Supplementary Information

Excited-State Palladium-Catalyzed Defluorinative Arylation of Polyfluoroarenes

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1. General Information

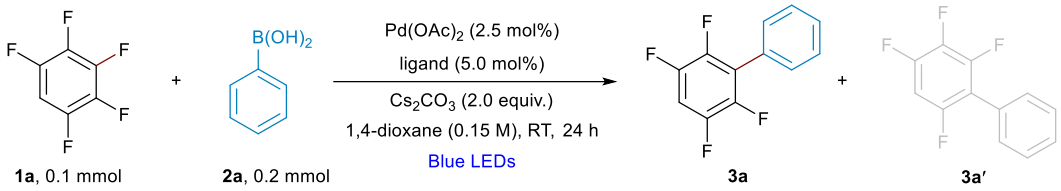
Unless otherwise noted, all reactions were carried out under argon in a screw cap glass reaction vial. All the reagents and solvents were bought from Sigma Aldrich, Alfa Aesar, VWR, and TCI in a sure-seal bottle and were used as received without drying. $Pd(OAc)_2$, Cs_2CO_3, and BrettPhos were obtained from Sigma Aldrich. All polyfluoroarenes and aryl boronic acids are commercially available and were used as received. Column chromatography was performed on silica gel (particle size 0.043–0.063 mm, 60 Å from Sepa Flash) by using the Biotage® Selekt System automatic purification system. A gradient elution using 100% pet. ether or DCM/pet. ether or, EtOAc/pet. ether was performed based on Merck aluminium TLC sheets (silica gel 60 F254), visualized by irradiation with UV light. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

1.1 Analytical Information

All isolated compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy, and gas chromatography-mass spectra (GC-MS). Copies of the ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR can be found in the supporting information. ^{1}H NMR spectra were recorded in deuterated solvents on Bruker Avance-II spectrometers at 400 or 500 MHz, with residual protic solvent as the internal standard ($CDCl_3$ referenced at 7.26 ppm). ^{13}C NMR spectra were recorded in deuterated solvents on Bruker Avance-II spectrometers at 101 or 125 MHz, with the central peak of the deuterated solvent as the internal standard ($CDCl_3$ referenced at 77.16 ppm). ^{19}F NMR spectra were recorded in deuterated solvents on Bruker Avance-II at 377 MHz. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz) rounded to the nearest 0.1 Hz. The ^{1}H NMR spectra are reported as δ/ppm downfield from tetramethylsilane (multiplicity, number of protons, assignment, coupling constant J/Hz). The ^{13}C NMR spectra are reported as δ/ppm and were obtained with ^{1}H decoupling and, if coupled to fluorine, multiplicity and coupling constant (Hz). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), b (broad), d (doublet), t (triplet), q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublets of doublets, dm = doublet of multiplets, m (multiplet); coupling constants (*J*) are in Hertz (Hz). All GC analysis was performed on an Agilent 7890A GC system with an FID detector using a J&W HP–5ms column (10 m, 0.1 mm I.D.), and mesitylene was used as an internal standard. All GCMS analysis (EI-MS, 70 eV) was done by Agilent 7890A GC system with a J&W DB–5ms column (30 m, 0.1 mm I.D.) connected with 5975C inert XL EI/CI MSD (with triple axis detector). All reaction mixtures were irradiated with 34 W Kessil KSH150B from 3 cm away. Regular fans are employed to maintain ambient temperature (T = 33 ± 2 °C).

2. Optimization Details

Table S1. Optimization of ligands for C(sp^2)–C(sp^2) cross-coupling

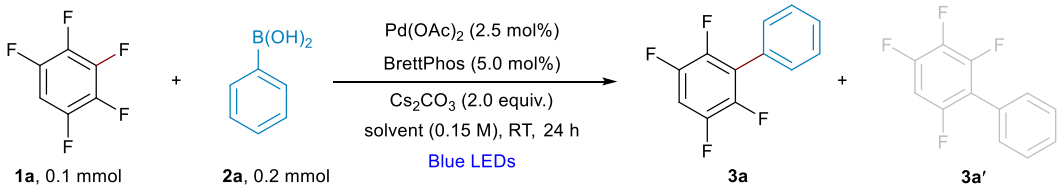


1a, 0.1 mmol **2a**, 0.2 mmol **3a** **3a′**

Entry	Additive (mol%)	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	BrettPhos	76	3
2	PPh_3	trace	trace
3	R-BINAP	np	np
4	DavePhos	np	np
5	RuPhos	np	np
6	XPhos	np	np
7	SPhos	np	np
8	Xantphos	np	np

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard. np = no product observed.

Table S2. Optimization of solvents for C(sp^2)–C(sp^2) cross-coupling

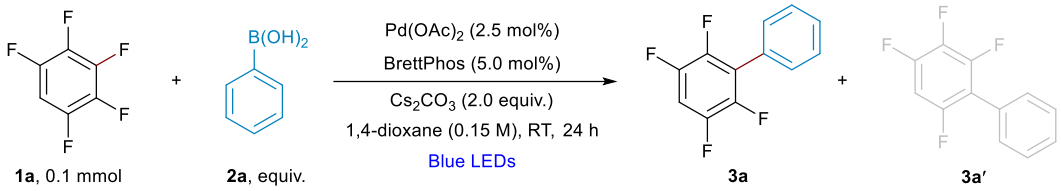


1a, 0.1 mmol **2a**, 0.2 mmol **3a** **3a′**

Entry	solvent	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	DMF	2	trace
2	DMSO	np	np
3	Toluene	44	2
4	HFIP	np	np
5	DMA	6	trace
6	DME	21	trace
7	MeCN	10	trace
8	THF	55	27

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard. np = no product observed.

Table S3. Optimization of loading of boronic acid for C(sp^2)–C(sp^2) cross-coupling

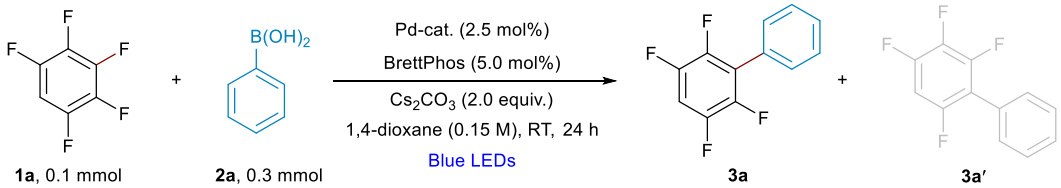


1a, 0.1 mmol **2a**, equiv. **3a** **3a′**

Entry	**2a** (equiv.)	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	1.0	25	trace
2	1.5	44	1
3	3.0	81	3
4	3.5	78	3

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard.

Table S4. Optimization of Pd-catalyst for C(sp^2)–C(sp^2) cross-coupling

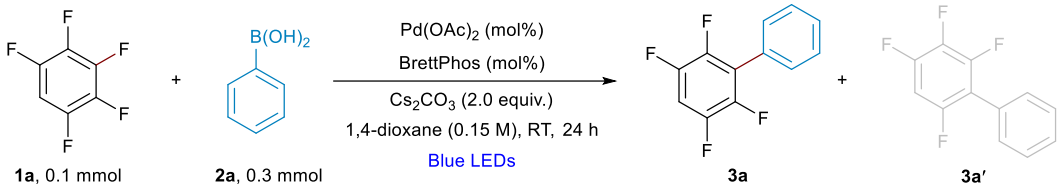


1a, 0.1 mmol **2a**, 0.3 mmol **3a** **3a′**

Entry	Pd-cat. (2.5 mol%)	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	$Pd(acac)_2$	np	np
2	$PdCl_2$	trace	trace
3	PdI_2	trace	trace
4	$Pd(TFA)_2$	37	1
5	$PdCl_2[P(cy)_3]_2$	trace	trace
6	$Pd(PPh_3)_2Cl_2$	trace	trace
7	$Pd(MeCN)_2Cl_2$	29	trace
8	$Pd(cod)Cl_2$	34	trace
9	$Pd(dppf)Cl_2$	trace	trace
10	$Pd(OAc)_2(PPh_3)_2$	trace	trace
11	$PdBr_2$	trace	trace
12	$Pd(hfacac)_2$	72	3
13	$[PdCl(C_3H_5)]_2$	trace	trace
14	$(PhCN)_2PdCl_2$	22	trace
15	$Pd(PPh_3)_4$	5	trace

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard. np = no product observed.

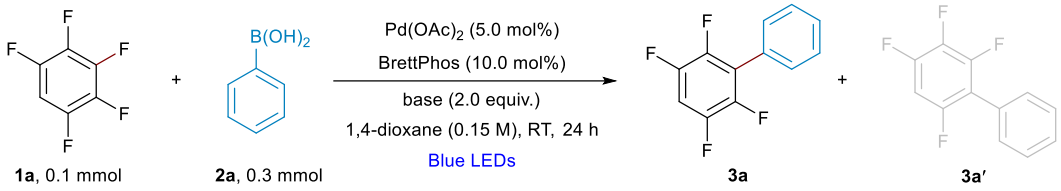
Table S5. Optimization of loading of Pd-cat and ligand for C(sp^2)–C(sp^2) cross-coupling



Entry	$Pd(OAc)_2$ (mol%)	BrettPhos (mol%)	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	2.5	5	76	2
2	5	10	86	3
3	7.5	15	84	8
4	10	20	89	6

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard.

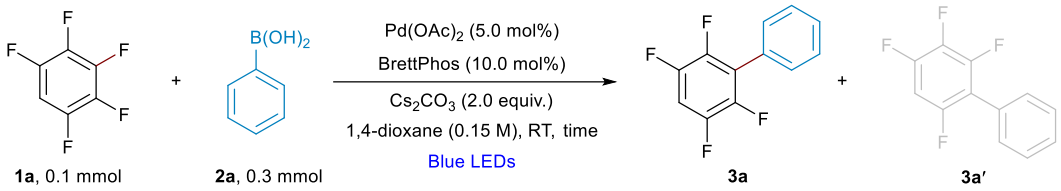
Table S6. Optimization of base for C(sp^2)–C(sp^2) cross-coupling



Entry	base (2.0 equiv.)	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	CsF	84	8
2	CsOAc	63	6
3	$CsHCO_3$	np	np
4	K_3PO_4	15	trace
5	KF	np	np
6	Na_2CO_3	np	np
7	K_2CO_3	80	8
8	KO*t*Bu	14	trace
9	DABCO	75	5
10	Piperidine	np	np
11	Bu_3N	19	trace
12	DIPEA	24	trace
13	Quinuclidine	72	6
14	N-Methylpiperidine	72	6

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard. np = no product observed.

Table S7. Optimization of reaction time for C(sp^2)–C(sp^2) cross-coupling

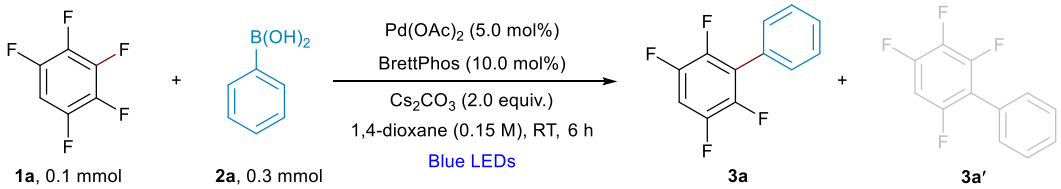


1a, 0.1 mmol **2a**, 0.3 mmol **3a** **3a′**

Entry	Time (h)	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	18	89	6
2	12	85	10
3	6	88(78)	5(3)
4	4	81	8

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard. Yield with parenthesis is that of the isolated product.

Table S8. Control experiment for C(sp^2)–C(sp^2) cross-coupling



1a, 0.1 mmol **2a**, 0.3 mmol **3a** **3a′**

Entry	**Condition**	% Yield of **3a**[a]	% Yield of **3a'**[a]
1	under dark at 40 °C	17	trace
2	w/o $Pd(OAc)_2$	np	np
3	w/o BrettPhos	np	np
4	w/o Cs_2CO_3	trace	trace

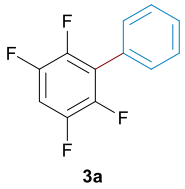
[a] Yields determined by GC-FID analysis using mesitylene as an internal standard.

3. General Procedure

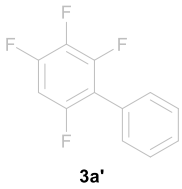
A. General Procedure for visible light induced Pd-catalyzed C(sp^2)–C(sp^2) cross-coupling:

A clean 4 mL screw cap glass reaction vial was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), BrettPhos (16.1 mg, 0.03 mmol, 10 mol%), aryl boronic acid (0.9 mmol, 3.0 equiv.) and then transferred into an argon-filled glove box. To that, Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.), and degassed 1,4-dioxane (2 mL) were then added followed by polyfluoroarene (0.3 mmol, 1.0 equiv.). The vial was then capped with Teflon septum, removed from the glove box, and irradiated using blue LEDs (34 W) while stirring at RT (under fan cooling) for 6 h. After 6 h, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL). The combined organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using silica gel (~100-200 mesh size) and pet. ether or pet. ether/DCM or, pet. ether/ethyl acetate was used as the eluent.

4. Characterization data of products



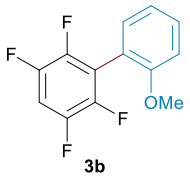
3a



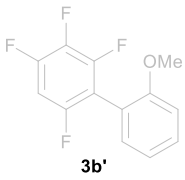
3a'

2,3,5,6-tetrafluoro-1,1'-biphenyl (3a): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and phenyl boronic acid (109.7 mg, 0.9 mmol). Pure **3a** was obtained with an inseparable regioisomeric mixture of **3a'** as an off-white solid (**3a**, 52.9 mg, 78% yield; **3a'**, 2.0 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 5H), 7.07 (tt, *J* = 9.7, 7.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.4 (dm, *J* = 244.2 Hz), 143.9 (dm, *J* = 247.2 Hz), 130.2, 129.3, 128.7, 127.6, 121.6 (t, *J* = 16.7 Hz), 105.0 (t, *J* = 22.8 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.31 (dt, *J* = 22.0, 11.2 Hz, 2F), -143.96 (dt, *J* = 19.0, 9.7 Hz, 2F). The data are in accordance with those reported in the literature.[1]



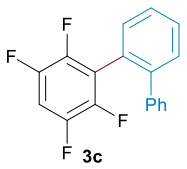
3b



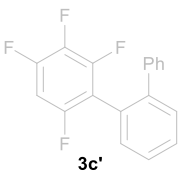
3b'

2,3,5,6-tetrafluoro-2'-methoxy-1,1'-biphenyl (3b): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (2-methoxyphenyl)boronic acid (136.8 mg, 0.9 mmol). Pure **3b** was obtained with an inseparable regioisomeric mixture of **3b'** as an off-white solid (**3b**, 33.8 mg, 44% yield; **3b'**, 1.5 mg, 2% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 1H), 7.28 – 7.25 (m, 1H), 7.12 – 7.01 (m, 3H), 3.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 146.0 (dm, *J* = 246.9 Hz), 144.2 (dm, *J* = 247.1 Hz), 131.7, 131.1, 120.7, 118.6 (t, *J* = 18.8 Hz), 116.5, 111.4, 105.0 (t, *J* = 22.7 Hz), 55.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -140.0 – -140.2 (m, 2F), -140.8 – -141.0 (m, 2F). The data are in accordance with those reported in the literature.[2]



3c

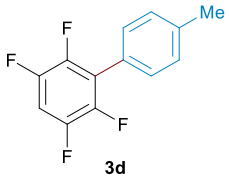


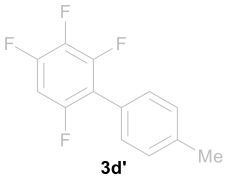
3c'

2,3,5,6-tetrafluoro-1,1':2',1''-terphenyl (3c): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and [1,1'-biphenyl]-2-ylboronic acid (178.2 mg, 0.9 mmol). Pure **3c** was obtained with an inseparable regioisomeric mixture of **3c'** as a white solid (**3c**, 80.6 mg, 89% yield; **3c'**, 2.7 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

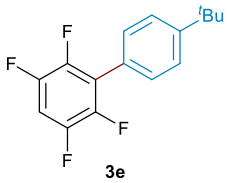
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 3H), 7.41 – 7.36 (m, 1H), 7.30 – 7.23 (m, 3H), 7.22 – 7.15 (m, 2H), 6.96 (tt, *J* = 9.6, 7.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.8 (dm, *J* = 248.4 Hz), 143.8 (dm, *J* = 246.7 Hz), 143.0, 140.6, 131.1, 130.4, 129.7, 128.7, 128.2, 127.5, 127.4, 126.1, 121.8 (t, *J* = 18.7 Hz), 105.2 (t, *J* = 22.7 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.4 – -

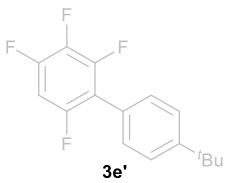
139.6 (m, 2F), -140.8 – -141.0 (m, 2F). The data are in accordance with those reported in the literature.[1]



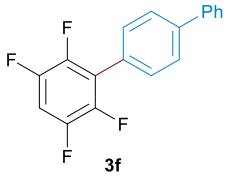


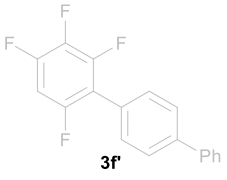
2,3,5,6-tetrafluoro-4'-methyl-1,1'-biphenyl (3d): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and *p*-tolylboronic acid (122.4 mg, 0.9 mmol). Pure **3d** was obtained with an inseparable regioisomeric mixture of **3d'** as a white solid (**3d**, 55.4 mg, 77% yield; **3d'**, 2.2 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.00 (m, 1H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3 (dm, *J* = 248.4 Hz), 143.9 (dm, *J* = 246.5 Hz), 139.4, 130.1, 129.5, 124.6, 121.7 (t, *J* = 16.7 Hz), 104.6 (t, *J* = 22.8 Hz), 21.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.3 – -139.5 (m, 2F), -143.9 – -144.2 (m, 2F). The data are in accordance with those reported in the literature.[3]





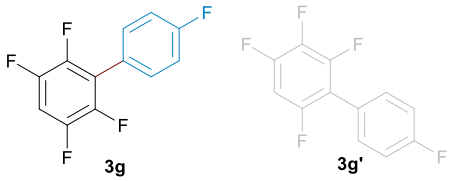
4'-(tert-butyl)-2,3,5,6-tetrafluoro-1,1'-biphenyl (3e): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-(*tert*-butyl)phenyl)boronic acid (160.2 mg, 0.9 mmol). Pure **3e** was obtained with an inseparable regioisomeric mixture of **3e'** as a white solid (**3e**, 79.6 mg, 94% yield; **3e'**, 2.5 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 2H), 7.49 – 7.37 (m, 2H), 7.06 (tt, *J* = 9.6, 7.3 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.5, 147.6 (ddd, *J* = 14.8, 10.6, 4.0 Hz), 145.2 (tt, *J* = 10.4, 4.9 Hz), 142.7 (dt, *J* = 13.8, 4.3 Hz), 129.9, 125.7, 121.6 (t, *J* = 16.5 Hz), 104.6 (t, *J* = 22.7 Hz), 34.9, 31.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.3 – -139.5 (m, 2F), -143.9 – -144.2 (m, 2F). The data are in accordance with those reported in the literature.[1]





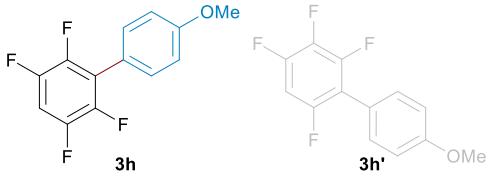
2,3,5,6-tetrafluoro-1,1':4',1''-terphenyl (3f): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and [1,1'-biphenyl]-4-ylboronic acid (178.2 mg, 0.9 mmol). Pure **3f** was obtained with an inseparable regioisomeric mixture of **3f'** as a white solid (**3f**, 55.3 mg, 61% yield; **3f'**, 2.7 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.14 (tt, *J* = 9.8, 7.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.9 (dm, *J* = 247.6 Hz), 144.4 (dm, *J* = 251.3 Hz), 142.6, 140.7, 131.1,

129.5, 128.4, 127.8, 127.7, 126.9, 121.6 (t, J = 16.7 Hz), 105.5 (t, J = 22.9 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.8 – -140.0 (m, 2F), -144.4 – -144.7 (m, 2F). The data are in accordance with those reported in the literature.[4]



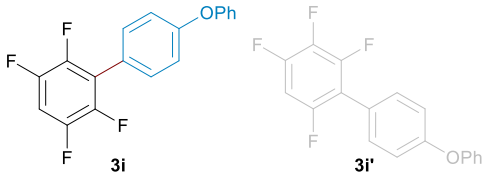
2,3,4',5,6-pentafluoro-1,1'-biphenyl (3g): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-fluorophenyl)boronic acid (125.9 mg, 0.9 mmol). Pure **3g** was obtained with an inseparable regioisomeric mixture of **3g'** as a white solid (**3g**, 43.9 mg, 60% yield; **3g'**, 2.9 mg, 4% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.19 (t, J = 8.7 Hz, 2H), 7.07 (ddd, J = 17.0, 9.6, 7.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.3 (d, J = 249.6, Hz), 147.6 – 147.3 (m), 145.2 – 144.9 (m), 142.6 – 142.4 (m), 132.17 (d, J = 8.5 Hz), 123.46, 120.65, 115.98 (d, J = 21.9 Hz), 105.15 (t, J = 22.7 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -111.4 – -111.6 (m, 1F), -138.9 – -139.0 (m, 2F), -143.9 – -144.1 (m, 2F).The data are in accordance with those reported in the literature.[1]



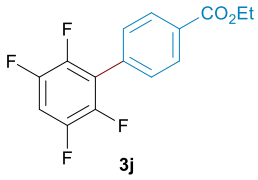
2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (3h): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-methoxyphenyl)boronic acid (136.8 mg, 0.9 mmol). Pure **3h** was obtained with an inseparable regioisomeric mixture of **3h'** as an off-white solid (**3h**, 59.2 mg, 77% yield; **3h'**, 2.3 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.8 Hz, 2H), 7.08 – 6.98 (m, 3H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.3, 146.4 (dm, J = 243.9 Hz), 143.9 (dm, J = 246.2 Hz), 131.5, 121.3 (t, J = 16.7 Hz), 119.6, 114.2, 104.4 (t, J = 22.8 Hz), 55.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.4 – -139.5 (m, 2F), -144.2 – -144.5 (m, 2F). The data are in accordance with those reported in the literature.[1]

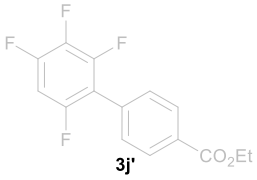


2,3,5,6-tetrafluoro-4'-phenoxy-1,1'-biphenyl (3i): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-phenoxyphenyl)boronic acid (192.6 mg, 0.9 mmol). Pure **3i** was obtained with an inseparable regioisomeric mixture of **3i'** as a white solid (**3i**, 58.2 mg, 61% yield; **3i'**, 2.9 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 4H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.09 (m, 4H), 7.09 – 7.00 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6, 156.3, 146.4 (dm, *J* = 245.6 Hz), 143.9 (dm, *J* = 245.0 Hz), 131.8, 130.8, 124.2, 121.8, 121.1 (t, *J* = 16.5 Hz), 119.9, 118.3, 104.7 (t, *J* = 22.8 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.0 – -139.2 (m, 2F), -144.0 – -144.2 (m, 2F).



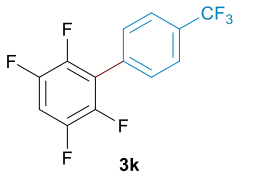
3j



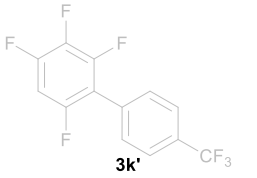
3j'

ethyl 2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carboxylate (3j): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-(ethoxycarbonyl)phenyl)boronic acid (174.6 mg, 0.9 mmol). Pure **3j** was obtained with an inseparable regioisomeric mixture of **3j'** as an off-white solid (**3j**, 67.1 mg, 75% yield; **3j'**, 2.7 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 4% ethyl acetate/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.04 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 146.3 (dm, *J* = 249.2 Hz), 143.7 (dm, *J* = 247.8 Hz), 132.0, 131.2, 130.3, 129.8, 120.6 (t, *J* = 16.5 Hz), 105.7 (t, *J* = 22.7 Hz), 61.4, 14.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -138.5 – -138.8 (m, 2F), -143.4 – -143.6 (m, 2F). The data are in accordance with those reported in the literature.[1]



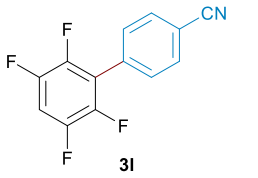
3k



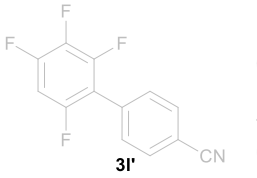
3k'

2,3,5,6-tetrafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (3k): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-(trifluoromethyl)phenyl)boronic acid (170.9 mg, 0.9 mmol). Pure **3k** was obtained with an inseparable regioisomeric mixture of **3k'** as an off-white solid (**3k**, 82.0 mg, 93% yield; **3k'**, 2.6 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.13 (ddd, *J* = 16.9, 9.5, 7.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3 (dm, *J* = 249.0 Hz), 143.7 (dm, *J* = 248.8 Hz), 131.7, 131.3, 130.8 (t, *J* = 2.2 Hz), 126.2 – 126.1 (m), 124.0 (q, *J* = 272.4 Hz), 120.3 (t, *J* = 16.7 Hz), 105.9 (t, *J* = 22.7 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.0 (s, 3F), -138.4 – -138.5 (m, 2F), -143.6 – -143.8 (m, 2F). The data are in accordance with those reported in the literature.[1]



3l

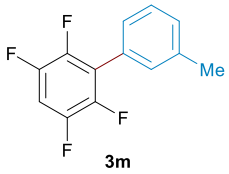


3l'

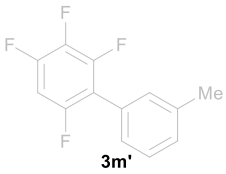
2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carbonitrile (3l): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-cyanophenyl)boronic acid (132.2 mg, 0.9 mmol). Pure **3l** was obtained with an

inseparable regioisomeric mixture of **3l'** as an off-white solid (**3l**, 71.6 mg, 95% yield; **3l'**, 1.5 mg, 2% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 5% ethyl acetate/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.15 (ddd, *J* = 16.9, 9.5, 7.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.6 – 142.4 (m, 2C), 132.5, 132.3, 131.1 (t, *J* = 2.2 Hz), 119.7 (t, *J* = 15.8 Hz), 118.3, 113.3, 106.3 (t, *J* = 22.7 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -137.9 – -138.0 (m, 2F), -143.4 – -143.5 (m, 2F). The data are in accordance with those reported in the literature.[5]



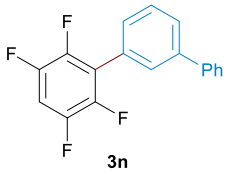
3m



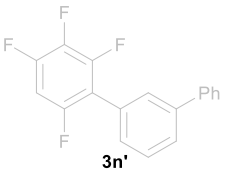
3m'

2,3,5,6-tetrafluoro-3'-methyl-1,1'-biphenyl (3m): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and *m*-tolylboronic acid (122.4 mg, 0.9 mmol). Pure **3m** was obtained with an inseparable regioisomeric mixture of **3m'** as a white solid (**3m**, 57.6 mg, 80% yield; **3m'**, 3.6 mg, 5% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 1H), 7.31 – 7.23 (m, 3H), 7.11 – 7.01(m, 1H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3 (dm, *J* = 248.7 Hz), 143.9 (dm, *J* = 243.2 Hz), 138.5, 130.8, 130.1, 128.6, 127.5, 127.3, 121.8 (t, *J* = 16.9 Hz), 104.8 (t, *J* = 22.7 Hz), 21.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.2 – -139.4 (m, 2F), -143.7 – -143.9 (m, 2F). The data are in accordance with those reported in the literature.[6]



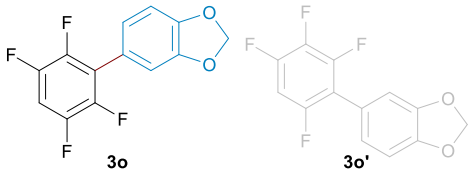
3n



3n'

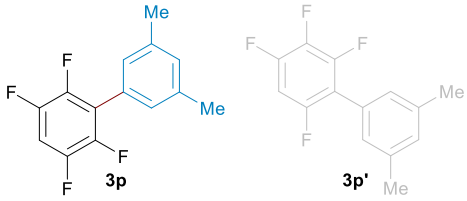
2,3,5,6-tetrafluoro-1,1':3',1''-terphenyl (3n): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and [1,1'-biphenyl]-3-ylboronic acid (178.2 mg, 0.9 mmol). Pure **3n** was obtained with an inseparable regioisomeric mixture of **3n'** as a white solid (3n, 60.7 mg, 67% yield; **3n'**, 2.7 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.7 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.11 (tt, *J* = 9.7 Hz, 7.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.4 (dm, *J* = 248.9 Hz), 143.9 (dm, *J* = 243.8 Hz), 141.9, 140.5, 129.2, 129.9, 129.0, 128.11, 128.05, 127.8, 127.4, 121.5 (t, *J* = 16.8 Hz), 105.1 (t, *J* = 22.8 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -138.8 – -139.1 (m, 2F), -143.5 – -143.7 (m, 2F).



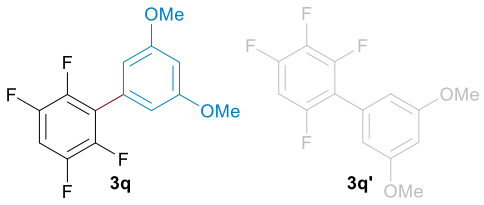
5-(2,3,5,6-tetrafluorophenyl)benzo[d][1,3]dioxole (3o): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and benzo[d][1,3]dioxol-5-ylboronic acid (149.3 mg, 0.9 mmol). Pure **3o** was obtained with an inseparable regioisomeric mixture of **3o'** as an off-white solid (**3o**, 66.4 mg, 82% yield; **3o'**, 4.0 mg, 5% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.01 (m, 1H). 7.00 – 6.89 (m, 3H), 6.06 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.5, 148.0, 146.3 (dm, J = 248.4 Hz), 143.9 (dm, J = 242.1 Hz), 124.3, 121.3 (t, J = 16.5 Hz), 120.7, 110.5, 108.7, 104.7 (t, J = 22.8 Hz), 101.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.1 – -139.3 (m, 2F), -143.8 – -144.0 (m, 2F). The data are in accordance with those reported in the literature.[5]



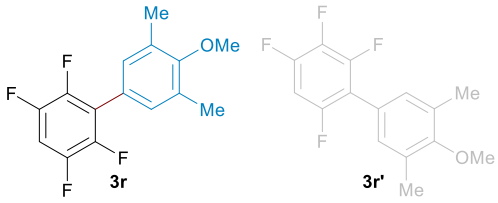
2,3,5,6-tetrafluoro-3',5'-dimethyl-1,1'-biphenyl (3p): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (3,5-dimethylphenyl)boronic acid (135.0 mg, 0.9 mmol). Pure **3p** was obtained with an inseparable regioisomeric mixture of **3p'** as an off-white solid (**3p**, 58.7 mg, 77% yield; **3p'**, 2.3 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.07 (s, 2H), 7.09 – 7.00 (m, 1H), 2.39 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3 (dm, J = 248.6 Hz), 143.5 (dm, J = 247.6 Hz), 138.3, 131.0, 127.9, 127.3, 122.0 (t, J = 17.1 Hz), 104.7 (t, J = 22.8 Hz), 21.4. **^{19}F NMR (377 MHz, $CDCl_3$)** -139.3 – -139.5 (m, 2F), -143.5 – -143.7 (m, 2F). The data are in accordance with those reported in the literature.[1]



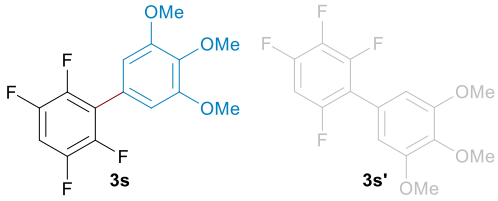
2,3,5,6-tetrafluoro-3',5'-dimethoxy-1,1'-biphenyl (3q): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (3,5-dimethoxyphenyl)boronic acid (163.8 mg, 0.9 mmol). Pure **3q** was obtained with an inseparable regioisomeric mixture of **3q'** as a pale yellow solid (**3q**, 74.7 mg, 87% yield; 3q', 2.6 mg, 3% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 10% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (tt, J = 9.7, 7.3 Hz, 1H), 6.60 – 6.53 (m, 3H), 3.83 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.9, 146.3 (dm, J = 248.7 Hz), 143.9 (dm, J = 240.0 Hz), 129.1, 121.6 (t, J = 16.8 Hz), 108.3, 105.0 (t, J = 22.7 Hz), 101.4, 55.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.0 – -139.2 (m, 2F), -142.9 – -143.2 (m, 2F).



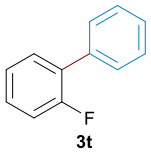
2,3,5,6-tetrafluoro-4'-methoxy-3',5'-dimethyl-1,1'-biphenyl (3r): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **3r** was obtained with an inseparable regioisomeric mixture of **3r'** as a white solid (**3r**, 51.1 mg, 60% yield; **3r'**, 4.3 mg, 5% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 15% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 2H), 7.02 (tt, *J* = 9.7, 7.3 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.8, 146.3 (dm, *J* = 248.4 Hz), 143.8 (dm, *J* = 243.2 Hz), 131.5, 130.7, 122.8, 121.5 (t, *J* = 16.8 Hz), 104.5 (t, *J* = 22.7 Hz), 59.8, 16.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.3 – -139.6 (m, 2F), -143.7 – -144.0 (m, 2F).



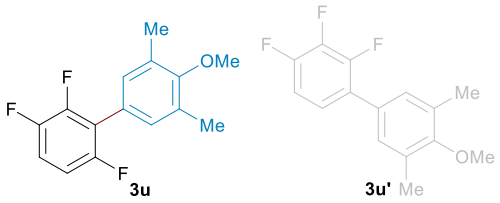
2,3,5,6-tetrafluoro-3',4',5'-trimethoxy-1,1'-biphenyl (3s): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluorobenzene (50.4 mg, 0.3 mmol) and (3,4,5-trimethoxyphenyl)boronic acid (190.8 mg, 0.9 mmol). Pure **3s** was obtained with an inseparable regioisomeric mixture of **3s'** as a white solid (**3s**, 61.6 mg, 65%; **3s'**, 0.95 mg, 1% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 15% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (tt, *J* = 9.6 Hz, 7.3 Hz, 1H), 6.65 (s, 2H), 3.91 (s, 3H), 3.87 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4, 146.3 (dm, *J* = 248.5 Hz), 143.8 (dm, *J* = 247.2 Hz), 138.8, 122.6, 121.5 (t, *J* = 16.6 Hz), 107.5, 104.8 (t, *J* = 22.7 Hz), 61.0, 56.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -139.0 – -139.2 (m, 2F), -143.2 – -143.4 (m, 2F). The data are in accordance with those reported in the literature.[7]



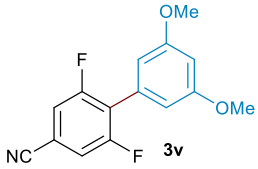
2-fluoro-1,1'-biphenyl (3t): The title compound was prepared according to the general procedure-A from 1,2-difluorobenzene (43.2 mg, 0.3 mmol) and phenylboronic acid (109.7 mg, 0.9 mmol). Pure **3t** was obtained as colorless liquid 43.7 mg, 67% yield after column chromatography of the crude reaction mixture (silica gel, gradient 100% pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.51 (m, 2H), 7.50 – 7.28 (m, 5H), 7.24 – 7.12 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.0, 136.0, 130.9 (d, *J* = 3.1 Hz), 129.2 (d, *J* = 2.9 Hz), 128.6, 127.8, 124.3 (d, *J* = 4.0 Hz), 116.4, 116.1. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -118.1. The data are in accordance with those reported in the literature.[8]



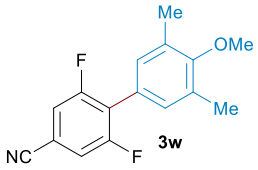
2,3,6-trifluoro-4'-methoxy-3',5'-dimethyl-1,1'-biphenyl (3u): The title compound was prepared according to the general procedure-A from 1,2,3,4-tetrafluorobenzene (45.0 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **3u** was obtained with an inseparable regioisomeric mixture of **3u'** as pale-yellow liquid (3u, 35.9 mg, 45% yield; **3u'**, 4.0 mg, 5% yield) after column chromatography of the crude reaction mixture (silica gel, gradient 15% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.04 (m, 3H), 6.89 (tdd, *J* = 9.1, 3.8, 2.2 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** 157.5, 155.4 (ddd, *J* = 244.3, 4.6, 2.5 Hz), 148.0 (ddd, *J* = 249.8, 14.2, 7.5 Hz), 147.6 (ddd, *J* = 244.9, 13.8, 3.5 Hz), 131.2, 130.7, 123.7, 120.3 (dd, *J* = 20.9, 15.3 Hz), 115.3 (dd, *J* = 19.3, 10.0 Hz), 110.9 (ddd, *J* = 25.7, 6.6, 4.3 Hz), 59.8, 16.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -119.6 (s, 1F), -137.6 – -137.8 (m, 1F), -142.2 – -142.4 (m, 1F).



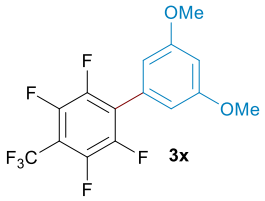
2,6-difluoro-3',5'-dimethoxy-[1,1'-biphenyl]-4-carbonitrile (3v): The title compound was prepared according to the general procedure-A from 3,4,5-trifluorobenzonitrile (47.1 mg, 0.3 mmol) and (3,5-dimethoxyphenyl)boronic acid (163.8 mg, 0.9 mmol). Pure **3v** was obtained as an off-white solid 97% (80.0 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% ethyl acetate/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.13 (m, 2H), 6.56 (s, 3H), 3.82 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.0 (dd, *J* = 252.9, 7.7 Hz), 160.9, 128.8, 124.3 (t, *J* = 18.7 Hz), 116.7 (d, *J* = 3.5 Hz), 116.3 – 115.4 (m), 112.5 (t, *J* = 12.1 Hz), 108.3, 101.4, 55.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -109.12 – -109.50 (m, 2F).



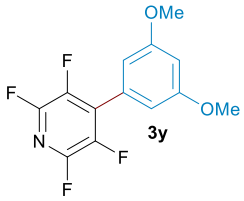
2,6-difluoro-4'-methoxy-3',5'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (3w): The title compound was prepared according to the general procedure-A from 3,4,5-trifluorobenzonitrile (47.1 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **3w** was obtained as an off-white solid 79% (64.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% ethyl acetate/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.11 (s, 2H), 3.78 (s, 3H), 2.34 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.0 (dd, *J* = 251.8, 7.9 Hz), 158.0, 131.4, 130.6, 124.2 (t, *J* = 18.6 Hz), 122.4, 116.8 (t, *J* = 3.3 Hz), 116.1 – 115.6 (m), 111.8 (t, *J* = 12.2 Hz), 59.8, 16.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -110.1 (s, 2F).



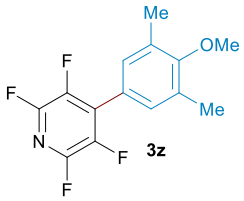
2,3,5,6-tetrafluoro-3',5'-dimethoxy-4-(trifluoromethyl)-1,1'-biphenyl (3x): The title compound was prepared according to the general procedure-A from 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (70.8 mg, 0.3 mmol) and (3,5-dimethoxyphenyl)boronic acid (163.8 mg, 0.9 mmol). Pure **3x** was obtained as an off-white solid 93% (98.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% DCM/pet. ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.58 (s, 3H), 3.83 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.1, 146.1 – 145.3 (m), 143.4 – 142.8 (m), 127.6, 125.1 (t, *J* = 16.2 Hz), 121.0 (d, *J* = 274.5 Hz), 108.2, 102.0, 55.6. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -56.37 (t, *J* = 21.0 Hz, 3F), -140.82 (ddd, *J* = 54.1, 19.8, 11.9 Hz, 4F).



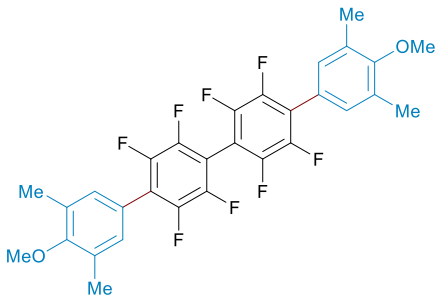
2,3,5,6-tetrafluoro-4-(4-methoxy-3,5-dimethylphenyl)pyridine (3y): The title compound was prepared according to the general procedure-A from perfluoropyridine (50.7 mg, 0.3 mmol) and (3,5-dimethoxyphenyl)boronic acid (163.8 mg, 0.9 mmol). Pure **3y** was obtained as an off-white solid 71% (61.1 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% DCM/pet. ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.95 – 6.30 (m, 3H), 3.83 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.1, 146.1 – 142.5 (m), 141.5 – 137.8 (m), 133.6 (t, *J* = 14.8 Hz), 127.4, 107.9, 102.5, 55.6. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -90.68 – -90.94 (m, 2F), -144.06 – -144.30 (m, 2F).



