

Pd-Catalyzed Decarboxylative Cross Coupling of Potassium Polyfluorobenzoates with Aryl Bromides, Chlorides, and Triflates

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Supporting Information

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Part1. General Information.....S2**a. Materials**

All the reactions were carried out in oven-dried Schlenk tubes under Argon atmosphere (purity $\geq 99.999\%$). The diglyme solvent was bought from Sigma Aldrich(Sure/Seal) without further purification. All aryl halides were bought from Alfa Aesar or Acros and used as is. Aryl triflates^{<1>} and tosylates^{<2>} were synthesized according to the literature methods^{<1>}. All the polyfluorobenzoic acids were purchased from Sigma Aldrich. Palladium(I I) acetate was purchased from Alfa Aesar (99.98% purity). All phosphine ligands were bought from Sigma-Aldrich, Strem or Alfa Aesar and used as is. All the other reagents and solvents mentioned in this text were bought from Sinopharm Chemical Reagent Co. Ltd or Alfa Aesar and purified when necessary.

b. Methods

¹H-NMR, ¹³C-NMR, ¹⁹F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl₃ unless otherwise noted. Data for ¹H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). ¹⁹F-NMR were recorded in CDCl₃ solutions and trifluorotoluene (TFT) ($\delta = -67.73$ ppm) was employed as an external standard. Data for ¹⁹F-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz).

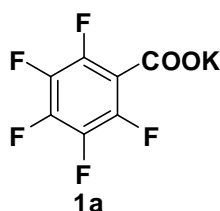
Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Elementary Analysis was carried out on Elementar Vario EL III elemental analyzer. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

Part2. Experimental Section.....S3**a. Synthesis of various potassium polyfluorobenzoates**

General procedure for the synthesis of potassium salts of the polyfluorobenzoic acids

According to the literature procedure^{<3>}, a 100ml, two-necked, round-bottomed flask was charged with the carboxylic acid (10.0 mmol) and ethanol (10ml). To this, a solution of potassium tert-butoxide (1.12g, 10 mmol) in ethanol (10 ml) was added dropwise over 30 min. After completion of addition, the reaction mixture was stirred for another 1h at room temperature. In many cases, a gradual formation of a white precipitate was observed. After removing about 2/3 of the ethanol solvent by slow evaporation on rotary evaporator, 20 ml diethyl ether was added. The resulting solid was collected by filtration, washed sequentially with ethanol (5ml x 2) and diethyl ether (10 ml x 2), transferred to a round-bottomed flask and dried under vacuum at 30°C for 2 h to provide the corresponding potassium salts in 91-99% yields.

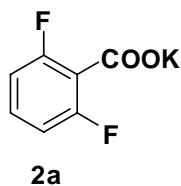
Potassium pentafluorobenzoate (**1a**)



According to the general procedure, compound **1a** was prepared from pentafluorobenzoic acid (4.24g, 20 mmol) yielding **1a** as a white crystal (4.95g, 99%).

¹⁹F-NMR (377 MHz, D₂O) δ -162.0- -161.9 (m, 2F), -155.8 (t, J_F = 21.0 Hz, 1F), -144.2 (dd, J_F = 7.2, 22.6 Hz, 2F).

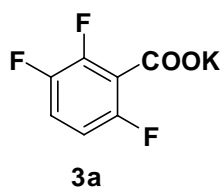
Potassium 2, 6-difluorobenzoate (**2a**)



According to the general procedure, compound **2a** was prepared from 2, 6-difluorobenzoic acid (1.58g, 10 mmol) yielding **2a** as a white solid (1.88g, 96%).

¹⁹F-NMR (377 MHz, D₂O) δ -116.0 (s, 2F).

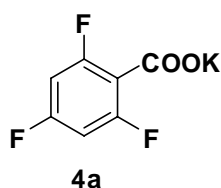
Potassium 2, 3, 6-trifluorobenzoate (**3a**)



According to the general procedure, compound **3a** was prepared from 2, 3, 6-trifluorobenzoic acid (1.76g, 10 mmol) yielding **3a** as a white solid (2.12g, 99%).

^{19}F -NMR (377 MHz, D_2O) δ -143.0 (dd, $J_{\text{F}} = 15.8, 23.0$ Hz, 1F), -139.4 (d, $J_{\text{F}} = 22.2.0$ Hz, 1F), -120.9 (d, $J_{\text{F}} = 16.2$ Hz, 1F).

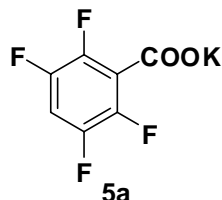
Potassium 2, 4, 6-trifluorobenzoate (4a)



According to the general procedure, compound **4a** was prepared from 2, 4, 6-trifluorobenzoic acid (1.76g, 10 mmol) yielding **4a** as a white solid (2.13g, 99%).

^{19}F -NMR (377 MHz, D_2O) δ -112.8 (d, $J_{\text{F}} = 6.8$ Hz, 2F), -108.4 (t, $J_{\text{F}} = 6.8$ Hz, 1F).

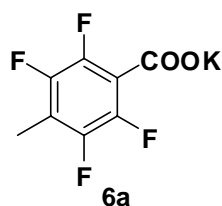
Potassium 2, 3, 5, 6-tetrafluorobenzoate (5a)



According to the general procedure, compound **5a** was prepared from 2, 3, 5, 6-tetrafluorobenzoic acid (1.94g, 10 mmol) yielding **5a** as a white solid (2.30g, 99%).

^{19}F -NMR (377 MHz, D_2O) δ -144.9 (dd, $J_{\text{F}} = 13.9, 23.7$ Hz, 2F), -139.1 (dd, $J_{\text{F}} = 13.6, 23.4$ Hz, 2F).

Potassium 2, 3, 5, 6-tetrafluoro-4-methylbenzoate (6a)

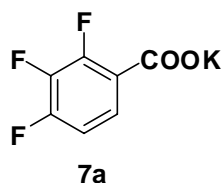


According to the general procedure, compound **6a** was prepared from 2, 3, 5, 6-tetrafluoro-p-toluic

acid (2.08g, 10 mmol) yielding **6a** as a white crystal (2.68g, 97%).

^{19}F -NMR (377 MHz, D_2O) δ -146.3 (dd, $J_{\text{F}} = 13.2, 23.0$ Hz, 2F), -143.8 (dd, $J_{\text{F}} = 13.2, 23.4$ Hz, 2F).

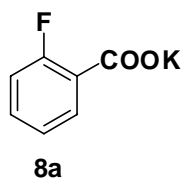
Potassium 2, 3, 4-trifluorobenzoate (**7a**)



According to the general procedure, compound **7a** was prepared from 2, 3, 4-trifluorobenzoic acid (1.76g, 10 mmol) yielding **7a** as a pale solid (2.03g, 95%).

^{19}F -NMR (377 MHz, D_2O) δ -161.2 (t, $J_{\text{F}} = 21.1$ Hz, 1F), -137.2 (dd, $J_{\text{F}} = 9.4, 21.1$ Hz, 1F), -132.7 (dd, $J_{\text{F}} = 9.4, 20.4$ Hz, 1F).

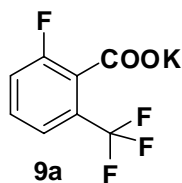
Potassium 2-fluorobenzoate (**8a**)



According to the general procedure, compound **4a** was prepared from 2-fluorobenzoic acid (1.40g, 10 mmol) yielding **8a** as a white solid (1.78g, 99%).

^{19}F -NMR (377 MHz, D_2O) δ -116.2 (s, 1F).

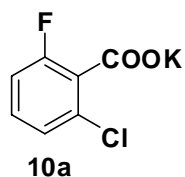
Potassium 2-fluoro-6-trifluoromethylbenzoate (**9a**)



According to the general procedure, compound **9a** was prepared from 2-fluoro-6-trifluoromethylbenzoic acid (2.08g, 10 mmol) yielding **9a** as a pale solid (2.38g, 97%). (This potassium salt can dissolve in ethanol).

^{19}F -NMR (377 MHz, D_2O) δ -117.8 (s, 1F), -59.9 (s, 3F).

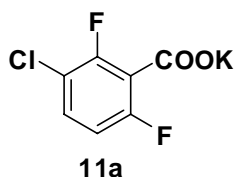
Potassium 2-fluoro-6-chlorobenzoate (**10a**)



According to the general procedure, compound **10a** was prepared from 2-fluoro-6-chlorobenzoic acid (1.74g, 10 mmol) yielding **10a** as a white solid (2.12g, 99%).

^{19}F -NMR (377 MHz, D_2O) δ -116.7 (s, 1F).

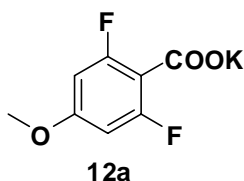
Potassium 3-chloro-2, 6-difluorobenzoate (11a)



According to the general procedure, compound **11a** was prepared from 3-chloro-2,6-difluorobenzoic acid (1.92g, 10 mmol) yielding **11a** as a white solid (2.23g, 97%).

^{19}F -NMR (377 MHz, D_2O) δ -116.8 (s, 2F).

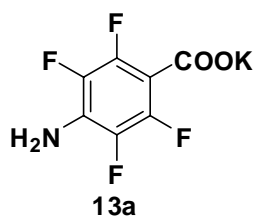
Potassium 2, 6-difluoro-4-methoxybenzoate (12a)



According to the general procedure, compound **12a** was prepared from 2,6-difluoro-4-methoxybenzoic acid (1.88g, 10 mmol) yielding **12a** as a white solid (2.12g, 94%).

^{19}F -NMR (377 MHz, D_2O) δ -113.8 (s, 2F).

Potassium 4-amino-2, 3, 5, 6-tetrafluorobenzoate (13a)



According to the general procedure, compound **13a** was prepared from 4-amino-2,3,5,6-tetrafluorobenzoic acid (2.09g, 10 mmol) yielding **13a** as a pale white solid (2.42g, 98%).

^{19}F -NMR (377 MHz, D_2O) δ -161.1 (dd, $J_{\text{F}} = 5.7, 20.0$ Hz, 2F), -146.5 (dd, $J_{\text{F}} = 6.0, 19.6$ Hz, 2F).

b. Optimization of the reaction conditions

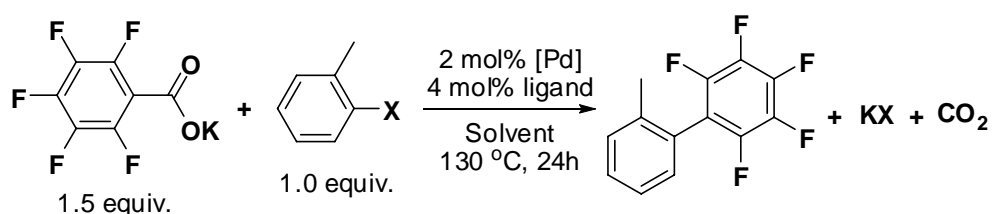
General procedures for the decarboxylative coupling of potassium pentafluorobenzoate with *o*-tolylhalides

General Procedure:

A 10ml oven-dried Schlenk tube was charged with Pd.source (See Table 1), ligand (See Table 1), and potassium pentafluorobenzoate (0.375mmol). The tube was evacuated and filled with argon (this procedure was repeated three times). Then *o*-tolylhalide (0.25mmol) and solvent (0.5 ml, See Table 1) were added with a syringe under a counter flow of argon. The tube was sealed with a screw cap, stirred at room temperature for 10 min, and connected to the Schlenk line which was full of argon, stirred in a preheated oil bath (130 °C) for the appointed time (24h). Upon completion of the reaction, the mixture was cooled to room temperature and diluted with diethyl ether, and the yields were determined by gas chromatography using biphenyl as the internal standard.

SI Table 1

Pd-catalyzed decarboxylative cross coupling of potassium pentafluorobenzoate with *o*-tolylhalide.^a

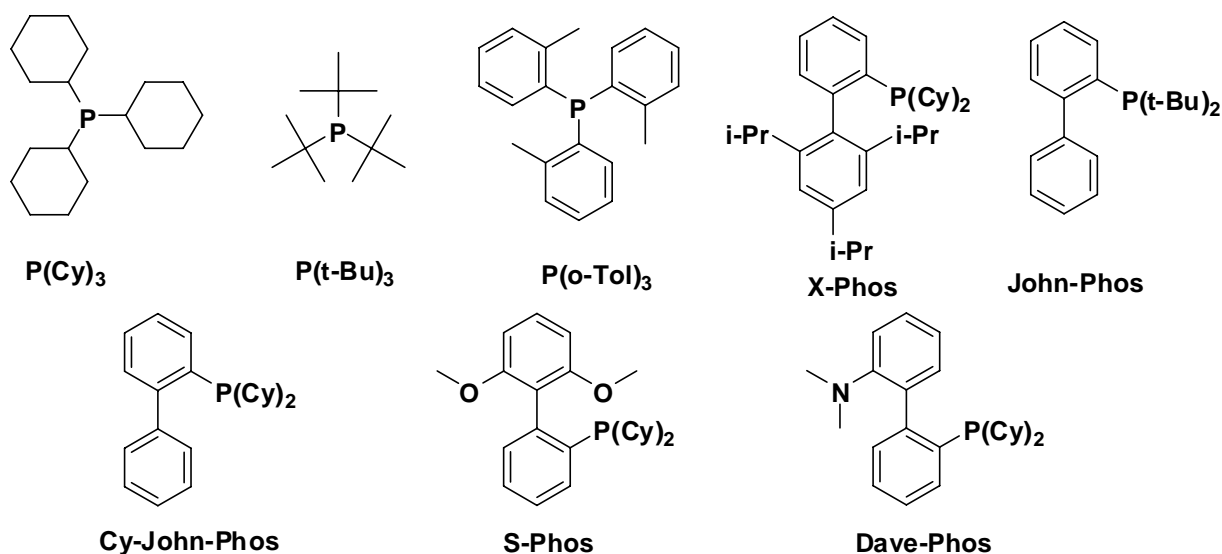


Entry	X	Pd Source	Ligand	Solvent	Yield% ^b
1	Cl	Pd(OAc) ₂	P(Cy) ₃	NMP	trace
2	Cl	Pd(OAc) ₂	P(Cy) ₃	DMA	trace
3	Cl	Pd(OAc) ₂	P(Cy) ₃	DMF	11
4	Cl	Pd(OAc) ₂	P(Cy) ₃	Mesitylene	n.r.
5	Cl	Pd(OAc) ₂	P(Cy) ₃	diglyme	88
6	Cl	Pd(OAc) ₂	P(<i>t</i> -Bu) ₃	diglyme	79
7	Cl	Pd(OAc) ₂	S-Phos	diglyme	85
8	Cl	Pd(OAc) ₂	Dave-Phos	diglyme	28
9	Cl	Pd(OAc) ₂	X-Phos	diglyme	88
10	Cl	Pd(OAc) ₂	Cy-JohnPhos	diglyme	56
11	Cl	Pd(OAc) ₂	JohnPhos	diglyme	15
12	Cl	Pd ₂ (dba) ₃	P(Cy) ₃	diglyme	84

13	Cl	Pd(TFA) ₂	P(Cy) ₃	diglyme	85
14	Cl	Pd(MeCN) ₂ Cl ₂	P(Cy) ₃	diglyme	73
15 ^c	Cl	Pd(OAc) ₂	P(Cy) ₃	diglyme	86
16	Br	Pd(OAc) ₂	P(Cy) ₃	diglyme	87
17	Br	Pd(OAc) ₂	P(o-Tol) ₃	diglyme	91

^a All the reactions were carried out at 0.25 mmol scale in 0.5 mL solvents. ^b GC yields using biphenyl as the internal standard. ^c 1 mol% Pd(OAc)₂ and 2 mol% ligand were used.

Some structures of the ligands mentioned in SI Table 1



c. General procedures for the coupling of potassium pentafluorobenzoate with aryl chlorides, bromides and triflates

General Procedure A:

A 10ml oven-dried Schlenk tube was charged with Pd(OAc)₂ (1%-2% mol, See Part 3), ligand (2%-4% mol PCy₃ or P(o-Tol)₃, See Part 3), appointed amount of potassium pentafluorobenzoate (0.30-0.375mmol, See Part 3) and the corresponding aryl electrophile (0.25 mmol) (if solid). The tube was evacuated and filled with argon (this procedure was repeated three times). Then aryl electrophile (0.25 mmol) (if liquid) and diglyme (0.5 ml) were added with a syringe under a counter flow of argon. The tube was sealed with a screw cap, stirred at room temperature for 10 min, and connected to the Schlenk line which was full of argon, stirred in a preheated oil bath (130 °C) for the appointed time (24h). Upon completion of the reaction, the mixture was cooled to room temperature, diluted with diethyl ether (20ml) and filtered through a short silica gel column to

remove the deposition. The organic layers were washed with water (20ml×3), and then with brine, dried over Na₂SO₄, and filtered, the solvents were removed via rotary vapor. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded the corresponding fluoroarene.

d. General procedures for the coupling of various potassium polyfluorobenzoates with 4-chloroanisole or 4-bromoanisole

General procedure B:

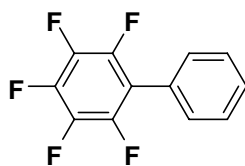
A 10ml oven-dried Schlenk tube was charged with Pd(OAc)₂ (4% mol), ligand (8% mol PCy₃ or P(o-Tol)₃, See Part 3), appointed amount of potassium polyfluorobenzoate (0.30-0.375mmol, See Part 3) and the corresponding aryl electrophile (0.25 mmol) (if solid). The tube was evacuated and filled with argon (this procedure was repeated three times). Then aryl electrophile (0.25 mmol) (if liquid) and diglyme (0.5 ml) were added with a syringe under a counter flow of argon. The tube was sealed with a screw cap, stirred at room temperature for 10 min, and connected to the Schlenk line which was full of argon, stirred in a preheated oil bath (140-160 °C) for the appointed time (24h). Upon completion of the reaction, the mixture was cooled to room temperature, diluted with diethyl ether (20ml) and filtered through a short silica gel column to remove the deposition. The organic layers were washed with water (20ml×3), and then with brine, dried over Na₂SO₄, and filtered, the solvents were removed via rotary vapor. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded the corresponding fluoroarene.

e. Genreal procedures for the selective decarboxylative cross couplings in Scheme 2

A 10ml oven-dried Schlenk tube was charged with Pd(OAc)₂ (0.02 mmol, 4.5 mg), P(o-Tol)₃ (0.04 mmol, 12.2 mg), potassium 2, 6-difluoro-4-methoxybenzoate (0.60 mmol, 136 mg) and 4-chlorobromobenzene (0.5 mmol, 96 mg). The tube was evacuated and filled with argon (this procedure was repeated three times). Then diglyme (1.0 ml) was added via a syringe under a counter flow of argon. The tube was sealed with a screw cap, stirred at room temperature for 10 min, and connected to the Schlenk line which was full of argon, stirred in a preheated oil bath (160 °C) for the appointed time (24h). Upon completion of the reaction, the mixture was cooled to room

temperature, diluted with diethyl ether (20ml) and filtered through a short silica gel column to remove the deposition. The organic layers were washed with water (20ml×3), and then with brine, dried over Na₂SO₄, and filtered, the solvents were removed via rotary vapor. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded 4'-chloro-2, 6-difluoro-4-methoxybiphenyl as a white solid (84 mg, 66%).

Pd(OAc)₂ (0.01 mmol, 2.2 mg), P(Cy)₃ (0.02 mmol, 5.6 mg), potassium 2, 3, 5, 6-tetrafluoro-4-methylbenzoate (0.30 mmol, 74 mg) and 4'-chloro-2, 6-difluoro-4-methoxybiphenyl (0.25 mmol, 64 mg) were placed in an oven-dried 10 ml Schlenk-tube, the reaction vessel was evacuated and filled with argon for three times. Then diglyme (0.5 ml) was added via a syringe under a counter flow of argon, the vessel was sealed with a screw cap, stirred at room temperature for 10 min, and connected to the Schlenk line which was full of argon, stirred at 140 °C for 24h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate or petroleum ether (20ml) and filtered through a short silica gel column to remove the deposition. The organic layers were washed with water (20ml×3), and then with brine, dried over Na₂SO₄, and filtered, the solvents were removed via rotary vapor. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded 4'-(2, 3, 5, 6-tetrafluoro-4-methylphenyl)-2, 6-difluoro-4-methoxybiphenyl as a white solid (81mg, 85%).

Part3. Characterization of the Products.....S11-S38**1. Compound name:** 2, 3, 4, 5, 6-pentafluorobiphenyl**Preparation procedure:**

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tricyclohexylphosphine (4% mol, 2.8 mg, 0.01 mmol), phenylchloride (28 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 56 mg (91%) of a white solid was obtained.

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), phenylbromide (39 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 54 mg (89%) of a white solid was obtained.

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tricyclohexylphosphine (4% mol, 2.8 mg, 0.01 mmol), phenyltriflate (56 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 46 mg (76%) of a white solid was obtained.

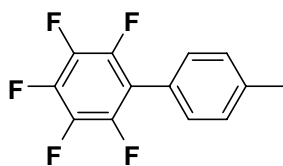
This compound is known.

Reference: Korenaga, T.; Kosaki, T.; Fukumura, R.; Ema, T.; Sakai, T. *Org. Lett.* **2005**, *7*, 4915 – 4918.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.39-7.42 (m, 2H), 7.44-7.48 (m, 3H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 115.9 (td, *J*_F = 3.8, 17.5 Hz), 126.4, 128.7, 129.3, 130.1, 137.8 (dm, *J*_F = 253.2Hz), 140.4 (dm, *J*_F = 253.2Hz), 144.2 (dm, *J*_F = 252.4Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.3 (m, 2F), -155.6 (t, *J*_F = 21.1 Hz, 1F), -143.2 (dd, *J*_F = 23.0, 8.3 Hz, 2F).

2. Compound name: 2, 3, 4, 5, 6-pentafluoro-4'-methylbiphenyl**Preparation procedure:**

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 4-chlorotoluene (32 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 59 mg (92%) of a white solid was obtained.

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tri(o-tolyl)phosphine (2% mol, 1.5 mg, 0.005 mmol), 4-bromotoluene (43 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 62 mg (96%) of a white solid was obtained.

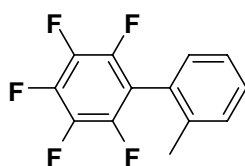
This compound is known.

Reference: Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754 – 8756.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 2.42 (s, 3H), 7.30 (s, 4H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 21.3, 116.0 (td, $J_F = 3.8, 17.3$ Hz), 123.4, 129.4, 130.0, 139.4, 137.8 (dm, $J_F = 249.0$ Hz), 140.2 (dm, $J_F = 251.5$ Hz), 144.4 (dm, $J_F = 249.4$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.5 (m, 2F), -156.2 (t, $J_F = 21.1$ Hz, 1F), -143.4 (dd, $J_F = 23.0, 8.3$ Hz, 2F).

3. Compound name: 2, 3, 4, 5, 6-pentafluoro-2'-methylbiphenyl

Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 2-chlorotoluene (32 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 54 mg (84%) of a white solid was obtained (room temperature ~10°C).

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tri(o-tolyl)phosphine (2% mol, 1.5 mg, 0.005 mmol), 2-bromotoluene (32 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 55 mg (86%) of a white solid was obtained

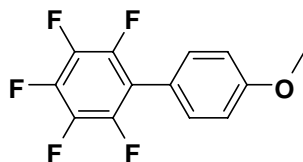
This compound is known.

Reference: Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, 8, 5097-5100.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 2.18 (s, 3H), 7.17-7.19 (m, 1H), 7.27-7.30 (m, 1H), 7.33-7.40 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 19.6, 115.5 (td, $J_F = 3.4, 17.2$ Hz), 125.9, 126.0, 129.6, 130.5, 130.6, 137.4, 137.7 (dm, $J_F = 250.8$ Hz), 140.6 (dm, $J_F = 252.0$ Hz), 144.1 (dm, $J_F = 244.8$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.3 (m, 2F), -155.4 (t, $J_F = 20.7$ Hz, 1F), -140.6 (dd, $J_F = 23.0, 8.3$ Hz, 2F).

4. Compound name: 2, 3, 4, 5, 6-pentafluoro-4'-methoxybiphenyl**Preparation procedure:**

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 4-chloroanisole (36 mg, 0.25 mmol),

potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 58 mg (85%) of a white solid was obtained

According to the general procedure A, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.02 mmol), 4-methoxyphenyl trifluoromethanesulfonate (64 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 54 mg (79%) of a white solid was obtained

This compound is known.

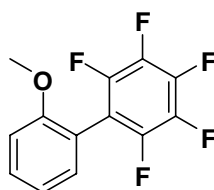
Reference: Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754 – 8756.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.85 (s, 3H), 6.99-7.02 (m, 2H), 7.34-7.36 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 114.2, 115.7 (td, $J_F = 3.4, 17.2$ Hz), 118.4, 131.4, 137.8 (dm, $J_F = 249.0$ Hz), 140.0 (dm, $J_F = 251.5$ Hz), 144.1 (dm, $J_F = 249.4$ Hz), 160.3.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.6 (m, 2F), -156.5 (t, $J_F = 21.5$ Hz, 1F), -143.6 (dd, $J_F = 23.4, 8.3$ Hz, 2F).

5. Compound name: 2, 3, 4, 5, 6-pentafluoro-2'-methoxybiphenyl



Preparation procedure:

According to the general procedure A, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.02 mmol), 2-chloroanisole (36 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 64 mg (94%) of a white solid was obtained

This compound is known.

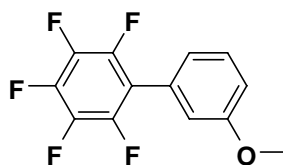
Reference: Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, 8, 5097-5100.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.81 (s, 3H), 7.01-7.07 (m, 2H), 7.21-7.23 (m, 1H), 7.43-7.47 (m, 1H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.6, 111.3, 112.8 (t, $J_F = 19.4$ Hz), 115.3, 120.6, 131.1, 131.7, 137.6 (dm, $J_F = 249.3$ Hz), 140.5(dm, $J_F = 251.1$ Hz), 144.5 (dm, $J_F = 248.3$ Hz), 157.1 .

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -163.2 (m, 2F), -156.2 (t, $J_F = 20.7$ Hz, 1F), -140.3 (dd, $J_F = 23.0, 8.3$ Hz, 2F).

6. Compound name: 2, 3, 4, 5, 6-pentafluoro-3'-methoxybiphenyl



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 3-chloroanisole (36 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 65 mg (96%) of a white solid was obtained

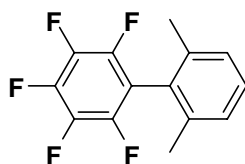
This compound is known.

Reference: Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, 128, 8754 – 8756.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.84 (s, 3H), 6.94 (s, 1H), 6.98-7.01 (m, 2H), 7.38-7.42 (t, $J = 8.0$ Hz, 1H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.2, 114.8 (td, $J_F = 3.4, 17.2$ Hz), 114.8, 115.8, 122.4, 127.5, 129.7, 137.8 (dm, $J_F = 250.8$ Hz), 140.4 (dm, $J_F = 252.0$ Hz), 144.2 (dm, $J_F = 246.4$ Hz), 159.7.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.2 (m, 2F), -155.6 (t, $J_F = 20.7$ Hz, 1F), -142.8 (dd, $J_F = 23.0, 8.3$ Hz, 2F).

7. Compound name: 2, 3, 4, 5, 6-pentafluoro-2',6'-dimethylbiphenyl**Preparation procedure:**

According to the general procedure A, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.02 mmol), 2-bromo-1,3-dimethylbenzene (46 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 55 mg (81%) of a white solid was obtained

This compound is known.

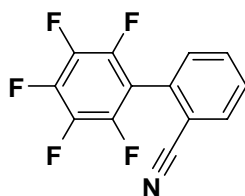
Reference: Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, 8, 5097-5100.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 2.08 (s, 6H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 20.1, 114.4 (td, *J_F* = 4.2, 21.1 Hz), 125.6, 127.7, 129.4, 137.4, 137.7 (dm, *J_F* = 252.0 Hz), 140.6 (dm, *J_F* = 252.1 Hz), 143.7 (dm, *J_F* = 244.2 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -161.9 (m, 2F), -155.2 (t, *J_F* = 20.7 Hz, 1F), -140.1 (dd, *J_F* = 23.4, 8.7 Hz, 2F).

HRMS calcd for C₁₄H₁₀F₄O (M⁺) 272.0624; found: 272.0626.

8. Compound name: 2',3',4',5',6'-pentafluorobiphenyl-2-carbonitrile**Preparation procedure:**

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol),

tricyclohexylphosphine (4% mol, 2.8 mg, 0.01 mmol), 2-chlorobenzonitrile (35 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 56 mg (83%) of a pale yellow solid was obtained.

This compound is known.

Reference: Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, 8, 5097-5100.

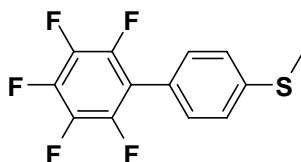
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.74 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.85 (dd, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 112.4 (td, *J*_F = 4.0, 18.0 Hz), 114.1, 116.8, 130.0, 130.1, 131.6, 133.0, 133.4, 137.8 (dm, *J*_F = 252.4 Hz), 141.7 (dm, *J*_F = 252.1 Hz), 144.2 (dm, *J*_F = 251.6 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -160.7 (m, 2F), -151.9 (t, *J*_F = 21.1 Hz, 1F), -140.1 (dd, *J*_F = 23.8, 8.3 Hz, 2F).

HRMS calcd for C₁₄H₁₀F₄O (M⁺) 269.0264; found: 269.0259.

9. Compound name: methyl(2',3',4',5',6'-pentafluorobiphenyl-4-yl)sulfane



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tri(o-tolyl)phosphine (2% mol, 1.5 mg, 0.005 mmol), (4-bromophenyl)(methyl)sulfane (51 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 68 mg (93%) of a white solid was obtained.

This compound is **new**.

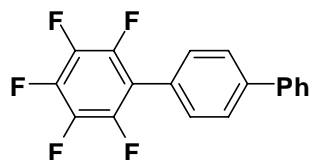
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 2.53 (s, 3H), 7.34 (s, 4H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 15.2, 115.4 (td, *J*_F = 3.8, 17.1 Hz), 122.6, 126.1, 130.4, 137.8 (dm, *J*_F = 251.4 Hz), 140.2 (dm, *J*_F = 252.5 Hz), 140.7, 144.1 (dm, *J*_F = 241.9 Hz).

^{19}F -NMR (377MHz, CDCl_3 , 293K, TFT): -162.2 (m, 2F), -155.7 (t, $J_{\text{F}} = 21.1$ Hz, 1F), -143.3 (dd, $J_{\text{F}} = 23.0, 7.9$ Hz, 2F).

HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{F}_4\text{O}$ (M^+) 290.0189; found: 290.0184.

10. Compound name: 4-perfluorophenylbiphenyl



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 4-chlorobiphenyl (47 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 72 mg (89%) of a white solid was obtained.

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tri(o-tolyl)phosphine (2% mol, 1.5 mg, 0.005 mmol), 4-bromobiphenyl (58 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 67 mg (84%) of a white solid was obtained.

This compound is known.

Reference: Birchall, J.M. et al.; JCPRB4; Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999); English; **1974**; 1715 – 1719.

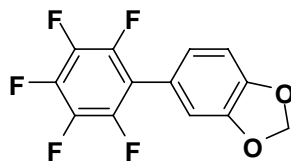
^1H -NMR (400 MHz, CDCl_3 , 293K, TMS): δ 7.38-7.42 (m, 1H), 7.46-7.52 (m, 4H), 7.64-7.66 (m, 2H), 7.71-7.74(m, 2H).

^{13}C -NMR (100MHz, CDCl_3 , 293K, TMS): δ 115.6 (td, $J_{\text{F}} = 4.2, 17.2$ Hz), 125.2, 127.2, 127.4, 127.8, 128.9, 130.5, 137.9 (dm, $J_{\text{F}} = 246.0$ Hz), 140.2, 140.4 (dm, $J_{\text{F}} = 252.0$ Hz), 142.2, 144.2 (dm, $J_{\text{F}} = 245.9$ Hz).

^{19}F -NMR (377MHz, CDCl_3 , 293K, TFT): -162.2 (m, 2F), -155.5 (t, $J_{\text{F}} = 20.7$ Hz, 1F), -143.1 (dd,

$J_F = 23.0, 8.3 \text{ Hz}, 2F$).

11. Compound name: 5-(perfluorophenyl)benzo[d][1,3]dioxole



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tri(o-tolyl)phosphine (2% mol, 1.5 mg, 0.005 mmol), 5-bromobenzo[d][1,3]dioxole (50 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 63 mg (87%) of a white solid was obtained.

This compound is known.

Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

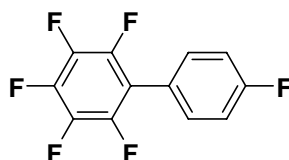
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 6.04 (s, 2H), 6.88-6.95 (m, 3H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 101.5, 108.6, 110.3, 115.7 (td, $J_F = 3.8, 17.2 \text{ Hz}$), 119.4, 124.2, 137.8 (dm, $J_F = 250.8 \text{ Hz}$), 140.2 (dm, $J_F = 252.0 \text{ Hz}$), 144.2 (dm, $J_F = 245.6 \text{ Hz}$), 148.0, 148.5.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.3 (m, 2F), -156.0 (t, $J_F = 20.7 \text{ Hz}$, 1F), -143.2 (dd, $J_F = 23.4, 8.3 \text{ Hz}, 2F$).

HRMS calcd for C₁₃H₅F₅O₂ (M⁺) 288.0210; found: 288.0212.

12. Compound name: 2, 3, 4, 4', 5, 6-hexafluorobiphenyl



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 1-chloro-4-fluorobenzene (33 mg, 0.25

mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 56 mg (86%) of a white solid was obtained.

This compound is known.

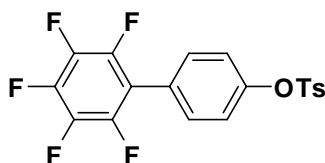
Reference: Do, H. Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128 – 1129.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.17-7.22 (m, 2H), 7.39-7.43 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 115.0 (td, *J*_F = 4.0, 17.0 Hz), 116.0 (d, *J*_F = 21.8 Hz), 122.3, 132.0 (d, *J*_F = 8.3 Hz), 137.9 (dm, *J*_F = 251.5 Hz), 140.5 (dm, *J*_F = 252.5 Hz), 144.2 (dm, *J*_F = 242.0 Hz), 163.2 (d, *J*_F = 248.3 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.0 (m, 2F), -155.2 (t, *J*_F = 21.1 Hz, 1F), -143.2 (dd, *J*_F = 22.6, 8.3 Hz, 2F), -111.3 (s, 1F) .

13. Compound name: 2', 3', 4', 5', 6'-pentafluorobiphenyl-4-yl 4-methylbenzenesulfonate



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tri(o-tolyl)phosphine (2% mol, 1.5 mg, 0.005 mmol), 4-bromophenyl 4-methylbenzenesulfonate (82 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 91 mg (88%) of a white needle-like crystal was obtained.

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 4-chlorophenyl 4-methylbenzenesulfonate (71 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 88 mg (85%) of a white needle-like crystal was obtained.

This compound is **new**.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 2.46 (s, 3H), 7.11-7.15 (dm, *J* = 8.8 Hz, 2H), 7.35 (t, *J*

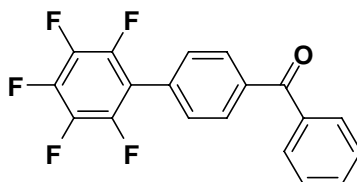
= 8.4 Hz, 4H), 7.76 (d, J = 8.4 Hz, 2H).

$^{13}\text{C-NMR}$ (100MHz, CDCl_3 , 293K, TMS): δ 21.7, 114.6 (td, J_{F} = 3.8, 16.8 Hz), 122.8, 125.2, 128.5, 129.9, 131.6, 132.3, 138.0 (dm, J_{F} = 253.2 Hz), 140.5 (dm, J_{F} = 253.2 Hz), 144.0 (dm, J_{F} = 246.9 Hz), 145.6, 150.1.

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -161.7 (m, 2F), -154.5 (t, J_{F} = 21.1 Hz, 1F), -143.0 (dd, J_{F} = 22.2, 8.3 Hz, 2F).

HRMS calcd for $\text{C}_{13}\text{H}_5\text{F}_5\text{O}_2$ (M^+) 414.0349; found: 414.0344.

14. Compound name: (2', 3', 4', 5', 6'-pentafluorobiphenyl-4-yl)(phenyl)methanone



Preparation procedure:

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tri(o-tolyl)phosphine (4% mol, 3.0 mg, 0.01 mmol), (4-bromophenyl)(phenyl)methanone (65.3 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 81 mg (93%) of a white solid was obtained.

This compound is **new**.

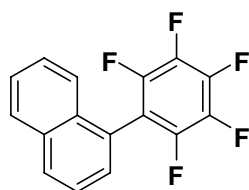
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 293K, TMS): δ 7.50-7.57 (m, 4H), 7.63 (t, J = 7.6 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H).

$^{13}\text{C-NMR}$ (100MHz, CDCl_3 , 293K, TMS): δ 114.9 (td, J_{F} = 3.9, 16.4 Hz), 128.4, 130.0, 130.16, 130.22, 130.4, 132.7, 137.1, 137.9 (dm, J_{F} = 251.6 Hz), 138.2, 140.8 (dm, J_{F} = 253.4 Hz), 144.1 (dm, J_{F} = 251.5Hz), 195.8.

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -161.5 (m, 2F), -154.1 (t, J_{F} = 20.7 Hz, 1F), -142.7 (dd, J_{F} = 23.0, 8.3 Hz, 2F).

HRMS calcd for $\text{C}_{13}\text{H}_5\text{F}_5\text{O}_2$ (M^+) 348.0574; found: 348.0575.

15. Compound name: 1-(perfluorophenyl) naphthalene



Preparation procedure:

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tricyclohexylphosphine (4% mol, 2.8 mg, 0.01 mmol), 1-bromonaphthalene (52 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 71 mg (97%) of a white solid was obtained.

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tricyclohexylphosphine (4% mol, 2.8 mg, 0.01 mmol), naphthalen-1-yl trifluoromethanesulfonate (69 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 65 mg (89%) of a white solid was obtained.

This compound is known.

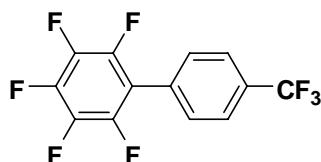
Reference: Do, H. Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128 - 1129;

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.45-7.63 (m, 5H), 7.94-8.04 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 144.4 (td, $J_F = 3.1, 19.5$ Hz), 123.8, 124.5, 125.2, 126.4, 127.1, 128.6, 129.0, 130.1, 131.5, 133.7, 137.8 (dm, $J_F = 251.7$ Hz), 140.9 (dm, $J_F = 252.5$ Hz), 144.6 (dm, $J_F = 246.1$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -161.9 (m, 2F), -154.7 (t, $J_F = 20.7$ Hz, 1F), -139.4 (dd, $J_F = 22.6, 7.9$ Hz, 2F).

16. Compound name: 2, 3, 4, 5, 6-pentafluoro-4'-(trifluoromethyl)biphenyl



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol),

tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 1-chloro-4-(trifluoromethyl)benzene (45 mg, 0.25 mmol), potassium pentafluorobenzoate (76 mg, 0.300 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether) 65 mg (83%) of a white solid was obtained.

This compound is known.

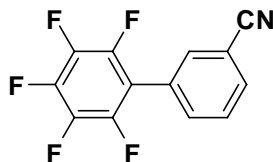
Reference: Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754 – 8756.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.55-7.57 (m, 2H), 7.76-7.78 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 114.6 (td, $J_F = 3.9, 16.5$ Hz), 123.8 (q, $J_F = 270.7$ Hz), 125.7 (q, $J_F = 3.6$ Hz), 130.2, 130.7, 131.6 (q, $J_F = 32.6$ Hz), 138.0 (dm, $J_F = 251.6$ Hz), 141.0 (dm, $J_F = 253.8$ Hz), 144.2 (dm, $J_F = 247.5$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -161.5 (m, 2F), -153.8 (t, $J_F = 20.7$ Hz, 1F), -142.9 (dd, $J_F = 21.9, 8.3$ Hz, 2F), -63.0 (s, 3F).

17. Compound name: 2', 3', 4', 5', 6'-pentafluorobiphenyl-3-carbonitrile



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 3-chlorobenzonitrile (35 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 66 mg (99%) of a pale yellow solid was obtained.

Reference: Adonin, N. Y.; Babushkin, D. E.; Parmon, V. N.; Bardin, V. V.; Kostin, G. A.; Mashukov, V. I.; Frohn, H. *Tetrahedron.* **2008**, *64*, 5920 - 5924;

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.61-7.70 (m, 2H), 7.74-7.78 (m, 2H).

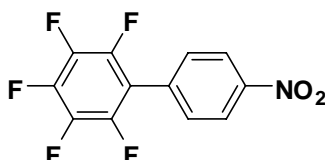
¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 113.4, 113.6 (td, $J_F = 3.8, 16.4$ Hz), 117.9, 127.8, 129.7, 132.8, 133.6, 134.4, 138.0 (dm, $J_F = 252.2$ Hz), 141.1 (dm, $J_F = 254.5$ Hz), 144.1 (dm, $J_F =$

252.0Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -160.9 (m, 2F), -152.8 (t, $J_F = 20.4$ Hz, 1F), -143.0 (dd, $J_F = 21.9, 8.7$ Hz, 2F).

HRMS calcd for C₁₃H₅F₅O₂ (M⁺) 269.0264; found: 269.0262.

18. Compound name: 2, 3, 4, 5, 6-pentafluoro-4'-nitrobiphenyl



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 1-chloro-4-nitrobenzene (39 mg, 0.25 mmol), potassium pentafluorobenzoate (76 mg, 0.300 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 70 mg (97%) of a pale yellow solid was obtained.

This compound is known.

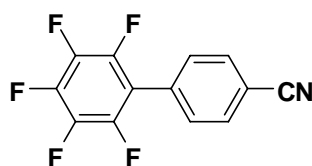
Reference: Korenaga, T.; Kosaki, T.; Fukumura, R.; Ema, T.; Sakai, T. *Org. Lett.* **2005**, *7*, 4915 – 4918.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.64-7.66 (m, 2H), 8.35-8.38 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 113.8 (td, $J_F = 3.4, 17.2$ Hz), 123.8, 131.3, 132.9, 138.0 (dm, $J_F = 252.4$ Hz), 141.3(dm, $J_F = 254.8$ Hz), 144.0(dm, $J_F = 259.0$ Hz), 148.2.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -160.8 (m, 2F), -152.5 (t, $J_F = 20.7$ Hz, 1F), -142.5 (dd, $J_F = 22.6, 8.7$ Hz, 2F).

19. Compound name: 2', 3', 4', 5', 6'-pentafluorobiphenyl-4-carbonitrile



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), 4-chlorobenzonitrile (35 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 66 mg (98%) of a pale yellow solid was obtained.

This compound is known.

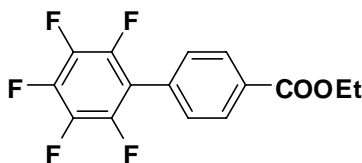
Reference: Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, *8*, 5097-5100.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.55-7.57 (m, 2H), 7.79-7.81 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 113.3, 114.1 (td, $J_F = 3.1, 17.7$ Hz), 118.0, 130.9, 131.1, 132.4, 137.9 (dm, $J_F = 251.8$ Hz), 141.1 (dm, $J_F = 254.9$ Hz), 144.0 (dm, $J_F = 247.4$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -160.9 (m, 2F), -152.8 (t, $J_F = 21.5$ Hz, 1F), -142.7 (dd, $J_F = 22.6, 7.2$ Hz, 2F).

20. Compound name: ethyl 2', 3', 4', 5', 6'-pentafluorobiphenyl-4-carboxylate



Preparation procedure:

According to the general procedure A, palladium (II) acetate (1% mol, 0.55 mg, 0.0025 mmol), tricyclohexylphosphine (2% mol, 1.4 mg, 0.005 mmol), ethyl 4-chlorobenzoate (46 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 75 mg (95%) of a white solid was obtained.

This compound is known.

Reference: Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754 – 8756.

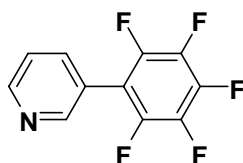
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 1.42 (t, $J = 7.2$ Hz, 3H), 4.42 (q, $J = 7.2$ Hz, 2H), 7.50-7.52 (m, 2H), 8.16-8.18 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 14.2, 61.2, 115.0 (td, $J_F = 4.2, 17.6$ Hz), 129.8, 130.2,

130.8, 131.3, 137.9 (dm, $J_F = 251.4$ Hz), 140.8 (dm, $J_F = 253.3$ Hz), 144.1 (dm, $J_F = 247.4$ Hz), 165.8.

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -161.6 (m, 2F), -154.2 (t, $J_F = 20.7$ Hz, 1F), -142.7 (dd, $J_F = 22.2, 8.3$ Hz, 2F).

21. Compound name: 3-(perfluorophenyl)pyridine



Preparation procedure:

According to the general procedure A, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 3-bromopyridine (40 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 50 mg (81%) of a yellow solid was obtained.

This compound is known.

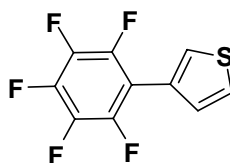
Reference: Do, H. Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128 – 1129.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 293K, TMS): δ 7.44-7.47 (m, 1H), 7.77-7.79 (m, 1H), 8.70 (s, 2H).

$^{13}\text{C-NMR}$ (100MHz, CDCl_3 , 293K, TMS): δ 112.5 (td, $J_F = 3.8, 17.1$ Hz), 122.9, 123.5, 137.4, 137.9 (dm, $J_F = 251.8$ Hz), 140.9 (dm, $J_F = 254.1$ Hz), 144.2 (dm, $J_F = 251.5$ Hz), 150.2, 150.3..

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -161.2 (m, 2F), -153.4 (t, $J_F = 21.1$ Hz, 1F), -142.9 (dd, $J_F = 23.0, 7.9$ Hz, 2F).

22. Compound name: 3-(perfluorophenyl)thiophene



Preparation procedure:

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tricyclohexylphosphine (4% mol, 2.8 mg, 0.010 mmol), 3-chlorothiophene (30 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 33 mg (52%) of a colorless liquid was obtained.

This compound is known.

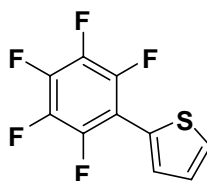
Reference: Do, H. Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128 – 1129.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.35-7.36 (m, 1H), 7.44-7.46 (m, 1H), 7.65 (s, 1H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 111.2 (td, $J_F = 4.2, 16.0$ Hz), 125.6, 125.7, 127.1 (t, $J = 4$ Hz), 128.1 (t, $J = 3.6$ Hz), 138.0 (dm, $J_F = 250.8$ Hz), 140.0 (dm, $J_F = 252.4$ Hz), 144.2 (dm, $J_F = 247.0$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -162.5 (m, 2F), -156.4 (t, $J_F = 20.7$ Hz, 1F), -142.0 (dd, $J_F = 22.2, 7.9$ Hz, 2F).

23. Compound name: 2-(perfluorophenyl)thiophene



Preparation procedure:

According to the general procedure A, palladium (II) acetate (2% mol, 1.1 mg, 0.005 mmol), tricyclohexylphosphine (4% mol, 2.8 mg, 0.010 mmol), 2-chlorothiophene (30 mg, 0.25 mmol), potassium pentafluorobenzoate (94 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 130 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 47 mg (75%) of a yellow solid was obtained.

This compound is known.

Reference: Do, H. Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128 – 1129.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 7.18-7.20 (m, 1H), 7.52-7.54 (m, 1H), 7.55-7.56 (m, 1H).

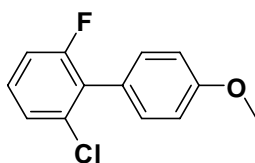
¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 110.0 (td, $J_F = 4.4, 15.5$ Hz), 126.3, 127.3, 128.2 (t, $J = 3.5$ Hz), 130.1 (t, $J = 5.0$ Hz), 138.0 (dm, $J_F = 250.9$ Hz), 139.9 (dm, $J_F = 253.1$ Hz), 144.0 (dm,

$J_F = 248.6$ Hz).

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -162.2 (m, 2F), -156.0 (t, $J_F = 21.1$ Hz, 1F), -140.0 (dd, $J_F = 7.9, 22.6$ Hz, 2F).

HRMS calcd for $\text{C}_{10}\text{H}_3\text{F}_5\text{S}$ (M^+) 249.9876; found: 249.9877.

24. Compound name: 2-chloro-6-fluoro-4'-methoxybiphenyl



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tri(o-tolyl)phosphine (8% mol, 6.0 mg, 0.020 mmol), 1-bromo-4-methoxybenzene (47 mg, 0.25 mmol), potassium 2-chloro-6-fluorobenzoate (64 mg, 0.300 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 40 mg (68%) of a colorless liquid was obtained.

This compound is known.

Reference: Becht, J.-M.; Catala, C.; Le Drian, C.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781.

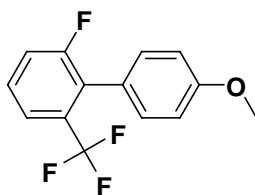
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 293K, TMS): δ 3.86 (s, 3H), 7.00 (d, $J = 8.8$ Hz, 2H), 7.04-7.08 (m, 1H), 7.20-7.25 (m, 1H), 7.27-7.31 (m, 3H)..

$^{13}\text{C-NMR}$ (100MHz, CDCl_3 , 293K, TMS): δ 55.2, 113.6, 114.2 (d, $J_F = 23.5$ Hz), 124.7, 125.4 (d, $J_F = 3.5$ Hz), 128.7 (d, $J_F = 9.5$ Hz), 128.72 (d, $J_F = 18.6$ Hz), 131.4, 134.6 (d, $J_F = 4.0$ Hz), 159.4, 160.5 (d, $J_F = 246.0$ Hz).

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -111.3 (s, 1F).

HRMS calcd for $\text{C}_{10}\text{H}_3\text{F}_5\text{S}$ (M^+) 236.0404; found: 236.0408.

25. Compound name: 2-fluoro-4'-methoxy-6-(trifluoromethyl) biphenyl



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tri(o-tolyl)phosphine (8% mol, 6.0 mg, 0.020 mmol), 1-bromo-4-methoxybenzene (47 mg, 0.25 mmol), potassium 2-fluoro-6-(trifluoromethyl)benzoate (92 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 50 mg (74%) of a colorless liquid was obtained.

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2-fluoro-6-(trifluoromethyl)benzoate (92 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 55 mg (81%) of a colorless liquid was obtained.

This compound is known.

Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

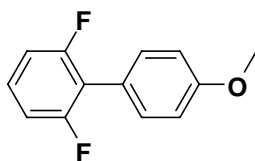
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.86 (s, 3H), 6.95-6.98 (dm, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 8.8 Hz, 1H), 7.40-7.46 (m, 1H), 7.55 (d, *J* = 7.6 Hz, 1H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.2, 113.4, 119.0 (d, *J*_F = 23.5 Hz), 121.6 (m), 123.4 (qd, *J*_F = 3.6, 272.7 Hz), 123.8, 128.8 (d, *J*_F = 8.7 Hz), 129.0 (d, *J*_F = 16.0 Hz), 130.9, 131.1 (qd, *J*_F = 2.7, 29.4 Hz), 159.6, 160.5 (d, *J*_F = 243.8 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -111.7 (s, 1F), -57.3 (s, 3F).

HRMS calcd for C₁₄H₁₀F₄O (M⁺) 270.0668; found: 270.0672.

26. Compound name: 2, 6-difluoro-4'-methoxybiphenyl



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tri(o-tolyl)phosphine (8% mol, 6.0 mg, 0.020 mmol), 1-bromo-4-methoxybenzene (47 mg, 0.25 mmol), potassium 2,6-difluorobenzoate (74 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 45 mg (82%) of a white solid was obtained.

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2,6-difluorobenzoate (74 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 47 mg (85%) of a white solid was obtained.

This compound is known.

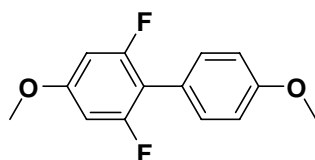
Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.82 (s, 3H), 6.89-6.98 (m, 4H), 7.17-7.24 (m, 1H), 7.36-7.39 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.2, 111.5 (dd, *J*_F = 7.3, 19.2 Hz), 113.8, 118.2 (t, *J*_F = 18.5 Hz), 121.2, 128.3 (t, *J*_F = 10.3 Hz), 131.5, 159.5, 160.2 (dd, *J*_F = 7.1, 246.3 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -114.8 (s, 2F).

HRMS calcd for C₁₃H₁₀F₂O (M⁺) 220.0700; found: 220.0706.

27. Compound name: 2,6-difluoro-4,4'-dimethoxybiphenyl**Preparation procedure:**

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tri(o-tolyl)phosphine (8% mol, 6.0 mg, 0.020 mmol), 1-bromo-4-methoxybenzene (47 mg, 0.25 mmol), potassium 2,6-difluoro-4-methoxybenzoate (85 mg, 0.375 mmol), and diglyme (0.5 mL)

were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 58 mg (92%) of a white solid was obtained.

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2,6-difluoro-4-methoxybenzoate (85 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 60 mg (96%) of a white solid was obtained.

This compound is **new**.

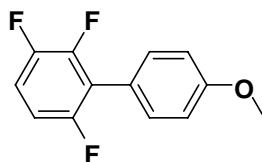
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.82 (s, 3H), 3.84 (s, 3H), 6.53 (dm, *J*_F = 9.6 Hz, 2H), 6.97 (d, *J*_F = 9.2 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.2, 55.7, 98.1 (dd, *J*_F = 9.1, 21.0 Hz), 110.6 (t, *J*_F = 19.3 Hz), 113.7, 121.4, 131.4, 159.1, 159.6 (t, *J*_F = 14.1 Hz), 160.6 (dd, *J*_F = 10.4, 254.7 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -113.8 (s, 2F).

HRMS calcd for C₁₃H₉F₃O (M⁺) 250.0805; found: 250.0811.

28. Compound name: 2, 3, 6-trifluoro-4'-methoxybiphenyl



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2,3,6-trifluorobenzoate (80 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 30 mg (51%) of a white solid was obtained.

This compound is known.

Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.86 (s, 3H), 6.87-6.93 (m, 1H), 6.99-7.02(m, 2H),

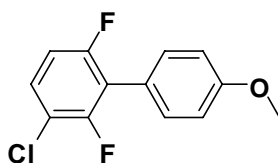
7.04-7.12 (m, 1H), 7.39-7.42 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 110.7 (dm, $J_F = 25.5$ Hz), 113.9, 115.1 (qd, $J_F = 1.1, 9.4$ Hz), 120.0 (dd, $J_F = 14.9, 20.4$ Hz), 120.4 (d, $J_F = 2.0$ Hz), 131.4, 147.45 (dd, $J_F = 3.6, 242.9$ Hz), 147.9 (dq, $J_F = 7.4, 247.9$ Hz), 155.3 (dm, $J_F = 242.7$ Hz), 159.8.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -142.2 (dd, $J_F = 15.1, 21.9$ Hz, 1F), -138.2 (dd, $J_F = 3.8, 21.5$ Hz, 1F), -120.0 (dd, $J_F = 4.1, 15.1$ Hz, 1F).

HRMS calcd for C₁₃H₉F₃O (M⁺) 238.0605; found: 238.0600.

29. Compound name: 3-chloro-2,6-difluoro-4'-methoxybiphenyl



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tri(o-tolyl)phosphine (8% mol, 6.0 mg, 0.020 mmol), 1-bromo-4-methoxybenzene (47 mg, 0.25 mmol), potassium 3-chloro-2,6-difluorobenzoate (69 mg, 0.300 mmol), and diglyme (0.5 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 47 mg (73%) of a colorless liquid was obtained.

This compound is **new**.

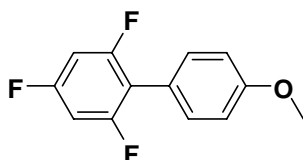
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.86 (s, 3H), 6.93 (td, $J = 8.8, 1.6$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.28-7.34 (m, 1H), 7.38 (d, $J = 8.8$ Hz, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 112.0 (dd, $J_F = 4.2, 24.7$ Hz), 113.9, 117.0 (dd, $J_F = 4.2, 19.1$ Hz), 119.7 (t, $J_F = 19.1$ Hz), 120.5, 128.6 (d, $J_F = 7.8$ Hz), 131.4, 155.5 (dd, $J_F = 7.3, 248.0$ Hz), 158.5 (dd, $J_F = 5.7, 246.4$ Hz), 159.8.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -115.5 (m, 1F), -114.3 (m, 1F).

HRMS calcd for C₁₃H₉F₃O (M⁺) 254.0310; found: 254.0304.

30. Compound name: 2, 4, 6-trifluoro-4'-methoxybiphenyl

**Preparation procedure:**

According to the general procedure B, palladium (II) acetate (4% mol, 4.4 mg, 0.02 mmol), tricyclohexylphosphine (8% mol, 11.2 mg, 0.040 mmol), 1-chloro-4-methoxybenzene (72 mg, 0.50 mmol), potassium 2,4,6-trifluorobenzoate (160 mg, 0.75 mmol), and diglyme (1.0 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 16 mg (14%) of a white solid was obtained.

This compound is known.

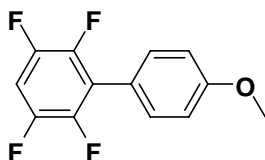
Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.85 (s, 3H), 6.74 (t, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 100.1-100.6 (m), 113.9, 114.7 (td, *J*_F = 4.8, 19.2 Hz), 120.4, 131.4, 159.6, 160.3 (ddd, *J*_F = 10.0, 14.8, 247.5 Hz), 161.4 (dt, *J*_F = 15.7, 247.0 Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -111.6 (d, *J*_F = 5.6, 2F), -109.9 (t, *J*_F = 5.6 Hz, 1F).

HRMS calcd for C₁₃H₉F₃O (M⁺) 238.0605; found: 238.06009.

31. Compound name: 2, 3, 5, 6-tetrafluoro-4'-methoxybiphenyl**Preparation procedure:**

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2,3,5,6-tetrafluorobenzoate (87 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 140 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 20

mg (31%) of a white solid was obtained.

This compound is known.

Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

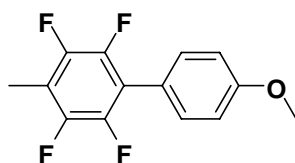
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.87 (s, 3H), 6.98-7.06 (m, 3H), 7.39-7.42 (m, 2H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 104.2 (t, *J*_F = 22.7 Hz), 114.1, 119.5, 121.2 (t, *J*_F = 16.2 Hz), 131.4, 143.8 (ddt, *J*_F = 4.4, 13.7, 250.8 Hz), 146.2 (dm, *J*_F = 245.7 Hz), 160.2.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -144.3 (dd, *J*_F = 13.6, 23.0 Hz, 2F), -139.5 (dd, *J*_F = 13.2, 23.0 Hz, 2F).

HRMS calcd for C₁₃H₈F₄O (M⁺) 256.0511; found: 256.0510.

32. Compound name: 2, 3, 5, 6-tetrafluoro-4'-methoxy-4-methylbiphenyl



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tri(o-tolyl)phosphine (8% mol, 6.0 mg, 0.020 mmol), 1-bromo-4-methoxybenzene (47 mg, 0.25 mmol), potassium 2,3,5,6-tetrafluoro-4-methylbenzoate (92 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 140 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 65 mg (96%) of a white solid was obtained.

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2,3,5,6-tetrafluoro-4-methylbenzoate (92 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 140 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 60 mg (89%) of a white solid was obtained.

This compound is known.

Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 2.31 (t, *J*_F = 2.0 Hz, 3H), 3.86 (s, 3H), 7.00 (d, *J* = 8.8

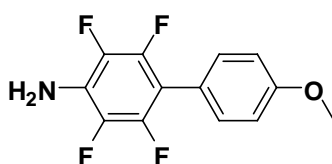
Hz, 2H), 7.39 (d, $J = 8.8$ Hz, 2H).

$^{13}\text{C-NMR}$ (100MHz, CDCl_3 , 293K, TMS): δ 7.44, 55.2, 114.0, 114.4 (t, $J_{\text{F}} = 19.1$ Hz), 117.6 (t, $J_{\text{F}} = 16.5$ Hz), 119.8, 131.4, 143.7 (dm, $J_{\text{F}} = 243.3$ Hz), 145.3 (dm, $J_{\text{F}} = 242.3$ Hz), 160.0.

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -146.0 (dd, $J_{\text{F}} = 12.4, 22.2$ Hz, 2F), -144.4 (dd, $J_{\text{F}} = 12.8, 22.6$ Hz, 2F).

HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{F}_4\text{O}$ (M^+) 270.0668; found: 270.0666.

33. Compound name: 2, 3, 5, 6-tetrafluoro-4'-methoxybiphenyl-4-amine



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 4-amino-2,3,5,6-tetrafluorobenzoate (93 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 140 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 58 mg (85%) of a yellow solid was obtained.

This compound is **new**.

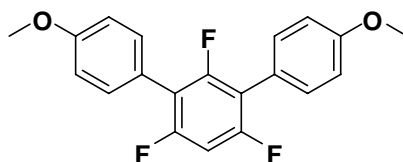
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 293K, TMS): δ 3.85 (s, 3H), 3.99 (s, br, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H),

$^{13}\text{C-NMR}$ (100MHz, CDCl_3 , 293K, TMS): δ 55.3, 108.1 (t, $J_{\text{F}} = 17.1$ Hz), 114.0, 120.1, 124.7-125.0 (m), 131.5, 136.9 (dm, $J_{\text{F}} = 236.6$ Hz), 144.1 (dm, $J_{\text{F}} = 240.5$ Hz), 159.5.

$^{19}\text{F-NMR}$ (377MHz, CDCl_3 , 293K, TFT): -162.4 (m, 2F), -146.9 (m, 2F).

HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{F}_4\text{O}$ (M^+) 271.0620; found: 271.0627.

34. Compound name: 1, 3-di-(*p*-methoxyphenyl)-2, 4, 6-trifluorobenzene

**Preparation procedure:**

According to the general procedure B, palladium (II) acetate (4% mol, 4.4 mg, 0.02 mmol), tricyclohexylphosphine (8% mol, 11.2 mg, 0.040 mmol), 1-chloro-4-methoxybenzene (72 mg, 0.50 mmol), potassium 2,4,6-trifluorobenzoate (160 mg, 0.75 mmol), and diglyme (1.0 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 18 mg (21%) of a white solid was obtained.

This compound is known.

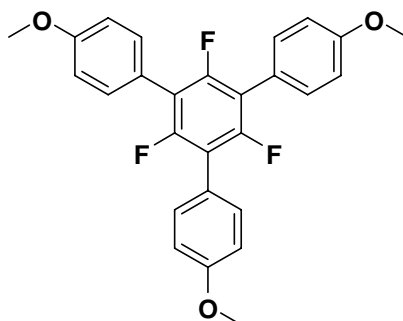
Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.85 (s, 6H), 6.84 (td, $J_F = 2.4, 9.6$ Hz, 1H), 7.00 (d, $J = 8.8$ Hz, 4H), 7.38 (d, $J = 8.4$ Hz, 4H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 100.2 (td, $J_F = 4.4, 15.5$ Hz), 113.9, 114.8 (m), 120.8, 131.5, 158.5 (dm, $J_F = 246.4$ Hz), 158.7 (dm, $J_F = 246.4$ Hz), 159.5.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -115.4 (t, $J_F = 6.8$ Hz, 1F), -113.8 (d, $J_F = 6.4$ Hz, 2F).

HRMS calcd for C₂₀H₁₅F₃O₂ (M⁺) 344.1024; found: 344.1023.

35. Compound name: 1, 3, 5-tri-(*p*-methoxyphenyl)-2, 4, 6-trifluorobenzene**Preparation procedure:**

According to the general procedure B, palladium (II) acetate (4% mol, 4.4 mg, 0.02 mmol), tricyclohexylphosphine (8% mol, 11.2 mg, 0.040 mmol), 1-chloro-4-methoxybenzene (72 mg, 0.50

mmol), potassium 2,4,6-trifluorobenzoate (160 mg, 0.75 mmol), and diglyme (1.0 mL) were reacted under 160 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 37 mg (49%) of a white solid was obtained.

This compound is **new**.

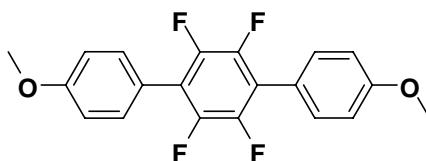
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.85 (s, 9H), 7.00 (d, *J* = 8.8 Hz, 6H), 7.42 (d, *J* = 8.4 Hz, 6H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 113.8, 114.5-114.9 (m), 121.0, 131.6, 155.8 (dt, *J*_F = 245.5 Hz), 159.5.

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -117.5 (s, 3F).

HRMS calcd for C₂₀H₁₅F₃O₂ (M⁺) 450.1443; found: 450.1436.

36. Compound name: 1, 4-di-(*p*-methoxyphenyl)-2,3,5,6-tetrafluorobenzene



Preparation procedure:

According to the general procedure B, palladium (II) acetate (4% mol, 2.2 mg, 0.01 mmol), tricyclohexylphosphine (8% mol, 5.6 mg, 0.020 mmol), 1-chloro-4-methoxybenzene (36 mg, 0.25 mmol), potassium 2,3,5,6-tetrafluorobenzoate (87 mg, 0.375 mmol), and diglyme (0.5 mL) were reacted under 140 °C for 24h. After column chromatography (petroleum ether/EtOAc gradient) 26 mg (58%) of a white solid was obtained.

This compound is known.

Reference: Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514-9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.

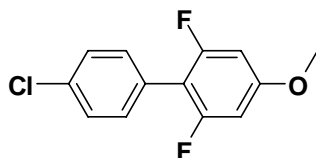
¹H-NMR (400 MHz, CDCl₃, 293K, TMS): δ 3.88 (s, 6H), 7.03 (d, *J* = 8.8 Hz, 4H), 7.46 (d, *J* = 8.8 Hz, 4H).

