Synthesis of Polyflourinated Biphenyls: Pushing the Boundaries of Suzuki-Miyaura Cross Coupling with Electron-Poor Substrates.

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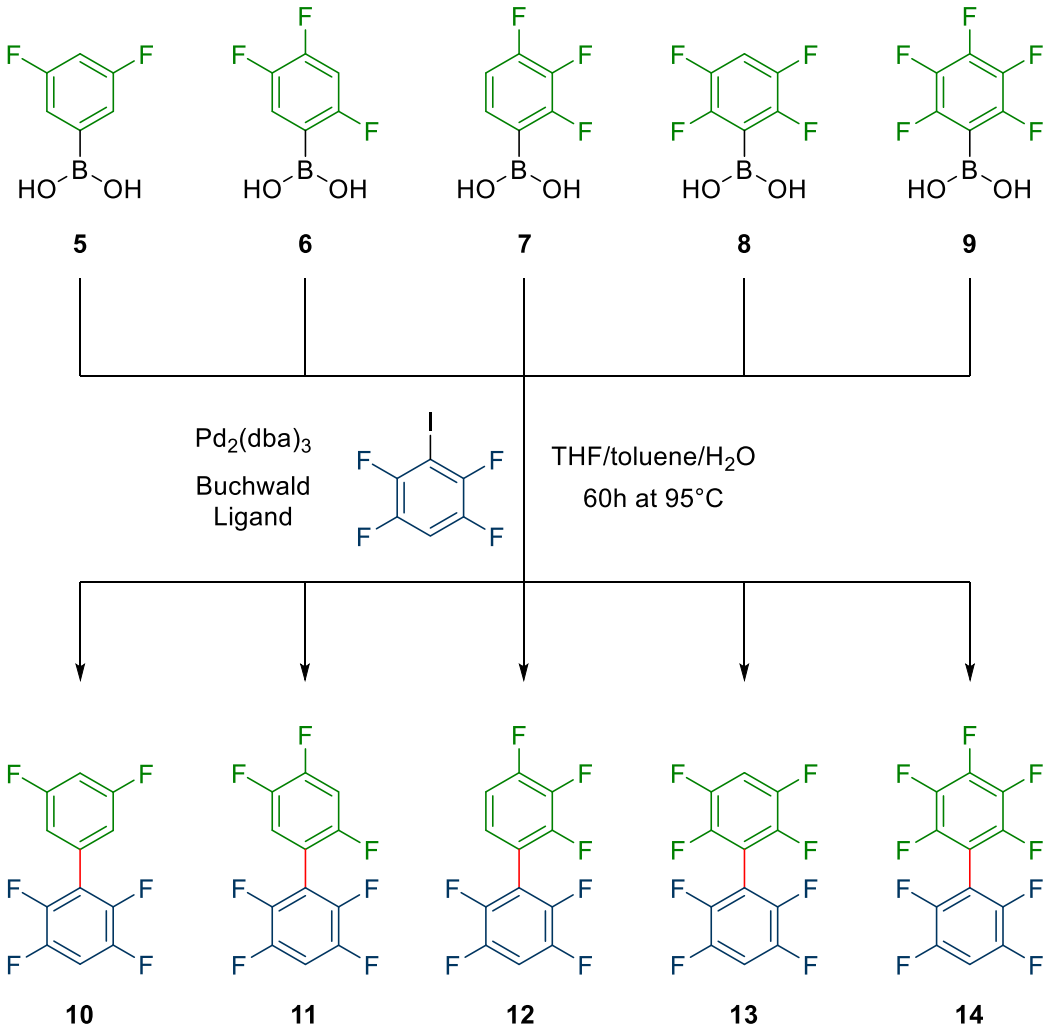
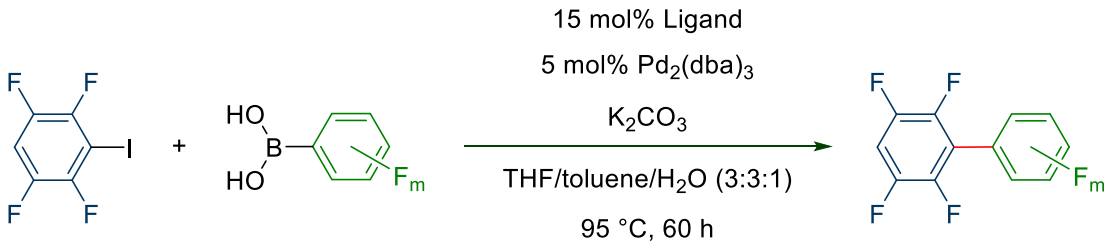
ADDITIONAL SCREENING DATA

Screening of boronic acid derivatives as nucleophiles



Scheme S1. Different boronic acids (**5**-**9**) which were tested as nucleophiles in the Suzuki Miyaura coupling and their corresponding products (**10**-**14**).

Table S1. Ligand Screening for the coupling of different fluorinated boronic acids to 2,3,5,6-tetrafluoroiodo-benzene.

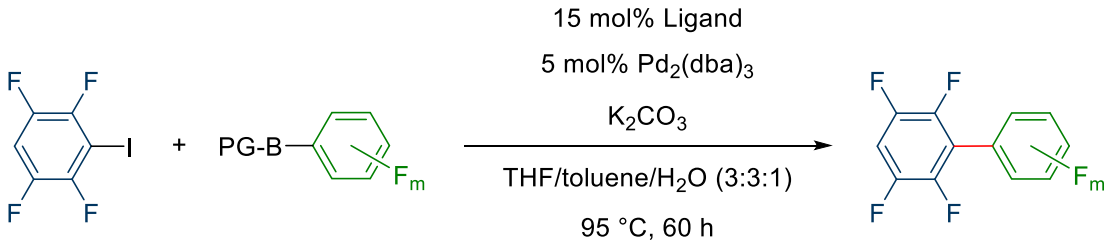


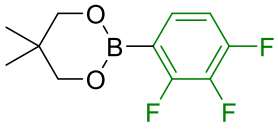
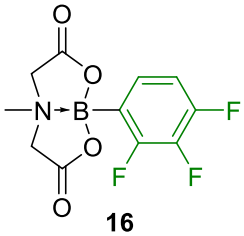
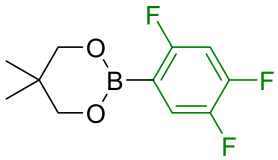
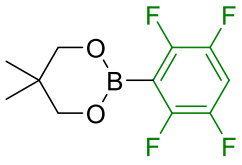
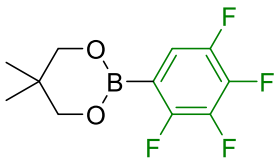
entry[a]	boronic acid	ligand	product	yield
1	**2**	CyJohnPhos	**3**	98%
2	**5**	CyJohnPhos	**10**	88%
3	**6**	CyJohnPhos[b]	**11**	35%
4	**7**	CyJohnPhos[b]	**12**	40%
5	**8**	CyJohnPhos	**13**	31%
6	**9**	CyJohnPhos	**14**	-
8	**5**	DavePhos	**10**	98%
9	**5**	MePhos	**10**	94%
10	**5**	RuPhos	**10**	90%
11	**5**	XPhos	**10**	99%
12	**5**	SPhos	**10**	94%
14	**6**	DavePhos[b]	**11**	36%
15	**6**	MePhos[b]	**11**	45%
16	**6**	RuPhos	**11**	47%
17	**6**	XPhos	**11**	45%
12	**6**	SPhos[b]	**11**	48%
14	**7**	DavePhos[b]	**12**	38%
15	**7**	MePhos[b]	**12**	86%
16	**7**	RuPhos	**12**	27%
17	**7**	XPhos	**12**	28%
18	**7**	SPhos[b]	**12**	74%
20	**8**	DavePhos	**13**	58%
21	**8**	MePhos	**13**	-
22	**8**	RuPhos	**13**	27%
23	**8**	XPhos	**13**	15%
24	**8**	SPhos[b]	**13**	-[c]
25	**8** without **1**	DavePhos	**13**	19%
26	**9**	DavePhos	**14**	-
27	**9**	MePhos	**14**	-
28	**9**	RuPhos	**14**	-
29	**9**	XPhos	**14**	-
30	**9**	SPhos	**14**	-

[a]Reactions were performed with 1 equiv. **1** and the corresponding boronic acid and 2.2 equiv. of Na_2CO_3 with 5 mol% $Pd_2(dba)_3$ and a 15 mol% of the corresponding ligand at 95°C for 60h on a 0.18 mmol scale. [b]contains significant amounts of a homocoupling side product (>2%). [c]complex product mixture.

Screening Data: Boronic Acid Protecting Groups

Table S2. Ligand Screening for the coupling of different fluorinated protected boronic acids to 2,3,5,6-tetrafluoroiodo-benzene.



entry[a]	protected boronic acid	ligand	product	yield
1	 15	CyJohnPhos	12	76%
2		DavePhos	12	84%
3		MePhos	12	79%
4		RuPhos	12	68%
5		XPhos	12	58%
6		SPhos	12	61%
7	 16	CyJohnPhos	12	80%
8		DavePhos	12	68%
9		MePhos	12	73%
10		RuPhos	12	80%
11		XPhos	12	61%
12		SPhos	12	51%
13	 17	CyJohnPhos[b]	11	78%
14		DavePhos[b]	11	52%
15		MePhos[b]	11	78%
16		RuPhos	11	63%
17		XPhos	11	30%
18		SPhos[b]	11	29%
19	 18	CyJohnPhos	13	20%
20		DavePhos	13	10%
21		MePhos	13	82%
22		RuPhos	13	39%
23		XPhos	13	-
24		SPhos	13	-
25	 19	CyJohnPhos	20	24%
26		DavePhos	20	62%
27		MePhos	20	10%
28		RuPhos	20	10%
29		XPhos	20	17%
30		SPhos	20	10%

[a]Reactions were performed with 1 equiv. **1** and the corresponding boronic acid and 2.2 equiv. of Na_2CO_3 with 5 mol% $Pd_2(dba)_3$ and a 15 mol% of the corresponding ligand at 95°C for 60h on a 0.18 mmol scale. [b]contains significant amounts of a homocoupling side product (>2%).

Table S3. Homocoupling in the reactions of **1** with the electrophiles **6** and **17**.

entry	ligand	homocoupling[a] (6; $B(OH)_2$)	homocoupling[a] (17; B-ester)
1	CyJohnPhos	30%	7%
2	DavePhos	22%	19%
3	MePhos	20%	9%
4	SPhos	8%	5%

[a]Homocoupling was determined by GC in the final product mixture.

SPECTROSCOPIC DATA

Polyfluorinated Biphenyls

2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl (3)

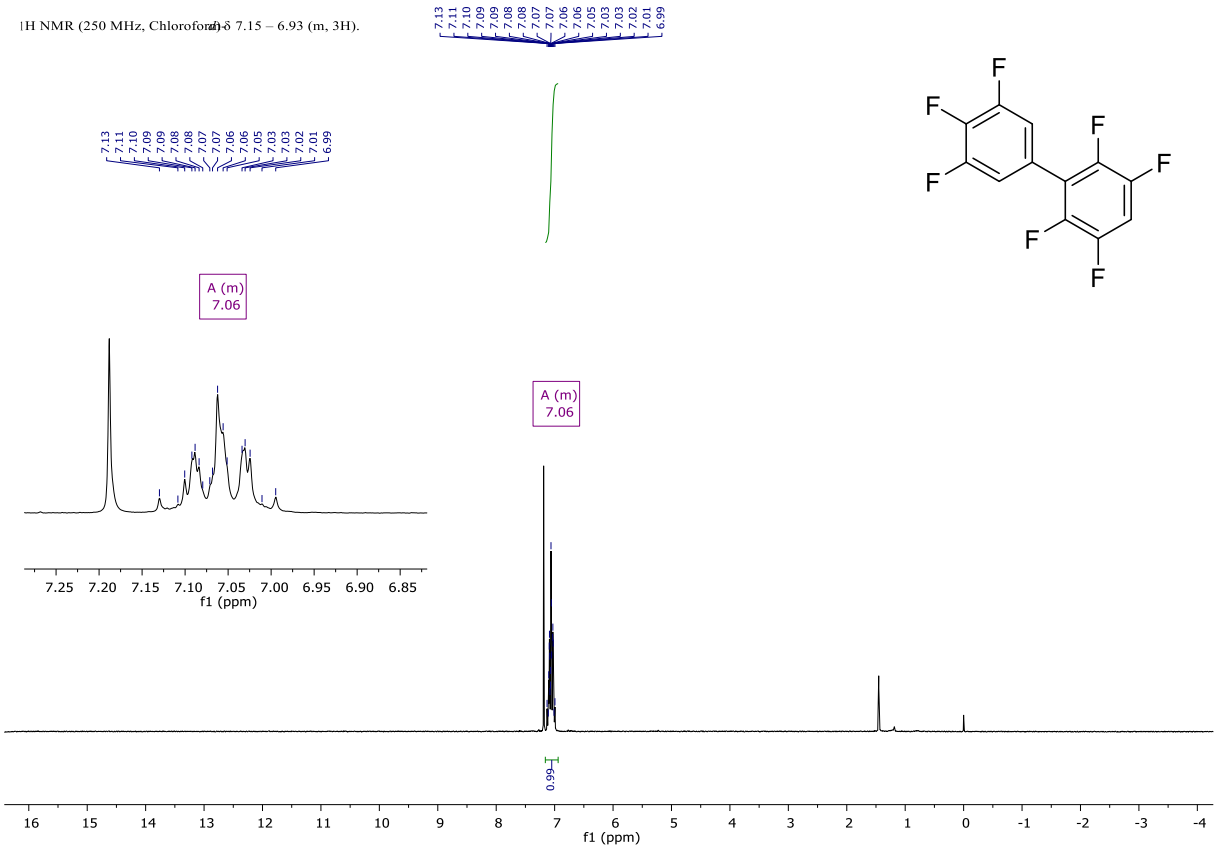


Figure S1 ^{1}H-NMR: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform-d) δ -133.34 (dd, J = 20.4, 8.0 Hz), -137.54 – -138.26 (m), -143.25 – -143.73 (m), -158.25 (tt, J = 20.7, 6.4 Hz).

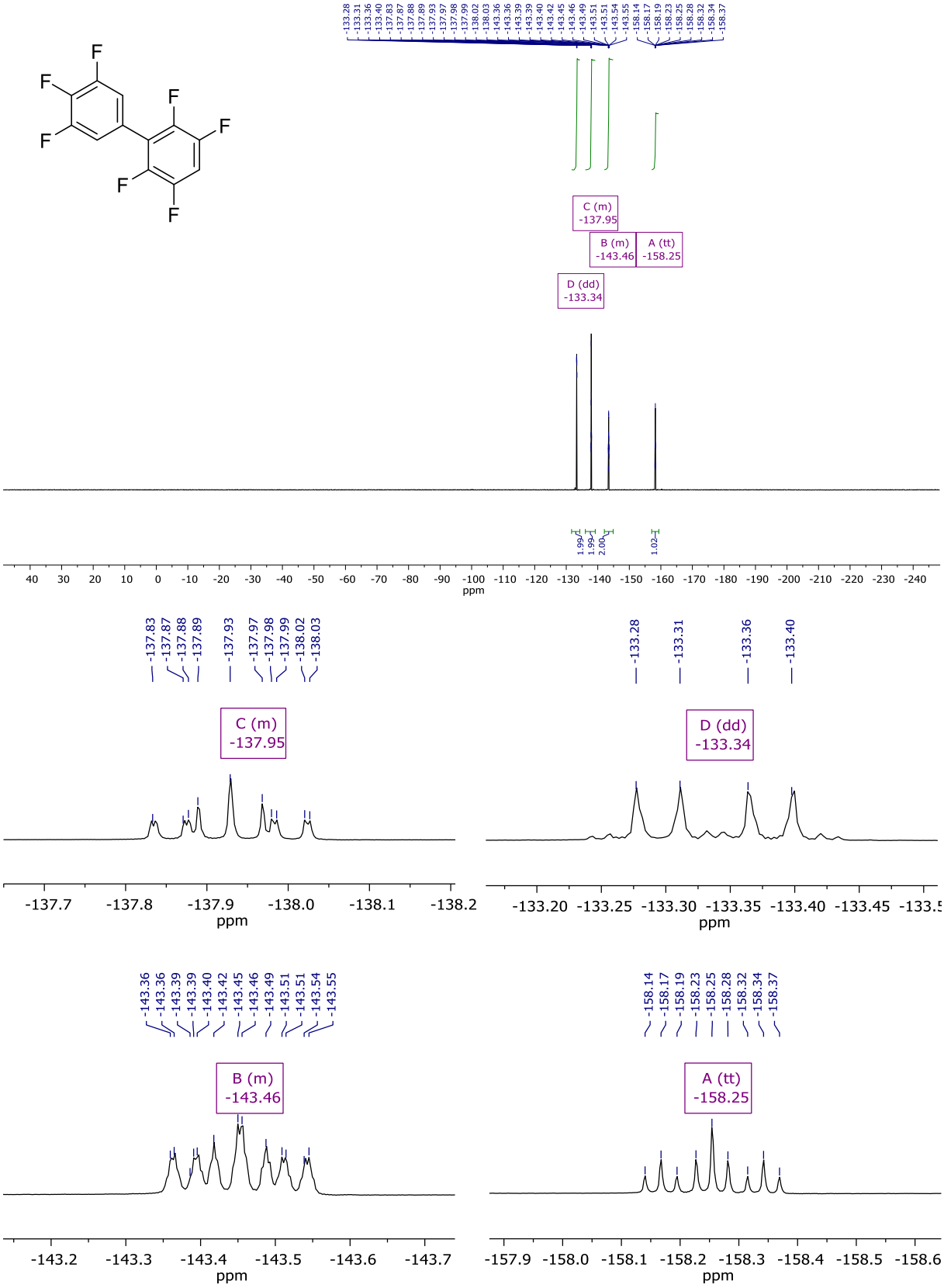


Figure S2 ^{19}F-NMR: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform-d) δ -133.34 (d, J = 20.5 Hz), -137.41 – -138.40 (m), -142.83 – -144.21 (m), -158.26 (t, J = 20.5 Hz).

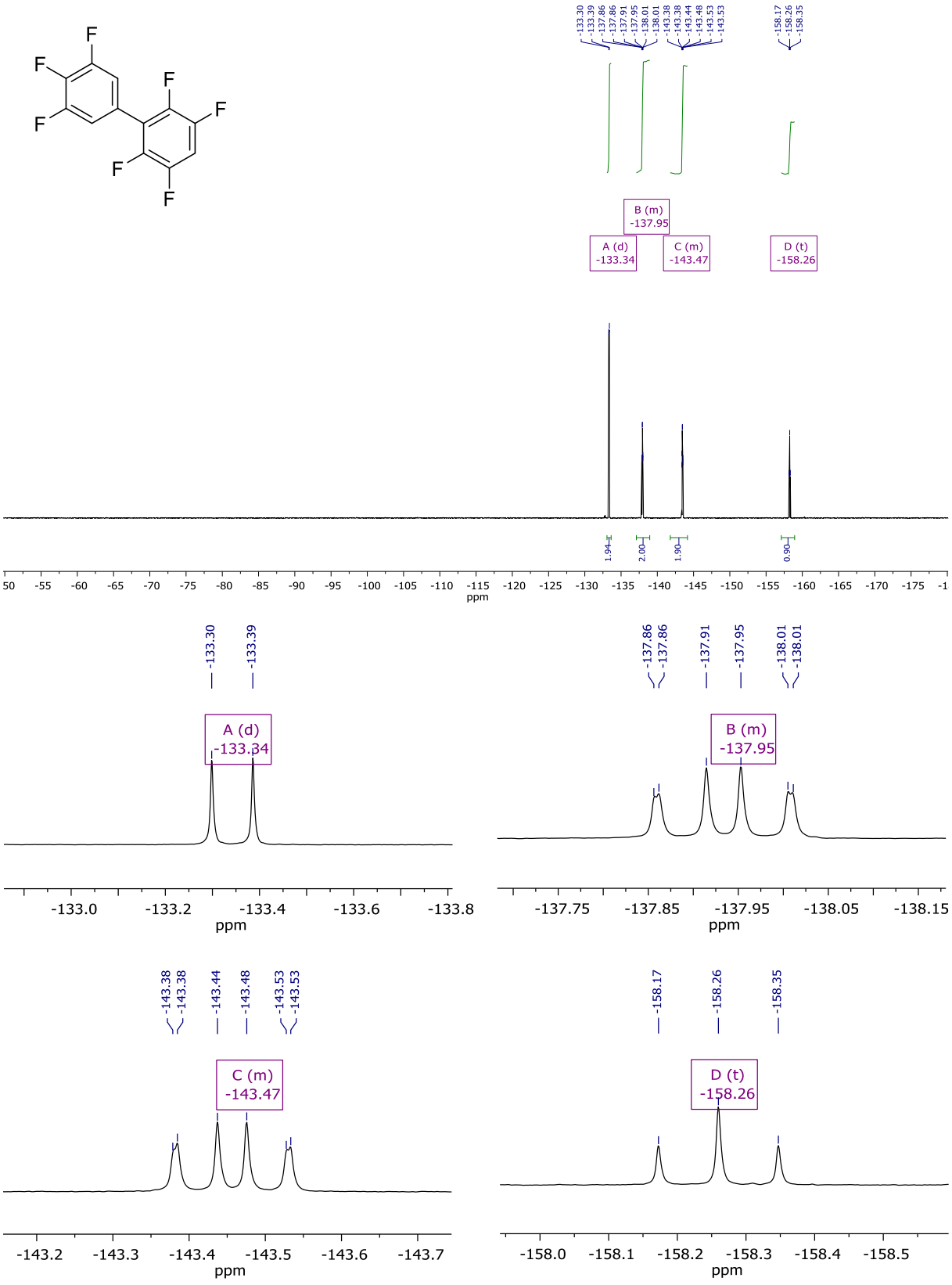


Figure S3 ^{19}F-NMR {^{1}H}: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

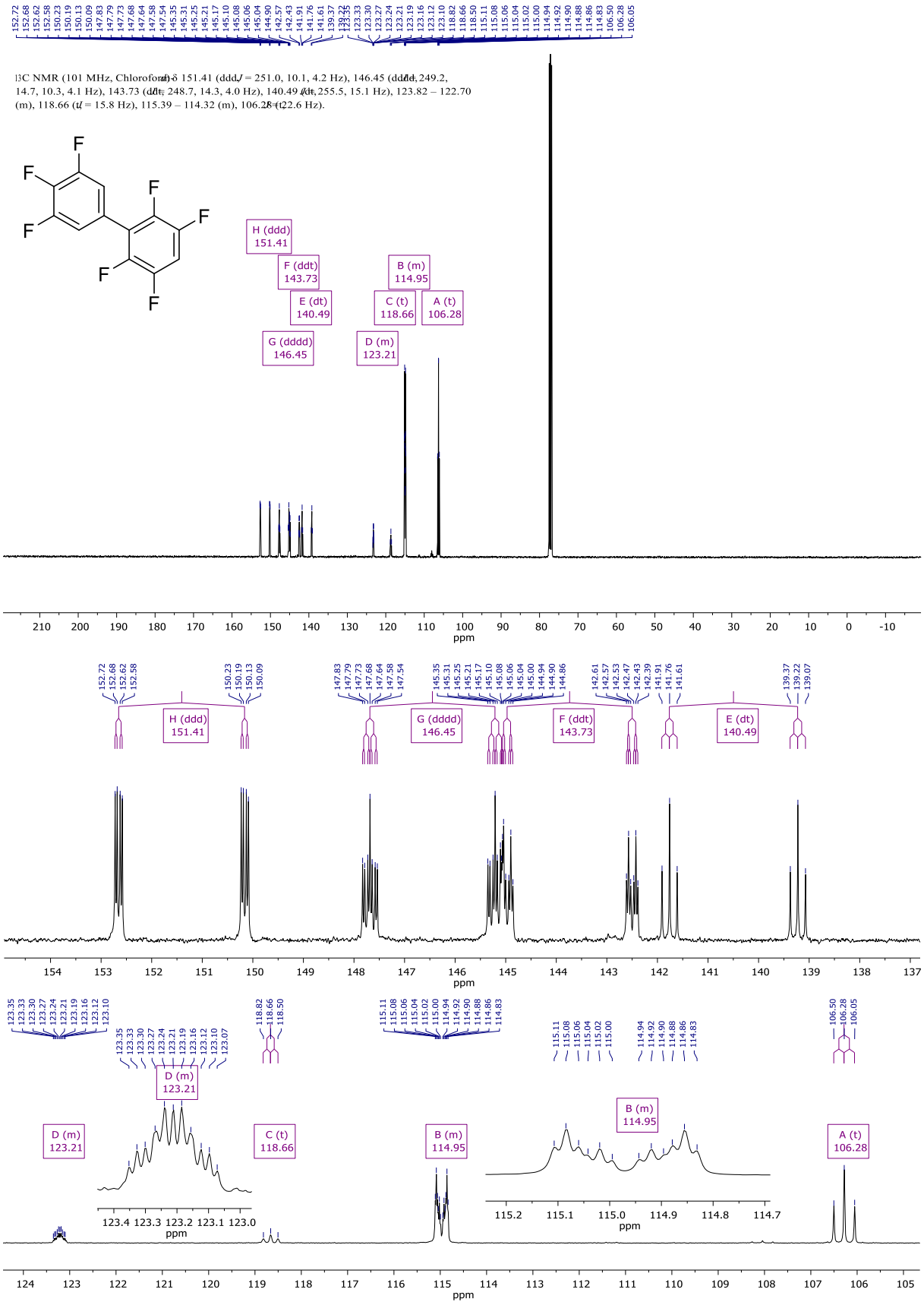


Figure S4 ^{13}C NMR: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

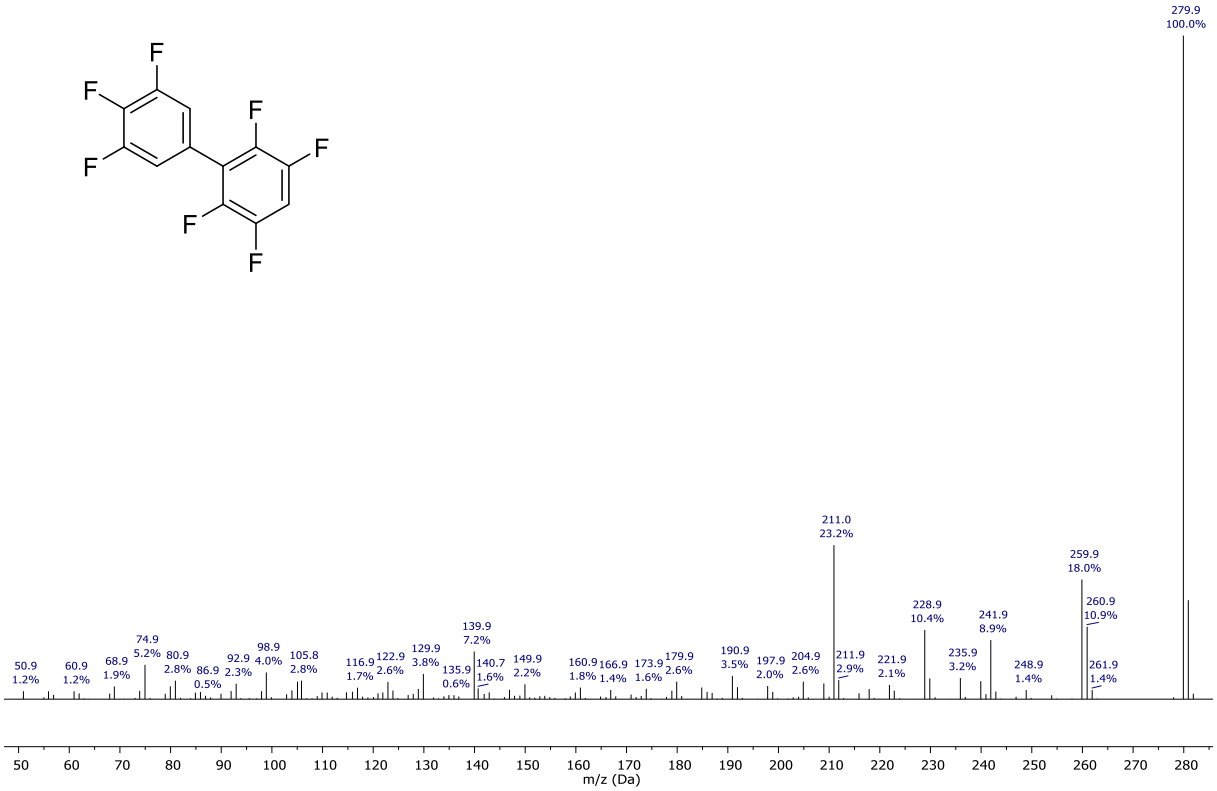


Figure S5 EI-Spectrum (EI⁺): 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

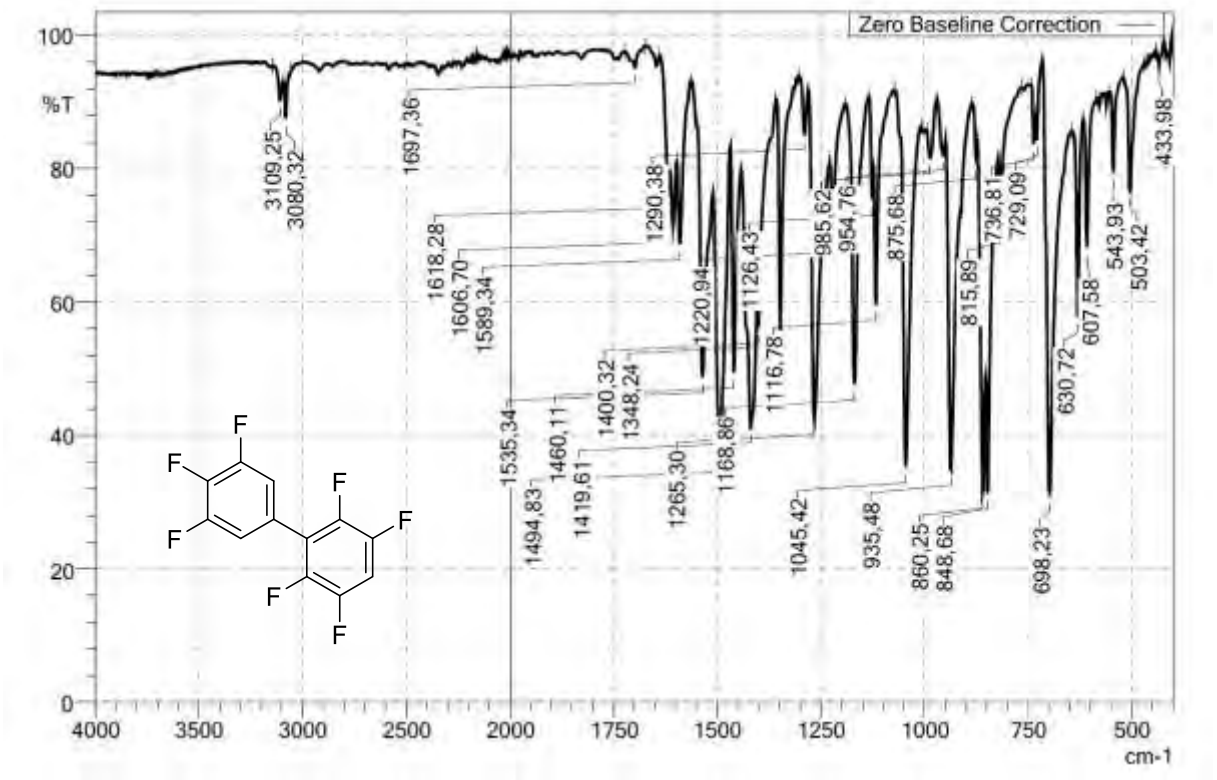


Figure S6 IR (ATR)-Spectrum: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl (10)

^{1}H NMR (250 MHz, Chloroform-d) δ 7.13 (tt, J = 9.7, 7.4 Hz, 1H), 7.02 (ddd, J = 6.5, 2.3, 1.2 Hz, 2H), 6.93 (tt, J = 8.9, 2.3 Hz, 1H).

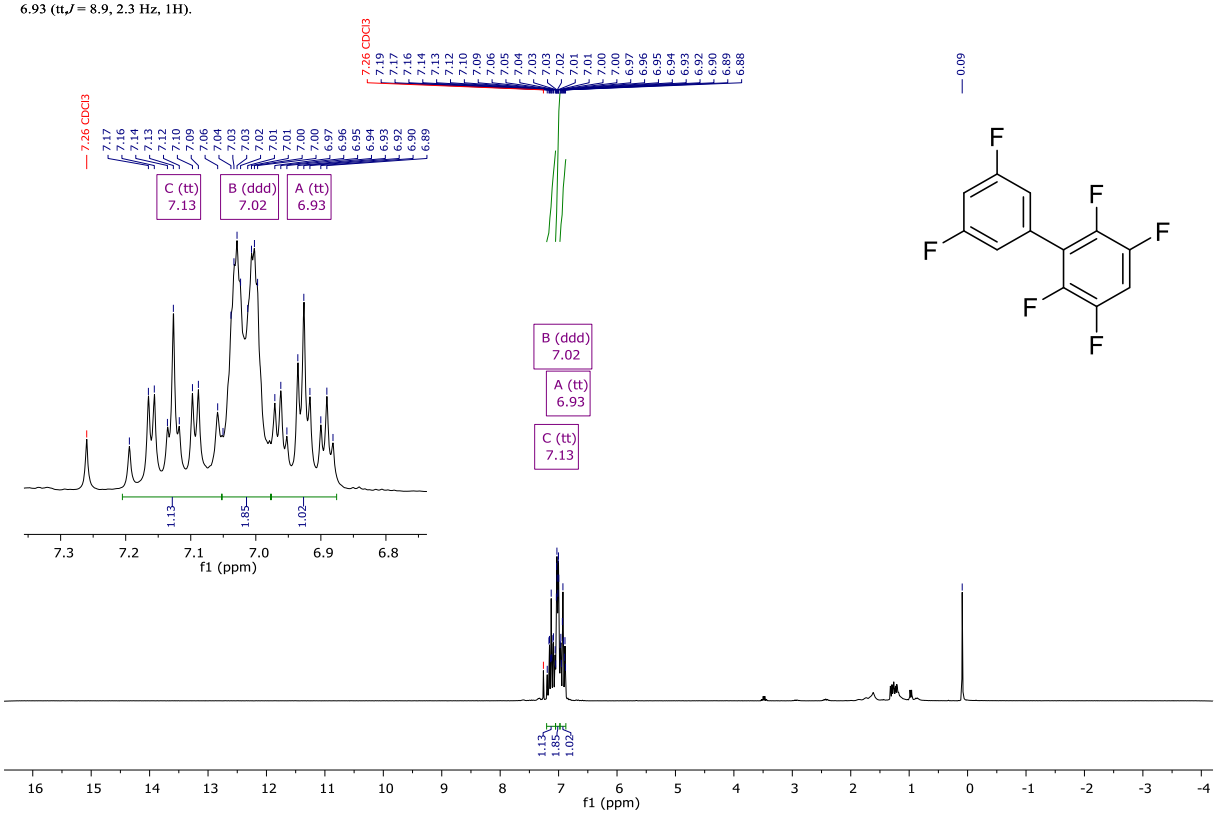


Figure S7 ^{1}H NMR: 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform-d) δ -108.98 , -138.28 (dd, J = 21.8, 12.8 Hz), -143.32 (dd, J = 21.9, 12.9 Hz).

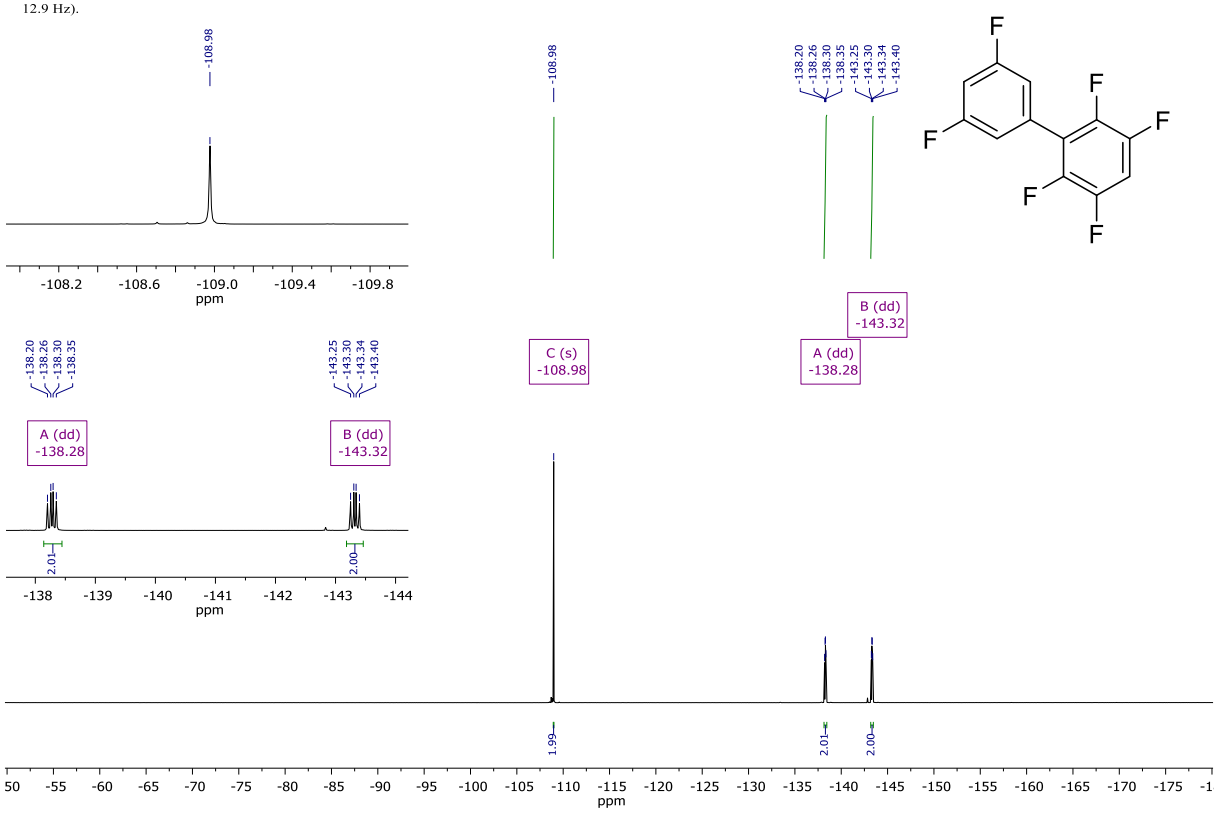


Figure S8 ^{19}F-NMR {^{1}H}: 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

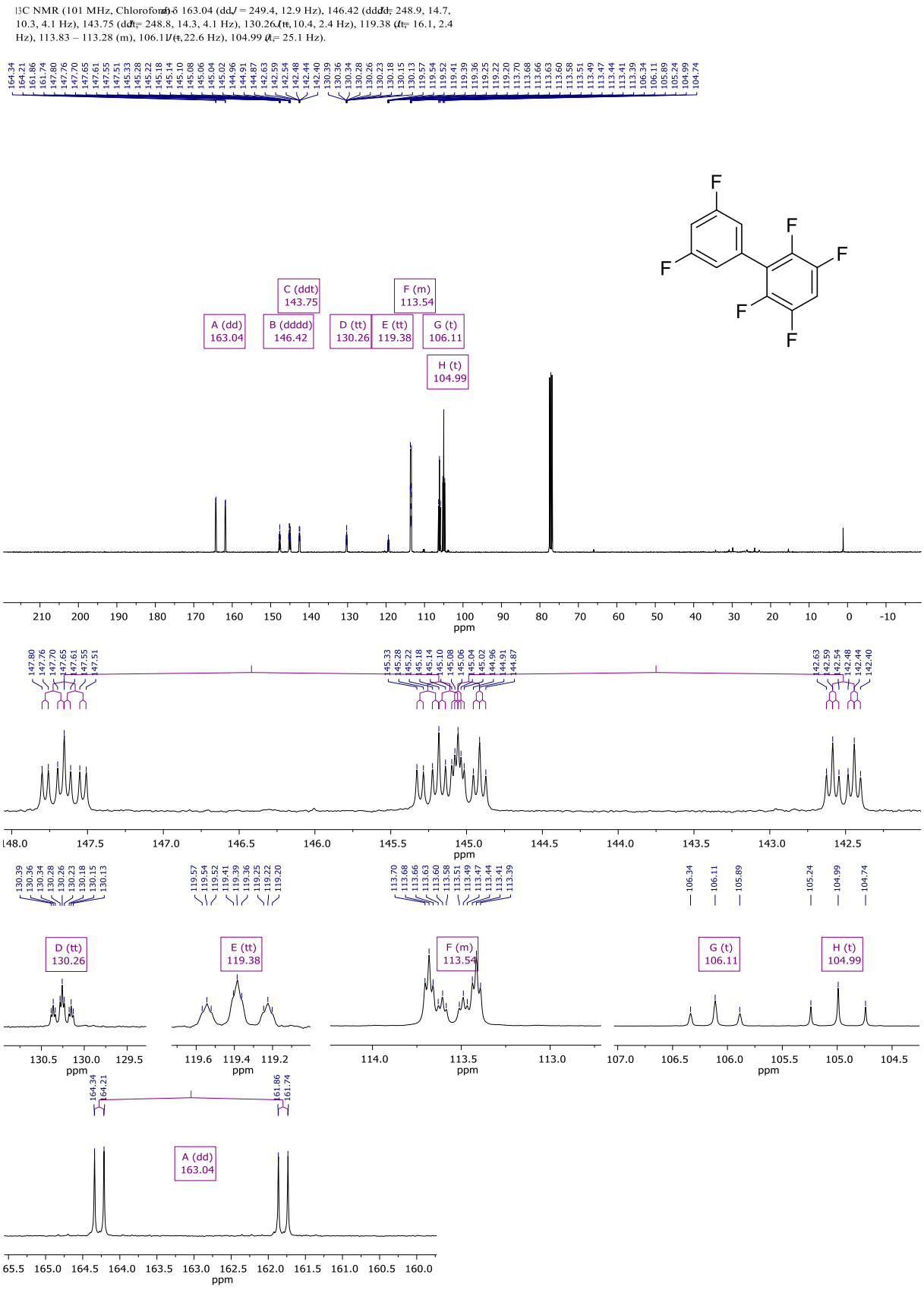


Figure S9 ^{13}C NMR: 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

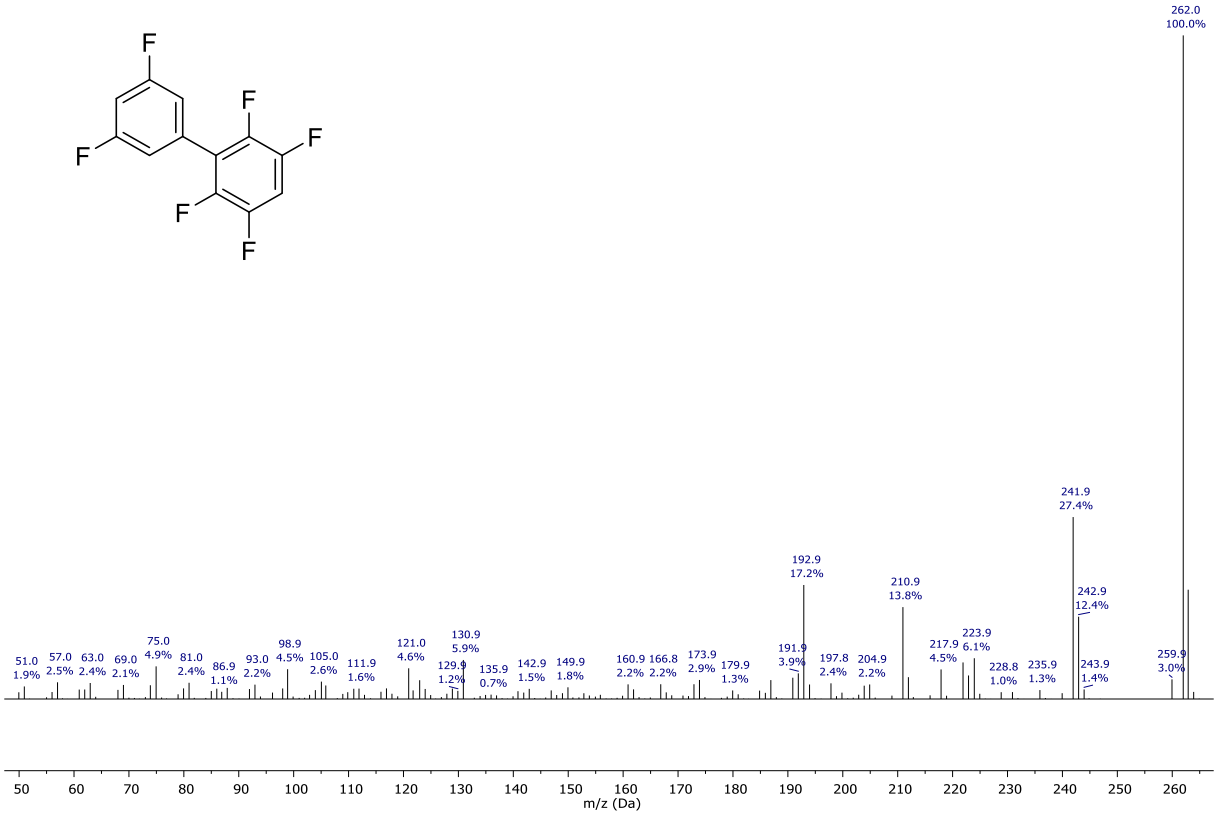


Figure S10 EI-Spectrum (EI⁺): 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

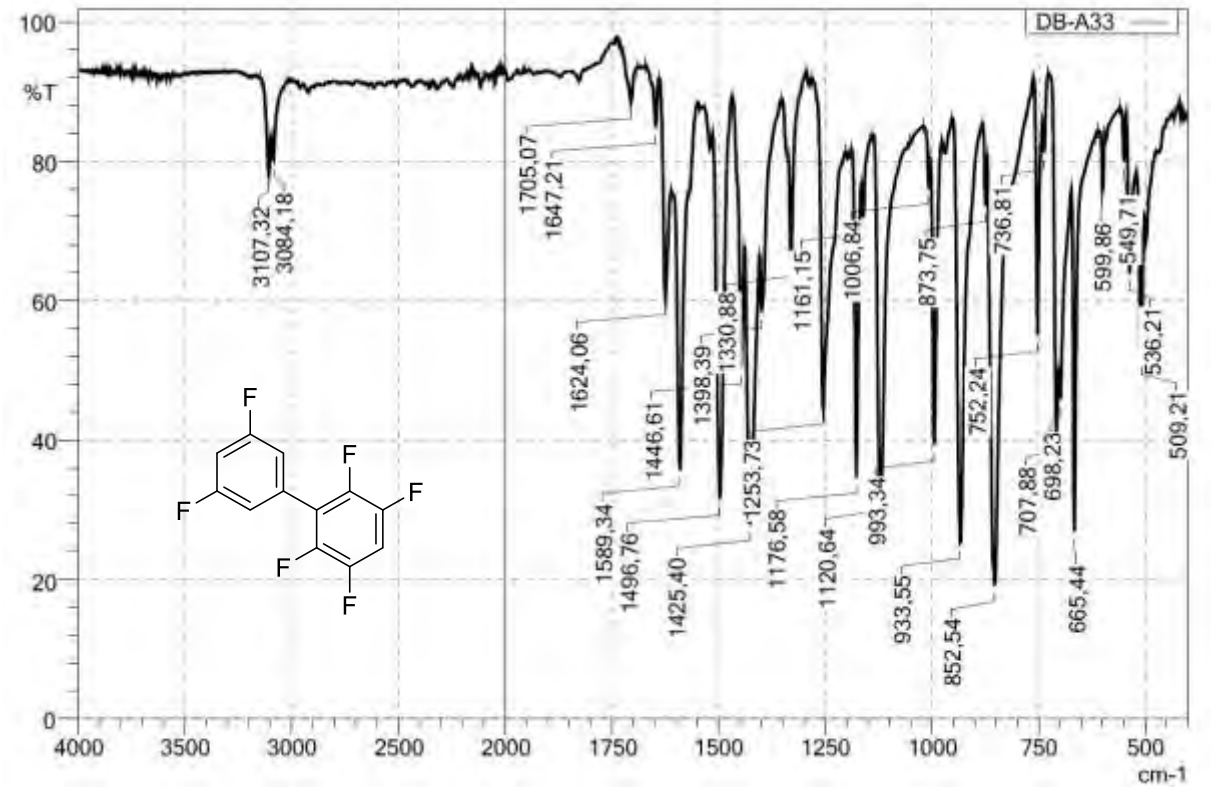


Figure S11 IR (ATR)-Spectrum: 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl (11)

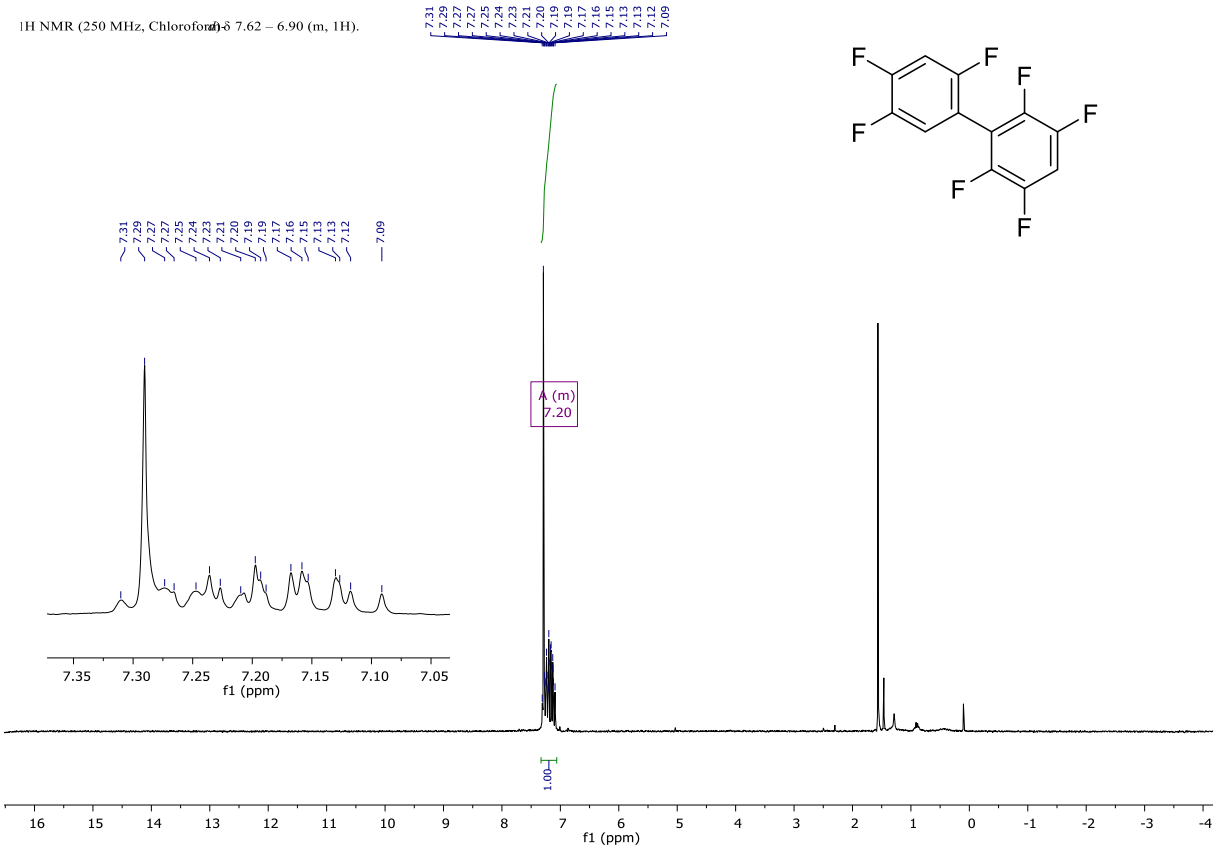


Figure S12 ^{1}H-NMR: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

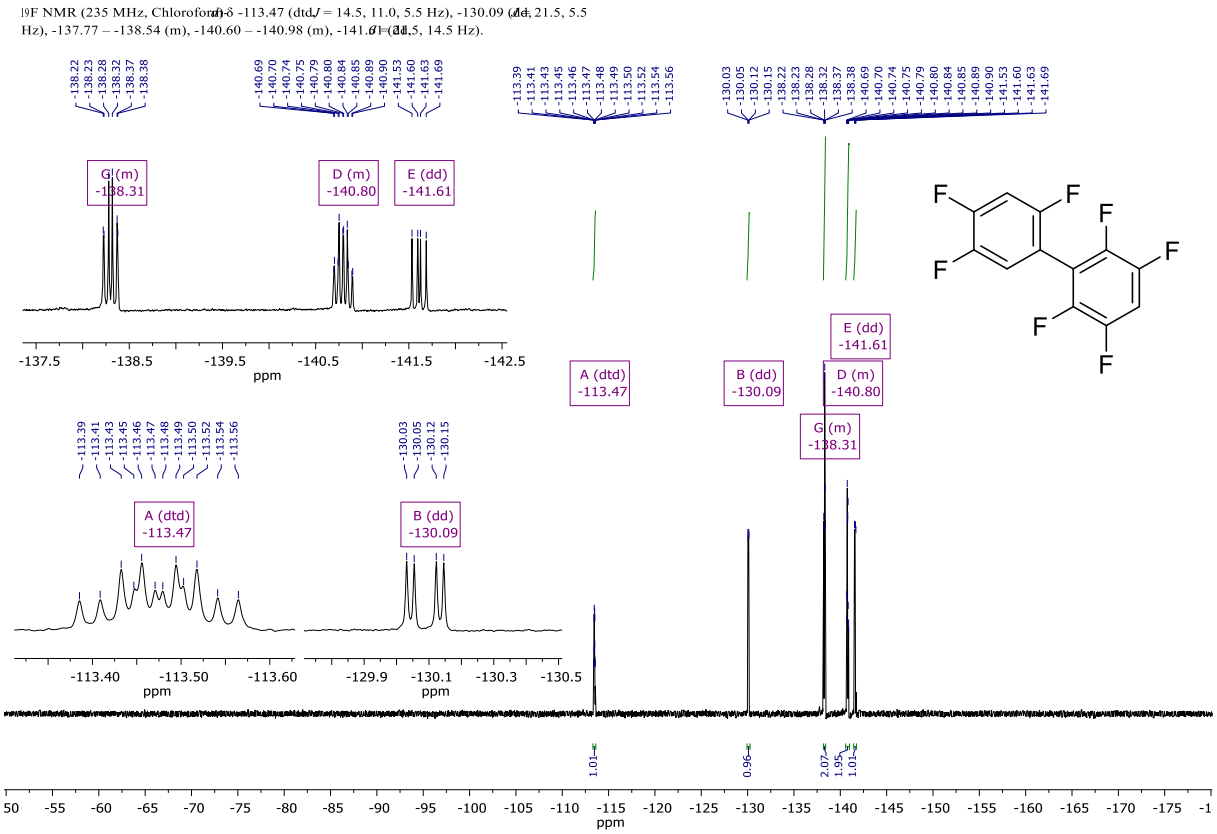


Figure S13 ^{19}F-NMR {^{1}H}: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

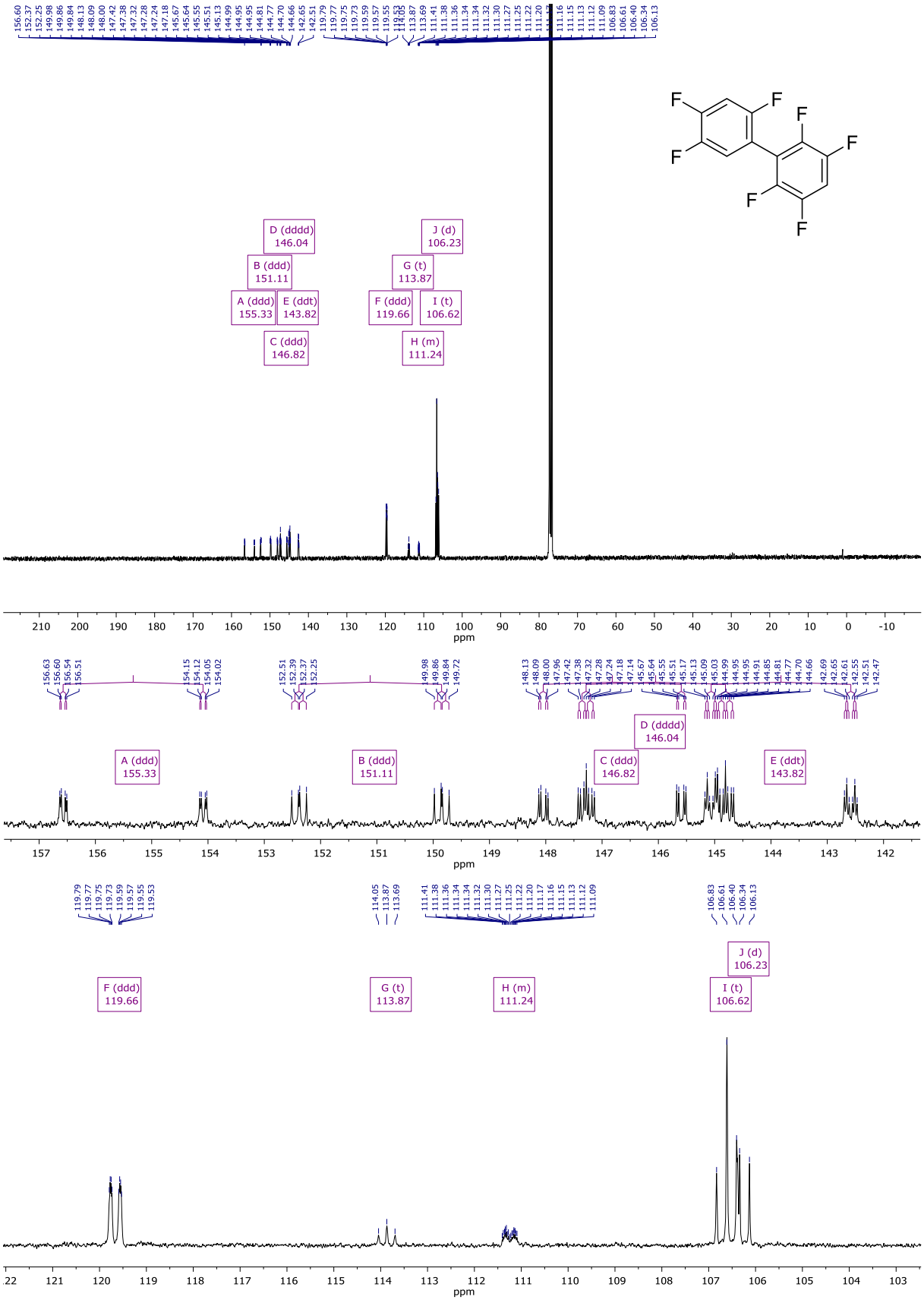


Figure S14^{13}C NMR: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

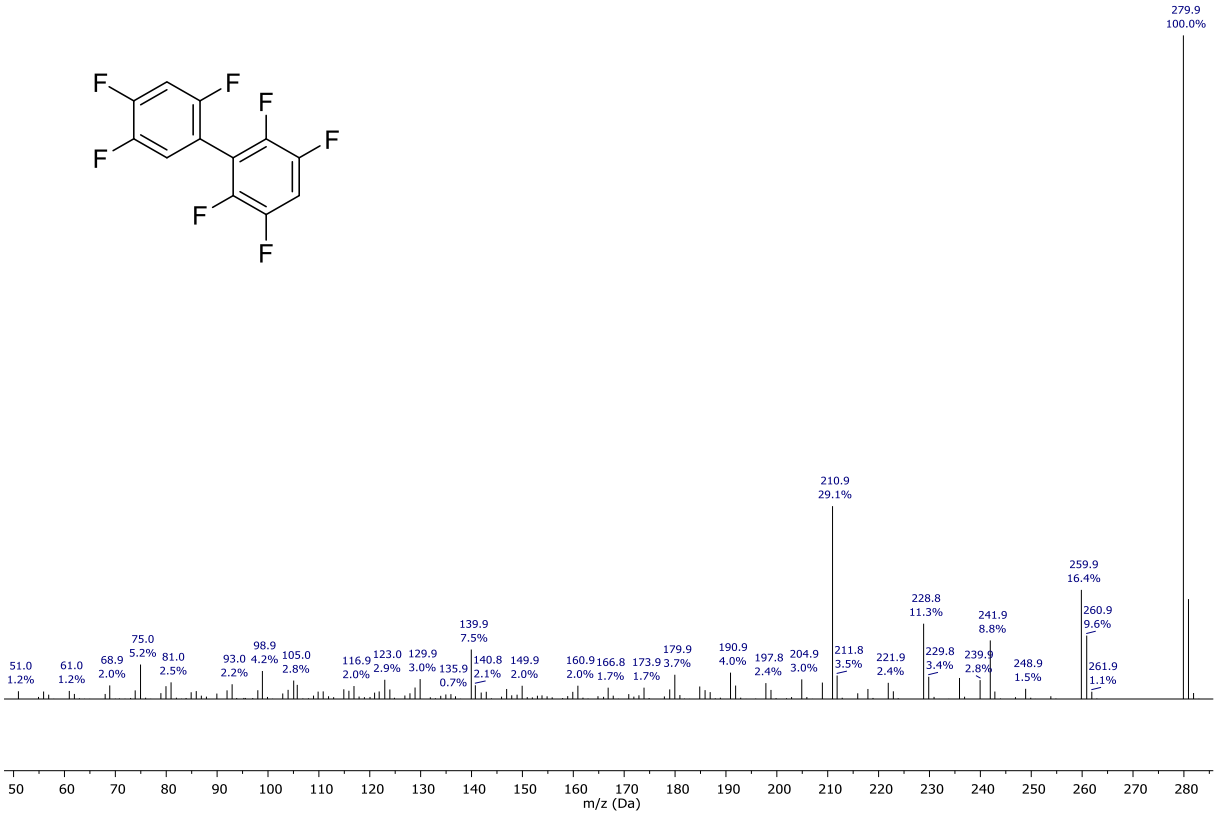


Figure S15 EI-Spectrum (EI⁺): 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

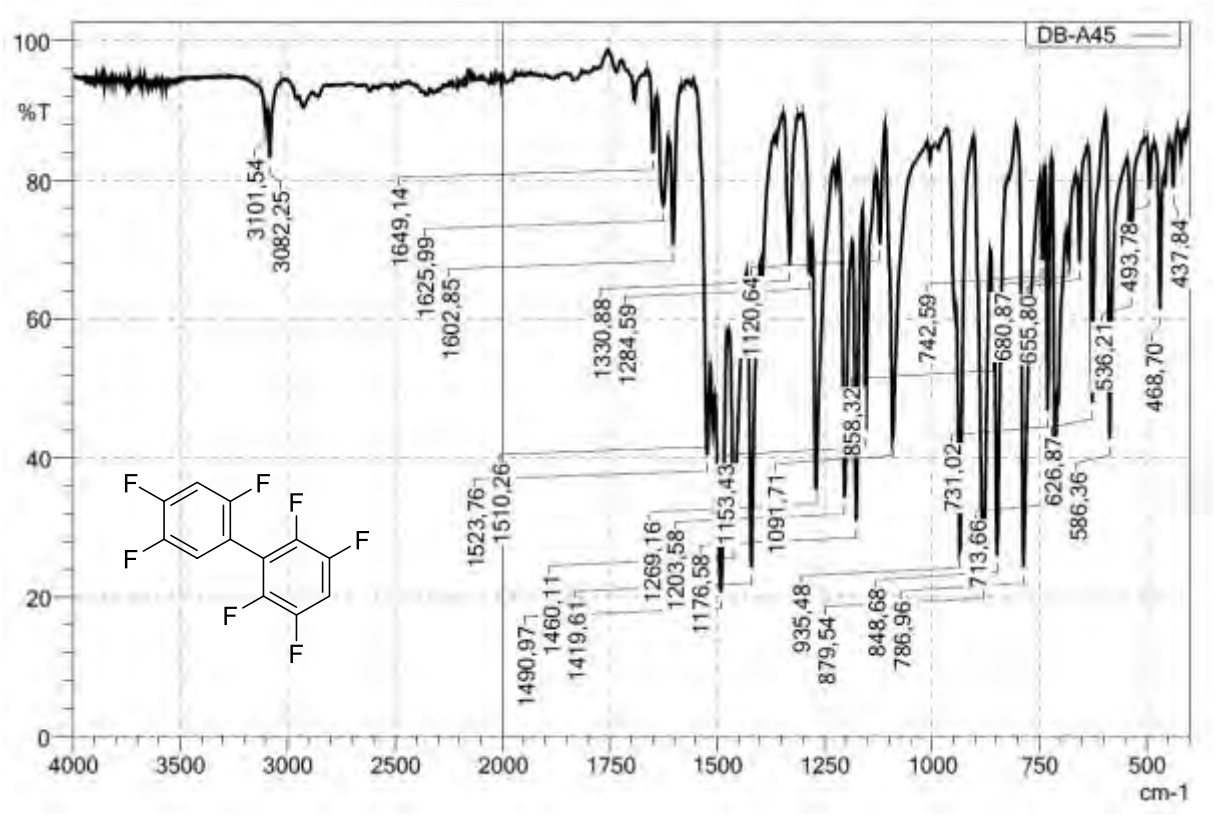


Figure S16 IR (ATR)-Spectrum: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl (12)

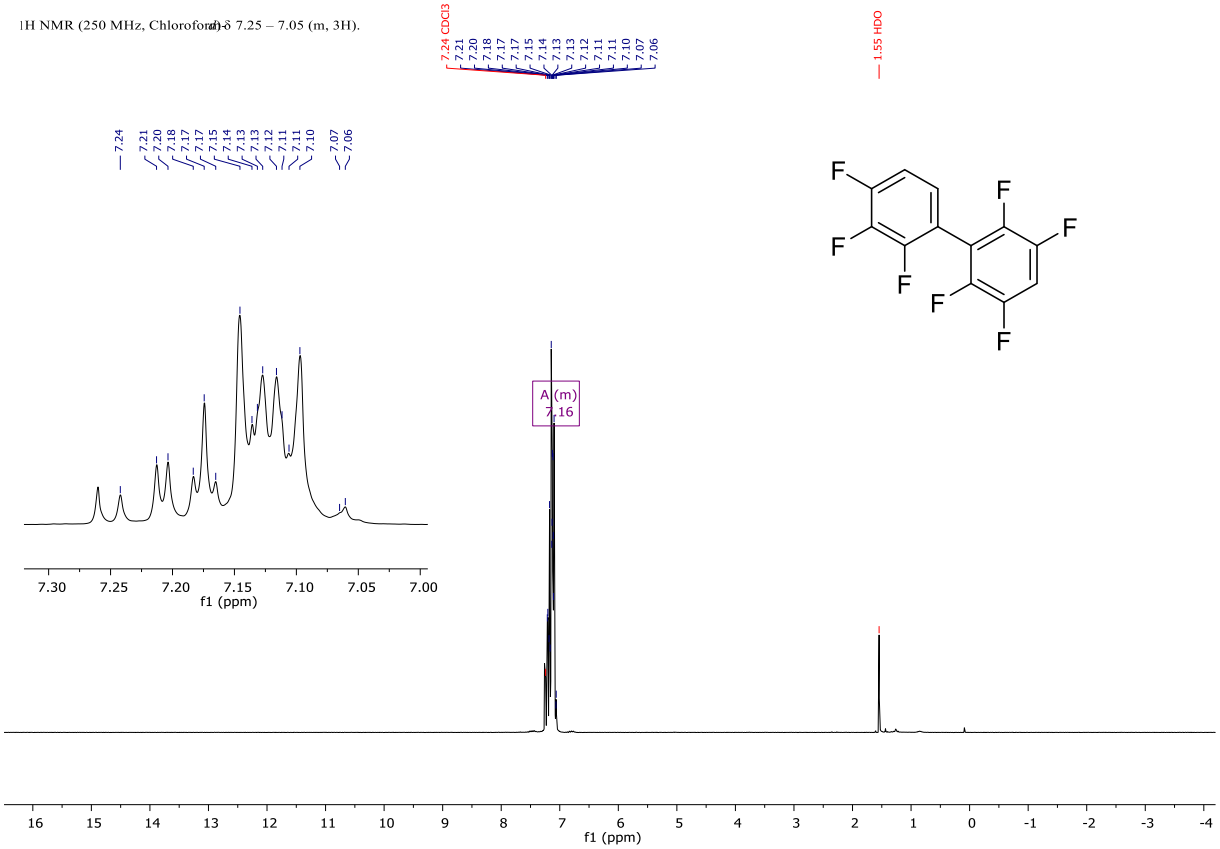


Figure S17 ^{1}H-NMR: 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl

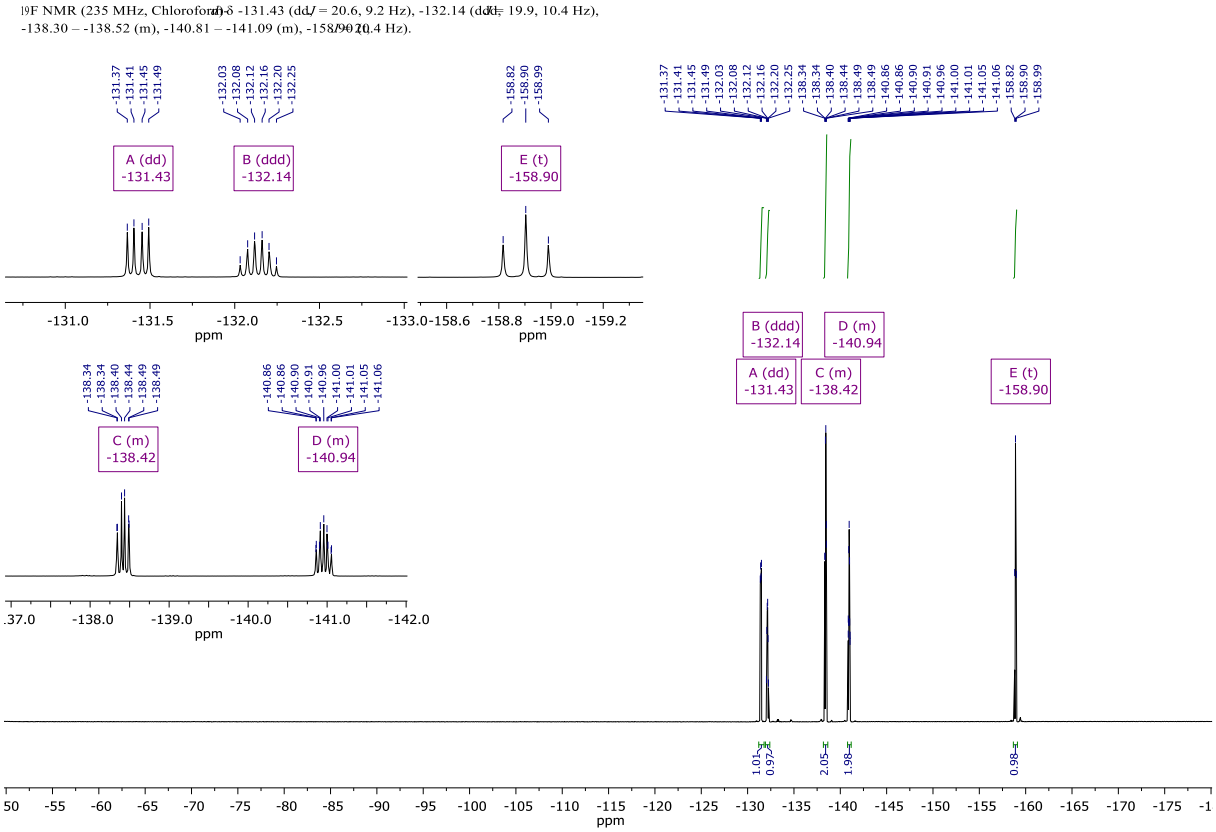


Figure S18 ^{19}F-NMR {^{1}H}: 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl

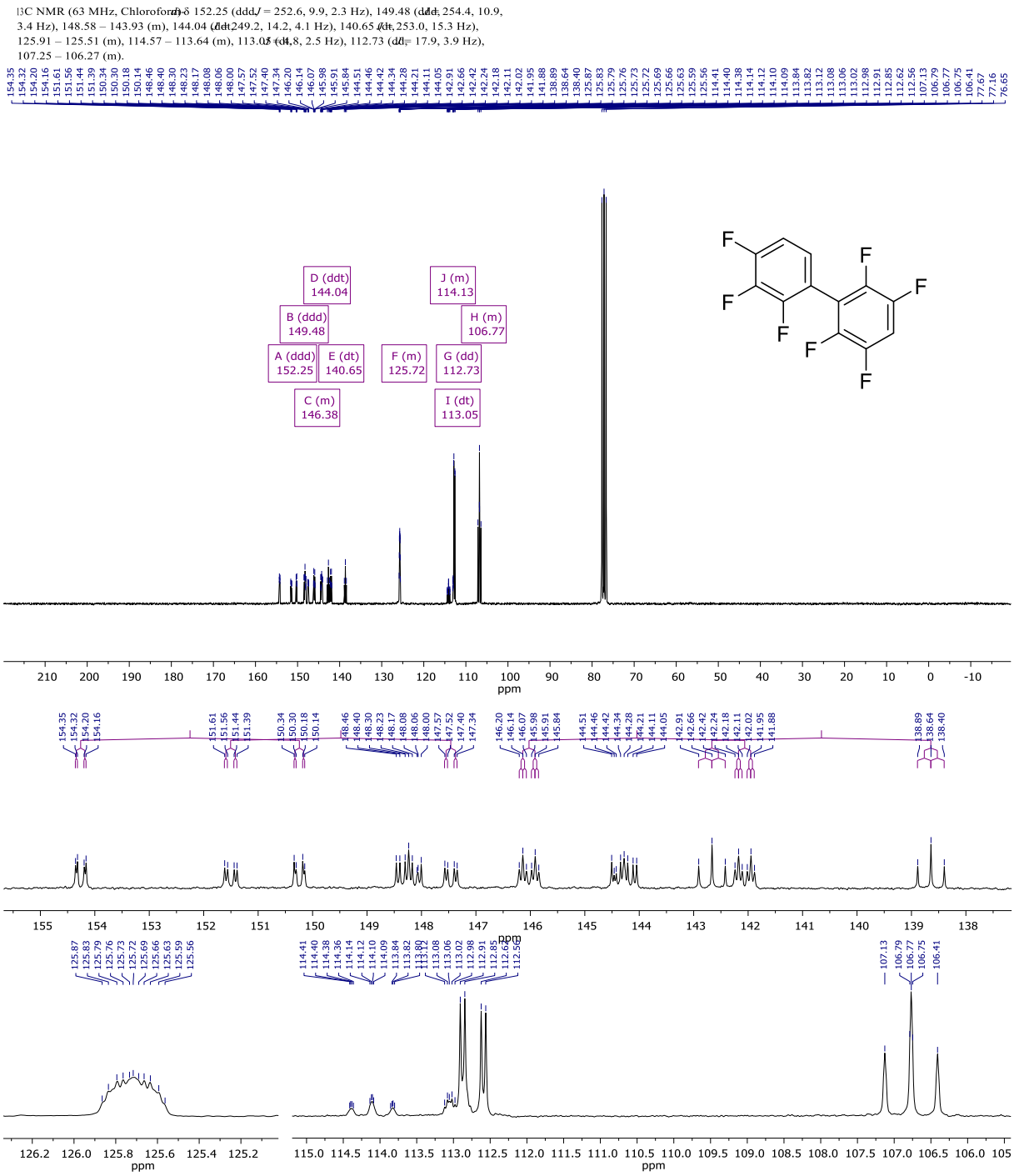


Figure S19 ^{13}C NMR: 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl

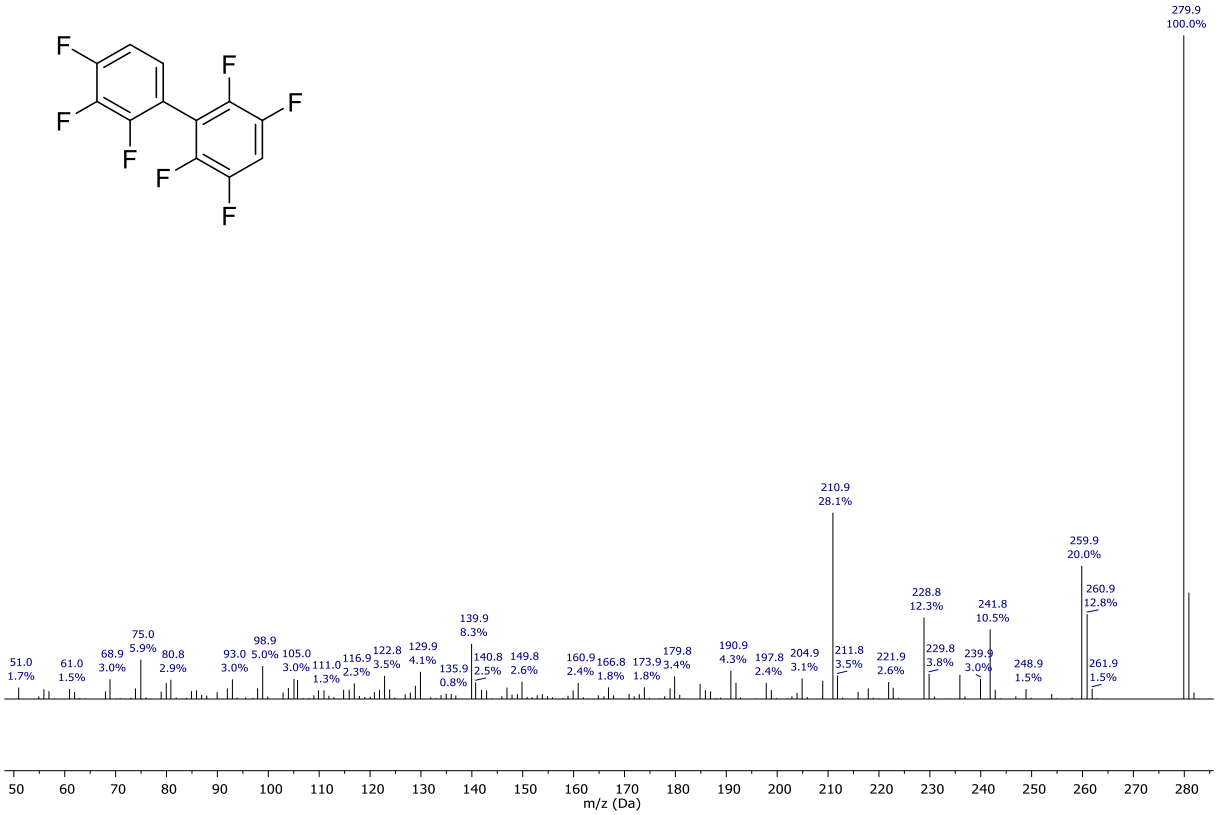


Figure S20 EI-Spectrum (EI⁺): 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl

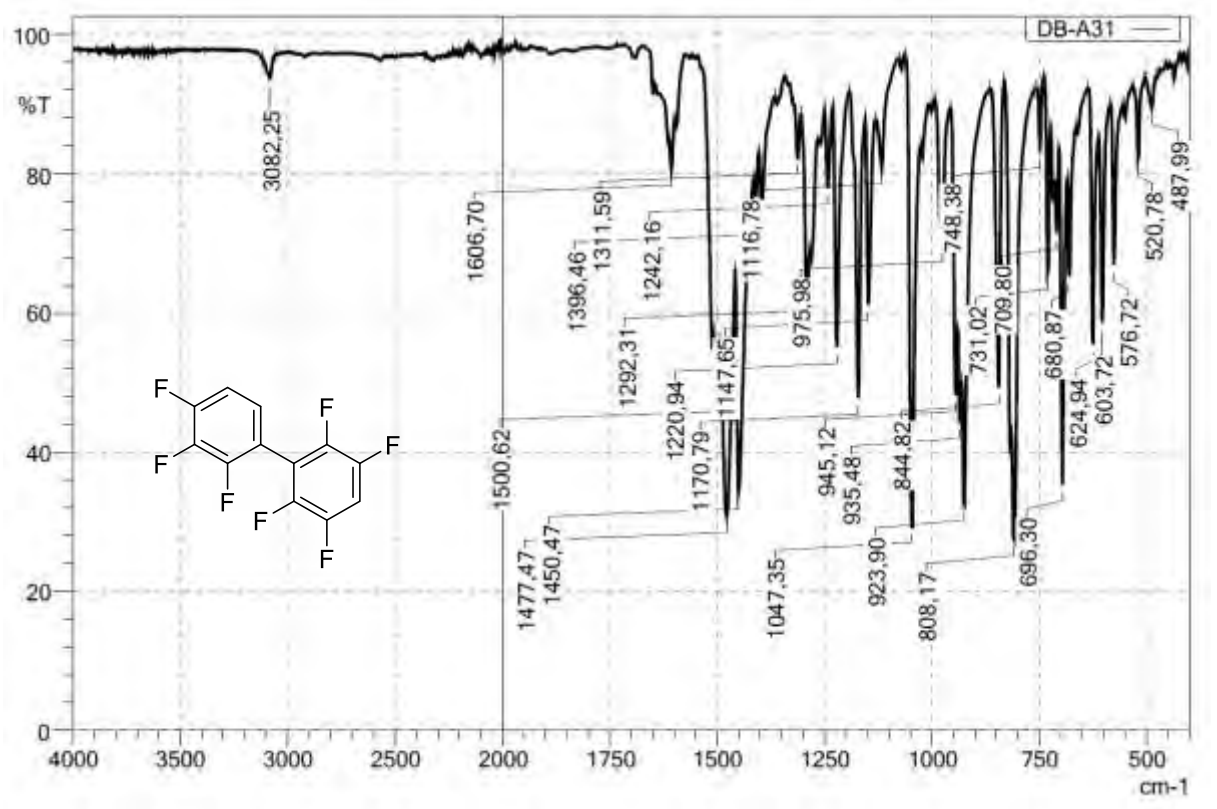


Figure S21 IR (ATR)-Spectrum: 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl

2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl (13)

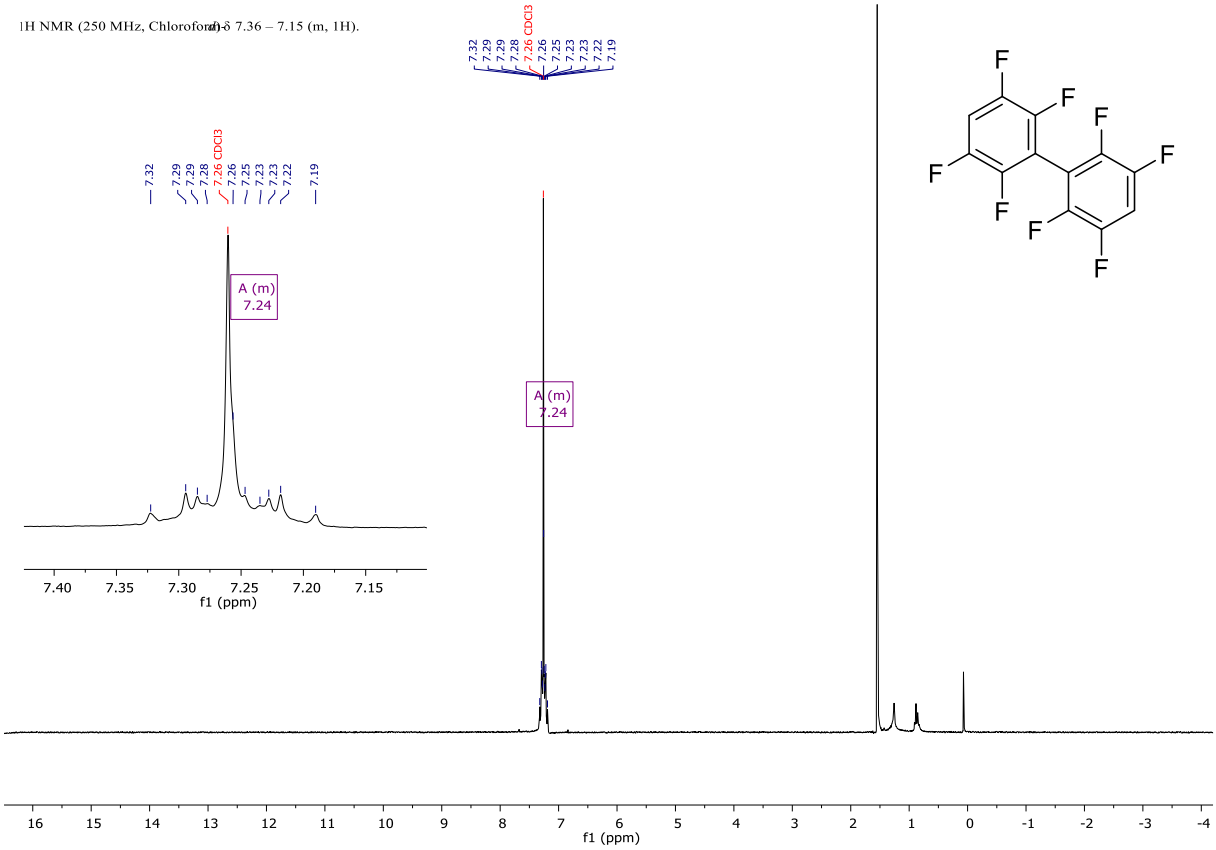


Figure S22 ^{1}H-NMR: 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

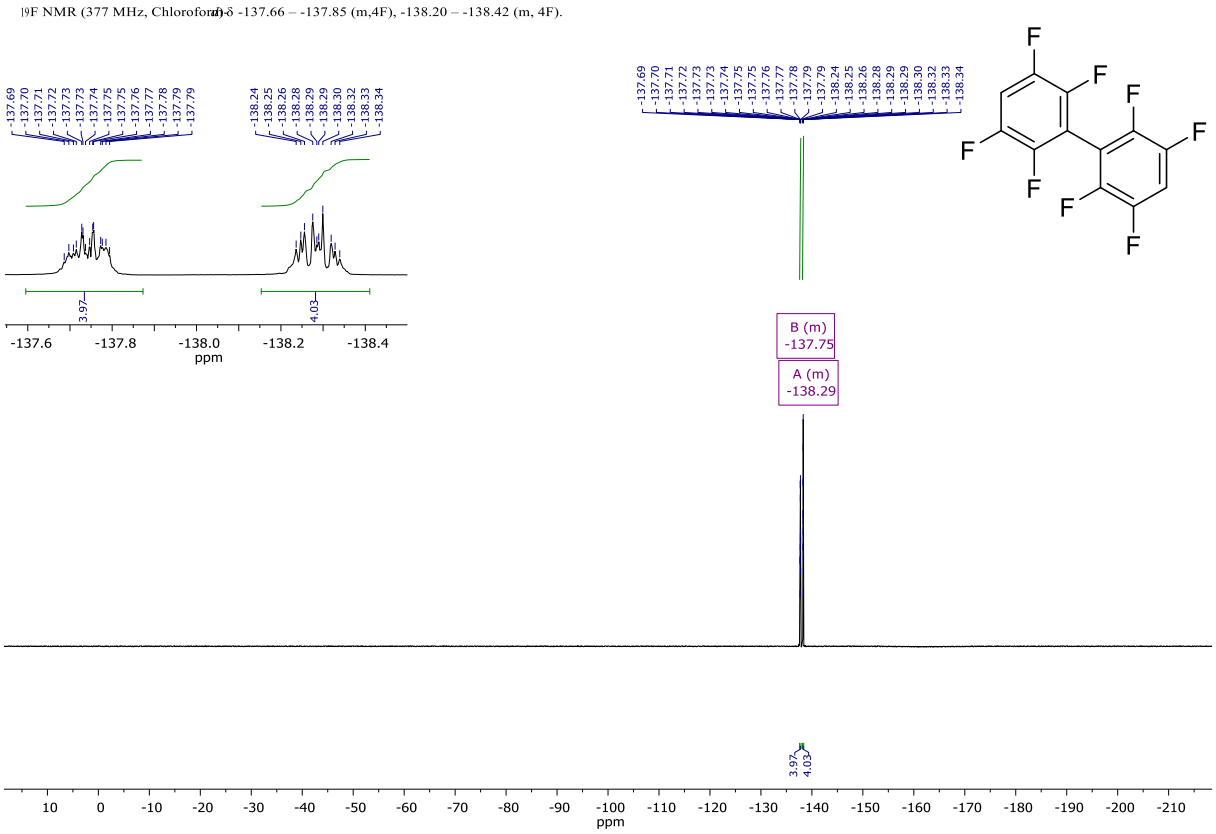


Figure S23 ^{19}F-NMR {^{1}H}: 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

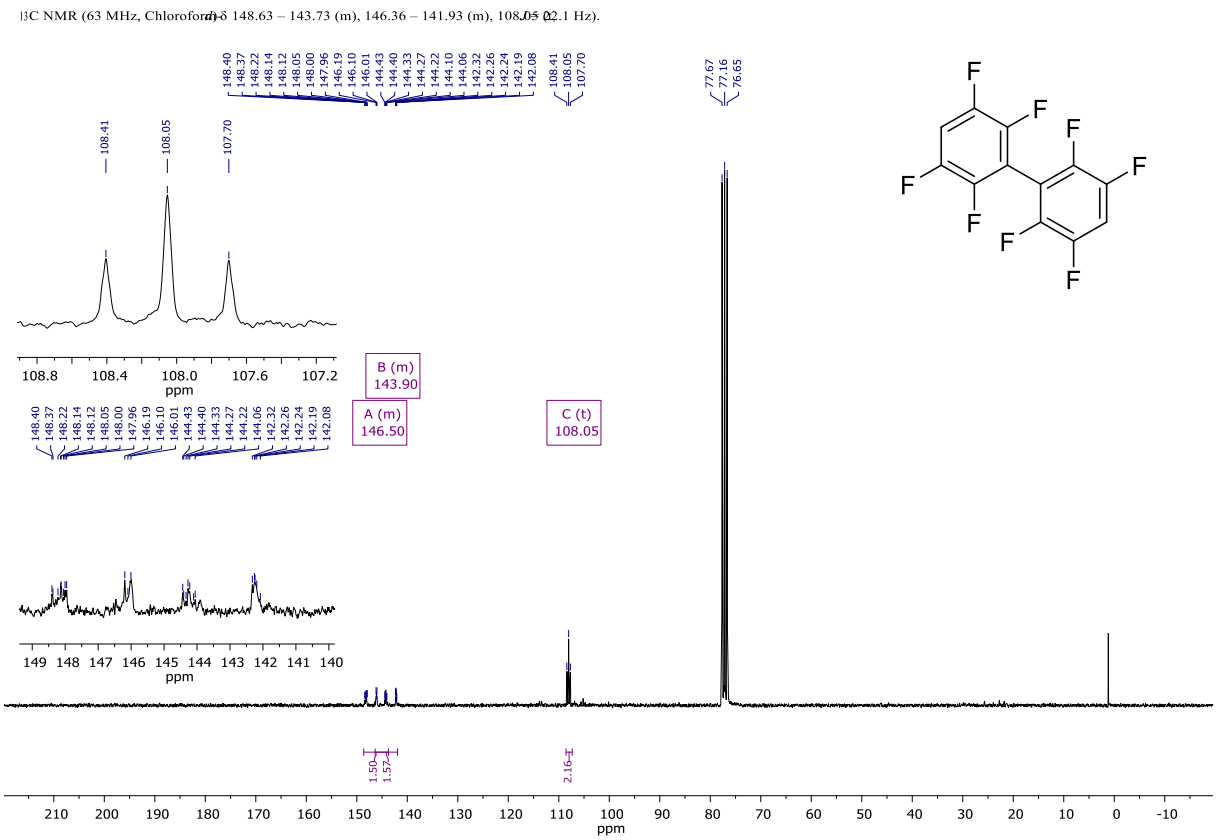


Figure S24 ^{13}C NMR: 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

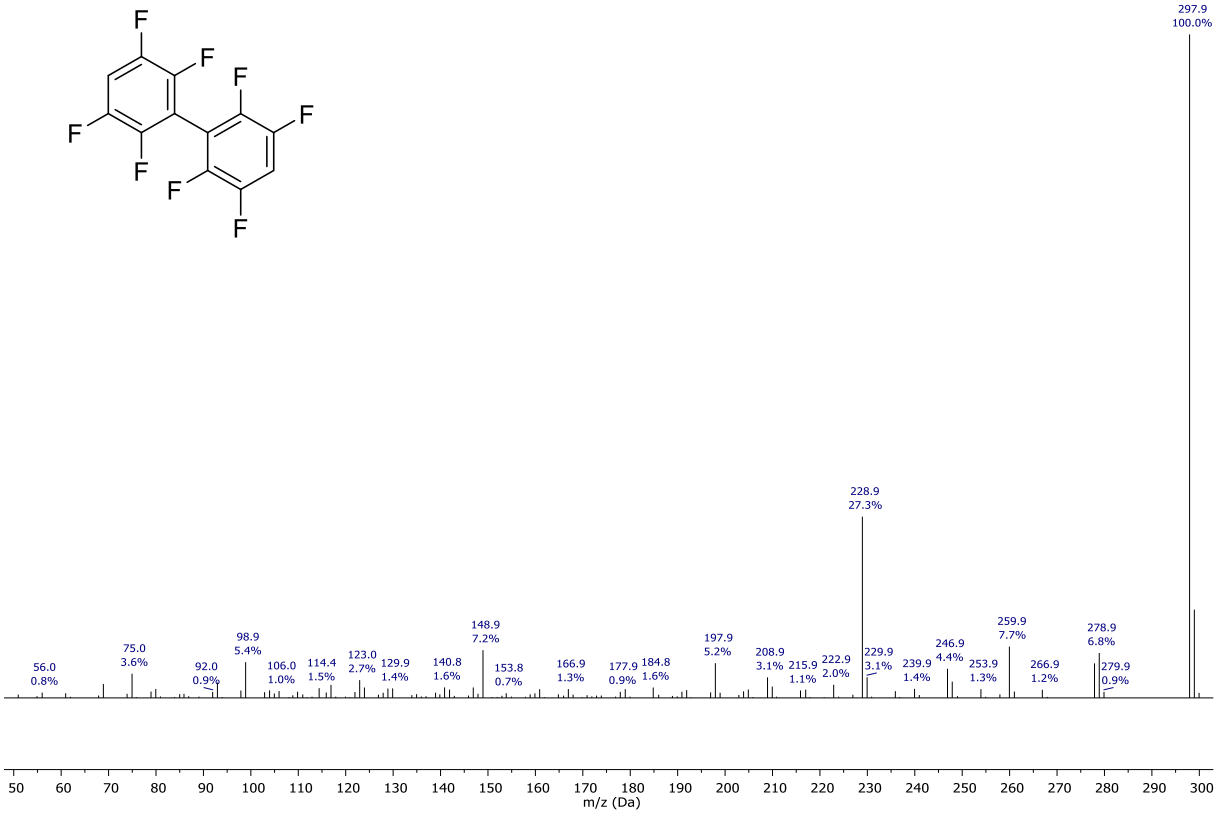


Figure S25 EI-Spectrum (EI$^+$): 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

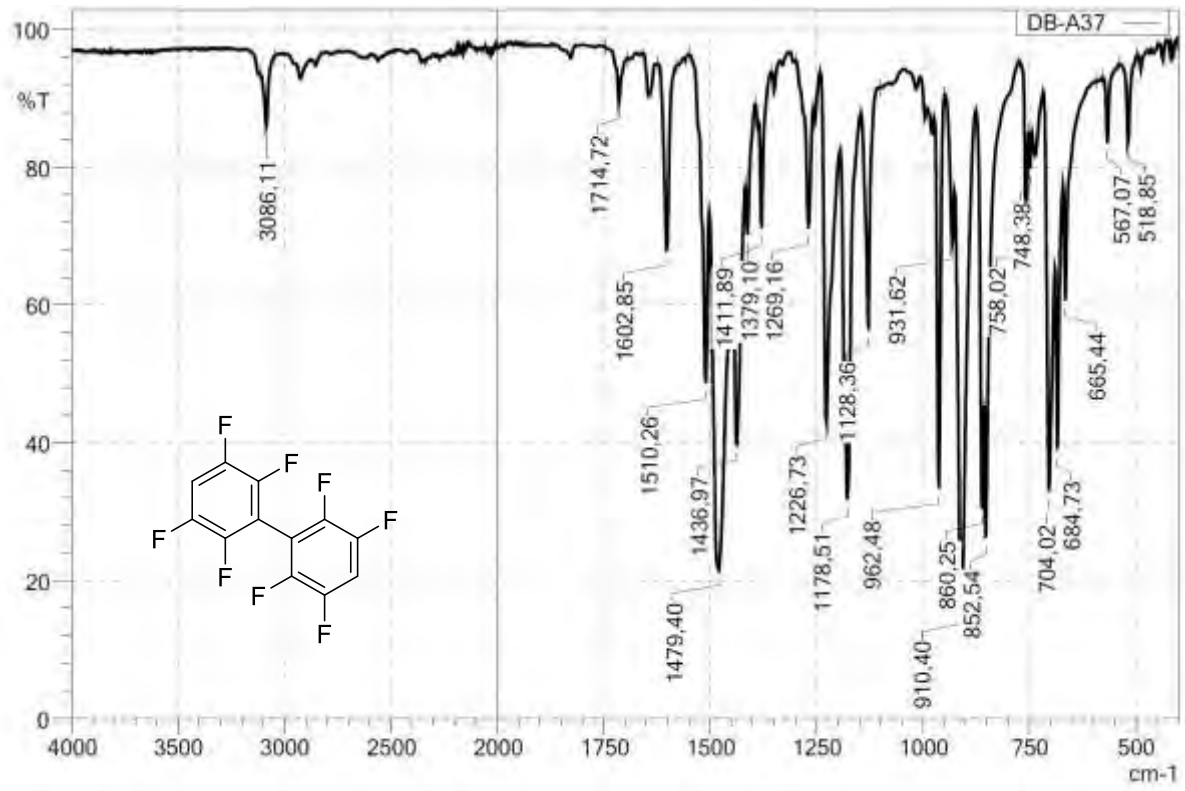


Figure S26 IR (ATR)- Spectrum: 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

2,2',3,3',4,5,5',6'-Octafluoro-1,1'-bipheny (20)

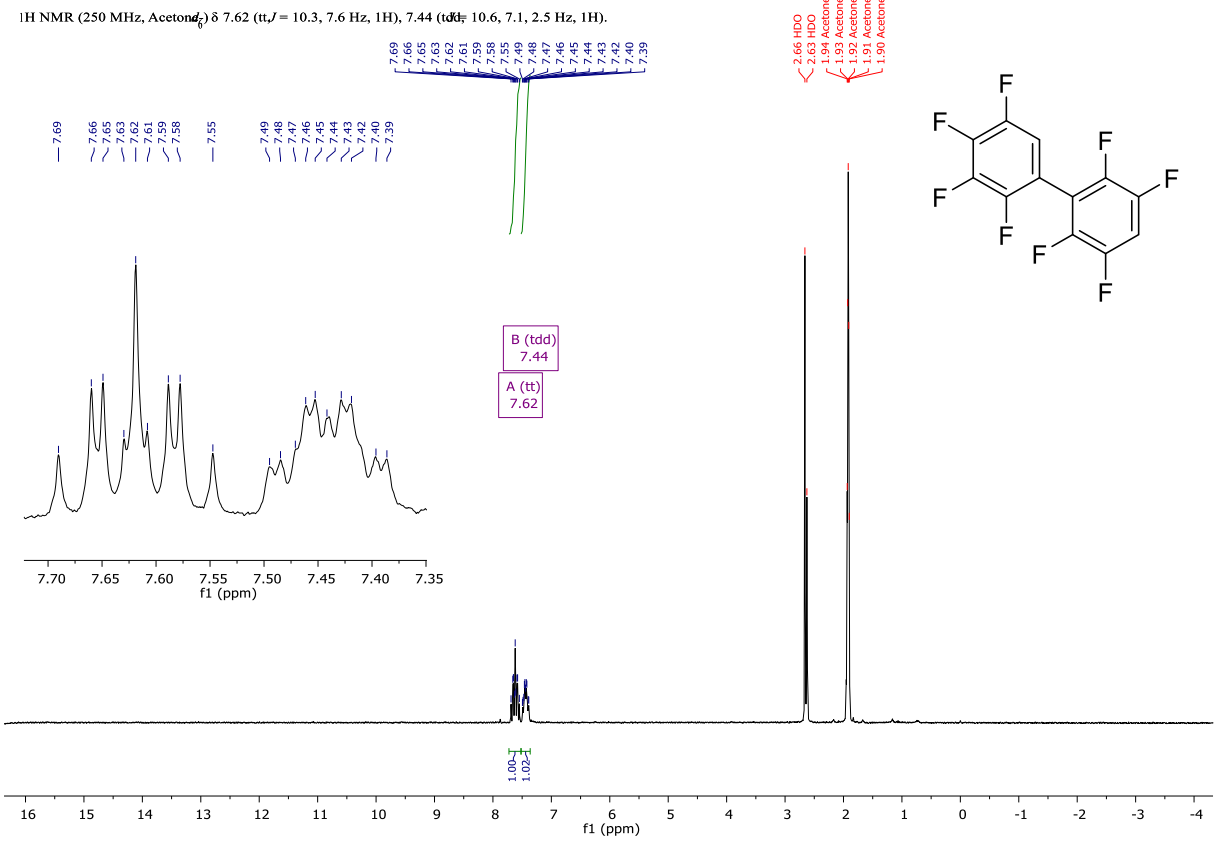


Figure S27 ^{1}H-NMR: 2,2',3,3',4,5,5',6'-Octafluoro-1,1'-biphenyl

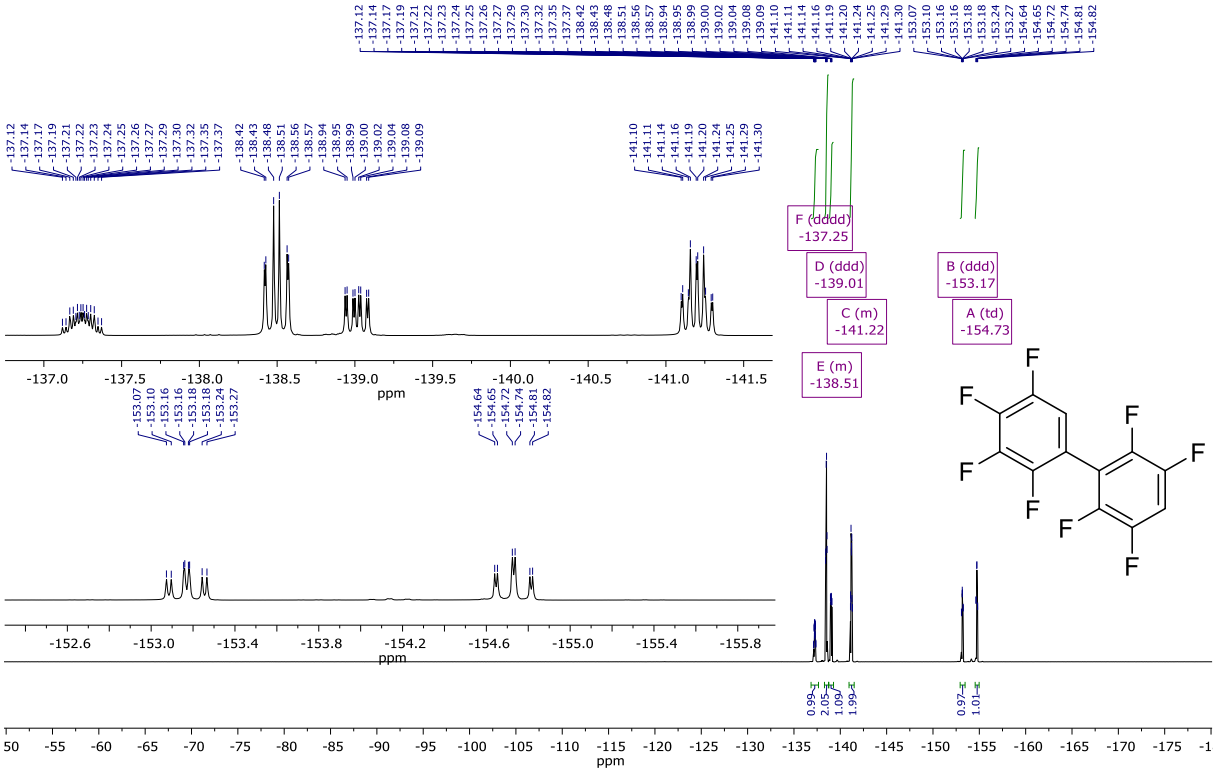


Figure S28 ^{19}F-NMR {^{1}H}: 2,2',3,3',4,5,5',6'-Octafluoro-1,1'-biphenyl

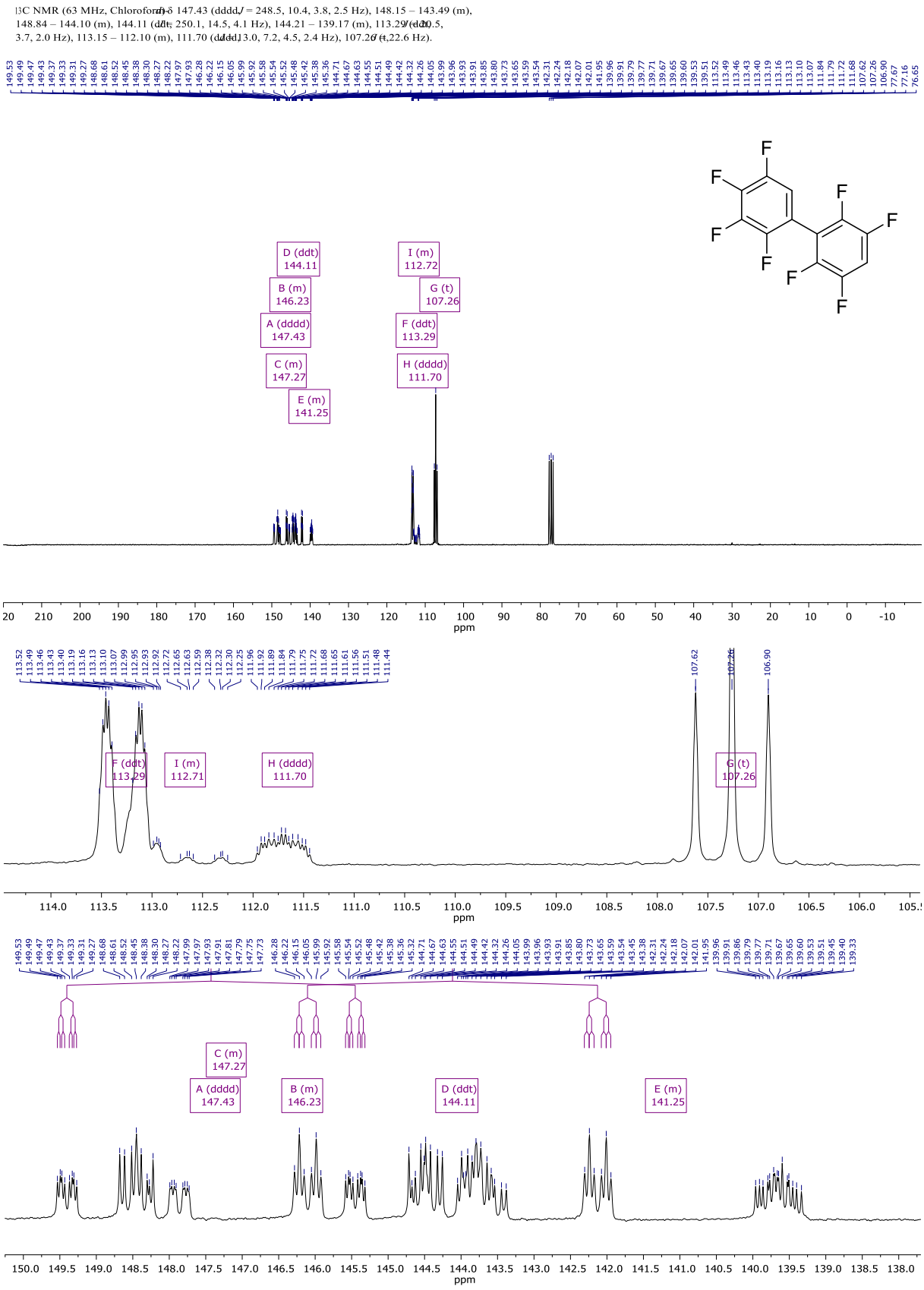


Figure S29 ^{13}C NMR: 2,2',3,3',4,5,5',6'-Octafluoro-1,1'-biphenyl

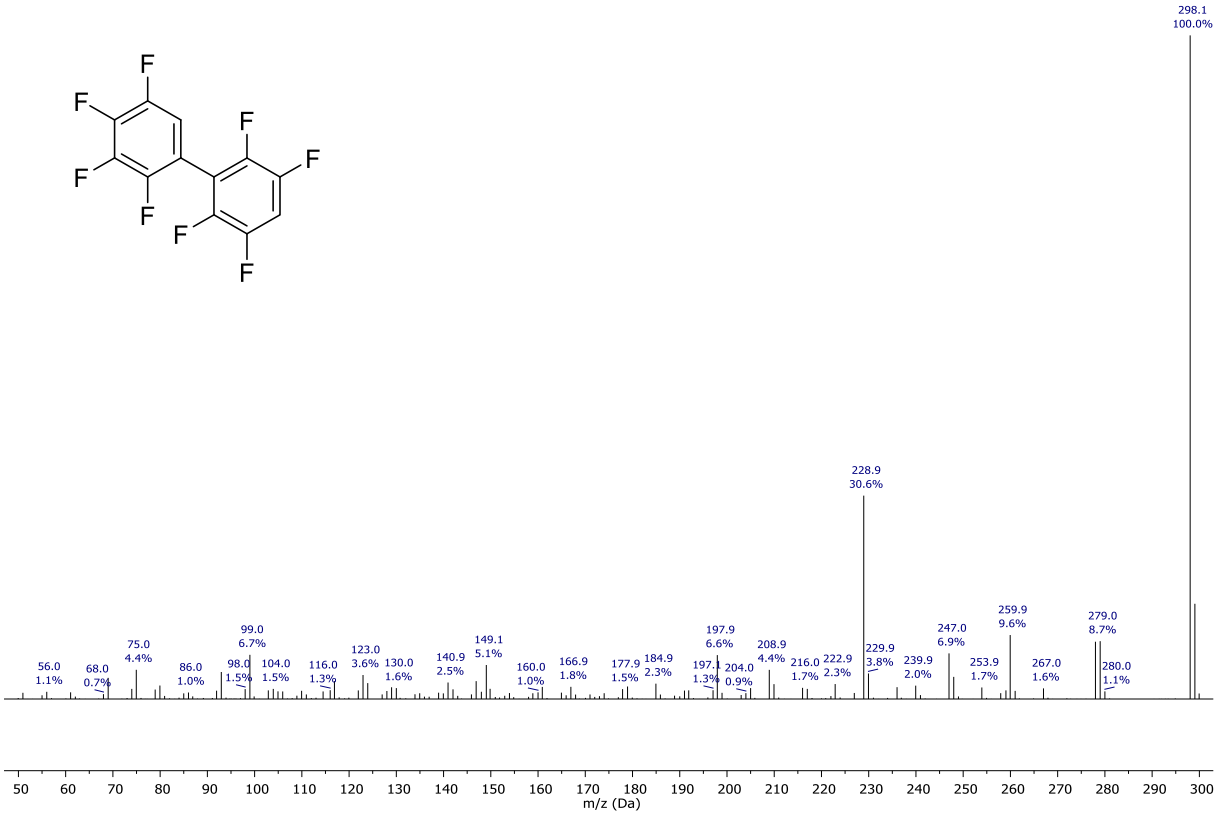


Figure S30 EI-Spectrum (EI$^+$): 2,2',3,3',4,5,5',6'-Octafluoro-1,1'-biphenyl

2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl (21)

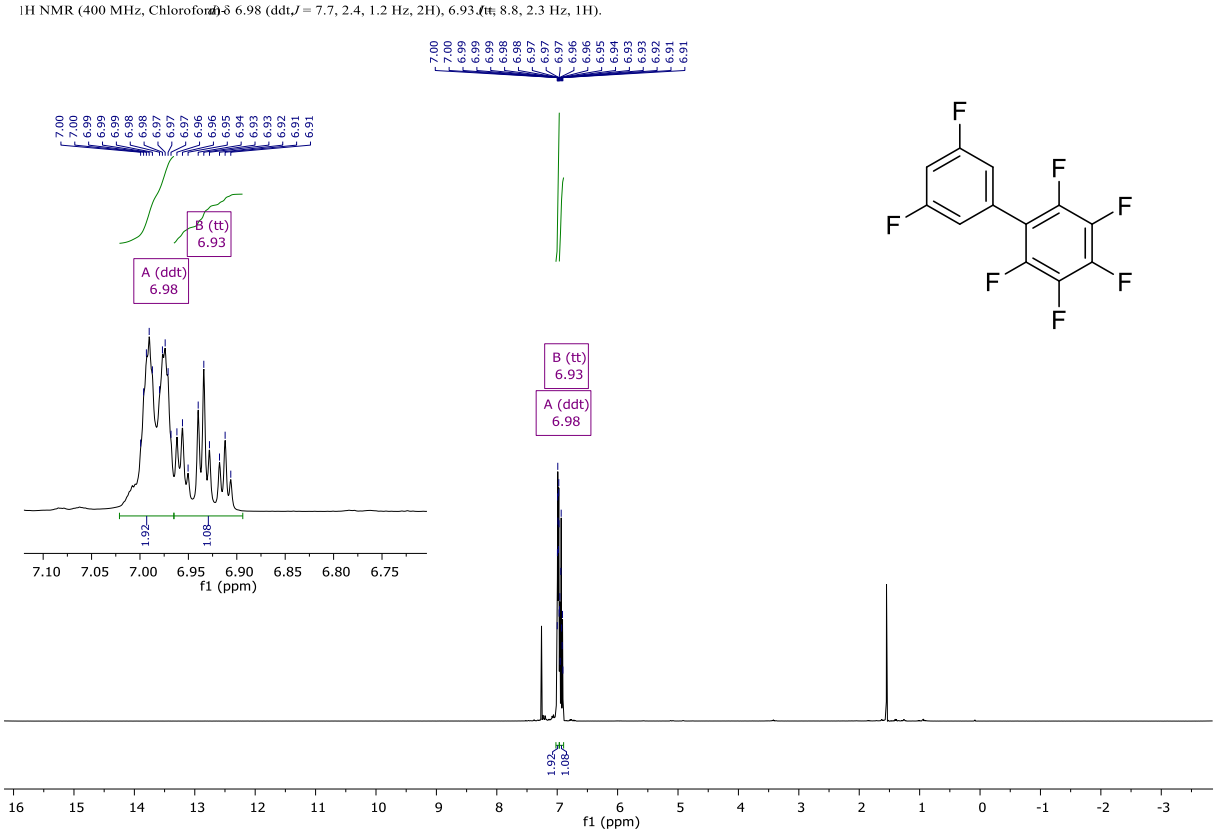


Figure S31 ^{1}H-NMR: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

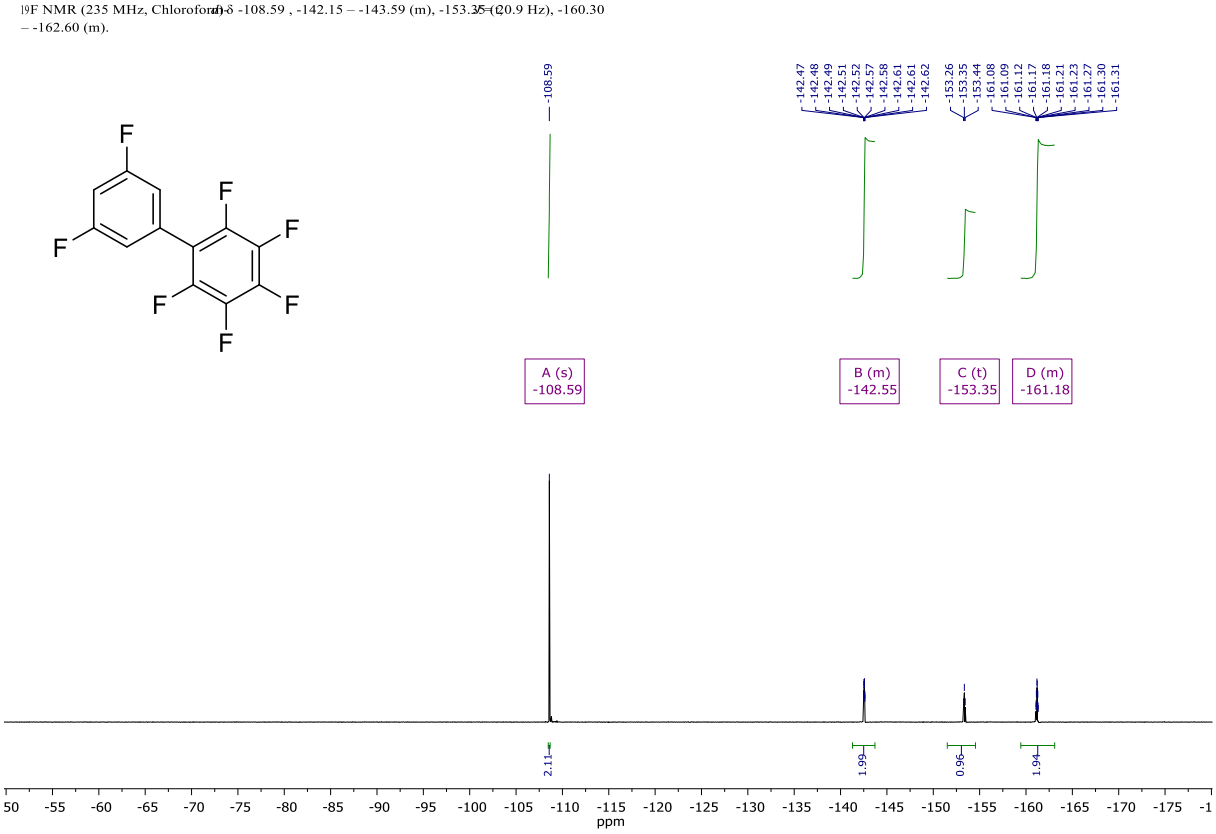


Figure S32 ^{19}F-NMR {^{1}H}: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

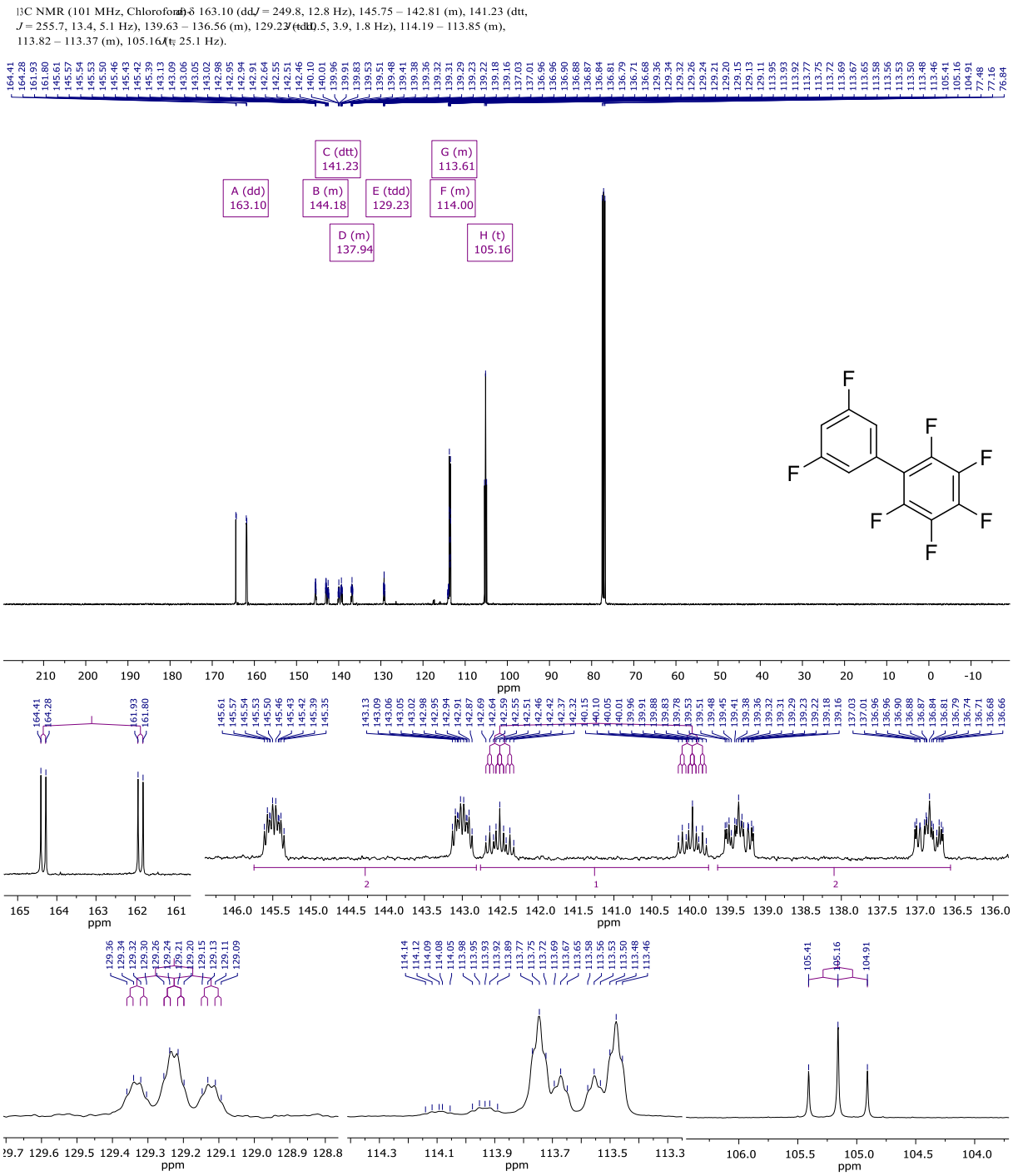


Figure S33 ^{13}C NMR: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

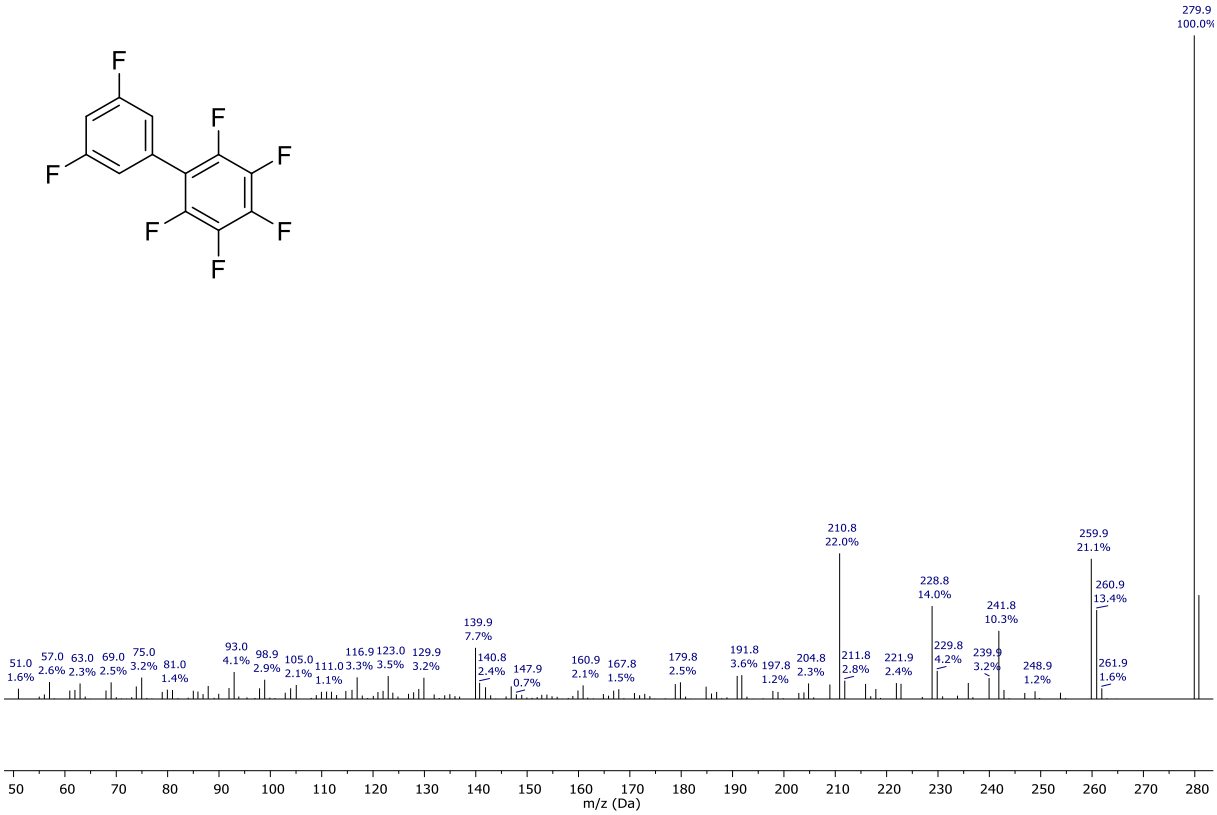


Figure S34 EI-Spectrum (EI⁺): 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

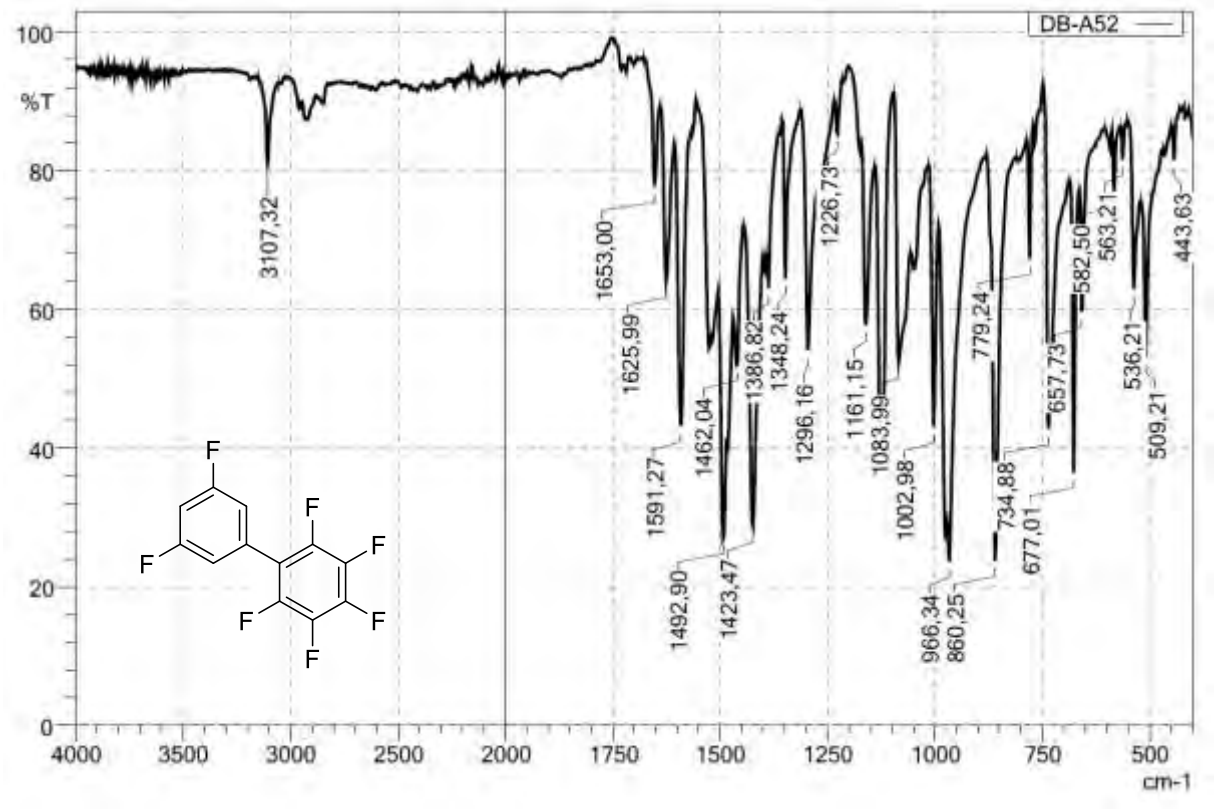


Figure S35 IR (ATR)-Spectrum: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl (22)

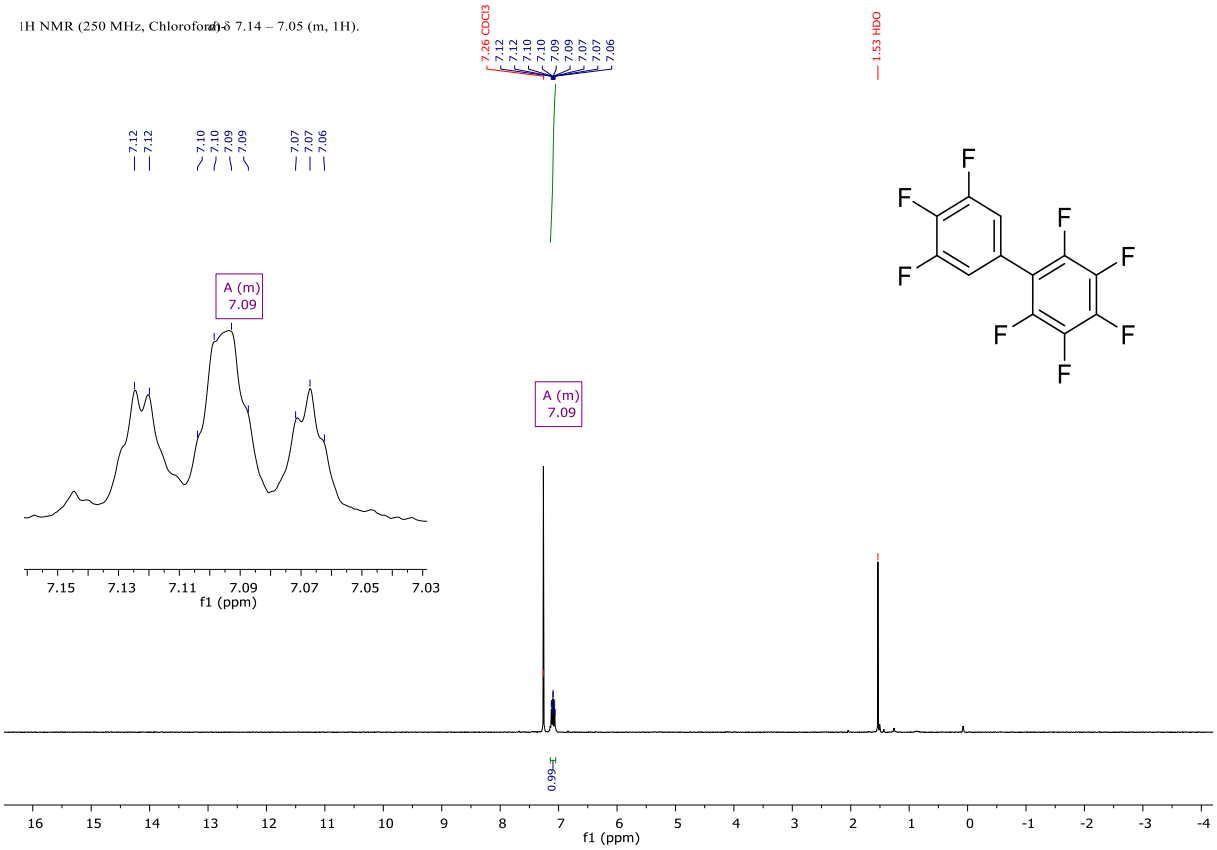


Figure S36 ^{1}H-NMR: 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

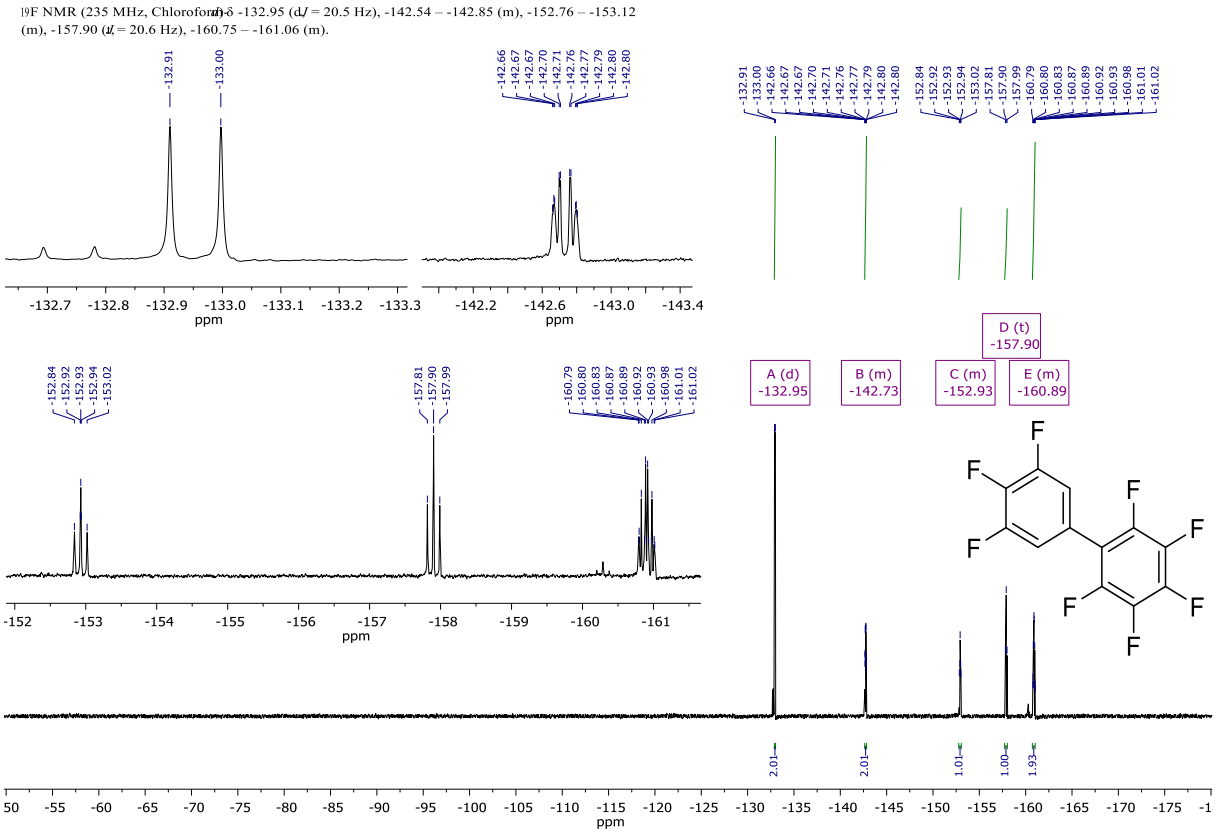


Figure S37 ^{19}F-NMR {^{1}H}: 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

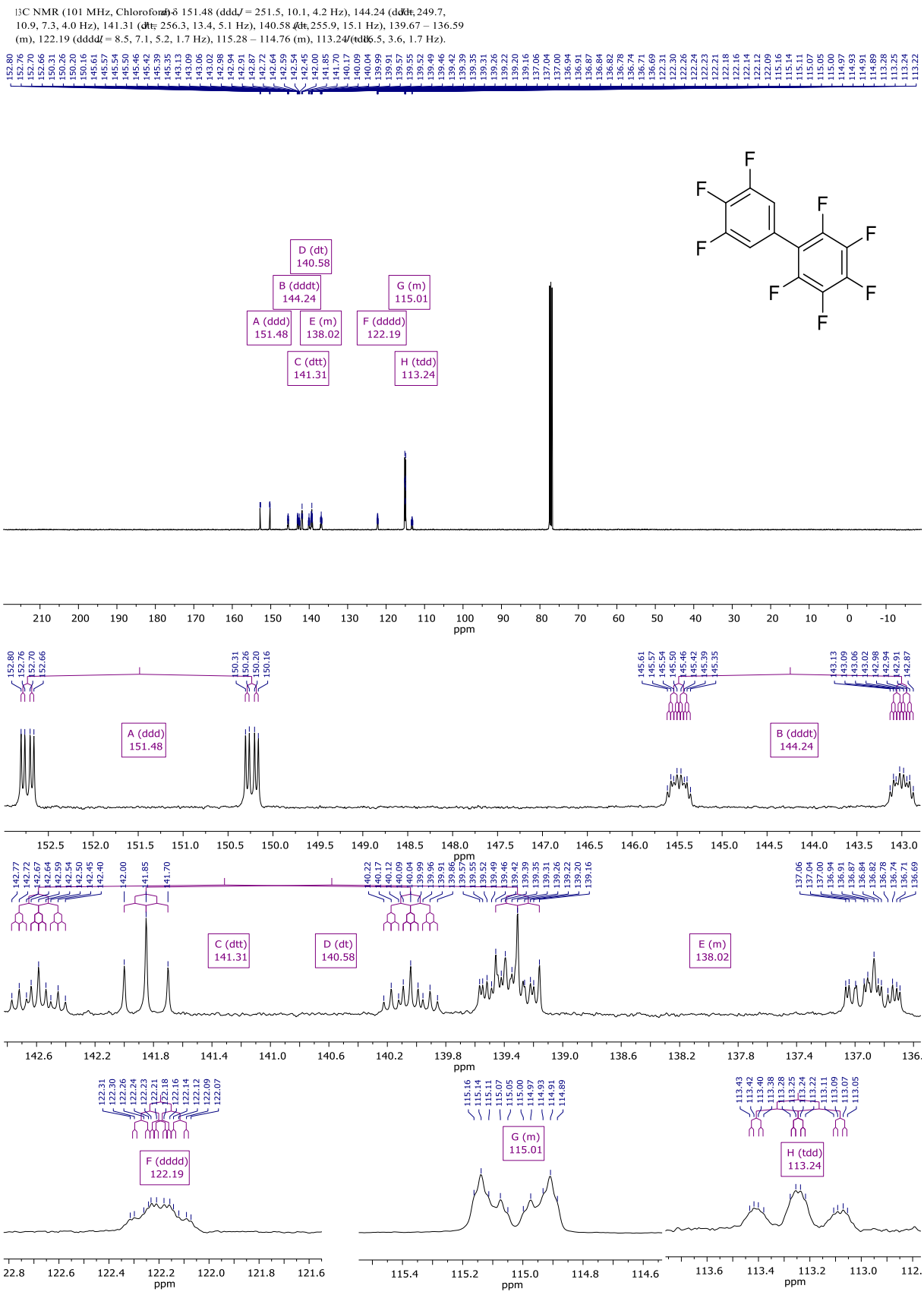


Figure S38 ^{13}C NMR: 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

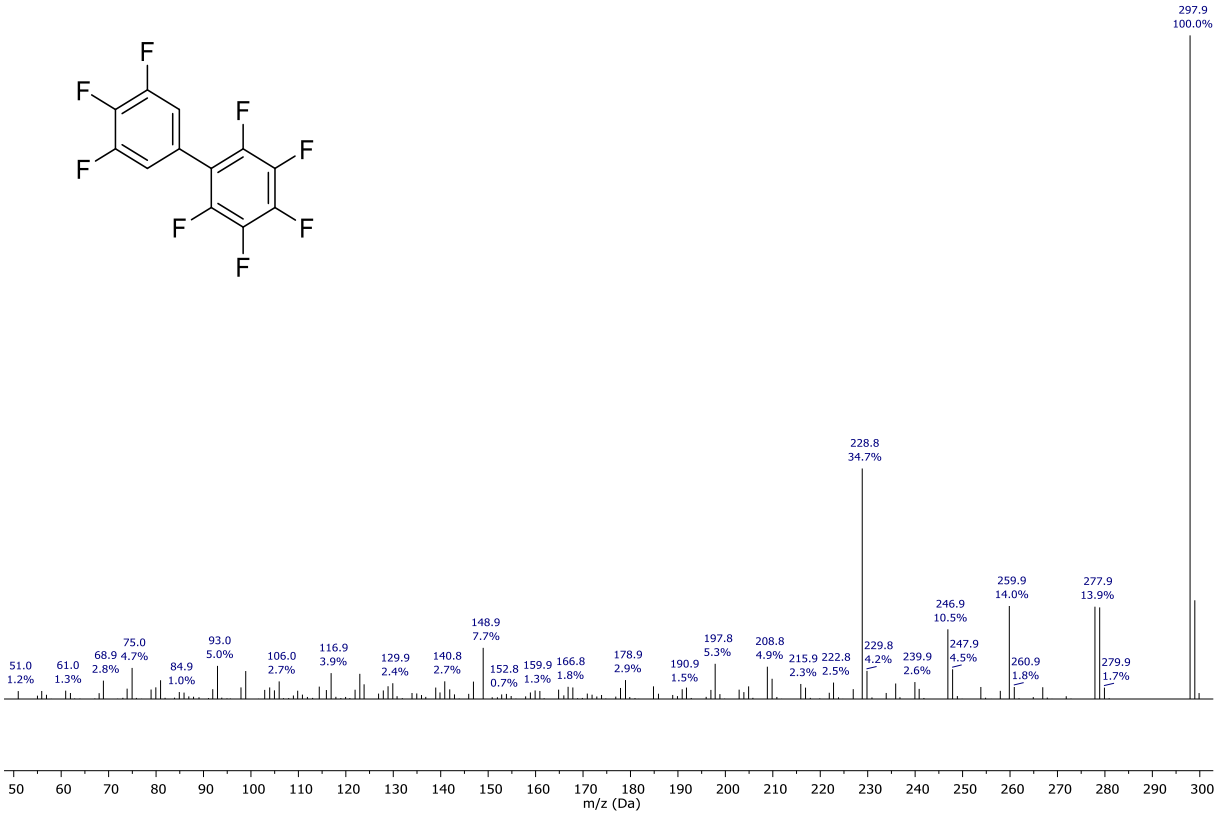


Figure S39 EI-Spectrum (EI⁺): 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

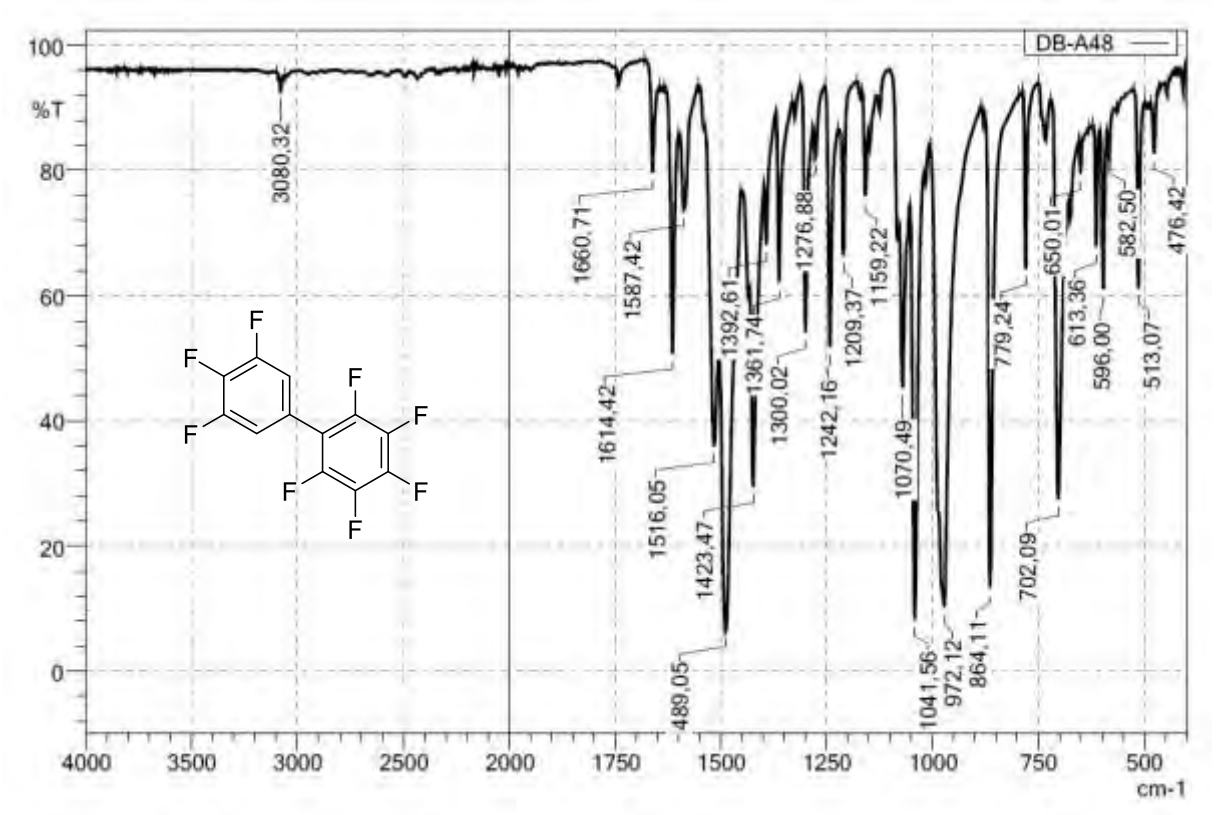


Figure S40 IR (ATR)-Spectrum: 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl (23)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.17 – 7.09 (m, 1H), 7.04 (ddd, J = 10.0, 8.8, 6.5 Hz, 1H).

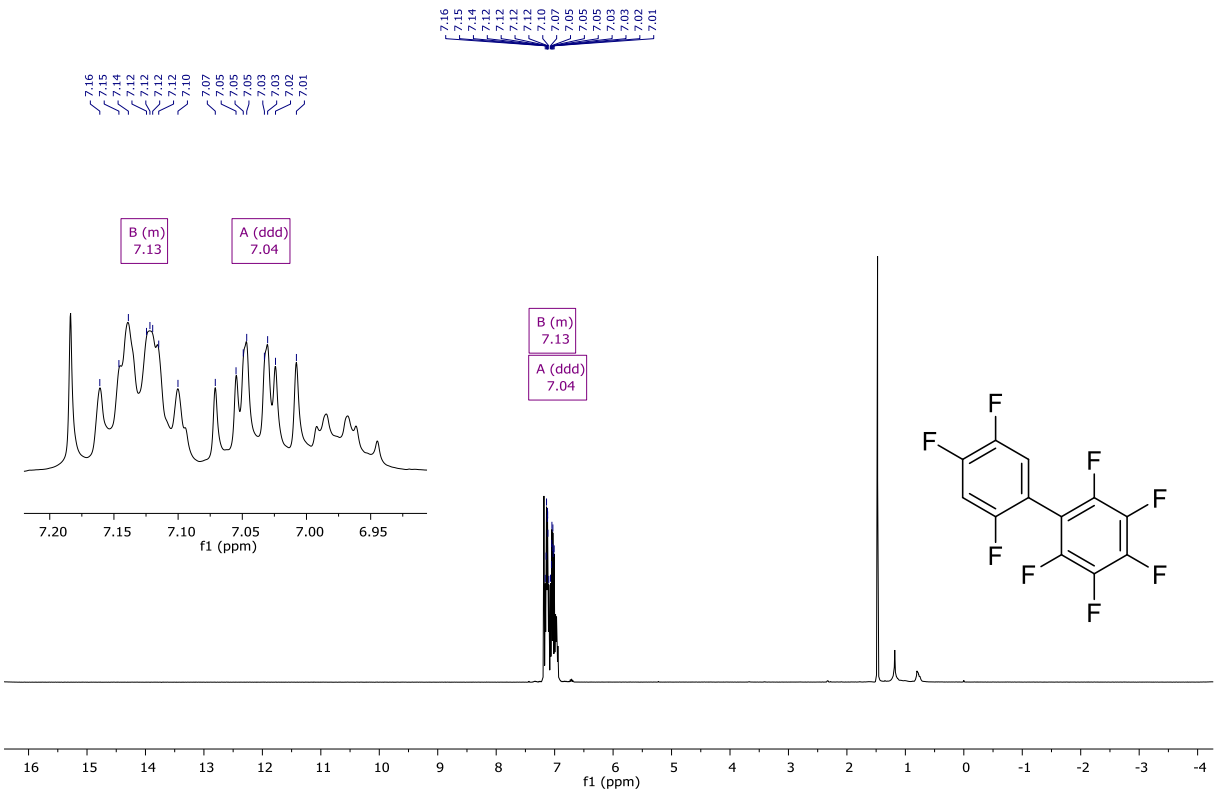


Figure S41 ^{1}H-NMR: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

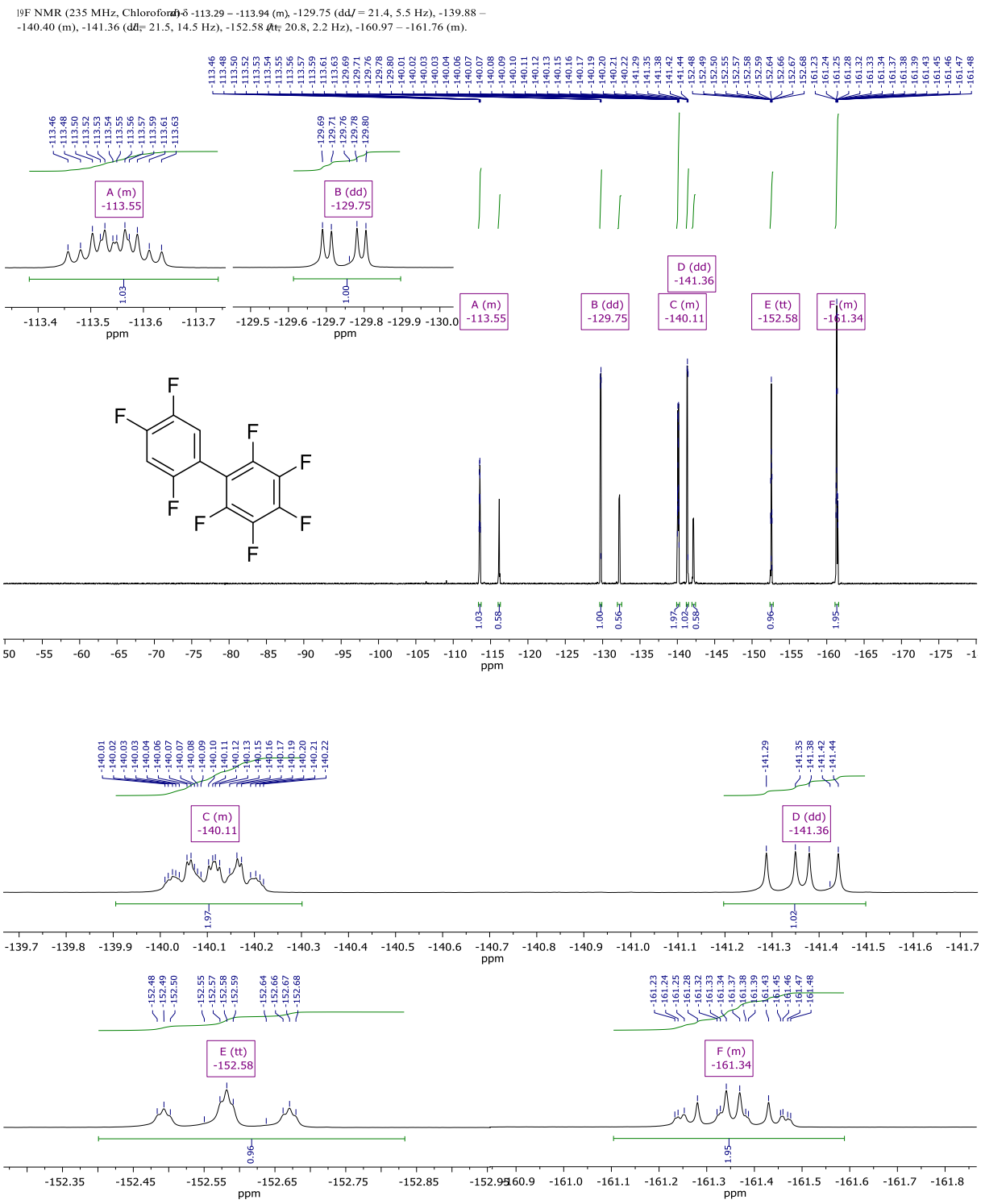


Figure S42 ^{19}F-NMR {^{1}H}: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

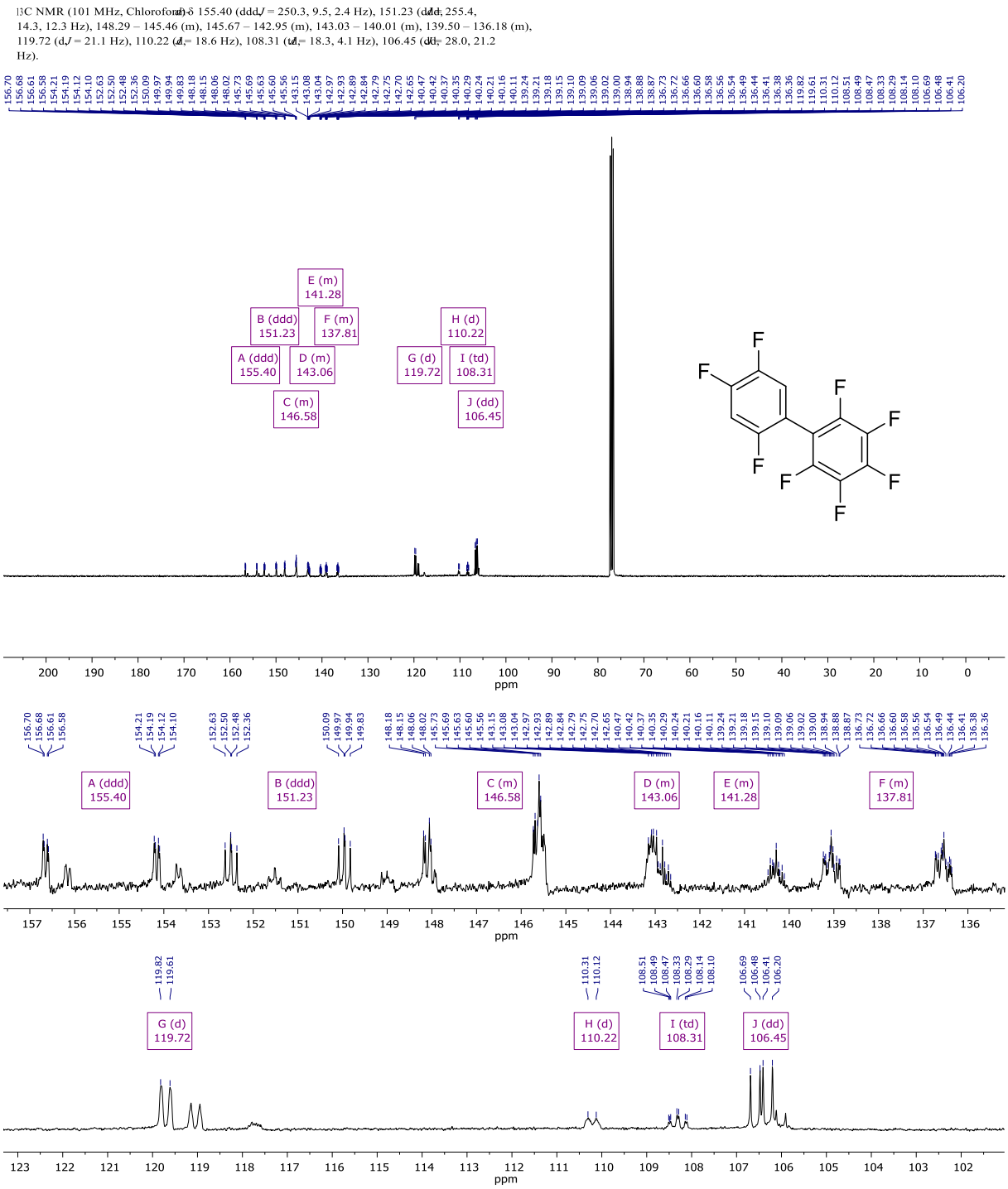


Figure S43 ^{13}C NMR: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

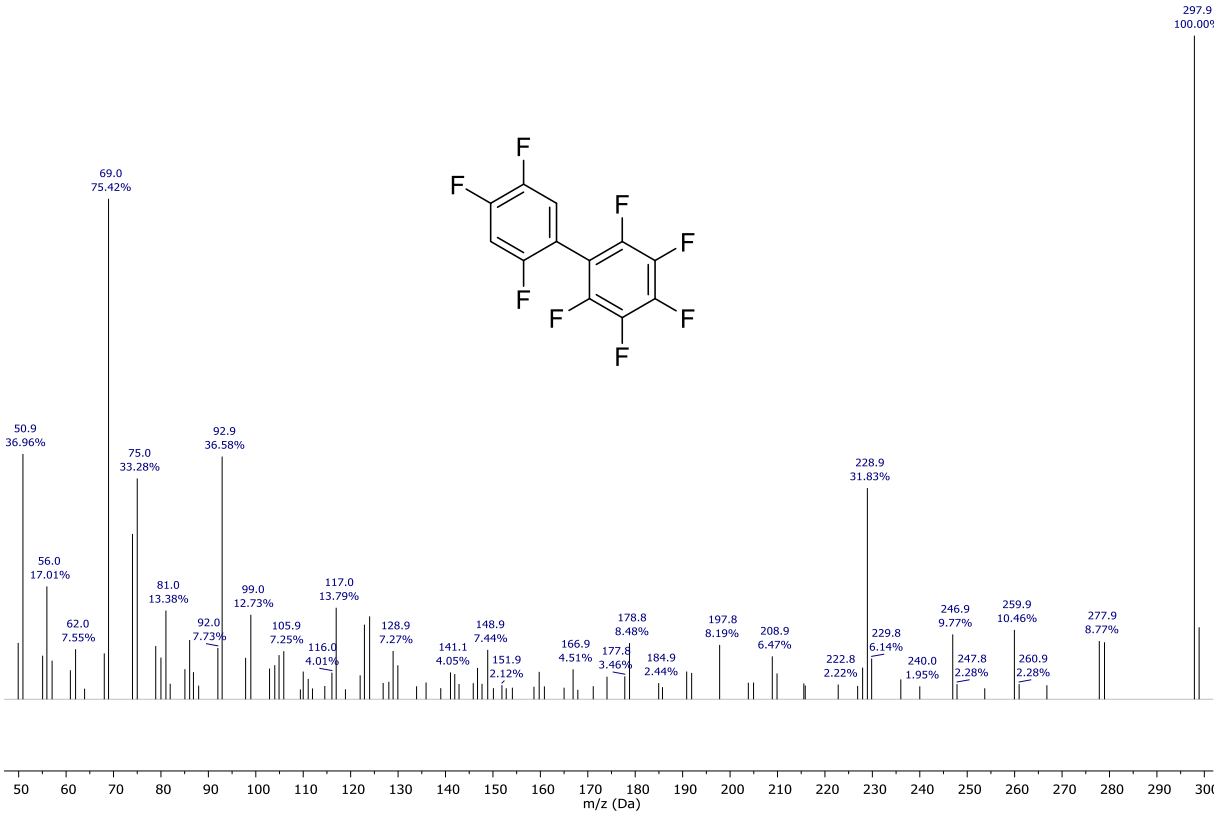


Figure S44 EI-Spectrum (EI⁺): 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

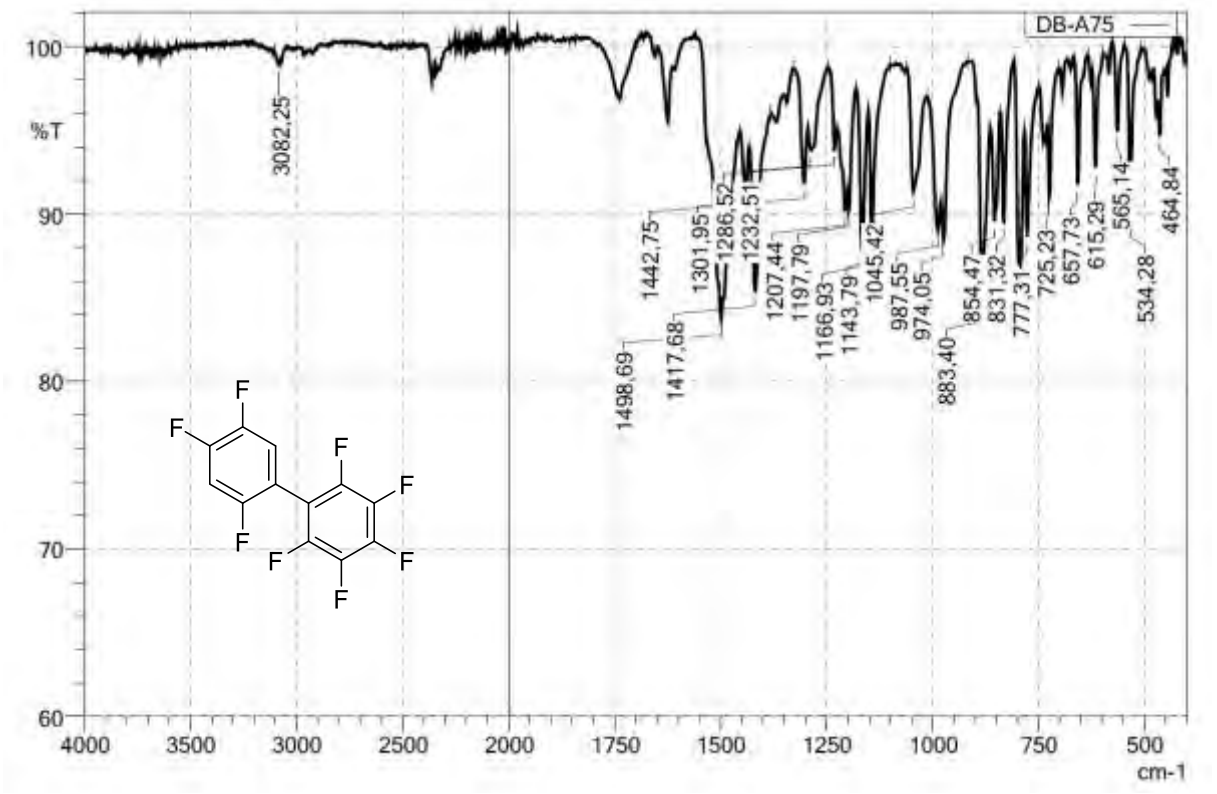


Figure S45 IR (ATR)-Spectrum: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

2,2',3,3',4,4',5,5',6-Nonafluoro-1,1'-biphenyl (24)

^{19}F NMR (377 MHz, Chloroform-d) δ -136.54 (dddd, J = 22.6, 20.9, 10.7, 5.6 Hz), -137.95 (ddd, J = 21.2, 12.0, 3.2 Hz), -139.76 (dddd, J = 23.2, 9.5, 6.7, 3.1 Hz), -151.35 (tt, J = 20.7, 2.4 Hz), -151.81 (td, J = 20.5, 5.5 Hz), -153.45 (td, J = 20.1, 3.4 Hz), -160.56 – -160.76 (m).