2,3,5,6-tetrafluoro-4-(4-methoxy-3,5-dimethylphenyl)pyridine (3z): The title compound was prepared according to the general procedure-A from perfluoropyridine (50.7 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **3z** was obtained as an off-white solid 37% (31.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% DCM/pet. ether).

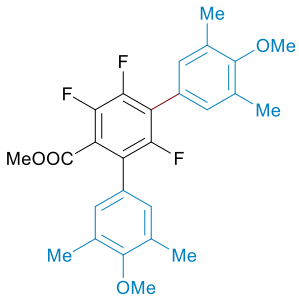
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (s, 2H), 3.80 (s, 3H), 2.36 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.0, 144.1 (dm, *J* = 245.4 Hz), 139.3 (dm, *J* = 258.7 Hz), 133.6 (t, *J* = 14.7 Hz), 132.0, 130.4, 121.3, 59.9, 16.3. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -91.1 – -91.4 (m, 2F), -145.0 – -145.3 (m, 2F).



2',2'',3',3'',5',5'',6',6''-octafluoro-4,4'''-dimethoxy-3,3''',5,5'''-tetramethyl-1,1':4',1'':4'',1'''-quaterphenyl (3aa): The title compound was prepared according to the general procedure-A from perfluoro-1,1'-biphenyl (100.2 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **3aa** was obtained as a white solid

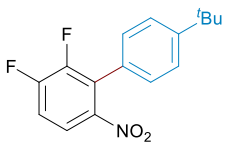
85% (144.4 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 50% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 3.82 (s, 6H), 2.39 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** 158.1, 144.3 (ddd, *J* = 54.4, 42.1, 14.0 Hz), 131.6, 130.7, 127.5, 122.7 (t, *J* = 16.8 Hz) 122.3, 105.7 (t, *J* = 15.8 Hz), 59.8, 16.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -138.9 – -139.1 (m, 4F), -142.9 (d, *J* = 12.2 Hz, 4F).



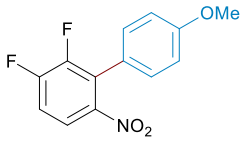
methyl 2',5',6'-trifluoro-4,4''-dimethoxy-3,3'',5,5''-tetramethyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3ab): The title compound was prepared according to the general procedure-A from methyl 2,3,4,5,6-pentafluorobenzoate (67.8 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **3ab** was obtained as yellowish orange sticky liquid 76% (104.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 80% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 7.01 (s, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 2.34 (s, 6H), 2.31 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.13, 157.7, 157.4, 151.9 (dm, *J* = 245.2 Hz), 146.3 (ddd, *J* = 252.0, 14.0 Hz, 7.0 Hz), 144.8 (ddd, *J* = 247.0, 15.3, 3.7 Hz), 131.3, 131.0, 130.7, 129.9, 127.4, 124.1 (dd, *J* = 21.1, 3.3 Hz), 123.1, 122.4 (dd, *J* = 14.7, 3.3 Hz), 121.8 (dd, *J* = 22.4, 15.2 Hz), 59.8, 52.8, 16.2, 16.2. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -119.9 (d, *J* = 14.7 Hz, 1F), -137.8 (d, *J* = 22.6 Hz, 1F), -143.8 (dd, *J* = 21.0, 15.6 Hz, 1F).



4'-(tert-butyl)-2,3-difluoro-6-nitro-1,1'-biphenyl (4a): The title compound was prepared according to the general procedure-A from 1,2,3-trifluoro-4-nitrobenzene (53.1 mg, 0.3 mmol) and ((4-(*tert*-butyl)phenyl)boronic acid (160.2 mg, 0.9 mmol). Pure **4a** was obtained as an off-white solid 97% yield (84.7 mg) after column chromatography of the crude reaction mixture (silica gel, gradient 4% DCM/pet. ether).

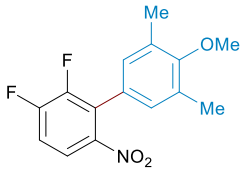
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (ddd, *J* = 9.1, 4.4, 2.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.24 (m, 3H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.1 (dd, *J* = 258.5, 14.0 Hz), 152.4, 151.9, 151.8, 148.1 (dd, *J* = 251.6, 13.5 Hz), 145.8, 128.5, 127.9 (d, *J* = 16.7 Hz), 126.2 (d, *J* = 1.6 Hz), 125.9, 120.5 (dd, *J* = 7.9, 4.4 Hz), 116.1 (d, *J* = 19.2 Hz), 34.9, 31.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -127.95 (d, *J* = 21.9 Hz, 1F), -132.67 – -135.32 (m, 1F).



2,3-difluoro-4'-methoxy-6-nitro-1,1'-biphenyl (4b): The title compound was prepared according to the general procedure-A from 1,2,3-trifluoro-4-nitrobenzene (53.1 mg, 0.3 mmol) and (4-methoxyphenyl)boronic acid (136.8 mg, 0.9 mmol). Pure **4b** was obtained as a yellow solid 87% (69.2 mg)

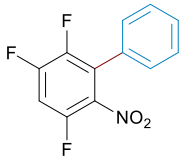
yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (ddd, *J* = 9.1, 4.4, 2.0 Hz, 1H), 7.39 – 7.19 (m, 3H), 7.12 – 6.97 (m, 2H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.4, 153.1 (dd, *J* = 258.1, 14.2 Hz), 148.1 (dd, *J* = 251.0, 13.4 Hz), 145.8, 130.2, 127.6 (d, *J* = 16.9 Hz), 121.2 (d, *J* = 1.8 Hz), 120.5 (dd, *J* = 8.0, 4.5 Hz), 116.0 (d, *J* = 19.2 Hz), 114.4, 55.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -127.20 – -128.77 (m, 1F), -134.96 (dd, *J* = 21.1, 5.6 Hz, 1F).



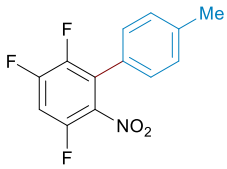
2,3-difluoro-4'-methoxy-3',5'-dimethyl-6-nitro-1,1'-biphenyl (4c): The title compound was prepared according to the general procedure-A from 1,2,3-trifluoro-4-nitrobenzene (53.1 mg, 0.3 mmol) and (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **4c** was obtained as a pale-yellow solid 84% (73.9 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% ethyl acetate/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (ddd, *J* = 9.1, 4.4, 2.0 Hz, 1H), 7.30 – 7.22 (m, 1H), 6.95 (s, 2H), 3.77 (s, 3H), 2.31 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.9, 153.1 (dd, *J* = 251.8, 14.2 Hz), 148.0 (dd, *J* = 251.2, 13.4 Hz), 145.7, 131.6, 129.2, 127.8 (d, *J* = 17.0 Hz) 124.5, 120.4 (dd, *J* = 8.0, 4.4 Hz), 116.0 (d, *J* = 19.2 Hz), 59.8, 16.2. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -128.0 (d, *J* = 22.4 Hz, 1F), -134.6 (dd, *J* = 21.0, 5.9 Hz, 1F).



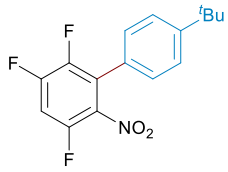
2,3,5-trifluoro-6-nitro-1,1'-biphenyl (4d): The title compound was prepared according to the general procedure-A from 1,2,3,5-tetrafluoro-4-nitrobenzene (58.5 mg, 0.3 mmol) and phenyl boronic acid (109.7 mg, 0.9 mmol). Pure **4d** was obtained as colorless liquid 51% (38.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 3H), 7.43 – 7.32 (m, 2H), 7.17 (td, *J* = 9.1, 6.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.6 (ddd, *J* = 258.7, 15.2, 11.7 Hz), 149.7 (ddd, *J* = 258.1, 11.2, 4.0 Hz), 144.2 (ddd, *J* = 250.1, 13.8, 3.8 Hz), 135.9 – 135.8 (m), 130.2, 129.2, 129.0, 127.8, 126.9 (d, *J* = 17.9 Hz), 105.9 (dd, *J* = 24.6, 22.7 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -123.88 – -124.20 (m, 1F), -125.75 – -126.52 (m, 1F), -140.77 (ddd, *J* = 19.2, 13.8, 4.4 Hz, 1F). The data are in accordance with those reported in the literature.[1, 9]



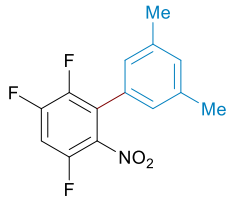
2,3,5-trifluoro-4'-methyl-6-nitro-1,1'-biphenyl (4e): The title compound was prepared according to the general procedure-A from 1,2,3,5-tetrafluoro-4-nitrobenzene (58.5 mg, 0.3 mmol) and *p*-tolylboronic acid (122.4 mg, 0.9 mmol). Pure **4e** was obtained as pale-yellow sticky liquid 53% (42.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% ethyl acetate/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 4H), 7.14 (m, 1H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.5 (ddd, *J* = 259.0, 15.4, 11.5 Hz), 149.6 (ddd, *J* = 256.8, 11.3, 4.1 Hz), 144.1 (ddd, *J* = 247.6, 13.5, 4.2 Hz), 140.4, 136.0 – 135.7 (m), 129.9, 128.8, 127.0 (d, *J* = 18.3 Hz), 124.7, 105.6 (dd, *J* = 24.7, 22.7 Hz), 21.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -123.59 – -125.11 (m, 1F), -125.49 – -127.62 (m, 1F), -140.63 – -141.64 (m, 1F). The data are in accordance with those reported in the literature.[7]



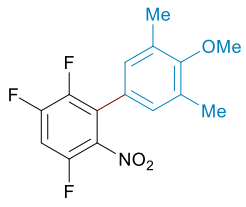
4'-(*tert*-butyl)-2,3,5-trifluoro-6-nitro-1,1'-biphenyl (4f): The title compound was prepared according to the general procedure-A from 1,2,3,5-tetrafluoro-4-nitrobenzene (58.5 mg, 0.3 mmol) and ((4-(*tert*-butyl)phenyl)boronic acid (160.2 mg, 0.9 mmol). Pure **4f** was obtained as colorless sticky liquid 62% (57.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 2H), 7.34 – 7.27 (m, 2H), 7.14 (td, *J* = 9.1, 6.2 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4, 151.6 (ddd, *J* = 258.5, 15.3, 12.0 Hz), 149.7 (ddd, *J* = 257.3, 11.4, 3.9 Hz), 144.307 (ddd, *J* = 249.7, 13.2, 3.9 Hz), 135.9 – 135.8 (m), 128.7, 127.0 (d, *J* = 18.6 Hz), 126.2, 124.7, 105.5 (dd, *J* = 24.6, 22.7 Hz), 35.0, 31.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -119.99 – -125.04 (m, 1F), -125.42 – -129.46 (m, 1F), -136.28 – -146.26 (m, 1F).



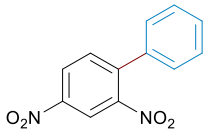
2,3,5-trifluoro-3',5'-dimethyl-6-nitro-1,1'-biphenyl (4g): The title compound was prepared according to the general procedure-A from 1,2,3,5-tetrafluoro-4-nitrobenzene (58.5 mg, 0.3 mmol) and (3,5-dimethylphenyl)boronic acid (135.0 mg, 0.9 mmol). Pure **4g** was obtained as an off-white solid 57% (48.1 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 2H), 7.00 – 6.91 (m, 2H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.6 (ddd, *J* = 258.8, 15.5, 11.7 Hz), 149.6 (ddd, *J* = 256.7, 11.0, 3.9 Hz), 144.1 (ddd, *J* = 249.3, 13.0, 4.1 Hz), 138.9, 136.0 – 135.7 (m), 131.9, 126.6, 127.0 (d, *J* = 18.3 Hz), 123.2, 105.5 (dd, *J* = 24.3, 23.6 Hz), 21.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -116.42 – -125.47 (m, 1F), -125.47 – -127.73 (m, 1F), -140.65 (dt, *J* = 23.7, 11.2 Hz, 1F).



2,3,5-trifluoro-4'-methoxy-3',5'-dimethyl-6-nitro-1,1'-biphenyl (4h): The title compound was prepared according to the general procedure-A from 1,2,3,5-tetrafluoro-4-nitrobenzene (58.5 mg, 0.3 mmol) (4-methoxy-3,5-dimethylphenyl)boronic acid (162.0 mg, 0.9 mmol). Pure **4h** was obtained as pale yellow solid 54% (50.4 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 20% DCM/pet. ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (td, *J* = 9.1, 6.2 Hz, 1H), 6.99 (s, 2H), 3.76 (s, 3H), 2.30 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 151.5 (ddd, *J* = 259.3, 15.3, 11.8 Hz), 149.6 (ddd, *J* = 257.9, 11.3, 4.0 Hz), 144.2 (ddd, *J* = 249.0, 13.3, 3.9 Hz), 136.0 – 135.5 (m), 132.0, 129.4, 126.8 (d, *J* = 18.0 Hz) 122.9, 105.4 (dd, *J* = 24.3, 23.0 Hz), 59.8, 16.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -124.6 (s, 1F), -126.8 (d, *J* = 22.8 Hz, 1F), -140.7 – -140.9 (m, 1F).

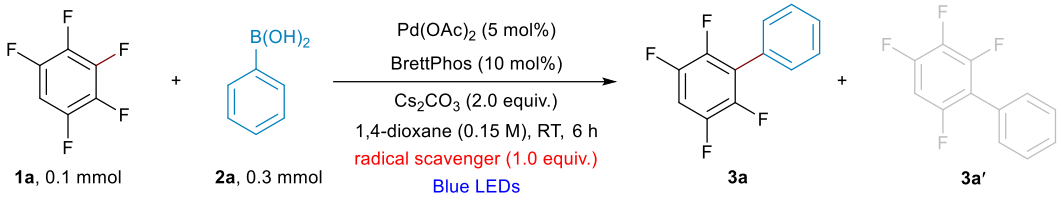


2,4-dinitro-1,1'-biphenyl (4i): The title compound was prepared according to the general procedure-A from 1-fluoro-2,4-dinitrobenzene (56.4 mg, 0.3 mmol) phenylboronic acid (109.7 mg, 0.9 mmol). Pure **4i** was obtained as a yellow solid 25% (18.3 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 9% ethyl acetate/pet. ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.3 Hz, 1H), 8.47 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.41 – 7.30 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.3, 147.0, 142.4, 135.4, 133.4, 129.7, 129.3, 127.8, 126.6, 119.9. The data are in accordance with those reported in the literature.[10]

5. Mechanistic Investigation

Radical quenching experiment



A clean 2 mL screw cap glass reaction vial was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol%), BrettPhos (5.4 mg, 0.01 mmol, 10 mol%), phenyl boronic acid (36.6 mg, 0.3 mmol, 3.0 equiv.) and then transferred into an argon-filled glove box. To that, Cs_2CO_3 (65.2 mg, 0.2 mmol, 2.0 equiv.), radical scavenger (0.1 mmol, 1.0 equiv.) and degassed 1,4-dioxane (666 μL) was added followed by 1,2,3,4,5-pentafluorobenzene (16.8 mg, 0.1 mmol, 1.0 equiv.). The vial was then capped with Teflon septum, removed from the glove box, and irradiated using blue LEDs (34 W) while stirring at RT (under fan cooling) for 6 h. After 6 h, the reaction was quenched *via* exposure to air. The reaction mixture was diluted with ethyl acetate and the desired product formation was analyzed by GC-MS and GC-FID analysis.

Entry	**Radical Scavenger (1.0 equiv.)**	% Yield of **3a**[a]
1	TEMPO	np
2	BHT	76%

[a] Yields determined by GC-FID analysis using mesitylene as an internal standard and yield of the minor regioisomer not taken under consideration. TEMPO = (2,2,6,6- Tetramethylpiperidin-1-yl)oxidanyl. BHT = 2,6-Di-tert-butyl-4-methylphenol. np = no product.

6. UV-Visible Spectroscopy Analysis

UV-visible spectroscopy was performed for each reaction component and combination of reaction components using a Cary 60 spectrophotometer (Agilent Technologies) at the concentrations present in the C(sp^2)−C(sp^2) cross-coupling reaction mixture.

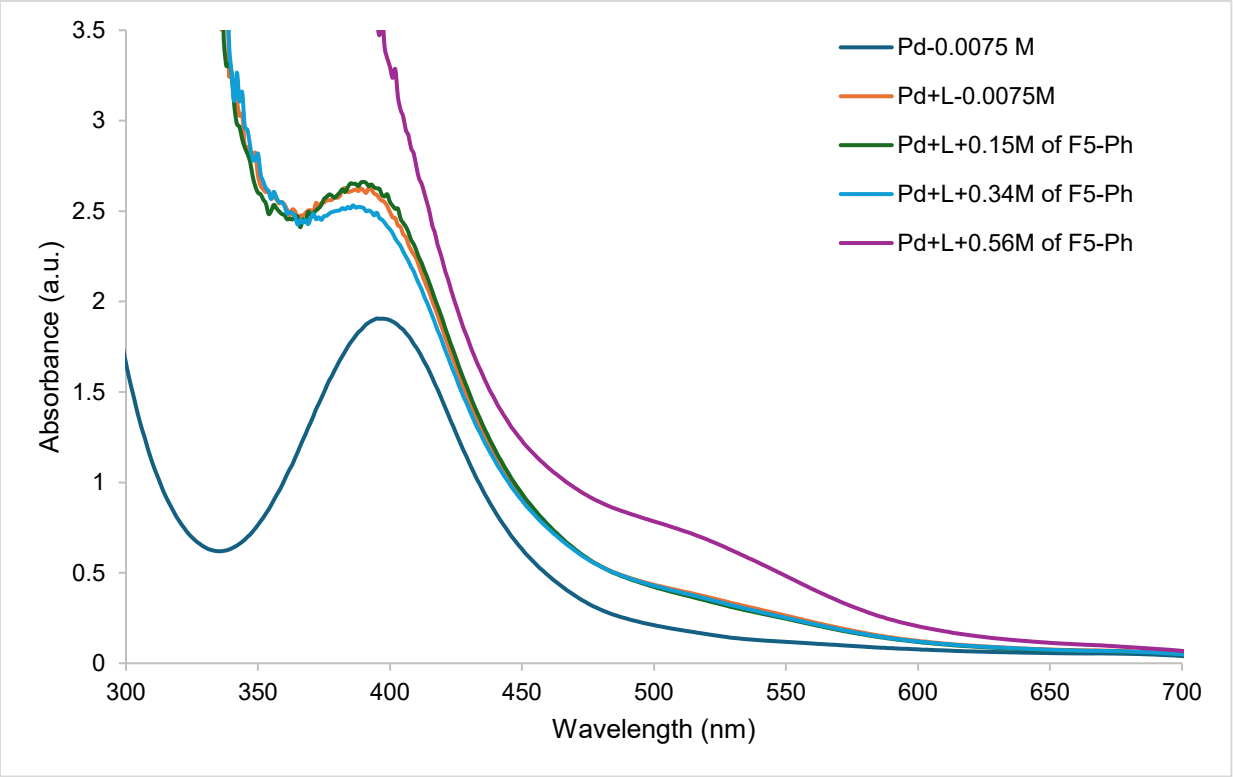
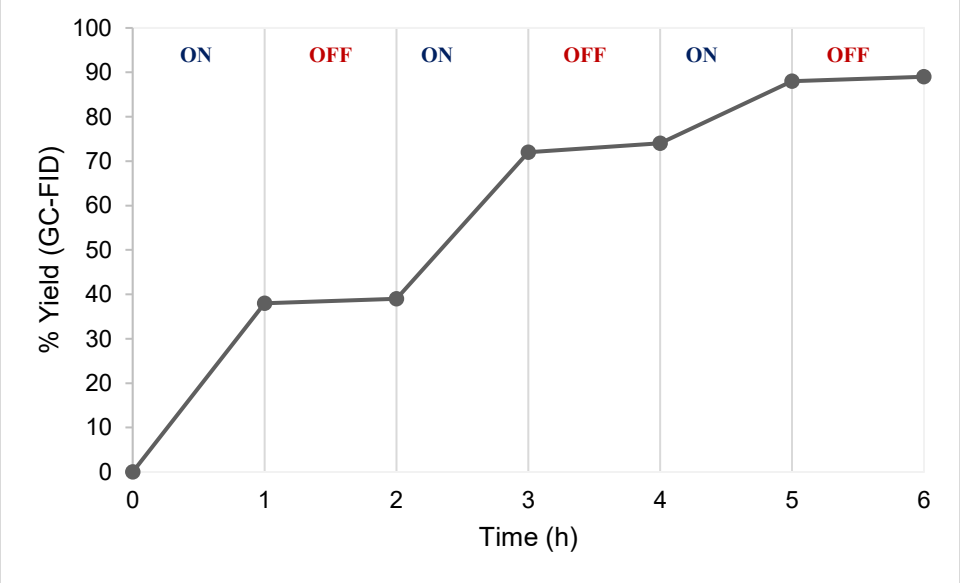


Fig. S1 UV-Vis spectra of reaction components: $Pd(OAc)_2$ (Pd), BrettPhos (L), 1,2,3,4,5-pentafluorobenzene (F5-Ph), individually and combined in 1,4-dioxane.

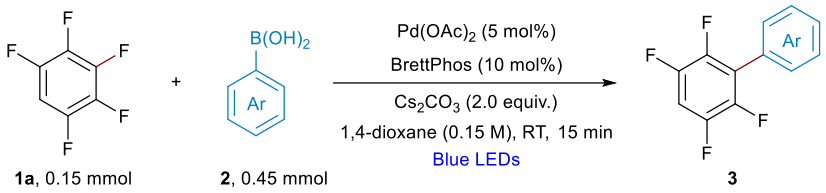
7. Effect of Light: On/Off Plot

A clean 2 mL screw cap glass reaction vial was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol%), BrettPhos (5.4 mg, 0.01 mmol, 10 mol%), phenyl boronic acid (36.6 mg, 0.3 mmol, 3.0 equiv.) and then transferred into an argon-filled glove box. To that, Cs_2CO_3 (65.2 mg, 0.2 mmol, 2.0 equiv.), and degassed 1,4-dioxane (666 μL) was added followed by 1,2,3,4,5-pentafluorobenzene (16.8 mg, 0.1 mmol, 1.0 equiv.) and mesitylene (0.1 mmol, 1.0 equiv.) as an internal standard and placed in front of the LEDs. The reaction was sequentially stirred under visible light irradiation and in the absence of light. Every one hour an aliquot of 30 μL was removed *via* syringe and analyzed by GC-FID. After a total of 6 h the determined yields were plotted against the reaction time.



8. Hammett Analysis of the C–F Arylation of Pentafluorobenzene with Substituted Arylboronic Acids

Experimental Procedure



A clean 2 mL screw cap glass reaction vial was charged with $Pd(OAc)_2$ (1.68 mg, 0.0075 mmol, 5 mol%), BrettPhos (8.05 mg, 0.015 mmol, 10 mol%), aryl boronic acid (0.9 mmol, 3.0 equiv.) and then transferred into an argon-filled glove box. To that, Cs_2CO_3 (97.7 mg, 0.3 mmol, 2.0 equiv.), and degassed 1,4-dioxane (1 mL) were then added followed by 1,2,3,4,5-pentafluorobenzene (25.21 mg, 0.15 mmol, 1.0 equiv.). The vial was then capped with Teflon septum, removed from the glove box, and irradiated using blue LEDs (34 W) while stirring at RT (under fan cooling, temperature 33±2 °C) for 15 mins. After 15 mins, the reaction mixture was diluted with diethyl ether and washed with water. The combined organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure (rotary evaporator, bath temperature 30 °C). 2,2,2-trifluoroethanol (TFE, 0.15 mmol, 1.0 equiv.) was added as an internal standard to the crude residue together with $CDCl_3$ and the sample was analyzed by quantitative ^{19}F NMR (377 MHz).

Quantification Method

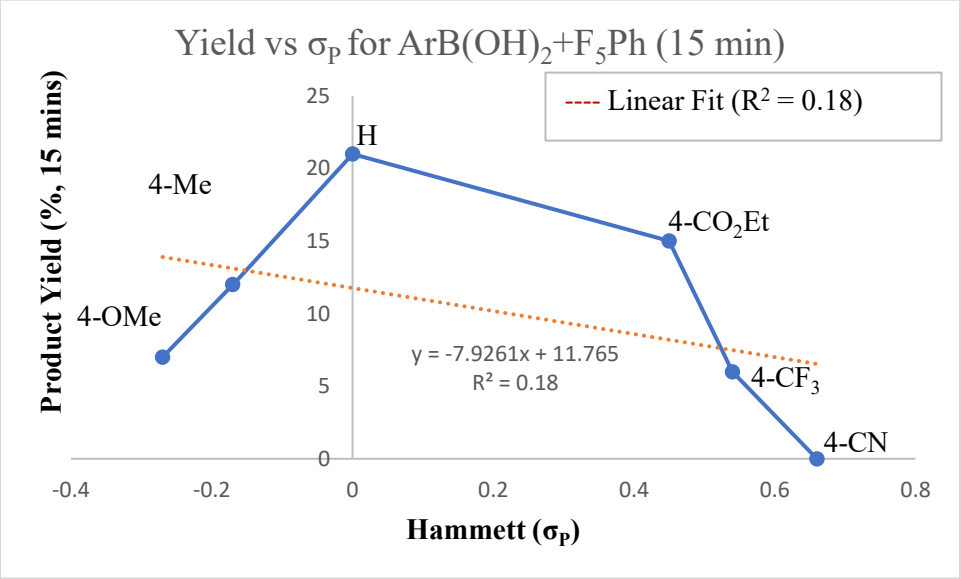
Product yields were determined by integration of the diagnostic aromatic ^{19}F resonances of each tetrafluorobiaryl product (δ around −144 ppm which corresponds to two fluorines in the products) relative to the TFE internal standard (δ −77.4 to −77.7 ppm, t, J = 8.3 Hz). Residual pentafluorobenzene was quantified independently from its isolated *para*-F resonance (δ −153 to −155 ppm), which does not overlap with any product or standard signal.

Table I. Hammett Data Set[a]

Entry	Ar-PhB(OH)$_2$	Hammett (σ_p)	Product yield (%, 15 min)[b]	Pentafluoro-benzene consumed[c]	Mass-balance gap[d]
1	4-OMe	−0.27	7	~95%	Large
2	4-Me	−0.17	12	>95%	Large
3	H	0.00	21	>95%	Large
4	4-CO_2Et	+0.45	15	~25%	Small
5	4-CF_3	+0.54	6	~14%	Small
6	4-CN	+0.66	0	~5%	Small

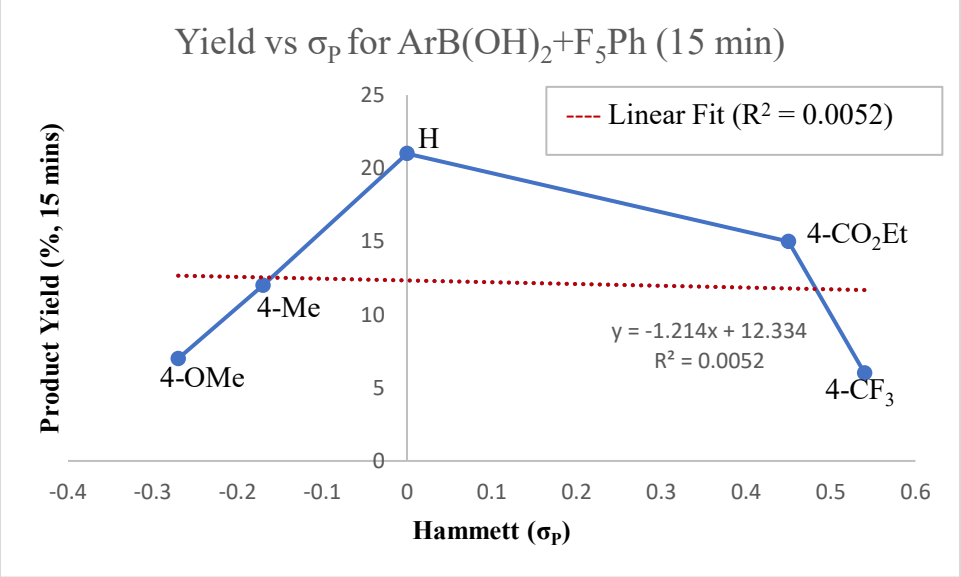
[a]All reactions run for 15 min under standard irradiation conditions; conversion and yield determined by quantitative ^{19}F NMR using TFE as internal standard (added post-work-up). [b]σ_p values from C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* 1991, **91**, 165-195. [c]estimated from disappearance of the pentafluorobenzene *para*-F resonance (δ −153 to −155 ppm) relative to the t = 0 reference. [d]difference between pentafluorobenzene consumed and product formed; a large gap indicates substantial non-productive consumption of pentafluorobenzene.

Figure I. Hammett Plot for six ArB(OH)$_2$



Product yield (%, 15 min) plotted against Hammett σ_p for the six arylboronic acid substituents examined. The dashed line is a least-squares fit to all six points and is shown for visual reference only (see analysis below).

Figure II. Hammett Plot for five ArB(OH)$_2$ excluding 4-CNC$_6$H$_4$B(OH)$_2$



Product yield (%, 15 min) plotted against Hammett σ_p for the five arylboronic acid substituents examined. The dashed line is a least-squares fit to all five points and is shown for visual reference only (see analysis below).

Table II. Regression Analysis

Regression model	Slope (ρ)	R^2	*p*-value
Yield (%) vs. σ_p - all six substituents	−7.93	0.18	0.40
Yield (%) vs. σ_p - excluding 4-CN	−1.21	0.0052	0.91

Linear regression of product yield (%) against σ_p, performed (i) across all six substituents and (ii) excluding 4-CN-$C_6H_4B(OH)_2$.

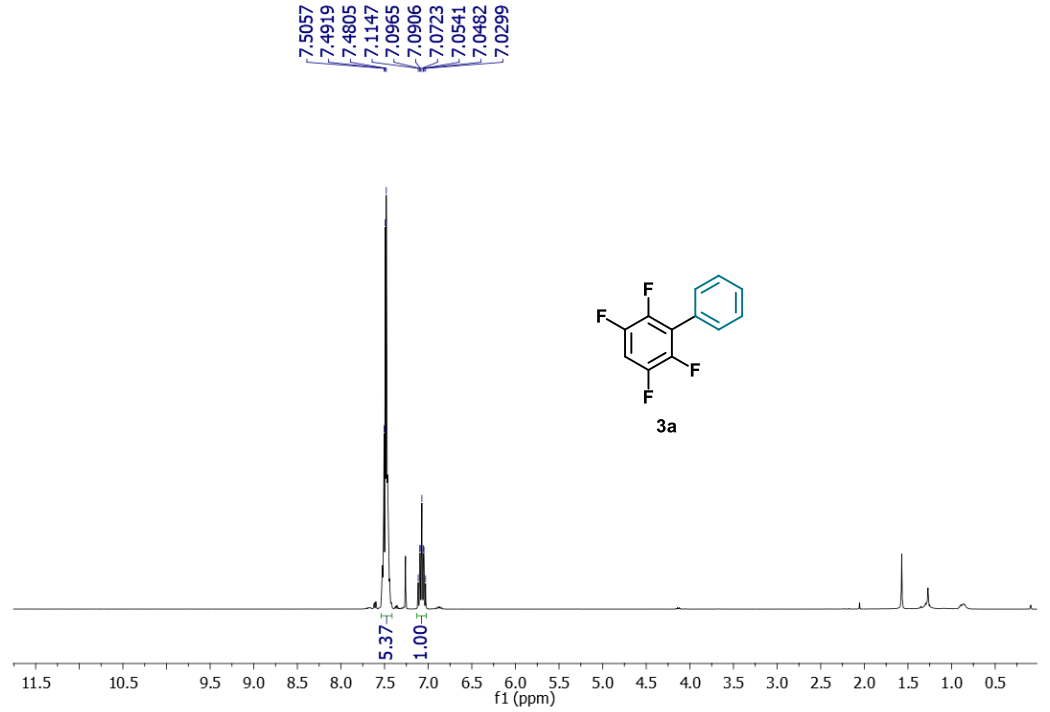
Hammett studies were conducted using six *para*-substituted arylboronic acids (σ_p = -0.27 to +0.66) under the standard reaction conditions, with product formation quantified by ^{19}F NMR spectroscopy after 15 min of reaction time (Table I, Figure I). However, the resulting plot of product yield *vs* σ_p did not exhibit a meaningful linear free-energy relationship (R^2 = 0.18 for the full data set; R^2 = 0.01 upon exclusion of the zero-yield 4-CN$C_6H_4B(OH)_2$ data point). Consequently, a statistically meaningful reaction constant (ρ) could not be extracted from the data.

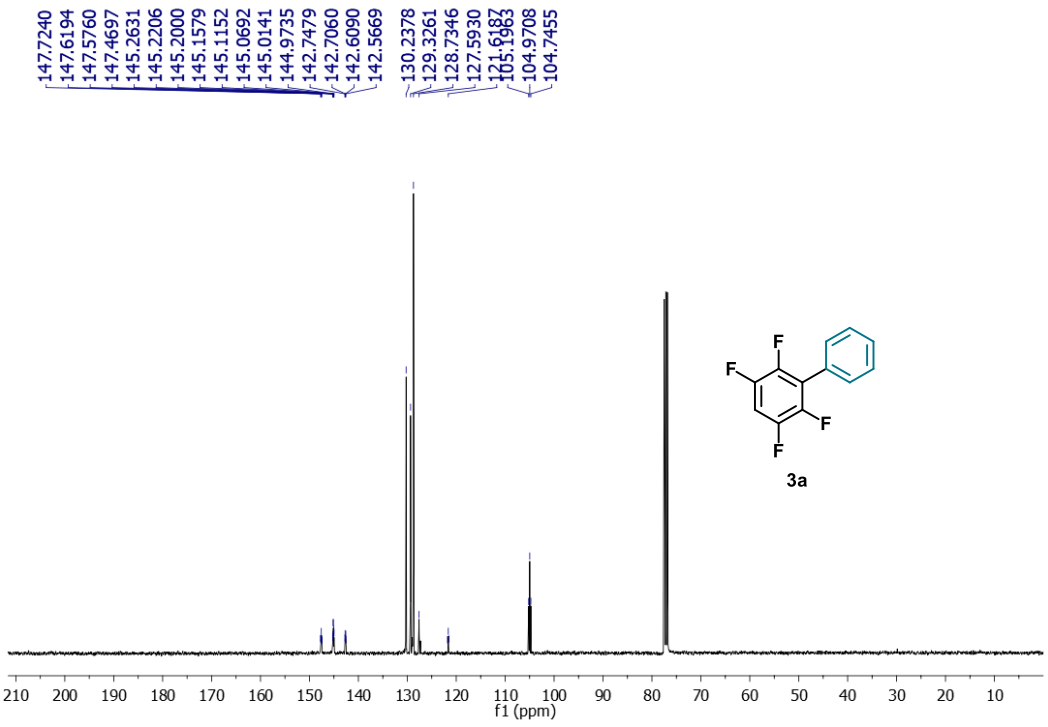
The Hammett plot displays a non-linear, U-shaped dependence, with diminished yields observed for both electron-rich and electron-poor aryl boronic acid substrates and the highest yield obtained for $PhB(OH)_2$. Based on the above results, it can be concluded that the observed yields depend on the combination of several electronically sensitive processes and not on a common single rate-determining step. The interpretation is consistent by quantitative ^{19}F NMR analysis (Table I, column 5) for electron-rich and unsubstituted aryl boronic acids (entries 1-3) where pentafluorobenzene was almost completely consumed despite relatively low product yields (7–21%). This result might indicate for the operation of a competing, non-productive light-mediated consumption pathway for the polyfluoroarene. On contrary, for the reaction with electron-deficient aryl boronic acids (entries 4-6), significant amounts of pentafluorobenzene remained unreacted. This effect turns out presumably due to less favorable conditions for transmetalation as the nucleophilicity of the boronic acid decreases.

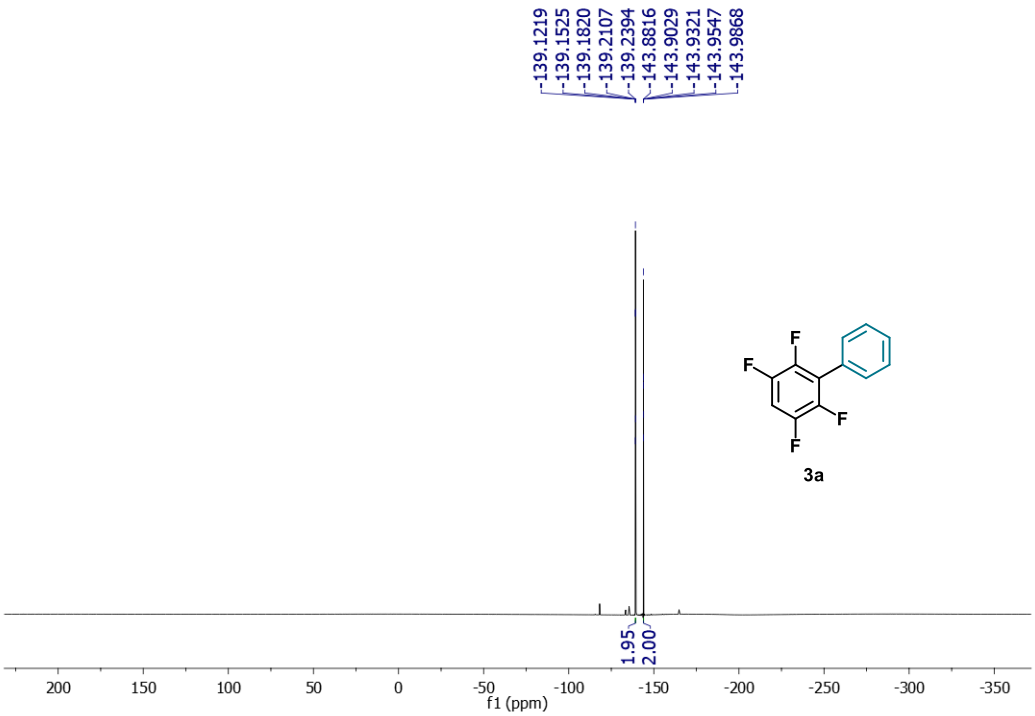
These combined observations suggest that there are at least two mechanistically distinct and substituent-sensitive pathways in the reaction, rather than a common rate-determining step. Under such conditions, assignment of a single Hammett reaction constant (ρ) would not provide a meaningful mechanistic interpretation. Therefore, we have not included a Hammett correlation in the main manuscript.