¹³C-NMR (100MHz, CDCl₃, 293K, TMS): δ 55.3, 114.2, 119.8, 131.4, 160.2. (Since this compound does not have good solubility in any of the deuterated solvents we tested, insufficient concentration was available to locate the F-splitting carbons in the ¹³C NMR.)

^{19}F -NMR (377MHz, CDCl_3 , 293K, TFT): -145.0 (s, 4F).

HRMS calcd for $\text{C}_{20}\text{H}_{14}\text{F}_4\text{O}_2$ (M^+) 362.0930; found: 362.0927.

37. Compound name: 4'-chloro-2,6-difluoro-4-methoxybiphenyl



Preparation procedure:

According to the general procedures for the selective decarboxylative cross couplings in Scheme 2 (SI Part 3, e)

This compound is **new**.

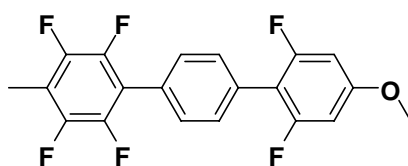
^1H -NMR (400 MHz, CDCl_3 , 293K, TMS): δ 3.83 (s, 3H), 6.54 (d, $J_{\text{F}} = 9.6$ Hz, 2H), 7.35-7.42 (m, 4H).

^{13}C -NMR (100MHz, CDCl_3 , 293K, TMS): δ 55.8, 98.2 (dd, $J_{\text{F}} = 8.6, 21.1$ Hz), 109.8 (t, $J_{\text{F}} = 19.2$ Hz), 127.8, 128.4, 131.6, 133.8, 160.3 (t, $J_{\text{F}} = 14.0$ Hz), 160.6 (dd, $J_{\text{F}} = 10.2, 245.5$ Hz).

^{19}F -NMR (377MHz, CDCl_3 , 293K, TFT): -113.7 (s, 2F).

HRMS calcd for $\text{C}_{20}\text{H}_{14}\text{F}_4\text{O}_2$ (M^+) 254.0310; found: 254.0306.

38. Compound name: 4'-(2,3,5,6-tetrafluoro-4-methylphenyl)-2,6-difluoro-4-methoxybiphenyl



Preparation procedure:

According to the general procedures for the selective decarboxylative cross couplings in Scheme 2 (SI Part 3, e)

This compound is **new**.

^1H -NMR (400 MHz, CDCl_3 , 293K, TMS): δ 2.33 (t, $J_{\text{F}} = 2.0$ Hz, 3H), 3.84 (s, 3H), 6.58 (d, $J_{\text{F}} = 9.6$ Hz, 2H), 7.51-7.57 (m, 4H).

¹³C-NMR (100MHz, C₆D₆, 293K, TMS): δ 7.0, 55.2, 98.6 (dd, $J_F = 8.7, 20.8$ Hz), 110.8 (t, $J_F = 18.8$ Hz), 115.4 (t, $J_F = 19.1$ Hz), 118.1 (t, $J_F = 16.3$ Hz), 130.4, 130.6, 130.9, 144.2 (dm, $J_F = 244.6$ Hz), 145.8 (dm, $J_F = 242.2$ Hz), 160.9 (t, $J_F = 14.0$ Hz), 161.2 (dd, $J_F = 10.2, 245.7$ Hz).

¹⁹F-NMR (377MHz, CDCl₃, 293K, TFT): -145.4 (dd, $J_F = 12.4, 22.2$ Hz, 2F), -144.0 (dd, $J_F = 12.8, 22.6$ Hz, 2F), 113.4 (s, 2F).

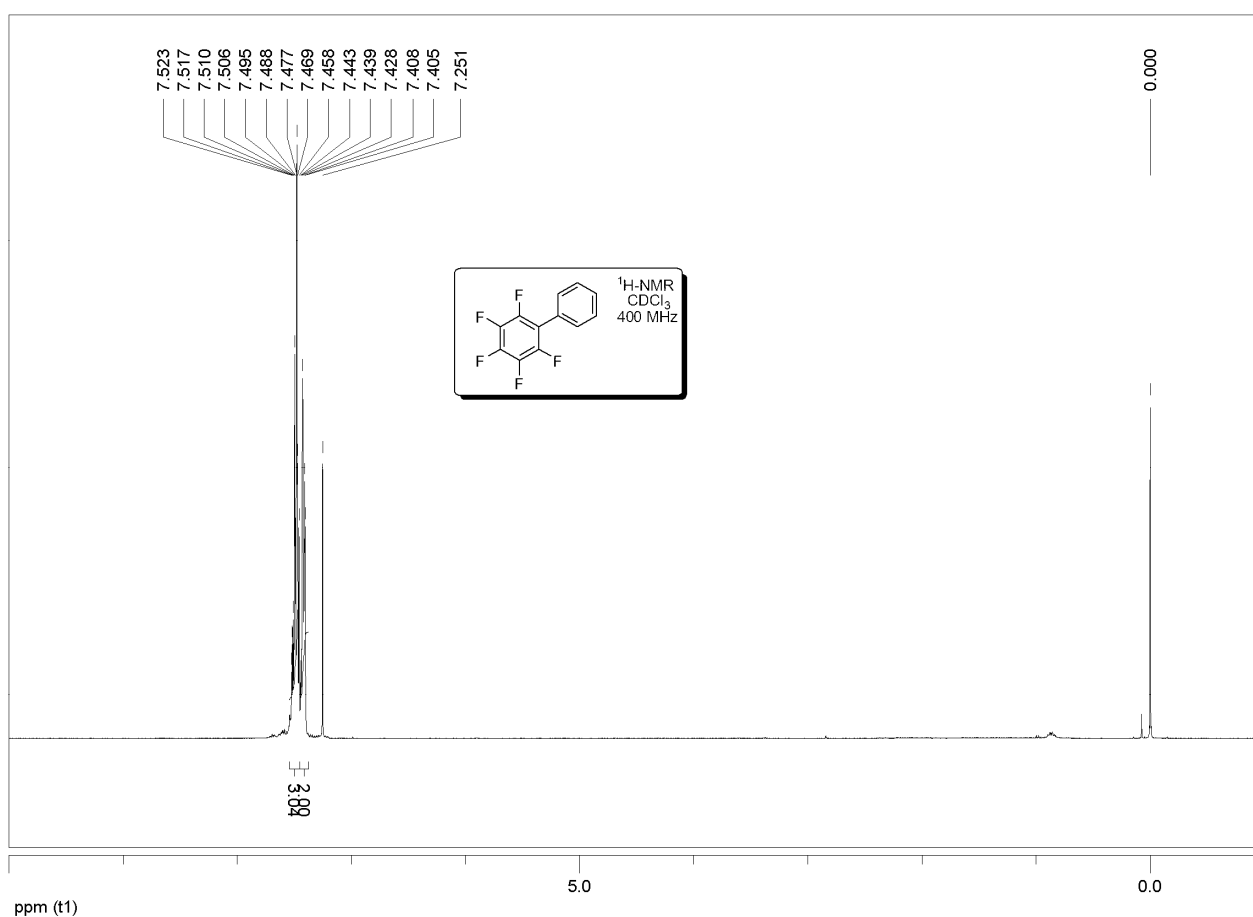
HRMS calcd for C₂₀H₁₄F₄O₂ (M⁺) 382.0792; found: 382.0793.

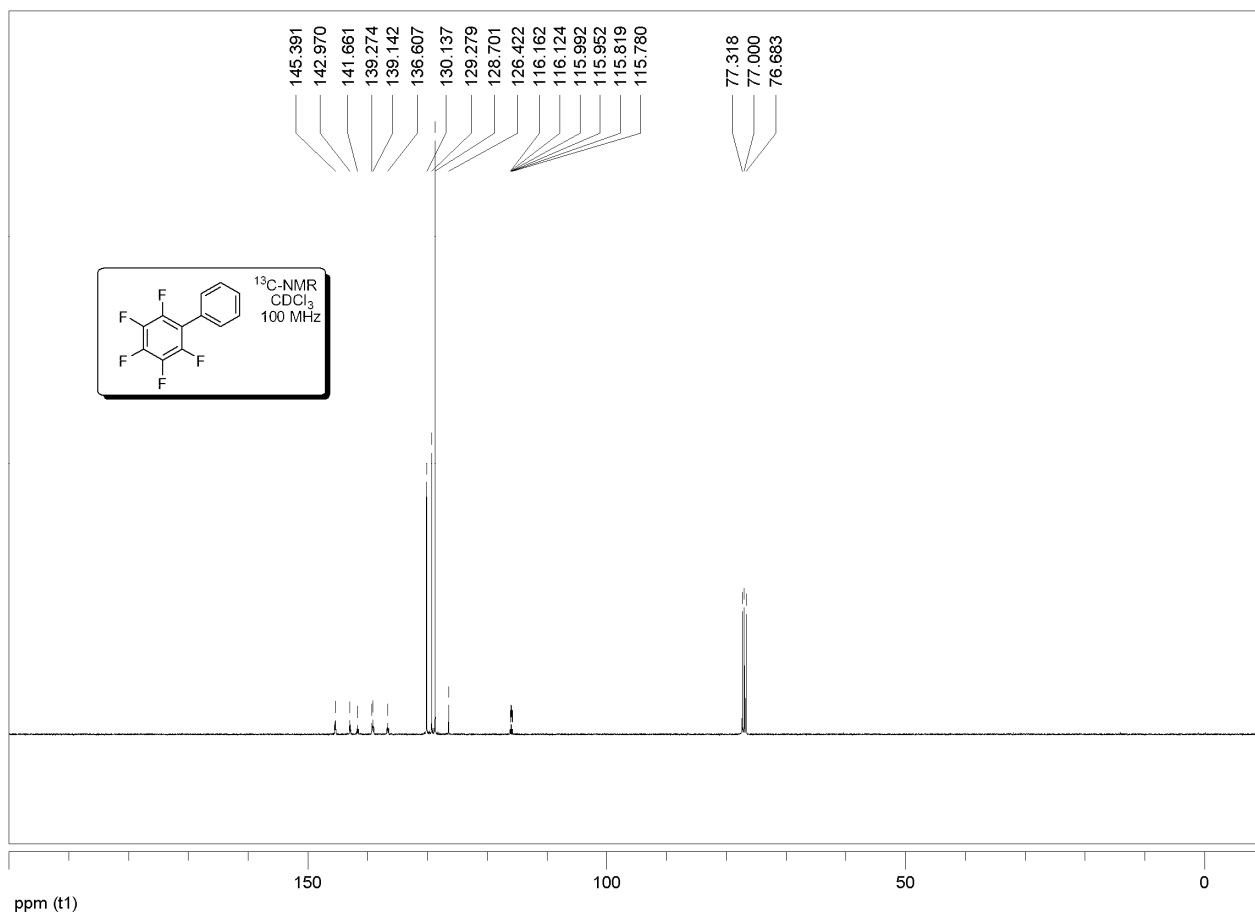
Part4. References.....S39

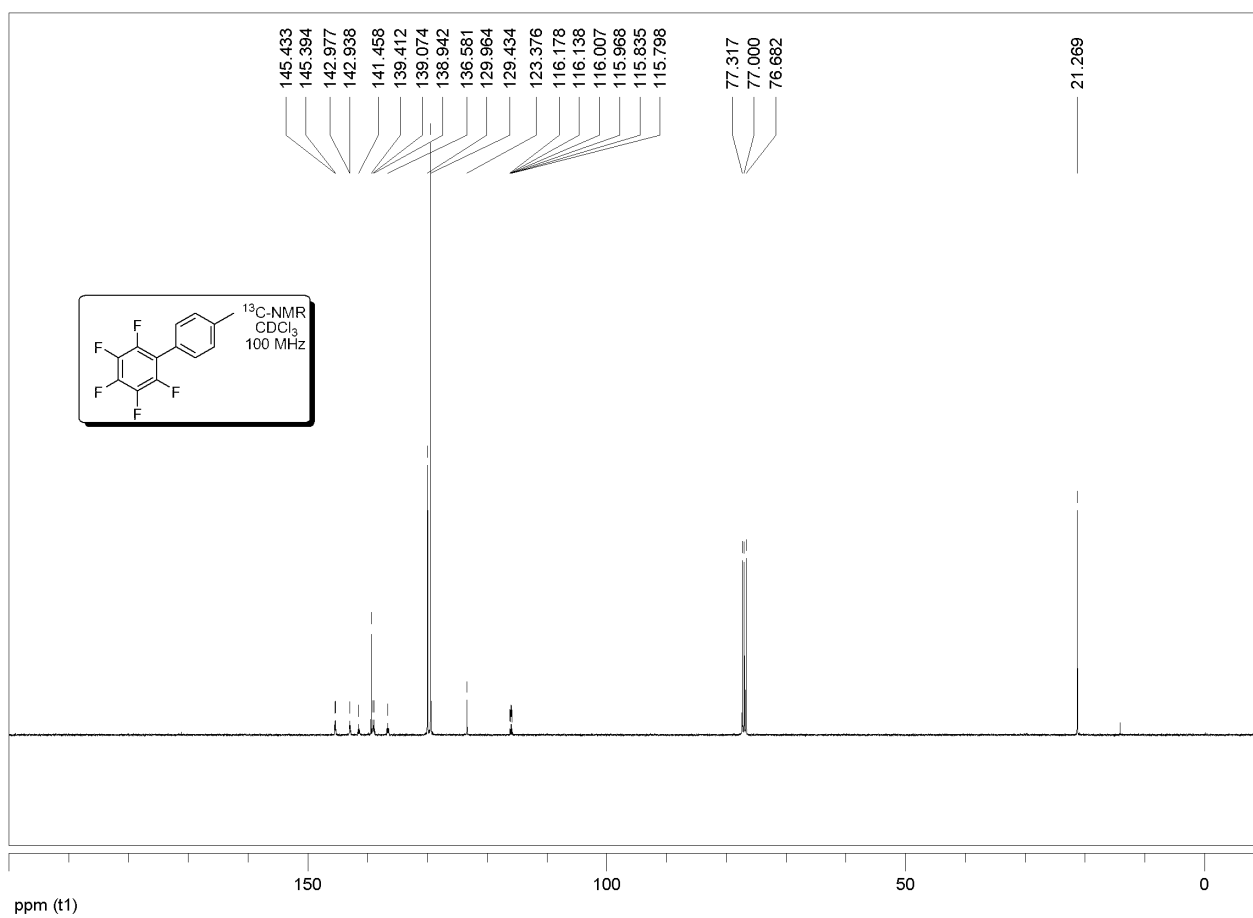
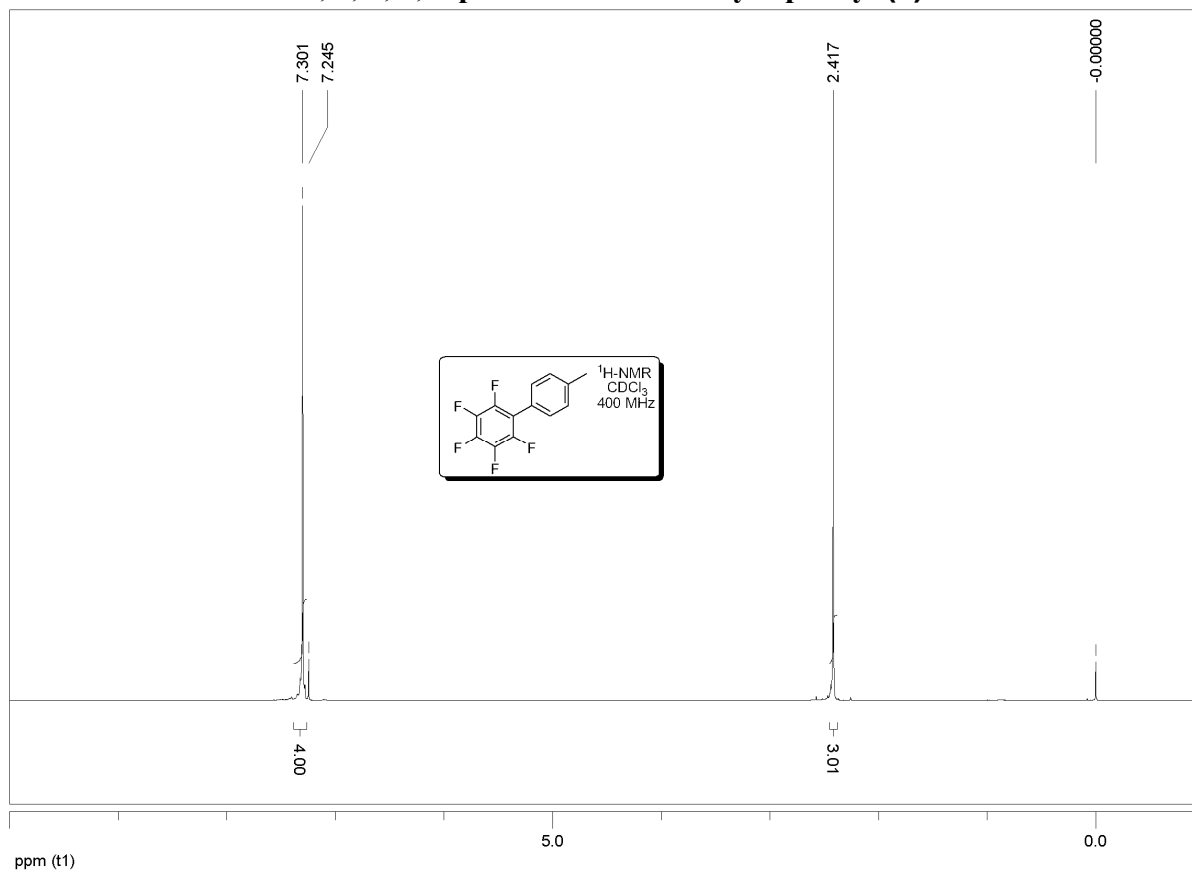
<1> Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 1137.

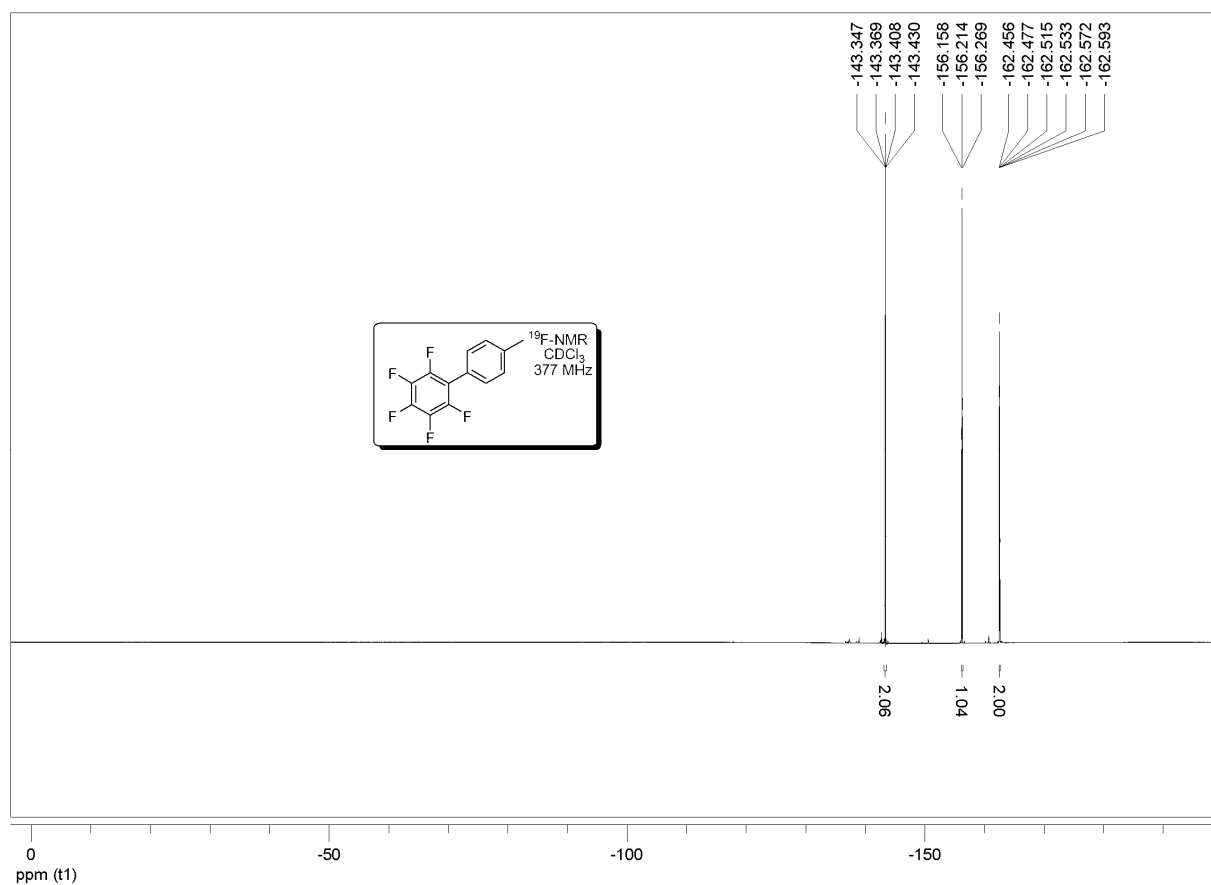
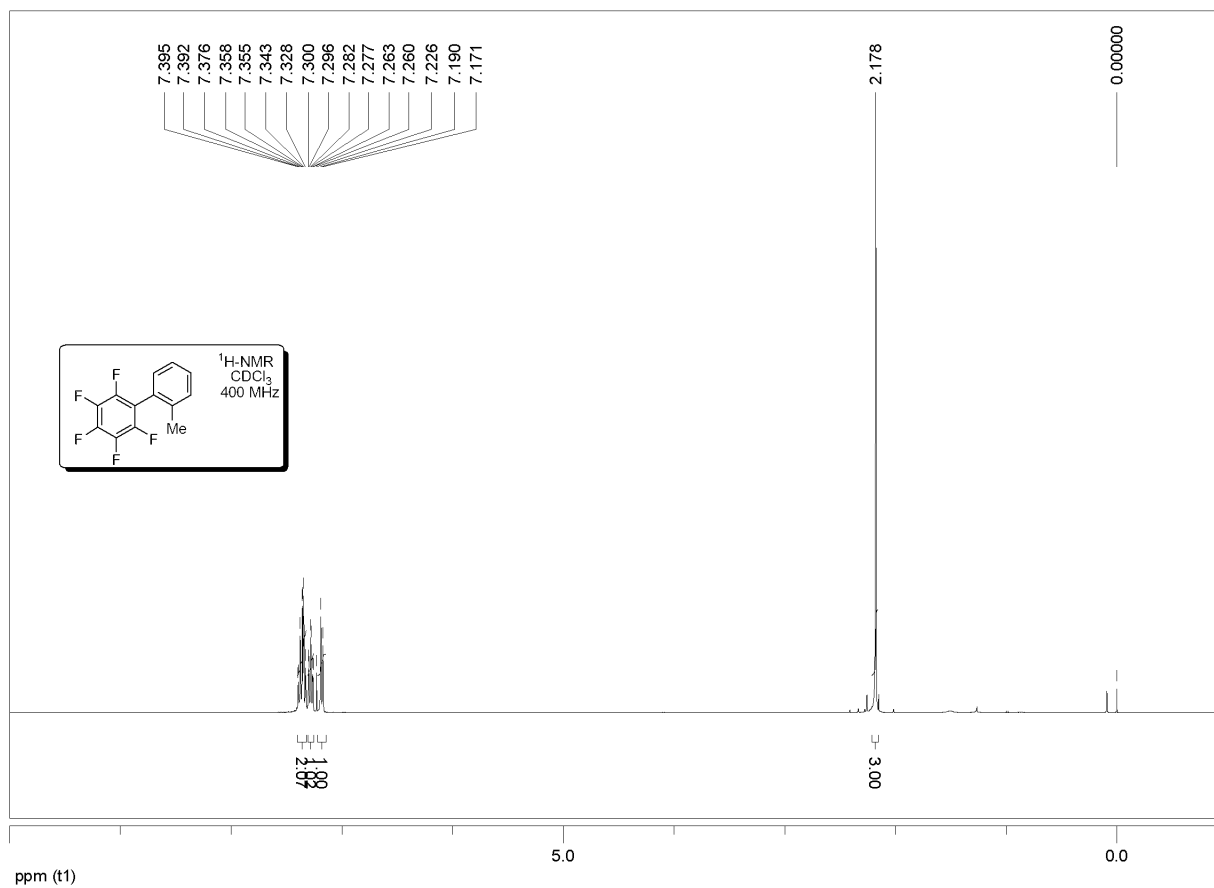
<2> Munday, R.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.*, **2008**, *130*, 2754.

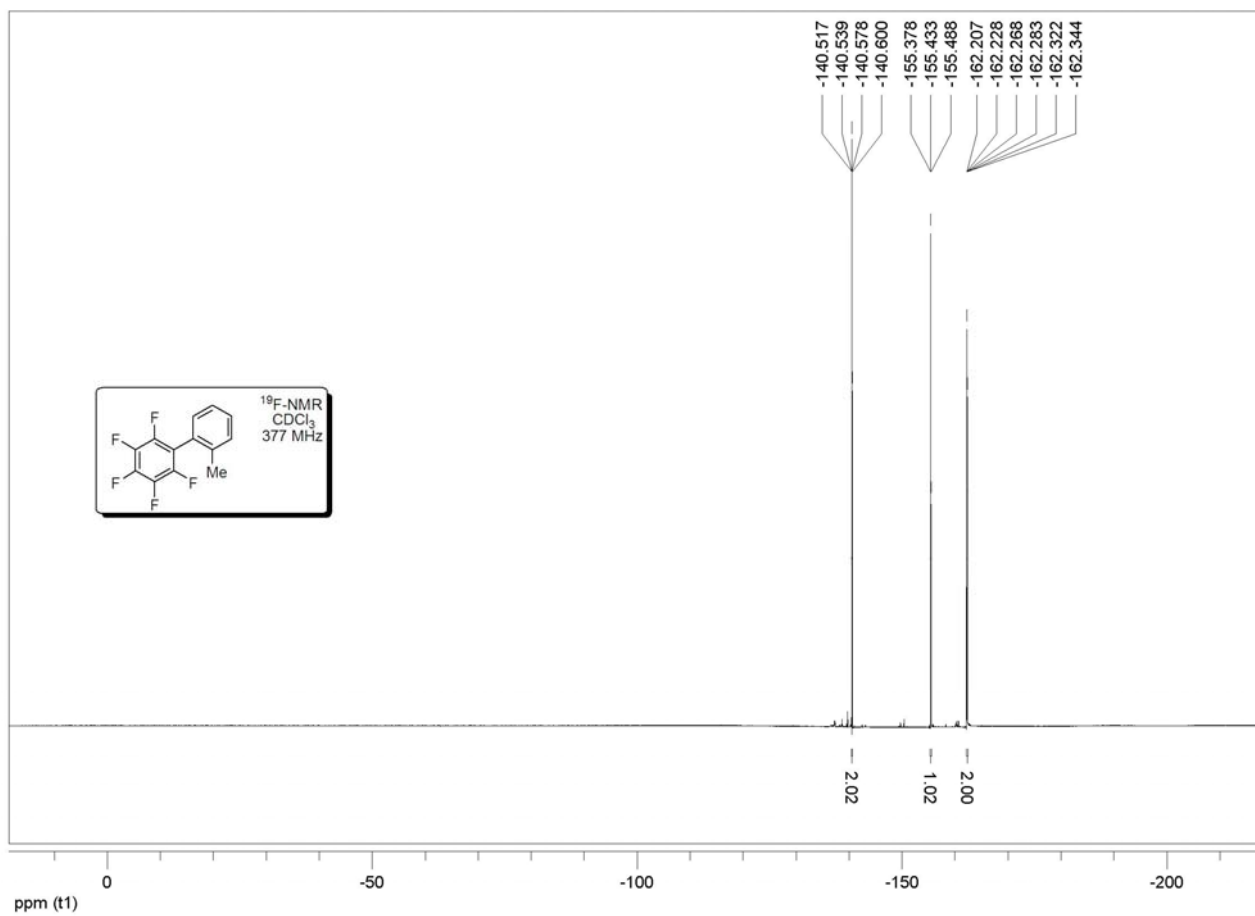
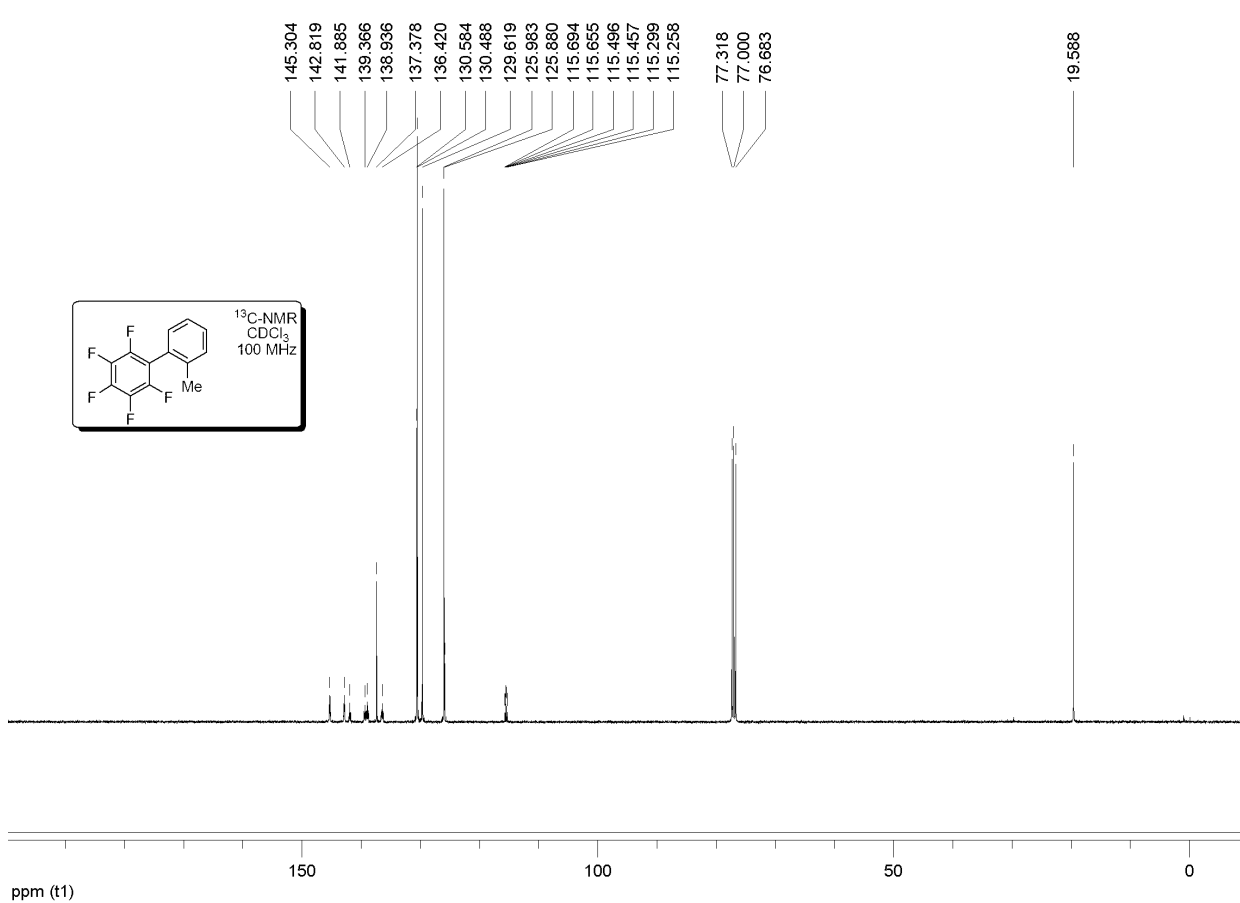
<3> Goossen, L. J.; Rodriguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248.

Part6. Copies of ¹H-NMR, ¹³C-NMR and ¹⁹F-NMR Spectra.....S39-S104**2, 3, 4, 5, 6-pentafluorobiphenyl (1)**

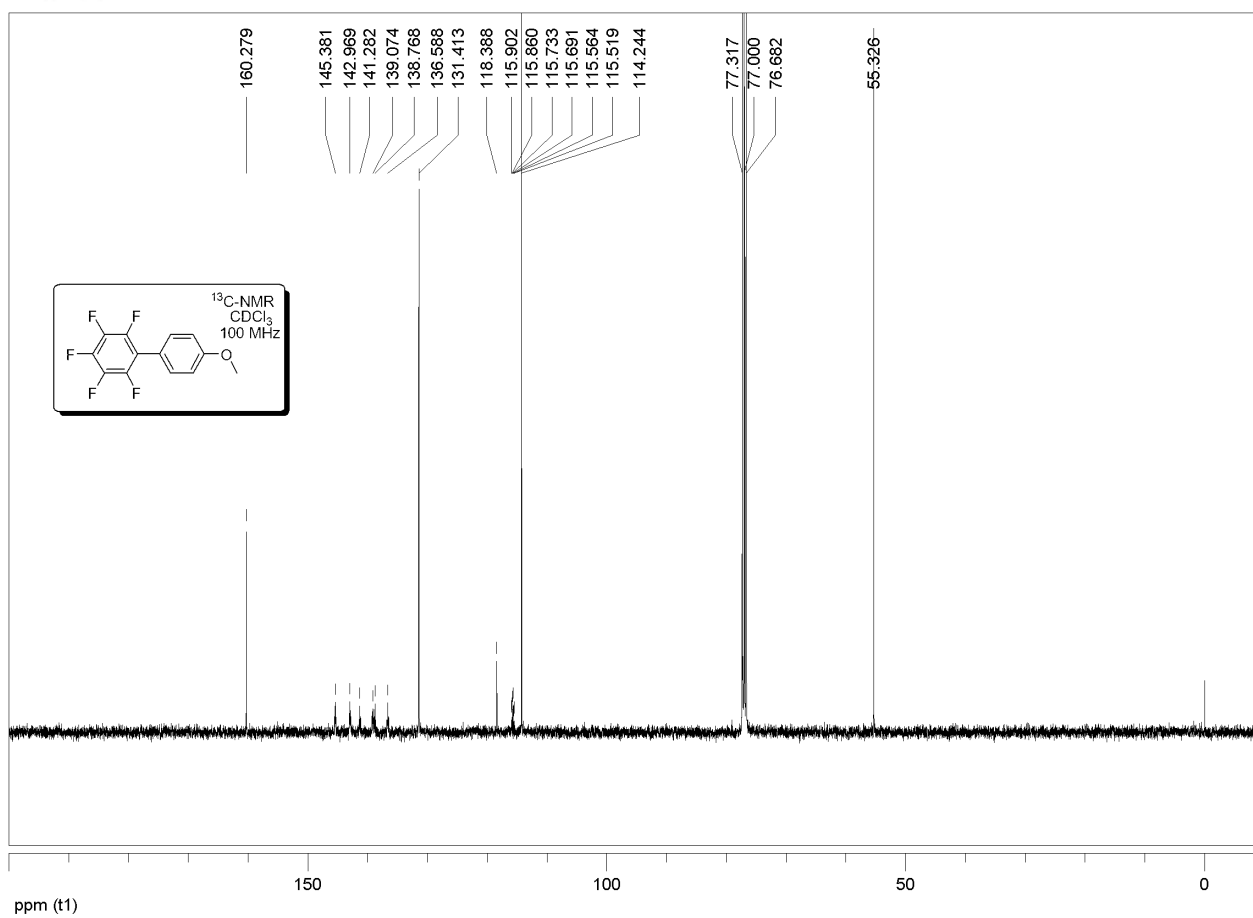
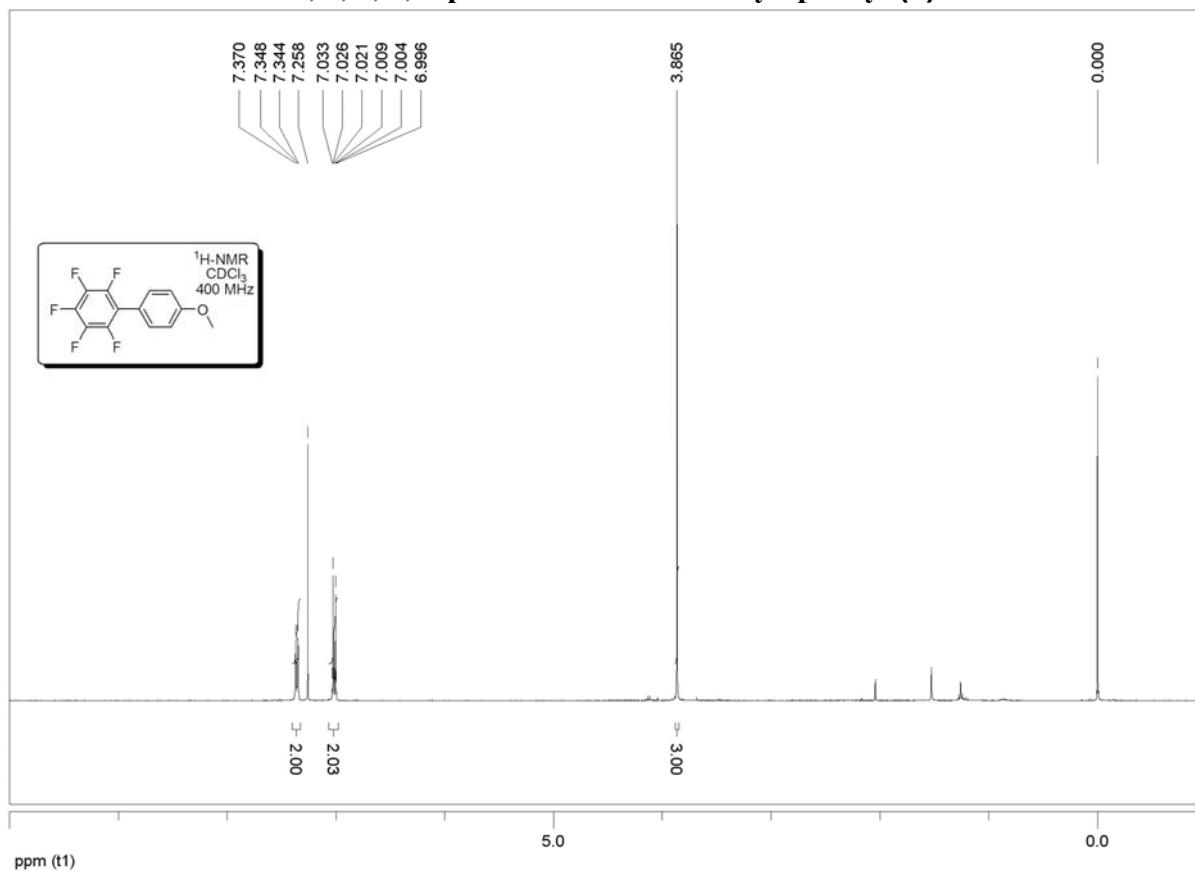


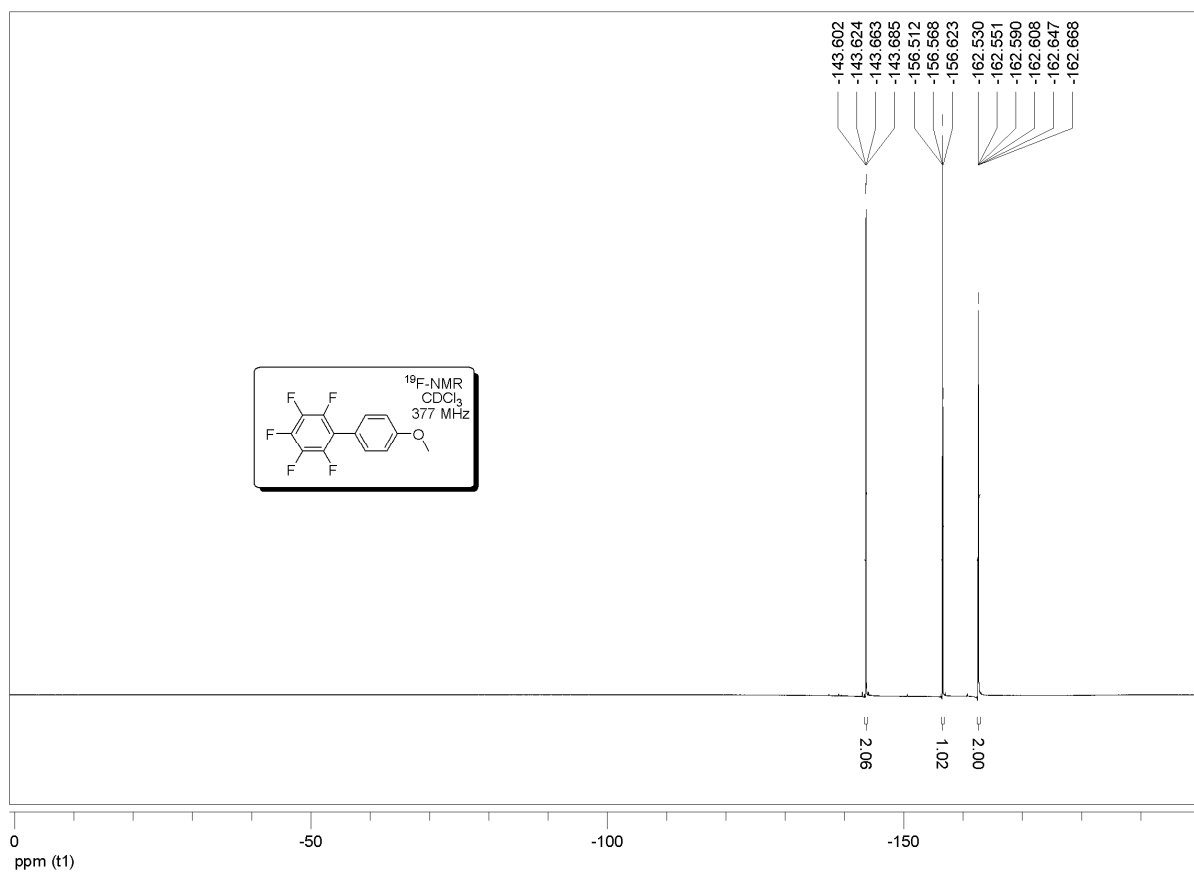
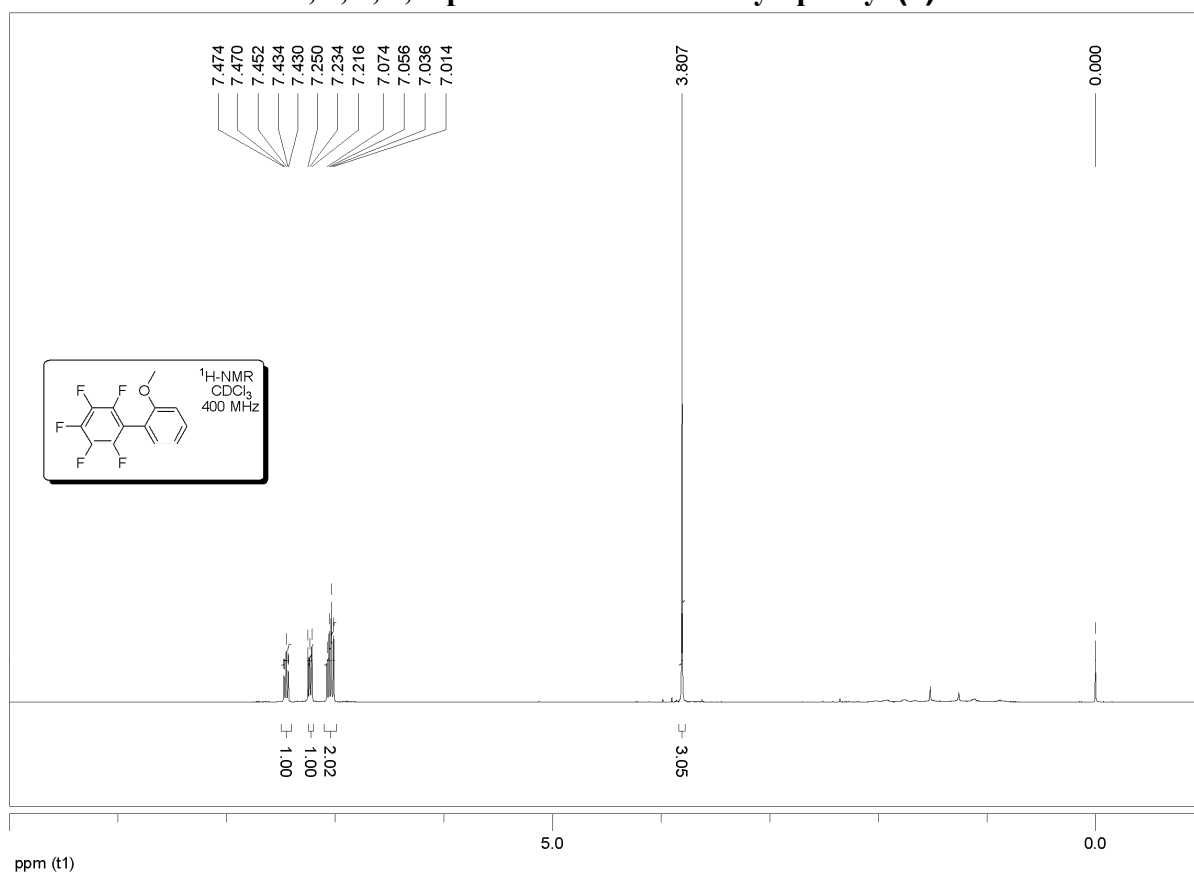
2, 3, 4, 5, 6-pentafluoro-4'-methylbiphenyl (2)

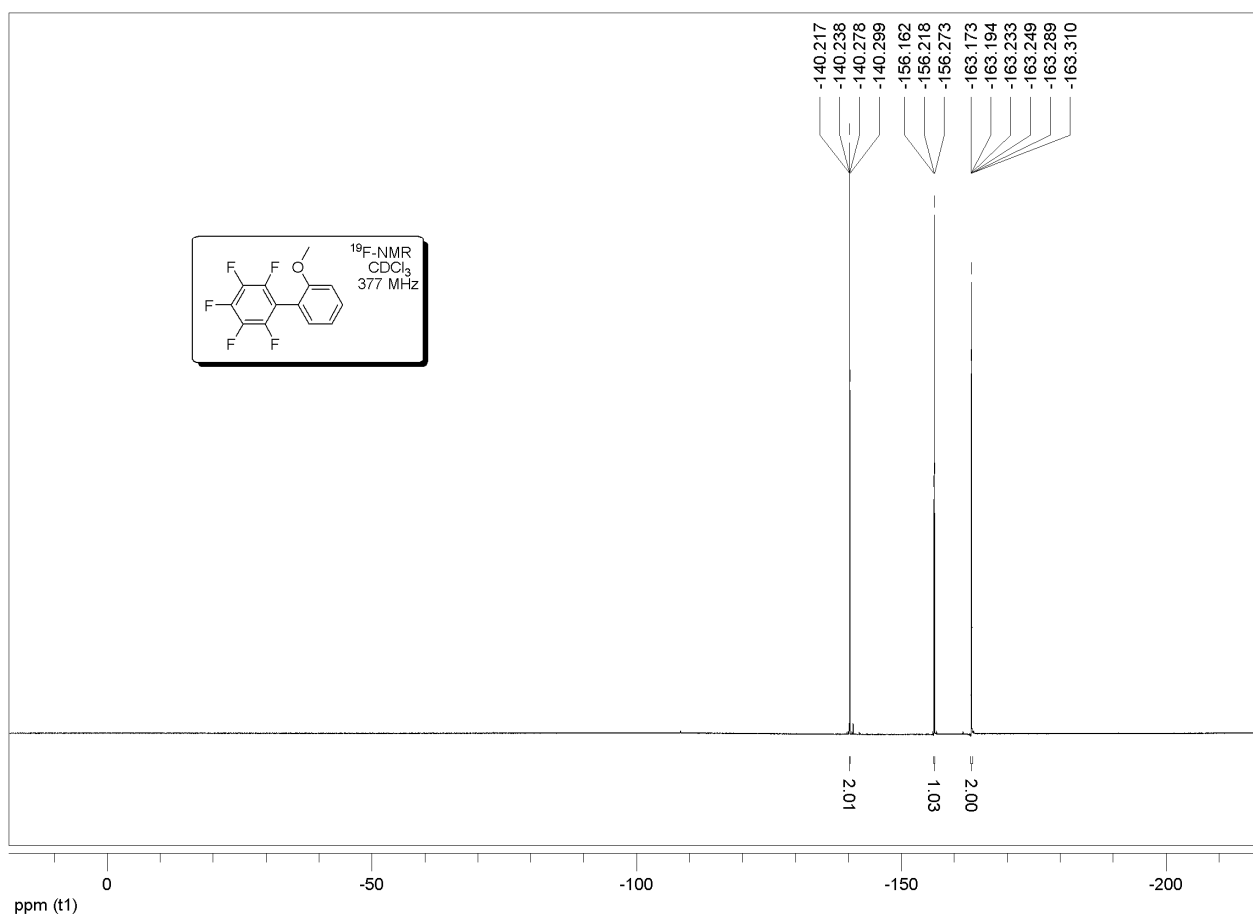
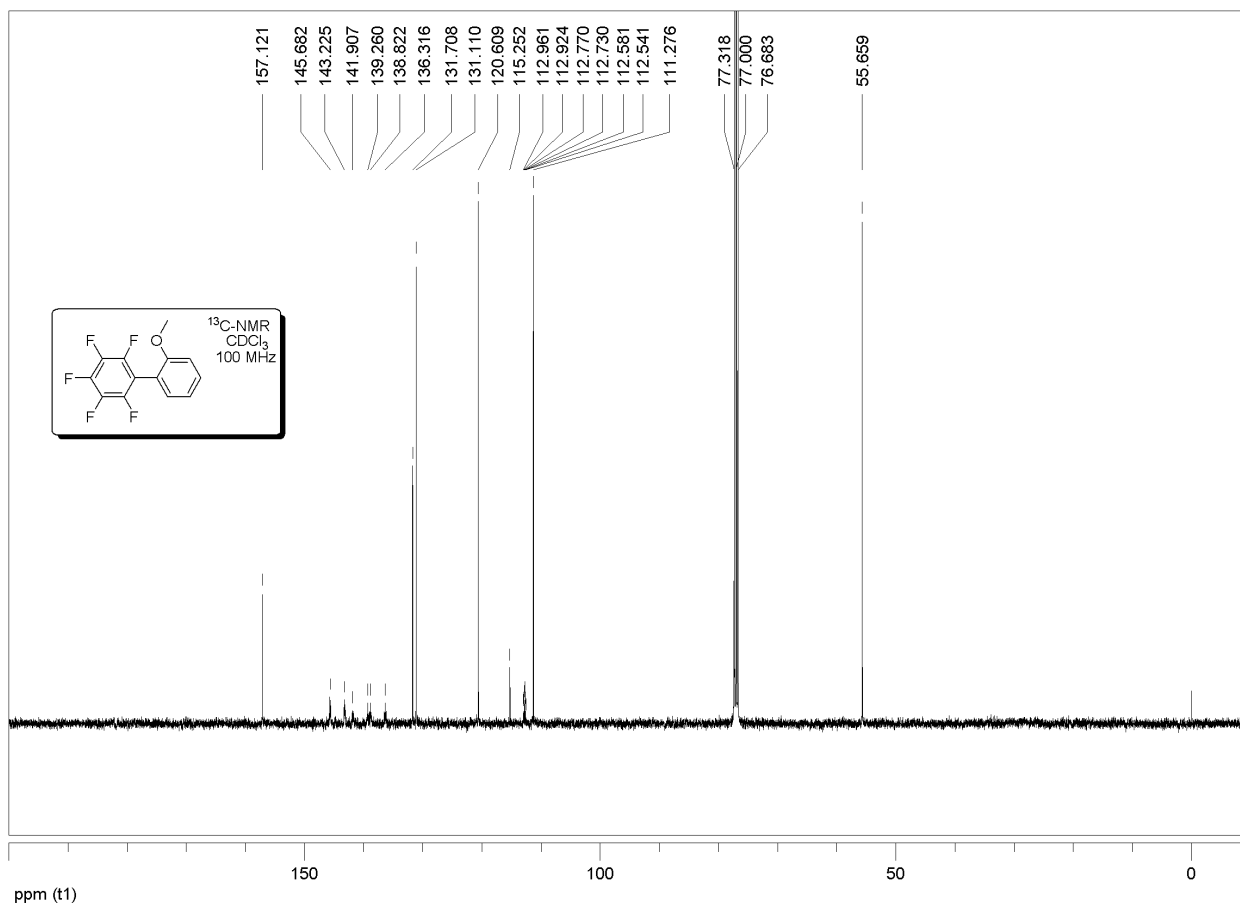
**2, 3, 4, 5, 6-pentafluoro-2'-methylbiphenyl (3)**



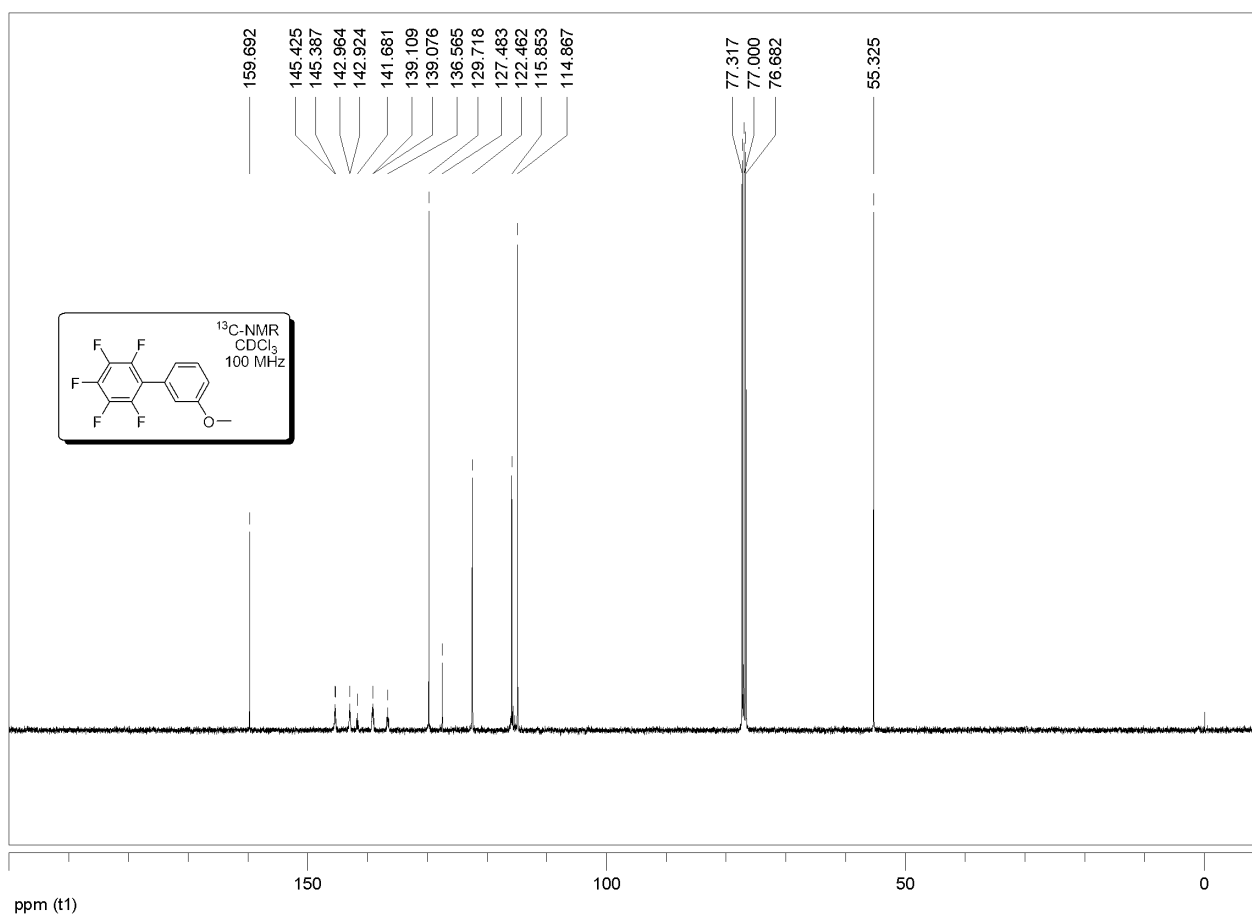
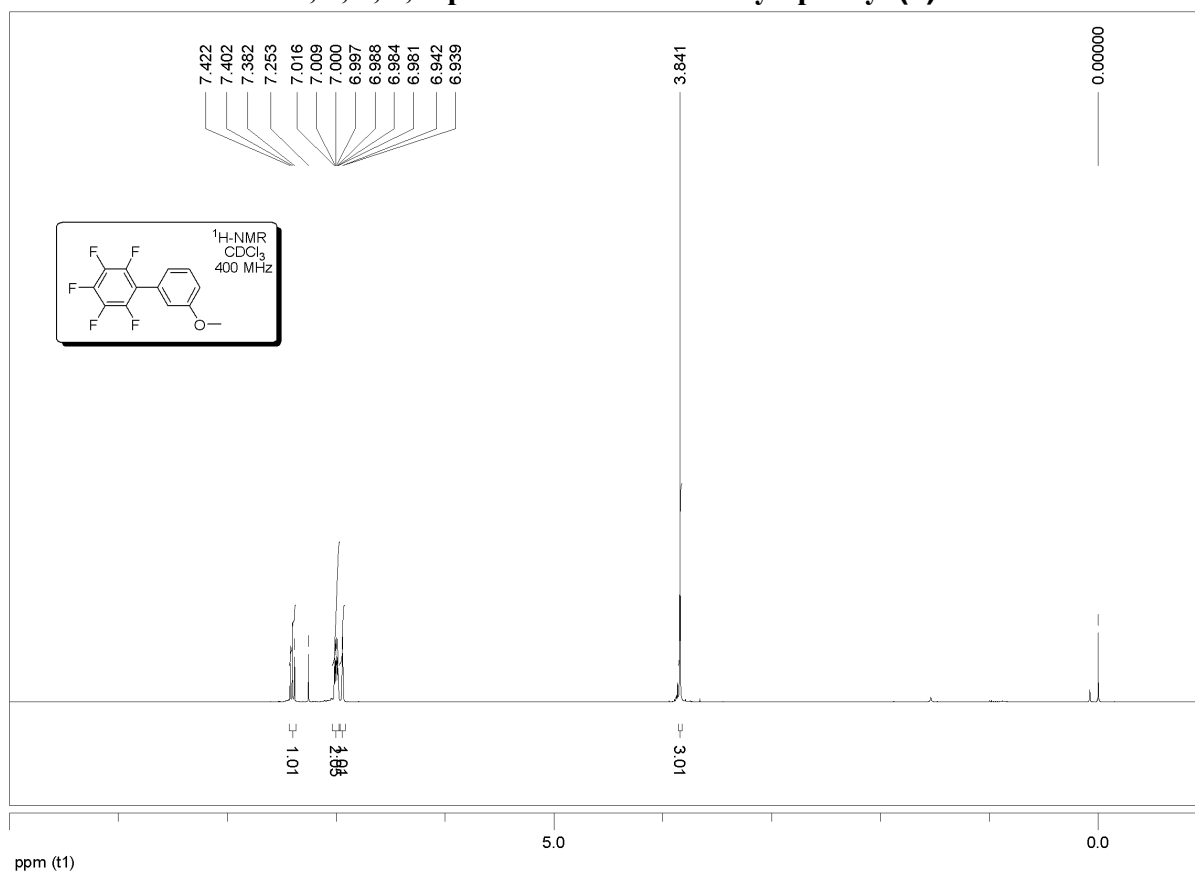
2, 3, 4, 5, 6-pentafluoro-4'-methoxybiphenyl (4)

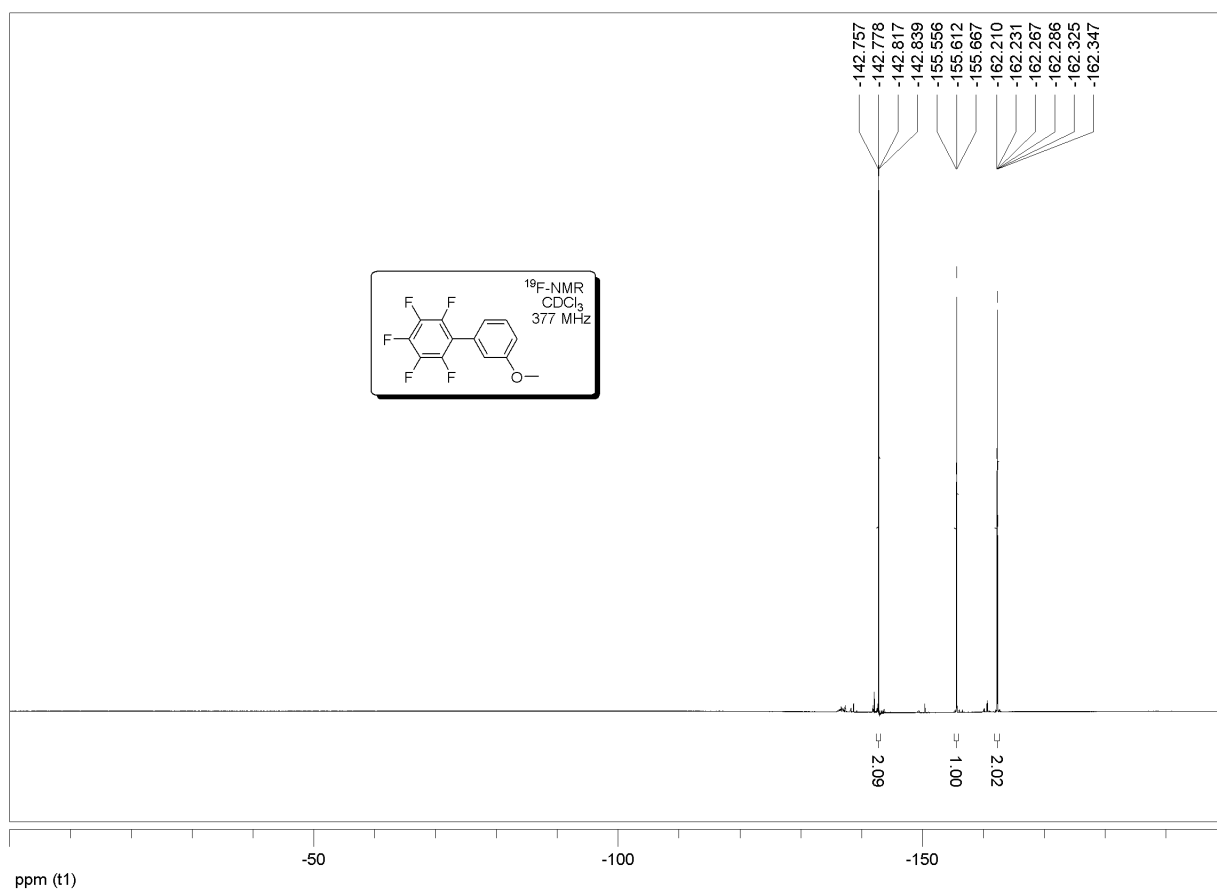
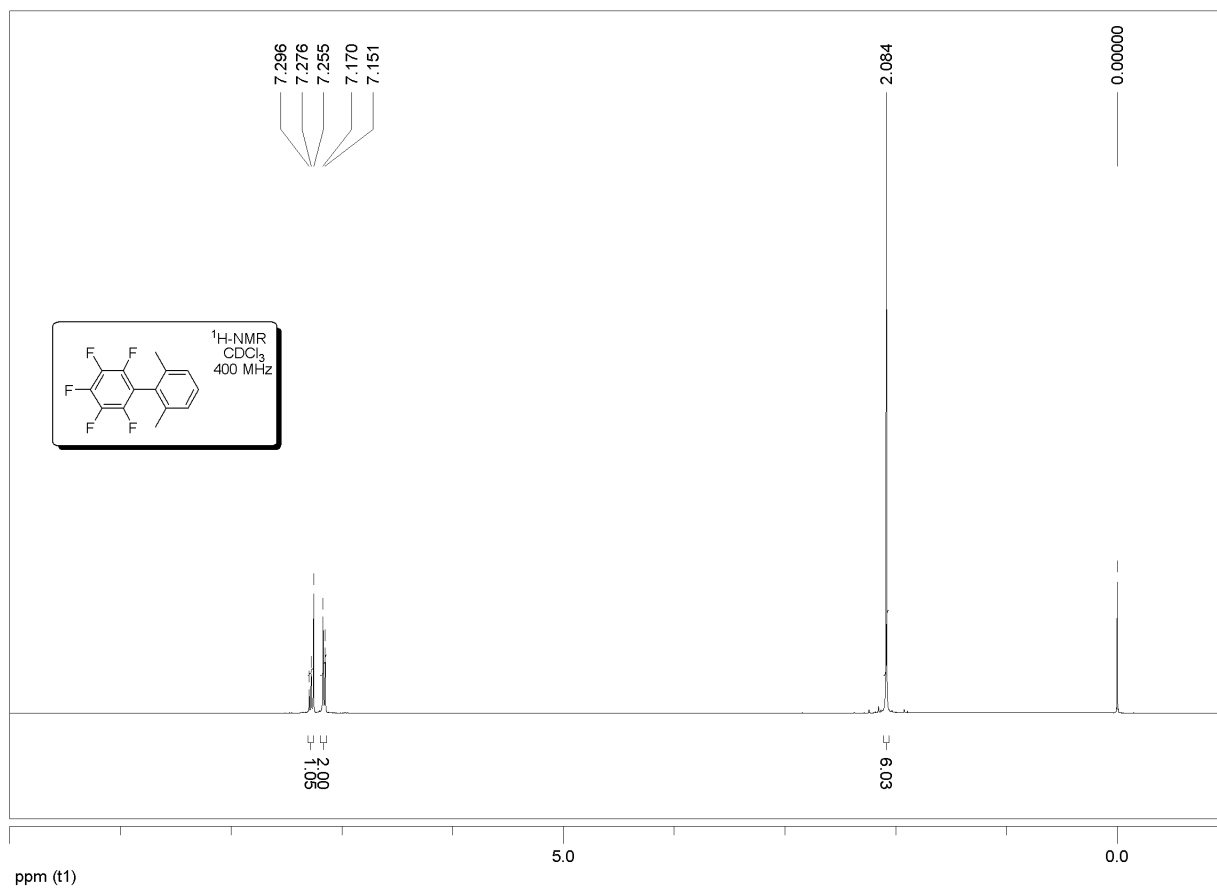


