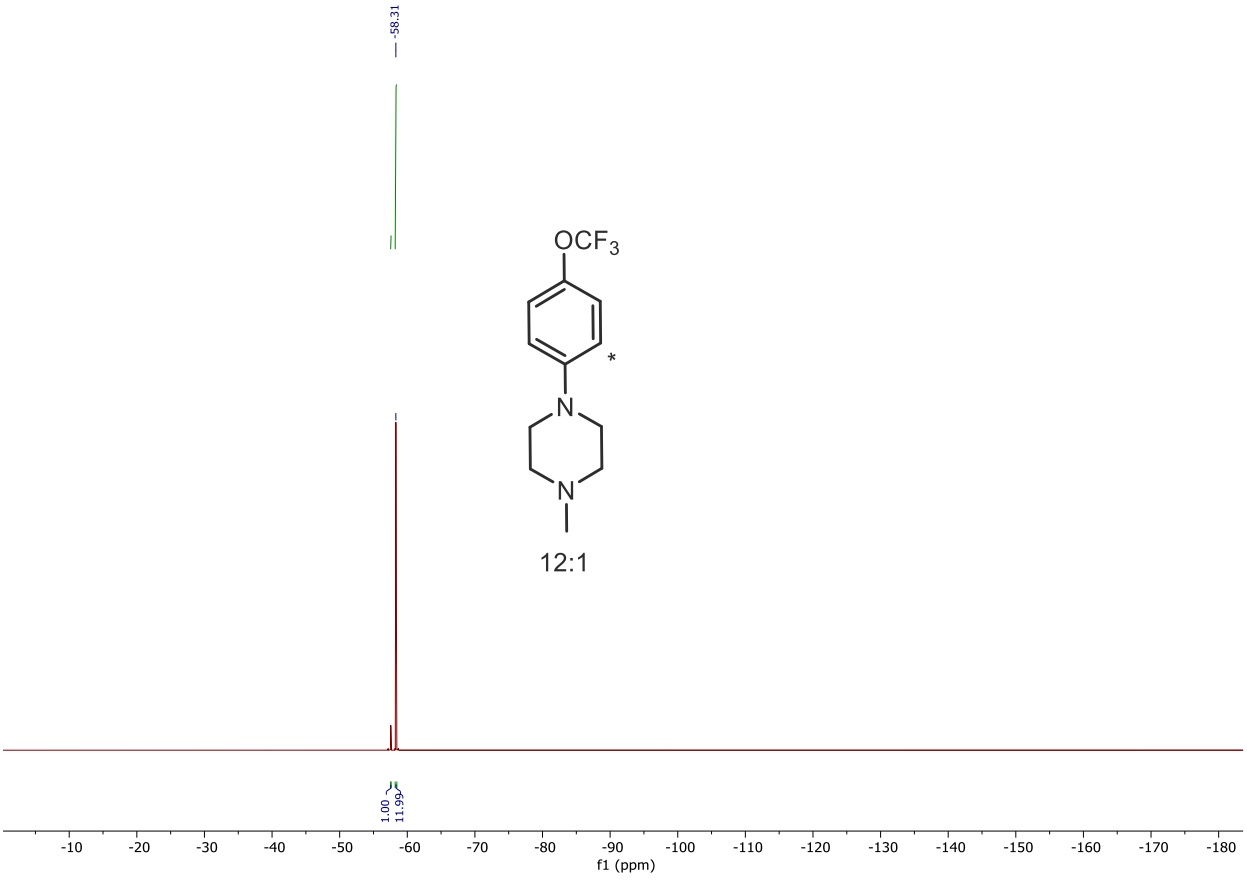
13C NMR



1-methyl-4-(4-trifluoromethoxyphenyl) piperazine (5n)

$CDCl_3$

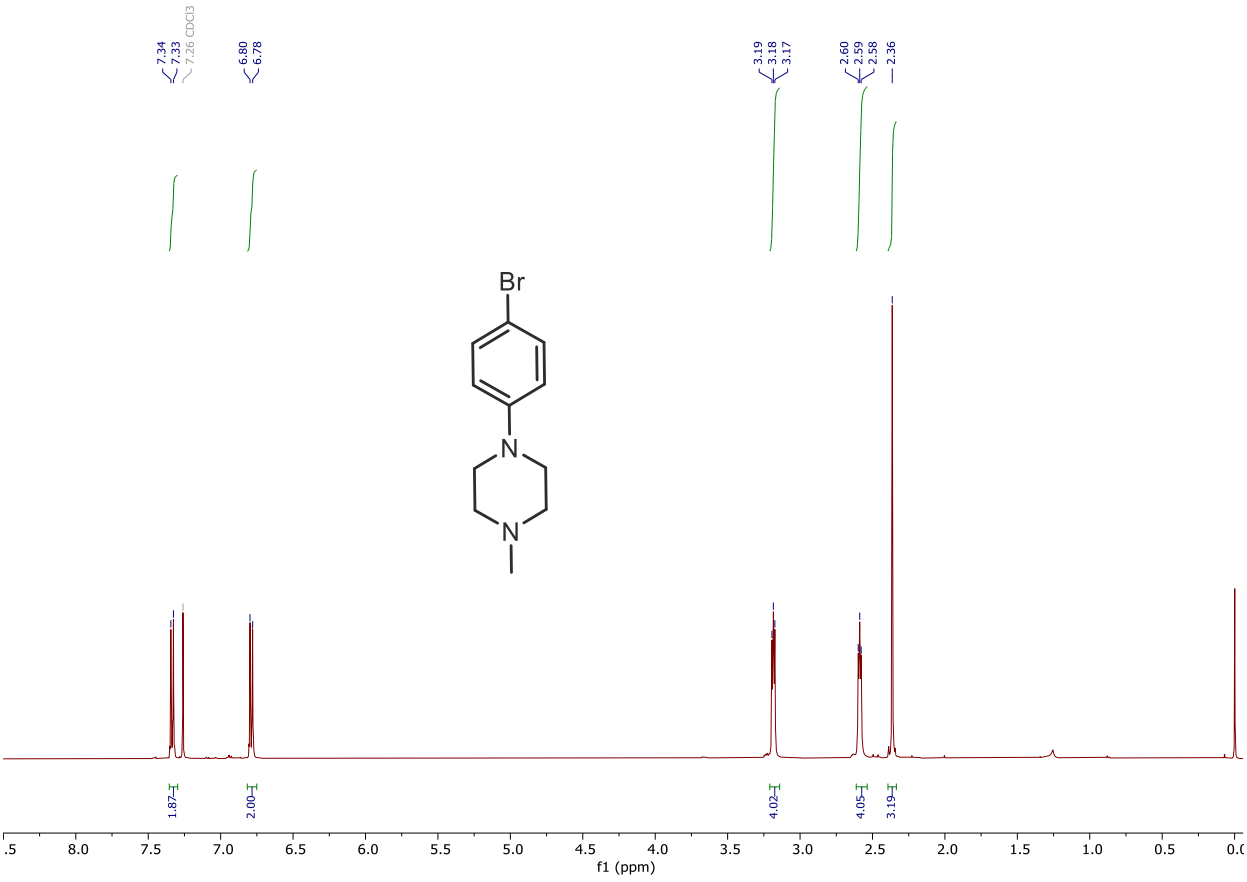
19F NMR



1-methyl-4-(4-bromophenyl) piperazine (5o)

$CDCl_3$

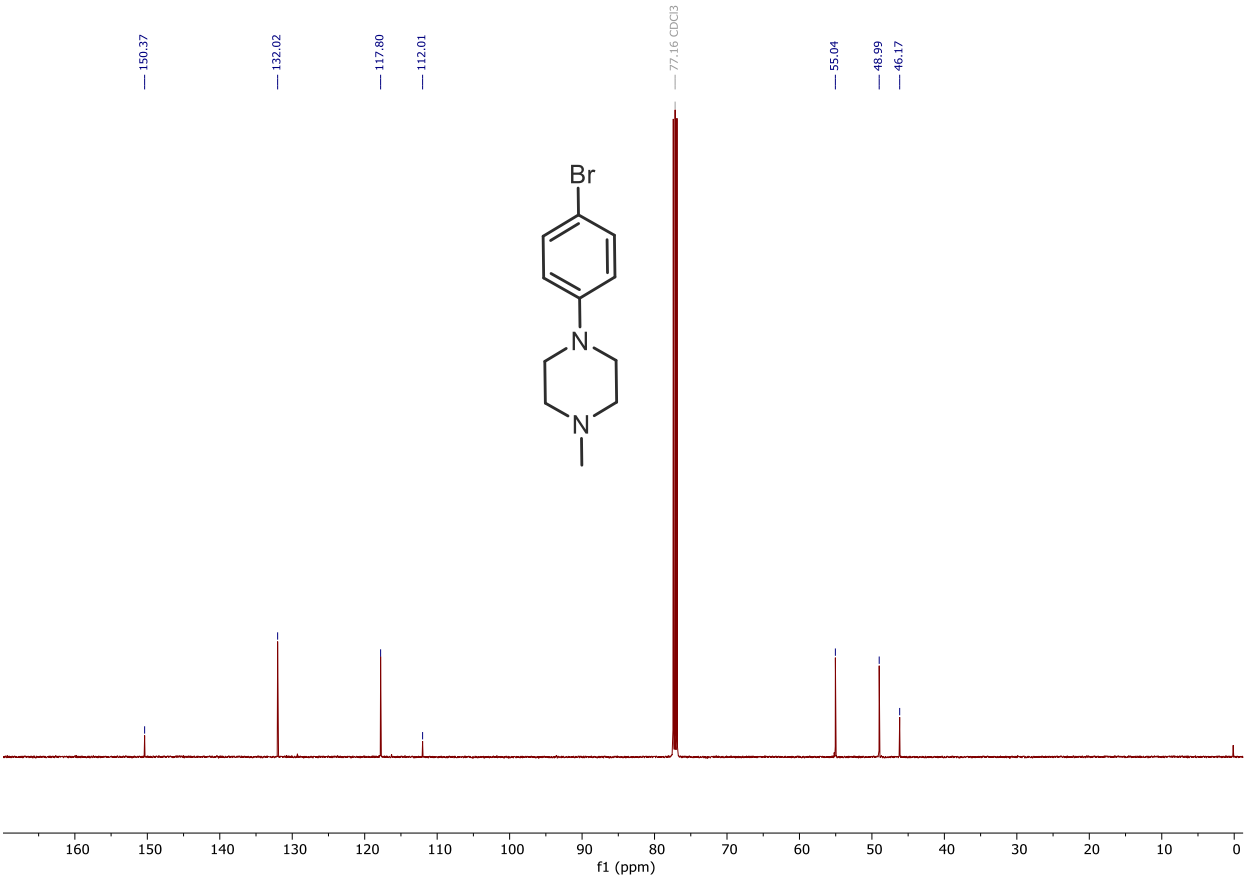
1H NMR



1-methyl-4-(4-bromophenyl) piperazine (5o)

$CDCl_3$

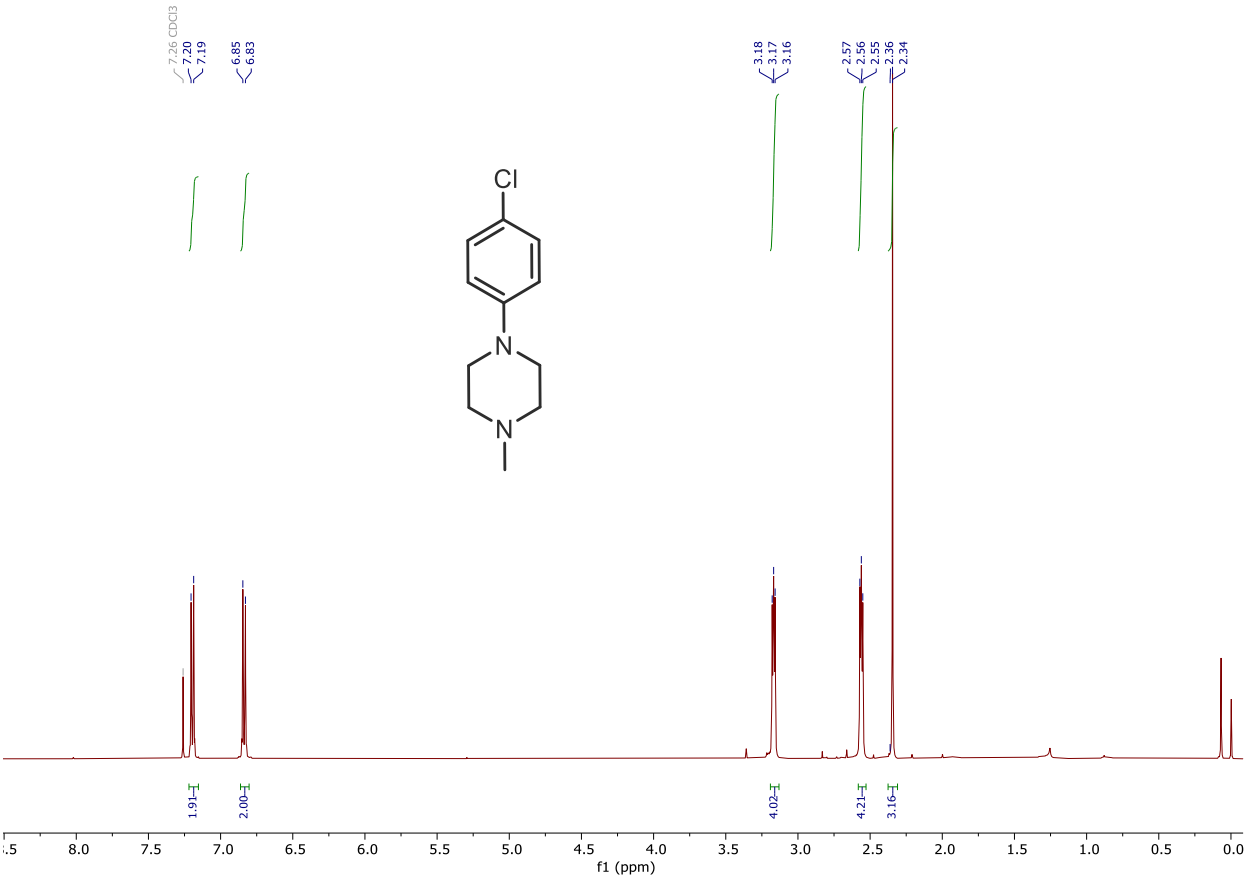
13C NMR



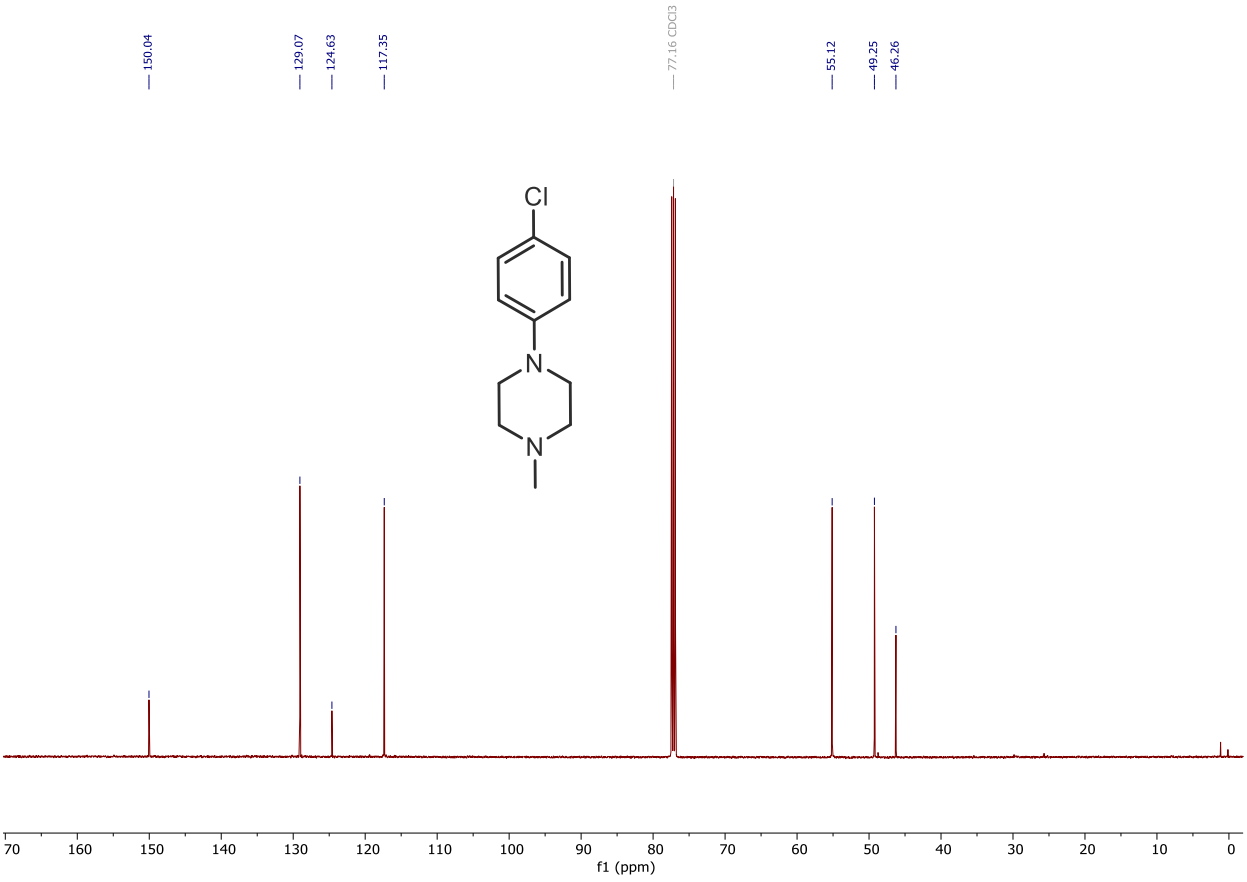
1-methyl-4-(4-chlorophenyl) piperazine (5p)

$CDCl_3$

1H NMR



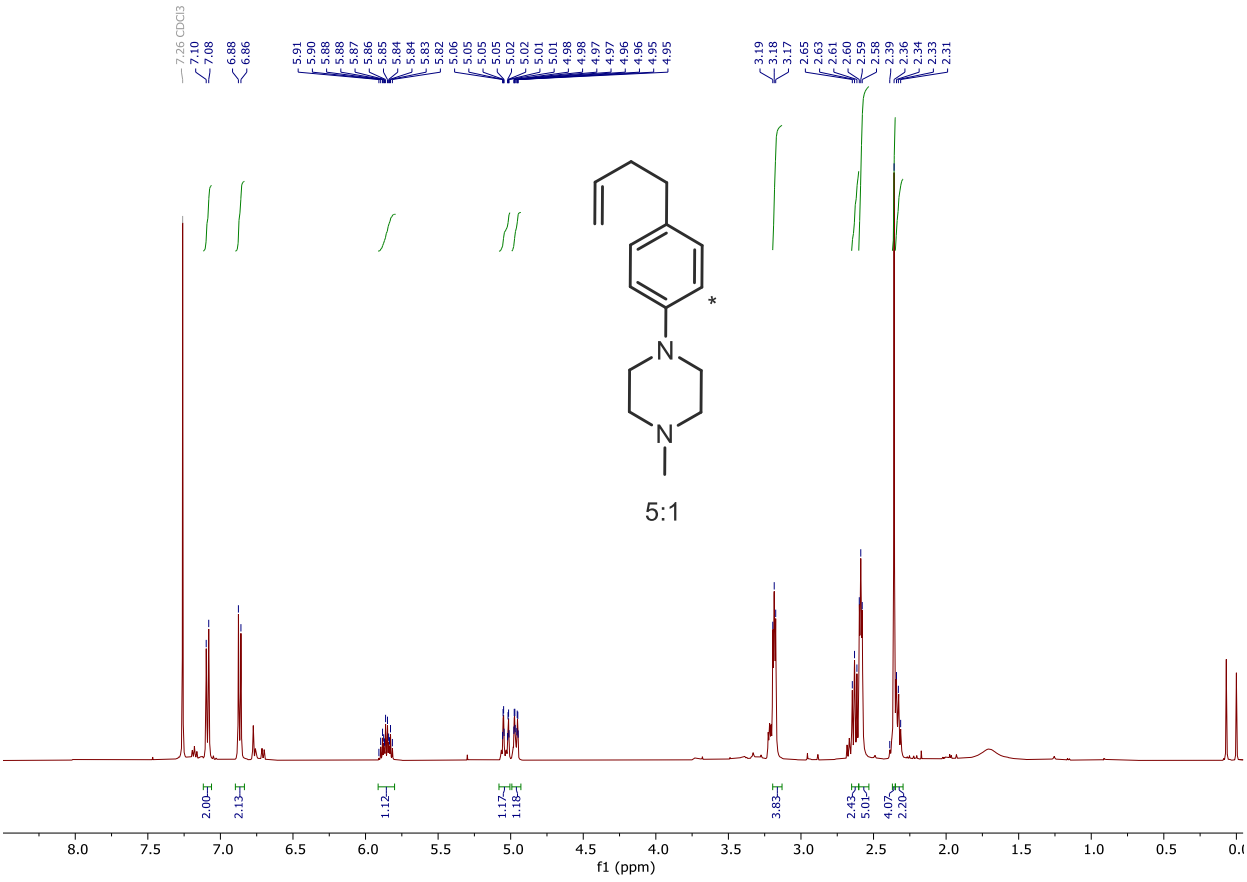
1-methyl-4-(4-chlorophenyl) piperazine (5p)
$CDCl_3$
13C NMR