9. NMR data of products

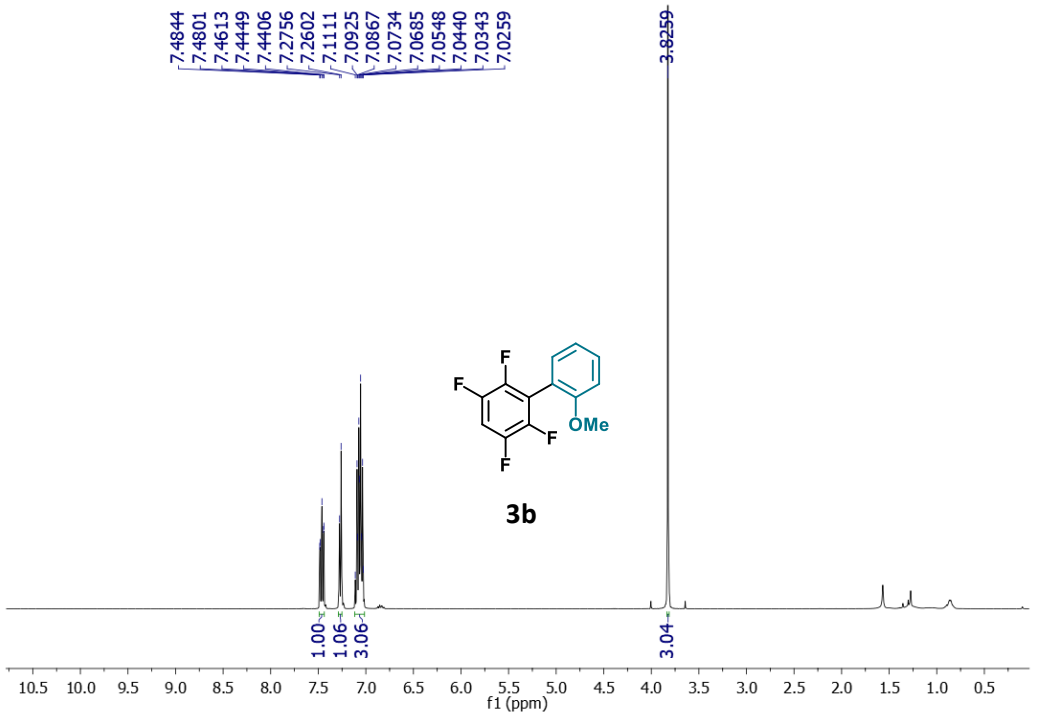
2,3,5,6-tetrafluoro-1,1'-biphenyl (3a):

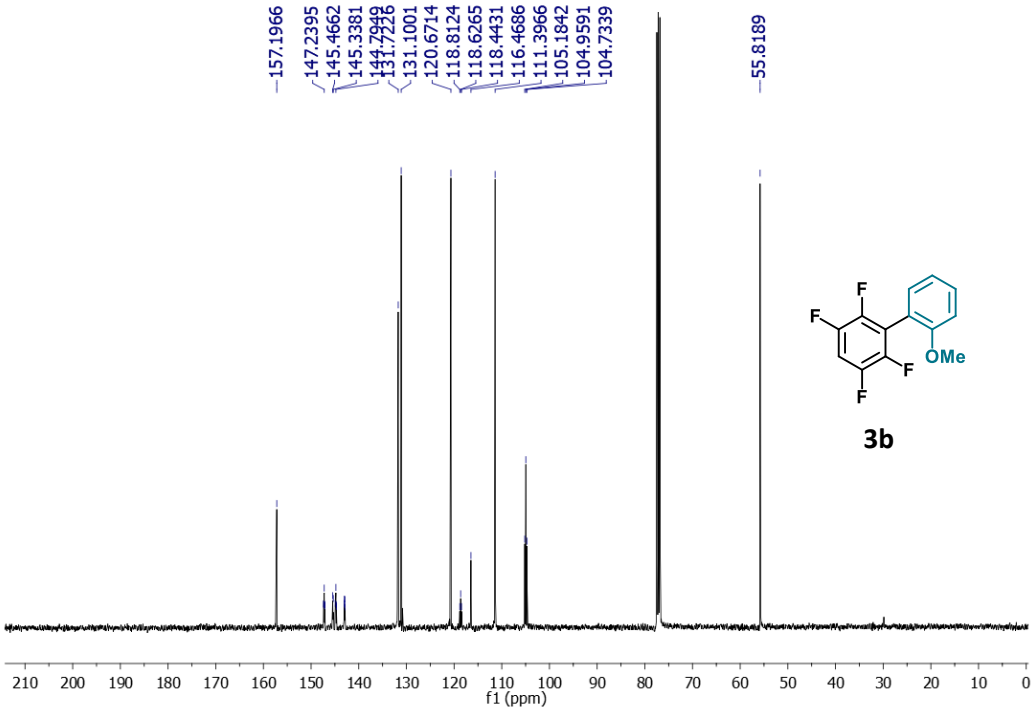


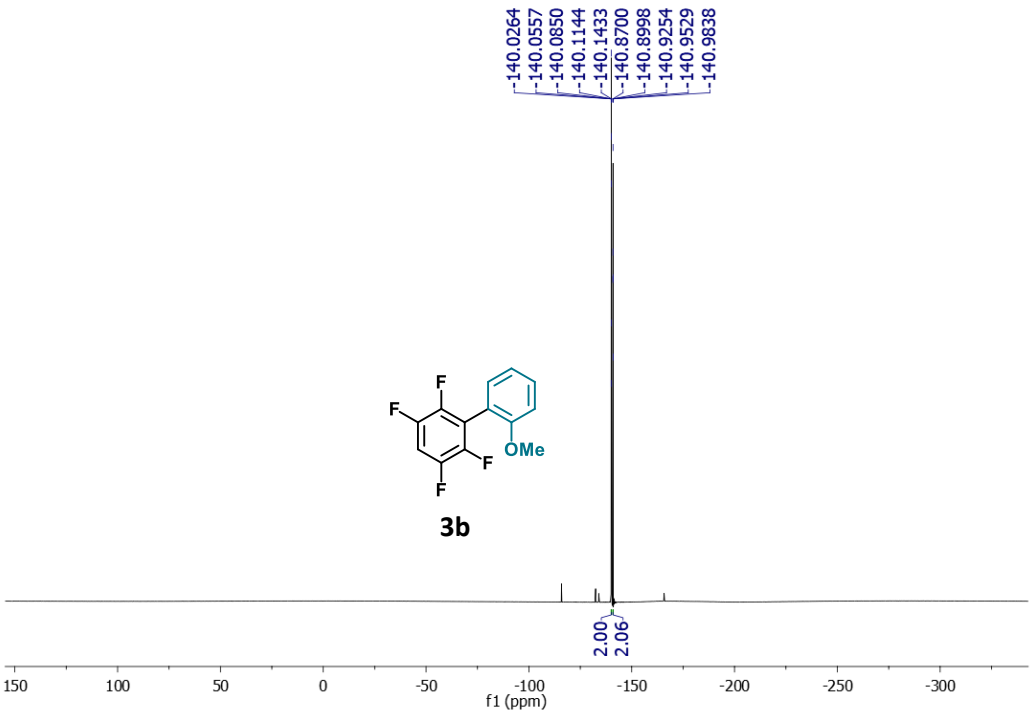



-139.1219
-139.1525
-139.1820
-139.2107
-139.2394
-143.8816
-143.9029
-143.9321
-143.9547
-143.9868
F
F
F
F
3a
1.95
2.00
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

2,3,5,6-tetrafluoro-2'-methoxy-1,1'-biphenyl (3b):



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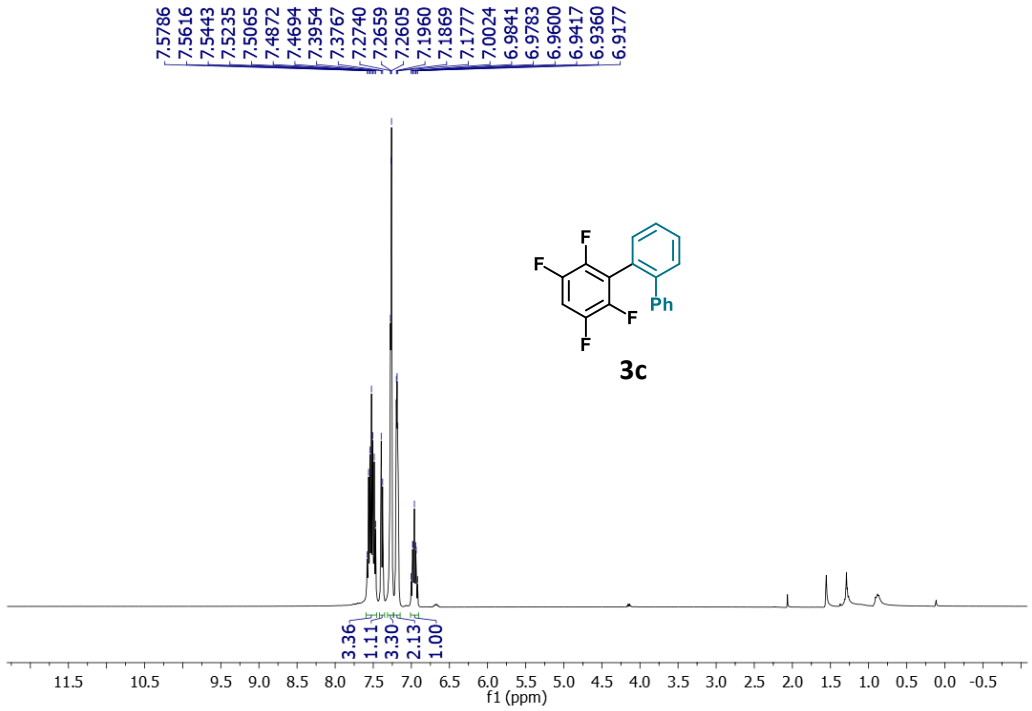
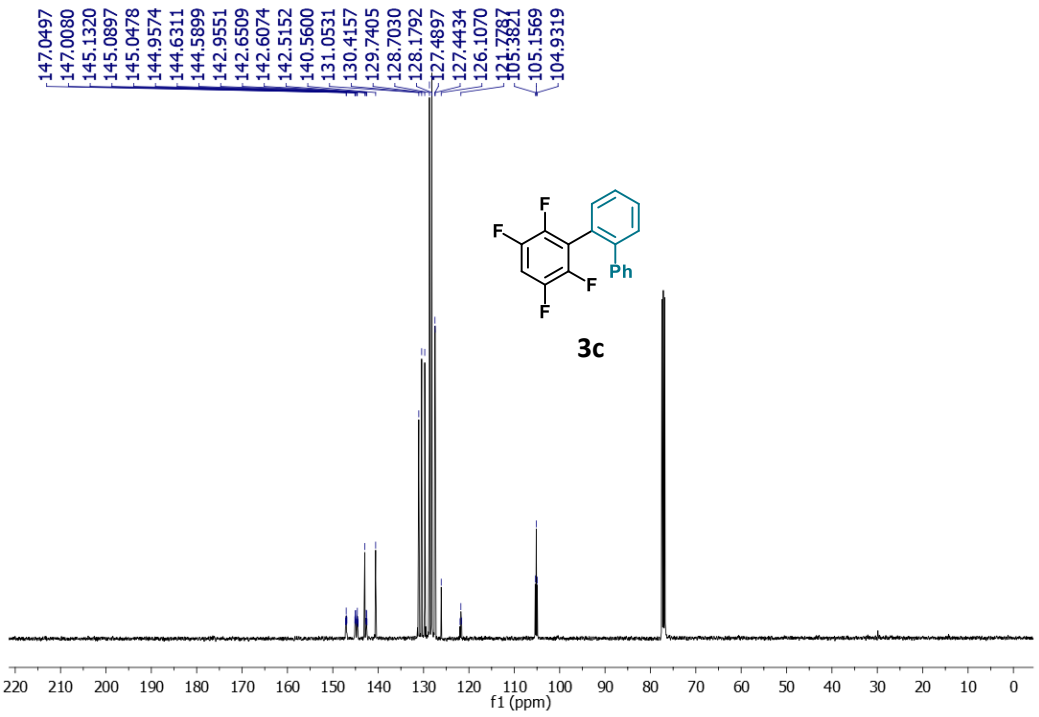
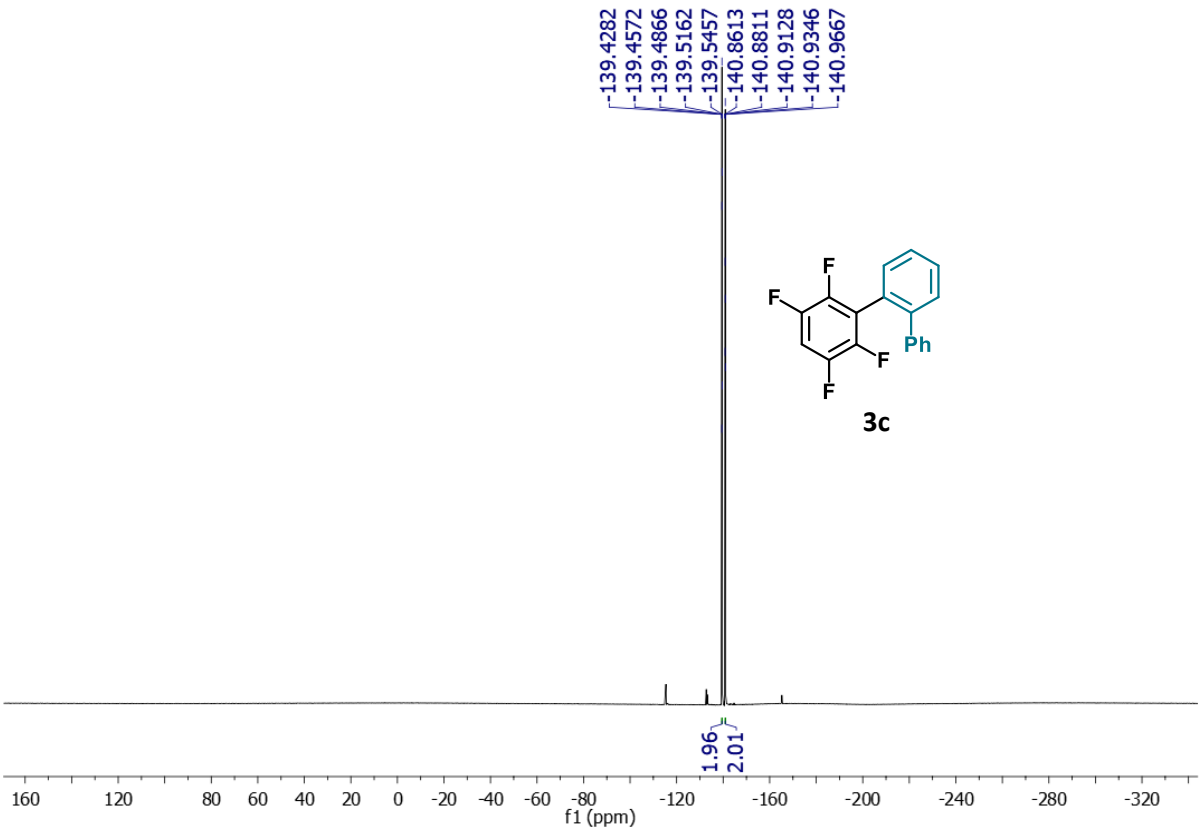
-140.8998
-140.9254
-140.9529
-140.9838
F
F
F
F
OMe
3b
2.00
2.06
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

2,3,5,6-tetrafluoro-1,1':2',1''-terphenyl (3c):



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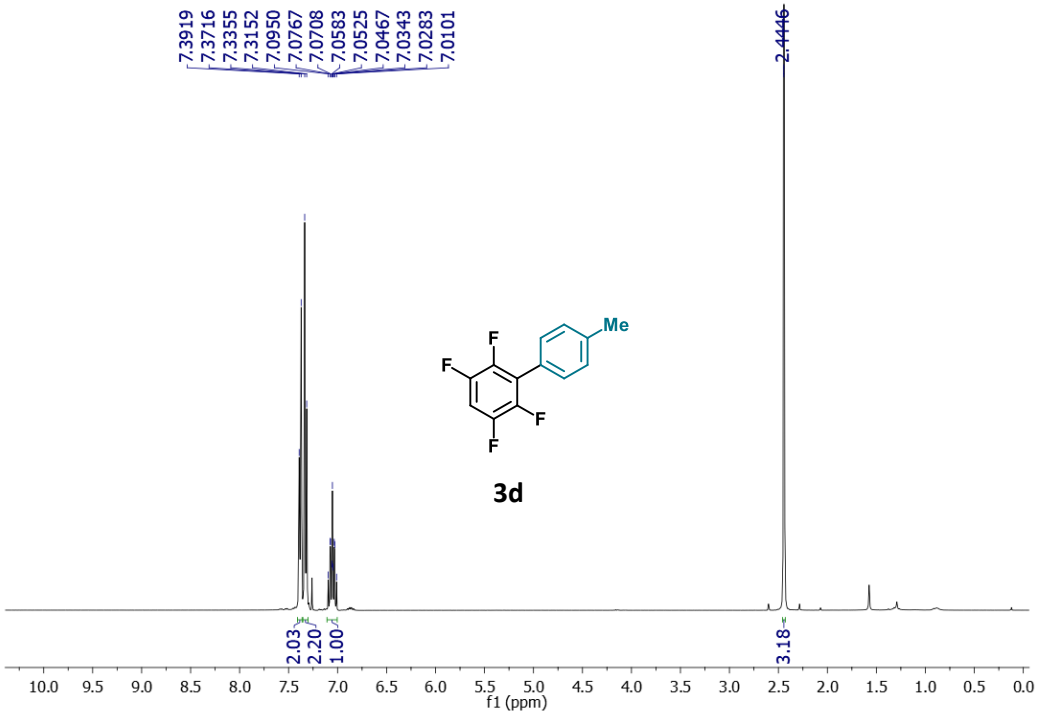
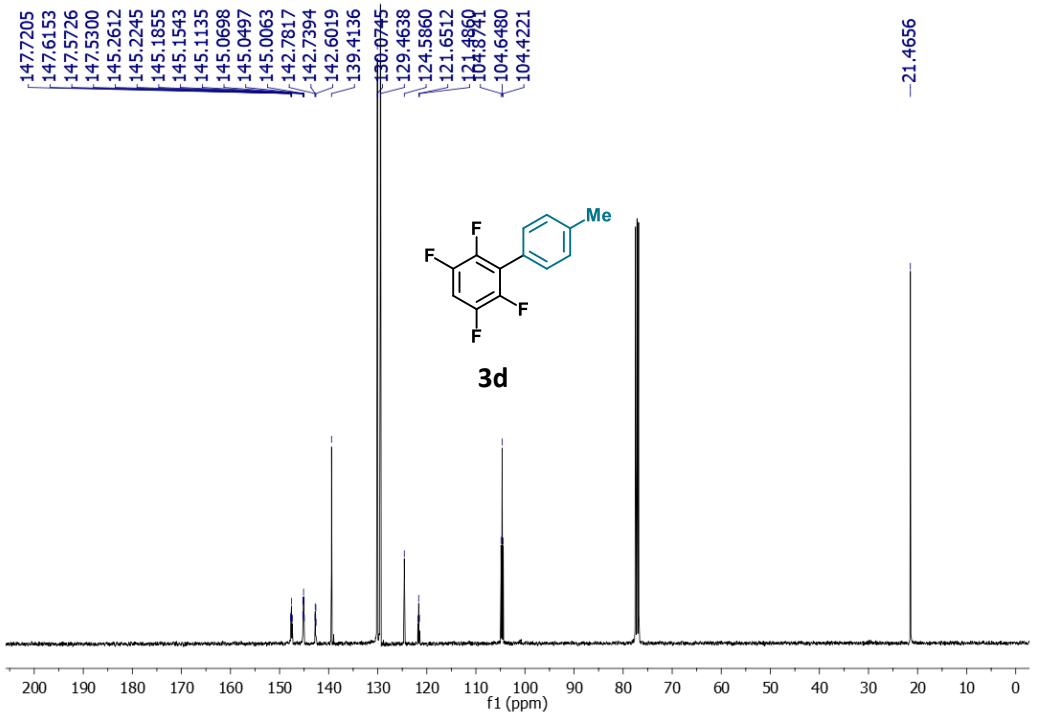
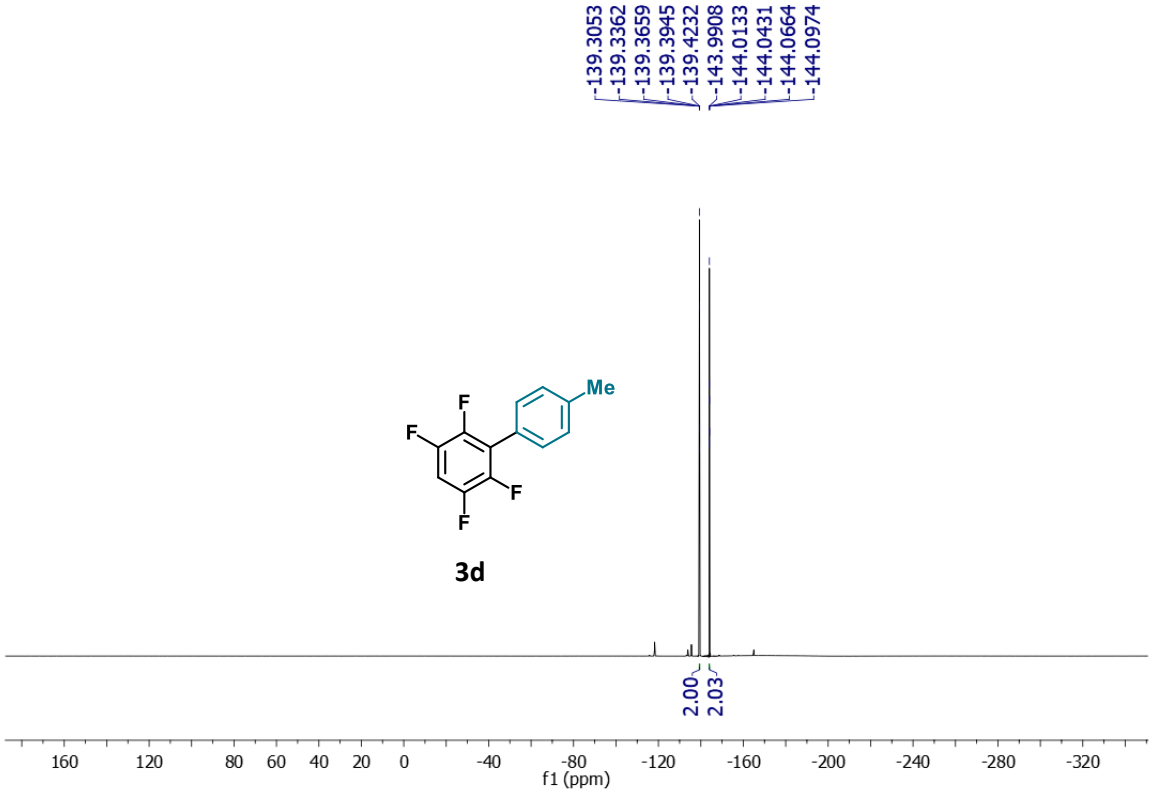
-139.4866
-139.5162
-139.5457
-140.8613
-140.8811
-140.9128
-140.9346
-140.9667
F
F
F
F
Ph
3c
1.96
2.01
160
120
80
60
40
20
0
-20
-40
-60
-80
-120
-160
-200
-240
-280
-320
f1 (ppm)

2,3,5,6-tetrafluoro-4'-methyl-1,1'-biphenyl (3d):



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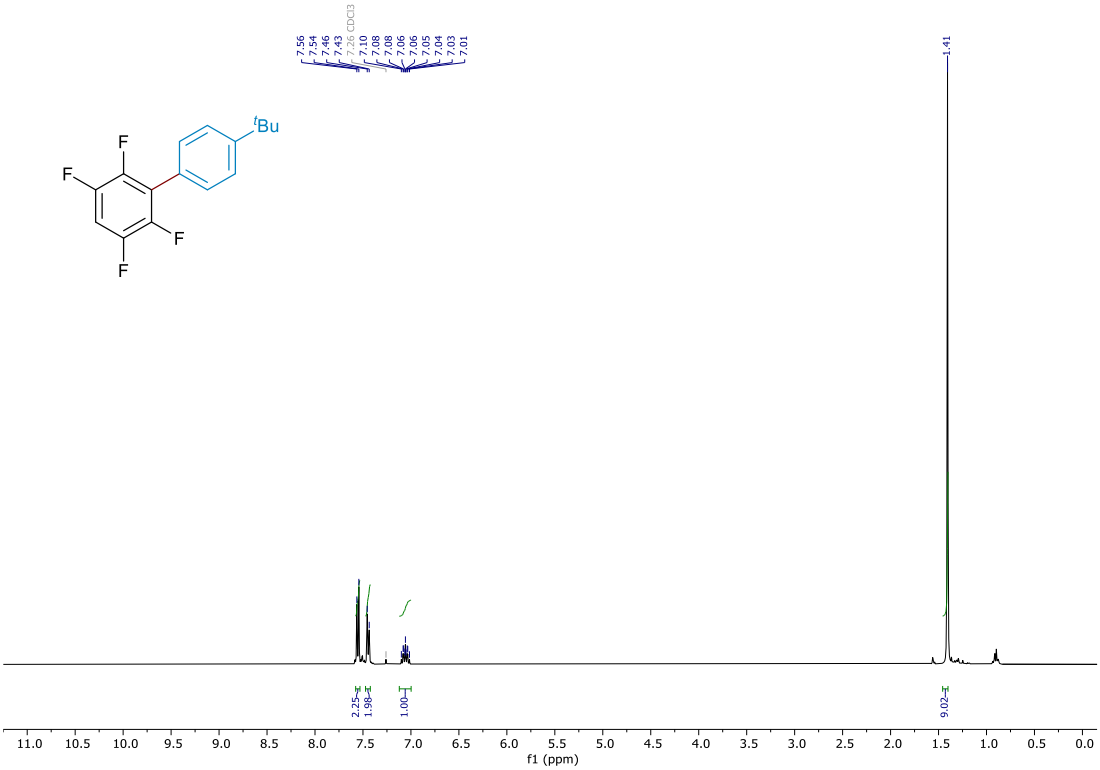
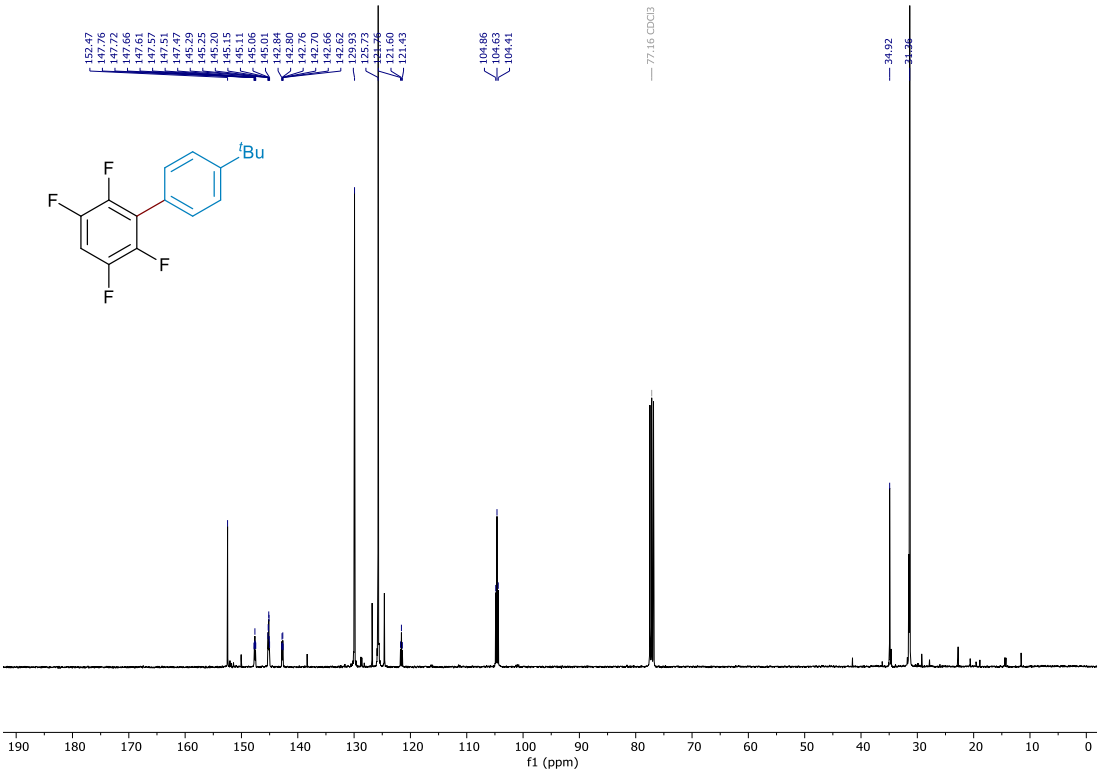
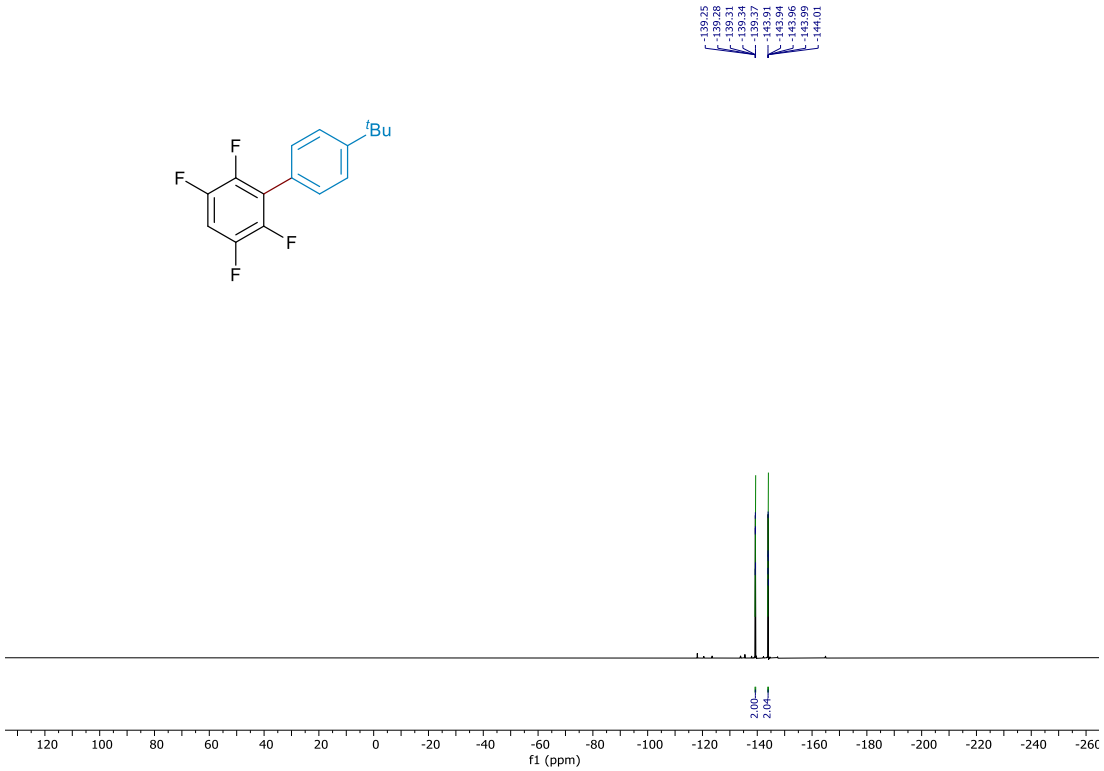
-139.3659
-139.3945
-139.4232
-143.9908
-144.0133
-144.0431
-144.0664
-144.0974
F
F
F
F
Me
3d
2.00
2.03
160
120
80
60
40
20
0
-40
-80
-120
-160
-200
-240
-280
-320
f1 (ppm)

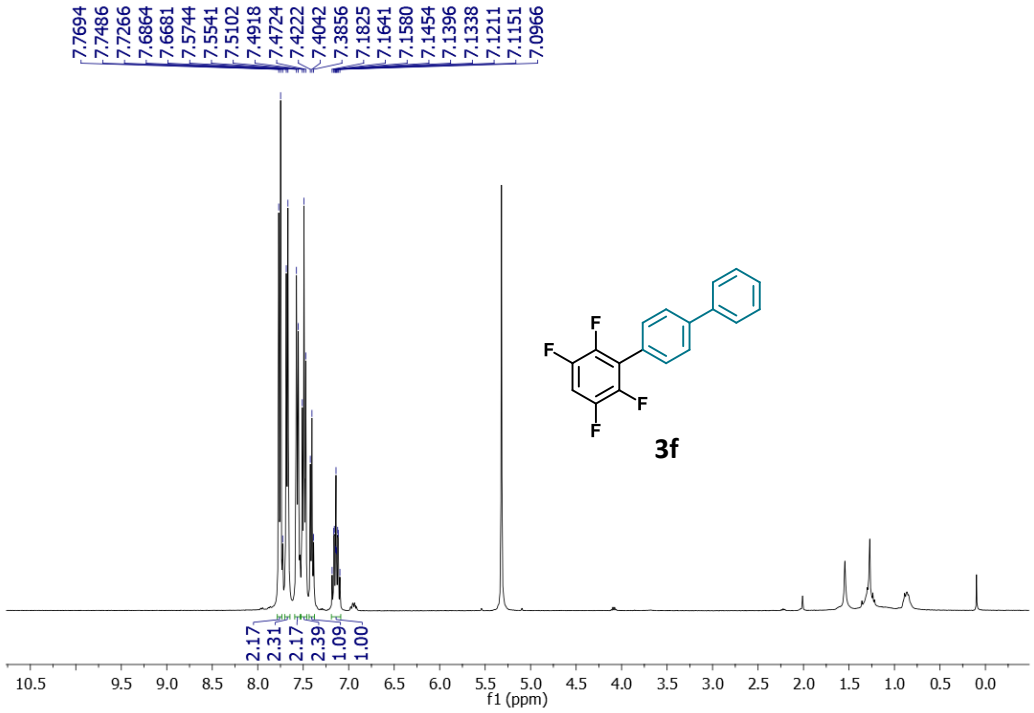
4'-(tert-butyl)-2,3,5,6-tetrafluoro-1,1'-biphenyl (3e):

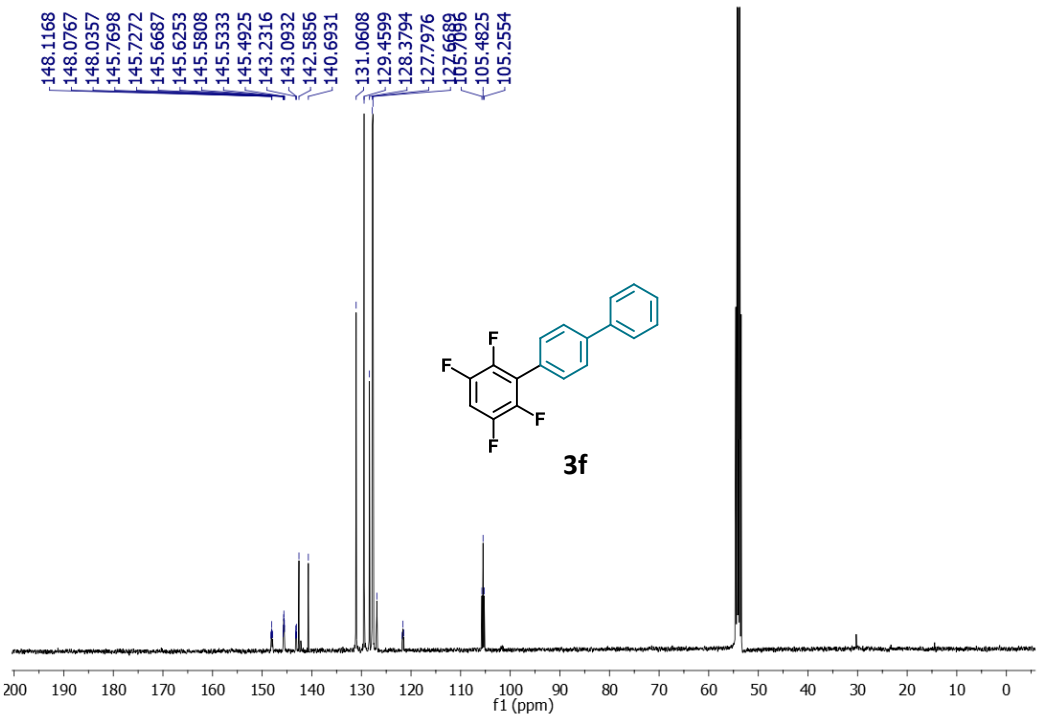


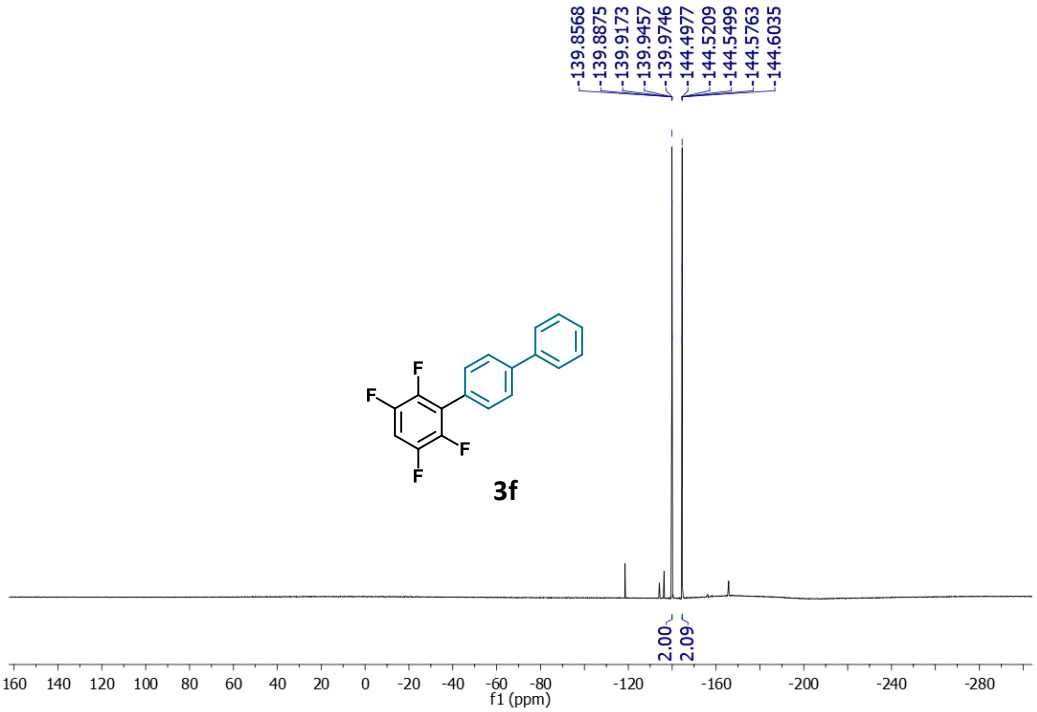



-139.25
-139.28
-139.31
-139.34
-139.37
-143.91
-143.94
-143.96
-143.99
-144.01
tBu
F
F
F
F
2.00
2.04
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

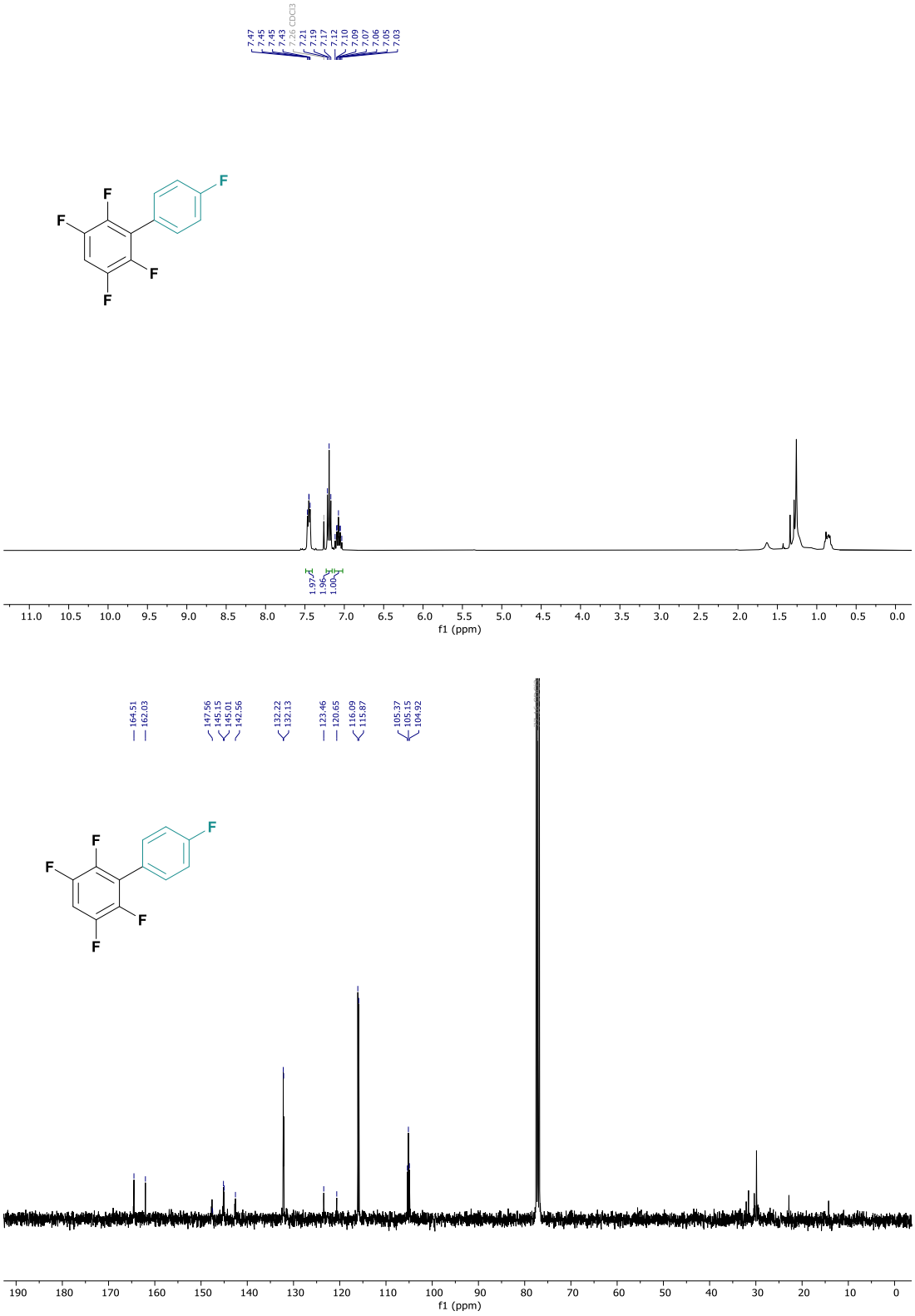
2,3,5,6-tetrafluoro-1,1':4',1''-terphenyl (3f):