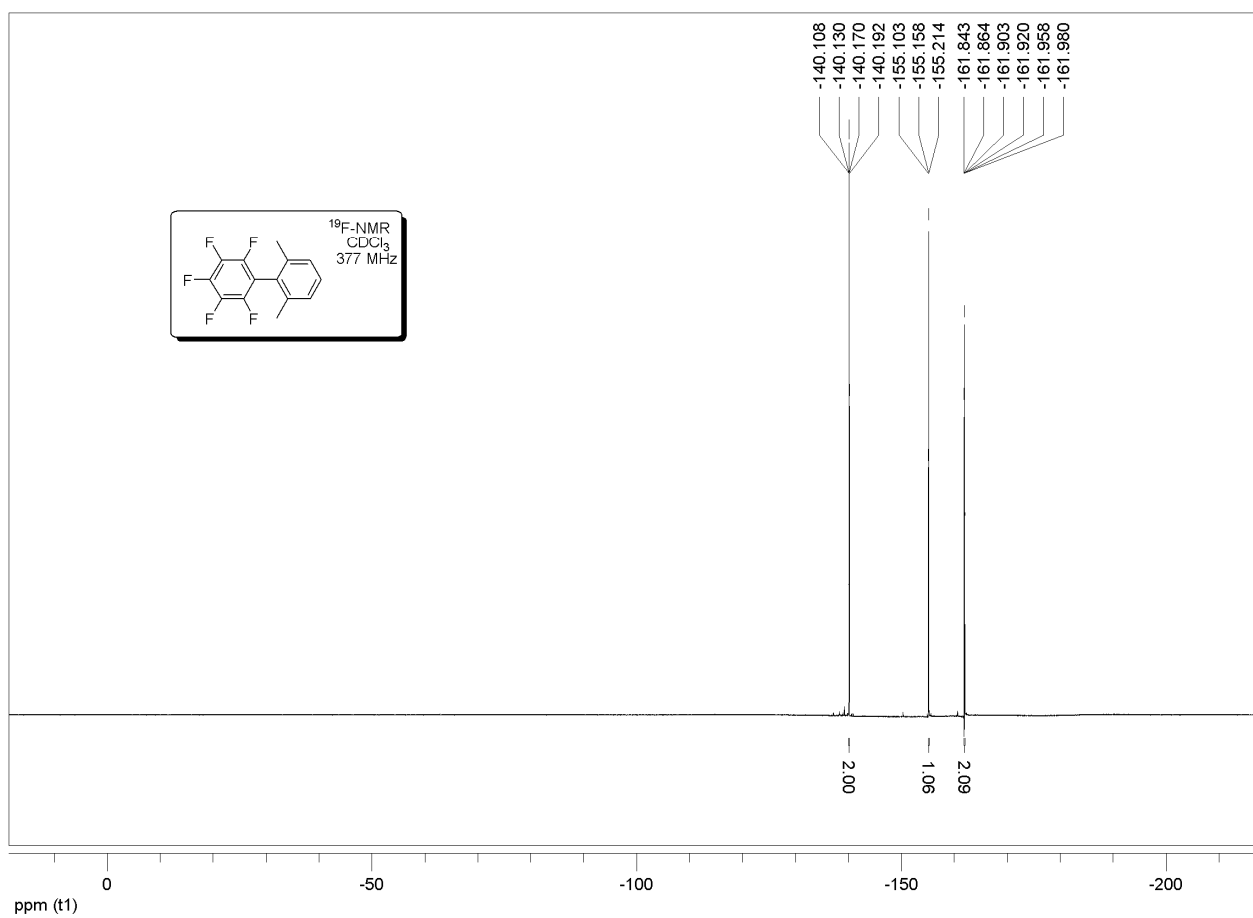
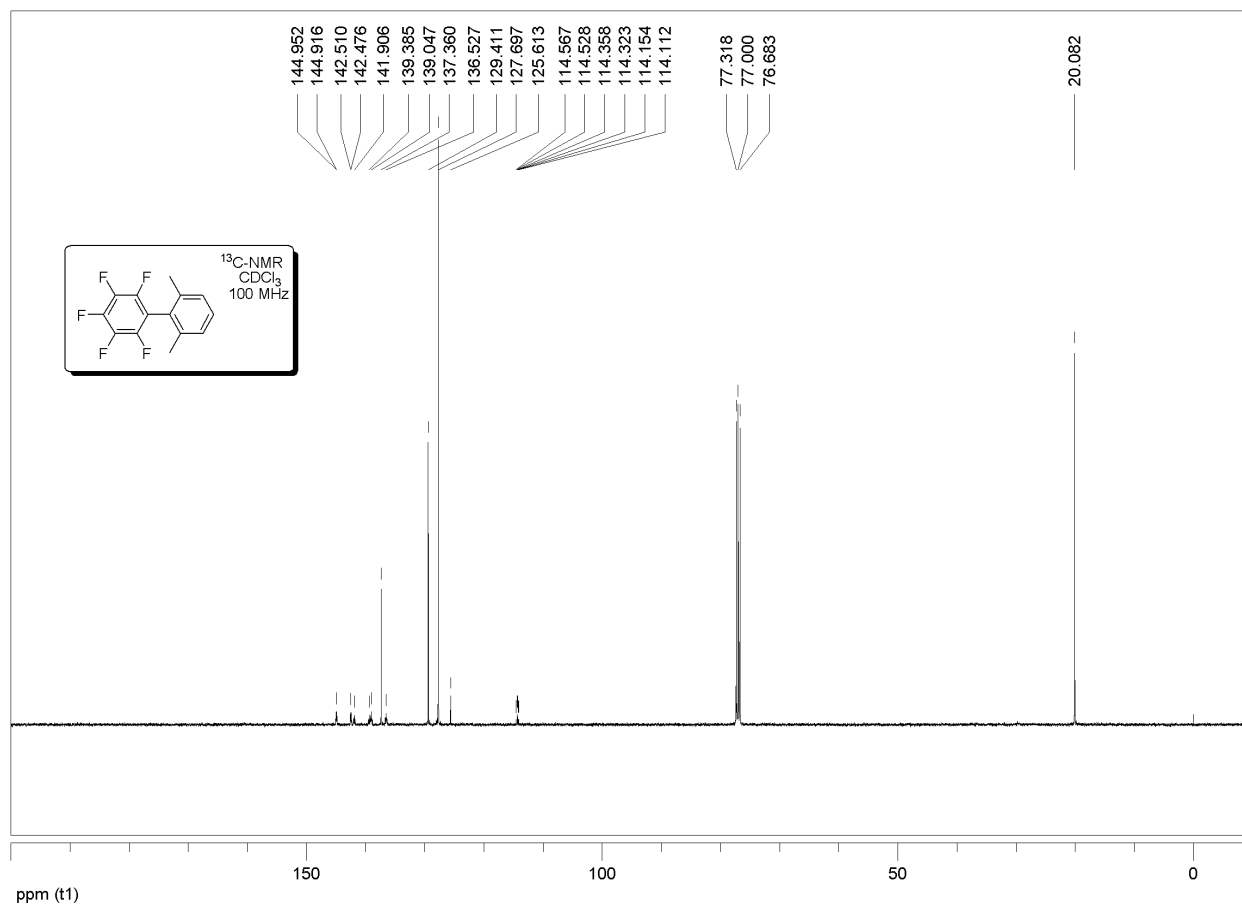
**2, 3, 4, 5, 6-pentafluoro-2'-methoxybiphenyl (5)**

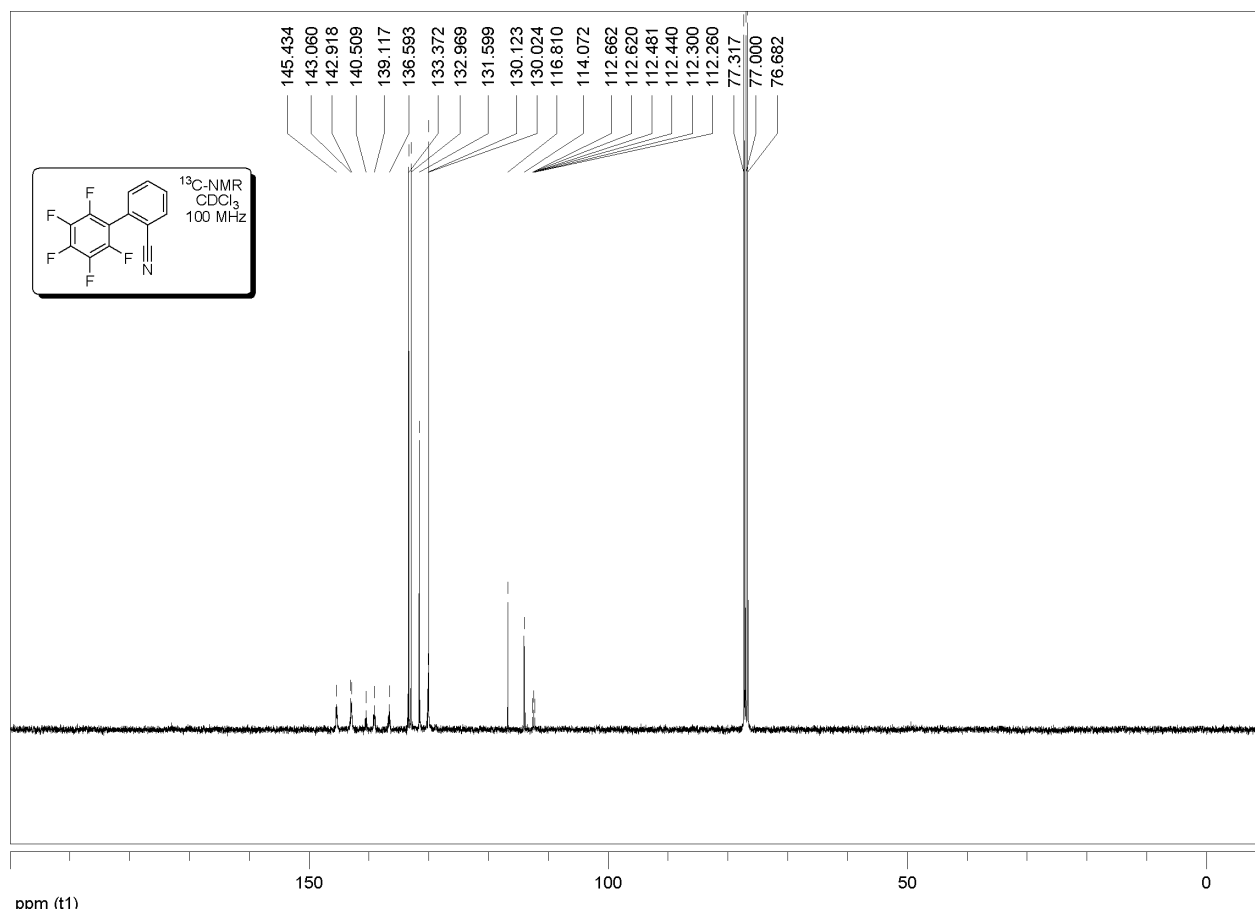
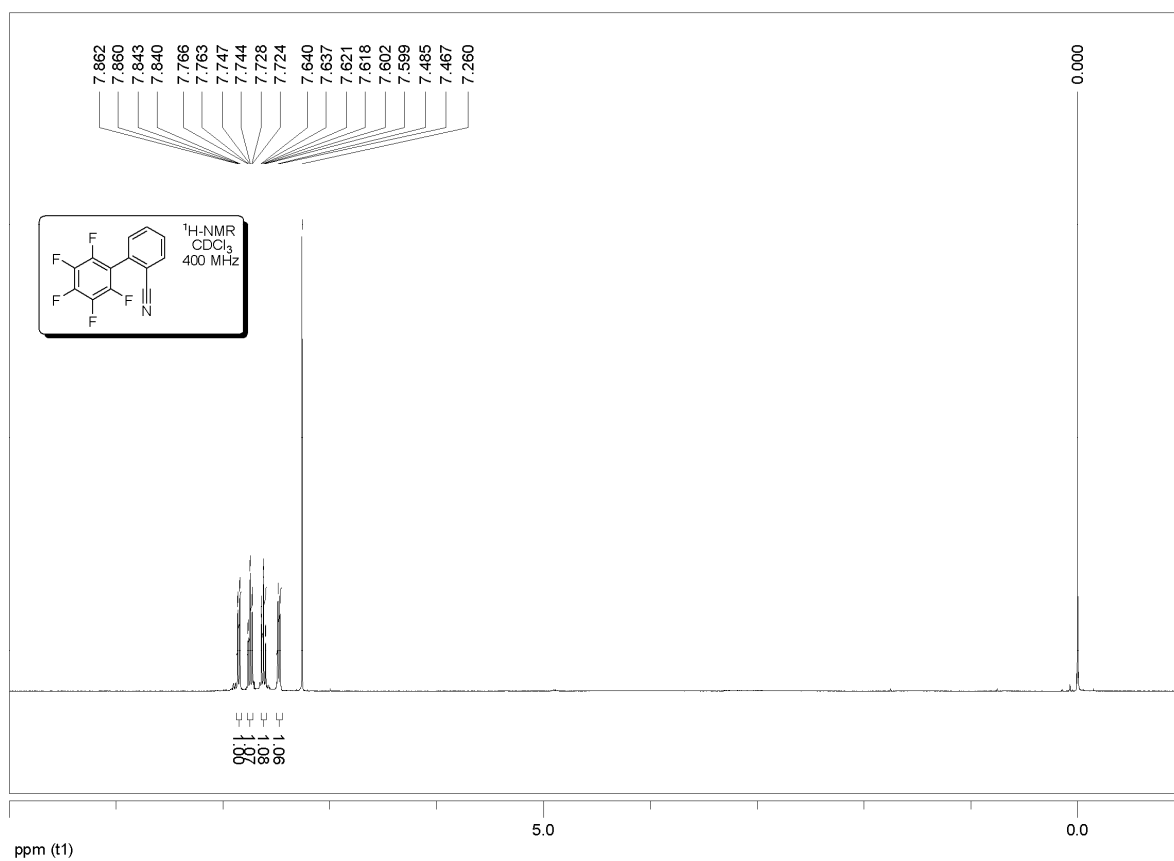


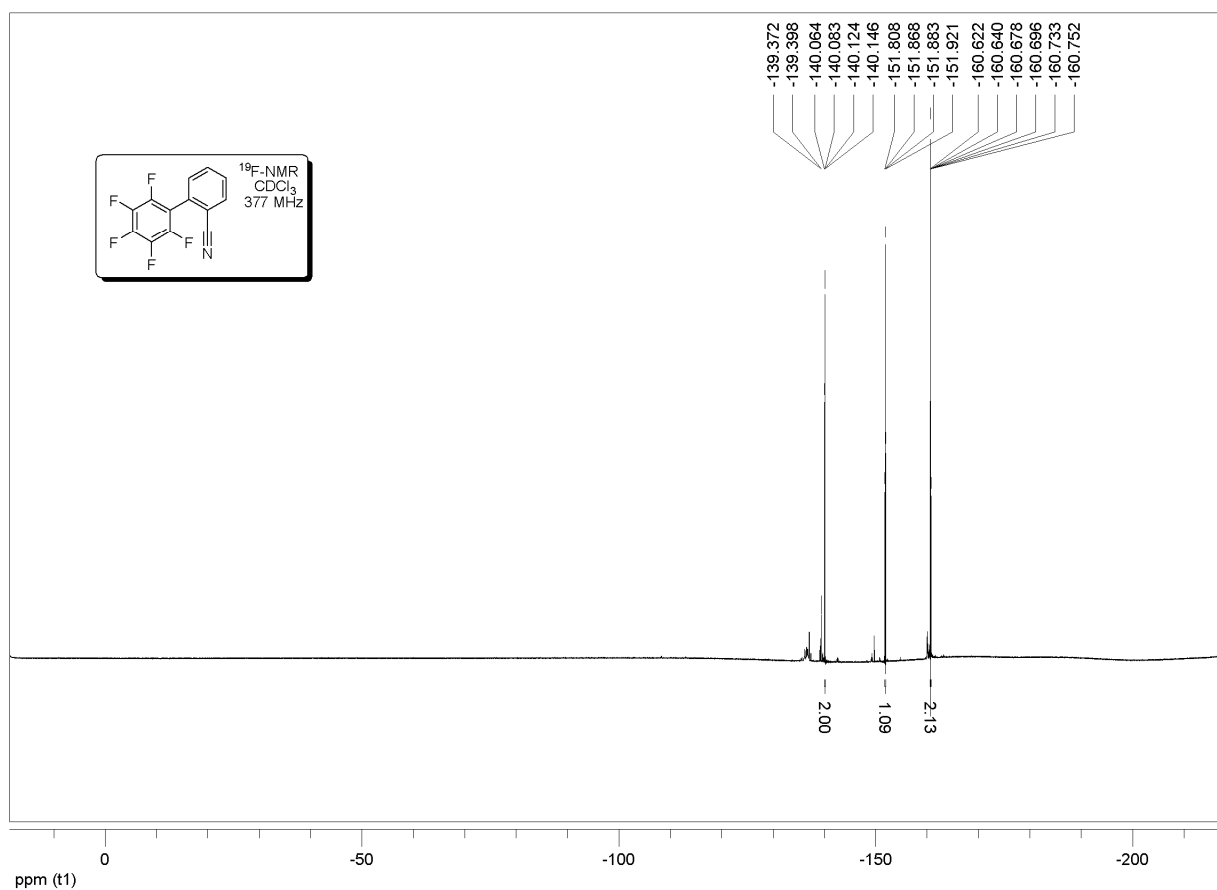
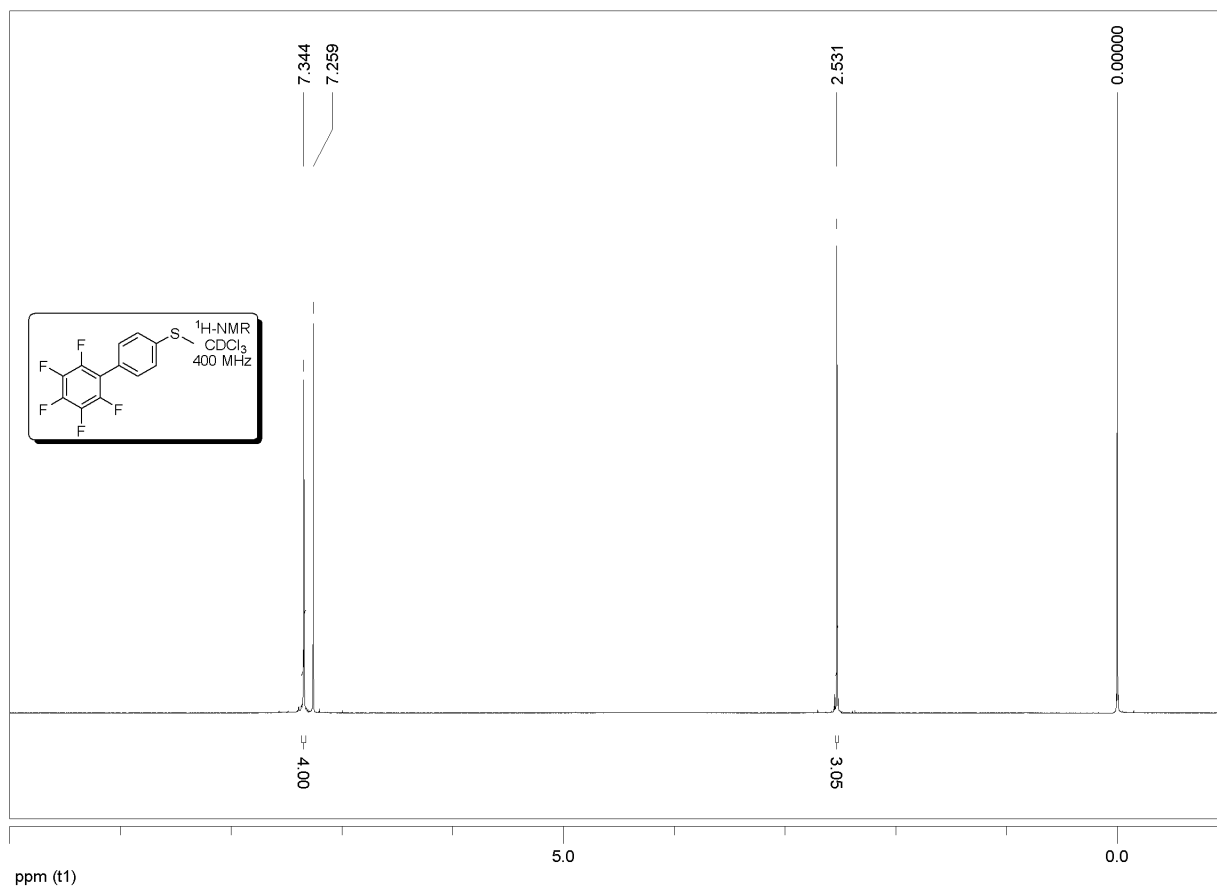
2, 3, 4, 5, 6-pentafluoro-3'-methoxybiphenyl (6)

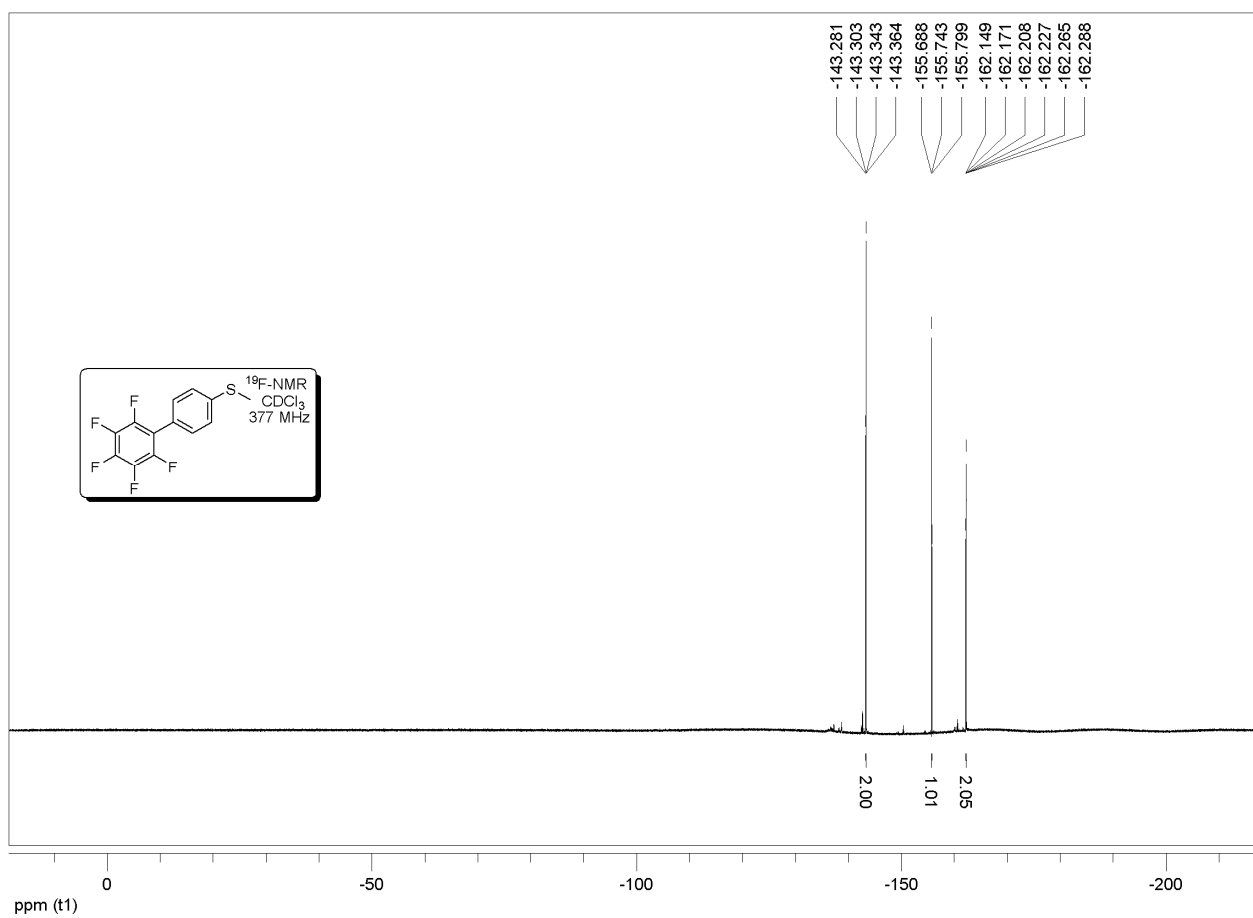
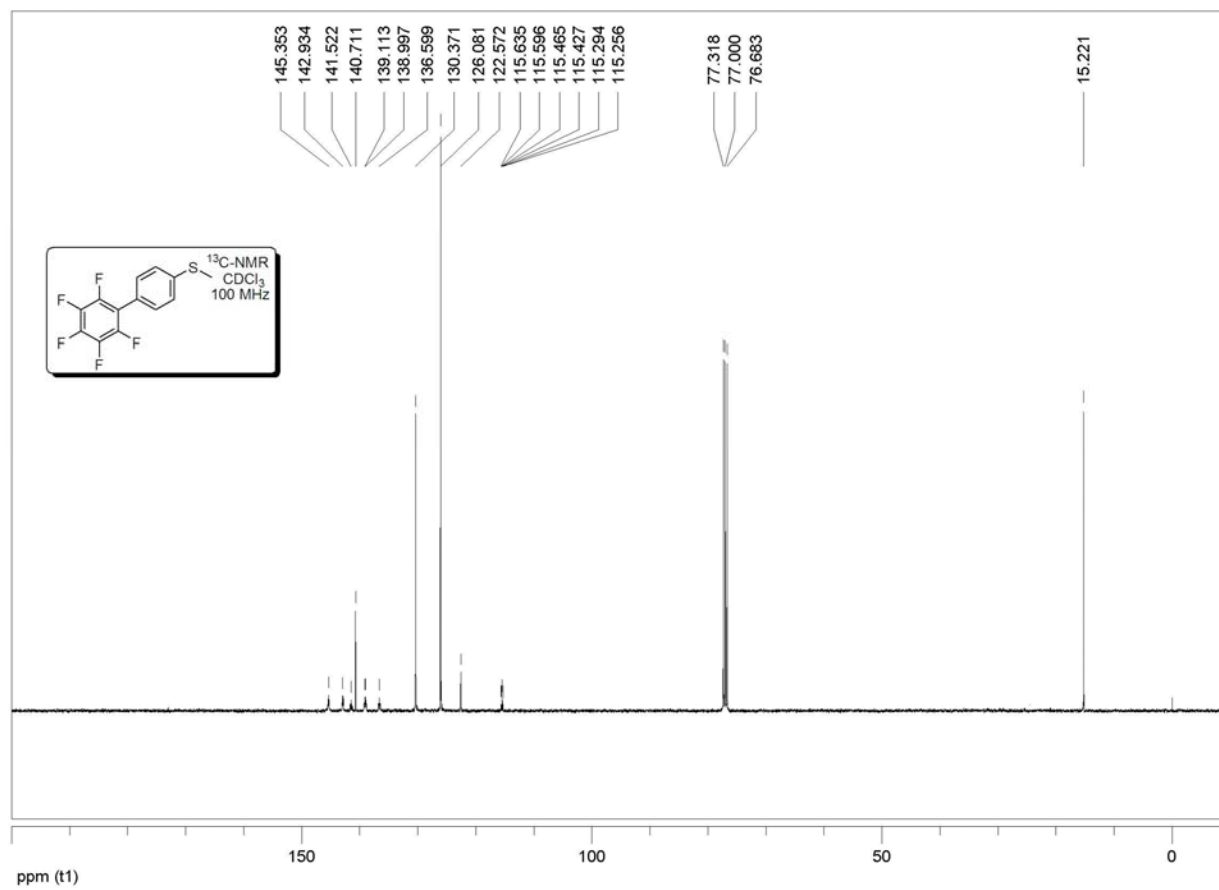


**2, 3, 4, 5, 6-pentafluoro-2',6'-dimethylbiphenyl (7)**

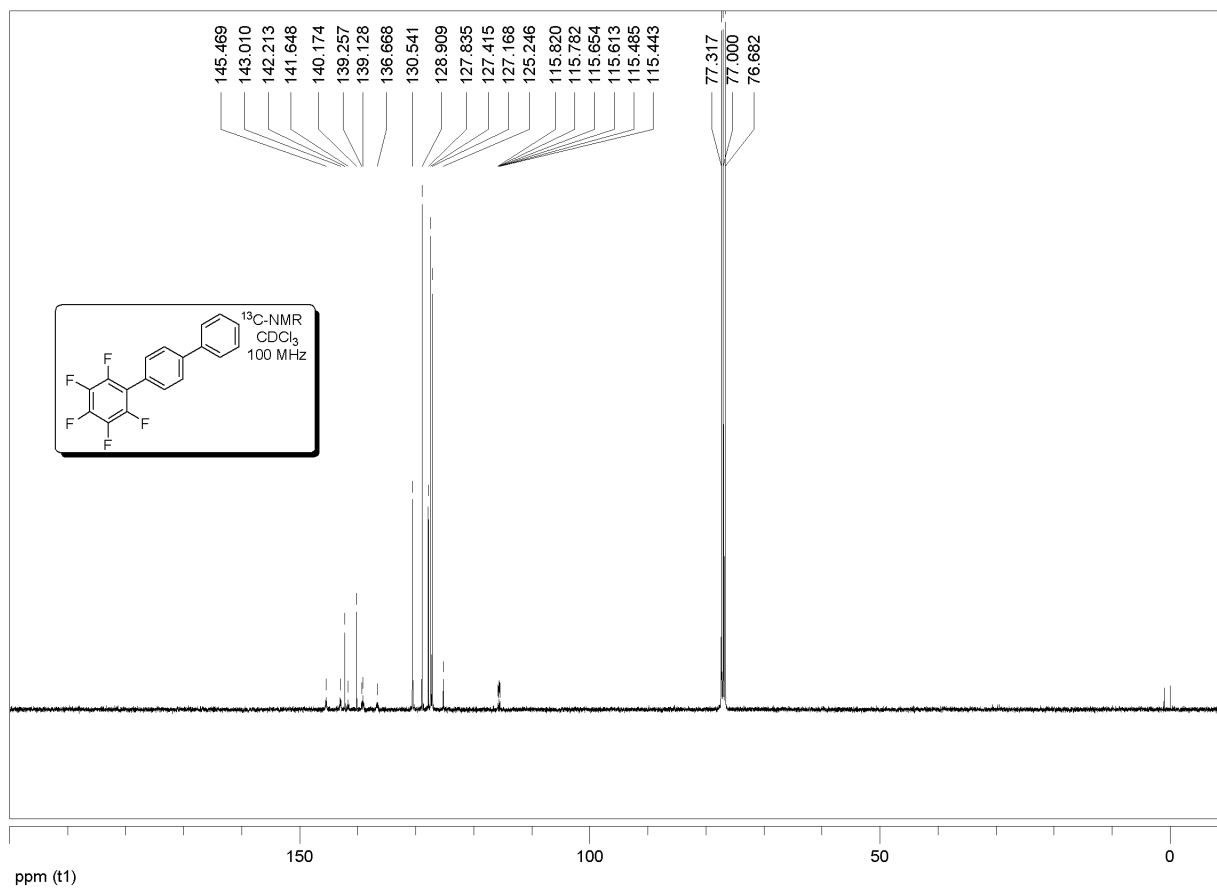
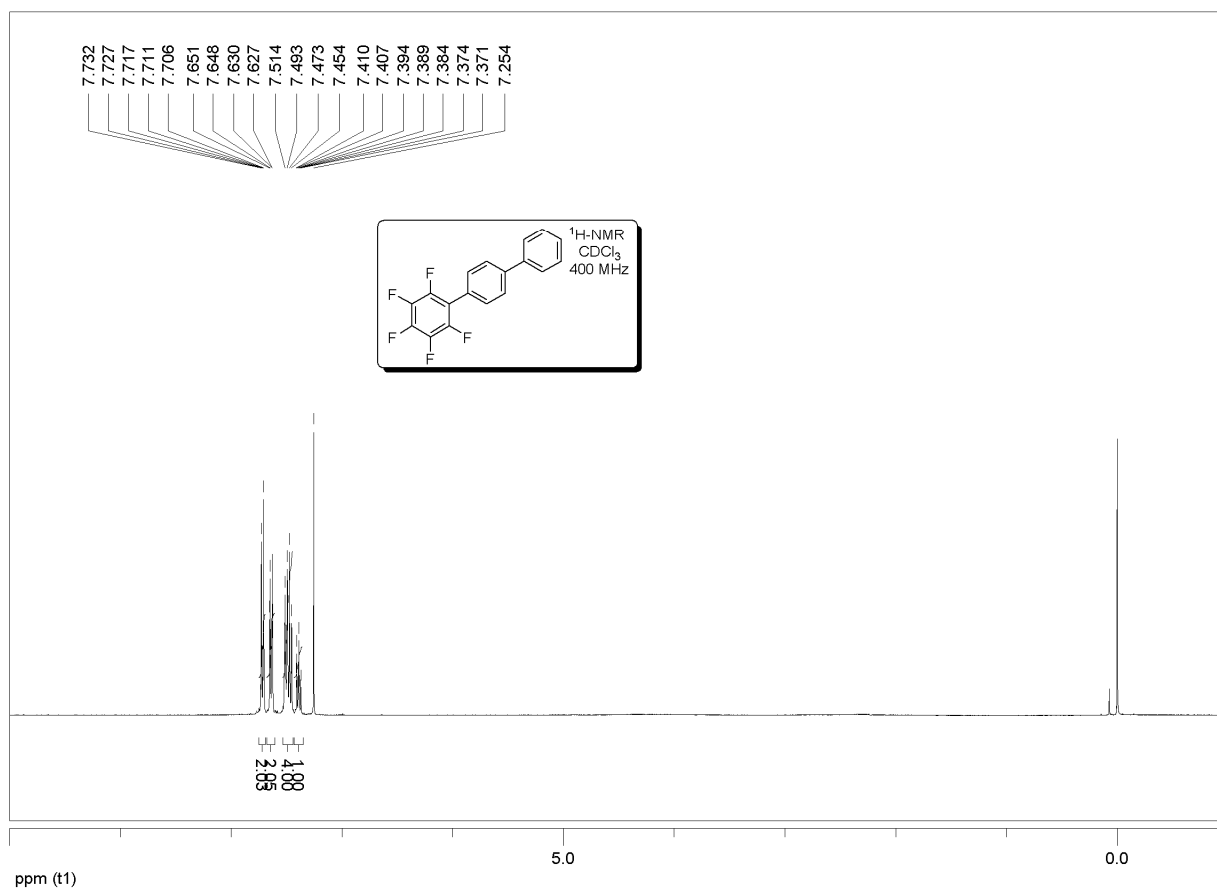


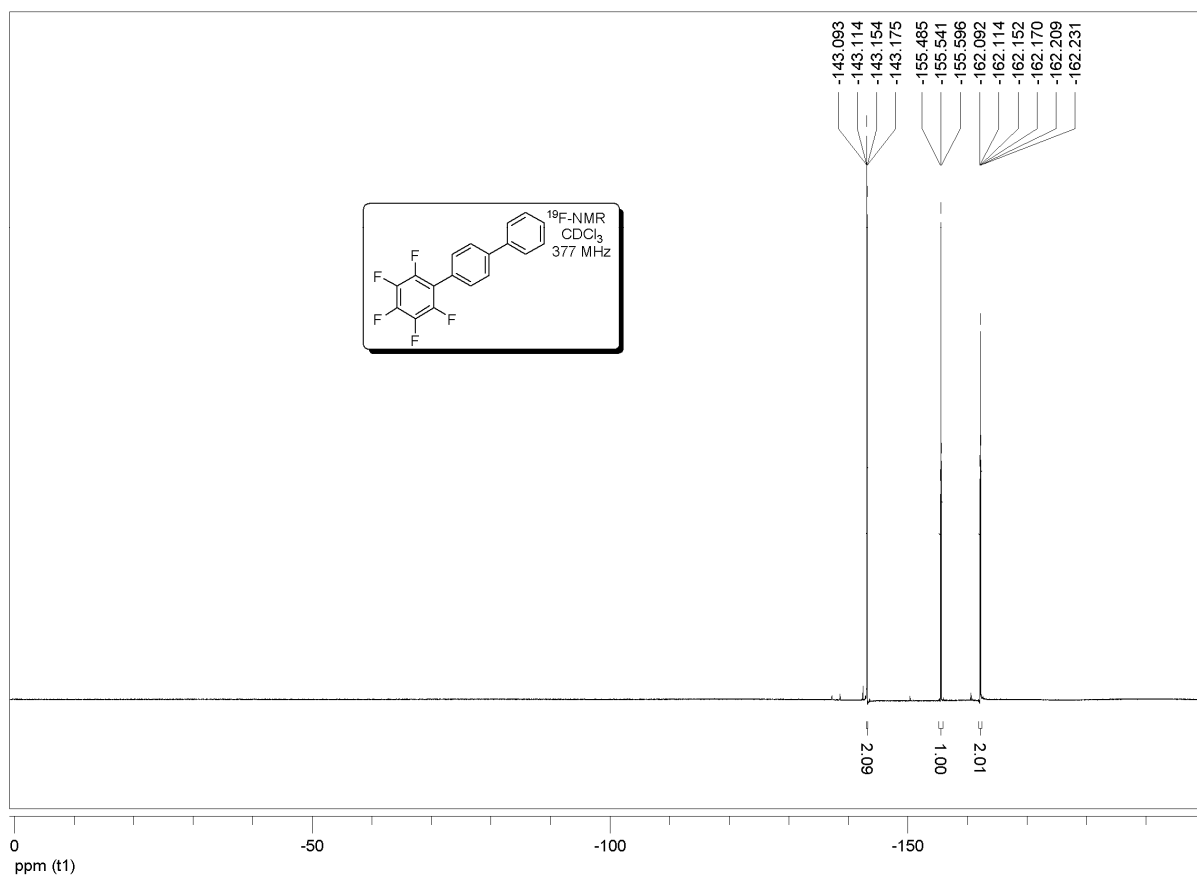
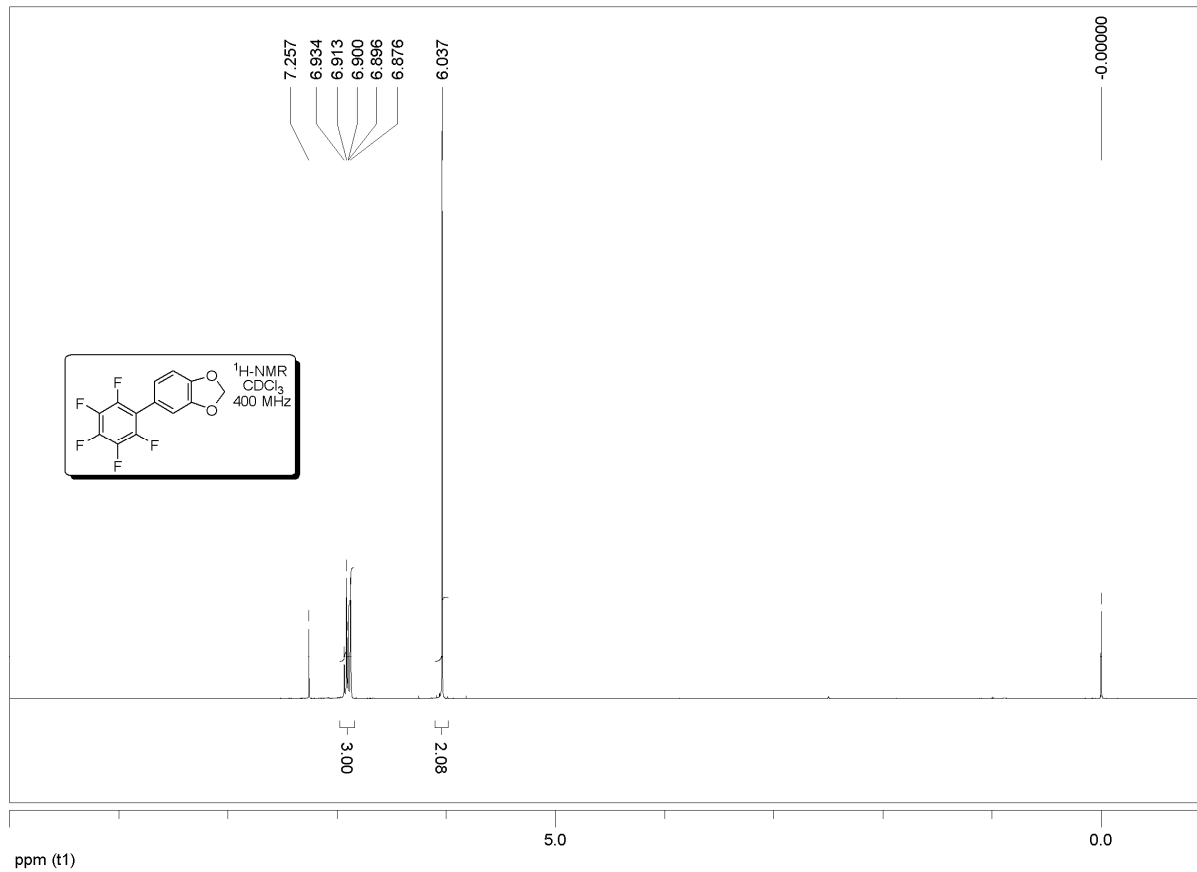
2', 3', 4', 5', 6'-pentafluorobiphenyl-2-carbonitrile (8)

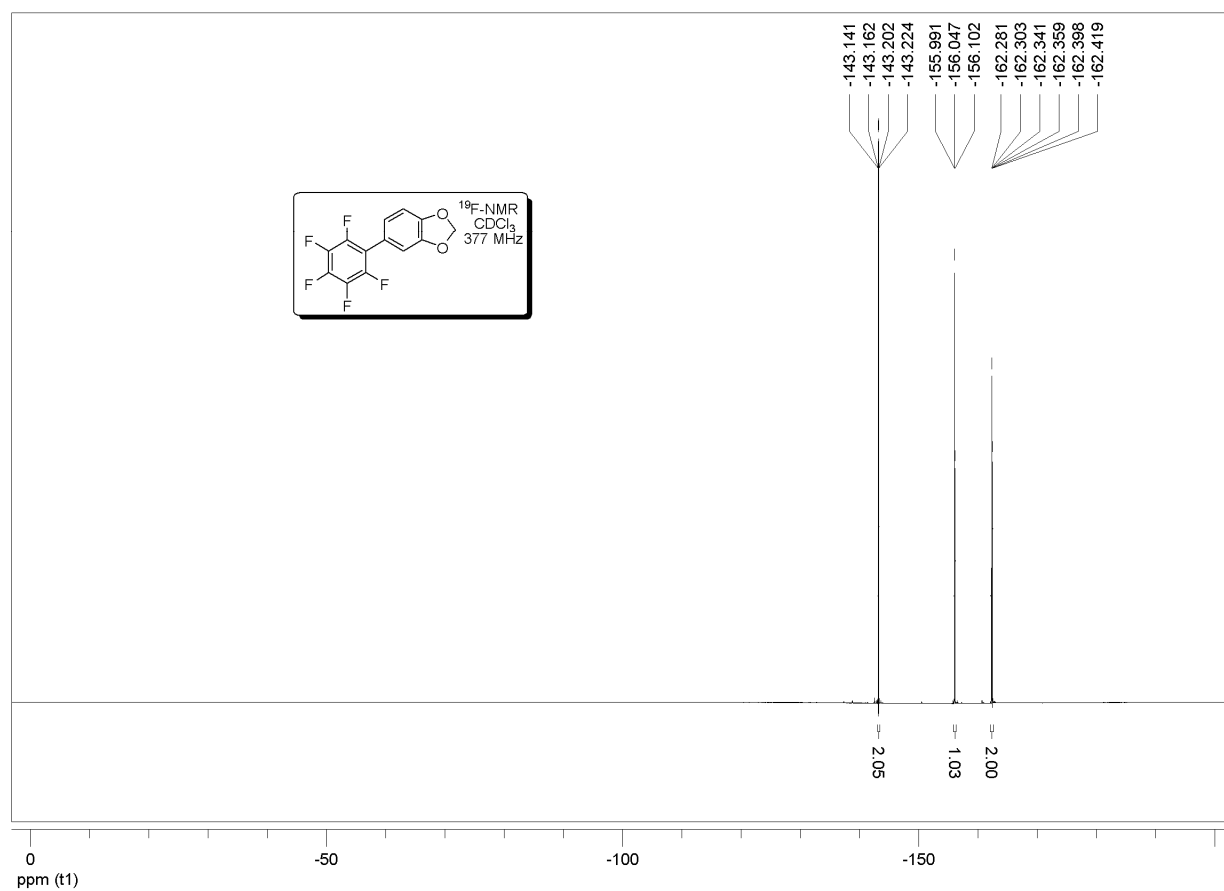
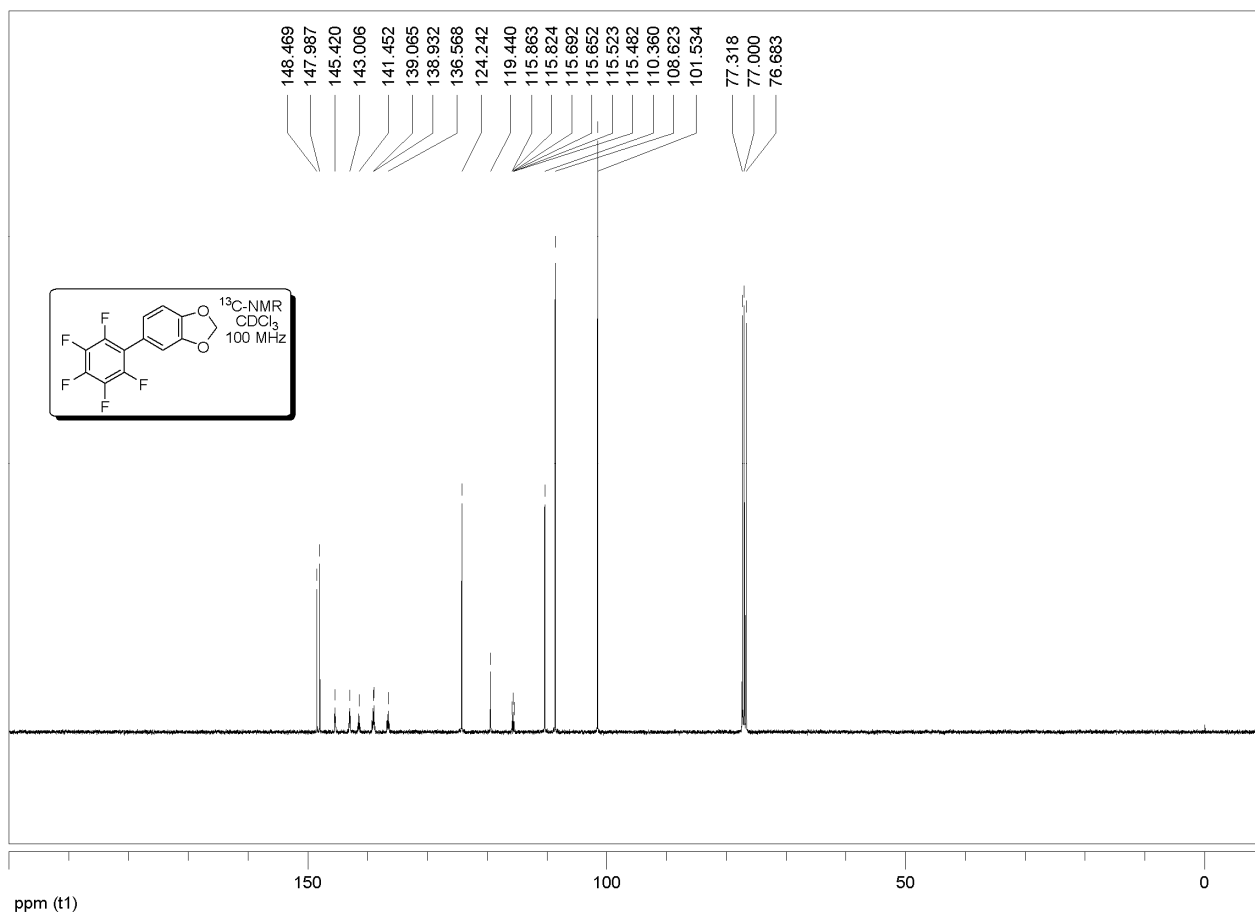
**methyl(2', 3', 4', 5', 6'-pentafluorobiphenyl-4-yl)sulfane (9)**

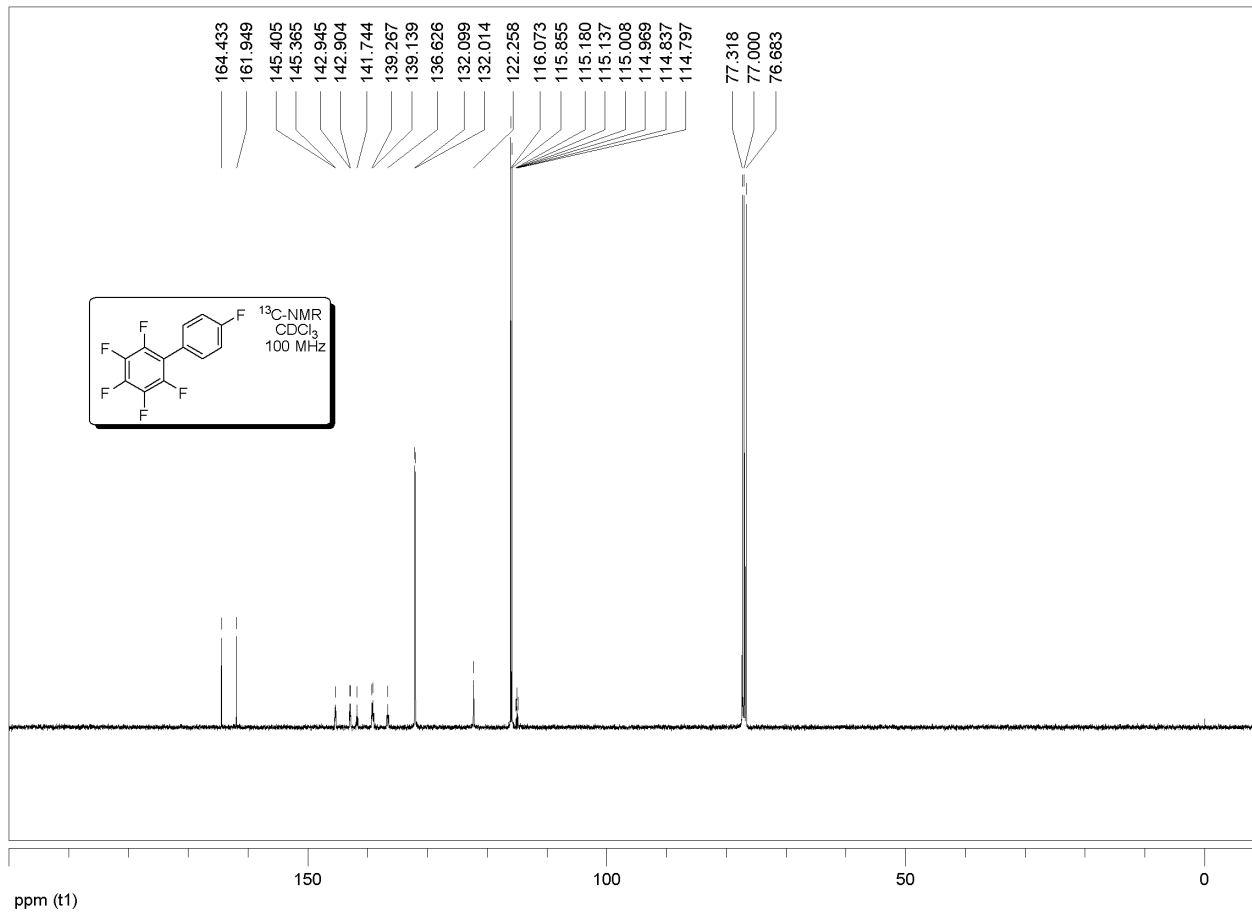
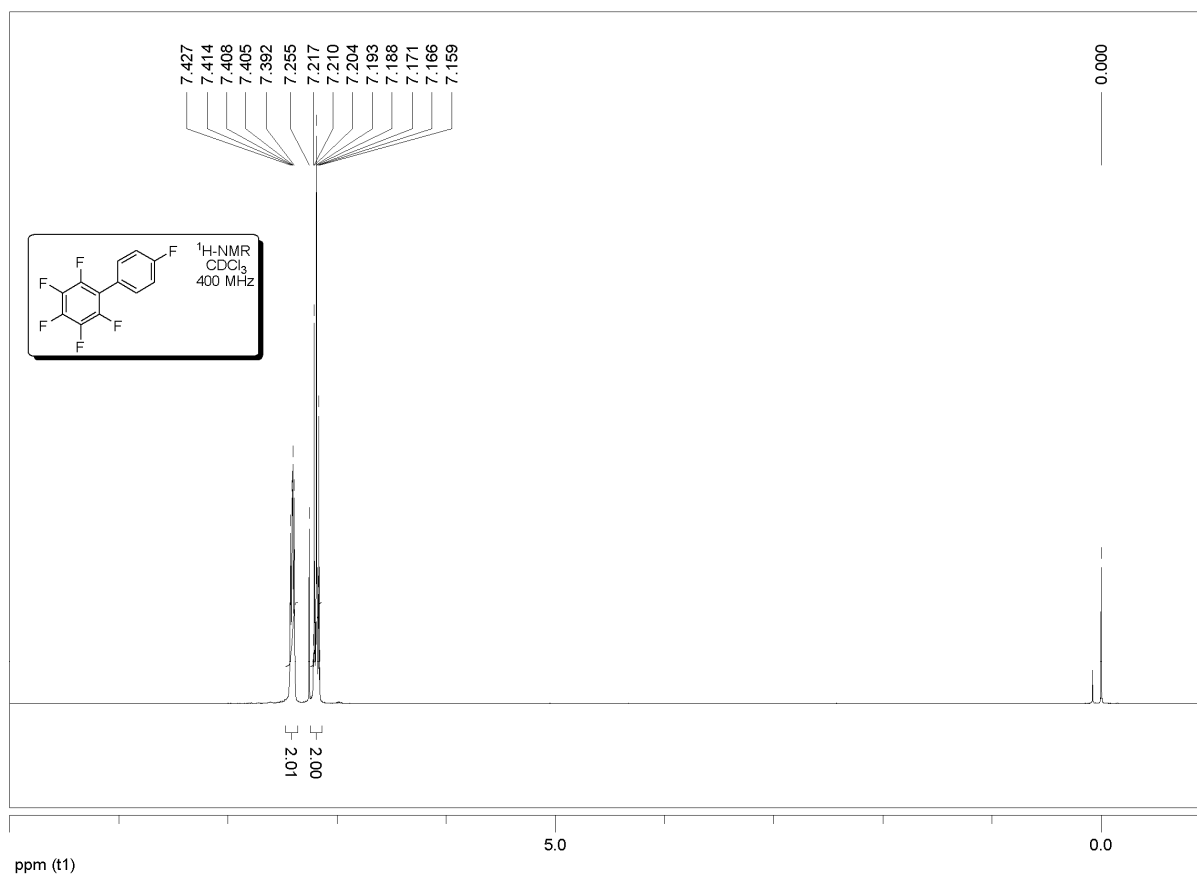


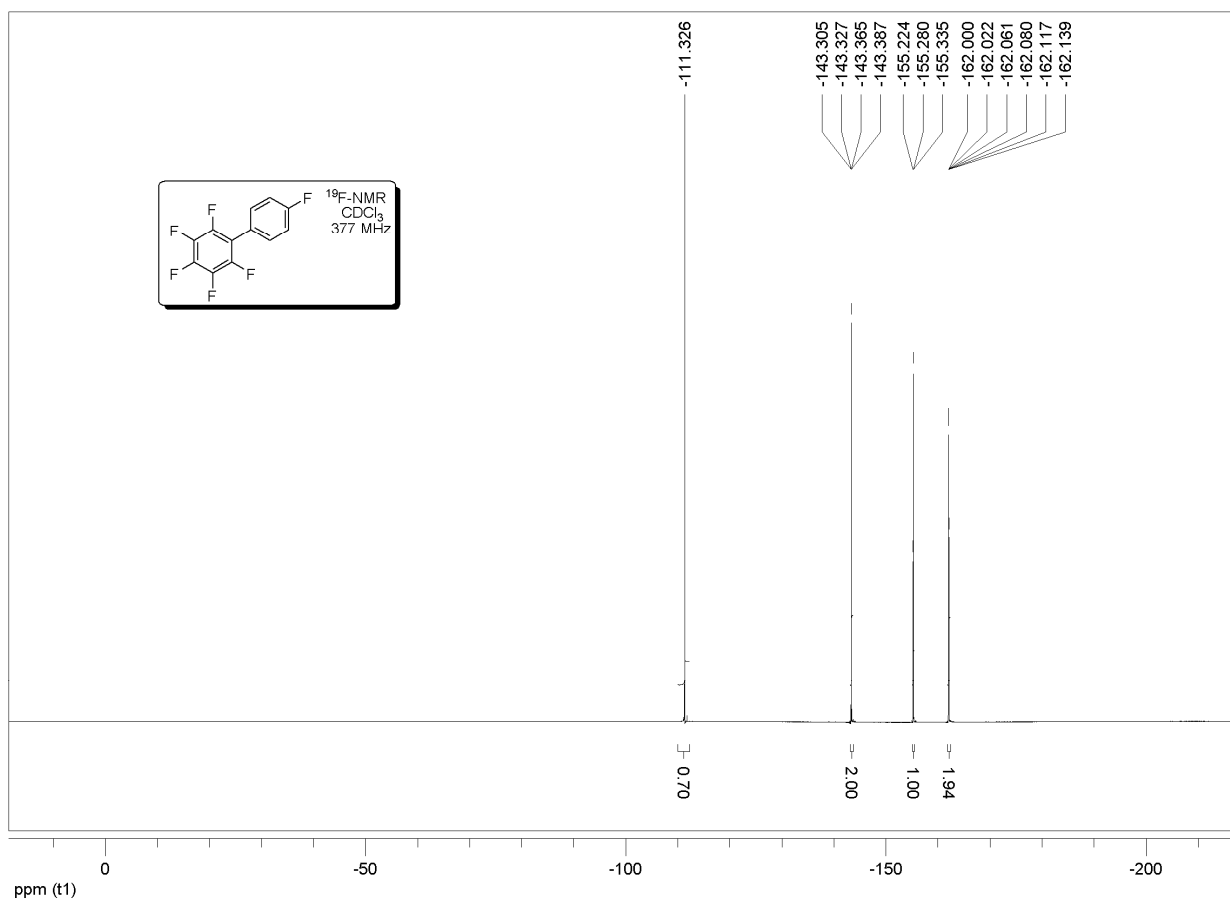
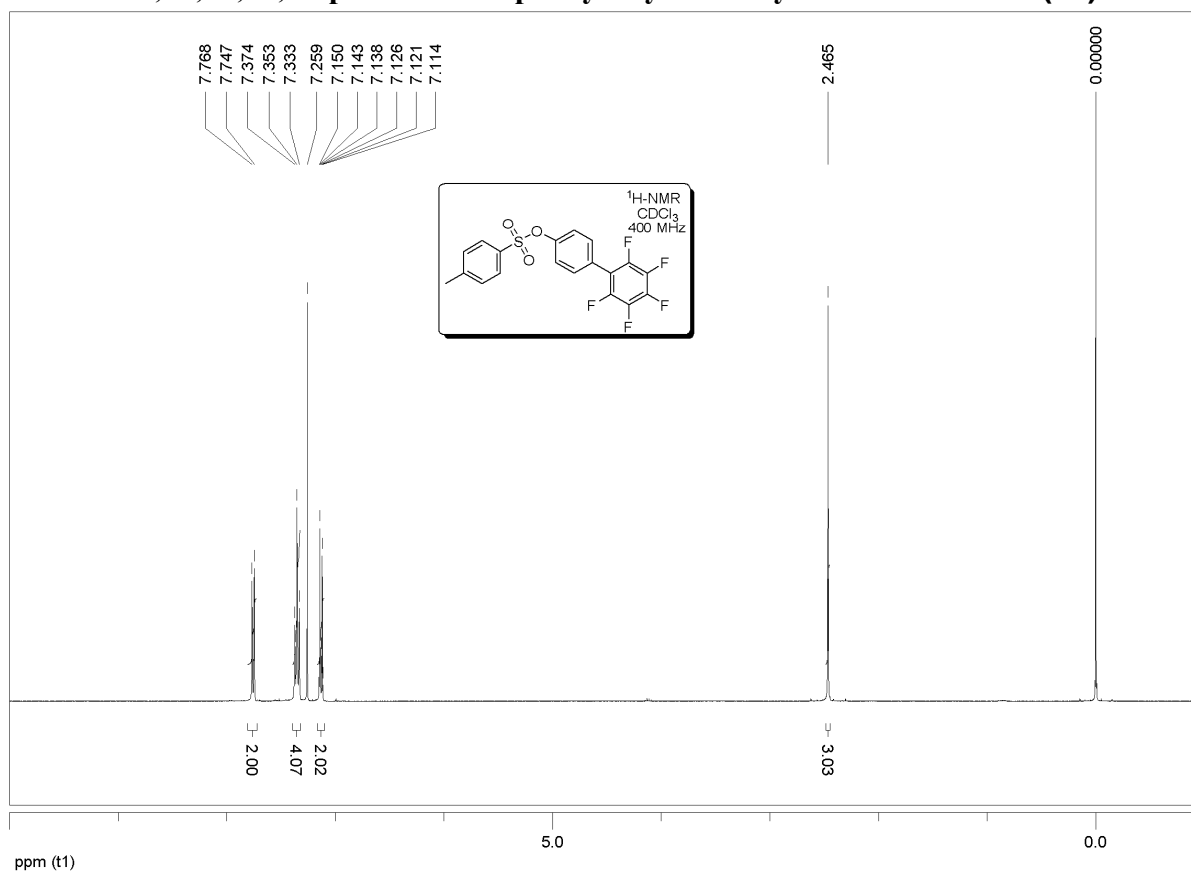
4-perfluorophenylbiphenyl (10)

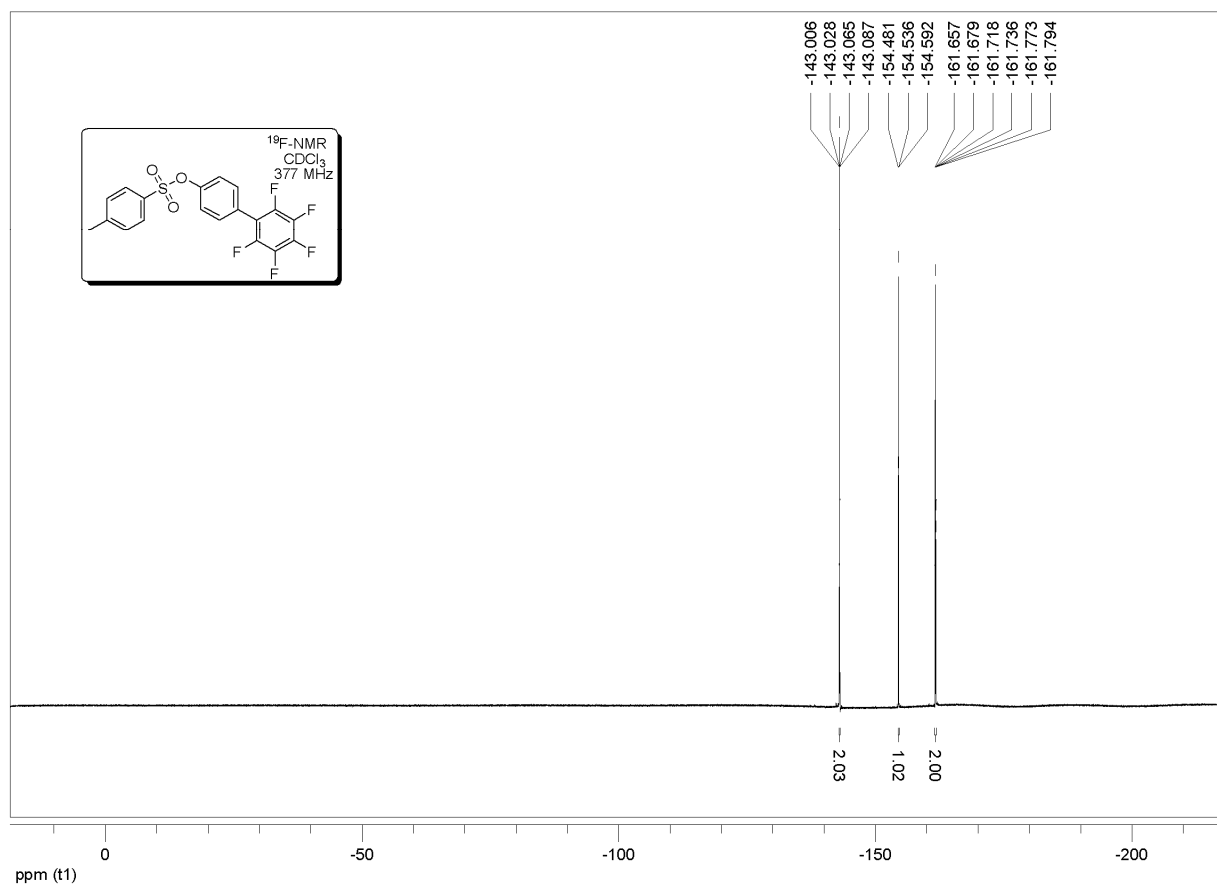
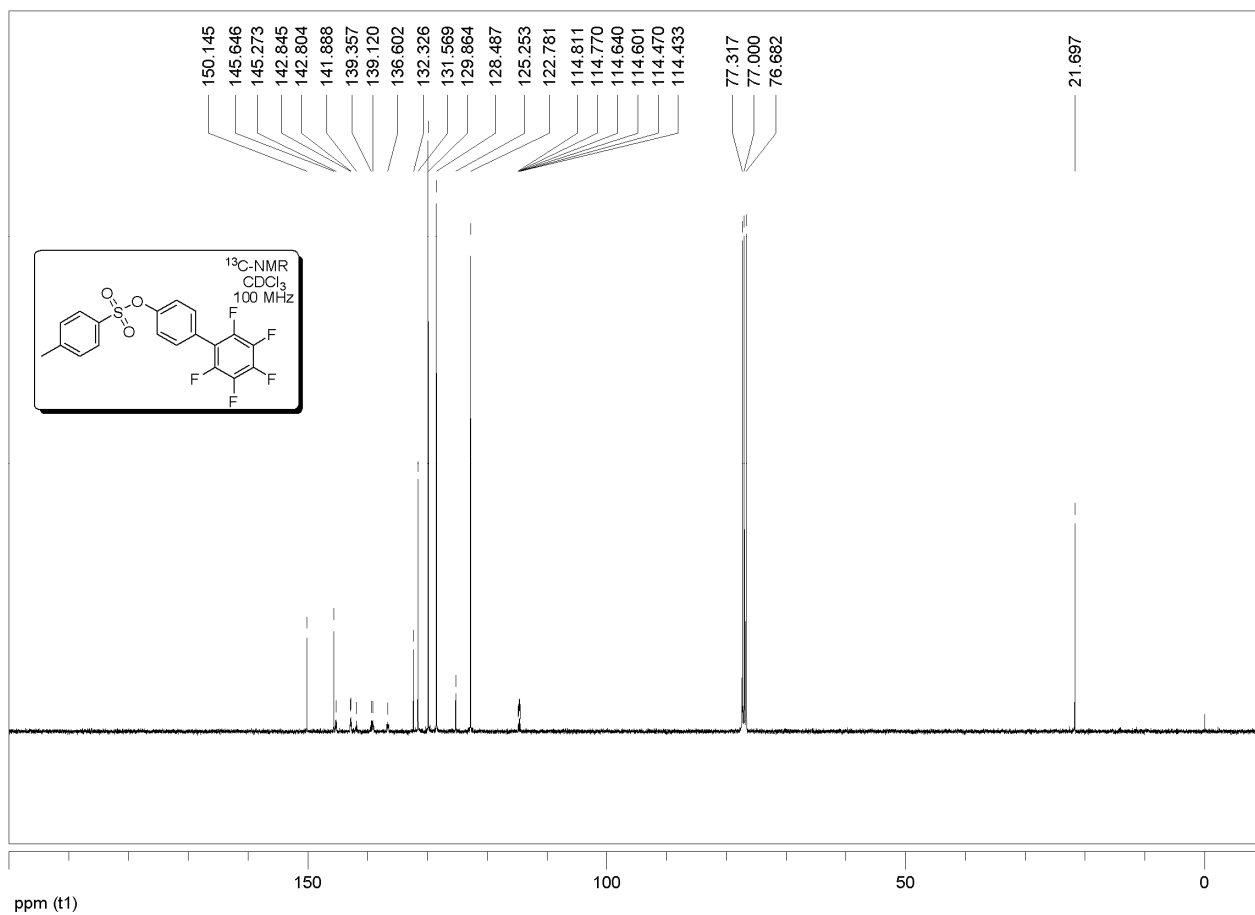


