Exploiting the Trifluoroethyl Group as a Precatalyst Ligand in Nickel-Catalyzed Suzuki-type Alkylations

Yi Yang,[†] Qinghai Zhou,[‡] Junjie Cai,[†] Teng Xue,[§] Yingle Liu,[†] Yan Jiang,[†] Yumei Su,[†] Lungwa Chung[‡]* and David A. Vicic[§]**

[†]Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, Sichuan University of Science & Engineering, Zigong 643000, China; [‡]Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China; [§]Department of Chemistry, Lehigh University, 6 E. Packer Avenue, Bethlehem, PA 18015, USA
E-mail: yangyiyoung@163.com; oscarchung@sustc.edu.cn; dav512@lehigh.edu

Supporting Information

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I. General specifications

All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All manipulations were conducted using standard Schlenk and high-vacuum techniques or in a nitrogen-filled glovebox. Solvents were distilled from Na/benzophenone or CaH_2. ^1H NMR and ^{13}C NMR spectra were recorded on a 500 MHz or 600 MHz spectrometer (TMS as internal standard). ^{19}F NMR was also recorded on a 400 MHz or 500 MHz spectrometer ($FCCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in parts per million, and coupling constants (*J*) are in hertz. High resolution mass spectrometry (EI/TOF or ESI-TOF) was performed at the Mass Spectrometry Facility.

Thin layer chromatography monitoring (TLC) was performed using precoated silica gel plate (0.2 mm thickness, GF254). Subsequent to elution, plates were first visualized using UV radiation (254 nm). Further visualization was conducted by staining with basic solution of potassium permanganate or acidic solution of cerric molybdate, followed by heating on a hot plate. Flash chromatography was performed using silica gel (200-300 mesh) with HPLC solvents. Columns were typically packed as slurry and equilibrated with petroleum ether prior to use.

II. Synthesis of precatalyst [(bipy)Ni(CH_2CF_3)$_2$]

A 100 mL round-bottom flask was charged with 2,2'-bipyridine (0.500 g, 3.20 mmol), Ni(COD)$_2$ (0.880 g, 3.20 mmol) and THF (40 mL). After stirring at room temperature for 12 h, a THF solution of CF_3CH_2I (0.740 g, 3.52 mmol in 10 mL of THF) were added to the flask. The reaction mixture was stirred overnight, and then the volatiles were removed under reduced pressure. The residue was redissolved in benzene (80 mL), and the suspension solution was passed through a sand-core glass funnel to remove the insoluble [(bipy)NiI_2]. After the solvent of the filtrate were removed under reduced pressure, the residue solid was washed with pentane (5 mL×2) and dried in *vacuo* to furnish [(bipy)Ni(CH_2CF_3)$_2$] as a dark red powder (0.252 g, Yield 41%). Suitable single crystals for X-ray analysis were obtained by recrystallization from THF/pentane solution at -25 °C. ^{1}H NMR (500 MHz, THF-d_8): δ 8.69 (d, J = 7.8 Hz, 2H), 8.23 (d, J = 7.8 Hz, 2H), 8.09 (dt, J = 7.8 Hz, 1.3 Hz, 2H), 7.59 (m, 2H), 1.06 (q, J = 16.2 Hz, 4H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -47.98 (t, J = 16.2 Hz, 6F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.22, 150.56, 139.39, 135.38 (q, J = 273.8 Hz), 127.16, 122.24, 6.11 (q, J = 23.6 Hz); Elemental analysis calcd (%) for $C_{14}H_{12}F_6N_2Ni$: C, 44.14; H, 3.18; found: C, 44.01; H, 3.27.

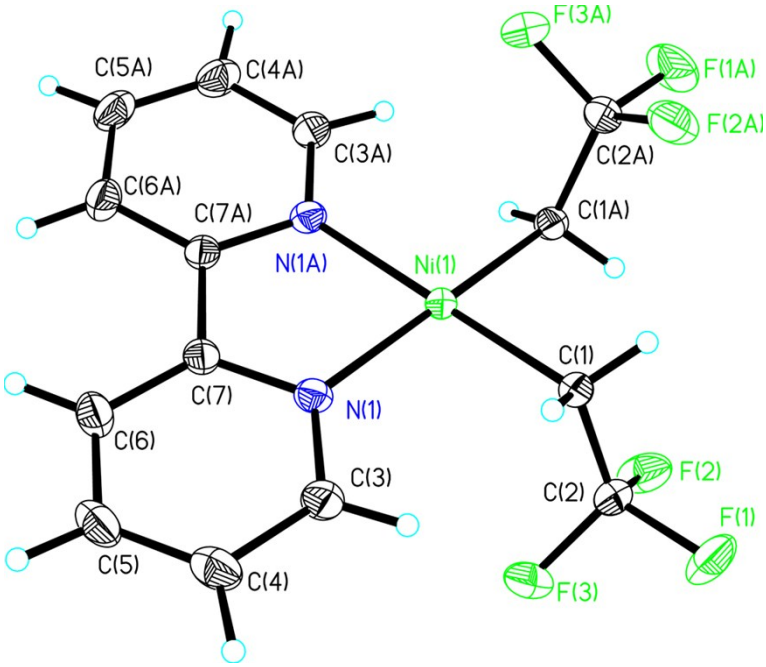
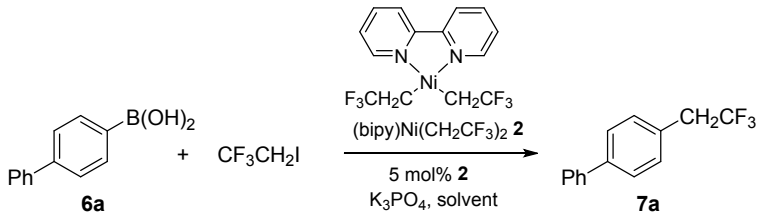


Figure S1. ORTEP diagram of [(bipy)Ni(CH_2CF_3)$_2$] (**2**). (CCDC 1436475)

III. Examination of the catalytic activities of [(bipy)Ni(CH_2CF_3)$_2$] and reaction condition optimization

4-biphenylboronic acid **2a** (1.5 equiv), base (2.0 equiv), followed by a solution of CF_3CH_2I (1.0 equiv) in the indicated solvent (1.0 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (5.0 mol%) in the indicated solvent (0.5 mL) was added dropwise into the reaction system subsequently. The Schlenck tube was screw capped and put into a preheated oil bath (80 ^oC). After stirring for 12-24 h, the reaction mixture was cooled to room temperature and poured into a saturated aqueous ammonium chloride solution (10.0 mL). The aqueous phase was extracted with ether three times (10.0 mL×3) and the combined organic phase was dried over sodium sulfate. After removing the solvent in *vacuo*, the residue was purified by flash chromatography on silica gel or preparative TLC to afford the corresponding $ArCH_2CF_3$ products.

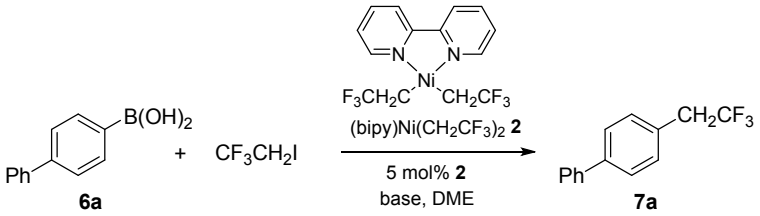
Table S1. Solvent effect on the precatalyst 2 catalyzed Suzuki-type trifluoroethylation



Entry	Base	Solvent	T/ ^oC	Isolated Yield
1	K_3PO_4	DME	80	93%
2	K_3PO_4	DMSO	80	91%
3	K_3PO_4	DMF	80	47%
4	K_3PO_4	CH_3CN	80	35%
5	K_3PO_4	toluene	80	43%
6	K_3PO_4	THF	80	54%

7	K_3PO_4	dioxane	80	78%

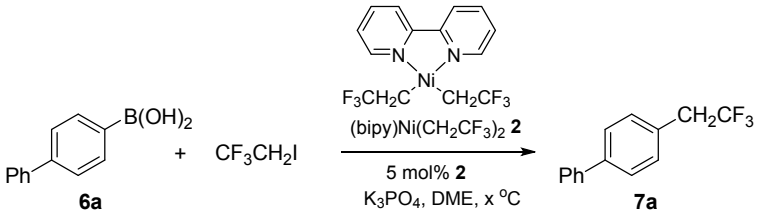
Table S2. Base effect on the precatalyst **2** catalyzed Suzuki-type trifluoroethylation



Entry	Base	Solvent	T/ °C	Isolated Yield
1	K_3PO_4	DME	80	93%
2	Na_2CO_3	DME	80	7%[a]
3	K_2CO_3	DME	80	23%[a]
4	Cs_2CO_3	DME	80	50%[a]
5	tBuOK	DME	80	Trace[b]
6	NaOAc	DME	80	ND[c]

[a]Partial dehydrofluorination of coupling product. [b]Complete dehydrofluorination of coupling product. [c]No conversion of CF_3CH_2I.

Table S3. Temperature effect of Suzuki-type trifluoroethylation[a]



Entry	Base	Solvent	T/ °C	Isolated Yield
1	K_3PO_4	DME	80	93%
2	K_3PO_4	DME	50	77%
3	K_3PO_4	DME	RT	<5%

[a]This experiment indicated the activation temperature of precatalyst [(bipy)Ni(CH_2CF_3)$_2$] is approximately 50

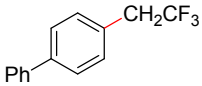
°C which is lower than the commercialized (TMEDA)Ni(*o*-tol)(Cl) (the lower bound of activation is 60 °C) (J. D. Shields, E. E. Gray and A. G. Doyle, *Org. Lett.*, 2015, **17**, 2166).

IV. Suzuki-type direct trifluoroethylation and alkylation of $ArB(OH)_2$ and characterization of Ar-R products

(a) Typical Procedure

Arylboronic acid (1.5 equiv), base (2.0 equiv), followed by a solution of CF_3CH_2I (0.4 mmol, 1.0 equiv) or the corresponding R-X (0.4 mmol, 1.0 equiv) in the DME solvent (1.0 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (5.0 mol%) in the DME solvent (0.5 mL) was added dropwise into the reaction system subsequently. The Schlenck tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 12-24 h, the reaction mixture was cooled to room temperature and poured into a saturated aqueous ammonium chloride solution (10.0 mL). The aqueous phase was extracted with ether three times (10.0 mL×3) and the combined organic phase was dried over sodium sulfate. After removing the solvent in *vacuo*, the residue was purified by flash chromatography on silica gel or preparative TLC to afford the corresponding Ar-CH_2CF_3 or Ar-R products.

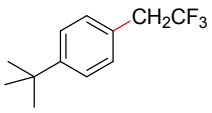
(b) Characterization of Ar-CH_2CF_3 and Ar-R Products



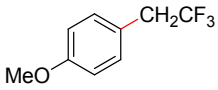
(7a). Colorless oil, TLC R_f (hexane) = 0.65, 91% yield (87 mg). A gram-scale synthesis was implemented as the following procedure and the isolated yield can be comparatively effective (83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.5 Hz, 3H), 3.40 (q, *J* = 10.8 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.85 (t, *J*= 10.8 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.12 (s), 140.53 (s), 130.60 (s), 129.14 (q, *J*= 2.9 Hz), 128.86 (s), 127.54 (s), 127.44 (s), 127.14 (s), 125.84 (q, *J* = 276.8 Hz), 39.92 (q, *J* = 29.8 Hz). MS (EI) *m/z* 236 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{14}H_{11}F_3$ 236.0813, found 236.0808.

Gram-scale synthesis procedure: 4-biphenylboronic acid (2.38 g, 12.0 mmol, 1.5 equiv), K_3PO_4 (5.10 g, 24.0 mmol, 3.0 equiv), followed by a solution of CF_3CH_2I (0.80 mL, 8.0 mmol, 1.0 equiv) in the DME solvent (20.0 mL) were loaded into a 100 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (76.0 mg, 2.5 mol%) in the DME solvent (5.0 mL) was added dropwise into

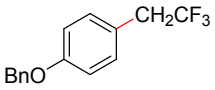
the reaction system subsequently. The Schlenck tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 24 h, the reaction mixture was cooled to room temperature and poured into a saturated aqueous ammonium chloride solution (100.0 mL). The aqueous phase was extracted with ether three times (70.0 mL × 3) and the combined organic phase was dried over sodium sulfate. After removing the solvent in *vacuo*, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether) afford the corresponding 4-(2,2,2-trifluoroethyl)-1,1'-biphenyl **7a** (1.57 g, yield 83%).



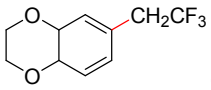
(7b). Colorless oil, TLC R_f (hexane) = 0.60, 79% yield (68 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.33 (q, *J* = 10.9 Hz, 2H), 1.33 (s, 9H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -65.97 (t, *J* = 10.9 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.27, 130.06, 127.35 (q, *J* = 2.7 Hz), 126.14 (q, *J* = 276.6 Hz), 125.83, 39.93 (q, *J* = 29.6 Hz), 34.75, 31.50. MS (EI) *m/z* 216 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{12}H_{15}F_3$ 216.1126, found 216.1120.



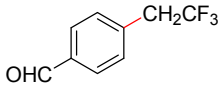
(7c). Colorless oil, TLC R_f (hexane) = 0.55, 86% yield (65 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.90-6.87 (m, 2H), 3.80 (s, 3H), 3.29 (q, *J* = 10.8 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -66.44 (t, *J* = 10.8 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.65, 131.46, 126.11 (q, *J* = 276.6 Hz), 122.35 (q, *J* = 2.8 Hz), 114.27, 55.42, 39.57 (q, *J* = 29.7 Hz); MS (EI) *m/z* 190 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_9H_9F_3O$ 190.0605, found 190.0608.



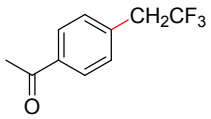
(7d). White solid, TLC R_f (hexane) = 0.55, 83% yield (88 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.37-7.33 (m, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.00-6.97 (m, 2H), 5.07 (s, 2H), 3.31 (q, *J* = 10.9 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -66.31 (t, *J* = 10.9 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.87, 137.02, 131.49, 128.83, 128.24, 127.68, 126.08 (q, *J* = 276.7 Hz), 122.63 (q, *J* = 2.8 Hz), 115.19, 70.21, 39.57 (q, *J* = 29.7 Hz). MS (EI) *m/z* 266 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{15}H_{13}F_3O$ 266.0918, found 266.0921.



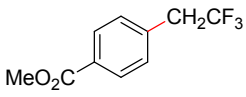
(7e). Light yellow oil, TLC R_f (hexane : EtOAc = 10 : 1) = 0.55, 80% yield (71 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.75 (dd, *J* = 8.3 Hz, 1.8 Hz, 1H), 4.23 (s, 4H), 3.24 (q, *J* = 10.8 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -66.26 (t, *J* = 10.8 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.71, 143.69, 126.02 (q, *J* = 276.7 Hz), 123.35, 121.60, 119.20, 117.60, 64.50, 64.48, 39.64 (q, *J* = 29.8 Hz). MS (EI) *m/z* 220 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{10}H_{11}F_3O_2$ 220.0711, found 220.0715.



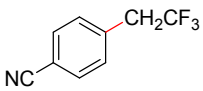
(7f). Light yellow oil, TLC R_f (hexane : EtOAc = 9 : 1) = 0.45, 70% yield (53 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 3.44 (q, *J* = 10.6 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -65.47 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.89, 136.92 (q, *J* = 2.8 Hz), 136.33, 131.10, 130.18, 125.52 (q, *J* = 277.0 Hz), 40.52 (q, *J* = 30.0 Hz). MS (EI) *m/z* 188 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_9H_7F_3O$ 188.0449, found 188.0447.



(7g). Colorless oil, TLC R_f (hexane : EtOAc = 5 : 1) = 0.48, 74% yield (60 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (dt, *J* = 8.3 Hz, 2.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 3.41 (q, *J* = 10.7 Hz, 2H), 2.58 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -65.57 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.74, 137.06, 135.45 (q, *J* = 2.7 Hz), 130.63, 128.84, 125.60 (q, *J* = 277.0 Hz), 40.33 (q, *J* = 30.0 Hz), 26.81. MS (EI) *m/z* 202 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{10}H_9F_3O$ 202.0605, found 202.0600.

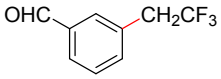


(7h). White solid, TLC R_f (hexane : EtOAc = 6 : 1) = 0.45, 80% yield (70 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.40 (q, *J* = 10.7 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -65.62 (t, *J* = 10.7 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.84, 135.28 (q, *J* = 2.6 Hz), 130.42, 130.24, 130.10, 125.62 (q, *J* = 276.9 Hz), 52.40, 40.35 (q, *J* = 30.0 Hz). MS (EI) *m/z* 218 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{10}H_9F_3O_2$ 218.0555, found 218.0552.

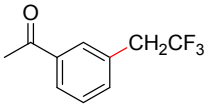


(7i). White solid, TLC R_f (hexane : EtOAc = 6 : 1) = 0.35, 72% yield (53 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 3.42 (q, *J* = 10.5 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -65.55 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (125

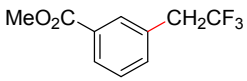
MHz, $CDCl_3$): δ 135.50 (q, *J* = 2.8 Hz), 132.65, 131.16, 125.33 (q, *J* = 277.0 Hz), 118.52, 112.56, 40.42 (q, *J* = 30.3 Hz). MS (EI) *m/z* 185 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_9H_6F_3N$ 185.0452, found 185.0452.



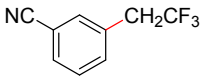
(7j). Yellow oil, TLC R_f (hexane : EtOAc = 9 : 1) = 0.45, 48% yield (36 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.83 (s, 1H), 7.57 (dt, *J* = 14.9, 7.6 Hz, 2H), 3.47 (q, *J* = 10.6 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.84 (t, *J* = 10.8 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.77 (s), 136.83 (s), 136.06 (s), 131.33 (q, *J* = 3.2 Hz), 131.13 (s), 129.49 (s), 128.19 (s), 125.44 (q, *J* = 276.8 Hz), 39.99 (q, *J* = 30.2 Hz). MS (EI) *m/z* 188 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_9H_7F_3O$ 188.0449, found 188.0447.



(7k). Yellow oil, TLC R_f (hexane : EtOAc = 5 : 1) = 0.50, 67% yield (54 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.90 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 3.44 (q, *J* = 10.7 Hz, 2H), 2.62 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.87 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.62 (s), 137.57 (s), 134.70 (s), 130.79 (q, *J* = 2.9 Hz), 129.95 (s), 129.03 (s), 128.21 (s), 125.53 (q, *J* = 276.9 Hz), 40.10 (q, *J* = 29.9 Hz), 26.64 (s). MS (EI) *m/z* 202 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{10}H_9F_3O$ 202.0605, found 202.0600.

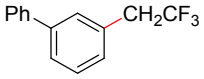


(7l). Colorless oil, TLC R_f (hexane : EtOAc = 6 : 1) = 0.45, 63% yield (55 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.99 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.43 (q, *J* = 10.7 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.91 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.62 (s), 134.57 (s), 131.33 (s), 130.72 (s), 130.54 (q, *J* = 2.9 Hz), 129.38 (s), 128.83 (s), 125.54 (q, *J* = 276.9 Hz), 52.26 (s), 40.04 (q, *J* = 30.0 Hz). MS (EI) *m/z* 218 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{10}H_9F_3O_2$ 218.0555, found 218.0552.

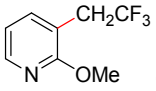


(7m). White solid, TLC R_f (hexane : EtOAc = 6 : 1) = 0.35, 44% yield (33 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.61 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 3.42 (q, *J* = 10.5 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.83 (t, *J* = 10.8 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.59 (s), 133.64 (s), 131.94 (s), 131.65 (q, *J* = 2.9 Hz), 129.64 (s), 125.16 (q, *J* = 277.0 Hz), 118.24 (s), 113.11 (s), 39.83 (q, *J* = 30.4 Hz). MS (EI) *m/z* 185 (M^+); HRMS (EI- TOF) *m/z* $[M]^+$ Calcd for $C_9H_6F_3N$ 185.0452, found

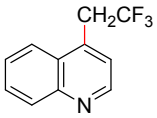
185.0452.



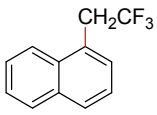
(7n). Colorless oil, TLC R_f (hexane) = 0.55, 74% yield (70 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (t, *J* = 8.7 Hz, 3H), 7.51 (s, 1H), 7.47 – 7.40 (m, 3H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 3.43 (q, *J* = 10.8 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.77 (t, *J* = 10.6 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.81 (s), 140.66 (s), 130.67(q, *J*= 5.6 Hz), 129.12 (s), 129.07 (s), 129.01 (s), 128.86 (s), 128.86 (s), 127.58 (s), 127.23(s), 127.23(s), 126.98 (s), 125.82 (q, *J* = 276.9 Hz), 40.33 (q, *J* = 29.7 Hz). MS (EI) *m/z* 236 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{14}H_{11}F_3$ 236.0813, found 236.0808.



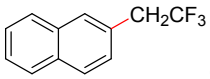
(7o). Colorless oil, TLC R_f (hexane: EtOAc = 5 : 1) = 0.40, 78% yield (60 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (dd, *J* = 5.0 Hz, 1.8 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 6.86 (dd, *J* = 7.3 Hz, 5.0 Hz, 1H), 3.95 (s, 3H), 3.40 (q, *J* = 10.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ -65.50 (t, *J* = 10.8 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.62, 147.01, 140.09, 126.02 (q, *J* = 277.3 Hz), 116.93, 113.48 (q, *J* = 2.8 Hz), 53.86, 33.62 (q, *J* = 30.6 Hz). MS (EI) *m/z* 191 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_8H_8F_3NO$ 191.0558, found 191.0554.



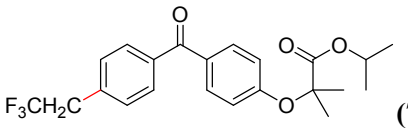
(7p). White solid, TLC R_f (hexane: EtOAc = 2 : 1) = 0.40, 82% yield (69 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.24 (s, 1H), 8.49 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.78 (ddd, *J* = 8.4 Hz, 6.9 Hz, 1.2 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 3.79 (q, *J* = 10.4 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -64.71 (t, *J* = 10.3 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.63, 145.63, 135.21, 131.25, 128.63, 127.63, 125.92 (q, *J* = 277.6 Hz), 122.93, 120.48, 34.60 (q, *J* = 30.9 Hz). MS (EI) *m/z* 211 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{11}H_8F_3N$ 211.0609, found 211.0601.



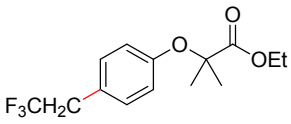
(7q). White solid, TLC R_f (hexane) = 0.55, 36% yield (30 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.59 (ddd, *J* = 8.5 Hz, 6.8 Hz, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.0 Hz, 6.9 Hz, 1.1 Hz, 1H), 7.50-7.46 (m, 2H), 3.87 (q, *J* = 10.6 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -64.66 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.09, 132.54, 129.66, 129.28, 129.05, 126.82, 126.61 (q, *J* = 2.3 Hz), 126.33 (q, *J* = 276.3 Hz), 126.10, 125.46, 123.79, 36.94 (q, *J* = 30.0 Hz). MS (EI) *m/z* 210 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{12}H_9F_3$ 210.0656, found 210.0662.



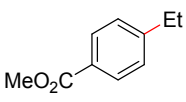
(7r). White solid, TLC R_f (hexane) = 0.57, 42% yield (35 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88-7.84 (m, 3H), 7.79 (s, 1H), 7.55-7.51 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 3.54 (q, *J* = 10.8 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -66.79 (t, *J* = 10.5 Hz, 3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.47, 133.08, 129.70, 128.59, 128.00, 127.90, 127.80, 126.61, 126.54, 126.13 (q, *J* = 277.0 Hz), 40.54 (q, *J* = 29.7 Hz). MS (EI) *m/z* 210 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{12}H_9F_3$ 210.0656, found 210.0662.



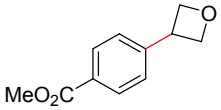
(7s). White solid, TLC R_f (hexane: EtOAc = 4 : 1) = 0.50, 61% yield (100 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 10.8, 8.5 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.09 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.46 (q, *J* = 10.7 Hz, 2H), 1.66 (s, 6H), 1.21 (s, 3H), 1.20 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.53 (t, *J* = 10.6 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.92 (s), 173.14 (s), 159.72 (s), 137.97 (s), 134.07 (s), 132.05 (s), 130.35 (s), 130.05 (s), 126.41 (s), 124.58 (s), 117.22 (s), 79.42 (s), 69.35 (s), 40.19 (q, *J* = 30.0 Hz), 25.38 (s), 21.53 (s). MS (ESI) *m/z* 409 ($M+H^+$); HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{22}H_{24}F_3O_4$ 409.1627, found 409.1633.



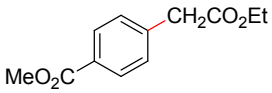
(7t). White solid, TLC R_f (hexane: EtOAc = 6 : 1) = 0.60, 44% yield (51 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 10.9 Hz, 2H), 1.60 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.44 (t, *J* = 10.5 Hz, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.38, 155.60, 131.16, 126.01 (q, *J* = 277.0 Hz), 123.75 (q, *J* = 6.2 Hz), 119.20, 79.38, 61.69, 39.64 (q, *J* = 29.9 Hz), 25.59, 14.24. MS (EI) *m/z* 290 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{14}H_{17}F_3O_3$ 290.1130, found 290.1137.



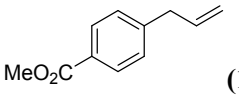
(13a). Colorless oil, TLC R_f (hexane: EtOAc = 6 : 1) = 0.60, 78% yield (51 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.22, 149.76, 129.71, 127.90, 127.65, 51.96, 28.96, 15.23.



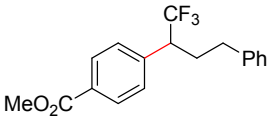
(13b). Colorless oil, TLC R_f (hexane: EtOAc = 6 : 1) = 0.55, 46% yield (35 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 5.11 (dd, *J* = 8.3, 6.1 Hz, 2H), 4.77 (t, *J* = 6.4 Hz, 2H), 4.32 – 4.22 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.85, 146.76, 130.12, 128.99, 126.83, 78.41, 52.13, 40.27. MS (EI) *m/z* 192 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0777.



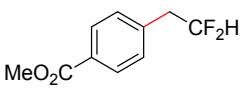
(13c). Colorless oil, TLC R_f (hexane: EtOAc = 6 : 1) = 0.55, 72% yield (64 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.67 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.86, 166.8, 139.29, 129.85, 129.35, 129.01, 61.10, 52.10, 41.38, 14.15. MS (EI) *m/z* 222 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{12}H_{14}O_4$ 222.0892, found 222.0891.



(13d). Colorless oil, TLC R_f (hexane: EtOAc = 6 : 1) = 0.65, 71% yield (50 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.95 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 5.06 (m, 2H), 3.90 (s, 3H), 3.44 (d, *J* = 6.7 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 167.12, 145.51, 136.41, 129.78, 128.63, 128.10, 116.60, 52.01, 40.16. MS (EI) *m/z* 176 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0833.

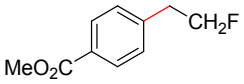


(13e). Light yellow solid, TLC R_f (hexane: EtOAc = 10 : 1) = 0.60, 75% yield (97 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.21 (s, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 3.94 (s, 3H), 3.28 (m, 1H), 2.57 (m, 1H), 2.38 (m, 2H), 2.22 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.40 (s, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.68, 140.17, 139.54, 130.25, 130.03, 129.30, 128.60, 128.38, 126.89 (q, *J* = 191.8 Hz), 126.40, 52.25, 49.11 (q, *J* = 26.9 Hz), 32.38, 30.02. MS (EI) *m/z* 322 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{18}H_{17}F_3O_2$ 322.1181, found 322.1190.

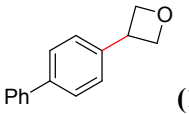


(13f). Light yellow oil, TLC R_f (hexane: EtOAc = 10 : 1) = 0.55, 41% yield (33 mg). ^{1}H

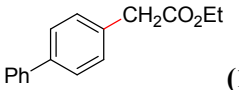
NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.95 (tt, *J* = 56.3, 4.5 Hz, 1H), 3.92 (s, 2H), 3.20 (td, *J* = 17.3, 4.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.80 (s), 137.52 (s), 129.95 (s), 129.90 (s), 129.48 (s), 116.05 (t, *J* = 241.7 Hz), 52.18 (s), 40.82 (t, *J* = 22.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.86 (s, 2F).



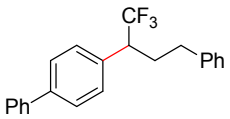
(13g). Light yellow oil, TLC R_f (hexane: EtOAc = 10 : 1) = 0.55, 58% yield (42 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.65 (dt, *J* = 47.0, 6.3 Hz, 2H), 3.91 (s, 3H), 3.07 (dt, *J* = 24.3, 6.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.08 (s), 142.78 (s), 130.00 (s), 129.12 (s), 128.88 (s), 83.60 (d, *J* = 169.7 Hz), 52.16 (s), 37.04 (d, *J* = 20.6 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -216.10 (s, 1F).



(14b). Colorless oil, TLC R_f (hexane: EtOAc = 20 : 1) = 0.60, 57% yield (48 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.10 (dd, *J* = 8.4, 6.1 Hz, 2H), 4.81 (t, *J* = 6.4 Hz, 2H), 4.31 – 4.22 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.76, 140.61, 140.07, 128.83, 127.50, 127.34, 127.28, 127.06, 78.92, 40.09. MS (EI) *m/z* 210 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{15}H_{14}O$ 210.1045, found 210.1054.

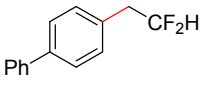


(14c). Colorless oil, TLC R_f (hexane: EtOAc = 10 : 1) = 0.50, 87% yield (84 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* =7.7 Hz, 2H), 7.54 (d, *J* =7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.31 (m, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.65, 140.85, 140.06, 133.22, 129.71, 128.79, 127.34, 127.29, 127.10, 60.97, 41.08, 14.24. MS (EI) *m/z* 240 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1144.

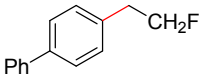


(14e). Light yellow solid, TLC R_f (hexane: EtOAc = 10 : 1) = 0.60, 90% yield (123 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 4H), 7.50 – 7.42 (m, 2H), 7.39 – 7.35 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 3.26 (m, 1H), 2.63 (m, 1H), 2.46 (m, 1H), 2.41 – 2.31 (m, 1H), 2.31 – 2.17 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.18 (s, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.36, 140.79, 140.69, 133.59, 129.80, 129.04, 128.74, 128.64,

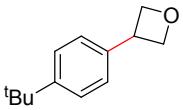
127.71, 127.67, 127.32, 127.15 (q, J = 279.4 Hz), 49.03 (q, J = 26.5 Hz), 32.72, 30.34. MS (EI) *m/z* 340 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{22}H_{19}F_3$ 340.1439, found 340.1435.



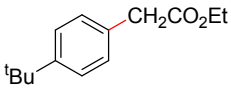
(14f). Light yellow solid, TLC R_f (hexane: EtOAc = 10 : 1) = 0.65, 75% yield (65 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (t, J = 8.6 Hz, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.37 – 7.27 (m, 3H), 5.94 (tt, J = 56.6, 4.6 Hz, 1H), 3.16 (td, J = 17.3, 4.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.80 (s), 140.64 (s), 131.58 (t, J = 5.9 Hz), 130.34 (s), 128.94 (s), 127.56 (s), 127.53 (s), 127.21 (s), 116.75 (t, J = 241.5 Hz), 40.69 (t, J = 21.9 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.70 (s, 2F).



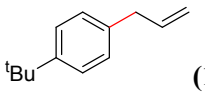
(14g). White solid, TLC R_f (hexane: EtOAc = 10 : 1) = 0.65, 78% yield (62 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.7 Hz, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 7.7 Hz, 2H), 4.66 (dt, J = 47.1, 6.5 Hz, 2H), 3.05 (dt, J = 23.4, 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.04 (s), 139.85 (s), 136.33 (d, J = 6.2 Hz), 129.51 (s), 128.89 (s), 127.44 (s), 127.33 (s), 127.18 (s), 84.14 (d, J = 169.2 Hz), 36.71 (d, J = 20.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -215.25 (s, 1F).



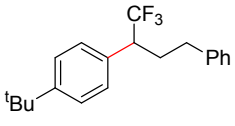
(15b). Colorless oil, TLC R_f (hexane: EtOAc = 20 : 1) = 0.60, 81% yield (62 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.08 – 5.01 (m, 2H), 4.79 (t, J = 6.4 Hz, 2H), 4.21 (p, J = 7.7 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.03, 138.51, 126.58, 125.67, 79.08, 39.96, 34.52, 31.38. MS (EI) *m/z* 190 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{13}H_{18}O$ 190.1358, found 190.1366.



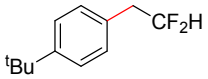
(15c). Colorless oil, TLC R_f (hexane: EtOAc = 10 : 1) = 0.55, 75% yield (66 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 1.31 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.85, 149.88, 131.12, 128.90, 125.51, 60.80, 40.90, 34.46, 31.36, 14.22. MS (EI) *m/z* 220 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1460.



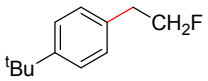
(15d). Colorless oil, TLC R_f (hexane) = 0.50, 69% yield (48 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 5.97 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.07 (dddd, *J* = 10.0, 4.2, 3.2, 1.4 Hz, 2H), 3.36 (d, *J* = 6.8 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.91, 137.64, 137.06, 128.21, 125.34, 115.64, 39.76, 34.40, 31.43. MS (EI) *m/z* 174 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{13}H_{18}$ 174.1409, found 174.1411.



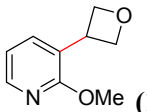
(15e). Light yellow oil, TLC R_f (hexane) = 0.50, 51% yield (65 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.27 (dd, *J* = 14.7 Hz, 7.1 Hz, 2H), 7.22 (d, *J* = 13.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 2H), 3.27–3.10 (m, 1H), 2.59 (m, 1H), 2.42 (m, 1H), 2.36–2.26 (m, 1H), 2.20 (m, 1H), 1.34 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.70 (s, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.30, 141.01, 131.48, 128.97, 128.69, 128.64, 126.38, 125.64, 127.52 (q, *J* = 280.1 Hz), 48.90 (q, *J* = 26.5 Hz), 34.76, 32.80, 31.54, 30.38. MS (EI) *m/z* 320 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{20}H_{23}F_3$ 320.1752, found 320.1760.



(15f). Light yellow oil, TLC R_f (hexane) = 0.50, 44% yield (35 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.22 (s, 2H), 5.95 (t, *J* = 56.6 Hz, 1H), 3.14 (t, *J* = 17.3 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.62 (s), 129.67 (s), 125.84 (s), 117.02 (t, *J* = 241.3 Hz), 40.63 (t, *J* = 21.8 Hz), 34.70 (s), 31.53 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.66 (dt, *J* = 56.7, 17.4 Hz, 2F).

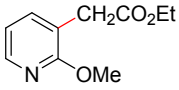


(15g). Colorless oil, TLC R_f (hexane) = 0.50, 56% yield (40 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.62 (dt, *J* = 47.1, 6.7 Hz, 2H), 2.99 (dt, *J* = 22.7, 6.7 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.56 (s), 133.98 (d, *J* = 6.7 Hz), 128.66 (s), 125.49 (s), 84.20 (d, *J* = 168.7 Hz), 36.40 (d, *J* = 20.3 Hz), 34.44 (s), 31.38 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -214.86 (s, 1F).

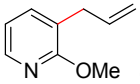


(16b). Yellow oil, TLC R_f (hexane: EtOAc = 4 : 1) = 0.40, 42% yield (28 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.0 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 6.92 (dd, *J* = 7.2, 5.1 Hz, 1H), 5.01 (dd, *J* = 8.5, 5.9 Hz, 2H), 4.81 (d, *J* = 13.3 Hz, 2H), 4.43 (p, *J* = 8.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.56, 145.06, 134.94, 123.58, 116.76, 65.86, 53.36, 34.55.

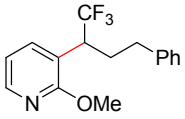
MS (EI) *m/z* 165 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_9H_{11}NO_2$ 165.0790, found 165.0788.



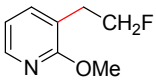
(16c). Colorless oil, TLC R_f (hexane: EtOAc = 4 : 1) = 0.40, 51% yield (40 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 4.9 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 6.89 – 6.81 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 3.58 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.09, 162.12, 145.69, 139.02, 117.53, 116.71, 60.85, 53.46, 35.56, 14.20. MS (EI) *m/z* 195 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{10}H_{13}NO_3$ 195.0895, found 195.0899.



(16d). Colorless oil, TLC R_f (hexane: EtOAc = 4 : 1) = 0.50, 67% yield (40 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.39 (d, *J* = 6.4 Hz, 1H), 6.83 (dd, *J* = 7.1, 5.0 Hz, 1H), 5.97 (ddt, *J* = 16.9, 10.4, 6.7 Hz, 1H), 5.10 – 5.05 (m, 2H), 3.96 (s, 3H), 3.33 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.95, 144.48, 137.62, 135.67, 122.86, 116.73, 116.28, 53.32, 33.82. MS (EI) *m/z* 149 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_9H_{11}NO$ 149.0841, found 149.0839.



(16e). Colorless oil, TLC R_f (hexane: EtOAc = 5 : 1) = 0.40, 85% yield (100 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.16 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.94 (dd, *J* = 7.4, 5.0 Hz, 1H), 3.94 (s, 3H), 3.89 (m, 1H), 2.54 (m, 1H), 2.47 (m, 1H), 2.36 – 2.26 (m, 1H), 2.18 – 2.07 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.54 (s, 3F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.64, 146.68, 128.63, 128.54, 127.14 (q, *J* = 280.9 Hz), 53.85, 40.54 (q, *J* = 26.8 Hz), 32.76, 30.39. MS (EI) *m/z* 295 (M^+); HRMS (EI-TOF) *m/z* $[M]^+$ Calcd for $C_{16}H_{16}F_3NO$ 295.1184, found 295.1180.



(16g). Yellow oil, TLC R_f (hexane: EtOAc = 5 : 1) = 0.45, 62% yield (39 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.4 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 6.84 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.64 (dt, *J* = 47.1, 6.3 Hz, 2H), 3.96 (s, 3H), 2.98 (dt, *J* = 23.8, 6.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.07 (s), 144.16 (s), 138.00 (s), 118.66 (d, *J* = 5.8 Hz), 115.75 (s), 81.27 (d, *J* = 167.4 Hz), 52.34 (s), 30.31 (d, *J* = 21.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -216.62 (s, 1F).

Table S4. The reference literatures of reported compounds

Known Compound Number	Reference
7a, 7b, 7d, 7e, 7f, 7g, 7h, 7i, 7k, 7n, 7q, 7r	Zhao, Y.; Hu, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 1033.
7c	Leng, F.; Wang, Y.; Li, H.; Li, J.; Zou, D.; Wu, Y.; Wu, Y. *Chem. Commun.* **2013**, *49*, 10697.
7j, 7l	Xu, S.; Chen, H.-H.; Dai, J.-J.; Xu, H.-J. *Org. Lett.* **2014**, *16*, 2306.
7m	Kautzky, J. A.; Wang, T.; Evans, R. W.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2018**, *140*, 6522.
7p	Akira, S.; Tetsuo, Y.; Hiroaki, I.; Masayuki, N.; Keiko, T.; Noriko, O. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3905.
13a	Rushworth, P. J.; Hulcoop, D. G.; Fox, D. J. *J. Org. Chem.* **2013**, *78*, 9517.
13b, 13c, 13d, 13f, 14f, 15f	Zhang, X.; Yang, C. *Adv. Synth. Catal.* **2015**, *357*, 2721.
14c	Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 9902.
15c	Chen, Z.; Wen, Y.; Fu, Y.; Chen, H.; Ye, M.; Luo, G. *Synlett* **2017**, *28*, 981.
15d	Mayer, M.; Czaplik, W. M.; Jacobi von Wangelin, A. *Adv. Synth. Catal.* **2010**, *352*, 2147.
16d	Struk, Ł.; Sośnicki, J. G. *Synthesis* **2012**, *44*, 735-746.
13g, 14g, 15g, 16g	Yang, Y.; Cai, J.; Luo, G.; Jiang, Y.; Su, Y.; Su, Y.; Li, C.; Zheng, Y.; Zeng, J.; Liu, Y. *Org. Chem. Front.* **2019**, dol:

	10.1039/C9QO00066F.