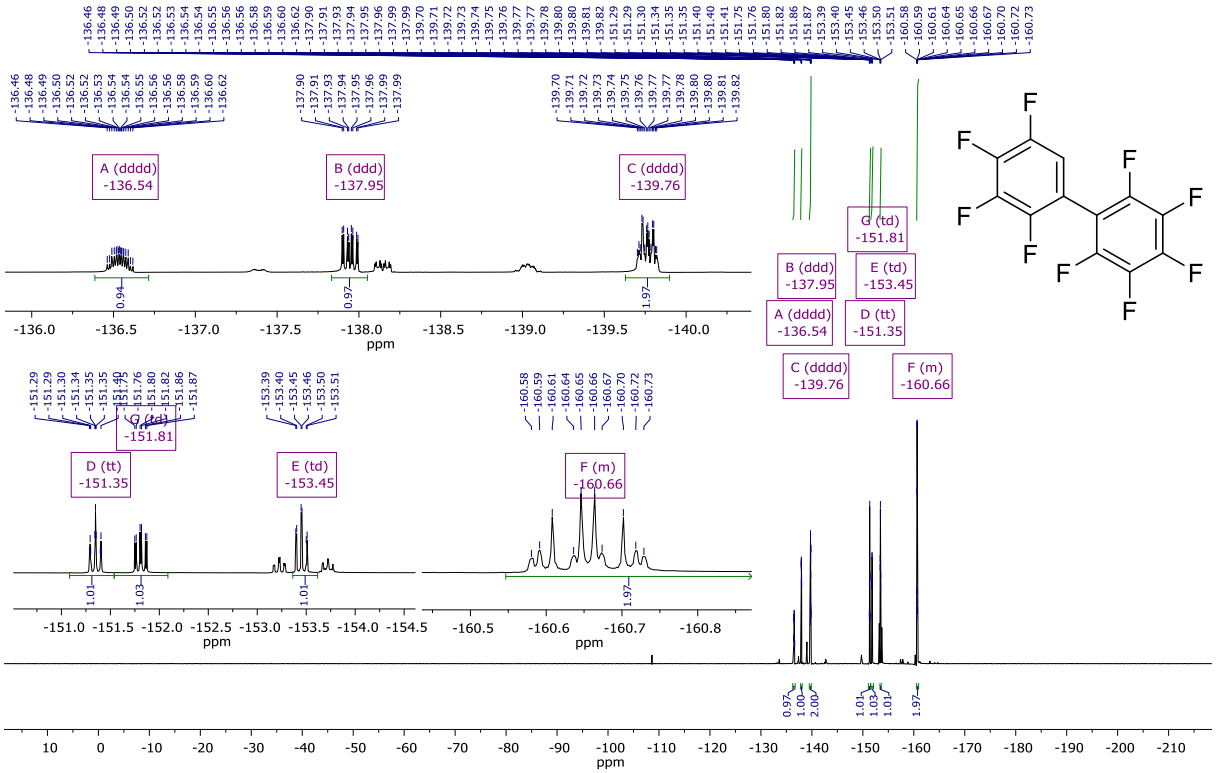


Figure S46 ^{19}F-NMR {^{1}H}: 2,2',3,3',4,4',5,5',6-Nonafluoro-1,1'-biphenyl

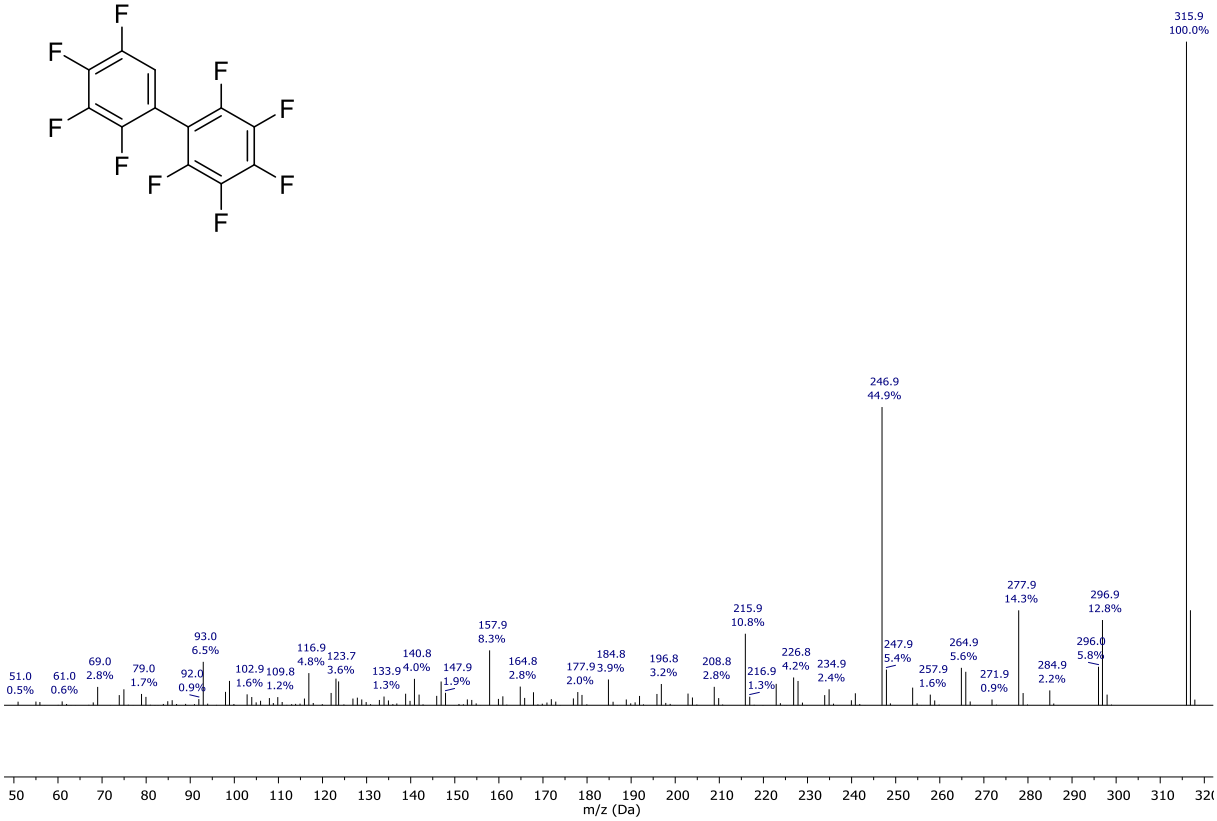


Figure S47 EI-Spectrum (EI^{+}): 2,2',3,3',4,4',5,5',6-Nonafluoro-1,1'-biphenyl

2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl (25)

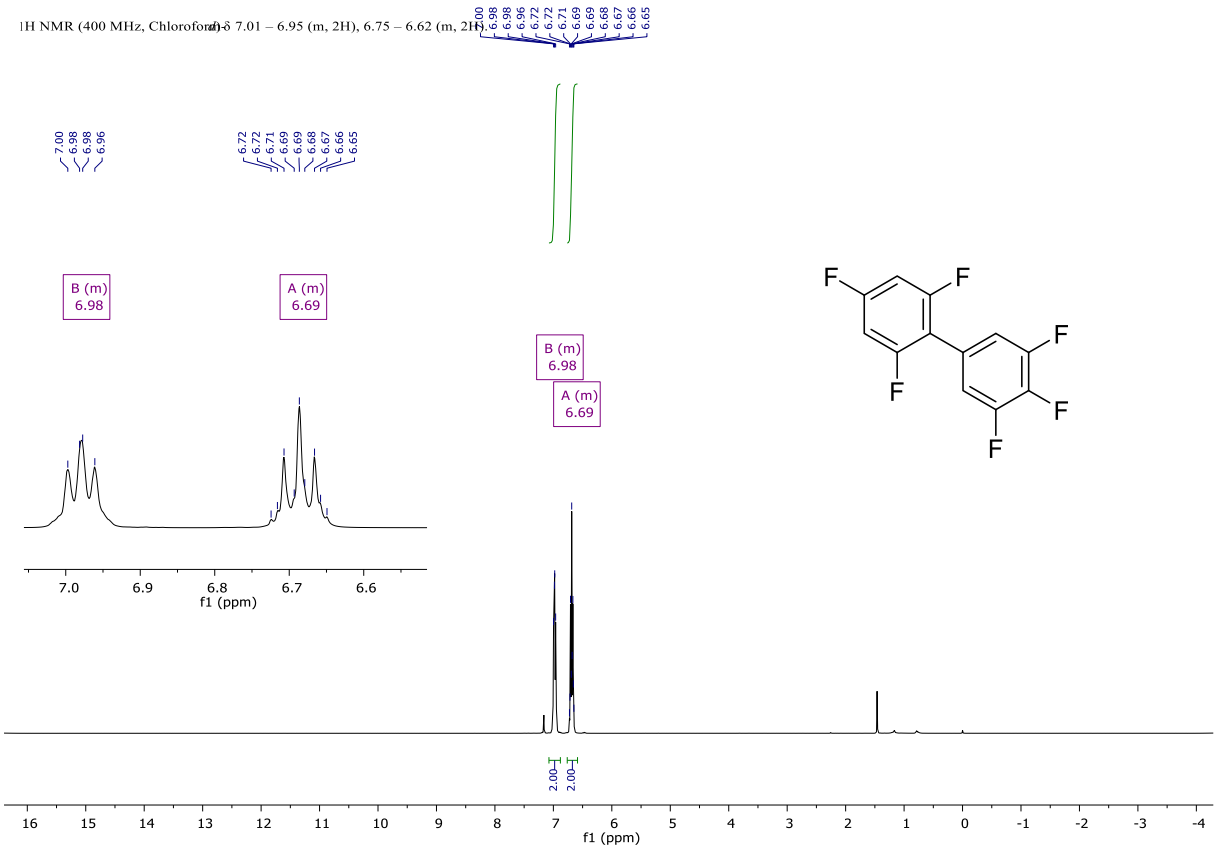


Figure S48 ^{1}H-NMR: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

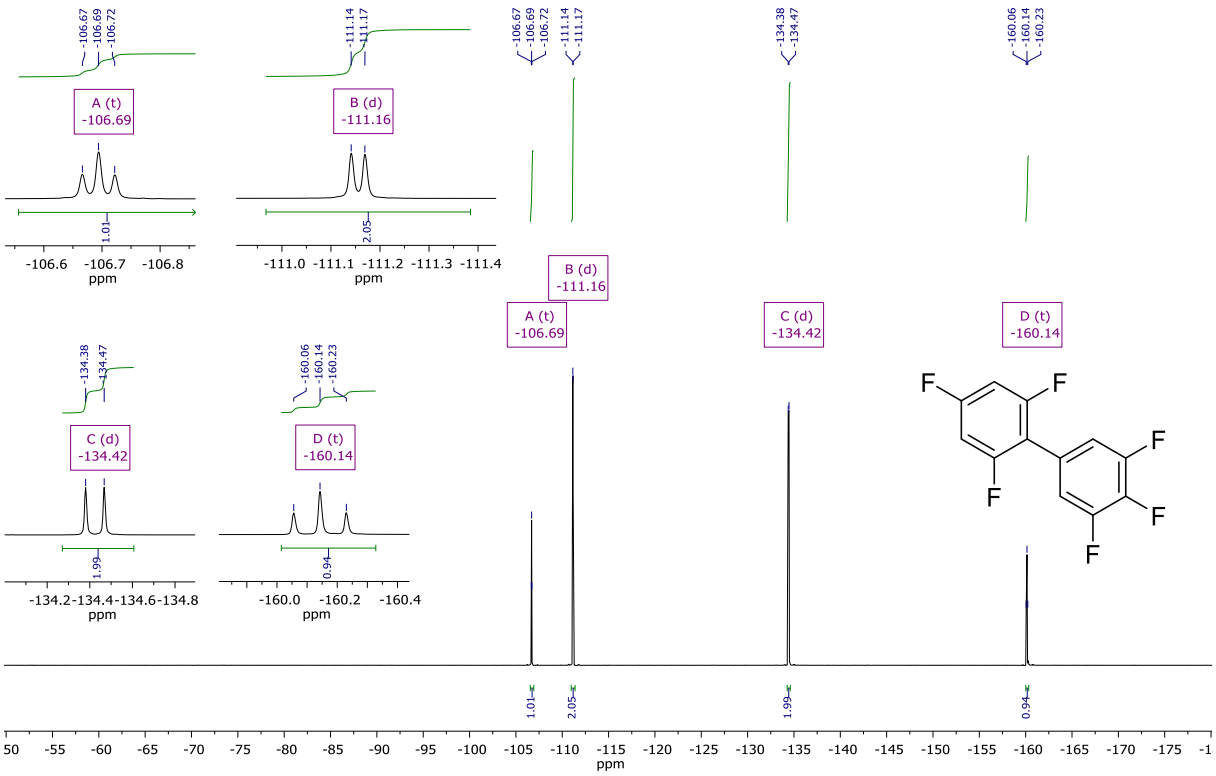


Figure S49 ^{19}F-NMR {^{1}H}: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

^{13}C NMR (101 MHz, Chloroform-d) δ 164.45 – 161.42 (m), 160.55 (ddd, J = 250.9, 14.7, 8.9 Hz), 151.57 (ddd, J = 249.7, 10.0, 4.2 Hz), 140.25 (dt, J = 253.8, 15.1 Hz), 124.59 (td, J = 9.0, 5.1 Hz), 115.50 – 114.86 (m), 112.75 (td, J = 19.5, 3.6 Hz), 101.97 – 100.81 (m).

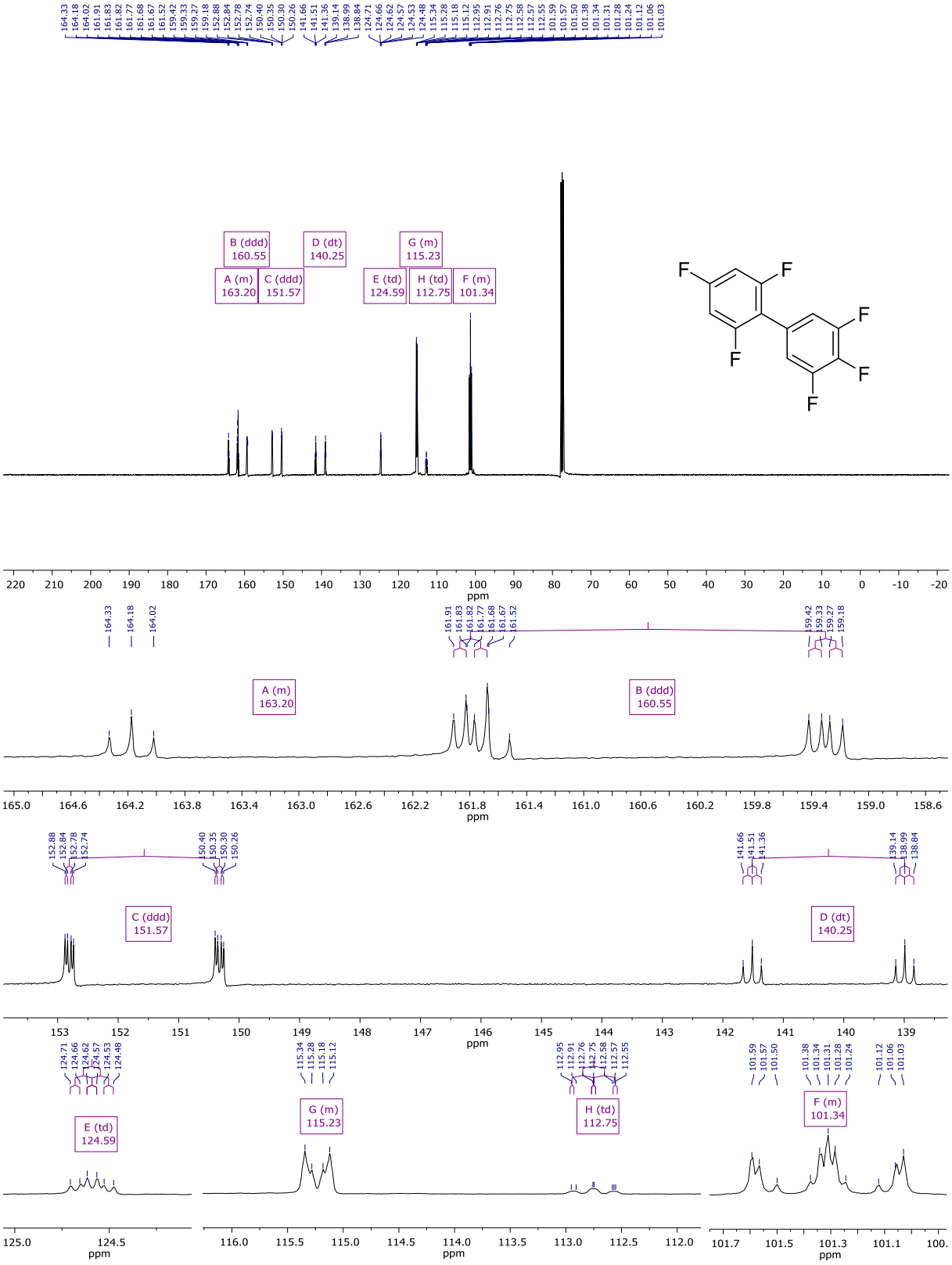


Figure S50 ^{13}C NMR: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

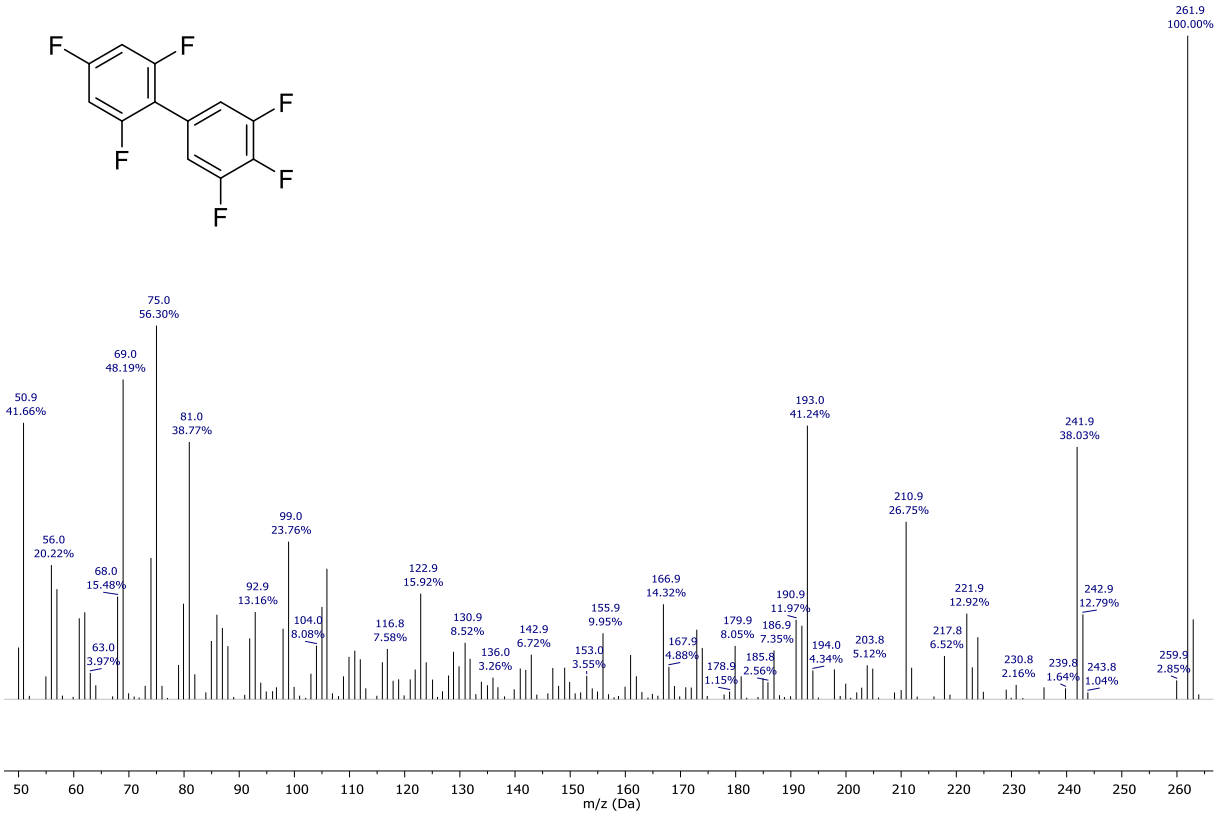


Figure S51 EI-Spectrum (EI⁺): 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

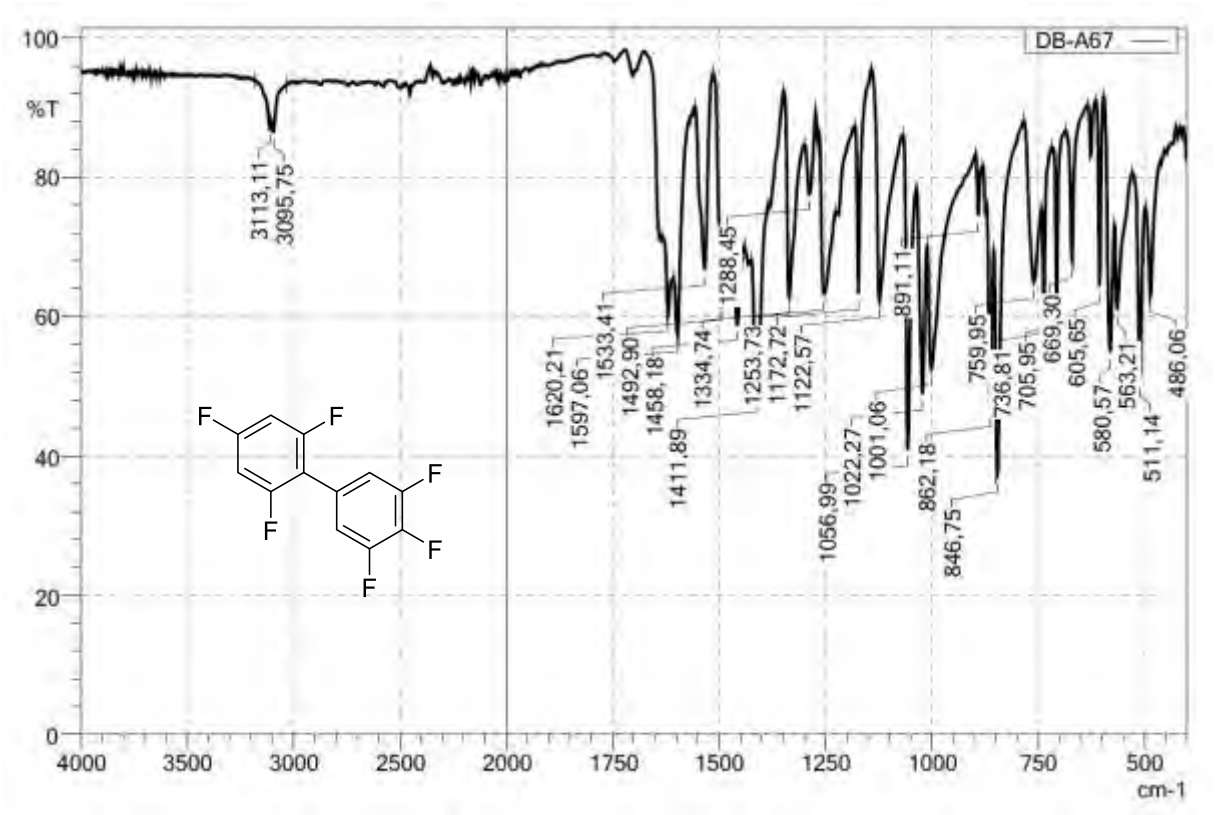


Figure S52 IR (ATR)-Spectrum: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl (26)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.19 (ddd, J = 10.3, 8.7, 6.4 Hz, 1H), 7.06 (ddd, J = 10.2, 8.9, 6.6 Hz, 1H), 6.84 – 6.74 (m, 2H).

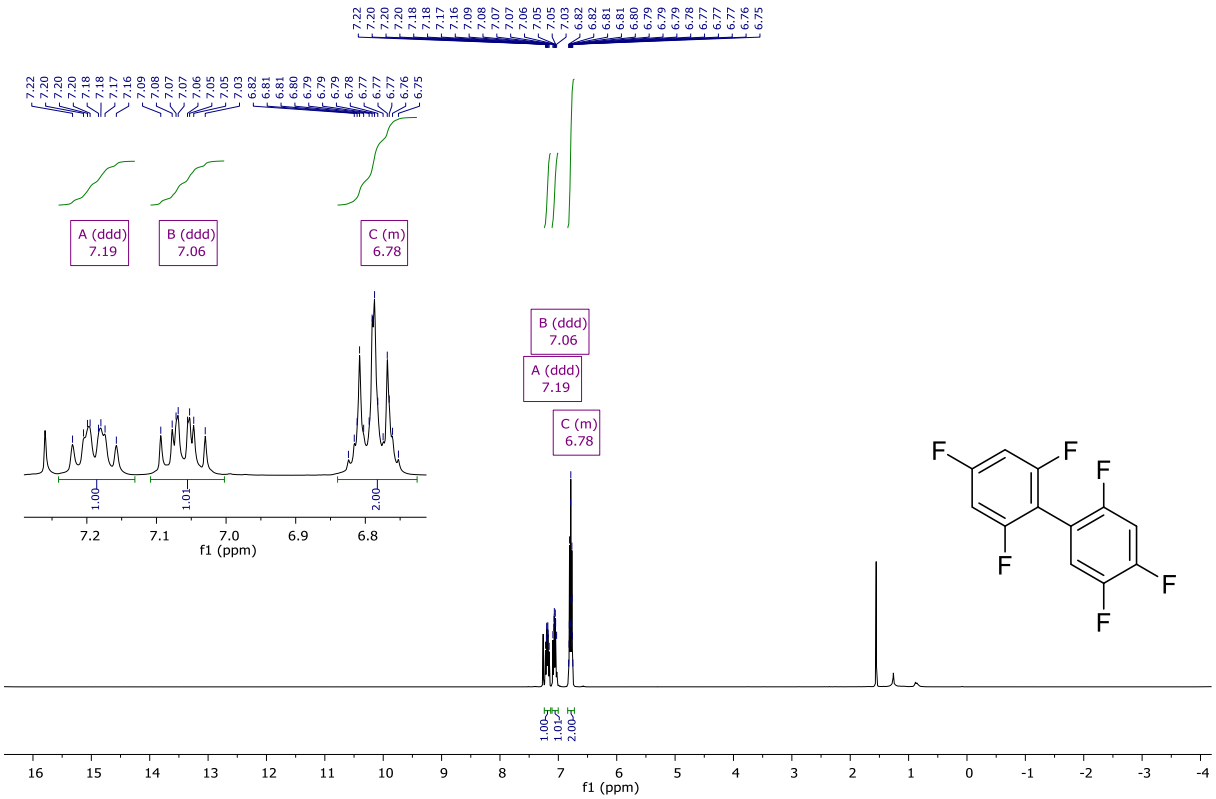


Figure S53 ^{1}H-NMR: 2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform-d) δ -106.33 (t, J = 6.9 Hz), -109.05 (dd, J = 10.8, 6.9 Hz), -114.09 (dtd, J = 14.6, 10.8, 5.0 Hz), -131.81 (dd, J = 21.5, 5.0 Hz), -142.46 (dd, J = 21.5, 14.6 Hz).

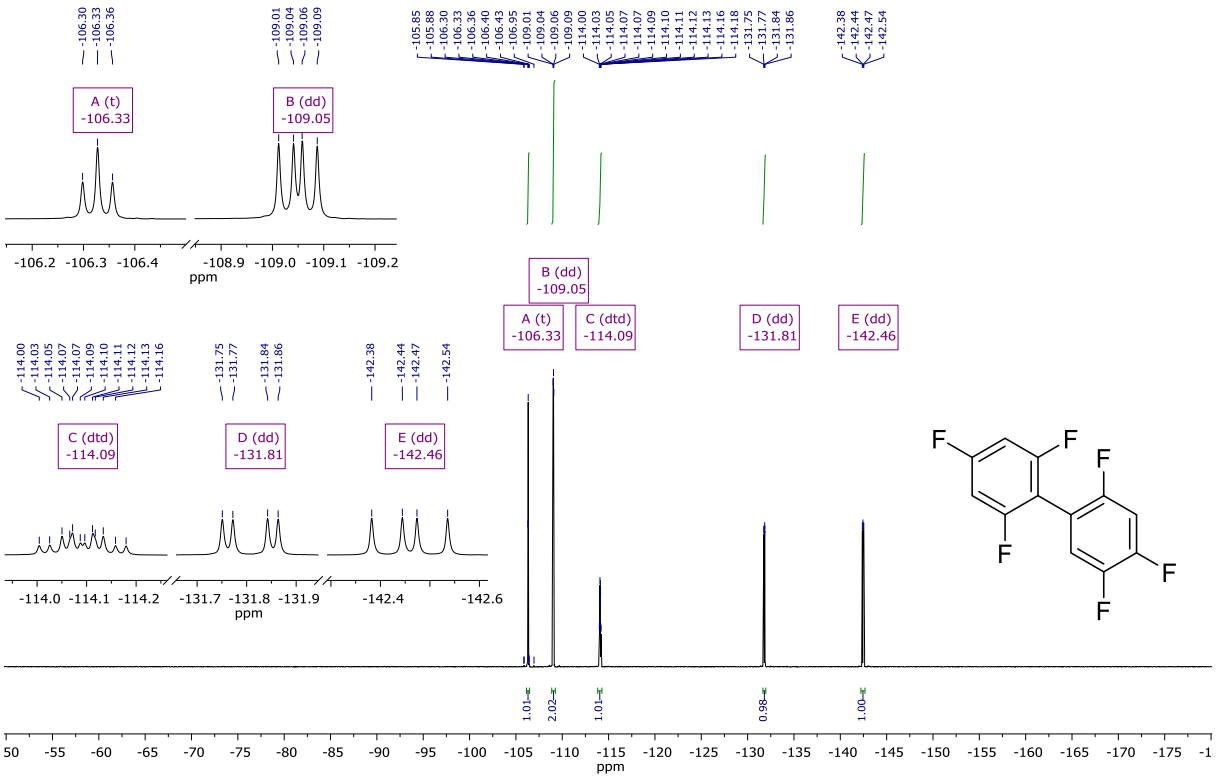


Figure S54 ^{19}F-NMR {^{1}H}: 2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl

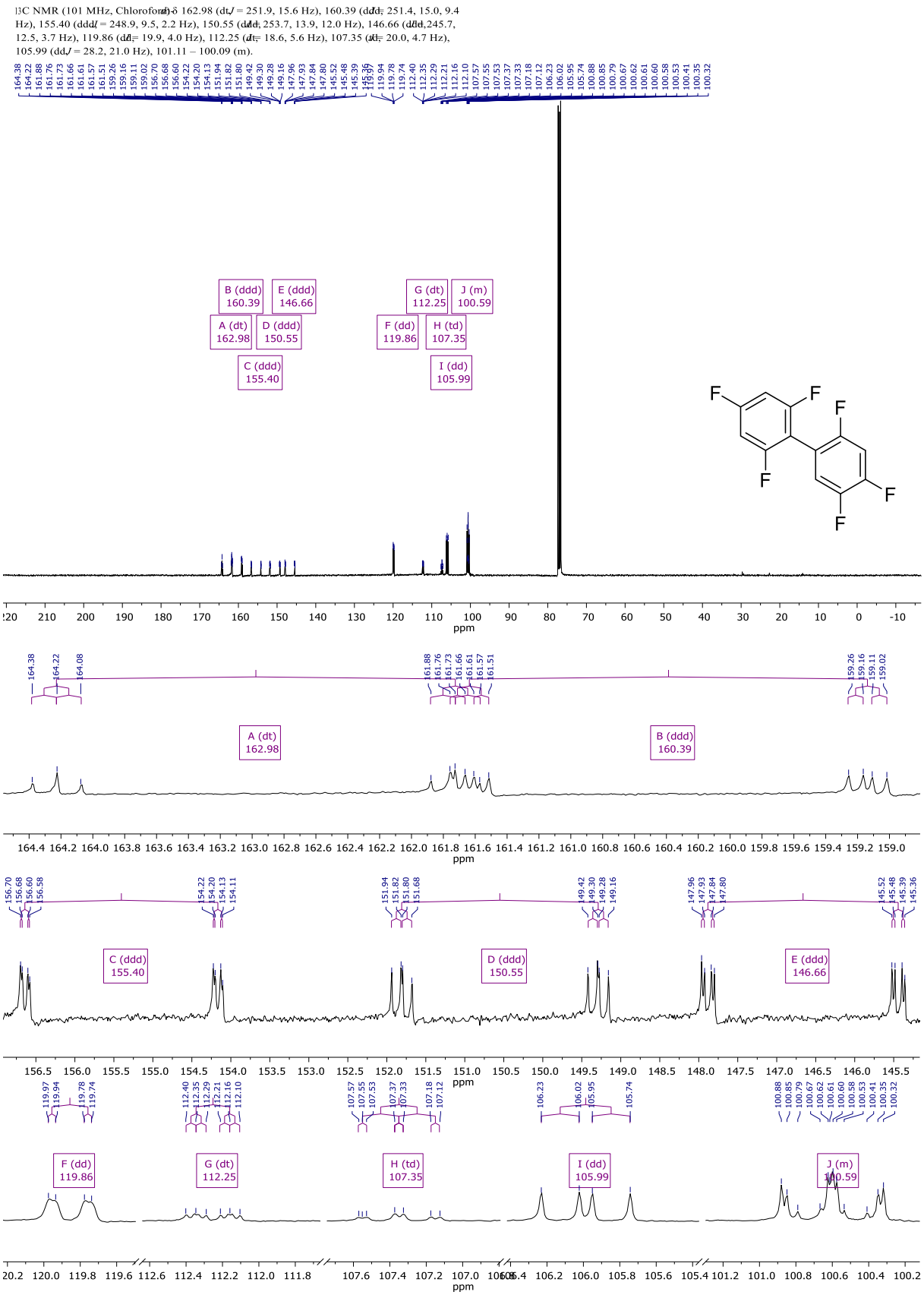


Figure S55 ^{13}C NMR: 2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl

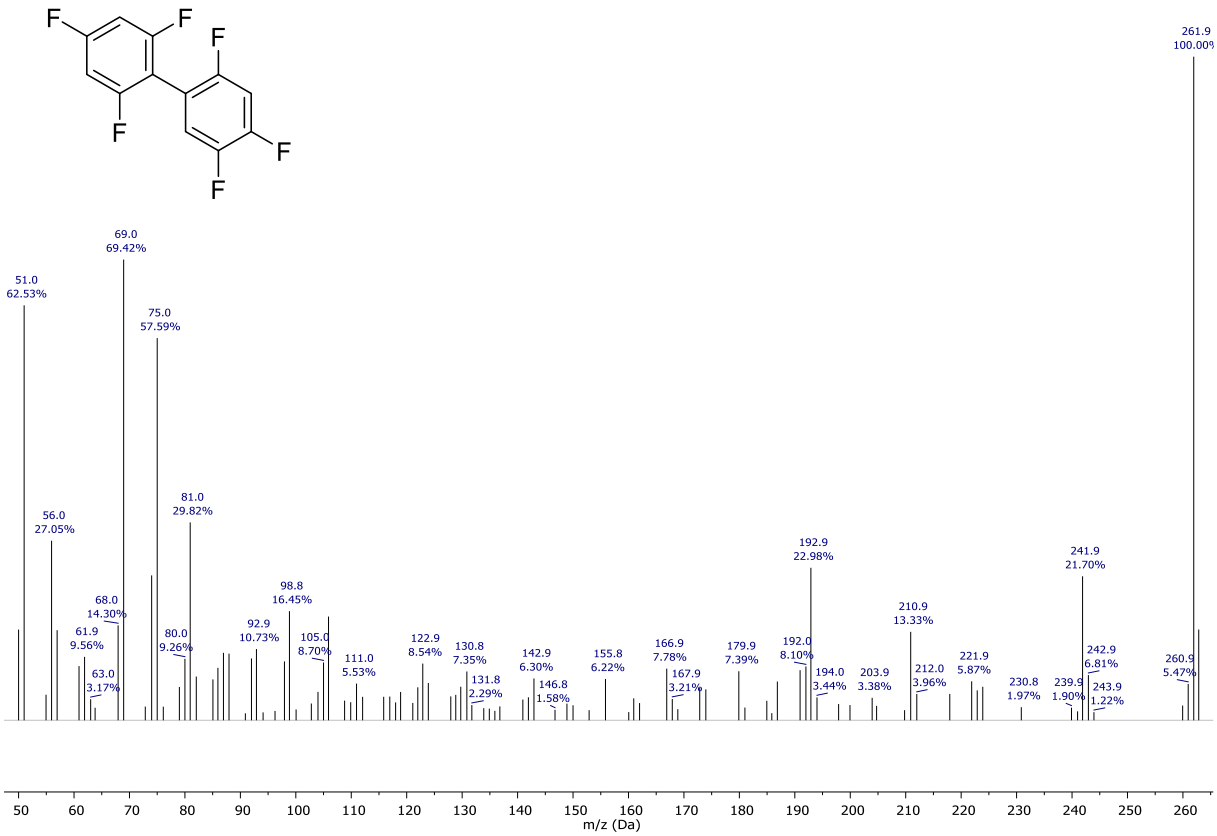


Figure S56 EI-Spectrum (EI⁺): 2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl

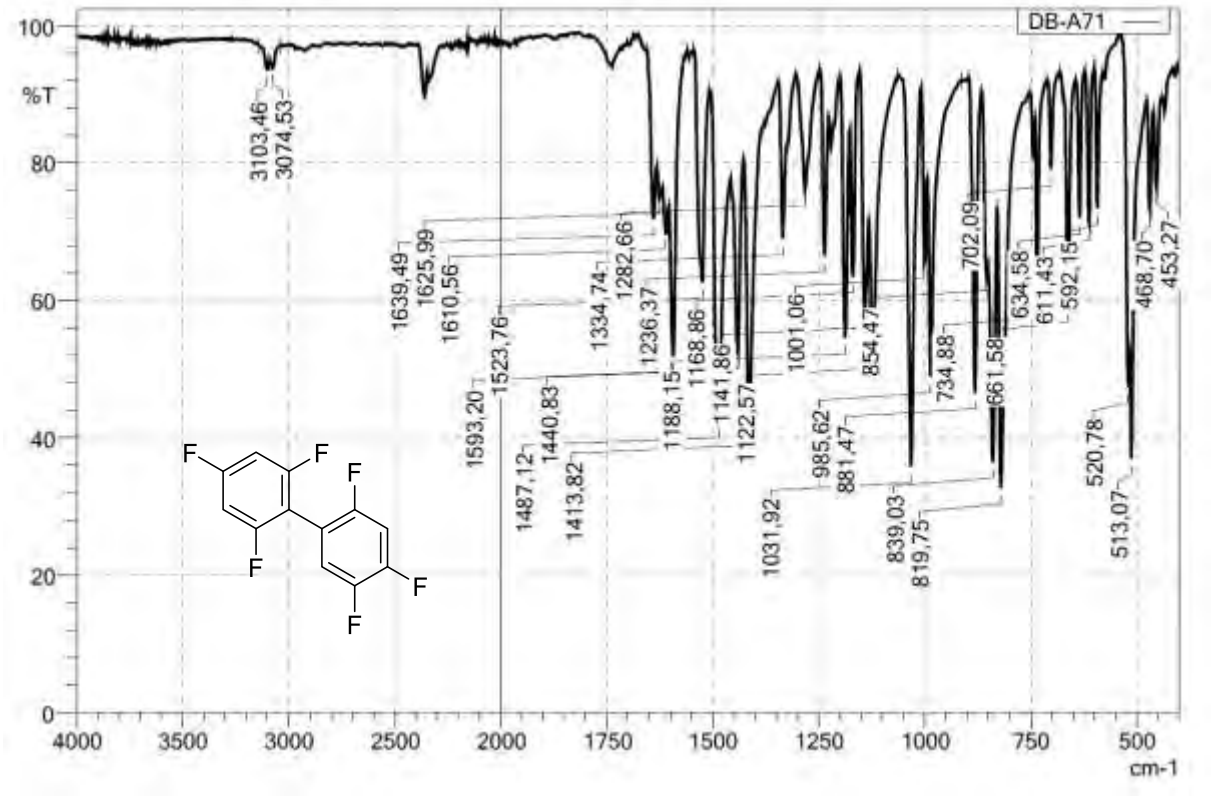


Figure S57 IR (ATR)-Spectrum: 2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl

2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl (27)

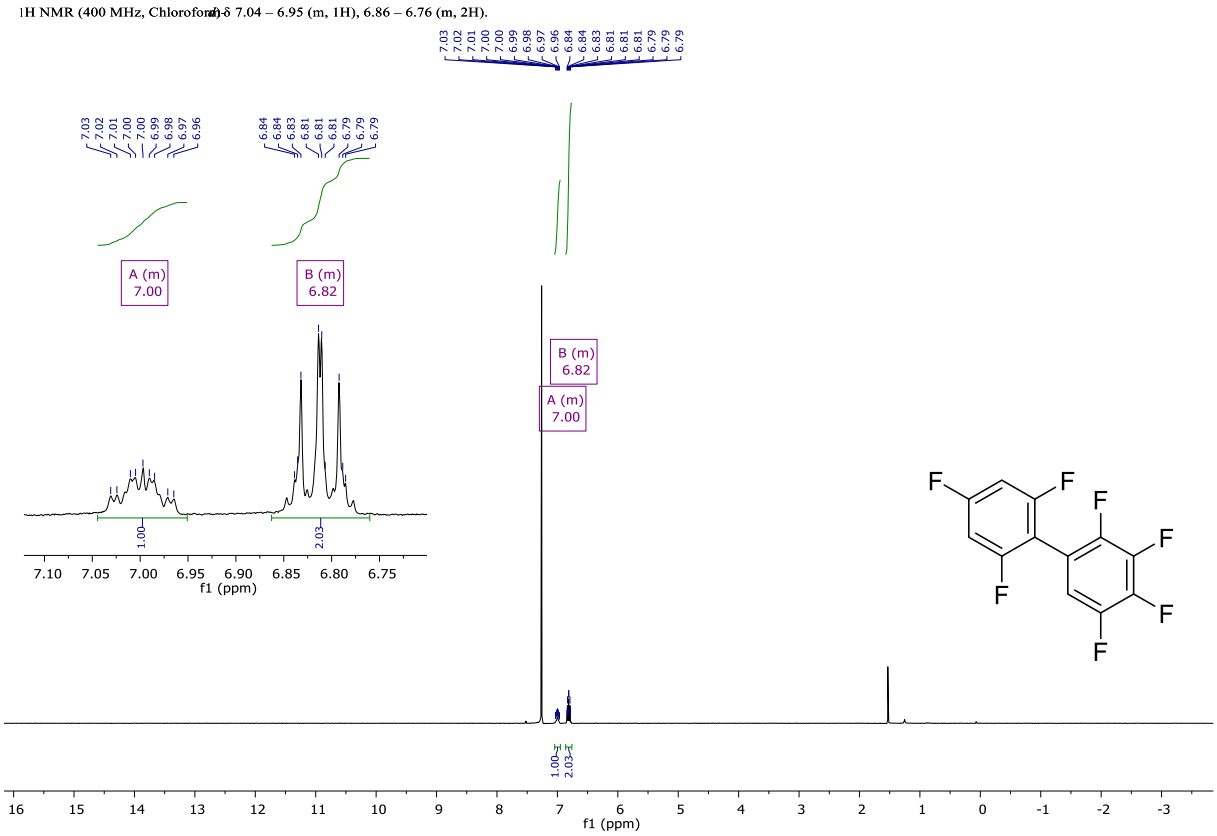


Figure S58 ^{1}H-NMR: 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

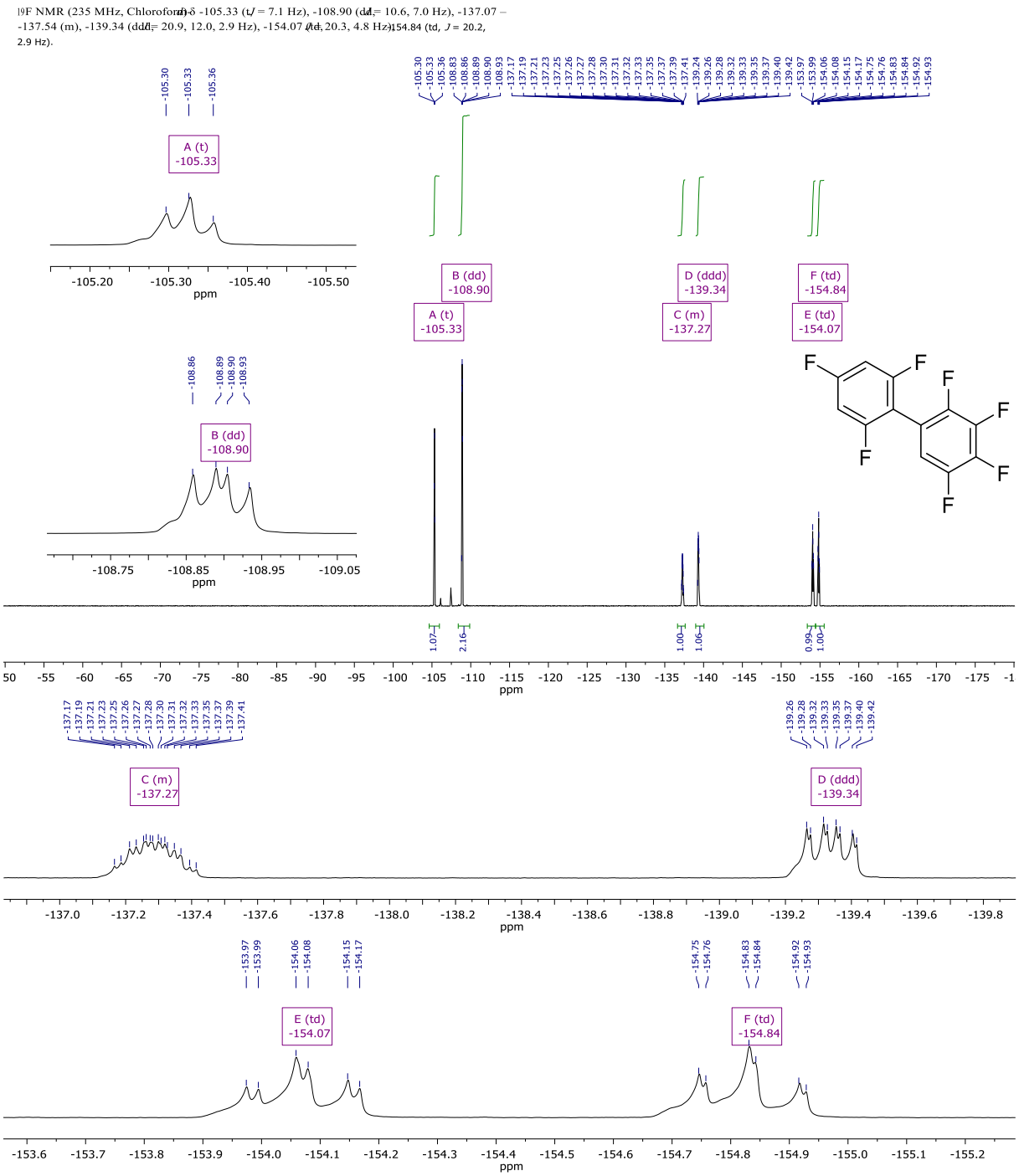


Figure S59 ^{19}F-NMR {^{1}H}: 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

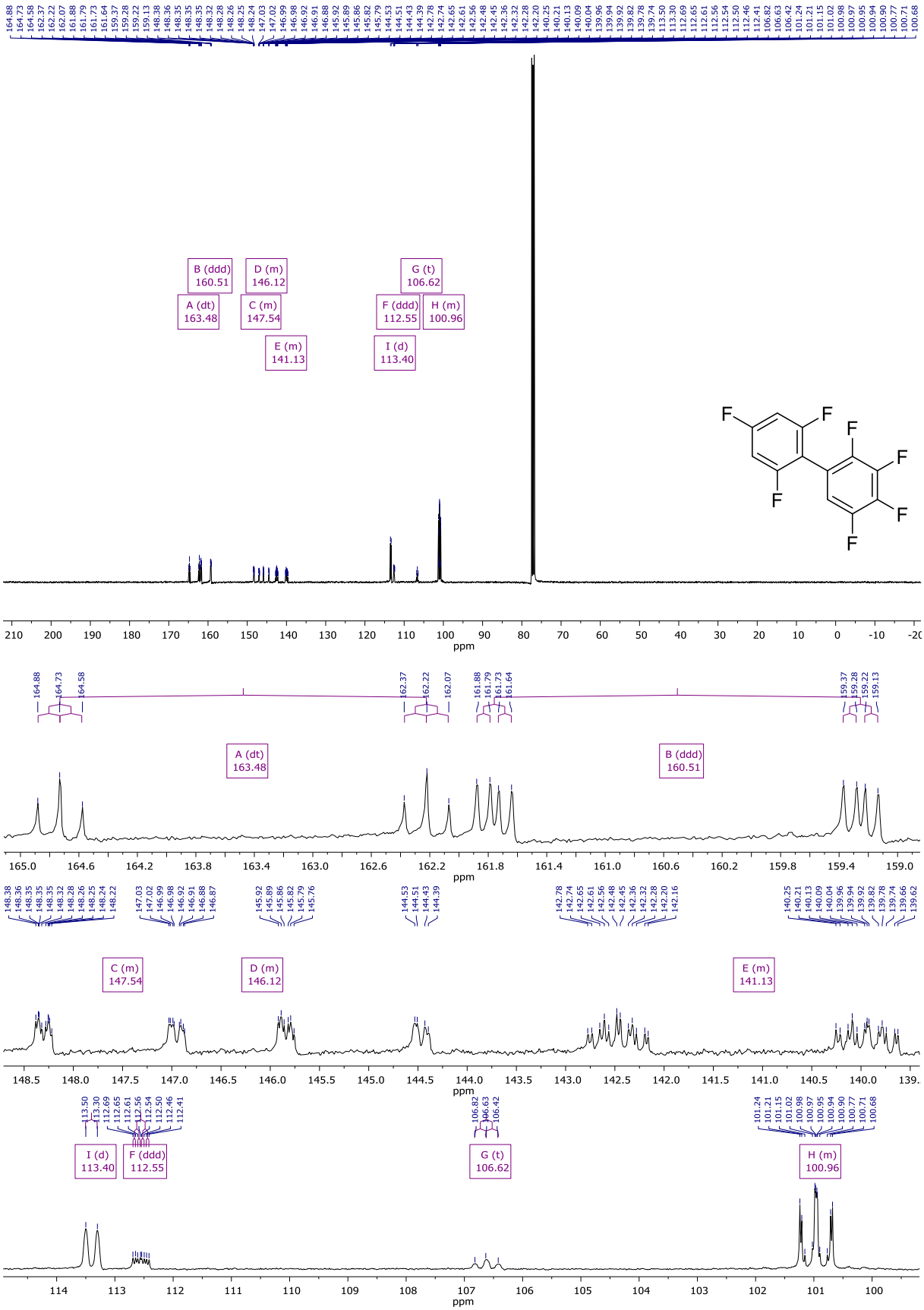


Figure S60 ^{13}C NMR: 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

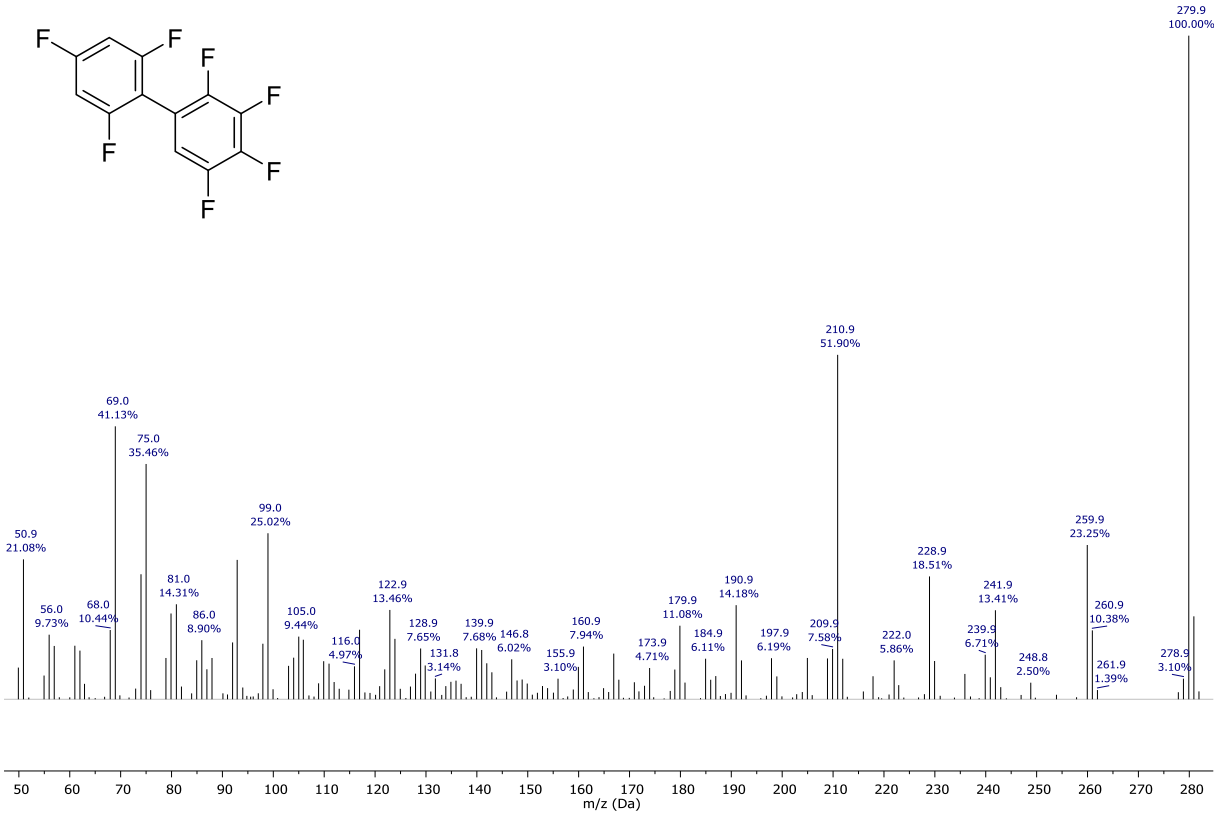


Figure S61 EI-Spectrum (EI⁺): 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

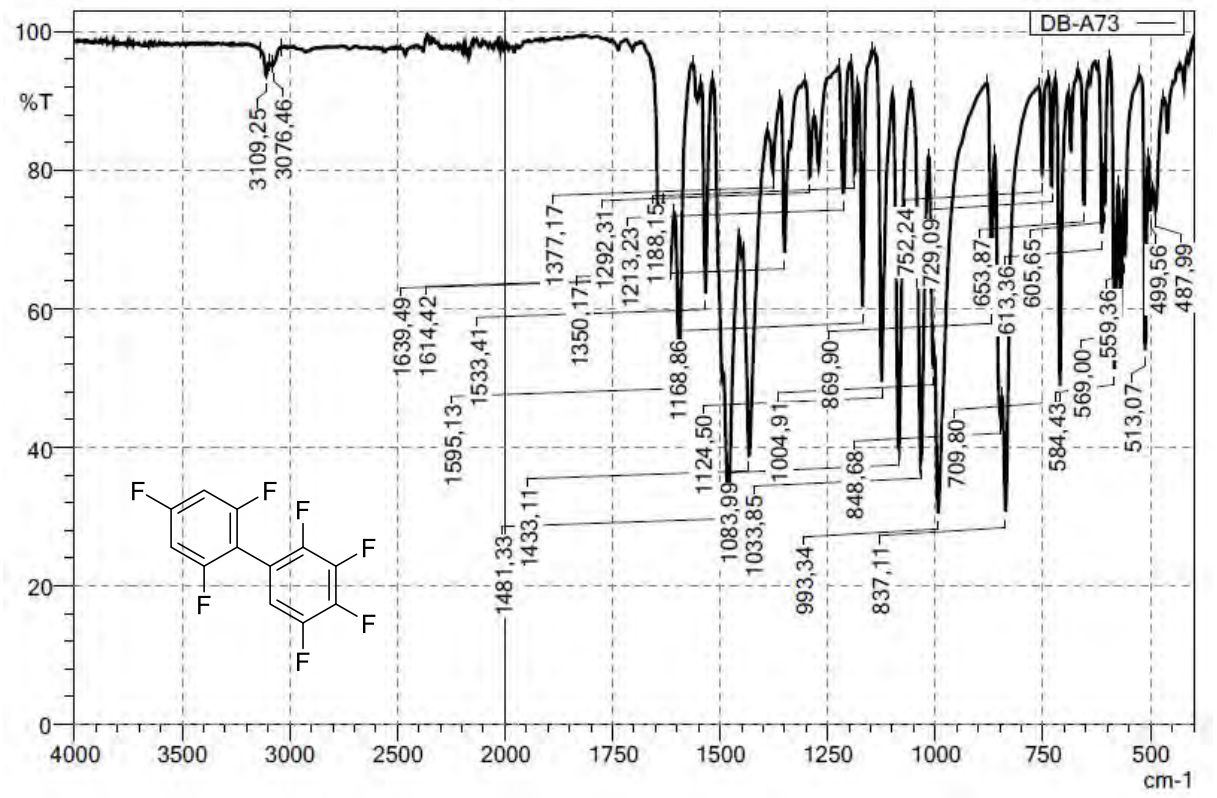


Figure S62 IR (ATR)-Spectrum: 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl (28)

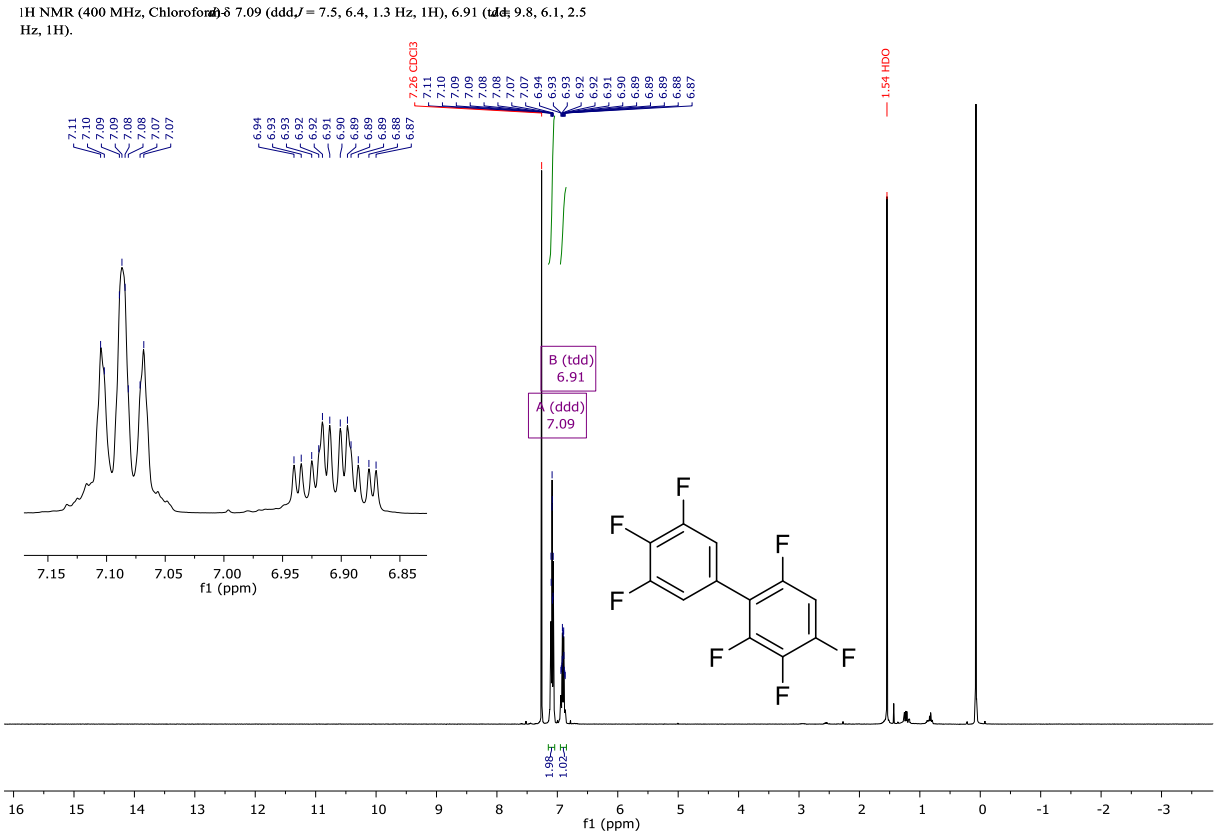


Figure S63 ^{1}H-NMR: 2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl

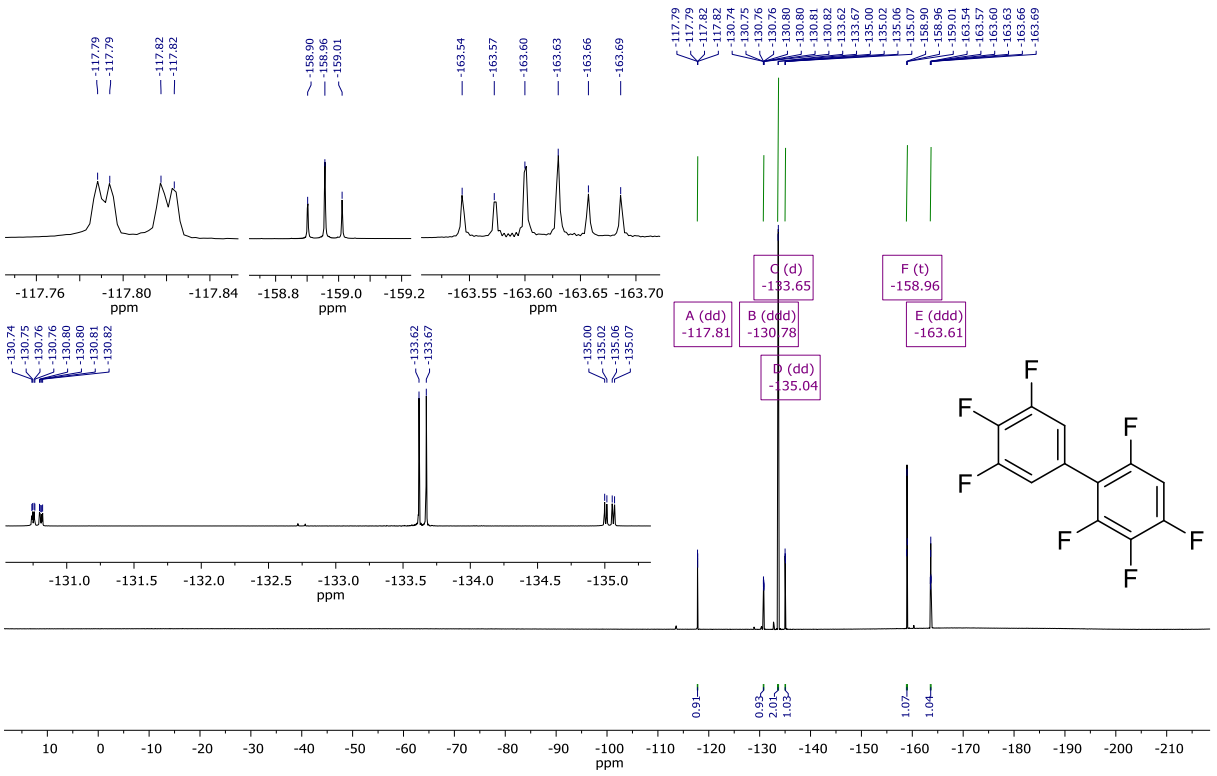


Figure S64 ^{19}F-NMR {^{1}H}: 2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl

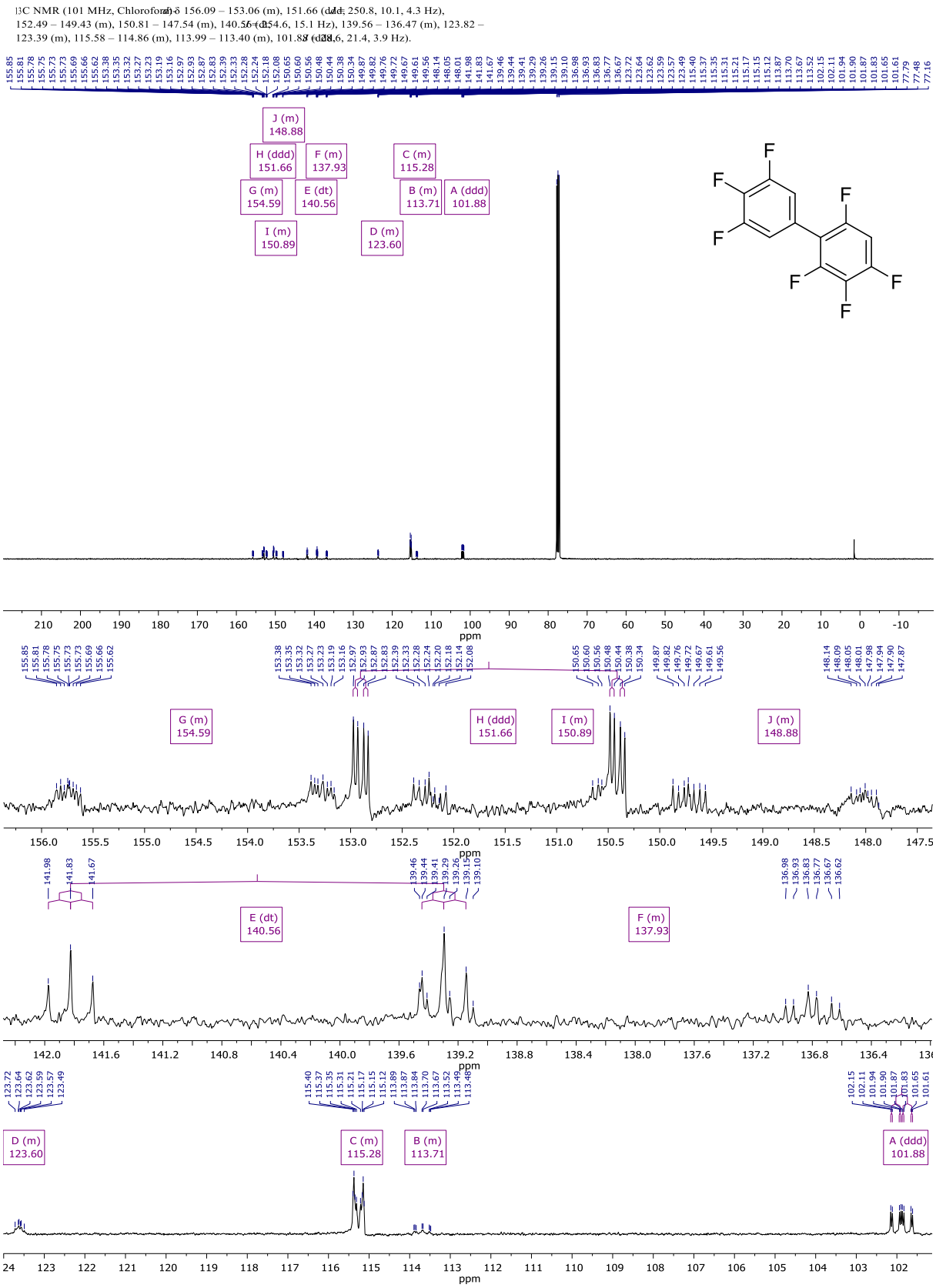


Figure S65 ^{13}C NMR: 2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl

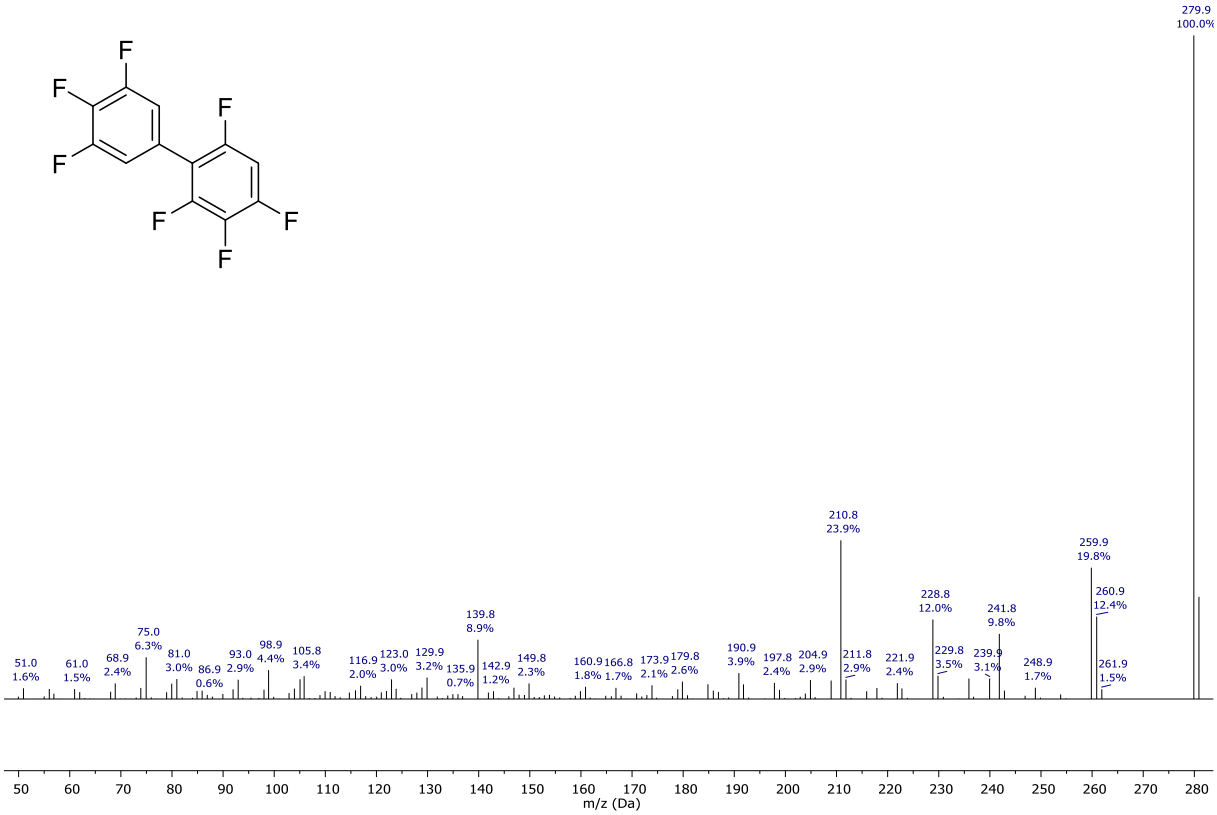


Figure S66 EI-Spectrum (EI⁺): 2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl

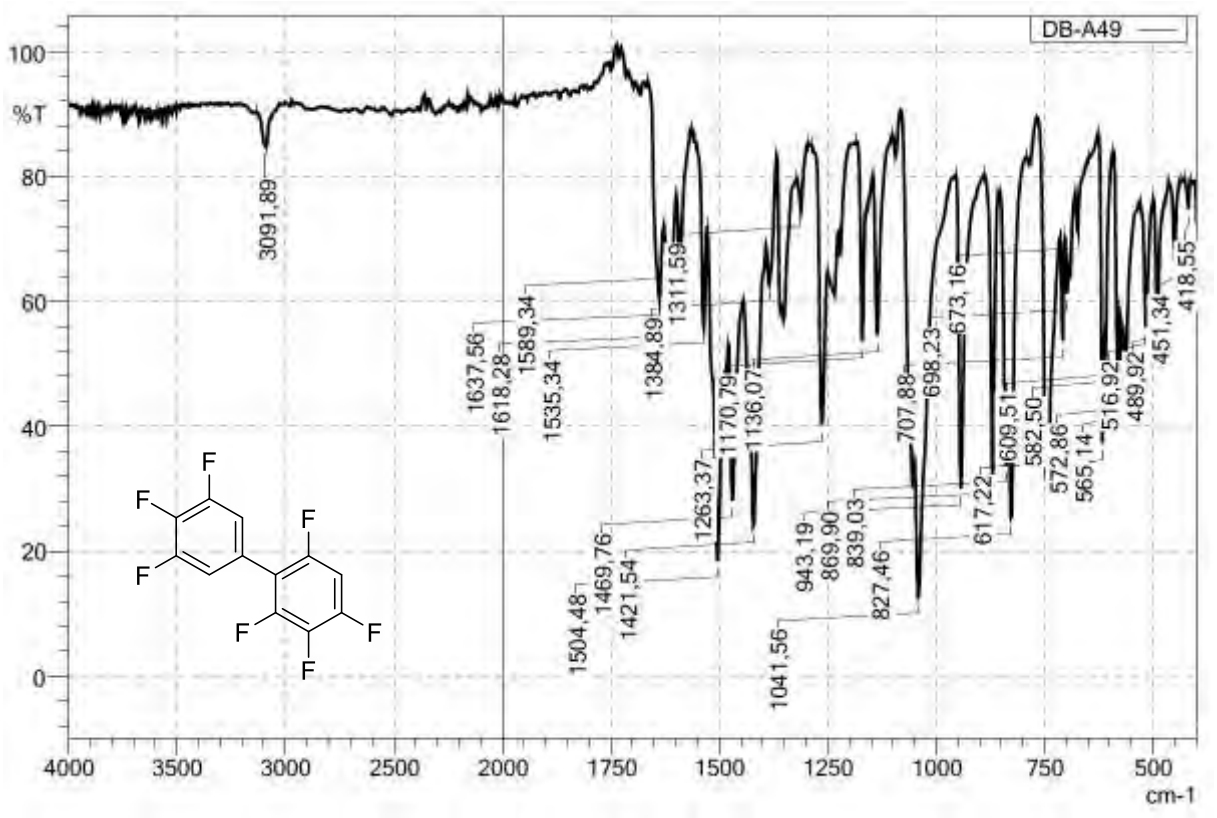


Figure S67 2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl

3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl (4)

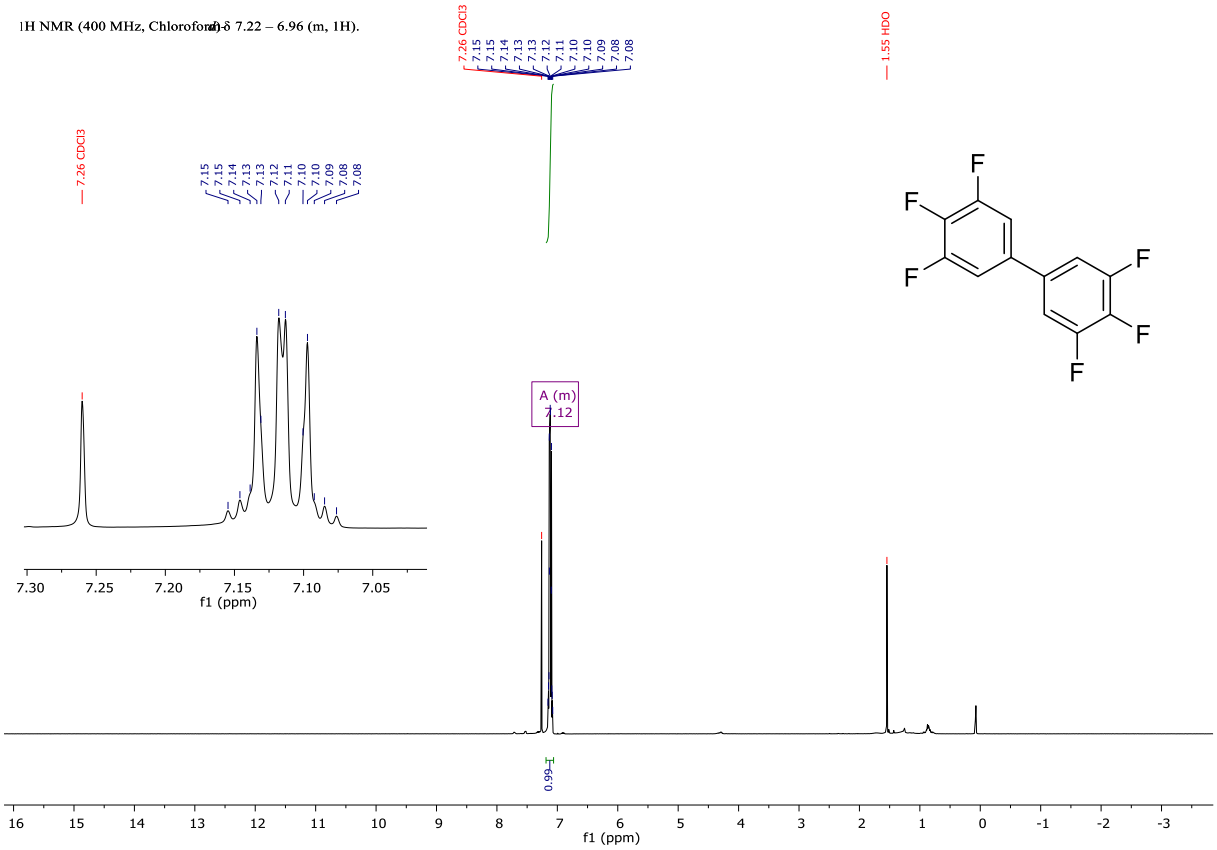


Figure S68 ^{1}H-NMR: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

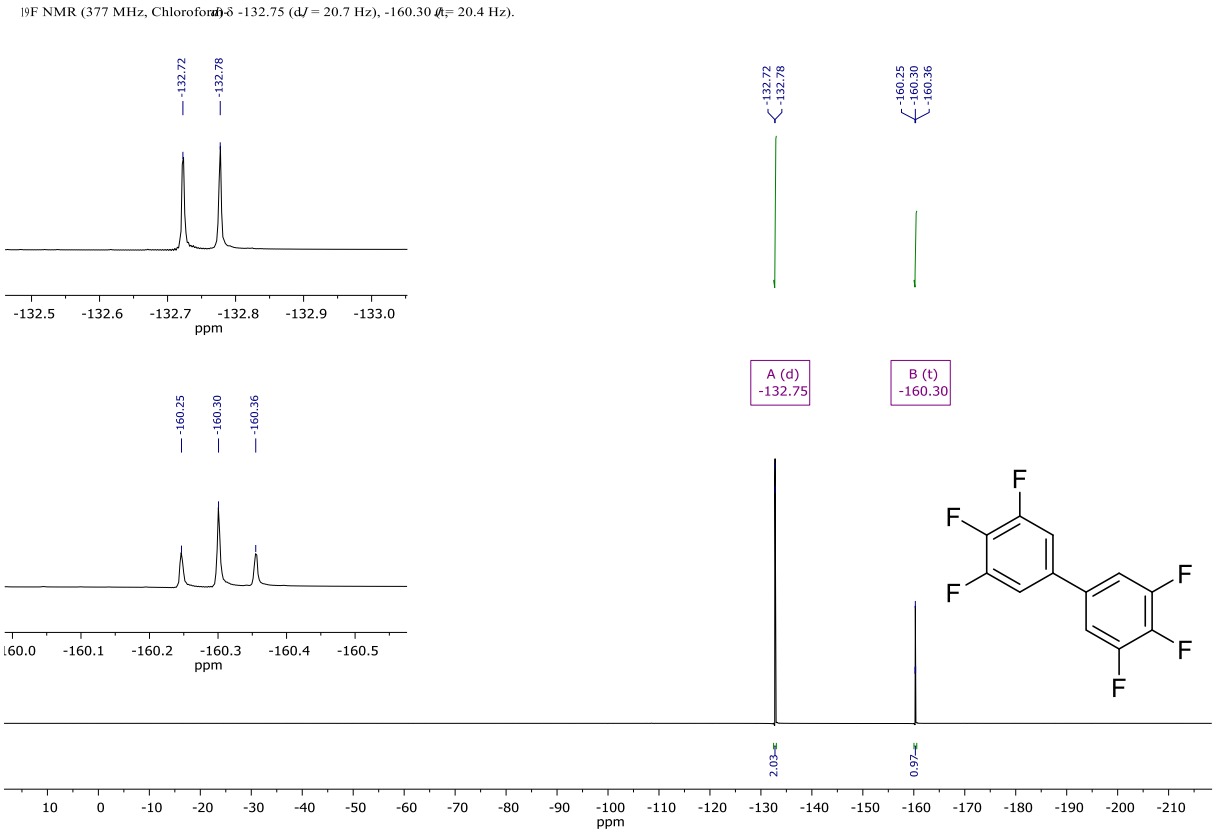


Figure S69 ^{19}F-NMR {^{1}H}: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

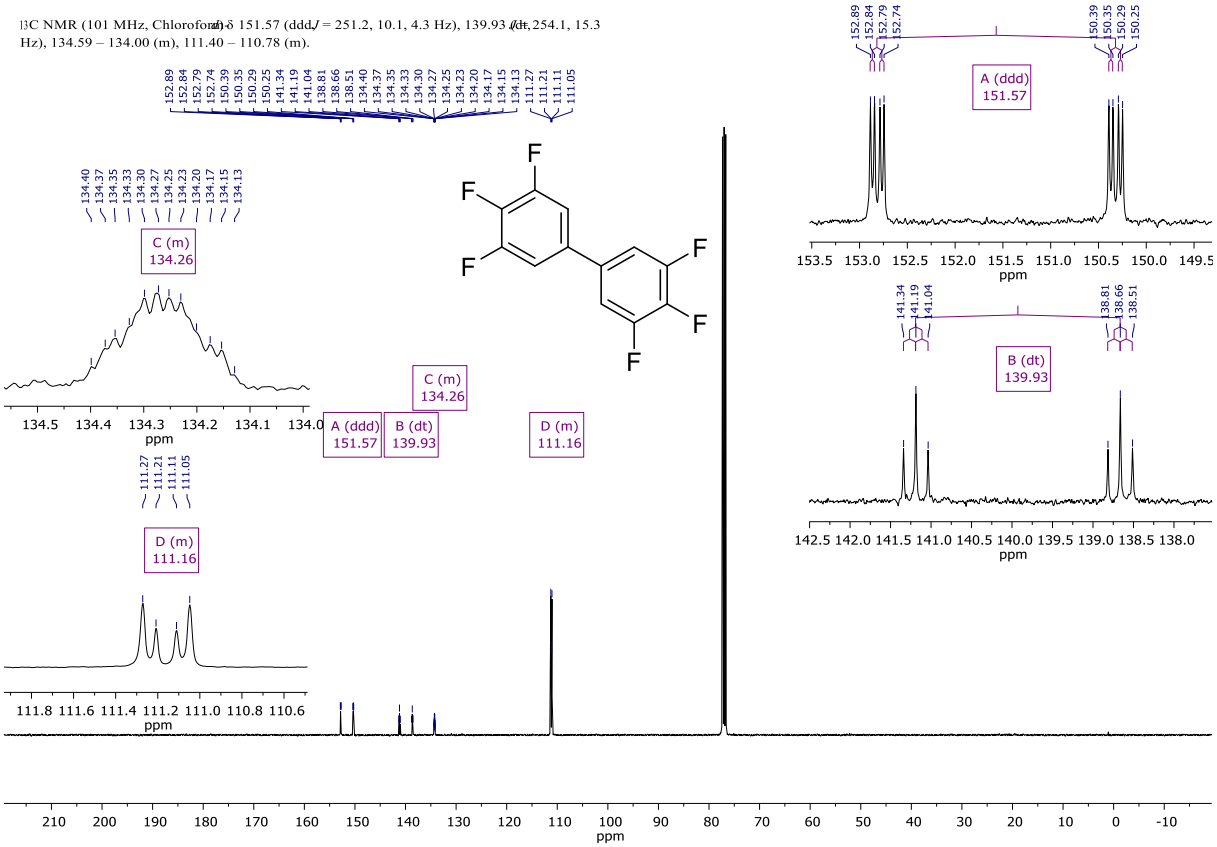


Figure S70 ^{13}C NMR: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

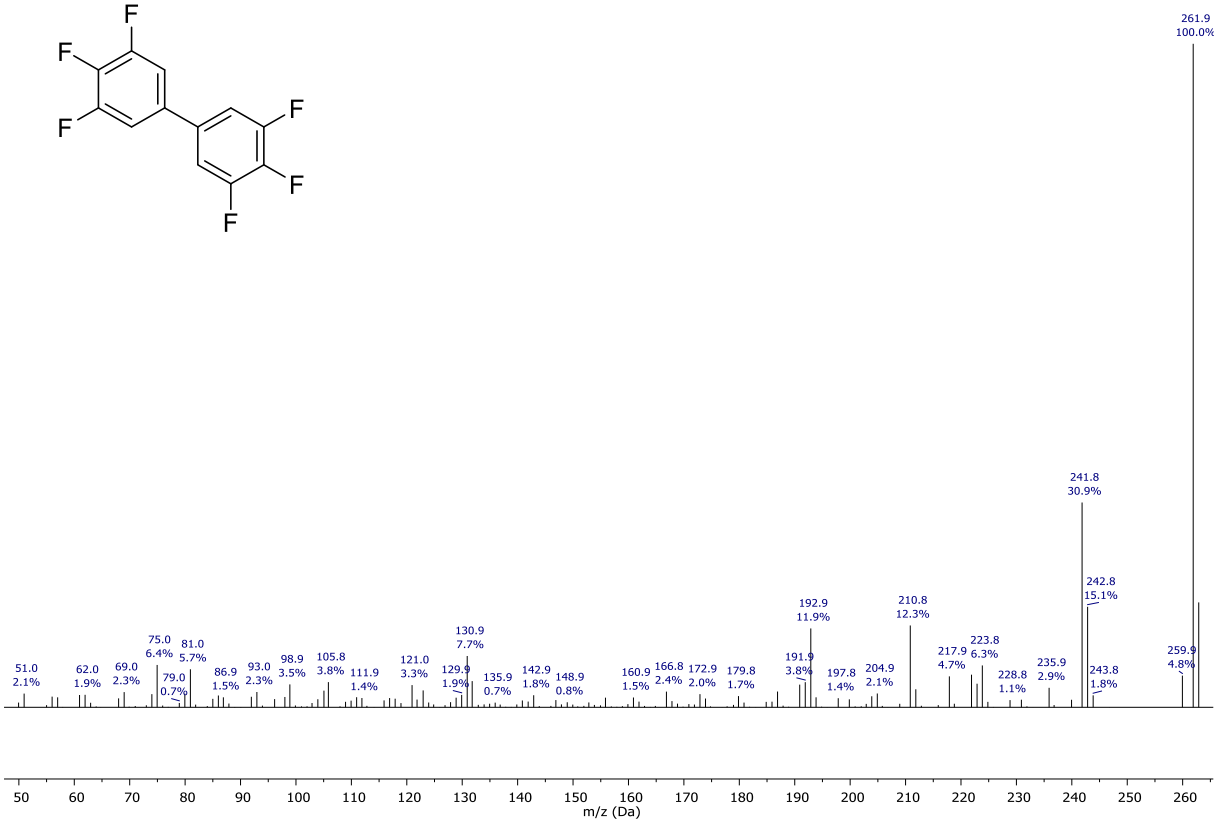


Figure S71 EI-Spectrum (EI$^+$): 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

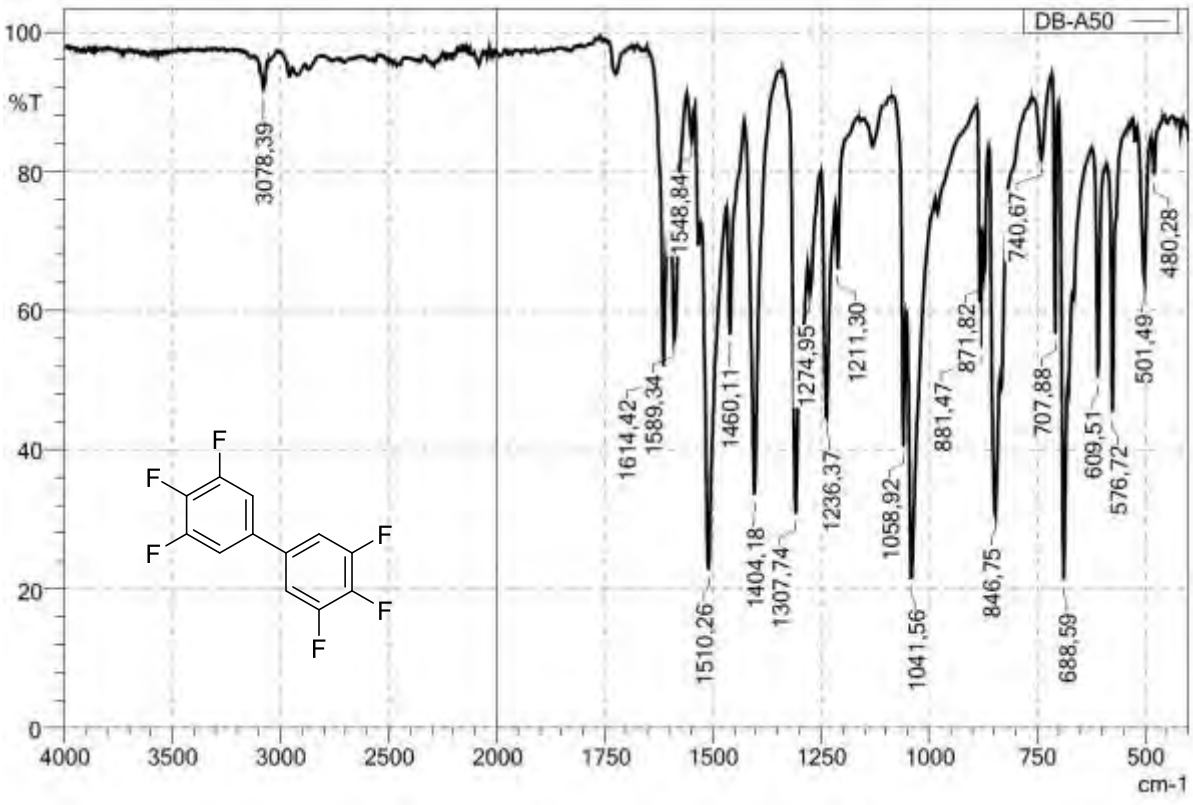


Figure S72 IR (ATR)-Spectrum: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl (29)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 (ddd, J = 10.5, 8.5, 7.0 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.05 (td, J = 9.9, 6.6 Hz, 1H).

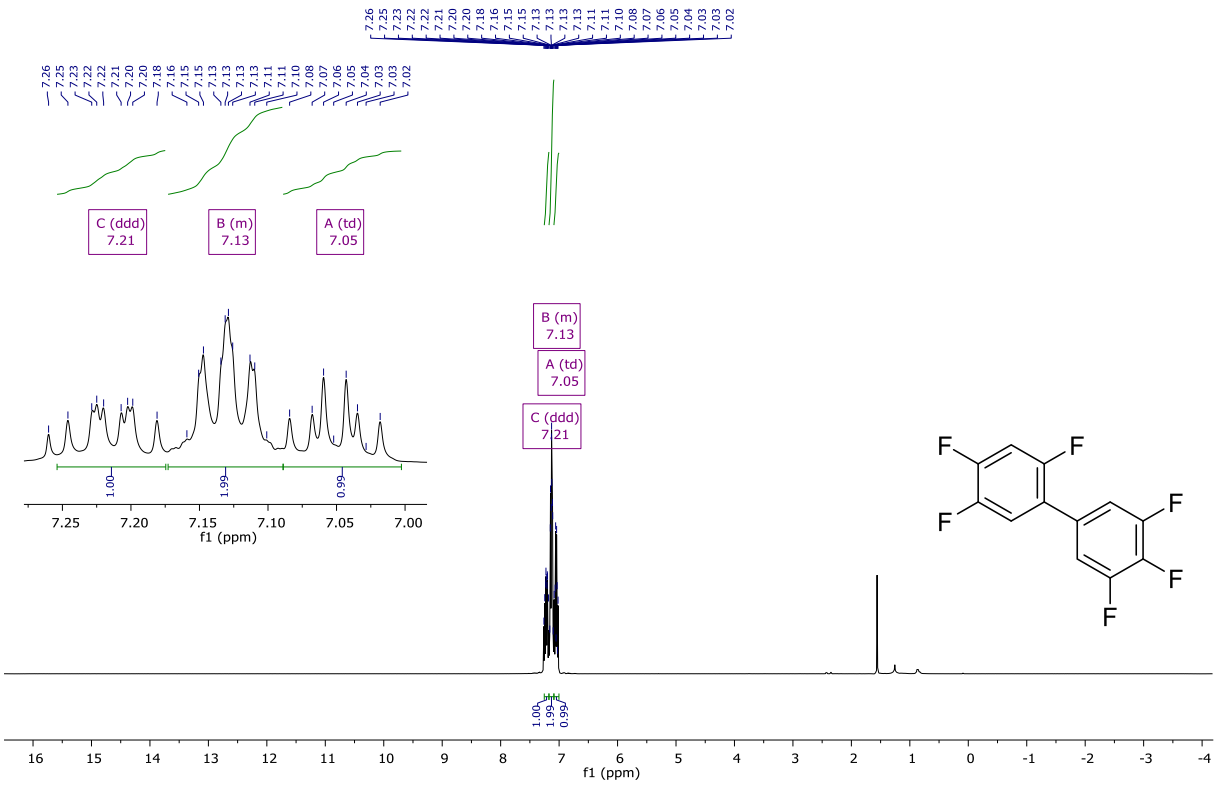


Figure S73 ^{1}H-NMR: 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform-d) δ -118.89 (dd, J = 15.3, 4.5 Hz), -132.60 (dd, J = 21.6, 4.4 Hz), -133.68 (dd, J = 20.5, 1.5 Hz), -141.60 (dd, J = 21.5, 15.1), -160.36 (t, J = 20.5).

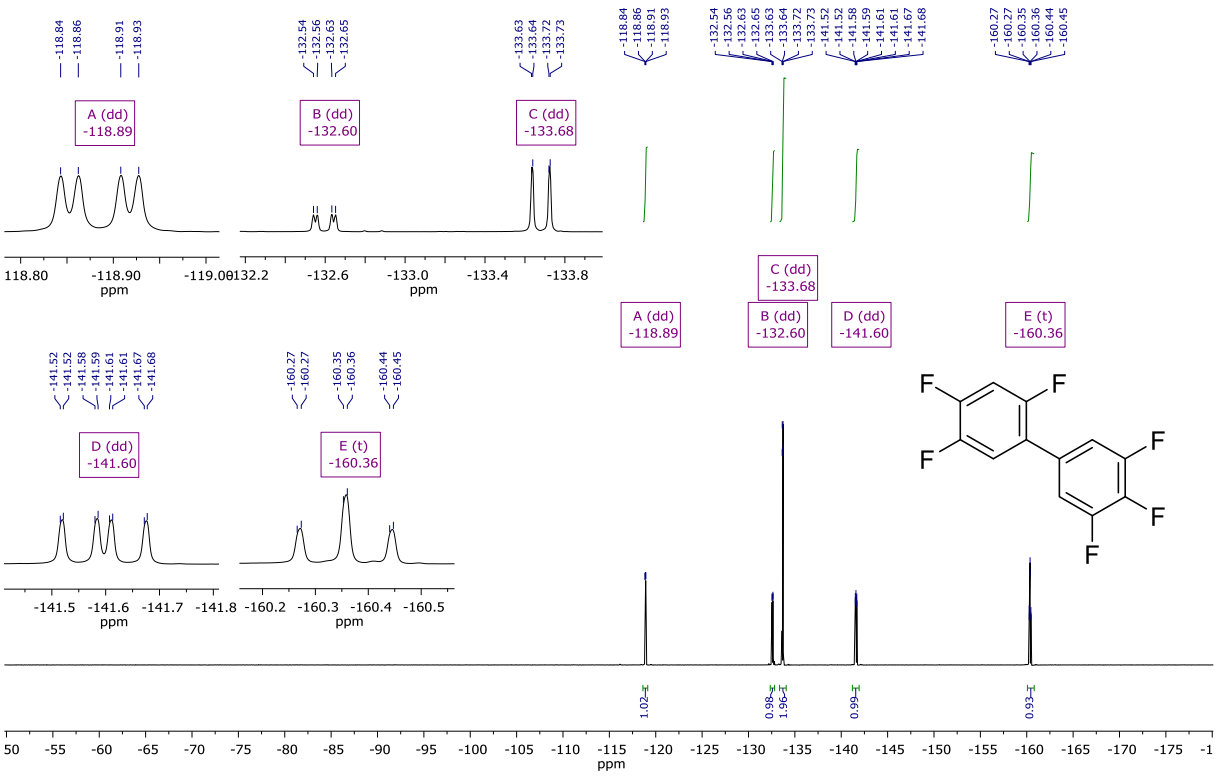


Figure S74 ^{19}F-NMR {^{1}H}: 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

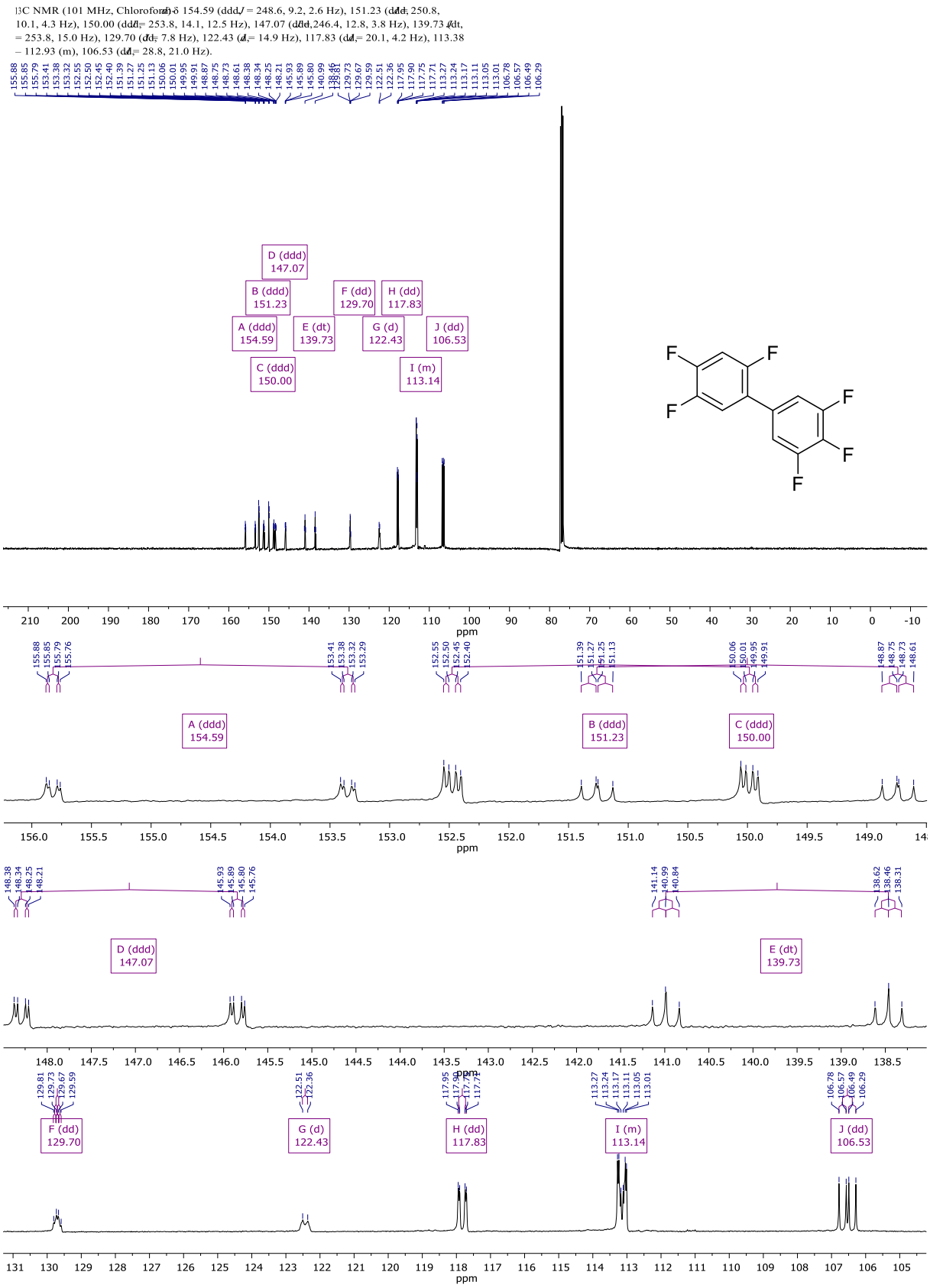


Figure S75 ^{13}C NMR: 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

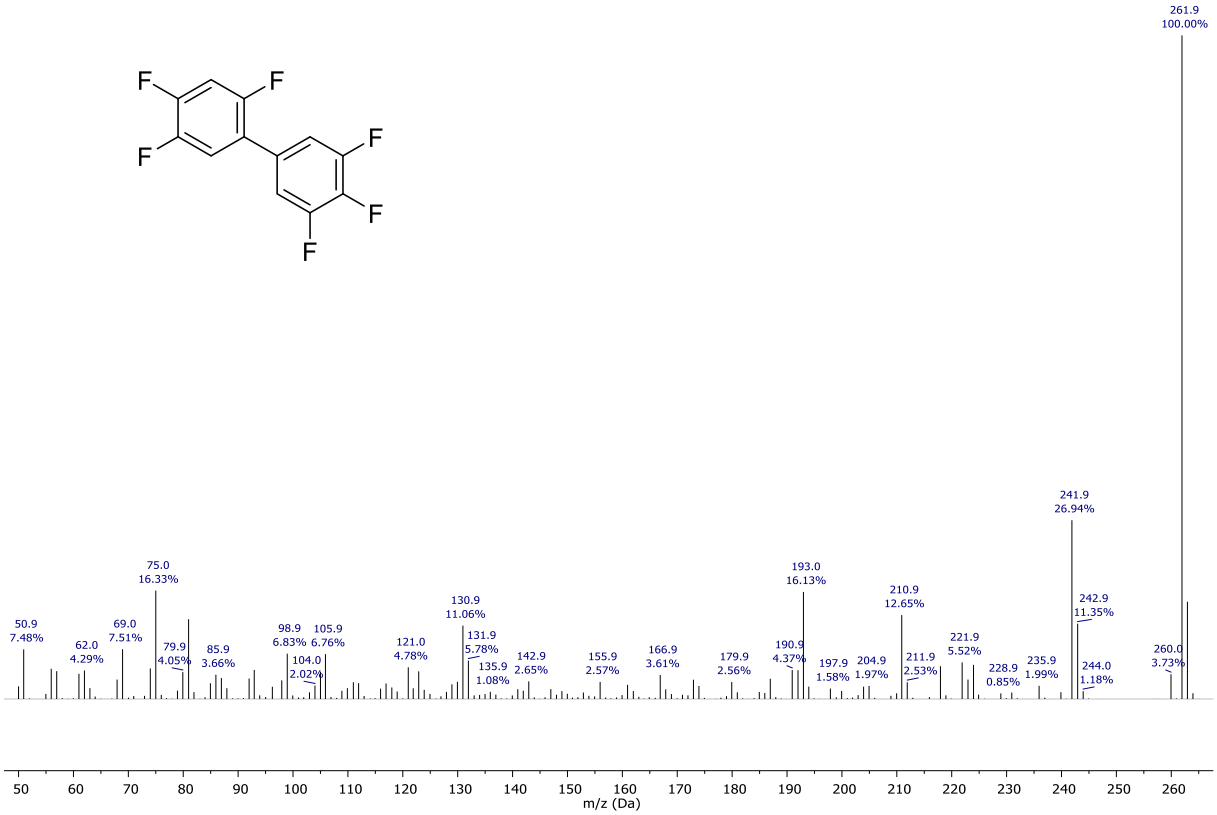


Figure S76 EI-Spectrum (EI⁺): 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

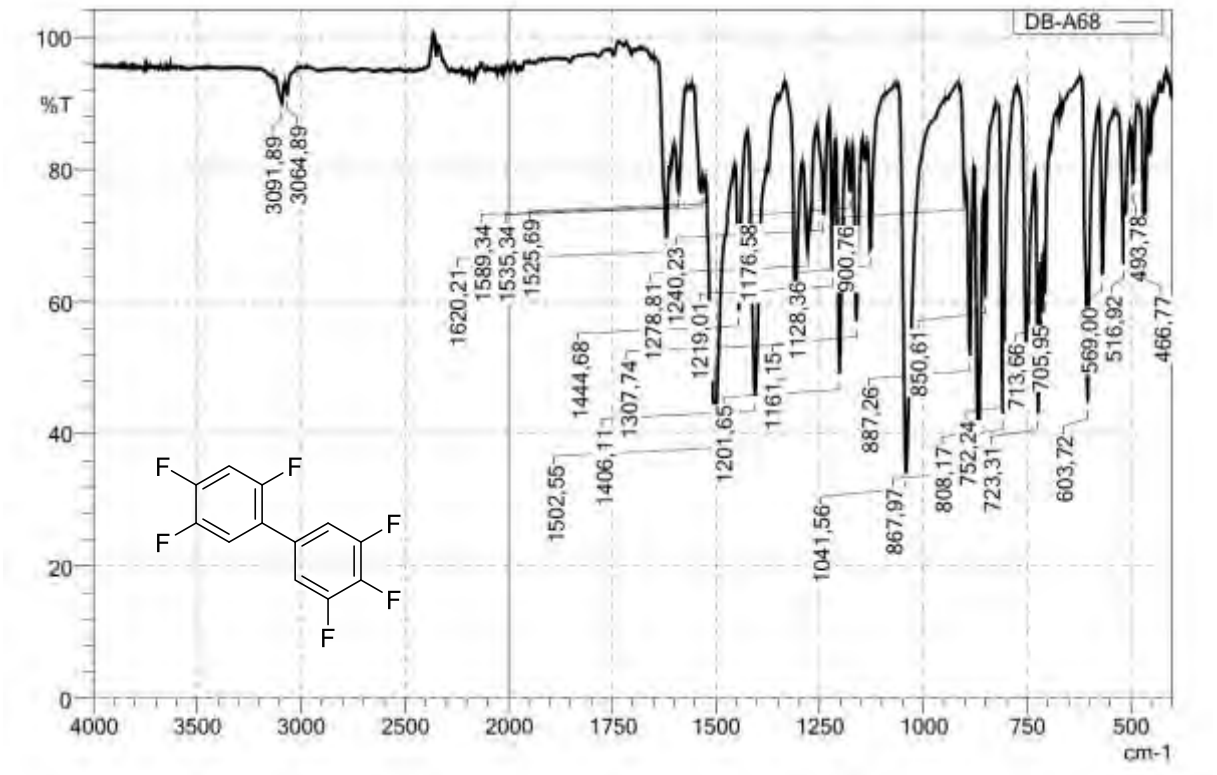


Figure S77 IR (ATR)-Spectrum: 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl (30)

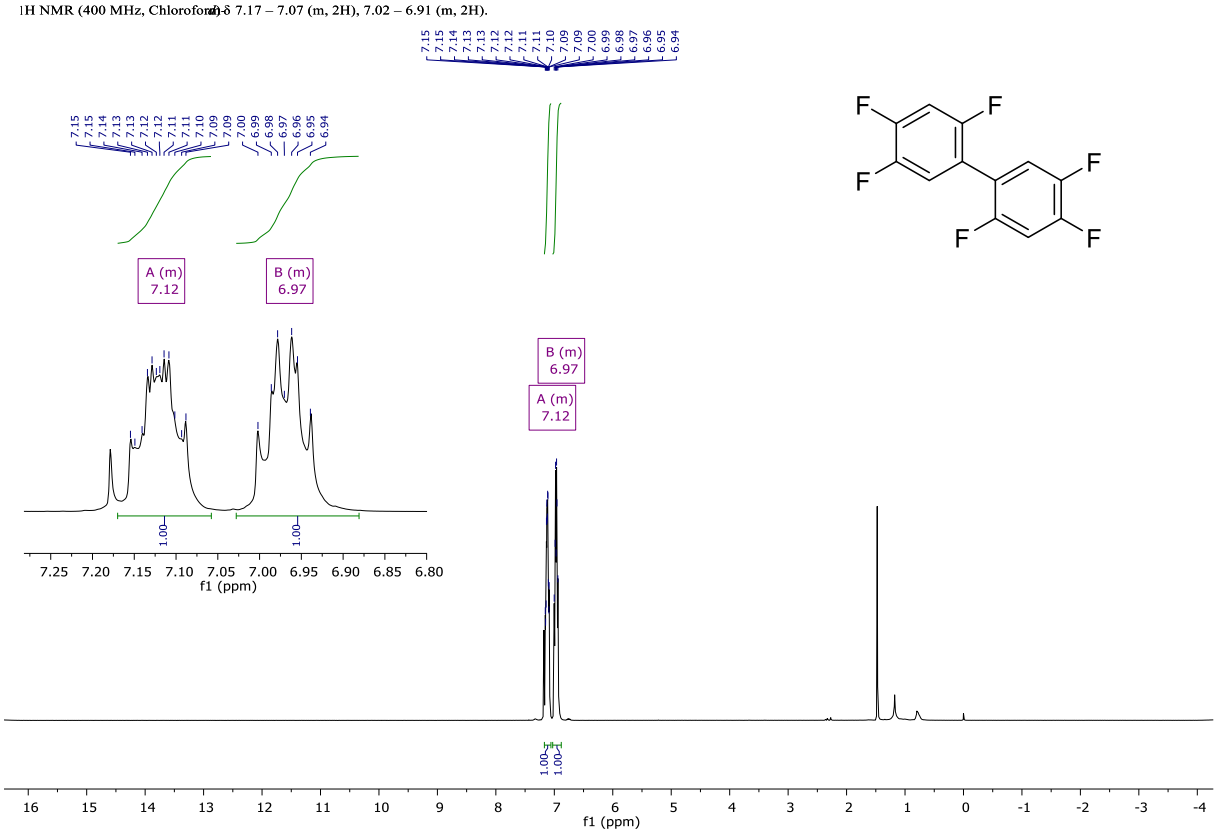


Figure S78 ^{1}H-NMR: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

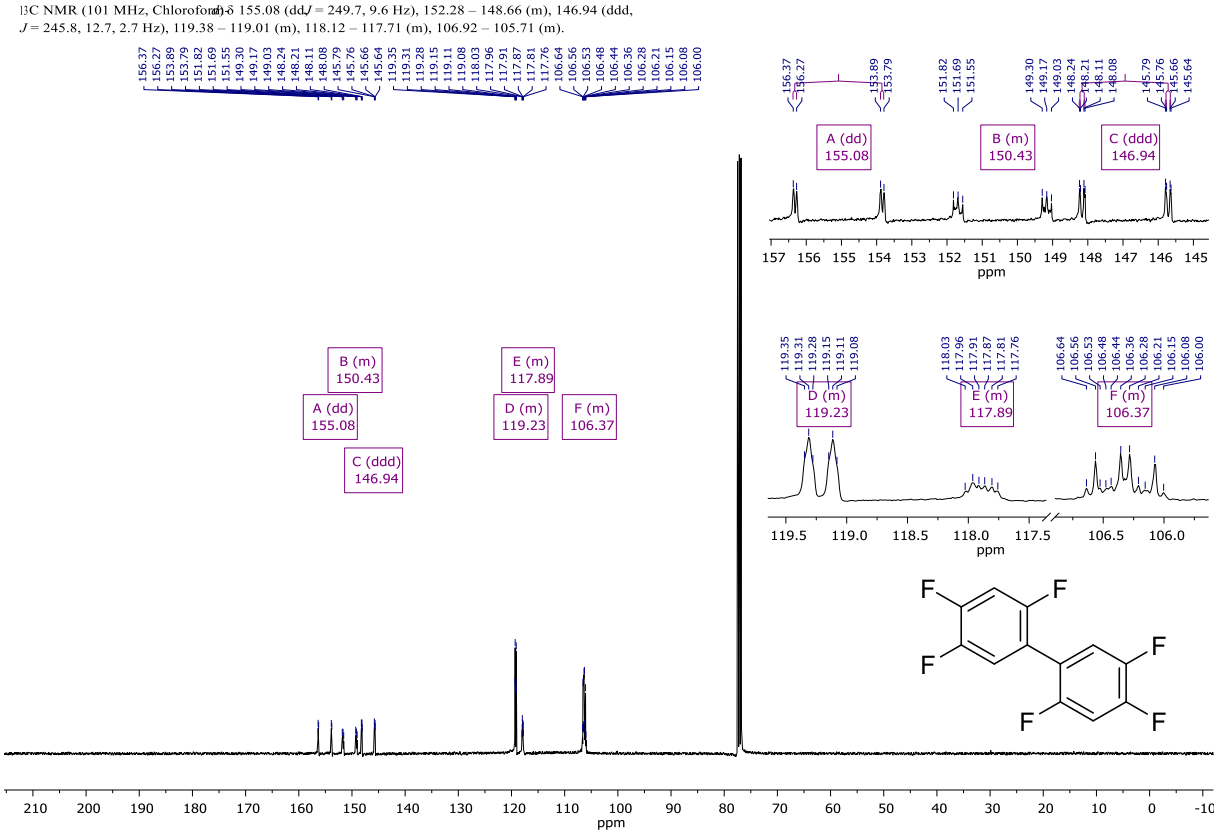


Figure S79 ^{13}C NMR: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

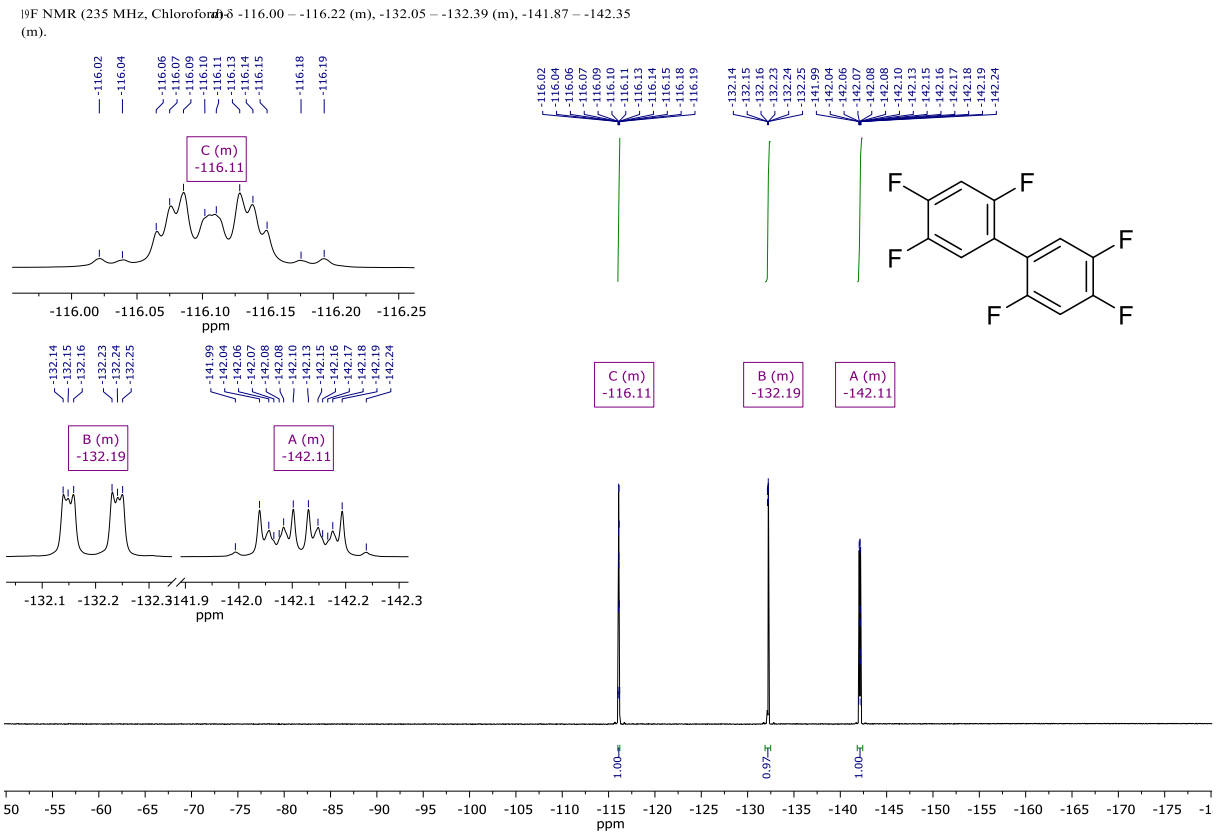


Figure S80 ^{19}F-NMR {^{1}H}: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

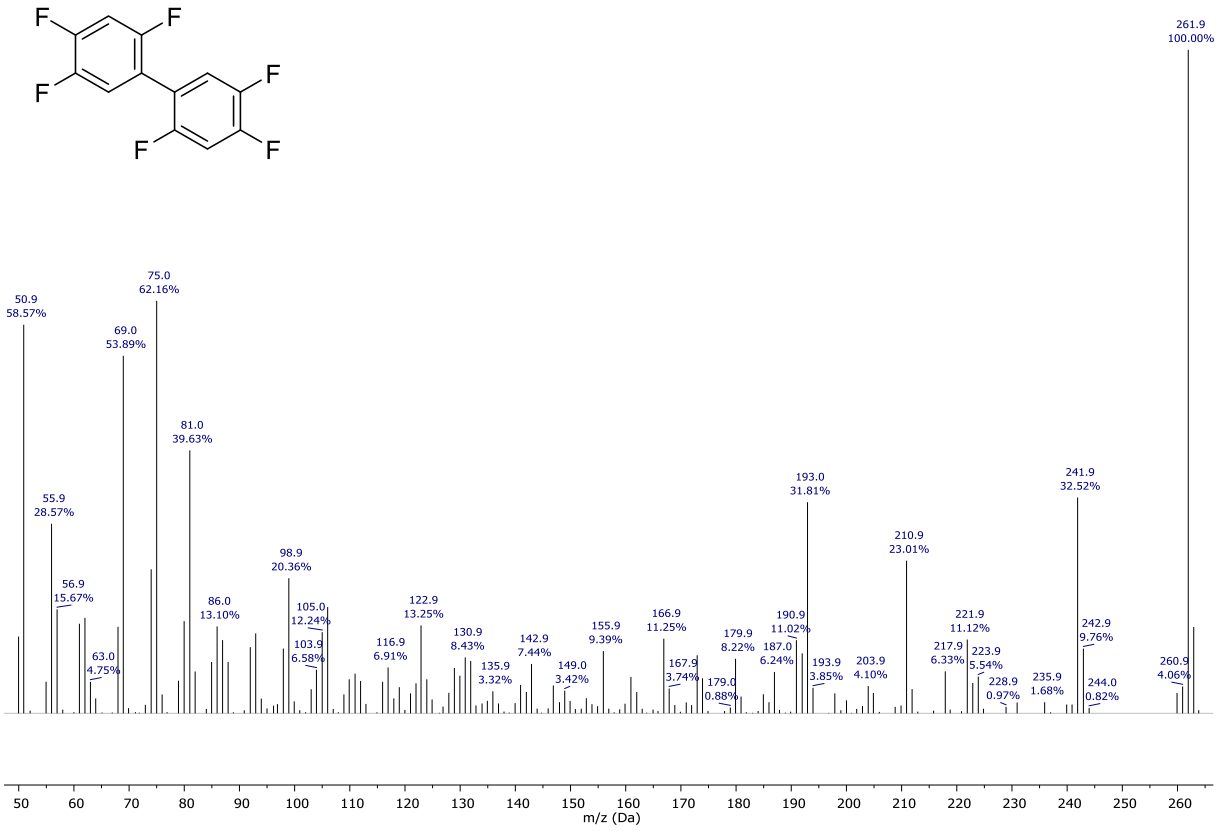


Figure S81 EI-Spectrum (EI^{+}): 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

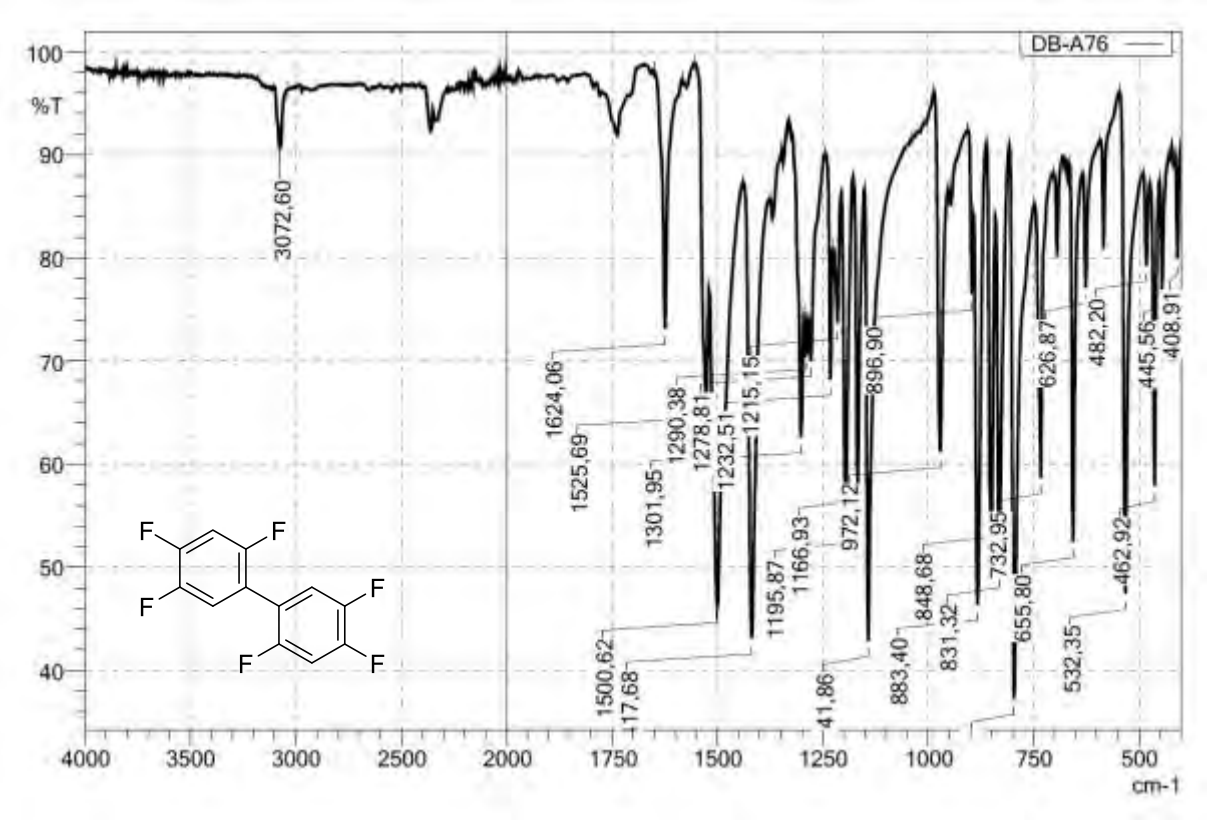


Figure S82 IR (ATR)-Spectrum: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl (31)

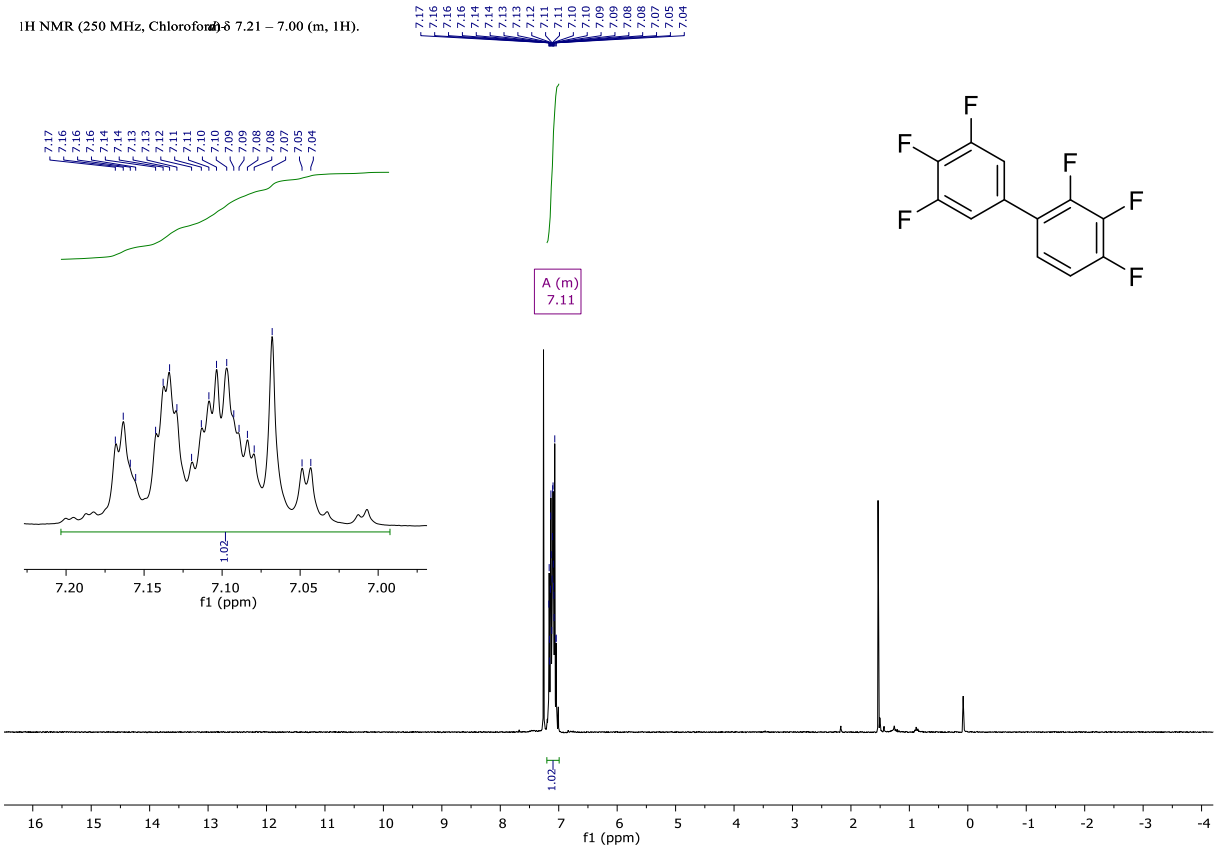


Figure S83 ^{1}H-NMR: 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl

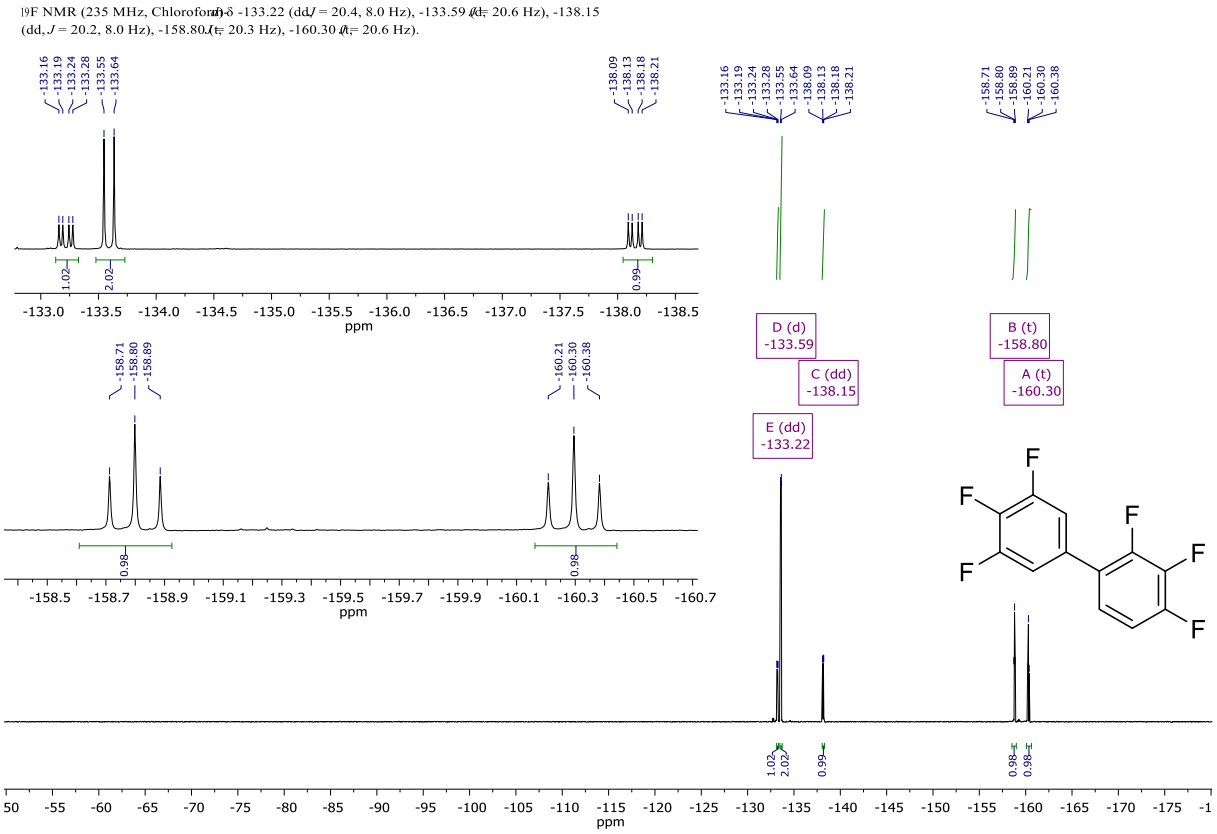


Figure S84 ^{19}F-NMR {^{1}H}: 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl

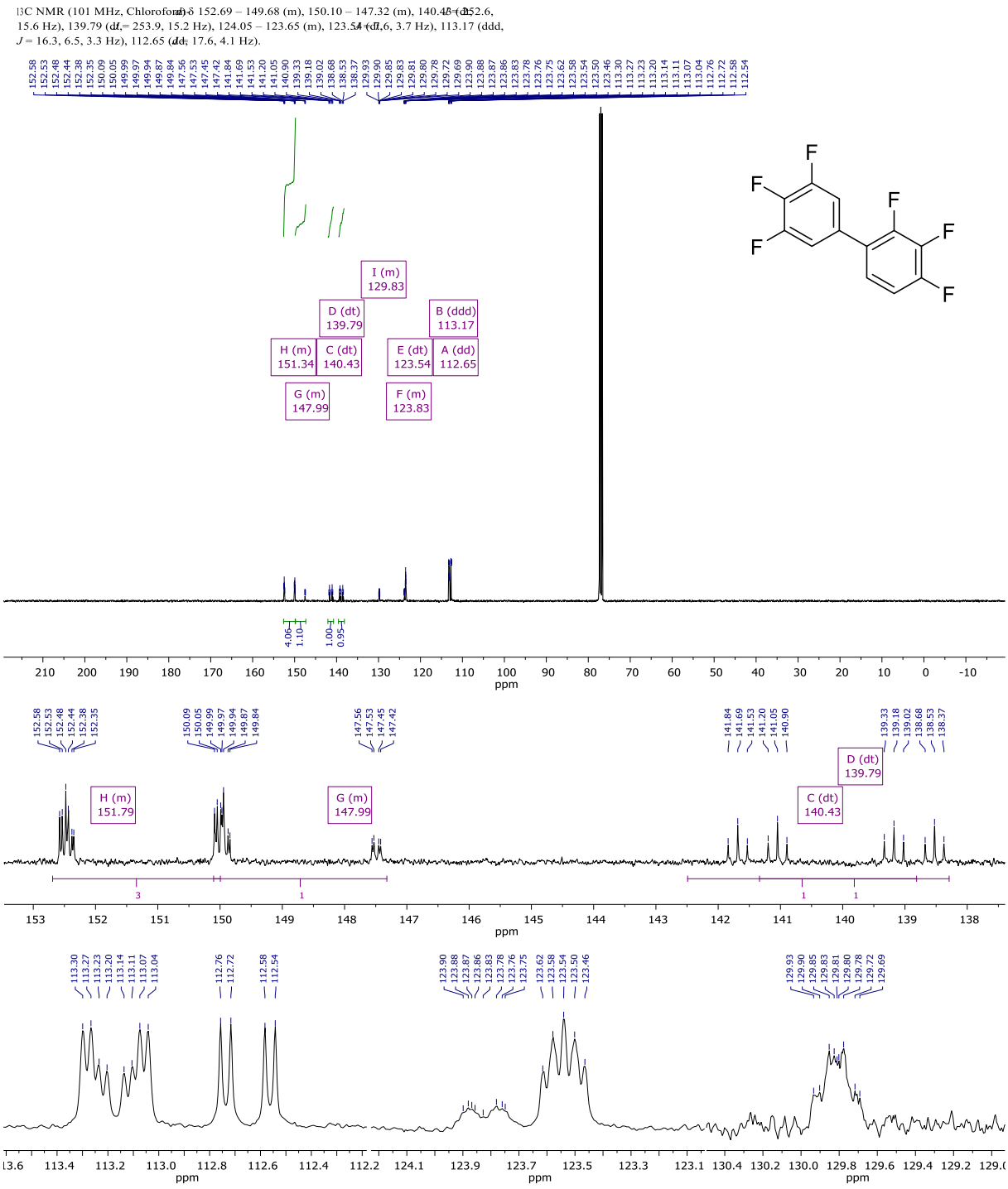


Figure S85 ^{13}C NMR: 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl

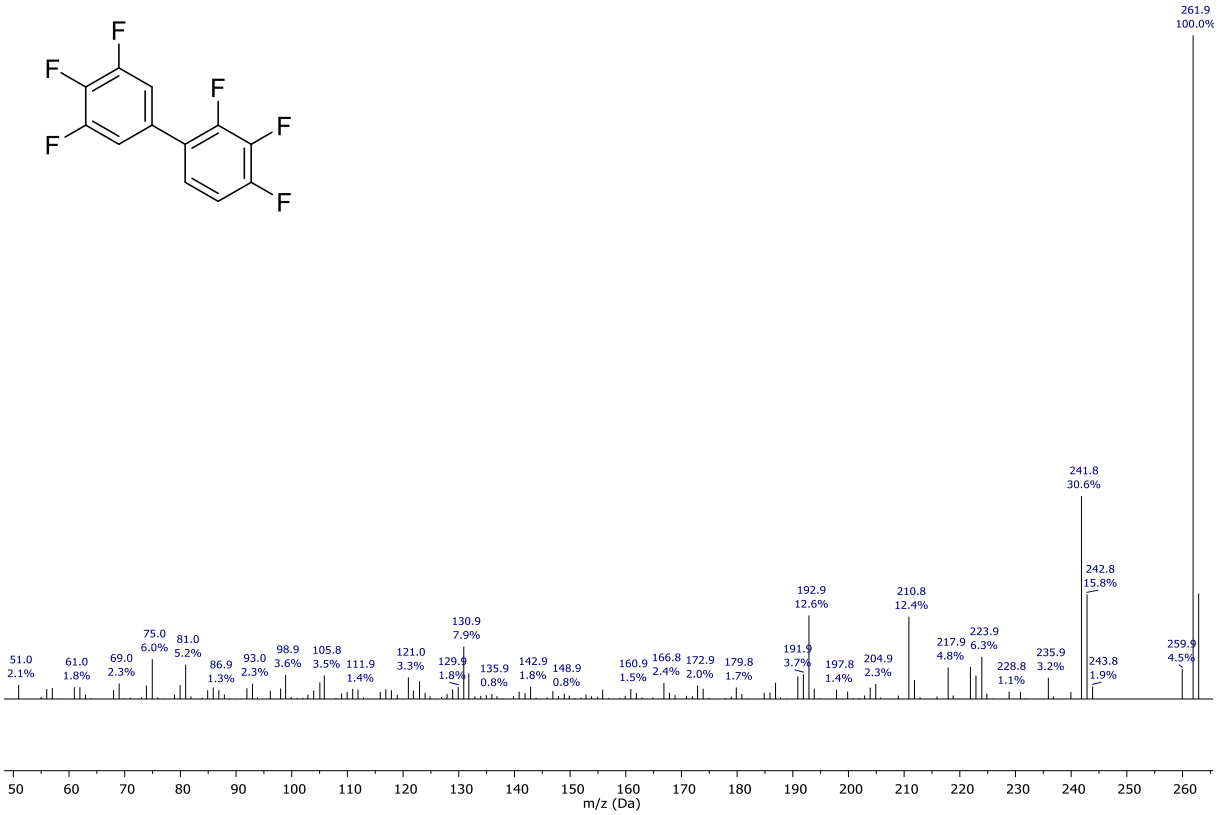


Figure S86 EI-Spectrum (EI⁺): 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl

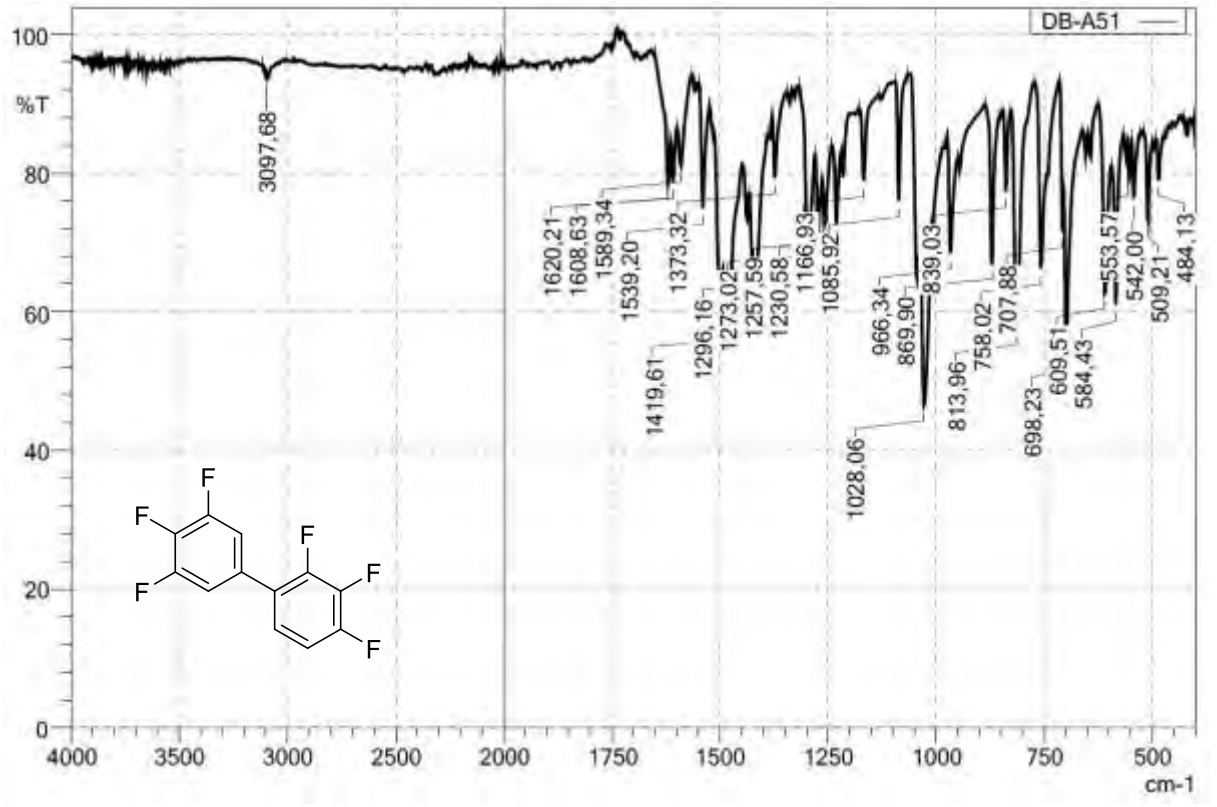


Figure S87 IR (ATR)-Spectrum: 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl

2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl (32)

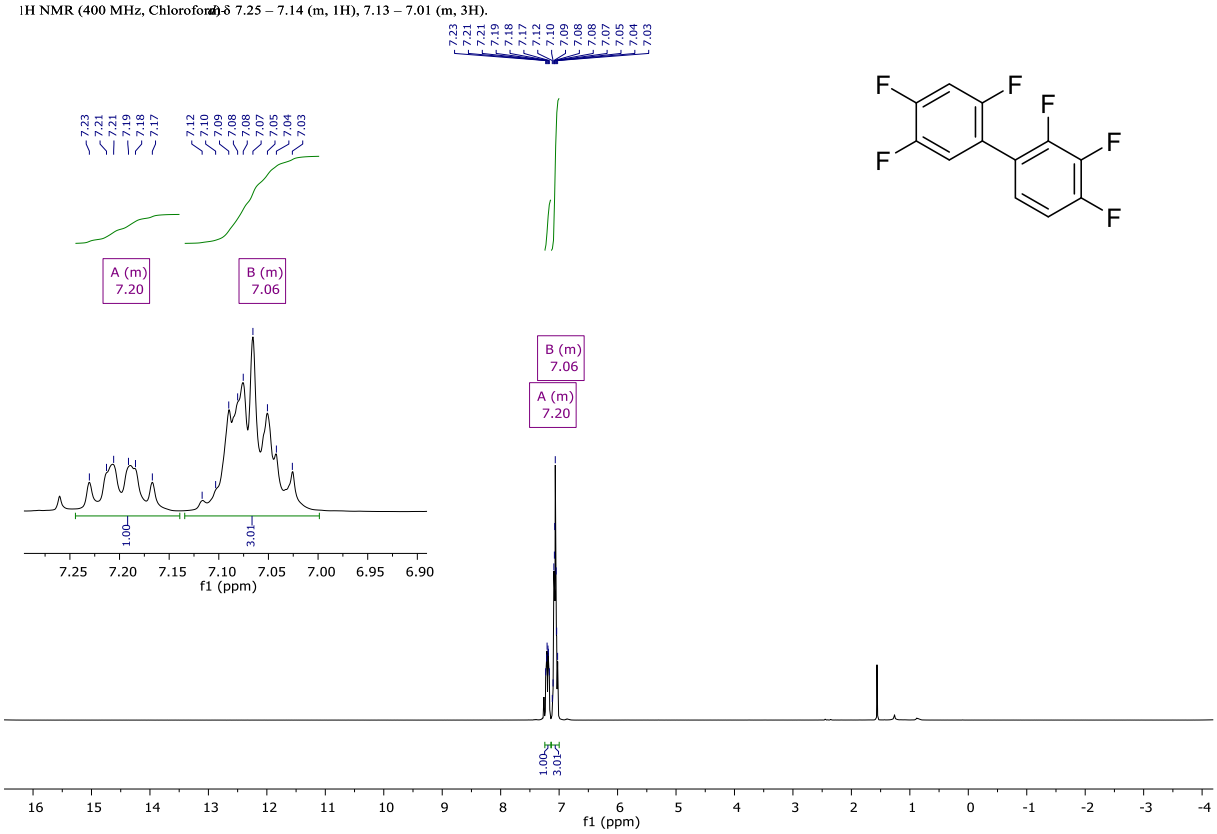


Figure S88 ^{1}H-NMR: 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

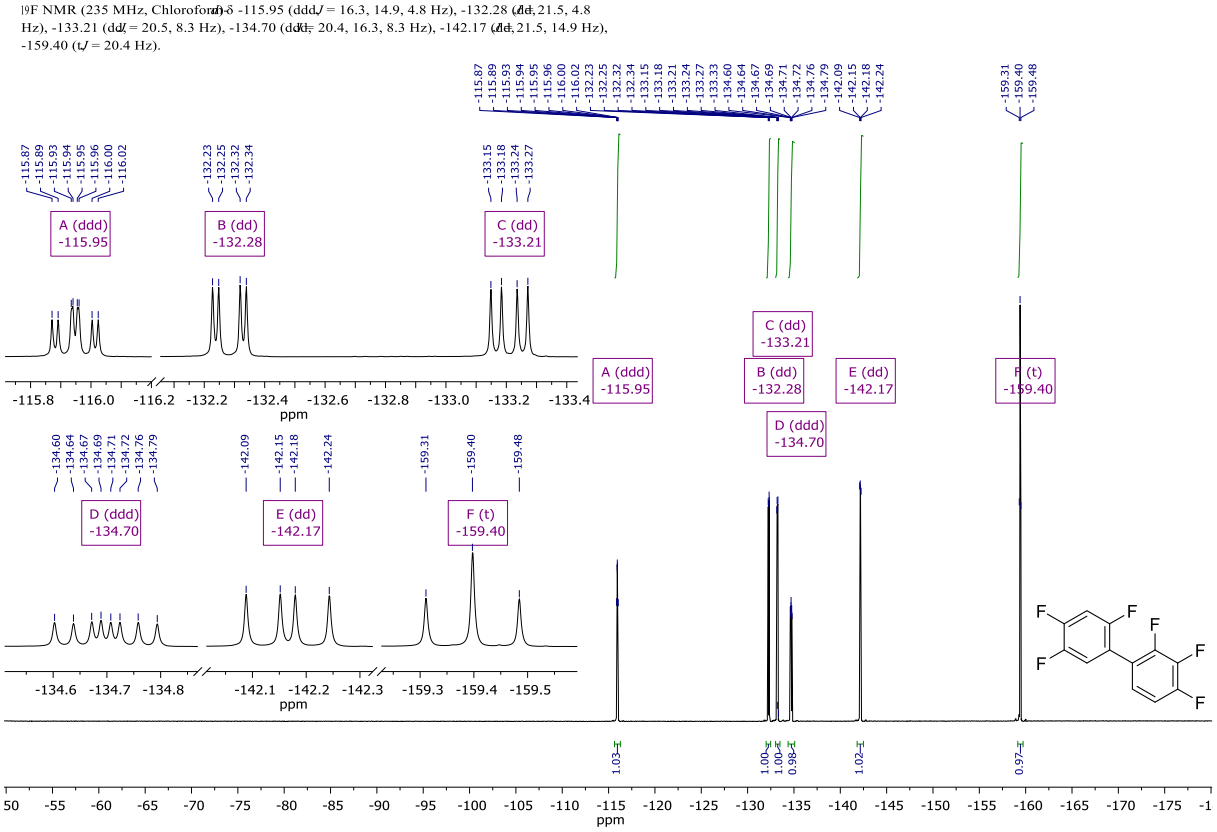


Figure S89 ^{19}F-NMR {^{1}H}: 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

