Electronic Supplementary Information

Transition Metal-free Electrochemical Fluorotrifluoromethylation of Styrenes

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1. General Information

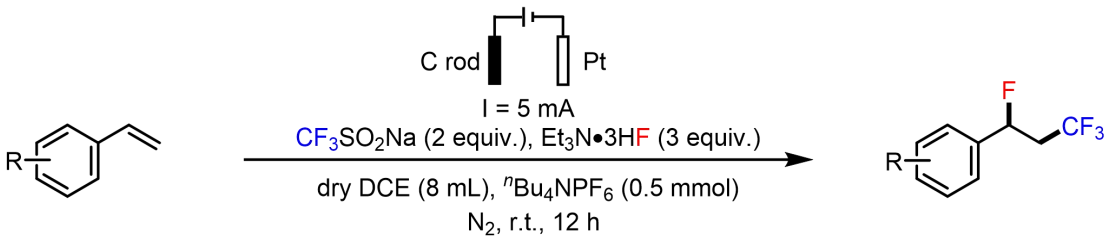
All reagents were purchased without further purification unless otherwise noted. Analytical thin-layer chromatography (TLC) was conducted with TLC silica gel GF254 under UV irradiation. Flash column chromatography was performed using silica gel 200-300 and columns were packed according to the dry or wet method. Nuclear Magnetic Resonance spectra were recorded on a Bruker Advance II 400 (400 MHz) or Bruker Advance III 400 (400 MHz) NMR spectrometer and ^{1}H NMR reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or $CDCl_3$ (δ 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dt (doublets of triplet), td (triplet of doublets) or m (multiplet). ^{13}C NMR spectra were recorded on a Bruker Advance II 400 (101 MHz) or Bruker Advance III 400 (101 MHz) NMR spectrometer and reported in ppm relative to $CDCl_3$ (77.0 ppm). F NMR spectra were recorded on a Bruker Advance II 400 (376 MHz) or Bruker Advance III 400 (376 MHz) NMR. Coupling constants were reported as a *J* value in Hz. GC-MS data were recorded on SHIMADZU™ GCMS-QP2010. HR-MS analyses were performed on a Thermo Scientific Q Exactive Focus Orbitrap LC-MS/MS System. LSV determination was performed on CHI 760E (CH Instruments, Ins) with glassy carbon as working electrode, $Ag/AgNO_3$ as reference electrode and a Pt wire as counter electrode. The instrument for bulk electrolysis is dual display potentiostat (DJS-292B) (Shanghai xinrui instruments Co., Ltd). Distyryls (**1a**, **1d**-**1u**) were prepared according to the previous report[1]. The GC yields were determined by internal standard method: internal standard (mesitylene, 25 μmol), pure products (25 μmol), 1/160 of the volume of reaction solution (note: the products were 160 × 25 μmol, calculated as 100% yields).

2. Experimental Procedures

2.1 Treatment of electrode materials

Pretreatment of carbon rod: the specification of the carbon rod is a cylindrical rod with a diameter of 6 mm and were sonicated with ethyl acetate for 10 min to remove organic molecules on the surface, and then washed with ethanol several times to remove ethyl acetate; Pretreatment of Pt sheet, BDD sheet, carbon fiber paper (CP): cutting into pieces of 1.0 cm×1.0 cm and ultrasonicated with ethyl acetate for 10 minutes to remove organic molecules on the surface, then washed with ethanol several times to remove ethyl acetate; Pretreatment of Fe sheet, cutting into pieces of 1.5 cm×1.0 cm and sonicated with acetone, 3.0 M of HCl aqueous solution and deionized water several times respectively to remove the impurities (organic molecules and oxide layer) on the surface of the materials[2].

2.2 The procedure for electrosynthesis in a two-electrode system



1a-u **2a-u**

Into an undivided cell with a carbon rod anode (2.5 cm^2) and a Pt sheet (1.0 cm^2), dry DCE (8 mL), $^nBu_4NBF_6$ (193.7 mg, 0.5 mmol), CF_3SO_2Na (0.8 mmol), $Et_3N•3HF$ (1.2 mmol) and freshly substrate **1** (0.4 mmol) were added. A constant current electrolysis with a current 5 mA was performed at room temperature. The electrochemical reaction under magnetic stirring (300 rpm) under nitrogen atmosphere. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at room temperature for 12 h. Then extract with ethyl acetate to obtain the organic phase. Then, the solvent was removed with a rotary evaporator. The pure products **2** were obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate (PE:EA = 50:1 to 20:1) as the eluent.

2.3 Experiments with GC-MS ananlysis

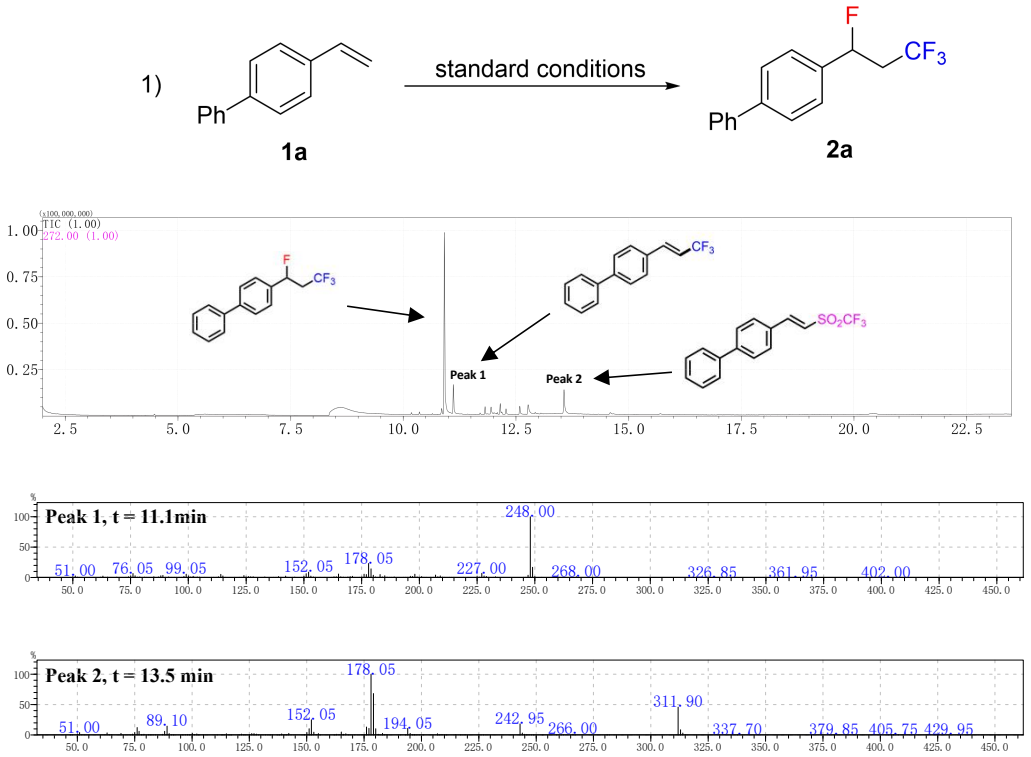
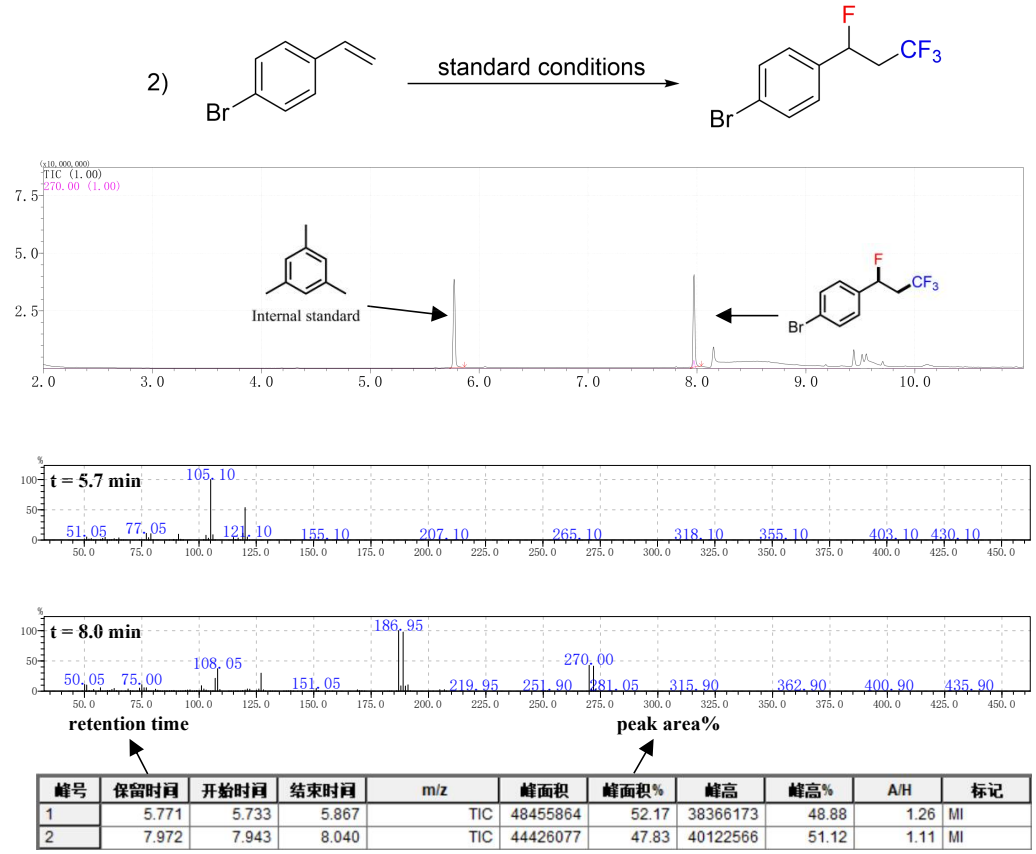
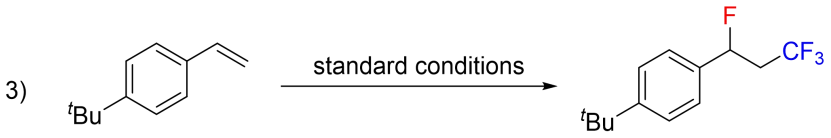


Figure S1. GC-MS analysis of the model reaction.

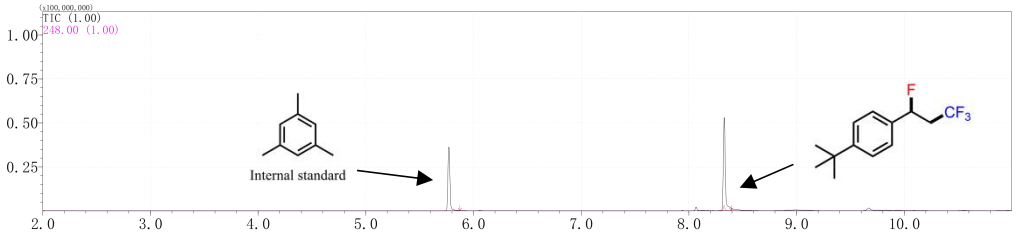


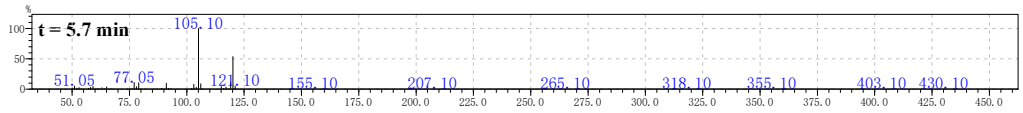
峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.733	5.867	TIC	48455864	52.17	38366173	48.88	1.26	MI
2	7.972	7.943	8.040	TIC	44426077	47.83	40122566	51.12	1.11	MI

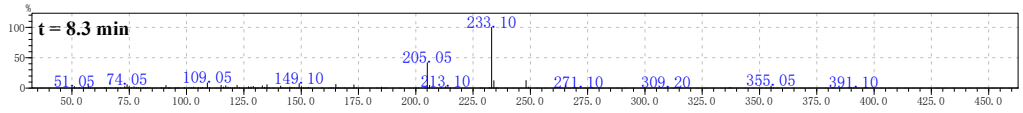
Figure S2. GC-MS analysis of the reaction from *p*-bromostyrene.



a) GC-MS of Internal standard and pure product



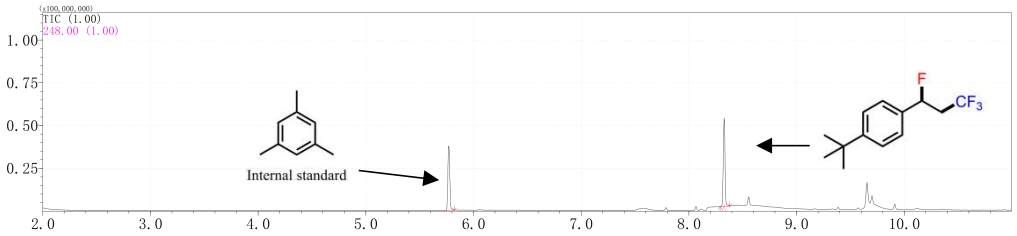


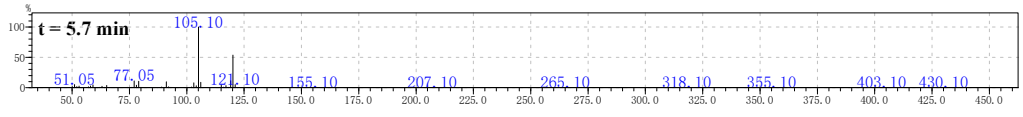


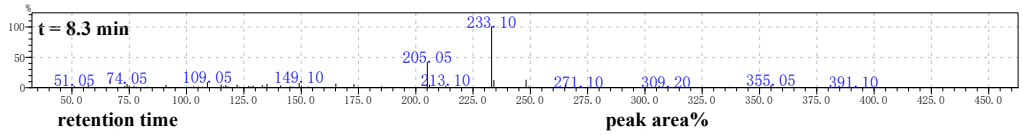
retention time peak area%

峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.727	5.873	TIC	46958109	40.45	36201122	40.65	1.30	MI
2	8.328	8.290	8.393	TIC	69121203	59.55	52847768	59.35	1.31	MI

b) GC-MS of Internal standard and reaction solution



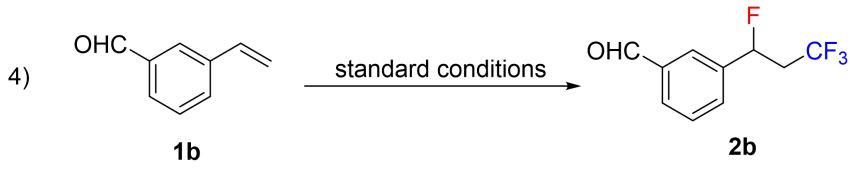




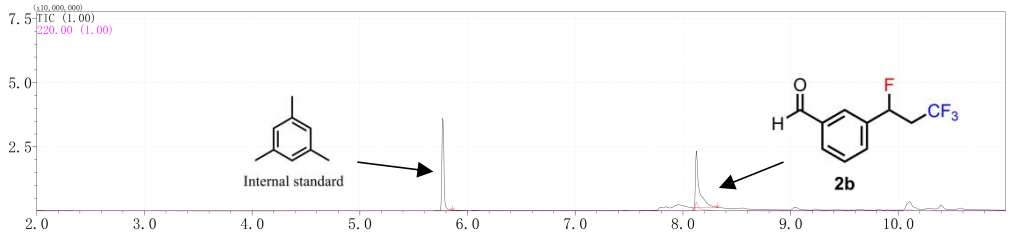
retention time peak area%

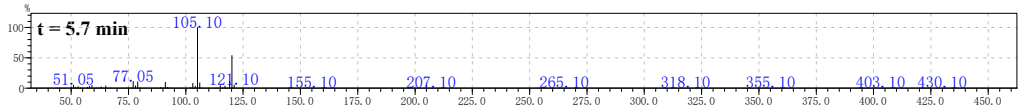
峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.727	5.823	TIC	47532606	44.60	37789494	42.21	1.26	MI
2	8.327	8.290	8.380	TIC	59046516	55.40	51734001	57.79	1.14	MI

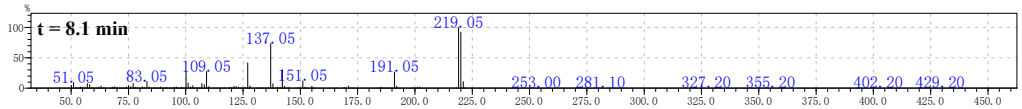
Figure S3. GC-MS analysis of *p-tert*-butylstyrene derived product.



a) GC-MS of Internal standard and pure product



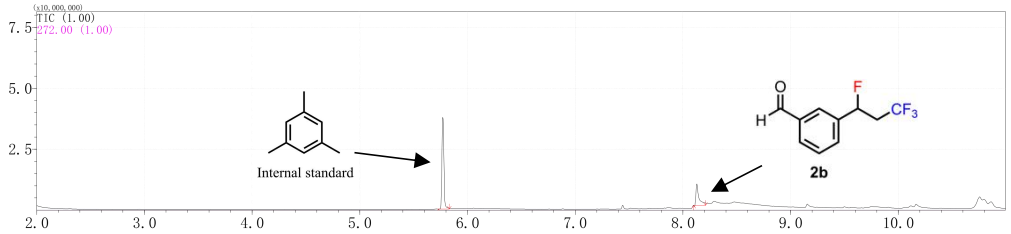


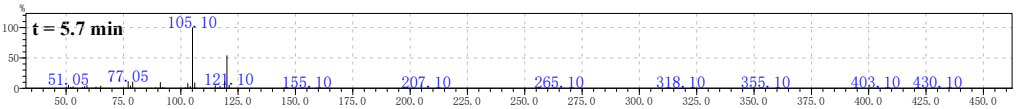


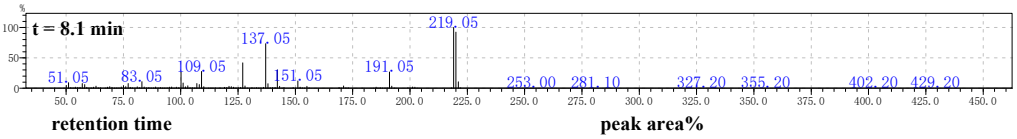
retention time peak area%

峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.703	5.863	TIC	48344848	47.00	36112273	62.00	1.34	MI
2	8.125	8.100	8.323	TIC	54524815	53.00	22137329	38.00	2.46	MI

b) GC-MS of Internal standard and reaction solution





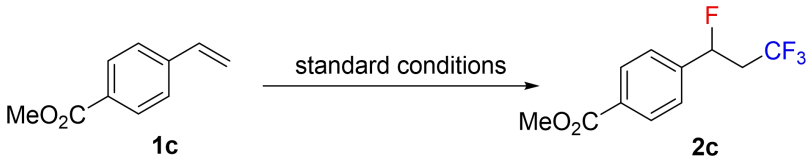


retention time peak area%

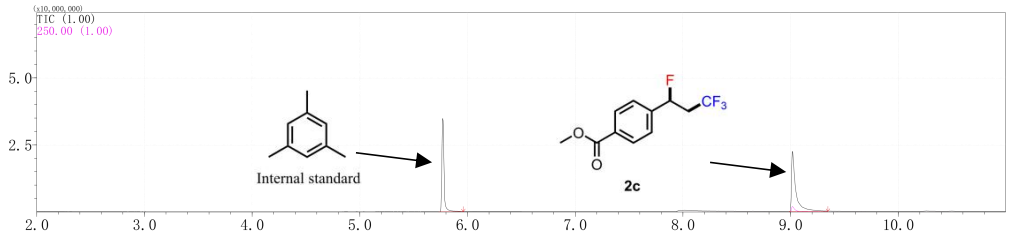
峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.730	5.830	TIC	48173273	73.80	37589237	81.07	1.28	MI
2	8.129	8.100	8.210	TIC	17097802	26.20	8776781	18.93	1.95	MI

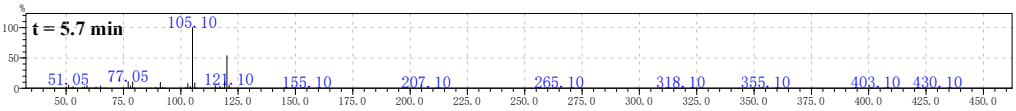
Figure S4. GC-MS analysis of **2b**.

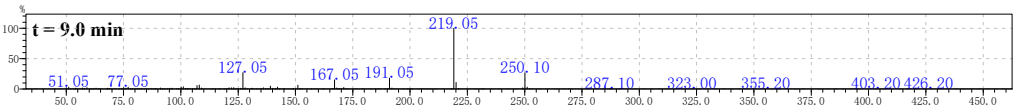
5)



a) GC-MS of Internal standard and pure product



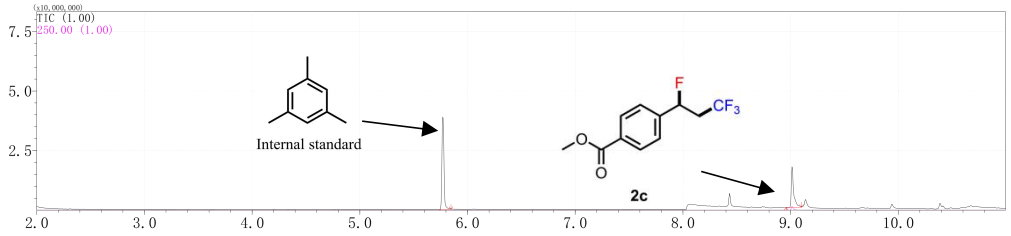


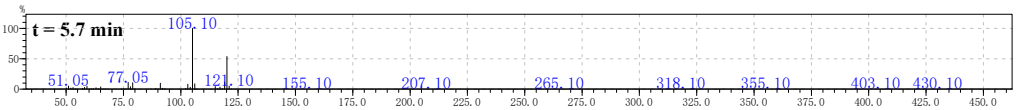


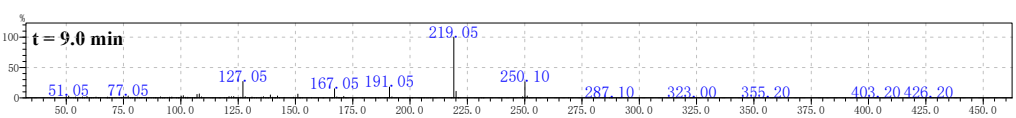
retention time peak area%

峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.737	5.960	TIC	48233397	43.83	34741956	60.75	1.39	MI
2	9.018	8.990	9.347	TIC	61811549	56.17	22445849	39.25	2.75	MI

b) GC-MS of Internal standard and reaction solution







retention time peak area%

峰号	保留时间	开始时间	结束时间	m/z	峰面积	峰面积%	峰高	峰高%	A/H	标记
1	5.771	5.743	5.847	TIC	51135915	65.81	38726717	69.38	1.32	MI
2	9.014	8.960	9.100	TIC	26566243	34.19	17090344	30.62	1.55	MI

Figure S5. GC-MS analysis of **2c**.

2.4 Complementary CV

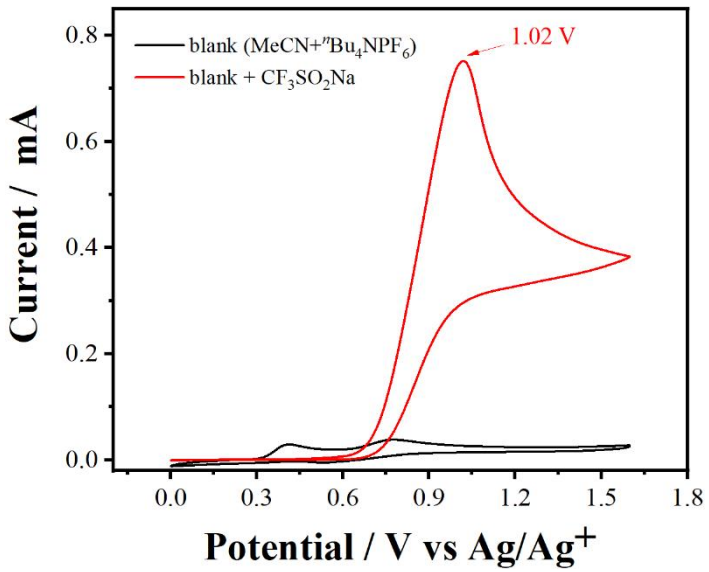


Figure S6. CV of CF_3SO_2Na in MeCN.

Test condition: ^{n}Bu$_4$NPF$_6$ (0.3 mmol), CF_3SO_2Na (0.4 mmol), MeCN (5.0 mL), glass carbon anode (4 mm diameter), Pt plate cathode (1cm × 1cm), scan rate was 0.1 V/s.

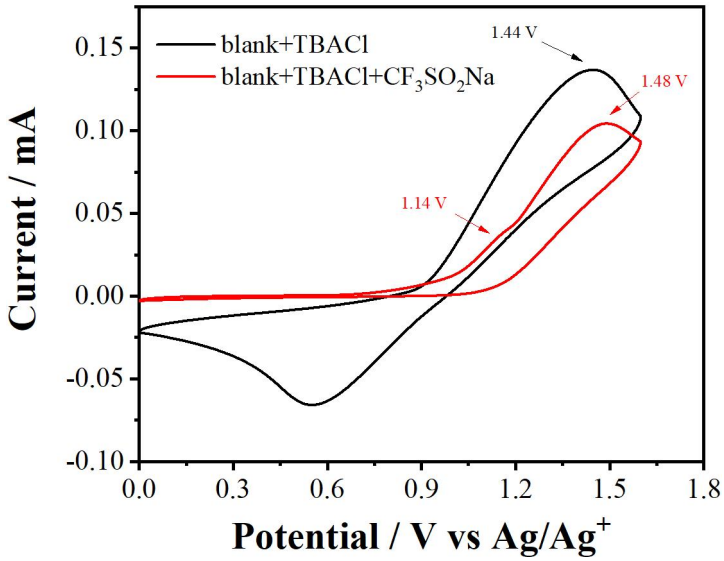
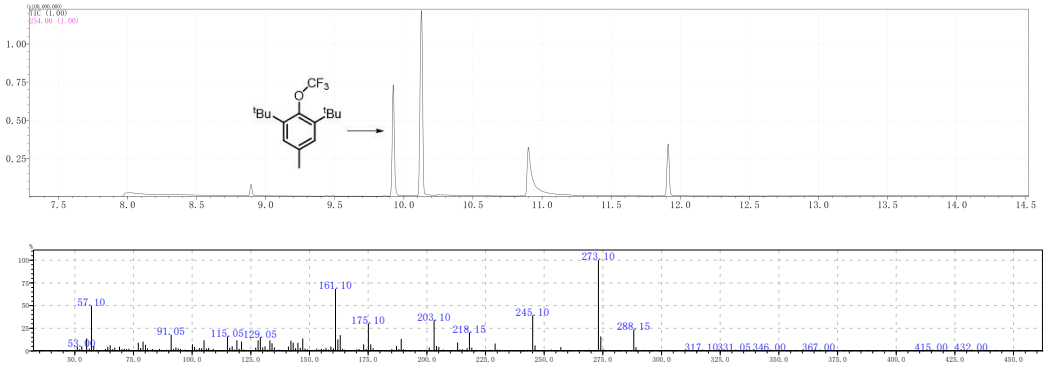


Figure S7. CV of TBACl and CF_3SO_2Na in DCE.

Test conditions: ^{n}Bu$_4$NPF$_6$ (0.3 mmol), TBACl (0.1mmol), CF_3SO_2Na (0.4 mmol), DCE (5.0 mL), glass carbon anode (4 mm diameter), Pt plate cathode (1cm × 1cm), scan rate was 0.1 V/s.

