Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis of Fluorinated Aminium Cations Coupled with Carborane Anions for Use as Strong One-Electron Oxidants

*Jillian J. Davidson, S. Olivia Gunther, Derek W. Leong, and Oleg. V. Ozerov**

Department of Chemistry, Texas A&M University, College Station Texas 77842

ozerov@chem.tamu.edu

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I. General considerations.

Unless otherwise specified all manipulations were performed under an atmosphere of Ar using a standard Schlenk line or a glovebox. Toluene, diethyl ether, hexanes, tetrahydrofuran, dichloromethane, Me_3SiCl, Me_3SiOTf, C_6D_6, 2,6-lutidine, CD_3CN, and CD_2Cl_2 were all dried over CaH_2, distilled or vacuum transferred, and then stored over molecular sieves in an Ar filled glove box. $Cs[HCB_{11}H_{11}]$ was purchased from Katchem. $K[(C_6F_5)_4]$ was purchased from Boulder Scientific Co. $Na[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ was purchased from Matrix Fine Chemicals Co. All other chemicals used were received from commercial venders. NMR spectra were recorded on Bruker Avance Neo 400 (^{1}H NMR, 400.200 MHz; ^{13}C NMR, 100.630 MHz; ^{19}F NMR, 376.564 MHz; ^{11}B NMR, 128.400 MHz, and ^{1}H NMR, 400.09 MHz; ^{13}C NMR, 100.603 MHz, respectively) and Varian Inova 500 spectrometer (^{1}H NMR, 499.703 MHz, ^{13}C NMR 125.580 MHz, ^{19}F NMR, 469.854 MHz). Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference (^{1}H NMR: δ 7.15 for C_6D_6; ^{13}C NMR: δ 128.06 for C_6D_6). ^{19}F NMR spectra were referenced externally using CF_3COOH (-78.5 ppm) respectively. Electron paramagnetic resonance spectra were recorded in a continuous wave X-band EleXsys EPR spectrometer at 298 K Electrochemical studies were carried out using a CH Instruments Model 700 D Series Electrochemical Analyzer and Workstation in conjunction with a three electrode cell. The working electrode was a CHI 104 glassy-carbon disk with a 3.0 mm diameter and the auxiliary electrode was composed of platinum wire. The third electrode, the reference electrode, was a $Ag/AgNO_3$ electrode. This was separated from solution by a fine porosity frit. CVs were conducted in dichloromethane with 0.3 M $[Bu_4N][PF_6]$ as the supporting electrolyte at scan rate of 100 mV/s. The concentrations of the analyte solutions were approximately 1.00×10^{-3} M. CVs were referenced to the Fc^+/Fc redox couple as recommended by IUPAC.[1,2] Atmospheric pressure chemical ionization (APCI) high resolution mass spectrometry (HRMS) experiments were performed using a Thermo Scientific Q Exactive Focus. Sample was injected into a 10 µL sample loop and carried using methanol (MeOH) as a mobile phase at a flow rate of 300 µL/min. Ultraviolent-visible (UV-vis) spectra were collected on a UV-2450 UV-Vis spectrophotometer (Shimadzu, Japan). Elemental analyses were performed by CALI Laboratories, Parsippany, NJ. Electrochemical data for **T1–3**[3] has been previously reported. Synthetic procedures for Na[$HCB_{11}Cl_{11}$],[4] Na[$MeCB_{11}Cl_{11}$],[5] **T4**,[6] **T5**,[7] **T7**,[8] and **T8**[9] have been previously reported.

II. Synthesis and characterization of triarylamines.

T4. A Schlenk flask was charged with bis(*p*-fluorophenyl)amine (0.95 g, 4.6 mmol), 4-fluoroiodobenzene (0.58 mL, 4.6 mmol), DPPF (76 mg, 0.14 mmol), $Pd(OAc)_2$ (10 mg, 0.045 mmol), sodium *tert*-pentoxide (0.56 g, 5.1 mmol), a stir bar, and toluene (25 mL). The reaction mixture was then placed in a 120 °C oil bath and refluxed for 24 h. After cooling the solution to room temperature the volatiles were removed under *vacuo* and the resulting brown oil was taken up in hexanes and filtered through a pad of silica gel. Concentration of the hexane solution and recrystallization at -35 °C resulted in the formation of colorless crystals which were collected and dried under vacuum to yield **T4** (0.35 g, 1.2 mmol, 25%). The ^{1}H, ^{13}C, and ^{19}F spectral data were in accordance with previously reported literature.[6] $E_{½}$ = 0.59 V vs Fc^+/Fc.

T5. A Schlenk flask was charged with bis(4-fluorophenyl)amine (2.9 g, 14 mmol), phenyl iodide (1.6 mL, 14 mmol), DPPF (77 mg, 0.14 mmol), $Pd(OAc)_2$ (16 mg, 0.070 mmol), sodium *tert*-pentoxide (1.7 g, 15 mmol), a stir bar, and toluene (20 mL). The reaction was then refluxed for 18 h and then the volatiles were removed under vacuum. The resulting brown oil was taken up in hexanes and filtered through a pad of Celite and then a pad of silica gel. The colorless solution was concentrated and stored at -35 °C. The resulting colorless crystals were then collected and dried to yield **T5** and a small amount of residual biphenyl. The biphenyl product was removed via vacuum distillation. **T5** was then isolated as a colorless solid (1.5 g, 5.3 mmol, 38%). The ^{1}H, ^{13}C, and ^{19}F spectral data were in accordance with previously reported literature.[7]

T6. A Schlenk flask was charged with bis(4-fluorophenyl)amine (1.1 g, 5.3 mmol), 4-iodobenzotrifluoride (0.78 mL, 5.3 mmol), DPPF (88 mg, 0.16 mmol), Pd(OAc)$_2$ (12 mg, 0.053 mmol), sodium *tert*-pentoxide (0.64 g, 5.8 mmol), a stir bar, and toluene (20 mL). The reaction was refluxed for 24 h and prior to removing the volatiles under vacuum. The resulting brown oil was taken up in hexanes and filtered through a pad of Celite and then a pad of silica gel. The colorless solution was concentrated and stored at -35 °C. Colorless crystals were then collected and dried to yield **T6** and a small amount of residual 4,4-bis(trifluoromethyl)-1,1-biphenyl. The biphenyl product was then removed via vacuum distillation. **T6** was isolated as a colorless powder (0.68 g, 1.9 mmol, 37%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.23 (d, J_{HF} = 9 Hz, 2H), 6.70-6.56 (m, 10H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 160.0 (d, J_{CF} = 244 Hz, *C*F), 151.1 (s), 142.9 (s), 127.4 (d, J_{CF} = 8 Hz), 126.7 (d, J_{CF} = 4 Hz), 124.9 (d, J_{CF} = 268 Hz, *C*F$_3$), 123.0 (d, J_{CF} = 32 Hz, *C*CF$_3$), 120.3 (s), 116.7 (d, J_{CF} = 23 Hz). ^{19}F NMR (376 MHz, C_6D_6): δ -63.9 (CF$_3$), -119.9 (CF). $E_{½}$ = 0.78 V vs Fc^{+}/Fc. HRMS (+APCI) m/z: [M]$^{+}$, calcd. For $C_{19}H_{12}F_5N^{+}$ 349.0884; Found 349.0886; [M+H]+, calcd for $C_{19}H_{13}F_5N^{+}$ 350.0963; Found 350.0965.

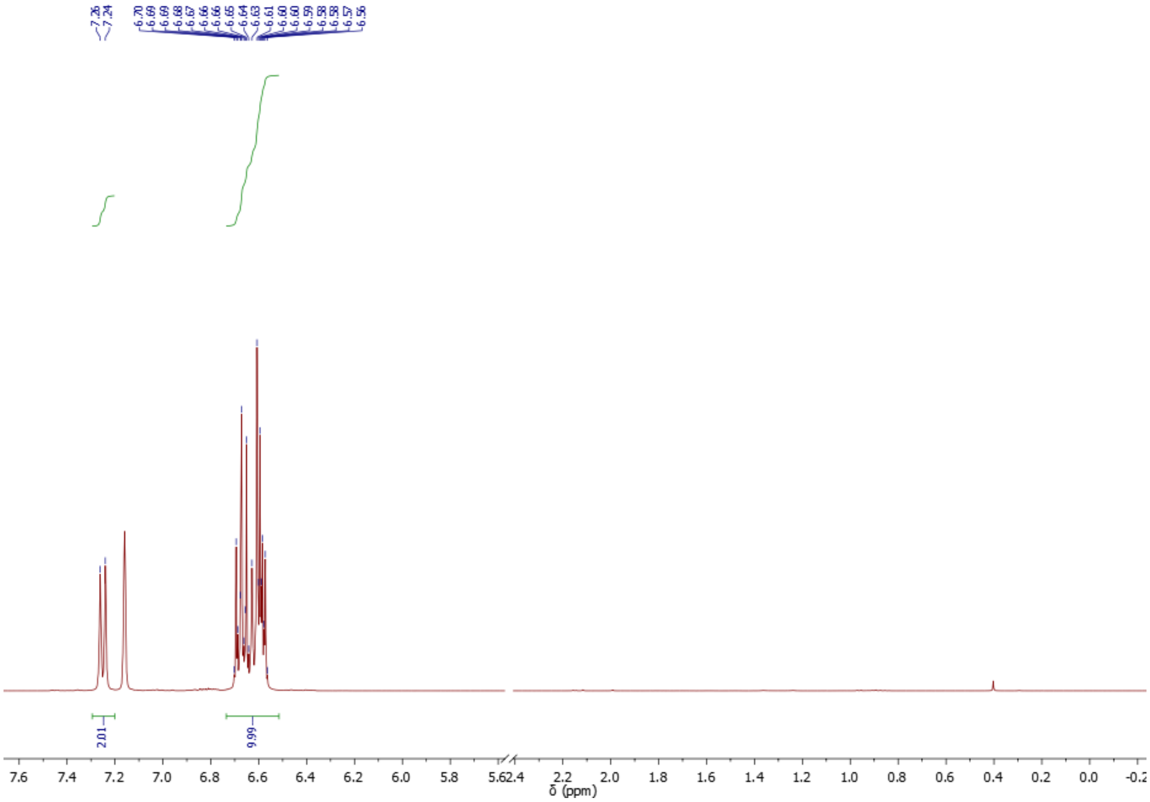

Figure S1. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **T6**. Residual water from the solvent is also observed.

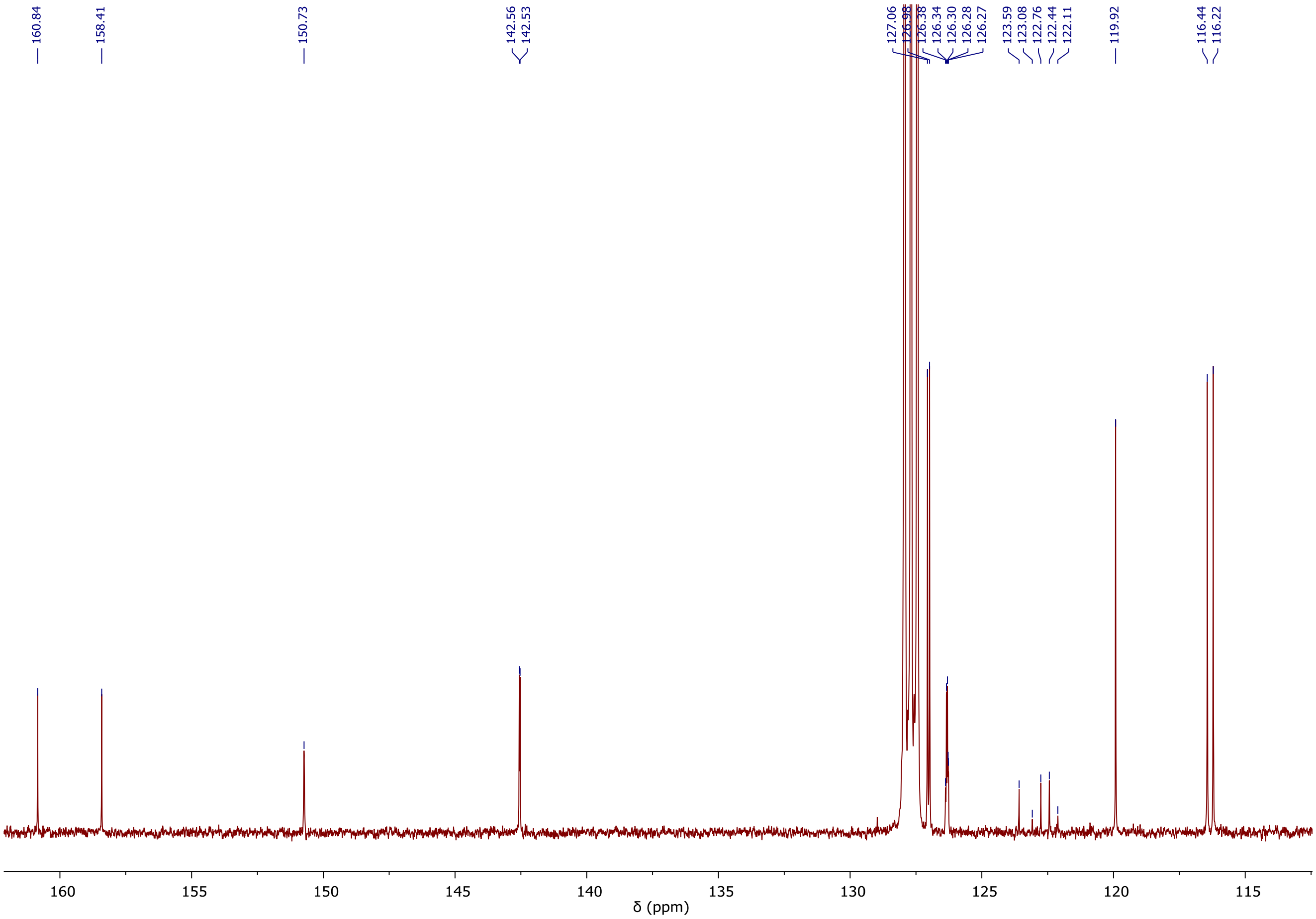

Figure S2. ${}^{13}C\{{}^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **T6**.

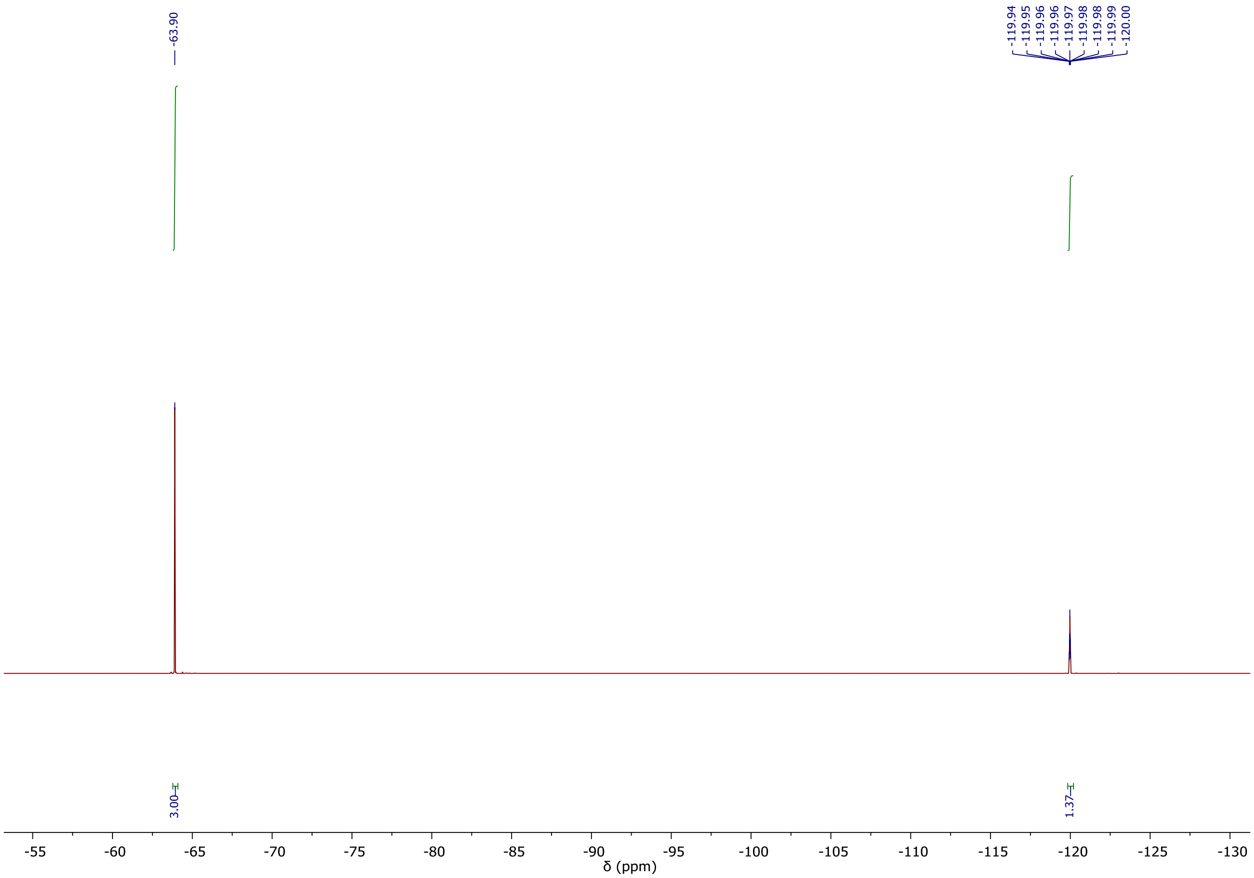

Figure S3. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T6**.