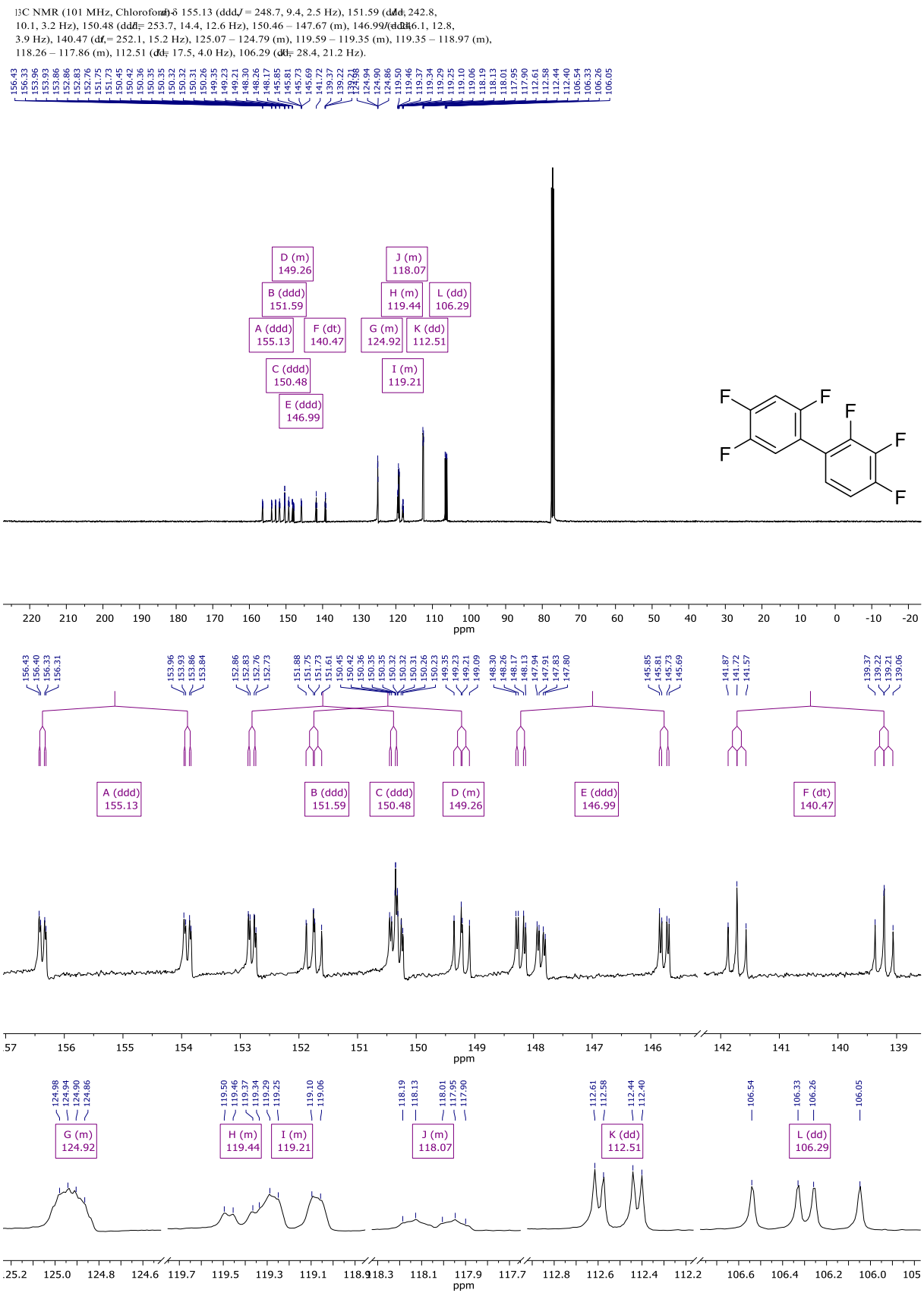


Figure S90 ^{13}C NMR: 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

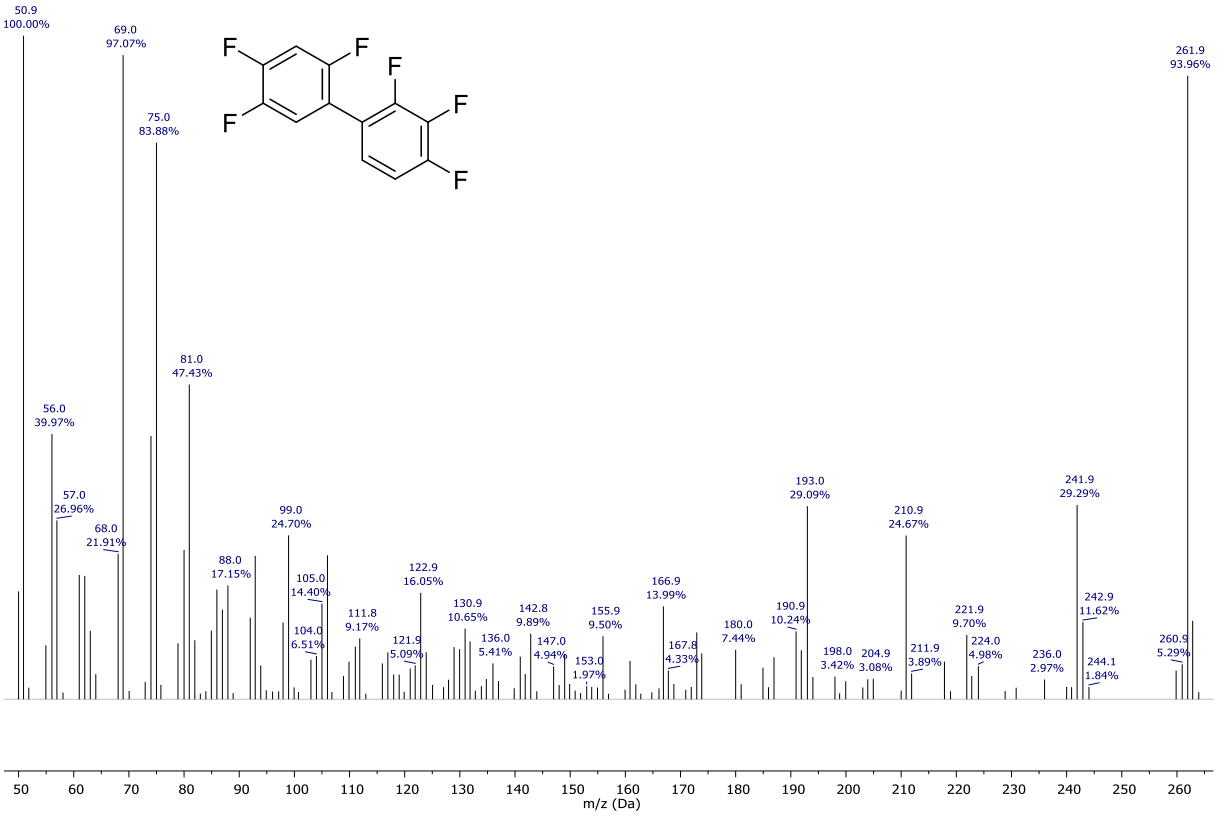


Figure S91 EI-Spectrum (EI⁺): 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

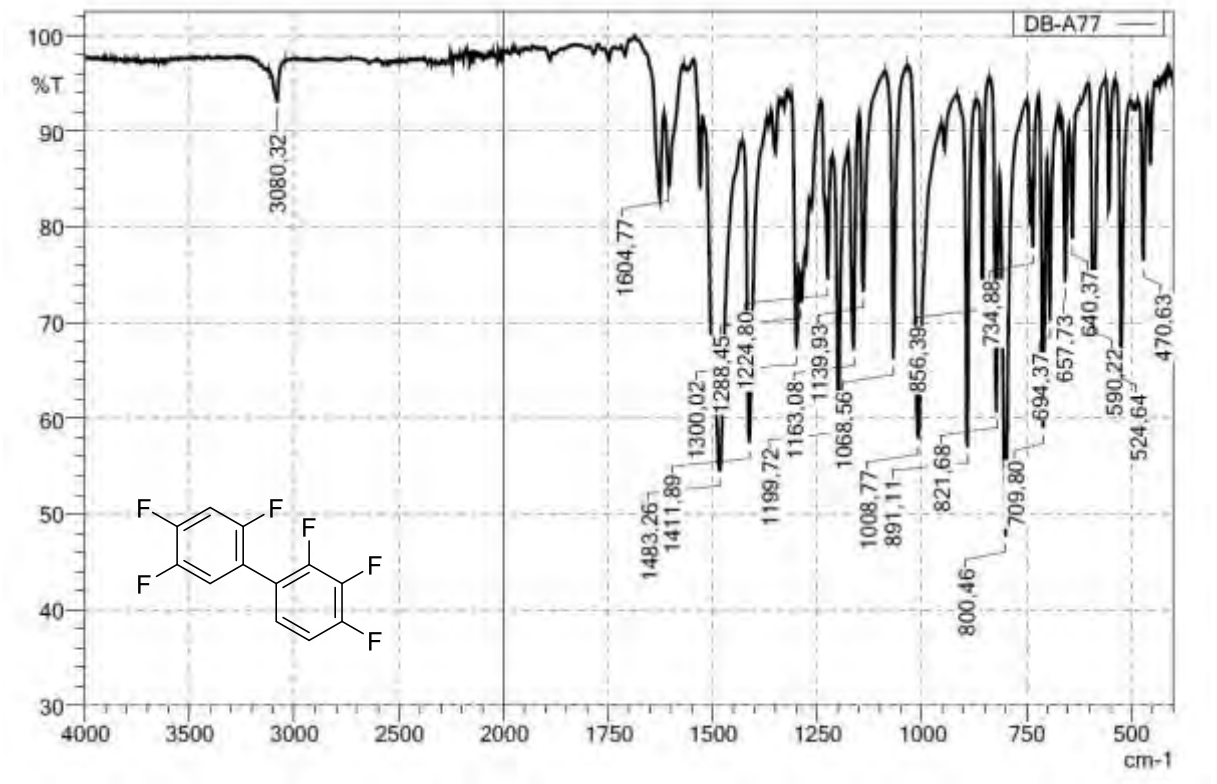


Figure S92 IR (ATR)-Spectrum: 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (33)

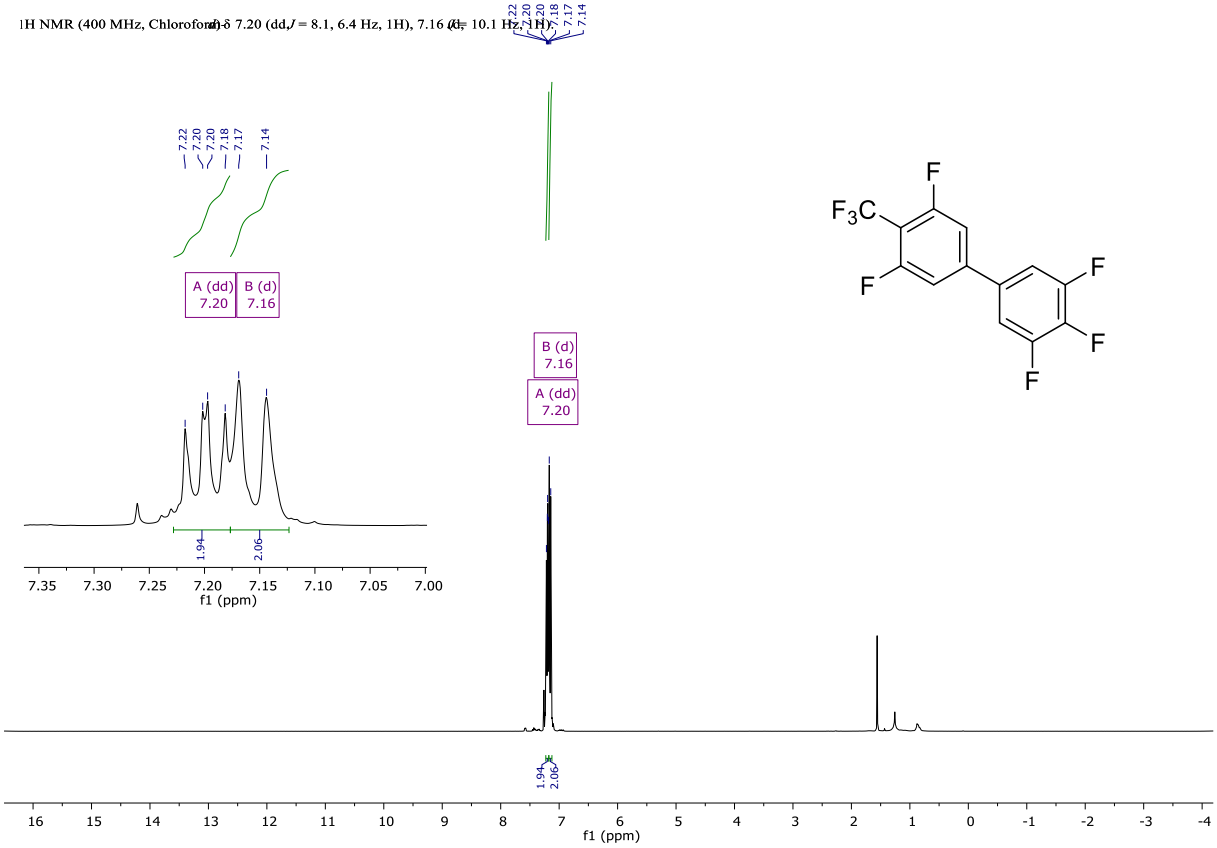


Figure S93 ^{1}H-NMR: 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

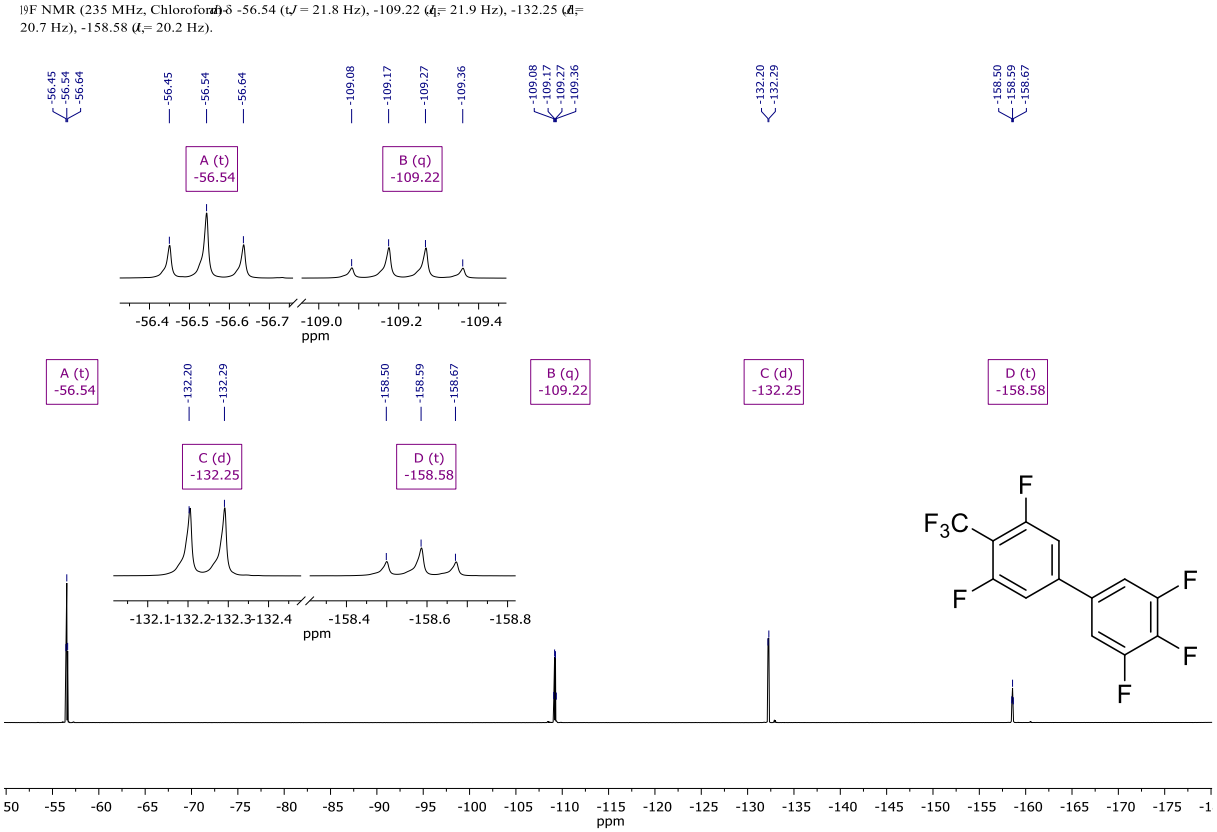


Figure S94 ^{19}F-NMR {^{1}H}: 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

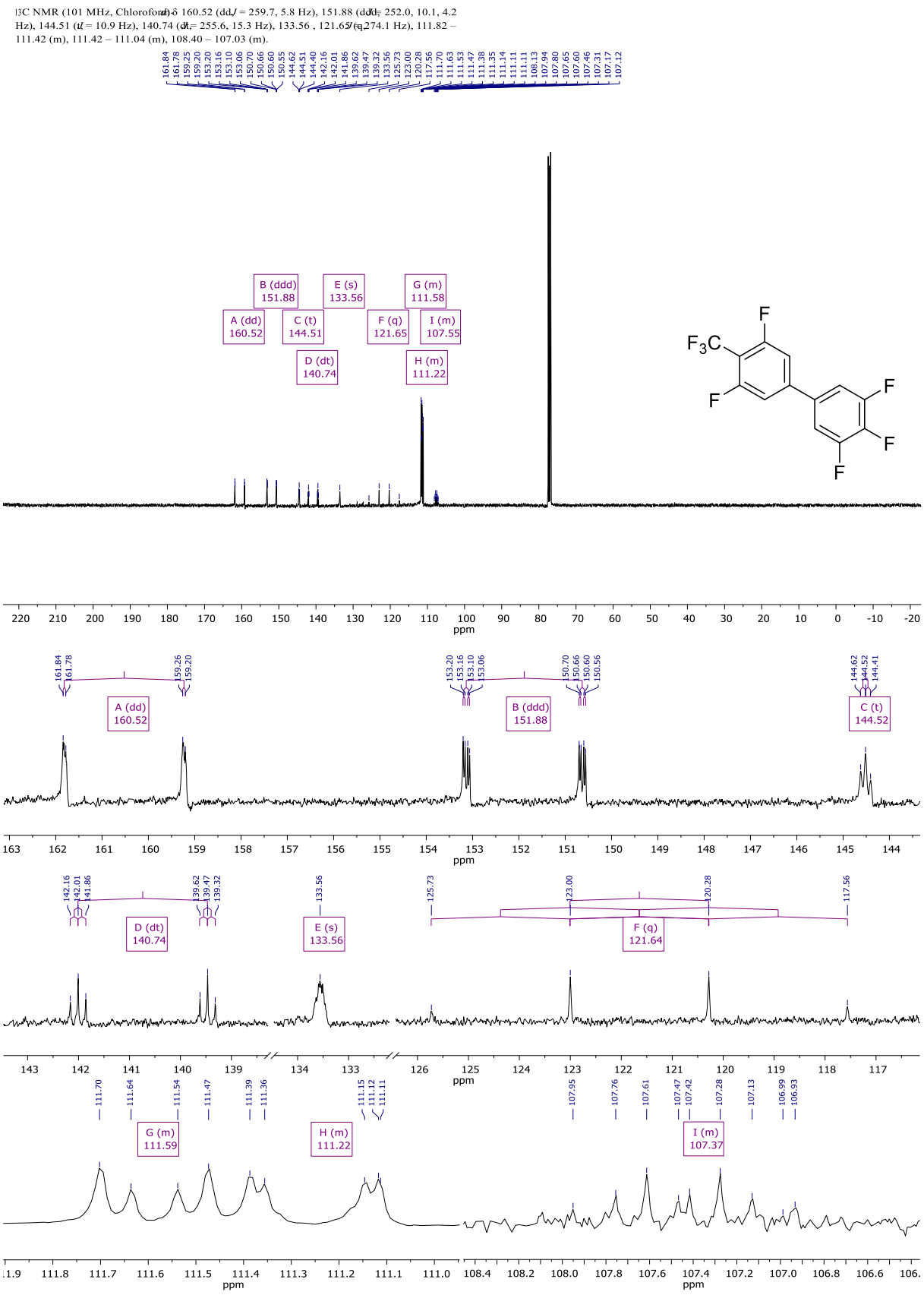


Figure S95 ^{13}C NMR: 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

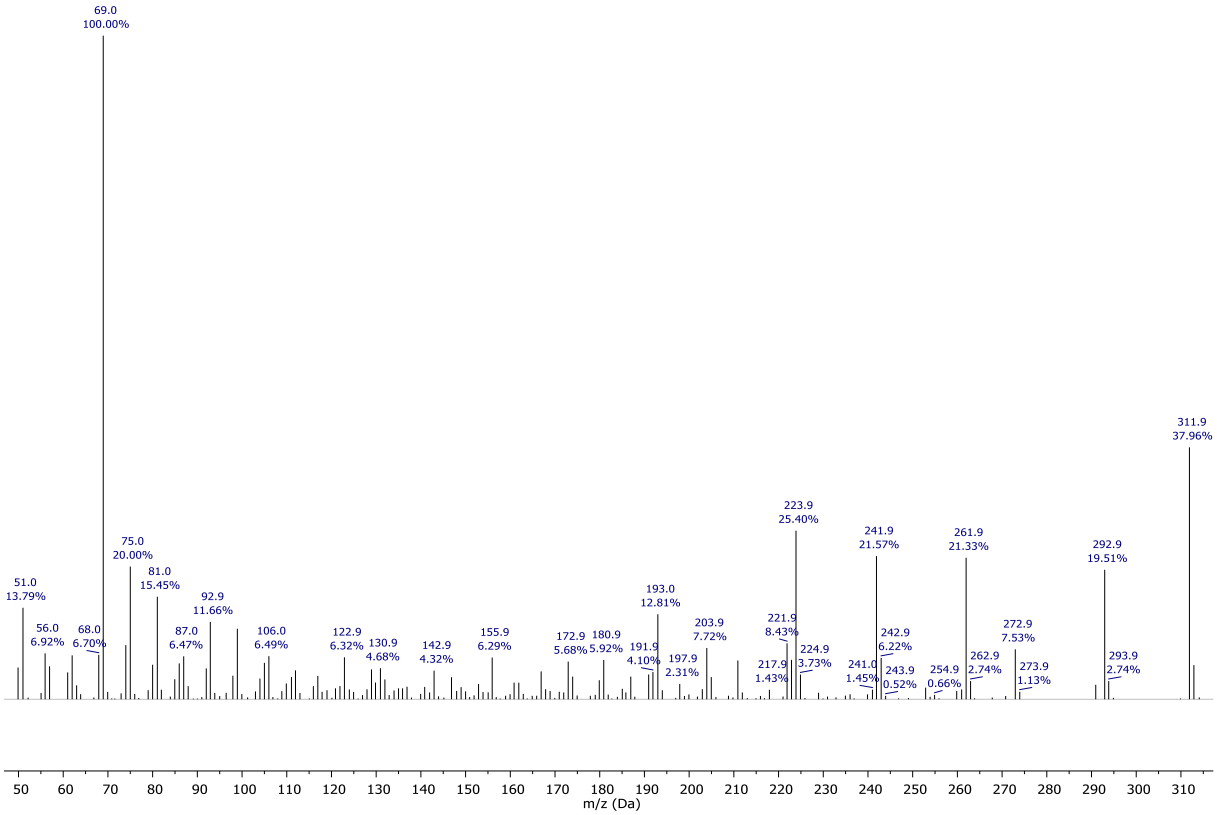


Figure S96 EI-Spectrum (EI⁺): 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

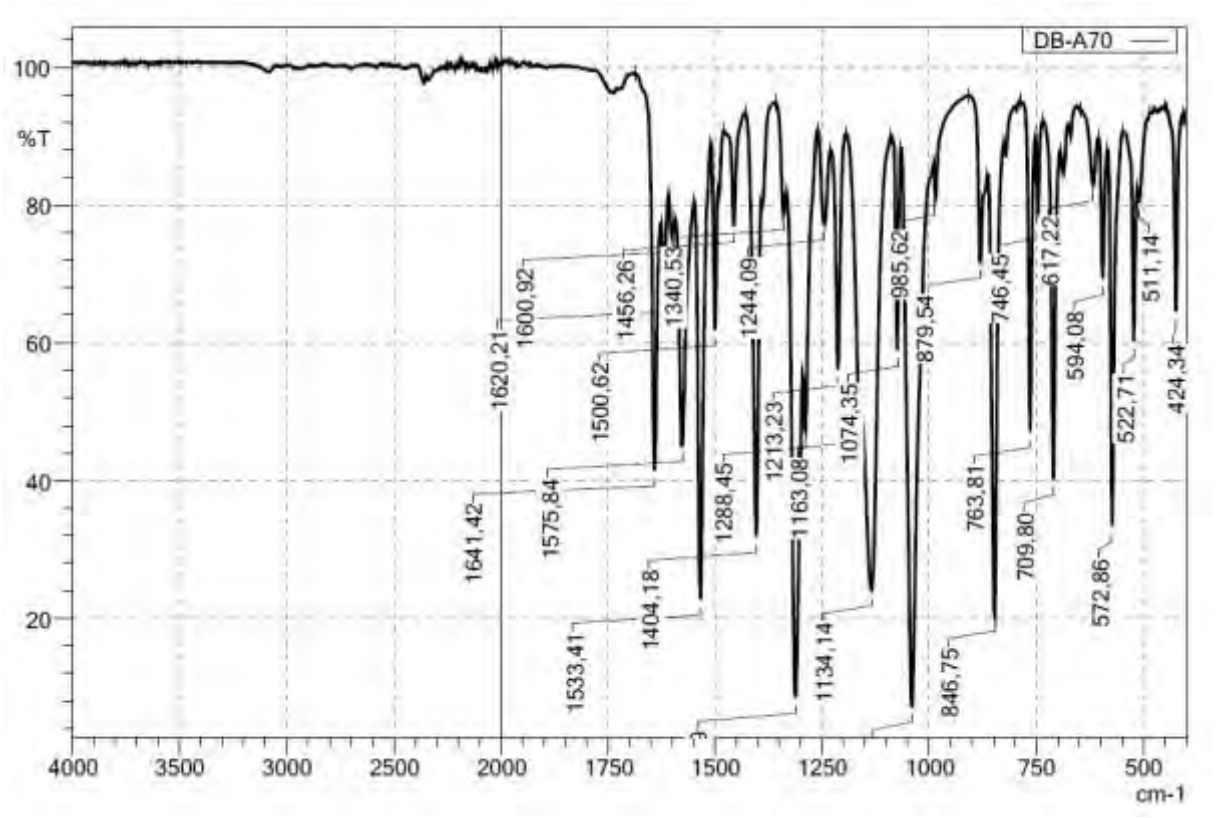


Figure S97 IR (ATR)-Spectrum: 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

Polyfluorinated Phenylpyridines

4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine (34)

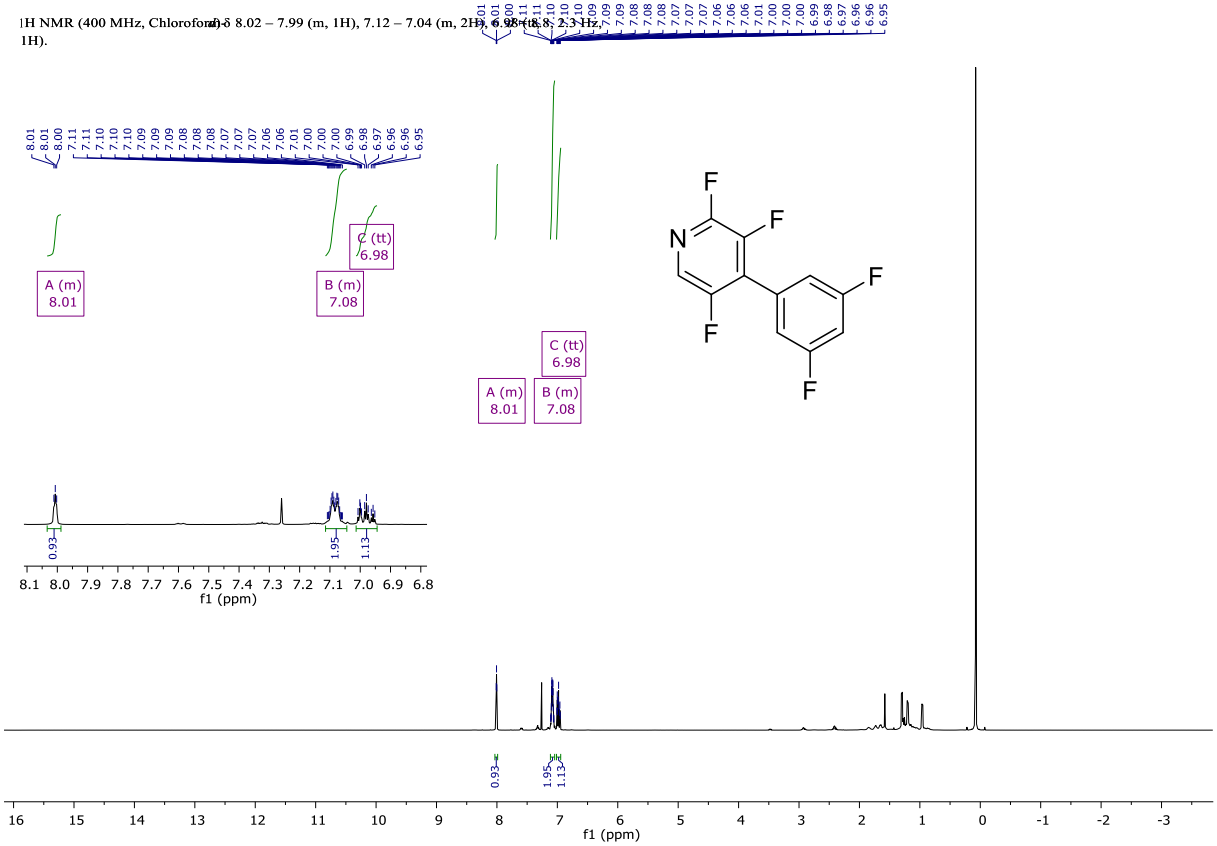


Figure S98 ^{1}H-NMR: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

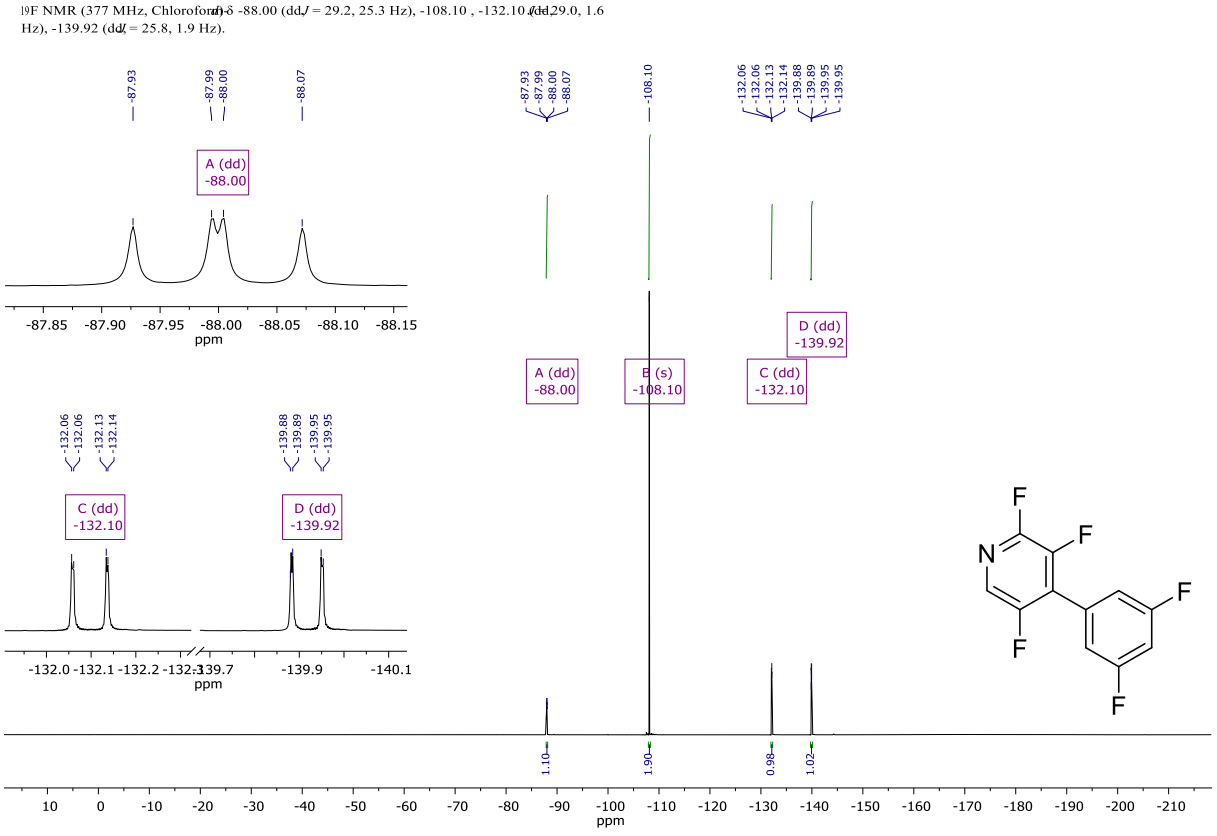


Figure S99 ^{19}F-NMR {^{1}H}: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

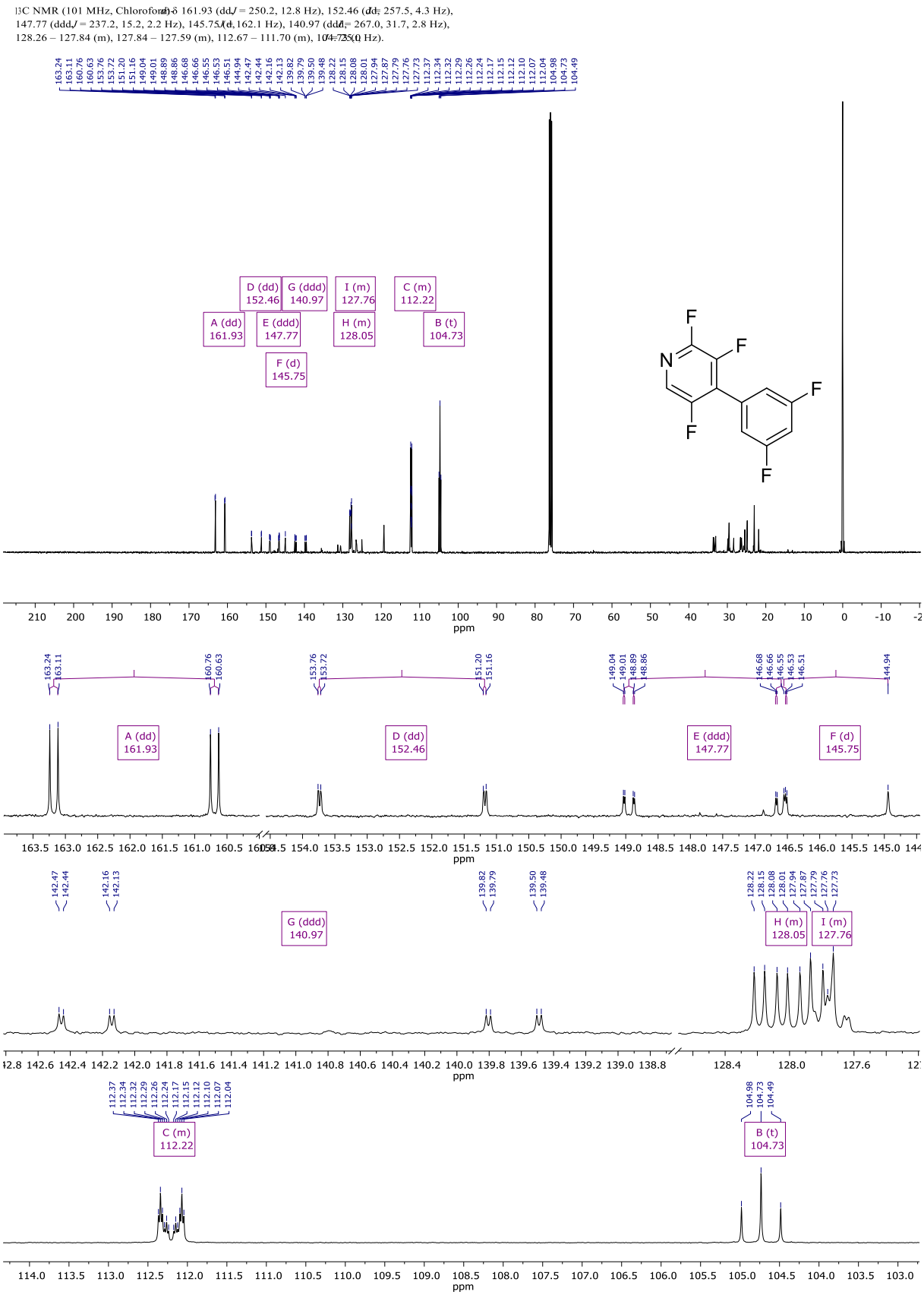


Figure S100 ^{13}C NMR: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

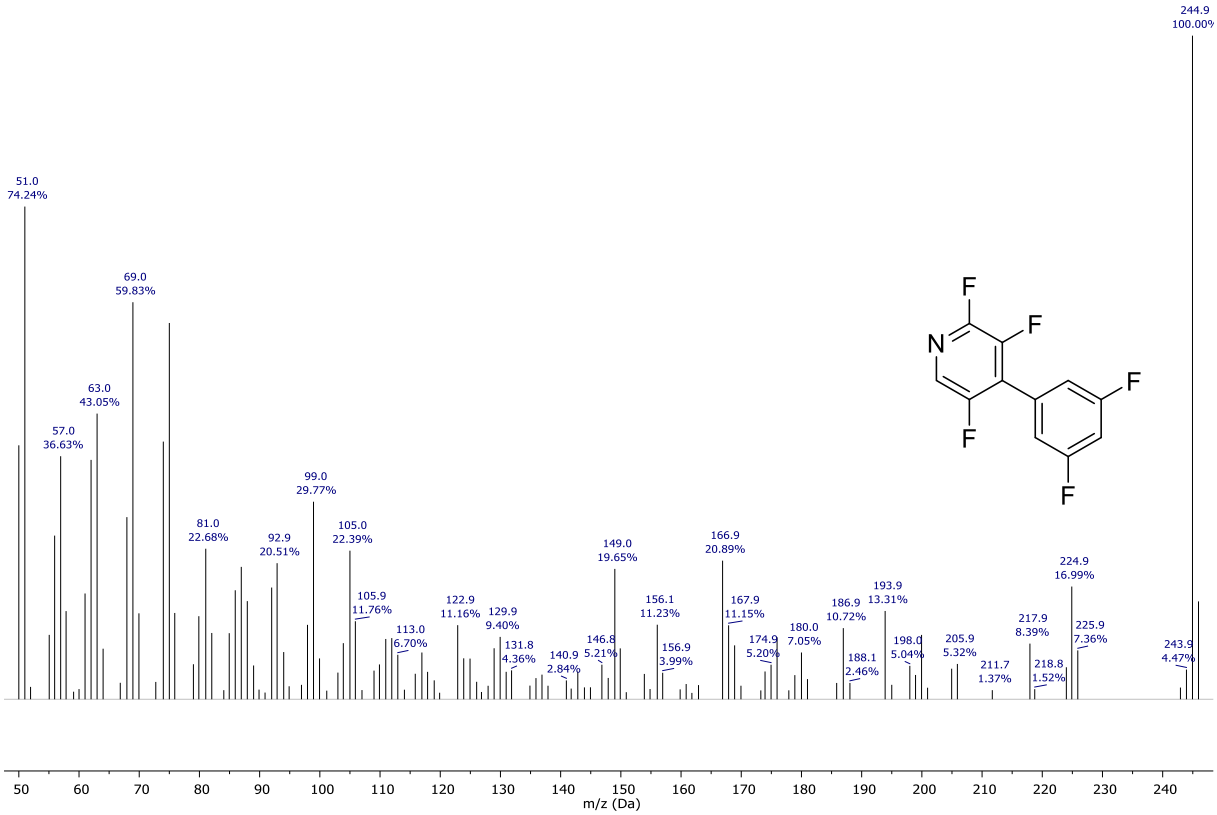


Figure S101 EI-Spectrum (EI⁺): 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

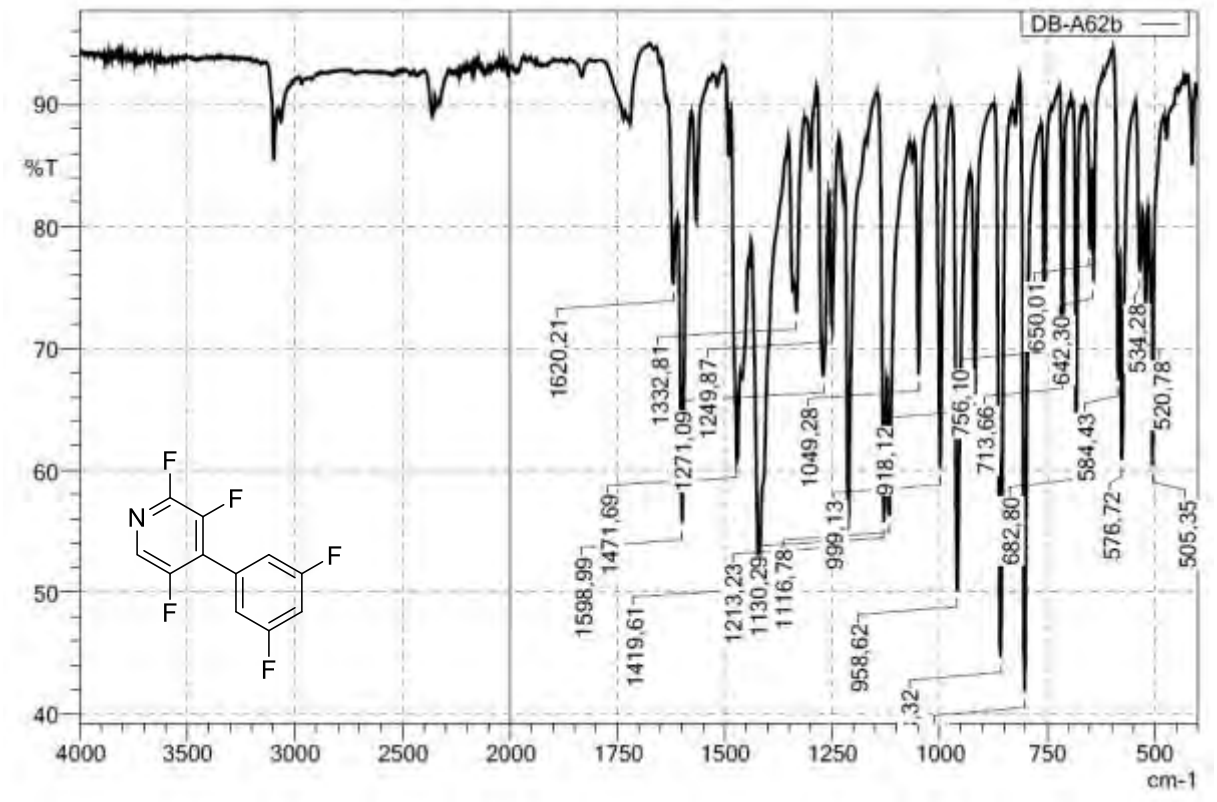


Figure S102 IR (ATR)-Spectrum: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine (35)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (t, J = 1.8 Hz, 1H), 7.18 – 7.10 (m, 2H).

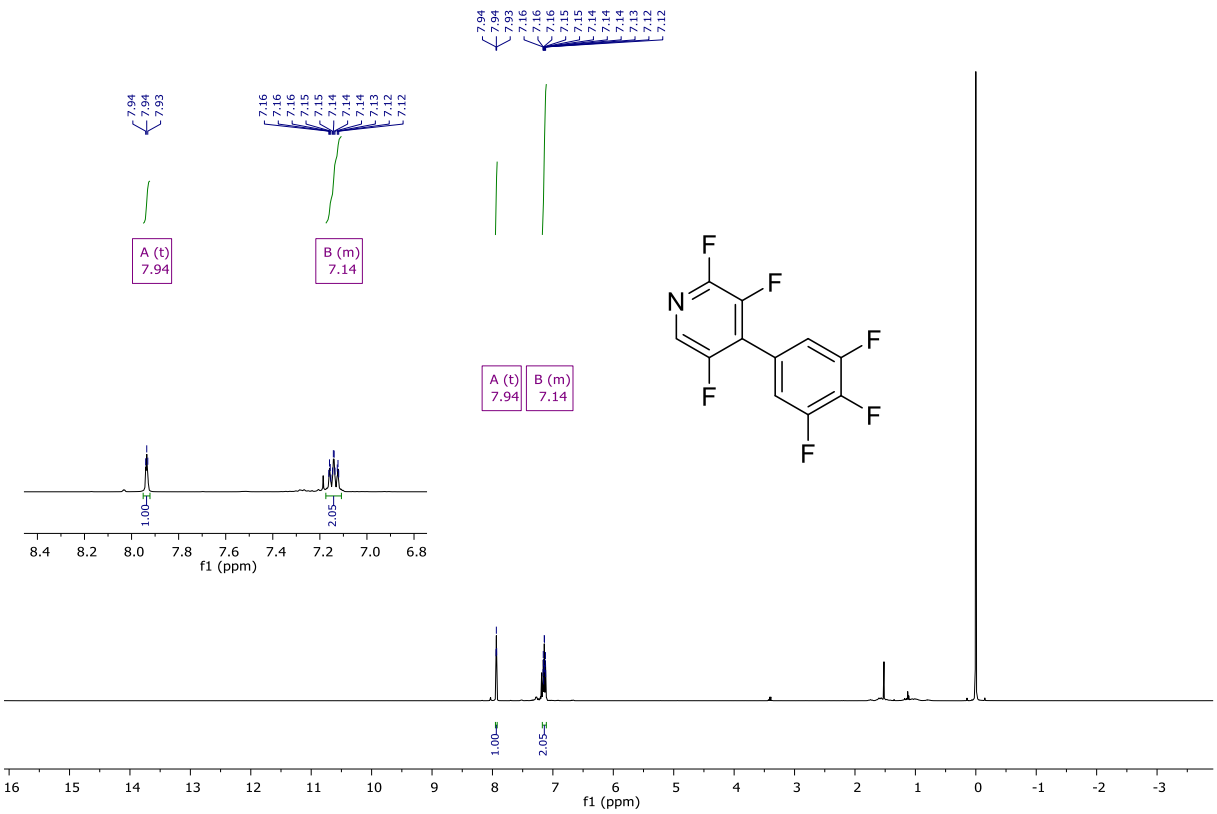


Figure S103 ^{1}H-NMR: 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

^{19}F NMR (377 MHz, Chloroform-d) δ -87.68 (dd, J = 29.3, 25.5 Hz), -132.35 (dd, J = 29.0, 1.4 Hz), -132.47 (d, J = 20.5 Hz), -140.16 (dt, J = 25.1 Hz), -156.38 (t, J = 20.4 Hz).

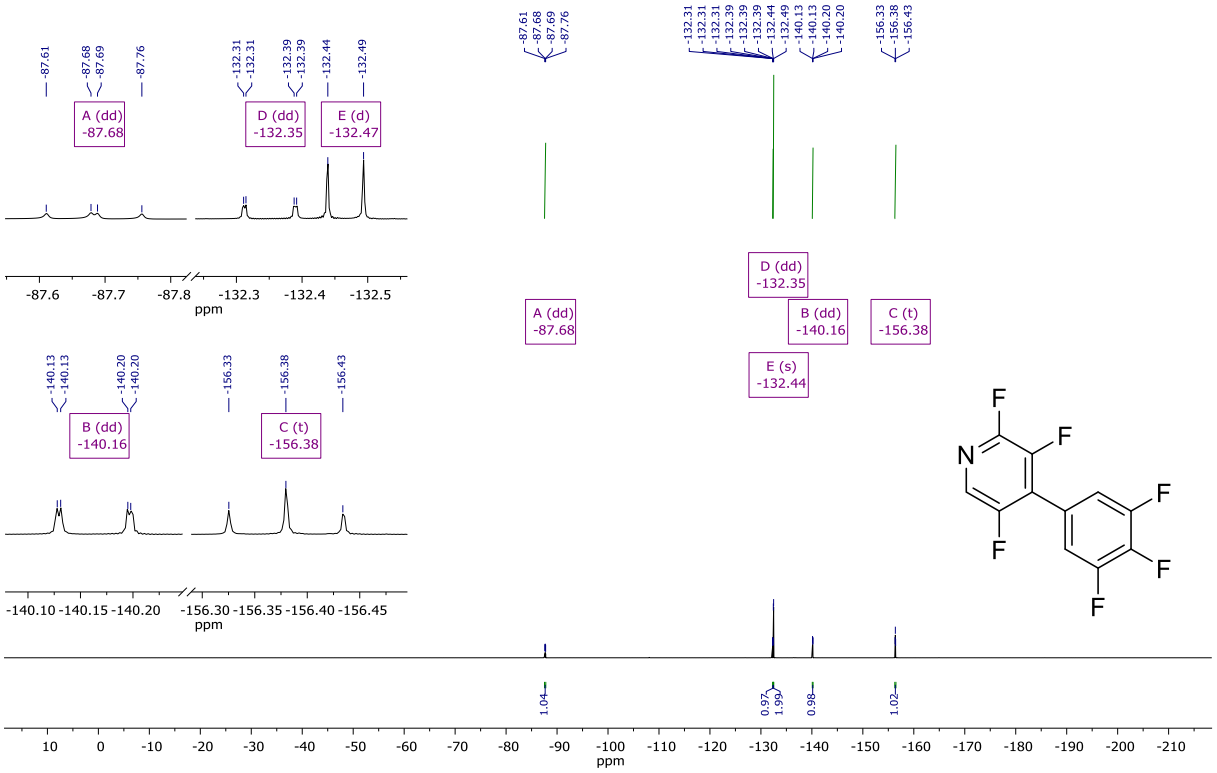


Figure S104 ^{19}F-NMR {^{1}H}: 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

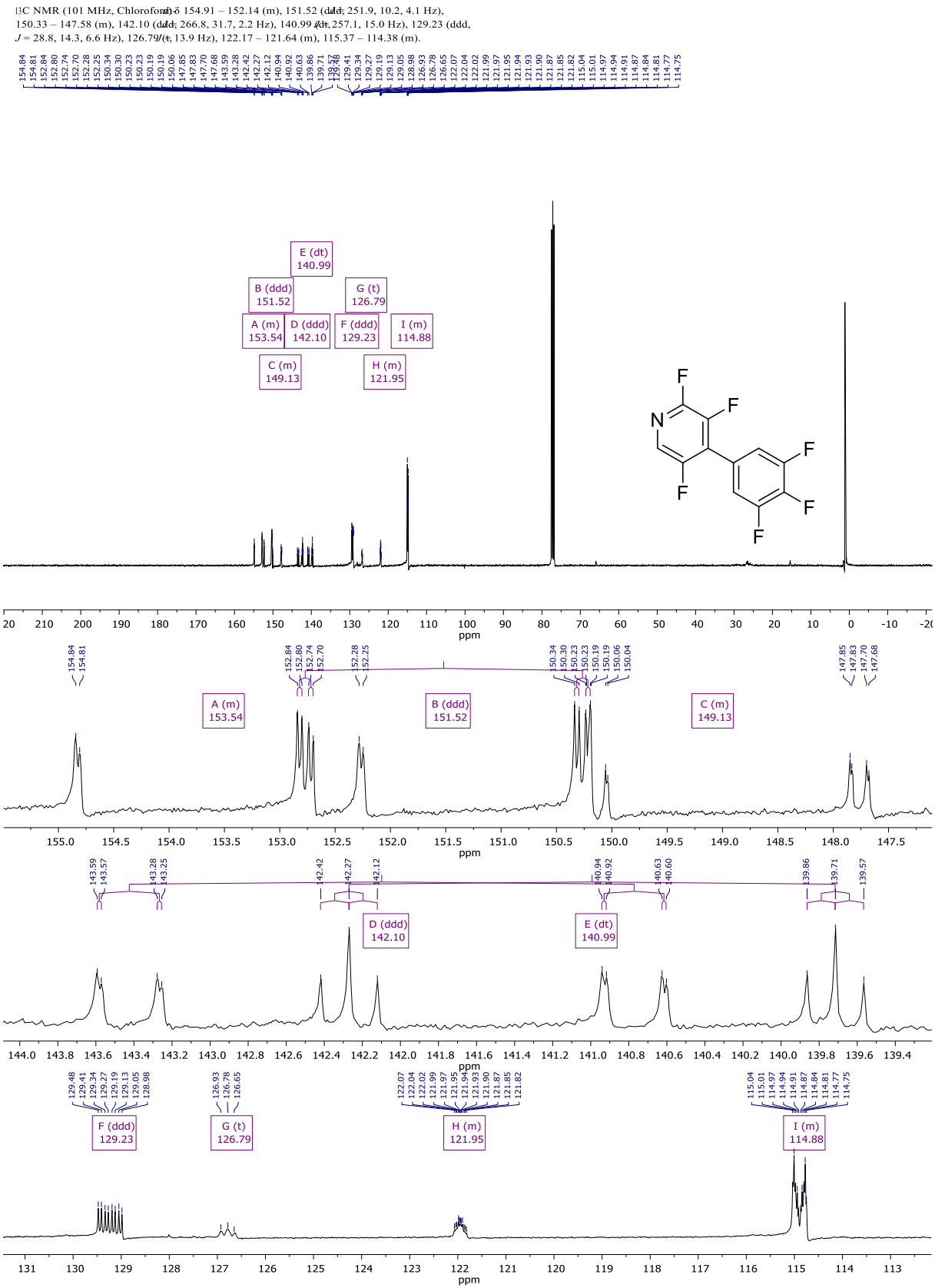


Figure S105 ^{13}C NMR: 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

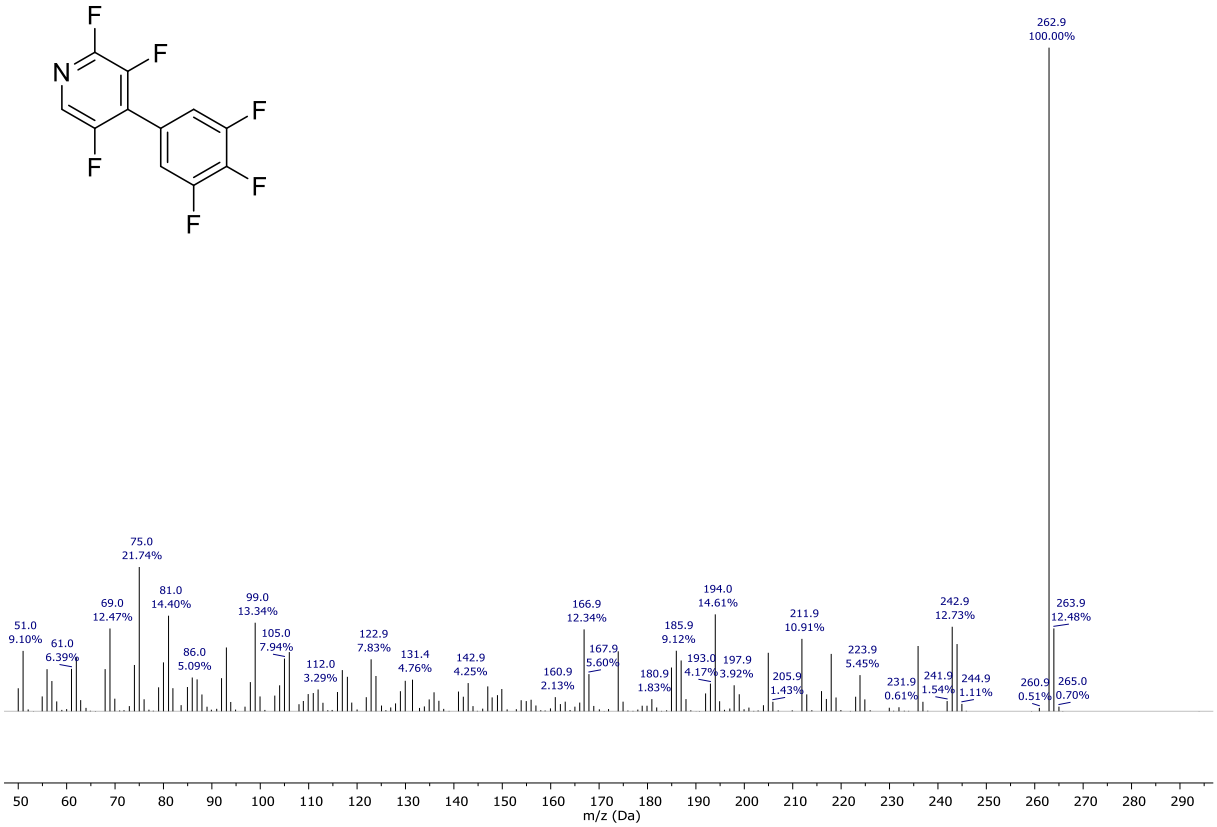


Figure S106 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

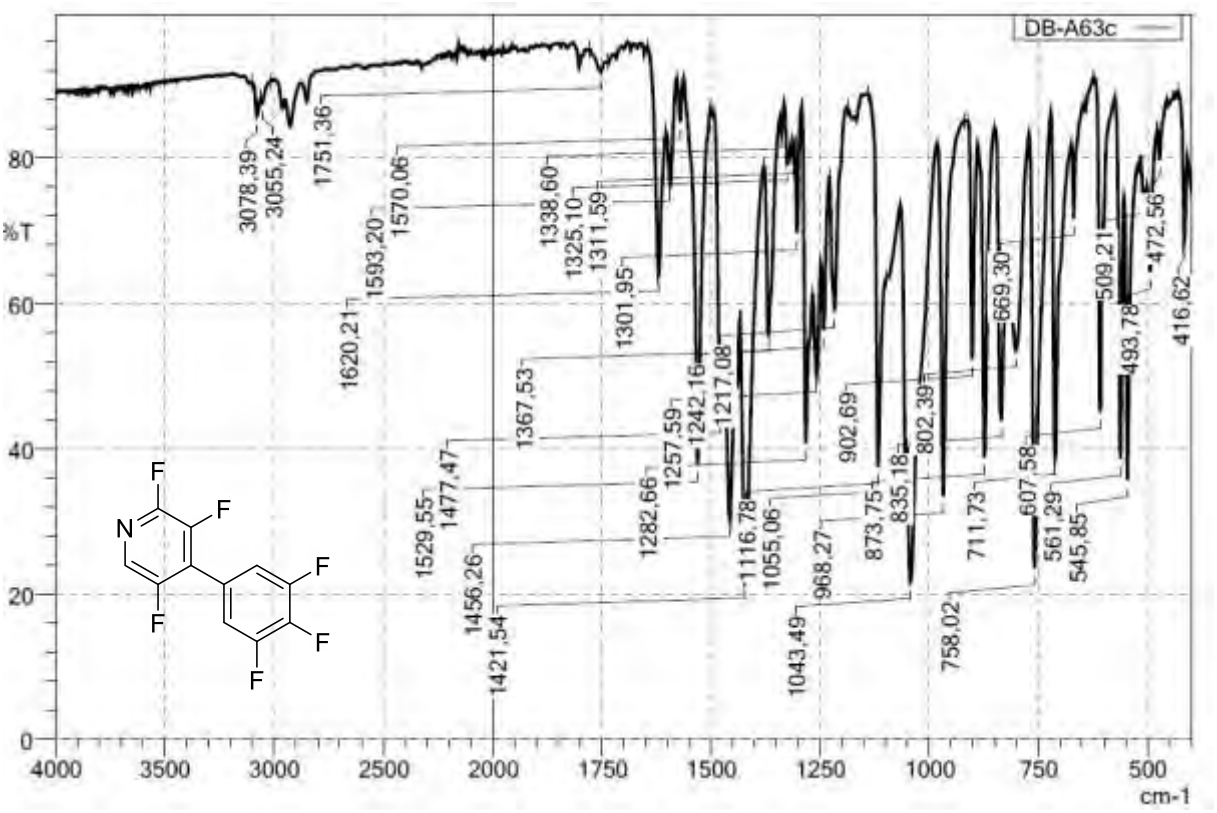


Figure S107 IR (ATR)-Spectrum: 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine (36)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 (dd, J = 2.2, 1.3 Hz, 1H), 7.21 – 7.09 (m, 2H).

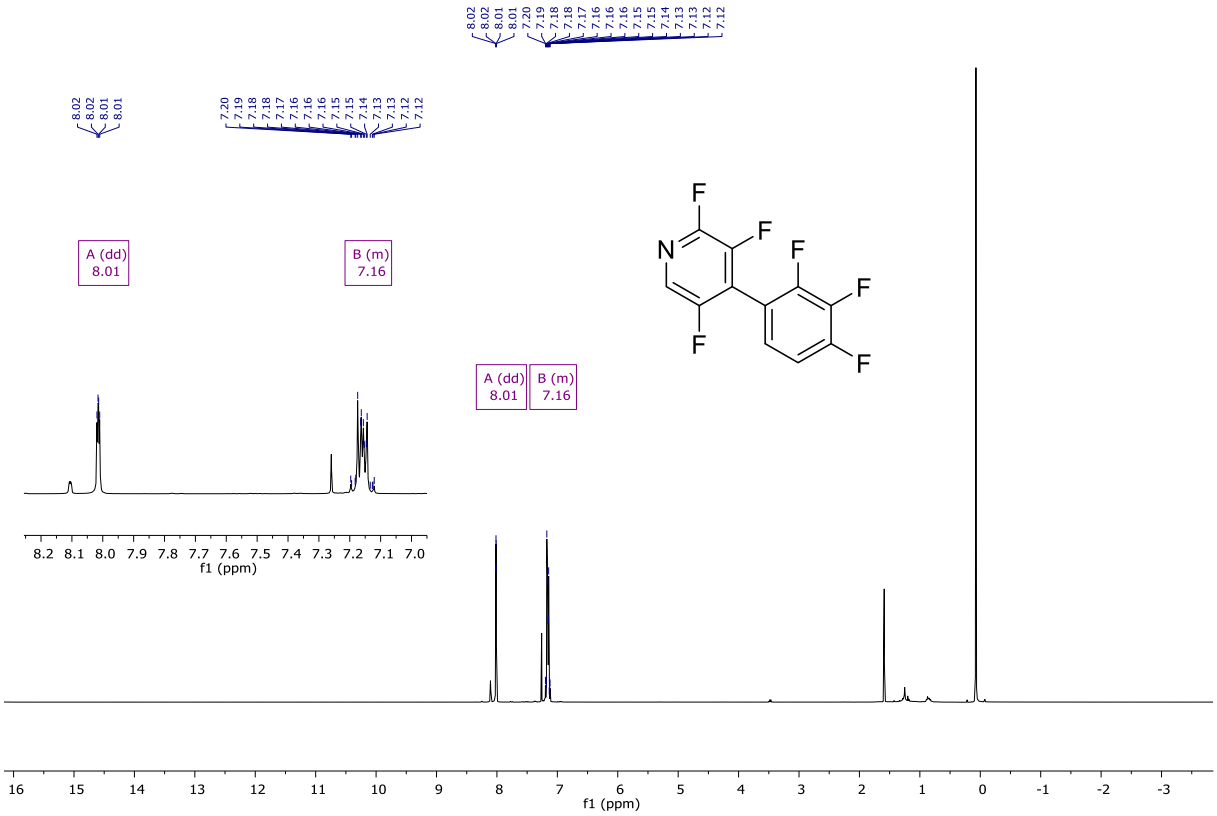


Figure S108 ^{1}H-NMR: 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

^{19}F NMR (377 MHz, Chloroform-d) δ -88.08 (dd, J = 29.1, 25.3 Hz), -129.78 (dd, J = 20.5, 10.0 Hz), -129.95 (dd, J = 29.2, 12.2 Hz), -130.95 – -131.42 (m), -136.97 (dd, J = 25.2, 12.2 Hz), -158.20 (t, J = 20.4 Hz).

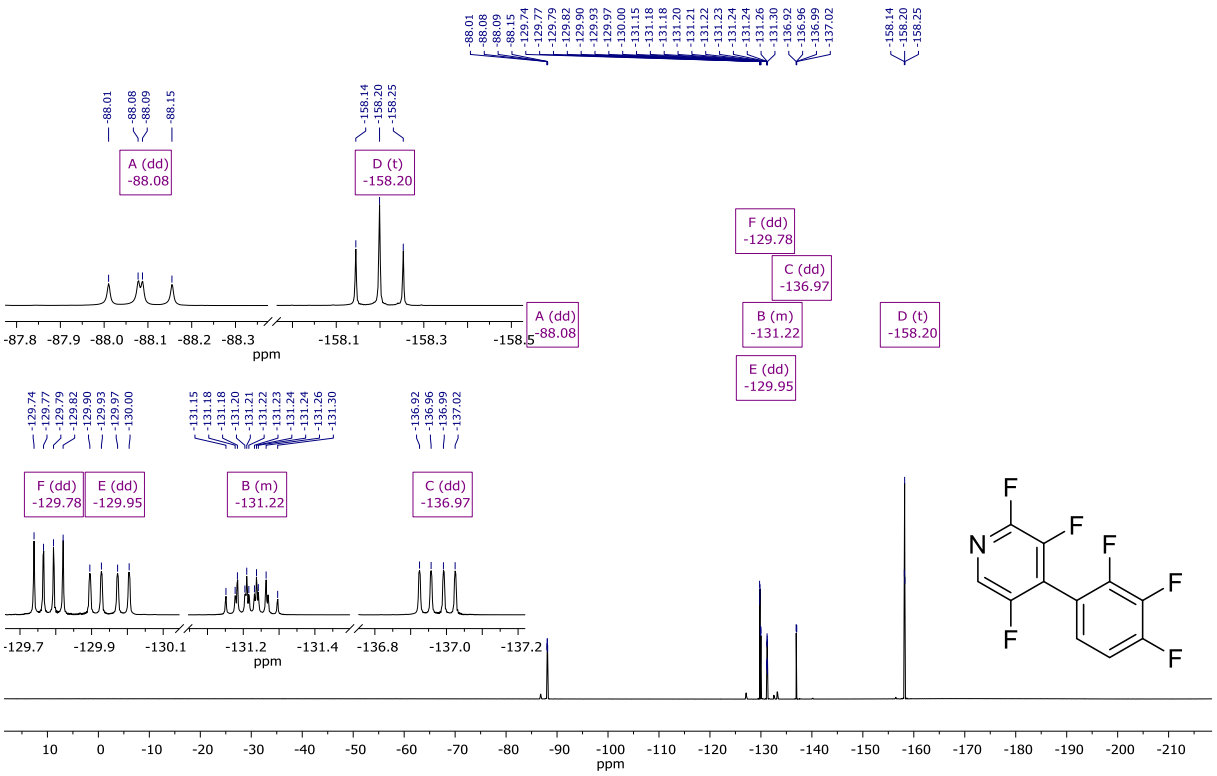


Figure S109 ^{19}F-NMR {^{1}H}: 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

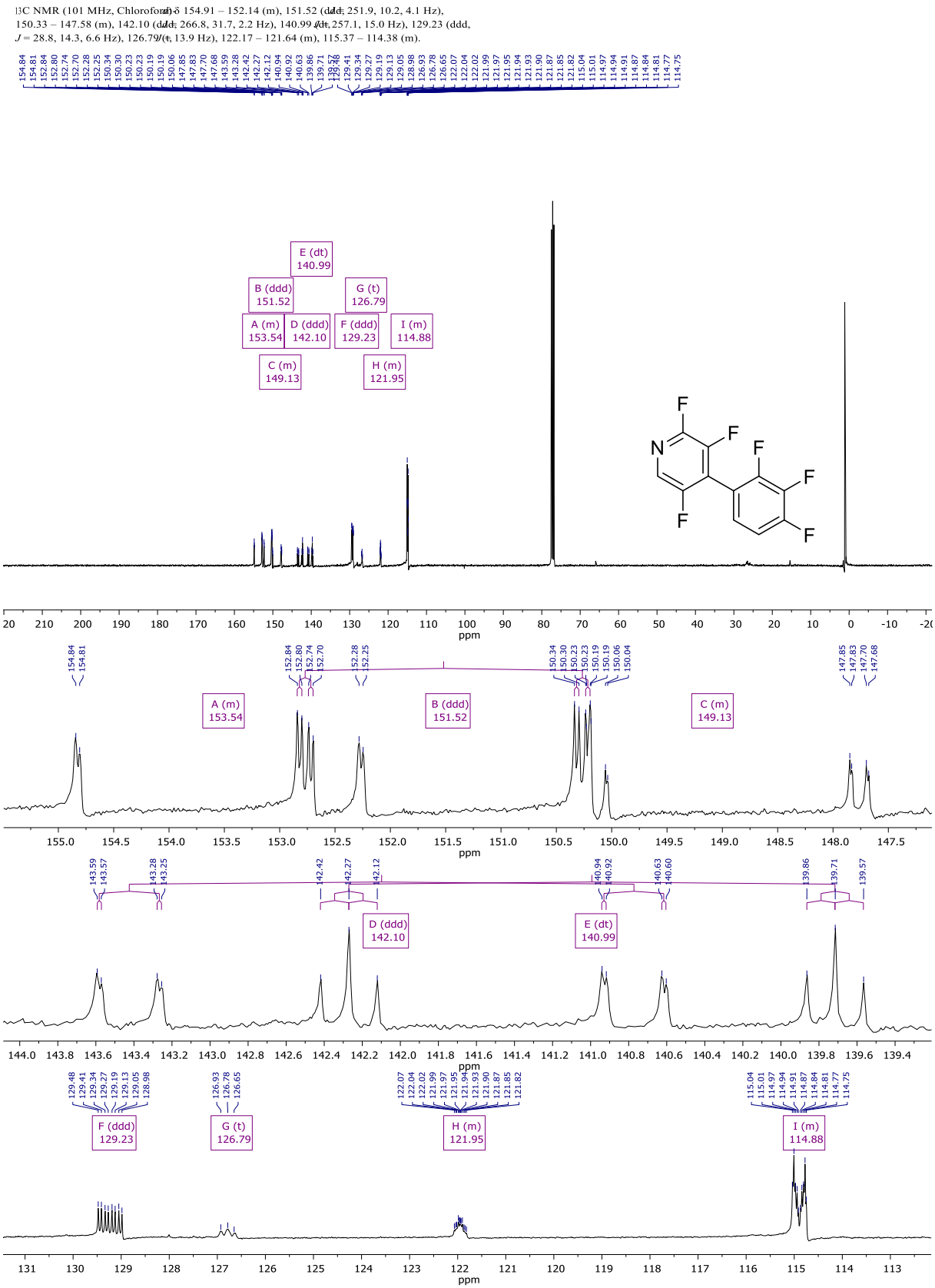


Figure 110^{13}C NMR: 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

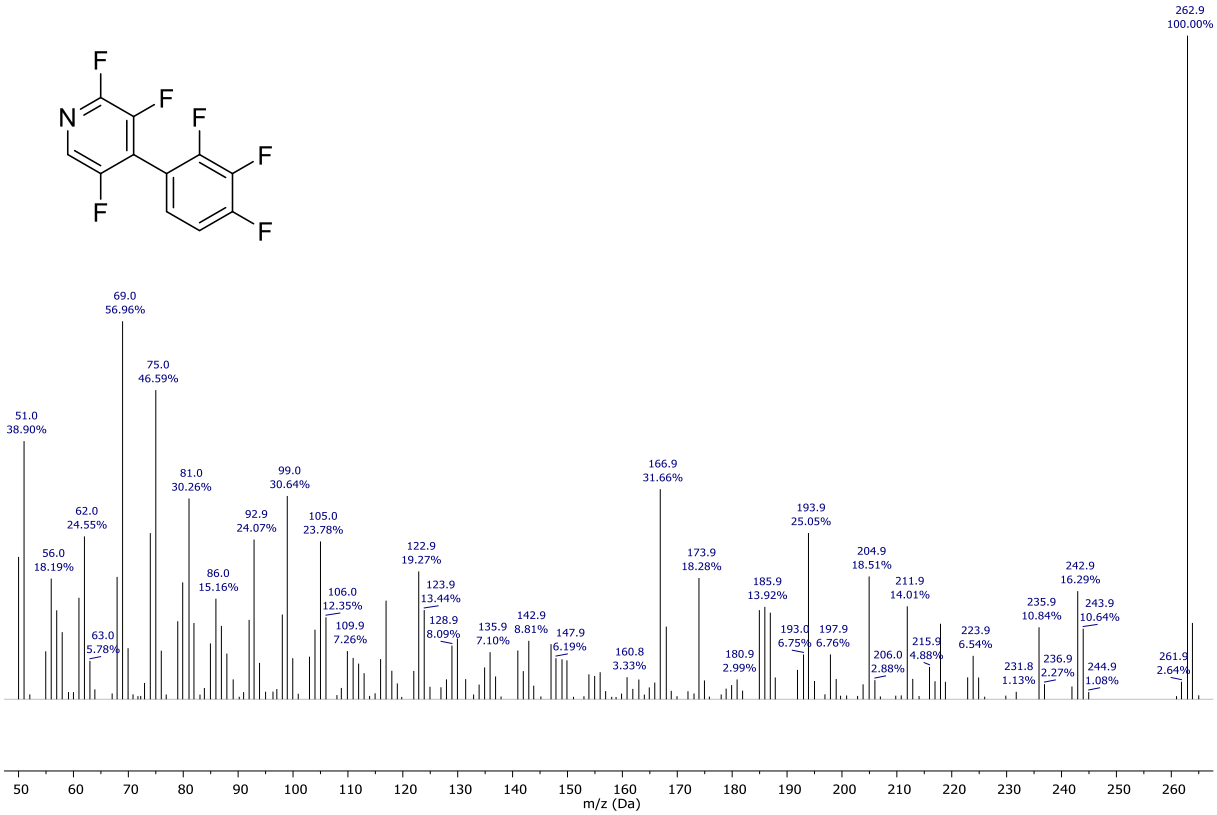


Figure S111 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

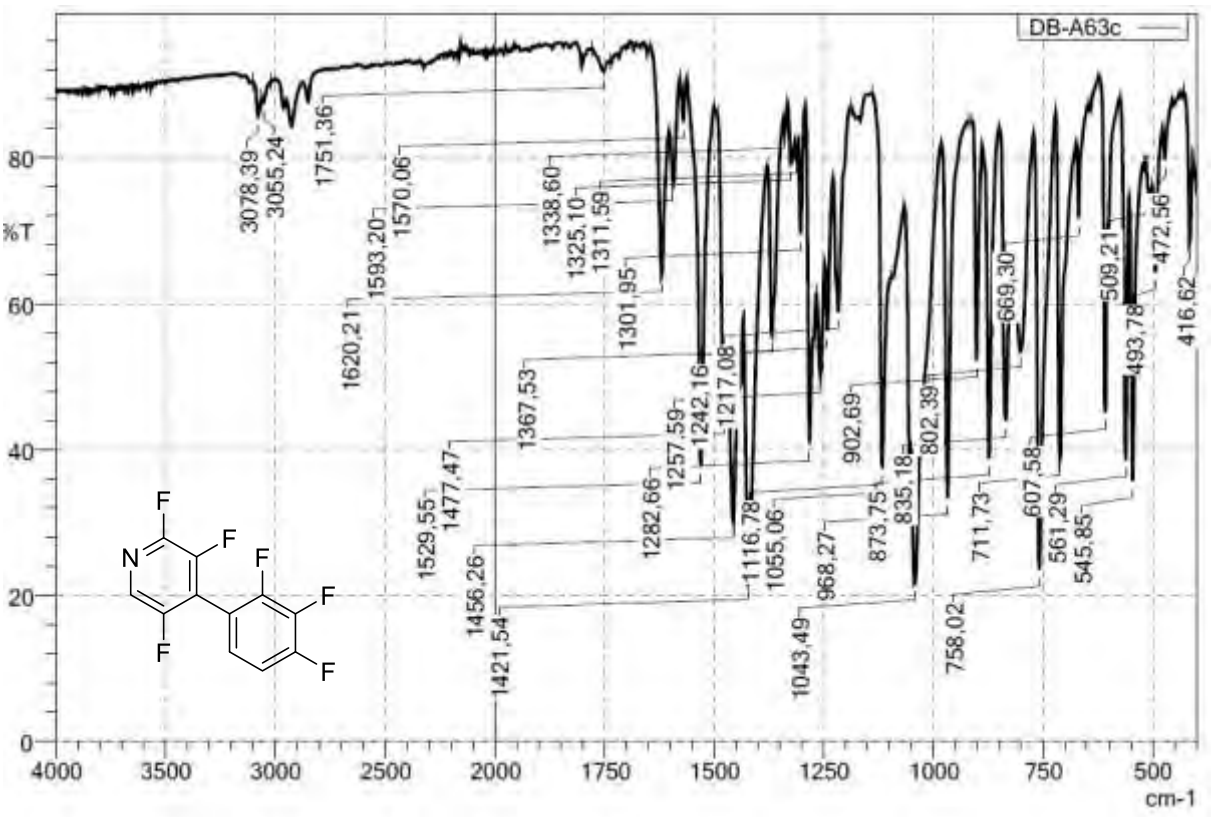


Figure S112 IR (ATR)-Spectrum: 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine (37)