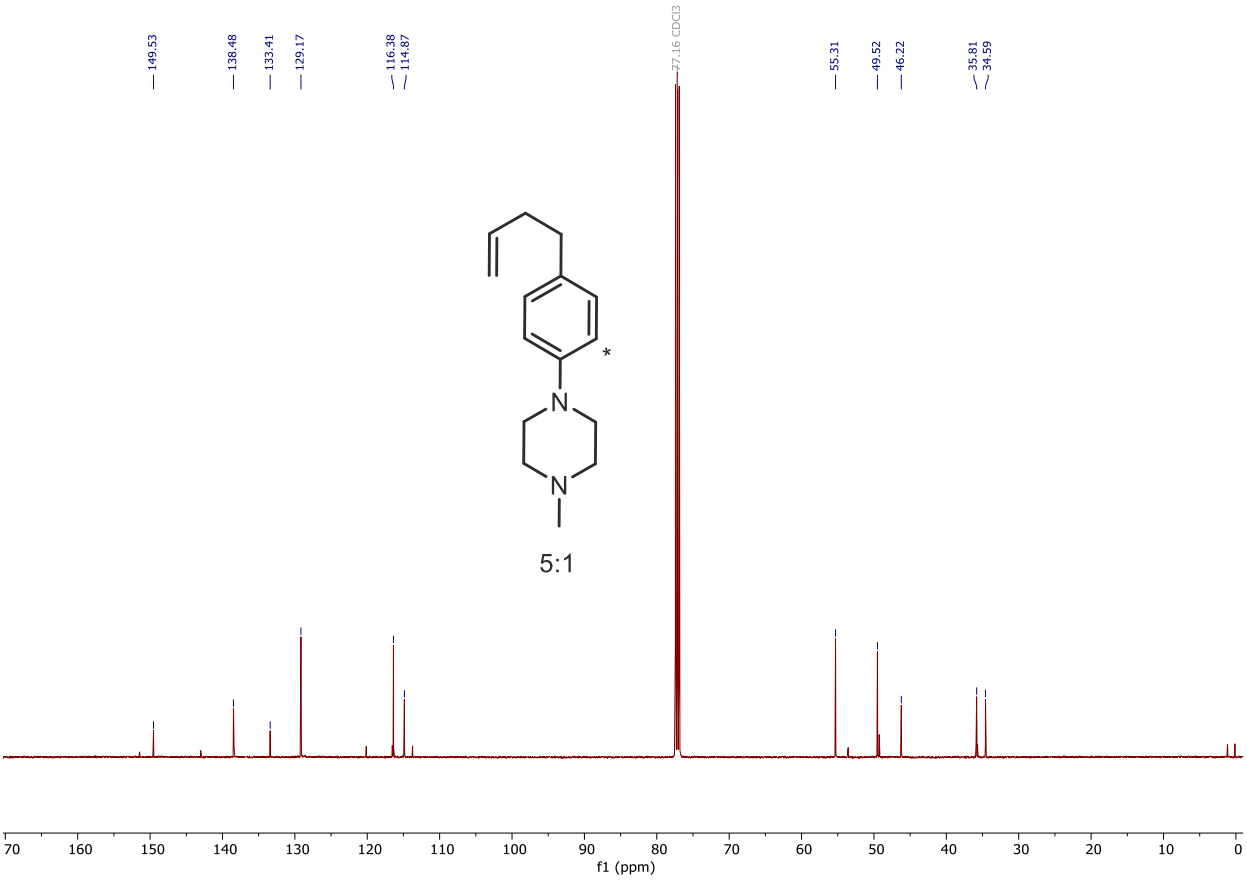
4-phenyl-1-butene piperazine (5q)

$CDCl_3$

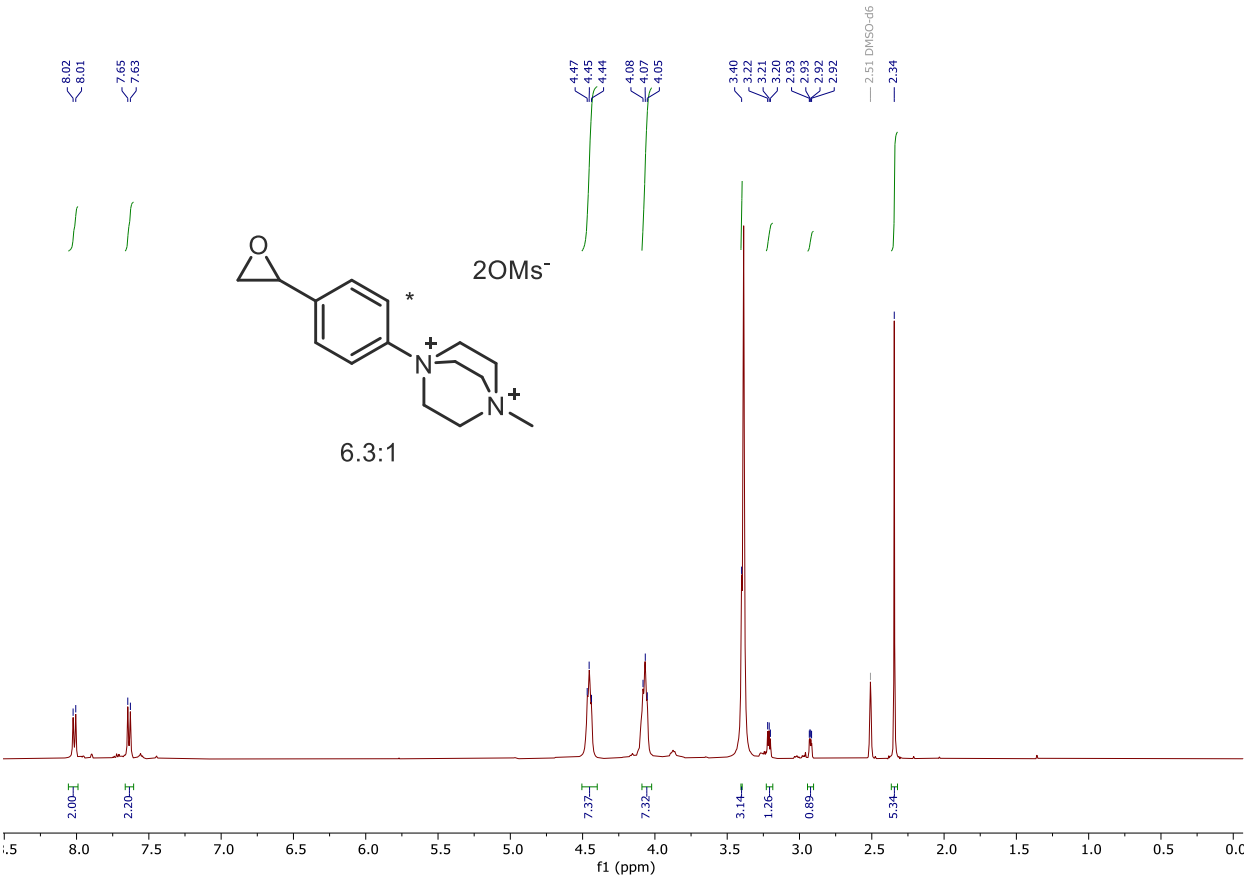
1H NMR



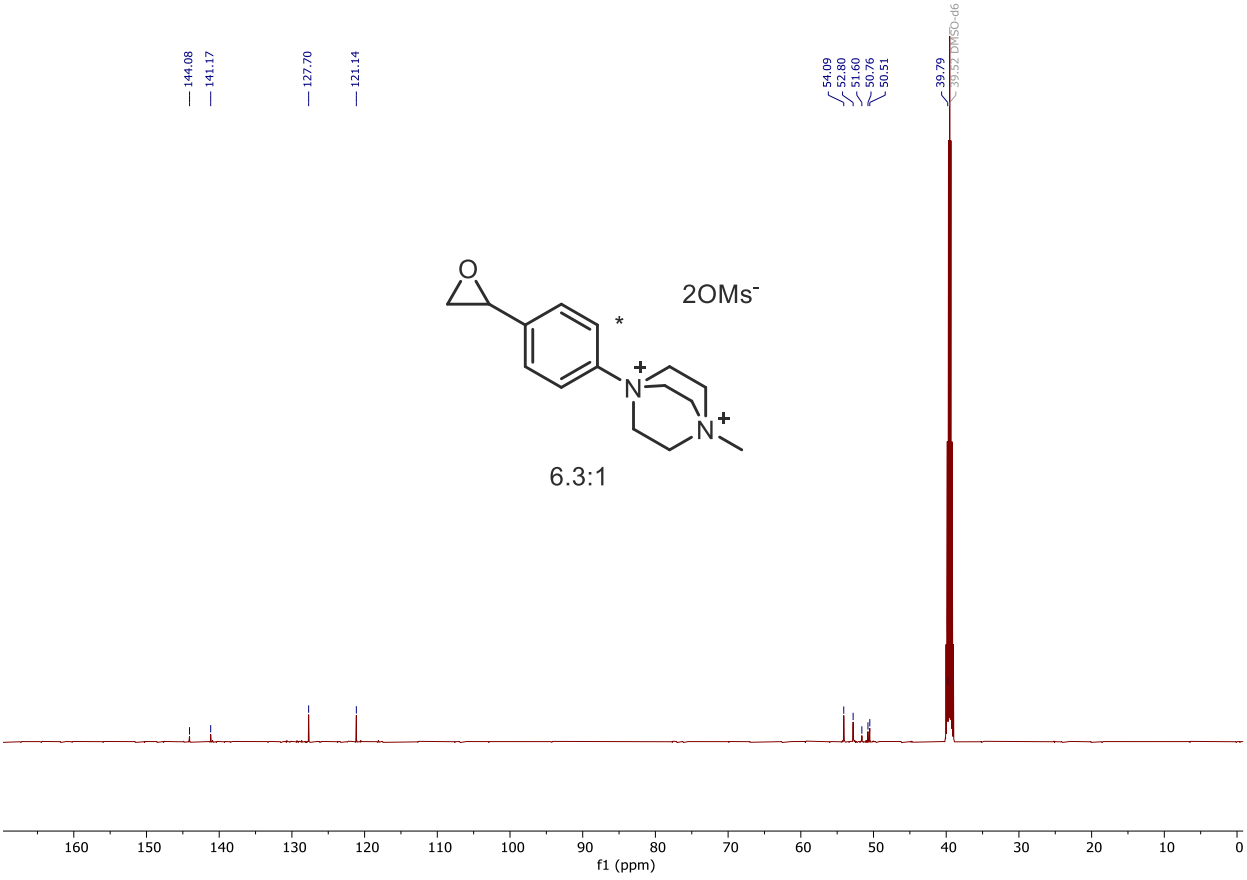
4-phenyl-1-butene piperazine (5q)
$CDCl_3$
13C NMR



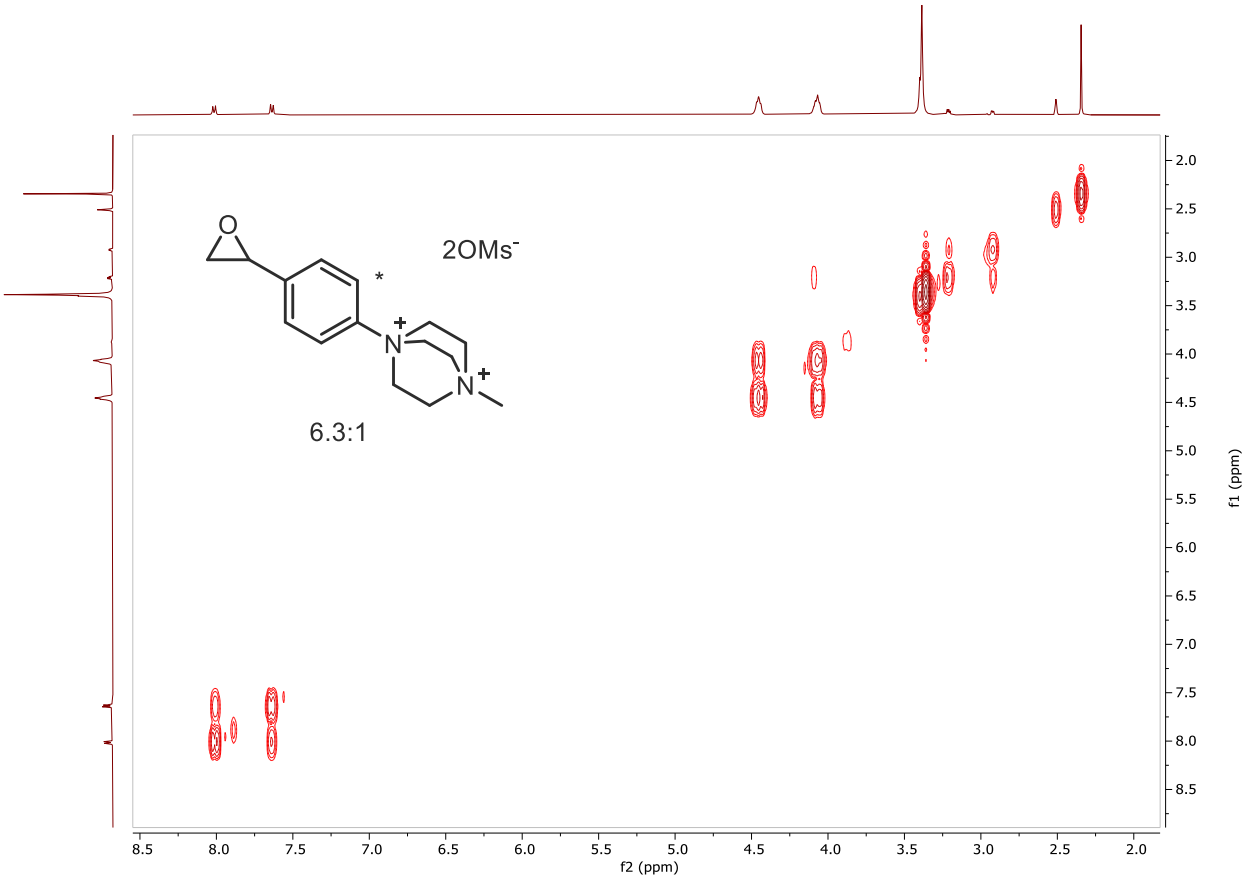
Styrene oxide DABCOnium salt (2r)
DMSO-d_6
1H NMR



Styrene oxide DABCOnium salt (2r)
DMSO-d_6
13C NMR



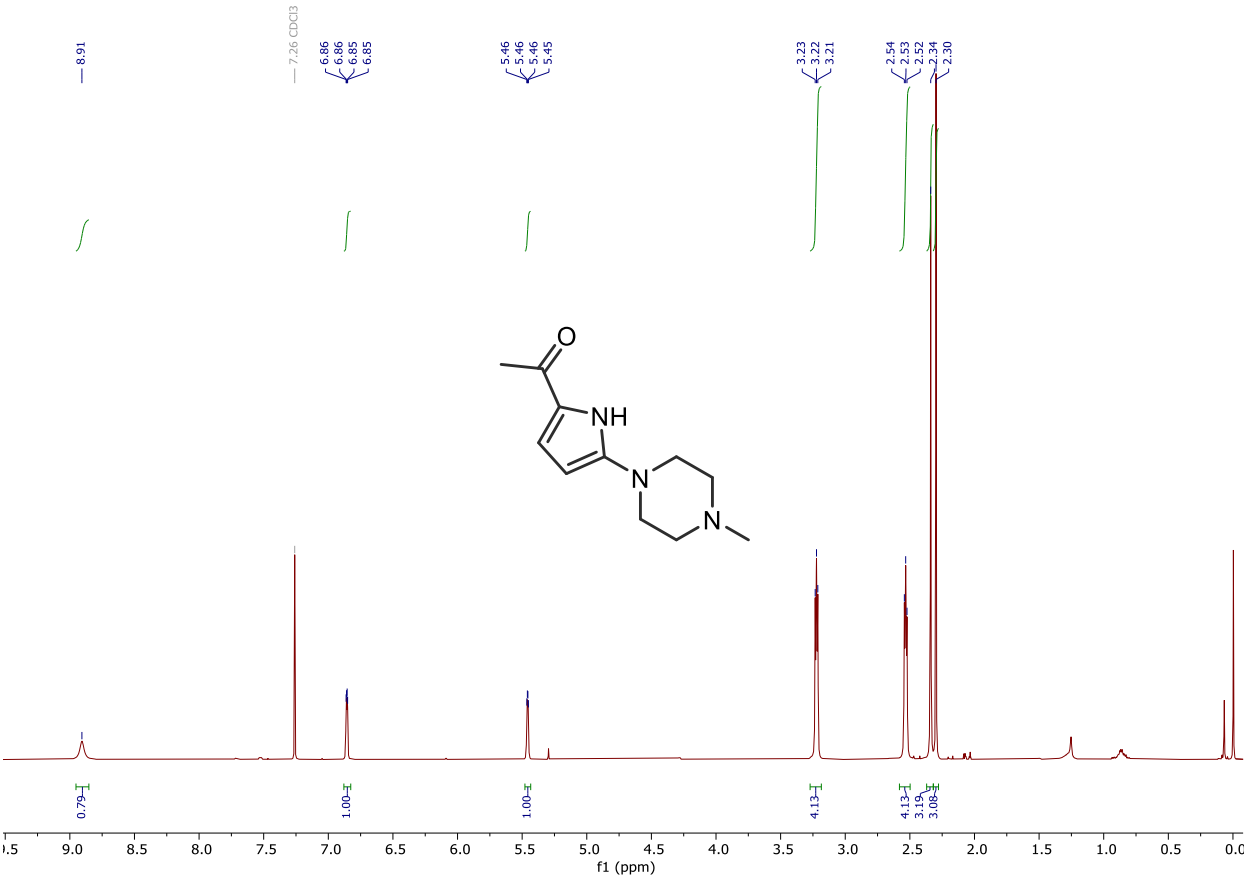
Styrene oxide DABCOnium salt (2r)
DMSO-d_6
COSY



2-Acetylpyrrole N-methyl piperazine (5s)

