Supporting Information for:

Nickel(IV)-Catalyzed C–H Trifluoromethylation of (Hetero)arenes

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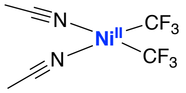
General Procedures

NMR spectra were obtained on a Varian VNMR 700 (699.76 MHz for ^{1}H; 175.95 MHz for ^{13}C; 224.51 MHz for ^{11}B; 283.29 MHz for ^{31}P) or a Varian VNMR 500 (500.09 MHz for ^{1}H; 470.56 MHz for ^{19}F) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F and ^{11}B chemical shifts are reported in ppm and are referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^{1}H NMR spectrum. Abbreviations used in the NMR data: s, singlet; d, doublet; t, triplet; q, quartet; dt, double of triplets; bq, broad quartet. Elemental analyses were conducted by Midwest Microlabs. X-ray crystallographic data were collected on a Bruker SMART APEX-I CCD-based X-ray diffractometer. Cyclic voltammetry was performed using a CHI600C potentiostat from CH Instruments. EPR spectra were collected at –176 ºC using a Bruker EMX ESR Spectrometer with a nitrogen-cooled cryostat. Flash chromatography was conducted using a Biotage Isolera One system with cartridges containing high performance silica gel. Cyclic voltammetry was performed using a CHI600C potentiostat from CH Instruments.

Materials and Methods

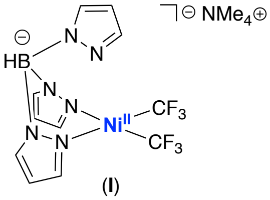
$Ni(PEt_3)_4$[1], $K[(Tp)Ni^{II}(C_6H_4\text{-}o\text{-}C_6H_4)]$[2], 2(2-fluorophenyl)pyridine,[3] 2(4-fluorophenyl)pyridine,[3] and 2-(2-bromophenyl)pyridine[4] were prepared according to literature procedures. $Ni(COD)_2$ and KTp were purchased from Strem. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor), 2,2'-bipyridine, *N*-fluorobenzenesulfonamide, and 2-picoline were purchased from Acros. Xenon difluoride was purchased from Matrix Solutions. 1-Fluoro-2,4,6-trimethylpyridinium triflate was purchased from TCI. Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaBAr_F$) was purchased from Astatech. Biphenylene was purchased from Oxchem. Dichloromethane (Fisher), pentane (Fisher), and tetrahydrofuran (Fisher) were de-aerated via a nitrogen sparge and were dried using a solvent purification system. Acetonitrile, *N,N*-dimethylformamide, dioxane, 1,2-dimethoxyethane, and pyridine were purchased from Acros, de-aerated via a nitrogen sparge, and stored over activated 3 Å molecular sieves. CD_3CN and C_6D_6 were obtained from Cambridge Isotopes Laboratories and were all sparged with N_2 before being stored over 3 Å molecular sieves under an N_2 atmosphere. Celite was dried under vacuum for 12 h at 50 °C. Unless otherwise noted, all glassware was dried overnight in an oven at 150 ºC and cooled under an inert atmosphere before use. All commercial reagents were used without further purification/drying unless explicitly stated in the experimental section.

II. Synthesis of Complexes



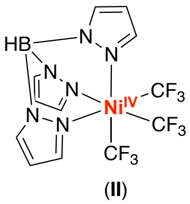
(**S1**)

Synthesis of [(MeCN)$_2$Ni^{II}(CF$_3$)$_3$] (S1). An oven-dried 500 mL round bottom flask equipped with a magnetic stir was charged with AgF (3.30 g, 26.0 mmol, 2 equiv), MeCN (250 mL), and TMSCF$_3$ (4.80 mL, 32.5 mmol, 2.5 equiv) in the glovebox. The mixture was stirred vigorously for 2 h and then NiBr$_2$·DME (4.01 g, 13.0 mmol, 1.0 equiv) was added. After stirring for 24 h, the reaction was transferred to several centrifuge tubes, which were sealed and centrifuged at 5000 rpm for 20 min. The yellow-orange supernatant was carefully separated from the gray pellet and reduced to dryness in vacuo. The resulting orange residue was dissolved in CH$_2$Cl$_2$ (100 mL) and filtered through a 3 cm Celite pad using vacuum filtration. The solvent was removed from the filtrate under vacuum to yield a dark yellow solid (2.79 g, 77% yield). The ^{19}F NMR spectrum matched that reported in the literature.[1]



(**I**)

Synthesis of [(Tp)Ni^{II}(CF$_3$)$_2$NMe$_4$] (I). A 20 mL scintillation vial equipped with a magnetic stir was charged with (MeCN)$_2$Ni^{II}(CF$_3$)$_3$ (**S1**) (178 mg, 0.64 mmol, 1.0 equiv), NMe$_4$Tp (183 mg, 0.64 mmol, 1.0 equiv), and MeCN (10 mL). The mixture was vigorously shaken for 1 min and then the solvent was removed under vacuum. The orange residue was washed with pentanes (2 x 10 mL) and diethyl ether (2 x 10 mL) and dried under vacuum to yield a light orange solid (299 mg, 97% yield). ^{1}H NMR and ^{19}F NMR spectra matched those reported in the literature.[2]



(**II**)

Synthesis of [(Tp)Ni^{IV}(CF$_3$)$_3$] (II): In a nitrogen atmosphere glovebox, an oven-dried 250 mL round bottom flask equipped with magnetic stir bar was charged with TpNi^{II}(CF$_3$)$_2$NMe$_4$] (**I**) (500 mg, 1.03 mmol, 1.0 equiv) and CH$_2$Cl$_2$ (250 mL). 2,8-Difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (496 mg, 1.13 mmol, 1.1 equiv) was added, and the reaction was vigorously stirred for 1.5 h. The brown reaction mixture was removed from the glovebox and filtered, and the filtrate was reduced to dryness under vacuum. The brown residue was purified by flash chromatography on silica gel (mobile phase:

hexanes/ethyl acetate with a gradient from 99:1 to 90:10). The product was obtained as a canary yellow solid (233 mg, 47% yield). ^{1}H, ^{19}F, ^{13}C, and ^{11}B NMR spectra matched those reported in the literature.[3]

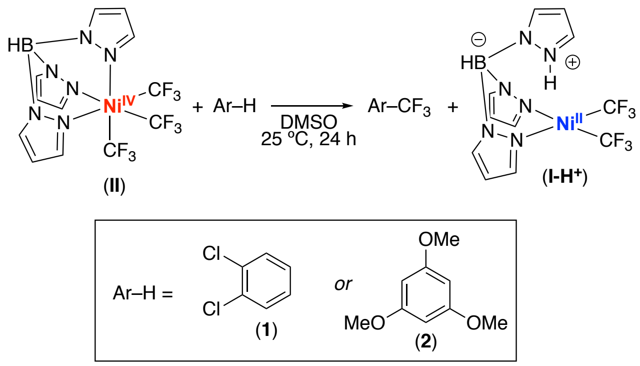
^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ 7.95 (s, 3H), 7.70 (s, 3H), 6.27 (s, 3H), 4.53 (bq, B–***H***, 1H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 °C) δ 144.1, 135.5, 108.8 (q, J_{CF} = 401 Hz), 105.9.

^{11}B NMR (225 MHz, $CDCl_3$, 23 °C): δ –4.50 (d, J_{BH} = 112 Hz, ***B***–H).

^{19}F NMR (470 MHz, $CDCl_3$, 23 °C): δ –18.4 (s, 3F)

III. Stoichiometric C–H Trifluoromethylation of Arenes



In a nitrogen-filled glovebox, a 4 mL glass vial equipped with a stir bar was charged with substrate (1.0 equiv, 5.0 equiv or neat), complex **II** (6 mg, 0.015 mmol, 1.0 equiv), and anhydrous DMSO (600 µL or 0 µL for entry 2). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, trifluorotoluene (1.53 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of the trifluoromethylated product was determined by ^{19}F NMR spectroscopy.

Table S1. Optimizing Ni^{IV}-mediated trifluoromethylation

Entry	Ar–H	equiv Ar–H	Yield (%)
1	**1**	1 equiv	<5 (~1:1 r.r.)
2	**1**	neat	9 (1:1.2 r.r.)
3	**2**	1 equiv	47
4	**2**	5 equiv	72

*Yields determined by ^{19}F NMR spectroscopy using trifluorotoluene as an internal standard

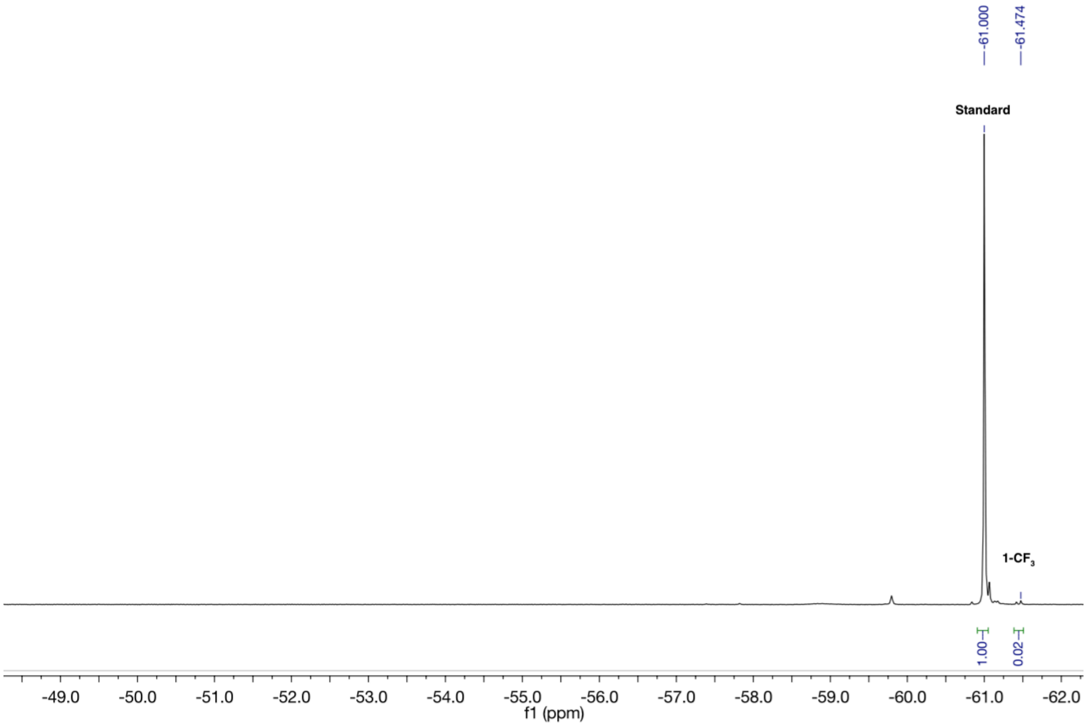


Figure S1. ^{19}F NMR spectrum showing formation of compound **1-CF$_3$** under conditions outlined in entry 1.

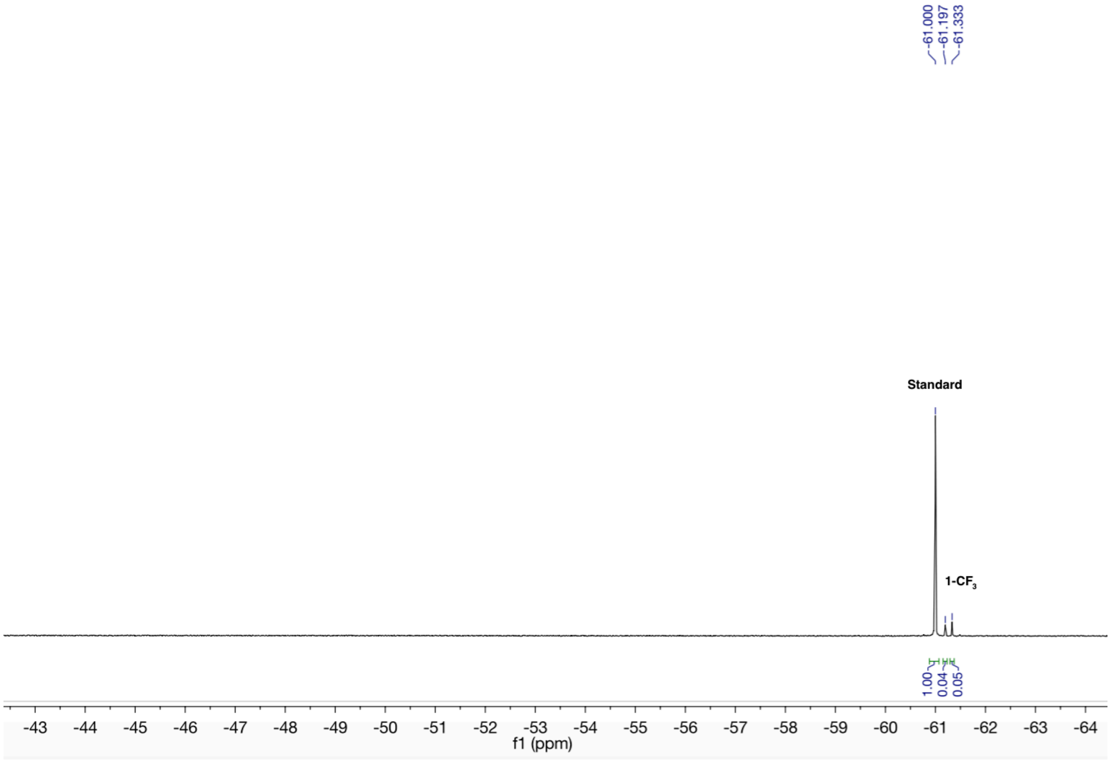


Figure S2. ^{19}F NMR spectrum showing formation of compound **1-CF$_3$** under conditions outlined in entry 2.

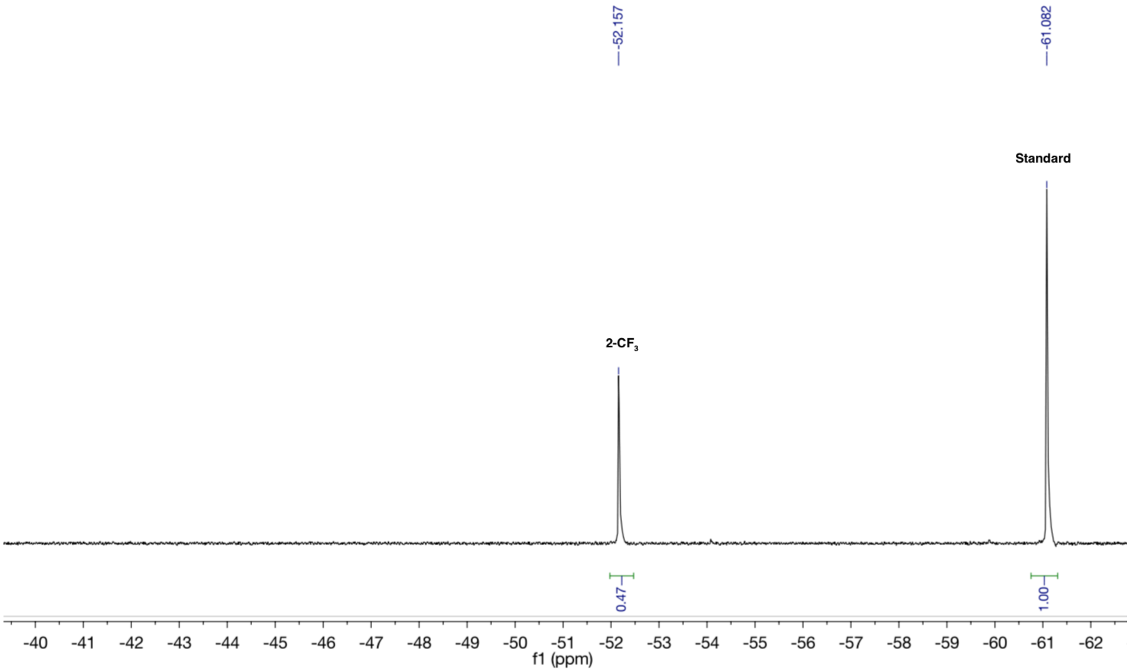


Figure S3. ^{19}F NMR spectrum showing formation of compound **2-CF$_3$** under conditions outlined in entry 3.

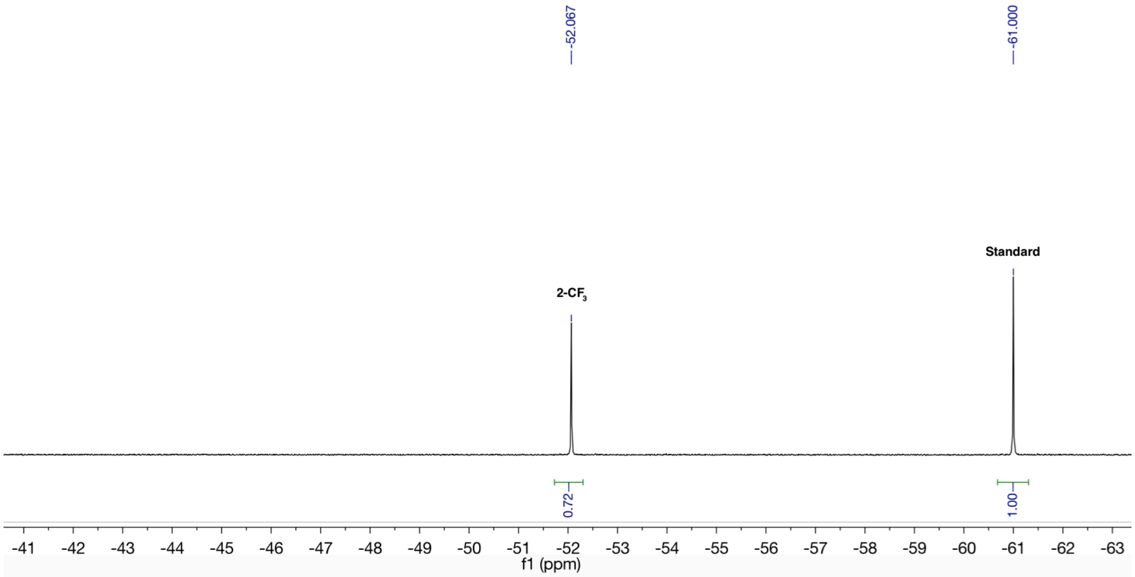
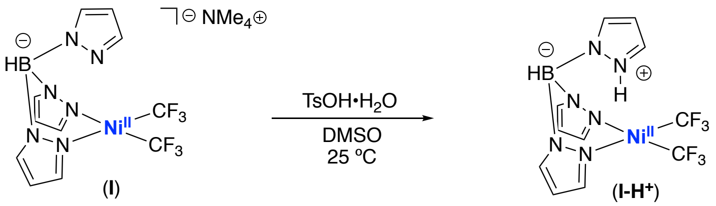


Figure S4. ^{19}F NMR spectrum showing formation of compound **2-CF$_3$** under conditions outlined in entry 4.



In a nitrogen-filled glovebox, a 4 mL glass vial equipped with a stir bar was charged with complex **I** (10 mg, 0.021 mmol, 1.0 equiv), trifluorotoluene (2.5 µL, 0.02 mmol, 1.0 equiv), and anhydrous DMSO (700 µL). This solution was added to a screw-top NMR tube, which was sealed and removed from the glovebox. A solution of TsOH•H_2O (7.8 mg, 0.041 mmol, 2.0 equiv) in DMSO (300 µL) was added to the NMR tube via syringe. The NMR tube was shaken, and then the reaction was analyzed by ^{19}F NMR spectroscopy. As shown in Figure S5, a significant upfield shift was observed for the CF_3 signal, consistent with the proposed protonation reaction. This new signal has the same chemical shift as that of the Ni^{II} product observed in the above trifluoromethylation reactions, indicating that this Ni^{II} product is the protonated derivative of complex **I** (**I-H$^+$**)

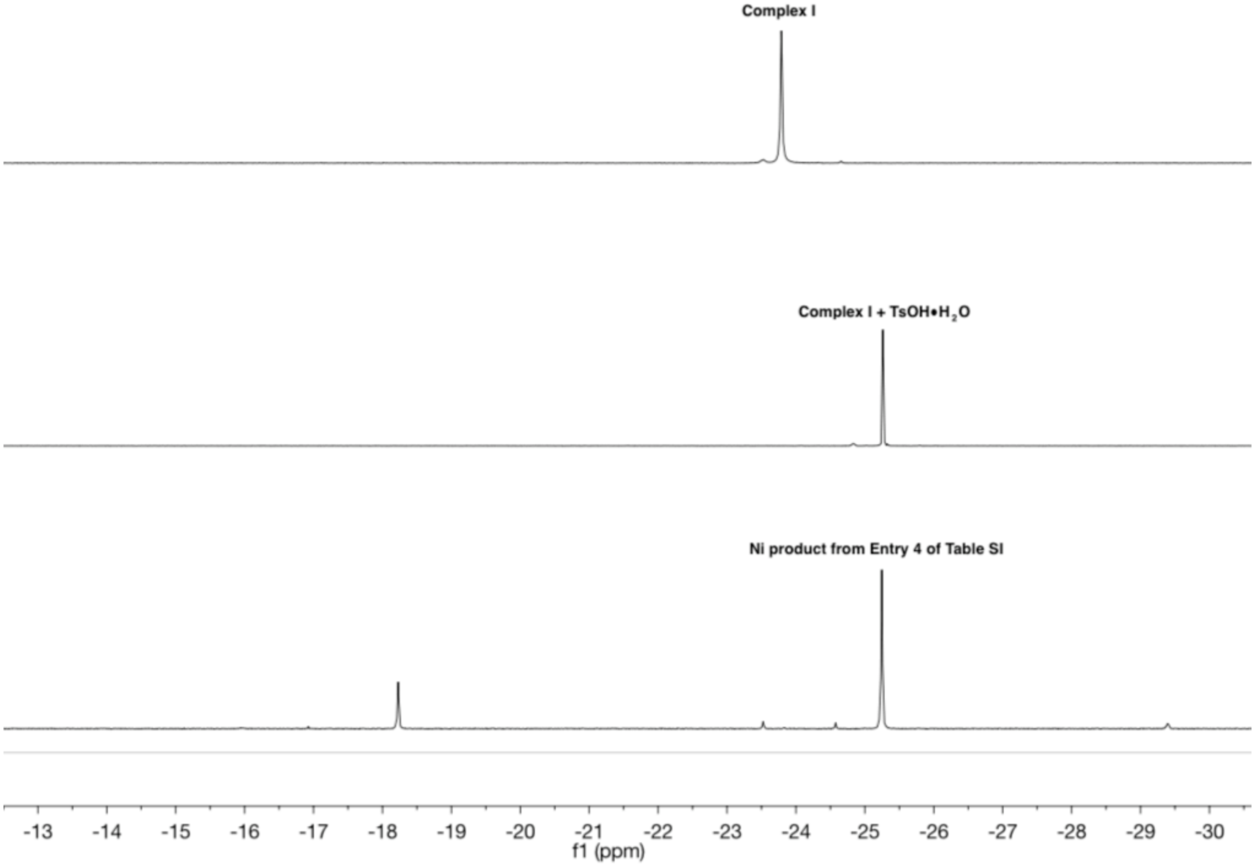
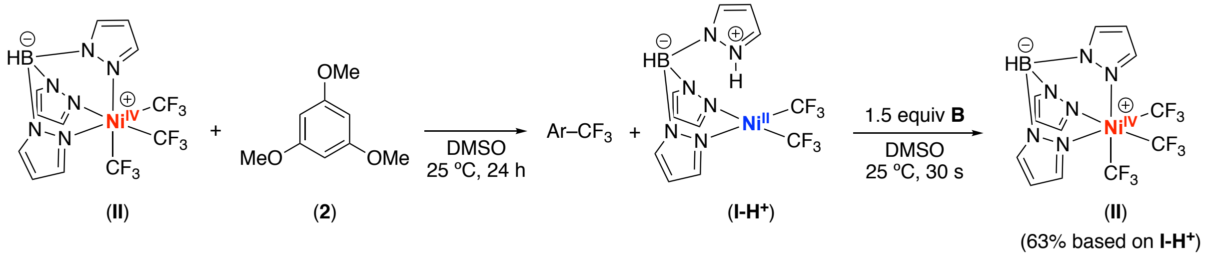
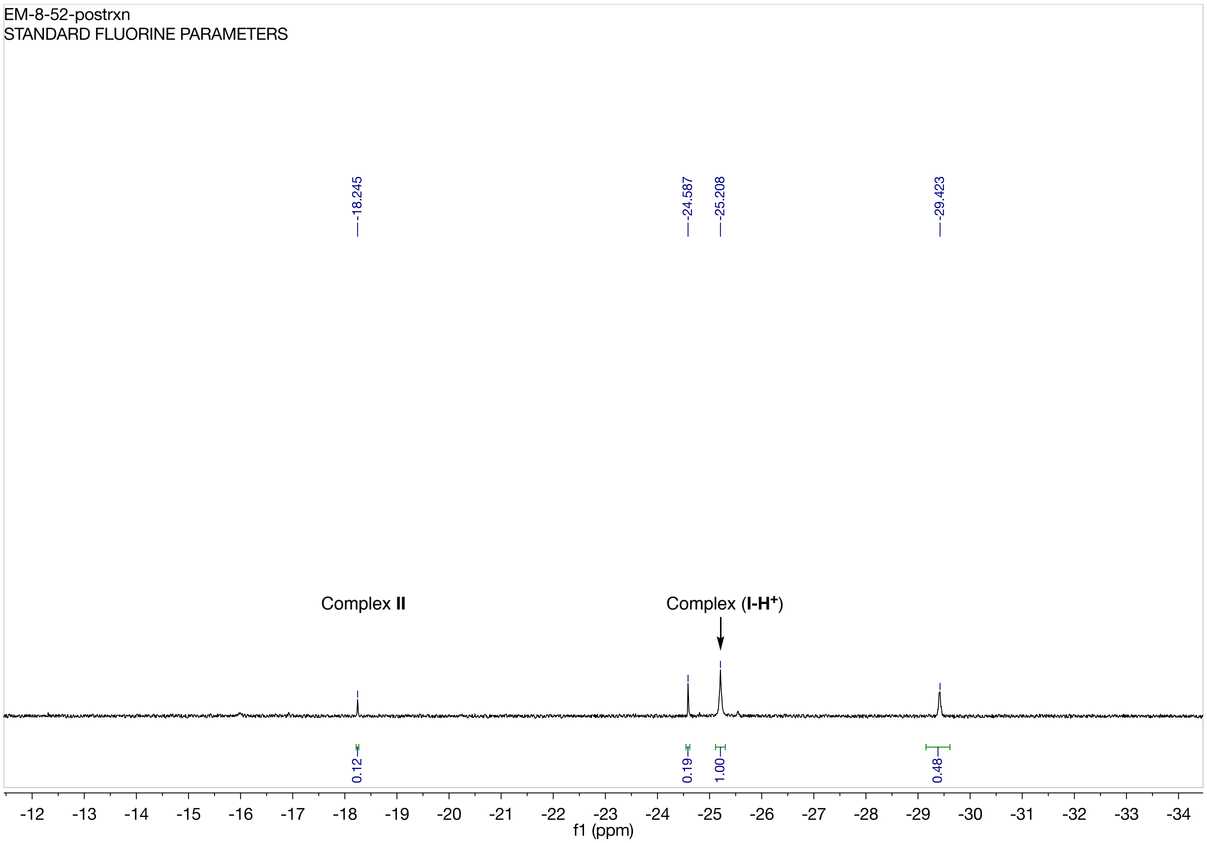


Figure S5. ^{19}F NMR spectrum showing formation of compound **I-H$^+$** through treatment of complex **I** with TsOH•H_2O.



In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (10.5 mg, 0.0625 mmol, 5 equiv), complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), and DMSO (625 µL). The reaction was stirred at room temperature for 2 h and then transferred to a screw-cap NMR tube and analyzed by ^{19}F NMR spectroscopy to confirm complete formation of **2-CF$_3$** and relative concentration of **I-H$^+$** (Figure S6a). A solution of **B** (8.2 mg, 0.0187 mmol, 1.5 equiv) in DMSO (100 µL) was added to this NMR tube, and the contents were shaken before the sample was inserted back into the spectrometer to determine the relative consumption of **I-H$^+$** and formation of **II** (Figure S6b).

a)



b)

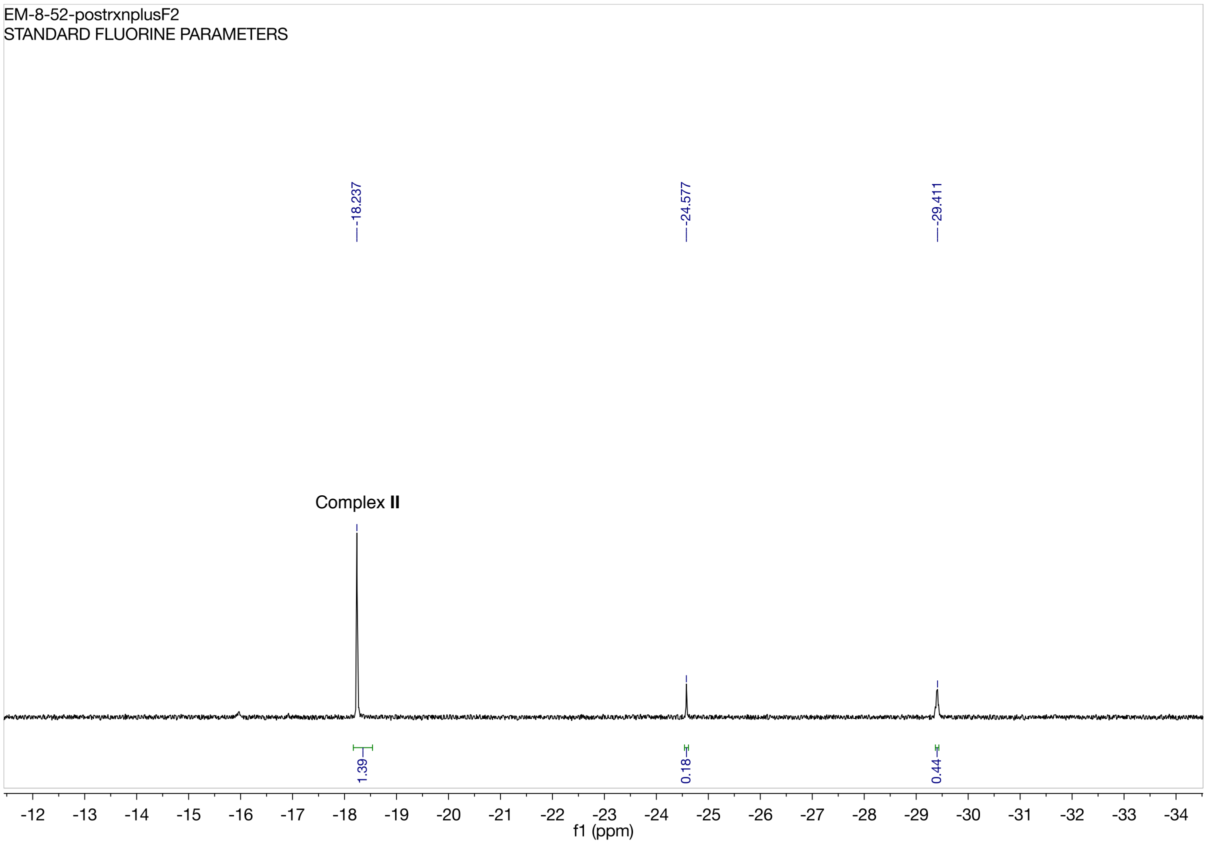
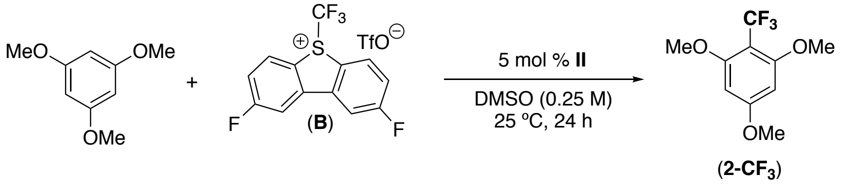


Figure S6. Determining ability of oxidant **B** to convert **I-H$^+$** into complex **II**. (a) ^{19}F NMR spectrum of reaction after stirring for 2 h. (b) ^{19}F NMR spectrum of reaction after addition of **B**

IV. Catalytic C–H Trifluoromethylation of Arenes

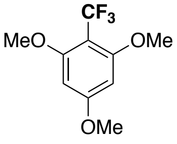


In a nitrogen-filled glovebox, a 4 mL glass vial equipped with a stir bar was charged with trimethoxybenzene (8 mg, 0.05 mmol, 1.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred inside the glovebox for 24 h at room temperature. After this time, trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **2-CF$_3$** was determined by ^{19}F NMR spectroscopy.

Table S2. Optimizing Ni^{IV}-catalyzed trifluoromethylation

Entry	Modification	Yield (%)
1	none	35
2	no **II**	0
3	no light	37
4	no **II**, 45 °C	4
5	no **II**, 65 °C	9
6	no **II**, 85 °C	7
7	no **II**, 105 °C	7
8	**I** as catalyst	25
9	**A** used as oxidant	25
10	0.025 M	20
11	2.5 M	40
12	MeCN solvent	24
13	Dioxane solvent	4
14	DMF solvent	35
15	THF solvent	1
16	60 °C	38
17	48 h	42
18	2 equiv arene	62
19	**5 equiv arene**	**93**
20	0.1 equiv Cp_2Co, 1.0 equiv $TsOH \cdot H_2O$	25

[*] Yields determined by ^{19}F NMR spectroscopy using trifluorotoluene as an internal standard and are based on oxidant.



(**2-CF₃**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL glass vial equipped with a stir bar was charged with trimethoxybenzene (42 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred inside the glovebox for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added and the yield of **2-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S7, 92% yield). Yield of **2-CF$_3$** obtained from reaction conducted in absence of **II** was 1% (Figure S8).

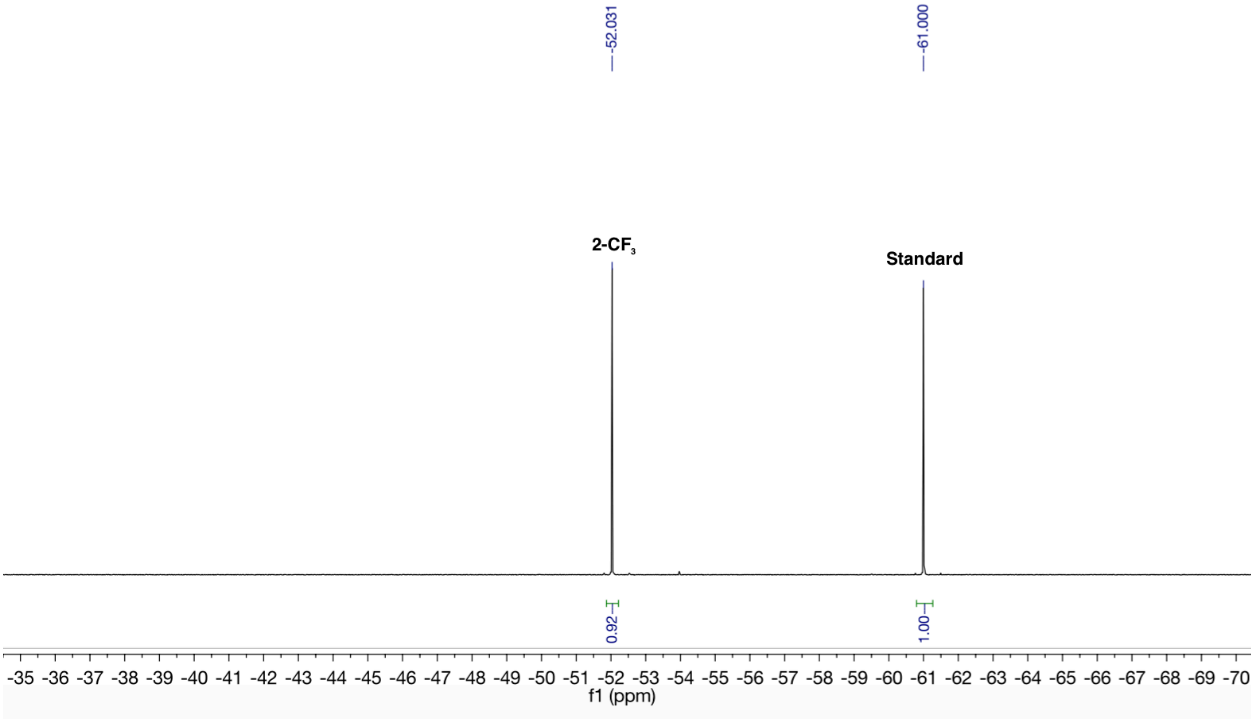


Figure S7. ^{19}F NMR spectrum showing formation of compound **2-CF$_3$**.

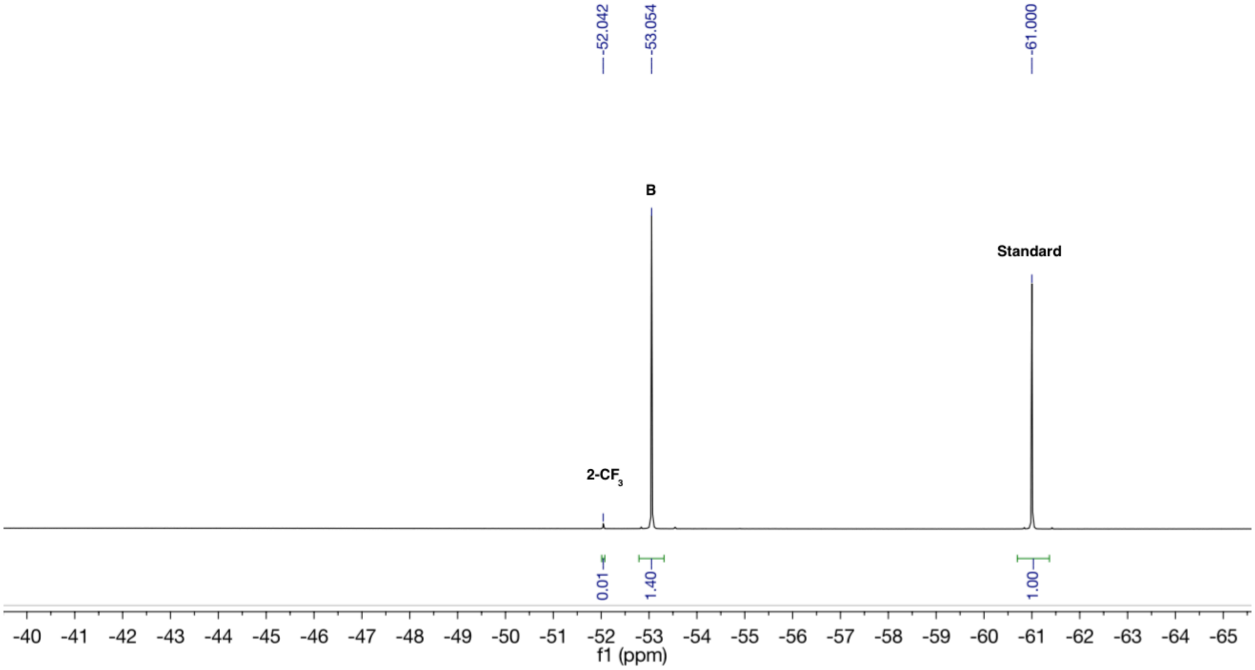
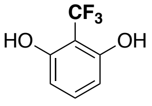
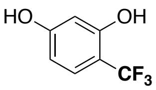


Figure S8. ^{19}F NMR spectrum of control reaction with compound **2** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL glass vial equipped with stir bar was charged with trimethoxybenzene (420 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred inside the glovebox for 24 h at room temperature. After this time, the reaction was removed from the glovebox, transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with Et_2O (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 100:0 to 90:10) to yield **2-CF$_3$** as a white crystalline solid (103 mg, 87% yield). ^{1}H, ^{19}F, and ^{13}C NMR spectra matched those reported in the literature.[4]



(3-CF$_3$-2)



(3-CF$_3$-4)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with resorcinol (28 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **3-**

CF_3-2 and **3-CF_3-4** were determined by ^{19}F NMR spectroscopy (Figure S9, 2 isomers, 2.5 : 1 ratio, 24% yield **3-CF_3-2** and 60% yield of **3-CF_3-4**, 84% combined yield). No **3-CF_3-2** or **3-CF_3-4** was detected from reaction conducted in absence of **II** (Figure S10).

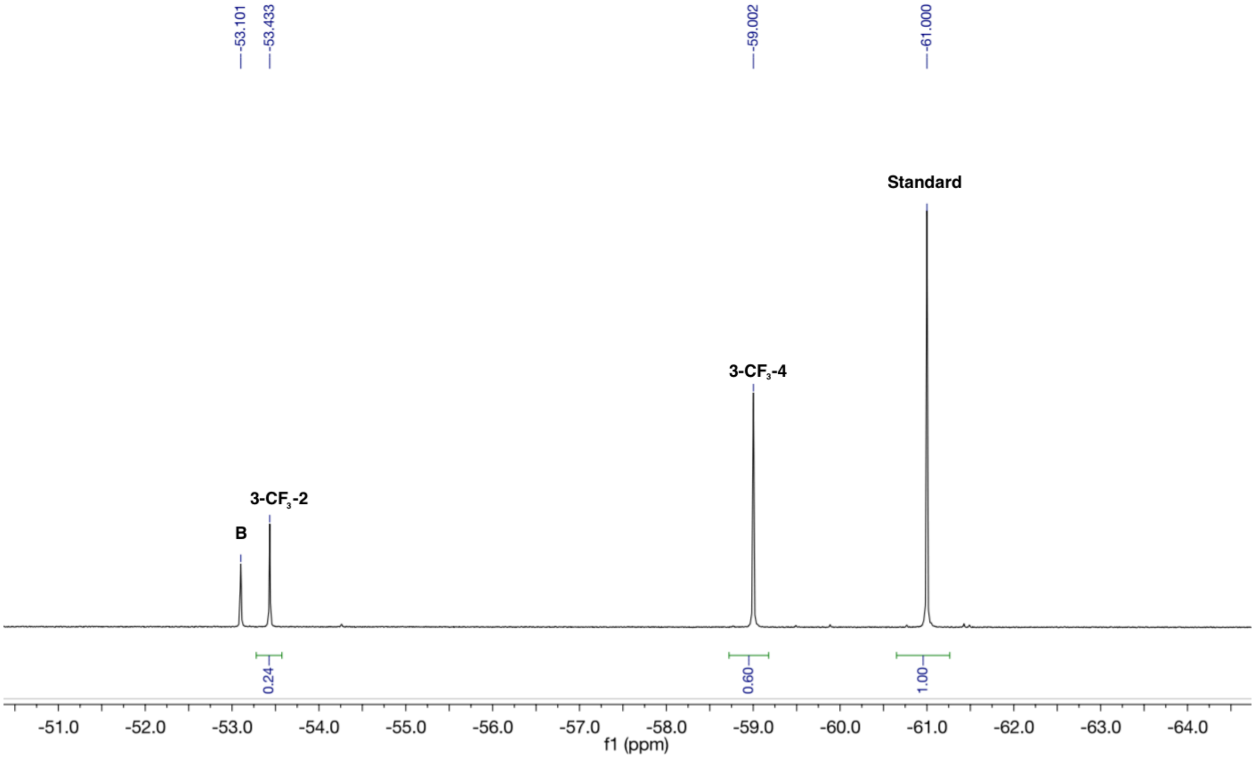


Figure S9. ^{19}F NMR spectrum showing formation of compound **3-CF_3**.

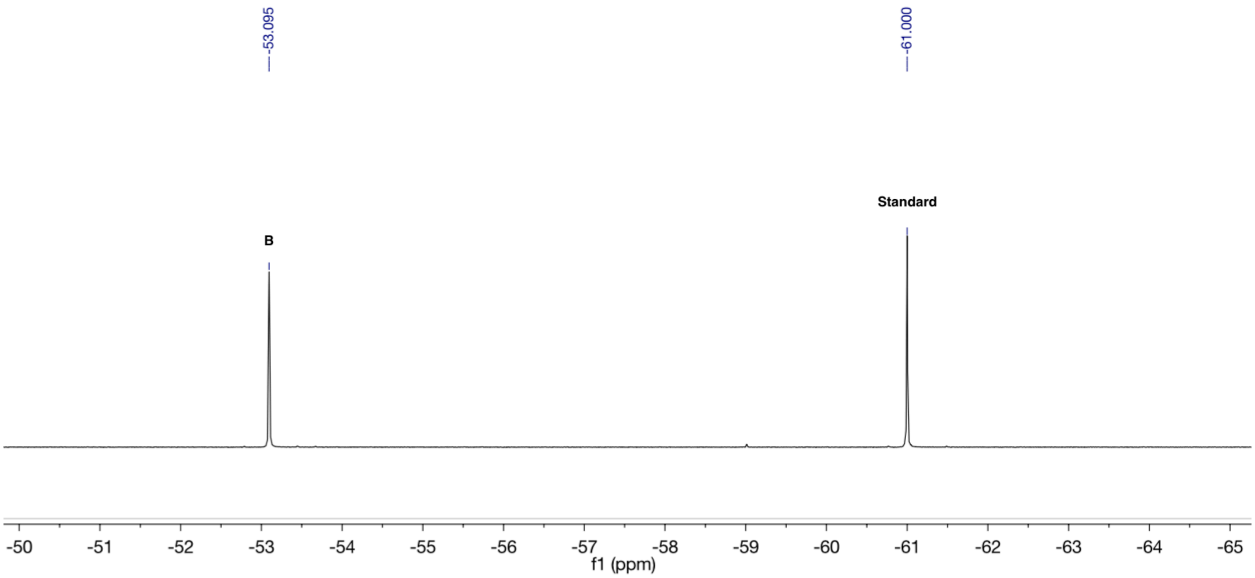


Figure S10. ^{19}F NMR spectrum of control reaction with compound **3** and **B** in absence of **II**.

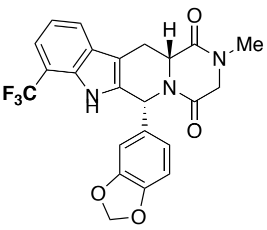
Isolation Scale: In a nitrogen-filled glovebox, a 20 mL glass vial equipped with stir bar was charged with resorcinol (275mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined screw cap and the reaction was stirred inside the glovebox for 24 h at room temperature. After this time, the reaction was removed from the glovebox, transferred to a separatory funnel. After this time, the reaction was removed from the glovebox, transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with Et_2O (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: 75:25 hexanes/EtOAc) to yield **3-CF$_3$-2** as a white powder (20 mg, 22% yield). We were unable to separate **3-CF$_3$-4** from residual starting material **3**.

NMR Data for 3-CF$_3$-2:

^{1}H NMR (700 MHz, $CDCl_3$, 23 °C): δ 7.23 (t, J_{HH} = 8.2 Hz, 1H), 6.50 (d, J_{HH} = 8.2 Hz, 2H), 5.74 (s, 2H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 °C): δ 154.9, 133.6, 125.1 (q, J_{CF} = 273.2 Hz), 109.8.

^{19}F NMR (470 MHz, $CDCl_3$, 23 °C): δ –54.2 (s).



(**4-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with tadalafil (97 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **4-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S11, 65% yield). Yield of **4-CF$_3$** obtained from reaction conducted in absence of **II** was 4% (Figure S12).

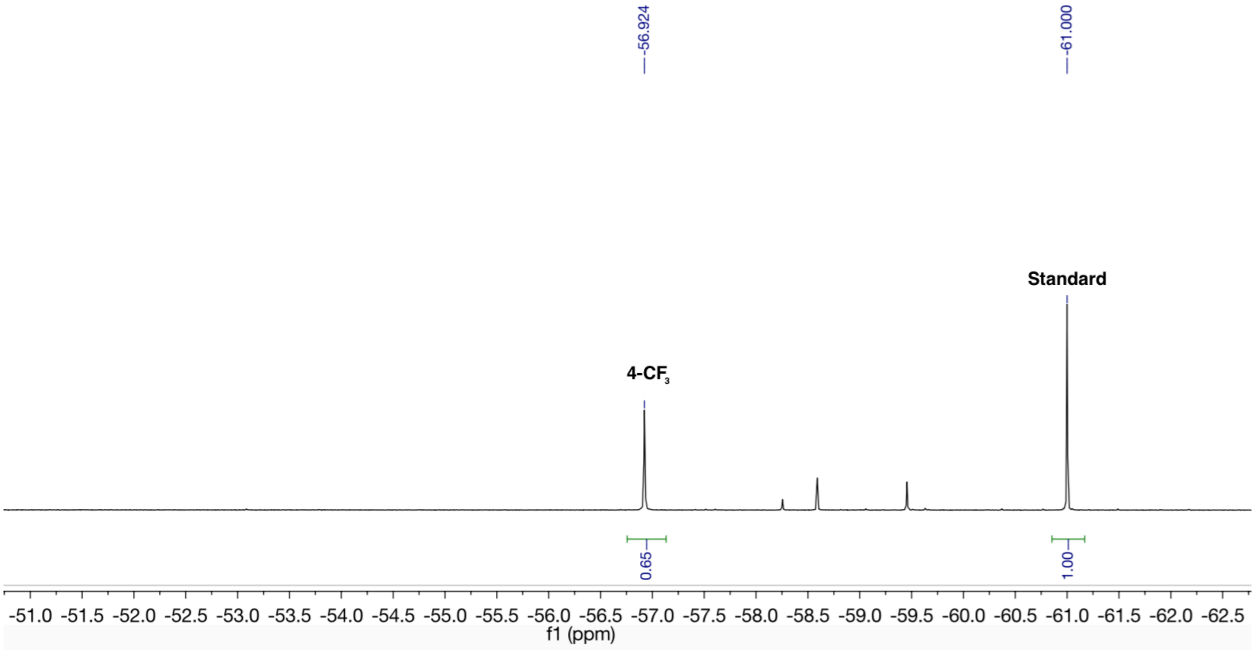


Figure S11. ^{19}F NMR spectrum showing formation of compound **4-CF$_3$**.