T8. A Schlenk flask was charged with diphenylamine (7.9 g, 0.46 mol), 4-iodobenzotrifluoride (6.7 mL, 0.46 mol), $Pd(OAc)_2$ (31 mg, 0.14 mmol), DPPF (0.10 g, 0.18 mmol), sodium *tert*-pentoxide (5.0 g, 0.46 mol), a stir bar, and toluene (25 mL). The reaction was then refluxed for 24 h after which time a small aliquot was analyzed by ^{19}F NMR analysis. Two products were observed at -63.8 and -65.2 ppm. The reaction was allowed to continue refluxing for an additional 24 hours. ^{19}F NMR analysis revealed the same reaction mixture. The volatiles were removed under vacuum. The residual diarylamine and 4,4-trifluoromethyl-1,1-biphenyl were removed via distillation. The remaining brown oil was then dissolved in hexanes and passed through a pad of Celite and then a pad of silica gel. Concentration of the hexanes solution and storage at -35 °C resulted in copious precipitation of **T8** as a colorless solid (7.9 g, 0.21 mol, 45%). The ^{1}H, ^{19}F, and ^{13}C NMR spectral data were in accordance with previously reported literature.[9]

T9. A Schlenk flask was charged with **T4** (84 mg, 0.28 mmol), a stir bar, and dichloromethane (5.0 mL). Br_2 (0.30 mL) was then added drop-wise. The reaction mixture was then stirred for 3 h prior to removal of the volatiles. The resulting tan solid was then dissolved in a minimal amount of hexanes and recrystallized to yield **T9** as colorless needles (0.14 g, 0.27 mmol, 95%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.08 (dd, 3H, J_{HF} = 7 Hz, J_{HH} = 3 Hz, Ar-*H*), 6.50 (m, 3H, Ar-*H*), 6.32 (m, 3H, Ar-*H*). ^{1}H{^{19}F δ -118.2} NMR (400 MHz, C_6D_6): δ 7.08 (d, 3H, J_{HH} = 3 Hz, Ar-*H*), 6.50 (dd, J_{HH} = 8 Hz, J_{HH} = 3 Hz, 3H, Ar-*H*), 6.32 (d, J_{HH} = 8 Hz, 3H, Ar-*H*). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 159.5 (d, J_{CF} = 245 Hz, *C*F), 141.9, 127.4 (m), 121.9, 121.7 (d, J_{CF} = 25 Hz), 114.7 (d, J_{CF} = 22 HZ). ^{19}F NMR (376 MHz, C_6D_6): δ -118.2 (q, J_{HF} = 7 Hz). $E_{½}$ = 1.05 V vs Fc^+/Fc. HRMS (+APCI) m/z: $[M+H]^+$, calcd. For $C_{18}H_{10}Br_3F_3N^+$ 535.8290; Found 535.8291.

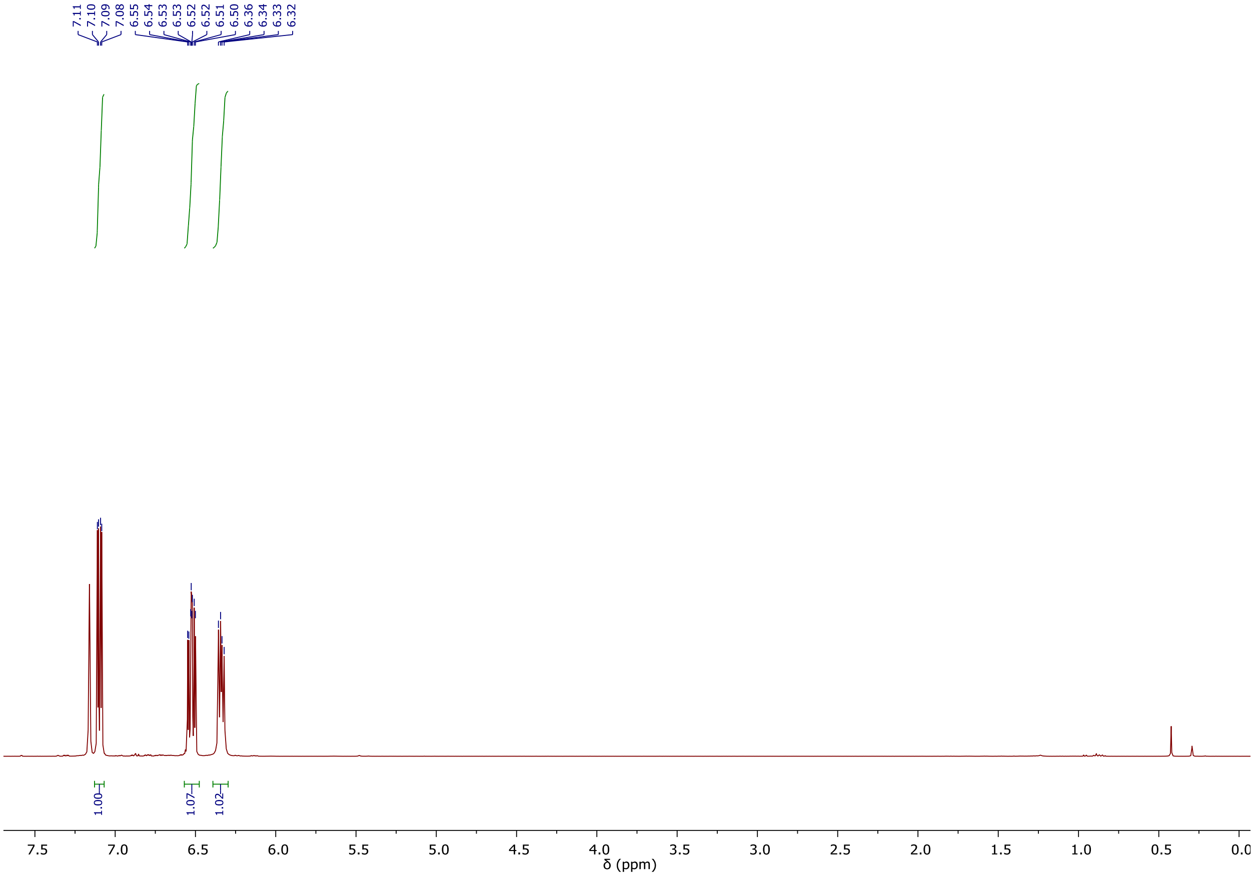

Figure S4. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **T9**. Water and silicone grease can also be observed.

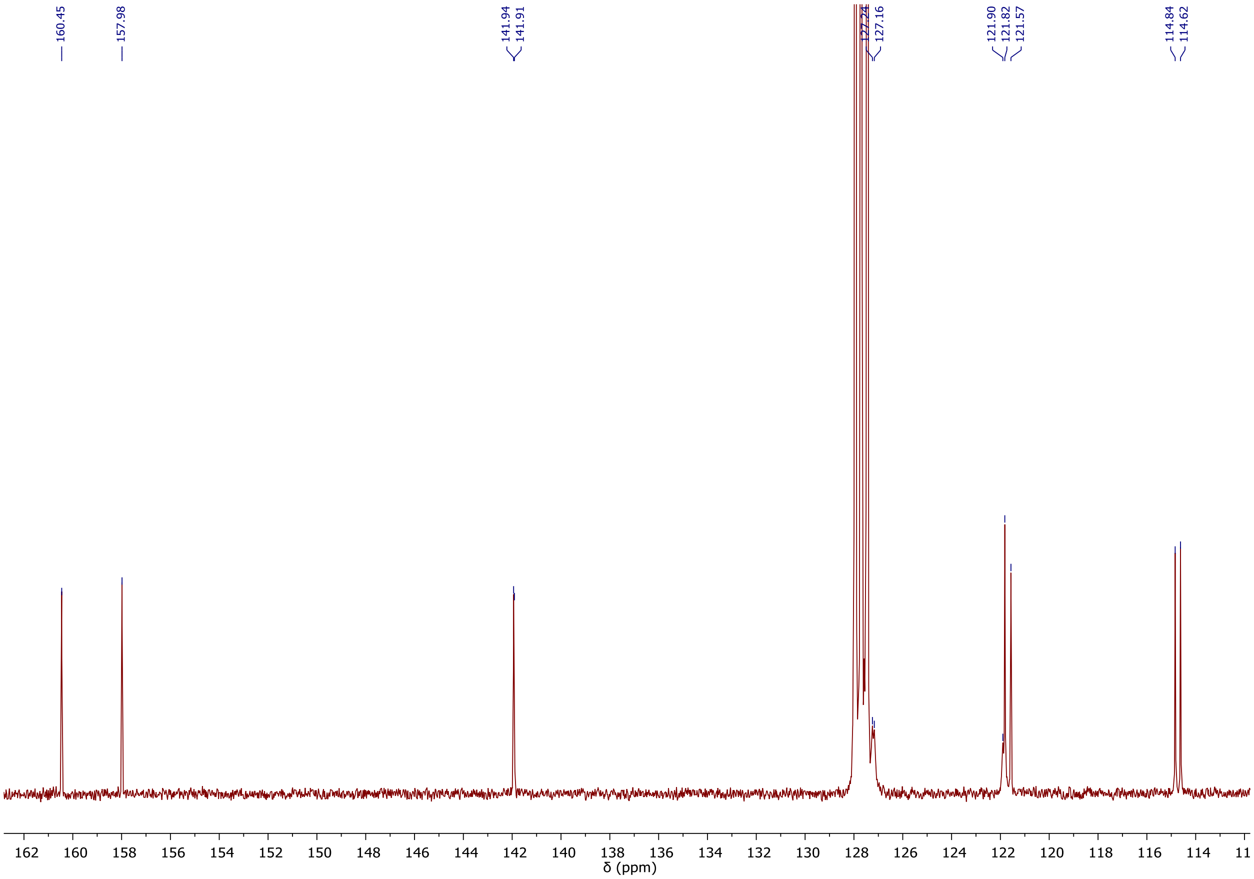

Figure S5. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **T9**.

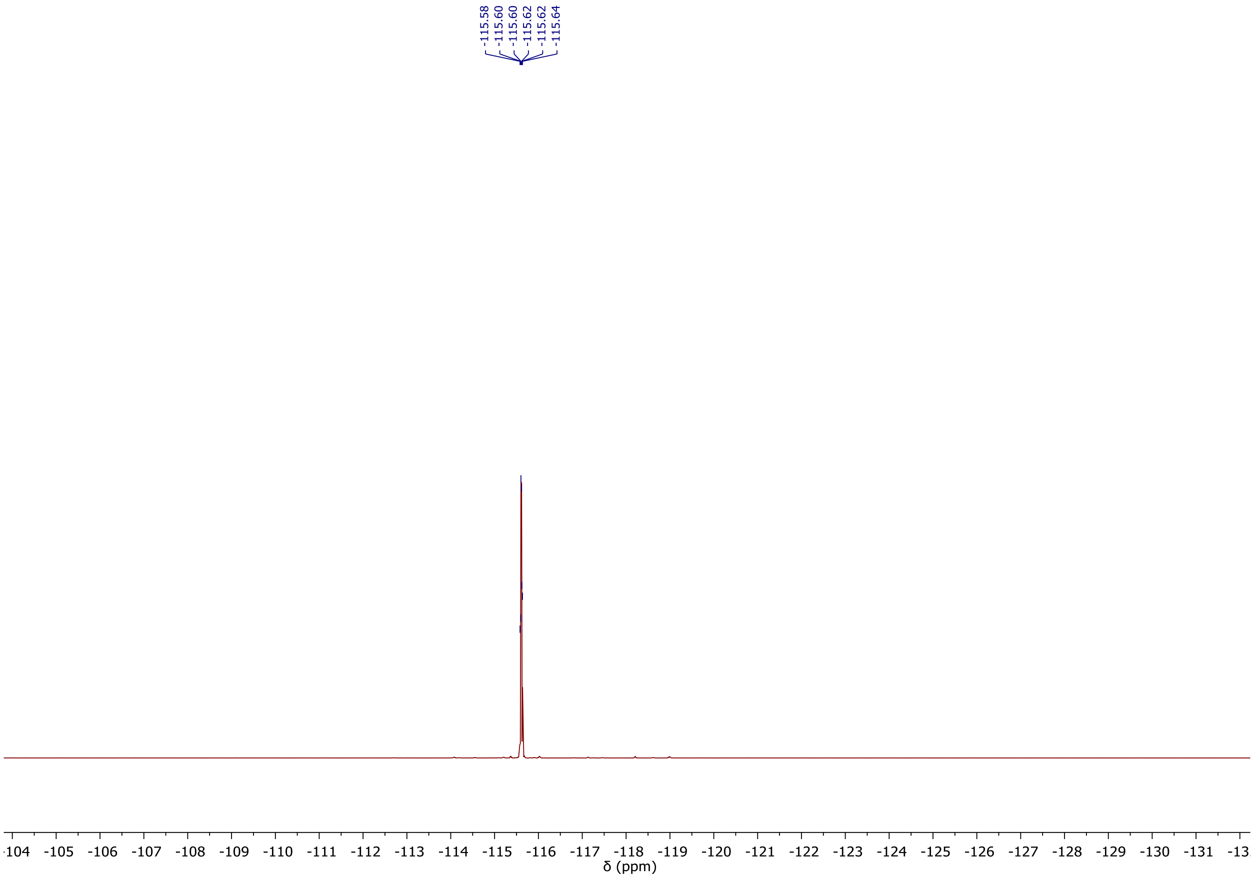

Figure S6. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T9**.

T10. A Schlenk flask was charged with **T5** (3.77 g, 13.4 mmol), dichloromethane (10 mL), and a stir bar. The reaction was stirred for 18 h after adding Br_2 (1.00 mL) in a drop-wise fashion. Removal of a small aliquot and analysis by ^{19}F NMR spectroscopy revealed a mixture of products. Br_2 (1.00 mL) was added a second time. The reaction was stirred for another 18 h. ^{19}F NMR analysis of a small aliquot of the reaction mixture revealed only one product at -117.7 ppm. The volatiles were next removed under vacuum and the resulting oil was taken up in hexanes and passed through a pad of silica gel. Concentration of the solution and storage at -35 °C resulted in the formation of green needles. Sublimation of the green crystals, while being heated under vacuum, gave **T10** as a colorless solid (5.45 mg, 9.22 mmol, 68%). ^{1}H NMR (400

MHz, C_6D_6): δ 7.57 (d, J_{HH} = 2 Hz, 1H), 7.06 (dd, J_{HF} = 8 Hz, J_{HH} = 3 Hz, 2H), 6.98 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H), 6.50 (m, 2H), 6.29 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 2H), 6.22 (d, J_{HH} = 9 Hz, 1H). $^1H\{^{19}F$ δ -117.7} NMR (400 MHz, C_6D_6): δ 7.57 (d, J_{HH} = 2 Hz, 1H), 7.06 (d, J_{HH} = 3 Hz, 2H), 6.98 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H), 6.50 (m, 2H), 6.29 (d, J_{HH} = 9 Hz, 2H), 6.22 (d, J_{HH} = 9 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 159.7 (d, J_{CF} = 249 Hz, *C*F), 144.8 (s, *C*N), 141.6, 141.5, 137.0, 131.0, 121.8 (m, overlapping signals), 121.5, 117.8, 114.8 (d, J_{CF} = 22 Hz). ^{19}F NMR (376 MHz, C_6D_6): δ -117.7 (m). $E_{½}$ = 1.11 V vs Fc^+/Fc. HRMS (+APCI) m/z: $[M+H]^+$, calcd. For $C_{18}H_{10}Br_4F_2N^+$ 597.7468; Found 597.7470.

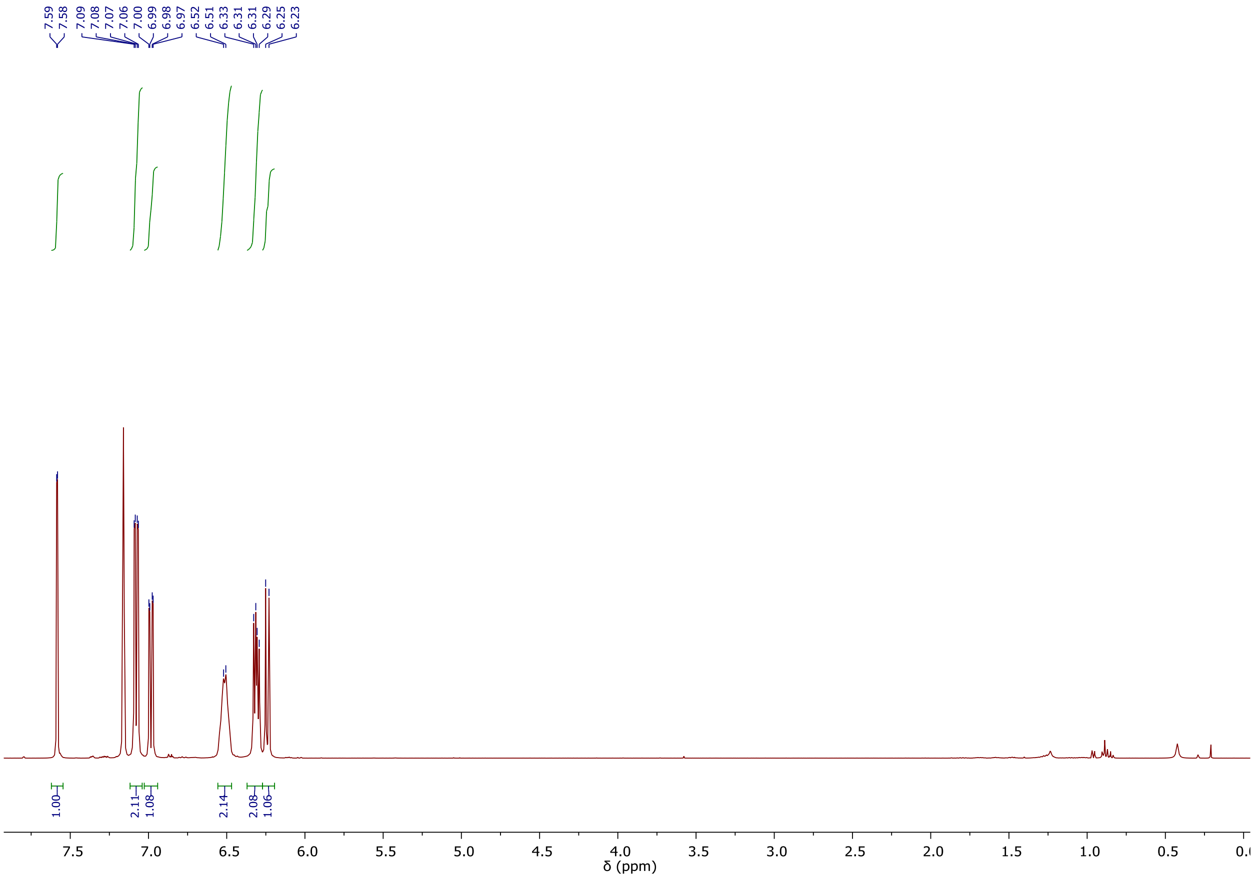

Figure S7. ^1H NMR spectrum (400 MHz, C_6D_6) of **T10**. Trace quantities of silicone grease, hexanes, and water are also observed.