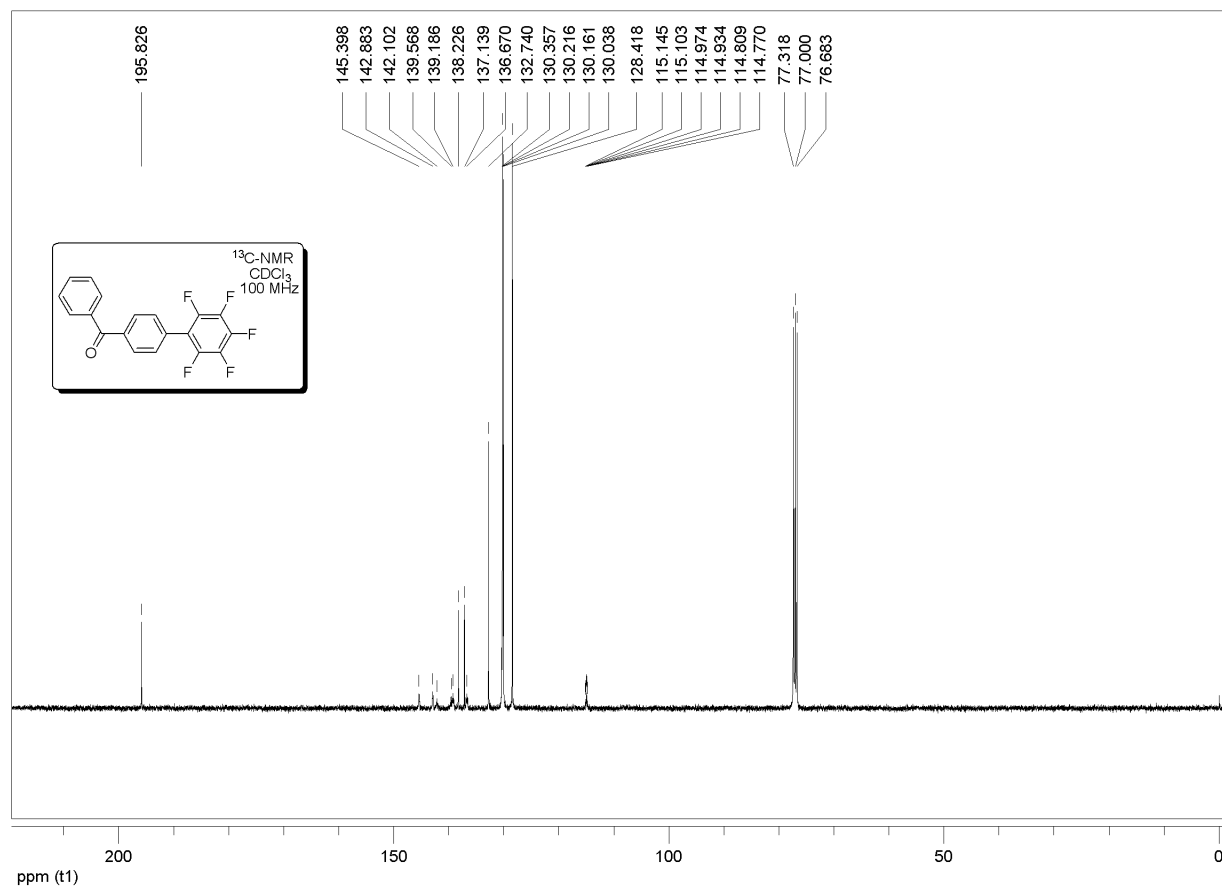
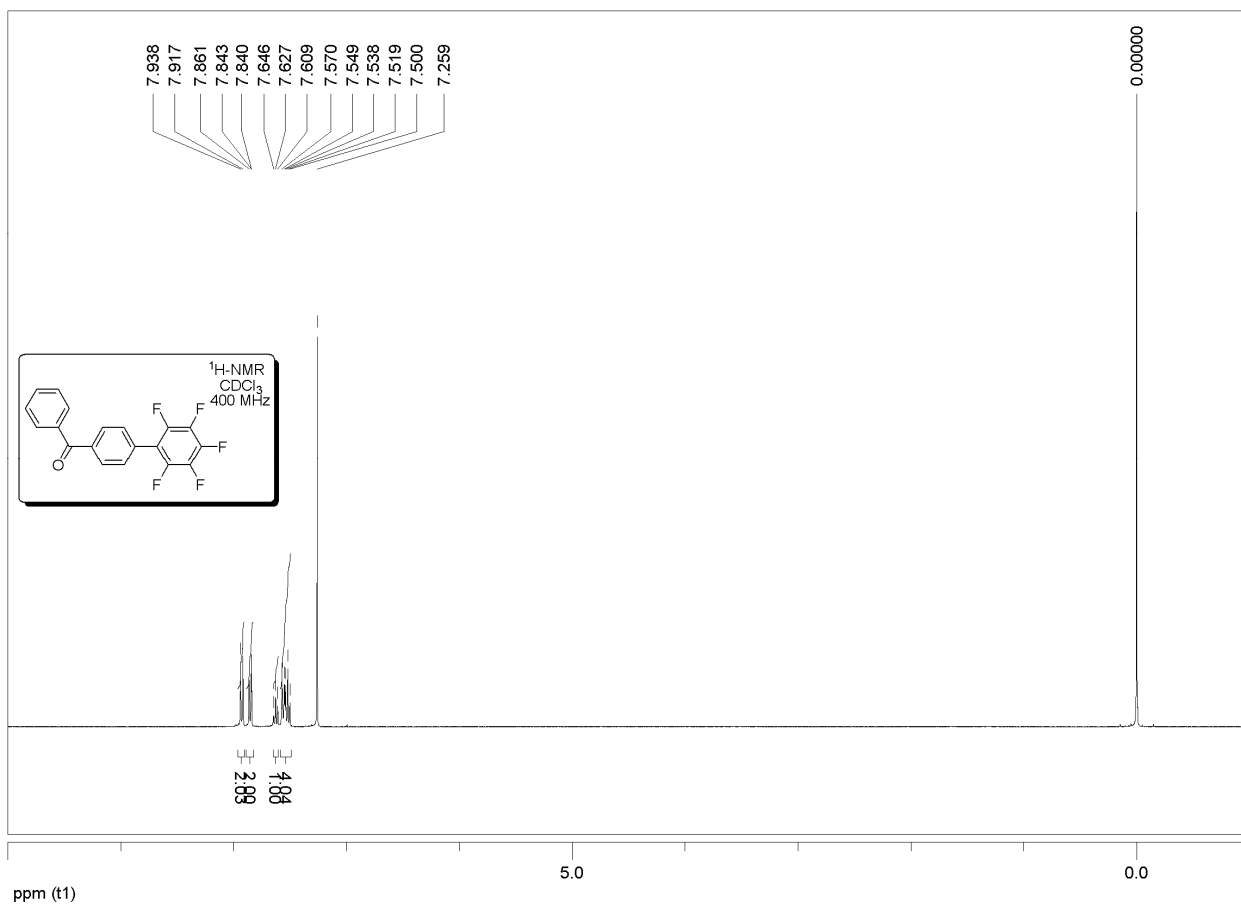
**5-(perfluorophenyl)benzo[d][1,3]dioxole (11)**

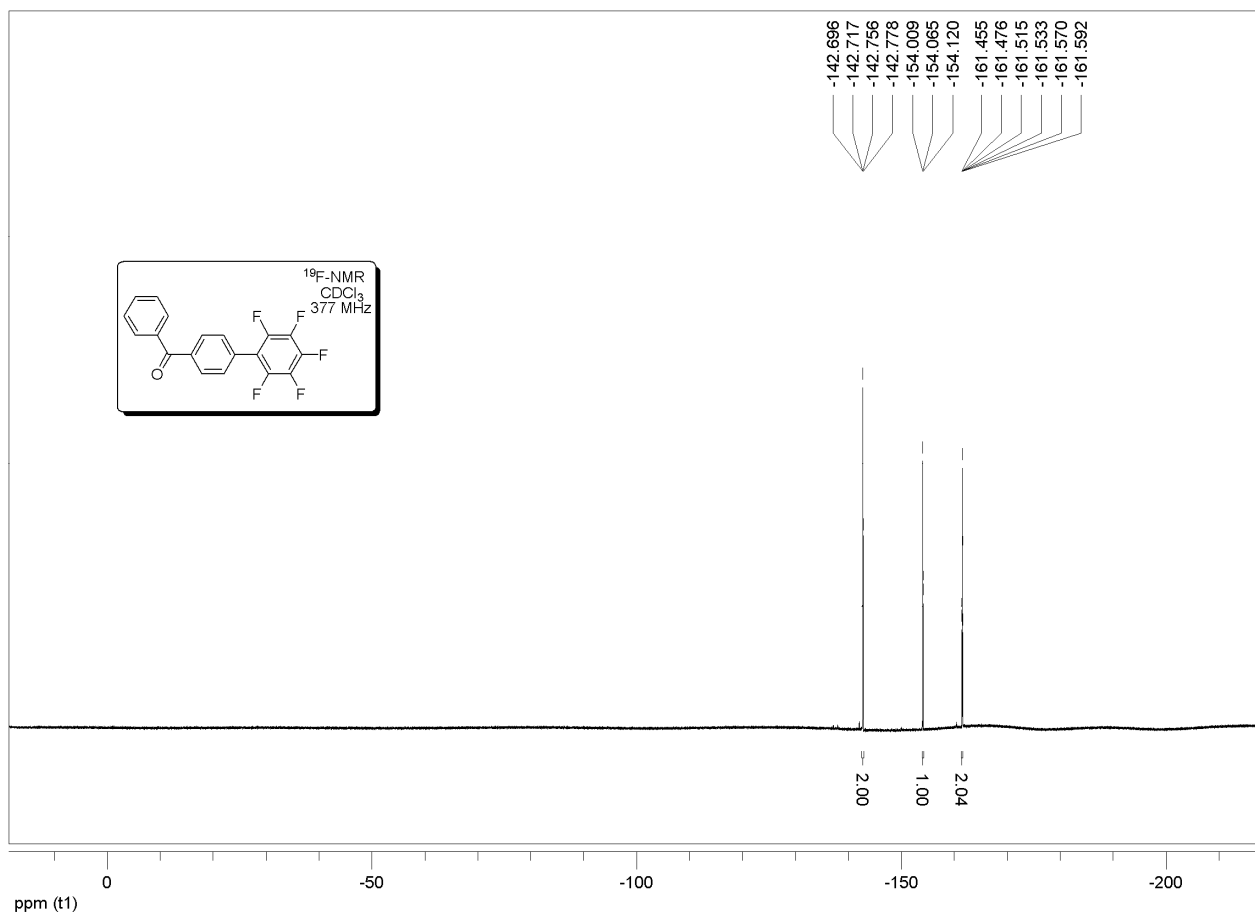
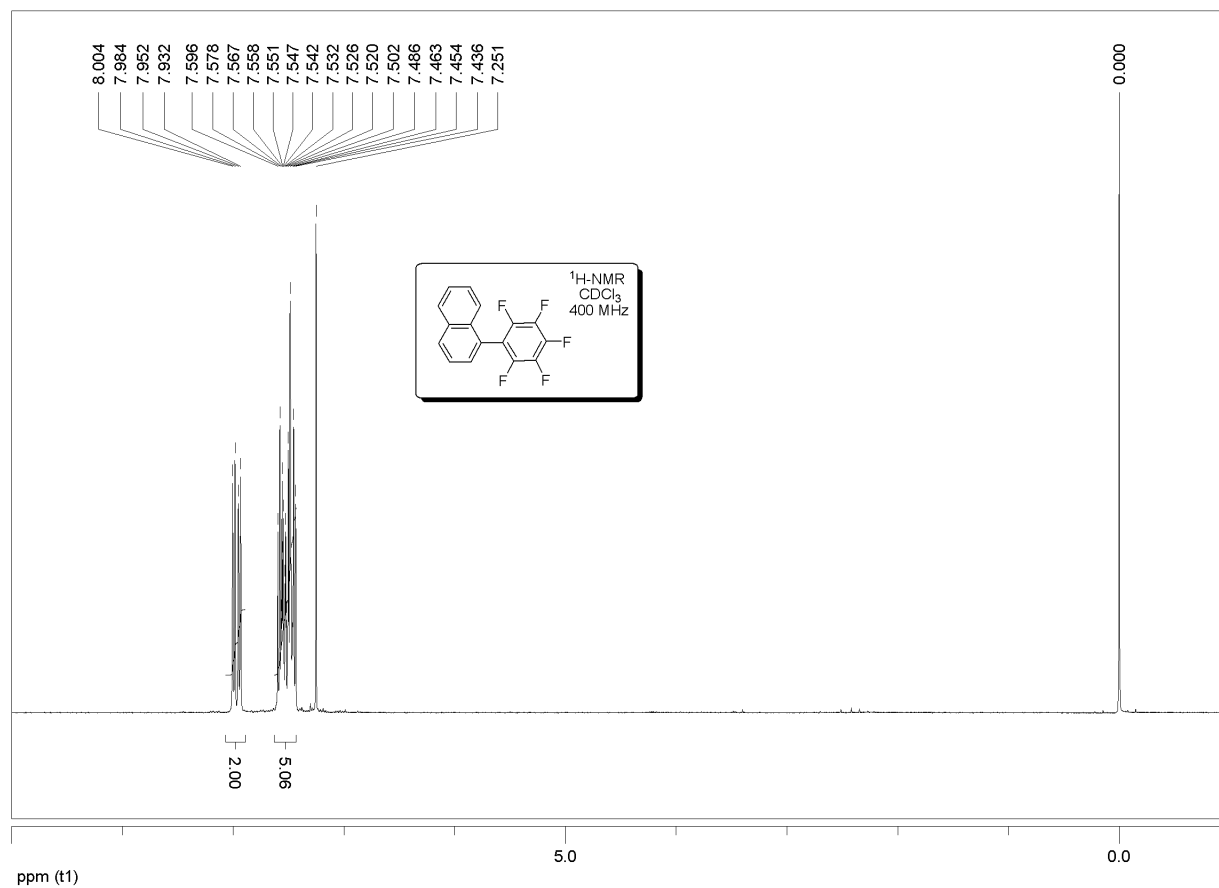


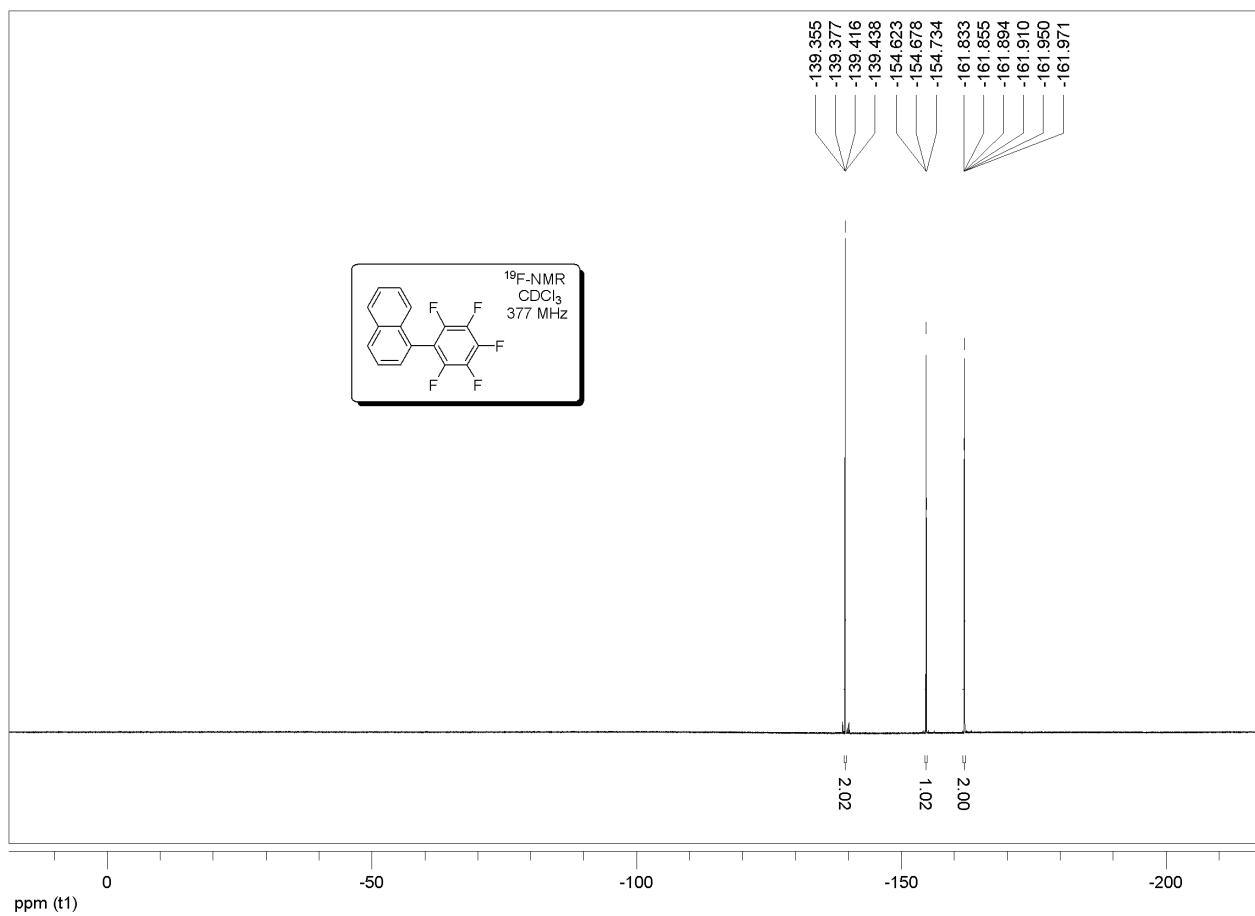
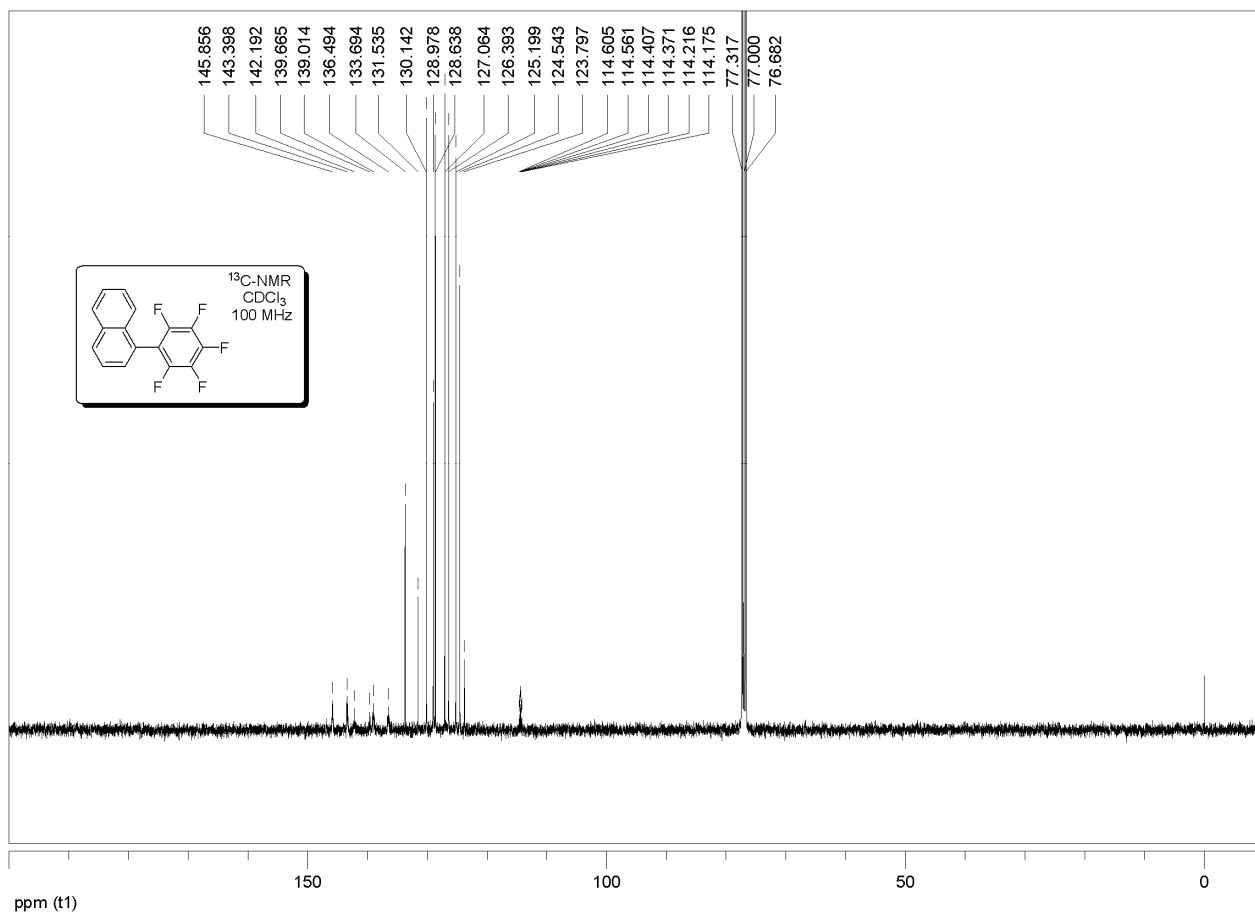
2, 3, 4, 4', 5, 6-hexafluorobiphenyl (12)

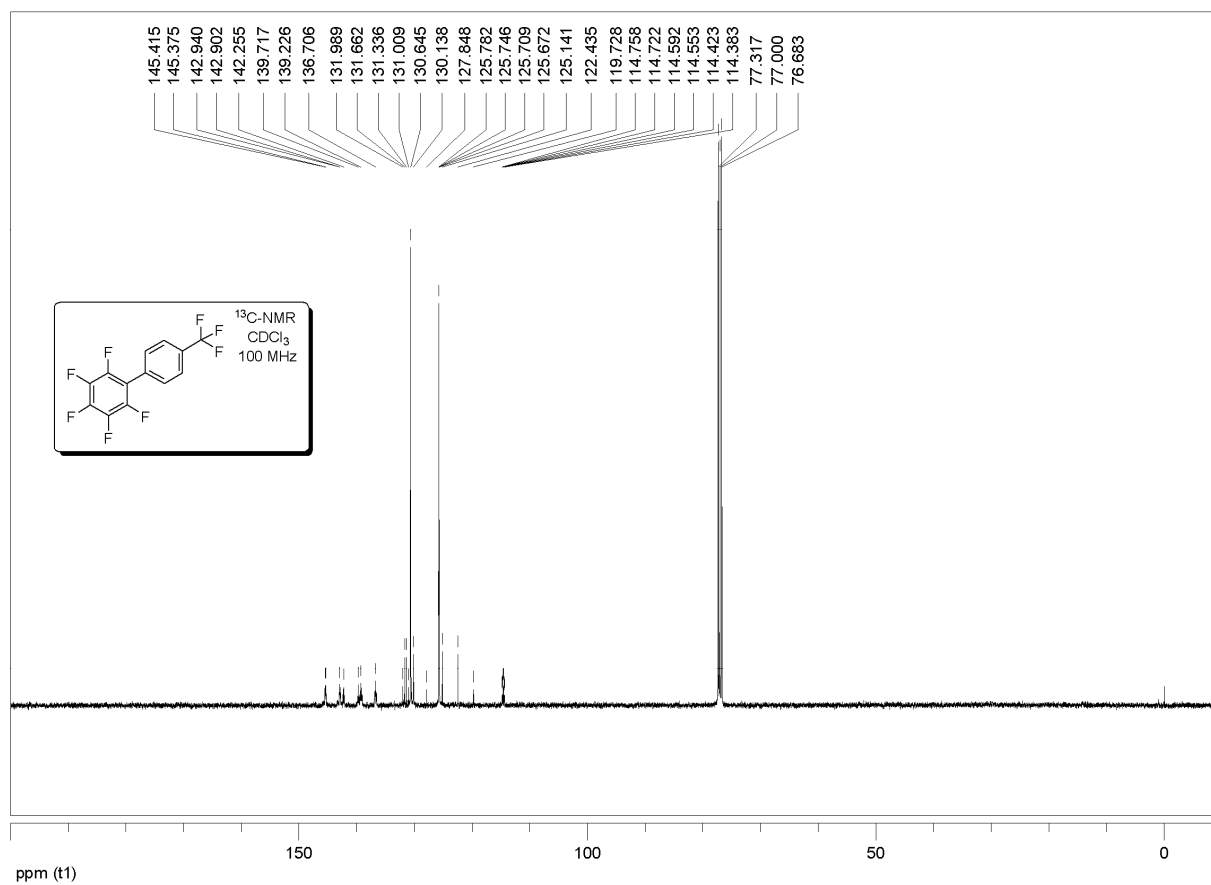
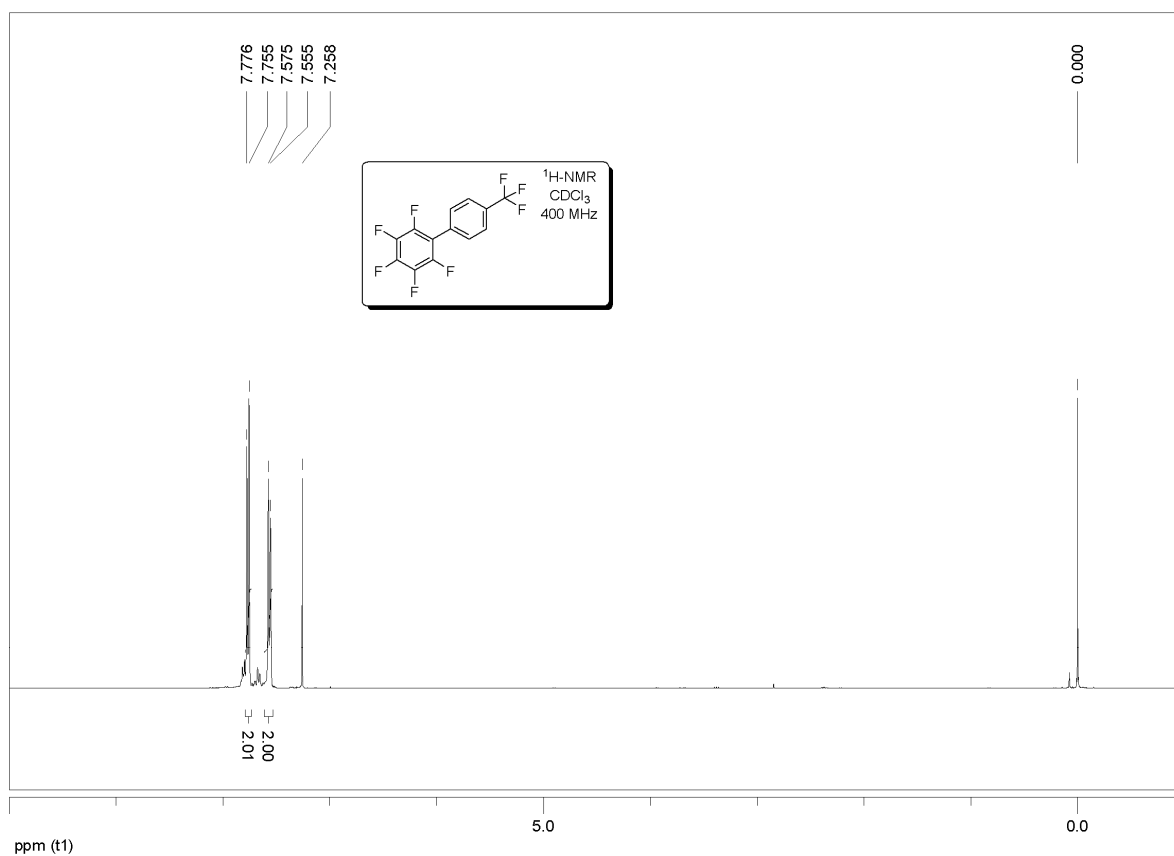
**2', 3', 4', 5', 6'-pentafluorobiphenyl-4-yl 4-methylbenzenesulfonate (13)**

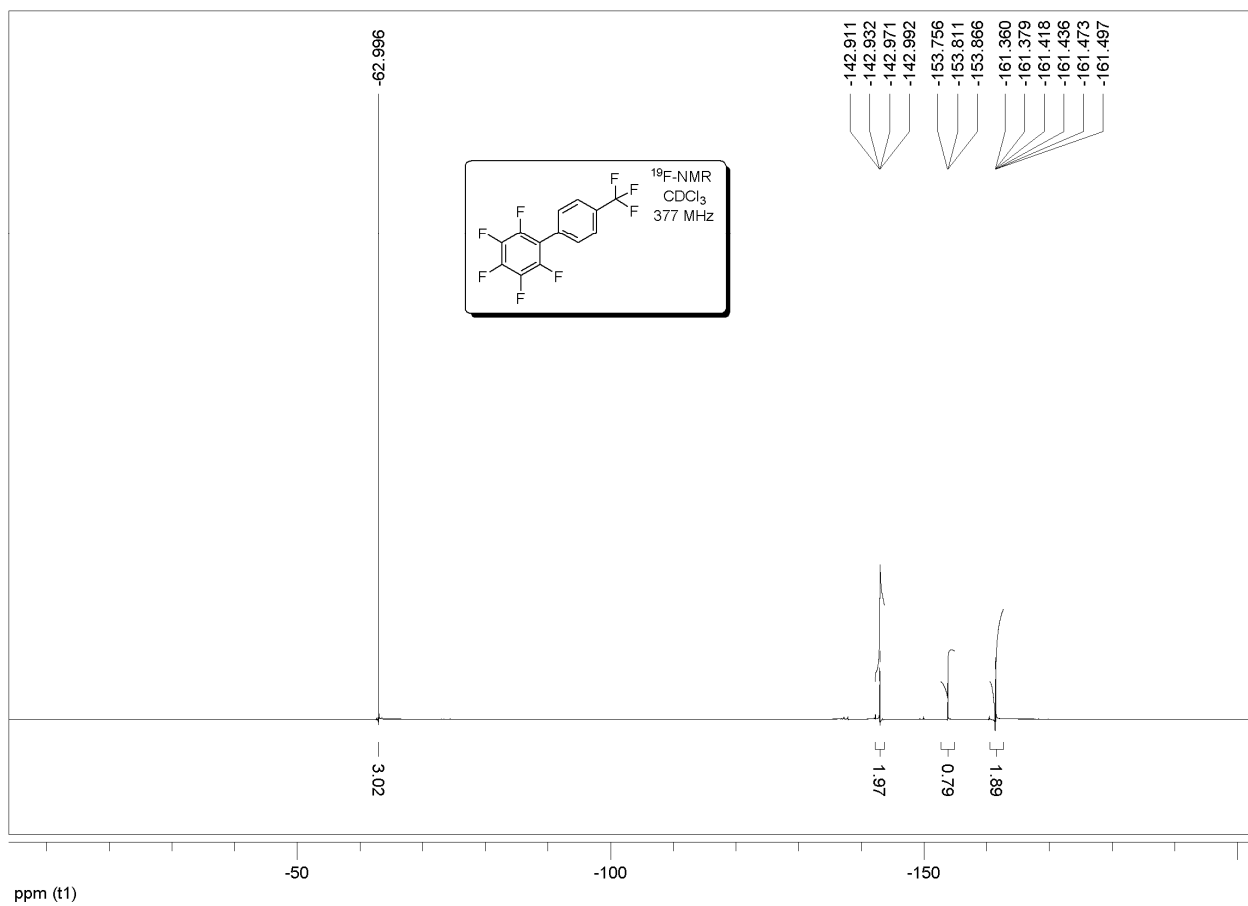
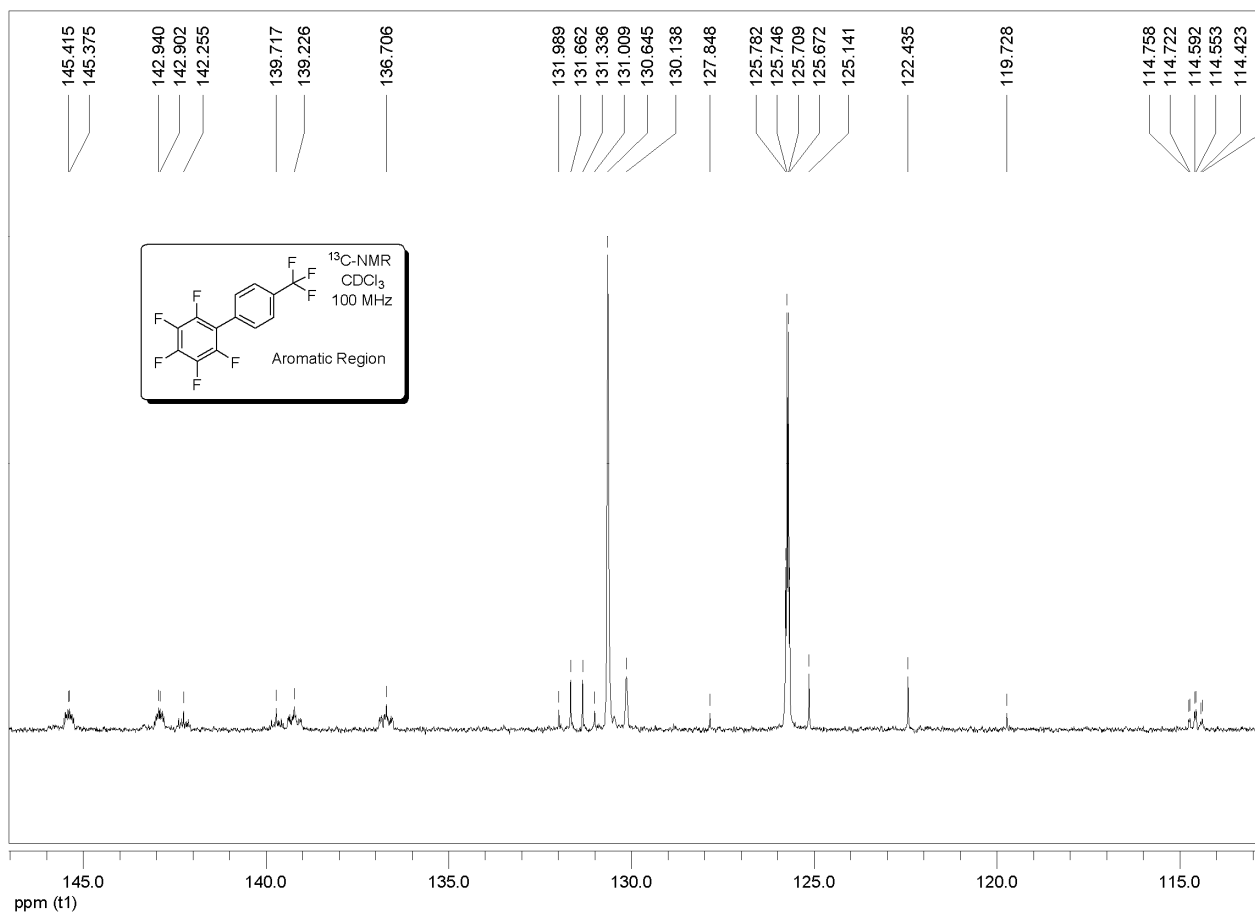


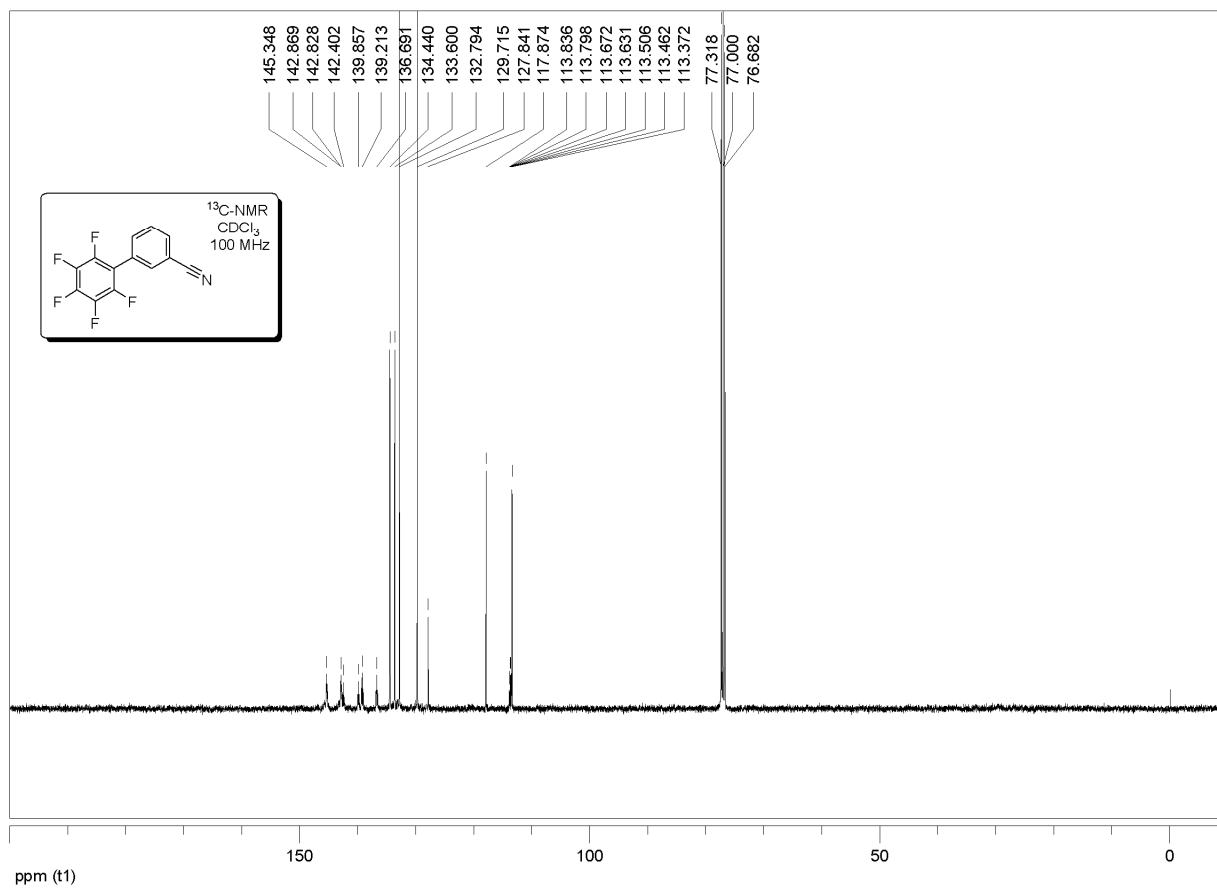
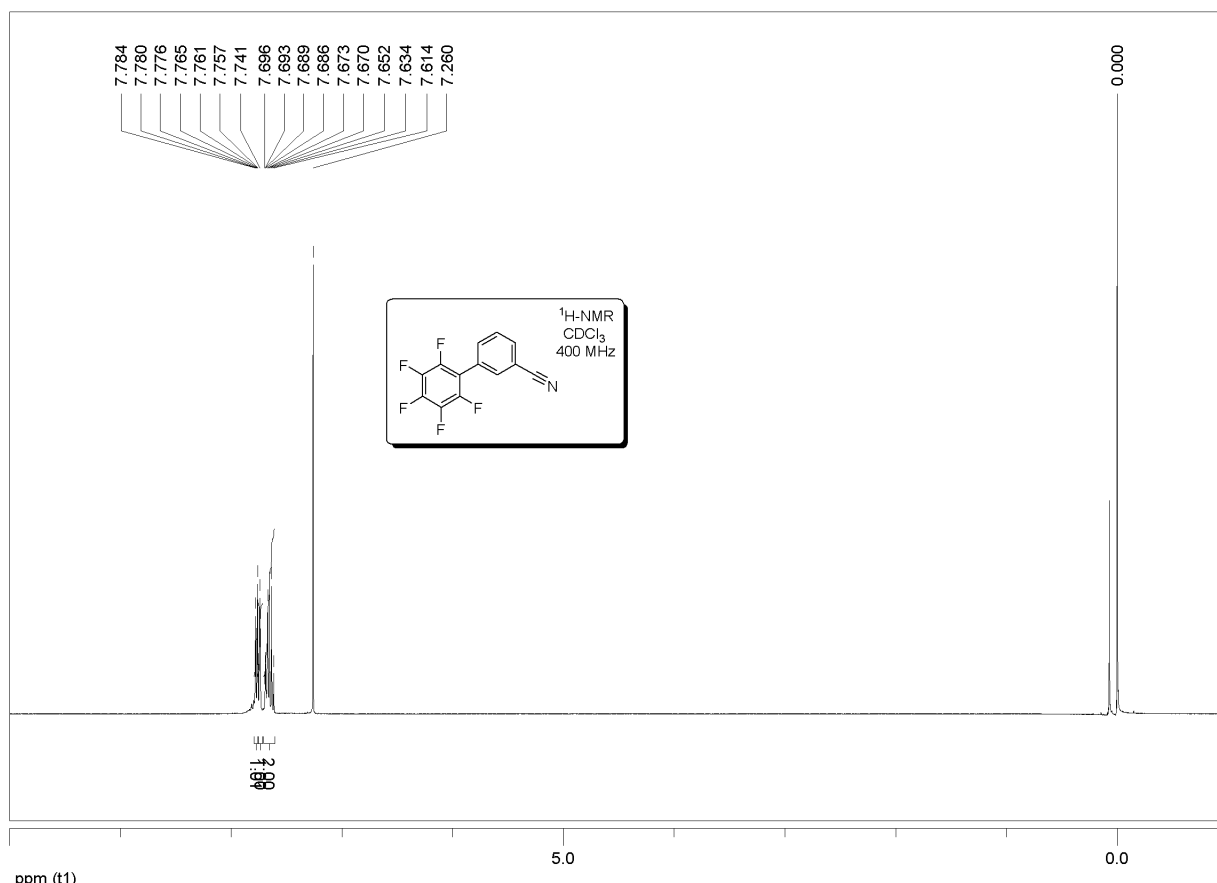
(2', 3', 4', 5', 6'-pentafluorobiphenyl-4-yl)(phenyl)methanone (14)

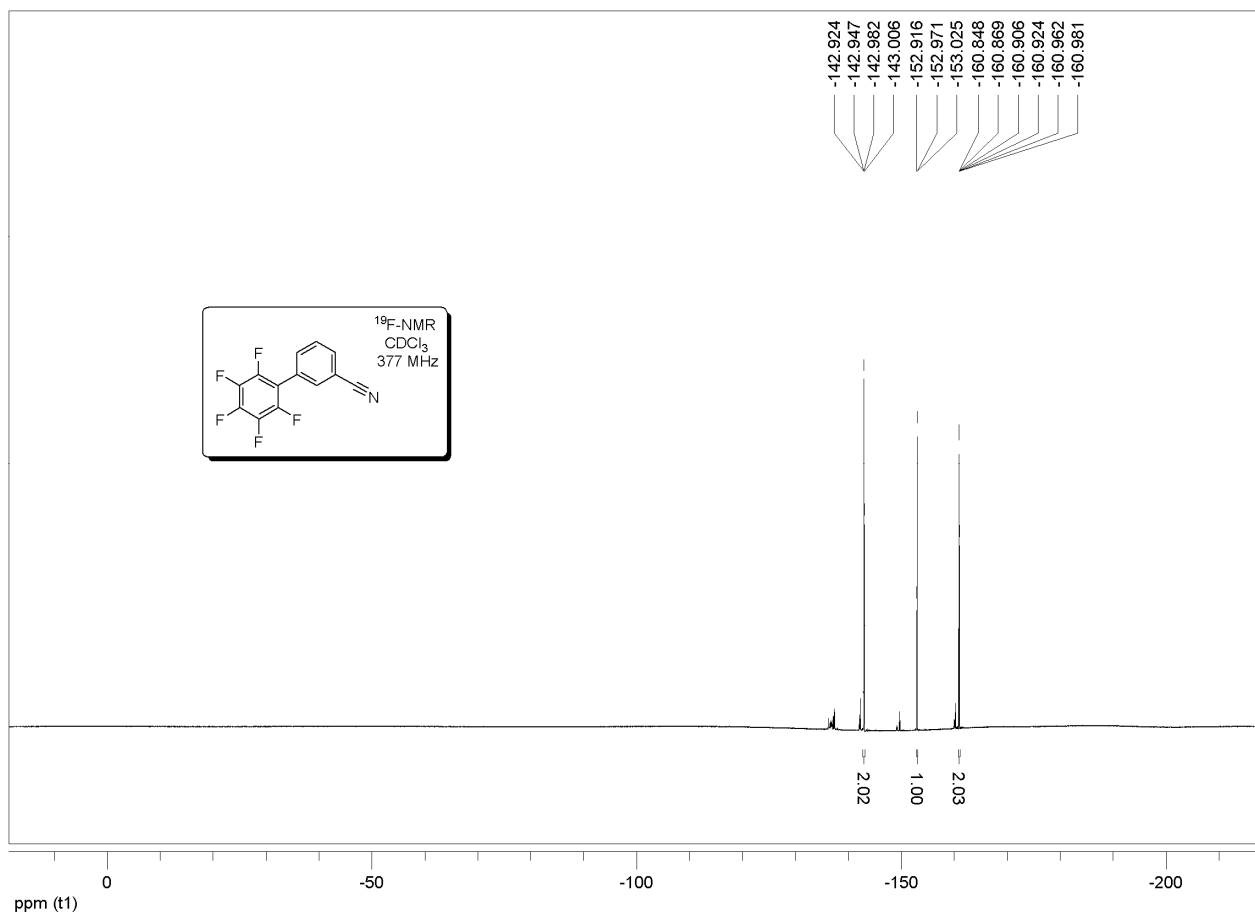
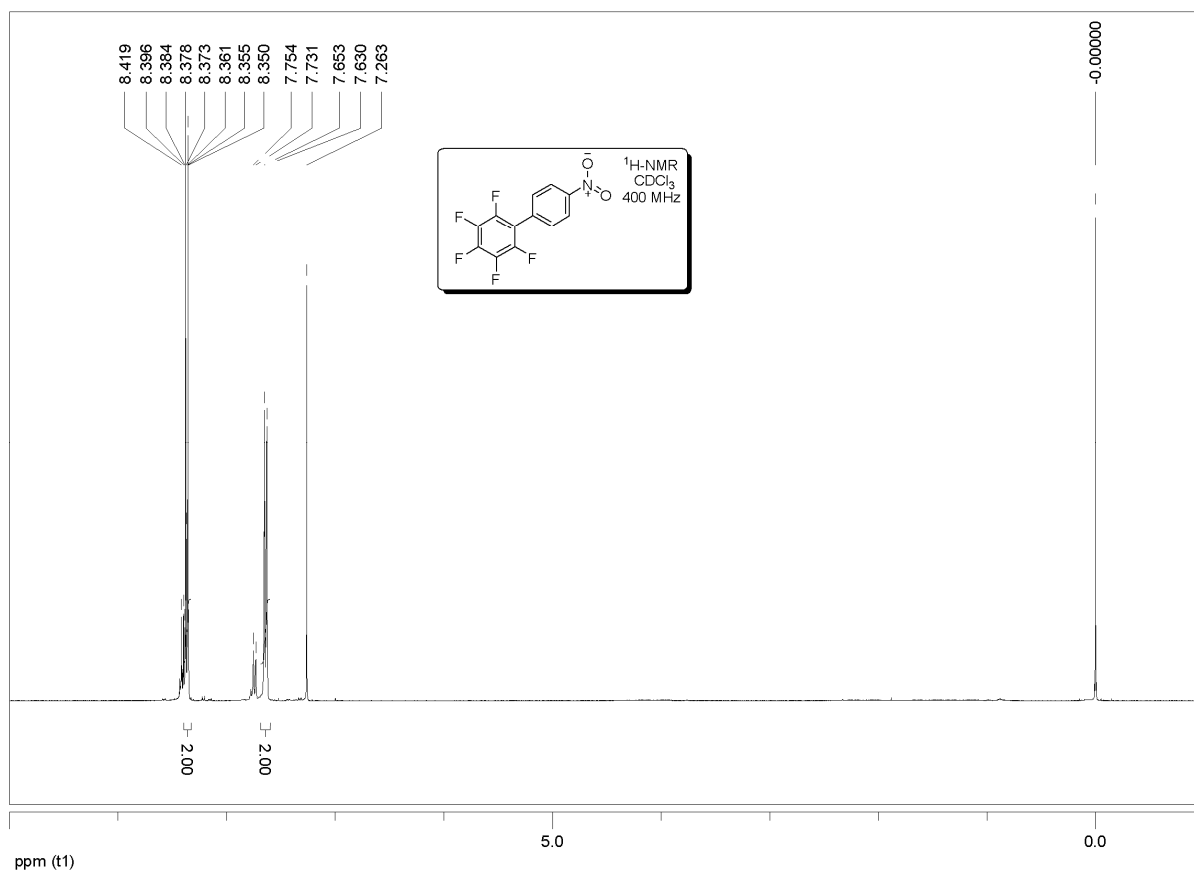
**1-(perfluorophenyl) naphthalene (15)**

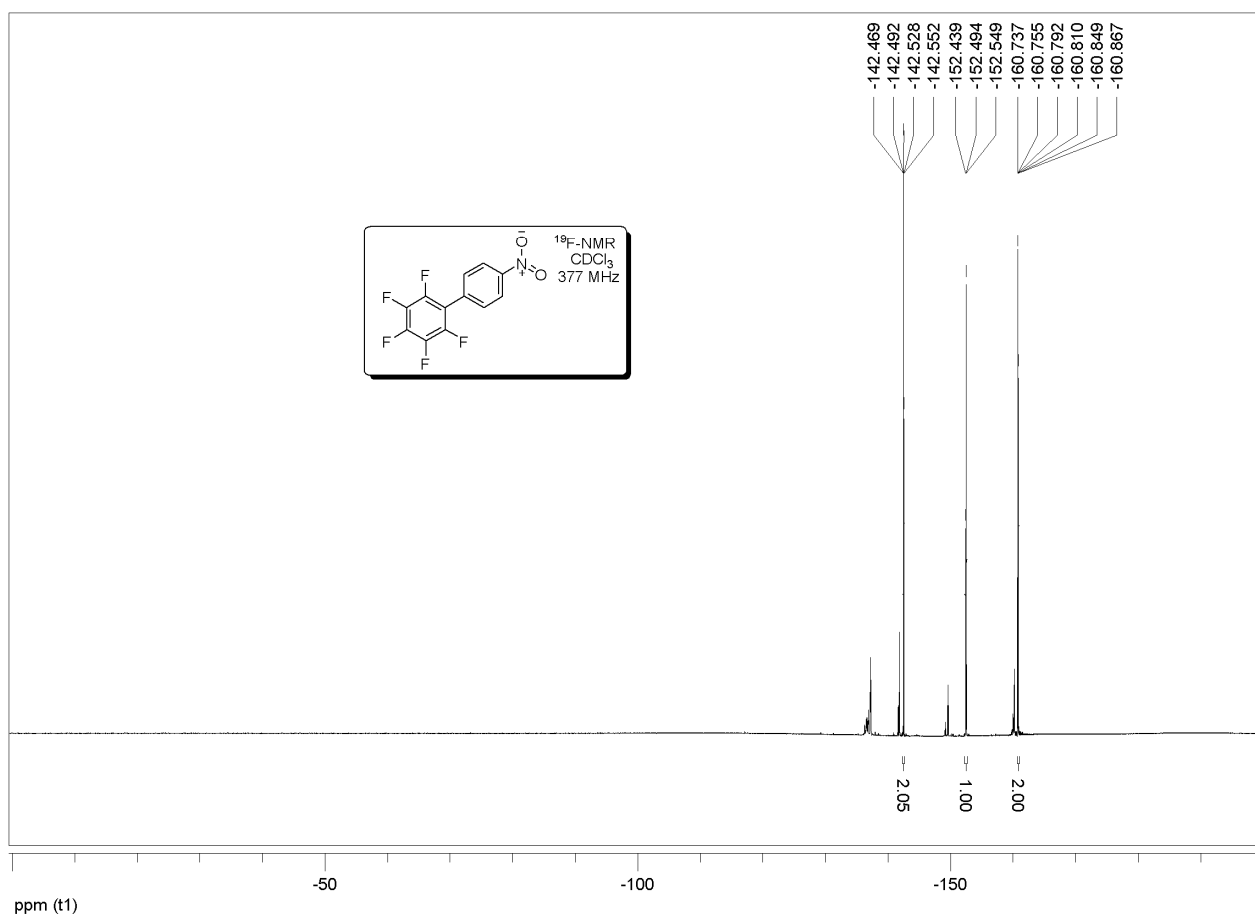
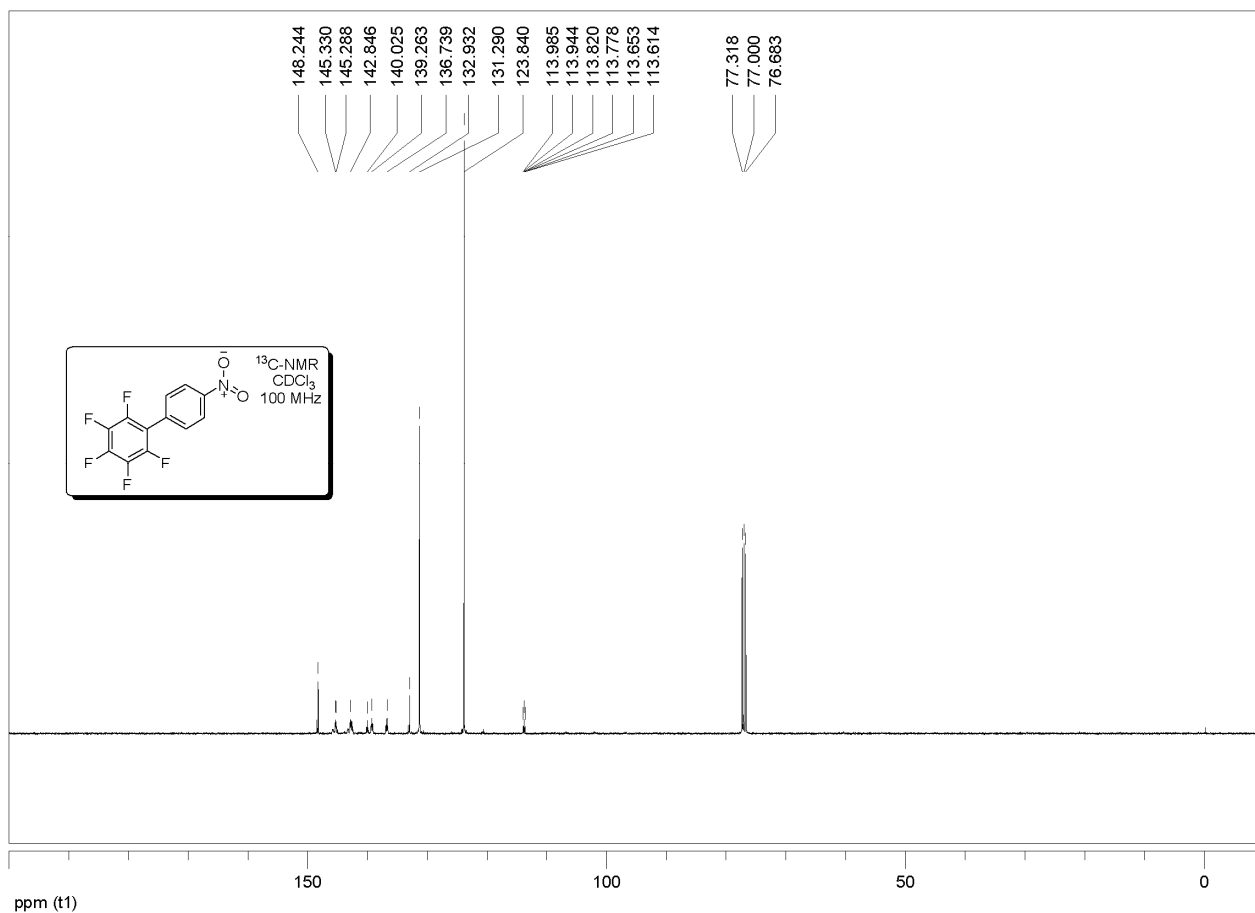


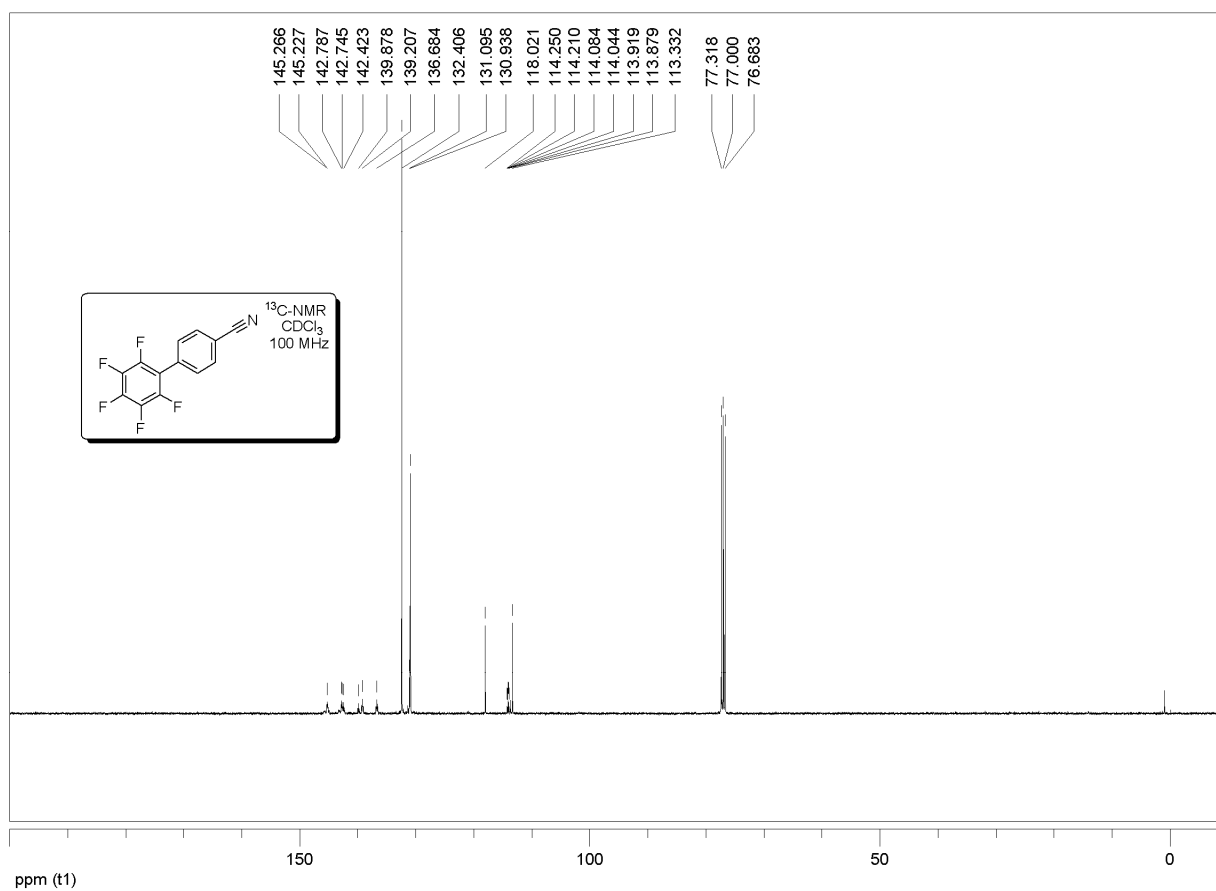
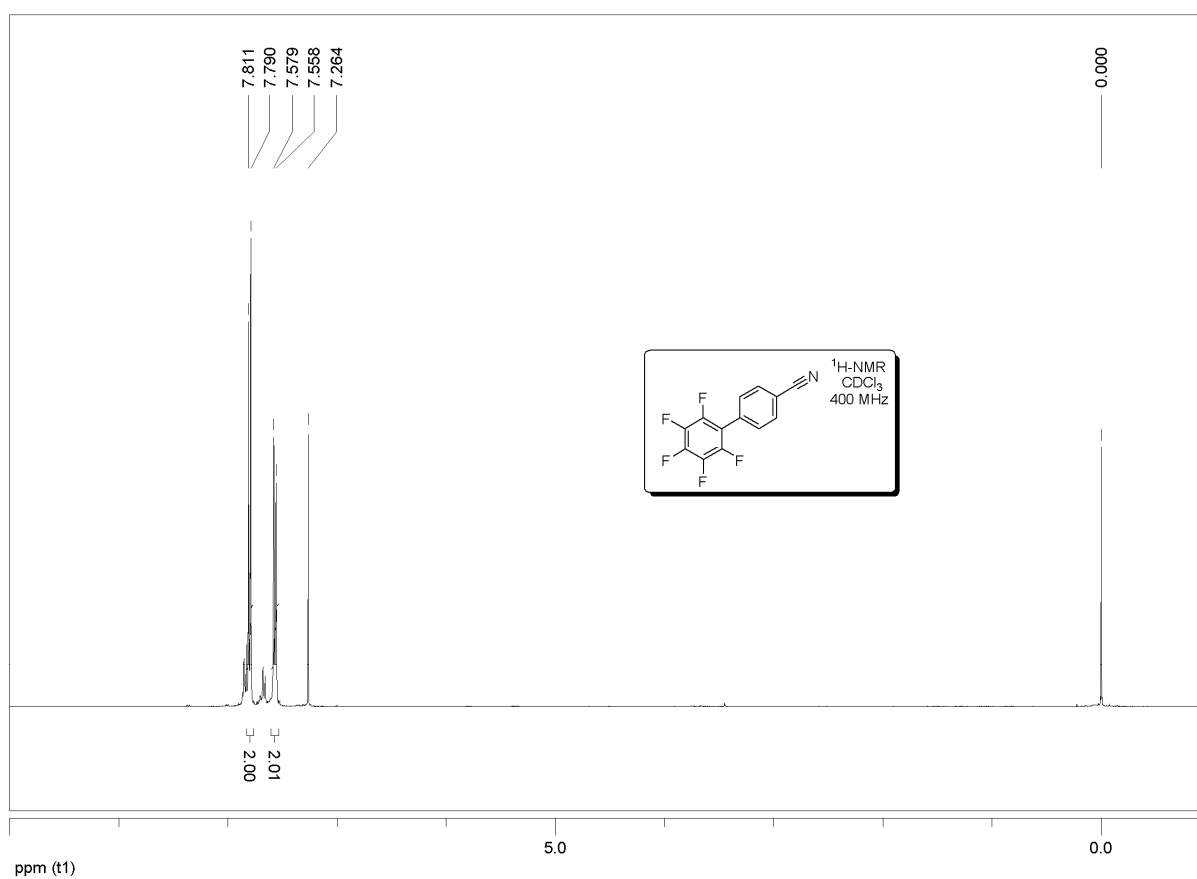
2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)biphenyl (16)