$CDCl_3$

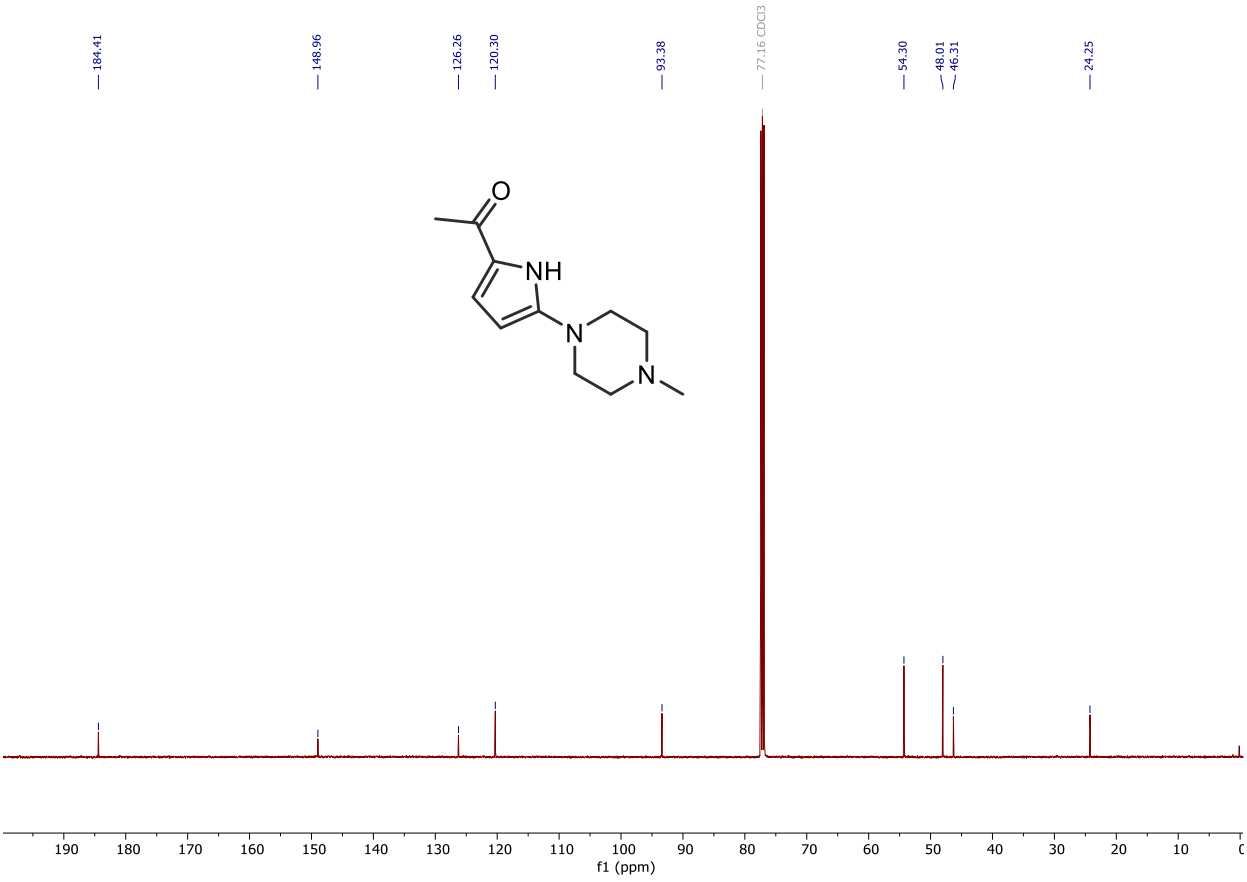
1H NMR



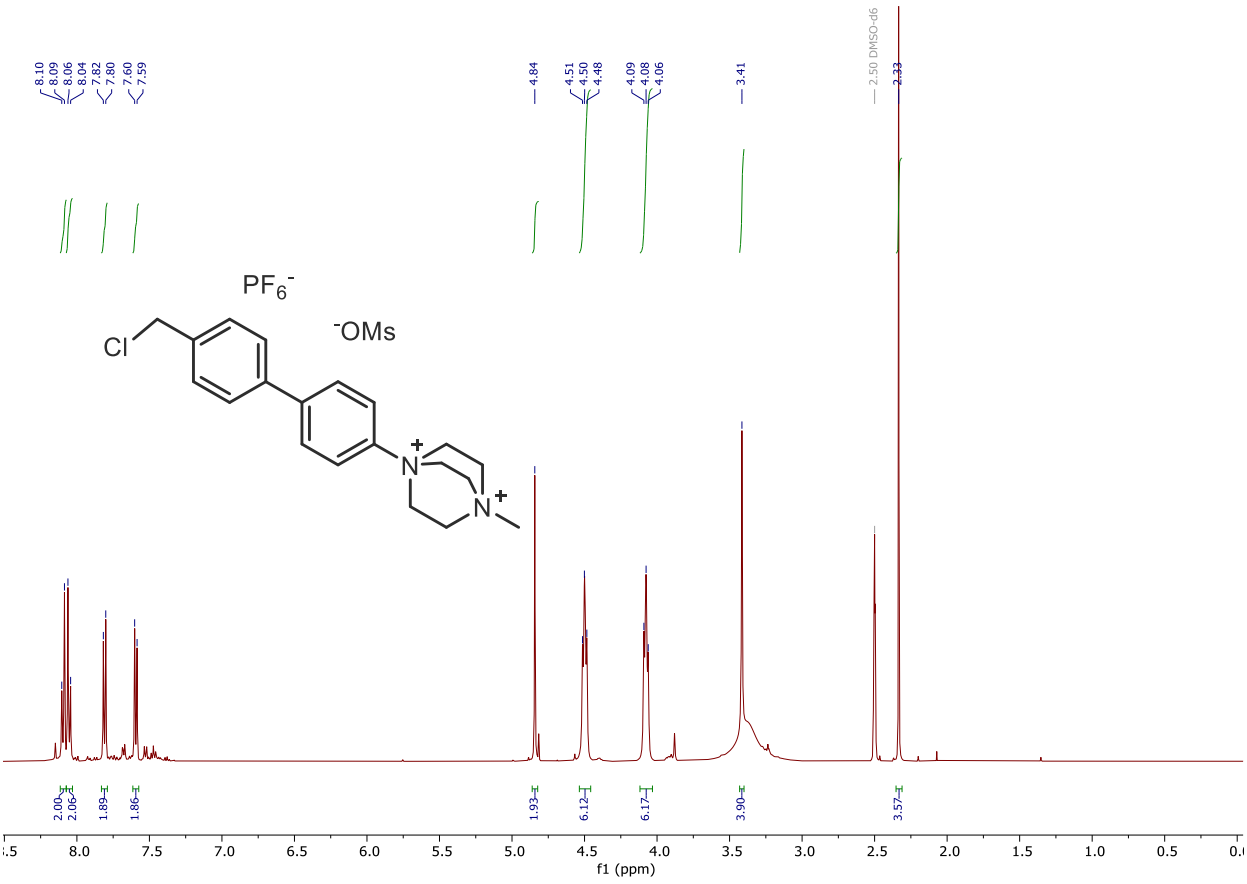
2-Acetylpyrrole N-methyl piperazine (5s)

$CDCl_3$

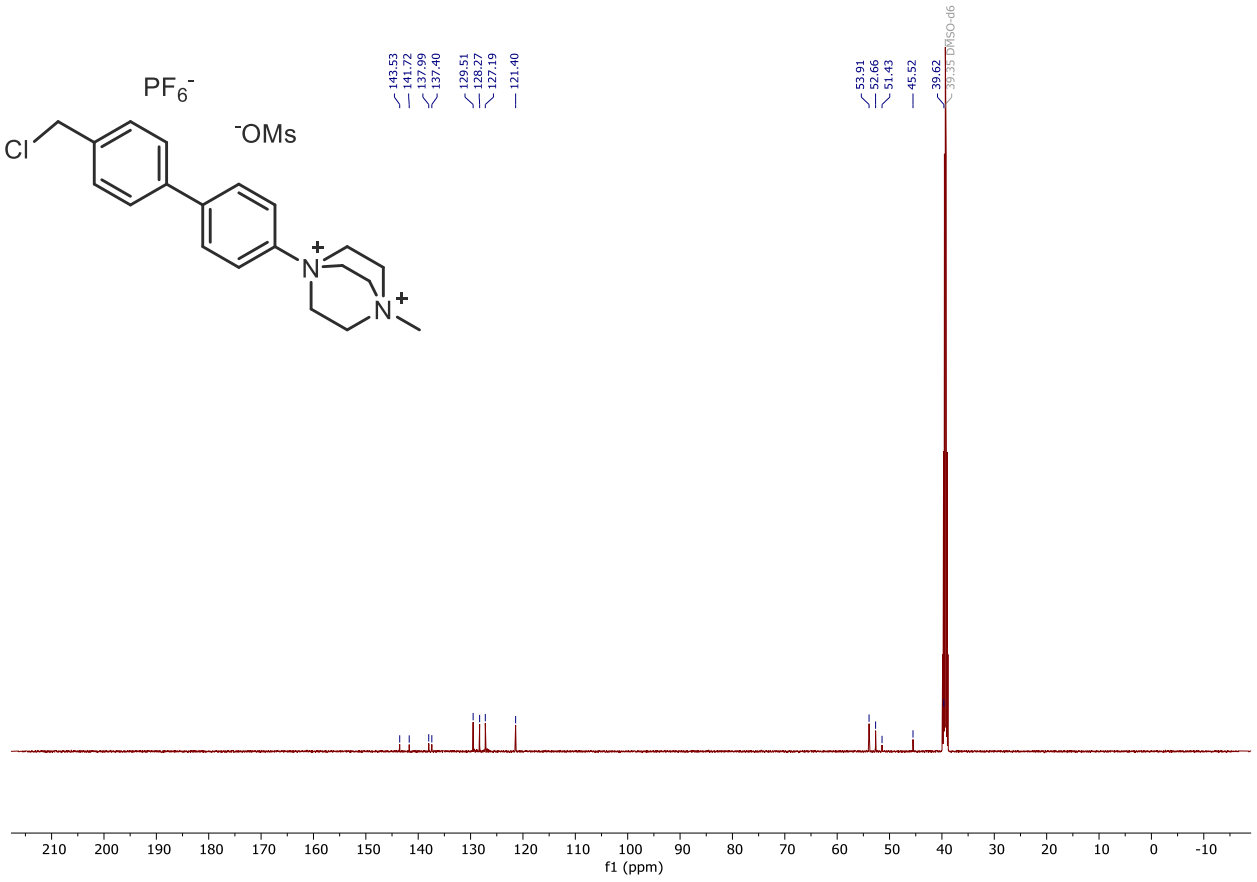
13C NMR



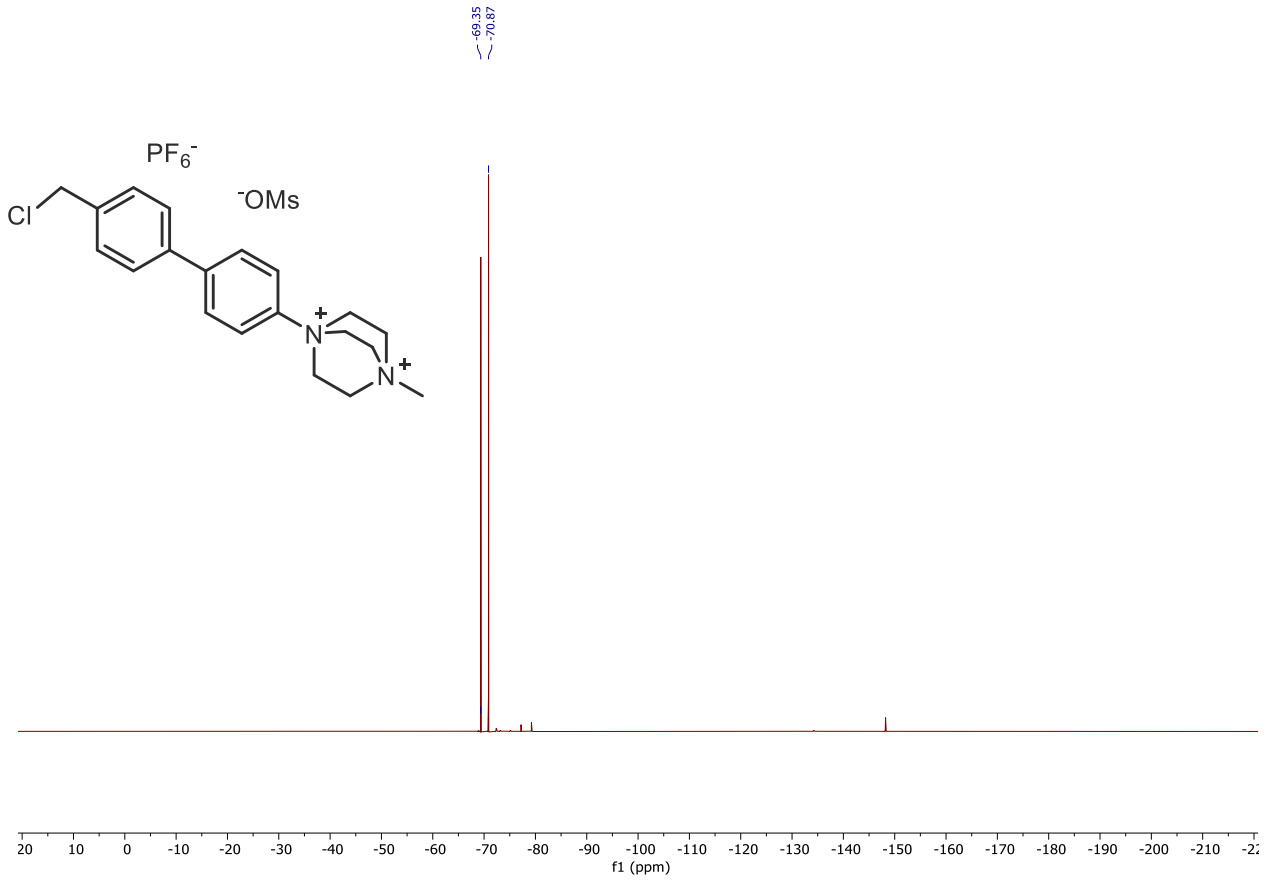
p-PhBzCl DABCOnium salt (2t)
DMSO-d_6
1H NMR



p-PhBzCl DABCOnium salt (2t)
DMSO-d_6
13C NMR



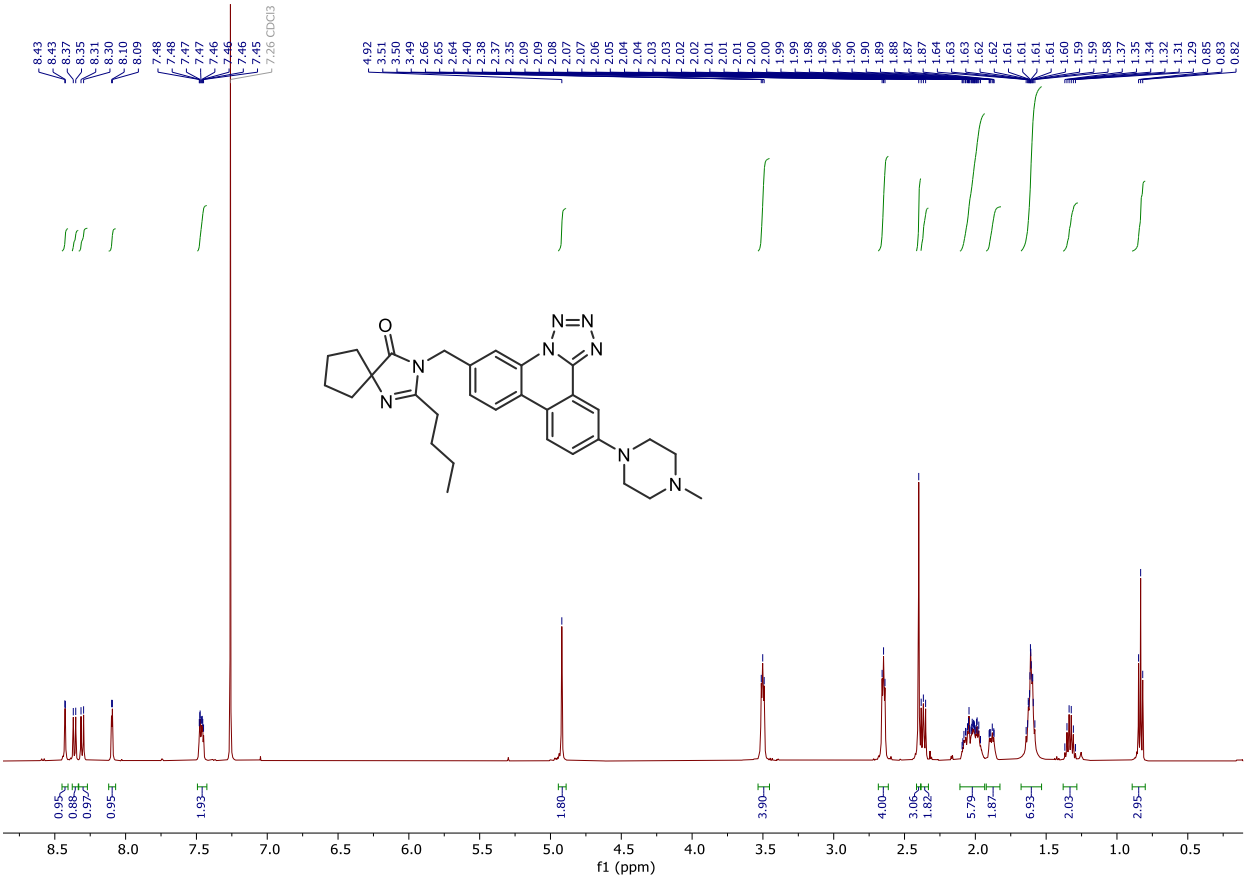
p-PhBzCl DABCOnium salt (2t)
DMSO-d_6
19F NMR



Irbesartan cyclicized N-Me piperazine (5u)