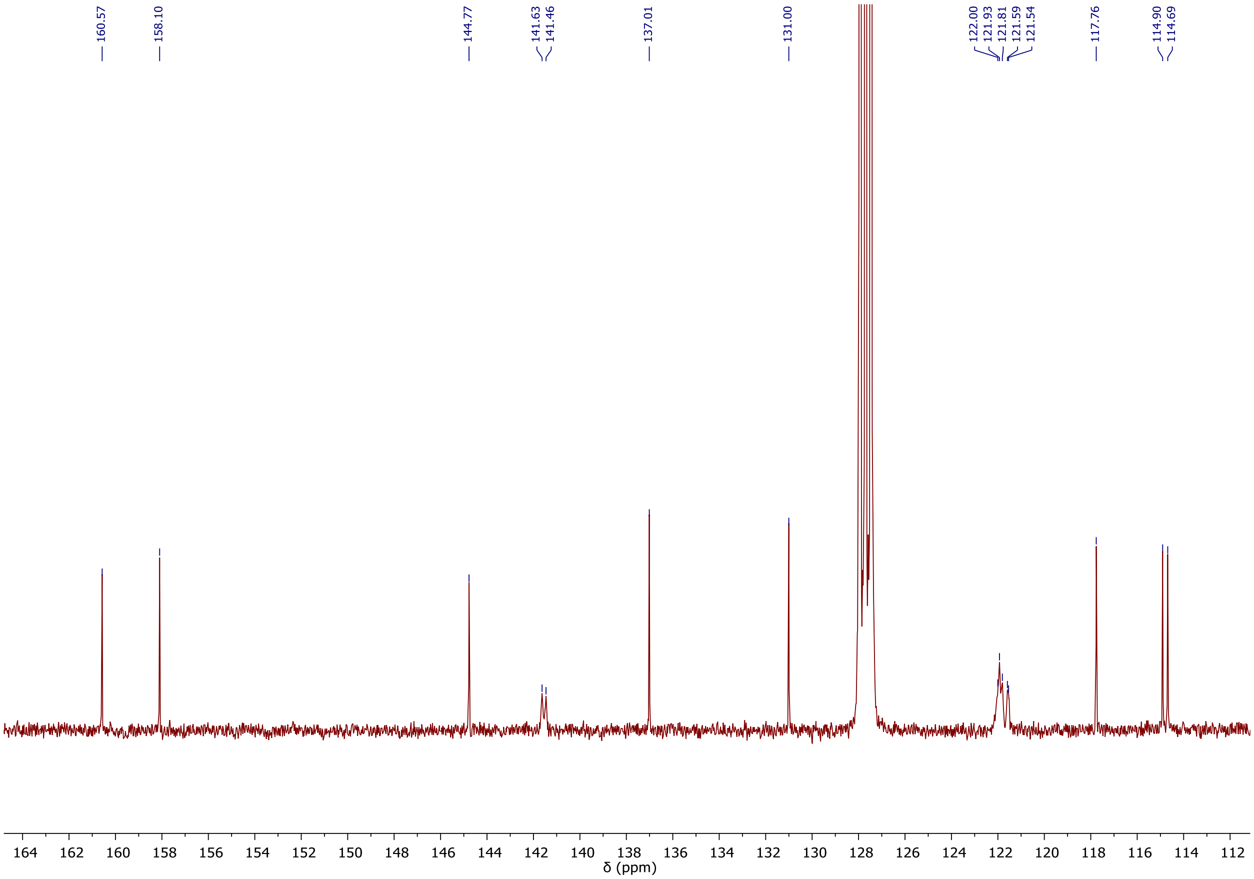

Figure S8. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **T10**.

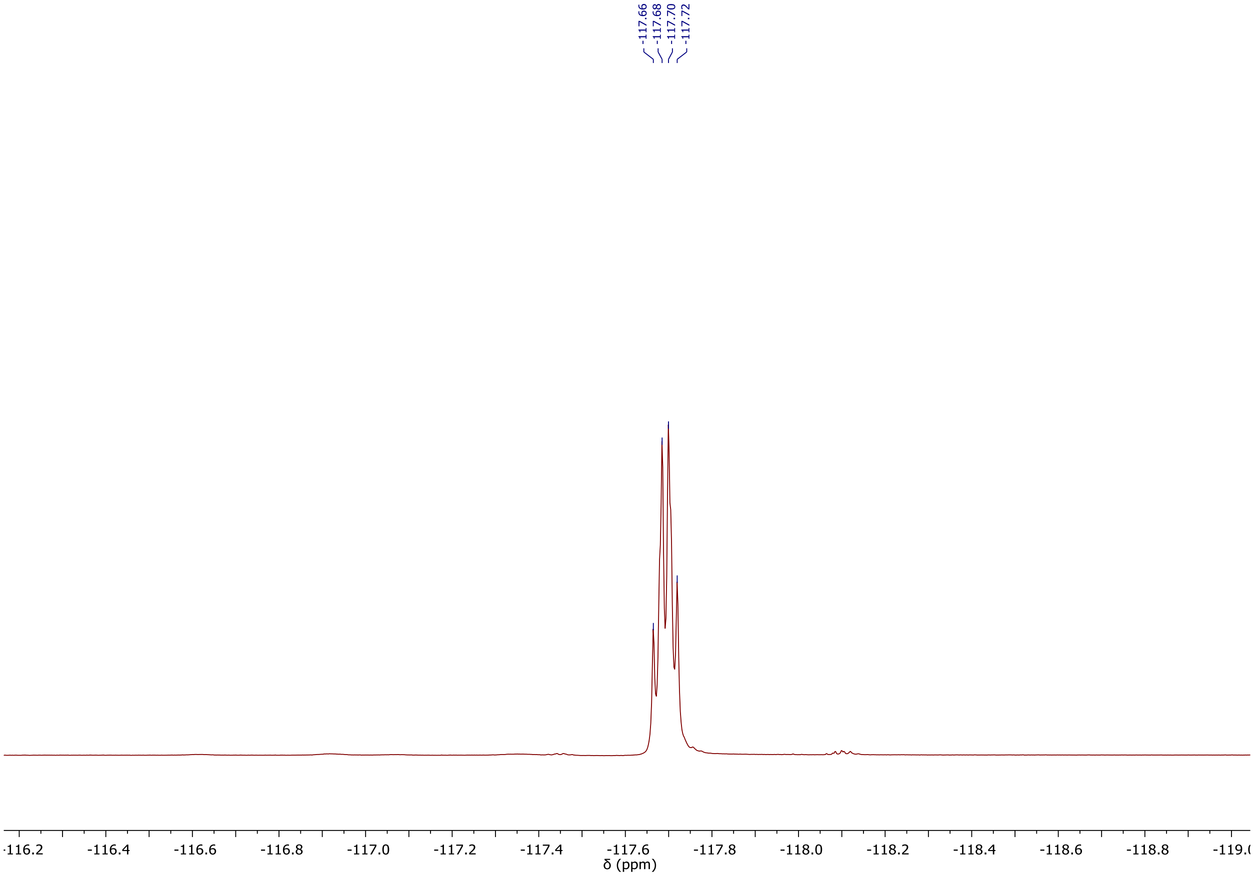

Figure S9. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T10**.

T11. A Schlenk flask was charged with **T6** (0.16 g, 0.47 mmol), dichloromethane (10 mL) and a stir bar. Br_2 (0.30 mL) was then added drop-wise to the solution while vigorously stirring. The reaction vessel was capped with a glass stopper and stirred for an additional 18 h. The volatiles were next removed under vacuum and the resulting brown solution was washed with cold hexanes (3 × 5 mL). **T11** was isolated as a tan powder (0.14 g, 0.23 mmol, 49%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.74 (d, J_{HH} = 2 Hz, 1H), 7.08-7.06 (m, 3H), 6.50-6.47 (m, 2H), 6.36 (dd, J_{HH} = 9 Hz, J_{HF} = 1 Hz, 1H), 6.31 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 1H), 6.32 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 1H). ^{1}H{^{19}F δ -117.0} NMR (400 MHz, C_6D_6): δ 7.74 (d, J_{HH} = 2 Hz, 1H), 7.08 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H), 7.06 (d, J_{HH} = 9 Hz, 2H), 6.50 (s, 1H), 6.48 (s, 1H), 6.36 (dd, J_{HH} =

9 Hz, J_{HF} = 1 Hz, 1H), 6.31 (d, J_{HH} = 9 Hz, 1H), 6.32 (d, J_{HH} = 9 Hz, 1H). ^{1}H{^{19}F δ -64.4} NMR (400 MHz, C_6D_6): δ 7.74 (d, J_{HH} = 2 Hz, 1H), 7.08 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H), 7.06-7.04 (m, 2H), 6.50-6.47 (m, 2H), 6.36 (d, J_{HH} = 9 Hz, 1H), 6.31 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 1H), 6.32 (dd, J_{HH} = 9 Hz, J_{HF} = 5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 159.9 (d, J_{CF} = 250 Hz, *C*F), 149.0 (s), 141.7 (d, J_{CF} = 3 Hz), 141.3 (s), 132.3 (q, J_{CF} = 4 Hz), 127.5 (q, J_{CF} = 34 Hz, *C*CF_3), 126.3 (s), 125.3 (q, J_{CF} = 4 Hz), 123.8 (q, J_{CF} = 273 Hz, *C*F_3), 122.7-122.5 (m), 122.1 (m, J_{CF} = 27 Hz), 120.9 (d, J_{CF} = 27 Hz), 115.3 (dd, J_{CF} = 8 Hz J_{CF} = 22 Hz). ^{19}F NMR (376 MHz, C_6D_6): δ -61.9 (s, CF_3), -114.4 (s, F). $E_{½}$ = 1.26 V vs Fc^+/Fc. HRMS (-APCI) m/z: [M-H]$^-$, calcd. For $C_{19}H_8Br_3F_5N^-$ 583.8111; Found 583.8101; [M-H+HCl]-, calcd. For $C_{19}H_9Br_3F_5NCl$- 619.7868; Found, 619.7878.

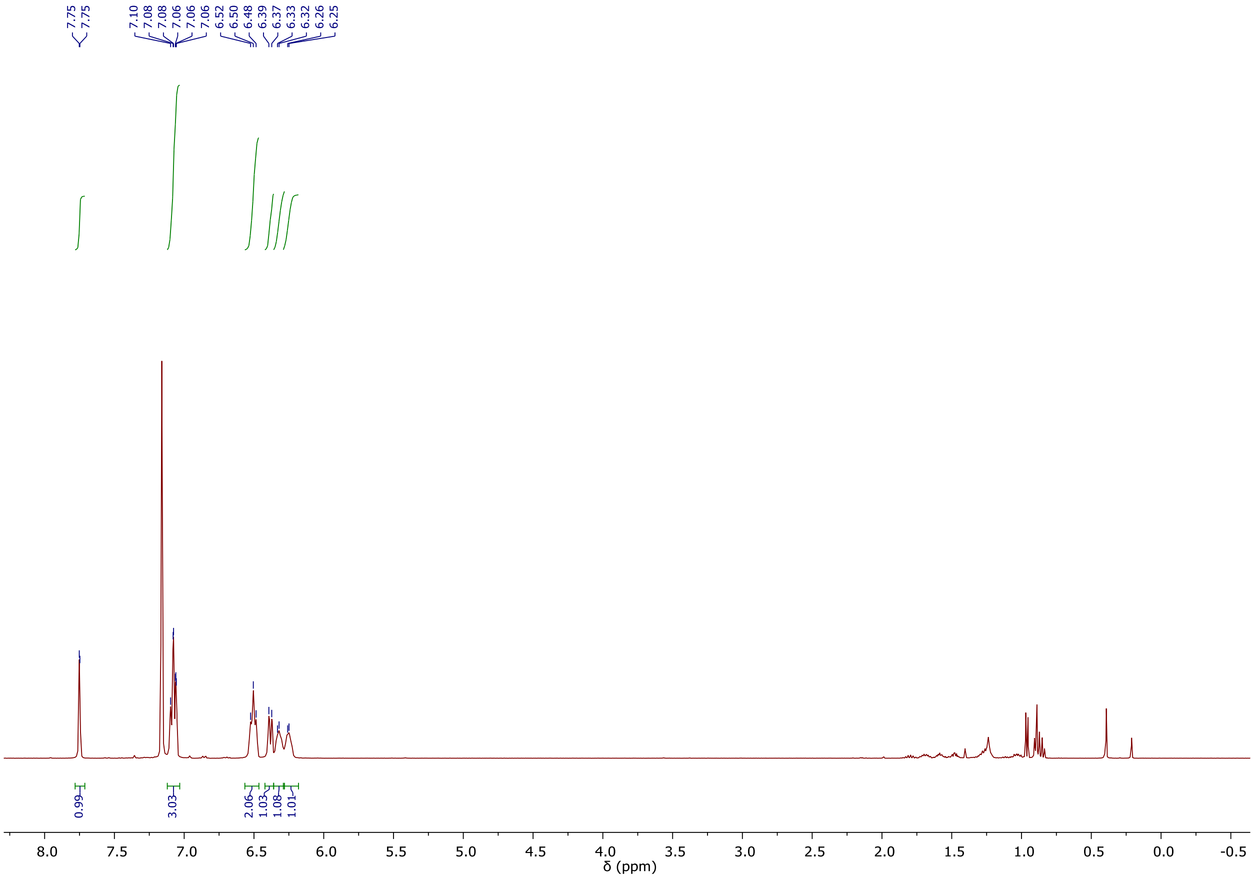

Figure S10. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **T11**. Residual hexanes, water, and silicone grease can be observed.

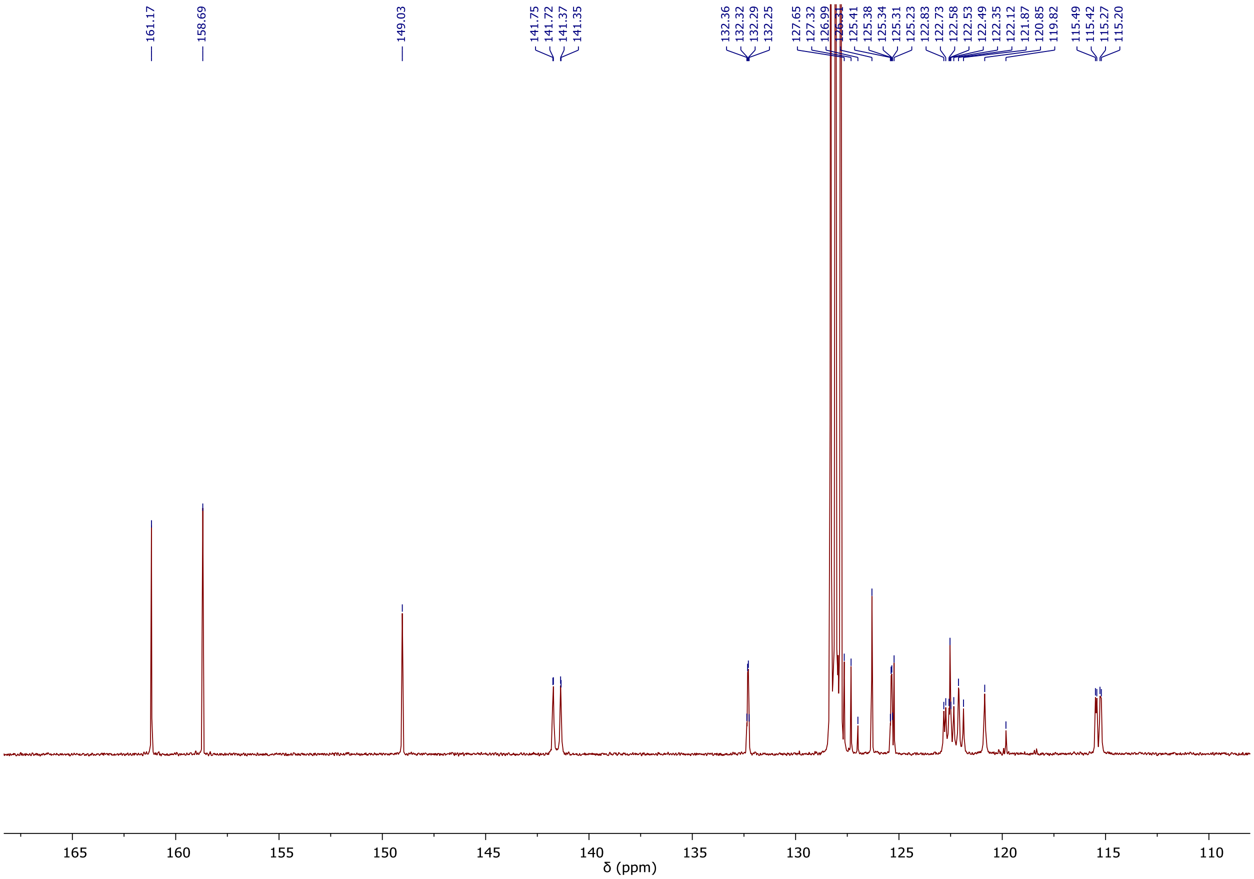

Figure S11. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **T11**.