V. Copies of ^{1}H NMR , ^{19}F NMR and ^{13}C NMR spectra

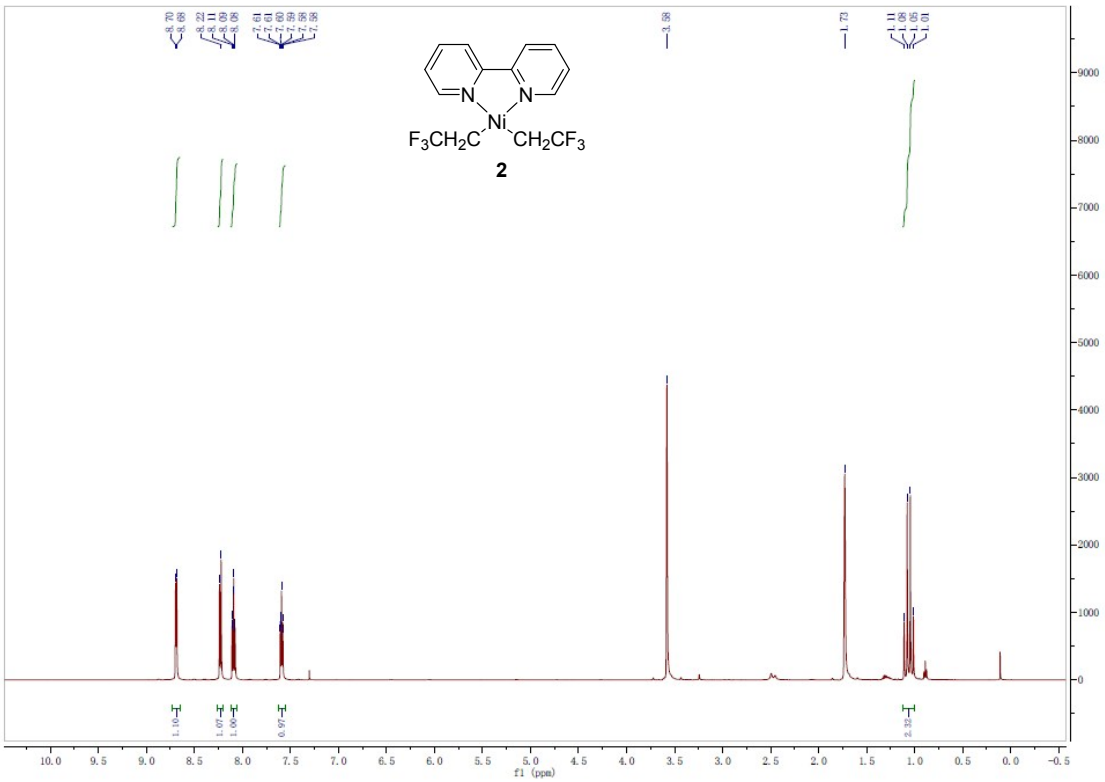


Figure S2. ^{1}H NMR of 2 in d_8-THF

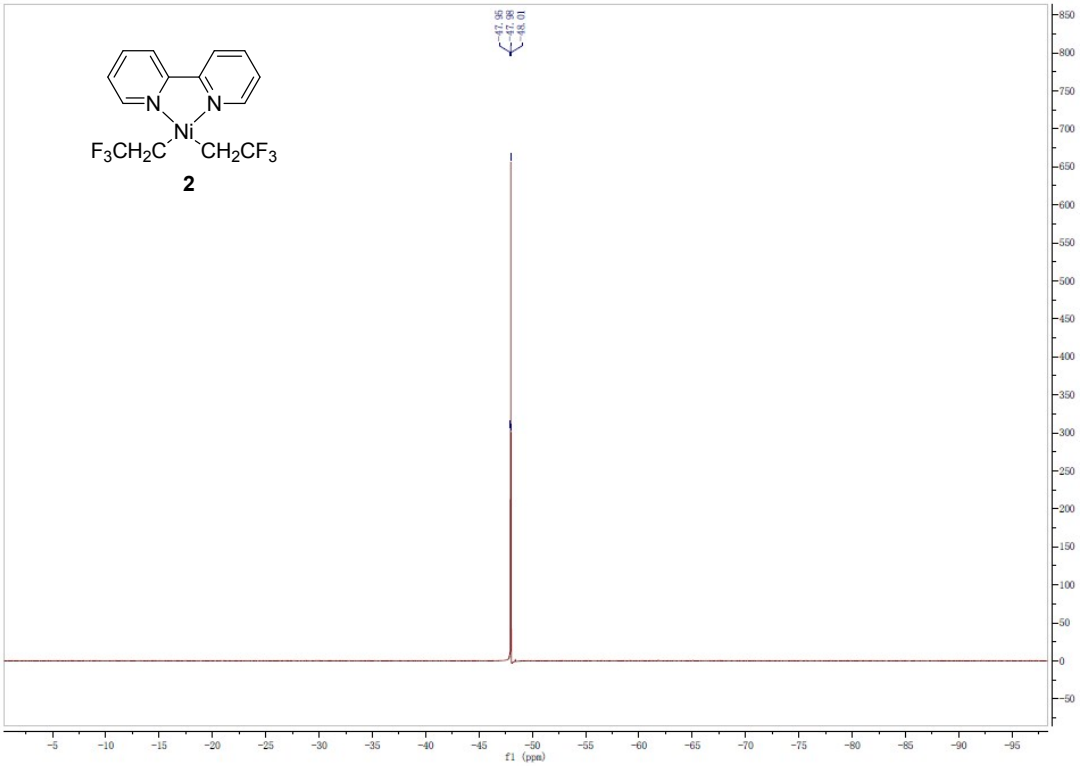


Figure S3. ^{19}F NMR of 2 in d_8-THF

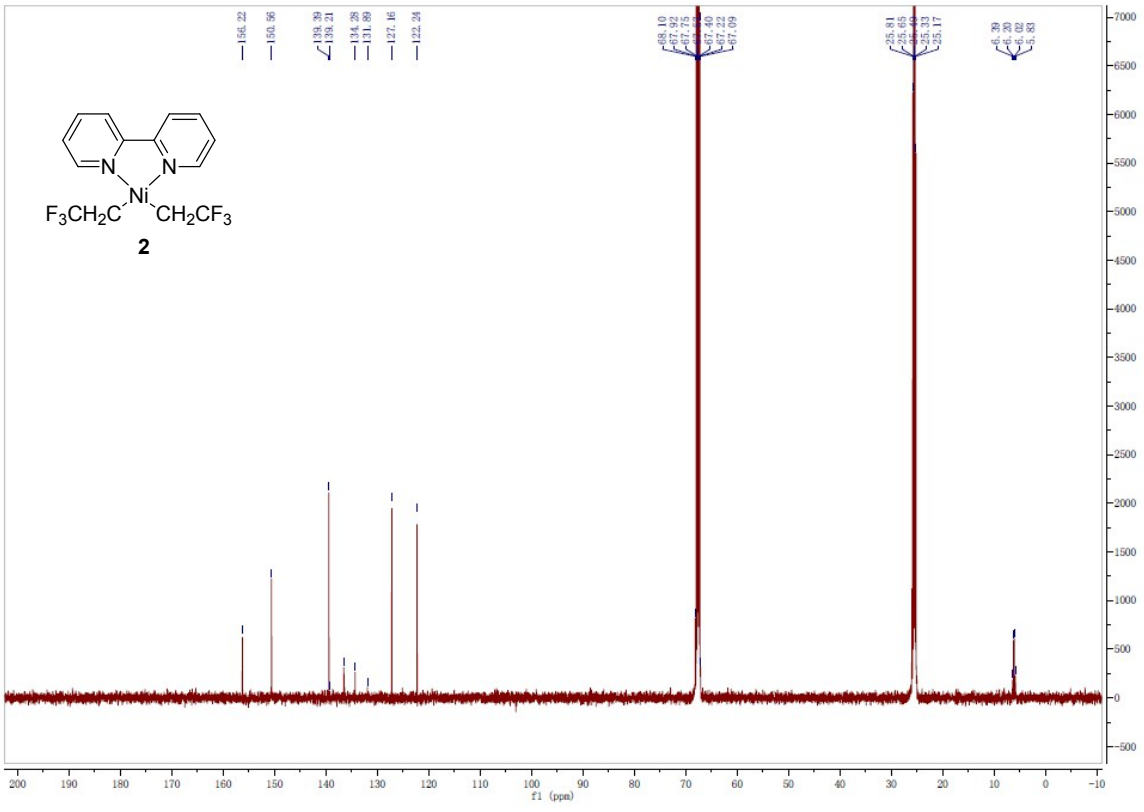


Figure S4. ^{13}C NMR of 2 in d_8-THF

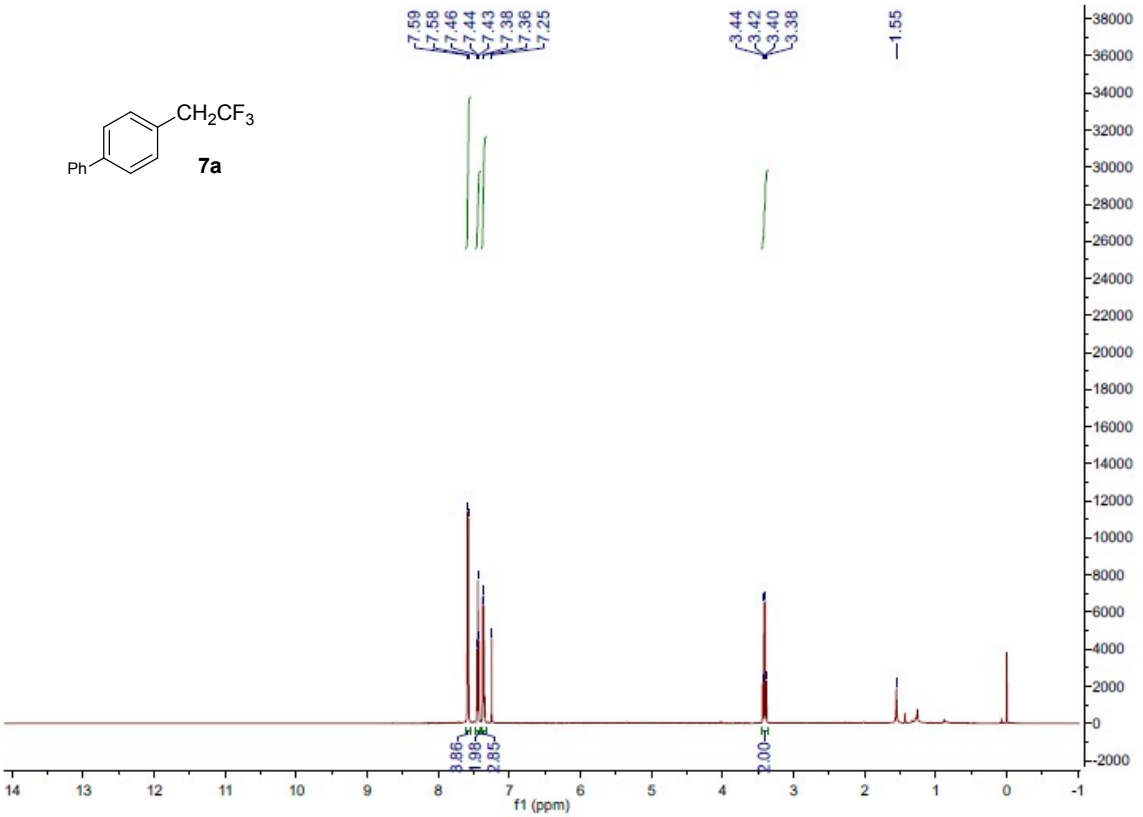


Figure S5. ^{1}H NMR of 7a in $CDCl_3$

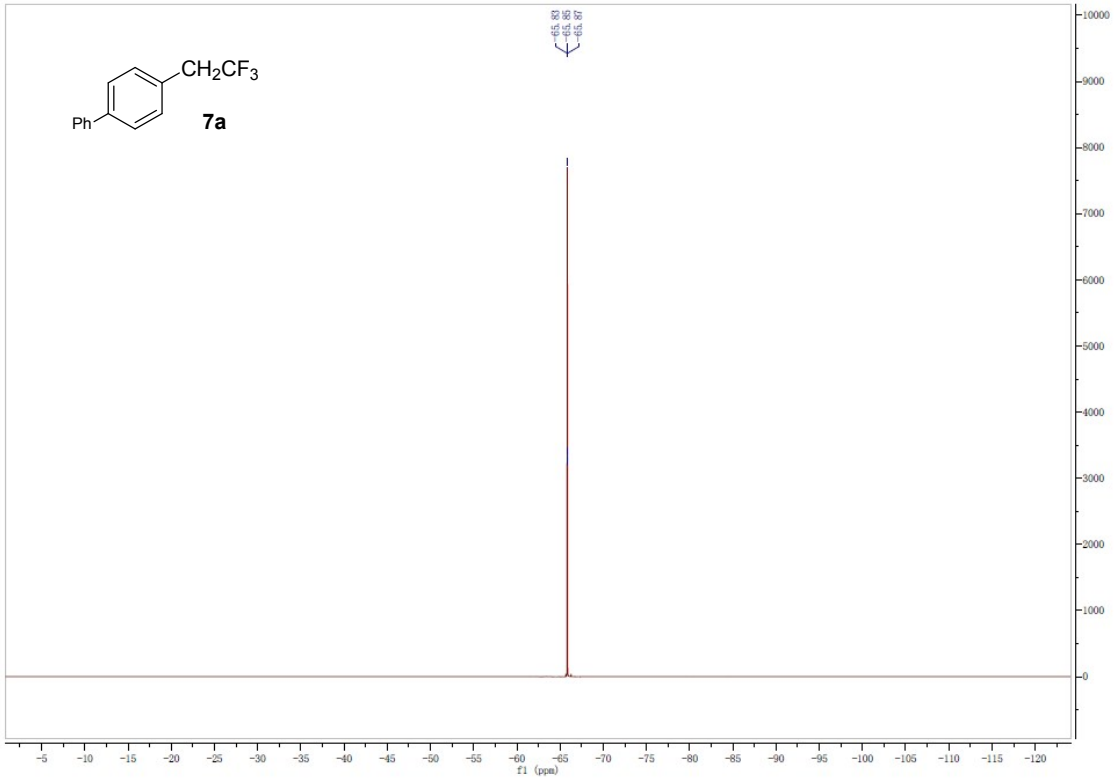


Figure S6. ^{19}F NMR of 7a in $CDCl_3$

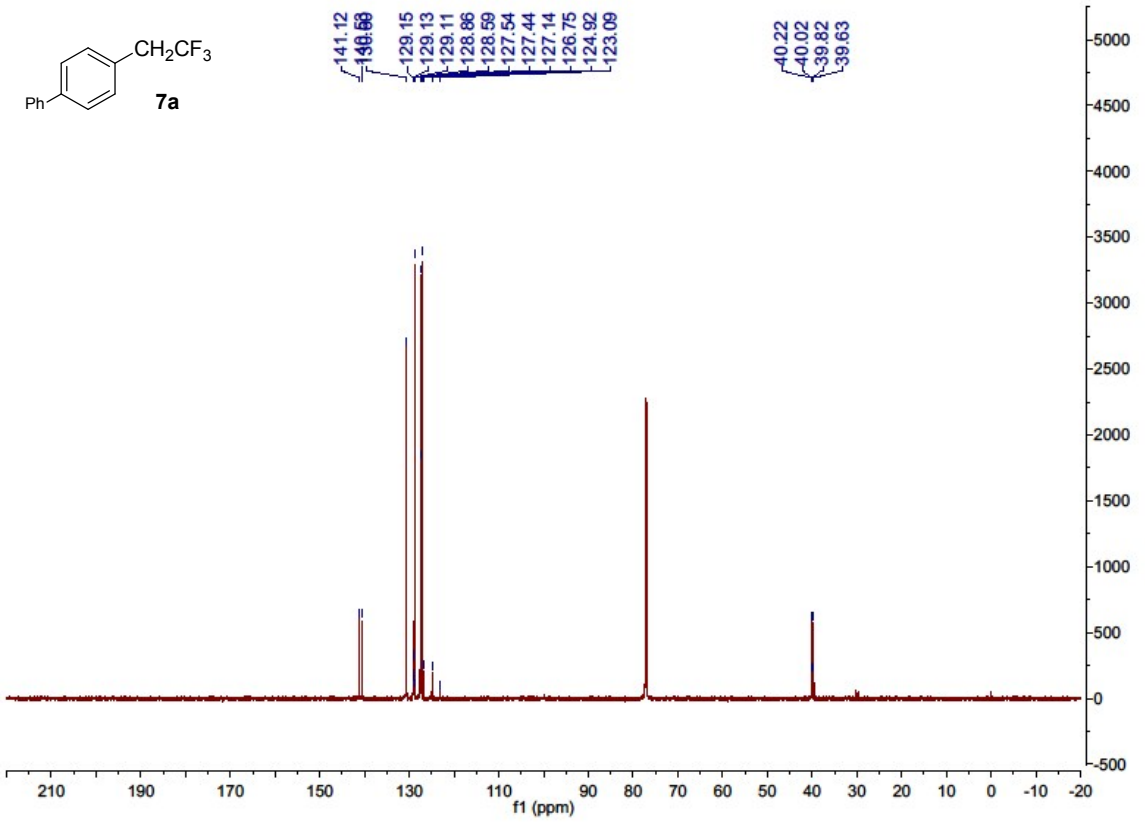


Figure S7. ^{13}C NMR of 7a in $CDCl_3$

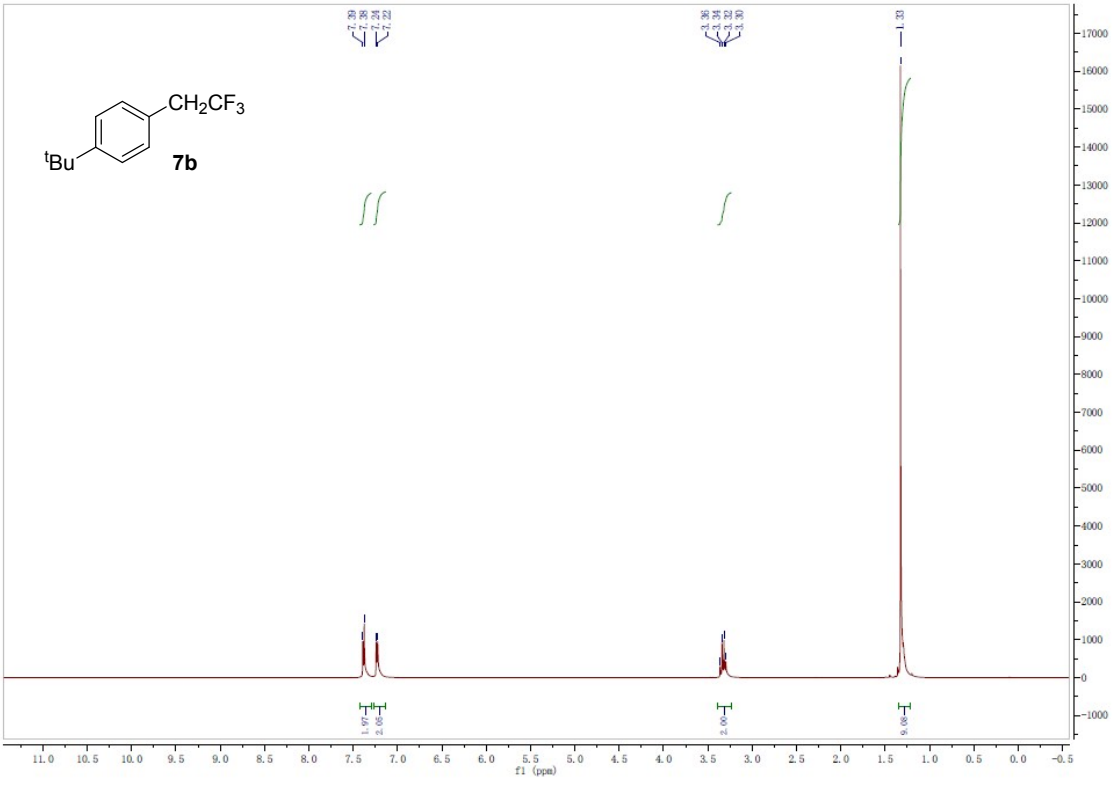


Figure S8. ^{1}H NMR of 7b in $CDCl_3$

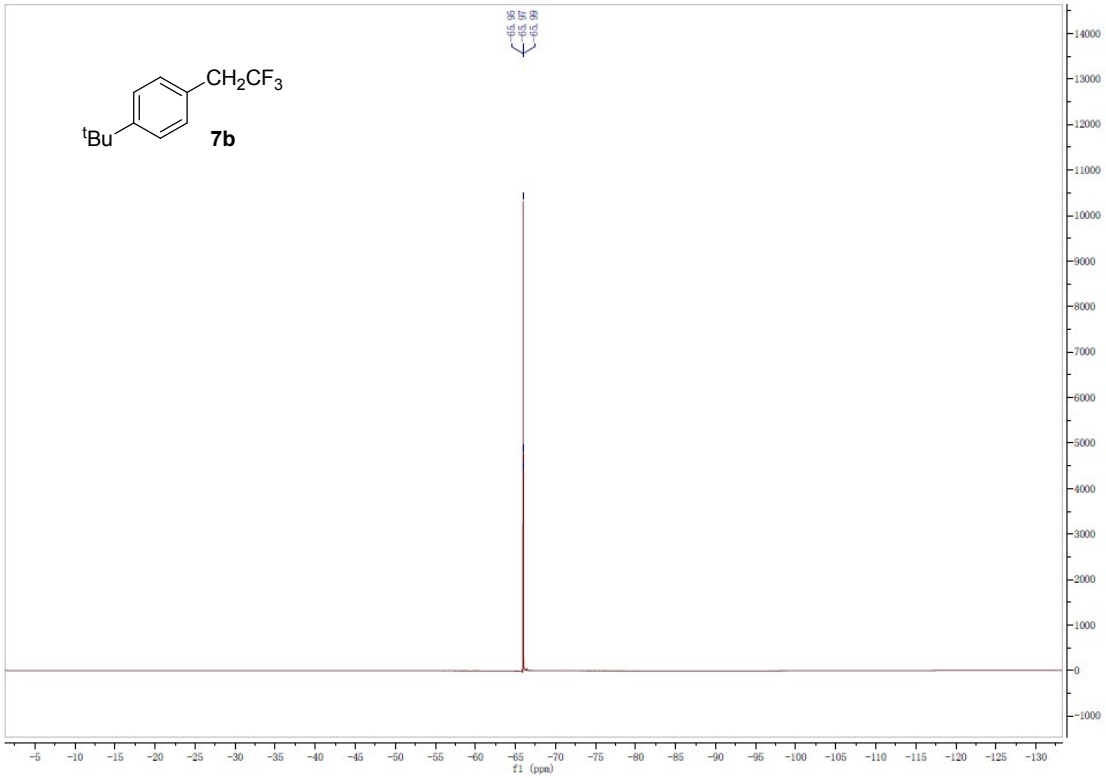


Figure S9. ^{19}F NMR of 7b in $CDCl_3$

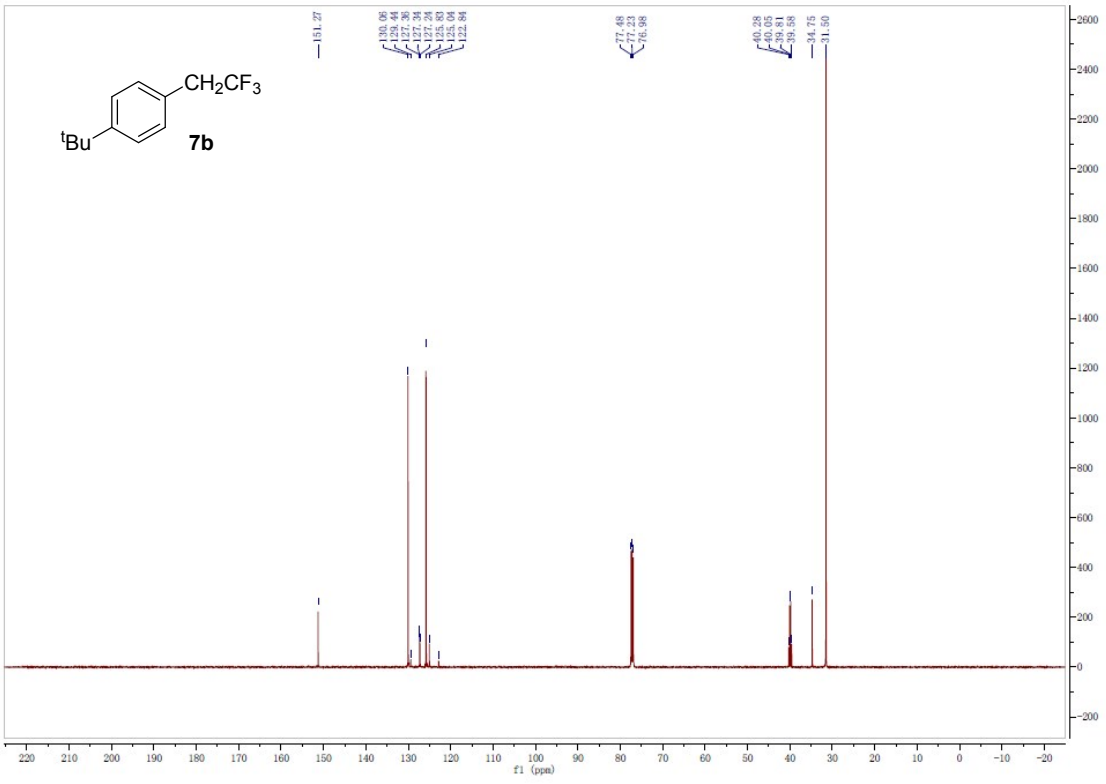


Figure S10. ^{13}C NMR of 7b in $CDCl_3$

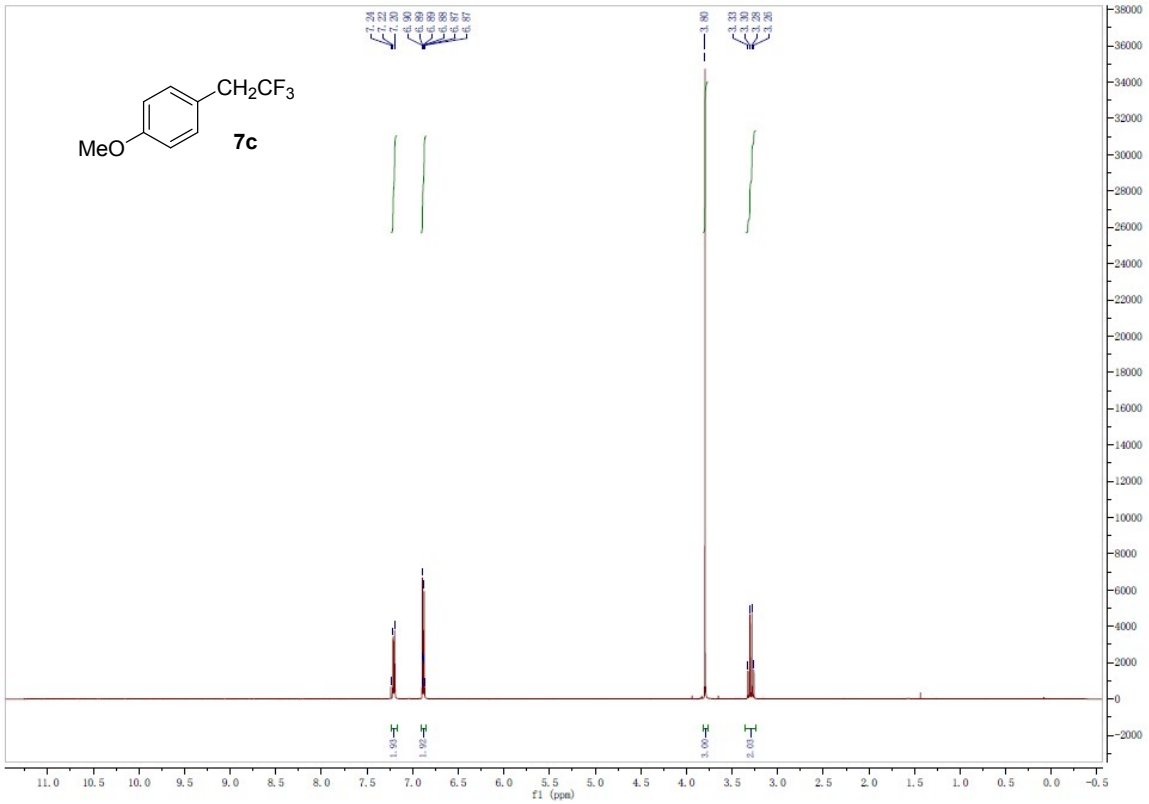


Figure S11. ^{1}H NMR of 7c in $CDCl_3$

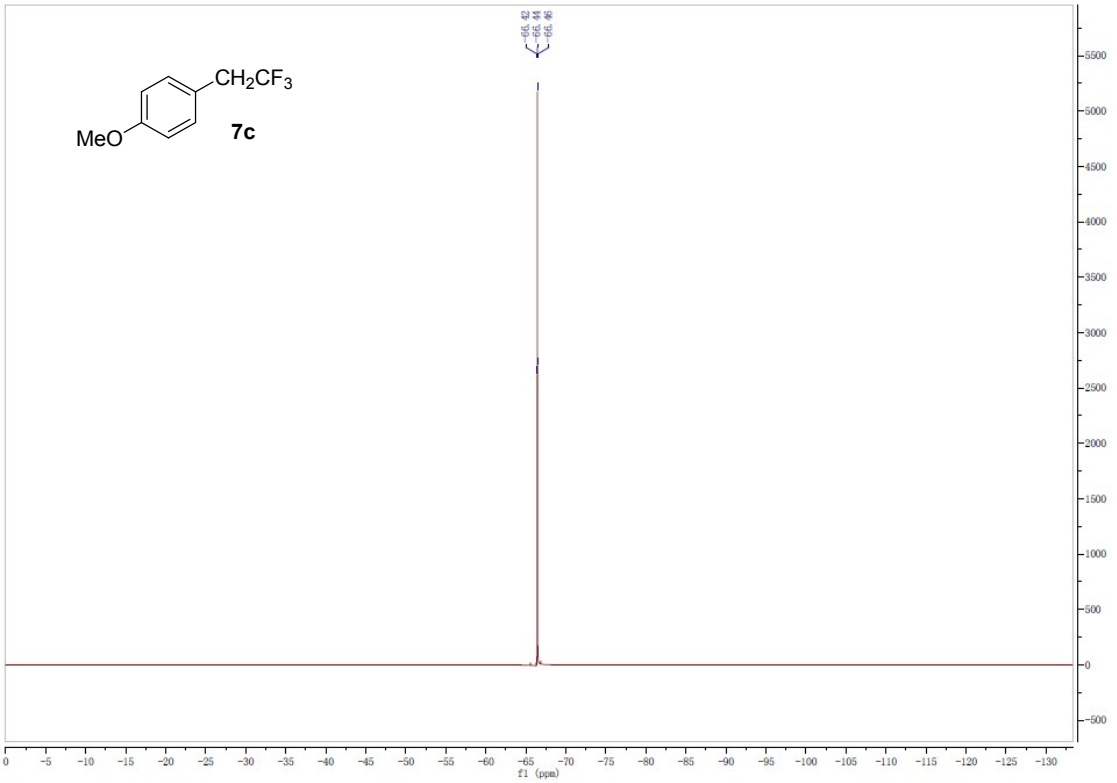


Figure S12. ^{19}F NMR of 7c in $CDCl_3$

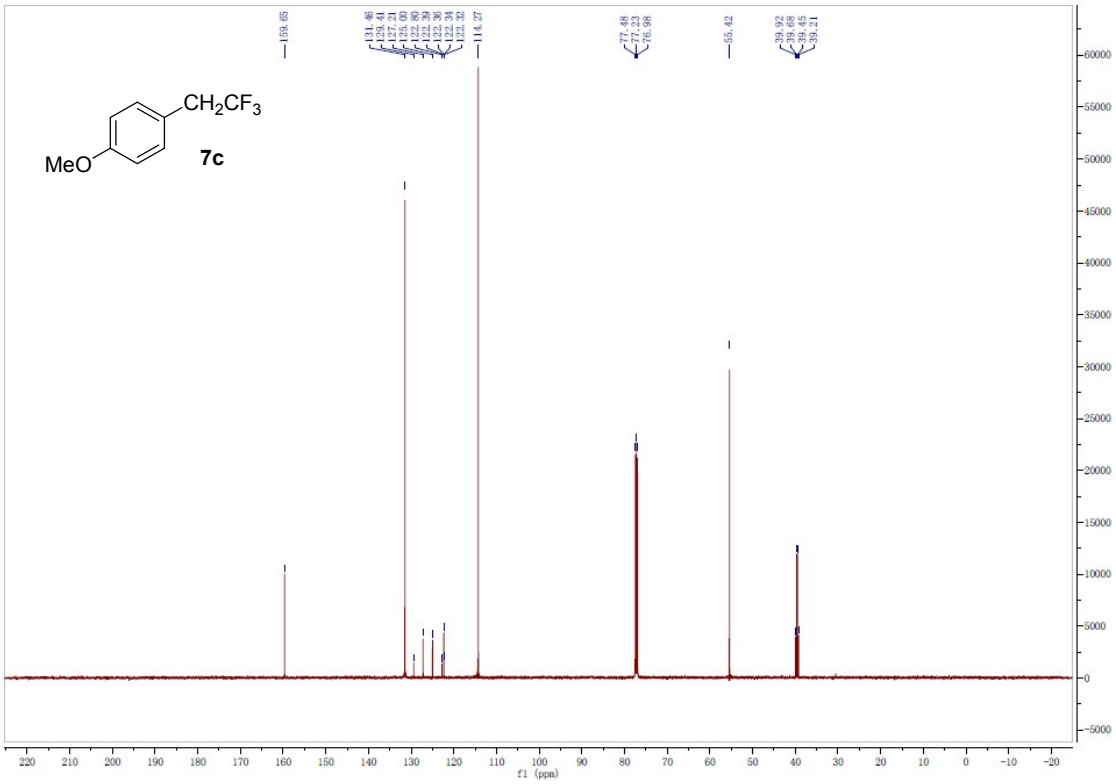


Figure S13. ^{13}C NMR of 7c in $CDCl_3$

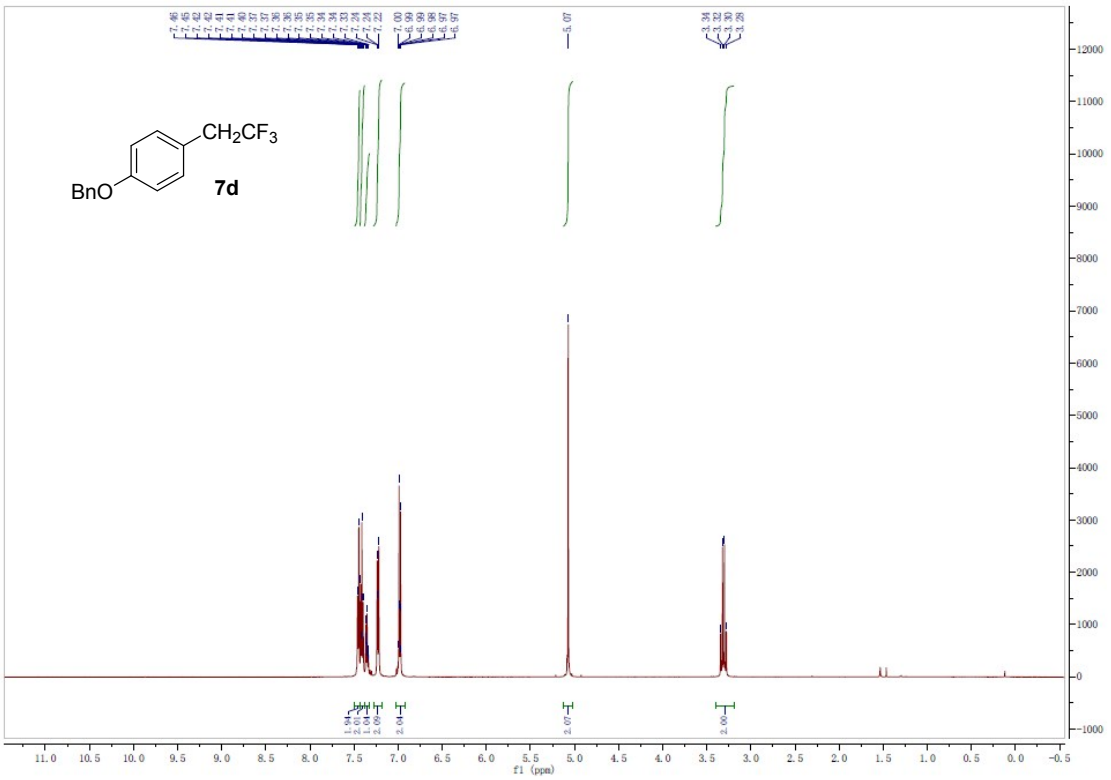


Figure S14. ^{1}H NMR of 7d in $CDCl_3$

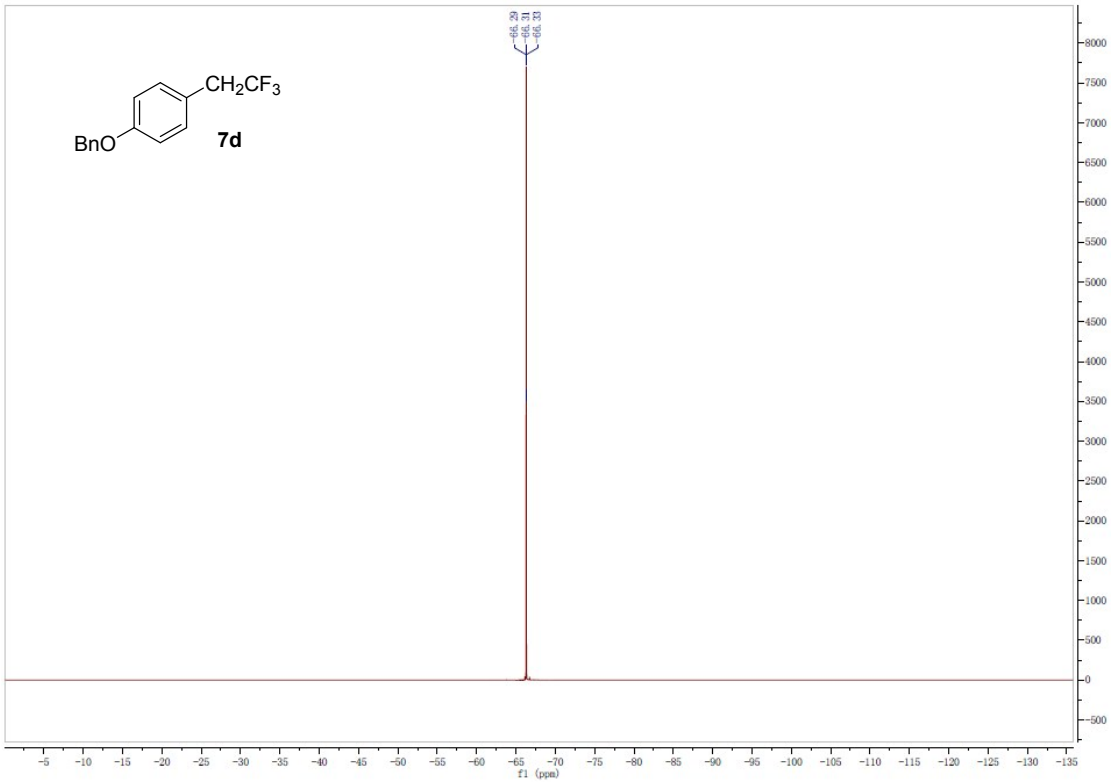


Figure S15. ^{19}F NMR of 7d in $CDCl_3$

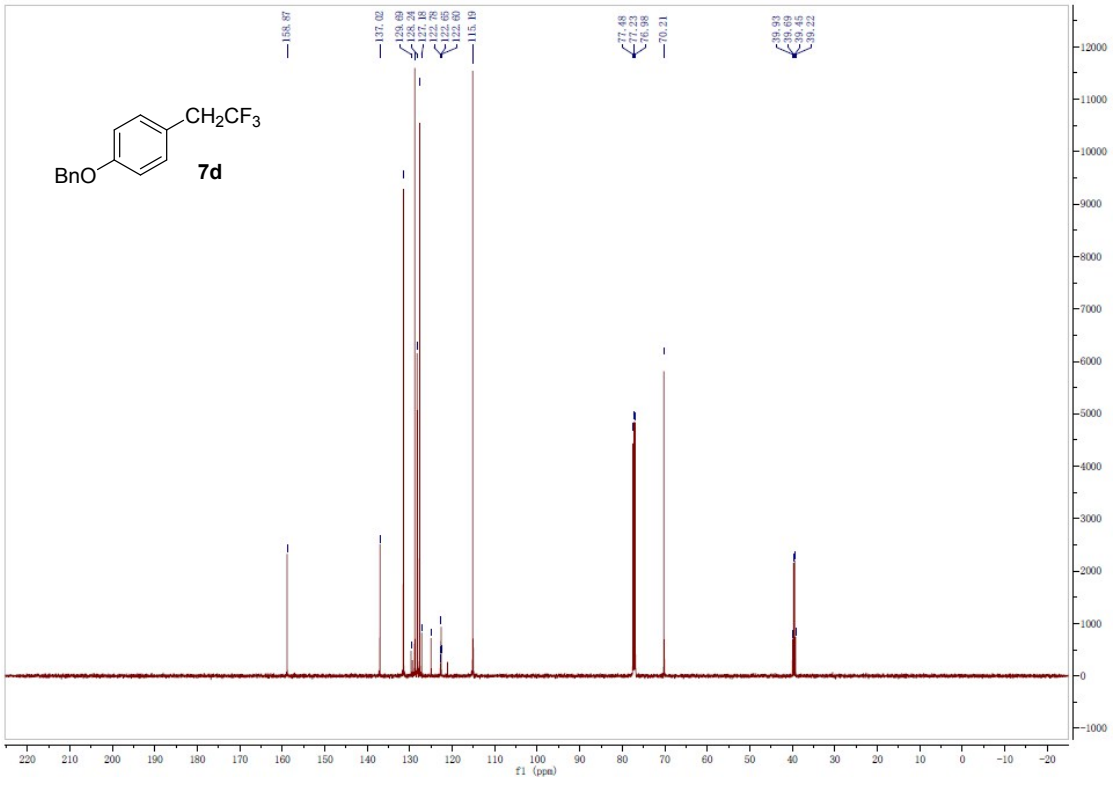


Figure S16. ^{13}C NMR of 7d in $CDCl_3$

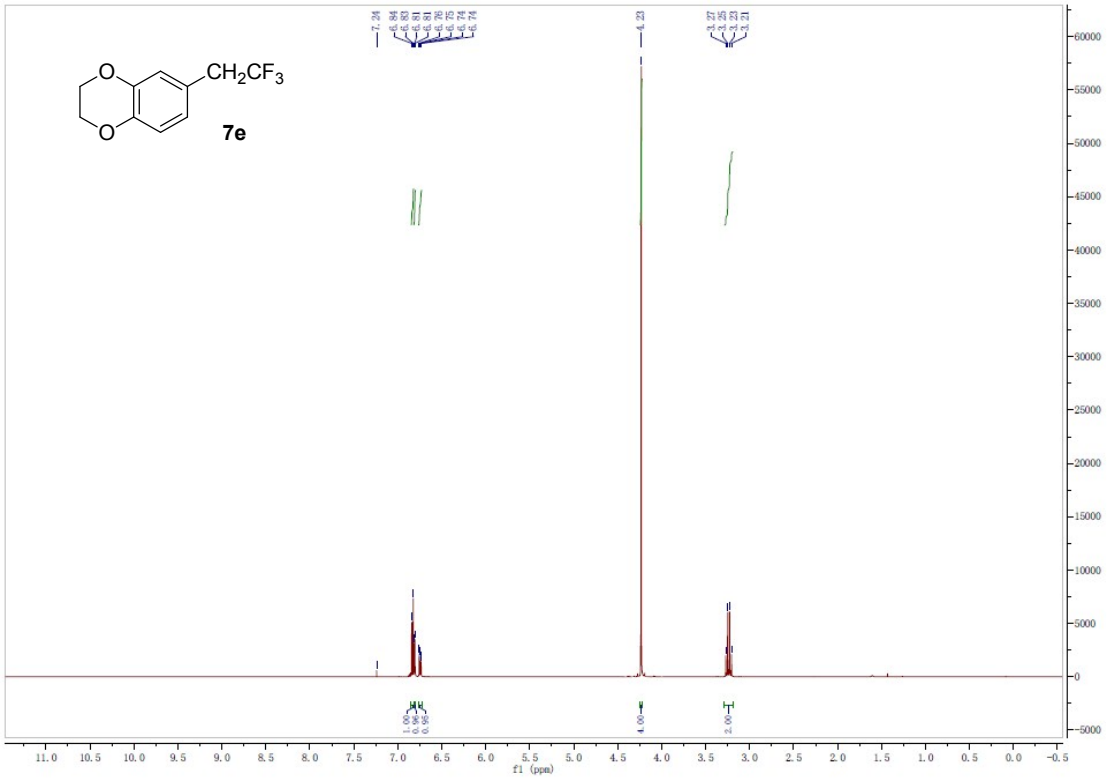


Figure S17. ^{1}H NMR of 7e in $CDCl_3$

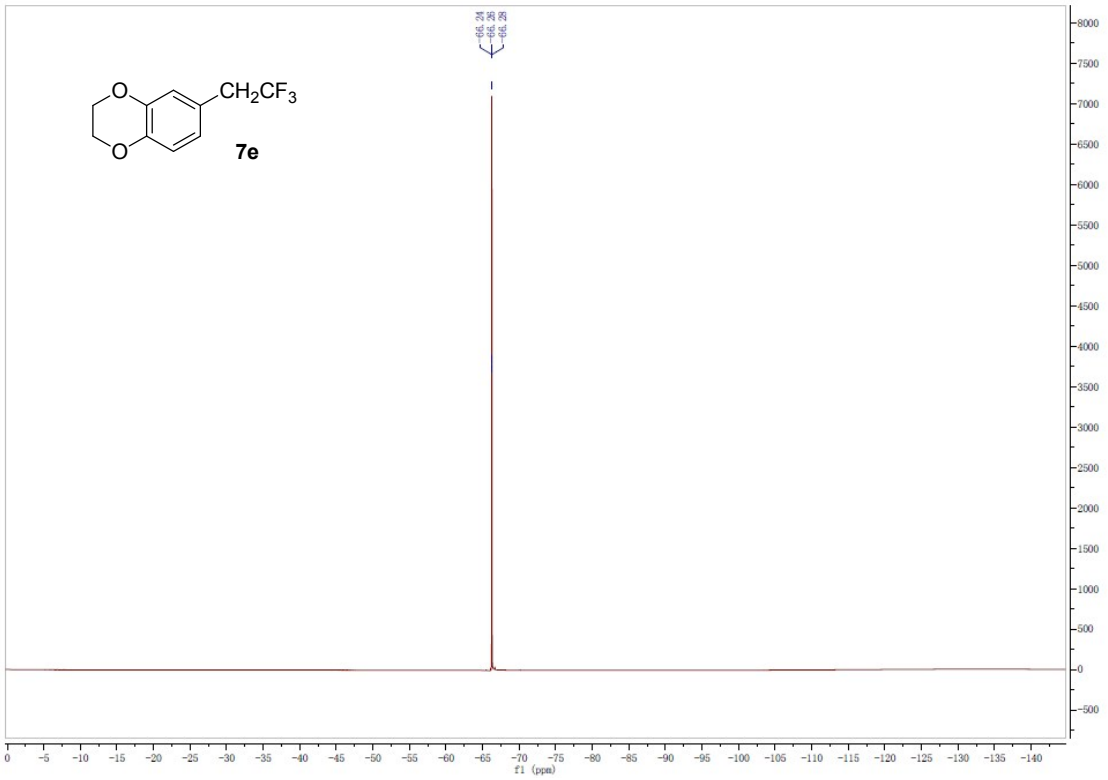


Figure S18. ^{19}F NMR of 7e in $CDCl_3$

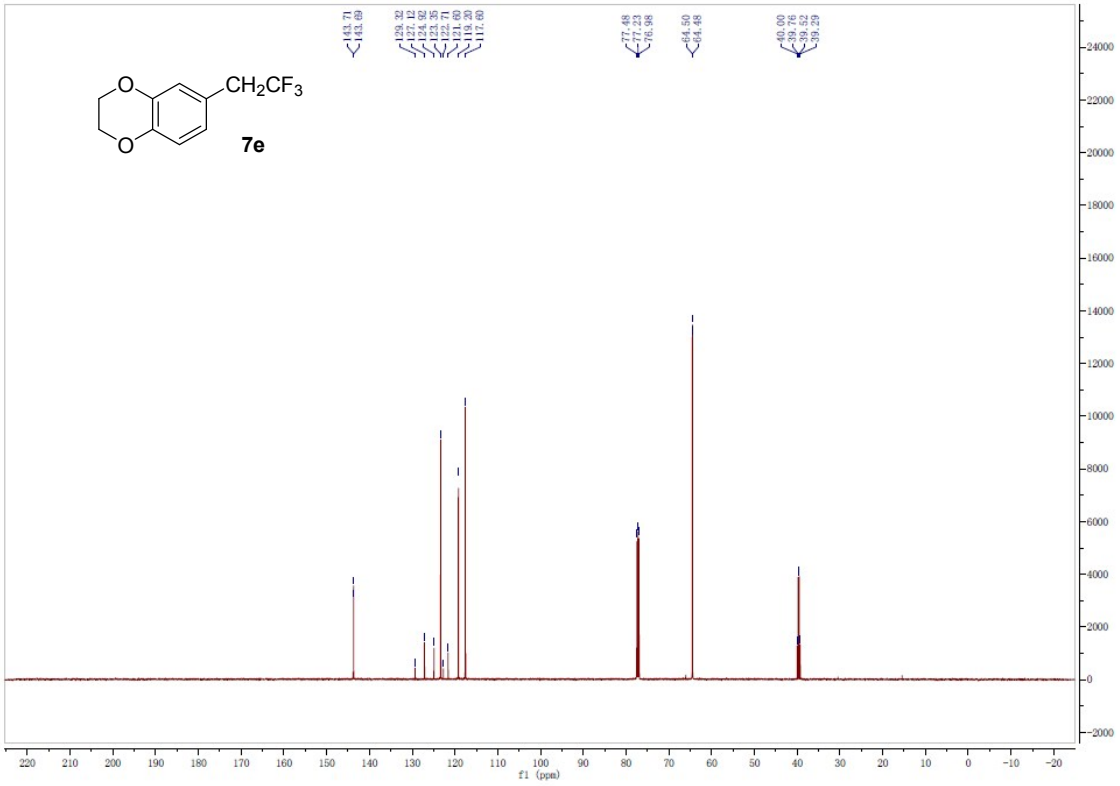


Figure S19. ^{13}C NMR of 7e in $CDCl_3$

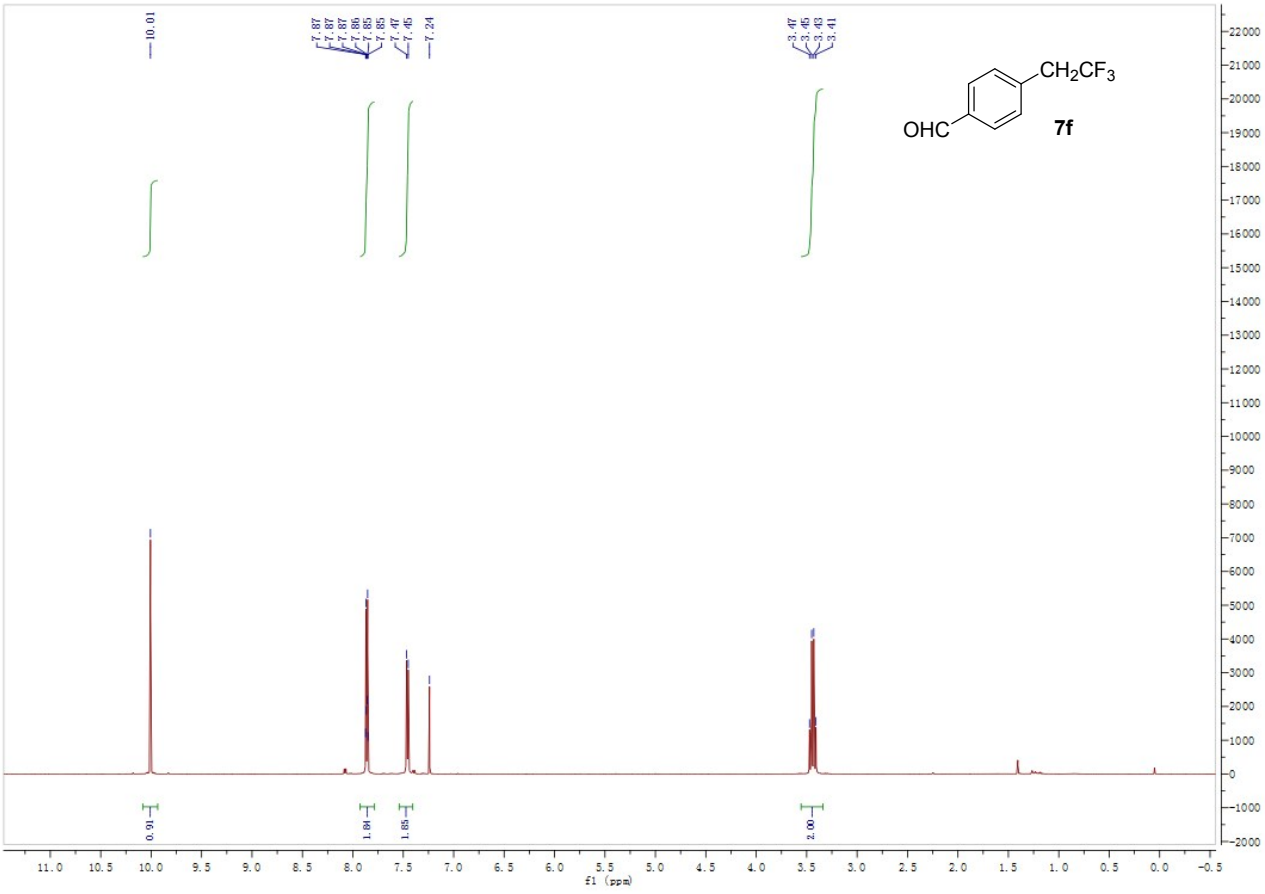


Figure S20. ^{1}H NMR of 7f in $CDCl_3$

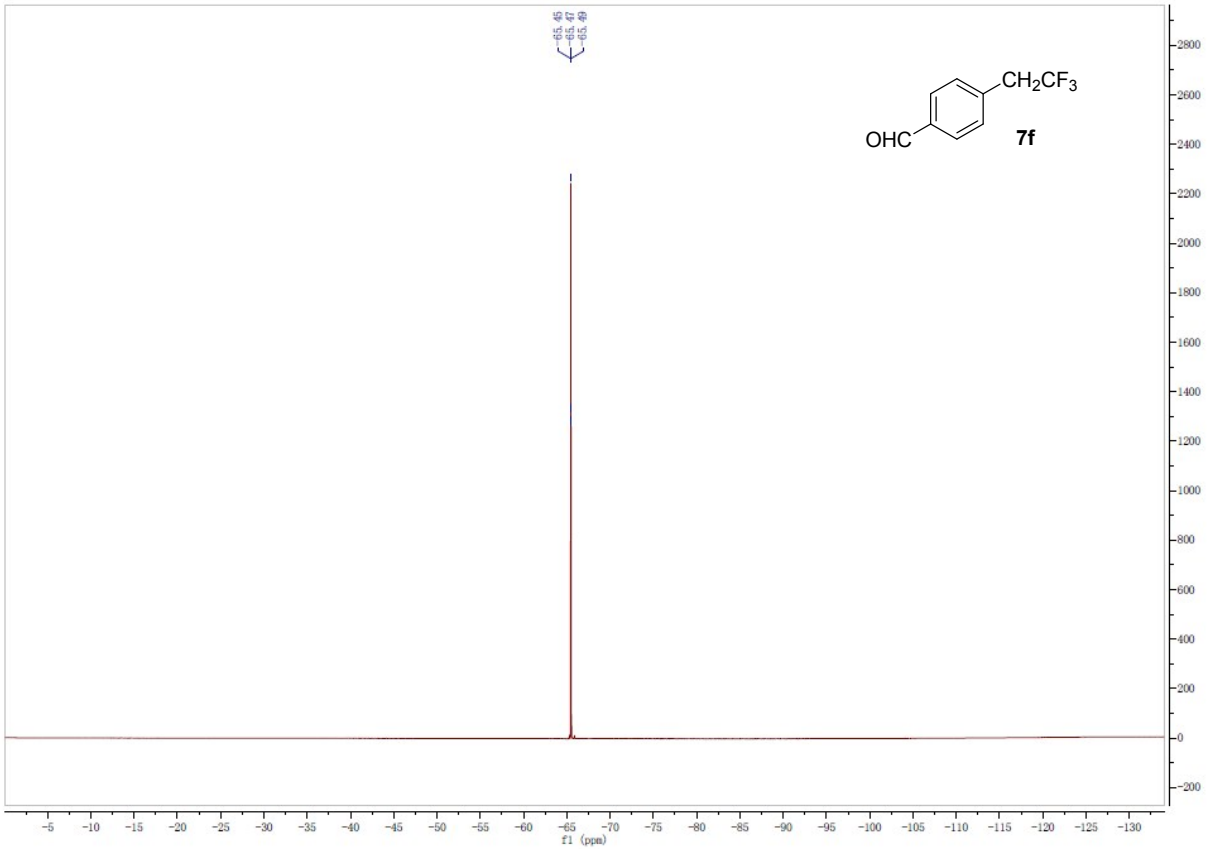


Figure S21. ^{19}F NMR of 7f in $CDCl_3$

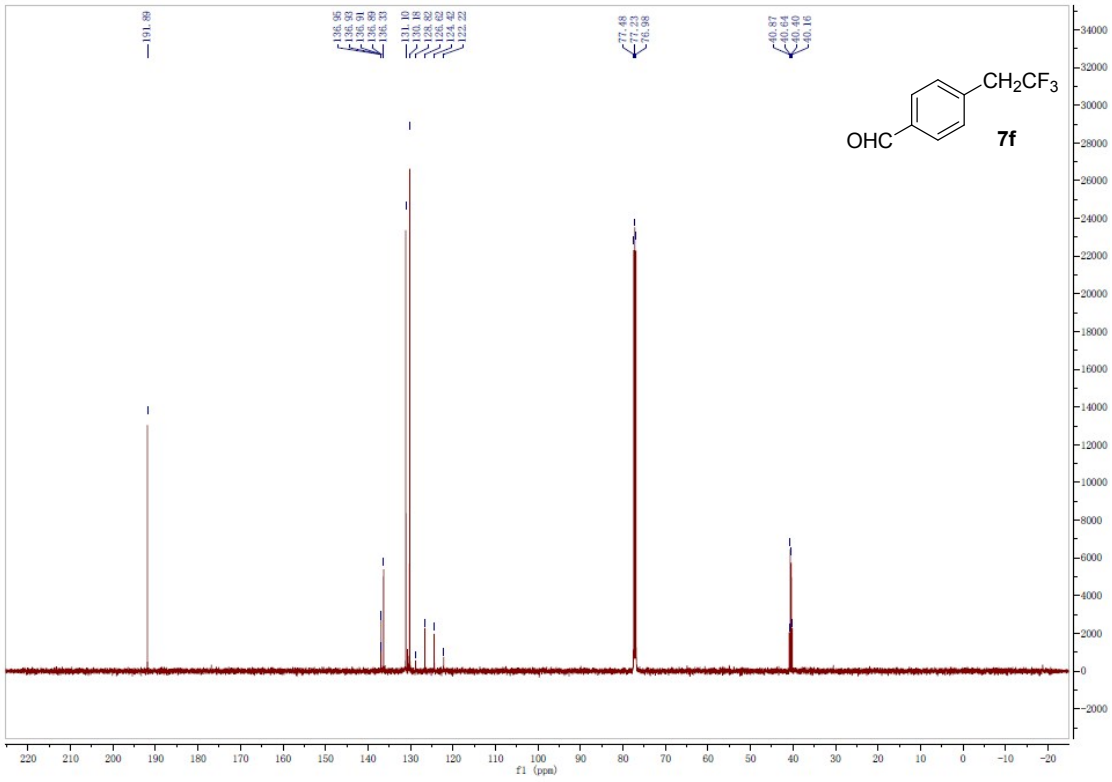


Figure S22. ^{13}C NMR of 7f in $CDCl_3$

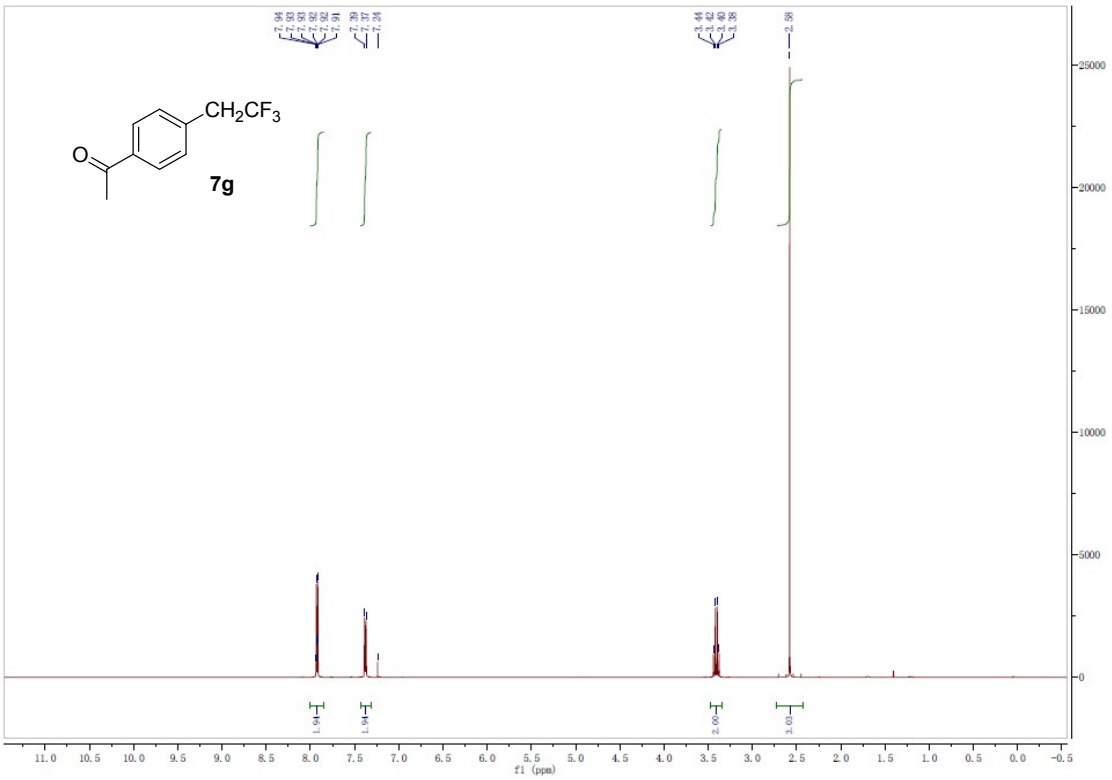


Figure S23. ^{1}H NMR of 7g in $CDCl_3$

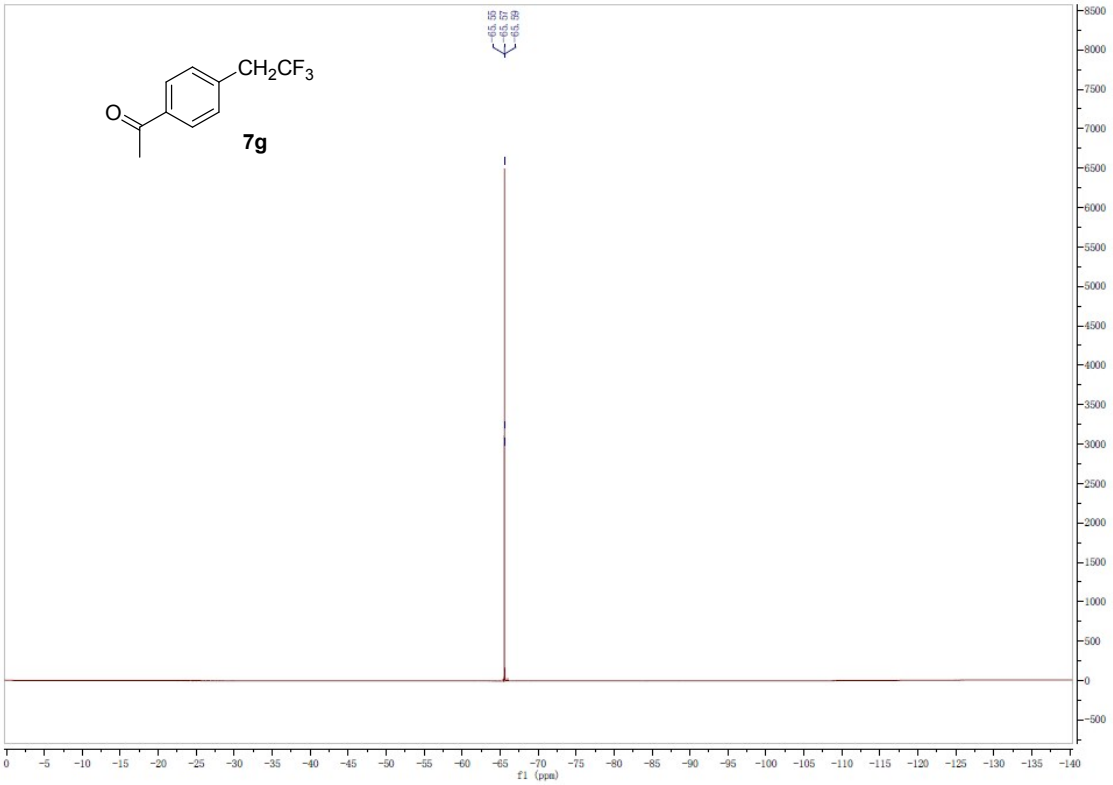


Figure S24. ^{19}F NMR of 7g in $CDCl_3$

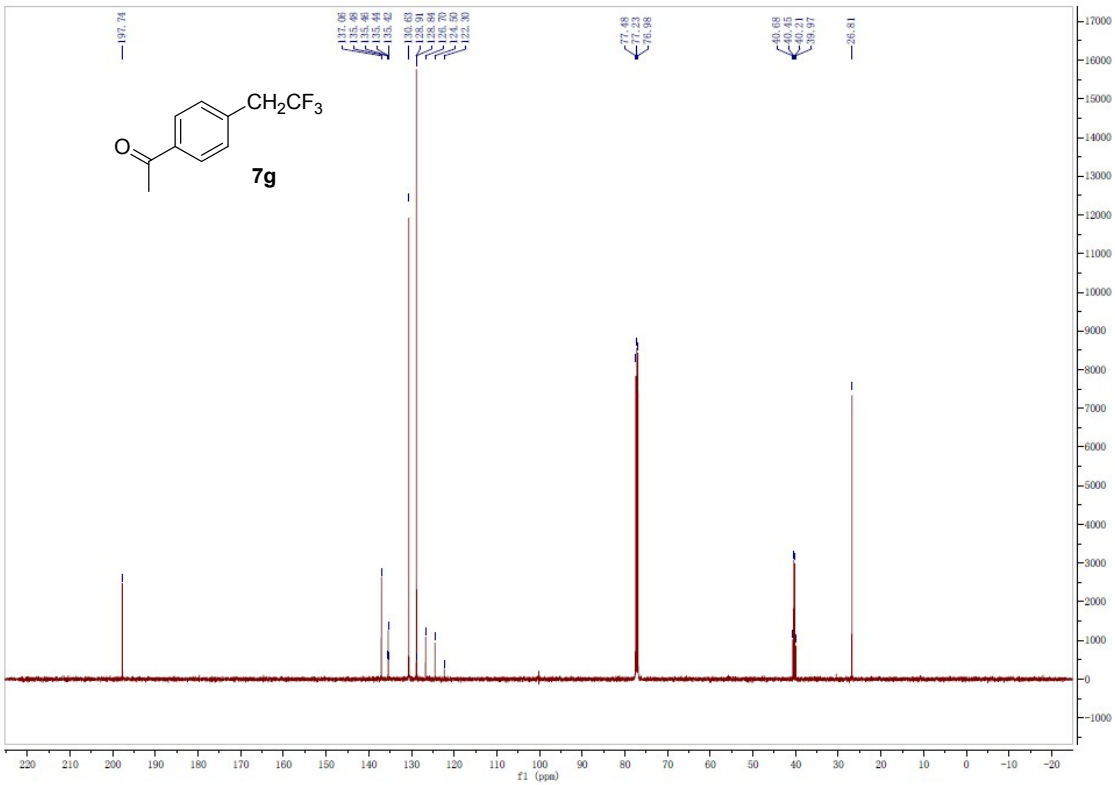


Figure S25. ^{13}C NMR of 7g in $CDCl_3$

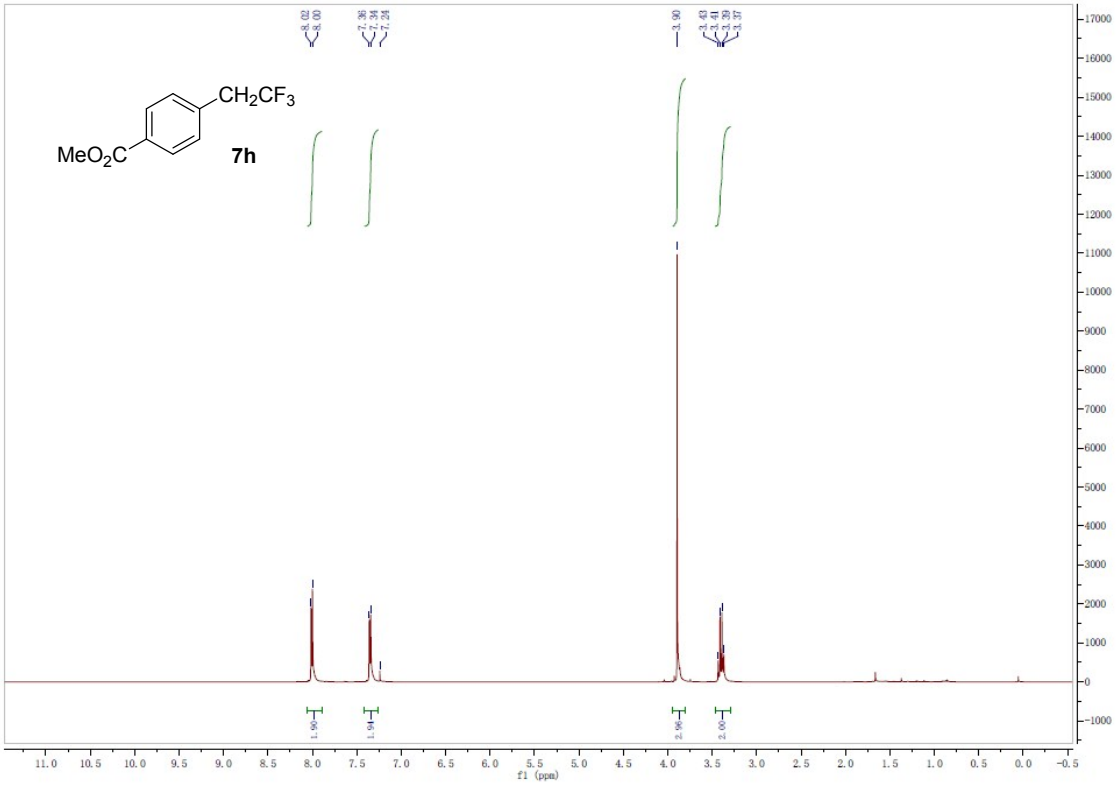


Figure S26. ^{1}H NMR of 7h in $CDCl_3$

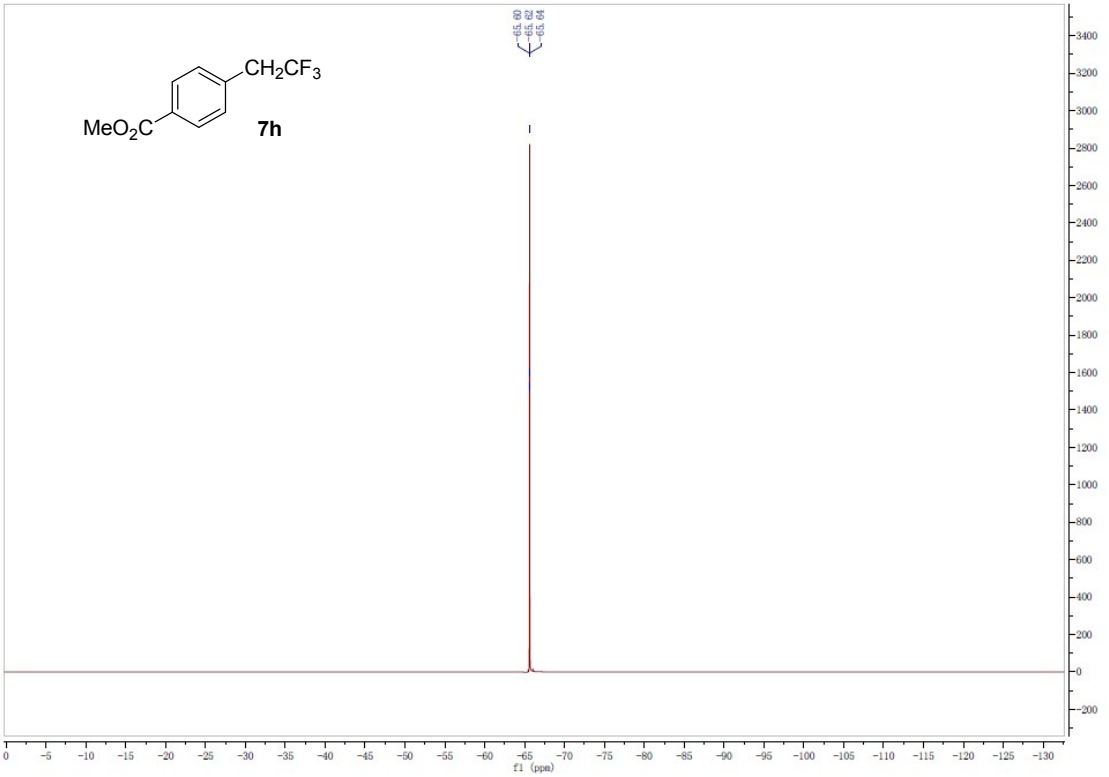


Figure S27. ^{19}F NMR of 7h in $CDCl_3$

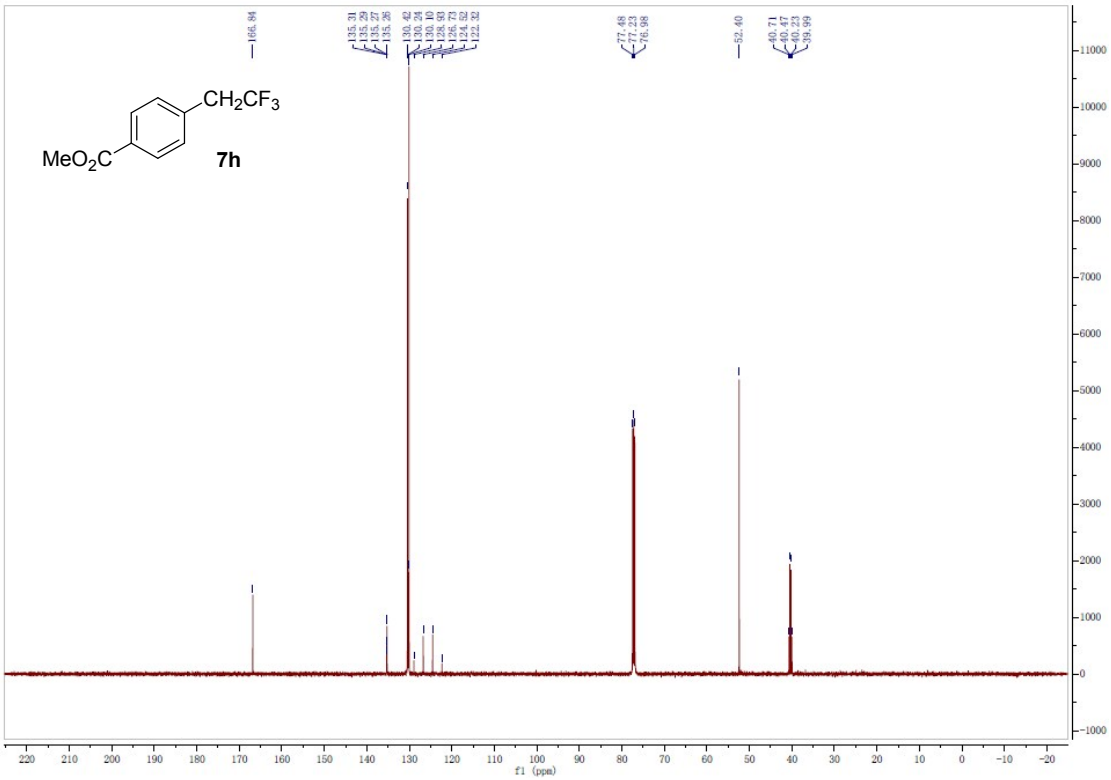


Figure S28. ^{13}C NMR of 7h in $CDCl_3$

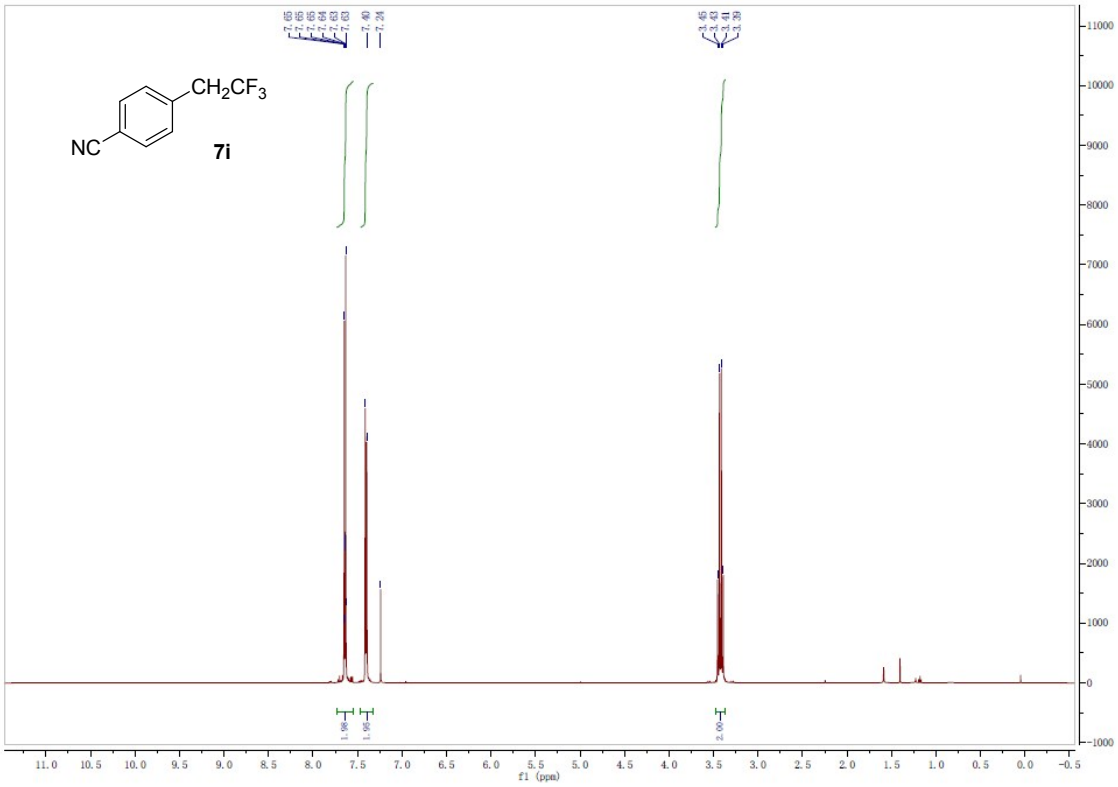


Figure S29. ^{1}H NMR of 7i in $CDCl_3$

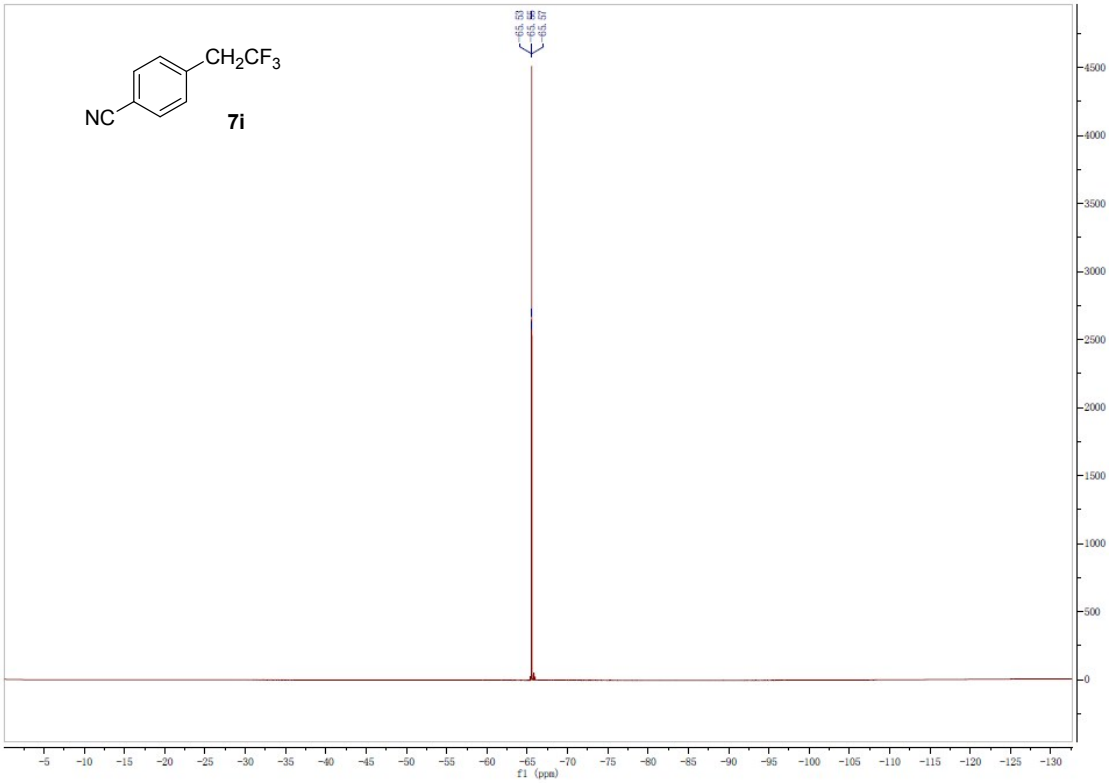


Figure S30. ^{19}F NMR of 7i in $CDCl_3$

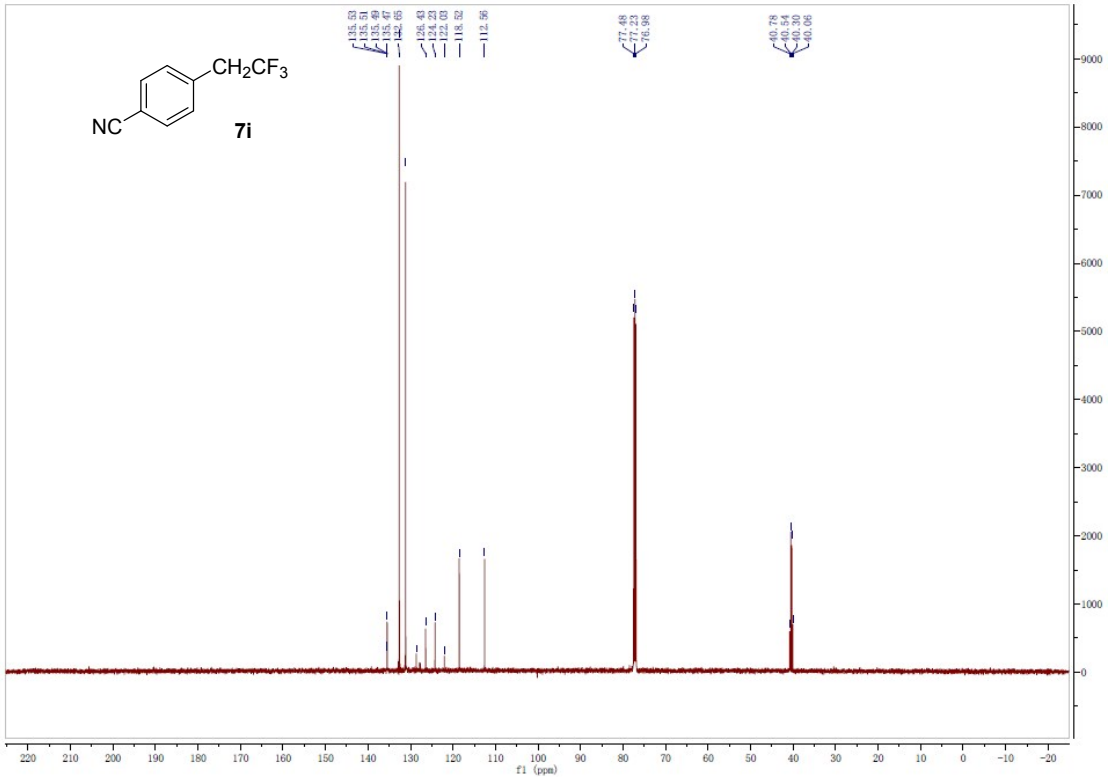


Figure S31. ^{13}C NMR of 7i in $CDCl_3$

