Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Diaryldifluoromethanes by Pd-Catalyzed Difluoroalkylation of Arylboronic Acids

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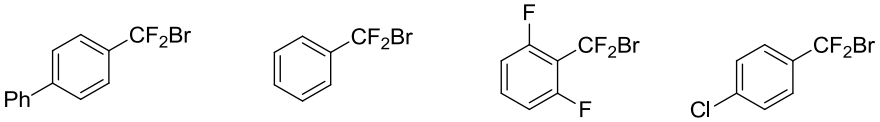
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM300, AM400, Agilent MR400 spectrometer. ^{19}F NMR was recorded on a Bruker AM300 and Agilent MR400 spectrometer ($CFCl_3$ as an outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using $PhCF_3$ as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air, and then purged on air and backfilled with argon at room temperature. 1,4-Dioxane was distilled from sodium immediately and degassed before used. Compounds **1a-b**,[1] and **1d-c**[2] were prepared according to references, in which compounds **1b-d** are known compounds.

Structures of Compounds 1a-d



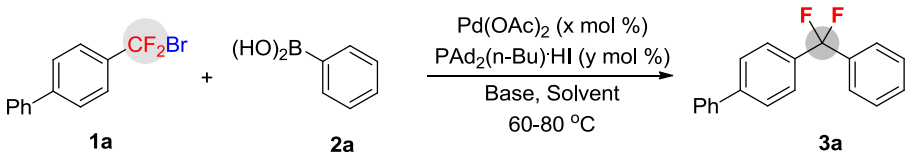
1a **1b** **1c** **1d**

4-(Bromodifluoromethyl)-1,1'-biphenyl (1a). The preparation of compound **1a** was according to reference. The product (72 % yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 57-59 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 9.6 Hz, 4H), 7.62-7.60 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 144.2 (t, *J* = 1.4 Hz), 139.7, 136.9 (t, *J* = 23.8 Hz), 129.0, 128.2, 127.3, 127.2, 124.8 (t, *J* = 5.2 Hz), 118.4 (t, *J* = 305.2 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2 (s, 2F). IR (thin film) ν_{max} 3082, 1922, 1609, 1570, 1488, 1406 cm^{-1}. MS (EI): m/z (%) 281 (M^+), 203 (100). HRMS: Calculated for $C_{13}H_9BrF_2$: 281.9856; Found: 281.9860.

Screens for Palladium-Catalyzed Cross-Coupling of 1a with 2a (Table S1).

A 25 mL of Schlenck tube equipped with a magnetic stir bar was charged with aryldifluoromethyl bromide **1a** (56.6 mg, 0.2 mmol, 1.0 equiv), phenylboronic acid **2a** (36.6 mg, 0.3 mmol, 1.5 equiv), palladium catalyst (1-5 mol %), phosphine ligand (5-10 mol %) under air, followed by addition of base (0.5-2.0 equiv). The vessel was evacuated and backfilled with Ar (3 times), solvent (2 mL) was then added. The Schlenck tube was screw capped and heated to 60-80 ºC. After stirring for 8 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2 mL). The yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (hexane 100%) to give product **3a** as a white solid.

Table S1.Optimization of Palladium-Catalyzed Cross-Coupling of 1a with 2a[a]

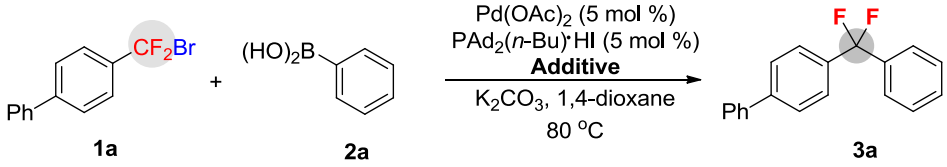


1a 2a 3a

Entry	Catalyst (x mol%)	Ligand (y mol%)	Base (equiv.)	Solvent	Temp/ºC	Results
1	**$Pd(OAc)_2$ (2.5)**	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	Dioxane	80	80%
2	**$Pd(OAc)_2$ (1)**	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	Dioxane	80	62%
3	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	Dioxane	**70**	48%
4	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	Dioxane	**60**	43%
5	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	**DMSO**	80	Trace
6	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	**Toluene**	80	87%
7	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	**DCE**	80	76%
8	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	**DMF**	80	Trace
9	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	**MeCN**	80	29%
10	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	K_2CO_3(2.0)	**THF**	80	73%
11	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**Cs_2CO_3(2.0)**	Dioxane	80	70%
12	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**Na_2CO_3(2.0)**	Dioxane	80	8%
13	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**K_3PO_4(2.0)**	Dioxane	80	83%
14	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**NaOAc(2.0)**	Dioxane	80	Trace
15	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**KOAc(2.0)**	Dioxane	80	9%
16	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**K_2CO_3(1.0)**	Dioxane	80	75%
17	$Pd(OAc)_2$ (5)	PAd_2(*n*-Bu) ·HI (10)	**K_2CO_3(0.5)**	Dioxane	80	50%
18	**$Pd(OAc)_2$ (5)**	**PAd_2(*n*-Bu) ·HI (10)**	**None**	Dioxane	80	NR
19	**$Pd(OAc)_2$ (5)**	**PAd_2(*n*-Bu) ·HI (7.5)**	K_2CO_3(2.0)	Dioxane	80	89%
20	**$Pd(OAc)_2$ (5)**	**PAd_2(*n*-Bu) ·HI (5)**	K_2CO_3(2.0)	Dioxane	80	97% (91%)

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), solvent (2 mL). [b]Determined by ^{19}F NMR using $PhCF_3$ as an internal standard and number in parenthesis is the isolated yield.

Radical Inhibition Experiments

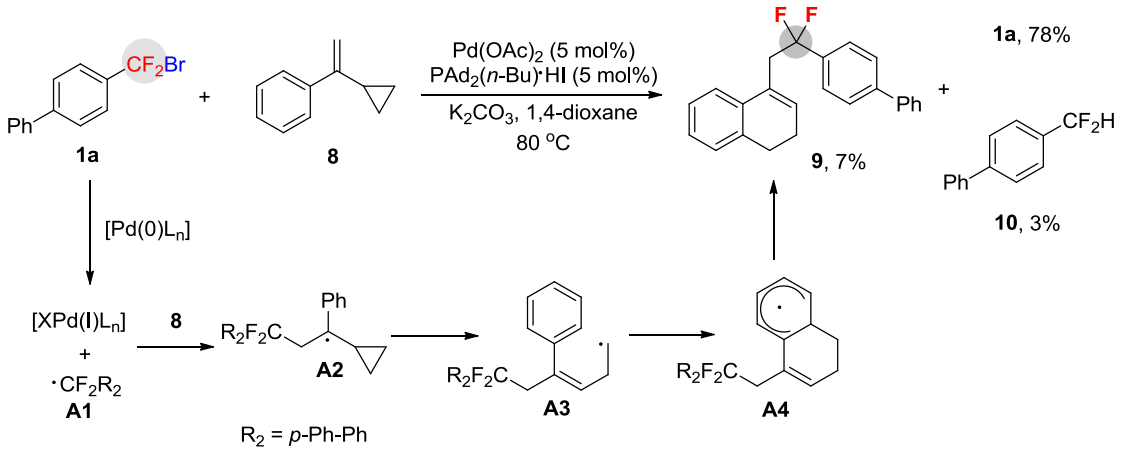


Entry	Additive	**3a**, yield (%)[a]
1	none	97
2	1,4-dinitrobenzene (0.2 equiv)	36
3	1,4-dinitrobenzene (1.0 equiv)	6

[a]Determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

A 25 mL of Schlenck tube equipped with a magnetic stir bar was charged with aryldifluoromethyl bromide **1a** (56.6 mg, 0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 0.05 equiv), PAd_2(*n*-Bu)•HI (4.9 mg, 0.01 mmol, 0.05 equiv) under air, followed by addition of K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) and additive. The vessel was evacuated and backfilled with Ar (3 times), solvent (2 mL) was then added. The Schlenck tube was screw capped and heated to 80 °C. After stirring for 8 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2 mL). The yield was determined by ^{19}F NMR before working up.

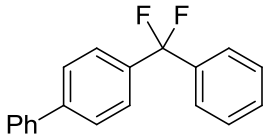
Radical Clock Experiment



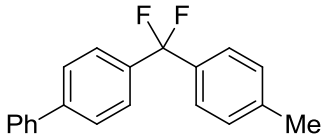
A 25 mL of Schlenck tube equipped with a magnetic stir bar was charged with aryldifluoromethyl bromide **1a** (56.6 mg, 0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 0.05 equiv), PAd_2(*n*-Bu)•HI (4.9 mg, 0.01 mmol, 0.05 equiv) under air, followed by addition of K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv). The vessel was evacuated and backfilled with Ar (3 times), compound **8** (43.3 mg, 0.3 mmol, 1.5 equiv) and 1,4-dioxane (2 mL) were then added. The Schlenck tube was screw capped and heated to 80 °C. After stirring for 8 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2 mL). The yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was filtrated through a pad of Celite® and washed with ethyl acetate (3×5 mL). The filtrate was concentrated. The residue was subjected to column chromatography on silica gel (hexane/EtOAc = 100:1) to afford the product **9** as a semi-solid. ^1H NMR (400 MHz, CDCl3) δ 7.58-7.56 (m, 4H), 7.49-7.44 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 1H), 7.16-7.10 (m, 3H), 5.89 (t, *J* = 4.4 Hz, 1H), 3.31 (t, *J* = 15.4 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.24-2.19 (m, 2H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.4 (t, *J* = 1.7 Hz), 140.3, 136.2, 136.1 (t, *J* = 26.9 Hz), 134.5, 131.6, 128.82, 128.78 (t, *J* = 3.9 Hz), 127.7, 127.4, 127.2, 126.81, 126.75, 126.5, 125.6 (t, *J* = 6.2 Hz), 123.2 (t, *J* = 1.8 Hz), 122.4 (t, *J* = 246.0 Hz), 42.1 (t, *J* = 28.8 Hz), 28.2, 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.3 (t, *J* = 15.6 Hz, 2F). IR (thin film) ν_{max} 3058, 3031, 2933, 2831, 1616, 1488, 1325, 1066 cm^{-1}. MS (EI): m/z (%) 346 (M^+), 203 (100). HRMS: Calculated for $C_{24}H_{20}F_2$: 346.1533; Found: 346.1532.

General Procedure for Palladium-Catalyzed Cross-Coupling of $ArCF_2Br$ 1 with Arylboronic Acids 2.

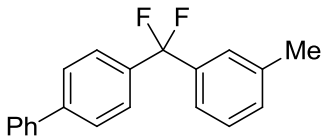
A 25 mL of Schlenck tube equipped with a magnetic stir bar was charged with aryldifluoromethyl bromide **1** (0.4 mmol, 1.0 equiv), phenylboronic acid **2** (0.6 mmol, 1.5 equiv), palladium catalyst (5 mol %), PAd_2(*n*-Bu)•HI (5 mol%) under air, followed by addition of K_2CO_3 (110.6 mg, 0.8mmol, 2.0 equiv). The vessel was evacuated and backfilled with Ar (3 times), dioxane (4 mL) was then added. The Schlenck tube was screw capped and heated to 80 °C. After stirring for 8 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography to give product **3**.



4-(Difluoro(phenyl)methyl)-1,1'-biphenyl (3a). The product (103 mg, 91% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 76-79℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.60-7.55 (m, 6H), 7.48-7.44 (m, 5H), 7.38 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.8 (t, *J* = 1.8 Hz), 140.2, 137.6 (t, *J* = 28.5 Hz), 136.5 (t, *J* = 28.7 Hz), 129.9 (t, *J* = 1.8 Hz), 128.9, 128.4, 127.8, 127.2, 127.1, 126.3 (t, *J* = 5.6 Hz), 125.8 (t, *J* = 5.6 Hz), 120.7 (t, *J* = 242.8 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -88.6 (s, 2F). IR (thin film) ν_{max} 3063, 2923, 1610, 1450, 1273, 1236, 1046 cm^{-1}. MS (EI): m/z (%) 280 (M^+, 100), 203, 127. HRMS: Calculated for $C_{19}H_{14}F_2$: 280.1064; Found: 280.1062.

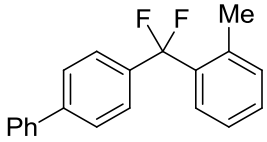


4-(Difluoro(*p*-tolyl)methyl)-1,1'-biphenyl (3b). The product (90 mg, 77% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 126-128℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.60-7.56 (m, 4H), 7.47-7.42 (m, 4H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.7 (t, *J* = 1.9 Hz), 140.2, 140.0 (t, *J* = 1.7 Hz), 136.7 (t, *J* = 28.9 Hz), 134.8 (t, *J* = 28.5 Hz), 129.1, 128.9, 127.7, 127.2, 127.1, 126.3 (t, *J* = 5.5 Hz), 125.8 (t, *J* = 5.5 Hz), 120.9 (t, *J* = 242.3 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.0 (s, 2F). IR (thin film) ν_{max} 3042, 2923, 1612, 1275, 1238, 1051, 838 cm^{-1}. MS (EI): m/z (%) 294 (M^+, 100), 203. HRMS: Calculated for $C_{20}H_{16}F_2$: 294.1220; Found: 294.1216.

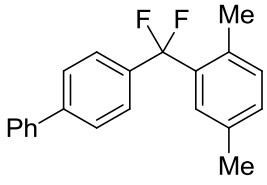


4-(Difluoro(m-tolyl)methyl)-1,1'-biphenyl (3c). The product (105 mg, 89% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 45-47℃. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.64-7.57 (m, 6H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.40-7.31 (m, 4H), 7.26-7.25 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.7 (t, *J* = 1.8 Hz), 140.2, 138.2, 137.6 (t, *J* = 28.3 Hz), 136.7 (t, *J* = 28.9 Hz), 130.6 (t, *J* = 1.6 Hz), 128.9, 128.3, 127.8, 127.2, 127.1, 126.4, 126.3 (t, *J* = 5.4 Hz), 122.9 (t, *J* = 5.7 Hz), 120.8 (t, *J* = 242.9 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.5 (s, 2F). IR (thin film) ν_{max} 3027, 2921, 1612, 1487, 1277, 1077, 969, 703 cm^{-1}. MS (EI): m/z (%) 294 (M^+, 100), 203. HRMS: Calculated for $C_{20}H_{16}F_2$: 294.1220; Found: 294.1219.

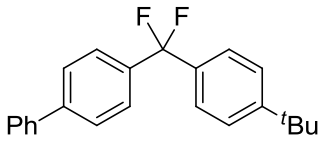


4-(Difluoro(o-tolyl)methyl)-1,1'-biphenyl (3d). The product (97 mg, 83% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 70-53℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 5H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.46 (m, 2H), 7.38 (m, 2H), 7.28 (dt, *J* = 21.2 Hz, *J* = 7.2 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.8 (t, *J* = 2.0 Hz), 140.2, 136.6 (t, *J* = 2.8 Hz), 136.2 (t, *J* = 28.2 Hz), 135.0 (t, *J* = 25.8 Hz), 131.9, 130.1 (t, *J* = 1.5 Hz), 128.9, 127.8, 127.2, 127.1, 126.6 (t, *J* = 5.2 Hz), 126.4 (t, *J* = 8.3 Hz), 125.6, 121.4 (t, *J* = 242.4 Hz), 20.3 (t, *J* = 2.5 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -86.5 (s, 2F). IR (thin film) ν_{max} 3058, 3027, 1933, 1605, 1565, 1402, 1224, 996, 840 cm^{-1}. MS (EI): m/z (%) 294 (M^+), 140 (100). HRMS: Calculated for $C_{20}H_{16}F_2$: 294.1220; Found: 294.1224.

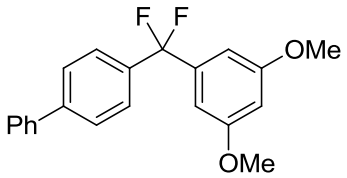


4-((2,5-Dimethylphenyl)difluoromethyl)-1,1'-biphenyl (3e). The product (101 mg, 82% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 58-59℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 8.0 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.15 (dd, *J* = 26.4 Hz, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.7 (t, *J* = 2.0 Hz), 140.2, 136.3 (t, *J* = 28.3 Hz), 135.1,

134.7 (t, *J* = 25.5 Hz), 133.3 (t, *J* = 2.9 Hz), 131.8, 130.7 (t, *J* = 1.5 Hz), 128.8, 127.8, 127.2, 127.0, 126.96 (t, *J* = 8.2 Hz), 126.6 (t, *J* = 5.2 Hz), 121.4 (t, *J* = 242.3 Hz), 21.1, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.4 (s, 2F). IR (thin film) ν_{max} 3027, 2926, 1599, 1486, 1008, 1030 cm^{-1}. MS (EI): m/z (%) 308 (M^+), 154 (100). HRMS: Calculated for $C_{21}H_{18}F_2$: 308.1377; Found: 308.1374.

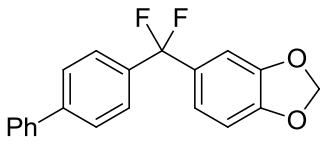


4-((4-(*tert*-Butyl)phenyl)difluoromethyl)-1,1'-biphenyl (3f). The product (90 mg, 67% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 126-128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 4H), 7.49-7.44 (m, 6H), 7.38 (t, *J* = 7.4 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 153.0 (t, *J* = 1.6 Hz), 142.7 (t, *J* = 1.8 Hz), 140.2, 136.7 (t, *J* = 28.9 Hz), 134.8 (t, *J* = 28.6 Hz), 128.9, 127.7, 127.2, 127.1, 126.3 (t, *J* = 5.5 Hz), 125.6 (t, *J* = 5.5 Hz), 125.3, 120.9 (t, *J* = 242.8 Hz), 34.7, 31.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.0 (s, 2F). IR (thin film) ν_{max} 2964, 2869, 1612, 1488, 1407, 1244, 1050 cm^{-1}. MS (EI): m/z (%) 336 (M^+), 321 (100). HRMS: Calculated for $C_{23}H_{22}F_2$: 336.1690; Found: 336.1697.

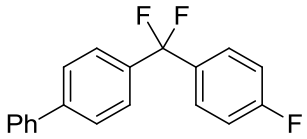


4-((3,5-Dimethoxyphenyl)difluoromethyl)-1,1'-biphenyl (3g). The product (111 mg, 82% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a light-brown solid. m.p. 65-68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.59-7.56 (m, 4H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 2H), 6.51 (s, 1H), 3.80 (s, 6H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 160.8, 142.8 (t, *J* = 1.8 Hz), 140.1, 139.6 (t, *J* = 28.7 Hz), 136.3 (t, *J* = 28.8 Hz), 128.8, 127.8, 127.14, 127.06, 126.2 (t, *J* = 5.5 Hz), 120.5 (t, *J* = 243.7 Hz), 104.0 (t, *J* = 5.8 Hz), 101.6, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 2F). IR (thin film) ν_{max} 3023, 2924, 1612, 1596,

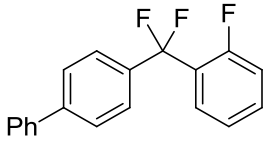
1459, 1336, 1205, 1055cm^{-1}. MS (EI): m/z (%) 340 (M^+, 100), 203. HRMS: Calculated for $C_{21}H_{18}F_2O_2$: 340.1275; Found: 340.1271.



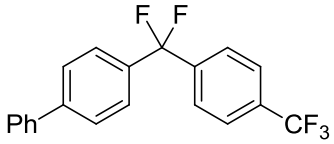
5-([1,1'-Biphenyl]-4-yldifluoromethyl)benzo[*d*][1,3]dioxole (3h). The product (55 mg, 42% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a white solid. m.p. 75-78 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 8.2 Hz, 3H), 7.58-7.57 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 148.8 (t, *J* = 1.7 Hz), 147.7, 142.8 (t, *J* = 1.7 Hz), 140.2, 136.5 (t, *J* = 28.8 Hz), 131.6 (t, *J* = 29.1 Hz), 128.9, 127.8, 127.2, 127.1, 126.3 (t, *J* = 5.4 Hz), 120.6 (t, *J* = 242.8 Hz), 120.1 (t, *J* = 6.2 Hz), 108.0, 106.6 (t, *J* = 5.5 Hz), 101.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.6 (s, 2F). IR (thin film) ν_{max} 2918, 2850, 1611, 1489, 1244, 1032 cm^{-1}. MS (EI): m/z (%) 324 (M^+, 100), 325, 171. HRMS: Calculated for $C_{20}H_{14}F_2O_2$: 324.0962; Found: 324.0965.



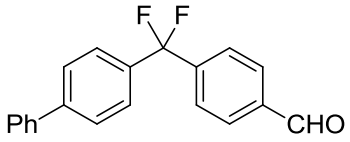
4-(Difluoro(4-fluorophenyl)methyl)-1,1'-biphenyl (3i). The product (102 mg, 86% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 83-86 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.60-7.52 (m, 6H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 163.5 (dt, *J* = 250.9 Hz, *J* = 1.9 Hz), 142.9 (t, *J* = 1.8 Hz), 140.1, 136.2 (t, *J* = 28.6 Hz), 133.7 (dt, *J* = 29.1 Hz, *J* = 3.2 Hz), 128.9, 128.05 (dt, *J* = 8.7 Hz, *J* = 5.5 Hz), 127.8, 127.2, 126.3 (t, *J* = 5.5 Hz), 120.4 (t, *J* = 242.8 Hz), 115.6, 115.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.3 (s, 2F), -110.94 to -110.98 (m, 1F). IR (thin film) ν_{max} 3079, 1605, 1511, 1275, 1236, 1053 cm^{-1}. MS (EI): m/z (%) 298 (M^+, 100), 203. HRMS: Calculated for $C_{19}H_{13}F_3$: 298.0969; Found: 298.0965.



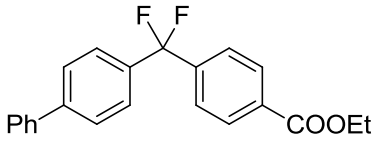
4-(Difluoro(2-fluorophenyl)methyl)-1,1'-biphenyl (3j). The product (86 mg, 73% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 77-79 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.58 (m, 7H), 7.45 (t, *J* = 7.6 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 9.6 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 159.7 (dt, *J* = 254.2 Hz, *J* = 3.8 Hz), 142.9 (t, *J* = 1.8 Hz), 140.1, 135.9 (t, *J* = 28.0 Hz), 132.1 (d, *J* = 8.4 Hz), 128.8, 127.8, 127.2, 127.1, 126.0 (dt, *J* = 5.5 Hz, *J* = 1.1 Hz), 125.1(dt, *J* = 29.1 Hz, *J* = 11.6 Hz), 123.9 (d, *J* = 3.8 Hz), 119.2 (t, *J* = 243.9 Hz), 116.7, 116.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.4 (d, *J* = 11.3 Hz, 2F), -112.6 to -112.7 (m, 1F). IR (thin film) ν_{max} 3053, 1618, 1490, 1237, 1220, 1055 cm^{-1}. MS (EI): m/z (%) 298 (M^+, 100), 203. HRMS: Calculated for $C_{19}H_{13}F_3$: 298.0969; Found: 298.0971.



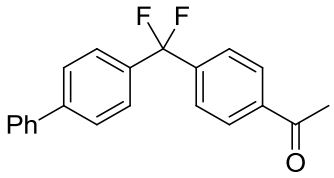
4-(Difluoro(4-(trifluoromethyl)phenyl)methyl)-1,1'-biphenyl (3k). The product (101 mg, 73% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 122-125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.64 (m, 6H), 7.60-7.55 (m, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 143.2 (t, *J* = 1.7 Hz), 141.3 (t, *J* = 29.2 Hz), 140.0, 135.7 (t, *J* = 28.3 Hz), 132.0 (q, *J* = 32.6 Hz), 128.9, 127.9, 127.3, 127.2, 126.3 (t, *J* = 5.6 Hz), 126.2 (t, *J* = 5.6 Hz), 125.6 (q, *J* =3.8 Hz), 123.7 (q, *J* = 273.7 Hz), 120.1 (t, *J* = 243.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s, 3F), -89.6 (s, 2F). IR (thin film) ν_{max} 3082, 1622, 1415, 1325, 1174, 1143, 1068 cm^{-1}. MS (EI): m/z (%) 348 (M^+), 203 (100). HRMS: Calculated for $C_{20}H_{13}F_5$: 348.0937; Found: 348.0941.



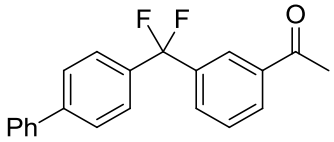
4-([1,1'-Biphenyl]-4-yldifluoromethyl)benzaldehyde (3l). The product (57 mg, 46% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a white solid. m.p. 100-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 191.5, 143.3 (t, *J* = 28.7 Hz), 143.2 (t, *J* = 1.8 Hz), 139.9, 137.2 (t, *J* = 1.4 Hz), 135.6 (t, *J* = 28.3 Hz), 129.8, 128.9, 127.9, 127.3, 127.2, 126.5 (t, *J* = 5.6 Hz), 126.1 (t, *J* = 5.6 Hz), 120.1 (t, *J* = 244.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.0 (s, 2F). IR (thin film) ν_{max} 3066, 3028, 2854, 1695, 1392, 1275, 1237, 1061 cm^{-1}. MS (EI): m/z (%) 308 (M^+), 280 (100). HRMS: Calculated for $C_{20}H_{14}F_2O$: 308.1013; Found: 308.1008.



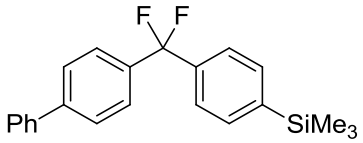
Ethyl 4-([1,1'-biphenyl]-4-yldifluoromethyl)benzoate (3m). The product (123 mg, 87% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a white solid. m.p. 107-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.59-7.54 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 165.7, 143.0 (t, *J* = 1.7 Hz), 141.7 (t, *J* = 28.8 Hz), 140.0, 135.9 (t, *J* = 28.4 Hz), 131.9 (t, *J* = 1.6 Hz), 129.7, 128.8, 127.8, 127.2, 127.1, 126.1 (t, *J* = 5.6 Hz), 125.8 (t, *J* = 5.6 Hz), 120.3 (t, *J* = 243.8 Hz), 61.2, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.7 (s, 2F). IR (thin film) ν_{max} 2992, 1713, 1412, 1274, 1112, 1063, cm^{-1}. MS (EI): m/z (%) 352 (M^+), 242 (100). HRMS: Calculated for $C_{22}H_{18}F_2O_2$: 352.1275; Found: 352.1270.



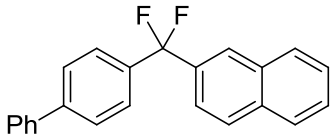
1-(4-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)ethanone (3n). The product (83 mg, 64% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a white solid. m.p. 95-97 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 9.0 Hz, 4H), 7.57 (t, *J* = 8.4 Hz, 4H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 197.2, 143.0 (t, *J* = 1.7 Hz), 141.9 (t, *J* = 28.8 Hz),139.9, 138.1, 135.8 (t, *J* = 28.4 Hz), 128.8, 128.4, 127.8, 127.2, 127.1, 126.1 (t, *J* = 5.6 Hz), 126.0 (t, *J* = 5.6 Hz), 120.2 (t, *J* = 243.8 Hz), 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.9 (s, 2F). IR (thin film) ν_{max} 3042, 2921, 1685, 1409, 1274, 1238, 1064, 1007 cm^{-1}. MS (EI): m/z (%) 322 (M^+), 307 (100). HRMS: Calculated for $C_{21}H_{16}F_2O$: 322.1169; Found: 322.1165.



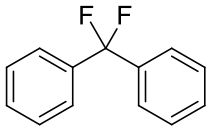
1-(3-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)ethanone (3o). The product (93 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a white solid. m.p. 57-60 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.60-7.56 (m, 5H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 197.2, 142.98 (t, *J* = 1.7 Hz), 139.9, 138.3 (t, *J* = 29.1 Hz), 137.3, 135.9 (t, *J* = 28.5 Hz), 130.2 (t, *J* = 5.4 Hz), 129.7, 128.9, 128.8, 127.8, 127.2, 127.1, 126.1 (t, *J* = 5.6 Hz), 125.5 (t, *J* = 5.6 Hz), 120.3 (t, *J* = 243.7 Hz), 26.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.9 (s, 2F). IR (thin film) ν_{max} 3357, 3070, 1686, 1257, 1212, 1057 cm^{-1}. MS (EI): m/z (%) 322 (M^+), 307 (100). HRMS: Calculated for $C_{21}H_{16}F_2O$: 322.1169; Found: 322.1165.



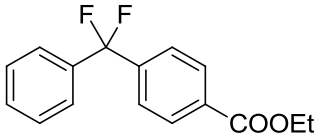
(4-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)trimethylsilane (3p). The product (120 mg, 85% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 117-119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.59-7.58 (m, 6H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 0.28 (s, 9H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.9 (t, *J* = 1.5 Hz), 142.8 (t, *J* = 1.7 Hz), 140.2, 137.9 (t, *J* = 28.6 Hz), 136.6 (t, *J* = 28.7 Hz), 133.4, 128.9, 127.8, 127.2, 127.1, 126.3 (t, *J* = 5.6 Hz), 124.9 (t, *J* = 5.6 Hz), 120.8 (t, *J* = 242.9 Hz), -1.25.^{19}F NMR (376 MHz, $CDCl_3$) δ -89.1 (s, 2F). IR (thin film) ν_{max} 3032, 2962, 1488, 1404, 1243, 1051 cm^{-1}. MS (EI): m/z (%) 352 (M^+), 337 (100). HRMS: Calculated for $C_{22}H_{22}F_2Si$: 352.1459; Found: 352.1454.



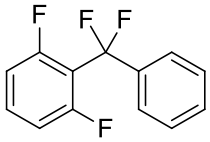
2-([1,1'-Biphenyl]-4-yldifluoromethyl)naphthalene (3q). The product (68 mg, 51% yield) was purified with silica gel chromatography (use Petroleum ether as eluent) as a white solid. m.p. 85-89 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.92-7.87 (m, 3H), 7.66-7.59 (m, 7H), 7.57-7.53 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 142.8 (t, *J* = 1.7 Hz), 140.1, 136.5 (t, *J* = 28.6 Hz), 134.8 (t, *J* = 28.1 Hz), 133.7, 132.5, 128.9, 128.7, 128.5, 127.8, 127.7, 127.22, 127.17, 127.13, 126.7, 126.4 (t, *J* = 5.5 Hz), 125.5 (t, *J* = 6.5 Hz), 123.0 (t, *J* =4.6 Hz), 121.0 (t, *J* = 242.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.4 (s, 2F). IR (thin film) ν_{max} 3057, 1601, 1488, 1402, 1250, 1191, 1062 cm^{-1}. MS (EI): m/z (%) 330 (M^+, 100), 331. HRMS: Calculated for $C_{23}H_{16}F_2$: 330.1220; Found: 330.1218.



1,2-Bis(phenyl)difluoromethane (3r). 1.0 equiv of H_2O was used. The product (35 mg, 42% yield) was purified with silica gel chromatography (use pentane as eluent) as a light-yellow oil. This is a known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.47-7.43 (m, 6H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 137.7 (t, *J* = 28.5 Hz), 129.8, 128.4, 125.8 (t, *J* = 5.7 Hz), 120.7 (t, *J* = 242.8 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 2F).

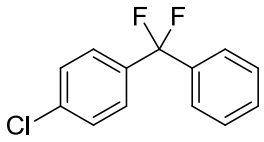


Ethyl 4-(difluoro(phenyl)methyl)benzoate (3s). 1.0 equiv of H_2O was used. The product (62 mg, 56% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a dark brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.50-7.48 (m, 2H), 7.43-7.41 (m, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 165.8, 141.8 (t, *J* = 28.7 Hz), 137.0 (t, *J* = 28.2 Hz), 131.8 (t, *J* = 1.6 Hz), 130.1 (t, *J* = 1.8 Hz), 129.6, 128.5, 125.8 (t, *J* = 5.6 Hz), 125.6 (t, *J* = 5.6 Hz), 120.2 (t, *J* = 243.8 Hz), 61.2, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.0 (s, 2F). IR (thin film) ν_{max} 3425, 2983, 1717, 1453, 1409, 1274 cm^{-1}. MS (EI): m/z (%) 276 (M^+), 231 (100). HRMS: Calculated for $C_{16}H_{14}F_2O_2$: 276.0962; Found: 276.0965.

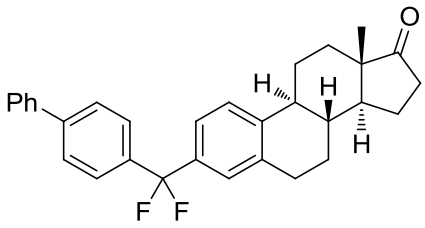


2-(Difluoro(phenyl)methyl)-1,3-difluorobenzene (3t). The product (64 mg, 66% yield) was purified with silica gel chromatography (use pentane as eluent) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.44-7.42 (m, 3H), 7.39-7.33 (m, 1H), 6.94 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 159.8 (dm, *J* = 256.8 Hz), 137.2 (t, *J* = 27.5 Hz), 131.8 (t, *J* = 10.9 Hz),

130.2 (t, J = 1.8 Hz), 128.5, 125.0 (t, J = 5.6 Hz), 118.7 (t, J = 247.0 Hz),112.7(m), 112.5 (m).^{19}F NMR (376 MHz, $CDCl_3$) δ -87.1 (t, J=28.2, 2F). -110.3 (tdd, J = 28.2 Hz, J = 9.1 Hz, J = 5.9 Hz, 2F). IR (thin film) ν_{max} 3068, 3034, 1623, 1605, 1453, 1225, 1127, 1038 cm^{-1}. MS (EI): m/z (%) 240 (M^+), 127 (100). HRMS: Calculated for $C_{13}H_8F_4$: 240.0562; Found: 240.0564.

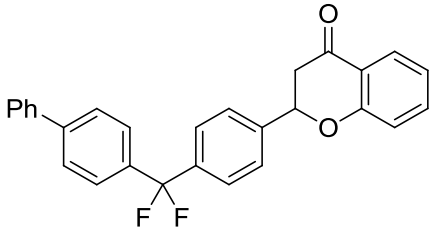


1-(4-Chlorophenyl)-1-phenyldifluoromethane (3u). The product (51 mg, 53% yield) was purified with silica gel chromatography (use pentane as eluent) as a colorless oil. This is a known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.47-7.43 (m, 5H), 7.40 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 137.1 (t, J = 28.4 Hz), 136.2 (t, J = 29.0 Hz), 136.0 (t, J = 2.1 Hz), 130.1 (t, J = 1.8 Hz), 128.7, 128.5, 127.3 (t, J = 5.5 Hz), 125.7 (t, J = 5.6 Hz), 120.3 (t, J = 243.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 2F).