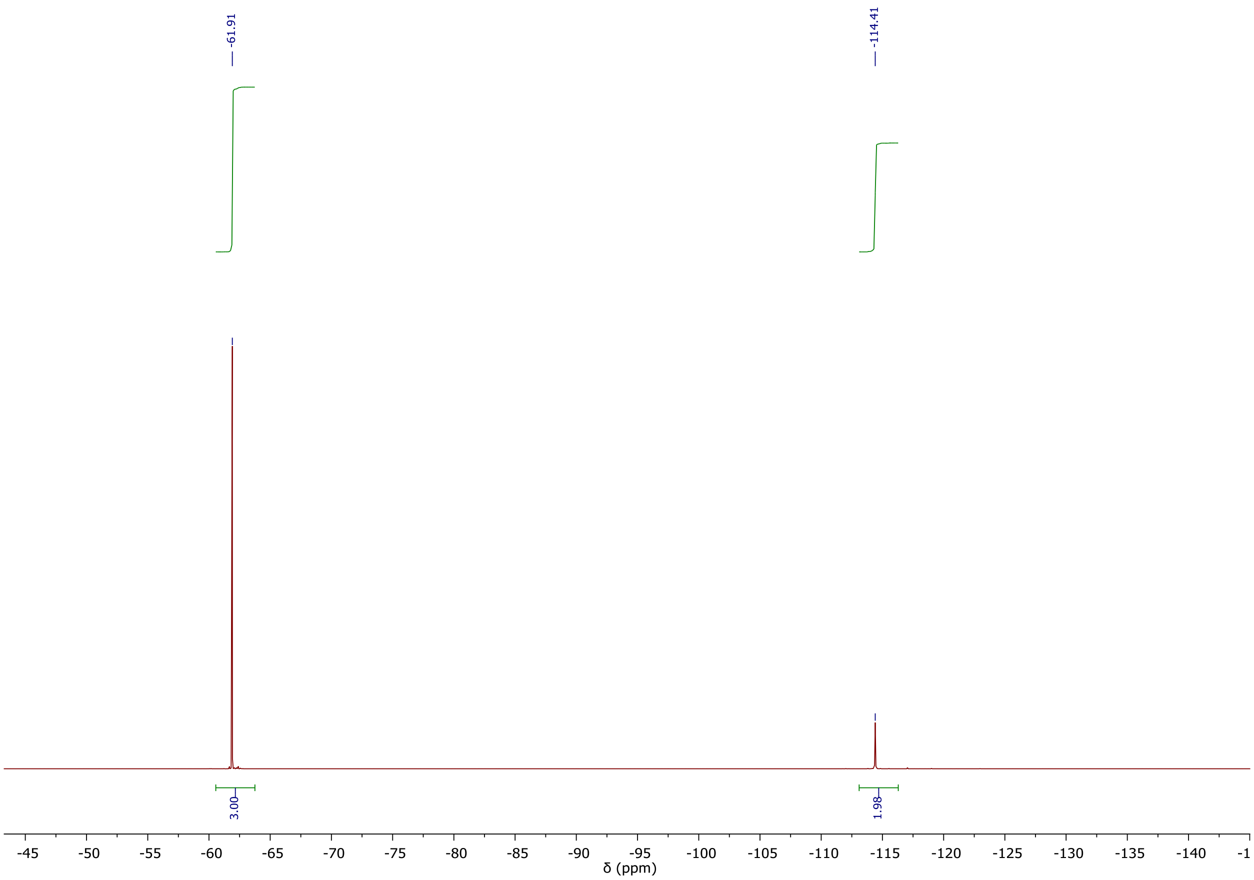

Figure S12. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T11**.

T12. A Schlenk flask was charged with diphenylamine (0.59 g, 3.5 mmol), 3-iodobenzotrifluoride (0.50 mL, 3.5 mmol), $Pd(OAc)_2$ (8.0 mg, 0.036 mmol), DPPF (58 mg, 0.10 mmol), sodium *tert*-pentoxide (0.38 g, 3.5 mmol), a stir bar, and toluene (10 mL). The reaction was then refluxed for 3 d and then the volatiles were removed under vacuum. The remaining brown oil was dissolved in hexanes and passed through a pad of silica gel. The solution was concentrated and recrystallized at -35 °C to give a pale yellow oil (^{19}F NMR (C_6D_6): δ 66.5 (s)). No further steps to purify the compound were taken. The oil was next dissolved in dichloromethane (10 mL) and Br_2 (0.30 mL) was added drop-wise. The reaction was stirred for

1 h and then the volatiles were removed under vacuum and the resulting brown solid was washed with cold hexanes (3 × 10 mL). The hexane washes were then collected and dried under vacuum to yield **T12** as a pale brown solid (0.42 g, 0.59 mmol, 17%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.47 (m, 2H), 7.19 (d, *J* = 20 Hz, 1 H), 7.06 (m, 1H), 6.92 (m, 2H), 6.35 (m, 2H), 6.15 (m, 1H). ^{19}F NMR (376 MHz, C_6D_6): δ -65.1z (s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 145.95, 143.01, 137.39, 136.06, 132.20, 131.27 (q, $J_{C–F}$ = 31.1 Hz, *C*CF_3), 130.30, 124.22, 123.48 (q, $J_{C–F}$ = 272 Hz, *C*F_3), 122.93, 120.24, 119.14 (q, $J_{C–F}$ = 6 Hz), 111.73. $E_{½}$ = 1.19 V vs Fc^+/Fc. HRMS (-APCI) m/z: $[M-H]^-$, calcd. For $C_{19}H_8Br_5F_3N^-$ 705.6479; Found 705.6493; $[M-H+HCl]^-$, calcd. For $C_{19}H_9Br_5F_3NCl^-$ 741.6246; Found 741.6261.

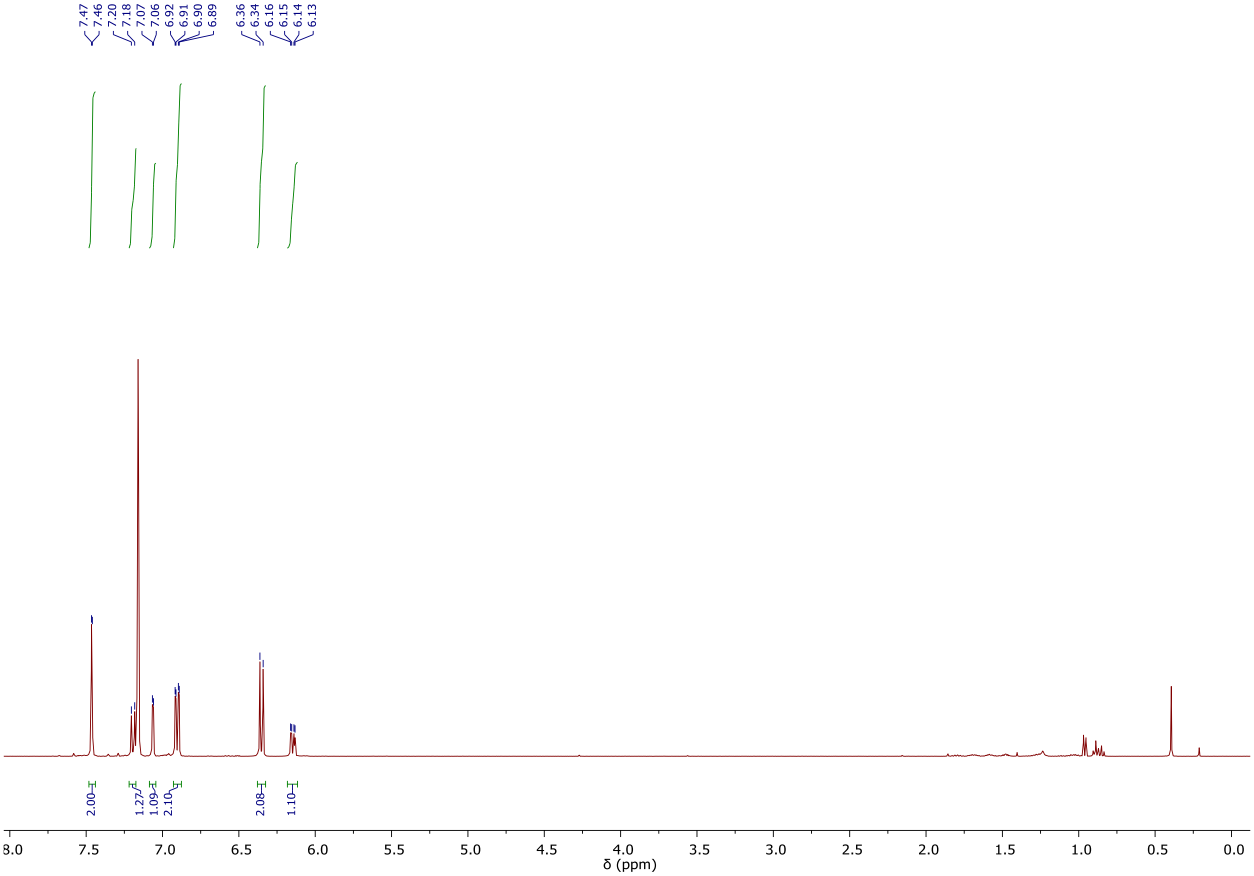

Figure S13. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **T12**. Hexanes, water, and silicone grease can be observed.

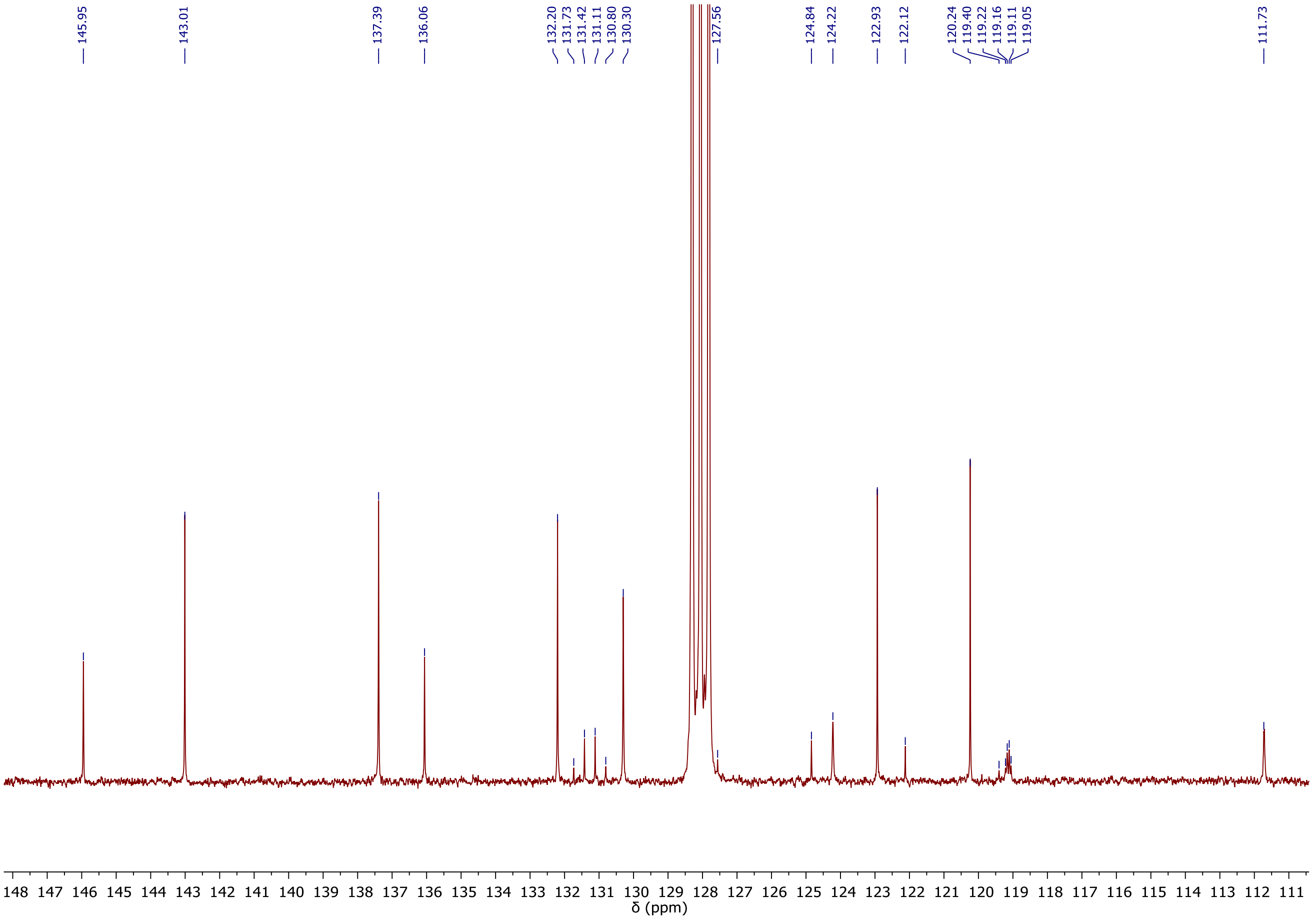

Figure S14. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **T12**

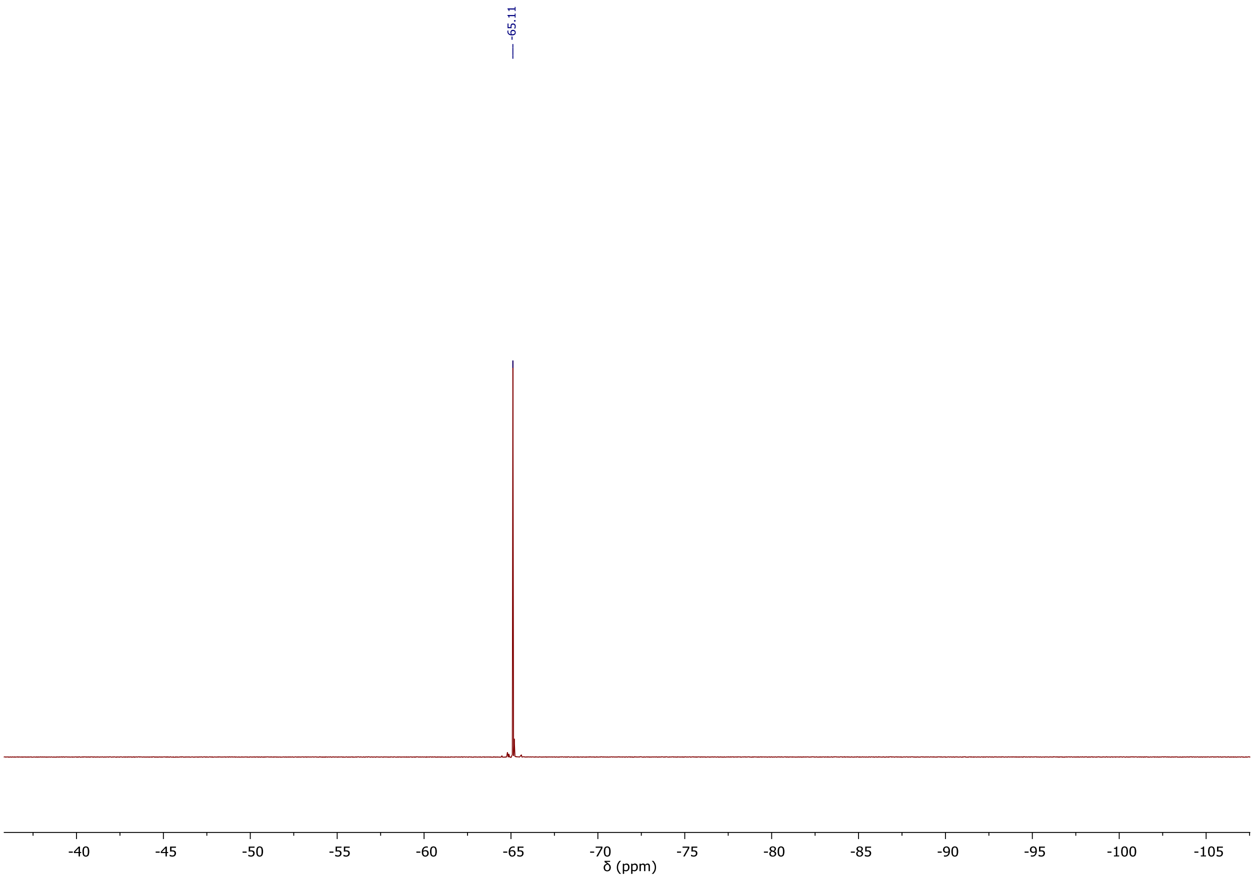

Figure S15. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T12**.

T13. A Schlenk flask was charged with **T8** (7.90 g, 20.7 mmol), dichloromethane (25 mL) and a stir bar. Br_2 (6.00 mL, 117 mmol) was then added in a drop-wise fashion in 6 portions. The reaction was capped and stirred for 1 h. The volatiles were then removed under vacuum and the resulting brown solid was dissolved in diethyl ether and filtered through a pad of Celite. The ethereal solution was then evaporated to dryness and the resulting brown solid was taken up in a 1:6 mixture (v/v) of diethyl ether and hexanes and stored at -35 °C. The resulting solid was isolated and dried under vacuum to yield a brown solid. Sublimation of the solid gave **T13** as a colorless solid. (8.07 g, 11.4 mmol, 55%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.71 (s, 1H, Ar-H), 7.54 (s, 2H, Ar-H), 7.07 (d, *J* = 7 Hz, 1H, Ar-H), 6.96 (dd, *J* = 8 Hz, *J* = 2 Hz, 2H, Ar-H), 6.32 (d, *J* = 8 Hz, 1H, Ar-H), 6.18 (d, *J* = 8 Hz, 1H, Ar-H), 6.10 (d, *J* = 8 Hz, Ar-H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 147.9 (s, *C*N), 143.7 (d, J_{CF} = 16 Hz, *C*N), 137.1 (s), 137.0 (s), 134.6 (s), 132.2 (q, J_{CF} = 4 Hz), 131.2 (d, J_{CF} = 4 Hz), 126.3 (s), 125.4 (q, J_{CF} = 4 Hz), 123.9 (q, J_{CF} = 270 Hz, *C*F_3), 122.9 (m, J_{CF} = 15 Hz, *C*CF_3), 118.8 (s), 118.4 (s). ^{19}F NMR (376 MHz. C_6D_6): δ -65.8 (m). $E_{½}$ = 1.32 V vs Fc^+/Fc. HRMS (-APCI) m/z: $[M-H]^-$, calcd. For $C_{19}H_8Br_5F_3N^-$ 705.6479; Found 705.6489; $[M-H+HCl]^-$, calcd. For $C_{19}H_9Br_5F_3NCl^-$ 741.6246; Found 741.6256.