2.5 The results of radical trapping experiments

a) The BHT group



b) The 1,1-diphenylethylene group

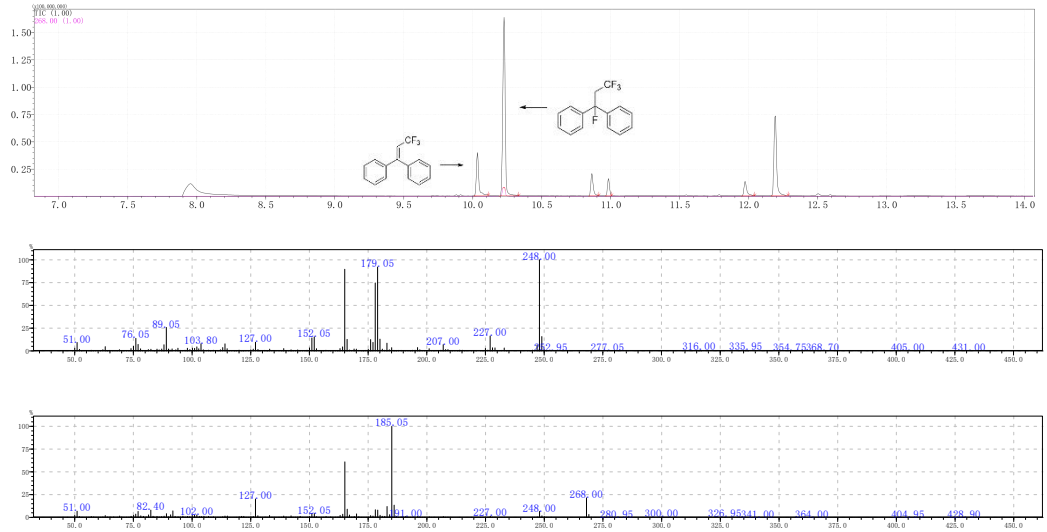
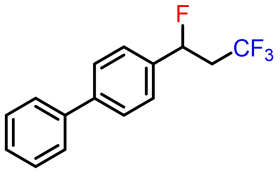


Figure S8. GC-MS of radical trapping reaction. (a) the BHT group; (b) the 1,1-diphenylethylene group.

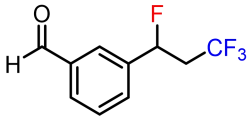
3. Characterization of Products

4-(1,3,3,3-Tetrafluoropropyl)-1,1'-biphenyl (2a)



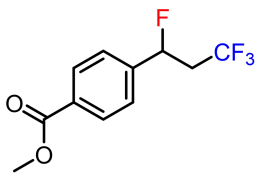
Yield: 70%. White solid. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.52-7.45 (m, 3H), 7.44-7.37 (m, 2 H), 5.83 (dd, *J* = 47.8, 6.7 Hz, 1 H), 2.97-2.84 (m, 1 H), 2.70-2.52 (m, 1 H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.14 (d, *J* = 2.0 Hz), 140.22, 140.21, 136.72 (d, *J* = 20.2 Hz), 128.86, 127.70, 127.51, 127.37, 127.09, 126.22, 126.16, 125.91 (d, *J* = 7.0 Hz), 125.11 (q, *J* = 275.7 Hz), 87.89 (dq, *J* = 172.7, 4.0 Hz), 41.31 (qd, *J* = 28.3, 25.3 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.83 (d, *J* = 7.7 Hz), -175.61 (q, *J* = 7.8 Hz).

3-(1,3,3,3-Tetrafluoropropyl)benzaldehyde (2b)



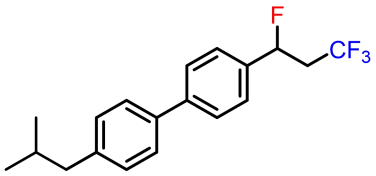
Yield: 20%. Colorless oil. The reaction time: 12 h.
^{1}H NMR (DMSO-*d*6, 400 MHz): δ 10.04 (s, 1H), 8.04 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 5.99 (dd, *J* = 47.9, 8 Hz, 1H), 3.25-3.17 (m, 1H), 3.10-2.96 (m, 1H).
^{13}C NMR (DMSO-*d*6, 101 MHz): δ 192.86, 138.84 (d, *J* = 20.2 Hz), 136.46, 132.14 (d, *J* = 6.1 Hz), 130.28, 129.61, 126.96 (d, *J* = 6.1 Hz), 125.85 (d, *J* = 278.8 Hz), 87.64 (dq, *J* = 172.71, 4.0 Hz).
^{19}F NMR (DMSO-*d*6, 376 MHz) δ -59.92 (d, *J* = 7.5 Hz), -172.81 (q, *J* = 7.5 Hz).

Methyl 4-(1,3,3,3-tetrafluoropropyl)benzoate (2c)



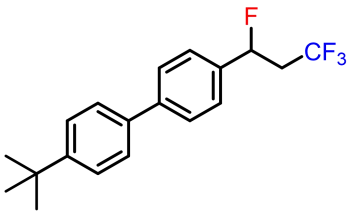
Yield: 36%. Colorless oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.82 (dd, *J* = 47.7, 9.2 Hz, 1H), 3.93 (s, 3H), 2.86-2.79 (m, 1H), 2.64-2.49 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.35, 142.50 (d, *J* = 19.2 Hz), 130.86, 130.84, 130.11, 129.92, 125.63, 125.56, 125.17 (d, *J* = 7.1 Hz), 124.87 (d, *J* = 278.8 Hz), 92.86, 91.08, 87.52(dq, *J* = 177.8, 4.0 Hz), 52.27, 41.39 (qd, *J* = 29.3, 25.2 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.14 (d, *J* = 7.5 Hz), -179.02 (q, *J* = 7.5 Hz).

4-Isobutyl-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2d)



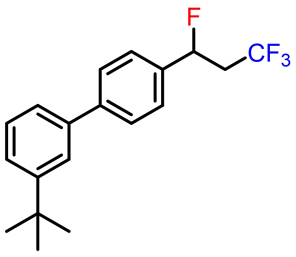
Yield: 55%. Light yellow oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.81 (dd, *J* = 47.9, 6.9 Hz, 1H), 2.95-2.83 (m, 1H), 2.70-2.54 (m, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.91 (dt, *J* = 13.5, 6.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.18 (d, *J* = 3.0 Hz), 141.41, 137.56, 136.37 (d, *J* = 20.2 Hz), 129.64, 127.36, 126.78, 125.88 (d, *J* = 6.1 Hz), 125.12 (q, *J* = 277.8 Hz), 87.97 (dq, J = 175.7, 3.0 Hz), 45.06, 41.43 (qd, *J* = 29.3, 26.2, Hz), 30.24, 22.39.
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.15 (d, *J* = 7.9 Hz), -174.72 (q, *J* = 7.9 Hz).

4-(Tert-butyl)-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2e)



Yield: 40%. White solid. Melting point: 75℃. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 5.81 (dd, *J* = 47.8, 6.9 Hz, 1H), 2.98-2.81 (m, 1H), 2.70-2.49 (m, 1H), 1.37 (s, 9H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.82, 142.06 (d, *J* = 2.0 Hz), 137.32, 136.41 (d, *J* = 20.2 Hz), 128.49, 127.40, 126.77, 125.88 (d, *J* = 7.1 Hz) ,125.83, 125.12 (q, *J* = 276.7 Hz), 87.96 (dq, *J* = 171.2, 4.04 Hz), 41.45 (qd, *J* = 29.3, 26.3 Hz), 34.57, 31.32.
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.18 (d, *J* = 7.9 Hz), -174.76 (q, *J* = 7.9 Hz).

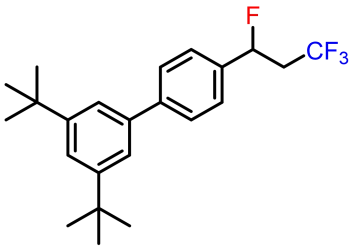
3-(Tert-butyl)-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2f)



Yield: 76%. Light blue transparent oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.59 (s, 1H), 7.46 – 7.38 (m, 5H), 5.82 (dd, *J* = 47.8, 6.8 Hz, 1H), 2.98-2.81 (m, 1H), 2.70-2.49 (m, 1H), 1.38 (s, 9H).

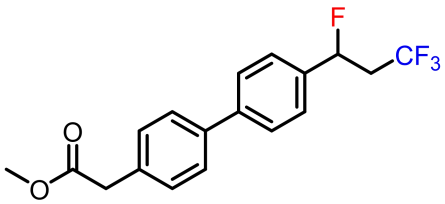
^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.78, 142.88 (d, *J* = 2.0 Hz), 140.07, 136.56 (d, *J* = 20.2 Hz), 128.59, 127.74, 125.86 (d, *J* = 6.1 Hz) , 125.12 (q, *J* = 276.7 Hz), 124.77, 124.39, 124.28, 123.75, 87.95 (dq, *J* = 172.7, 3.0 Hz), 41.47 (qd, *J* = 28.3, 26.3 Hz), 34.83, 31.38.
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.13 (d, *J* = 8.0 Hz), -174.85 (q, *J* = 7.9 Hz).

3,5-Di-tert-butyl-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2g)



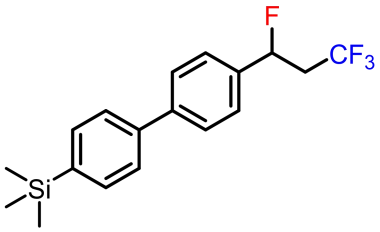
Yield: 75%. Light blue transparent oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.48-7.46 (m, 1H), 7.44 (s, 1H), 7.43-7.38 (m, 3H), 5.82 (dd, *J* = 47.8, 6.8 Hz, 1H), 2.99-2.81 (m, 1H), 2.70-2.49 (m, 1H), 1.39 (s, 18H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.31, 143.53 (d, *J* = 2.0 Hz), 139.75, 136.39 (d, *J* = 20.2 Hz), 127.89, 125.81 (q, *J* = 7.1 Hz), 125.13 (q, *J* = 278.7 Hz), 121.88, 121.65, 87.99 (dq, *J* = 171.7, 4.0 Hz), 41.48 (qd, *J* = 29.29, 25.25 Hz), 34.99, 31.51.
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.13 (d, *J* = 8.0 Hz), -174.67 (q, *J* = 7.9 Hz).

Methyl 2-(4'-(1,3,3,3-tetrafluoropropyl)-[1,1'-biphenyl]-4-yl)acetate (2h)



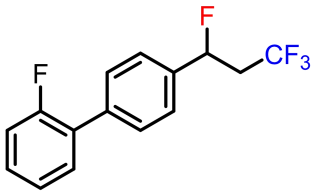
Yield: 60%. White solid. Melting point: 91.7℃. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 5.81 (dd, *J* = 46.5, 10.6 Hz, 1H), 3.72 (s, 3H), 3.69 (d, *J* = 4.3 Hz, 2H), 2.97-2.81 (m, 1H), 2.67-2.49 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.88, 141.73 (d, *J* = 3.0 Hz), 139.10, 136.73 (d, *J* = 20.2 Hz), 133.51, 129.79, 127.46, 127.29, 126.47, 125.91 (d, *J* = 6.1 Hz), 125.08 (q, *J* = 276.7 Hz), 87.89 (dq, *J* = 171.7, 3.0 Hz), 61.06, 52.10, 41.41 (qd, *J* = 29.29, 25.25 Hz), 40.75.
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.14 (d, *J* = 7.8 Hz), -175.06 (q, *J* = 7.8 Hz).
HRMS (ESI^+): calculated for $C_{18}H_{16}F_4O_2^+$ $[M + H]^+$: 341.1160; found: 341.1158.

Trimethyl(4'-(1,3,3,3-tetrafluoropropyl)-[1,1'-biphenyl]-4-yl)silane (2i)



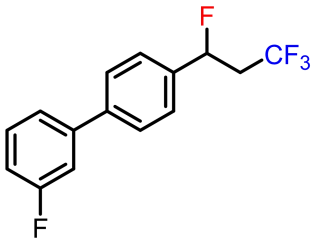
Yield: 54%. Light blue oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.57 (m, 6H), 7.43 (d, *J* = 7.6 Hz, 2H), 5.88 (dd, *J* = 48.4, 6.7 Hz, 1H), 2.97-2.80 (m, 1H), 2.71-2.46 (m, 1H), 0.31 (s, 9H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.82 (d, *J* = 2.0 Hz), 140.58, 136.44 (d, *J* = 19.2 Hz), 133.91, 129.42, 127.58, 126.44, 125.58 (d, *J* = 7.1 Hz), 125.23 (q, *J* = 221.2 Hz), 87.58 (dq, *J* = 172.7, 3.0 Hz), 41.13 (qd, *J* = 29.29, 25.25 Hz), 29.36.
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.18 (d, *J* = 8.0 Hz), -175.04 (q, *J* = 7.9 Hz).

2-Fluoro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2j)



Yield: 53%. Colorless oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.36-7.13 (m, 4H), 5.82 (dd, *J* = 47.8, 6.9 Hz, 1H), 2.96-2.80 (m, 2H), 2.70-2.49 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.96, 158.49, 137.15 (d, *J* = 20.2 Hz), 136.79, 136.79, 130.63 (d, *J* = 3.0 Hz), 129.48 (d, *J* = 3.0 Hz), 129.38, 128.15 (d, *J* = 13.1 Hz), 127.15, 125.52 (d, *J* = 7.0 Hz), 125.09 (q, *J* = 276.7 Hz), 124.47 (d, *J* = 3.0 Hz), 116.19 (d, *J* = 23.2 Hz), 87.88 (dq, *J* = 173.7, 3.0 Hz), 41.48 (qd, *J* = 28.28, 25.25 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.73 (d, *J* = 7.6 Hz), -118.59 (q, *J* = 7.8 Hz), -176.36 (q, *J* = 7.7 Hz).

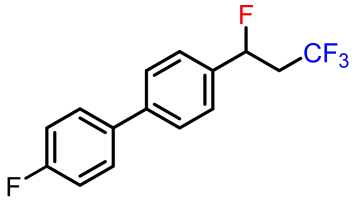
3-Fluoro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2k)



Yield: 52%. Colorless oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.45-7.29 (m, 5H), 7.15 (t, *J* = 8.7 Hz, 2H), 5.82 (dd, *J* = 47.8, 6.6 Hz, 1H), 2.98-2.80 (m, 1H), 2.70-2.49 (m, 1H).

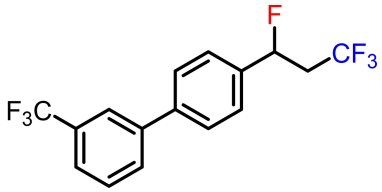
^{13}C NMR ($CDCl_3$, 101 MHz): δ 163.19 (d, *J* = 247.4 Hz), 142.49 (d, *J* = 8.1 Hz), 140.90, 137.37 (d, *J* = 20.2 Hz), 130.37 (d, *J* = 8.1 Hz), 127.56, 127.38, 126.15, 126.00 (d, *J* = 6.1 Hz), 123.83, 122.76 (d, *J* = 3.0 Hz), 114.39 (d, J = 48.5 Hz), 114.18 (d, J = 49.5 Hz), 87.80 (d, *J* = 175.7 Hz), 41.52 (qd, *J* = 29.3, 26.2, Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.13 (d, *J* = 8.0 Hz), -112.80, -175.63 (q, *J* = 7.8 Hz).

4-Fluoro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2l)



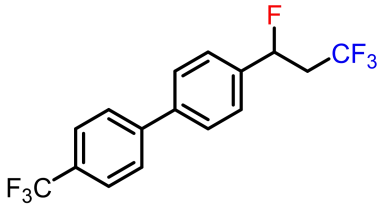
Yield: 59%. Colorless oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.55 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 5.82 (dd, *J* = 47.8, 6.6 Hz, 1H), 2.98-2.80 (m, 1H), 2.70-2.49 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.69 (d, *J* = 248.5 Hz), 141.23 (d, *J* = 2.0 Hz), 136.76 (d, *J* = 20.2 Hz), 136.37 (d, *J* = 3.0 Hz), 129.48, 128.72 (d, *J* = 8.0 Hz), 127.44, 125.98 (d, *J* = 6.1 Hz), 125.07 (q, *J* = 276.7 Hz), 115.78 (d, *J* = 21.2 Hz), 87.88 (dq, *J* = 172.7, 3.0 Hz), 41.46 (qd, *J* = 29.29, 26.26 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.13 (d, *J* = 7.7 Hz), -114.98, -175.16 (q, *J* = 7.4 Hz).

3'-(1,3,3,3-Tetrafluoropropyl)-3-(trifluoromethyl)-1,1'-biphenyl (2m)



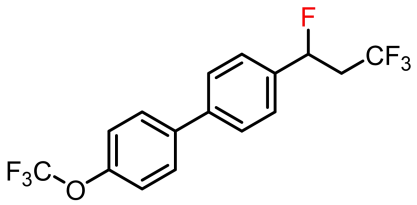
Yield: 67%. Light blue transparent oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.70-7.62 (m, 3H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 5.83 (dd, *J* = 47.7, 6.5 Hz, 1H), 2.97-2.81 (m, 1H), 2.69-2.52 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.06, 140.71 (d, *J* = 2.0 Hz), 137.62 (d, *J* = 20.0 Hz), 131.32 (d, *J* = 32.2 Hz), 130.41, 129.38, 127.67, 126.11 (d, *J* = 7.1 Hz), 125.57 (q, *J* = 277.8 Hz), 124.17 (q, *J* = 46.5 Hz), 124.13 (q, *J* = 46.5 Hz), 87.82 (d, *J* = 176.8 Hz), 41.43 (qd, *J* = 29.3, 26.2, Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.66 (d, *J* = 8.2 Hz), -64.12 (d, *J* = 7.9 Hz), -175.88 (q, *J* = 7.8 Hz).

4-(1,3,3,3-Tetrafluoropropyl)-4'-(trifluoromethyl)-1,1'-biphenyl (2n)



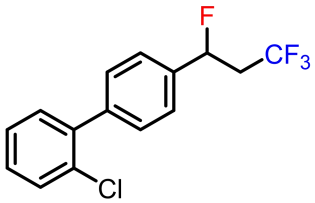
Yield: 61%. White solid. Melting point: 68.5℃. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.62 (m, 6H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.84 (dd, *J* = 47.7, 6.5 Hz, 1H), 3.02-2.76 (m, 1H), 2.74-2.47 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.76, 140.70 (d, *J* = 2.1 Hz), 137.78 (d, *J* = 19.8 Hz), 129.80 (d, *J* = 32.4 Hz), 129.23 (d, J = 6.1 Hz), 129.21 (q, *J* = 218.2 Hz), 124.2 (q, *J* = 272.7 Hz), 126.09 (d, *J* = 6.1 Hz), 125.83 (q, *J* = 4.0 Hz), 125.05 (q, *J* = 278.8 Hz), 87.80 (dq, *J* = 176.8, 2.0 Hz), 41.43 (qd, *J* = 29.4, 26.4 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.48, -64.13 (d, *J* = 7.8 Hz), -175.93 (q, *J* = 7.8 Hz).

4-(1,3,3,3-Tetrafluoropropyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (2o)



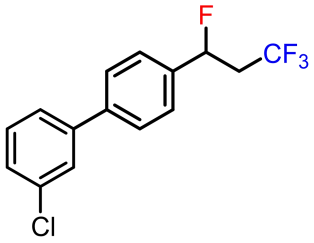
Yield: 60%. Colorless oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.58 (m, 4H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.82 (dd, *J* = 47.7, 6.5 Hz, 1H), 2.96-2.81 (m, 1H), 2.69-2.52 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 148.93 (d, *J* = 2.0 Hz), 140.79 (d, *J* = 2.0 Hz), 138.97, 137.18 (d, *J* = 20.2 Hz), 128.49, 127.55, 126.42, 126.03 (q, *J* = 278.8 Hz), 125.13 (q, *J* = 278.8 Hz), 87.83 (dq, *J* = 176.8, 4.0 Hz), 41.45 (qd, *J* = 29.3, 26.3 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -58.33, -64.64 (d, *J* = 6.9 Hz), -176.03 (q, *J* = 7.0 Hz).

2-Chloro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2p)



Yield: 67%. Colorless oil. The reaction time: 12 h.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.47 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35-7.28 (m, 3H), 5.83 (dd, *J* = 47.8, 7.1 Hz, 1H), 2.99-2.80 (m, 1H), 2.72-2.50 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.34 (d, *J* = 2.0 Hz), 139.61, 137.10 (d, *J* = 20.2 Hz), 132.40, 131.24, 130.03, 129.96, 129.83, 128.89, 128.86, 127.35, 126.92, 125.47, 125.44 (d, *J* = 6.1 Hz), 125.11 (q, *J* = 277.8 Hz), 87.90 (dq, *J* = 172.7, 3.0 Hz), 41.50 (qd, *J* = 29.29, 26.26 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.19 (d, *J* = 7.8 Hz), -175.75 (q, *J* = 7.7 Hz).

3-Chloro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2q)



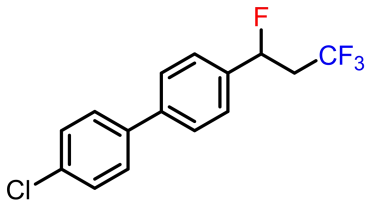
Yield: 71%. Colorless oil. The reaction time: 12 h.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 1H), 7.47-7.32 (m, 5H), 5.82 (dd, *J* = 47.7, 6.6 Hz, 1H), 2.98-2.79 (m, 1H), 2.71-2.48 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.07, 140.76, 140.75, 137.40 (d, *J* = 20.2 Hz), 134.79, 130.11, 129.17, 127.72, 127.56, 127.27, 126.01 (d, *J* = 6.1 Hz), 125.27, 125.04 (q, *J* = 275.7 Hz), 87.81 (dq, *J* = 173.7, 3.0 Hz), 41.47 (qd, *J* = 28.28, 26.26 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.11 (d, *J* = 8.0 Hz), -175.67 (q, *J* = 7.9 Hz).

4-Chloro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2r)



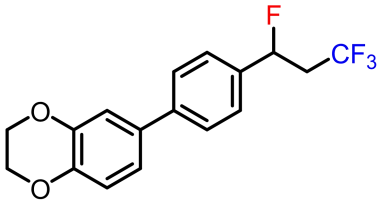
Yield: 58%. White solid. Melting point: 87℃. The reaction time: 12 h.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.46-7.35 (m, 4H), 5.82 (dd, *J* = 47.7, 6.5 Hz, 1H), 2.92-2.85 (m, 1H), 2.70-2.48 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.95 (d, *J* = 2.0 Hz), 138.68, 137.11 (d, *J* = 20.2 Hz), 133.89, 129.04, 128.36, 127.41, 126.02 (d, *J* = 6.1 Hz), 125.06 (q, *J* = 277.8 Hz), 87.84 (dq, *J* = 172.7, 3.0 Hz), 41.45 (qd, *J* = 29.29, 26.26 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.11 (d, *J* = 7.7 Hz), -175.39 (q, *J* = 7.6 Hz).

6-(4-(1,3,3,3-Tetrafluoropropyl)phenyl)-2,3-dihydrobenzo[b][1,4]dioxine (2s)



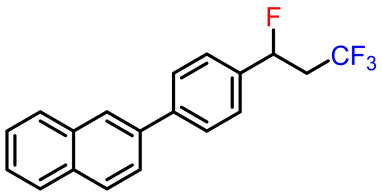
Yield: 35%. Colorless oil. The reaction time: 12 h.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.40 (m, 3H), 7.38 (s, 1H), 7.19-6.98 (m, 2H), 6.96-6.83 (m, 1H), 5.79 (dd, *J* = 47.7, 6.9 Hz, 1H), 4.29 (d, *J* = 8.4 Hz, 4H), 2.97-2.78 (m, 1H), 2.70-2.47 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.76, 143.52, 141.59, 136.33, 136.13, 133.74, 130.02, 127.43, 127.11, 125.92, 125.86, 125.04, 124.98, 121.43, 120.13, 119.38, 117.67, 115.85, 112.66, 88.82, 88.79, 87.08, 87.04, 64.41, 41.71, 41.43, 41.14.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.16 (d, *J* = 7.7 Hz), -174.66 (q, *J* = 7.8 Hz).

2-(4-(1,3,3,3-Tetrafluoropropyl)phenyl)naphthalene (2t)



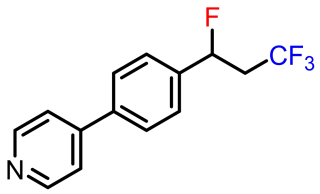
Yield: 48%. Colorless oil. The reaction time: 12 h.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (s, 1H), 7.96-7.86 (m, 3H), 7.80-7.71 (m, 3H), 7.57-7.48 (m, 4H), 5.85 (dd, *J* = 46.5, 10.7 Hz, 1H), 2.98-2.84 (m, 1H), 2.73-2.51 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.12 (d, *J* = 2.0 Hz), 137.54, 136.80 (d, *J* = 20.2 Hz), 133.60, 132.78, 128.59, 128.21, 127.83, 127.66, 126.45, 126.20, 126.00 (d, *J* = 7.1 Hz), 125.29, 125.18 (q, *J* = 290.9 Hz), 87.94 (dq, *J* = 172.7, 3.0 Hz), 41.48 (qd, *J* = 29.29, 26.26 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.09 (d, *J* = 8.0 Hz), -175.06 (q, *J* = 8.0 Hz).

4-(4-(1,3,3,3-Tetrafluoropropyl)phenyl)pyridine (2u)



Yield: 63%. Colorless oil. The reaction time: 12 h.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69 (d, *J* = 4.6 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 4H), 5.83 (dd, *J* = 49.0, 10.7 Hz, 1H), 2.97-2.79 (m, 1H), 2.71-2.49 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.28, 147.44, 139.05 (d, *J* = 2.0 Hz), 138.67 (d, *J* = 19.2 Hz), 127.50, 126.16 (d, *J* = 7.1 Hz), 124.96 (q, *J* = 276.7 Hz), 121.60, 87.67 (dq, *J* = 174.7, 3.0 Hz), 41.45 (qd, *J* = 28.28, 26.26 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.08 (d, *J* = 7.8 Hz), -176.61 (q, *J* = 7.7 Hz).

HRMS (ESI^+): calculated for $C_{14}H_{11}F_3N^+$ $[M + H]^+$: 251.0922; found: 251.0918.

4. References

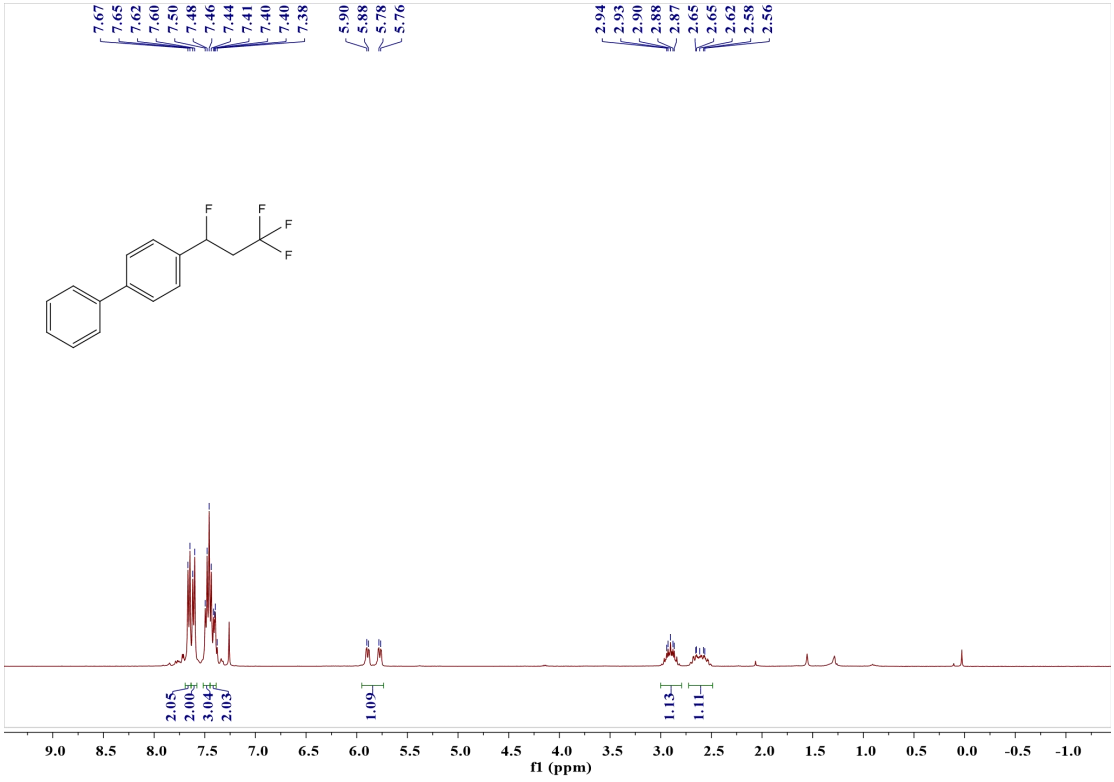
(1) Pfeifer, L.; Gouverneur, V. Controlled Single and Double Iodofluorination of Alkynes with DIH- and HF-Based Reagents. *Org. Lett.* **2018**, *20*, 1576-1579.