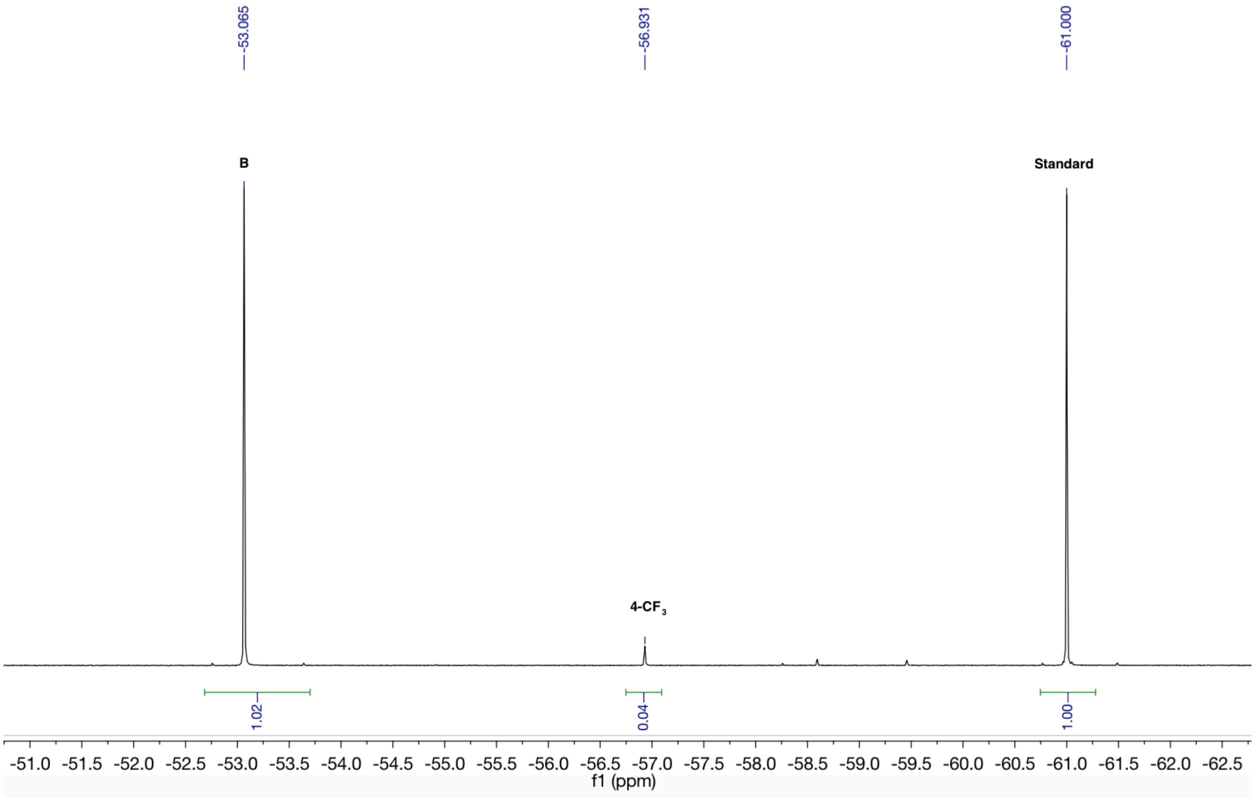
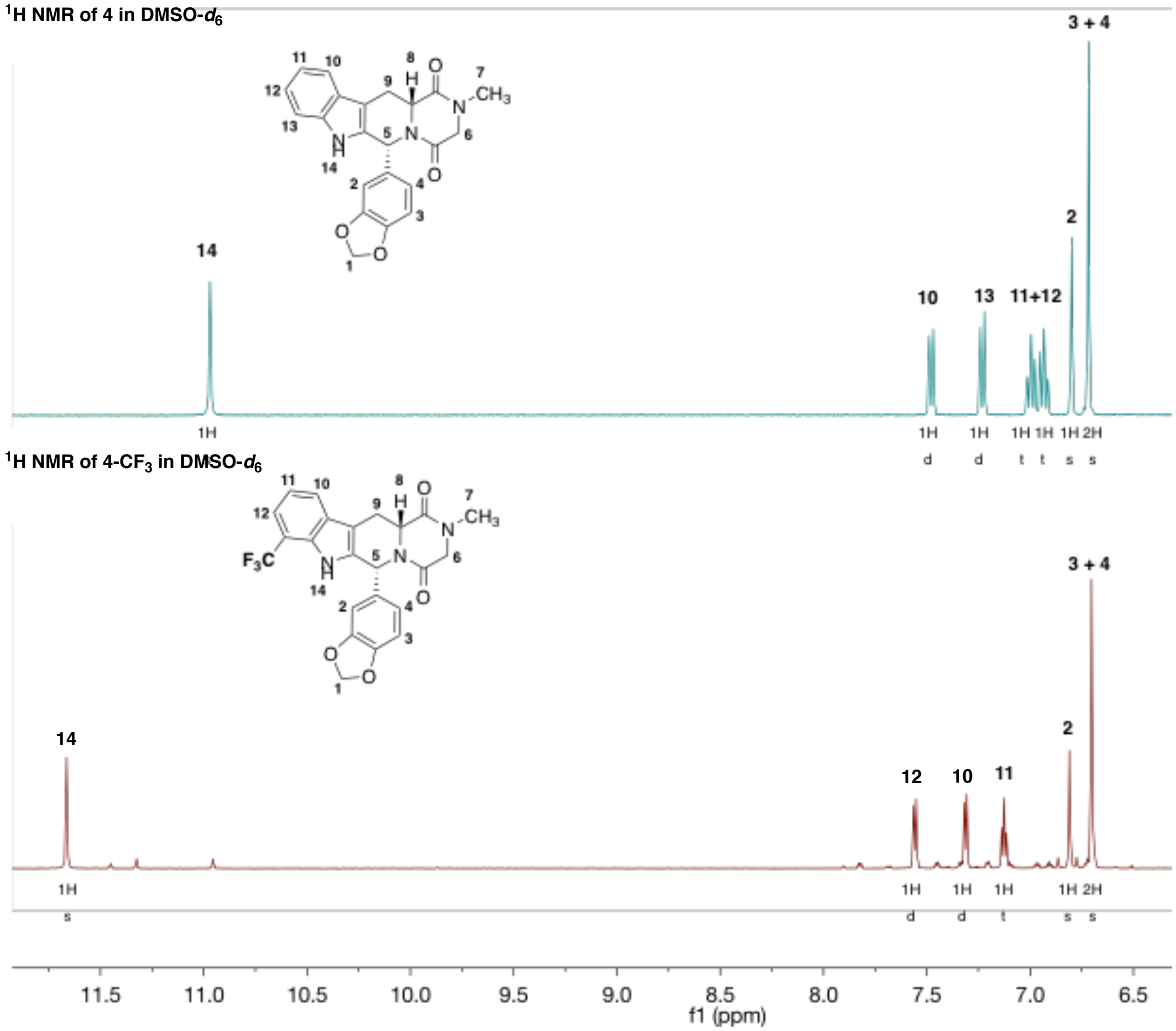


Figure S12. ^{19}F NMR spectrum of control reaction with compound **4** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with tadalafil (487 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox, and transferred to a separatory funnel. Ethyl acetate (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with EtOAc (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on reverse-phase silica gel (mobile phase: MeCN/H_2O) with a gradient from 100:0 to 90:10) to yield **4-CF$_3$** as a white powder (49 mg, 43% yield). The structure of the product was assigned as depicted in Figure S13 and was informed by the assigned ^{1}H NMR data for **4**.[5]


^{1}H NMR of 4 in DMSO-d_6

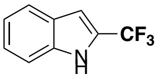
^{1}H NMR of 4-CF$_3$ in DMSO-d_6

Figure S13. ^{1}H NMR spectra and assignment of the aromatic regions of **4** and **4-CF$_3$**.

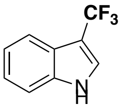
^{1}H NMR (700 MHz, DMSO-d_6, 23 °C): δ 11.75 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 6.90 (s, 1H), 6.79 (s, 2H), 6.18 (s, 1H), 5.93 (s, 2H), 4.42 (dd, J = 11.8, 3.9 Hz, 1H), 4.16 (d, J = 17.0 Hz, 1H), 3.96 (d, J = 17.0 Hz, 1H), 3.64-3.60 (m, 1H), 3.01 – 2.96 (m, 1H), 2.93 (s, 3H).

^{13}C NMR (176 MHz, DMSO-d_6, 23 °C): δ 167.2, 166.7, 147.5, 146.6, 137.5, 137.4, 136.9, 126.2, 121.4, 120.73, 119.6, 118.9, 117.3 (***CF$_3$*** extracted from HMBC), 116.6, 108.6, 107.34, 103.9, 101.4, 55.9, 55.5, 51.8, 33.3, 24.6.

^{19}F NMR (470 MHz, DMSO-d_6, 23 °C): δ –57.1 (s).



(5-CF$_3$-2)



(5-CF$_3$-3)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with indole (30 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **5-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S14, 2 : 1 ratio of isomers, 43% yield **5-CF$_3$-2** and 21% yield of **5-CF$_3$-3**, 64% combined yield). Reaction conducted in absence of **II** yielded 2% **5-CF$_3$-2** and 3% **5-CF$_3$-3** (Figure S15).

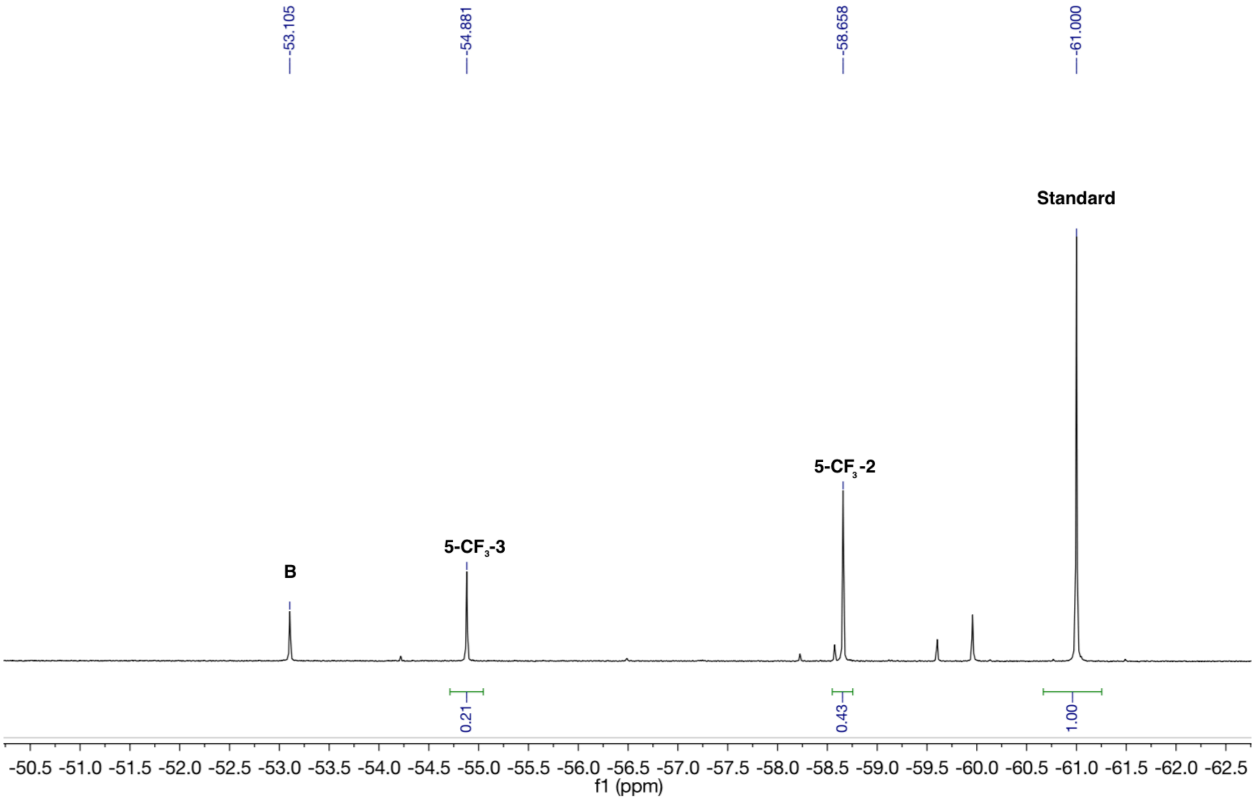


Figure S14. ^{19}F NMR spectrum showing formation of compound **5-CF$_3$-2** and **5-CF$_3$-3**.

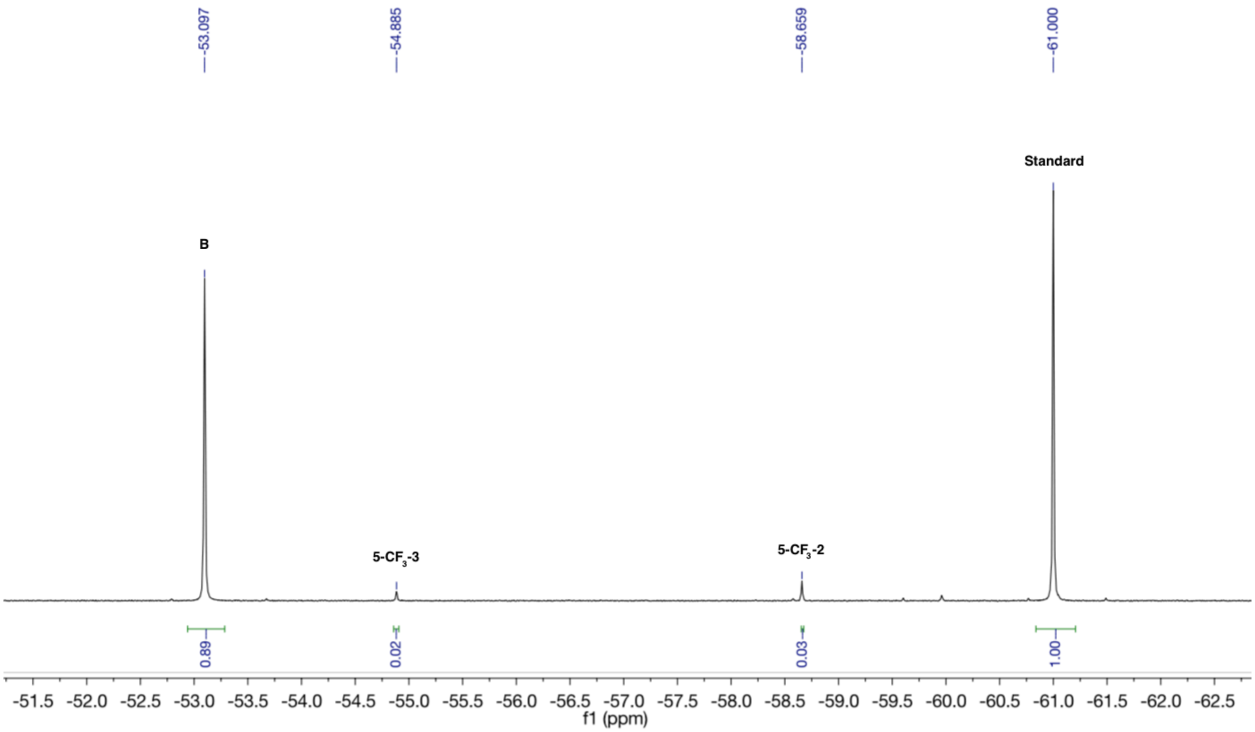
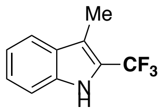


Figure S15. ^{19}F NMR spectrum of control reaction with compound **5** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with indole (293 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined screw cap and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with Et_2O (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 99:1 to 95:5) to yield the major product of **5-CF$_3$-2** as a white solid (29 mg, 32% yield). ^{1}H, ^{19}F, and ^{13}C NMR spectra matched those reported in the literature.[6]



(**6-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with 3-methylindole (33 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and

anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **6-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S16, 100% yield). Reaction conducted in absence of **II** yielded 14% **6-CF$_3$** (Figure S17).

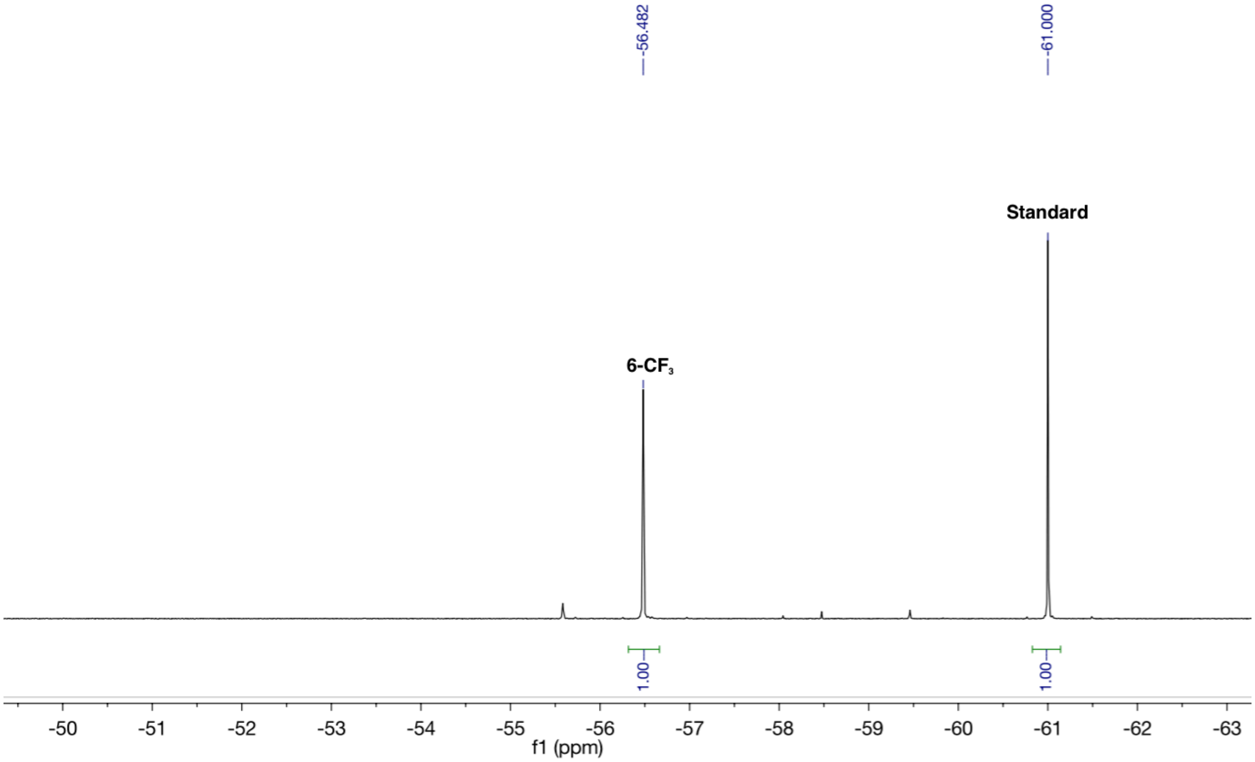


Figure S16. ^{19}F NMR spectrum showing formation of compound **6-CF$_3$**.

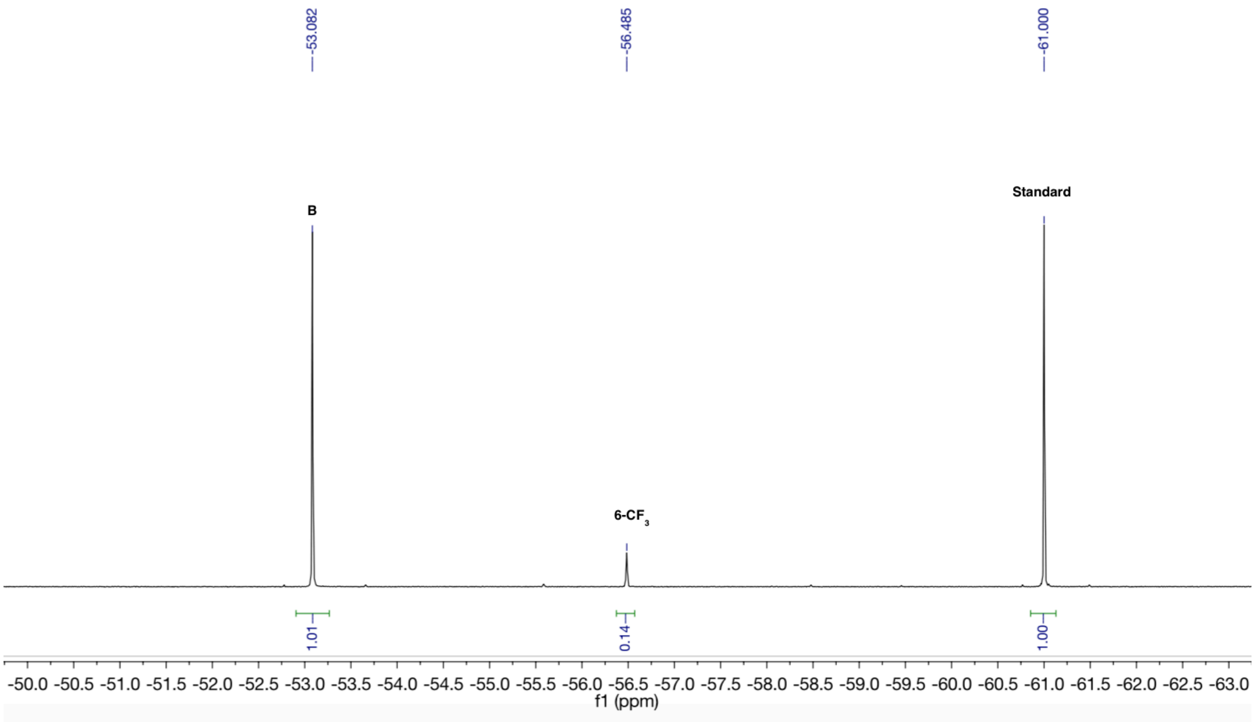
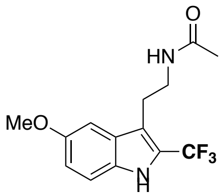


Figure S17. ^{19}F NMR spectrum of control reaction with compound **6** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with 3-methylindole (328 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with Et_2O (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 100:0 to 55:45) to yield **6-CF$_3$** as an off-white crystalline solid (91 mg, 91% yield). ^1H, ^{19}F, and ^{13}C NMR spectra matched those reported in the literature.[4]



(**7-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with melatonin (58 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-

dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **7-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S18, 67% yield). Reaction conducted in absence of **II** yielded 12% **7-CF$_3$** (Figure S19).

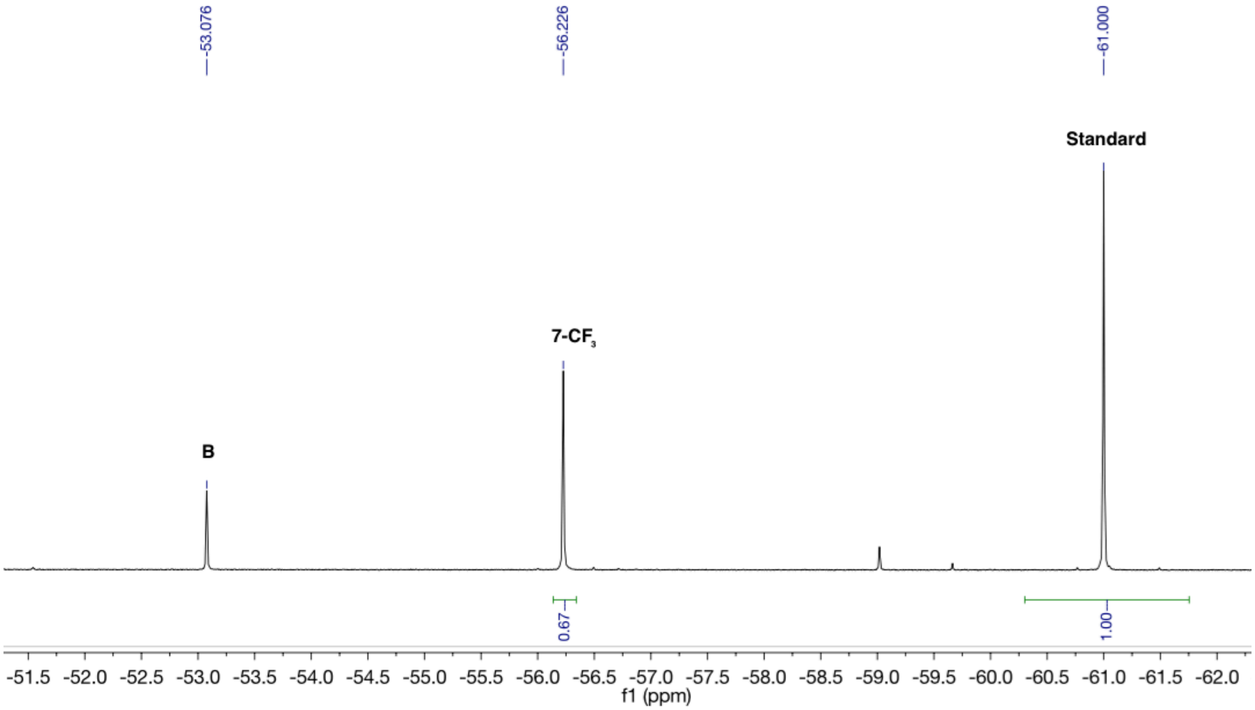


Figure S18. ^{19}F NMR spectrum showing formation of compound **7-CF$_3$**.

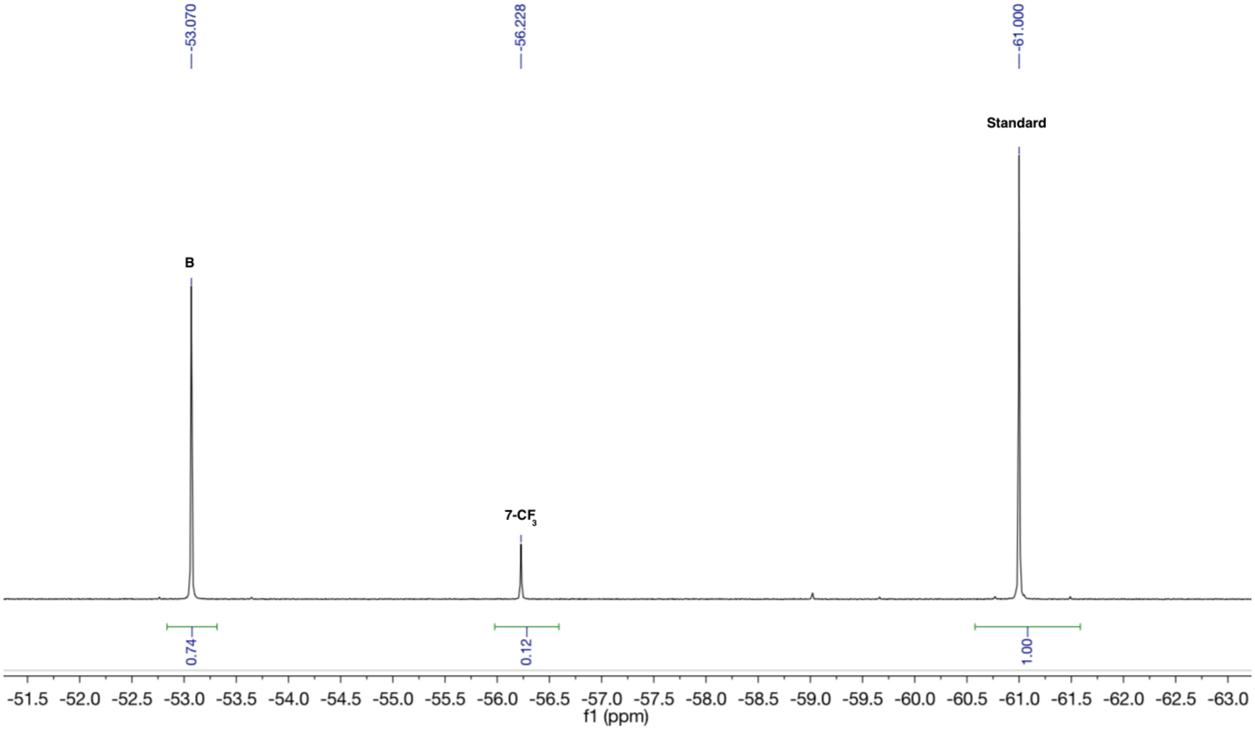
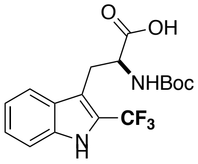


Figure S19. ^{19}F NMR spectrum of control reaction with compound **7** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with melatonin (581 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol%), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with Et_2O (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: 100% ethyl acetate) to yield **7-CF$_3$** as a white powder (96 mg, 64% yield). ^{1}H, ^{19}F, and ^{13}C NMR spectra matched those reported in the literature.[7]



(**8-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with boc-L-tryptophan (76 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and

anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **8-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S20, 81% yield). Reaction conducted in absence of **II** yielded 7% **8-CF$_3$** (Figure S21).

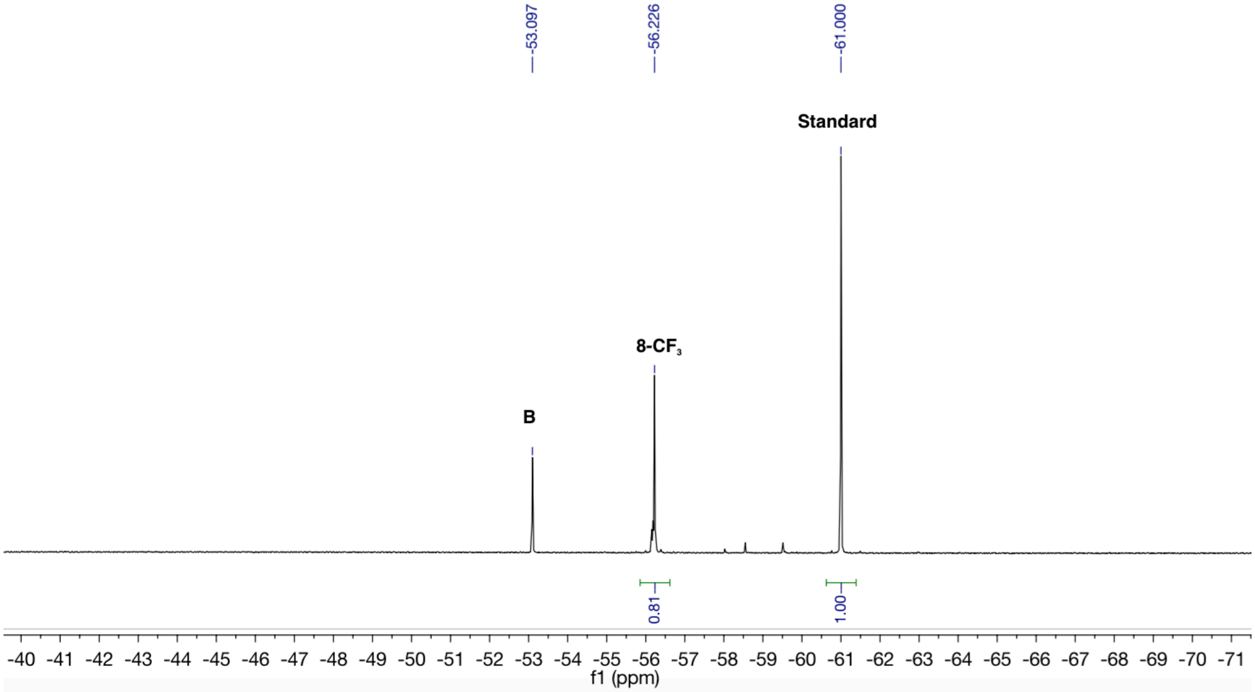


Figure S20. ^{19}F NMR spectrum showing formation of compound **8-CF$_3$**.

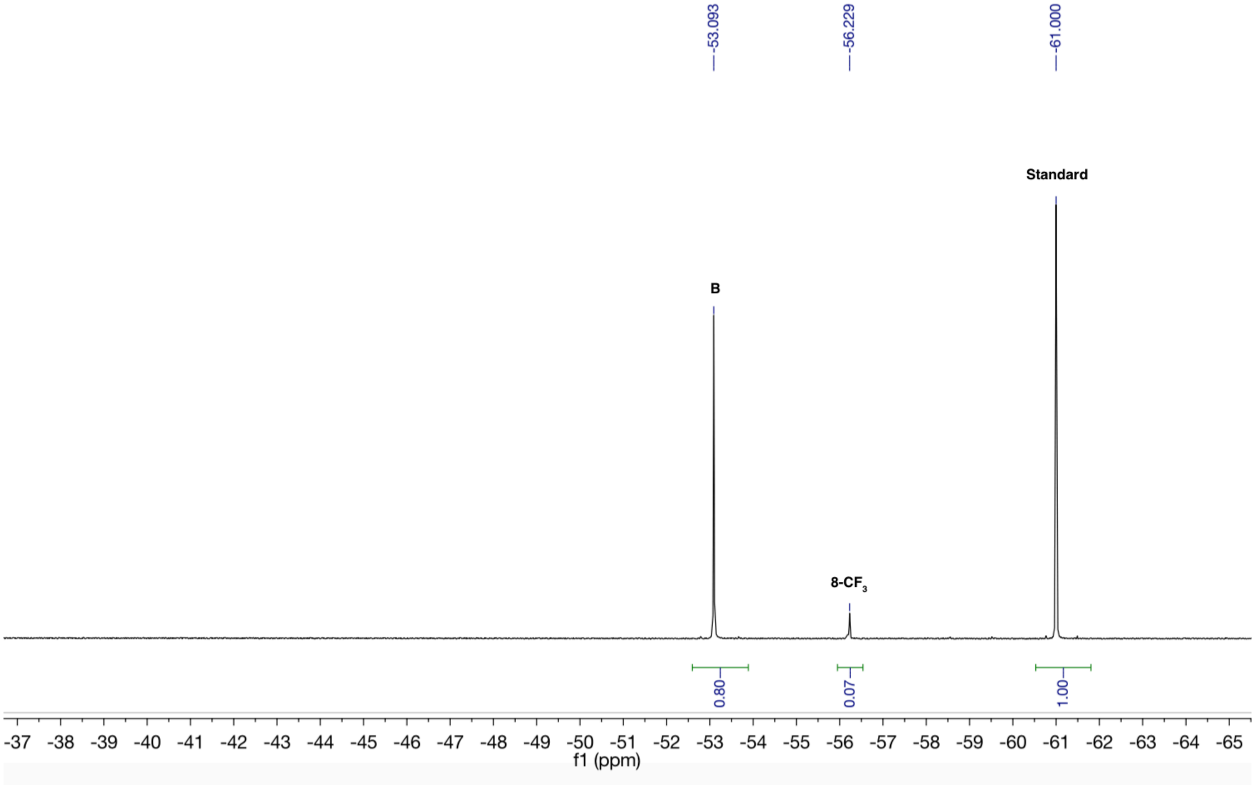


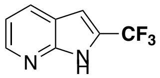
Figure S21. ^{19}F NMR spectrum of control reaction with compound **8** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with Boc-L-tryptophan (760 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. EtOAc (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with EtOAc (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: 1% AcOH, 28% EtOAc, 71% hexanes). Fractions containing **8-CF$_3$** were combined and washed with saturated aqueous $NaHCO_3$ (3 x 25 mL), dried over Mg_2SO_4, and concentrated in vacuo to yield **8-CF$_3$** as a white powder (120 mg, 64% yield).

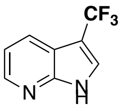
^{1}H NMR (700 MHz, $CDCl_3$, 23 °C): δ 8.59 (br. d, 1H), 7.73 (dd, *J* = 24.0, 6.5 Hz, 1H), 7.37 (dd, *J* = 24.0, 8.0 Hz, 1H), 7.31 (q, *J* = 8.0 Hz, 1H), 7.18 (m, 1H), 6.82 (s, 1H), 5.15 (s, 1H), 4.58 (bd, 1H), 3.47 (m, 1H), 3.27 (s, 1H), 1.36 (s, 6H), 0.99 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 °C): δ 175.3, 156.3, 155.4, 135.2, 127.7, 127.4, 124.9, 121.7 (q, J_{CF} = 269 Hz), 120.9, 120.3, 113.6, 112.5, 111.7, 81.1, 80.2, 28.1, 27.5.

^{19}F NMR (470 MHz, $CDCl_3$, 23 °C): δ –57.8 (s).



(**9-CF$_3$-2**)



(**9-CF$_3$-3**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with 7-azaindole (30 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **9-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S22, 3 : 1 ratio of isomers, 60% yield of **9-CF$_3$-2** and 19% yield of **9-CF$_3$-3**, 79% combined yield). Reaction conducted in absence of **II** yielded 0% **9-CF$_3$-2** and 0% **9-CF$_3$-3** (Figure S23).

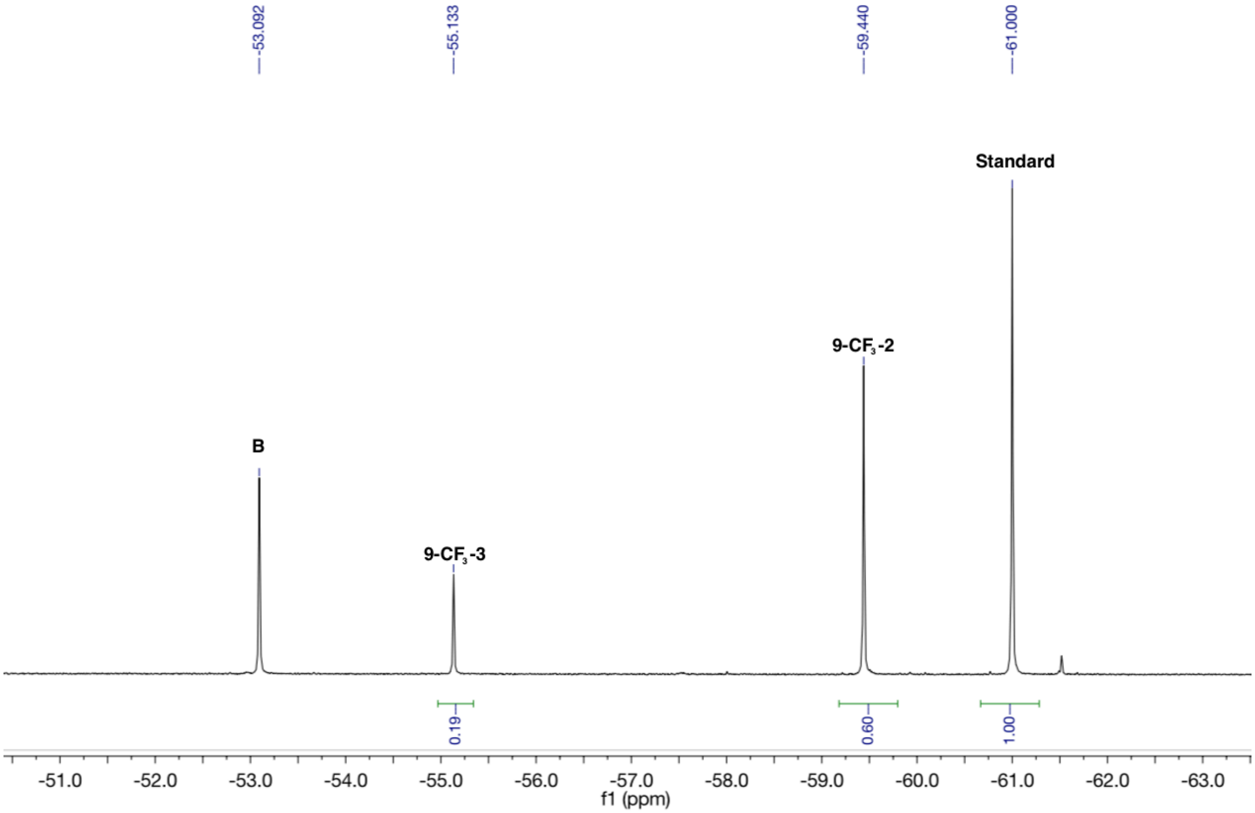


Figure S22. ^{19}F NMR spectrum showing formation of compound **9-CF$_3$**.

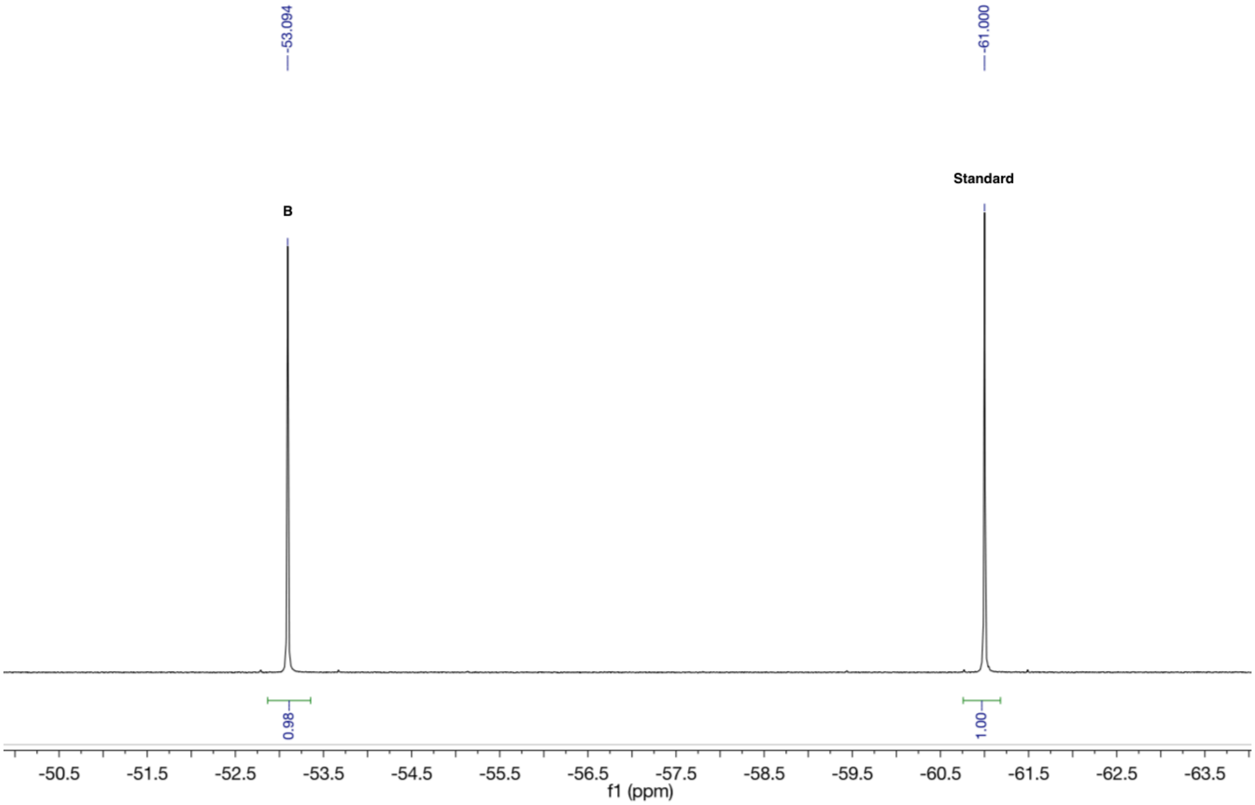


Figure S23. ^{19}F NMR spectrum of control reaction with compound **9** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with 7-azaindole (295 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol%), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. EtOAc (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with EtOAc (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 100:0 to 65:35) to yield **9-CF$_3$-2** as a white powder (59 mg, 63% yield) and **9-CF$_3$-3** as a white powder (7 mg, 7% yield).

Characterization for 9-CF$_3$-2:

^{1}H NMR (700 MHz, $CDCl_3$, 23 °C): δ 12.06 (br. s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.62 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 6.23 (m).

^{13}C NMR (176 MHz, $CDCl_3$, 23 °C): δ 147.6 (q, J_{CF} = 34.2 Hz), 140.0, 129.8, 129.1, 123.2, 122.6 (q, J_{CF} = 273.2 Hz), 112.1 (q, J_{CF} = 2.7 Hz), 100.9.

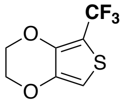
^{19}F NMR (470 MHz, $CDCl_3$, 23 °C): δ –65.5 (s).

Characterization for 9-CF$_3$-3:

^{1}H NMR (700 MHz, $CDCl_3$, 23 °C): δ 14.00 (br. s, 1H), 8.48 (d, J = 4.4 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 7.21 (dd, J = 4.4, 7.9 Hz, 1H), 6.89 (s).

^{13}C NMR (176 MHz, $CDCl_3$) δ 148.49, 144.5, 131.4, 127.22 (q, J_{CF} = 39.2 Hz), 121.2 (q, J_{CF} = 268.2 Hz), 119.8, 116.9, 101.4 (q, J_{CF} = 3.5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$, 23 °C): δ –61.1 (s).



(**10-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with 3,4-ethylenedioxythiophene (27 µL, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **10-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S24, 41% yield). Reaction conducted in absence of **II** yielded 1% **10-CF$_3$** (Figure S25).

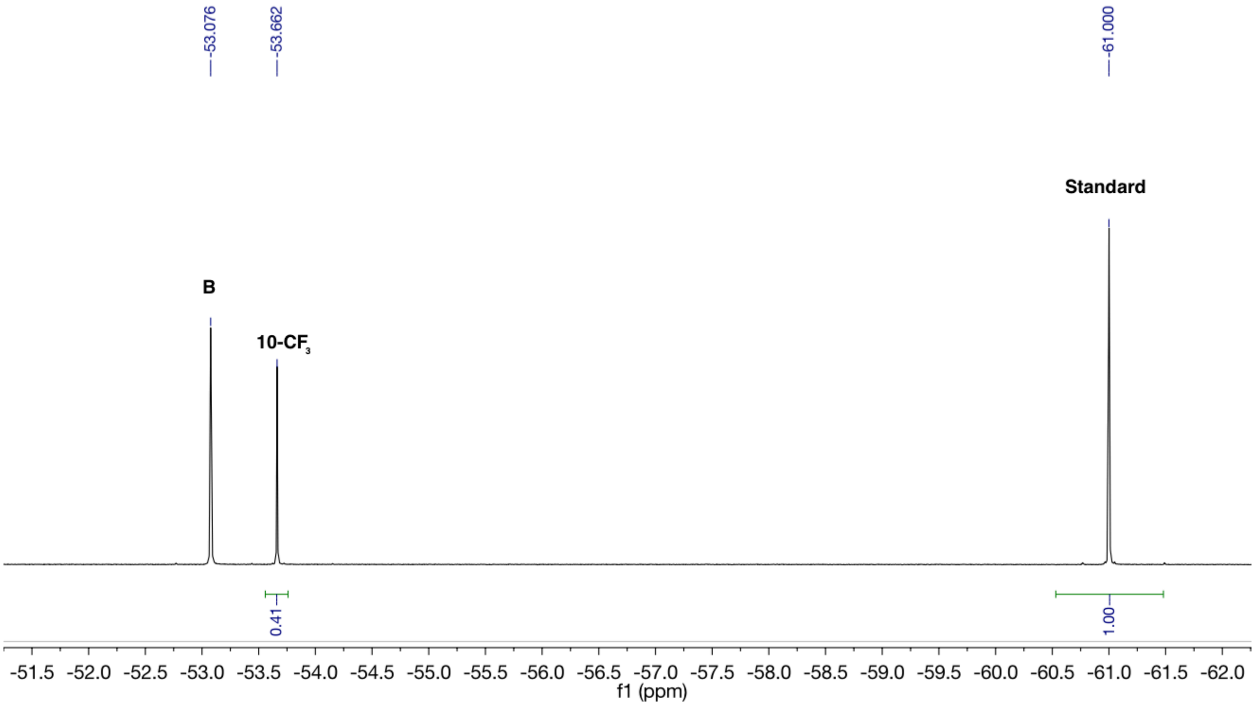


Figure S24. ^{19}F NMR spectrum showing formation of compound **10-CF$_3$**.