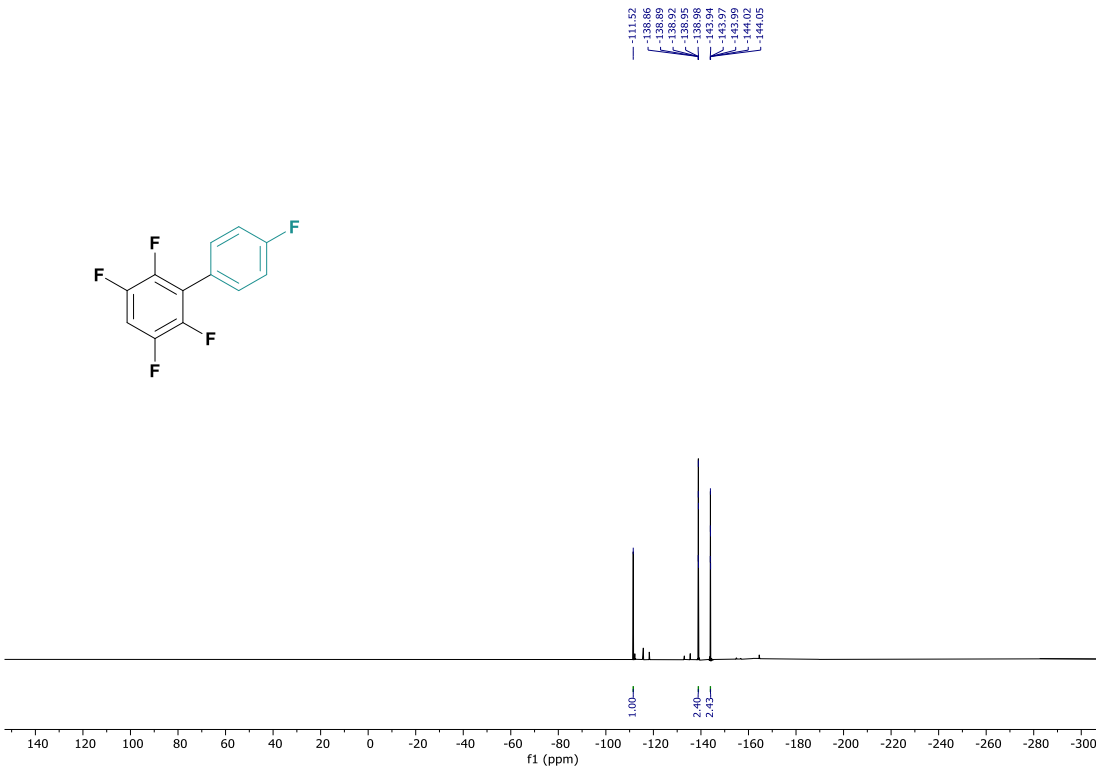




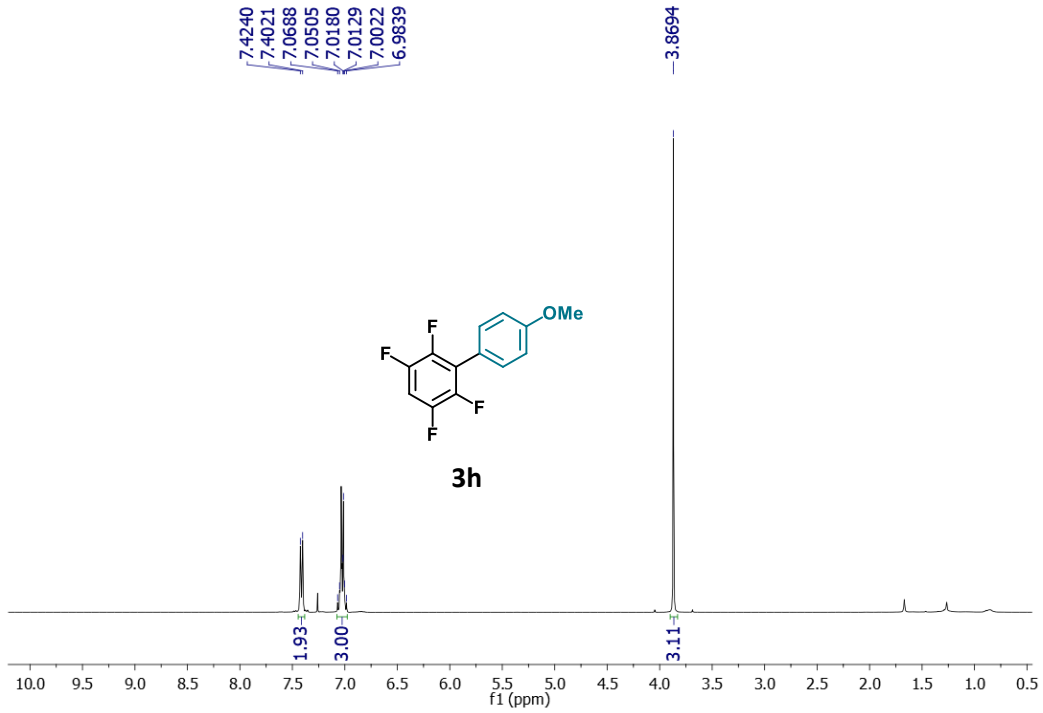

-139.8568
-139.8875
-139.9173
-139.9457
-139.9746
-144.4977
-144.5209
-144.5499
-144.5763
-144.6035
F
F
F
F
3f
2.00
2.09
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

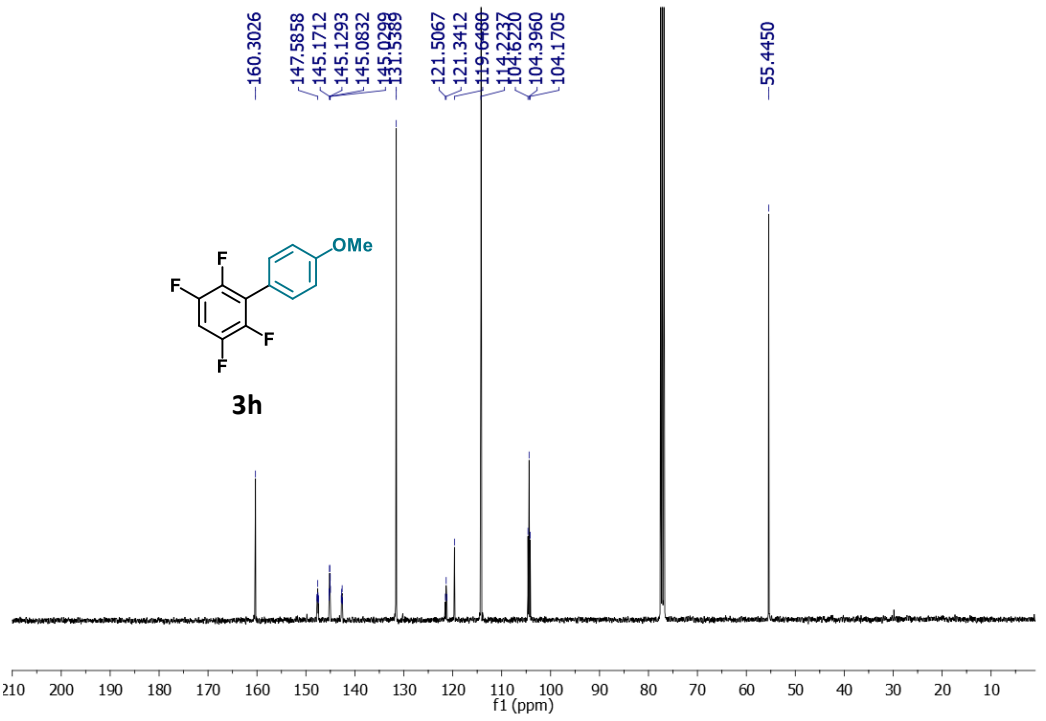
2,3,4',5,6-pentafluoro-1,1'-biphenyl (3g):

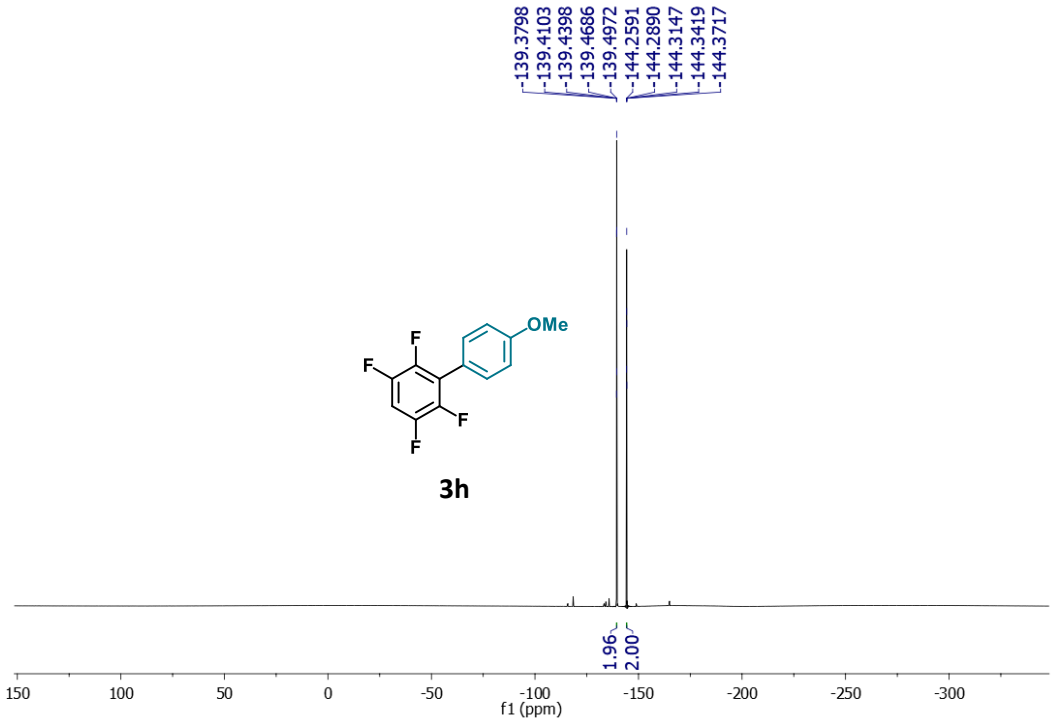



-111.52
-138.86
-138.89
-138.92
-138.95
-138.98
-143.94
-143.97
-143.99
-144.02
-144.05
F
F
F
F
1.00
2.40
2.43
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

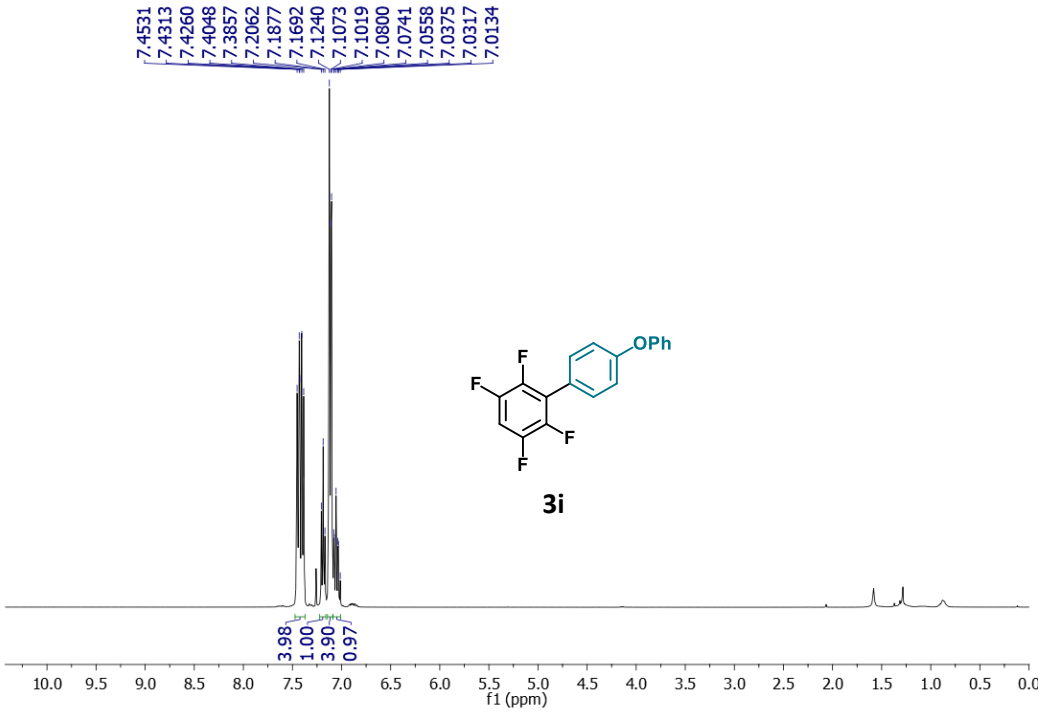
2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (3h):

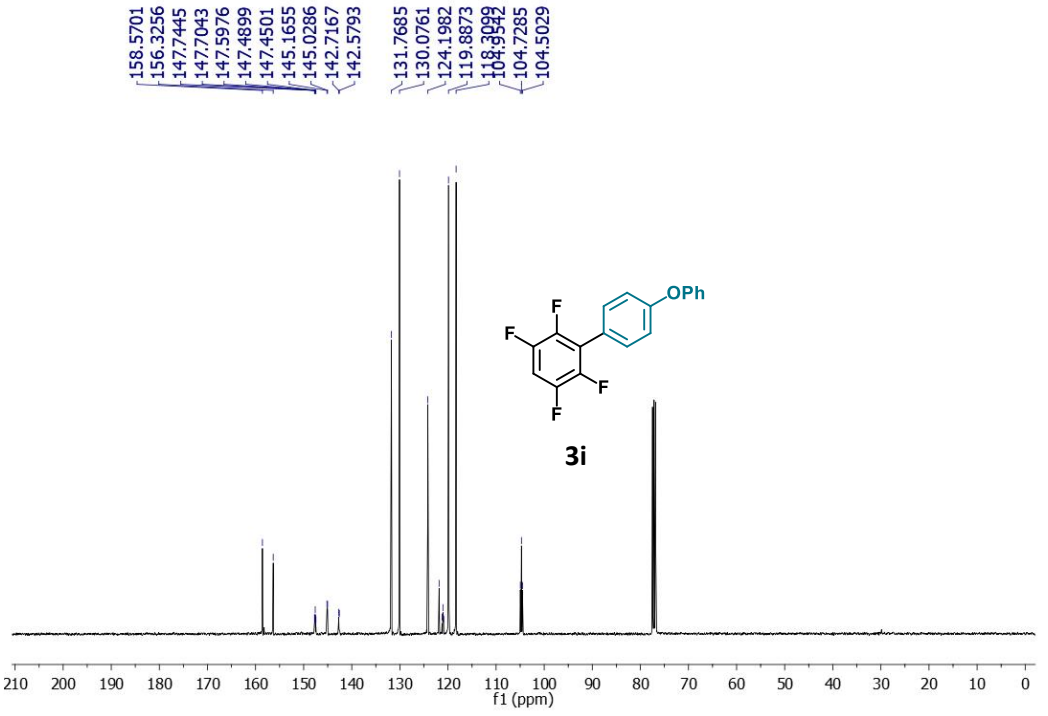


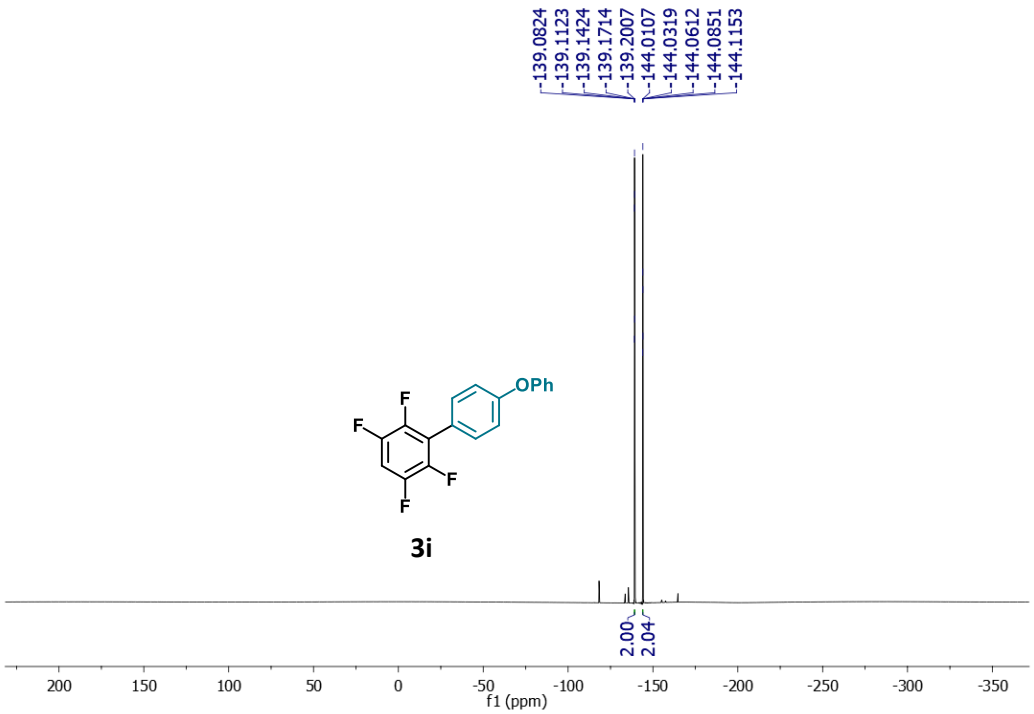



-139.3798
-139.4103
-139.4398
-139.4686
-139.4972
-144.2591
-144.2890
-144.3147
-144.3419
-144.3717
OMe
F
F
F
F
3h
1.96
2.00
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

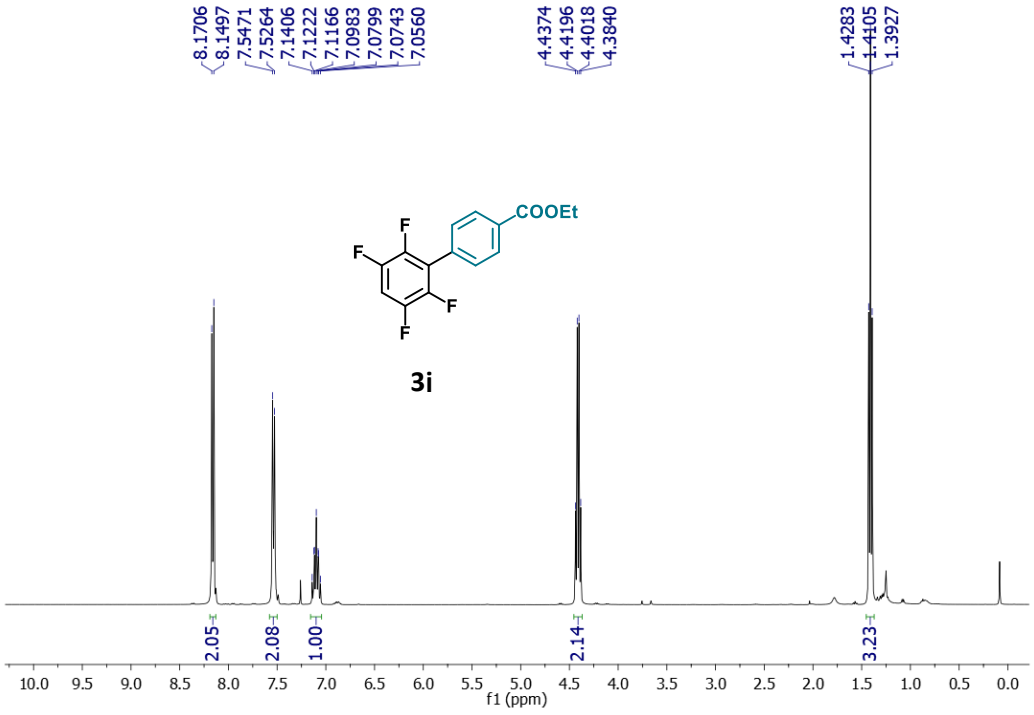
2,3,5,6-tetrafluoro-4'-phenoxy-1,1'-biphenyl (3i):

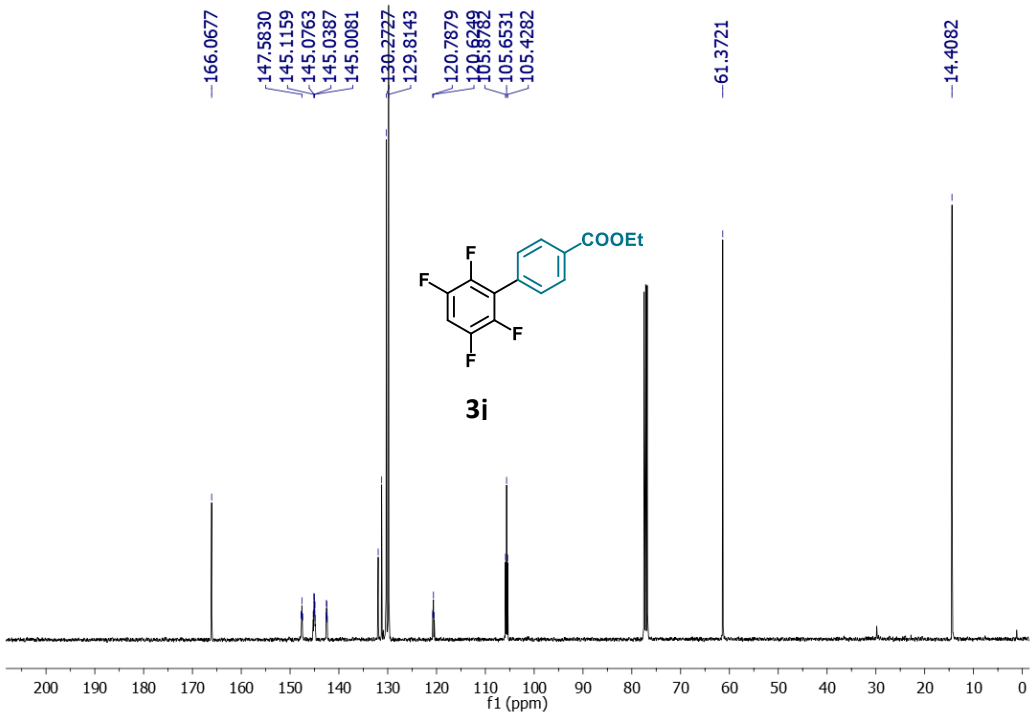


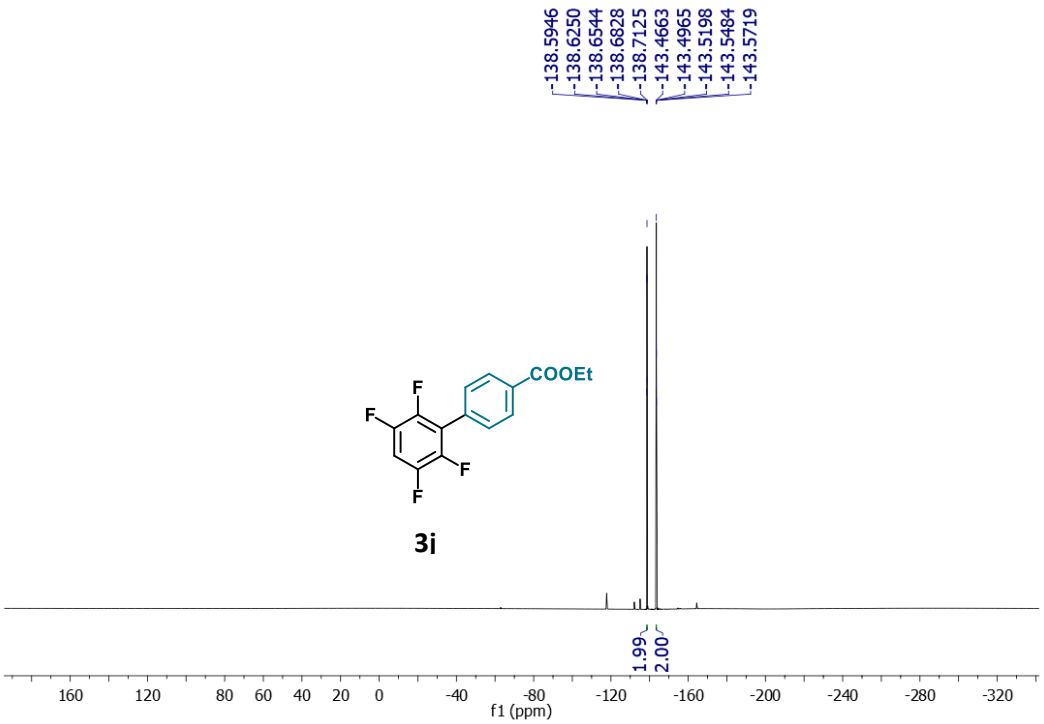



-139.0824
-139.1123
-139.1424
-139.1714
-139.2007
-144.0107
-144.0319
-144.0612
-144.0851
-144.1153
OPh
F
F
F
F
3i
2.00
2.04
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

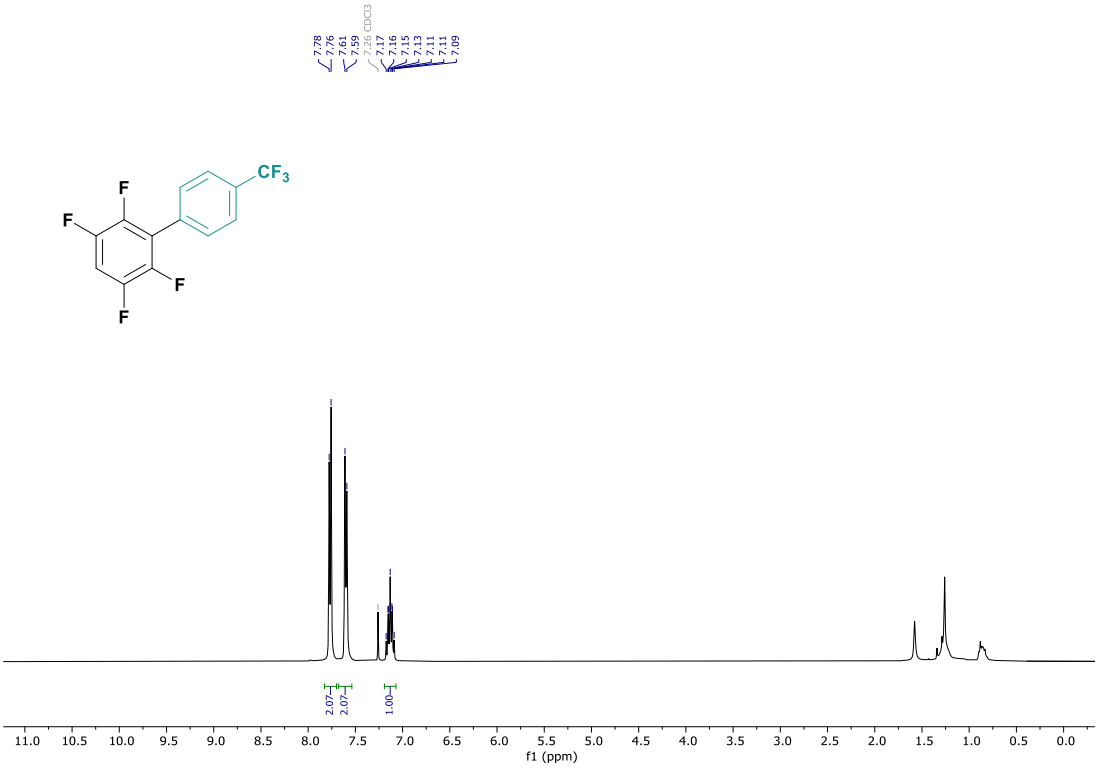
Ethyl 2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carboxylate (3j):

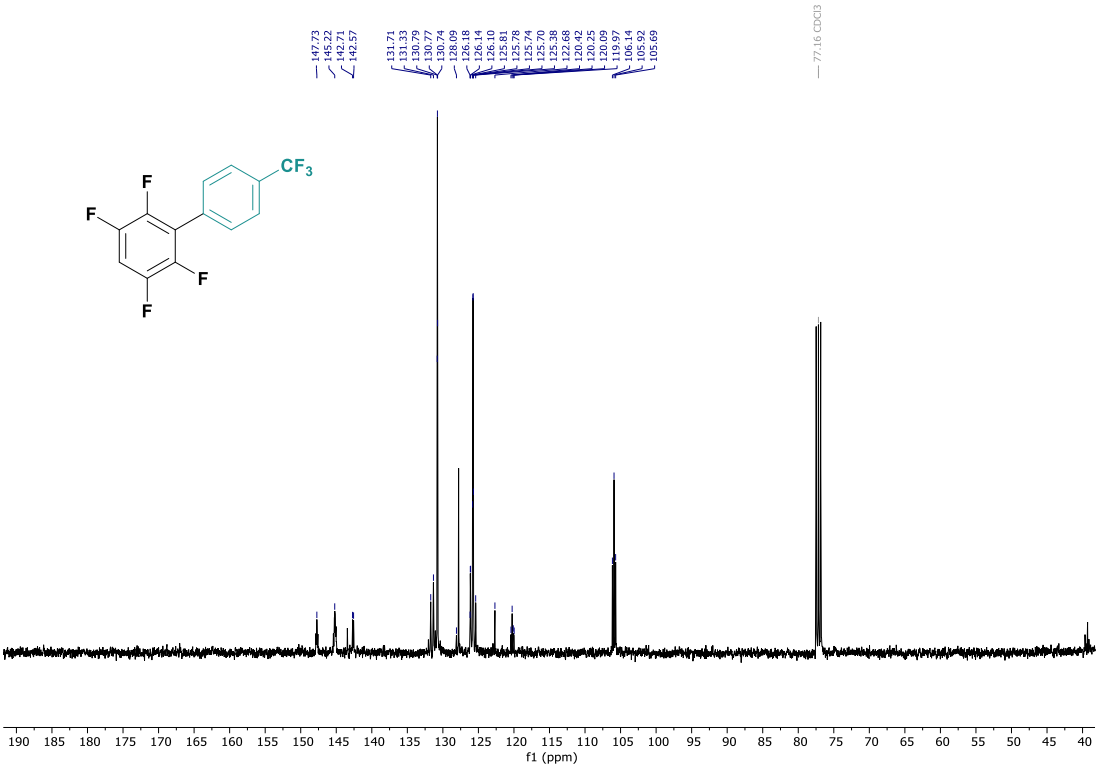


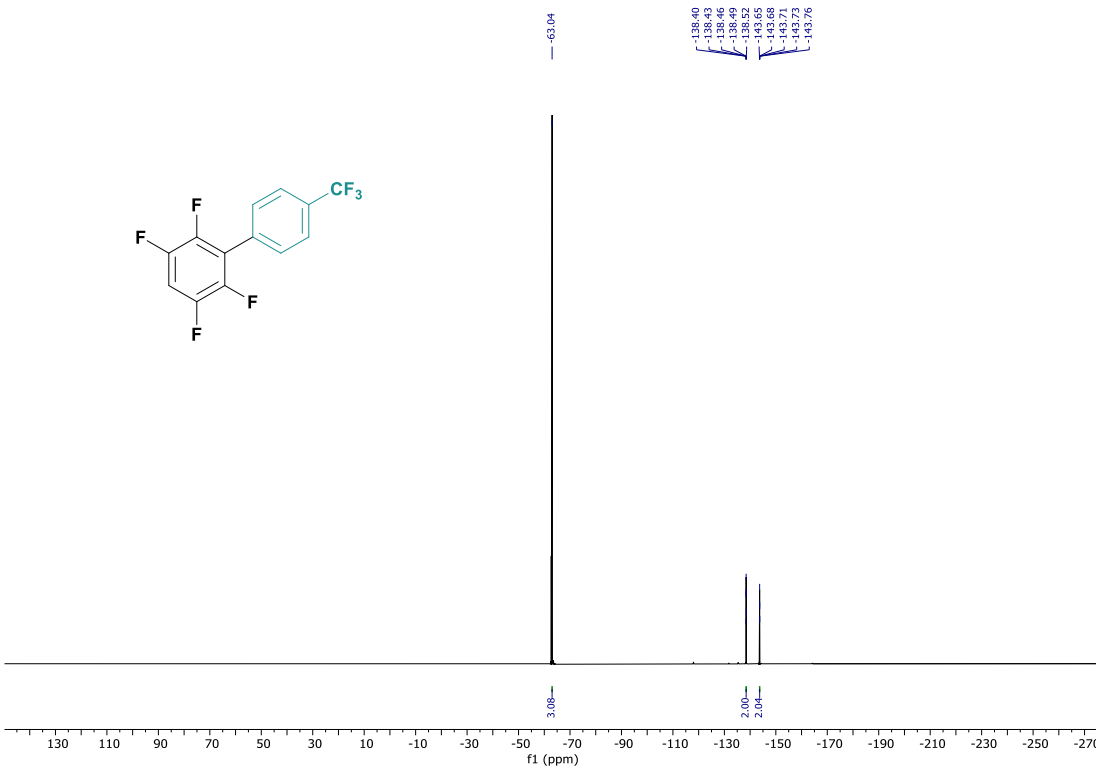



-138.5946
-138.6250
-138.6544
-138.6828
-138.7125
-143.4663
-143.4965
-143.5198
-143.5484
-143.5719
COOEt
F
F
F
F
3i
1.99
2.00
160
120
80
60
40
20
0
-40
-80
-120
-160
-200
-240
-280
-320
f1 (ppm)

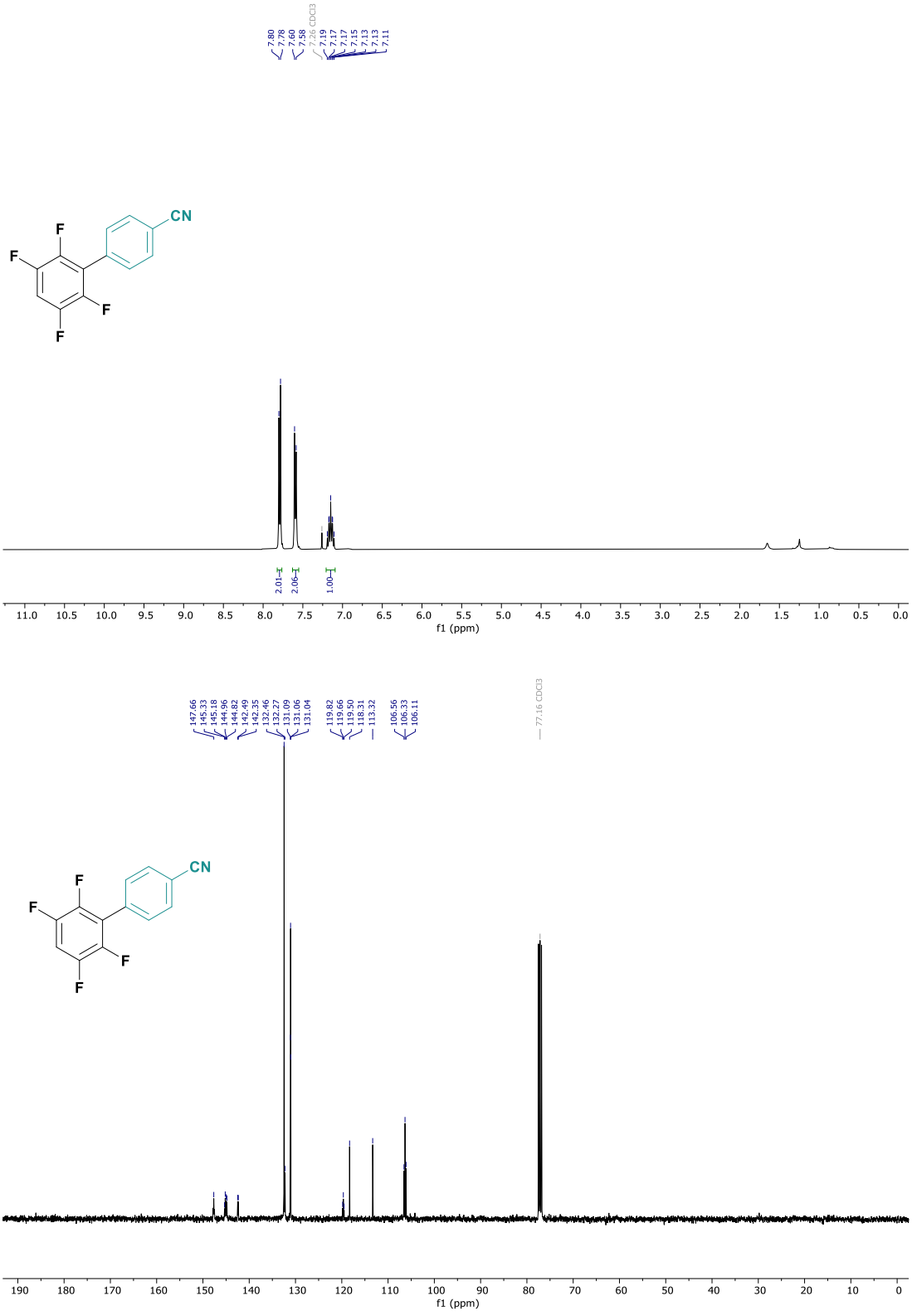
2,3,5,6-tetrafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (3k):





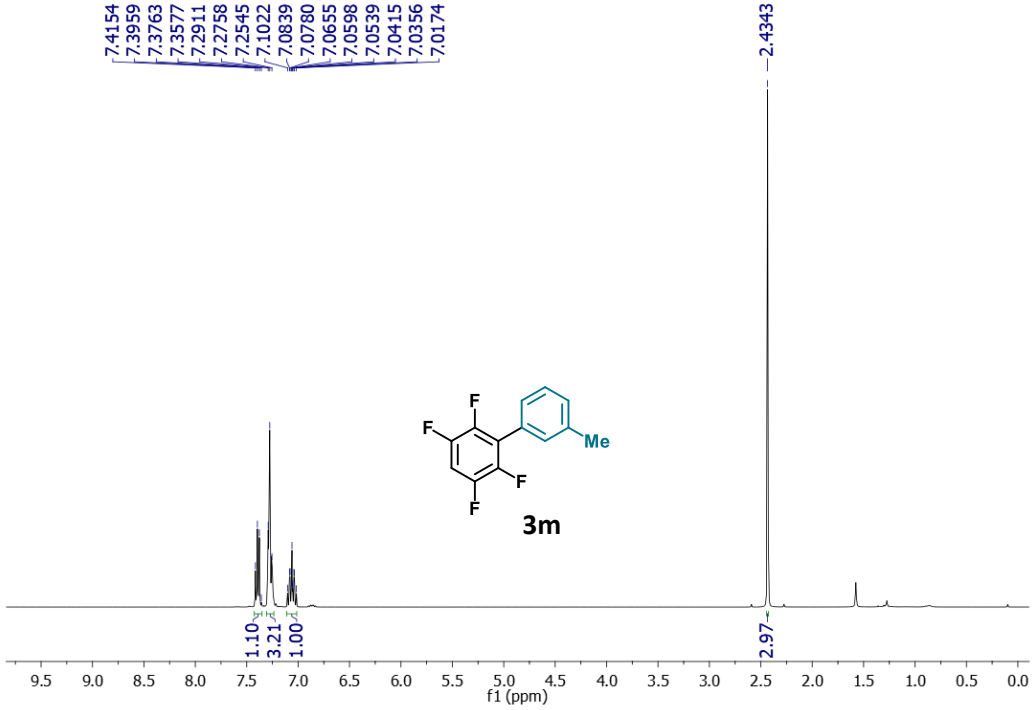

-63.04
-138.40
-138.43
-138.46
-138.49
-138.52
-143.65
-143.68
-143.71
-143.73
-143.76
F
F
F
F
CF3
3.08
2.00
2.04
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

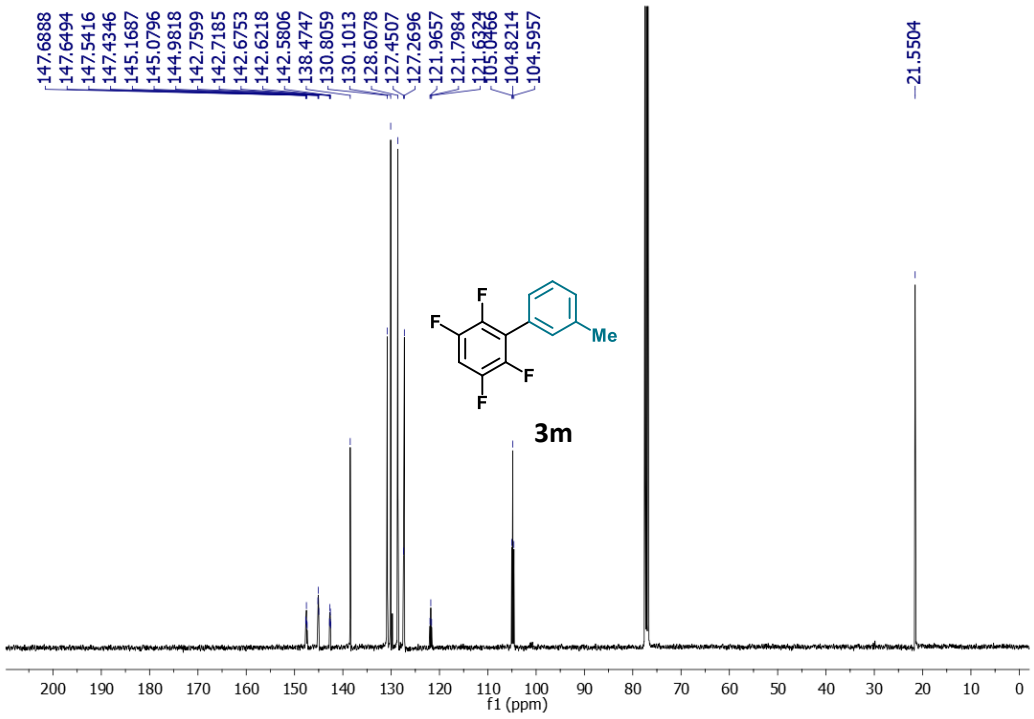
2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carbonitrile (3l):