(8*R*,9*S*,13*S*,14*S*)-3-([1,1'-Biphenyl]-4-yldifluoromethyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (5). The reaction was carried out in 0.3 mmol scale. The product (108 mg, 79% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a light yellow solid. m.p. 59-62 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 6H), 7.46 (t, J = 7.6 Hz, 2H), 7.40-7.30 (m, 4H), 2.97-2.94 (m, 2H), 2.56-2.49 (m, 1H), 2.46-2.42 (m, 1H), 2.21-2.14 (m, 1H), 2.12-1.98 (m, 4H), 1.68-1.44 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 220.6, 142.6, 141.6, 140.2, 136.8, 136.7 (t, J = 29.0 Hz), 135.1 (t, J = 28.6 Hz), 128.8, 127.7, 127.14, 127.05, 126.2(t, J = 5.5 Hz), 125.4,123.1(t, J = 5.6 Hz),120.8 (t, J = 242.5 Hz), 50.4, 47.9, 44.4, 37.9, 35.8, 31.5, 29.4, 26.3, 25.6, 21.5, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.2 (s, 2F). IR (thin film) ν_{max} 2930, 1738, 1612, 1417, 1240, 1085 cm^{-1}. MS (EI): m/z (%) 456 (M^+), 203

(100). HRMS: Calculated for $C_{31}H_{30}F_4O$: 456.2265; Found: 456.2261.



2-(4-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)chroman-4-one (7). The reaction was carried out in 0.3 mmol scale. The product (105 mg, 82% yield) was purified with silica gel chromatography (Petroleum ether/AcOEt = 30/1) as a light-yellow solid. m.p. 162-166 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 1H), 7.67-7.64 (m, 4H), 7.61-7.58 (m, 5H), 7.56-7.51 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 5.53 (dd, *J* = 13.2 Hz, *J* = 2.8 Hz, 1H), 3.08 (dd, *J* = 16.8 Hz, *J* = 13.2 Hz, 1H), 2.92 (dd, *J* = 16.8 Hz, *J* = 3.2 Hz, 1H). ^{13}C NMR (101.0 MHz, $CDCl_3$) δ 191.4, 161.3, 142.9 (t, *J* = 1.5 Hz), 140.5 (t, *J* = 1.6 Hz), 140.1, 138.1 (t, *J* = 28.9 Hz), 136.3, 136.2 (t, *J* = 28.6 Hz), 128.9, 127.8, 127.2, 127.1, 126.4 (t, *J* = 5.5 Hz), 126.2 (t, *J* = 5.5 Hz), 126.15, 121.8, 120.9, 120.5 (t, *J* = 243.3 Hz), 118.1, 79.0, 44.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 2F). IR (thin film) ν_{max} 1698, 1608, 1463, 1301, 1227, 1053 cm^{-1}. MS (EI): m/z (%) 426 (M^+), 147 (100). HRMS: Calculated for $C_{28}H_{20}F_2O_2$: 426.1431; Found: 426.1436.

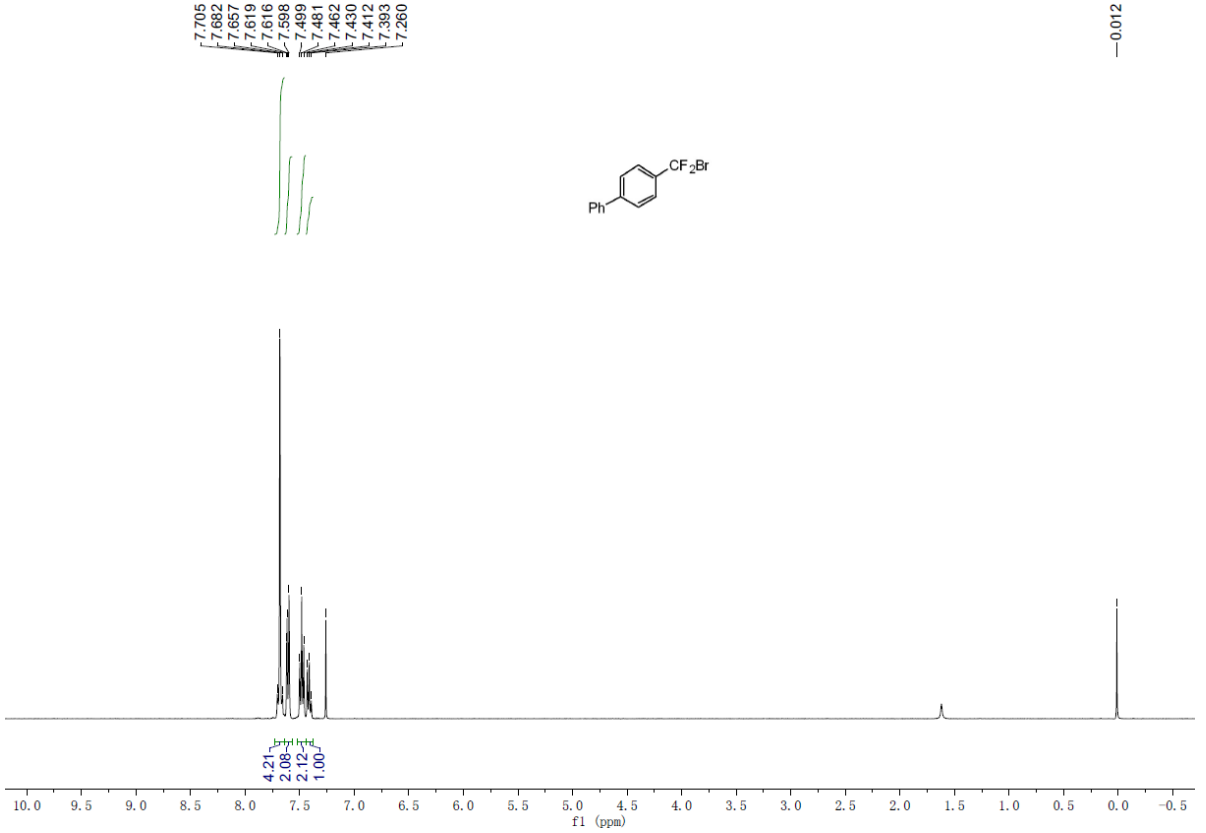
References:

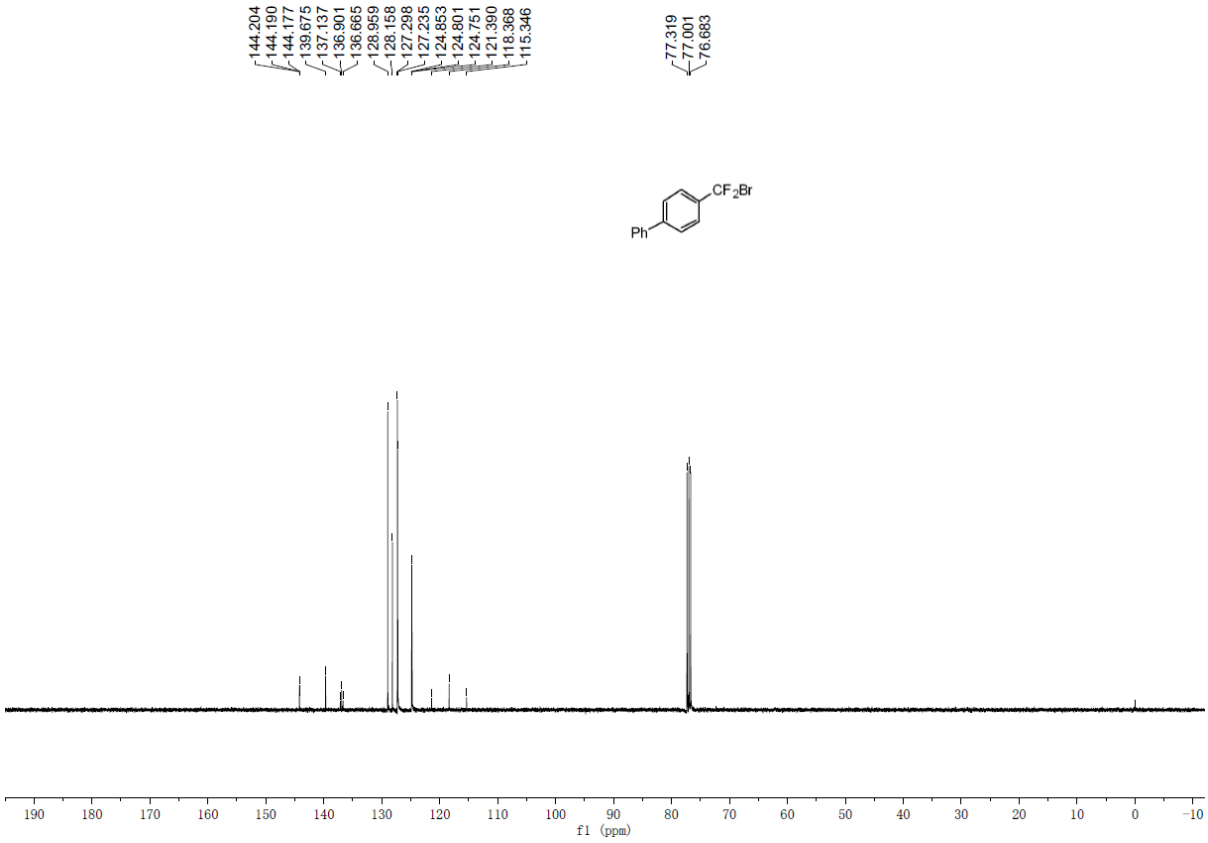
(1). J. He and C. U. Pittman, *Synth.Commun.*, 1999, **29**, 855.

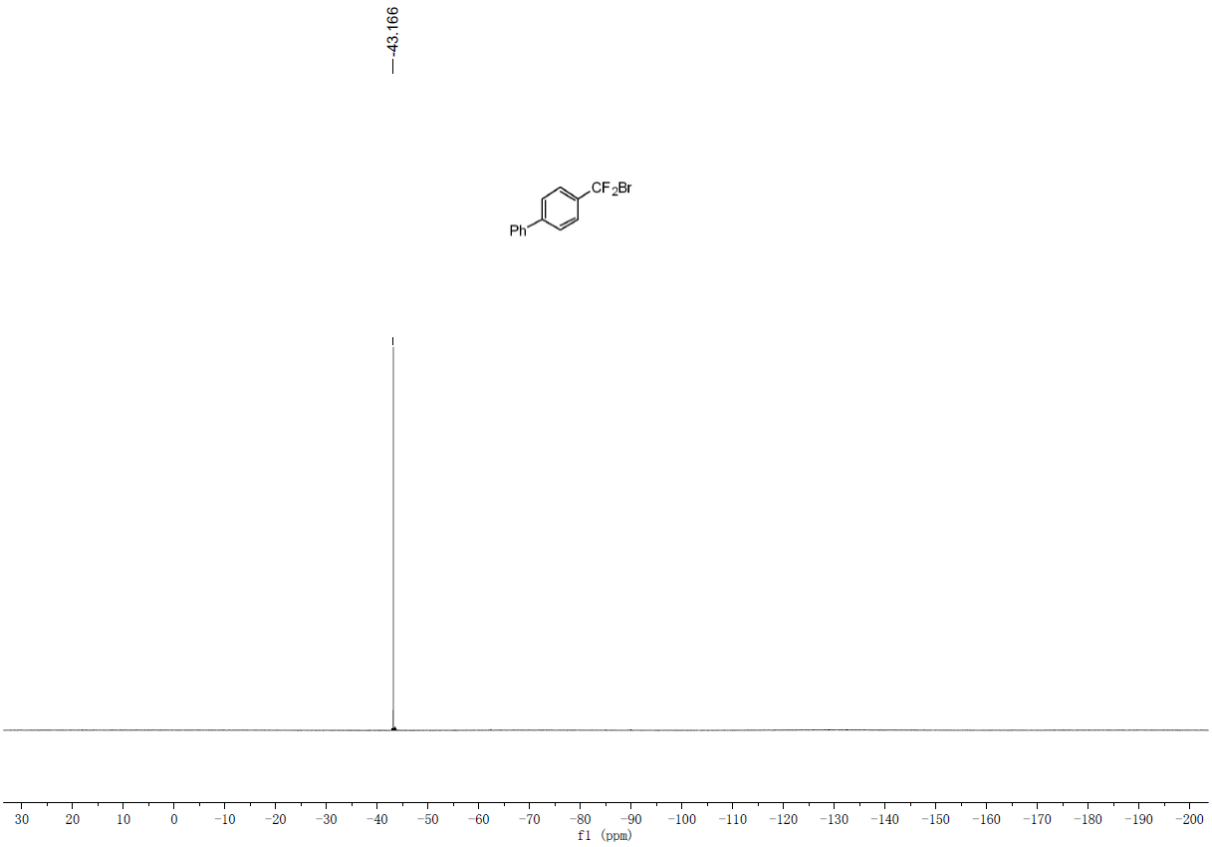
(2). C.-D.-G. Geraldine, WO 2009121939, 2009.

(3). Y. Chang, A. Tewari, A.-I. Adi and C. Bae, *Tetrahedron*, 2008, **64**, 9837.

4-(Bromodifluoromethyl)-1,1'-biphenyl (1a).



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Ph
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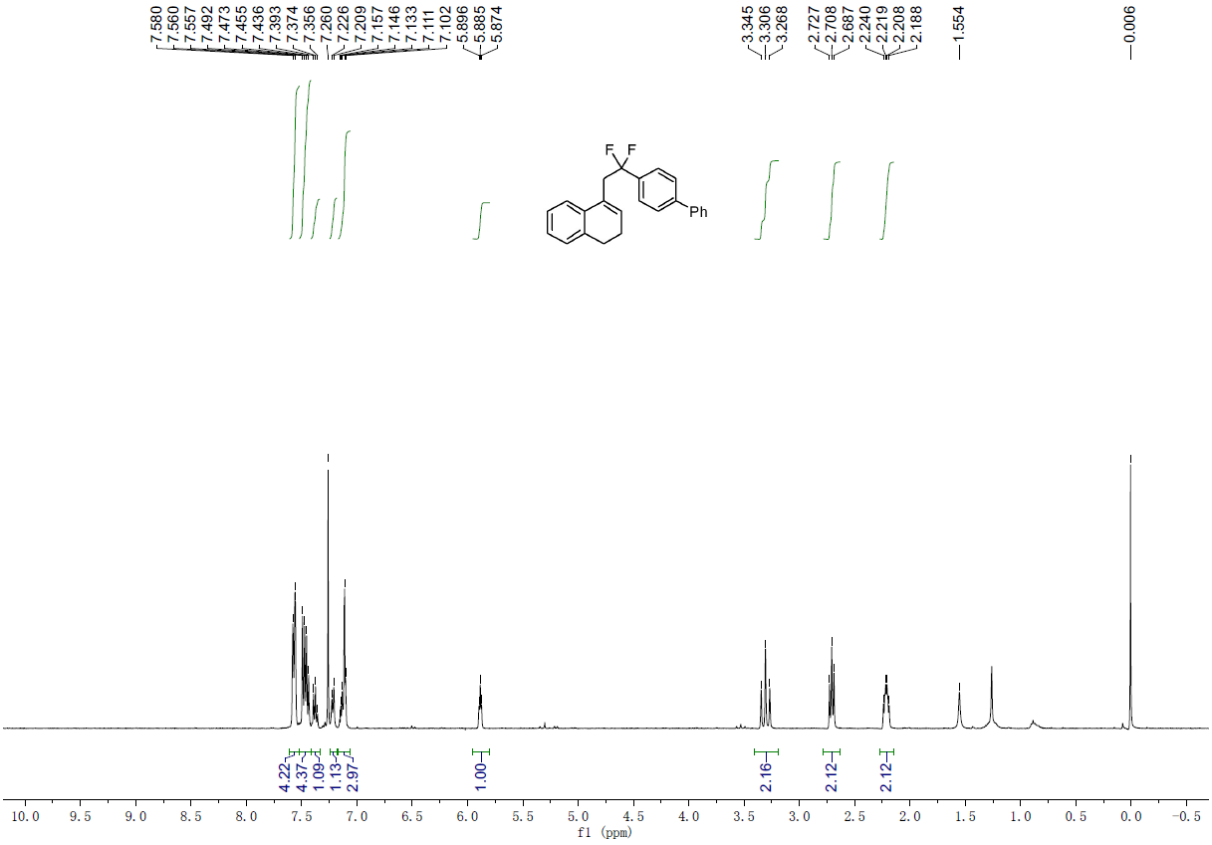
f1 (ppm)

Compound 9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7.356
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7.226
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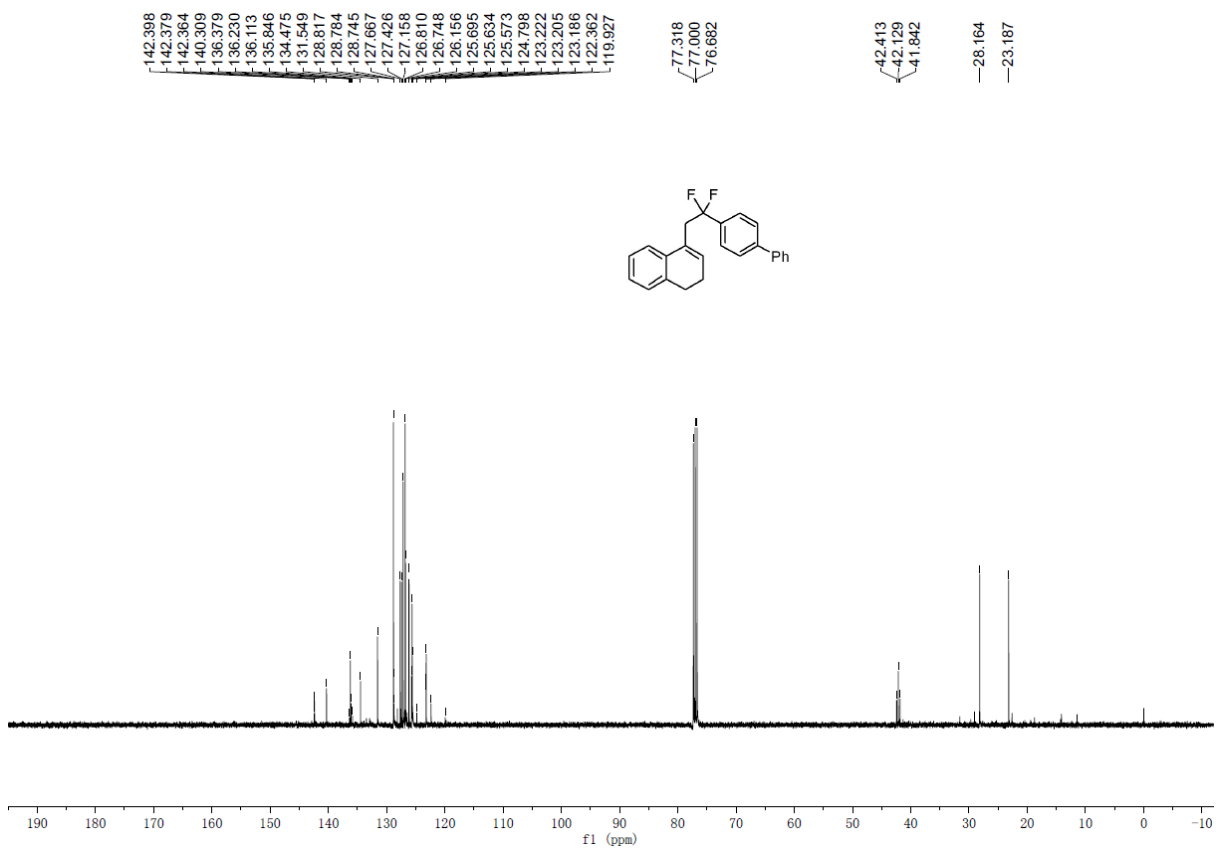
7.157
7.146
7.133
7.111
7.102
5.896
5.885
5.874
3.345
3.306
3.268
2.727
2.708
2.687
2.240
2.219
2.208
2.188
1.554
0.006
F
F
Ph
4.22
4.37
1.09
1.13
2.97
1.00
2.16
2.12
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.810
126.748
126.156
125.695
125.634
125.573
124.798
123.222
123.205
123.186
122.362
119.927
77.318
77.000
76.682
42.413
42.129
41.842
28.164
23.187
F
F
Ph
190
180
170
160
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140
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120
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100
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80
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40
30
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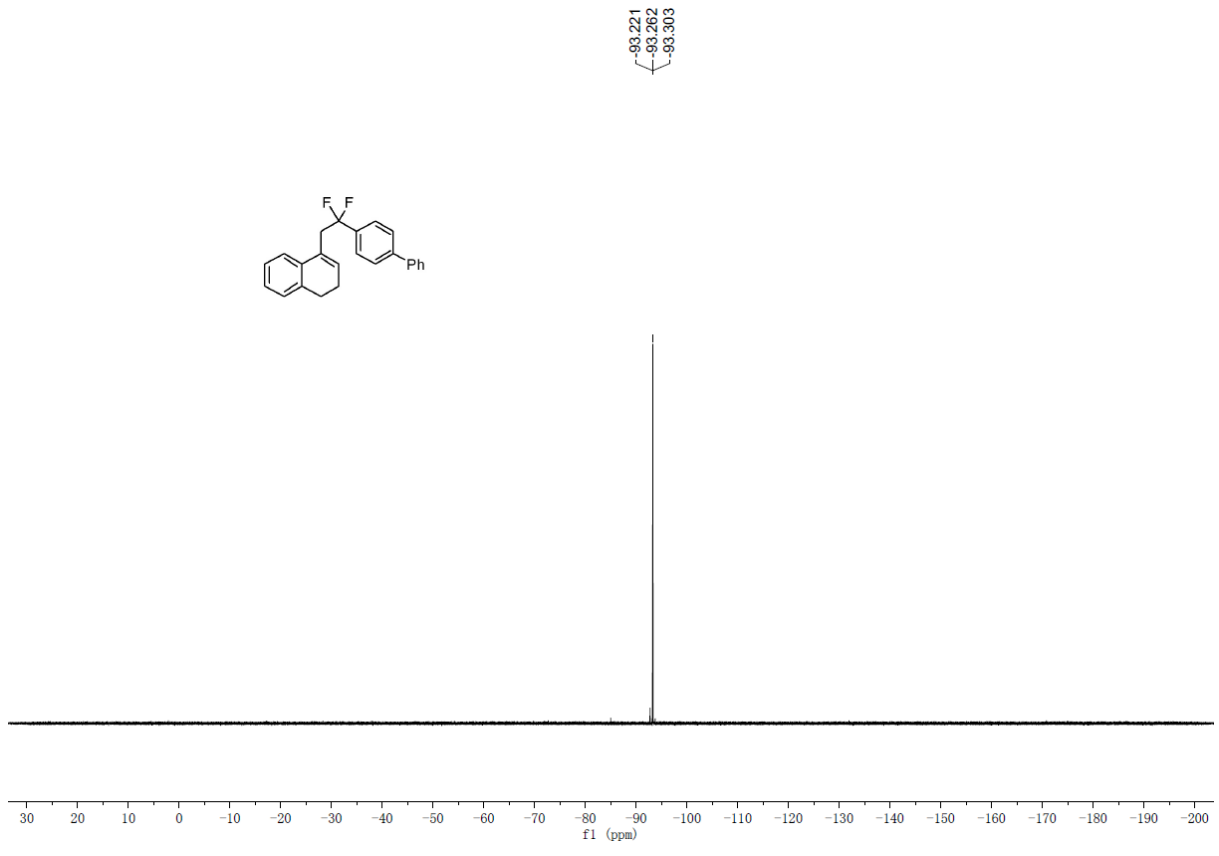
0
-10
f1 (ppm)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-93.303
F
F
Ph
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20
10
0
-10
-20
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-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
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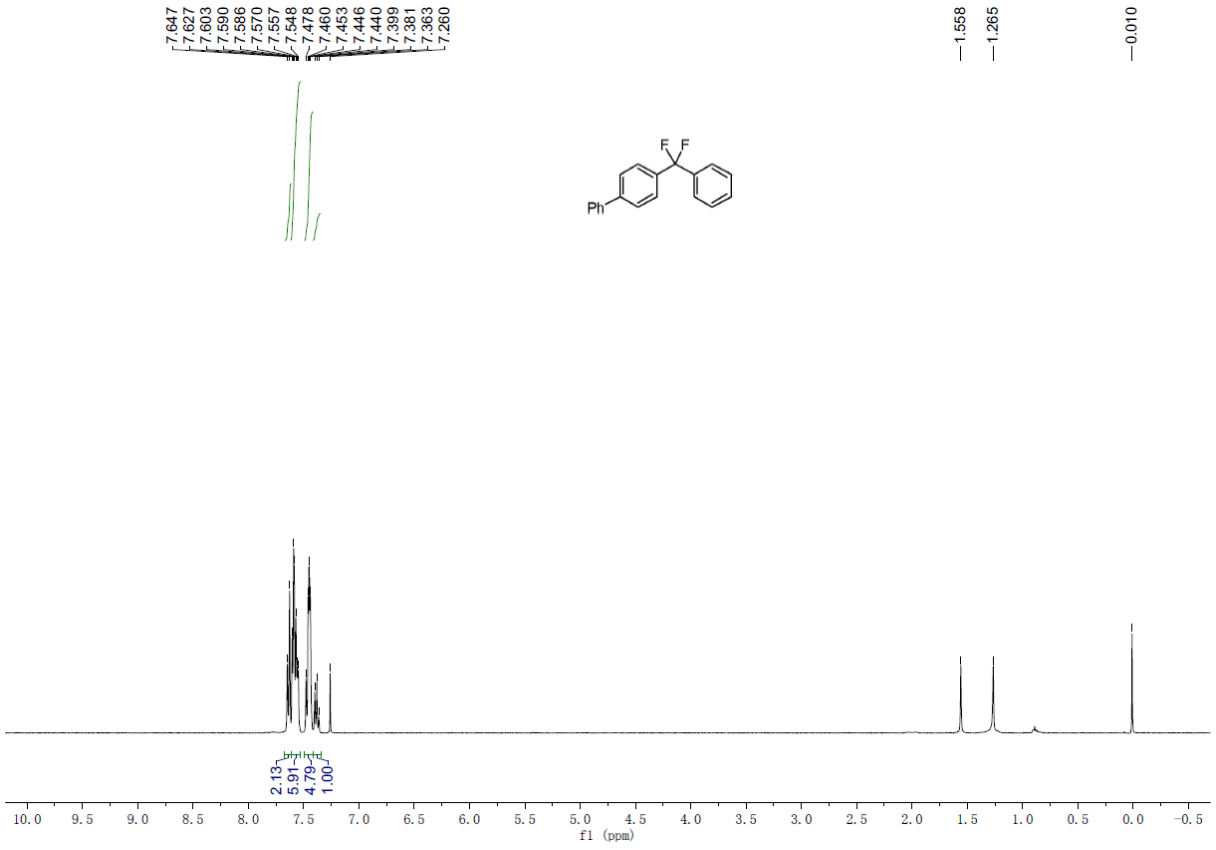
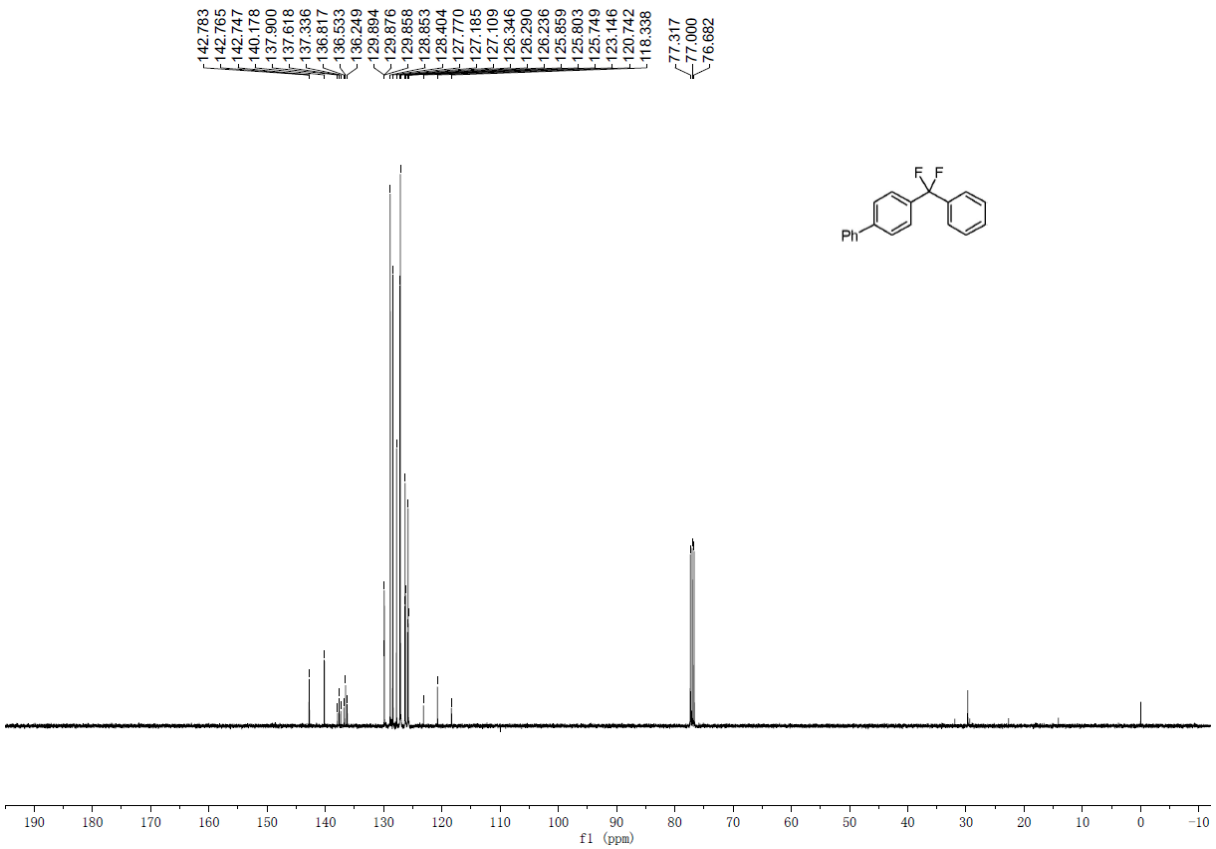
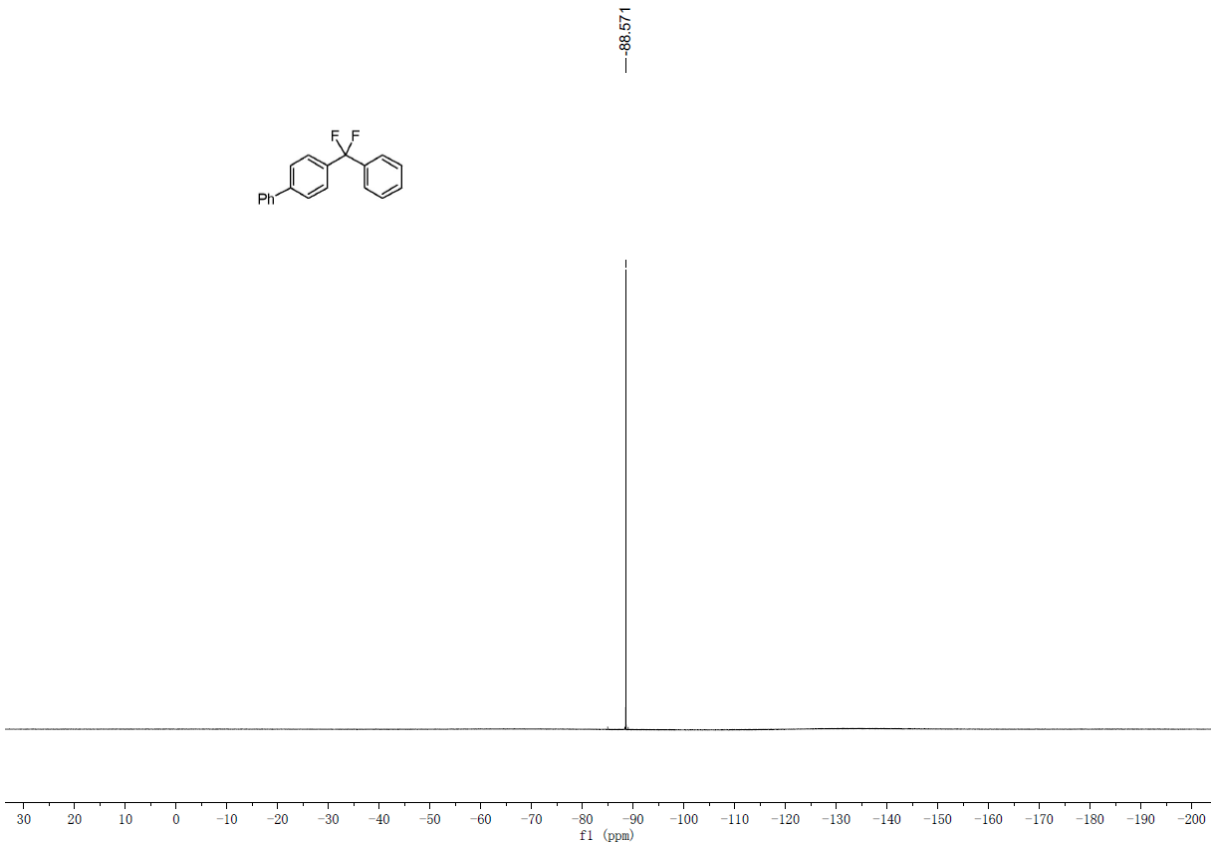
-160
-170
-180
-190
-200
f1 (ppm)

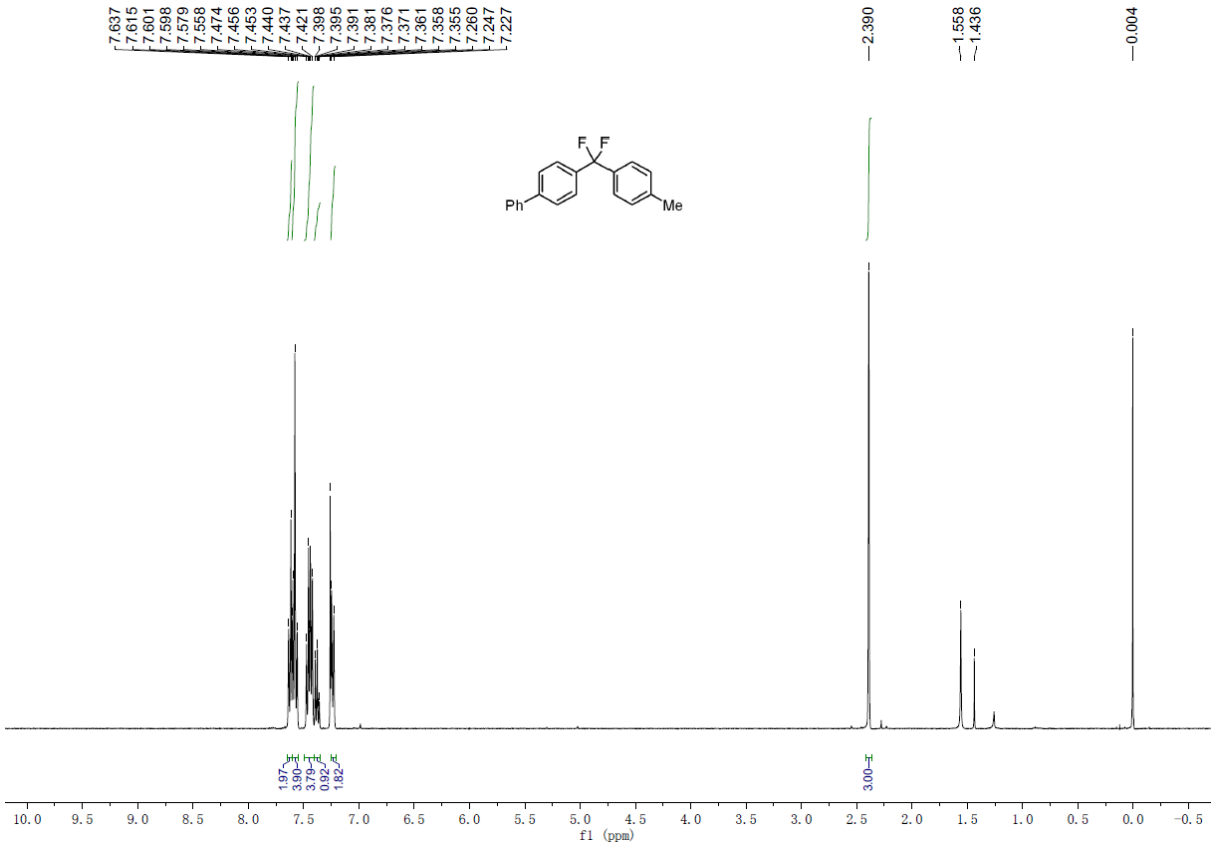
4-(Difluoro(phenyl)methyl)-1,1'-biphenyl (3a).