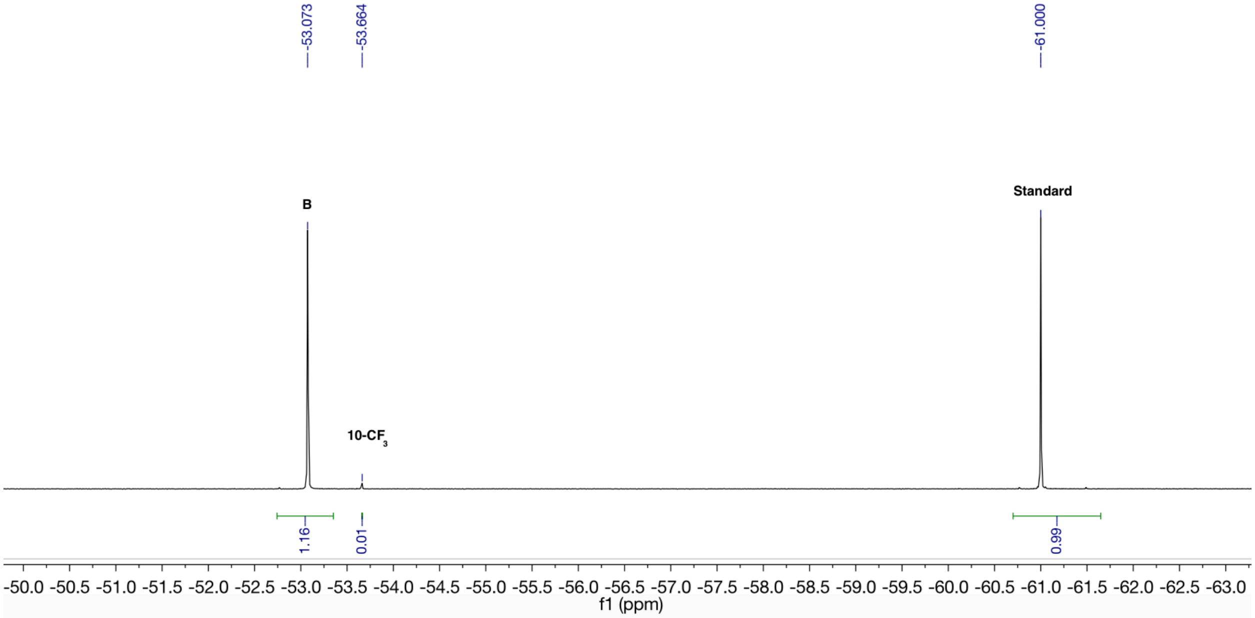


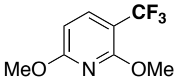
Figure S25. ^{19}F NMR spectrum of control reaction with compound **10** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with stir bar was charged with 3,4-ethylenedioxythiophene (267 µL, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol%), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. EtOAc (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with EtOAc (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 100:0 to 90:10) to yield **10-CF$_3$** as a clear oil (33 mg, 31% yield). ^{1}H, ^{19}F, and ^{13}CNMR spectra matched reported values.[8]

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 6.49 (s, 1H), 4.31-4.30 (m, 2H), 4.23-4.22 (m, 2H)

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 141.9 (q, J_{CF} = 3.2 Hz), 141.3, 122.2 (q, J_{CF} = 244.4 Hz), 104.4 (q, J_{CF} = 39.1 Hz), 102.1,64.9, 64.2.

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –55.4 (s).



(**11-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with 2,6-dimethoxypyridine (33 µL, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **11-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S26, 42% yield). Reaction conducted in absence of **II** yielded 0% **11-CF$_3$** (Figure S27).

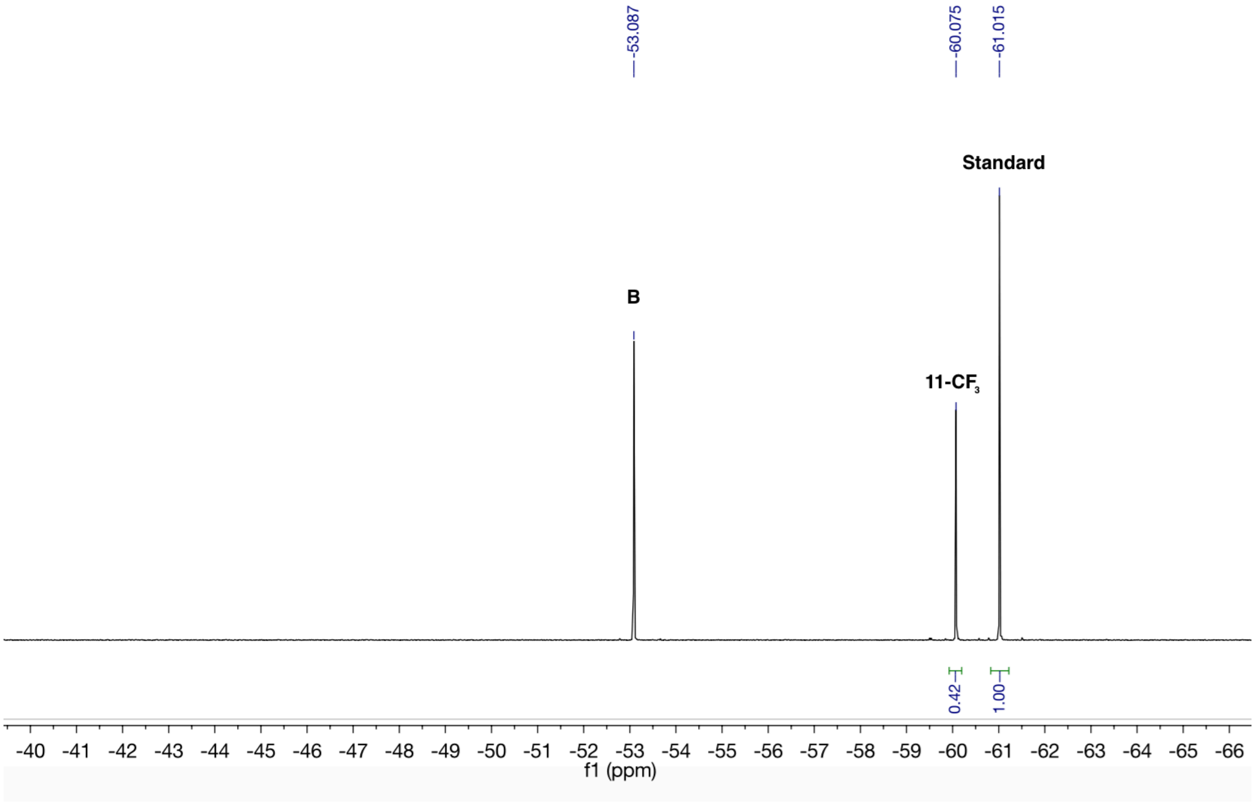


Figure S26. ^{19}F NMR spectrum showing formation of compound **11-CF$_3$**.

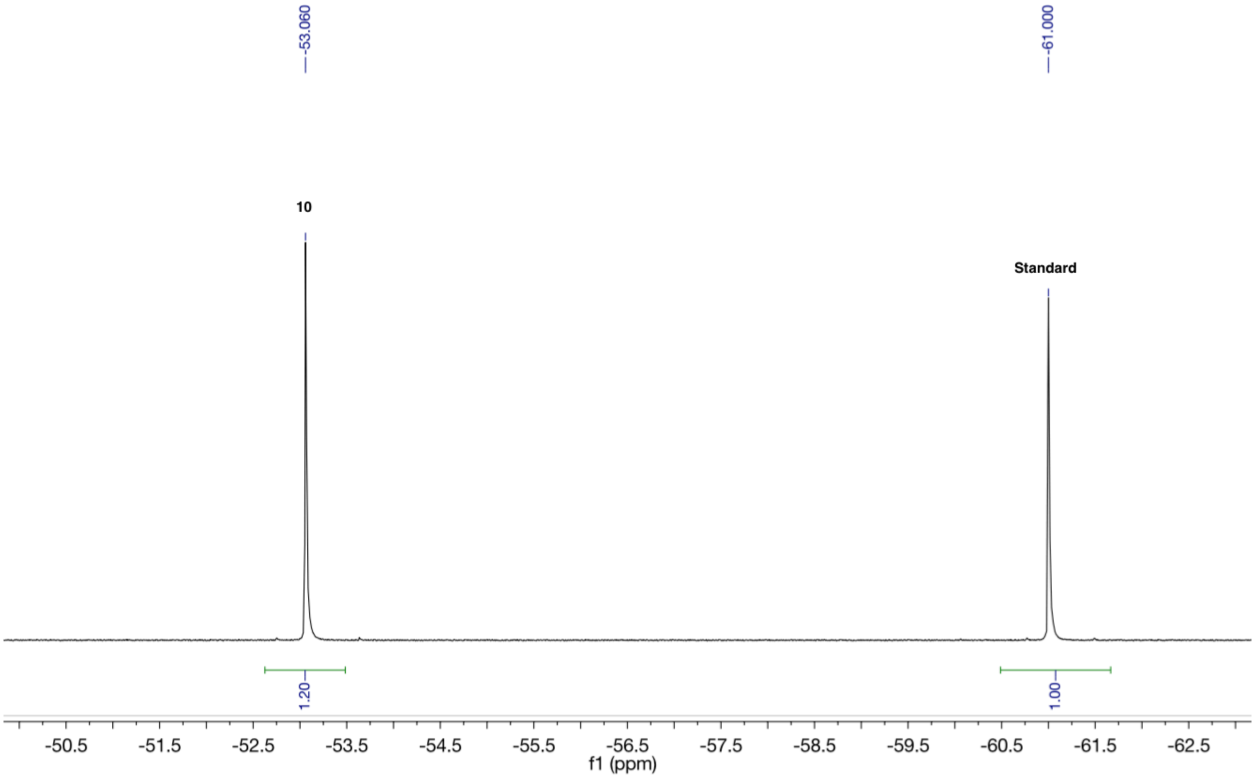
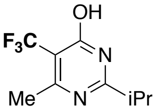


Figure S27. ^{19}F NMR spectrum of control reaction with compound **11** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL vial equipped with a stir bar was charged with 2,6-dimethoxypyridine (330 µL, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol %), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with Et_2O (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: 100% pentanes) to yield **11-CF$_3$** as a clear oil (35 mg, 34% yield). ^{1}H, ^{19}F, and ^{13}C NMR spectra matched those reported in the literature.[9]



(**12-CF$_3$**)

NMR Scale: In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with 2-isopropyl-6-methyl-4-pyrimidol (38 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and

anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **12-CF$_3$** was determined by ^{19}F NMR spectroscopy (Figure S28, 67% yield). Reaction conducted in absence of **II** yielded 0% **12-CF$_3$** (Figure S29).

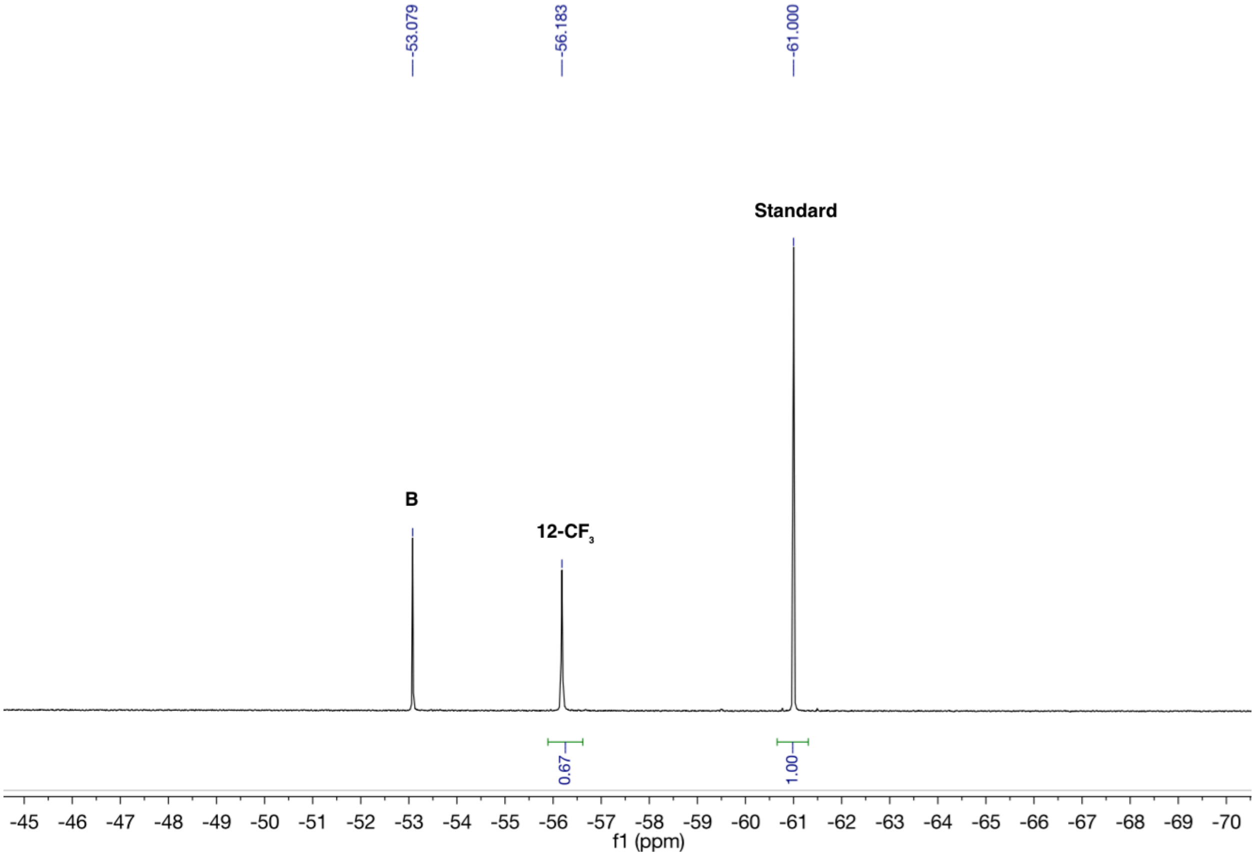


Figure S28. ^{19}F NMR spectrum showing formation of compound **12-CF$_3$**.

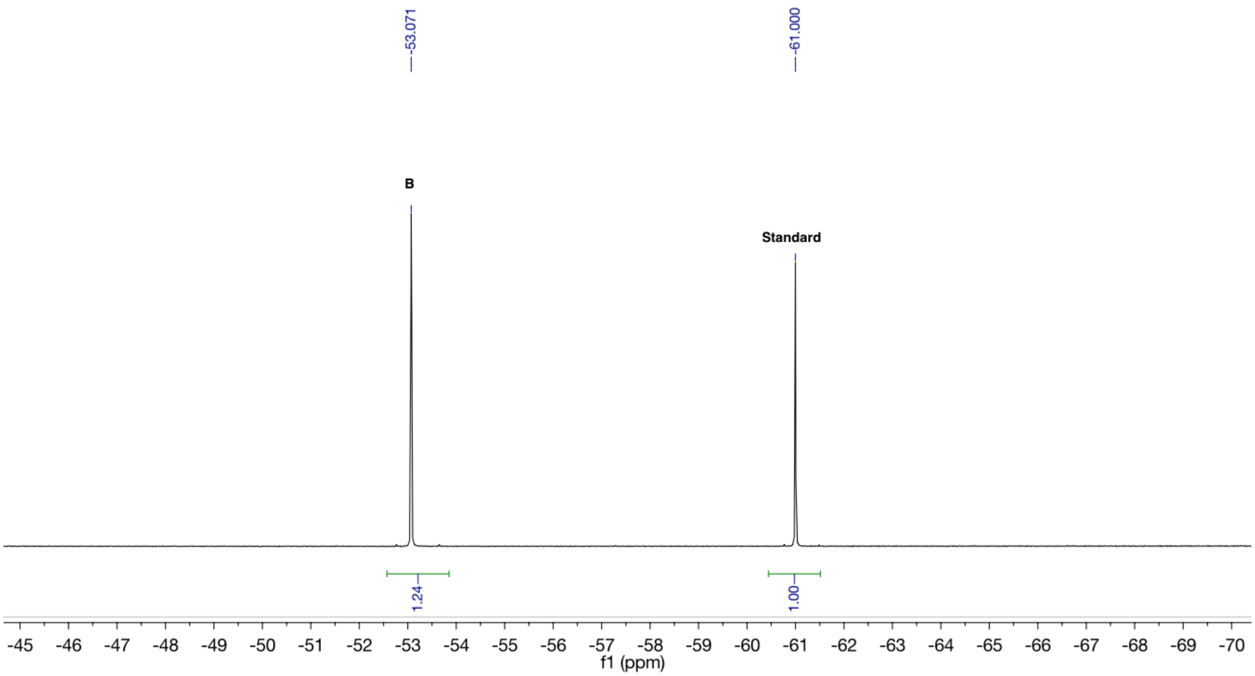


Figure S29. ^{19}F NMR spectrum of control reaction with compound **12** and **B** in absence of **II**.

Isolation Scale: In a nitrogen-filled glovebox, a 20 mL glass vial equipped with stir bar was charged with 2-isopropyl-6-methyl-4-pyrimidol (380 mg, 2.5 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 220 mg, 0.50 mmol, 1.0 equiv), complex **II** (12 mg, 0.025 mmol, 5 mol%), and anhydrous DMSO (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. After this time, the reaction was removed from the glovebox and transferred to a separatory funnel. Et_2O (60 mL) was added, and the organic layer was then washed with DI H_2O (2 x 25 mL). The aqueous layers were combined and re-extracted with EtOAc (60 mL). The organic layers were combined and washed with DI H_2O (4 x 25 mL), 5% aqueous LiCl (1 x 25 mL), and sat. aqueous NaCl (1 x 25 mL). The organic extracts were dried over Mg_2SO_4 and concentrated in vacuo. The deep purple residue was purified by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 100:0 to 70:30) to yield **12-CF$_3$** as a white powder (57 mg, 52% yield).

^{1}H NMR (700 MHz, $CDCl_3$, 23 °C): δ 12.67 (br. s, 1H), 2.93 (hept, J_{HH} = 7.0 Hz, 1H), 2.52 (q, J_{HF} = 2.8 Hz, 3H), 1.34 (d, J_{HH} = 7.0 Hz, 6H).

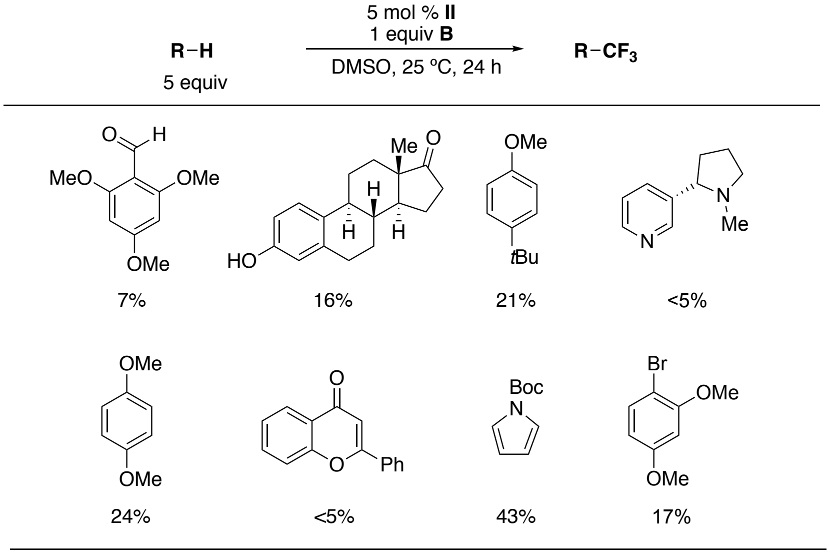
^{13}C NMR (176 MHz, $CDCl_3$, 23 °C): δ 167.7, 167.4, 161.4, 123.6 (q, J_{CF} = 273.3 Hz), 112.0 (q, J_{CF} = 30.6 Hz), 34.7, 23.9, 20.0.

^{19}F NMR (470 MHz, $CDCl_3$, 23 °C): δ –57.7 (s).

Investigation of Other Substrates

In a nitrogen-filled glovebox, a 4 mL vial equipped with a stir bar was charged with substrate (5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), and anhydrous DMSO (0.9 mL). Complex **II** (100 µL of a 0.025 M stock solution in DMSO) was then added. The vial was sealed with a Teflon-lined cap, and the reaction was stirred for 24 h at room temperature. Trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) was added, and the yield of **R-CF$_3$** was determined by ^{19}F NMR spectroscopy (Table S3).

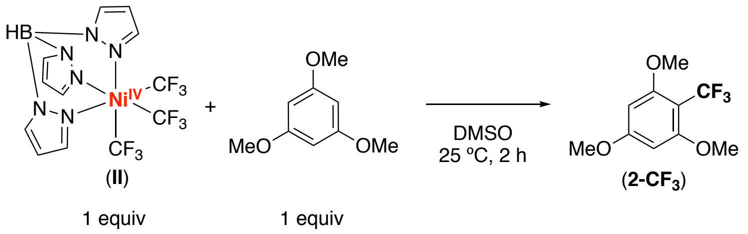
Table S3. Other substrates examined



*Yields determined by ^{19}F NMR spectrsocopy using trifluorotoluene as an internal standard

V. Mechanistic Studies

In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (2.1 mg, 0.0125 mmol, 1 equiv) and anhydrous DMSO (100 µL). To a separate 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (425 µL). This yellow solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene was added to the NMR tube, which was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the consumption of complex **II** and production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S30).



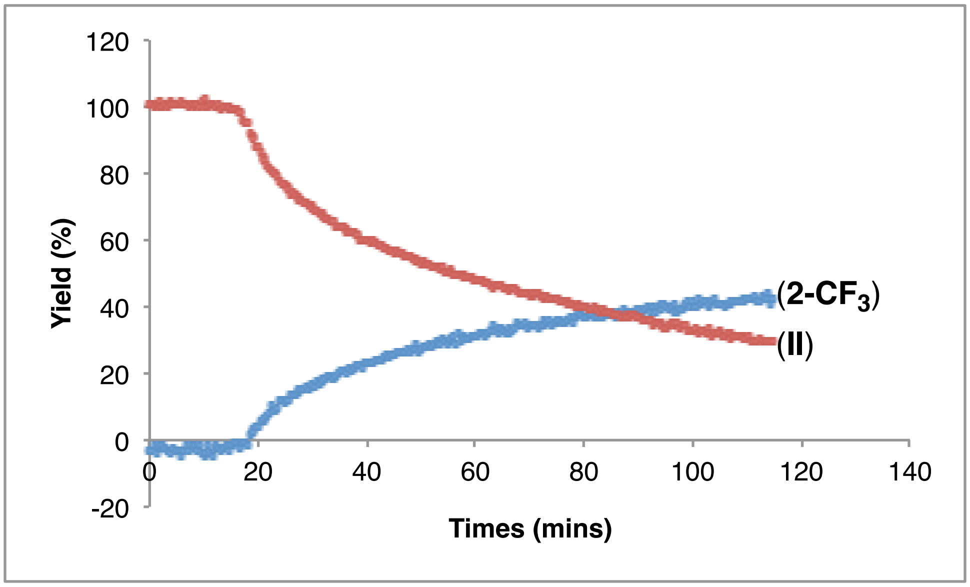
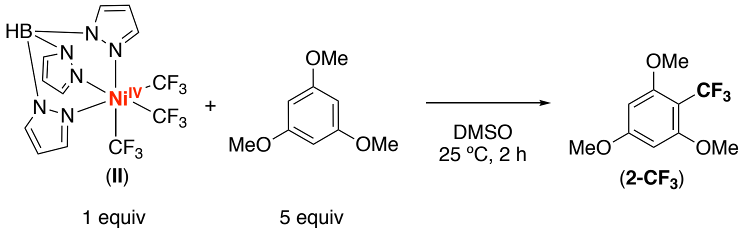


Figure S30. Reaction profile for the trifluoromethylation of 1 equiv trimethoxybenzene with complex **II**.

In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (10.5 mg, 0.0625 mmol, 5 equiv) and anhydrous DMSO (100 µL). To a separate 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (425 µL). This yellow solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene was added to the NMR tube, which was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the consumption of complex **II** and production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S31).



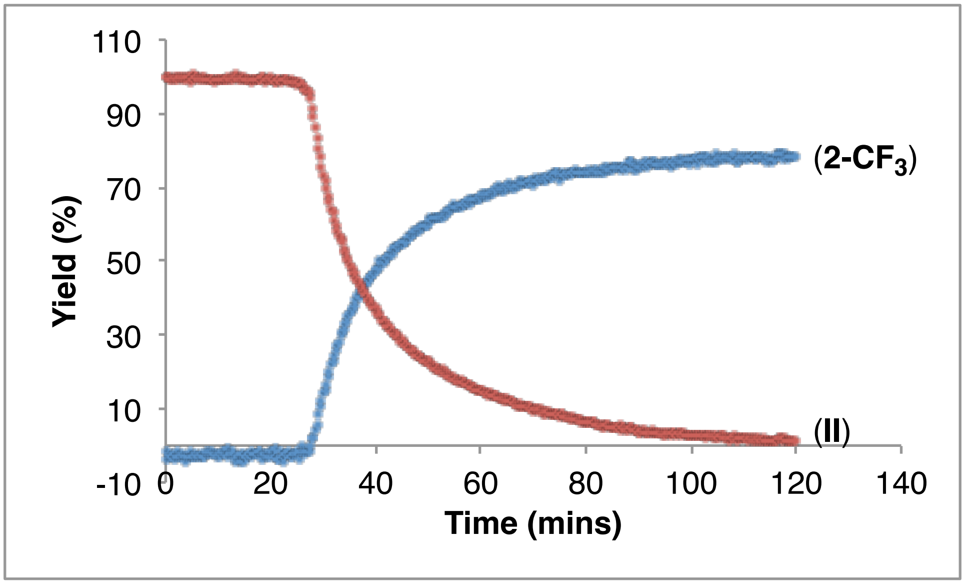
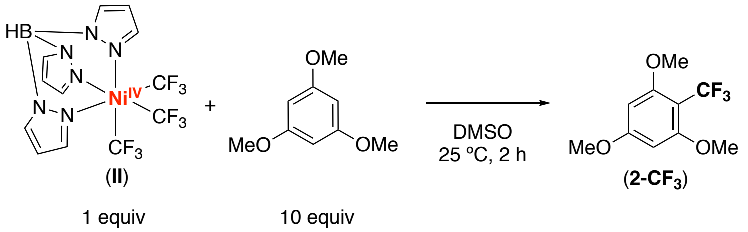


Figure S31. Reaction profile for the trifluoromethylation of 5.0 equiv trimethoxybenzene with complex **II**.

In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (21.0 mg, 0.0625 mmol, 10 equiv) and anhydrous DMSO (100 µL). To a separate 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (425 µL). This yellow solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene was added to the NMR tube, which was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the consumption of complex **II** and production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S32).



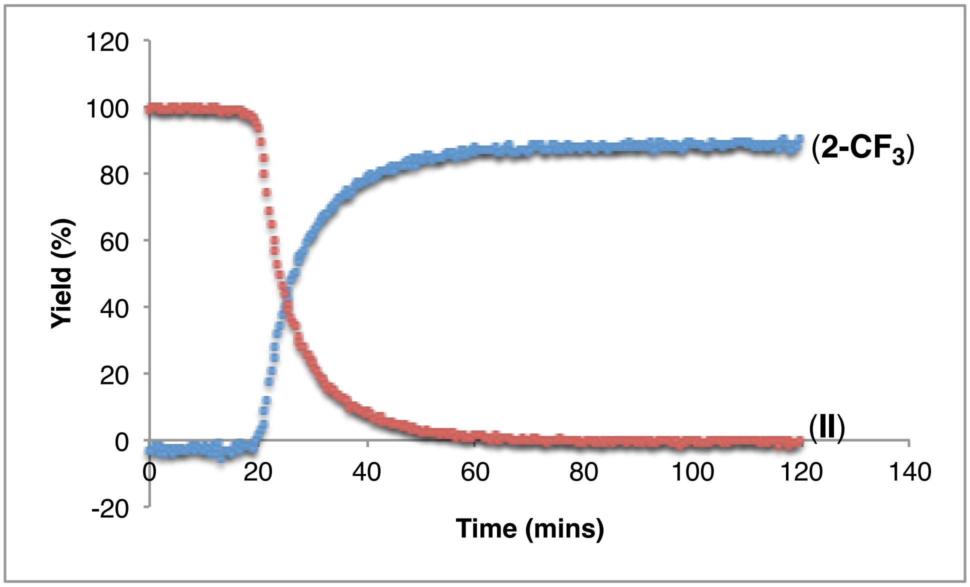
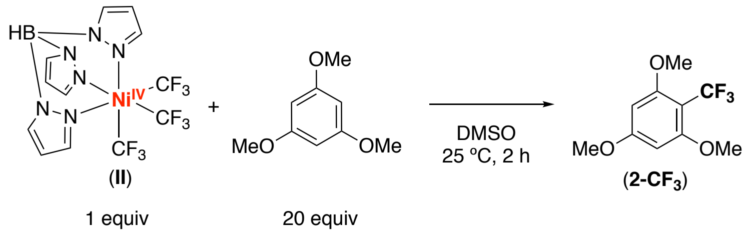


Figure S32. Reaction profile for the trifluoromethylation of 10.0 equiv trimethoxybenzene with complex **II**.

In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (42.0 mg, 0.25 mmol, 20 equiv) and anhydrous DMSO (100 µL). To a separate 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (425 µL). This yellow solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene was added to the NMR tube, which was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the consumption of complex **II** and production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S33).



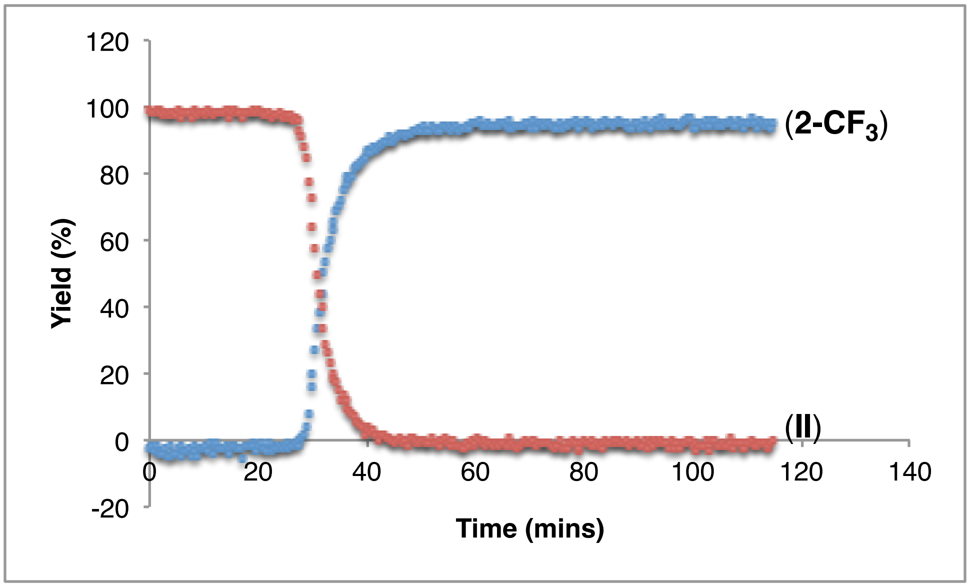
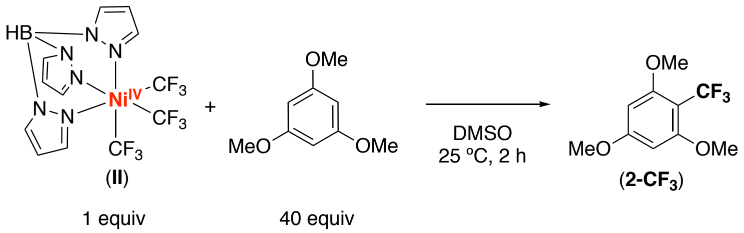


Figure S33. Reaction profile for the trifluoromethylation of 20.0 equiv trimethoxybenzene with complex **II**.

In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (84.1 mg, 0.5 mmol, 40 equiv) and anhydrous DMSO (100 µL). To a separate 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL, 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (425 µL). This yellow solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene was added to the NMR tube, which was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the consumption of complex **II** and production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S34).



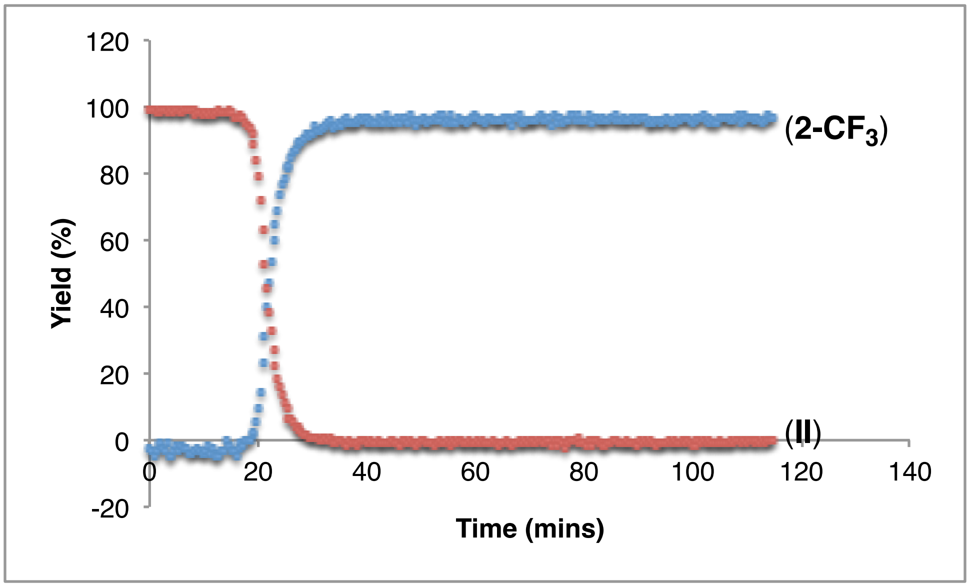


Figure S34. Reaction profile for the trifluoromethylation of 40.0 equiv trimethoxybenzene with complex **II**.

Using the data acquired in the above series of reactions, the initial rate of the reaction after completion of the induction period was determined through fitting this region of the reaction profile. These rates were plotted against substrate concentration. The initial rate was observed to increase with increasing concentration of trimethoxybenzene until saturation was reached at approximately 10 equiv of trimethoxybenzene.

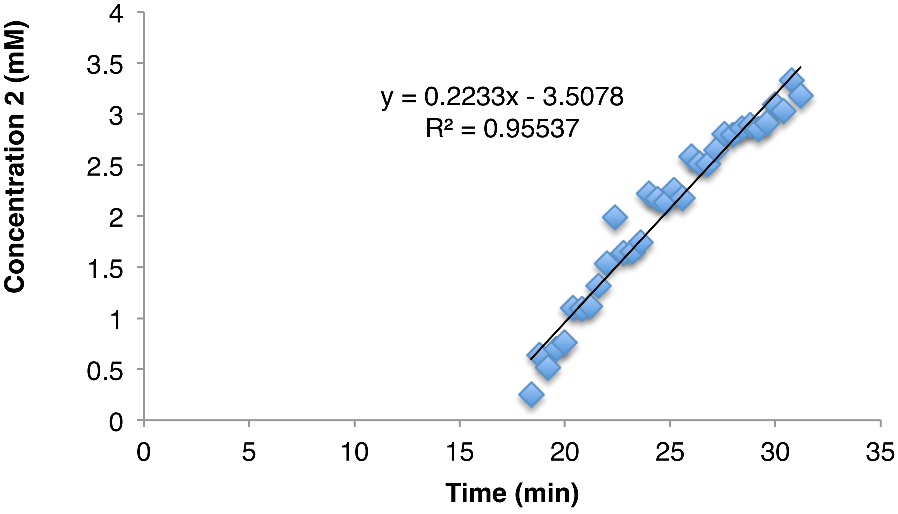


Figure S35. Fit region of reaction progress profile for the trifluoromethylation of 1.0 equiv trimethoxybenzene with complex **II**.

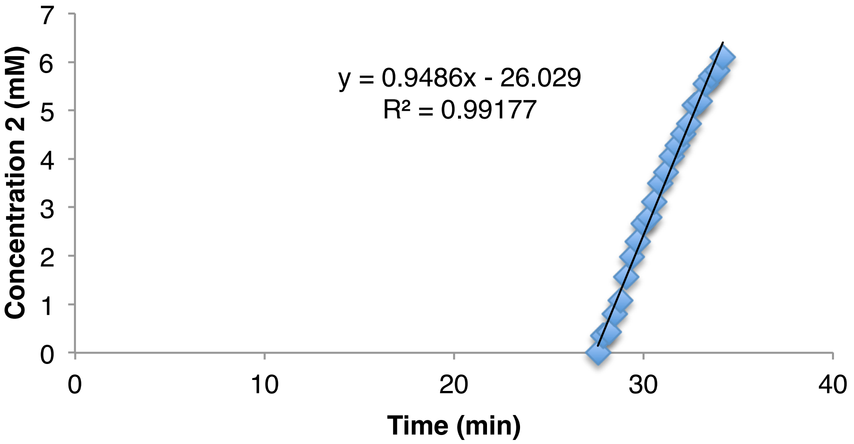


Figure S36. Fit region of reaction progress profile for the trifluoromethylation of 5.0 equiv trimethoxybenzene with complex **II**.

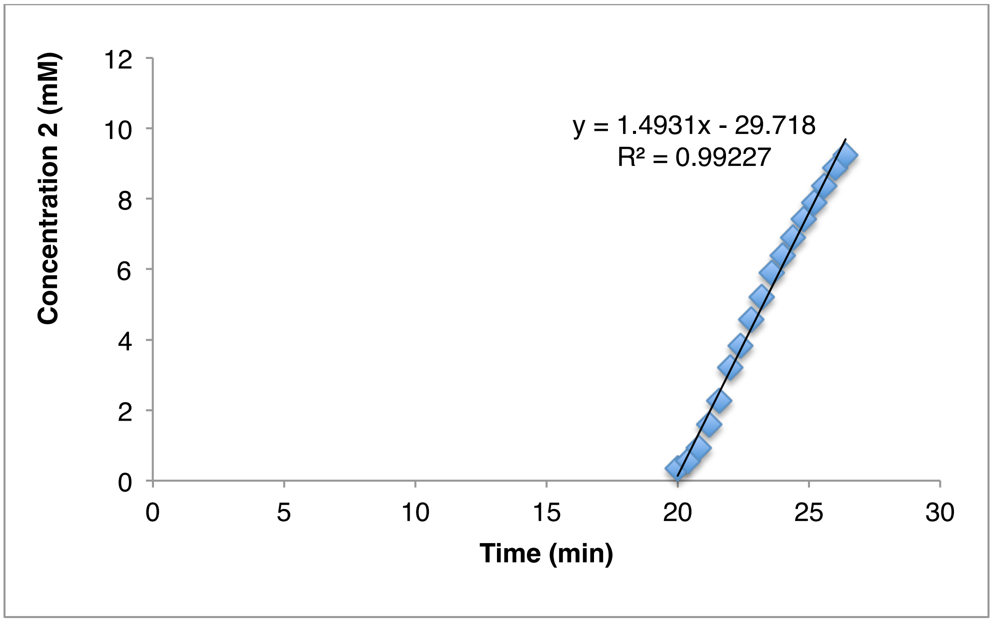


Figure S37. Fit region of reaction progress profile for the trifluoromethylation of 10.0 equiv trimethoxybenzene with complex **II**.

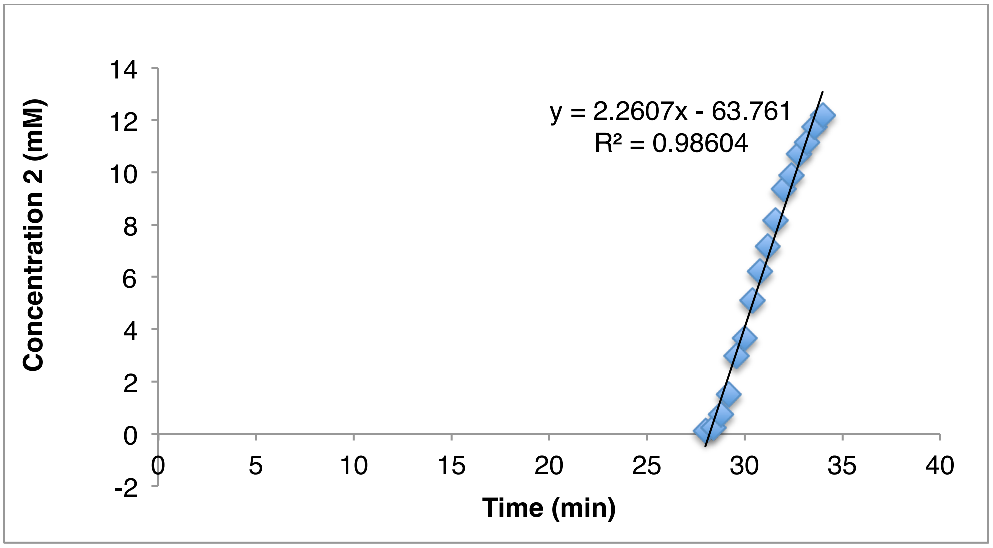


Figure S38. Fit region of reaction progress profile for the trifluoromethylation of 20.0 equiv trimethoxybenzene with complex **II**.

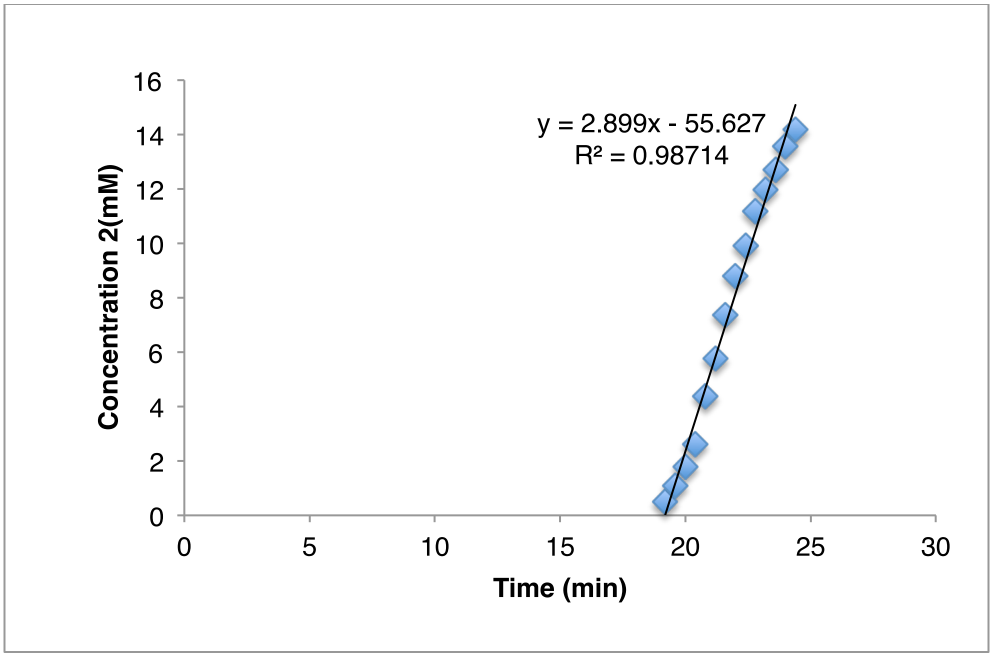


Figure S39. Fit region of reaction progress profile for the trifluoromethylation of 40.0 equiv trimethoxybenzene with complex **II**.

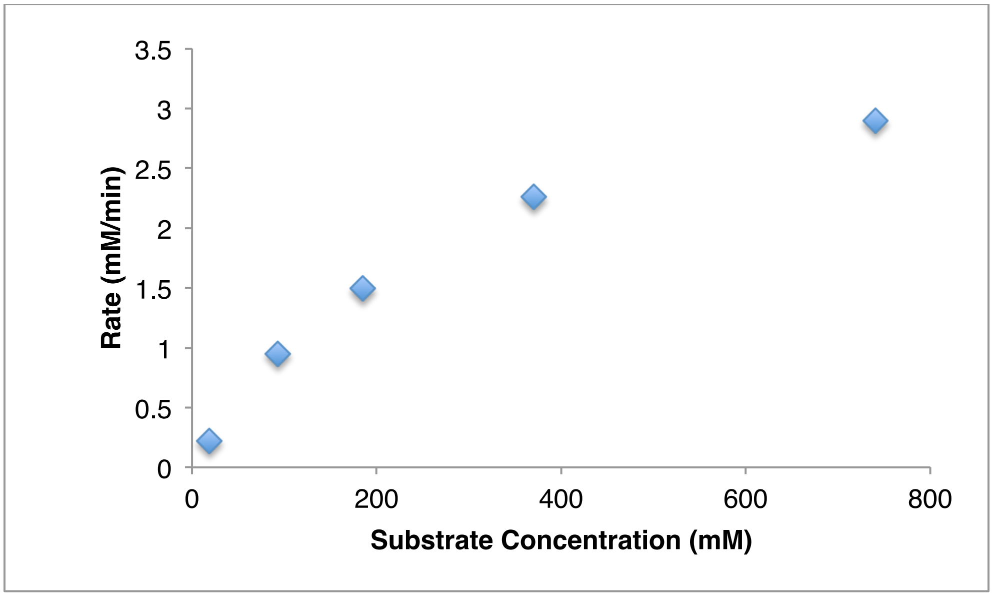


Figure S40. Initial rate vs. concentration data for the trifluoromethylation of trimethoxybenzene with complex **II**.

In a nitrogen-filled glovebox, a 4 mL vial was charged with N-Boc pyrrole (11 µL, 0.0625 mmol, 5 equiv) and anhydrous DMSO (100 µL). To a separate 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (425 µL). This yellow solution was added to a septum screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of N-Boc pyrrole was added to the NMR tube, which was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the consumption of complex **II** and production of product **S2** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S41).

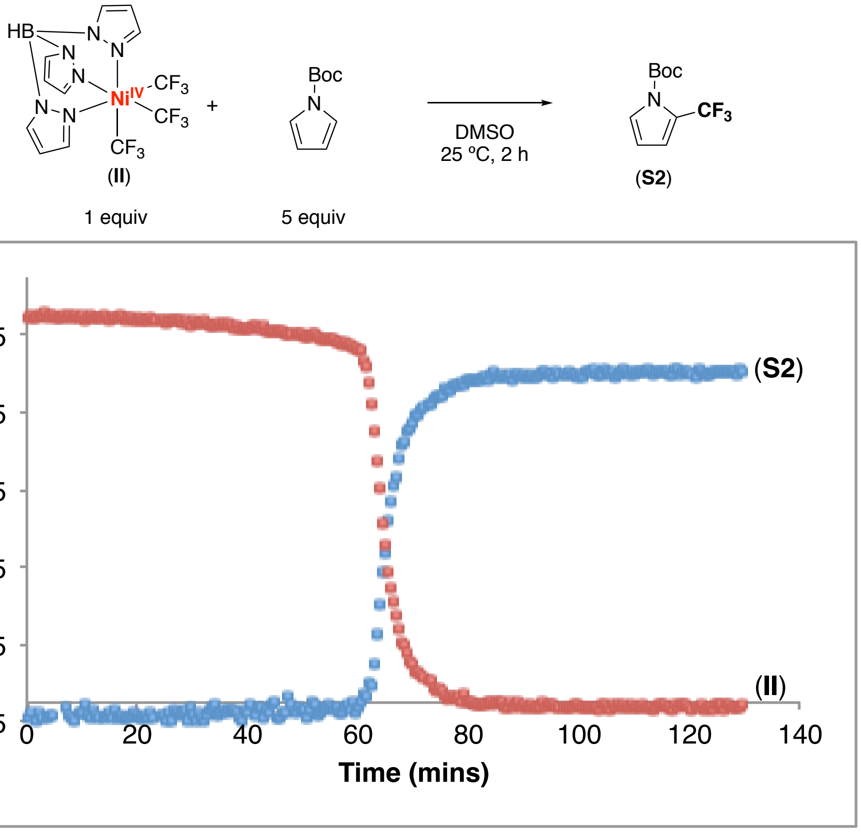
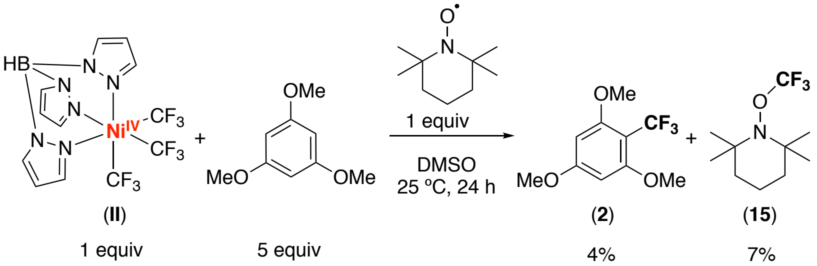


Figure S41. Reaction profile for the trifluoromethylation of N-Boc pyrrole with complex **II**.



In a nitrogen-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with trimethoxybenzene (10.5 mg, 0.0625 mmol, 5 equiv), TEMPO (1.95 mg, 0.0125 mmol, 1 equiv), complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (1 mL). The vial was sealed, and the reaction was stirred at room temperature for 24 h. The reaction was then transferred to a screw-cap NMR tube and analyzed by ^{19}F NMR spectroscopy. The yield of **2** was 4% and TEMPO–CF$_3$ (**15**) was detected in 7% yield (Figure S42).[10]

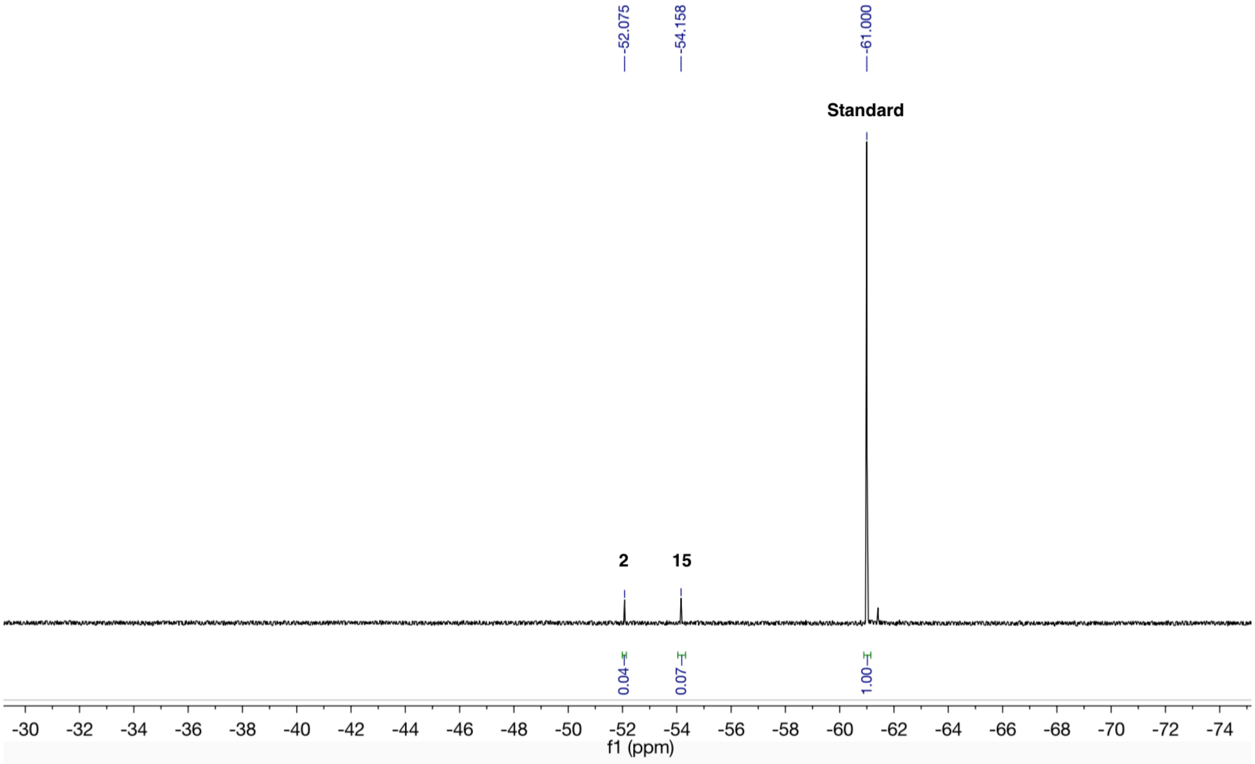
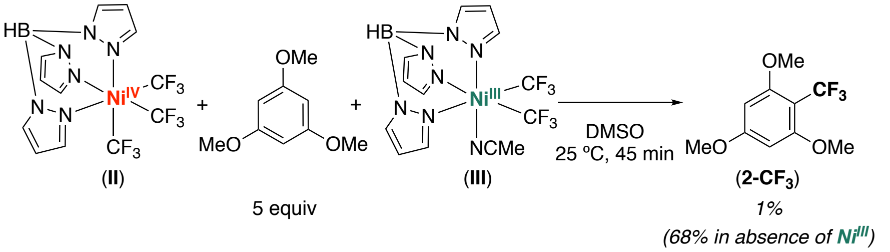


Figure S42. Trifluoromethylation of trimethoxybenzene by complex **II** in the presence of TEMPO.