$CDCl_3$

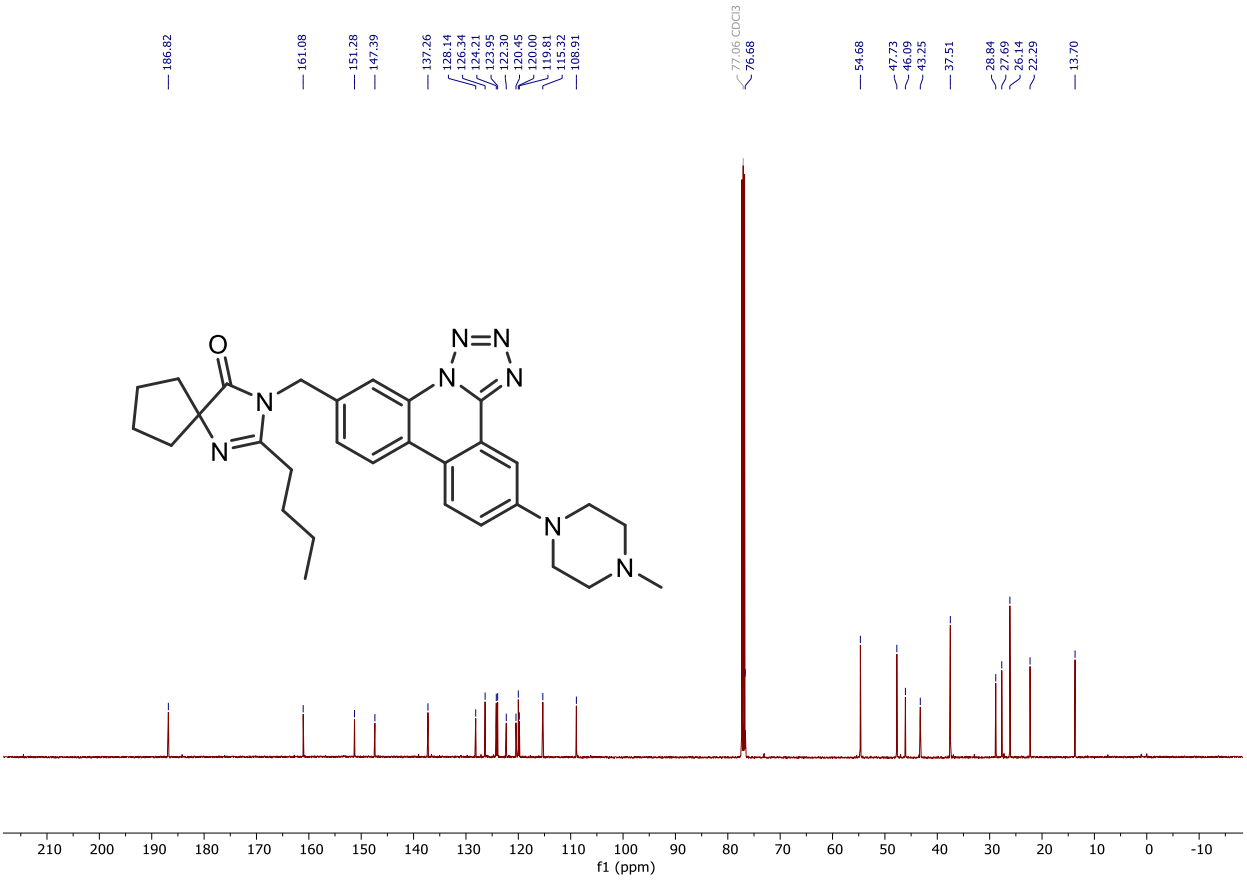
1H NMR



Irbesartan cyclicized N-Me piperazine (5u)

$CDCl_3$

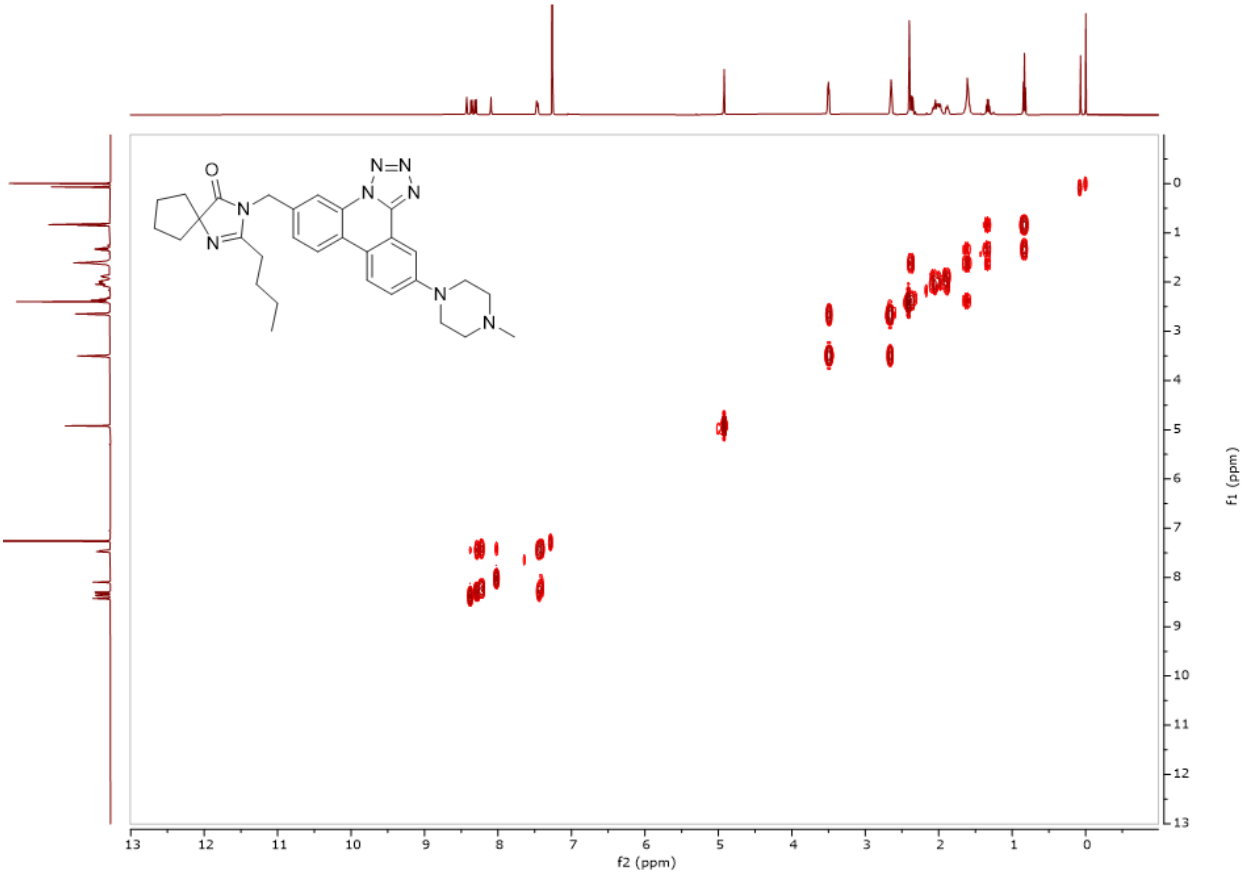
13C NMR



Irbesartan cyclicized N-Me piperazine (5u)

$CDCl_3$

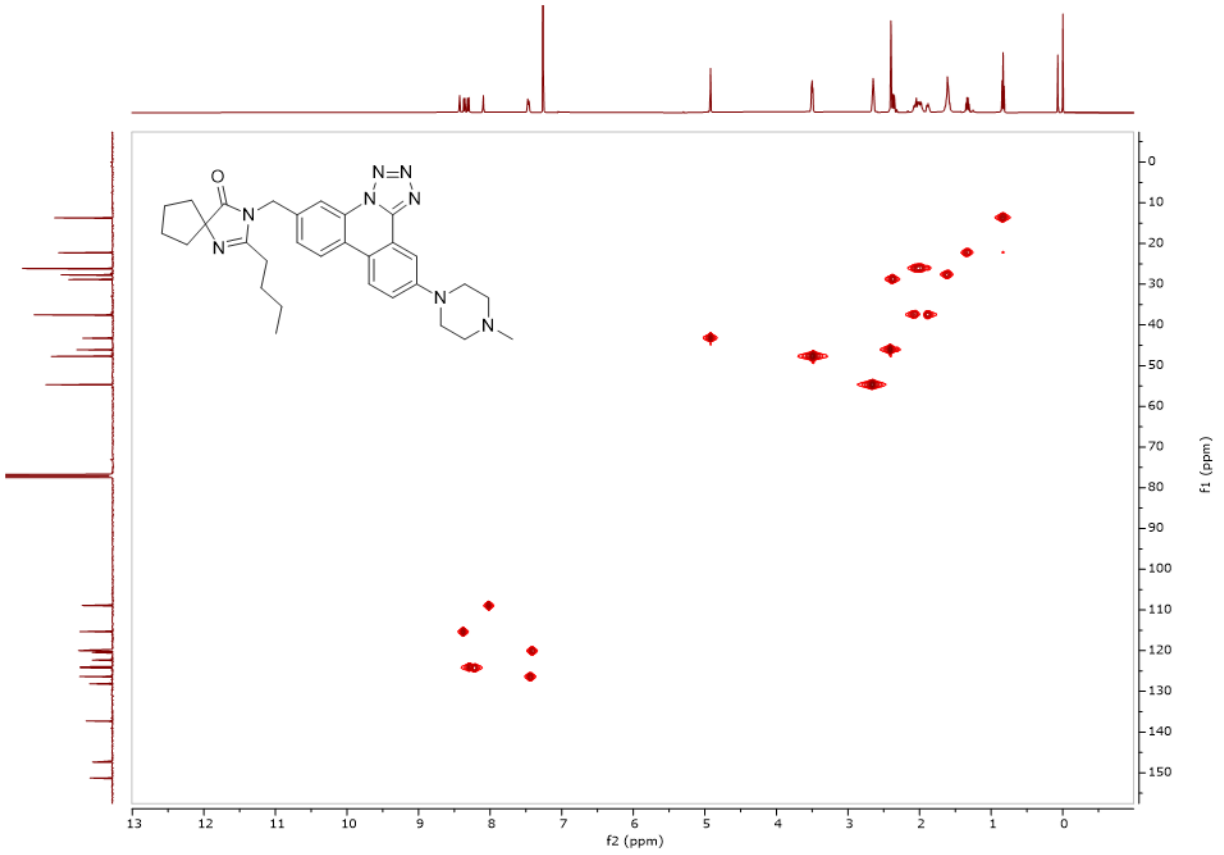
COSY



Irbesartan cyclicized N-Me piperazine (5u)

$CDCl_3$

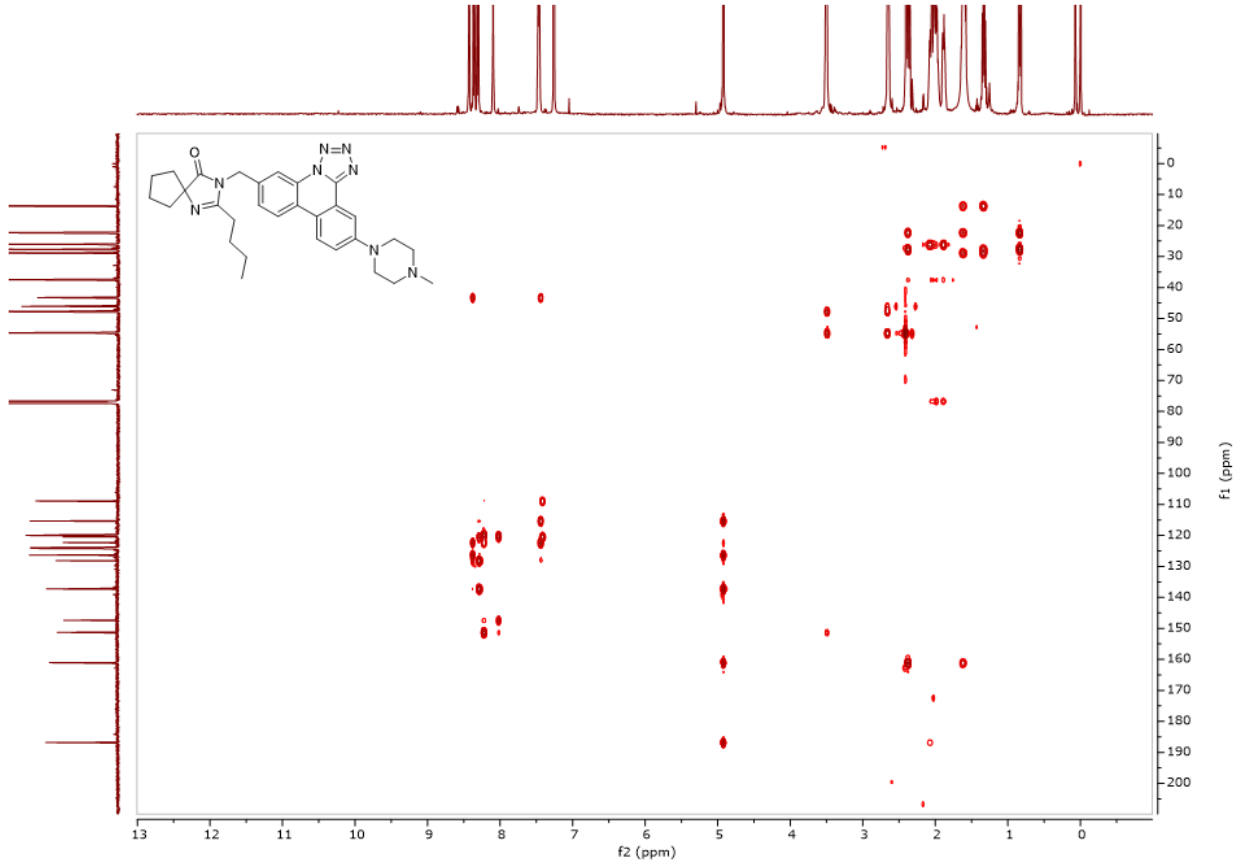
HSQC



Irbesartan cyclicized N-Me piperazine (5u)

$CDCl_3$

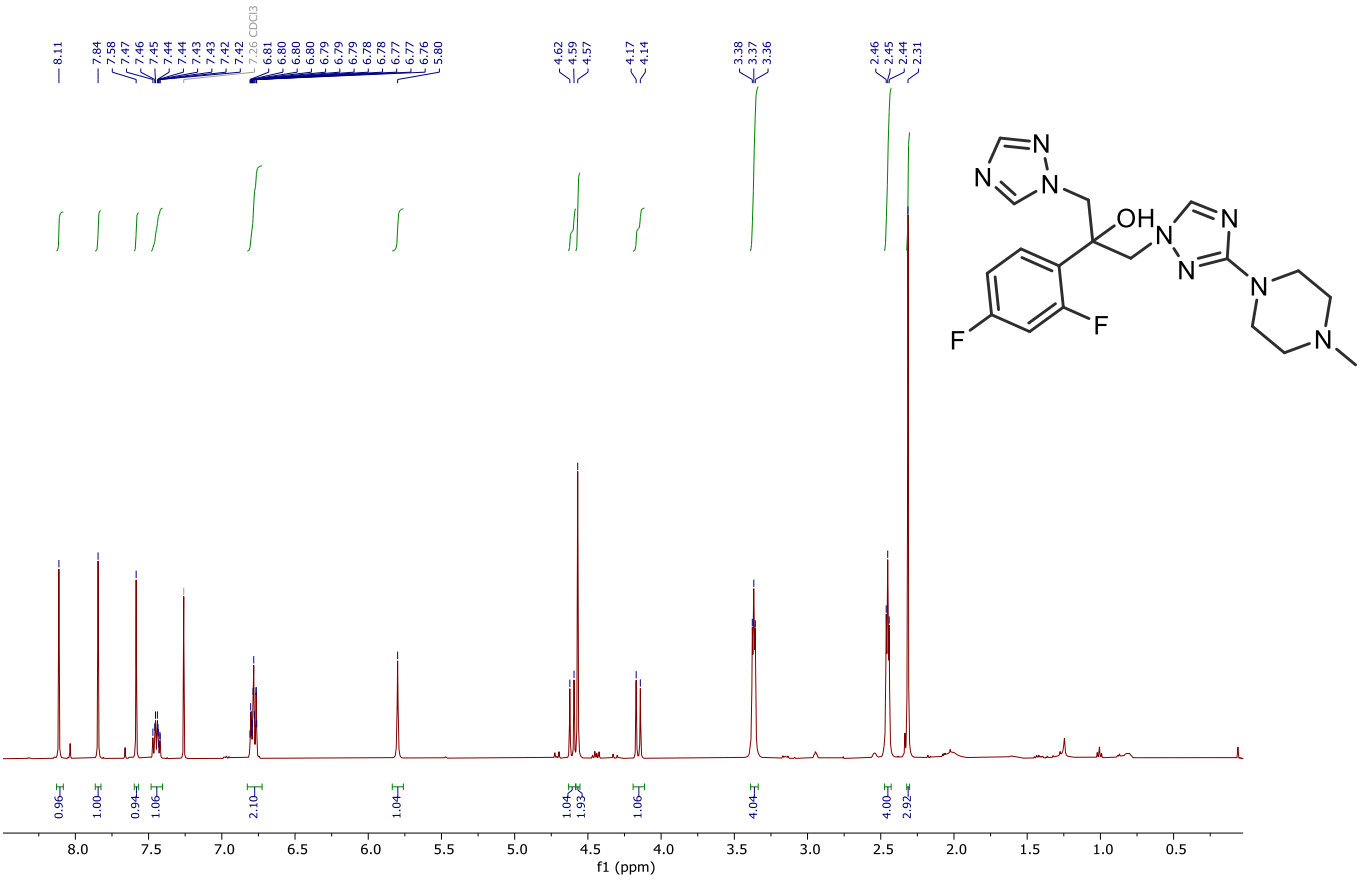
HMBC



Fluconazole N-Me piperazine (5v)

$CDCl_3$

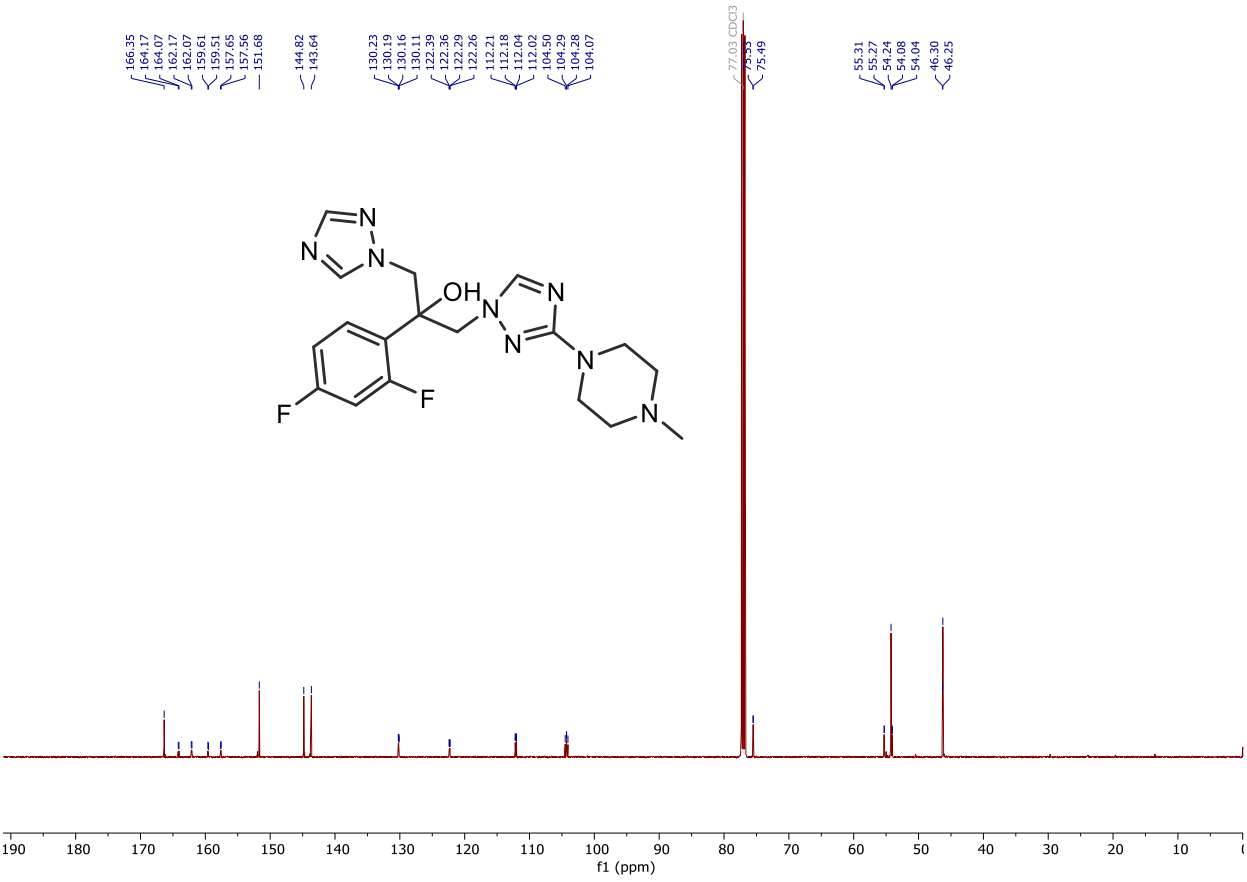
1H NMR



Fluconazole N-Me piperazine (5v)