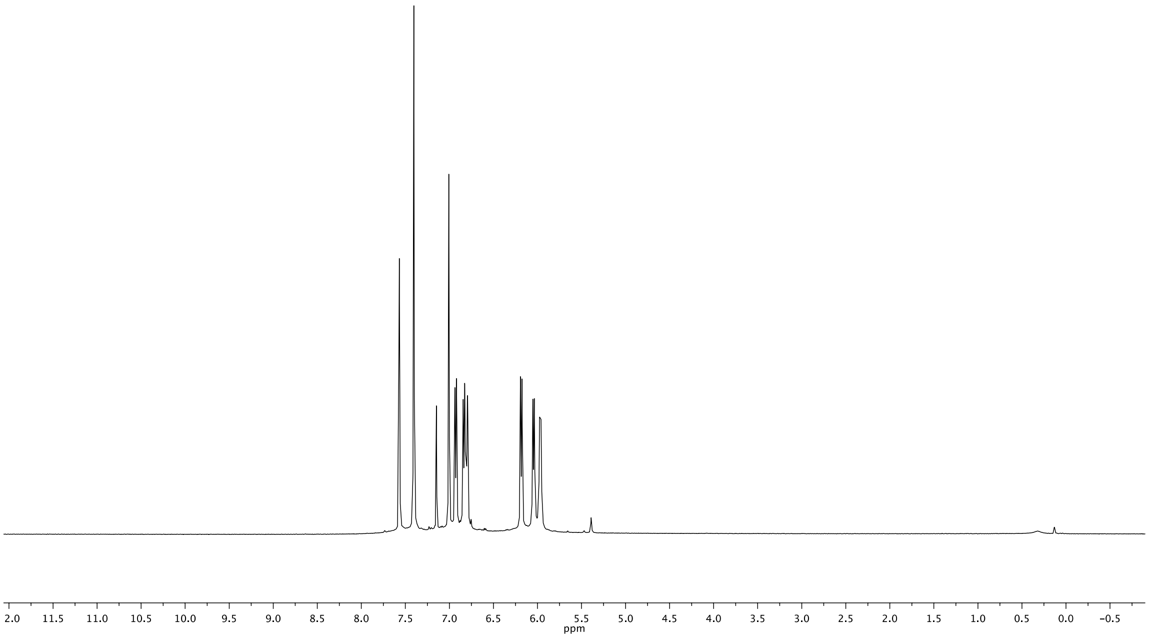

Figure S16. ^1H NMR spectrum of **T13** (C_6D_6, 500 MHz). Trace quantities of water and silicone grease are observed.

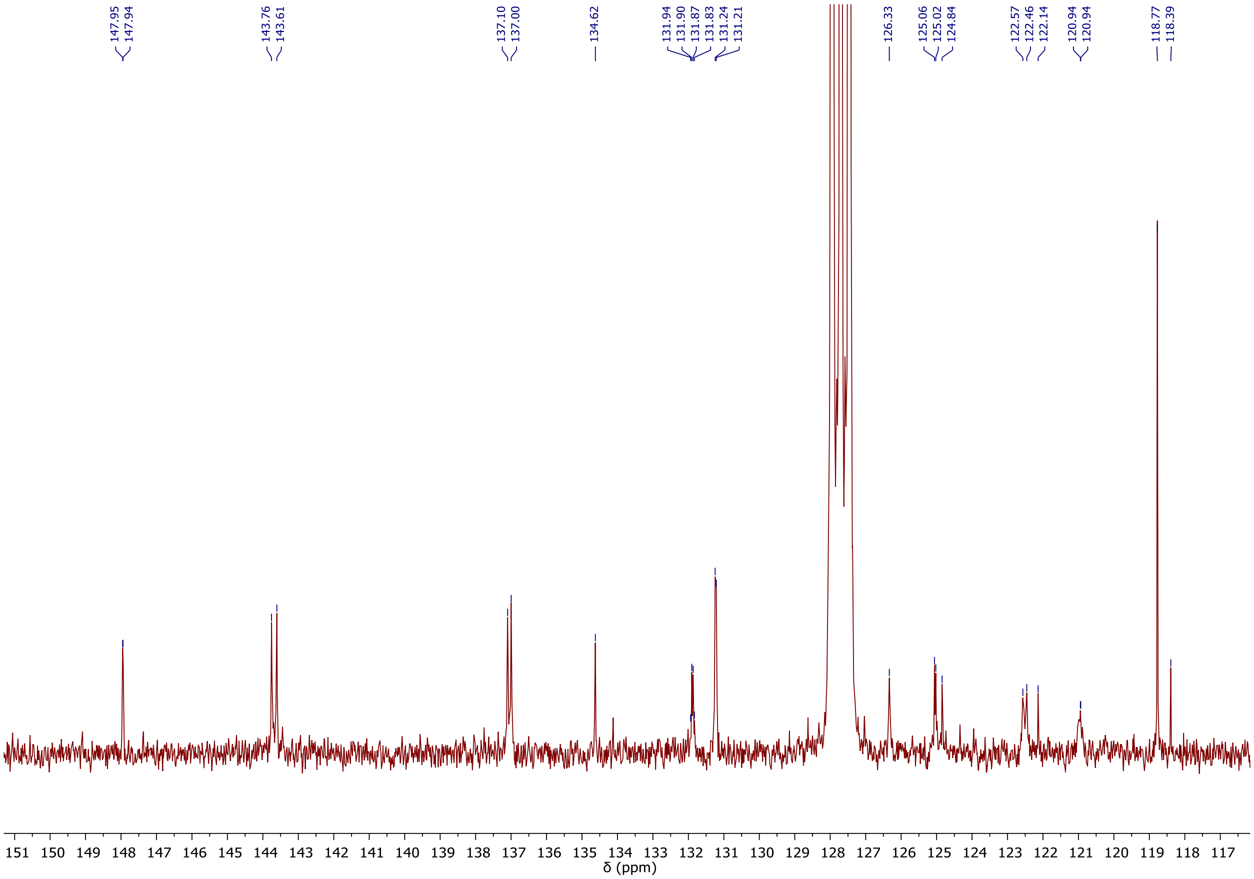

Figure S17. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) spectrum of **T13.**

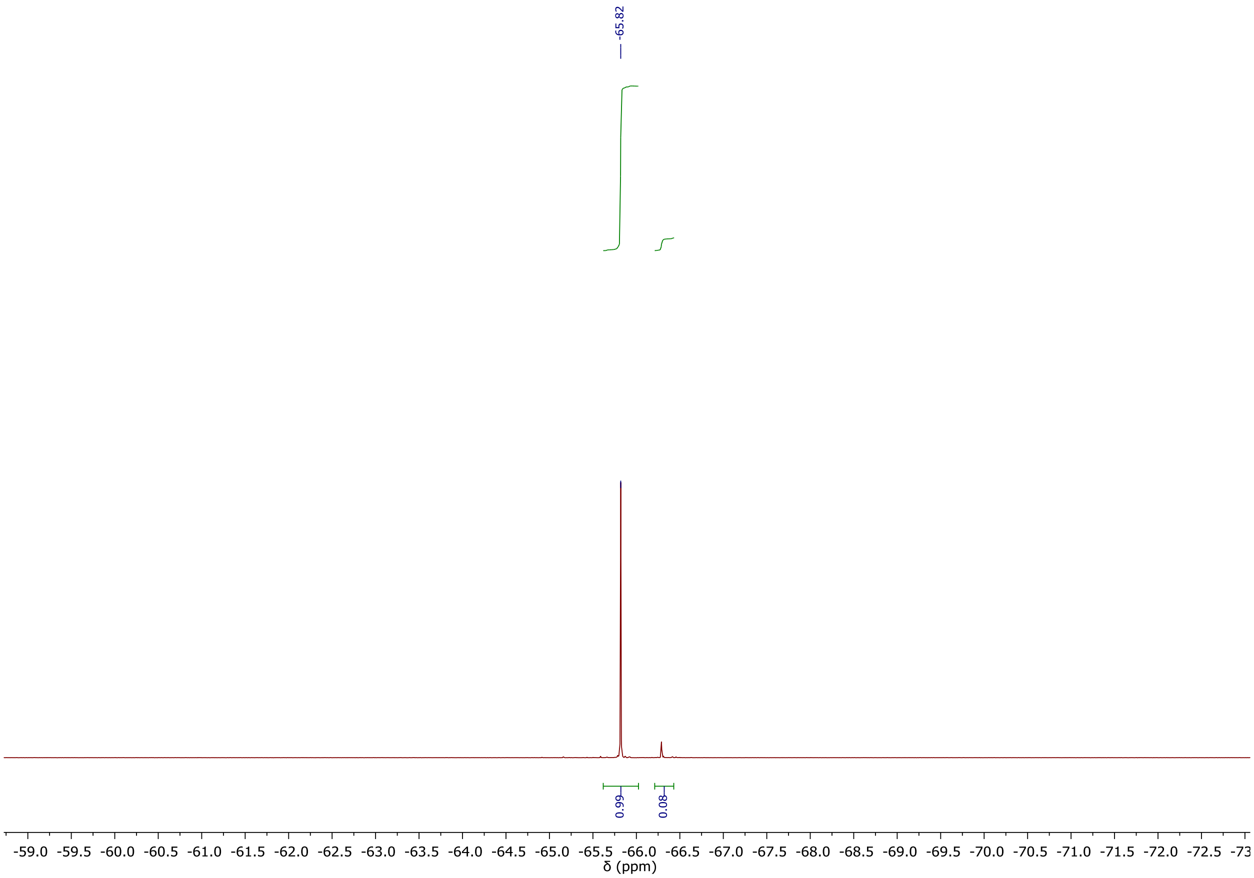

Figure S18. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T13** in >93% purity.

T14. A Schlenk flask was charged with **T5** (342 mg, 1.22 mmol), *N*-bromosuccinimide (217 mg, 1.22 mmol), a stir bar, and dichloromethane (10 mL). The reaction mixture was stirred for 18 h and then the volatiles were removed under vacuum. The resulting solid was dissolved in hexanes and passed through a pad of silica gel. The volatiles were again removed and the solid was dissolved in a minimal amount of hexamethydisiloxane and stored at -35 °C. The resulting colorless crystals were then collected and dried to yield **T14** (199 mg, 0.553 mmol, 45%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.11 (d, J_{HH} = 9 Hz, 2H), 6.65 (m, 4H), 6.59 (m, 4H), 6.51 (d, J_{HH} = 9 Hz, 2H). ^{1}H{^{19}F δ -121.3} NMR (400 MHz, C_6D_6): δ 7.11 (d, J_{HH} = 9 Hz, 2H), 6.65 (d, J_{HH} = 9

Hz, 4H), 6.59 (d, J_{HH} = 9 Hz, 4H), 6.51 (d, J_{HH} = 9 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ 159.4 (d, J_{CF} = 245 Hz, *C*F), 147.0 (s, *C*N), 143.3 (d, J_{CF} = 3 Hz, *C*N), 132.2 (s), 125.9 (d, J_{CF} = 8 Hz), 124.0 (s), 116.1 (d, J_{CF} = 22 Hz), 114.6 (s). ^{19}F NMR (376 MHz, C_6D_6): δ -121.3 (m). $E_{1/2}$ = 0.63 V Fc^{+}/Fc. HRMS (+APCI) m/z: $[M+H]^{+}$, calcd. For $C_{18}H_{13}BrF_2N^{-}$ 360.0194; Found 360.0196.

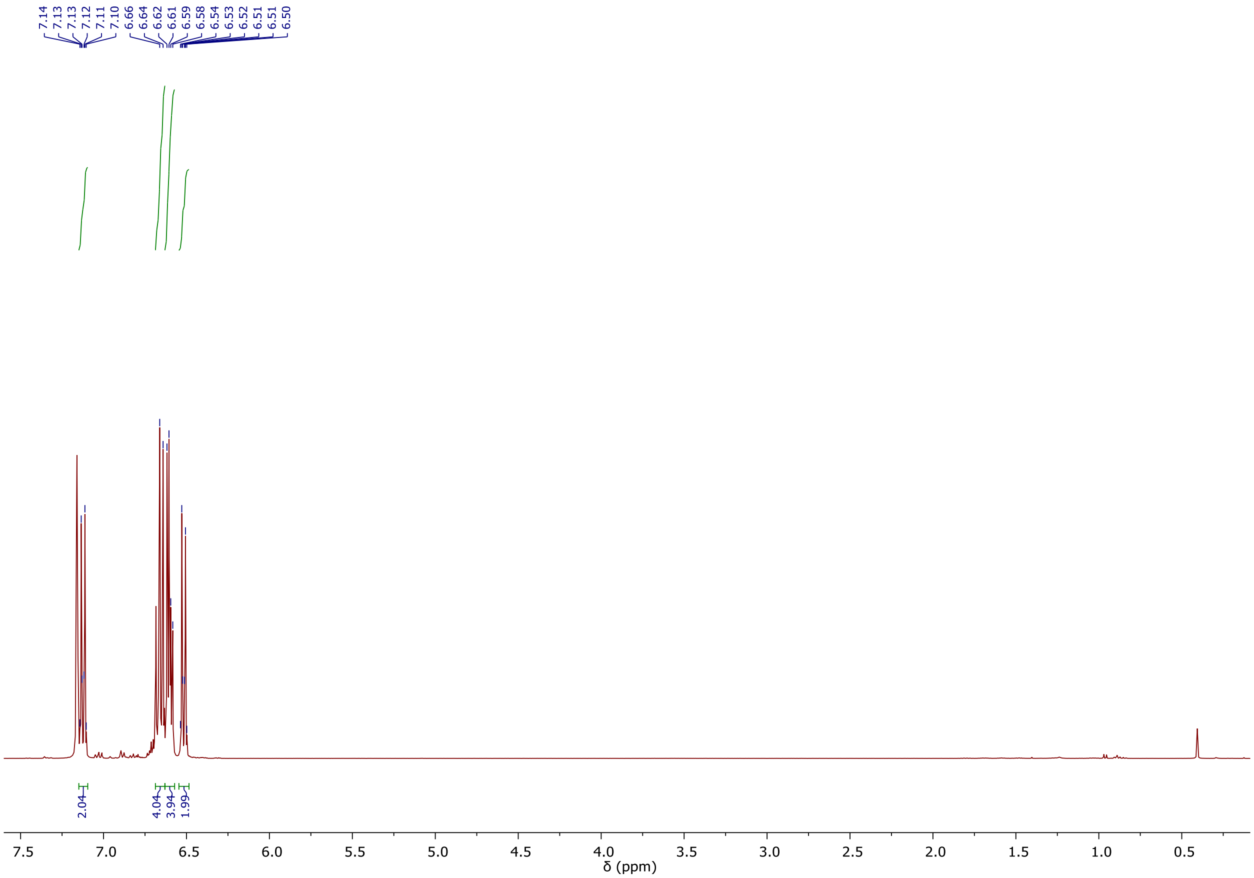

Figure S19. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **T14**. Water and residual hexanes are also observed.

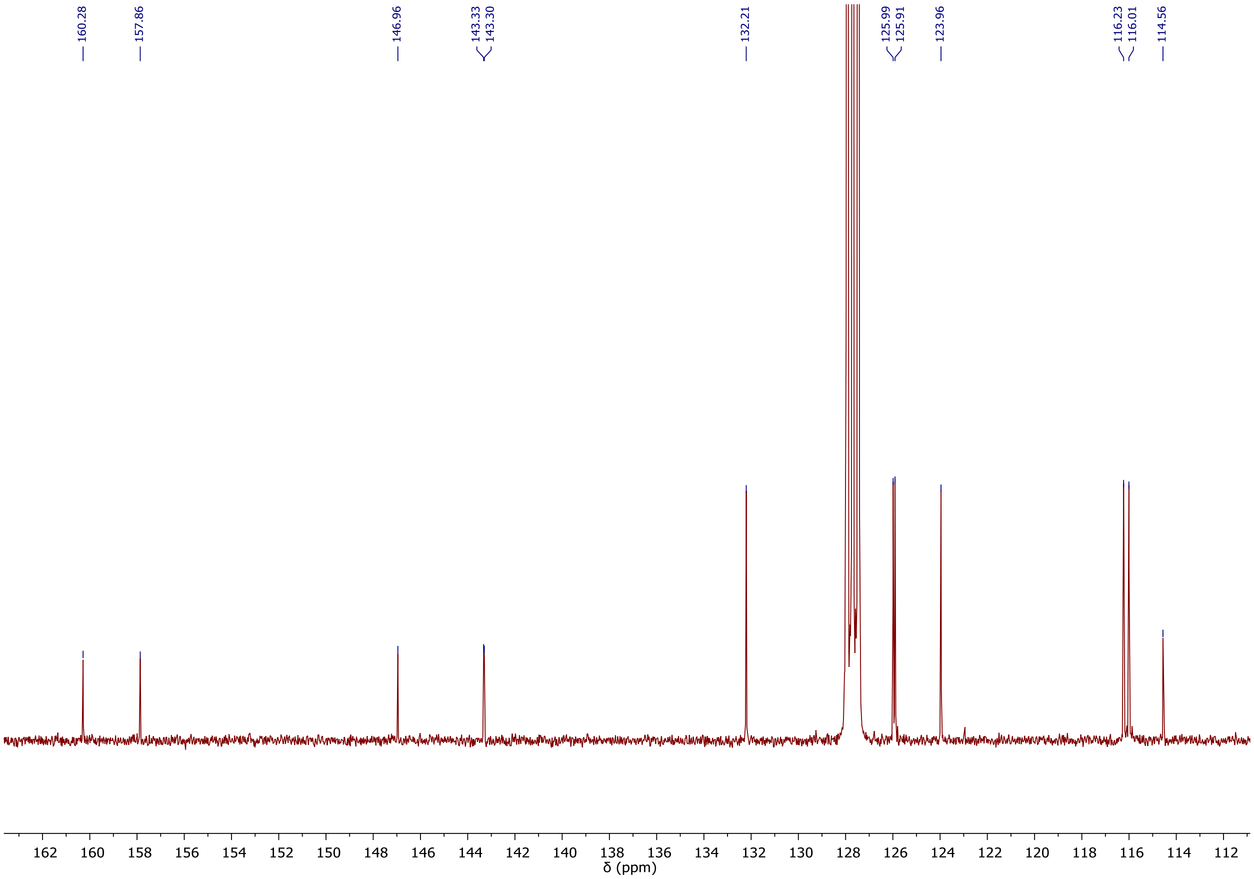

Figure S20. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of **T14**.