(2) C. Liu, R. Li, W. Zhou, Y. Liang, Y. Shi, R.-L. Li, Y. Ling, Y. Yu, J. Li, B. Zhang, Selectivity Origin of Organic Electrosynthesis Controlled by Electrode Materials: A Case Study on Pinacols, *ACS Catal.* **2018,** *11*, 8958-8967.

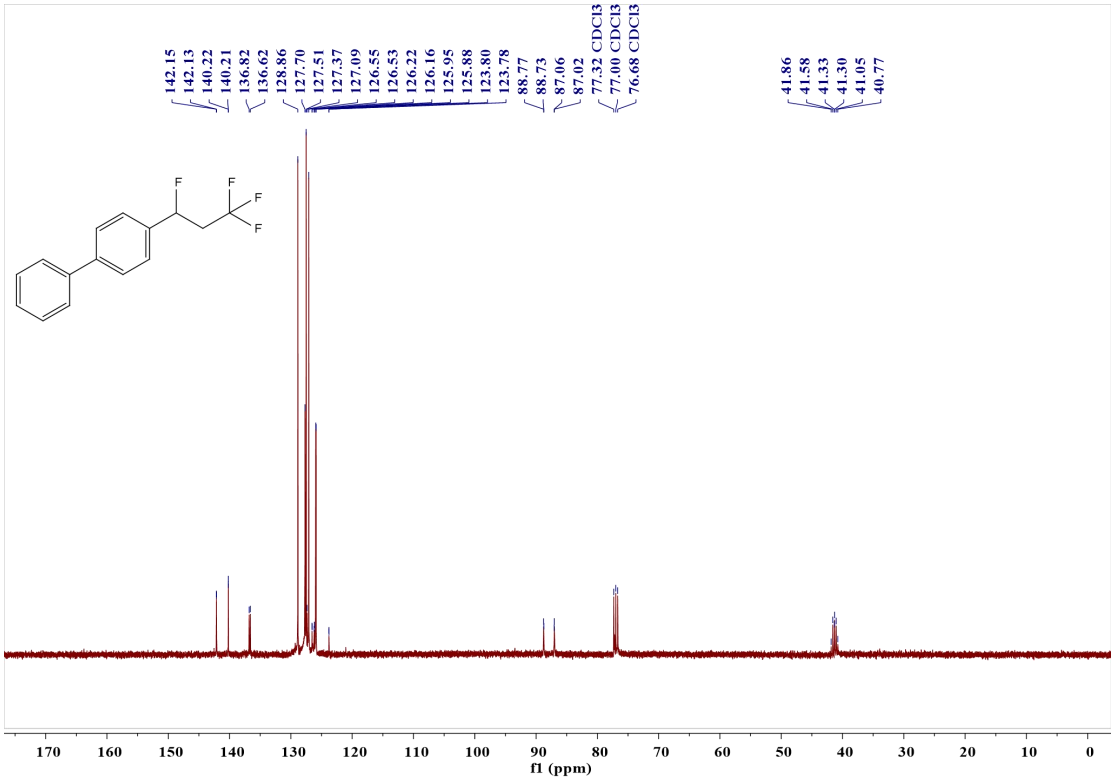
5. NMR spectra of Products

4-(1,3,3,3-Tetrafluoropropyl)-1,1'-biphenyl (2a)

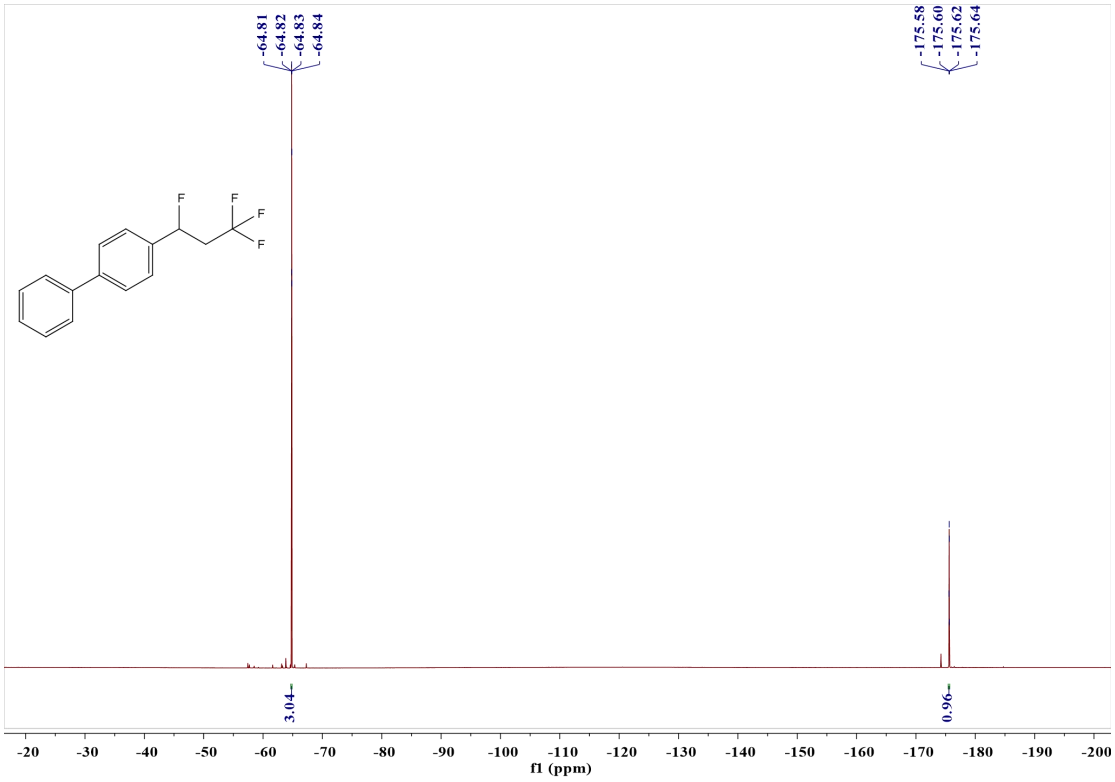
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

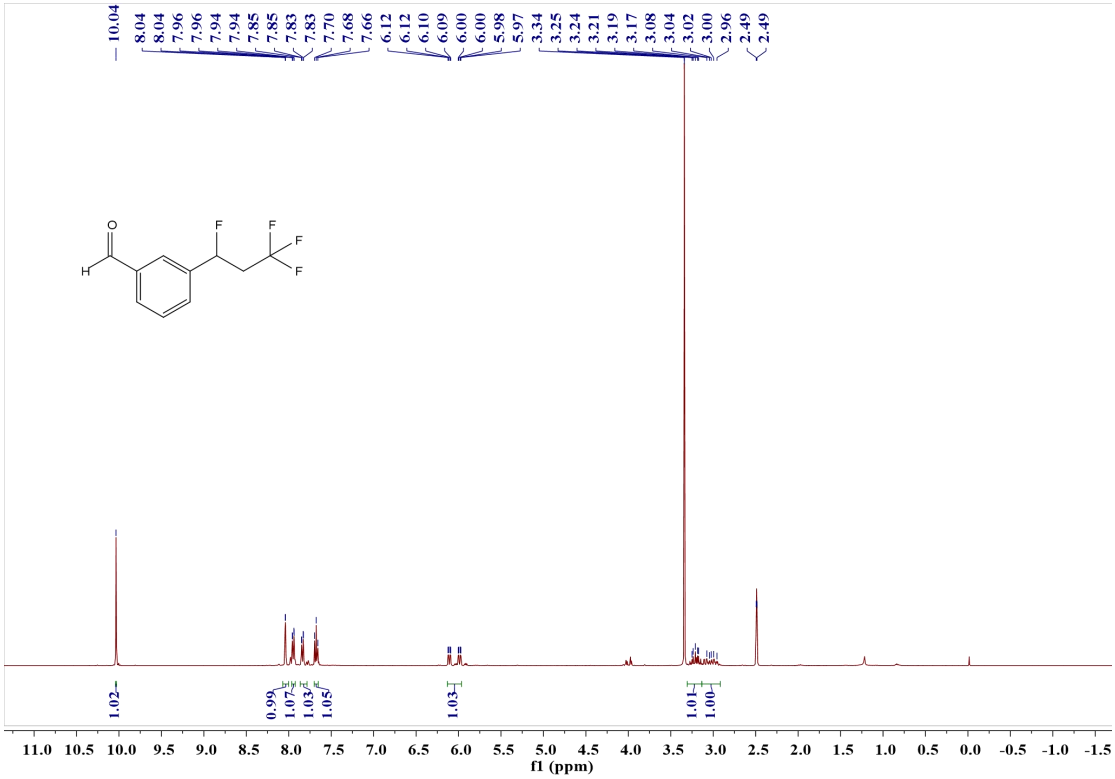


(^{19}F NMR, $CDCl_3$, 376 MHz)

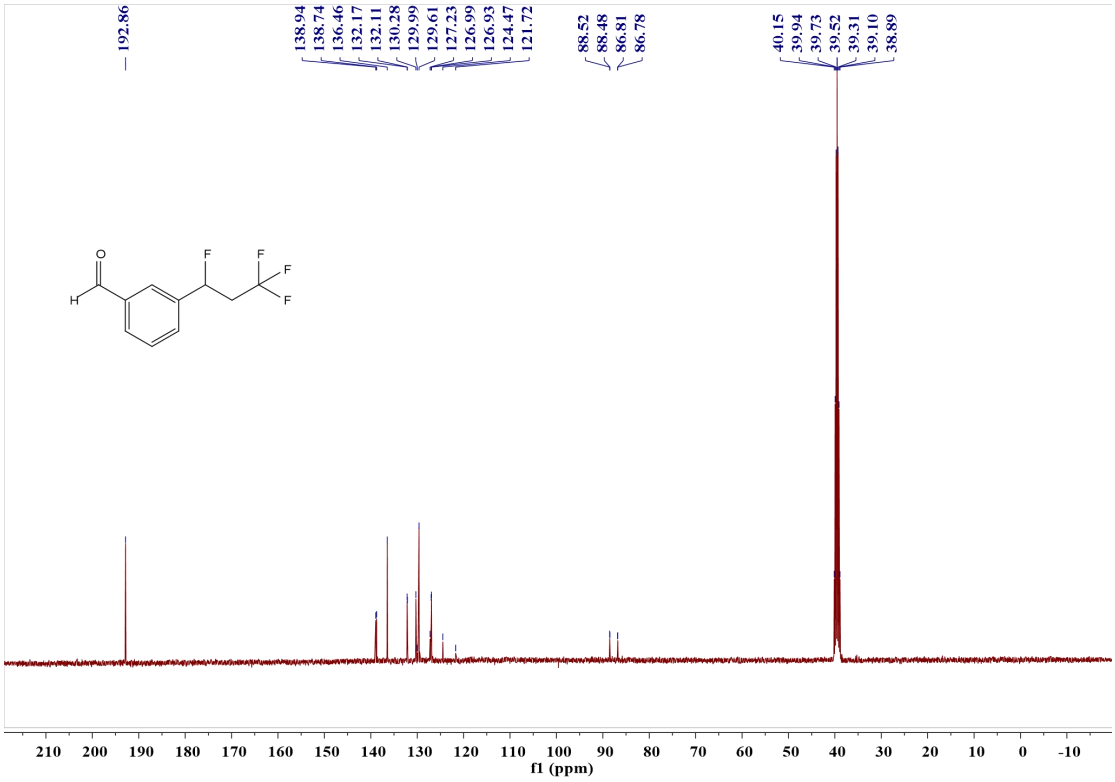


3-(1,3,3,3-tetrafluoropropyl)benzaldehyde (2b)

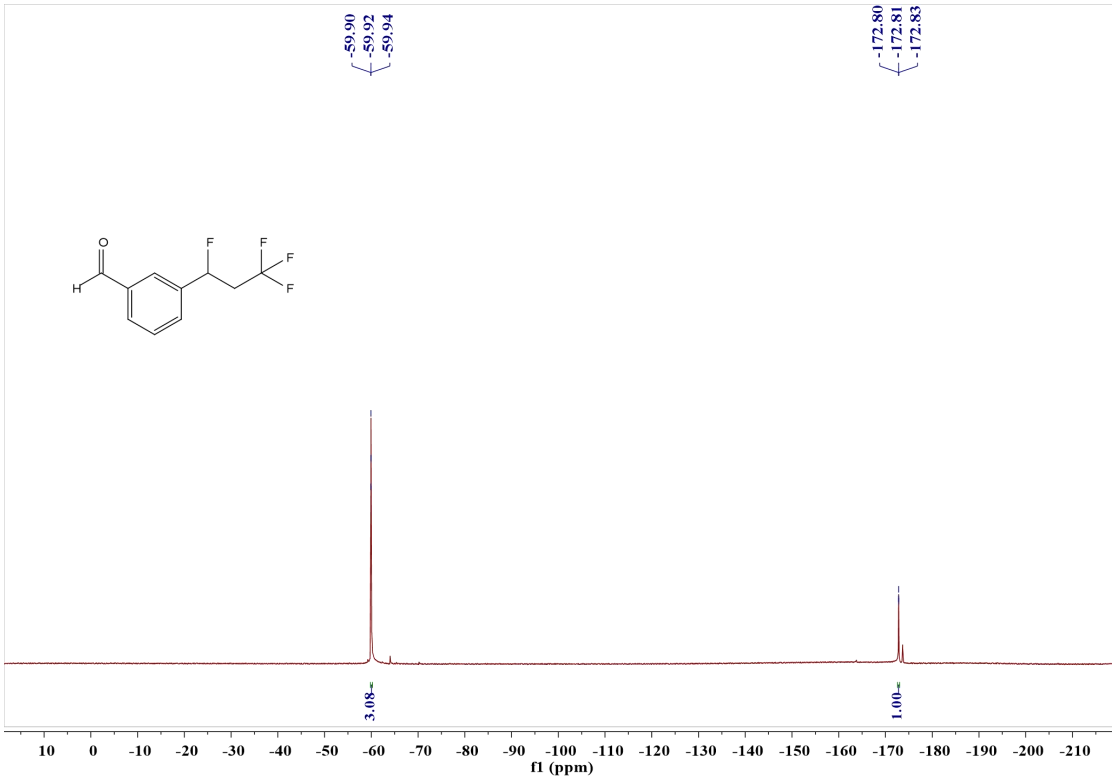
(^{1}H NMR, DMSO-*d*6, 400 MHz)



(^{13}C NMR, DMSO-*d*6, 101 MHz)

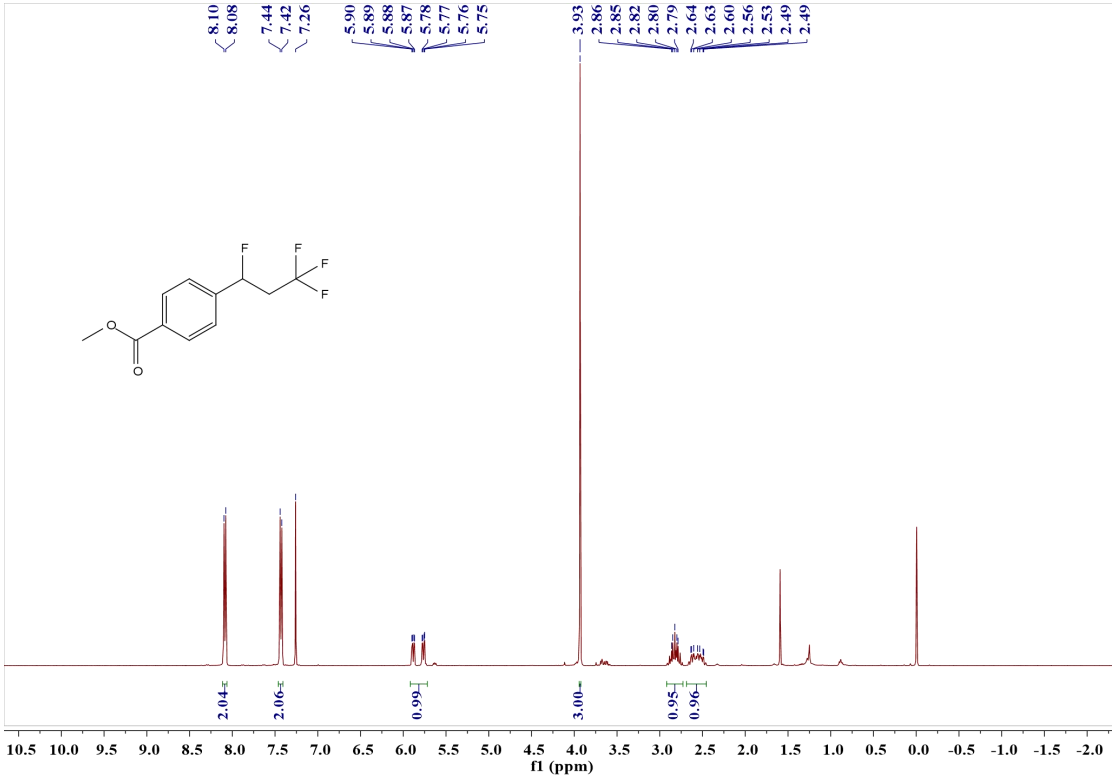


(^{19}F NMR, DMSO-*d*6, 376 MHz)

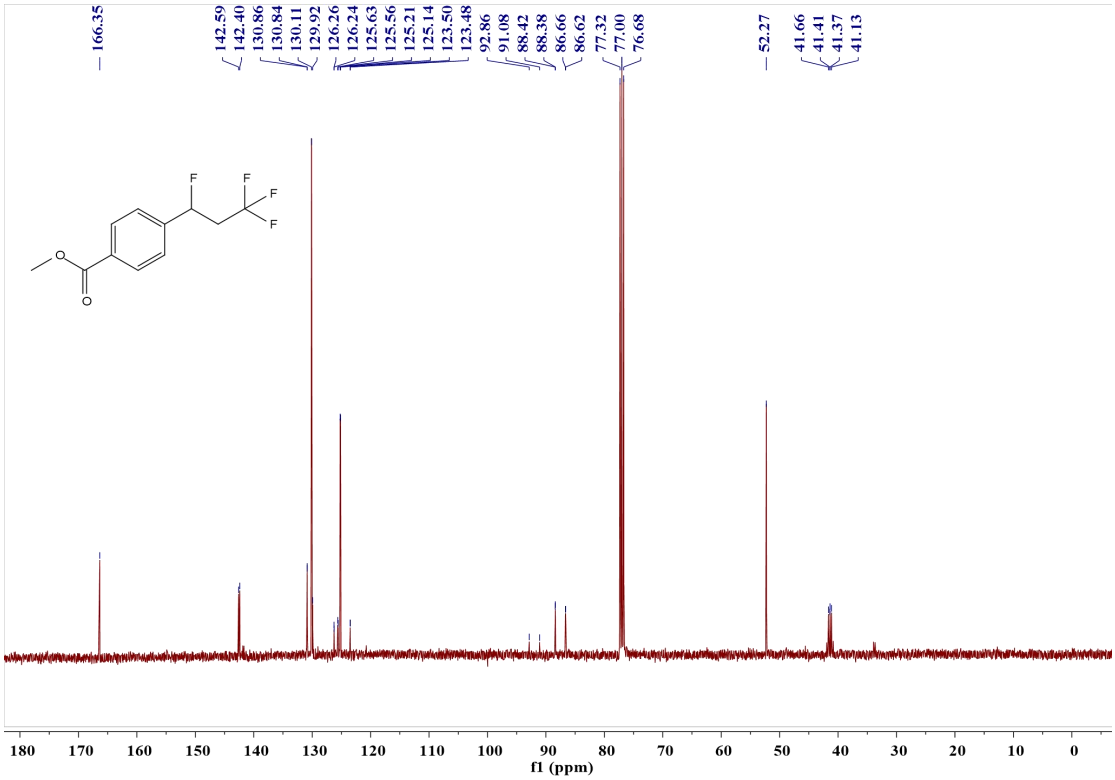


methyl 4-(1,3,3,3-tetrafluoropropyl)benzoate (2c)

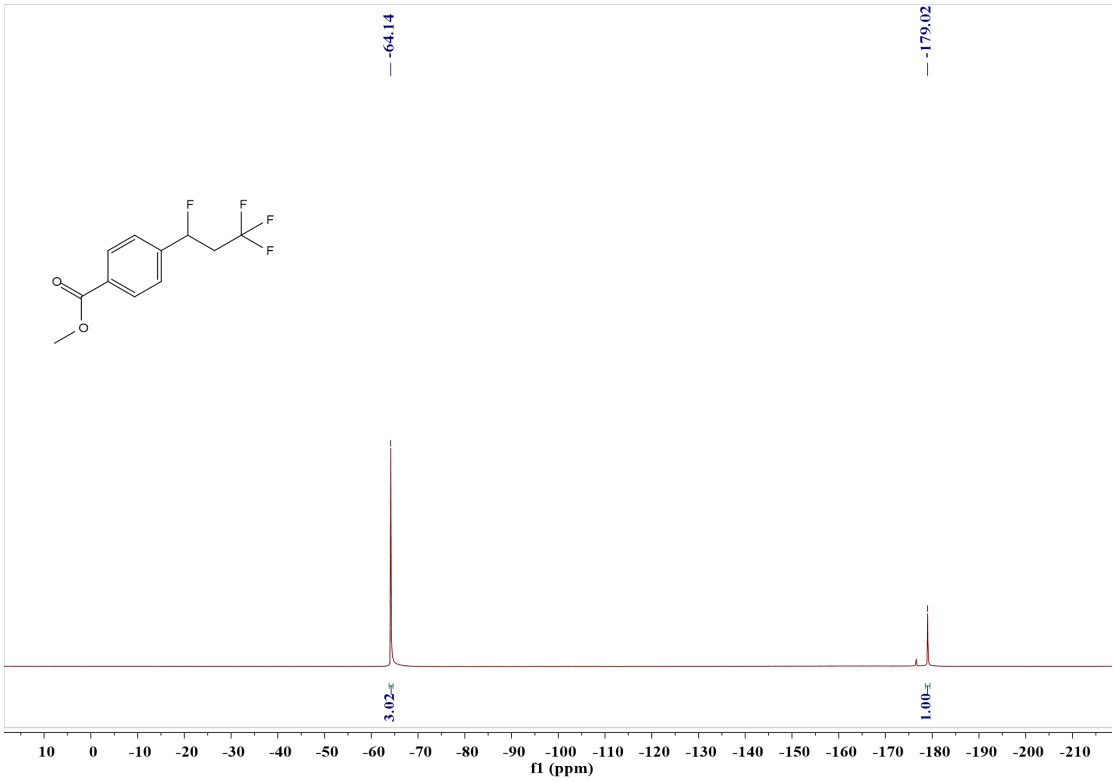
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

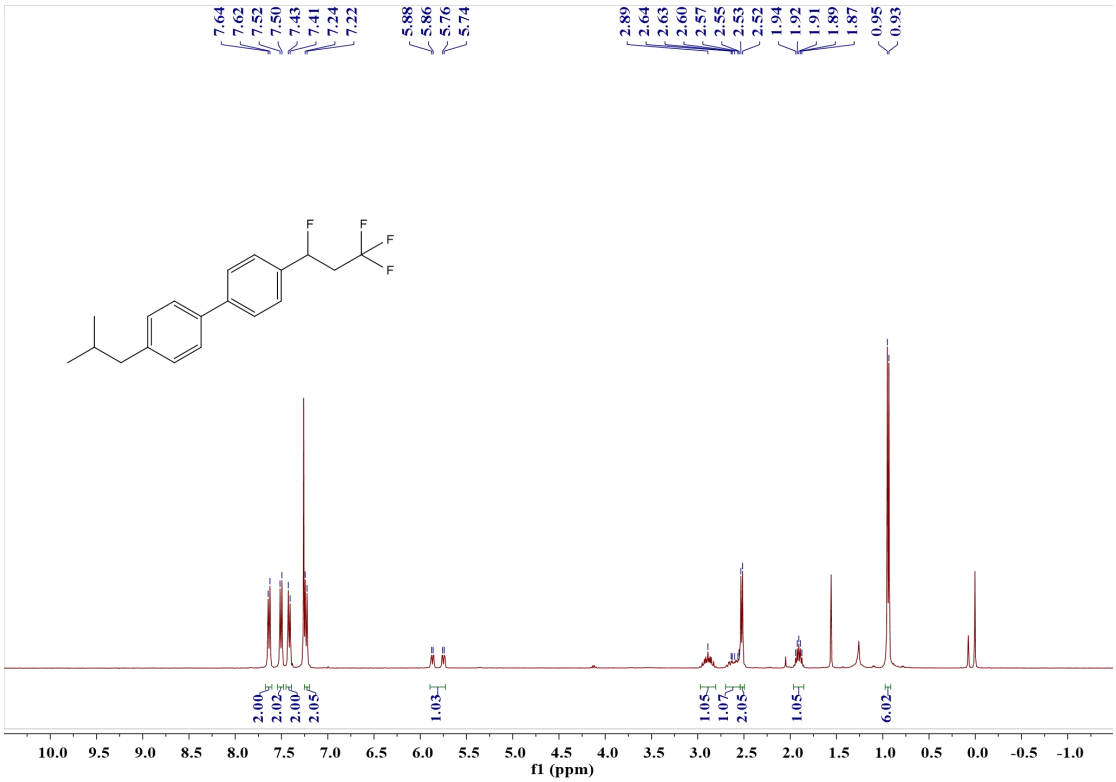


(^{19}F NMR, $CDCl_3$, 376 MHz)

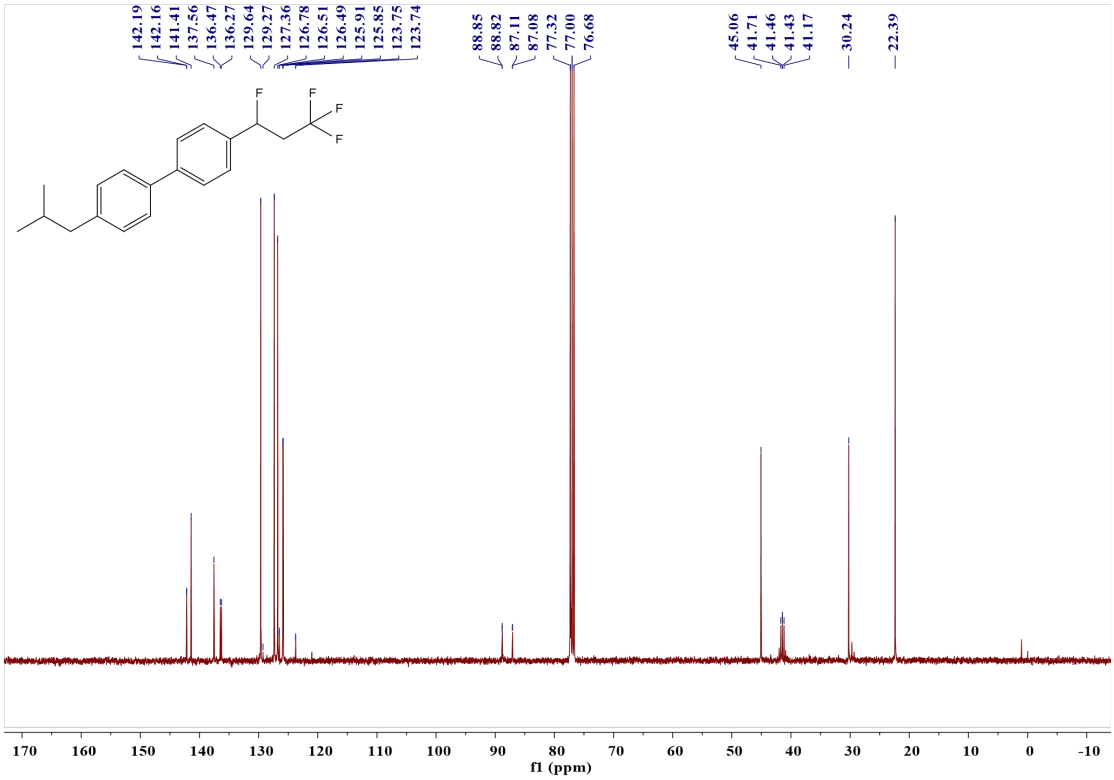


4-Isobutyl-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2d)