In a nitrogen-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with trimethoxybenzene (10.5 mg, 0.0625 mmol, 5 equiv), complex **III** (5.6 mg, 0.0125 mmol, 1 equiv), complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL , 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (1 mL). The vial was sealed, and the reaction was stirred at room temperature for 45 min. The reaction was then transferred to a screw-cap NMR tube and the analyzed by ^{19}F NMR spectroscopy. The yield of **2-CF$_3$** was 1% (Figure S43).

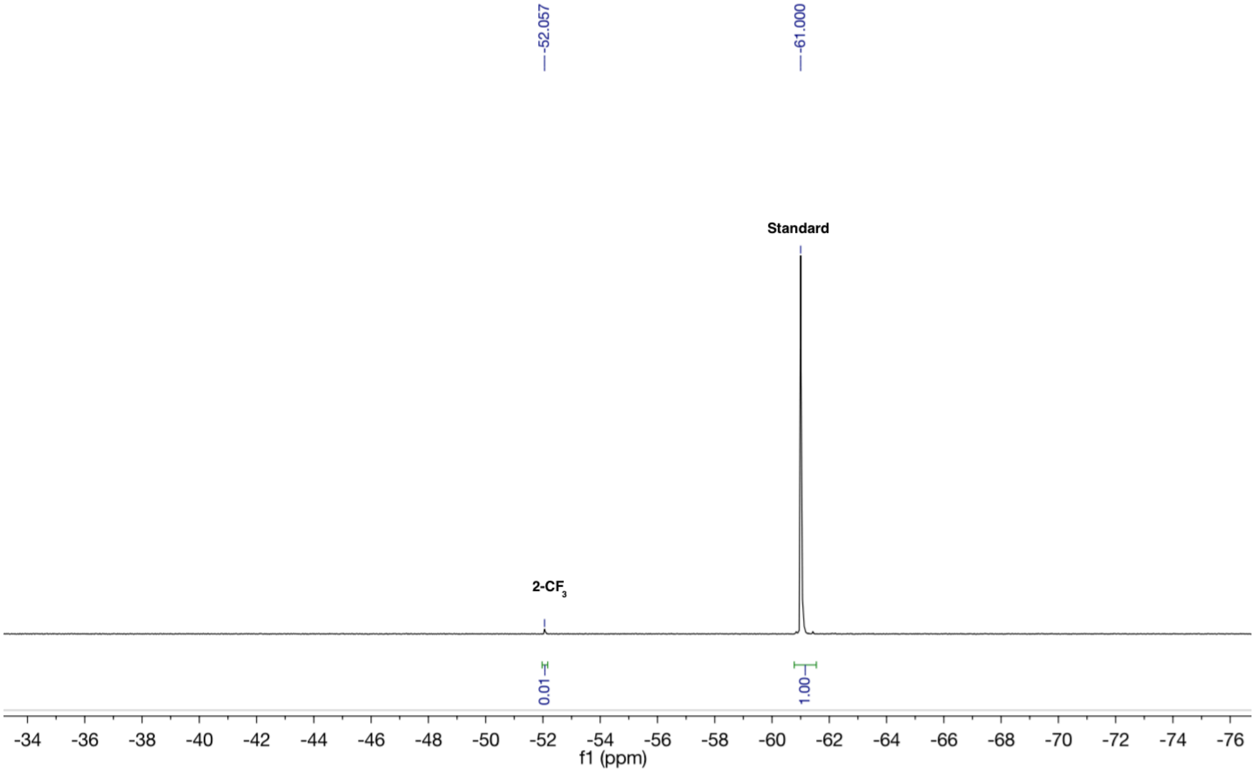
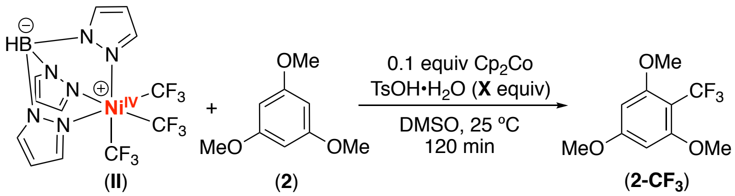


Figure S43. Trifluoromethylation of trimethoxybenzene by complex **II** in the presence of complex **III**.



In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (11 mg, 0.0625 mmol, 5 equiv), cobaltocene (0.25 mg, 0.00125 mmol, 0.1 equiv), and anhydrous DMSO (200 µL). A second 4 mL vial was charged with TsOH•H$_2$O (0, 0.1, or 1.0 equiv) and anhydrous DMSO (200 µL). To a third 4 mL vial was added complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL, 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (600 µL). This yellow solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. To this NMR tube was added the solution of trimethoxybenzene and cobaltocene, immediately followed by addition of the TsOH•H$_2$O solution. The NMR tube was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored by tracking the production of **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S44).

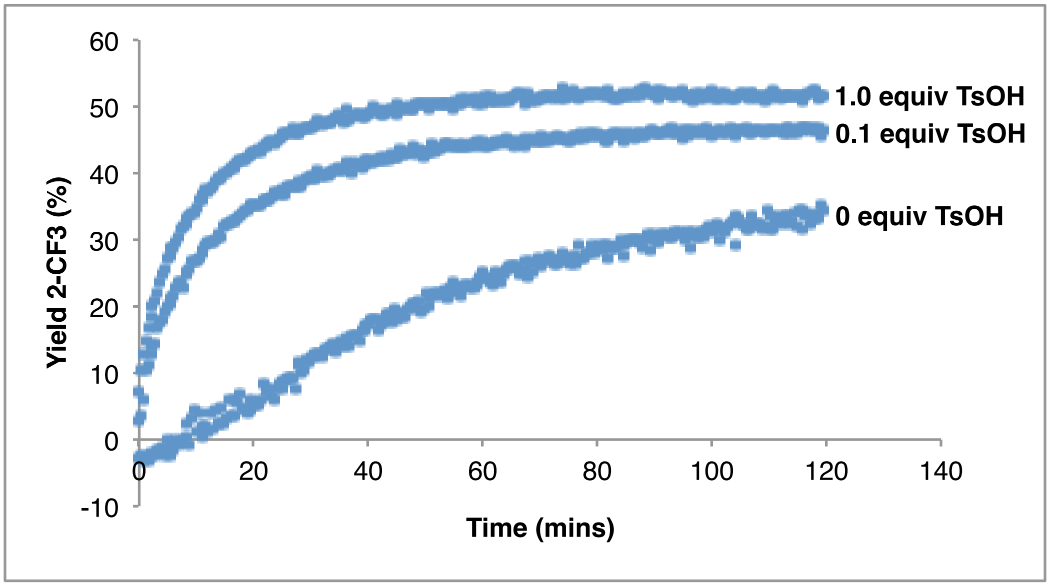
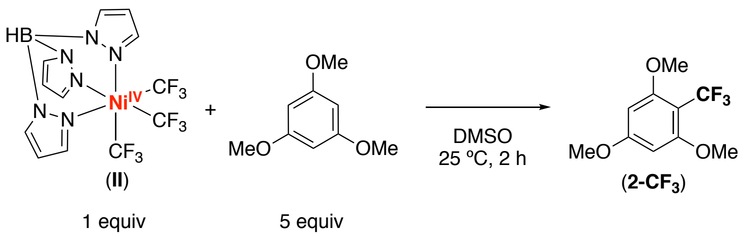
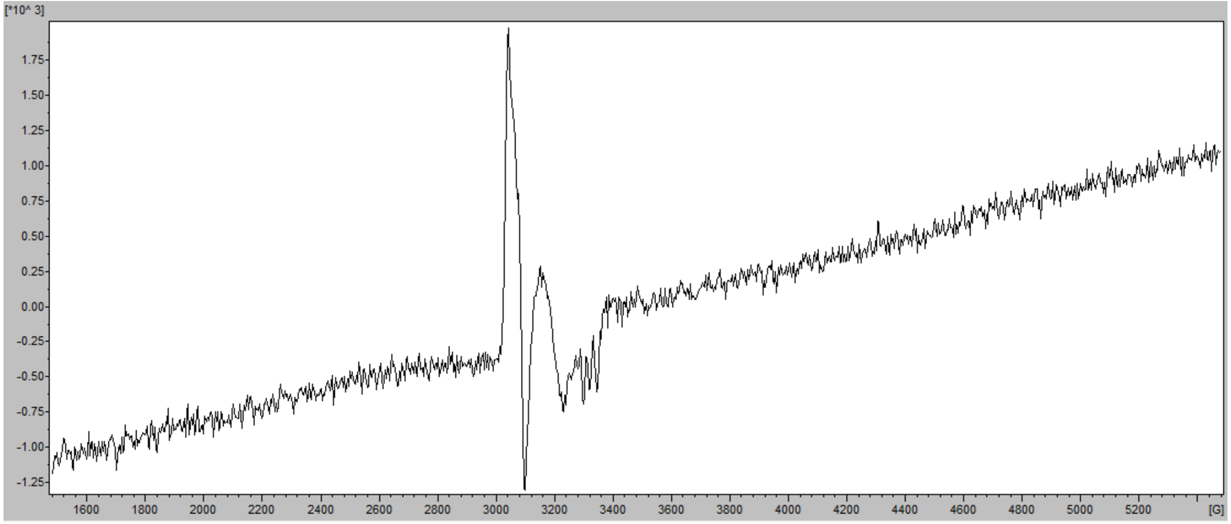


Figure S44. Reaction profile for the trifluoromethylation of trimethoxybenzene with complex **II** in the presence of cobaltocene and varying amounts of TsOH•H$_2$O.

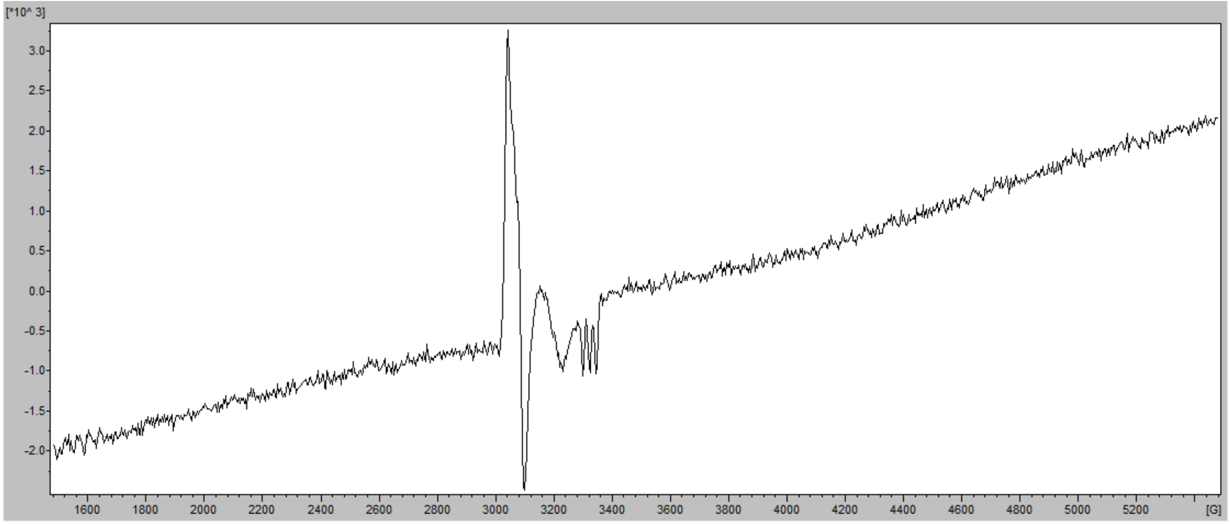


In a nitrogen-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with trimethoxybenzene (10.5 mg, 0.0625 mmol, 5 equiv), complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), and anhydrous DMSO (600 µL). Two drops of the reaction mixture were removed after 30 s, 35 min, 45 min, and 85 mins of stirring. These samples were diluted in 300 µL of PrCN that had been precooled to –35 °C and transferred to an EPR tube. The EPR tube was sealed, removed from the glovebox, and flash-frozen in liquid nitrogen until analysis.

(**a**)



(**b**)



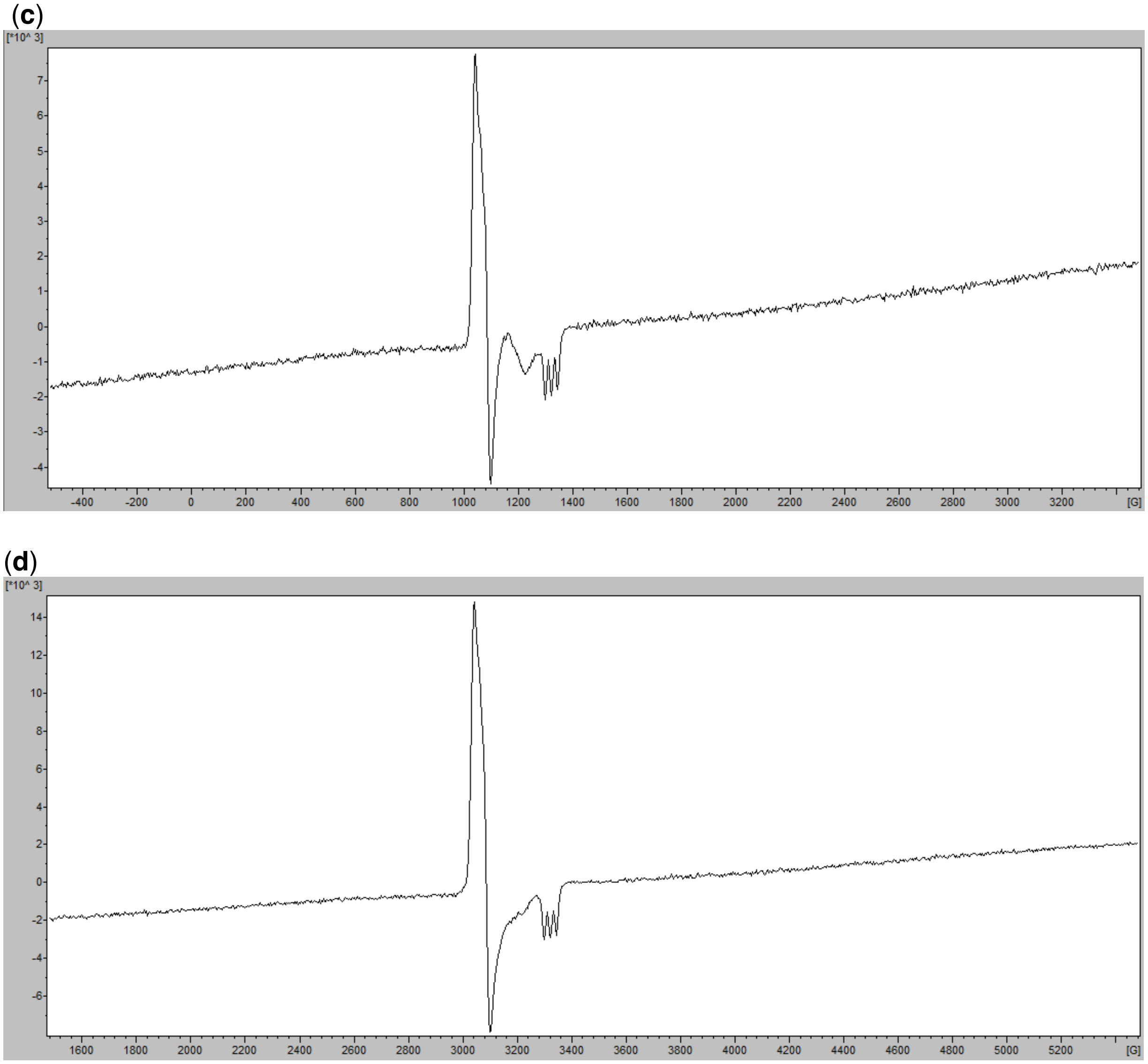
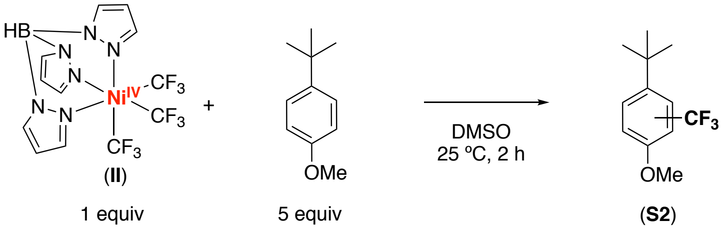
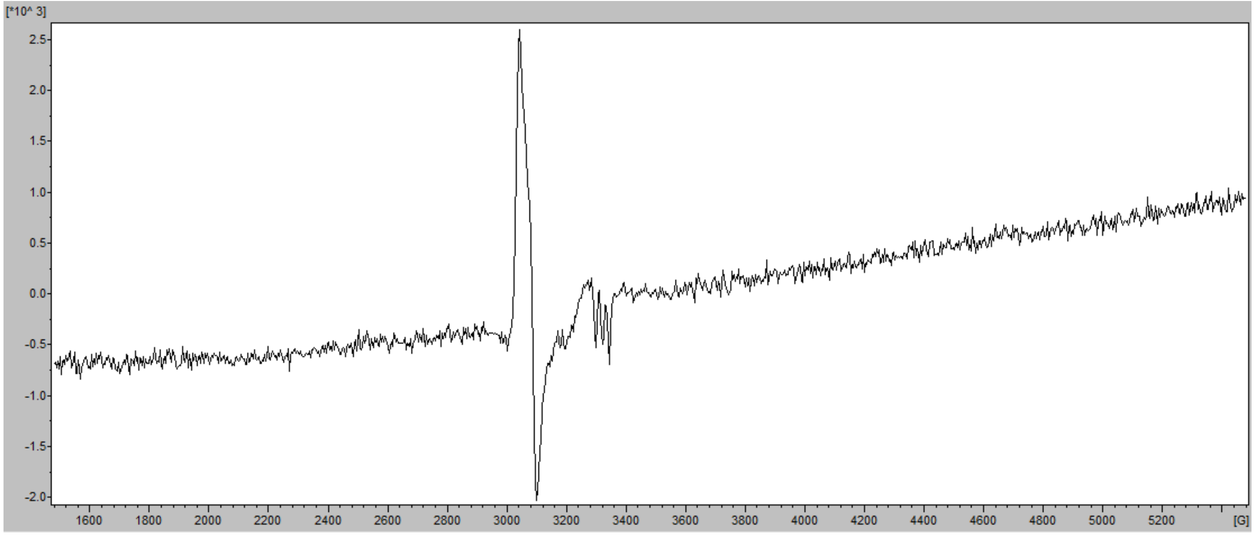


Figure S45. EPR spectra of aliquots of the complex **II**-mediated trifluoromethylation of trimethoxybenzene taken (**a**) 30 s, (**b**) 35 min, (**c**) 45 min, and (**d**) 85 min after the start of the reaction.

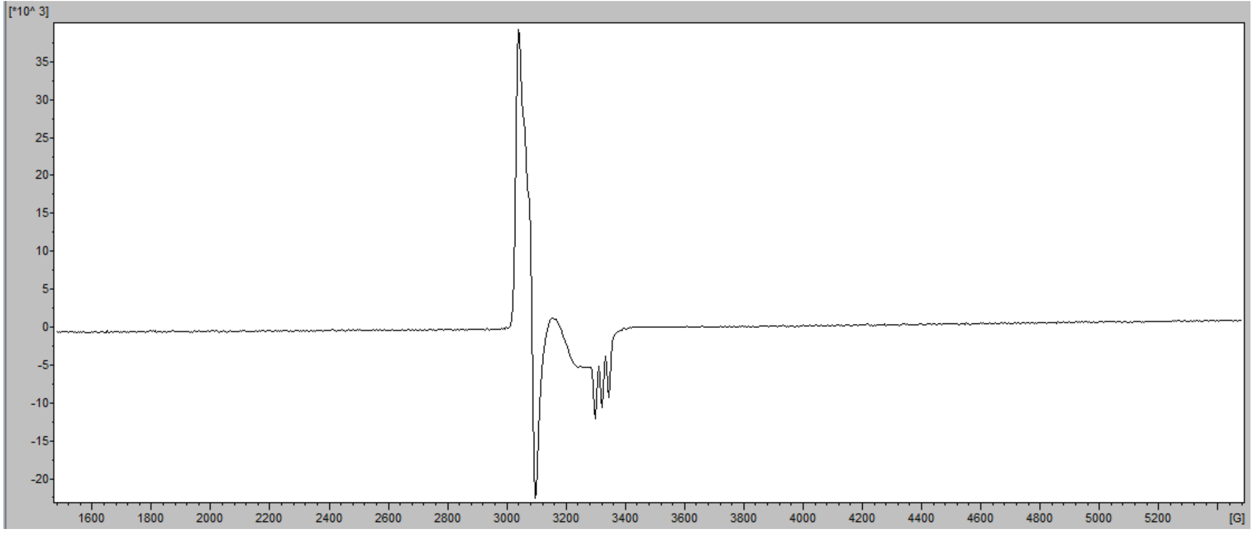


In a nitrogen-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with 4-*tert*-butylanisole (11 µL, 0.0625 mmol, 5 equiv), complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), and anhydrous DMSO (600 µL). Two drops of the reaction mixture were removed after 30 s, 20 min, 25 min, 30 min, 40 min, and 120 min of stirring. These samples were diluted in 300 µL PrCN that had been precooled to –35 ºC and transferred to an EPR tube. The EPR tube was sealed, removed from the glovebox, and flash-frozen in liquid nitrogen until analysis.

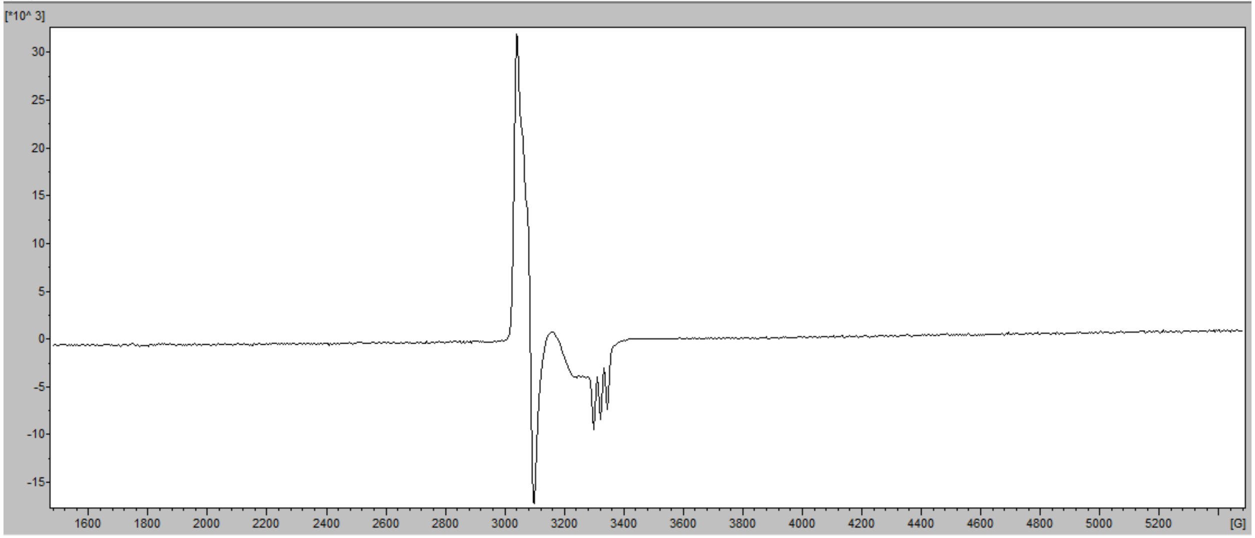
(**a**)



(**b**)



(**c**)


[*10^ 3]
30
25
20
15
10
5
0
-5
-10
-15
1600
1800
2000
2200
2400
2600
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3400
3600
3800
4000
4200
4400
4600
4800
5000
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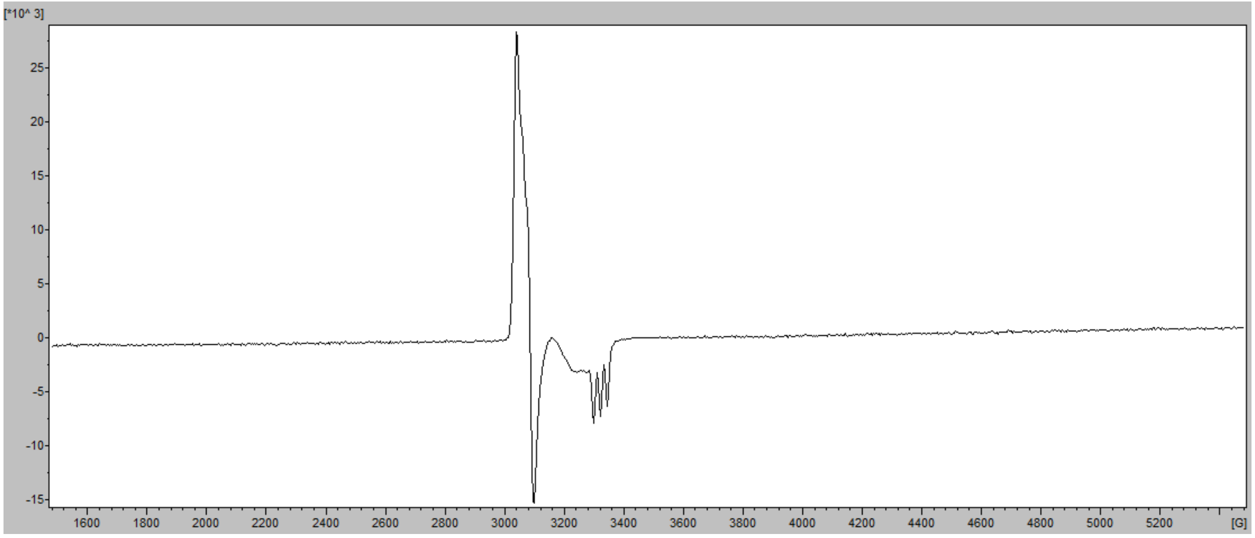
[G]

(**d**)


[*10^ 3]
25
20
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-15
1600
1800
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4800
5000
5200
[G]

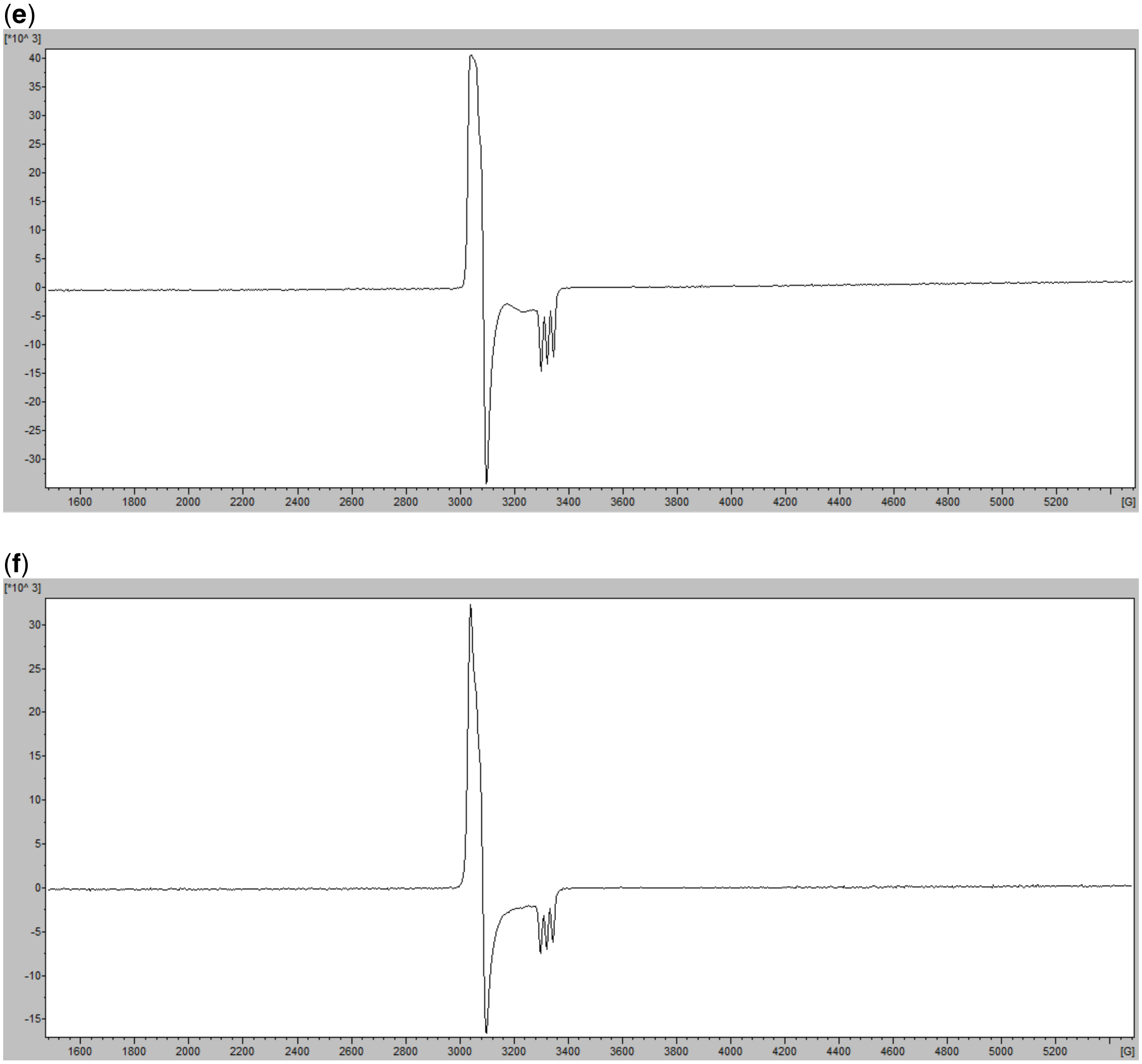
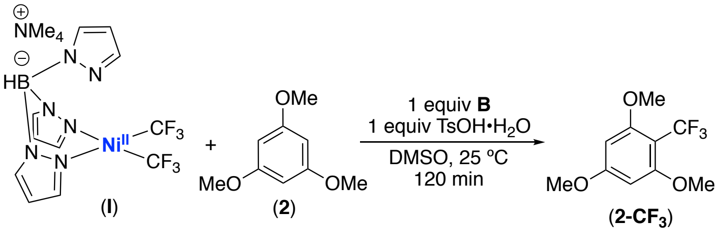


Figure S46. EPR spectra of aliquots of the complex **II**-mediated trifluoromethylation of 4-*tert*-butylanisole taken (**a**) 30 s, (**b**) 20 min, (**c**) 25 min, (**d**) 30 min, (**e**) 40 min, and (**f**) 120 min after the start of the reaction.



In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (11 mg, 0.0625 mmol, 5 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 5.5 mg, 0.0125 mmol, 1.0 equiv), and anhydrous DMSO (100 µL). A second 4 mL vial was charged with TsOH•H_2O (2.4 mg, 0.0125 mmol, 1.0 equiv) and anhydrous DMSO (200 µL). A third 4 mL vial was charged complex **I** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL, 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (600 µL). This orange solution was added to a screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene and **B** was added via syringe to this NMR tube immediately followed by the solution of TsOH, and the contents were shaken vigorously. The NMR tube was then immediately inserted into the spectrometer. Reaction progress was monitored through production of **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S47).

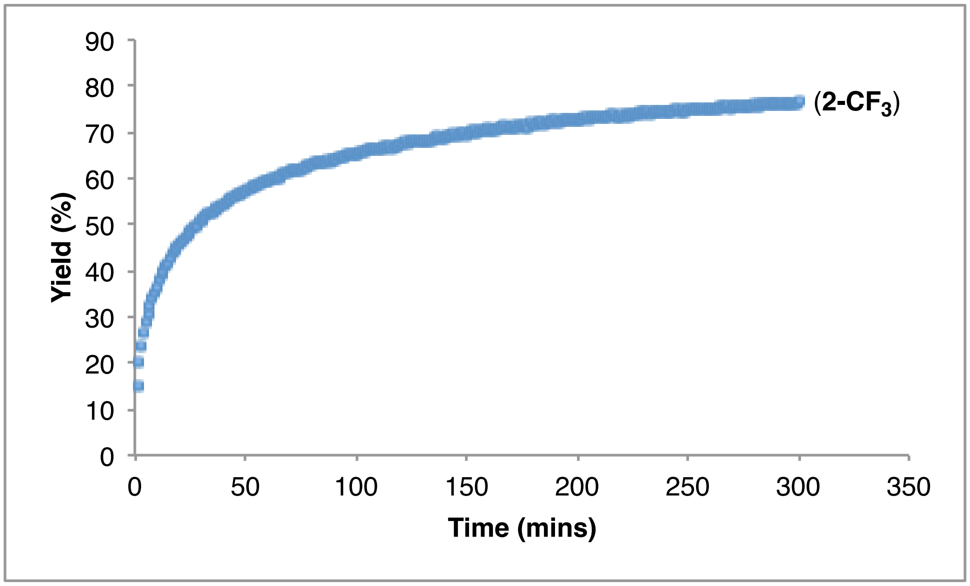
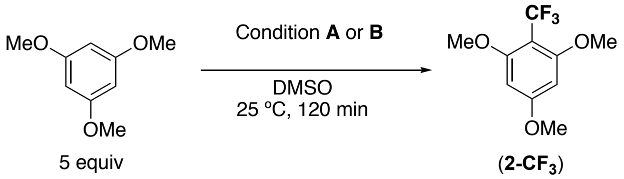


Figure S47. Reaction profile for the trifluoromethylation of trimethoxybenzene mediated by complex **I** in the presence of **B** and TsOH.



Condition **A**: In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (11 mg, 0.0625 mmol, 5 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 5.5 mg, 0.0125 mmol, 1.0 equiv), and anhydrous DMSO (200 µL). A second 4 mL vial was charged complex **I** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL, 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (600 µL). This orange solution was added to a septum screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene and **B** was added via syringe to this NMR tube, and the contents were shaken vigorously. The NMR tube was then immediately inserted into the spectrometer. Reaction progress was monitored through production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S48).

Condition **B**: In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (11 mg, 0.0625 mmol, 5 equiv) and anhydrous DMSO (200 µL). A second 4 mL vial was charged complex **II** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL, 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (600 µL). This yellow solution was added to a septum screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene was added via syringe to this NMR tube, and the contents were shaken vigorously. The NMR tube was then immediately inserted into the spectrometer. Reaction progress was monitored through production of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S48).

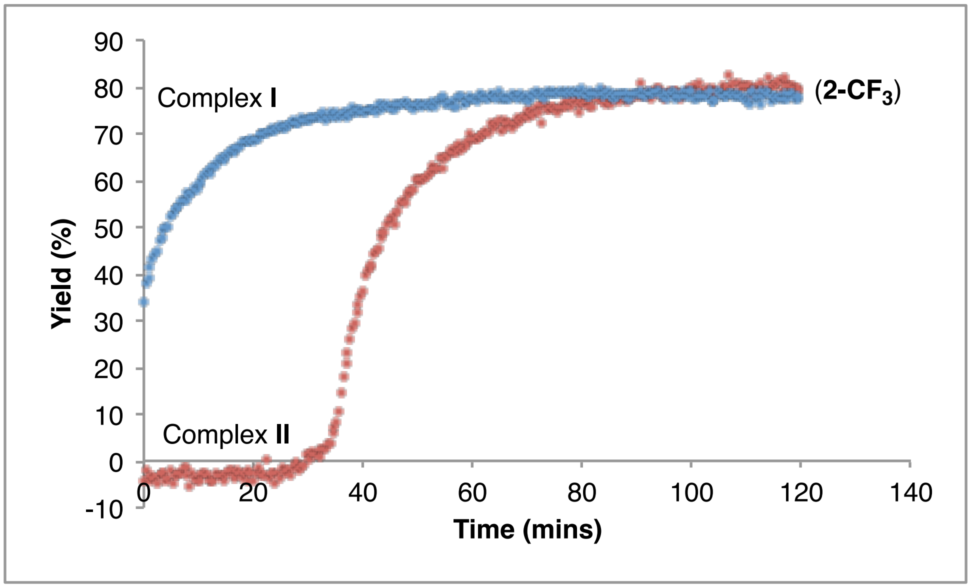
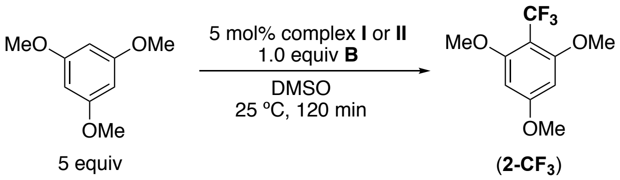


Figure S48. Reaction profile for the trifluoromethylation of trimethoxybenzene mediated by complex **I** (condition **A**, blue line) or complex **II** (condition **B**, red line).



In a nitrogen-filled glovebox, a 4 mL glass vial was charged with trimethoxybenzene (42 mg, 0.25 mmol, 5.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) as an internal standard, and anhydrous DMSO (700 µL). This solution was transferred to a septum screw-cap NMR tube, which was then sealed and removed from the glovebox. Complex **I** (1.2 mg, 0.0025 mmol, 0.05 equiv) or complex **II** (1.2 mg, 0.0025 mmol, 0.05 equiv) was dissolved in anhydrous DMSO (300 µL) and then added to the NMR tube via syringe. The NMR tube was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored through tracking the appearance of product **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S49).

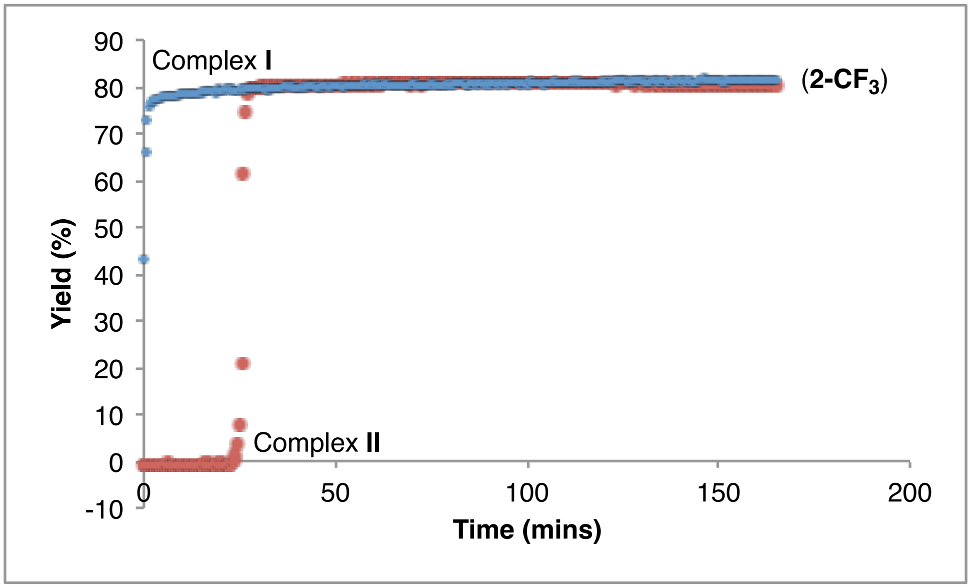
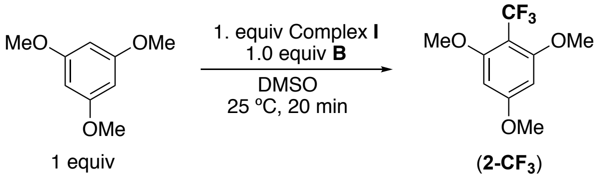


Figure S49. Reaction profile for the trifluoromethylation of trimethoxybenzene catalyzed by complex **I** (blue line) or complex **II** (red line).



In a nitrogen-filled glovebox, a 4 mL vial was charged with trimethoxybenzene (2.1 mg, 0.0125 mmol, 1 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 5.5 mg, 0.0125 mmol, 1.0 equiv), and anhydrous DMSO (200 µL). A second 4 mL vial was charged complex **I** (6.0 mg, 0.0125 mmol, 1 equiv), trifluorotoluene (1.53 µL, 0.0125 mmol, 1 equiv) as an internal standard, and DMSO (600 µL). This orange solution was added to a septum screw-cap NMR tube, which was then sealed and removed from the glovebox. The solution of trimethoxybenzene and **B** was added via syringe to this NMR tube, and the contents were shaken vigorously. The NMR tube was then immediately inserted into the spectrometer. Reaction progress was monitored through the appearance and consumption of complex **II** and production of **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S50).

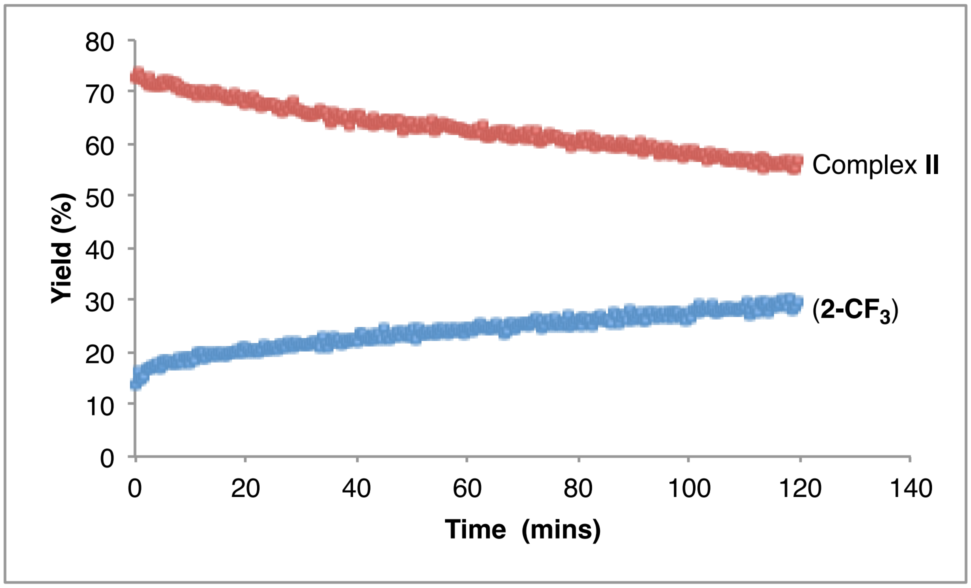
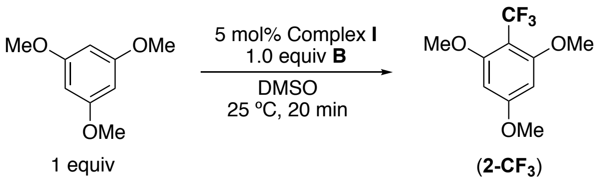


Figure S50. Tracking the formation and consumption of complex **II** during the trifluoromethylation of trimethoxybenzene mediated by complex **I**.



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In a nitrogen-filled glovebox, a 4 mL glass vial was charged with trimethoxybenzene (8.4 mg, 0.05 mmol, 1.0 equiv), 2,8-difluoro-5-(trifluoromethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate (**B**, 22 mg, 0.05 mmol, 1.0 equiv), trifluorotoluene (6.14 µL, 0.05 mmol, 1.0 equiv) as an internal standard, and anhydrous DMSO (700 µL). This solution was transferred to a septum screw-cap NMR tube, which was then sealed and removed from the glovebox. Complex **I** (1.2 mg, 0.0025 mmol, 0.05 equiv) was dissolved in anhydrous DMSO (300 µL) and then added to the NMR tube via syringe. The NMR tube was shaken vigorously and immediately inserted into the spectrometer. Reaction progress was monitored through tracking the appearance and consumption of complex **II** and production of **2-CF$_3$** by ^{19}F NMR spectroscopy over the course of 2 h (400 spectra acquired total, Figure S51).

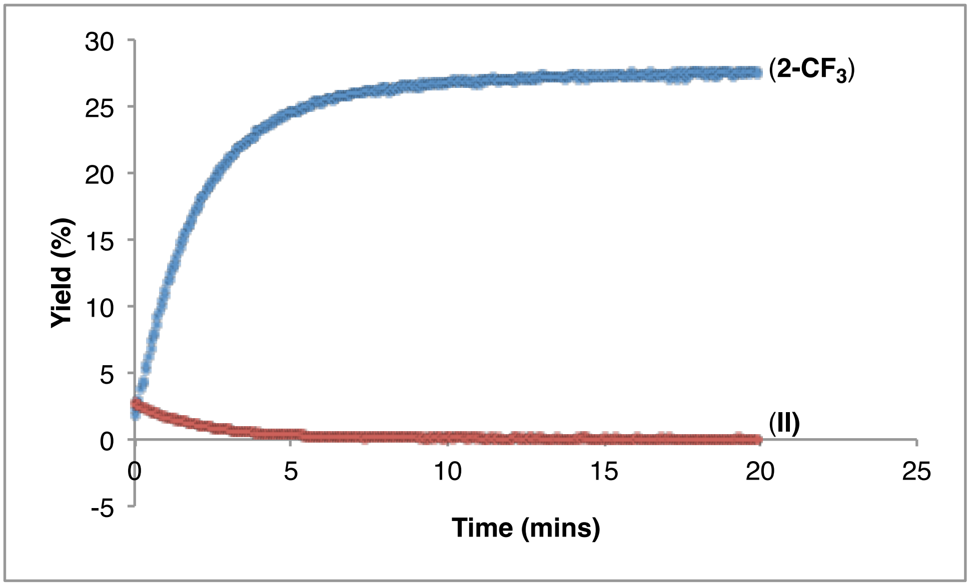


Figure S51. Tracking the formation and consumption of complex **II** during the trifluoromethylation of trimethoxybenzene catalyzed by complex **I**.

VI. Cyclic Voltammetry Data

In a nitrogen atmosphere glovebox, a 20 mL vial was charged with complex **II** (9.5 mg, 0.02 mmol) and 2 ml 0.1 M NBu_4PF_6 solution in MeCN. To the vial was added a 3 mm glassy carbon disc working electrode, a Ag/Ag^+ reference electrode composed of Ag wire in a fritted chamber containing 0.01 M $AgBF_4$ and 0.1 M NBu_4PF_6 solution in MeCN, and a Pt wire counter electrode. A cyclic voltammogram was acquired at a scan rate of 100 mV/s (Figure S52).

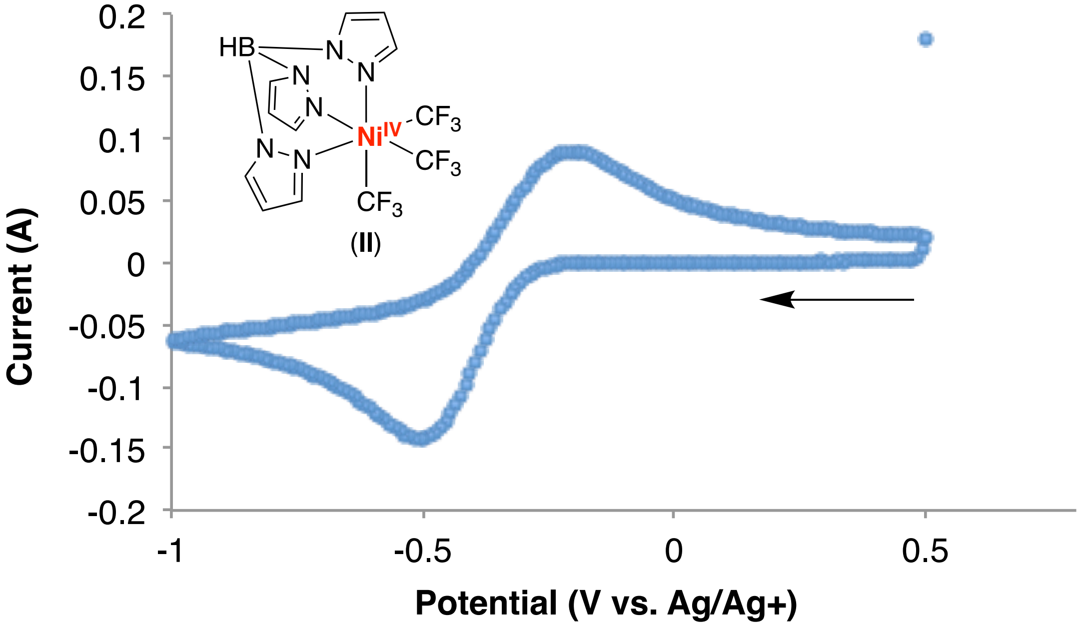
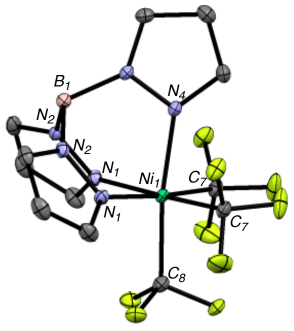


Figure S52. Cyclic voltammogram of complex **II** acquired at a scan rate of 100 mV/s.