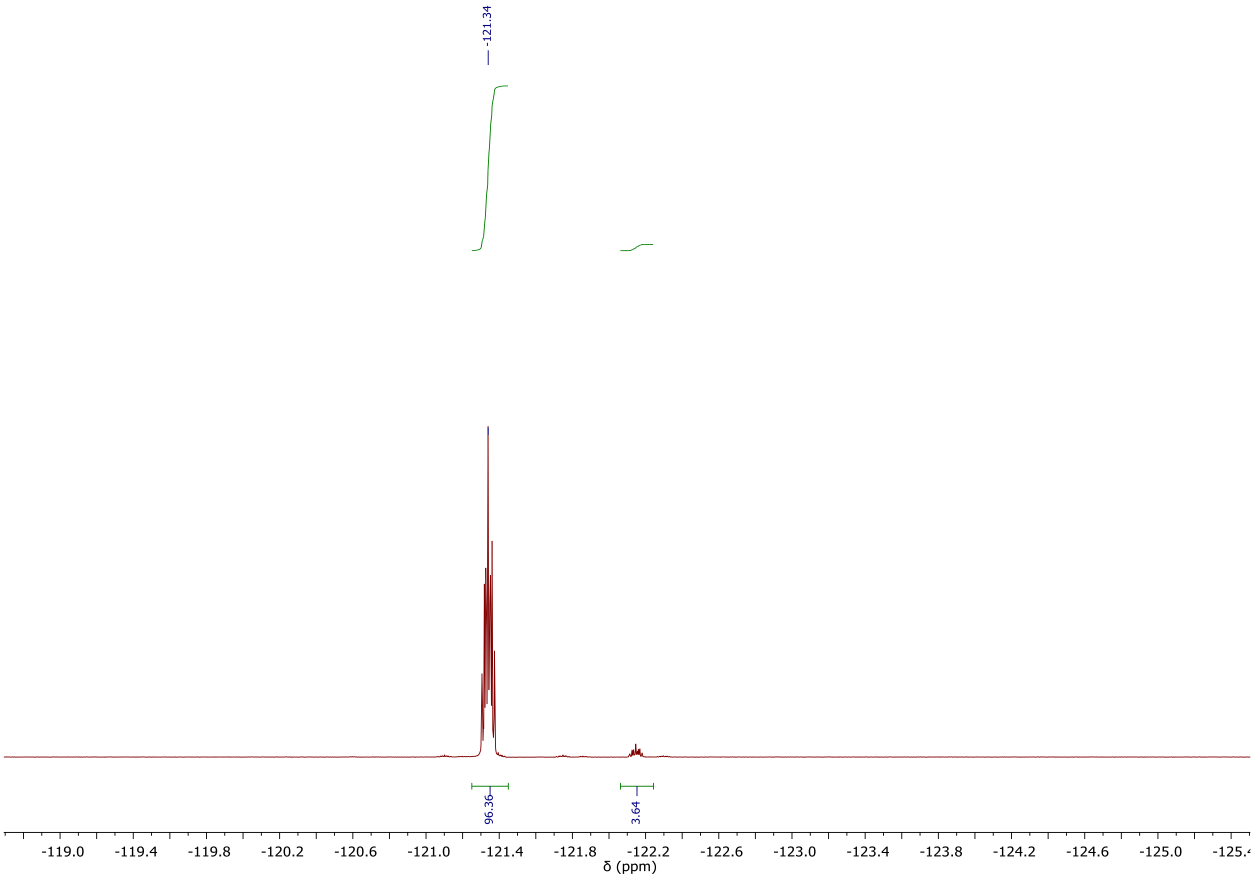

Figure S21. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **T14** in >96% purity.

Reaction of T1 with 3 equivalents N-bromosuccinimide. A Schlenk flask was charged with **T1** (110 mg, 0.228 mmol), a stir bar, and dichloromethane (5 mL). *N*-bromosuccinimide (122 mg, 0.685 mmol) was then added slowly to the solution while stirring vigorously. After 18 h the solution was passed over a pad of Celite and the volatiles were removed under vacuum. NMR analysis of the resulting colorless solid revealed a mixture of products.

Reaction of T1 with Br_2. A Schlenk flask was charged with **T1** (0.15 g, 0.31 mmol), a stir bar, and chloroform (5 mL). Br_2 (50 mg, 0.31 mmol) was then added drop-wise to the solution while stirring vigorously. After 18 h ethanol was added to the reaction mixture resulting in copious precipitation. NMR analysis of the resulting colorless solid revealed a mixture of products.

Reaction of T1 with Br_2 and $FeBr_3$. A Schlenk flask was charged with **T1** (0.41 g, 0.86 mmol), a stir bar, $FeBr_3$ (20 mg), and a chloroform/trifluoroacetic acid mixture (5 mL:5 mL). Br_2 (0.89 mg, 5.6 mmol) was then added drop-wise to the solution while stirring vigorously. The reaction was then refluxed for 1 week at 100 °C resulting in a colorless precipitate. NMR analysis of the precipitate revealed a mixture of products.

Reaction of T1 with Br_2 and $SbCl_5$. A Schlenk flask was charged with **T1** (82 mg, 0.17 mmol), a stir bar, and chloroform (5 mL). A Br_2 (0.50 ml, 9.7 mmol)/$SbCl_5$(1 mL) solution in dichloromethane was then added drop-wise to the solution while stirring vigorously. After 3 d the volatiles were removed and the resulting solid was dissolved in chloroform. Addition of ethanol to the chloroform solution resulted in copious precipitation. The solid was collected and washed with ethanol (3 × 5 mL). NMR analysis of the resulting colorless solid revealed a mixture of products.

III. Synthesis of aminium salts.

T1[$CHB_{11}Cl_{11}$]. A Schlenk flask was charged with Na[$CHB_{11}Cl_{11}$] (628 mg, 1.15 mmol), **T1** (555 mg, 1.15 mmol), $PhI(OAc)_2$ (185 mg, 0.575 mmol), and dichloromethane (10 mL). Me_3SiCl (209 µL, 1.15 mmol) was then added to the colorless solution resulting in a color change to royal blue. The solution was stirred for 30 min and then the volatiles were removed extensively under vacuum. The resulting blue powder was dissolved in dichloromethane and filtered through a pad of Celite. The solution was then layered with pentane and slow diffusion at -35 °C resulted in the isolation of **T1[$CHB_{11}Cl_{11}$]** (457 mg, 40%) as a paramagnetic blue powder. Elemental Analysis Calculated: C, 22.73; H, 1.31. Found C, 22.87; H, 1.17.

T10[$CHB_{11}Cl_{11}$]. A Schlenk flask was charged with Na[$CHB_{11}Cl_{11}$] (0.25 g, 0.46 mmol), **T10** (0.27 g, 0.46 mmol), $PhI(OAc)_2$ (74 mg, 0.23 mmol), and dichloromethane (7 mL). Me_3SiCl (58 µL, 0.46 mmol) was then added to the colorless solution resulting in a color change to green. The solution was then stirred for 30 min and then the volatiles were removed extensively under vacuum. The resulting green powder was then dissolved in dichloromethane and filtered through a pad of Celite. The solution was then layered with pentane and slow diffusion at -35 °C resulted in the isolation of a green powder. Multinuclear NMR analysis (^{1}H and ^{19}F) did not reveal the characteristic peaks of **T10** suggesting the oxidation has occurred. Elemental Analysis Calculated: C, 20.60; H, 0.91; N, 1.48, Found: C, 20.40; H, 0.90; N, 1.25.

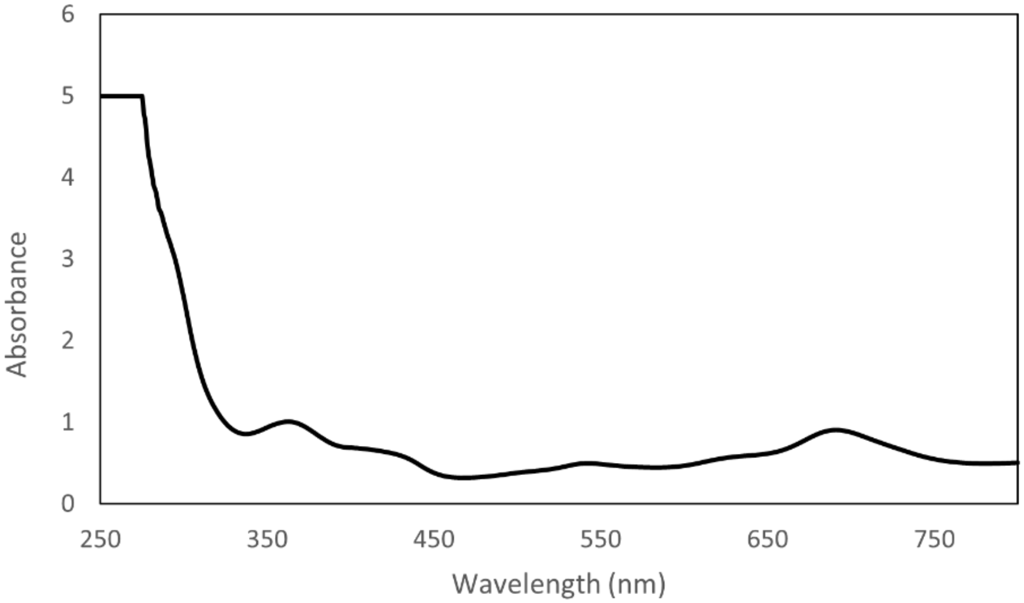

Figure S22. UV-Vis of **T10[$CHB_{11}Cl_{11}$]** in CH_2Cl_2 (0.4 mM).

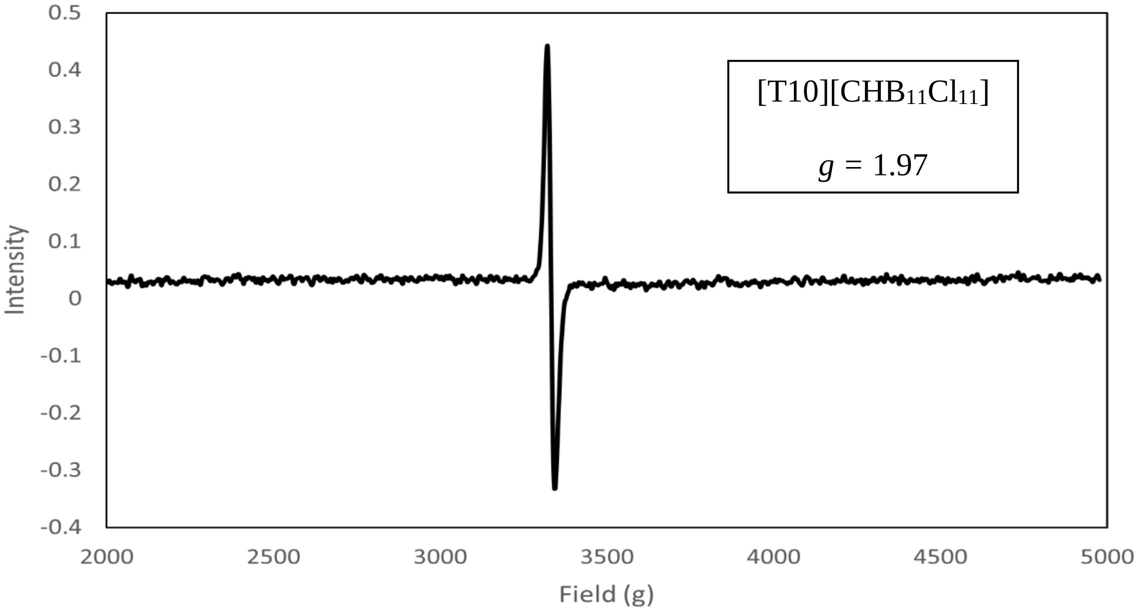

Figure S23. X-Band EPR of **T10[$CHB_{11}Cl_{11}$]** (solid) at 298K, with a microwave frequency of 9.40 GHz and a power of 0.6 mW.

T13[$CHB_{11}Cl_{11}$]. A Schlenk flask was charged with Na[$CHB_{11}Cl_{11}$] (400 mg, 0.734 mmol), **T13** (523 mg, 0.734 mmol), PhI(OAc)$_2$ (118 mg, 0.367 mmol), and dichloromethane (10 mL). Me_3SiOTf (132 µL, 0.734 mmol) was then added to the colorless solution resulting in a color change to royal blue. The solution was stirred for 30 min and then the volatiles were removed extensively under vacuum. The resulting blue powder was then dissolved in dichloromethane and filtered through a pad of Celite. The solution was then layered with pentane and slow diffusion at -35 °C resulted in the isolation of **T13[$CHB_{11}Cl_{11}$]** (864 mg, 0.700 mmol, 95%) as a blue powder. Elemental Analysis Calculated: C, 19.54; H, 0.82; N, 1.14, Found: C, 19.87; H, 0.75; N, 1.03.

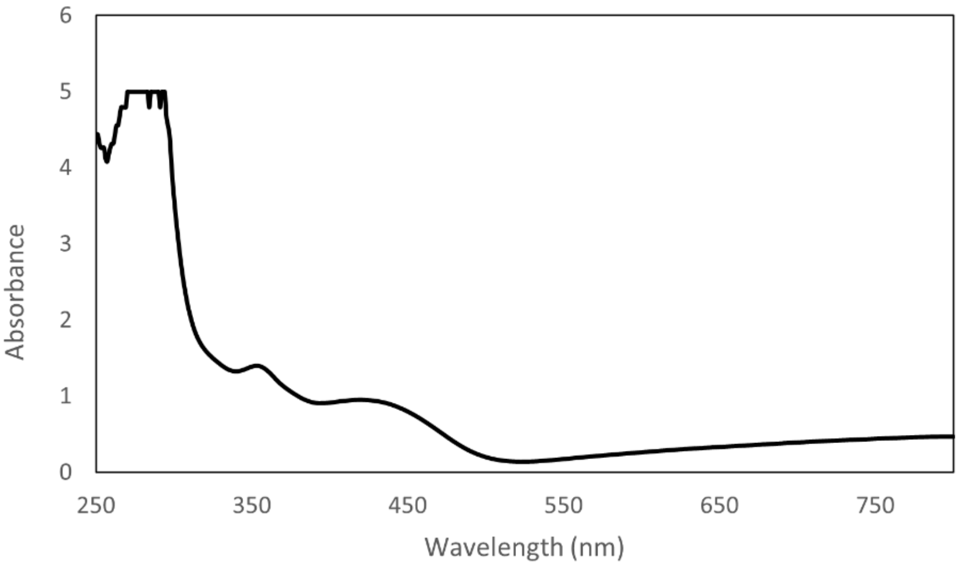

Figure S24. UV-Vis of **T13[$CHB_{11}Cl_{11}$]** in CH_2Cl_2 (0.4 mM).

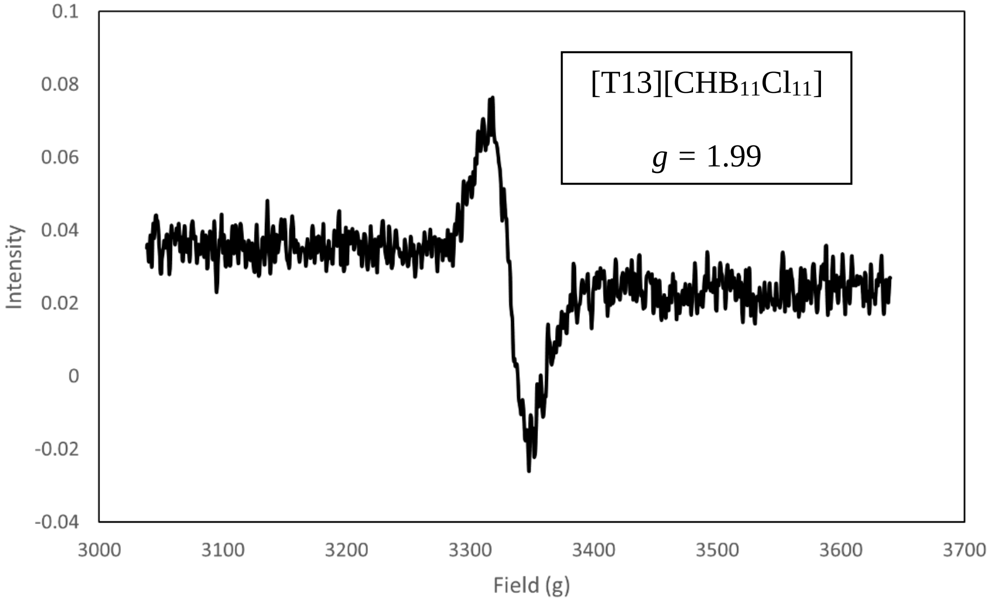

Figure S25. X-Band EPR of **T13[$CHB_{11}Cl_{11}$]** (solid) at 298K, with a microwave frequency of 9.40 GHz and a power of 0.6 mW.

T13[$B(C_6F_5)_4$]. A Schlenk flask was charged with K[**$B(C_6F_5)_4$**] (76.8 mg, 0.107 mmol), **T13** (75.7 mg, 0.107 mmol), $PhI(OAc)_2$ (17.1 mg, 0.054 mmol), and dichloromethane (10 mL). Me_3SiOTf (20 µL, 0.107 mmol) was then added to the colorless solution resulting in a color change to royal blue. The solution was stirred for 30 min and then the volatiles were removed under vacuum. The resulting blue oil was then dissolved in dichloromethane and filtered through a pad of Celite. The volatiles were removed and the blue oil was redissolved in dichloromethane and layered with pentane in a 1:2 ratio and placed in a freezer at -35 °C resulted in the isolation of **T13[$B(C_6F_5)_4$]** (122 mg, 0.700 mmol, 82%) as a blue oil that dries to a sticky blue powder. Only the $BArF_{20}$ anion is observable by NMR. ^{19}F NMR (376 MHz, CD_2Cl_2) : δ -132.9 (s), -163.5 (t, J_{FF} = 19 MHz), -167.23 (s).

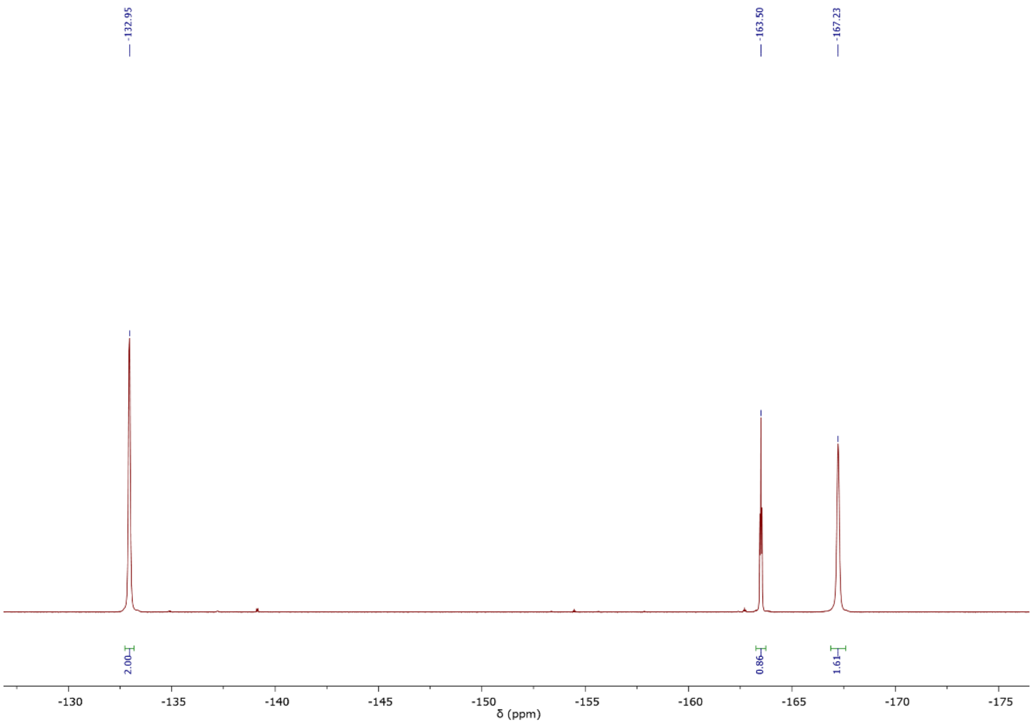

Figure S26. ^{19}F NMR (376 MHz, CD_2Cl_2) spectrum of T13[B(C_6F_5)$_4$].