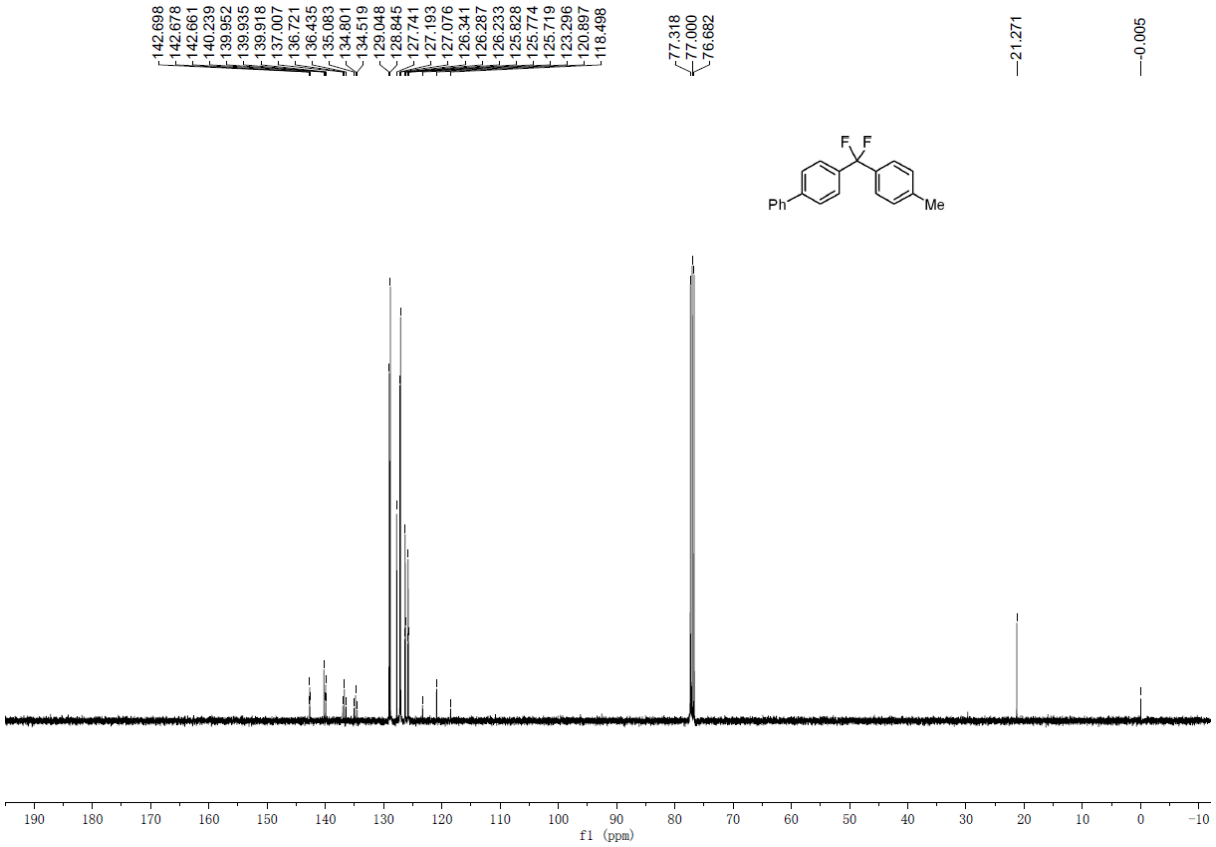






4-(Difluoro(*p*-tolyl)methyl)-1,1'-biphenyl (3b).

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126.287
126.233
125.828
125.774
125.719
123.296
120.897
118.498
77.318
77.000
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Ph
Me
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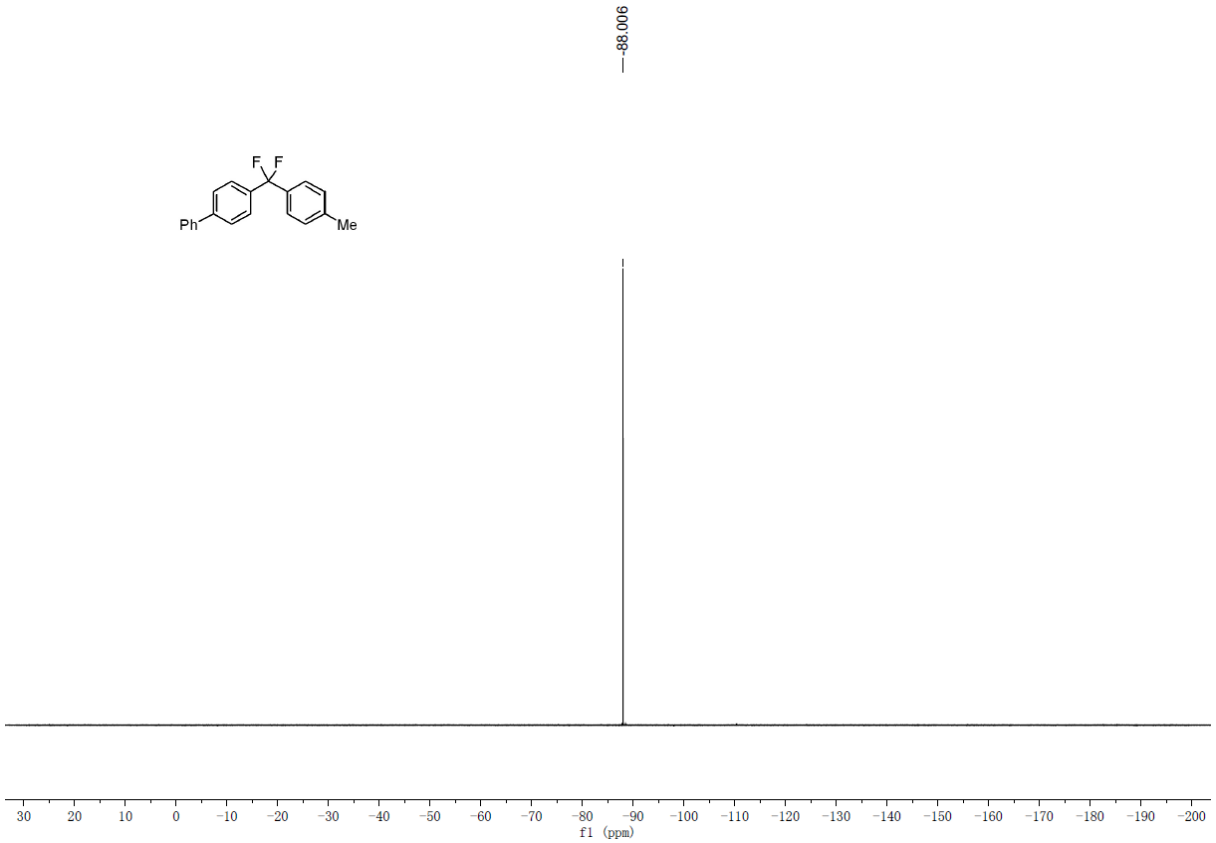
f1 (ppm)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F F
Ph
Me
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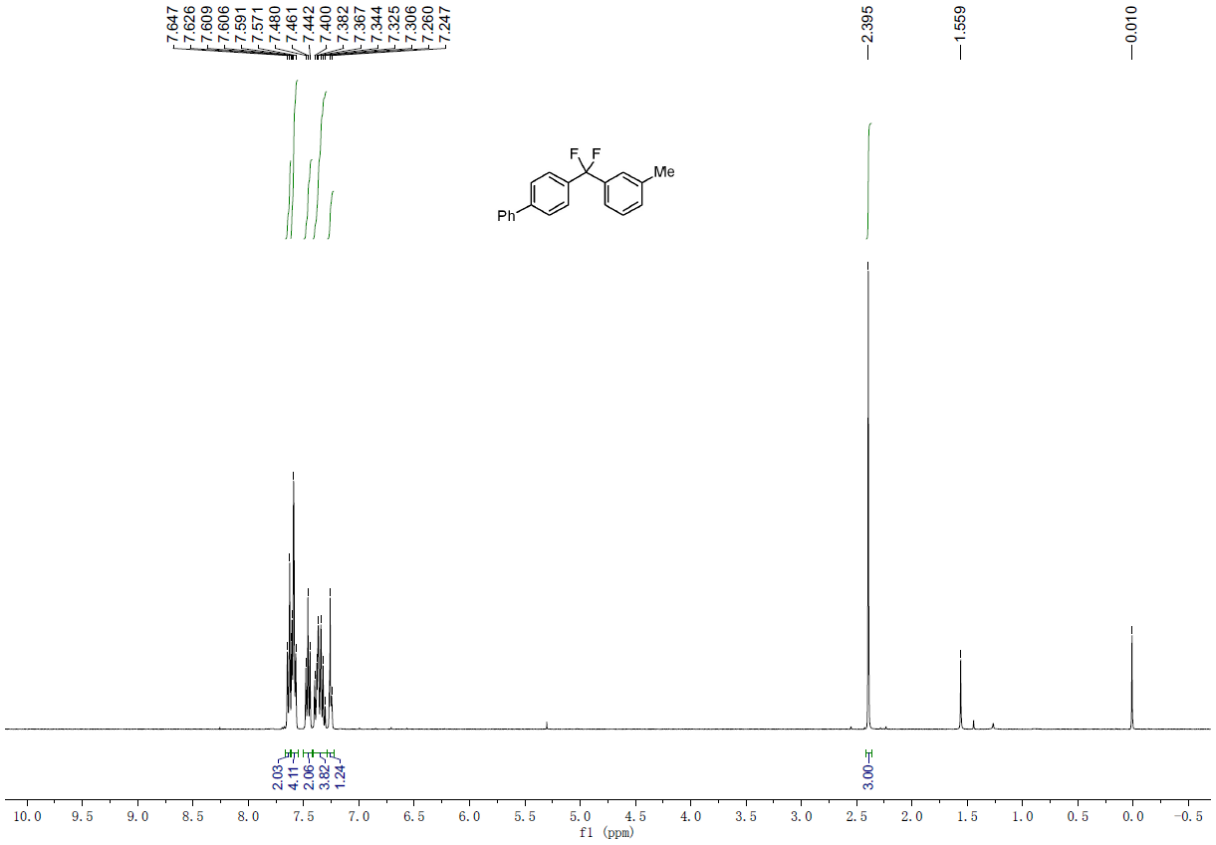
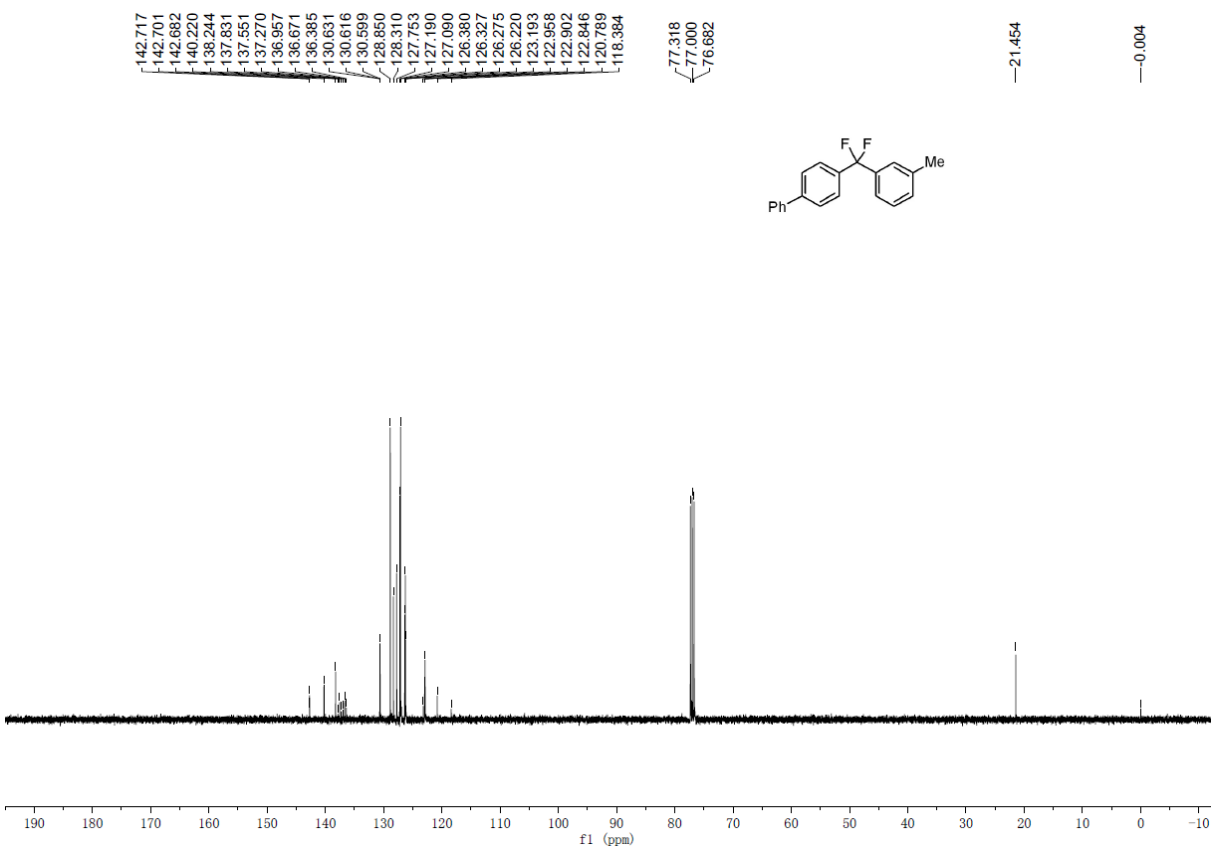
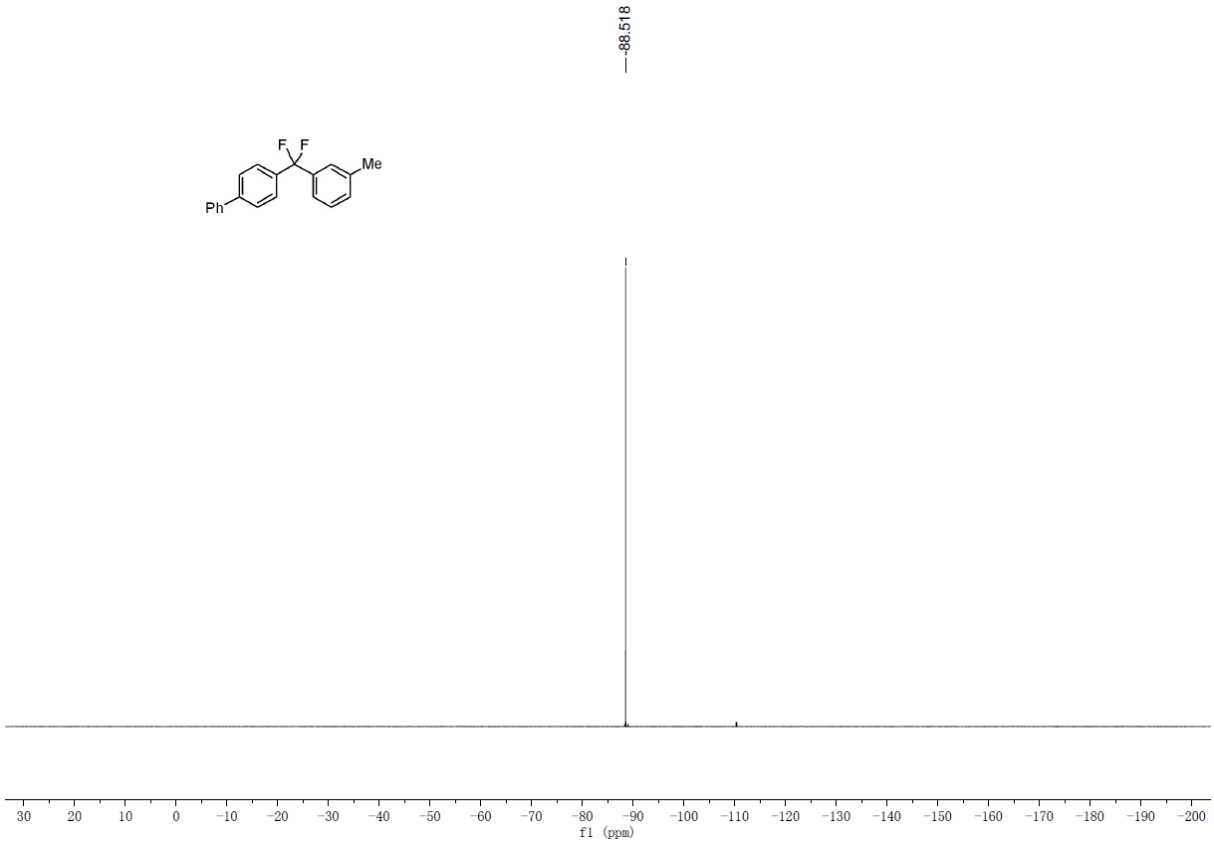
f1 (ppm)

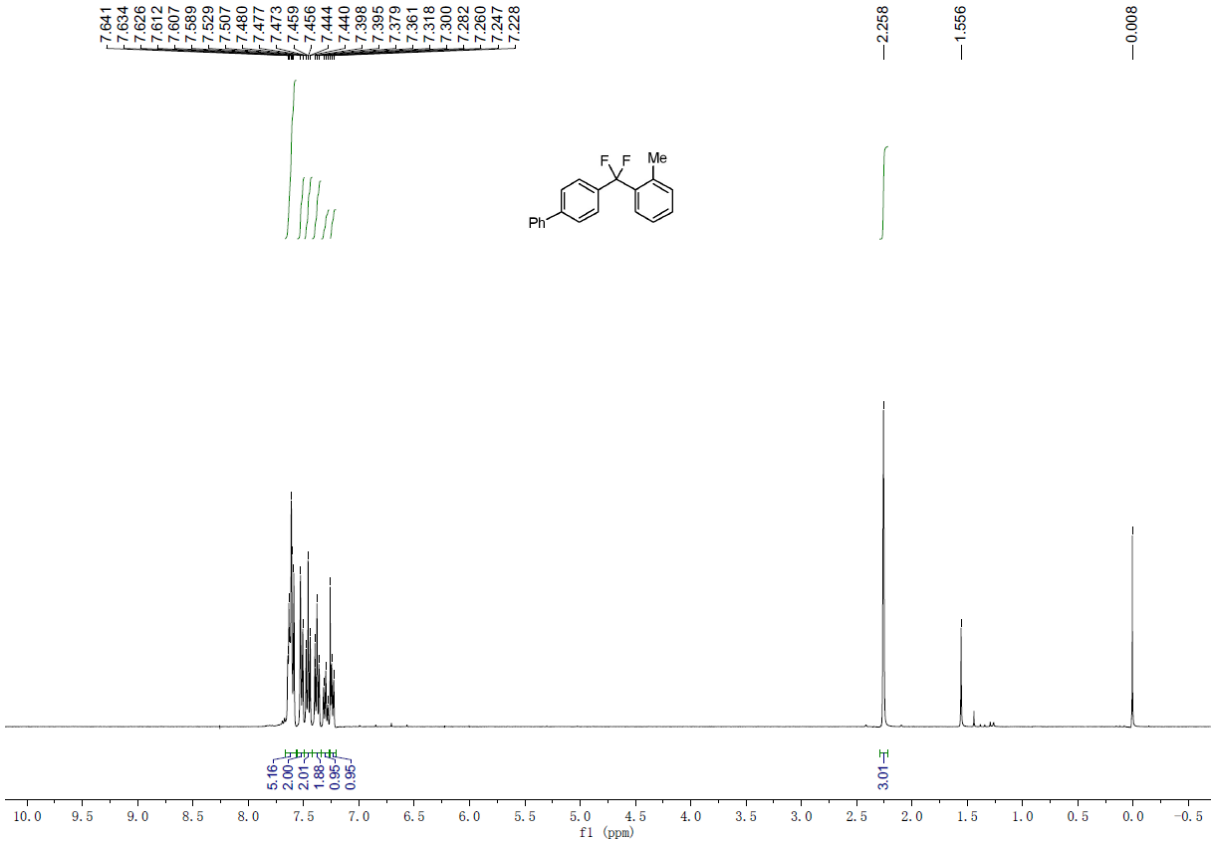
4-(Difluoro(m-tolyl)methyl)-1,1'-biphenyl (3c).

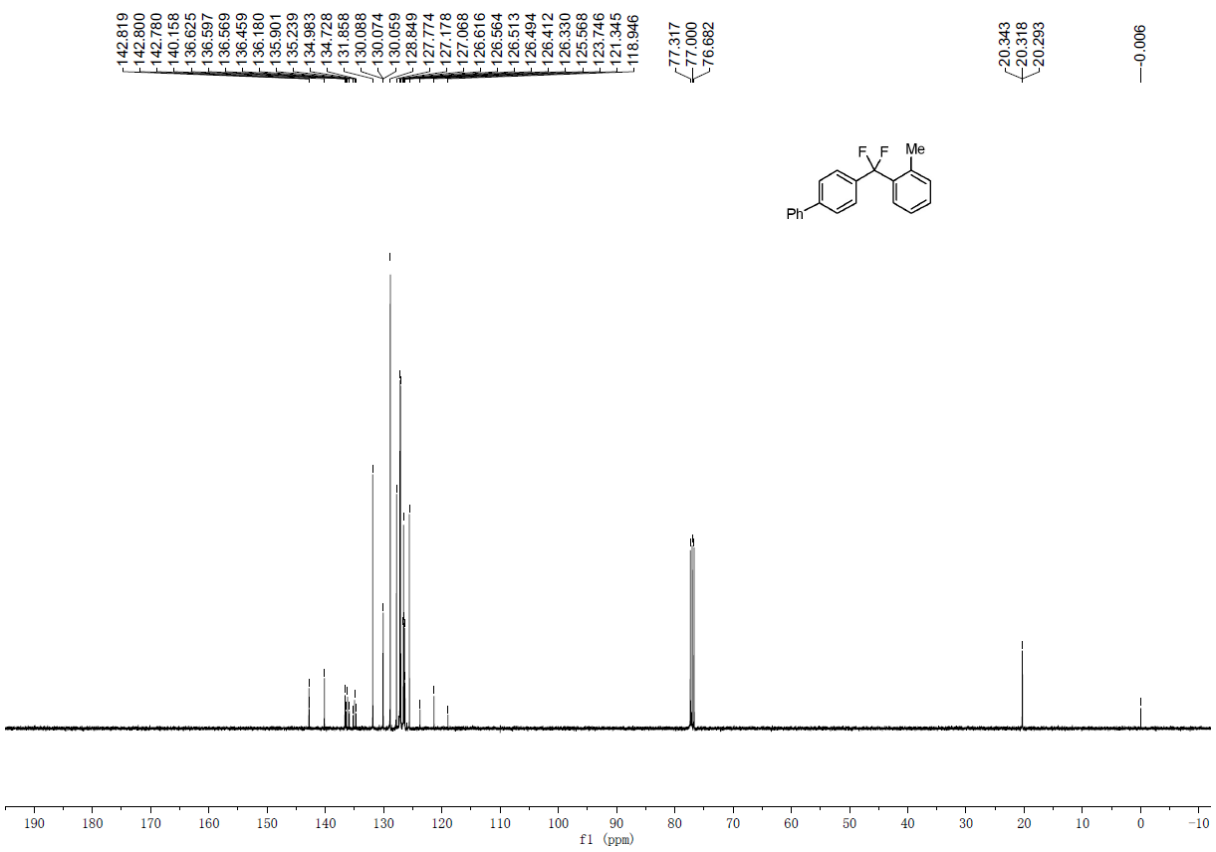






4-(Difluoro(o-tolyl)methyl)-1,1'-biphenyl (3d).

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121.345
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Me
Ph
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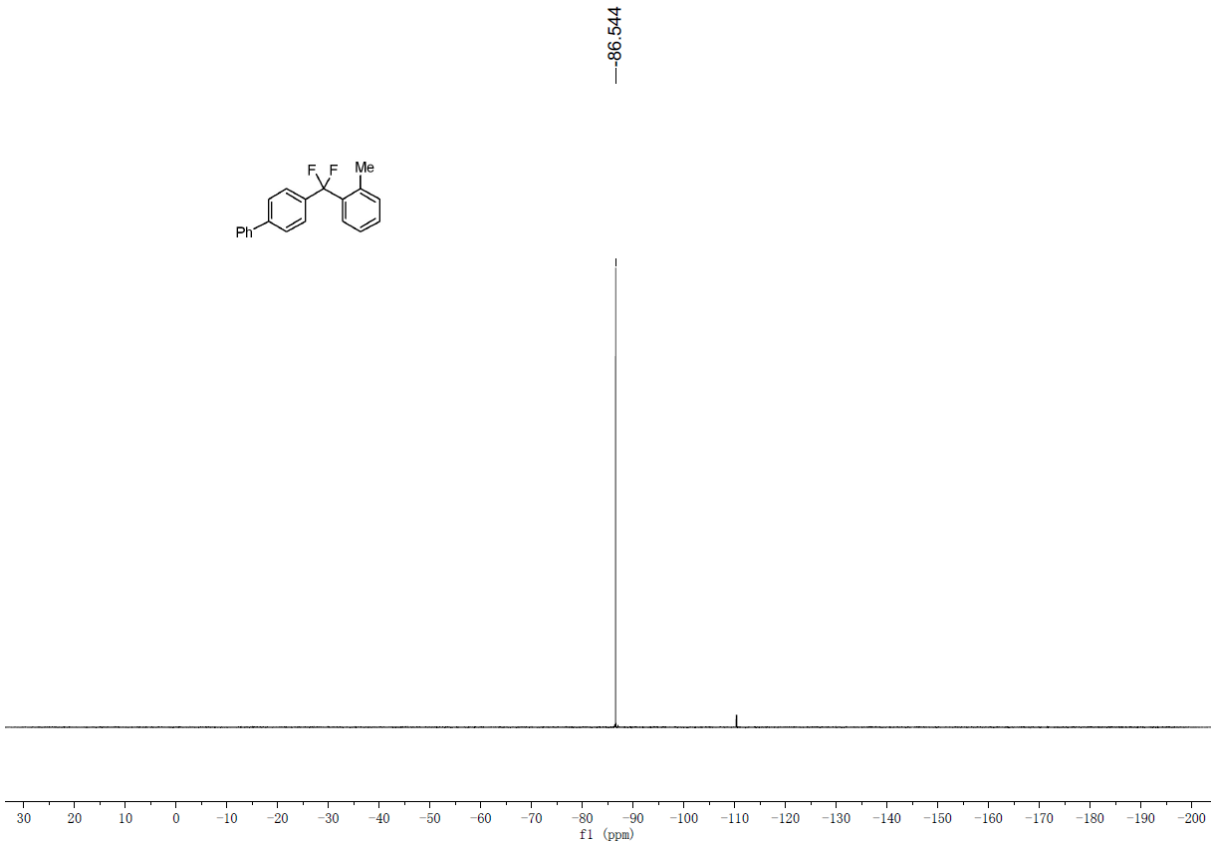
f1 (ppm)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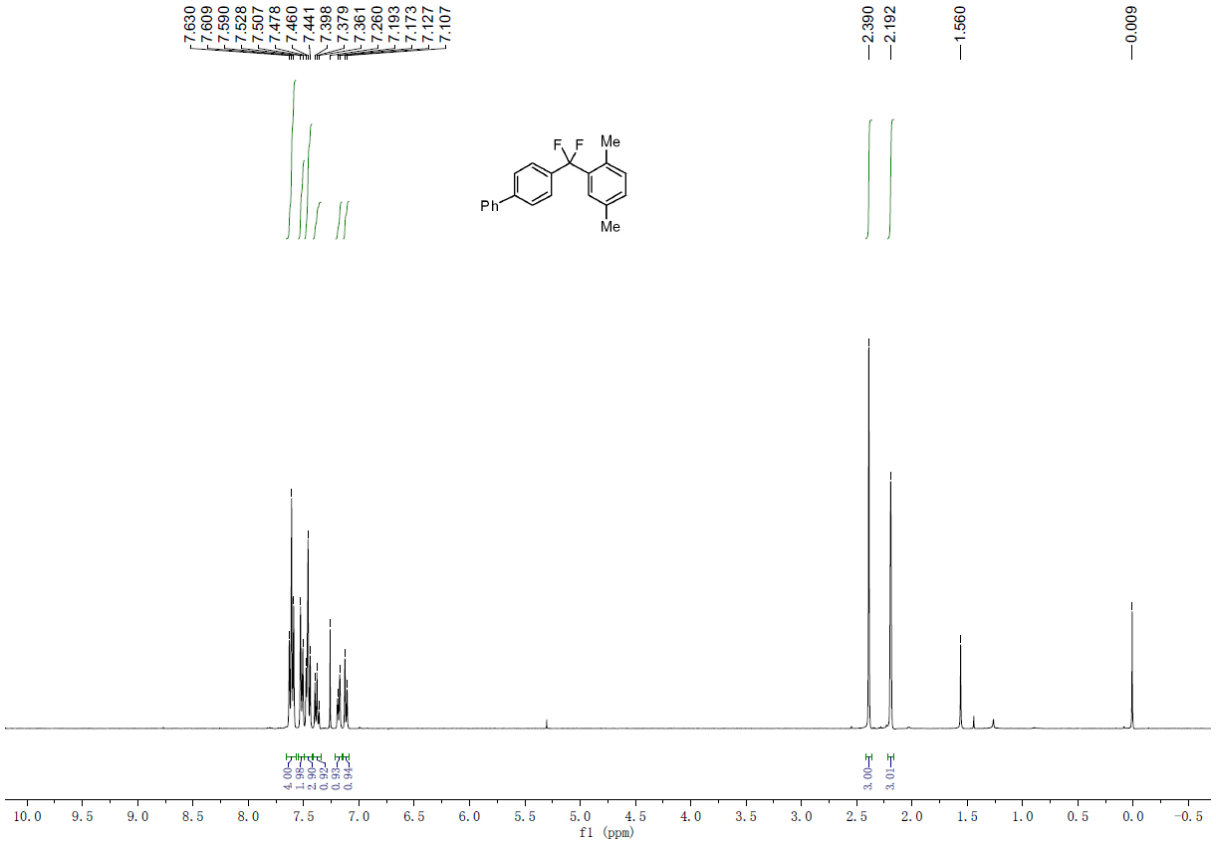
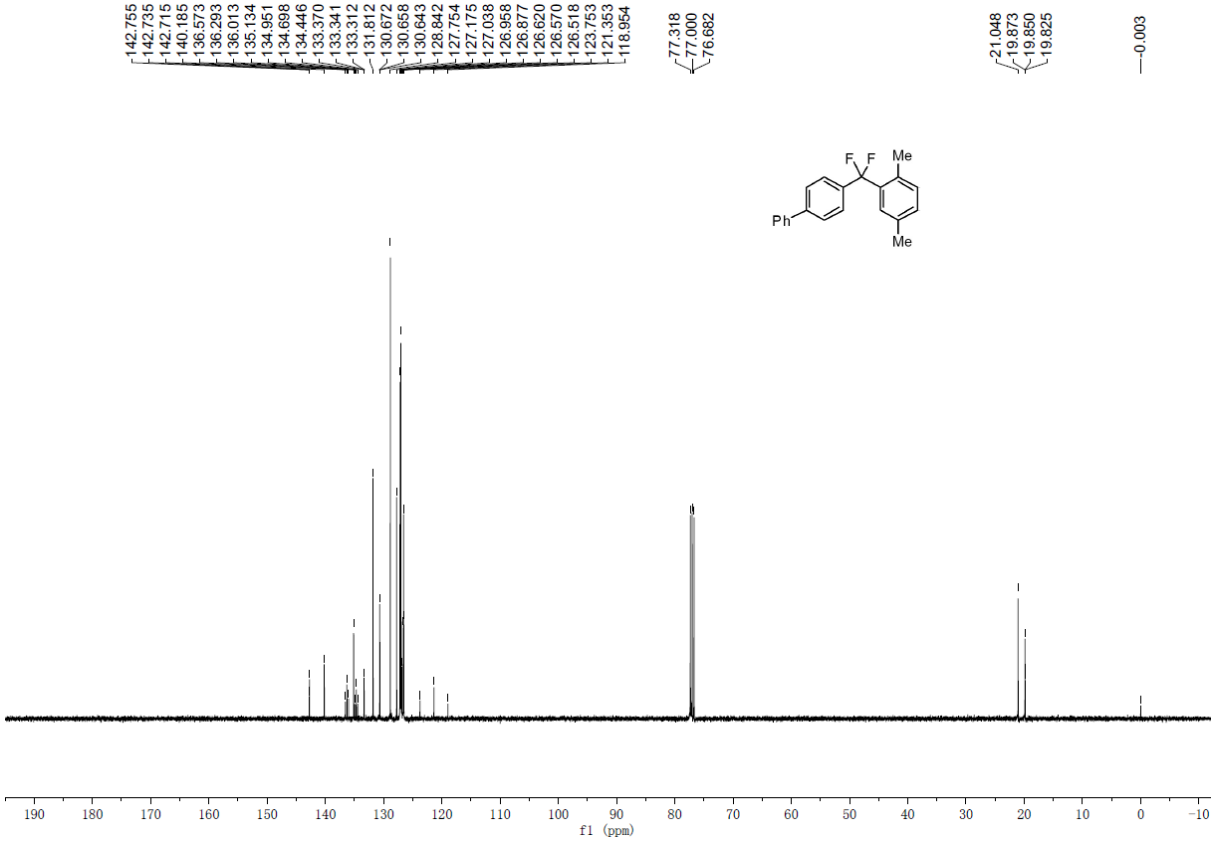
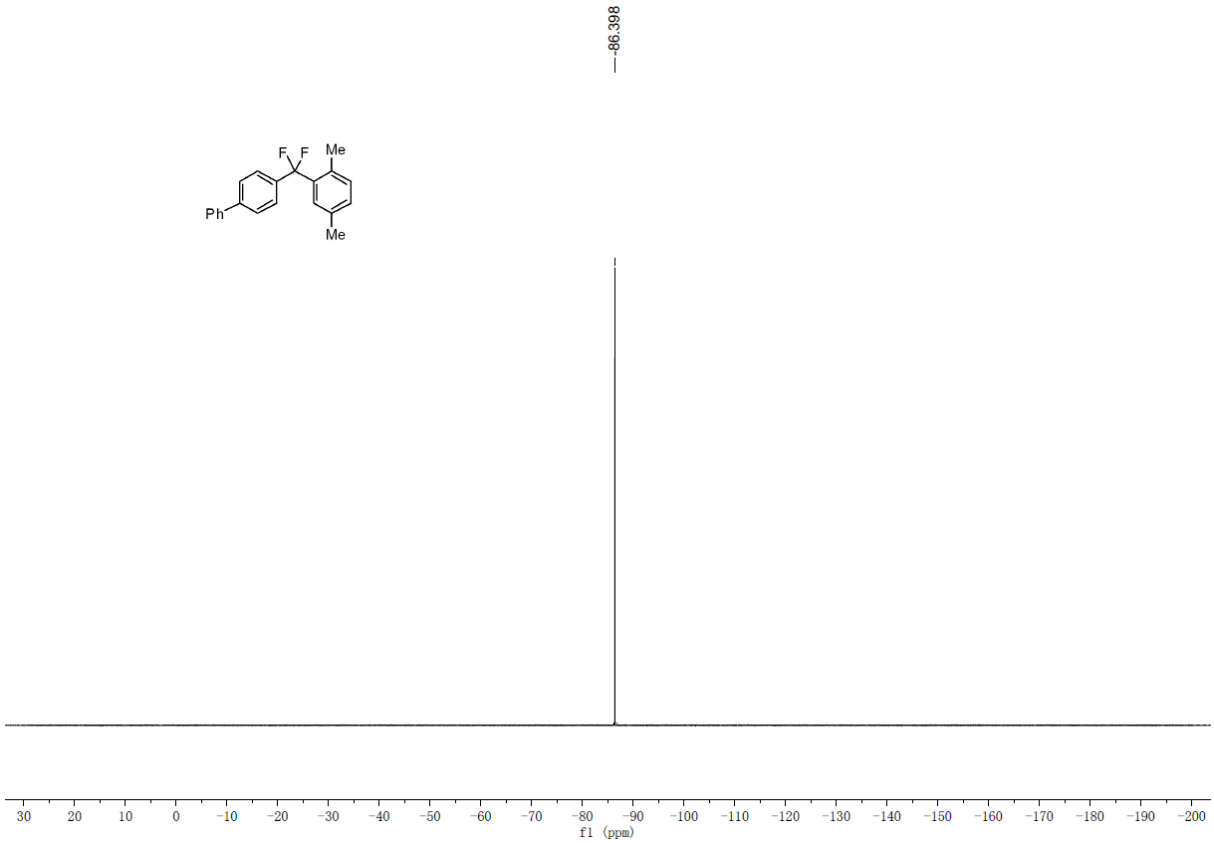
f1 (ppm)