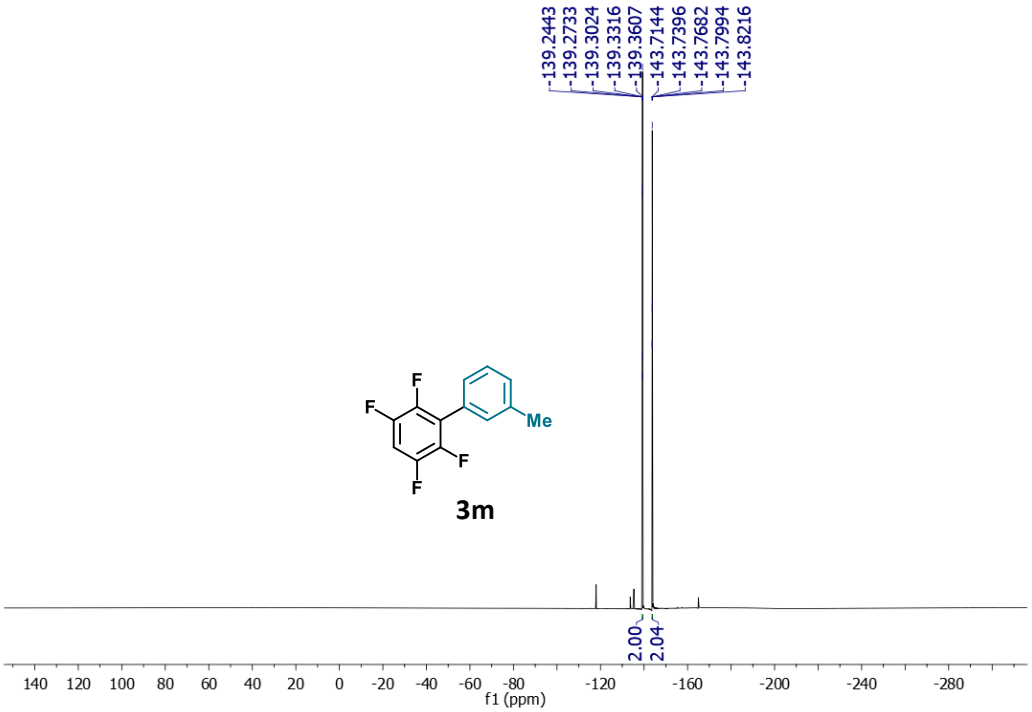



-137.90
-137.93
-137.96
-137.99
-138.02
-143.41
-143.44
-143.47
-143.49
F
F
F
F
CN
2.00
2.03
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

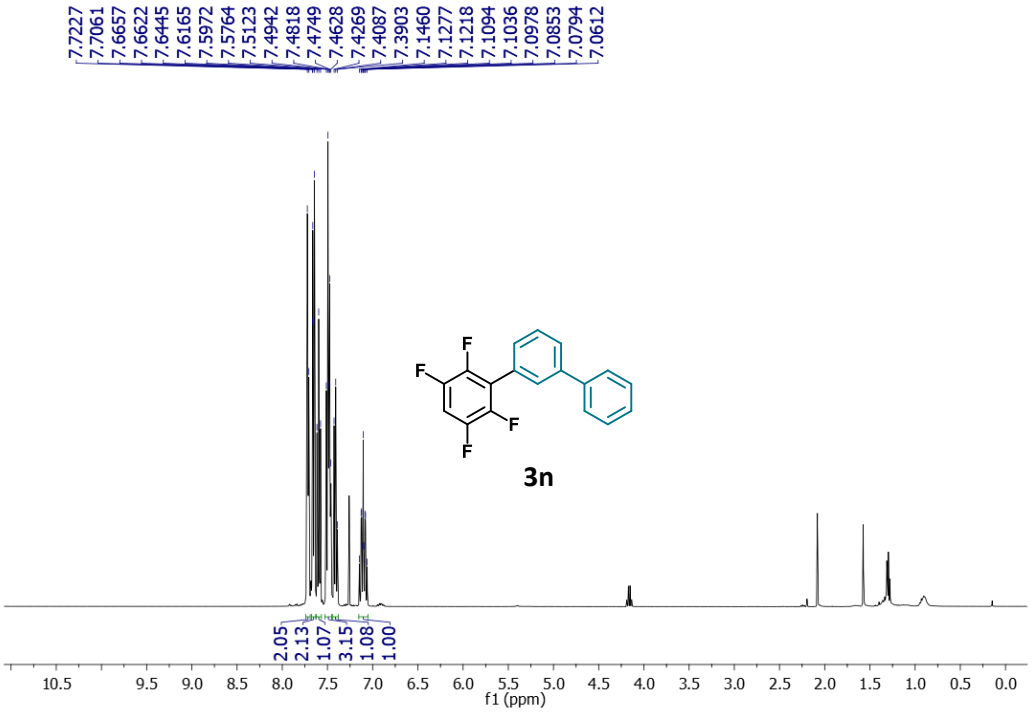
2,3,5,6-tetrafluoro-3'-methyl-1,1'-biphenyl (3m):

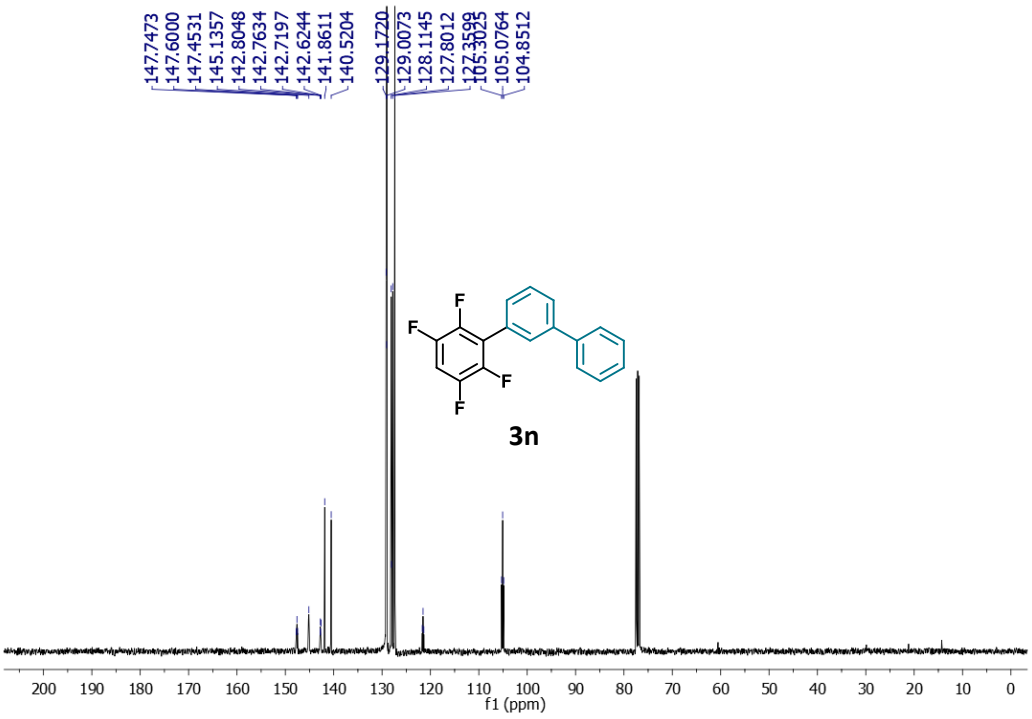


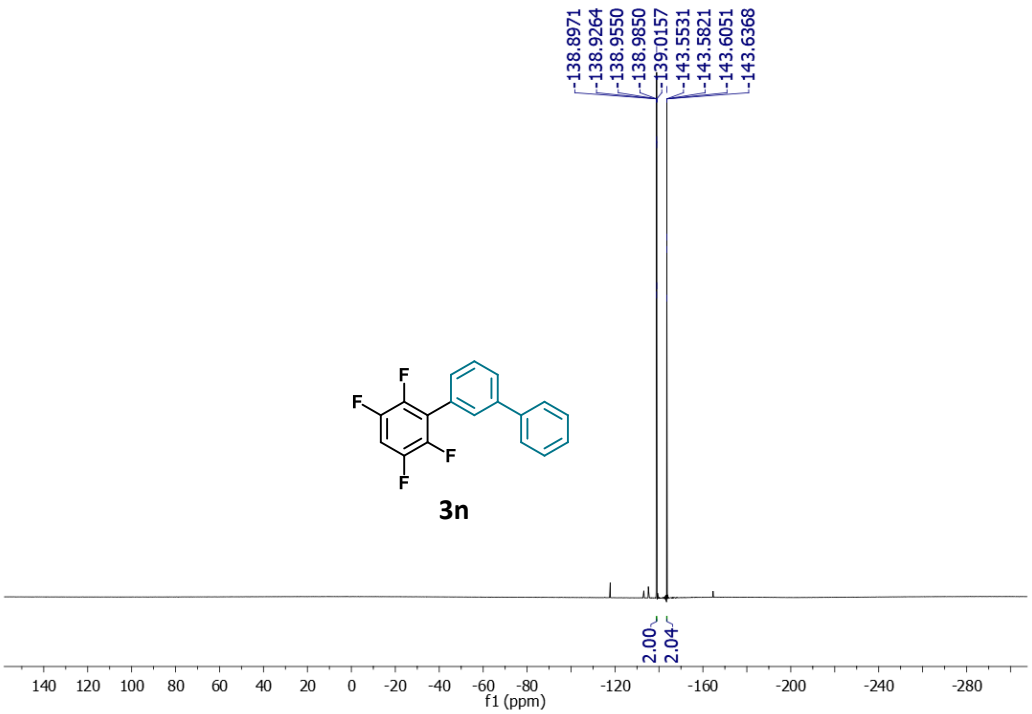



-139.2443
-139.2733
-139.3024
-139.3316
-139.3607
-143.7144
-143.7396
-143.7682
-143.7994
-143.8216
F
F
F
F
Me
3m
2.00
2.04
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

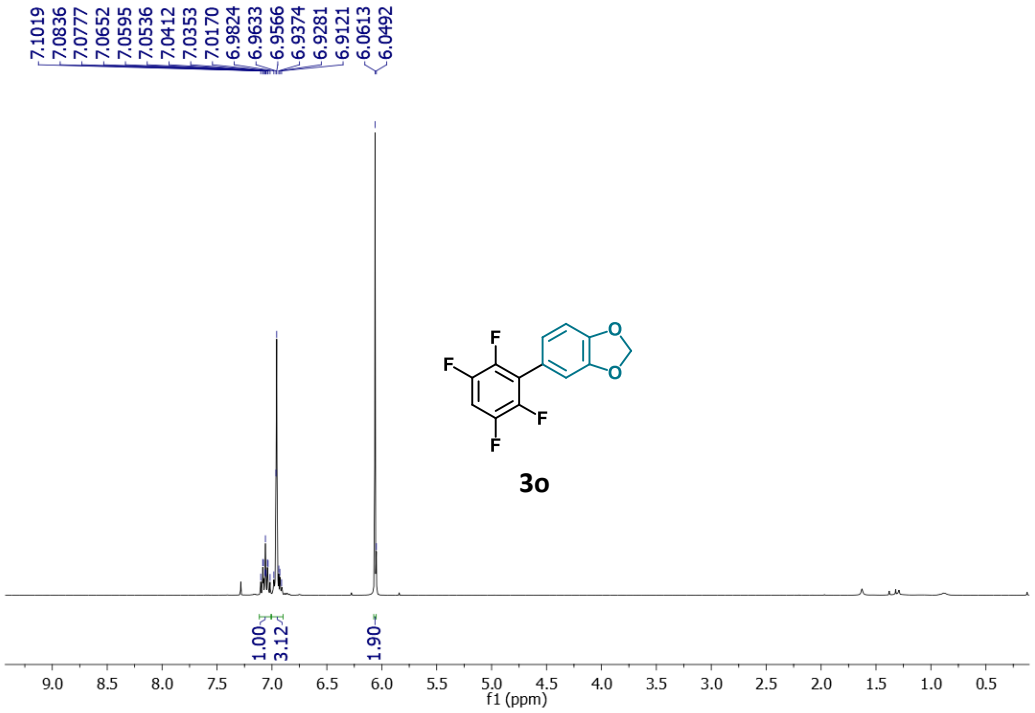
2,3,5,6-tetrafluoro-1,1':3',1''-terphenyl (3n):

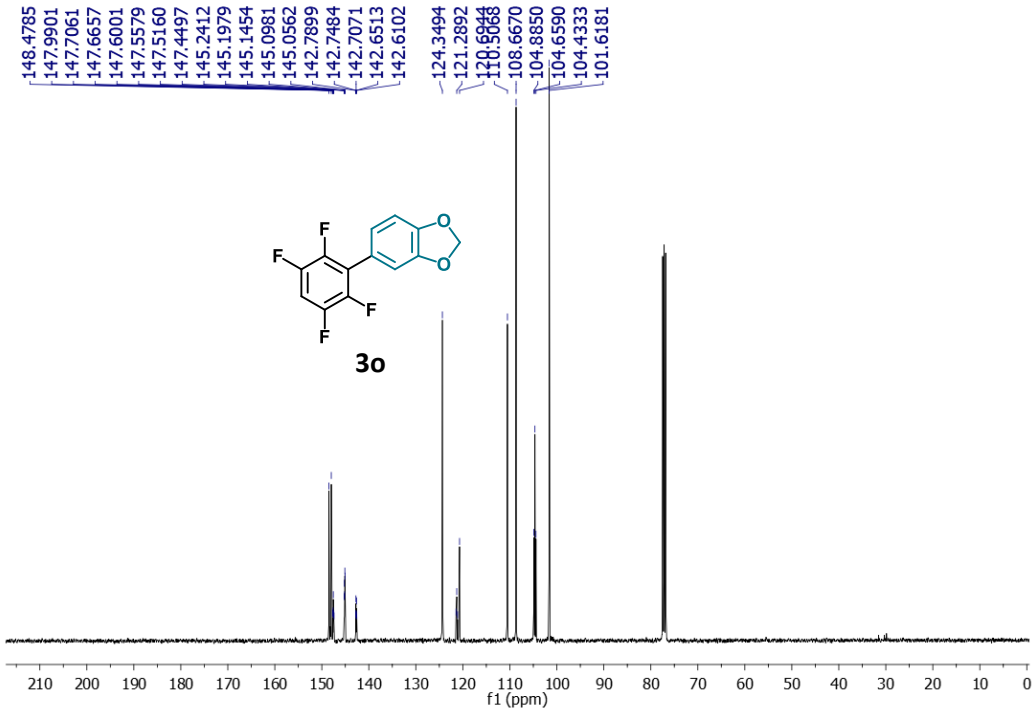


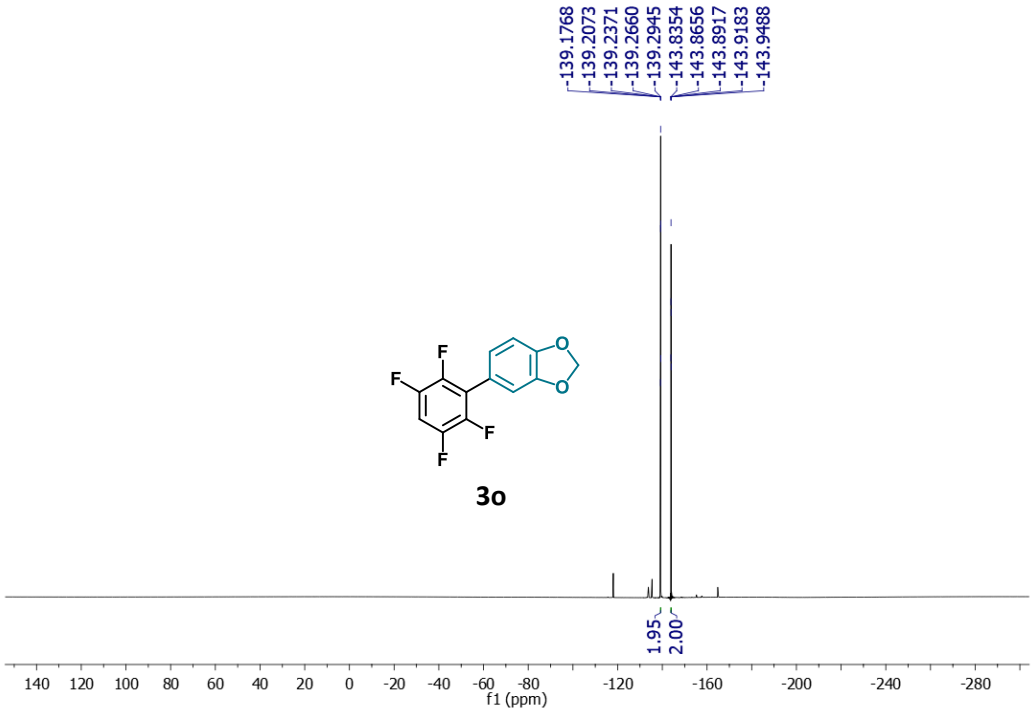



138.8971
138.9264
138.9550
138.9850
139.0157
143.5531
143.5821
143.6051
143.6368
F
F
F
F
3n
2.00
2.04
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

5-(2,3,5,6-tetrafluorophenyl)benzo[d][1,3]dioxole (3o):

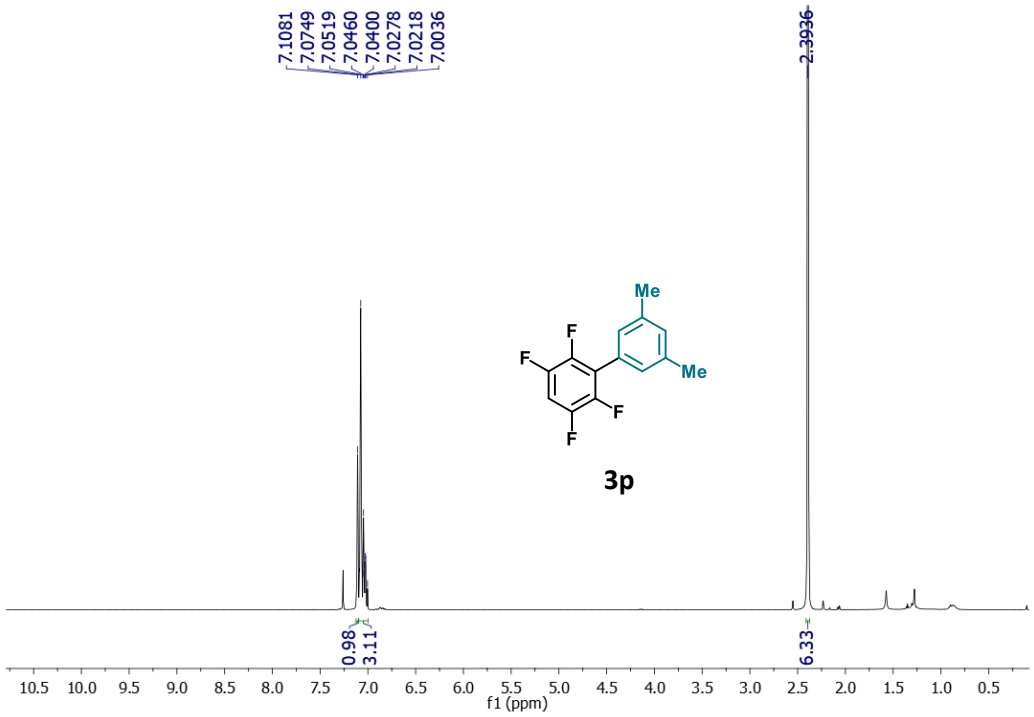


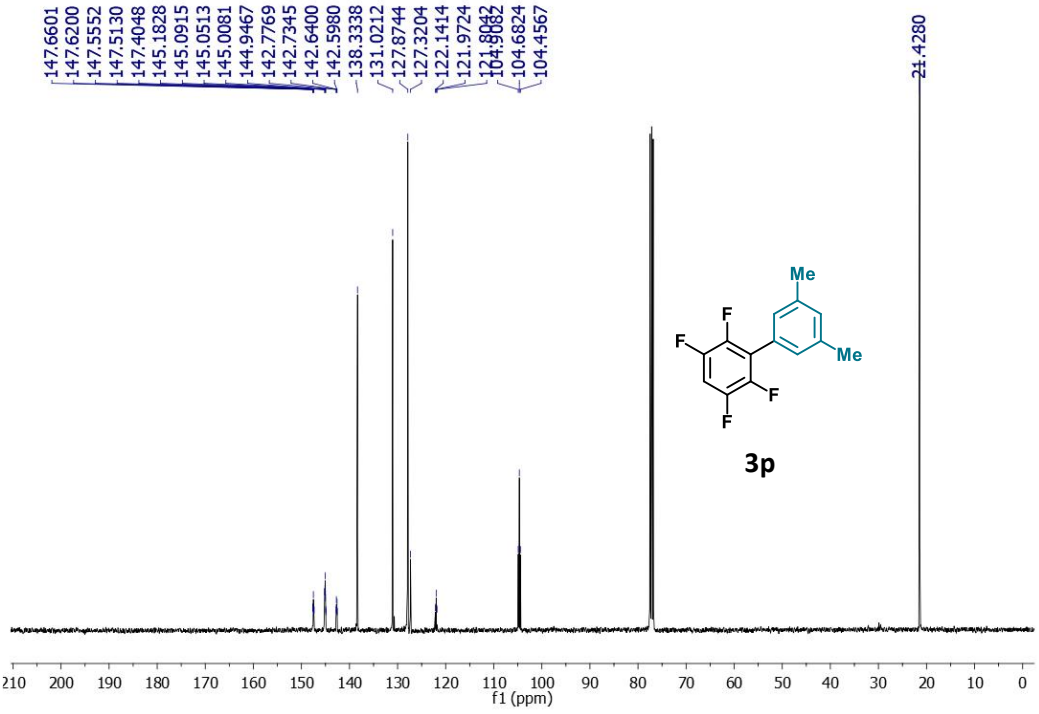


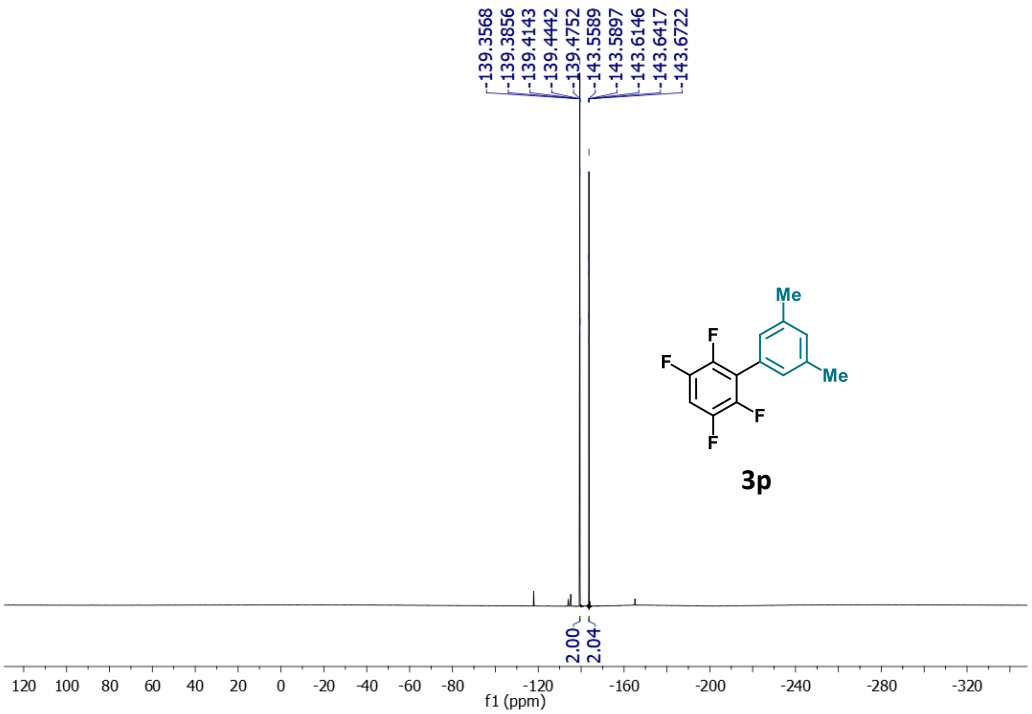

-139.1768
-139.2073
-139.2371
-139.2660
-139.2945
-143.8354
-143.8656
-143.8917
-143.9183
-143.9488
F
F
F
F
O
O
1.95
2.00
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

3o

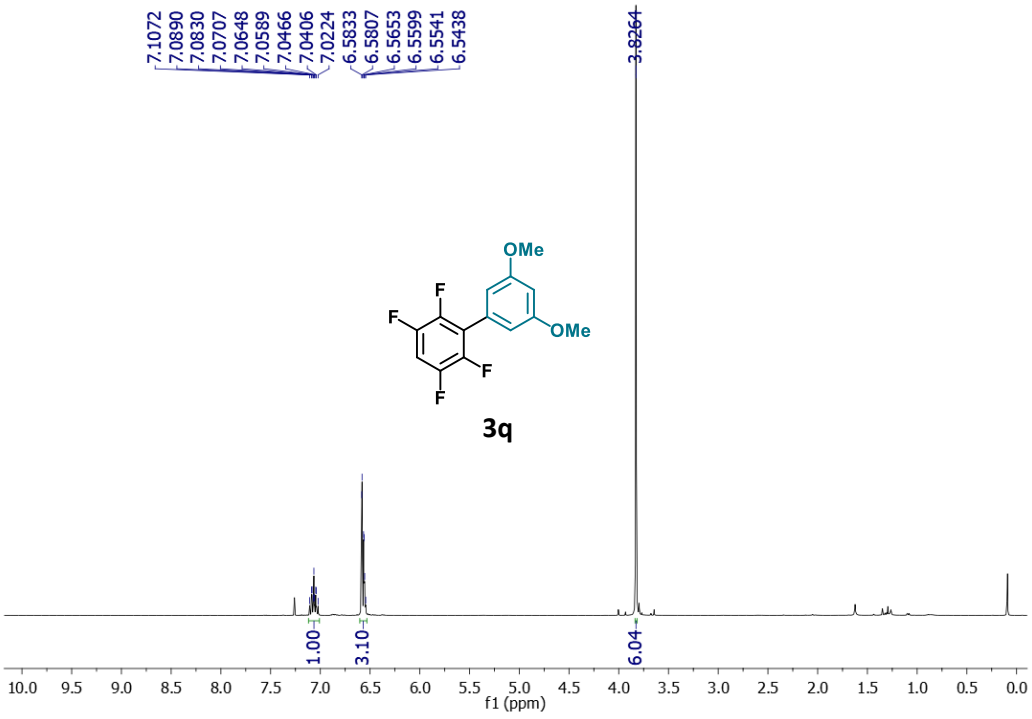
2,3,5,6-tetrafluoro-3',5'-dimethyl-1,1'-biphenyl (3p):

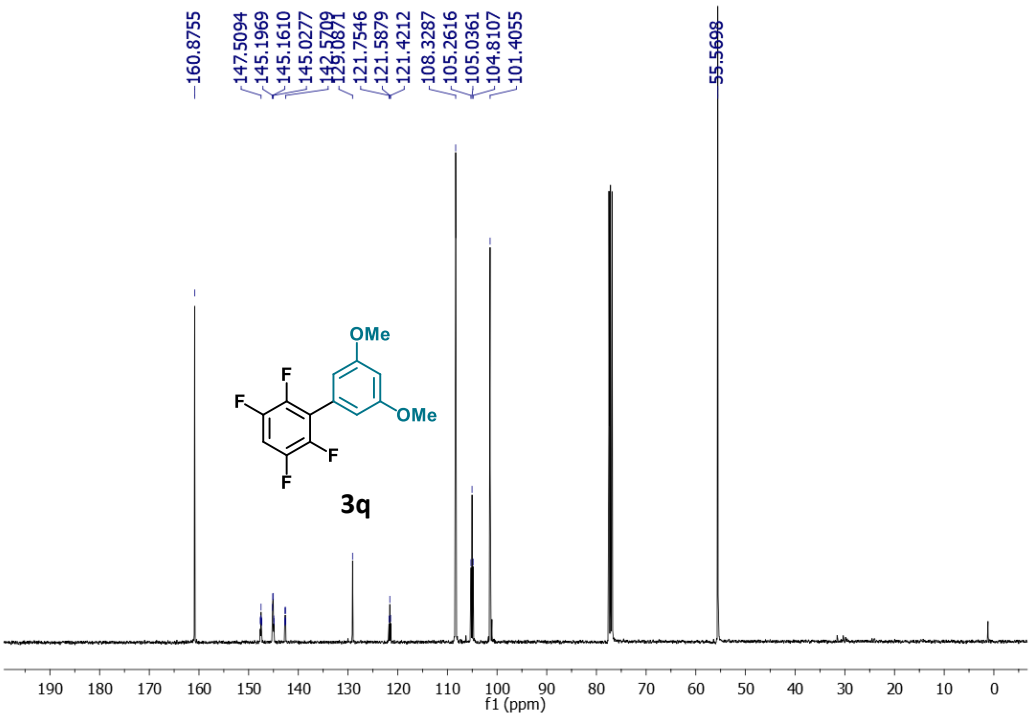


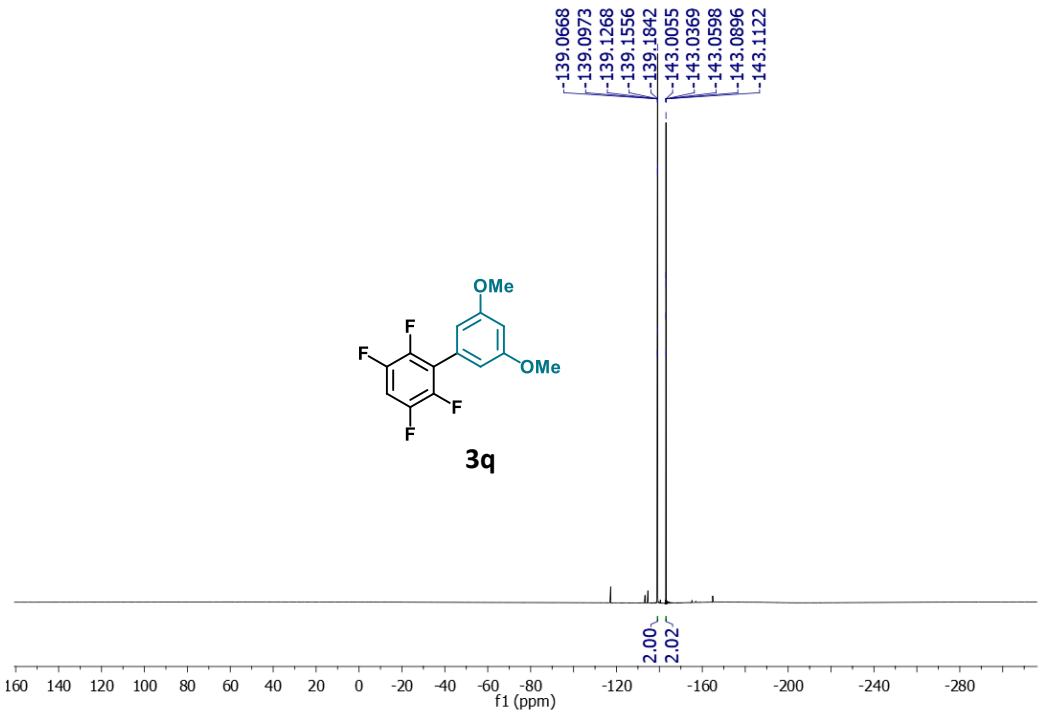



-139.3568
-139.3856
-139.4143
-139.4442
-139.4752
-143.5589
-143.5897
-143.6146
-143.6417
-143.6722
Me
F
F
Me
F
F
3p
2.00
2.04
120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280 -320
f1 (ppm)

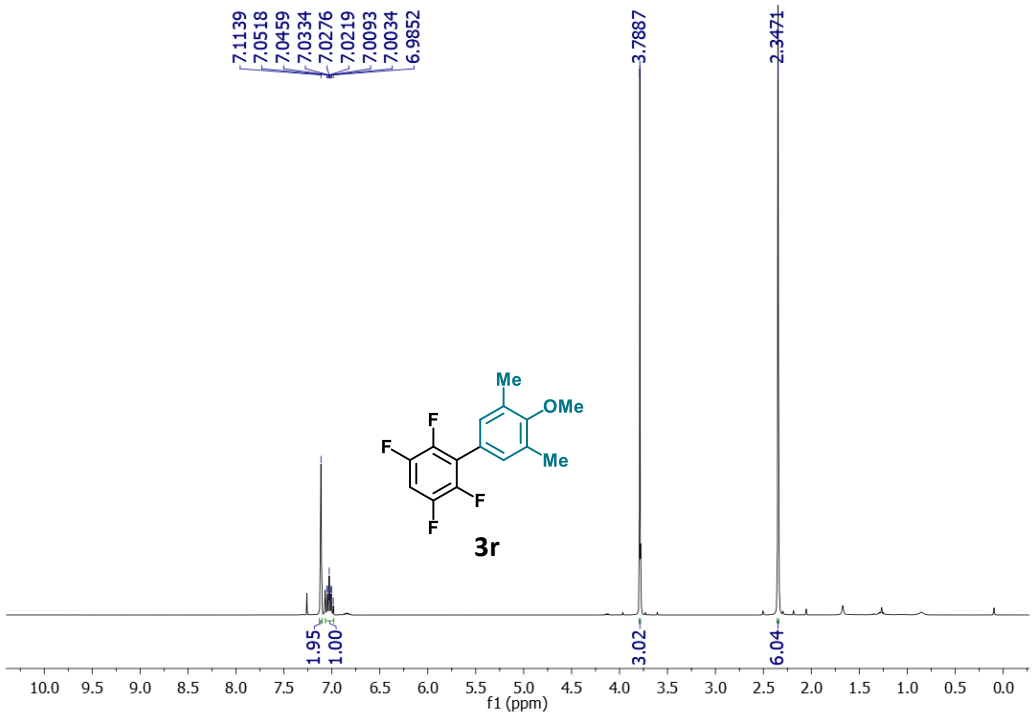
2,3,5,6-tetrafluoro-3',5'-dimethoxy-1,1'-biphenyl (3q):

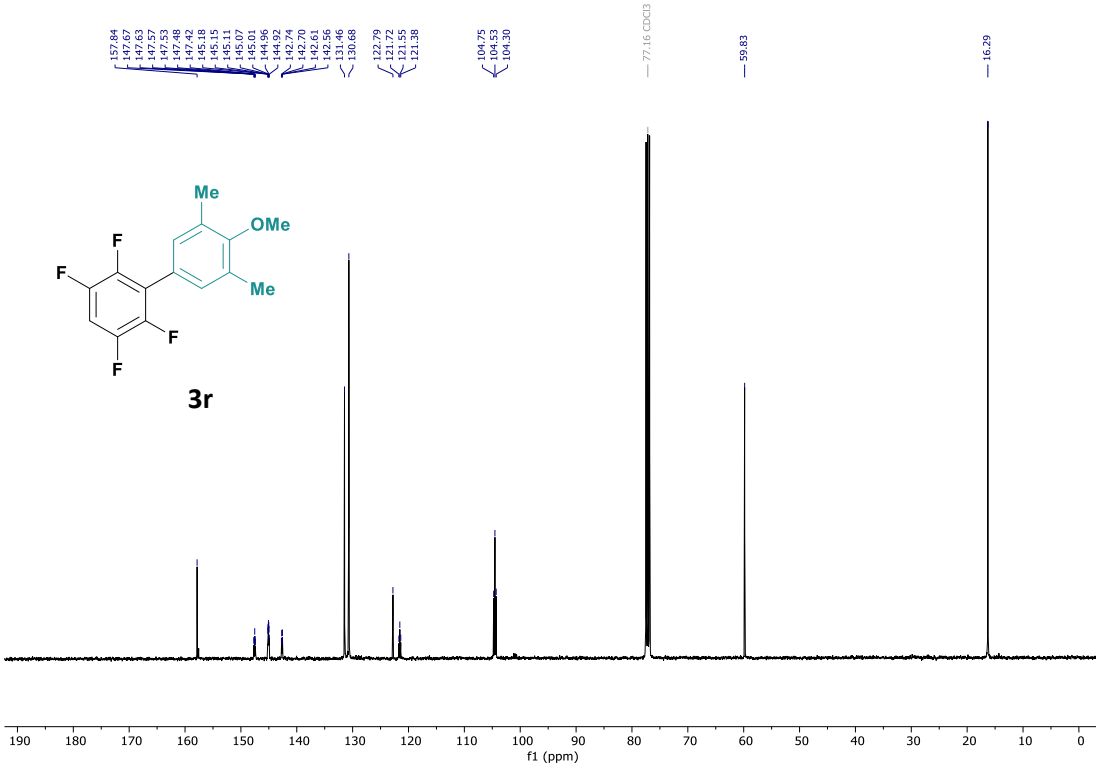


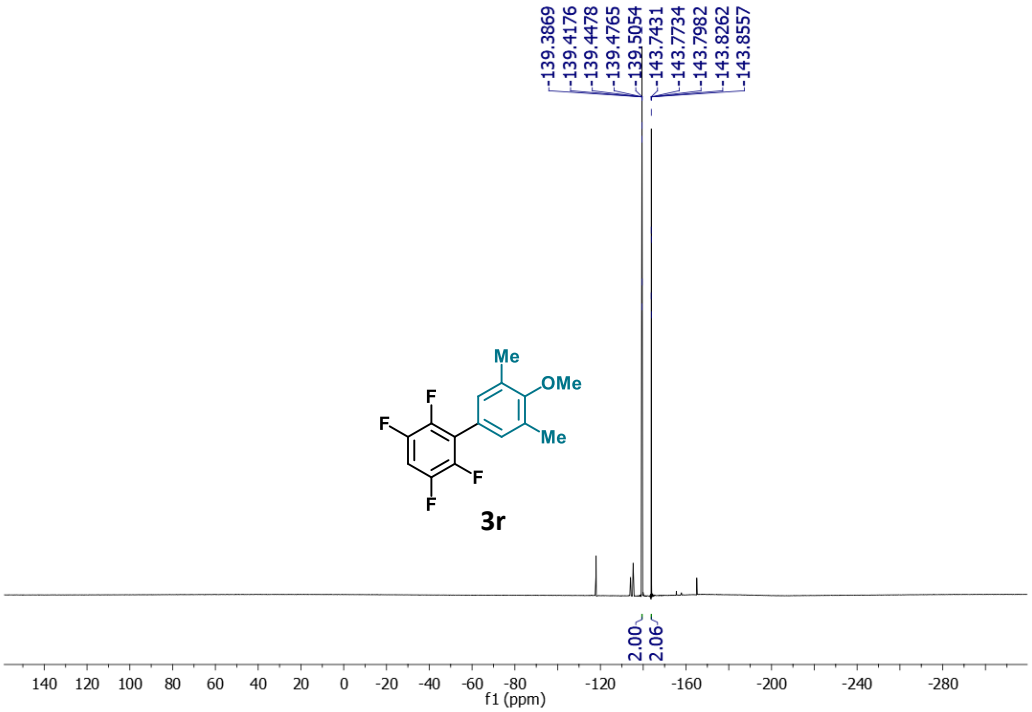



139.0668
139.0973
139.1268
139.1556
139.1842
143.0055
143.0369
143.0598
143.0896
143.1122
OMe
OMe
F
F
F
F
3q
2.00
2.02
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

2,3,5,6-tetrafluoro-4'-methoxy-3',5'-dimethyl-1,1'-biphenyl (3r):