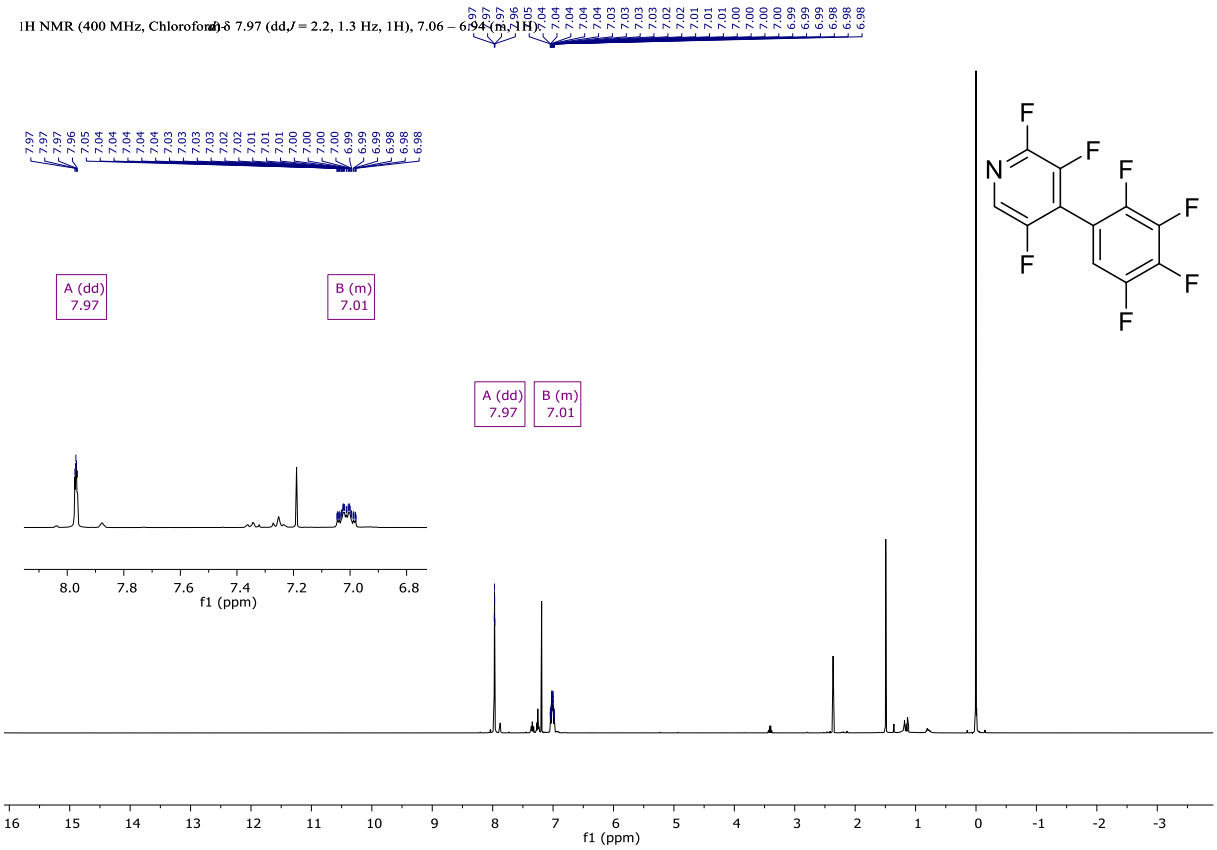


Figure 113 ^{1}H-NMR: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

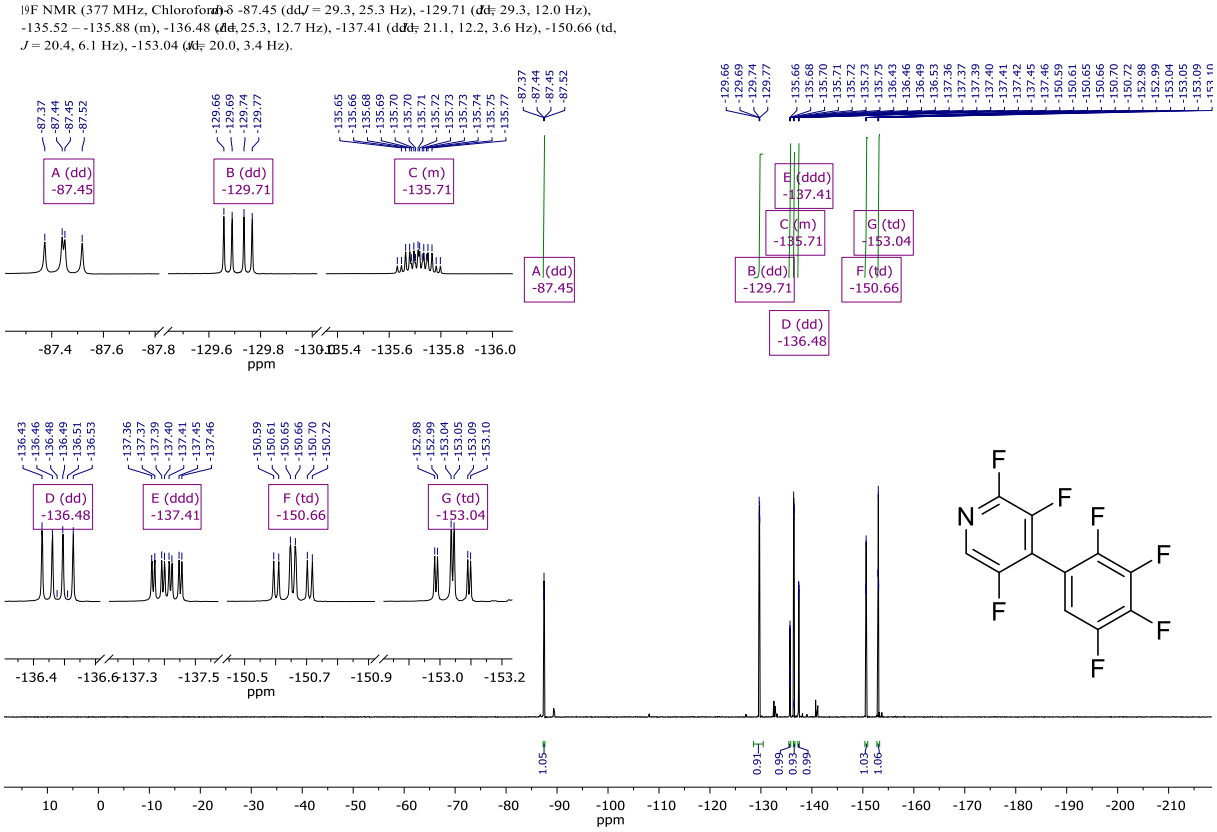


Figure S114 ^{19}F-NMR {^{1}H}: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

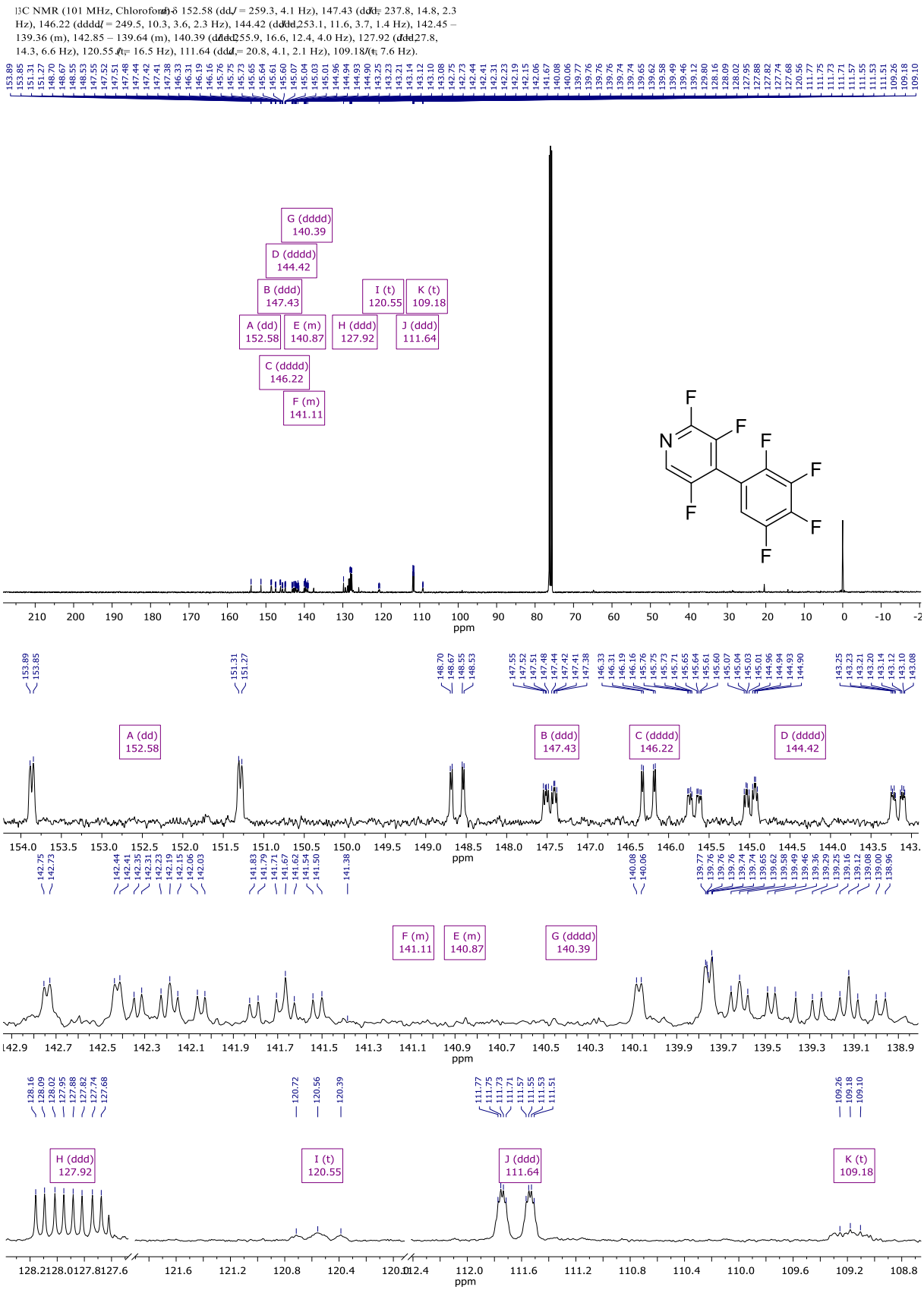


Figure S115 ^{13}C NMR: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

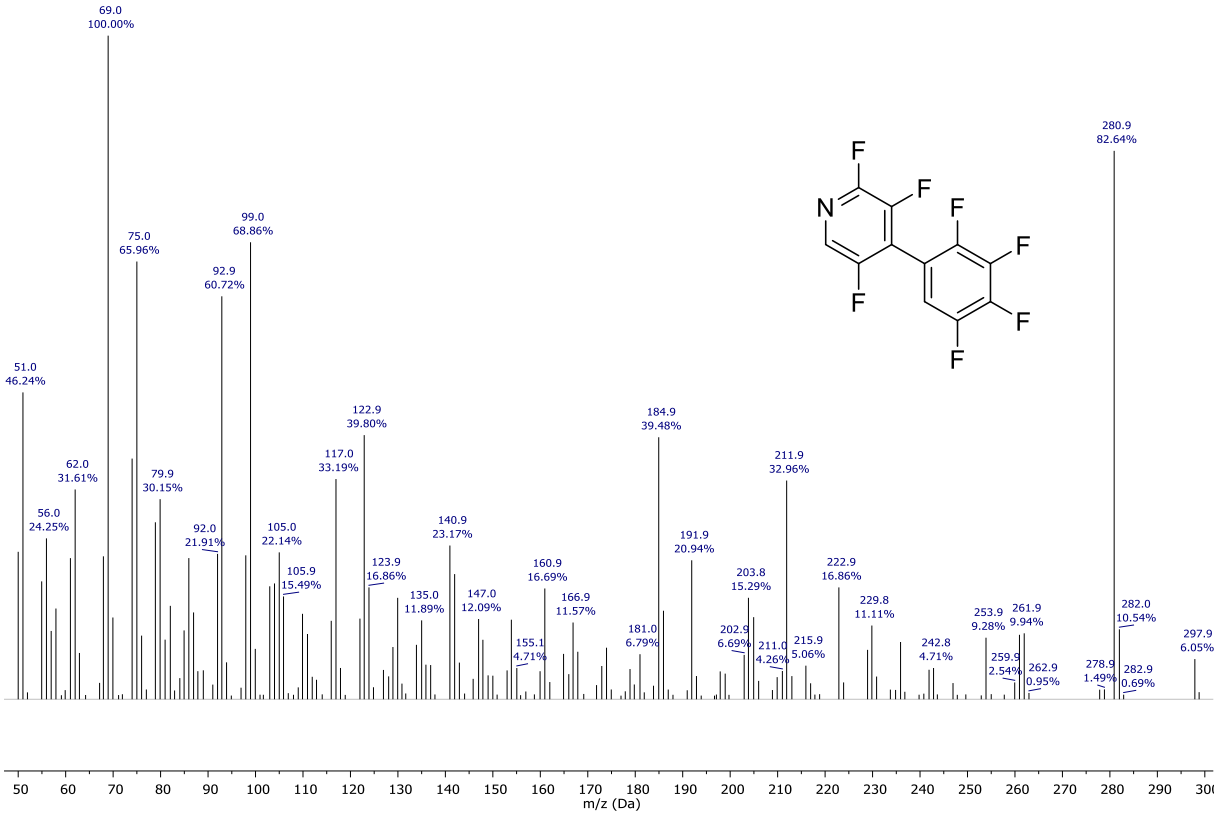


Figure S116 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

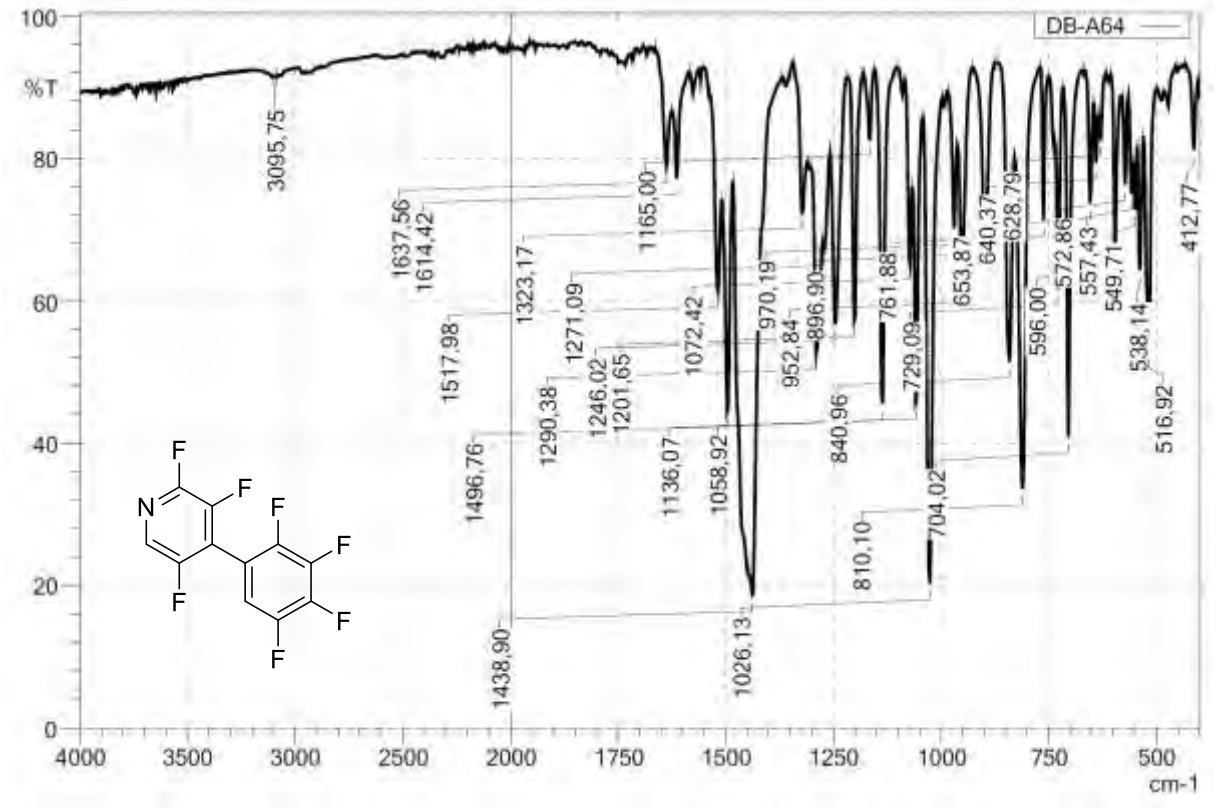


Figure S117 IR (ATR)-Spectrum: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

4-(3,5-Difluorophenyl)-2,3,5,6-tetrafluoropyridine (38)

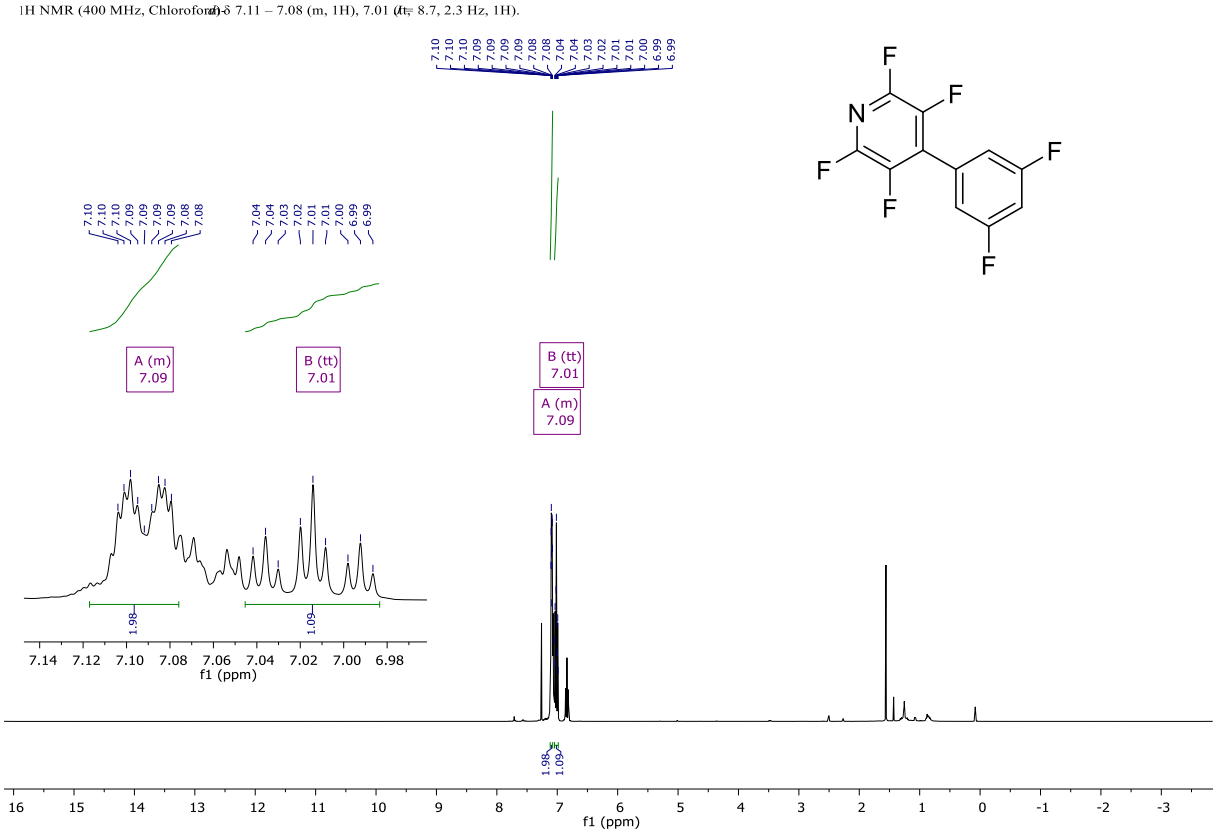


Figure S118 ^{1}H-NMR: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

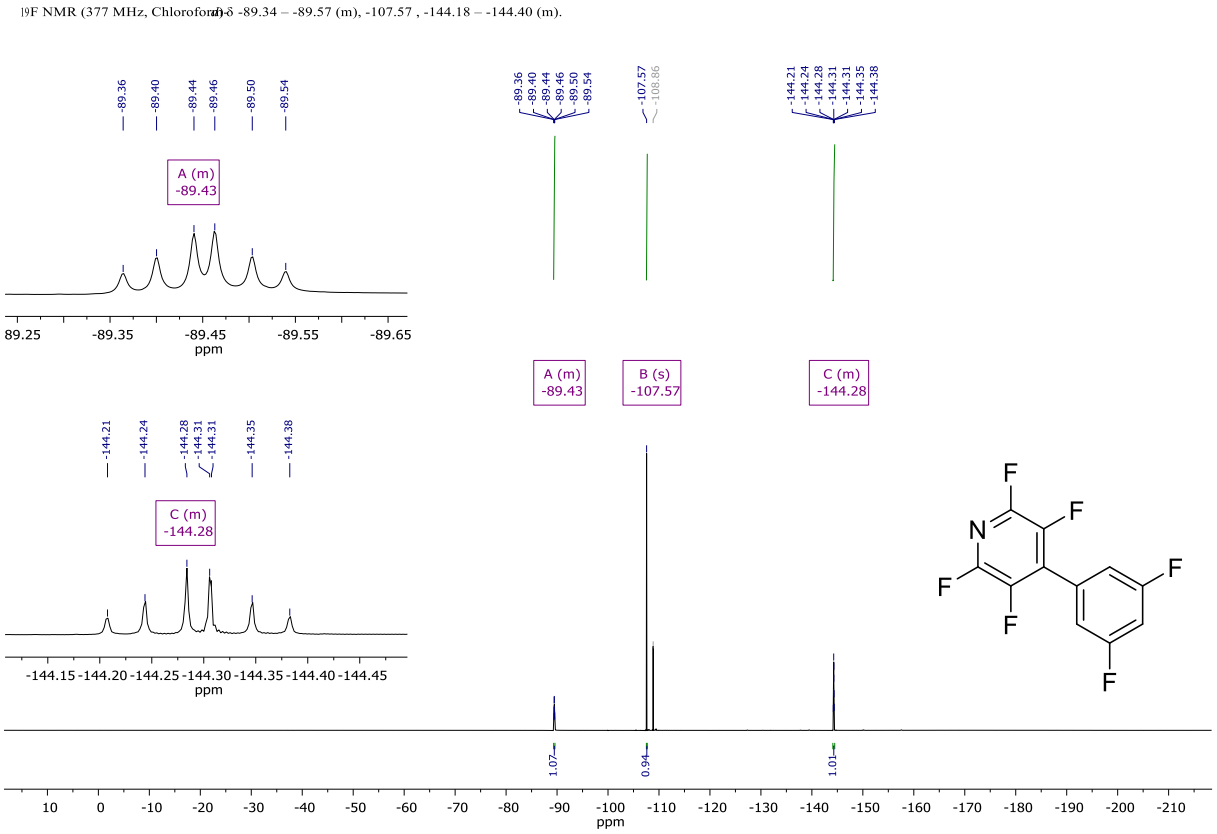


Figure S119 ^{19}F-NMR {^{1}H}: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

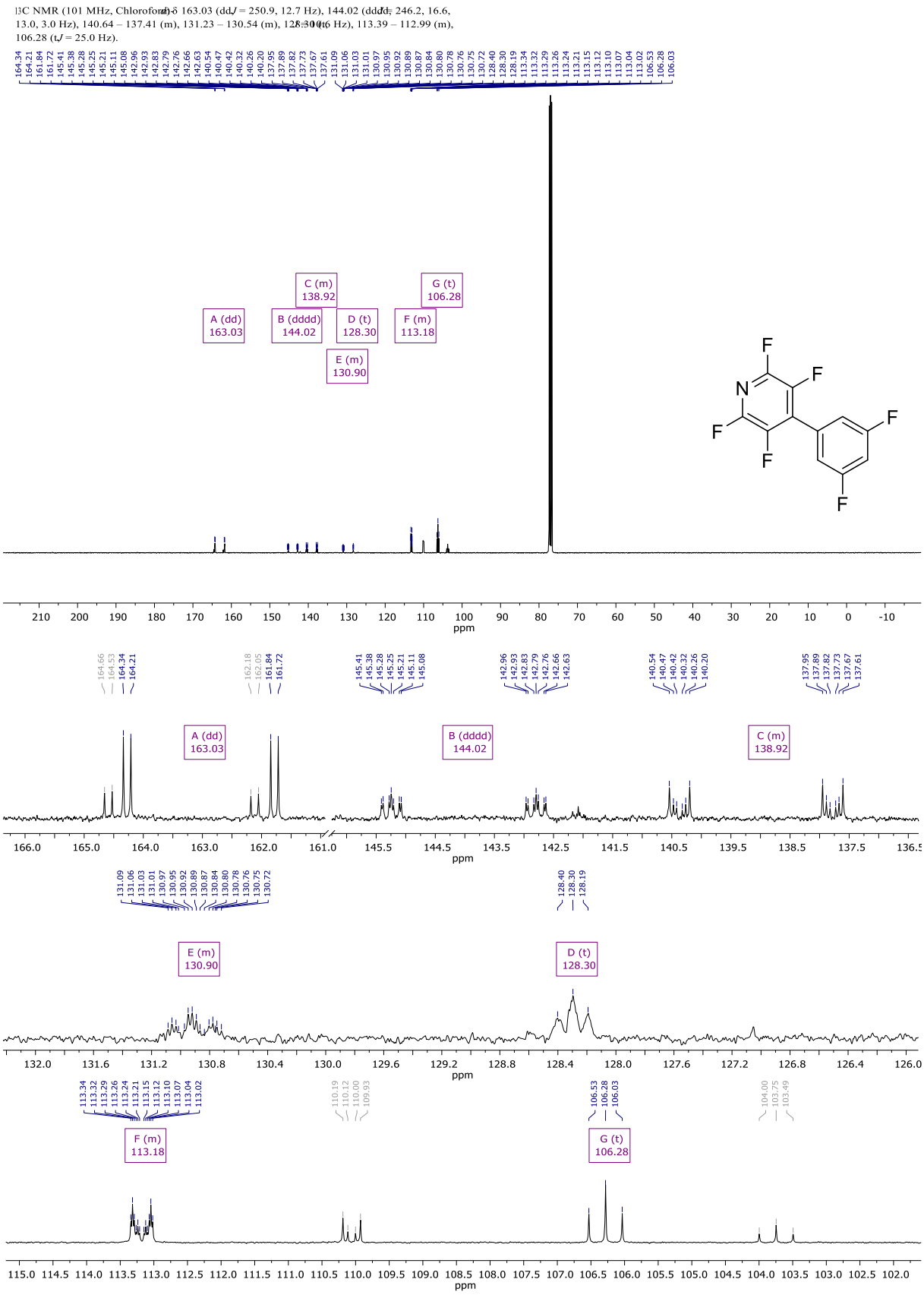


Figure S120 ^{13}C NMR: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

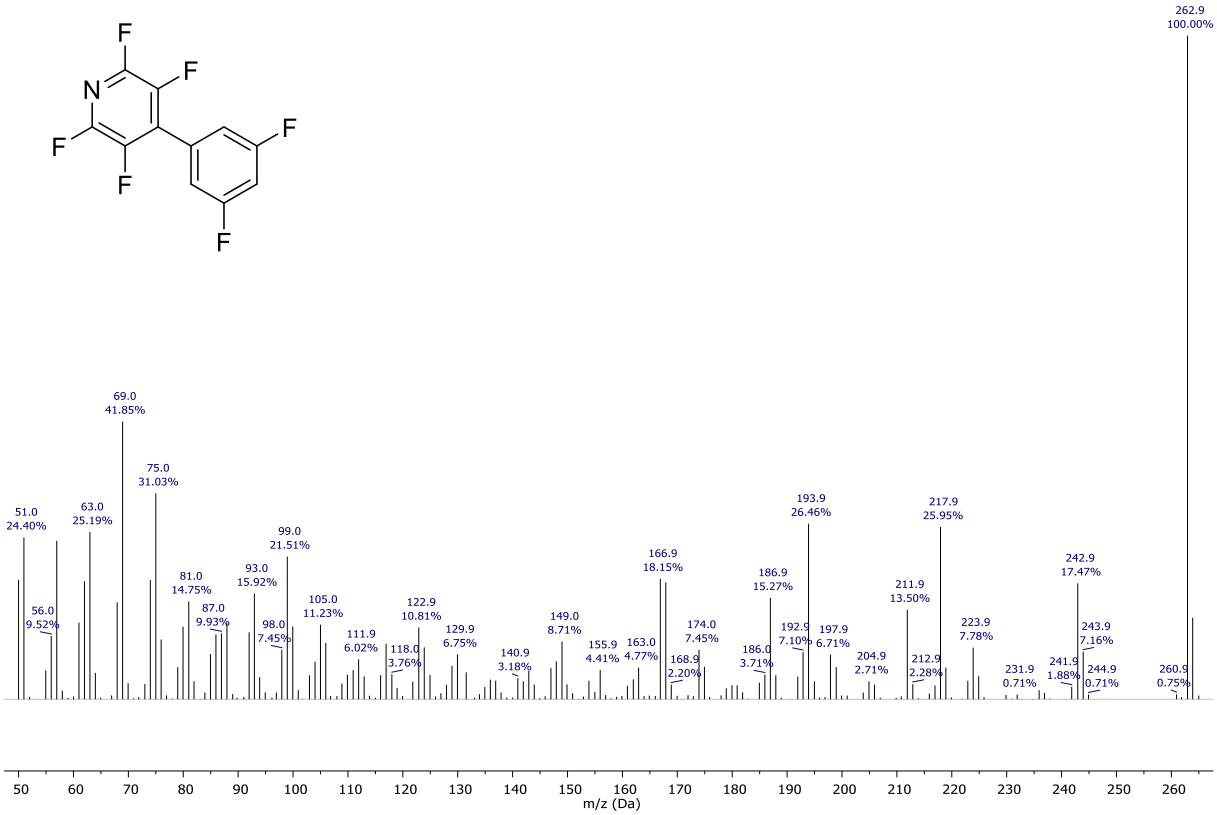


Figure S121 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

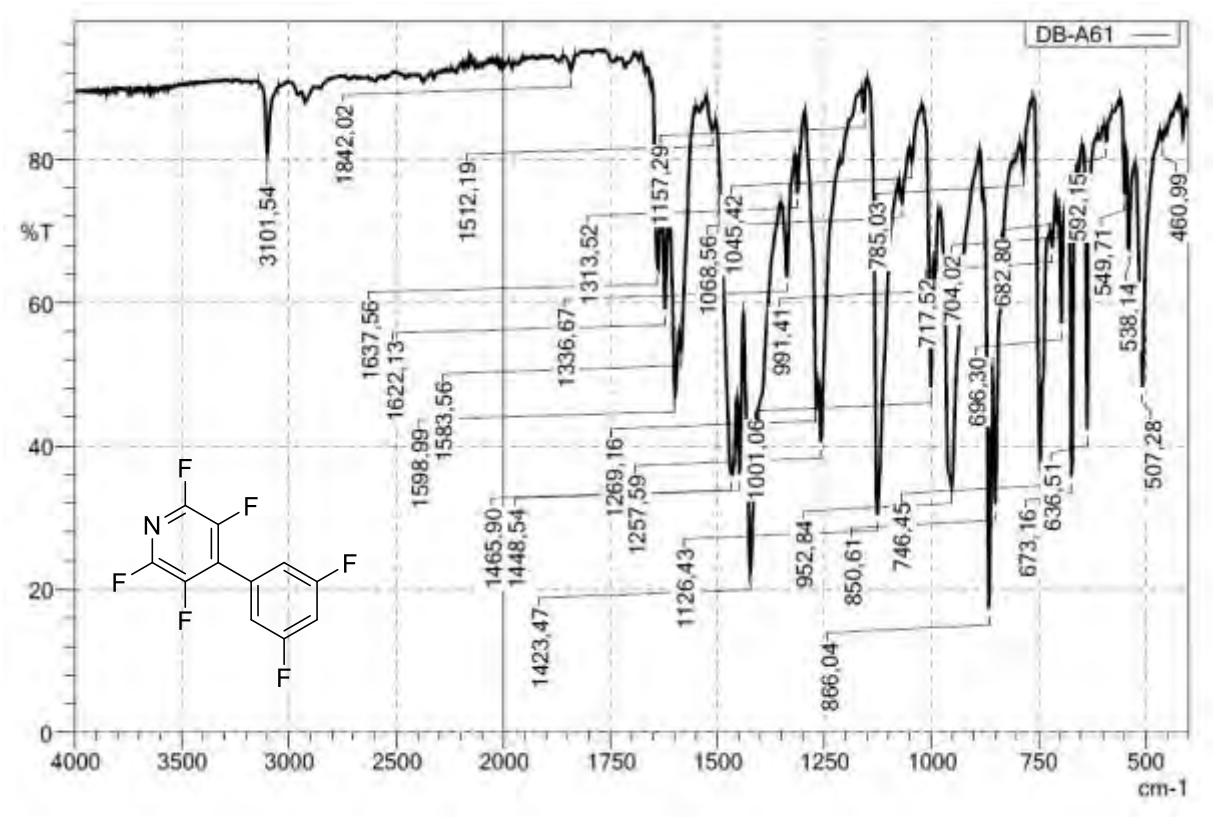


Figure S122 IR (ATR)-Spectrum: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine (39)

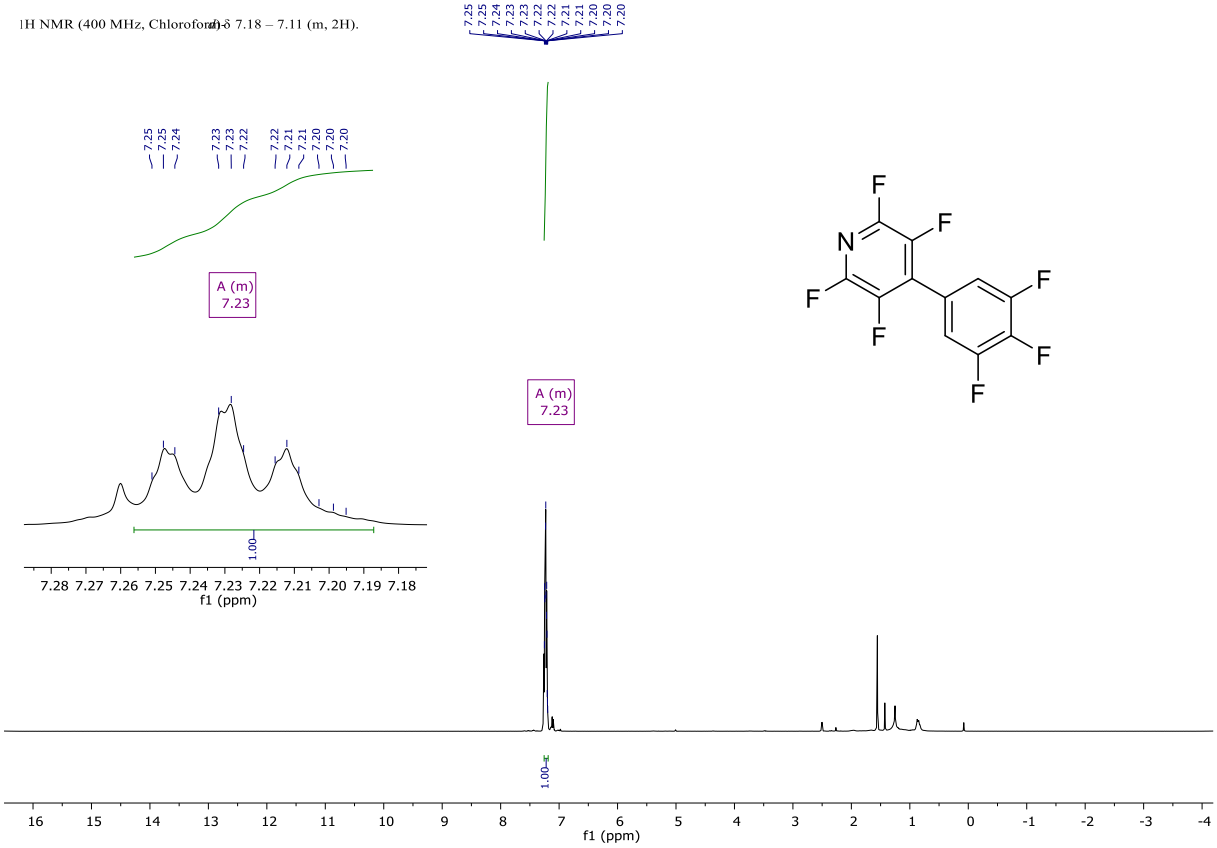


Figure S123 ^{1}H-NMR: 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

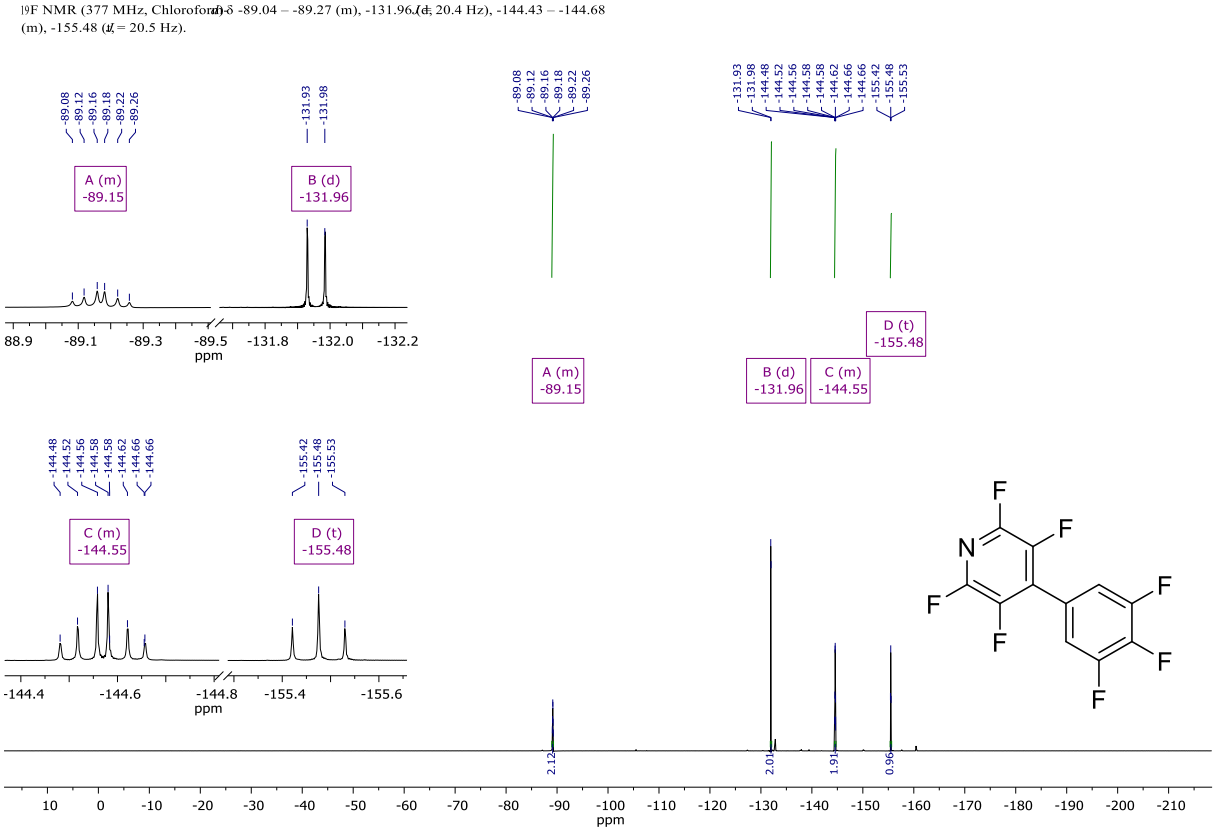


Figure S124 ^{19}F-NMR {^{1}H}: 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

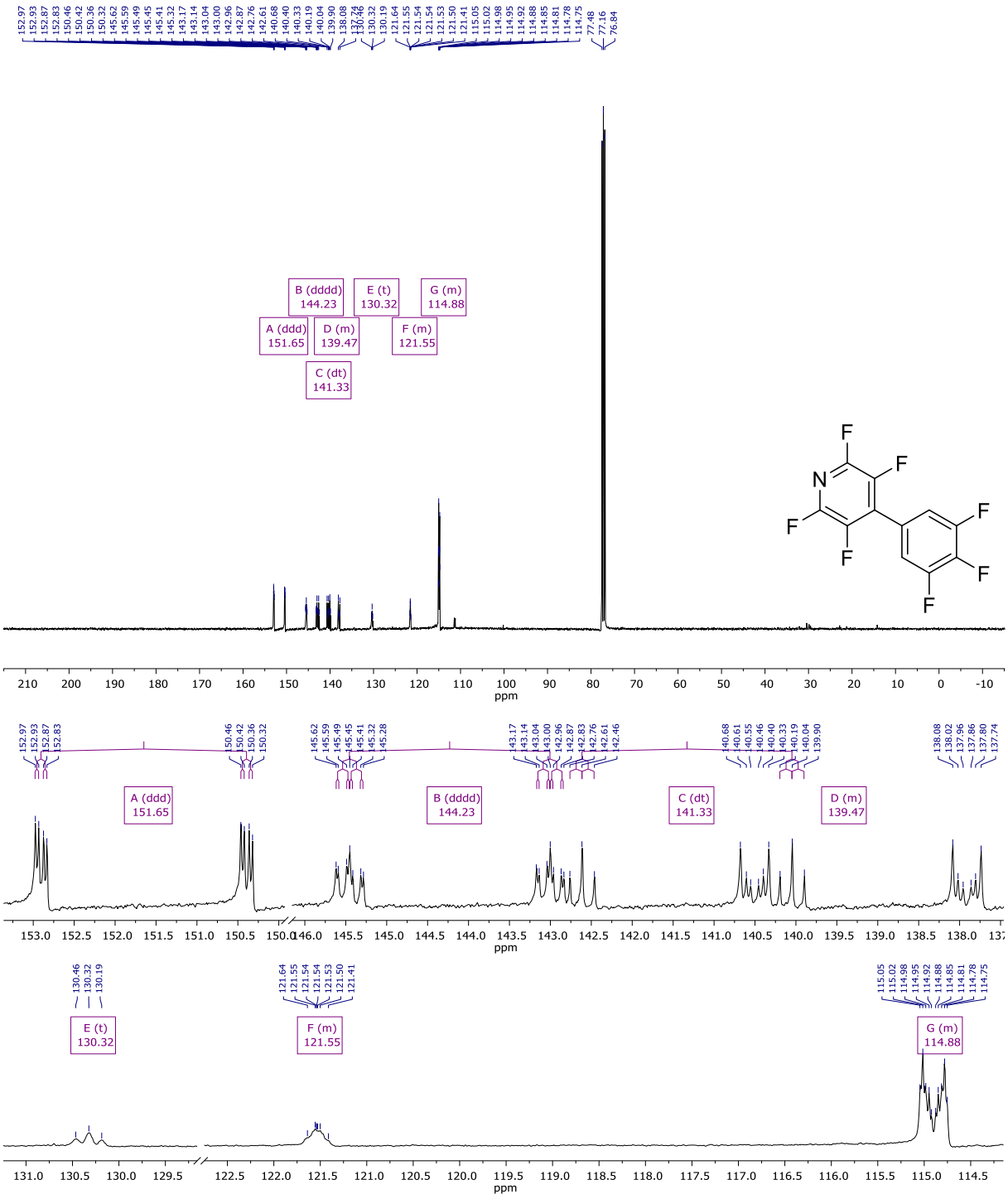


Figure S125 ^{13}C NMR: 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

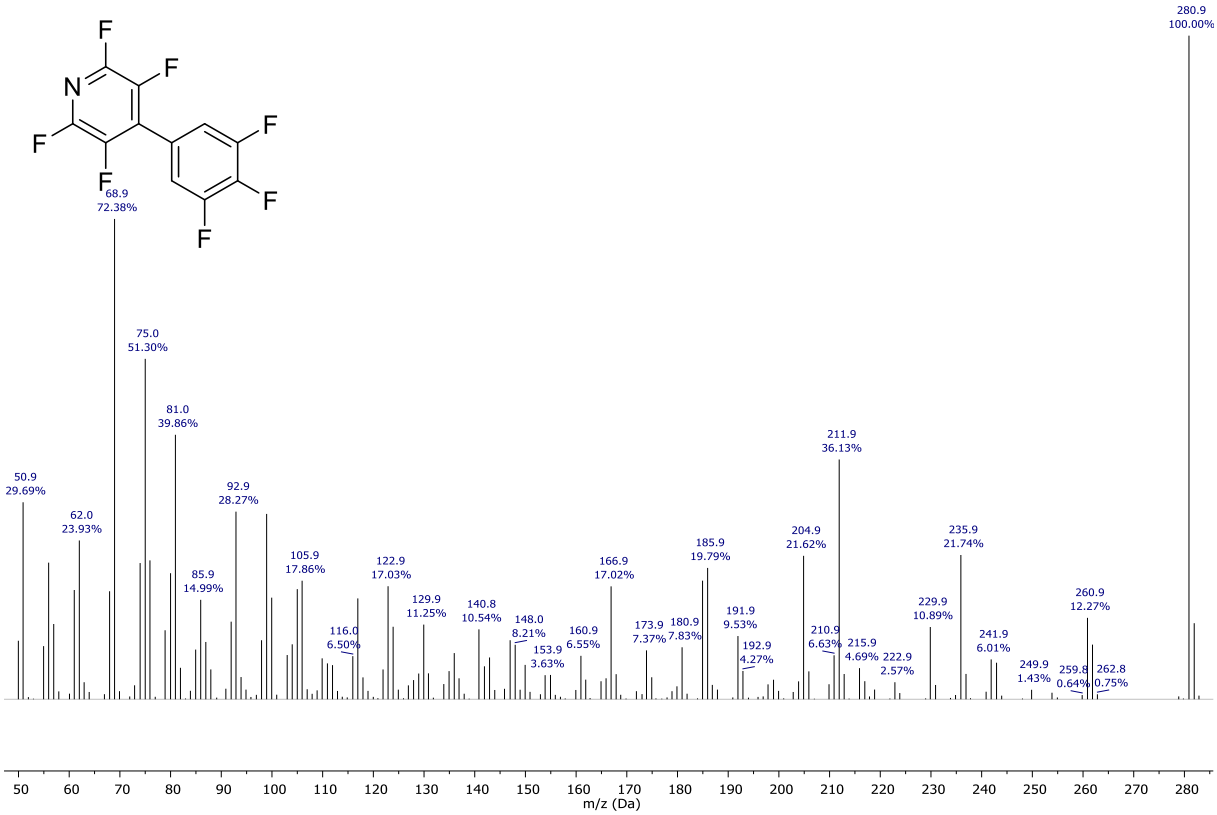


Figure S126 EI-Spectrum (EI⁺): 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

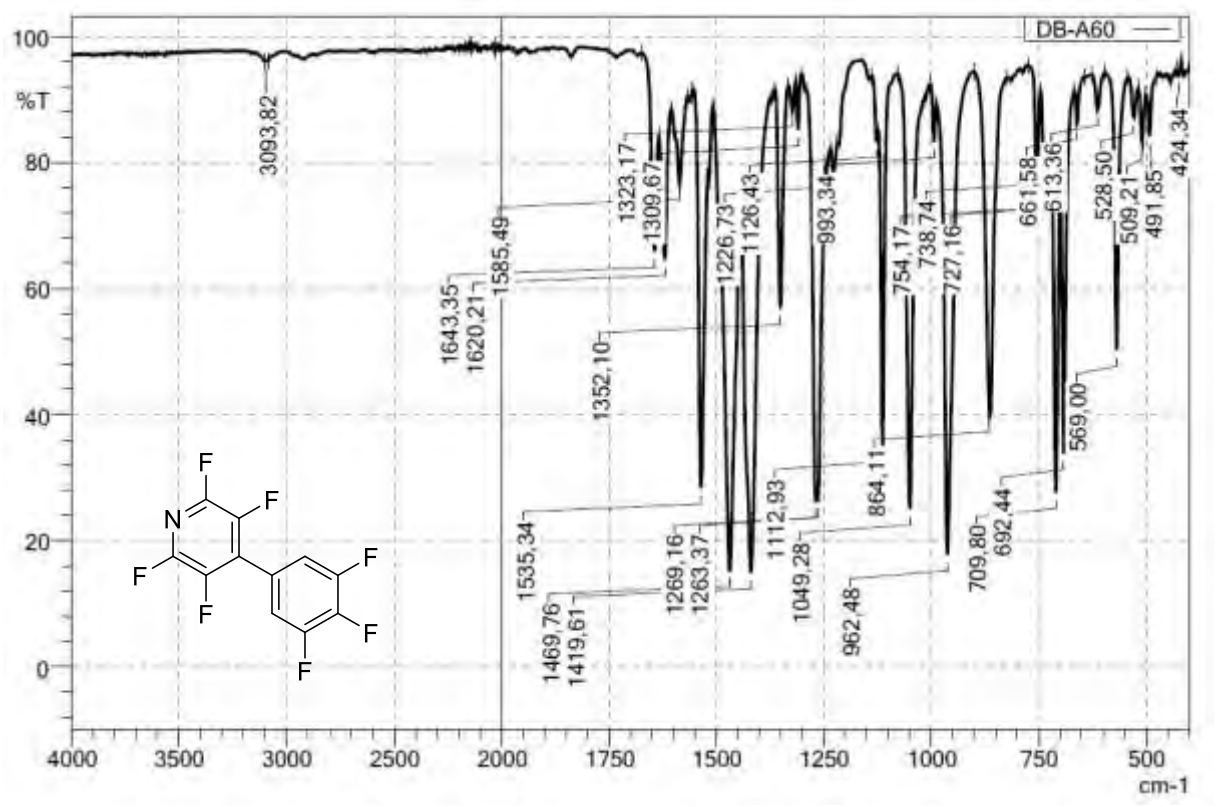


Figure S127 IR (ATR)-Spectrum: 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

Iodobenzenes and Iodopyridines

1,2,4,5-Tetrafluoro-3-iodobenzene (1)

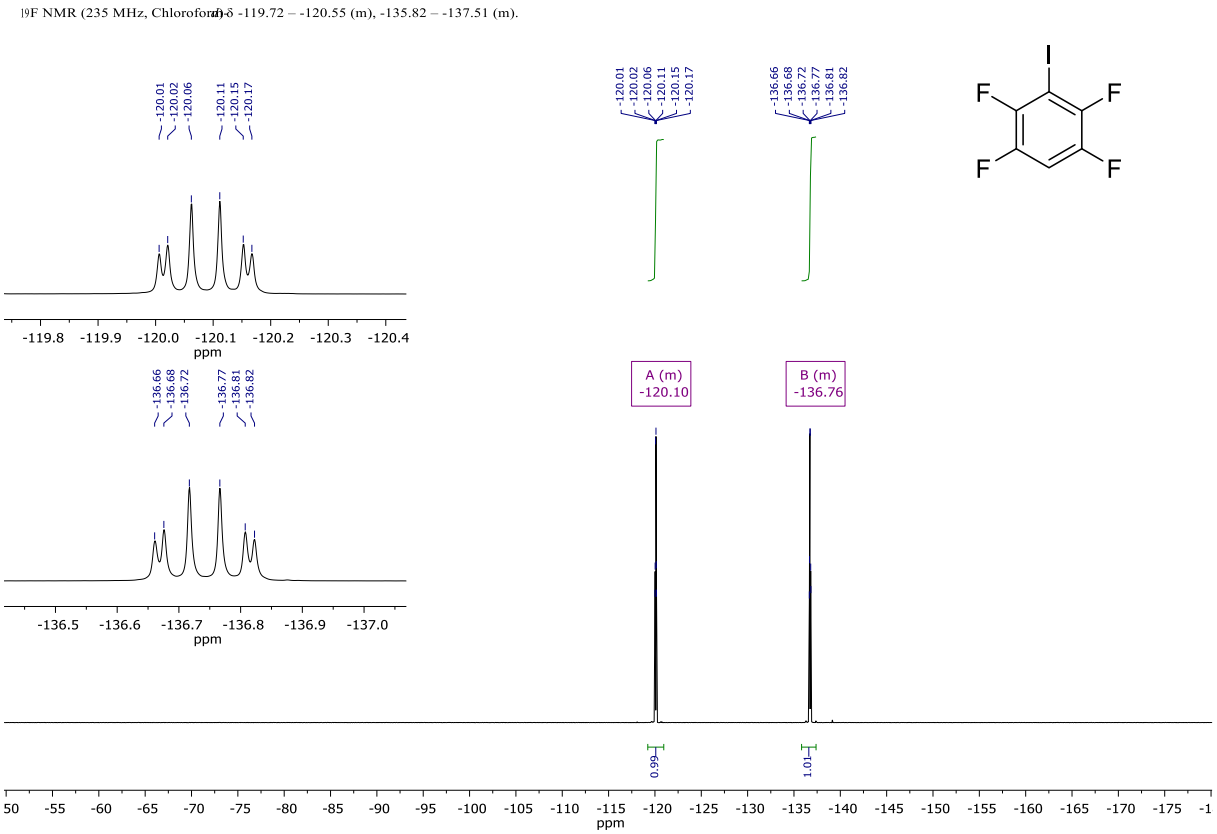


Figure S128 ^{19}F-NMR {^{1}H}: 1,2,4,5-Tetrafluoro-3-iodobenzene

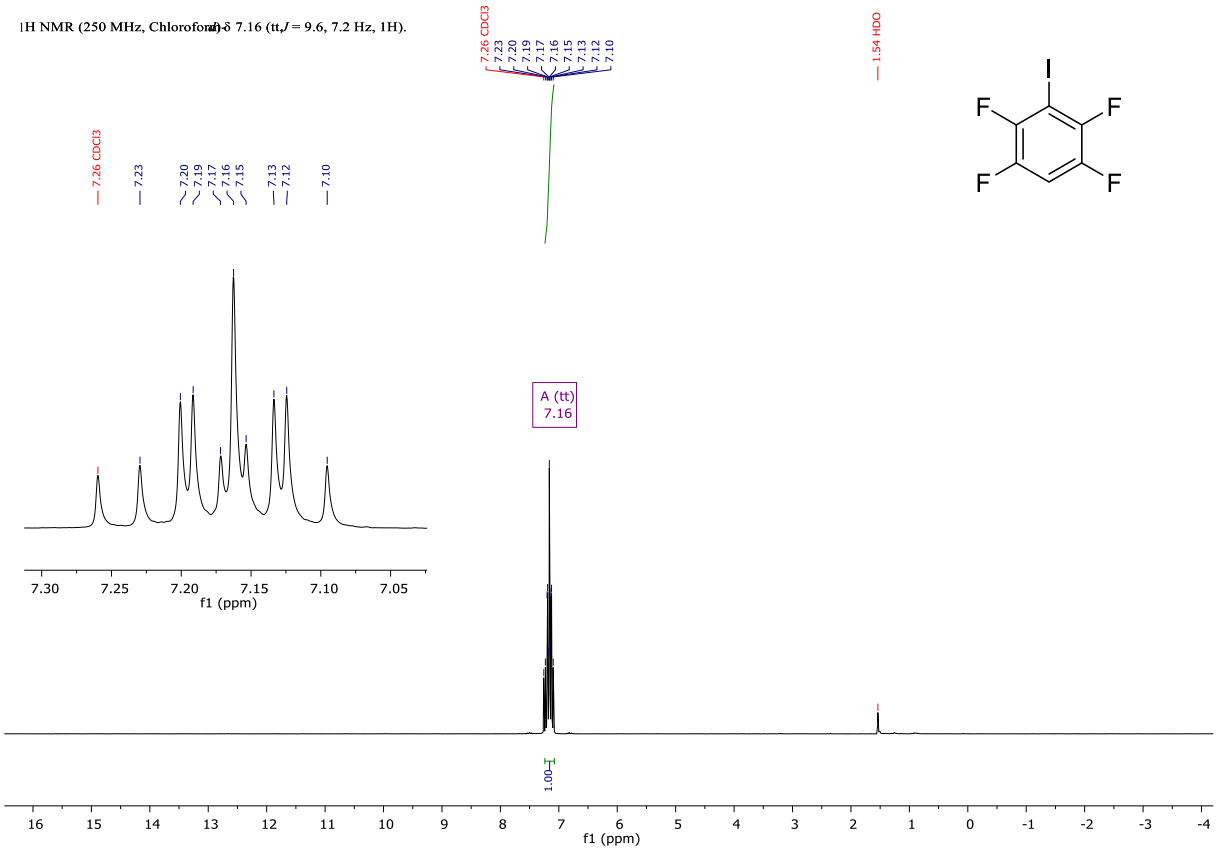


Figure S129 ^{1}H-NMR: 1,2,4,5-Tetrafluoro-3-iodobenzene

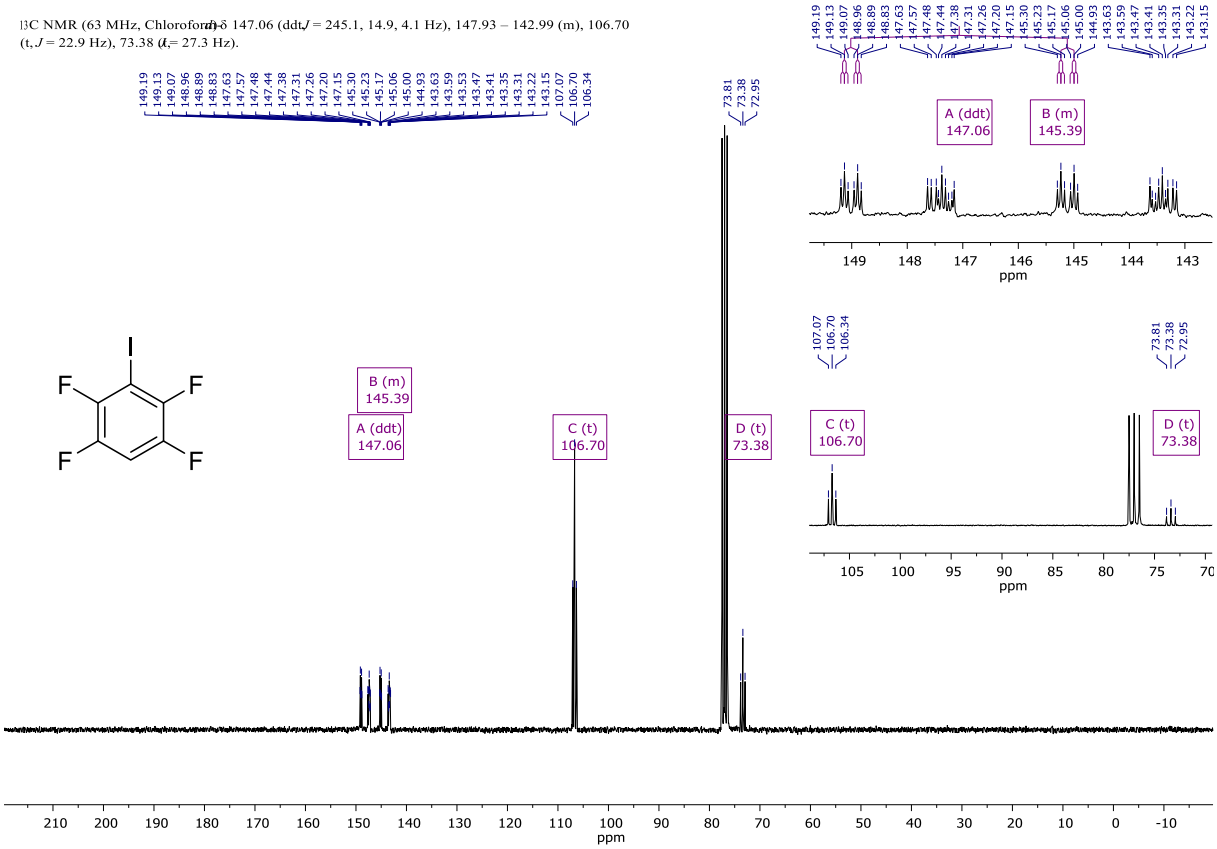


Figure S130 ^{13}C NMR: 1,2,4,5-Tetrafluoro-3-iodobenzene

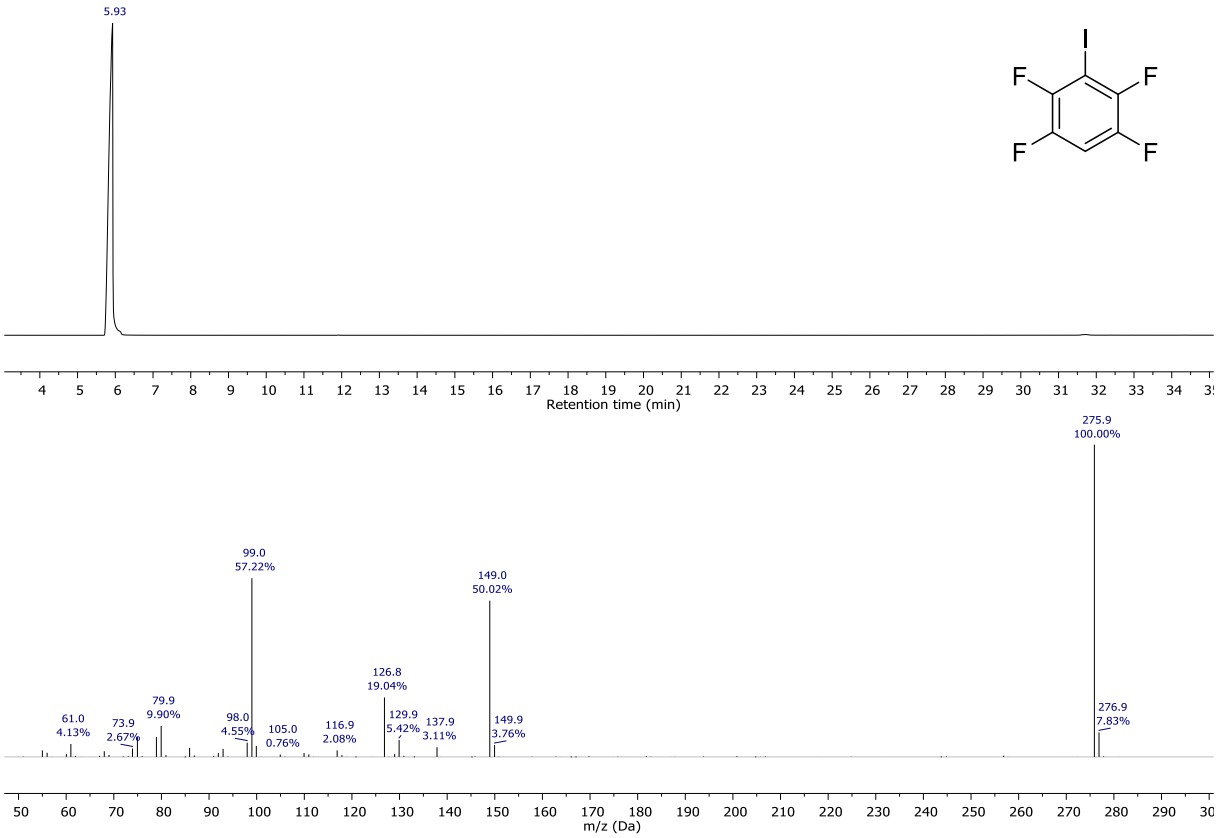


Figure S131 GC/MS-Spectrum with EI-Spectrum (EI$^+$): 1,2,4,5-Tetrafluoro-3-iodobenzene

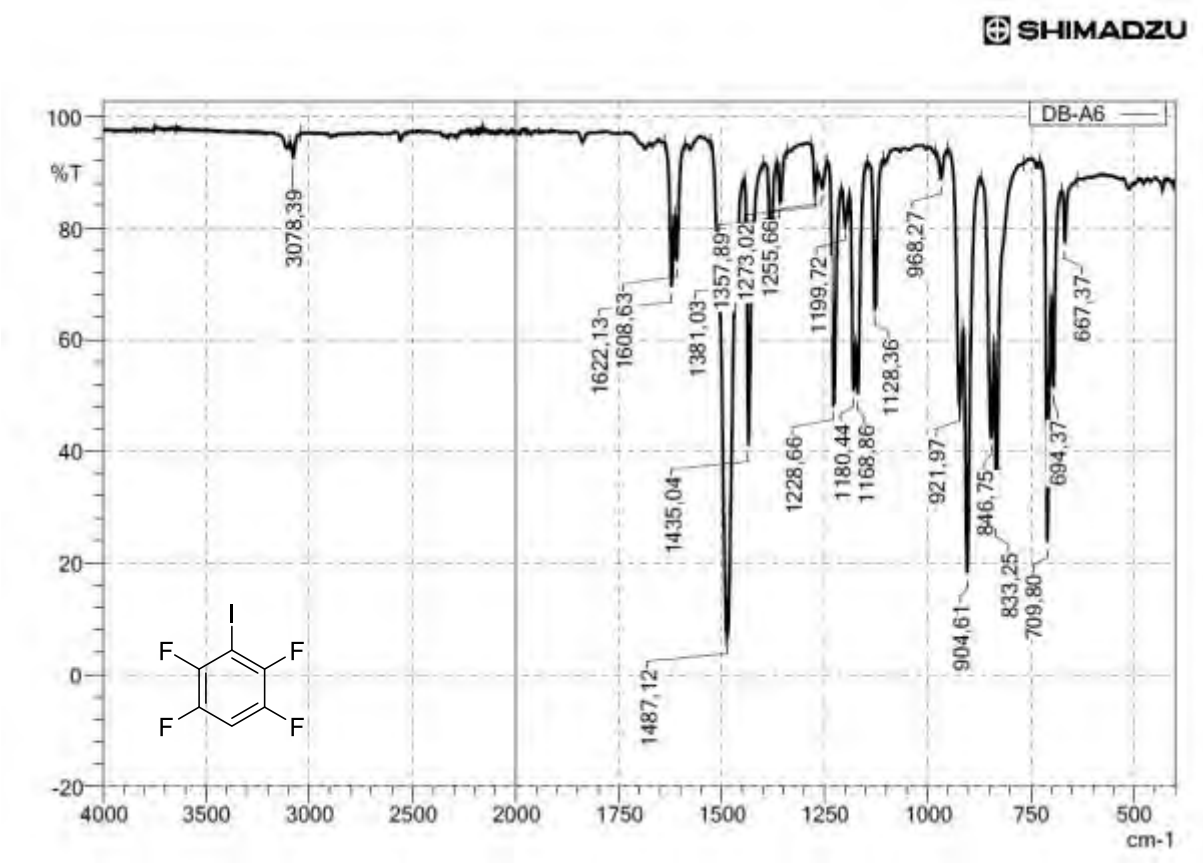


Figure S132 IR (ATR)-Spectrum: 1,2,4,5-Tetrafluoro-3-iodobenzene

1,2,3,5-Tetrafluoro-4-iodobenzene (40)

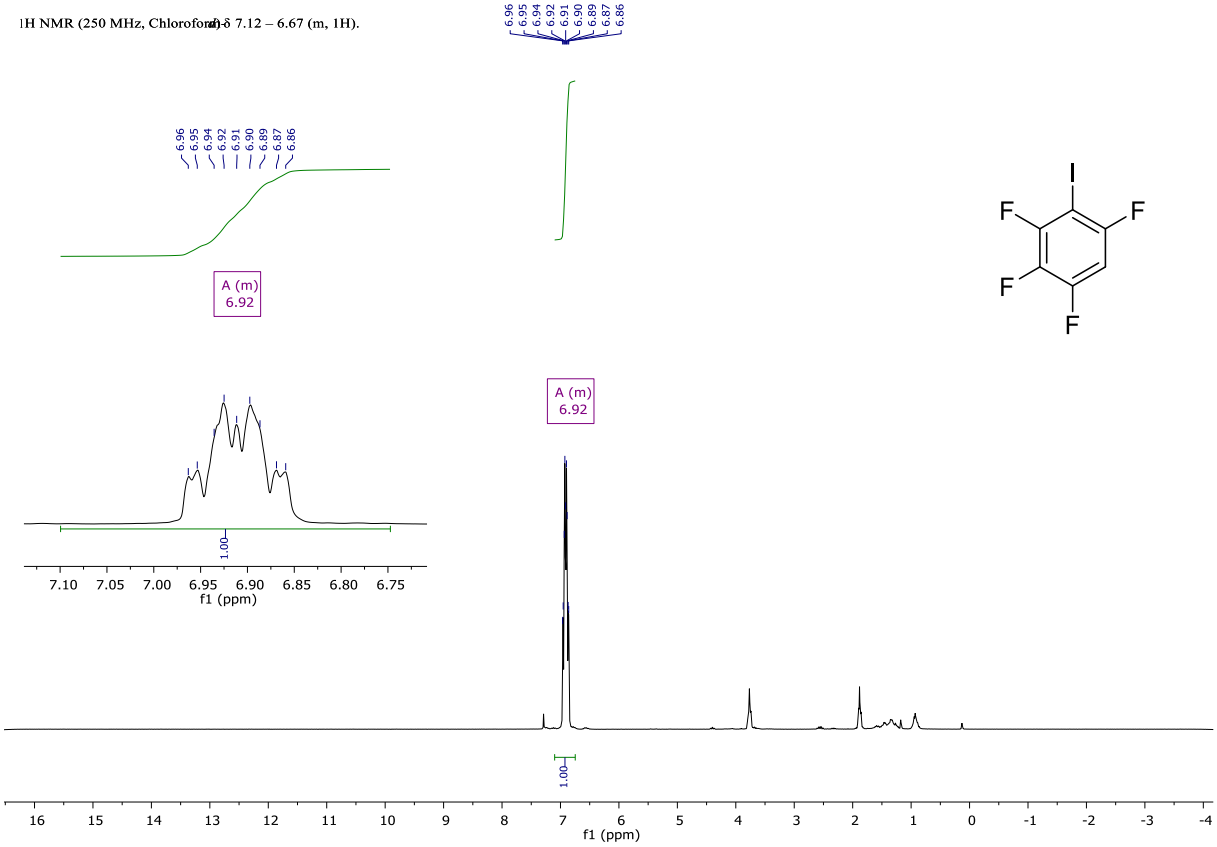


Figure S133 ^{1}H-NMR: 1,2,3,5-Tetrafluoro-4-iodobenzene

^{19}F NMR (235 MHz, Chloroform-d) δ -96.19 (d, J = 9.7 Hz), -111.72 (ddd, J = 22.3, 5.2, 2.6 Hz), -131.07 (ddd, J = 20.4, 4.8, 2.4 Hz), -161.84 (ddd, J = 21.8, 21.3, 9.7 Hz).