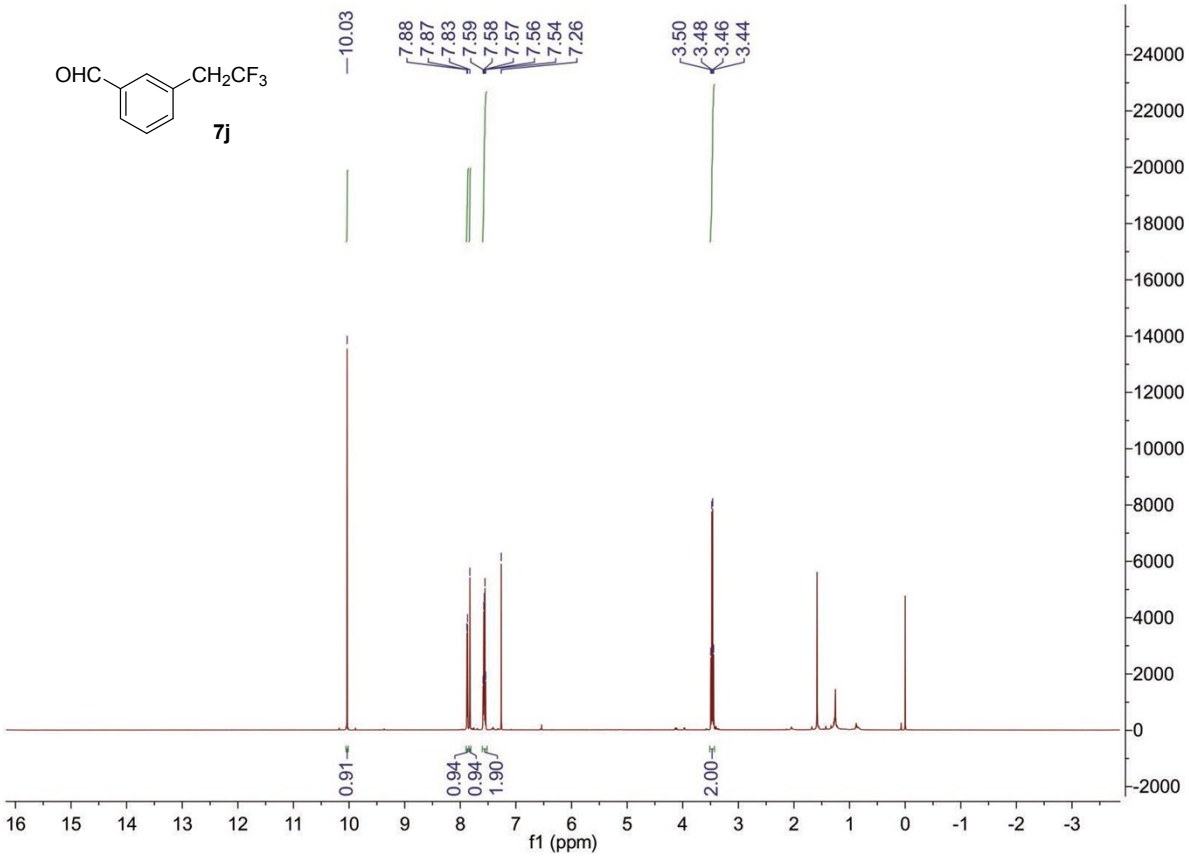


Figure S32. ^{1}H NMR of 7j in $CDCl_3$

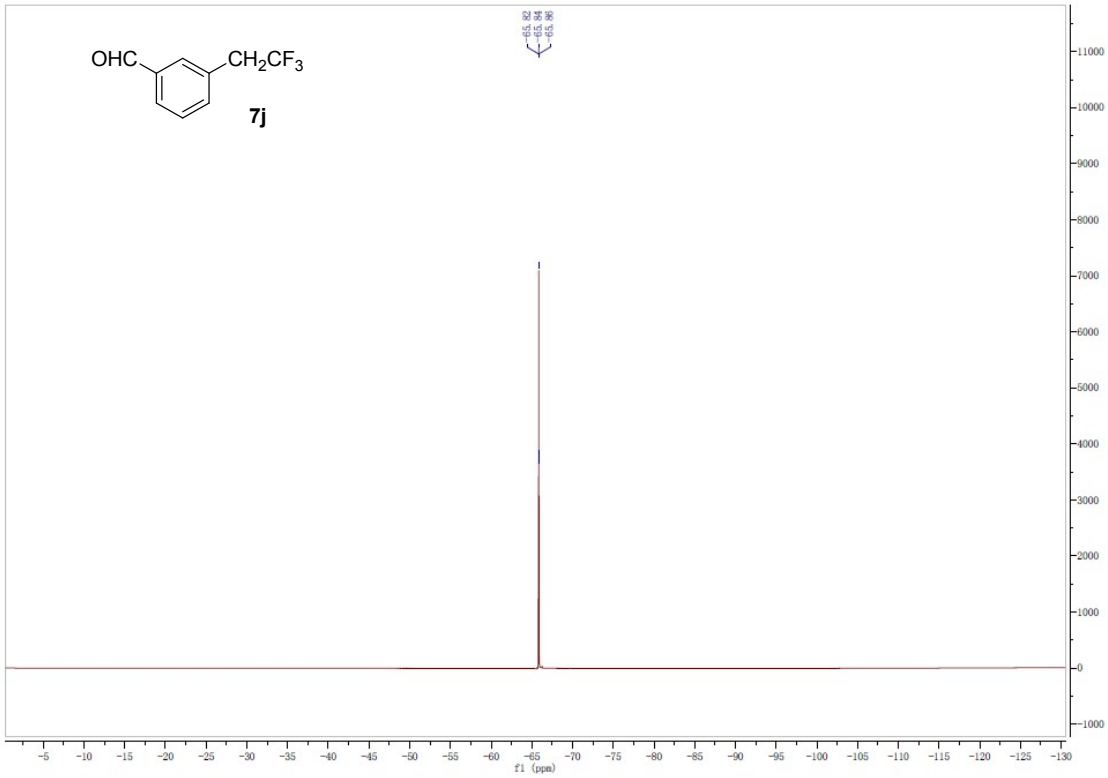


Figure S33. ^{19}F NMR of 7j in $CDCl_3$

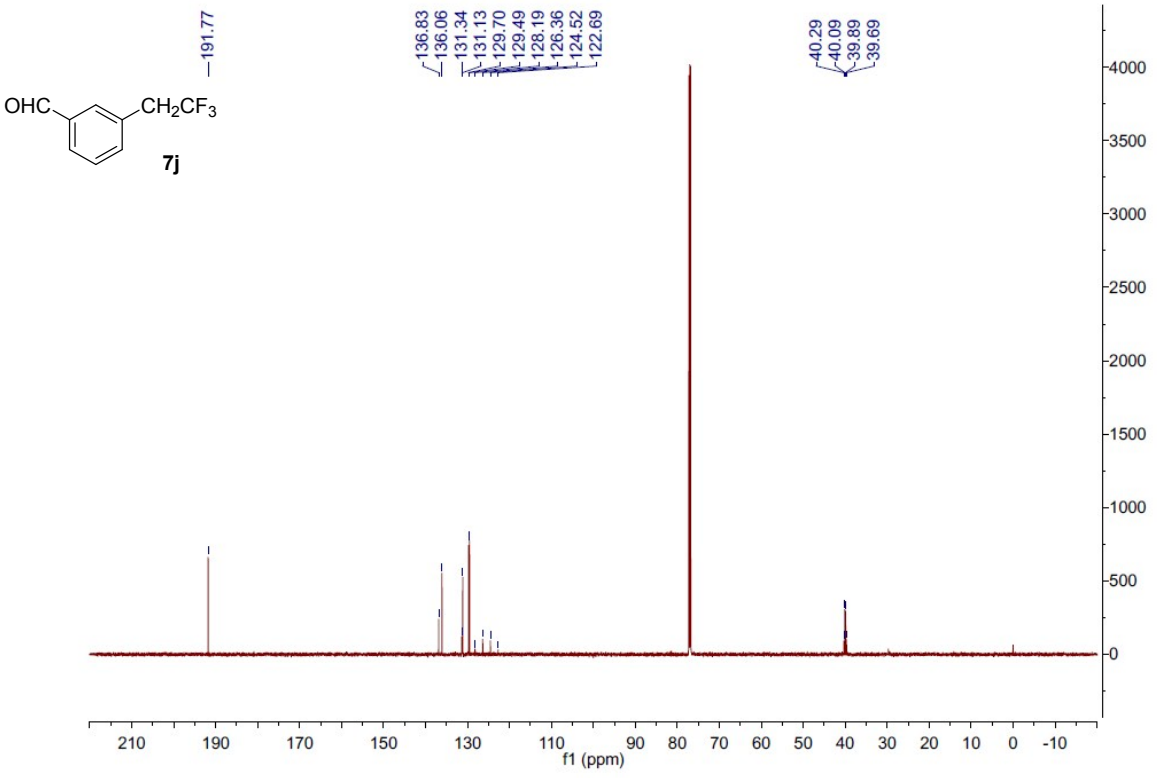


Figure S34. ^{13}C NMR of 7j in $CDCl_3$

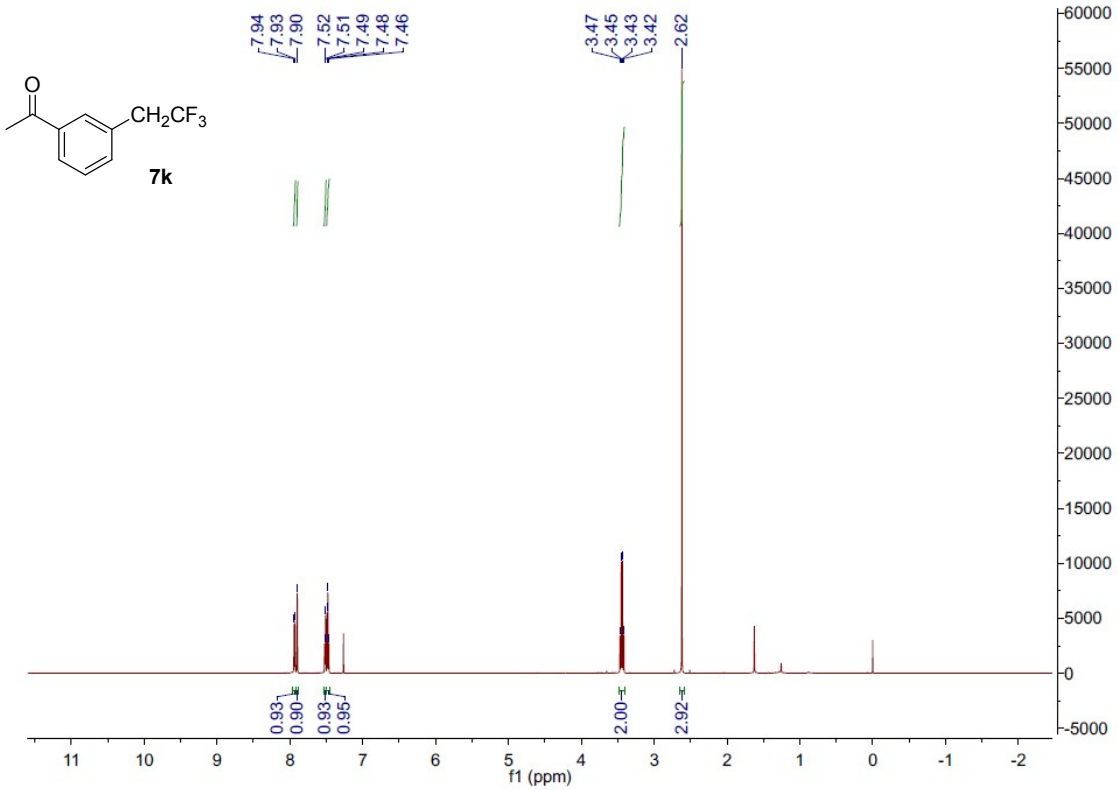


Figure S35. ^{1}H NMR of 7k in $CDCl_3$

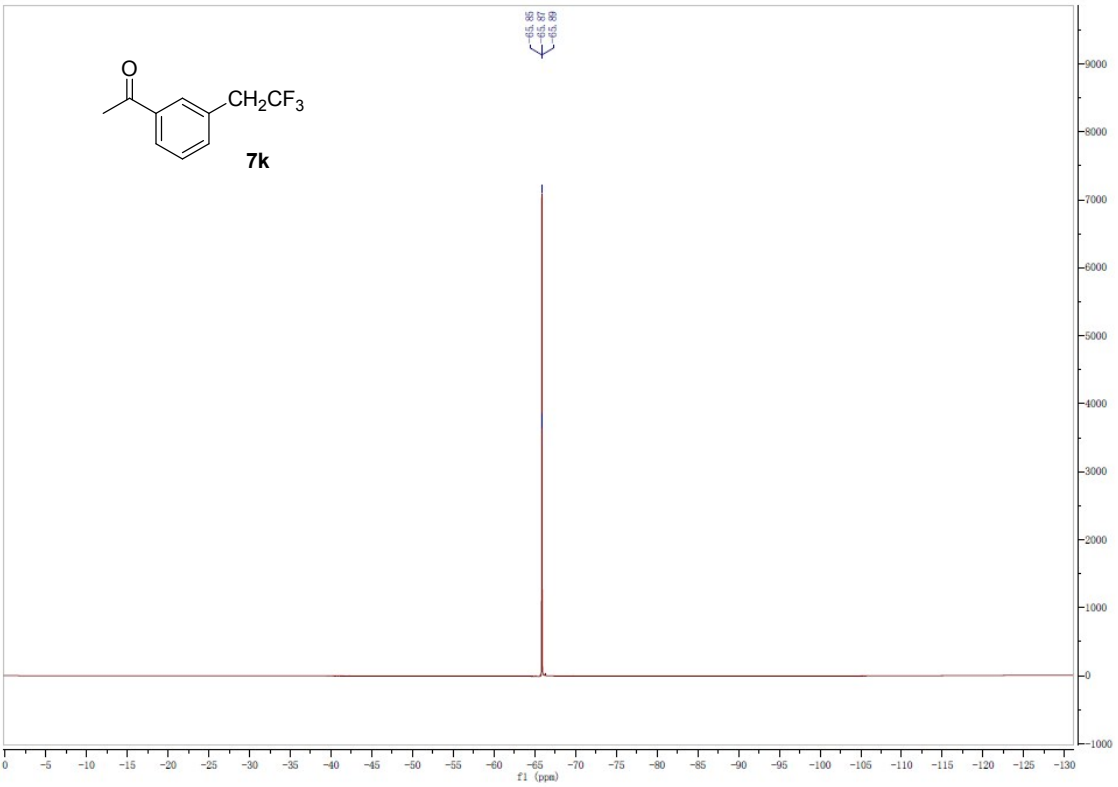


Figure S36. ^{19}F NMR of 7k in $CDCl_3$

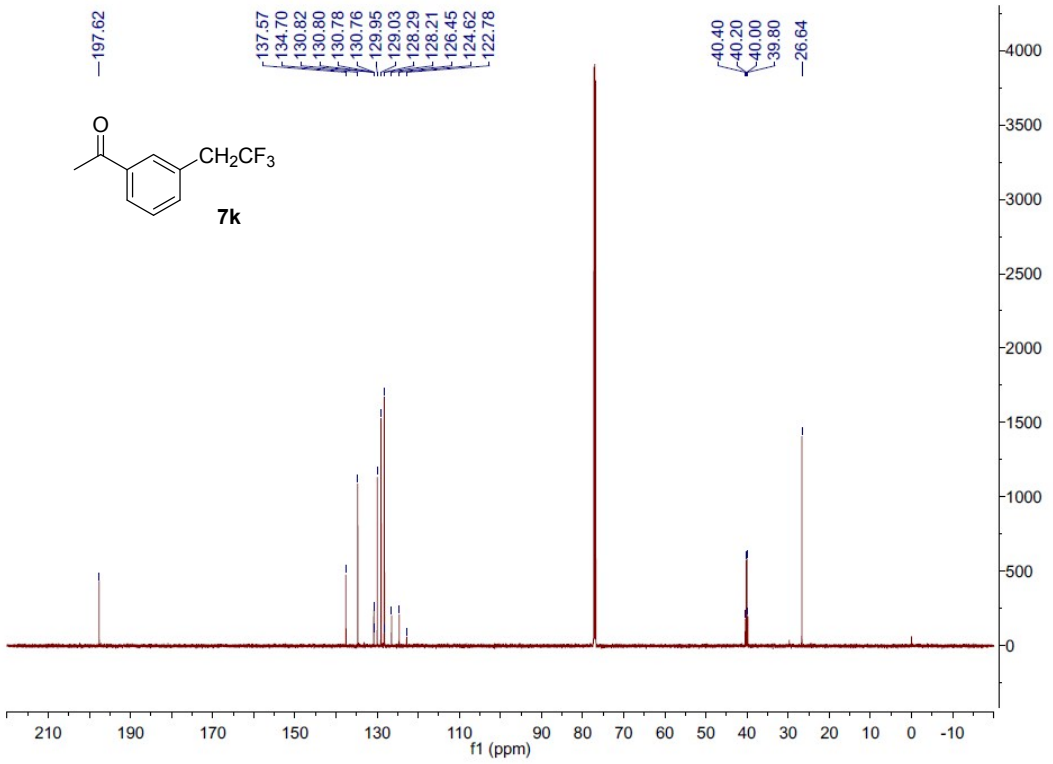


Figure S37. ^{13}C NMR of 7k in $CDCl_3$

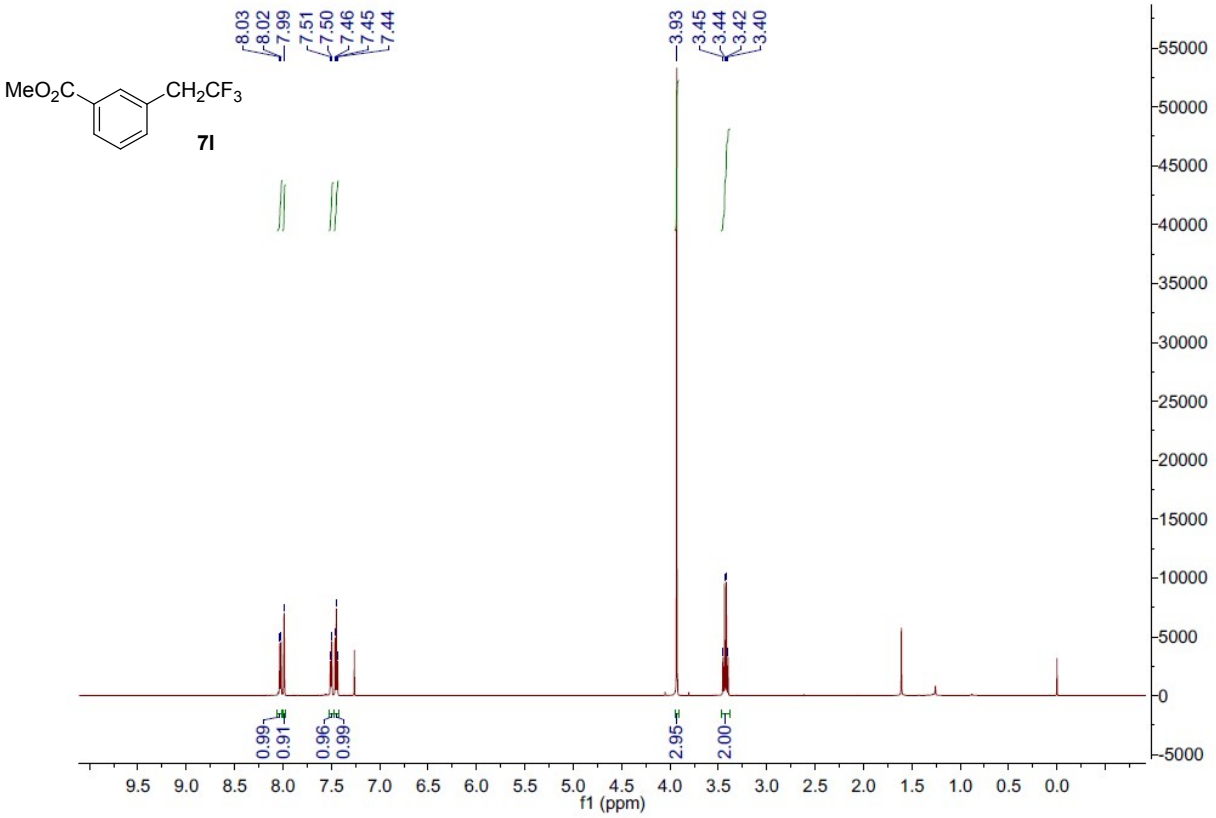


Figure S38. ^{1}H NMR of 7l in $CDCl_3$

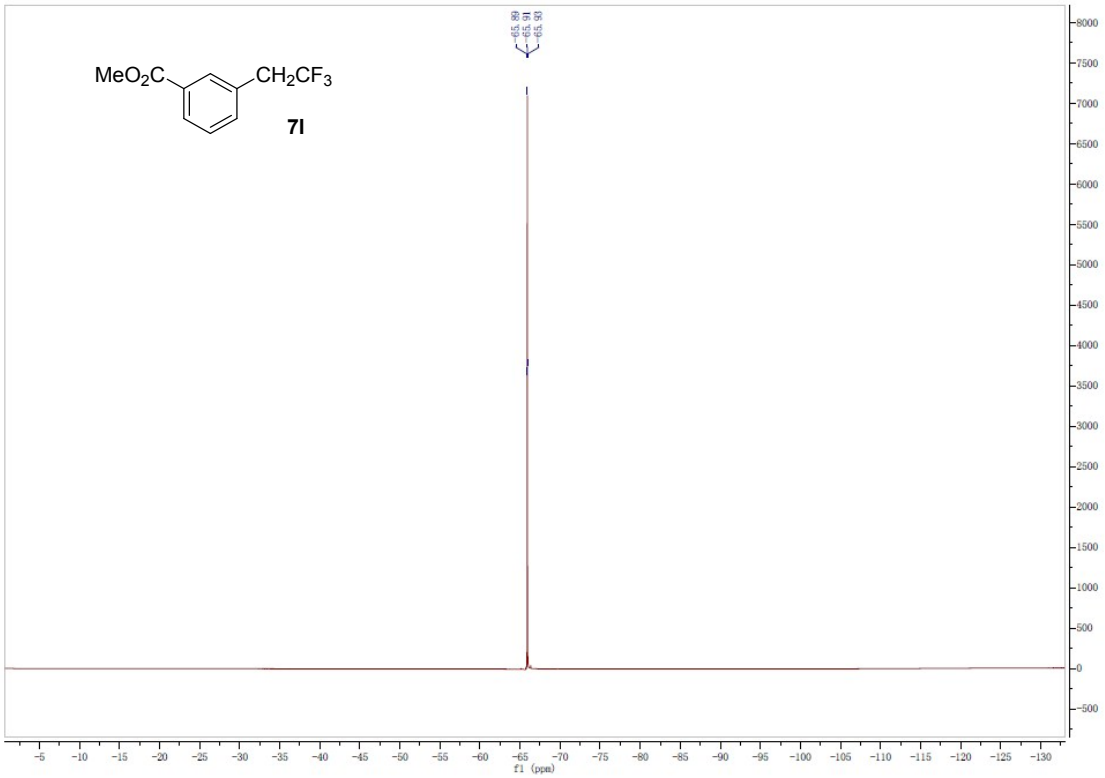


Figure S39. ^{19}F NMR of 7l in $CDCl_3$

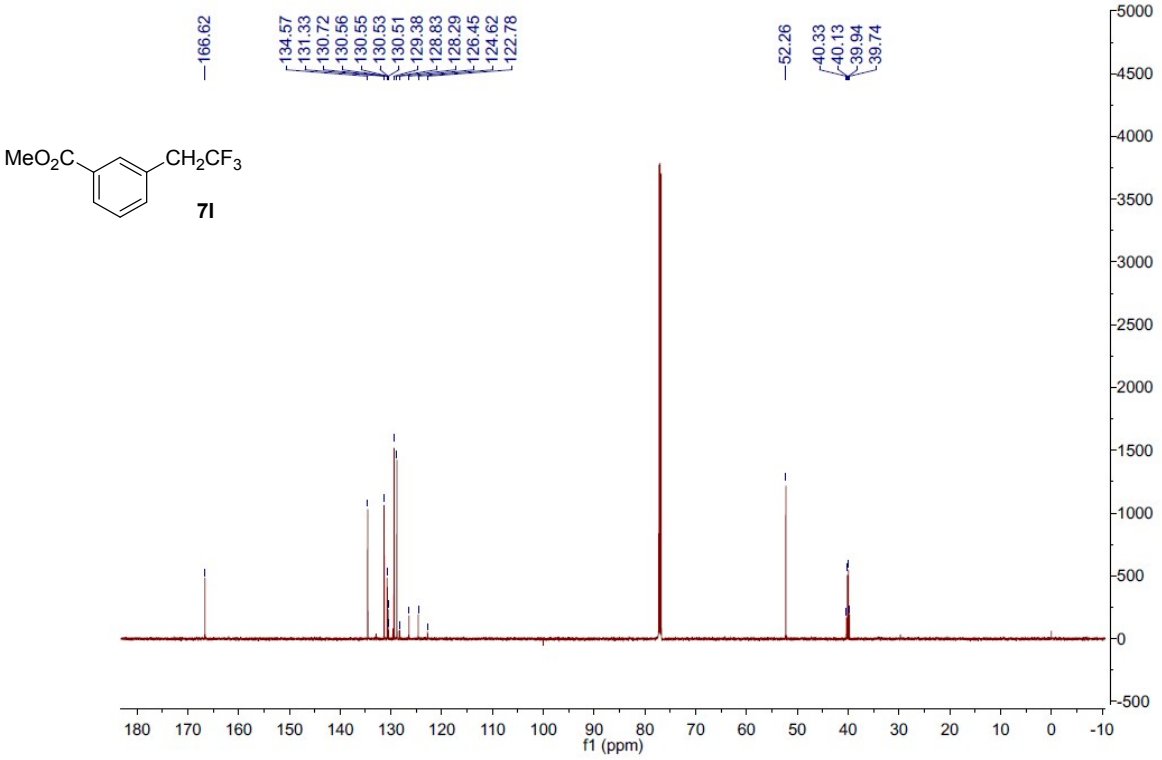


Figure S40. ^{13}C NMR of 7l in $CDCl_3$

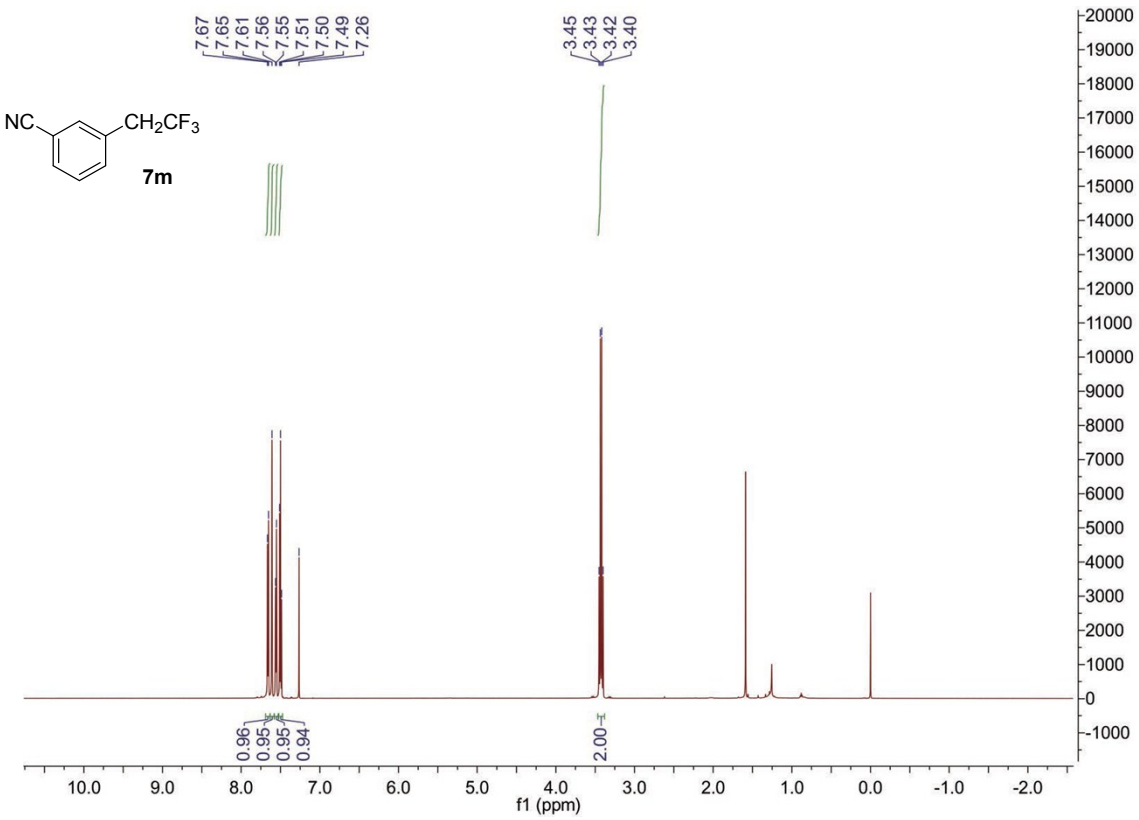


Figure S41. ^{1}H NMR of 7m in $CDCl_3$

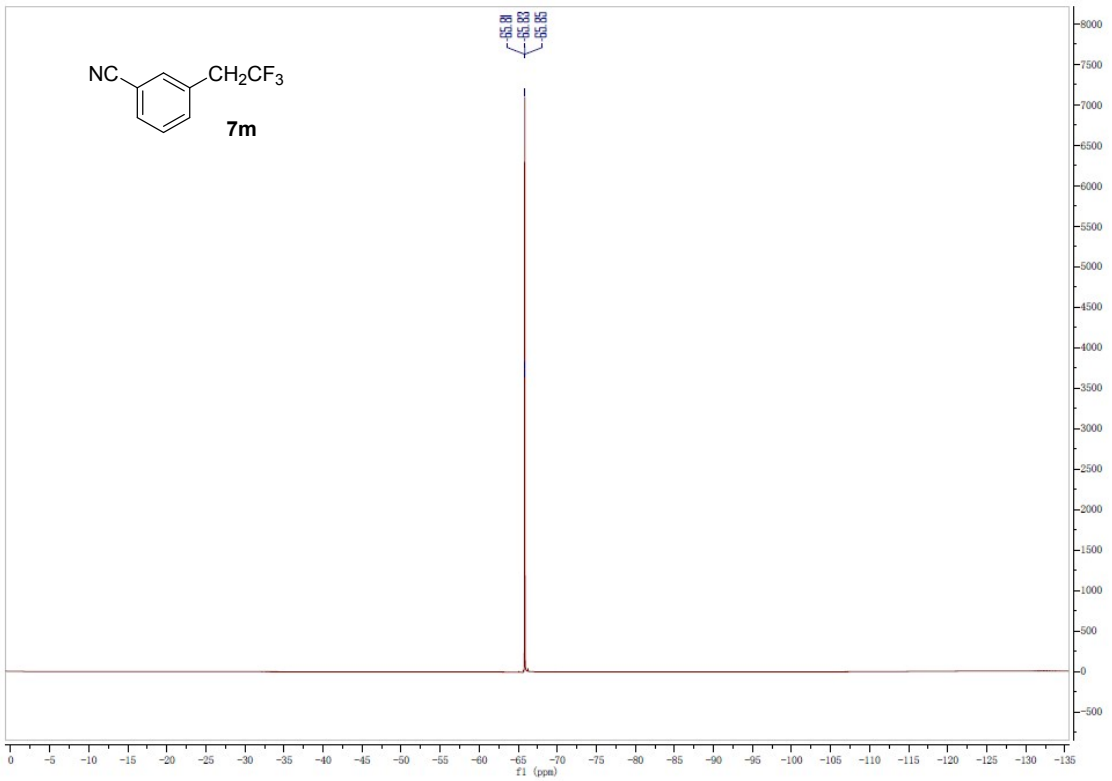


Figure S42. ^{19}F NMR of 7m in $CDCl_3$

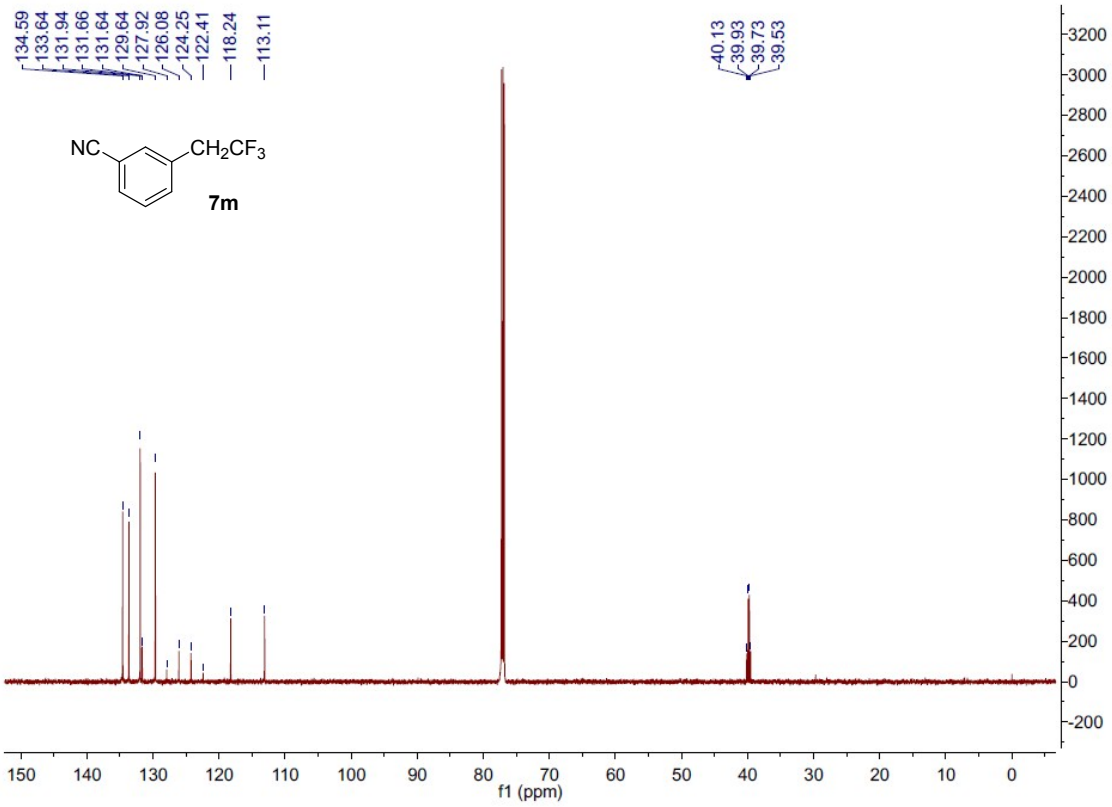


Figure S43. ^{13}C NMR of 7m in $CDCl_3$

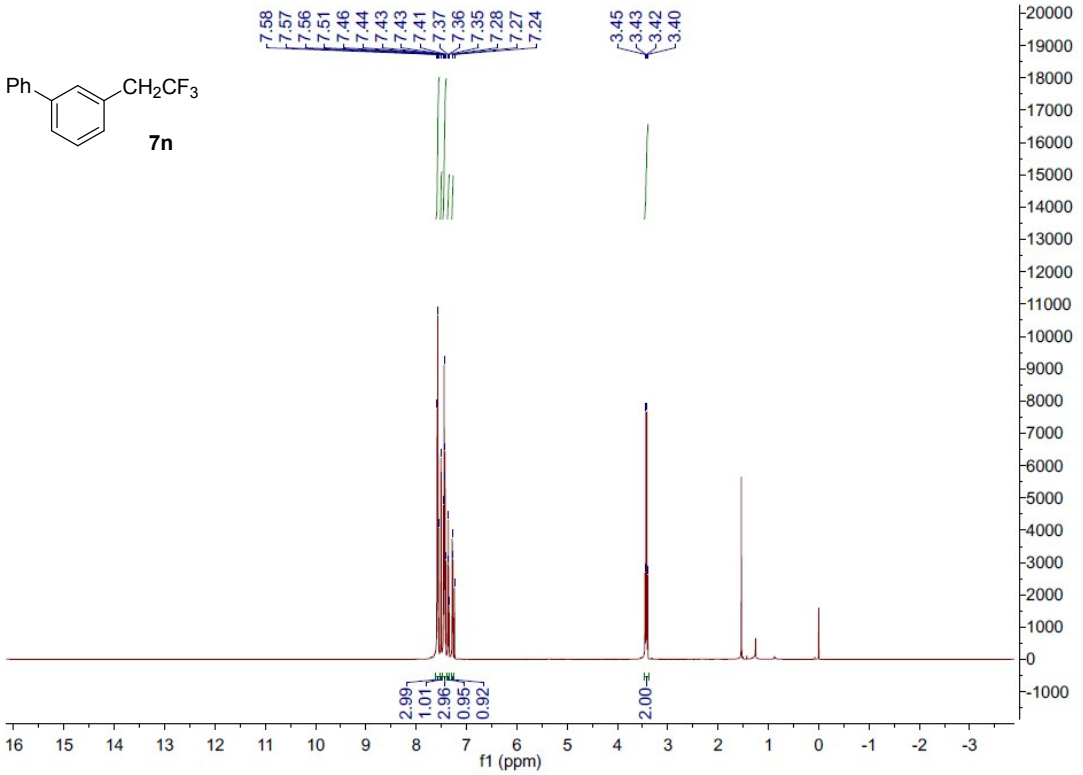


Figure S44. ^{1}H NMR of 7n in $CDCl_3$

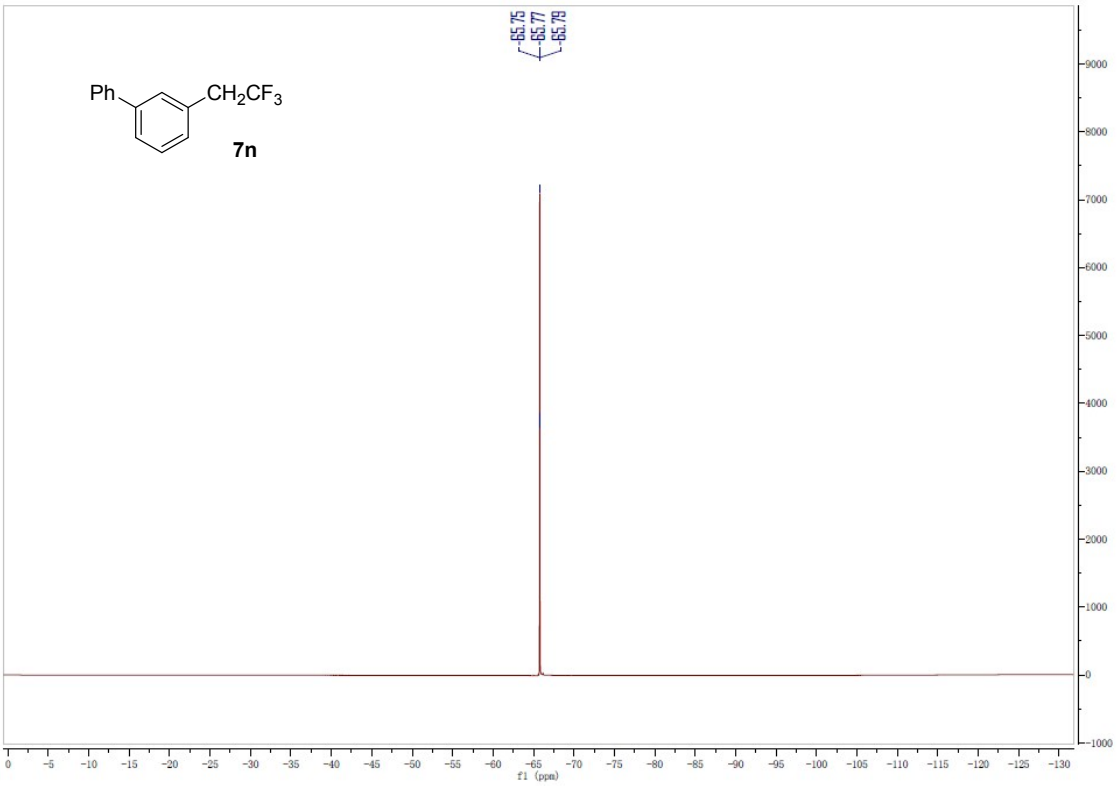


Figure S45. ^{19}F NMR of 7n in $CDCl_3$

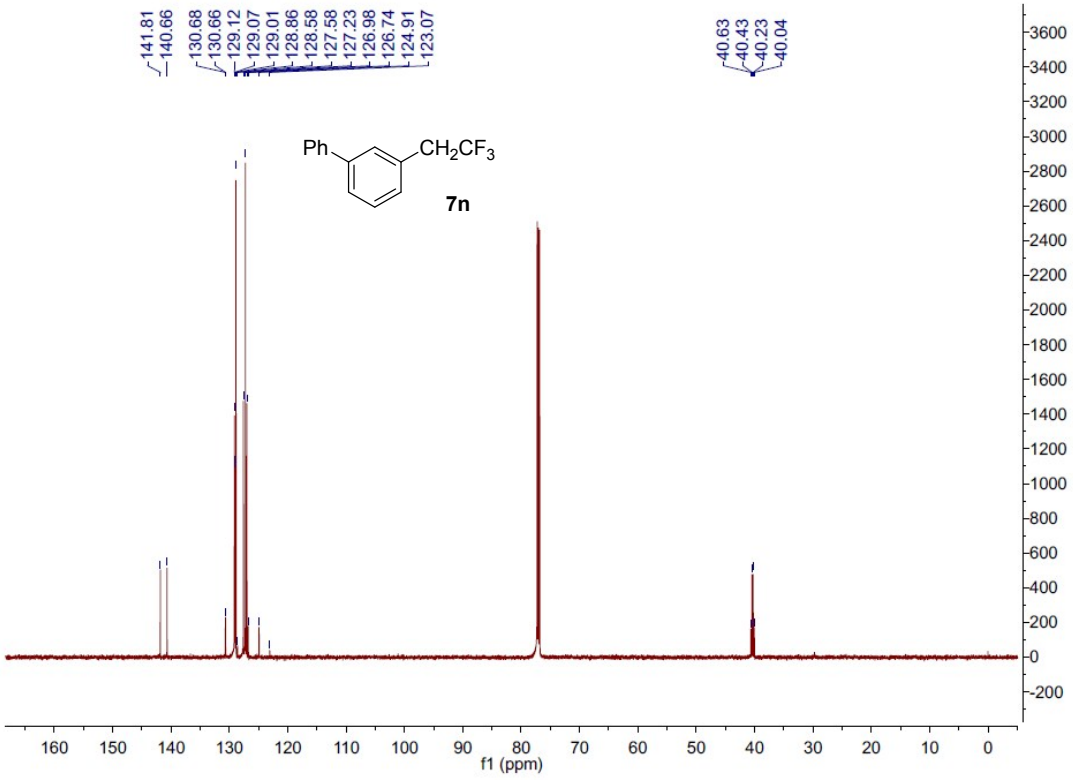


Figure S46. ^{13}C NMR of 7n in $CDCl_3$

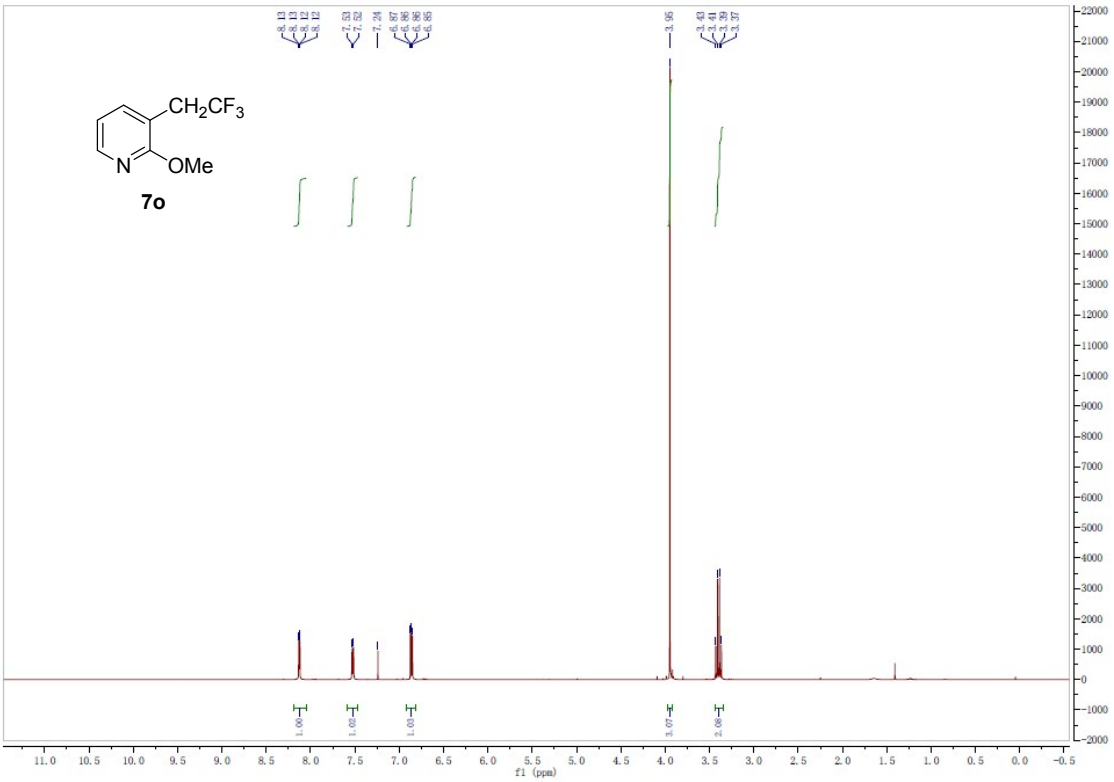


Figure S47. ^{1}H NMR of 7o in $CDCl_3$

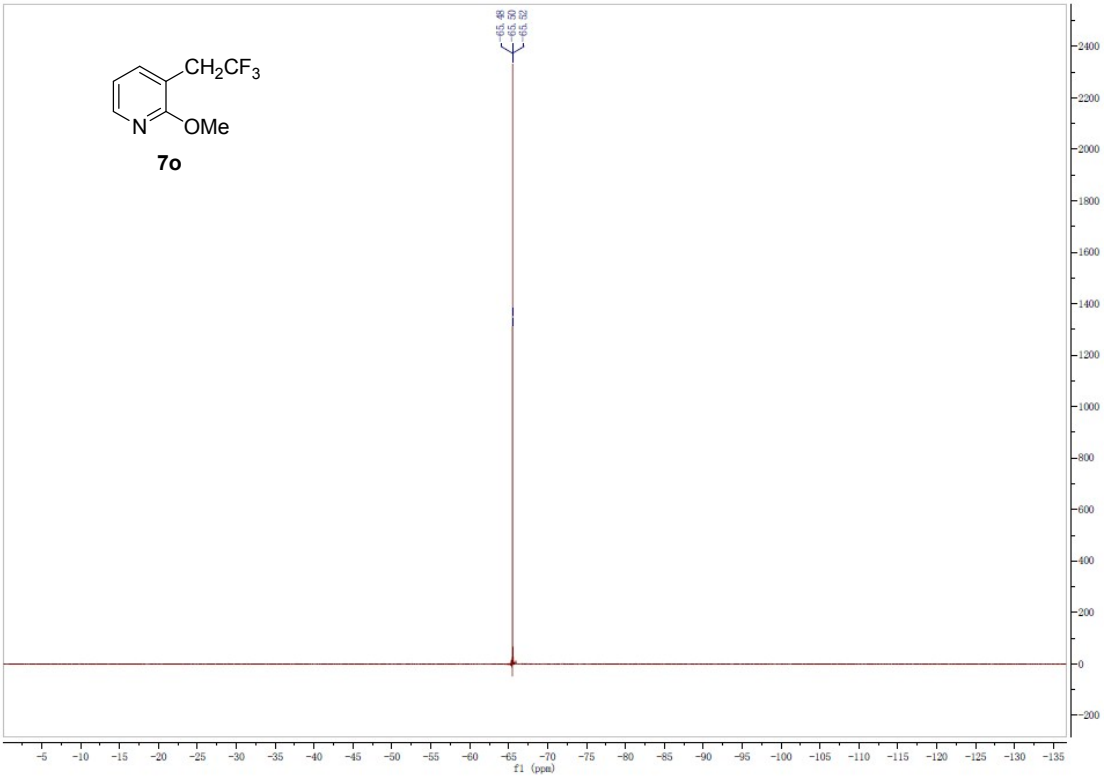


Figure S48. ^{19}F NMR of 7o in $CDCl_3$

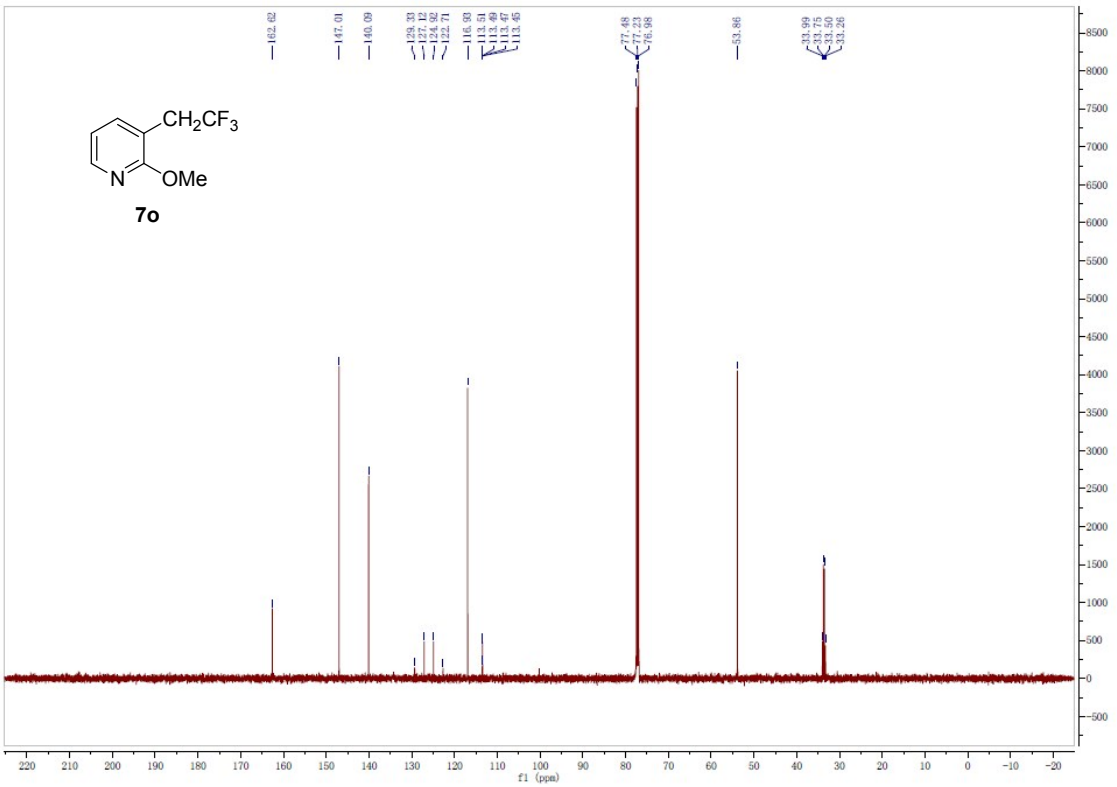


Figure S49. ^{13}C NMR of 7o in $CDCl_3$

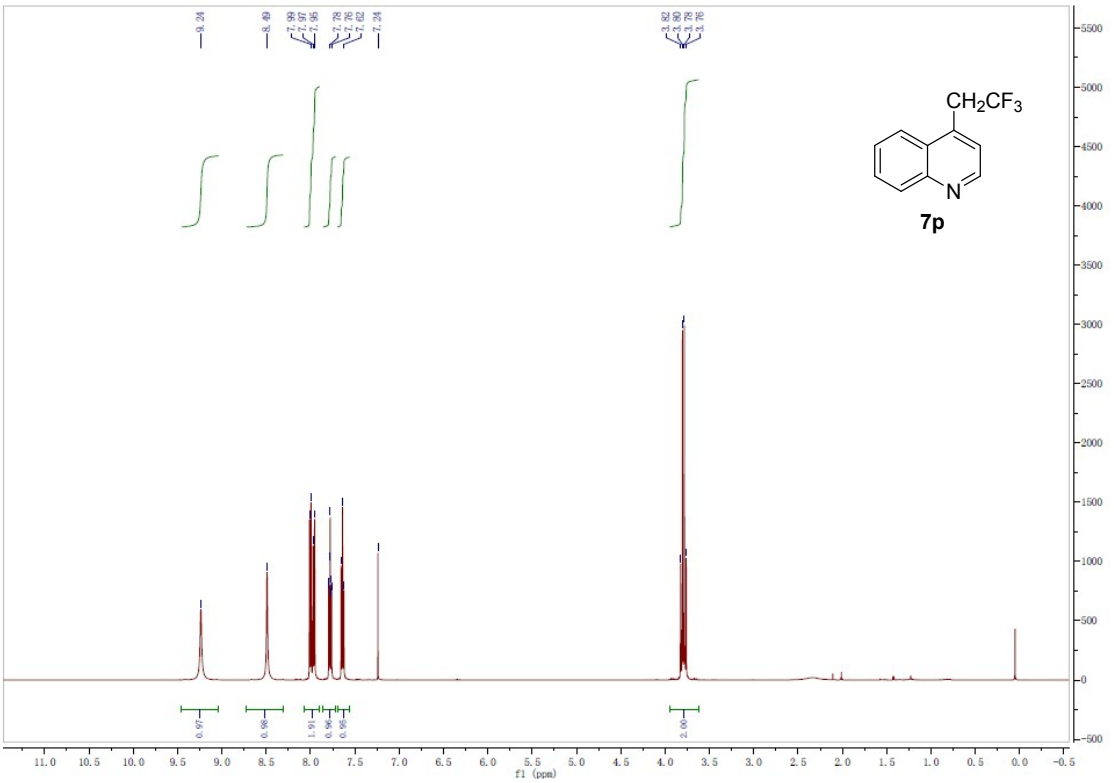


Figure S50. ^{1}H NMR of 7p in $CDCl_3$

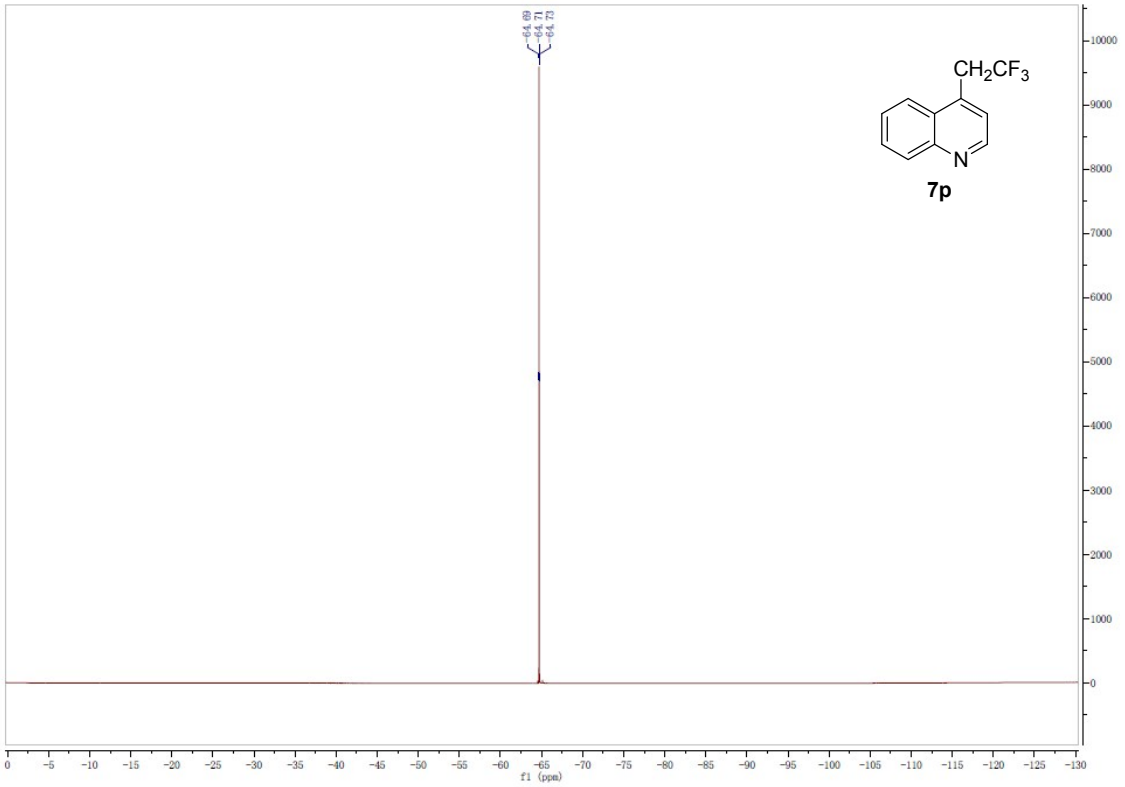


Figure S51. ^{19}F NMR of 7p in $CDCl_3$

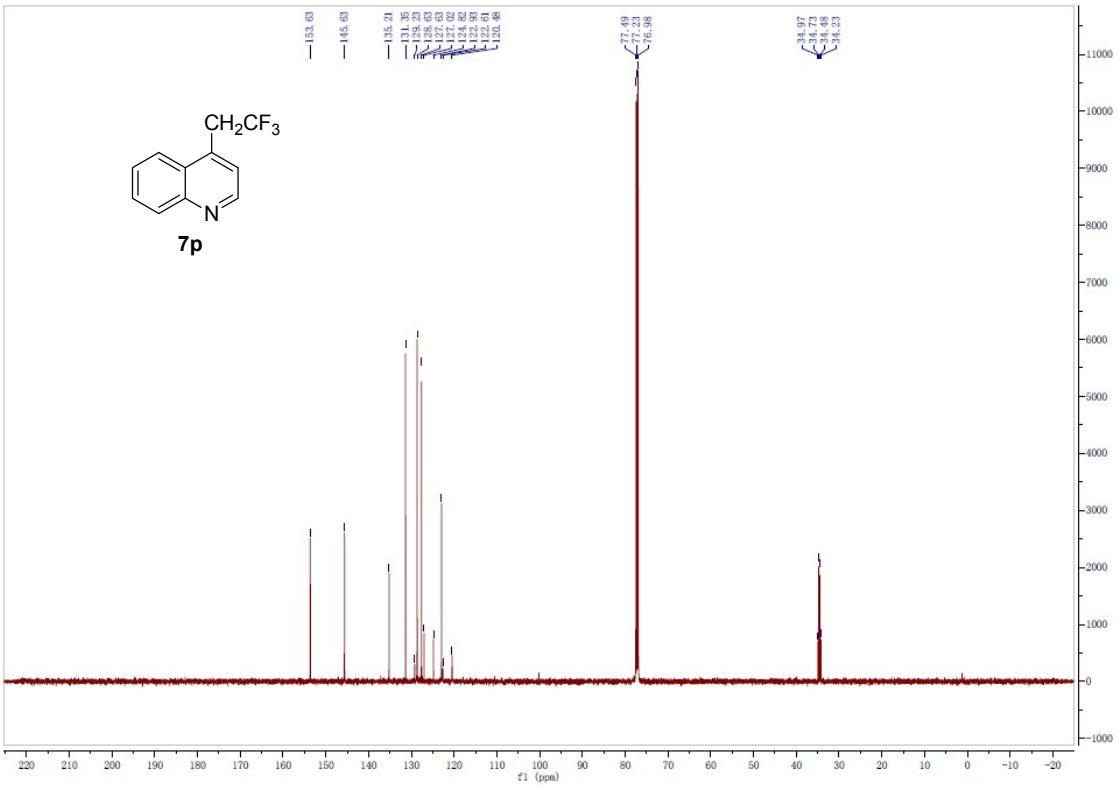


Figure S52. ^{13}C NMR of 7p in $CDCl_3$

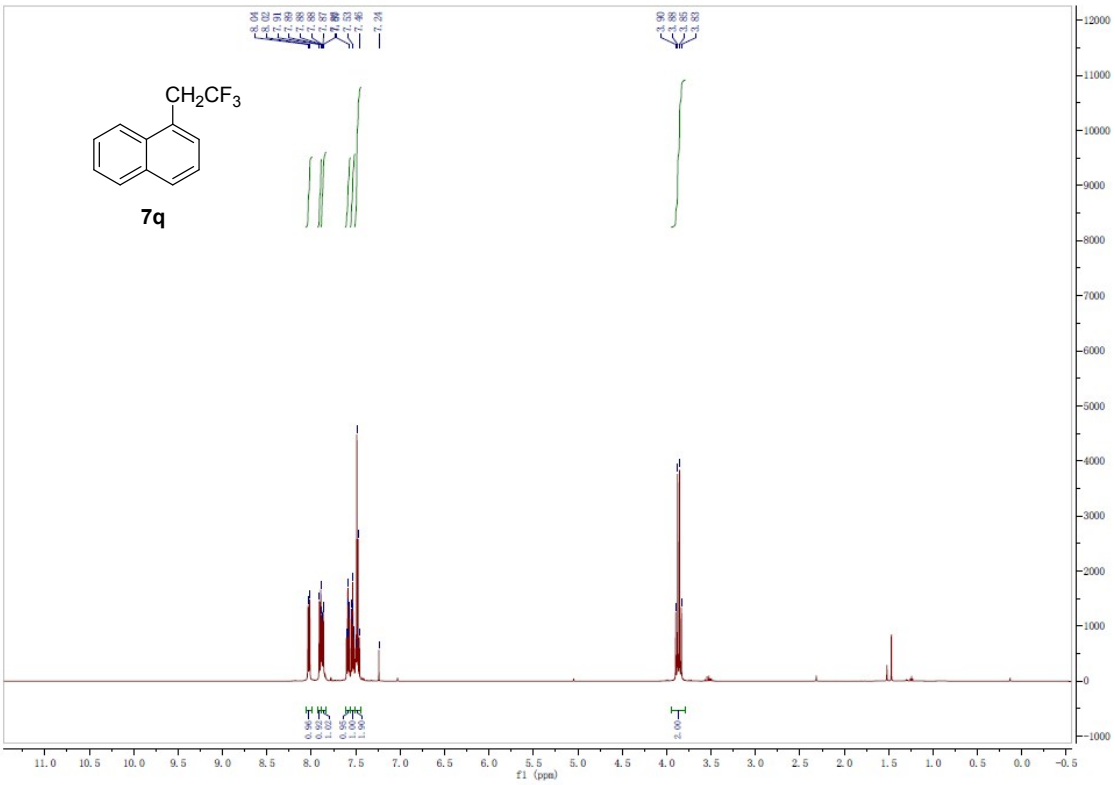


Figure S53. ^{1}H NMR of 7q in $CDCl_3$

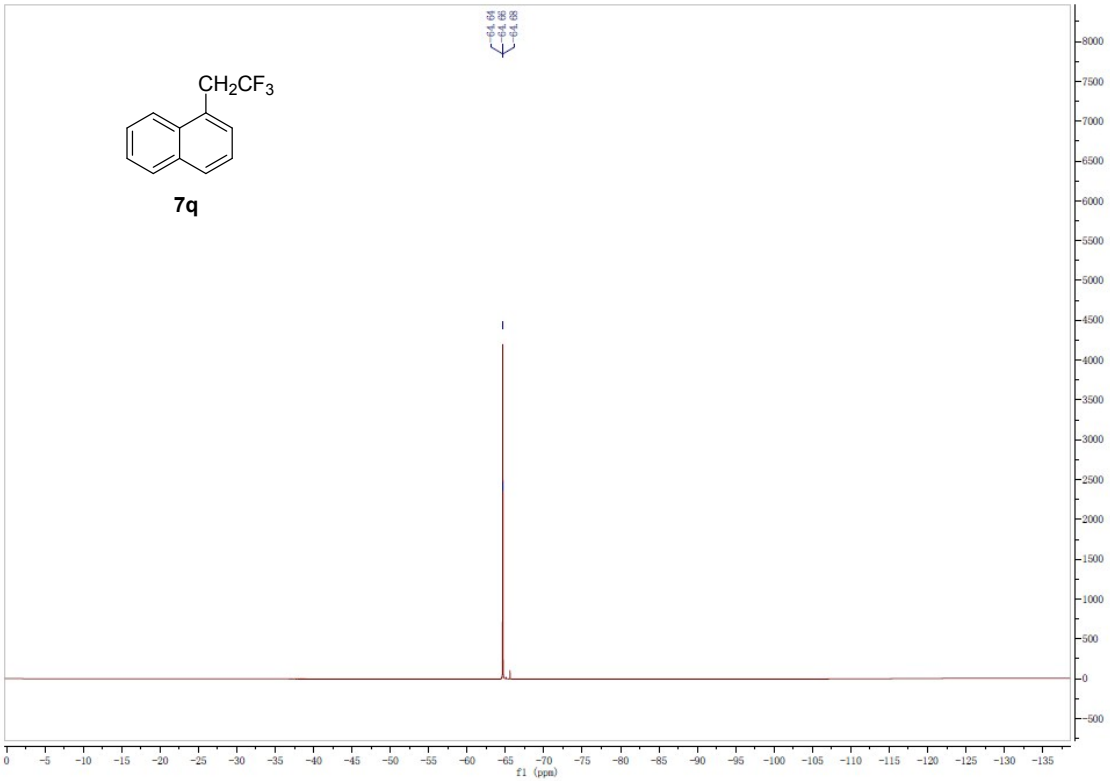


Figure S54. ^{19}F NMR of 7q in $CDCl_3$

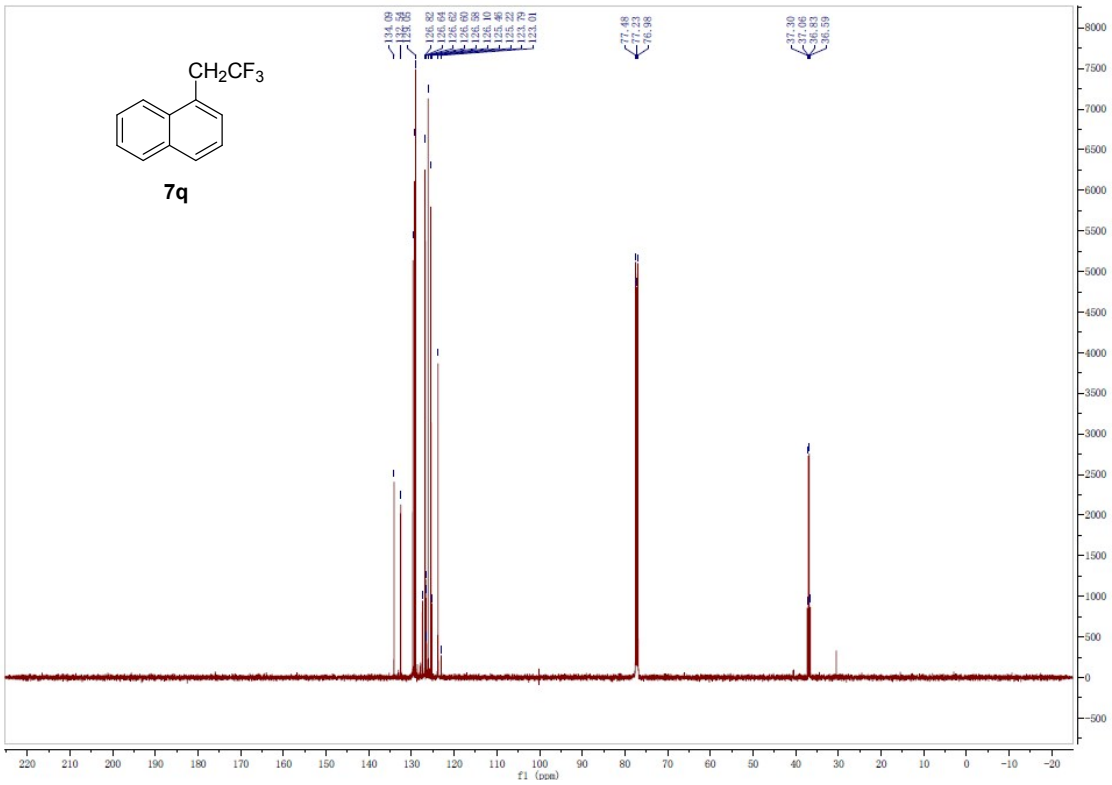


Figure S55. ^{13}C NMR of 7q in $CDCl_3$

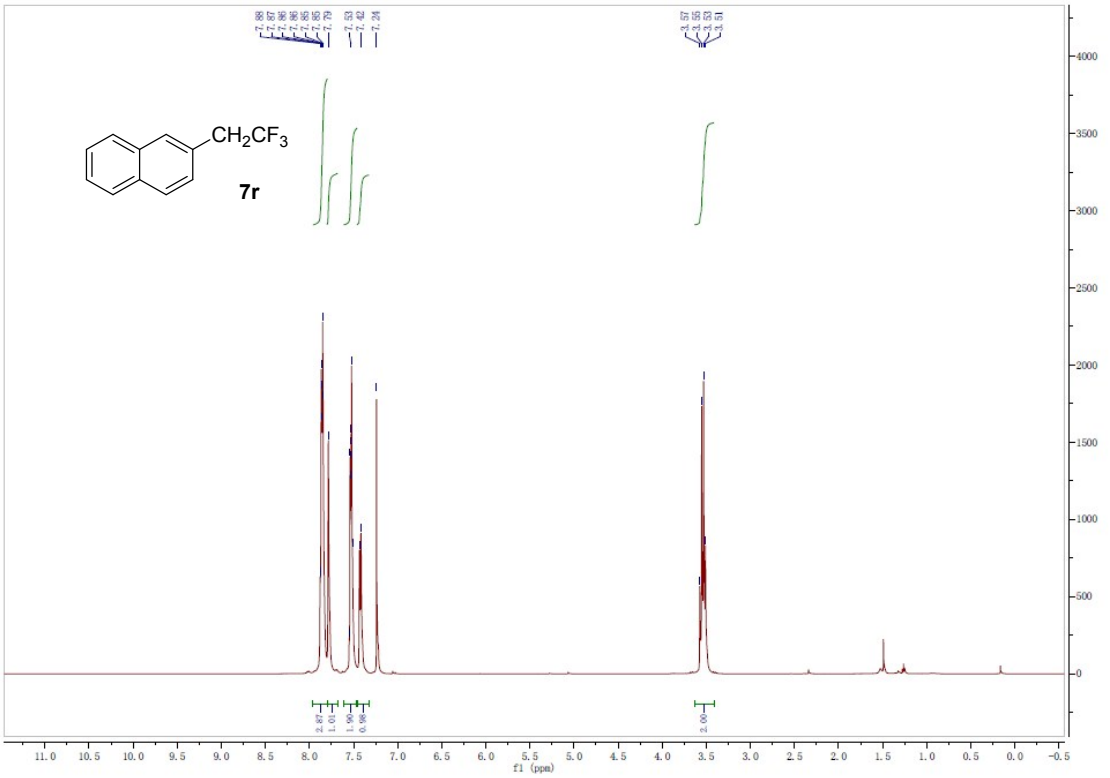


Figure S56. ^{1}H NMR of 7r in $CDCl_3$

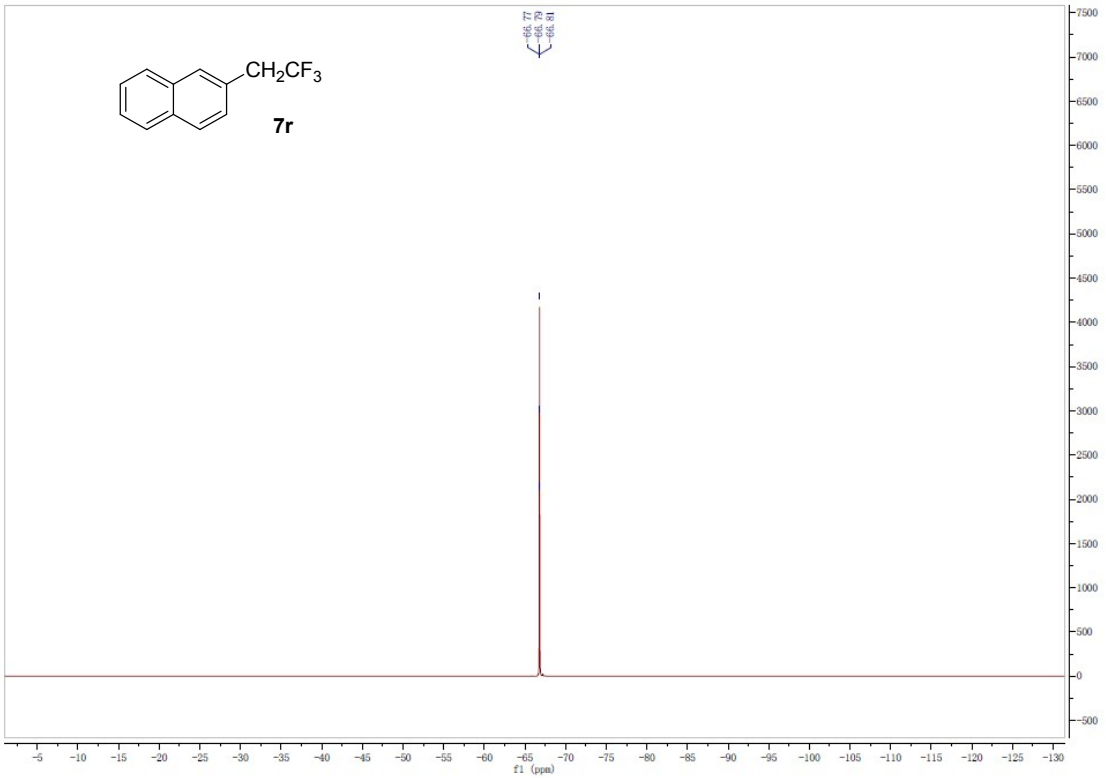


Figure S57. ^{19}F NMR of 7r in $CDCl_3$

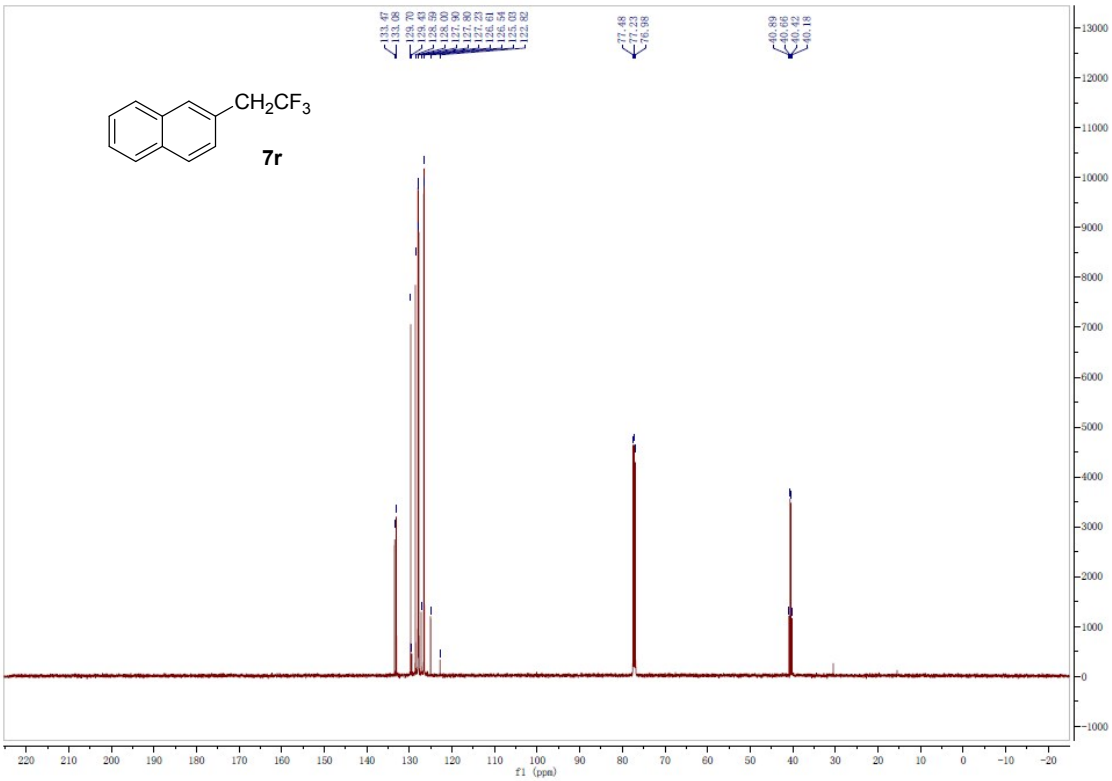


Figure S58. ^{13}C NMR of 7r in $CDCl_3$

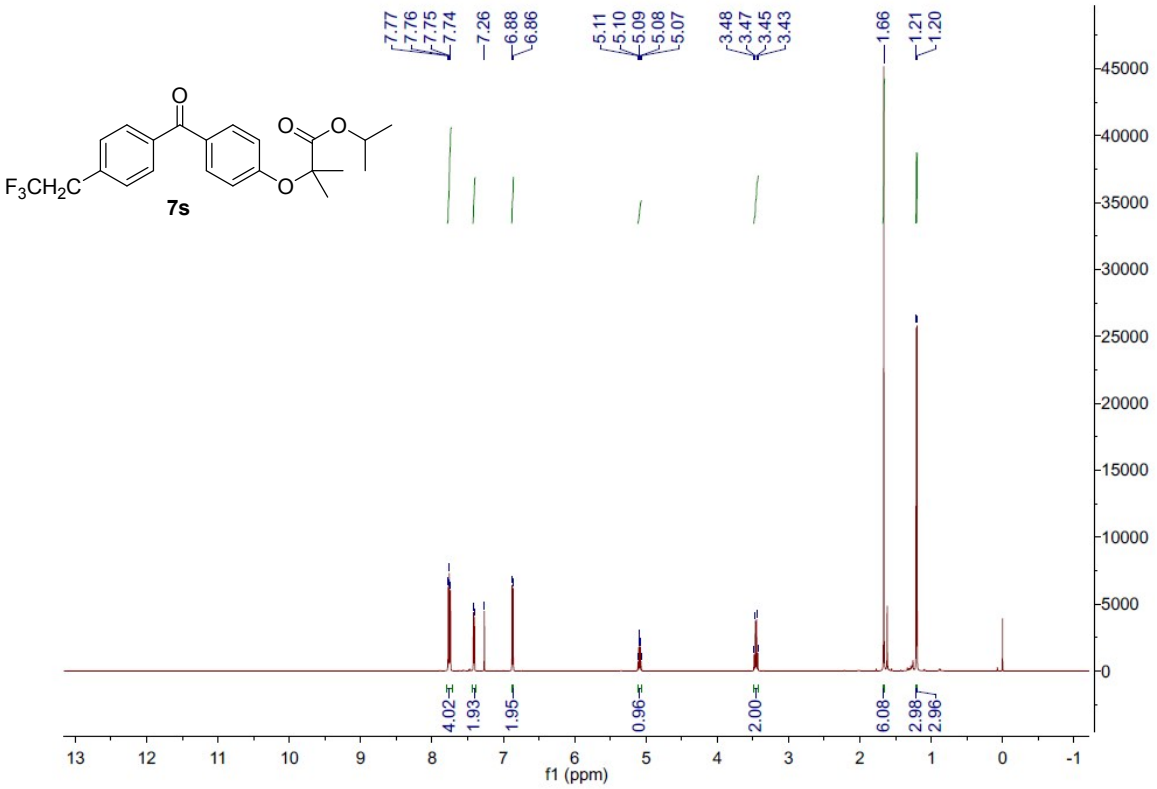


Figure S59. ^{1}H NMR of 7s in $CDCl_3$

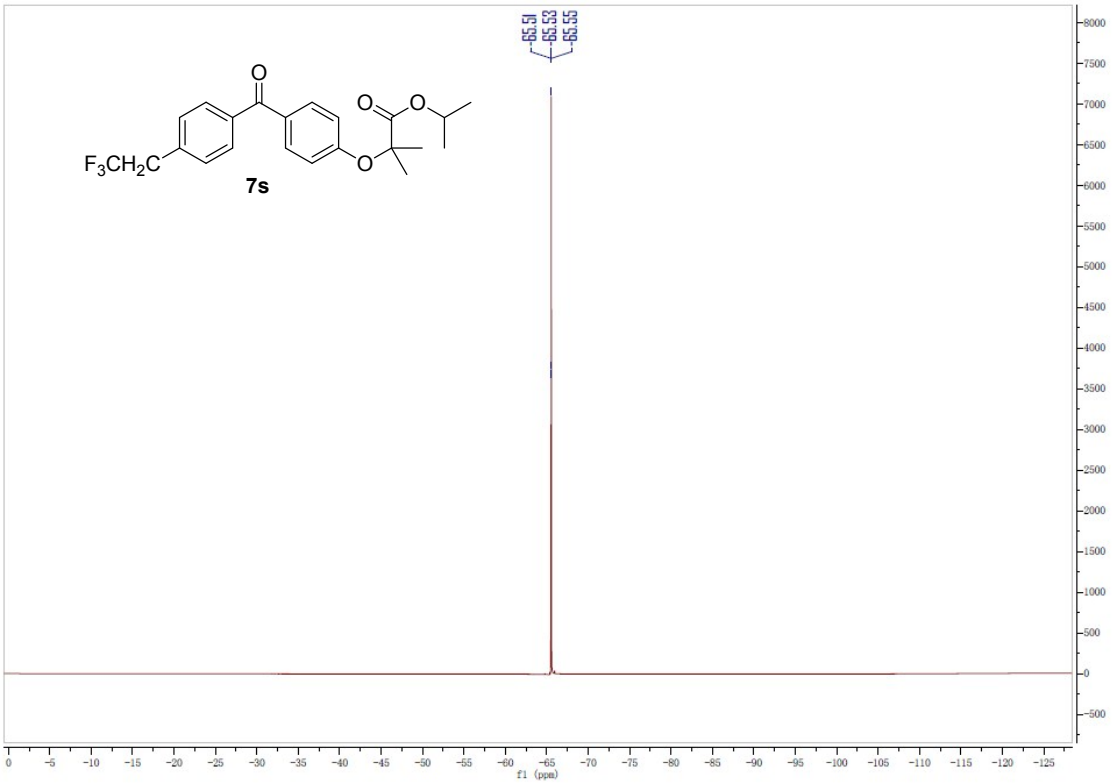


Figure S60. ^{19}F NMR of 7s in $CDCl_3$

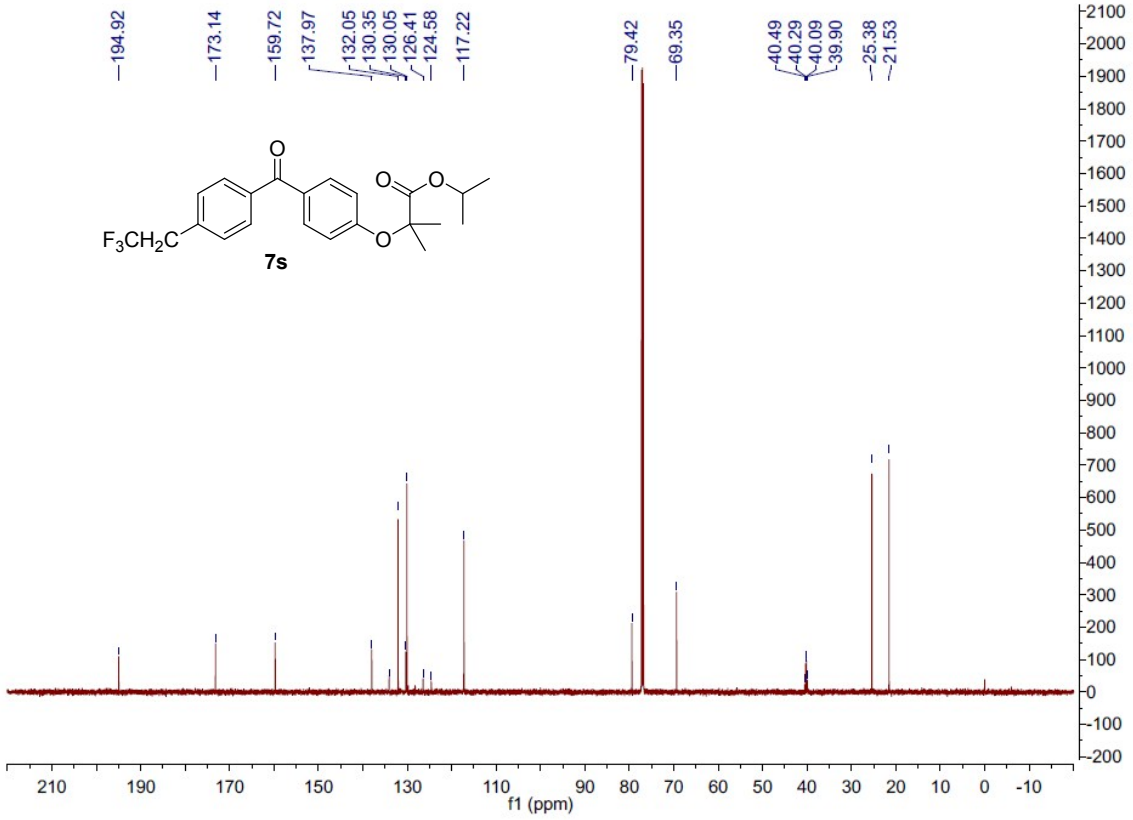


Figure S61. ^{13}C NMR of 7s in $CDCl_3$

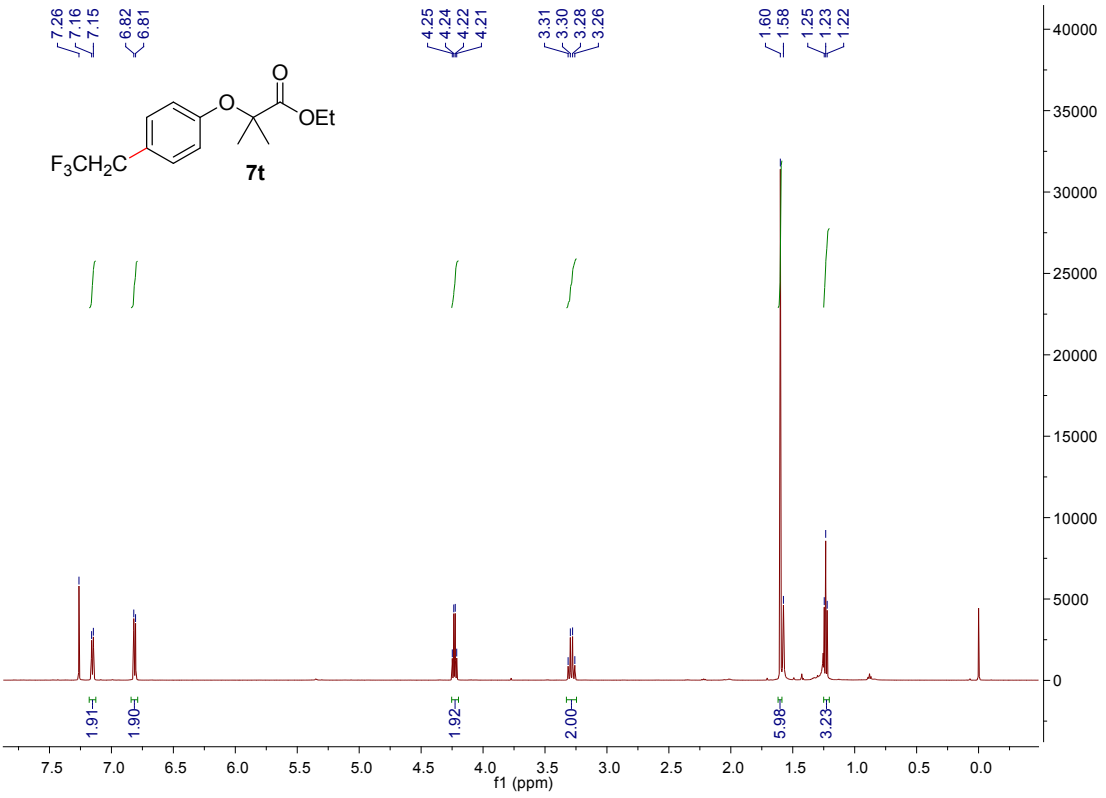