VII. X-Ray Crystallography Data



Structure Determination.

Yellow blocks of **II** were grown from a dimethylformamide/acetonitrile solution of the compound at 25 °C. A crystal of dimensions 0.16 x 0.10 x 0.05 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 23763 reflections to a maximum 2θ value of 138.47° of which 1600 were independent and 1589 were greater than 2σ(I). The final cell constants (Table S4) were based on the xyz centroids of 18004 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group Pnma with Z = 4 for the formula $C_{12}H_{10}BN_6F_9Ni$. The comples lies on a mirror plane of the crystal lattice. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0296 and wR2 = 0.0791 [based on I > 2sigma(I)], R1 = 0.0297 and wR2 = 0.0792 for all data. Additional details are presented in Table S4 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S4. Crystal Data and Structural Refinement for **II.**

Empirical Formula	$C_{12}H_{10}BF_9N_6Ni$
Formula Weight	478.78
Temperature	85 (2) K
Wavelength	1.54184 A
Crystal System	Orthorhombic
Space Group	Pnma
Unit Cell Dimensions	a = 14.48910(10) Å, α = 90° b = 18.8696(2) Å, β = 90° c = 8.52640(10) Å, γ = 90°
Volume	1640.564(19) A^3
Z	4
Calculated Density	1.938 Mg/m^3
Absorption Coefficient	2.781 mm^{-1}
F(000)	952
Crystal Size	0.160x0.100x0.050 mm
Theta Range for Data Collection	5.516 to 69.235 deg.
Limiting Indices	$-18 \le h \le 19$, $-16 \le k \le 16$, $-9 \le l \le 9$
Reflections Collected	23763
Unique Reflections	1600
Completeness to Theta	99.8%
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 to 0.71377
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	1600 / 0 / 146
Goodness-of-Fit on F^2	1.116
Final R Indices [$I > 2\sigma(I)$]	R1 = 0.0296, wR2 = 0.0791
R indices (all data)	R1 = 0.0297, wR2 = 0.0792
Extinction coefficient	0.0023(2)
Largest Difference Peak and Hole	0.389 and -0.448 A^{-3}

VII. Computational Details

Gaussian 09 was used at the B3LYP[11] level of density functional theory (DFT) for geometry optimization. The Stuttgart/Dresden ECP (SDD) was used to describe Ni,[12] and the 6-31G(d) basis set was used for other atoms to form basis set BS1. Computation was carried out for dimethylsulfoxide as the solvent utilizing the IEFPCM (SCRF) model. To further refine energies obtained from the B3LYP/BS1 calculations, single point energy calculations were computed for all structures at the B3LYP-D3 level.[13] These calculations employed a larger basis set (BS2) utilizing the quadrupole-ξ valence polarized def2-QZVP[14] basis set on Ni along with the corresponding ECP and the 6-311+G(2d,p) basis set on other atoms. All thermodynamic data were calculated at the standard state (298.15 K and 1 atm). To estimate the corresponding Gibbs free energies (ΔG), entropy corrections were calculated at the B3LYP/BS1 level and added to the single point potential energies. Additional corrections for compression of 1 mol of an ideal gas from 1 atm to the 1 M solution phase standard state (1.89 kcal/mol),[15] and for presence of DMSO solvent as a ligand (1.6 kcal/mol),[16] were applied. All transition structures contained one imaginary frequency, exhibiting atom displacements consistent with the anticipated reaction pathway. The nature of transition structures was confirmed by intrinsic reaction coordinate (IRC) searches, vibrational frequency calculations, and potential energy surface scans.

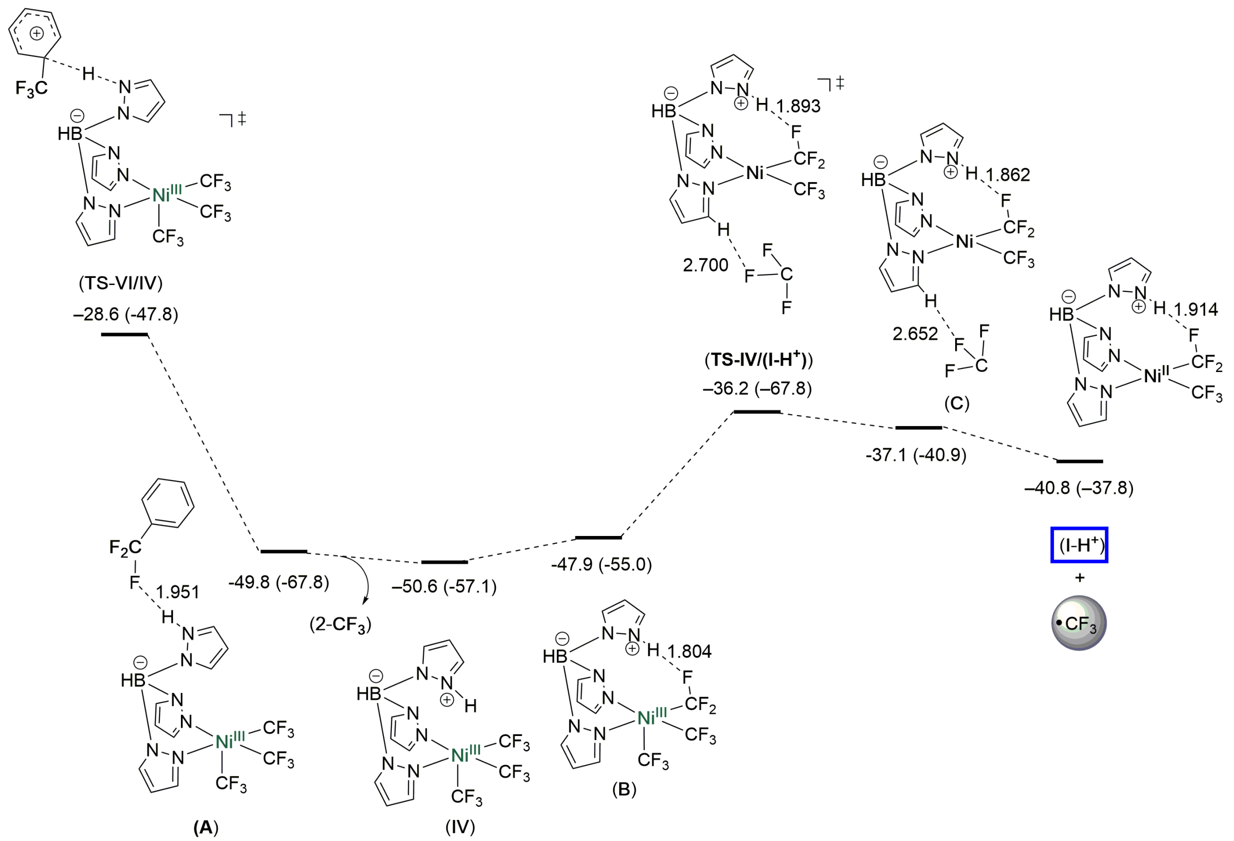
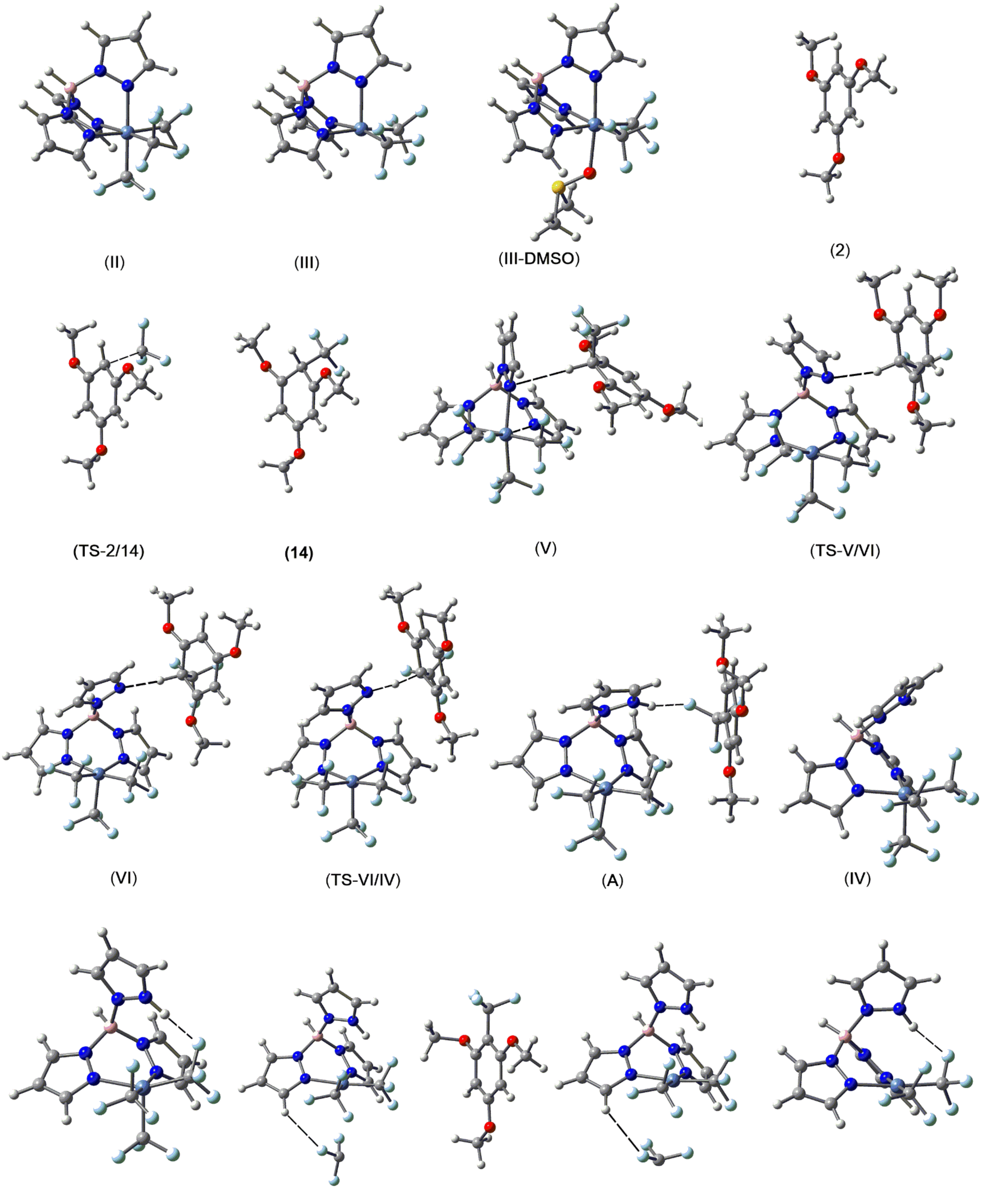


Figure S53. Energy profile including omitted species in Figure 6. Energies ΔG (ΔH) in kcal/mol relative to ($CF_3^{\cdot}$ + **2**), as for Figure 6.



(II) (III) (III-DMSO) (2)

(TS-2/14) **(14)** (V) (TS-V/VI)

(VI) (TS-VI/IV) (A) (IV)

(B) **(TS-IV/I-H$^+$)** (2-CF$_3$) **(C)** (I-H$^+$)

Figure S54. Gaussview diagrams for initiation step (**II**, **III** and DMSO adduct of **III**), and structures for Figure 6 and Figure S53 in the order of occurrence in the propagation sequence**.**

Energies of calculated species and Cartesian coordinates

All calculations related to thermodynamic effects are obtained using B3LYP/BS1; single-point data, listed immediately after BS1 data, are calculated using BS2 and B3LYP-D3.

(2)
E(RB3LYP) = -575.815130657
Zero-point correction= 0.198947 (Hartree/Particle)
Thermal correction to Energy= 0.211010
Thermal correction to Enthalpy= 0.211954
Thermal correction to Gibbs Free Energy= 0.161027
Sum of electronic and zero-point Energies= -575.616183
Sum of electronic and thermal Energies= -575.604121
Sum of electronic and thermal Enthalpies= -575.603177
Sum of electronic and thermal Free Energies= -575.654104
E(UB3LYP) = -913.732972289

24
(2)

C	-0.429819	-0.623460	-0.009644
C	0.977189	-0.693592	-0.013687
C	1.708932	0.490604	-0.015798
C	1.066345	1.744357	-0.014119
C	-0.325155	1.785692	-0.010172
C	-1.089557	0.602298	-0.007914
H	1.445543	-1.669287	-0.014916
H	1.677398	2.637729	-0.015924
H	-2.168717	0.684682	-0.004953
O	3.072648	0.546721	-0.019446
O	-1.062633	-1.832634	-0.007671
O	-1.055956	2.938441	-0.008092
C	-0.357147	4.179681	-0.010783
H	-1.125031	4.954855	-0.009241
H	0.271030	4.286757	0.881824
H	0.266242	4.285561	-0.906872
C	3.798034	-0.679218	-0.021826
H	3.574419	-1.274414	-0.915487
H	4.853318	-0.401901	-0.025256
H	3.580325	-1.274417	0.873296
C	-2.487131	-1.848731	-0.003610
H	-2.895274	-1.360458	-0.896877
H	-2.773849	-2.901501	-0.002525
H	-2.890236	-1.360150	0.891767

(2-CF$_3$)
E(RB3LYP) = -912.838721890
Zero-point correction= 0.203225 (Hartree/Particle)
Thermal correction to Energy= 0.219052

Thermal correction to Enthalpy= 0.219996
Thermal correction to Gibbs Free Energy= 0.159557
Sum of electronic and zero-point Energies= -912.635497
Sum of electronic and thermal Energies= -912.619670
Sum of electronic and thermal Enthalpies= -912.618726
Sum of electronic and thermal Free Energies= -912.679165
E(RB3LYP) = -913.175346310

27

(2-CF_3)

C	-0.516650	-0.786301	-0.091085
C	0.872128	-0.960266	-0.347704
C	1.667569	0.192305	-0.444222
C	1.129597	1.471893	-0.259109
C	-0.231016	1.613401	0.013310
C	-1.057448	0.481231	0.095642
H	1.791986	2.321966	-0.358064
H	-2.110557	0.628638	0.295091
O	2.999882	0.119124	-0.776008
O	-1.255905	-1.923220	-0.044229
O	-0.856569	2.801811	0.204407
C	-0.080563	3.998669	0.133352
H	-0.778372	4.814969	0.323042
H	0.707785	4.005835	0.894644
H	0.366919	4.122601	-0.859396
C	3.904630	0.155584	0.334544
H	3.779260	-0.729126	0.968936
H	4.910067	0.159578	-0.090560
H	3.756770	1.061377	0.934678
C	-2.655452	-1.824382	0.217499
H	-3.164276	-1.242007	-0.558956
H	-3.028033	-2.849185	0.208515
H	-2.844179	-1.373833	1.198477
C	1.385858	-2.361130	-0.535143
F	1.088293	-3.156214	0.525166
F	0.838486	-2.959288	-1.625942
F	2.723846	-2.441872	-0.693170

(3)

E(UB3LYP) = -913.391706659
Zero-point correction= 0.213160 (Hartree/Particle)
Thermal correction to Energy= 0.229452
Thermal correction to Enthalpy= 0.230396
Thermal correction to Gibbs Free Energy= 0.168343
Sum of electronic and zero-point Energies= -913.178547
Sum of electronic and thermal Energies= -913.162255
Sum of electronic and thermal Enthalpies= -913.161311
Sum of electronic and thermal Free Energies= -913.223363
E(UB3LYP) = -913.732972289

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(3)

C	-0.434248	-0.675617	-0.078247
C	1.040376	-0.815998	-0.391903
C	1.765417	0.496412	-0.182938
C	1.100335	1.702222	-0.117743
C	-0.304835	1.745008	-0.080844
C	-1.057594	0.534964	-0.003484
H	1.698381	2.603779	-0.051952
H	-2.124474	0.615520	0.168315
O	3.135780	0.526047	-0.208423
O	-1.022583	-1.889197	0.090777
O	-1.051627	2.887458	-0.041094
C	-0.371165	4.138248	-0.063660
H	-1.149273	4.903055	-0.055554
H	0.268716	4.261230	0.818770
H	0.237103	4.245056	-0.970067
C	3.843168	-0.469546	0.537820
H	3.746730	-1.461451	0.084578
H	4.892329	-0.169420	0.512872
H	3.499115	-0.501906	1.578734
C	-2.417423	-1.917126	0.386638
H	-3.001946	-1.483374	-0.433319
H	-2.678008	-2.969274	0.506897
H	-2.632760	-1.373039	1.314071
C	1.246601	-1.330209	-1.838935
F	0.636191	-2.514860	-2.051033
F	0.764287	-0.460104	-2.751024
F	2.559532	-1.512069	-2.114836
H	1.455319	-1.614644	0.240592

(15)

E(UB3LYP) = -913.360870228
Zero-point correction= 0.210976 (Hartree/Particle)
Thermal correction to Energy= 0.227663
Thermal correction to Enthalpy= 0.228608
Thermal correction to Gibbs Free Energy= 0.164426
Sum of electronic and zero-point Energies= -913.149894
Sum of electronic and thermal Energies= -913.133207
Sum of electronic and thermal Enthalpies= -913.132263
Sum of electronic and thermal Free Energies= -913.196444
E(UB3LYP) = -913.705924784

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(15)

C	-0.419936	-0.607829	0.175345
C	1.008124	-0.696533	0.100721
C	1.737747	0.519386	0.151396

C	1.091865	1.756435	0.051216
C	-0.303500	1.794223	0.007728
C	-1.070704	0.608261	0.083183
H	1.696454	2.654136	0.036652
H	-2.149702	0.694274	0.088244
O	3.094375	0.569855	0.227721
O	-1.033479	-1.813515	0.292988
O	-1.032904	2.937126	-0.087937
C	-0.341206	4.183280	-0.152704
H	-1.114416	4.948078	-0.235838
H	0.249684	4.357299	0.754072
H	0.314610	4.227801	-1.029964
C	3.824444	-0.639534	0.441604
H	3.662065	-1.356930	-0.368836
H	4.875342	-0.348124	0.462527
H	3.556294	-1.100158	1.399702
C	-2.459740	-1.846000	0.305670
H	-2.871212	-1.449328	-0.629758
H	-2.733264	-2.896703	0.409306
H	-2.861591	-1.276704	1.151957
C	1.308813	-1.408453	-1.986812
F	2.017462	-2.558653	-1.979784
F	0.140967	-1.633526	-2.612878
F	2.001022	-0.494523	-2.692438
H	1.455833	-1.622477	0.441923

(I-H$^+$)
E(RB3LYP) = -1549.23879783
Zero-point correction= 0.242421 (Hartree/Particle)
Thermal correction to Energy= 0.264897
Thermal correction to Enthalpy= 0.265841
Thermal correction to Gibbs Free Energy= 0.189744
Sum of electronic and zero-point Energies= -1548.996377
Sum of electronic and thermal Energies= -1548.973901
Sum of electronic and thermal Enthalpies= -1548.972957
Sum of electronic and thermal Free Energies= -1549.049054
E(RB3LYP) = -1548.62353727

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(I-H$^+$)

N	-0.381315	-1.445727	0.781929
C	-1.230482	-1.968408	1.682375
H	-2.294627	-1.968632	1.499078
C	-0.475962	-2.444943	2.748111
H	-0.836459	-2.936220	3.638251
C	0.849253	-2.165702	2.411243
C	3.920990	0.469019	1.621891
C	4.091026	1.830283	1.811931
H	4.933110	2.334272	2.262089

C	2.924614	2.407147	1.289233
H	2.635737	3.445272	1.244613
H	4.560839	-0.367161	1.863555
H	1.764060	-2.375065	2.945702
N	2.101786	1.461520	0.817267
C	-1.258438	1.415502	-1.142704
F	-1.580811	0.060173	-1.383171
F	-2.426550	1.913890	-0.653176
F	-1.168723	1.959333	-2.408621
N	2.723416	0.262616	1.023724
N	0.896264	-1.551816	1.216949
B	2.196545	-1.057721	0.444944
H	3.026340	-1.909128	0.588999
Ni	0.393481	1.539254	-0.171173
N	1.879063	-0.849953	-1.035147
C	2.314481	-1.562911	-2.101107
C	1.205702	0.210198	-2.804889
C	1.904836	-0.918758	-3.256599
H	2.887596	-2.467155	-1.956114
H	0.698839	0.976926	-3.369497
H	2.087006	-1.217633	-4.277950
N	1.194411	0.251279	-1.466519
C	-0.411368	2.775755	1.044149
F	0.407453	3.338437	1.999324
F	-1.432081	2.223925	1.787002
F	-0.970464	3.875923	0.424505
H	-0.612524	-0.965708	-0.089094

(II)
E(RB3LYP) = -1886.22006890
Zero-point correction= 0.246992 (Hartree/Particle)
Thermal correction to Energy= 0.272231
Thermal correction to Enthalpy= 0.273176
Thermal correction to Gibbs Free Energy= 0.193259
Sum of electronic and zero-point Energies= -1885.973077
Sum of electronic and thermal Energies= -1885.947837
Sum of electronic and thermal Enthalpies= -1885.946893
Sum of electronic and thermal Free Energies= -1886.026810
E(RB3LYP) = -1885.71523360

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(II)

N	0.392171	-1.229722	1.291628
C	-0.322449	-1.954798	2.169878
H	-1.383715	-1.811013	2.270876
C	0.511634	-2.835956	2.864400
H	0.227951	-3.546731	3.625947
C	1.780161	-2.593897	2.356058
C	3.774839	1.347734	1.379787

C	3.297946	2.648954	1.456683
H	3.833386	3.533223	1.768153
C	1.965106	2.562597	1.043628
H	1.238463	3.349813	0.944643
H	4.747374	0.930483	1.597374
H	2.738770	-3.033095	2.591562
N	1.650826	1.290297	0.743507
C	-0.318583	1.704043	-1.410283
F	-0.566865	1.170579	-2.627636
F	-1.342883	2.543092	-1.160671
F	0.783140	2.466623	-1.557210
N	2.775488	0.552634	0.949962
N	1.686537	-1.630509	1.418629
B	2.798143	-0.945581	0.608885
H	3.866655	-1.426097	0.853767
Ni	-0.004340	0.313781	-0.034825
N	2.453941	-1.095178	-0.881839
C	3.135491	-1.724982	-1.858778
C	1.226136	-0.971983	-2.666252
C	2.384478	-1.668095	-3.024594
H	4.099993	-2.166045	-1.652674
H	0.375801	-0.721119	-3.275908
H	2.636096	-2.069709	-3.994667
N	1.274429	-0.622366	-1.368904
C	-1.593494	-0.691595	-0.657414
C	-1.145943	1.302860	1.249807
F	-1.210944	-1.758980	-1.385905
F	-2.316681	-1.182357	0.375150
F	-2.463035	0.006349	-1.413476
F	-1.007348	0.788224	2.487740
F	-2.464831	1.299985	0.973091
F	-0.793237	2.604395	1.343407

(III)
E(UB3LYP) = -1548.63365576
Zero-point correction= 0.230503 (Hartree/Particle)
Thermal correction to Energy= 0.252465
Thermal correction to Enthalpy= 0.253409
Thermal correction to Gibbs Free Energy= 0.178429
Sum of electronic and zero-point Energies= -1548.403153
Sum of electronic and thermal Energies= -1548.381191
Sum of electronic and thermal Enthalpies= -1548.380246
Sum of electronic and thermal Free Energies= -1548.455226
E(UB3LYP) = -1548.00352339

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(III)

N	0.445819	-1.139452	1.279022
C	-0.340127	-1.962766	1.987148

H	-1.410926	-1.822689	1.995800
C	0.440974	-2.915030	2.654428
H	0.102884	-3.707833	3.304710
C	1.748625	-2.608686	2.298671
C	3.879561	1.430638	1.433203
C	3.400320	2.731394	1.516705
H	3.933376	3.609906	1.848434
C	2.070269	2.648218	1.078903
H	1.321881	3.421673	0.987953
H	4.849200	1.015316	1.667395
H	2.685617	-3.071788	2.572596
N	1.771608	1.384315	0.755411
C	-0.357145	1.613249	-1.449009
F	-1.154797	0.894455	-2.306642
F	-1.033044	2.753462	-1.191240
F	0.732995	1.994457	-2.160105
N	2.886568	0.637855	0.973777
N	1.730426	-1.540976	1.473463
B	2.871202	-0.875208	0.666232
H	3.928231	-1.375265	0.923171
Ni	0.130186	0.382046	-0.007161
N	2.512416	-1.074566	-0.828110
C	3.171796	-1.728013	-1.807175
C	1.232644	-1.012957	-2.585378
C	2.388013	-1.713341	-2.954152
H	4.145731	-2.156139	-1.618278
H	0.364594	-0.756083	-3.173104
H	2.619355	-2.144988	-3.916387
N	1.315667	-0.634013	-1.301387
C	-1.200170	1.245334	1.137447
F	-1.248111	0.718684	2.388452
F	-2.454643	1.085343	0.621204
F	-1.014993	2.574254	1.325715

(III-DMSO)

E(UB3LYP) = -2101.84231915
Zero-point correction= 0.312221 (Hartree/Particle)
Thermal correction to Energy= 0.341279
Thermal correction to Enthalpy= 0.342223
Thermal correction to Gibbs Free Energy= 0.251393
Sum of electronic and zero-point Energies= -2101.530098
Sum of electronic and thermal Energies= -2101.501040
Sum of electronic and thermal Enthalpies= -2101.500096
Sum of electronic and thermal Free Energies= -2101.590926
E(UB3LYP) = -2101.32910149

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(III-DMSO)

N	0.636709	-1.228471	1.318428

C	-0.048332	-2.066302	2.111659
H	-1.122575	-2.005065	2.165698
C	0.826421	-2.918853	2.797881
H	0.574114	-3.693093	3.507056
C	2.089841	-2.539461	2.367087
C	3.862879	1.591790	1.497080
C	3.275197	2.844698	1.604276
H	3.731620	3.759210	1.953607
C	1.956053	2.653273	1.161837
H	1.147852	3.363750	1.074058
H	4.863385	1.253417	1.726322
H	3.070880	-2.911139	2.625988
N	1.760361	1.376275	0.814419
C	-0.139641	1.674457	-1.393513
F	-1.026750	1.336476	-2.366095
F	-0.566800	2.865370	-0.885855
F	1.018414	1.983653	-2.044224
N	2.937217	0.728883	1.020201
N	1.954730	-1.528690	1.482438
B	3.048159	-0.773022	0.694560
H	4.136557	-1.192947	0.971129
Ni	0.152017	0.223868	-0.089726
N	2.752869	-0.977110	-0.811293
C	3.524709	-1.473097	-1.802106
C	1.564428	-0.877592	-2.623754
C	2.800679	-1.429292	-2.987396
H	4.526618	-1.820189	-1.594158
H	0.708047	-0.632522	-3.234804
H	3.120797	-1.748237	-3.968118
N	1.545523	-0.615388	-1.310393
C	-1.331330	0.992201	0.950056
F	-1.816398	0.113718	1.876441
F	-2.423258	1.349230	0.218138
F	-0.978242	2.096823	1.663328
S	-1.180849	-2.626603	-1.166010
C	-2.658095	-3.379077	-0.412241
H	-2.589041	-3.228739	0.666151
H	-3.553156	-2.892512	-0.807974
H	-2.660583	-4.448871	-0.637307
C	-1.610877	-2.945277	-2.906943
H	-2.567711	-2.469232	-3.136110
H	-0.816514	-2.521882	-3.523336
H	-1.662534	-4.026290	-3.062209
O	-1.367213	-1.097782	-0.976705

(IV)

E(UB3LYP) = -1886.82470305
Zero-point correction= 0.255385 (Hartree/Particle)
Thermal correction to Energy= 0.282818

Thermal correction to Enthalpy= 0.283762
Thermal correction to Gibbs Free Energy= 0.195256
Sum of electronic and zero-point Energies= -1886.569318
Sum of electronic and thermal Energies= -1886.541885
Sum of electronic and thermal Enthalpies= -1886.540941
Sum of electronic and thermal Free Energies= -1886.629447
E(UB3LYP) = -1886.33627564

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(IV)

N	-0.183393	-2.158633	0.598414
C	-1.123954	-2.460499	1.509795
H	-2.003100	-3.022496	1.232492
C	-0.714815	-1.921508	2.723249
H	-1.229925	-1.975536	3.669496
C	0.501535	-1.288255	2.455850
C	3.962005	0.258583	1.635288
C	4.213988	1.596430	1.887452
H	5.073282	2.023608	2.382216
C	3.109366	2.272909	1.349292
H	2.896418	3.329391	1.315426
H	4.537399	-0.628127	1.858459
H	1.167711	-0.748900	3.112119
N	2.245897	1.405570	0.811901
C	-1.272019	1.507173	-0.939751
F	-1.726764	0.240217	-0.651154
F	-2.275722	2.340916	-0.572503
F	-1.245871	1.583300	-2.301713
N	2.773418	0.157993	0.991444
N	0.809425	-1.432868	1.156558
B	2.148286	-1.087845	0.368635
H	2.901516	-2.017145	0.450273
Ni	0.492987	1.678207	-0.155780
N	1.808258	-0.827246	-1.102389
C	2.254010	-1.513971	-2.185385
C	1.241503	0.329184	-2.849953
C	1.906181	-0.811545	-3.325344
H	2.788534	-2.444181	-2.057994
H	0.811498	1.148630	-3.402935
H	2.105880	-1.079292	-4.352020
N	1.181788	0.317011	-1.515075
C	-0.340923	2.539098	1.381102
F	0.524361	2.815595	2.400179
F	-1.289501	1.722132	1.948020
F	-0.961151	3.723111	1.134071
H	-0.176417	-2.342176	-0.397436
C	1.086915	3.389544	-1.126163
F	0.124676	4.010891	-1.883992
F	1.530922	4.380495	-0.267675

F	2.140762	3.201980	-1.995051

(V)
E(UB3LYP) = -2799.64781567
Zero-point correction= 0.459726 (Hartree/Particle)
Thermal correction to Energy= 0.504665
Thermal correction to Enthalpy= 0.505609
Thermal correction to Gibbs Free Energy= 0.376772
Sum of electronic and zero-point Energies= -2799.188090
Sum of electronic and thermal Energies= -2799.143151
Sum of electronic and thermal Enthalpies= -2799.142206
Sum of electronic and thermal Free Energies= -2799.271044
E(UB3LYP) = -2799.50892198

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(V)

N	-0.146822	-1.058348	0.732270
C	-1.236190	-1.474836	1.385717
H	-2.154457	-0.912314	1.306888
C	-0.972599	-2.665759	2.088223
H	-1.651132	-3.241808	2.700993
C	0.360234	-2.939311	1.811926
C	3.893685	-0.043047	1.365380
C	3.988610	1.341045	1.394145
H	4.764324	1.940457	1.847294
C	2.844163	1.783689	0.711667
H	2.522680	2.789719	0.493714
H	4.542835	-0.809013	1.765202
H	1.001748	-3.750409	2.126985
N	2.104267	0.743971	0.304714
C	1.162156	1.802487	-2.394107
F	0.726986	1.538315	-3.683357
F	0.957233	3.159786	-2.264727
F	2.538135	1.693123	-2.491640
N	2.760375	-0.378479	0.708173
N	0.830043	-1.960466	1.003113
B	2.218296	-1.782717	0.366570
H	2.974700	-2.628790	0.760519
Ni	0.356404	0.506798	-0.974920
N	2.080319	-1.882975	-1.172896
C	2.616282	-2.793790	-2.014567
C	1.401660	-1.357430	-3.166106
C	2.206691	-2.495705	-3.307314
H	3.248405	-3.582808	-1.633149
H	0.886657	-0.776011	-3.914232
H	2.457061	-3.020845	-4.217218
N	1.331373	-0.996140	-1.879097
C	-1.399217	-0.082326	-1.774431
C	-0.598523	1.966316	-0.164020

F	-1.422448	-1.419434	-2.097649
F	-2.517927	0.076802	-0.985733
F	-1.718118	0.553260	-2.947496
F	-1.315309	1.581918	0.939629
F	-1.492600	2.613136	-0.963558
F	0.228148	2.952465	0.299114
C	-1.568035	0.672298	5.297089
C	-0.600816	-0.364711	5.342152
C	0.590758	-0.191576	4.688268
C	0.957008	1.106605	3.996920
C	-0.190915	2.092973	3.921271
C	-1.372862	1.877317	4.570285
H	-0.822582	-1.292132	5.848156
H	1.275499	0.880472	2.971143
H	-2.192230	2.582278	4.536631
O	0.100785	3.141994	3.181337
O	1.546058	-1.092356	4.596769
O	-2.736688	0.588206	5.893739
C	-0.901409	4.155270	2.956357
H	-0.429589	4.878099	2.294706
H	-1.770230	3.707288	2.469854
H	-1.179427	4.625526	3.902992
C	-3.108364	-0.576676	6.667482
H	-4.096899	-0.346015	7.059435
H	-3.154567	-1.456875	6.022413
H	-2.402179	-0.726632	7.486857
C	1.397929	-2.367509	5.261323
H	0.542867	-2.903446	4.843875
H	2.321168	-2.904038	5.052328
H	1.279432	-2.215278	6.336916
C	2.183096	1.752581	4.701938
F	1.882467	2.044895	5.983807
F	3.240310	0.928445	4.701685
F	2.557591	2.887243	4.095526

(VI)
E(UB3LYP) = -2799.64666350
Zero-point correction= 0.459506 (Hartree/Particle)
Thermal correction to Energy= 0.504545
Thermal correction to Enthalpy= 0.505490
Thermal correction to Gibbs Free Energy= 0.375635
Sum of electronic and zero-point Energies= -2799.187158
Sum of electronic and thermal Energies= -2799.142118
Sum of electronic and thermal Enthalpies= -2799.141174
Sum of electronic and thermal Free Energies= -2799.271029
E(UB3LYP) = -2799.49942104

67
(VI)

N	0.326726	-1.446722	1.934862
C	-0.871734	-2.021467	2.081873
H	-1.391813	-1.951440	3.029918
C	-1.282787	-2.664718	0.899871
H	-2.199436	-3.205724	0.713364
C	-0.242575	-2.434539	0.014210
C	3.458530	0.660289	1.185982
C	3.540969	2.027097	0.962508
H	4.217549	2.732025	1.422096
C	2.543201	2.287343	0.015768
H	2.264371	3.219972	-0.447337
H	4.022212	0.013750	1.842464
H	-0.121284	-2.726217	-1.018526
N	1.897029	1.157935	-0.305397
C	1.207848	1.966416	-3.228861
F	1.036826	1.445044	-4.499473
F	0.648877	3.219773	-3.309548
F	2.563808	2.204995	-3.145806
N	2.468204	0.154594	0.419354
N	0.705812	-1.697967	0.652027
B	2.137659	-1.336685	0.179302
H	2.964462	-1.997186	0.756388
Ni	0.502235	0.734420	-1.736317
N	2.265488	-1.600583	-1.337758
C	3.006479	-2.544571	-1.959740
C	2.067584	-1.243586	-3.472612
C	2.906784	-2.356163	-3.330578
H	3.553287	-3.274771	-1.380949
H	1.729363	-0.742877	-4.365672
H	3.378667	-2.932527	-4.112359
N	1.685242	-0.793558	-2.271016
C	-1.058132	-0.030385	-2.658521
C	-0.694668	2.032128	-0.951275
F	-0.810985	-1.228684	-3.275345
F	-2.096976	-0.302540	-1.802621
F	-1.587001	0.752371	-3.640683
F	-1.180457	1.525940	0.229586
F	-1.786277	2.436218	-1.648581
F	-0.064756	3.198836	-0.606646
C	-1.483529	0.849021	6.191844
C	-0.759471	-0.350601	6.416754
C	0.307000	-0.641804	5.605589
C	0.785682	0.299442	4.524970
C	-0.148714	1.461206	4.283099
C	-1.196432	1.733586	5.117316
H	-1.064860	-1.031460	7.197103
H	0.863218	-0.270962	3.574532
H	-1.857165	2.576902	4.970285
O	0.161478	2.135162	3.191660

O	1.041024	-1.734311	5.672391
O	-2.506833	1.216807	6.932937
C	-0.635764	3.276410	2.807321
H	-0.227547	3.598299	1.853163
H	-1.679582	2.977875	2.683495
H	-0.544356	4.063669	3.559985
C	-2.946472	0.420408	8.057411
H	-3.776023	0.978642	8.486742
H	-3.288513	-0.558754	7.714536
H	-2.139926	0.320240	8.787181
C	0.763332	-2.730508	6.681389
H	-0.243884	-3.131637	6.543329
H	1.506324	-3.509333	6.521948
H	0.874892	-2.295493	7.677718
C	2.216039	0.785390	4.876955
F	2.264615	1.260219	6.140051
F	3.098758	-0.223272	4.782198
F	2.632682	1.763390	4.061419

(A)
E(UB3LYP) = -2799.67698693
Zero-point correction= 0.460114 (Hartree/Particle)
Thermal correction to Energy= 0.505109
Thermal correction to Enthalpy= 0.506053
Thermal correction to Gibbs Free Energy= 0.377738
Sum of electronic and zero-point Energies= -2799.216873
Sum of electronic and thermal Energies= -2799.171878
Sum of electronic and thermal Enthalpies= -2799.170934
Sum of electronic and thermal Free Energies= -2799.299249
E(UB3LYP) = -2799.53015957

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(A)

N	0.858196	-1.695948	1.941230
C	-0.284903	-2.231527	2.401052
H	-0.641228	-2.001802	3.394312
C	-0.812432	-3.026716	1.390994
H	-1.722407	-3.605286	1.420928
C	0.081217	-2.908385	0.325134
C	4.118462	-0.035133	0.851291
C	4.281581	1.335364	0.760853
H	5.107894	1.926990	1.125116
C	3.132361	1.786000	0.094390
H	2.852792	2.788111	-0.188376
H	4.752566	-0.799963	1.275630
H	0.063327	-3.361317	-0.654528
N	2.326480	0.761031	-0.195717
C	0.980909	2.070750	-2.648094
F	0.498642	1.743586	-3.903266

F	0.454629	3.315507	-2.402349
F	2.324421	2.301110	-2.855483
N	2.935559	-0.369364	0.276539
N	1.088651	-2.087500	0.669244
B	2.446745	-1.772786	-0.094909
H	3.273634	-2.583408	0.216863
Ni	0.582565	0.643638	-1.220564
N	2.169935	-1.843546	-1.596268
C	2.686158	-2.708263	-2.502674
C	1.506937	-1.164368	-3.548553
C	2.283192	-2.312038	-3.766957
H	3.302035	-3.534474	-2.178183
H	1.006030	-0.525686	-4.258396
H	2.519822	-2.779576	-4.710954
N	1.439360	-0.886588	-2.242282
C	-1.199665	0.205723	-1.853282
C	-0.230866	1.769112	0.143224
F	-1.216492	-0.703632	-2.870654
F	-1.935656	-0.380899	-0.852168
F	-1.946010	1.243230	-2.314301
F	-0.248530	1.047573	1.316505
F	-1.497640	2.240971	0.005328
F	0.517222	2.880124	0.405075
C	-1.996060	0.859654	5.605785
C	-1.040578	-0.061074	6.050081
C	0.285890	0.095256	5.633686
C	0.677666	1.150440	4.775766
C	-0.311936	2.080212	4.361610
C	-1.637239	1.924474	4.772073
H	-1.315519	-0.873715	6.704922
H	1.467885	-1.021813	2.398271
H	-2.410179	2.616036	4.466366
O	0.083451	3.113541	3.583620
O	1.275024	-0.753241	6.011991
O	-3.309010	0.805654	5.940798
C	-0.901536	4.003849	3.059021
H	-0.349080	4.717381	2.447757
H	-1.619746	3.468175	2.430201
H	-1.426009	4.534866	3.861109
C	-3.762463	-0.248849	6.790358
H	-4.834285	-0.088626	6.911884
H	-3.589189	-1.229684	6.333047
H	-3.273680	-0.207722	7.770412
C	0.967164	-1.842464	6.882183
H	0.245078	-2.527011	6.423086
H	1.911717	-2.363322	7.041935
H	0.578893	-1.485544	7.842540
C	2.112488	1.198563	4.344894
F	2.973735	1.297968	5.385247

F	2.481577	0.032702	3.688858
F	2.420855	2.190841	3.497317

(B)
E(UB3LYP) = -1886.82480987
Zero-point correction= 0.255999 (Hartree/Particle)
Thermal correction to Energy= 0.283111
Thermal correction to Enthalpy= 0.284055
Thermal correction to Gibbs Free Energy= 0.196507
Sum of electronic and zero-point Energies= -1886.568811
Sum of electronic and thermal Energies= -1886.541699
Sum of electronic and thermal Enthalpies= -1886.540755
Sum of electronic and thermal Free Energies= -1886.628302
E(UB3LYP) = -1886.33315496

40
(B)

N	-0.428464	-1.488328	0.905542
C	-1.196021	-2.097745	1.824312
H	-2.271839	-2.094658	1.732045
C	-0.351605	-2.660001	2.774461
H	-0.632879	-3.229210	3.646543
C	0.938822	-2.344790	2.348020
C	3.844030	0.307670	1.762071
C	4.028411	1.628590	2.134931
H	4.853917	2.049208	2.689338
C	2.909204	2.297673	1.623392
H	2.661899	3.345498	1.660465
H	4.451592	-0.569117	1.932624
H	1.896395	-2.591953	2.781773
N	2.094453	1.441517	0.990566
C	-1.272455	1.418478	-1.152609
F	-1.487039	0.024746	-1.219047
F	-2.440174	1.883593	-0.644394
F	-1.272156	1.807774	-2.456900
N	2.681654	0.211093	1.073901
N	0.881707	-1.628612	1.211856
B	2.129305	-1.052076	0.407264
H	2.963709	-1.909408	0.464006
Ni	0.486355	1.785829	-0.264327
N	1.775184	-0.762833	-1.057604
C	2.099146	-1.534891	-2.124620
C	1.300238	0.390731	-2.839380
C	1.806733	-0.838141	-3.284103
H	2.532347	-2.513221	-1.975889
H	0.943898	1.234032	-3.409922
H	1.951189	-1.163209	-4.303381
N	1.284389	0.434077	-1.503747
C	-0.429998	2.871092	1.016041

F	0.377285	3.514473	1.898802
F	-1.209055	2.043651	1.782866
F	-1.245762	3.834610	0.522362
H	-0.728154	-0.981360	0.071441
C	1.261493	3.418696	-1.203178
F	0.413829	4.004054	-2.106523
F	1.644172	4.444668	-0.369198
F	2.395111	3.125444	-1.923082

(C)
E(UB3LYP) = -1886.79738433
Zero-point correction= 0.255132 (Hartree/Particle)
Thermal correction to Energy= 0.283244
Thermal correction to Enthalpy= 0.284188
Thermal correction to Gibbs Free Energy= 0.191394
Sum of electronic and zero-point Energies= -1886.542253
Sum of electronic and thermal Energies= -1886.514140
Sum of electronic and thermal Enthalpies= -1886.513196
Sum of electronic and thermal Free Energies= -1886.605990
E(UB3LYP) = -1886.31093599

40
(C)

N	-0.329002	-1.591769	0.883947
C	-1.105522	-2.189950	1.802504
H	-2.176053	-2.238681	1.669845
C	-0.276782	-2.665966	2.812000
H	-0.568199	-3.207142	3.698499
C	1.014640	-2.307668	2.423080
C	3.877076	0.507130	1.647870
C	3.988172	1.865375	1.893318
H	4.812469	2.388058	2.355046
C	2.791990	2.410194	1.405172
H	2.463130	3.436222	1.393836
H	4.556061	-0.308846	1.848344
H	1.964151	-2.488807	2.904651
N	2.005686	1.449692	0.902290
C	-1.414215	1.234522	-0.949015
F	-1.636799	-0.144177	-1.199250
F	-2.590830	1.617264	-0.380227
F	-1.449793	1.796296	-2.205309
N	2.683698	0.272147	1.051921
N	0.971623	-1.649392	1.252354
B	2.207224	-1.055240	0.446215
H	3.087217	-1.863134	0.533673
Ni	0.269696	1.472598	-0.051403
N	1.827752	-0.822110	-1.015669
C	2.257815	-1.487973	-2.114580
C	1.078196	0.271158	-2.734257

C	1.798984	-0.821955	-3.238607
H	2.864045	-2.376340	-2.012516
H	0.541549	1.044515	-3.261293
H	1.965289	-1.082755	-4.273056
N	1.099576	0.268937	-1.396417
C	-0.571531	2.622645	1.221318
F	0.250525	3.268289	2.119653
F	-1.469813	1.959353	2.031904
F	-1.292055	3.658250	0.661504
H	-0.626257	-1.099214	0.039253
C	1.866022	4.288082	-1.928109
F	2.851284	3.402591	-1.878776
F	1.598065	4.778079	-0.723304
F	0.780085	3.771665	-2.487592

CF$_3$·
E(UB3LYP) = -337.547888258
Zero-point correction= 0.011982 (Hartree/Particle)
Thermal correction to Energy= 0.015442
Thermal correction to Enthalpy= 0.016386
Thermal correction to Gibbs Free Energy= -0.014746
Sum of electronic and zero-point Energies= -337.535906
Sum of electronic and thermal Energies= -337.532446
Sum of electronic and thermal Enthalpies= -337.531502
Sum of electronic and thermal Free Energies= -337.562635
E(UB3LYP) = -337.679772015

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CF$_3$

C	-0.404373	0.697838	0.028452
F	0.057529	1.350372	1.087905
F	0.057582	-0.545957	-0.006919
F	-1.730886	0.718499	-0.007167

DMSO
E(RB3LYP) = -553.191876389
Zero-point correction= 0.079967 (Hartree/Particle)
Thermal correction to Energy= 0.085598
Thermal correction to Enthalpy= 0.086542
Thermal correction to Gibbs Free Energy= 0.051645
Sum of electronic and zero-point Energies= -553.111909
Sum of electronic and thermal Energies= -553.106278
Sum of electronic and thermal Enthalpies= -553.105334
Sum of electronic and thermal Free Energies= -553.140231
E(RB3LYP) = -553.303548287

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DMSO

S	-0.612779	1.728626	-0.776974

C	0.213004	0.317452	0.040210
H	0.308005	0.516387	1.111697
H	-0.367838	-0.592342	-0.135628
H	1.203038	0.216208	-0.410654
C	-2.145638	1.682729	0.218033
H	-2.768052	2.519887	-0.106878
H	-2.668529	0.740093	0.032597
H	-1.899386	1.788605	1.278570
O	0.147381	2.990707	-0.383544

(TS-IV/I-H+)
E(UB3LYP) = -1886.79427390
Zero-point correction= 0.254785 (Hartree/Particle)
Thermal correction to Energy= 0.282188
Thermal correction to Enthalpy= 0.283133
Thermal correction to Gibbs Free Energy= 0.191597
Sum of electronic and zero-point Energies= -1886.539489
Sum of electronic and thermal Energies= -1886.512085
Sum of electronic and thermal Enthalpies= -1886.511141
Sum of electronic and thermal Free Energies= -1886.602677
E(UB3LYP) = -1886.30969388

40
(TS-IV/I-H+)

N	-0.374896	-1.609248	0.868058
C	-1.192674	-2.171393	1.773621
H	-2.259977	-2.194583	1.611373
C	-0.405556	-2.651085	2.814120
H	-0.735993	-3.169874	3.700311
C	0.905374	-2.331850	2.457372
C	3.893447	0.380121	1.684757
C	4.042007	1.739295	1.905035
H	4.879689	2.246938	2.359373
C	2.862170	2.308439	1.403896
H	2.558968	3.342657	1.375063
H	4.549536	-0.450390	1.901130
H	1.835704	-2.529372	2.969080
N	2.051609	1.360332	0.917232
C	-1.351765	1.256479	-0.963421
F	-1.625582	-0.104126	-1.243410
F	-2.524822	1.682679	-0.419692
F	-1.327741	1.844312	-2.211934
N	2.694681	0.167418	1.090923
N	0.913024	-1.692484	1.275633
B	2.184981	-1.149556	0.489155
H	3.035843	-1.985645	0.596905
Ni	0.321764	1.420785	-0.036308
N	1.834093	-0.915602	-0.979529
C	2.256788	-1.601174	-2.068794

C	1.114340	0.173546	-2.712936
C	1.816899	-0.937956	-3.202116
H	2.844149	-2.500620	-1.954177
H	0.592856	0.949310	-3.251325
H	1.983176	-1.212748	-4.232938
N	1.129023	0.185916	-1.374899
C	-0.499802	2.571505	1.249639
F	0.328766	3.161219	2.179486
F	-1.432986	1.914469	2.026617
F	-1.177643	3.644963	0.710648
H	-0.635319	-1.117140	0.011723
C	1.388417	4.543405	-1.948075
F	1.992549	5.541119	-2.576246
F	1.400858	4.727564	-0.632365
F	1.929011	3.374119	-2.273568