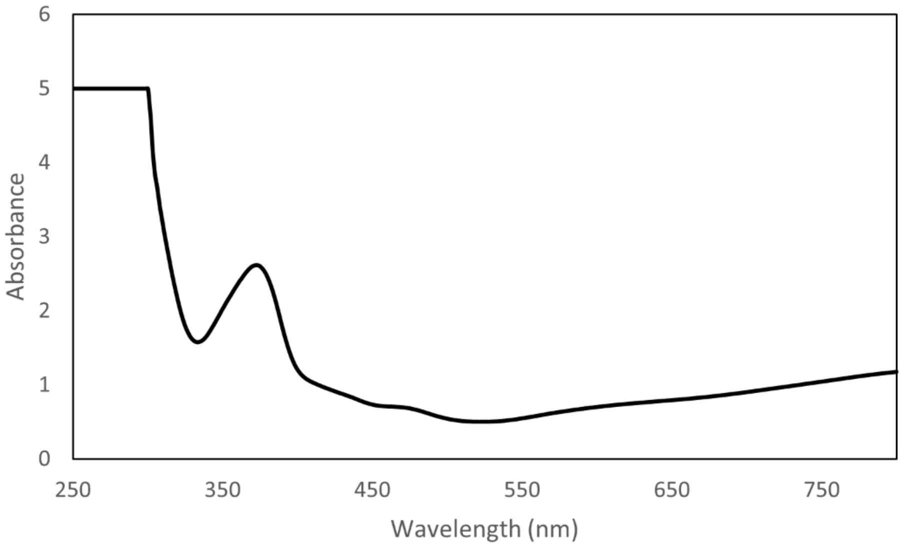

Figure S27. UV-Vis of T13[B(C_6F_5)$_4$] in CH_2Cl_2 (0.4 mM).

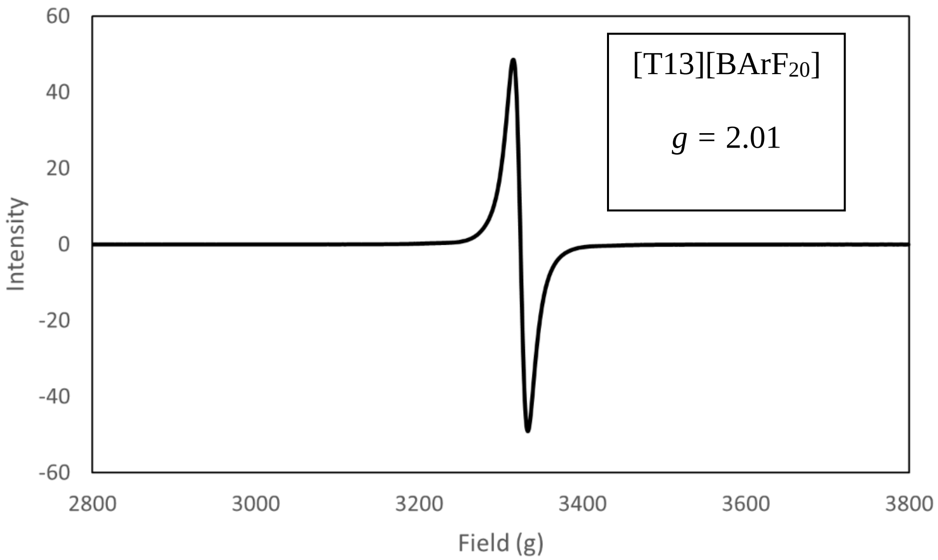

Figure S28. X-Band EPR of **T13[B(C_6F_5)$_4$]** (solid) at 298K, with a microwave frequency of 9.34 GHz and a power of 0.6 mW.

Attempted isolation of T13[B(C_6H_3-3,5-(CF_3)$_2$)$_4$]. A Schlenk flask was charged with Na[B(C_6H_3-3,5-(CF_3)$_2$)$_4$] (89.7 mg, 0.101 mmol), **T13** (71.6 mg, 0.101 mmol), PhI(OAc)$_2$ (16.2 mg, 0.051 mmol), and dichloromethane (10 mL). Me_3SiOTf (18 µL, 0.101 mmol) was then added to the colorless solution resulting in a color change to dark brown. The solution was stirred for 30 min and then the volatiles were removed under vacuum to yield a brown solid. The solid was dissolved in CD_2Cl_2 for NMR analysis and yielded a black solution. By ^{1}H NMR the reaction yielded a mixture of arene products and by ^{19}F NMR the –CF_3 groups present in the amine and the anion do not remain intact.

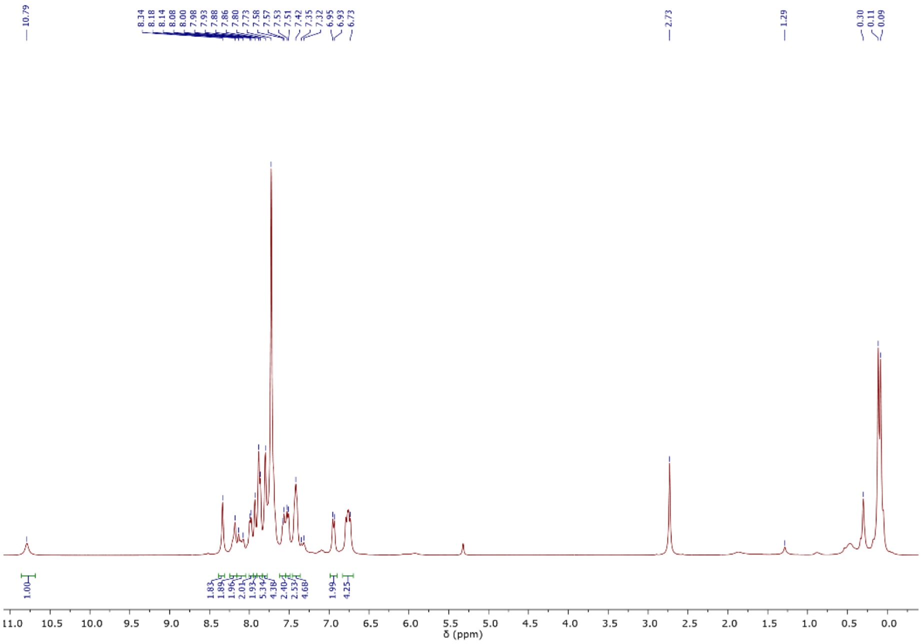

Figure S29. ^{1}H NMR (400 MHz, CD_2Cl_2) of the black solution from the attempted synthesis of **T13[B(C_6H_3-3,5-(CF_3)$_2$)$_4$]**.

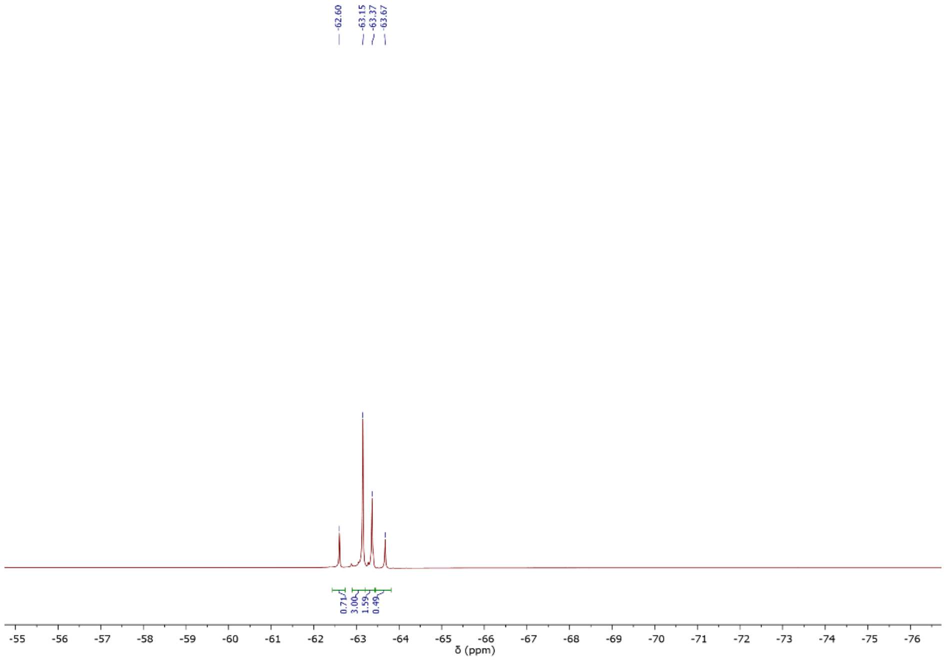

Figure S30. ^{19}F NMR (376 MHz, CD_2Cl_2) of the black solution from the attempted synthesis of **T13[B(C_6H_3-3,5-(CF_3)$_2$)$_4$]**.

Reaction of T13[$CHB_{11}Cl_{11}$] with ferrocene. A J. Young tube was charged with **T13[$CHB_{11}Cl_{11}$]** (32 mg, 0.029 mmol), ferrocene (6.2 mg, 0.033 mmol), C_6F_6 (4.0 μL, 0.034 mmol), and C_6D_6 (1.2 mL). An immediate solution color change from blue to yellow is observed in conjunction with formation of blue crystals. ^{1}H NMR analysis demonstrates formation of one equivalent of **T13** (Figure 2.18). A signal corresponding to ferrocene was still observed but was shifted to 4.23 ppm and was very broad. By ^{19}F NMR analysis approximately one equivalent of amine was observed relative to the C_6F_6.

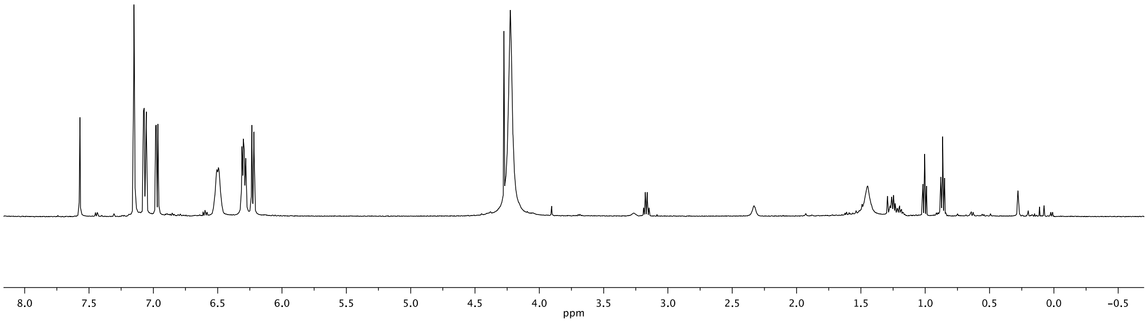

Figure S31. ^{1}H NMR (500 MHz) analysis of the reaction of **T13[$CHB_{11}Cl_{11}$]** with ferrocene in the presence of C_6F_6 in C_6D_6. The spectrum is contaminated with silicone grease, diethyl ether, hexanes and dichloromethane.

Cascade reduction starting with T13[$CHB_{11}Cl_{11}$]. 66 mg (0.0538 mmol) of **T13[$CHB_{11}Cl_{11}$]** was added to a J. Young tube and dissolved in 600 μL of CD_2Cl_2 resulting in a dark green solution. After ^{19}F NMR spectrum (NMR entry 1 in **Fig. S32**) was recorded, the J. Young tube was brought back into the box and 32 mg (0.0538 mmol) of **T10** was added to the J. Young tube, and upon mixing there was a gradual color change to blue-green. After mixing for 5 min an ^{19}F NMR spectrum was recorded (NMR entry 2 in **Fig. S32**). Since there appeared to be an equilibrium between the two oxidized aminiums, the reaction was stirred for an additional 30 minutes and another ^{19}F NMR spectrum was recorded (entry 3 in **Fig. S32**) and showed minimal change in the reaction mixture. The J. Young tube was pumped back into the box and 16 mg (0.0538 mmol) of **T4** was added to the mixture. Upon addition there was an immediate color change to royal blue. An ^{19}F NMR spectrum was recorded (entry 4 in **Fig. S32**) for the mixture, and showed production of the neutral **T10** and **T13**. The J. Young tube was brought back into the glovebox and 10 mg (0.0538 mmol) ferrocene was added. There was an immediate color change to olive green. An ^{19}F NMR spectrum was recorded and **T4** was observed (entry 5 in **Fig. S32**). The ^{19}F NMR resonances of **T10** and **T4** overlap with each other.

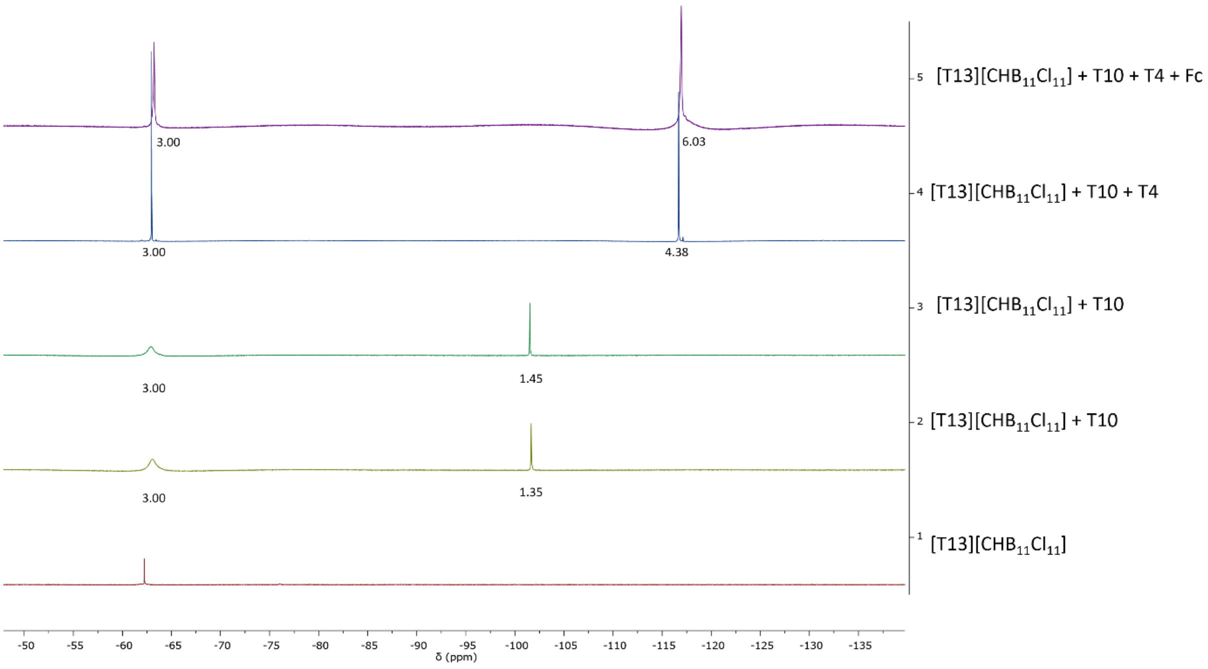

Figure S32. ^{19}F NMR (472 MHz) spectra of the cascade reaction starting with **T13[CHB$_{11}$Cl$_{11}$]**

T13[CMeB$_{11}$Cl$_{11}$]. A Schlenk flask was charged with Na[CMeB$_{11}$Cl$_{11}$] (65 mg, 0.12 mmol), **T13** (84 mg, 0.12 mmol), PhI(OAc)$_2$ (19 mg, 0.058 mmol), and dichloromethane (4 mL).

Me_3SiOTf (22 µL, 0.12 mmol) was then added to the colorless solution resulting in a color change to royal blue. The solution was stirred for 30 min and then the volatiles were removed extensively under vacuum. The resulting blue powder was then dissolved in dichloromethane and filtered through a pad of Celite. The solution was layered with pentane and slow diffusion at -35 °C resulted in the isolation of **T13[$CMeB_{11}Cl_{11}$]** (0.11 g) as a blue powder.

Attempted isolation of T13[$CHB_{11}Cl_{11}$] with Me_3SiCl. A Schlenk flask was charged with Na[$CHB_{11}Cl_{11}$] (0.13 g, 0.24 mmol), **T13** (0.17 mg, 0.24 mmol), $PhI(OAc)_2$ (39 mg, 0.12 mmol), and dichloromethane (5 mL). Me_3SiCl (39 µL, 0.24 mmol) was then added to the colorless solution. No color change was observed. The solution was stirred for 1 h and then the volatiles were removed extensively under vacuum. The neutral amine is observed by multinuclear NMR analysis (^1H and ^{19}F) suggesting the oxidation has not occurred.

IV. Electrochemical Analysis

Electrochemical studies were carried out using a CH Instruments Model 700 D Series Electrochemical Analyzer and Workstation in conjunction with a three-electrode cell. The working electrode was a CHI 104 glassy-carbon disk with a 3.0 mm diameter and the auxiliary electrode was composed of platinum wire. The third electrode, the reference electrode, was a Ag/AgNO$_3$ electrode. This was separated from solution by a fine porosity frit. CVs were conducted in dichloromethane with 0.1–0.3 M [Bu$_4$N][PF$_6$] as the supporting electrolyte at scan rate of 100 mV/s. The concentration of the analyte solutions were approximately 0.1–0.3 M. CVs were referenced to the Fc/Fc$^+$ redox couple, which can be observed in all of the following figures.