Figure S62. ^{1}H NMR of 7t in $CDCl_3$

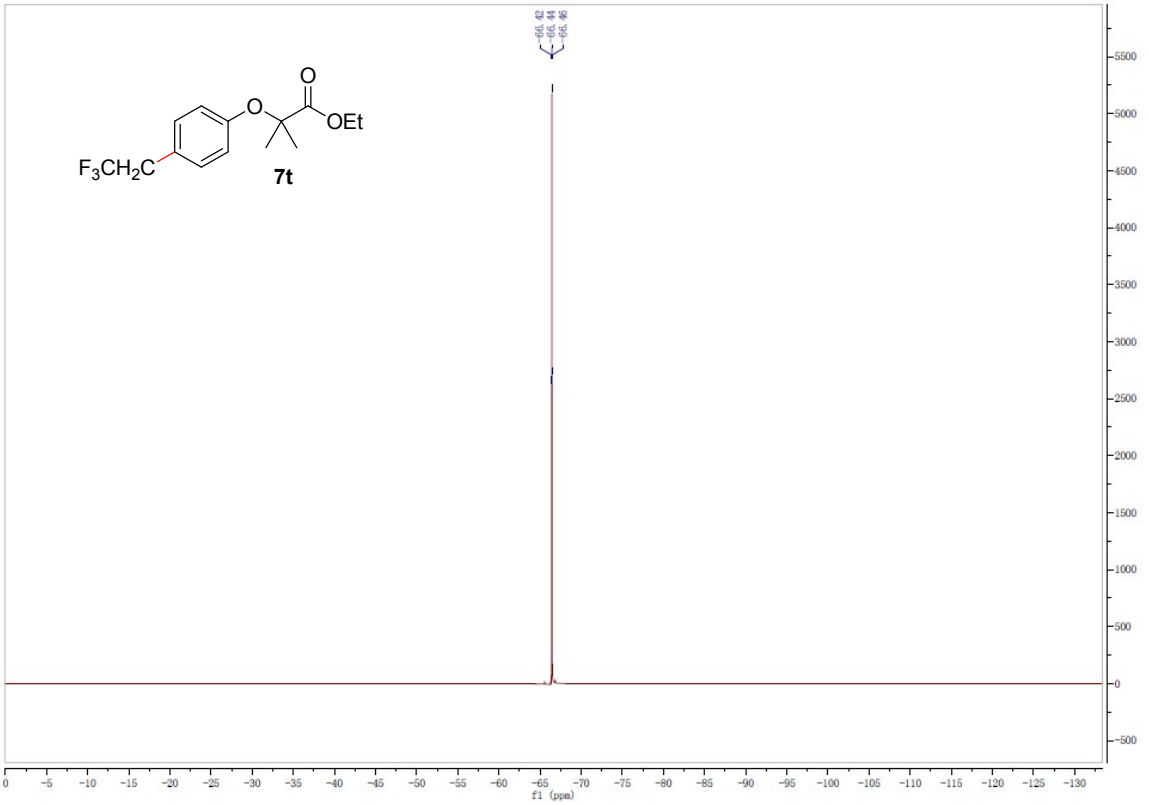


Figure S63. ^{19}F NMR of 7t in $CDCl_3$

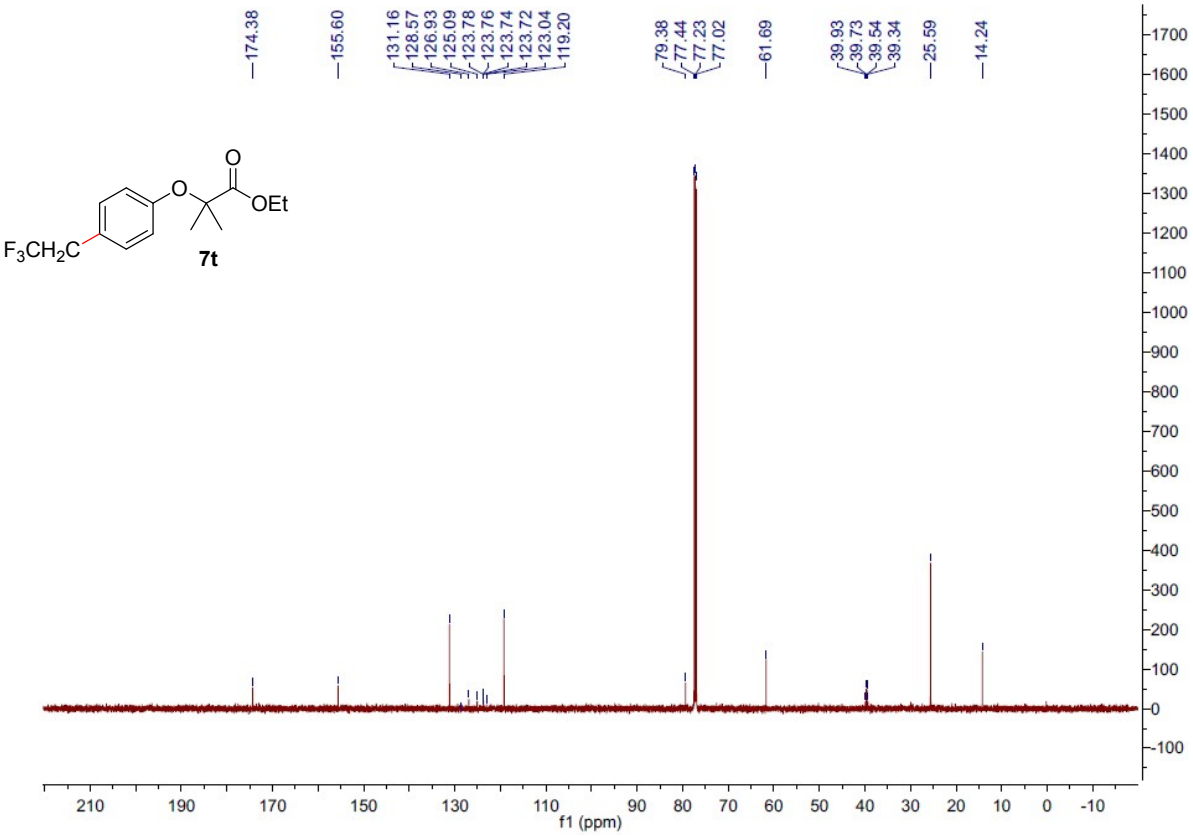


Figure S64. ^{13}C NMR of 7t in $CDCl_3$

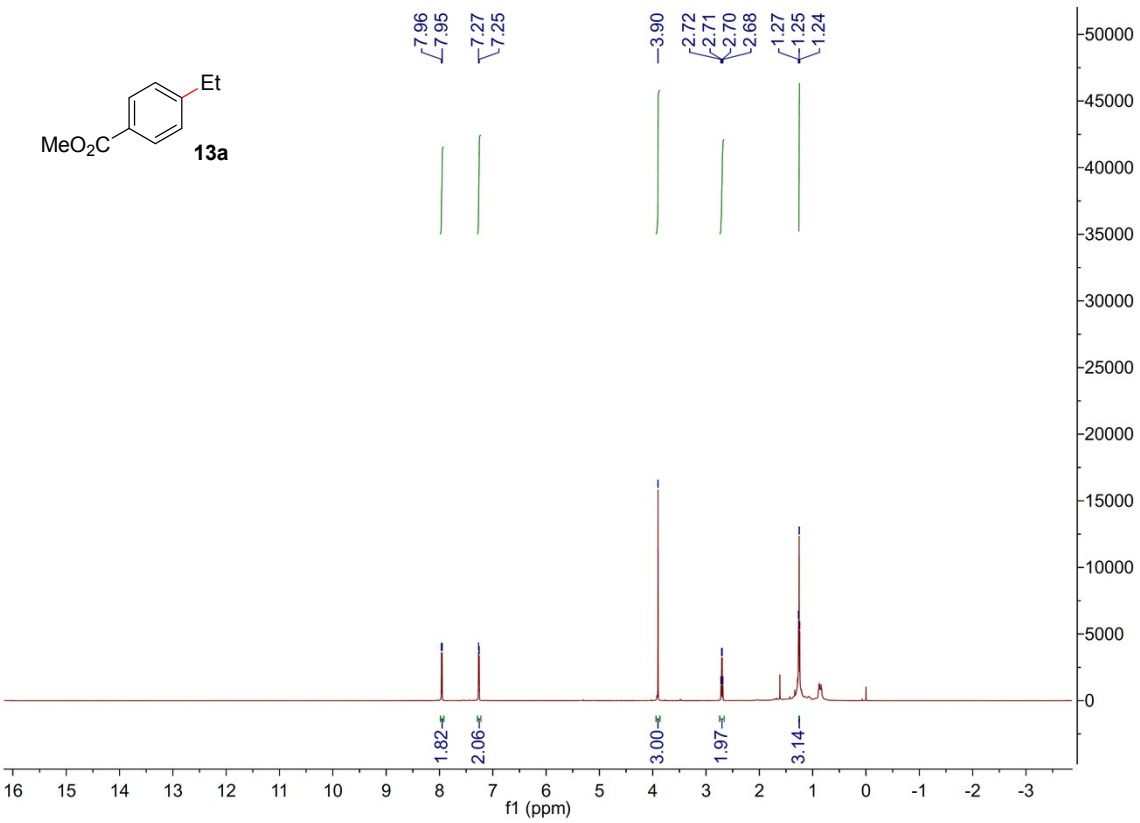


Figure S65. ^{1}H NMR of 13a in $CDCl_3$

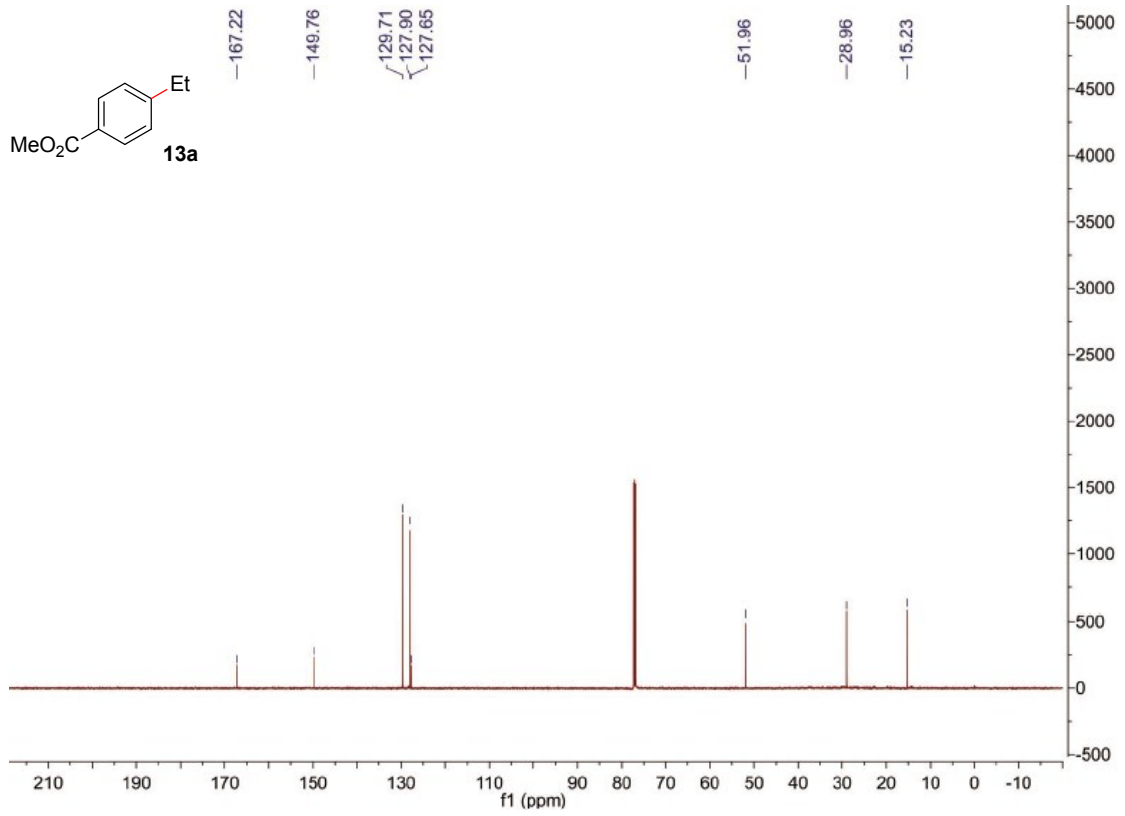


Figure S66. ^{13}C NMR of 13a in $CDCl_3$

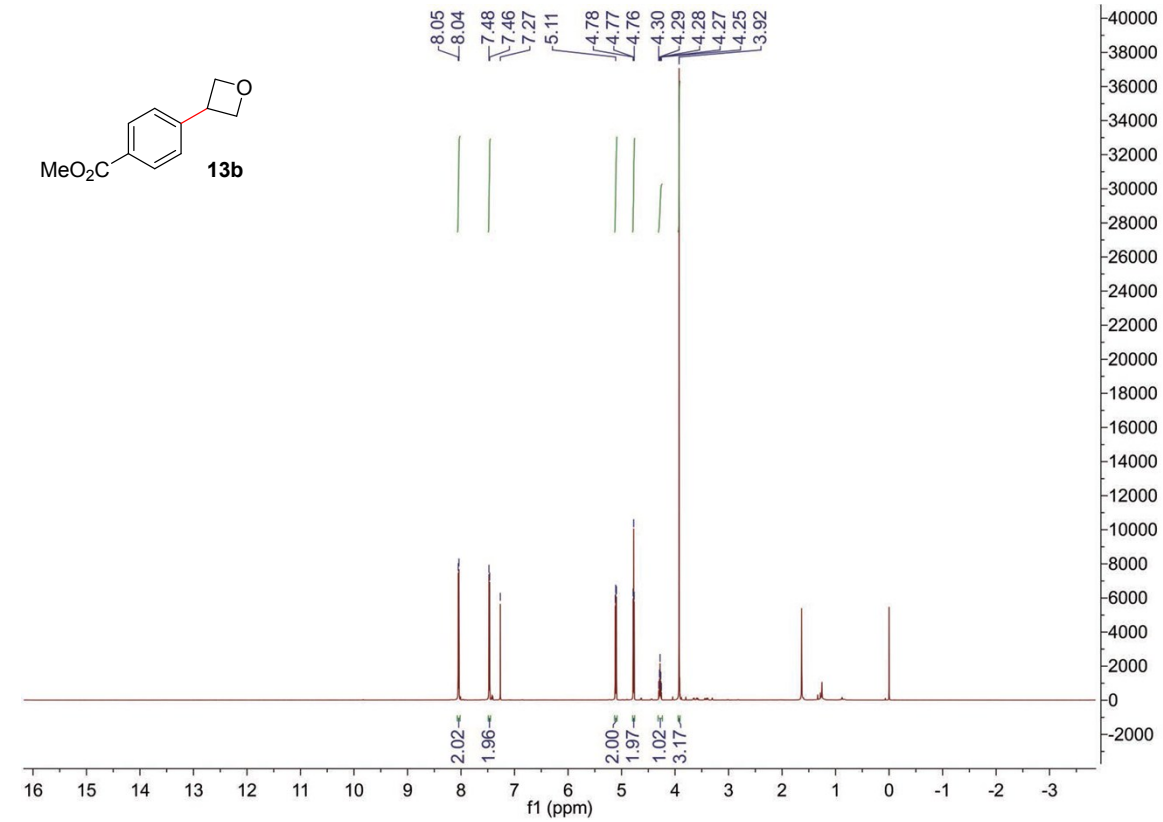


Figure S67. ^{1}H NMR of 13b in $CDCl_3$

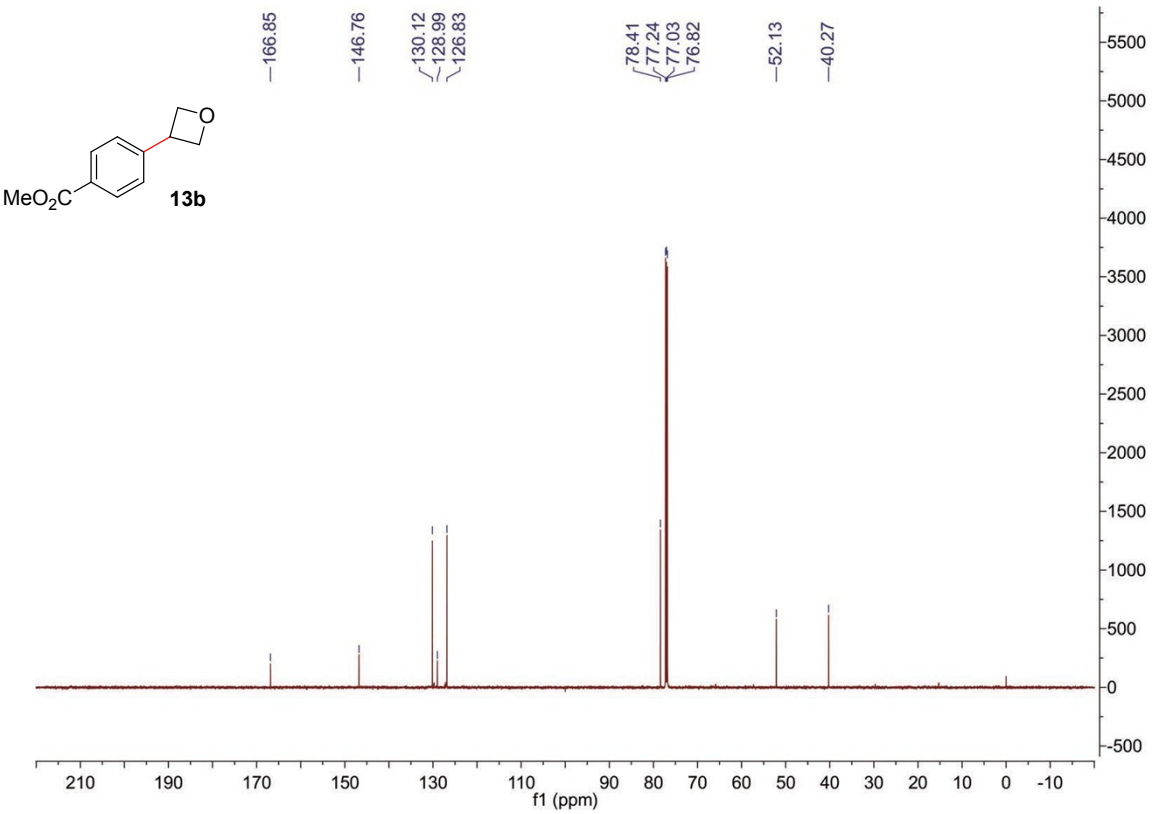


Figure S68. ^{13}C NMR of 13b in $CDCl_3$

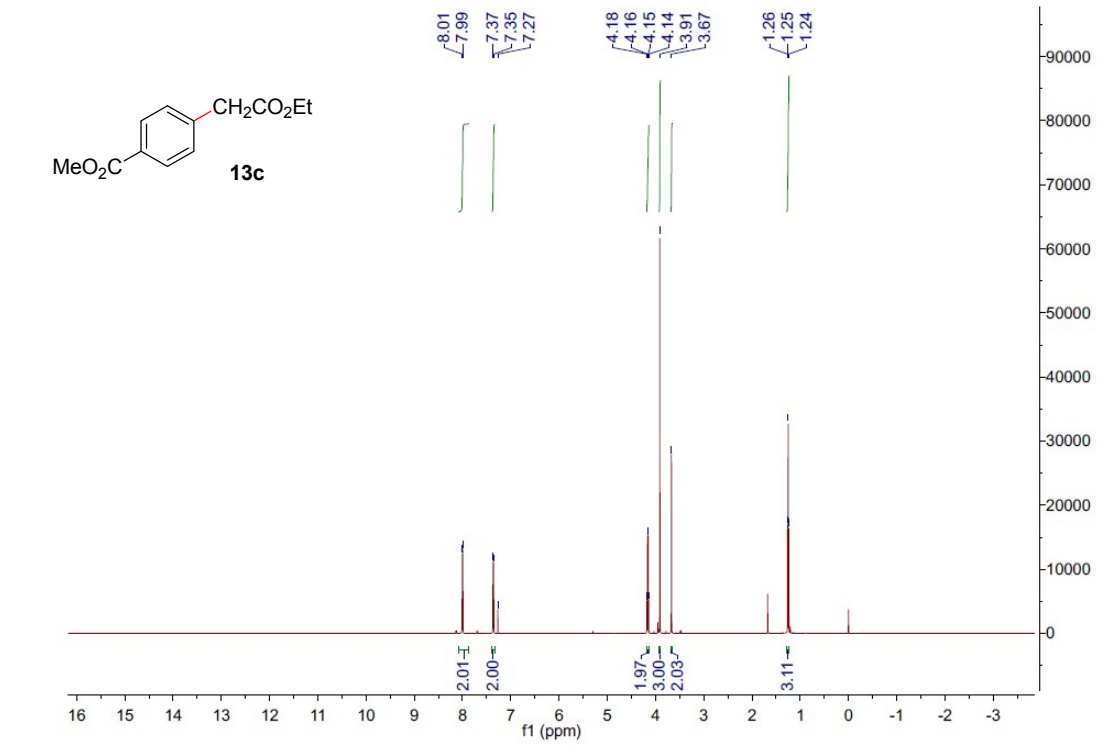


Figure S69. ^{1}H NMR of 13c in $CDCl_3$

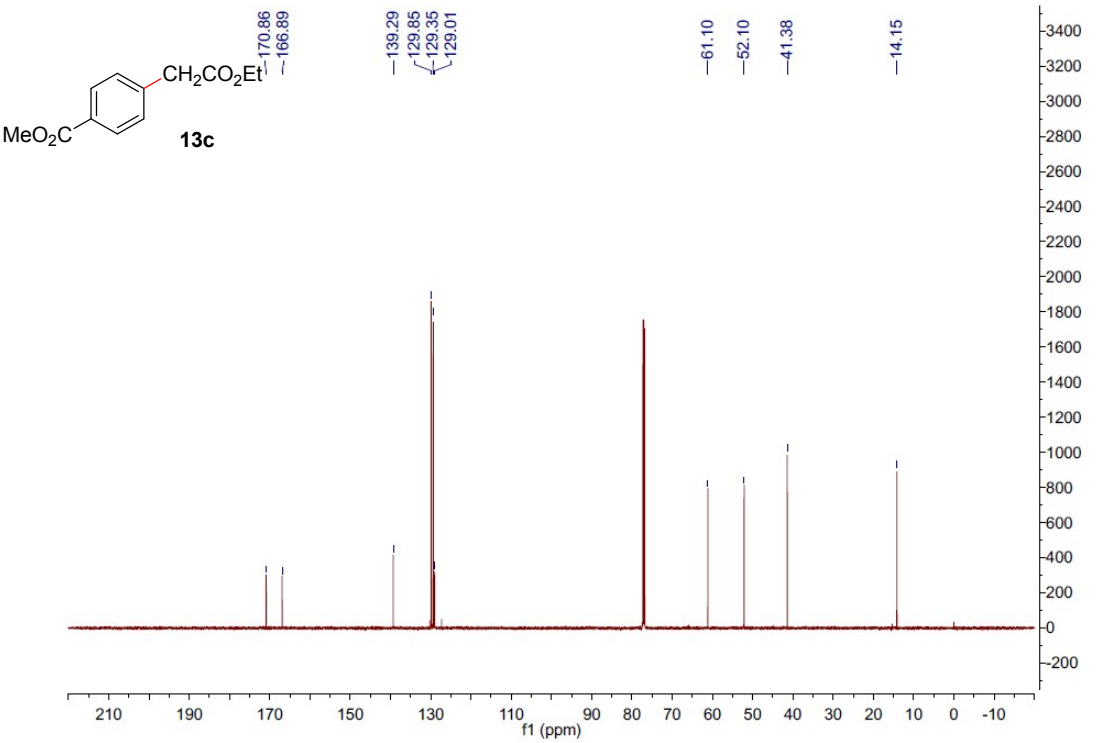


Figure S70. ^{13}C NMR of 13c in $CDCl_3$

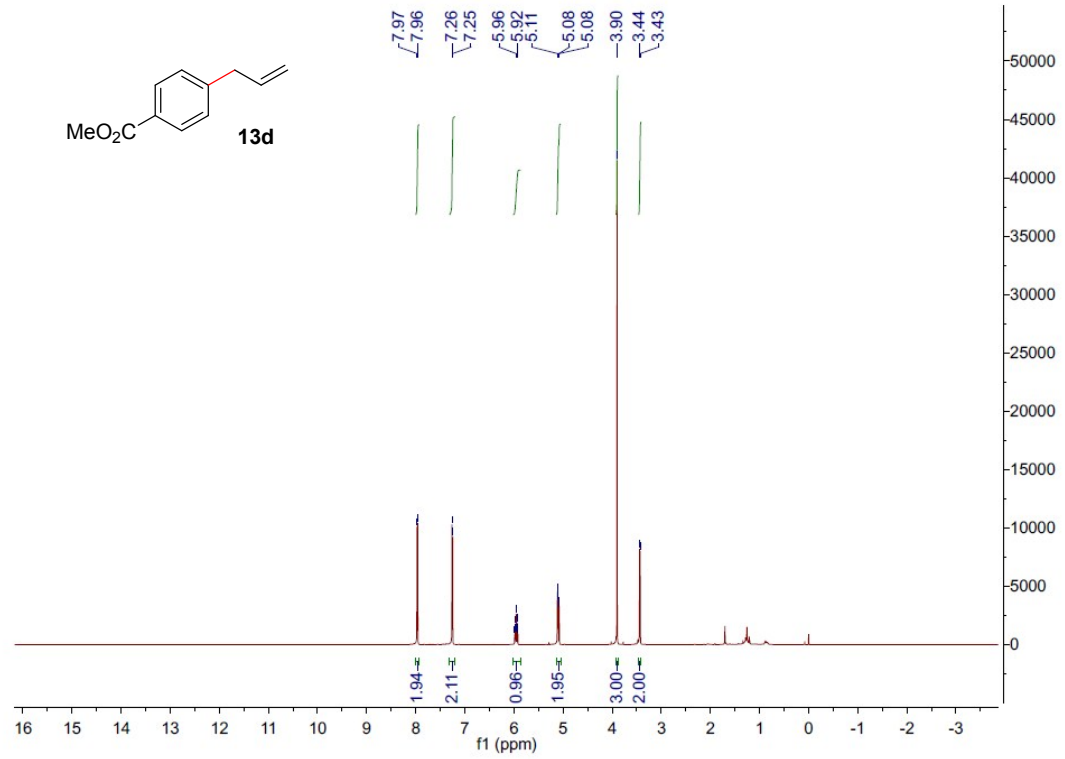


Figure S71. ^{1}H NMR of 13d in $CDCl_3$

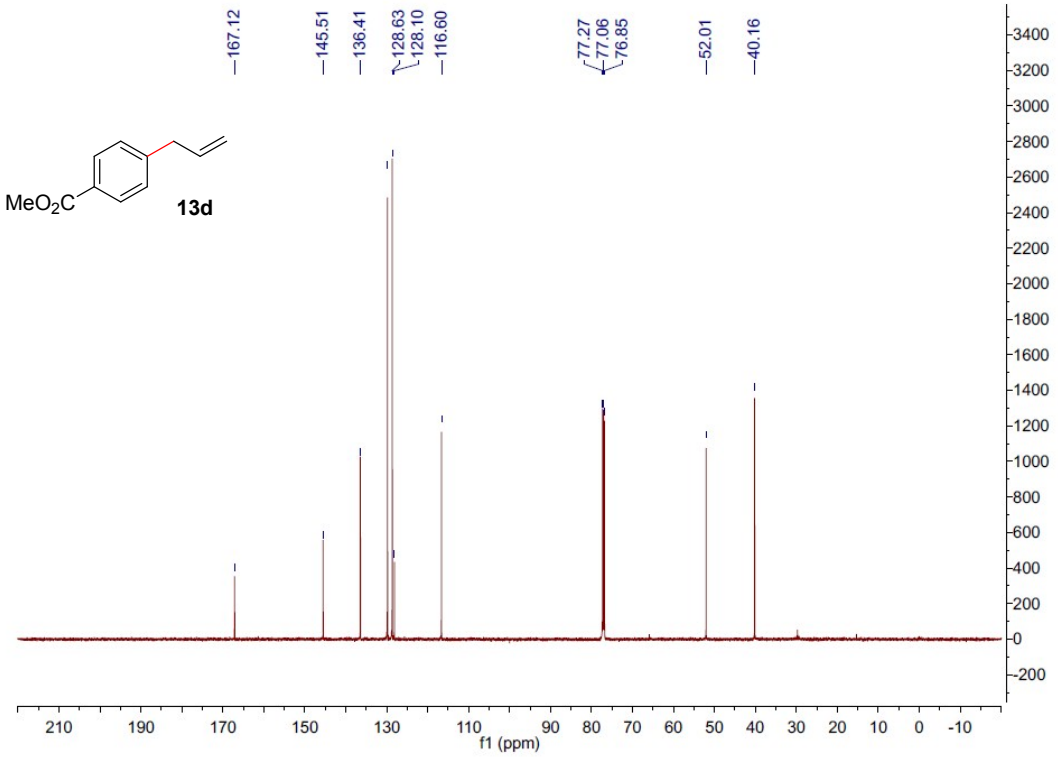


Figure S72. ^{13}C NMR of 13d in $CDCl_3$

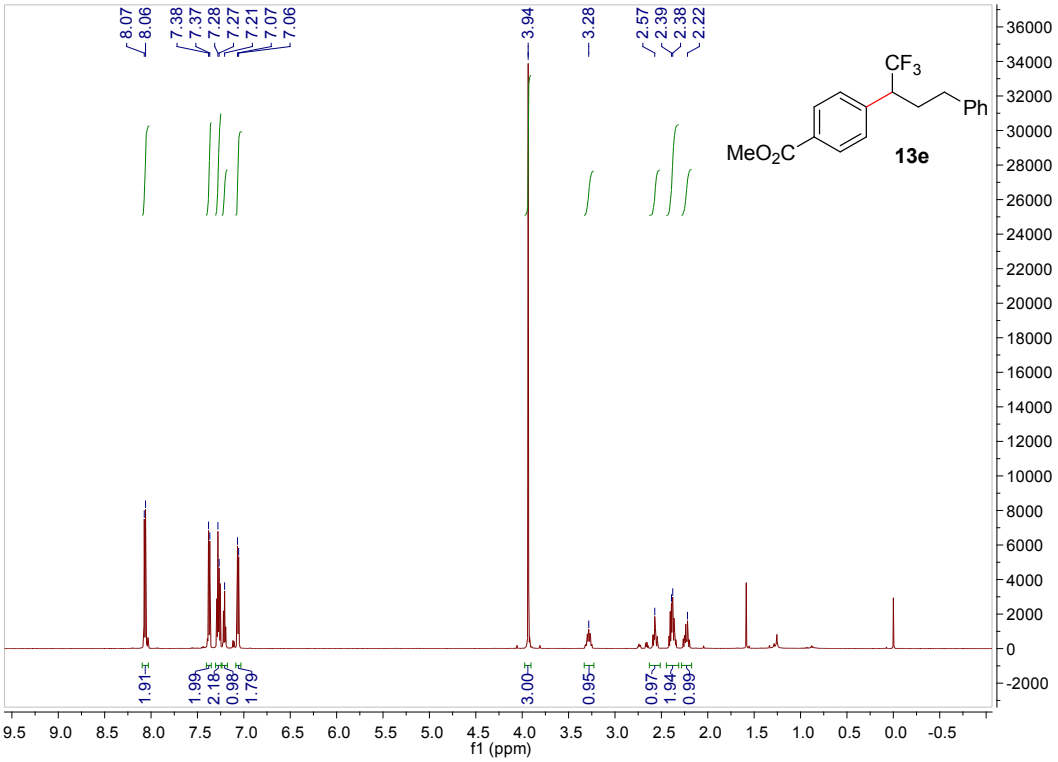


Figure S73. ^{1}H NMR of 13e in $CDCl_3$

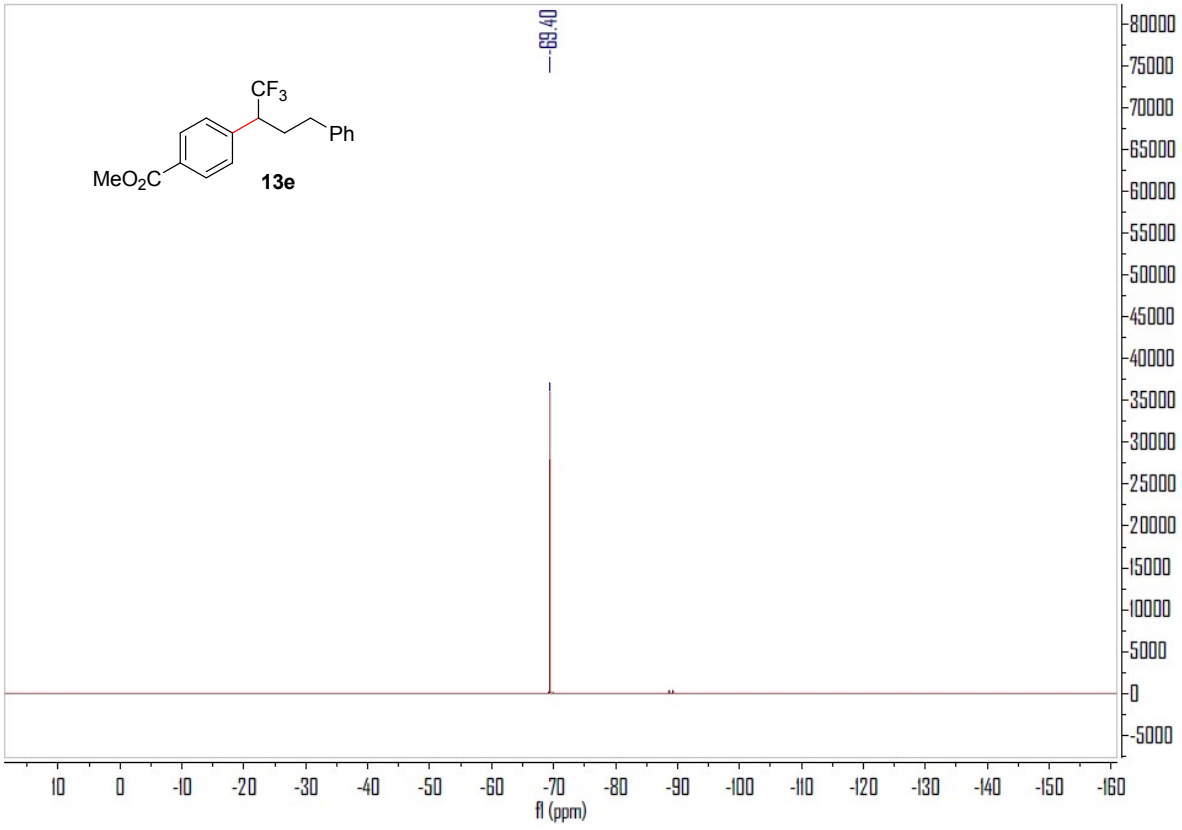


Figure S74. ^{19}F NMR of 13e in $CDCl_3$

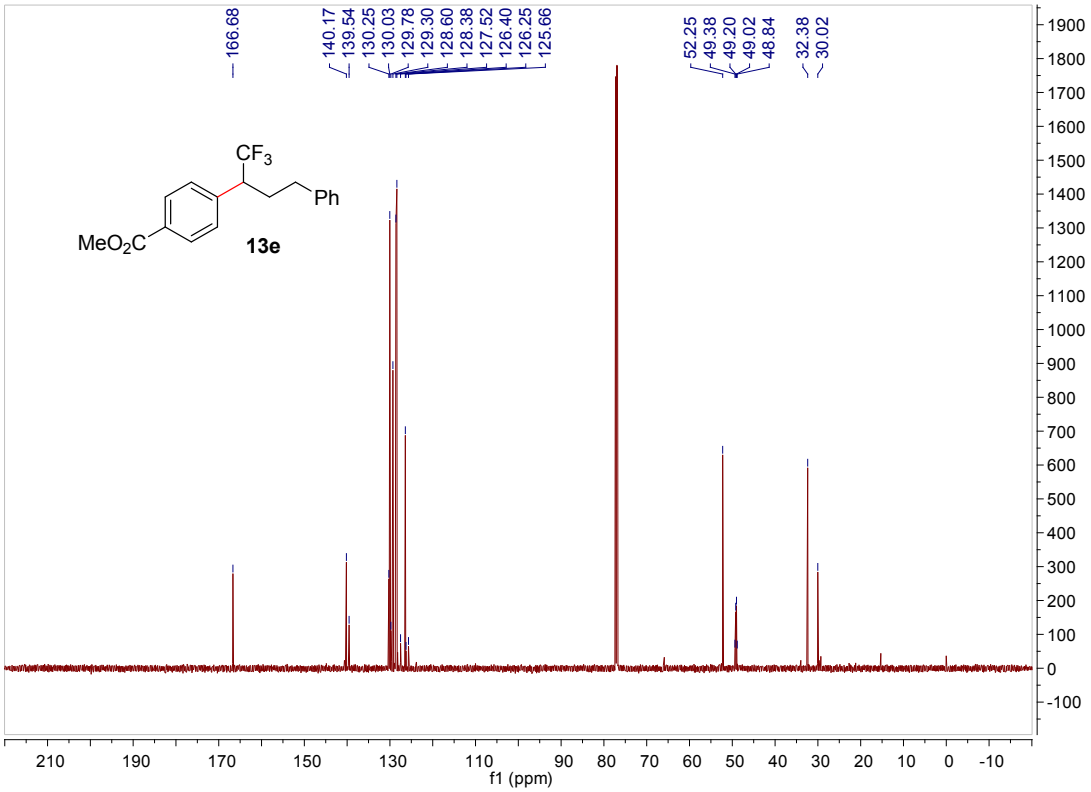


Figure S75. ^{13}C NMR of 13e in $CDCl_3$

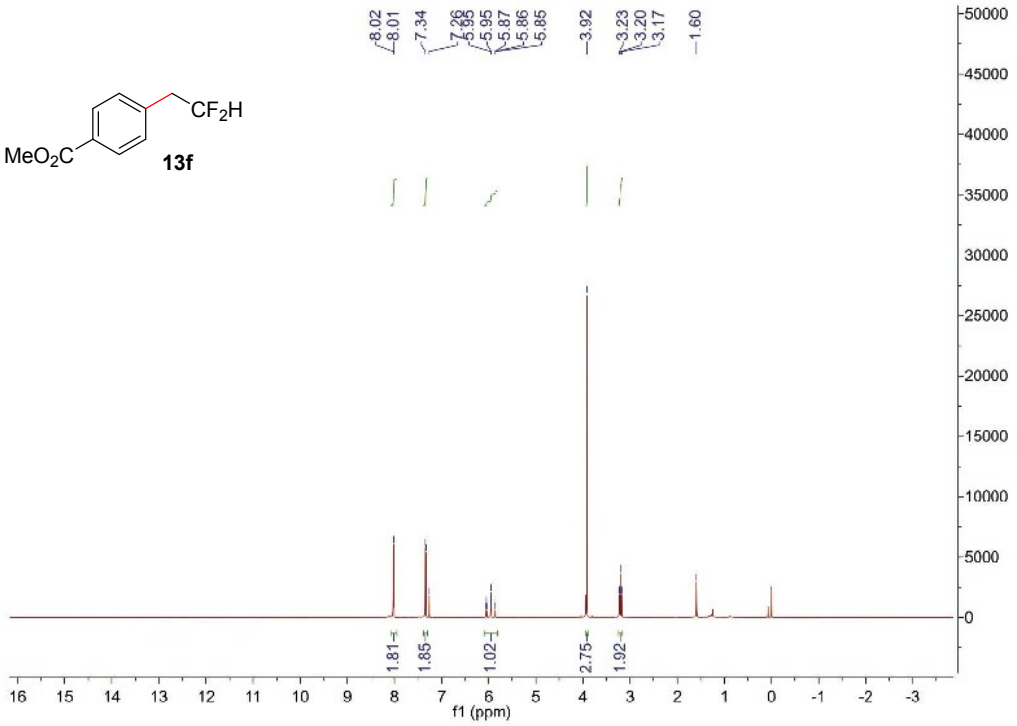


Figure S76. ^{1}H NMR of 13f in $CDCl_3$

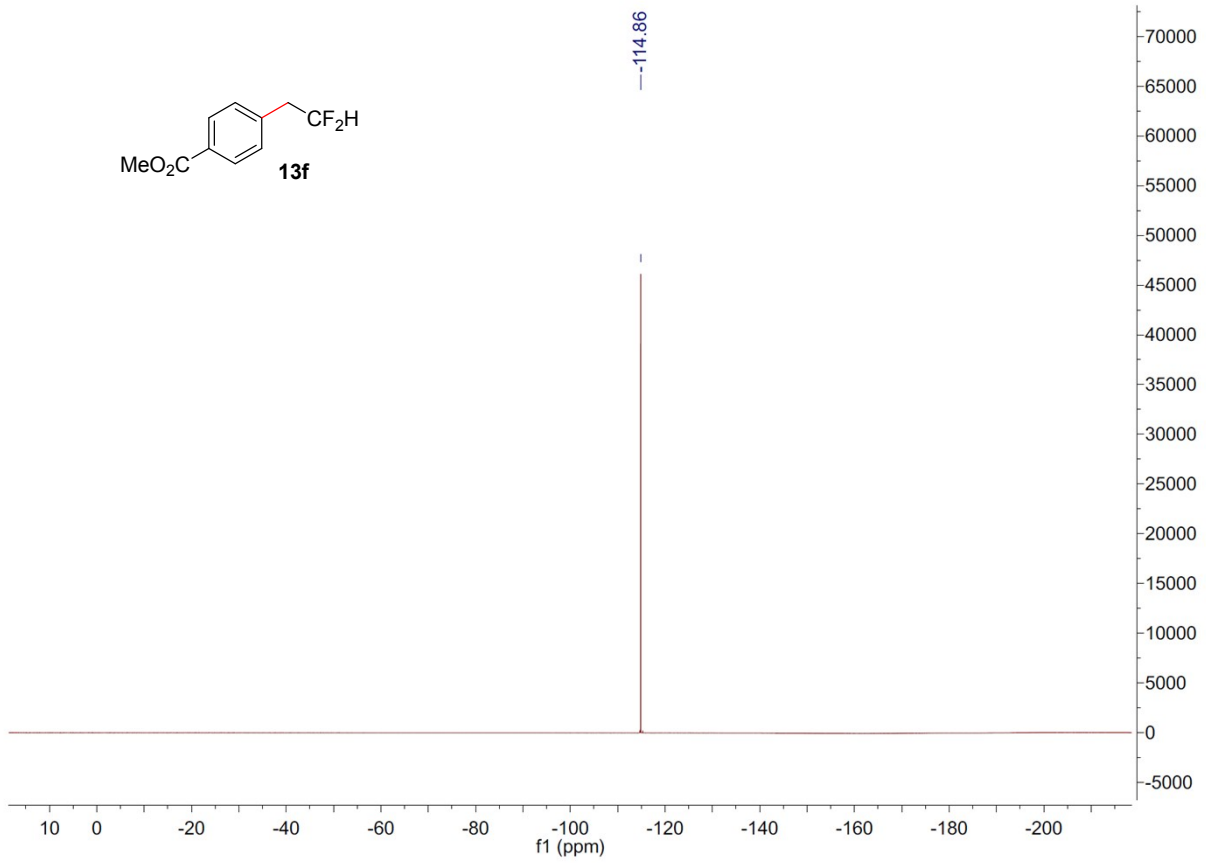


Figure S77. ^{19}F NMR of 13f in $CDCl_3$

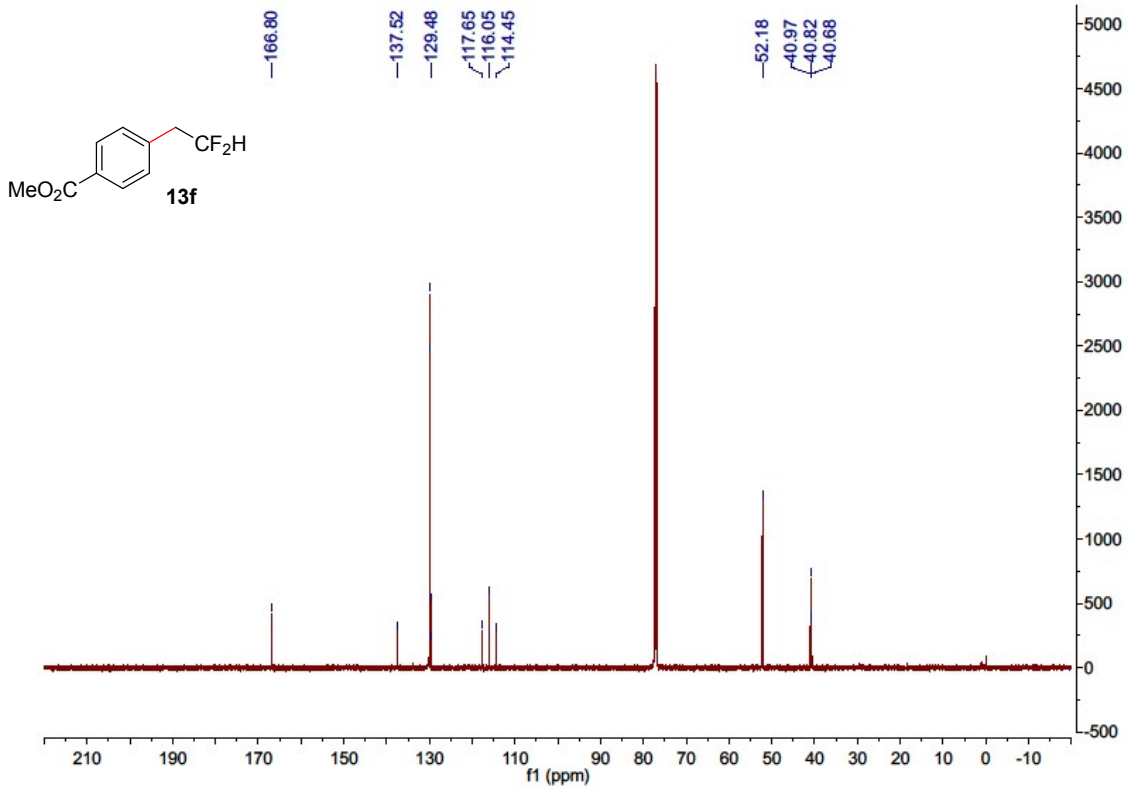


Figure S78. ^{13}C NMR of 13f in $CDCl_3$

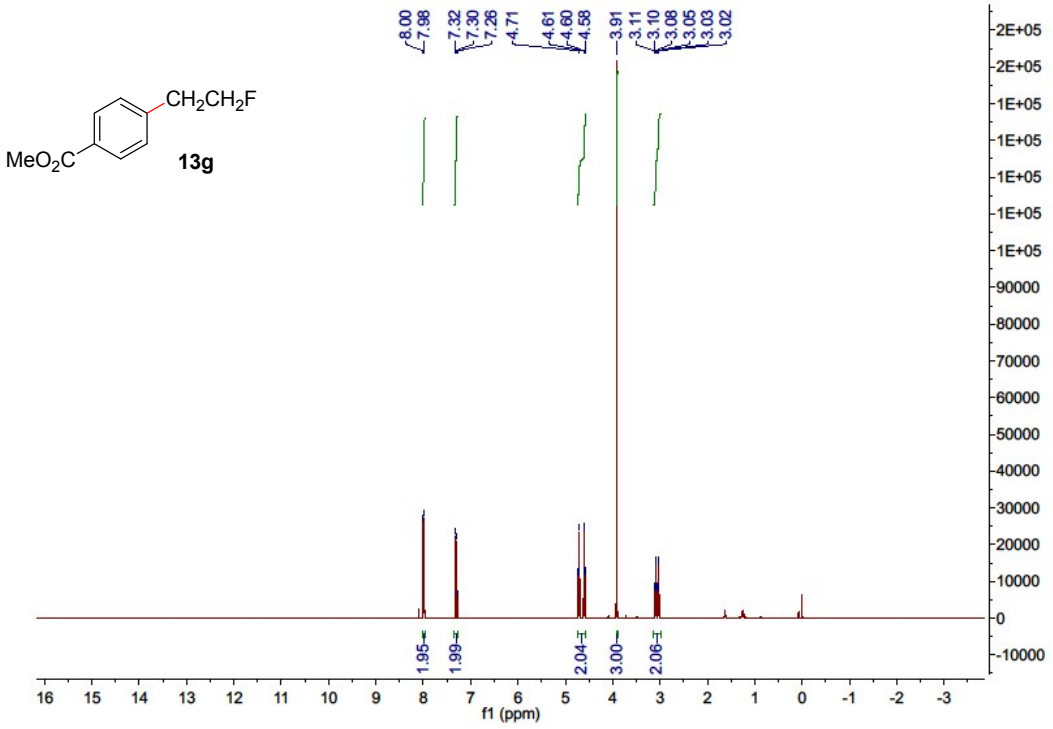


Figure S79. ^{1}H NMR spectra of 1**3g** in $CDCl_3$

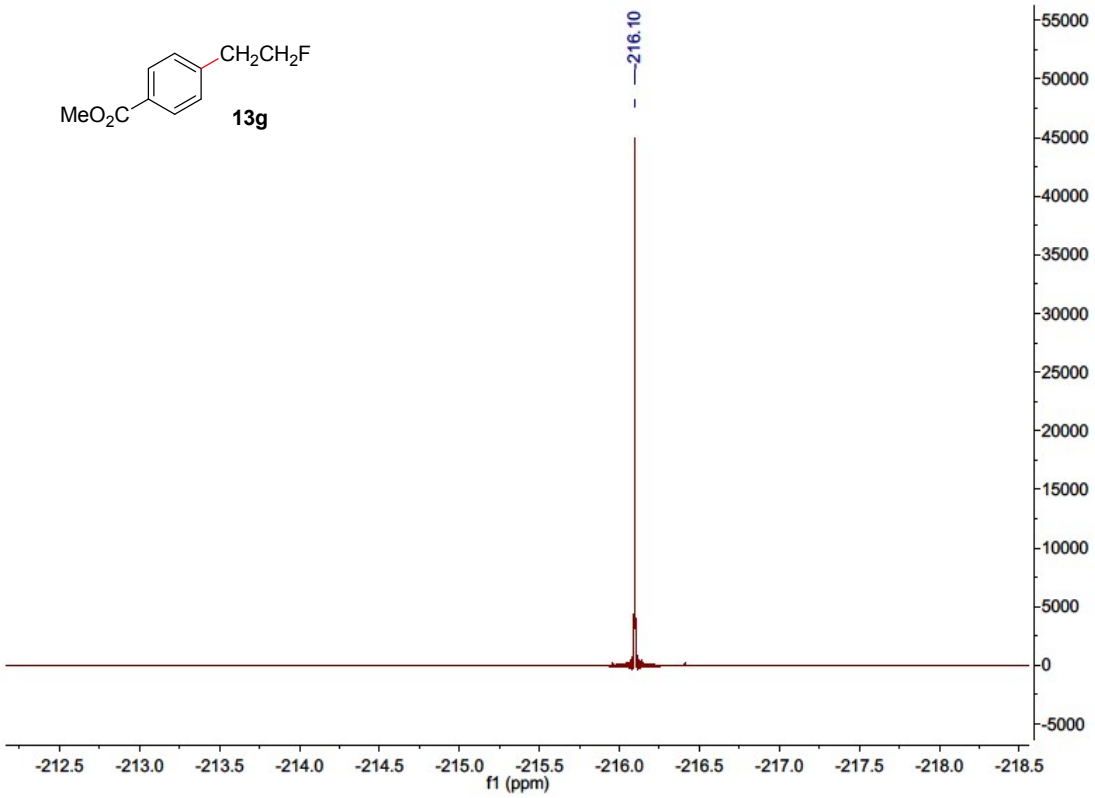


Figure S80. ^{19}F NMR spectra of 1**3g** in $CDCl_3$

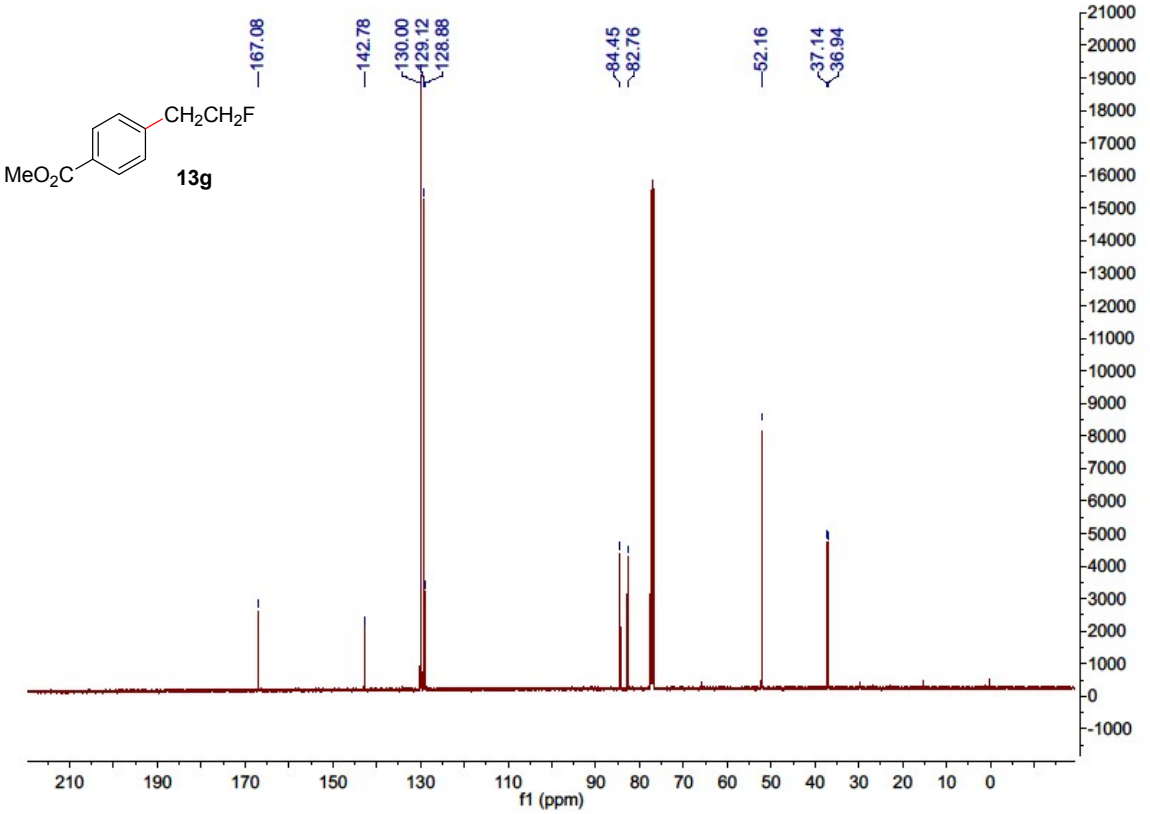


Figure S81. ^{13}C NMR spectra of **3g** in $CDCl_3$

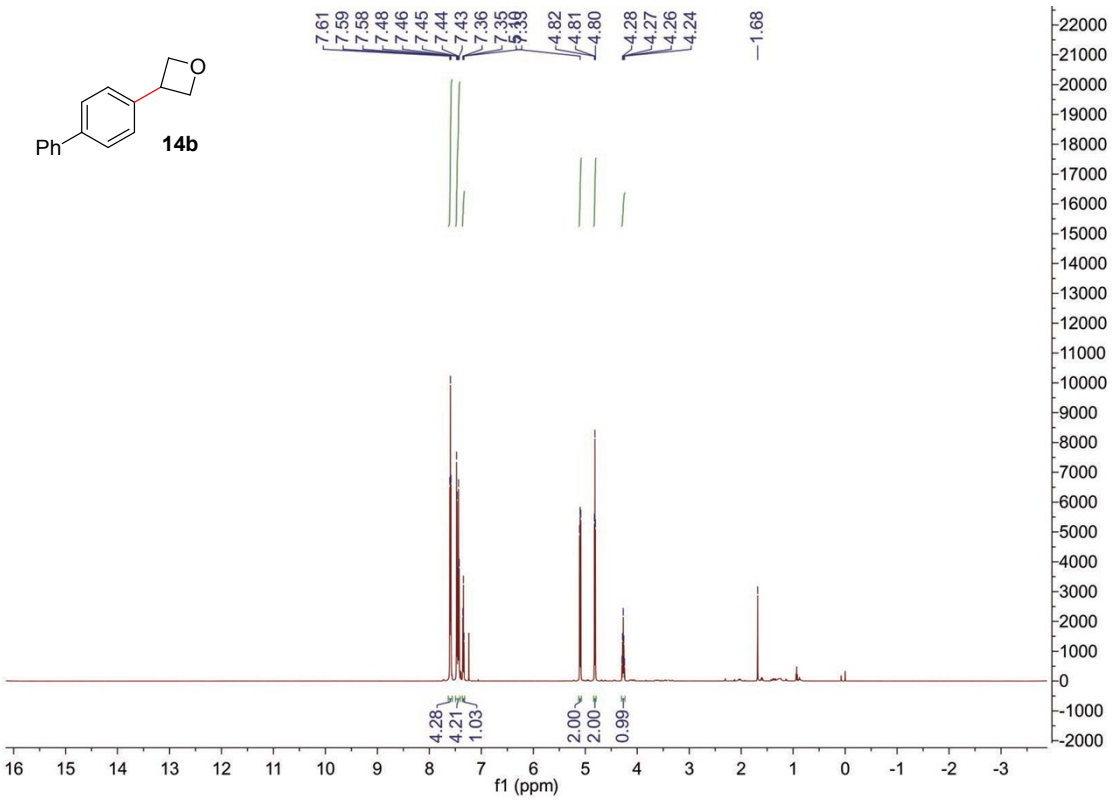


Figure S82. ^{1}H NMR of 14b in $CDCl_3$

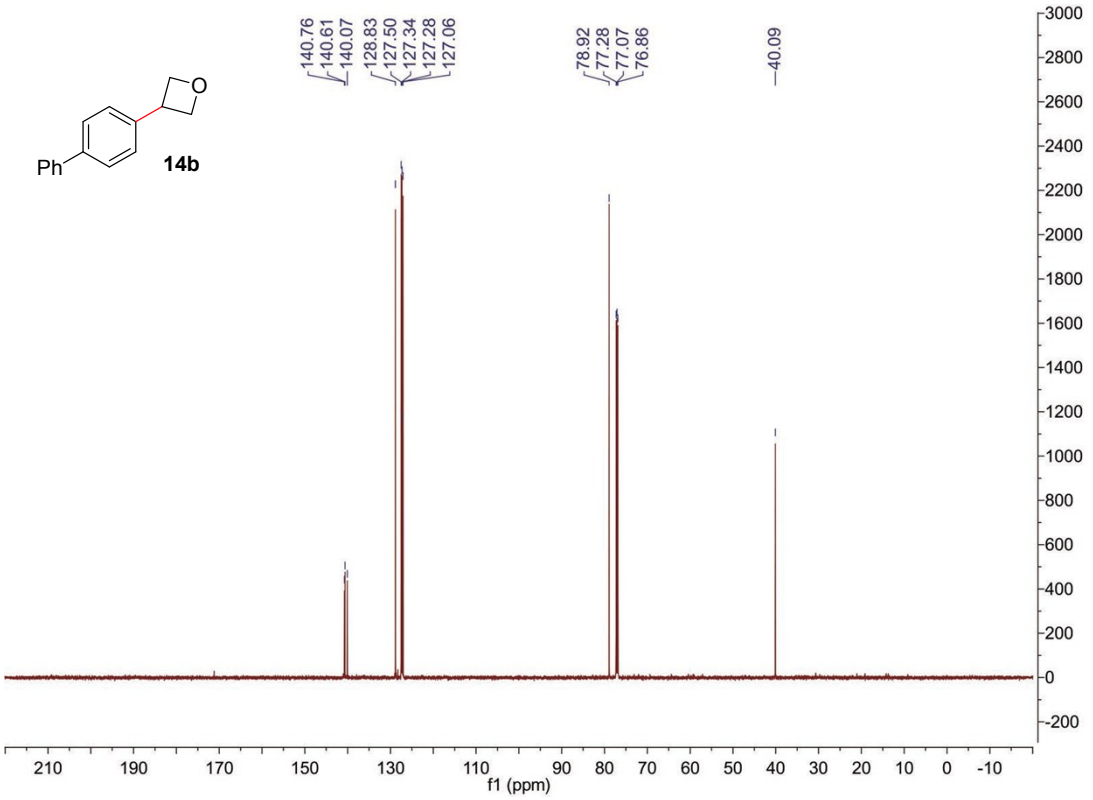


Figure S83. ^{13}C NMR of 14b in $CDCl_3$

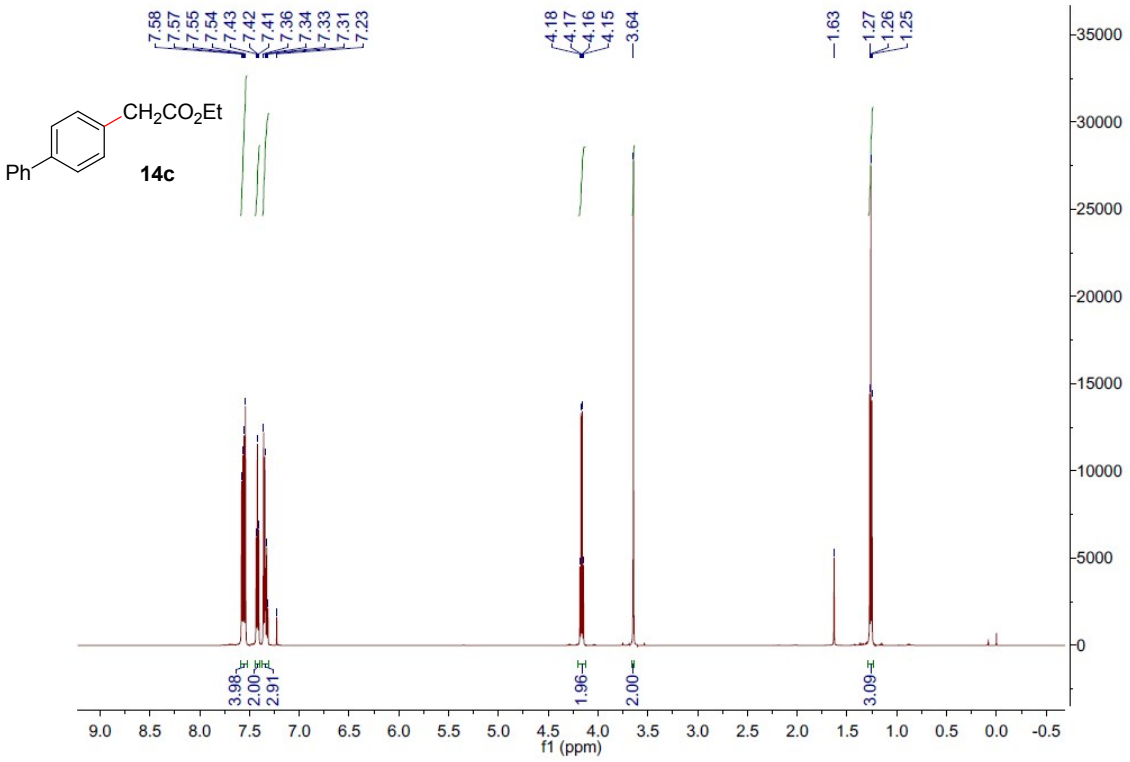


Figure S84. ^{1}H NMR of 14c in $CDCl_3$

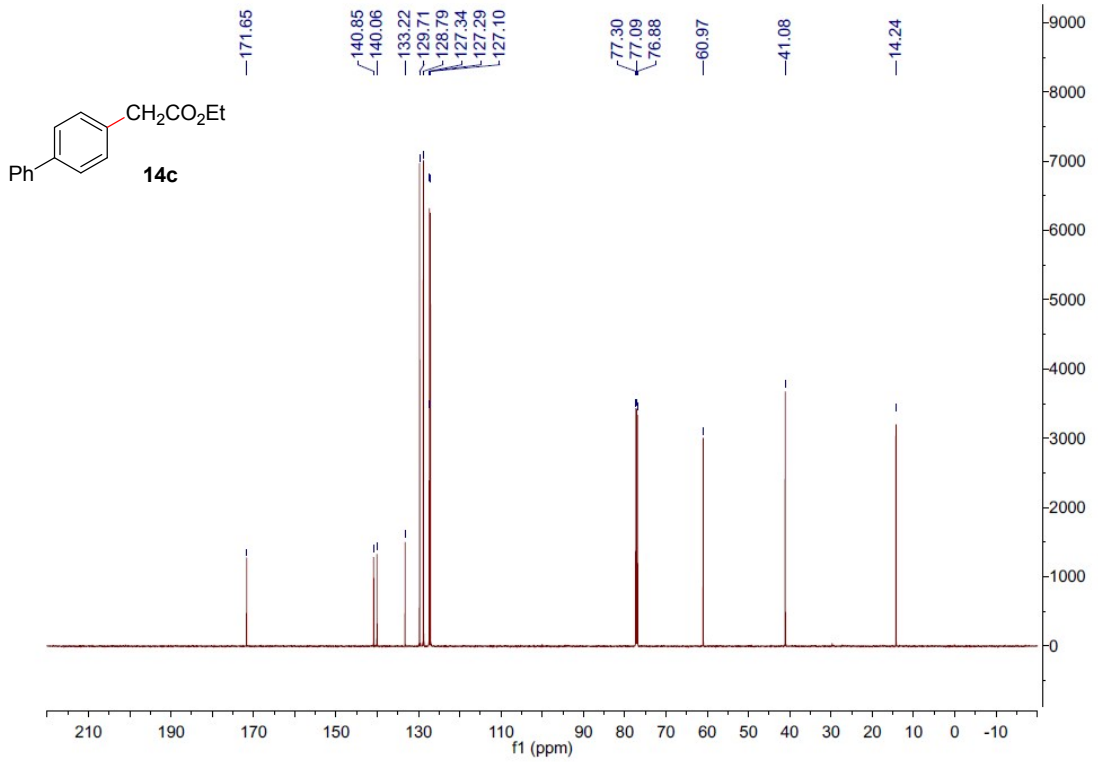


Figure S85. ^{13}C NMR of 14c in $CDCl_3$

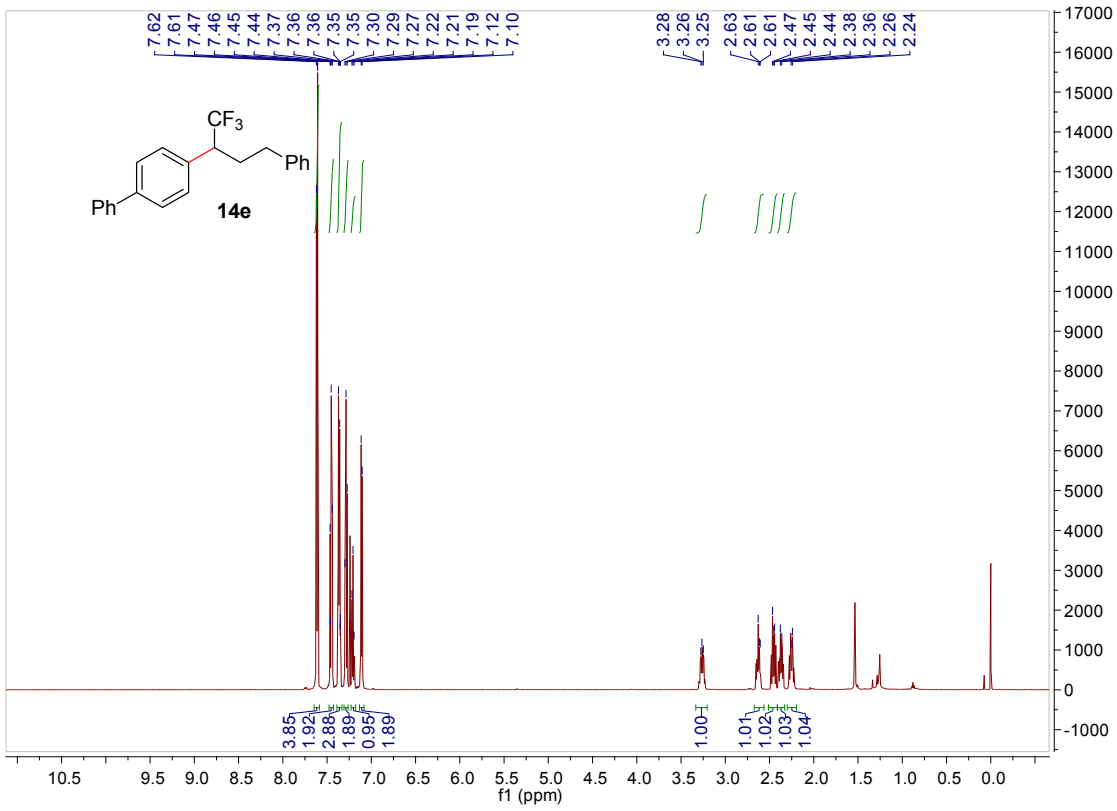


Figure S86. ^{1}H NMR of 14e in $CDCl_3$

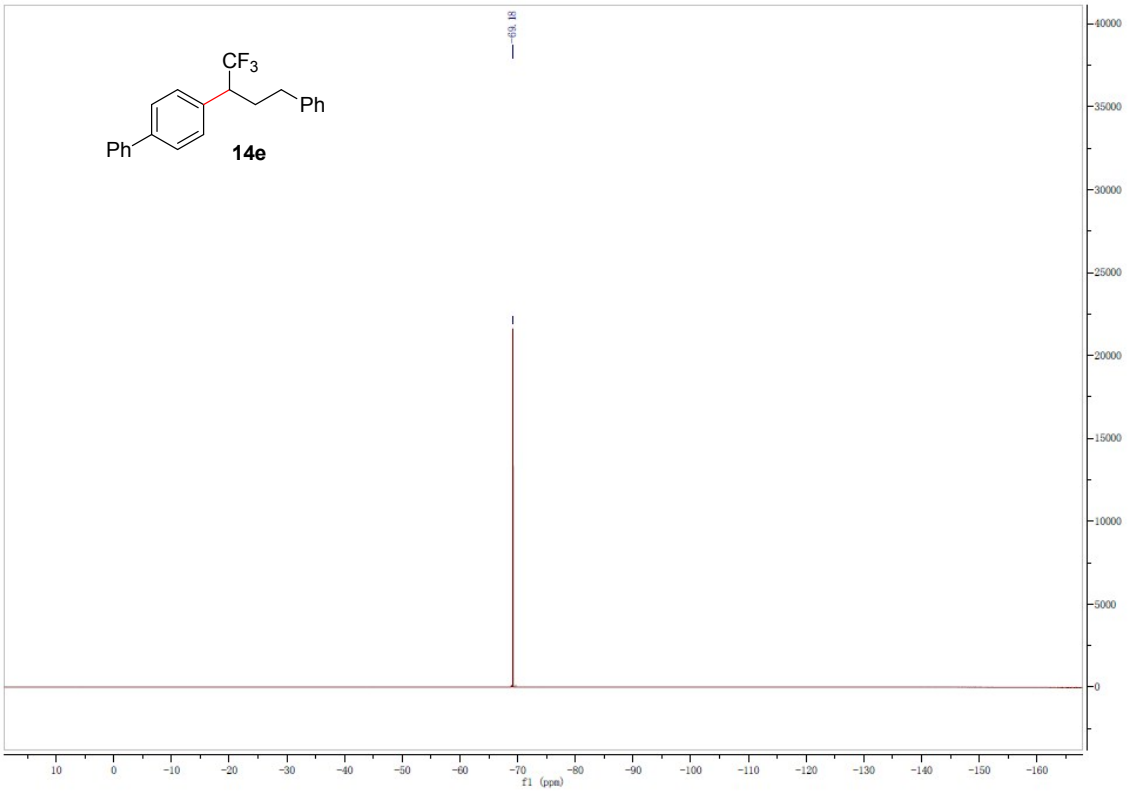


Figure S87. ^{19}F NMR of 14e in $CDCl_3$

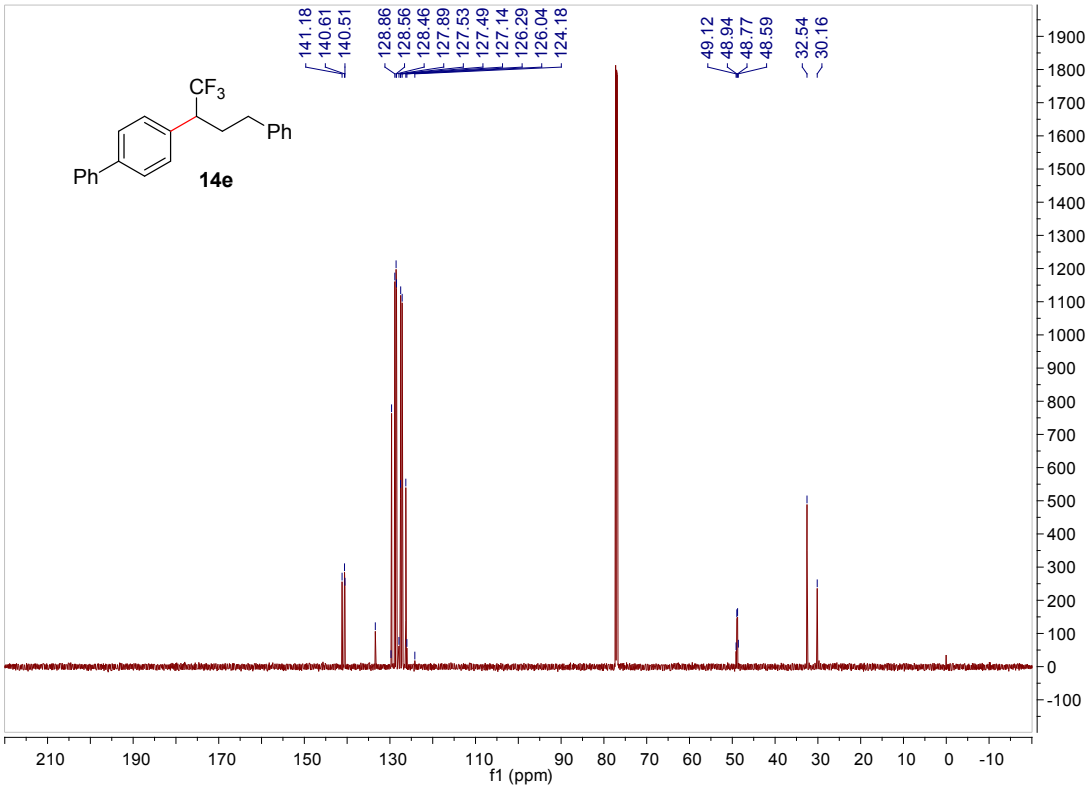


Figure S88. ^{13}C NMR of 14e in $CDCl_3$

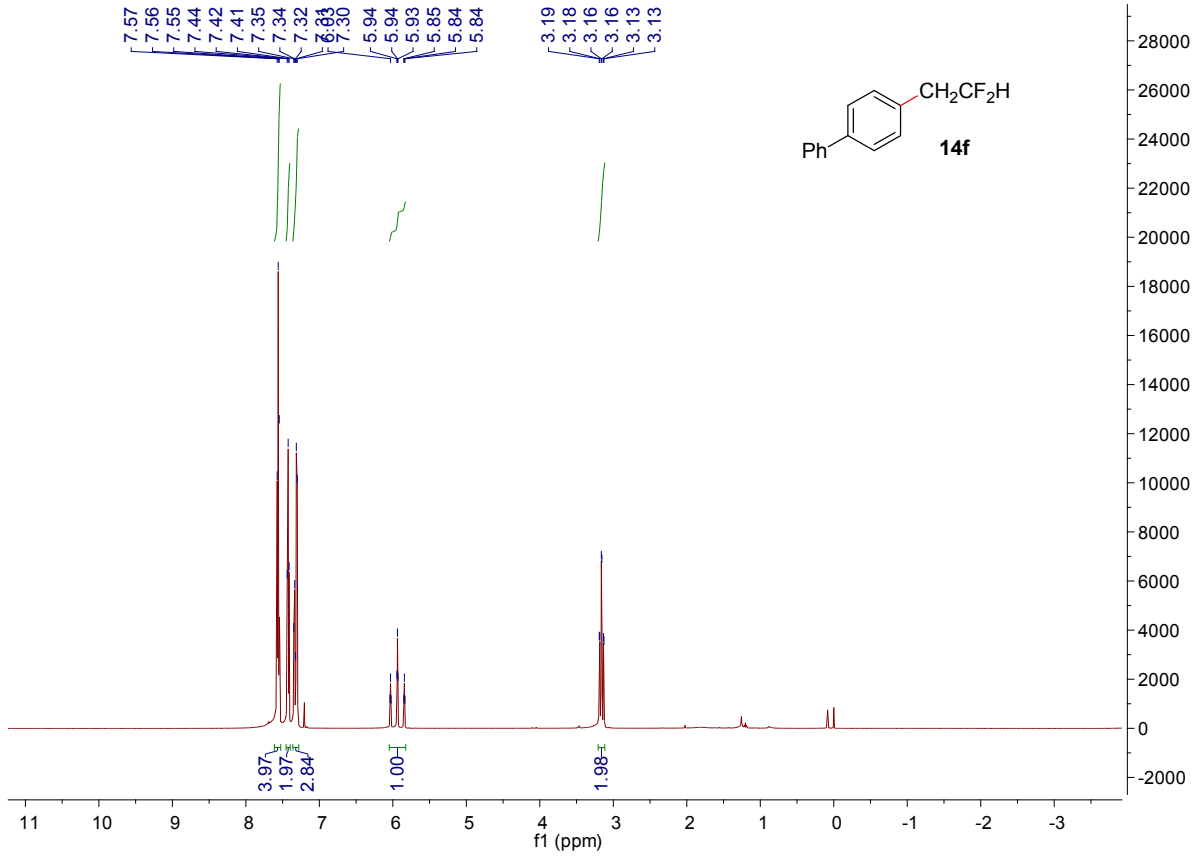


Figure S89. ^{1}H NMR of 14f in $CDCl_3$

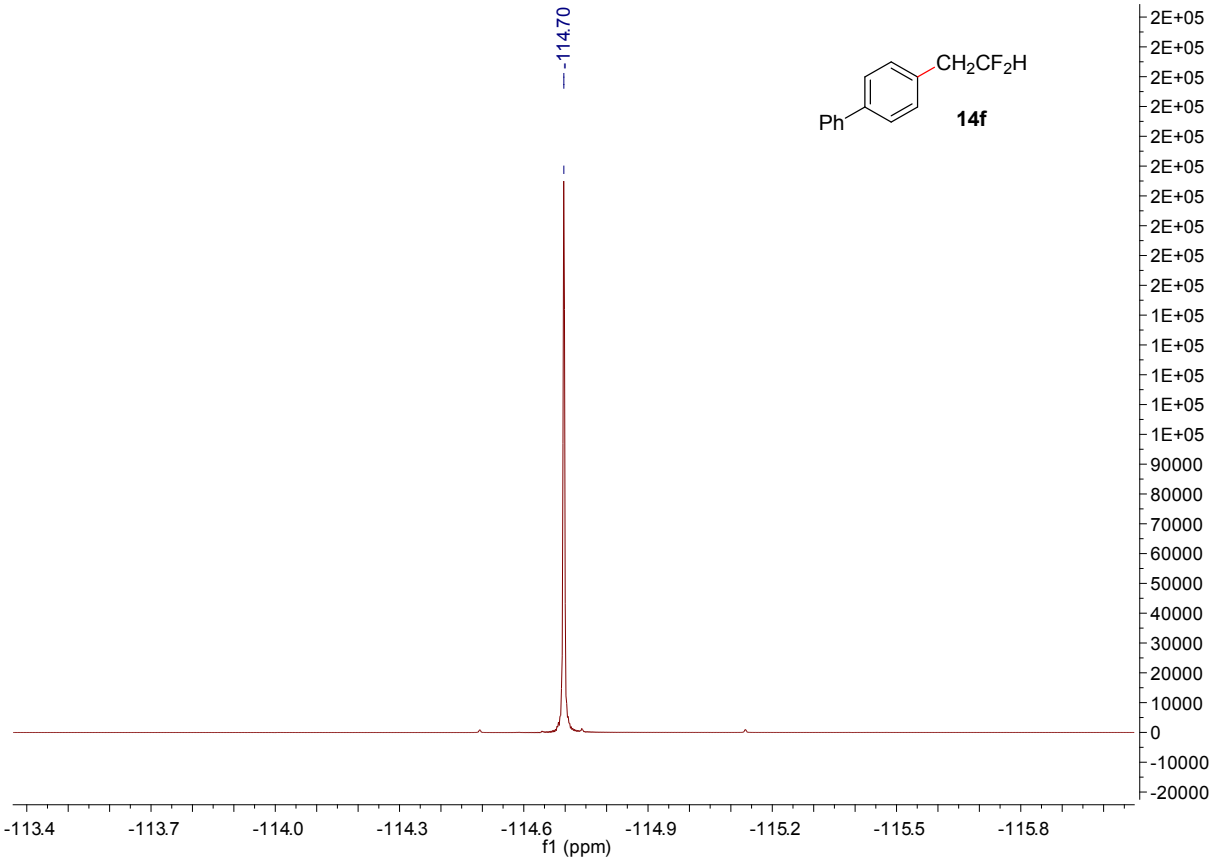


Figure S90. ^{19}F NMR of 14f in $CDCl_3$

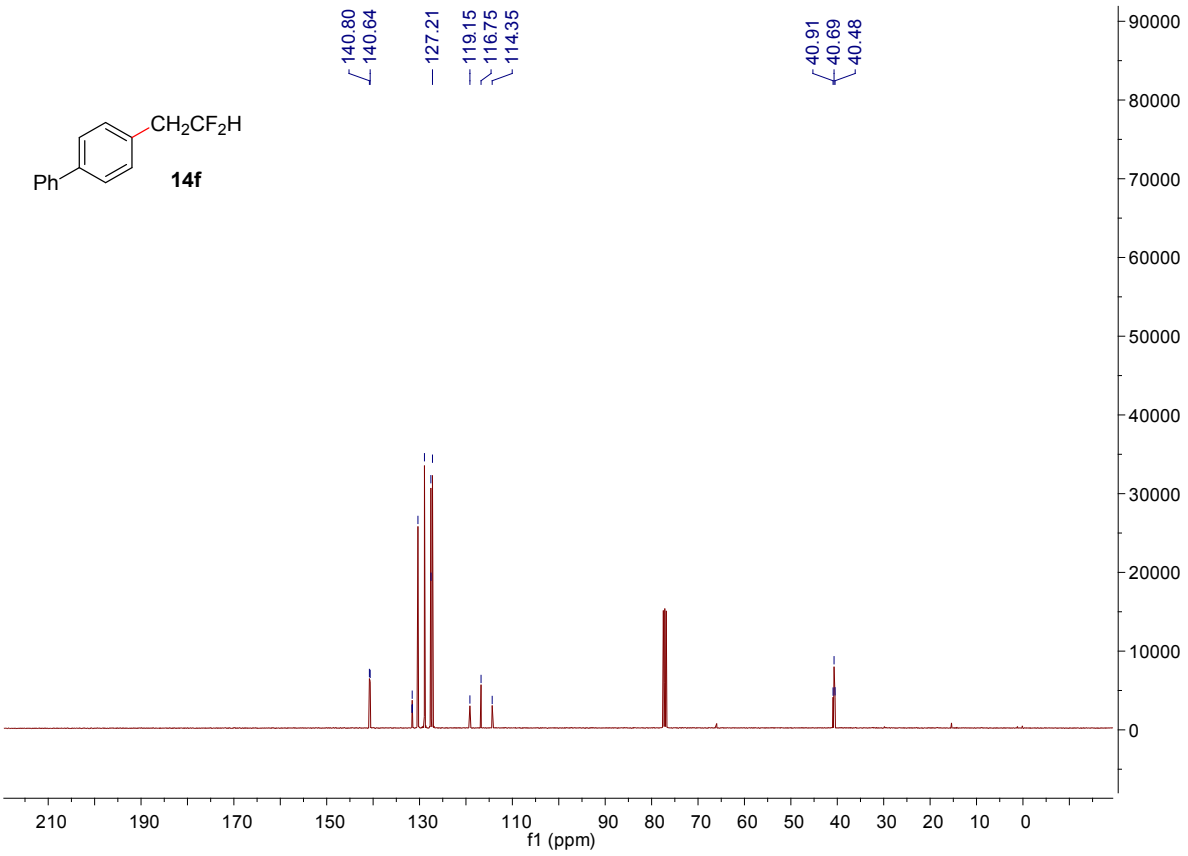


Figure S91. ^{13}C NMR of 14f in $CDCl_3$