(TS-V/VI)
E(UB3LYP) = -2799.64259851
Zero-point correction= 0.459374 (Hartree/Particle)
Thermal correction to Energy= 0.503726
Thermal correction to Enthalpy= 0.504671
Thermal correction to Gibbs Free Energy= 0.376236
Sum of electronic and zero-point Energies= -2799.183225
Sum of electronic and thermal Energies= -2799.138872
Sum of electronic and thermal Enthalpies= -2799.137928
Sum of electronic and thermal Free Energies= -2799.266363
E(UB3LYP) = -2799.49683454

67
(TS-V/VI)

N	0.481012	1.175219	-0.956249
C	1.111930	1.425626	-2.110182
H	1.666199	0.635302	-2.602179
C	0.947773	2.766167	-2.507867
H	1.344147	3.260888	-3.383229
C	0.165947	3.317295	-1.504806
C	-0.316159	1.499472	2.913196
C	-0.495018	0.299913	3.584451
H	-0.197697	0.056727	4.593669
C	-1.145139	-0.525275	2.657774
H	-1.490193	-1.540752	2.766299
H	0.131924	2.429881	3.230227
H	-0.214259	4.321673	-1.376925
N	-1.339348	0.125630	1.502894
C	-3.926823	-1.267088	0.842612
F	-4.982156	-1.675559	0.059034
F	-3.597170	-2.386858	1.578754
F	-4.498952	-0.423449	1.771236

N	-0.828238	1.379265	1.667206
N	-0.100355	2.349174	-0.591156
B	-1.022816	2.508574	0.641057
H	-0.793593	3.566974	1.168499
Ni	-2.381070	-0.398562	-0.202809
N	-2.525292	2.524650	0.234225
C	-3.361628	3.586024	0.253012
C	-4.484558	1.790558	-0.355743
C	-4.629492	3.162990	-0.121617
H	-2.994377	4.562062	0.535227
H	-5.219542	1.060637	-0.655069
H	-5.526891	3.757771	-0.205713
N	-3.215734	1.415305	-0.144102
C	-2.874551	-0.473895	-2.122429
C	-1.496576	-2.095949	-0.416142
F	-2.315382	0.607060	-2.763930
F	-2.533189	-1.539079	-2.902907
F	-4.225552	-0.342274	-2.308812
F	-0.447801	-2.016461	-1.292023
F	-2.288785	-3.107534	-0.868140
F	-0.944755	-2.585017	0.734487
C	5.188916	-0.946084	-1.166917
C	5.111557	0.431907	-0.836746
C	4.082185	0.866073	-0.042434
C	3.073305	-0.080766	0.567967
C	3.168560	-1.489247	0.026192
C	4.207155	-1.892018	-0.764808
H	5.832889	1.127037	-1.238901
H	2.063944	0.303494	0.334728
H	4.300222	-2.903171	-1.137052
O	2.148436	-2.235133	0.400101
O	3.852203	2.118910	0.291427
O	6.150380	-1.450880	-1.909255
C	2.058211	-3.603727	-0.048464
H	1.116231	-3.965651	0.354503
H	2.039559	-3.636193	-1.140613
H	2.899249	-4.182234	0.341982
C	7.223872	-0.624520	-2.417360
H	7.870365	-1.311346	-2.959960
H	6.826432	0.134190	-3.095250
H	7.769972	-0.164225	-1.590964
C	4.728313	3.164917	-0.183306
H	4.701116	3.204879	-1.275128
H	4.327178	4.083578	0.239855
H	5.746399	2.993349	0.174843
C	3.220929	-0.073244	2.112064
F	4.479122	-0.408692	2.469054
F	2.960624	1.142944	2.616943
F	2.385403	-0.942191	2.696146

(TS-VI/IV)
E(UB3LYP) = -2799.63751301
Zero-point correction= 0.455127 (Hartree/Particle)
Thermal correction to Energy= 0.499394
Thermal correction to Enthalpy= 0.500338
Thermal correction to Gibbs Free Energy= 0.374811
Sum of electronic and zero-point Energies= -2799.182386
Sum of electronic and thermal Energies= -2799.138119
Sum of electronic and thermal Enthalpies= -2799.137175
Sum of electronic and thermal Free Energies= -2799.262702
E(UB3LYP) = -2799.49350189

67
(TS-VI/IV)

N	0.257728	-1.158771	2.231874
C	-0.929578	-1.756977	2.404138
H	-1.467785	-1.639215	3.334727
C	-1.278008	-2.478382	1.259174
H	-2.169799	-3.061393	1.084872
C	-0.220746	-2.267437	0.385962
C	3.550465	0.940823	1.101237
C	3.632092	2.265518	0.702595
H	4.370258	2.998336	0.992485
C	2.536352	2.442561	-0.151507
H	2.225495	3.320426	-0.694444
H	4.171423	0.361830	1.766878
H	-0.066914	-2.625865	-0.620110
N	1.837700	1.305541	-0.258764
C	1.050240	1.852533	-3.199058
F	0.821286	1.228037	-4.412134
F	0.486848	3.097298	-3.353638
F	2.408811	2.092193	-3.200133
N	2.463354	0.379122	0.525001
N	0.695101	-1.464544	0.980631
B	2.132844	-1.123544	0.454399
H	2.961349	-1.726741	1.081748
Ni	0.399782	0.754679	-1.583028
N	2.206612	-1.538125	-1.028690
C	2.943140	-2.524492	-1.588686
C	1.928706	-1.379419	-3.177709
C	2.792872	-2.462079	-2.965807
H	3.521669	-3.191779	-0.966325
H	1.551950	-0.967430	-4.100410
H	3.247897	-3.099891	-3.708820
N	1.578265	-0.826946	-2.010018
C	-1.177625	-0.061280	-2.414601
C	-0.776440	2.094442	-0.833029
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F	-2.170196	-0.319842	-1.500867
F	-1.764639	0.673157	-3.398781
F	-1.200952	1.650411	0.397606
F	-1.904520	2.445365	-1.500037
F	-0.143883	3.280365	-0.587942
C	-1.552049	0.686035	5.817129
C	-0.804769	-0.477165	6.097225
C	0.410557	-0.653628	5.464475
C	0.918416	0.280804	4.444705
C	0.087295	1.482885	4.231820
C	-1.117602	1.647838	4.879843
H	-1.166817	-1.205685	6.806709
H	0.726443	-0.380716	3.302957
H	-1.763426	2.493886	4.689278
O	0.538425	2.308099	3.290900
O	1.211321	-1.695007	5.671783
O	-2.721873	0.957238	6.387782
C	-0.255240	3.442675	2.898212
H	0.296448	3.904488	2.081763
H	-1.233104	3.115341	2.537840
H	-0.362283	4.140770	3.733115
C	-3.286872	0.054262	7.356574
H	-4.226269	0.514140	7.659577
H	-3.478945	-0.922917	6.904754
H	-2.624812	-0.045975	8.220904
C	0.852073	-2.696540	6.640837
H	-0.078043	-3.192729	6.349998
H	1.674569	-3.409983	6.631664
H	0.753072	-2.248950	7.633679
C	2.437961	0.455958	4.533993
F	2.856777	0.537501	5.821048
F	3.089433	-0.595696	3.979296
F	2.888535	1.561056	3.920590

IX. References

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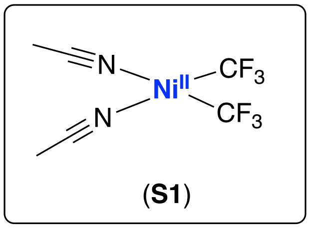
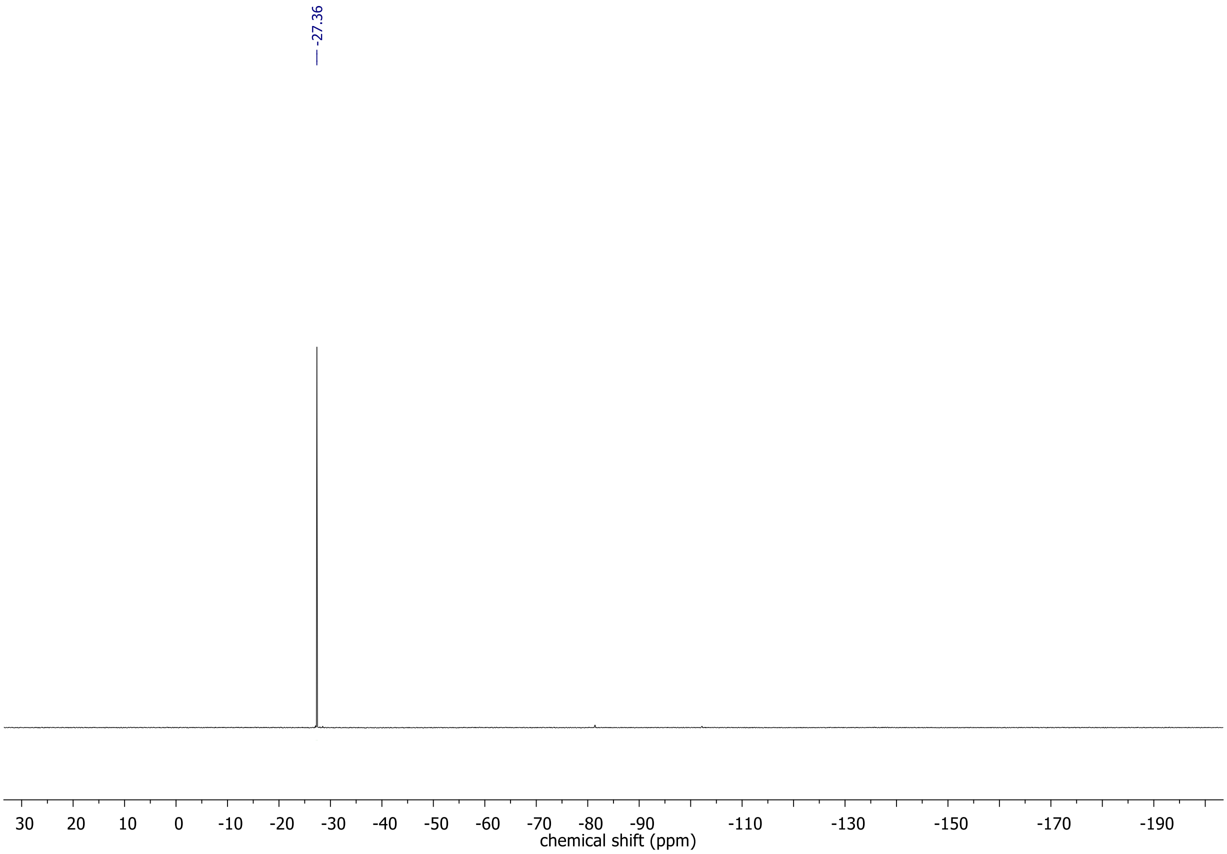
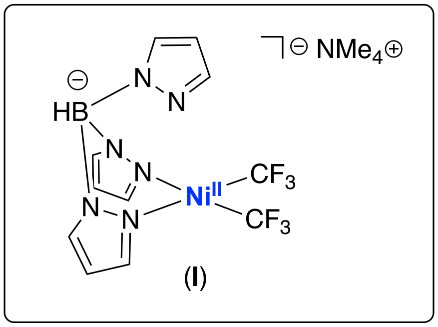
X. Spectral Data

^{19}F NMR Spectrum of S1 at 23 °C (CD_3CN)





^{1}H NMR Spectrum of I at 23 °C (acetone-d_6)



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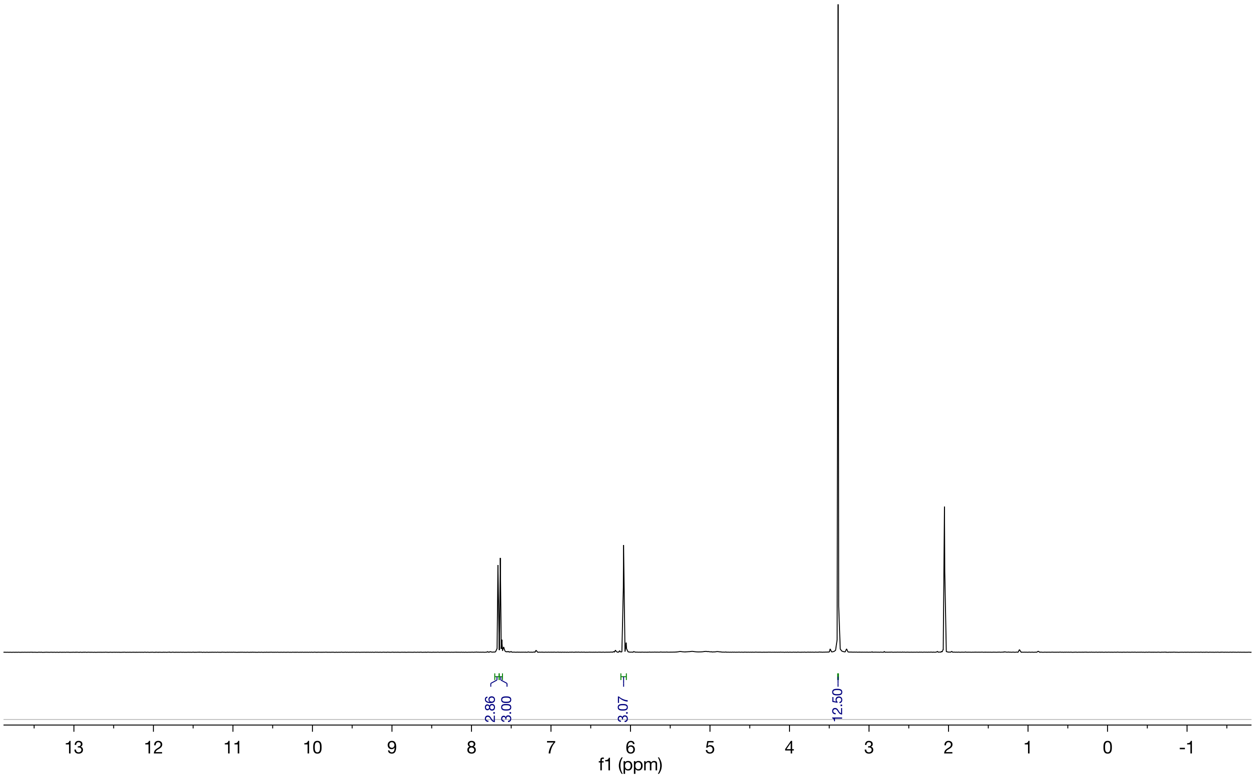

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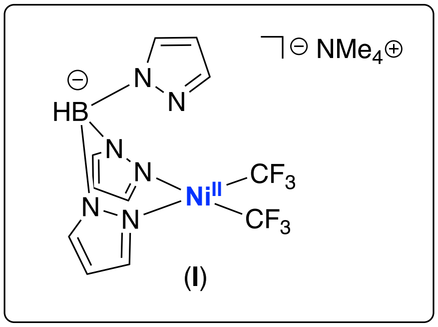

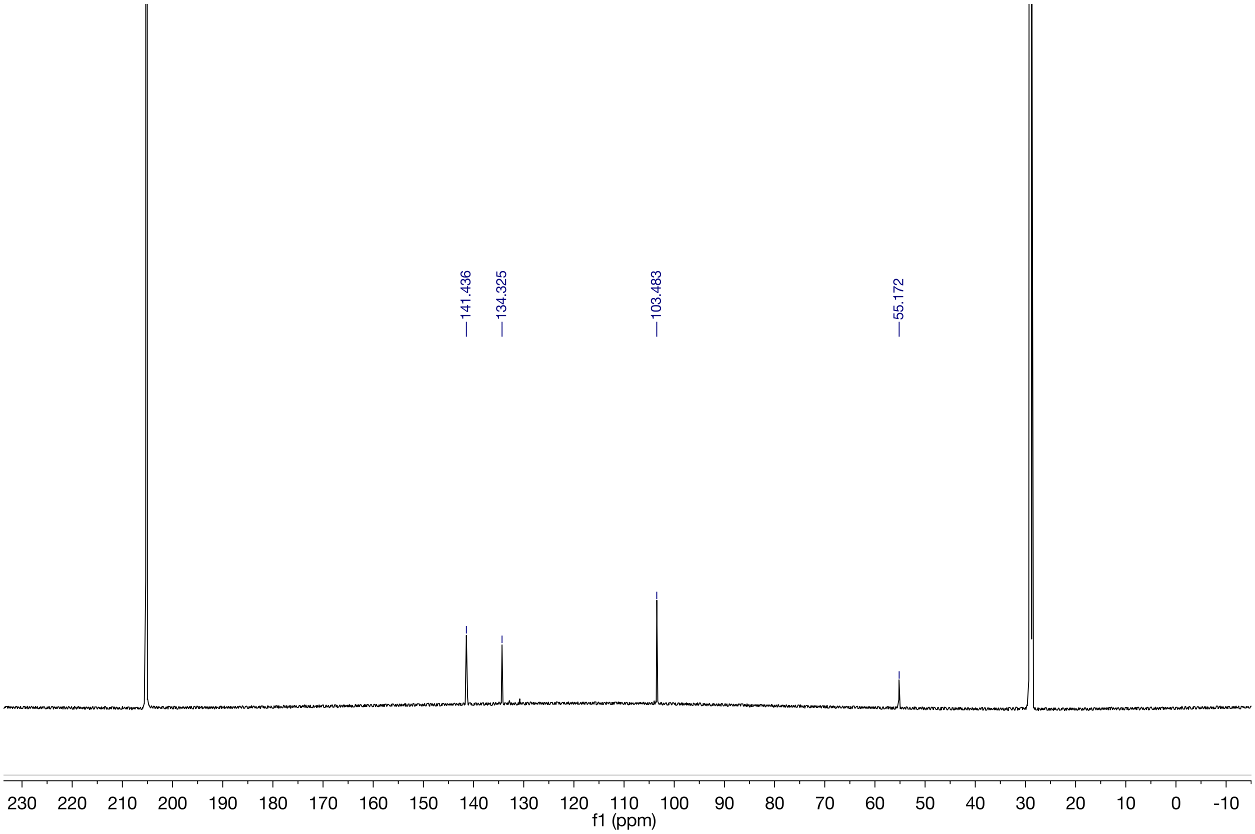

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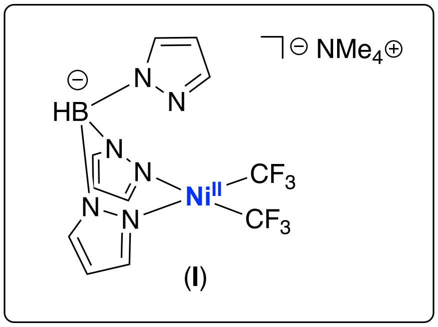

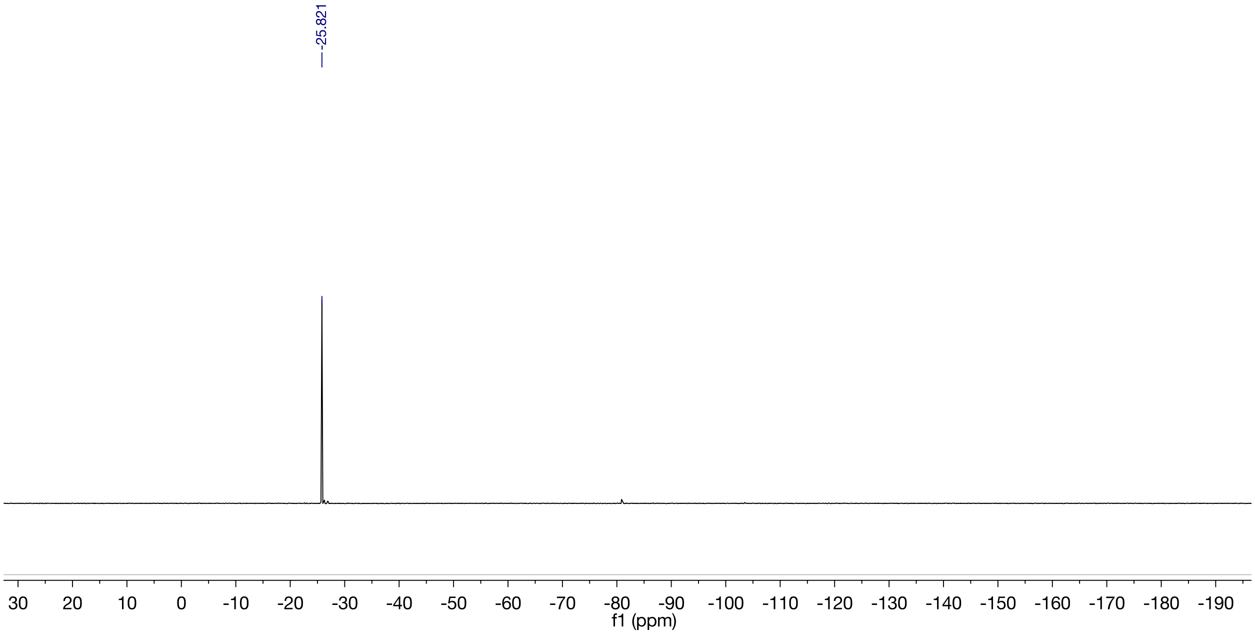

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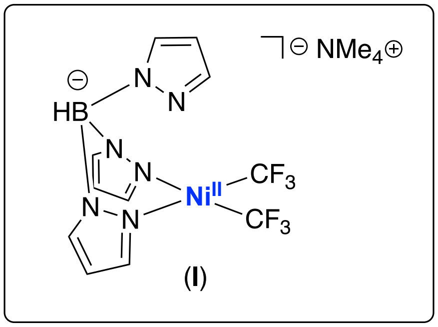

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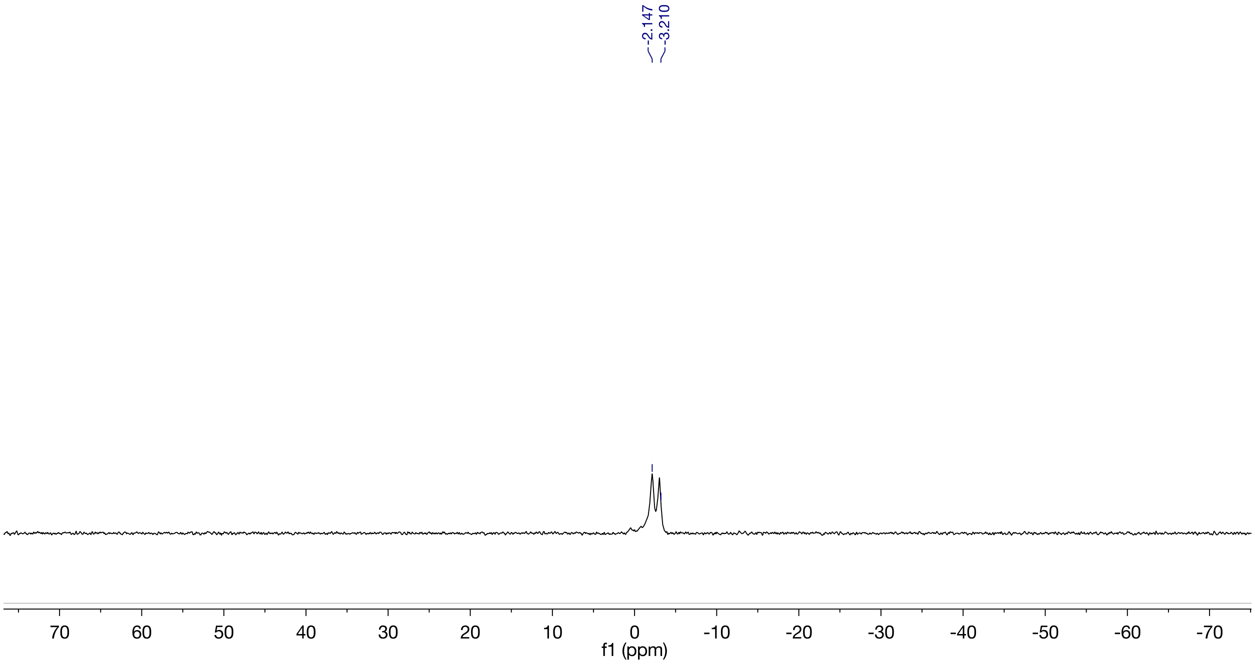

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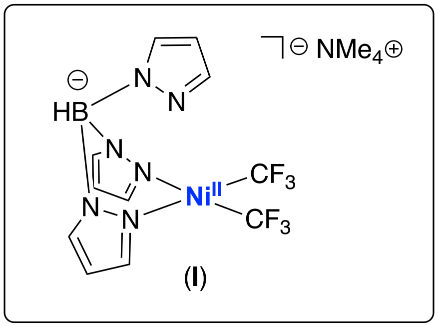

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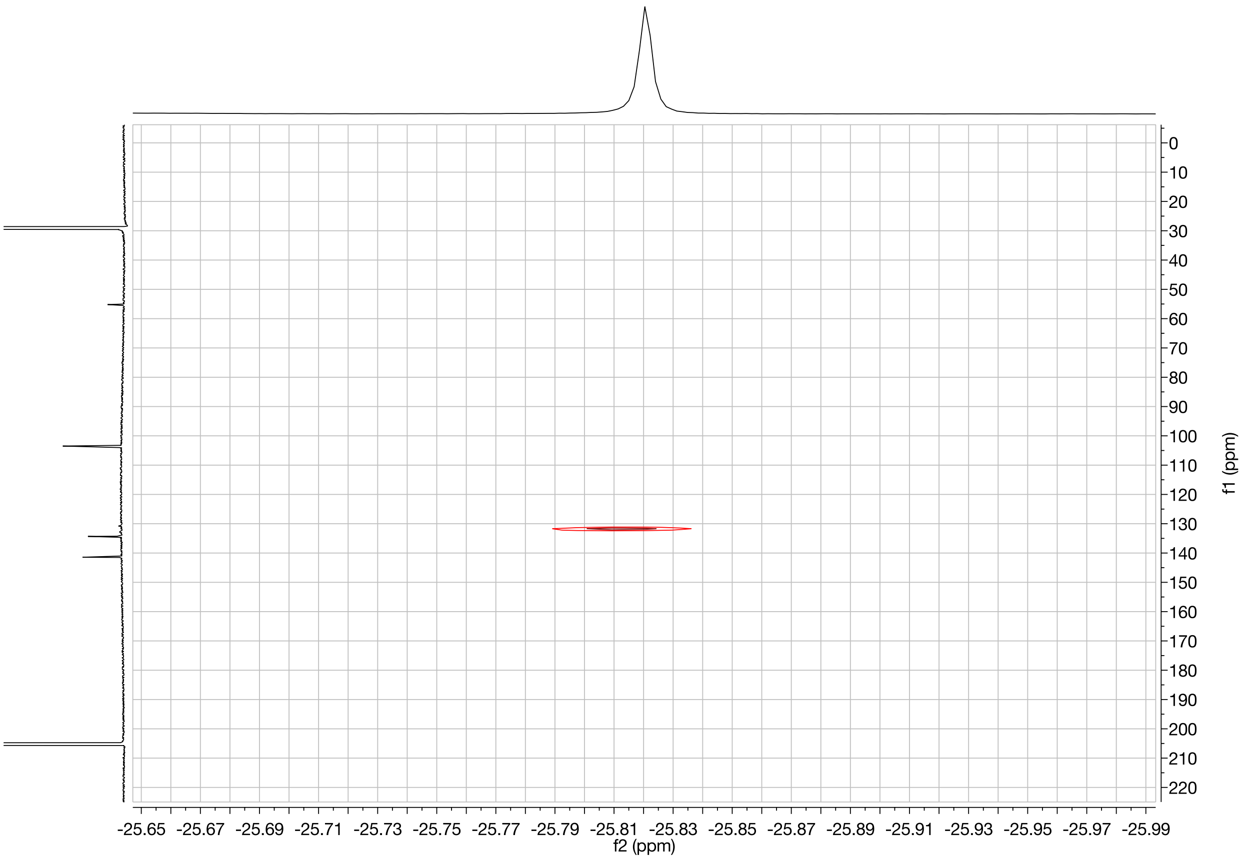

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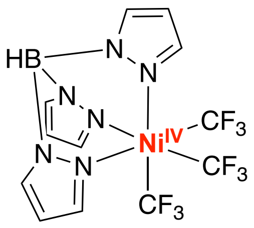

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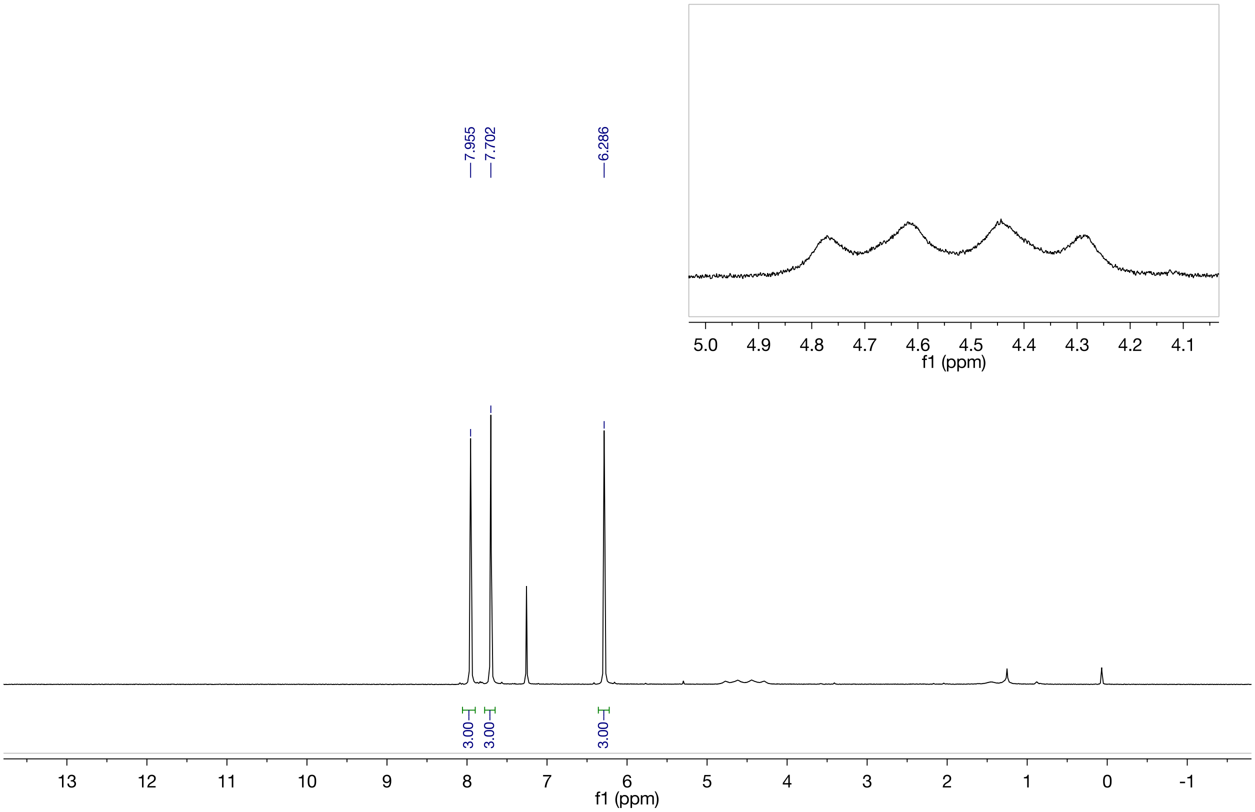

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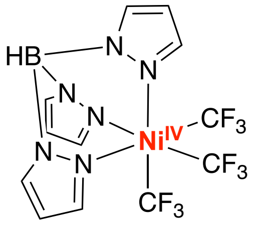

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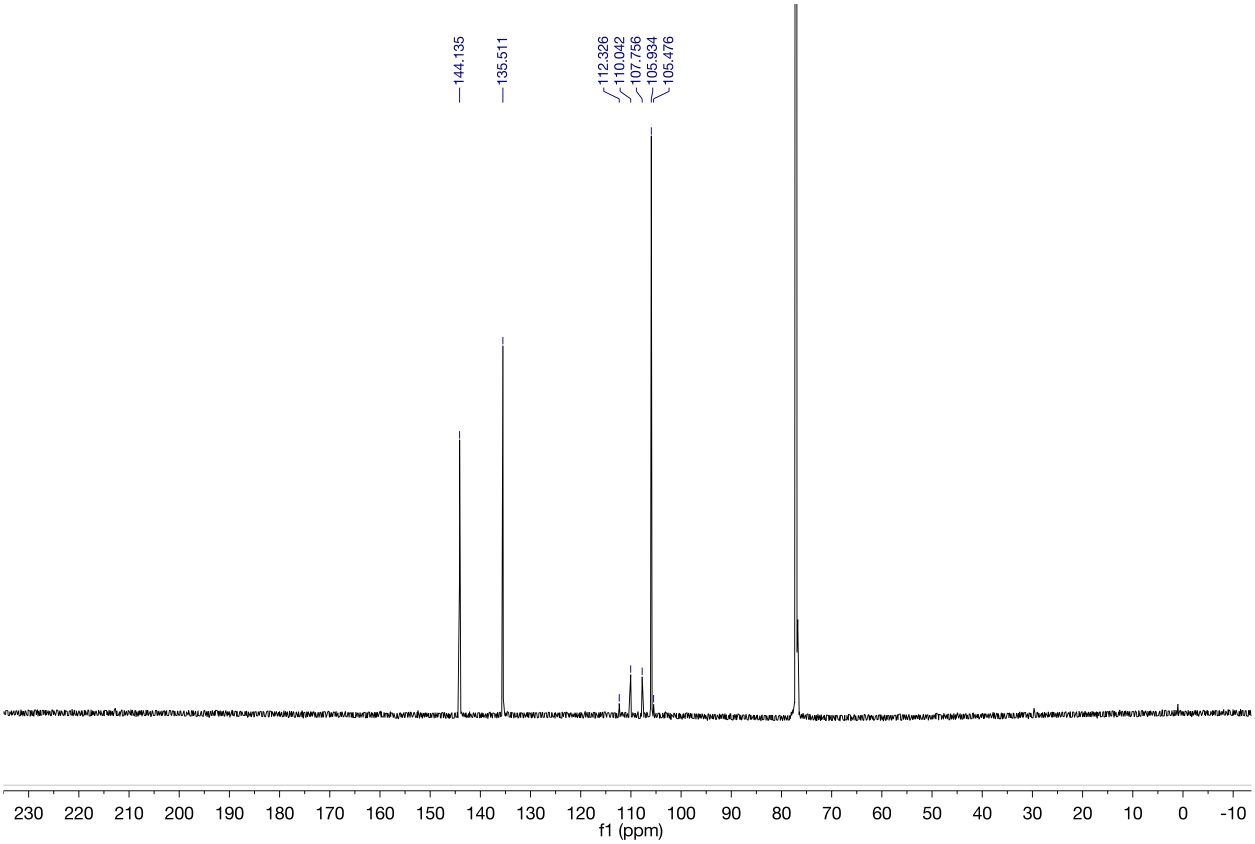

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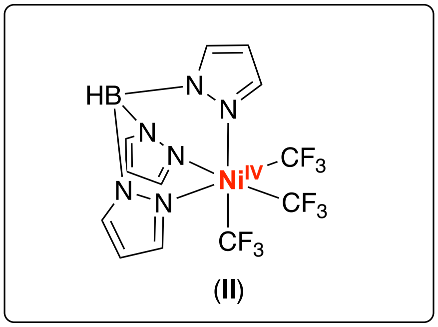

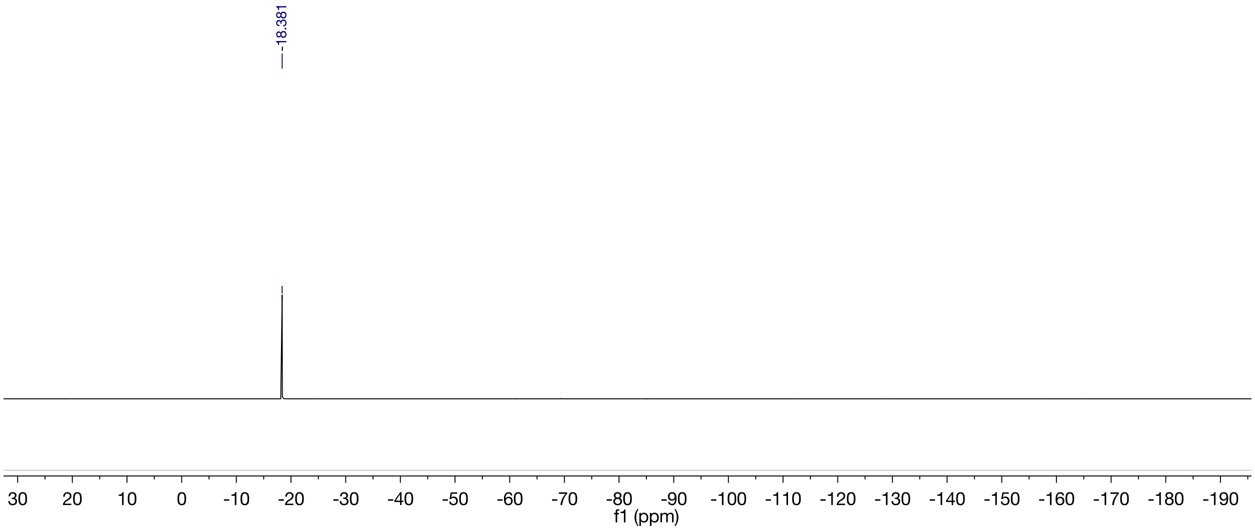

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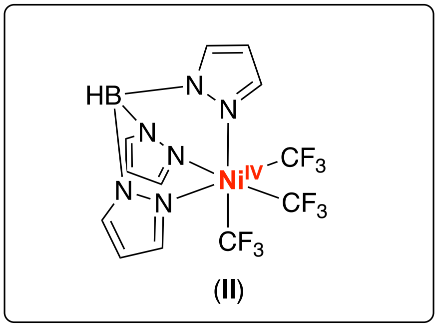

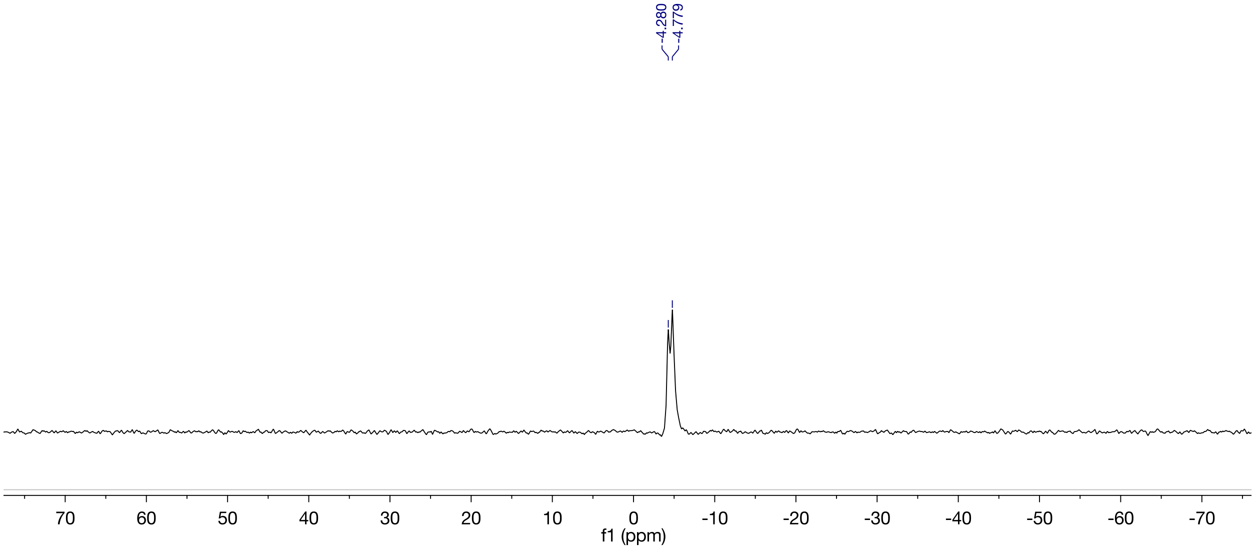

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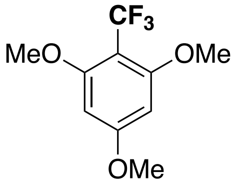

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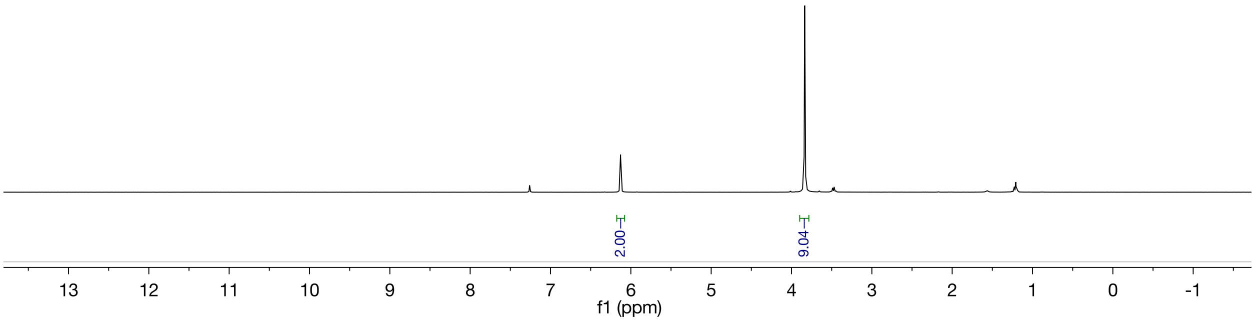

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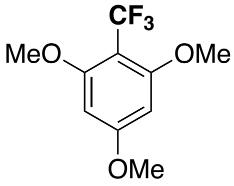

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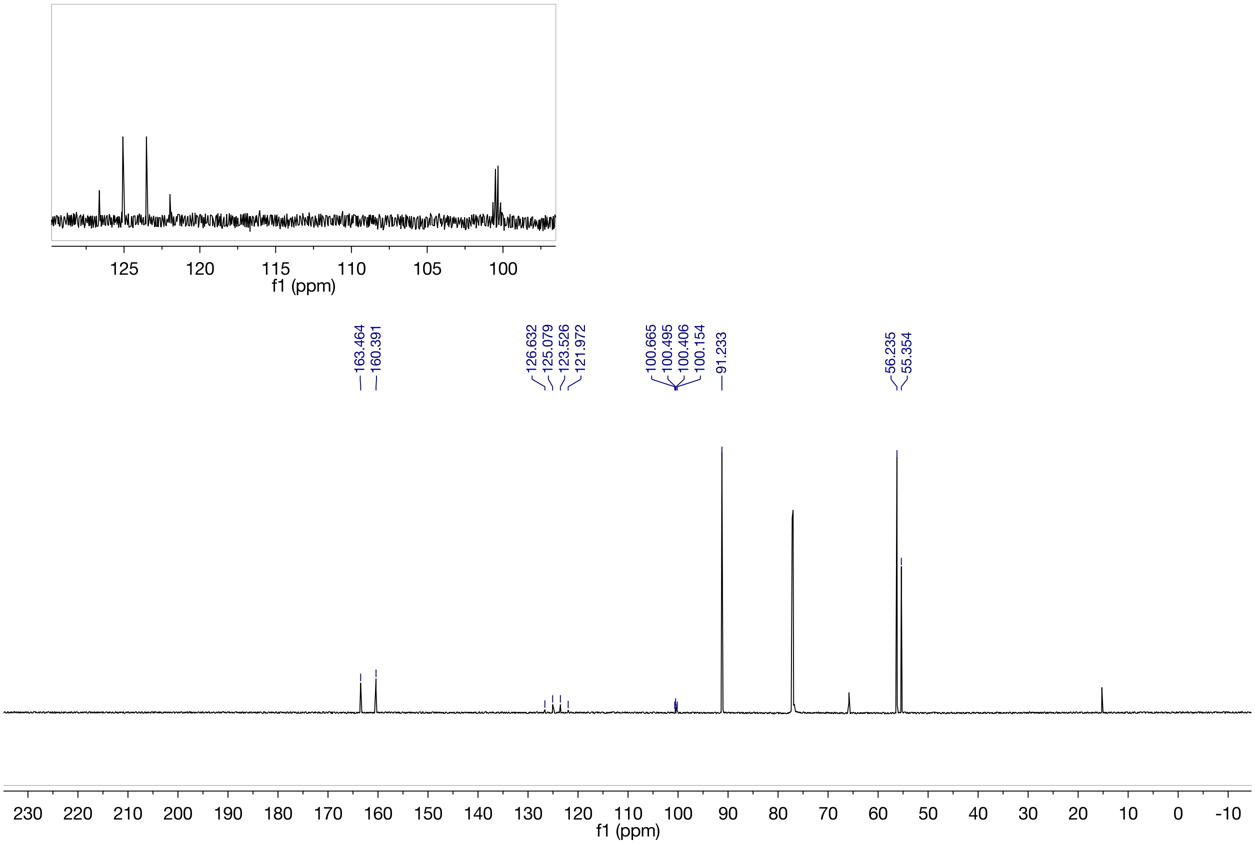
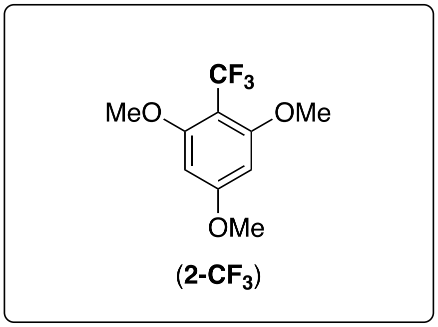


^{19}F NMR Spectrum of 2-CF$_3$ at 23 °C ($CDCl_3$)



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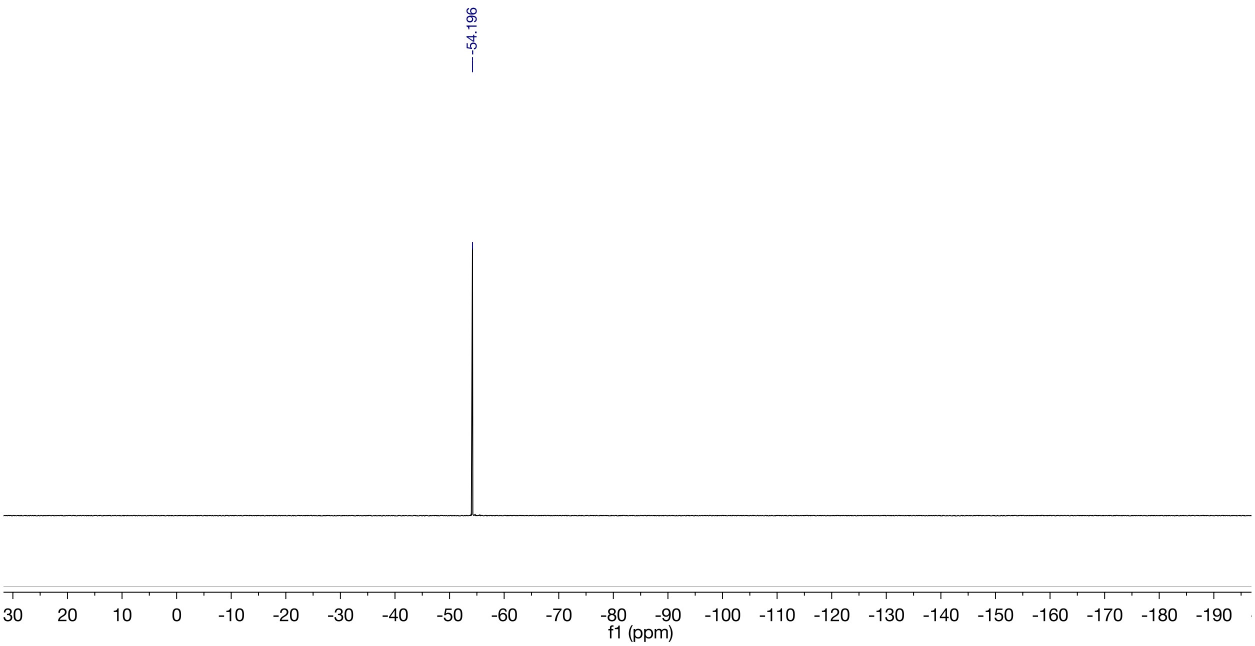

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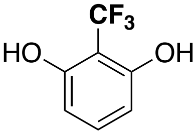

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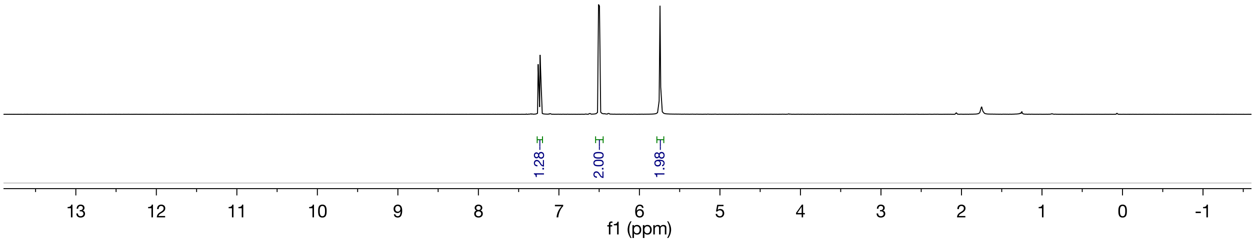

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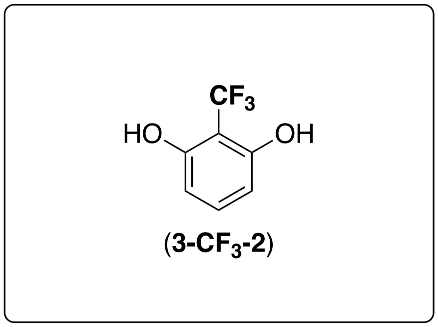