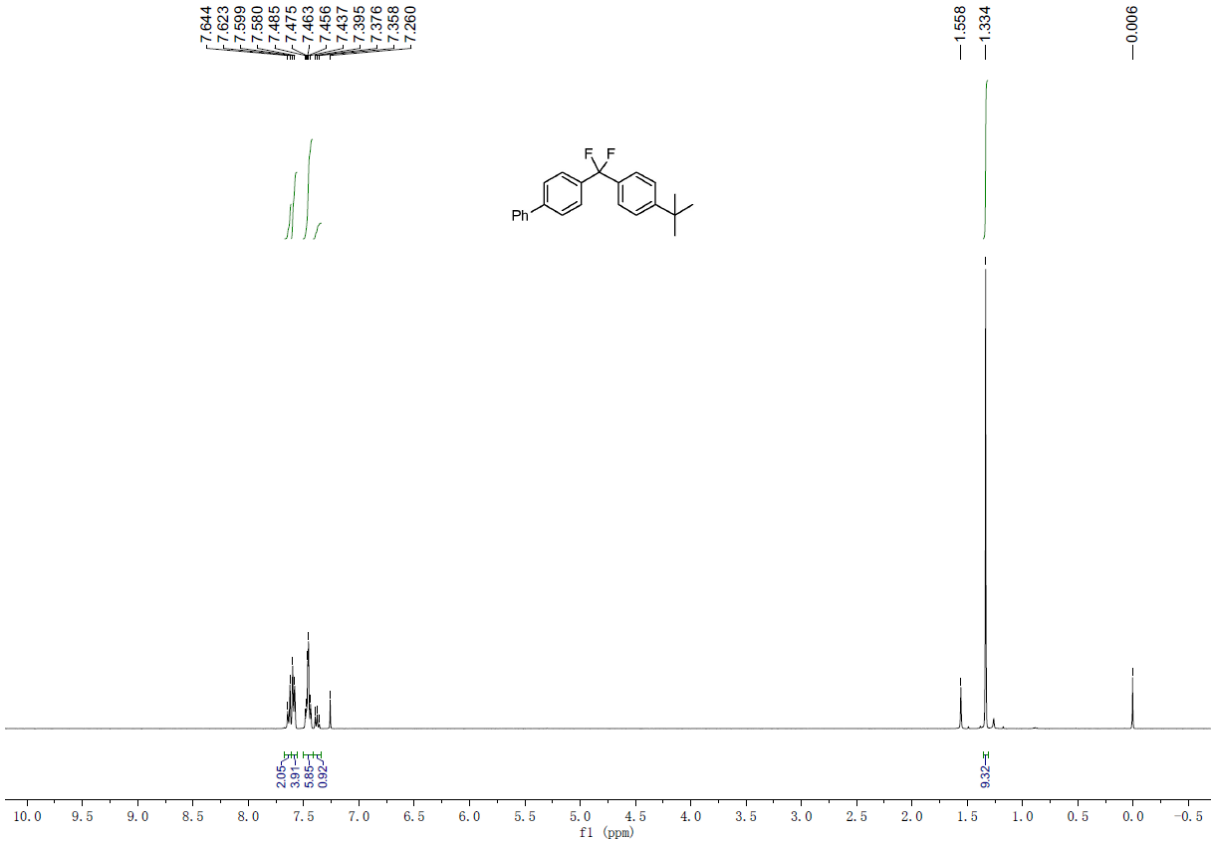
4-((2,5-Dimethylphenyl)difluoromethyl)-1,1'-biphenyl (3e).

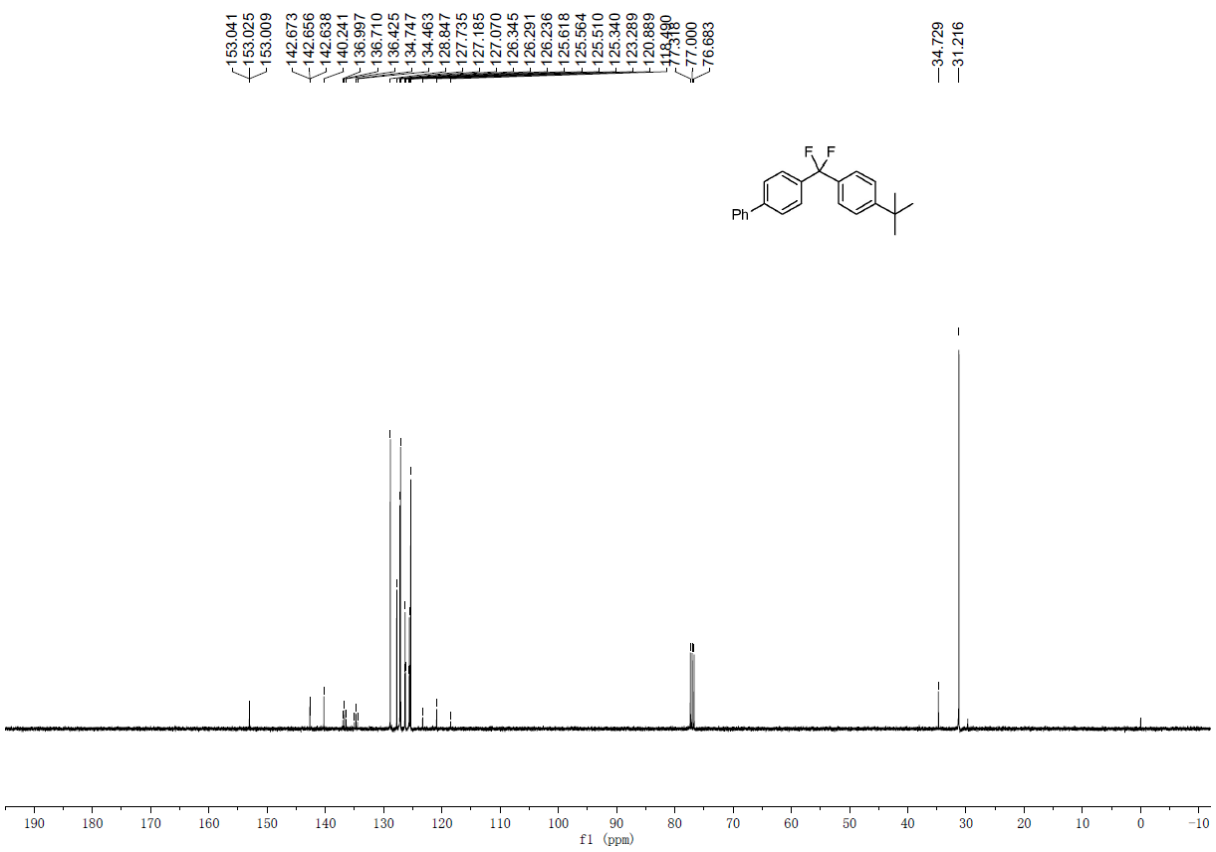






4-((4-(*tert*-Butyl)phenyl)difluoromethyl)-1,1'-biphenyl (3f).

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F
Ph
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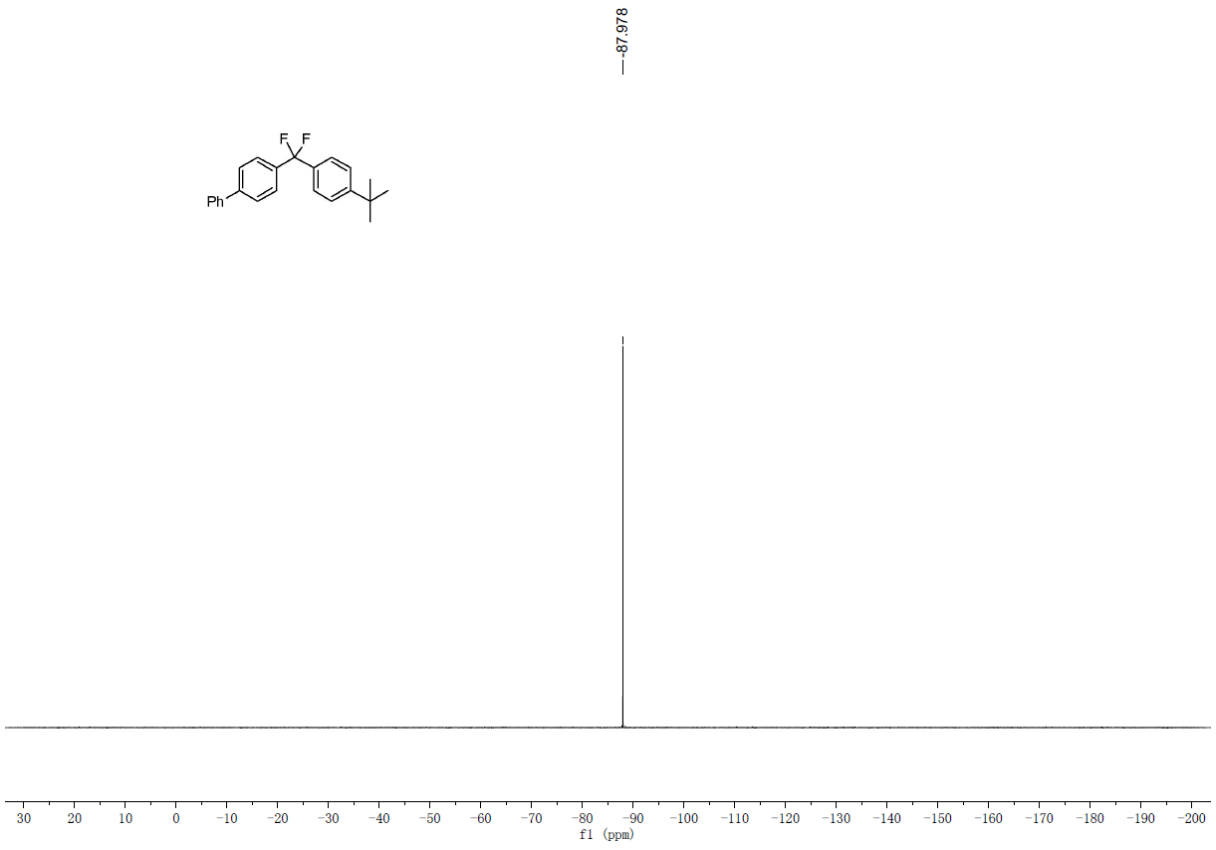
f1 (ppm)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-140
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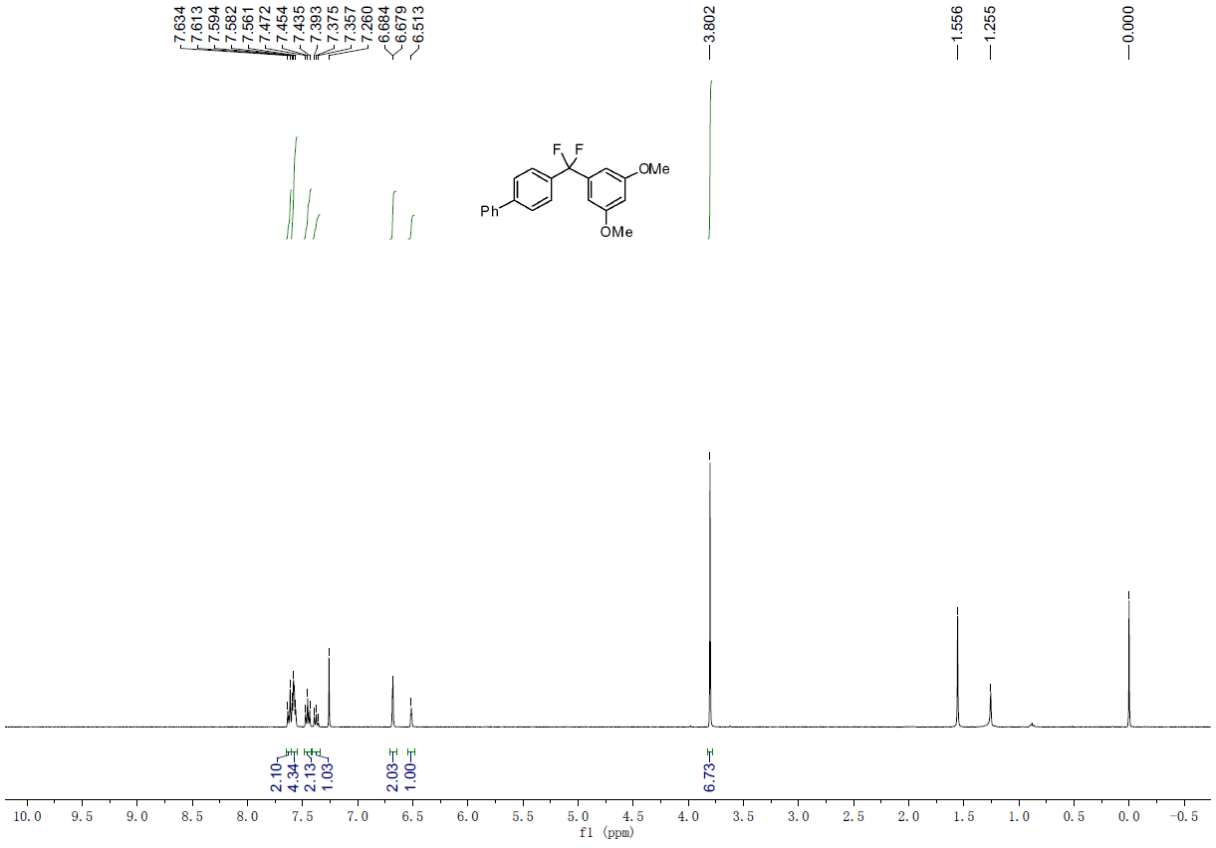
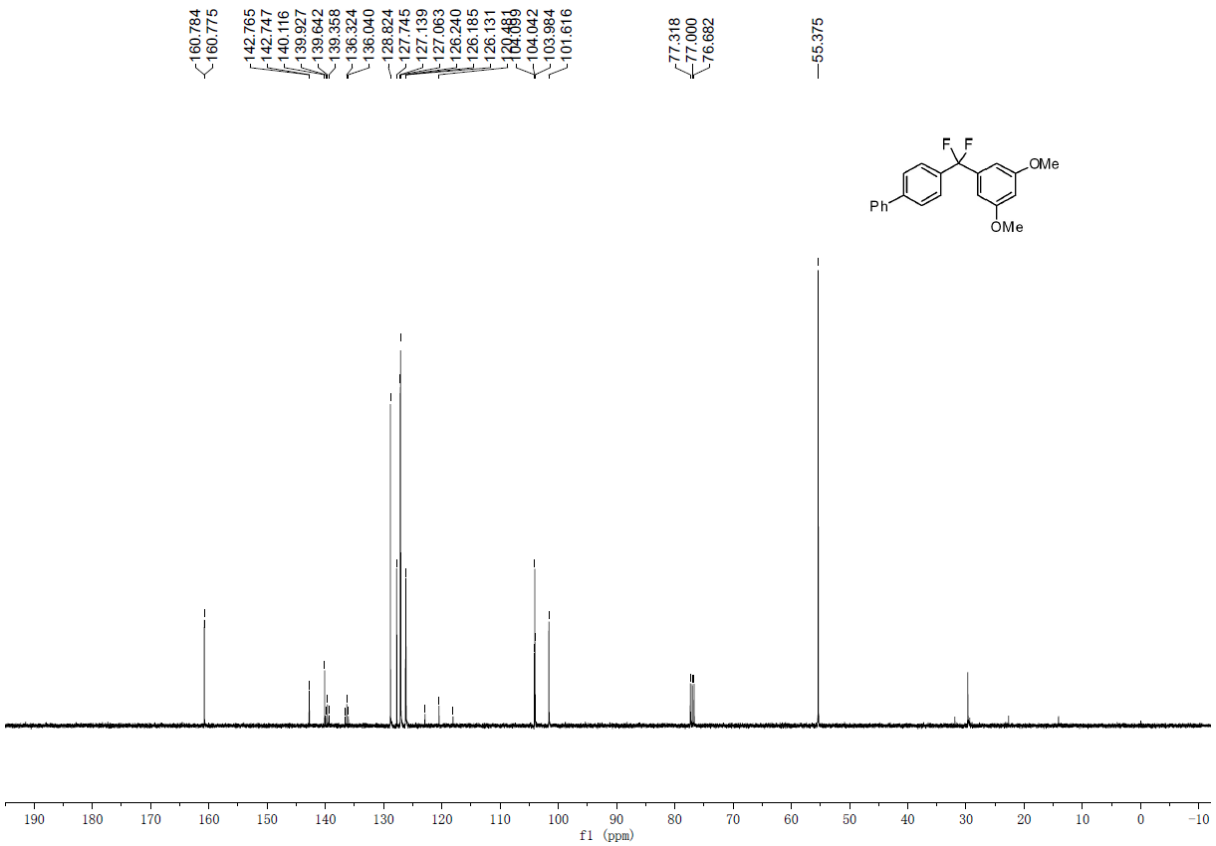
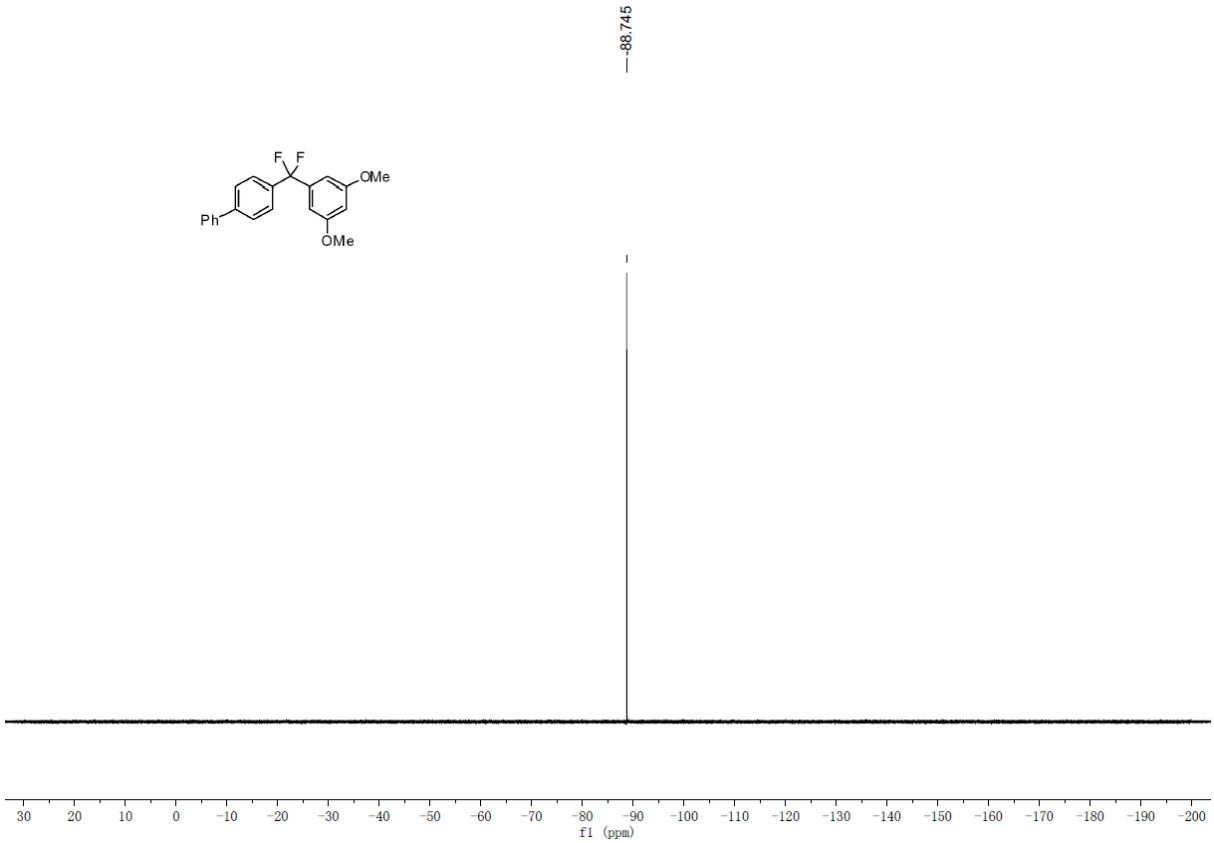
f1 (ppm)

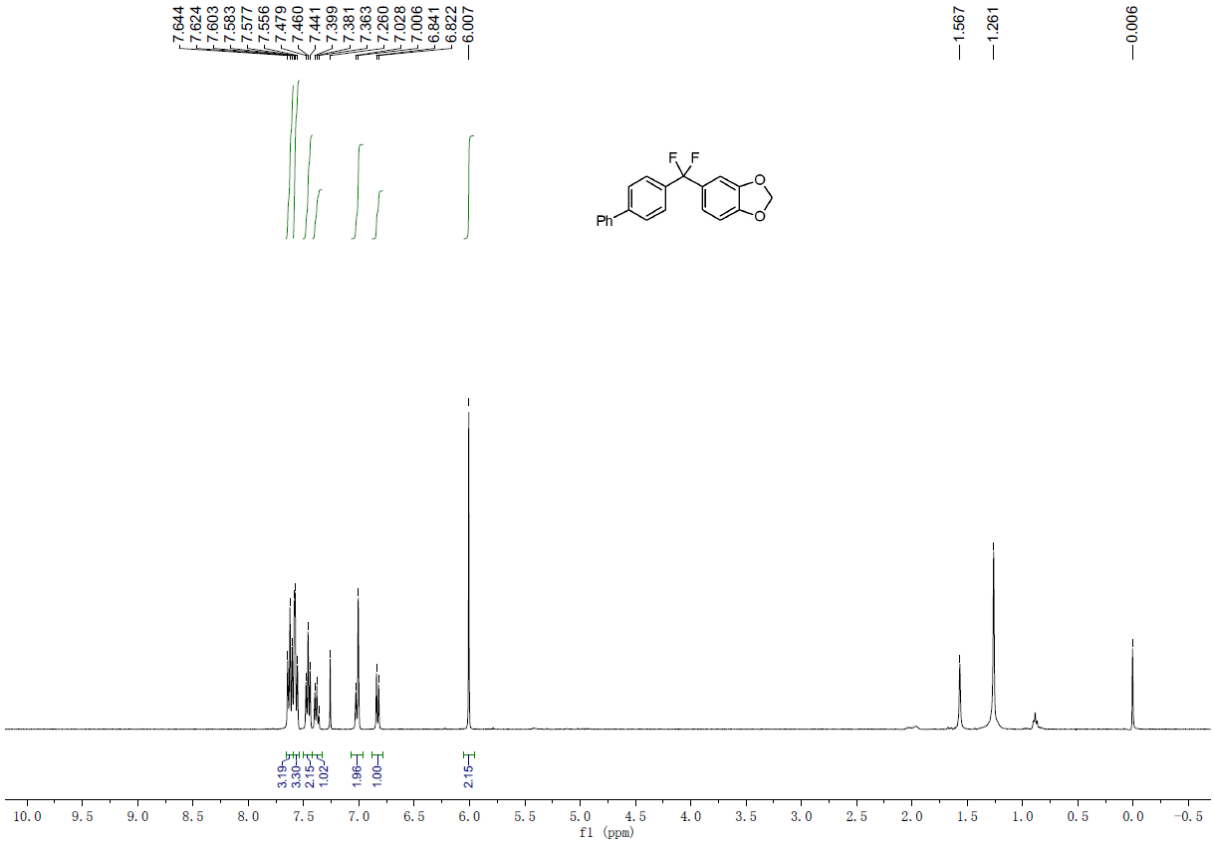
4-((3,5-Dimethoxyphenyl)difluoromethyl)-1,1'-biphenyl (3g).







5-([1,1'-Biphenyl]-4-yldifluoromethyl)benzo[*d*][1,3]dioxole (3h).

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127.185
127.089
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126.256
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123.028
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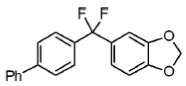
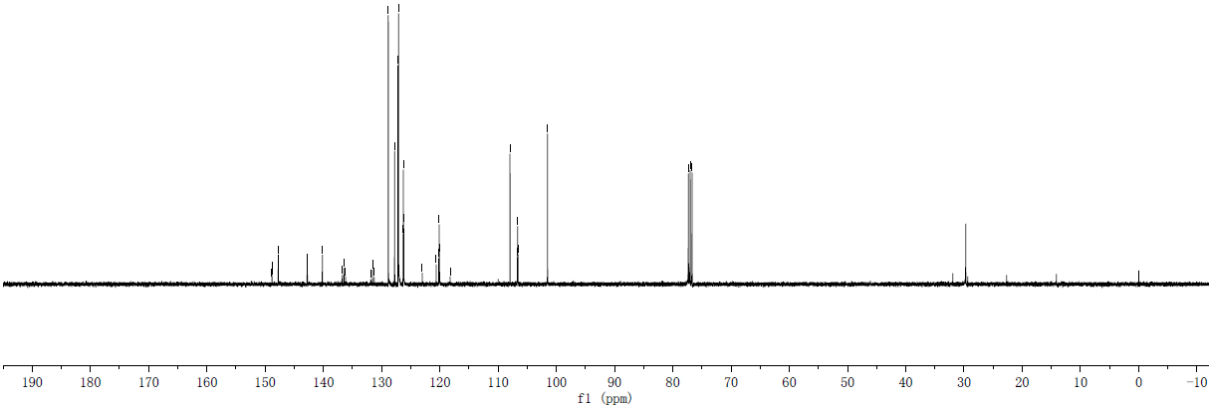
77.000
76.682


F
F
Ph
O
O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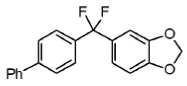
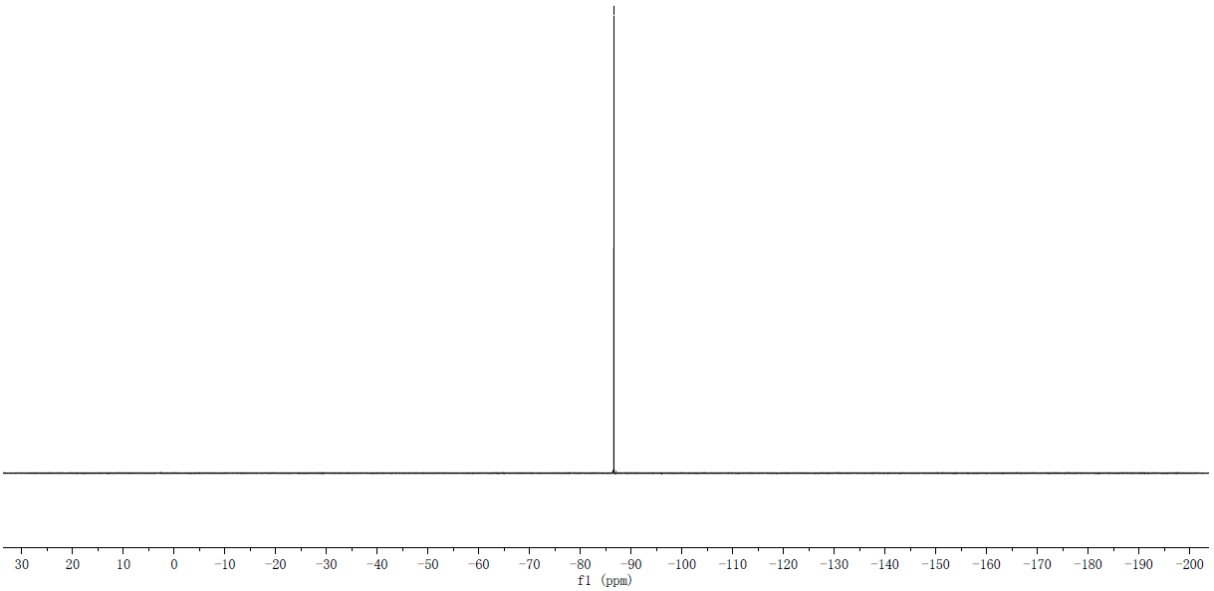
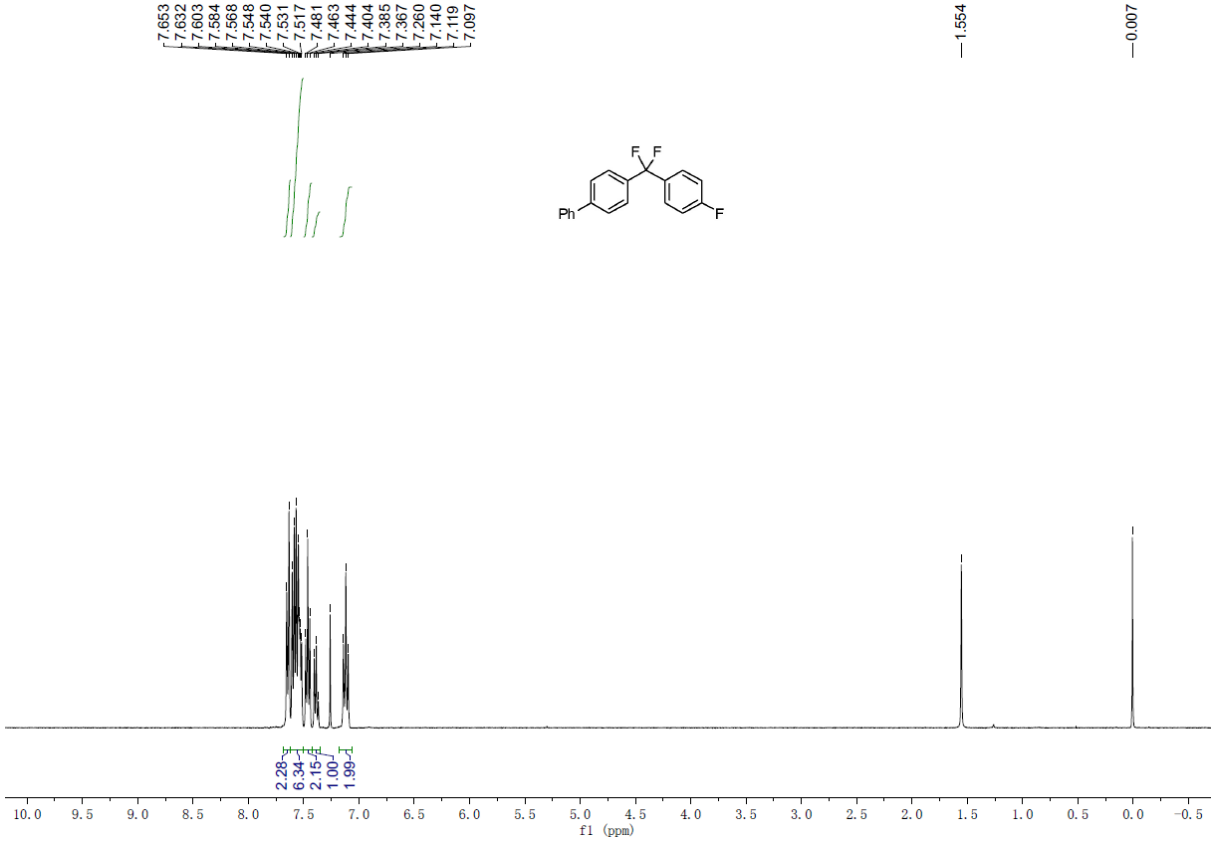
-10
f1 (ppm)