$CDCl_3$

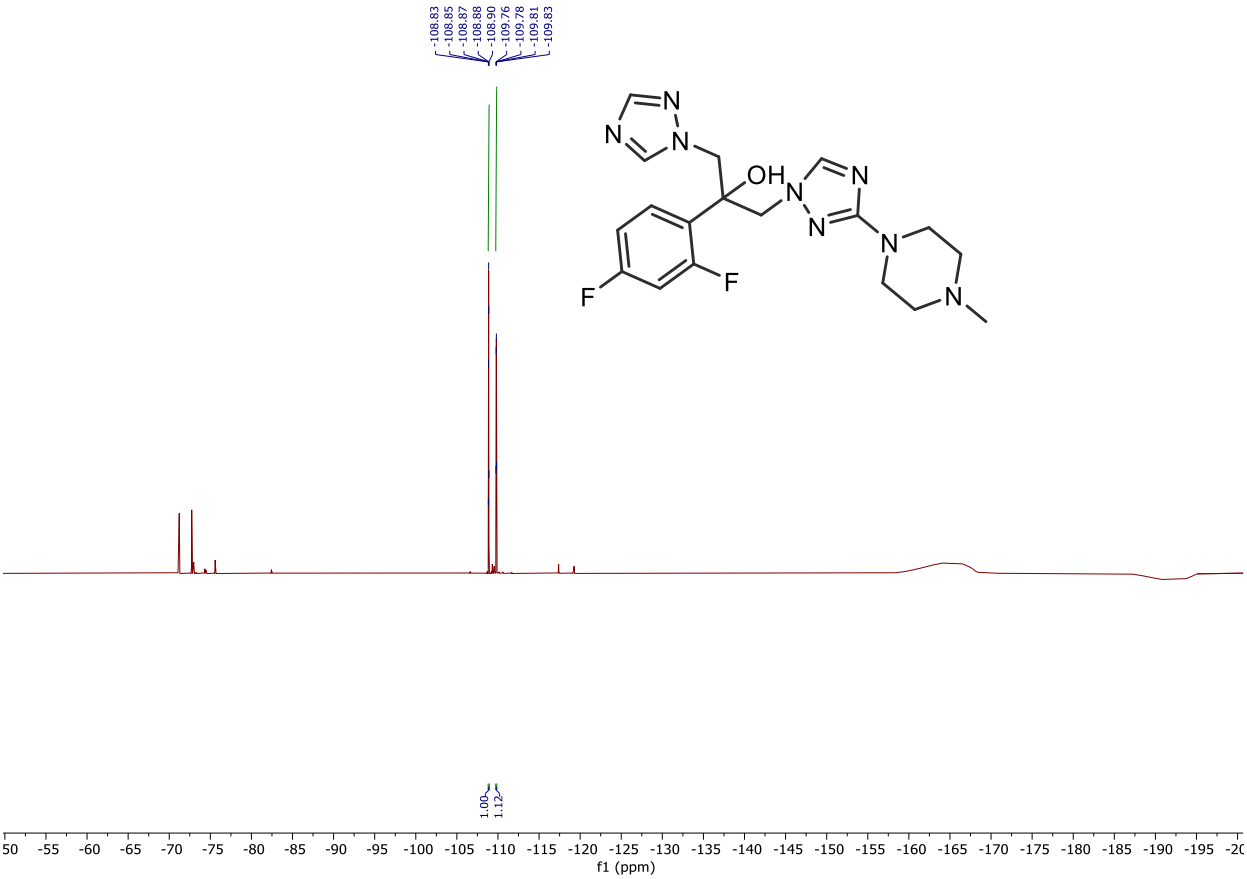
13C NMR



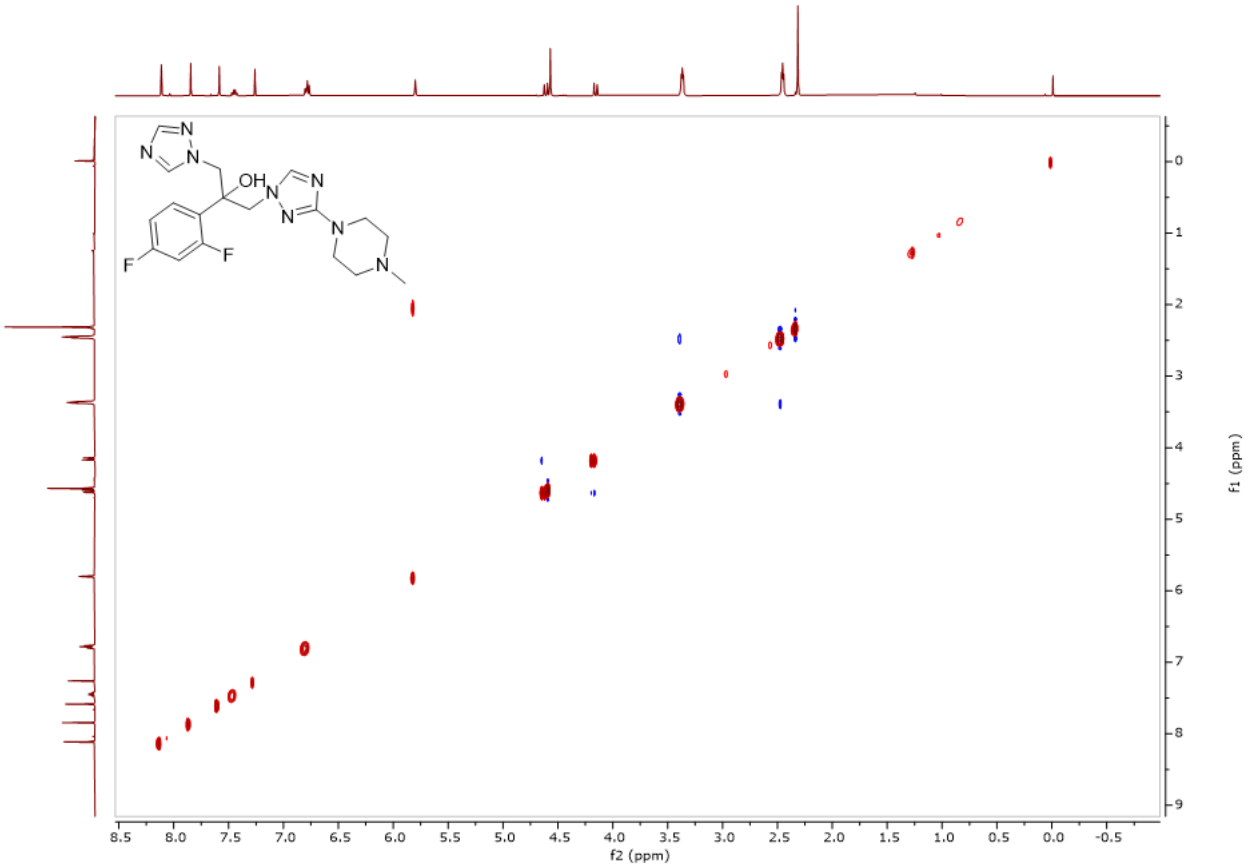
Fluconazole N-Me piperazine (5v)

$CDCl_3$

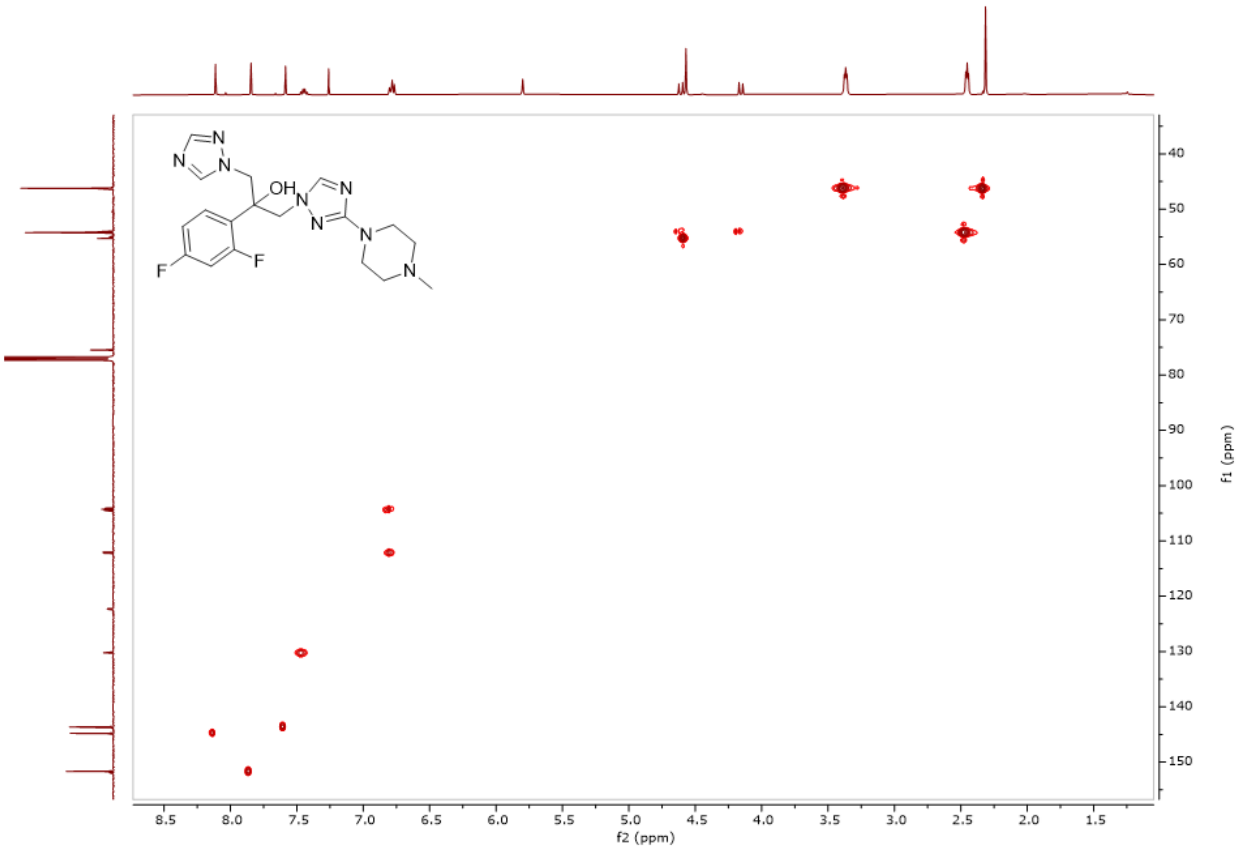
19F NMR



Fluconazole N-Me piperazine (5v)
$CDCl_3$
NOESY



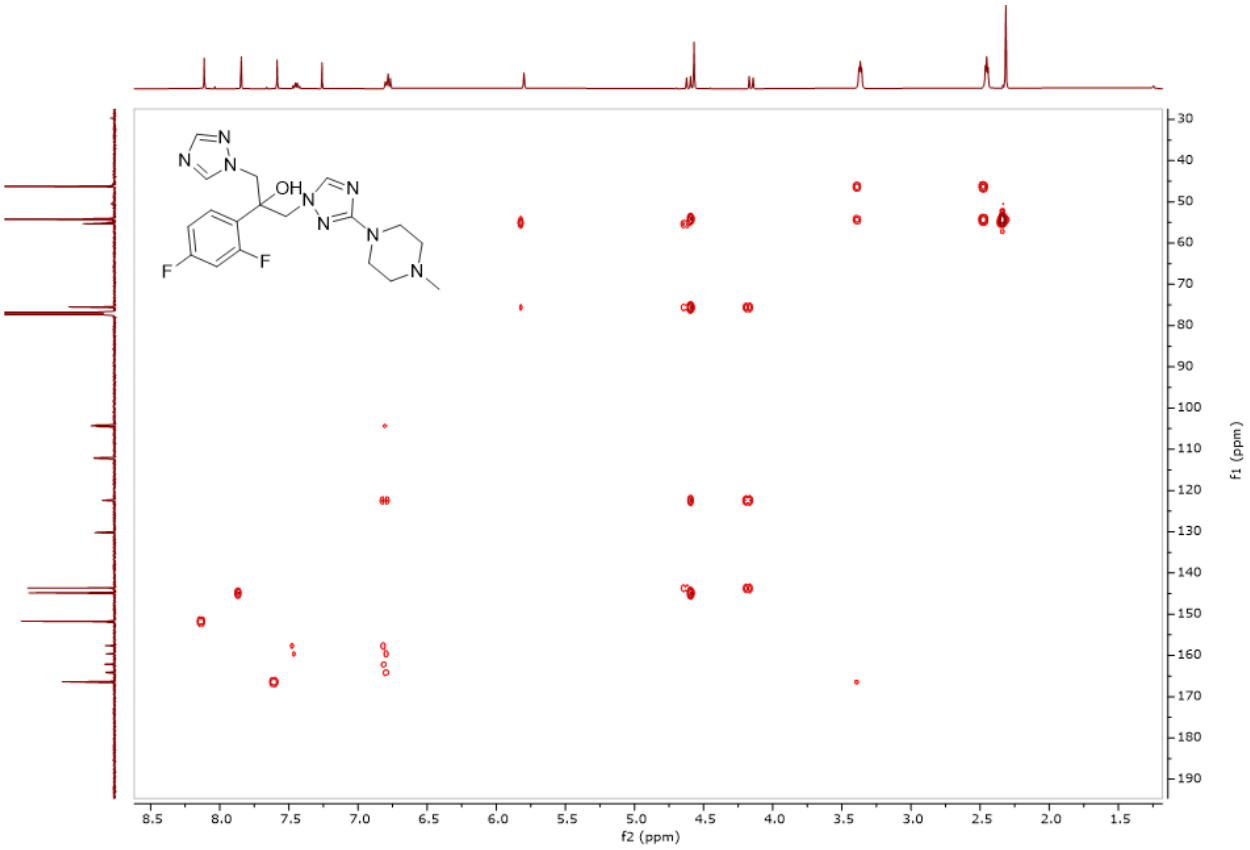
Fluconazole N-Me piperazine (5v)
$CDCl_3$
HSQC



Fluconazole N-Me piperazine (5v)

$CDCl_3$

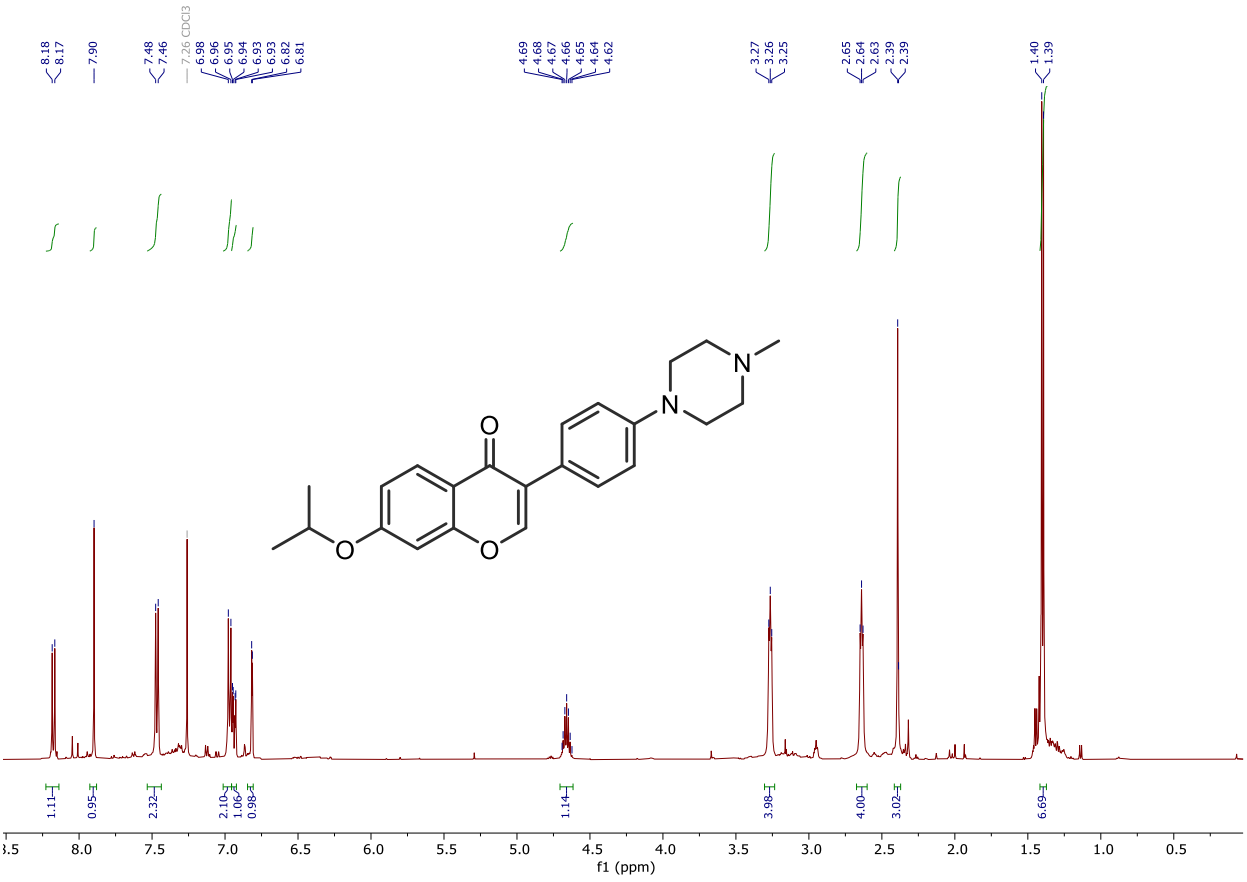
HMBC



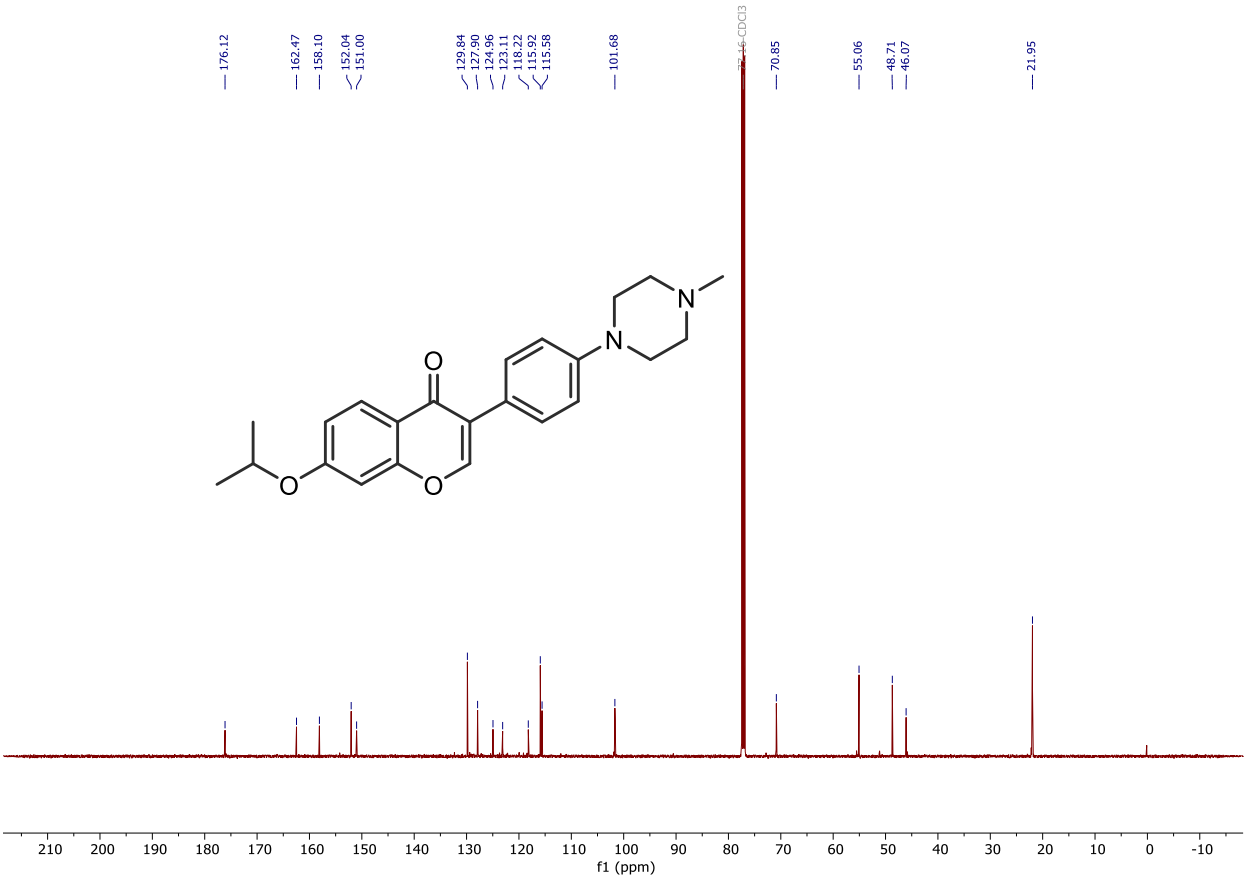
Ipriflavone N-Me piperazine (5w)