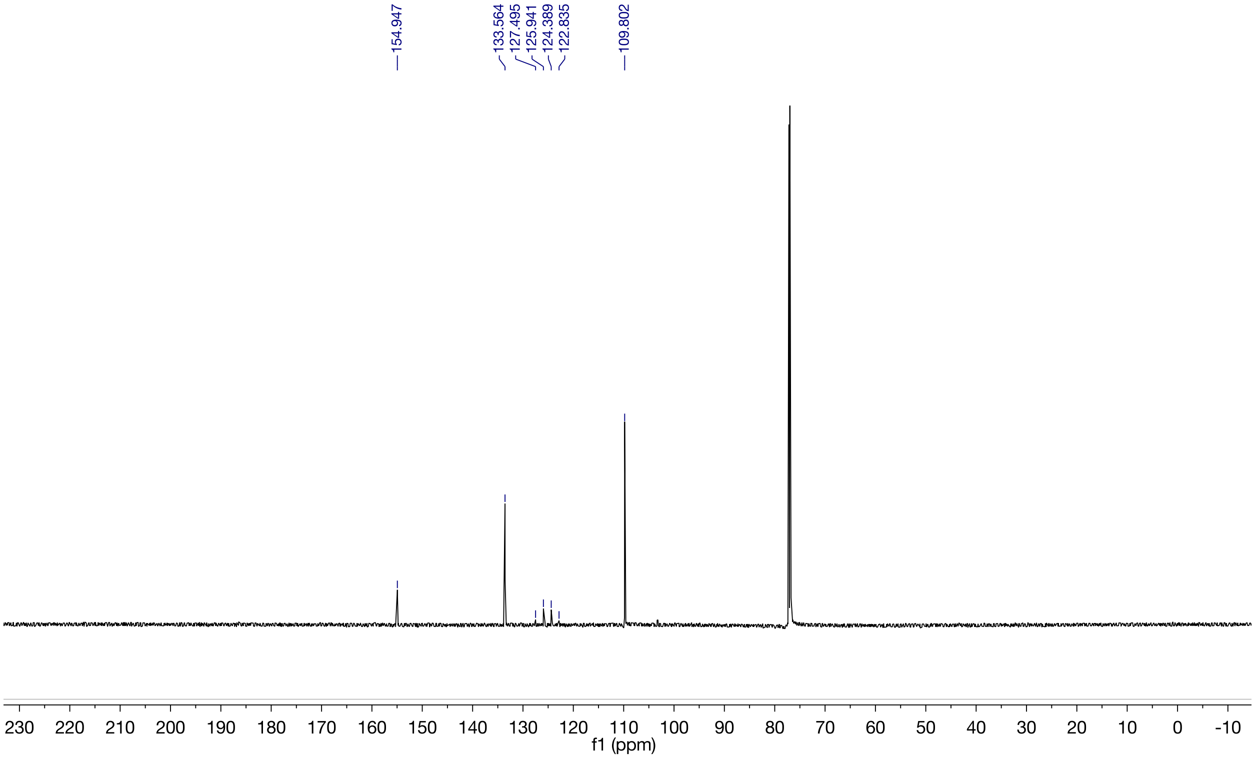

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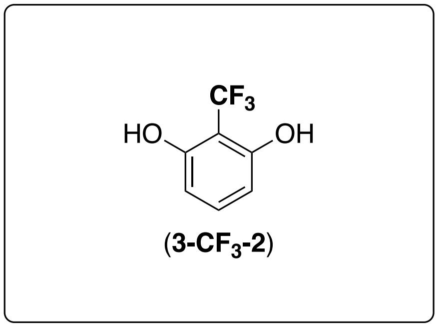
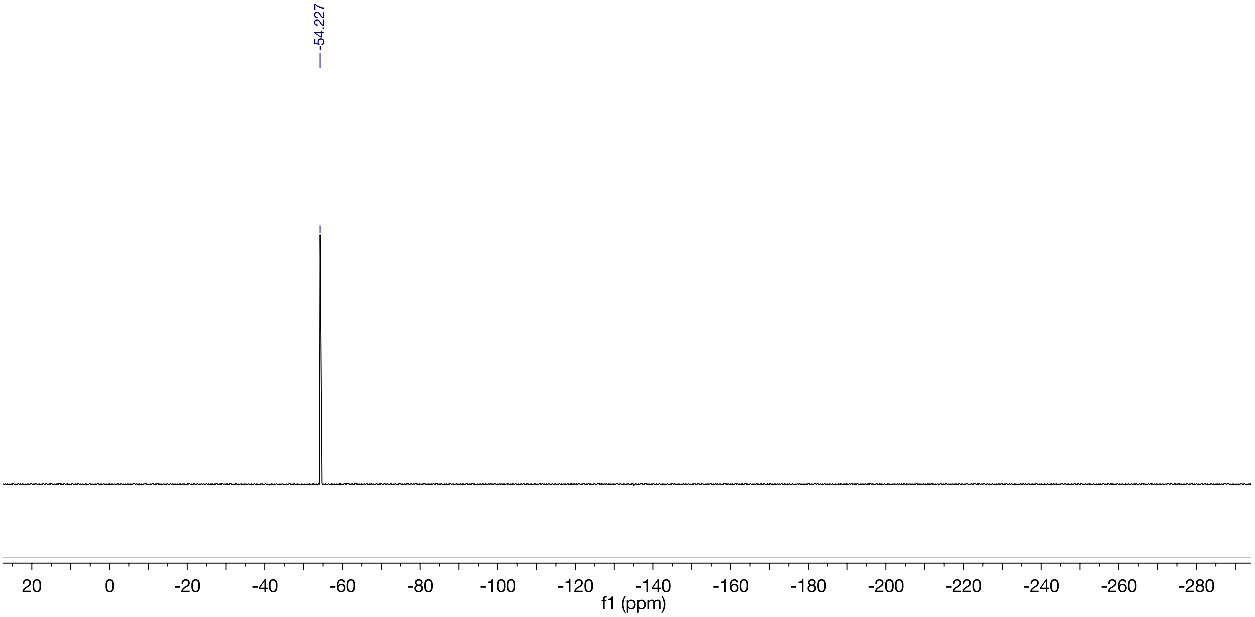

(**3-CF$_3$-2**)



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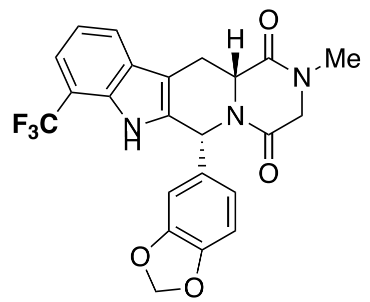

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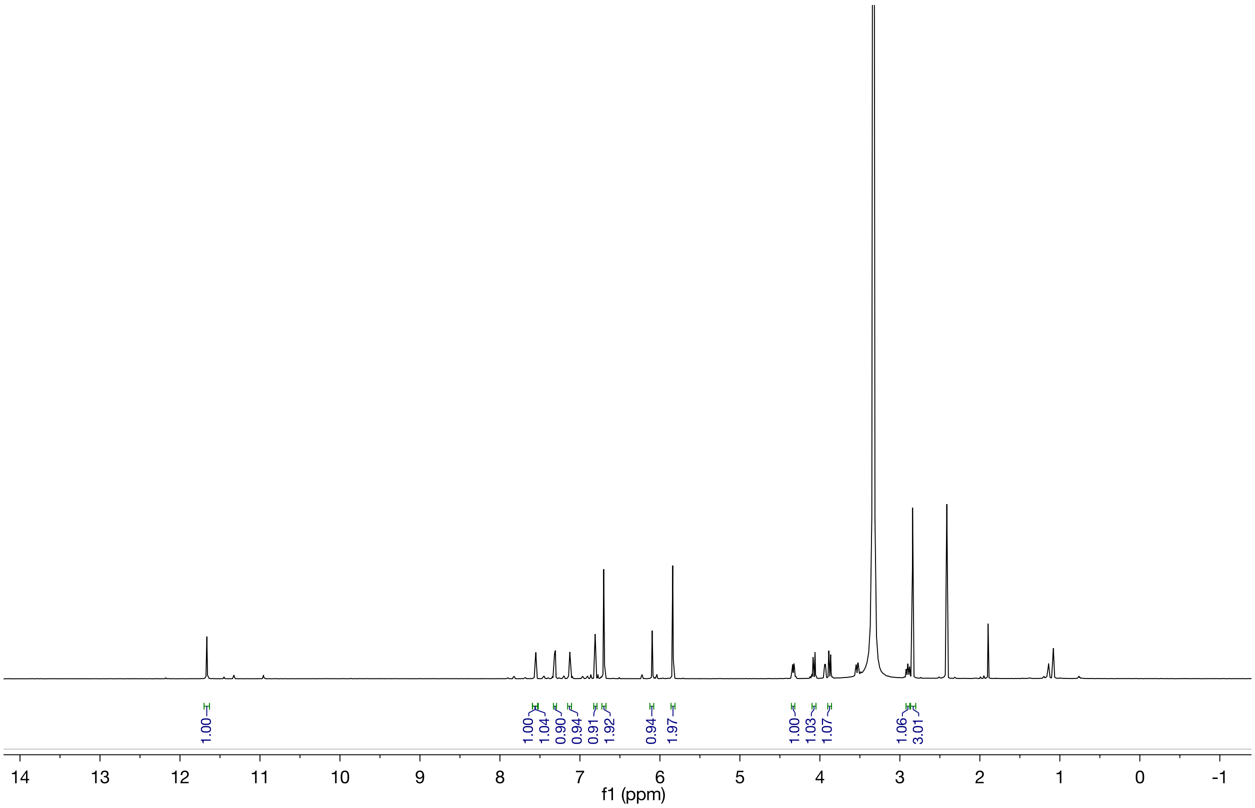

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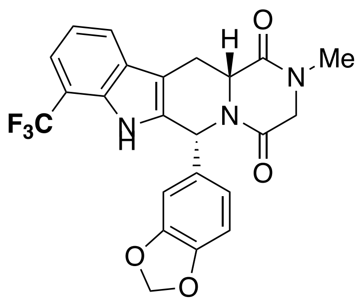
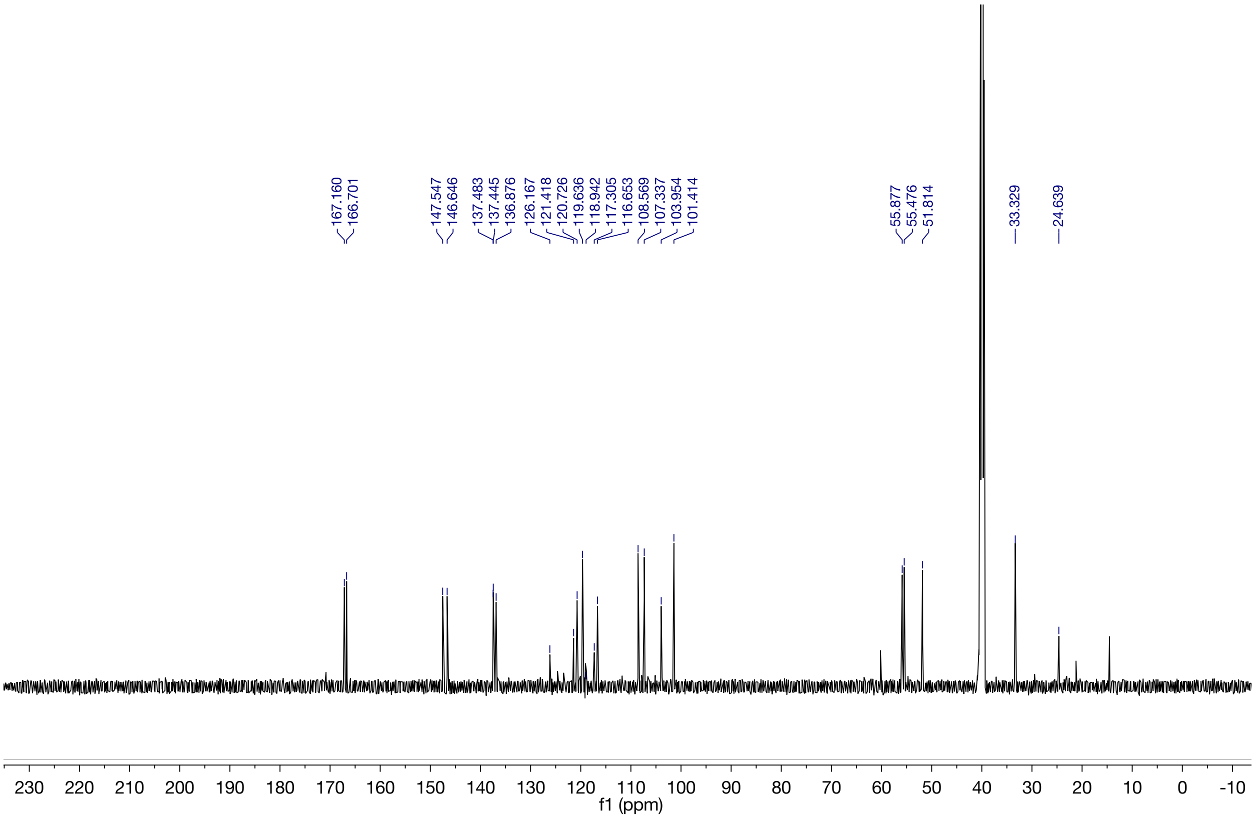


(**4-CF$_3$**)



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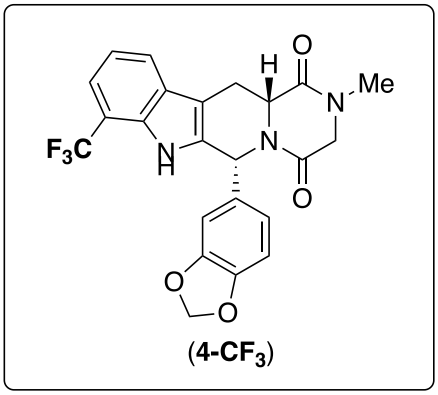
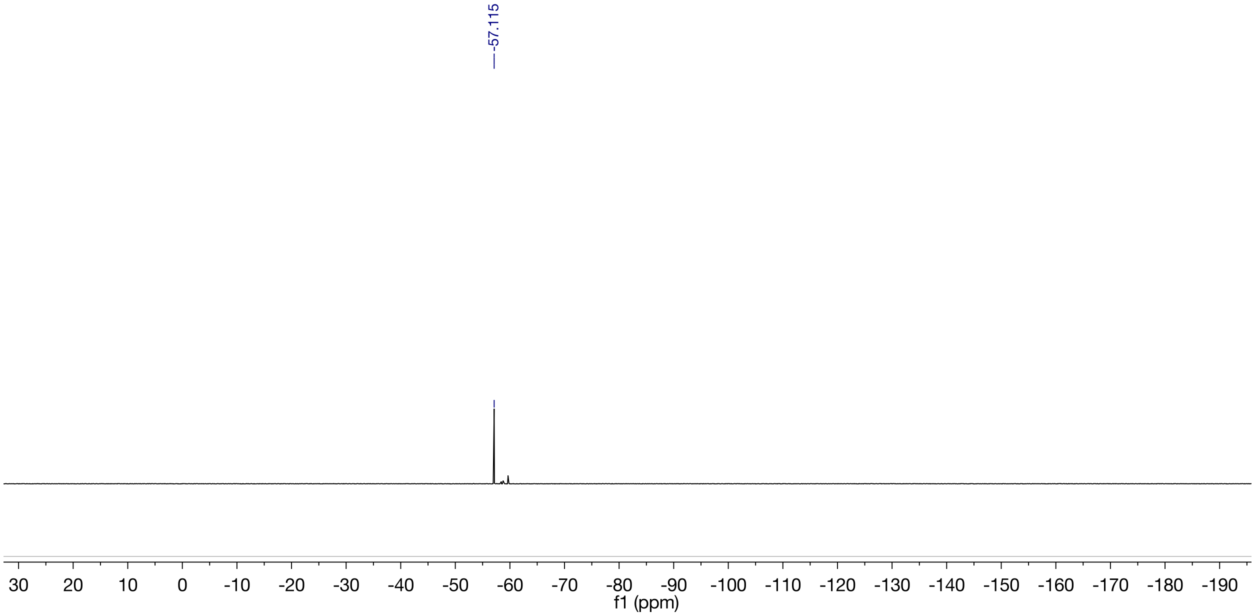


(**4-CF$_3$**)



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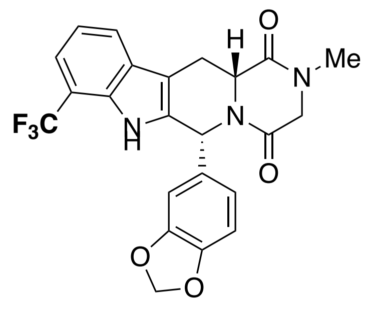
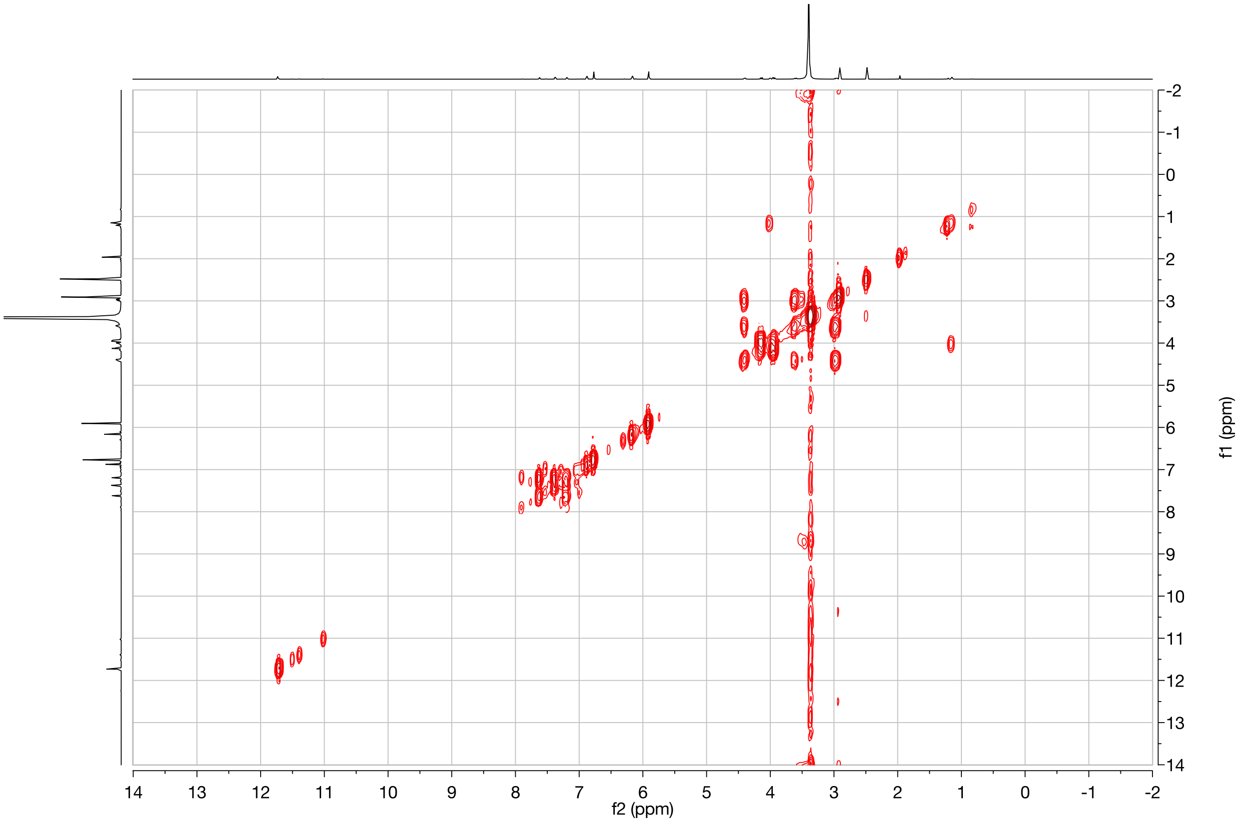
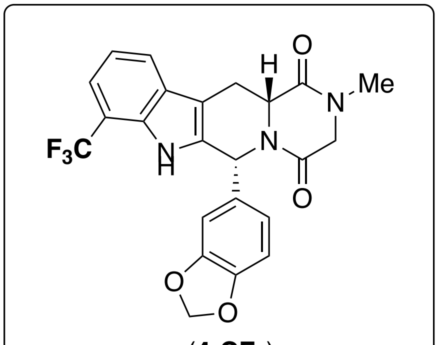


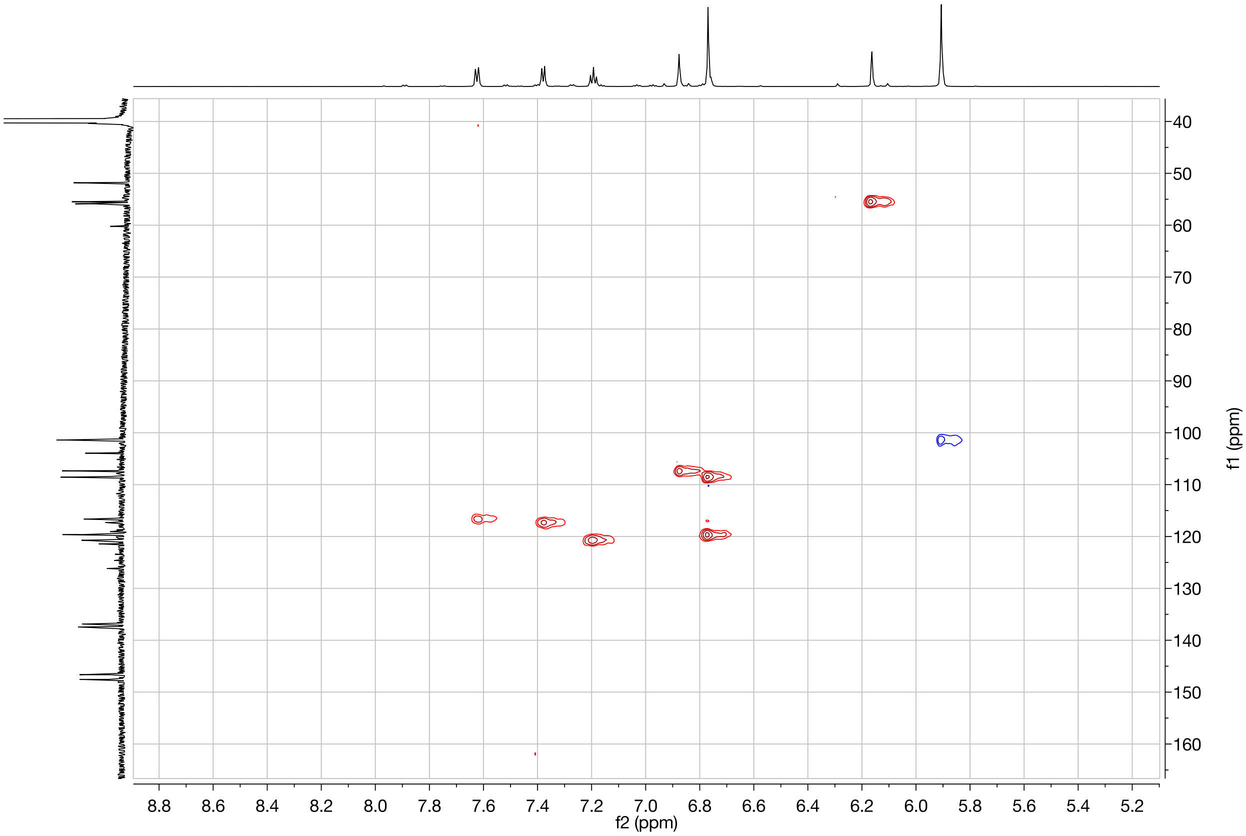
(**4-CF$_3$**)



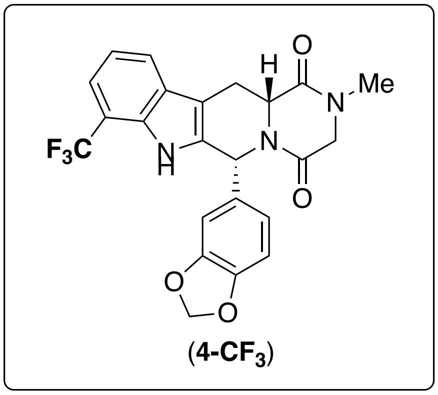
^{1}H–^{13}C HSQC Spectrum of 4-CF$_3$ at 23 °C (DMSO-d_6)



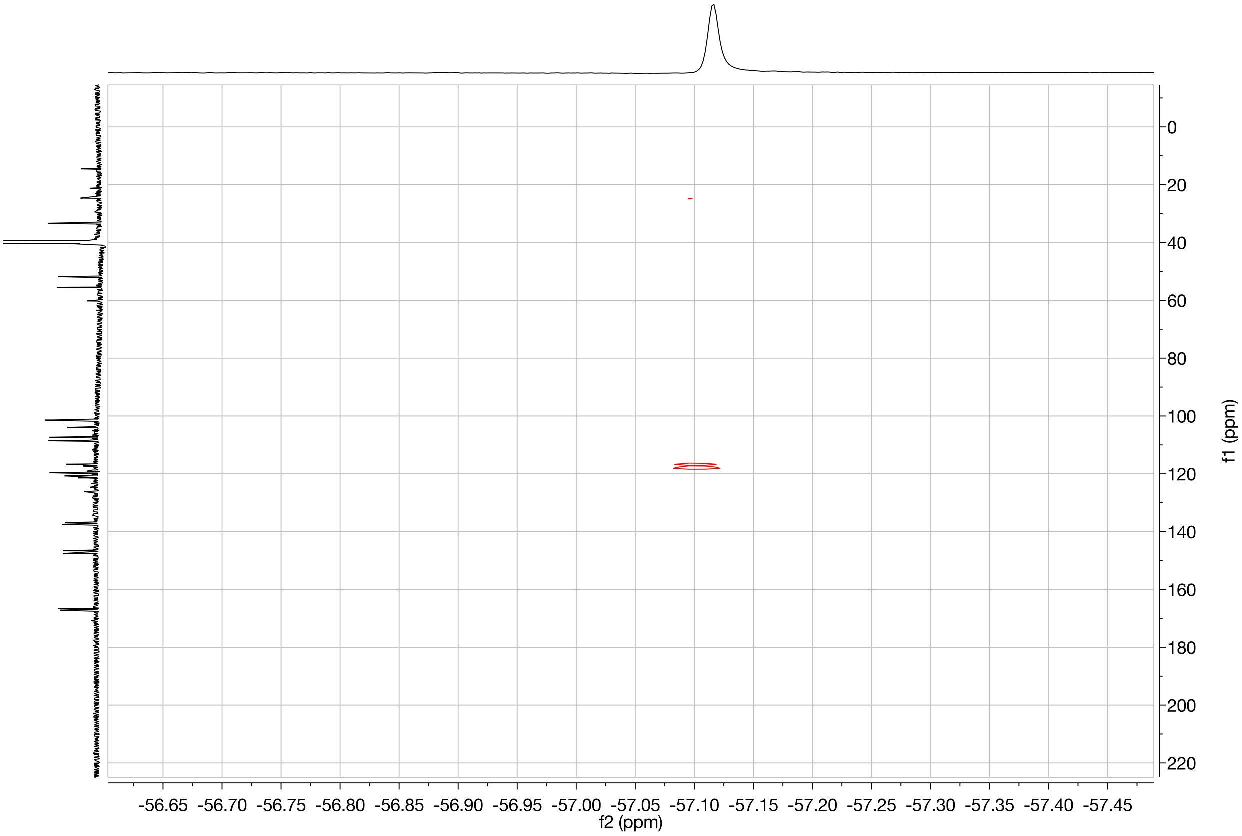
(**4-CF$_3$**)



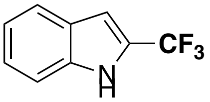
^{19}F–^{13}C HMBC Spectrum of 4-CF$_3$ at 23 °C (DMSO-d_6)



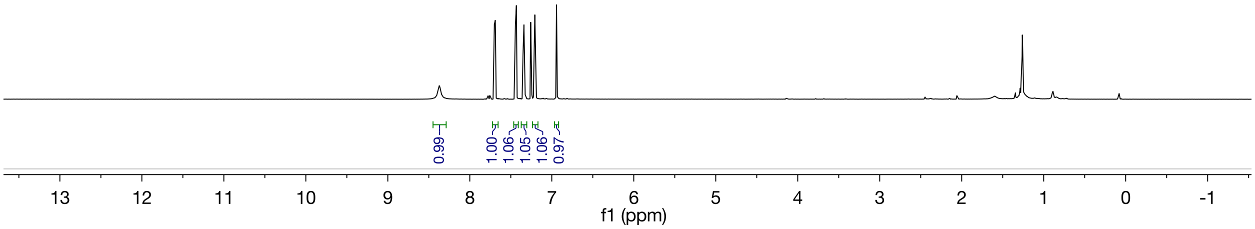
(**4-CF$_3$**)



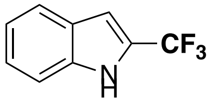
^{1}H NMR Spectrum of 5-CF$_3$-2 at 23 °C (CDCl$_3$)



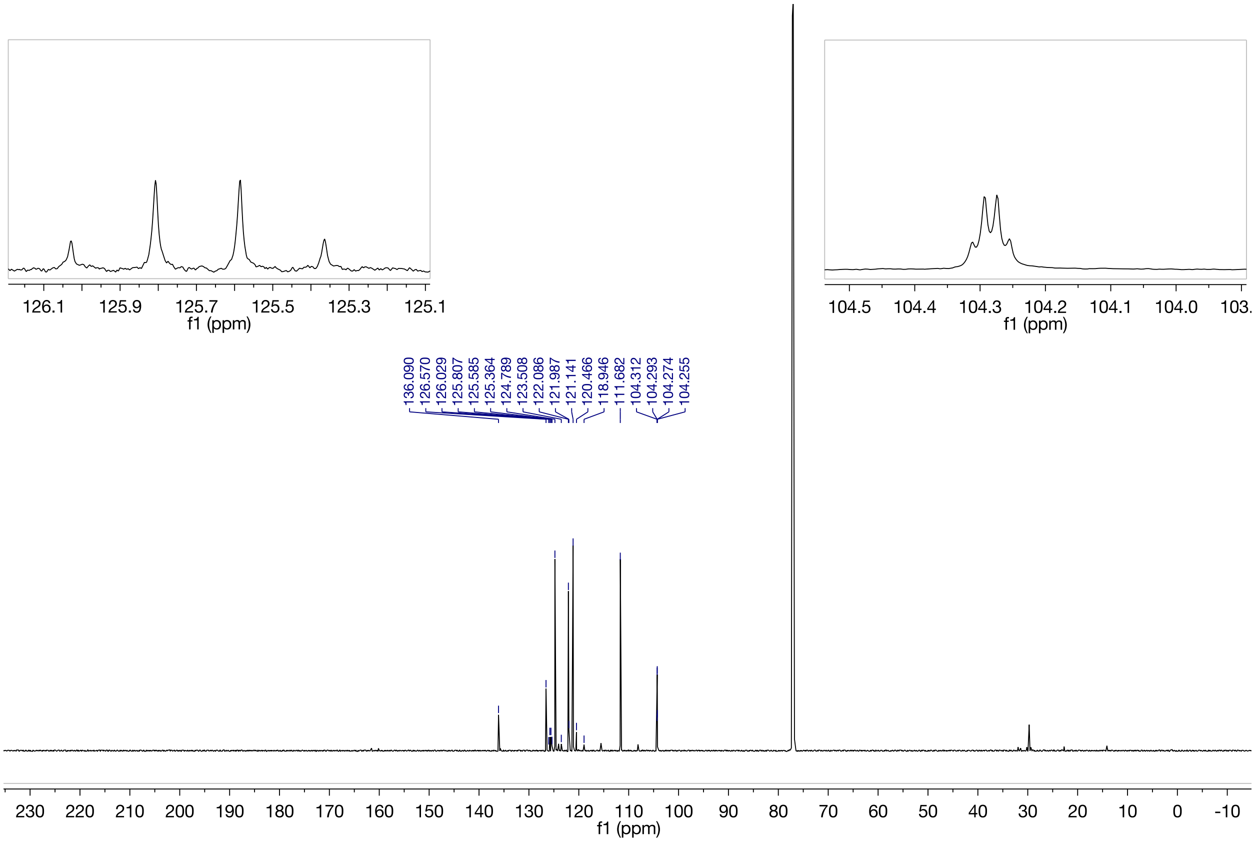
(**5-CF$_3$-2**)



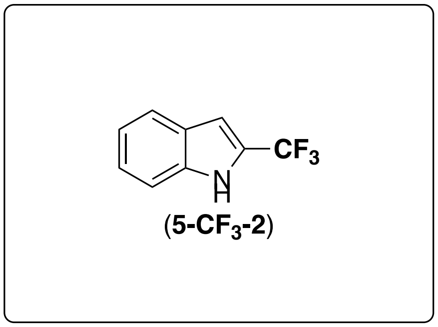
^{13}C NMR Spectrum of 5-CF$_3$-2 at 23 °C (CDCl$_3$)



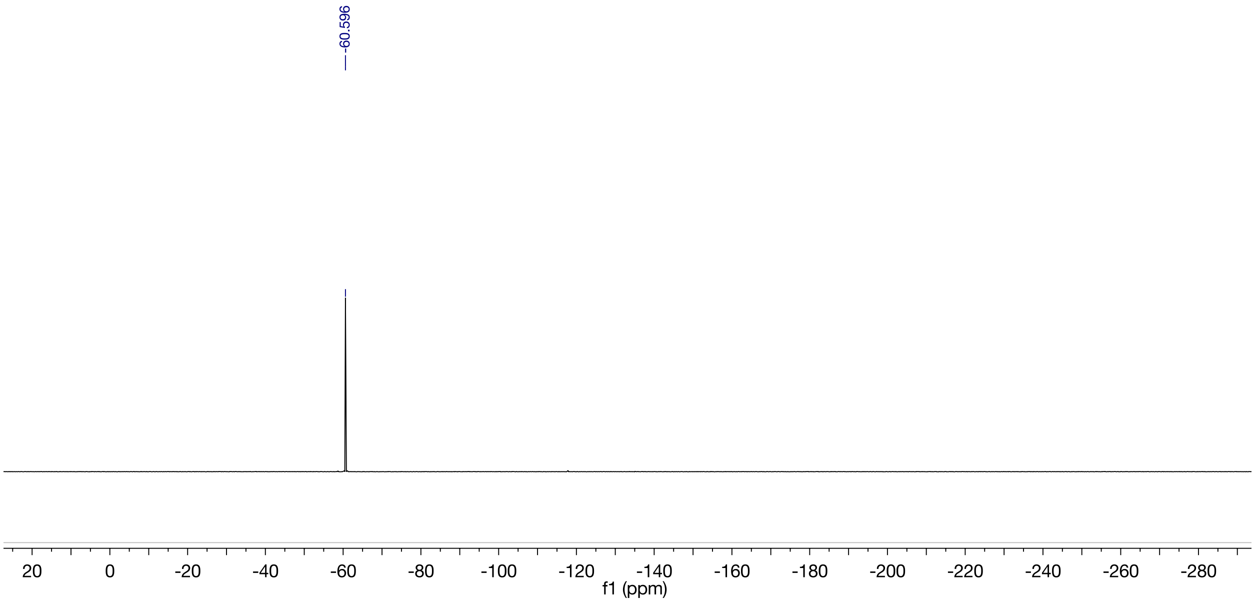
(**5-CF$_3$-2**)



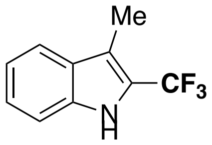
^{19}F NMR Spectrum of 5-CF$_3$-2 at 23 °C (CDCl$_3$)



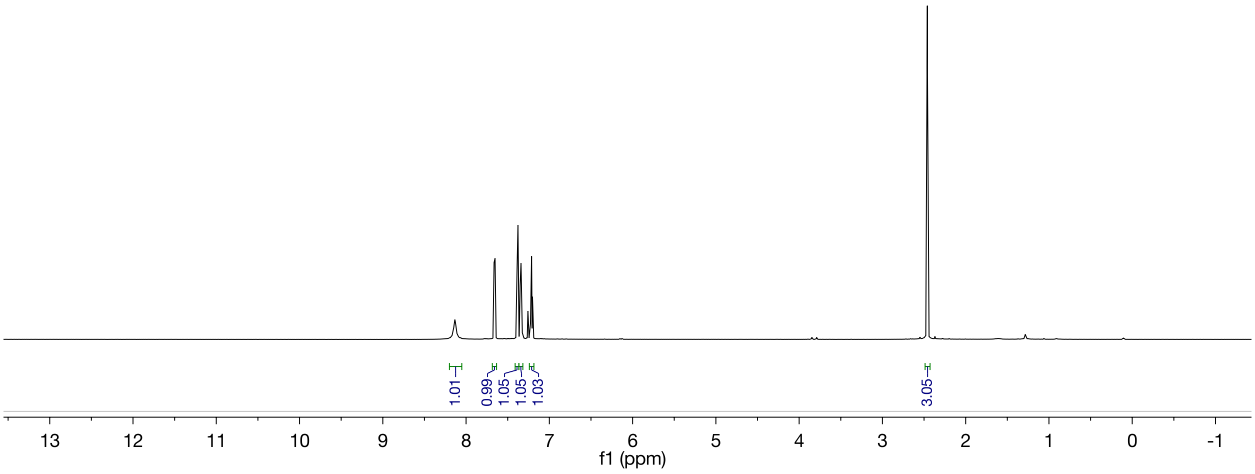
(**5-CF$_3$-2**)



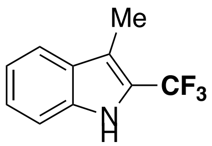
^{1}H NMR Spectrum of 6-CF$_3$ at 23 °C (CDCl$_3$)



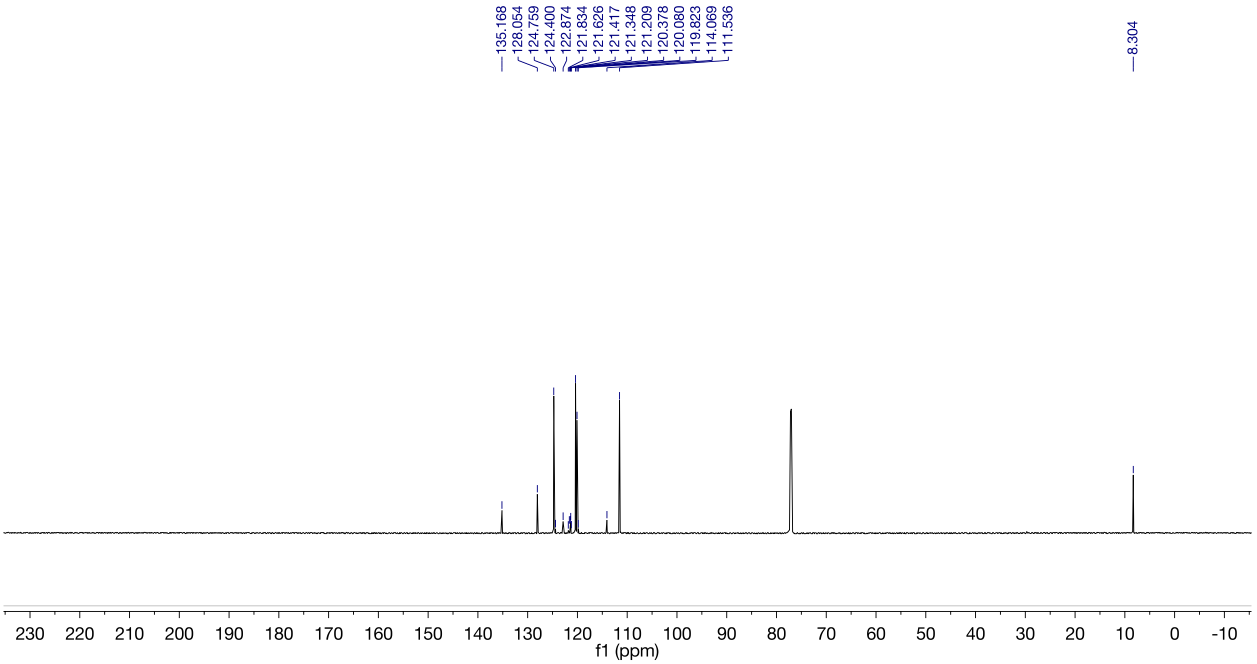
(**6-CF$_3$**)



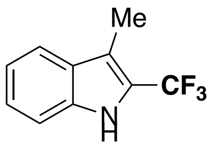
^{13}C NMR Spectrum of 6-CF$_3$ at 23 °C (CDCl$_3$)



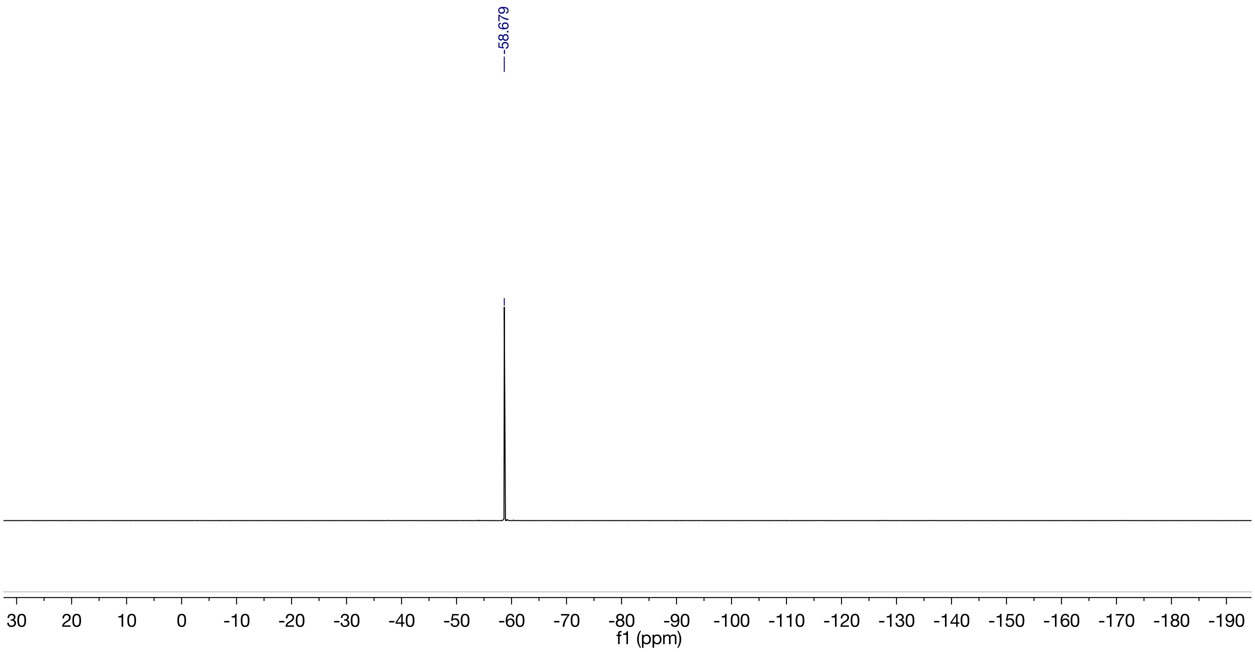
(6-CF$_3$)



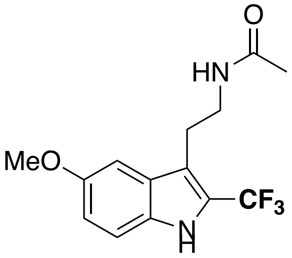
^{19}F NMR Spectrum of 6-CF$_3$ at 23 °C (CDCl$_3$)



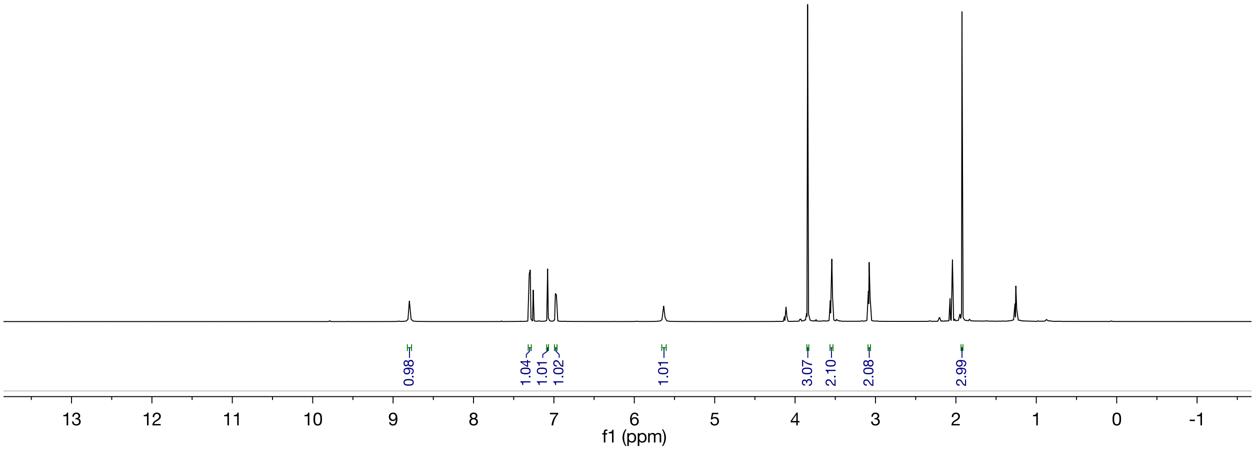
(**6-CF$_3$**)



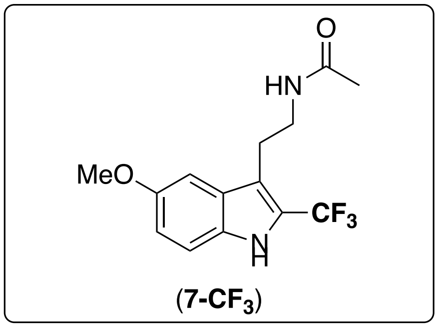
^{1}H NMR Spectrum of 7-CF_3 at 23 °C ($CDCl_3$)



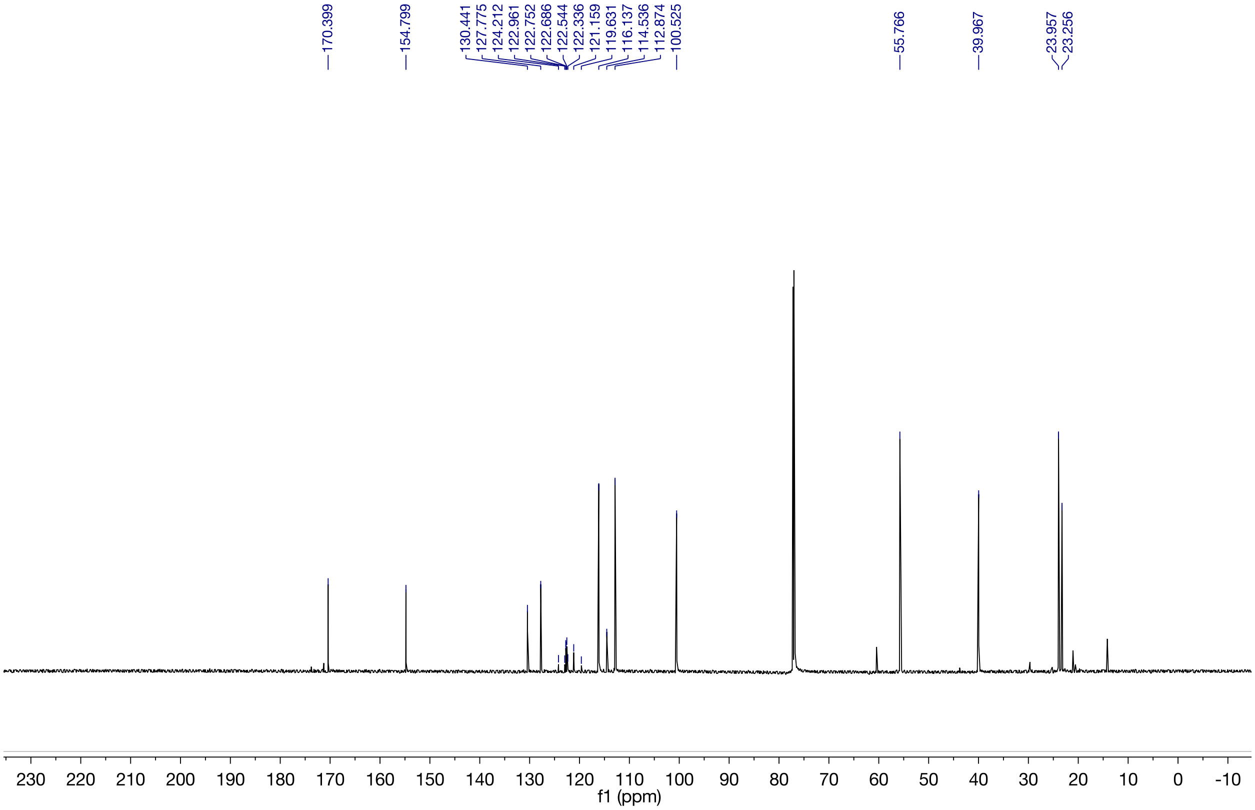
(**7-CF_3**)



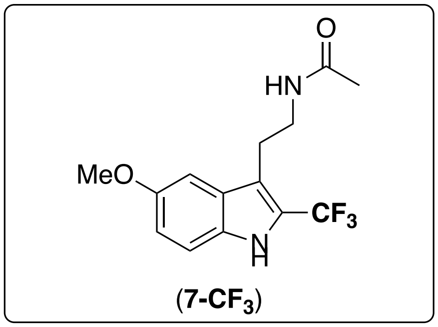
^{13}C NMR Spectrum of 7-CF$_3$ at 23 °C (CDCl$_3$)