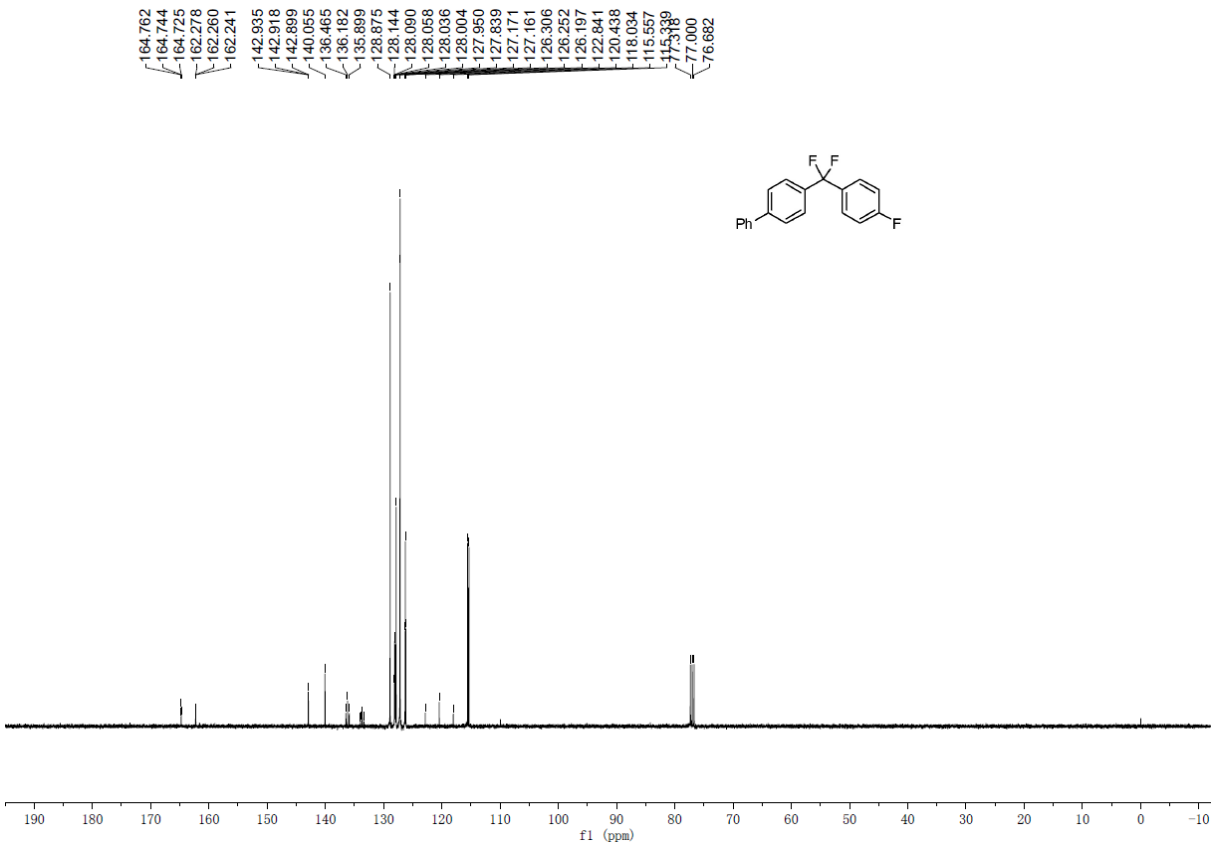

-86.596


F
F
Ph
O
O

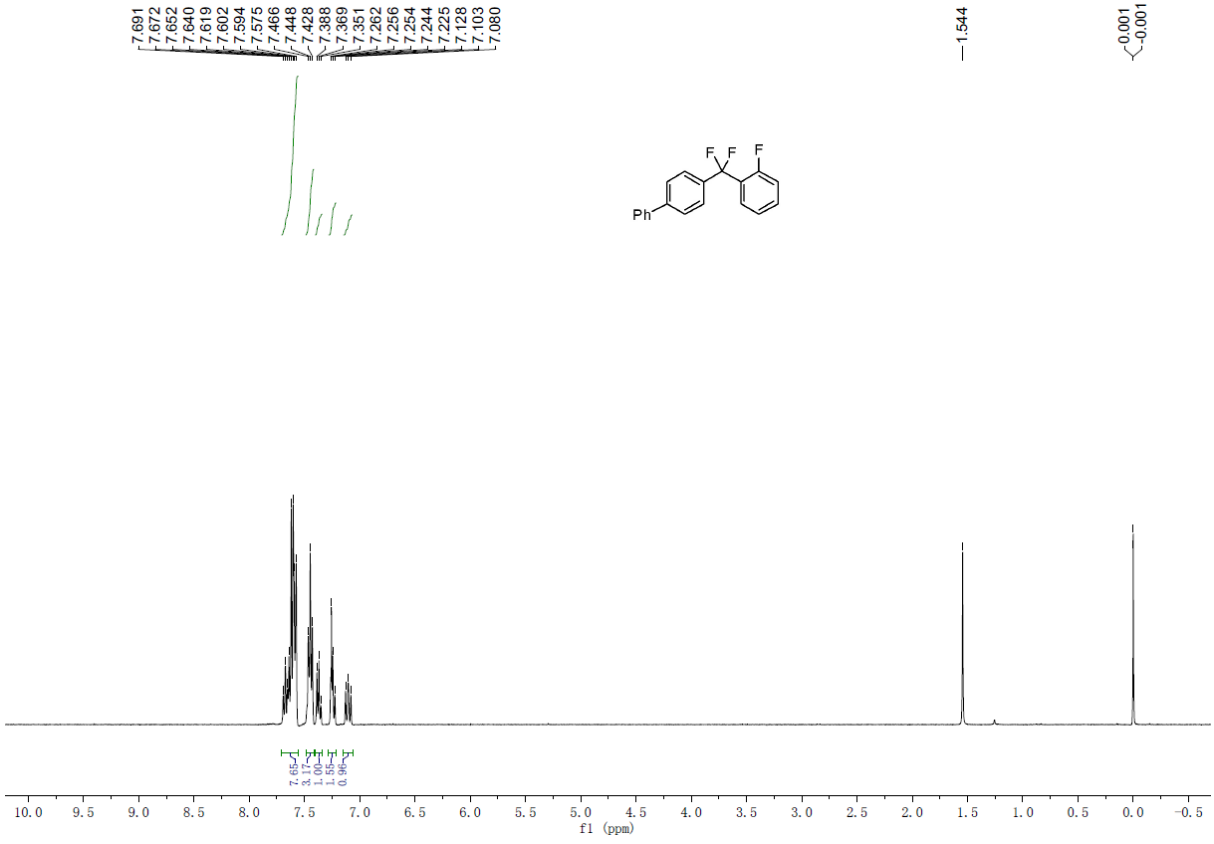

30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

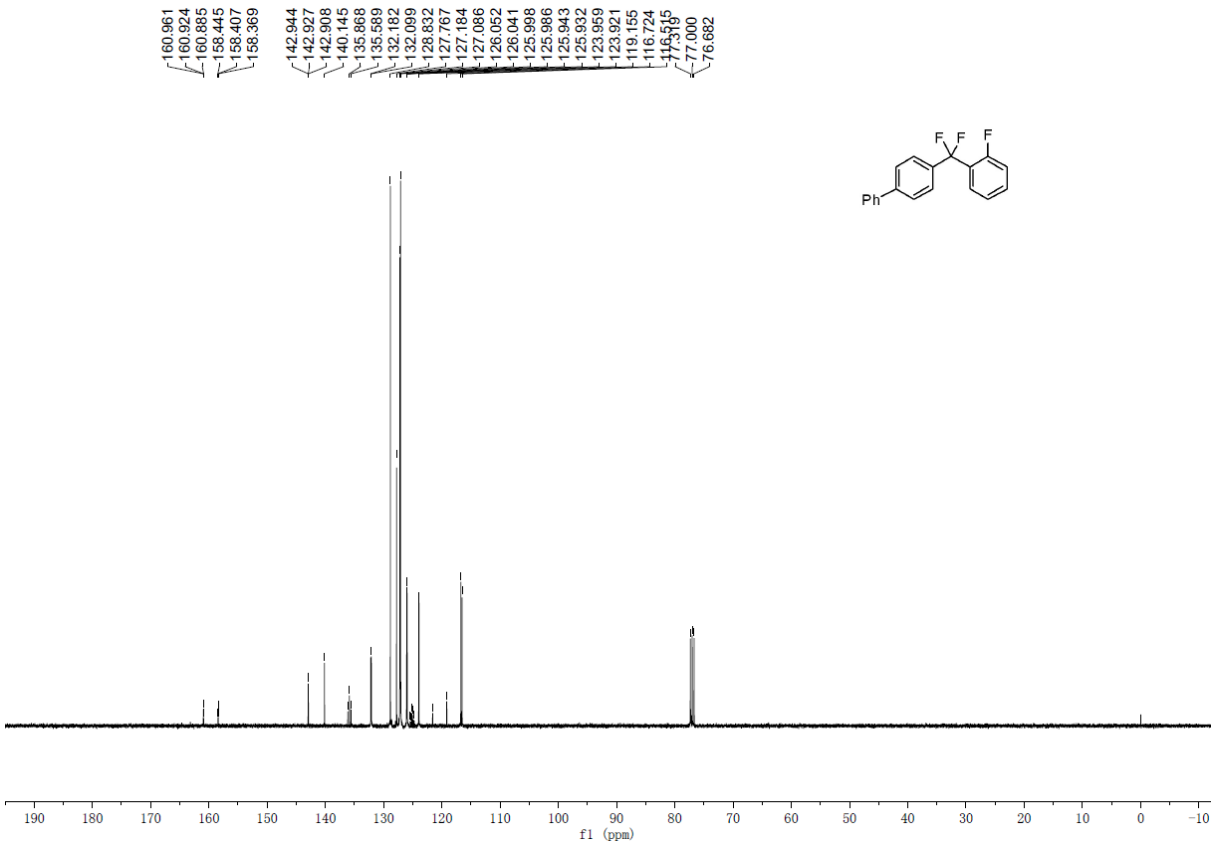
4-(Difluoro(4-fluorophenyl)methyl)-1,1'-biphenyl (3i).

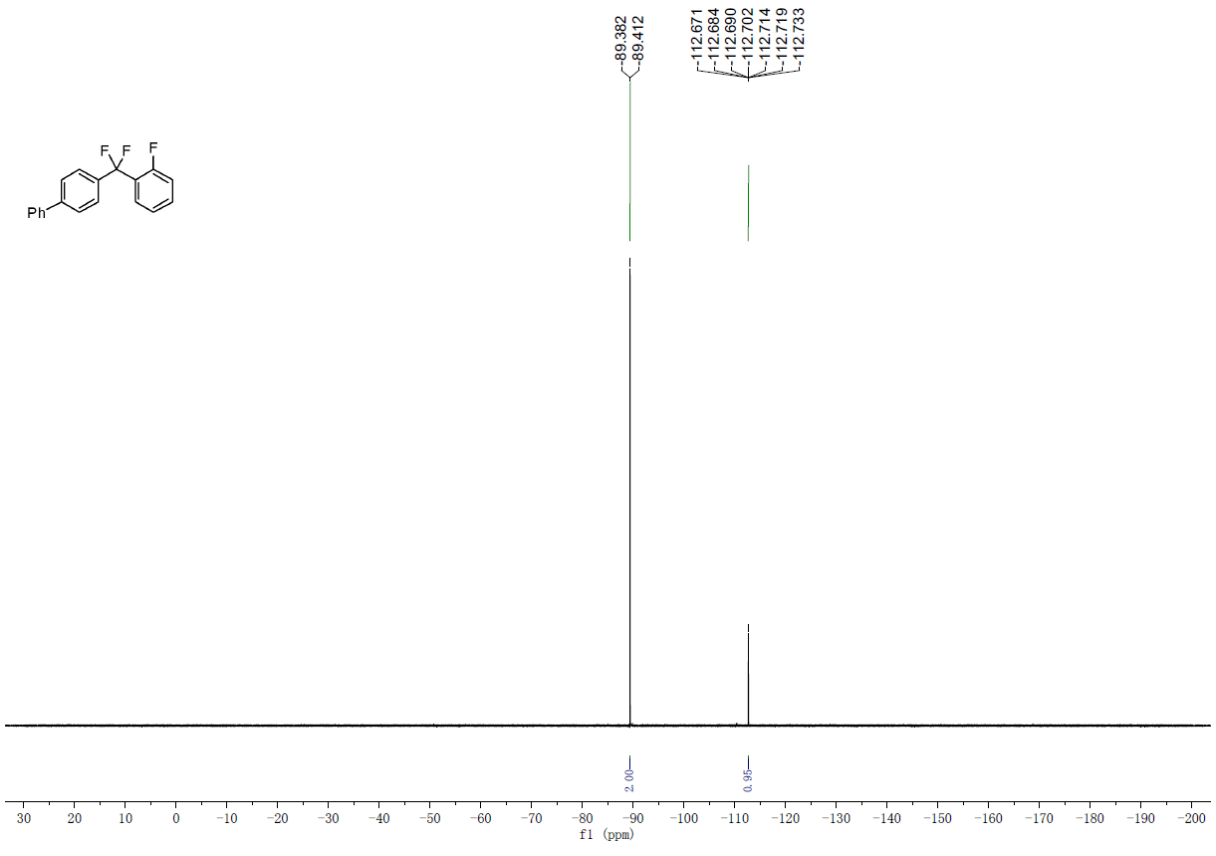




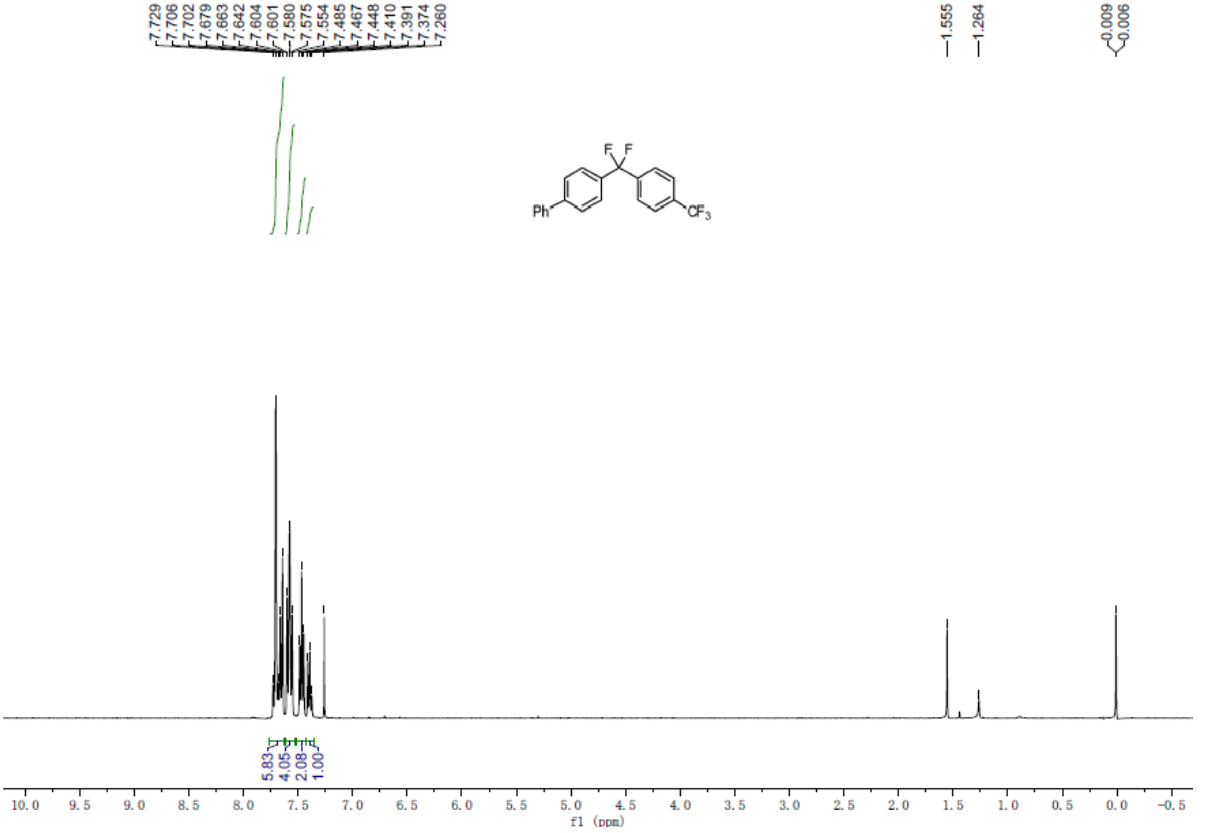
4-(Difluoro(2-fluorophenyl)methyl)-1,1'-biphenyl (3j).

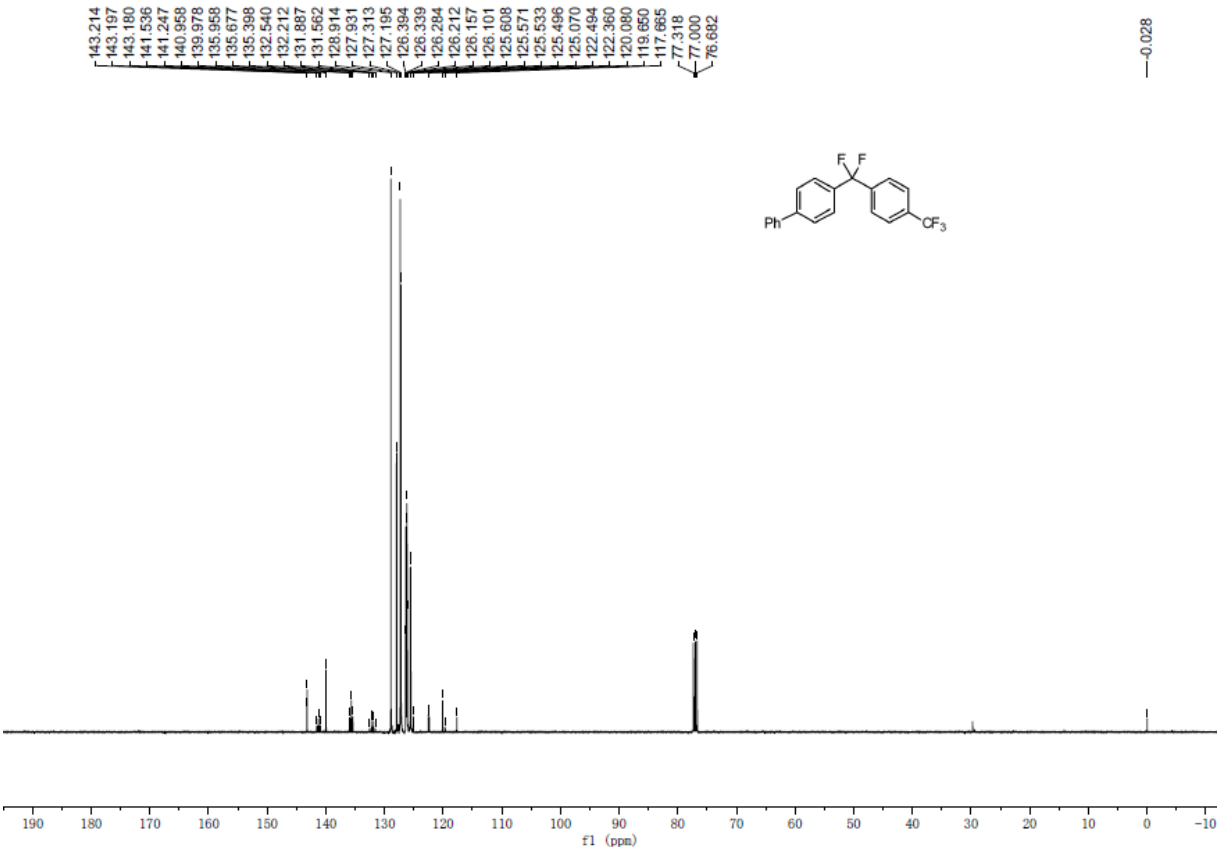



160.961
160.924
160.885
158.445
158.407
158.369
142.944
142.927
142.908
140.145
135.868
135.589
132.182
132.099
128.832
127.767
127.184
127.086
126.052
126.041
125.998
125.986
125.943
125.932
123.959
123.921
119.155
116.724
116.515
77.319
77.000
76.682
F
F
F
Ph
f1 (ppm)

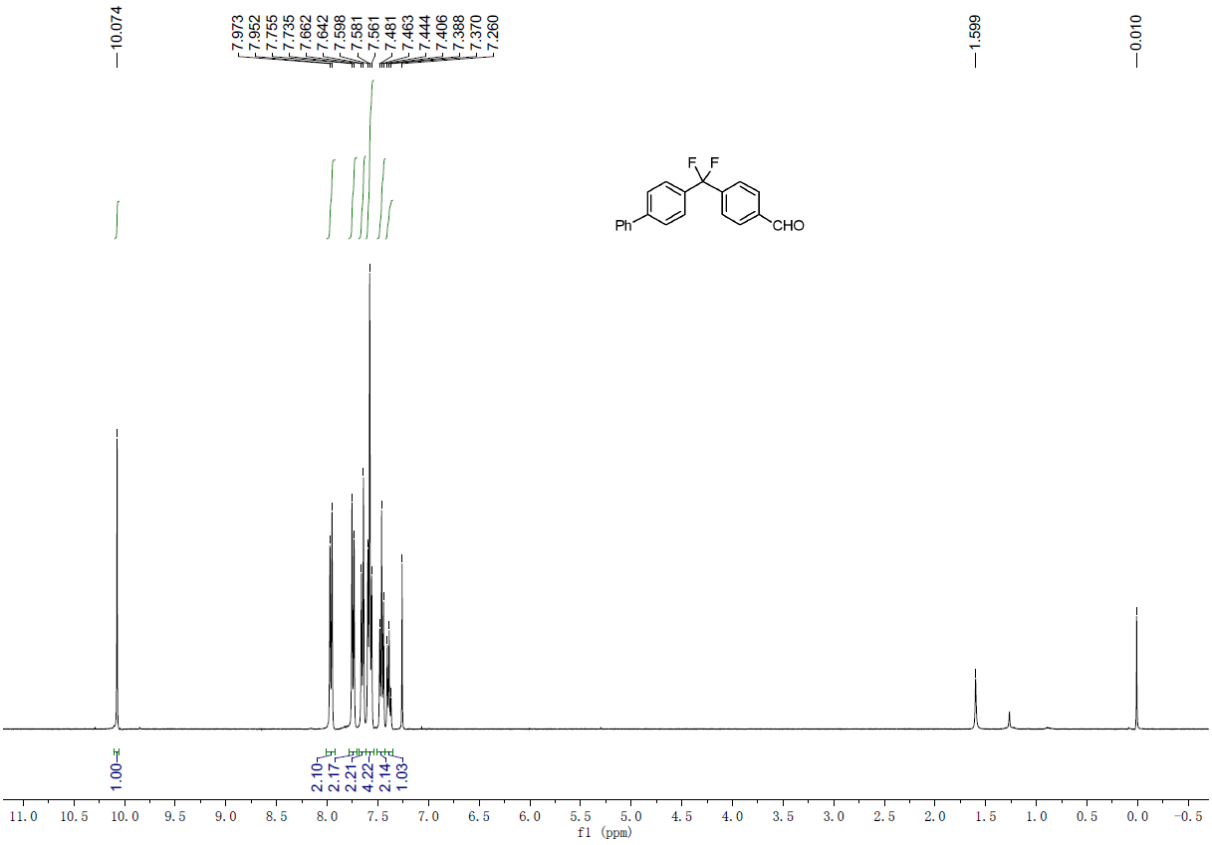

89.382
89.412
112.671
112.684
112.690
112.702
112.714
112.719
112.733
F
F
F
Ph
2.00
0.95
f1 (ppm)

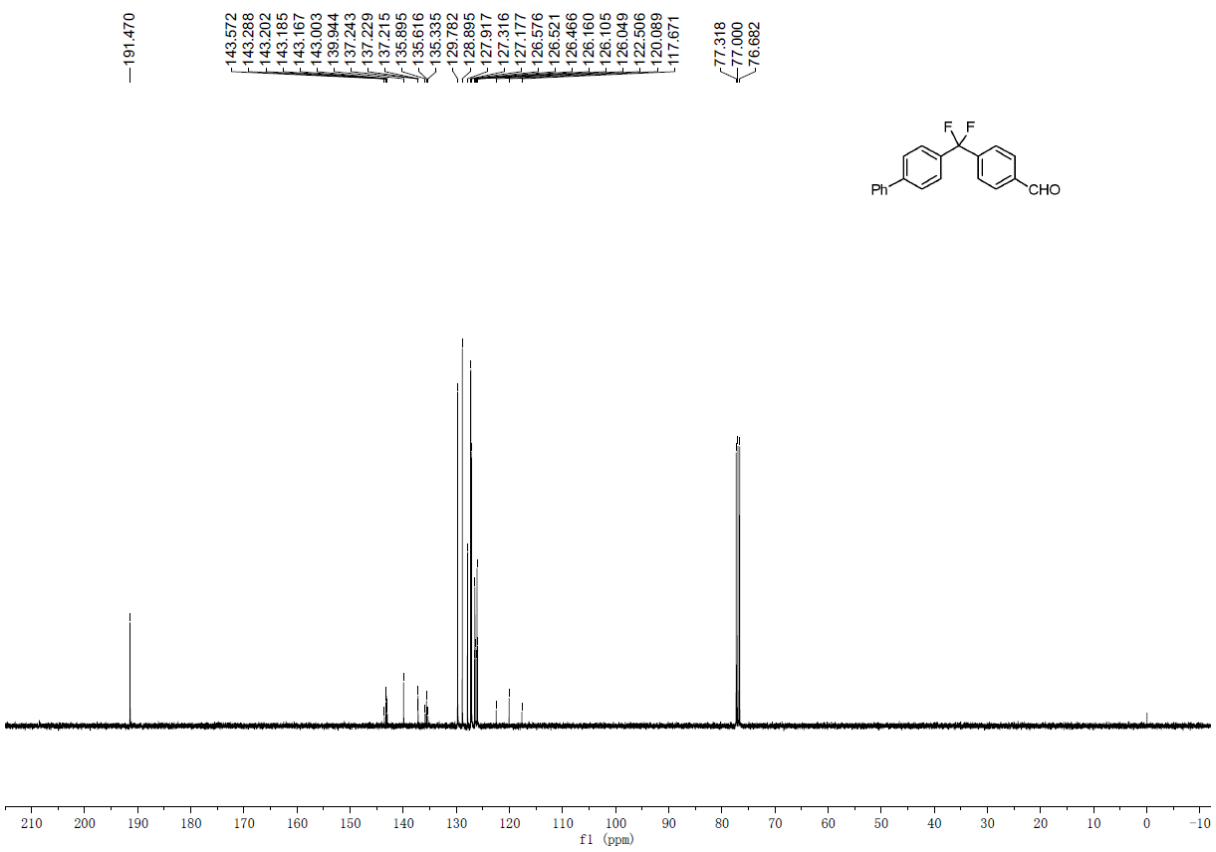
4-(Difluoro(4-(trifluoromethyl)phenyl)methyl)-1,1'-biphenyl (3k).

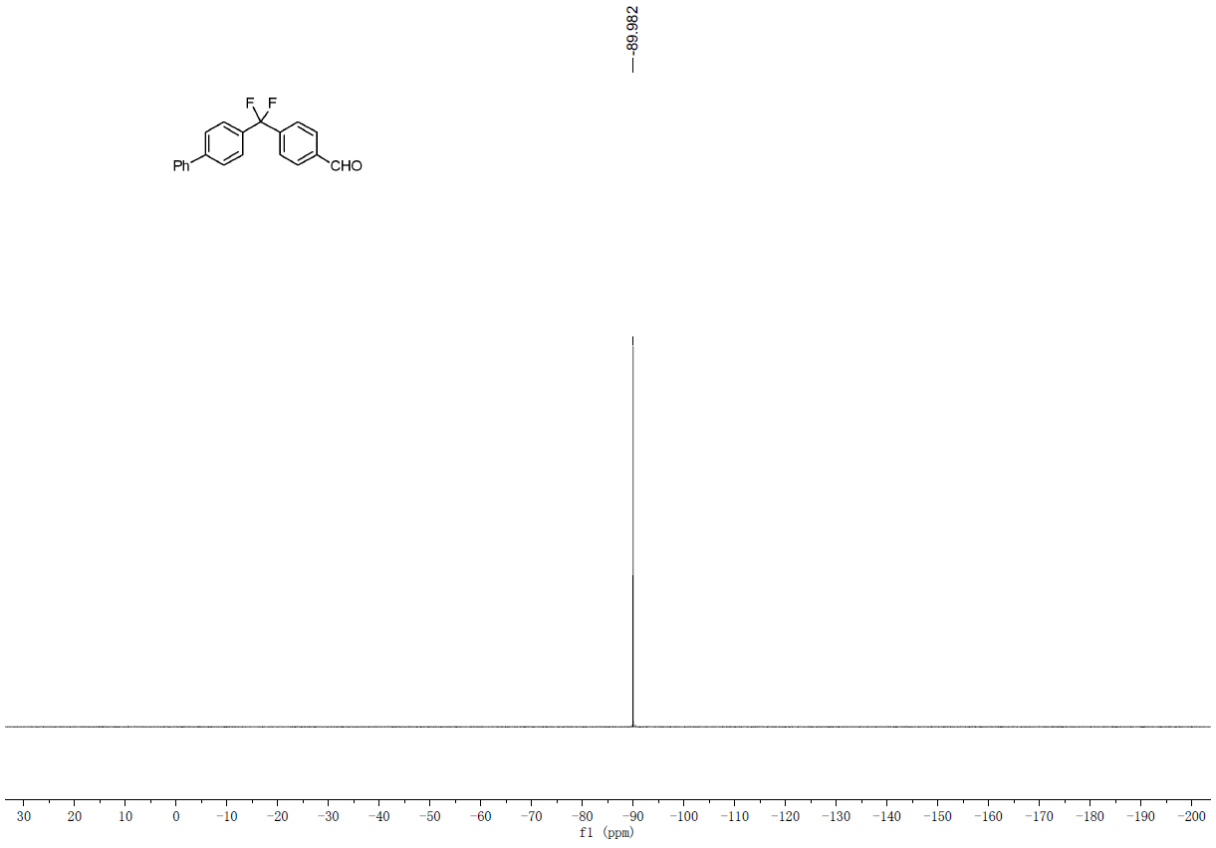




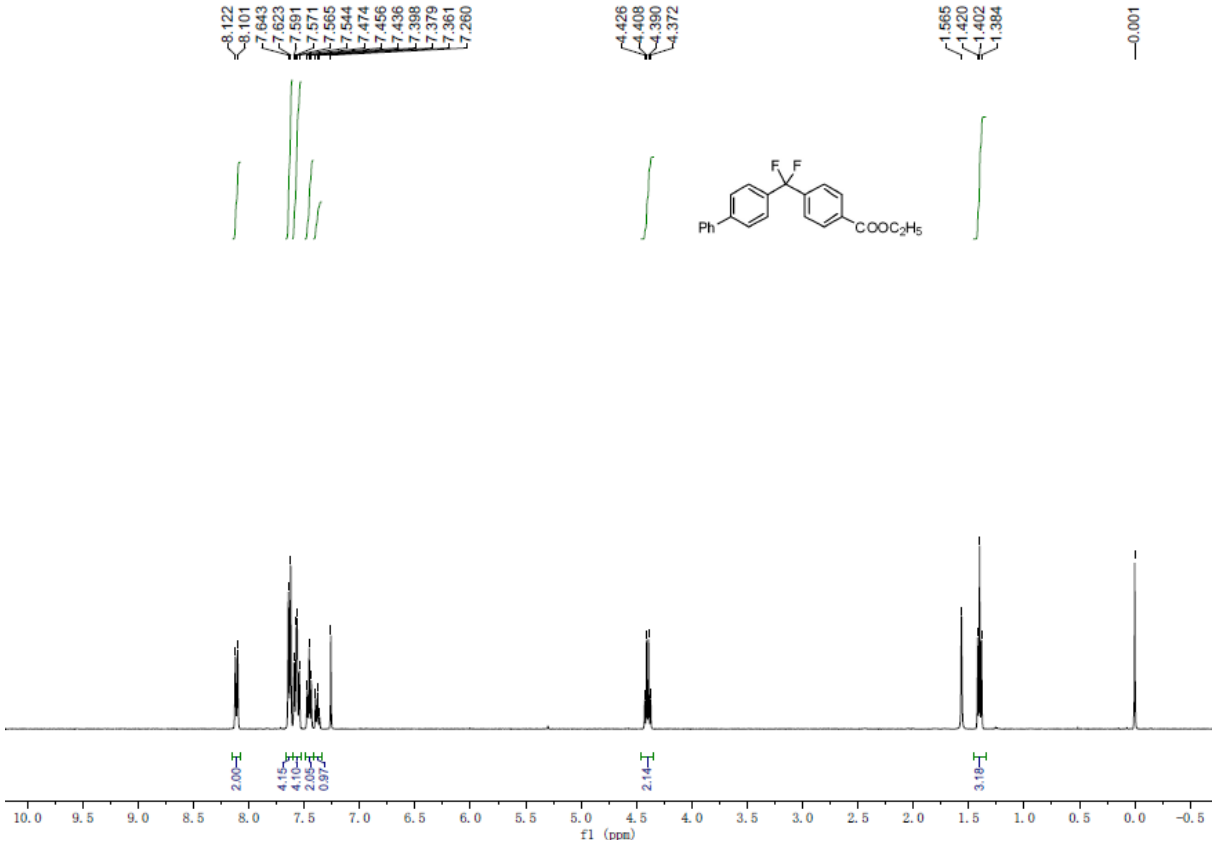
4-([1,1'-Biphenyl]-4-yldifluoromethyl)benzaldehyde (3l).