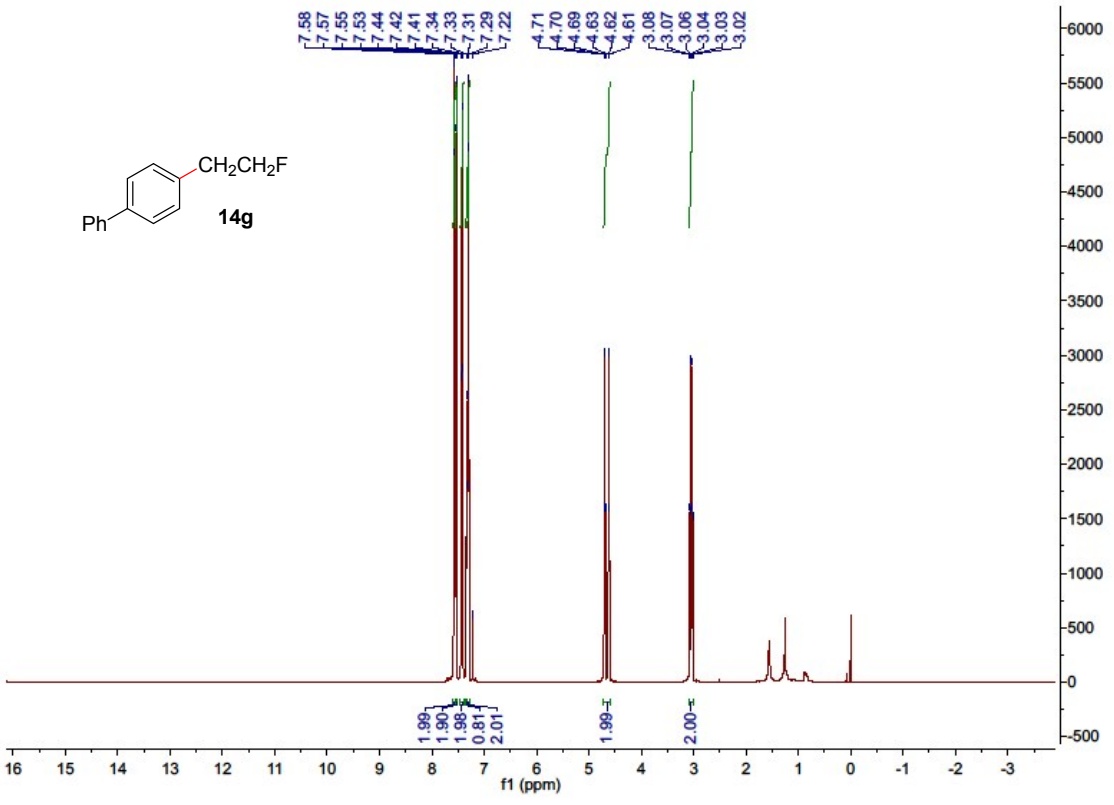


Figure S92. ^{1}H NMR of 14g in $CDCl_3$

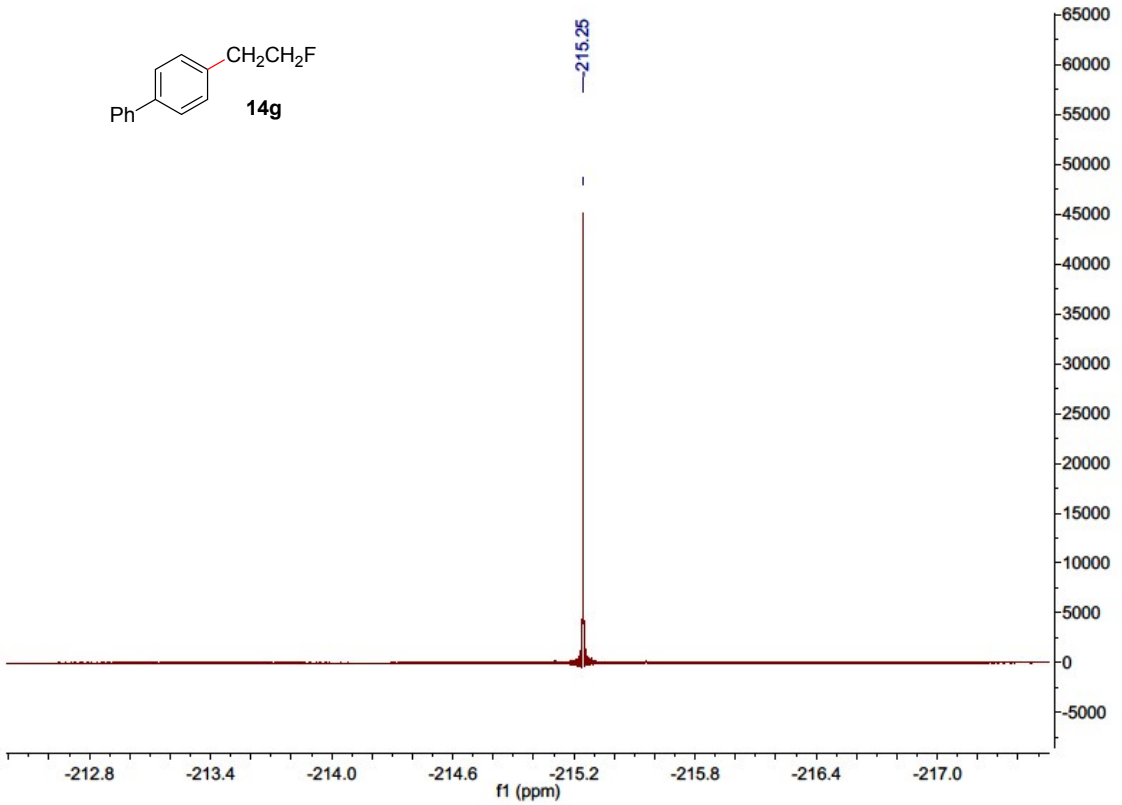


Figure S93. ^{19}F NMR of 14g in $CDCl_3$

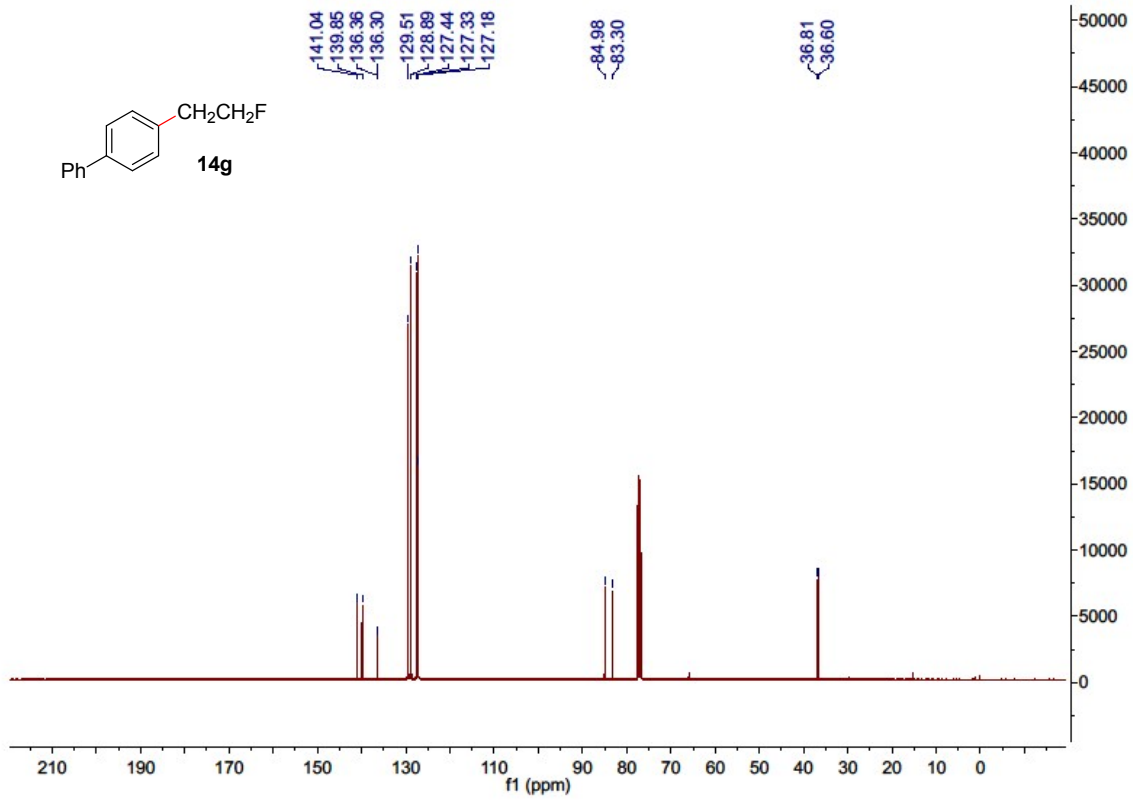


Figure S94. ^{13}C NMR of 14g in $CDCl_3$

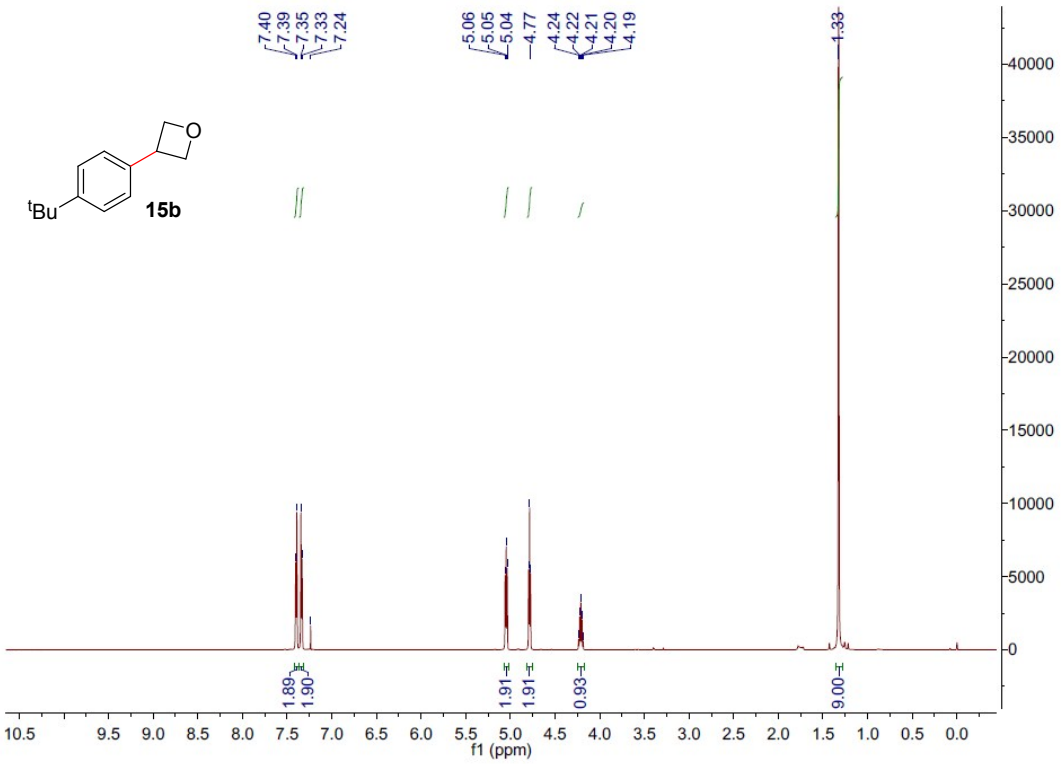


Figure S95. ^{1}H NMR of 15b in $CDCl_3$

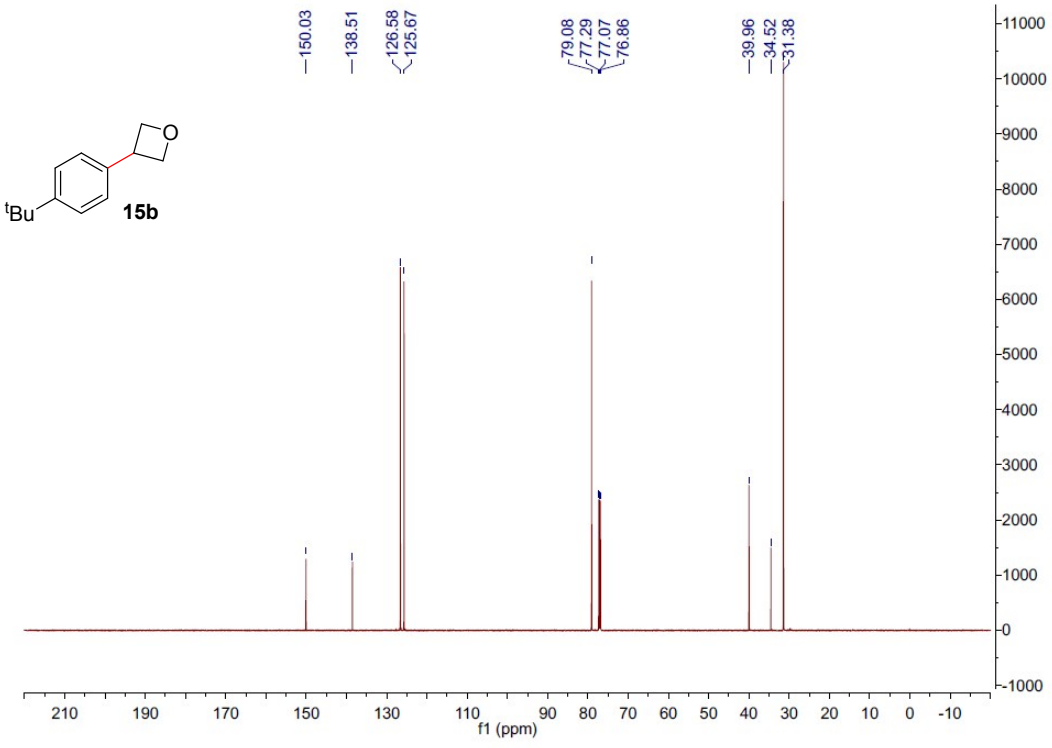


Figure S96. ^{13}C NMR of 15b in $CDCl_3$

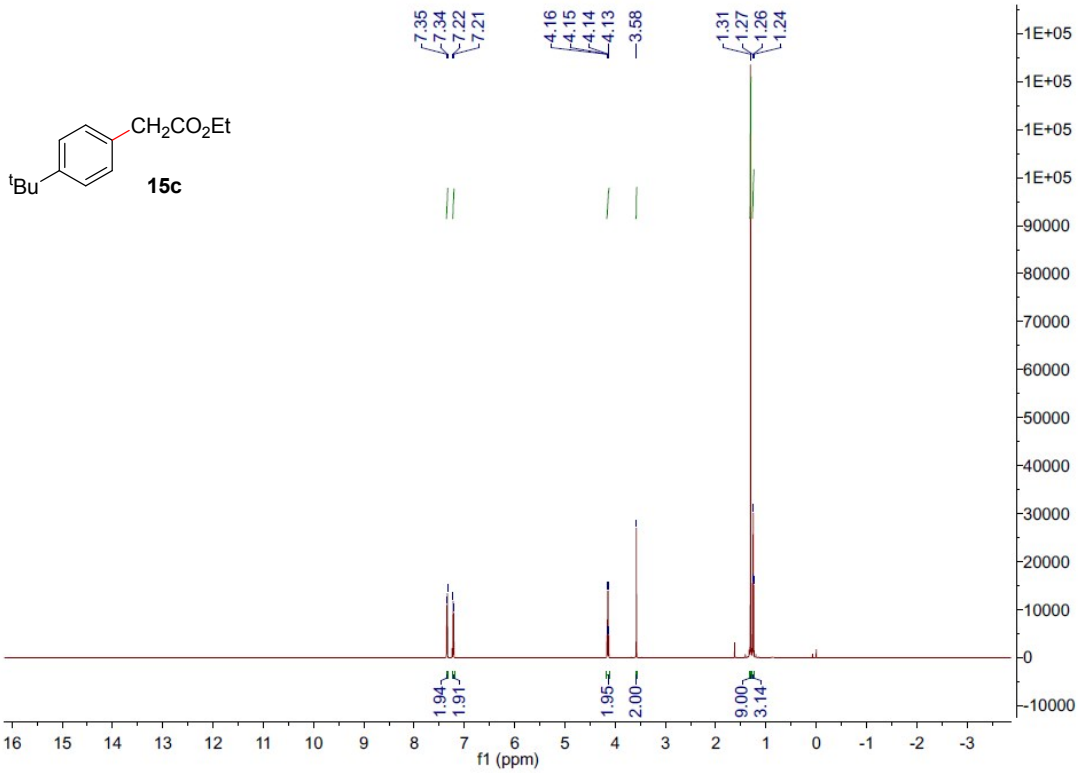


Figure S97. ^{1}H NMR of 15c in $CDCl_3$

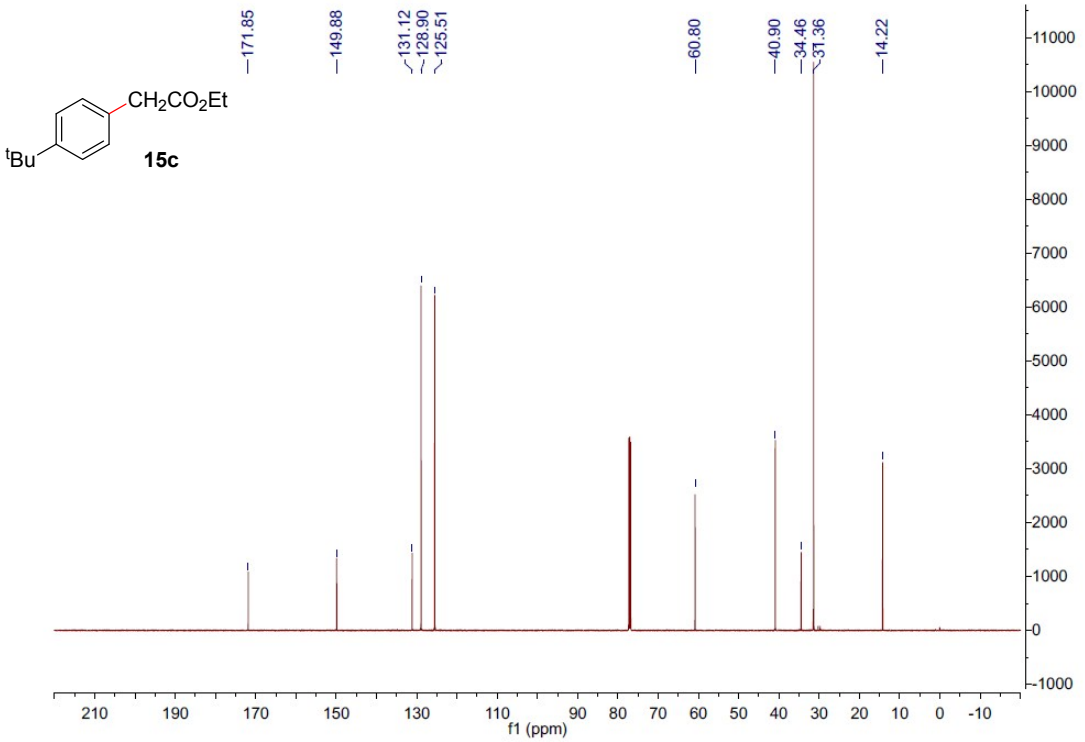


Figure S98. ^{13}C NMR of 15c in $CDCl_3$

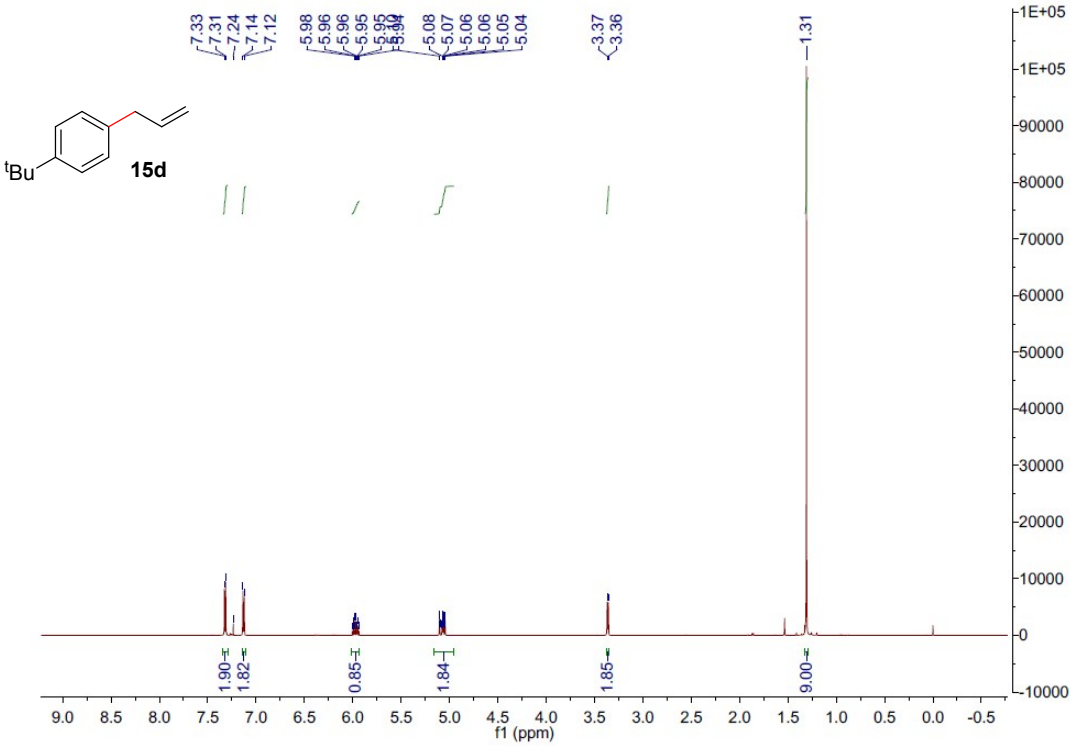


Figure S99. ^{1}H NMR of 15d in $CDCl_3$

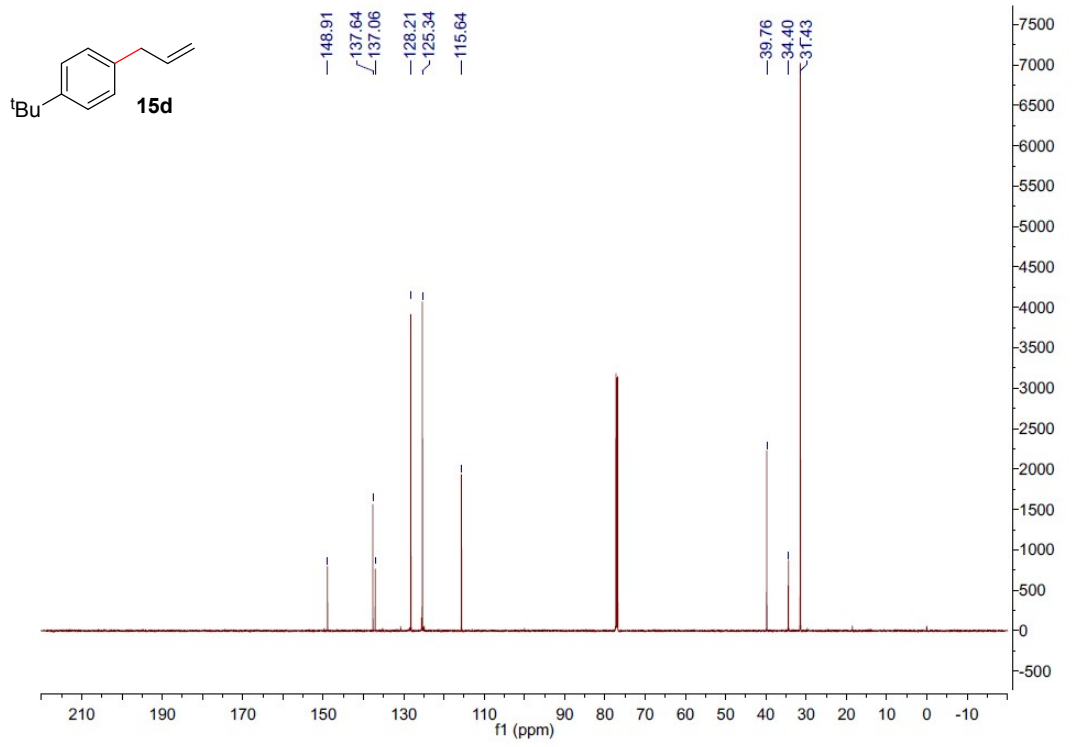


Figure S100. ^{13}C NMR of 15d in $CDCl_3$

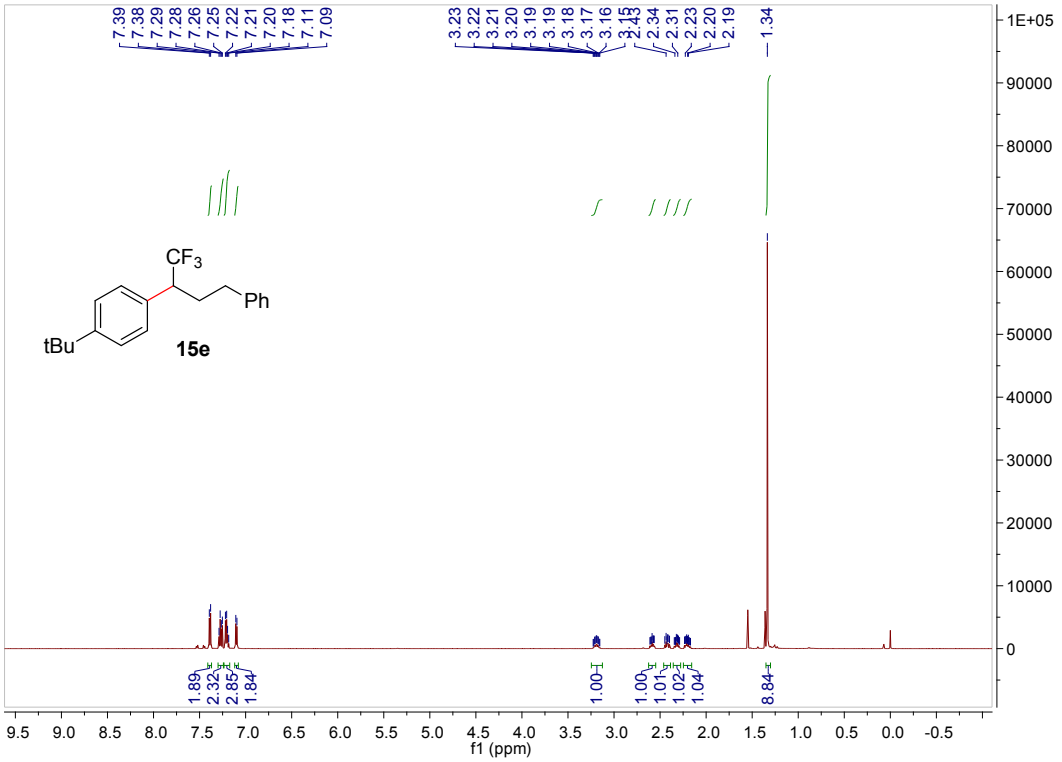


Figure S101. ^{1}H NMR of 15e in $CDCl_3$

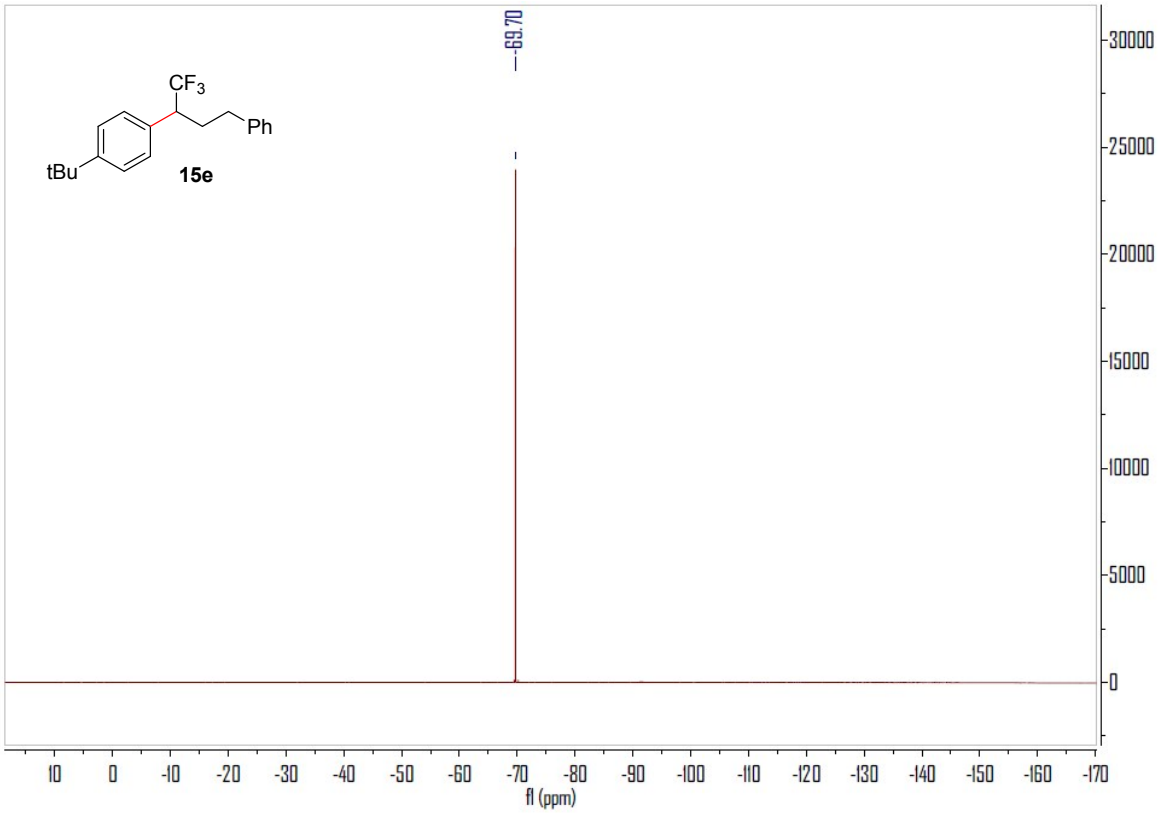


Figure S102. ^{19}F NMR of 15e in $CDCl_3$

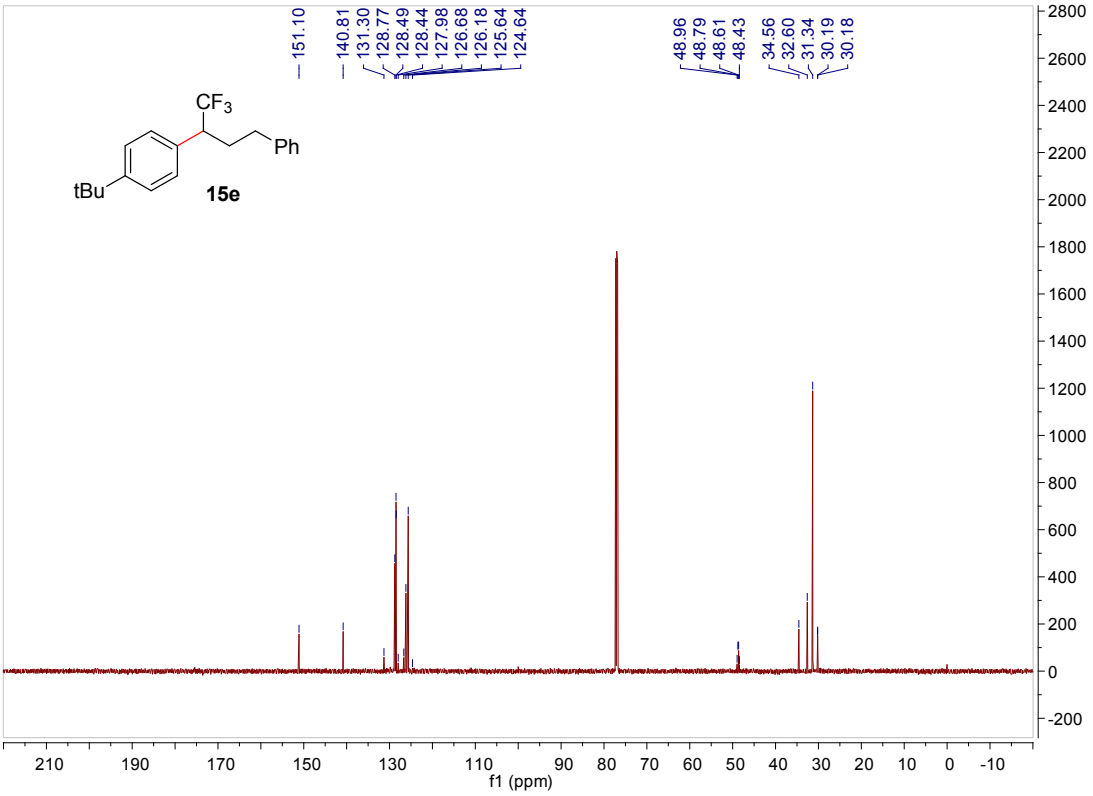


Figure S103. ^{13}C NMR of 15e in $CDCl_3$

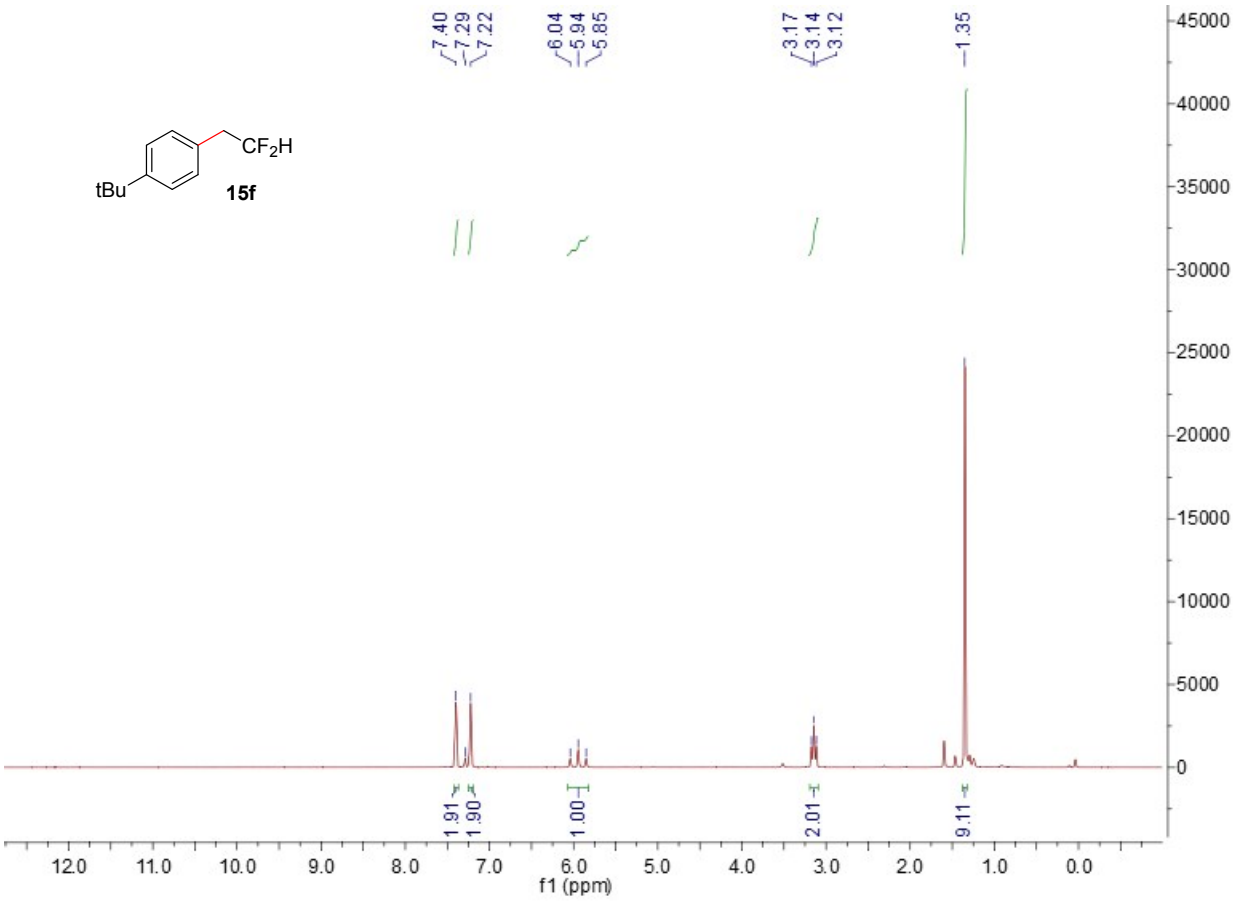


Figure S104. ^{1}H NMR of 15f in $CDCl_3$

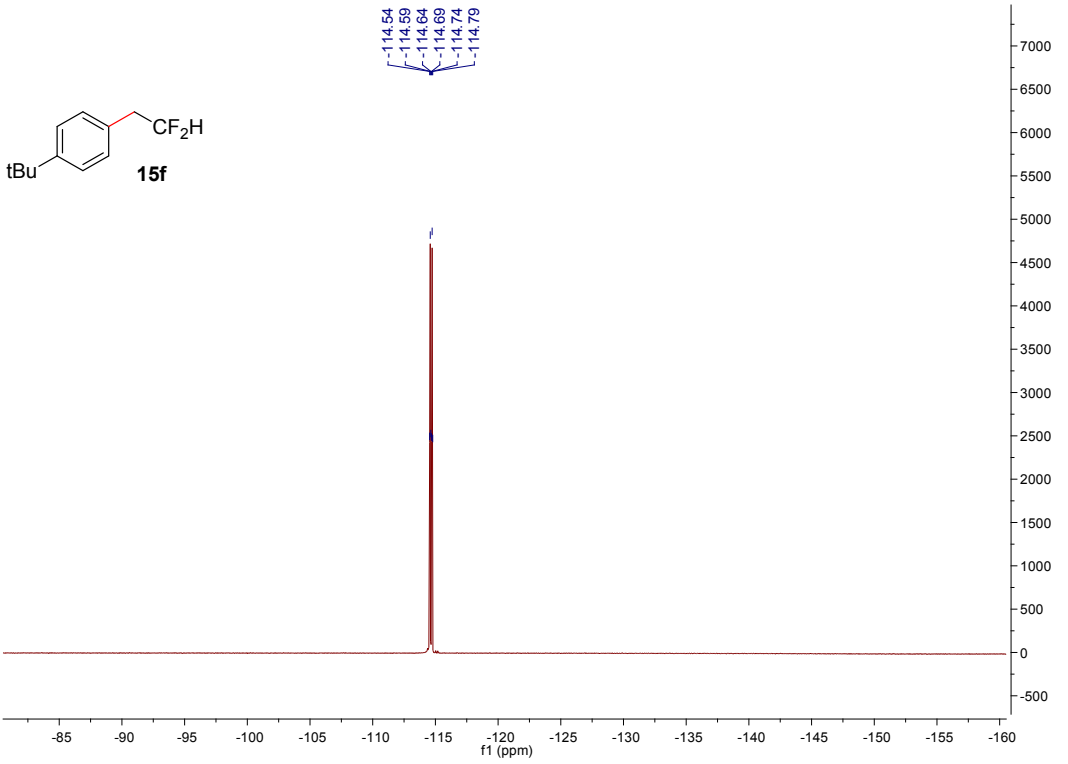


Figure S105. ^{19}F NMR of 15f in $CDCl_3$

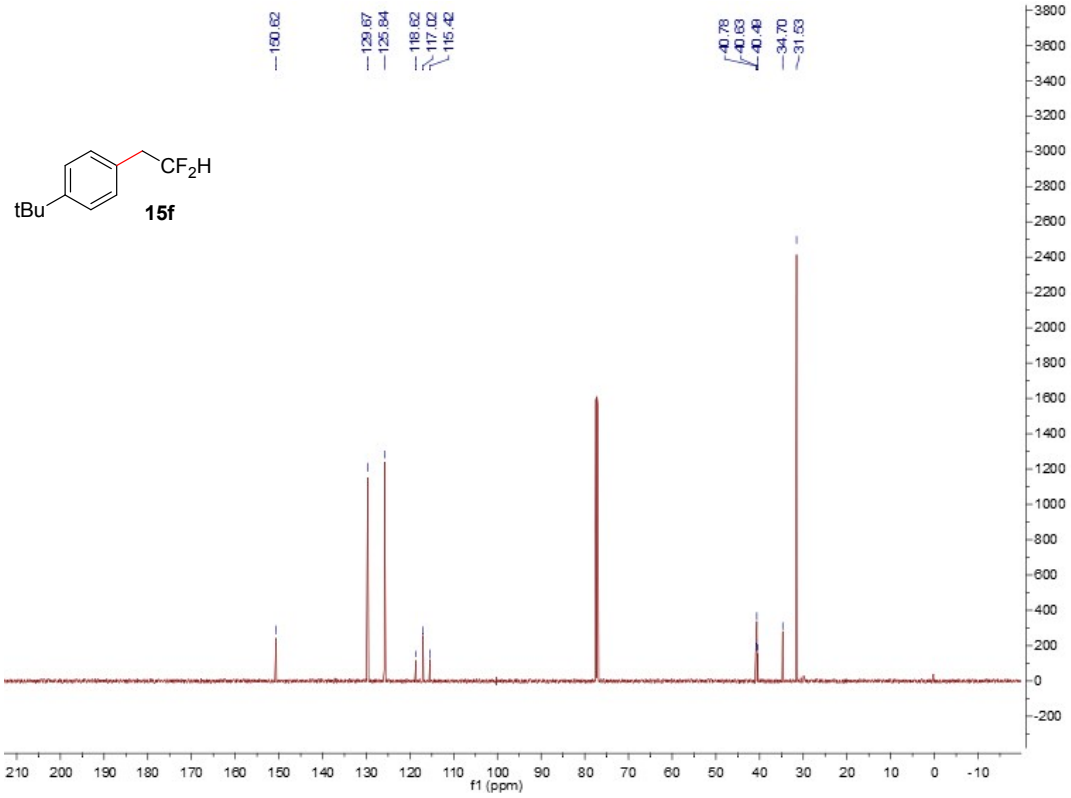


Figure S106. ^{13}C NMR of 15f in $CDCl_3$

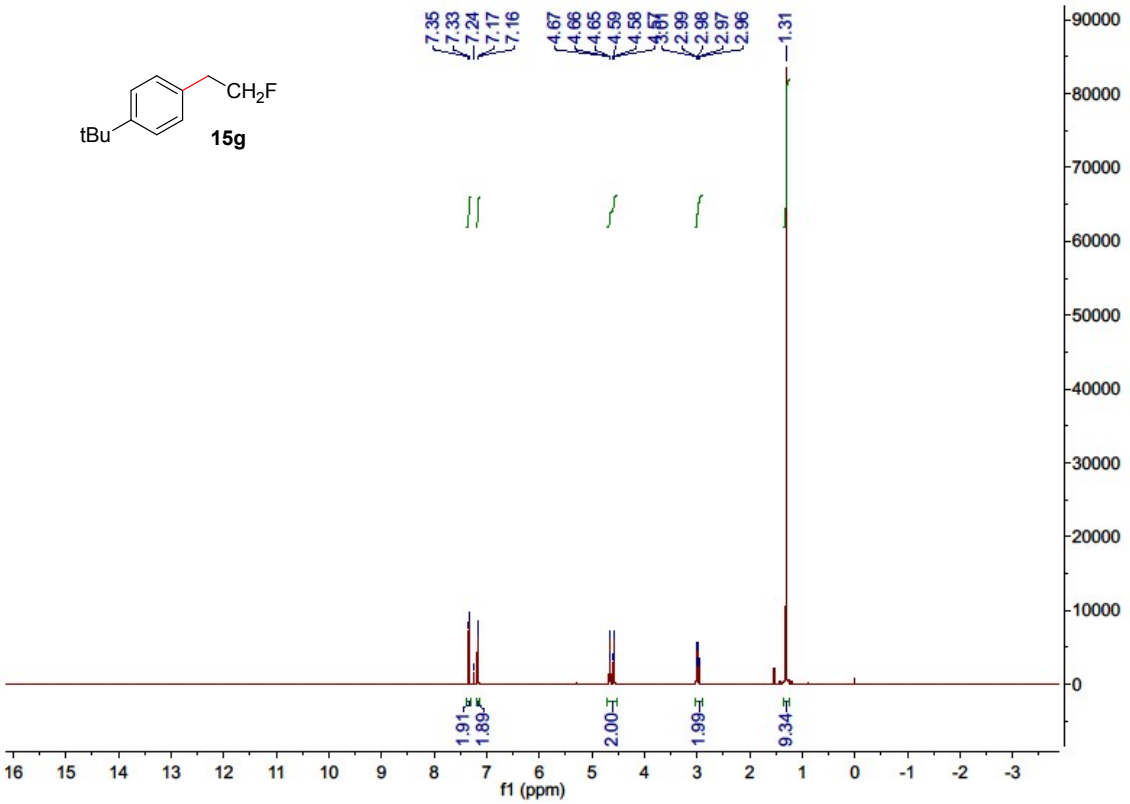


Figure S107. ^{1}H NMR of 15g in $CDCl_3$

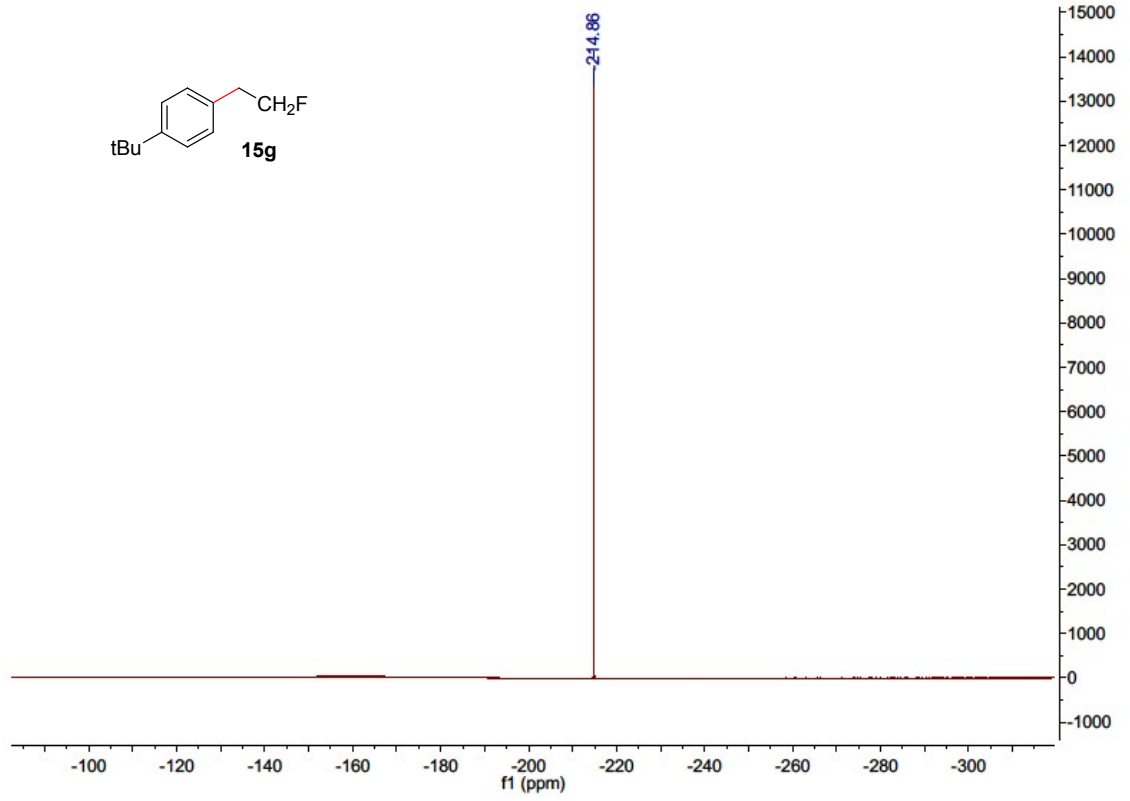


Figure S108. ^{19}F NMR of 15g in $CDCl_3$

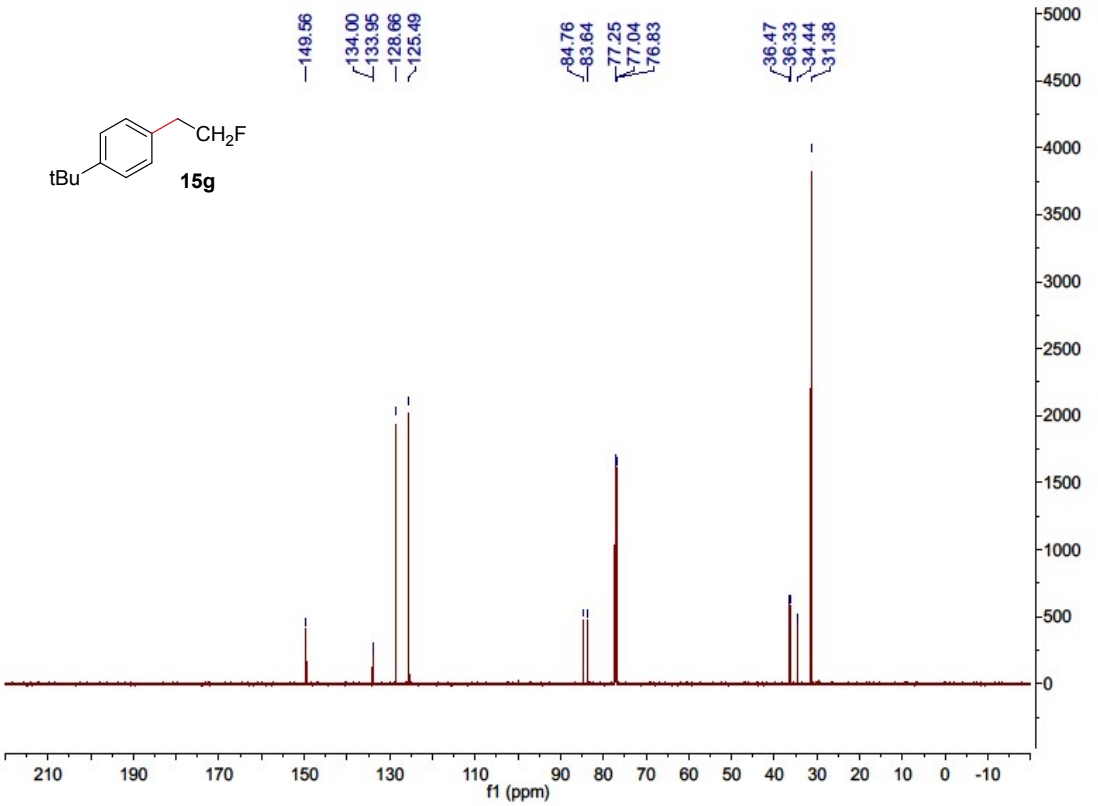


Figure S109. ^{13}C NMR of 15g in $CDCl_3$

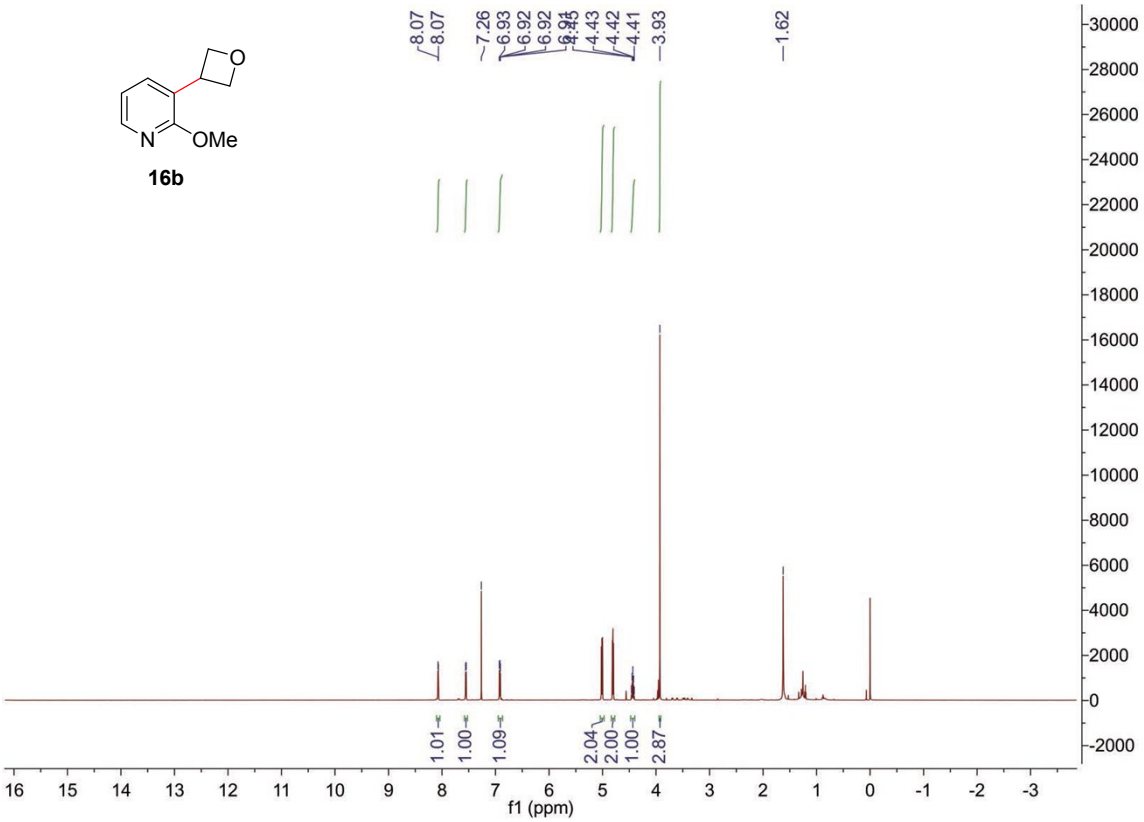


Figure S110. ^{1}H NMR of 16b in $CDCl_3$

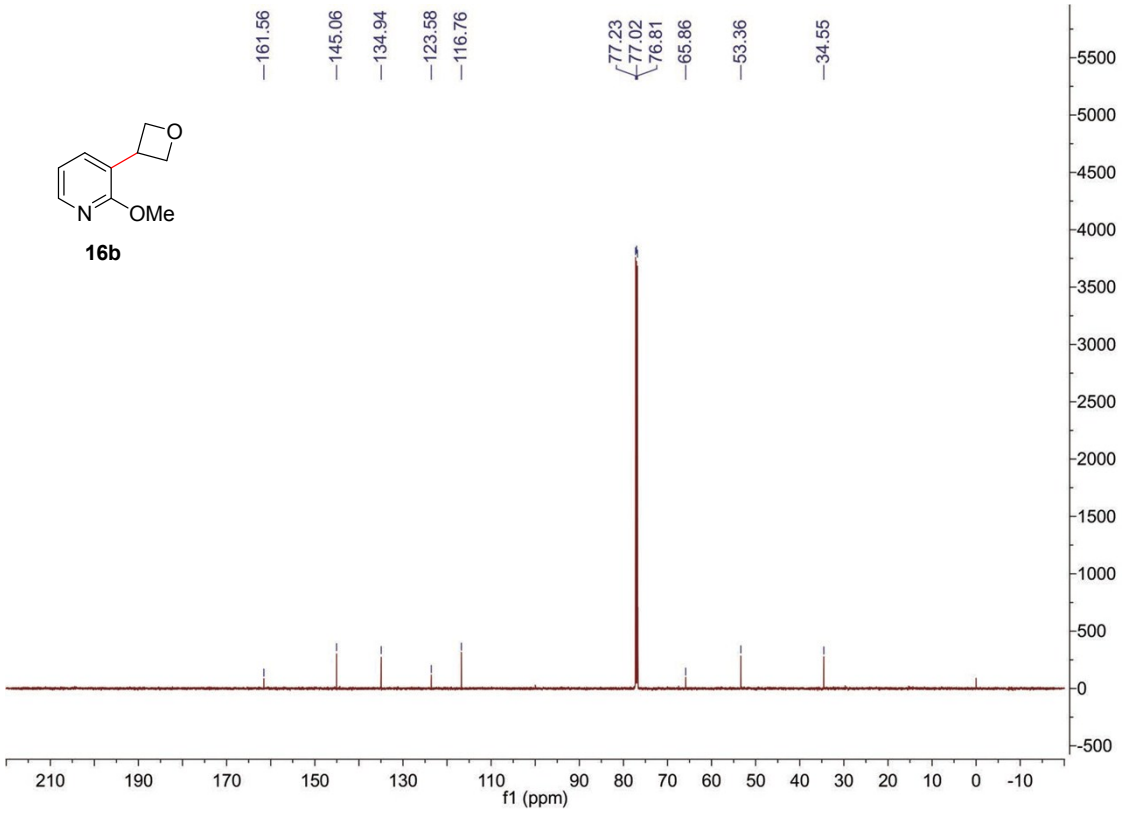


Figure S111. ^{13}C NMR of 16b in $CDCl_3$

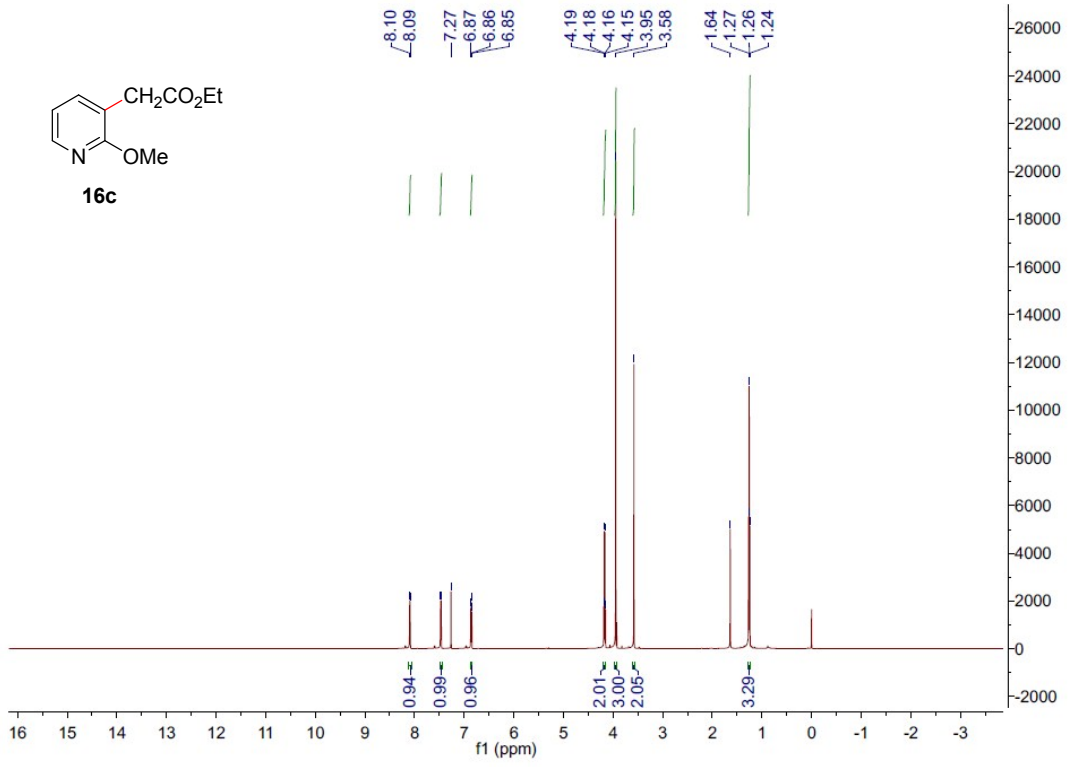


Figure S112. ^{1}H NMR of 16c in $CDCl_3$

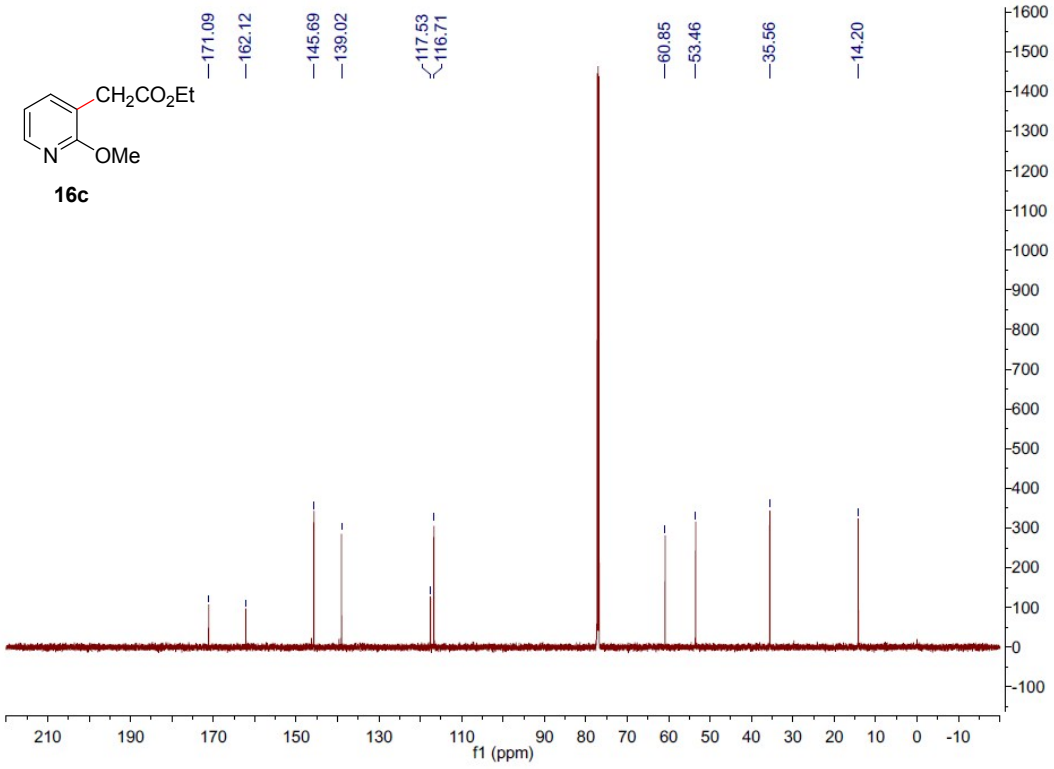


Figure S113. ^{13}C NMR of 16c in $CDCl_3$

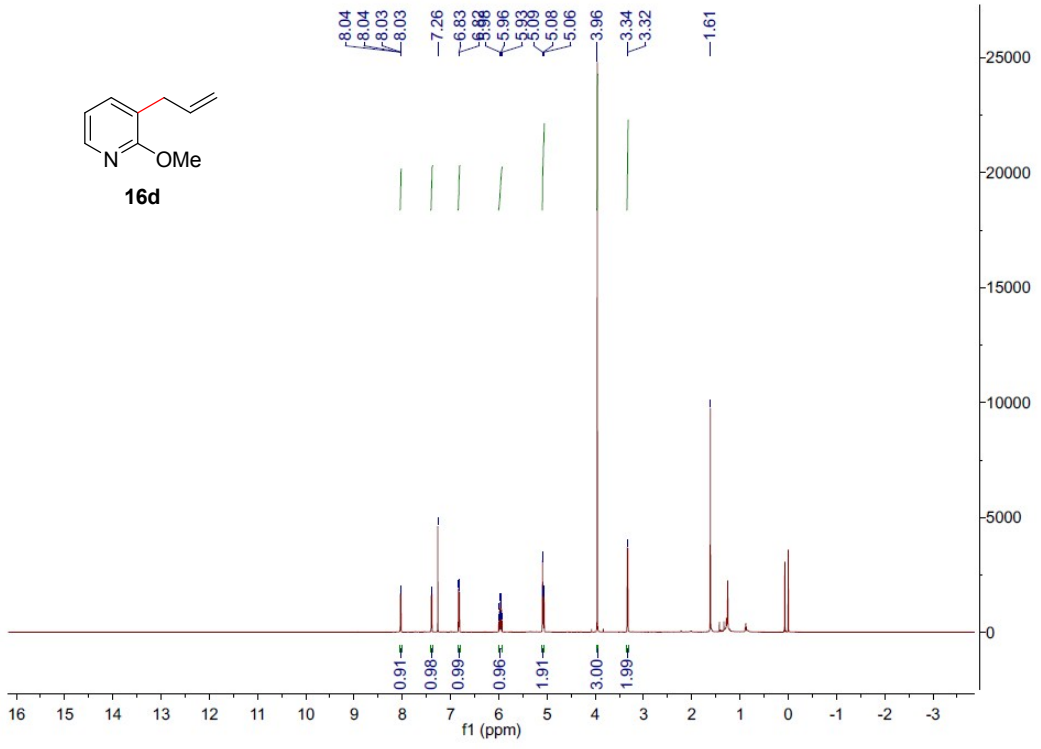


Figure S114. ^{1}H NMR of 16d in $CDCl_3$

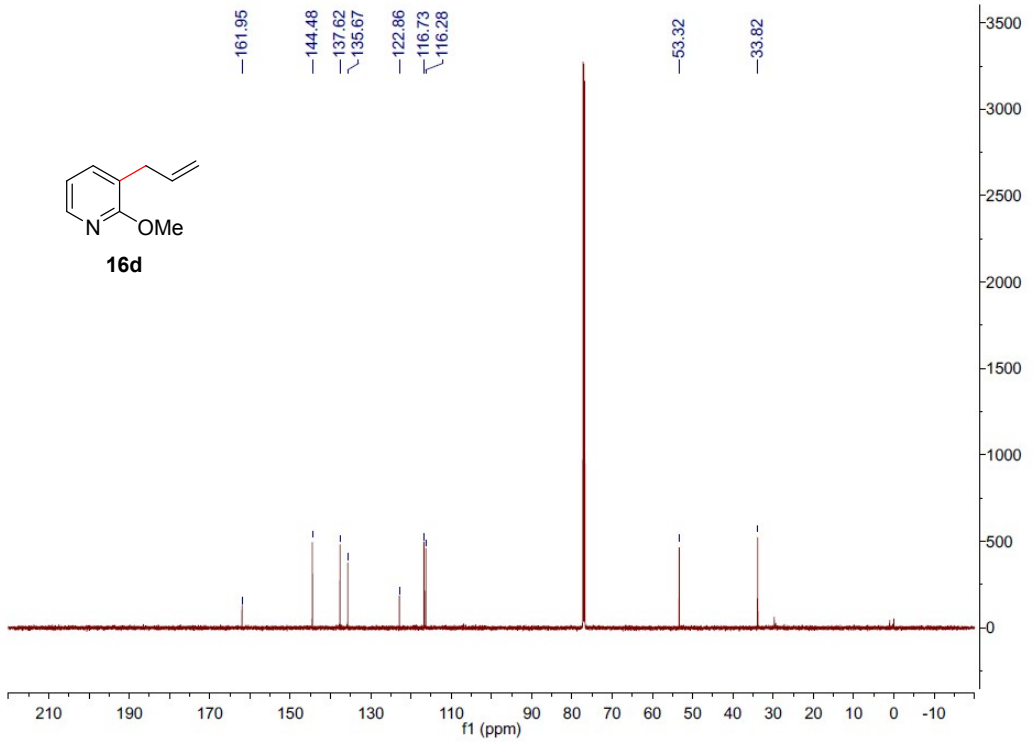


Figure S115. ^{13}C NMR of 16d in $CDCl_3$

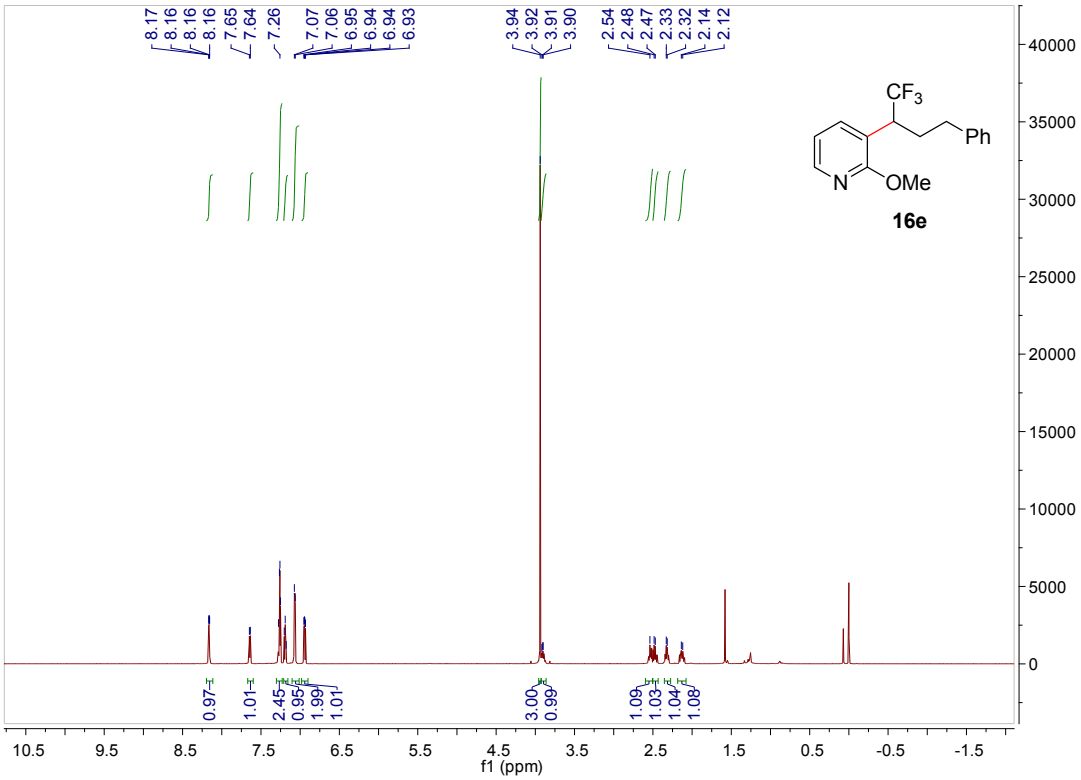


Figure S116. ^{1}H NMR of 16e in $CDCl_3$

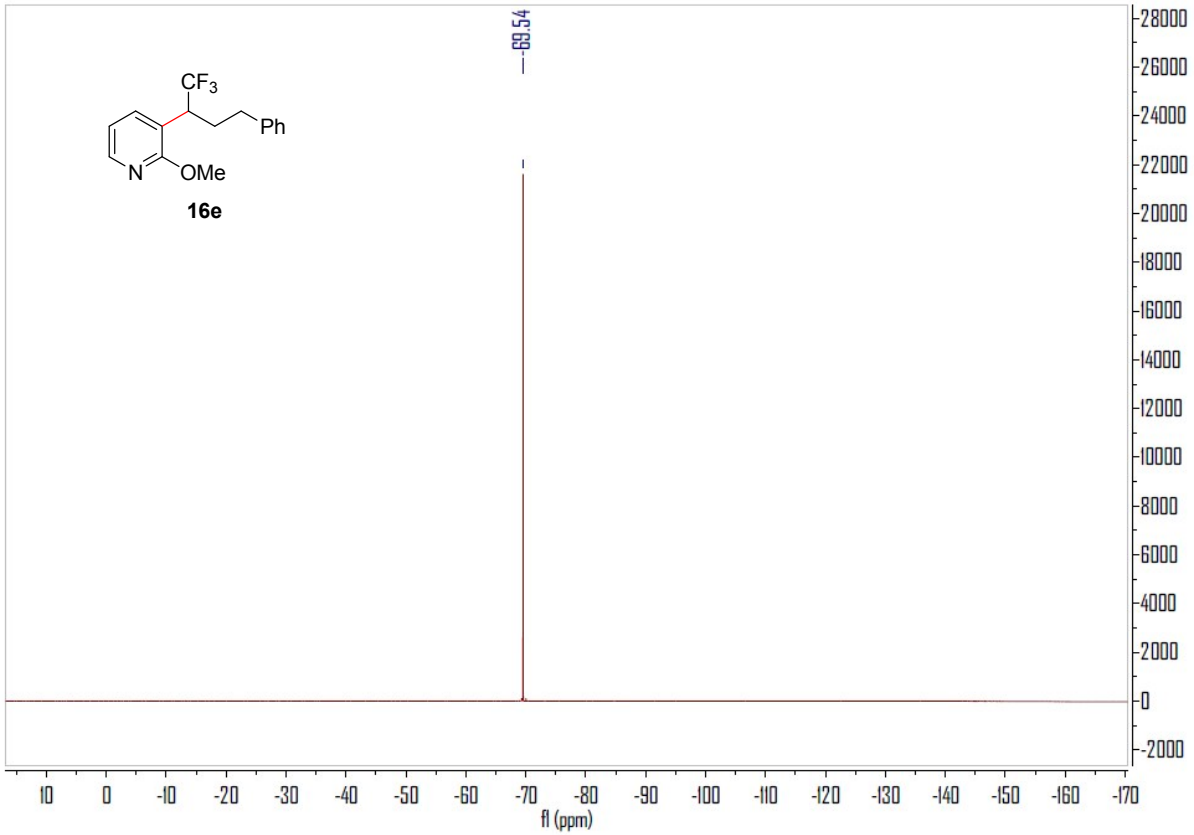


Figure S117. ^{19}F NMR of 16e in $CDCl_3$

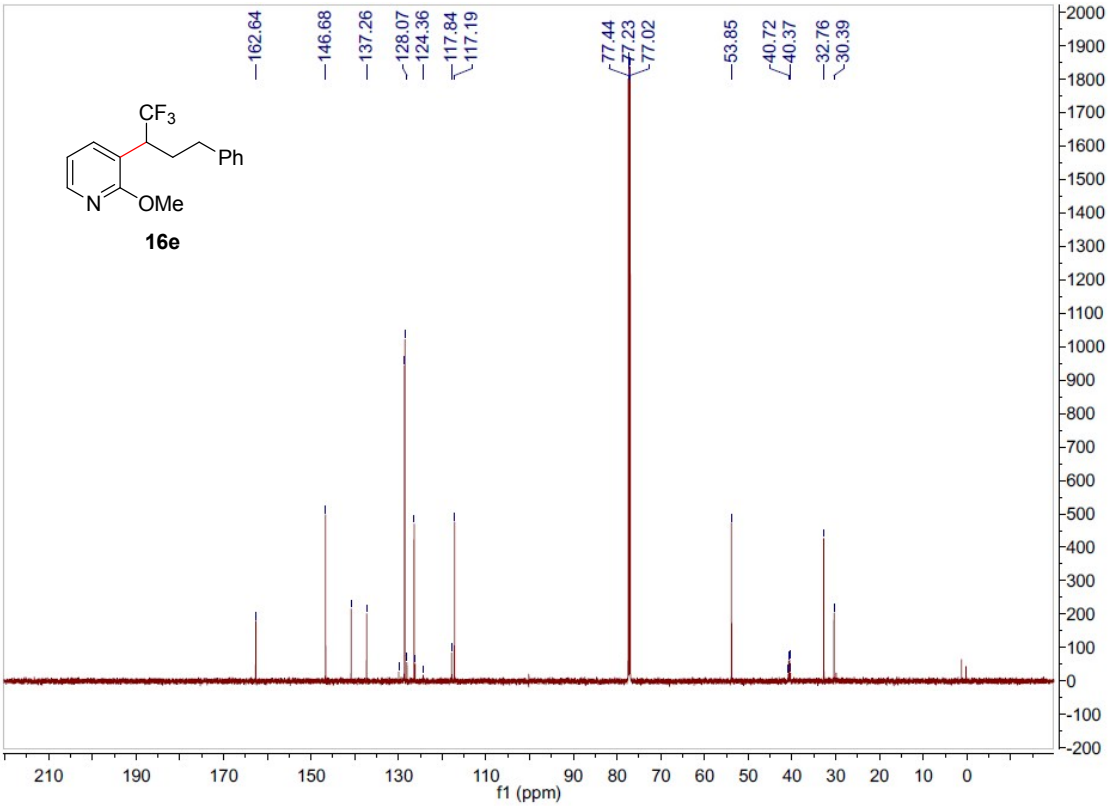


Figure S118. ^{13}C NMR of 16e in $CDCl_3$

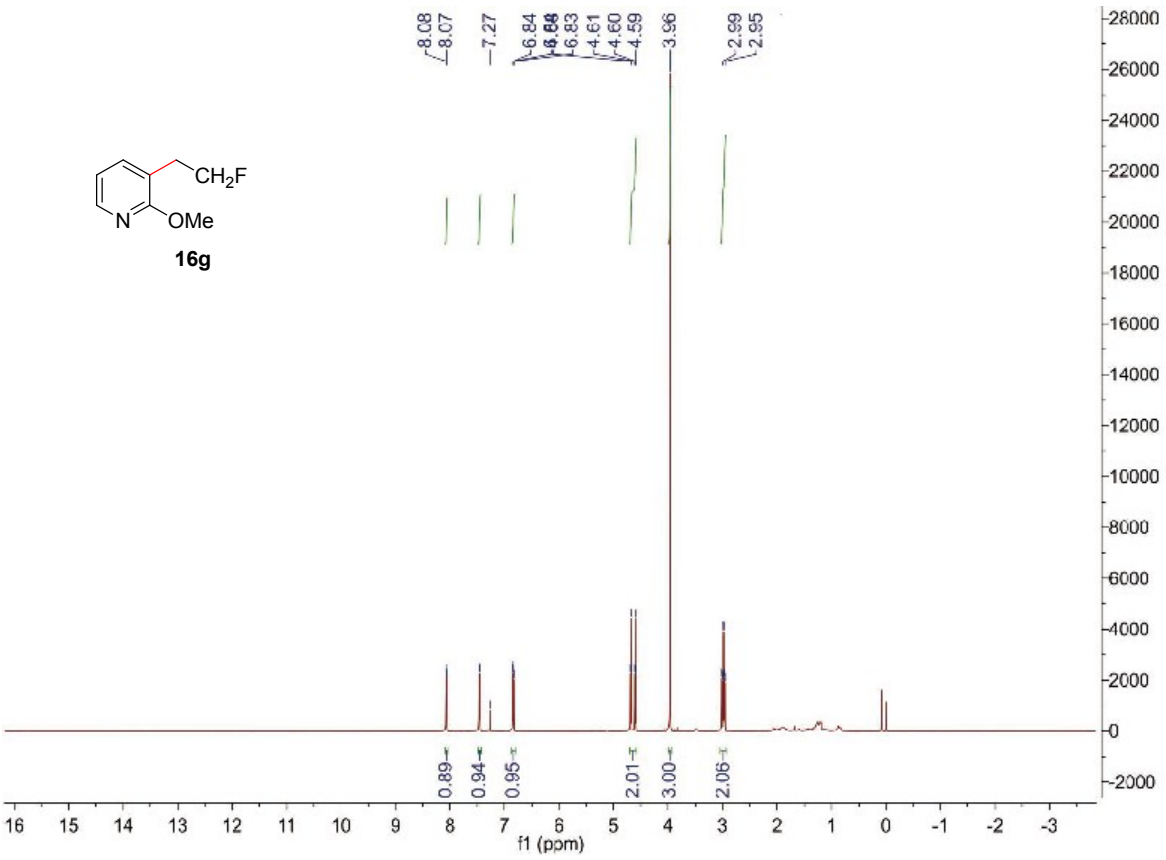


Figure S119. ^{1}H NMR of 16g in $CDCl_3$

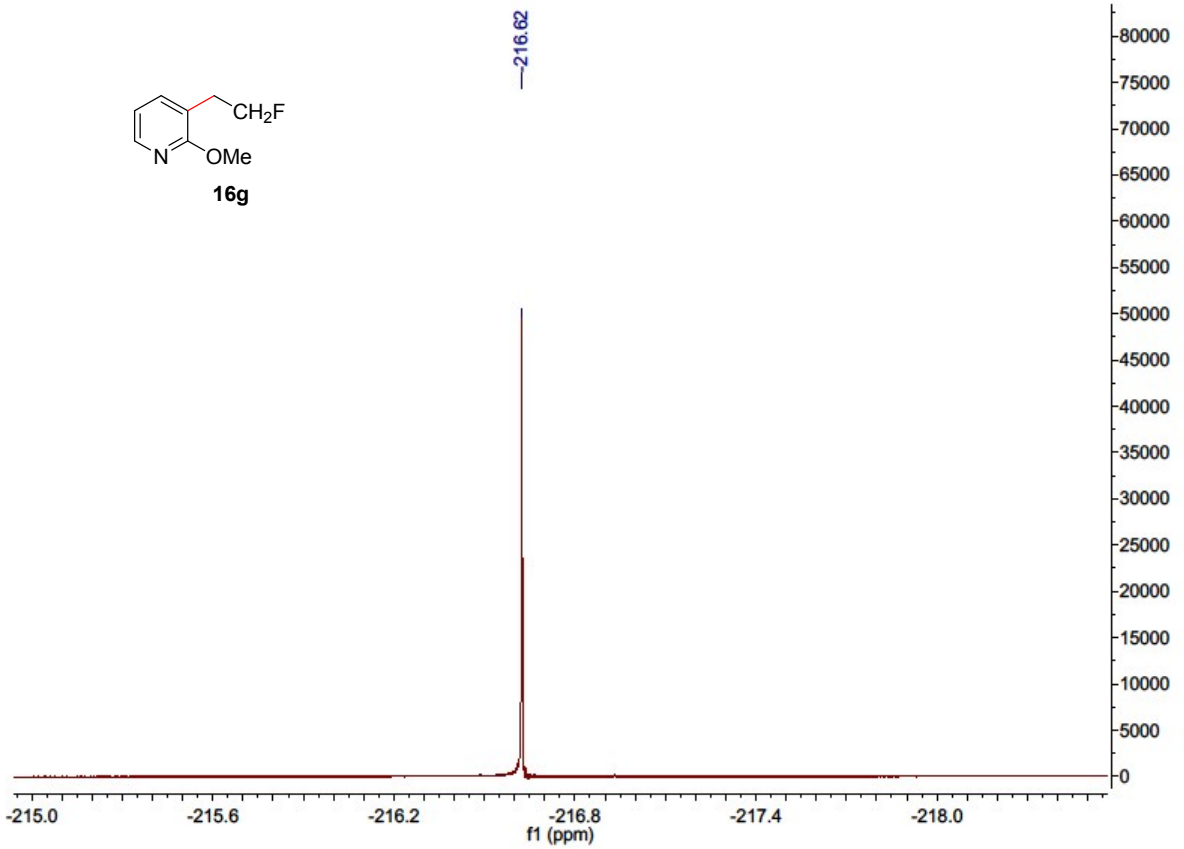


Figure S120. ^{19}F NMR of 16g in $CDCl_3$

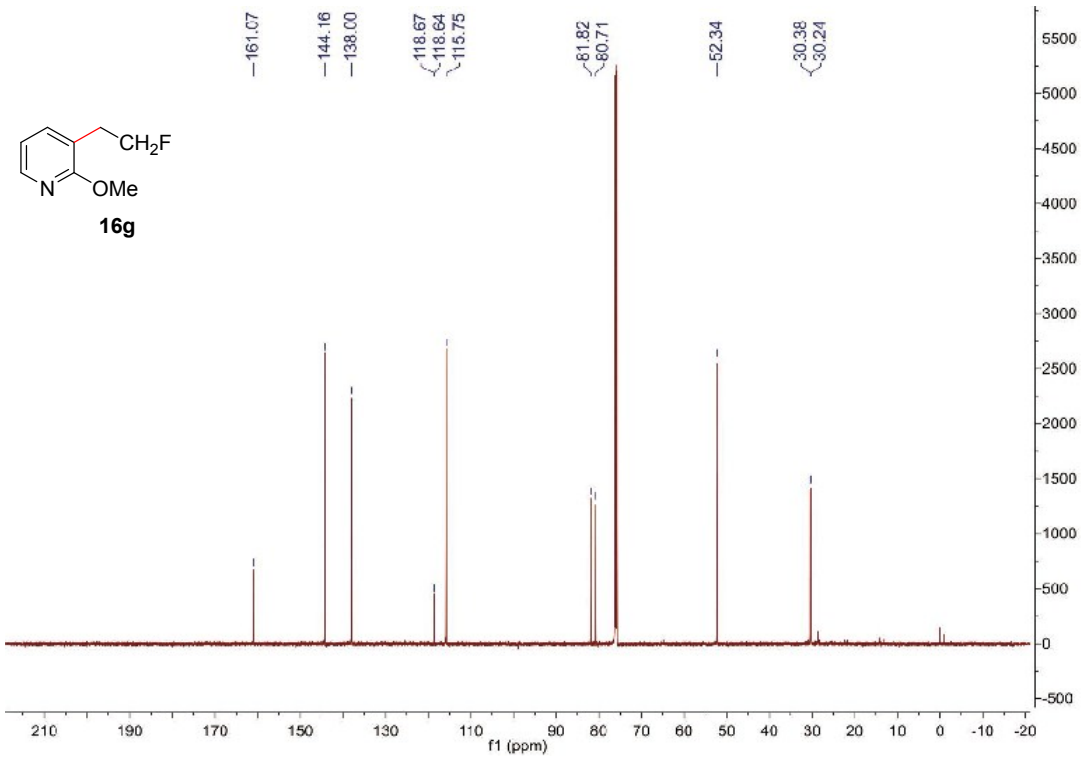


Figure S121. ^{13}C NMR of 16g in $CDCl_3$