$CDCl_3$

1H NMR



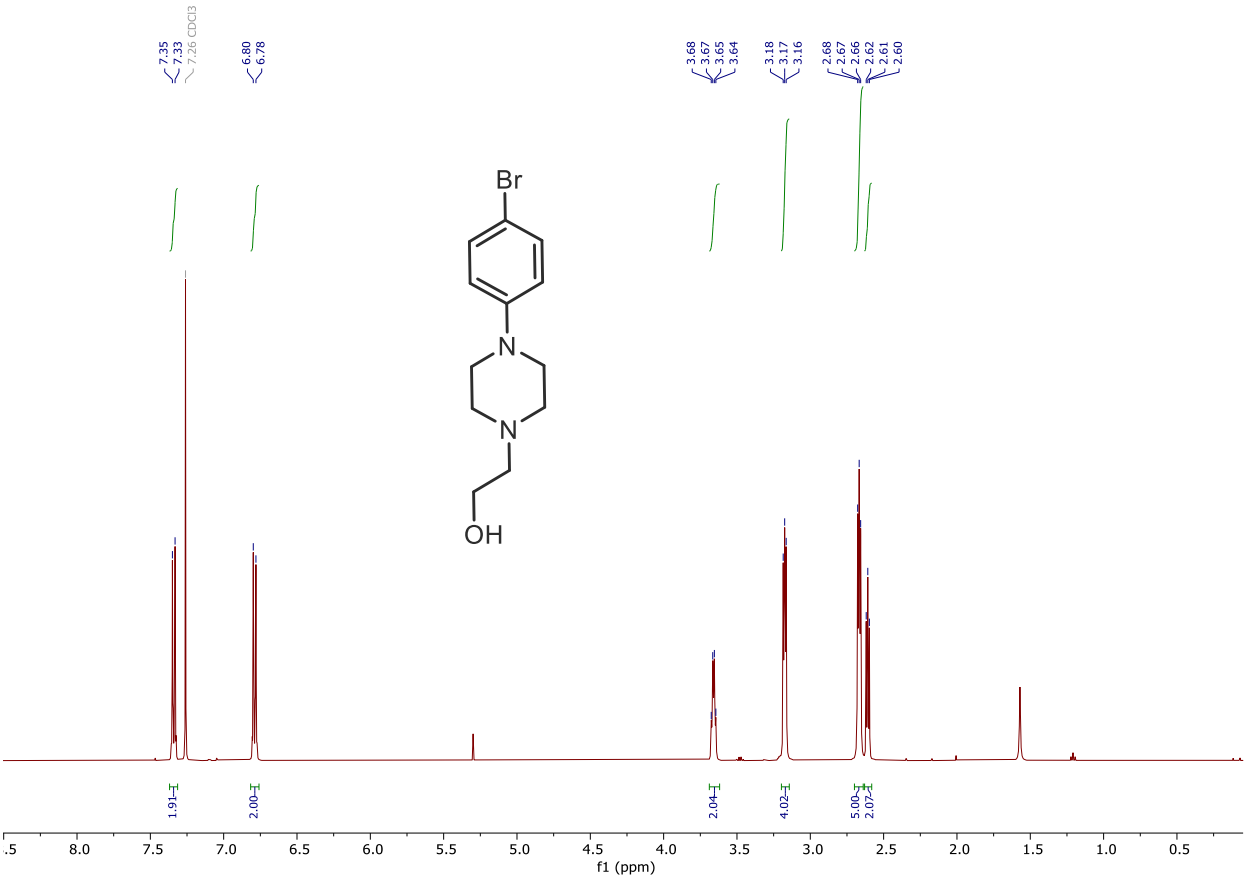
Ipriflavone N-Me piperazine (5w)
$CDCl_3$
13C NMR



1-(2-hydroxyethyl)-4-(4-bromophenyl) piperazine (5x)

$CDCl_3$

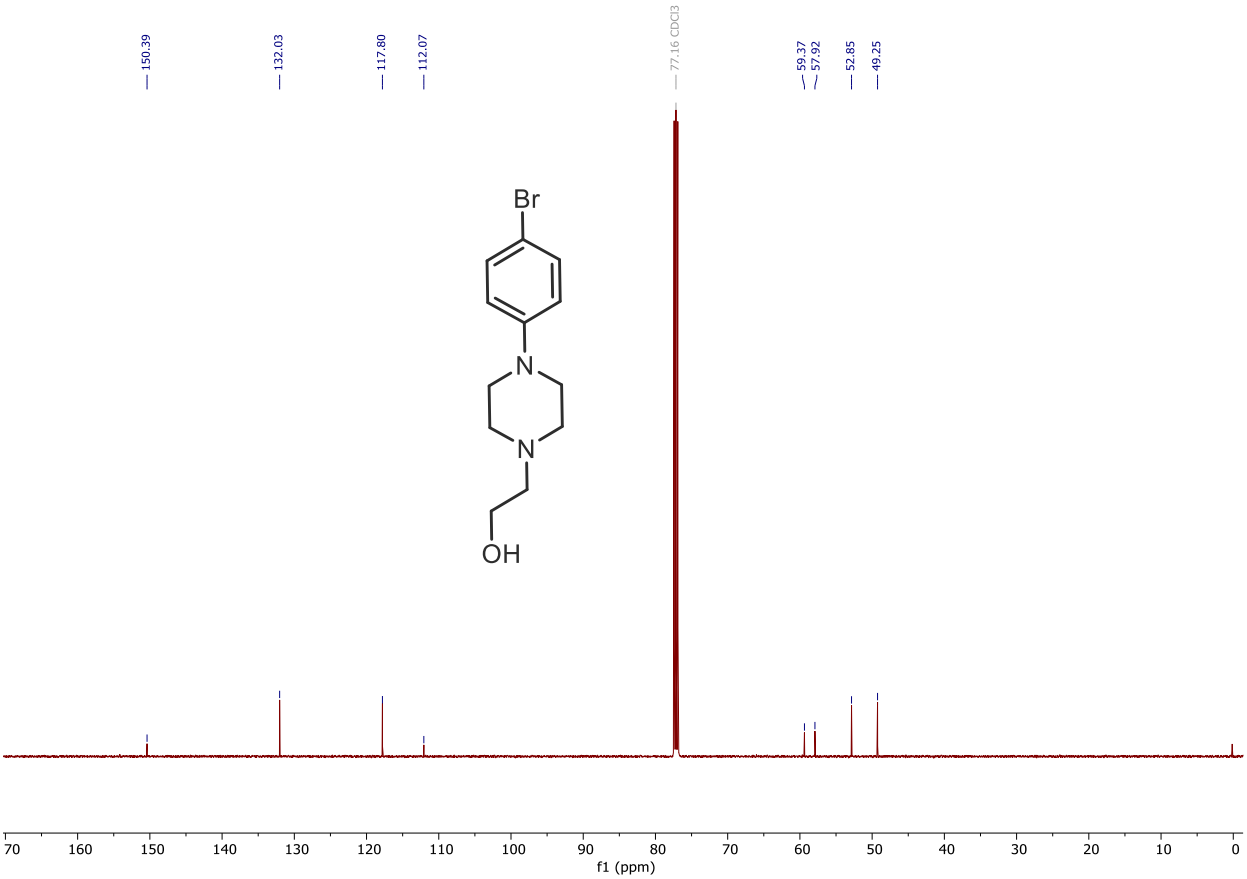
1H NMR



1-(2-hydroxyethyl)-4-(4-bromophenyl) piperazine (5x)

$CDCl_3$

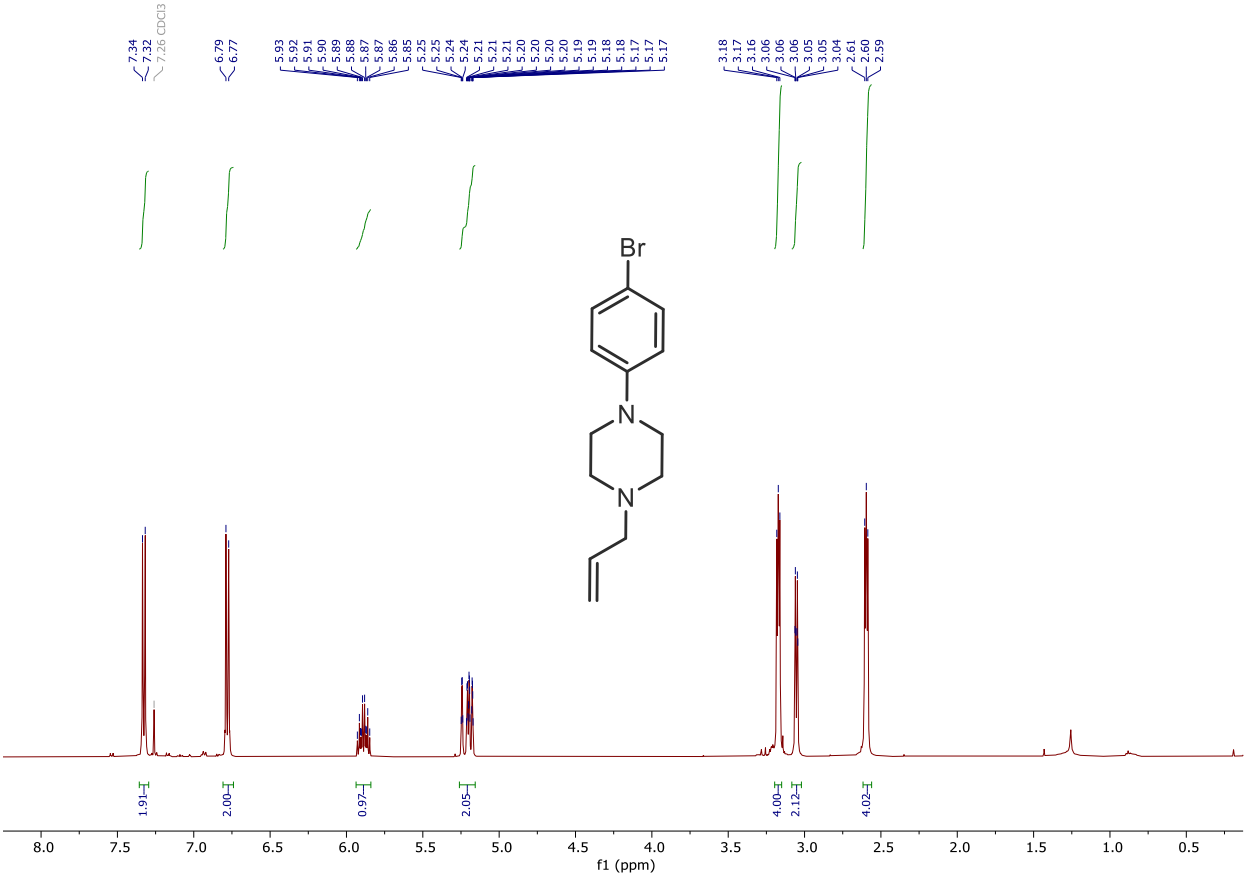
13C NMR



1-allyl-4-(4-bromophenyl) piperazine (5y)

$CDCl_3$

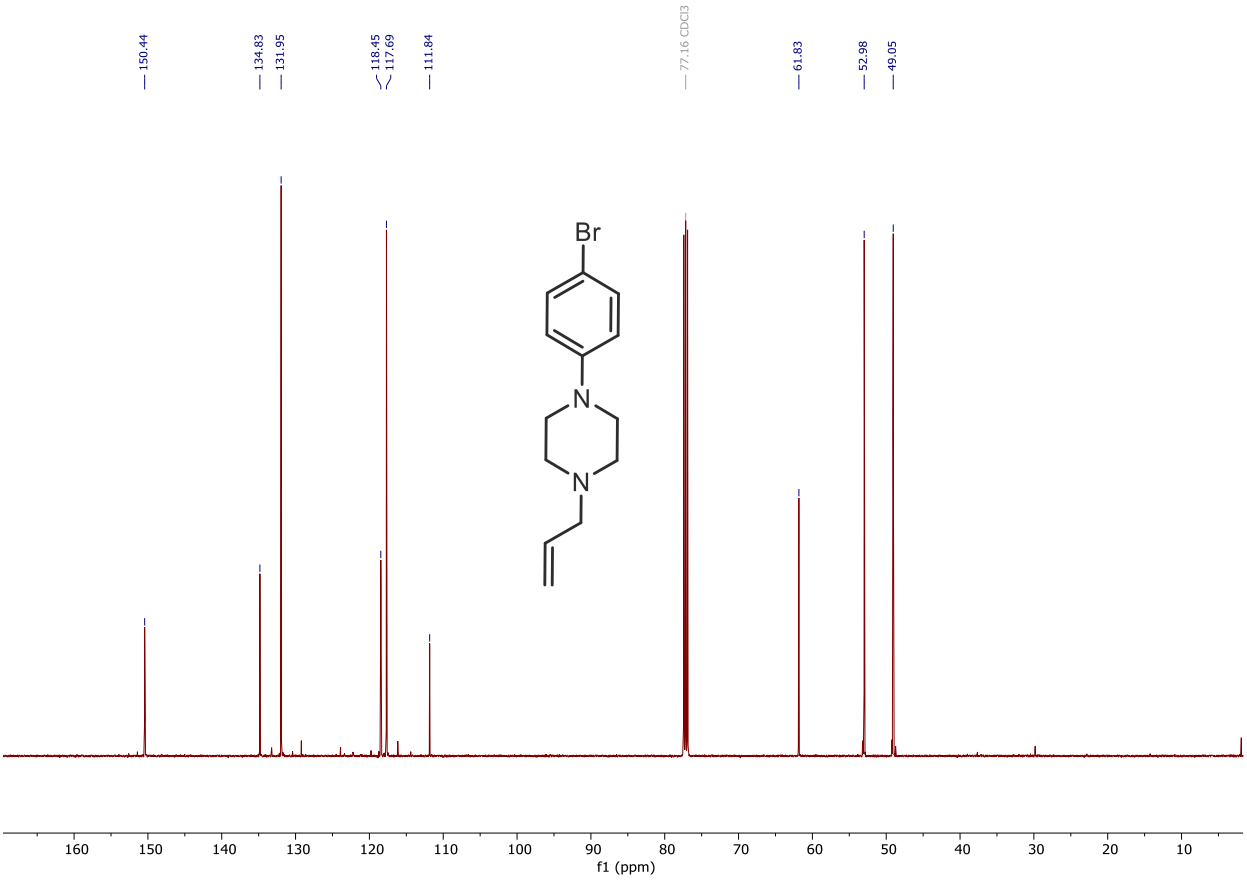
1H NMR



1-allyl-4-(4-bromophenyl) piperazine (5y)

$CDCl_3$

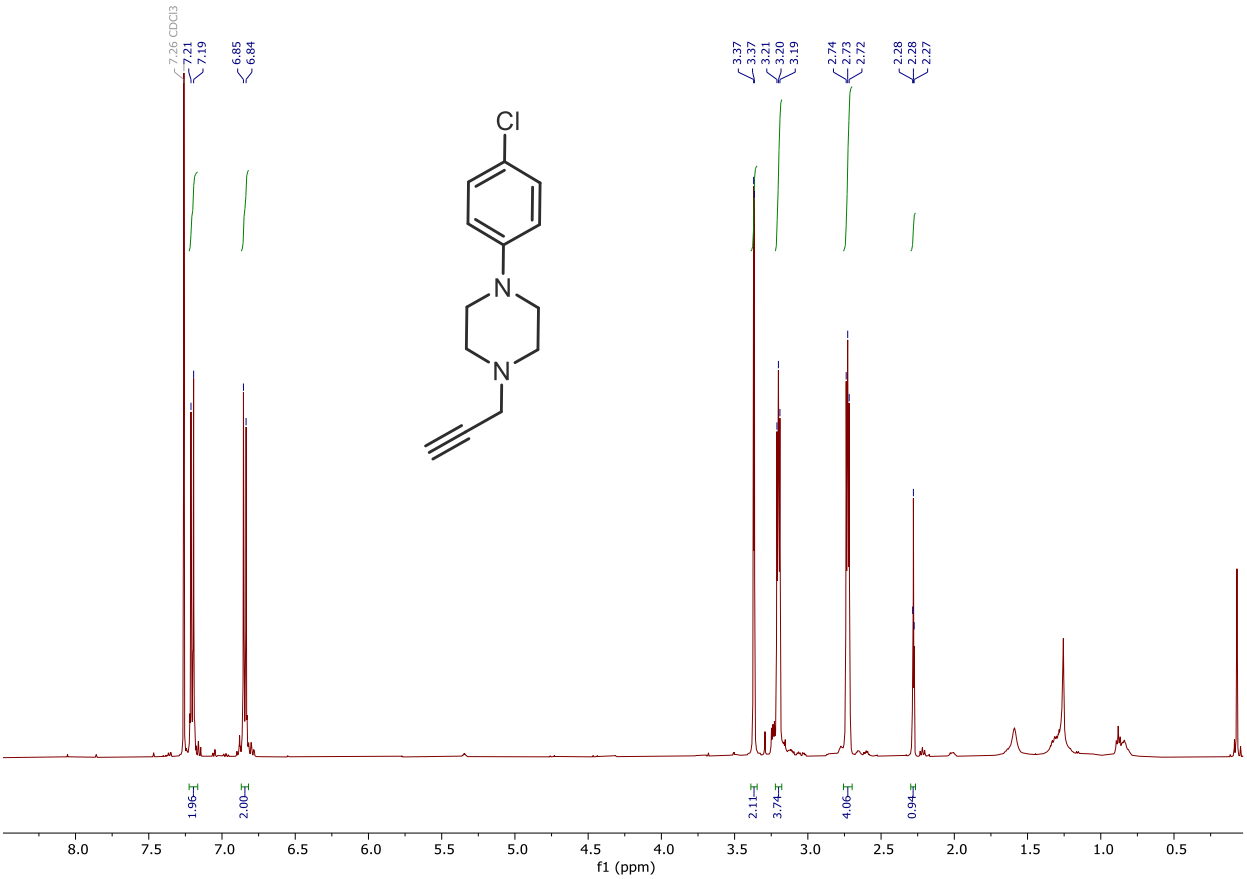
13C NMR



1-propargyl-4-(4-chlorophenyl) piperazine (5z)