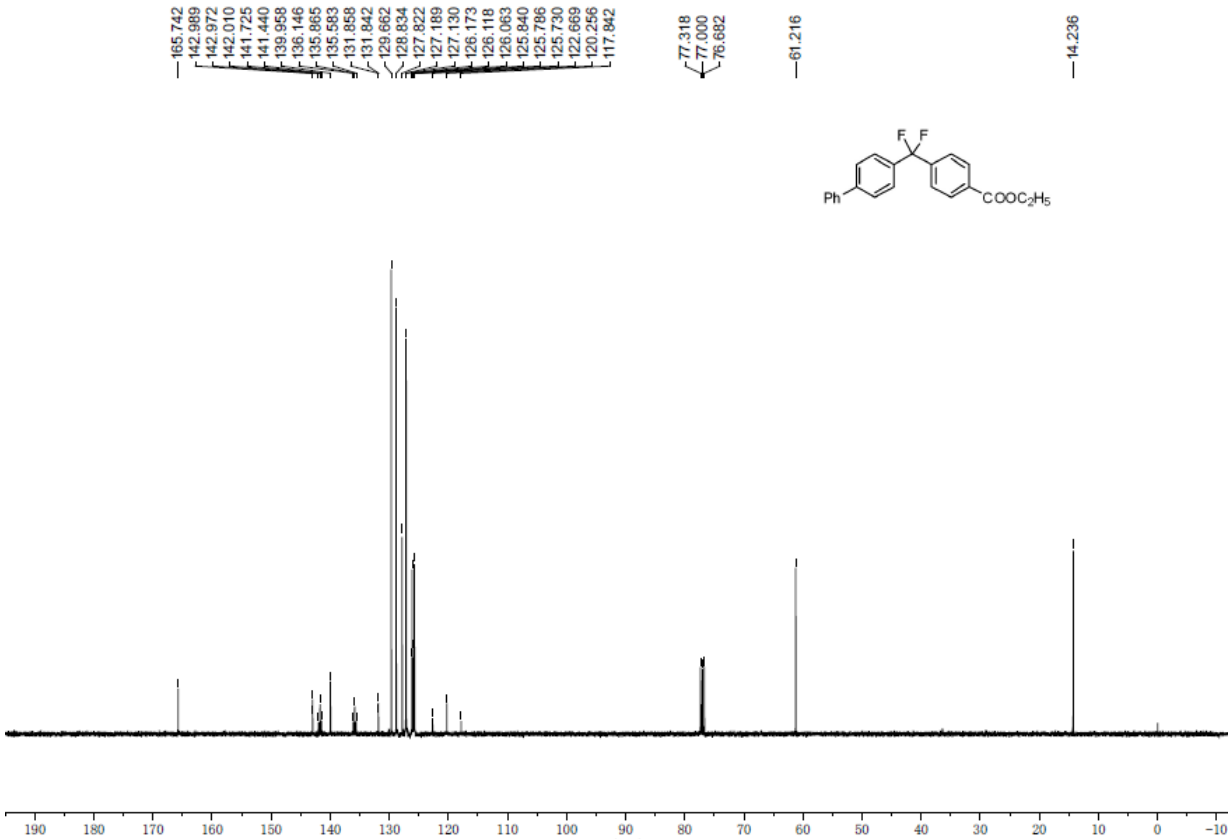


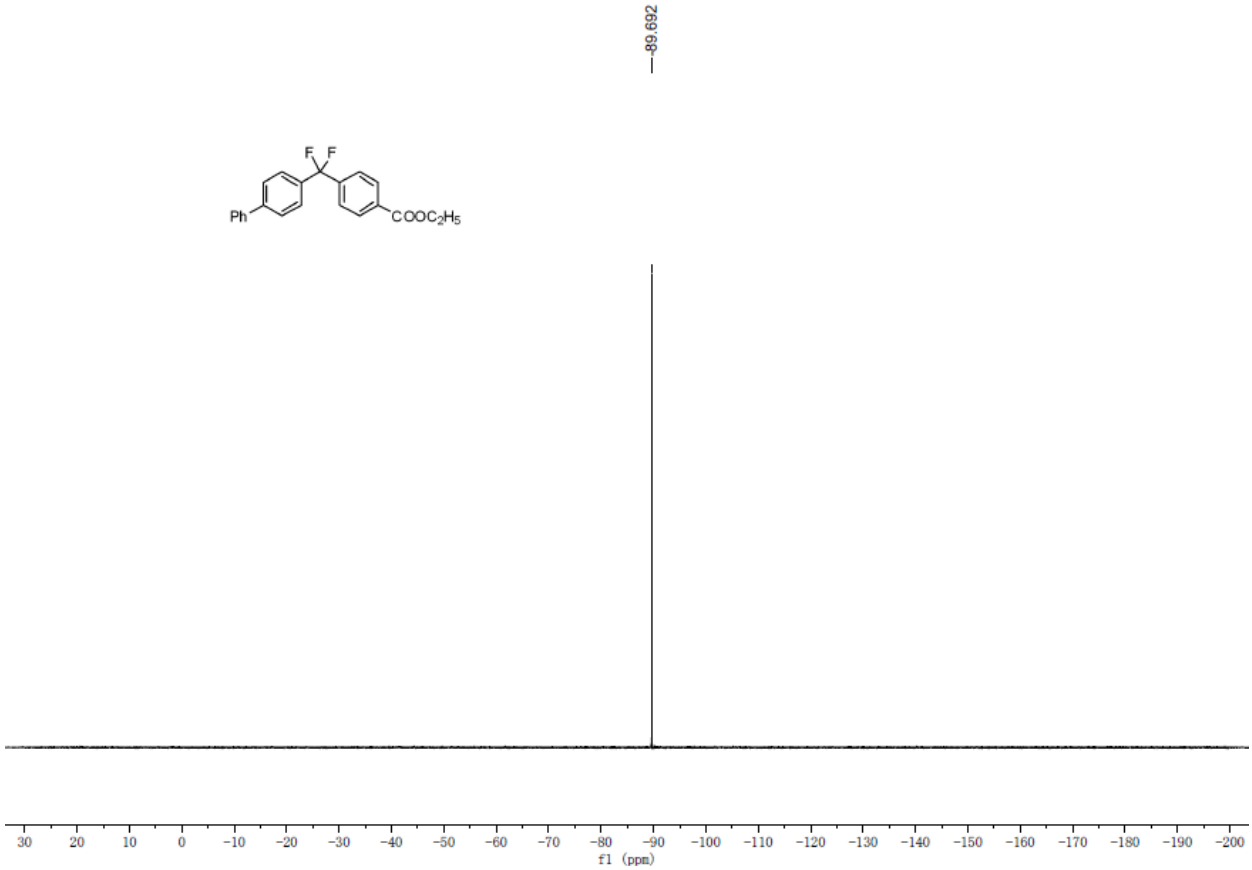

191.470
143.572
143.288
143.202
143.185
143.167
143.003
139.944
137.243
137.229
137.215
135.895
135.616
135.335
129.782
128.895
127.917
127.316
127.177
126.576
126.521
126.466
126.160
126.105
126.049
122.506
120.089
117.671
77.318
77.000
76.682
F
F
Ph
CHO
f1 (ppm)


-89.982
F
F
Ph
CHO
f1 (ppm)

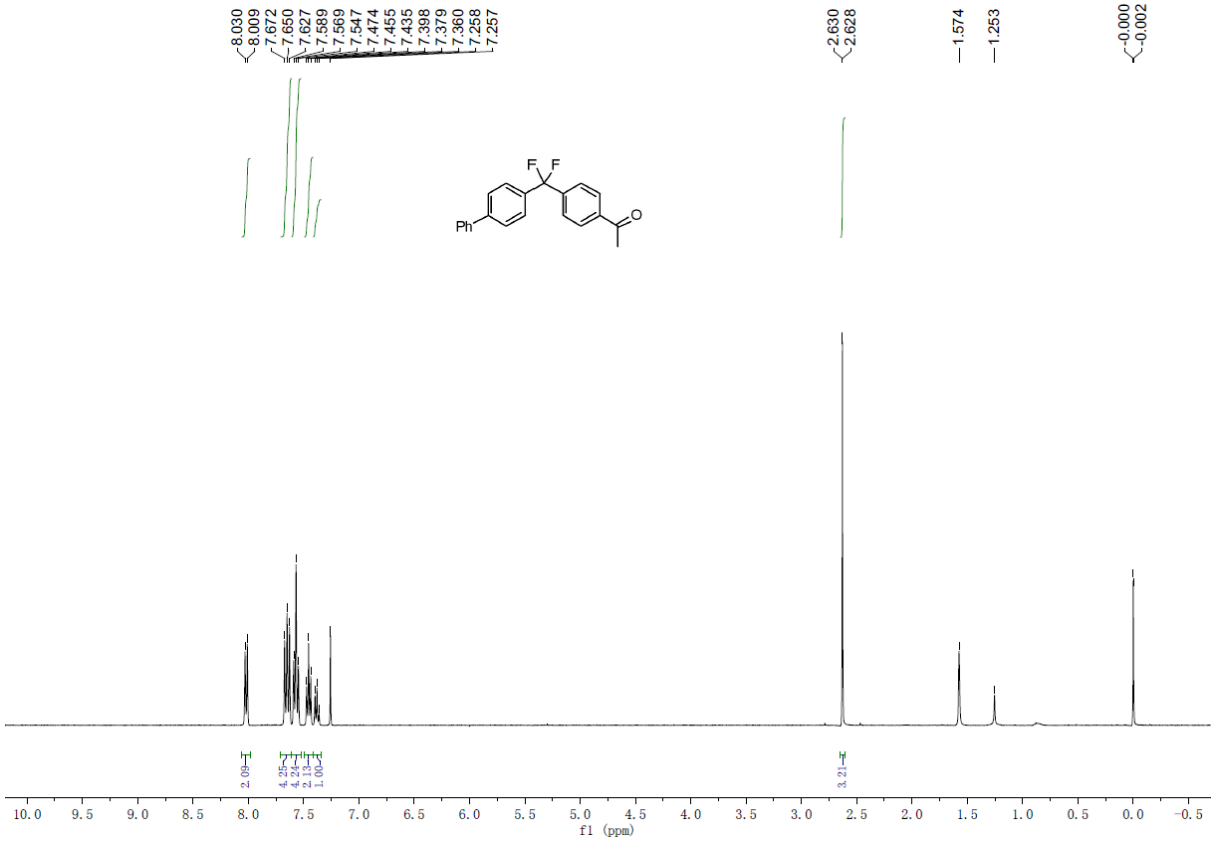
Ethyl 4-([1,1'-biphenyl]-4-yldifluoromethyl)benzoate (3m).

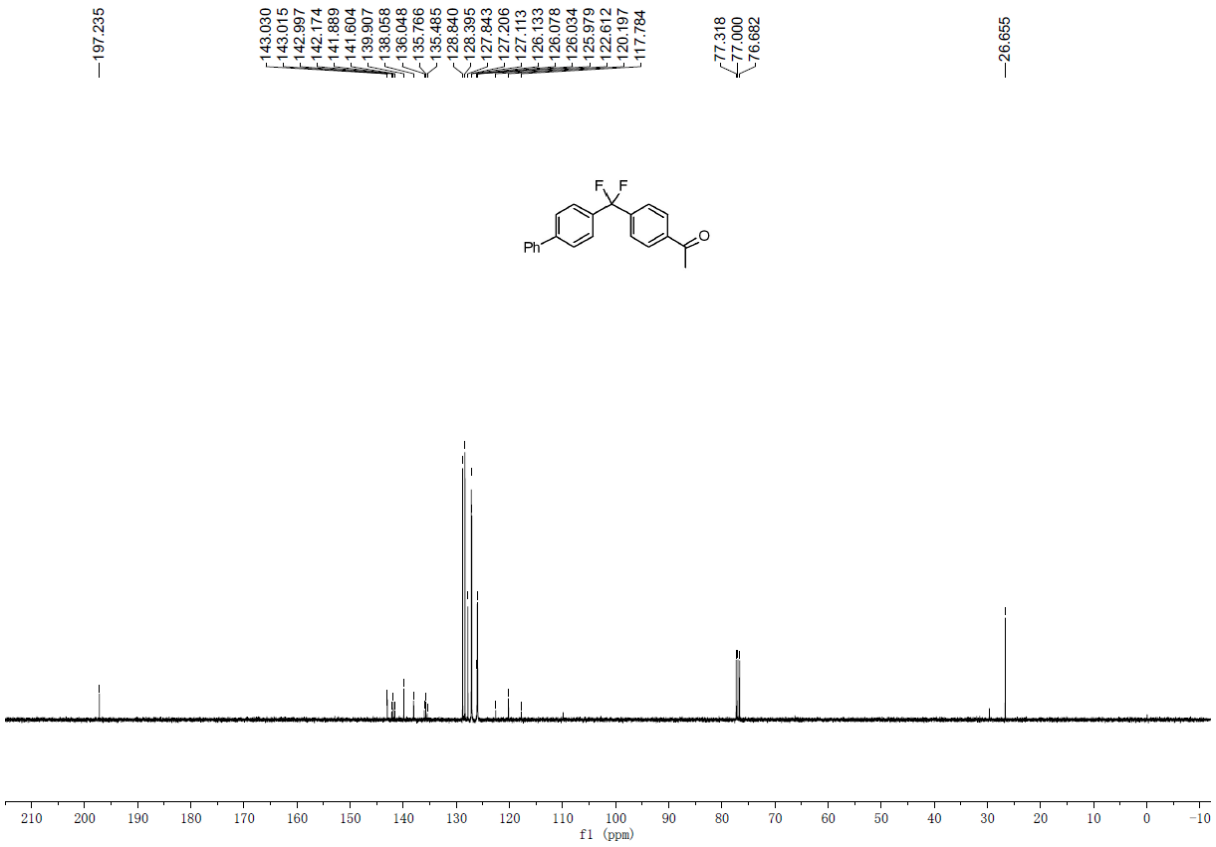


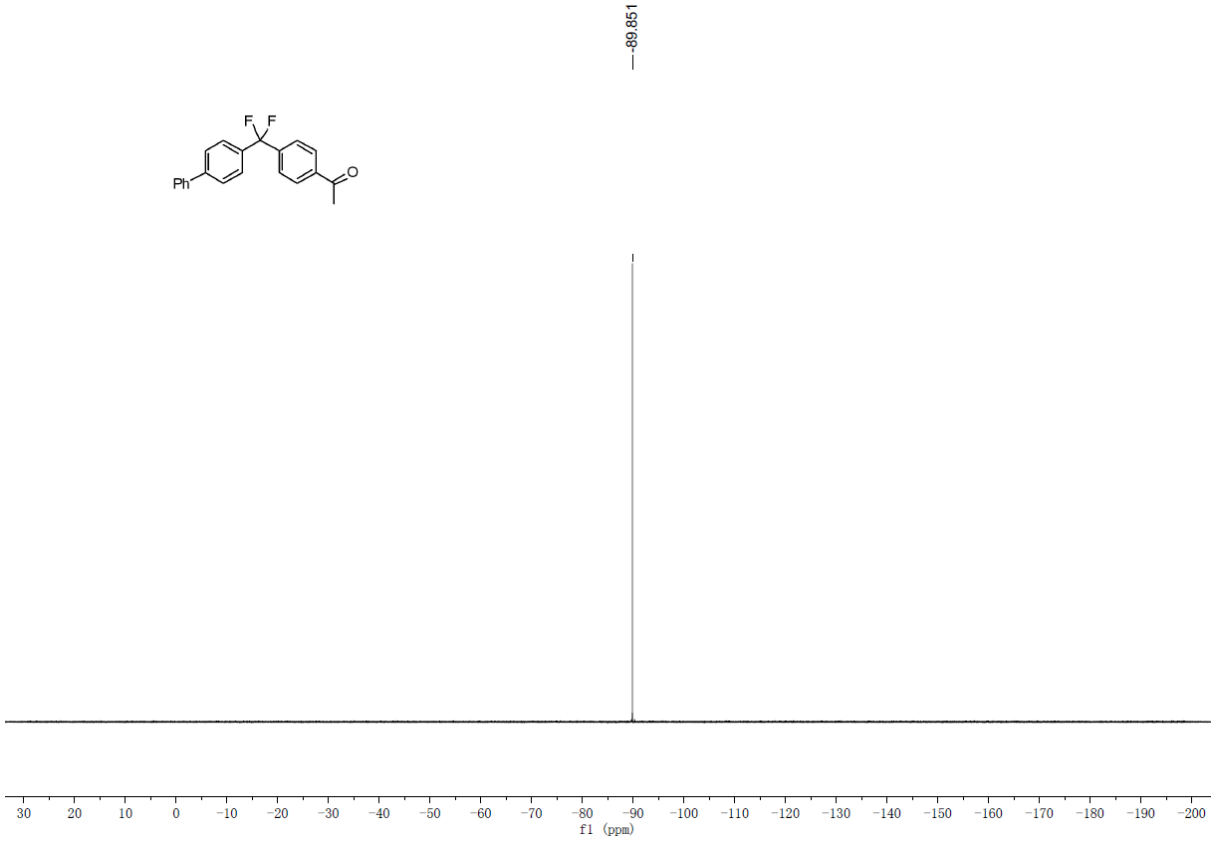




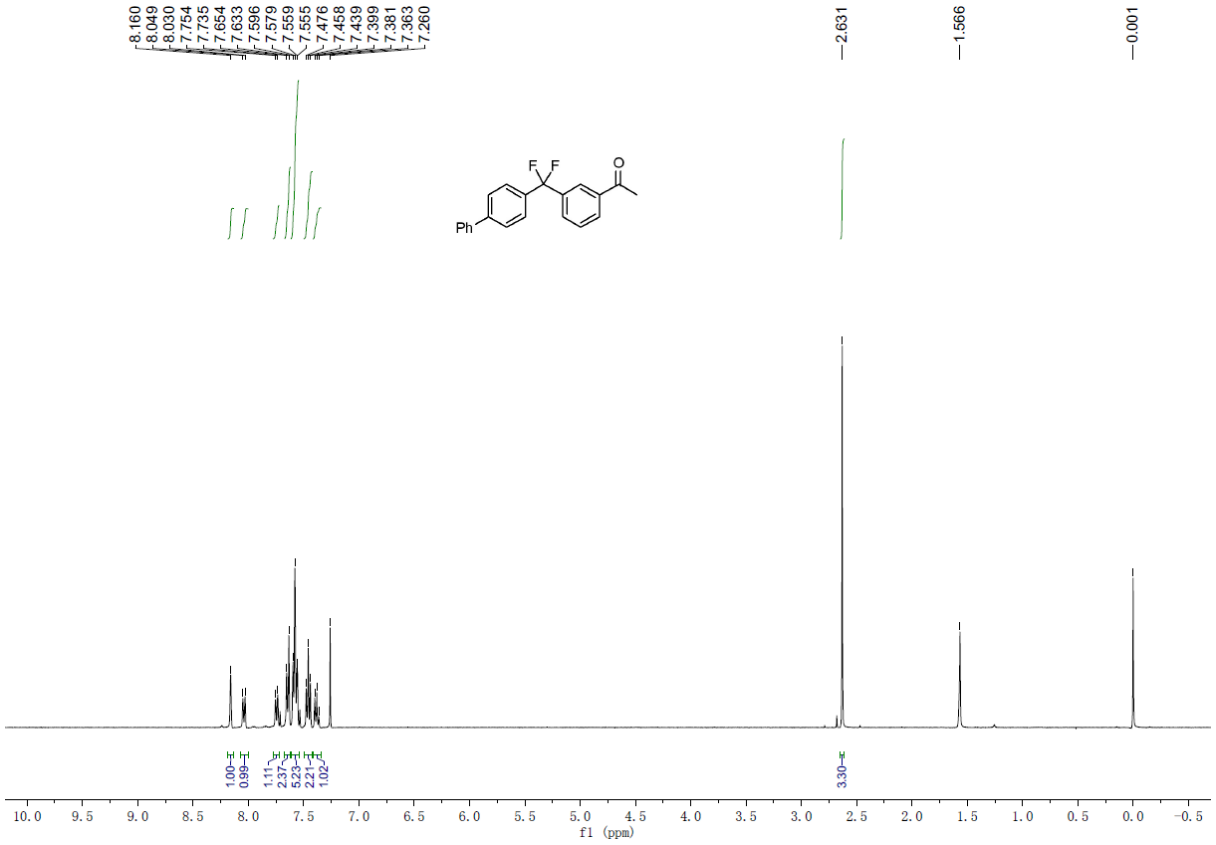
1-(4-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)ethanone (3n).

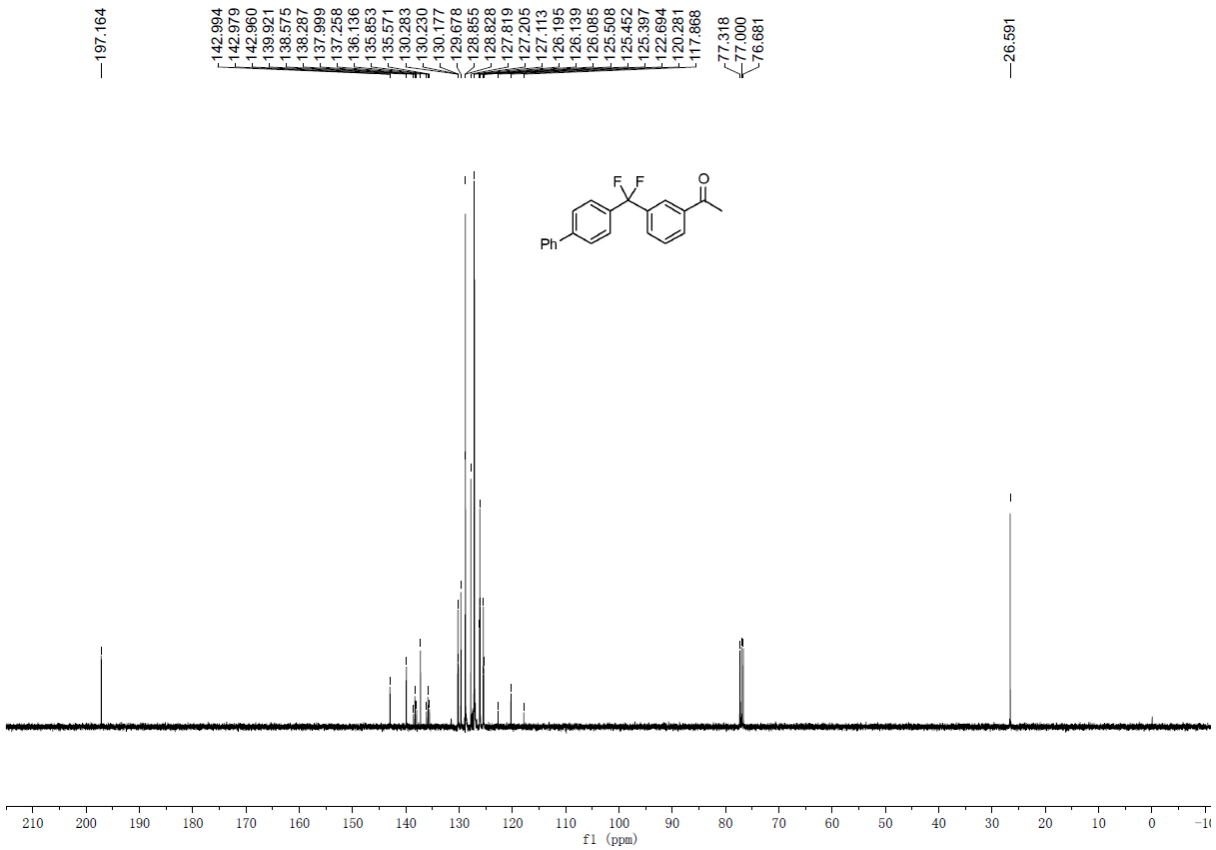


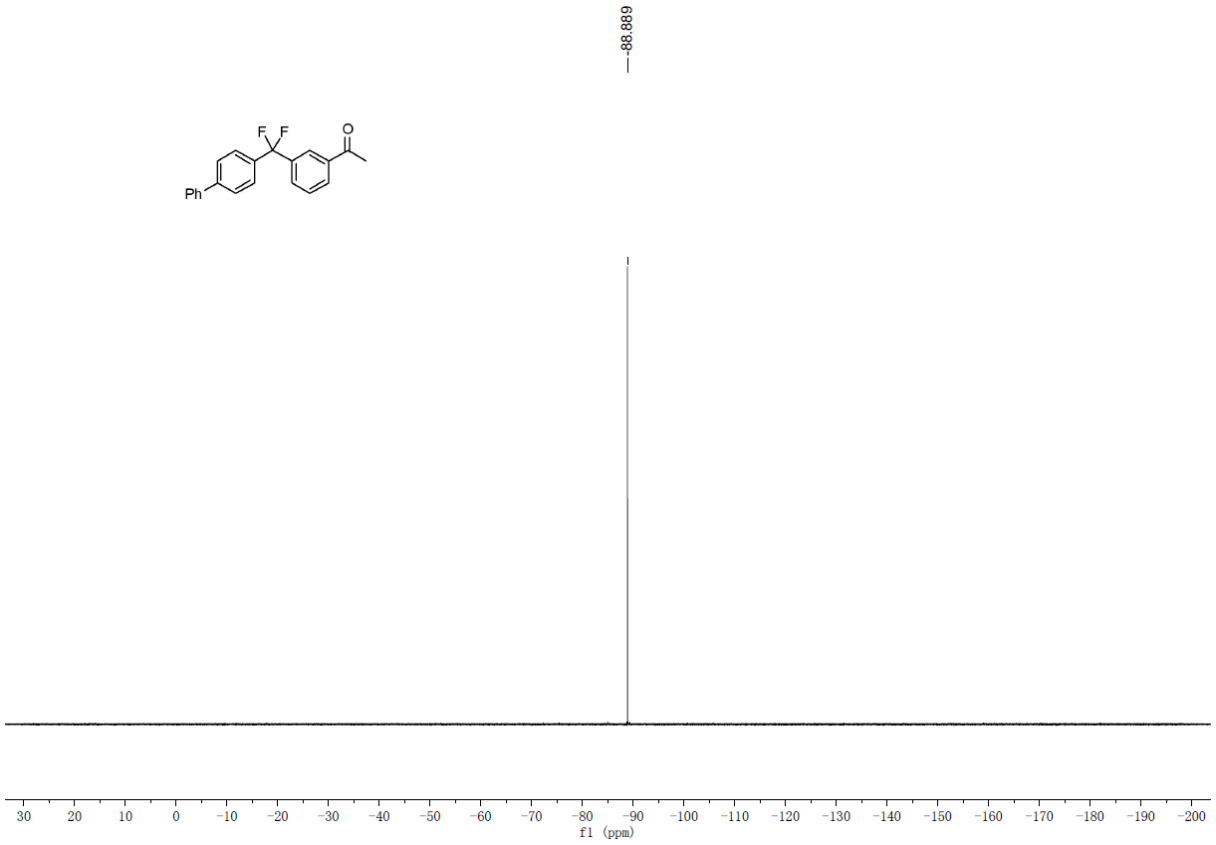

197.235
143.030
143.015
142.997
142.174
141.889
141.604
139.907
138.058
136.048
135.766
135.485
128.840
128.395
127.843
127.206
127.113
126.133
126.078
126.034
125.979
122.612
120.197
117.784
77.318
77.000
76.682
26.655
F
F
Ph
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-89.851
F
F
Ph
O
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

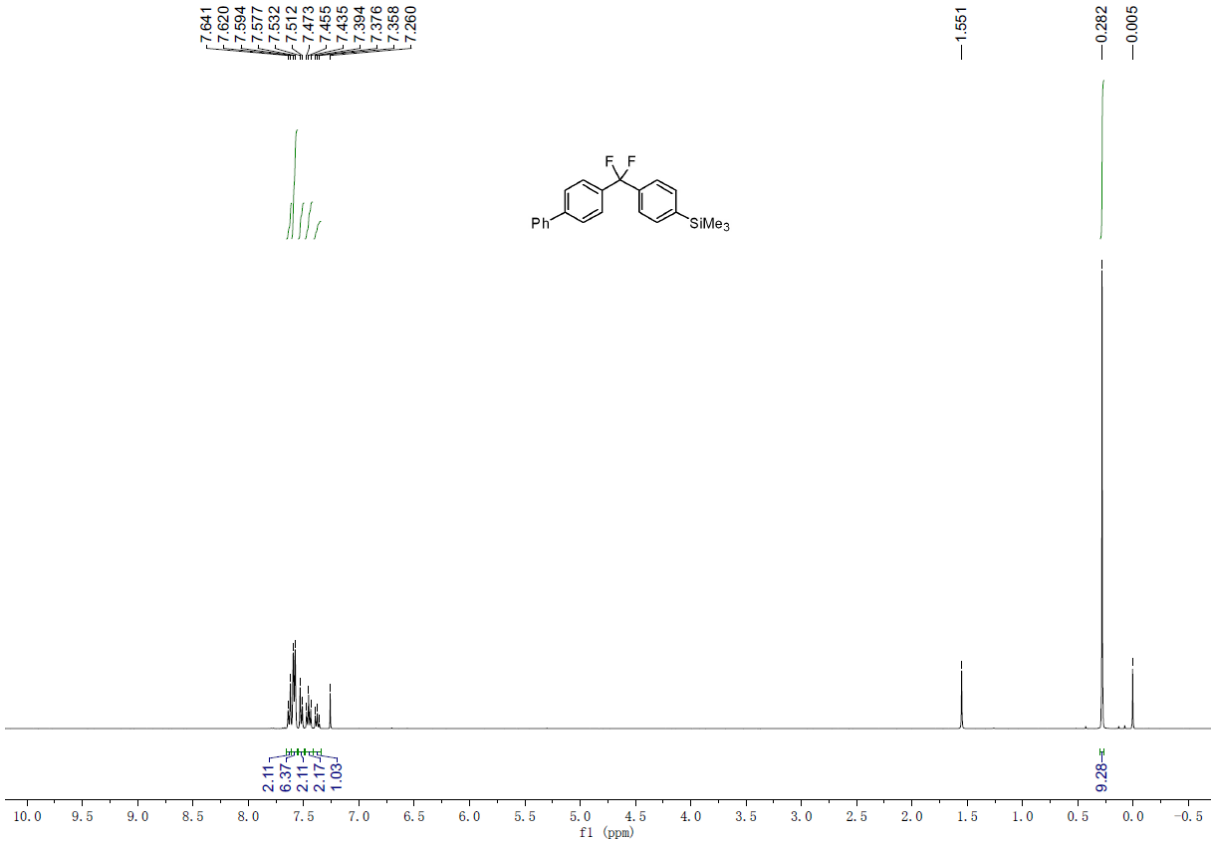
1-(3-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)ethanone (3o).

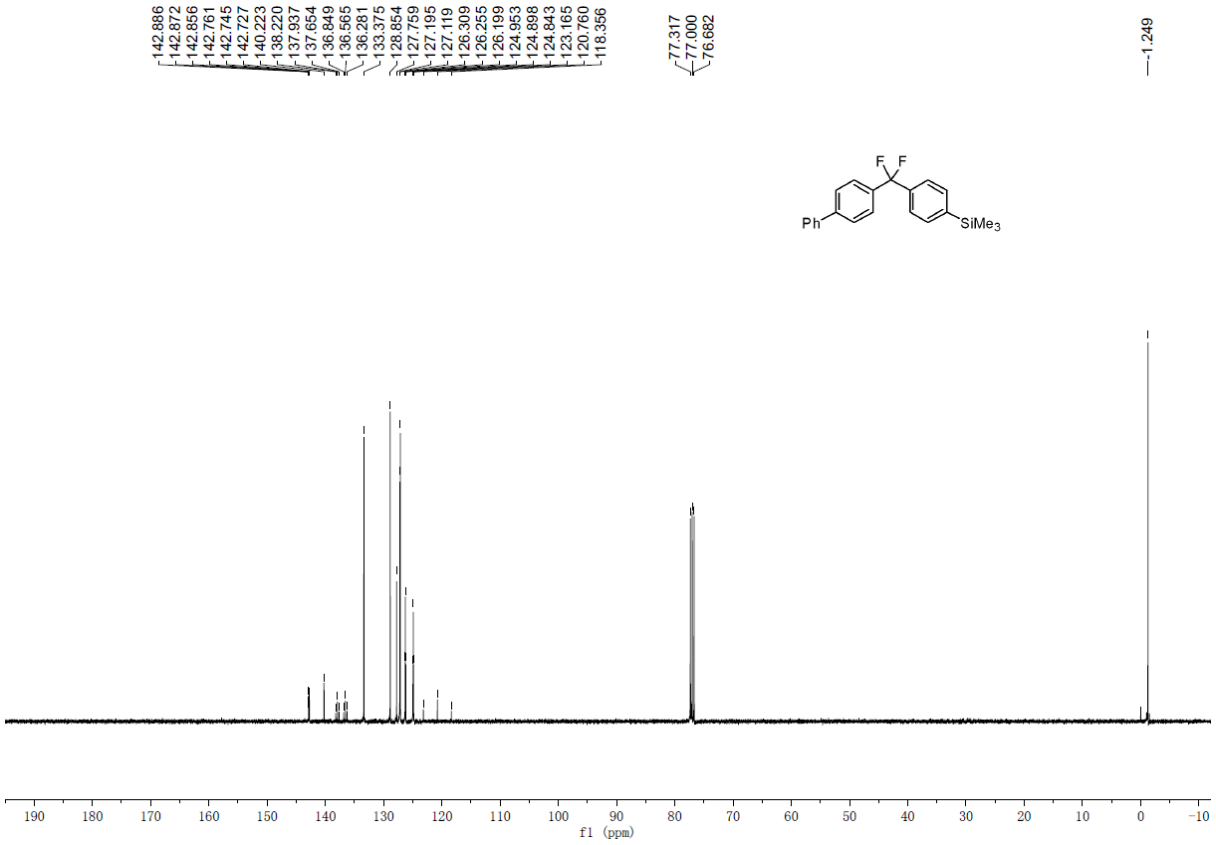


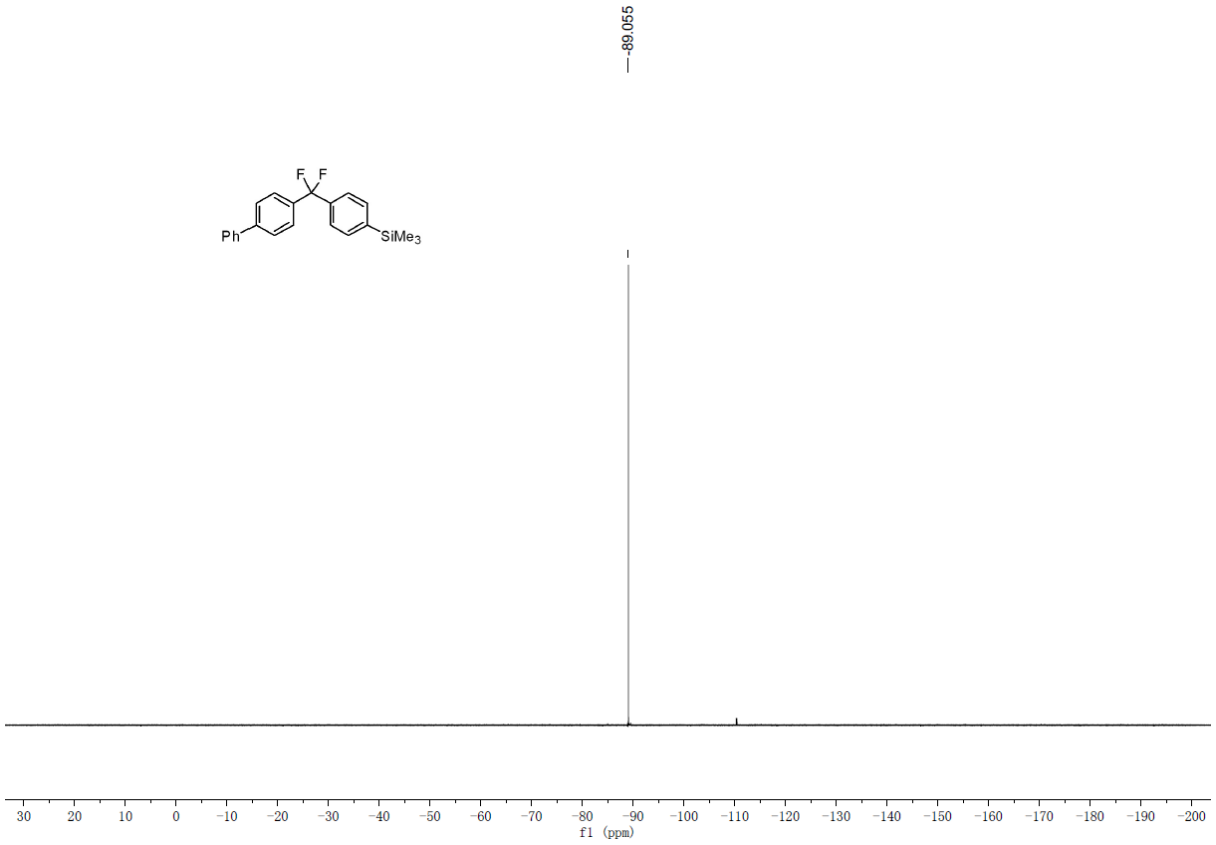




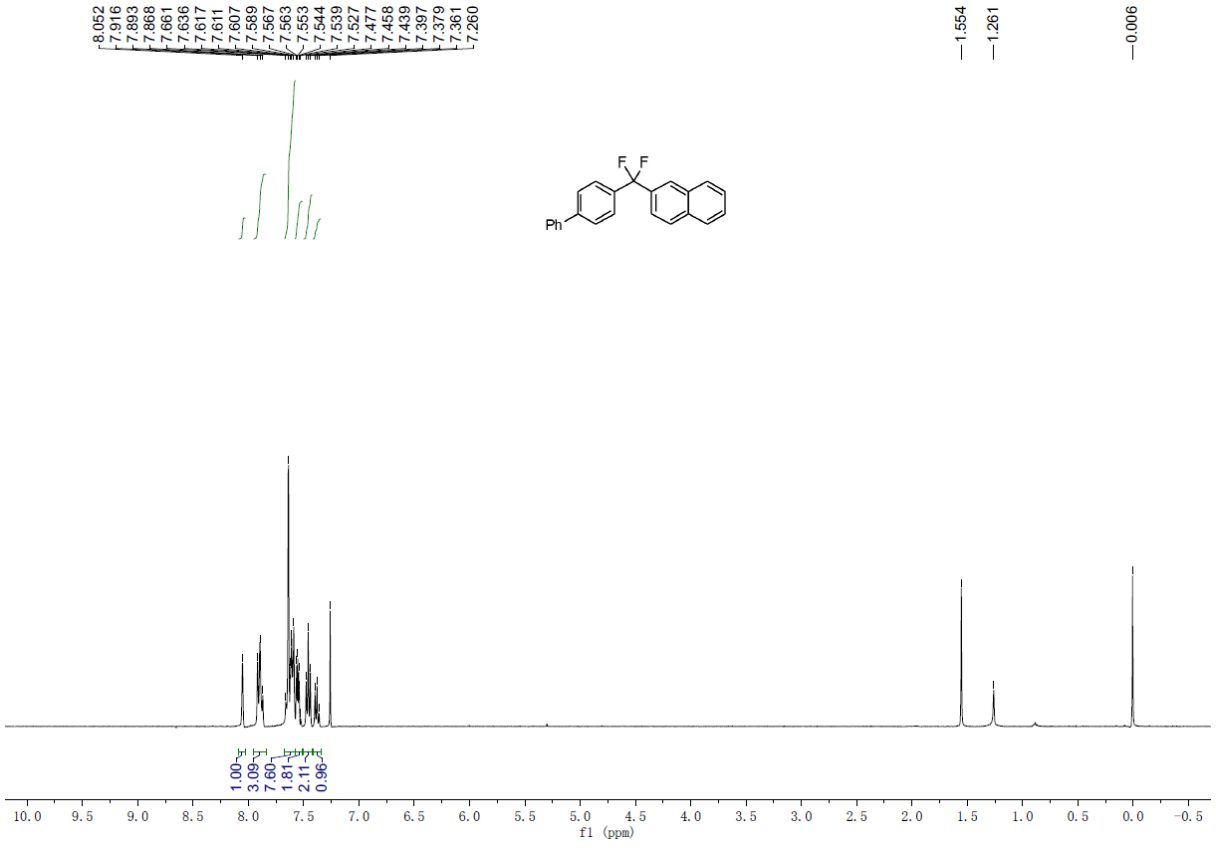
(4-([1,1'-Biphenyl]-4-yldifluoromethyl)phenyl)trimethylsilane (3p).