VI. Control experiments for mechanistic studies

(a) Control experiments for identifying the roles of trifluoroethyl ligands in precatalyst 2

i) Continuous NMR monitoring of (bipy)Ni(CH_2CF_3)$_2$ upon heating

$$\underset{\mathbf{2}}{(bipy)Ni(CH_2CF_3)_2} \xrightarrow[heat]{d^6\text{-DMSO}} \underset{\mathbf{2a}}{(bipy)Ni(F)(CH_2CF_3)} + CH_2{=}CF_2$$

The precatalyst (bipy)Ni(CH_2CF_3)$_2$ **2** (4.6 mg) was dissolved in d^6-DMSO (0.5 mL) with addition of $PhCF_3$ (3.0 μL) as internal standard which was loaded into a J. Young NMR tube. The solution was heated at the indicated temperature for fixed time and then recorded by a 400M NMR instrument. It was found that the decomposition of **2** started at a slight heating (approximately 40-50 ^oC) for an evolvement of $CH_2{=}CF_2$. When the temperature was elevated further to 60-80 ^oC, fast extrusion of $CH_2{=}CF_2$ from **2** was observed. Attempts to fingerprint the transient [(bipy)Ni(F)(CH_2CF_3)] **2a** via NMR were unsuccessful which might be attributed to the mentioned redistribution reaction to afford [(bipy)Ni(CH_2CF_3)$_2$].

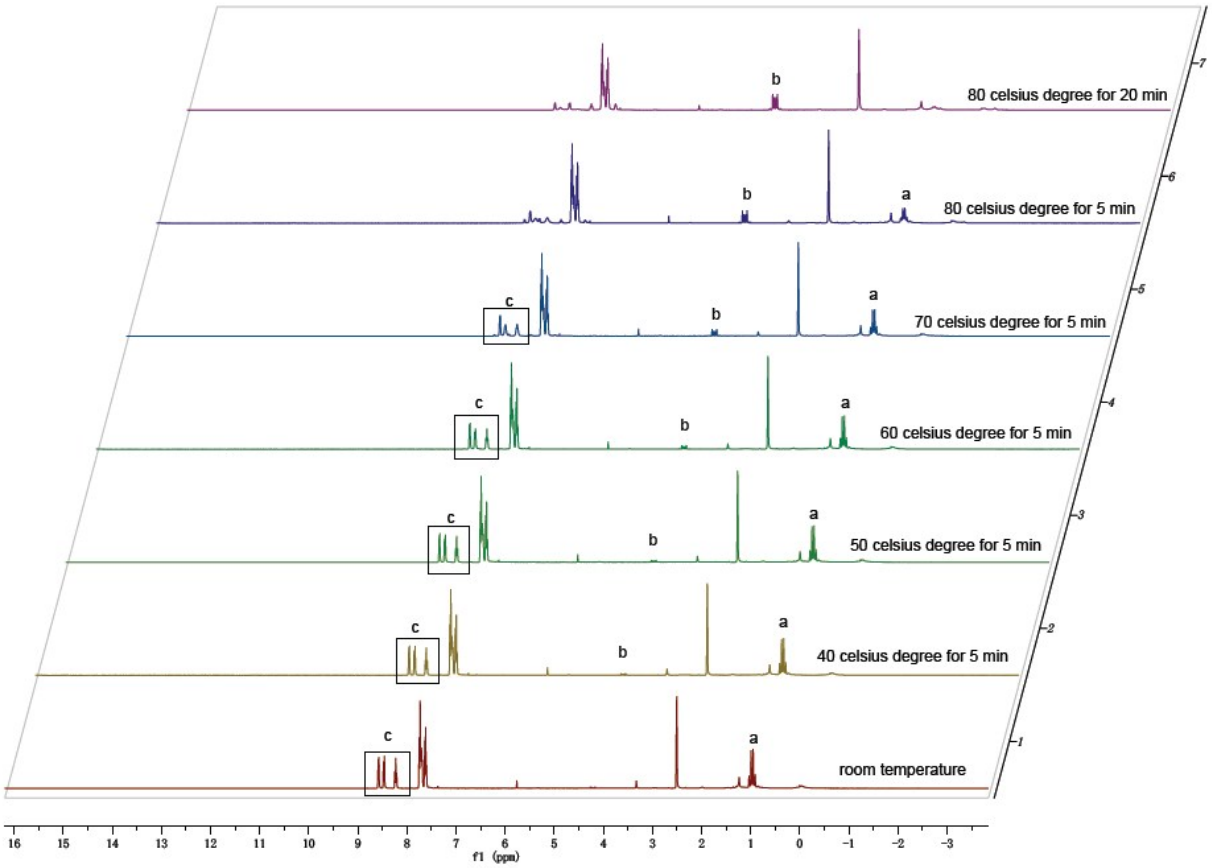


Figure S122. ^{1}H NMR spectrums of precatalyst 2 in a variable temperature experiment

[a]methylene peaks of precatalyst **2**; [b]CH_2=CF_2 gas peaks; [c]bipy peaks of precatalyst **2**.

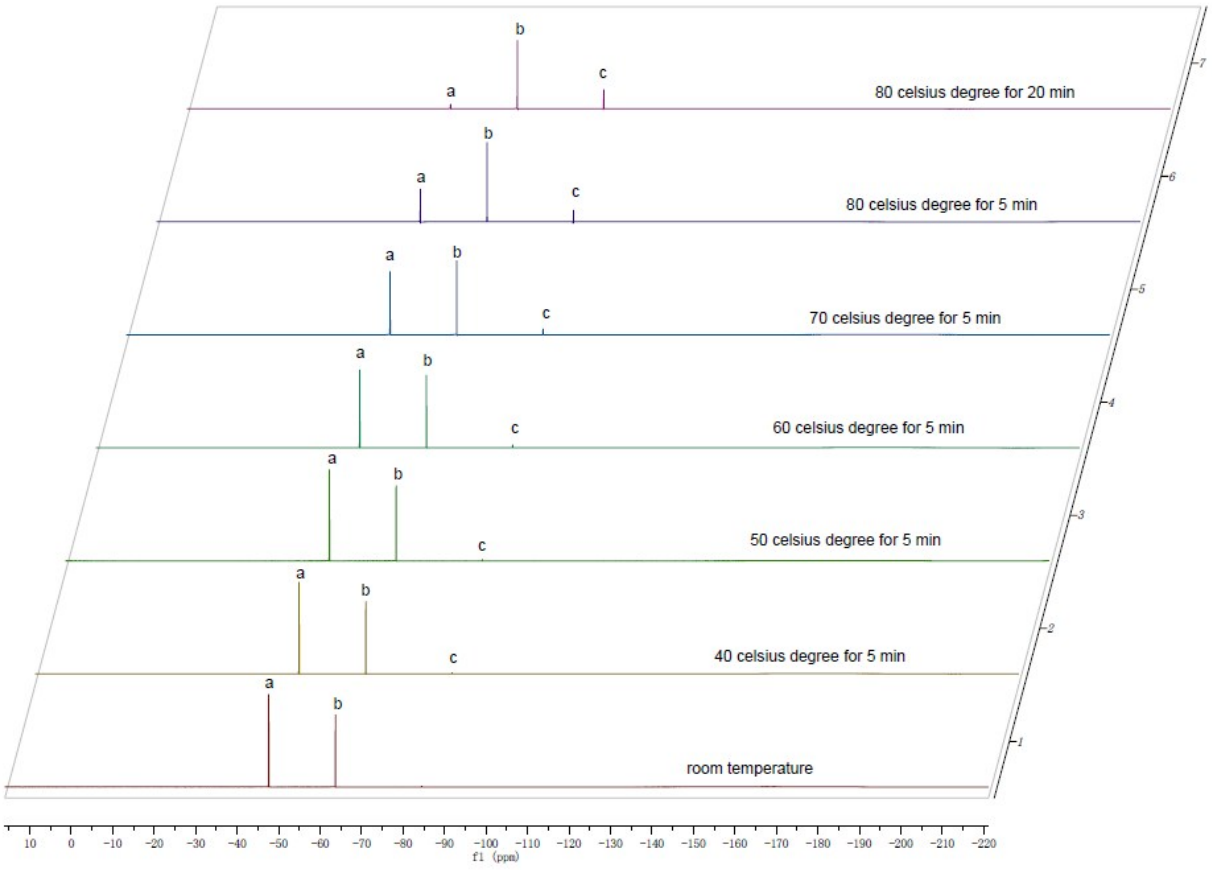
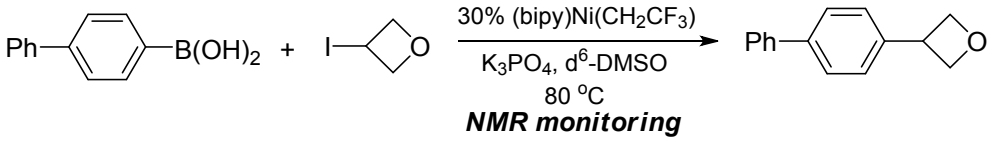


Figure S123. ^{19}F NMR spectrums of precatalyst 2 in a variable temperature experiment

[a]trifluoromethyl peak of precatalyst **2**; [b]trifluorotoluene (internal standard); [c]CH_2=CF_2 gas peaks.

ii) NMR experiments for identifying the role of trifluoroethyl groups bound to nickel



4-biphenylboronic acid (0.075 mmol, 1.5 equiv), K_3PO_4 (0.10 mmol, 3.0 equiv), followed by a solution of 3-iodooxetane (0.05 mmol, 1.0 equiv) and $PhCF_3$ (0.05 mmol, internal standard for ^{19}F NMR) in the d^6-DMSO solvent (0.5 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (30.0 mol%) in the d^6-DMSO solvent (0.5 mL) was added dropwise into the reaction system subsequently (*increasing the catalyst loading for clear identification of the reaction initiation*). The Schlenck tube was screw capped and put into a preheated oil bath (80 ^{o}C). After stirring for the indicated time, the reaction mixture was cooled to room temperature and recorded by ^{1}H and ^{19}F NMR. The result indicated the gradual consumption of 3-iodooxetane, the formation of product **9b** as well as the extrusion of CH_2=CF_2 from precatalyst **2**.