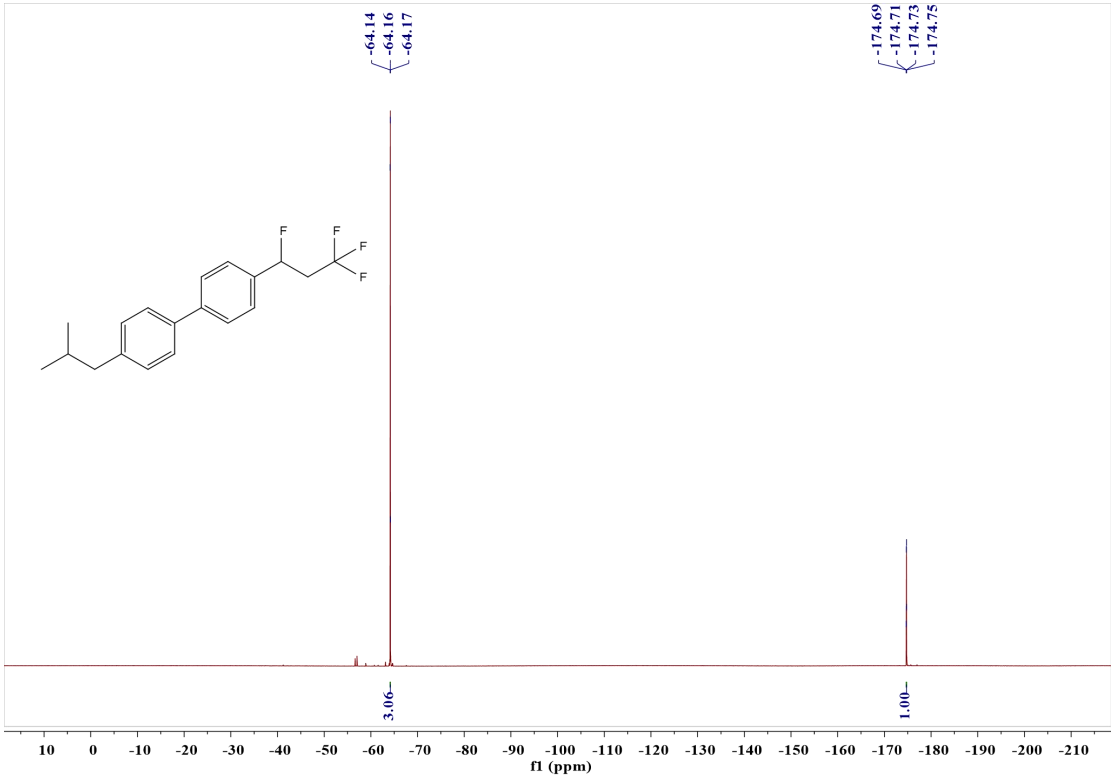
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

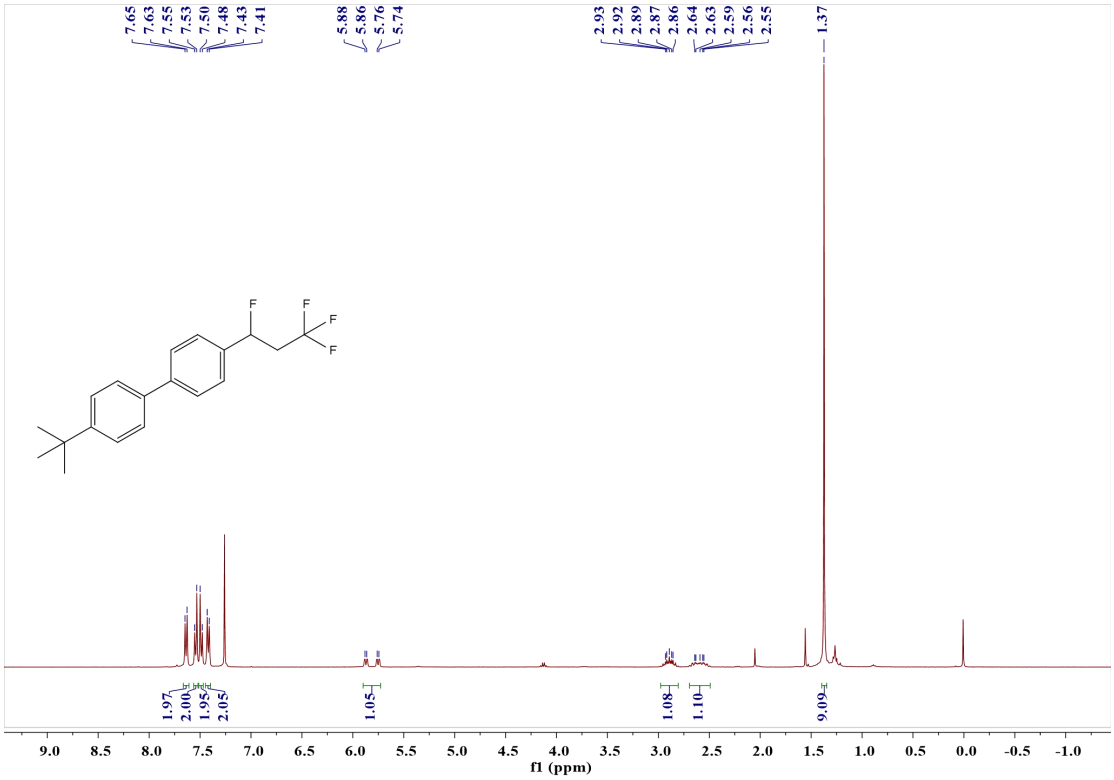


(^{19}F NMR, $CDCl_3$, 376 MHz)

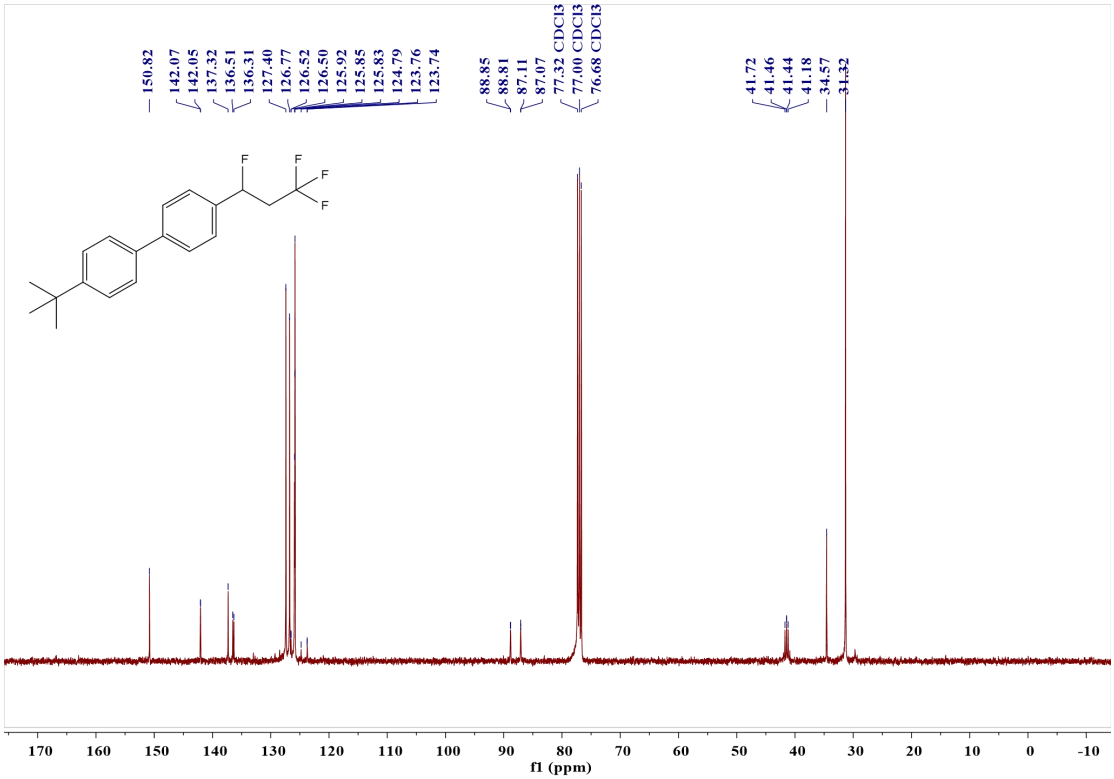


4-(Tert-butyl)-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2e)

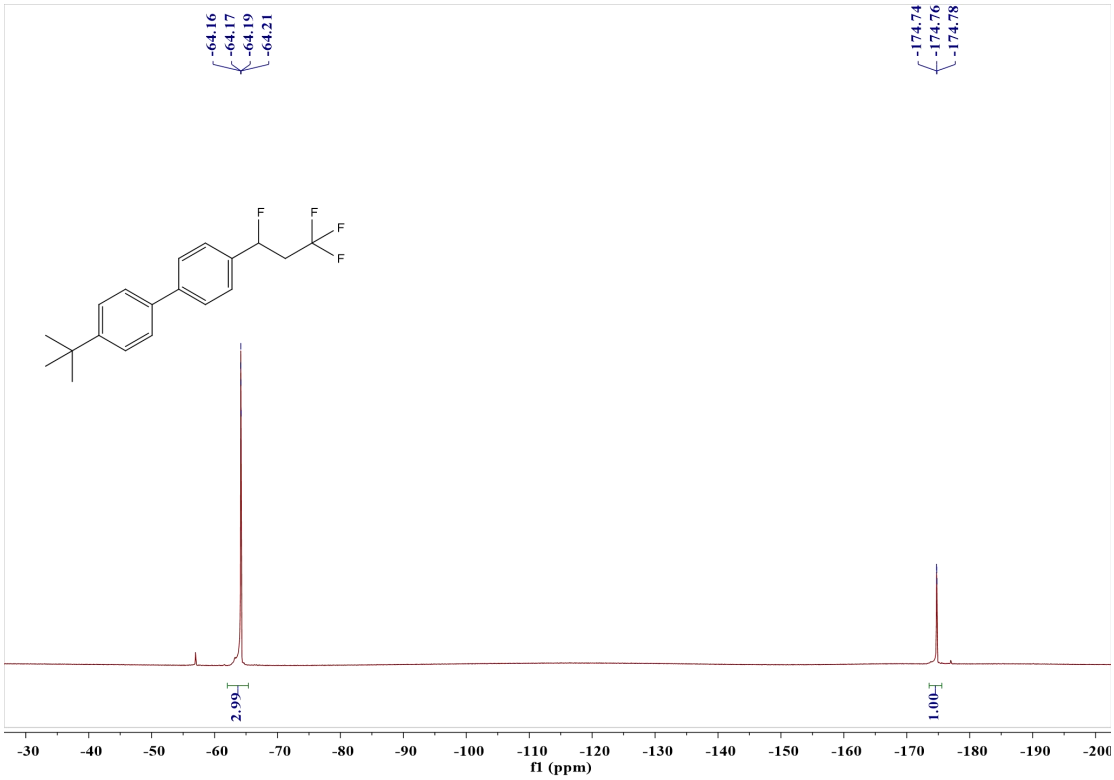
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

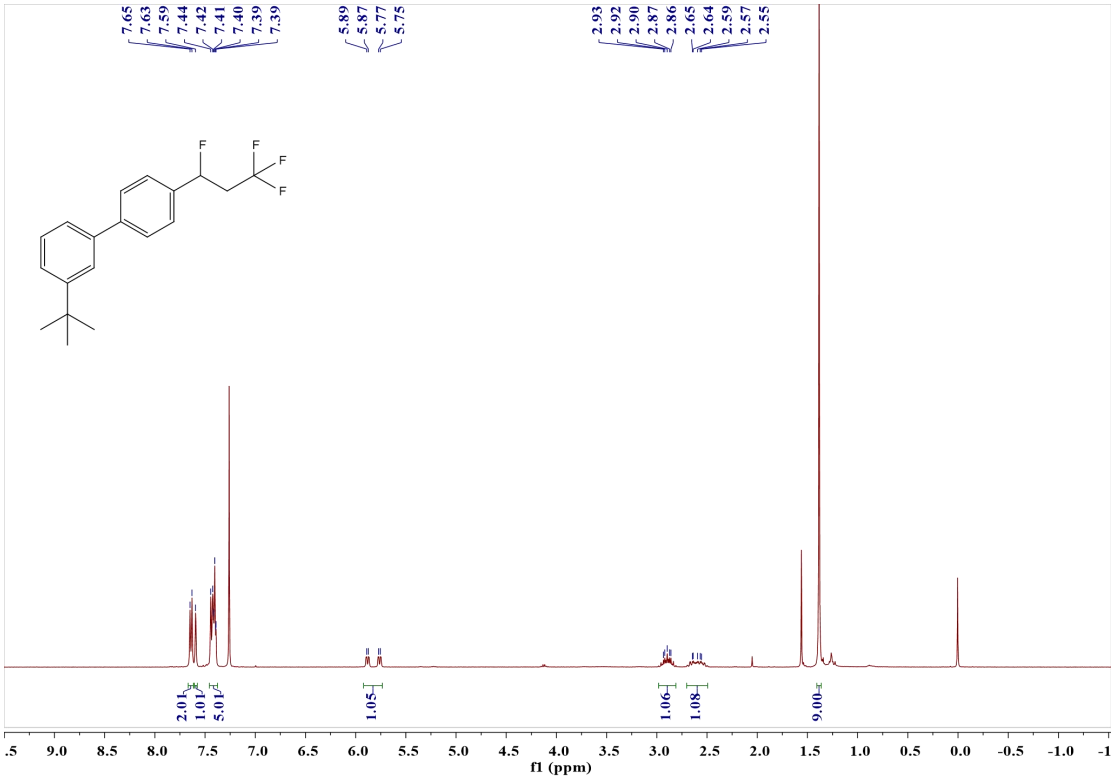


(^{19}F NMR, $CDCl_3$, 376 MHz)

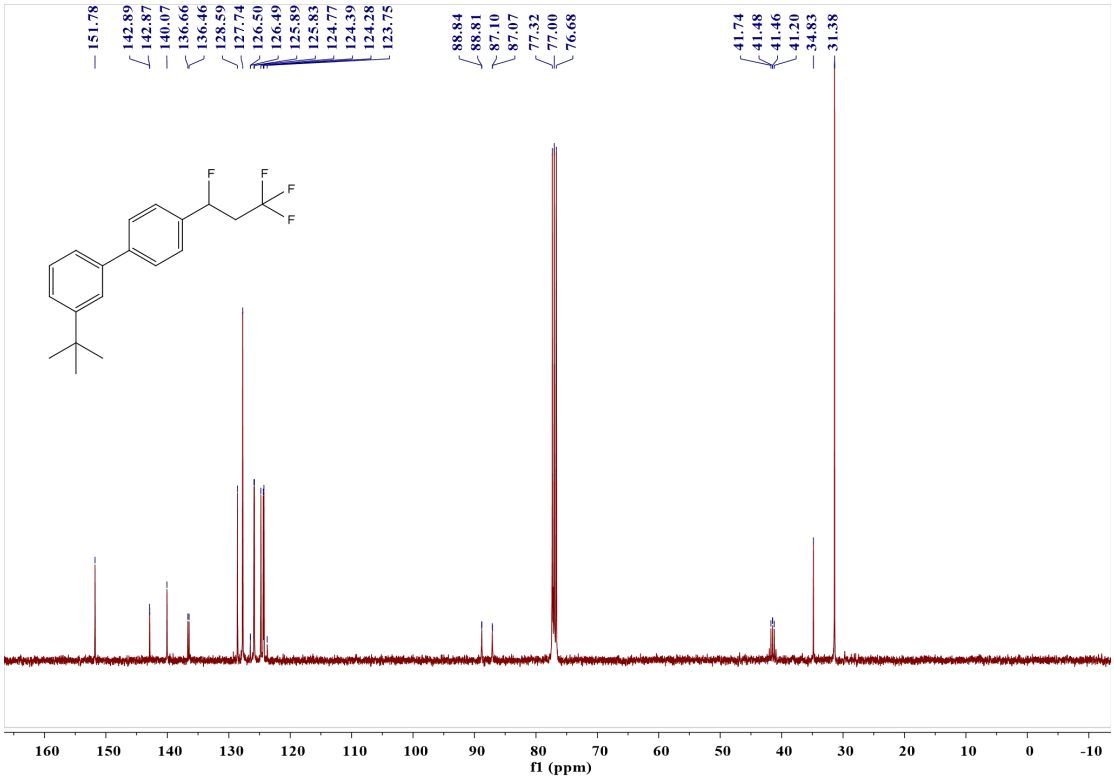


3-(Tert-butyl)-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2f)

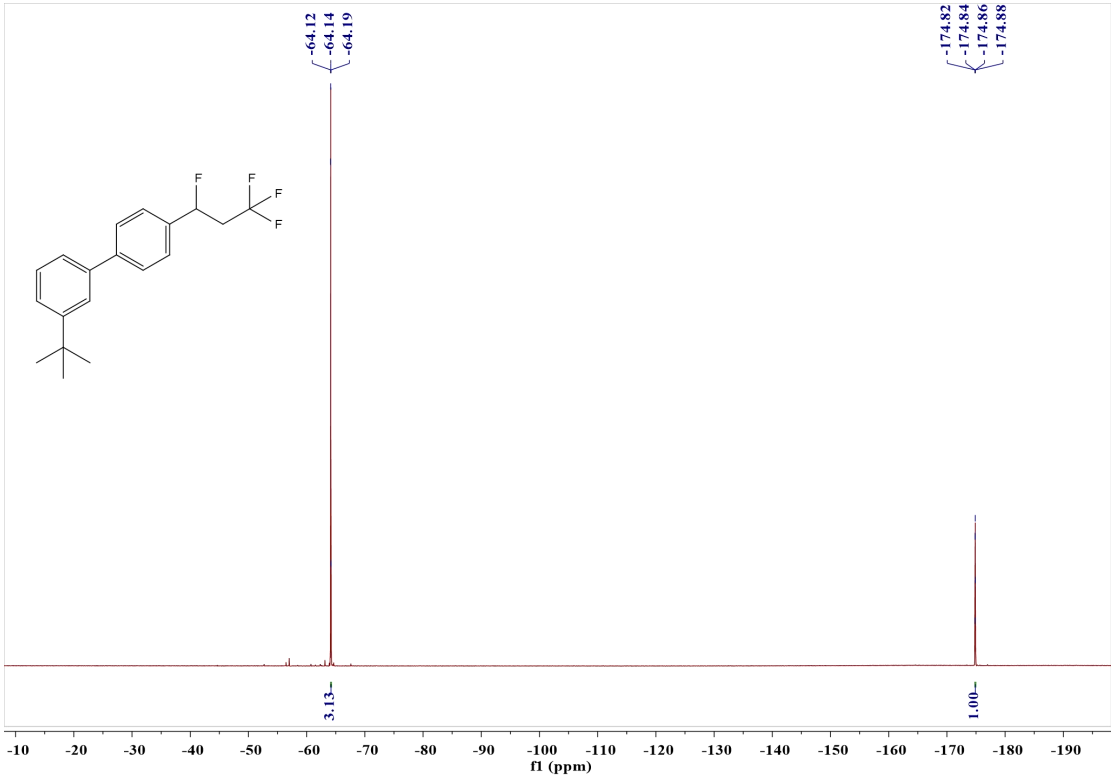
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

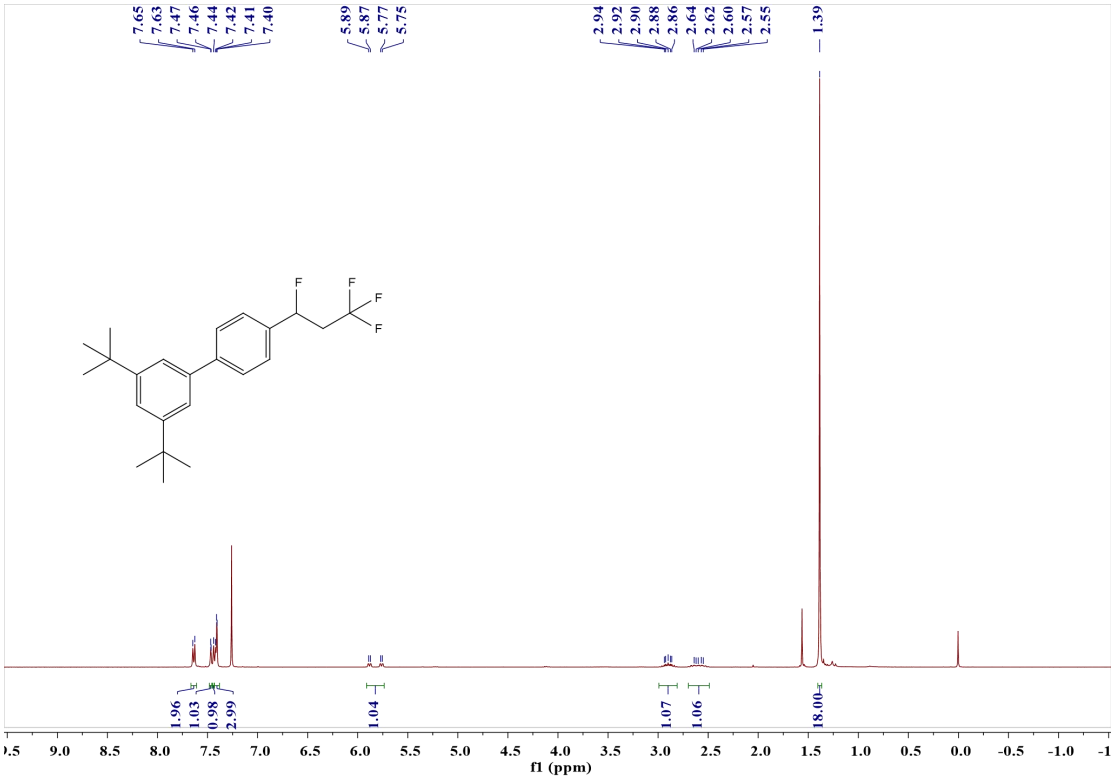


(^{19}F NMR, $CDCl_3$, 376 MHz)

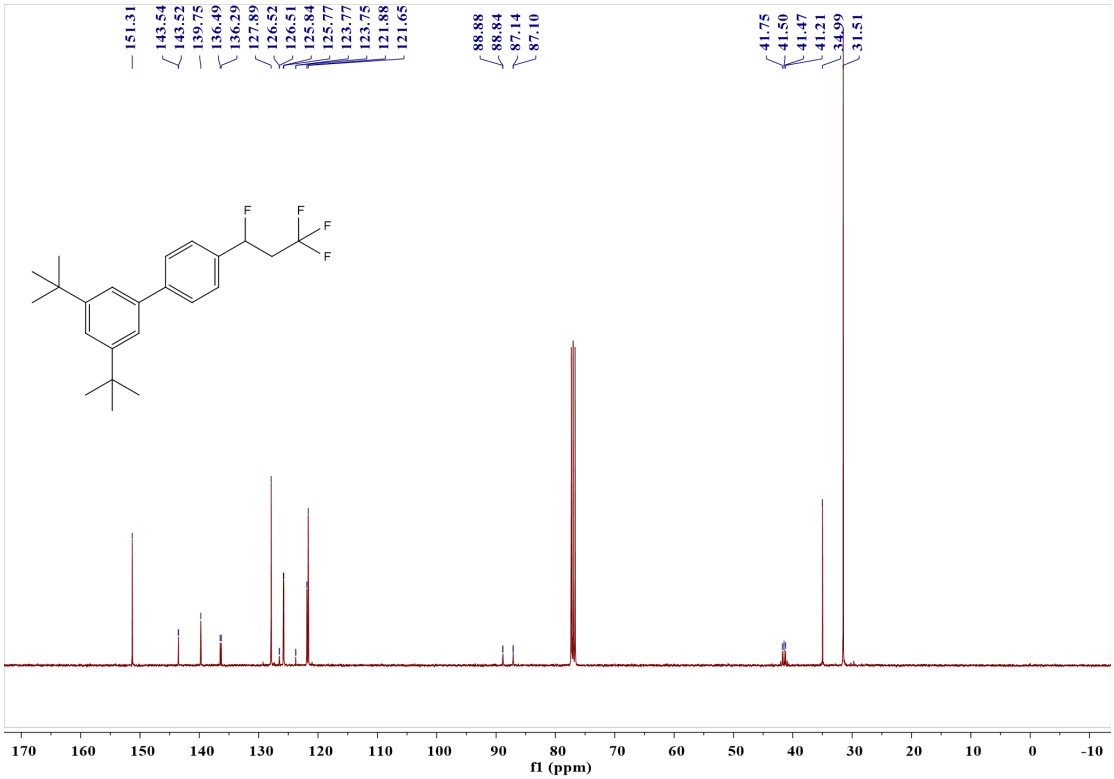


3,5-Di-tert-butyl-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2g)

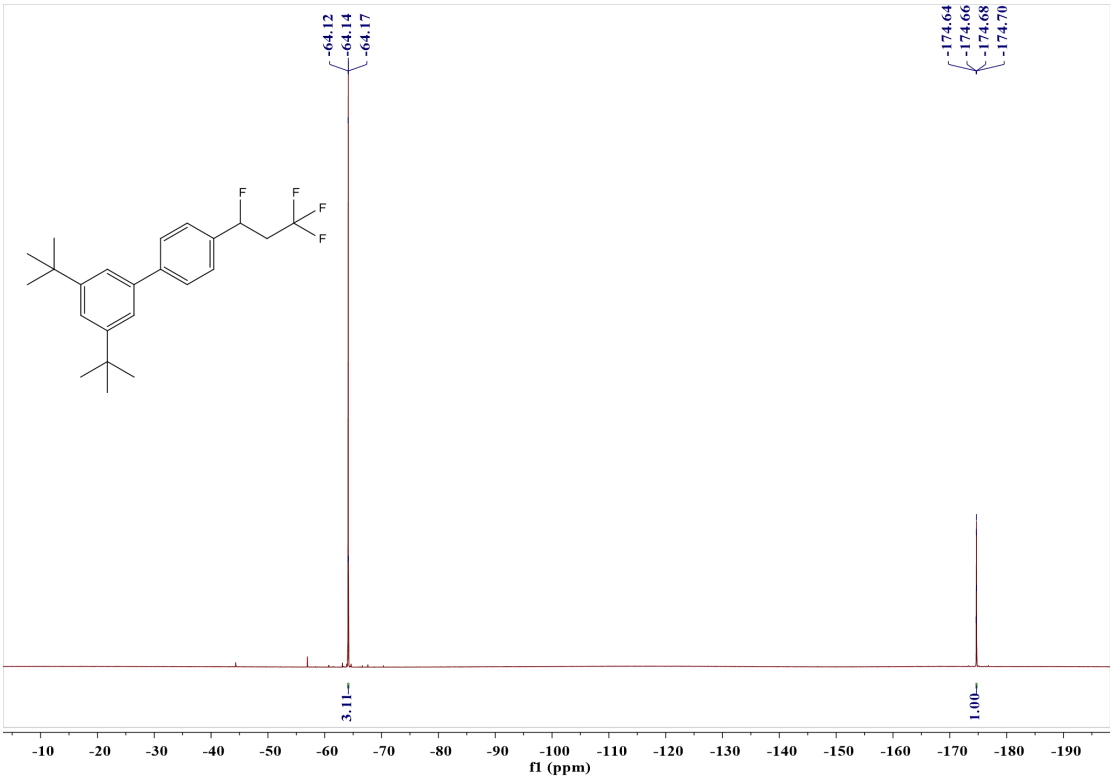
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