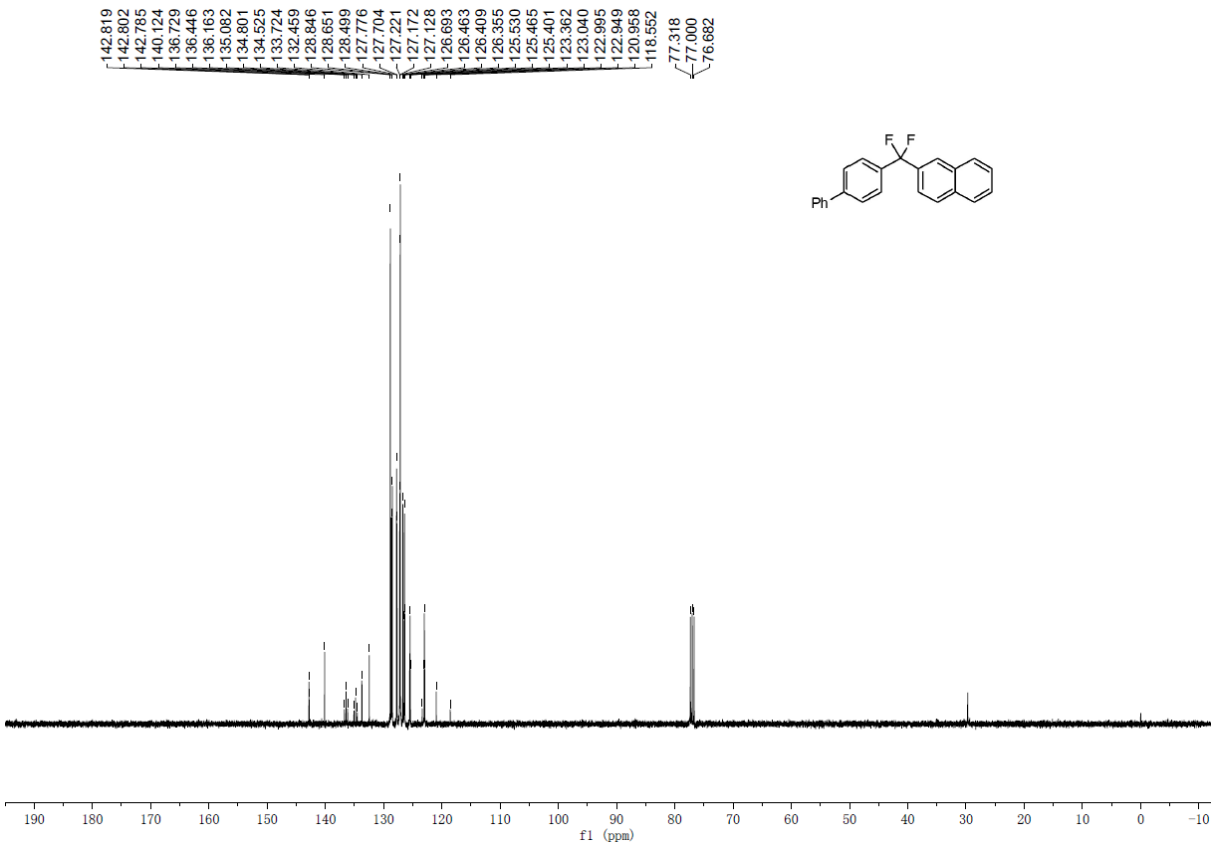


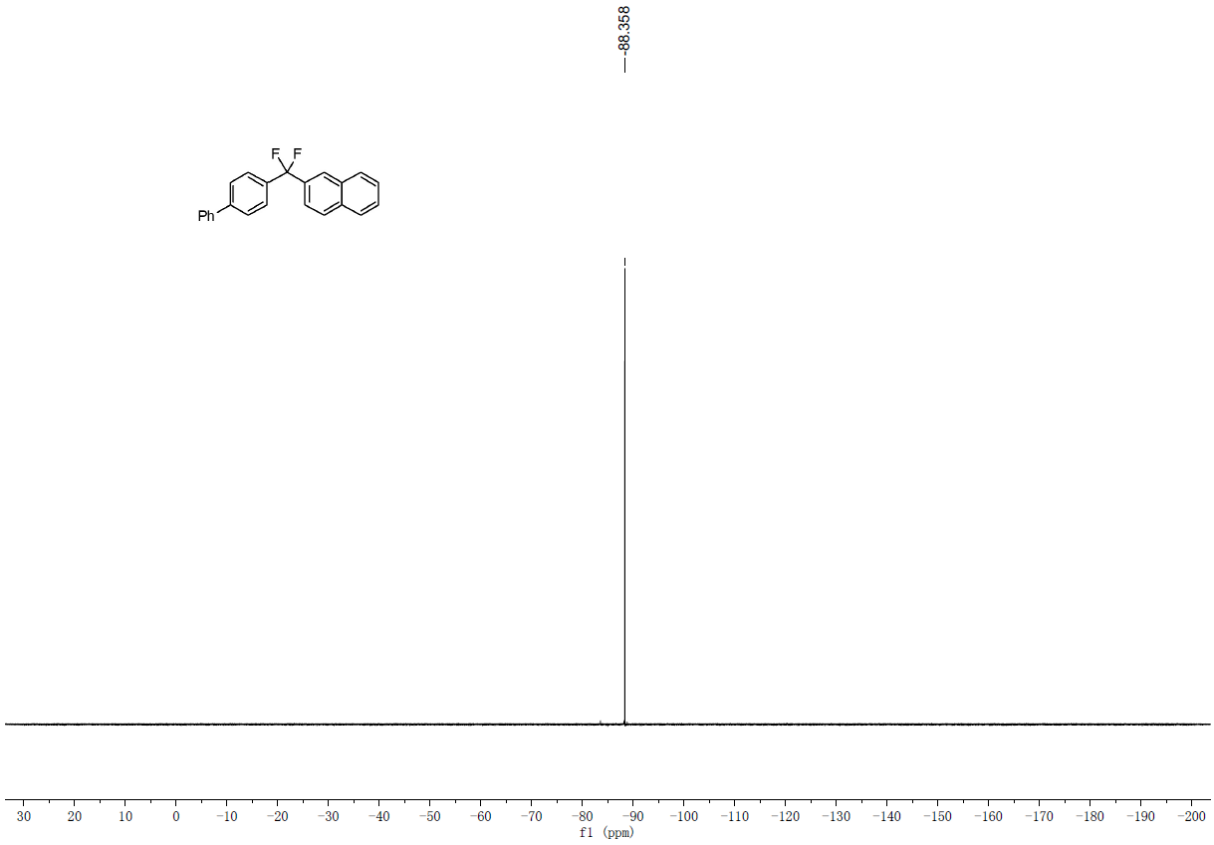

142.886
142.872
142.856
142.761
142.745
142.727
140.223
138.220
137.937
137.654
136.849
136.565
136.281
133.375
128.854
127.759
127.195
127.119
126.309
126.255
126.199
124.953
124.898
124.843
123.165
120.760
118.356
77.317
77.000
76.682
1.249
F
F
Ph
SiMe3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-89.055
F
F
Ph
SiMe3
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

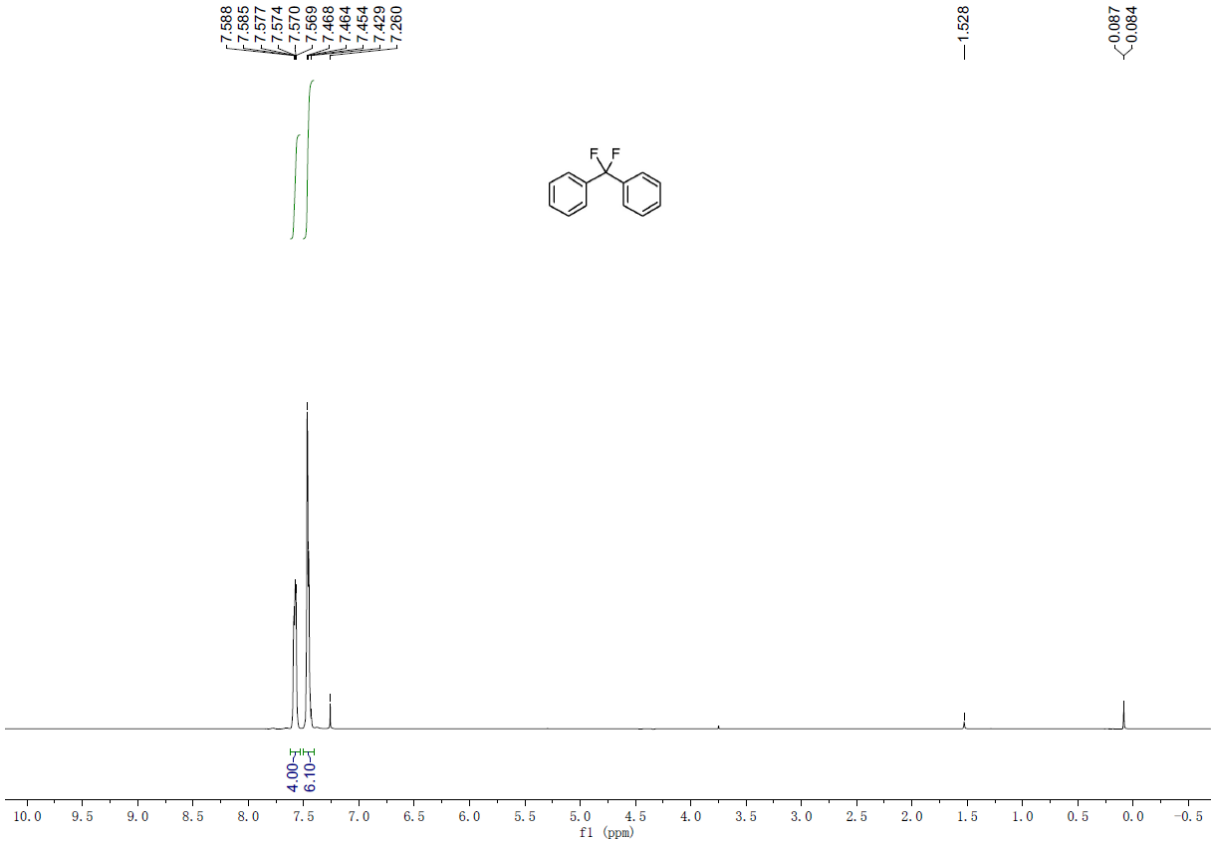
2-([1,1'-Biphenyl]-4-yldifluoromethyl)naphthalene (3q).

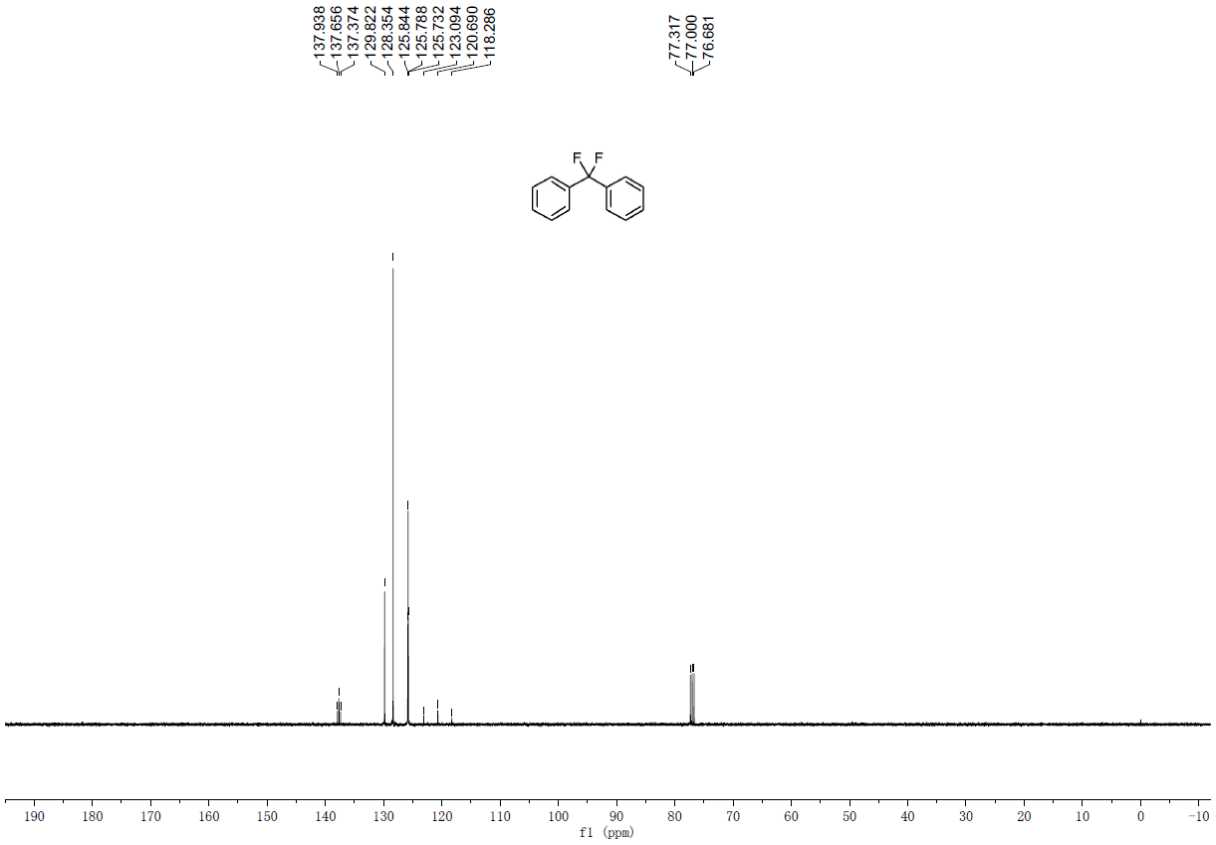


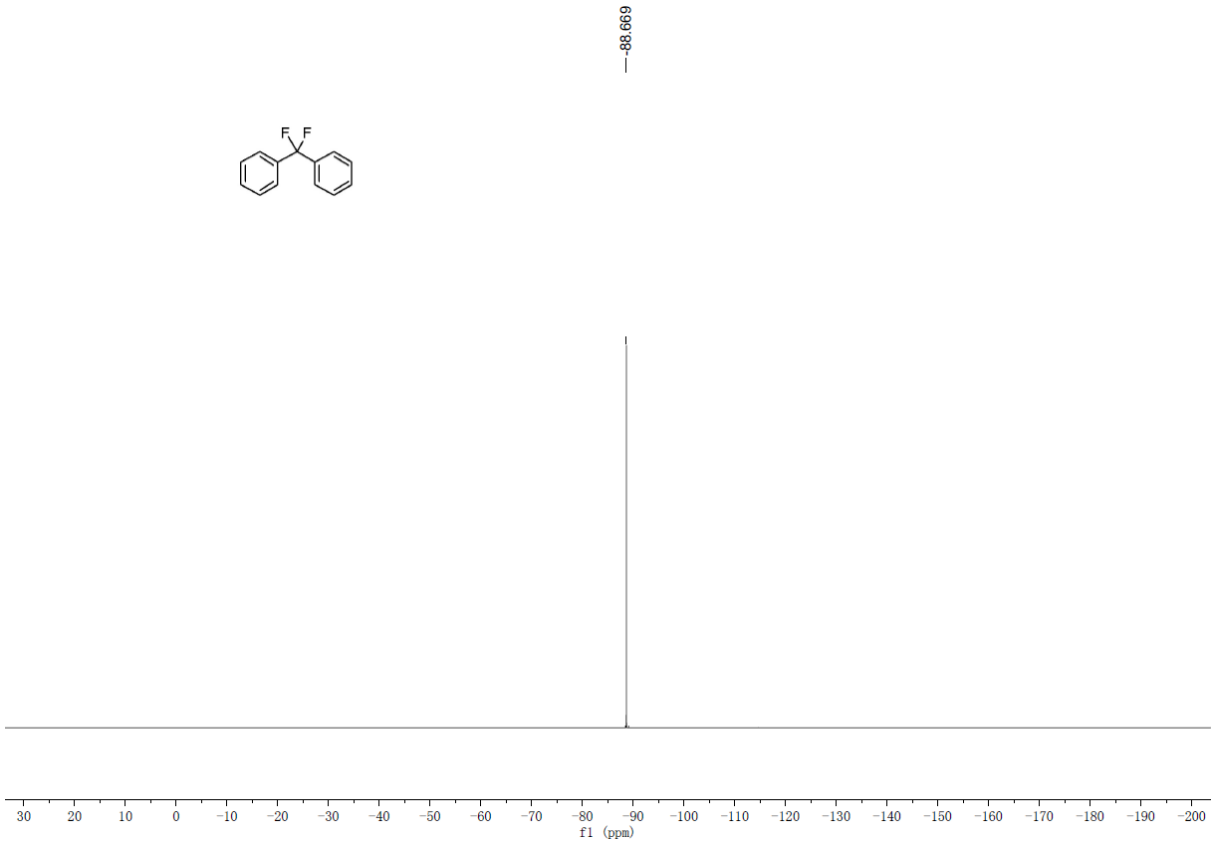




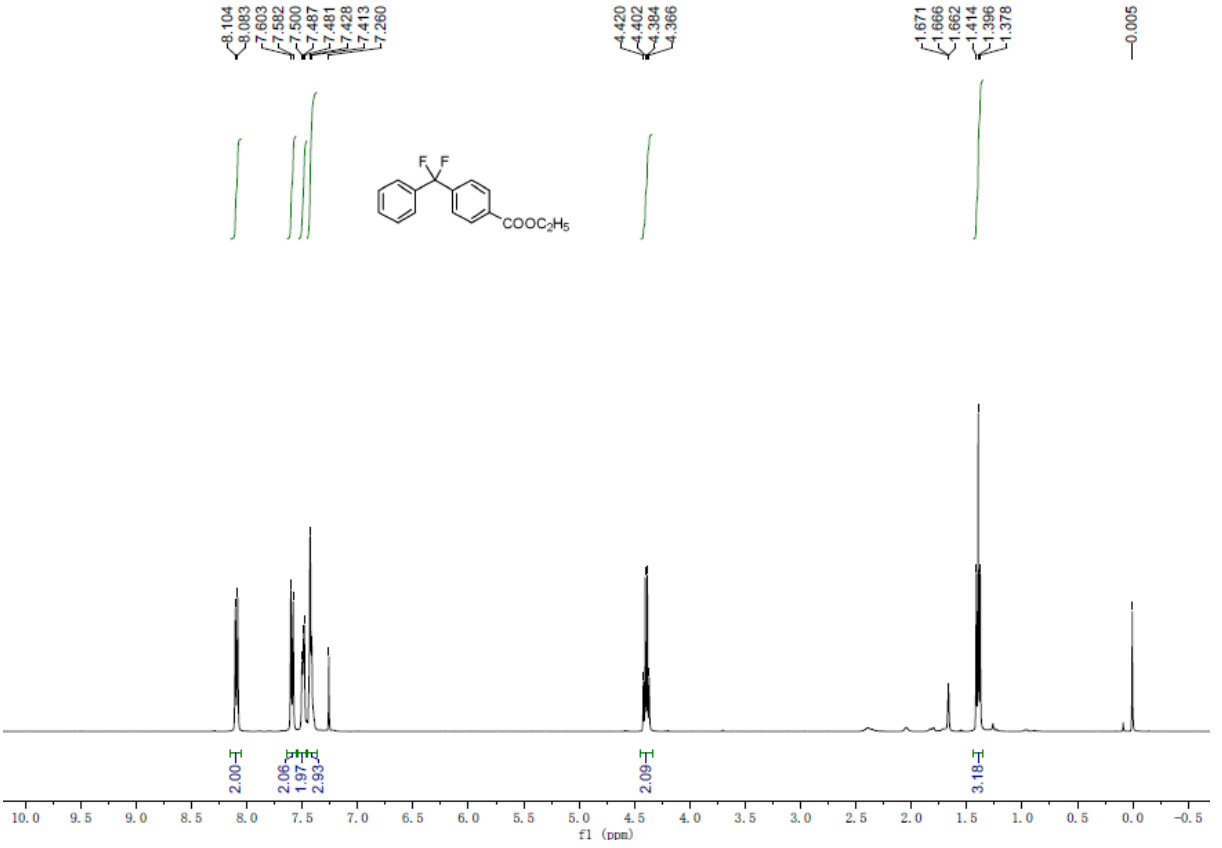
1,2-Bis(phenyl)difluoromethane (3r).

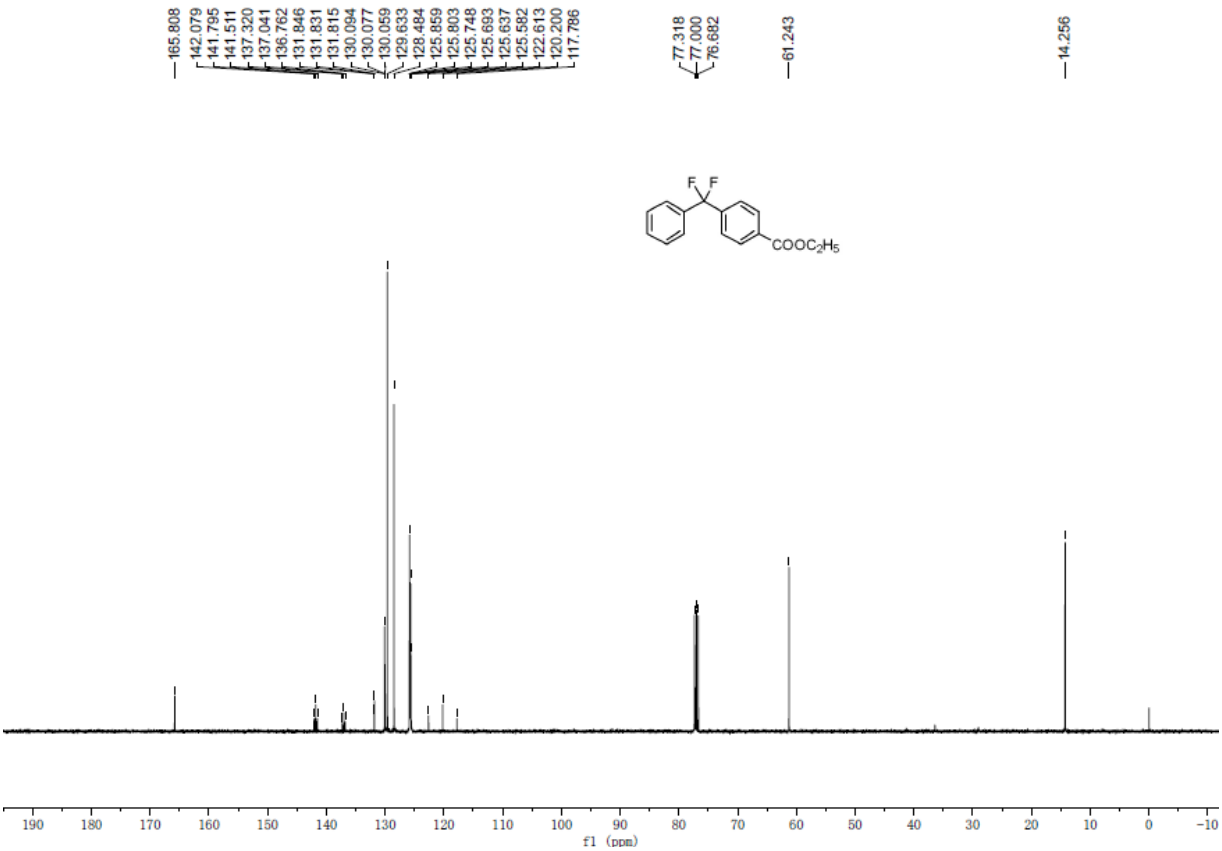


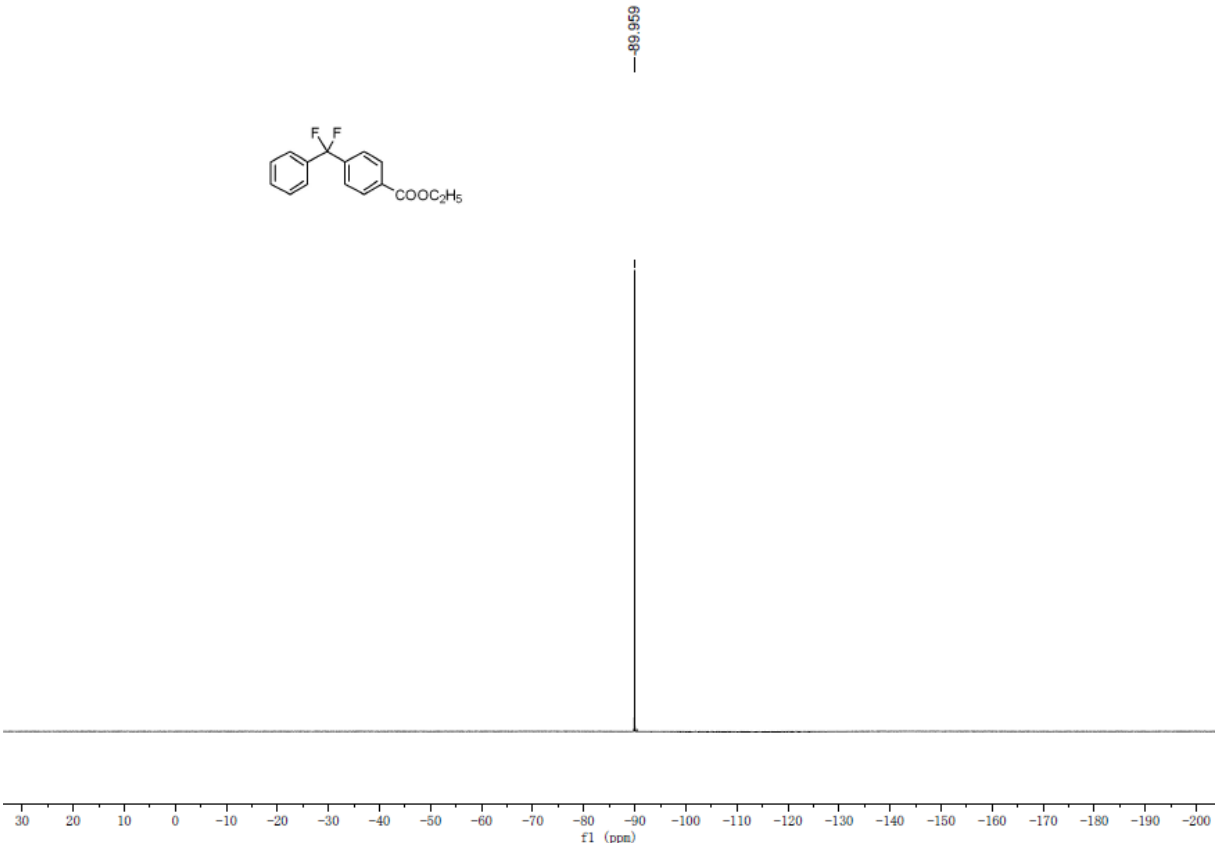

137.938
137.656
137.374
129.822
128.354
125.844
125.788
125.732
123.094
120.690
118.286
77.317
77.000
76.681
F F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-88.669
F F
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

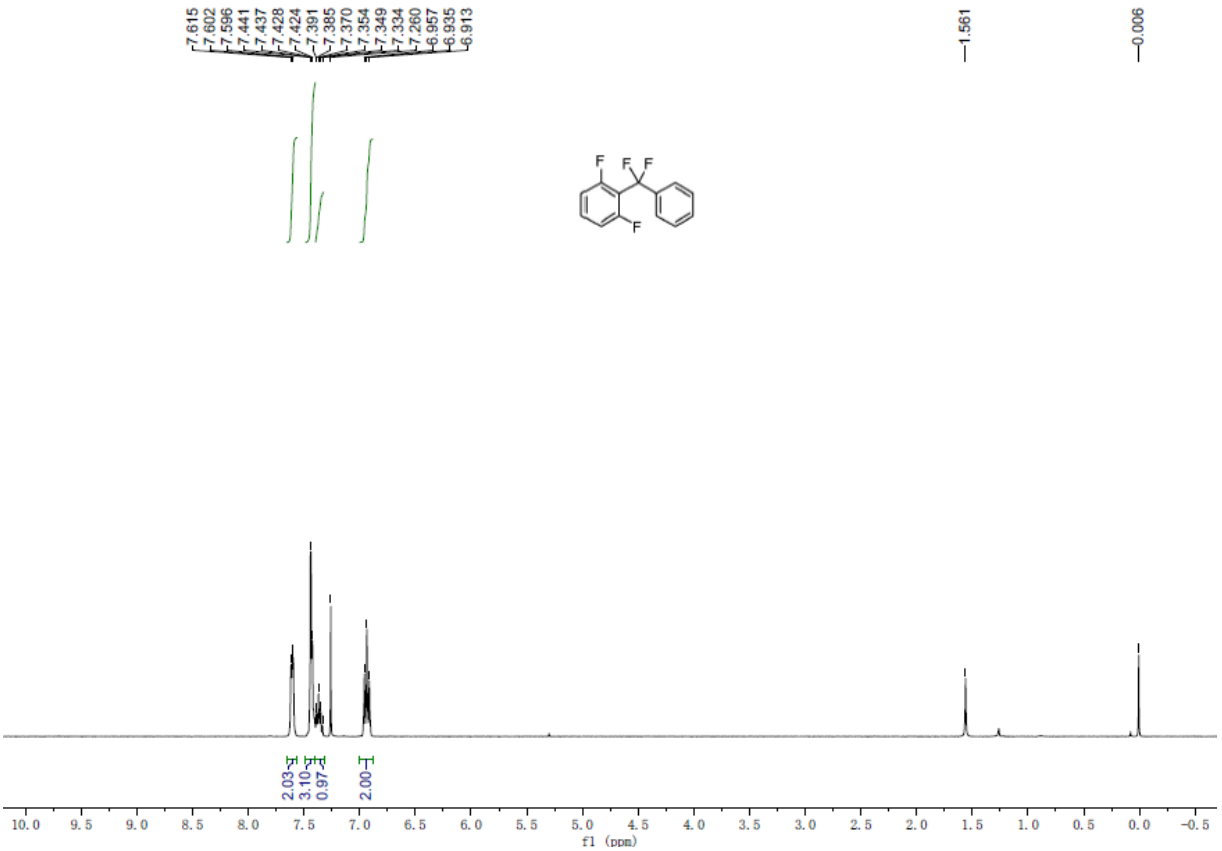
Ethyl 4-(difluoro(phenyl)methyl)benzoate (3s).