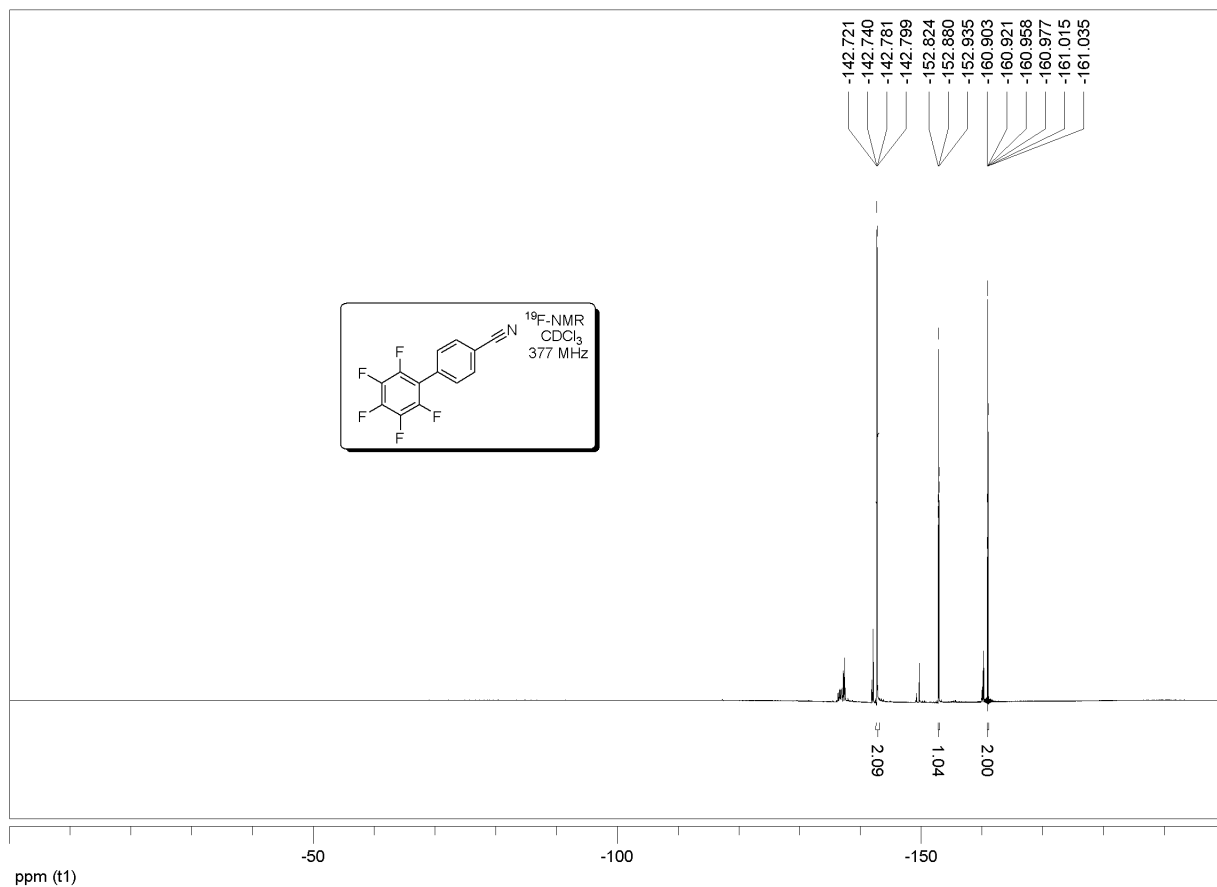
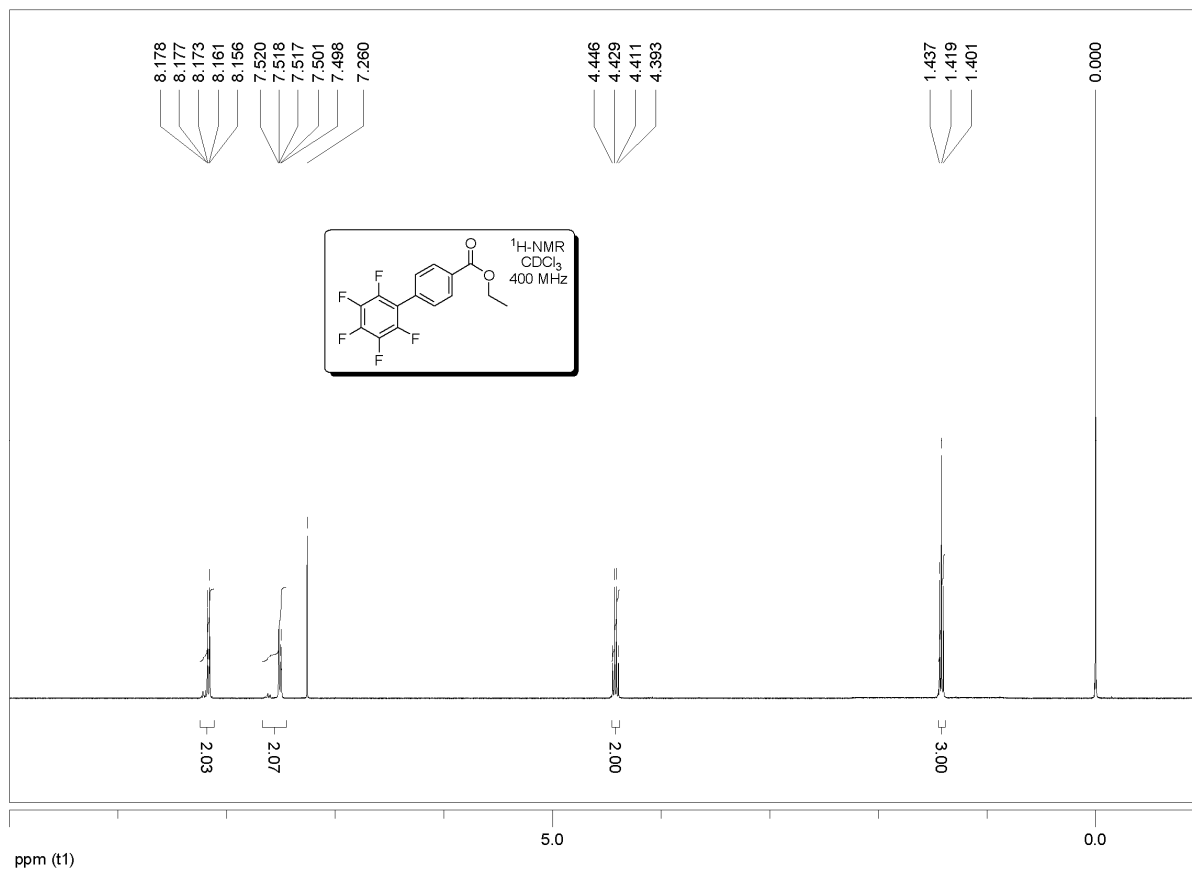


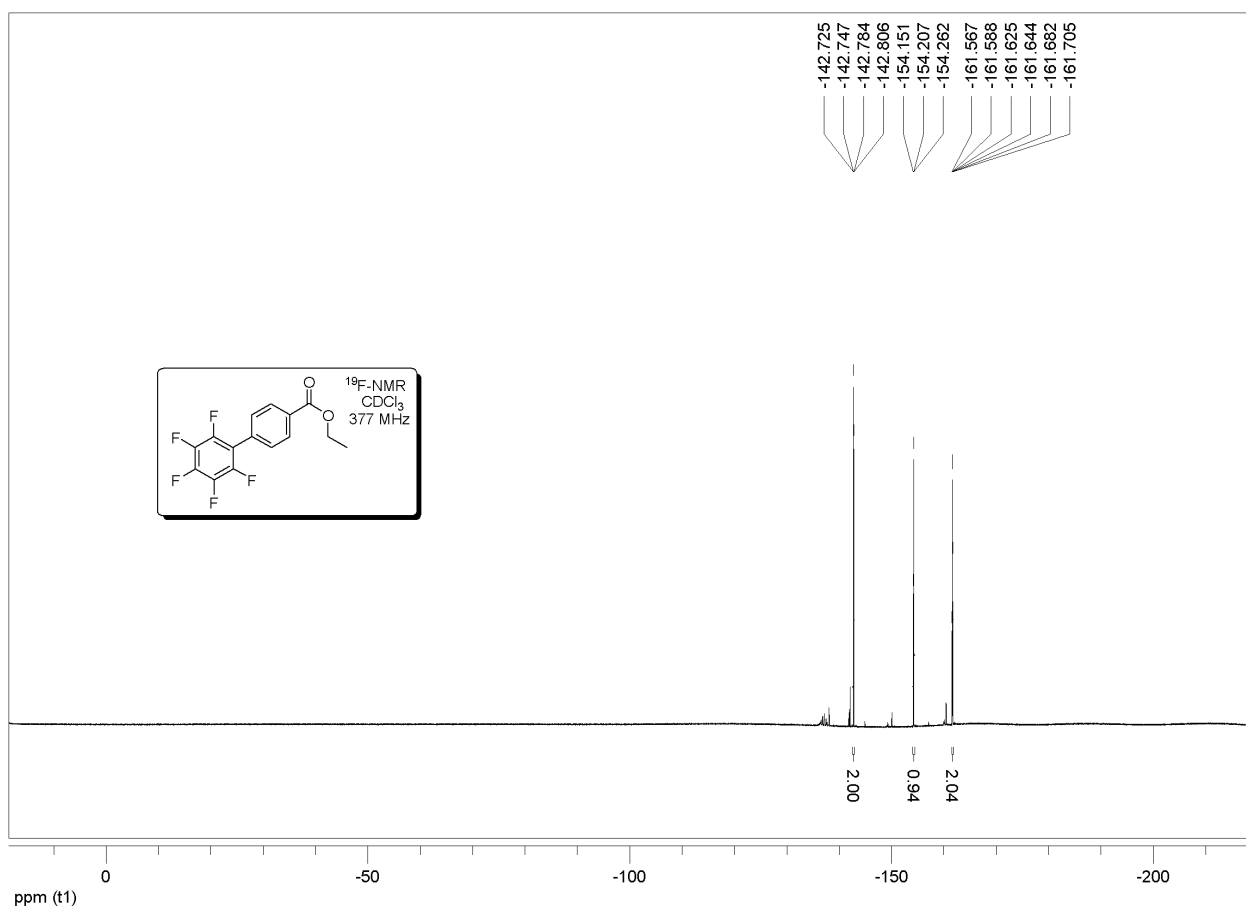
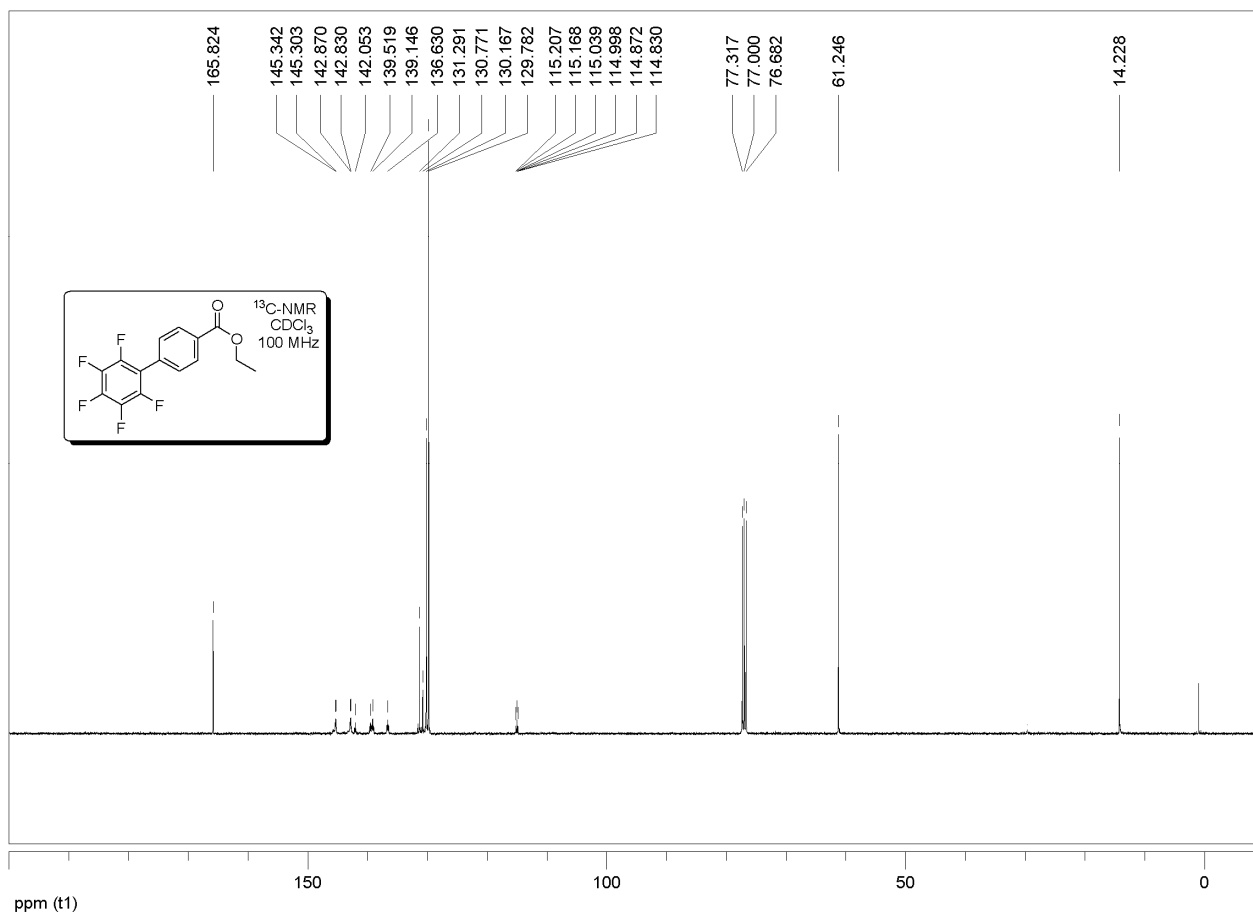
2', 3', 4', 5', 6'-pentafluorobiphenyl-3-carbonitrile (17)

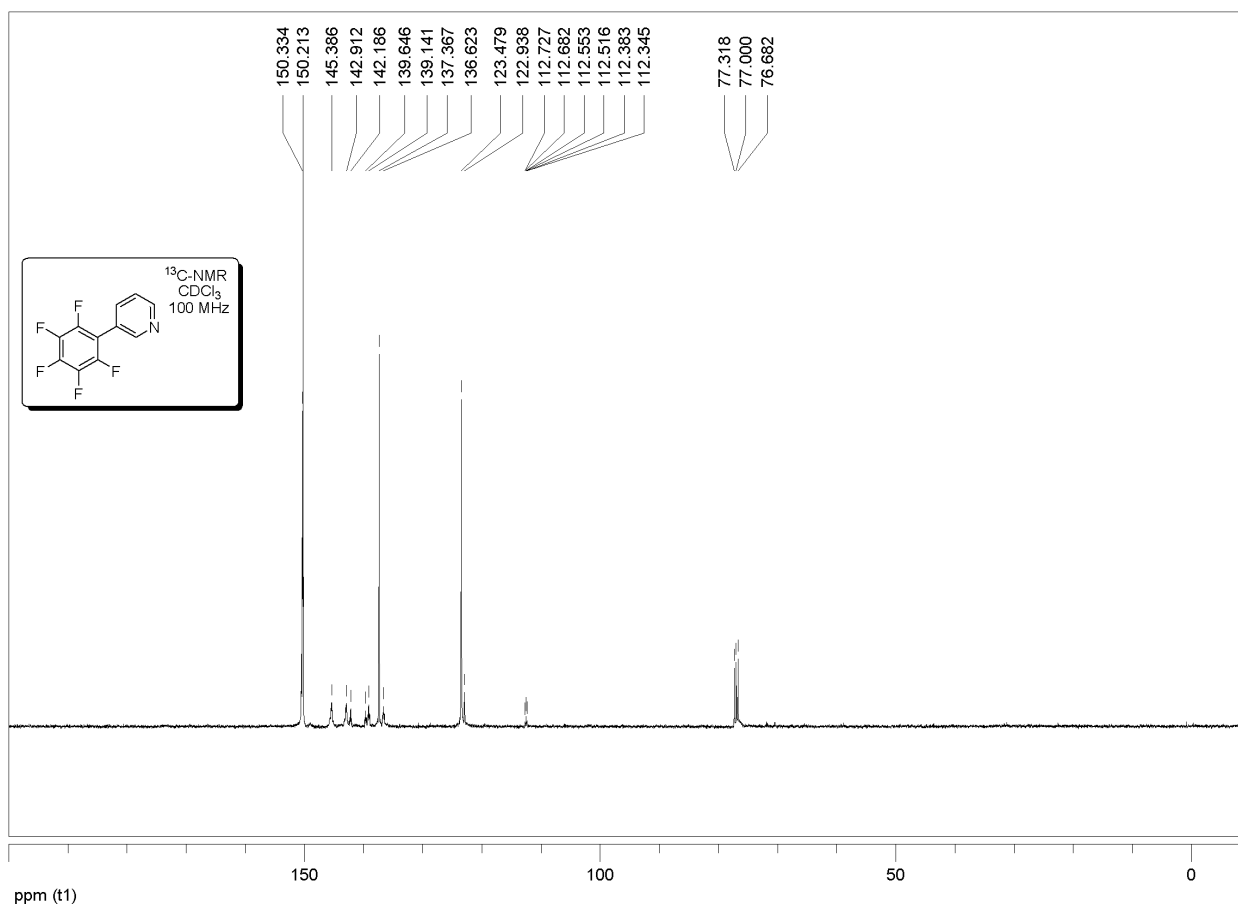
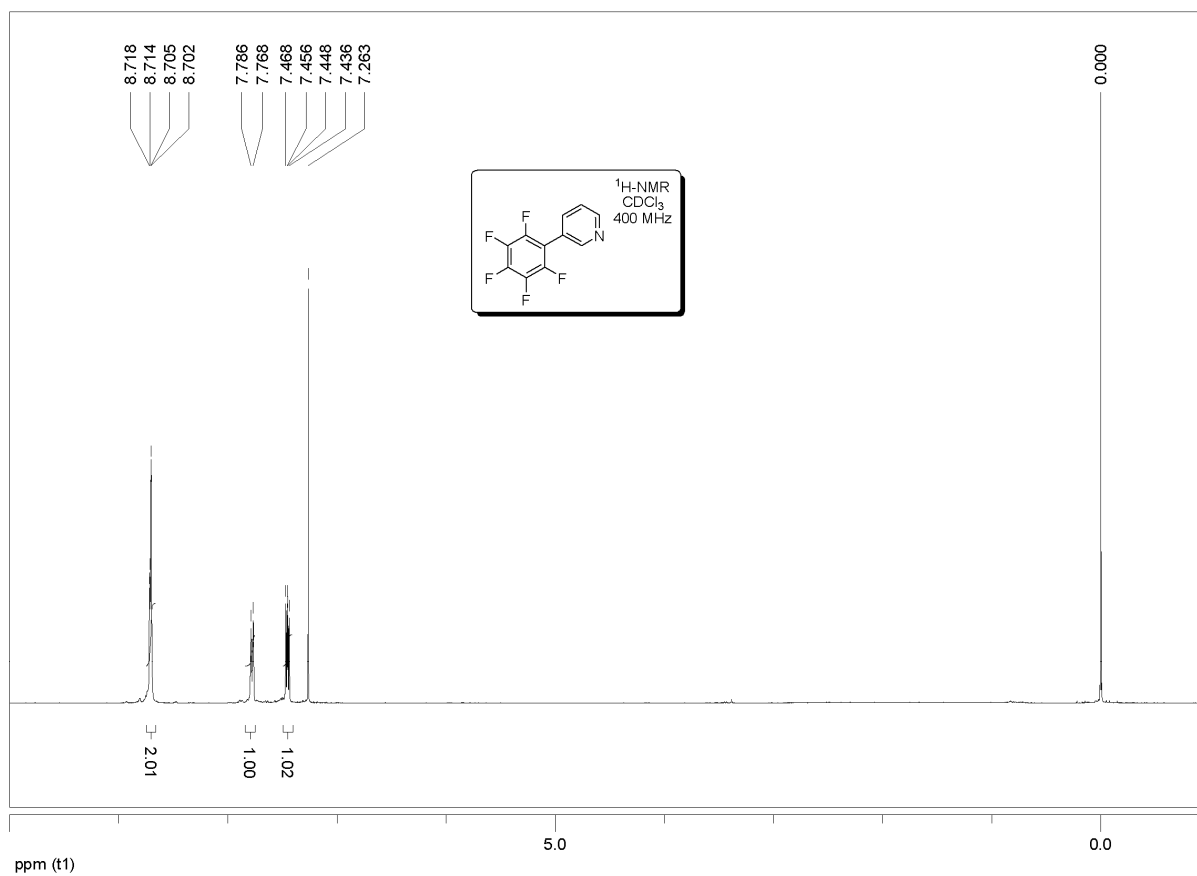
**2, 3, 4, 5, 6-pentafluoro-4'-nitrophenyl (18)**

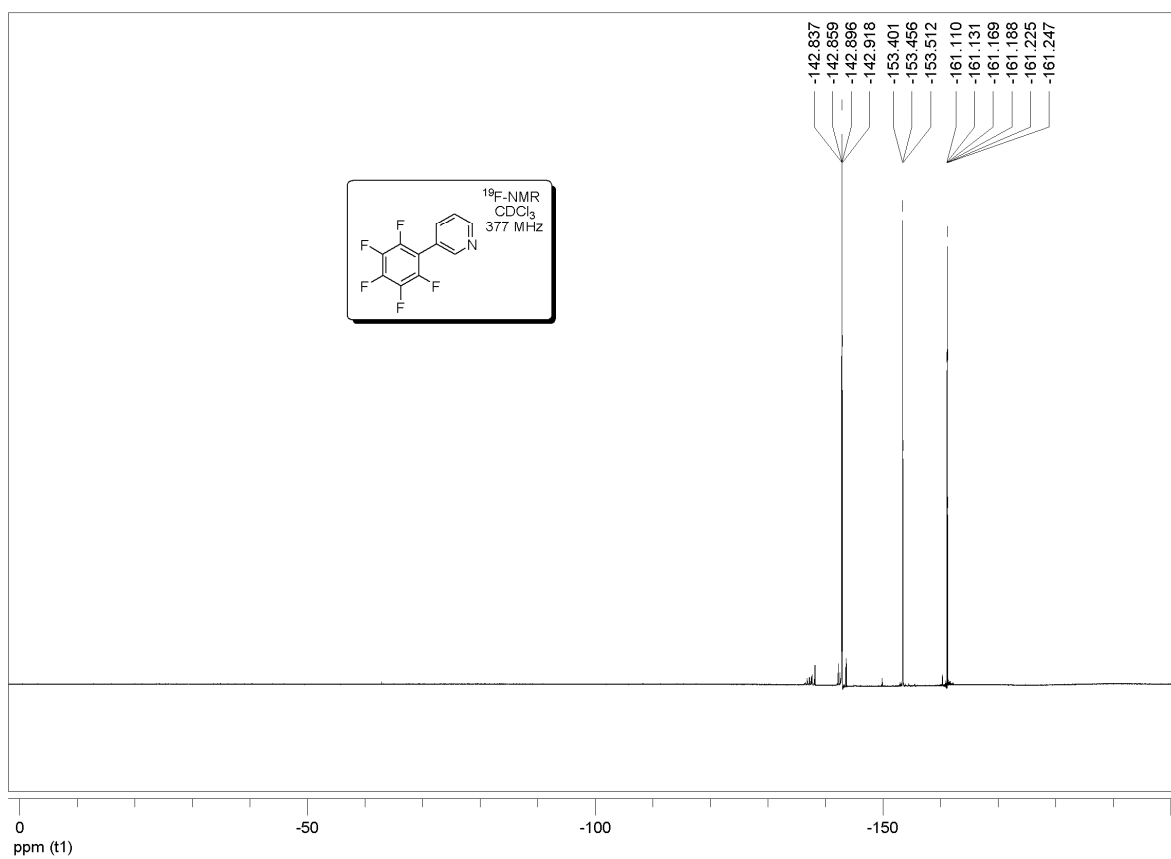
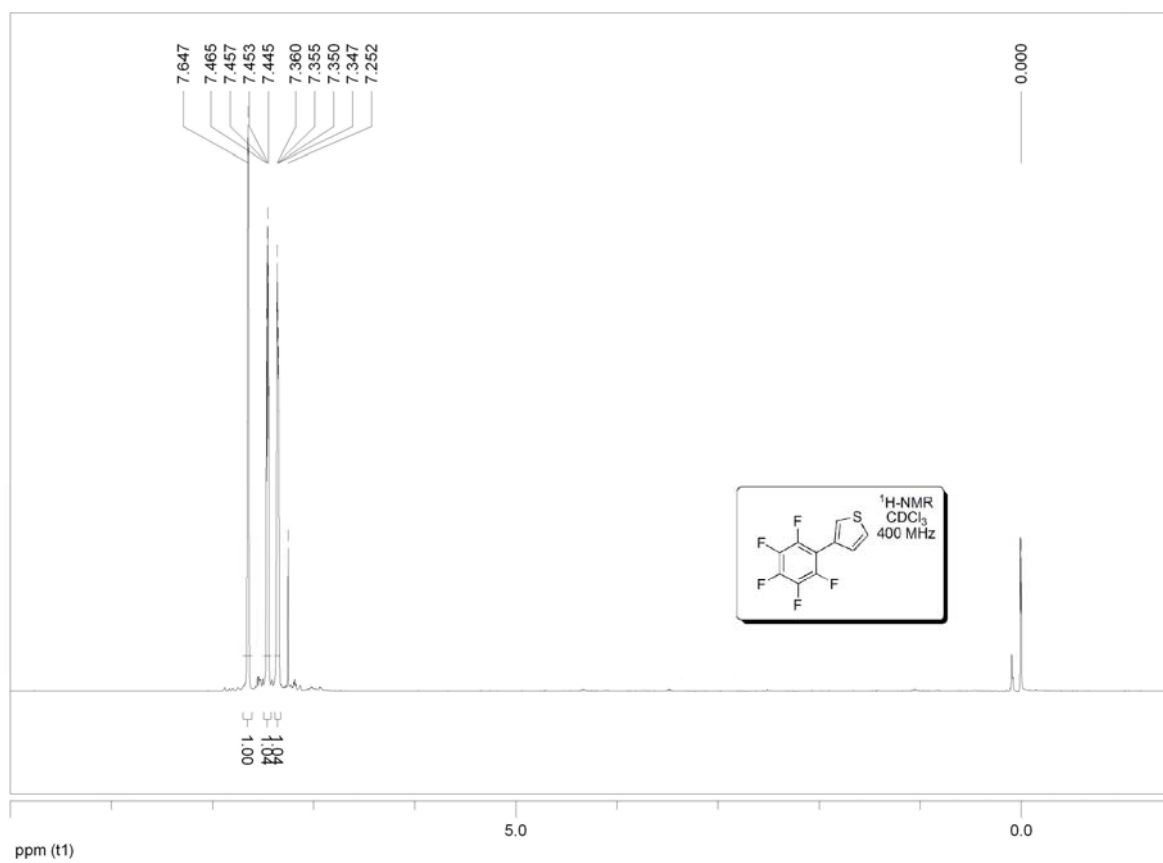


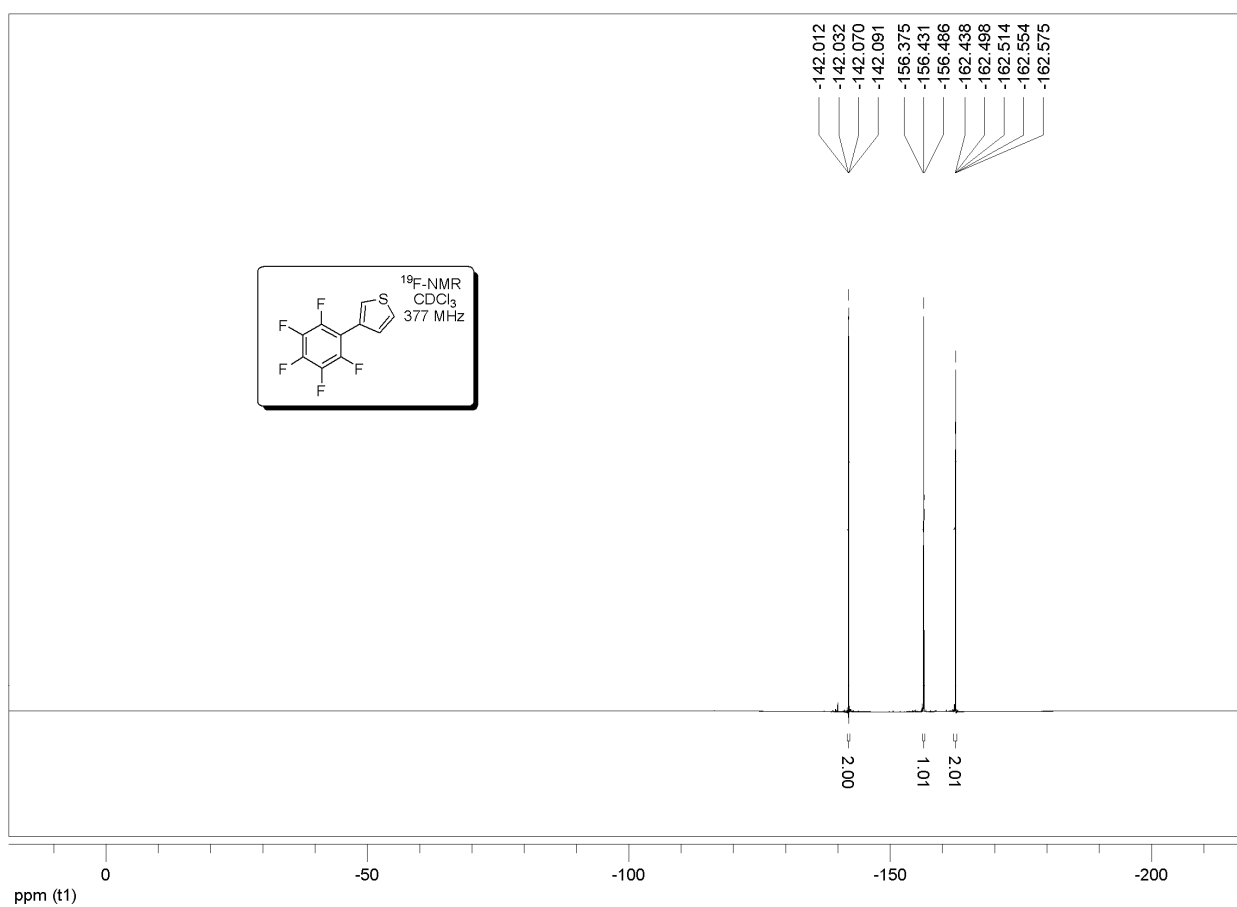
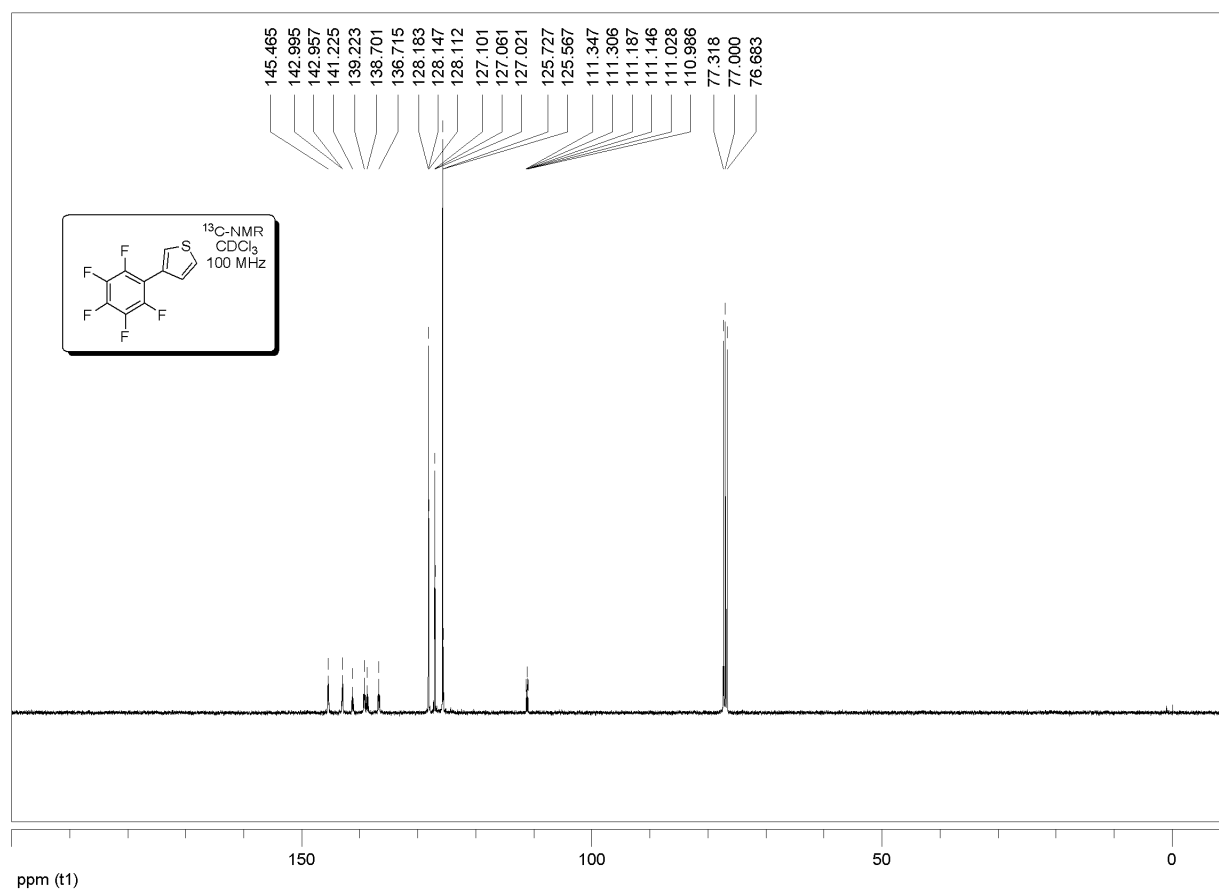
2', 3', 4', 5', 6'-pentafluorobiphenyl-4-carbonitrile (19)

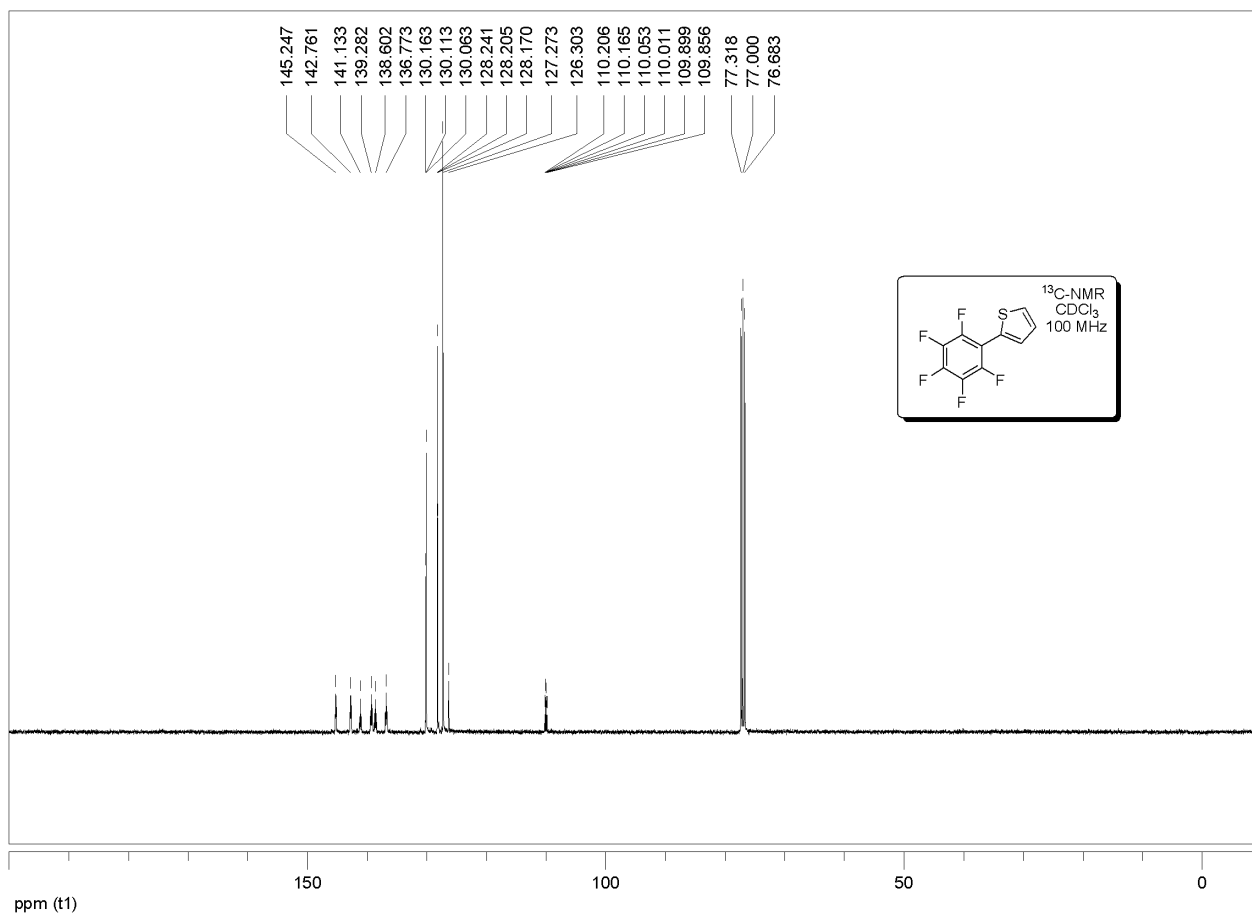
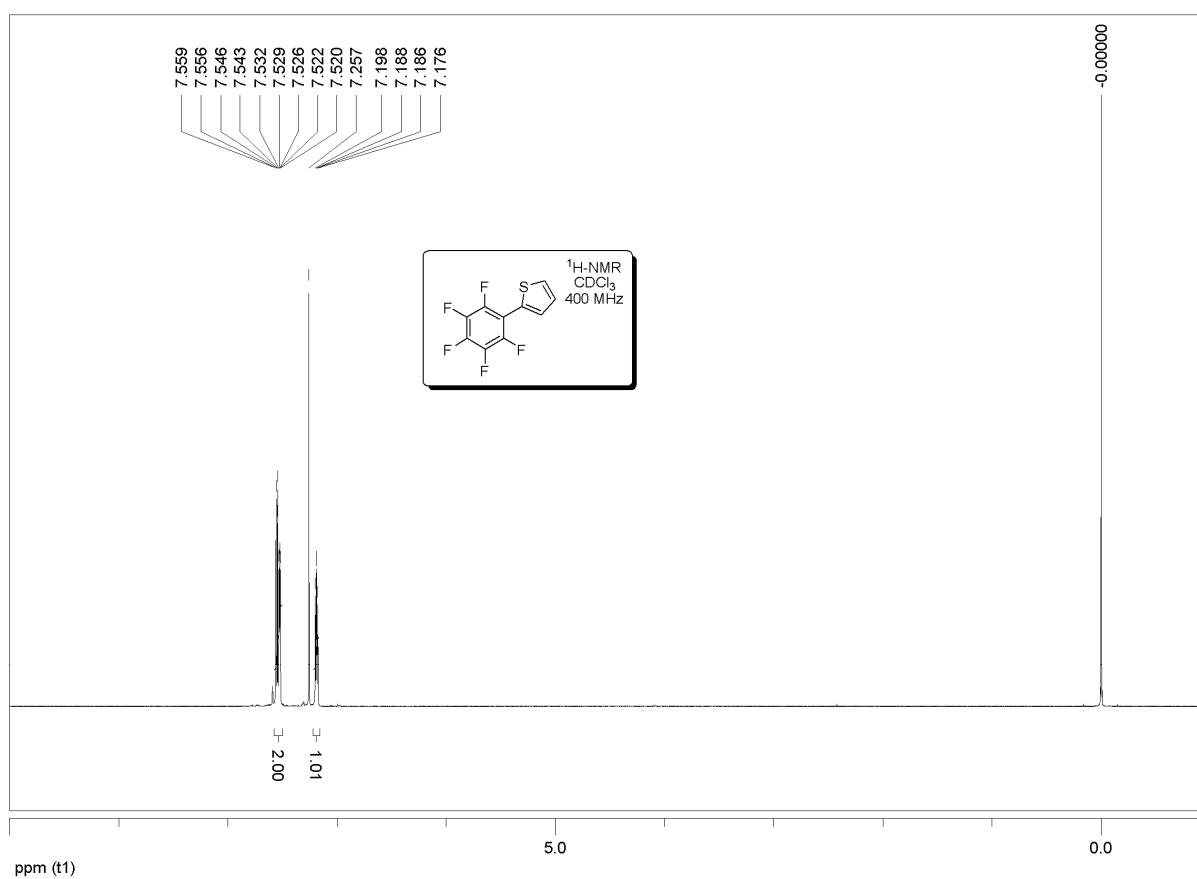
**ethyl 2', 3', 4', 5', 6'-pentafluorobiphenyl-4-carboxylate (20)**

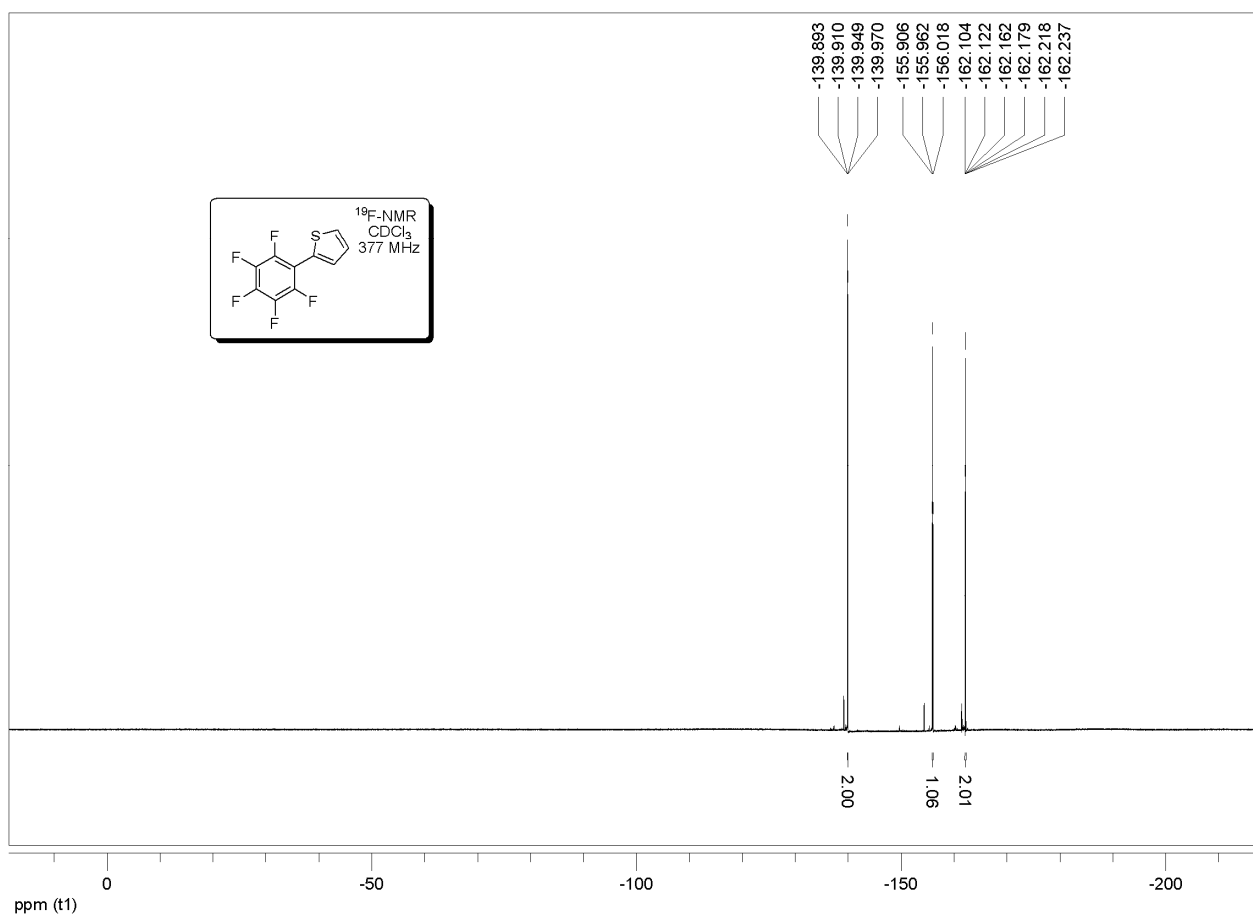
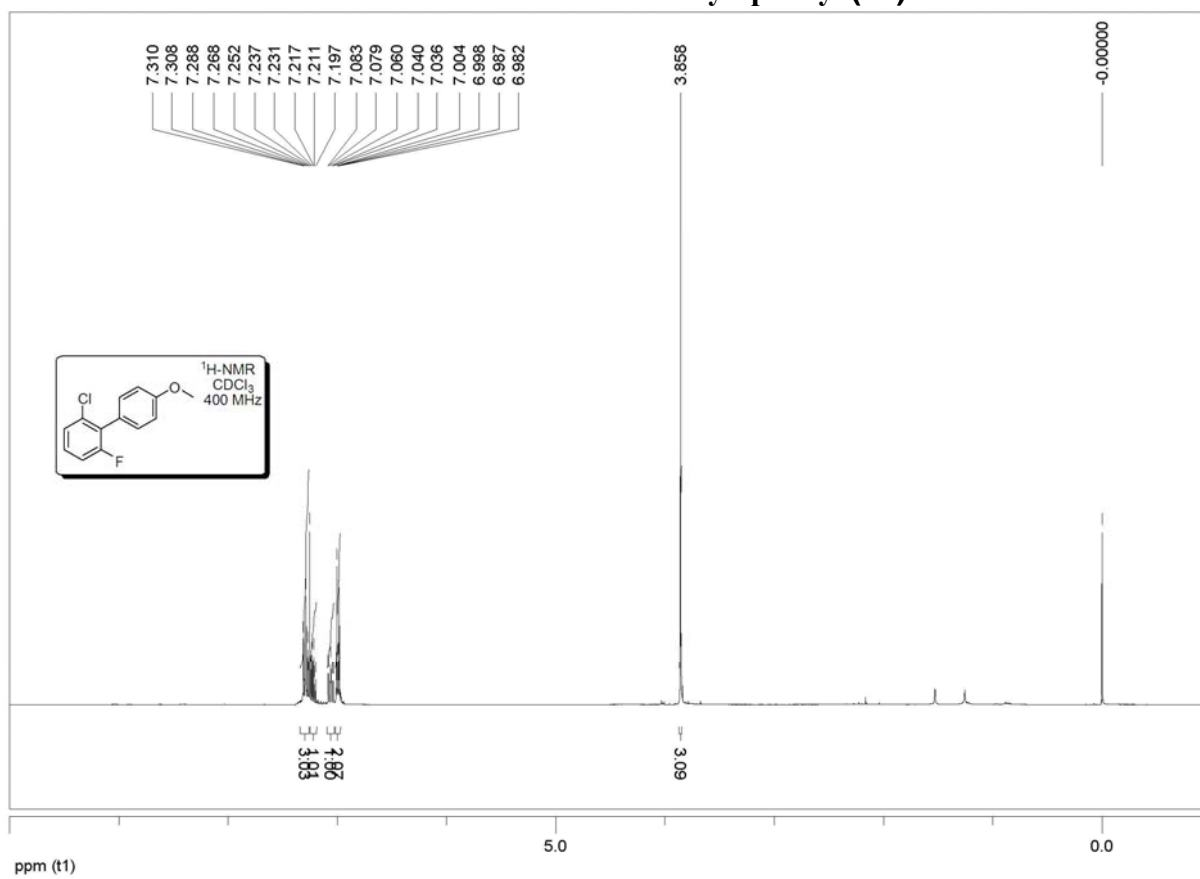


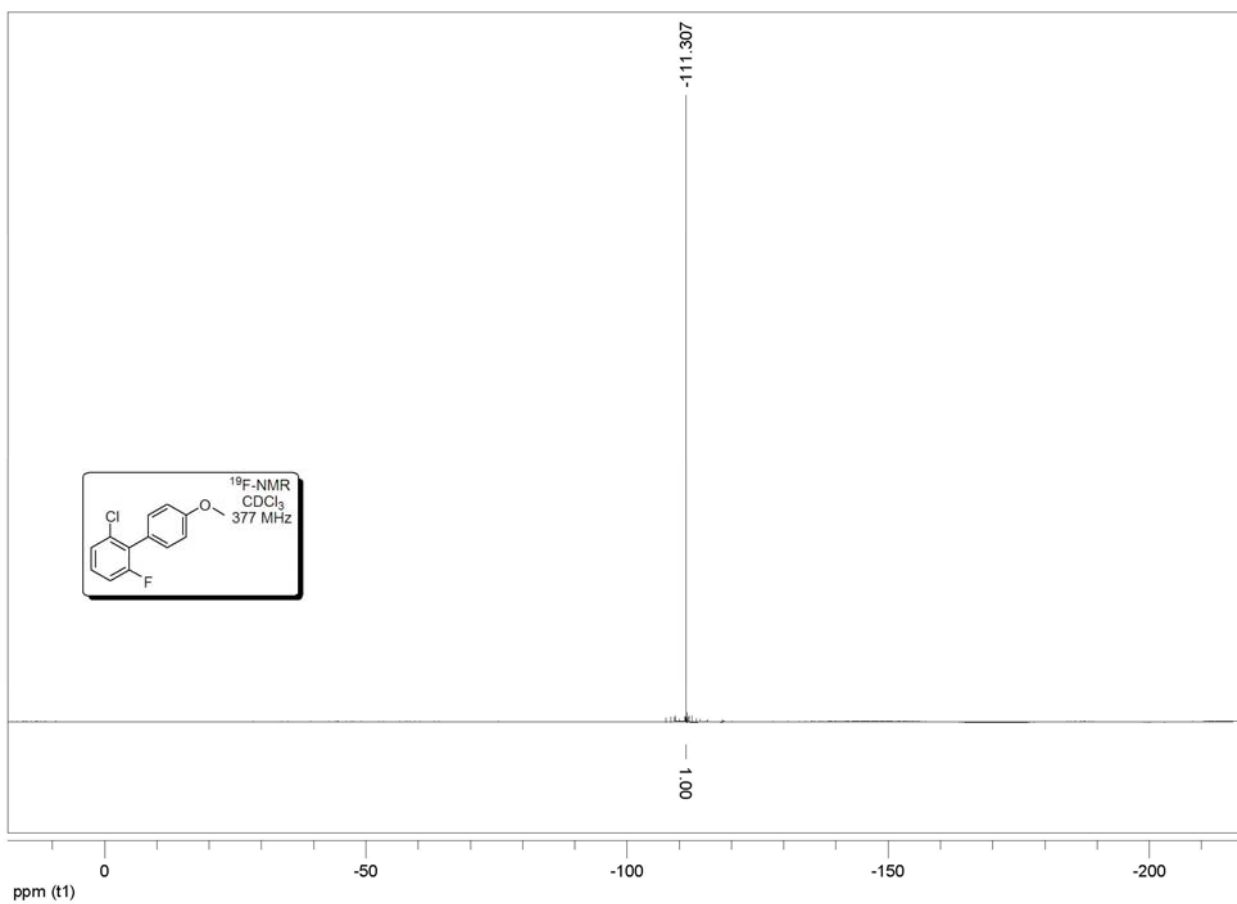
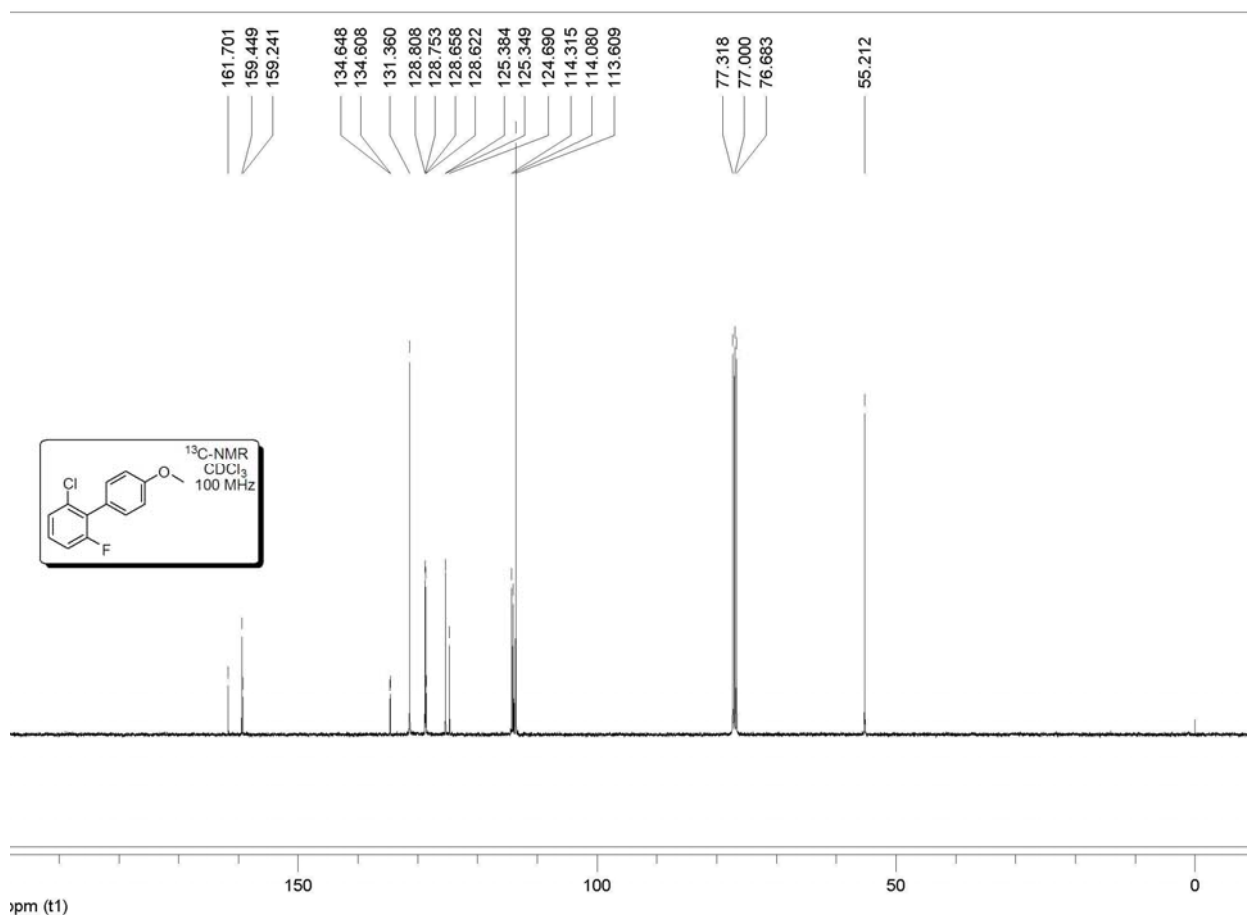
3-(perfluorophenyl)pyridine (21)

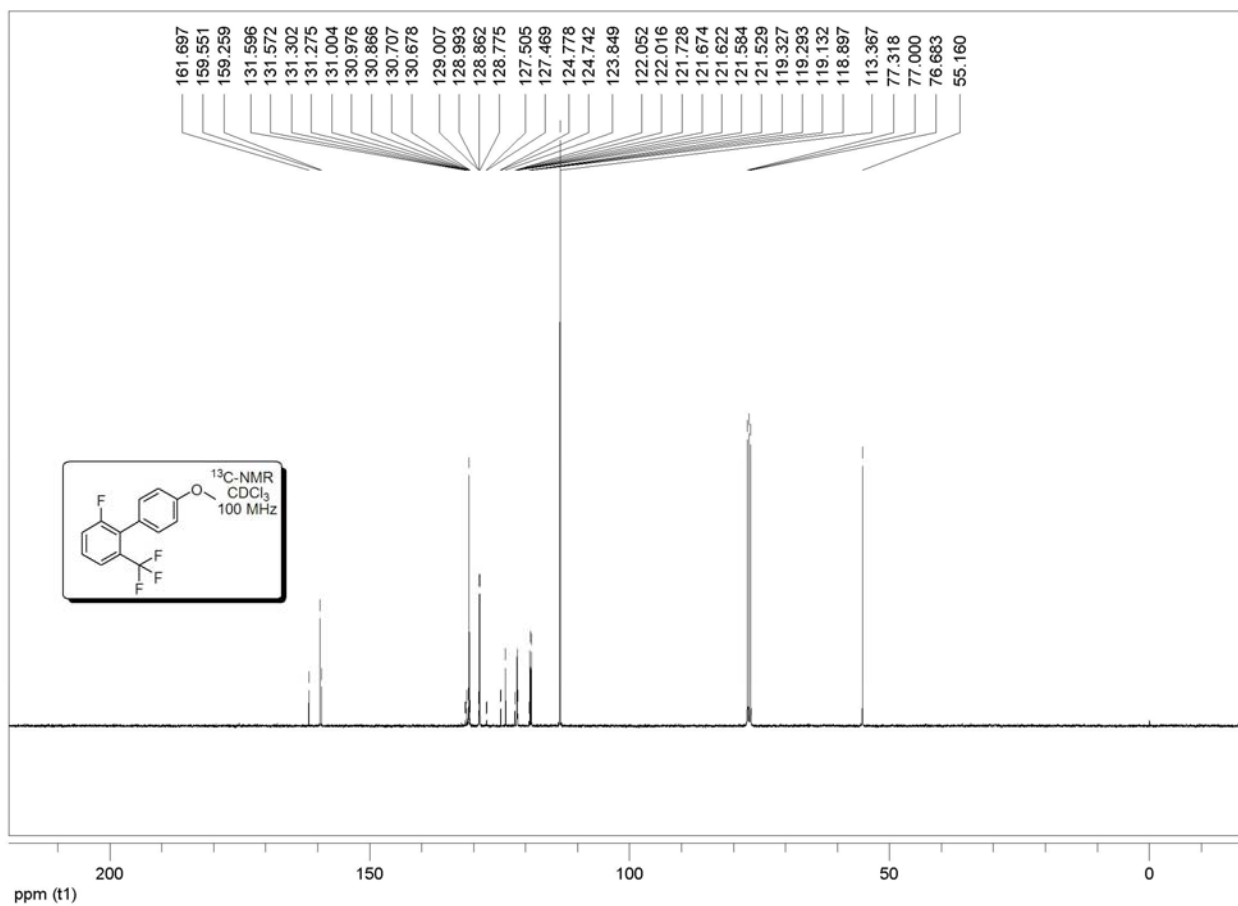
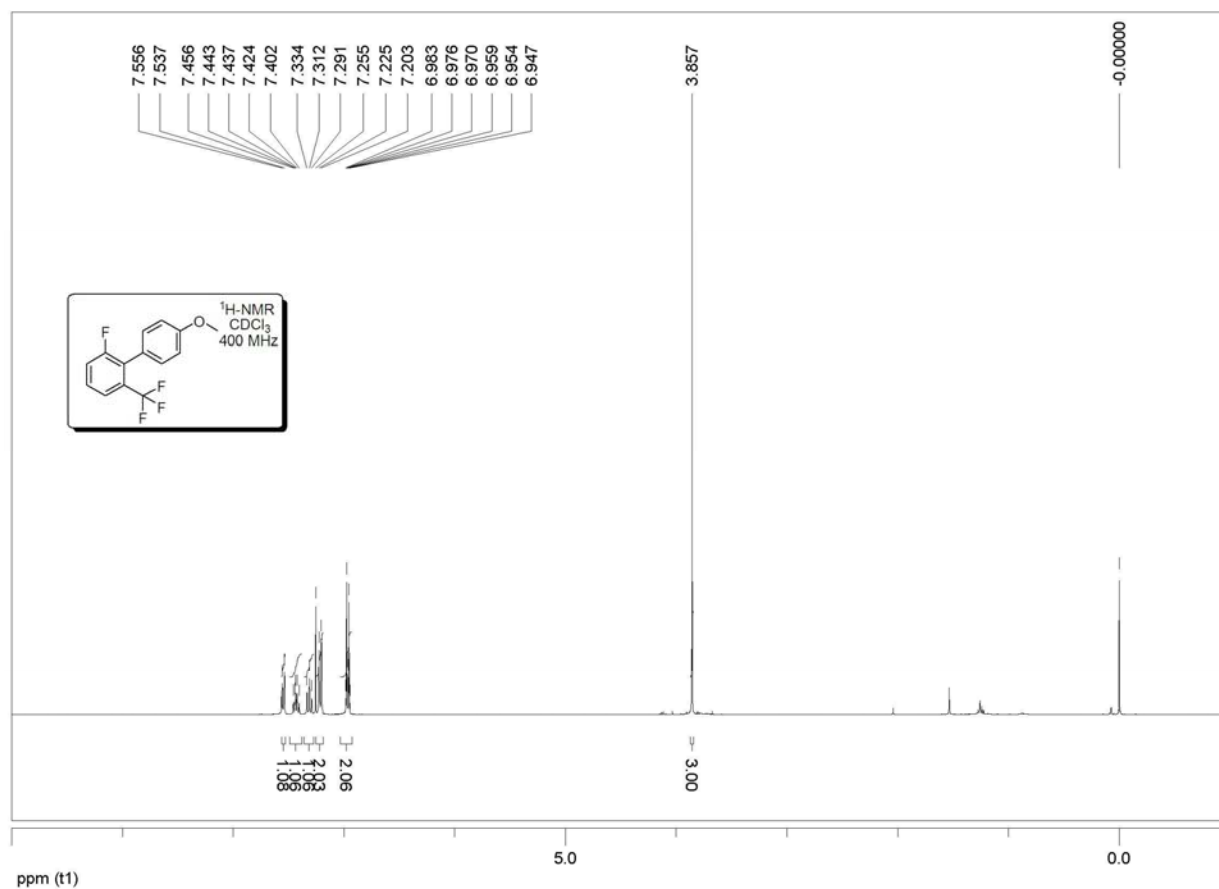
**3-(perfluorophenyl)thiophene (22)**

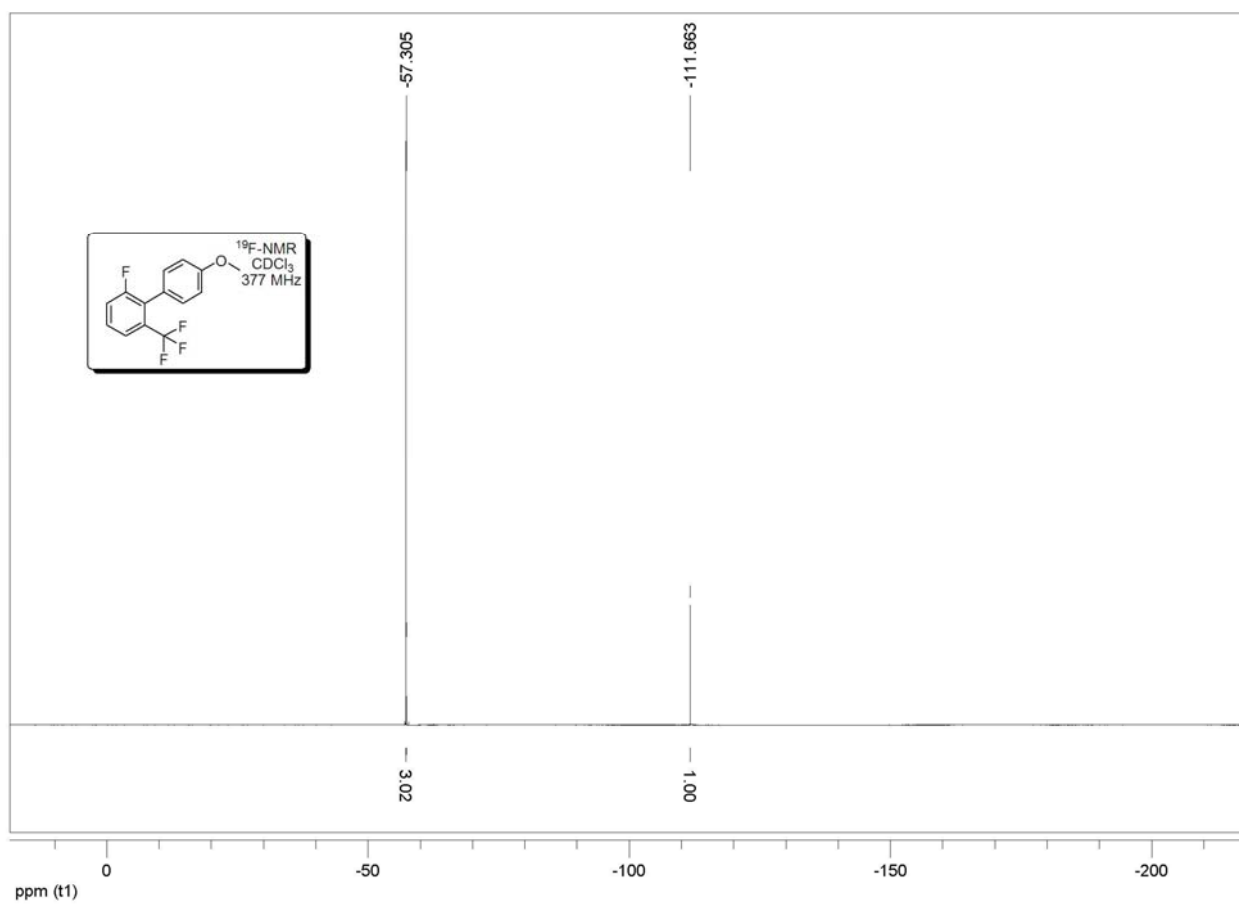
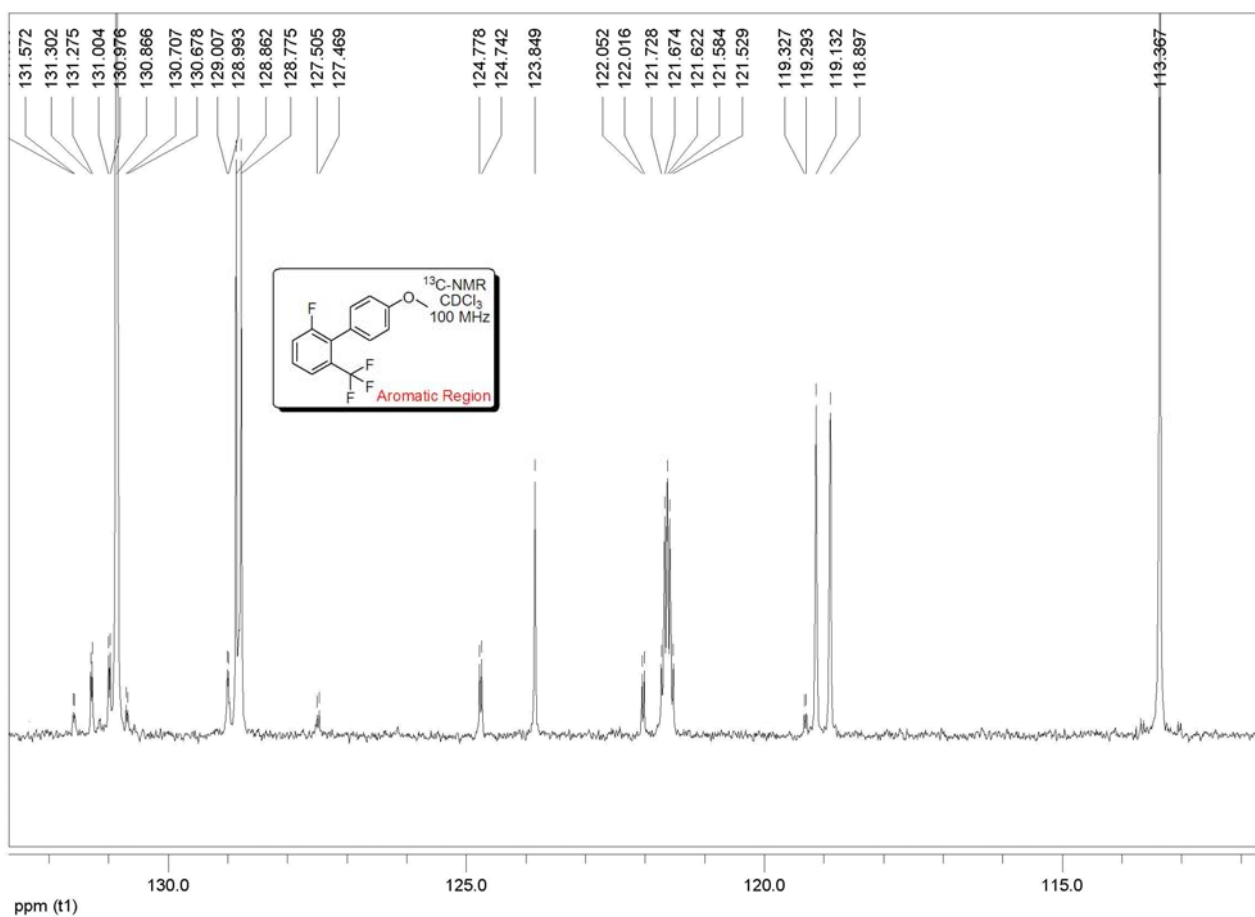