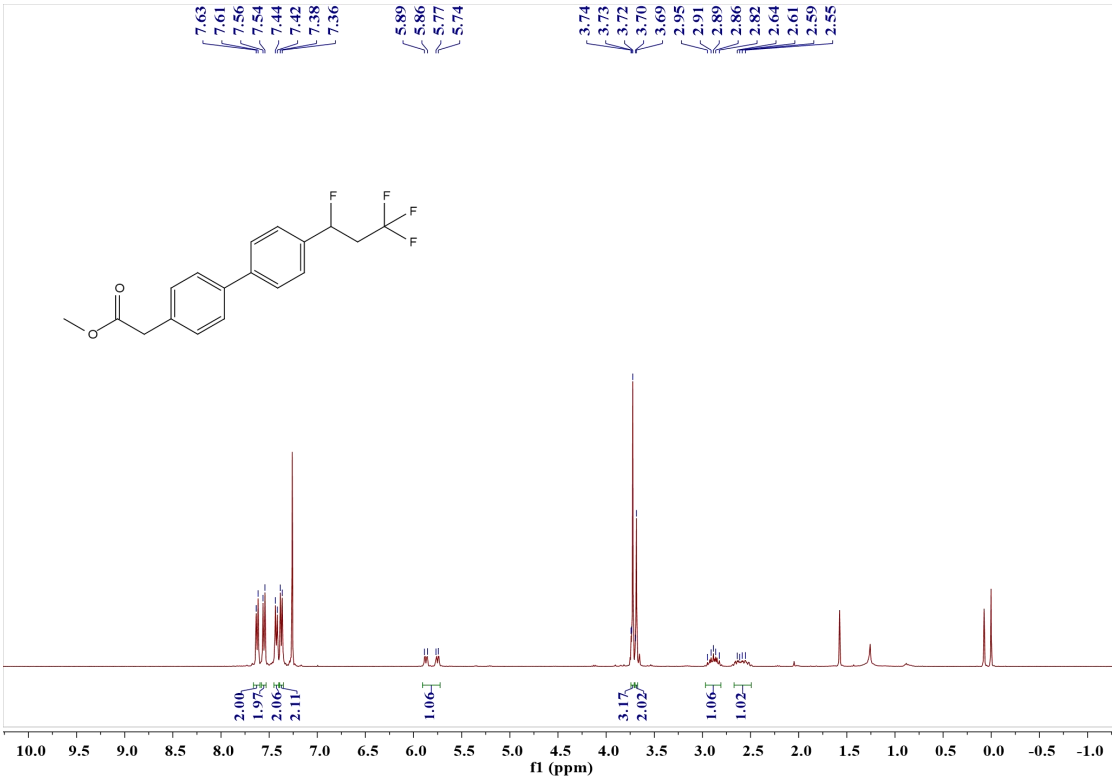


(^{19}F NMR, $CDCl_3$, 376 MHz)

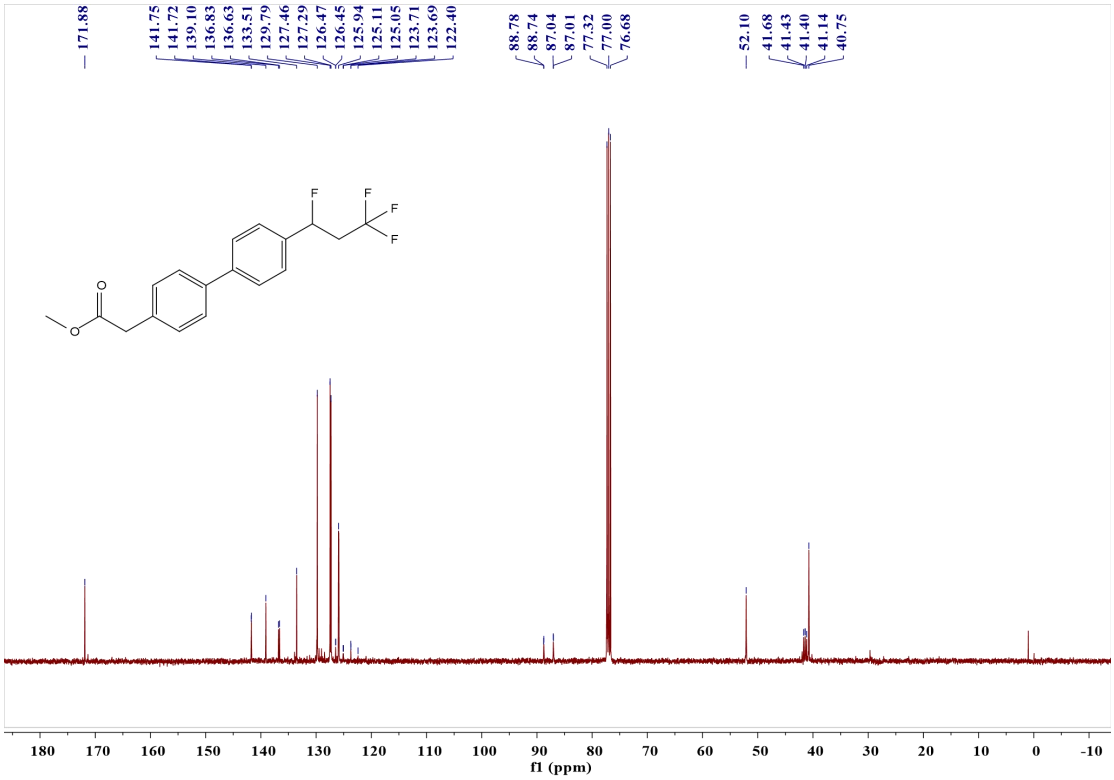


Methyl 2-(4'-(1,3,3,3-tetrafluoropropyl)-[1,1'-biphenyl]-4-yl)acetate (2h)

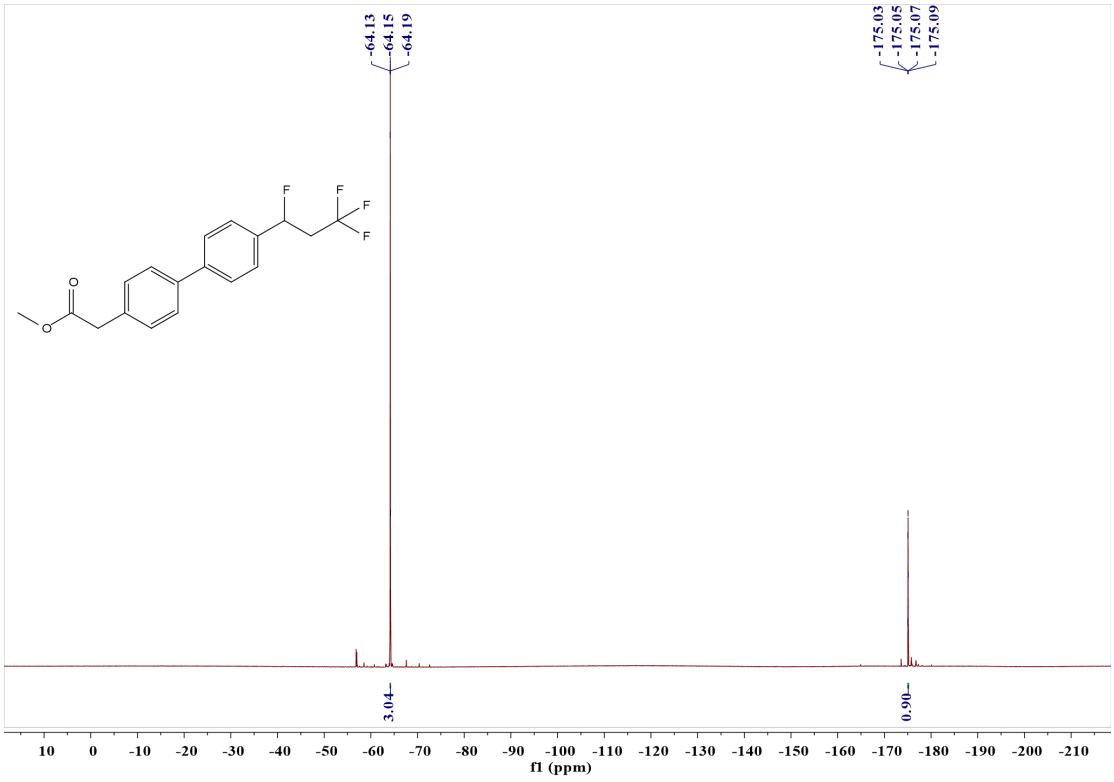
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

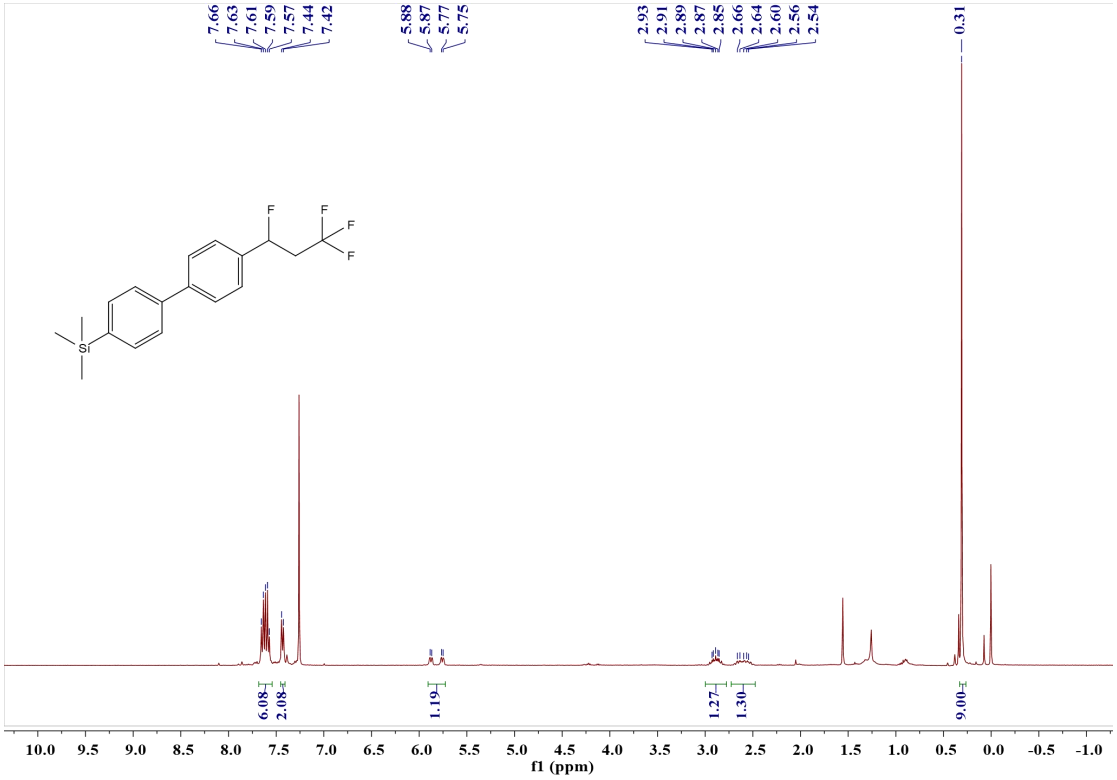


(^{19}F NMR, $CDCl_3$, 376 MHz)

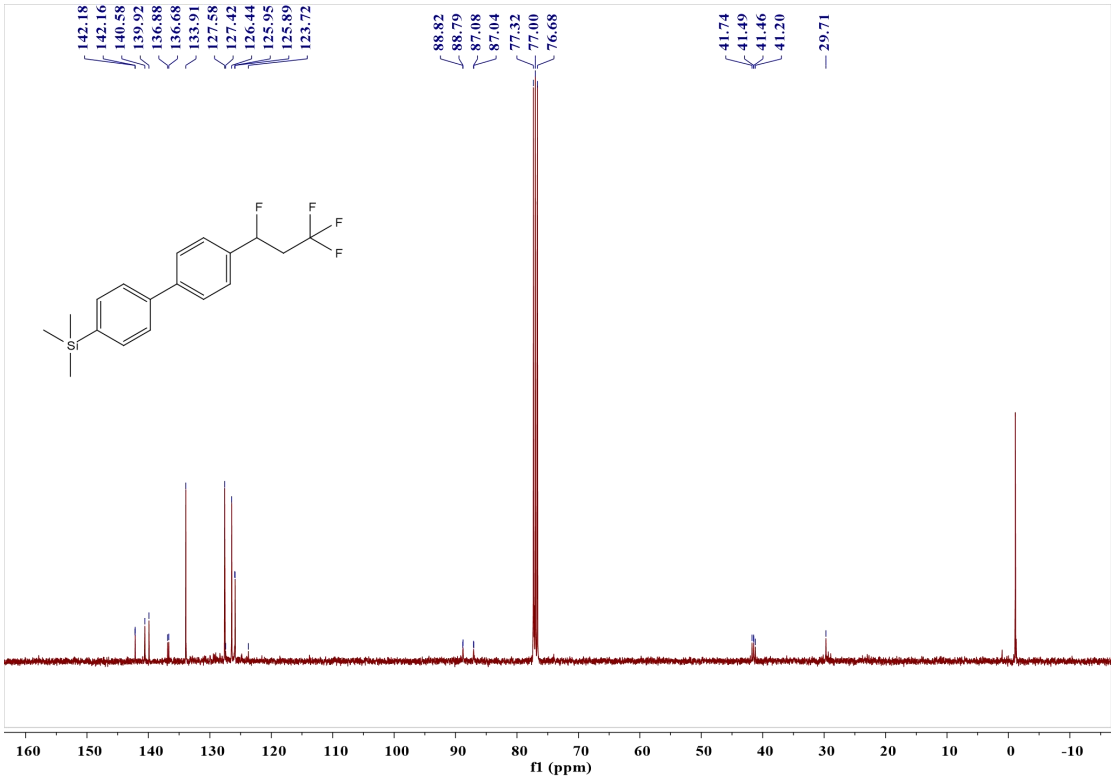


Trimethyl(4'-(1,3,3,3-tetrafluoropropyl)-[1,1'-biphenyl]-4-yl)silane (2i)

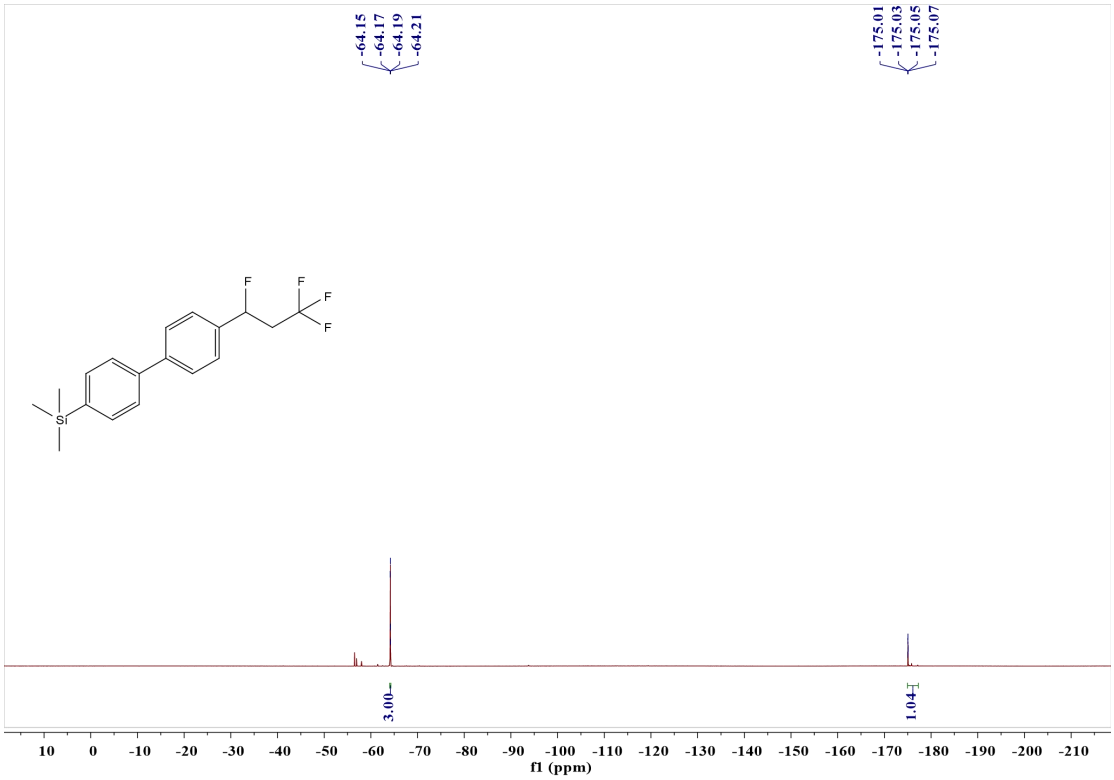
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

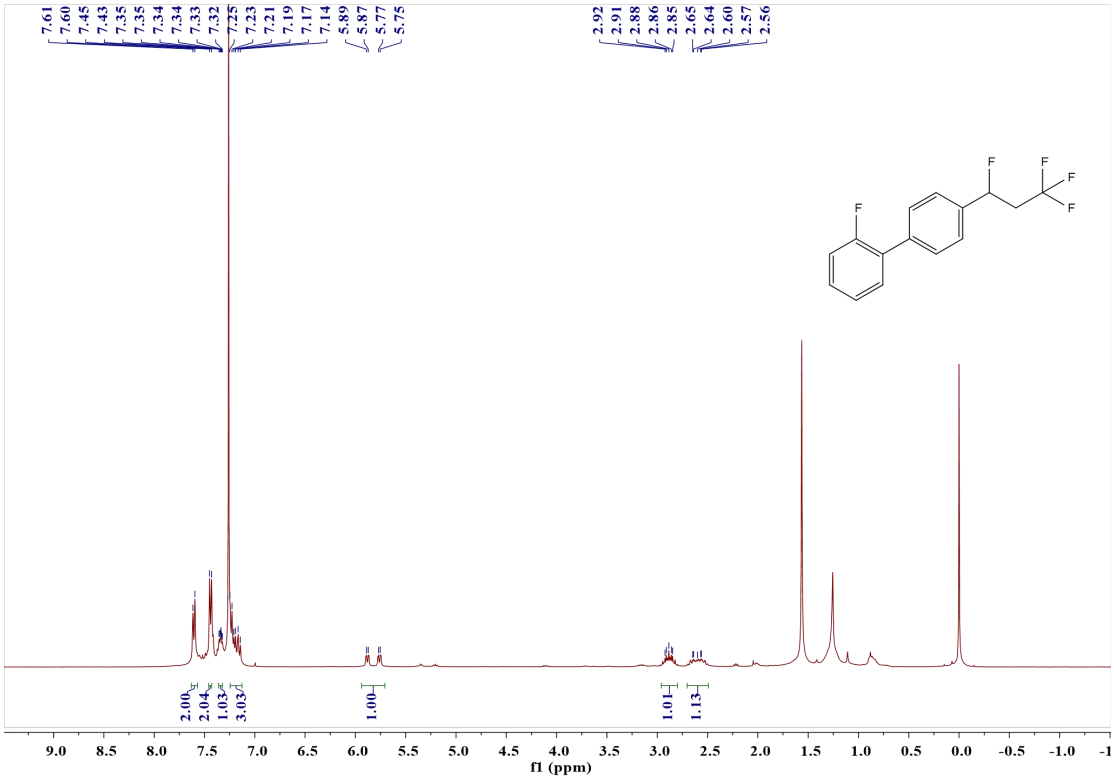


(^{19}F NMR, $CDCl_3$, 376 MHz)

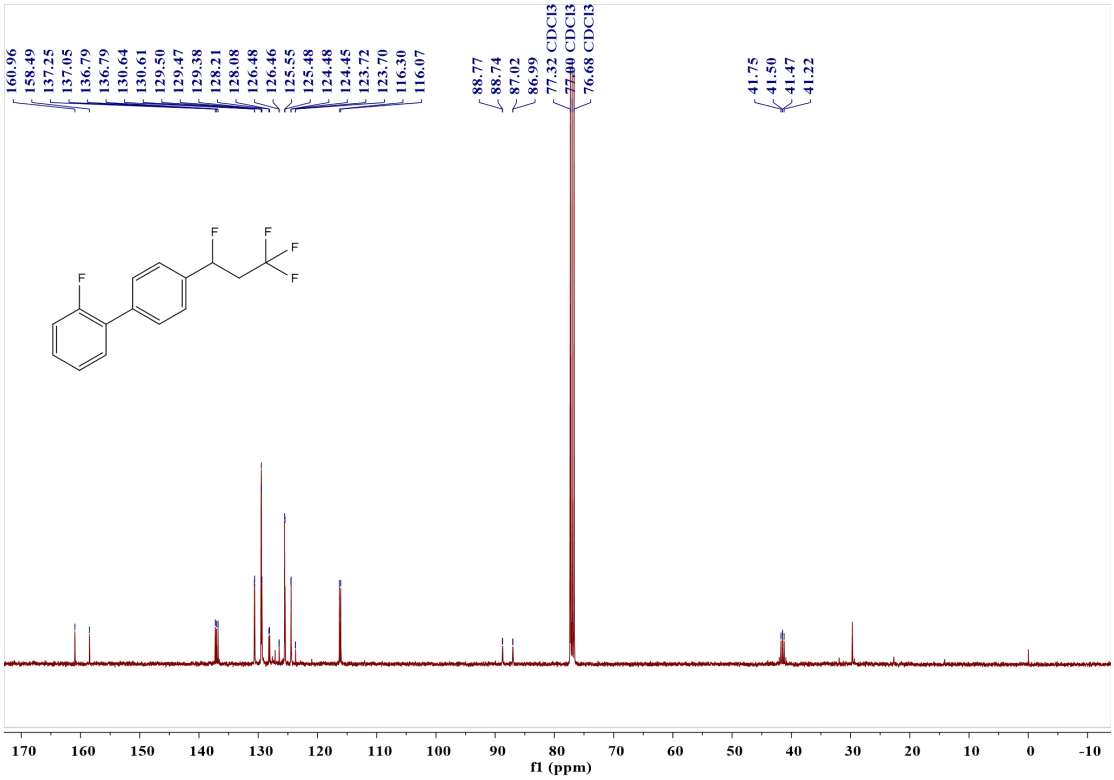


2-Fluoro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2j)

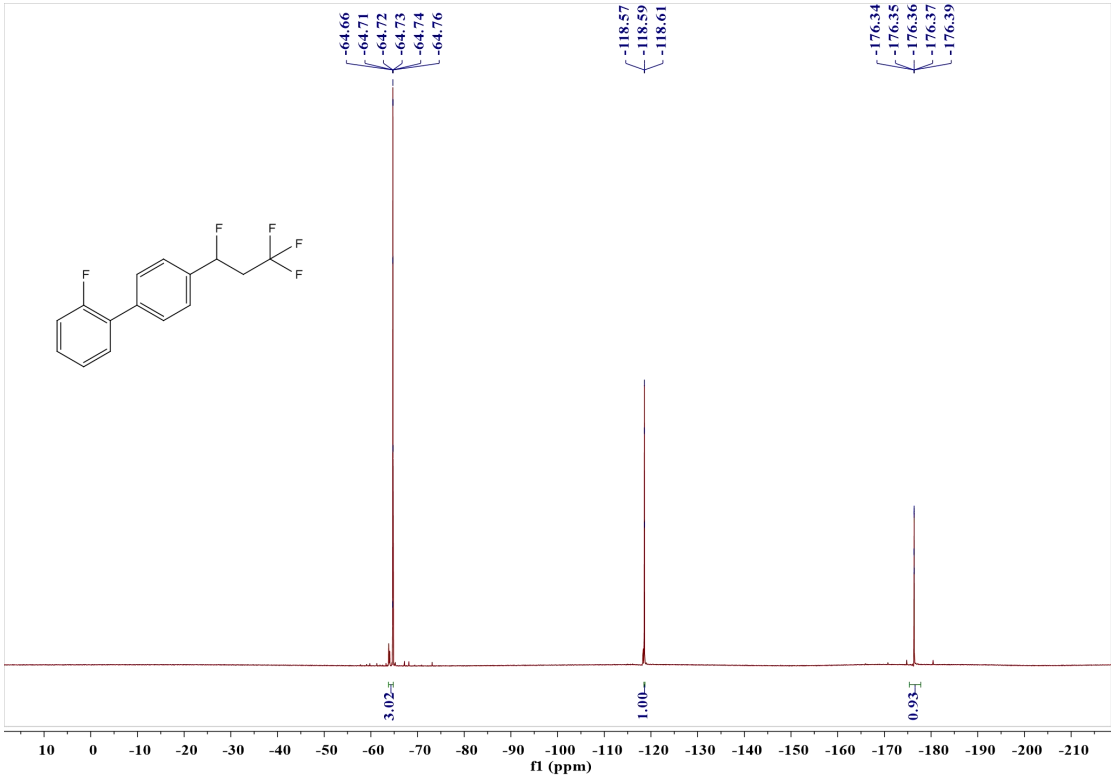
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

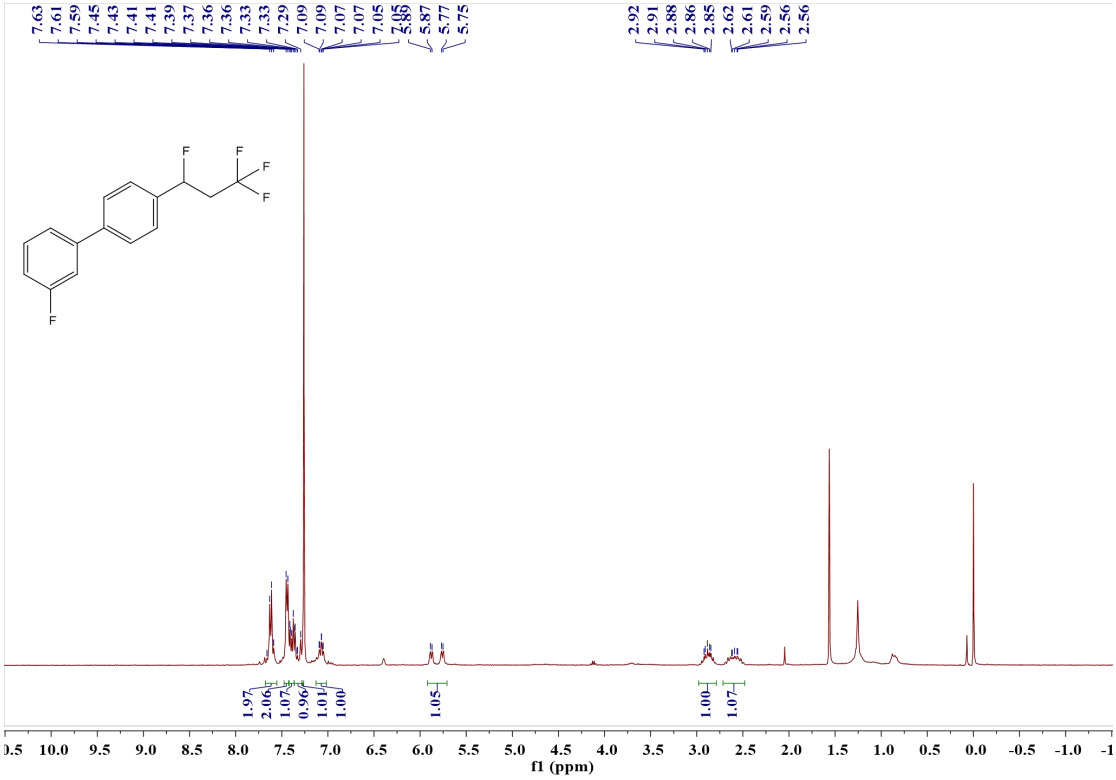


(^{19}F NMR, $CDCl_3$, 376 MHz)