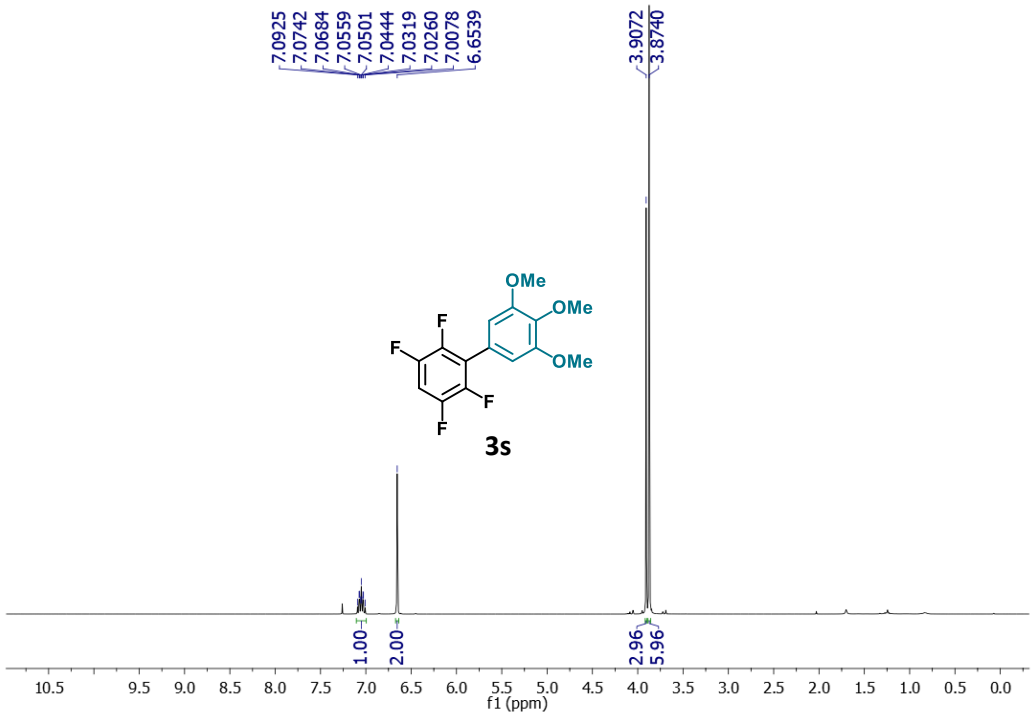


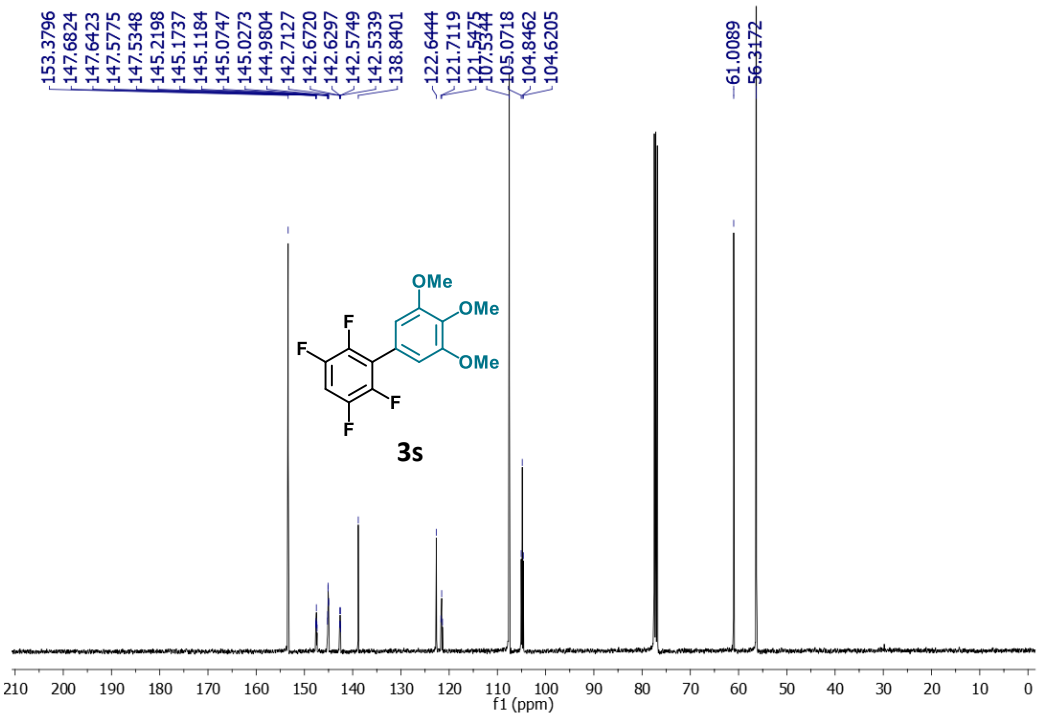


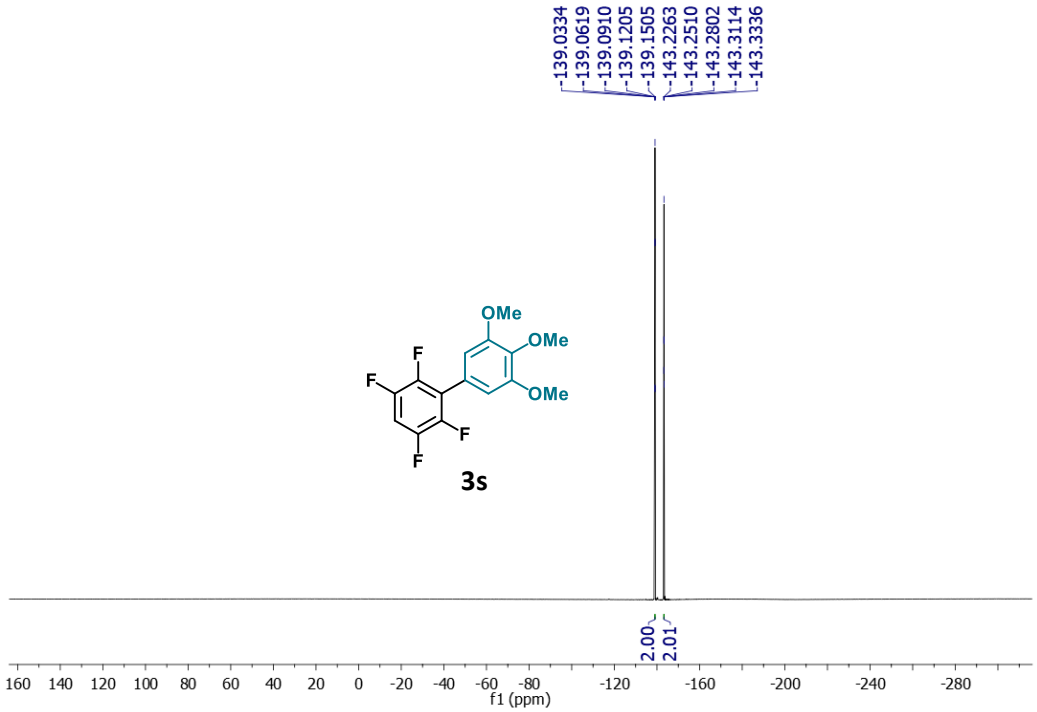

-139.3869
-139.4176
-139.4478
-139.4765
-139.5054
-143.7431
-143.7734
-143.7982
-143.8262
-143.8557
Me
OMe
Me
F
F
F
F
3r
2.00
2.06
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

3o

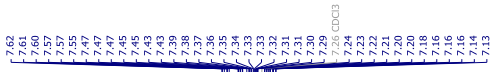
2,3,5,6-tetrafluoro-3',4',5'-trimethoxy-1,1'-biphenyl (3s):

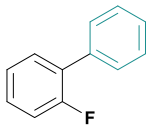


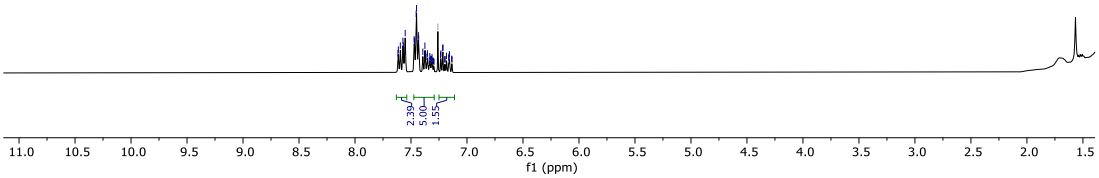


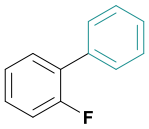

-139.0334
-139.0619
-139.0910
-139.1205
-139.1505
-143.2263
-143.2510
-143.2802
-143.3114
-143.3336
OMe
OMe
OMe
F
F
F
F
3s
2.00
2.01
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

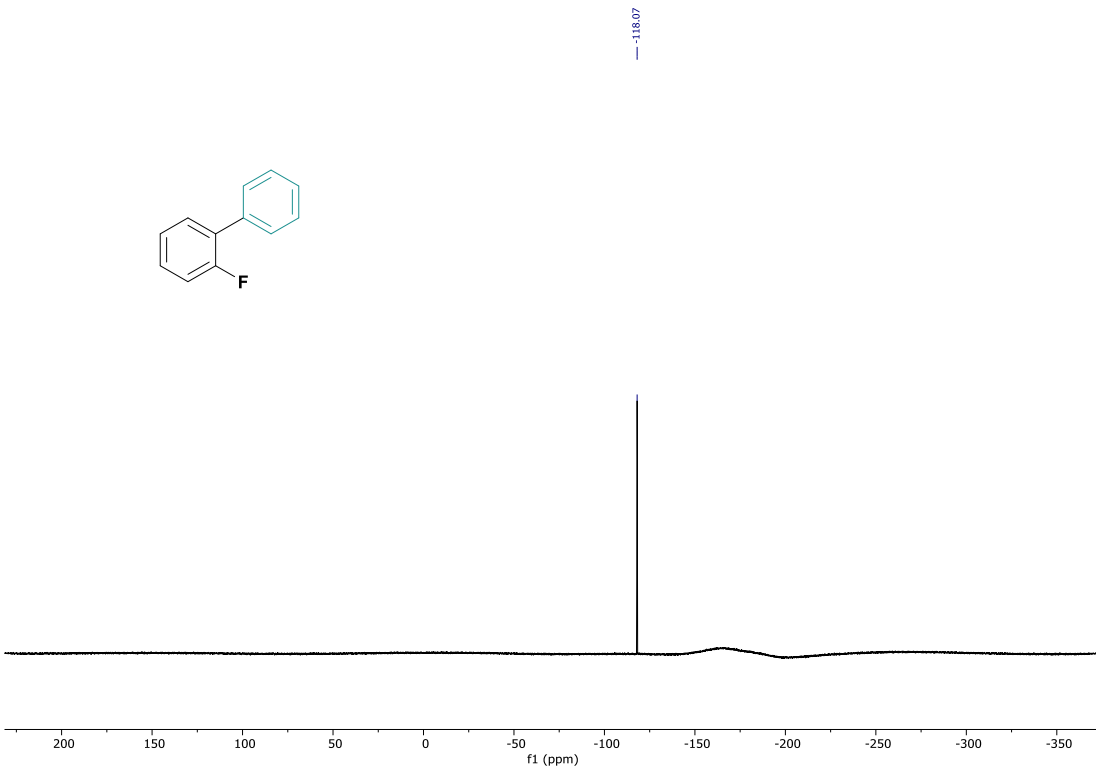
2-fluoro-1,1'-biphenyl (3t):



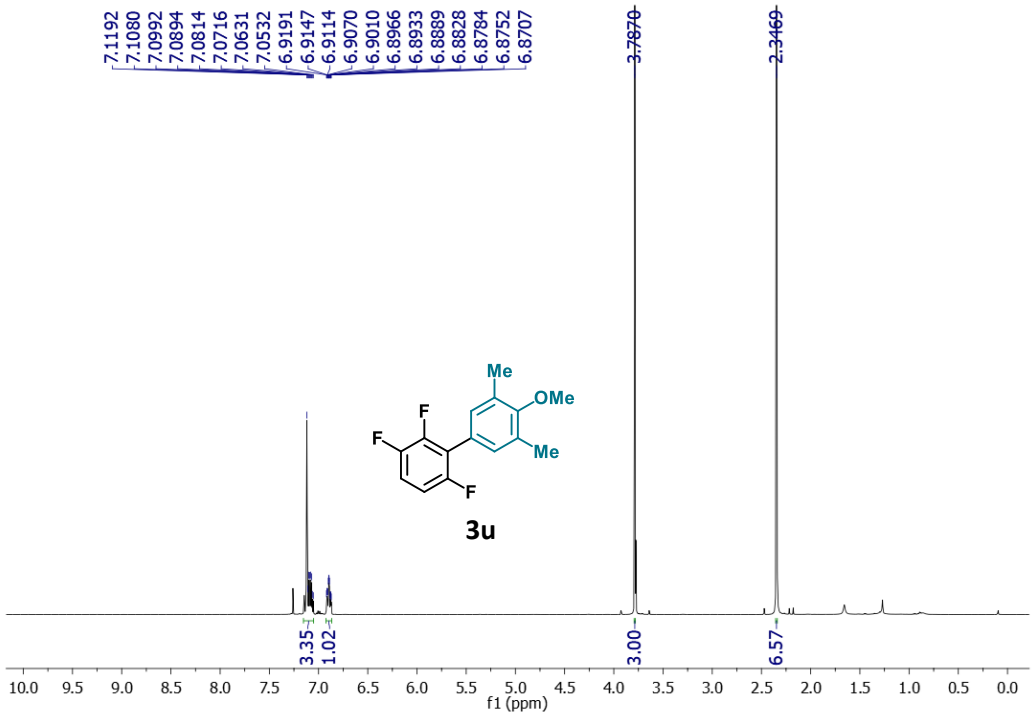


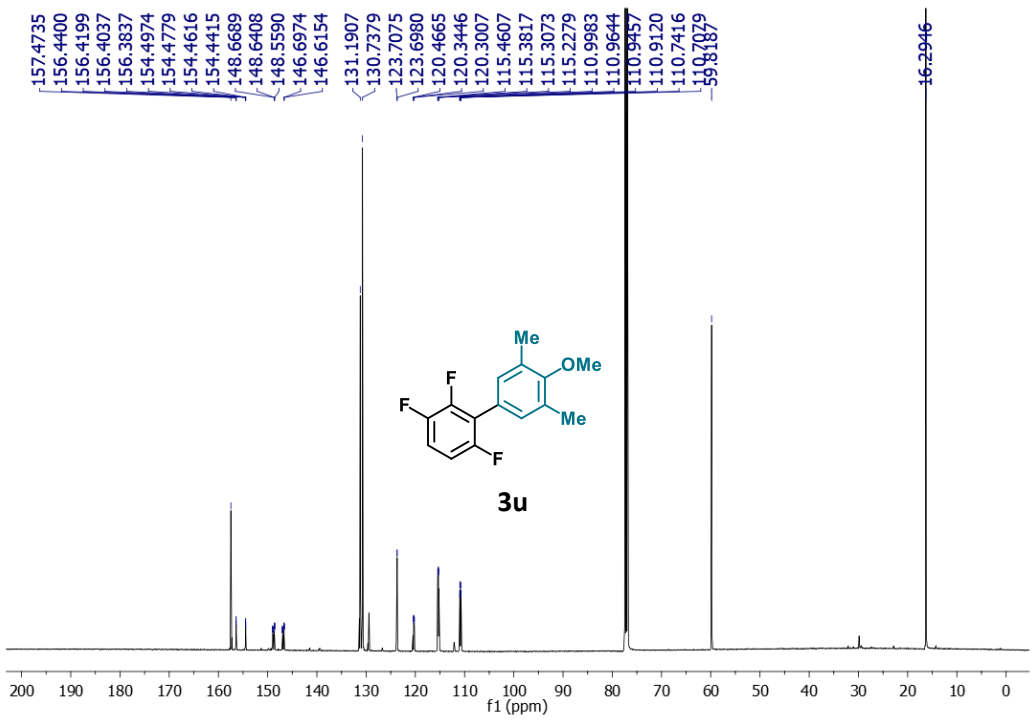


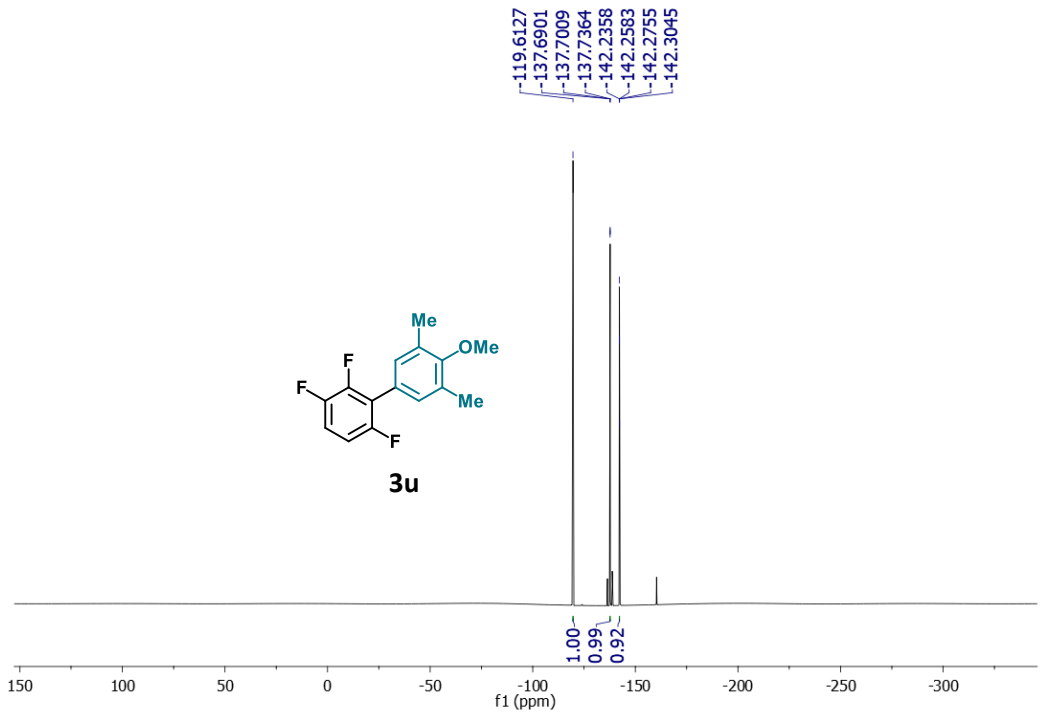



-118.07
F
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

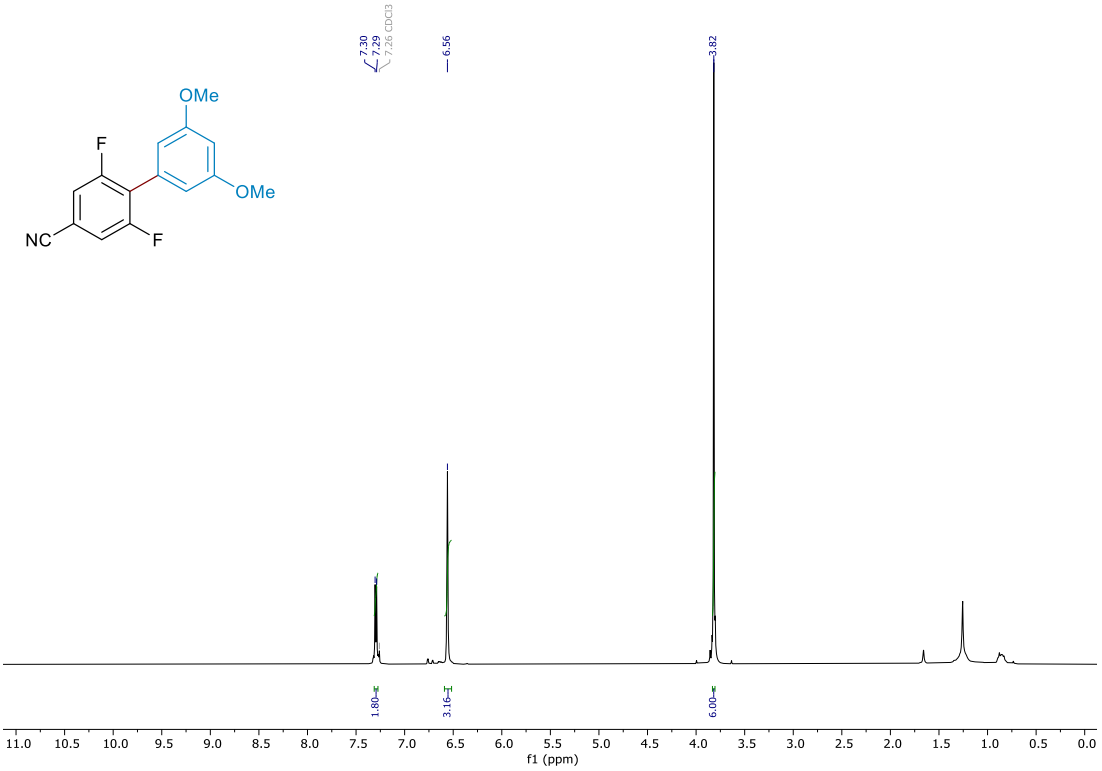
2,3,6-trifluoro-4'-methoxy-3',5'-dimethyl-1,1'-biphenyl (3u):

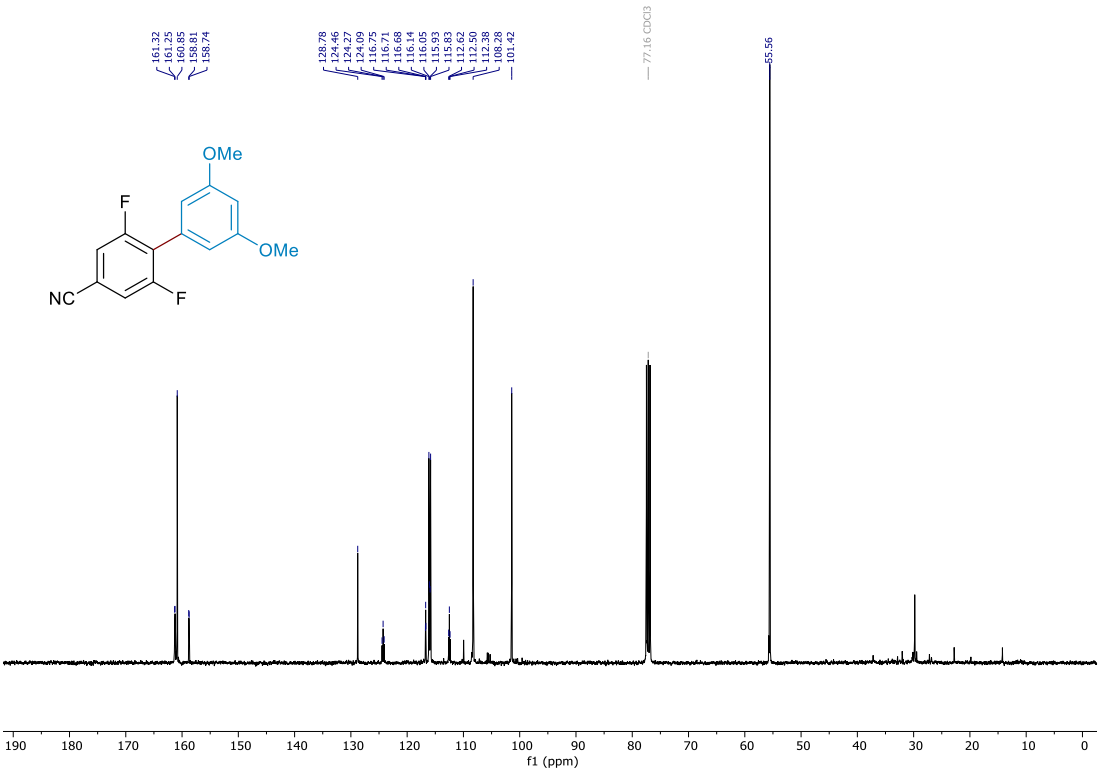


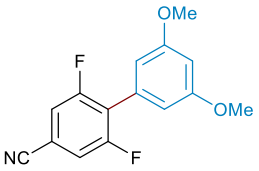



-119.6127
-137.6901
-137.7009
-137.7364
-142.2358
-142.2583
-142.2755
-142.3045
Me
OMe
Me
F
F
F
3u
1.00
0.99
0.92
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

2,6-difluoro-3',5'-dimethoxy-[1,1'-biphenyl]-4-carbonitrile (3v):

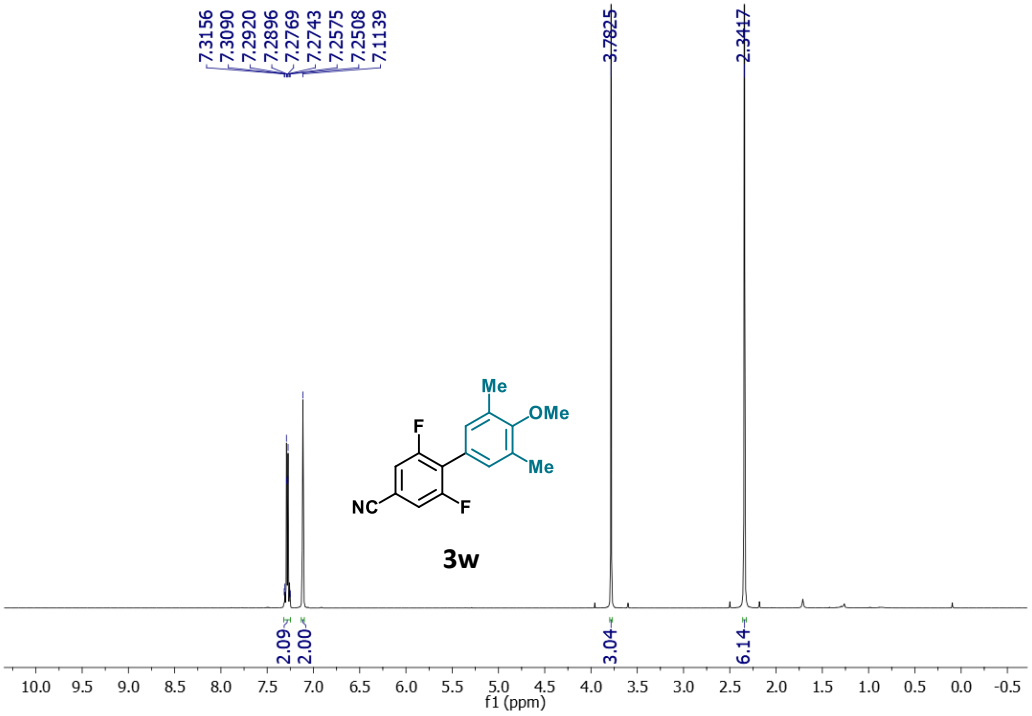


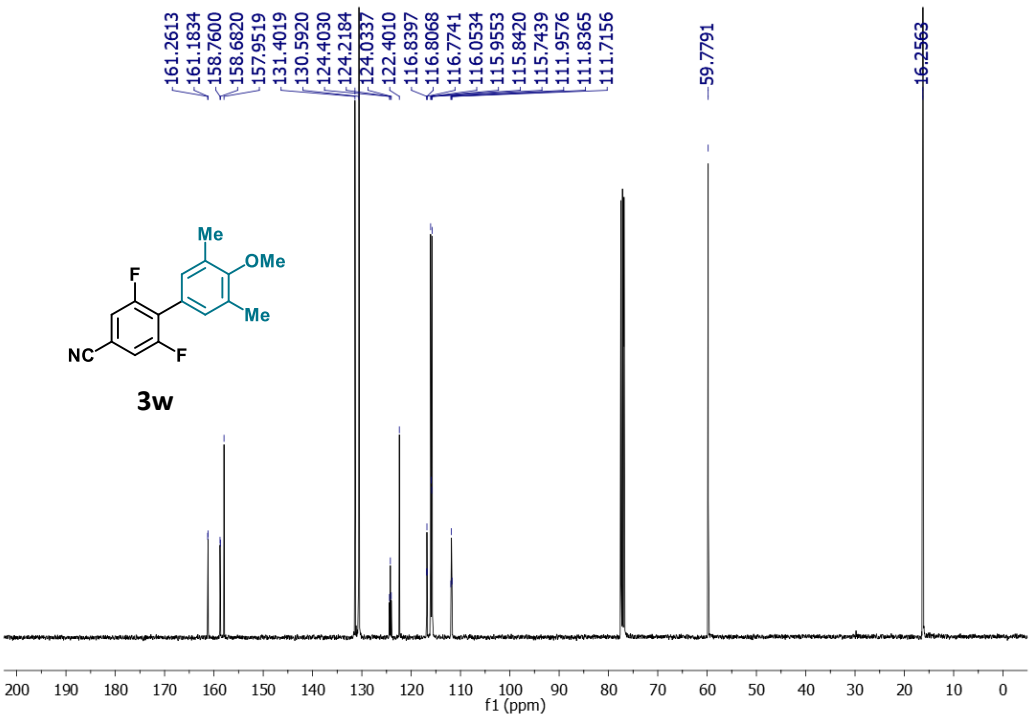


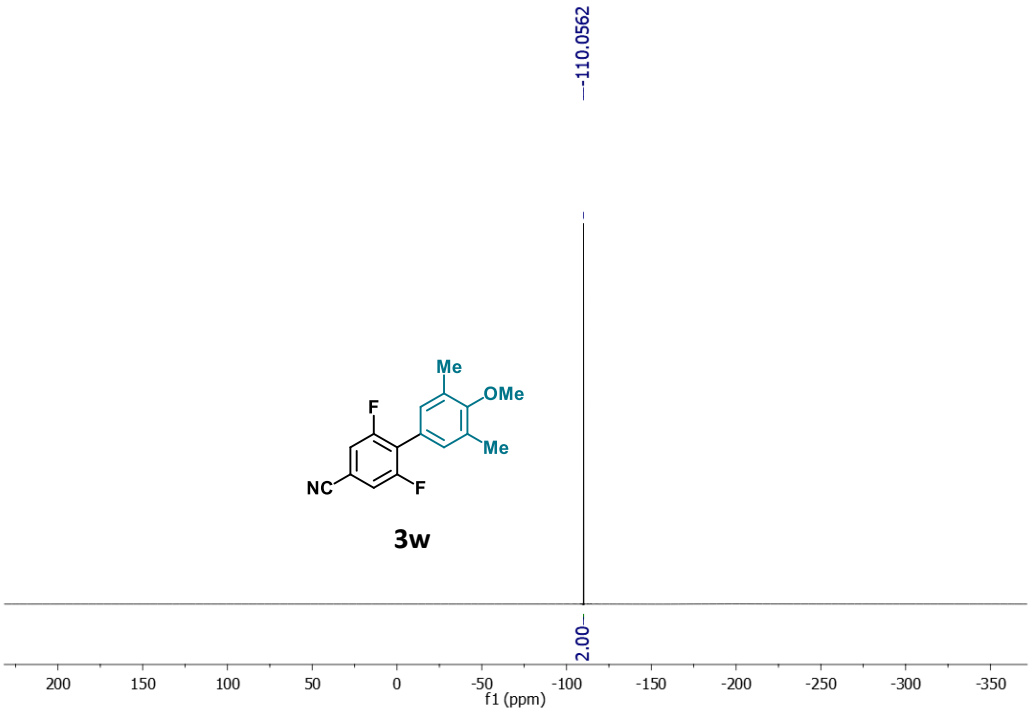

OMe
F
OMe
NC
F

-109.30
2.00
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-26
f1 (ppm)

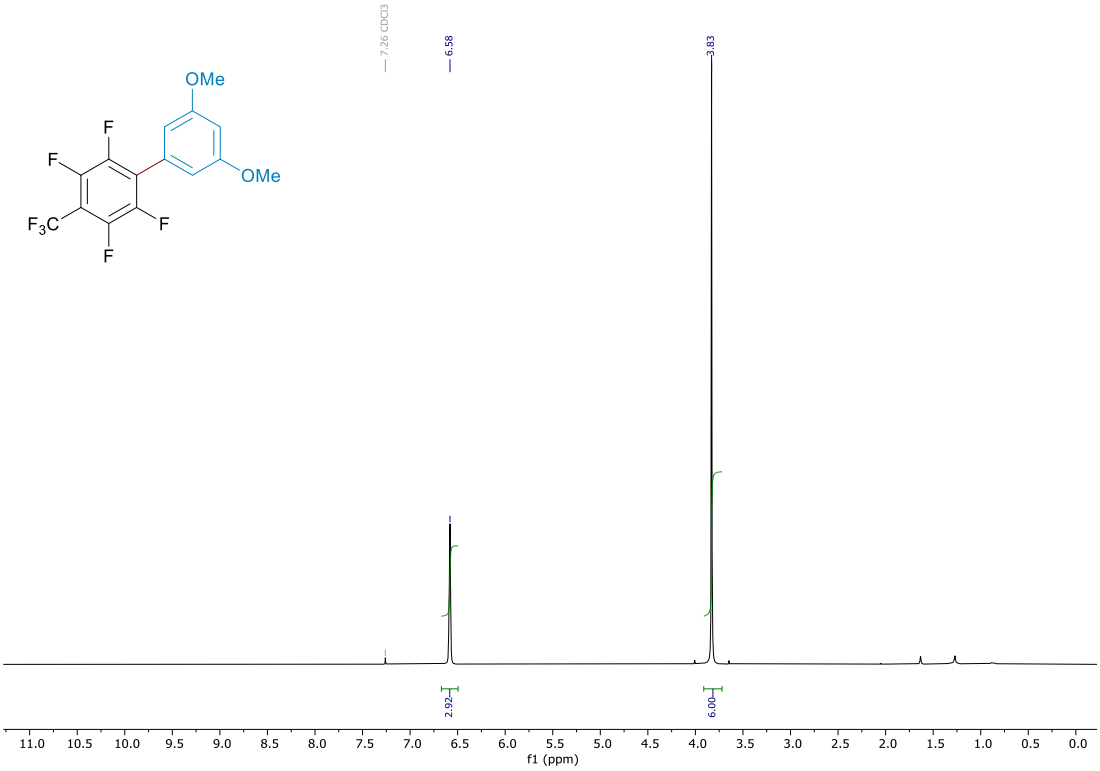
2,6-difluoro-4'-methoxy-3',5'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (3w):

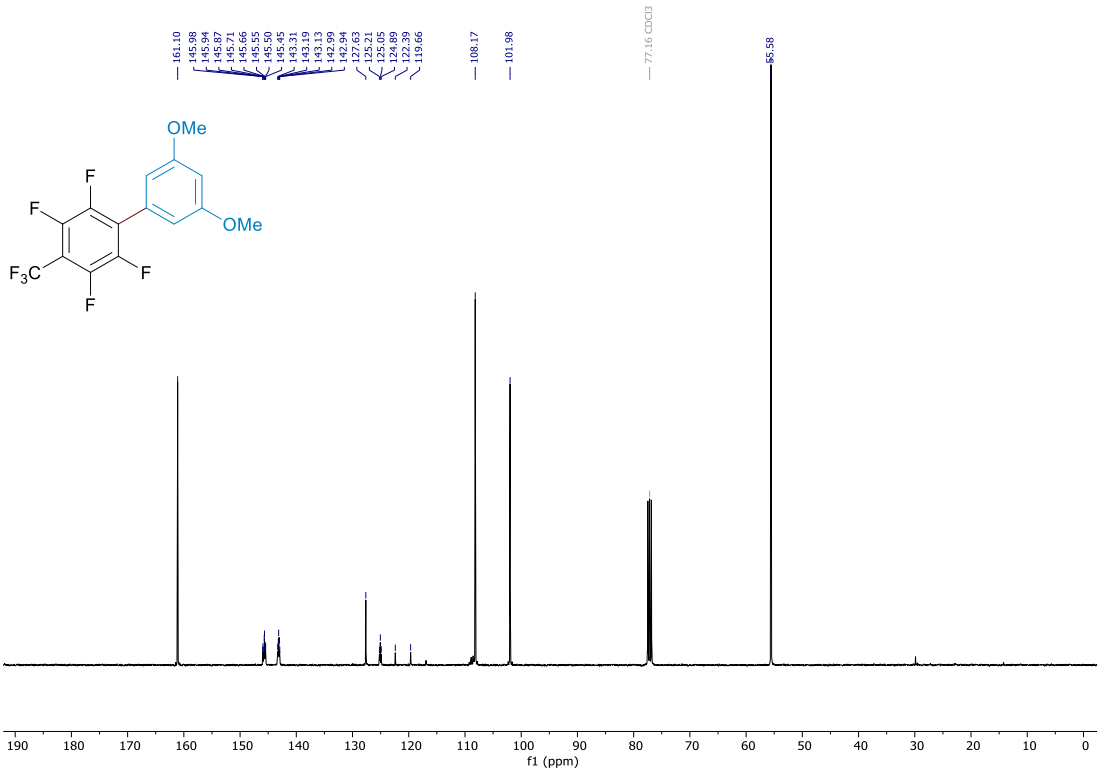


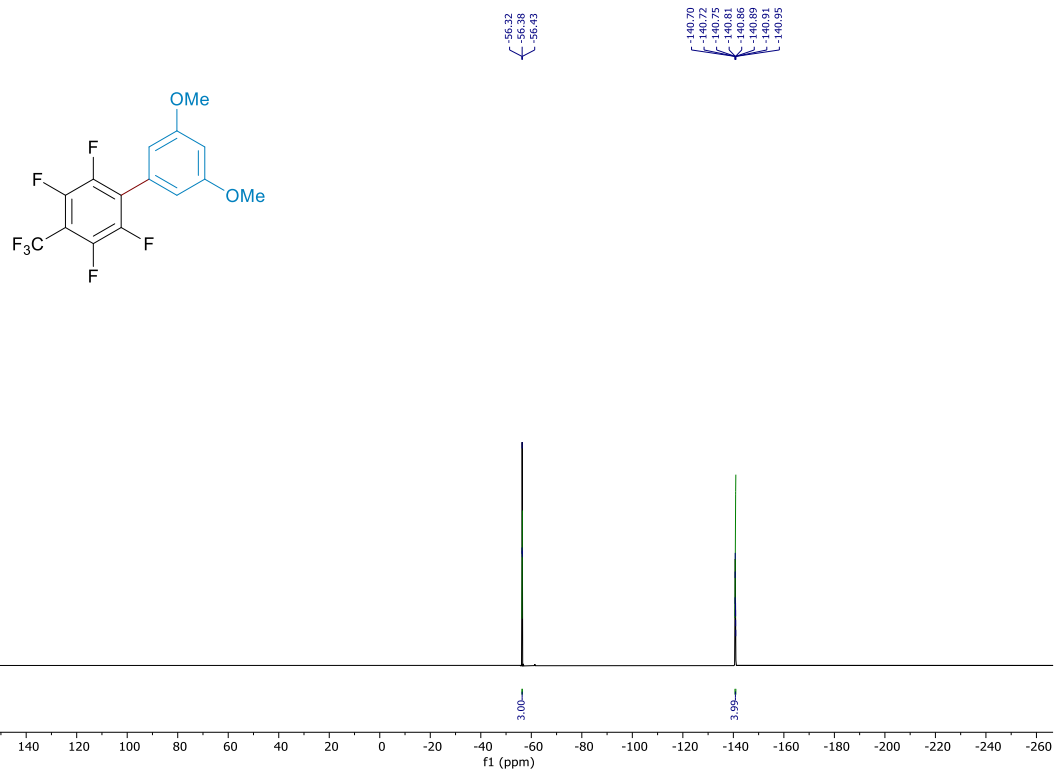



-110.0562
Me
OMe
F
Me
NC
F
3w
2.00
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

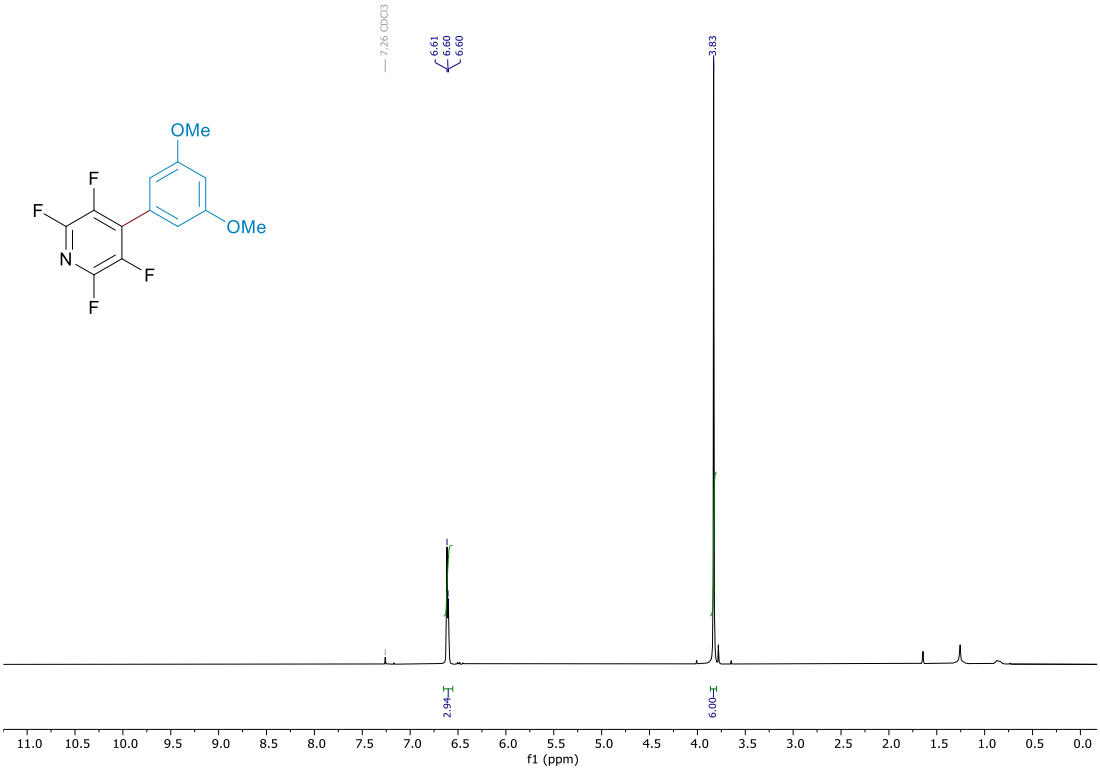
2,3,5,6-tetrafluoro-3',5'-dimethoxy-4-(trifluoromethyl)-1,1'-biphenyl (3x):

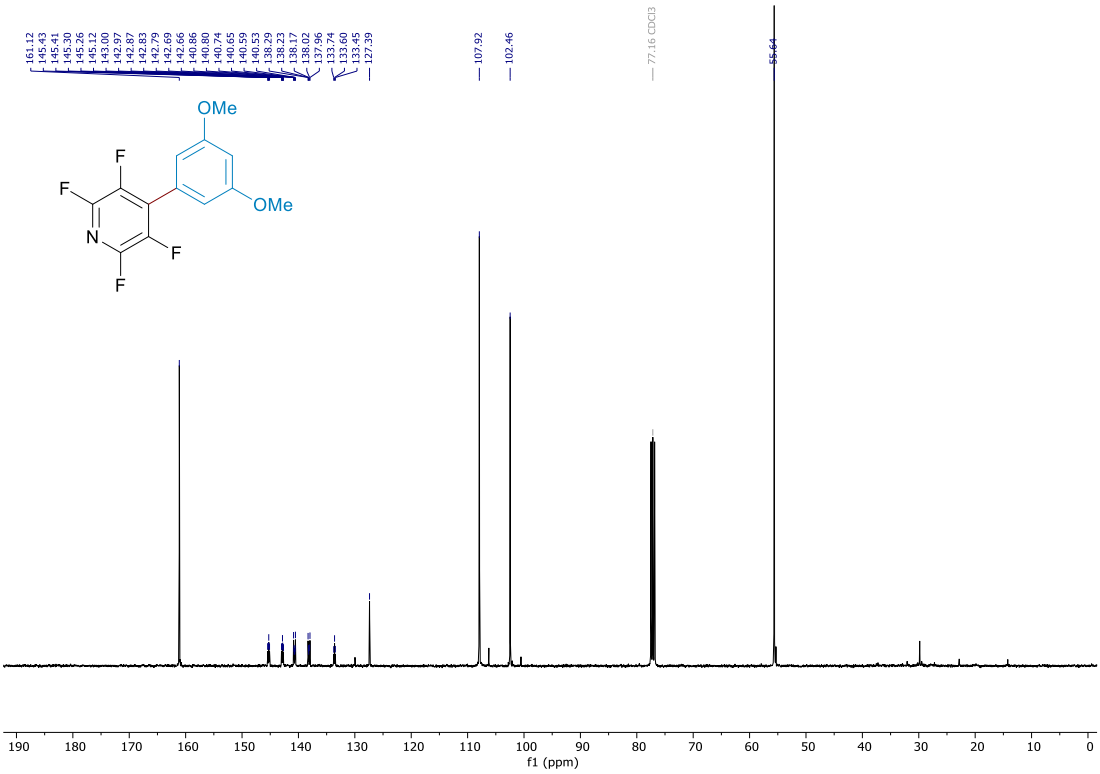


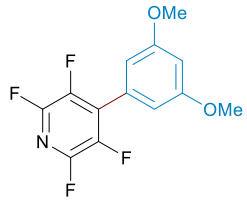



-56.32
-56.38
-56.43
-140.70
-140.72
-140.75
-140.81
-140.86
-140.89
-140.91
-140.95
OMe
OMe
F
F
F
F3C
F
3.00
3.99
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