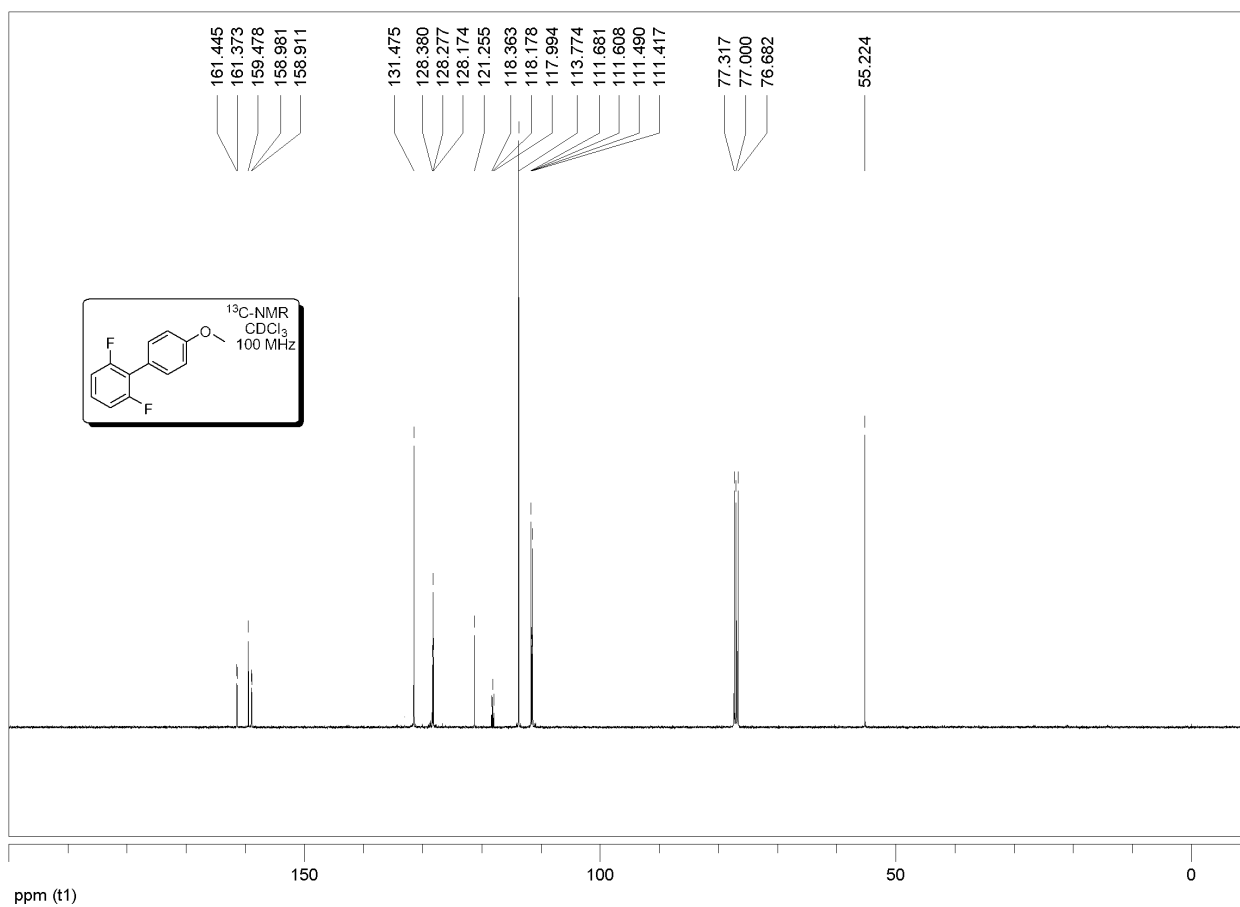
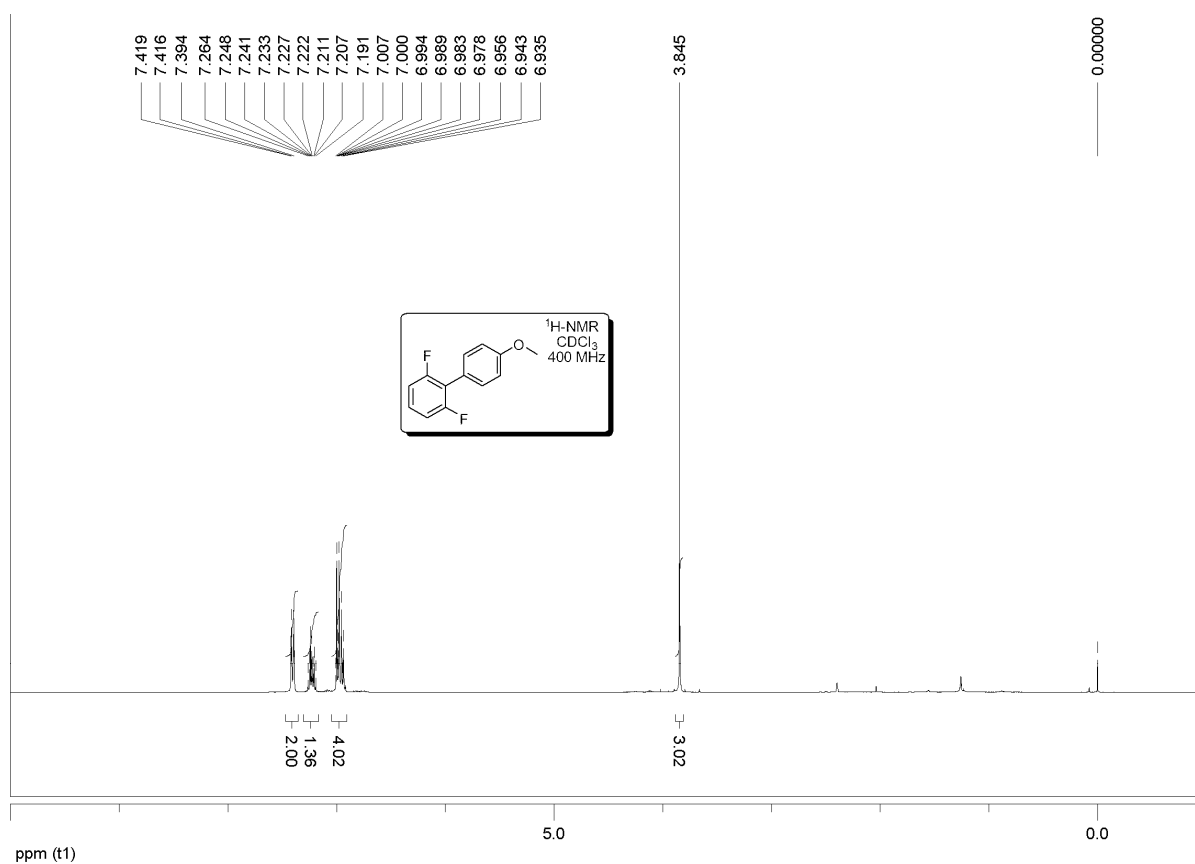
2-(perfluorophenyl)thiophene (23)

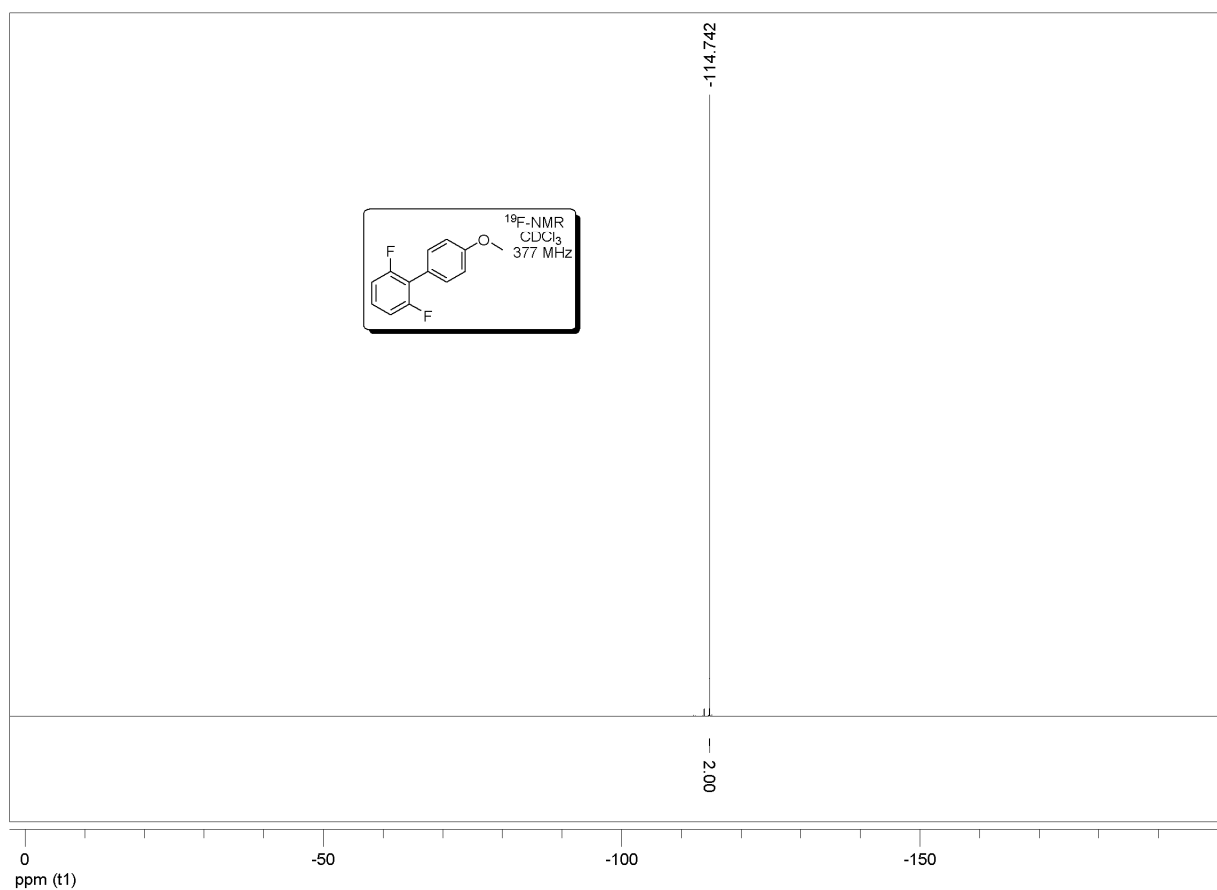
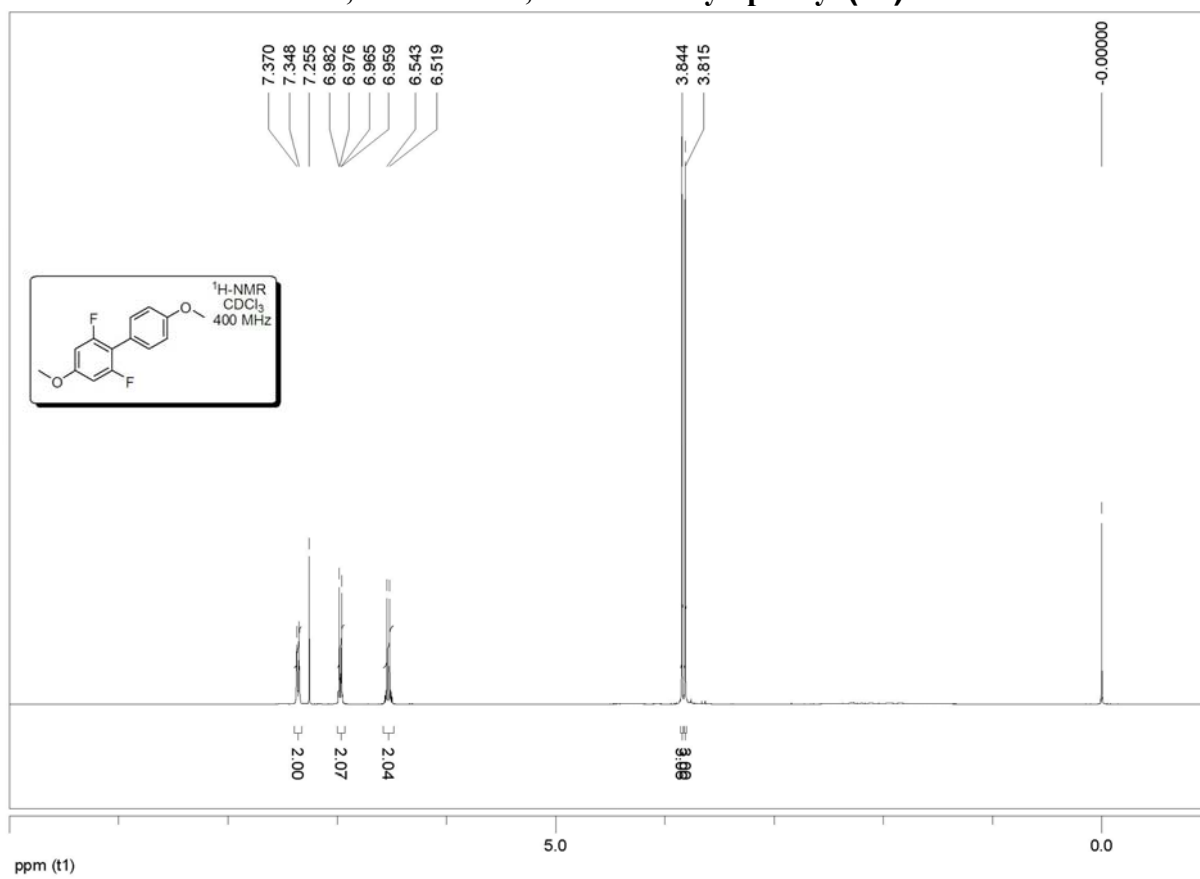
**2-chloro-6-fluoro-4'-methoxybiphenyl (24)**

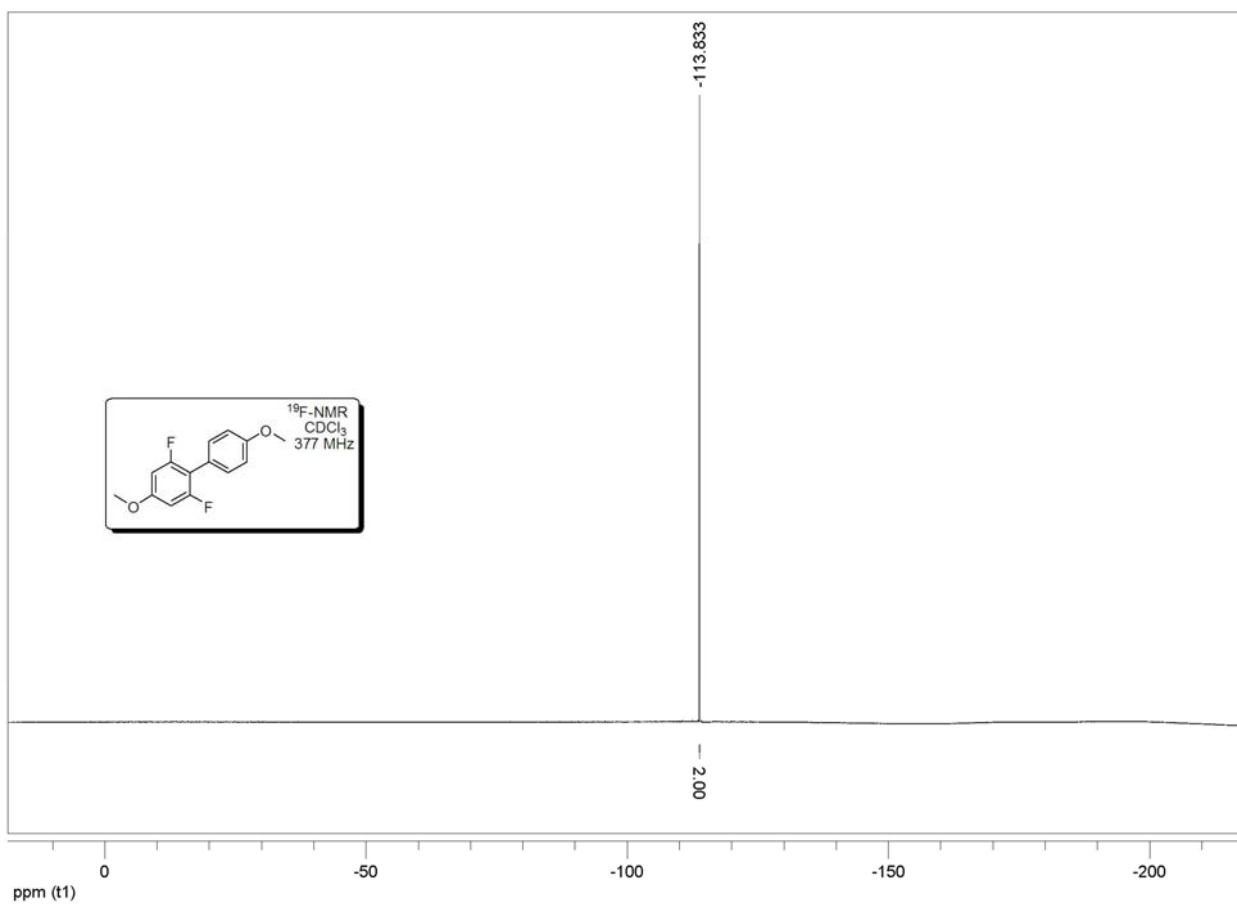
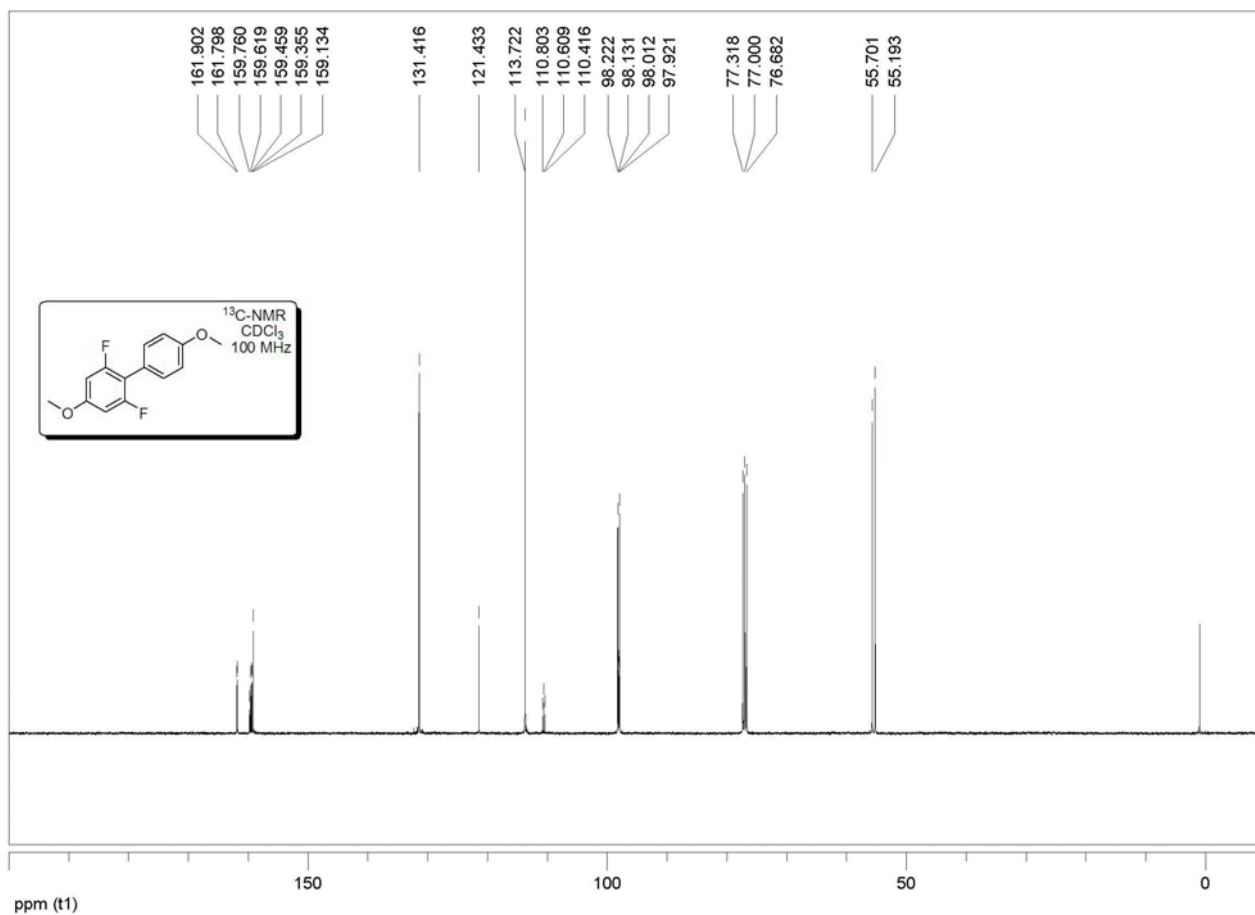


2-fluoro-4'-methoxy-6-(trifluoromethyl) biphenyl (25)

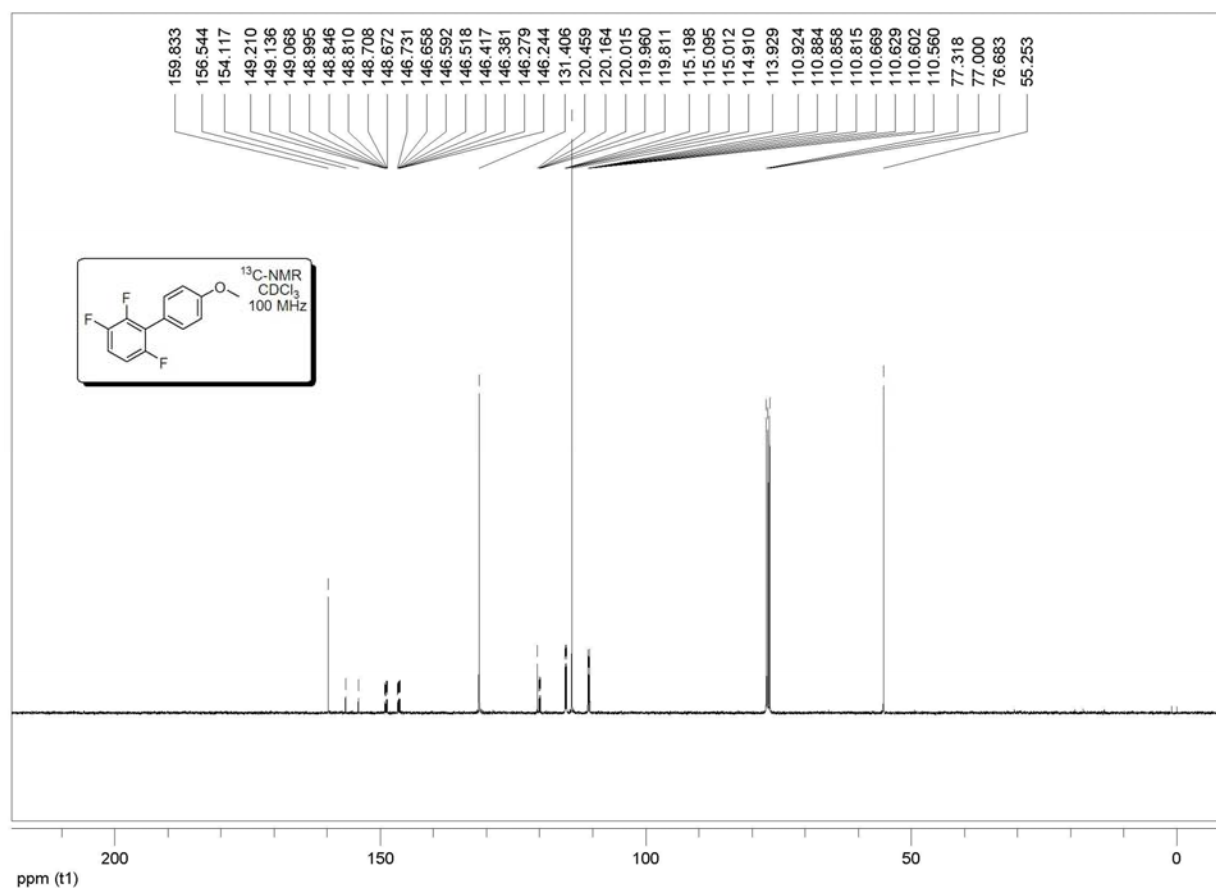
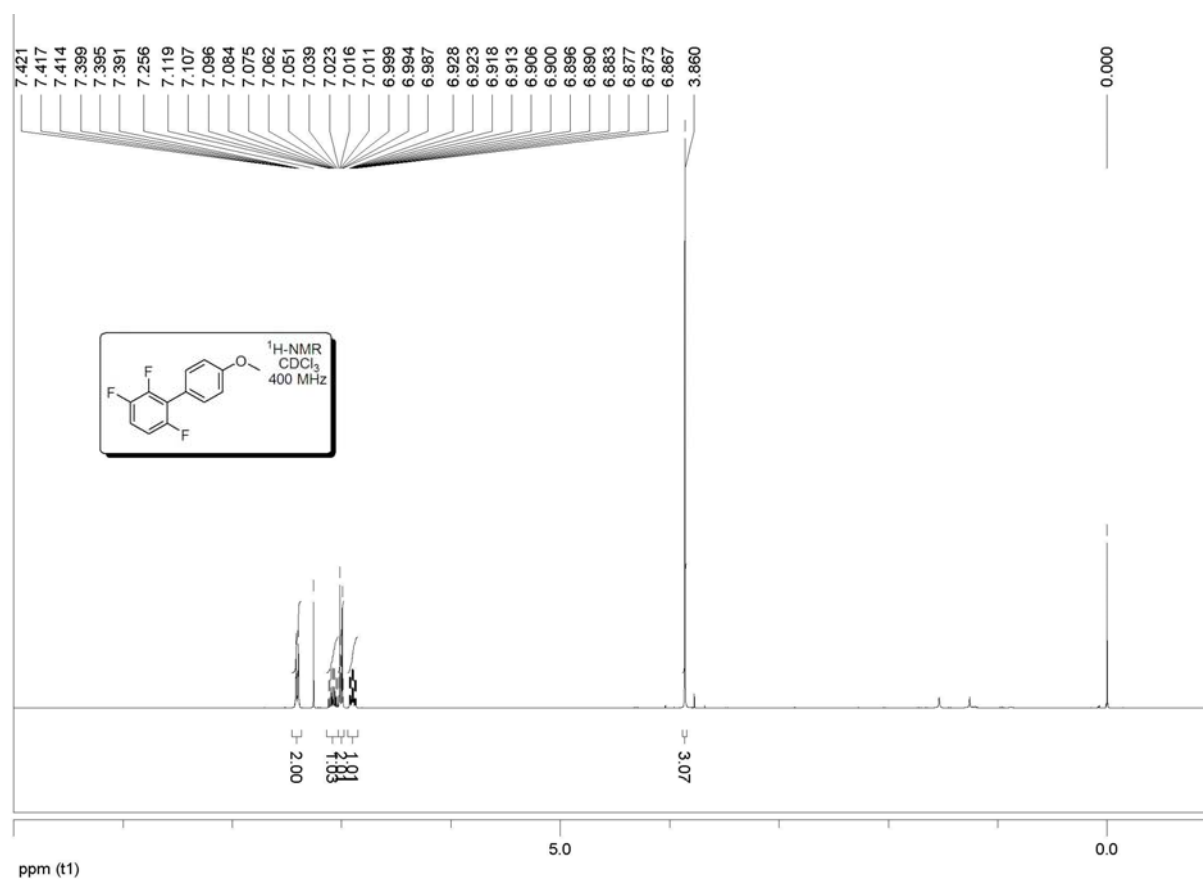


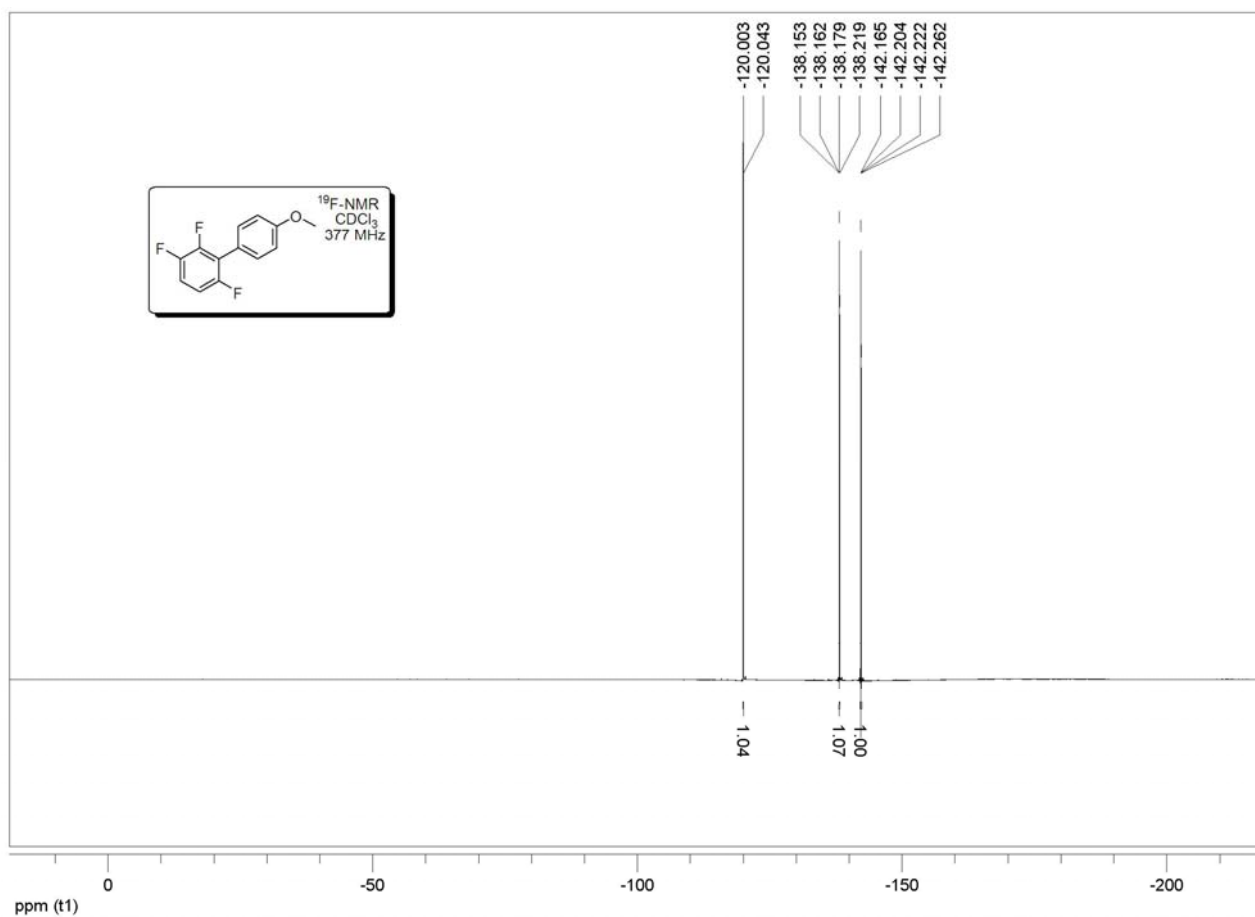
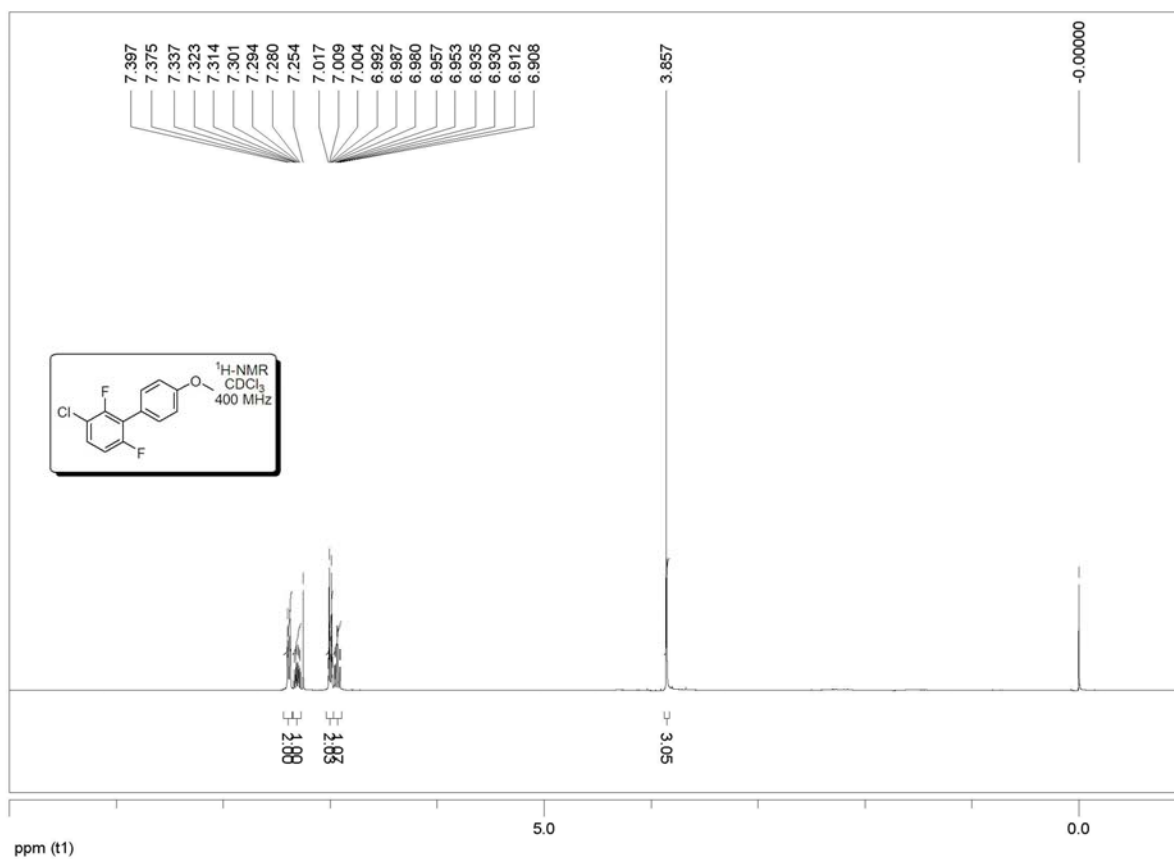
2, 6-difluoro-4'-methoxybiphenyl (26)

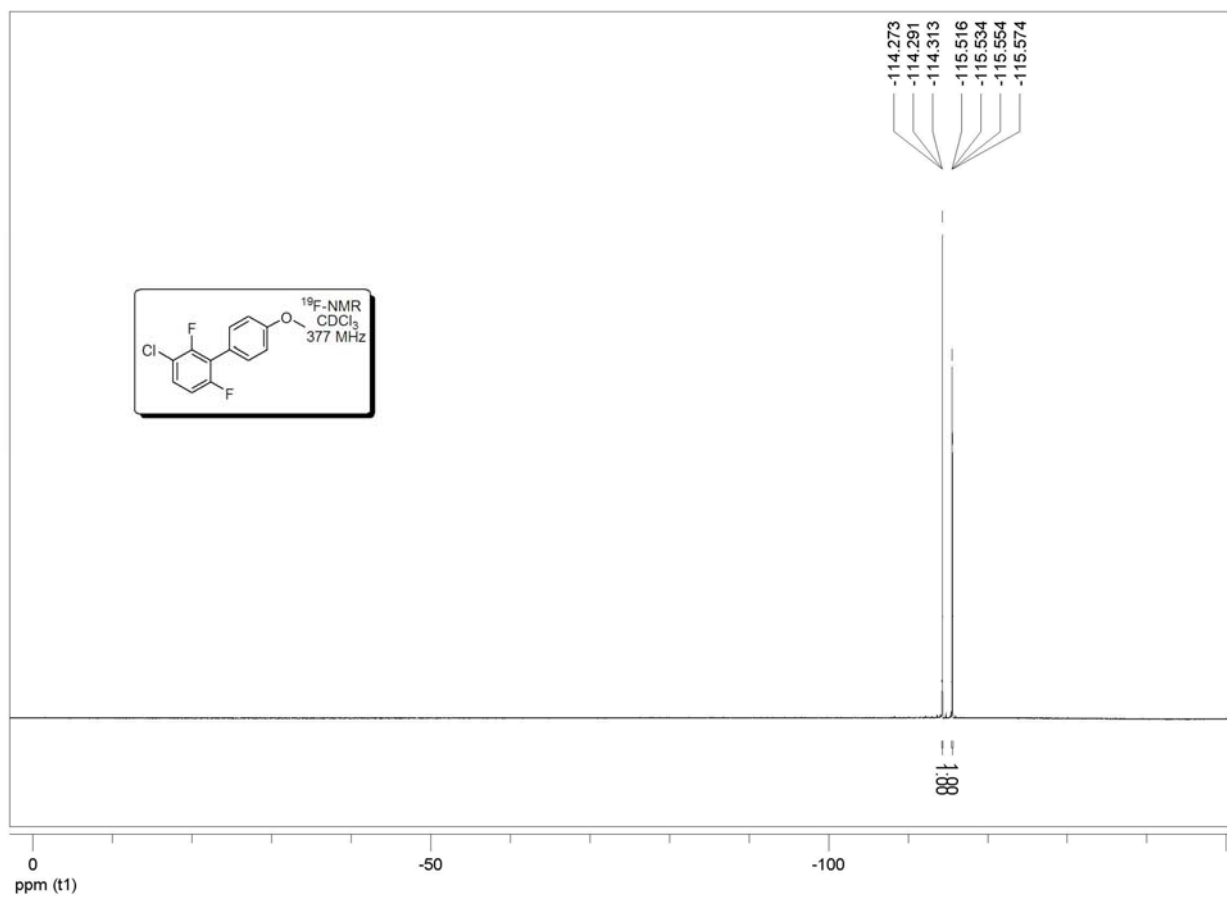
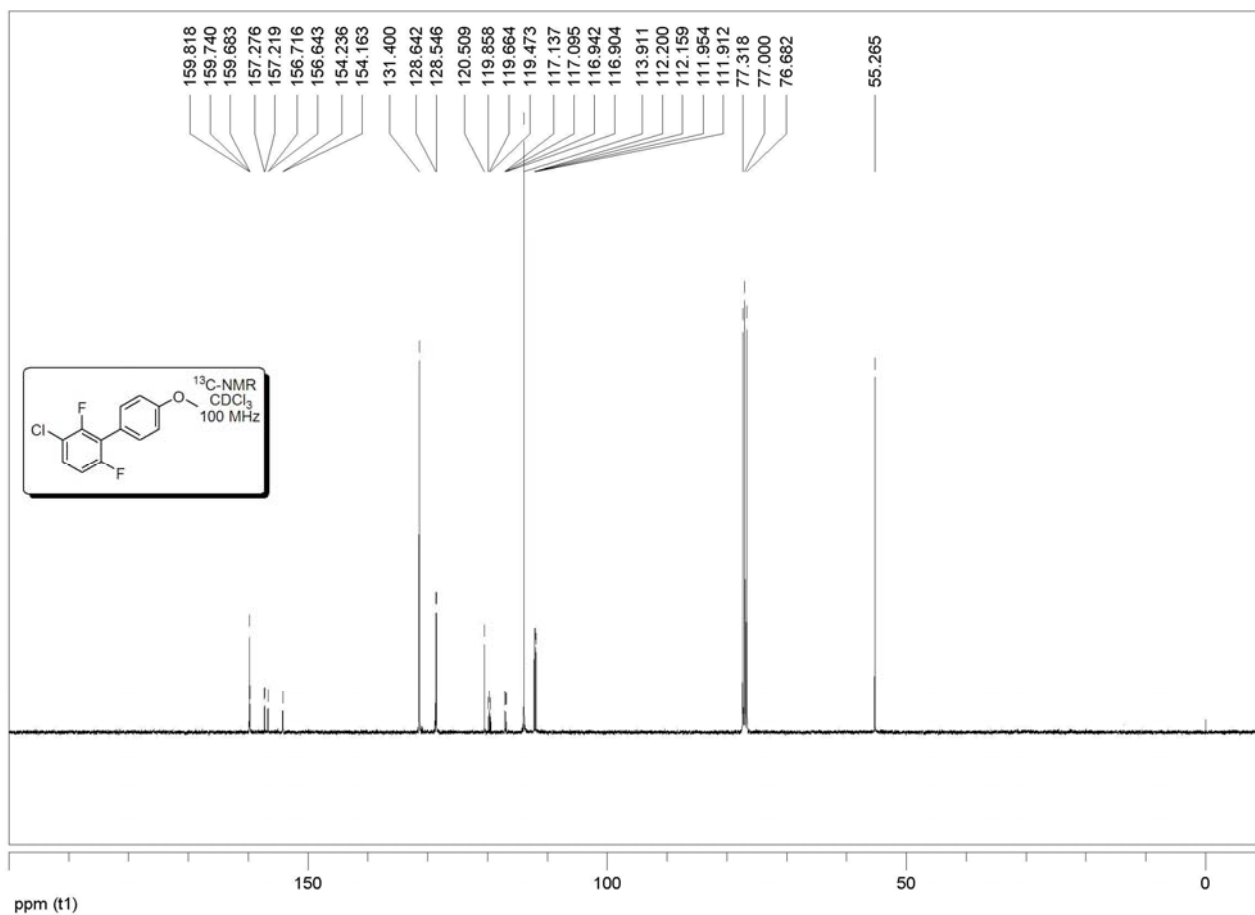
**2, 6-difluoro-4, 4'-dimethoxybiphenyl (27)**

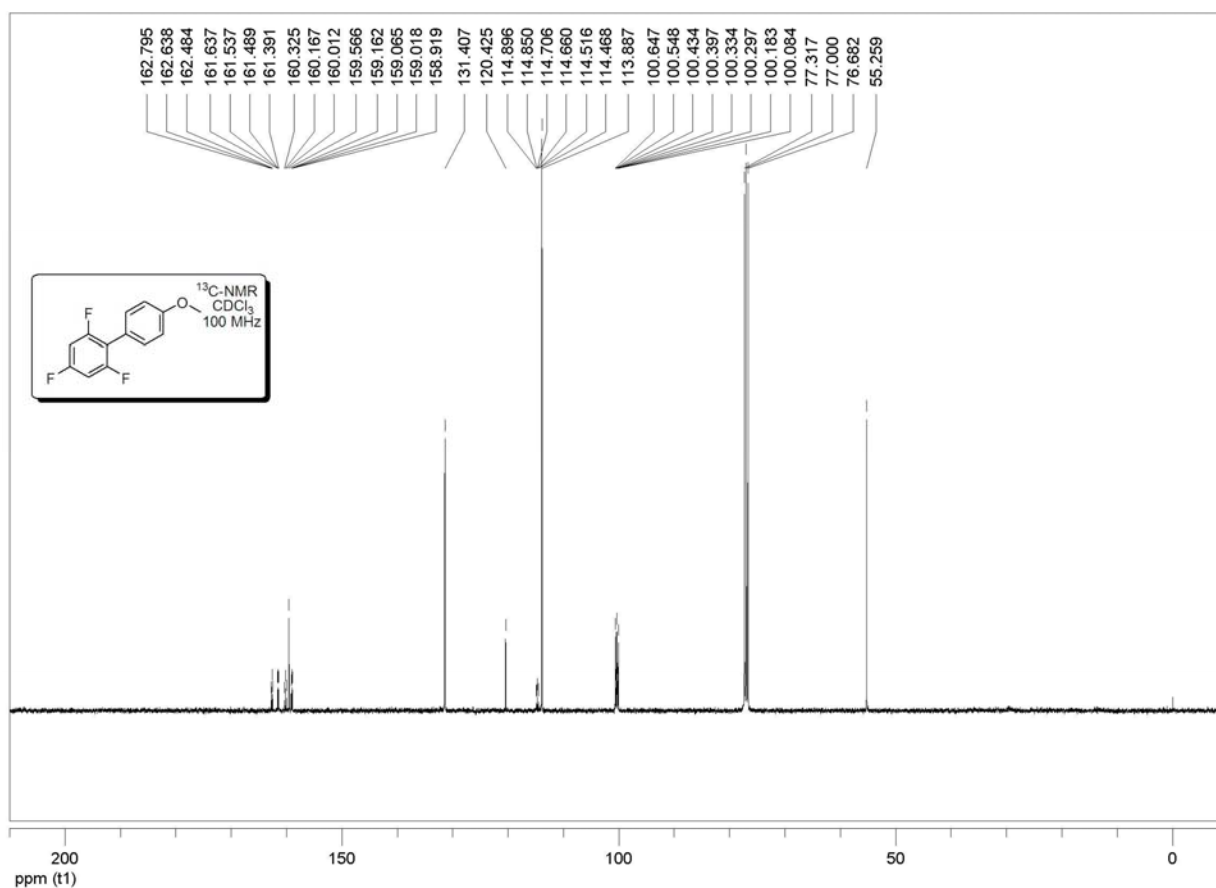
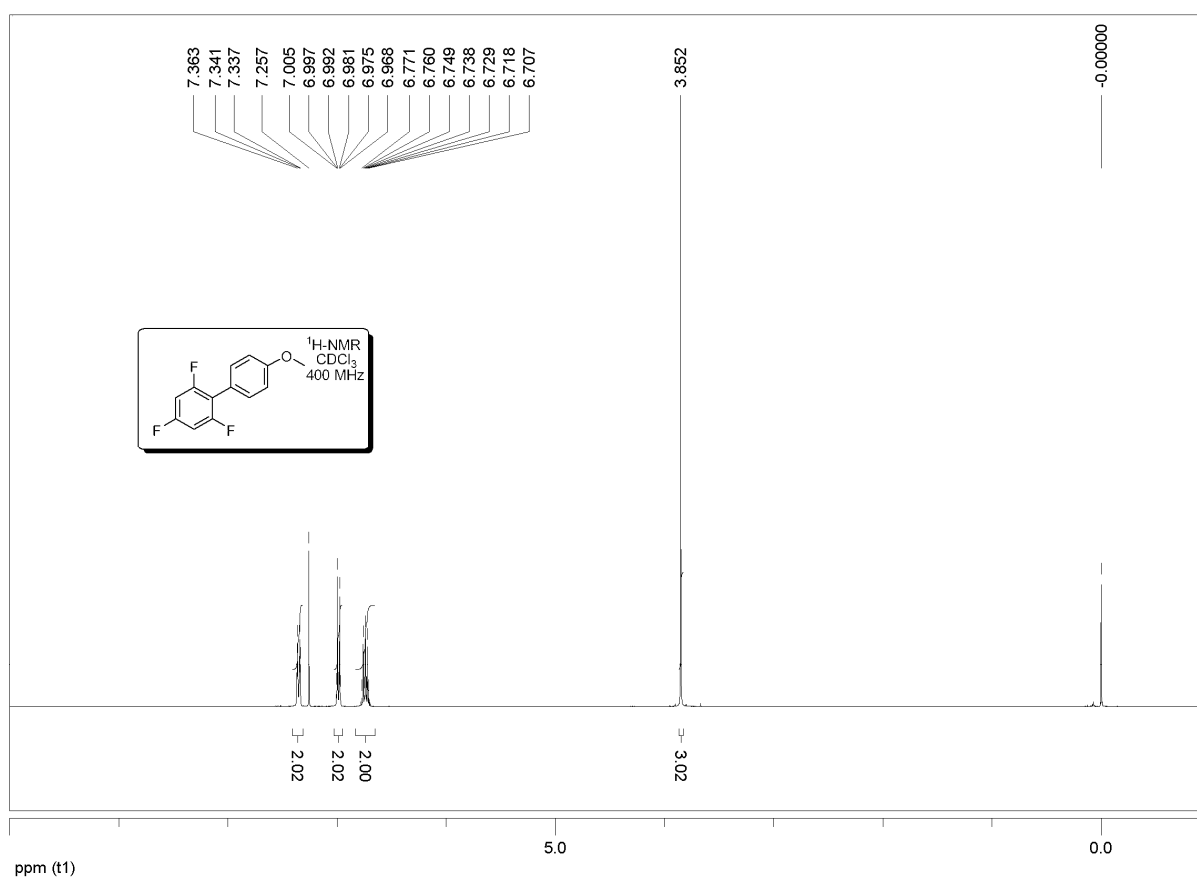


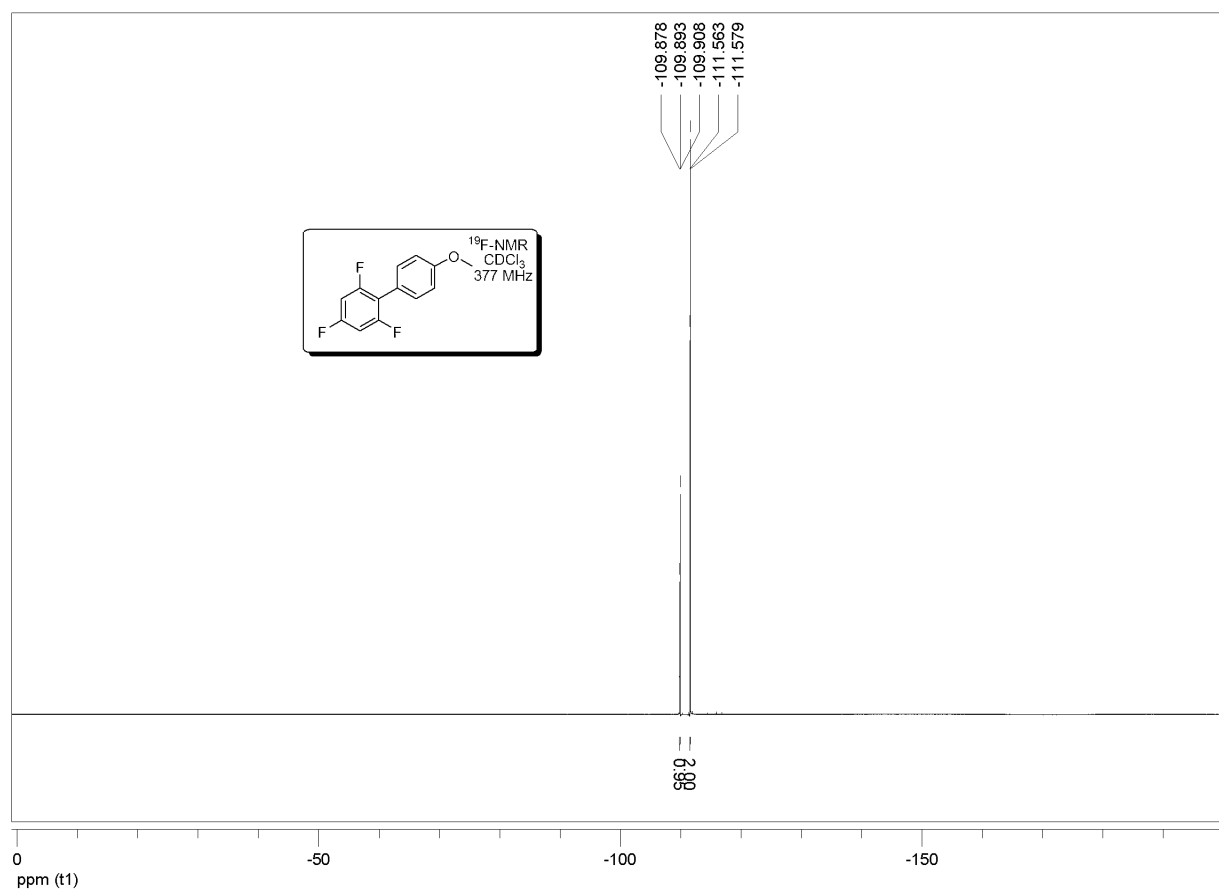
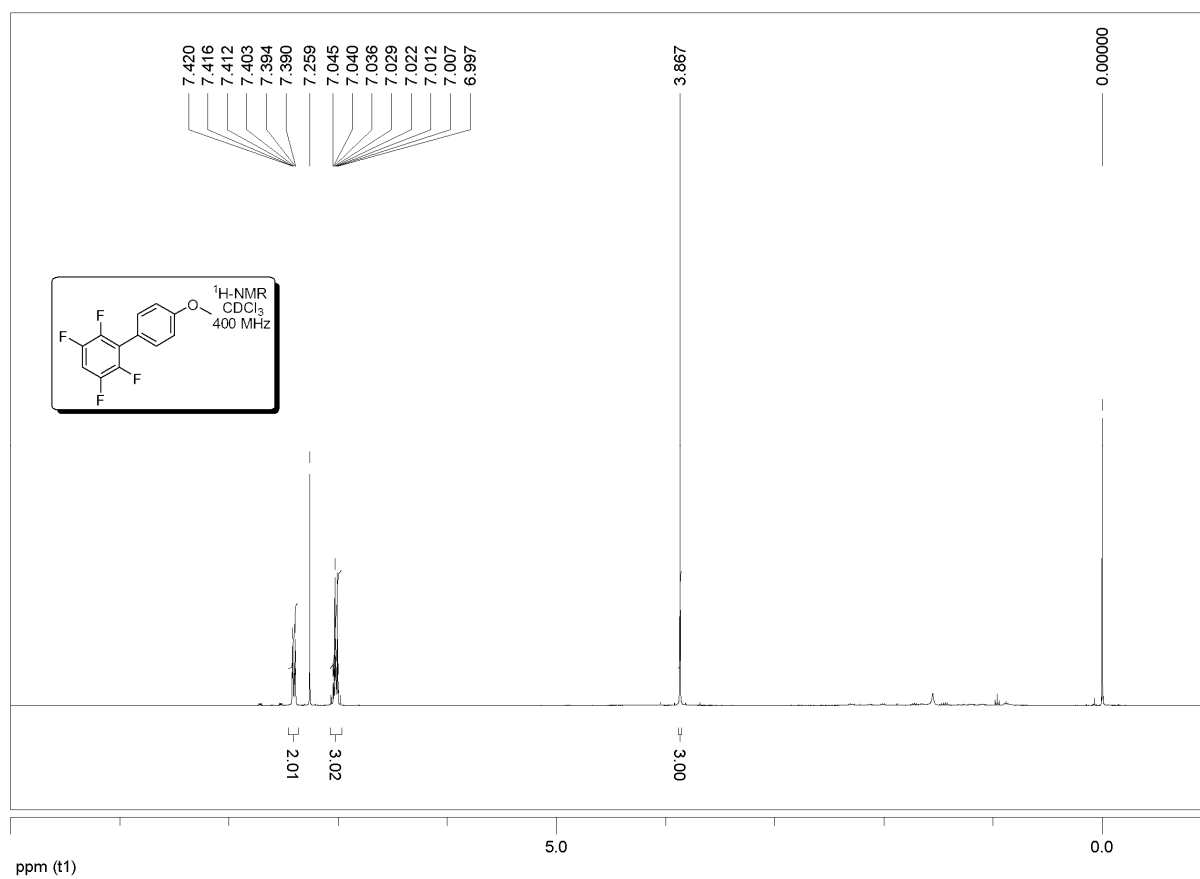
2, 3, 6-trifluoro-4'-methoxybiphenyl (28)

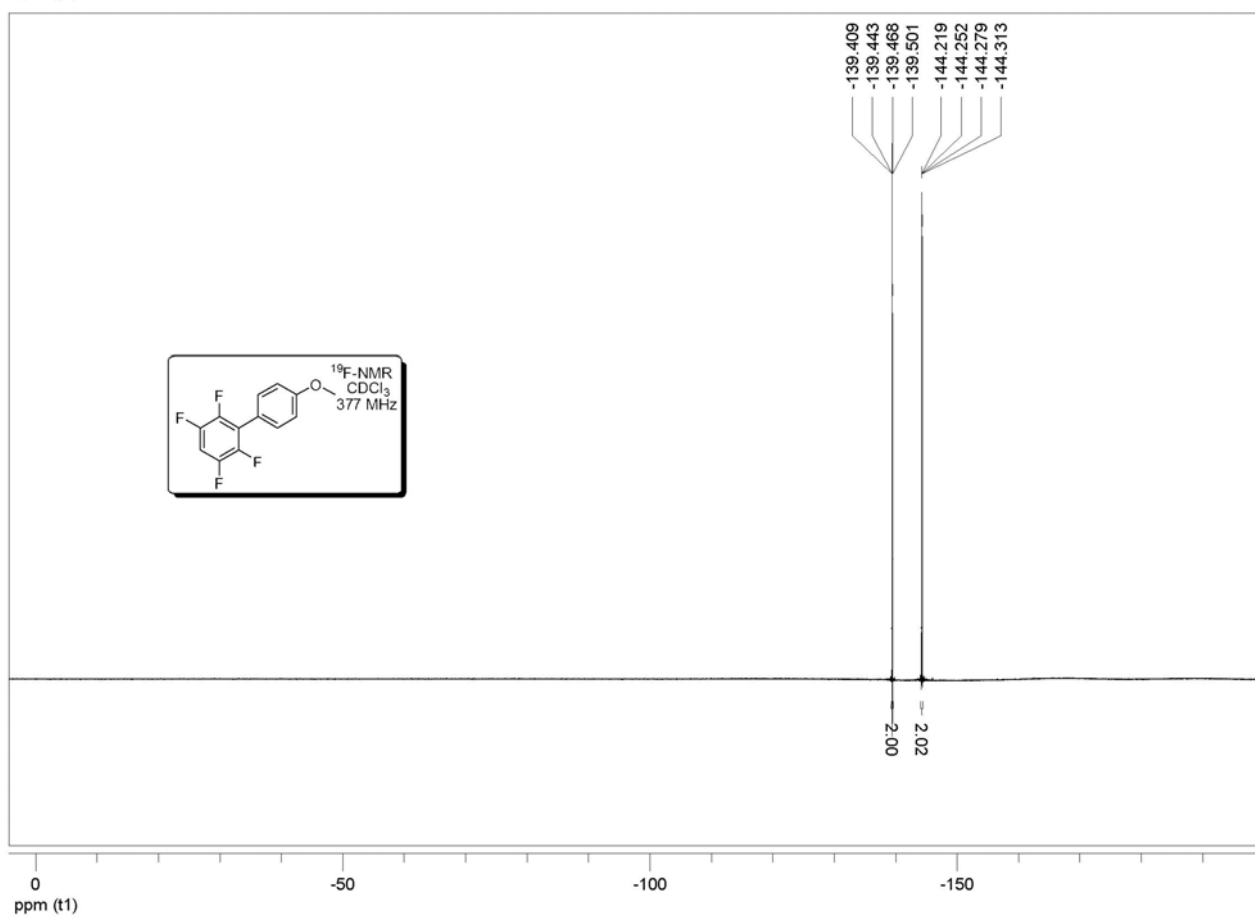
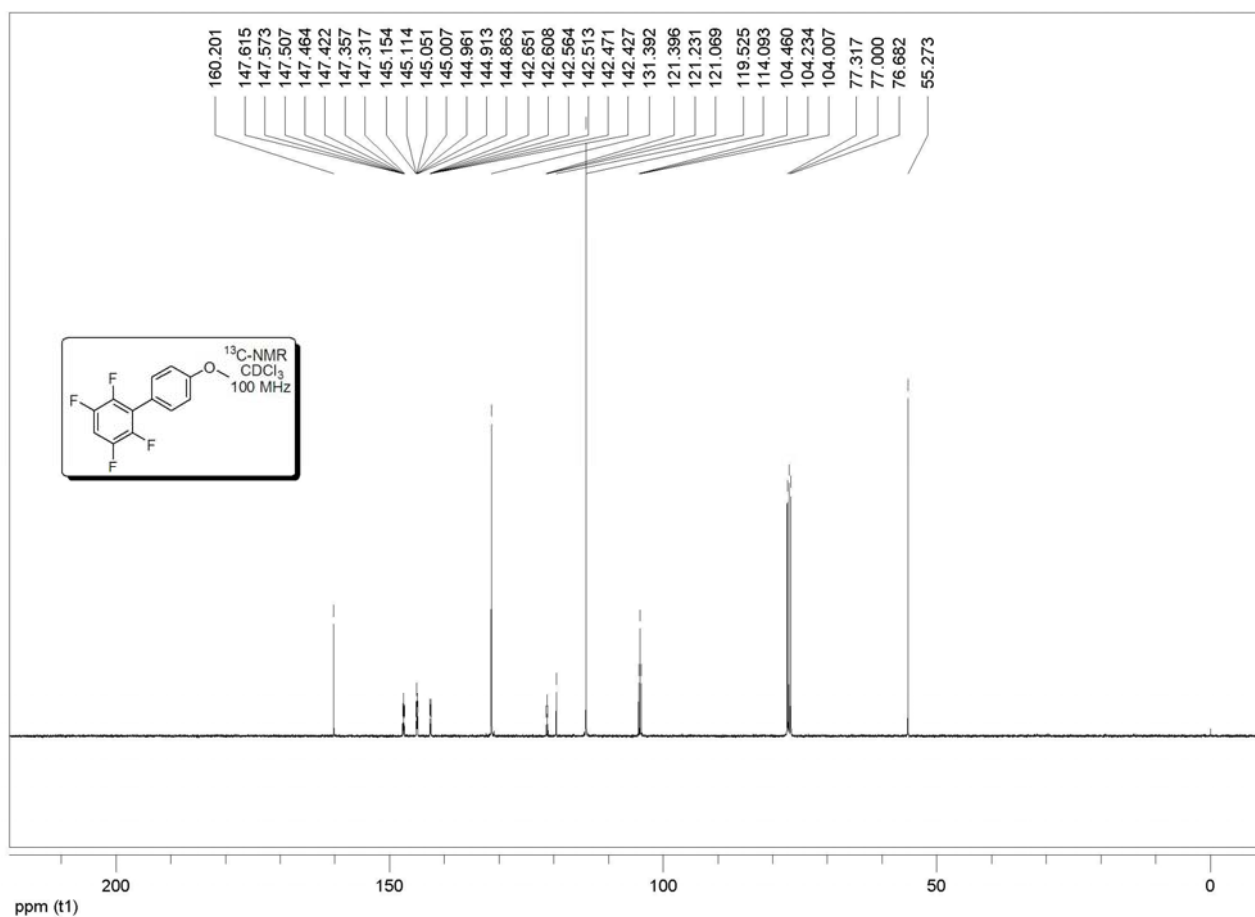