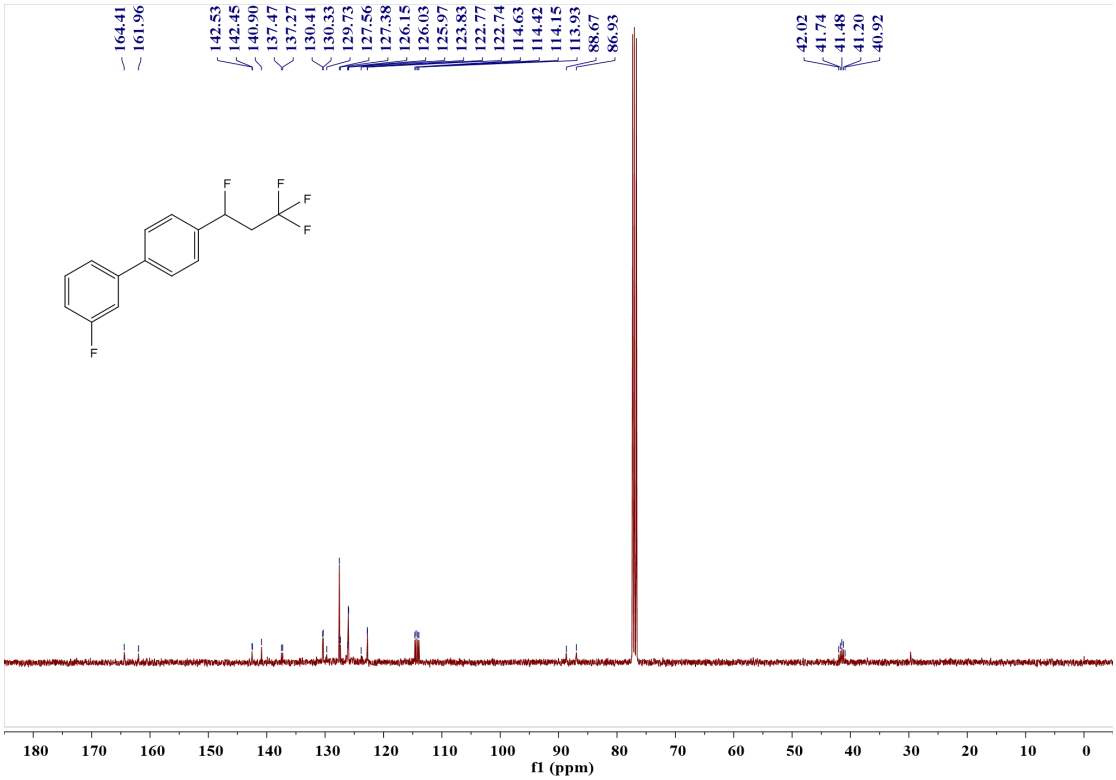


3-Fluoro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2k)

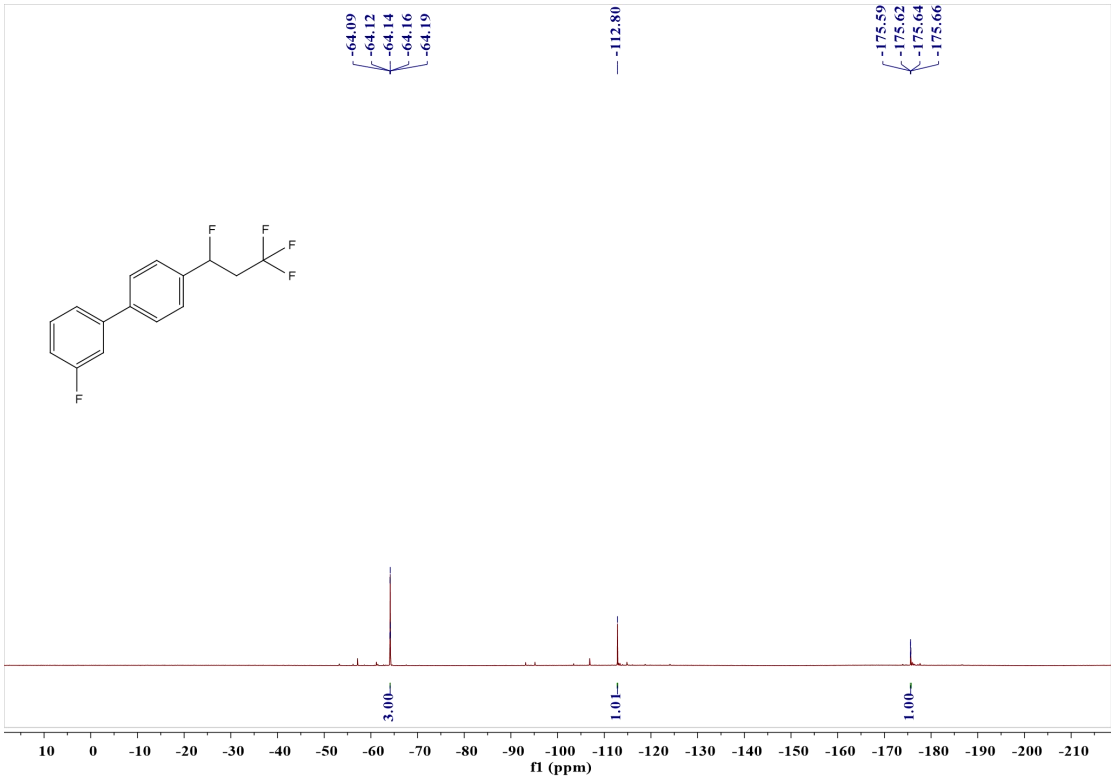
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

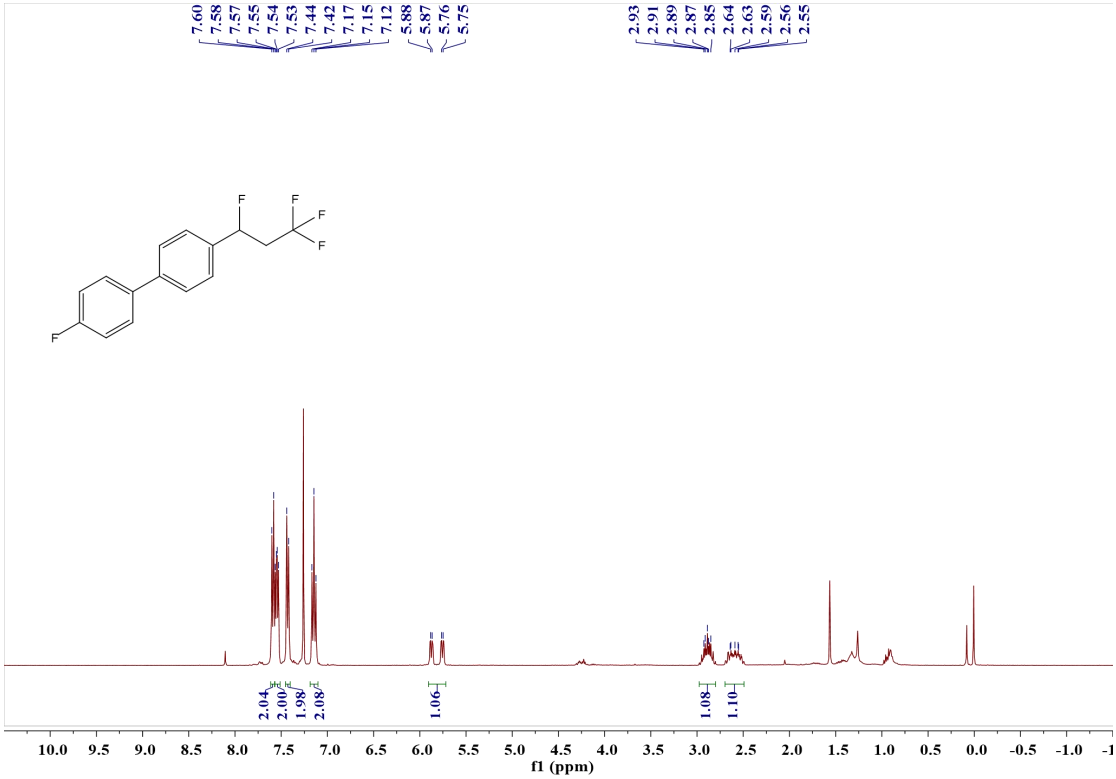


(^{19}F NMR, $CDCl_3$, 376 MHz)

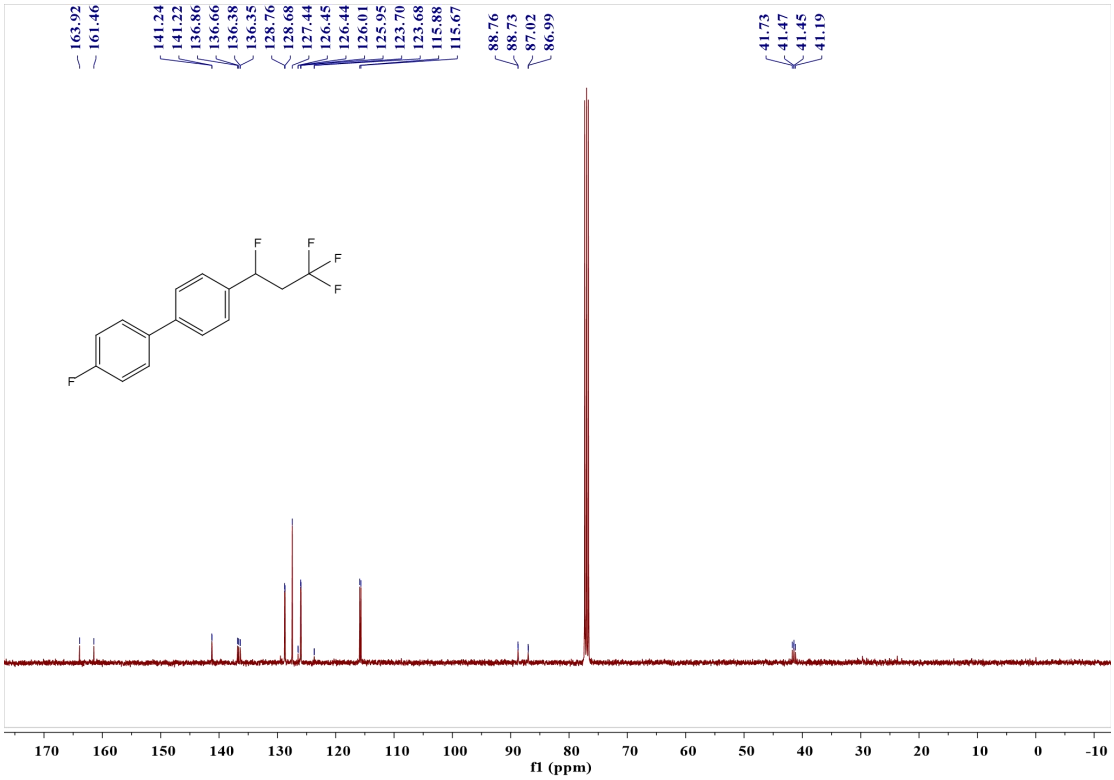


4-Fluoro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2l)

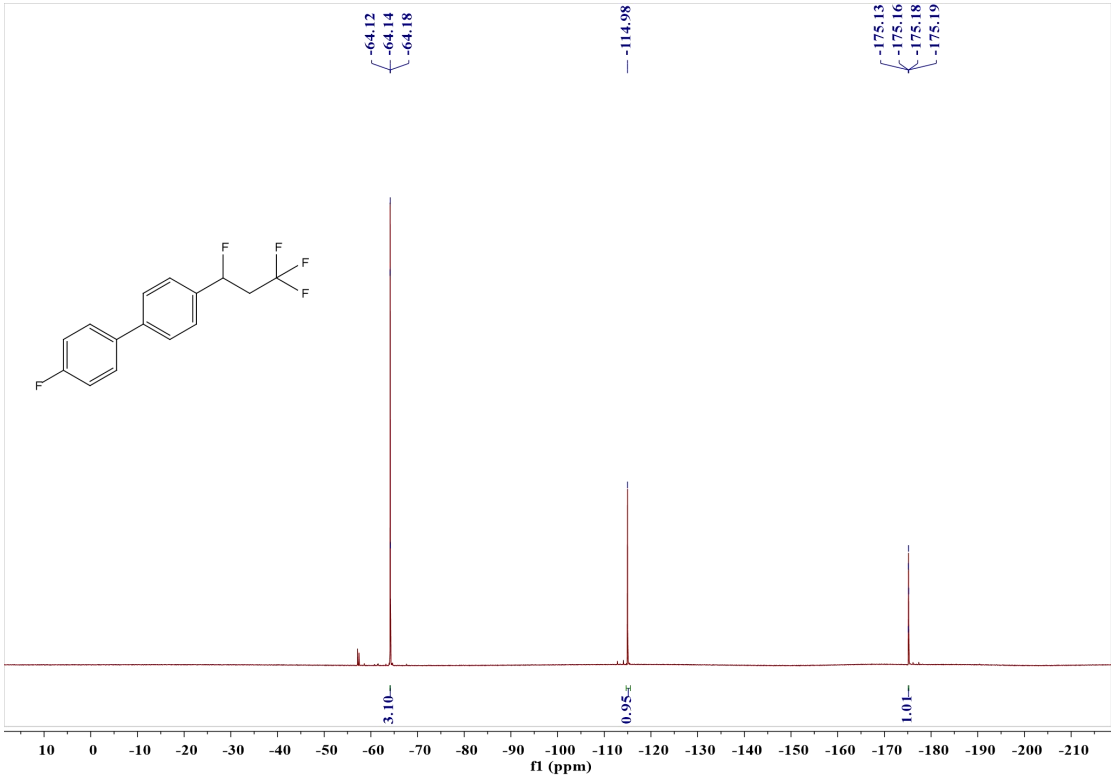
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

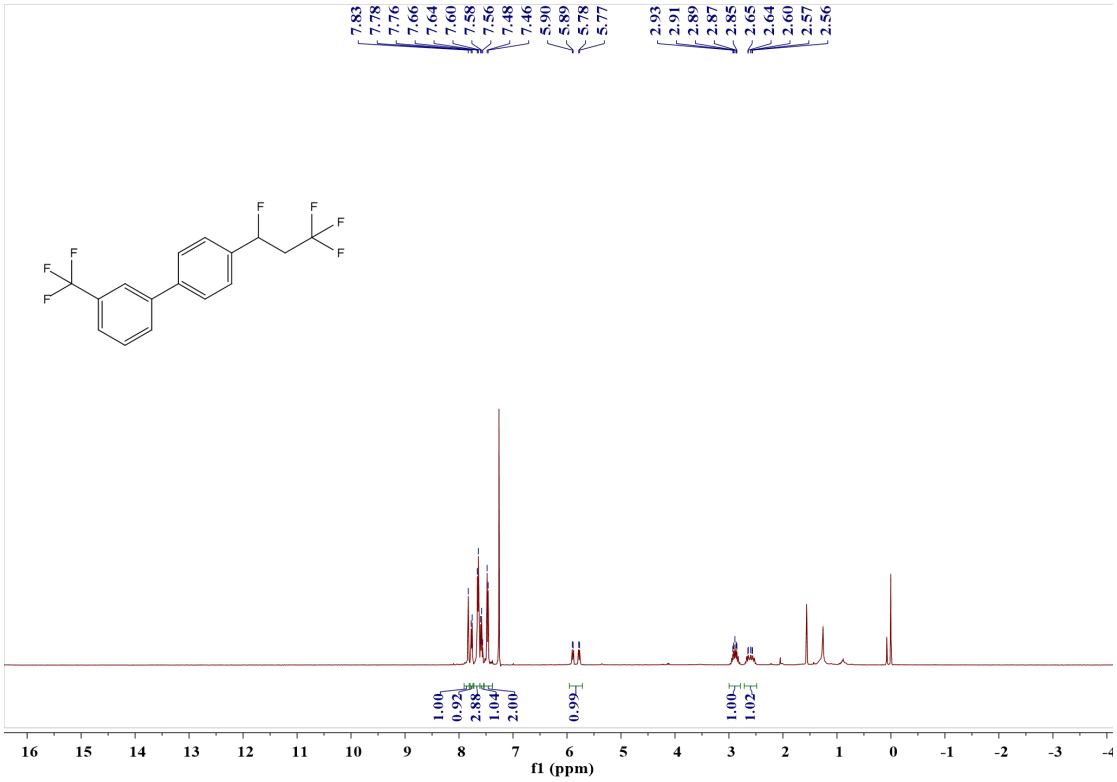


(^{19}F NMR, $CDCl_3$, 376 MHz)

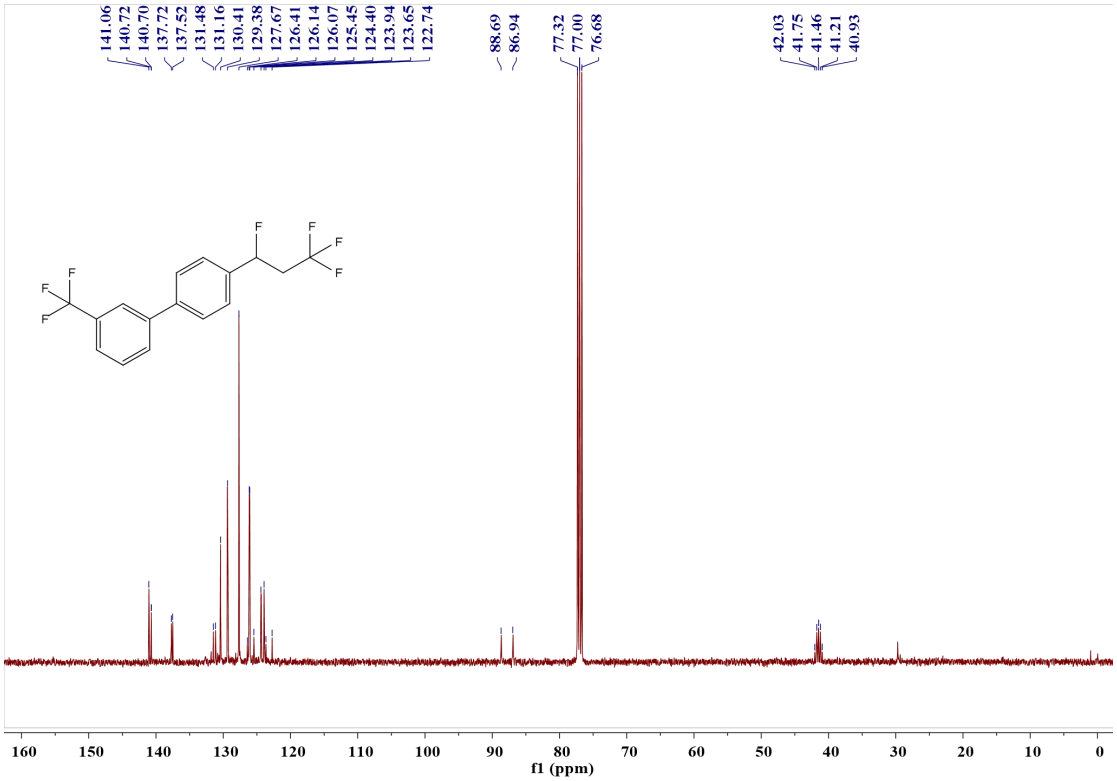


4'-(1,3,3,3-Tetrafluoropropyl)-3-(trifluoromethyl)-1,1'-biphenyl (2m)

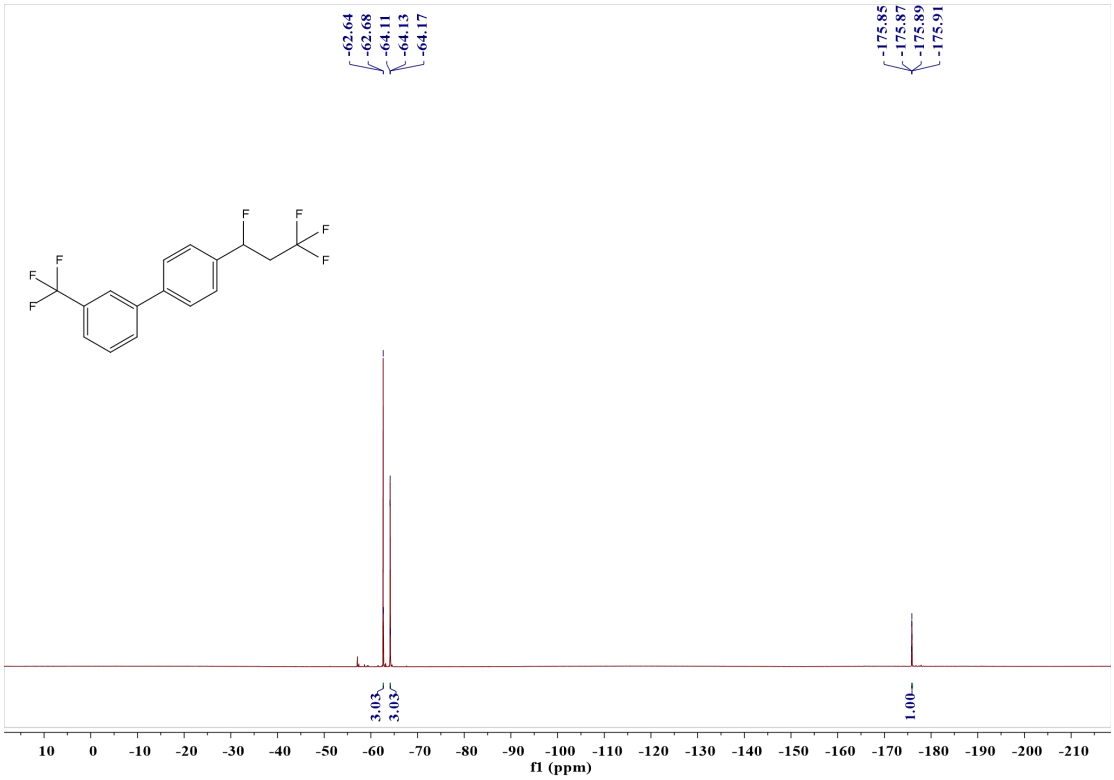
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

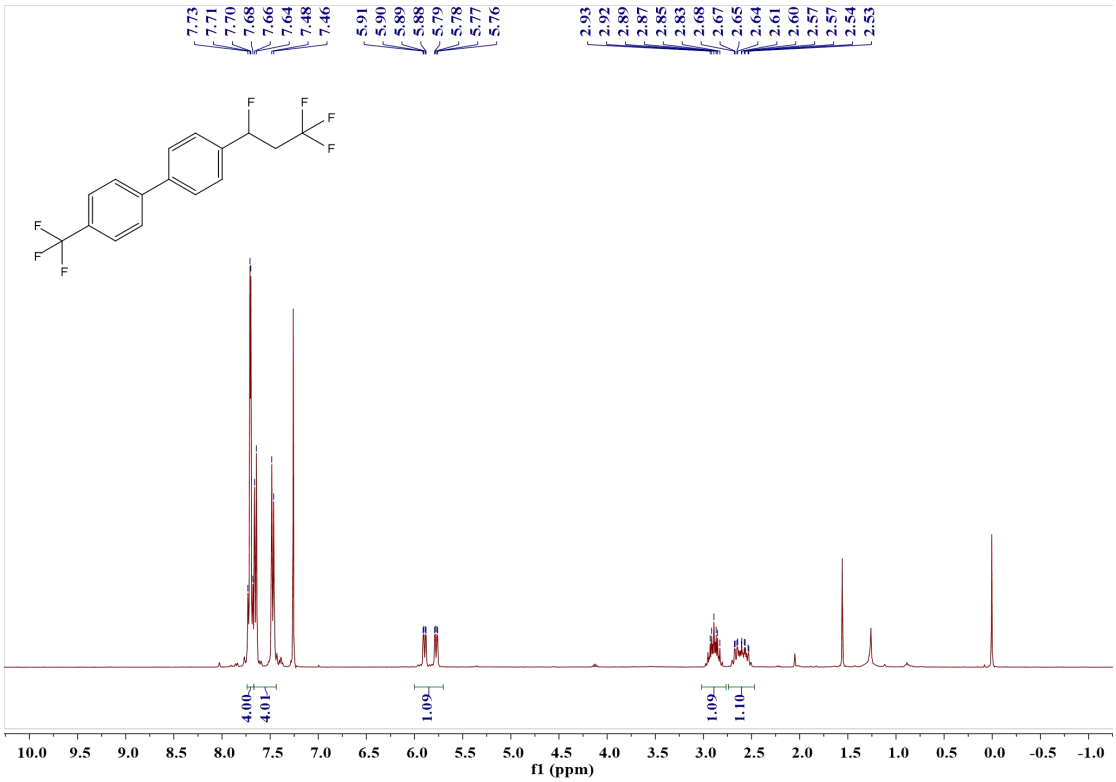


(^{19}F NMR, $CDCl_3$, 376 MHz)

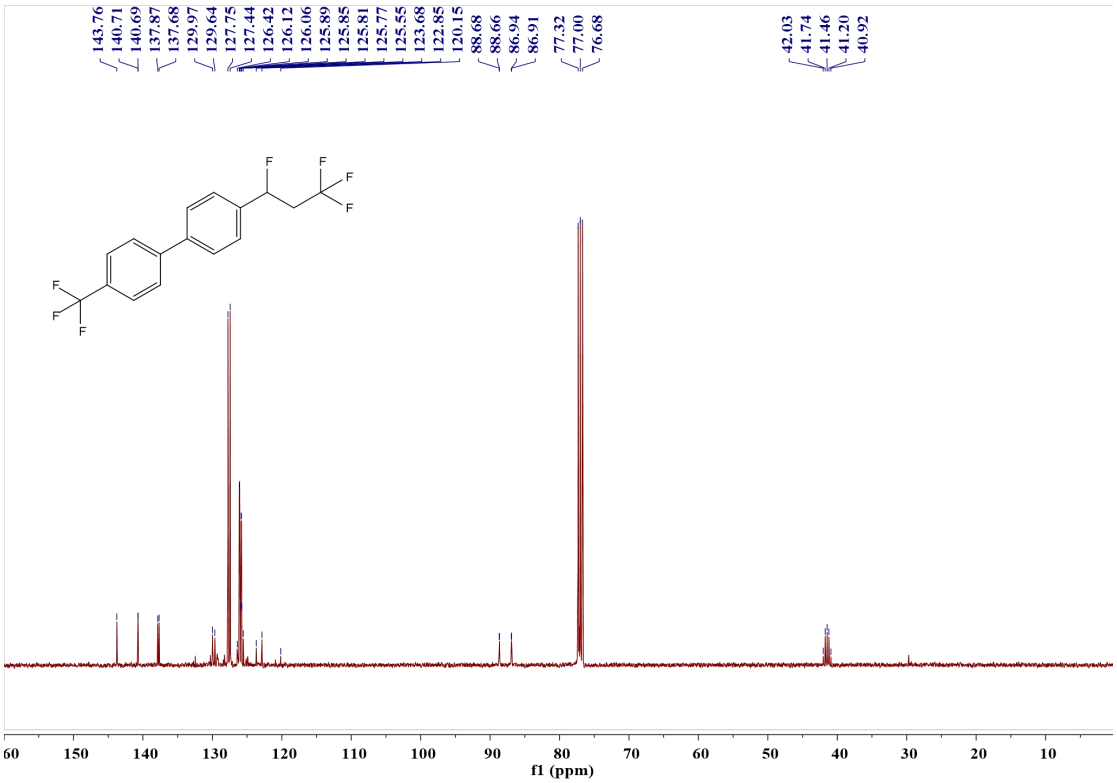


4-(1,3,3,3-Tetrafluoropropyl)-4'-(trifluoromethyl)-1,1'-biphenyl (2n)

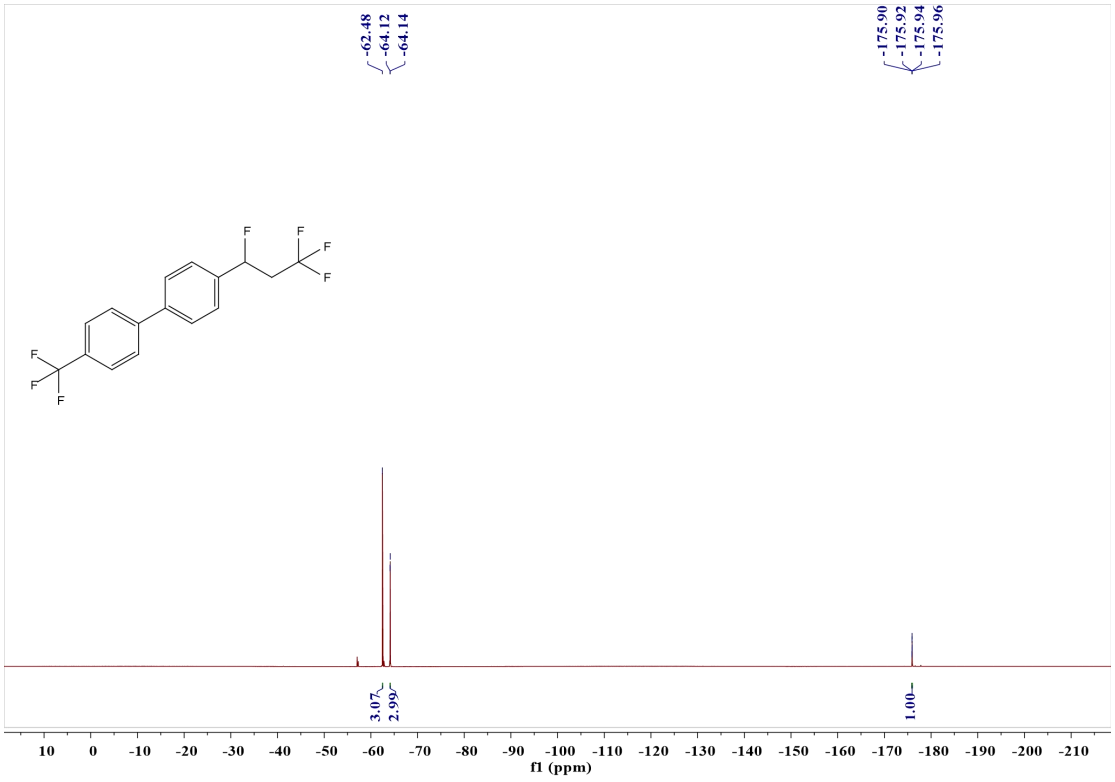
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