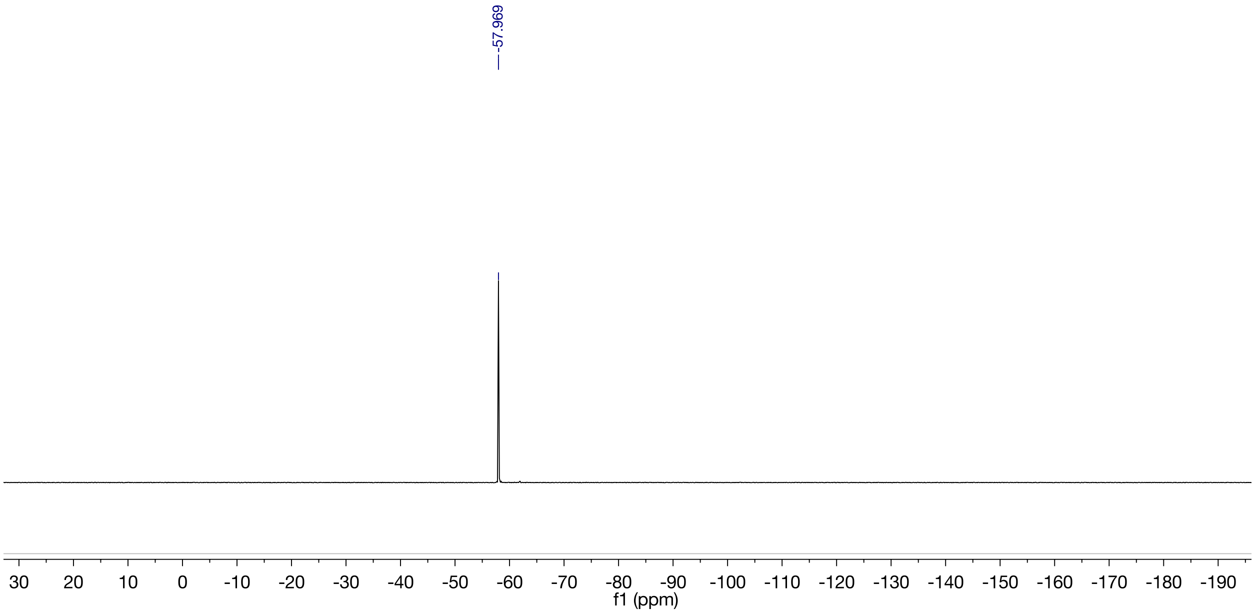


(**7-CF$_3$**)

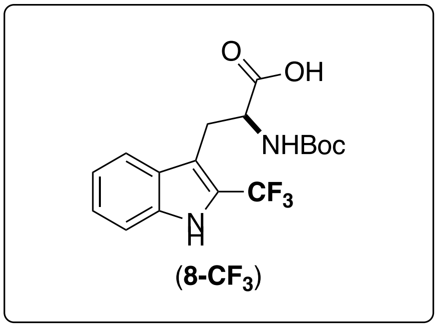


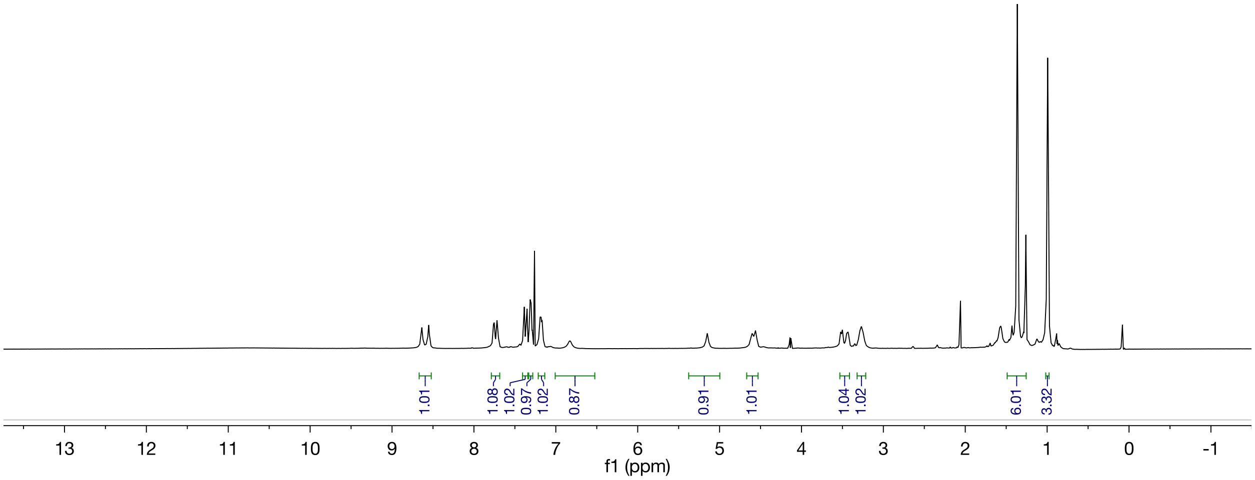
^{19}F NMR Spectrum of 7-CF$_3$ at 23 °C (CDCl$_3$)



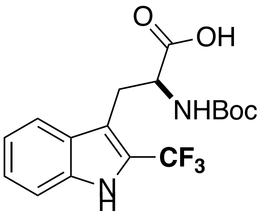


^{1}H NMR Spectrum of 8-CF$_3$ at 23 °C (CDCl$_3$)

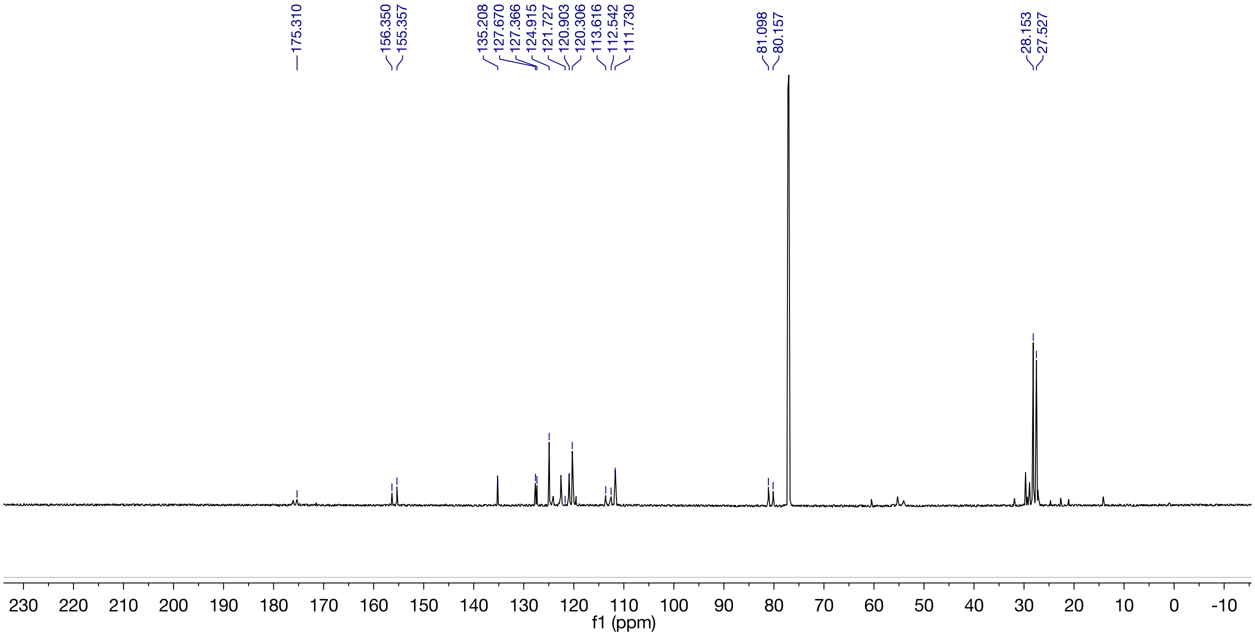

(**8-CF$_3$**)



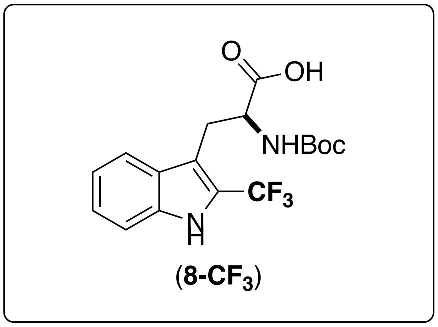
^{13}C NMR Spectrum of 8-CF$_3$ at 23 °C (CDCl$_3$)



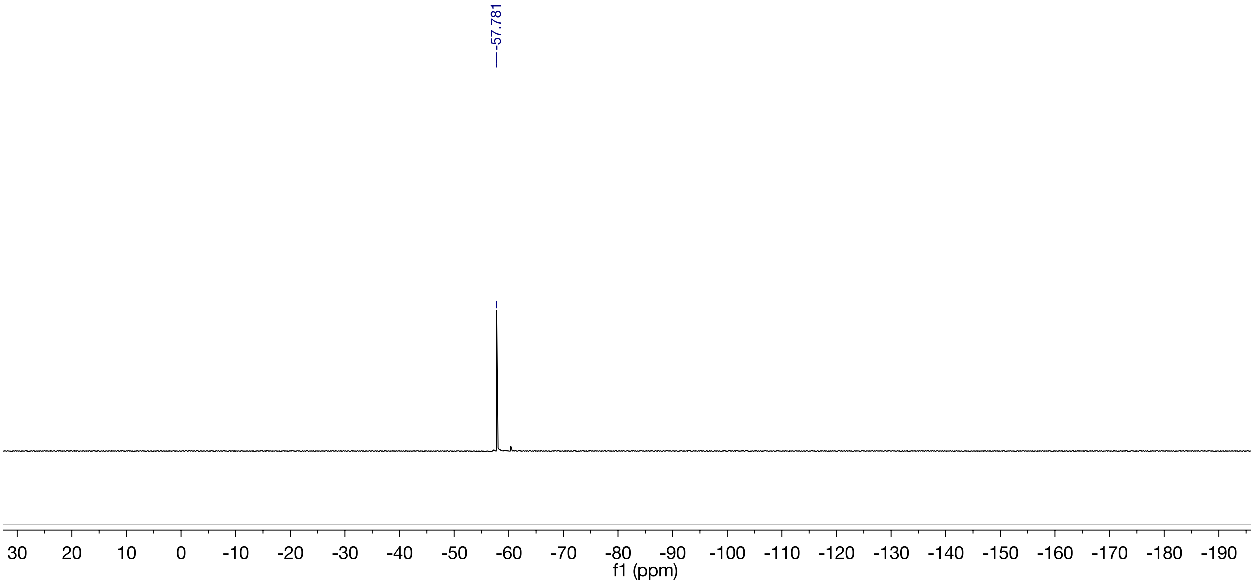
(**8-CF$_3$**)



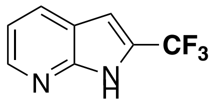
^{19}F NMR Spectrum of 8-CF$_3$ at 23 °C (CDCl$_3$)



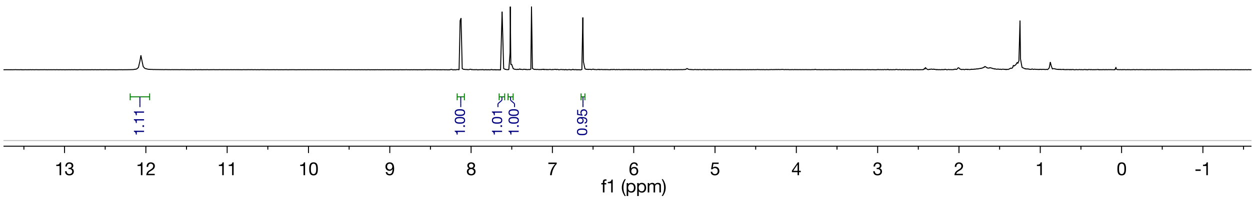
(**8-CF$_3$**)



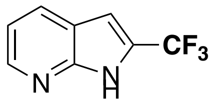
^{1}H NMR Spectrum of 9-CF$_3$-2 at 23 °C (CDCl$_3$)

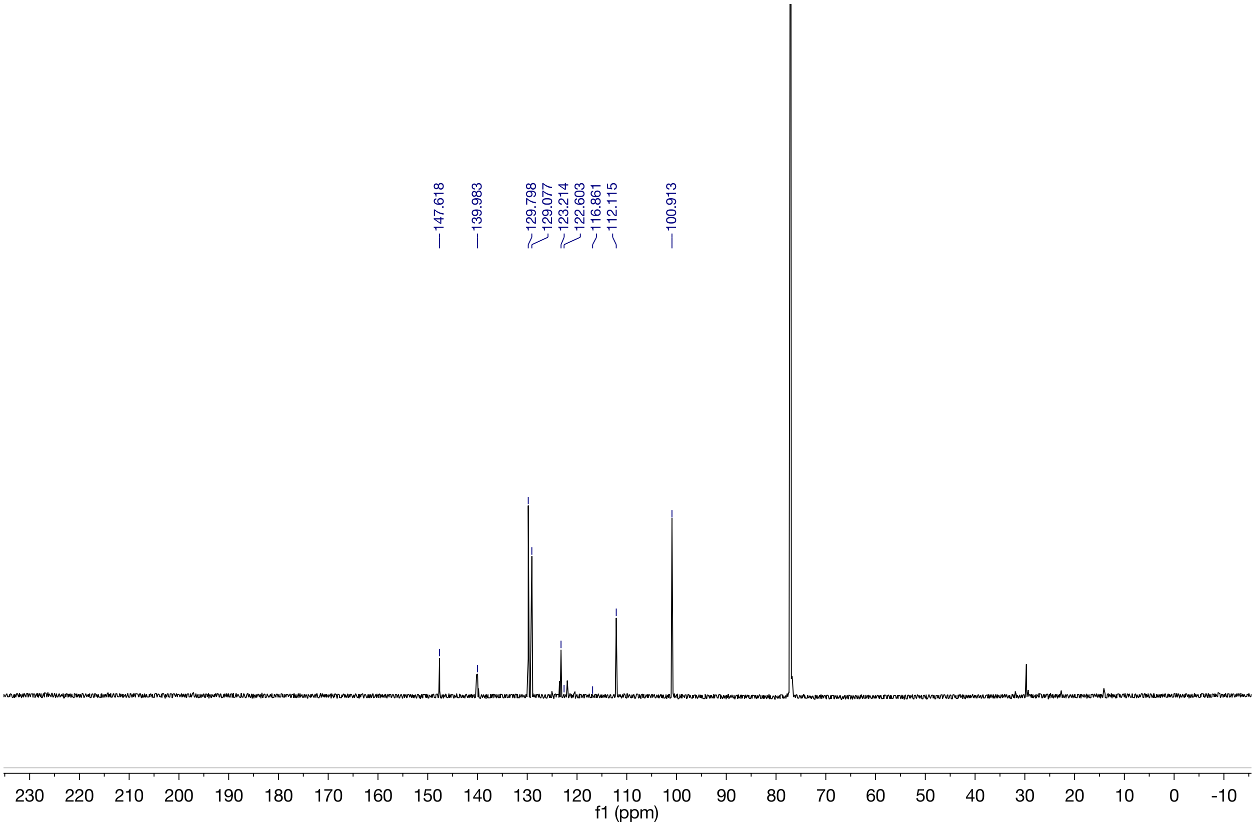


(9-CF$_3$-2)

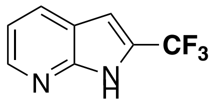


^{13}C NMR Spectrum of 9-CF$_3$-2 at 23 °C (CDCl$_3$)

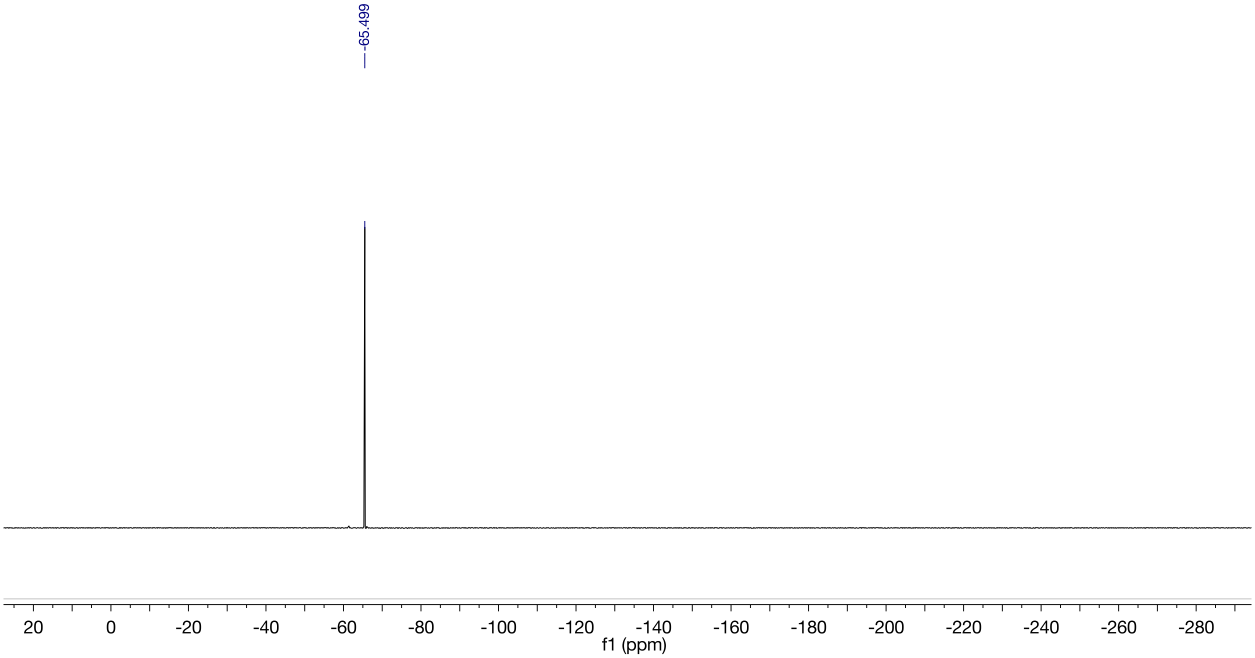

(**9-CF$_3$-2**)



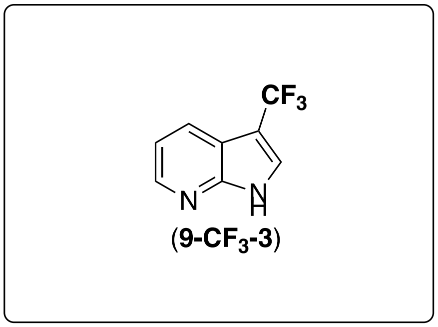
^{19}F NMR Spectrum of 9-CF$_3$-2 at 23 °C (CDCl$_3$)

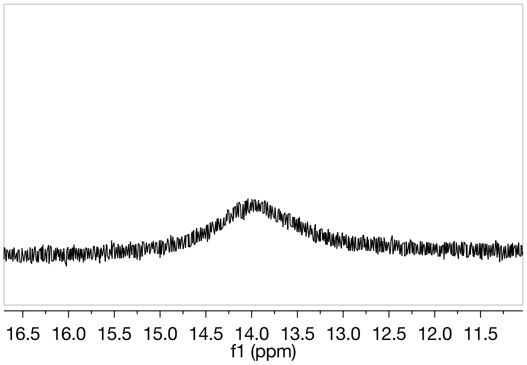


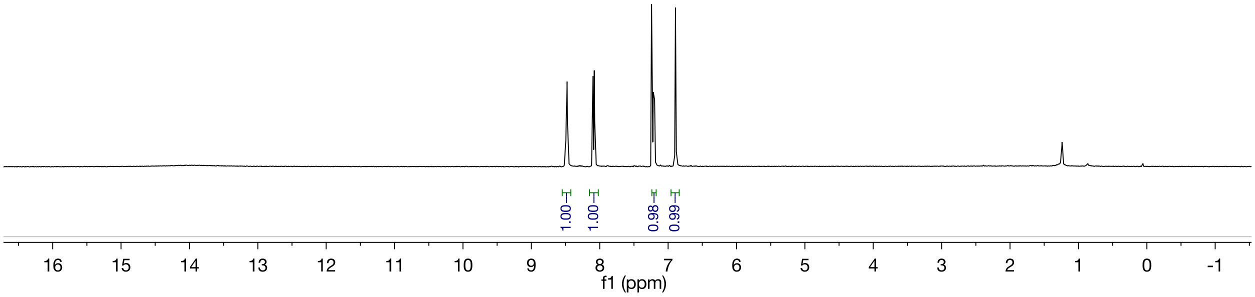
(**9-CF$_3$-2**)



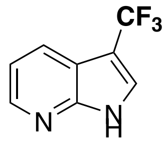
^{1}H NMR Spectrum of 9-CF$_3$-3 at 23 °C (CDCl$_3$)



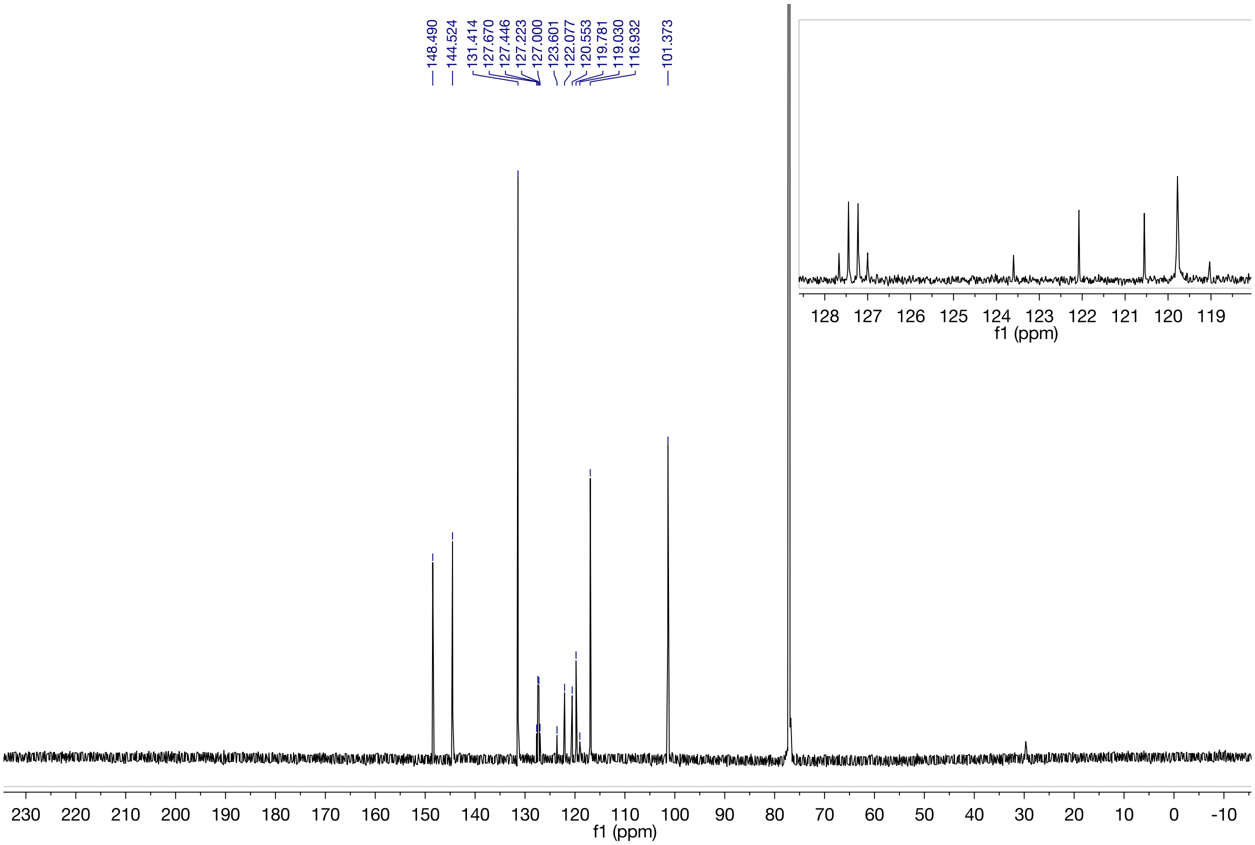




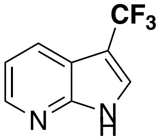
^{13}C NMR Spectrum of 9-CF$_3$-3 at 23 °C (CDCl$_3$)



(**9-CF$_3$-3**)



^{19}F NMR Spectrum of 9-CF$_3$-3 at 23 °C (CDCl$_3$)



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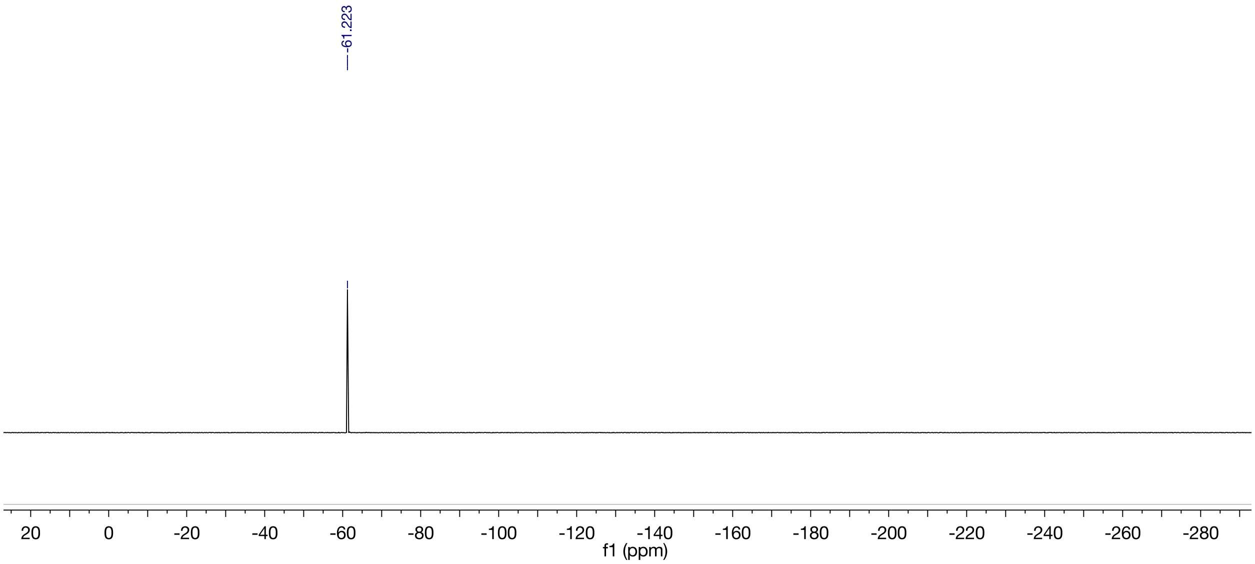
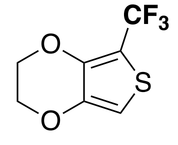


^{1}H NMR Spectrum of 10-CF$_3$ at 23 °C (CDCl$_3$)



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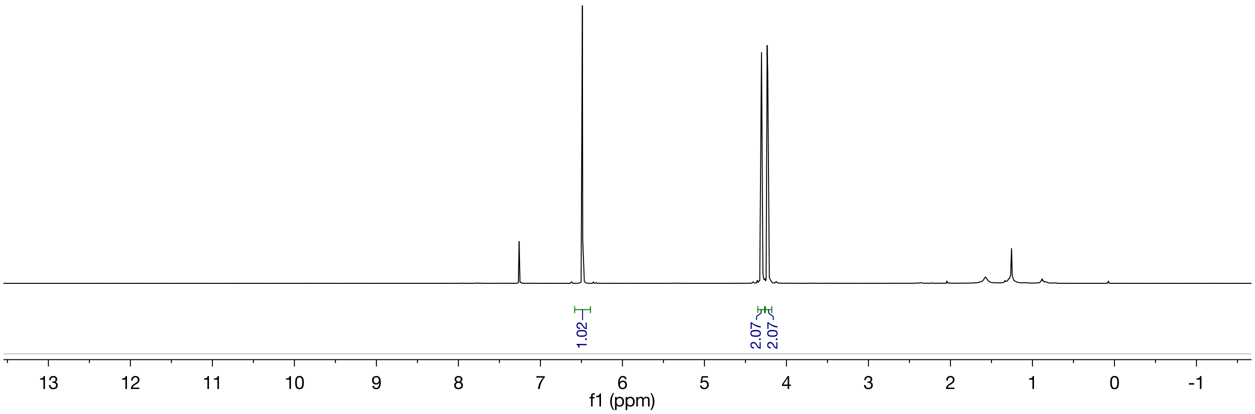
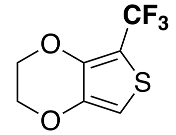
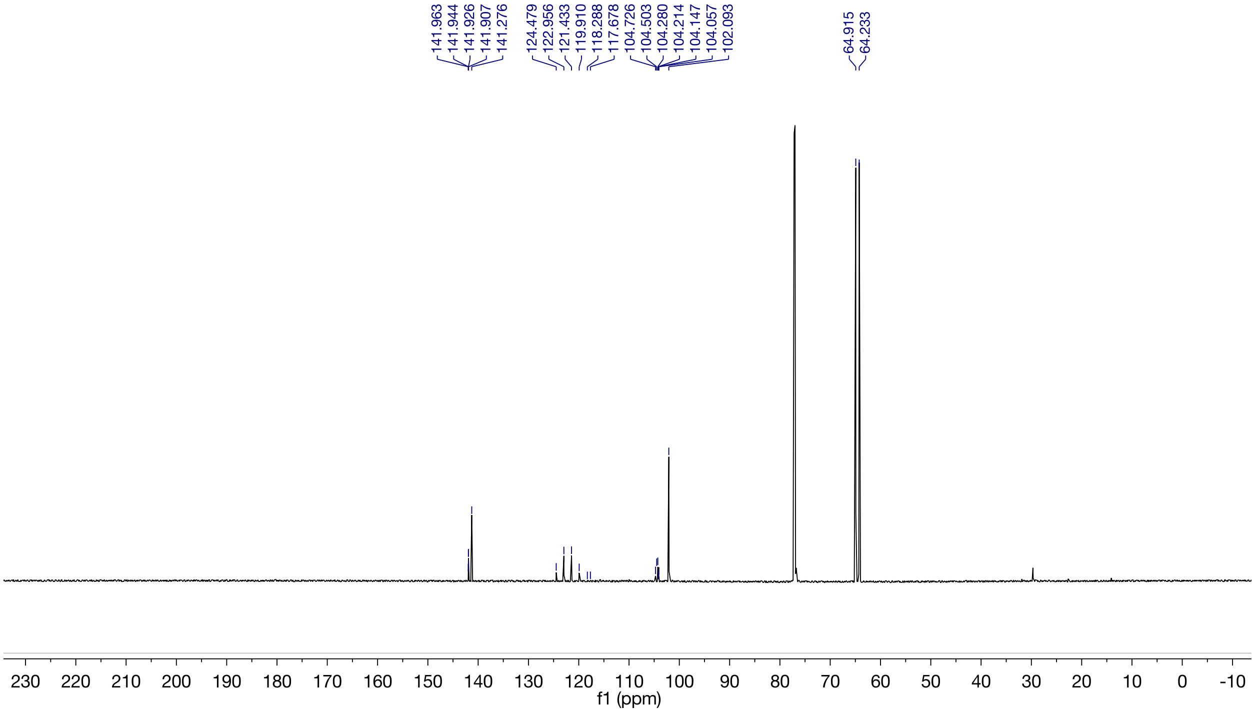


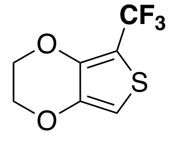
^{13}C NMR Spectrum of 10-CF$_3$ at 23 °C (CDCl$_3$)



(**10-CF$_3$**)



^{19}F NMR Spectrum of 10-CF_3 at 23 °C ($CDCl_3$)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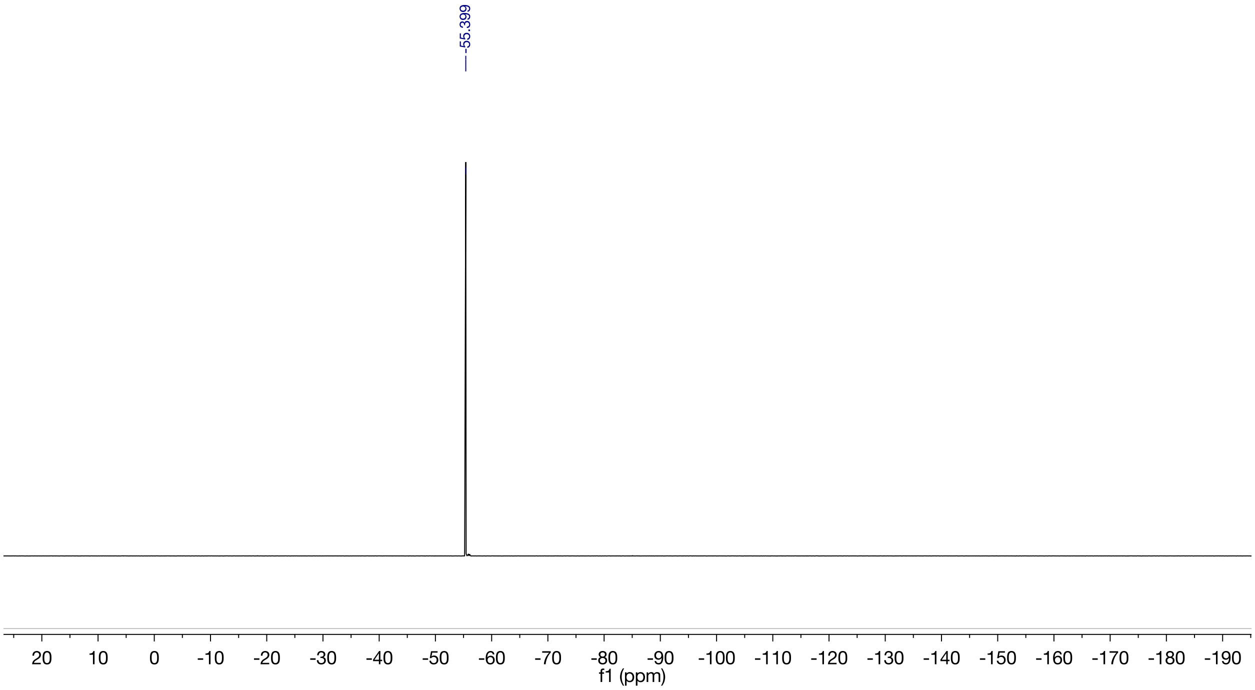
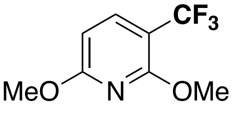
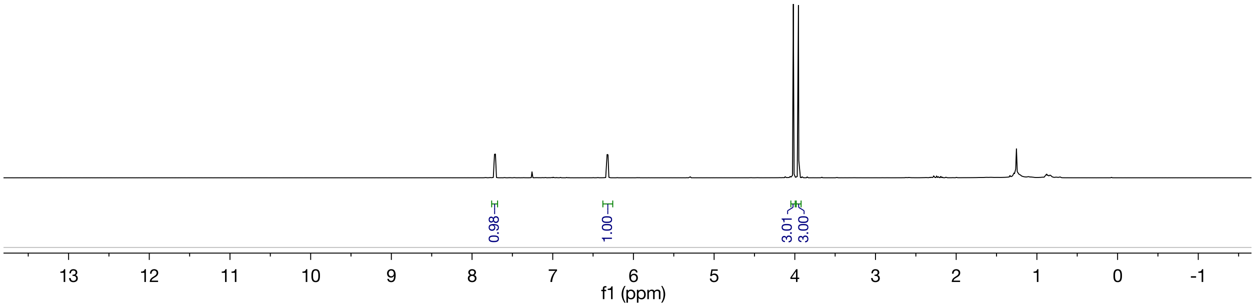


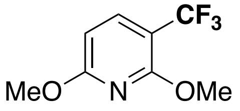
^{1}H NMR Spectrum of 11-CF$_3$ at 23 °C (CDCl$_3$)



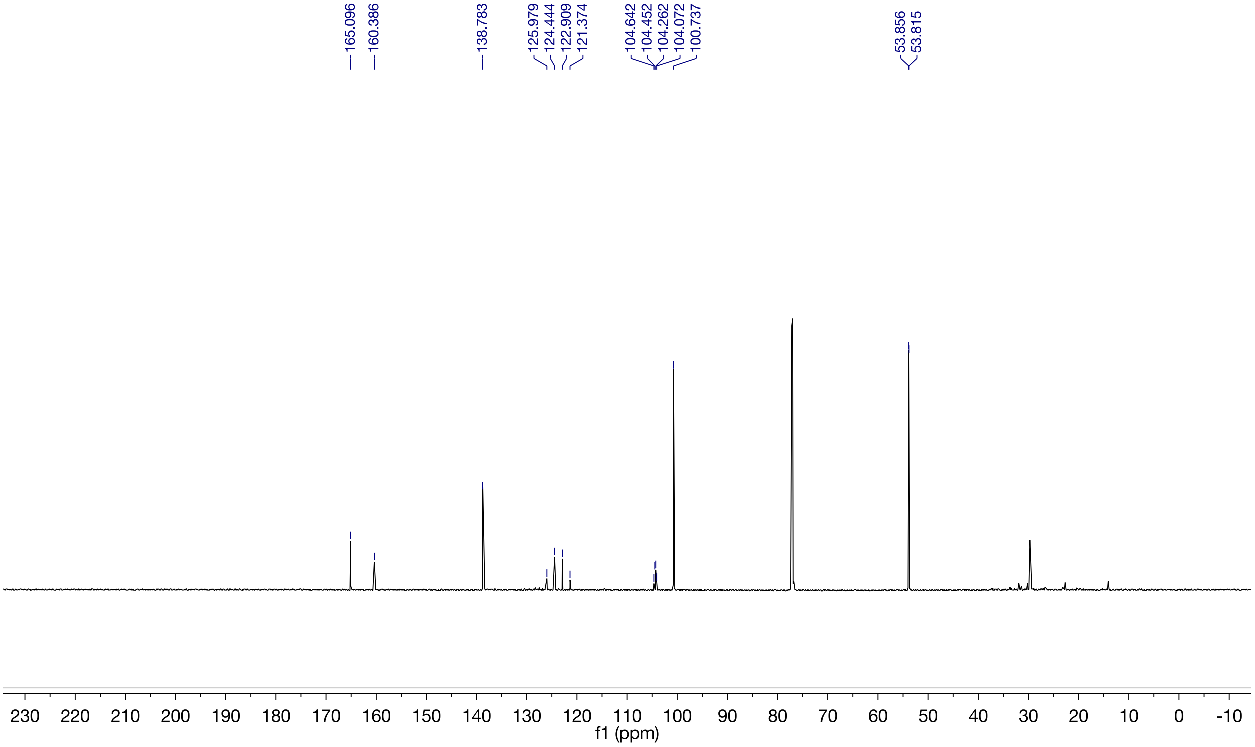
(**11-CF$_3$**)



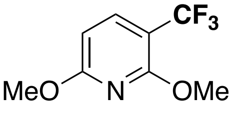
^{13}C NMR Spectrum of 11-CF$_3$ at 23 °C (CDCl$_3$)



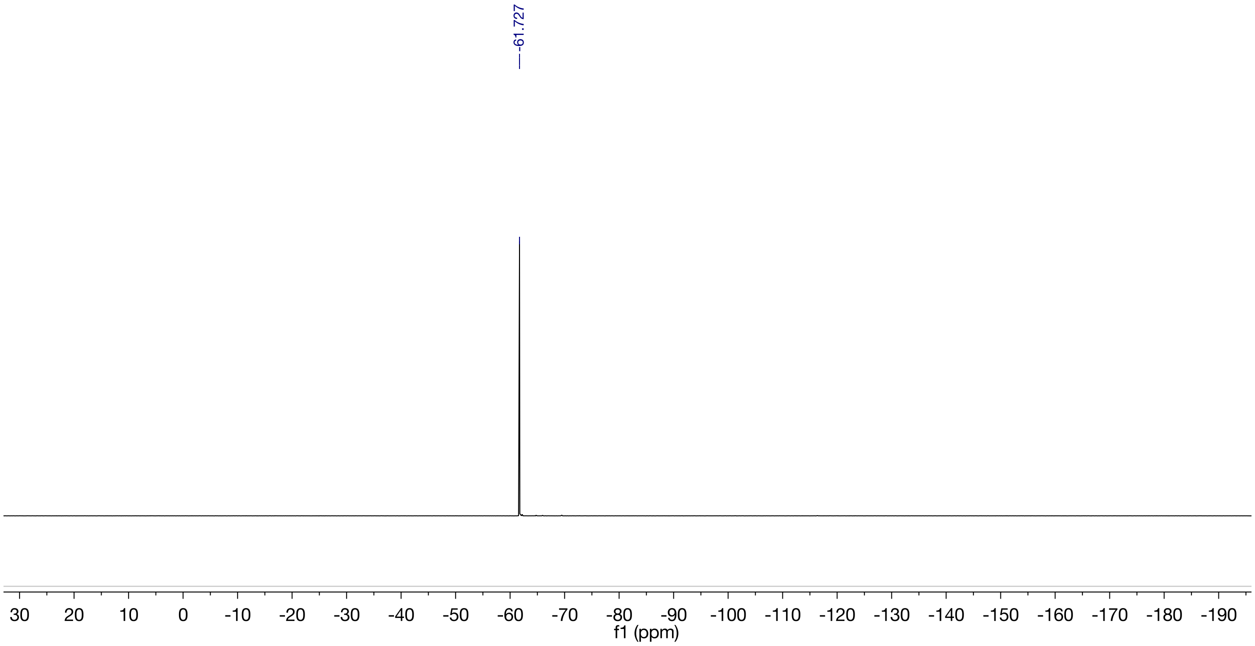
(**11-CF$_3$**)



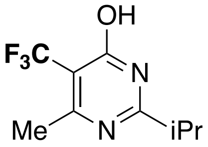
^{19}F NMR Spectrum of 11-CF_3 at 23 °C ($CDCl_3$)



(**11-CF_3**)



^{1}H NMR Spectrum of 11-CF$_3$ at 23 °C (CDCl$_3$)



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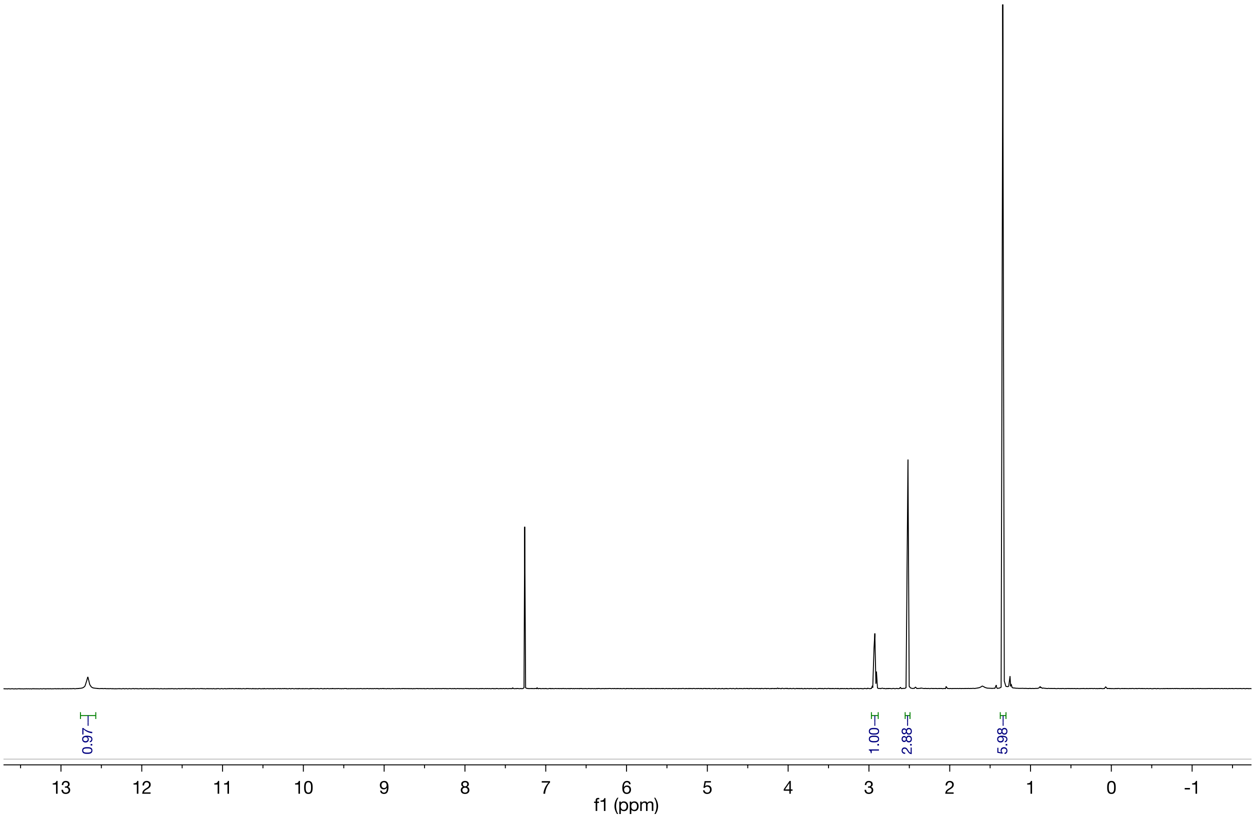
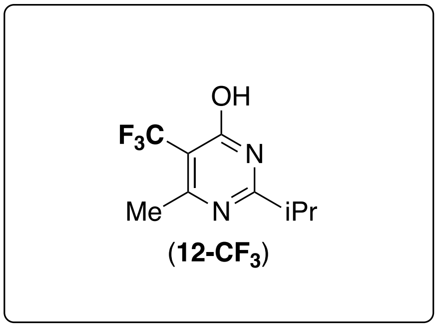
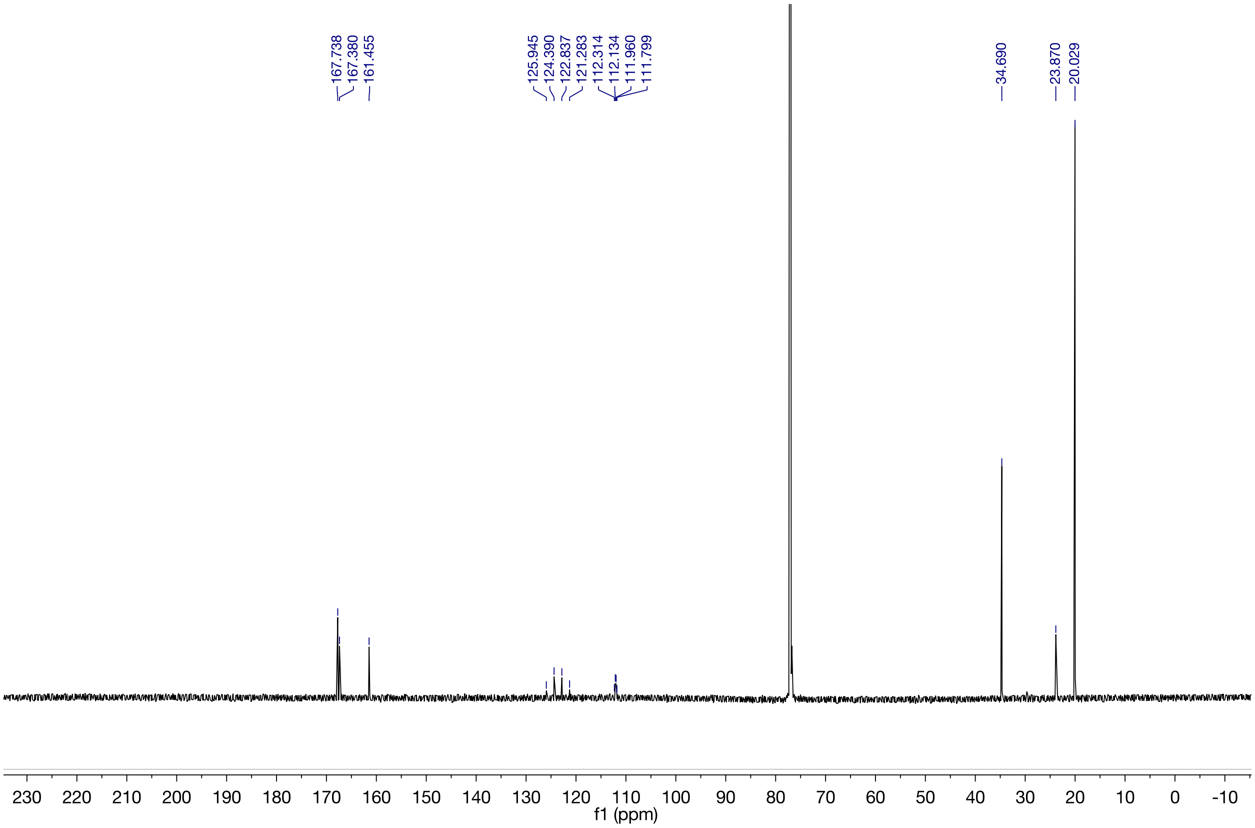


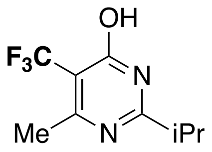
^{13}C NMR Spectrum of 11-CF$_3$ at 23 °C (CDCl$_3$)



(**12-CF$_3$**)



^{19}F NMR Spectrum of 11-CF_3 at 23 °C ($CDCl_3$)



(**12-CF_3**)