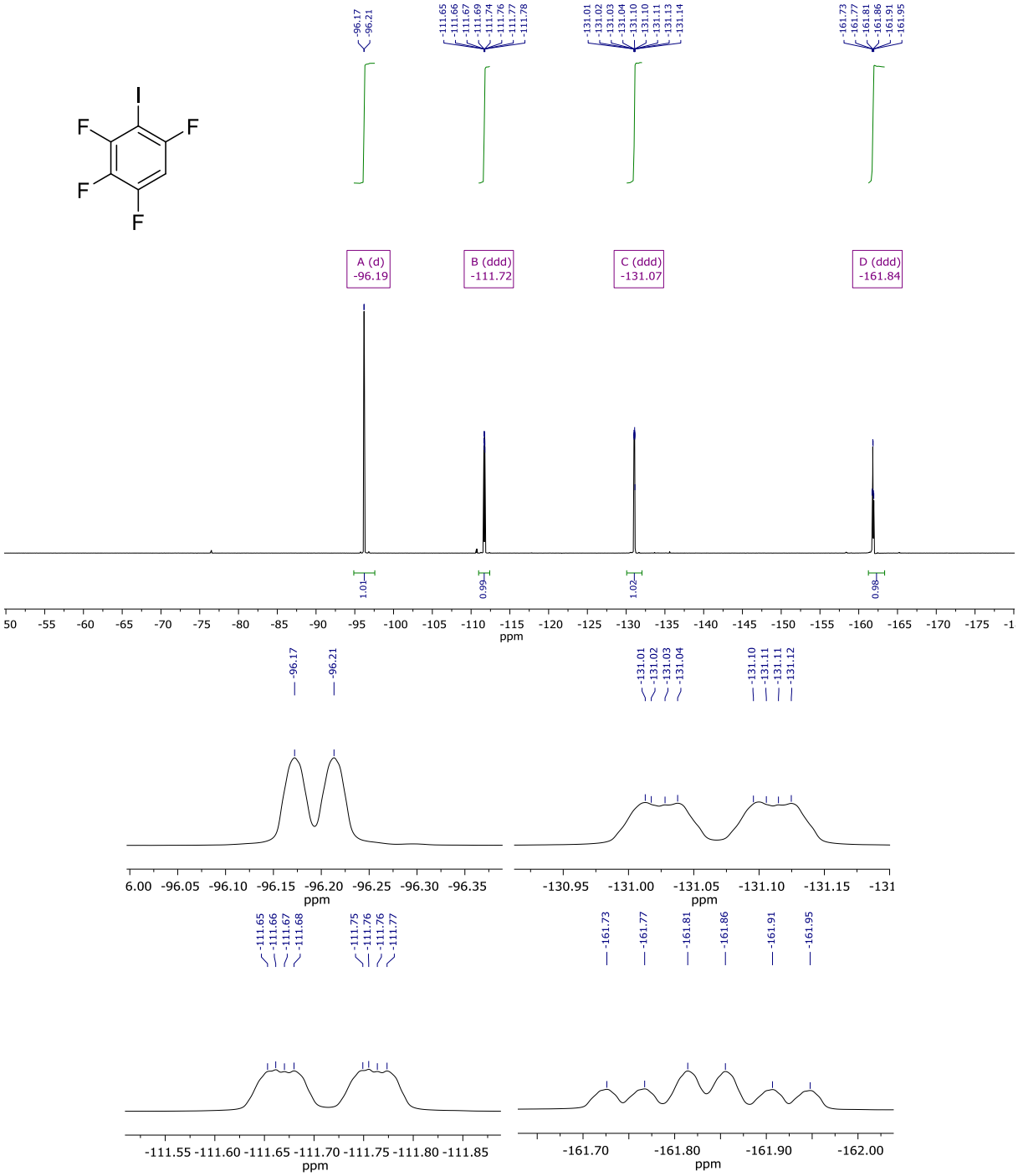


Figure S134 ^{19}F-NMR {^{1}H}: 1,2,3,5-Tetrafluoro-4-iodobenzene

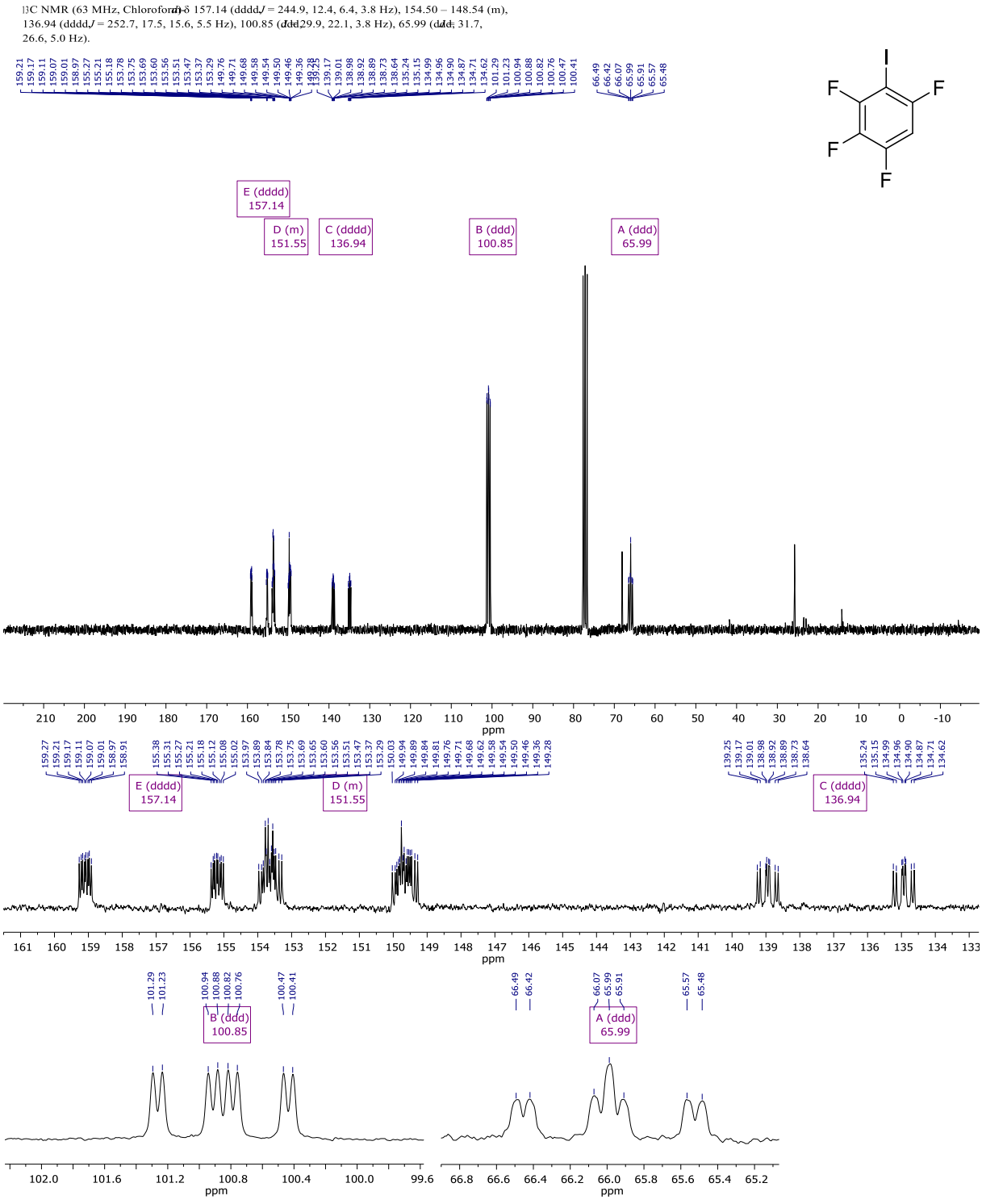


Figure S135 ^{13}C NMR: 1,2,3,5-Tetrafluoro-4-iodobenzene

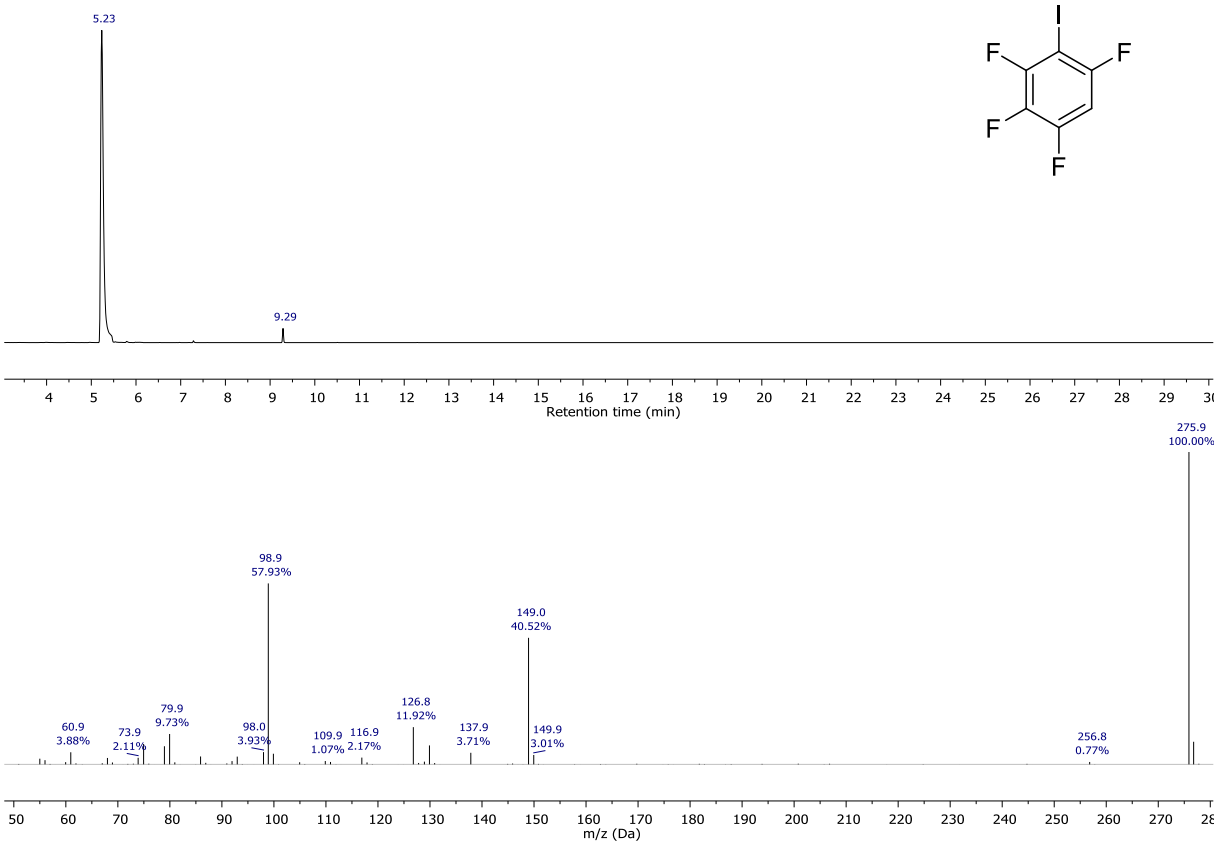


Figure S136 GC/MS-Spectrum EI-Spectrum (EI$^+$): 1,2,3,5-Tetrafluoro-4-iodobenzene

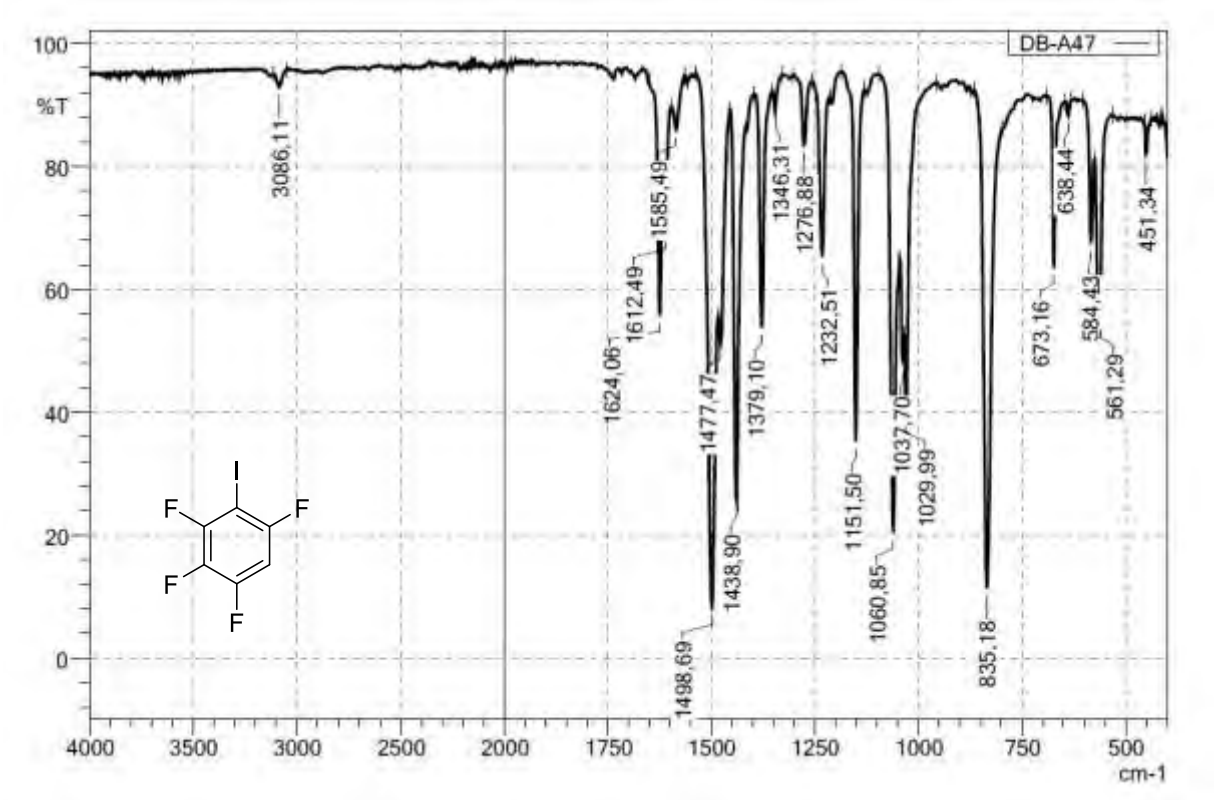


Figure S137 IR (ATR)-Spectrum: 1,2,3,5-Tetrafluoro-4-iodobenzene

2,3,5-Trifluoro-4-iodopyridine (41)

^{1}H NMR (250 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 1H).

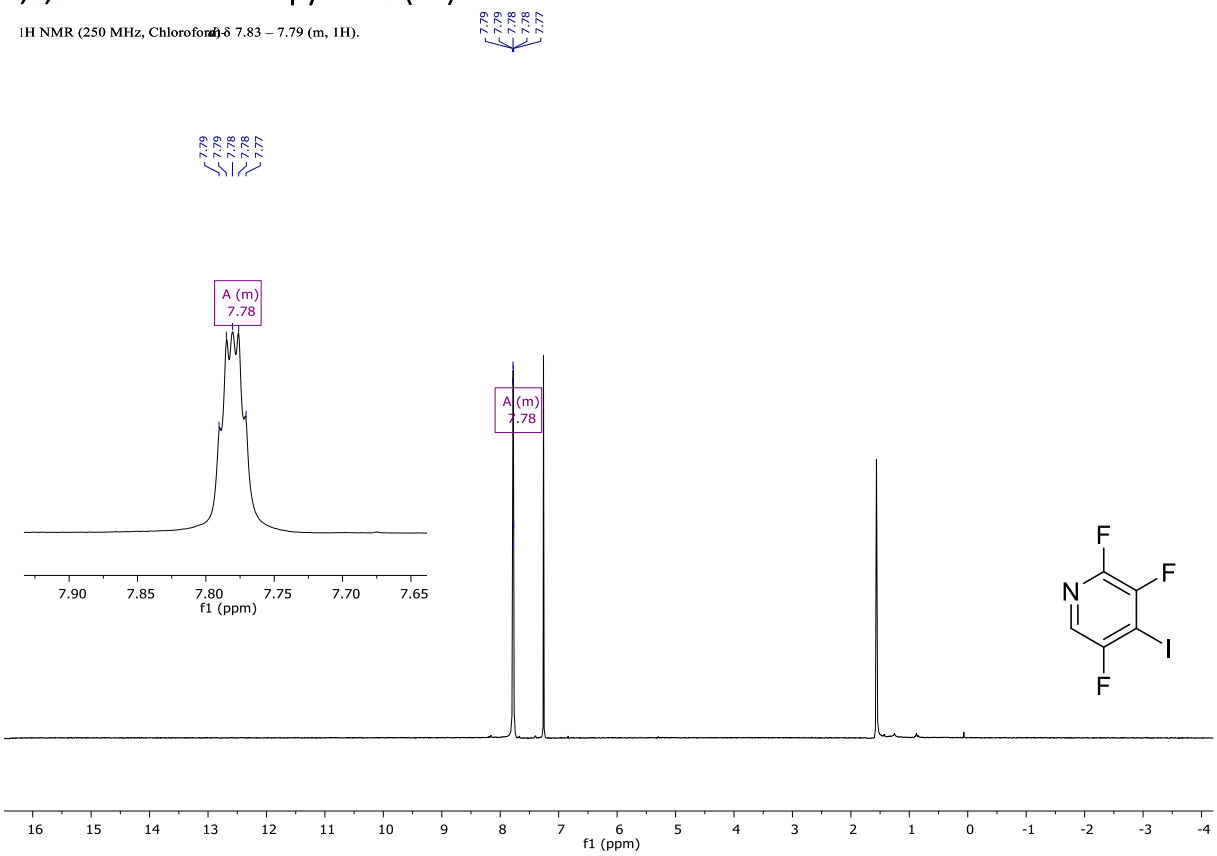


Figure S138 ^{1}H-NMR: 2,3,5-Trifluoro-4-iodopyridine

^{19}F NMR (235 MHz, Chloroform-*d*) δ -87.89 (t_J = 26.4 Hz), -111.85 (d_J = 27.2 Hz), -116.94 (d_J = 24.7 Hz).

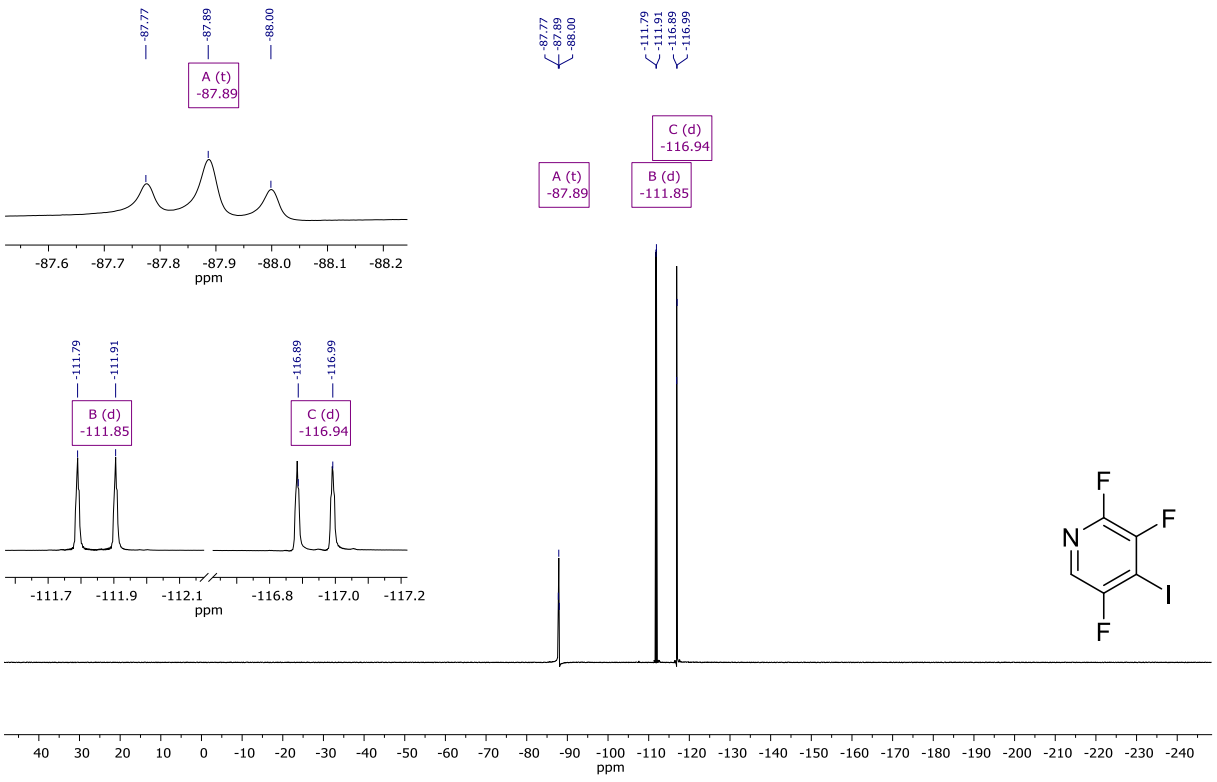


Figure S139 ^{19}F-NMR {^{1}H}: 2,3,5-Trifluoro-4-iodopyridine

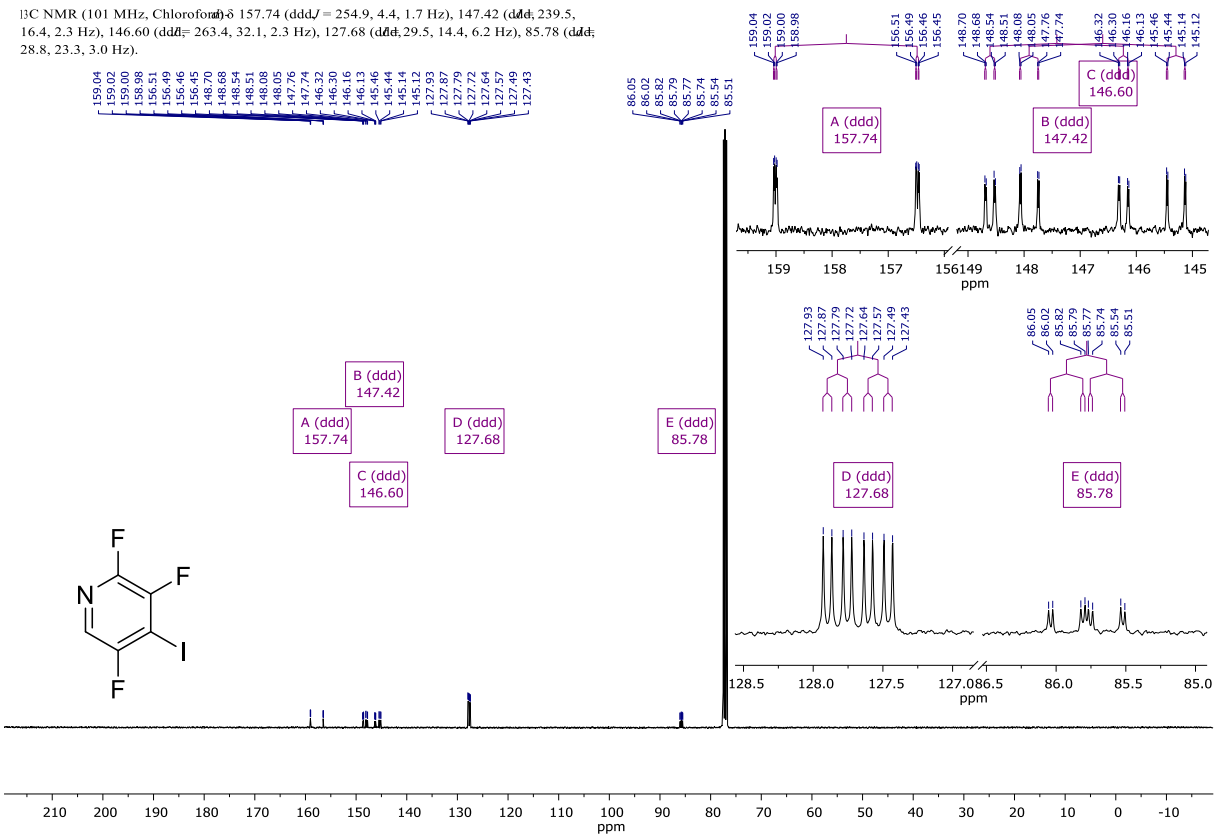


Figure S140 ^{13}C NMR: 2,3,5-Trifluoro-4-iodopyridine

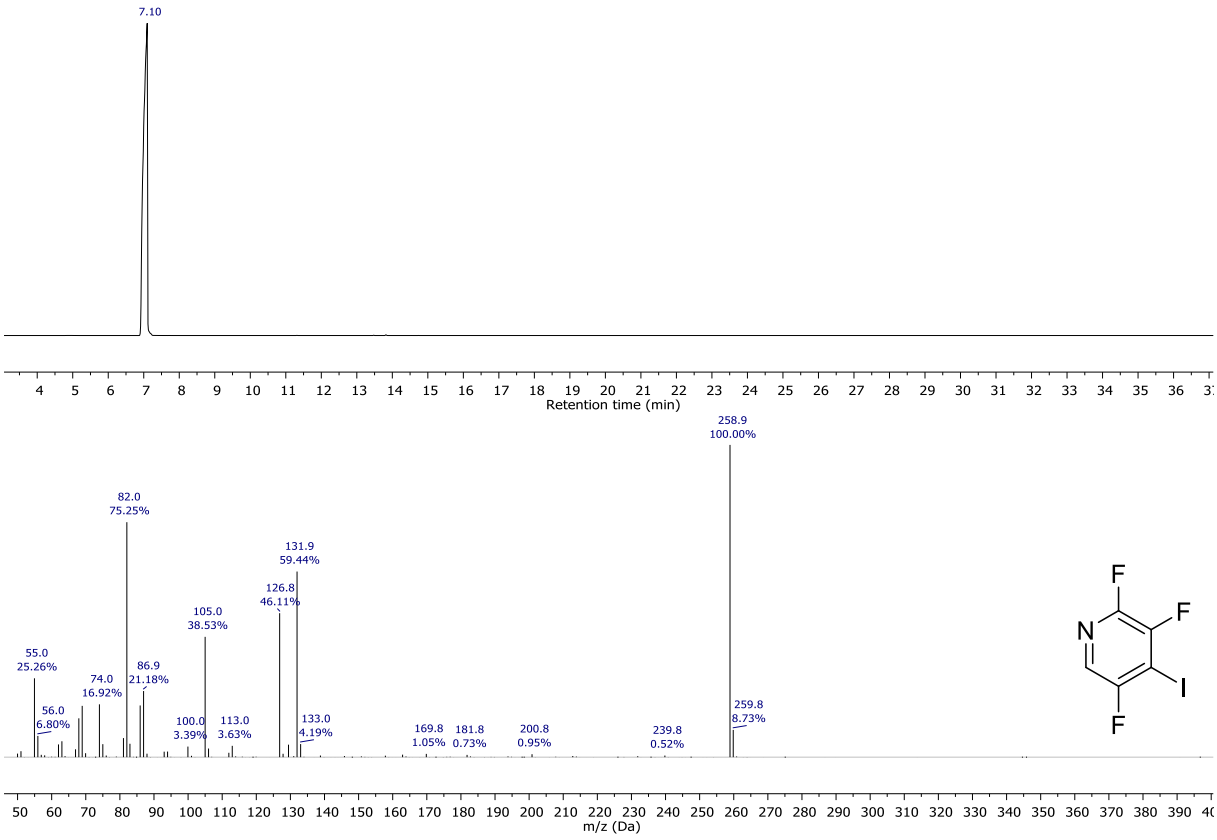


Figure S141 GC/MS-Spectrum with EI-Spectrum (EI$^+$): 2,3,5-Trifluoro-4-iodopyridine

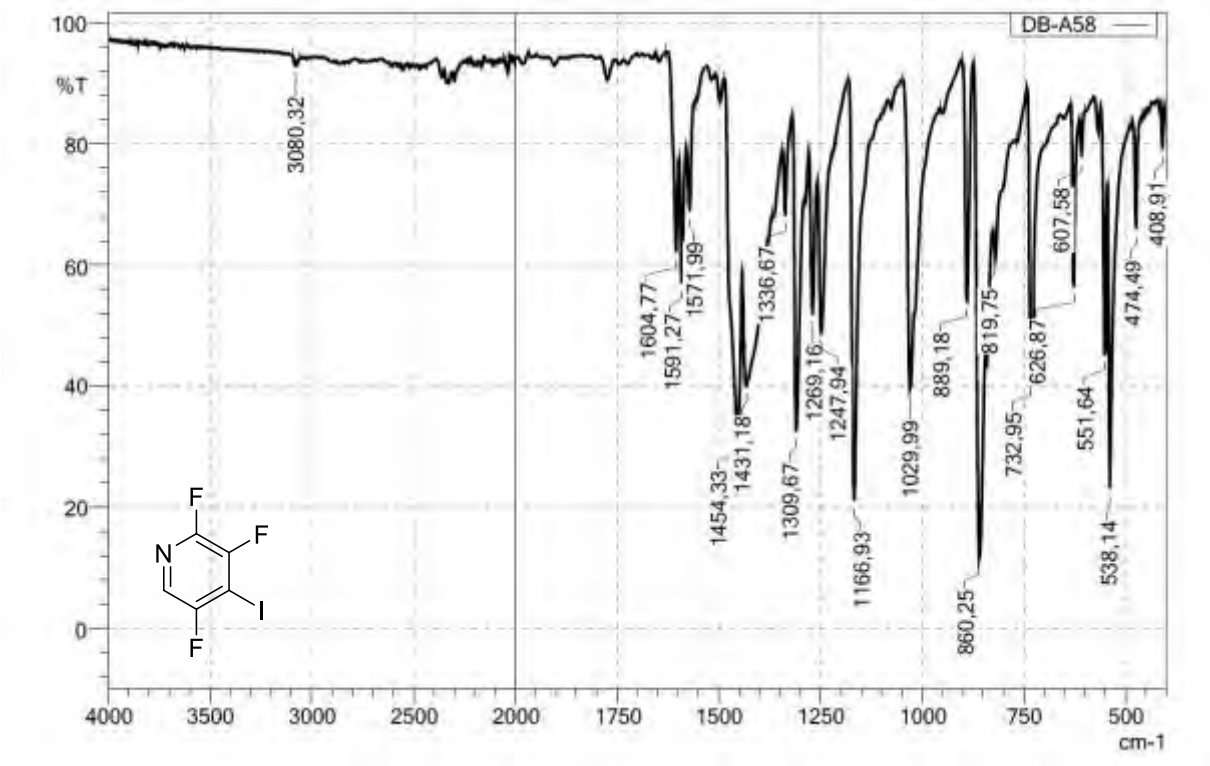


Figure S142 IR (ATR)-Spectrum: 2,3,5-Trifluoro-4-iodopyridine

2,3,5,6-Tetrafluoro-4-iodopyridine (42)

^{19}F NMR (235 MHz, Chloroform-*d*) δ -89.38 (dq, *J* = 28.0, 12.9 Hz), -122.33 – -123.18 (m).

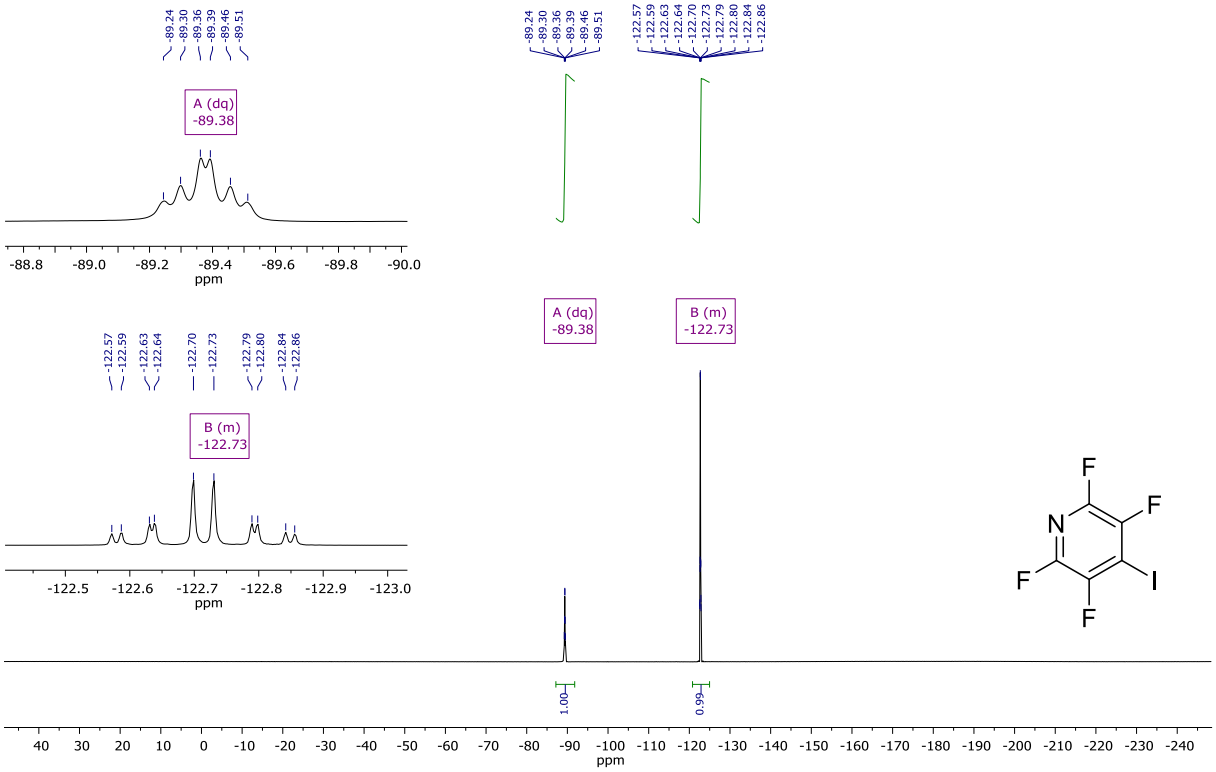


Figure S143 ^{19}F-NMR {^{1}H}: 2,3,5,6-Tetrafluoro-4-iodopyridine

^{13}C NMR (63 MHz, Chloroform-*d*) δ 145.98 – 141.01 (m), 145.05 – 140.23 (m), 88.64 (t, *J* = 15.8, 2.3 Hz).

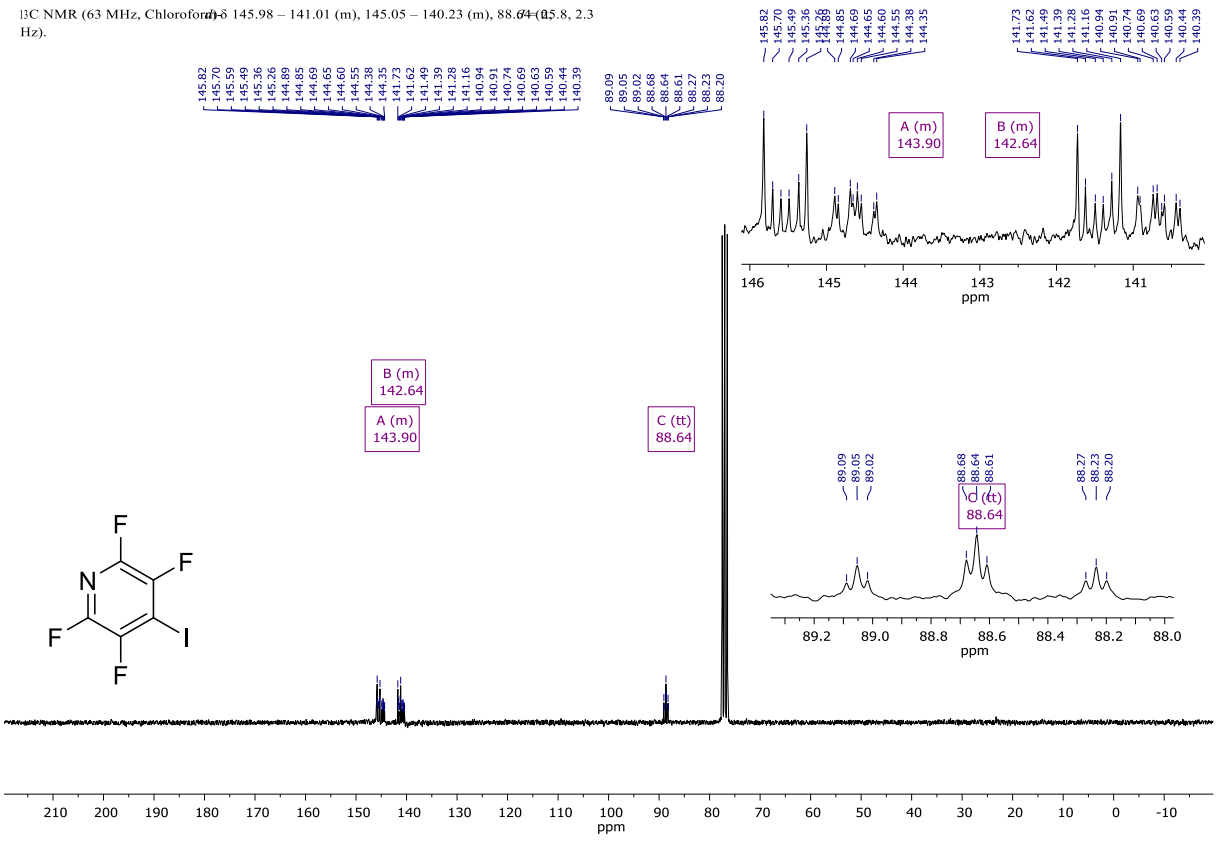


Figure S144 ^{13}C NMR: 2,3,5,6-Tetrafluoro-4-iodopyridine

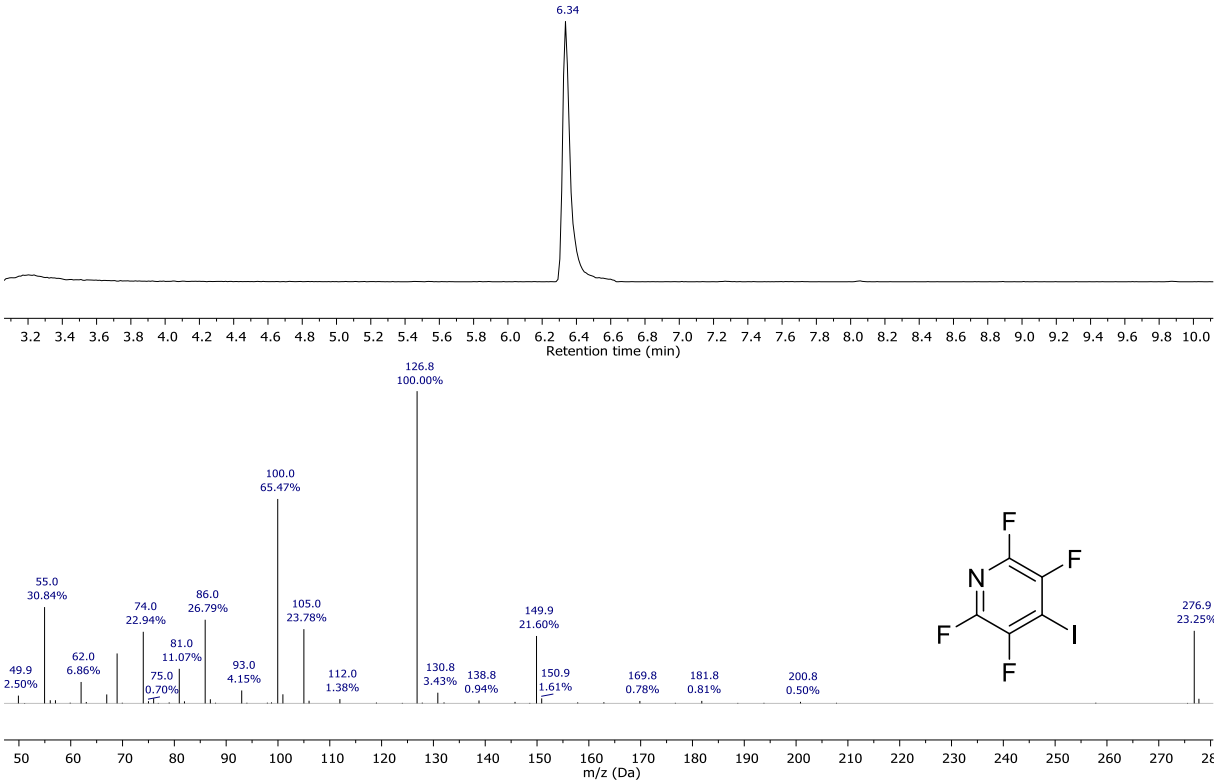


Figure S145 GC/MS-Spectrum with EI-Spectrum (EI^+): 2,3,5,6-Tetrafluoro-4-iodopyridine

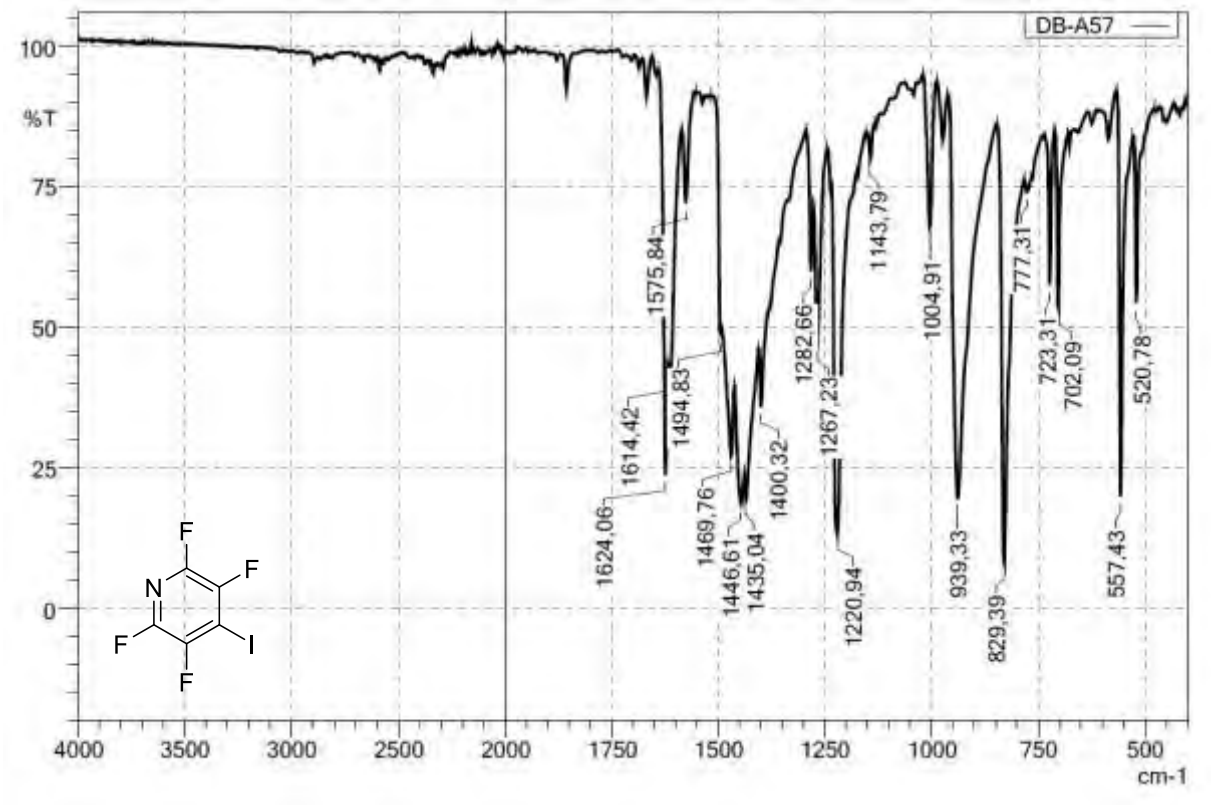


Figure S146 IR (ATR)-Spectrum: 2,3,5,6-Tetrafluoro-4-iodopyridine

Boronic acids

(2,4,5-Trifluorophenyl)boronic acid (6)

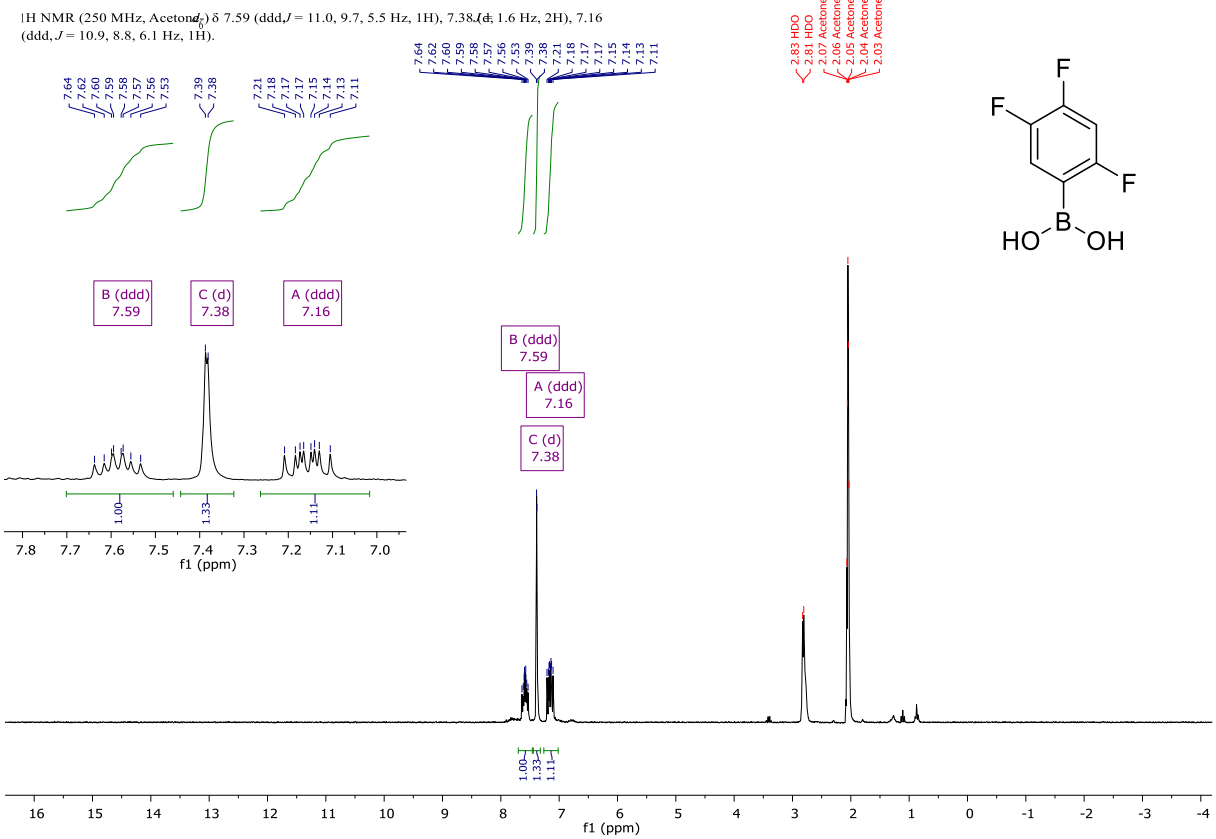


Figure S147 ^{1}H-NMR: (2,4,5-Trifluorophenyl)boronic acid

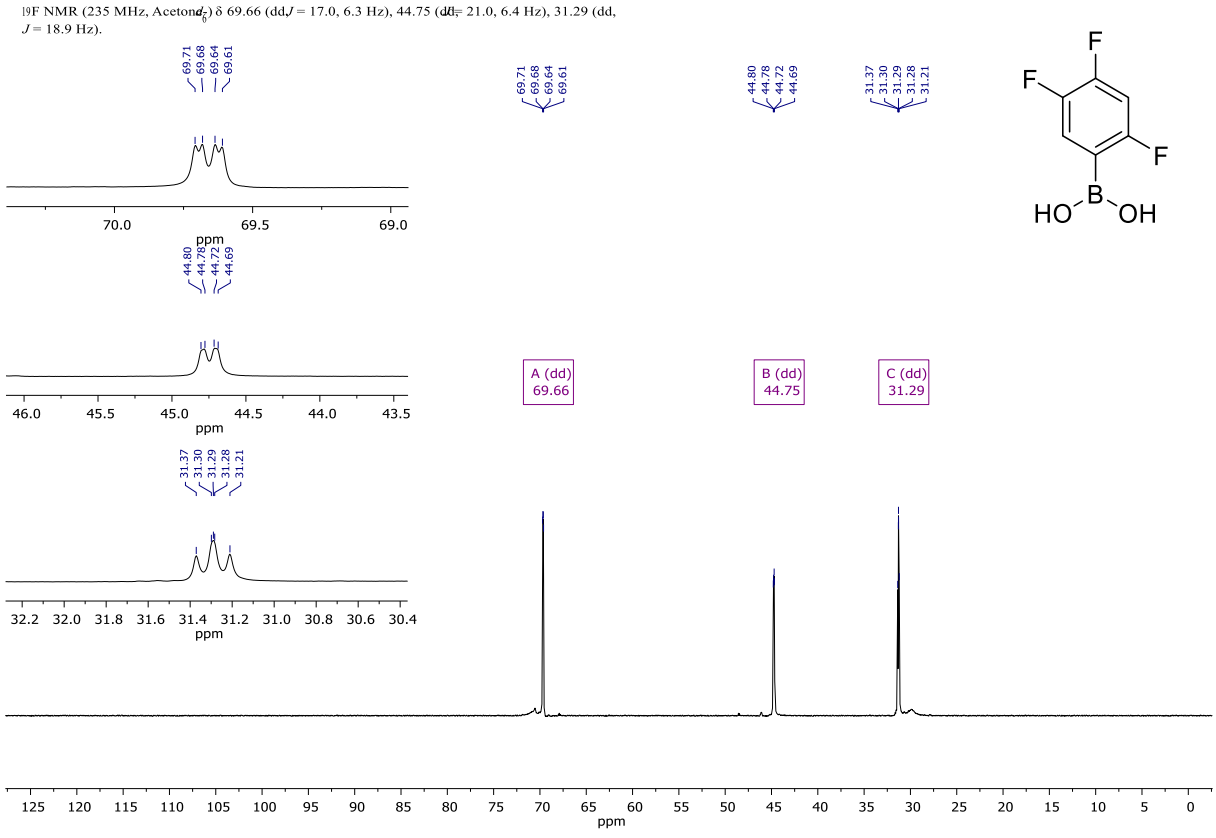


Figure S148 ^{19}F-NMR {^{1}H}: (2,4,5-Trifluorophenyl)boronic acid

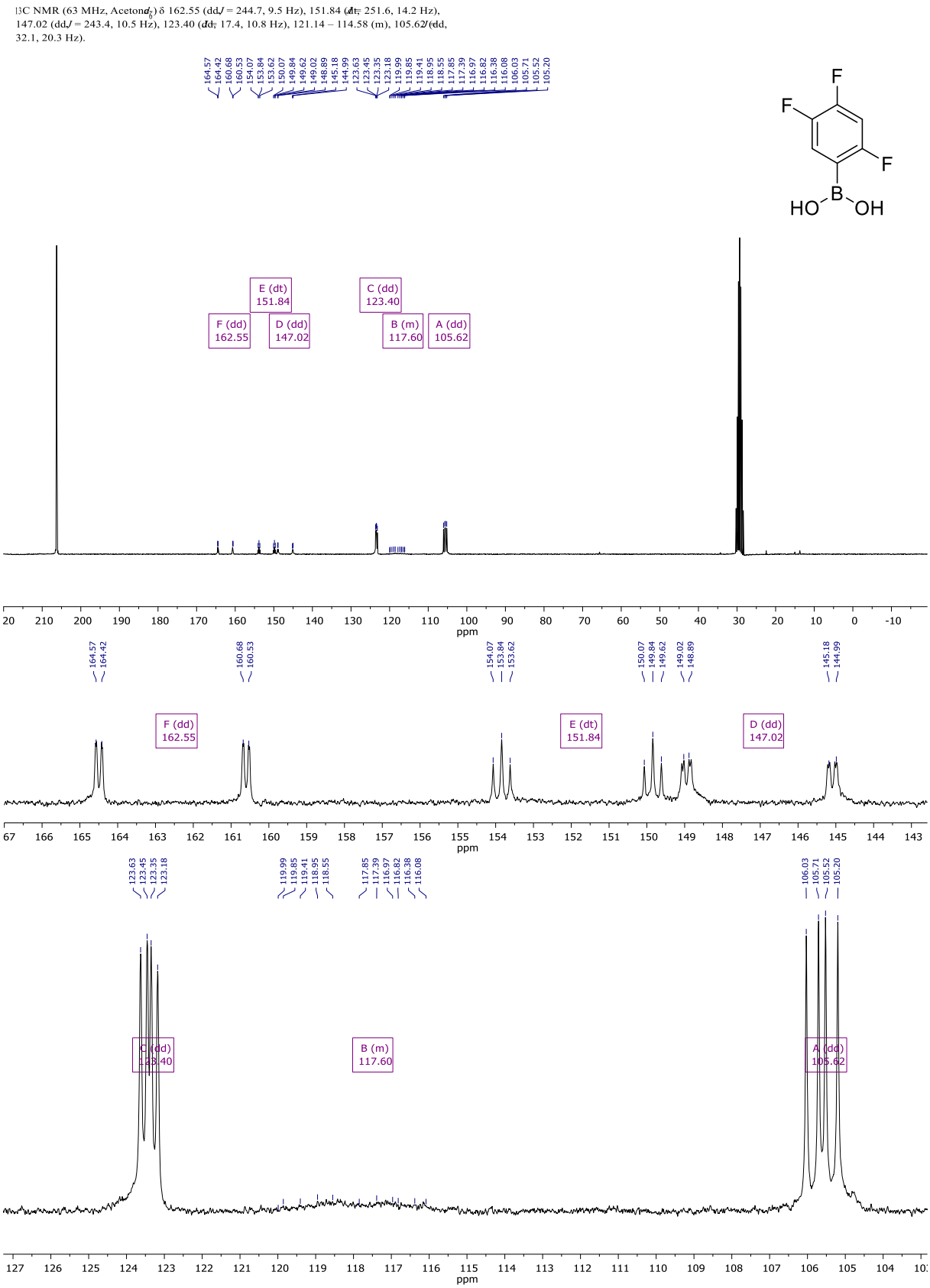


Figure S149 ^{13}C NMR: (2,4,5-Trifluorophenyl)boronic acid

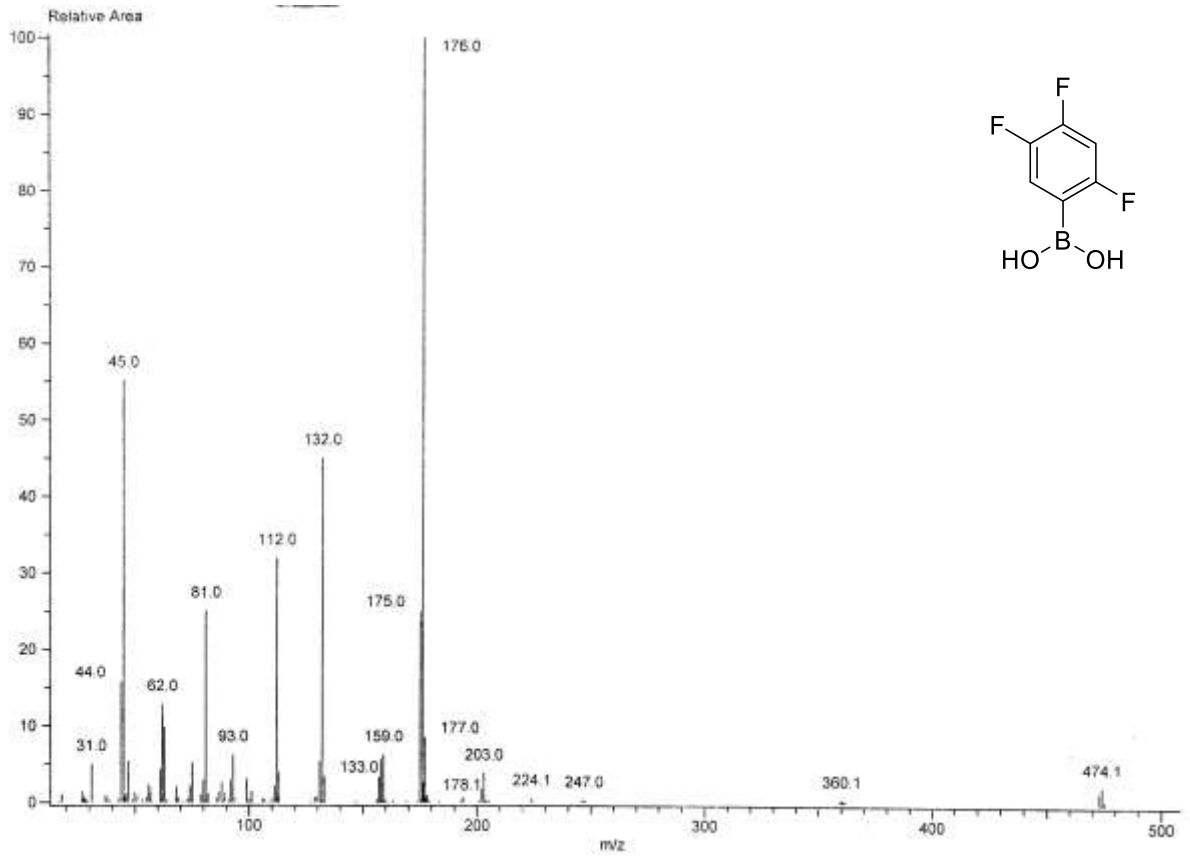


Figure S150 EI-Spectrum (EI⁺): (2,4,5-Trifluorophenyl)boronic acid

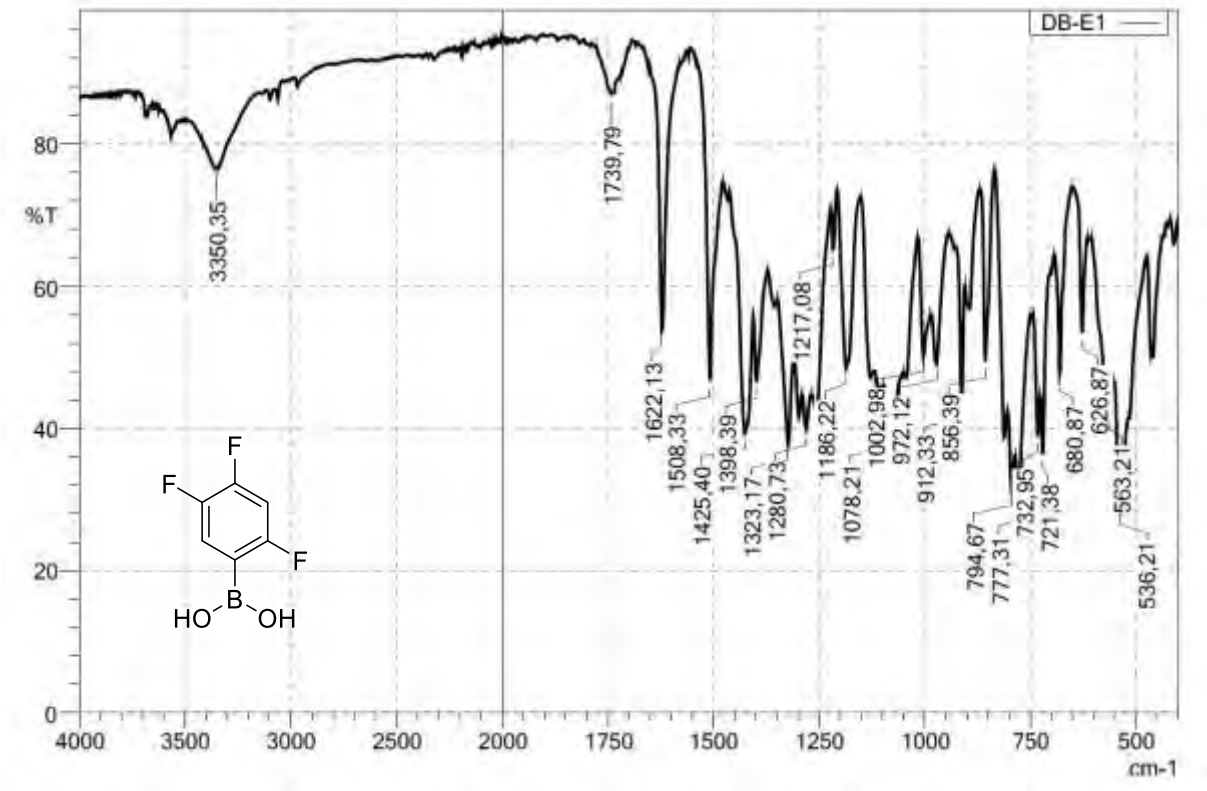


Figure S151 IR (ATR)-Spectrum: (2,4,5-Trifluorophenyl)boronic acid

(2,3,4-Trifluorophenyl)boronic acid (7)

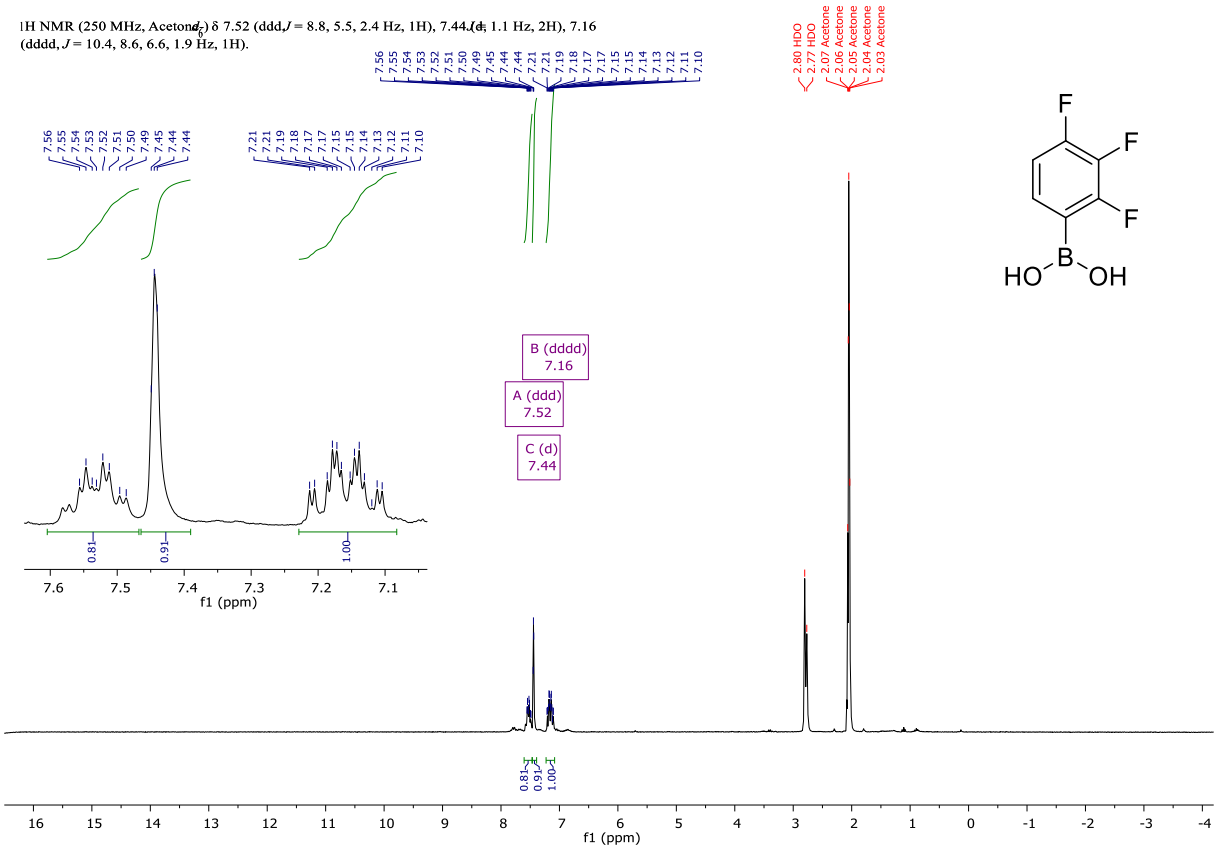


Figure S152 ^{1}H-NMR: (2,3,4-Trifluorophenyl)boronic acid

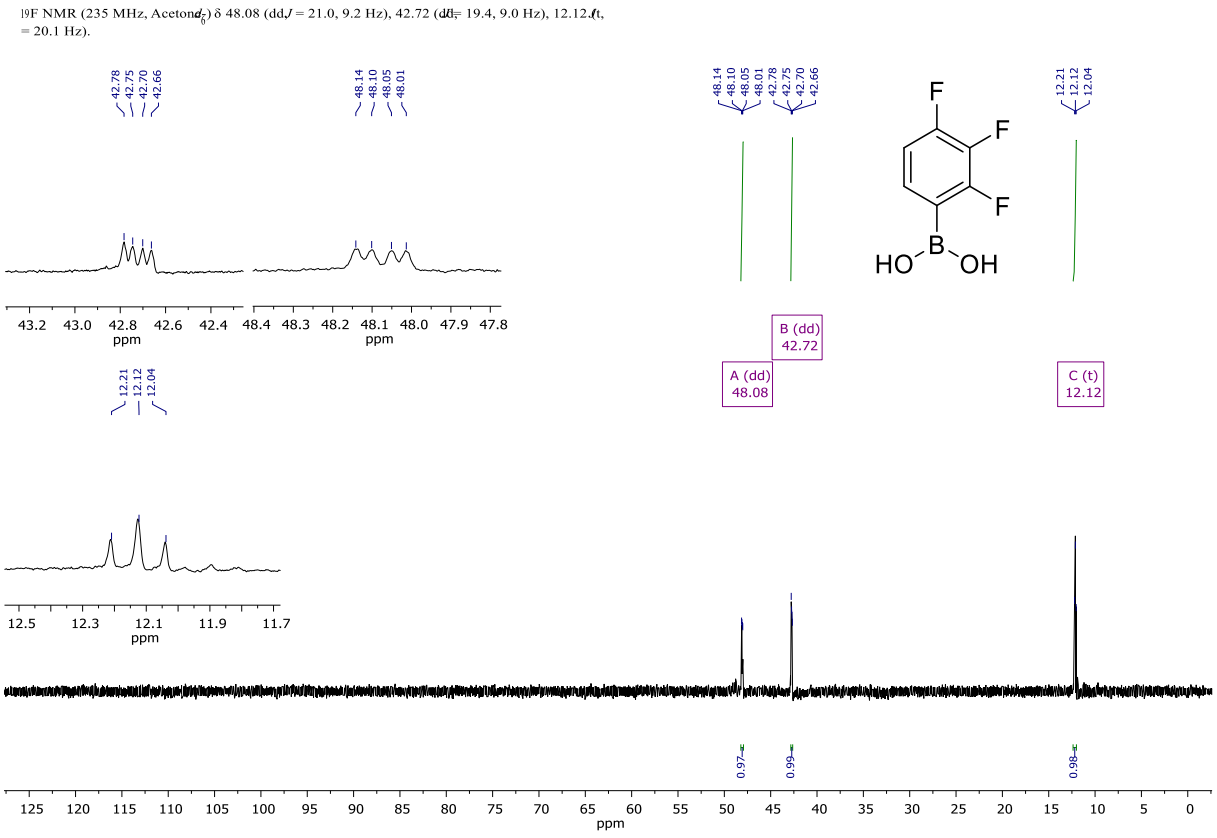


Figure S153 ^{19}F-NMR {^{1}H}: (2,3,4-Trifluorophenyl)boronic acid

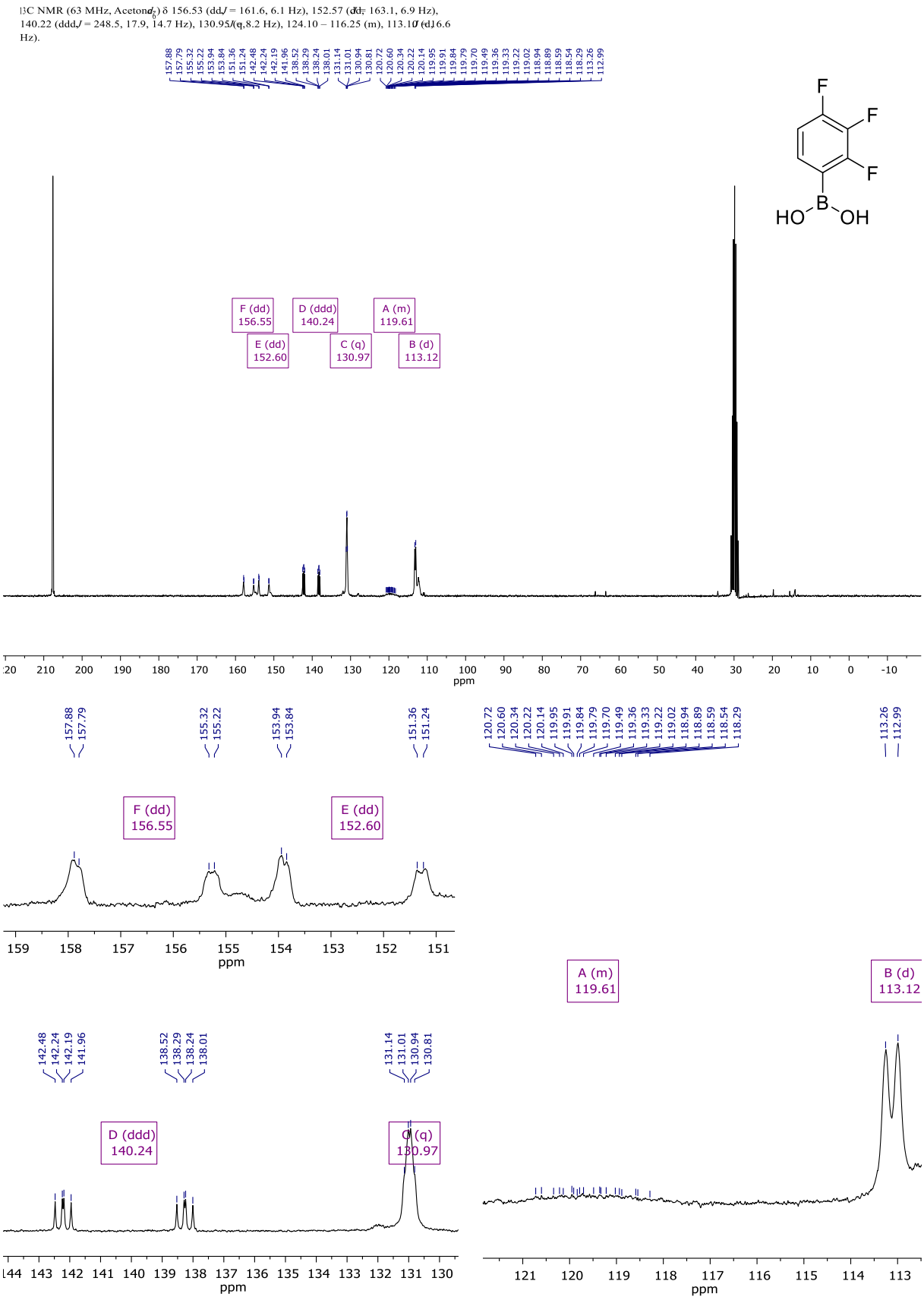


Figure S154 ^{13}C NMR: (2,3,4-Trifluorophenyl)boronic acid

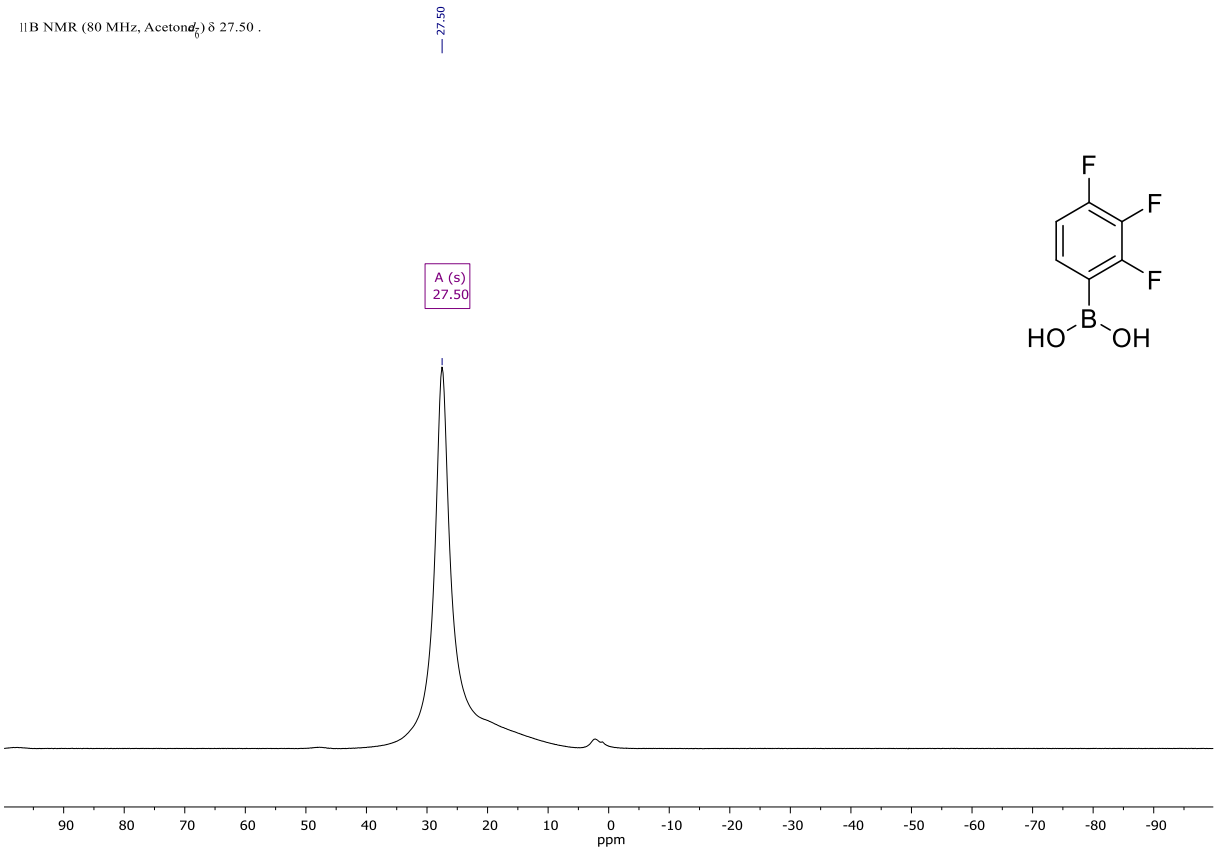


Figure S155 ^{11}B-NMR: (2,3,4-Trifluorophenyl)boronic acid

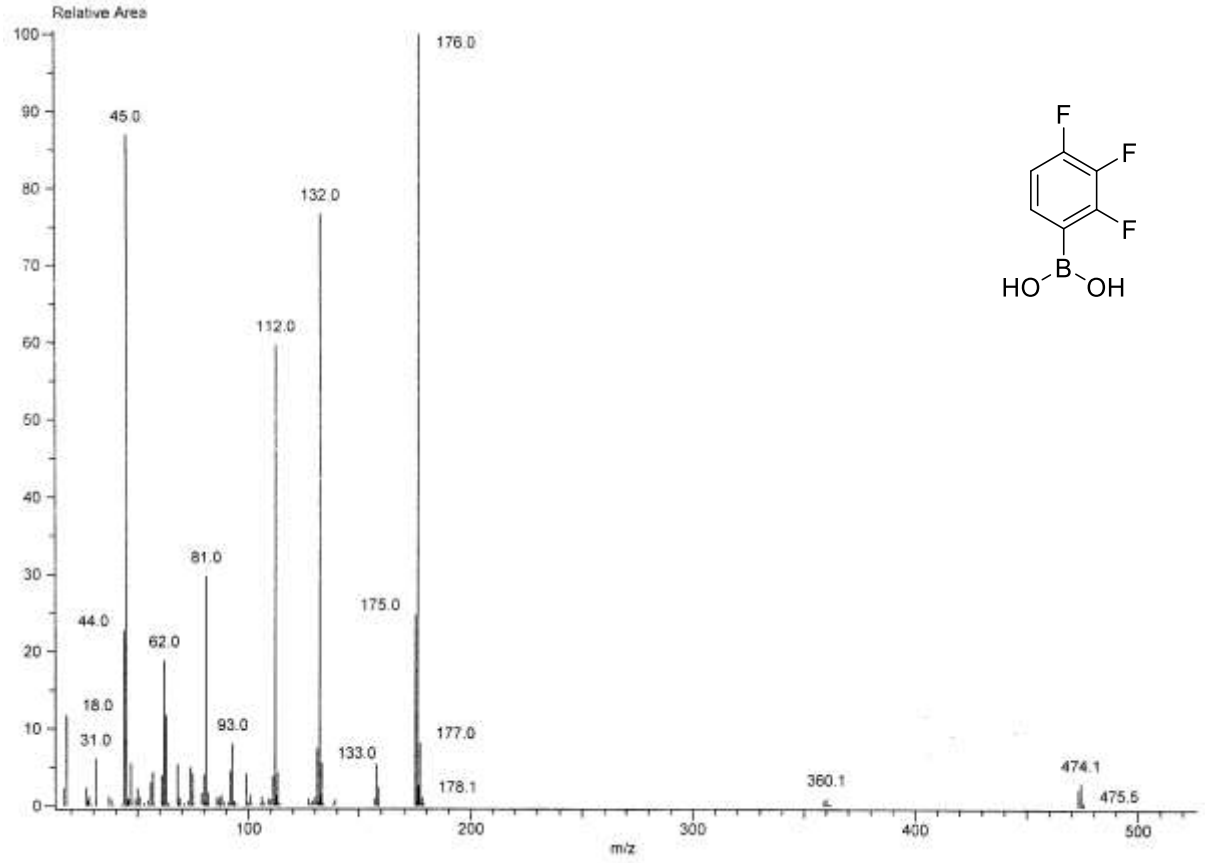


Figure S156 EI-Spectrum (EI$^+$): (2,3,4-Trifluorophenyl)boronic acid

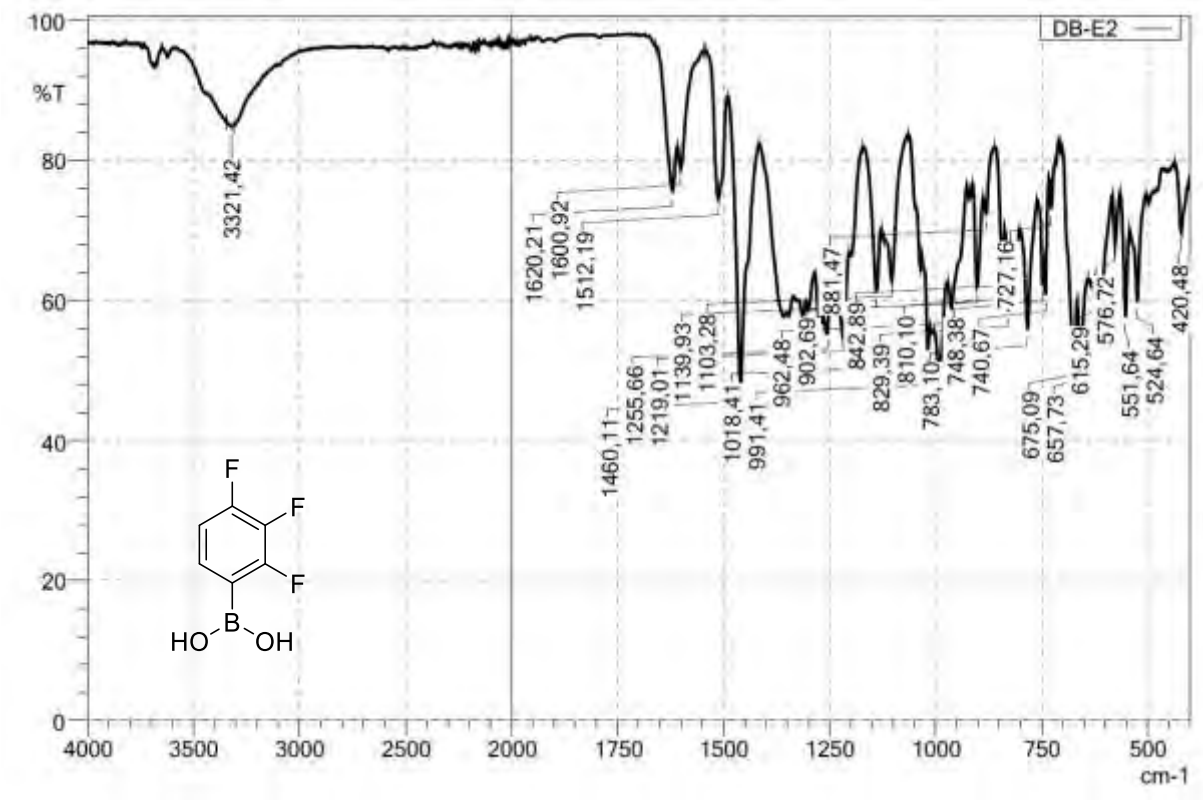


Figure S157 IR (ATR)-Spectrum: (2,3,4-Trifluorophenyl)boronic acid

Boronic acid esters

5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane (15)