4-(3,5-dimethoxyphenyl)-2,3,5,6-tetrafluoropyridine (3y):

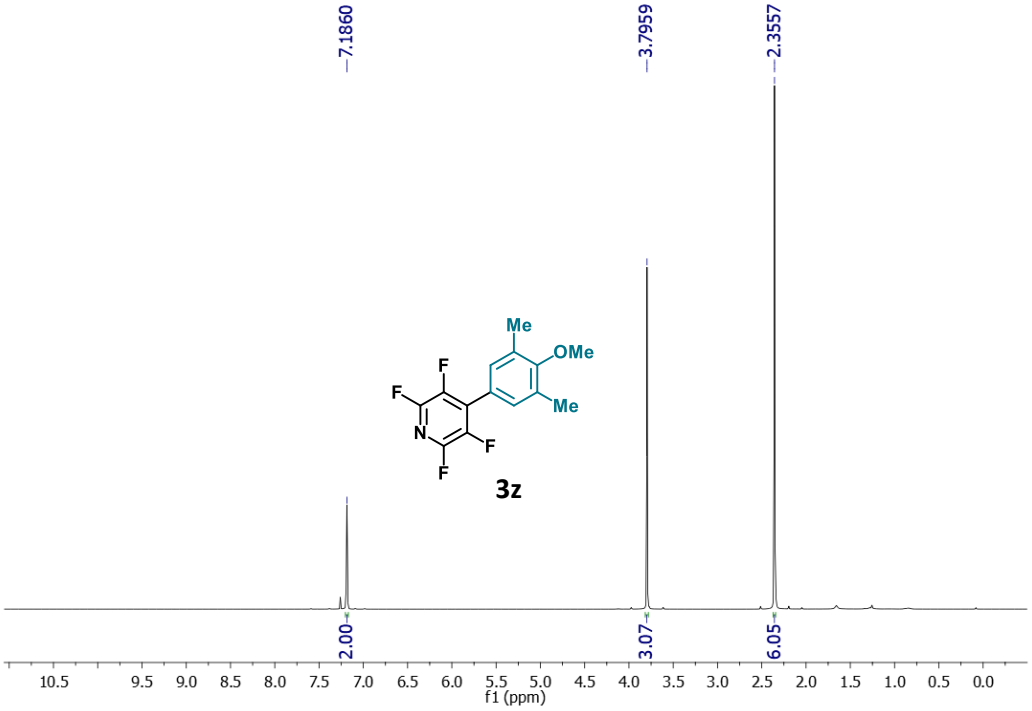


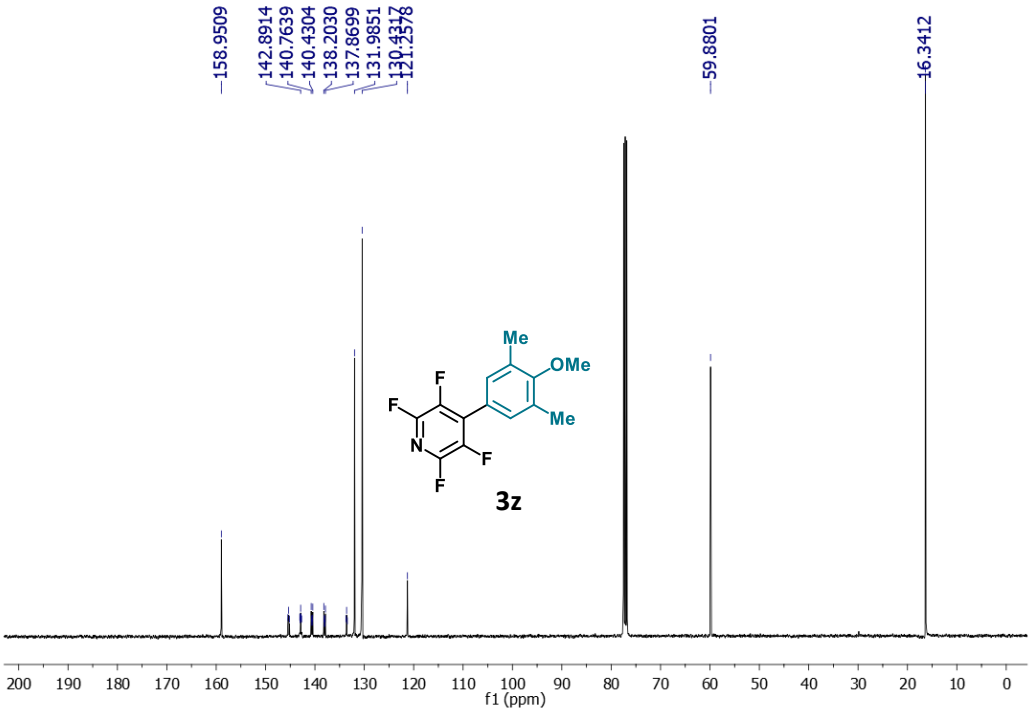


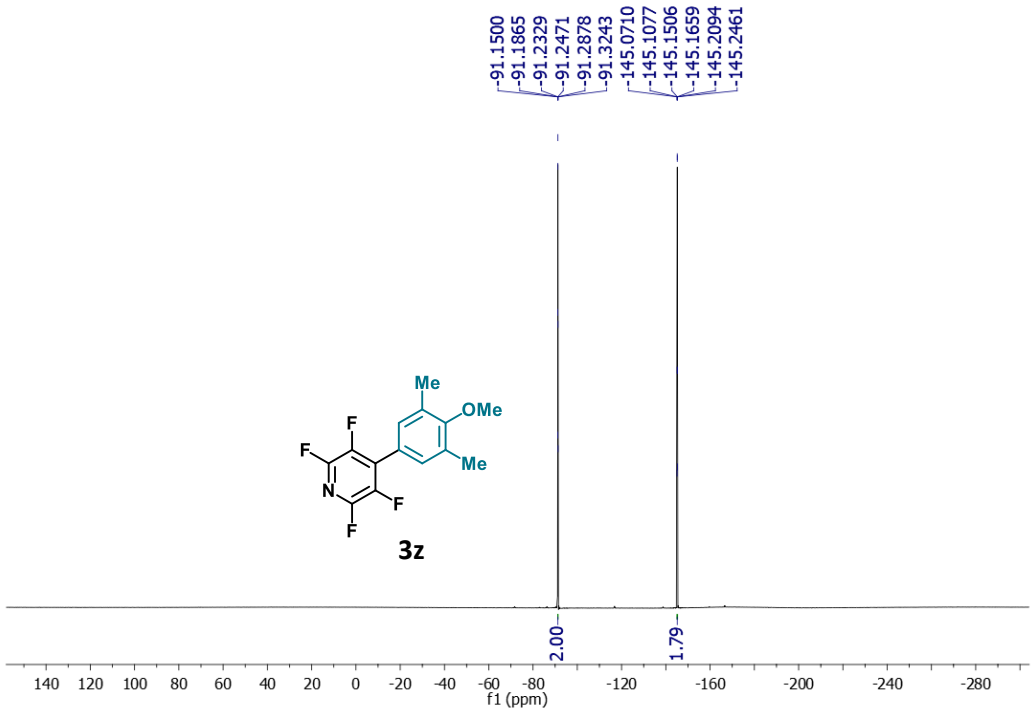

OMe
F
F
N
F
F
OMe

-90.74
-90.77
-90.81
-90.83
-90.87
-90.91
-144.11
-144.14
-144.18
-144.20
-144.24
-144.28
2.21
2.00
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

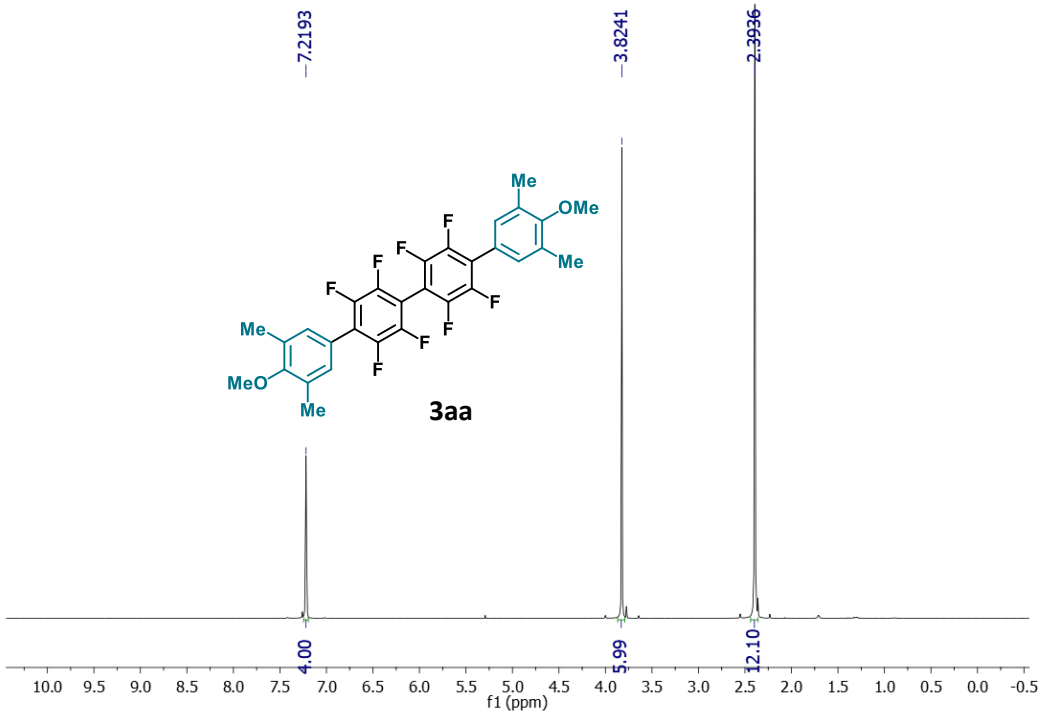
2,3,5,6-tetrafluoro-4-(4-methoxy-3,5-dimethylphenyl)pyridine (3z):

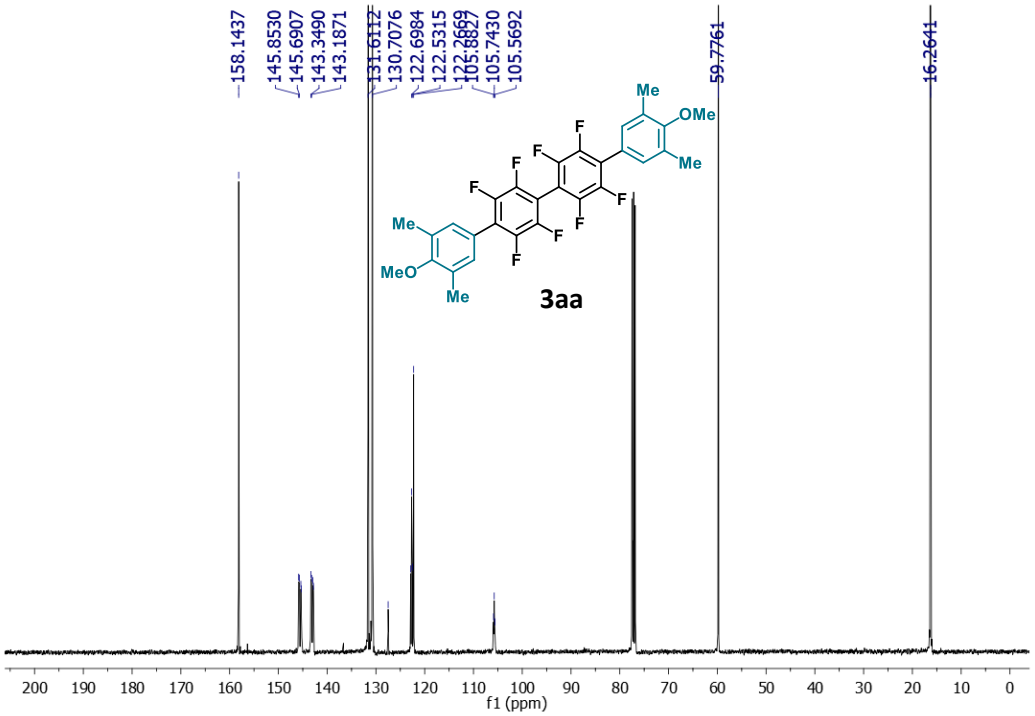


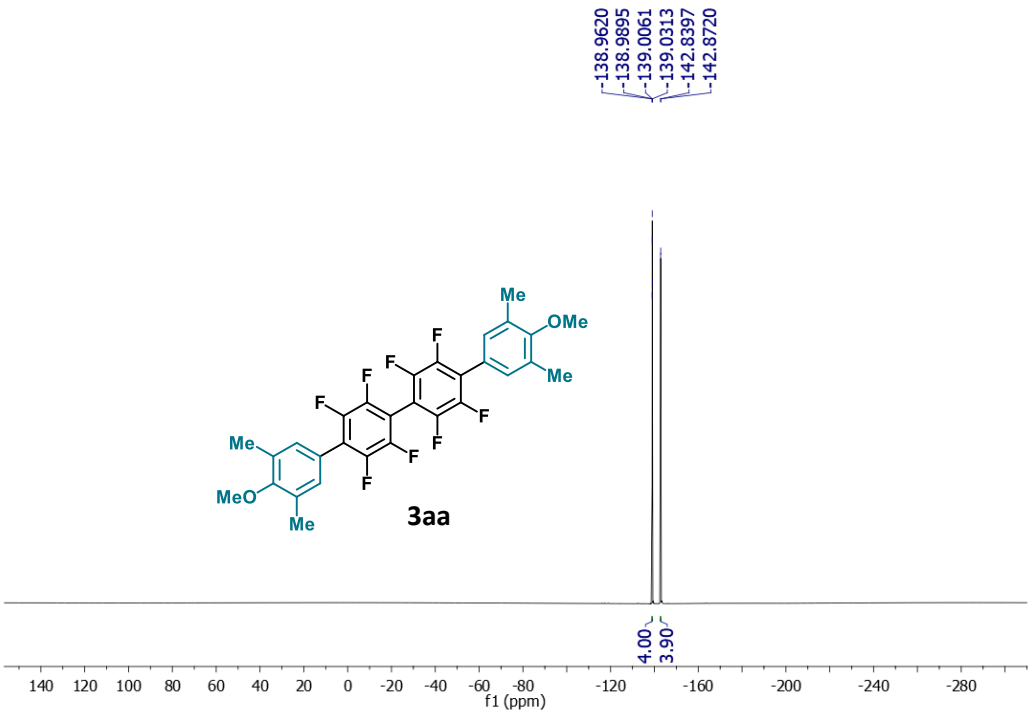



-91.1500
-91.1865
-91.2329
-91.2471
-91.2878
-91.3243
-145.0710
-145.1077
-145.1506
-145.1659
-145.2094
-145.2461
Me
OMe
Me
F
F
N
F
F
3z
2.00
1.79
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

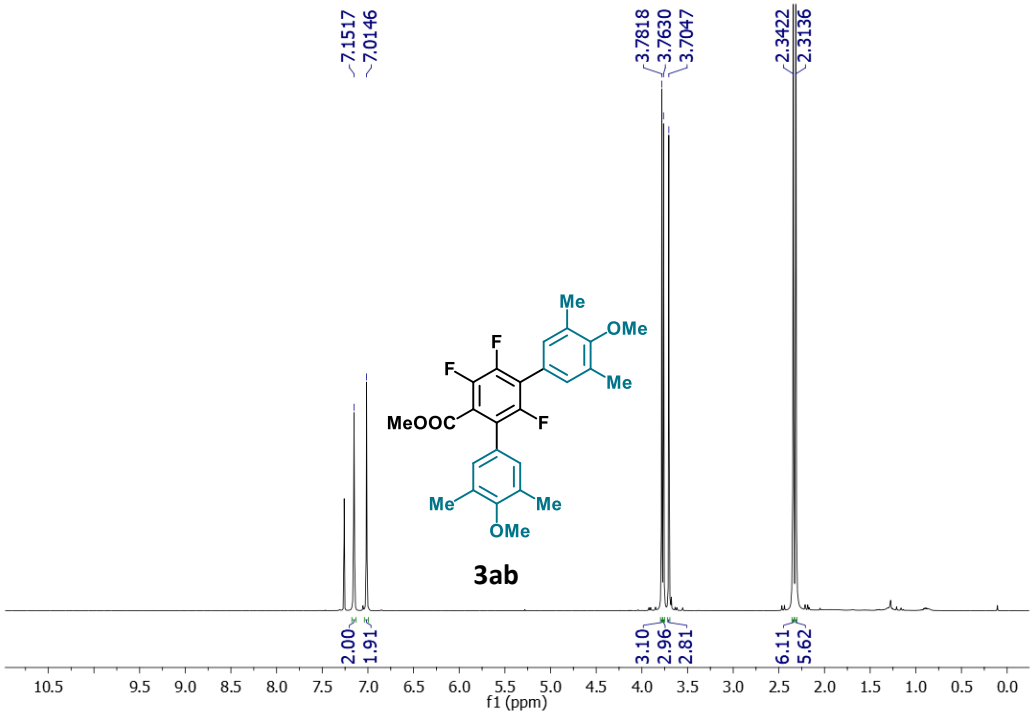
2',2'',3',3'',5',5'',6',6''-Octafluoro-4,4'''-dimethoxy-3,3''',5,5'''-tetramethyl-1,1':4',1'':4'',1'''-quaterphenyl (3aa):

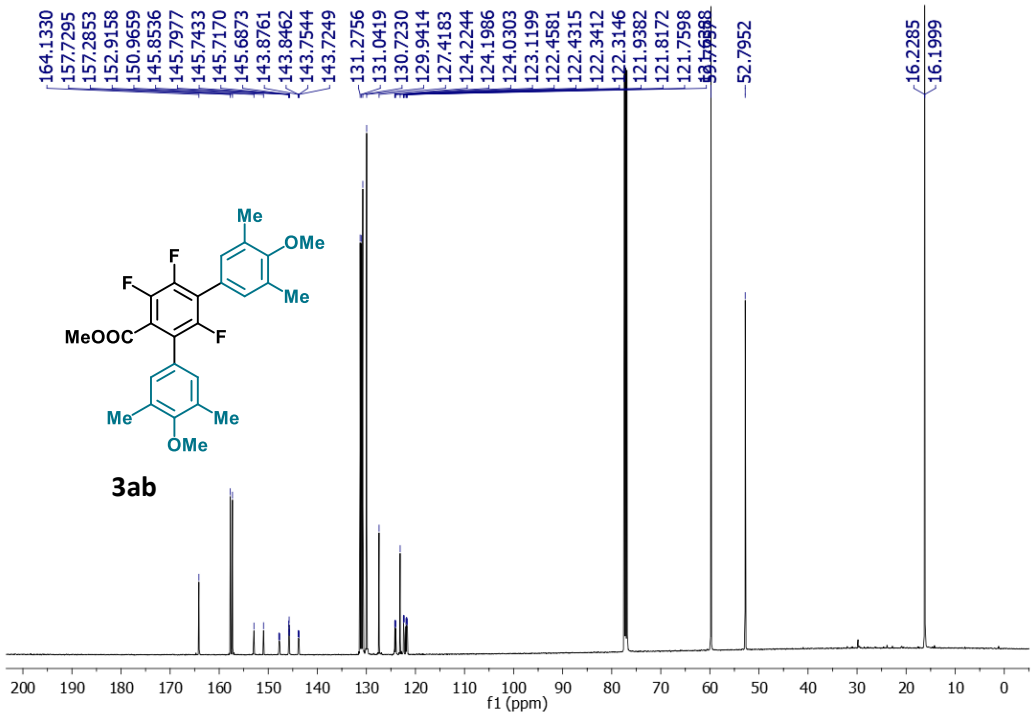


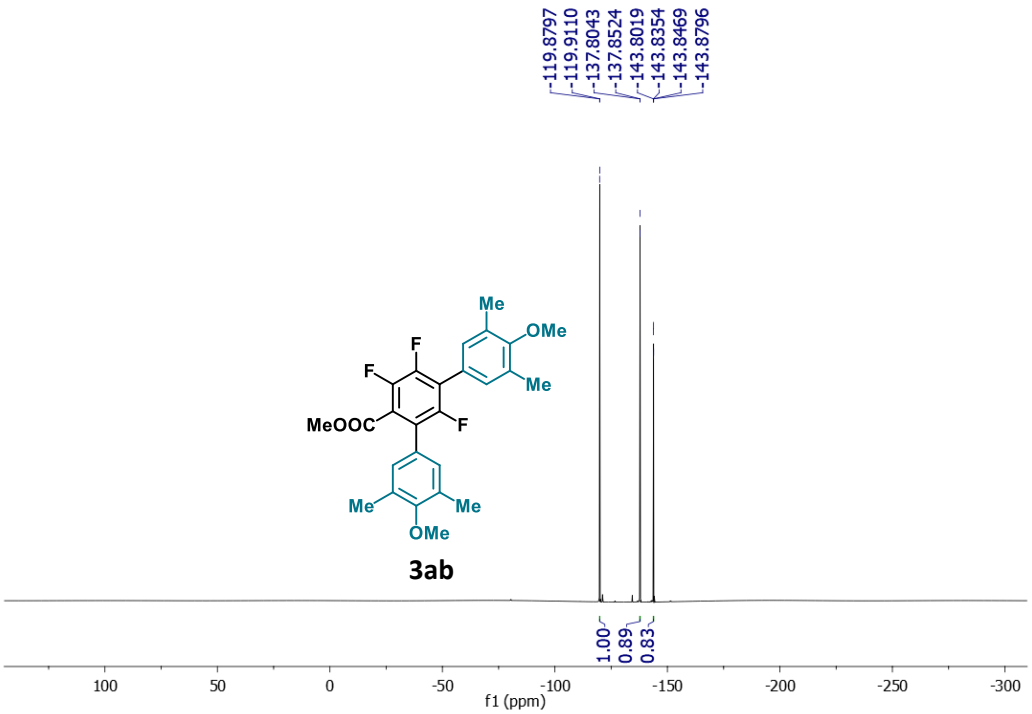



138.9620
138.9895
139.0061
139.0313
142.8397
142.8720
Me
OMe
Me
F
F
F
F
F
F
F
F
Me
MeO
Me
3aa
4.00
3.90
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

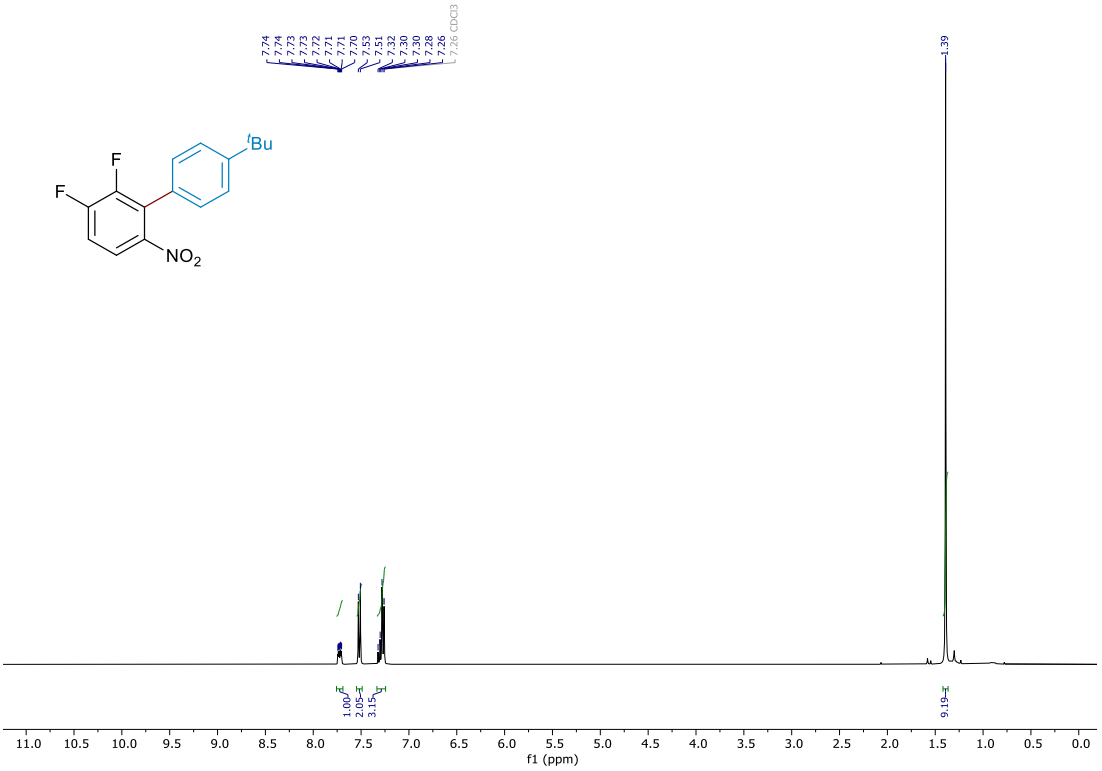
Methyl 2',5',6'-trifluoro-4,4''-dimethoxy-3,3'',5,5''-tetramethyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3ab):

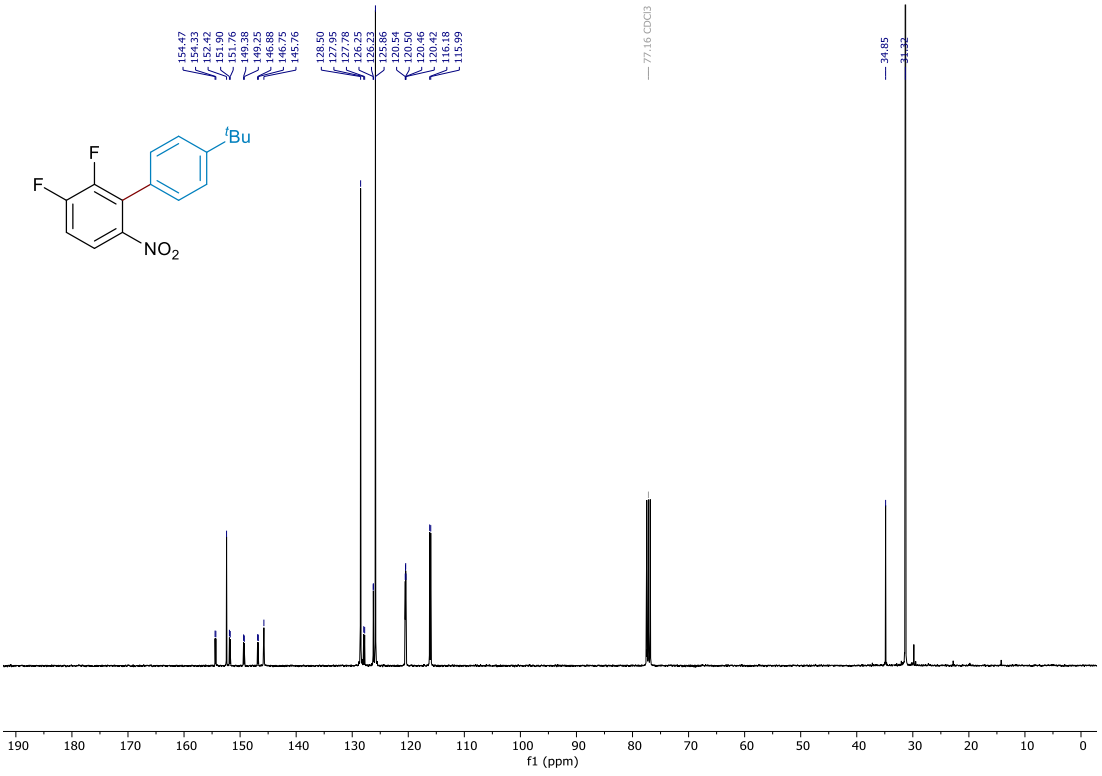


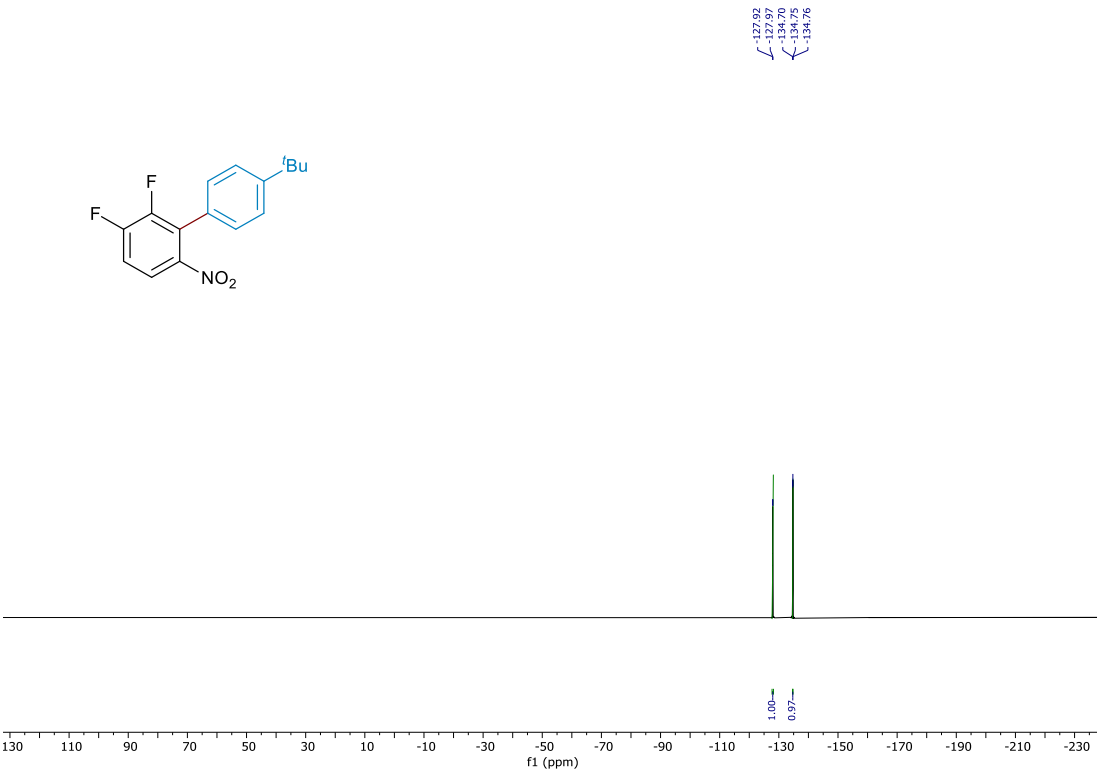



-119.8797
-119.9110
-137.8043
-137.8524
-143.8019
-143.8354
-143.8469
-143.8796
Me
OMe
F
F
Me
MeOOC
F
Me
Me
OMe
3ab
1.00
0.89
0.83
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

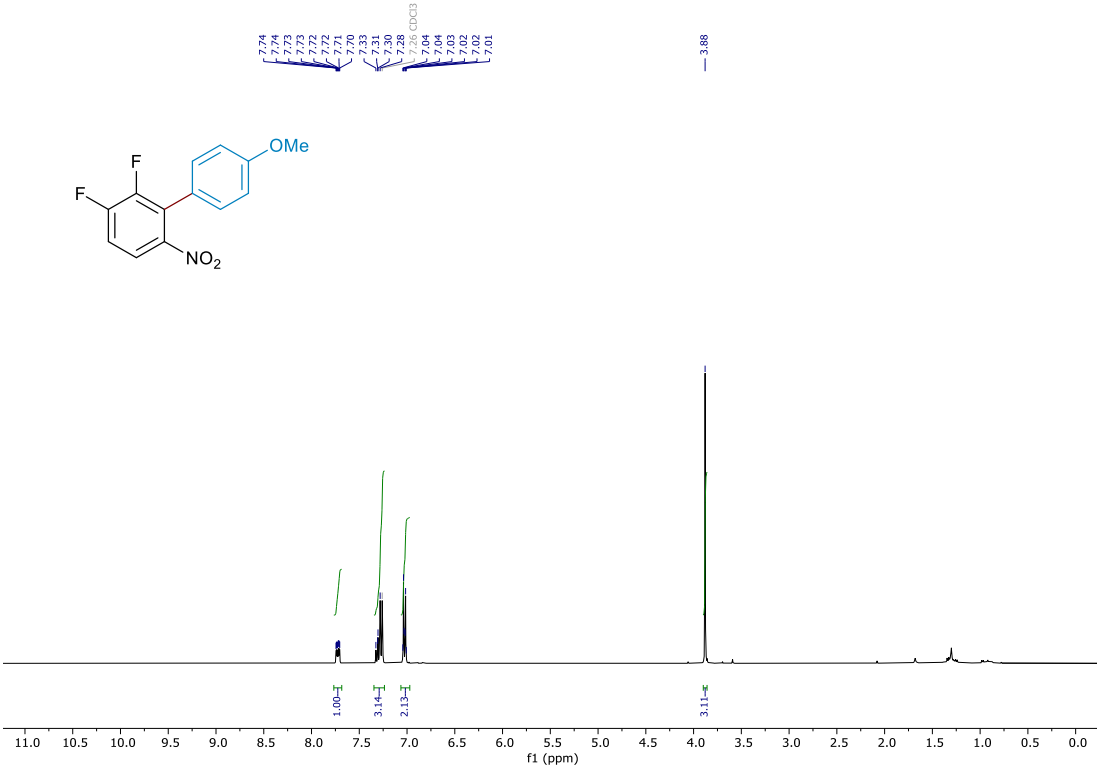
4'-(*tert*-butyl)-2,3-difluoro-6-nitro-1,1'-biphenyl (4a):

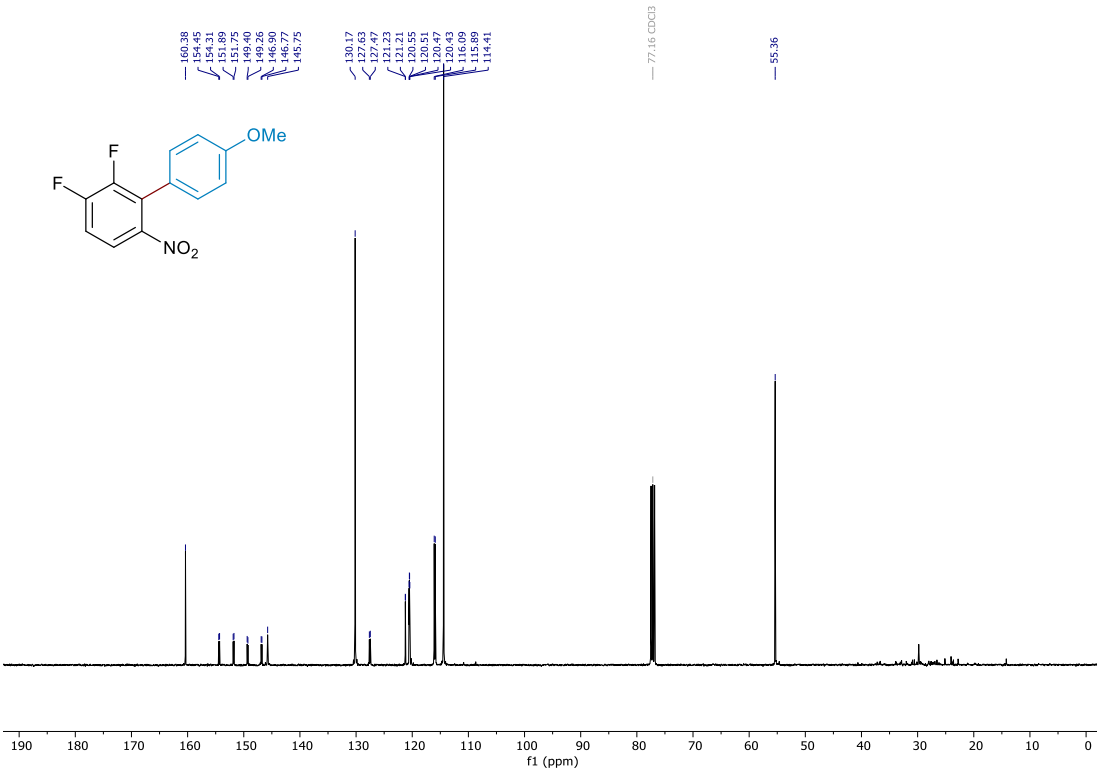


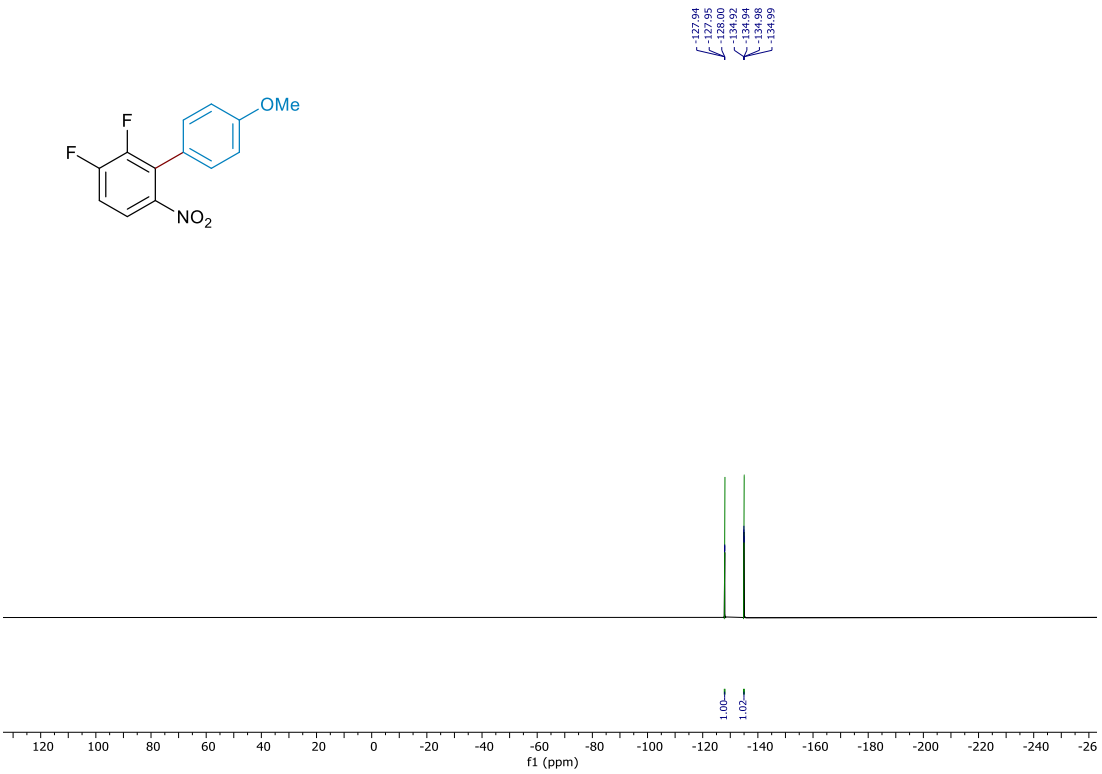



-127.92
-127.97
-134.70
-134.75
-134.76
F
F
tBu
NO2
1.00
0.97
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

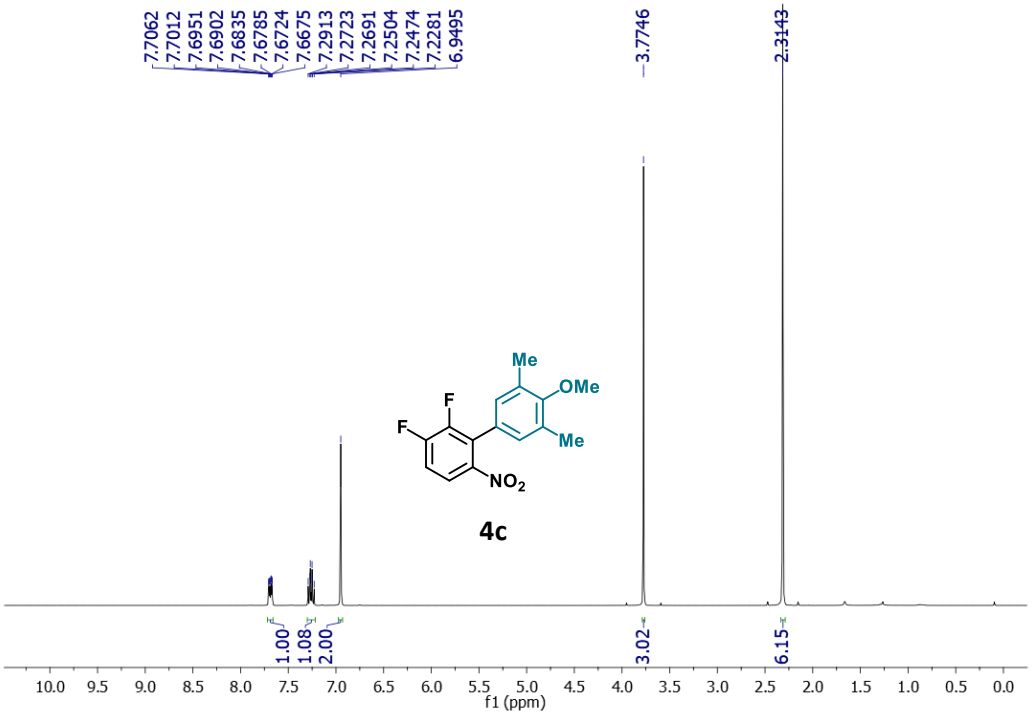
2,3-difluoro-4'-methoxy-6-nitro-1,1'-biphenyl (4b):