$CDCl_3$

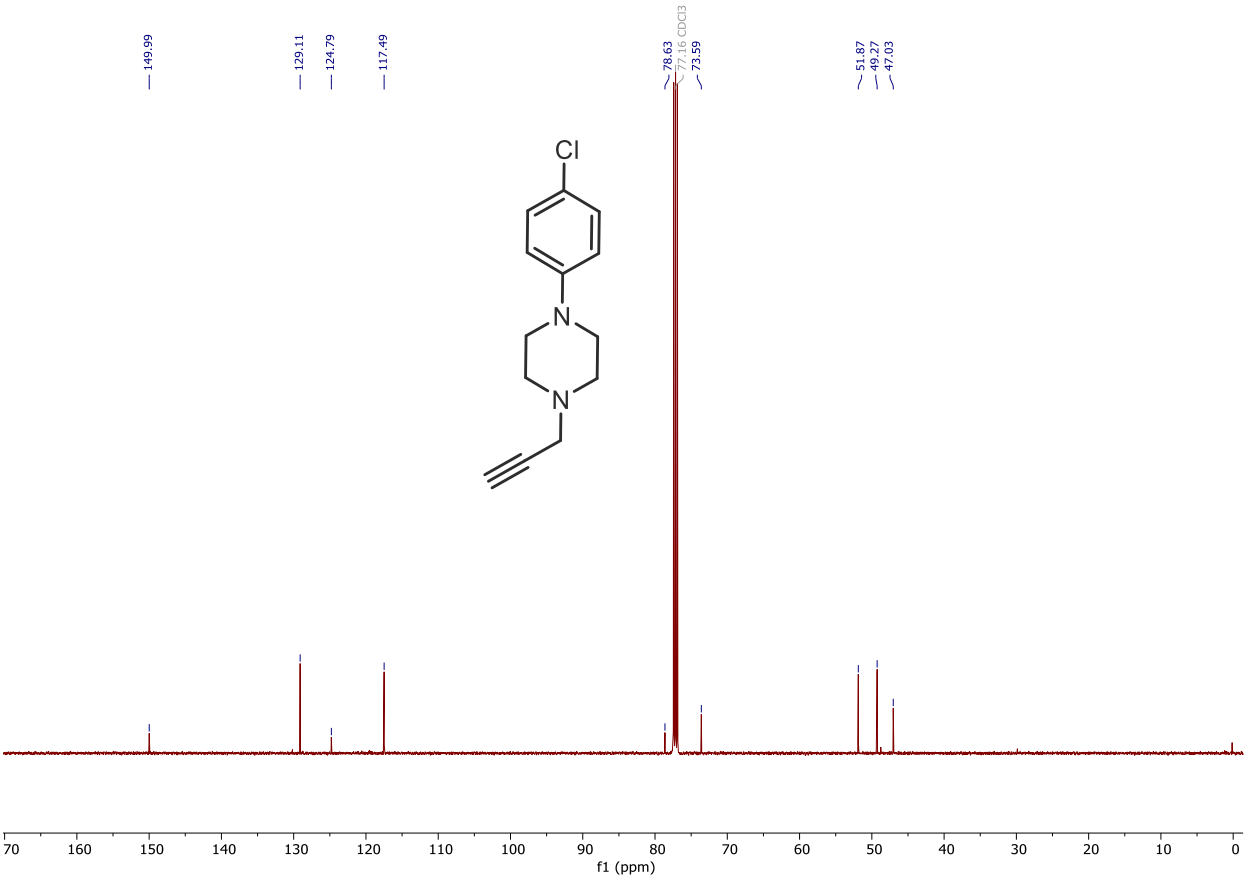
1H NMR



1-propargyl-4-(4-chlorophenyl) piperazine (5z)

$CDCl_3$

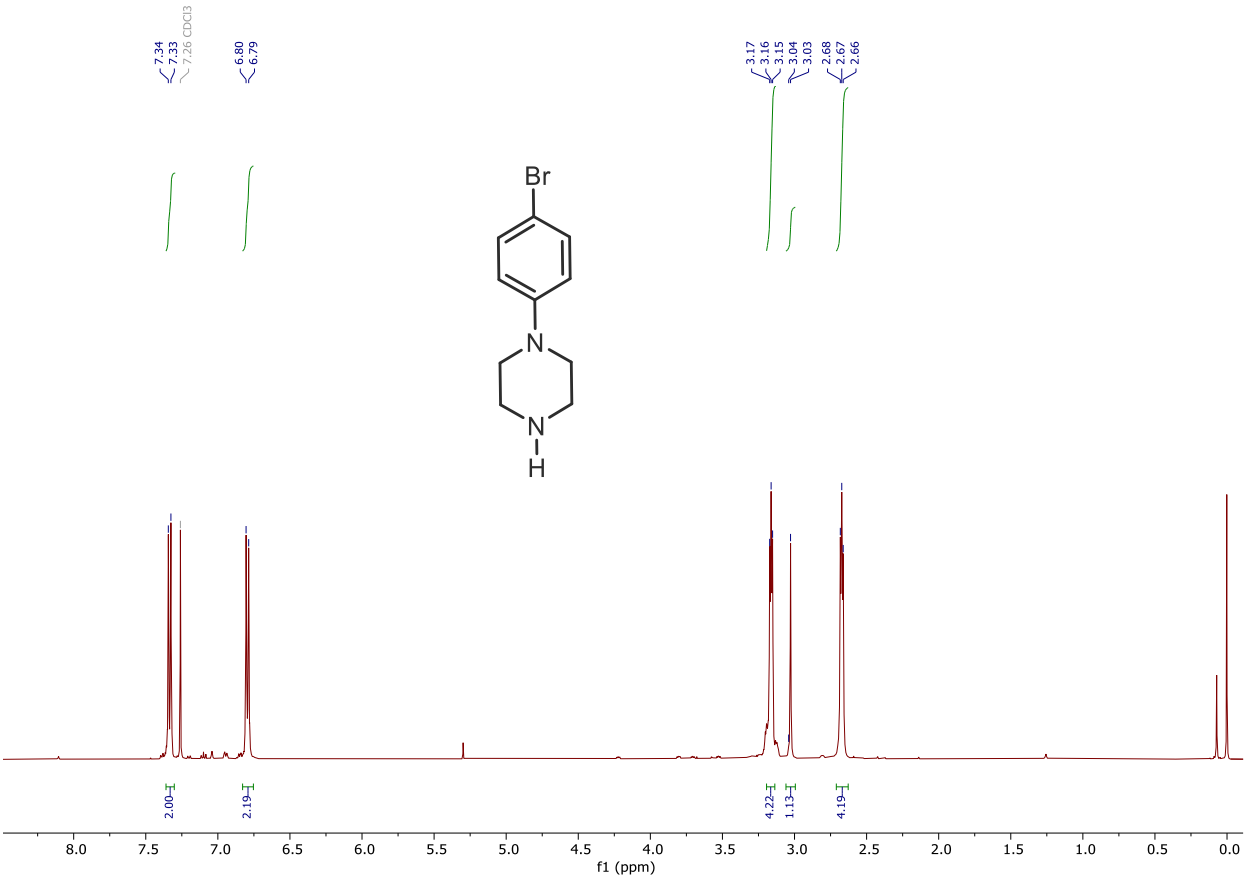
13C NMR



1-(4-bromophenyl) piperazine (5aa)

$CDCl_3$

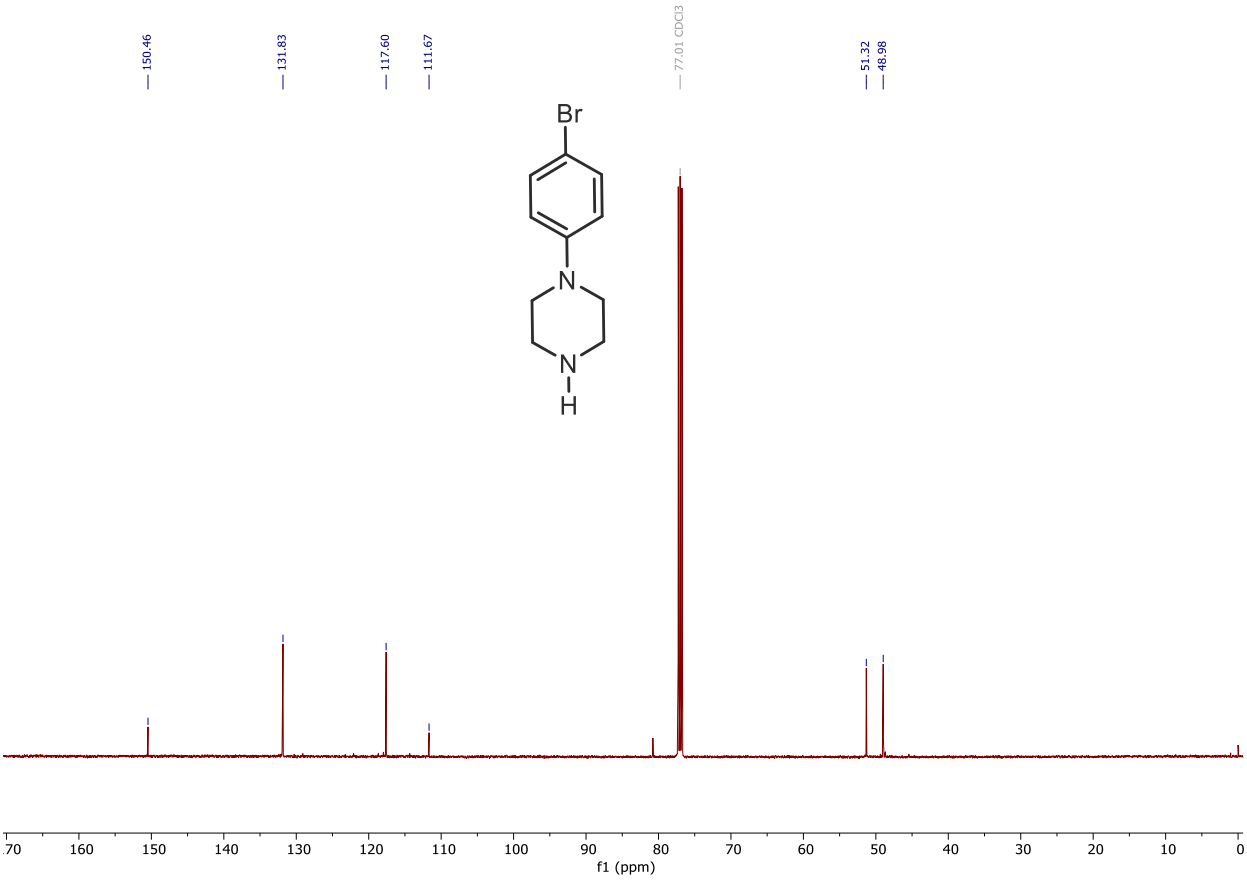
1H NMR



1-(4-bromophenyl) piperazine (5aa)

$CDCl_3$

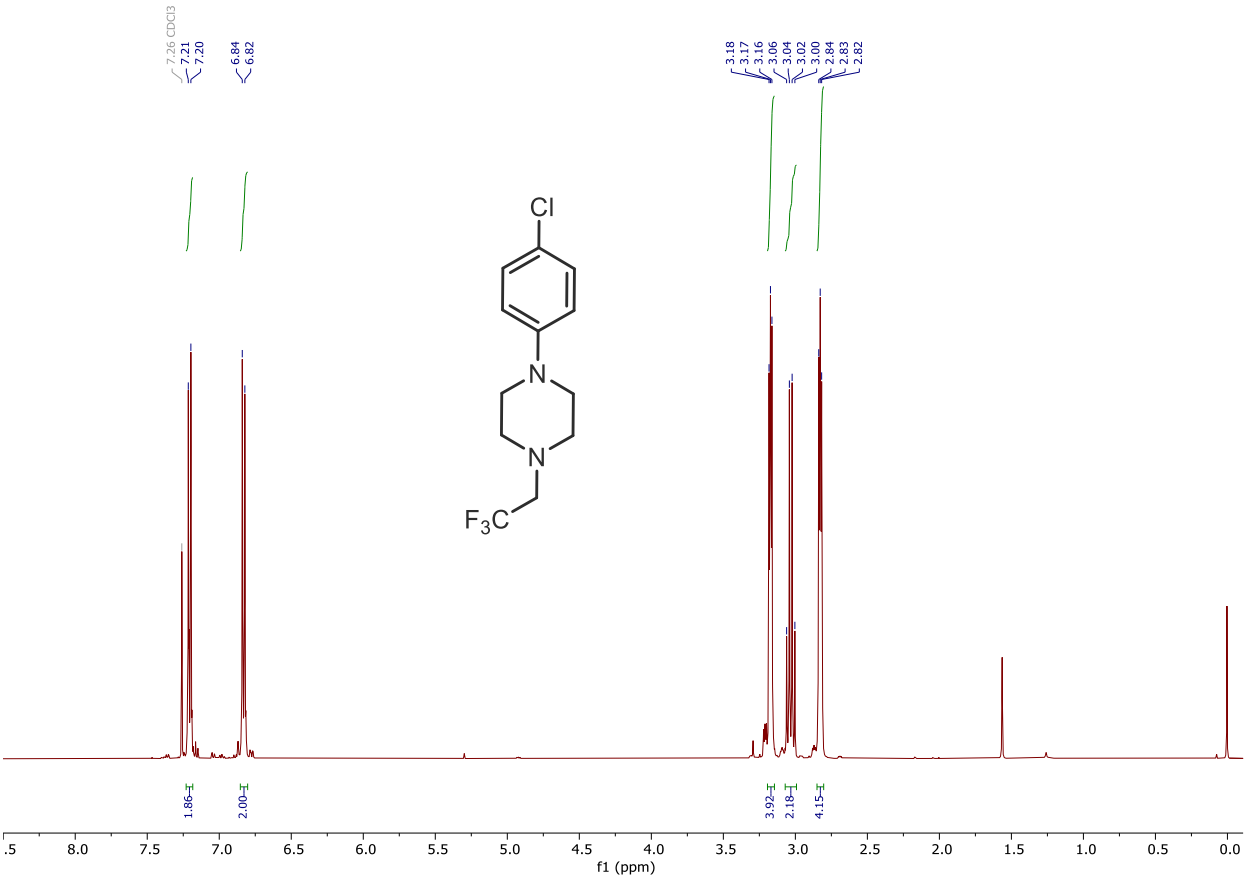
13C NMR



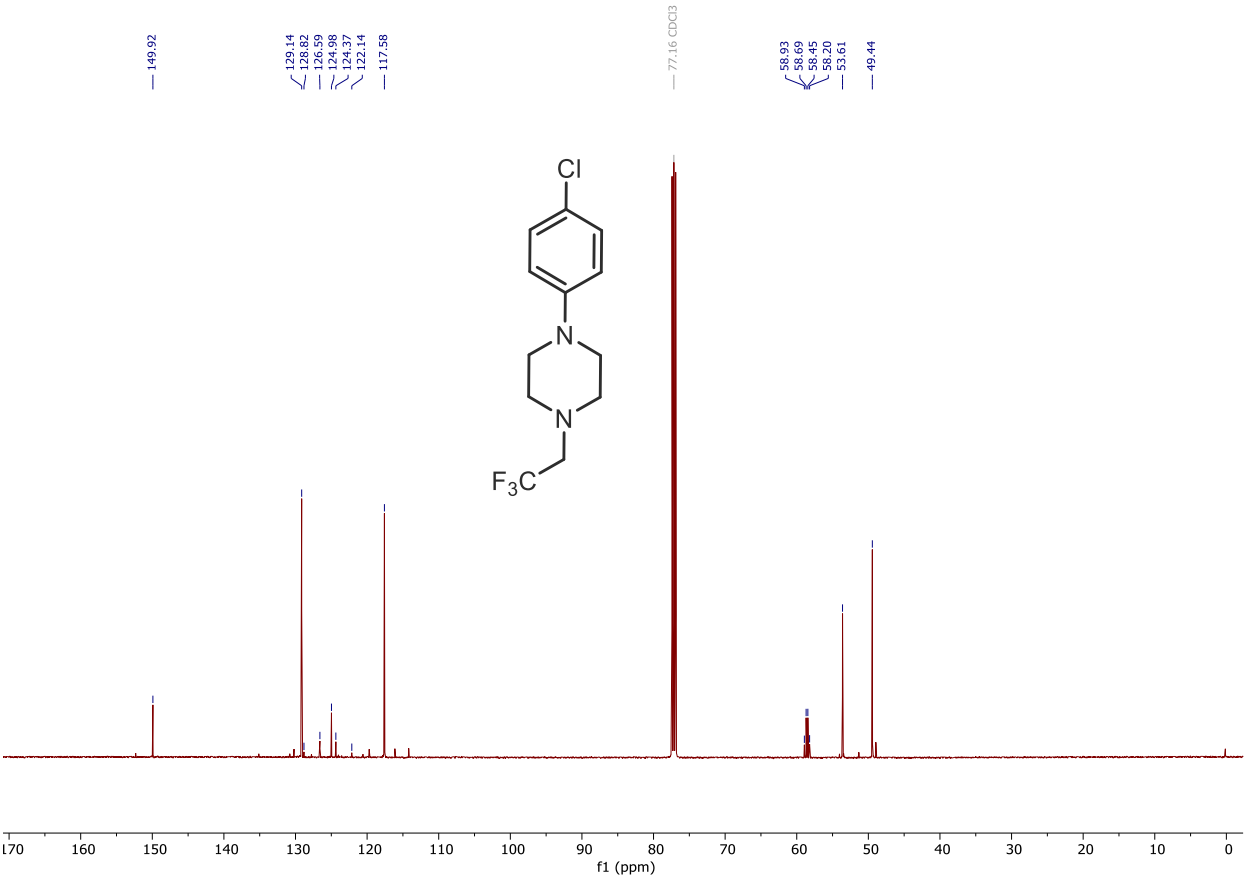
1-(2,2,2-trifluoroethyl)-4-(4-chlorophenyl) piperazine (5ab)

$CDCl_3$

1H NMR



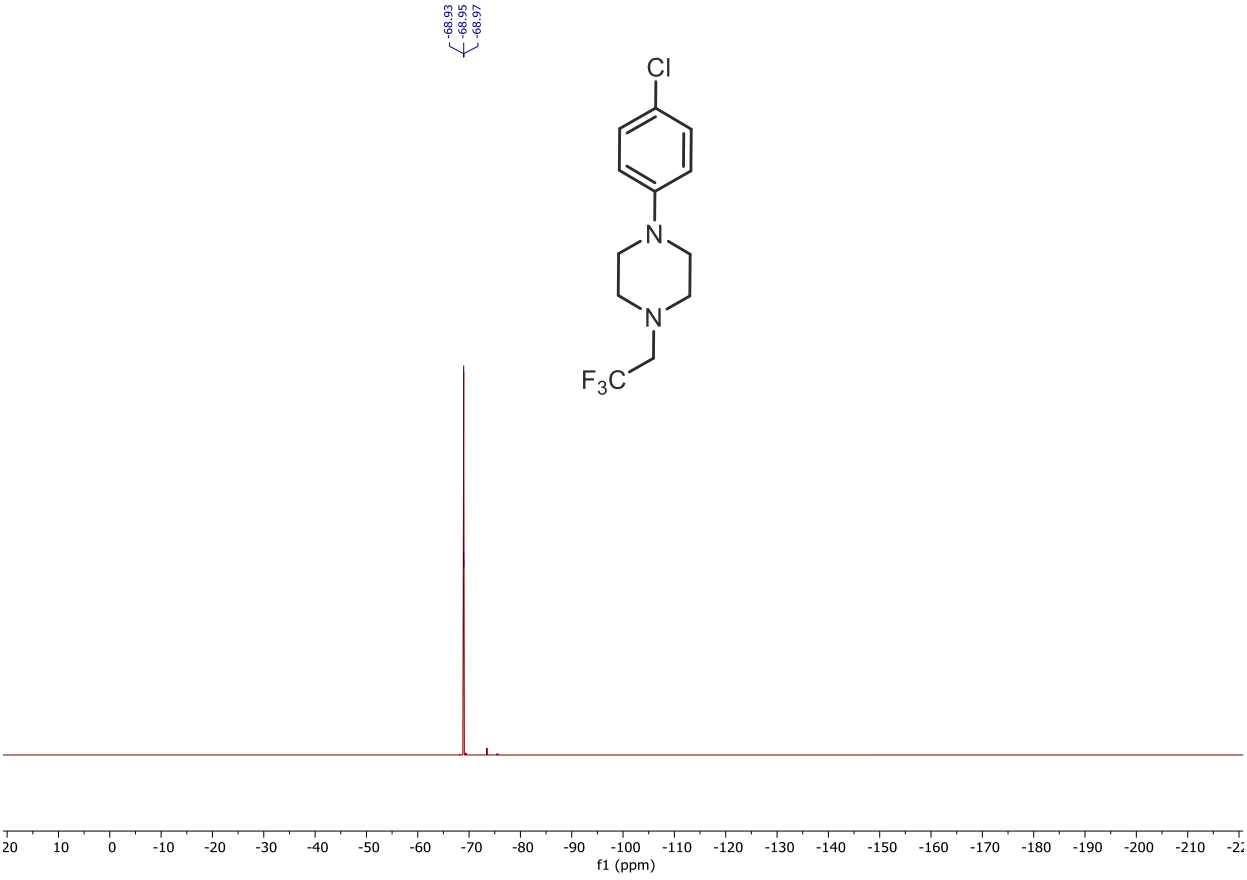
1-(2,2,2-trifluoroethyl)-4-(4-chlorophenyl) piperazine (5ab)
$CDCl_3$
13C NMR