**3-chloro-2,6-difluoro-4'-methoxybiphenyl (29)**

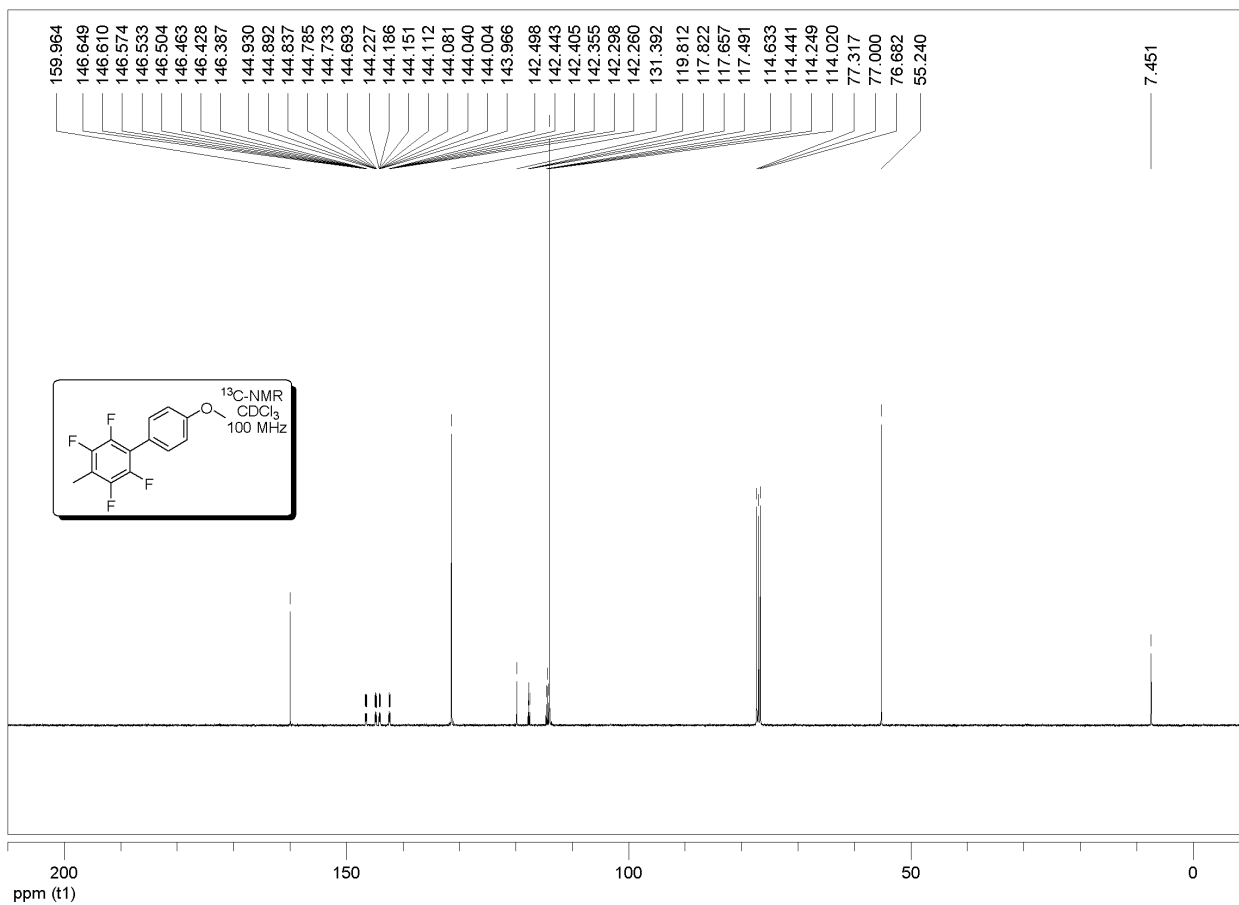
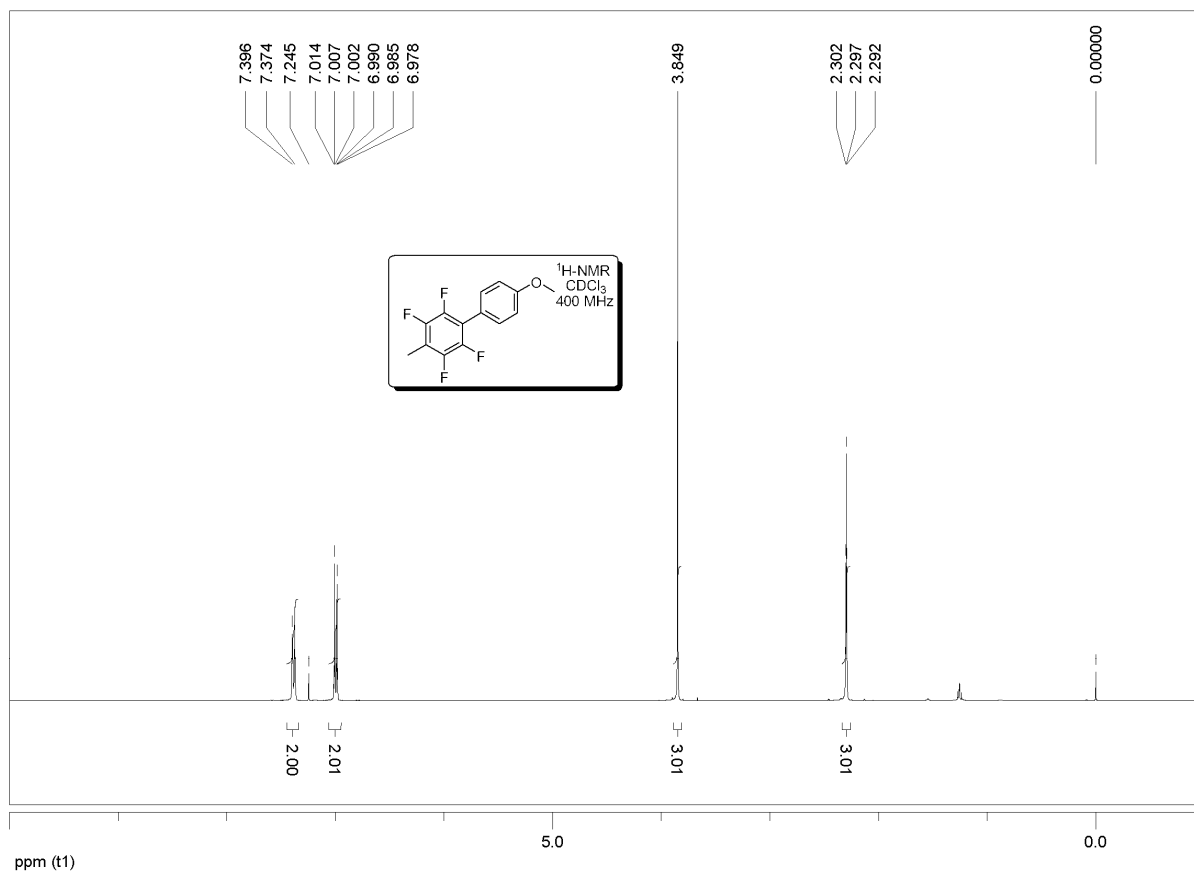


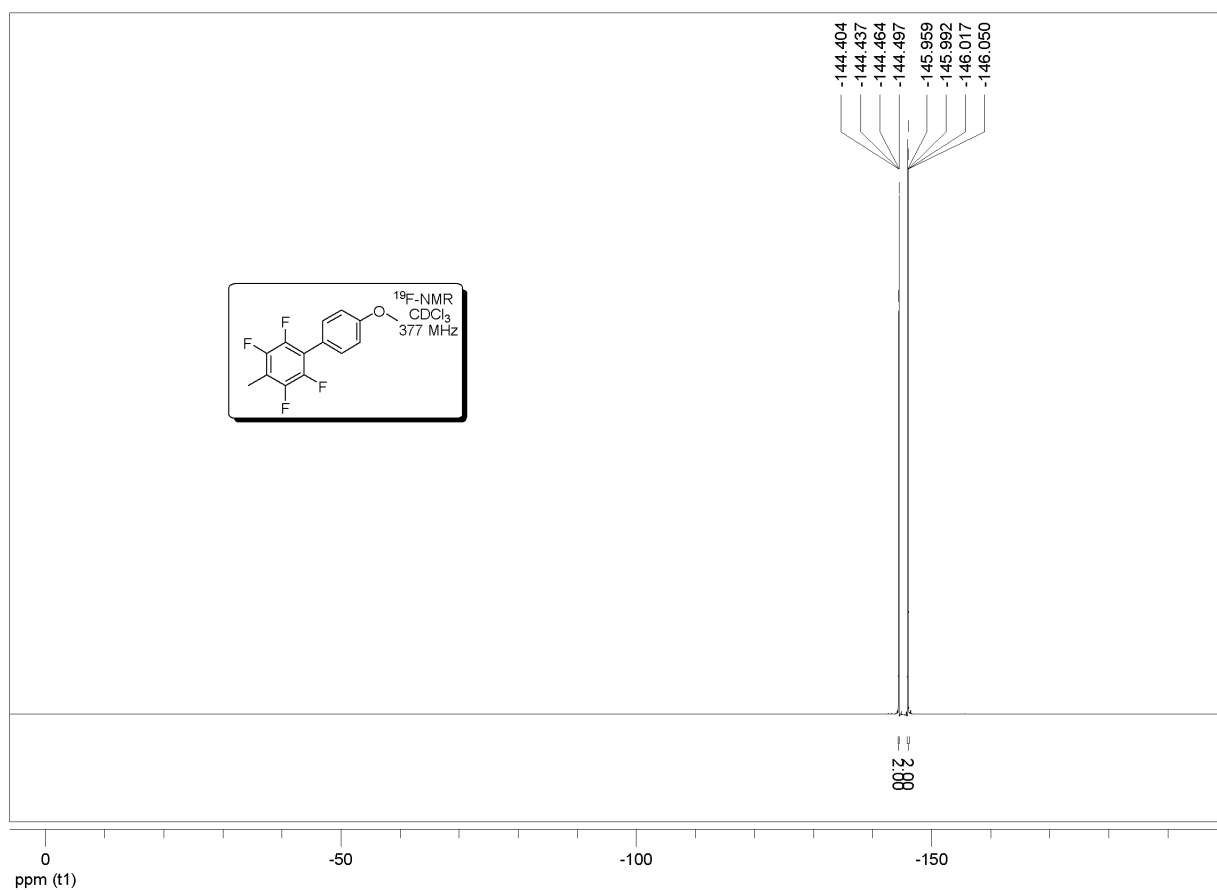
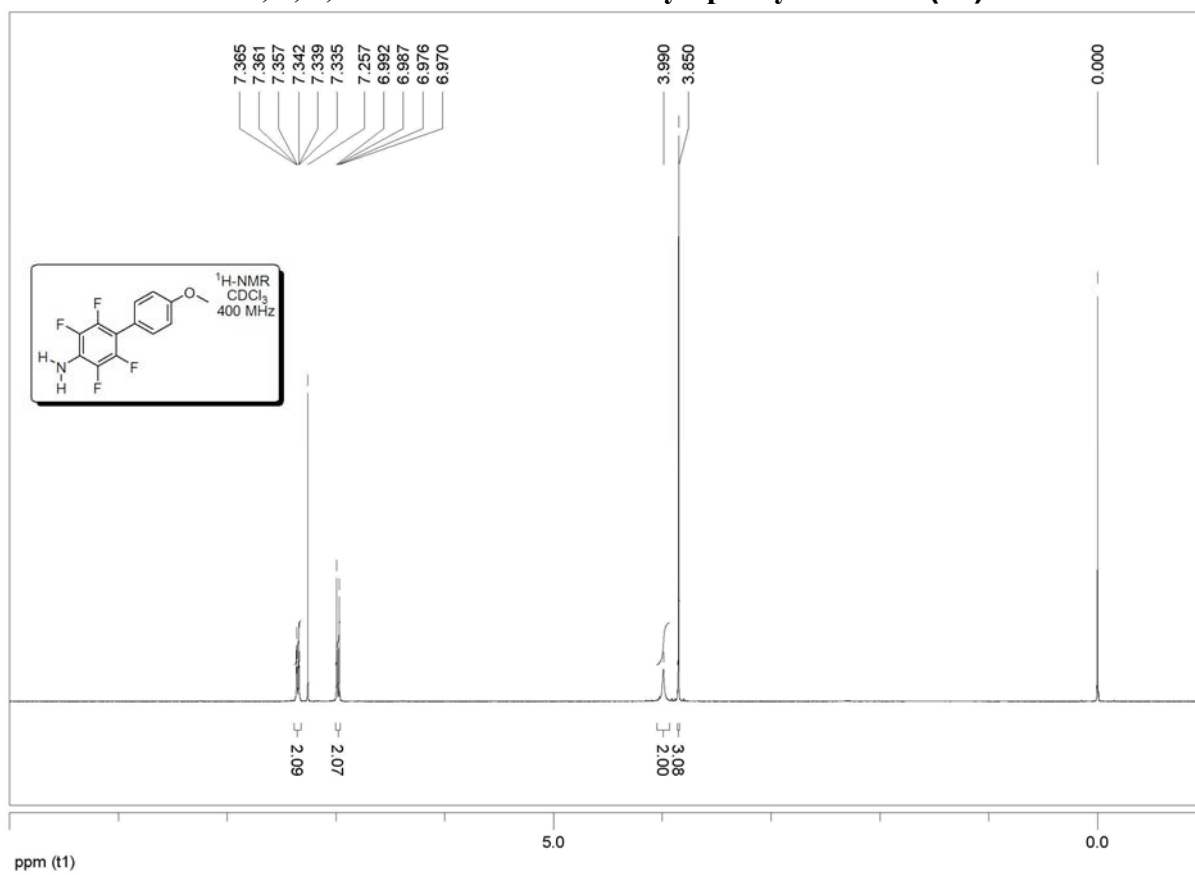
2, 4, 6-trifluoro-4'-methoxybiphenyl (30)

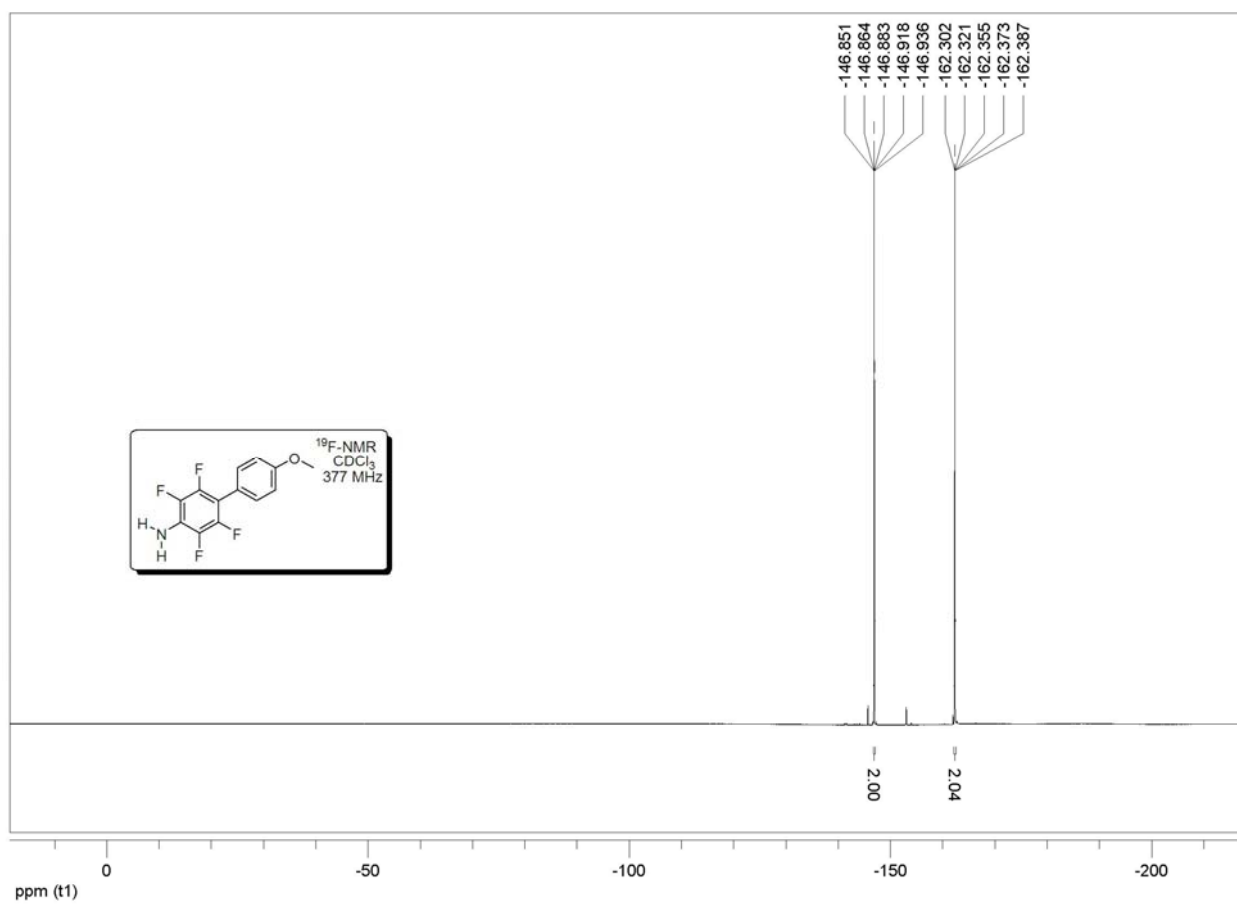
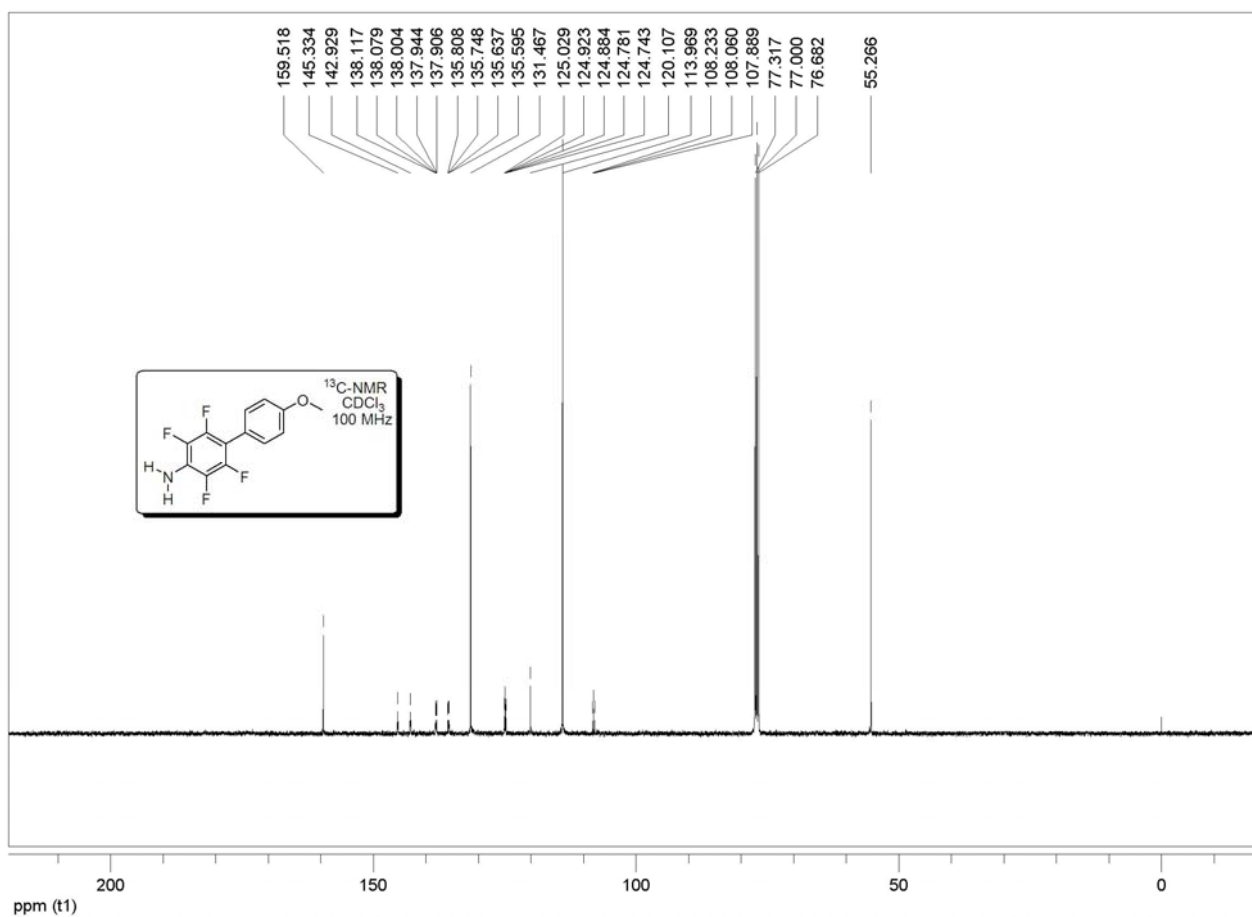
**2, 3, 5, 6-tetrafluoro-4'-methoxybiphenyl (31)**

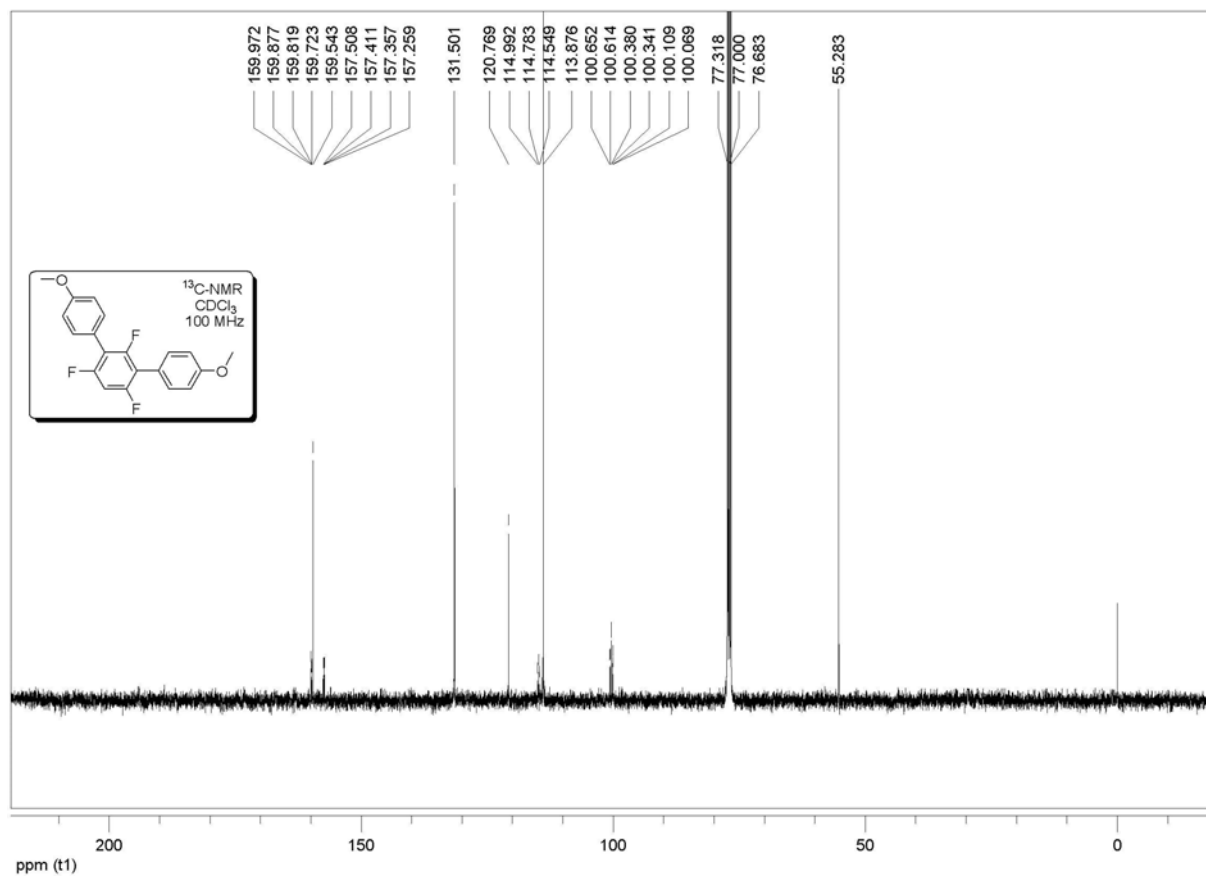
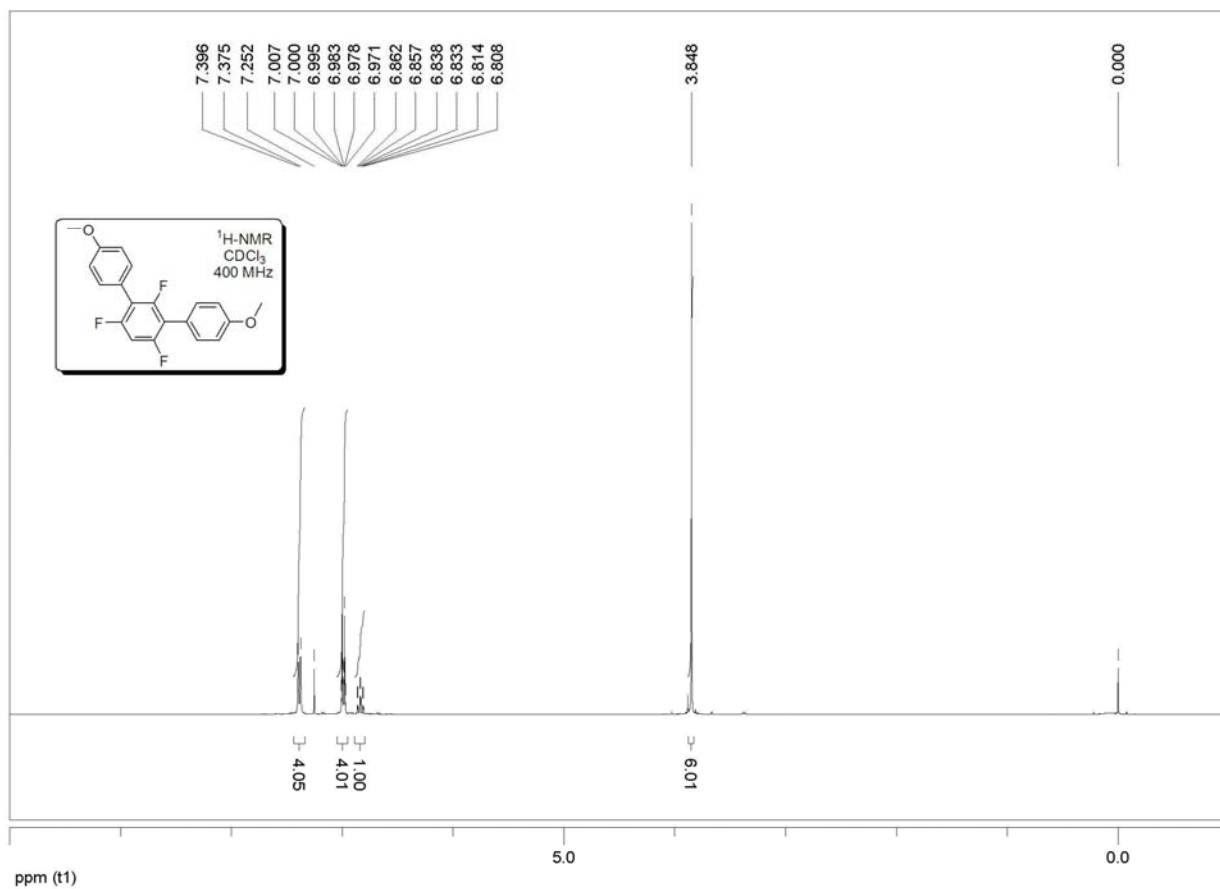


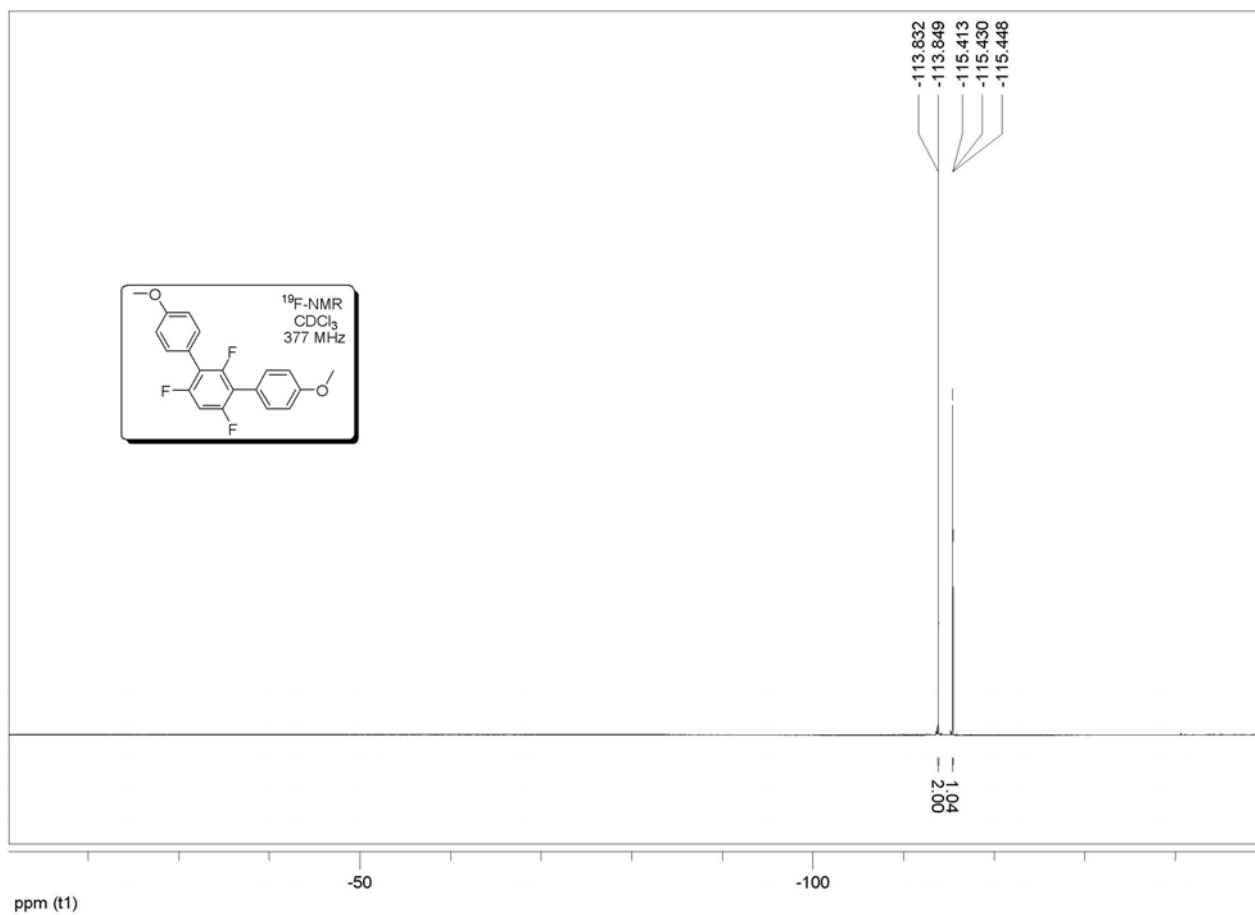
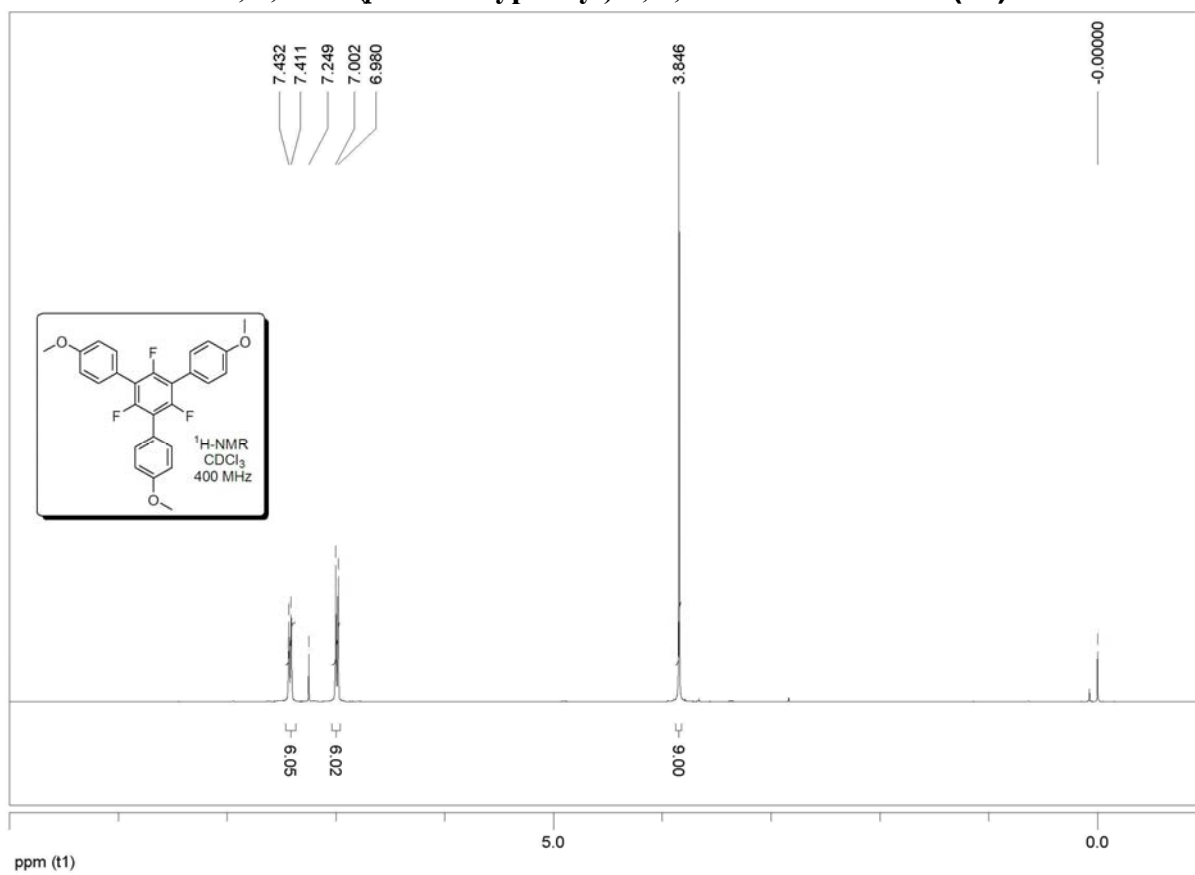
2, 3, 5, 6-tetrafluoro-4'-methoxy-4-methylbiphenyl (32)

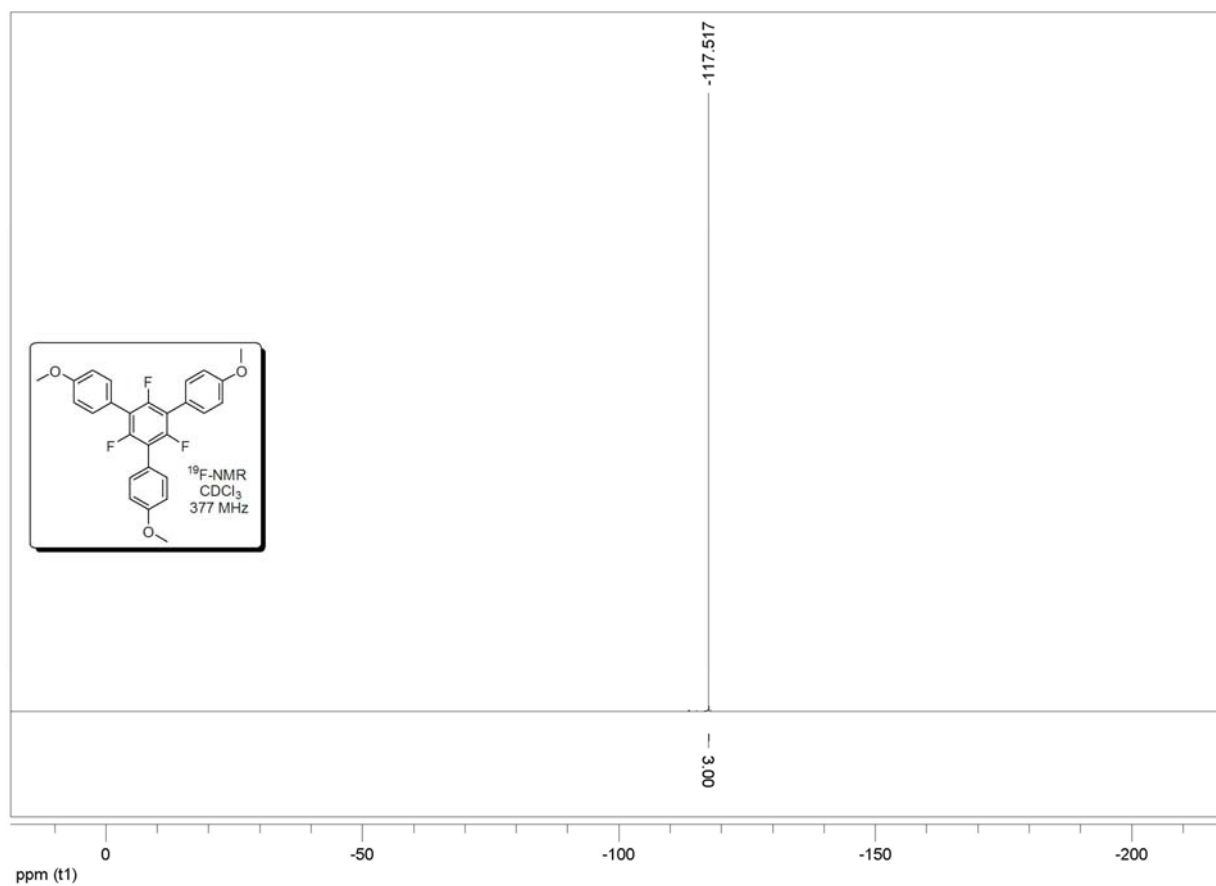
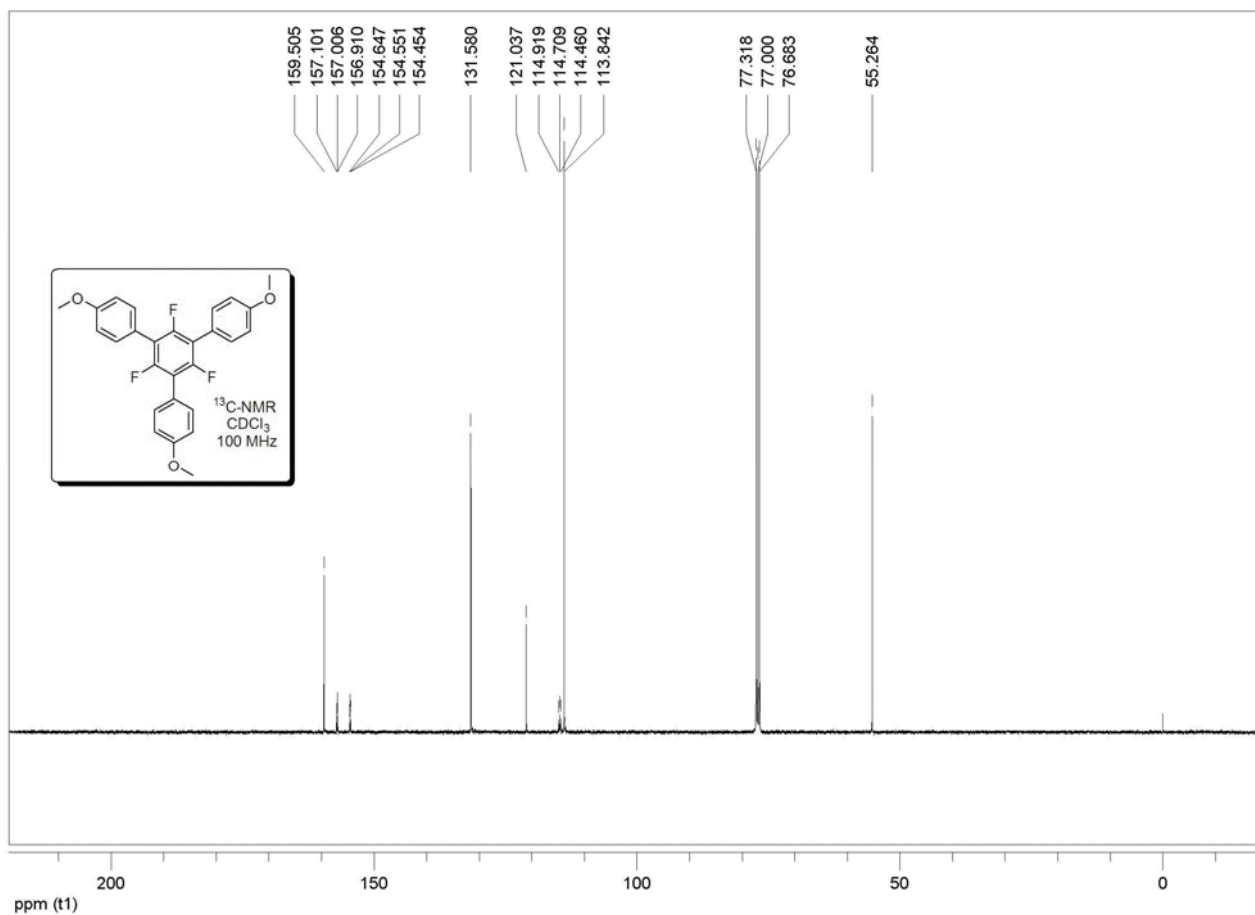


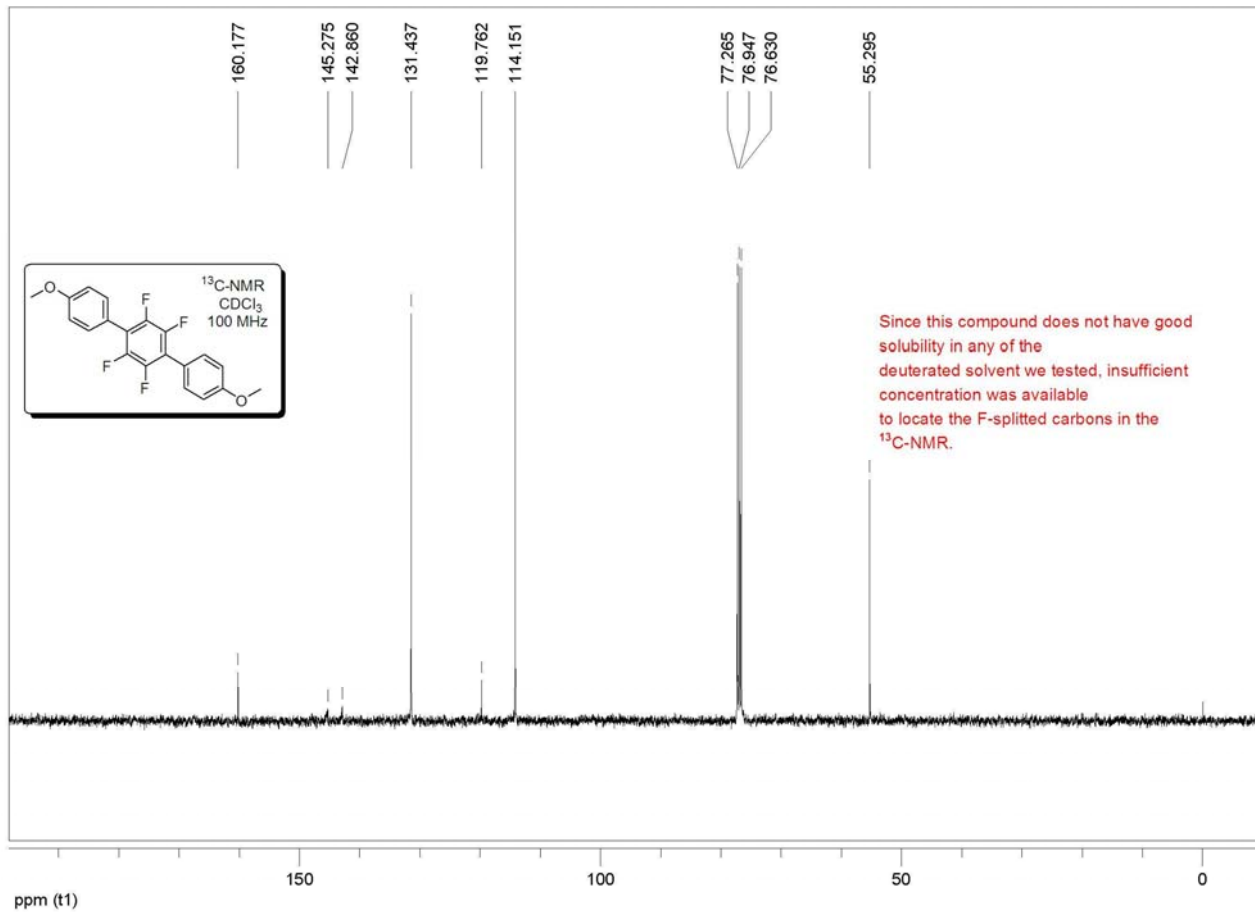
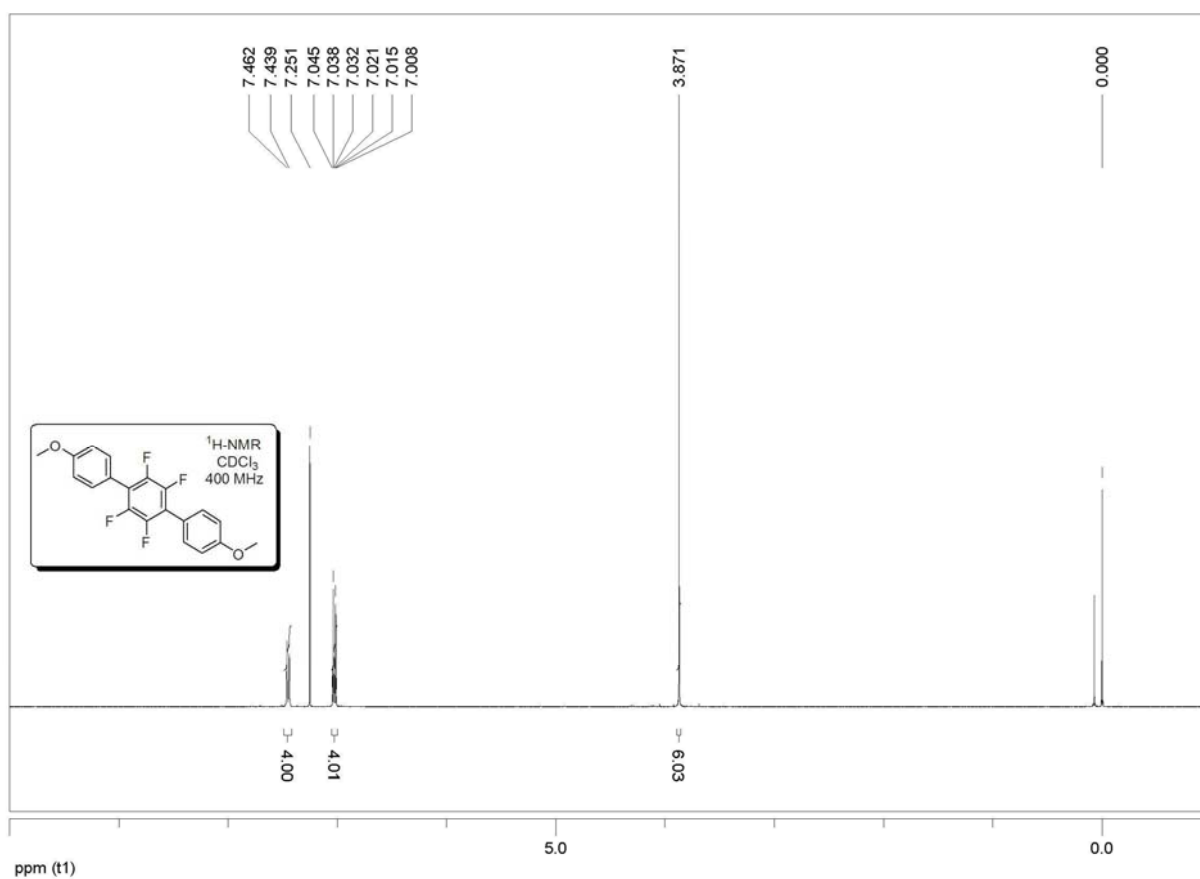
**2, 3, 5, 6-tetrafluoro-4'-methoxybiphenyl-4-amine (33)**

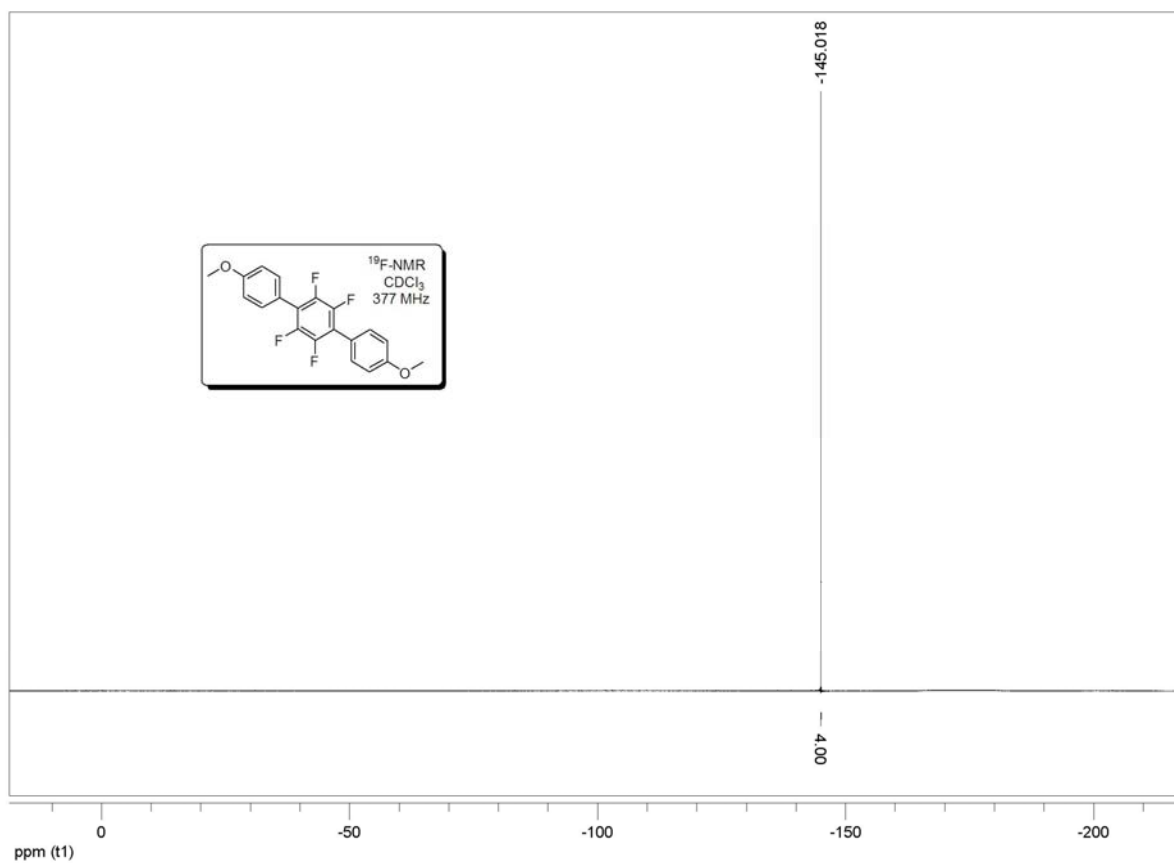
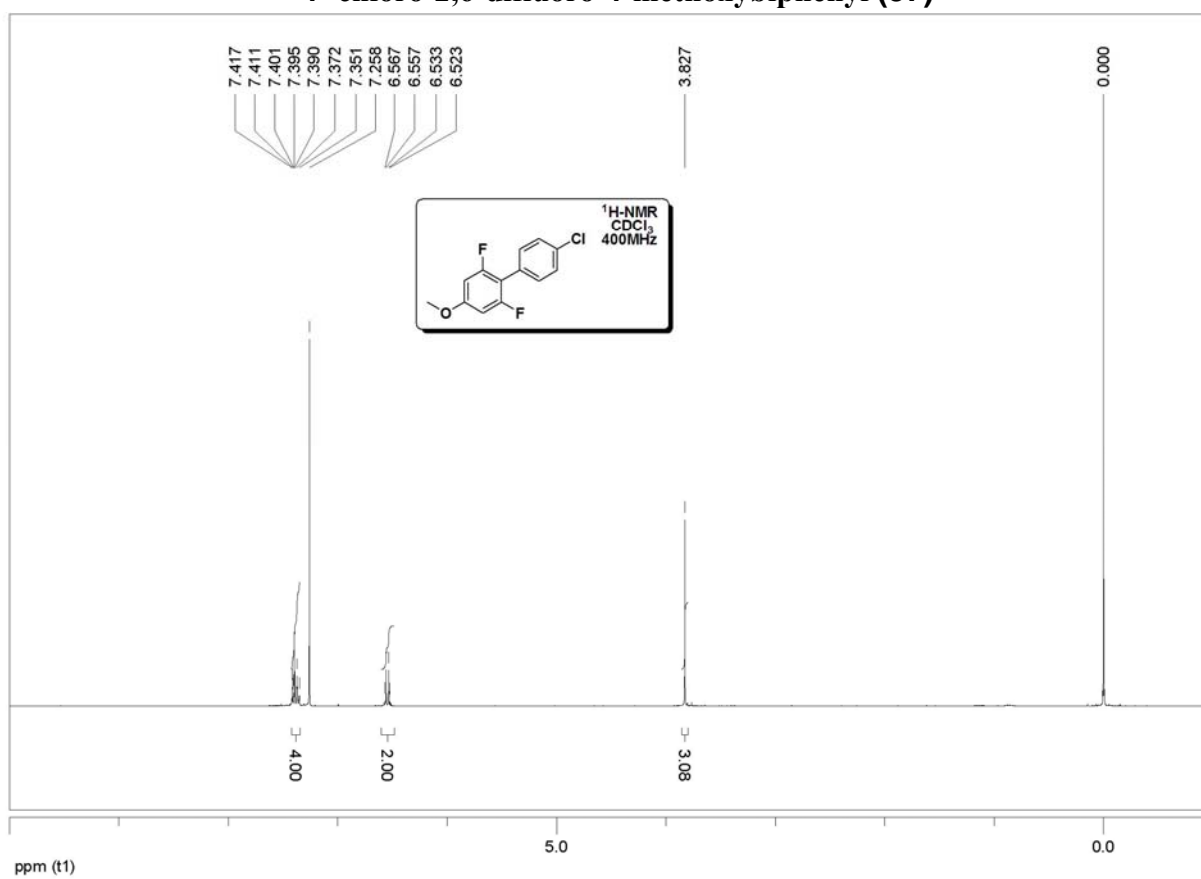


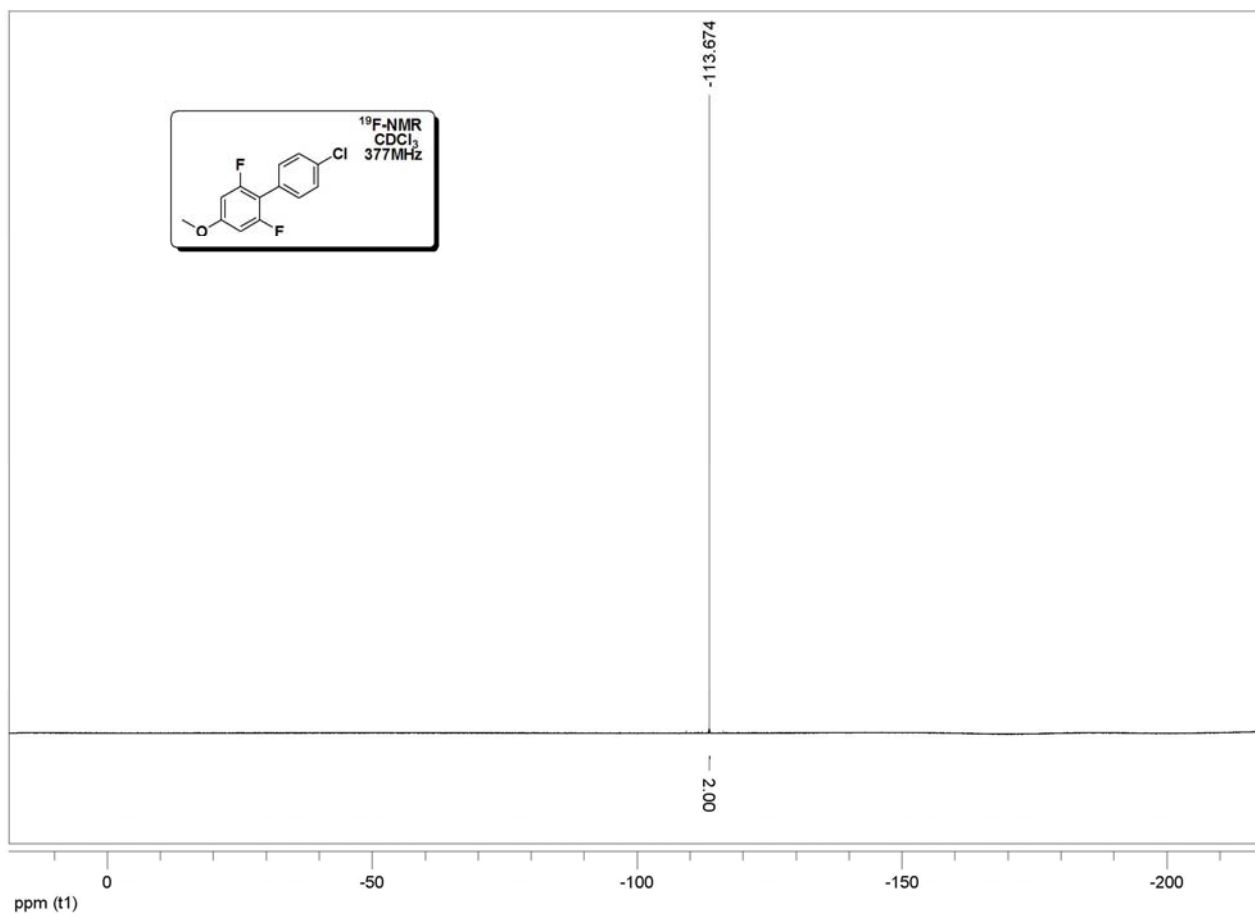
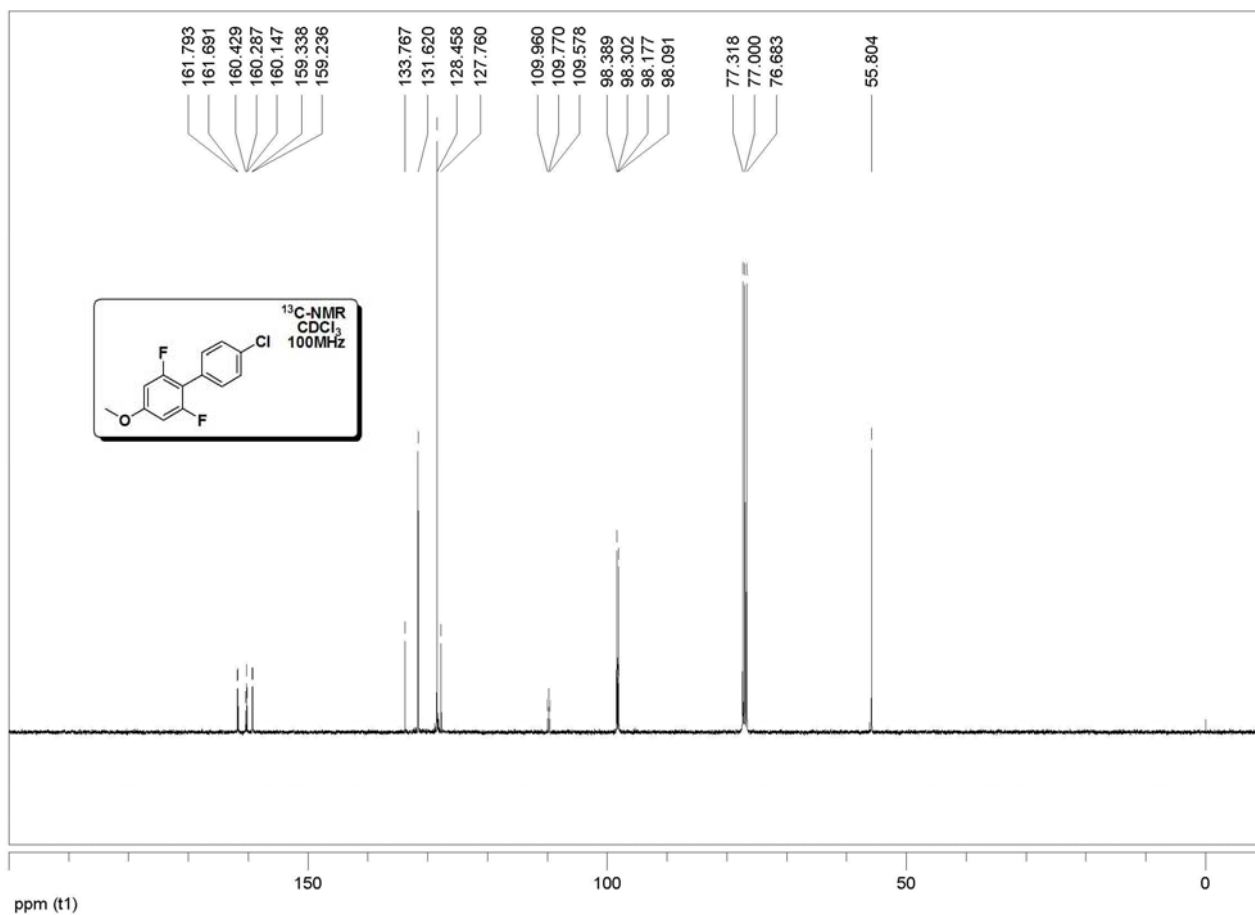
1, 3-di-(*p*-methoxyphenyl)-2, 4, 6-trifluorobenzene (34)

**1, 3, 5-tri(*p*-methoxyphenyl)-2, 4, 6-trifluorobenzene (35)**

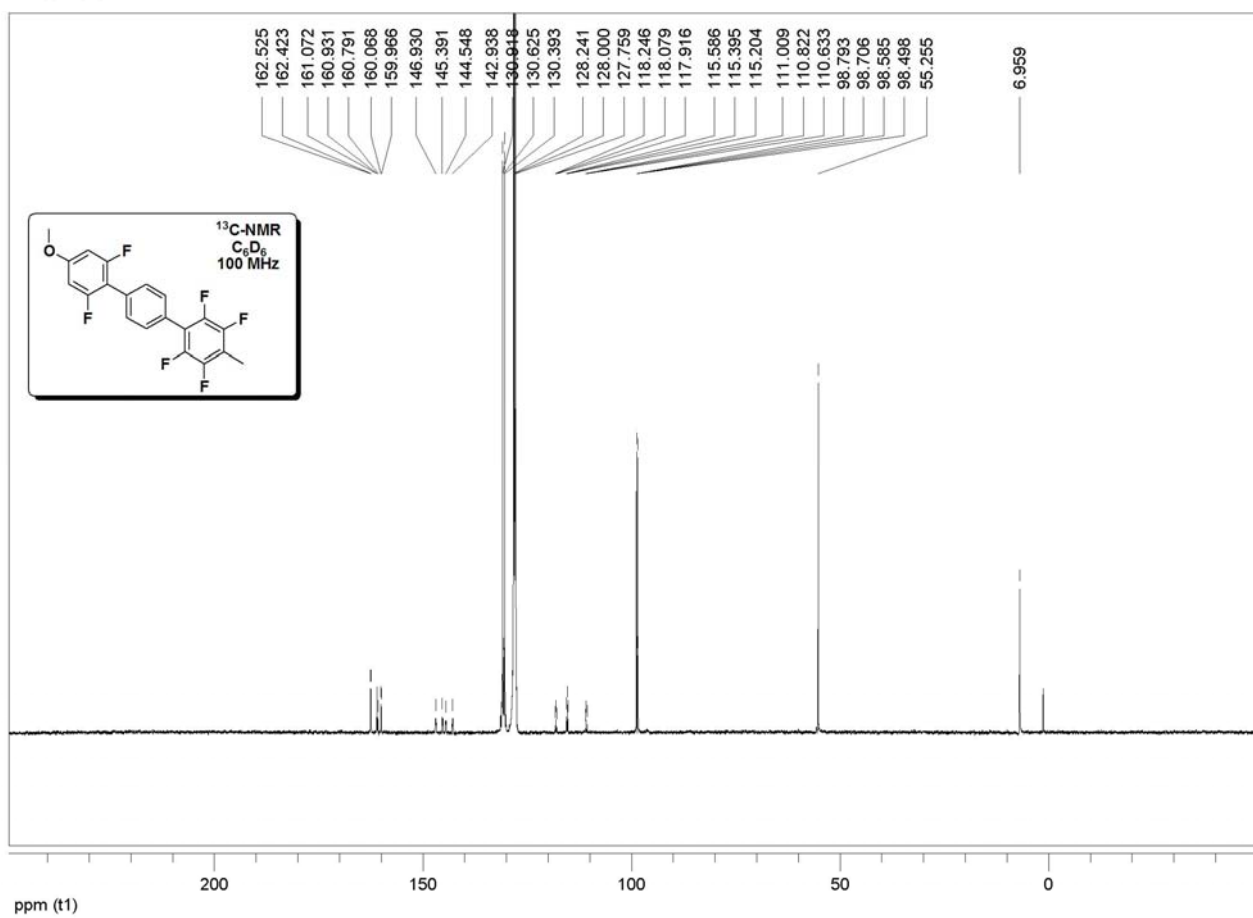
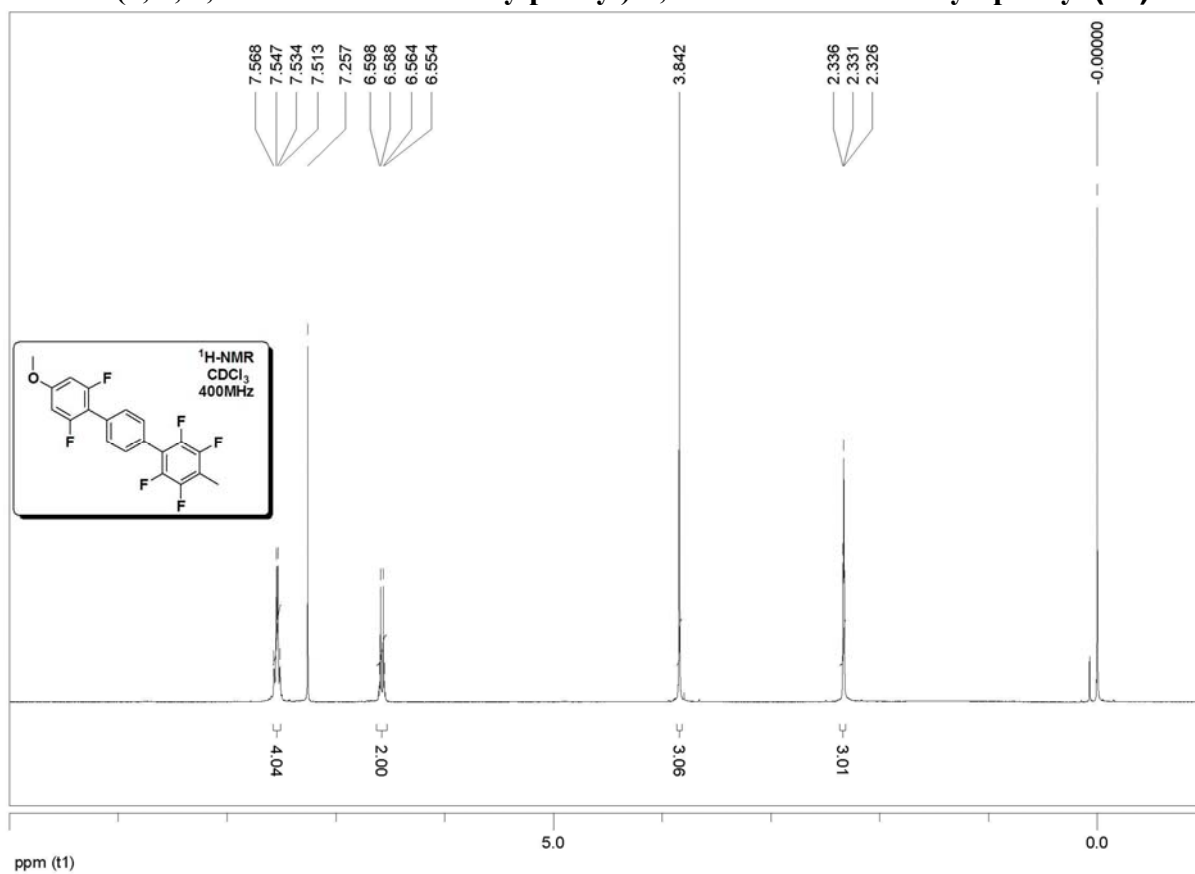