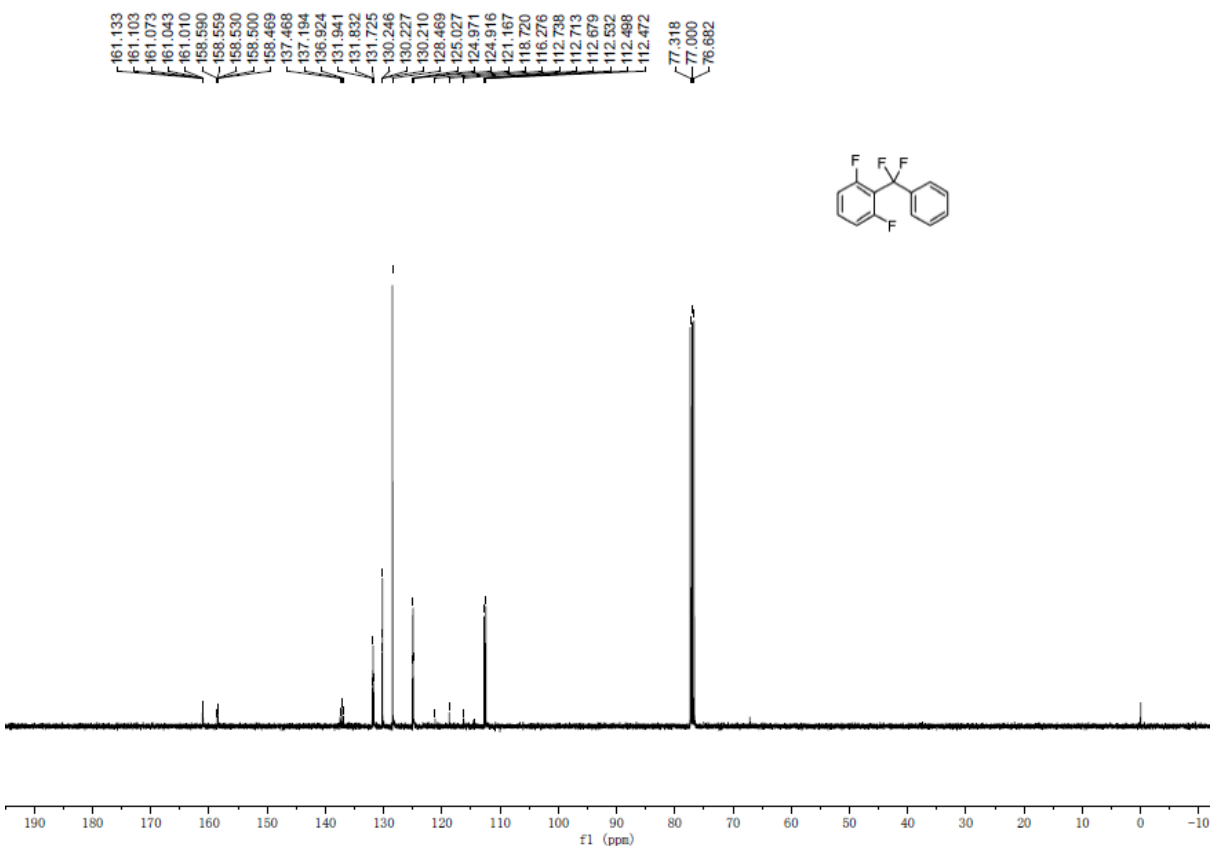


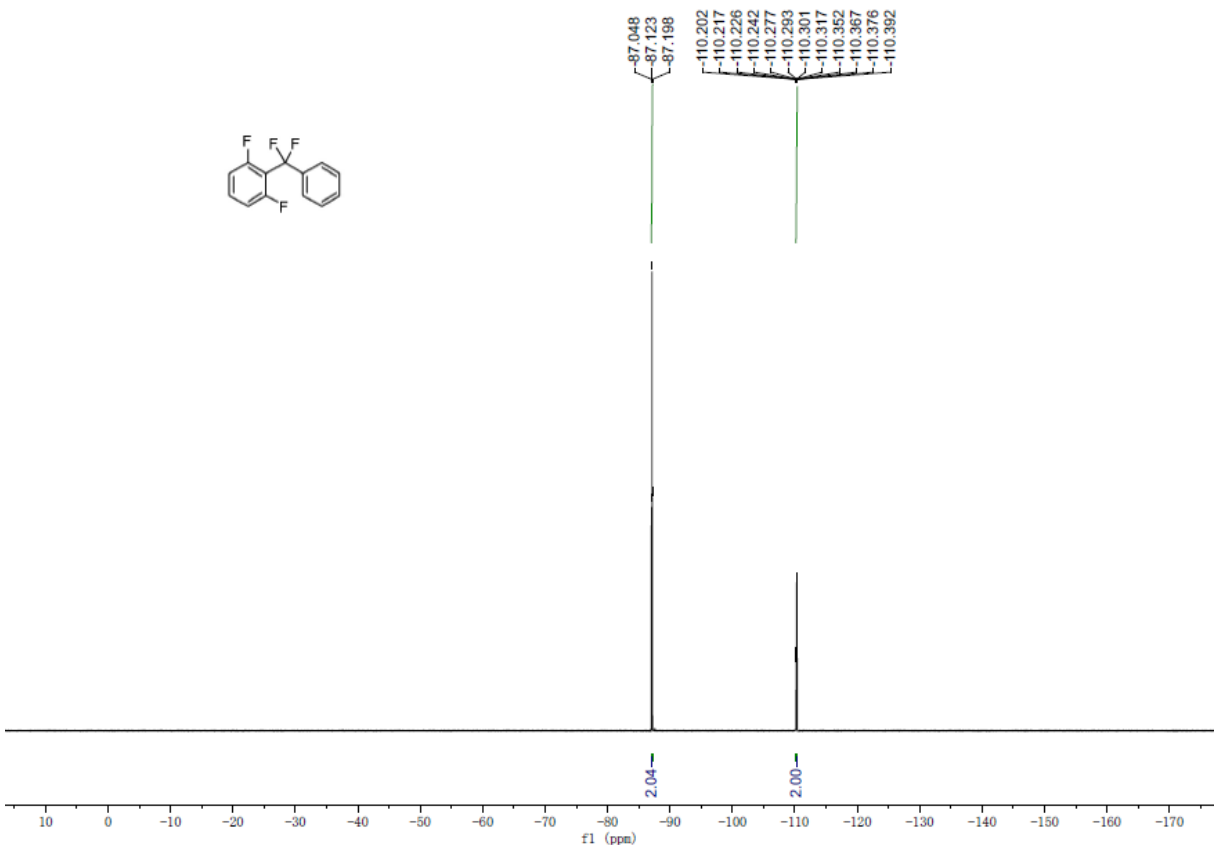




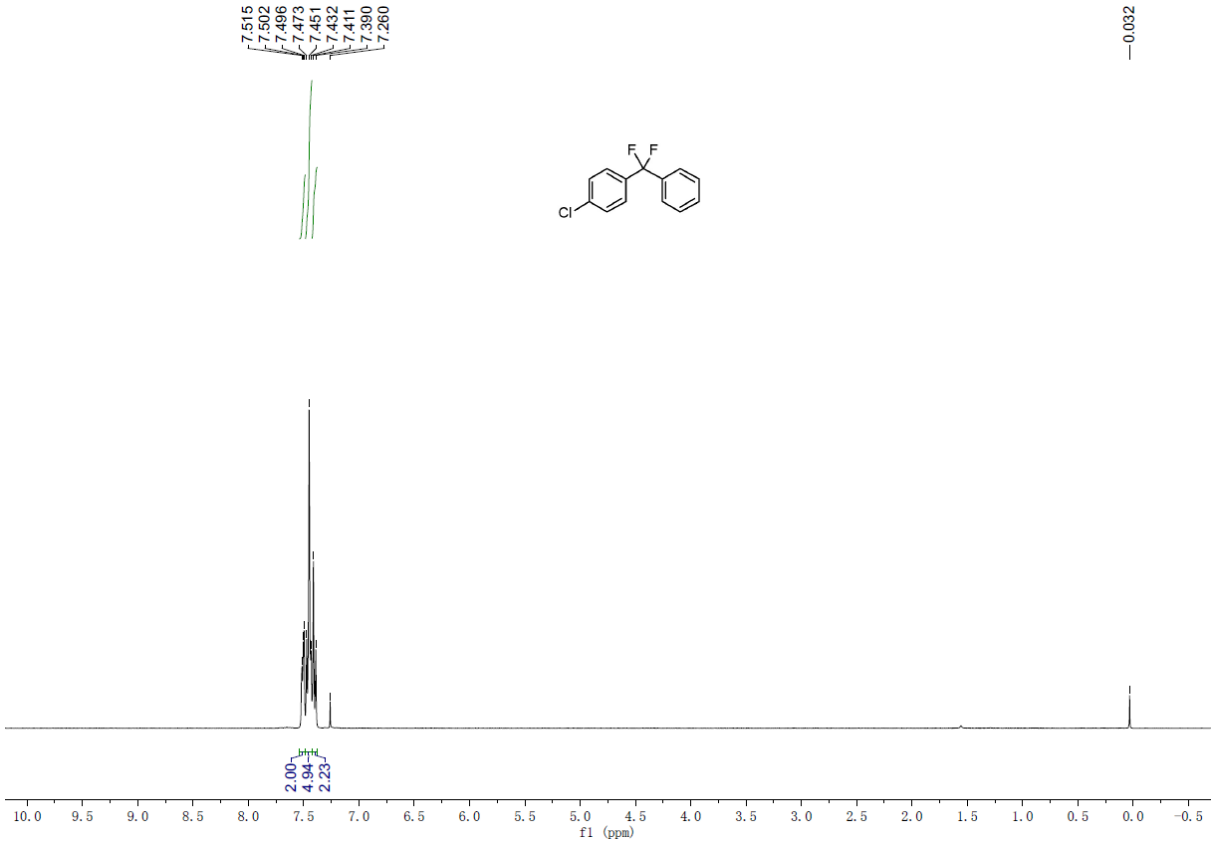
2-(Difluoro(phenyl)methyl)-1,3-difluorobenzene (3t).

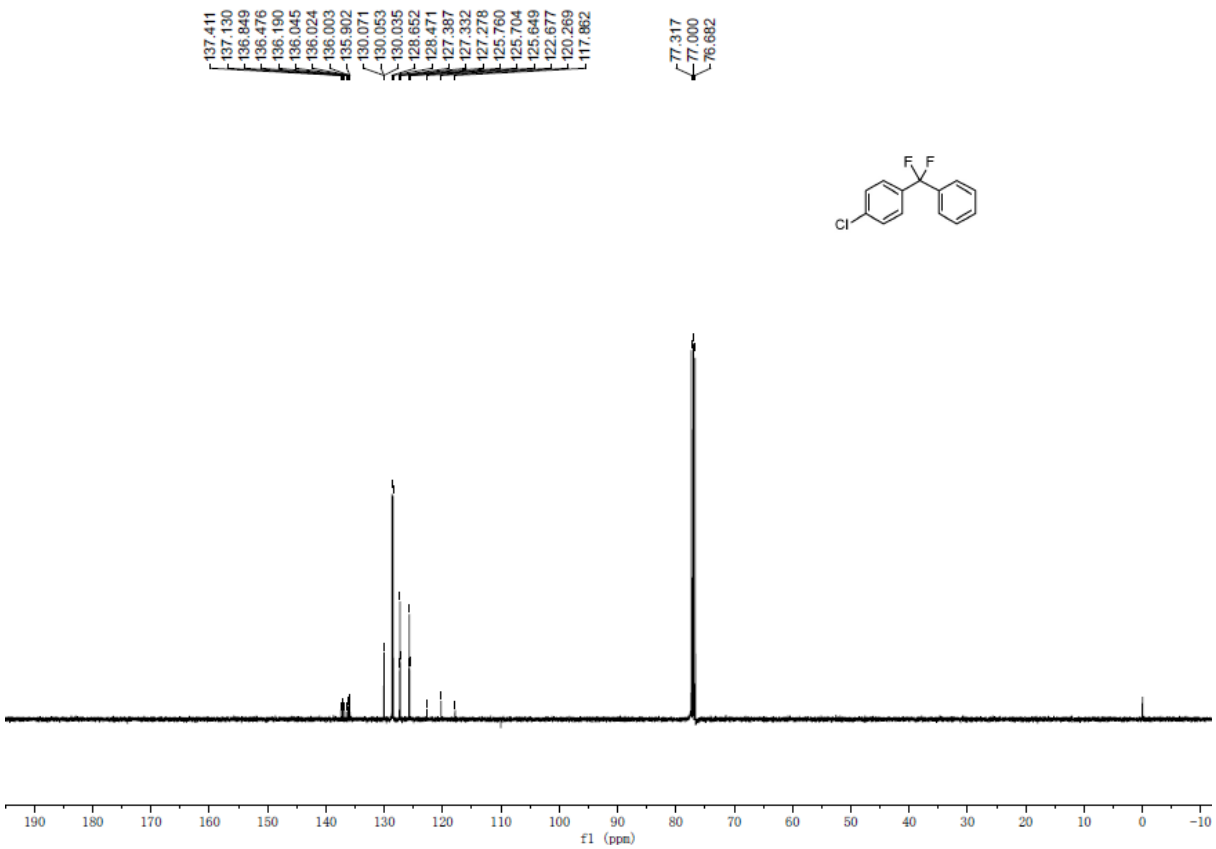


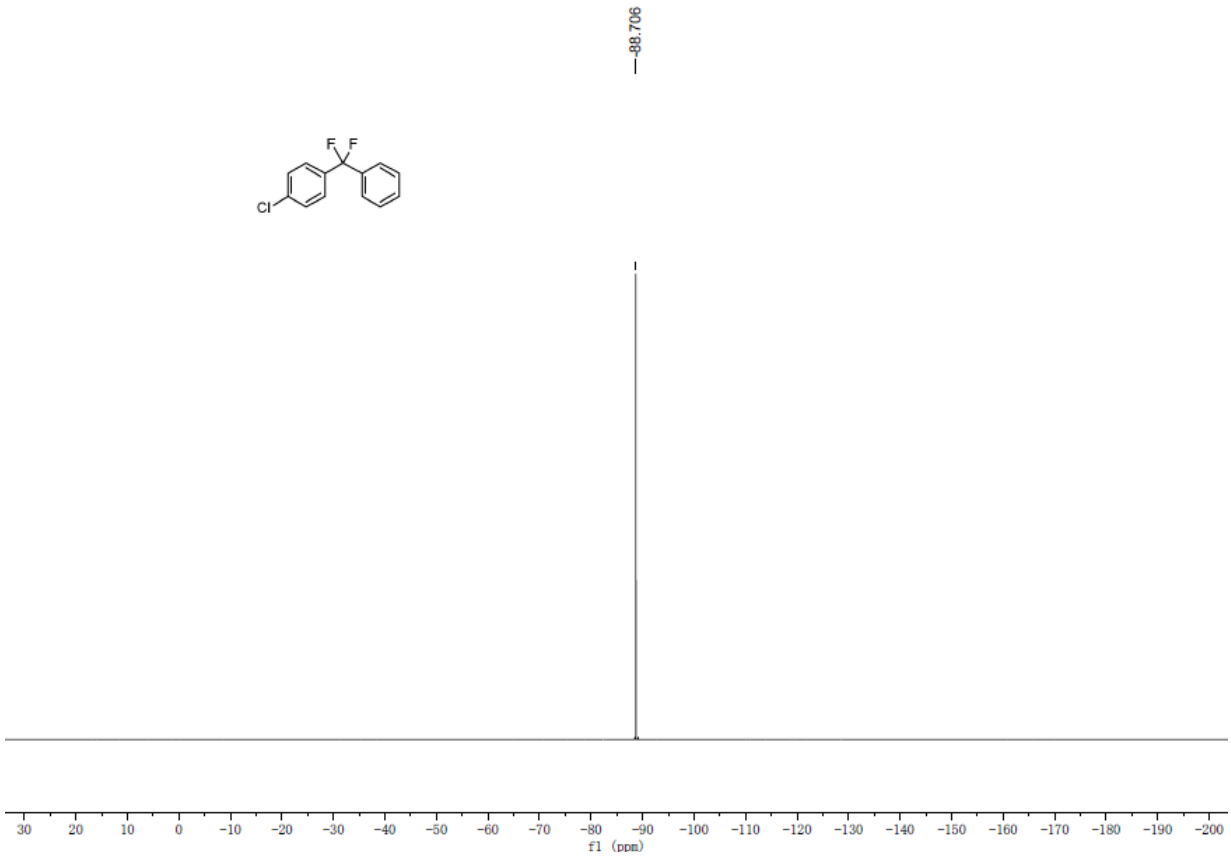

161.133
161.103
161.073
161.043
161.010
158.590
158.559
158.530
158.500
158.469
137.468
137.194
136.924
131.941
131.832
131.725
130.246
130.227
130.210
128.469
125.027
124.971
124.916
121.167
118.720
116.276
112.738
112.713
112.679
112.532
112.498
112.472
77.318
77.000
76.682
F
F
F
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-87.048
-87.123
-87.198
-110.202
-110.217
-110.226
-110.242
-110.277
-110.293
-110.301
-110.317
-110.352
-110.367
-110.376
-110.392
F
F
F
F
2.04
2.00
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
f1 (ppm)

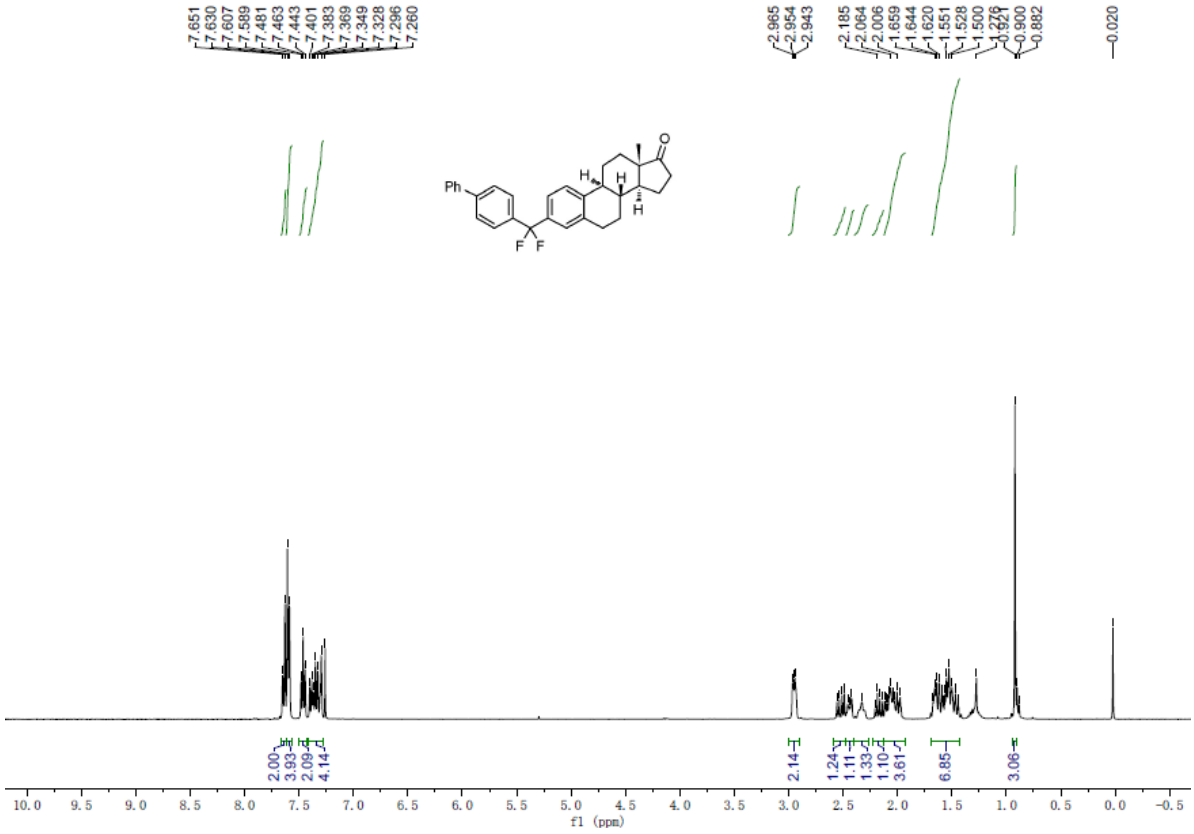
1-(4-Chlorophenyl)-1-phenyldifluoromethane (3u).

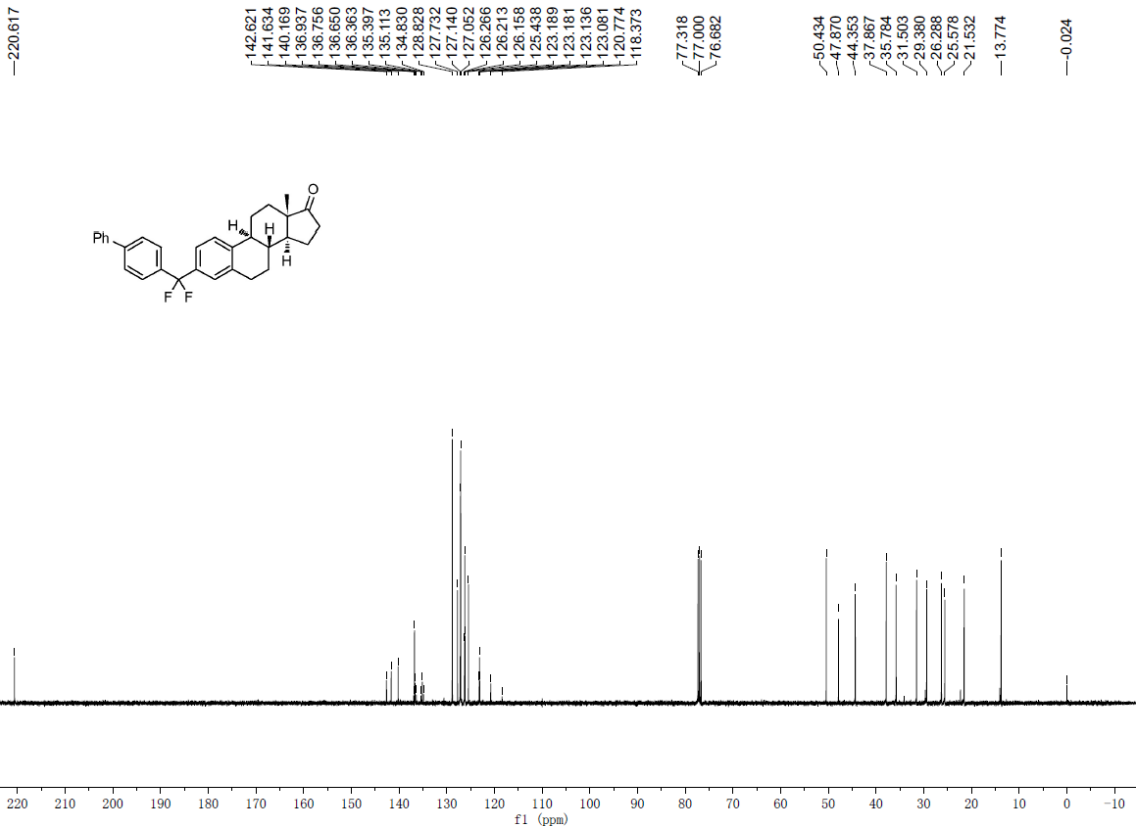


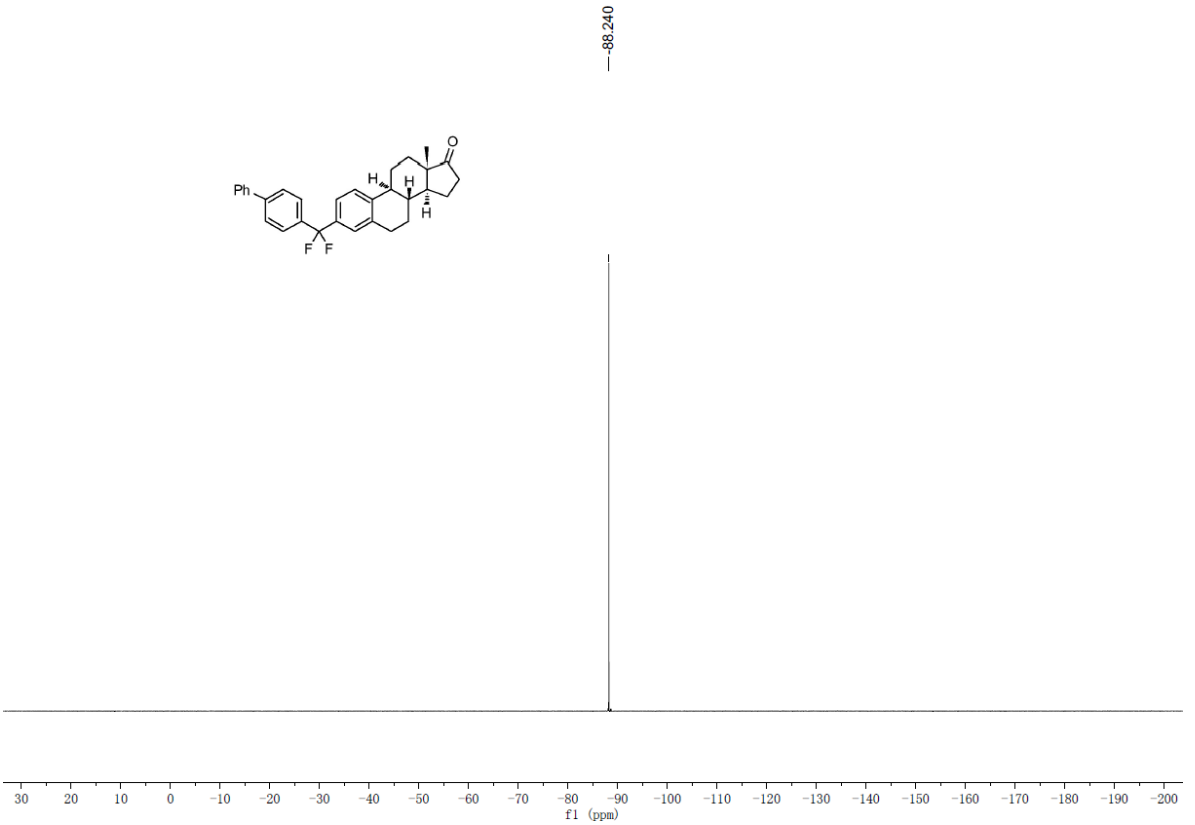



-88.706
F F
Cl
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

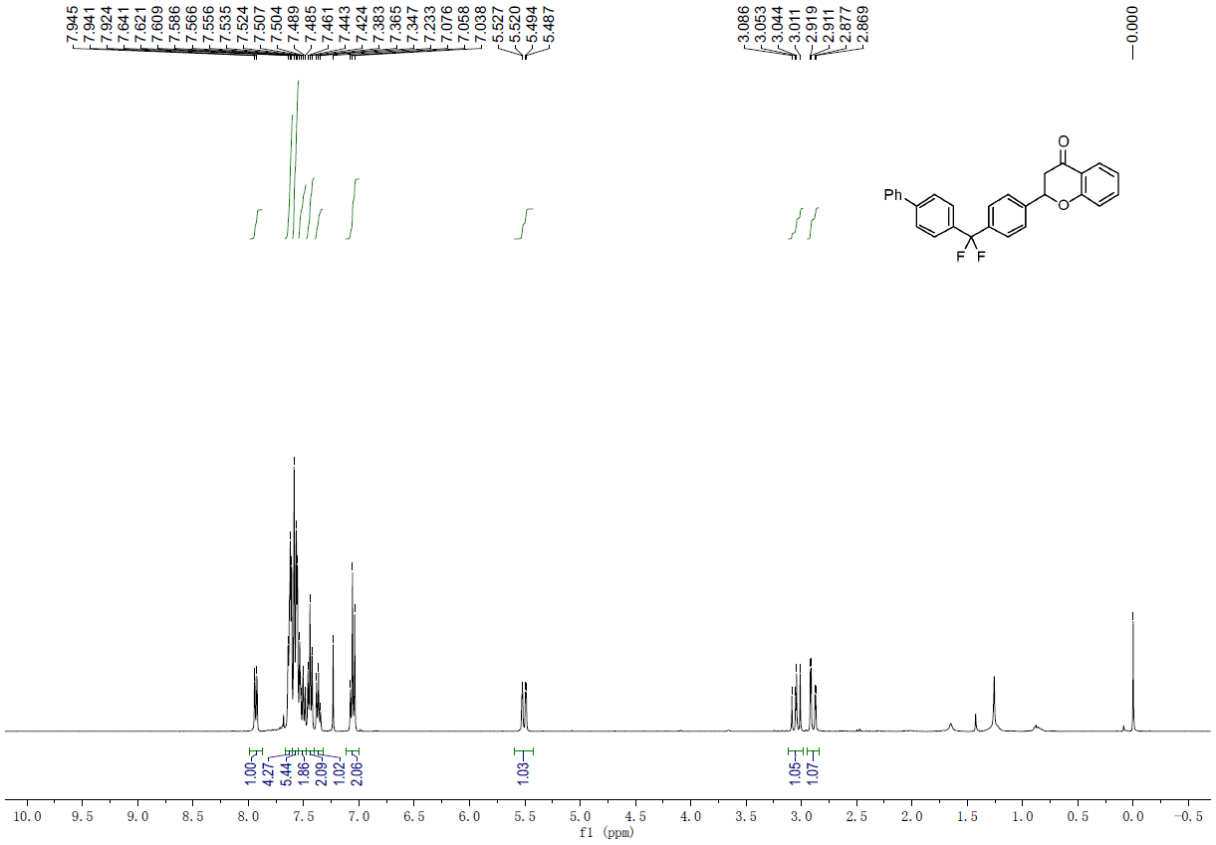
Compound (5).

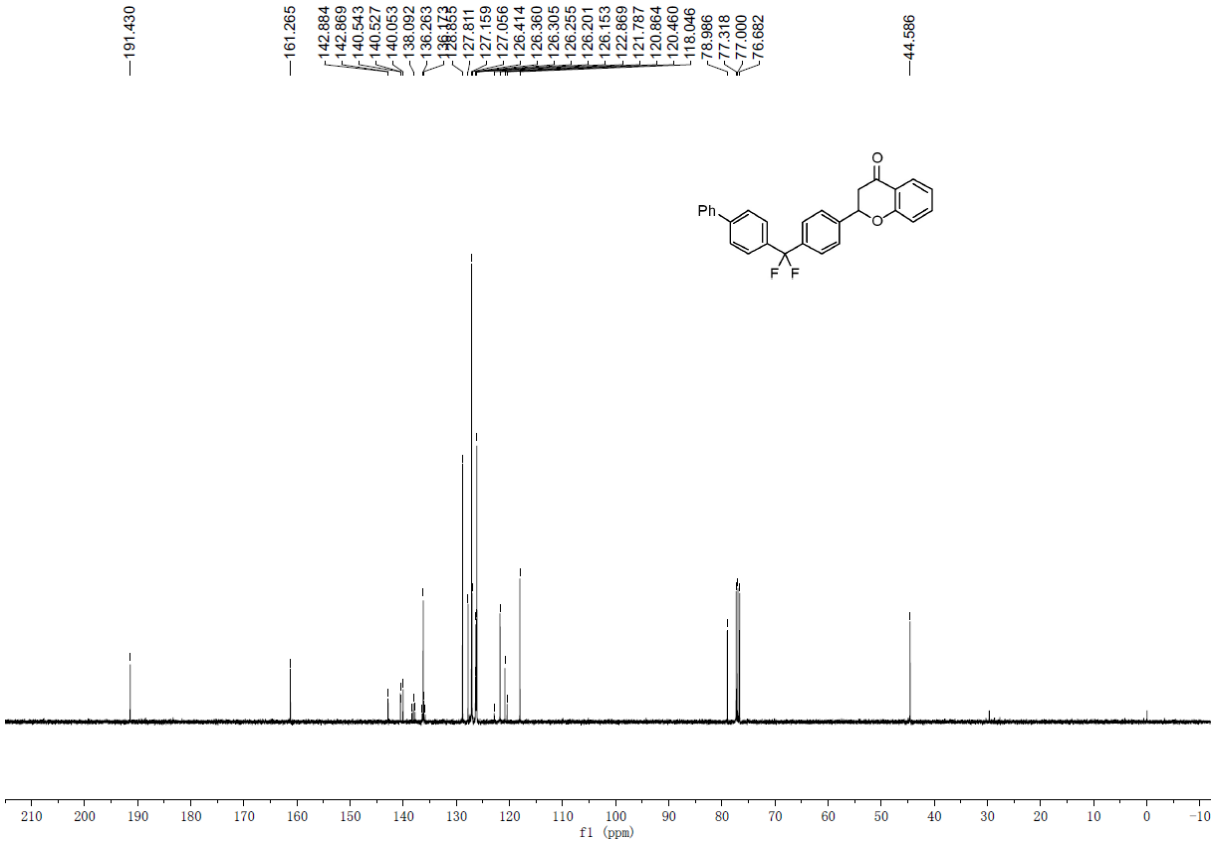

7.651
7.630
7.607
7.589
7.481
7.463
7.443
7.401
7.383
7.369
7.349
7.328
7.296
7.260
2.965
2.954
2.943
2.185
2.064
2.006
1.659
1.644
1.620
1.551
1.528
1.500
1.276
0.900
0.882
0.020
Ph
H
H
H
O
F F
2.00
3.93
2.09
4.14
2.14
1.24
1.11
1.33
1.10
3.61
6.85
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

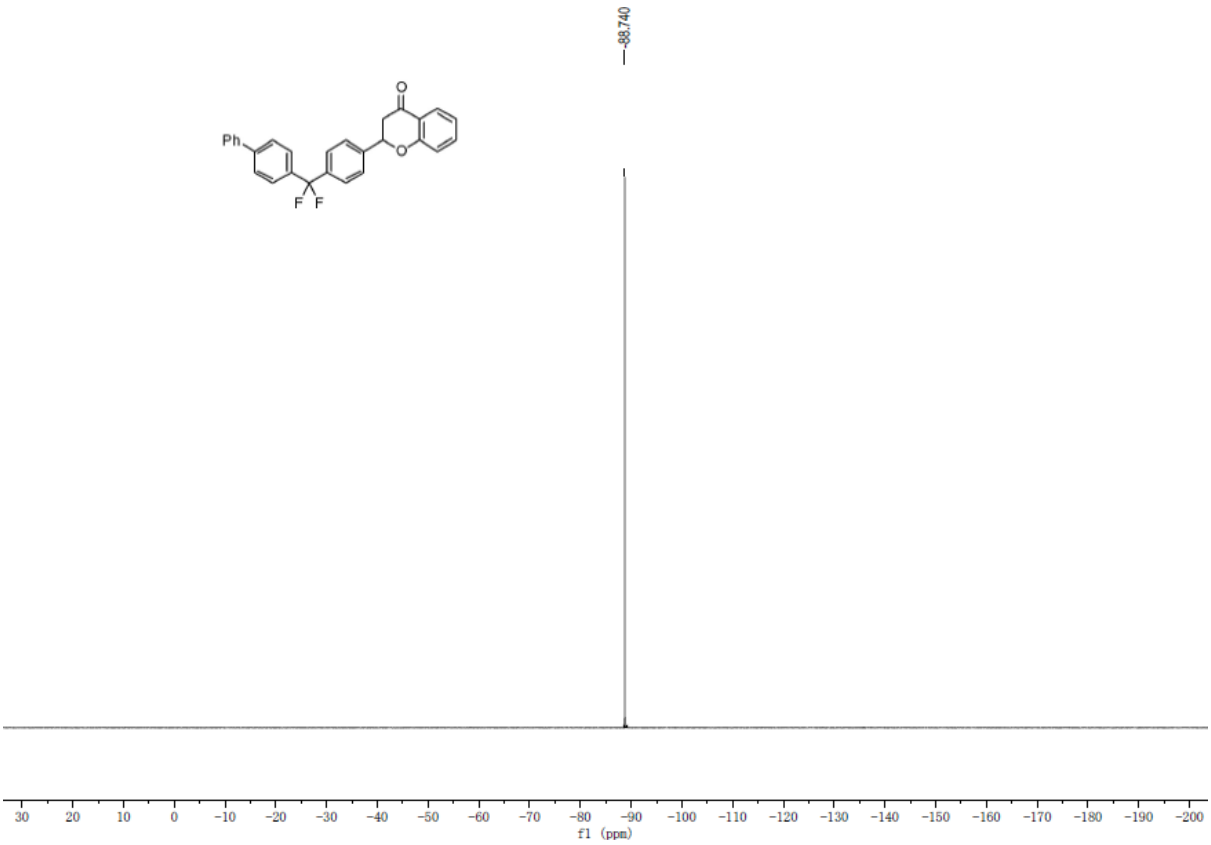

220.617
142.621
141.634
140.169
136.937
136.756
136.650
136.363
135.397
135.113
134.830
128.828
127.732
127.140
127.052
126.266
126.213
126.158
125.438
123.189
123.181
123.136
123.081
120.774
118.373
77.318
77.000
76.682
50.434
47.870
44.353
37.867
35.784
31.503
29.380
26.288
25.578
21.532
13.774
0.024
Ph
F F
H
H
H
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-88.240
Ph
F F
H
H
H
O
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

Compound 7.


7.945
7.941
7.924
7.641
7.621
7.609
7.586
7.566
7.556
7.535
7.524
7.507
7.504
7.489
7.485
7.461
7.443
7.424
7.383
7.365
7.347
7.233
7.076
7.058
7.038
5.527
5.520
5.494
5.487
3.086
3.053
3.044
3.011
2.919
2.911
2.877
2.869
0.000
Ph
O
F F
1.00
4.27
5.44
1.86
2.09
1.02
2.06
1.03
1.05
1.07
f1 (ppm)


191.430
161.265
142.884
142.869
140.543
140.527
140.053
138.092
136.263
127.811
127.159
127.056
126.414
126.360
126.305
126.255
126.201
126.153
122.869
121.787
120.864
120.460
118.046
78.986
77.318
77.000
76.682
44.586
Ph
O
F F
f1 (ppm)


-88.740
Ph
O
O
F F
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)