1-(2,2,2-trifluoroethyl)-4-(4-chlorophenyl) piperazine (5ab)

$CDCl_3$

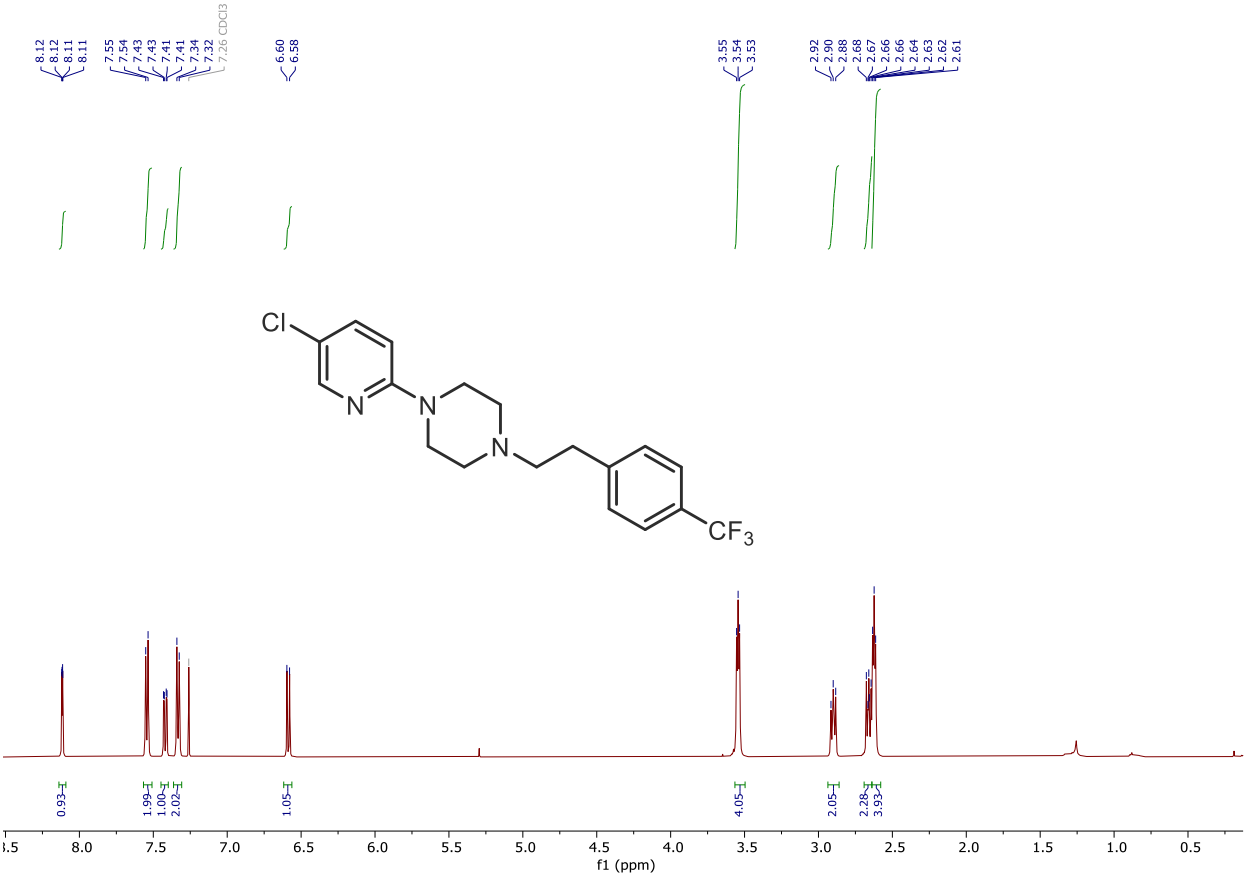
19F NMR



3-chloropyridine N-EtPhCF_3 piperazine (5ac)

$CDCl_3$

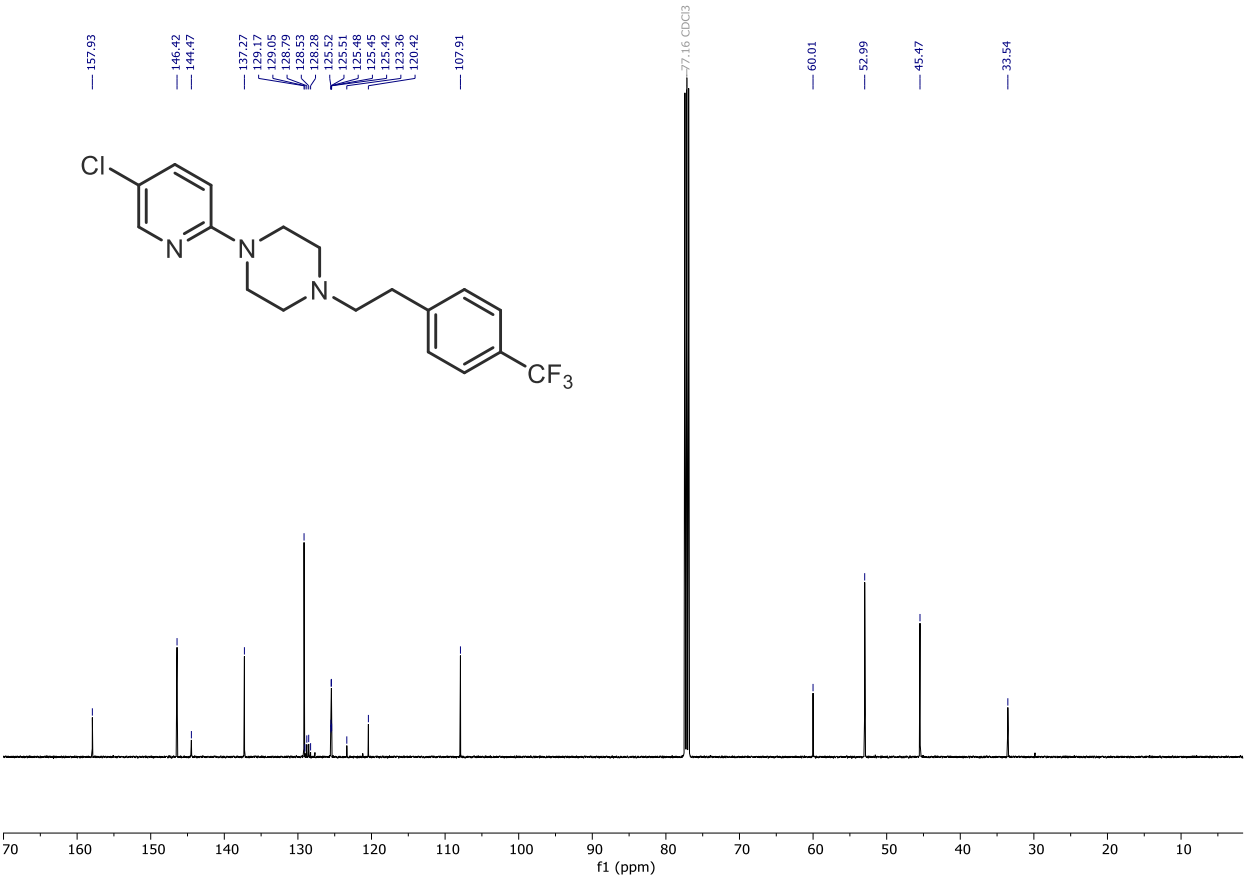
1H NMR



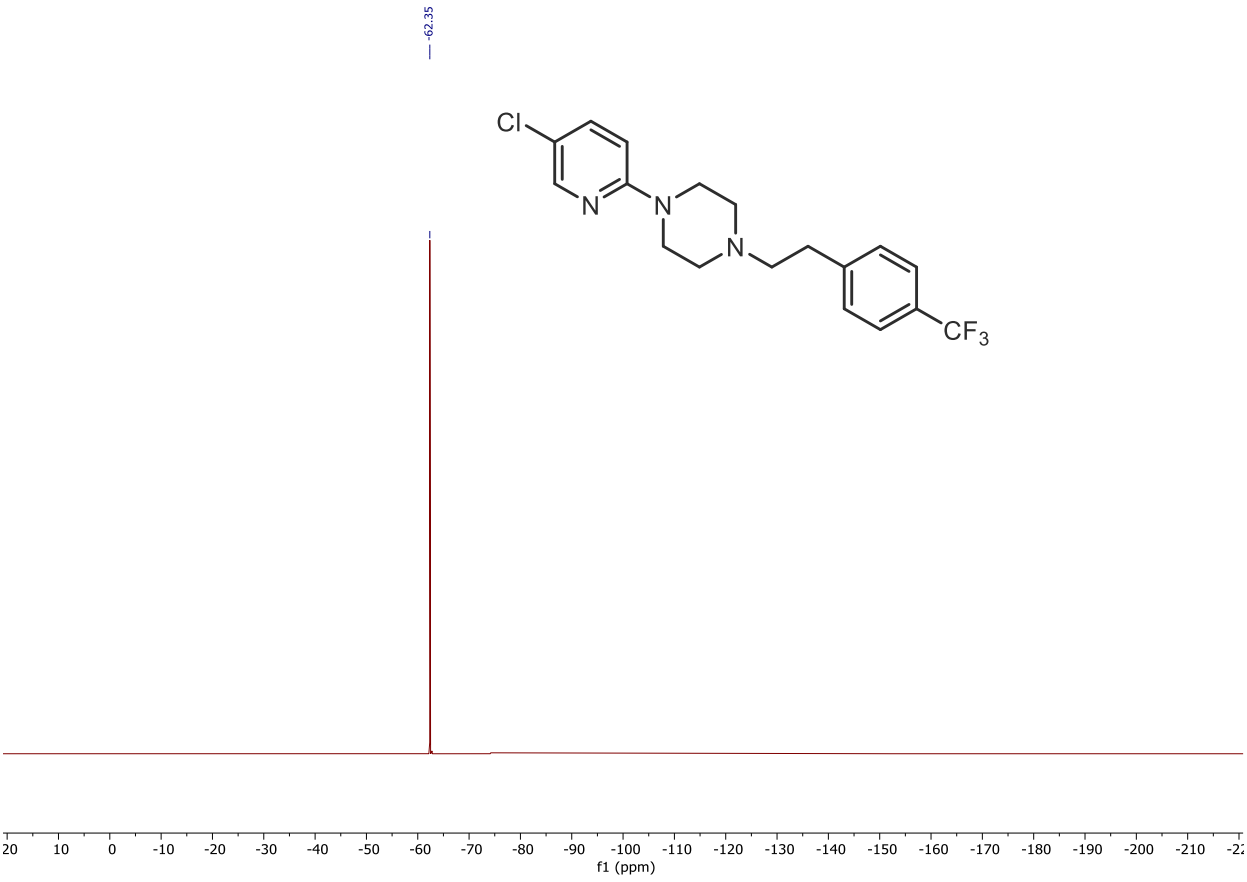
3-chloropyridine N-EtPhCF_3 piperazine (5ac)

$CDCl_3$

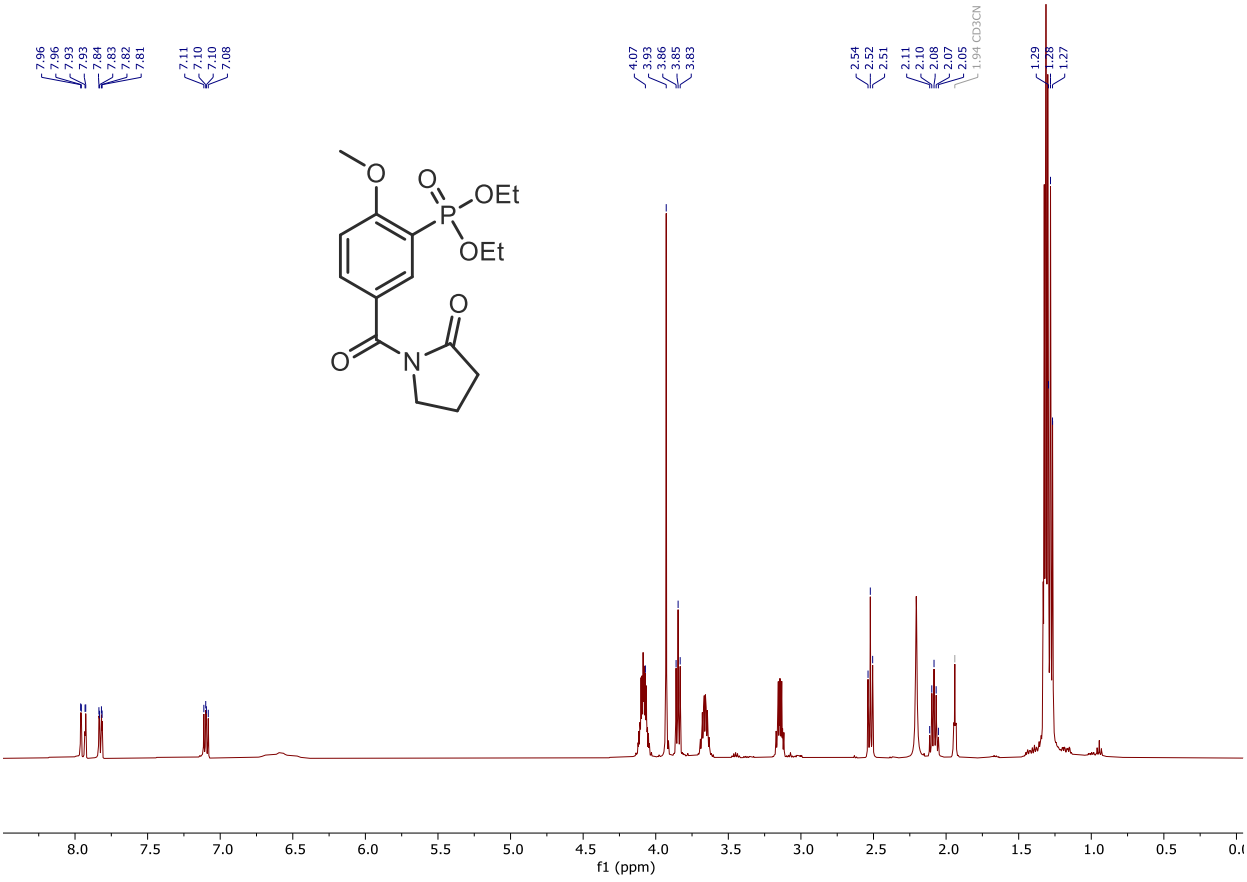
13C NMR



3-chloropyridine N-EtPhCF_3 piperazine (5ac)
$CDCl_3$
19F NMR



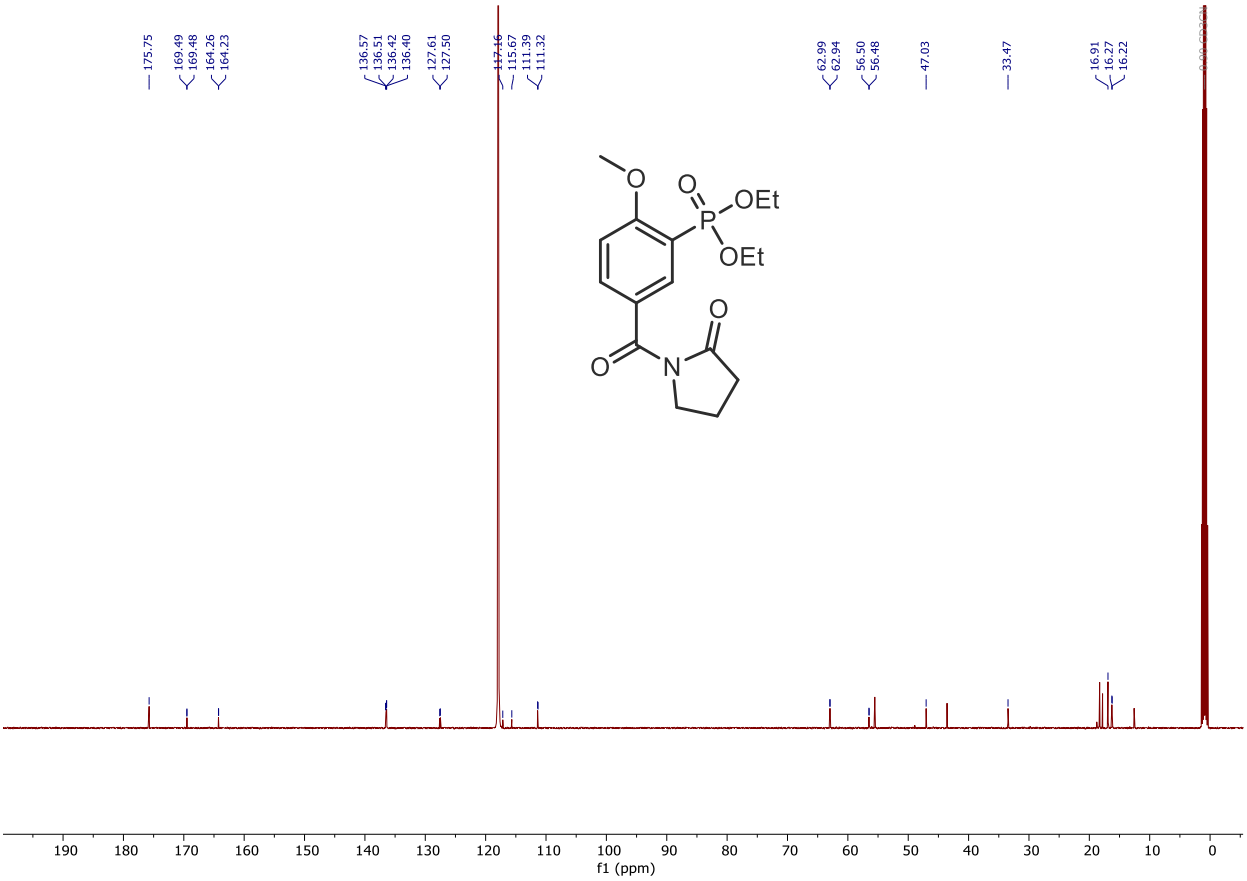
Aniraceteam Phosphonate Ester (6)
CD_3CN
1H NMR



Aniraceteam Phosphonate Ester (6)

CD_3CN

13C NMR



Aniraceteam Phosphonate Ester (6)
CD_3CN
31P NMR