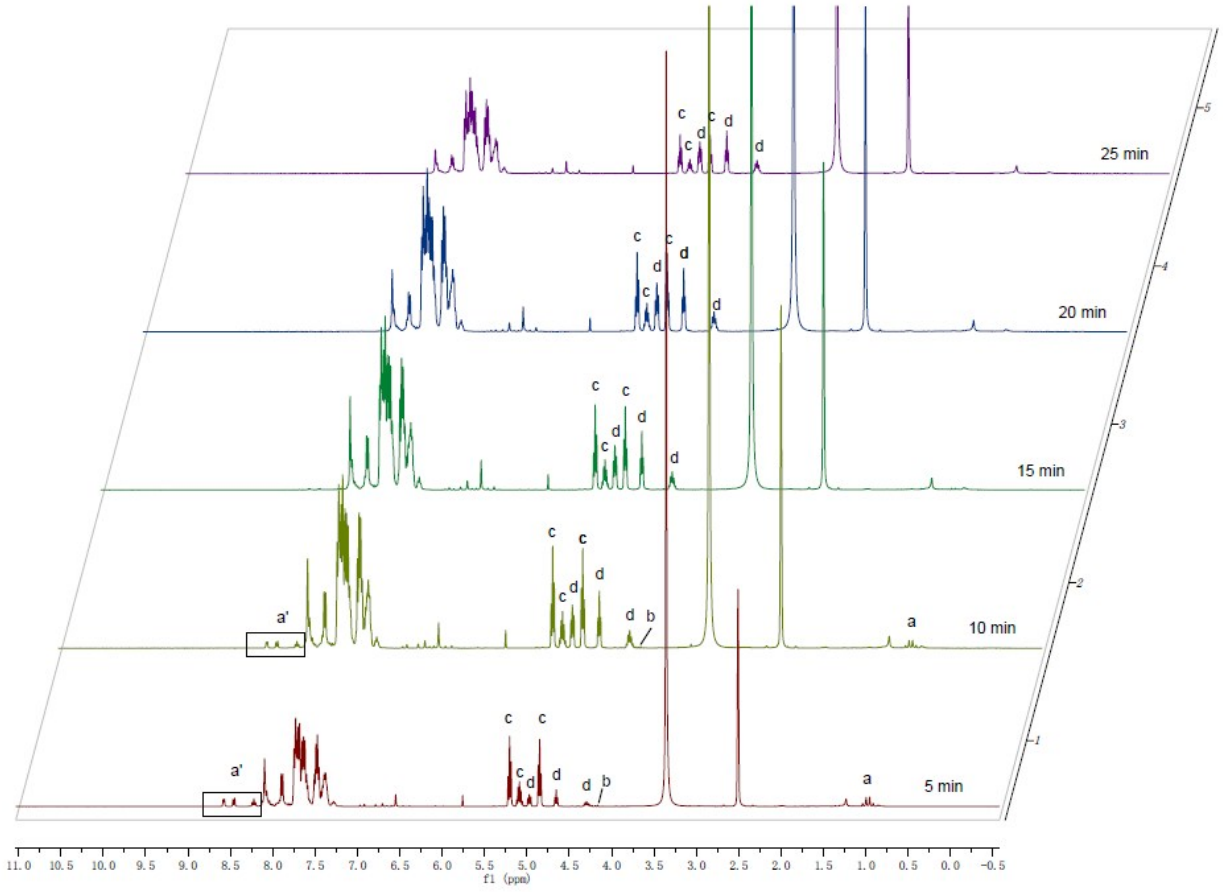


Figure S124. ^{1}H NMR monitoring of the synthetic reaction of product 14b

[a]methylene peaks of precatalyst **2**; [a']bipy peaks of precatalyst **2**; [b]CH_2=CF_2 gas peaks; [c]3-iodooxetane; [d]product **14b**

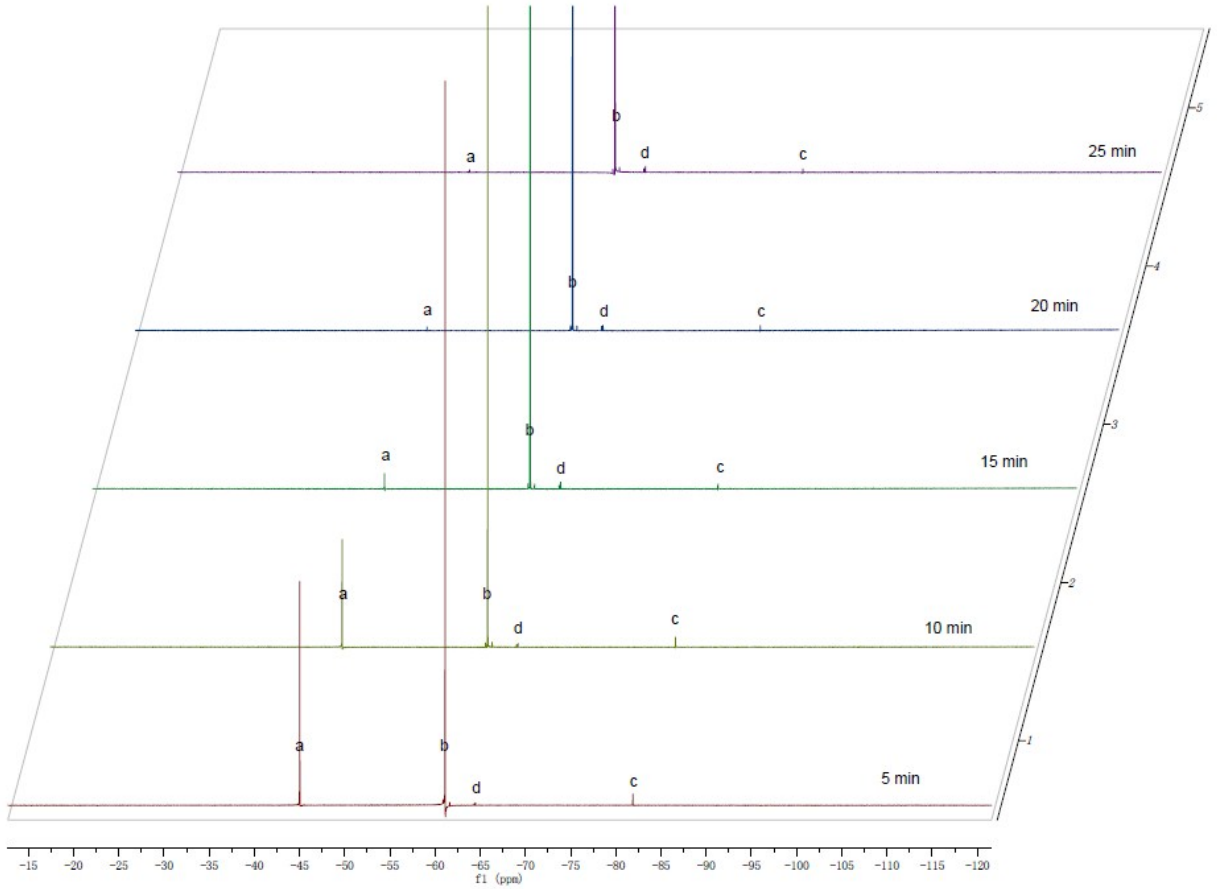
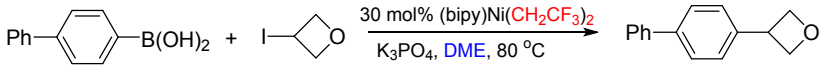


Figure S125. ^{19}F NMR monitoring of the synthetic reaction of product 14b

[a]trifluoromethyl peak of precatalyst **2**; [b]trifluorotoluene (internal standard); [c]CH_2=CF_2 gas peaks; [d]Ar-CH_2CF_3 **7a** (produced from the retained CF_3CH_2 group during the initiation step of catalytic cycle).

(iii) GC-MS analysis for identifying the role of trifluoroethyl groups bound to nickel



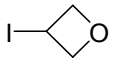
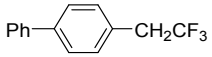
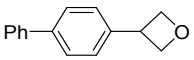
65% isolated yield

GC-MS identified products:		(Ar= 4-biphenyl)
CH_2=CF_2	Ar—CH_2CF_3	$CH_3OCH(Ar)CH_2OCH_3$
detected in the reaction system (proof for eliminative extrusion)	isolated yield 11%	or its regioisomer noticeble formation
m/z 64	*m/z* 236	*m/z* 242

4-biphenylboronic acid (0.3 mmol, 1.5 equiv), K_3PO_4 (0.6 mmol, 3.0 equiv), followed by a solution of 3-iodooxetane (0.2 mmol, 1.0 equiv) in the DME solvent (0.5 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (30.0 mol%) in the DME solvent (0.5 mL) was added dropwise into the reaction system subsequently (increasing the catalyst loading for clear identification of the reaction initiation). The Schlenck tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 24 h, the reaction mixture was cooled to room

temperature and poured into a saturated aqueous ammonium chloride solution (10.0 mL). The aqueous phase was extracted with ether three times (10.0 mL×3). The combined organic phase was analyzed by GC-MS with the *p*-xylene internal standard. The organic phase was condensed in *vacuo* to remove solvent, and the residue was purified by flash chromatography on preparative TLC to fingerprint the $ArCH_2CF_3$ mark **7a** (11% yield) and obtain the desired product **14b** (65% yield).

Table S5. GC-MS analysis for probing roles of trifluoroethyl groups bound to nickel

Retention time/minute	Detected species	Area%
1.62	$F_2C{=}CH_2$	Trace[a]
8.56		3.30
12.98	Biphenyl	13.50
13.44	Bipyridine	5.77
13.80		2.38
17.37	$CH_3OCH(Ar)CH_2OCH_3$	1.16
18.18 (desired product)		12.92

[a]$F_2C{=}CH_2$ was detected in trace amount in GC-MS due to the volatility of its gaseous properties. It could be observed clearly in ^{19}F NMR (Figure S104).