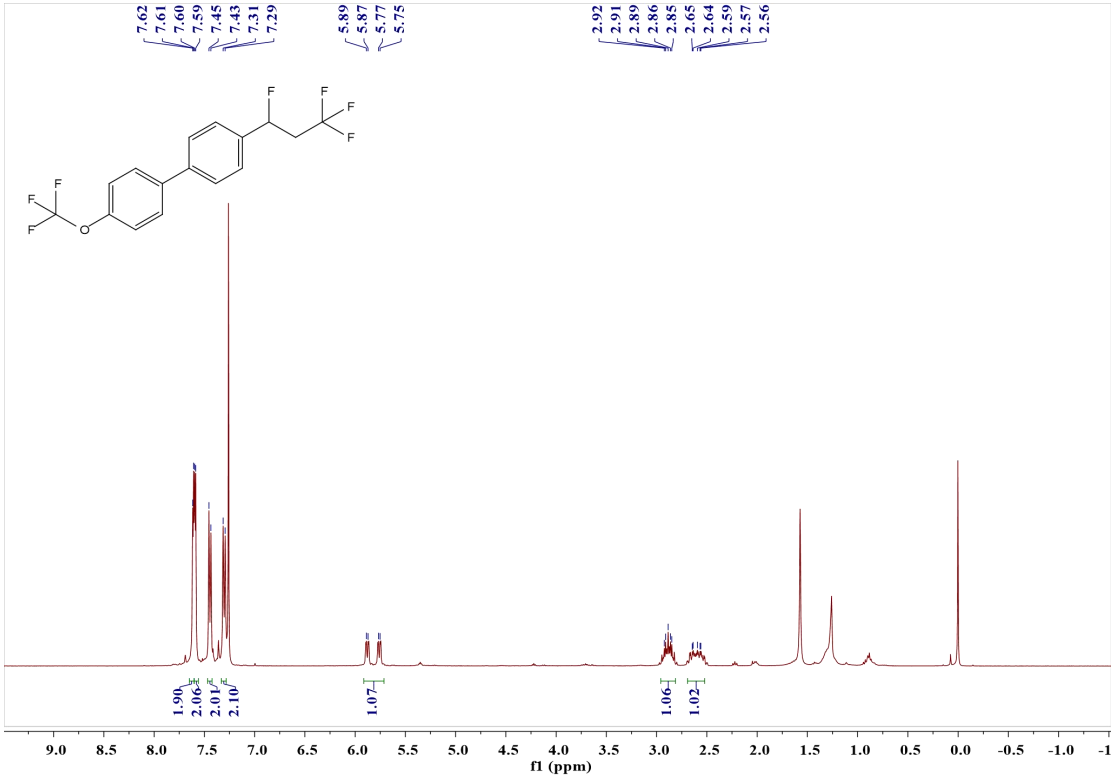


(^{19}F NMR, $CDCl_3$, 376 MHz)

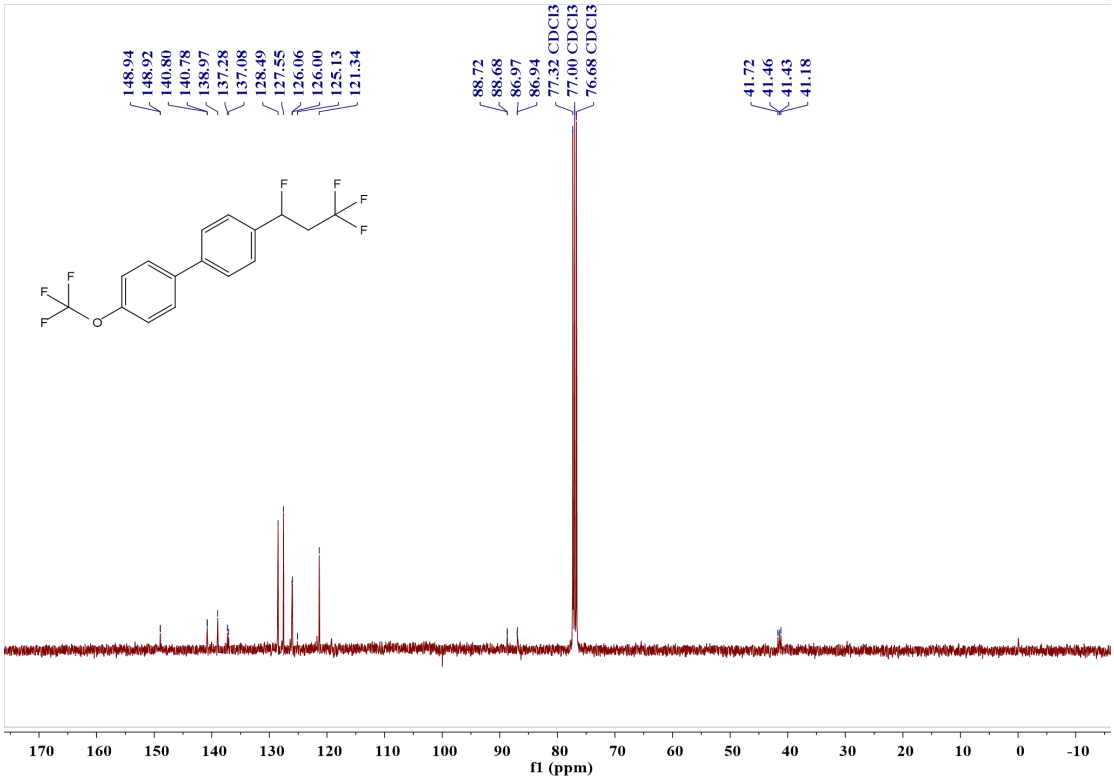


4-(1,3,3,3-Tetrafluoropropyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (2o)

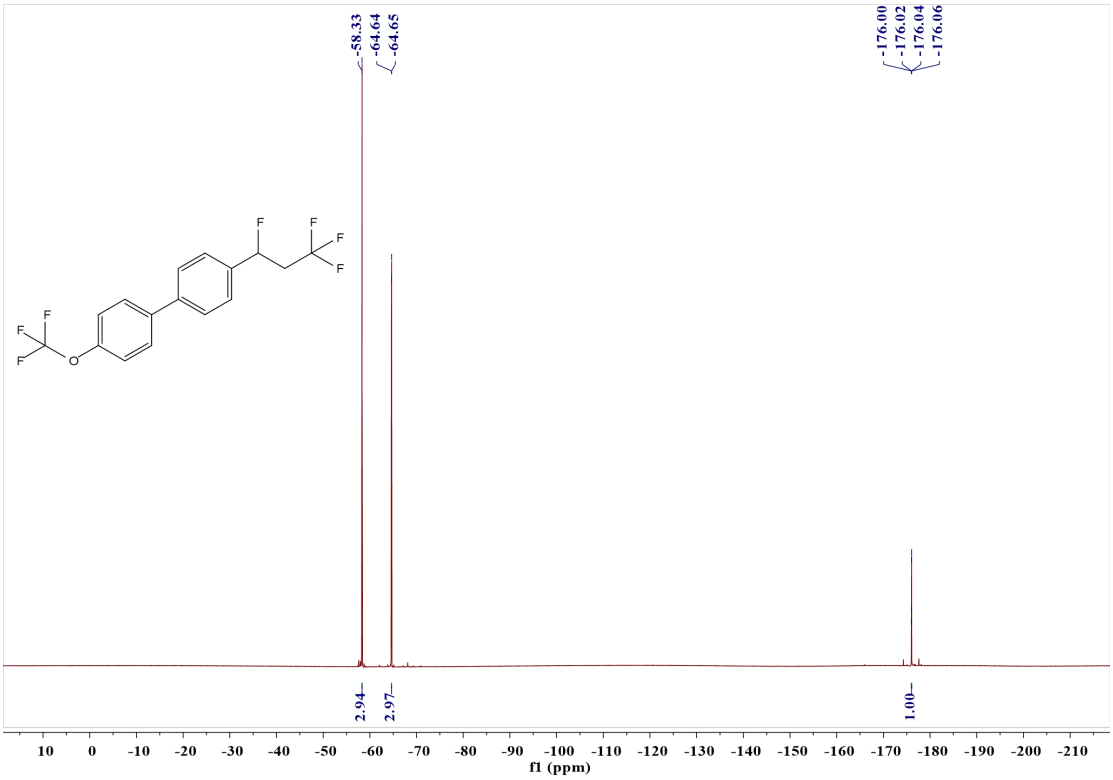
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

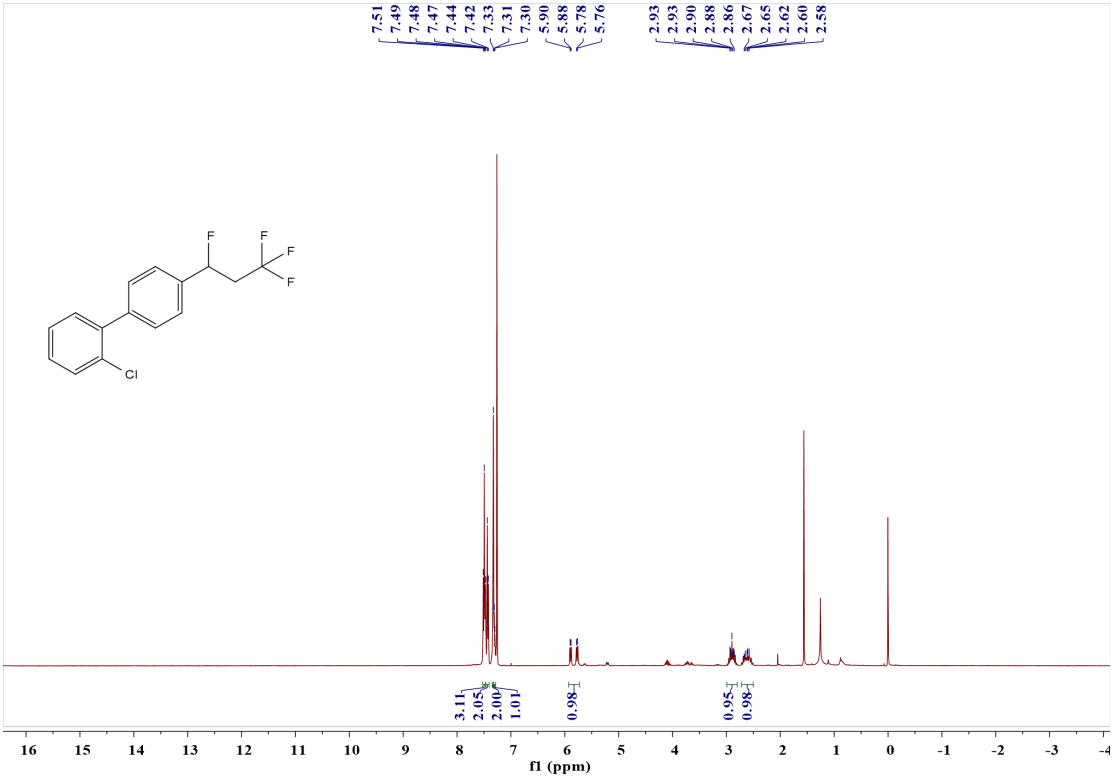


(^{19}F NMR, $CDCl_3$, 376 MHz)

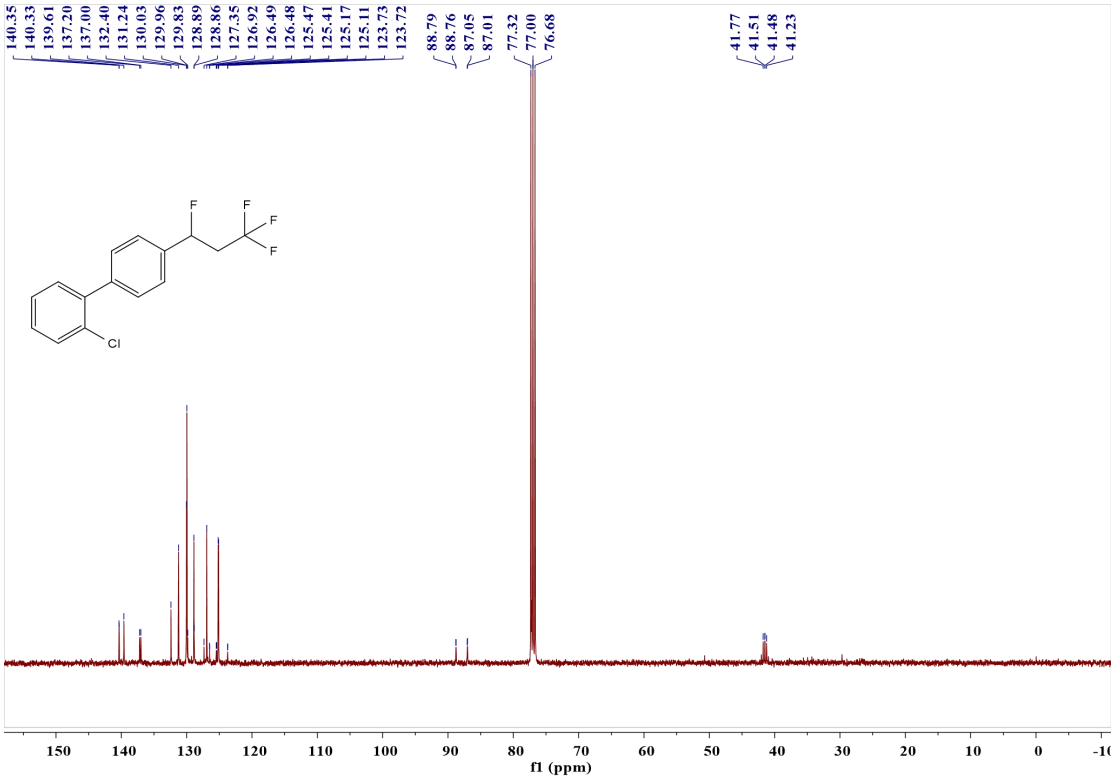


2-Chloro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2p)

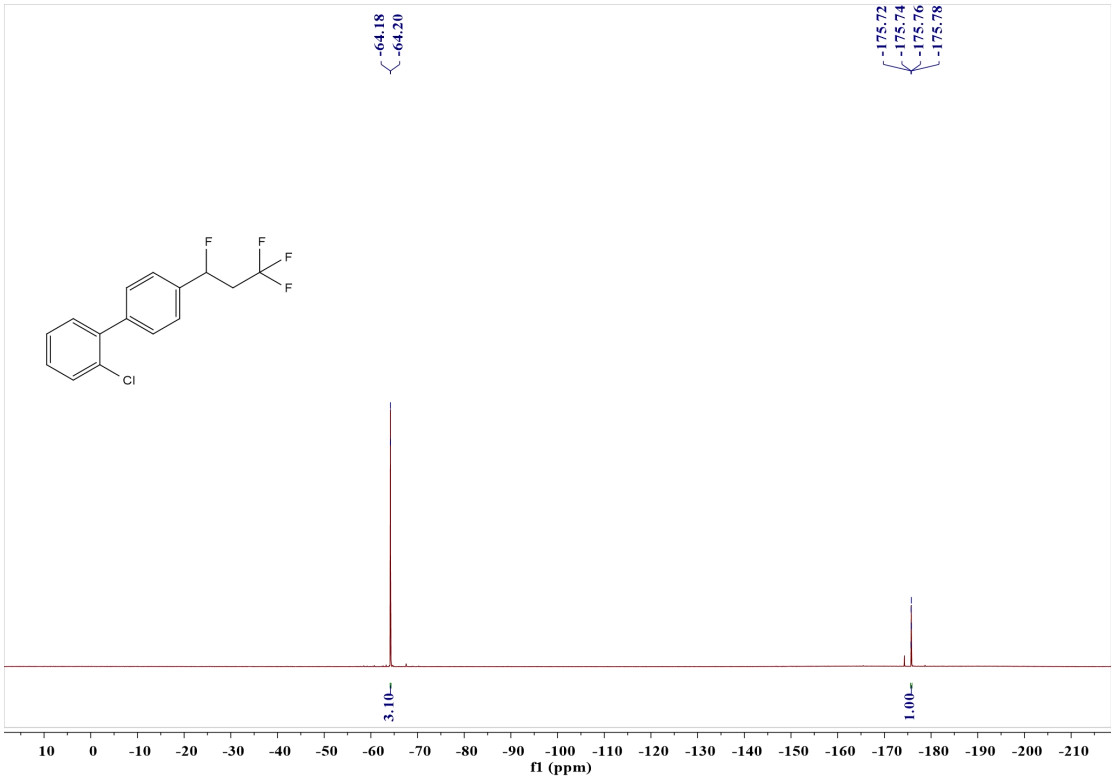
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

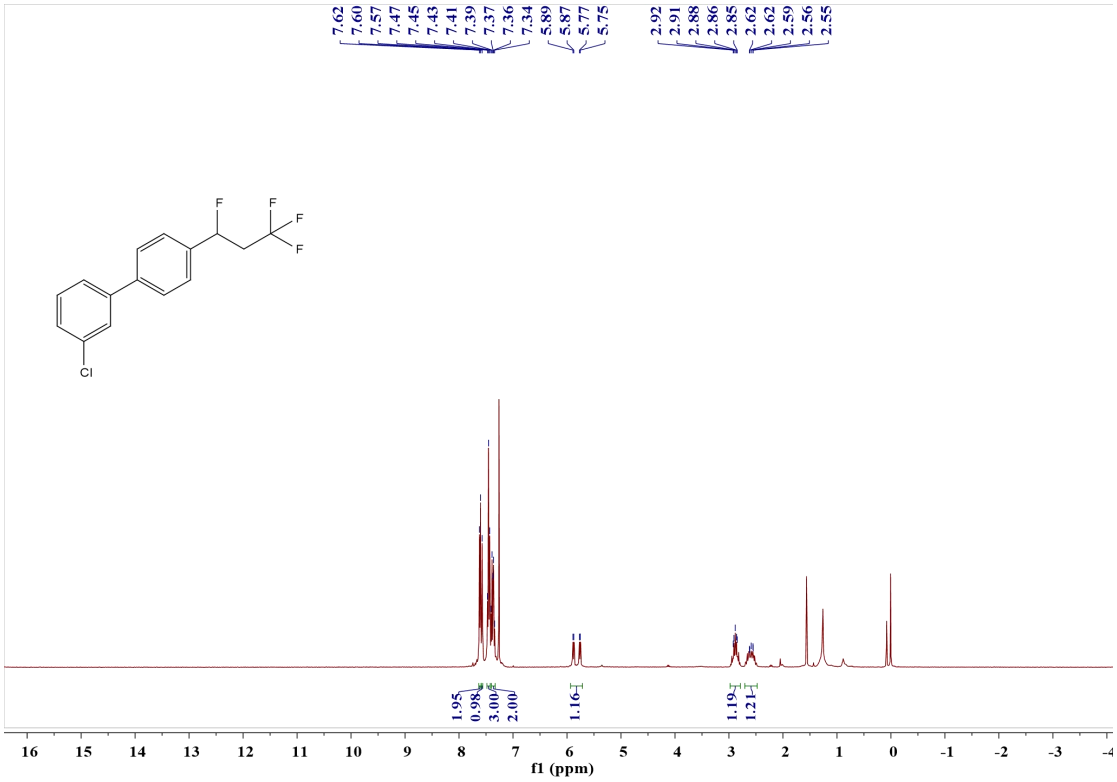


(^{19}F NMR, $CDCl_3$, 376 MHz)

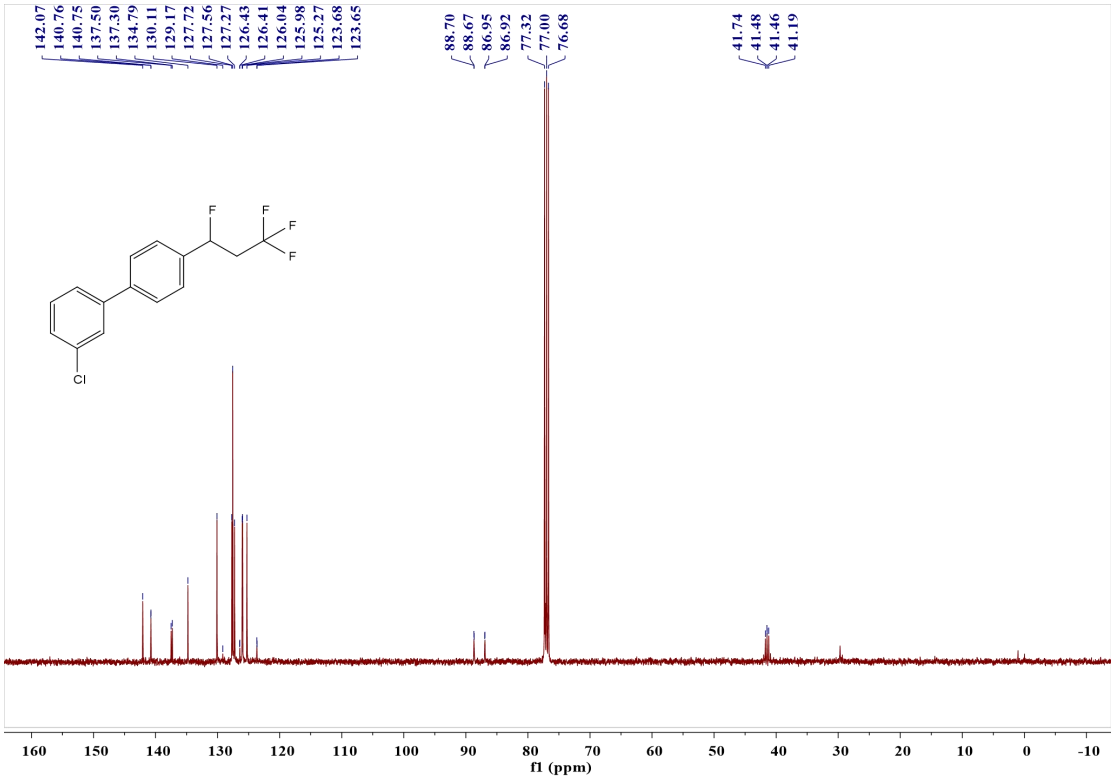


3-Chloro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2q)

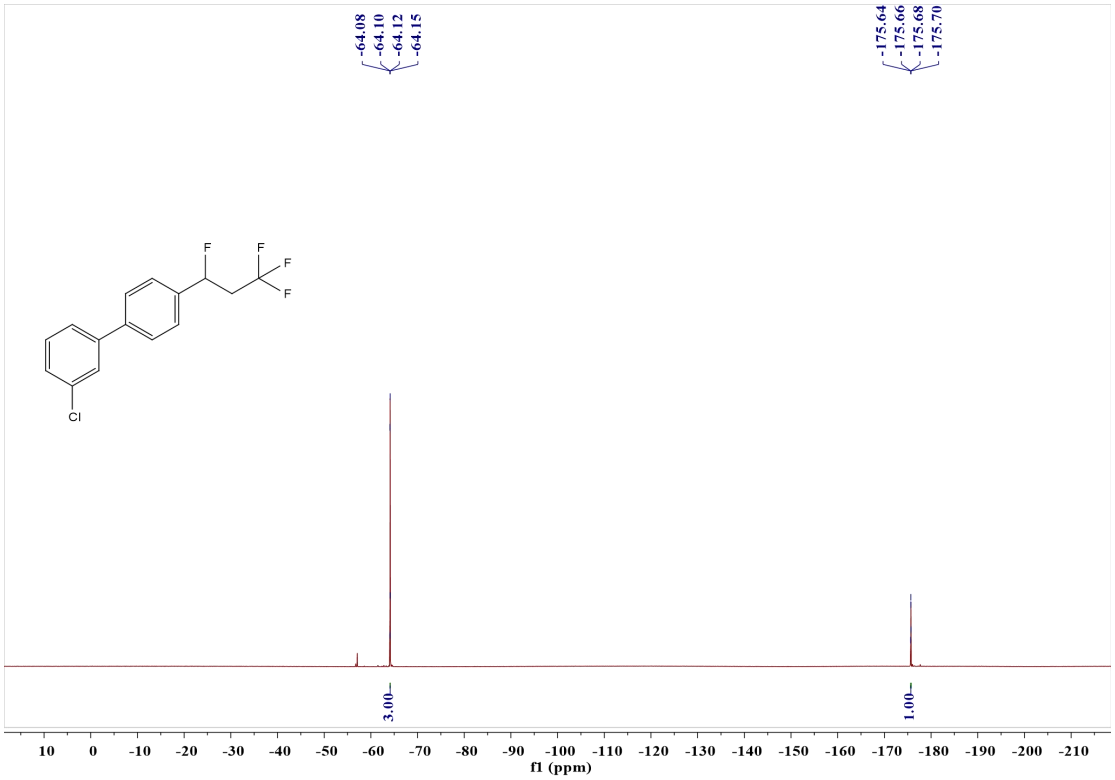
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

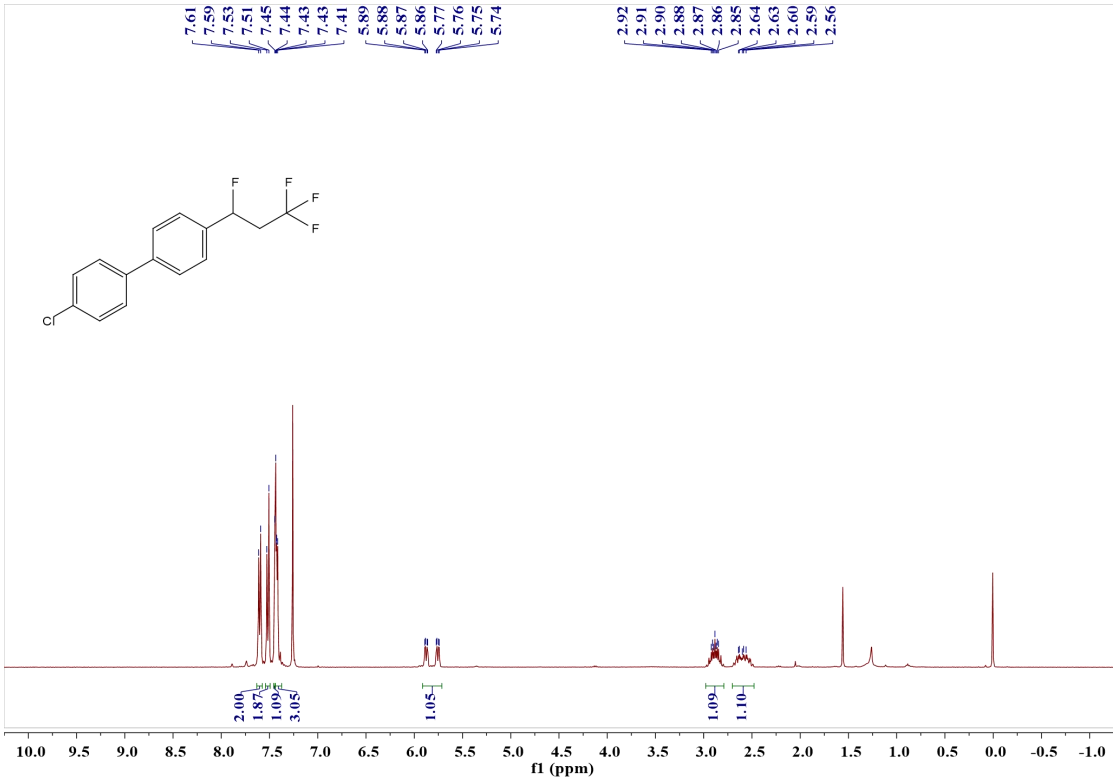


(^{19}F NMR, $CDCl_3$, 376 MHz)