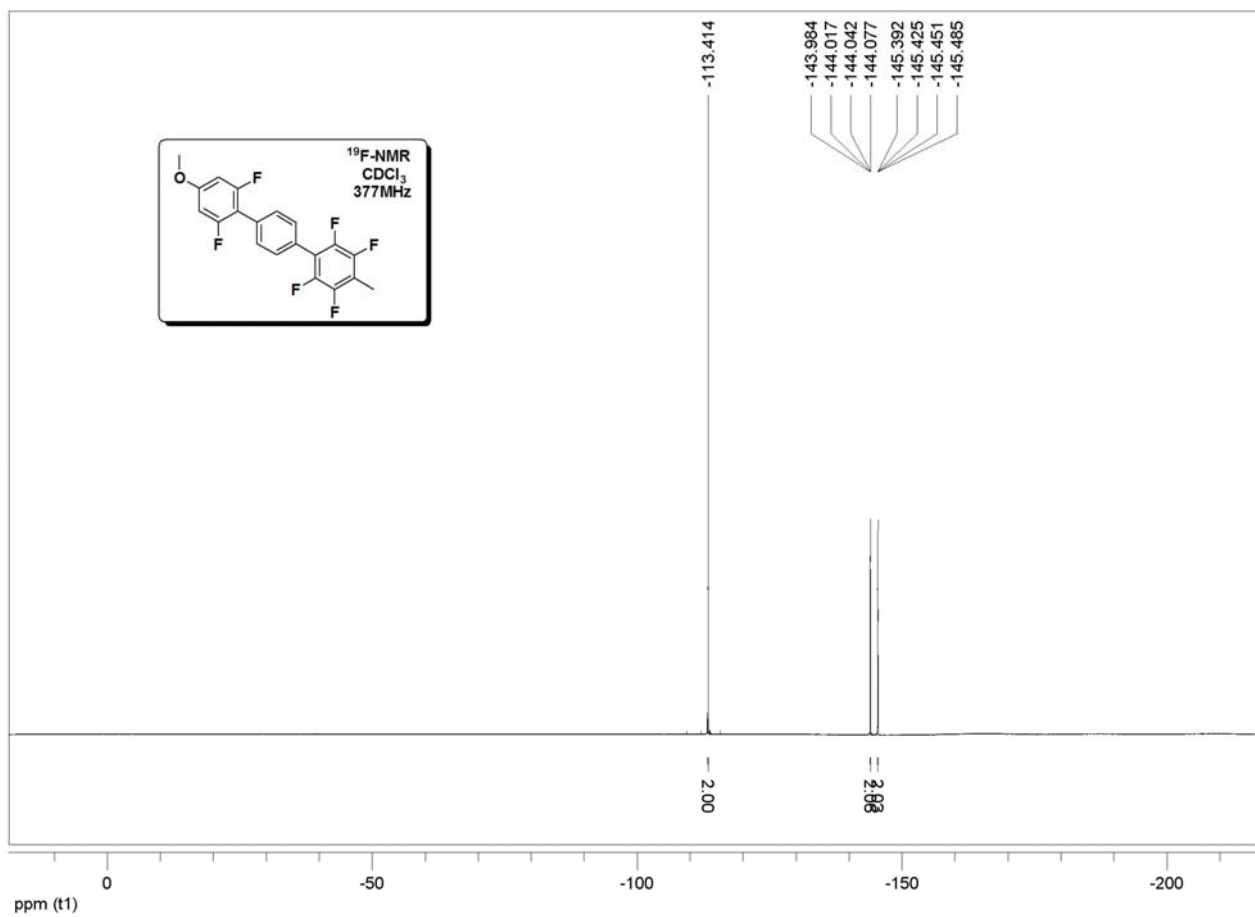
1, 4-di-(p-methoxyphenyl)-2, 3, 5, 6-tetrafluorobenzene (36)

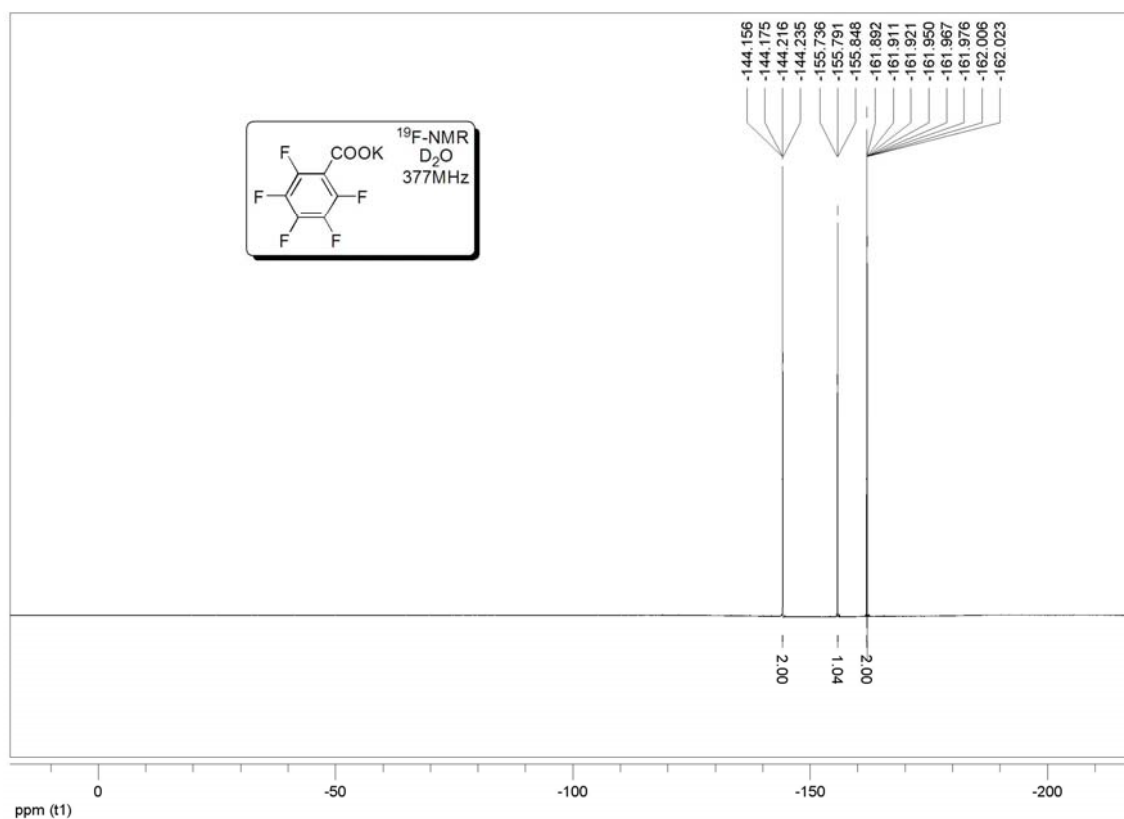
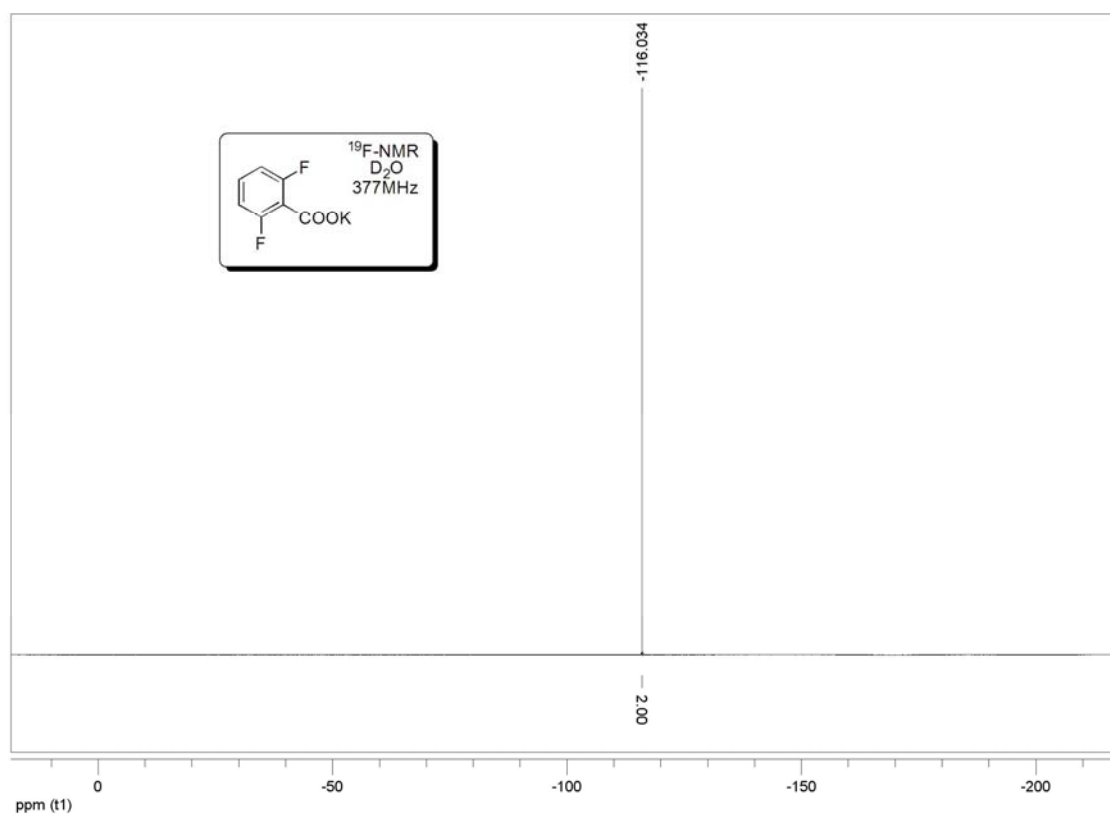
**4'-chloro-2,6-difluoro-4-methoxybiphenyl (37)**



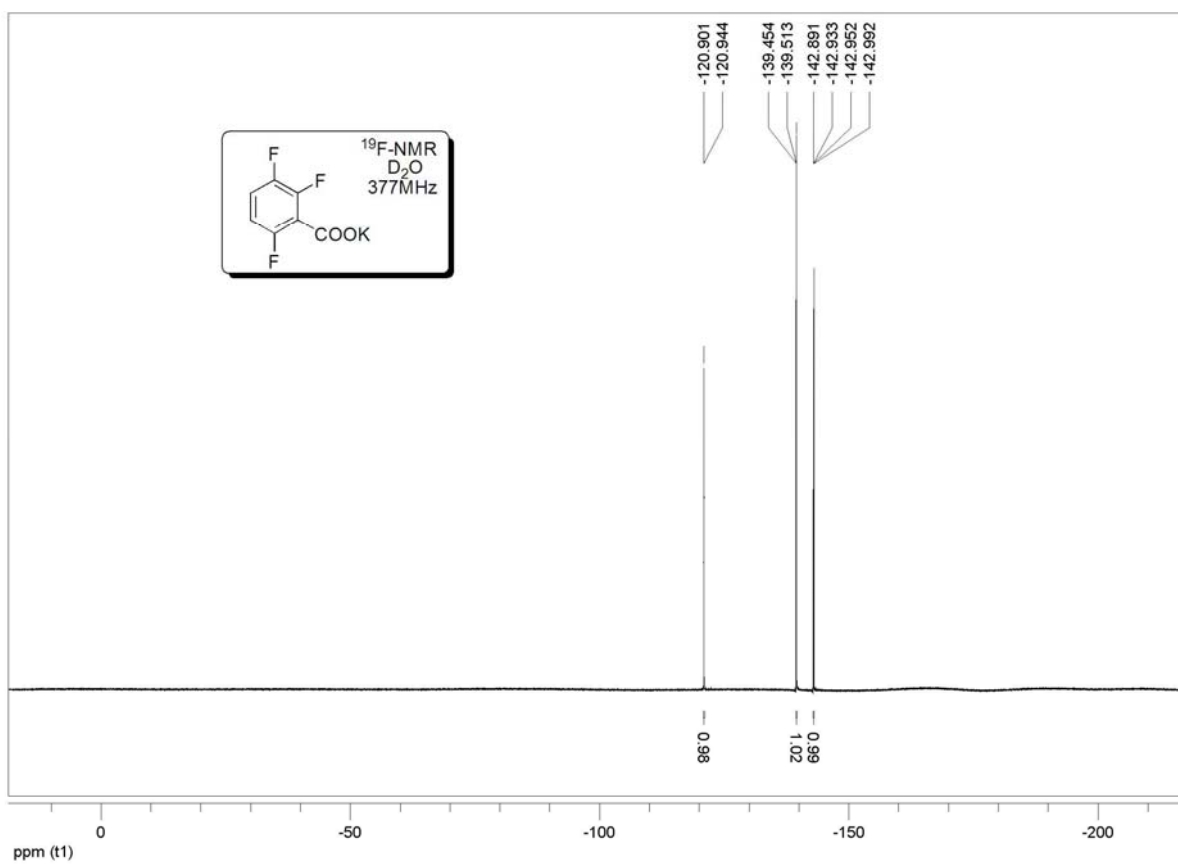
4'-(2, 3, 5, 6-tetrafluoro-4-methylphenyl)-2, 6-difluoro-4-methoxybiphenyl (38)



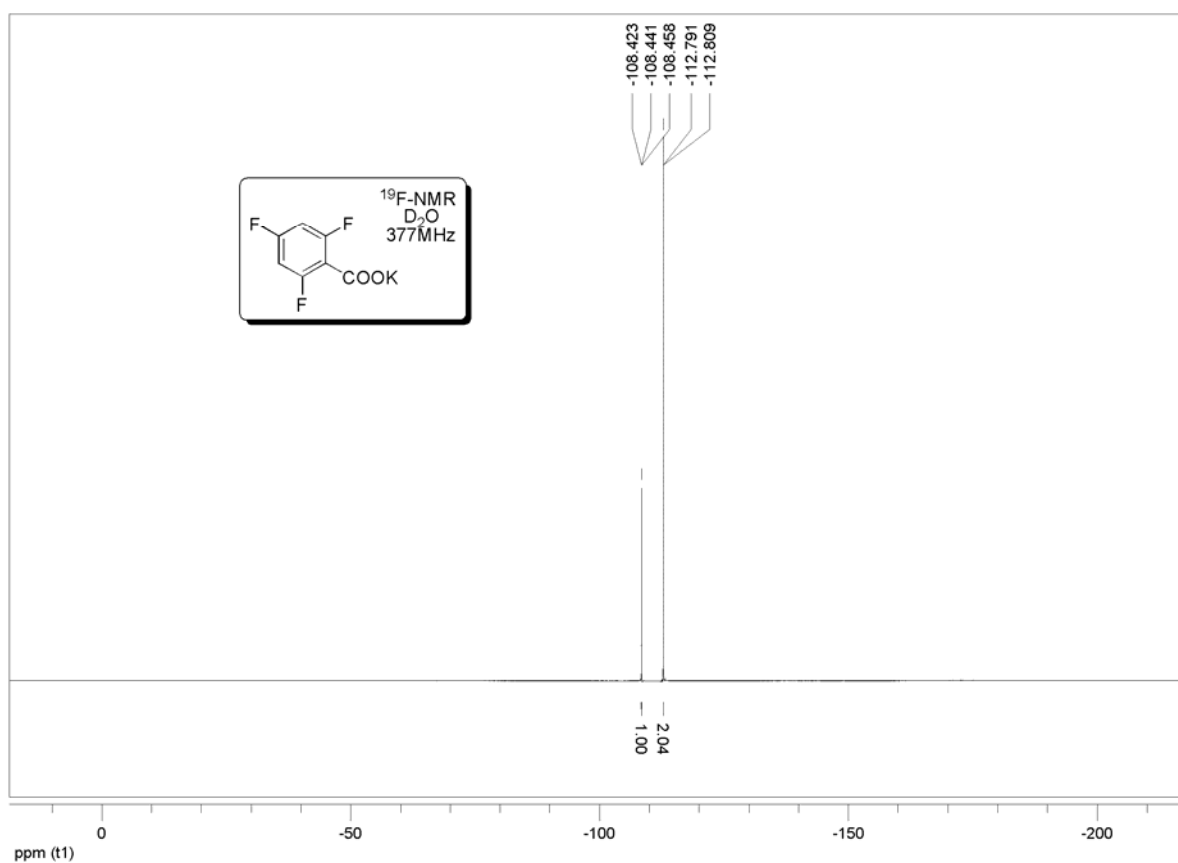


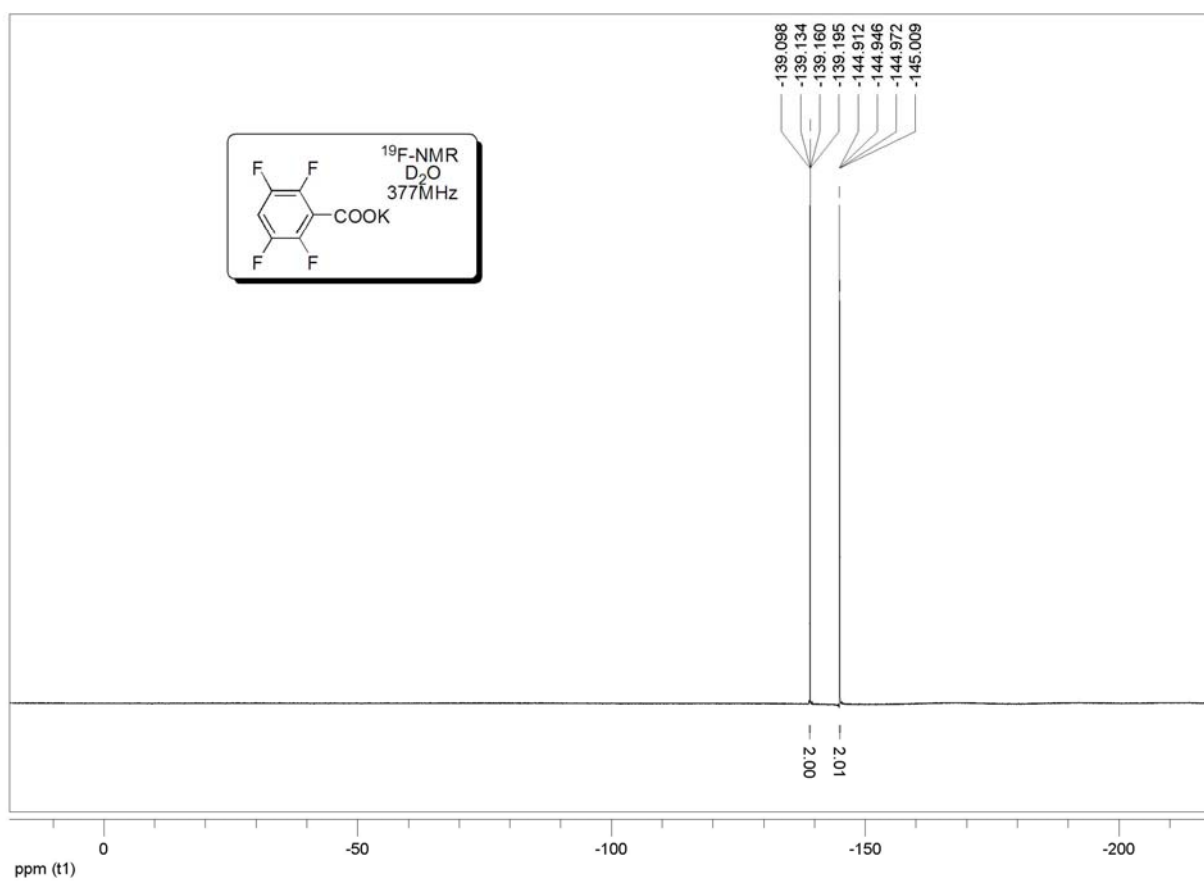
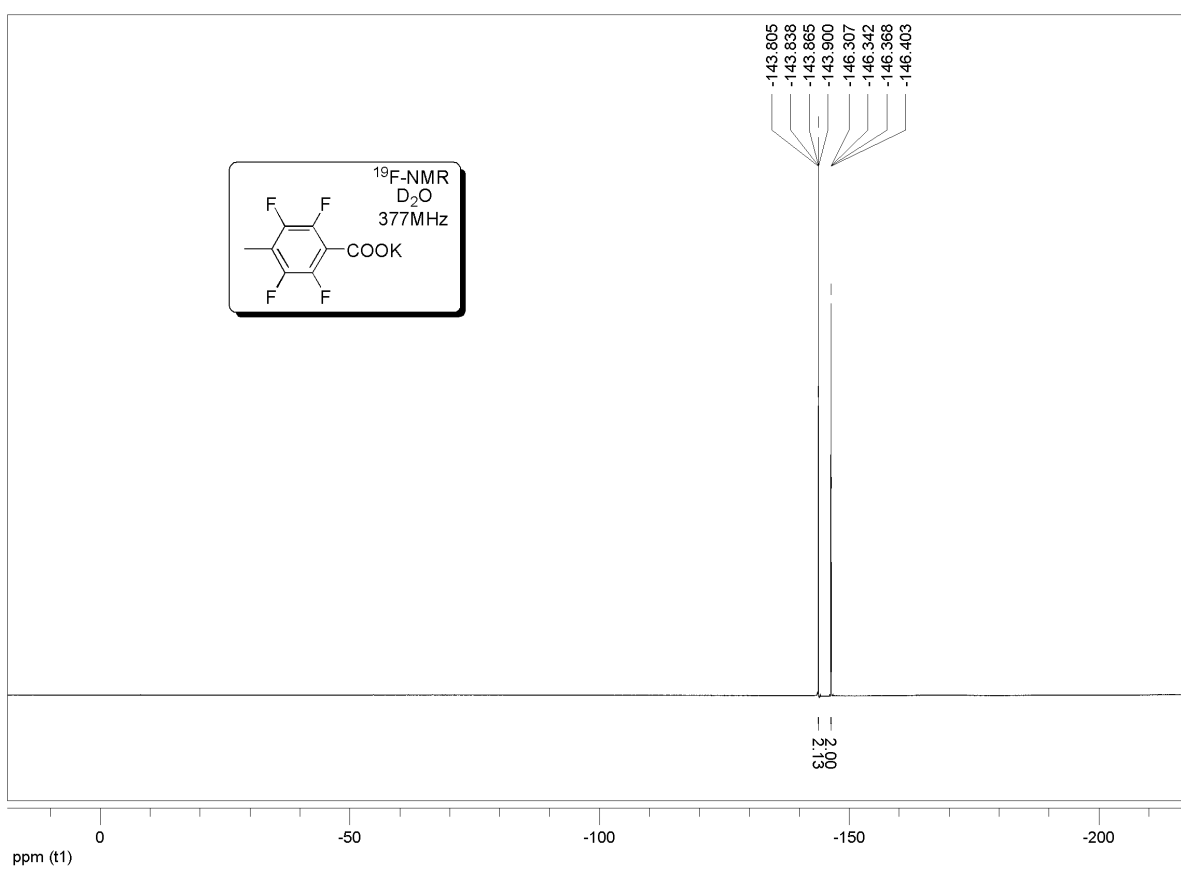
^{19}F -NMR Spectra of the Potassium salts:**Potassium pentafluorobenzoate (1a)****Potassium 2,6-difluorobenzoate (2a)**

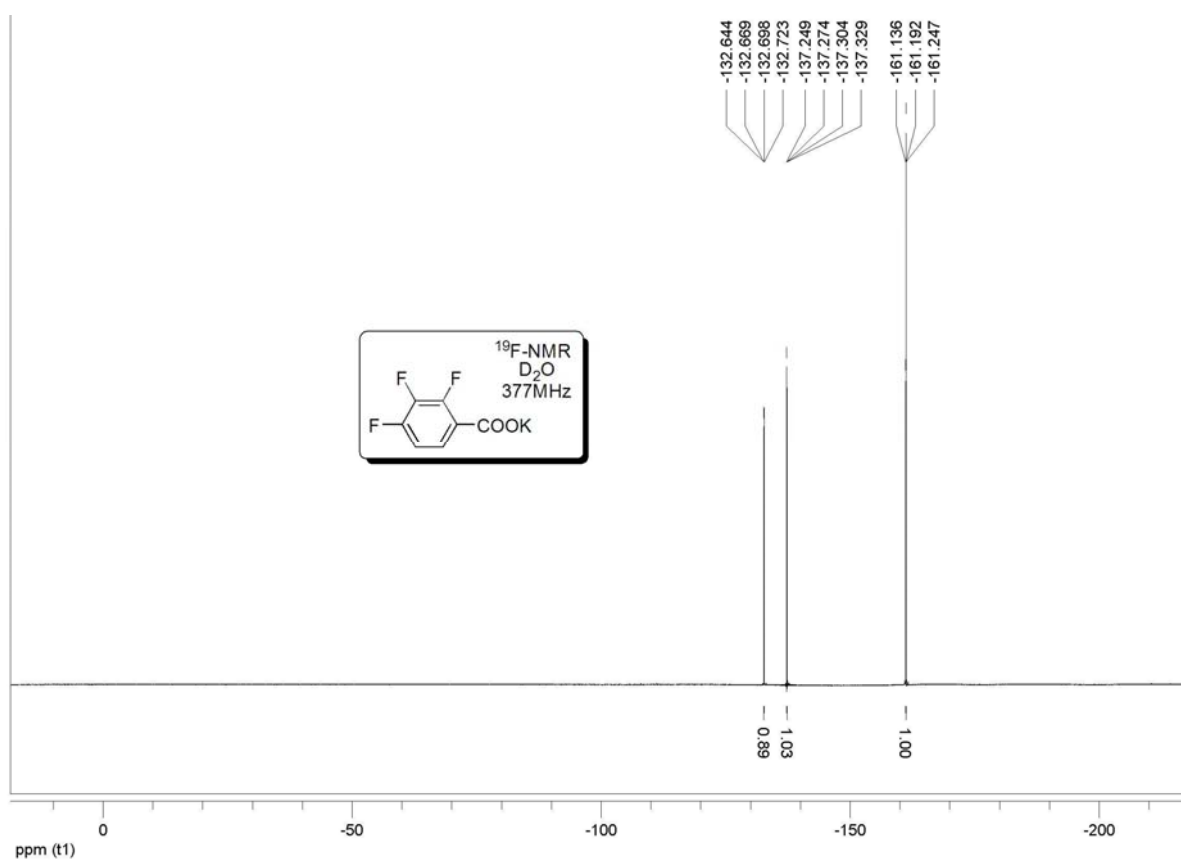
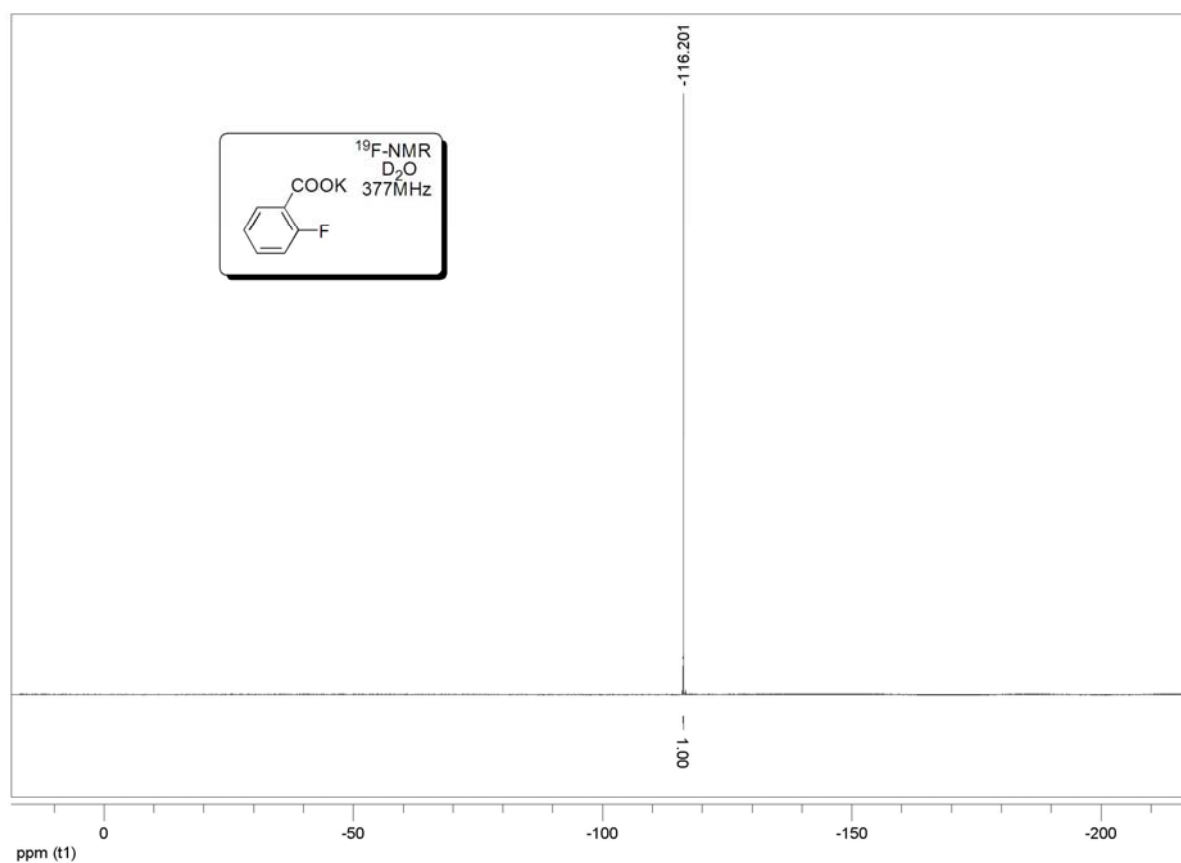
Potassium 2, 3, 6-trifluorobenzoate (3a)

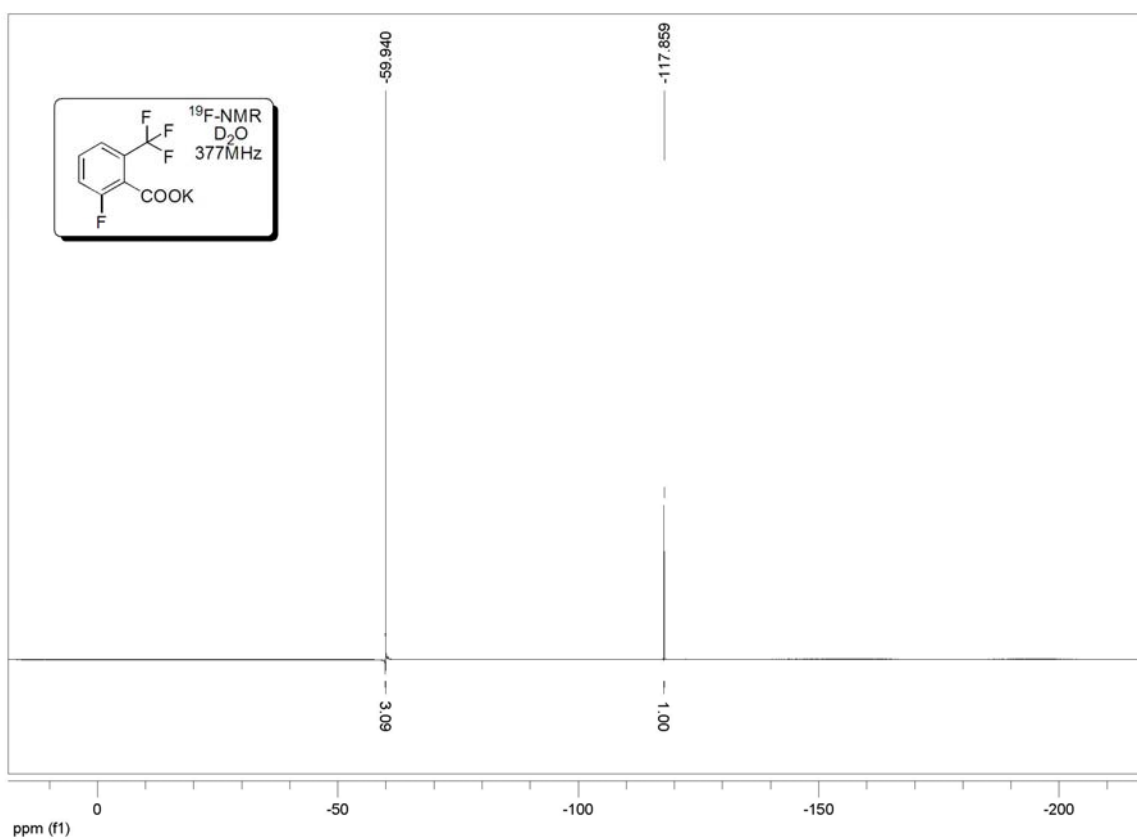
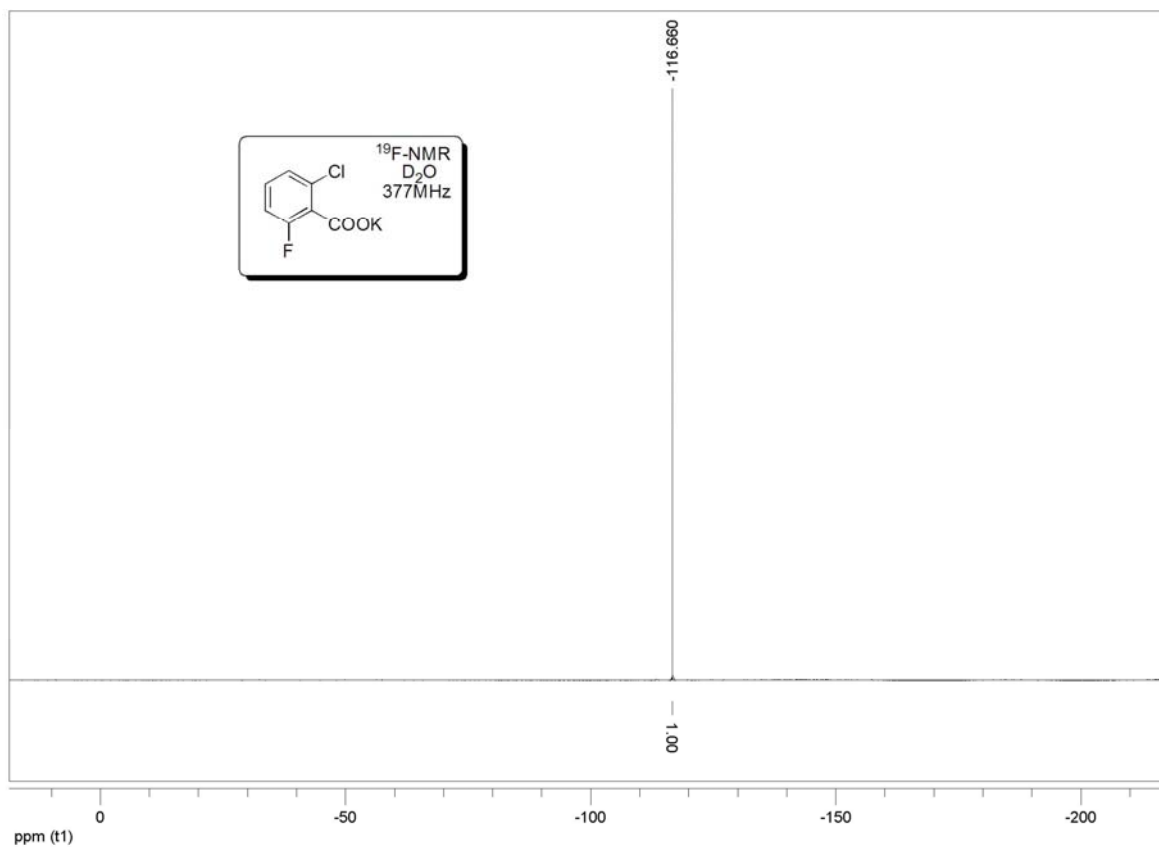


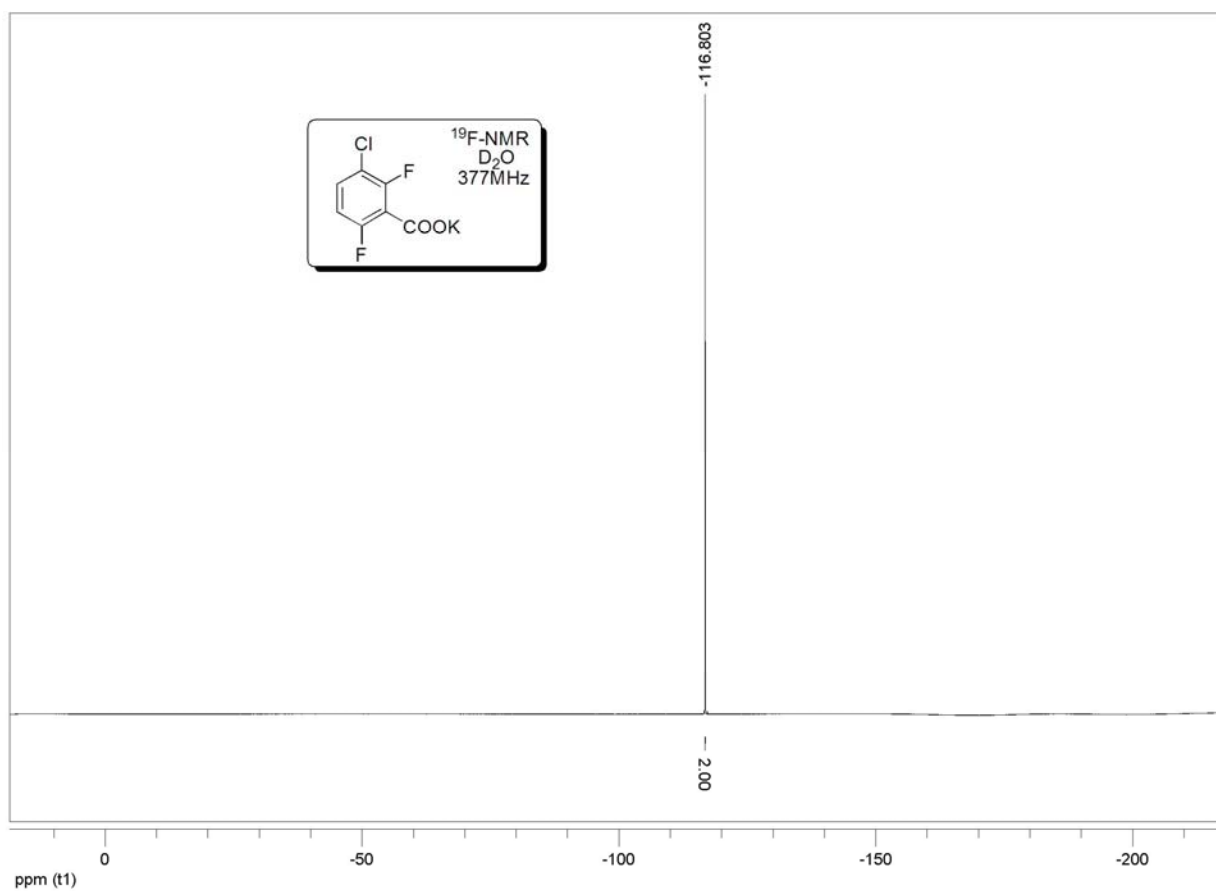
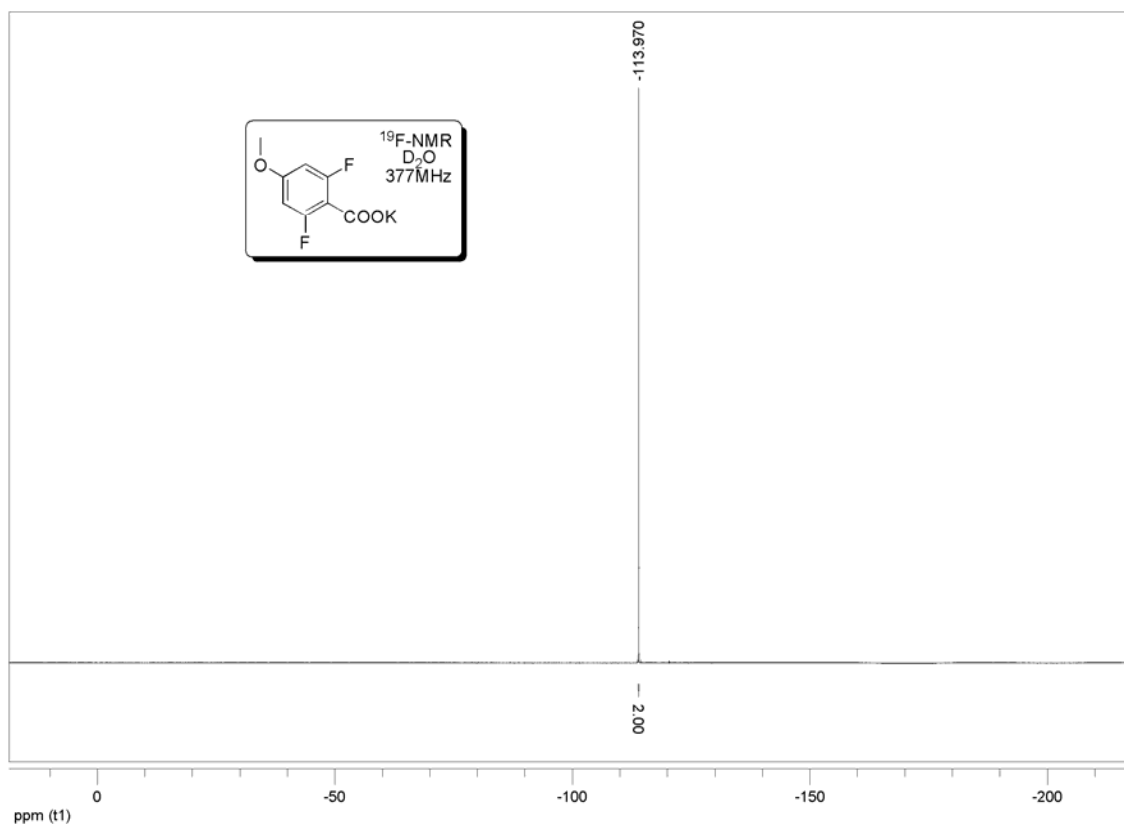
Potassium 2, 4, 6-trifluorobenzoate (4a)

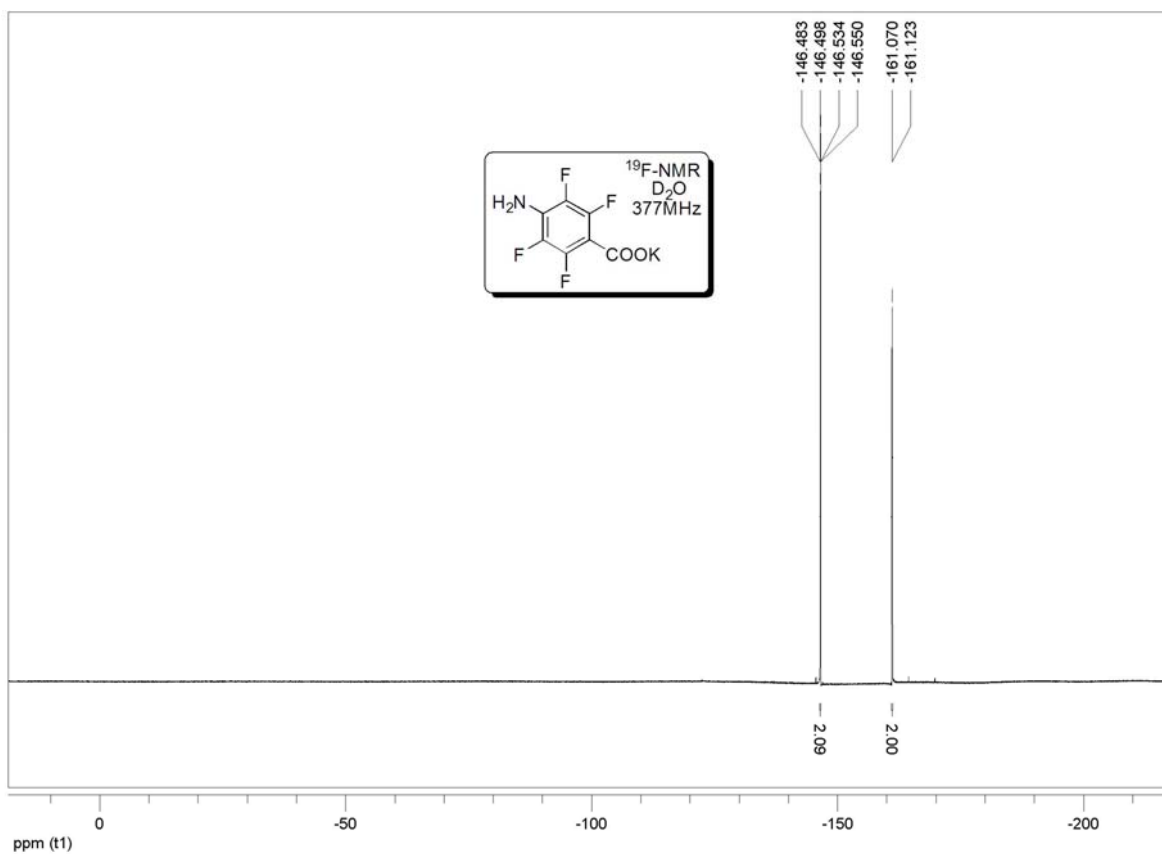


Potassium 2, 3, 5, 6-tetrafluorobenzoate (5a)**Potassium 2, 3, 5, 6-tetrafluoro-4-methylbenzoate (6a)**

Potassium 2, 3, 4-trifluorobenzoate (7a)**Potassium 2-fluorobenzoate (8a)**

Potassium 2-fluoro-6-trifluoromethylbenzoate (9a)**Potassium 2-fluoro-6-chlorobenzoate (10a)**

Potassium 3-chloro-2, 6-difluorobenzoate (11a)**Potassium 2, 6-difluoro-4-methoxybenzoate (12a)**

Potassium 4-amino-2,3,5,6-tetrafluorobenzoate (13a)

Part7. Computational Section.....S105-S115**Computational method:**

All calculations were performed using Gaussian03 suite of program.¹ Density functional theory method was used, employing B3LYP hybrid functional.² Geometry optimization was done using a combined basis set where LANL2DZ³ was used for Pd and P atom and 6-31G(d) for the rest. Extra d functions was added to P atom.⁴ Frequency calculation was done at the same level of theory as geometry optimization, to confirm the stationary points to be minima or saddle points. For saddle points, intrinsic reaction coordinate analysis (IRC)⁵ was done to verify that they connect the right reactants and products on the potential energy surface. Single point energy calculations were done using B3LYP method at a larger basis set, that is, LANL2DZ was used for Pd and P, and 6-311+G(d, p) was used for the rest. Solvent effect was accounted for using self-consistent reaction field (SCRF) method, using CPCM model and UAHF radii.⁶ Diglyme was used as the solvent.

Reference:

1. Frisch, M. J.; *Gaussian 03, revision D. 01*; Gaussian, Inc.: Wallingford, CT, **2004**.
2. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
3. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 299–310.
4. Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237-240.
5. (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363–368. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161. (c) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523–5527.
6. (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001. (b) M Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.

Optimized structures:

IN0			
Pd	-1.3375	-0.0000	0.0000
P	0.8837	0.0001	-0.0001
C	1.7345	1.5541	-0.5805
H	2.8271	1.4570	-0.5424
H	1.4288	1.7727	-1.6080
H	1.4260	2.3939	0.0492
C	1.7345	-0.2742	1.6360
H	2.8270	-0.2579	1.5324
H	1.4286	0.5058	2.3396
H	1.4268	-1.2399	2.0479
C	1.7344	-1.2800	-1.0553
H	2.8270	-1.2006	-0.9872
H	1.4261	-2.2791	-0.7333
H	1.4291	-1.1521	-2.0981

IN1			
Pd	0.8167	-0.5329	0.0096
P	2.8683	0.3722	-0.0060
C	-4.0875	-0.7647	-0.0290
C	-2.3854	0.9812	0.0308
C	-5.0808	0.2172	-0.0349
H	-4.3431	-1.8189	-0.0497
C	-3.3934	1.9477	0.0242
H	-1.3314	1.2483	0.0554
C	-4.7377	1.5705	-0.0084
H	-6.1248	-0.0825	-0.0607
H	-3.1212	2.9993	0.0449
H	-5.5157	2.3284	-0.0132
C	-2.7551	-0.3607	0.0040
Cl	-1.4931	-1.6098	0.0125
C	3.9050	0.1974	1.5347
H	4.8866	0.6752	1.4224
H	3.3785	0.6521	2.3793
H	4.0460	-0.8643	1.7587
C	2.9810	2.2128	-0.2865
H	2.4202	2.7341	0.4954
H	4.0204	2.5646	-0.2776
H	2.5269	2.4606	-1.2508
C	4.0640	-0.2448	-1.2975
H	5.0392	0.2529	-1.2226

H	4.2018	-1.3237	-1.1785
H	3.6452	-0.0668	-2.2926

TS1

Pd	0.3484	-0.9826	0.0001
P	2.1502	0.4705	0.0001
C	-2.0045	0.4388	-1.2219
C	-2.0048	0.4386	1.2218
C	-2.5541	1.7218	-1.2079
H	-1.8149	-0.0782	-2.1560
C	-2.5544	1.7216	1.2079
H	-1.8155	-0.0786	2.1559
C	-2.8270	2.3711	0.0000
H	-2.7806	2.2092	-2.1530
H	-2.7811	2.2089	2.1531
H	-3.2674	3.3639	0.0001
C	-1.6830	-0.1710	-0.0000
Cl	-1.7594	-2.1933	-0.0001
C	2.2151	1.6474	1.4395
H	3.0501	2.3526	1.3493
H	1.2750	2.2050	1.4896
H	2.3226	1.0805	2.3692
C	2.2145	1.6474	-1.4394
H	1.2744	2.2050	-1.4891
H	3.0495	2.3526	-1.3497
H	2.3215	1.0805	-2.3692
C	3.8829	-0.2127	-0.0003
H	4.6333	0.5872	-0.0003
H	4.0275	-0.8395	0.8849
H	4.0272	-0.8393	-0.8856

IN2

Pd	-0.4759	0.9591	-0.0002
C	1.1739	-0.1538	-0.0000
C	1.7680	-0.5028	1.2146
C	1.7676	-0.5037	-1.2146
C	2.9686	-1.2238	1.2069
H	1.3223	-0.2033	2.1579
C	2.9681	-1.2247	-1.2069
H	1.3216	-0.2048	-2.1580
C	3.5673	-1.5891	0.0001
H	3.4358	-1.4894	2.1521
H	3.4350	-1.4909	-2.1520
H	4.4999	-2.1467	0.0001

Cl	0.4896	3.0813	-0.0001
P	-1.7285	-0.9889	0.0001
C	-1.5025	-2.1126	-1.4527
H	-0.4518	-2.4077	-1.5161
H	-2.1299	-3.0061	-1.3629
H	-1.7656	-1.5774	-2.3700
C	-3.5530	-0.6500	0.0004
H	-3.8184	-0.0670	-0.8866
H	-4.1272	-1.5834	0.0008
H	-3.8180	-0.0665	0.8872
C	-1.5020	-2.1122	1.4531
H	-1.7653	-1.5769	2.3703
H	-2.1289	-3.0060	1.3635
H	-0.4511	-2.4067	1.5166

IN3

Pd	-1.4307	-0.2199	-0.0544
C	-2.9178	1.0749	0.3008
C	-3.3659	1.9220	-0.7220
C	-3.4014	1.2597	1.6030
C	-4.2731	2.9499	-0.4406
H	-2.9970	1.8006	-1.7376
C	-4.3084	2.2894	1.8798
H	-3.0621	0.6169	2.4117
C	-4.7479	3.1346	0.8593
H	-4.6038	3.6078	-1.2409
H	-4.6670	2.4298	2.8969
H	-5.4529	3.9329	1.0758
P	-3.0184	-1.7810	-0.4713
O	0.5817	-1.1628	-0.3274
C	1.1085	-0.0500	-0.0208
O	0.4119	0.9710	0.2623
C	2.6065	0.0608	0.0081
C	3.3946	-0.9463	0.5758
C	3.2631	1.1708	-0.5346
C	4.7836	-0.8532	0.6094
C	4.6523	1.2731	-0.5213
C	5.4129	0.2589	0.0554
F	2.8326	-2.0213	1.1383
F	5.5162	-1.8212	1.1735
F	6.7448	0.3523	0.0768
F	5.2606	2.3346	-1.0636
F	2.5749	2.1560	-1.1179
C	-4.1535	-2.2049	0.9245

H	-4.7163	-1.3140	1.2148
H	-4.8488	-3.0003	0.6344
H	-3.5644	-2.5377	1.7842
C	-4.1617	-1.4395	-1.8830
H	-4.8758	-2.2597	-2.0145
H	-4.7014	-0.5087	-1.6909
H	-3.5789	-1.3188	-2.8010
C	-2.2250	-3.3927	-0.9118
H	-2.9783	-4.1604	-1.1213
H	-1.5886	-3.2538	-1.7902
H	-1.5882	-3.7199	-0.0851

TS2

Pd	1.4932	-0.2625	-0.5770
C	3.1776	-0.7981	0.3431
C	4.3216	-1.0542	-0.4291
C	5.4341	-1.6779	0.1452
C	5.4253	-2.0247	1.4982
C	4.2998	-1.7494	2.2777
C	3.1839	-1.1270	1.7076
H	4.3459	-0.7849	-1.4829
H	6.3085	-1.8881	-0.4660
H	6.2935	-2.5026	1.9440
H	4.2876	-2.0168	3.3317
H	2.3152	-0.9182	2.3282
P	1.7970	1.8871	0.0112
C	1.2545	2.9457	-1.3945
C	3.4789	2.4824	0.4755
C	0.7095	2.3807	1.4172
H	0.2642	2.6009	-1.7011
H	1.9437	2.8242	-2.2346
H	1.2233	3.9988	-1.0931
H	4.1817	2.2632	-0.3325
H	3.4562	3.5627	0.6578
H	3.8180	1.9627	1.3747
H	0.8628	3.4383	1.6617
H	0.9289	1.7704	2.2973
H	-0.3288	2.2258	1.1155
O	-0.2643	0.1597	-1.6658
C	-1.3022	-0.6044	-1.8277
O	-1.4828	-1.4241	-2.7151
C	-2.4188	-0.3986	-0.7929
C	-3.2131	-1.4762	-0.3777
C	-4.2540	-1.3191	0.5362

C	-4.5391	-0.0587	1.0531
C	-3.7679	1.0317	0.6637
C	-2.7267	0.8488	-0.2424
F	-2.9768	-2.7166	-0.8132
F	-4.9799	-2.3746	0.9265
F	-5.5392	0.1017	1.9258
F	-4.0304	2.2498	1.1616
F	-2.0236	1.9554	-0.5673

IN4

Pd	0.8686	-0.4211	-0.0036
C	0.5550	1.5715	-0.0025
C	0.3724	2.2610	1.2071
C	0.3533	2.2627	-1.2080
C	-0.0335	3.6006	1.2104
H	0.5315	1.7545	2.1568
C	-0.0526	3.6022	-1.2029
H	0.4989	1.7580	-2.1608
C	-0.2462	4.2740	0.0059
H	-0.1830	4.1151	2.1568
H	-0.2168	4.1181	-2.1460
H	-0.5594	5.3146	0.0090
P	3.1028	-0.0279	-0.0081
O	-0.7714	-4.0087	0.0415
C	-0.2695	-2.9028	0.0221
O	0.9742	-2.5586	0.0091
C	-1.2117	-1.6514	0.0102
C	-1.7340	-1.1487	-1.1936
C	-1.7369	-1.1269	1.2033
C	-2.7091	-0.1566	-1.2152
C	-2.7118	-0.1344	1.2044
C	-3.1973	0.3477	-0.0105
F	-1.2943	-1.6357	-2.3615
F	-3.1704	0.3256	-2.3738
F	-4.1170	1.3121	-0.0204
F	-3.1753	0.3698	2.3526
F	-1.2989	-1.5913	2.3810
C	4.0069	-1.6331	-0.0891
H	3.7491	-2.1412	-1.0218
H	5.0898	-1.4755	-0.0360
H	3.6766	-2.2727	0.7329
C	3.7658	0.9622	-1.4183
H	3.3121	1.9563	-1.4082
H	4.8553	1.0532	-1.3475

H	3.5062	0.4708	-2.3605
C	3.7605	0.8196	1.4946
H	3.5133	0.2283	2.3811
H	4.8480	0.9360	1.4301
H	3.2911	1.8023	1.5882

TS3

Pd	-0.9704	-0.5585	-0.0000
C	-0.8466	1.4453	-0.0000
C	-0.7669	2.1531	-1.2081
C	-0.7665	2.1530	1.2080
C	-0.6099	3.5443	-1.2059
H	-0.8104	1.6241	-2.1571
C	-0.6094	3.5442	1.2059
H	-0.8096	1.6239	2.1570
C	-0.5348	4.2439	0.0000
H	-0.5425	4.0778	-2.1513
H	-0.5417	4.0776	2.1513
H	-0.4138	5.3239	0.0000
P	-3.2811	-0.3542	0.0000
O	1.4555	-3.5437	0.0000
C	0.5141	-2.8207	0.0001
O	-0.7138	-2.7578	0.0001
C	1.2026	-0.9256	-0.0000
C	1.8612	-0.5951	1.1876
C	1.8612	-0.5952	-1.1876
C	3.1059	0.0189	1.2133
C	3.1059	0.0189	-1.2133
C	3.7267	0.3232	-0.0000
F	1.2805	-0.8800	2.3698
F	3.7161	0.3317	2.3645
F	4.9211	0.9162	-0.0000
F	3.7161	0.3316	-2.3646
F	1.2806	-0.8801	-2.3698
C	-4.0193	0.5170	-1.4545
H	-5.1102	0.5711	-1.3699
H	-3.6051	1.5270	-1.5143
H	-3.7554	-0.0192	-2.3711
C	-4.0191	0.5168	1.4548
H	-3.6052	1.5269	1.5145
H	-5.1100	0.5707	1.3704
H	-3.7549	-0.0194	2.3712
C	-4.1129	-2.0078	-0.0000
H	-3.8003	-2.5708	0.8841

H	-5.2035	-1.9041	0.0000
H	-3.8004	-2.5707	-0.8843

IN5

Pd	-0.8042	-0.7672	-0.0054
C	-0.9279	1.2264	0.0067
C	-0.9874	1.9245	-1.2030
C	-1.0057	1.9085	1.2244
C	-1.1770	3.3120	-1.1881
H	-0.8681	1.4029	-2.1473
C	-1.1949	3.2962	1.2250
H	-0.9019	1.3747	2.1637
C	-1.2875	3.9992	0.0222
H	-1.2254	3.8530	-2.1302
H	-1.2574	3.8248	2.1733
H	-1.4299	5.0764	0.0282
P	-3.2026	-1.0449	-0.0068
C	1.2261	-0.5143	-0.0030
C	1.9556	-0.4277	-1.1833
C	1.9548	-0.4485	1.1792
C	3.3433	-0.3083	-1.2071
C	3.3425	-0.3296	1.2058
C	4.0384	-0.2606	0.0001
F	1.3188	-0.4549	-2.3798
F	4.0194	-0.2395	-2.3657
F	5.3742	-0.1517	0.0015
F	4.0180	-0.2814	2.3659
F	1.3174	-0.4965	2.3745
C	-4.0698	-0.2907	1.4483
H	-3.7960	0.7660	1.5171
H	-5.1579	-0.3809	1.3578
H	-3.7425	-0.7883	2.3664
C	-4.0732	-0.2697	-1.4488
H	-5.1613	-0.3537	-1.3528
H	-3.7927	0.7858	-1.5087
H	-3.7548	-0.7603	-2.3739
C	-3.8623	-2.7836	-0.0189
H	-4.9580	-2.7960	-0.0172
H	-3.5025	-3.3071	-0.9103
H	-3.4995	-3.3210	0.8629

TS4

Pd	0.9457	-0.5864	-0.0001
C	0.2828	1.3814	0.0001

C	0.3769	2.0862	1.2136
C	0.3769	2.0865	-1.2133
C	0.6002	3.4651	1.2049
H	0.2688	1.5660	2.1564
C	0.6002	3.4653	-1.2044
H	0.2688	1.5663	-2.1562
C	0.7154	4.1618	0.0003
H	0.6799	3.9941	2.1517
H	0.6799	3.9945	-2.1510
H	0.8832	5.2354	0.0004
P	3.2919	-1.0764	-0.0001
C	-1.0686	-0.1308	-0.0000
C	-1.7991	-0.2967	1.1842
C	-1.7992	-0.2964	-1.1842
C	-3.1642	-0.5634	1.2035
C	-3.1642	-0.5631	-1.2035
C	-3.8539	-0.6936	0.0000
F	-1.1834	-0.2008	2.3826
F	-3.8180	-0.7166	2.3642
F	-5.1645	-0.9609	0.0000
F	-3.8182	-0.7161	-2.3642
F	-1.1836	-0.2002	-2.3826
C	4.2320	-0.3793	1.4438
H	5.3079	-0.5708	1.3578
H	4.0600	0.6999	1.4967
H	3.8600	-0.8269	2.3706
C	4.2319	-0.3787	-1.4437
H	4.0597	0.7005	-1.4962
H	5.3078	-0.5699	-1.3579
H	3.8599	-0.8259	-2.3707
C	3.8538	-2.8514	-0.0003
H	4.9472	-2.9297	0.0003
H	3.4595	-3.3598	0.8852
H	3.4604	-3.3594	-0.8864

PhCl

C	1.2161	-0.1786	0.0000
C	1.2074	-1.5745	0.0000
C	0.0000	-2.2751	0.0000
C	-1.2074	-1.5745	0.0000
C	-1.2161	-0.1786	0.0000
C	0.0000	0.5037	0.0000
Cl	0.0000	2.2648	0.0000
H	2.1491	0.3748	0.0000

H	2.1515	-2.1122	0.0000
H	0.0000	-3.3612	0.0000
H	-2.1515	-2.1122	0.0000
H	-2.1491	0.3748	0.0000

IN6

C	0.1675	-0.0000	-0.0000
C	-0.5758	-1.1827	-0.1266
C	-1.9679	-1.1953	-0.1272
C	-2.6697	0.0000	0.0000
C	-1.9679	1.1953	0.1272
C	-0.5758	1.1827	0.1266
C	1.6541	-0.0000	-0.0000
C	2.3694	-0.9453	0.7528
C	3.7629	-0.9429	0.7526
C	4.4650	0.0000	0.0000
C	3.7629	0.9429	-0.7526
C	2.3694	0.9453	-0.7528
H	1.8330	-1.6808	1.3429
H	4.2997	-1.6797	1.3437
H	5.5515	-0.0000	0.0000
H	4.2997	1.6797	-1.3437
H	1.8331	1.6808	-1.3429
F	0.0478	2.3632	0.2695
F	-2.6329	2.3491	0.2601
F	-4.0054	0.0000	0.0000
F	-2.6329	-2.3491	-0.2601
F	0.0477	-2.3632	-0.2695

CO2

C	0.0000	0.0000	0.0000
O	0.0000	0.0000	1.1692
O	0.0000	0.0000	-1.1692

KCl

K	0.0000	0.0000	1.2900
Cl	0.0000	0.0000	-1.4418

C6F5COOK

C	1.9980	1.2035	-0.0466
C	0.6053	1.1905	-0.0370
C	-0.1203	0.0000	-0.0000
C	0.6053	-1.1905	0.0371
C	1.9981	-1.2034	0.0466

C	2.6967	-0.0000	0.0000
F	-0.0278	2.3722	-0.1000
C	-1.6474	-0.0001	0.0001
O	-2.2096	-0.6947	-0.8895
F	-0.0277	-2.3722	0.1000
F	2.6699	-2.3628	0.1038
F	4.0356	0.0001	0.0000
F	2.6698	2.3629	-0.1038
O	-2.2096	0.6944	0.8897
K	-4.4916	0.0001	-0.0001