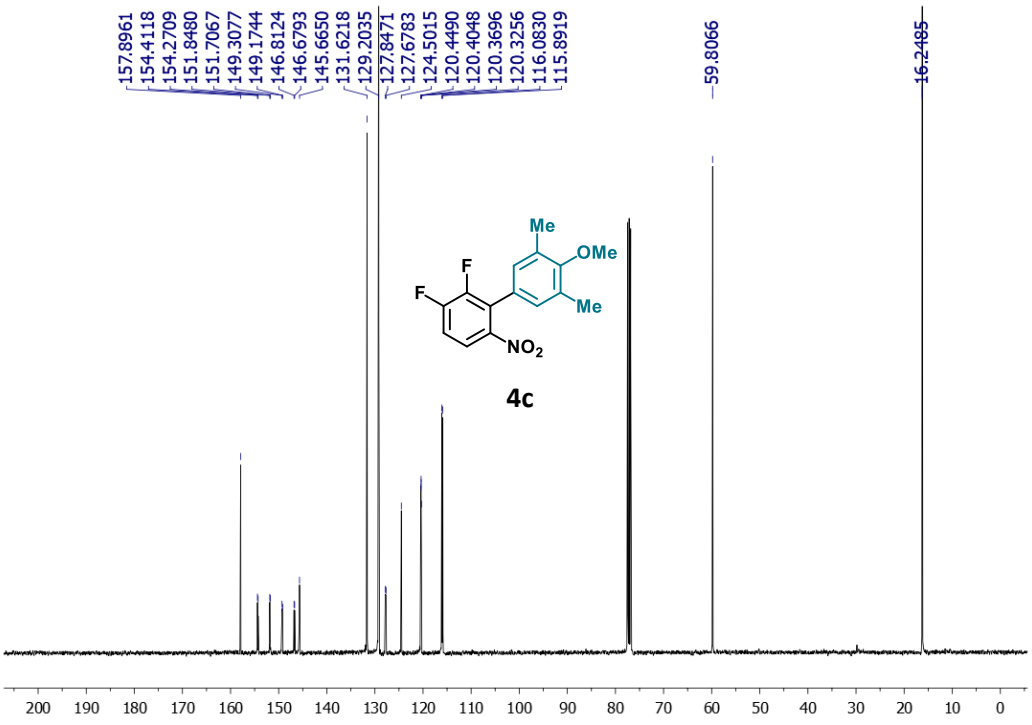


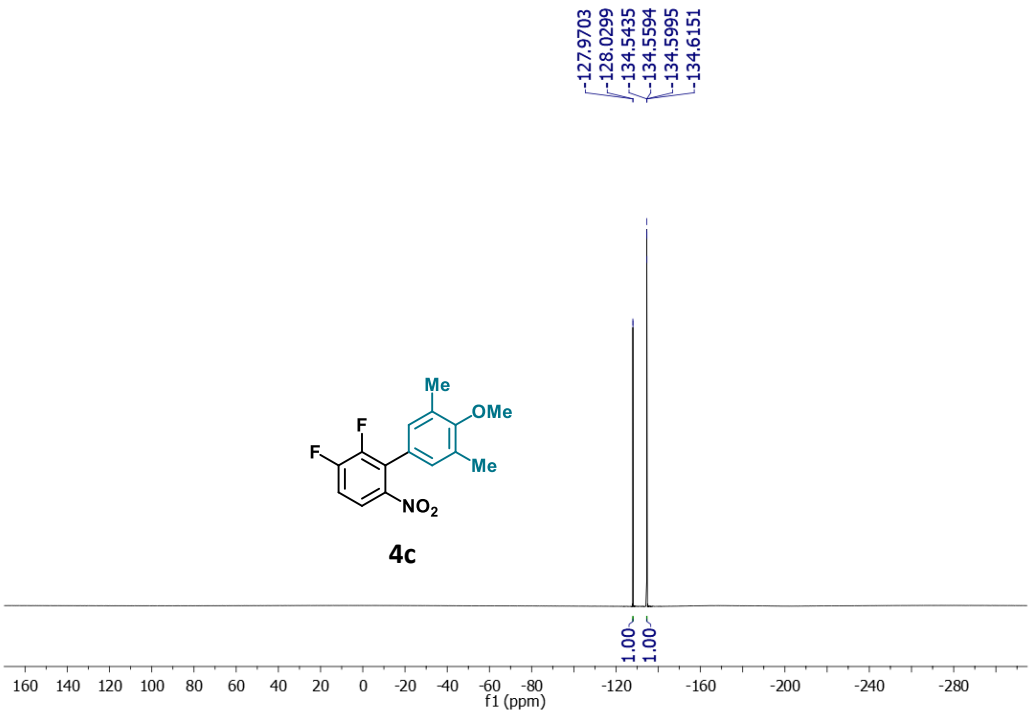



-127.94
-127.95
-128.00
-134.92
-134.94
-134.98
-134.99
F
F
OMe
NO2
1.00
1.02
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-26
f1 (ppm)

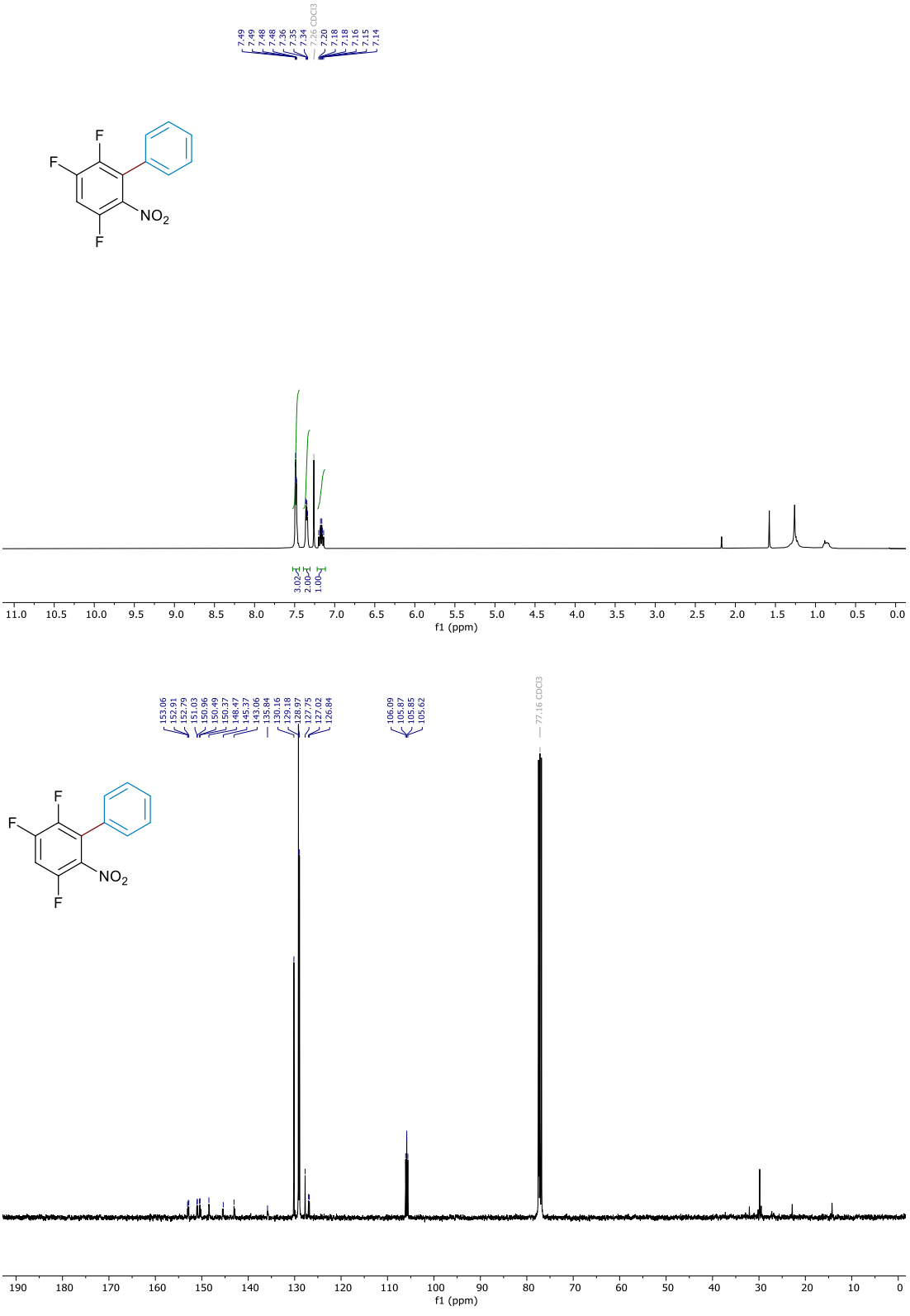
2,3-difluoro-4'-methoxy-3',5'-dimethyl-6-nitro-1,1'-biphenyl (4c):

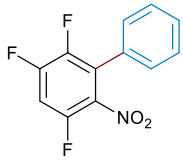





-127.9703
-128.0299
-134.5435
-134.5594
-134.5995
-134.6151
Me
OMe
F
F
Me
NO2
4c
1.00
1.00
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

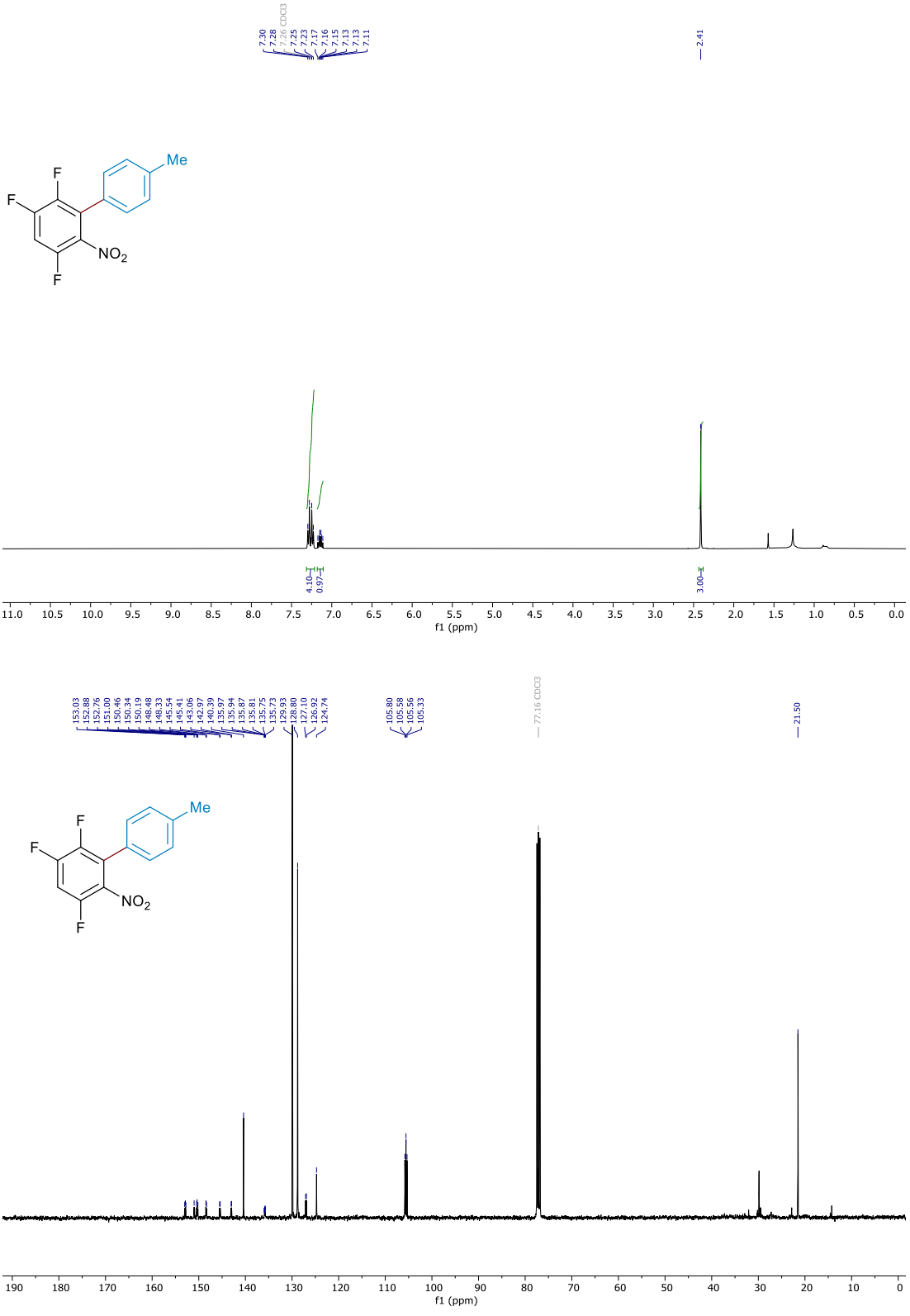
2,3,5-trifluoro-6-nitro-1,1'-biphenyl (4d):

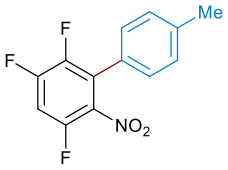



F
F
NO2
F

-124.06
-126.26
-126.77
-126.92
-140.72
-140.74
-140.76
-140.78
-140.79
-140.81
-140.83
1.00
1.06
1.04
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

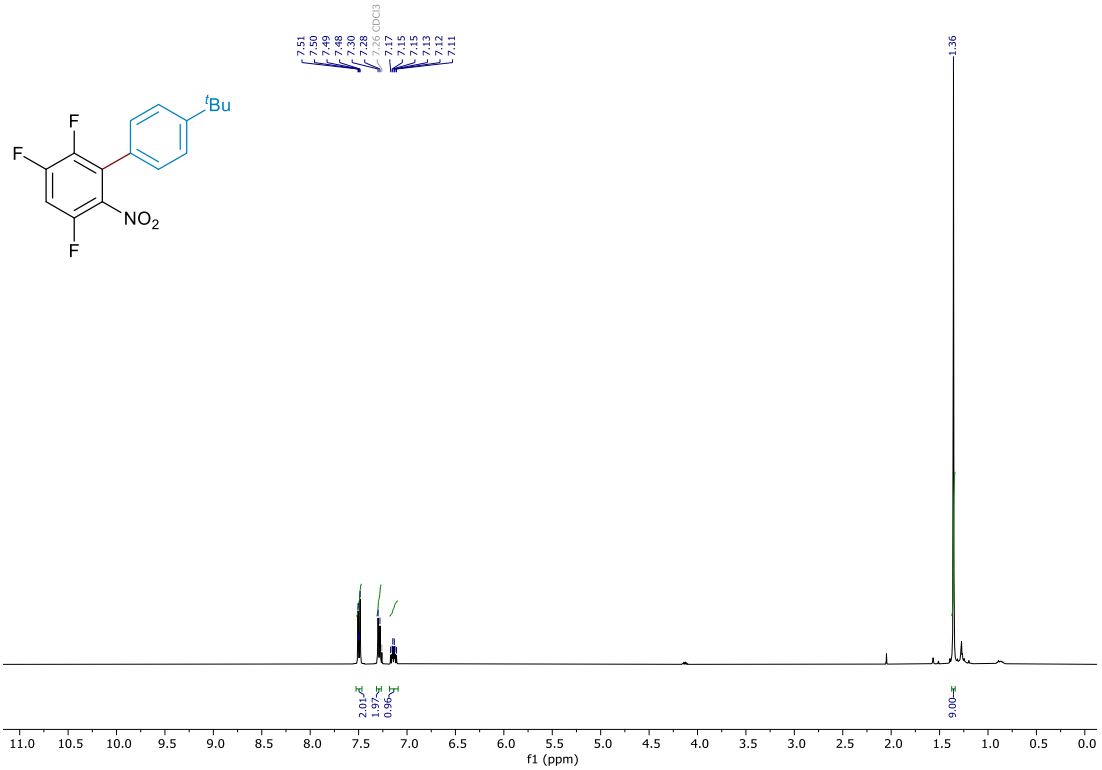
2,3,5-trifluoro-4'-methyl-6-nitro-1,1'-biphenyl (4e):

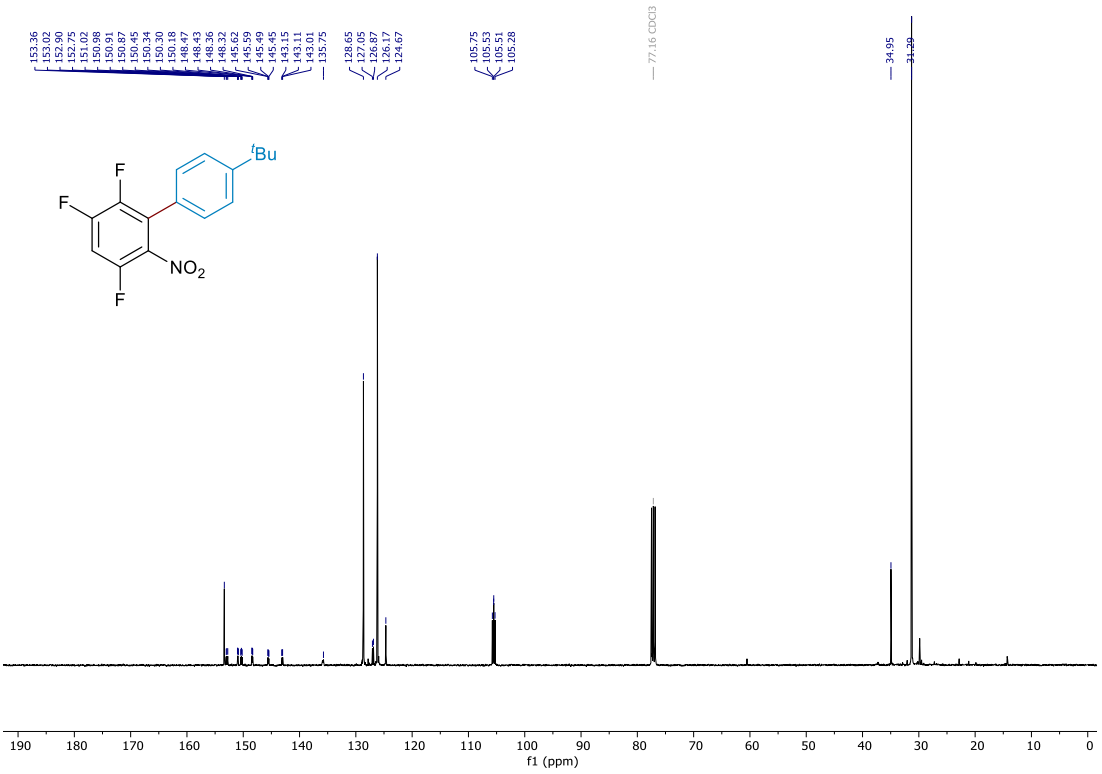


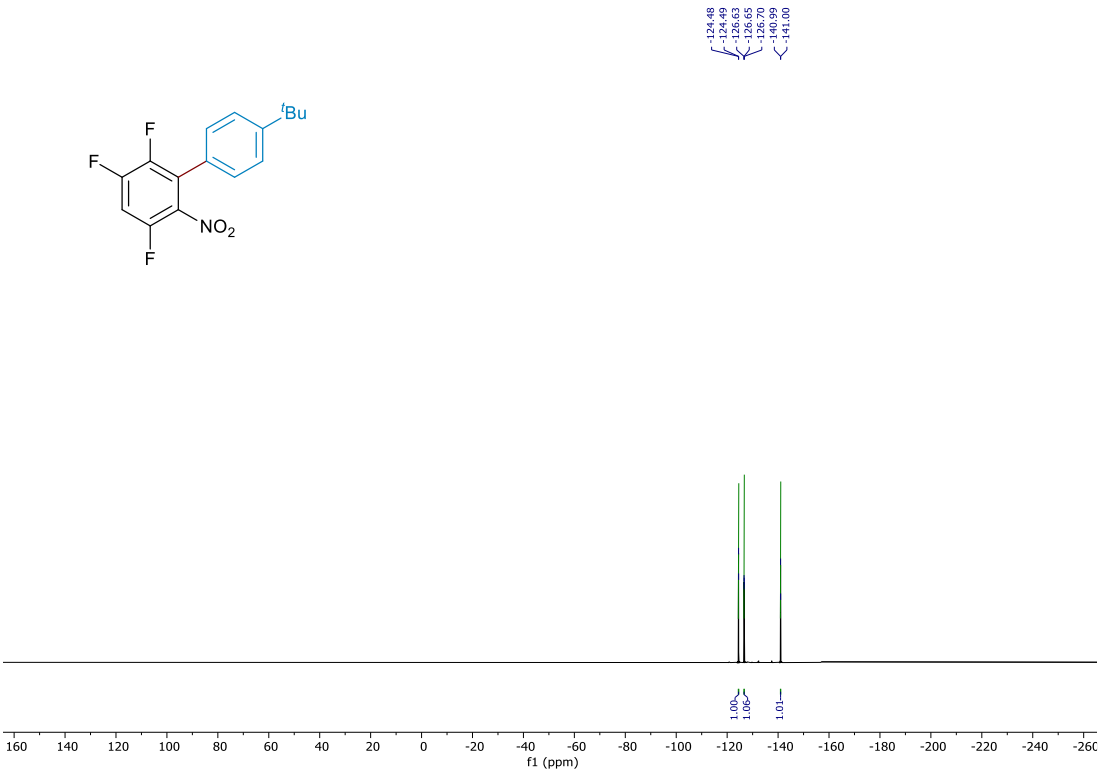

Me
F
F
NO2
F

-124.31
-124.32
-126.54
-126.58
-126.60
-140.93
-140.94
-140.96
-140.98
-141.02
1.00
1.09
1.08
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

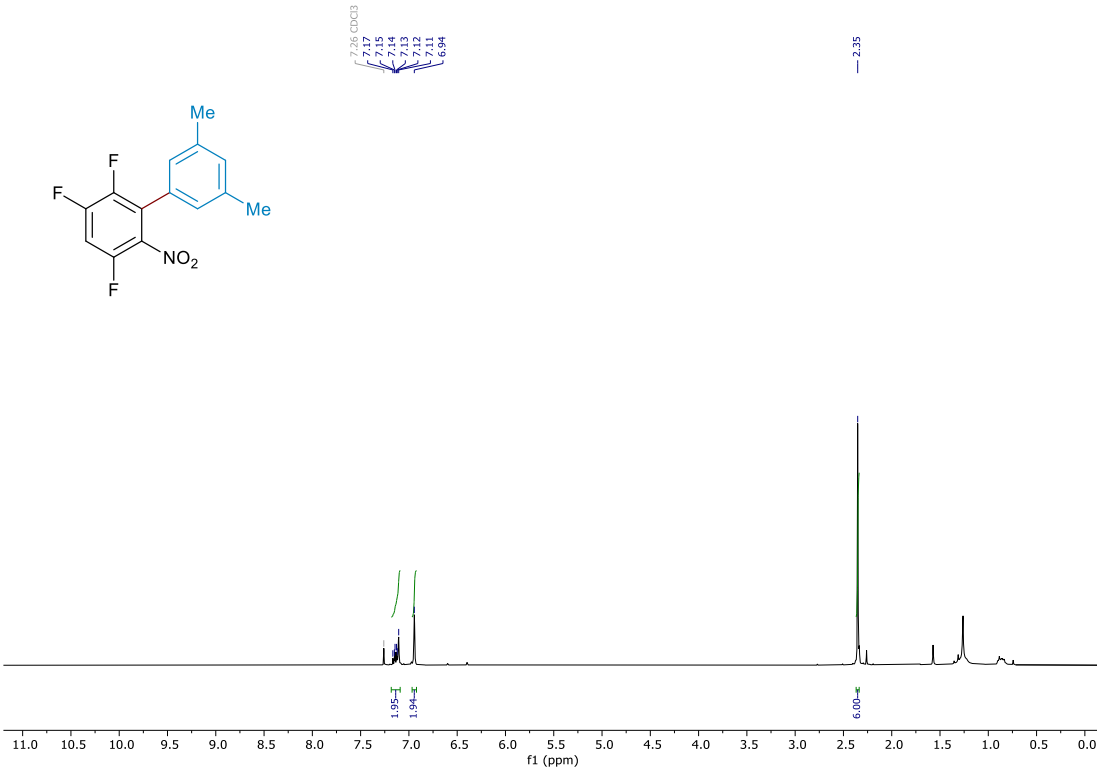
4'-(tert-butyl)-2,3,5-trifluoro-6-nitro-1,1'-biphenyl (4f):

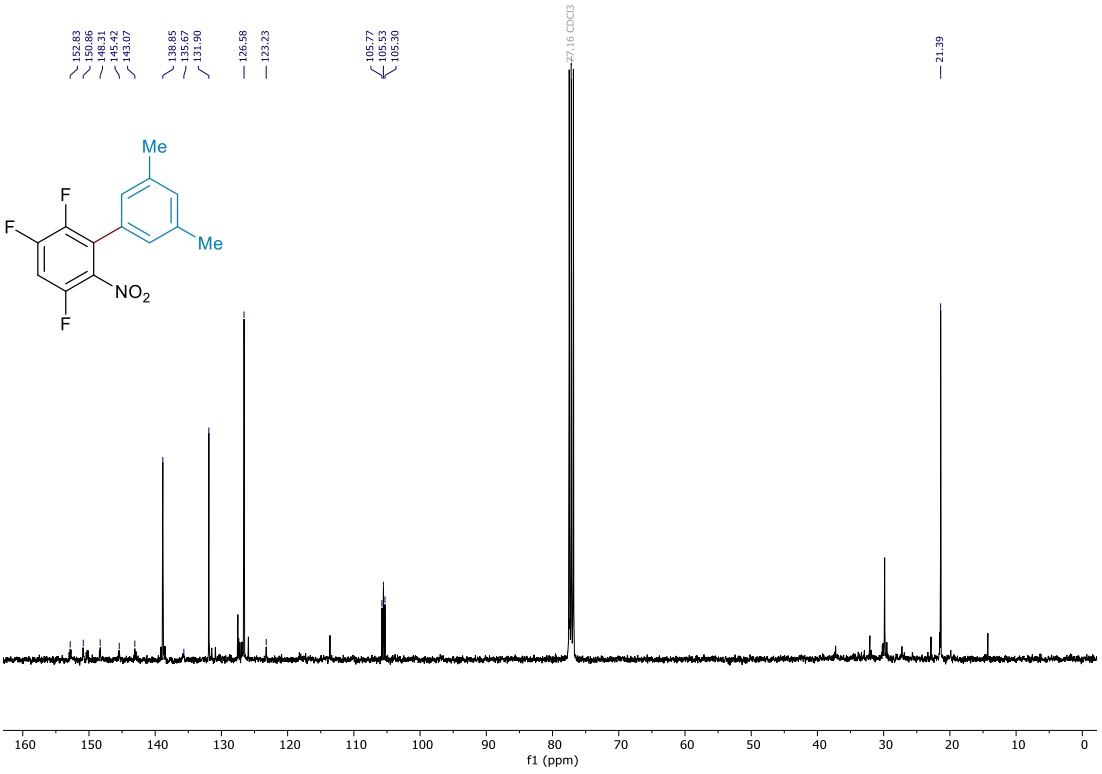


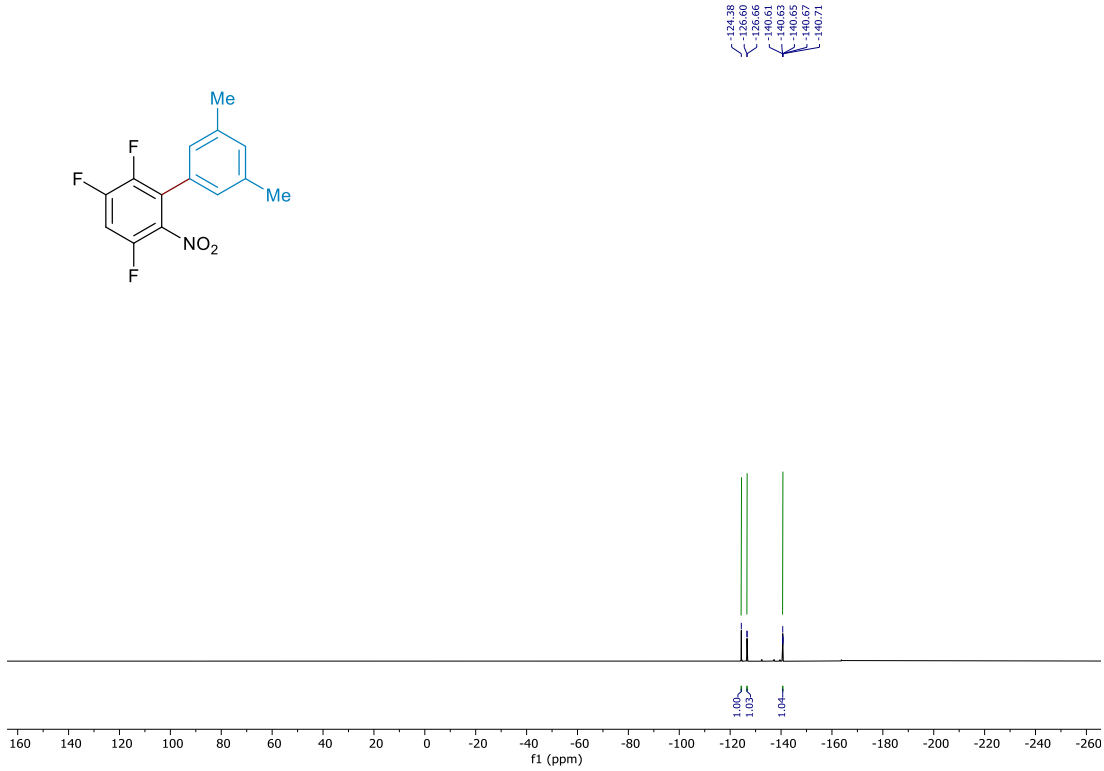



-124.48
-124.49
-126.63
-126.65
-126.70
-140.99
-141.00
F
F
F
NO2
tBu
1.00
1.06
1.01
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

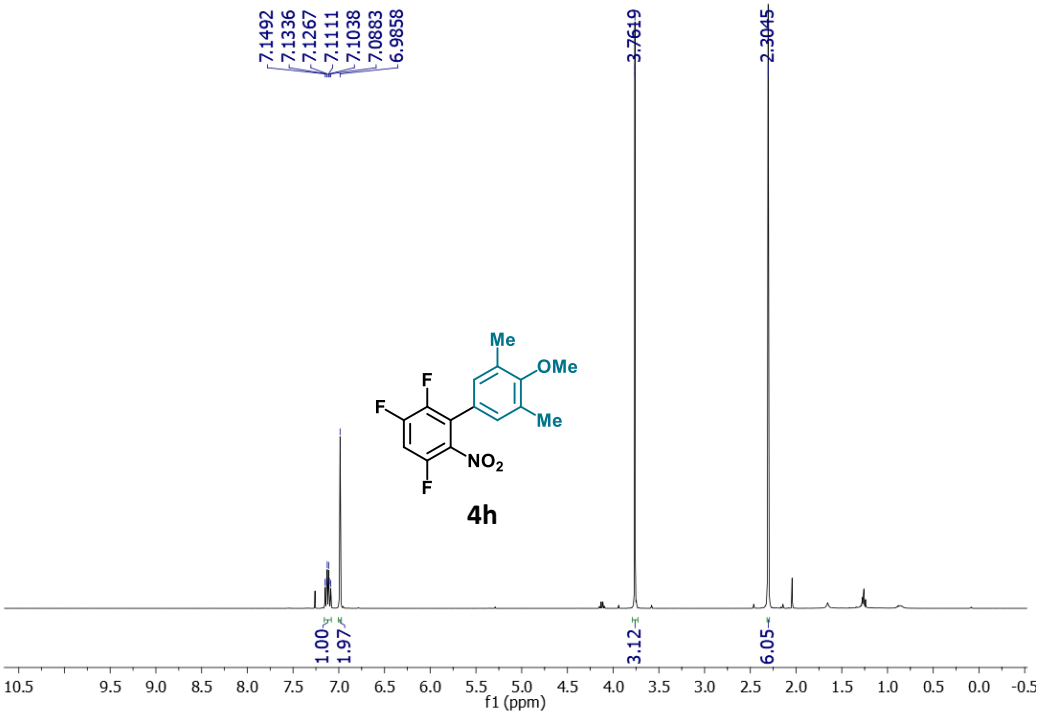
2,3,5-trifluoro-3',5'-dimethyl-6-nitro-1,1'-biphenyl (4g):

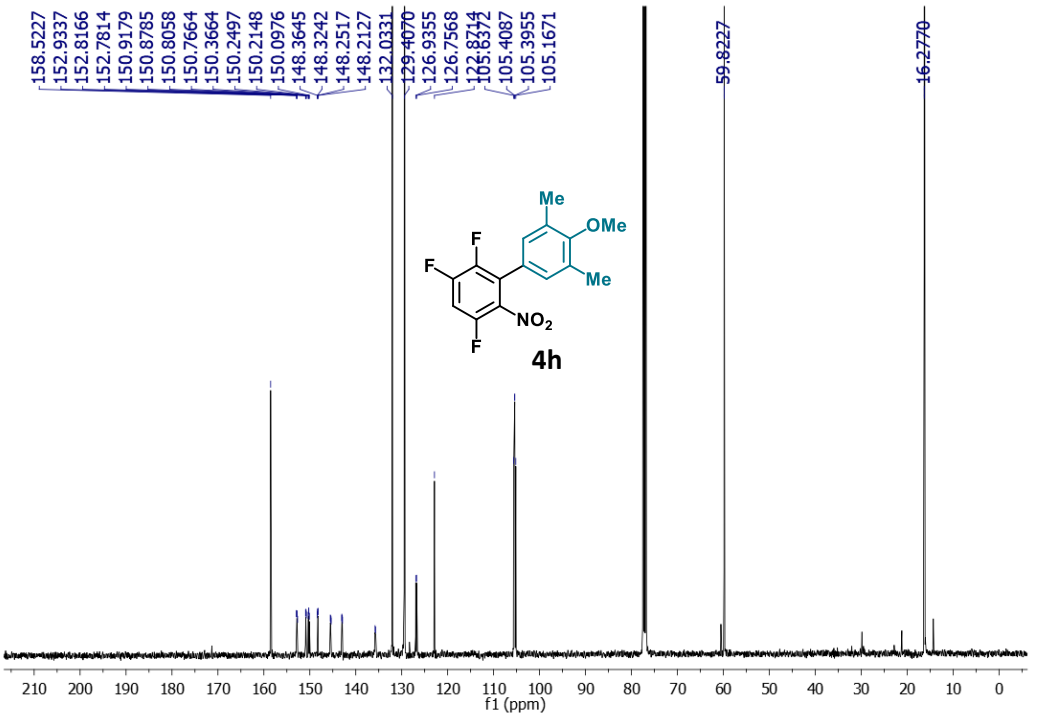


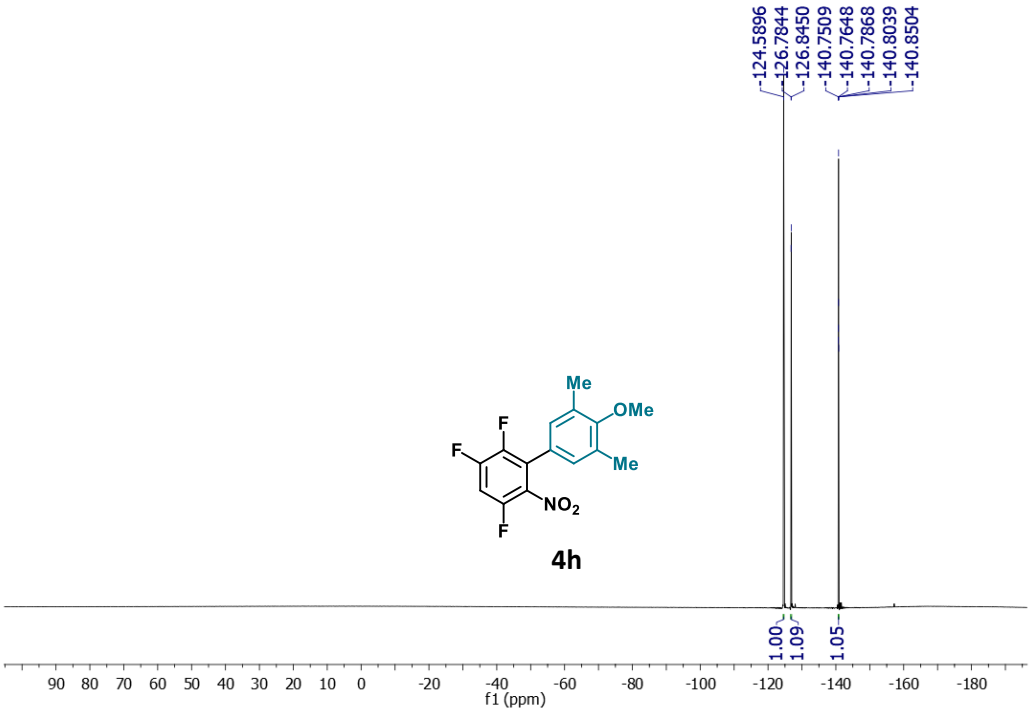



-124.38
-126.60
-126.66
-140.61
-140.63
-140.65
-140.67
-140.71
Me
F
F
Me
NO2
F
1.00
1.03
1.04
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

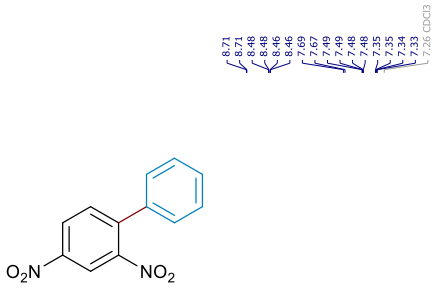
2,3,5-trifluoro-4'-methoxy-3',5'-dimethyl-6-nitro-1,1'-biphenyl (4h):

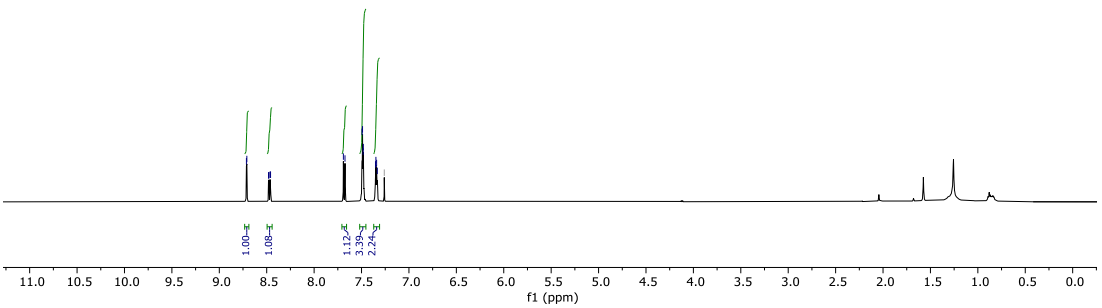


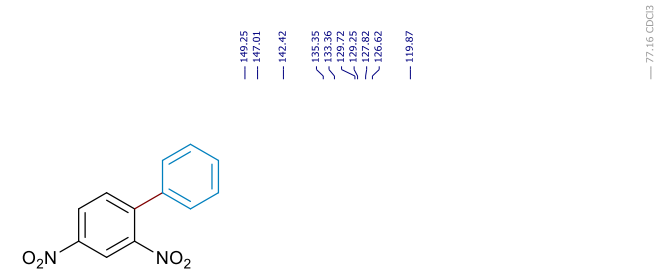


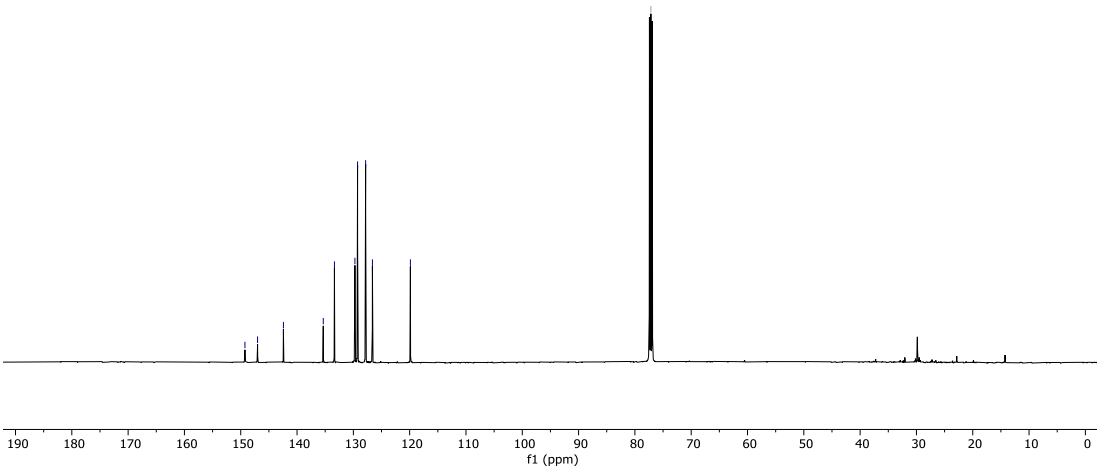

-124.5896
-126.7844
-126.8450
-140.7509
-140.7648
-140.7868
-140.8039
-140.8504
Me
OMe
Me
F
F
F
NO2
4h
1.00
1.09
1.05
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

2,4-dinitro-1,1'-biphenyl (4i):









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