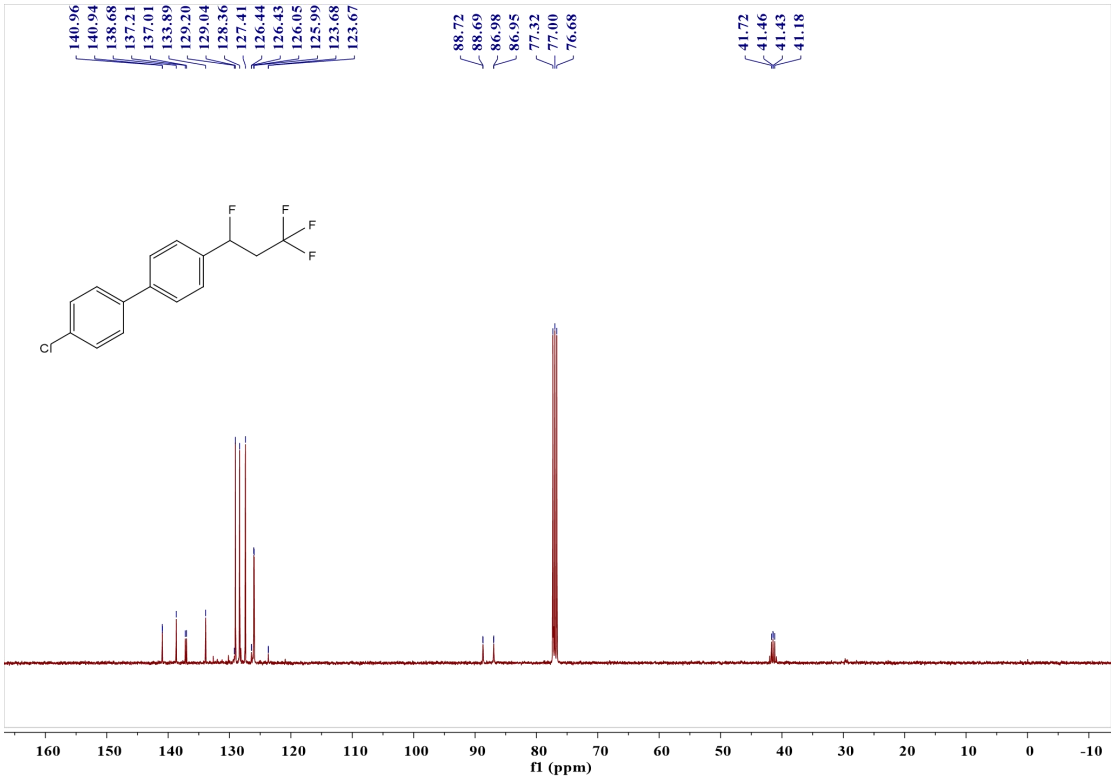


4-Chloro-4'-(1,3,3,3-tetrafluoropropyl)-1,1'-biphenyl (2r)

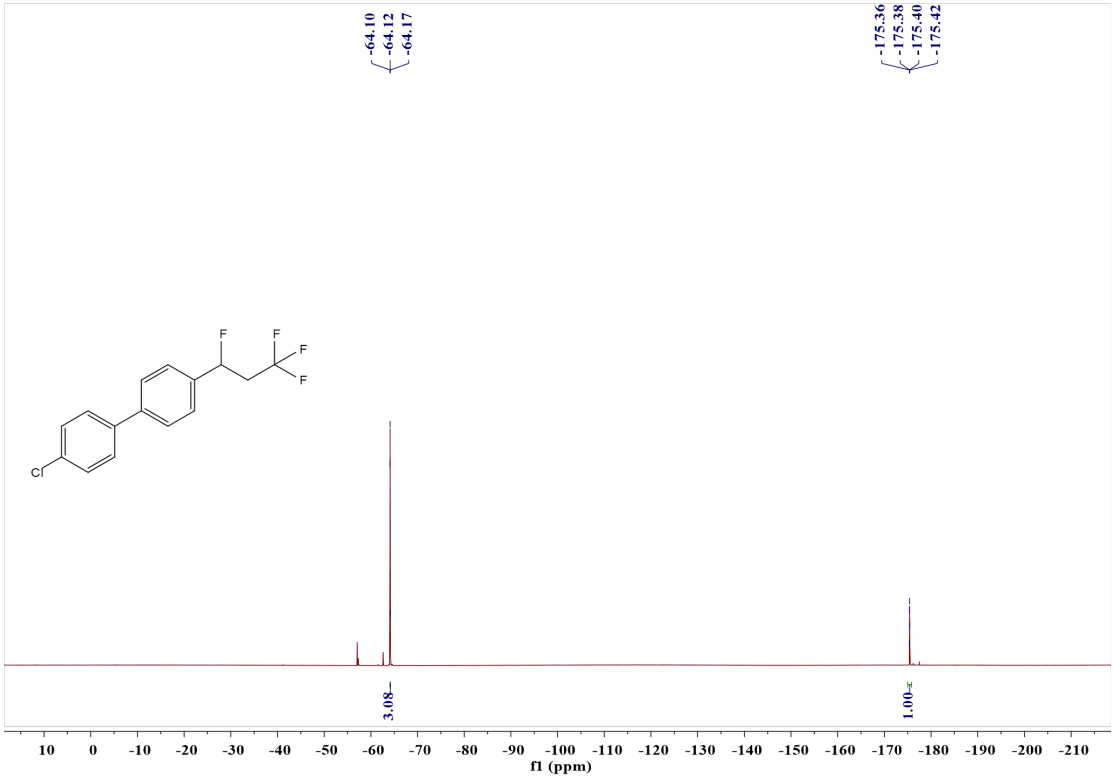
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

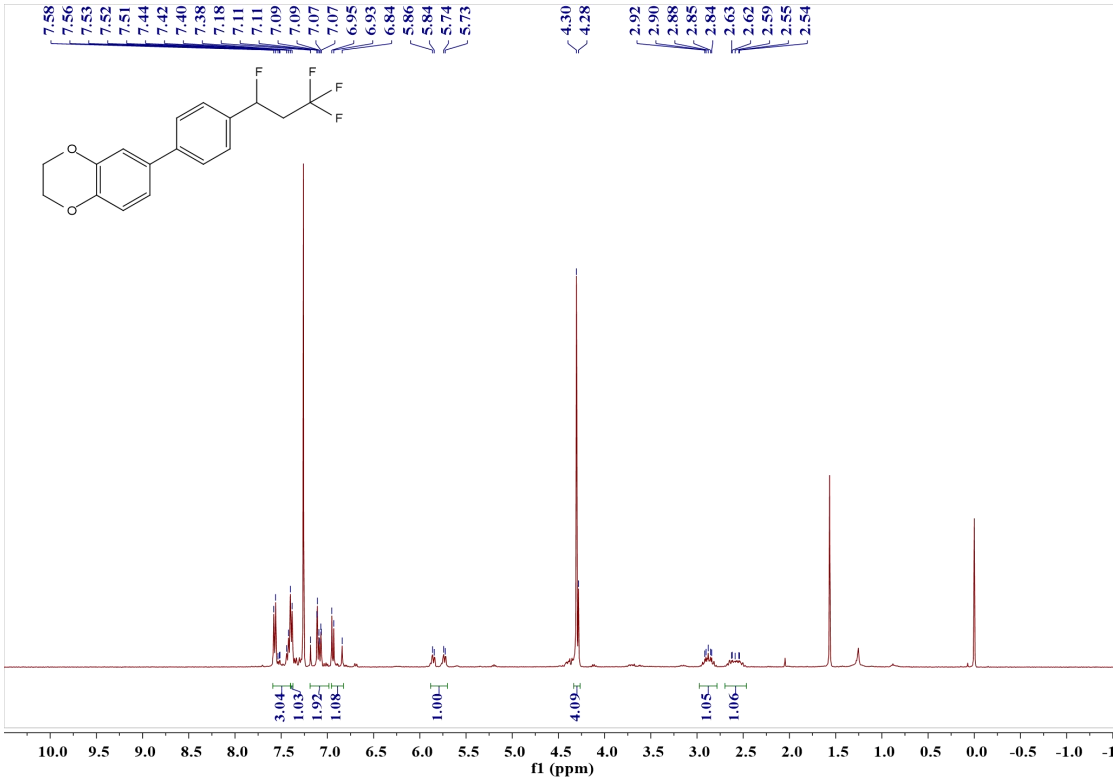


(^{19}F NMR, $CDCl_3$, 376 MHz)

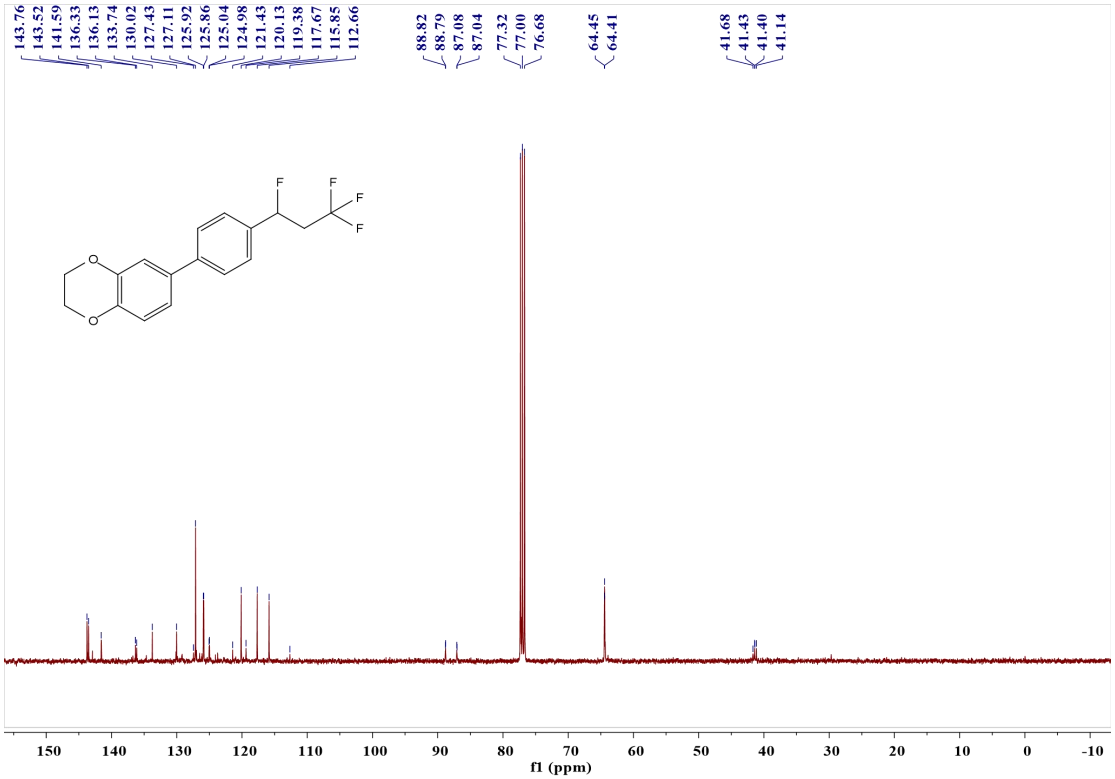


6-(4-(1,3,3,3-Tetrafluoropropyl)phenyl)-2,3-dihydrobenzo[b][1,4]dioxine (2s)

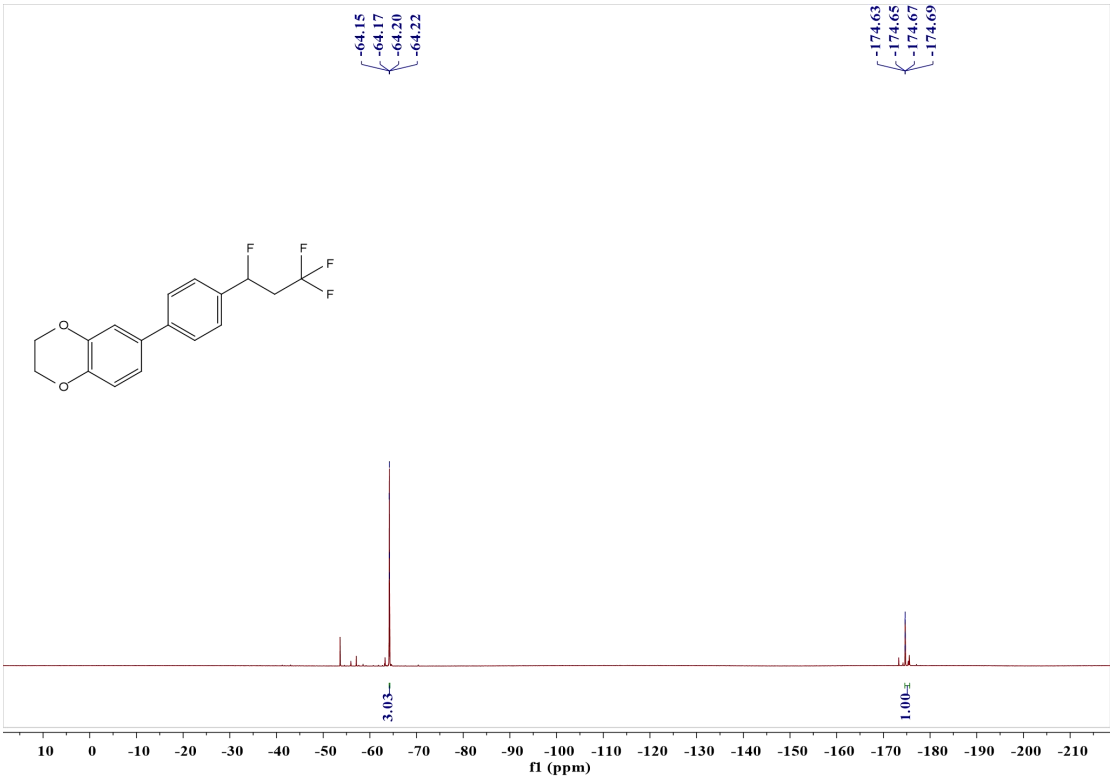
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

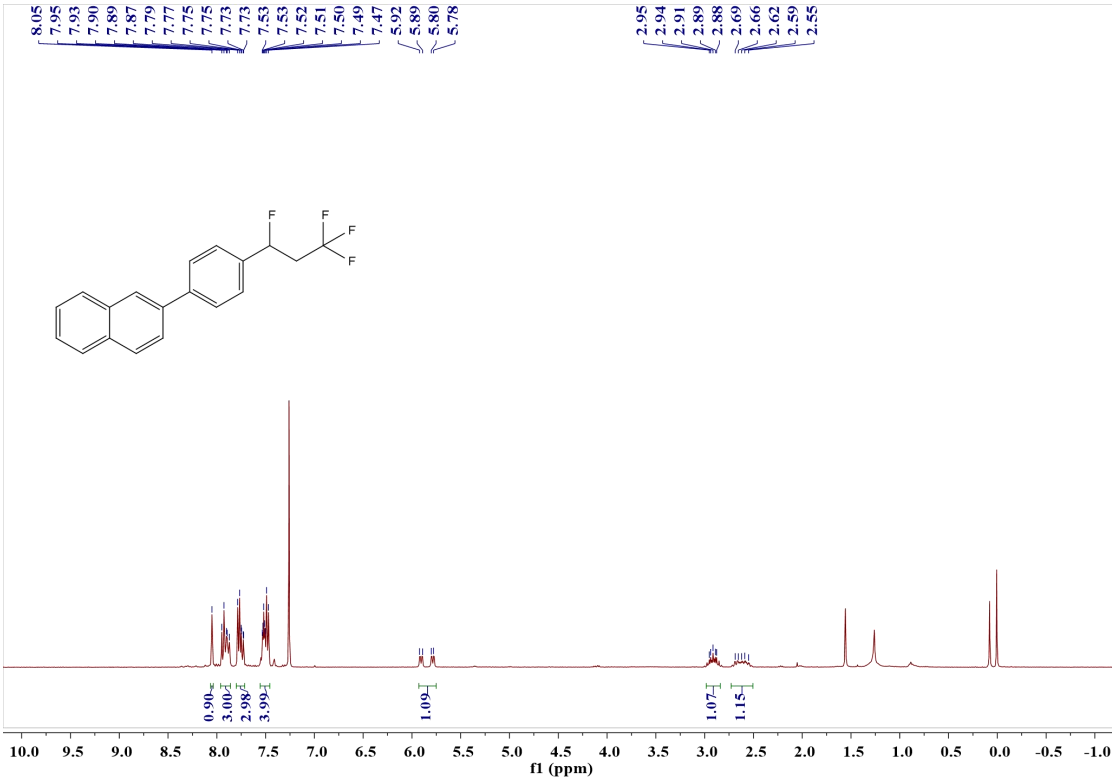


(^{19}F NMR, $CDCl_3$, 376 MHz)

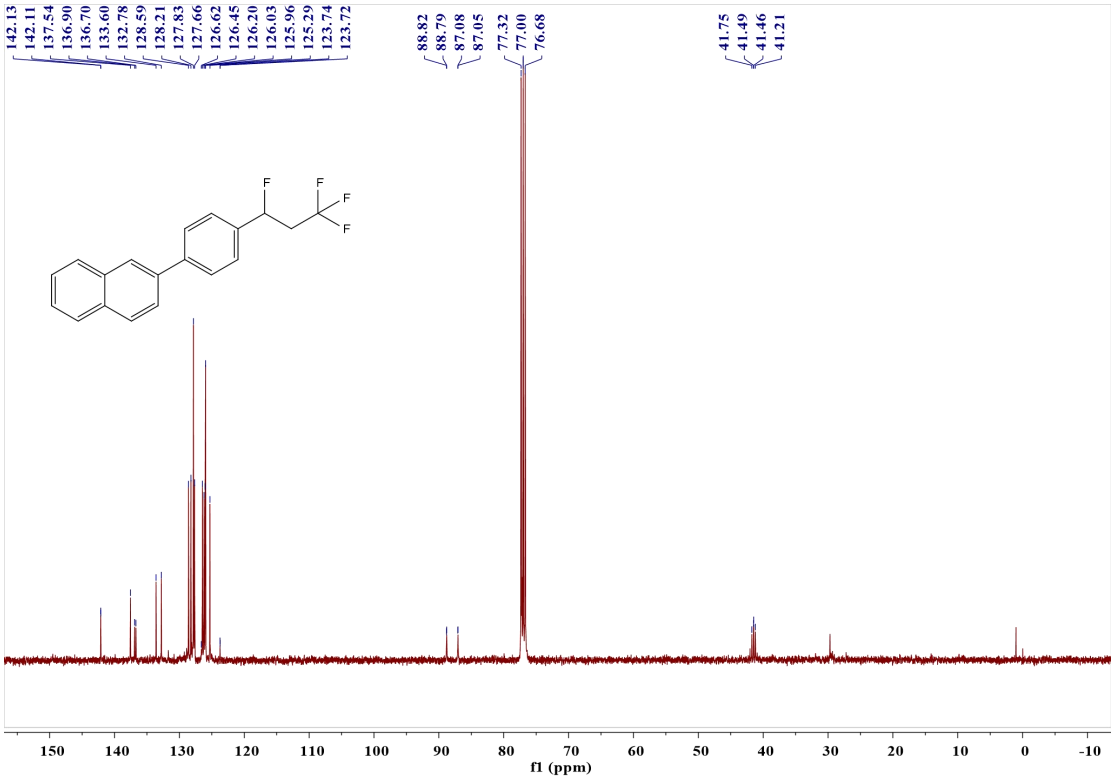


2-(4-(1,3,3,3-Tetrafluoropropyl)phenyl)naphthalene (2t)

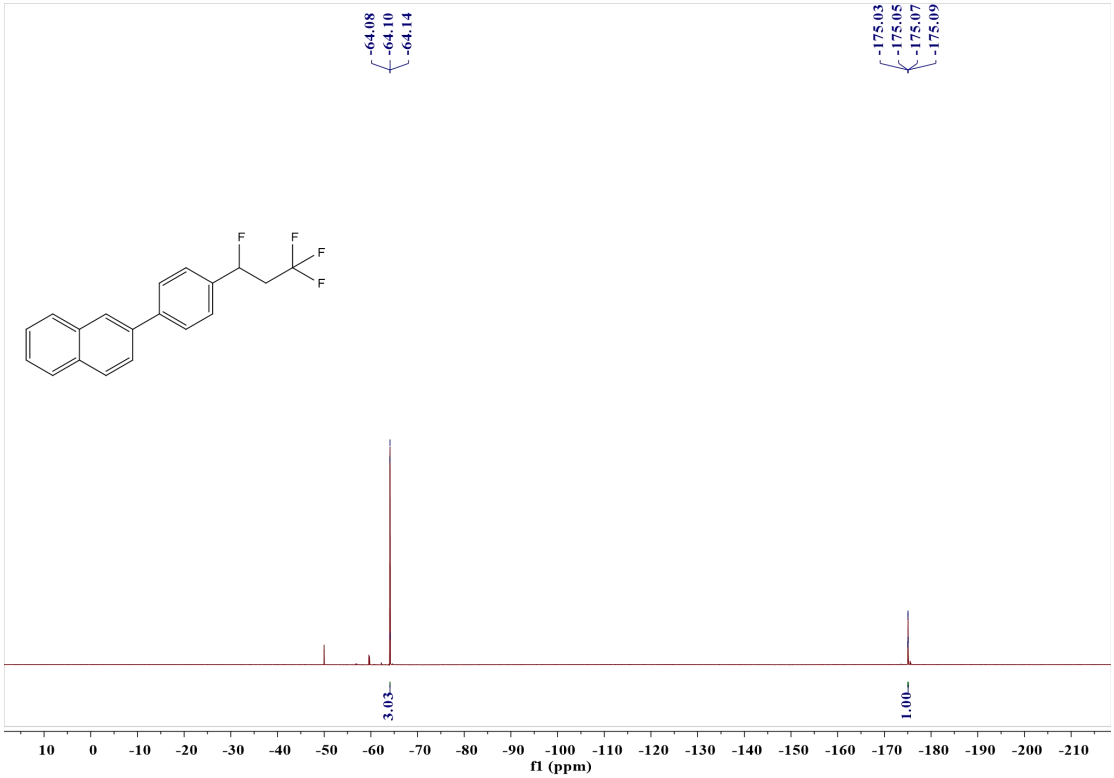
(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)

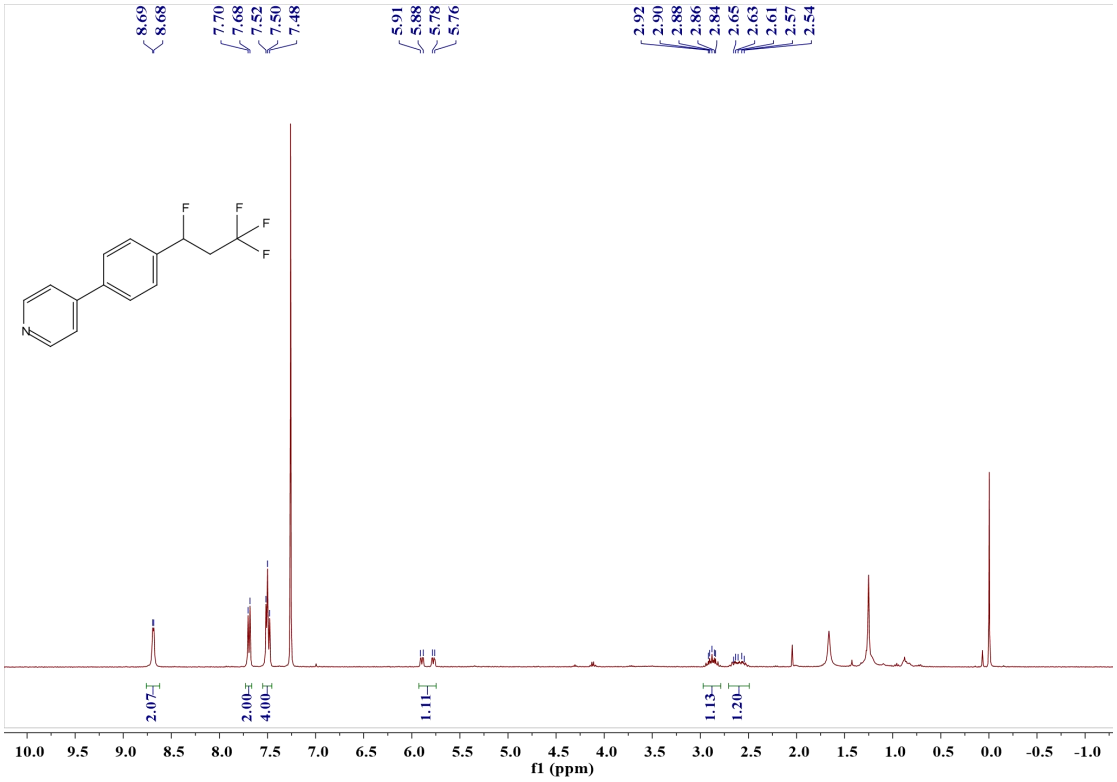


(^{19}F NMR, $CDCl_3$, 376 MHz)

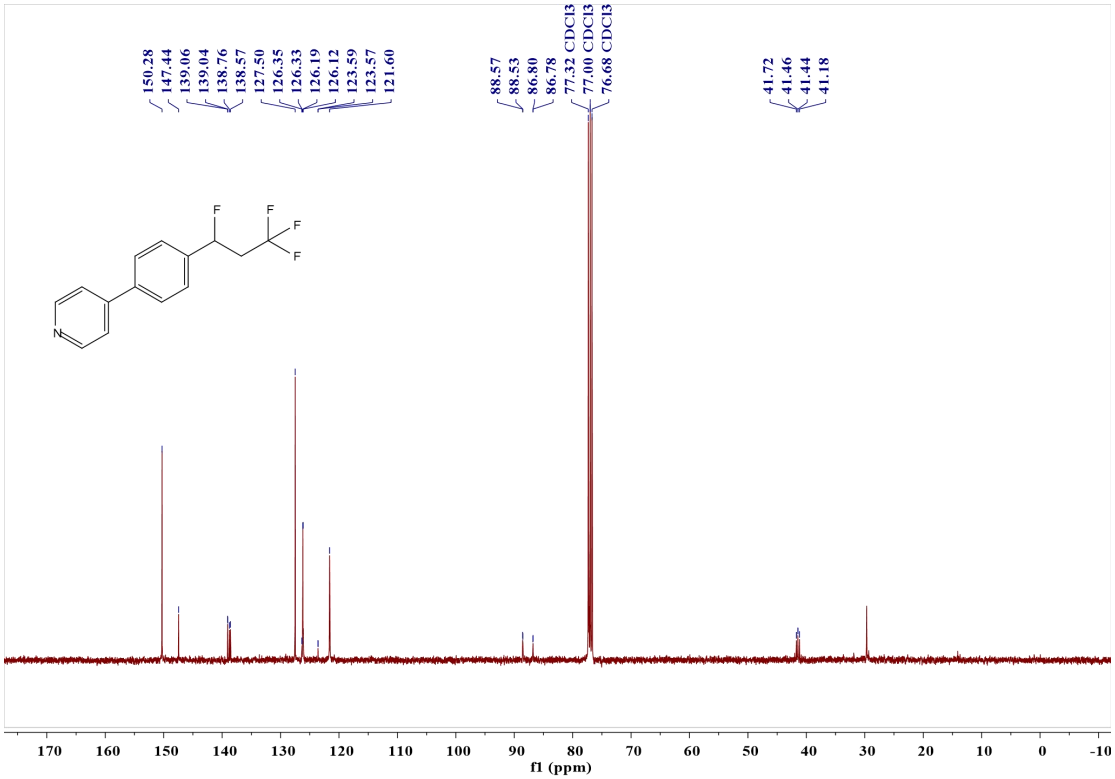


4-(4-(1,3,3,3-Tetrafluoropropyl)phenyl)pyridine (2u)

(^{1}H NMR, $CDCl_3$, 400 MHz)



(^{13}C NMR, $CDCl_3$, 101 MHz)



(^{19}F NMR, $CDCl_3$, 376 MHz)