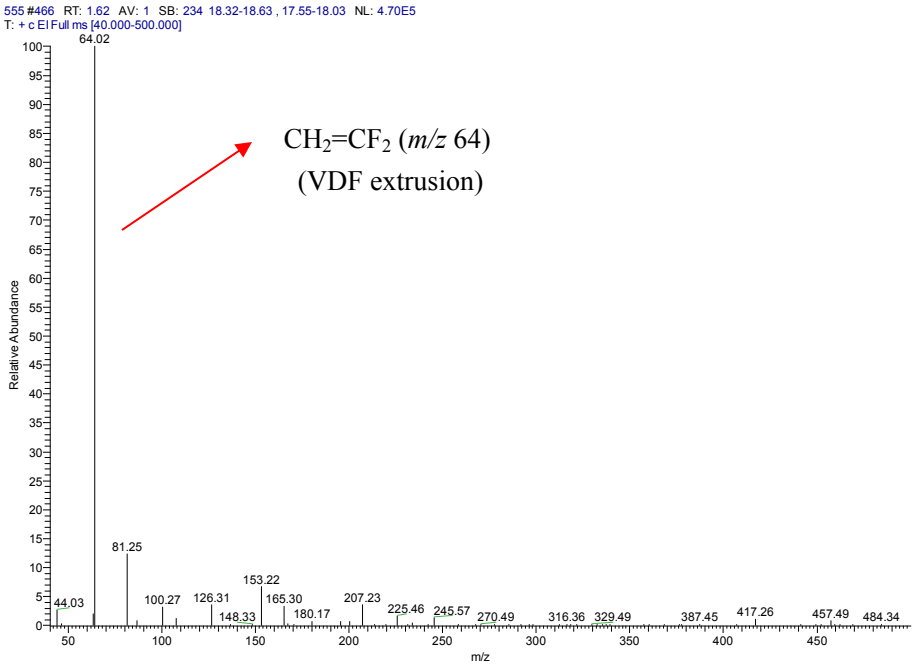
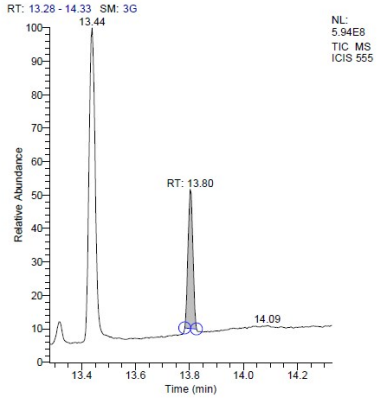
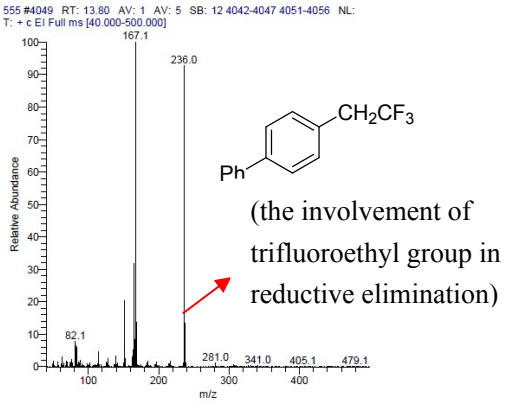


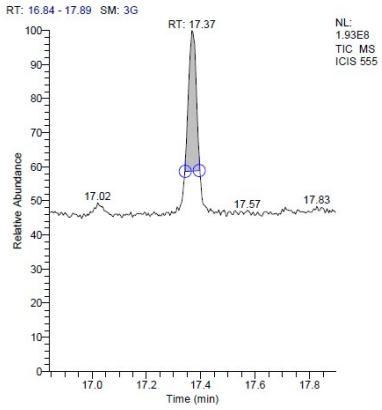
Figure S126. Detection of $CH_2{=}CF_2$ by GC-MS

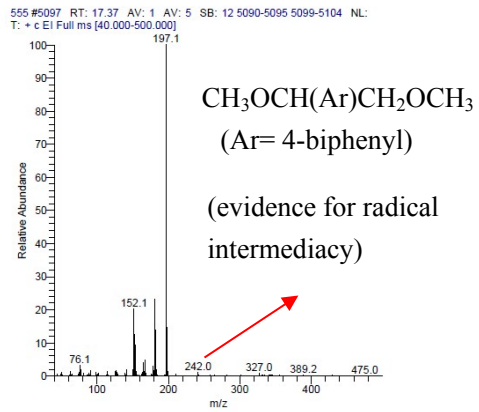




RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
13.80	77	787	56.14	C14H11F3	34239-04	4-Trifluoromethyldiphenylmethane	2.38
	7				-8		

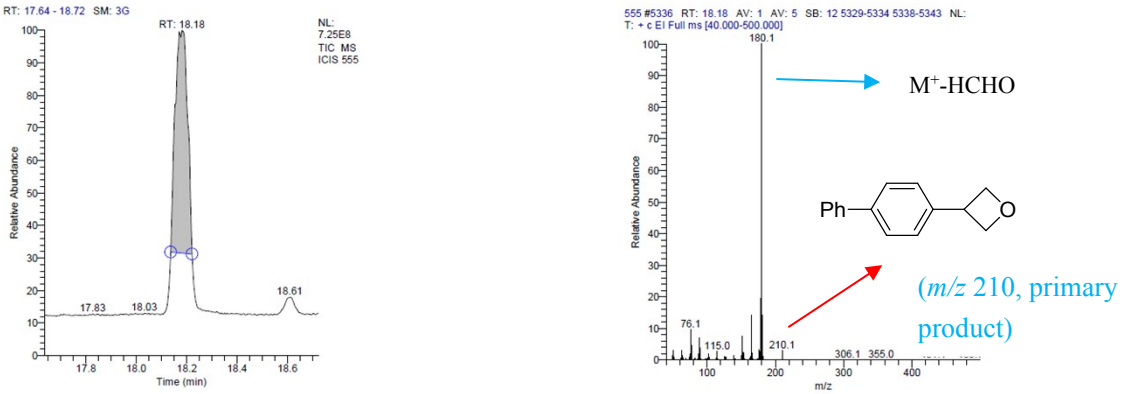
Figure S127. Detection of the Ar-CH_2CF_3 mark by GC-MS





RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
17.37	72	734	18.90	C14H15N	22750-87	2,3-Dimethyl-4-biphenylamine	1.16
	1				-4		

Figure S128. Detection of $CH_3OCH(Ar)CH_2OCH_3$ by GC-MS



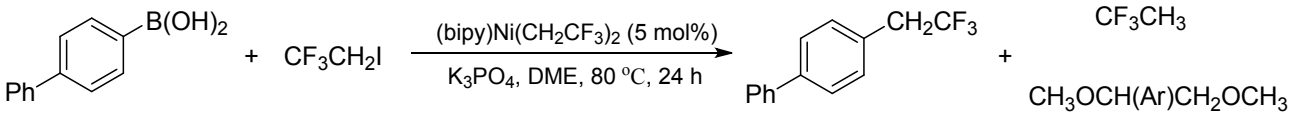
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
18.18	91 9	929	59.35	C14H12	2350-89-2	1,1'-Biphenyl, 4-ethenyl-	12.92

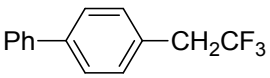
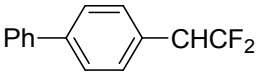
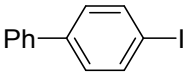
Figure S129. Detection of the product 14b by GC-MS

(b) Evidences for solvent-caged radical reactions

i) Detection of CF_3CH_3 (CF_3CH_2 radical abstracts ethereal α-hydrogen) and $CH_3OCH(Ar)$ CH_2OCH_3 to support the DME solvent-caged reactions

Table S6. GC-MS analysis of the coupling between CF_3CH_2I and 4-biphenylboronic acid



Retention time/minute	Detected species	Area%
1.64	**CF_3CH_3**	Trace[a]
12.98	Ph-Ph	8.42
13.44	Bipy	5.02
13.81		17.38
14.26		0.50
16.33		6.94
17.37	**$CH_3OCH(Ar)CH_2OCH_3$**	9.79

[a]CF_3CH_3 was detected in trace amount in GC-MS due to the volatility of its gaseous properties.

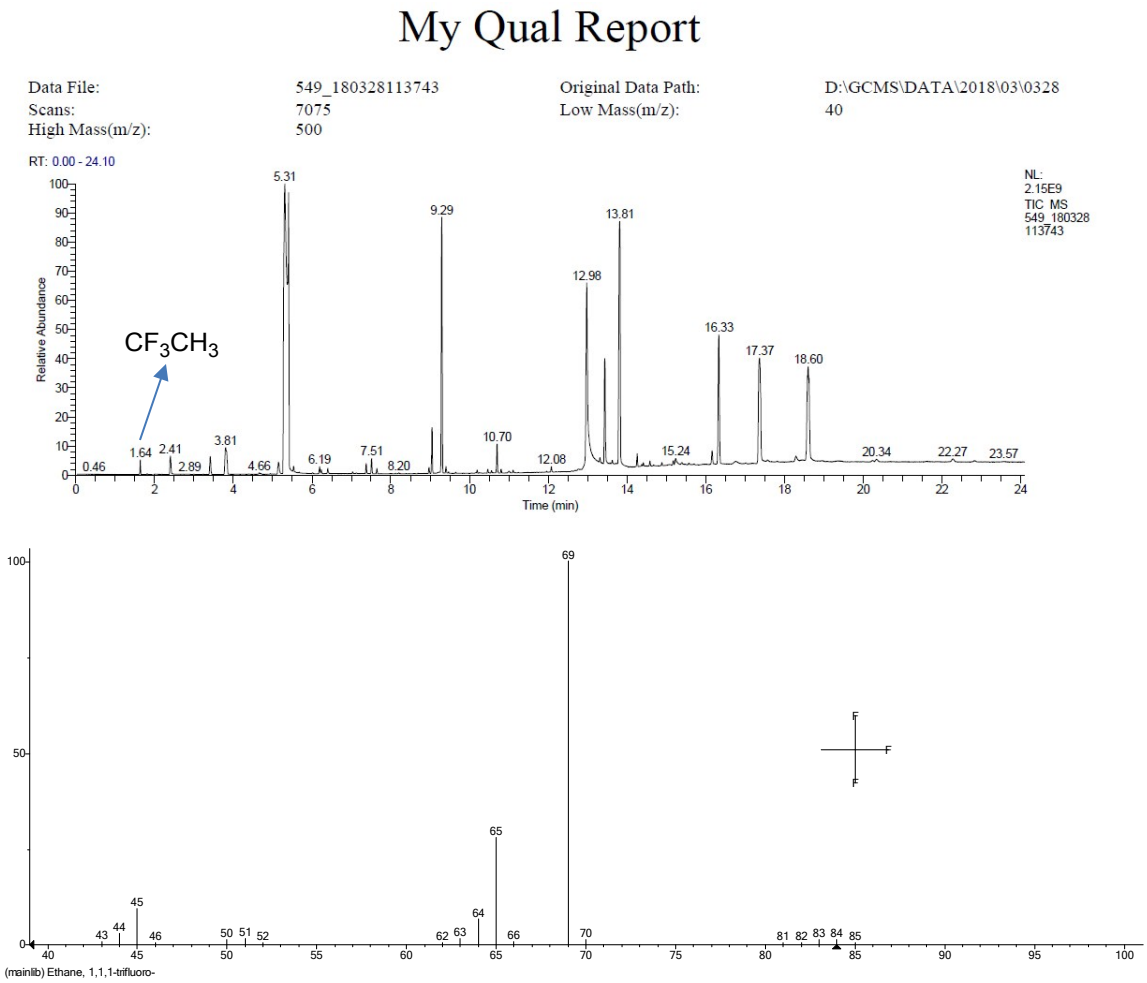
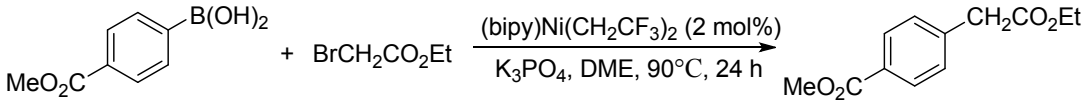
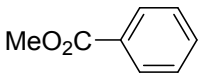
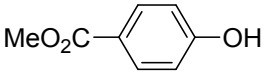
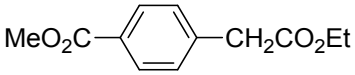


Figure S130. Detection CF_3CH_3 by GC-MS (CF_3CH_2 radical abstracts ethereal α-hydrogen)

ii) Detection of EtOAc ($EtOOCCH_2$ radical abstracts ethereal α-hydrogen) to support the DME solvent-caged reactions

Table S7. GC-MS analysis of the coupling between $BrCH_2CO_2Et$ and 4-biphenylboronic acid



Retention time/minute	Detected species	Area%
4.65	**CH_3COOEt**	1.76
10.55		6.36
13.22		0.41
14.83		11.78

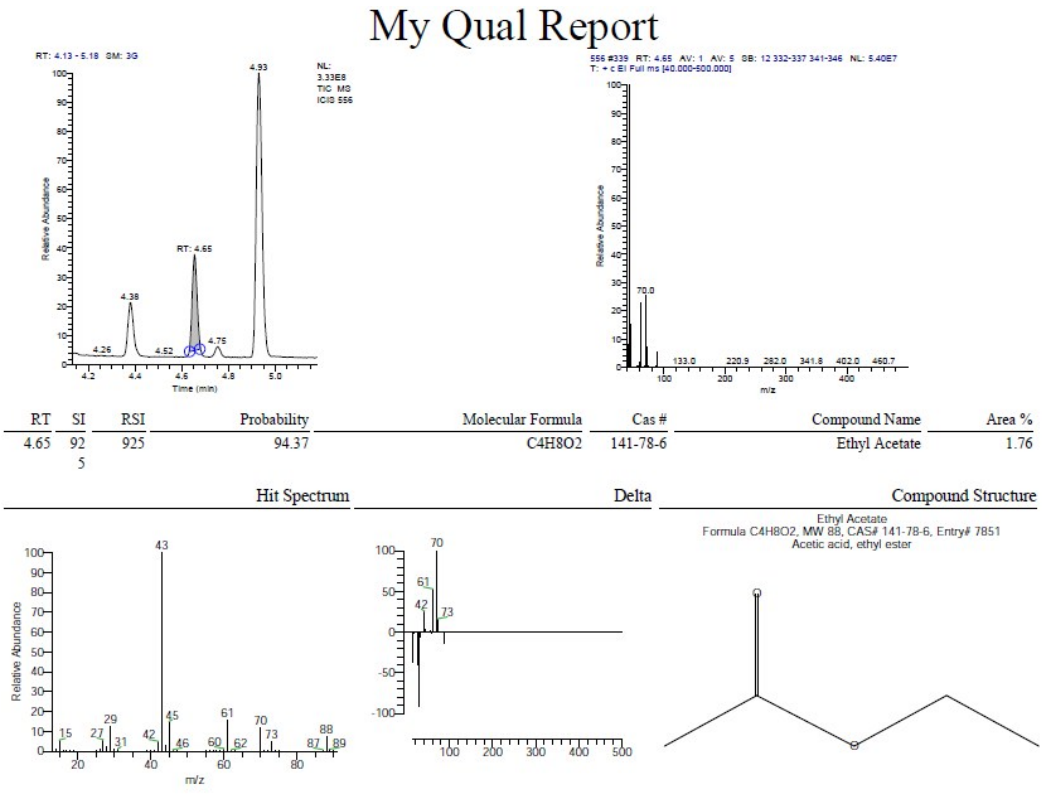


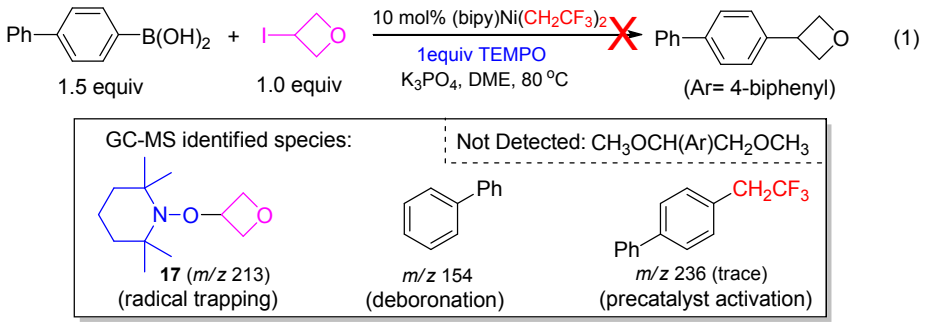
Figure S131. Detection of EtOAc by GC-MS ($EtOOCCH_2$ radical abstracts ethereal α-hydrogen)

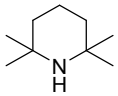
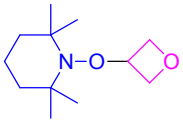
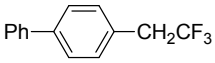
(c) TEMPO radical trapping experiments

Example 1: 4-biphenylboronic acid (0.3 mmol, 1.5 equiv), K_3PO_4 (0.4 mmol, 2.0 equiv), TEMPO (0.2 mmol, 1.0 equiv), followed by a solution of 3-iodooxetane (0.2 mmol, 1.0 equiv) in the DME solvent (0.5 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (10.0 mol%) in the DME solvent (0.5 mL) was added dropwise into the reaction system subsequently.

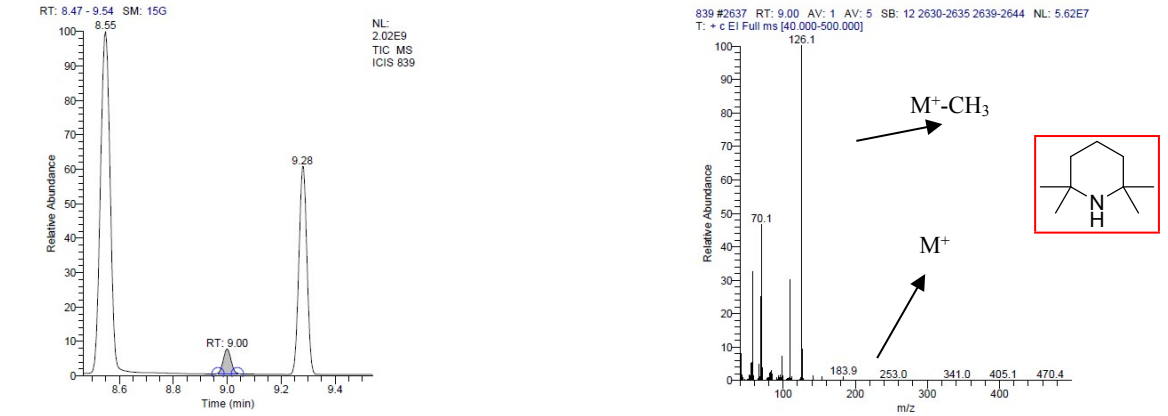
Table S8. GC-MS analysis of TEMPO radical trapping for the coupling reaction of 4-biphenylboronic acid and 3-iodooxetane

a Radical inhibition test



Retention time/minute	Detected species	Area%
8.29	*p*-xylene(internal standard)	14.84
8.55	3-iodooxetane	7.20
9.00		0.42
10.28		trace[a]
10.96	TEMPO	12.10
12.96	Biphenyl	16.67
13.79		0.07

[a]This species was dectected in trace amount possibly due to its instability.



RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
9.00	885	891	90.47	C9H19N	768-66-1	Piperidine, 2,2,6,6-tetramethyl-	0.42

Figure S132. Detection of 2,2,6,6-tetramethylpiperidine by GC-MS

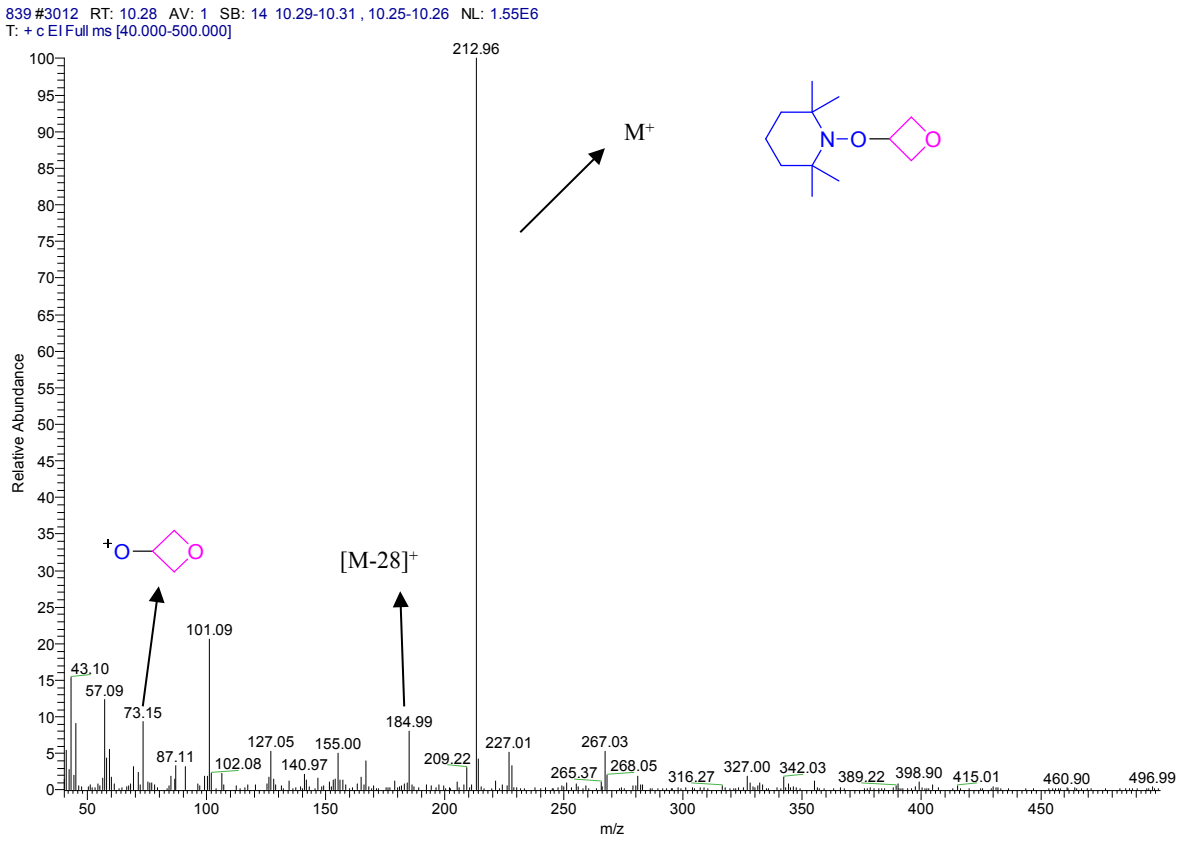
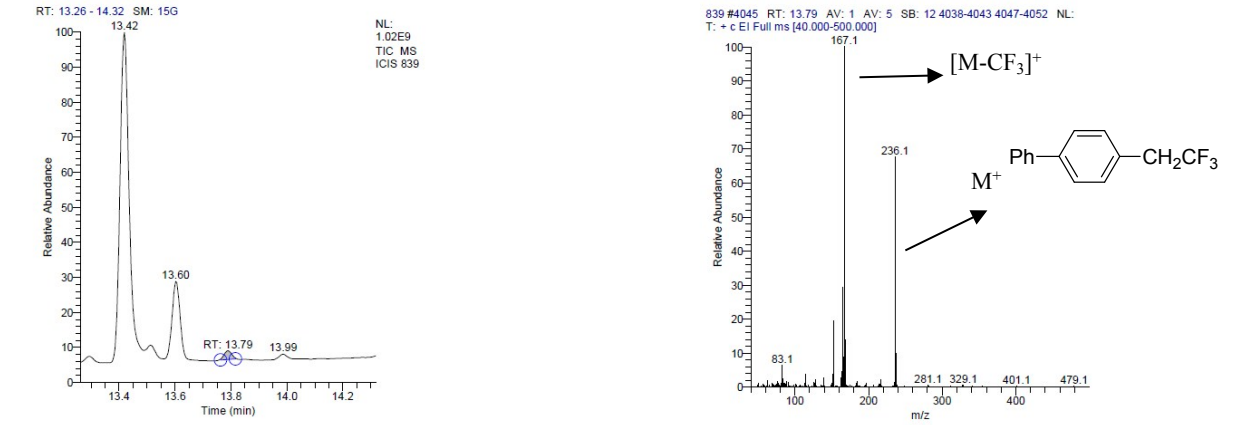


Figure S133. Detection of 2,2,6,6-tetramethyl-1-(oxetan-3-yloxy)piperidine by GC-MS

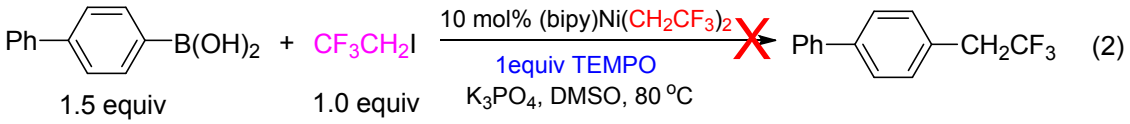


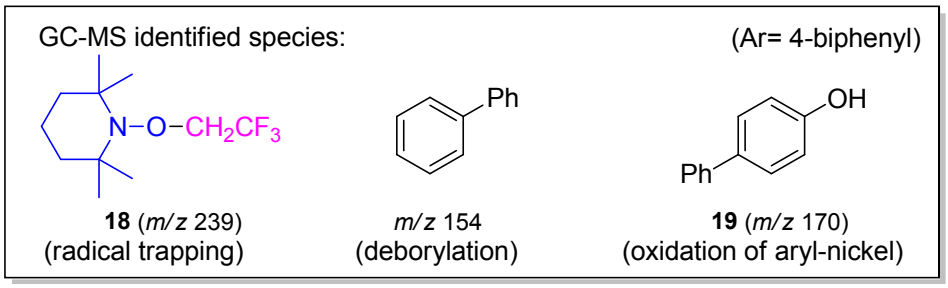
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
13.79	77 2	785	48.19	C14H11F3	34239-04 -8	4-Trifluoromethyldiphenylmethane	0.07

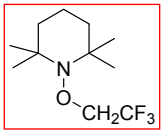
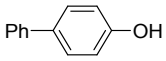
Figure S134. Detection of Ar-CH_2CF_3 by GC-MS (Ar= 4-biphenyl)

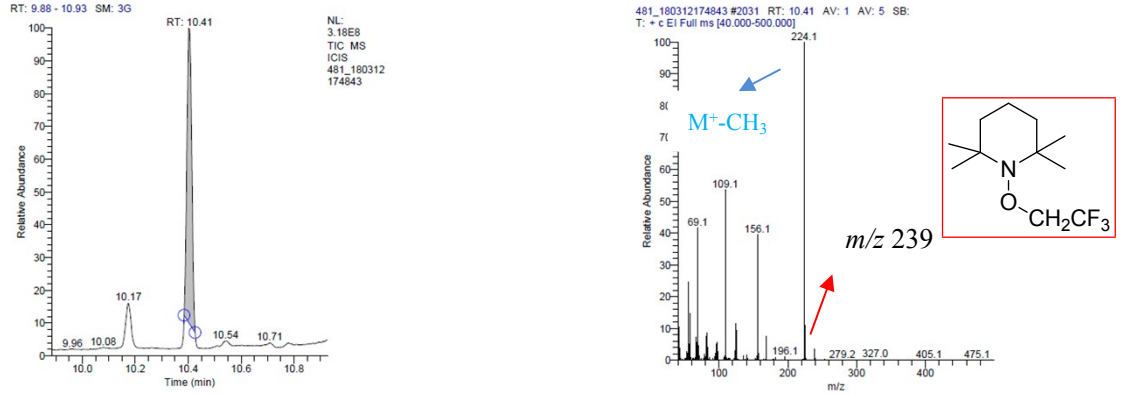
Example 2: 4-biphenylboronic acid (0.3 mmol, 1.5 equiv), K_3PO_4 (0.6 mmol, 3.0 equiv), TEMPO (0.2 mmol, 1.0 equiv), followed by a solution of CF_3CH_2I (0.2 mmol, 1.0 equiv) in the DMSO solvent (0.5 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (10.0 mol%) in the DMSO solvent (0.5 mL) was added dropwise into the reaction system subsequently. The Schlenck tube was screw capped and put into a preheated oil bath (80 ^oC). After stirring for 24 h, the reaction mixture was cooled to room temperature and poured into a saturated aqueous ammonium chloride solution (10.0 mL). The aqueous phase was extracted with ether three times (10.0 mL×3). The combined organic phase was analyzed by GC-MS with the *p*-xylene internal standard.

Table S9. GC-MS analysis of TEMPO radical trapping for the coupling reaction of 4-biphenylboronic acid and CF_3CH_2I



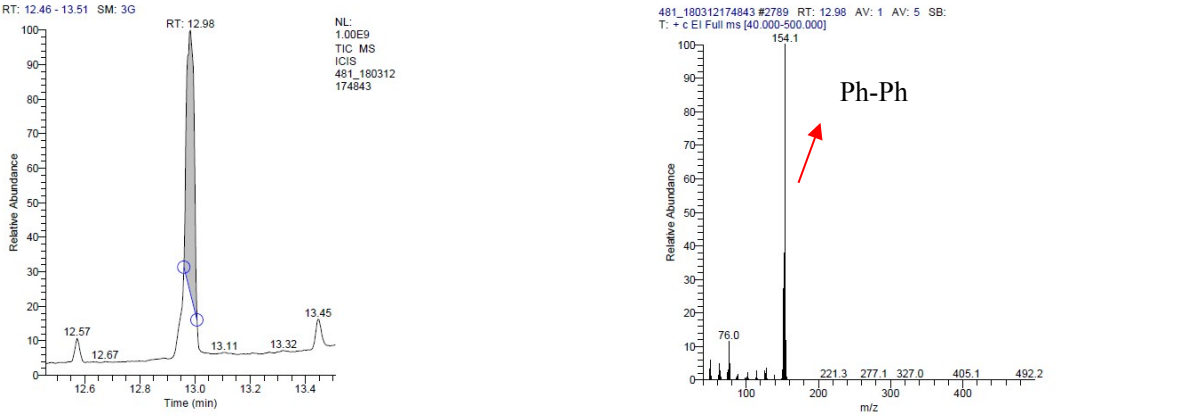


Retention time/minute	Detected species	Area%
3.79	CF_3CH_2I	10.92
8.31	*p*-xylene (internal standard)	20.27
10.41		3.82
10.98	TEMPO	21.93
12.98	Biphenyl	15.14
13.45	Bipyridine	0.90
15.24		1.51



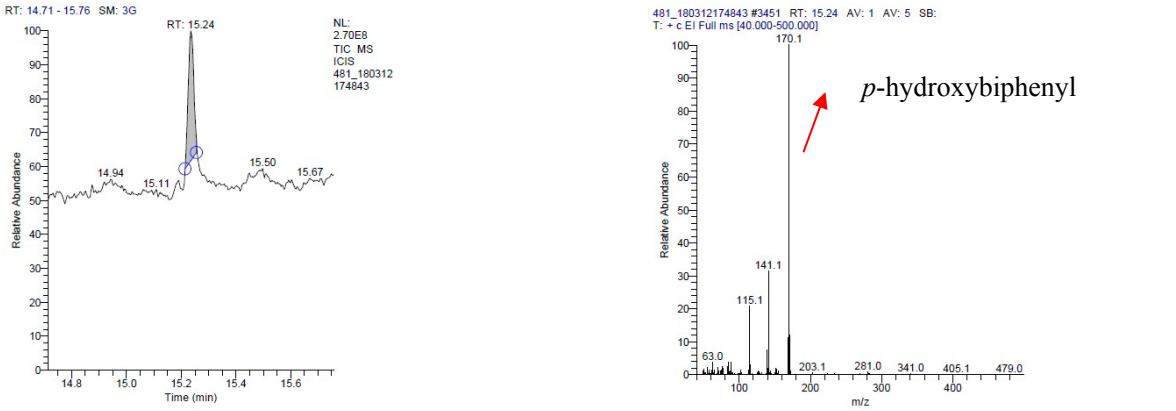
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
10.41	584	636	18.75	C18H24F6N2O4	NA	1,9-Dioxa-4,12-diazadispiro[4.2.4.2]tetradecane, 4,12-bis(trifluoroacetyl)-3,3,11,11-tetramethyl-	3.82

Figure S135. Detection of TEMPO-CH_2CF_3 by GC-MS



RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
12.98	953	955	77.85	C12H10	92-52-4	Biphenyl	15.14

Figure S136. Detection of biphenyl by GC-MS



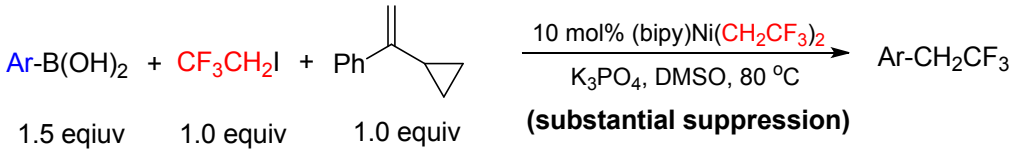
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
15.24	908	923	39.09	C12H10O	92-69-3	p-Hydroxybiphenyl	1.51

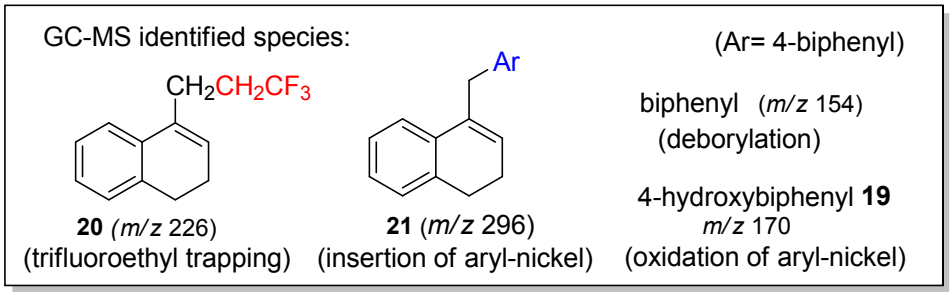
Figure S137. Detection of *p*-hydroxybiphenyl by GC-MS

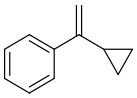
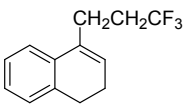
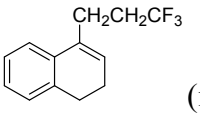
(c) Radical clock experiment

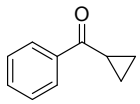
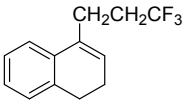
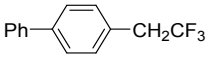
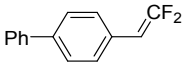
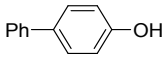
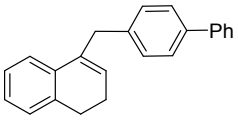
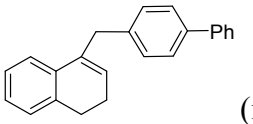
4-biphenylboronic acid (0.3 mmol, 1.5 equiv), K_3PO_4 (0.6 mmol, 3.0 equiv), followed by a solution of CF_3CH_2I (0.2 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 equiv) in the DMSO solvent (0.5 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The precatalyst **2** (10.0 mol%) in the DMSO solvent (0.5 mL) was added dropwise into the reaction system subsequently. The Schlenck tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 24 h, the reaction mixture was cooled to room temperature and poured into a saturated aqueous ammonium chloride solution (10.0 mL). The aqueous phase was extracted with ether three times (10.0 mL×3). The combined organic phase was analyzed by GC-MS with the *p*-xylene internal standard.

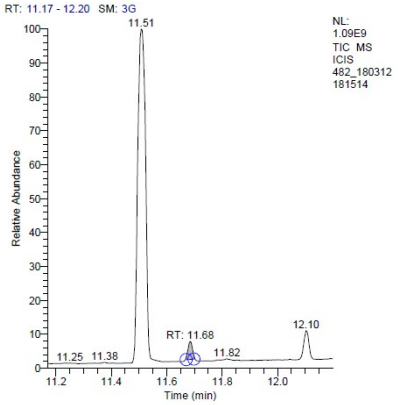
Table S10. GC-MS result of radical clock experiment

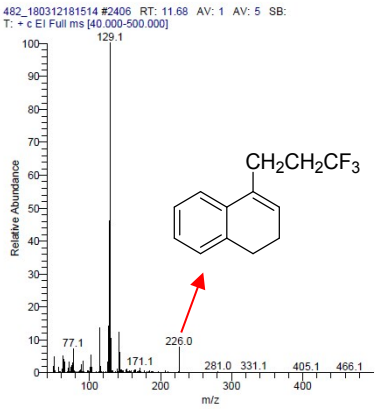




Retention time/minute	Detected species	Area%
3.80	CF_3CH_2I	7.71
8.31	*p*-xylene (internal standard)	16.15
11.51		12.59
11.68		0.49
12.10	 (its isomer)	0.80

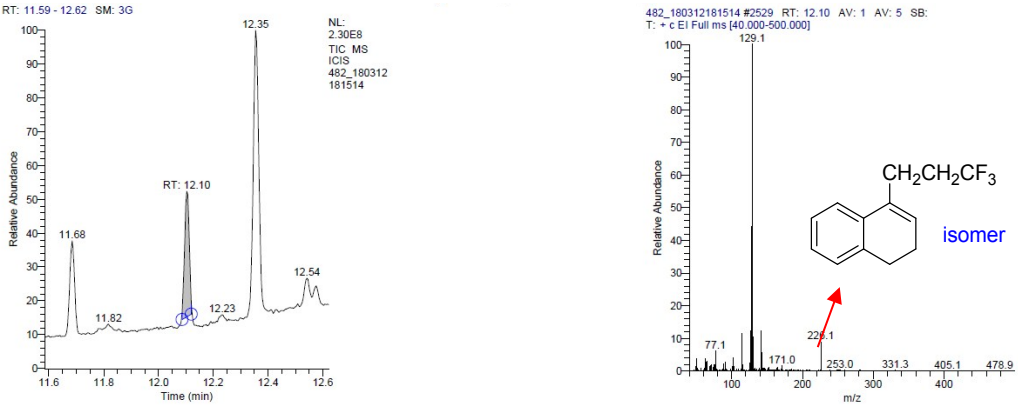
12.35		1.69
12.89	 (its isomer)	2.17
12.98	Biphenyl	11.35
13.80		1.71
14.26		0.44
15.23		1.46
15.57		0.49
16.19	 (its isomer)	0.85





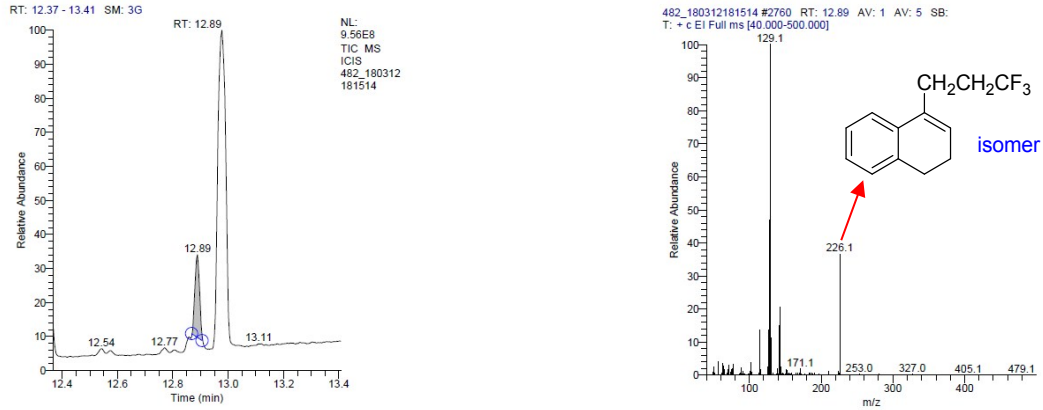
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
11.68	78 8	844	16.18	C11H12	NA	Cyclopropene, 2,3-dimethyl-3-phenyl-	0.49

Figure S138. Detection of trapping of CF_3CH_2 radical by radical-clock



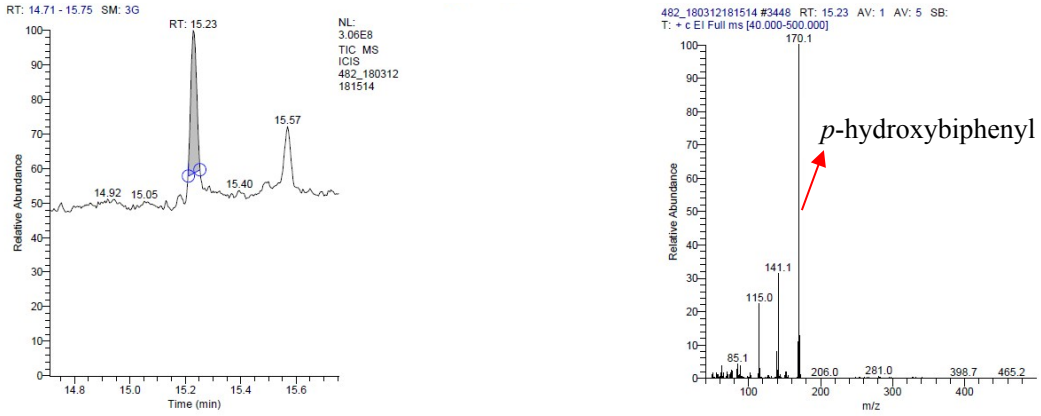
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
12.10	767	823	15.84	C12H14	NA	(1-Ethylbuta-1,3-dienyl)benzene	0.80

Figure S139. Detection of trapping of CF_3CH_2 radical by radical-clock (an isomeric product)



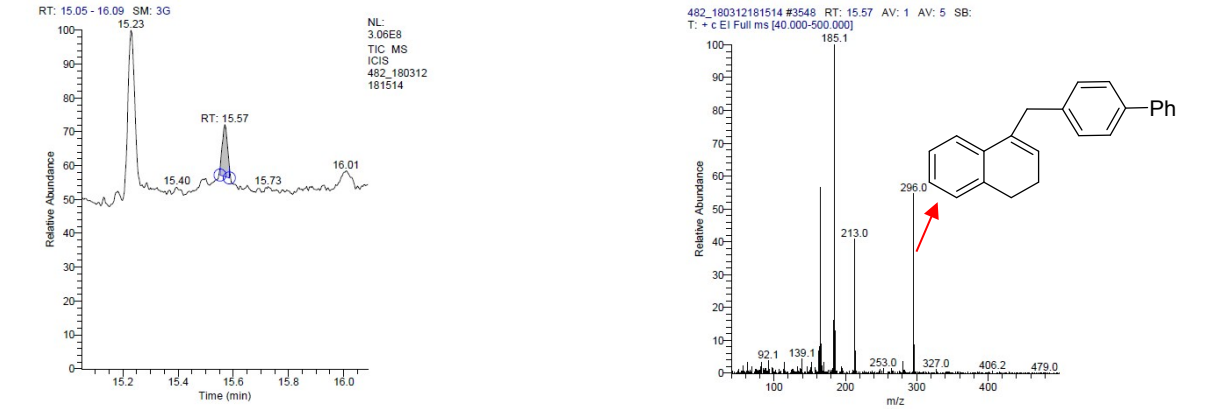
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
12.89	702	830	12.55	C11H12	NA	Cyclopropene, 2,3-dimethyl-3-phenyl-	2.17

Figure S140. Detection of trapping of CF_3CH_2 radical by radical-clock (another isomer)



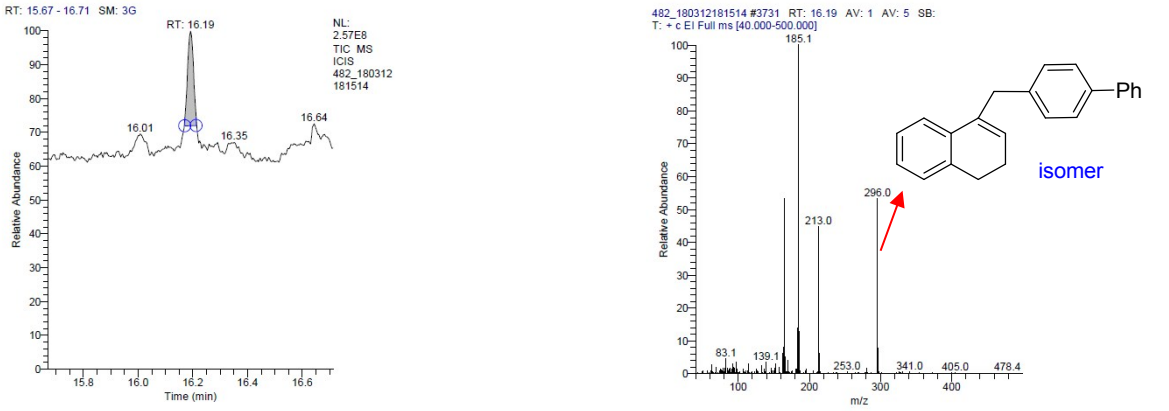
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
15.23	912	924	42.01	C12H10O	92-69-3	p-Hydroxybiphenyl	1.46

Figure S141. Detection of *p*-hydroxybiphenyl in radical-clock experiment



RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
15.57	524	681	18.59	C14H13F	74764-42-4	Benzene, 1-fluoro-3-(1-phenylethyl)-	0.49

Figure S142. Detection of trapping of Aryl moiety by radical-clock

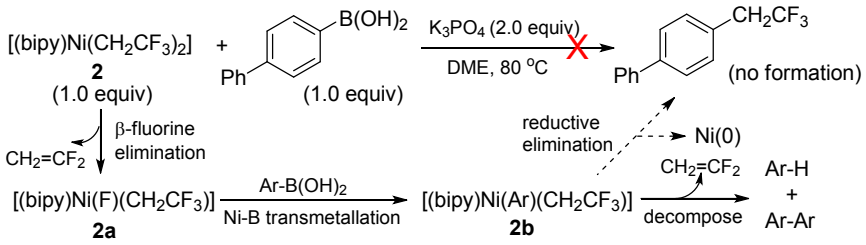


RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
16.19	53 2	689	18.57	C14H13F	74764-42 -4	Benzene, 1-fluoro-3-(1-phenylethyl)-	0.85

Figure S143. Detection of trapping of Aryl moiety by radical-clock (an isomeric product)

(d) Questioning over Ni(0)/Ni(II) or Ni(I)/Ni(III) catalytic cycle

i) Stoichiometric reaction of 4-biphenylboronic acid and 2 for verifying Ni(0)/Ni(II) cycle



GC-MS identified products:		Not detected:
$CH_2=CF_2$	biphenyl	Ar-CH_2CF_3
detected in reaction system (proof for eliminative extrusion)	deboronative product	F-CH_2CF_3
m/z 64	*m/z* 154	CF_3CH_2-CH_2CF_3 (Ar= 4-biphenyl)

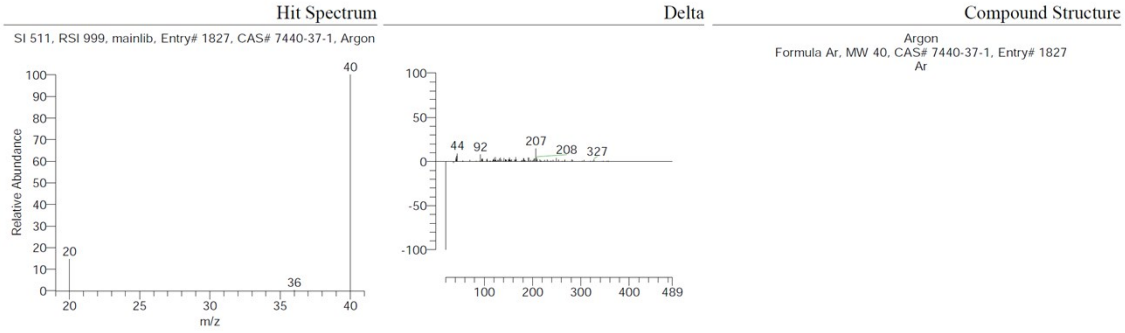
4-biphenylboronic acid (0.2 mmol, 1.0 equiv), K_3PO_4 (0.4 mmol, 2.0 equiv), followed by a solution of precatalyst **2** (0.2 mmol, 1.0 equiv) in the DME solvent (1 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The Schlenck tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 24 h, the reaction mixture was filtrated through a PTFE filter and analyzed by GC-MS.

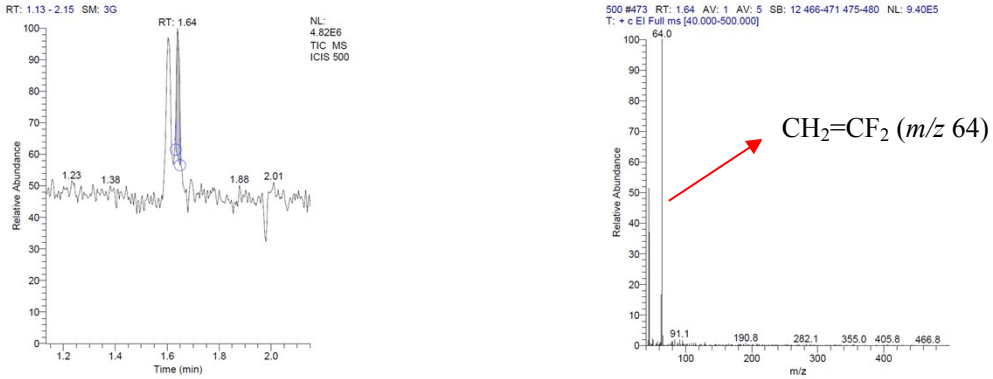
Table S11. GC-MS analysis for probing the catalytic cycle of Ni(0)/Ni(II)

Retention Time/minute	Detected species	Area%
1.64	$CF_2=CF_2$ (*m/z* 64)	0.03%[a]
12.91	Biphenyl (*m/z* 154)	37.39%

[a]$F_2C=CH_2$ was detected in trace amount in GC-MS due to the volatility of its gaseous properties.

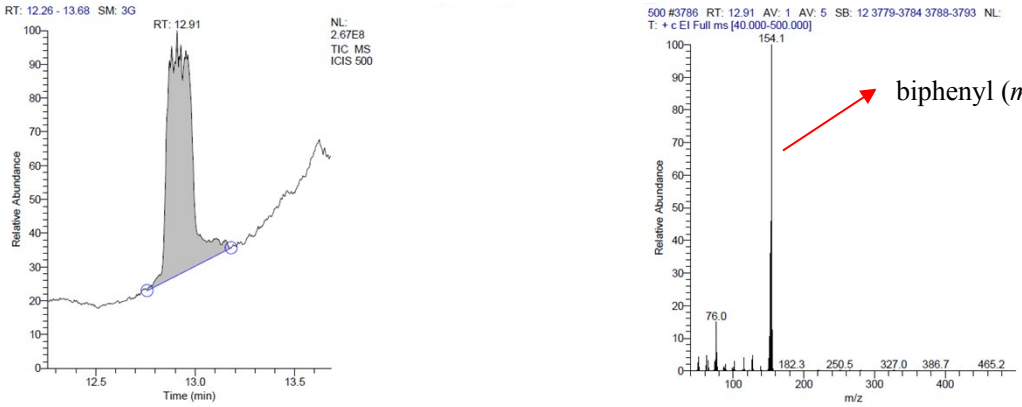
RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
1.60	511	999	50.16	Ar	7440-37-1	Argon	0.04





RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
1.64	762	899	90.09	C2H2F2	75-38-7	Ethene, 1,1-difluoro-	0.03

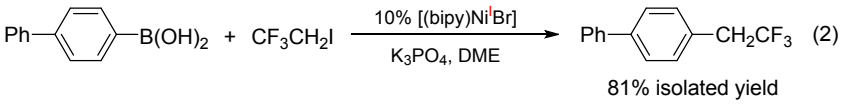
Figure S144. Detection of CH_2=CF_2 by GC-MS



RT	SI	RSI	Probability	Molecular Formula	Cas #	Compound Name	Area %
12.91	928	930	70.46	C12H10	92-52-4	Biphenyl	37.39

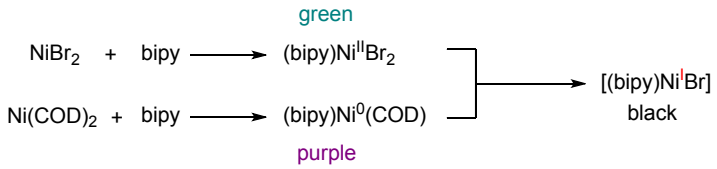
Figure S145. Detection of debornative product biphenyl by GC-MS

ii) Coupling reaction under the catalysis of Ni(I) precatalyst for verifying Ni(I)/Ni(III) cycle



4-biphenylboronic acid (0.3 mmol, 1.5 equiv), K_3PO_4 (0.6 mmol, 3.0 equiv), followed by a solution of CF_3CH_2I (0.2 mmol, 1.0 equiv) in the DME solvent (0.5 mL) were loaded into a 25 mL of Schlenck tube which was subject to evacuating/flushing with nitrogen gas three times. The presumed catalyst (bipy)$Ni^{I}Br$ (0.02 mmol, 1.0 equiv) was added into the reaction system subsequently. The Schlenck tube was screw capped and put into a preheated oil bath (80 ^{o}C). After stirring for 24 h, the reaction mixture was cooled to room temperature and poured into a saturated aqueous ammonium chloride solution (10.0 mL). The aqueous phase was extracted with ether three times (10.0 mL×3). After removing the solvent in vacuo, the residue was purified by flash chromatography on silica gel to afford the corresponding $ArCH_2CF_3$ product (38 mg, isolated yield 81%).

iii) Procedure for the preparation of [(bipy)$Ni^{I}Br$]



Analogous to the preparation method of (dppf)$Ni^{(I)}Cl$ of Hazari group (Guard, L. M.; Mohadjer Beromi, M.; Brudvig, G. W.; Hazari, N.; Vinyard, D. J. *Angew. Chem. Int. Ed.* **2015**, *54*, 13352.), the presumed catalyst [(bipy)$Ni^{I}Br$] was prepared according to the following procedure. To a THF solution (5.0 mL) of bipyridine (0.5 mmol) was added nickel(II) bromide (0.5 mmol) and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture exhibited a suspended solution of green color. Meanwhile, a reaction mixture of $Ni(COD)_2$ (0.5 mmol) and bipyridine (0.5 mmol) in the solution of THF was also stirred at room temperature for 24 h to accomplish the coordination step (a purple solution was formed). The two reaction solutions were combined together and stirred at room temperature for an extra 24 h. A dark black precipitate was produced in the combined reaction solution and was filtrated. The black solid was washed with ether (10.0 mL) and pentane (10.0 mL), and dried in *vacuo* to furnish the presumed [(bipy)$Ni^{I}Br$] as a dark black powder (271 mg, Estimated Yield 92%). The insolubility of presumed catalyst [(bipy)$Ni^{I}Br$] in organic solvent made NMR charaterization failed. Thus, XPS (X-ray Photoelectron Spectroscopy) and IR were used to characterize the presumable [(bipy)$Ni^{I}Br$]. The XPS of [(bipy)$Ni^{I}Br$] illustrated

the peaks corresponding to Ni(I) at 855.486 eV which was negatively shifted by 0.214 eV in comparison with a known $K_2[Ni^{(I)}(CN)_3]$ ($Ni^{(I)}$ at 855.70 eV) (Figure S123). The IR spectra of [(bipy)Ni^{I}Br] (KBr pellets method) showed strong absorption bands in the ranges of 1599-1441 cm^{-1} for the stretching mode of pyridine ring, which were blue shifted toward higher frequency as compared to the free bipyridine.

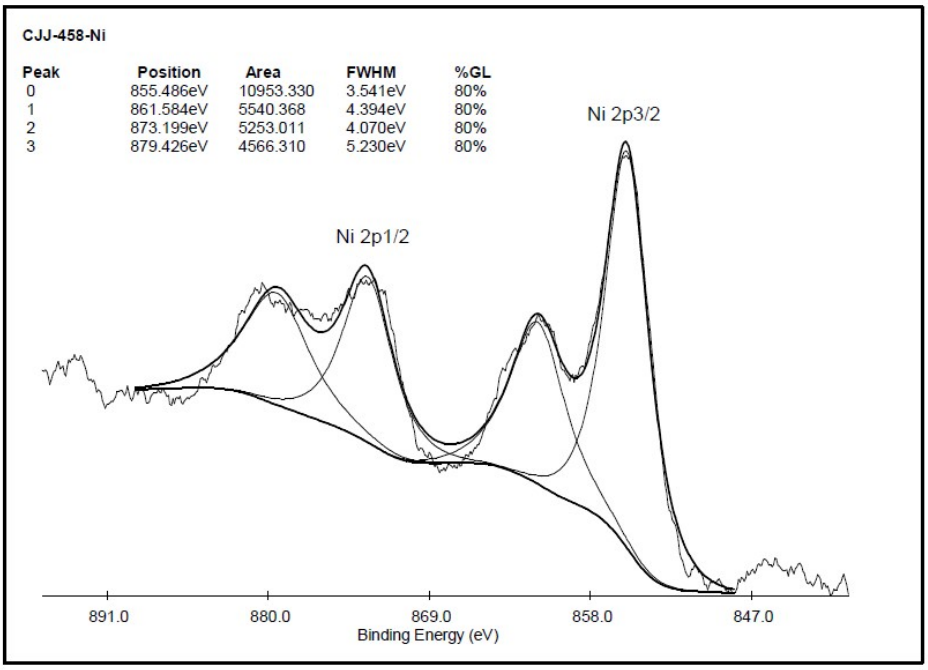


Figure S146. XPS (X-ray Photoelectron Spectroscopy) analysis of [(bipy)Ni^{I}Br]

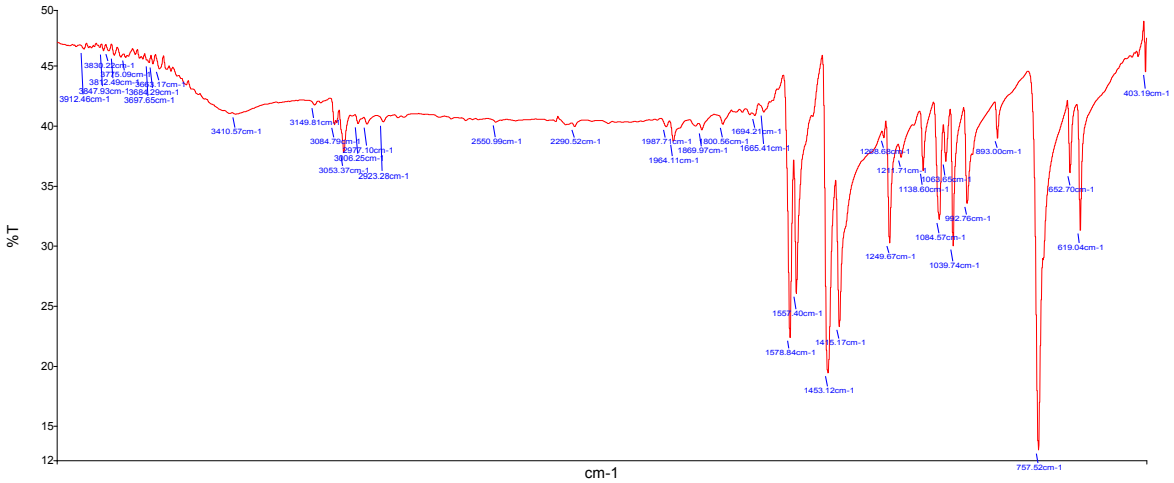


Figure S147. IR spectra of 2,2'-bipyridine

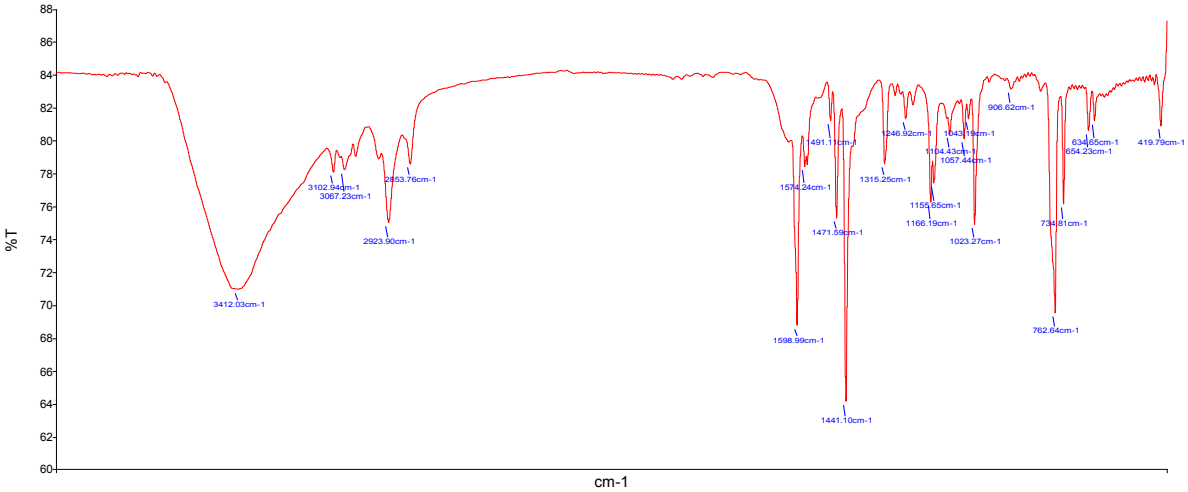


Figure S148. IR spectra of [(bipy)Ni^{I}Br