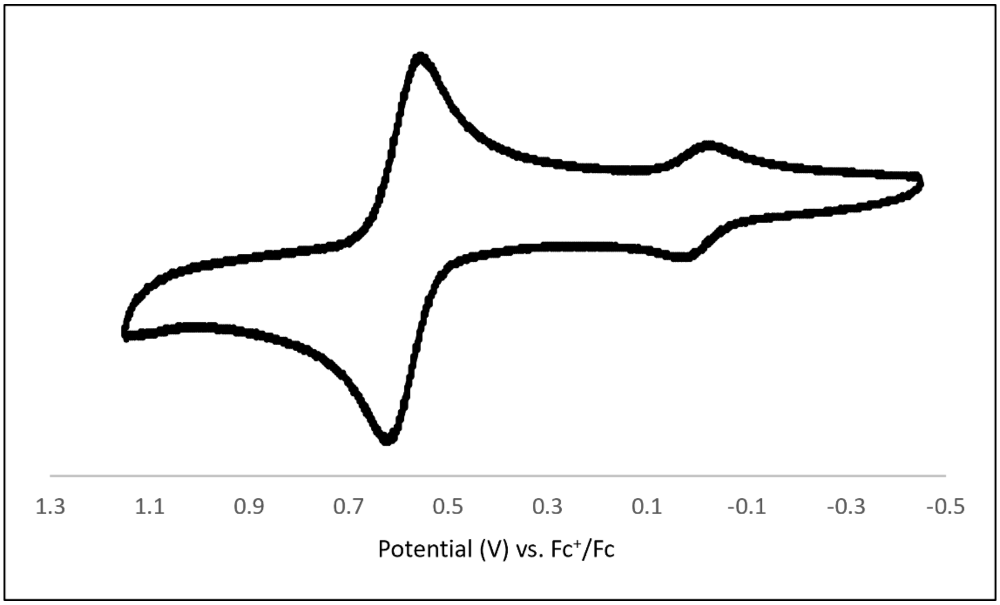

Figure S33. Cyclic voltammogram of **T4** in CH$_2$Cl$_2$ at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.3 M [Bu$_4$N][PF$_6$] as the supporting electrolyte and resulted in a measured potential (E$_{1/2}$) equal to 0.59 V vs Fc$^{+/0}$ as shown.

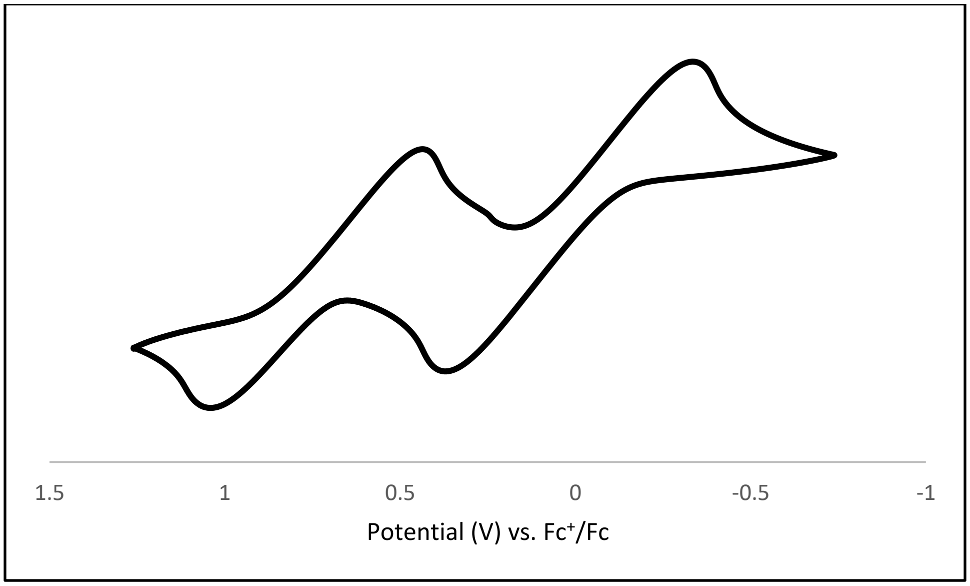

Figure S34. Cyclic voltammogram of **T4** in fluorobenzene at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 0.74 V vs $Fc^{+/0}$ as shown.

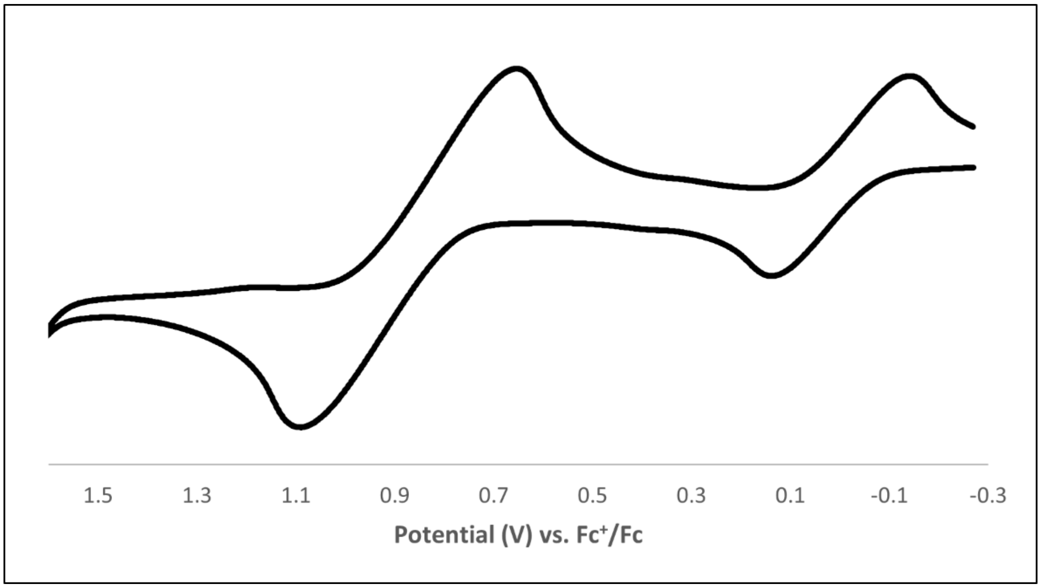

Figure S35. Cyclic voltammogram of **T6** in CH_2Cl_2 at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.3 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 0.78 V vs $Fc^{+/0}$ as shown.

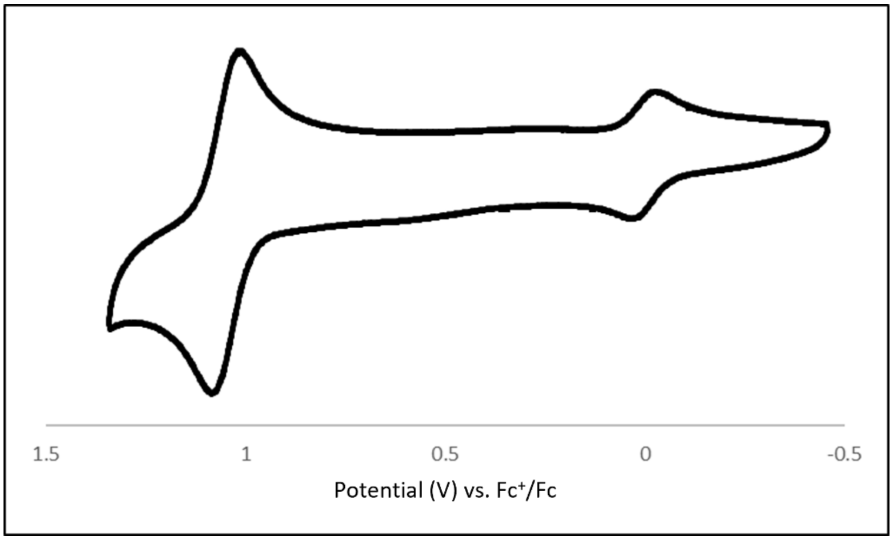

Figure S36. Cyclic voltammogram of **T9** in CH_2Cl_2 at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.3 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 1.05 V vs $Fc^{+/0}$ as shown.

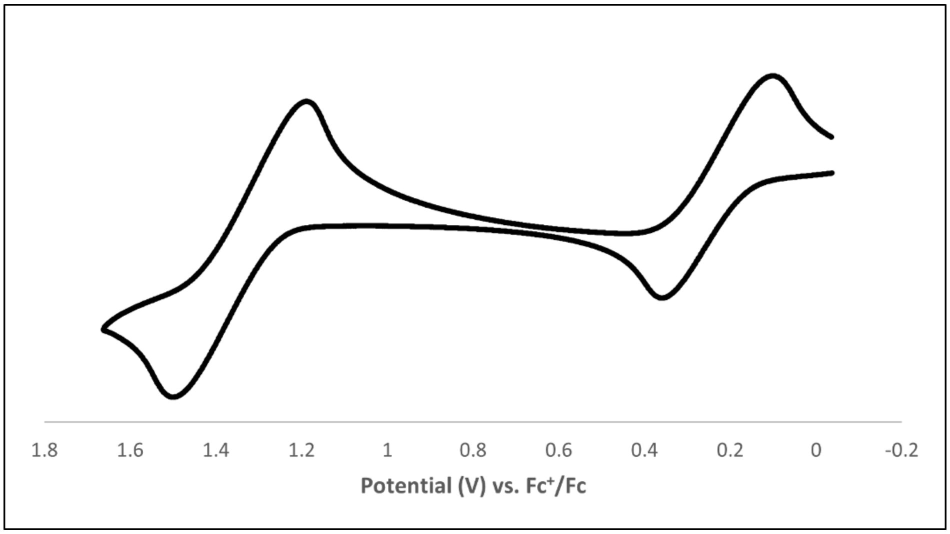

Figure S37. Cyclic voltammogram of **T10** in CH_2Cl_2 at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 1.11 V vs $Fc^{+/0}$ as shown.

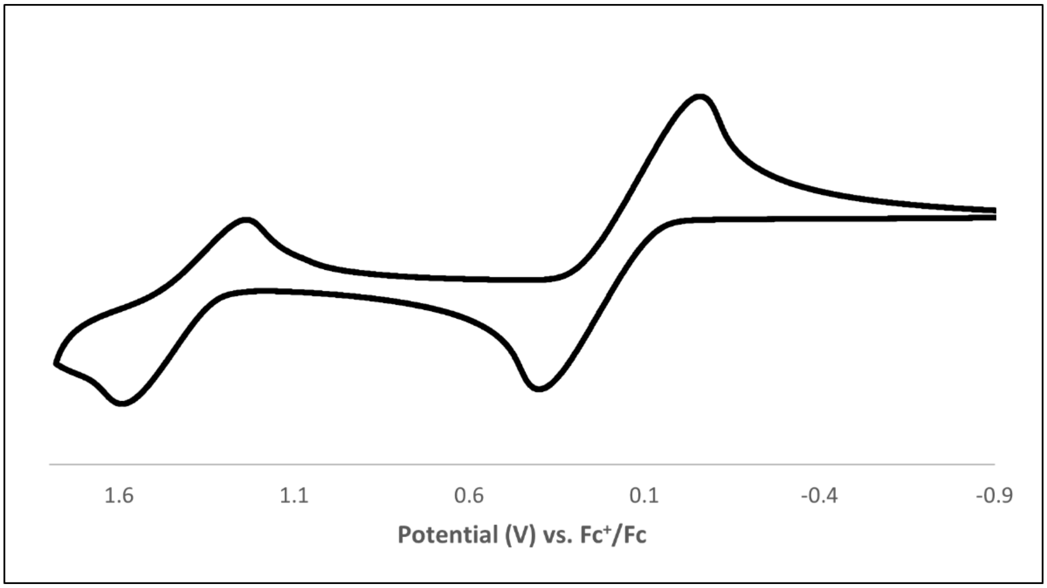

Figure S38. Cyclic voltammogram of **T11** in CH_2Cl_2 at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 1.26 V vs $Fc^{+/0}$ as shown

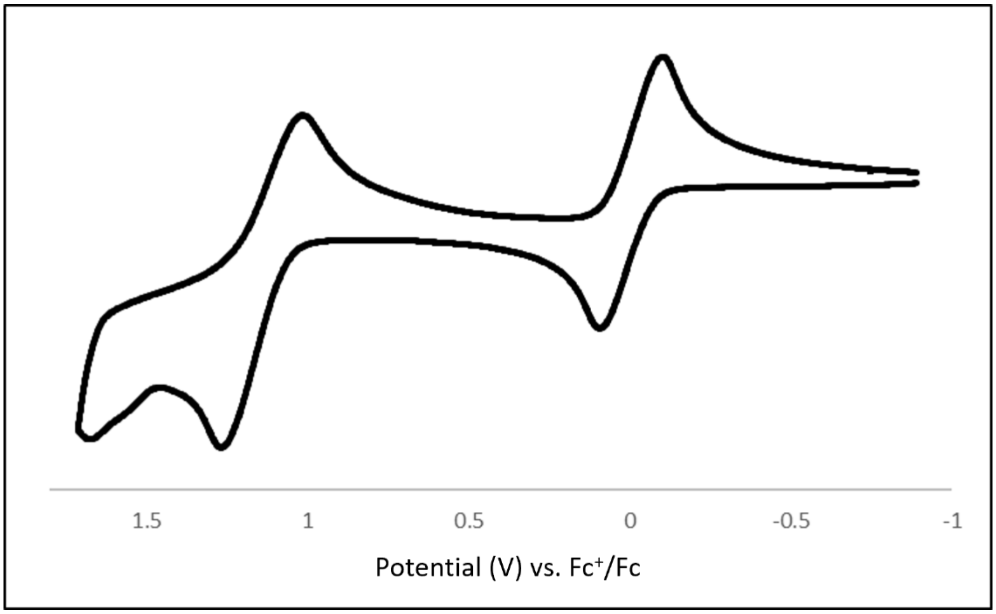

Figure S39. Cyclic voltammogram of **T12** in CH_2Cl_2 at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 1.19 V vs $Fc^{+/0}$ as shown.

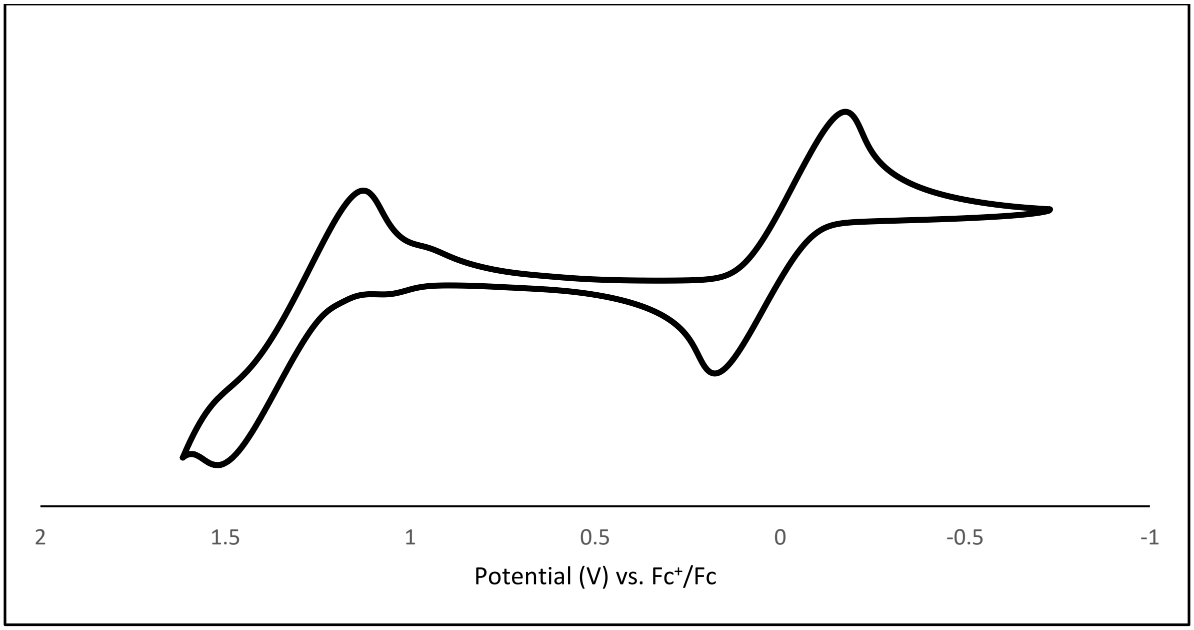

Figure S40. Cyclic voltammogram of **T13** in fluorobenzene at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 1.32 V vs $Fc^{+/0}$ as shown.

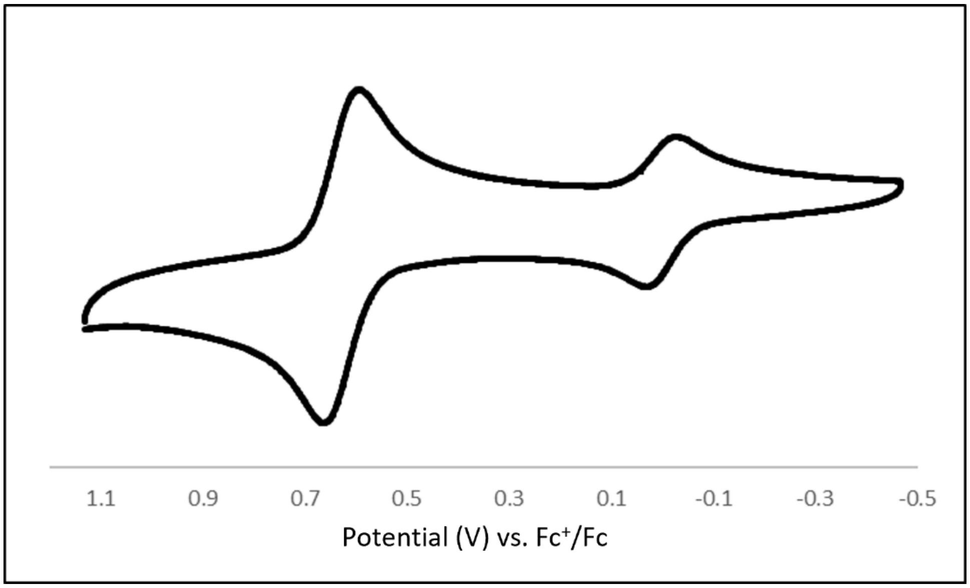

Figure S42. Cyclic voltammogram of **T14** in CH_2Cl_2 at 27 °C. The rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.3 M $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 0.63 V vs $Fc^{+/0}$ as shown.

V. ESI References

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