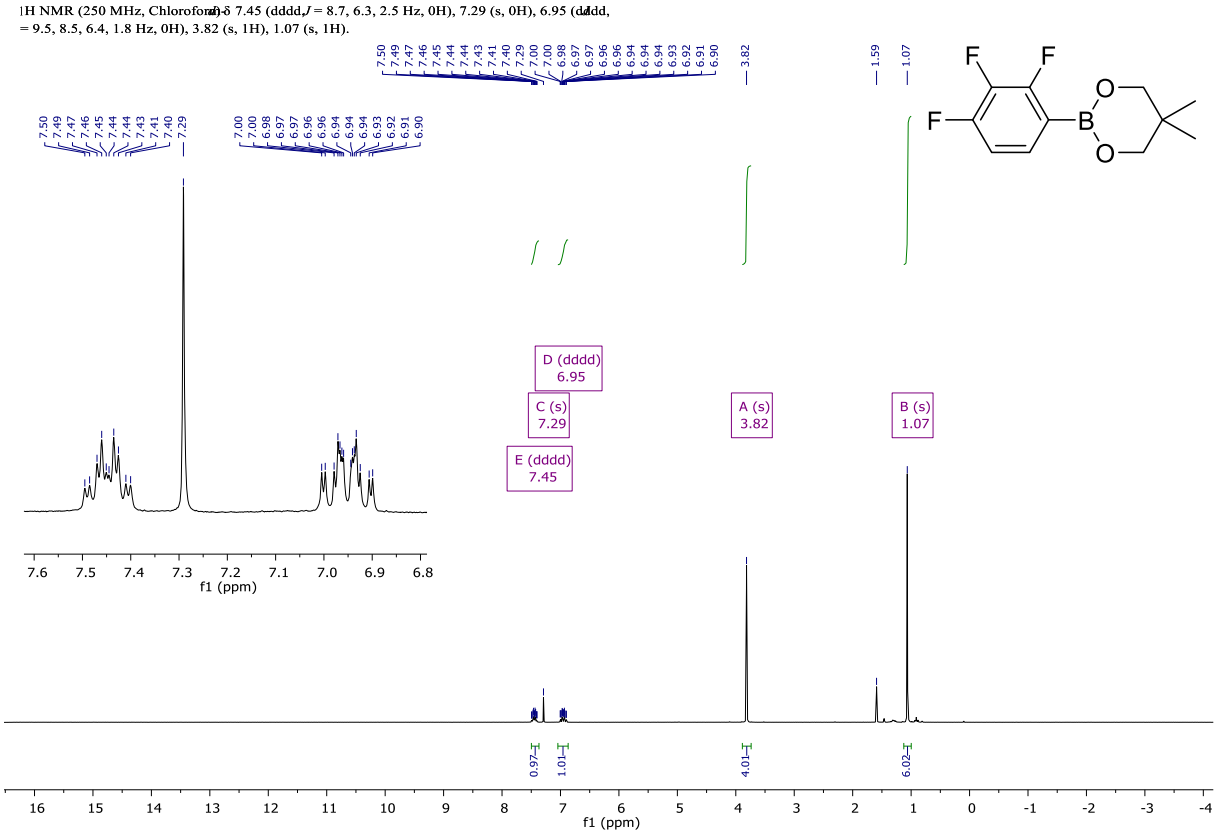


Figure S158 ^{1}H-NMR: 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

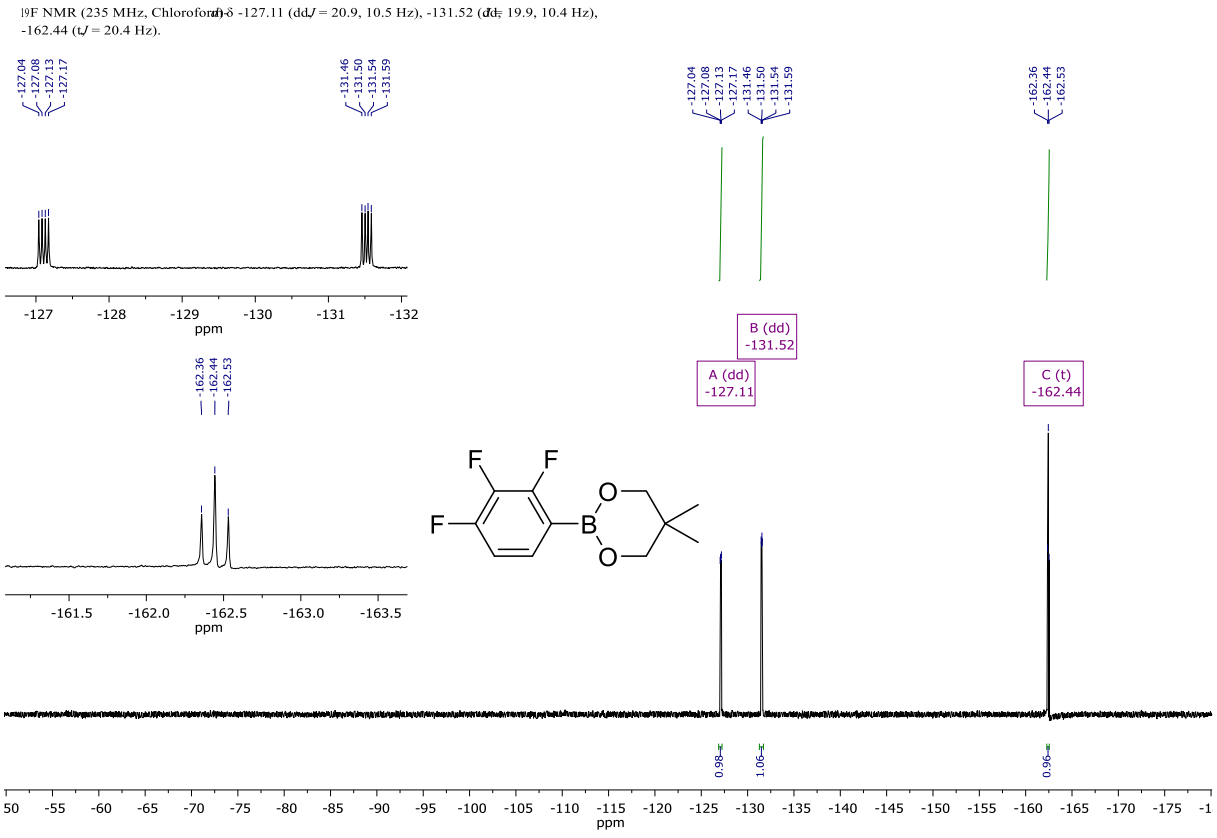


Figure S159 ^{19}F-NMR {^{1}H}: 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

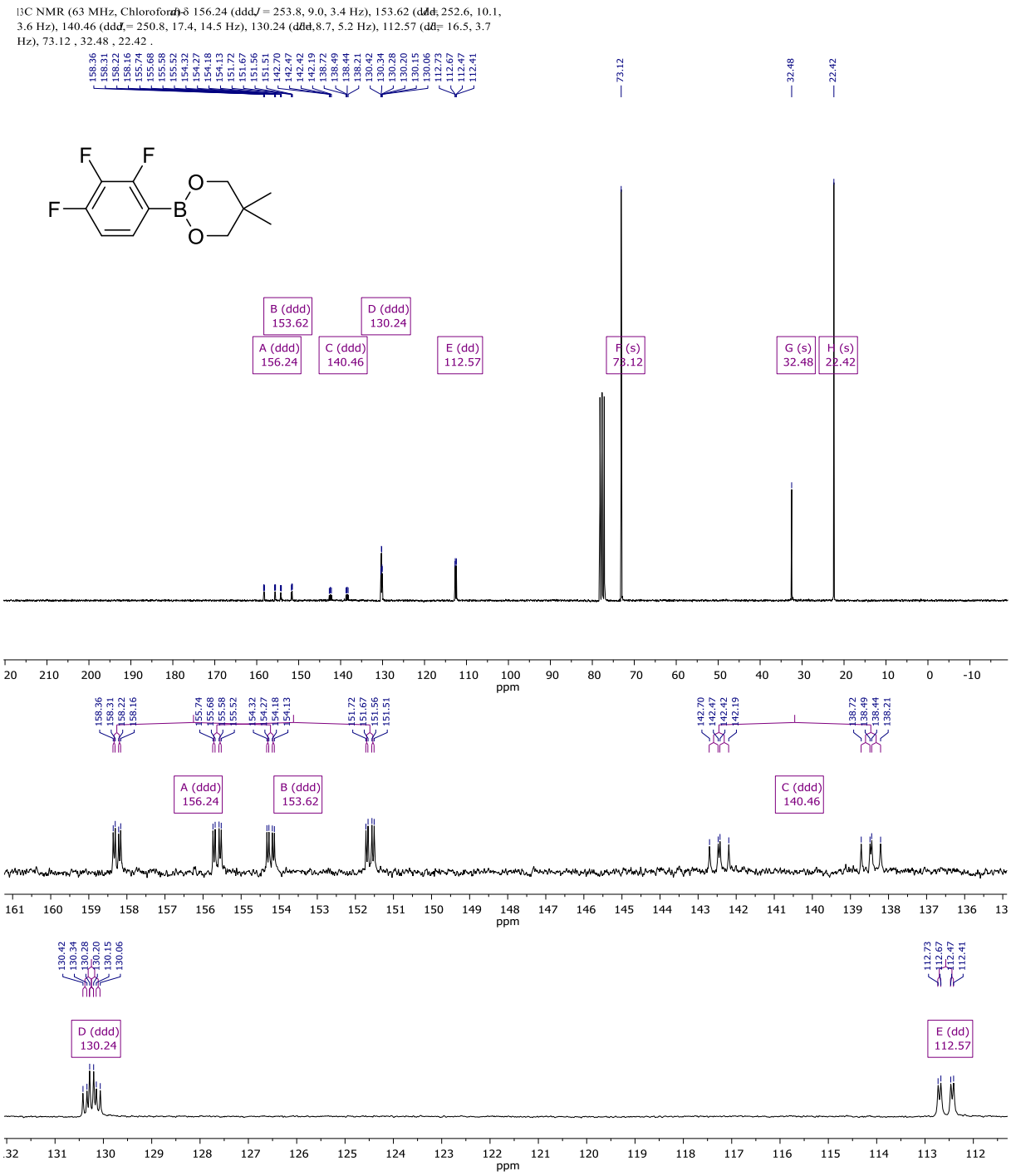


Figure S160 ^{13}C NMR: 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

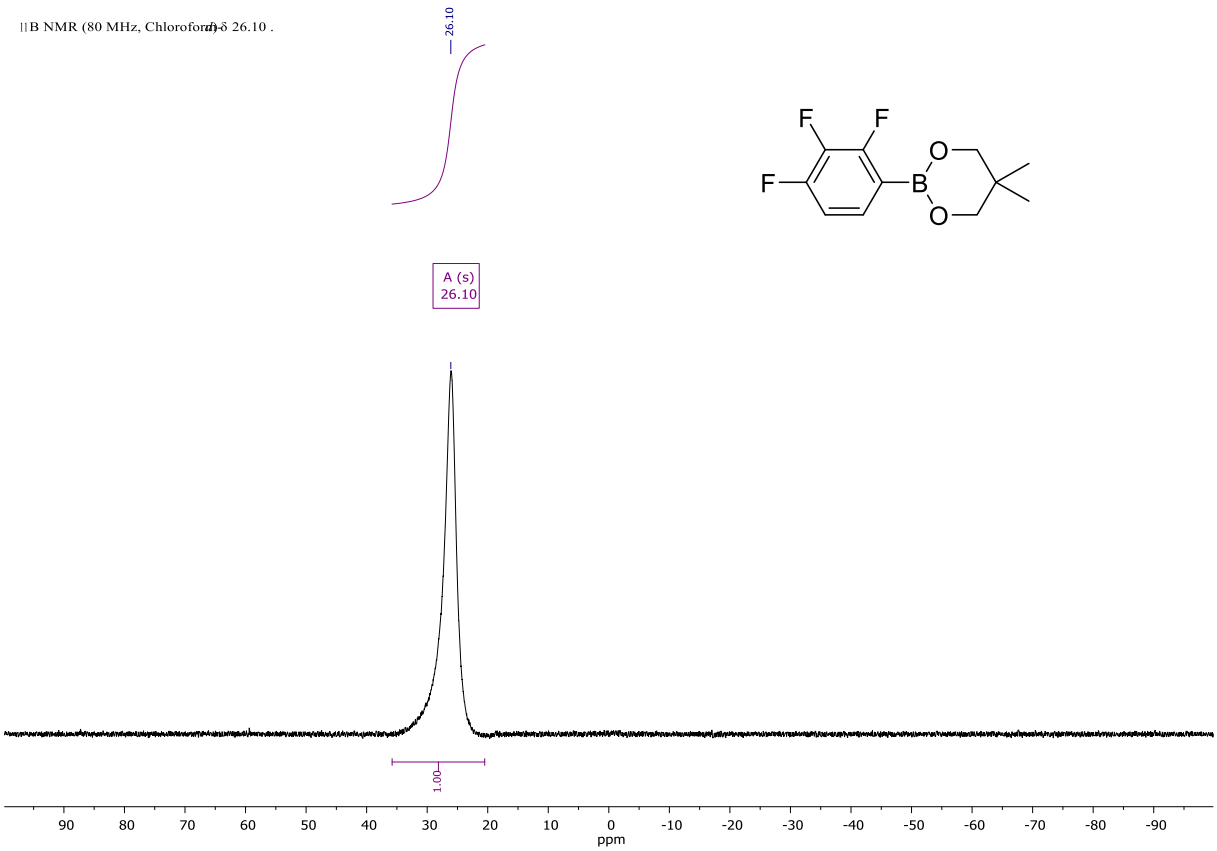


Figure S161 ^{11}B-NMR: 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

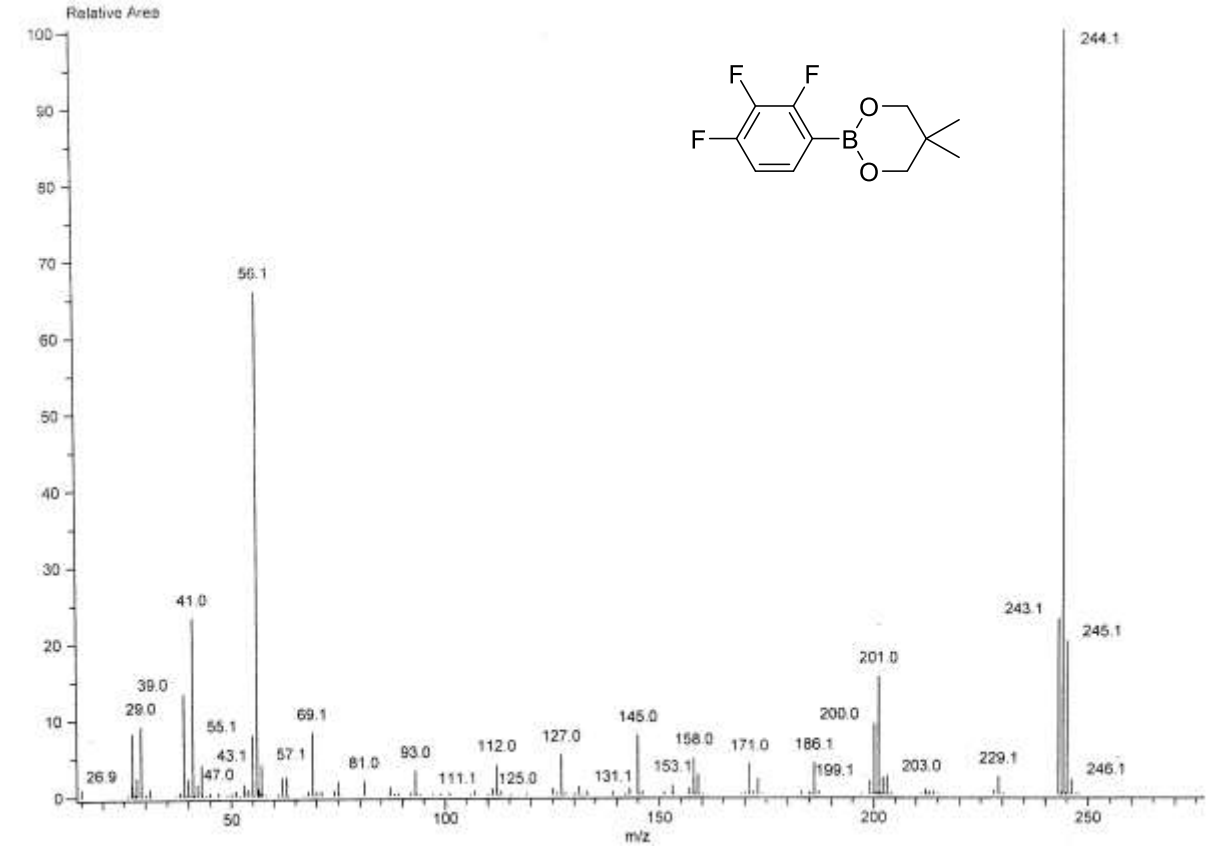


Figure S162 EI-Spectrum (EI$^+$): 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

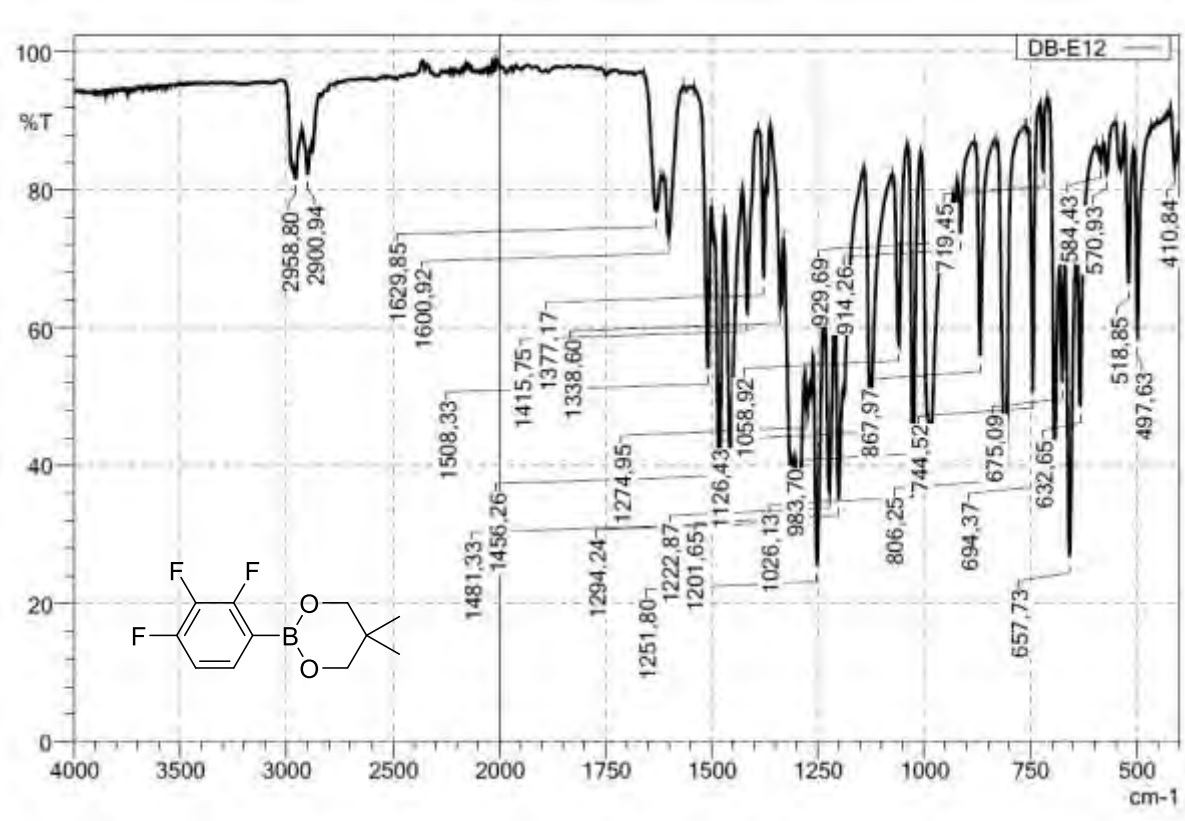


Figure S163 IR (ATR)-Spectrum: 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane (17)

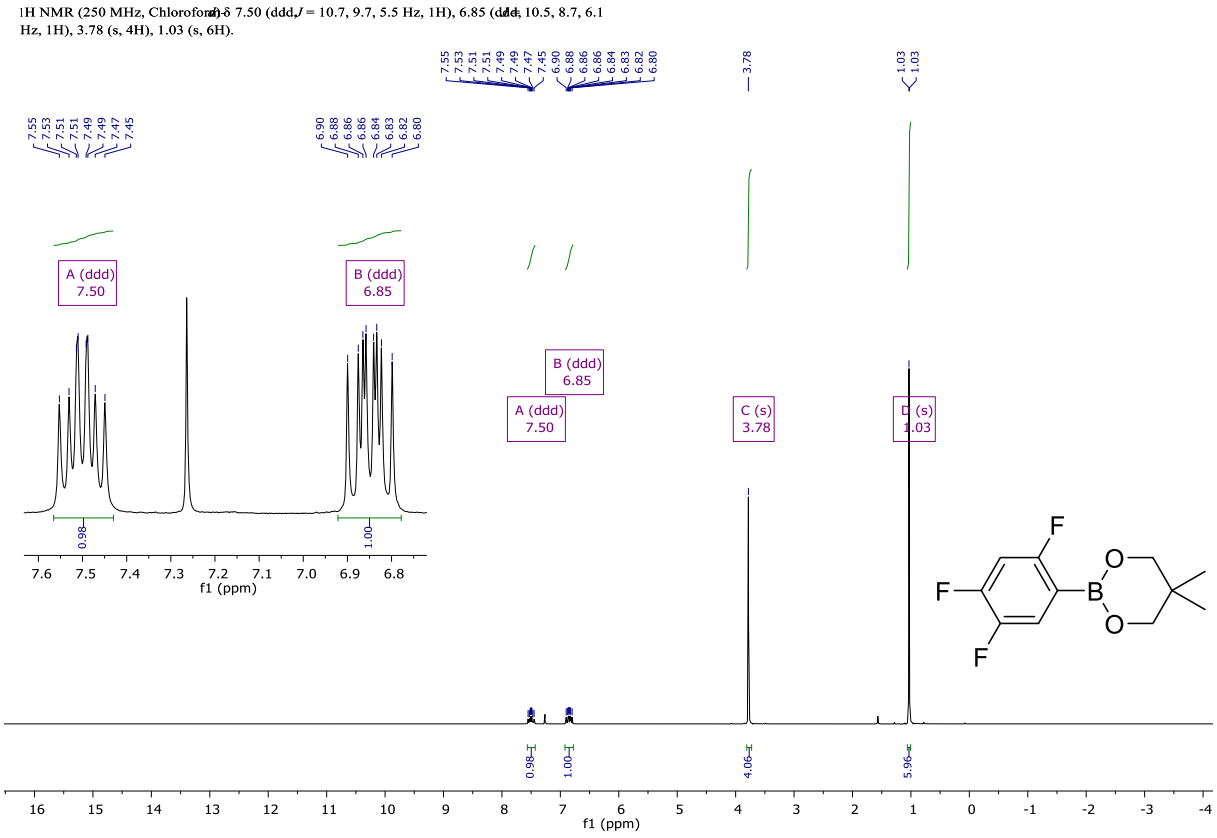


Figure S164 ^{1}H-NMR: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

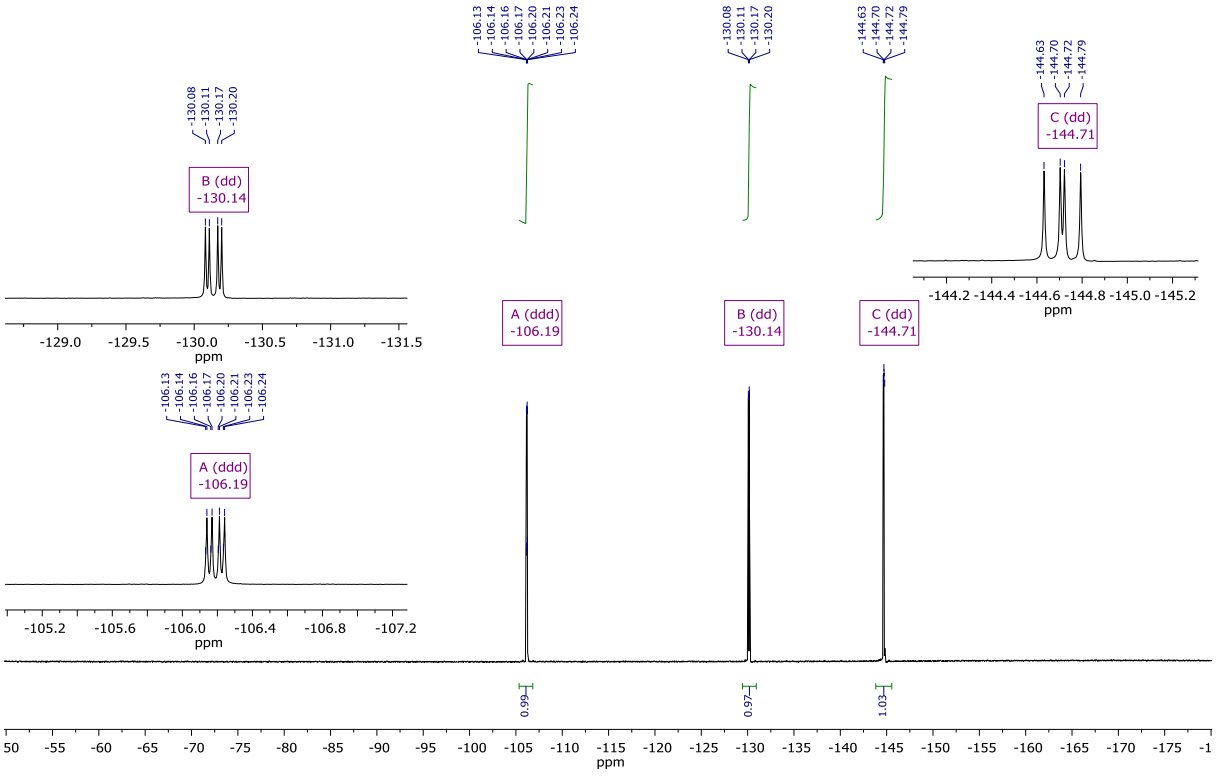


Figure S165: ^{19}F-NMR {^{1}H}: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

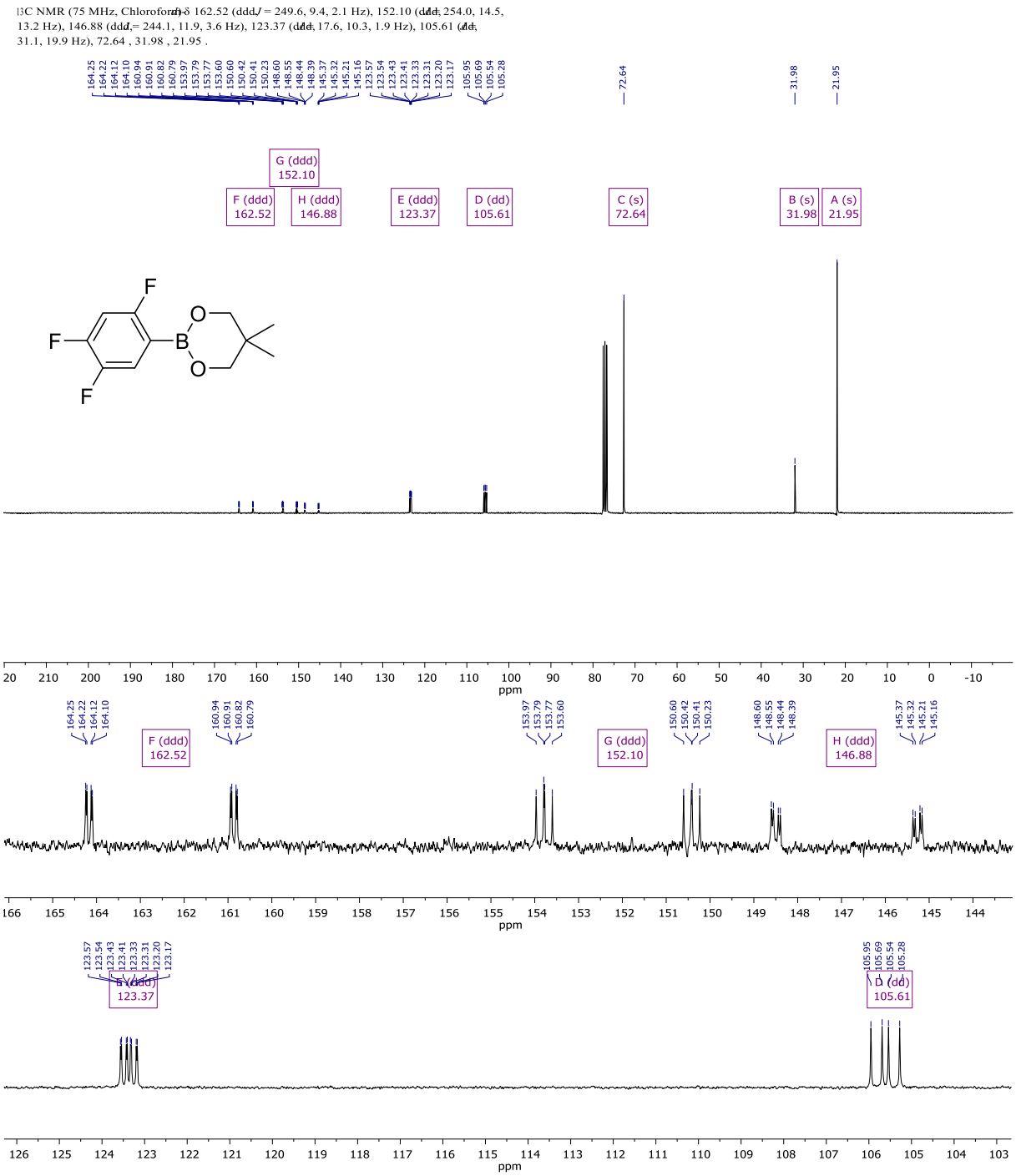


Figure S166 ^{13}C NMR: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

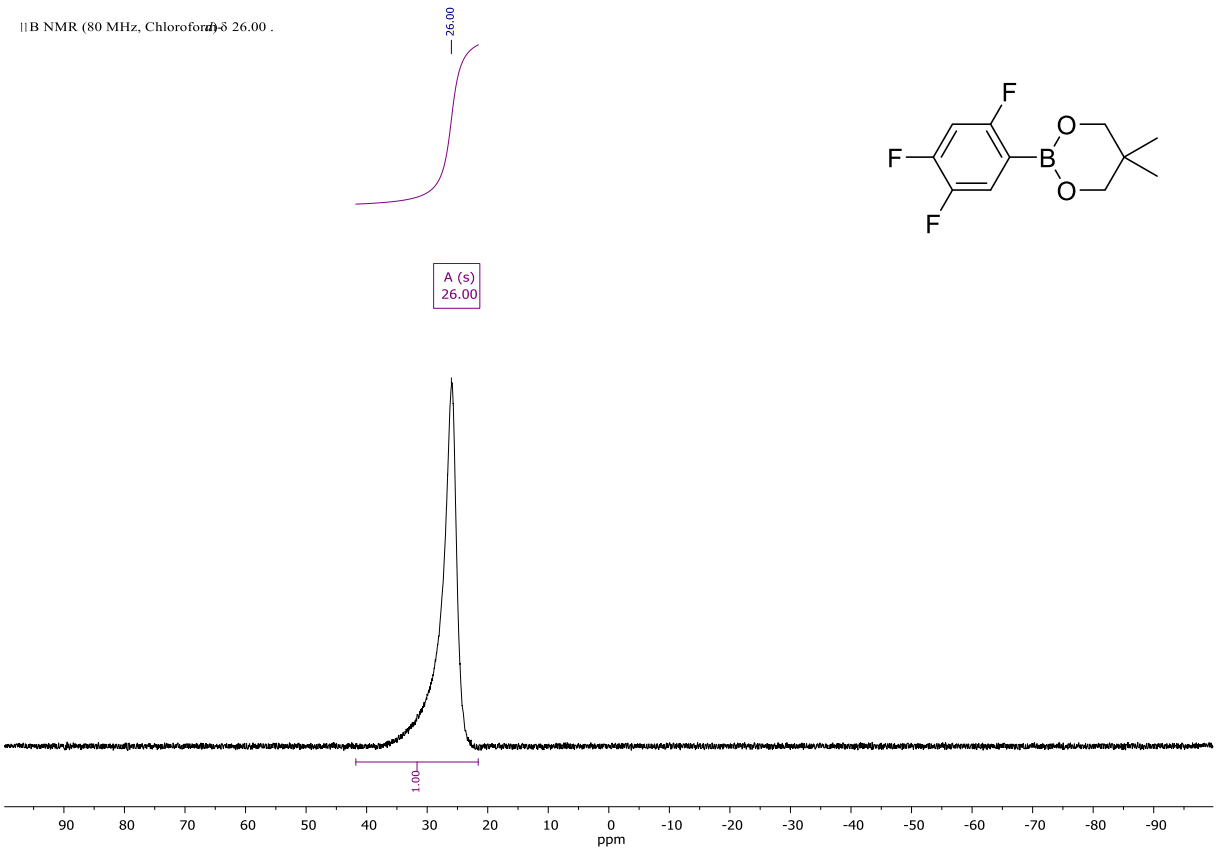


Figure S167 ^{11}B-NMR: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

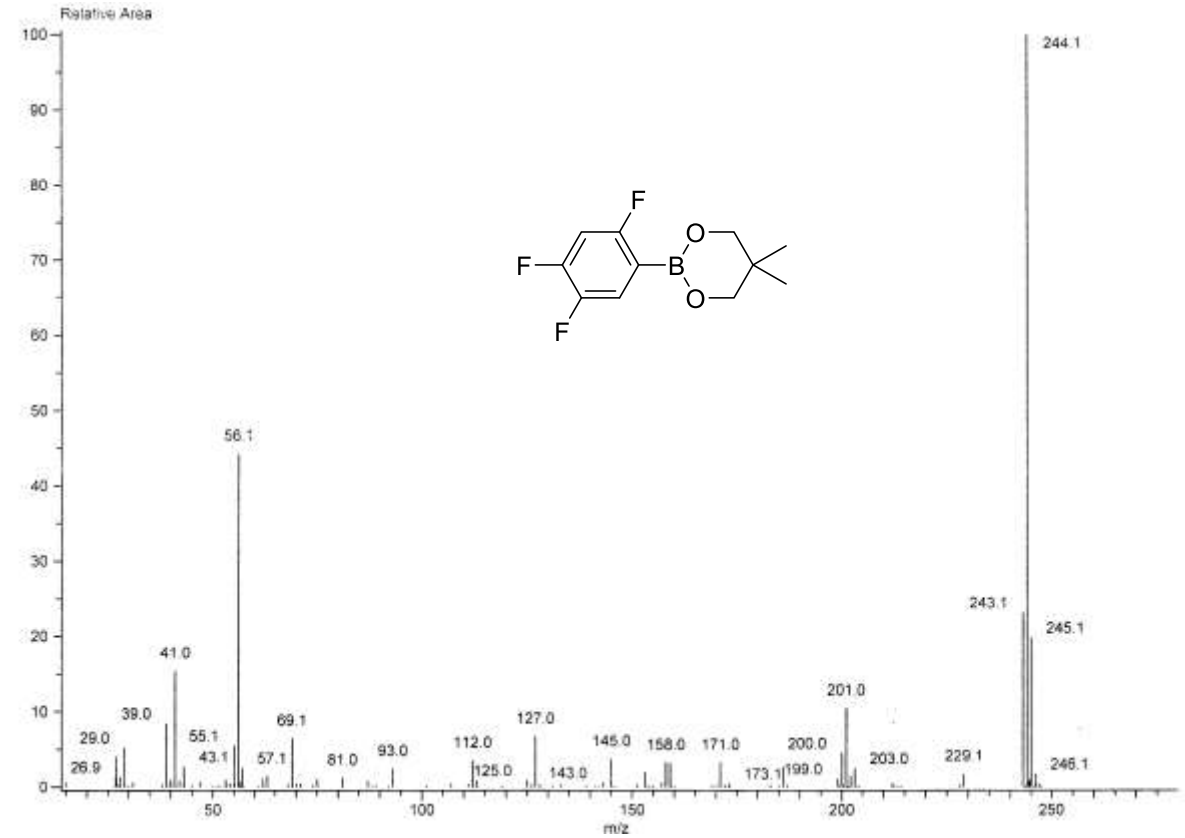


Figure S168 EI-Spectrum (EI$^+$): 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

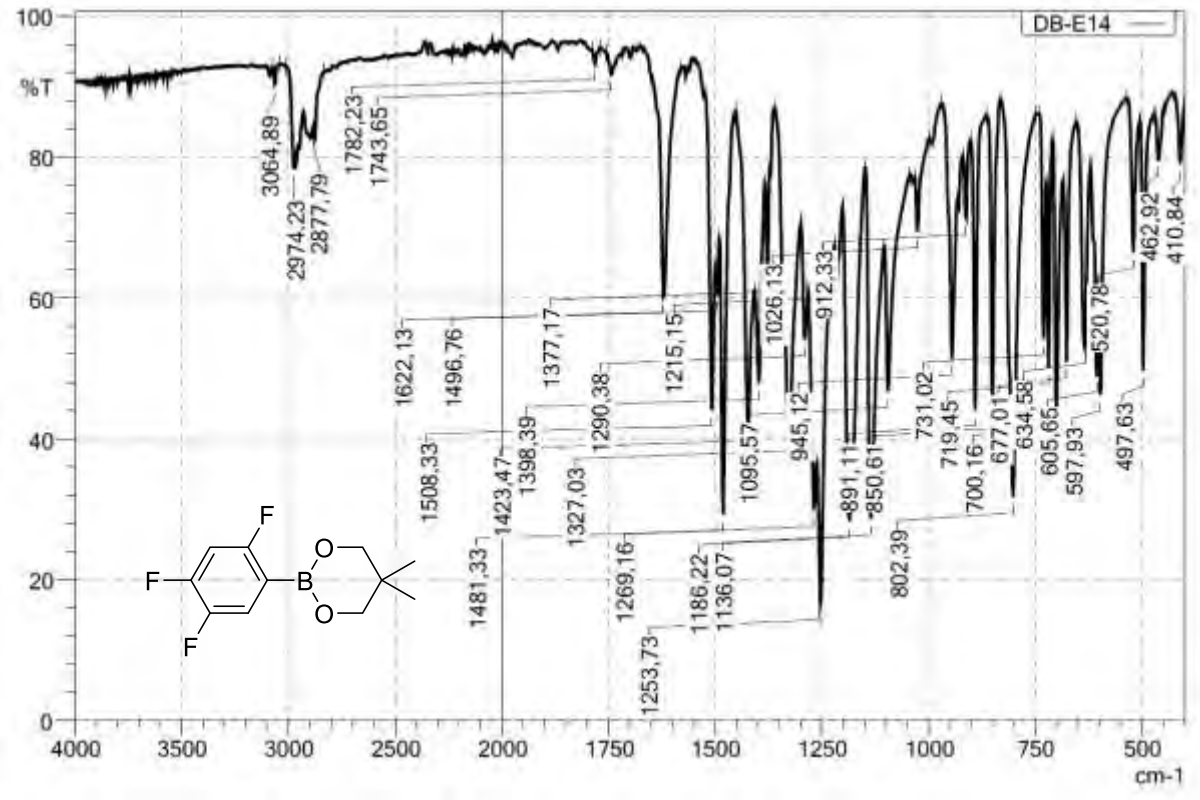


Figure S169 IR (ATR)-Spectrum: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane (18)

^{1}H NMR (250 MHz, Chloroform-d) δ 7.04 (tt, J = 9.6, 7.4 Hz, 1H), 3.82 (s, 4H), 1.07 (s, 6H).

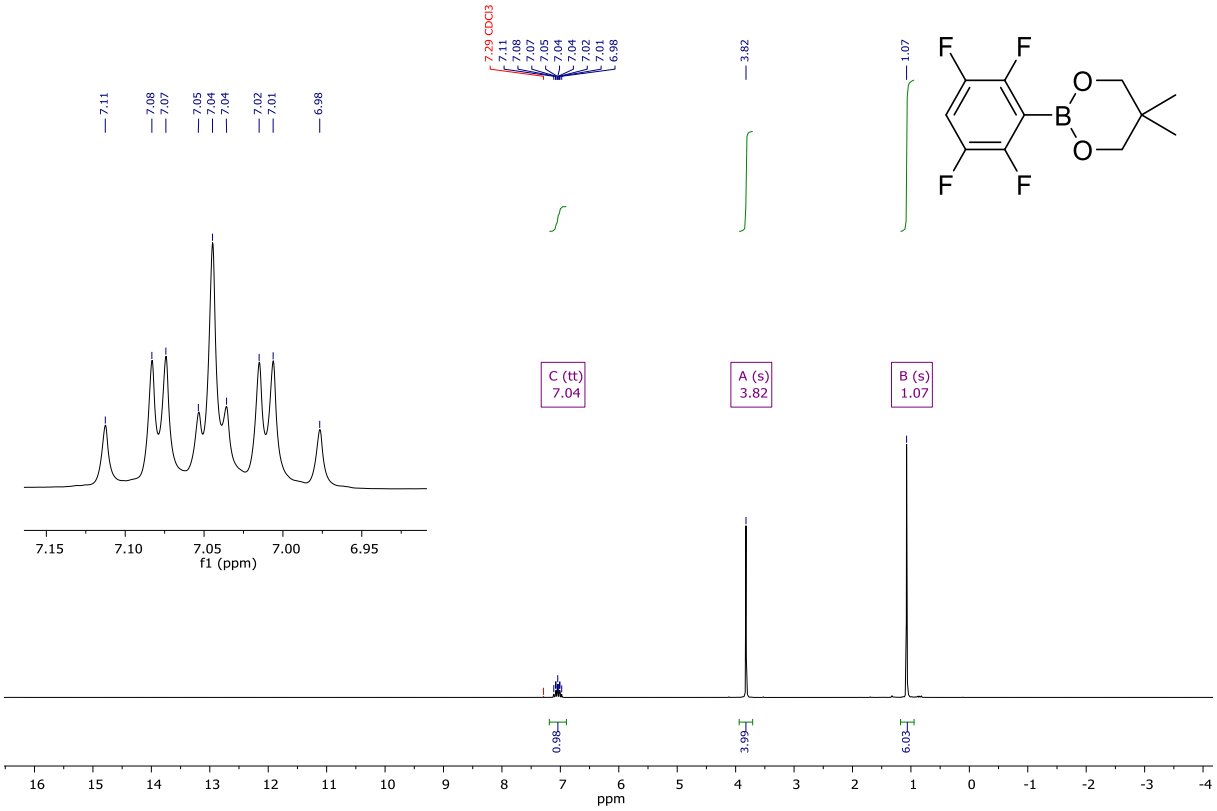


Figure S170 ^{1}H-NMR: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

^{19}F NMR (235 MHz, Chloroform-d) δ -133.33 (dd, J = 22.5, 14.7 Hz), -139.91 (dd, J = 22.4, 14.7 Hz).

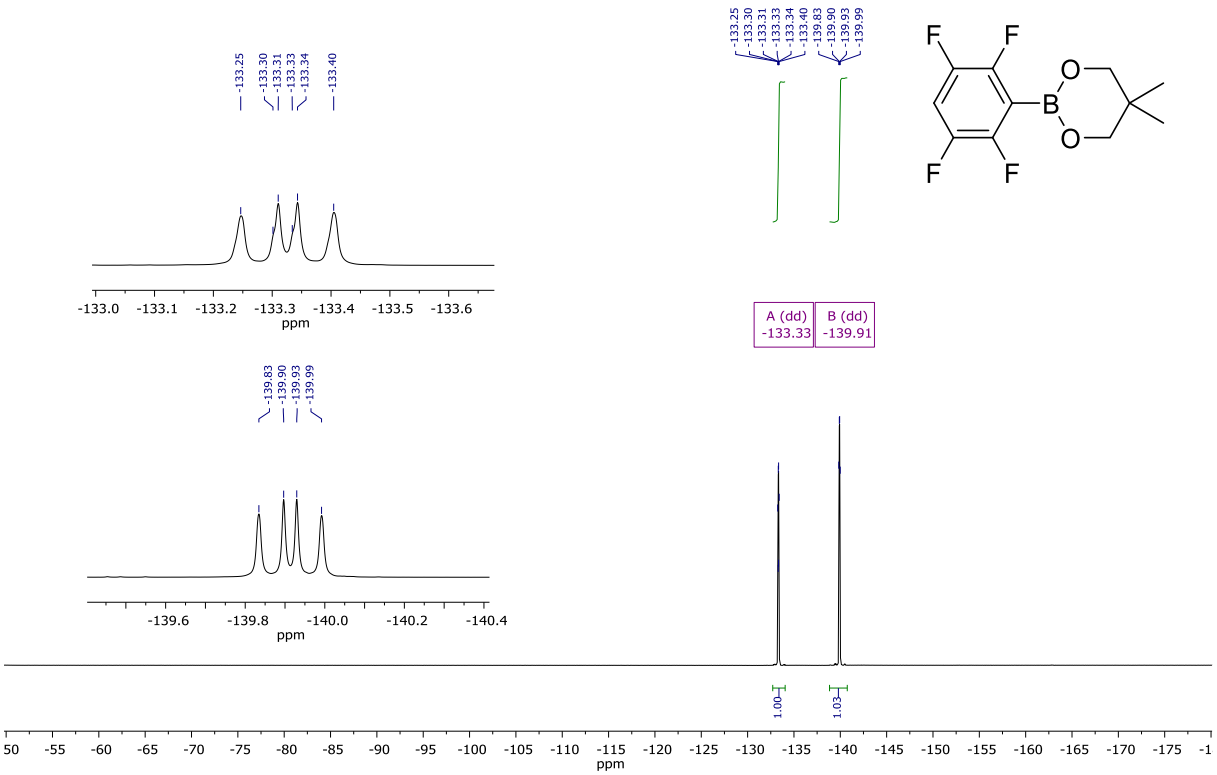


Figure S171 ^{19}F-NMR {^{1}H}: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

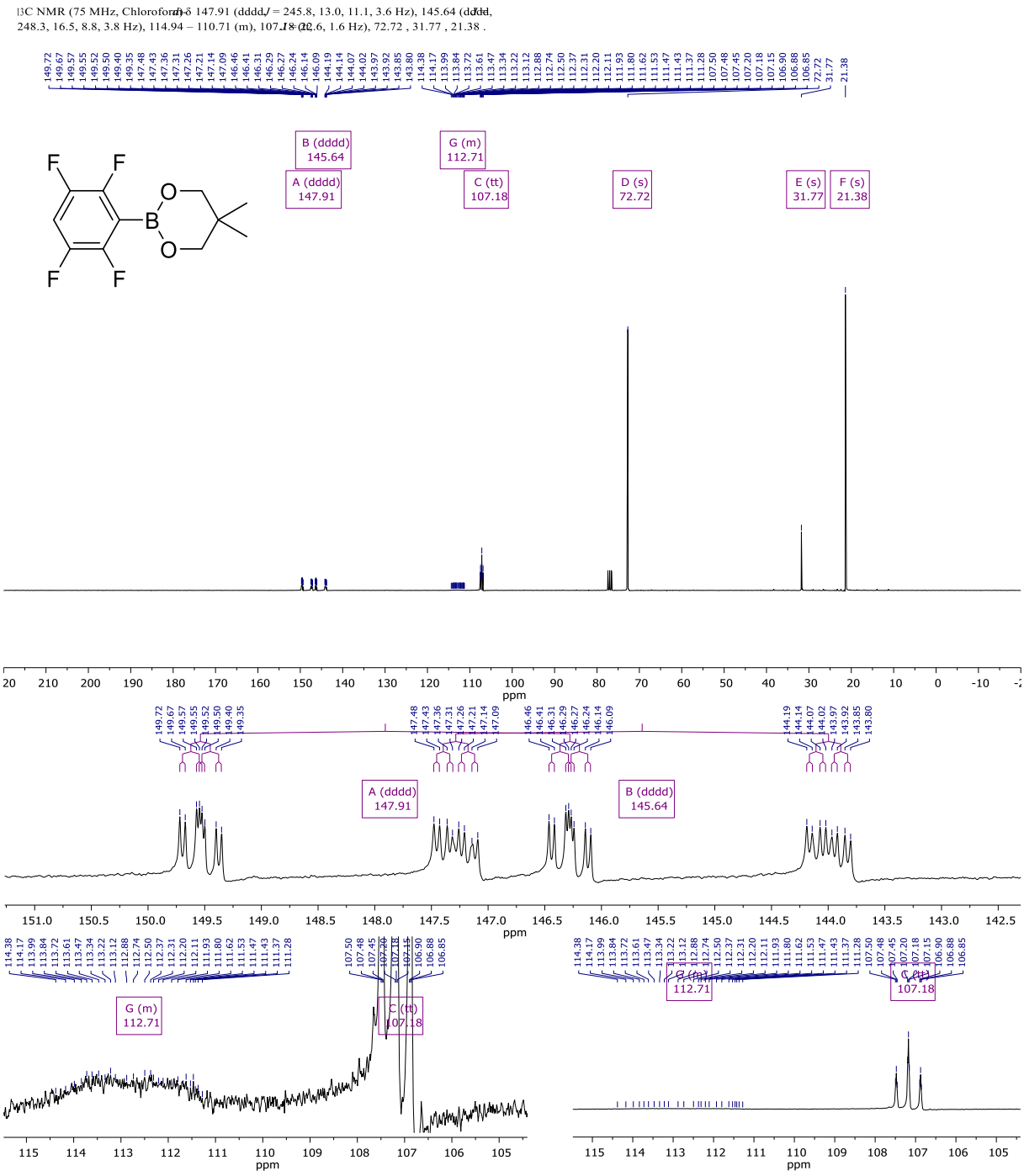


Figure S172 ^{13}C NMR: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

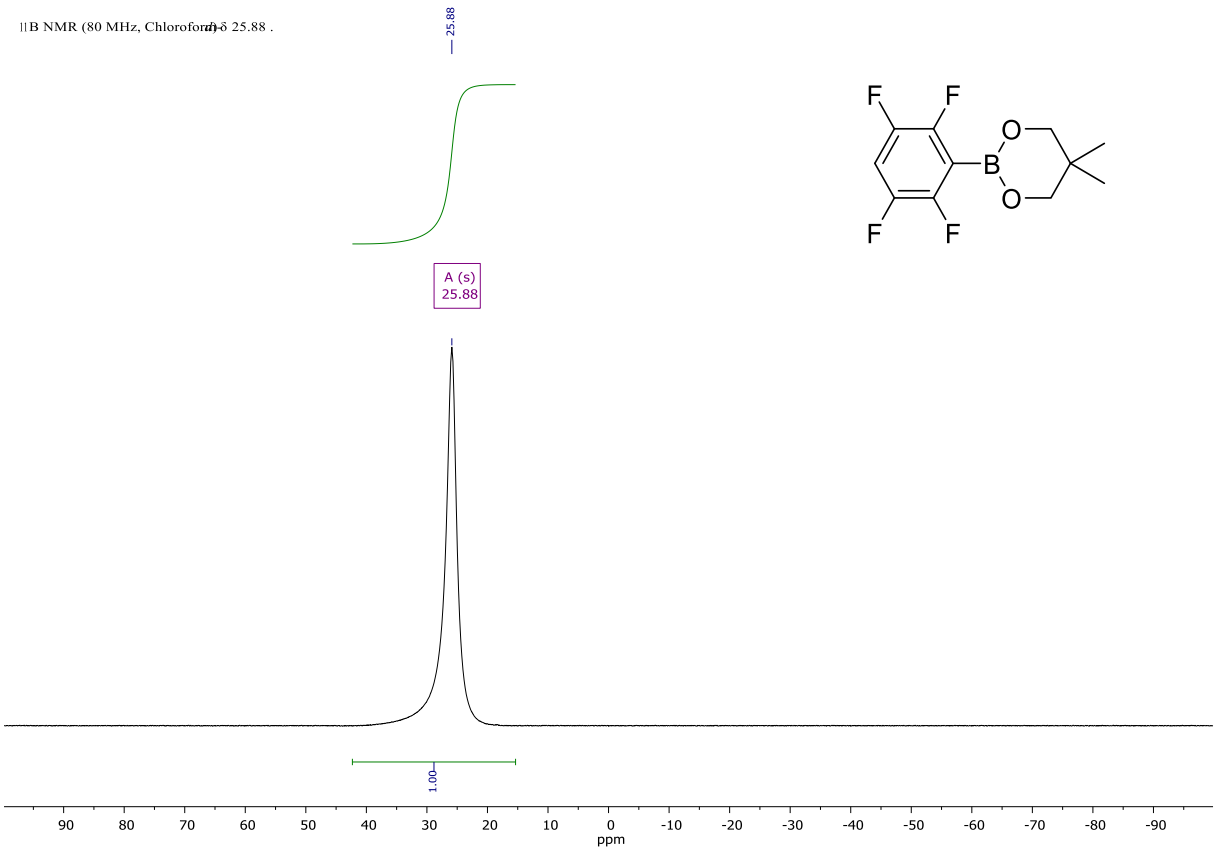


Figure S173 ^{11}B-NMR: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

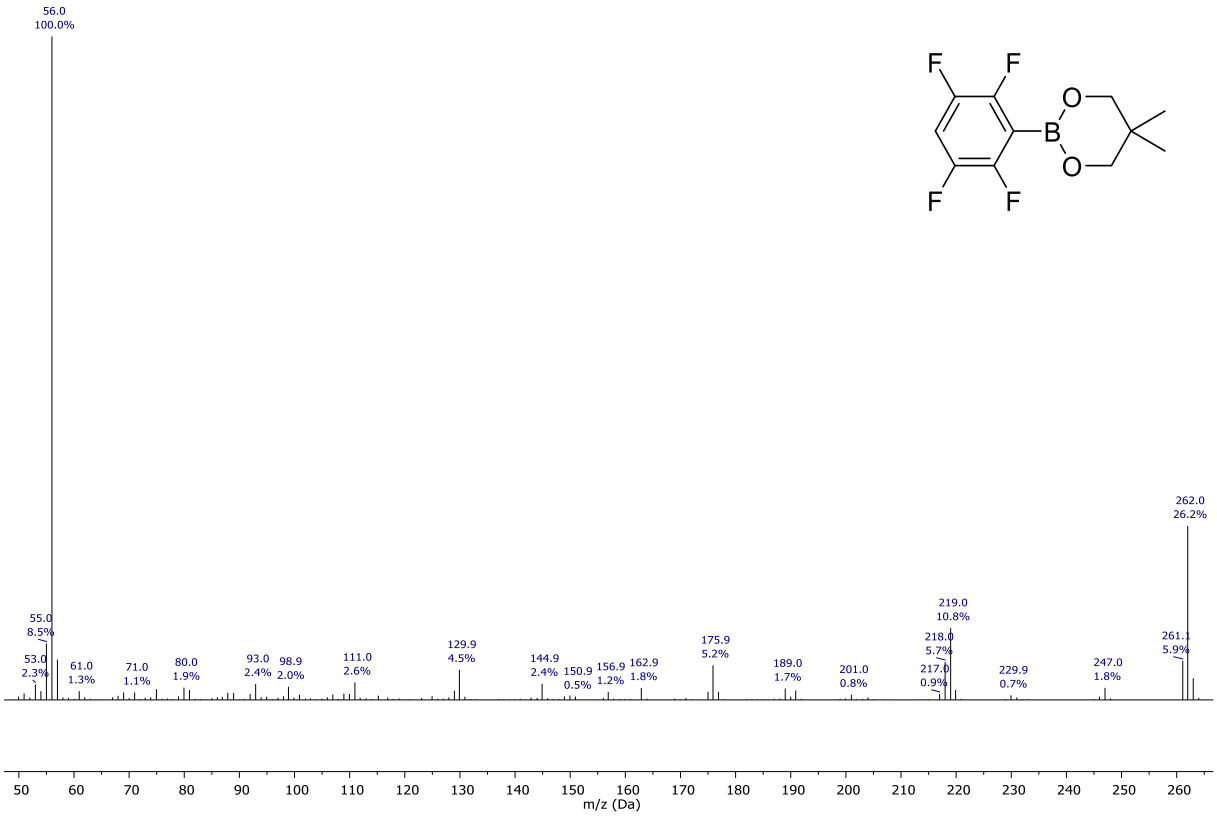


Figure S174 EI-Spectrum (EI$^+$): 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

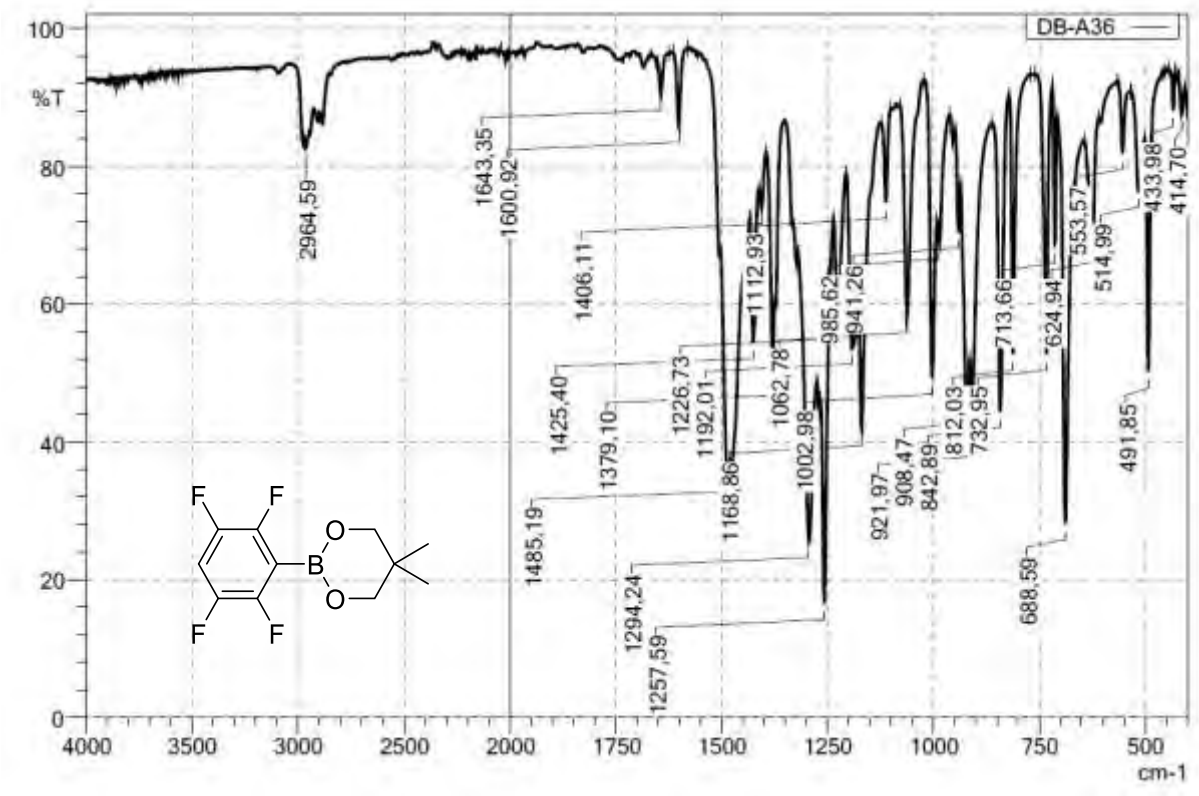


Figure S175 IR (ATR)-Spectrum: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione (16)

^{1}H NMR (250 MHz, DMSO-d_6) δ 7.39 – 7.20 (m, 1H), 4.43 (dd, J = 17.3, 0.9 Hz, 1H), 4.12 (d, J = 17.3 Hz, 1H), 2.65 (s, 1H).

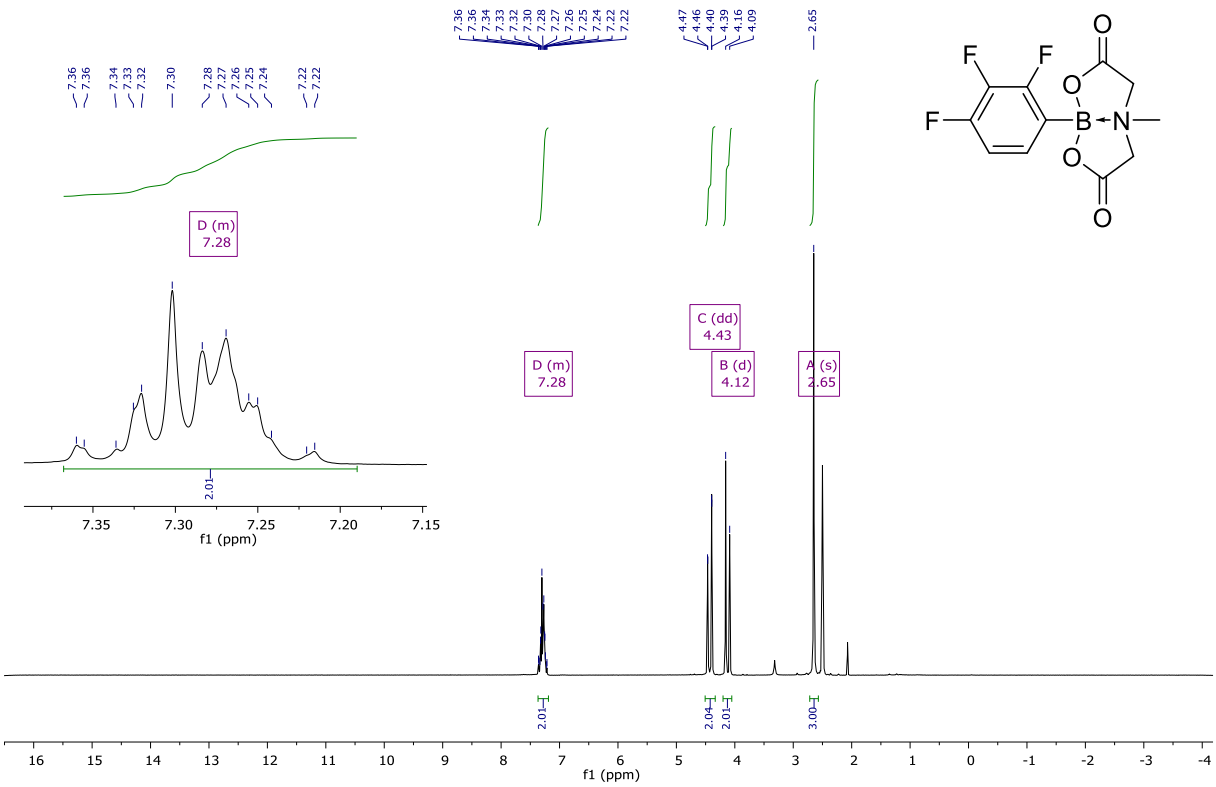


Figure S176 ^{1}H-NMR: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

^{19}F NMR (235 MHz, DMSO-d_6) δ -128.90 (dd, J = 23.0, 8.2 Hz), -134.33 (dd, J = 21.0, 8.2 Hz), -163.02 (dd, J = 23.0, 20.9 Hz).

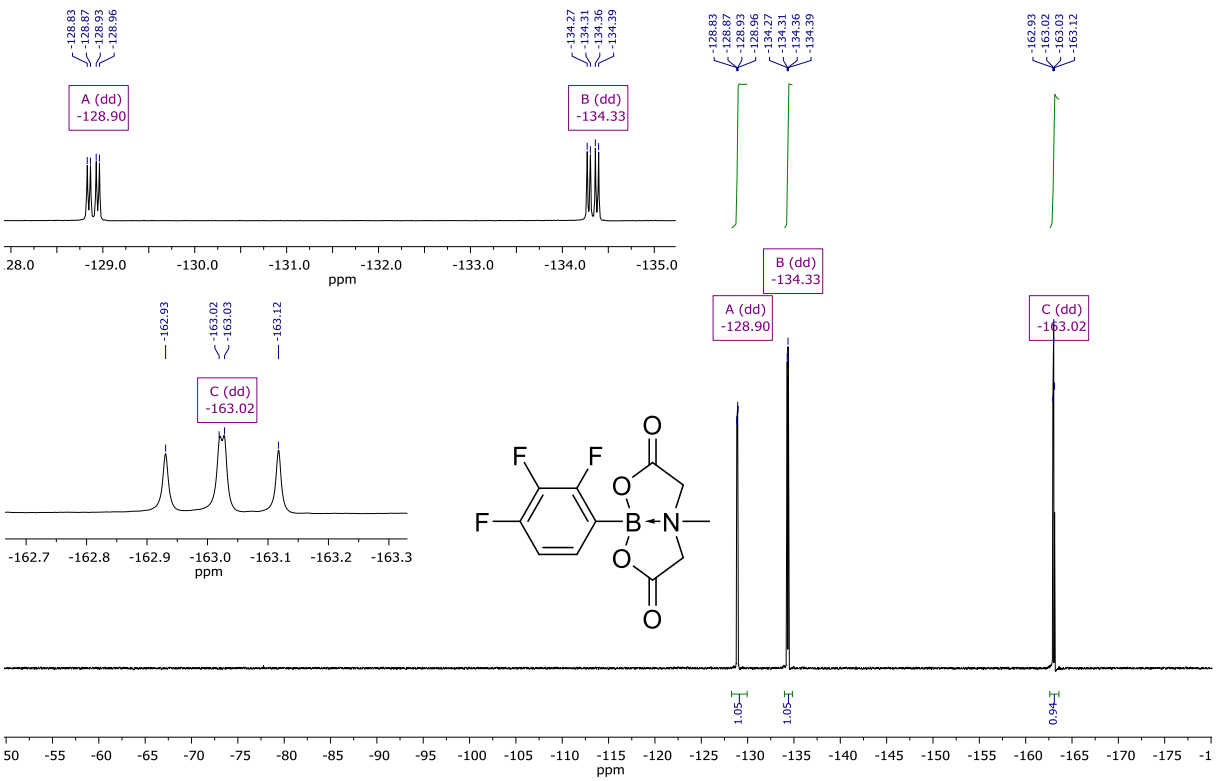


Figure S177 ^{19}F-NMR {^{1}H}: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

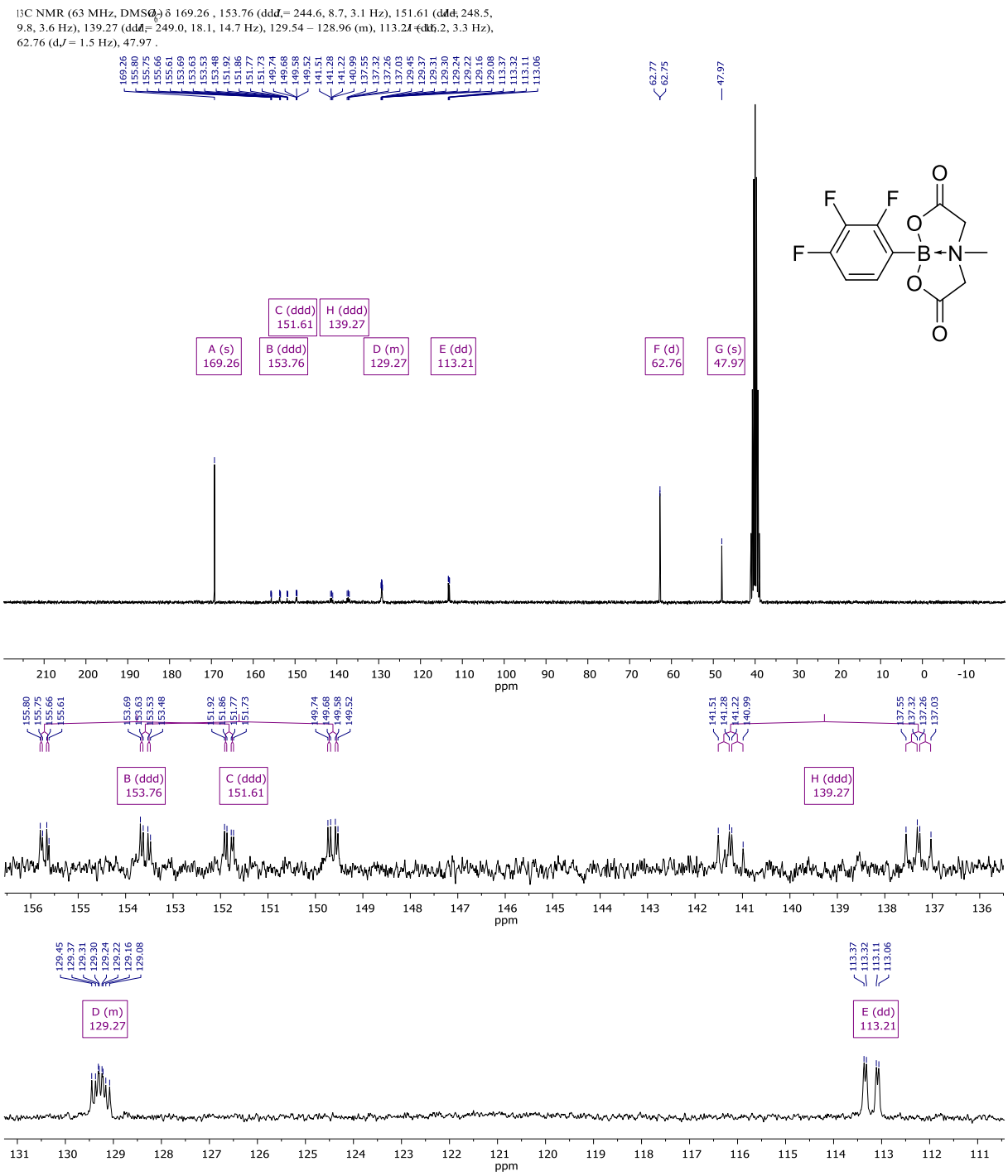


Figure S178 ^{13}C NMR: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

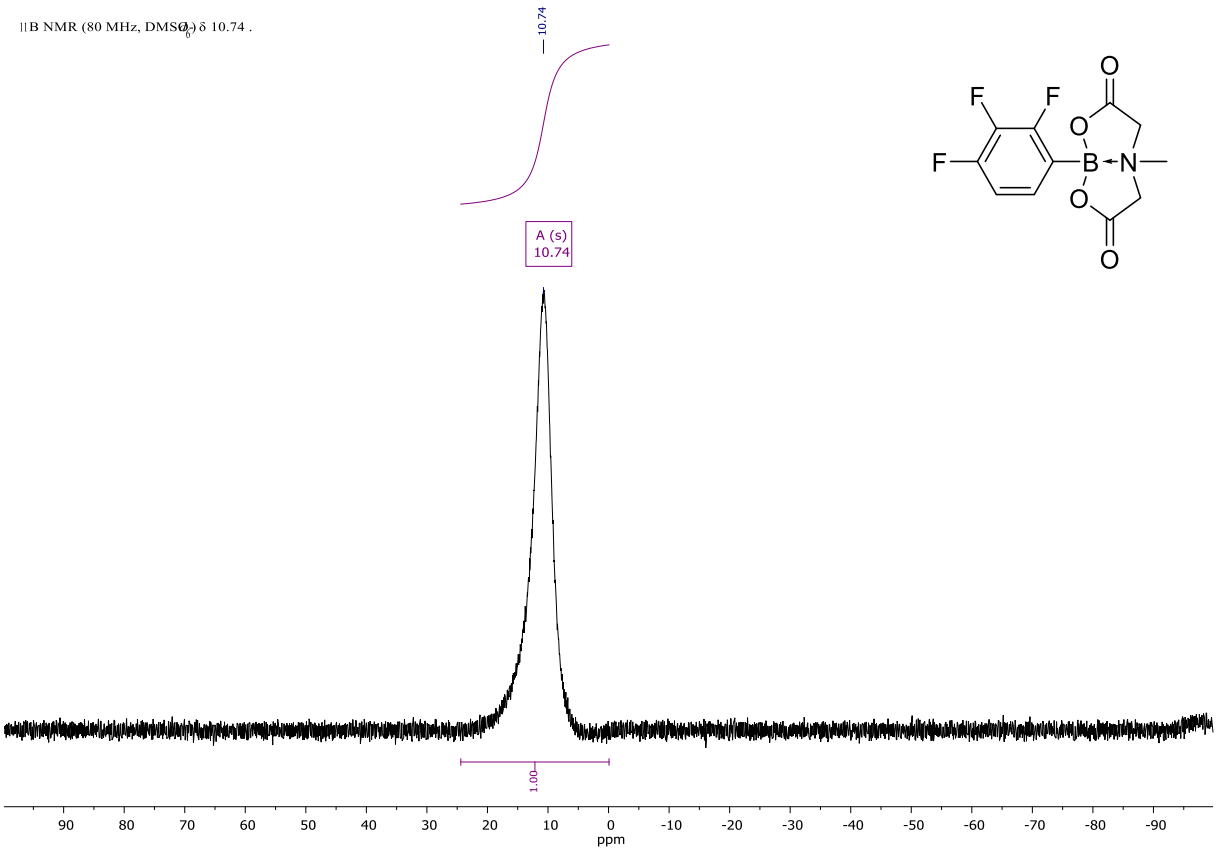


Figure S179 ^{11}B-NMR: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

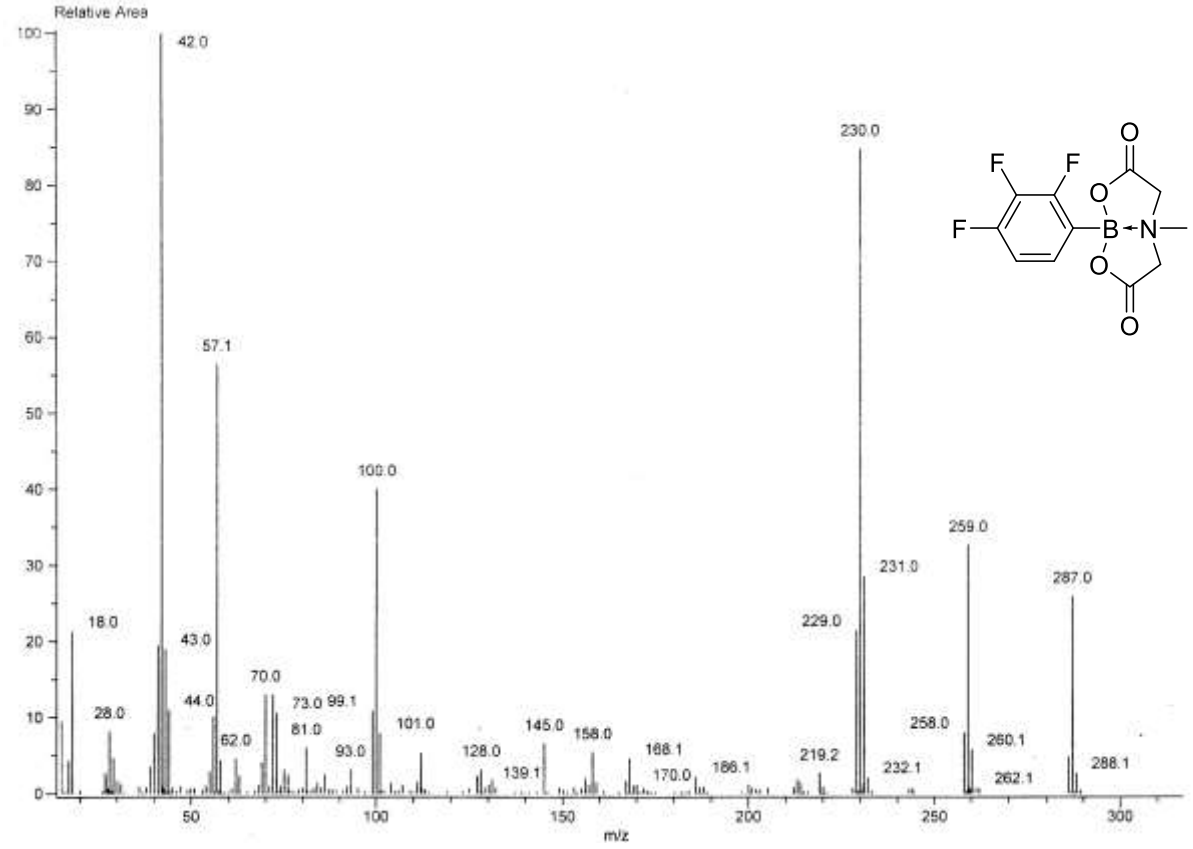


Figure S180 EI-Spectrum (EI$^+$): 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

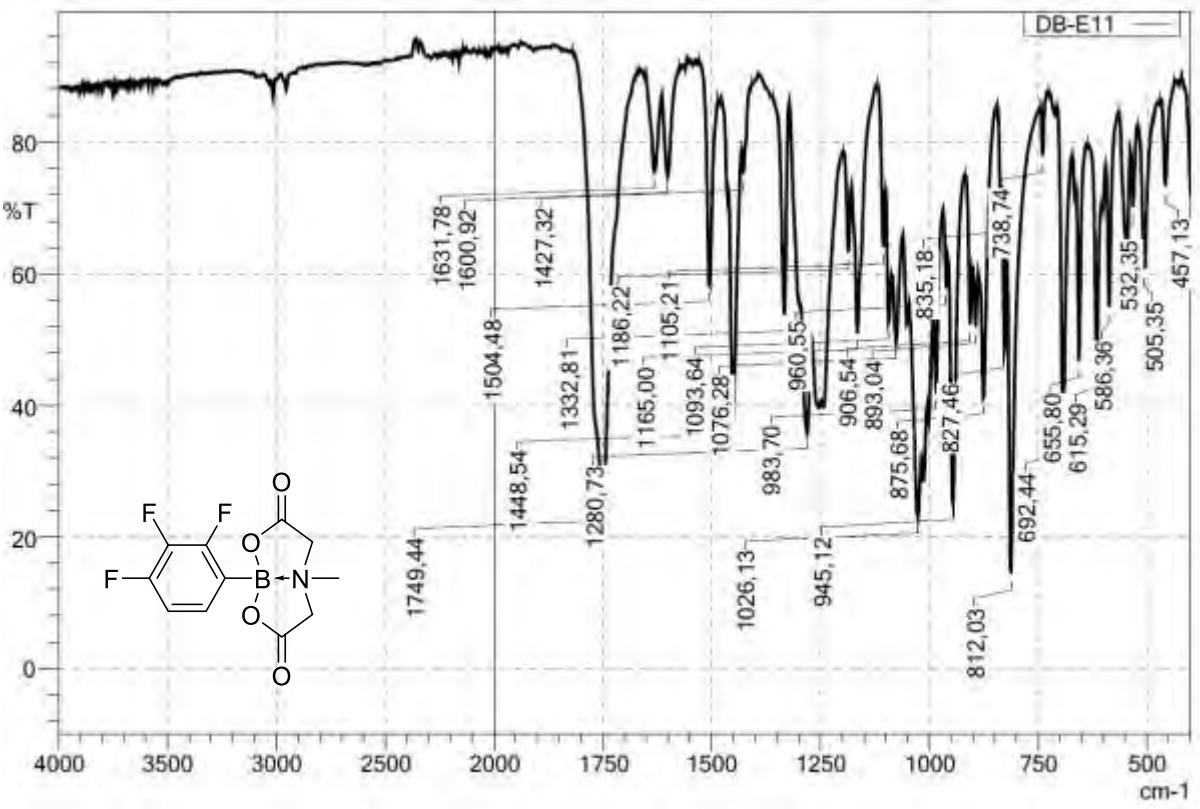


Figure S181 IR (ATR)-Spectrum: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione