

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

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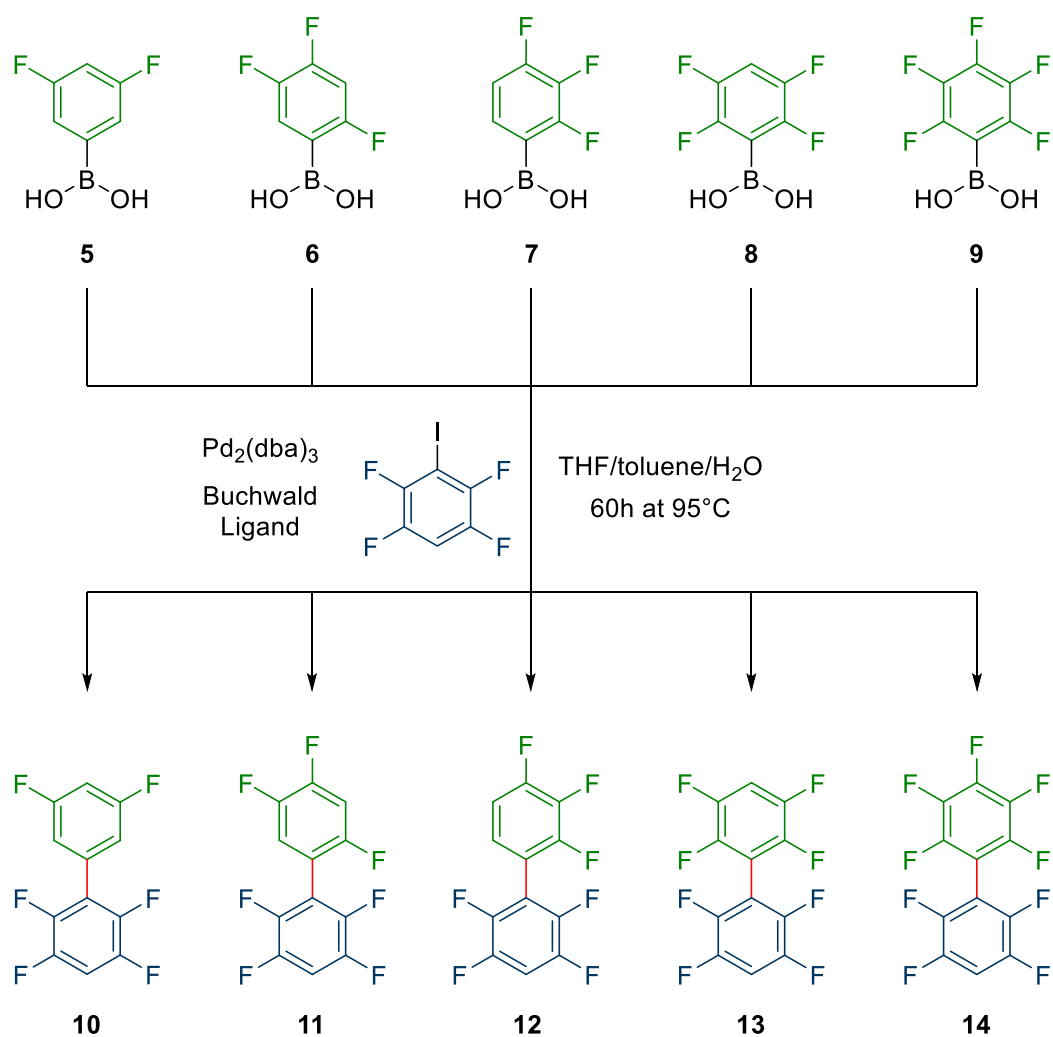
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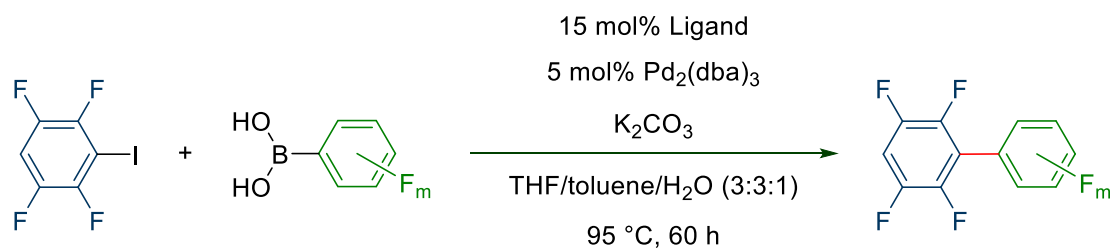
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ADDITIONAL SCREENING DATA

Screening of boronic acid derivatives as nucleophiles



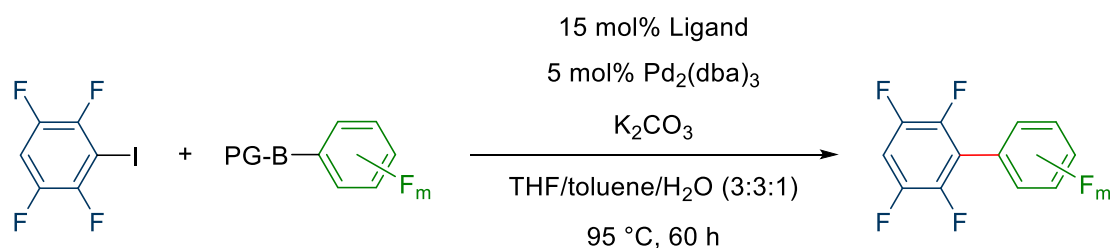
Scheme S1. Different boronic acids (**5-9**) which were tested as nucleophiles in the Suzuki Miyaura coupling and their corresponding products (**10-14**).

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	-

^aReactions were performed with 1 equiv. **1** and the corresponding boronic acid and 2.2 equiv. of Na₂CO₃ with 5 mol% Pd₂(dba)₃ and a 15 mol% of the corresponding ligand at 95°C for 60h on a 0.18 mmol scale. ^bcontains significant amounts of a homocoupling side product (>2%). ^ccomplex 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%

^aReactions were performed with 1 equiv. **1** and the corresponding boronic acid and 2.2 equiv. of Na₂CO₃ with 5 mol% Pd₂(dba)₃ and a 15 mol% of the corresponding ligand at 95°C for 60h on a 0.18 mmol scale. ^bcontains significant amounts of a homocoupling side product (>2%).

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

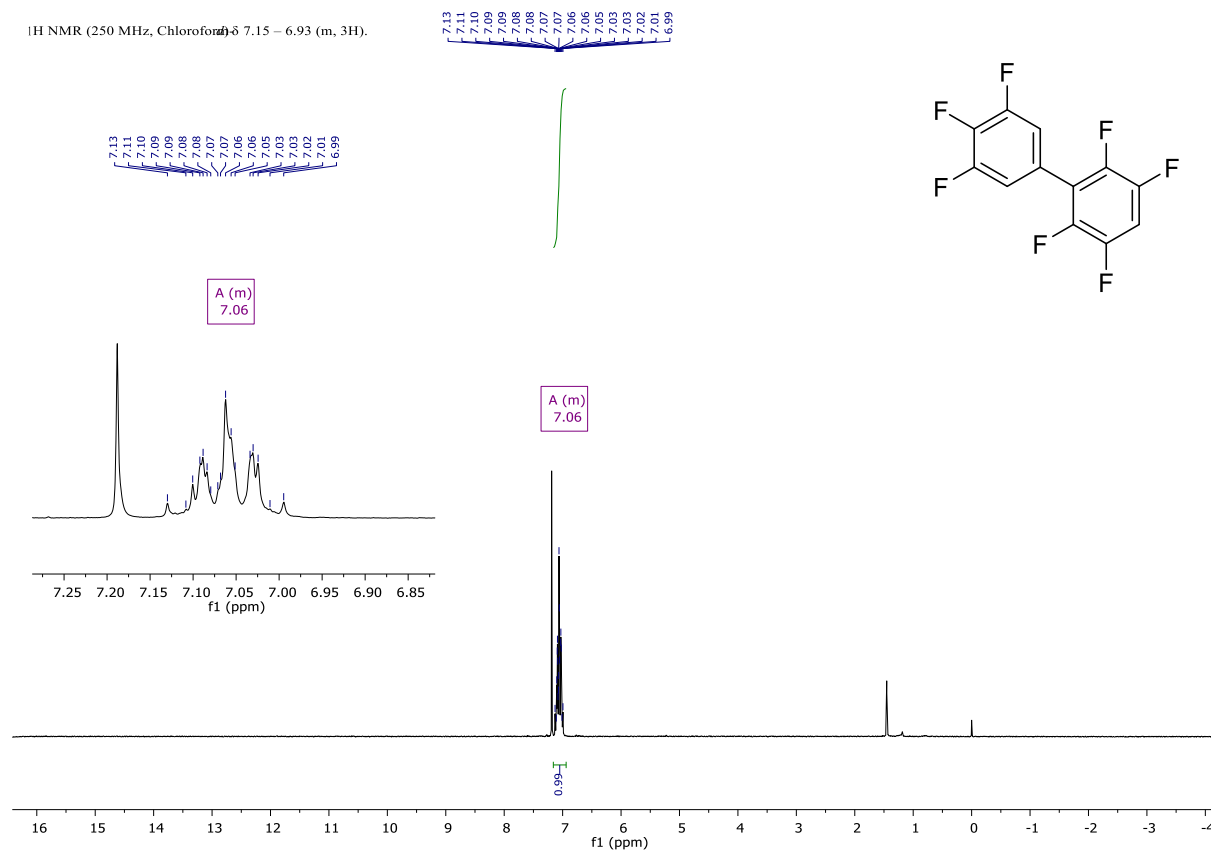
entry	ligand	homocoupling ^a (6 ; B(OH) ₂)	homocoupling ^a (17 ; B-ester)
1	CyJohnPhos	30%	7%
2	DavePhos	22%	19%
3	MePhos	20%	9%
4	SPhos	8%	5%

^aHomocoupling 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 ¹H-NMR: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform- d_3) 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).

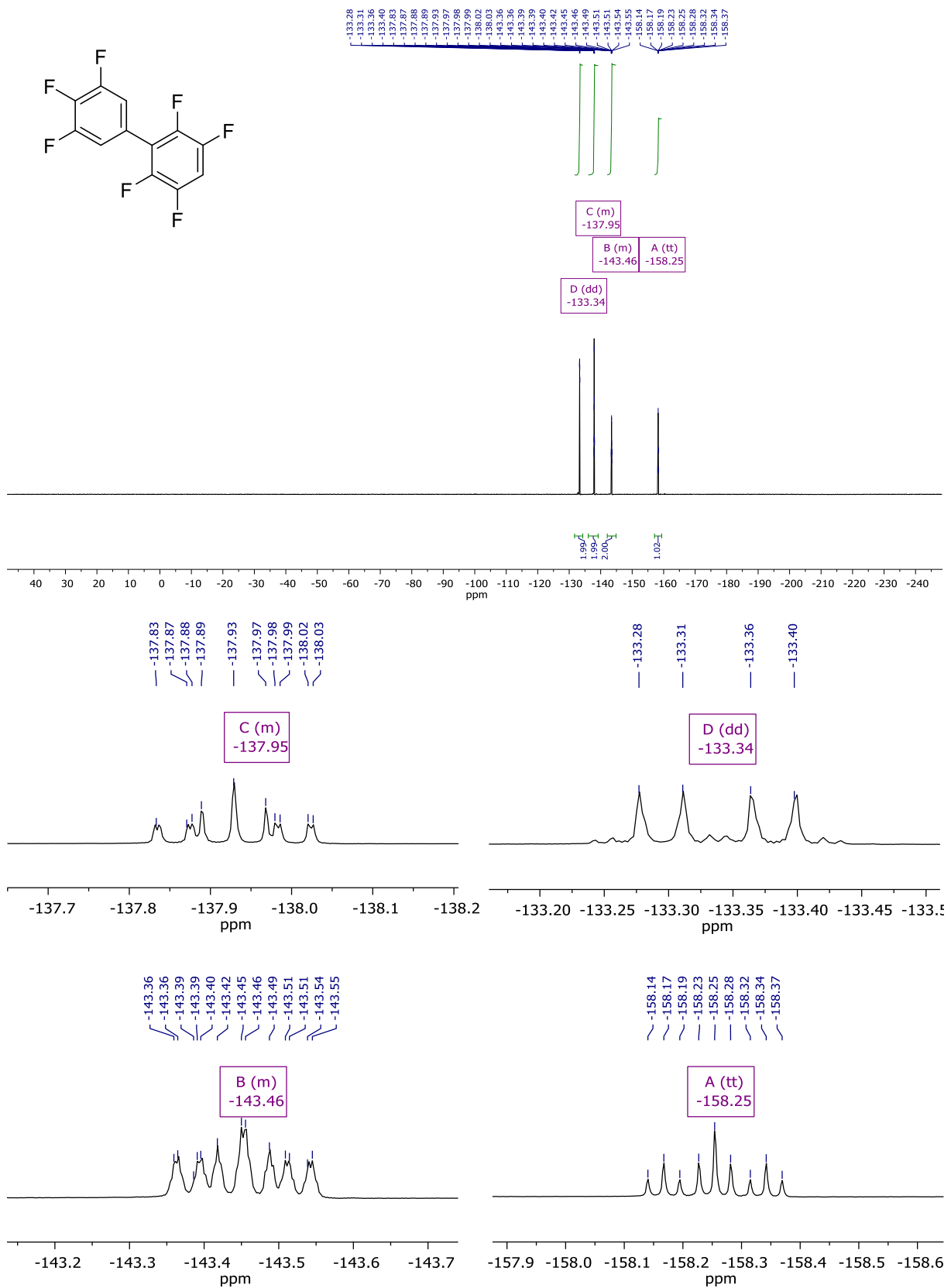


Figure S2 ^{19}F -NMR: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

^{19}F NMR (235 MHz, Chloroform- d_3) 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).

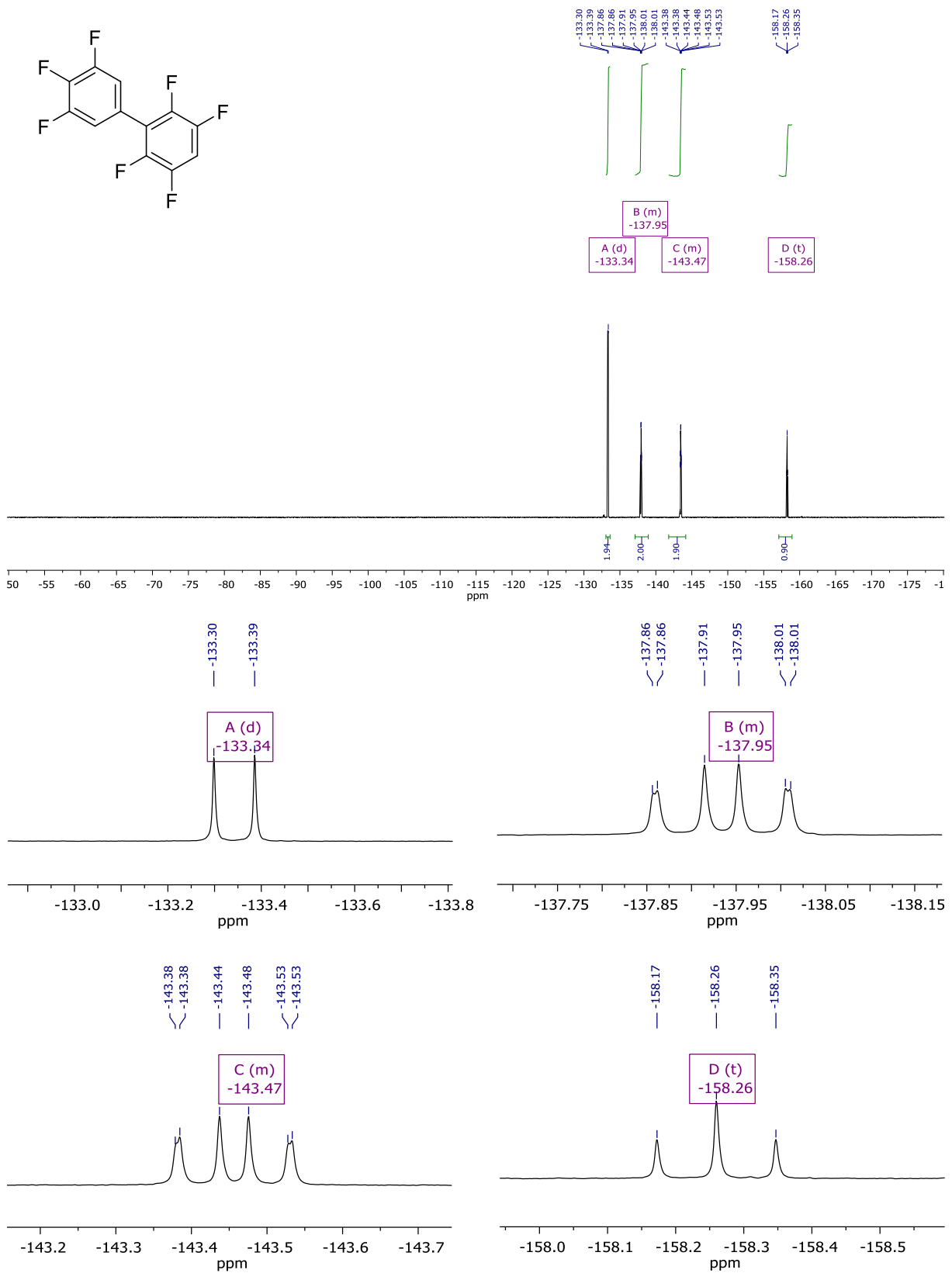
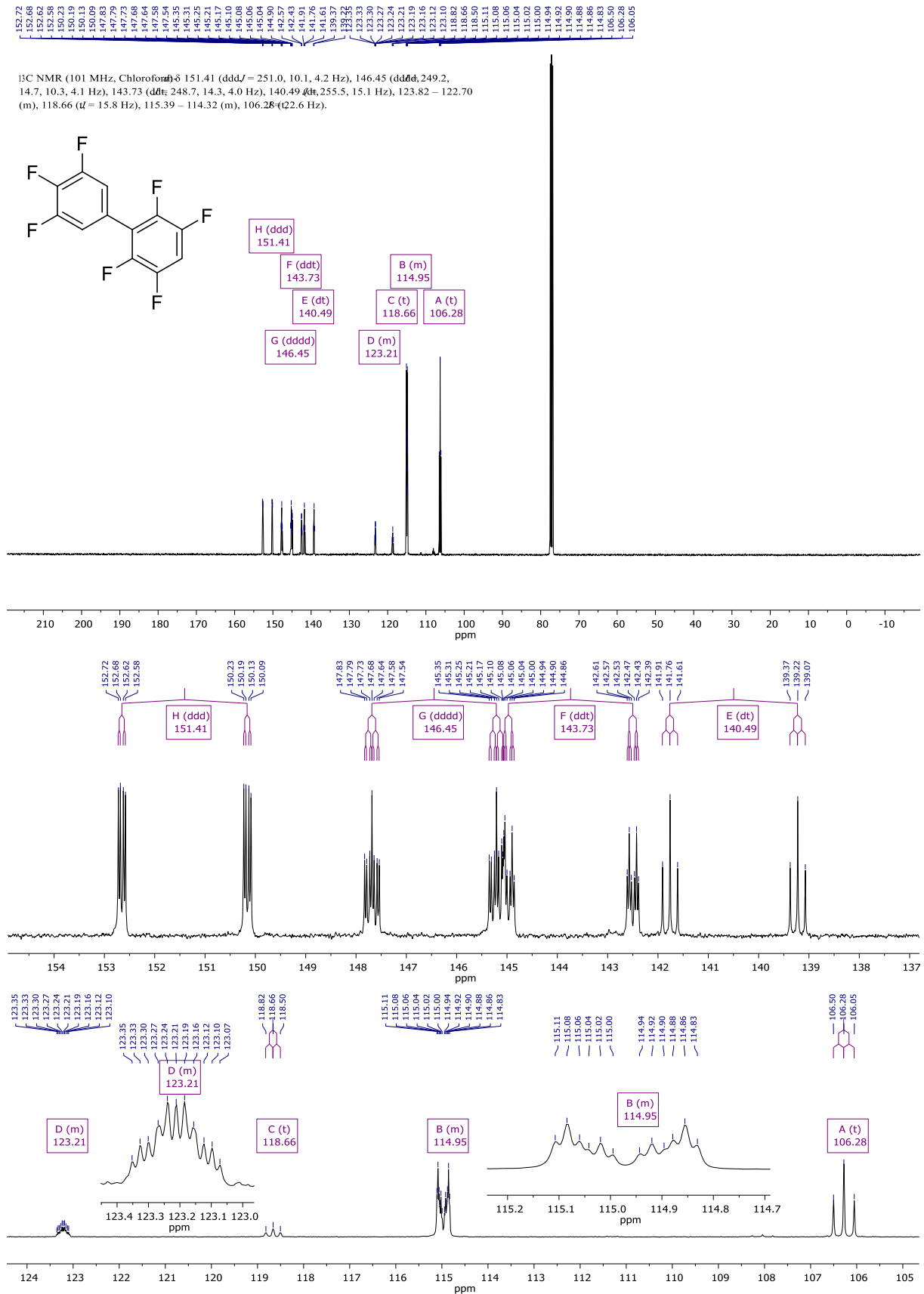


Figure S3 ^{19}F -NMR [^1H]: 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

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

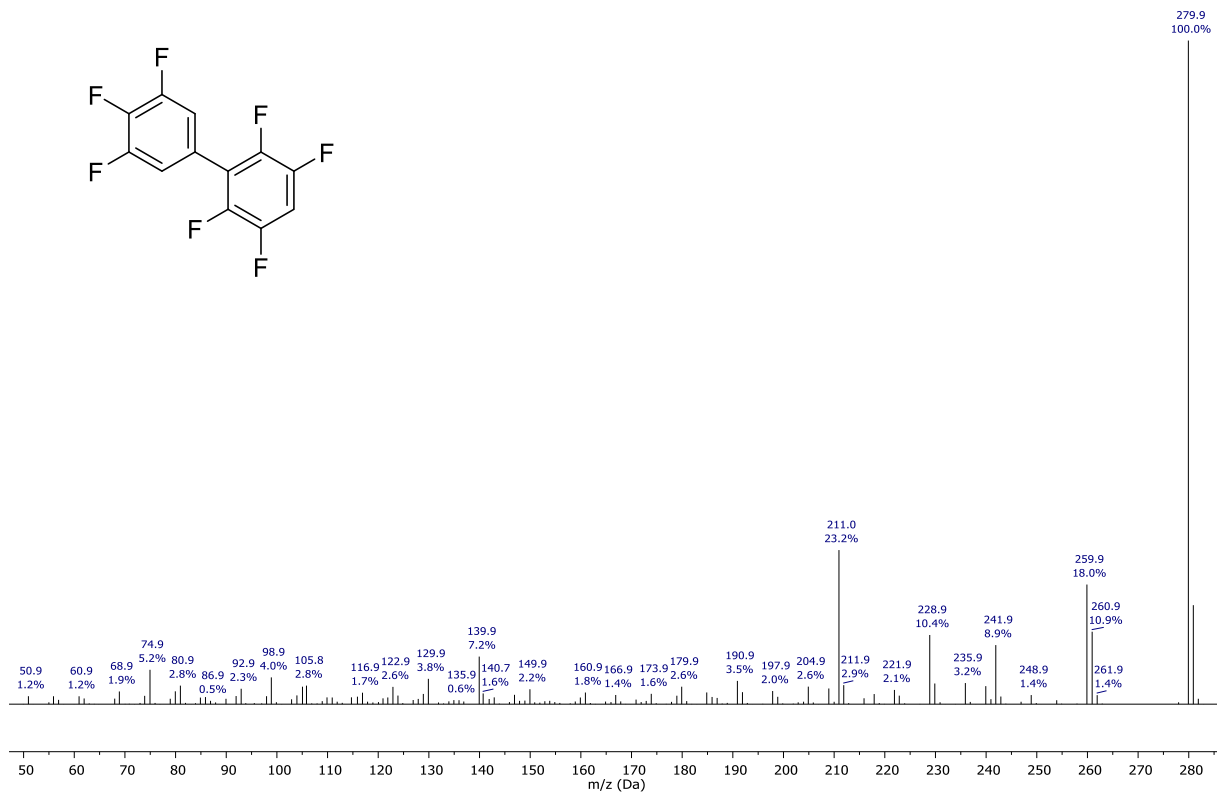
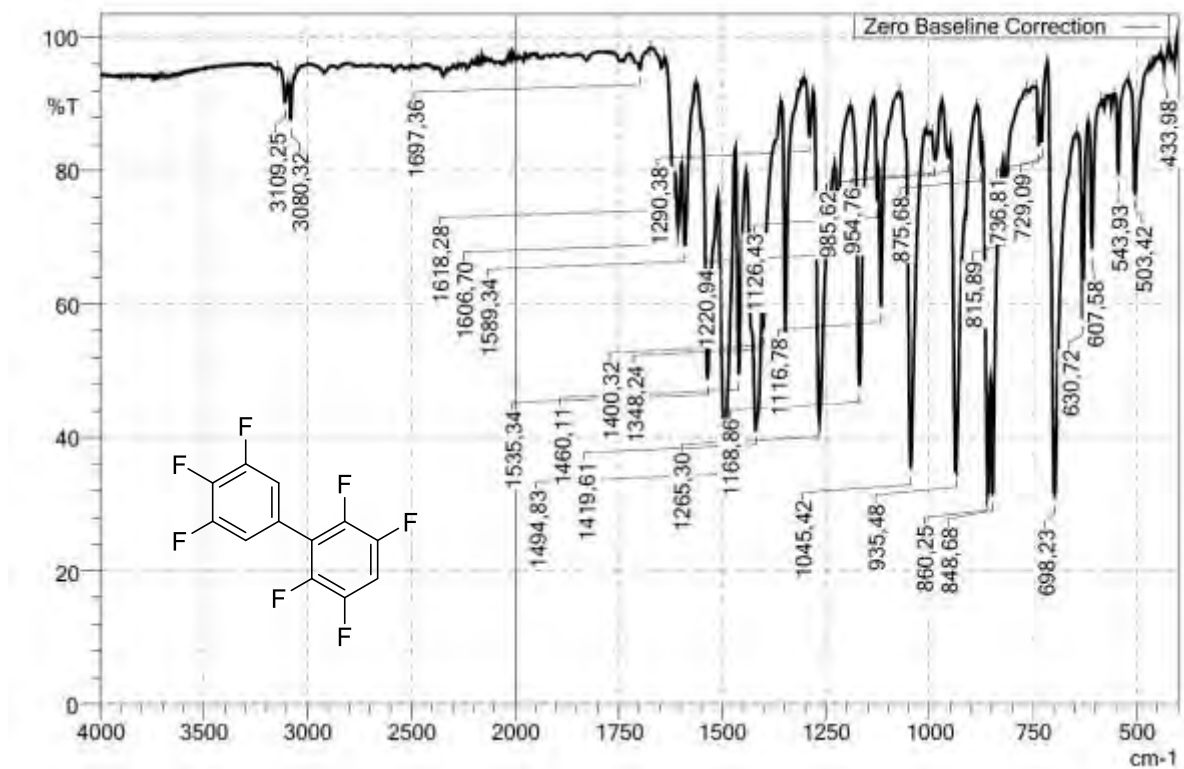
Figure S5 EI-Spectrum (EI⁺): 2,3,3',4',5,5',6-Heptafluoro-1,1'-biphenyl

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)

$^1\text{H NMR}$ (250 MHz, Chloroform- d_3) 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).

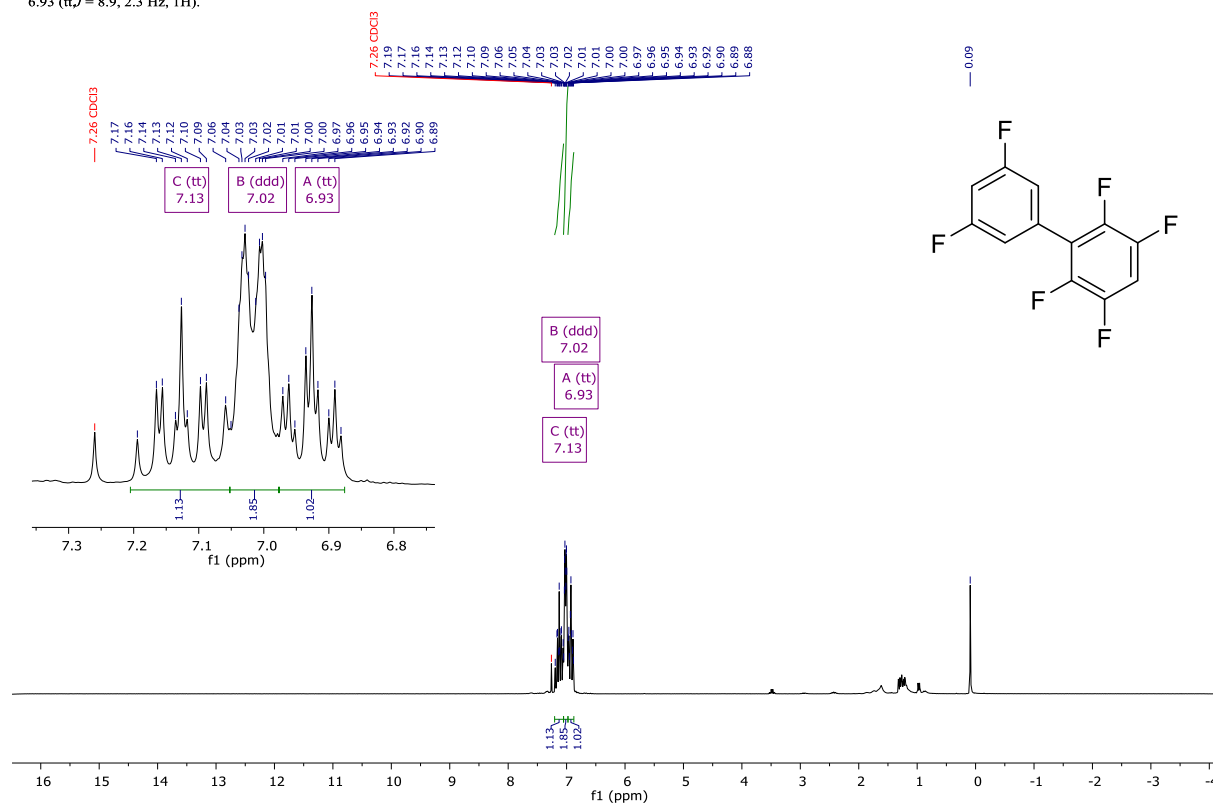


Figure S7 $^1\text{H NMR}$: 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

$^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) δ -108.98, -138.28 (dd, $J = 21.8, 12.8$ Hz), -143.32 (dd, $J = 21.9, 12.9$ Hz).

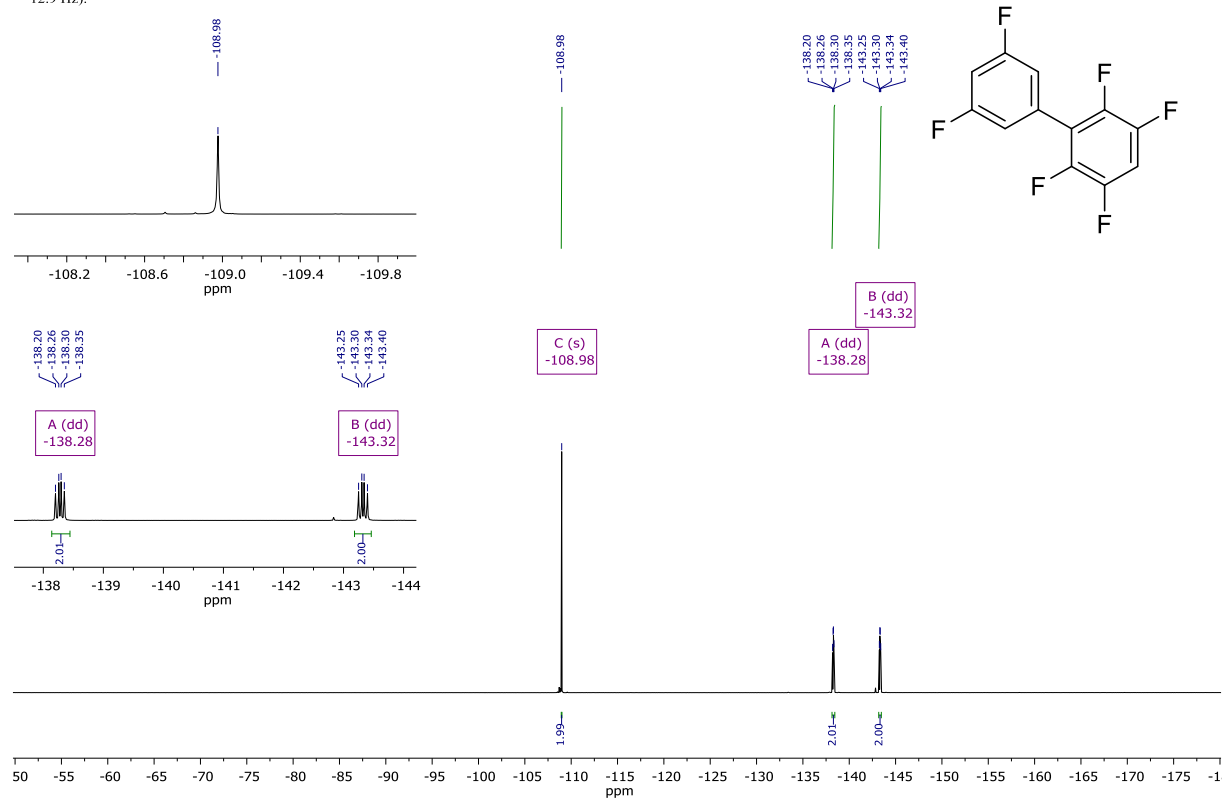


Figure S8 $^{19}\text{F NMR}$ (^1H): 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

^{13}C NMR (101 MHz, Chloroform- d_3) δ 163.04 (dd), 146.42 (ddd), 143.75 (dd), 142.63 (dd), 142.59 (dd), 142.48 (dd), 142.40 (dd), 142.39 (dd), 130.36 (dd), 130.34 (dd), 130.28 (dd), 130.26 (dd), 130.23 (dd), 130.15 (dd), 130.13 (dd), 119.57 (dd), 119.54 (dd), 119.52 (dd), 119.41 (dd), 119.39 (dd), 119.38 (dd), 119.25 (dd), 119.22 (dd), 119.20 (dd), 113.70 (dd), 113.68 (dd), 113.63 (dd), 113.58 (dd), 113.51 (dd), 113.49 (dd), 113.47 (dd), 113.44 (dd), 113.39 (dd), 113.38 (dd), 113.37 (dd), 113.36 (dd), 113.35 (dd), 113.34 (dd), 113.33 (dd), 113.32 (dd), 113.31 (dd), 113.30 (dd), 113.29 (dd), 113.28 (dd), 113.27 (dd), 113.26 (dd), 113.25 (dd), 113.24 (dd), 113.23 (dd), 113.22 (dd), 113.21 (dd), 113.20 (dd), 113.19 (dd), 113.18 (dd), 113.17 (dd), 113.16 (dd), 113.15 (dd), 113.14 (dd), 113.13 (dd), 113.12 (dd), 113.11 (dd), 113.10 (dd), 113.09 (dd), 113.08 (dd), 113.07 (dd), 113.06 (dd), 113.05 (dd), 113.04 (dd), 113.03 (dd), 113.02 (dd), 113.01 (dd), 113.00 (dd), 106.11 (dd), 105.89 (dd), 105.24 (dd), 104.99 (dd), 104.74 (dd).

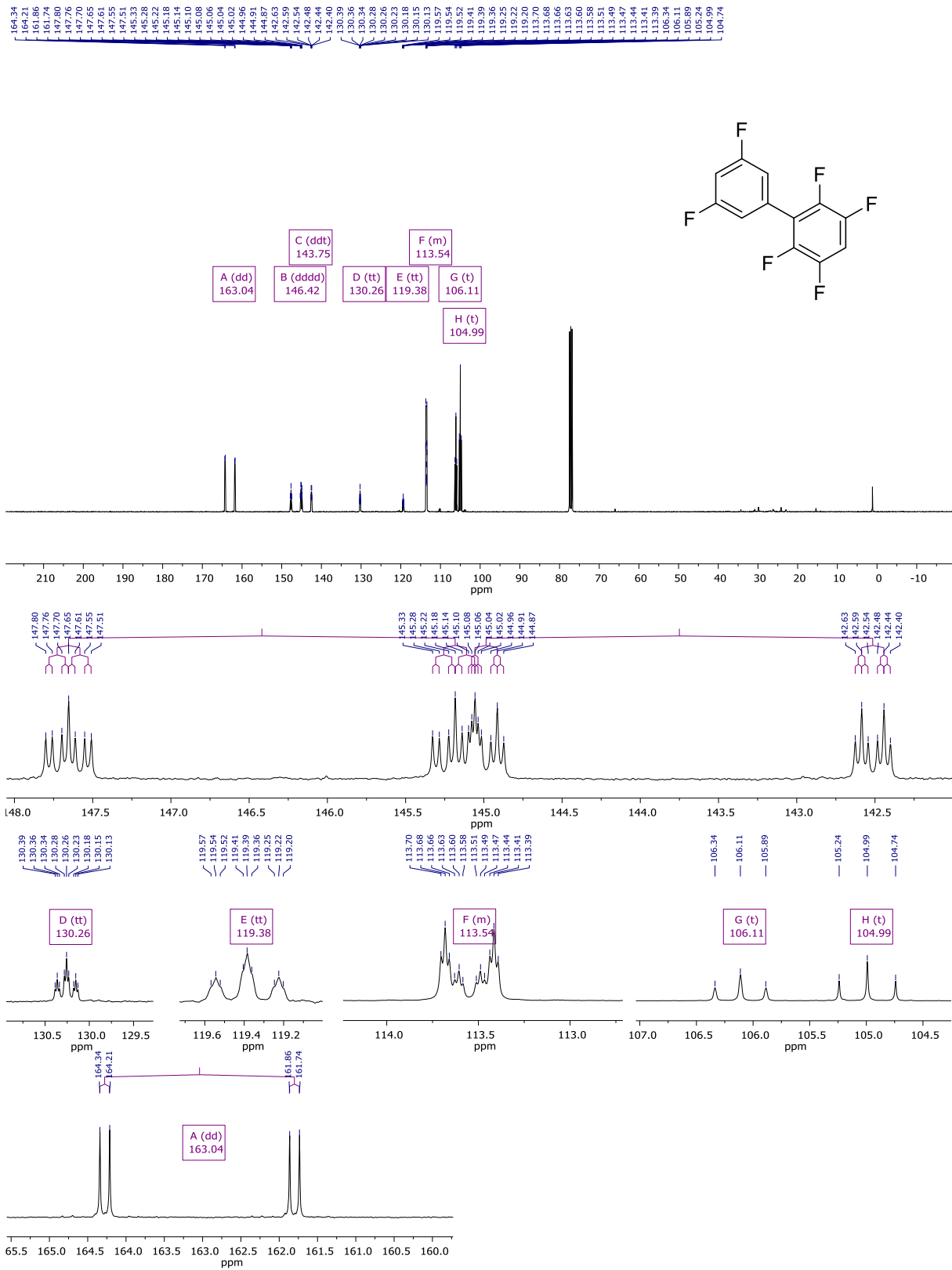


Figure S9 ^{13}C NMR: 2,3,3',5',6-hexafluoro-1,1'-biphenyl

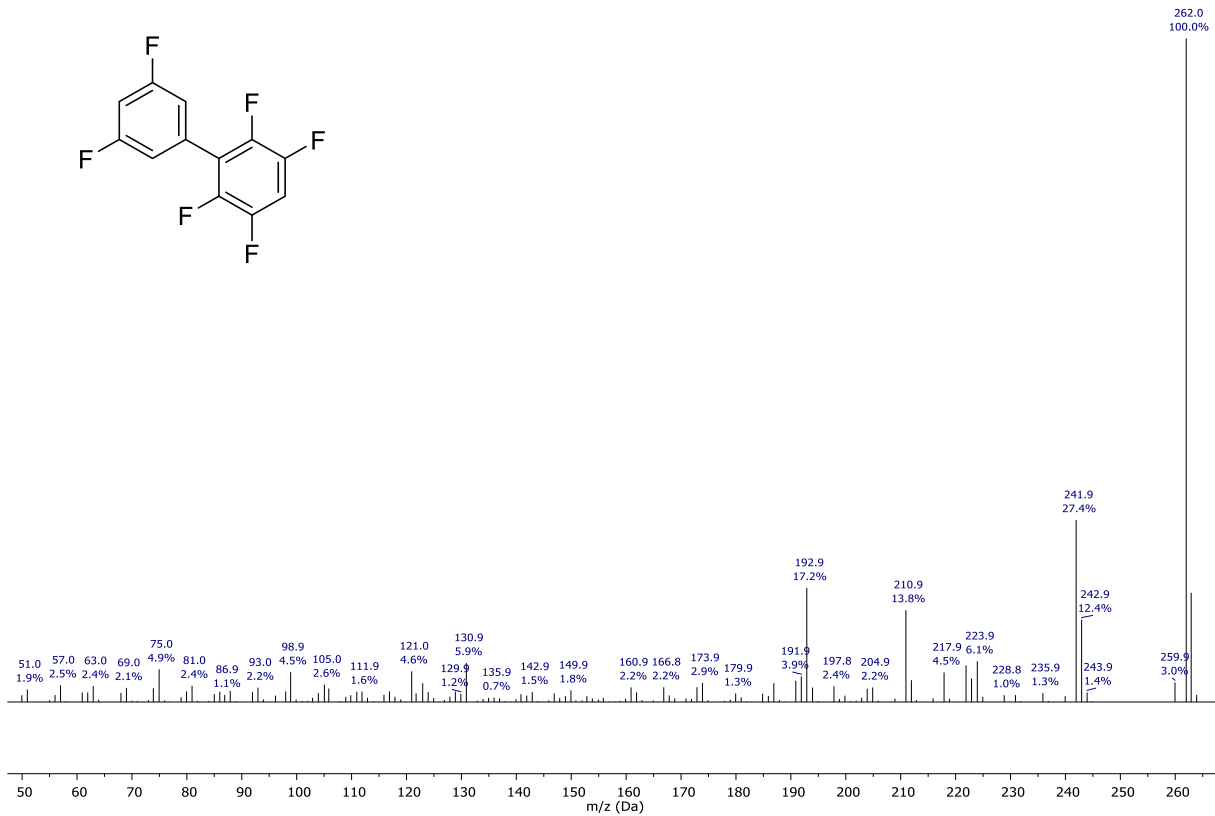
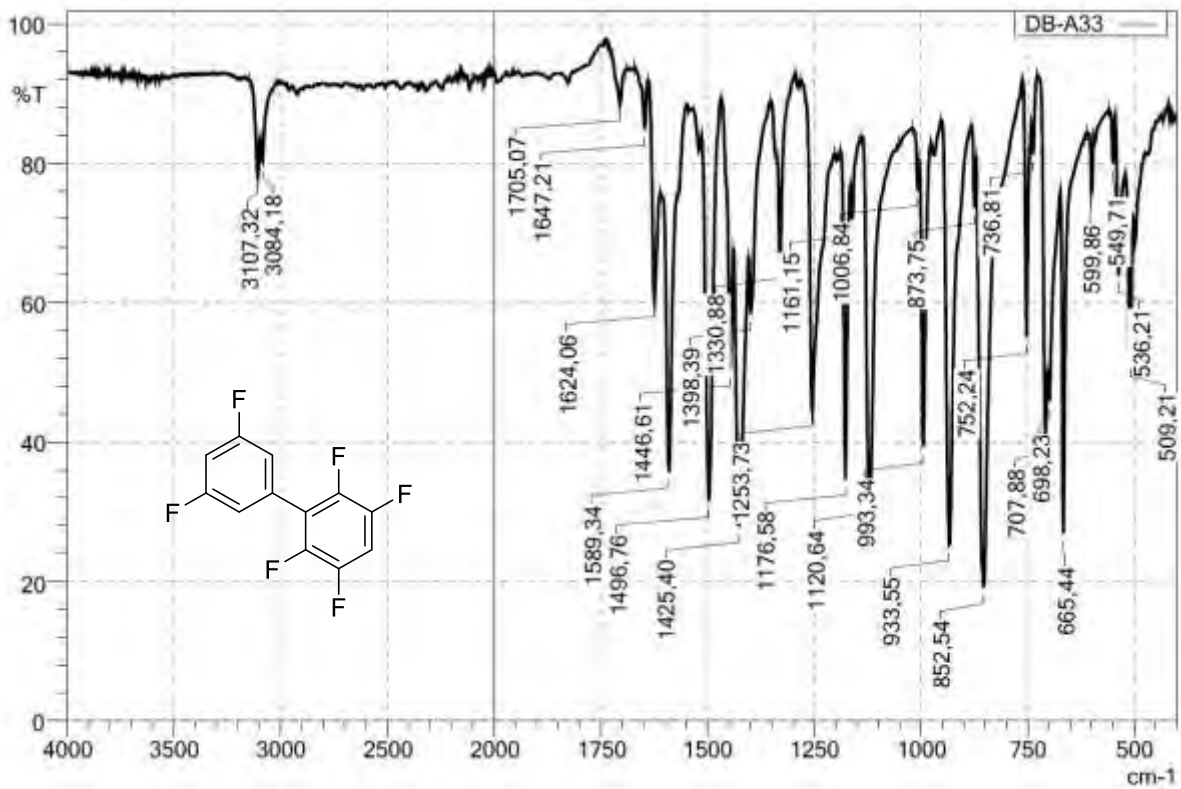
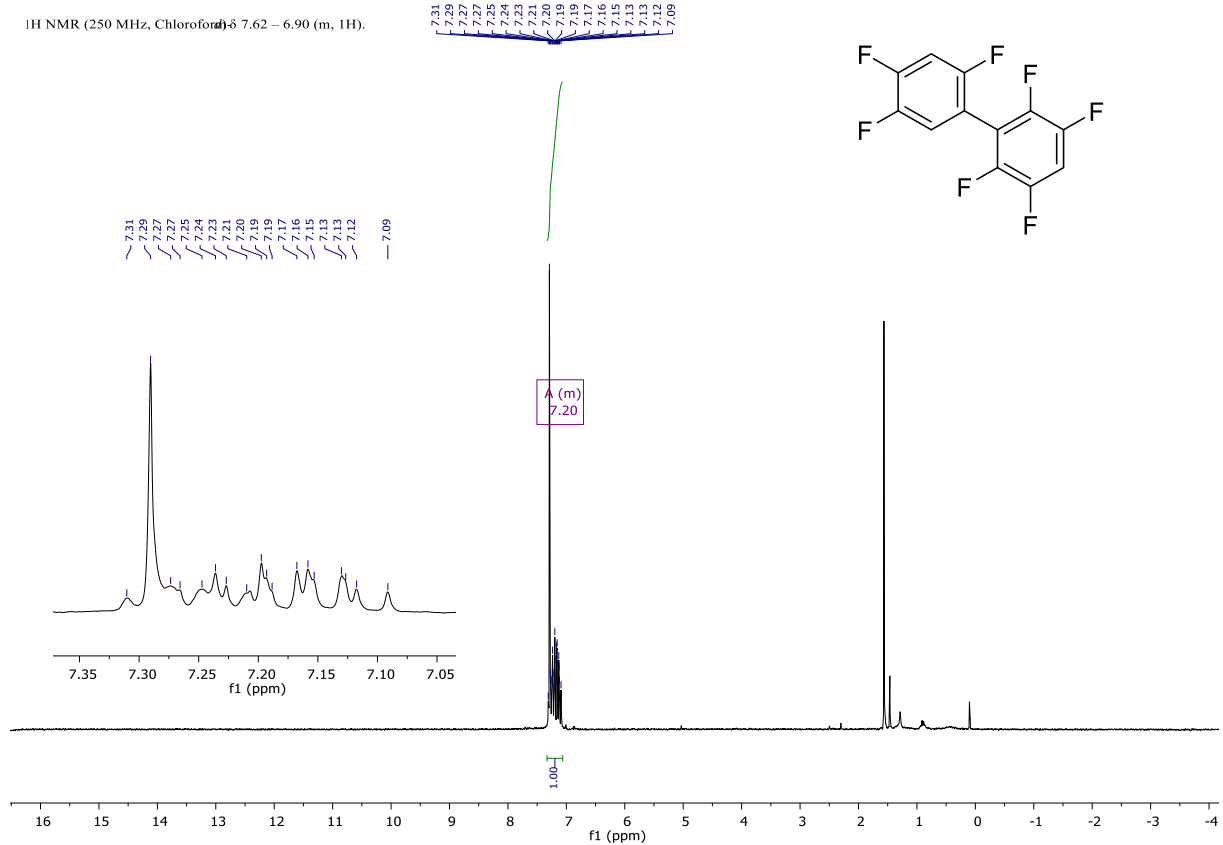
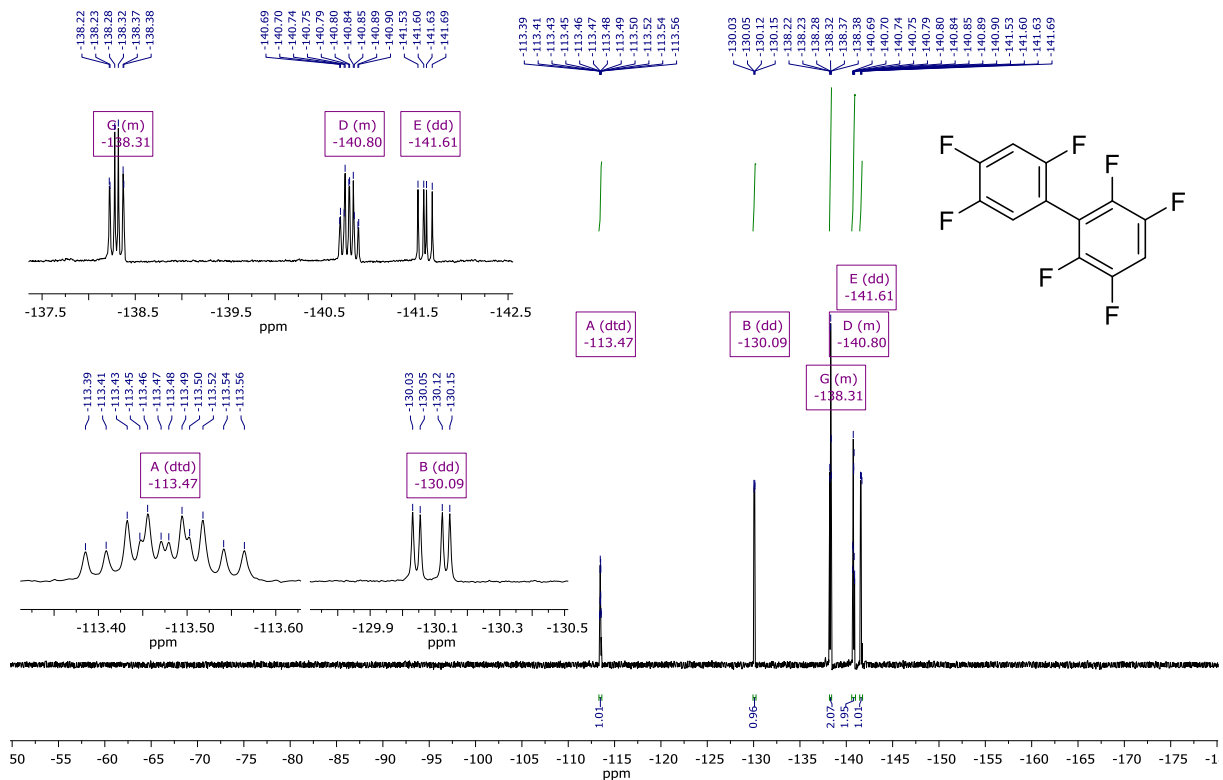
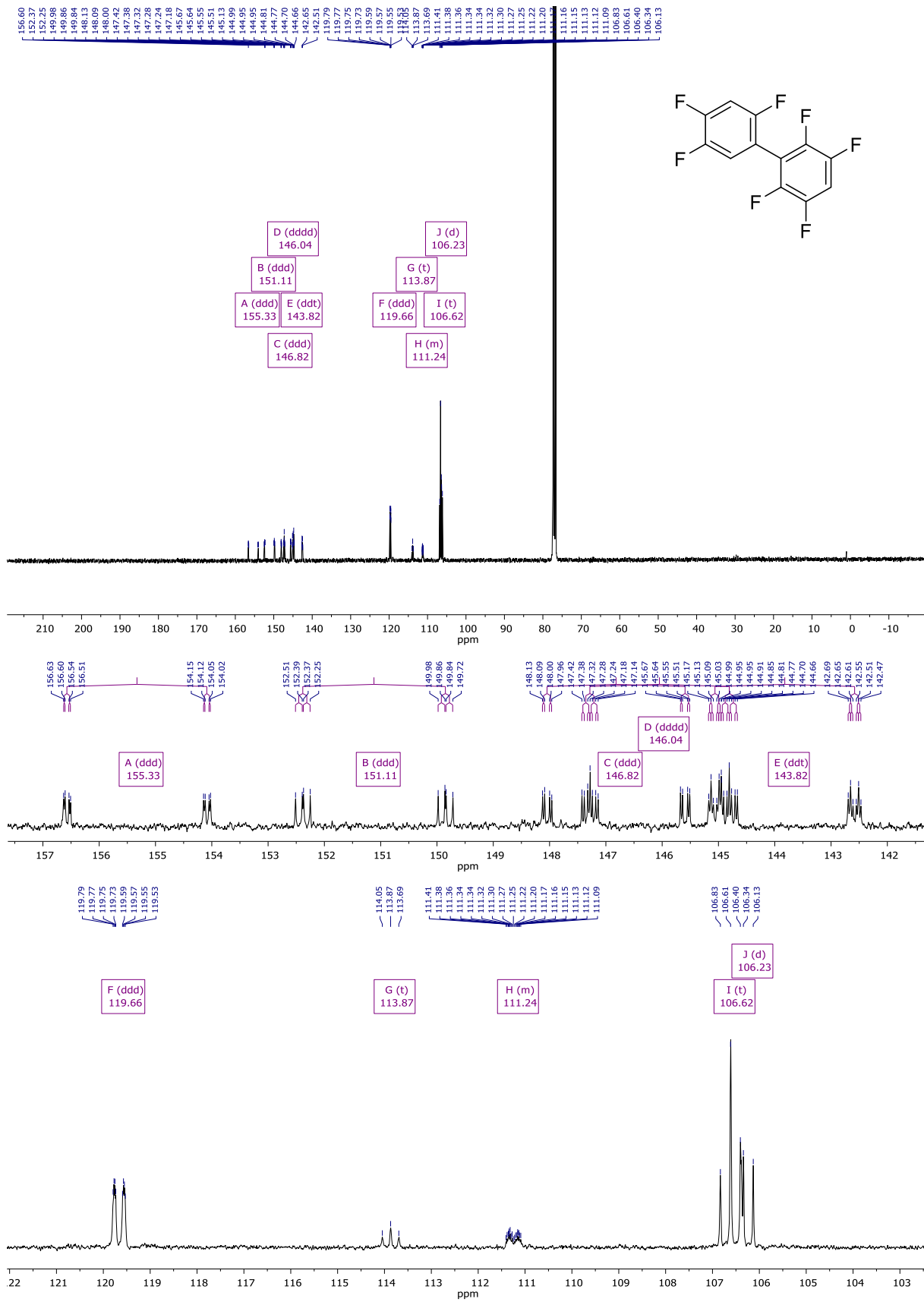
Figure S10 EI-Spectrum (EI⁺): 2,3,3',5,5',6-Hexafluoro-1,1'-biphenyl

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)

¹H NMR (250 MHz, Chloroform-d) δ 7.62 – 6.90 (m, 1H).Figure S12 ¹H-NMR: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl¹⁹F NMR (235 MHz, Chloroform-d) δ -113.47 (dtd, J = 14.5, 11.0, 5.5 Hz), -130.09 (dd, 21.5, 5.5 Hz), -137.77 – -138.54 (m), -140.60 – -140.98 (m), -141.61 (dd, 5, 14.5 Hz).Figure S13 ¹⁹F-NMR {¹H}: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

Figure S14¹³C NMR: 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

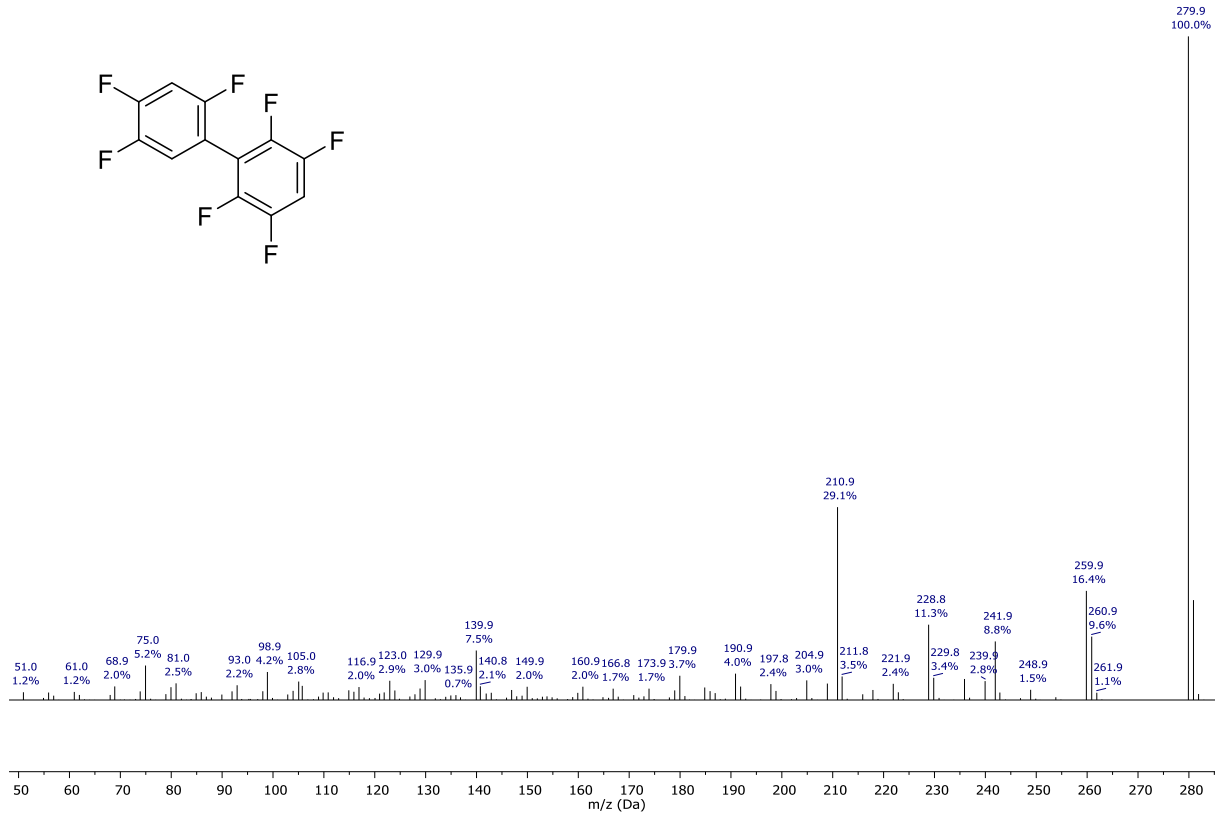
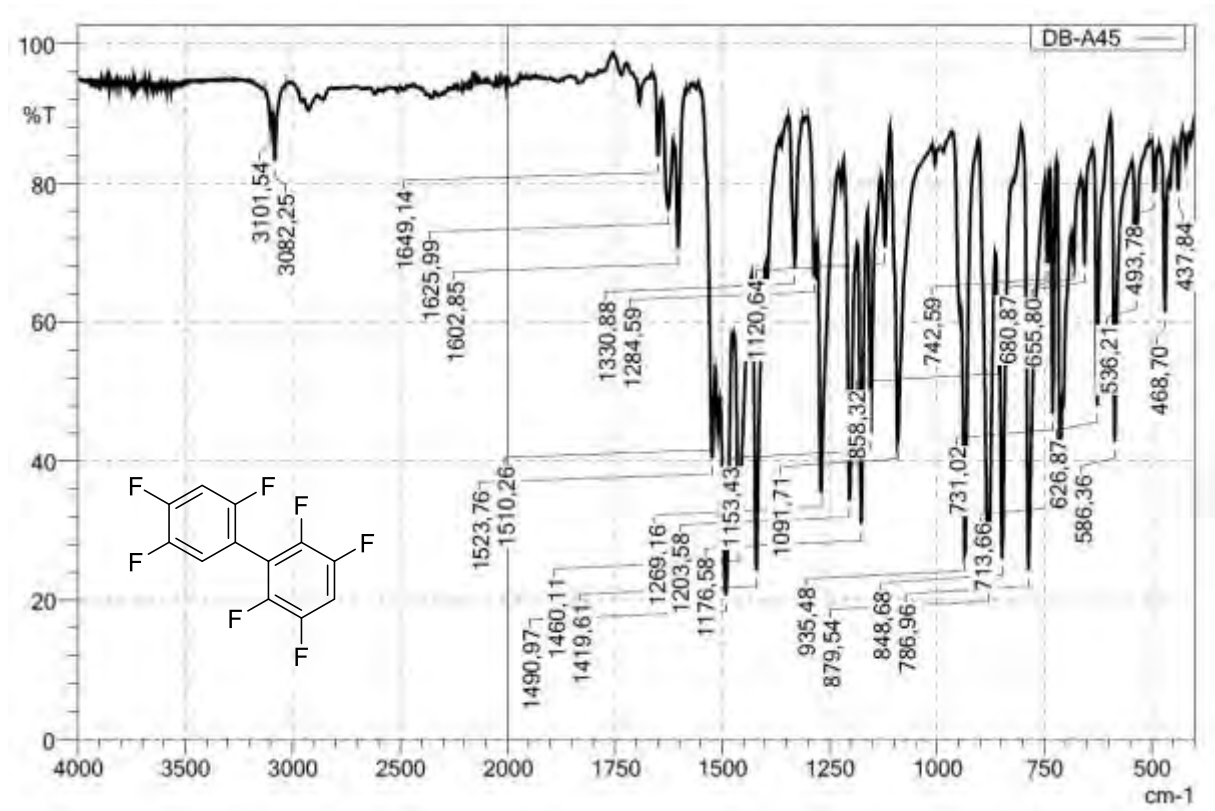
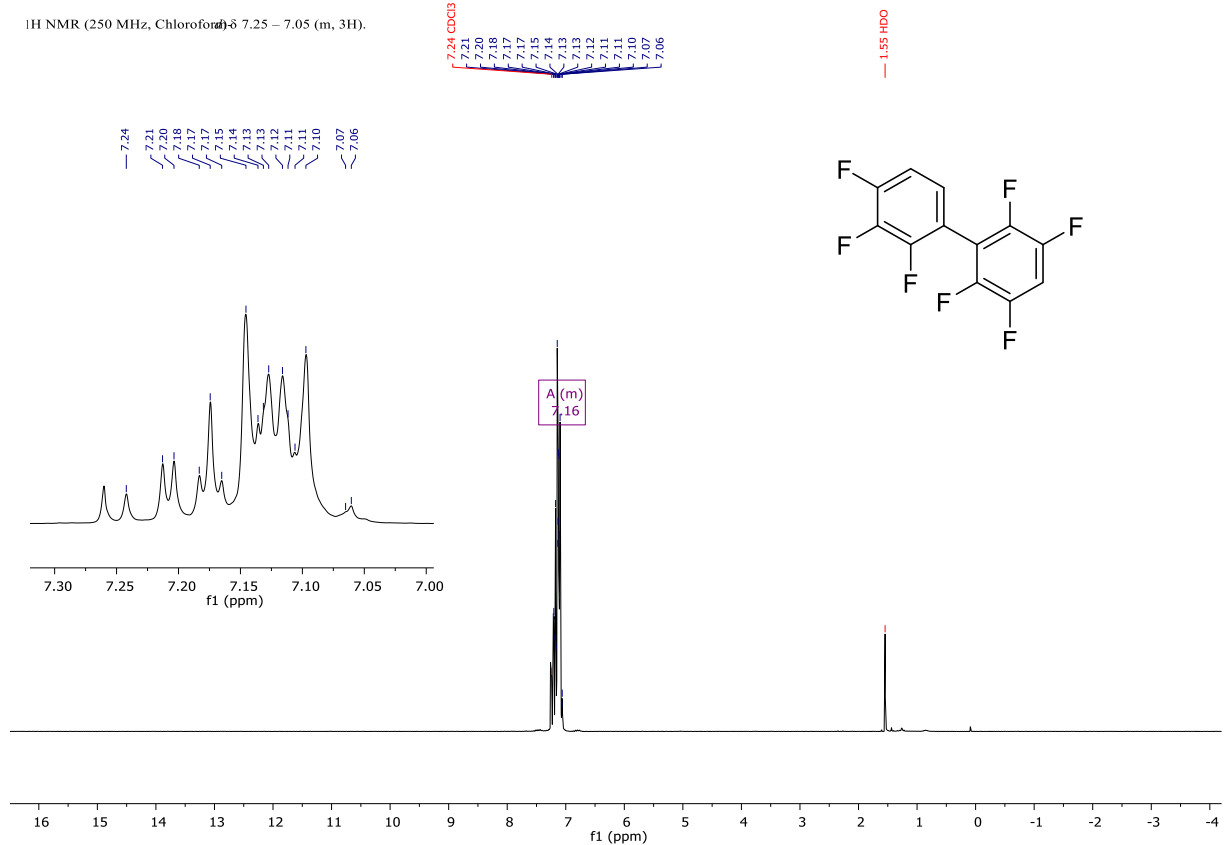
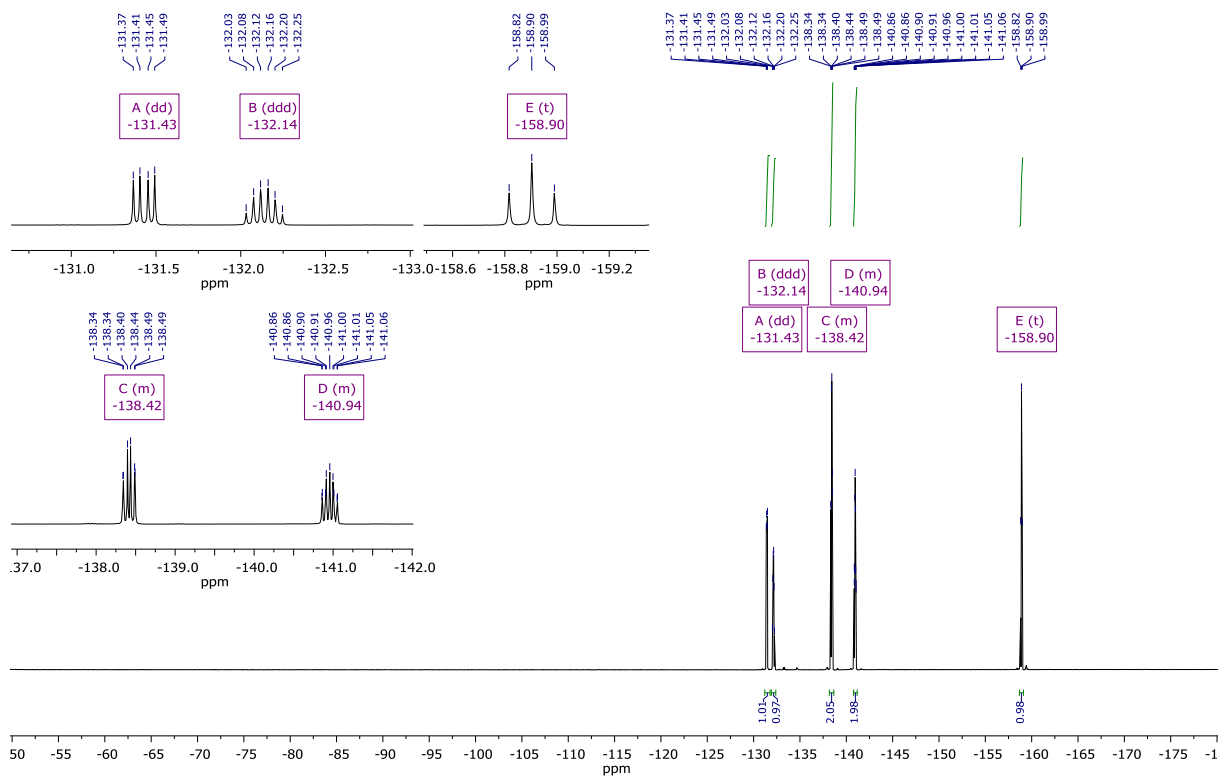
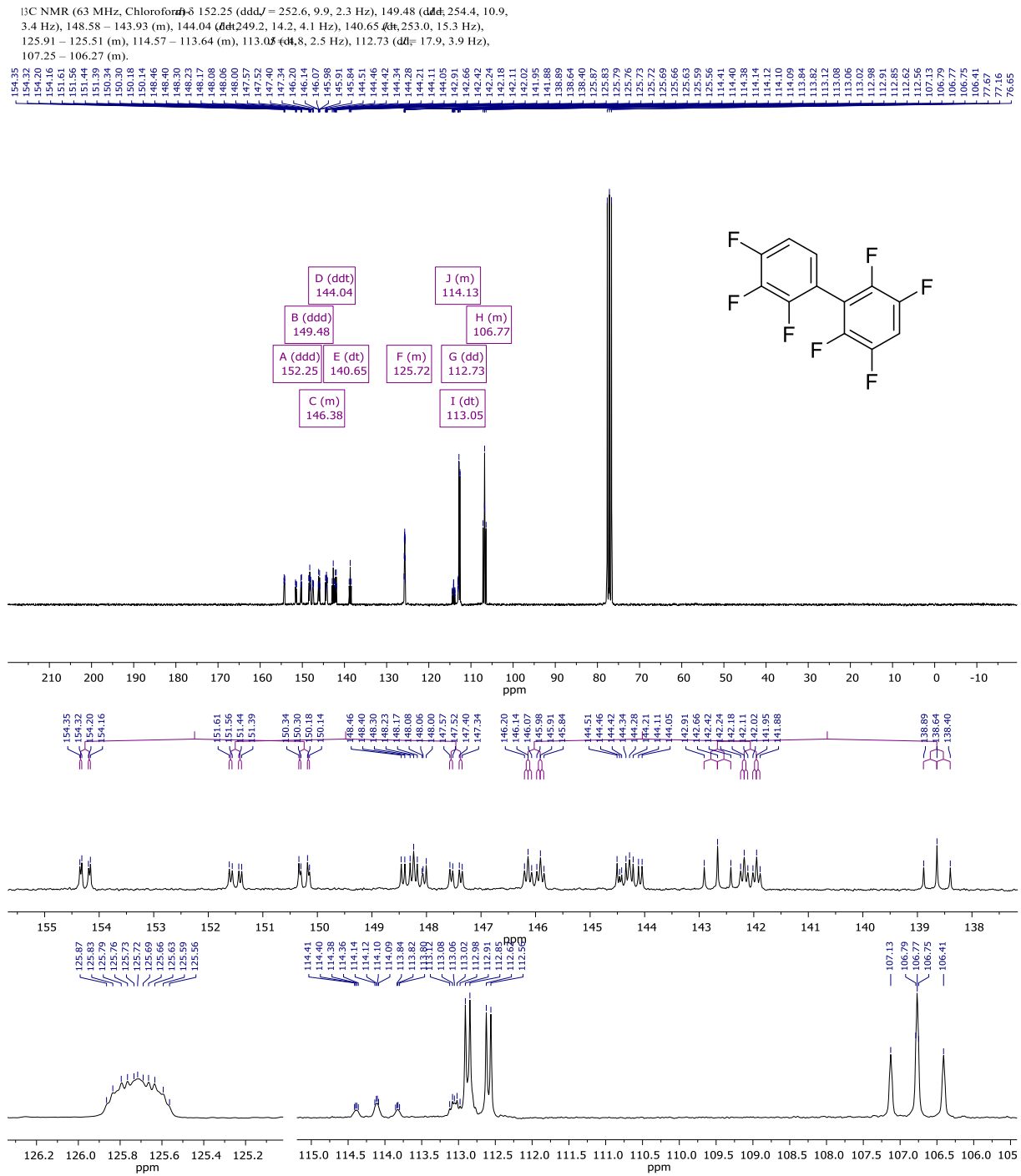
Figure S15 EI-Spectrum (EI⁺): 2,2',3,4',5,5',6-Heptafluoro-1,1'-biphenyl

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)

¹H NMR (250 MHz, Chloroform-d) δ 7.25 – 7.05 (m, 3H).Figure S17 ¹H-NMR: 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl¹⁹F NMR (235 MHz, Chloroform-d) δ -131.43 (dd, J = 20.6, 9.2 Hz), -132.14 (ddd, J = 19.9, 10.4 Hz), -138.30 – -138.52 (m), -140.81 – -141.09 (m), -158.82 (t, J = 10.4 Hz).Figure S18 ¹⁹F-NMR {¹H}: 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

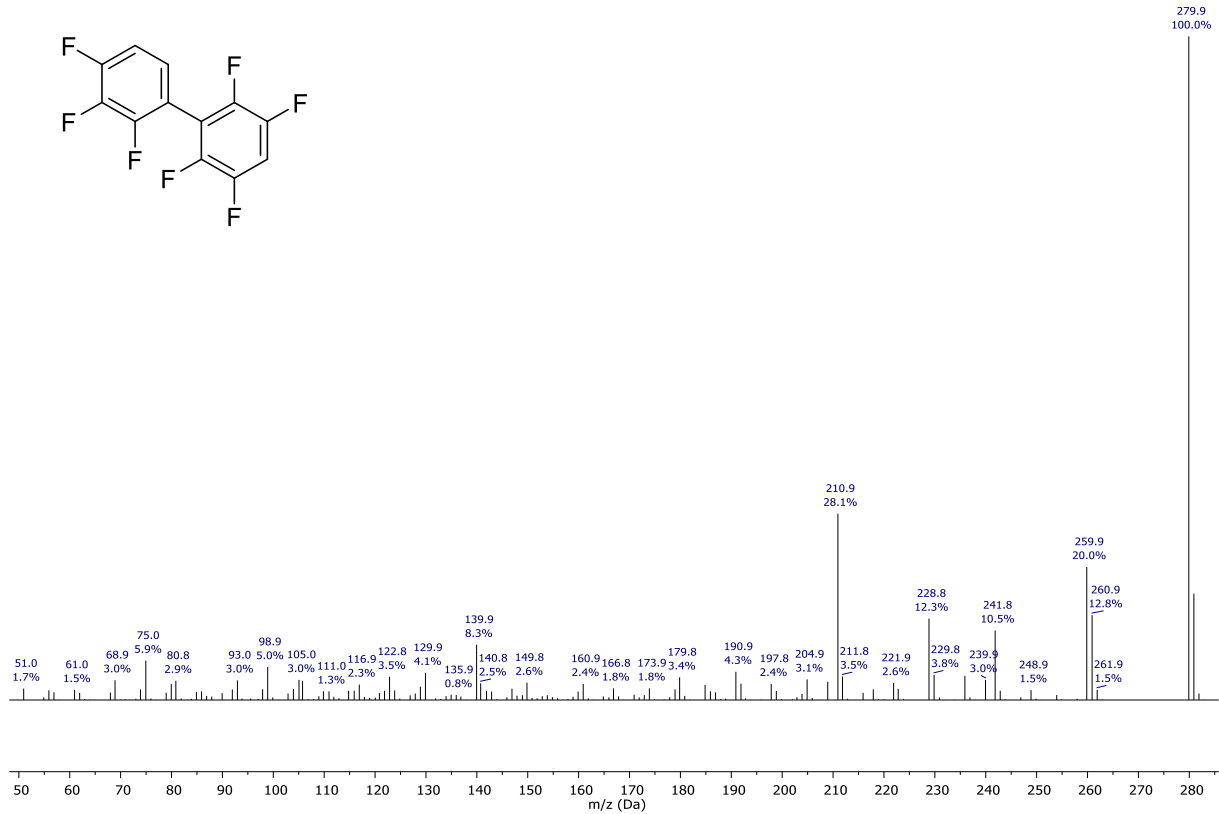
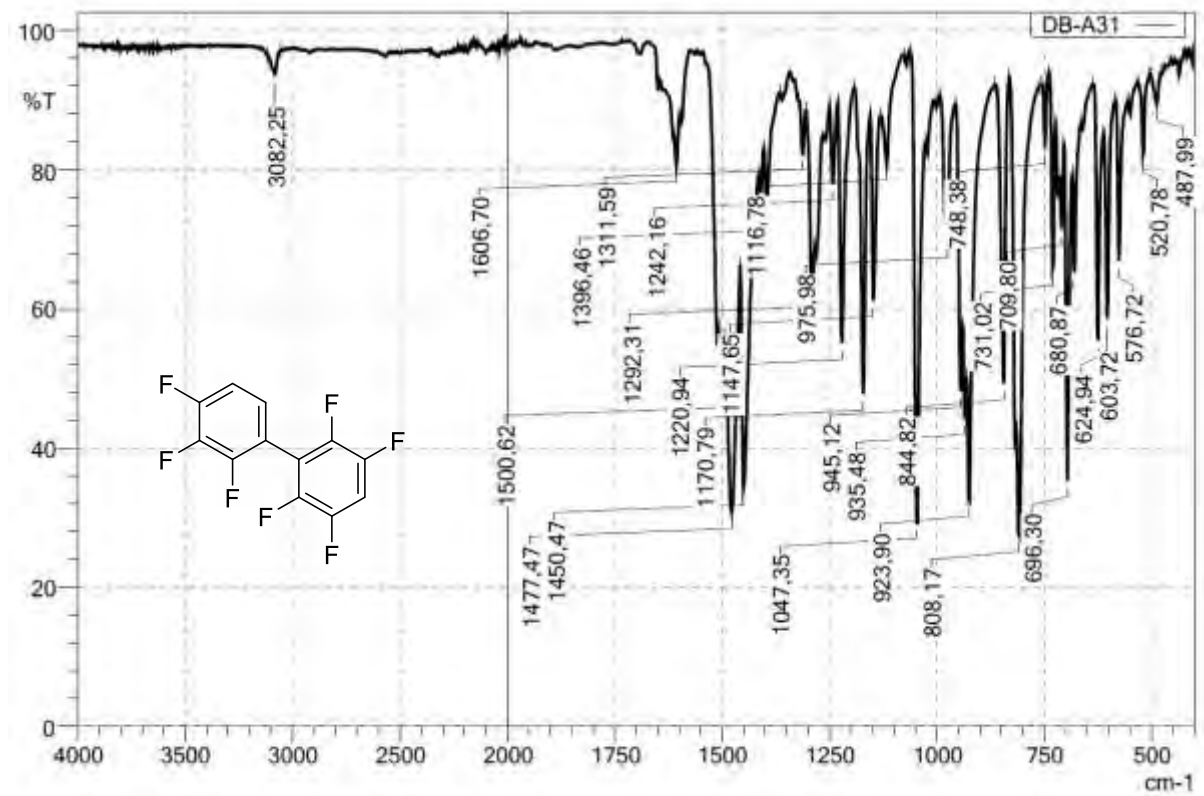
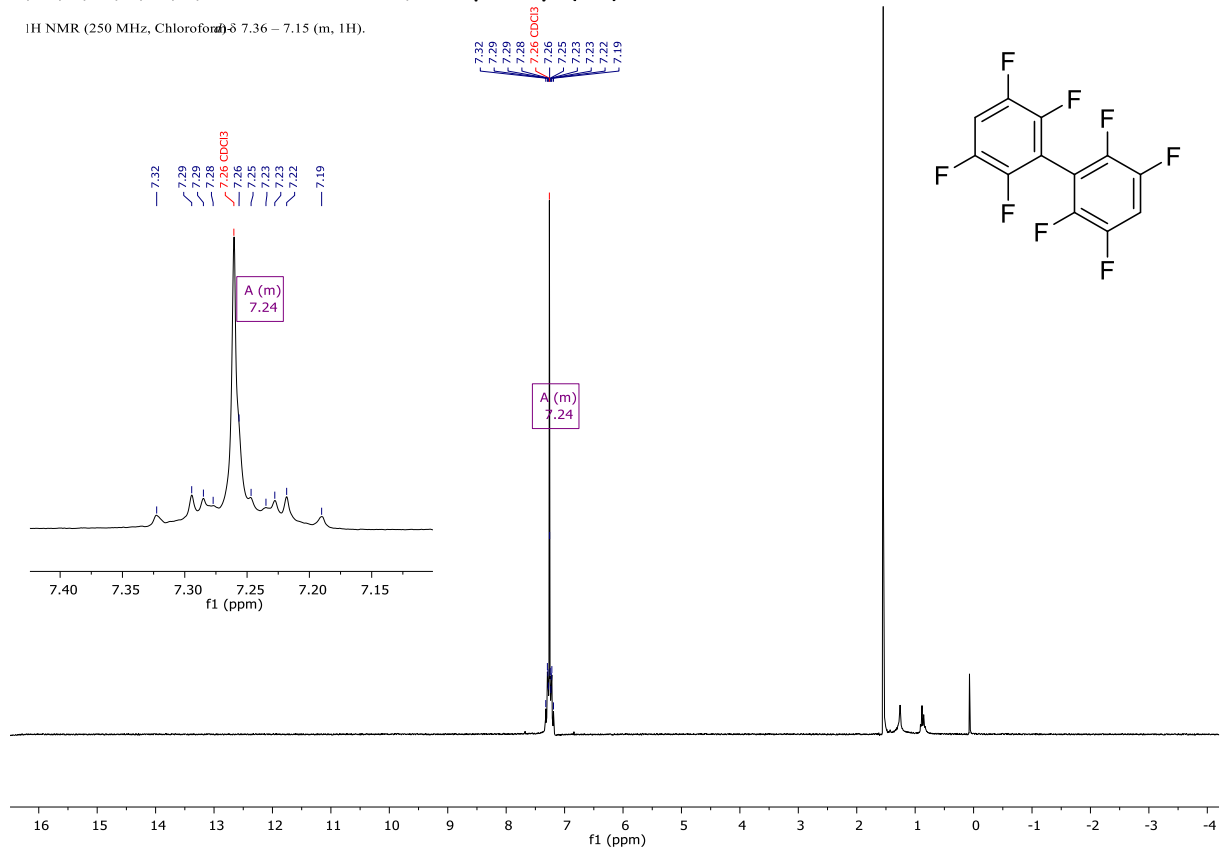
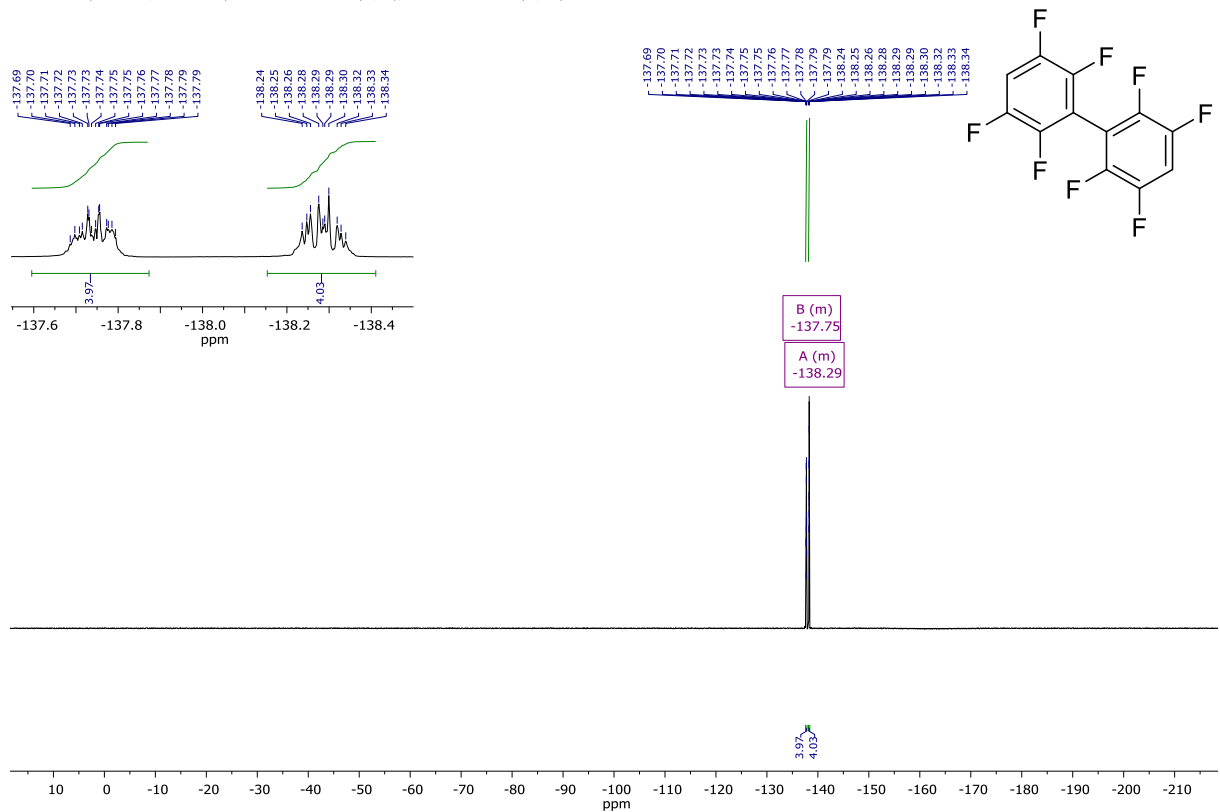
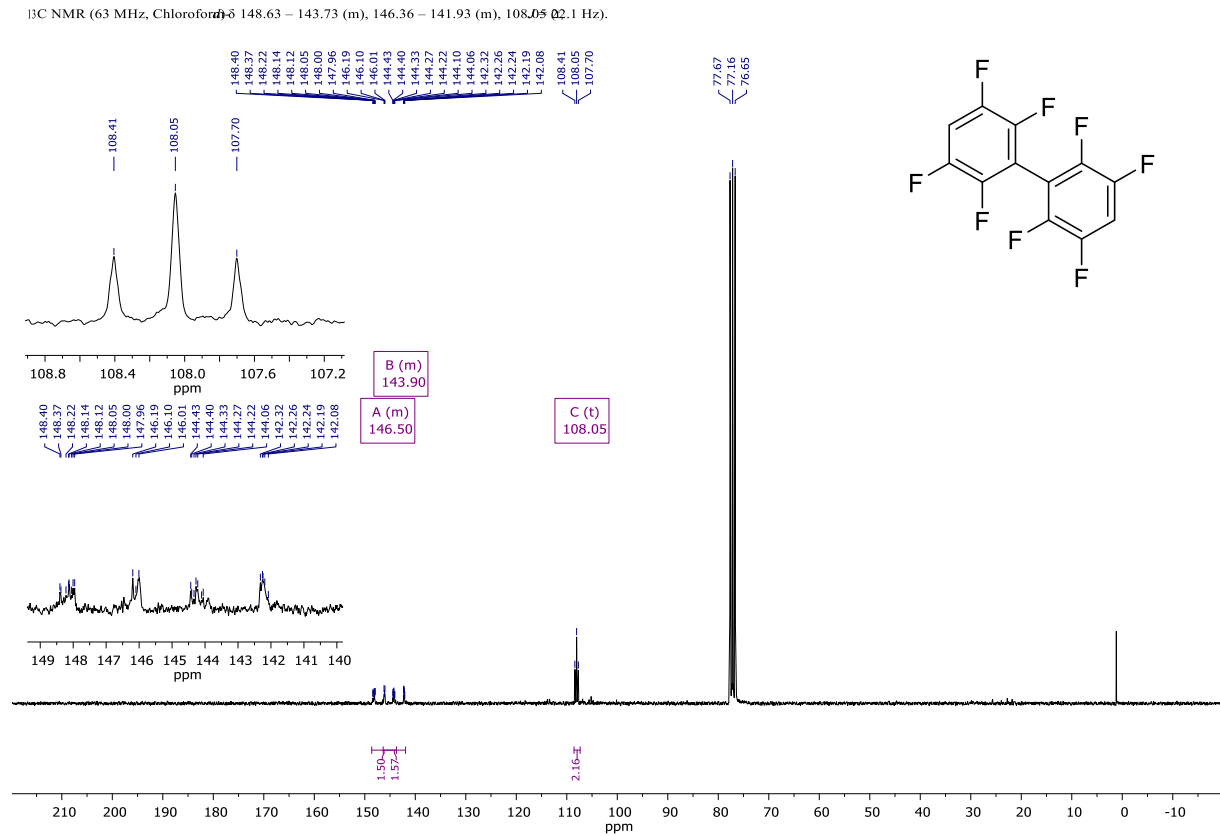
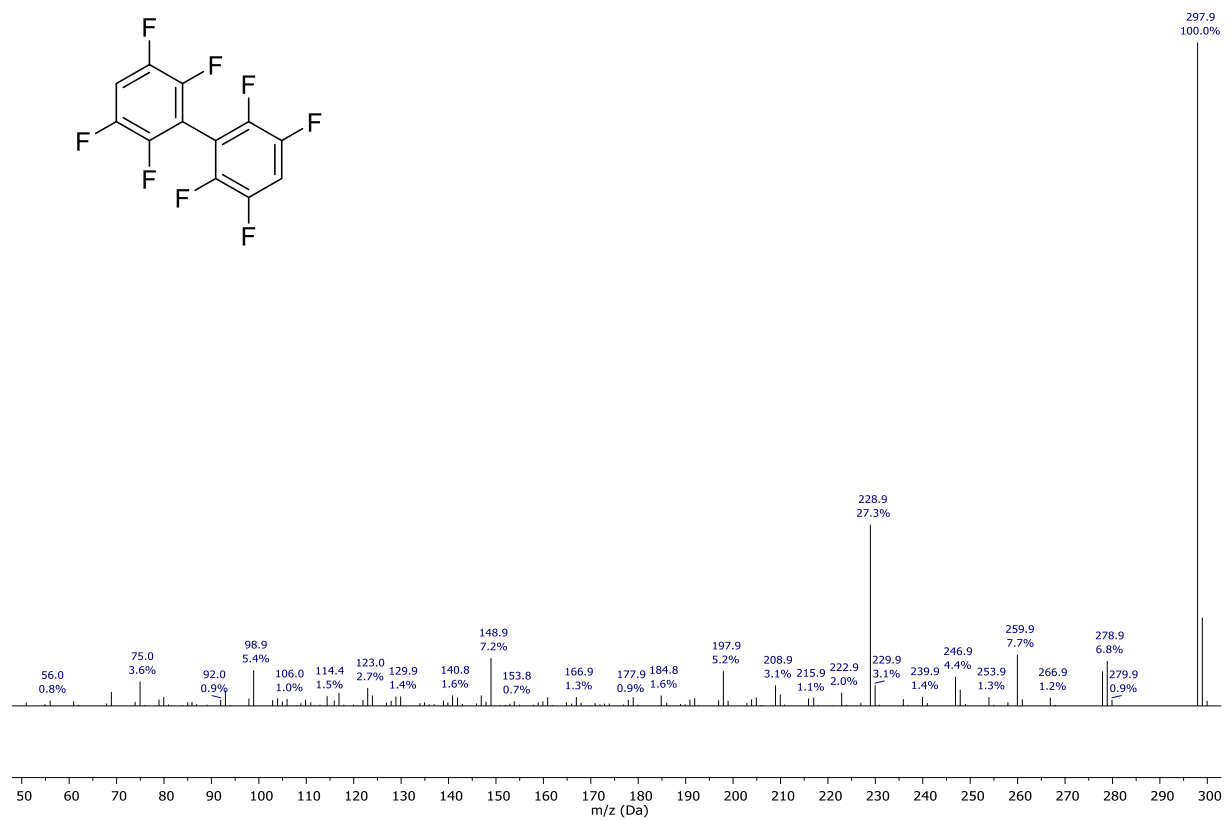
Figure S20 EI-Spectrum (EI⁺): 2,2',3,3',4,5',6'-Heptafluoro-1,1'-biphenyl

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)

 $^1\text{H NMR}$ (250 MHz, Chloroform- d_3) δ 7.36 – 7.15 (m, 1H).Figure S22 $^1\text{H-NMR}$: 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl $^{19}\text{F NMR}$ (377 MHz, Chloroform- d_3) δ -137.66 – -137.85 (m, 4F), -138.20 – -138.42 (m, 4F).Figure S23 $^{19}\text{F-NMR}$ $\{^1\text{H}\}$: 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'-biphenylFigure S25 EI-Spectrum (EI $^+$): 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

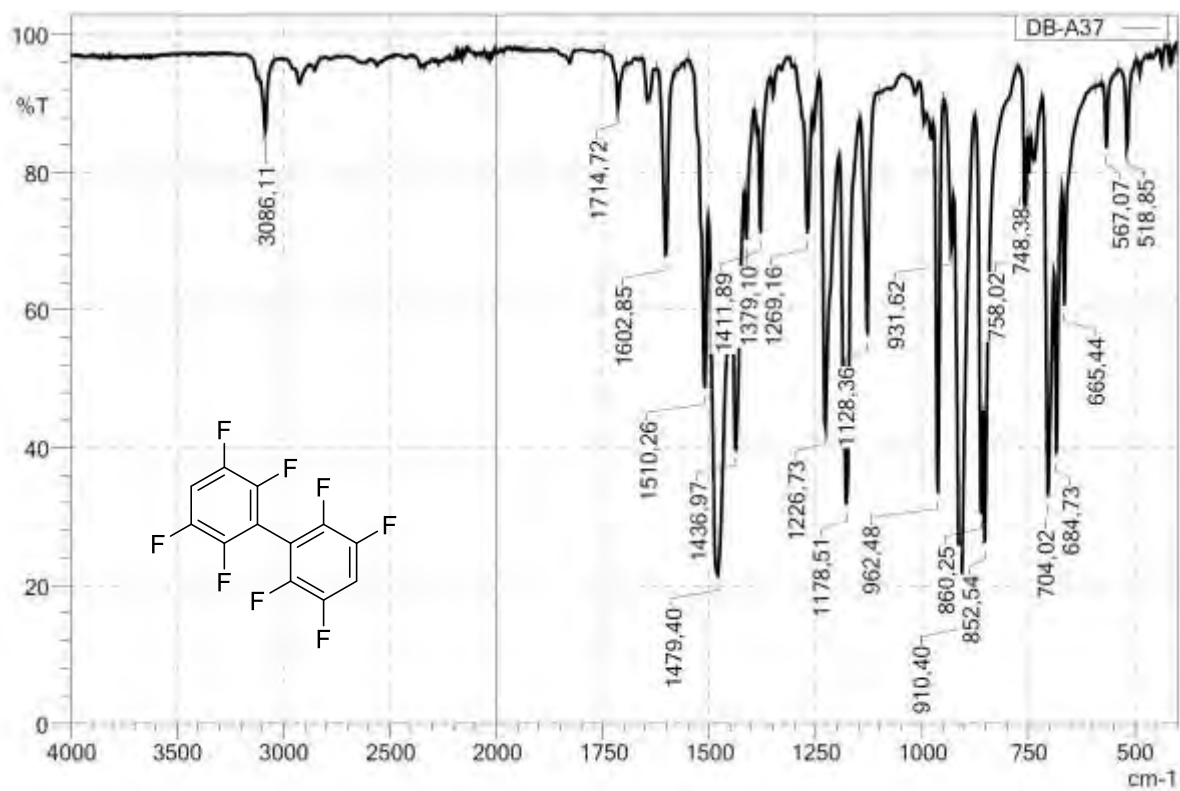
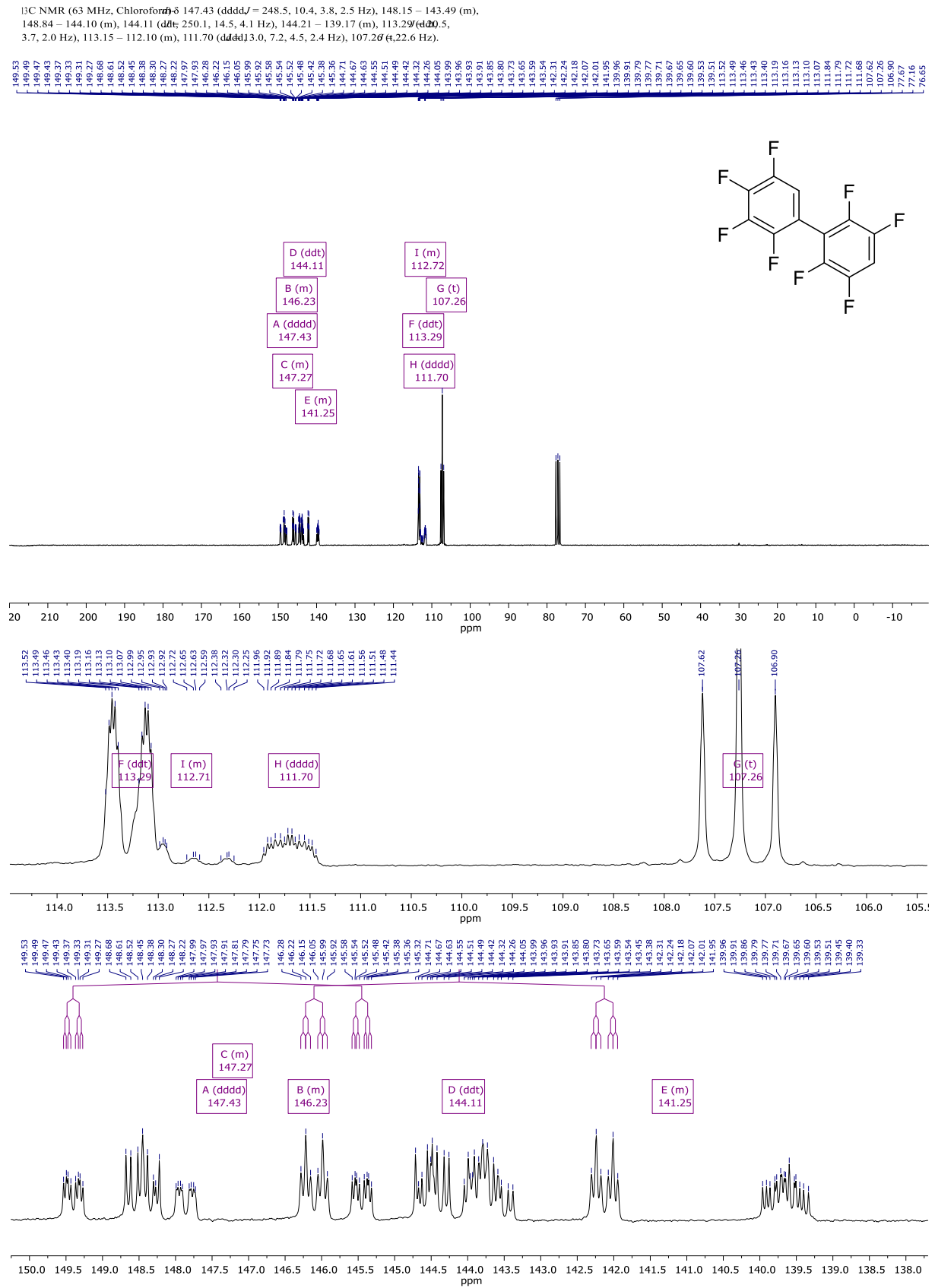


Figure S26 IR (ATR)- Spectrum: 2,2',3,3',5,5',6,6'-Octafluoro-1,1'-biphenyl

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

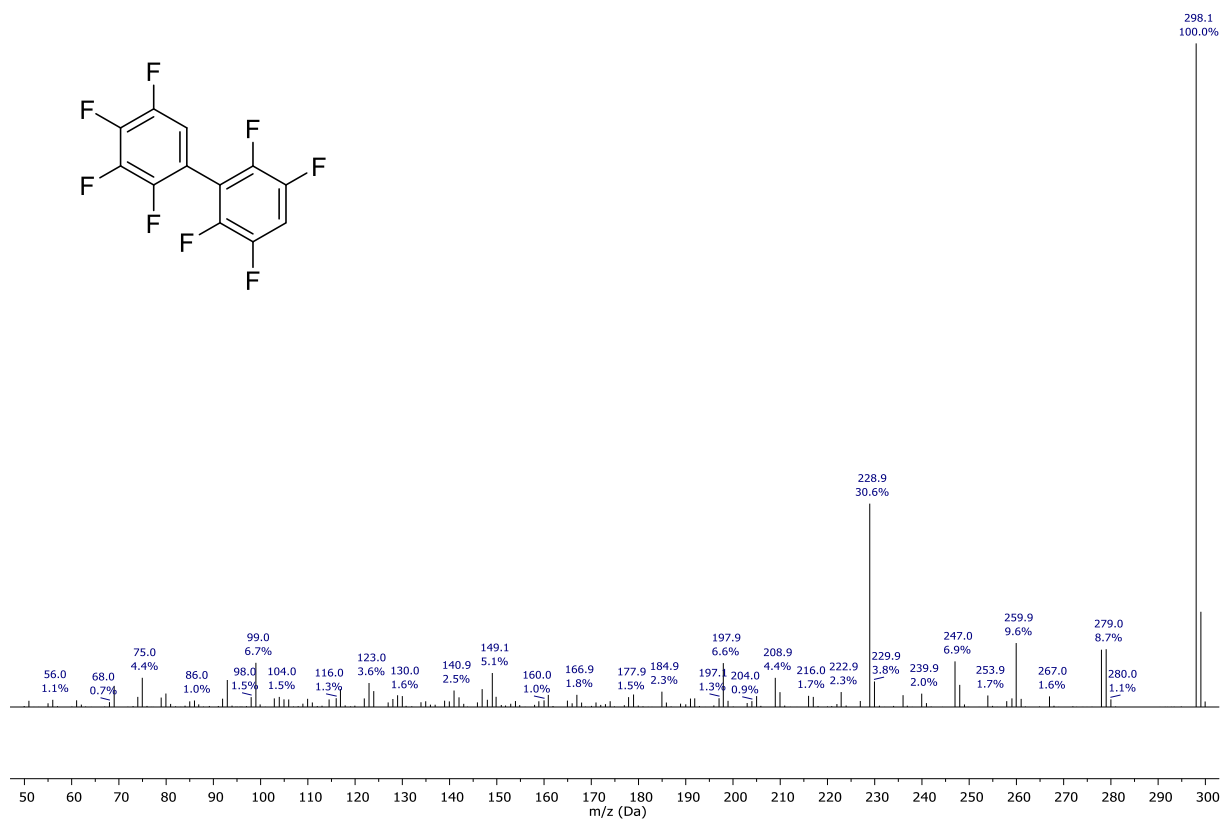
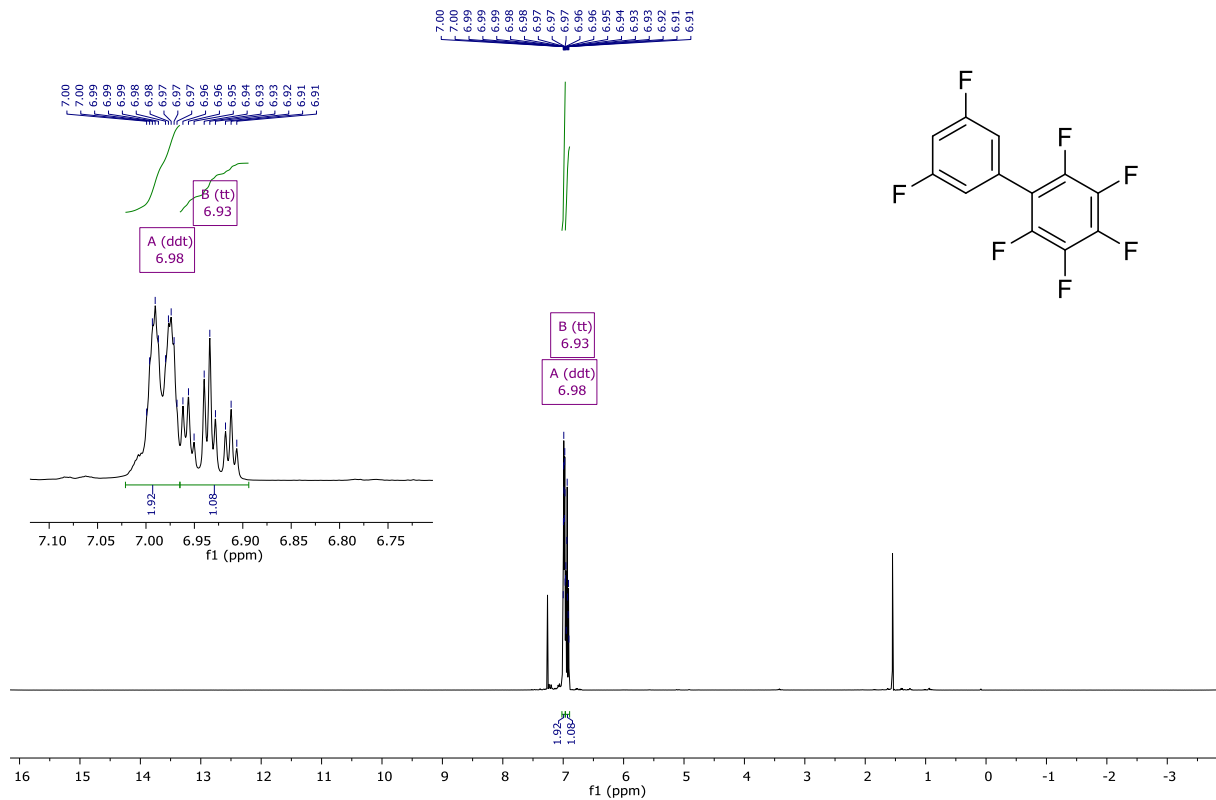
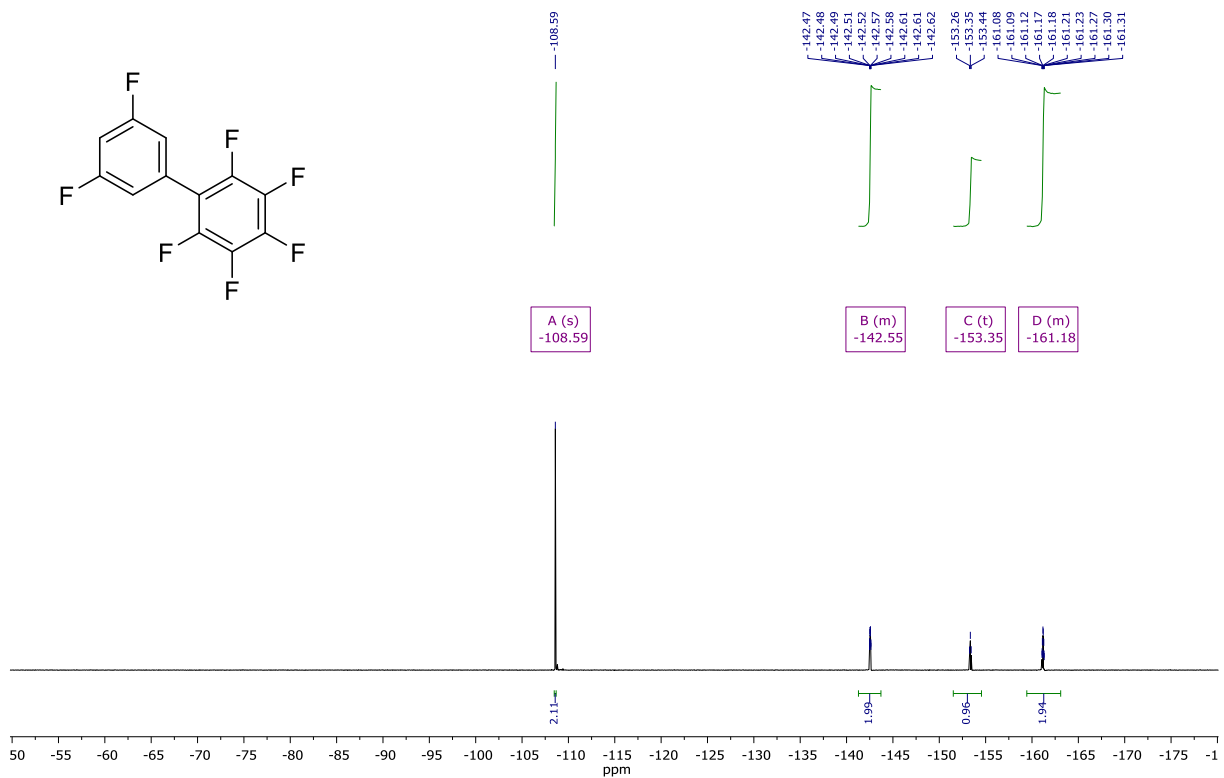


Figure S30 EI-Spectrum (EI⁺): 2,2',3,3',4,5,5',6'-Octafluoro-1,1'-biphenyl

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

¹H NMR (400 MHz, Chloroform-d) δ 6.98 (ddt, *J* = 7.7, 2.4, 1.2 Hz, 2H), 6.93 (tt, 8.8, 2.3 Hz, 1H).Figure S31 ¹H-NMR: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl¹⁹F NMR (235 MHz, Chloroform-d) δ -108.59, -142.15 – -143.59 (m), -153.35 (20.9 Hz), -160.30 – -162.60 (m).Figure S32 ¹⁹F-NMR {¹H}: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

^{13}C NMR (101 MHz, Chloroform- d) δ 163.10 (dd), 145.75 – 142.81 (m), 141.23 (dt),
 $J = 255.7, 13.4, 5.1$ Hz), 139.63 – 136.56 (m), 129.23 (td), 5, 3.9, 1.8 Hz), 114.19 – 113.85 (m),
 113.82 – 113.37 (m), 105.16 (t), 25.1 Hz).

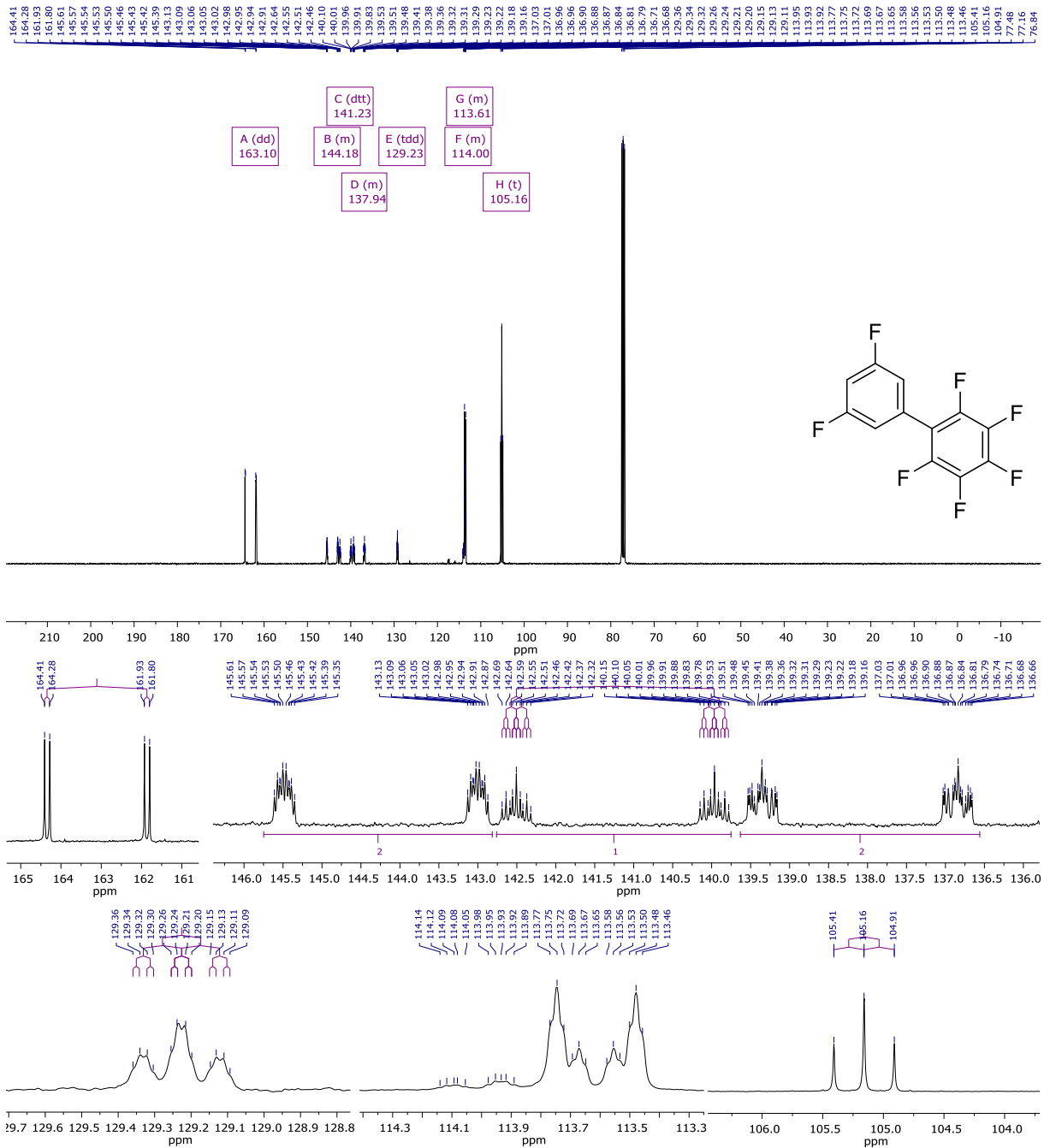


Figure S33 ^{13}C NMR: 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

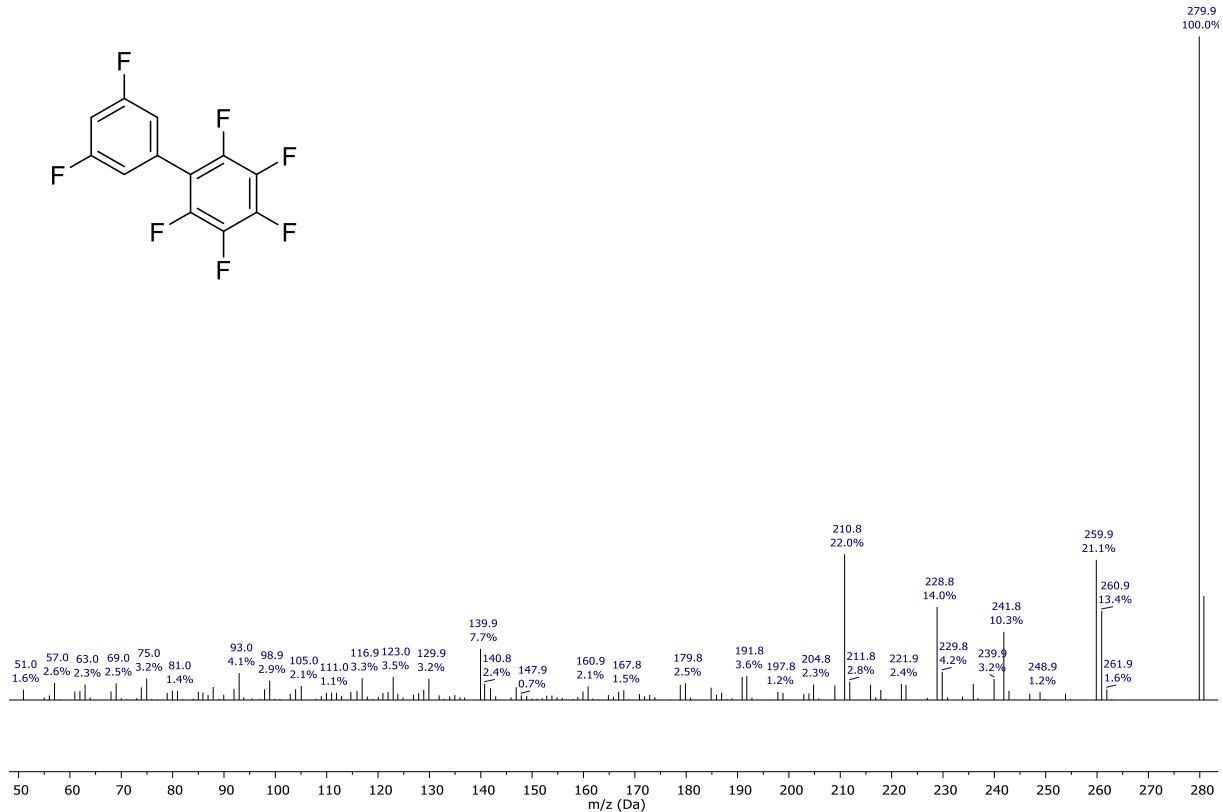
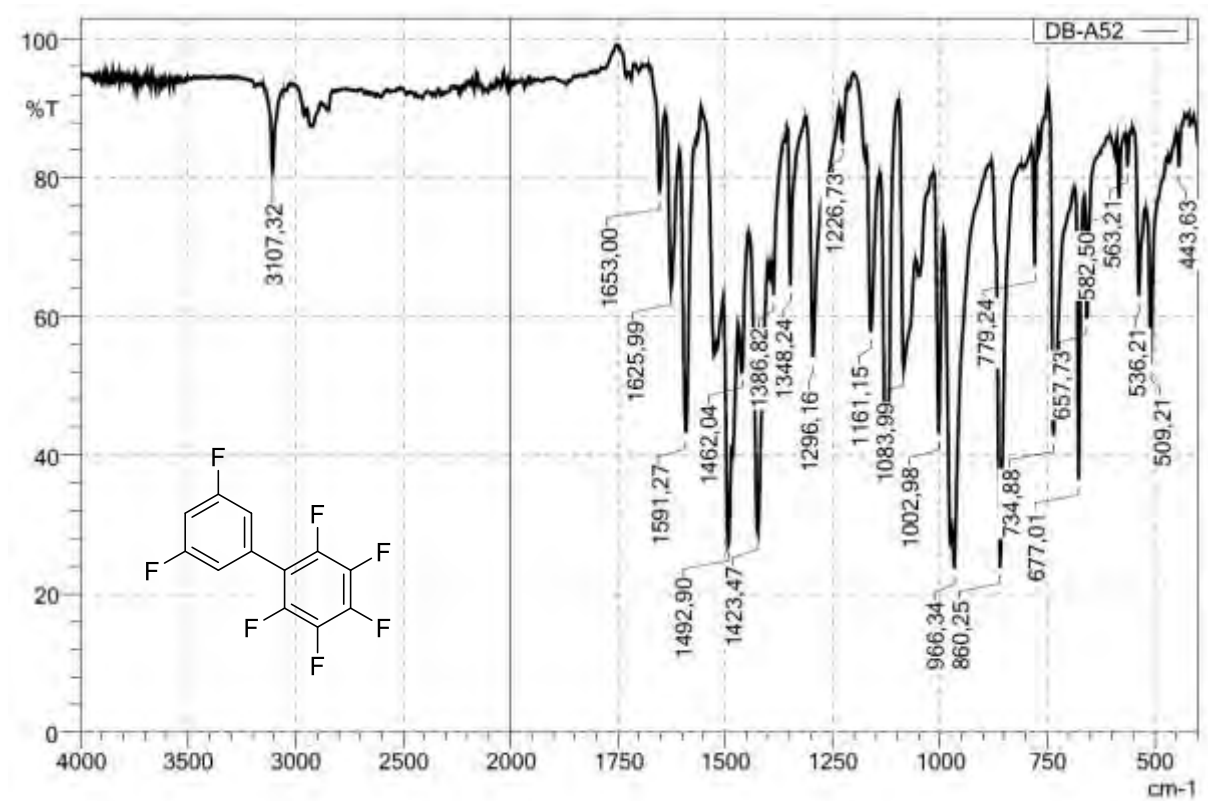
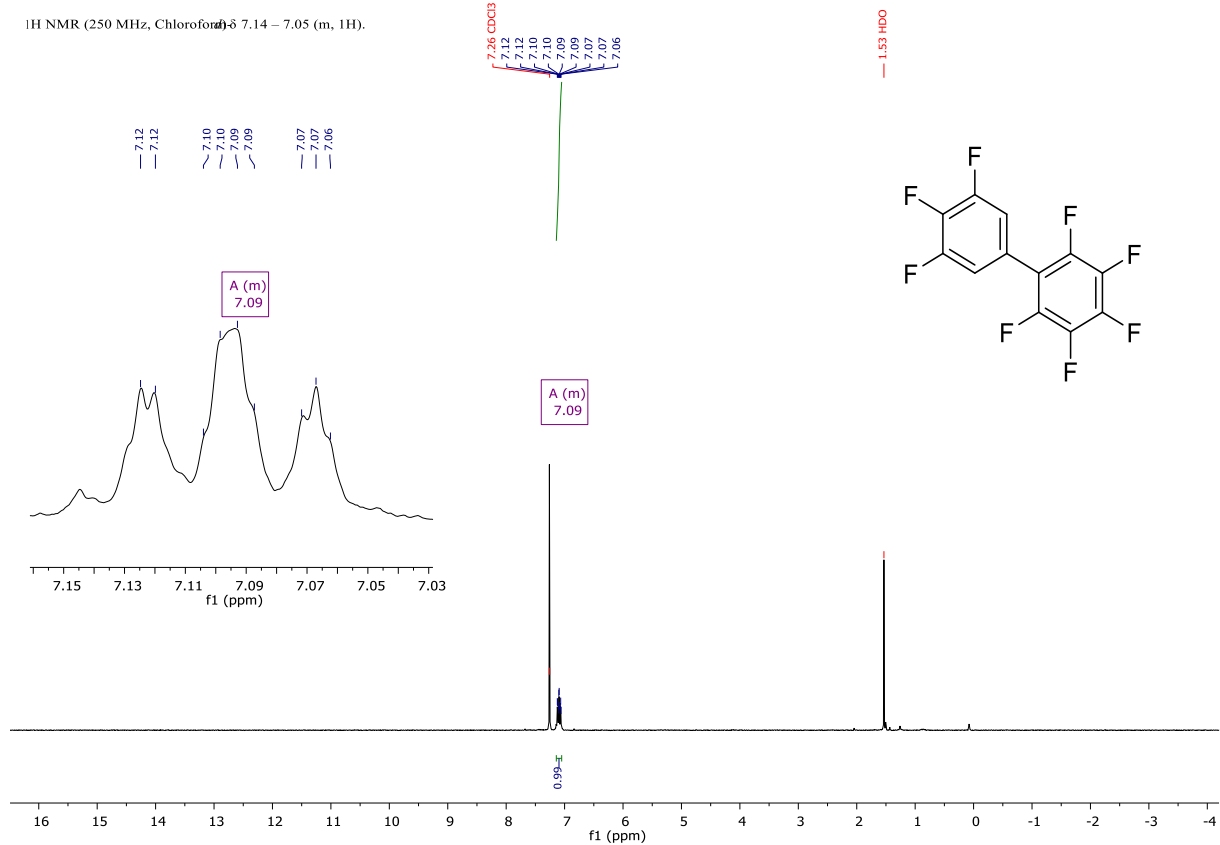
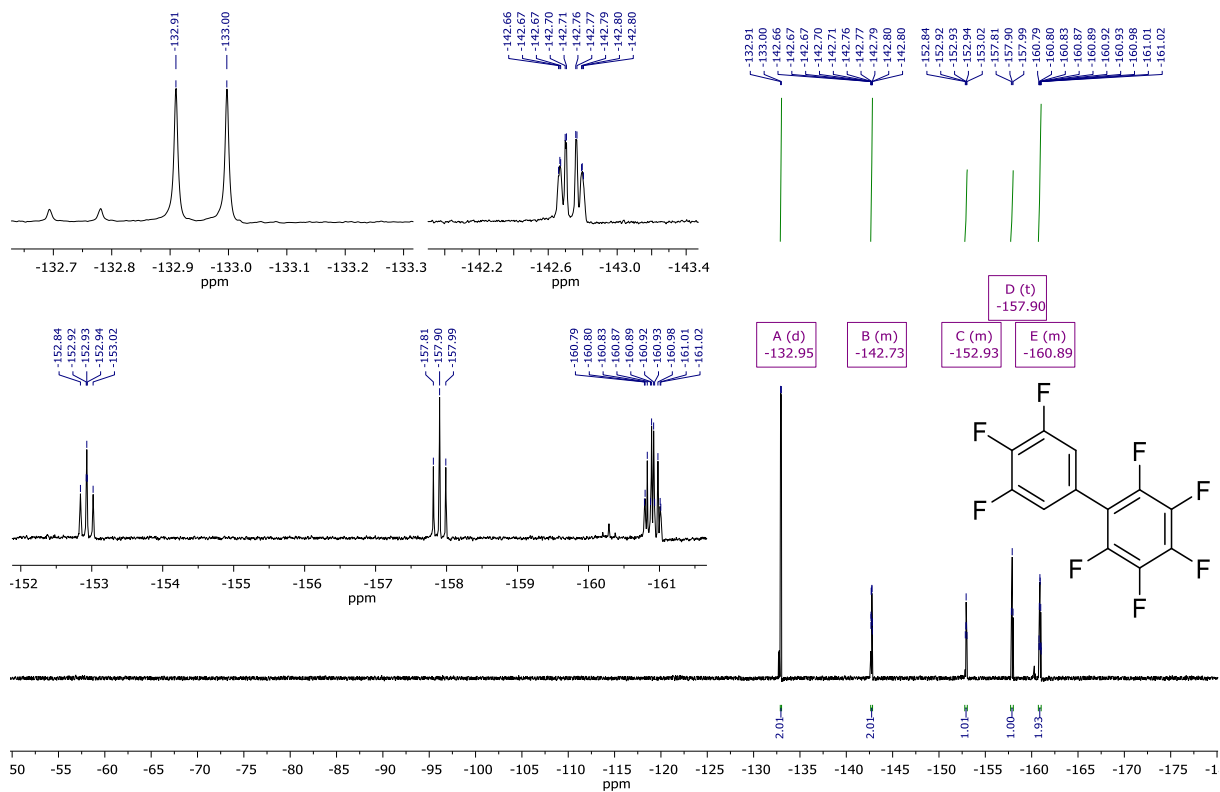
Figure S34 EI-Spectrum (EI⁺): 2,3,3',4,5,5',6-Heptafluoro-1,1'-biphenyl

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)

¹H NMR (250 MHz, Chloroform-d) δ 7.14 – 7.05 (m, 1H).Figure S36 ¹H-NMR: 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl¹⁹F NMR (235 MHz, Chloroform-d) δ -132.95 (d/ = 20.5 Hz), -142.54 – -142.85 (m), -152.76 – -153.12 (m), -157.90 (d/ = 20.6 Hz), -160.75 – -161.06 (m).Figure S37 ¹⁹F-NMR {¹H}: 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

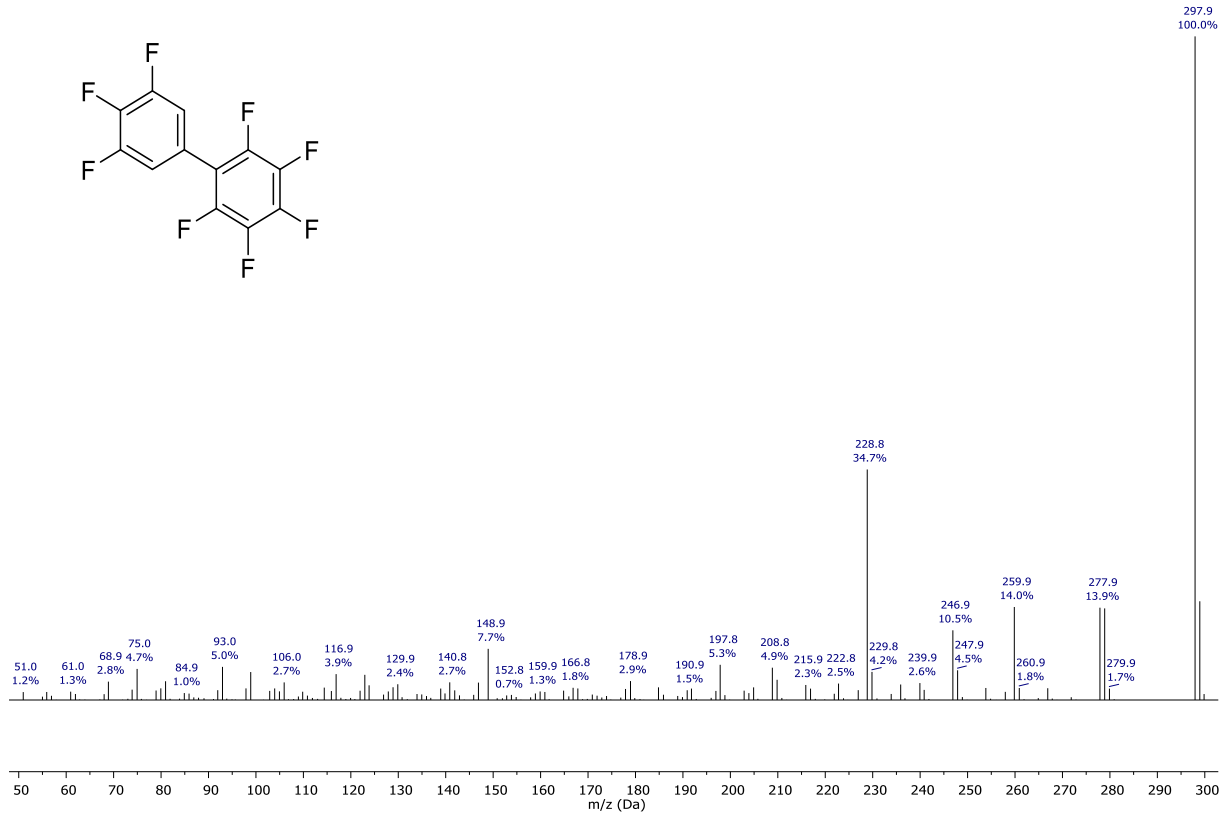
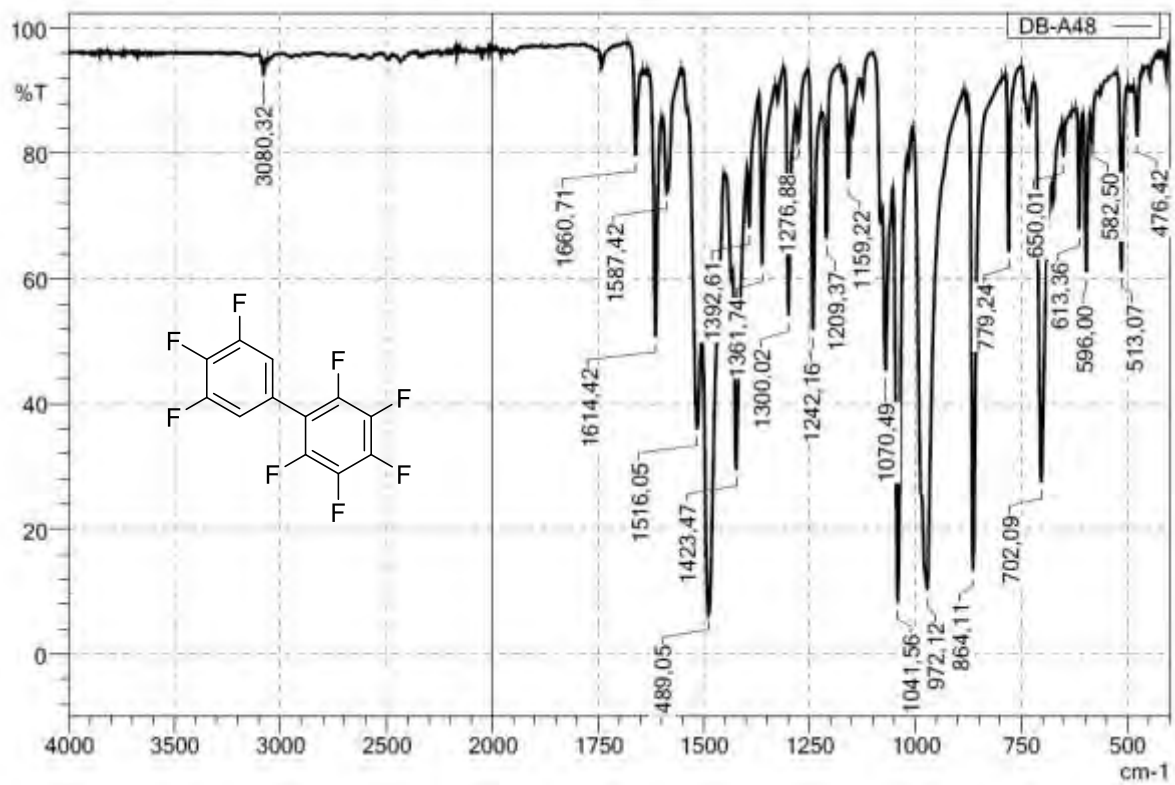
Figure S39 EI-Spectrum (EI⁺): 2,3,3',4,4',5,5',6-Octafluoro-1,1'-biphenyl

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)

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

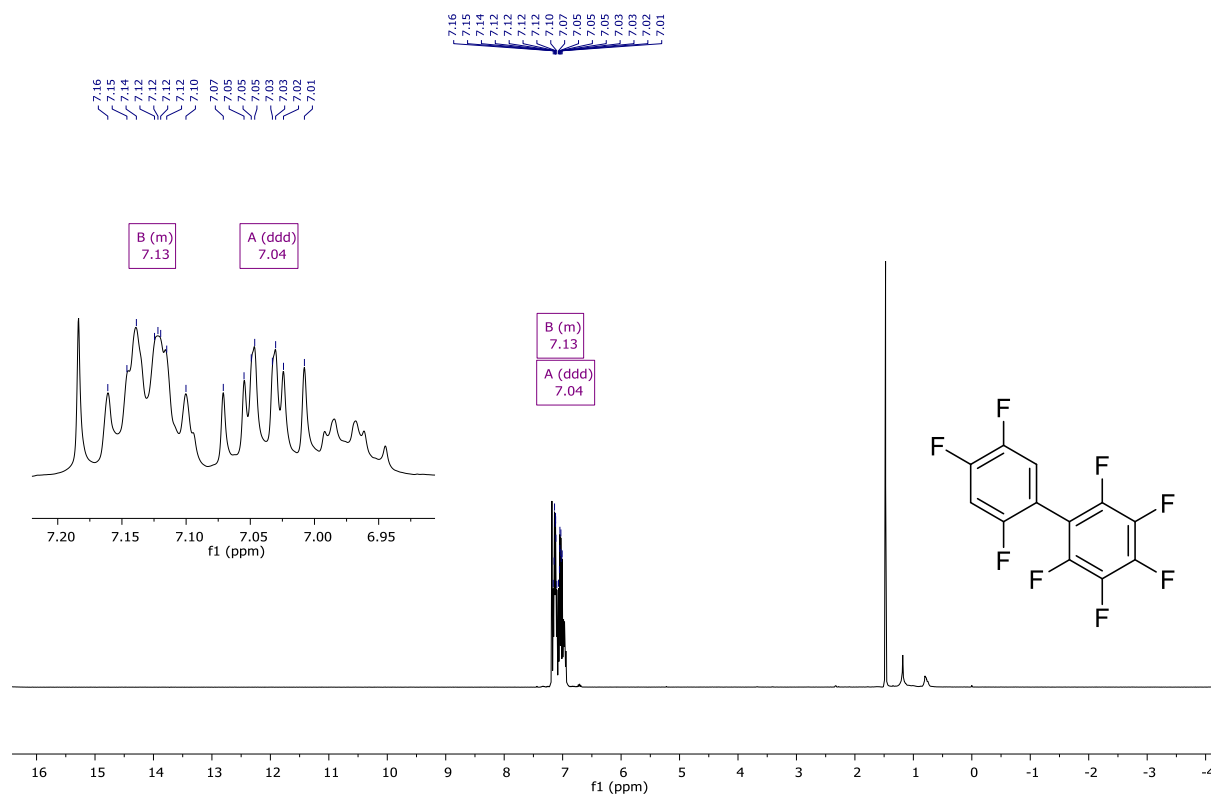
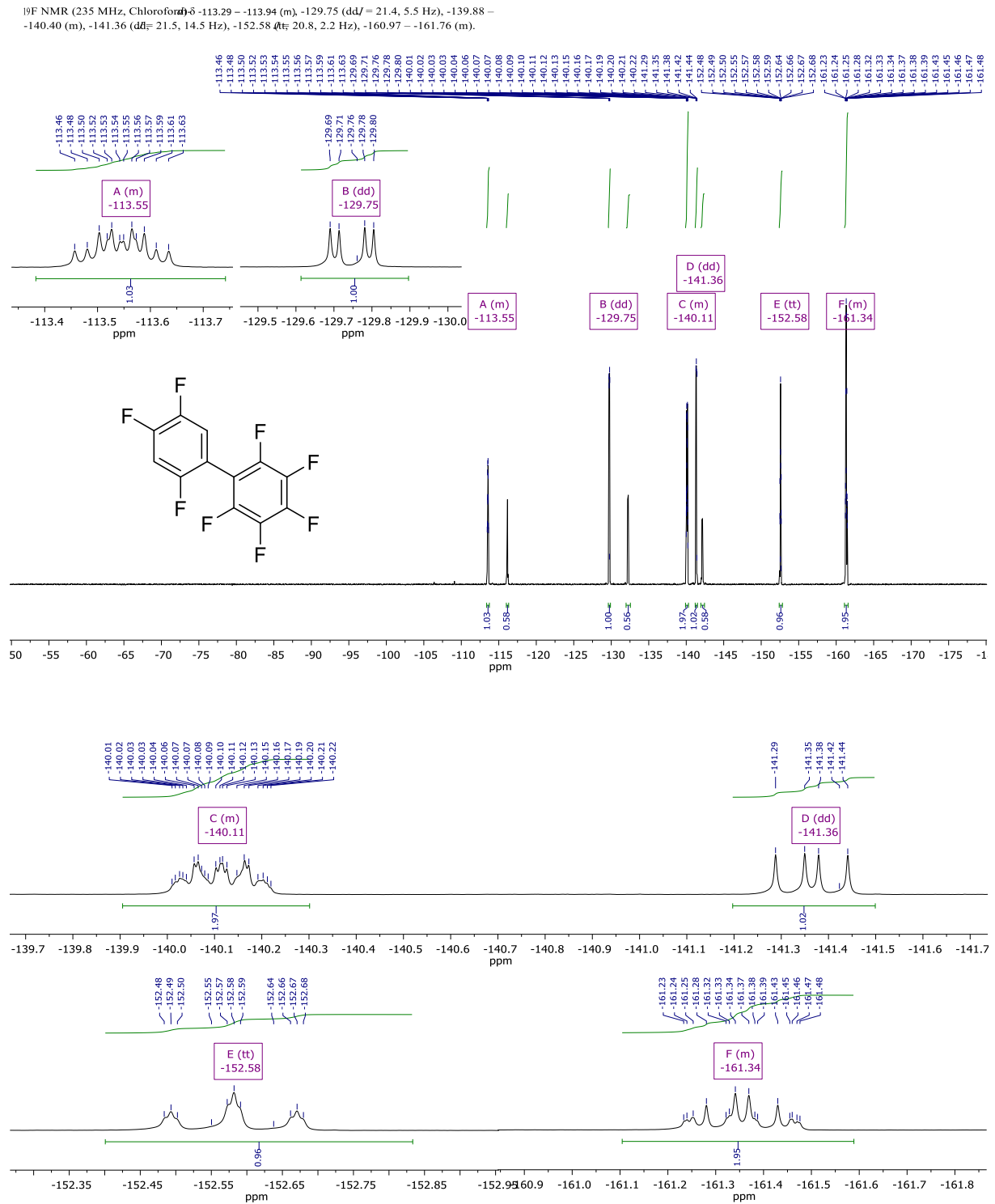


Figure S41 ¹H-NMR: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

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

^{13}C NMR (101 MHz, Chloroform- d_3) δ 155.40 (ddd, $J = 250.3, 9.5, 2.4$ Hz), 151.23 (ddd, 255.4, 14.3, 12.3 Hz), 148.29 – 145.46 (m), 145.67 – 142.95 (m), 143.03 – 140.01 (m), 139.50 – 136.18 (m), 119.72 ($d, J = 21.1$ Hz), 110.22 ($d, J = 18.6$ Hz), 108.31 ($td, J = 18.3, 4.1$ Hz), 106.45 ($dd, J = 28.0, 21.2$ Hz).

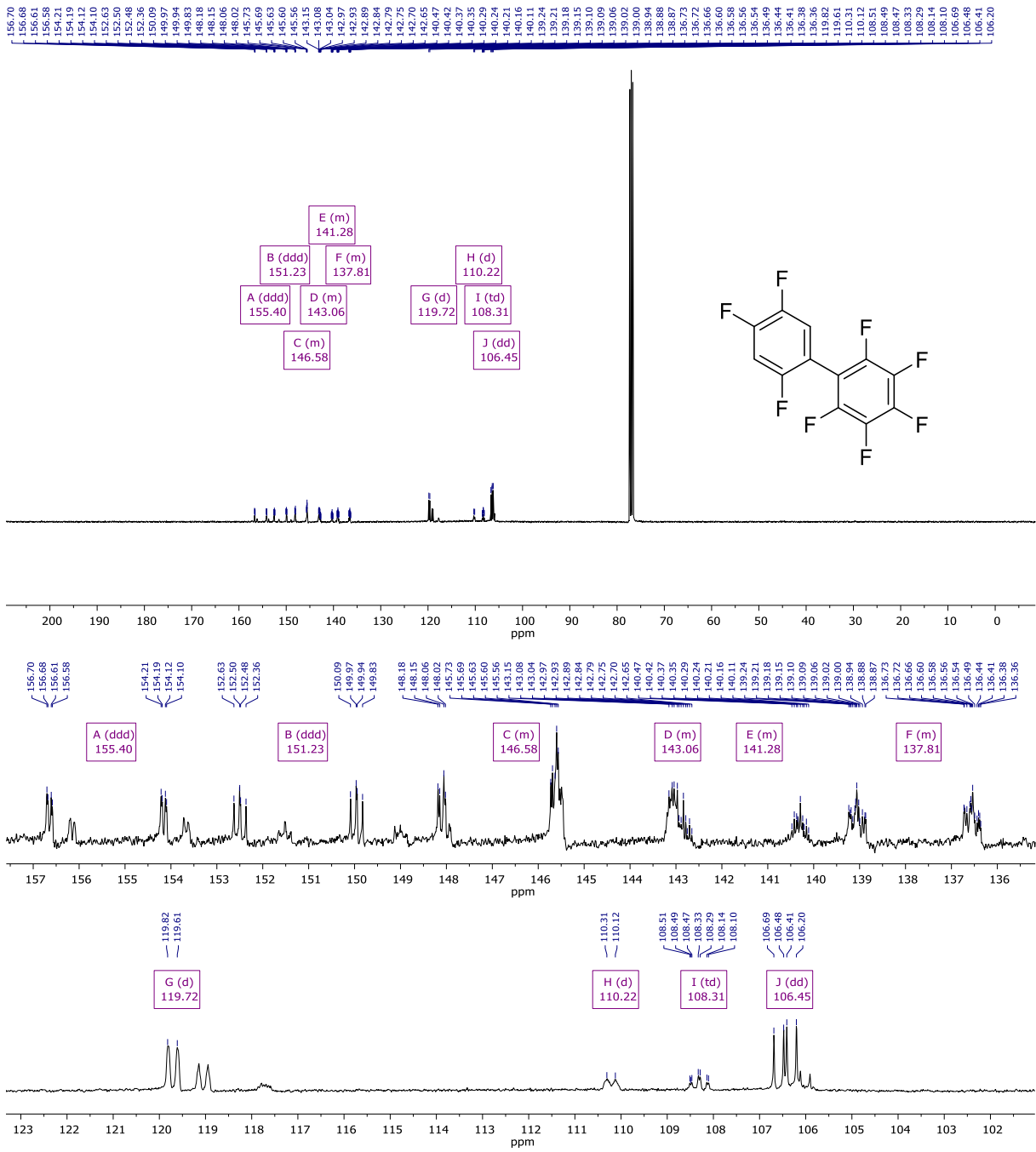


Figure S43 ^{13}C NMR: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

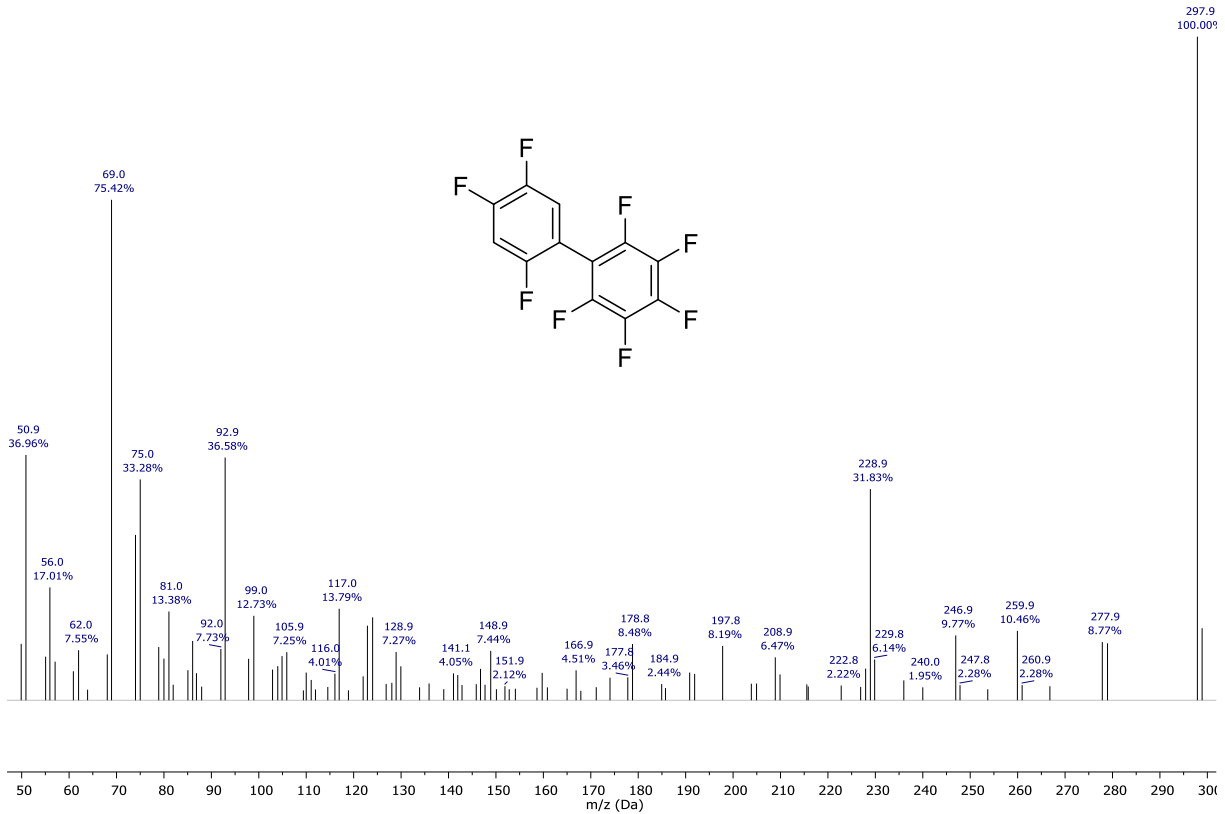
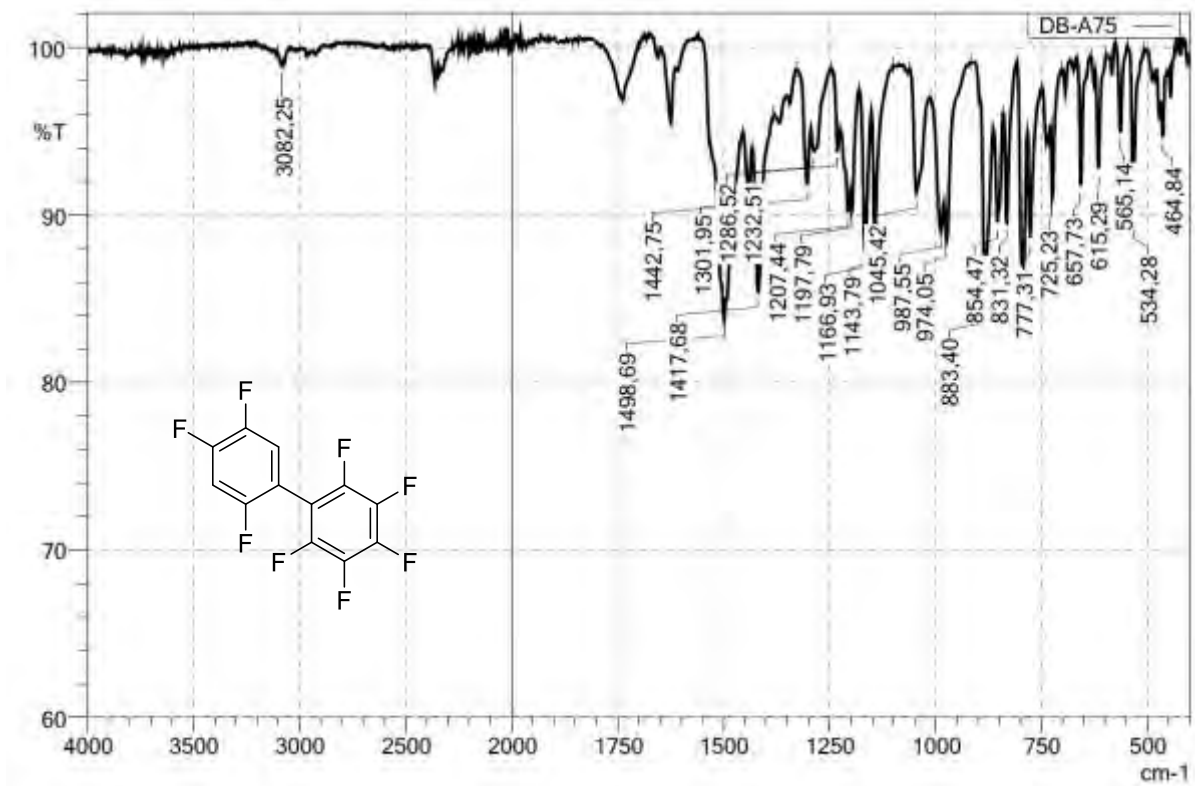
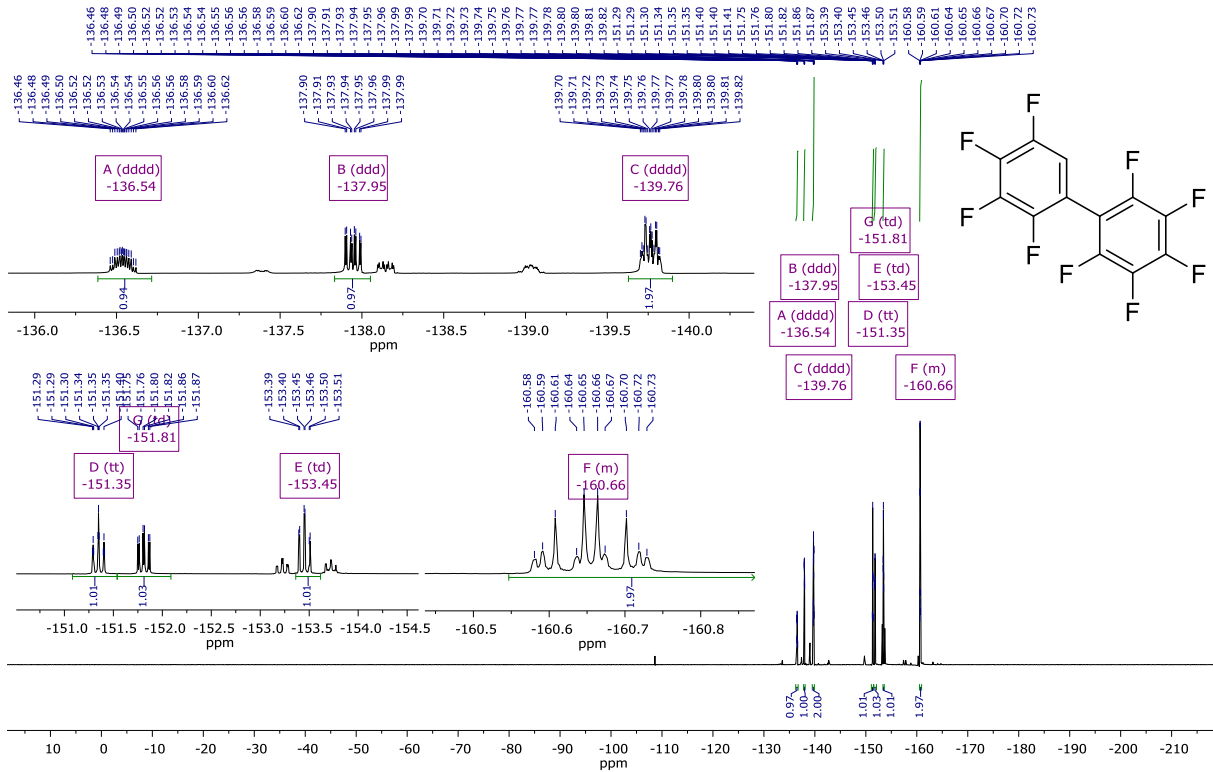
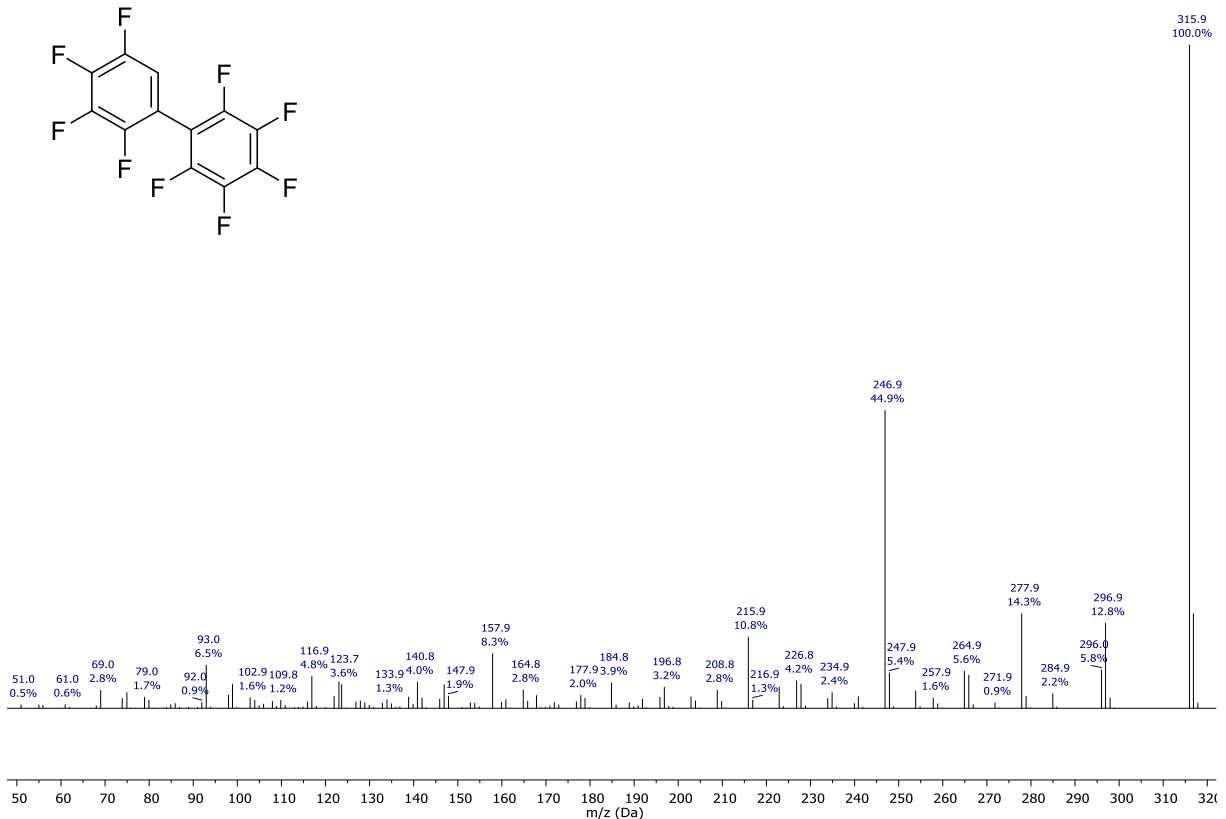
Figure S44 EI-Spectrum (EI⁺): 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

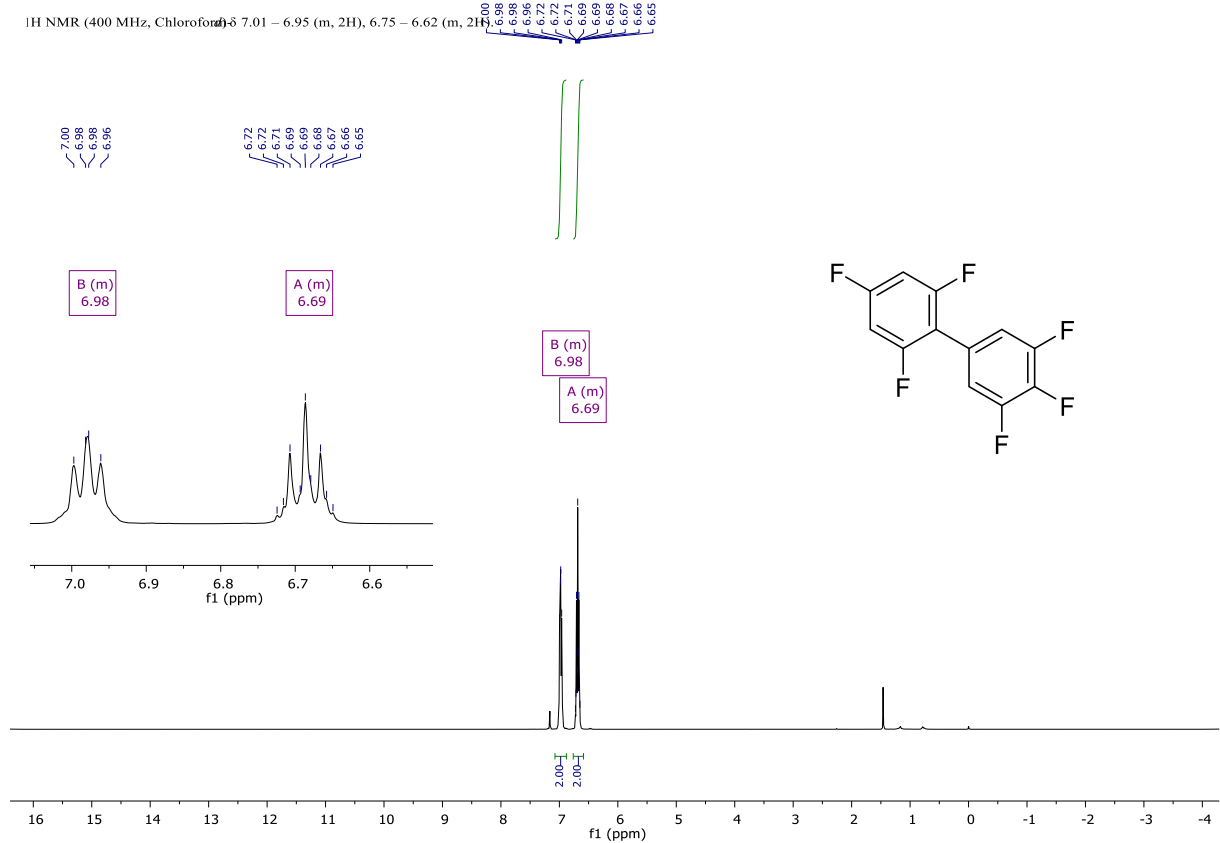
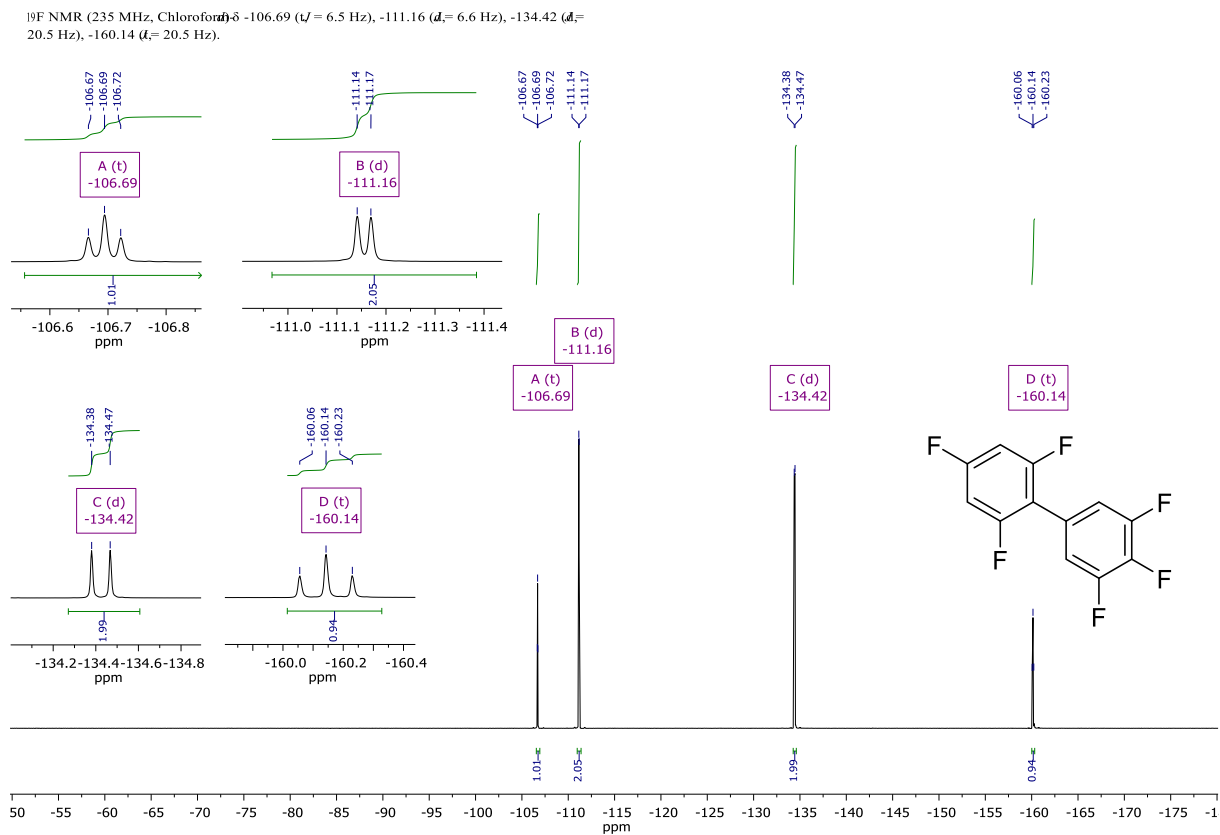
Figure S45 IR (ATR)-Spectrum: 2,2',3,4,4',5,5',6-Octafluoro-1,1'-biphenyl

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

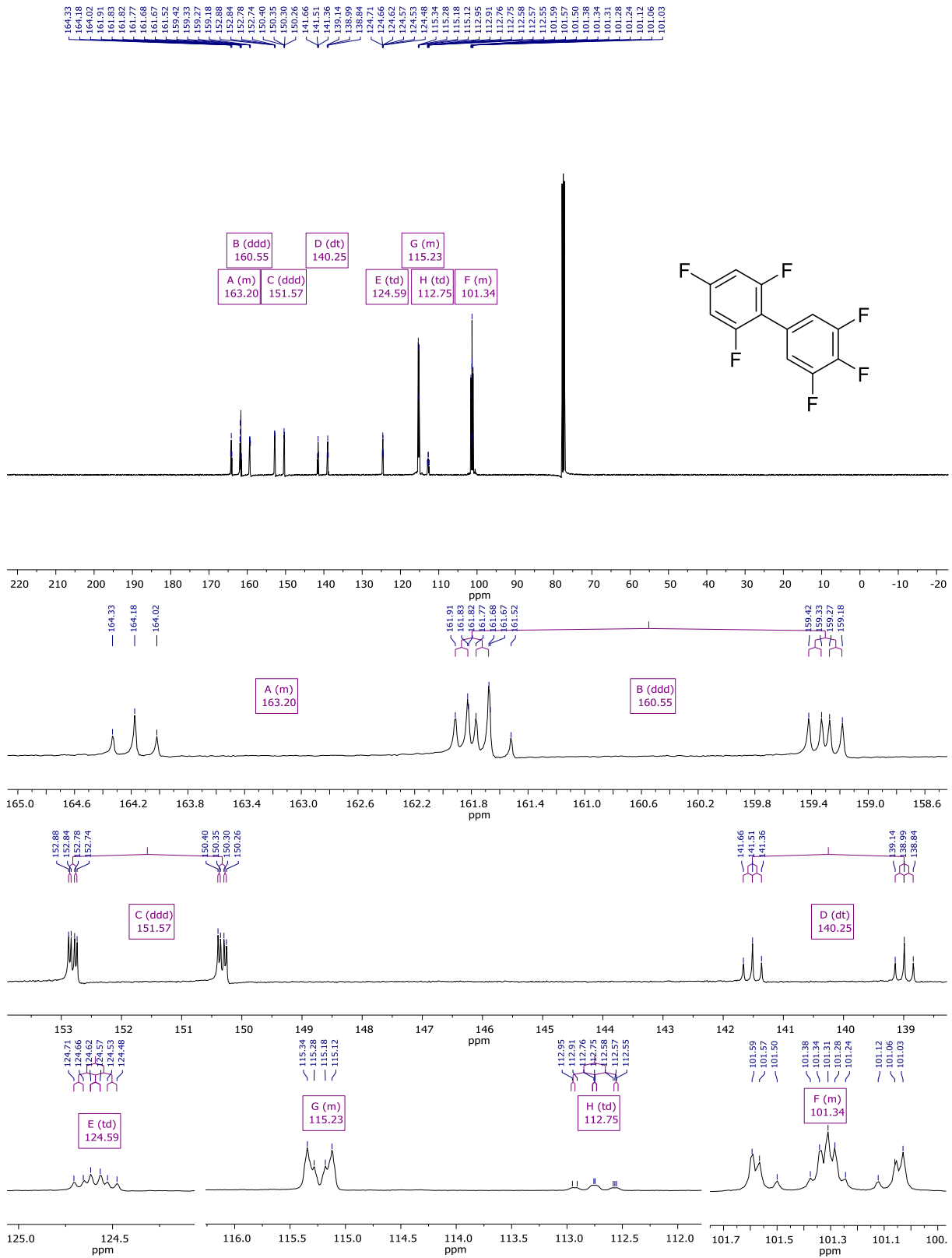
^{19}F NMR (377 MHz, Chloroform- d_3) δ -136.54 (dddd, $J = 22.6, 20.9, 10.7, 5.6$ Hz), -137.95 (ddd, 21.2, 12.0, 3.2 Hz), -139.76 (ddd, $J = 23.2, 9.5, 6.7, 3.1$ Hz), -151.35 (tt, 20.7, 2.4 Hz), -151.81 (xt, $J = 20.5, 5.5$ Hz), -153.45 (xt, $J = 20.1, 3.4$ Hz), -160.56 (-160.76 (m).

Figure S46 ^{19}F -NMR (^1H): 2,2',3,3',4,4',5,5',6-Nonafluoro-1,1'-biphenylFigure 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 $^1\text{H-NMR}$: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenylFigure S49 $^{19}\text{F-NMR}$ $\{^1\text{H}\}$: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

^{13}C NMR (101 MHz, Chloroform- d_3) δ 164.45 – 161.42 (m), 160.55 (ddd; 250.9, 14.7, 8.9 Hz),
 151.57 (ddd/ ν = 249.7, 10.0, 4.2 Hz), 140.25 (dt; 253.8, 15.1 Hz), 124.59 (td; 9.0, 5.1 Hz), 115.50
 – 114.86 (m), 112.75 (ν / ν = 19.5, 3.6 Hz), 101.97 – 100.81 (m).



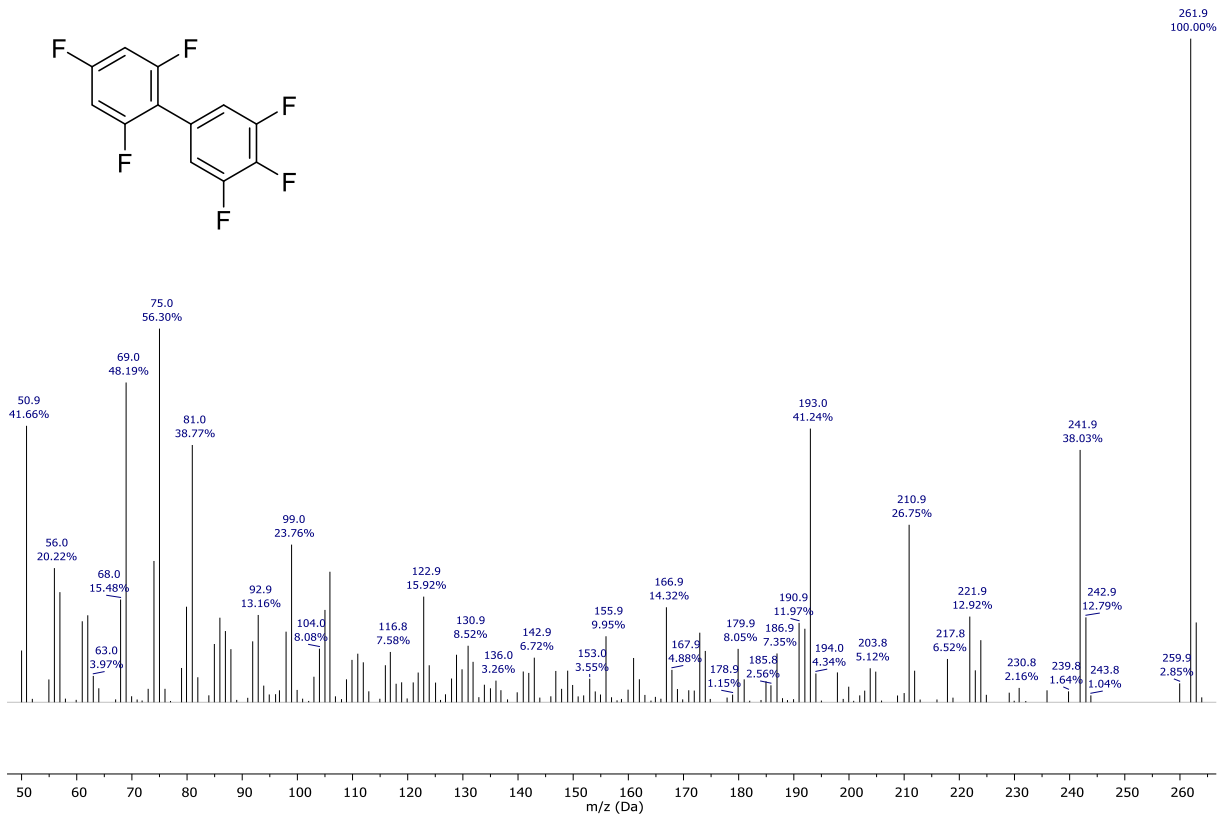
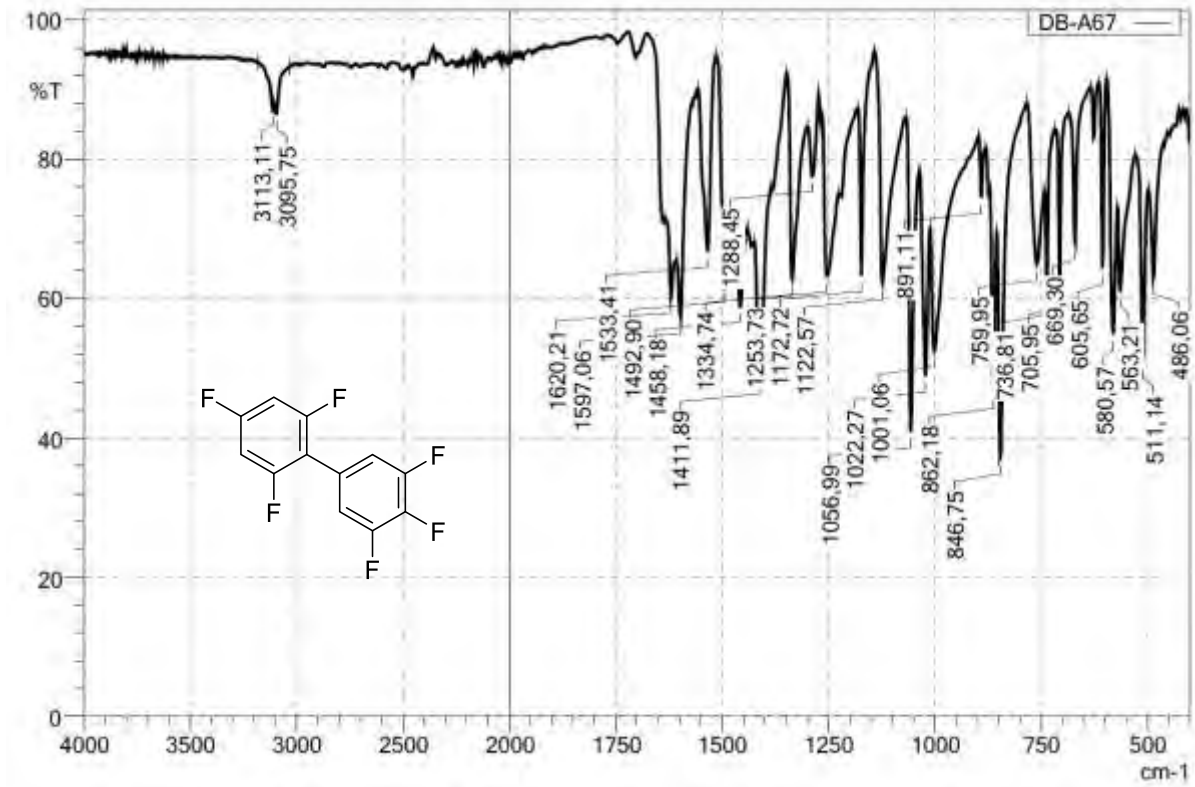
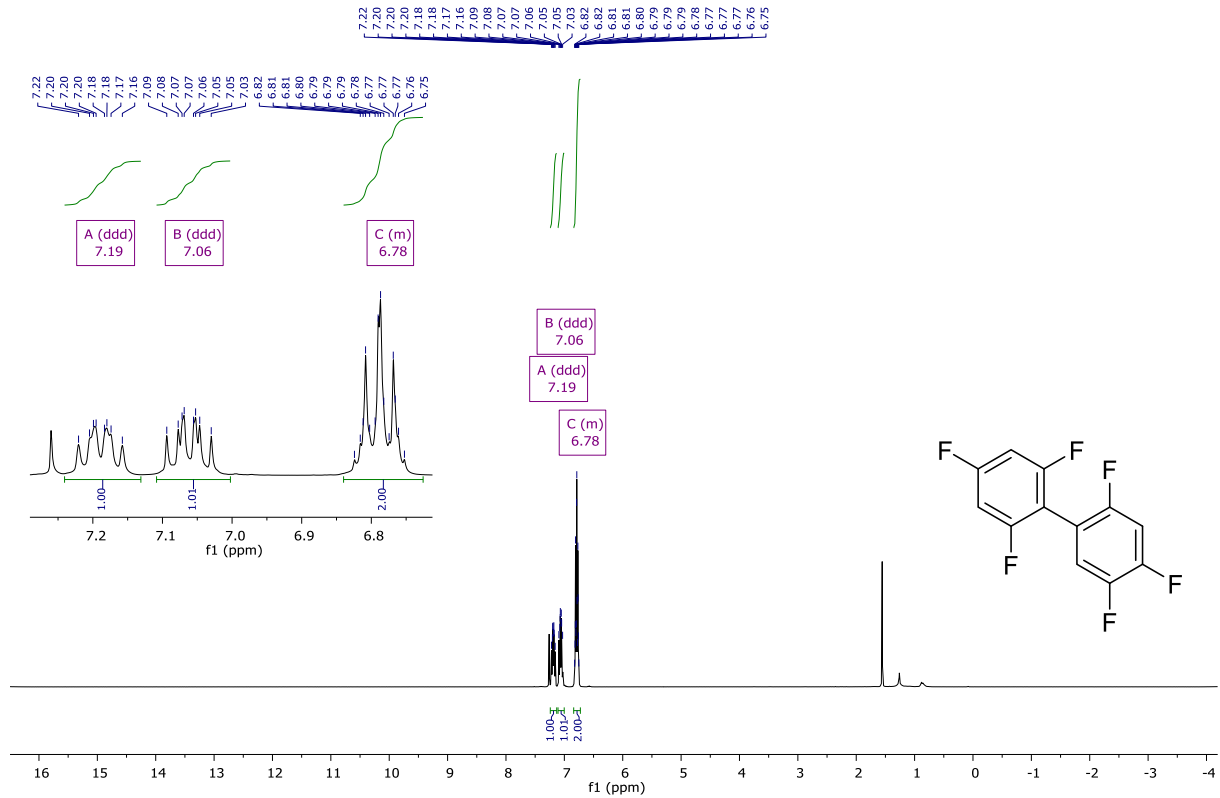
Figure S51 EI-Spectrum (EI⁺): 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

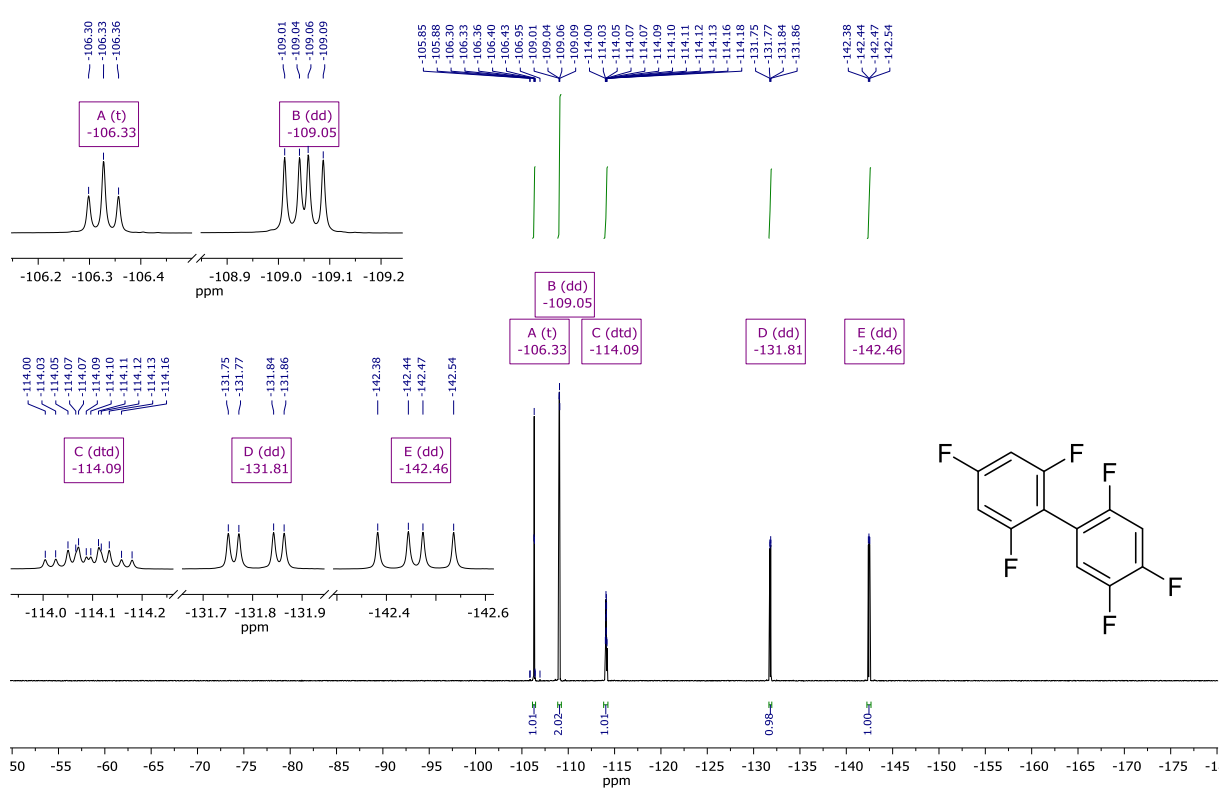
Figure S52 IR (ATR)-Spectrum: 2,3',4,4',5',6-Hexafluoro-1,1'-biphenyl

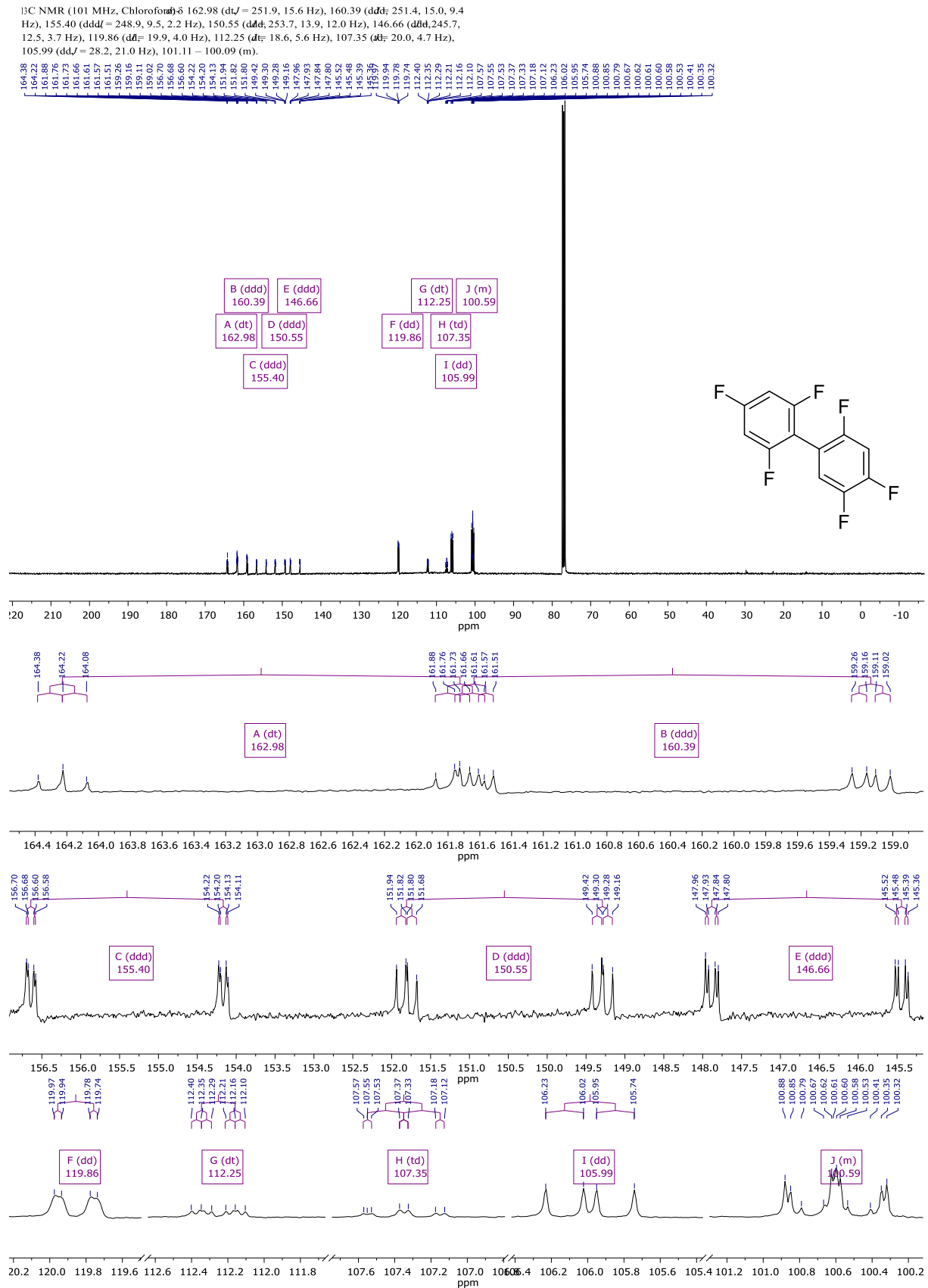
2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl (26)

$^1\text{H NMR}$ (400 MHz, Chloroform- d_3) δ 7.19 (ddd, $J = 10.3, 8.7, 6.4$ Hz, 1H), 7.06 (ddd, 10.2, 8.9, 6.6 Hz, 1H), 6.84 – 6.74 (m, 2H).

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

$^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) 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, 21.5, 5.0 Hz), -142.46 (dd, 21.5, 14.6 Hz).

Figure S54 $^{19}\text{F-NMR}$ [^1H]: 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

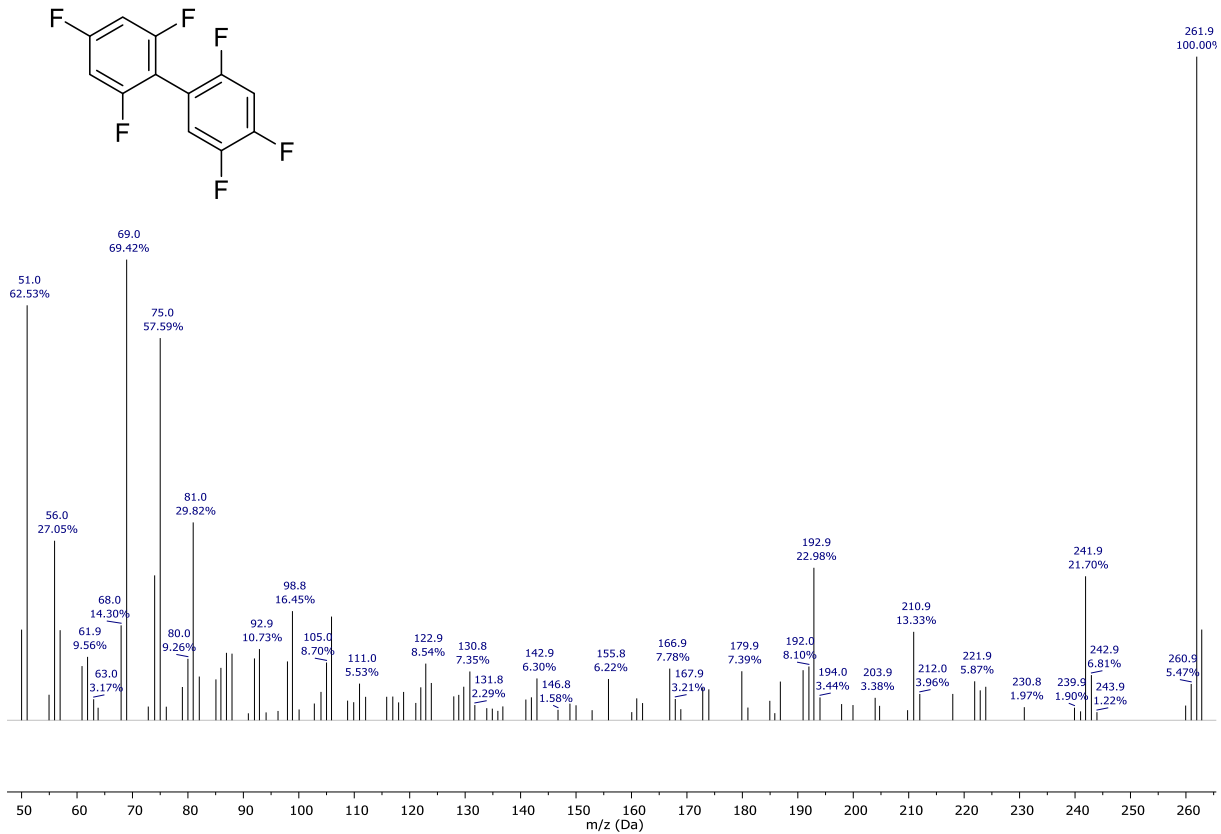
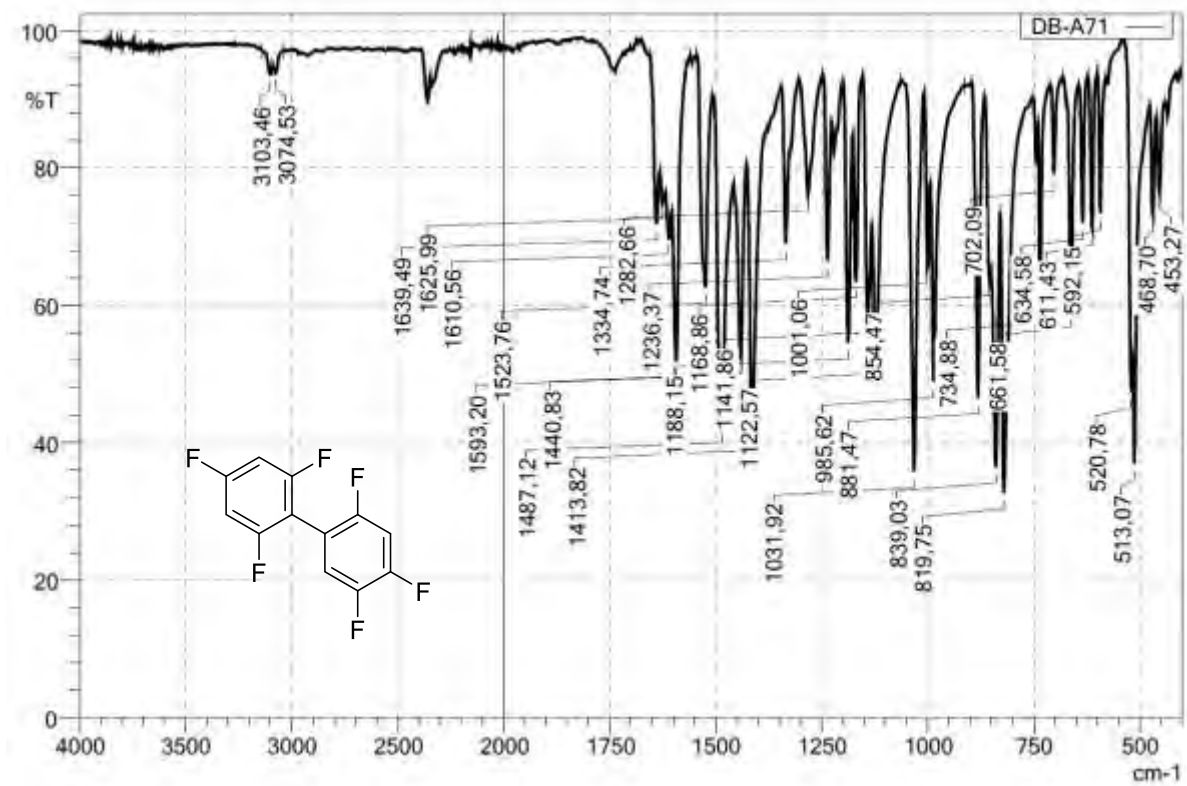
Figure S56 EI-Spectrum (EI⁺): 2,2',4,4',5,6'-Hexafluoro-1,1'-biphenyl

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)

¹H NMR (400 MHz, Chloroform-d) δ 7.04 – 6.95 (m, 1H), 6.86 – 6.76 (m, 2H).

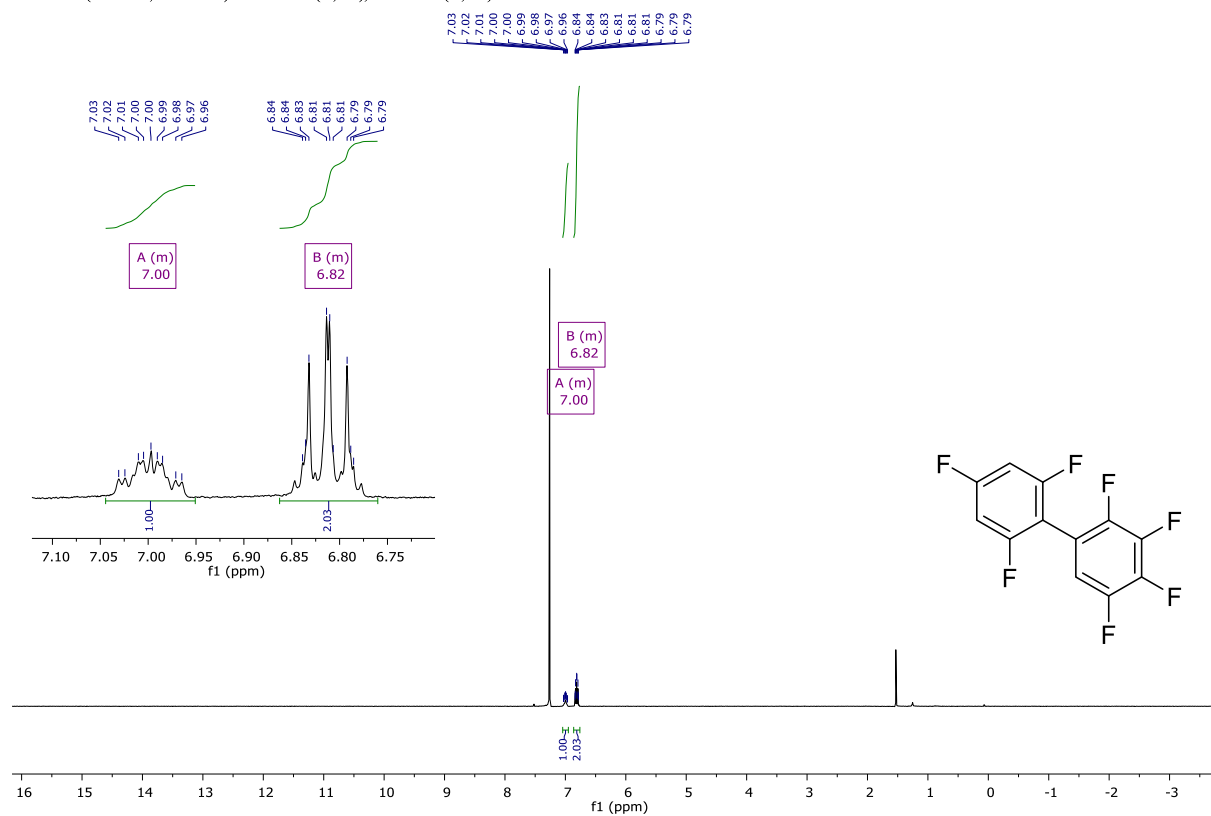
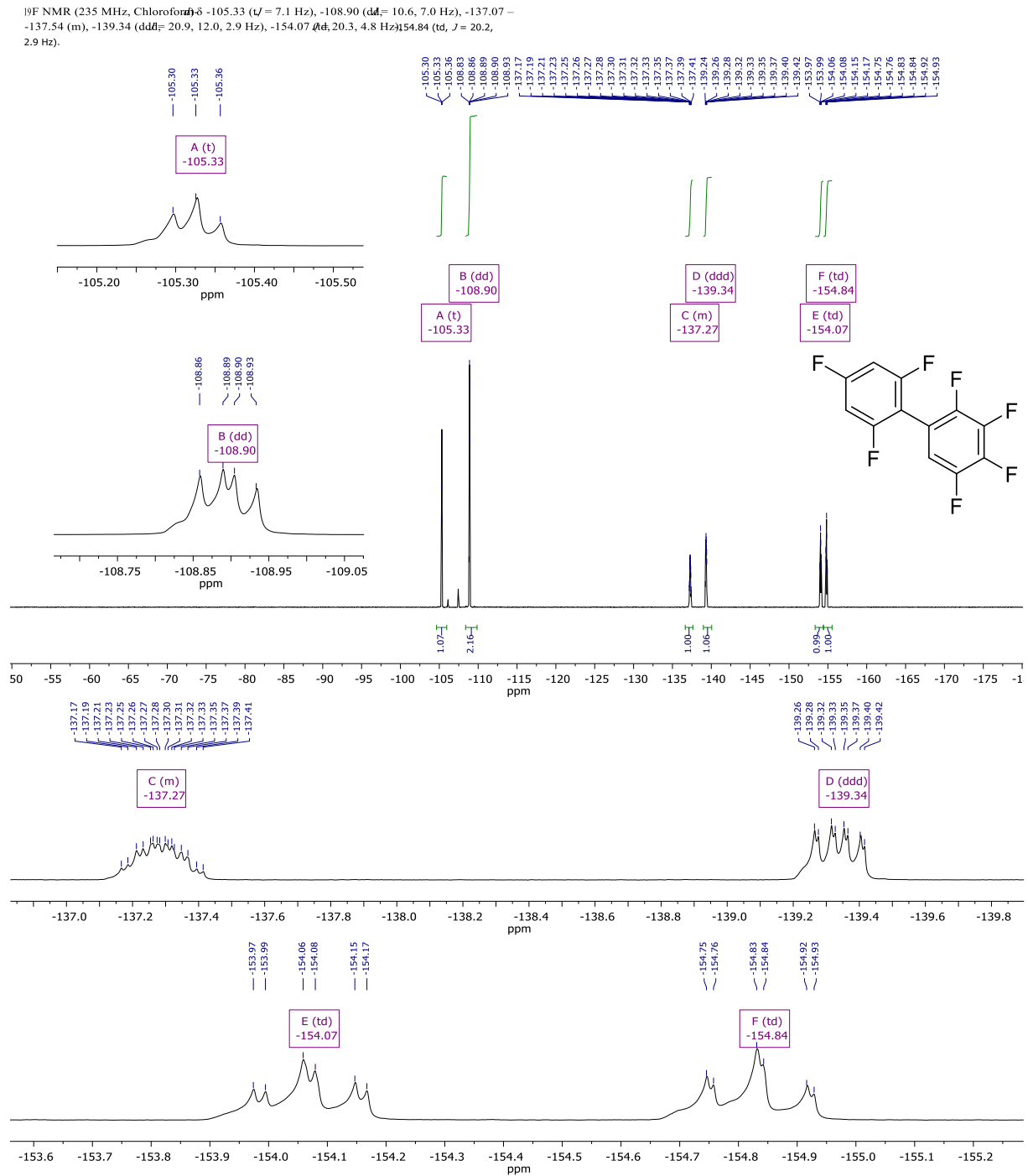
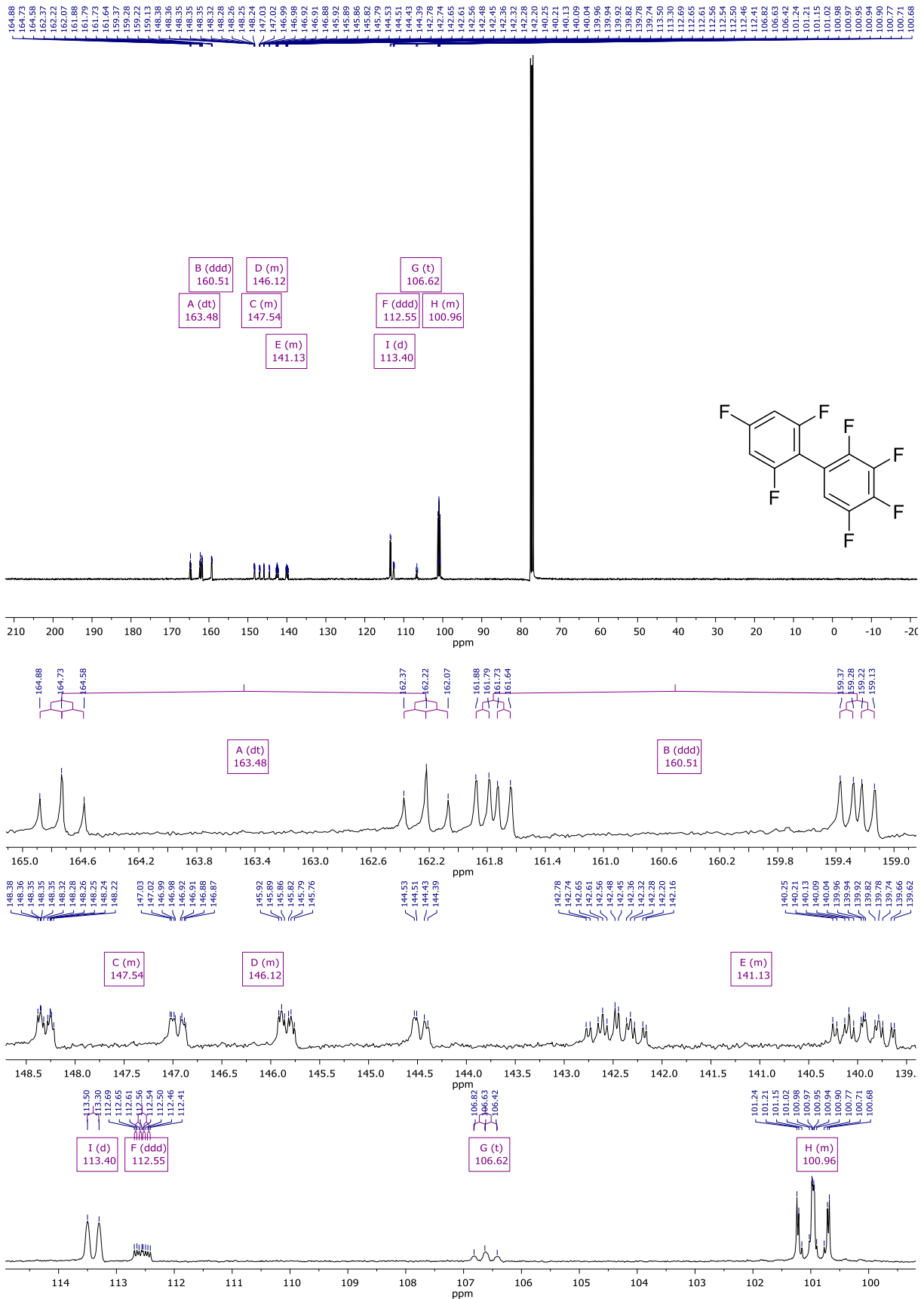


Figure S58 ¹H-NMR: 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

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

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

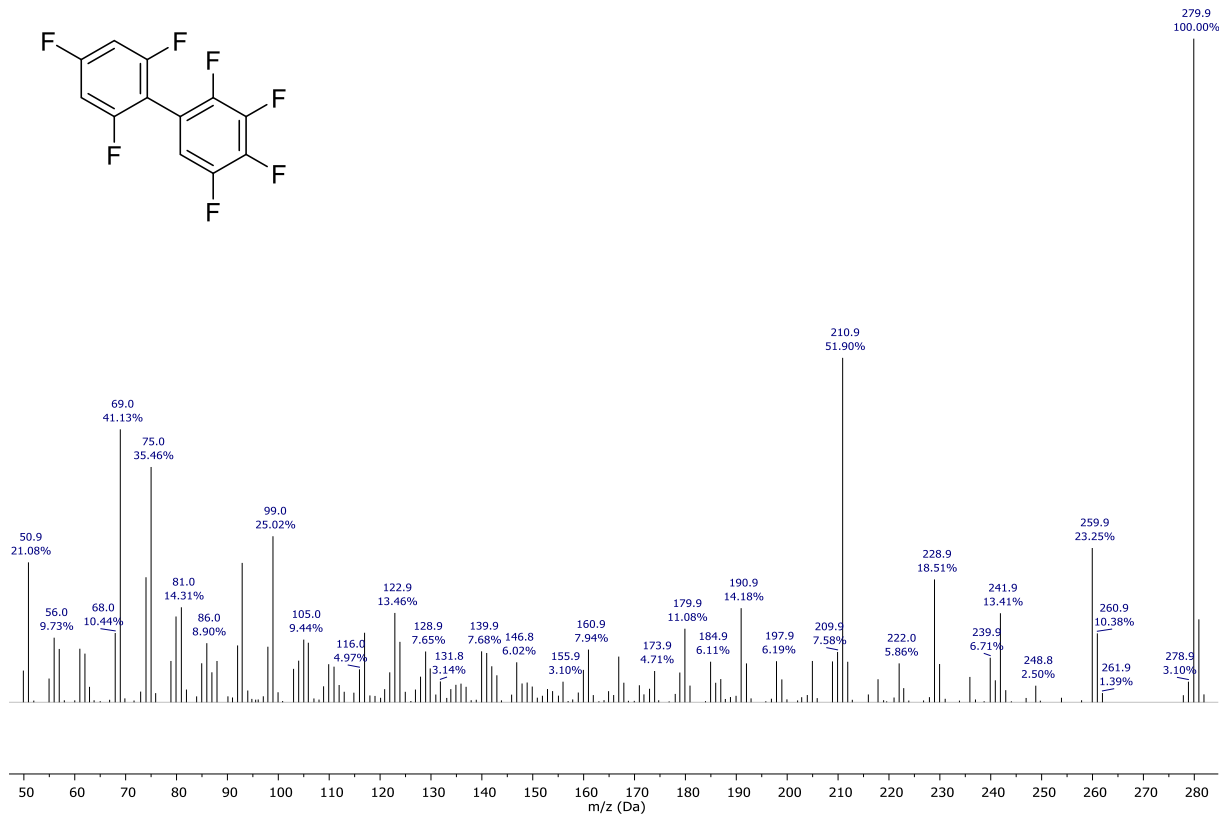
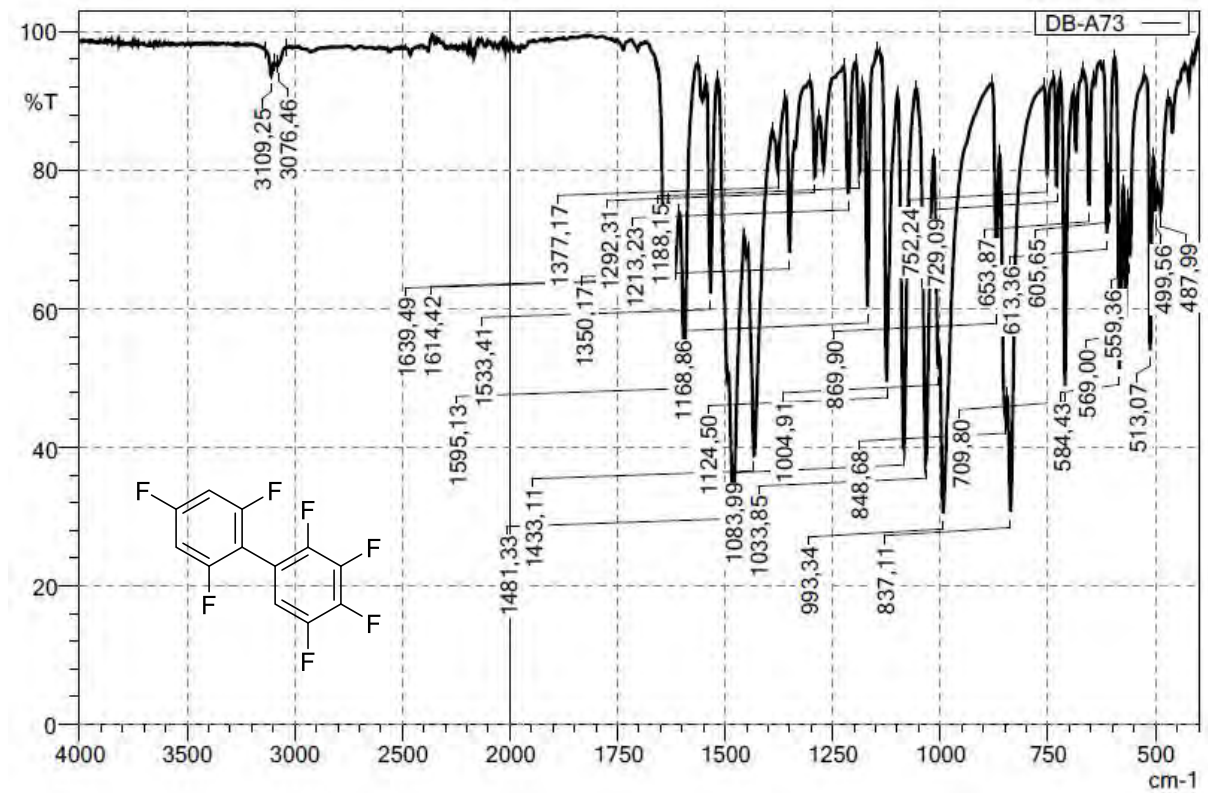
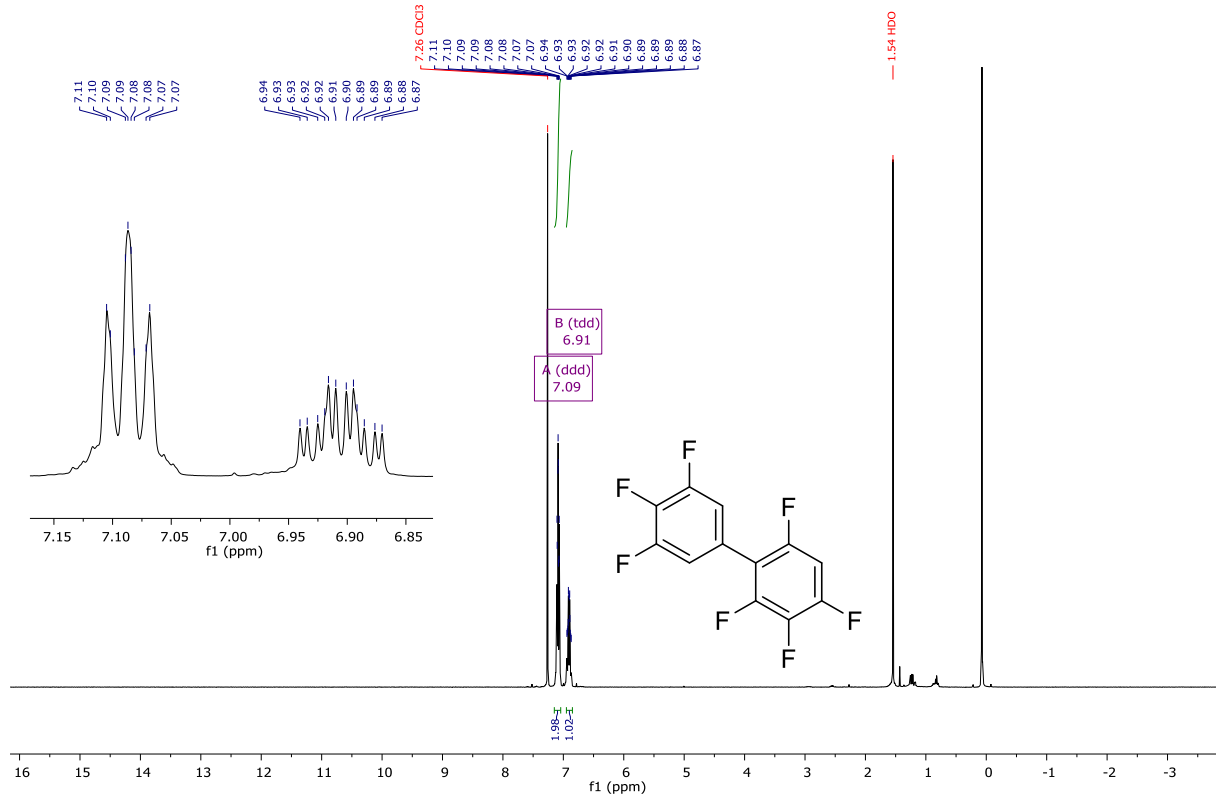
Figure S61 EI-Spectrum (EI⁺): 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

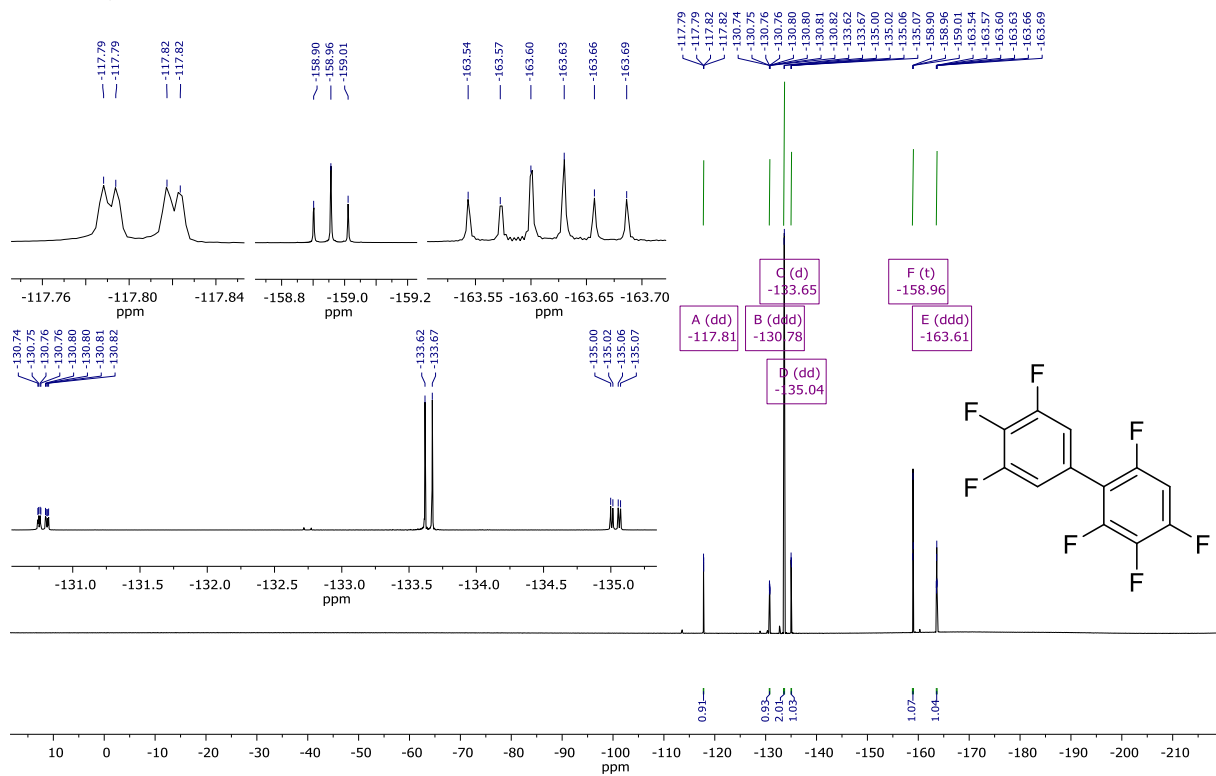
Figure S62 IR (ATR)-Spectrum: 2,2',3,4,4',5,6'-Heptafluoro-1,1'-biphenyl

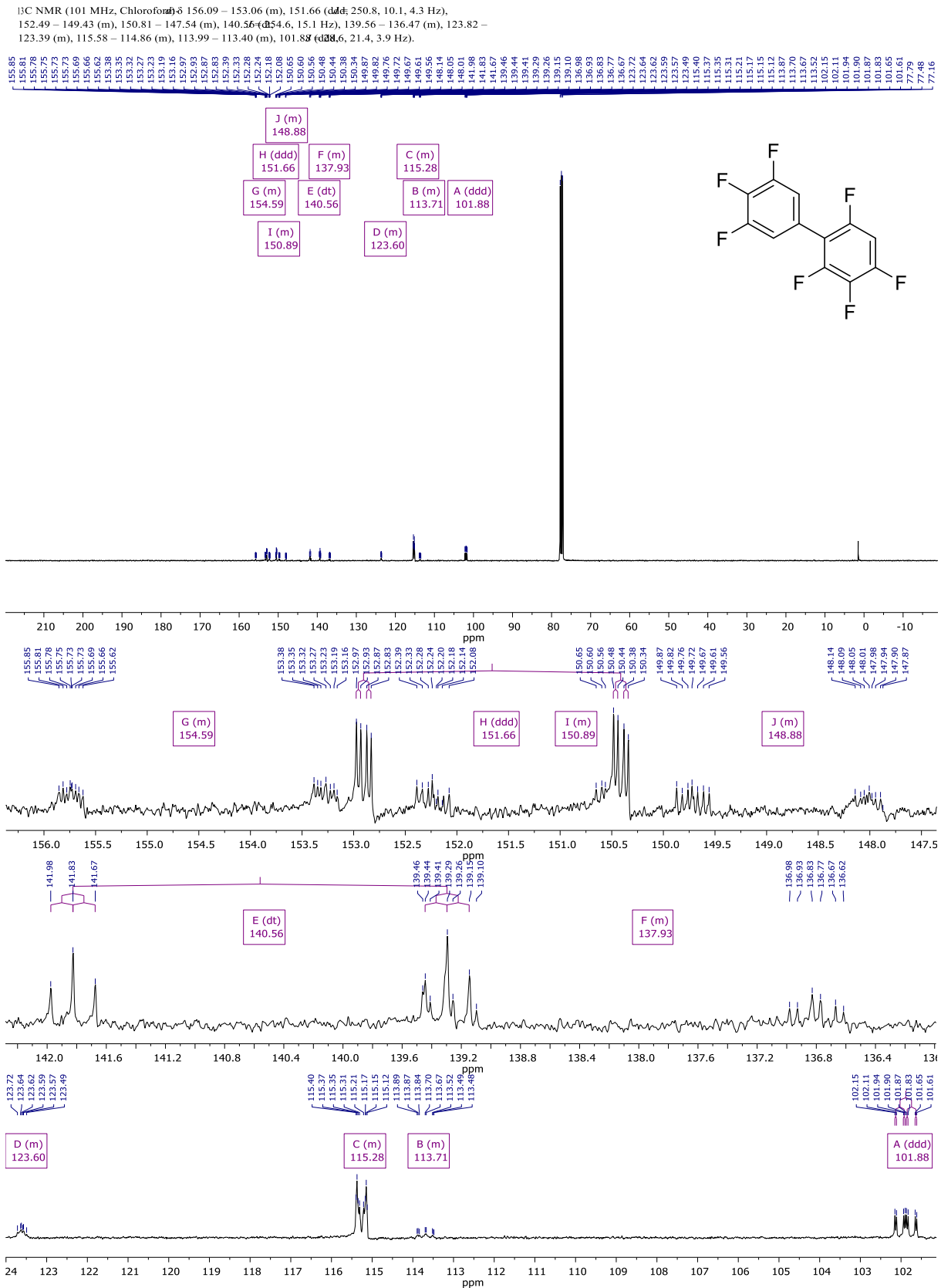
2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl (28)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.09 (ddd, $J = 7.5, 6.4, 1.3$ Hz, 1H), 6.91 (tdd, 9.8, 6.1, 2.5 Hz, 1H).

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

$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -117.81 (dd, $J = 11.1, 2.2$ Hz), -130.78 (ddt, 21.7, 6.4, 2.4 Hz), -133.65 (d, 20.5 Hz), -135.04 (dd, 21.3, 6.3 Hz), -158.96 (t, 20.6 Hz), -163.61 (ddd, 21.2, 10.9 Hz).

Figure S64 $^{19}\text{F-NMR}$ $\{^1\text{H}\}$: 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

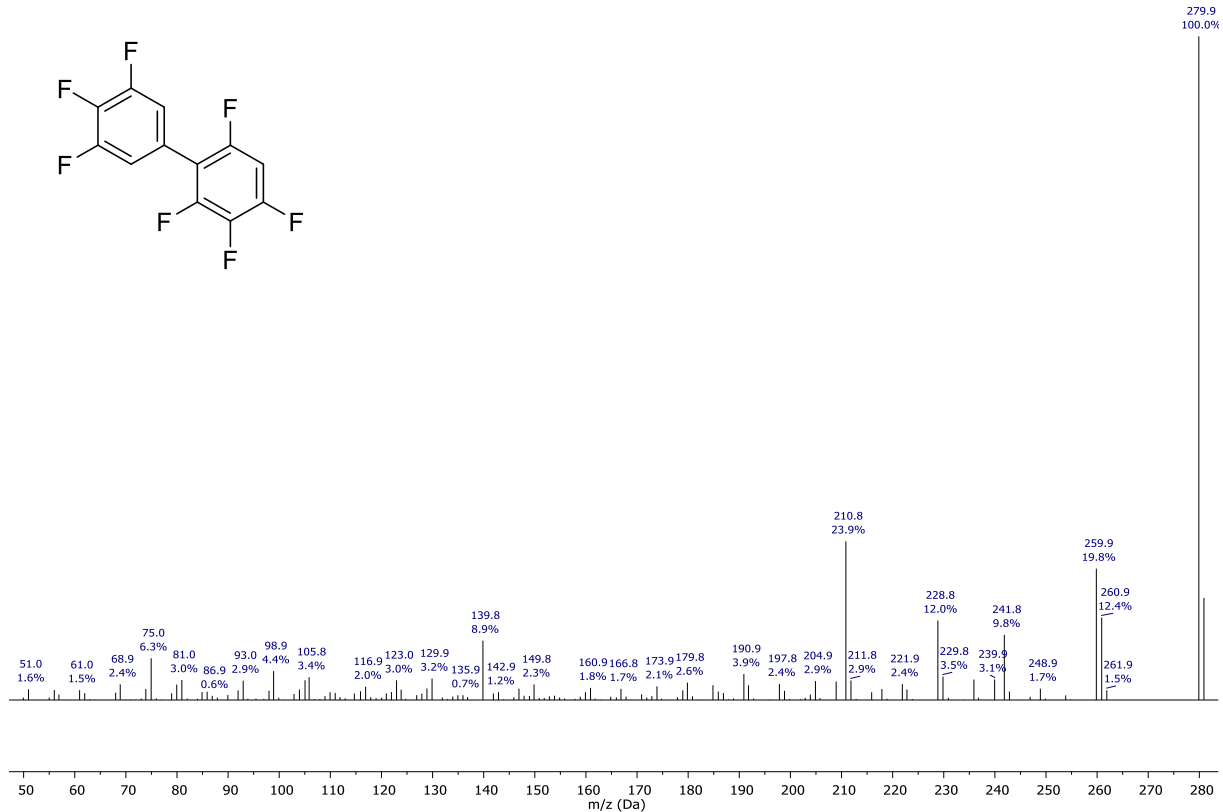
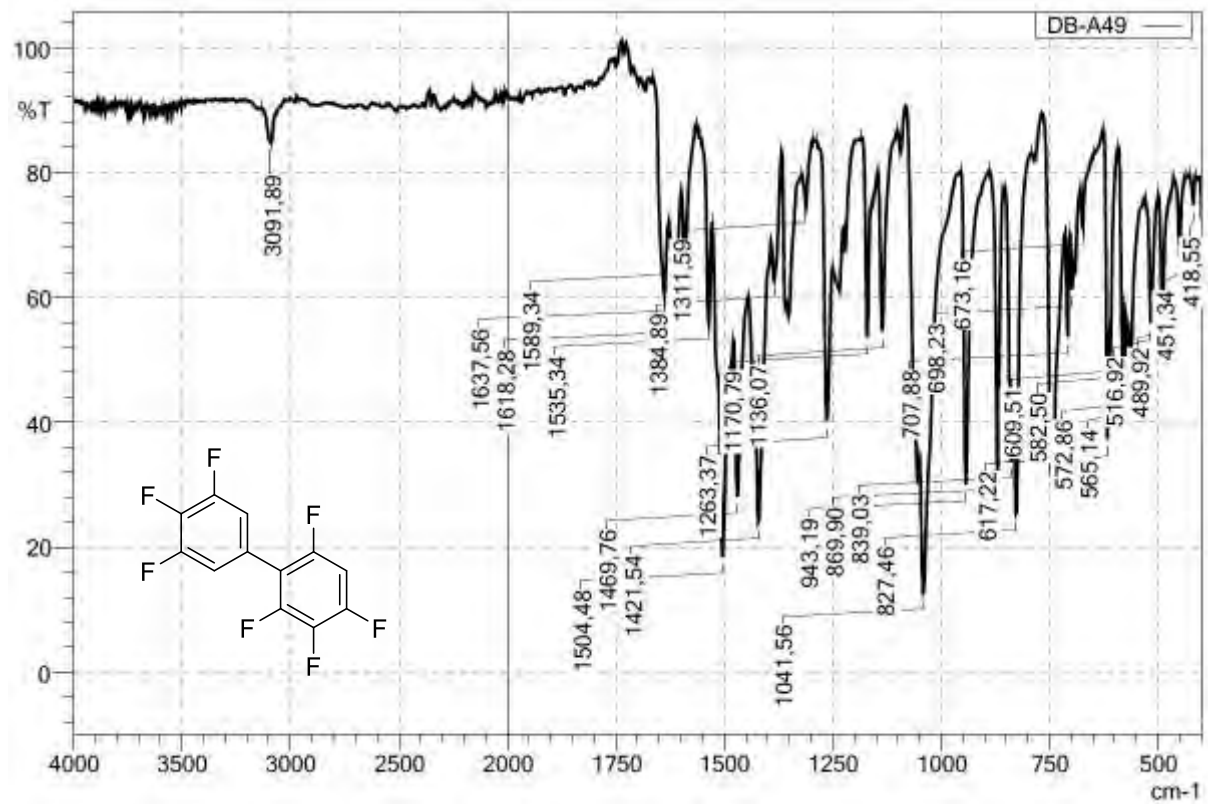
Figure S66 EI-Spectrum (EI⁺): 2,3,3',4,4',5',6-Heptafluoro-1,1'-biphenyl

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

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

$^1\text{H NMR}$ (400 MHz, Chloroform- d_3) δ 7.22 – 6.96 (m, 1H).

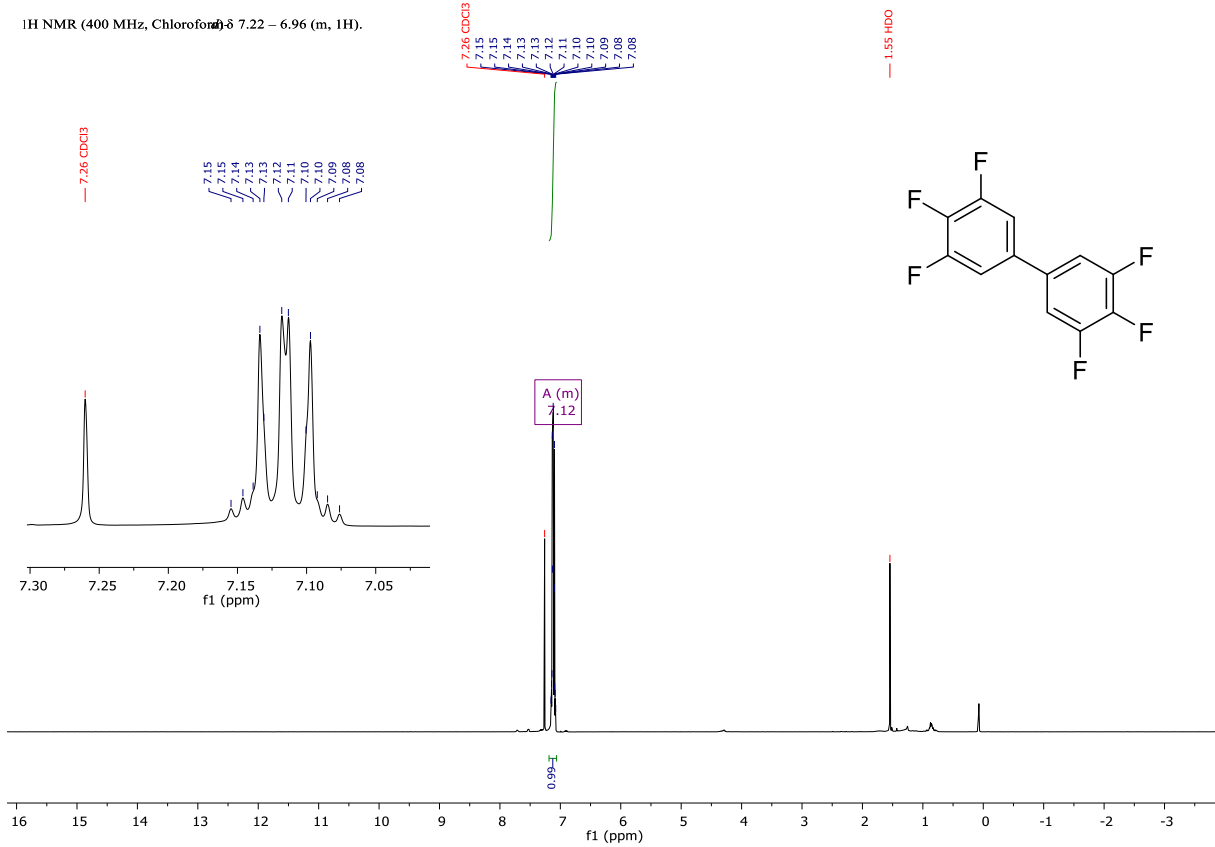


Figure S68 $^1\text{H-NMR}$: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

$^{19}\text{F NMR}$ (377 MHz, Chloroform- d_3) δ -132.75 (d, $J = 20.7$ Hz), -160.30 (t, $J = 20.4$ Hz).

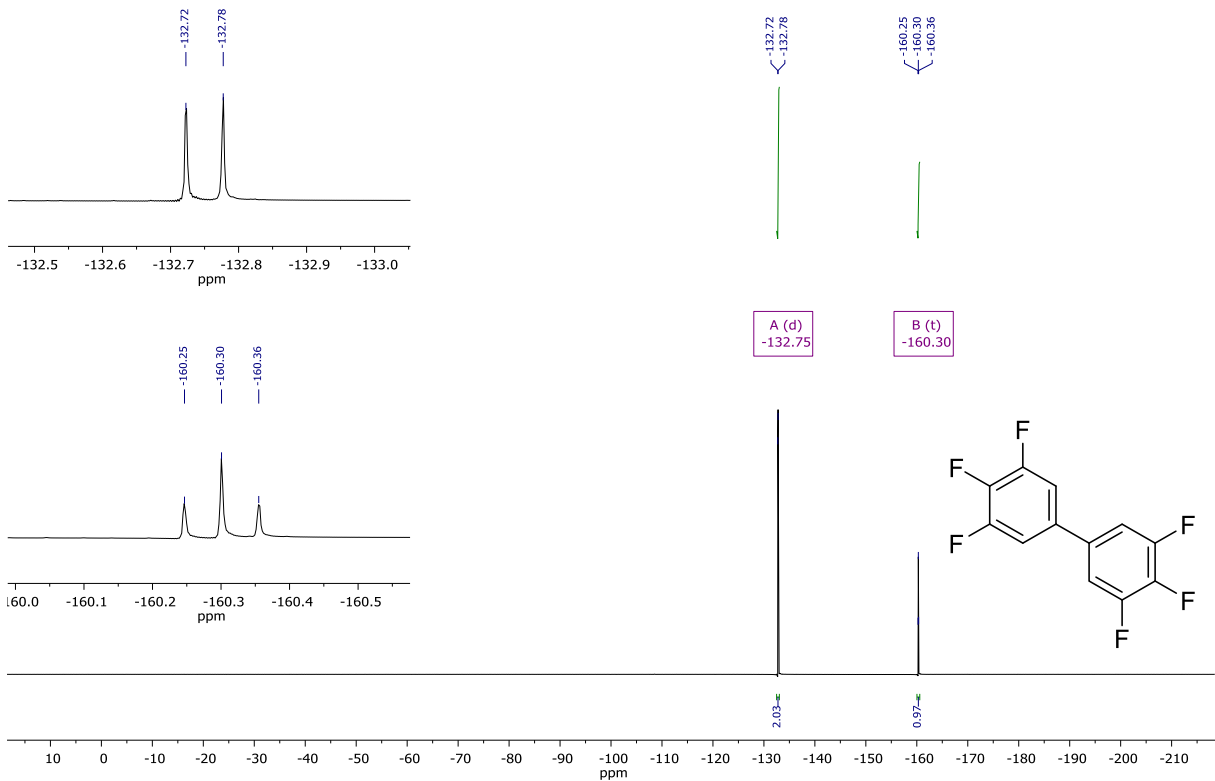
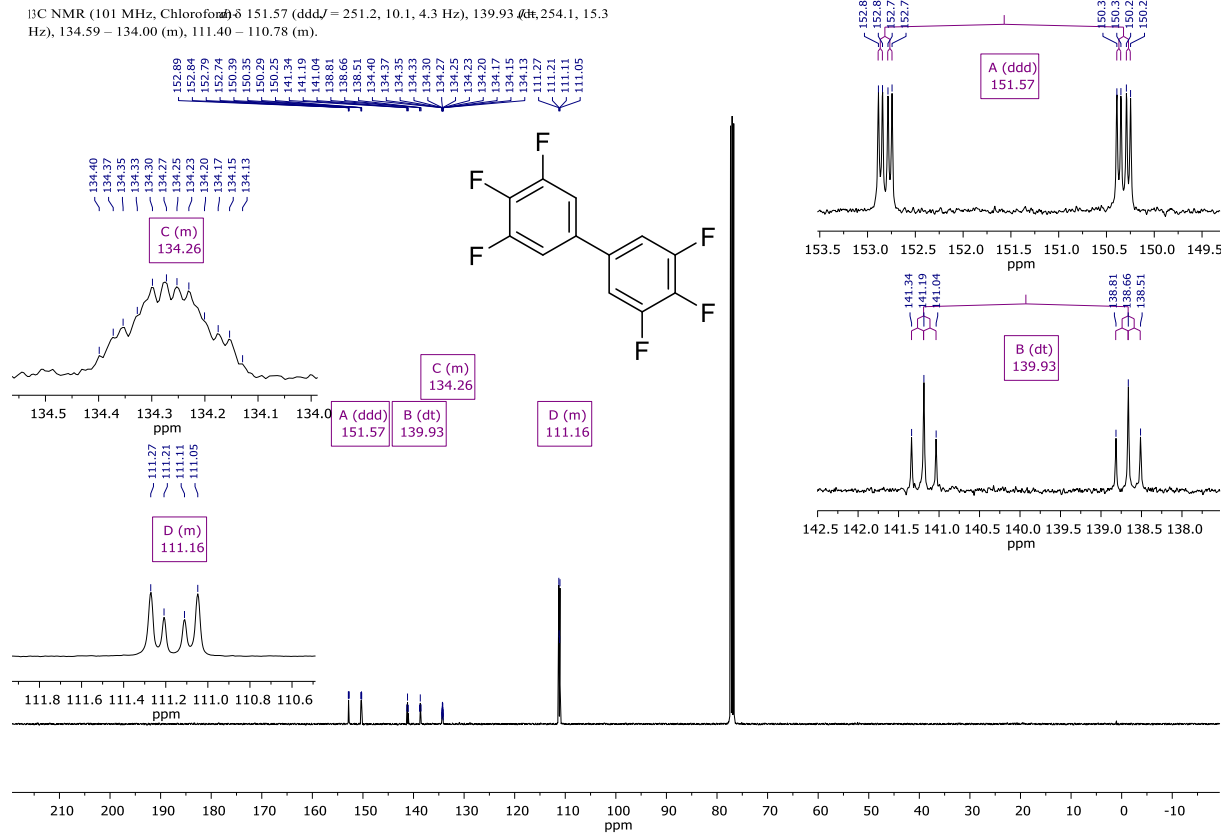
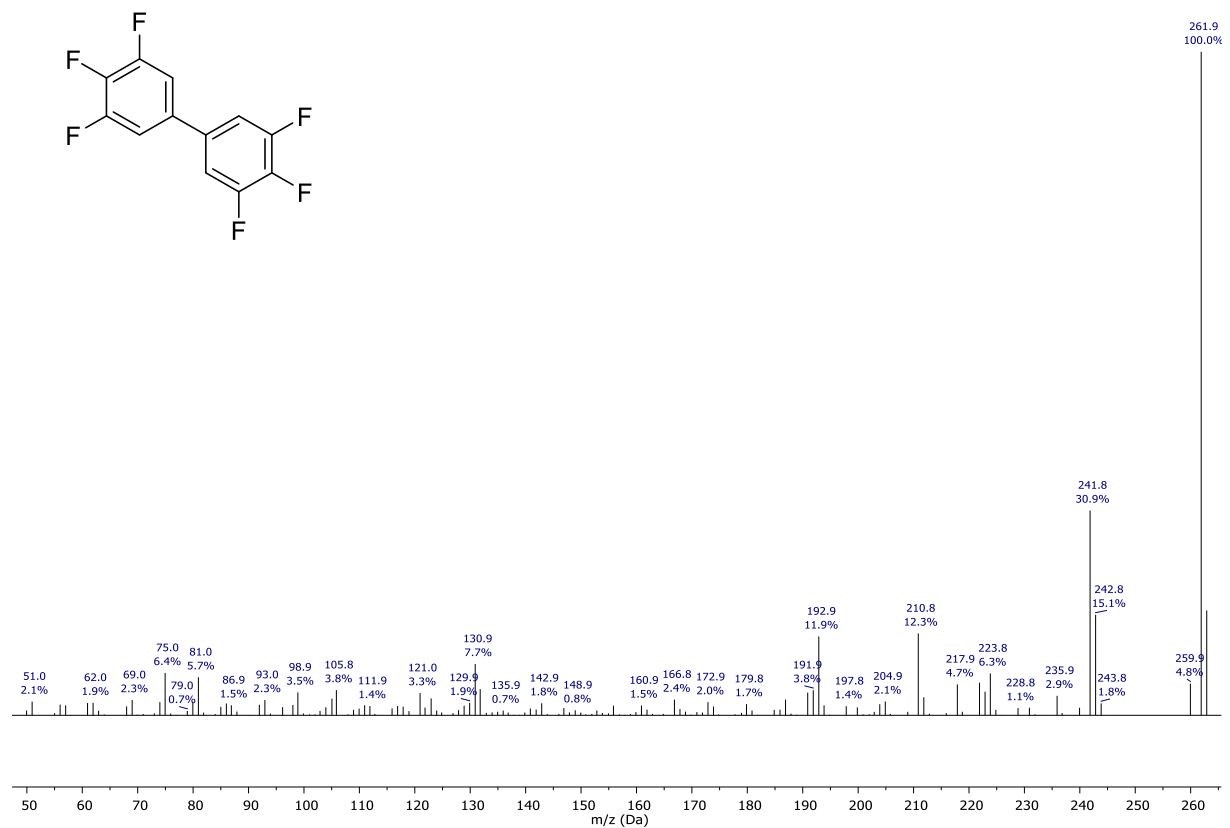


Figure S69 $^{19}\text{F-NMR}$ $\{^1\text{H}\}$: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

Figure S70 ^{13}C NMR: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenylFigure S71 EI-Spectrum (EI $^+$): 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

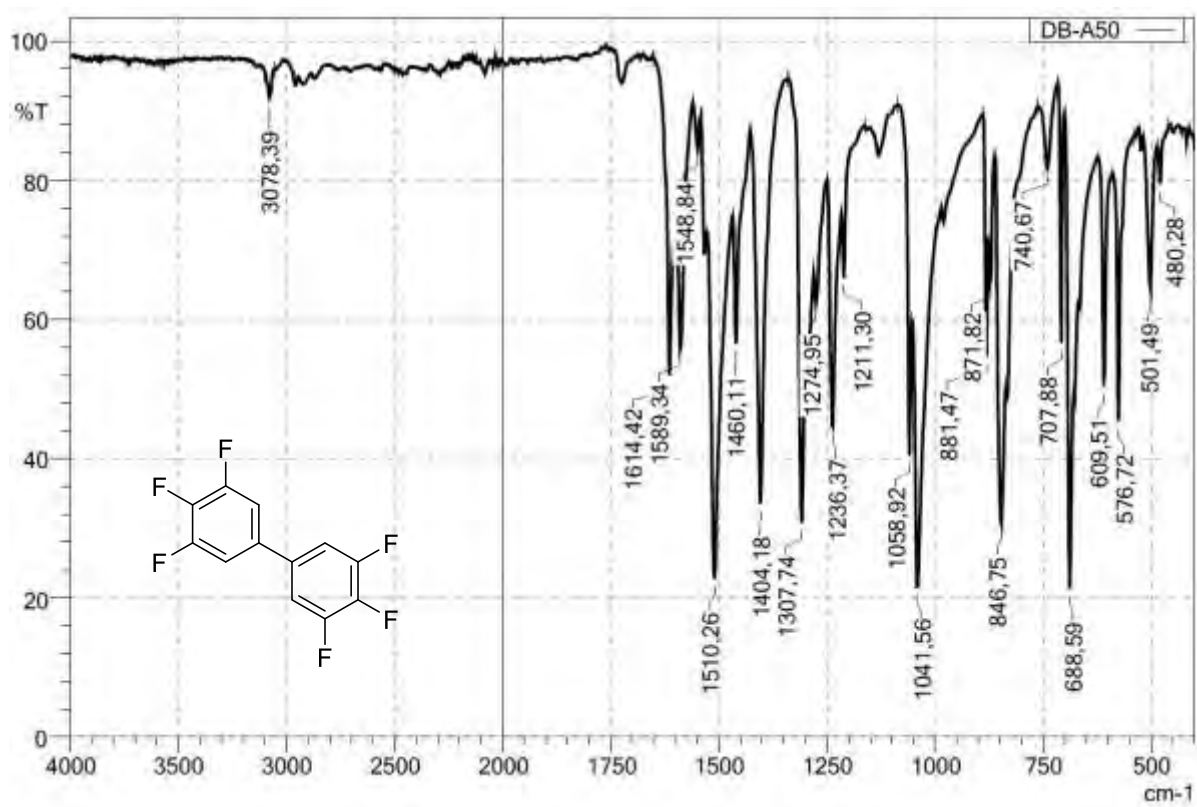
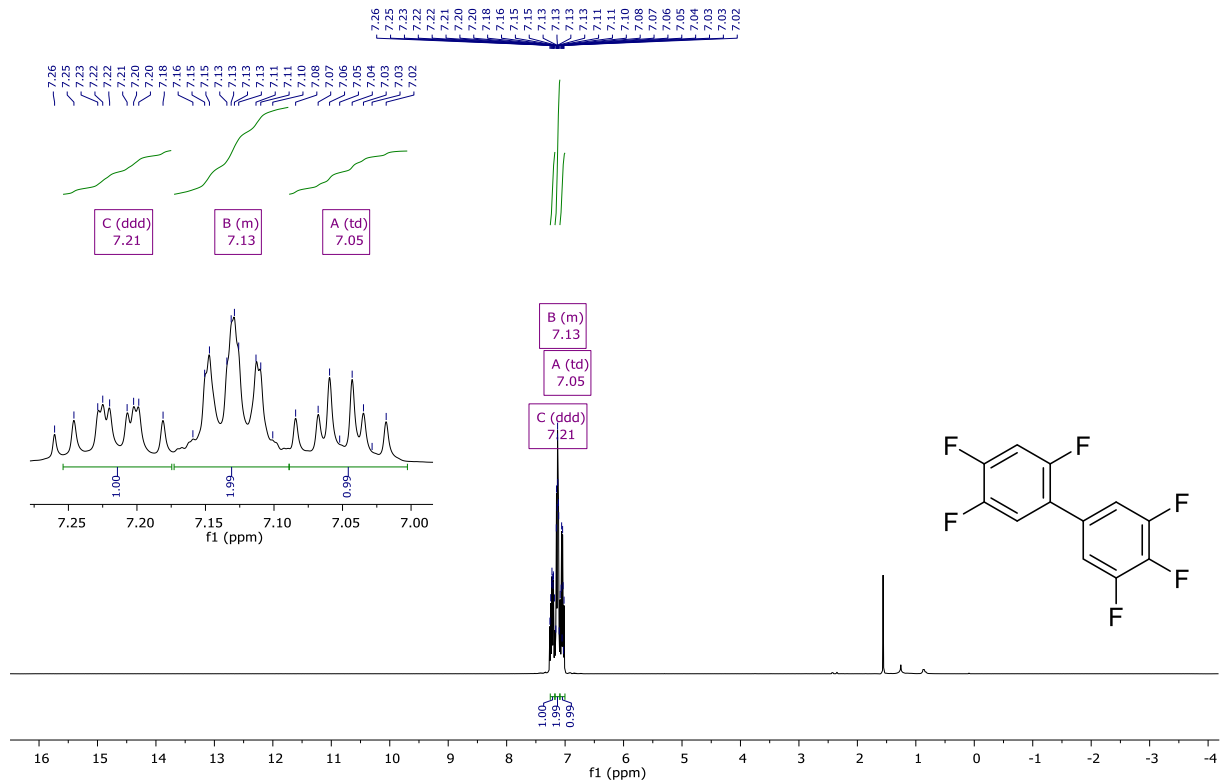


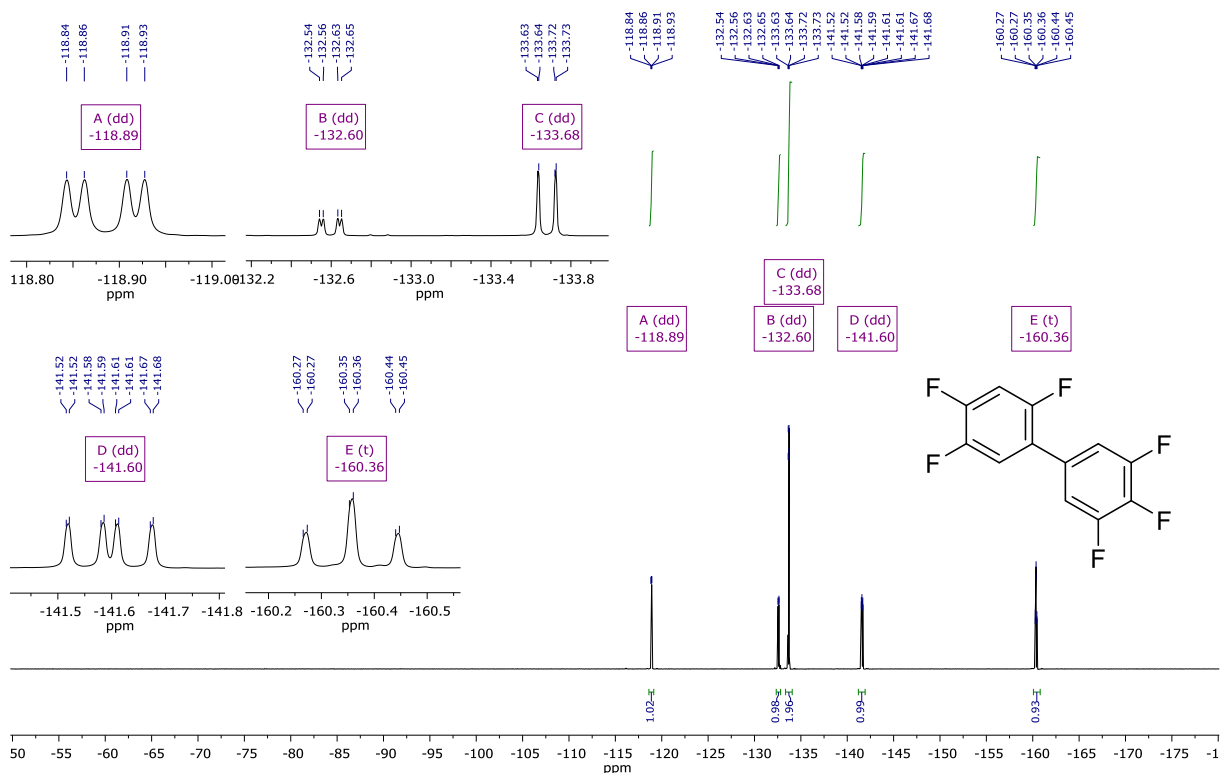
Figure S72 IR (ATR)-Spectrum: 3,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

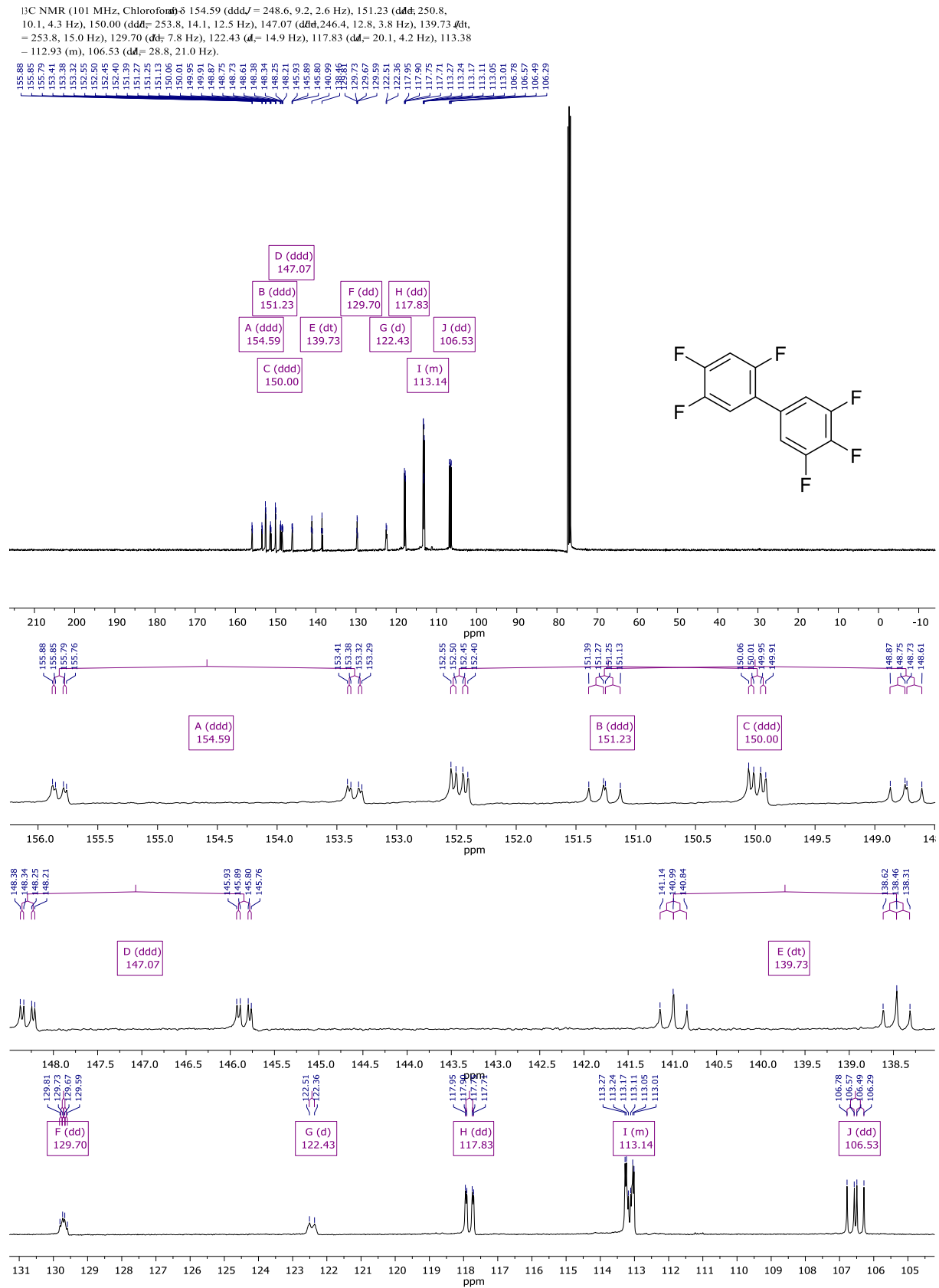
2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl (29)

$^1\text{H NMR}$ (400 MHz, Chloroform- d_3) 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 $^1\text{H-NMR}$: 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

$^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) 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 $^{19}\text{F-NMR}$ [^1H]: 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

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

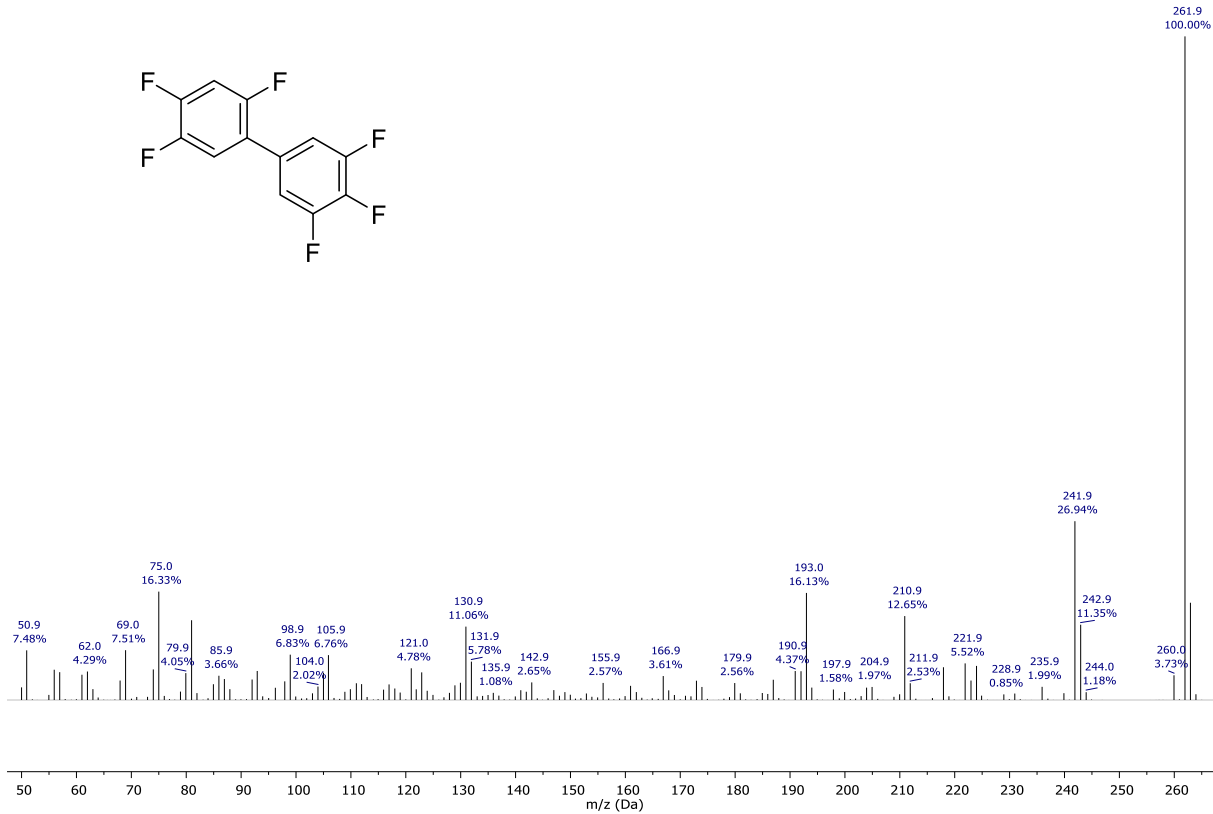
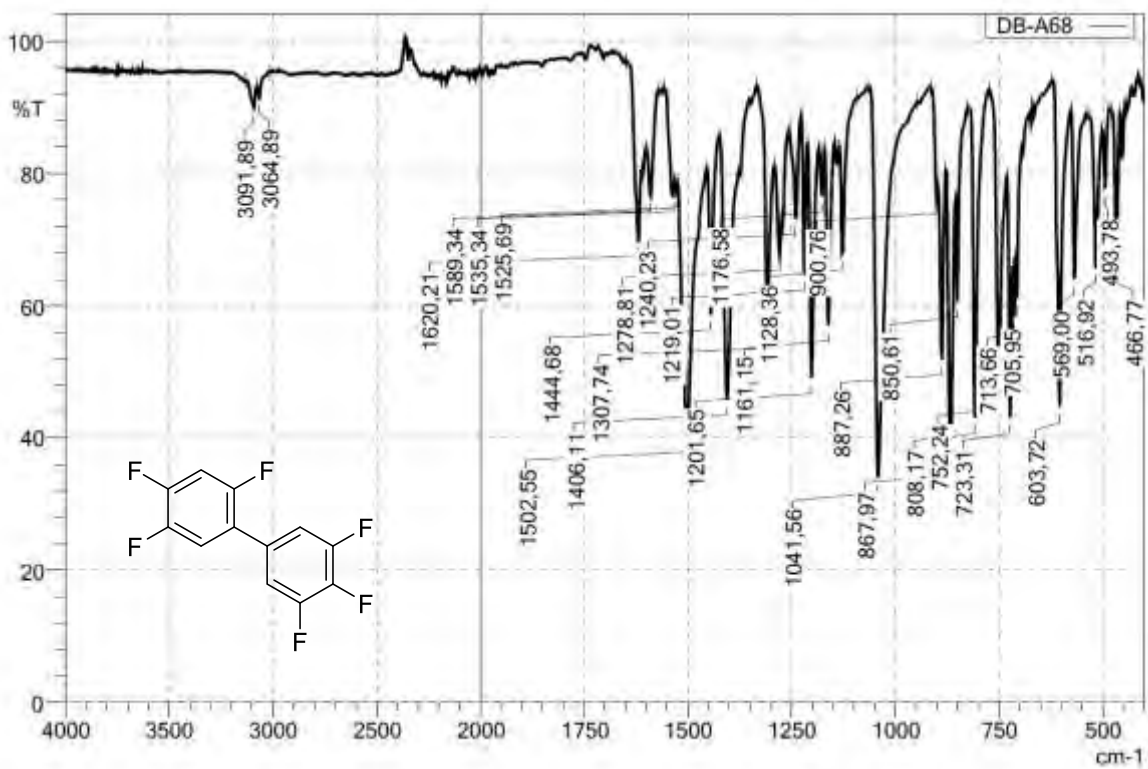
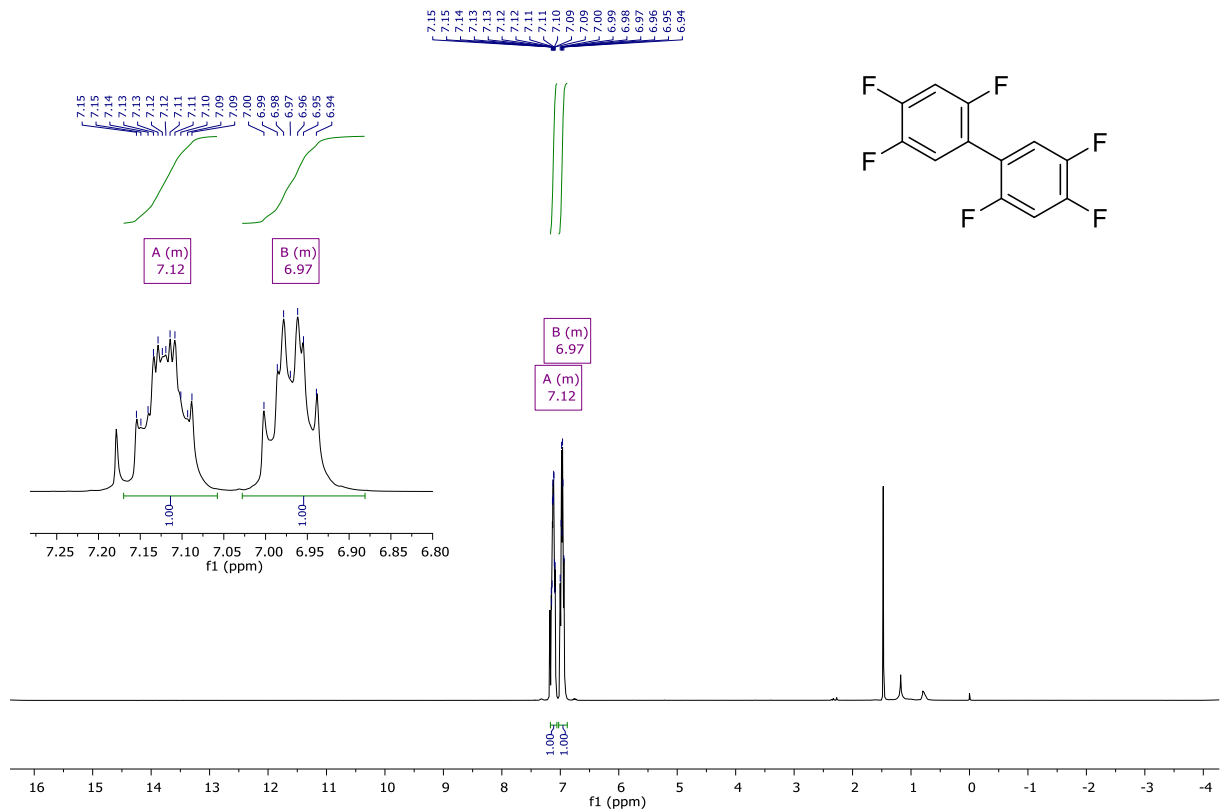
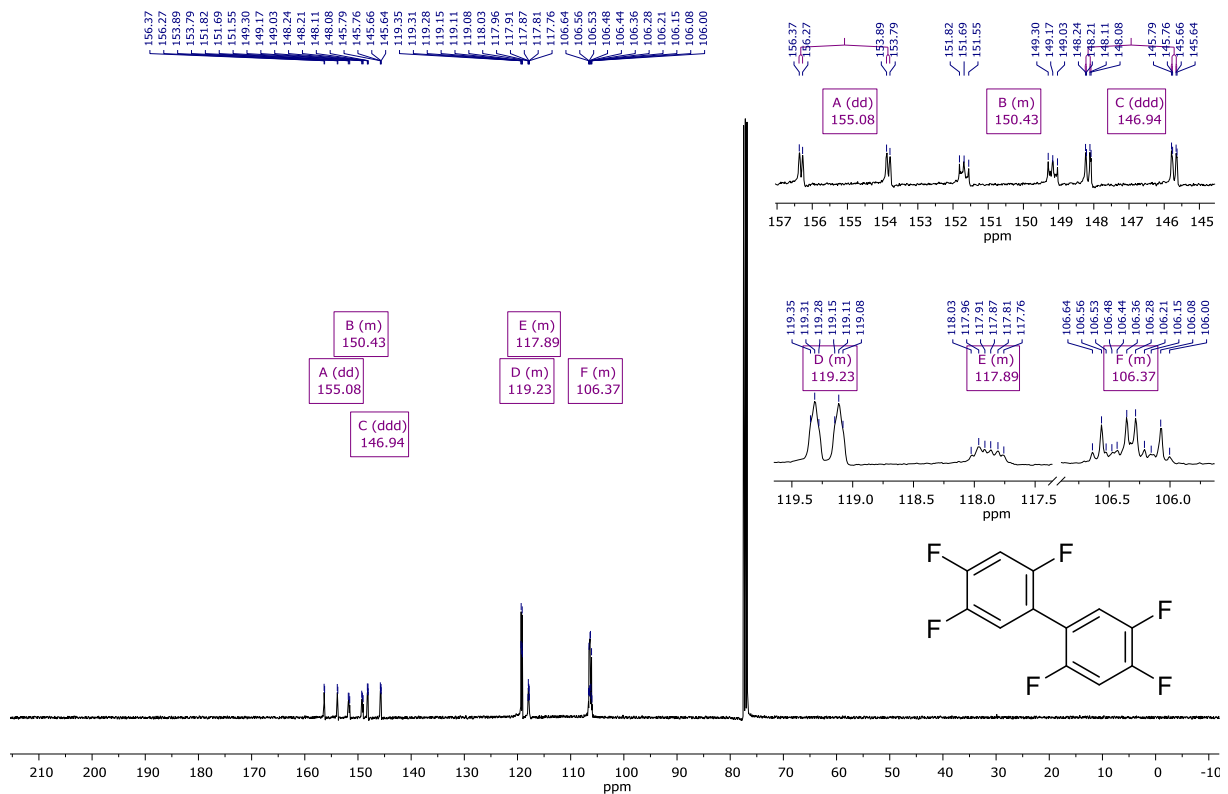
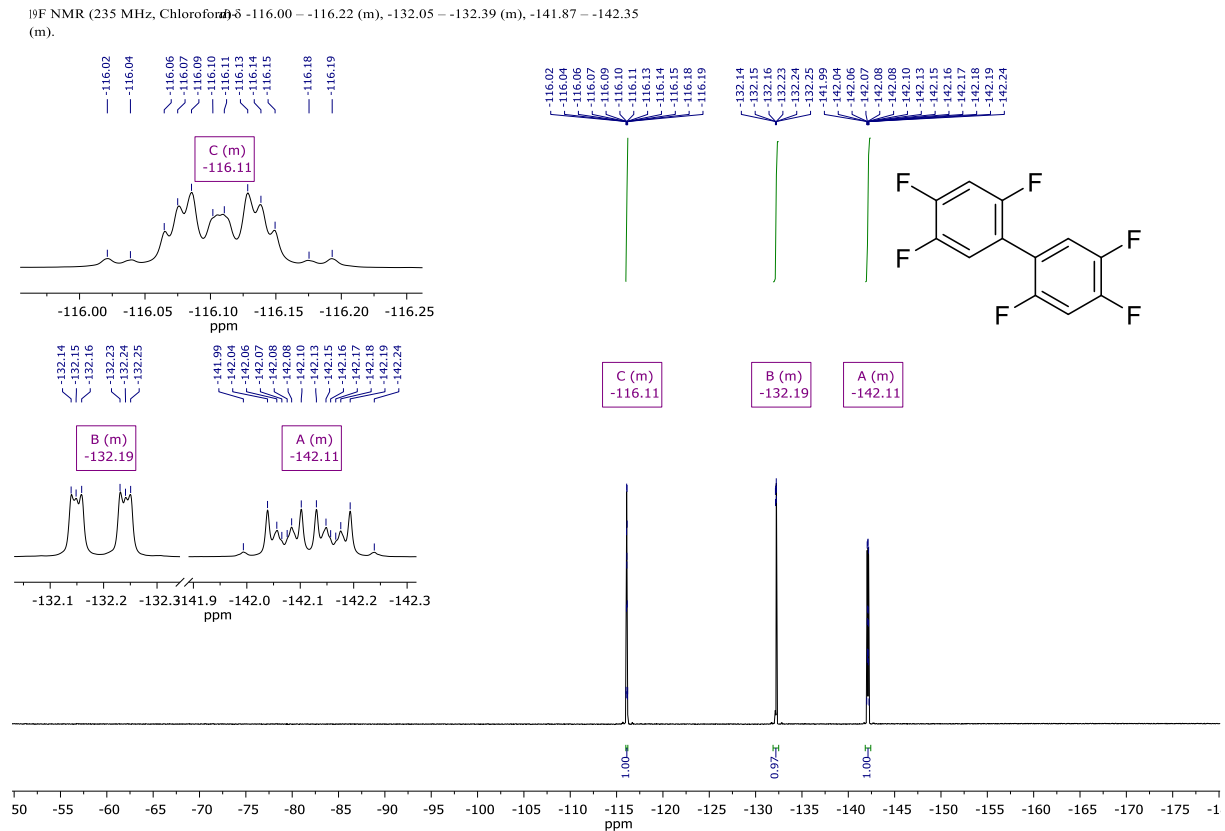
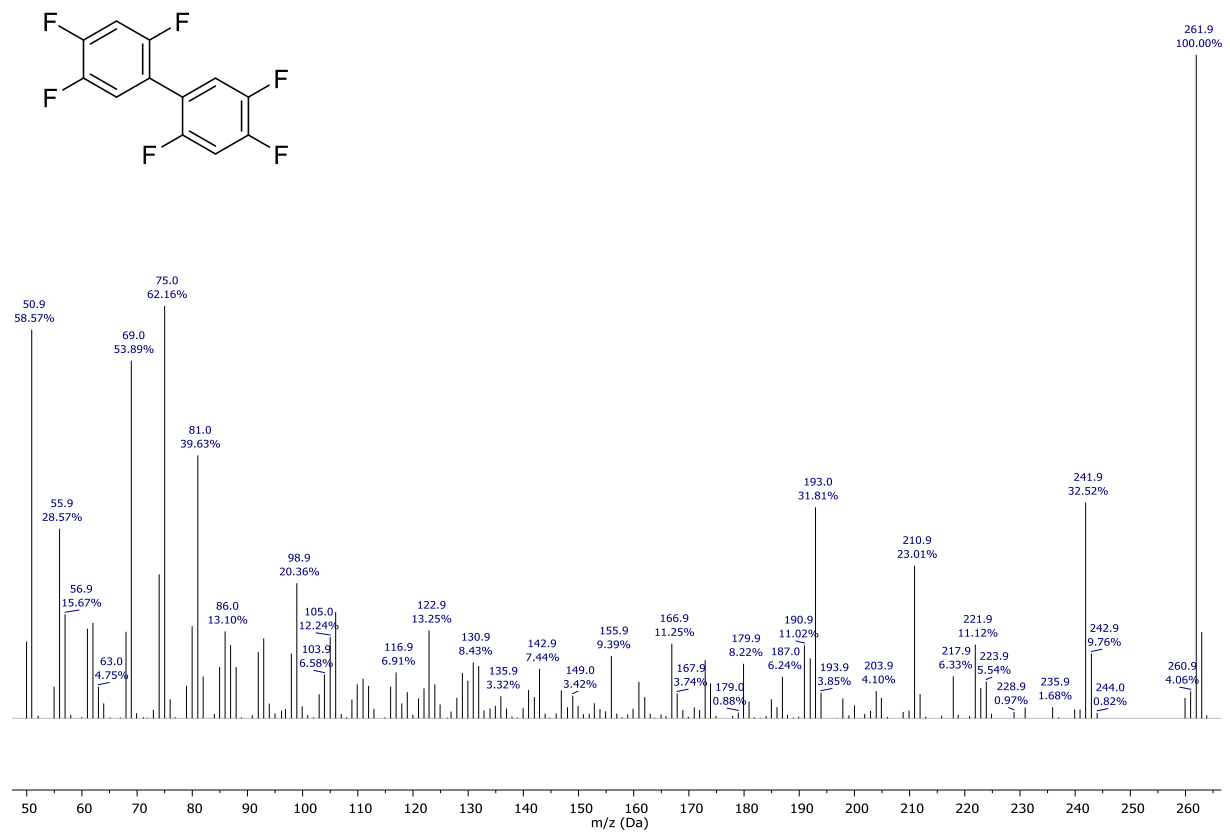
Figure S76 EI-Spectrum (EI⁺): 2,3',4,4',5,5'-Hexafluoro-1,1'-biphenyl

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)

¹H NMR (400 MHz, Chloroform-d) δ 7.17 – 7.07 (m, 2H), 7.02 – 6.91 (m, 2H).Figure S78 ¹H-NMR: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl¹³C NMR (101 MHz, Chloroform-d) δ 155.08 (dd/ = 249.7, 9.6 Hz), 152.28 – 148.66 (m), 146.94 (ddd), J = 245.8, 12.7, 2.7 Hz), 119.38 – 119.01 (m), 118.12 – 117.71 (m), 106.92 – 105.71 (m).Figure S79 ¹³C NMR: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

Figure S80 ^{19}F -NMR $\{^1\text{H}\}$: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenylFigure S81 EI-Spectrum (EI $^+$): 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

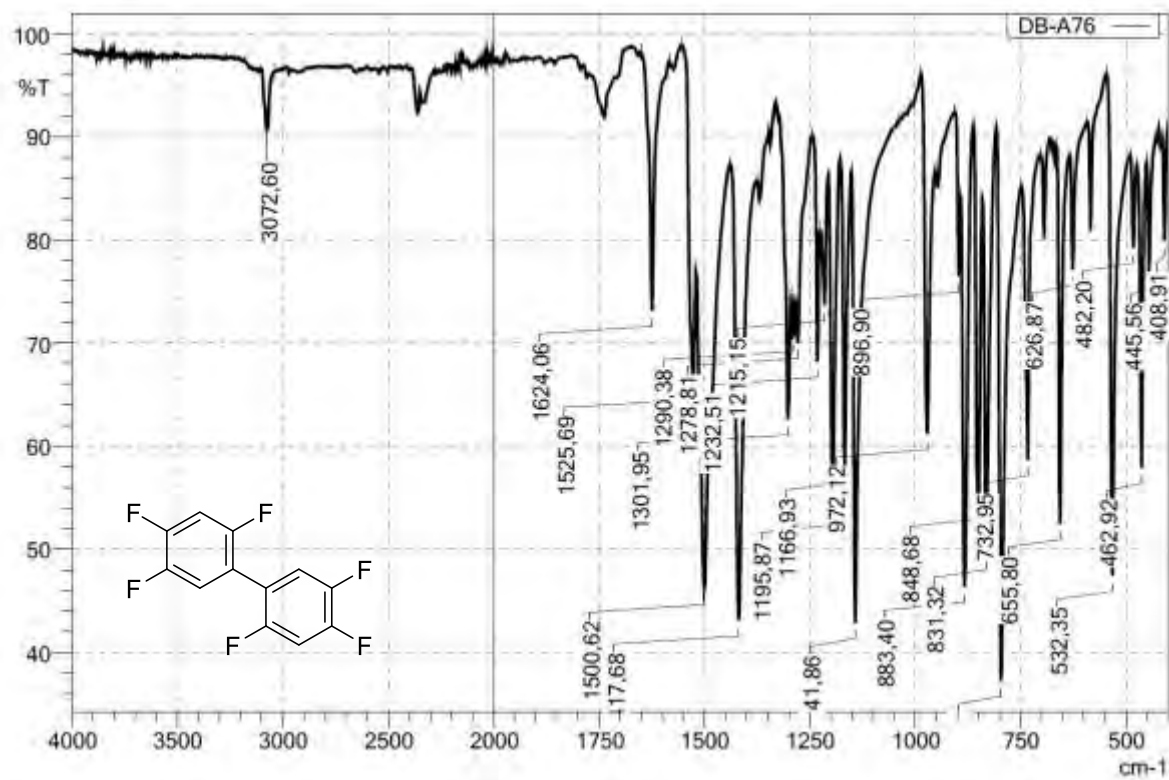
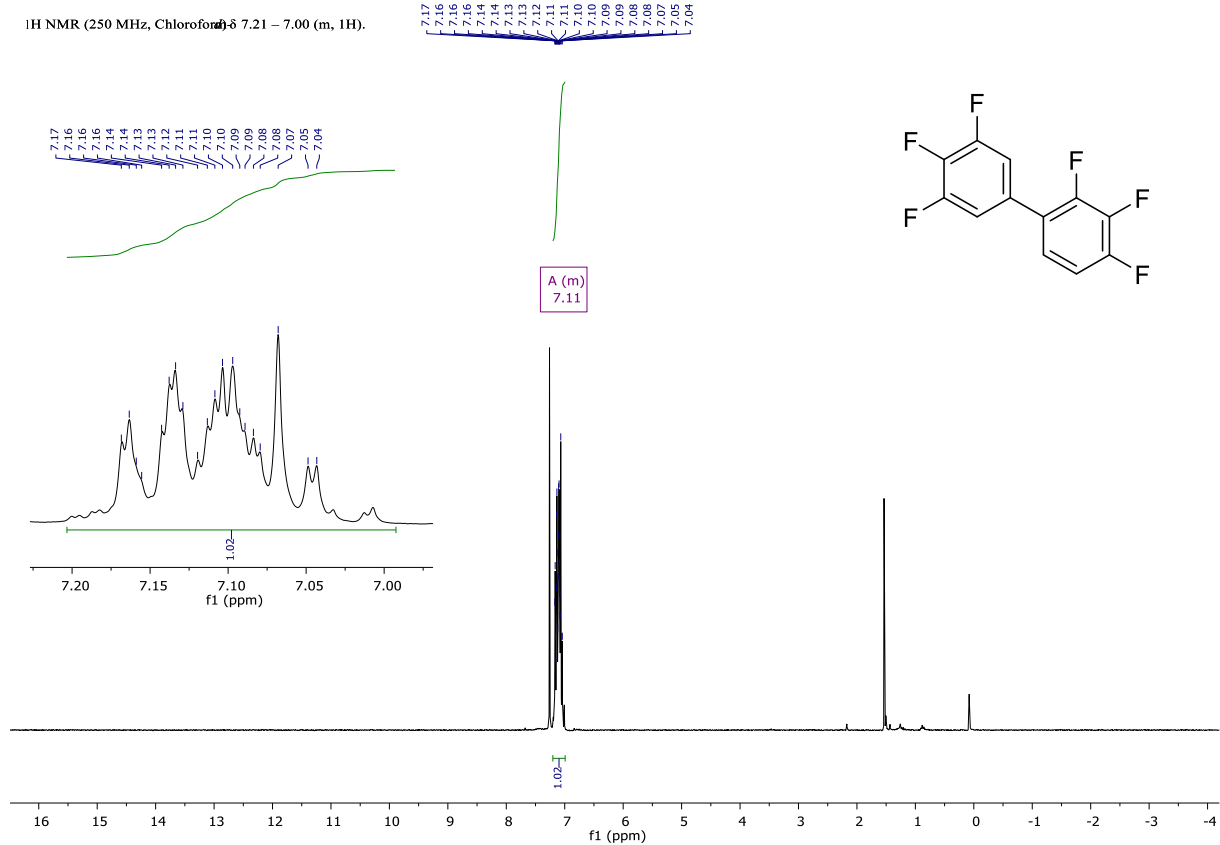
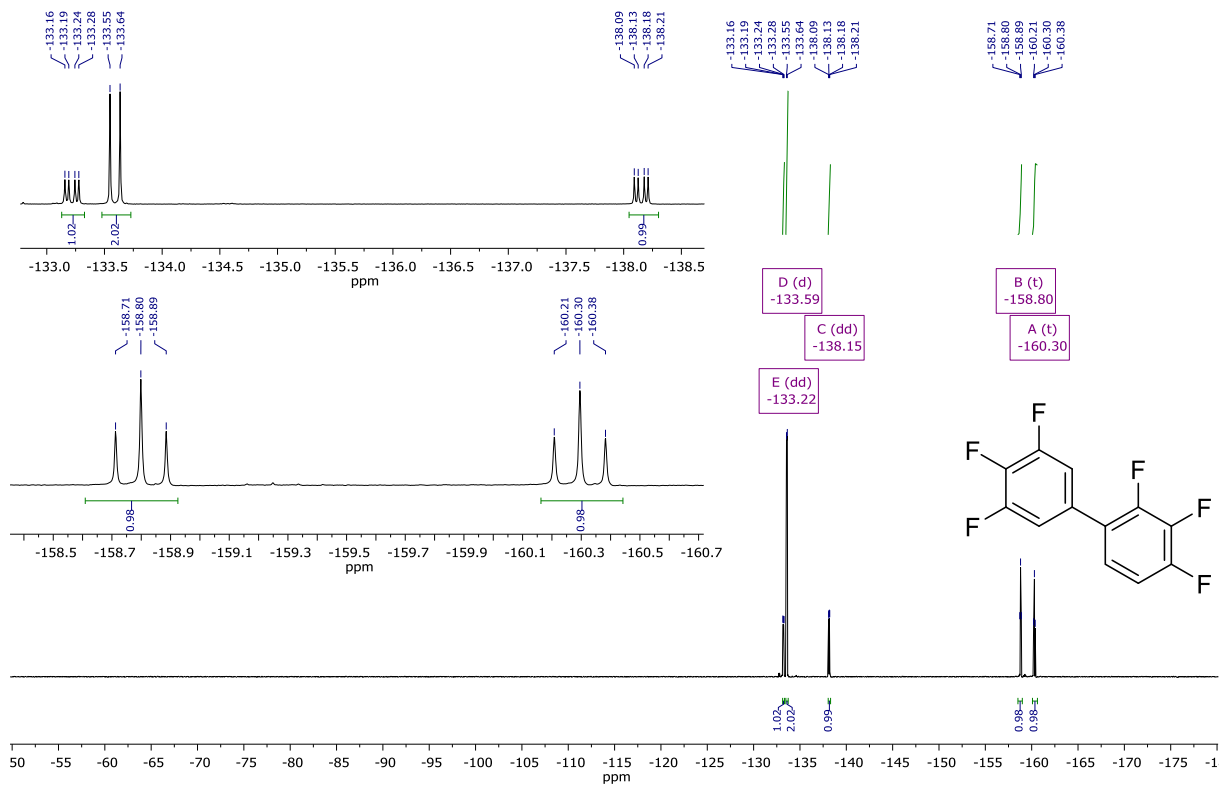
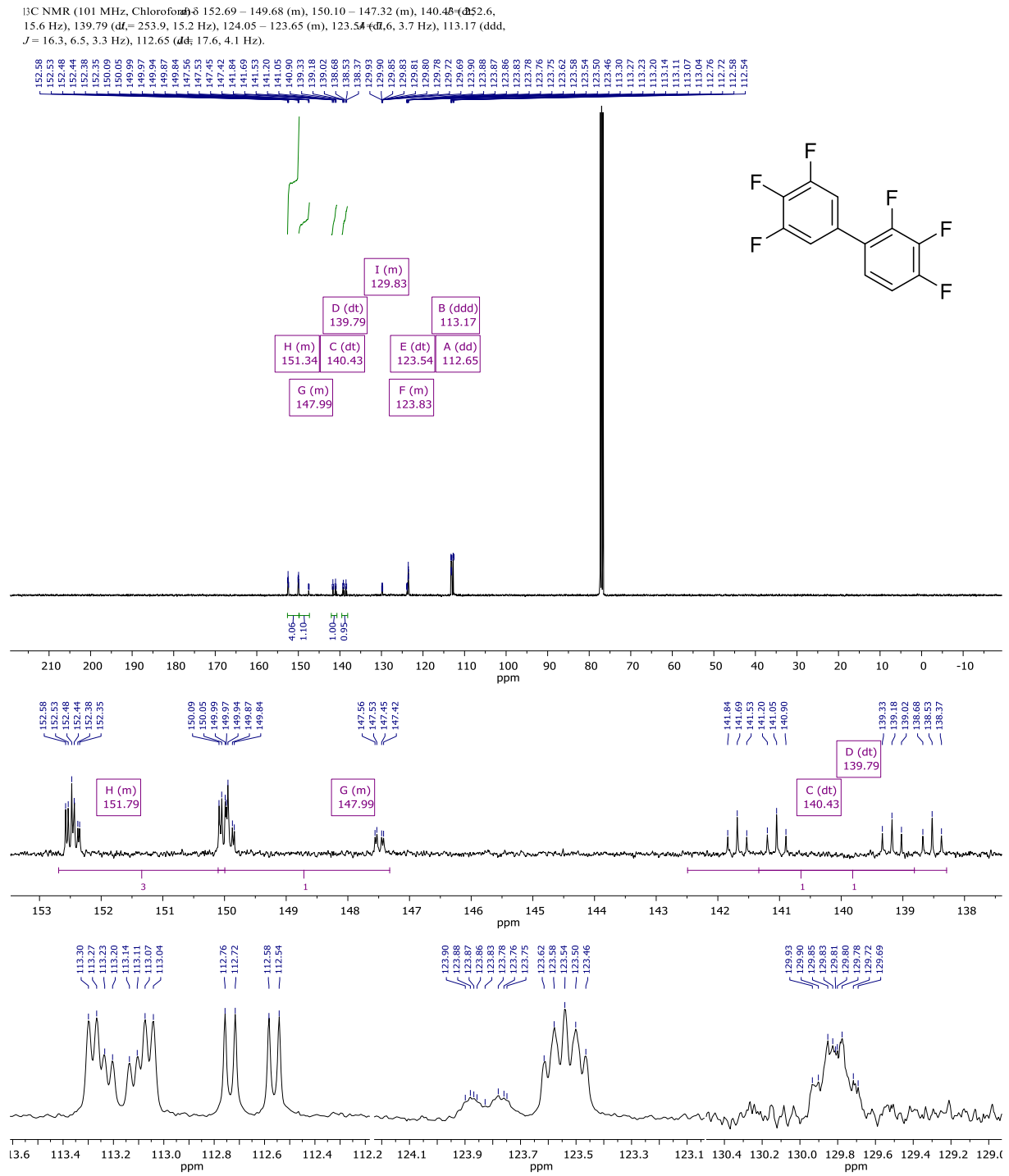


Figure S82 IR (ATR)-Spectrum: 2,2',4,4',5,5'-Hexafluoro-1,1'-biphenyl

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

¹H NMR (250 MHz, Chloroform-d) δ 7.21 – 7.00 (m, 1H).Figure S83 ¹H-NMR: 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl¹⁹F NMR (235 MHz, Chloroform-d) δ -133.22 (dd, $J = 20.4, 8.0$ Hz), -133.59 (t, $J = 20.6$ Hz), -138.15 (dd, $J = 20.2, 8.0$ Hz), -158.80 (t, $J = 20.3$ Hz), -160.30 (t, $J = 20.6$ Hz).Figure S84 ¹⁹F-NMR {¹H}: 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

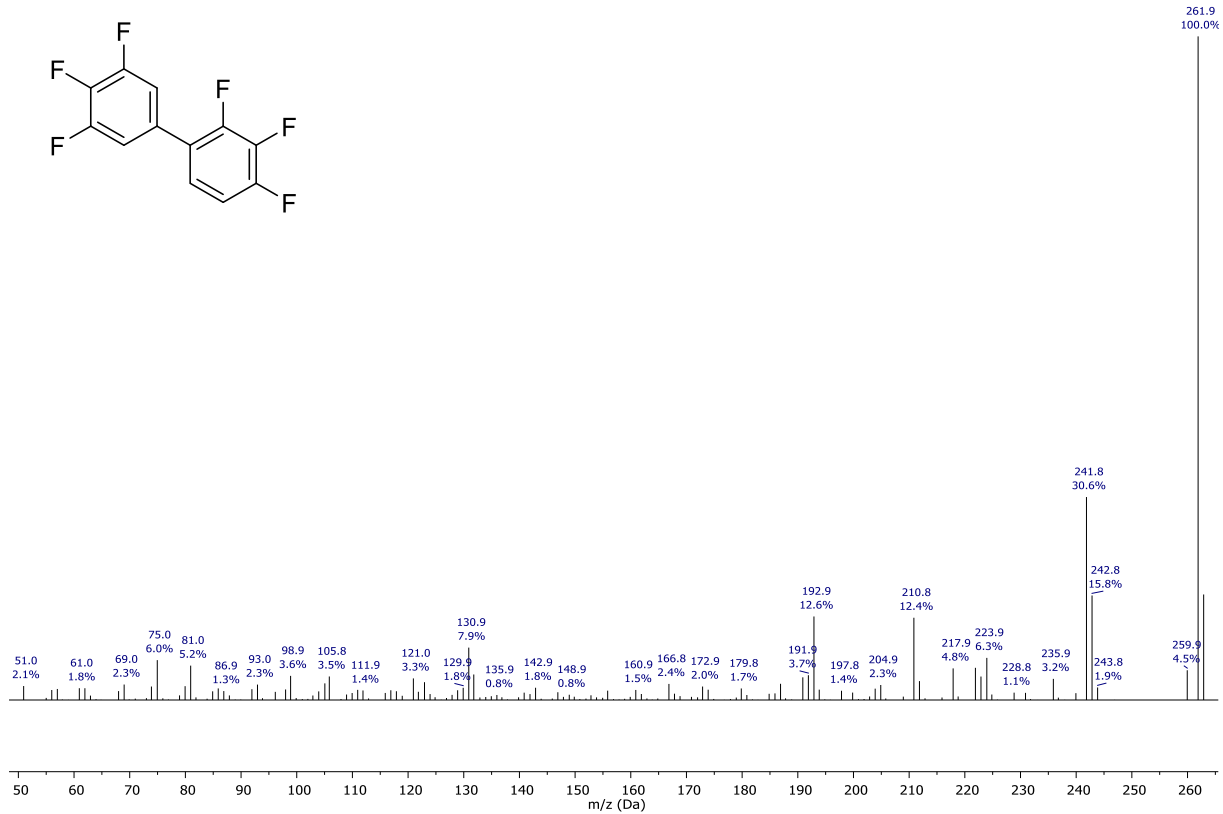
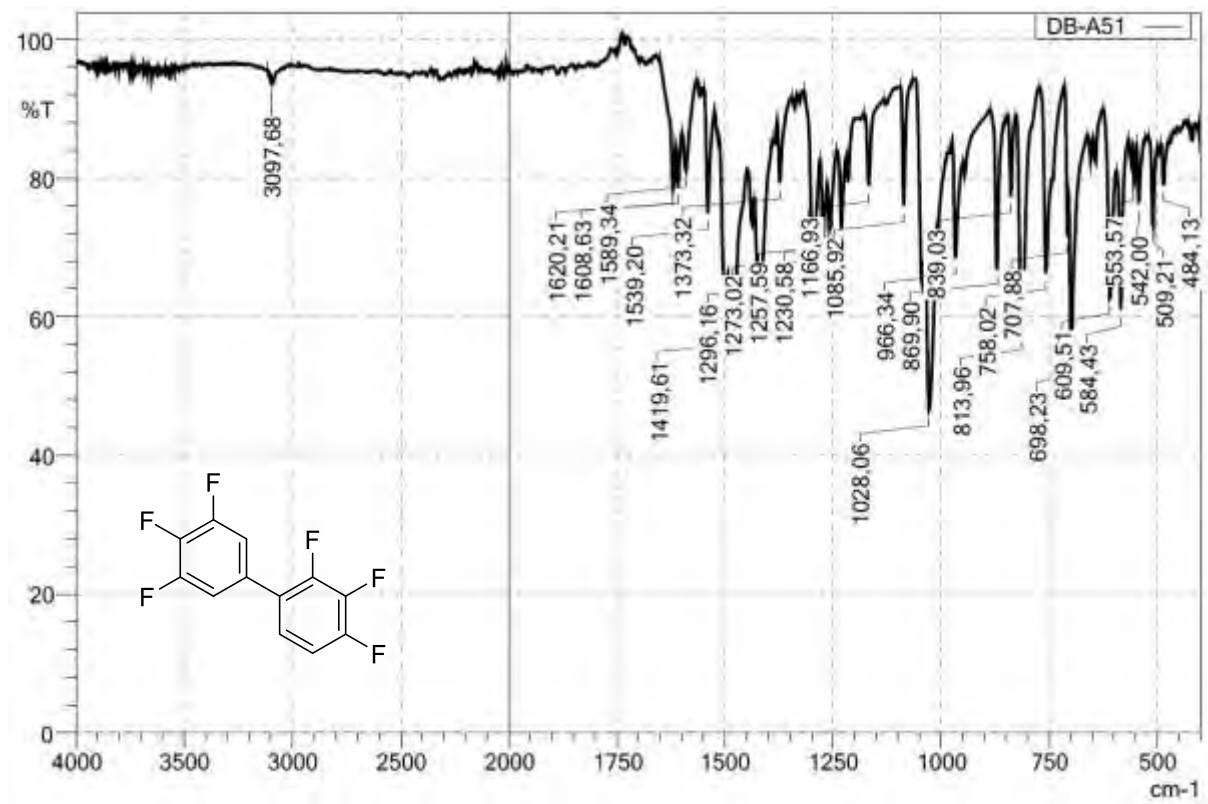
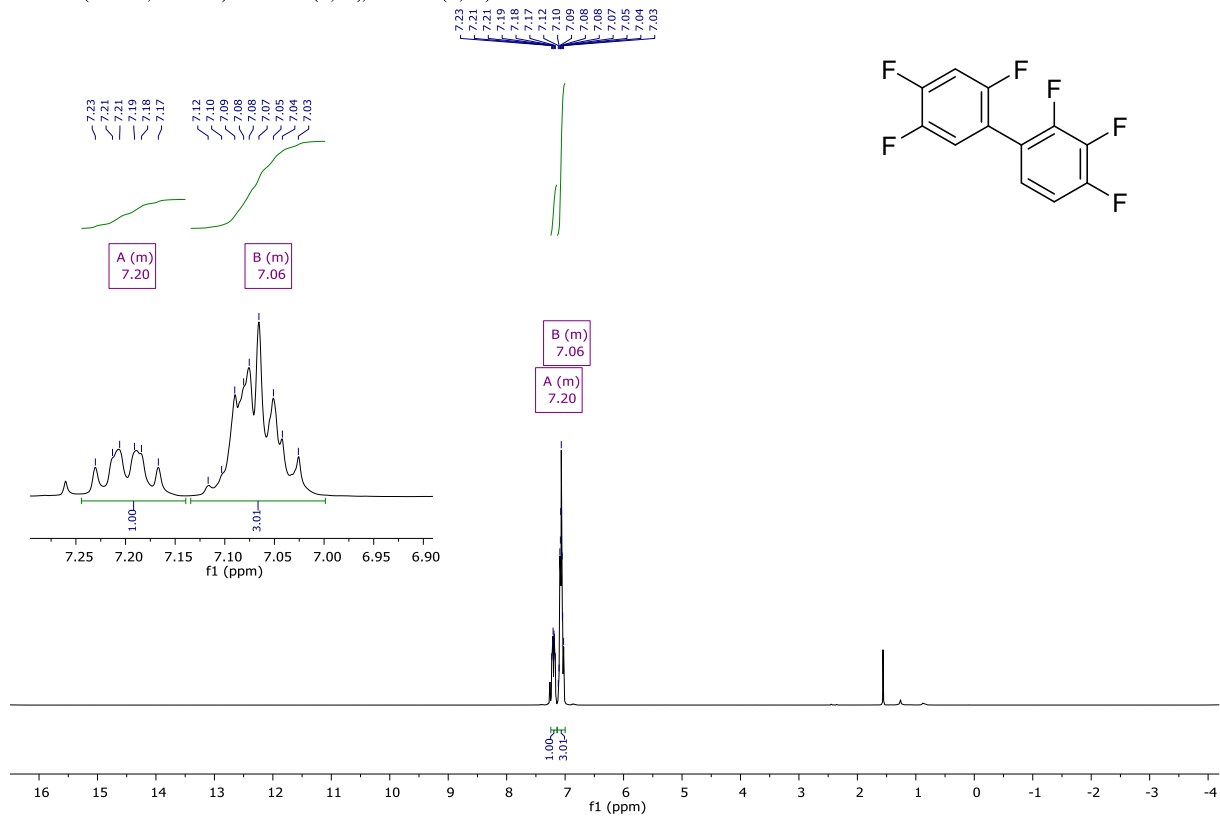
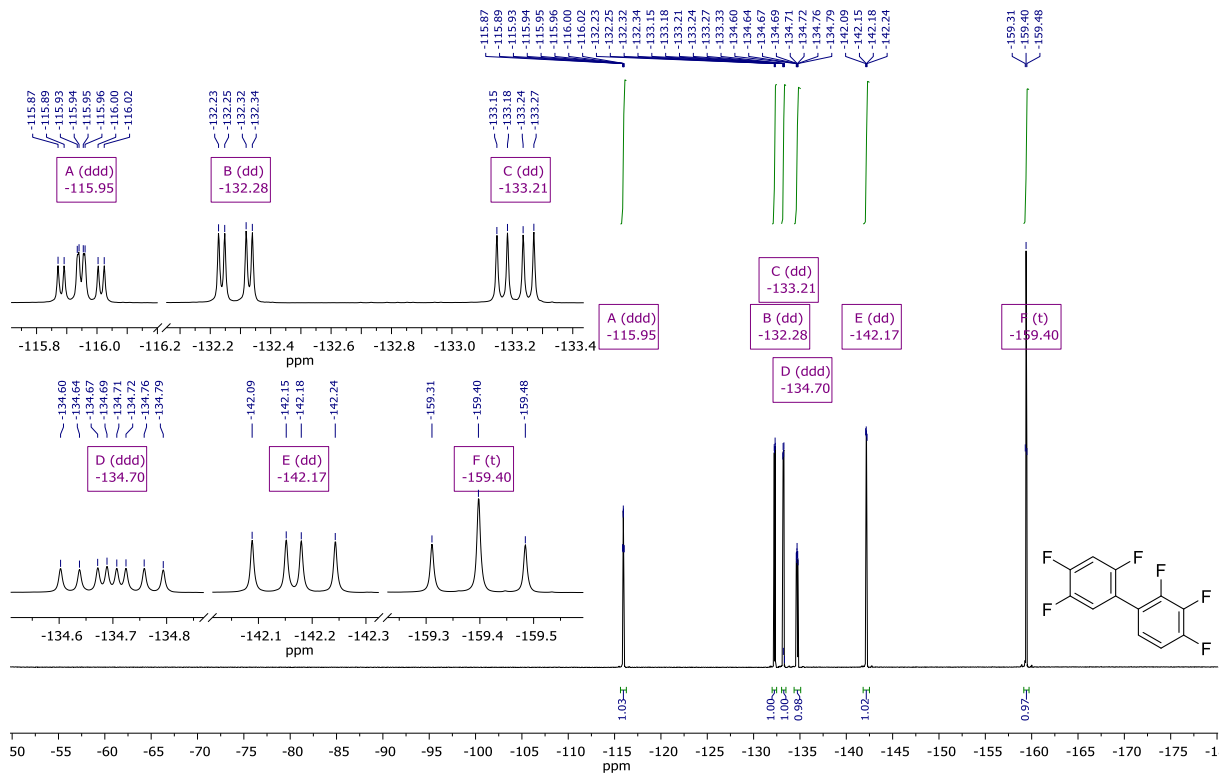
Figure S86 EI-Spectrum (EI⁺): 2,3,3',4,4',5'-Hexafluoro-1,1'-biphenyl

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)

 $^1\text{H NMR}$ (400 MHz, Chloroform- d_3) δ 7.25 – 7.14 (m, 1H), 7.13 – 7.01 (m, 3H).Figure S88 $^1\text{H-NMR}$: 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl $^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) δ -115.95 (ddd, J = 16.3, 14.9, 4.8 Hz), -132.28 (dd, 21.5, 4.8 Hz), -133.21 (dd, J = 20.5, 8.3 Hz), -134.70 (ddd, 20.4, 16.3, 8.3 Hz), -142.17 (dd, 21.5, 14.9 Hz), -159.40 (J = 20.4 Hz).Figure S89 $^{19}\text{F-NMR}$ $\{^1\text{H}\}$: 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

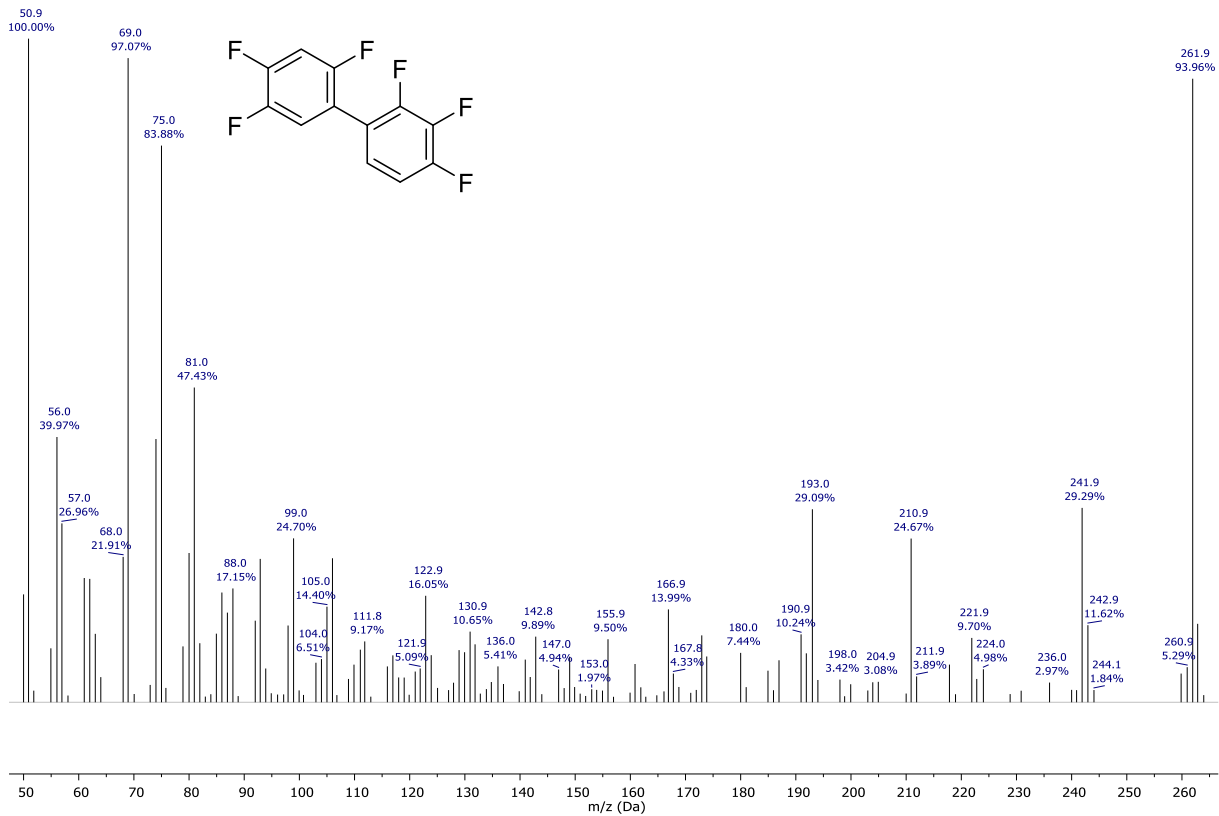
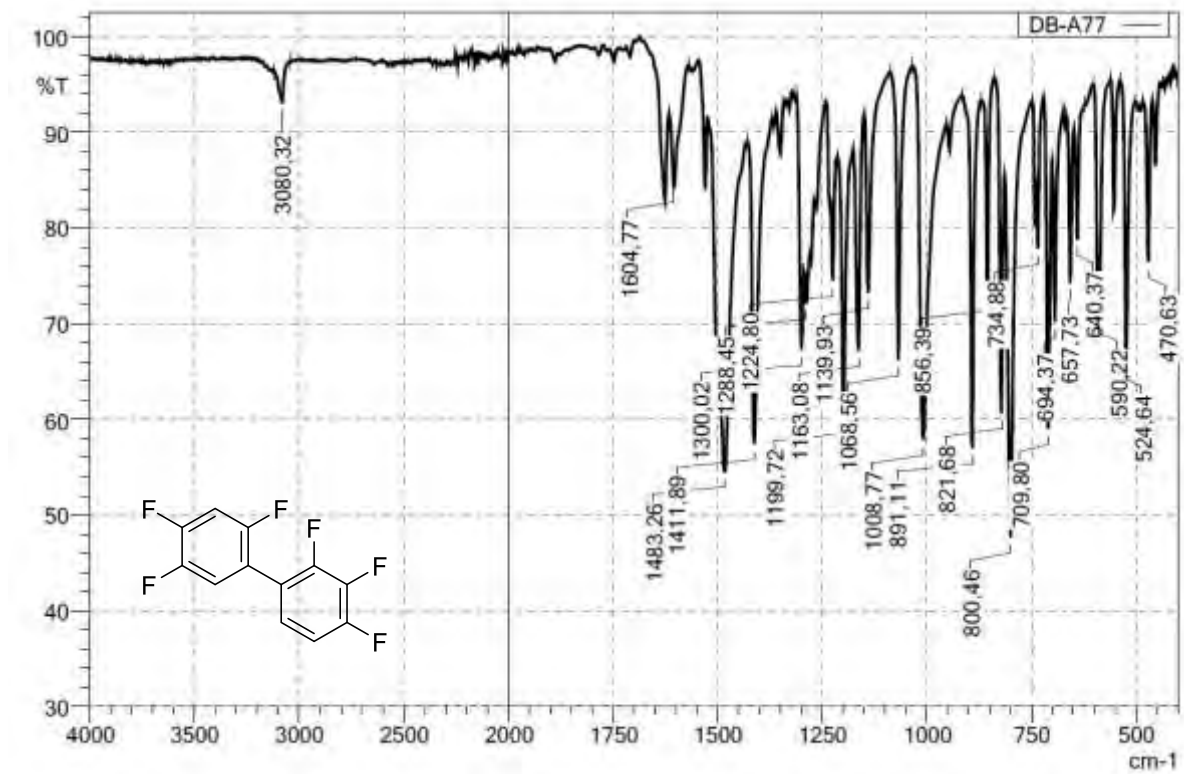
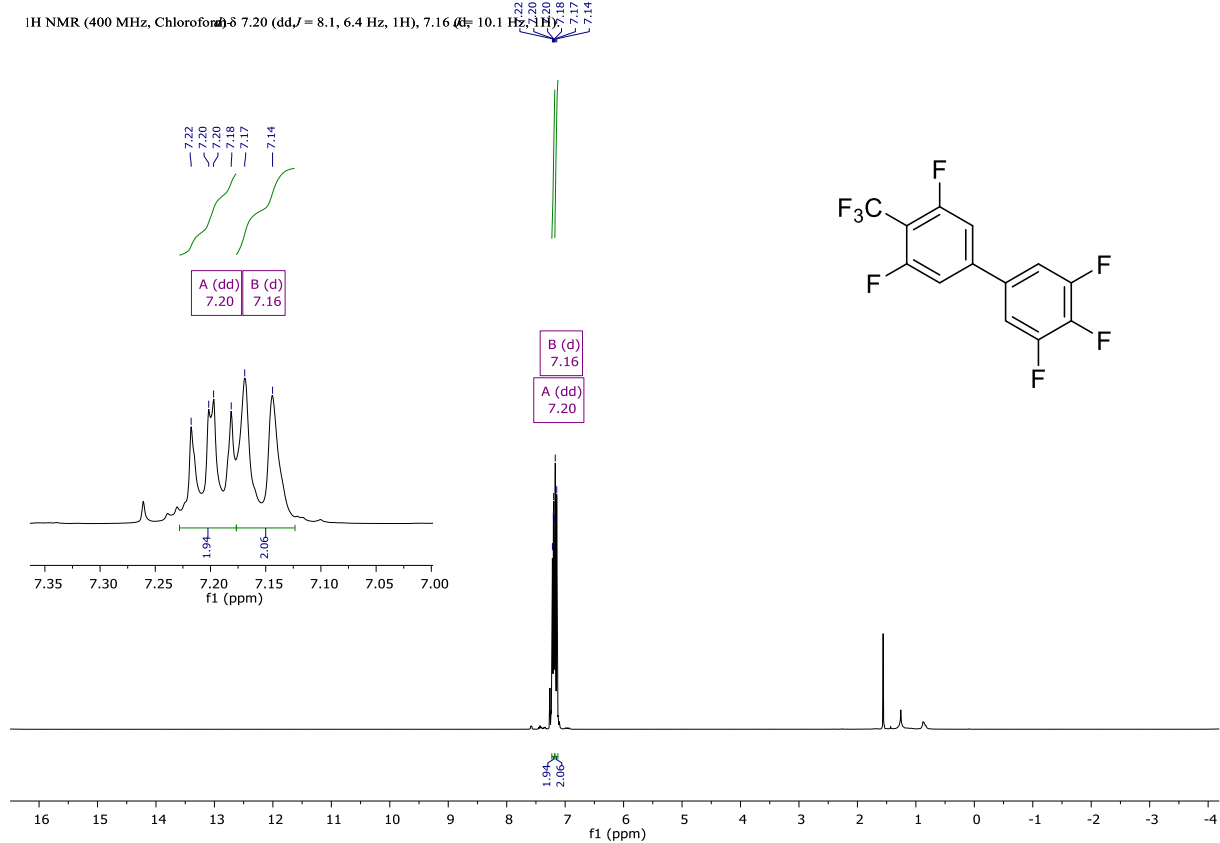
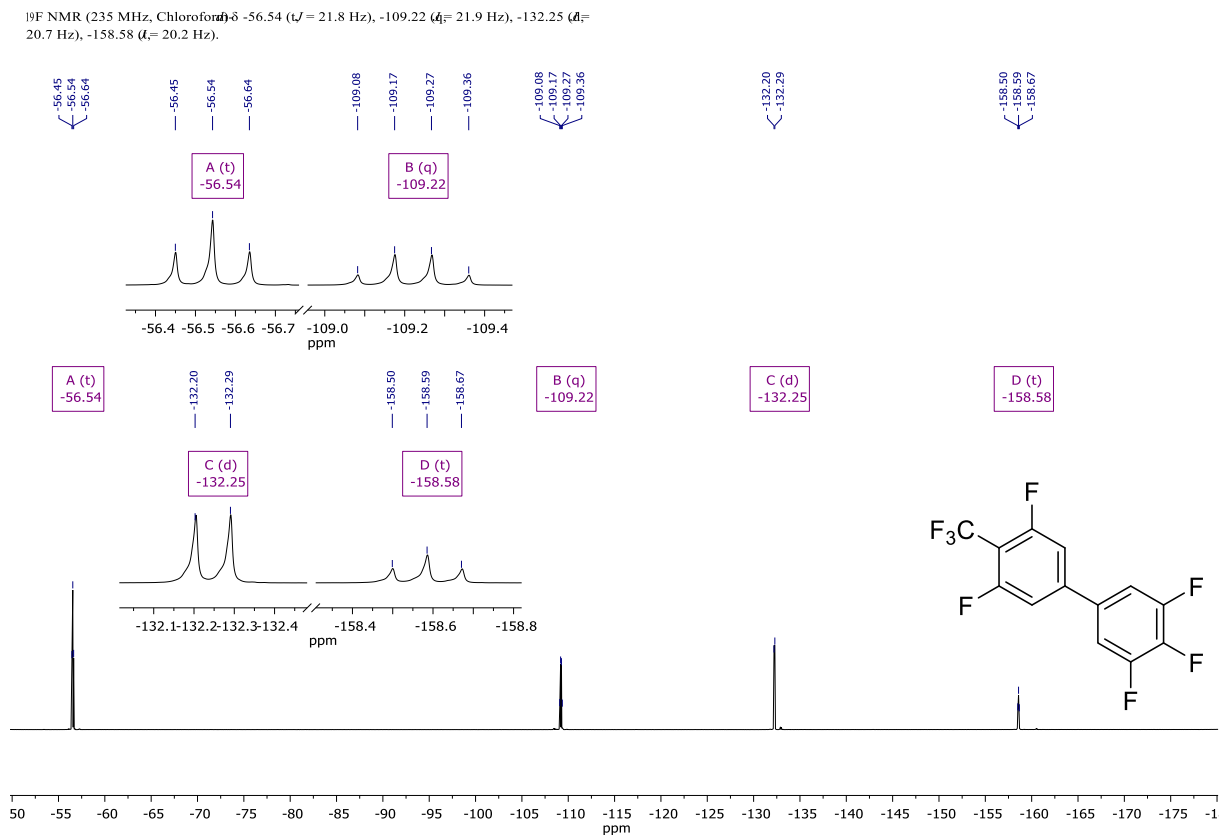
Figure S91 EI-Spectrum (EI⁺): 2,2',3,4,4',5'-Hexafluoro-1,1'-biphenyl

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

^{13}C NMR (101 MHz, Chloroform- d_3) δ 160.52 (dd, $J = 259.7, 5.8$ Hz), 151.88 (ddd, 252.0, 10.1, 4.2 Hz), 144.51 ($t = 10.9$ Hz), 140.74 (dt, $dt = 255.6, 15.3$ Hz), 133.56, 121.65 (q, 274.1 Hz), 111.82 – 111.42 (m), 111.42 – 111.04 (m), 108.40 – 107.03 (m).

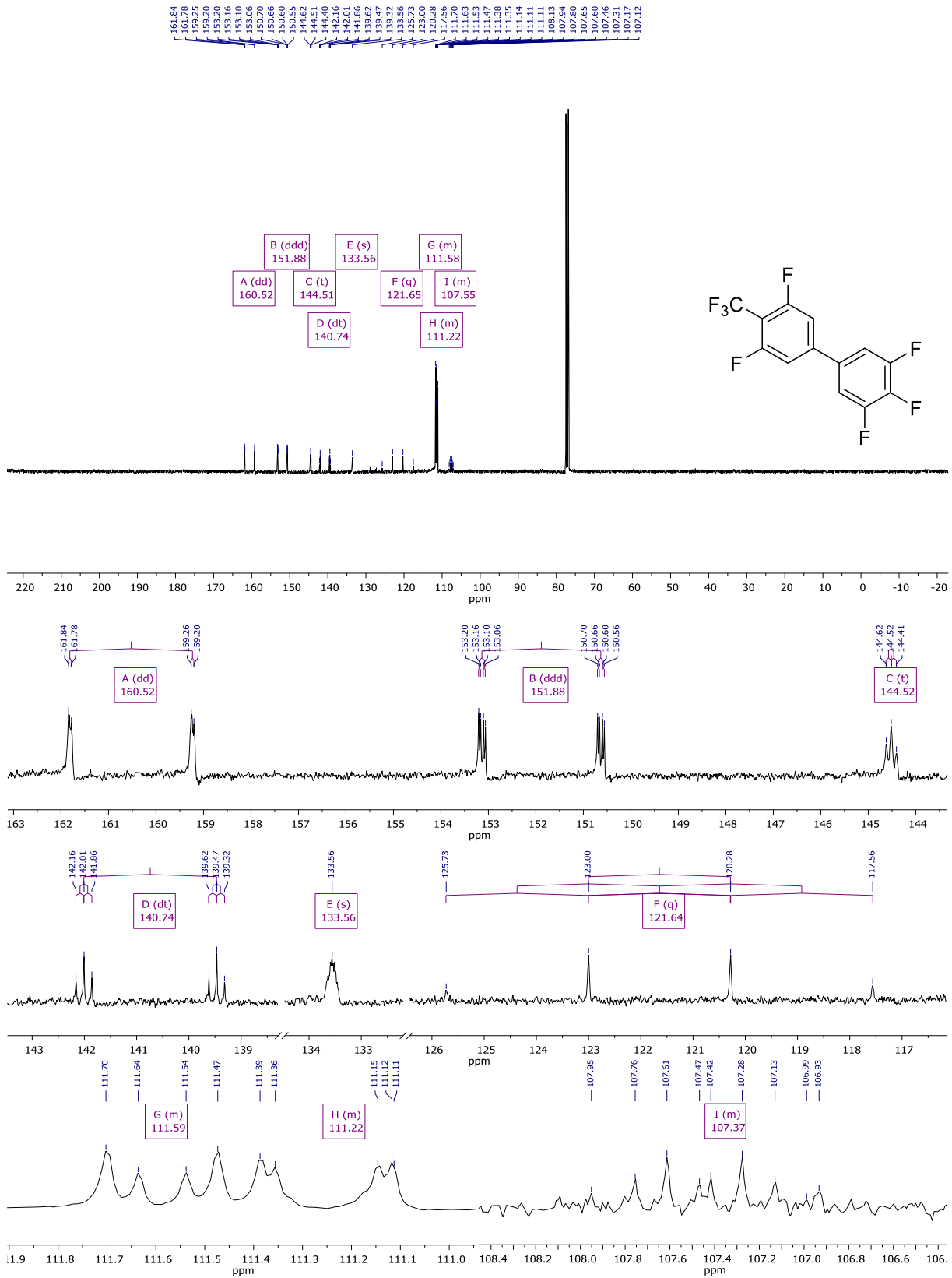


Figure S95 ^{13}C NMR: 3,3',4,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

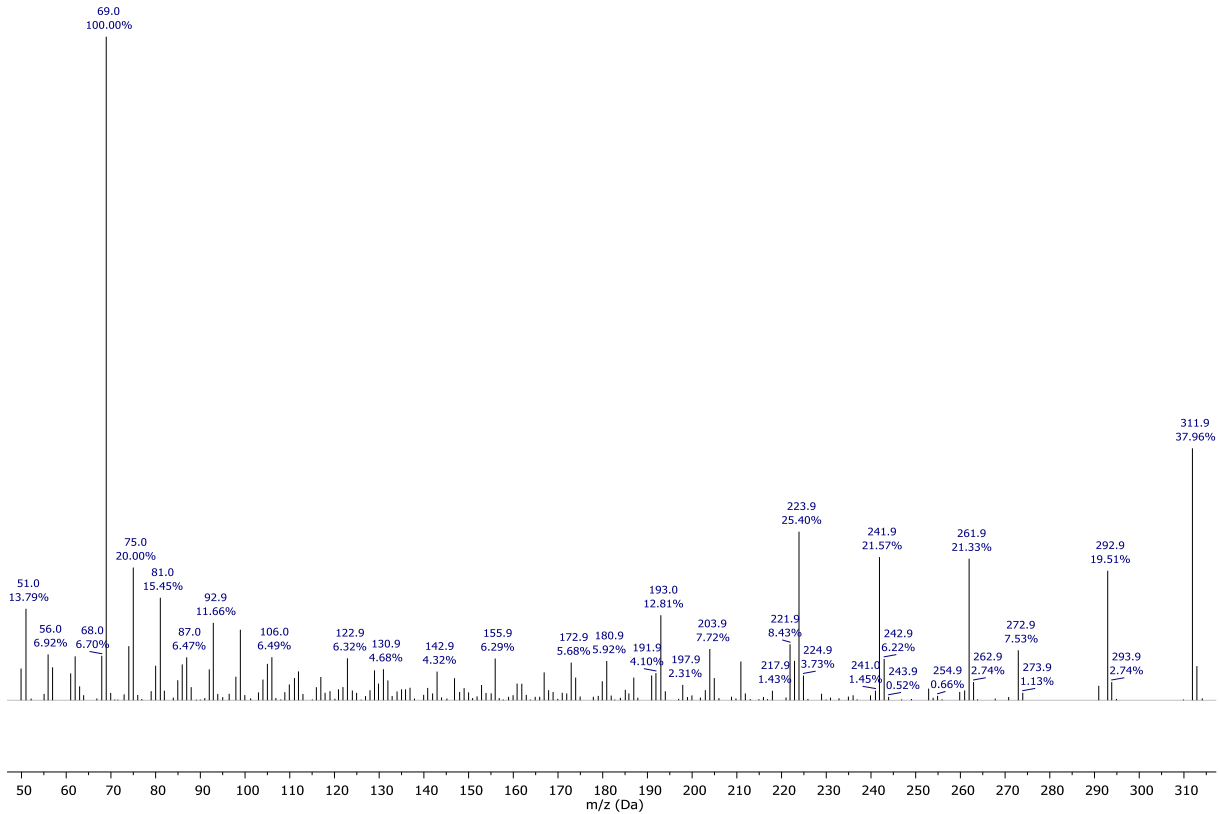


Figure S96 EI-Spectrum (EI⁺): 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

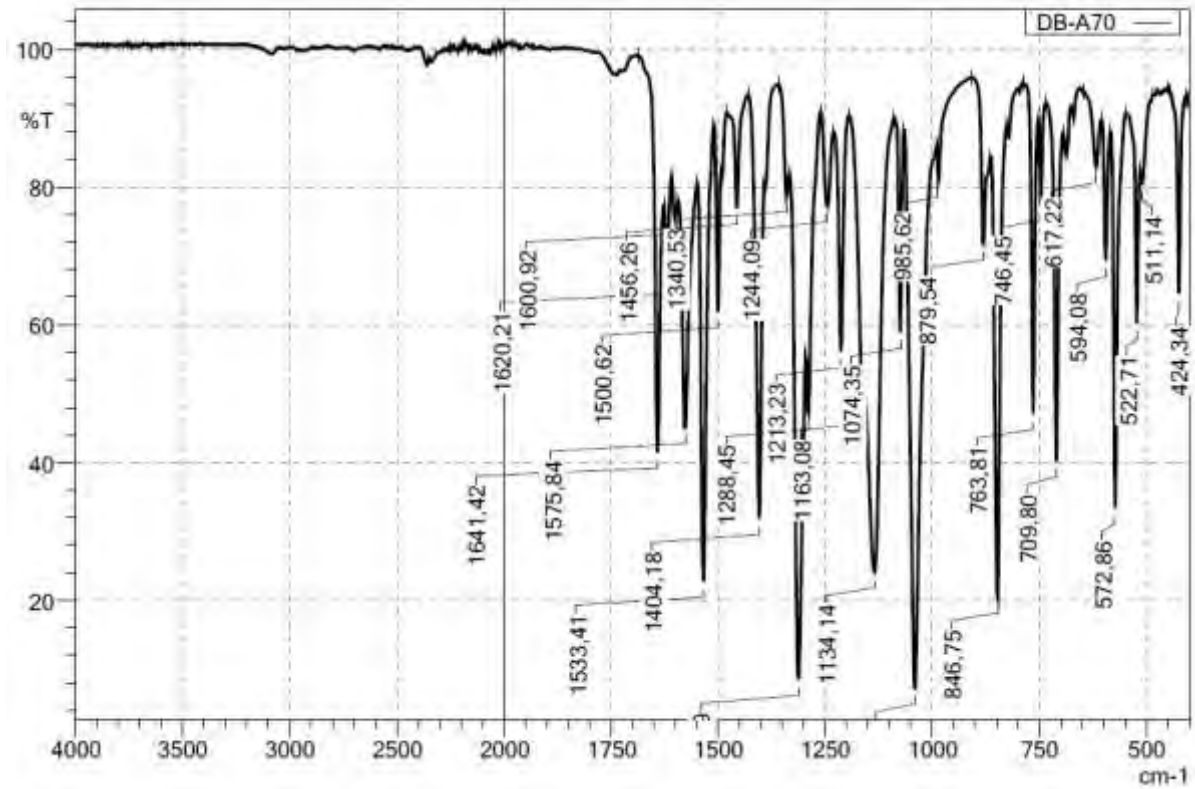
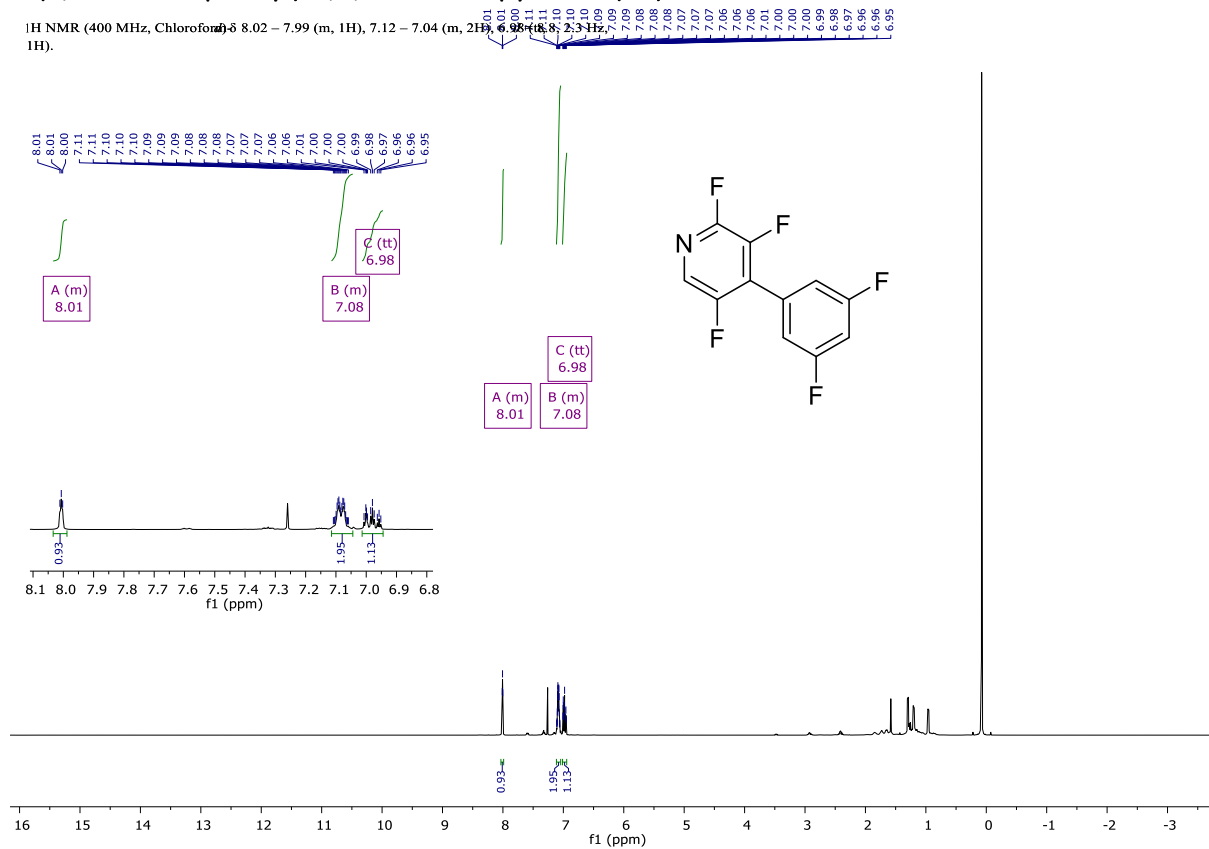
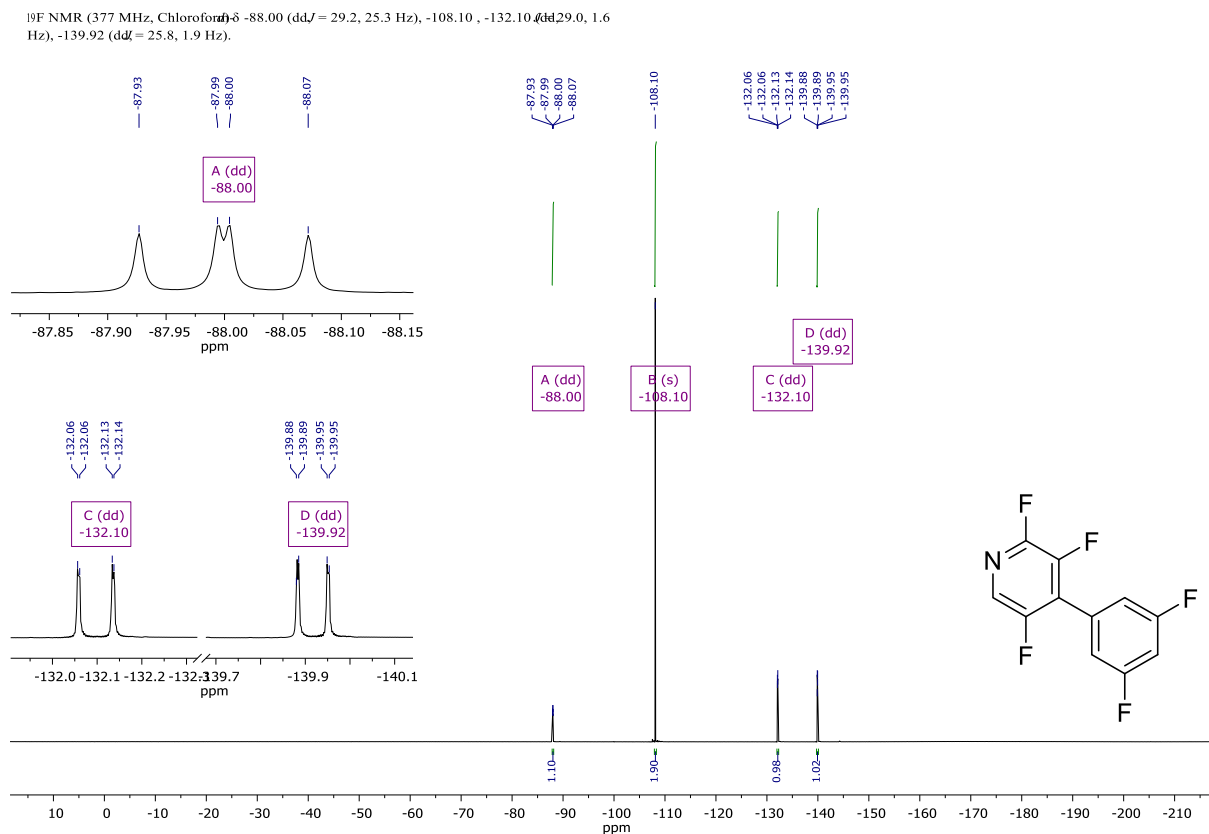


Figure S97 IR (ATR)-Spectrum: 3,3',4,5,5'-Pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl

Polyfluorinated Phenylpyridines

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

Figure S98 ¹H-NMR: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridineFigure S99 ¹⁹F-NMR {¹H}: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

^{13}C NMR (101 MHz, Chloroform- d_3) δ 161.93 (dd/ J = 250.2, 12.8 Hz), 152.46 (dd; 257.5, 4.3 Hz), 147.77 (ddd/ J = 237.2, 15.2, 2.2 Hz), 145.75 (d, 162.1 Hz), 140.97 (ddd = 267.0, 31.7, 2.8 Hz), 128.26 – 127.84 (m), 127.84 – 127.59 (m), 112.67 – 111.70 (m), 104.73 (t).

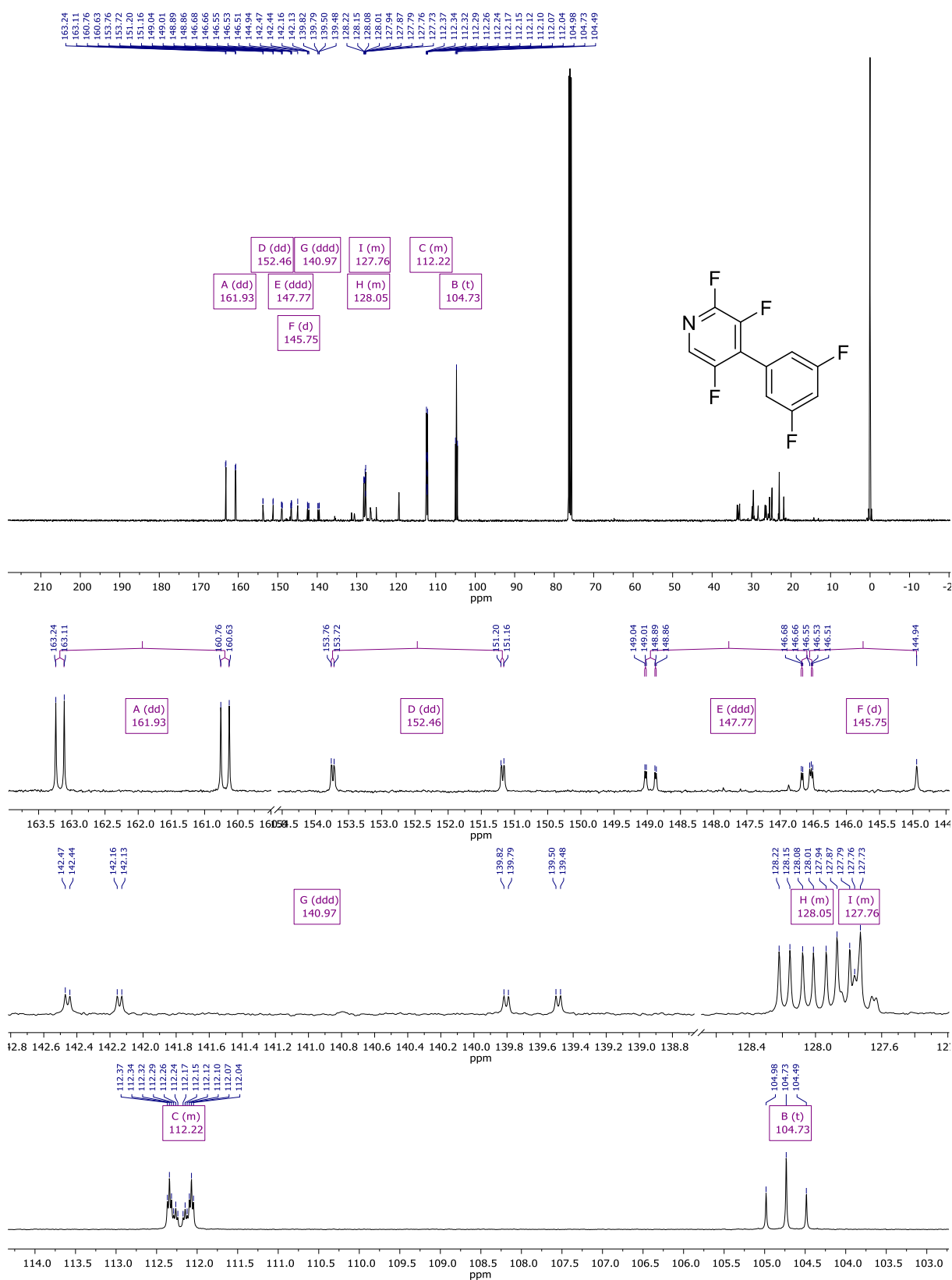


Figure S100 ^{13}C NMR: 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

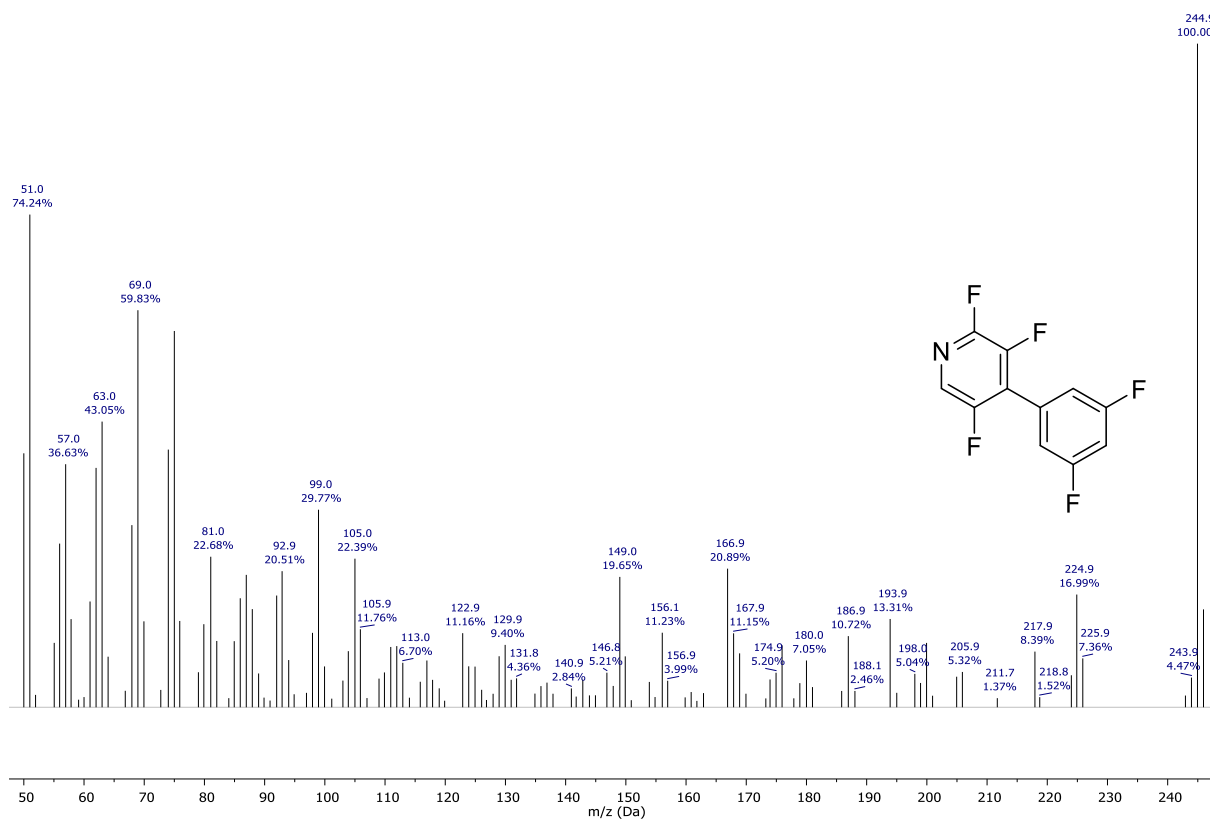
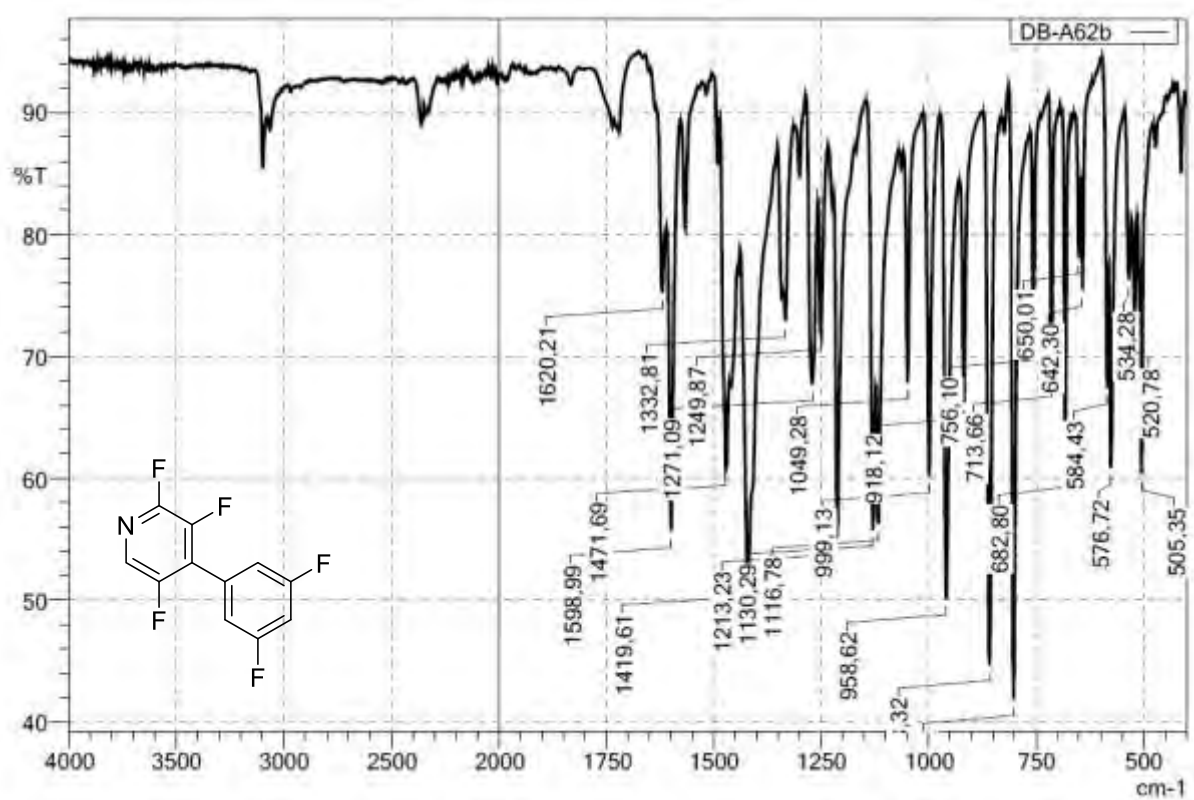
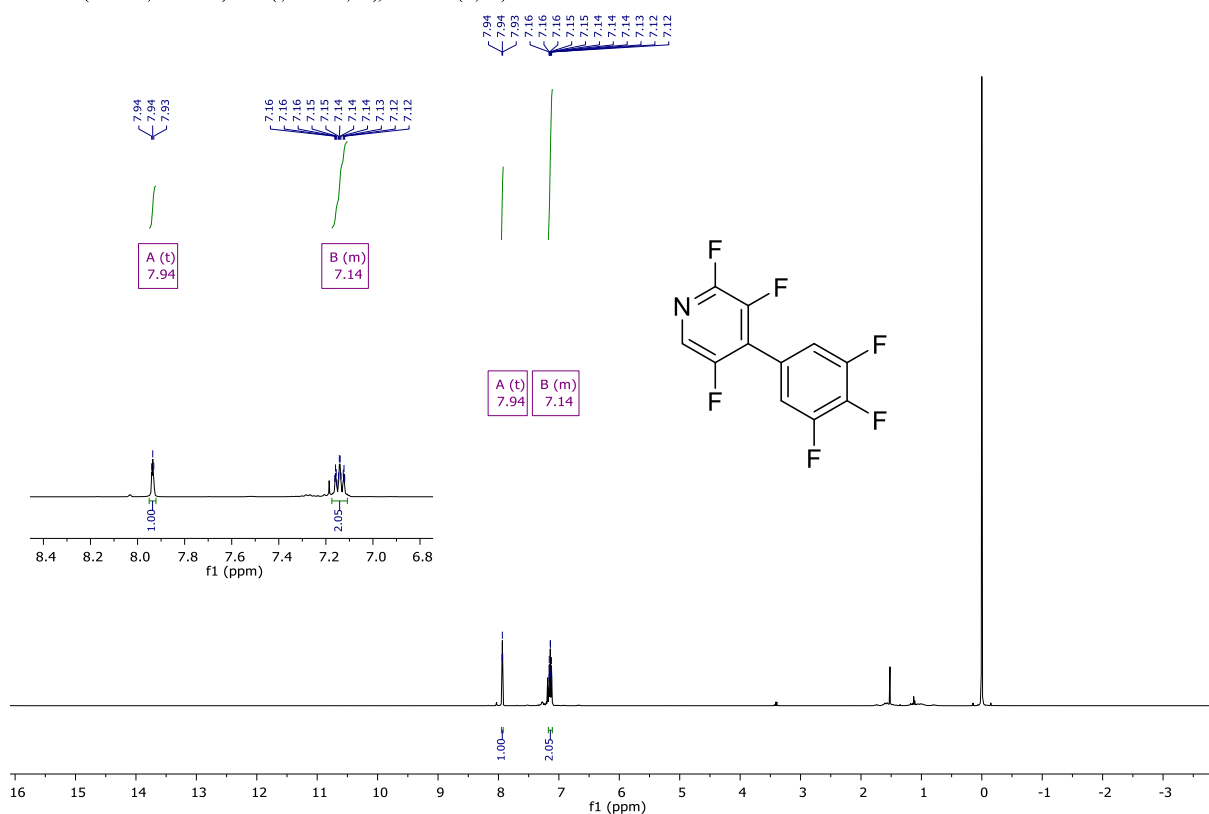
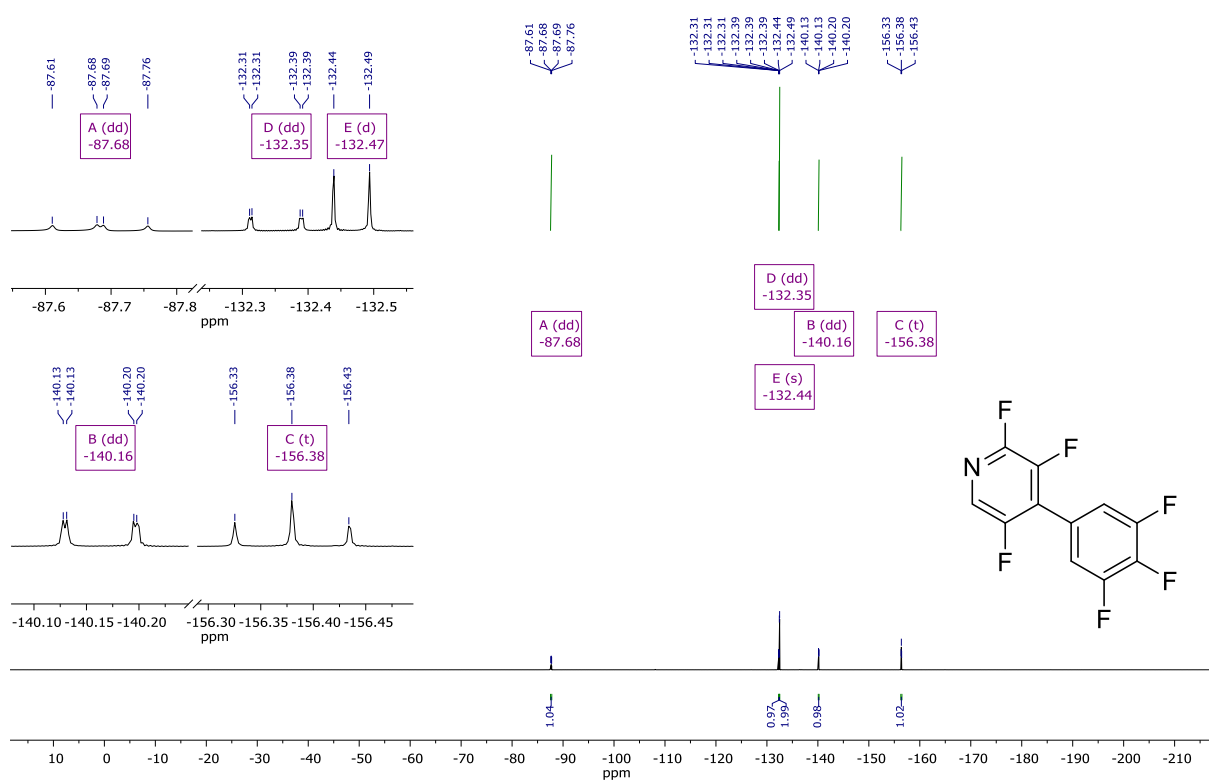
Figure S101 EI-Spectrum (EI⁺): 4-(3,5-Difluorophenyl)-2,3,5-trifluoropyridine

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

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

¹H NMR (400 MHz, Chloroform-d) δ 7.94 (t, $J = 1.8$ Hz, 1H), 7.18 – 7.10 (m, 2H).Figure S103 ¹H-NMR: 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine¹⁹F 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 (d, $J = 25.1$ Hz), -156.38 (t, $J = 20.4$ Hz).Figure S104 ¹⁹F-NMR {¹H}: 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

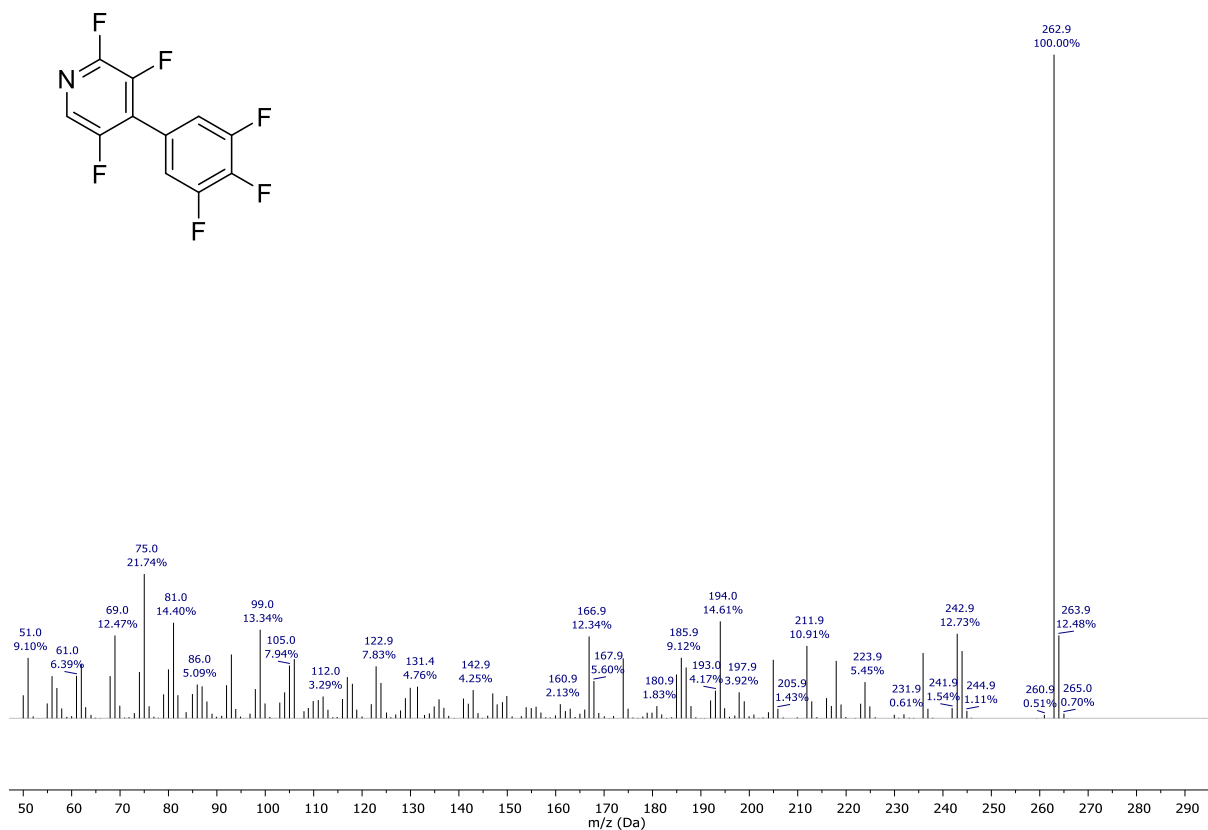
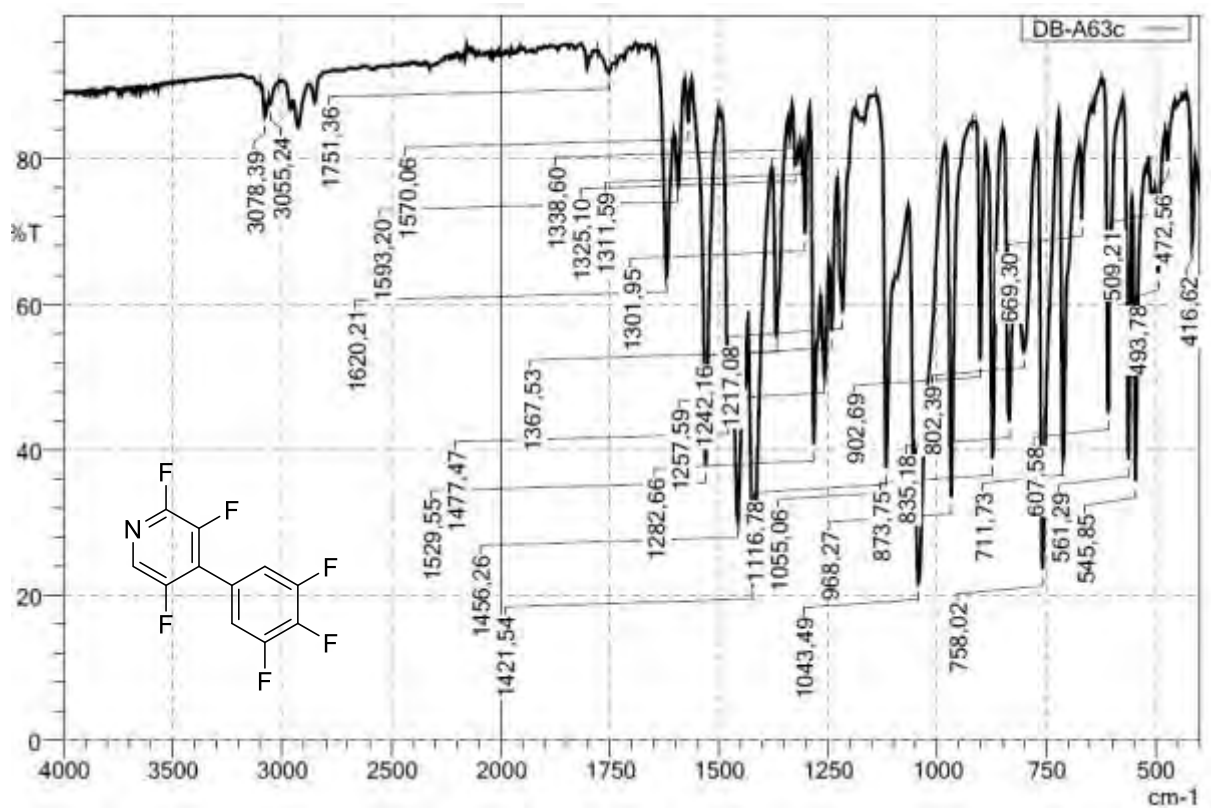
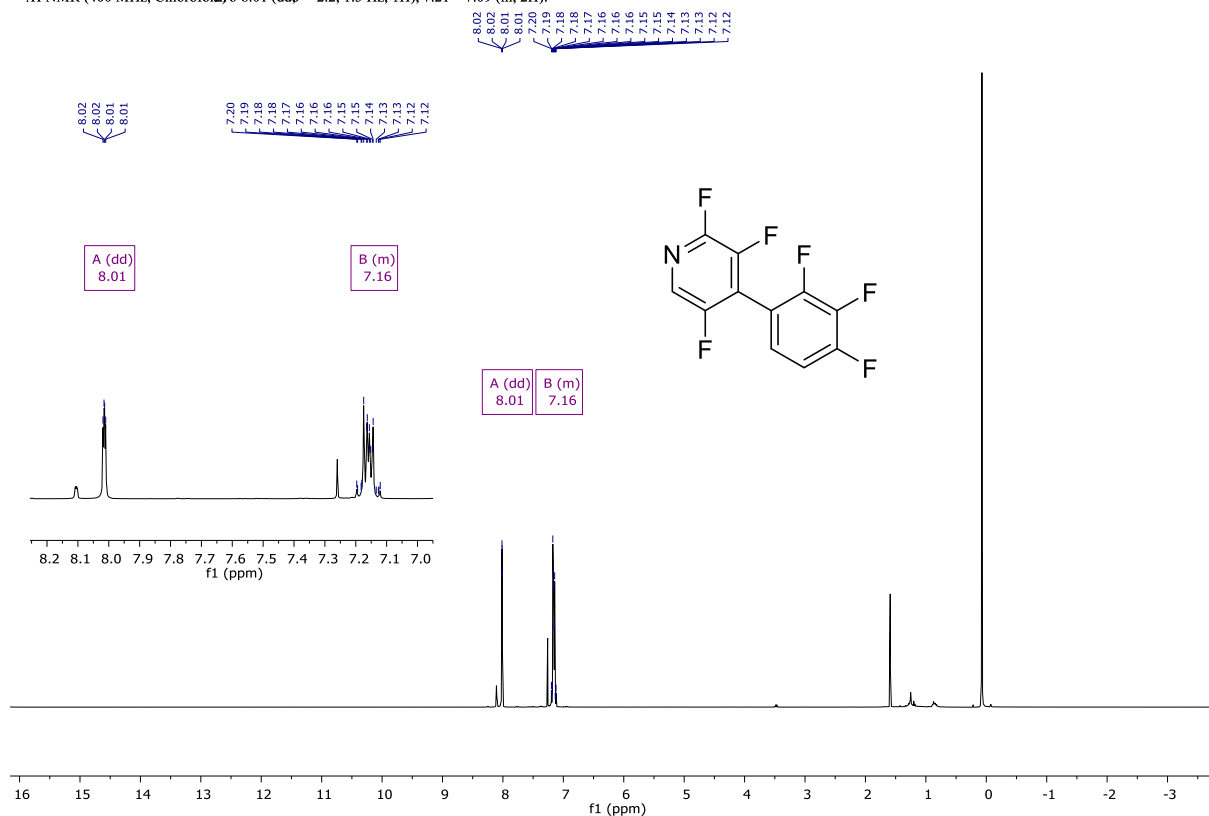
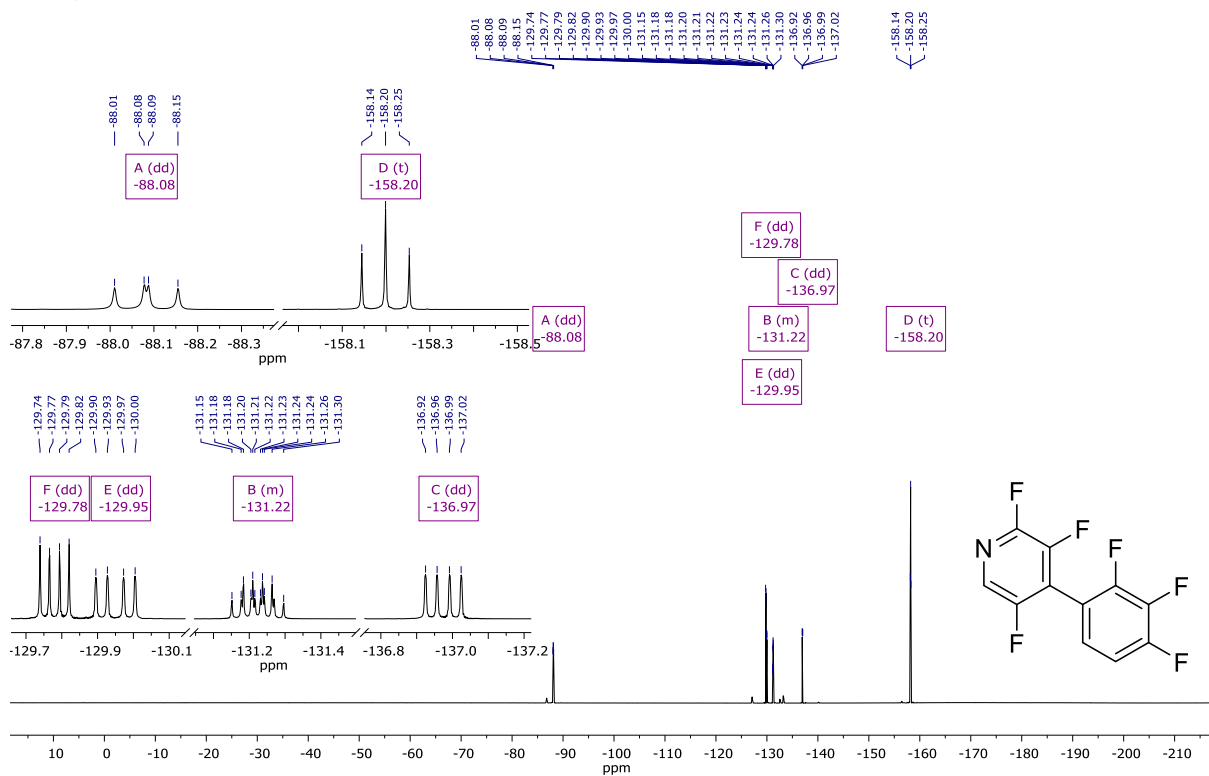
Figure S106 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(3,4,5-trifluorophenyl)pyridine

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)

 $^1\text{H NMR}$ (400 MHz, Chloroform- d_3) δ 8.01 (dd, $J = 2.2, 1.3$ Hz, 1H), 7.21 – 7.09 (m, 2H).Figure S108 $^1\text{H-NMR}$: 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine $^{19}\text{F NMR}$ (377 MHz, Chloroform- d_3) 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, $J = 5.2, 12.2$ Hz), -158.20 (t, 20.4 Hz).Figure S109 $^{19}\text{F-NMR}$ { ^1H }: 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

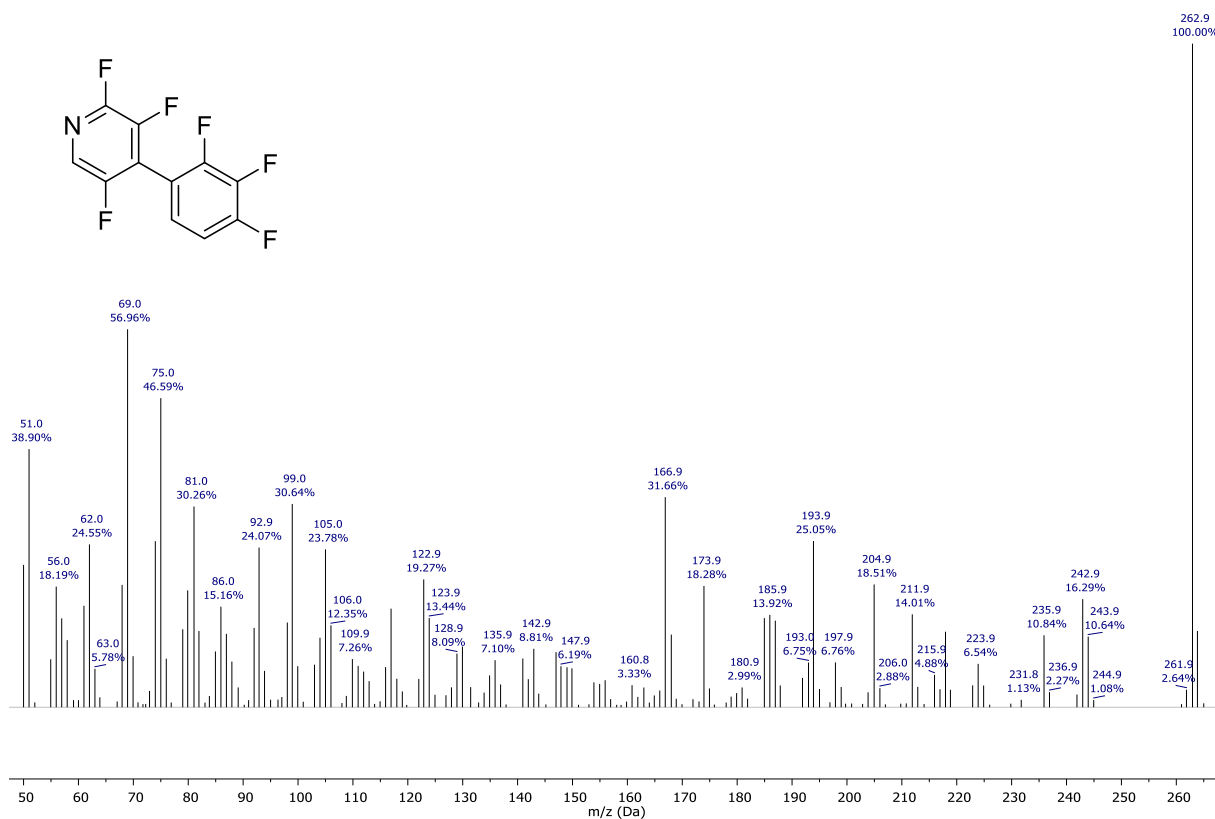
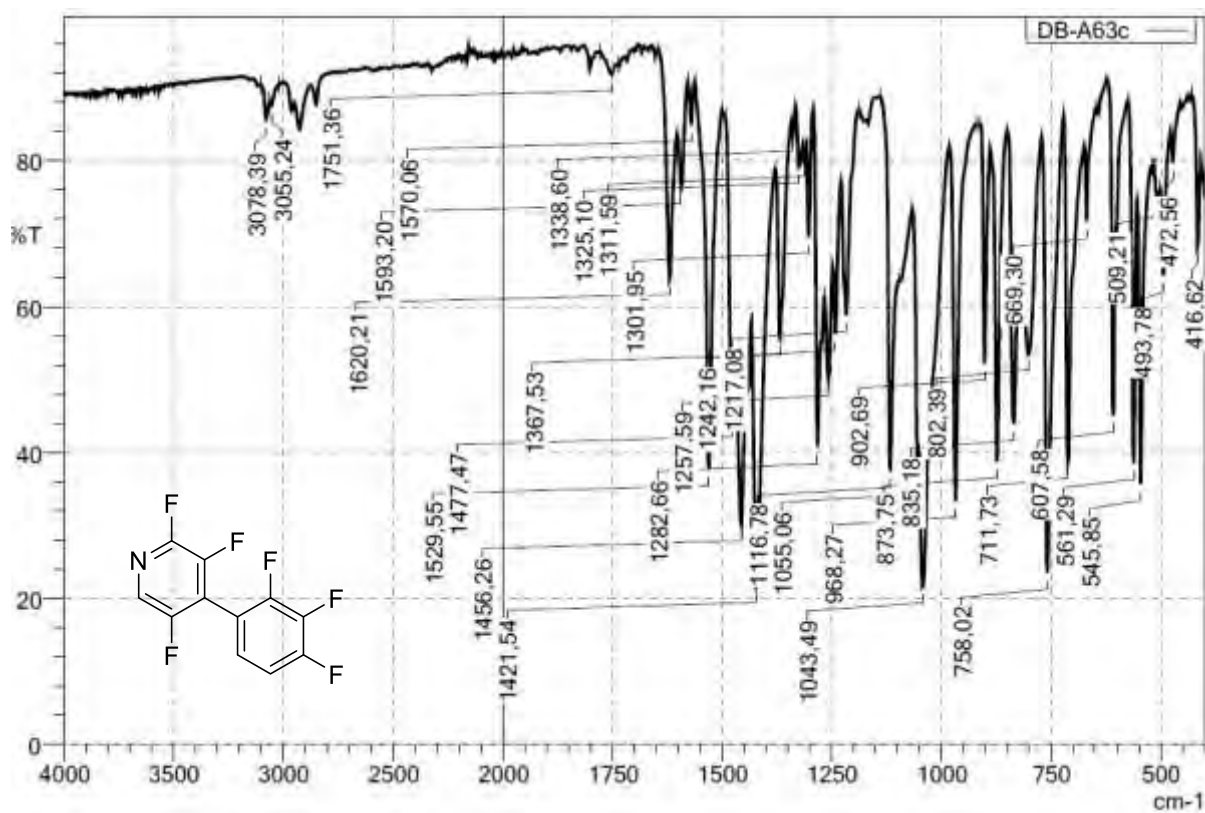
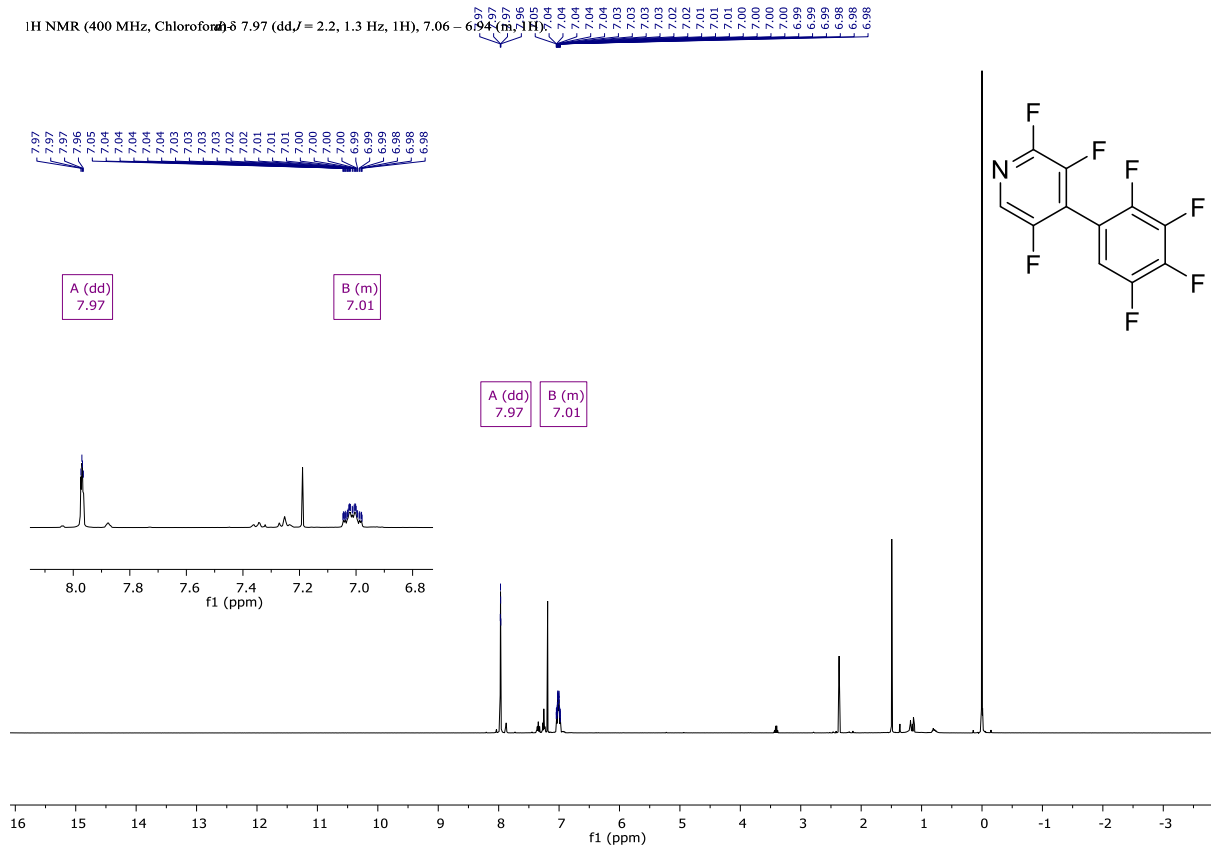
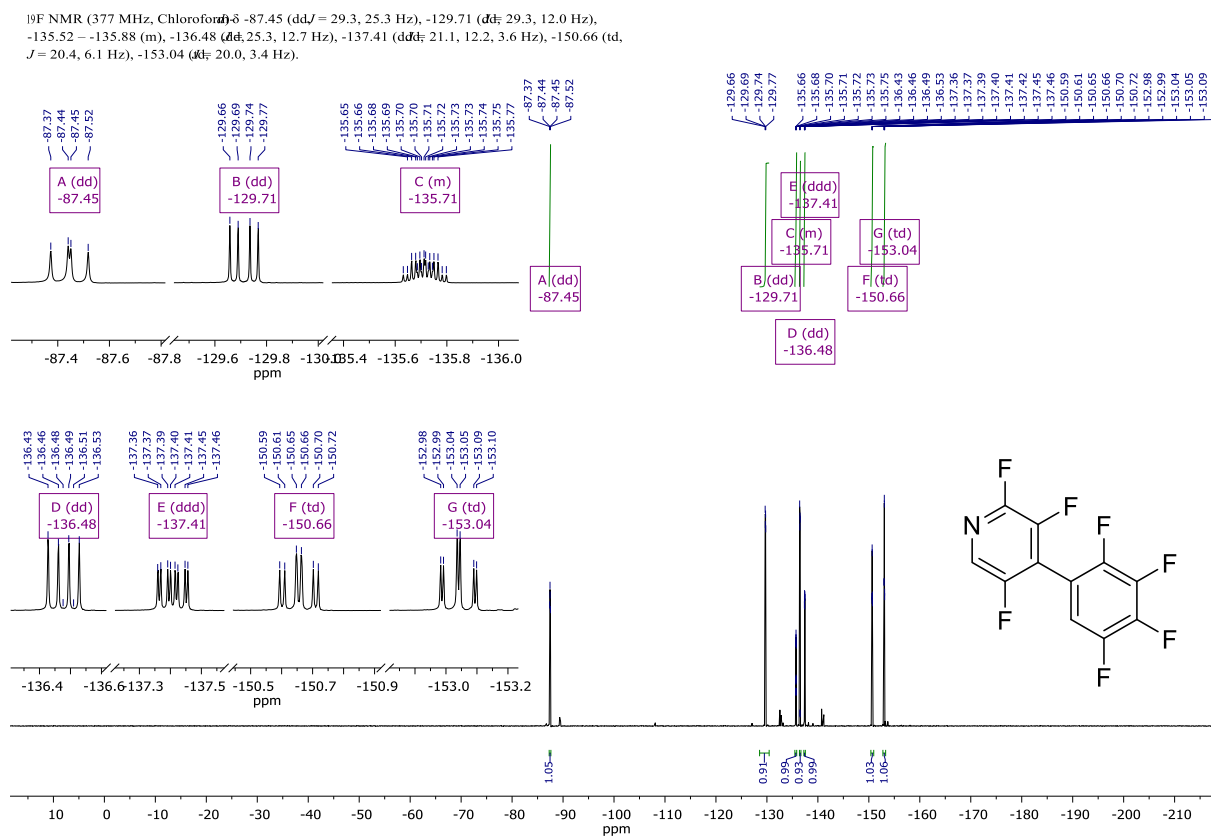
Figure S111 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(2,3,4-trifluorophenyl)pyridine

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 S113 ¹H-NMR: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridineFigure S114 ¹⁹F-NMR {¹H}: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

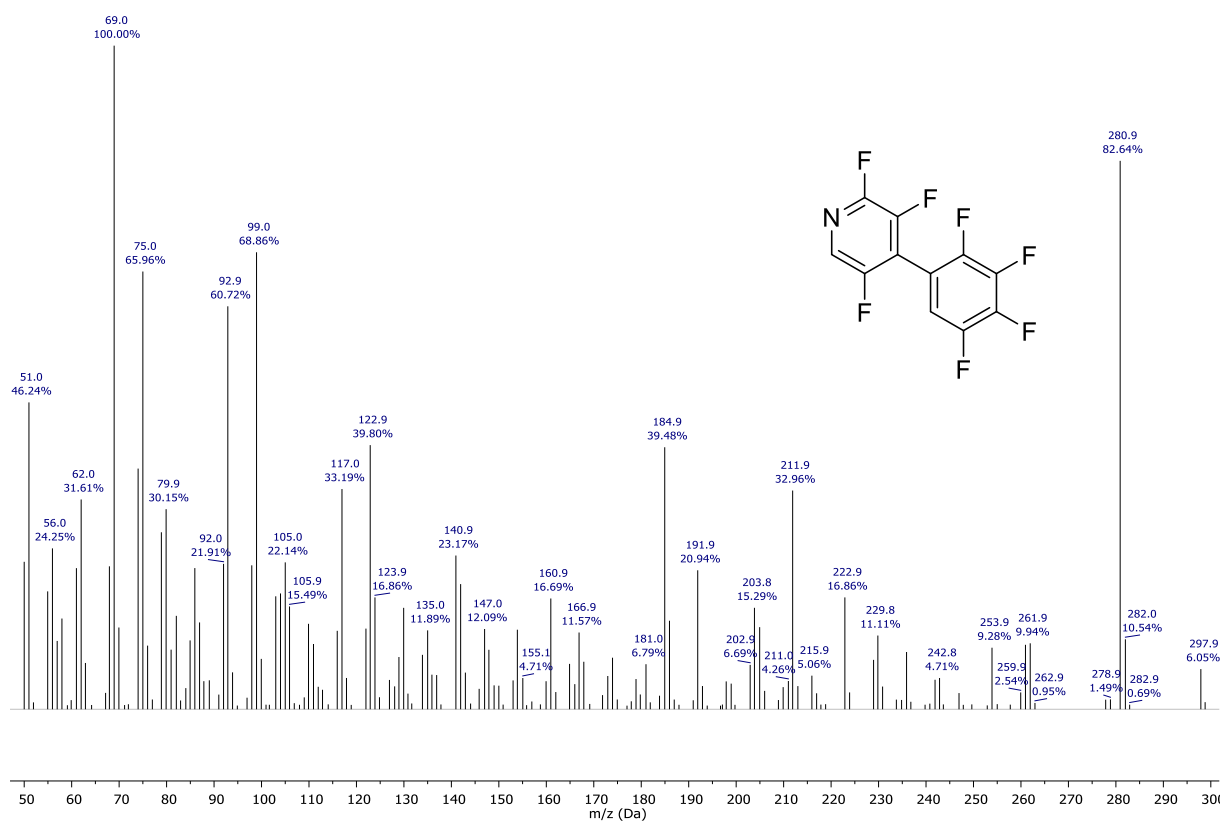
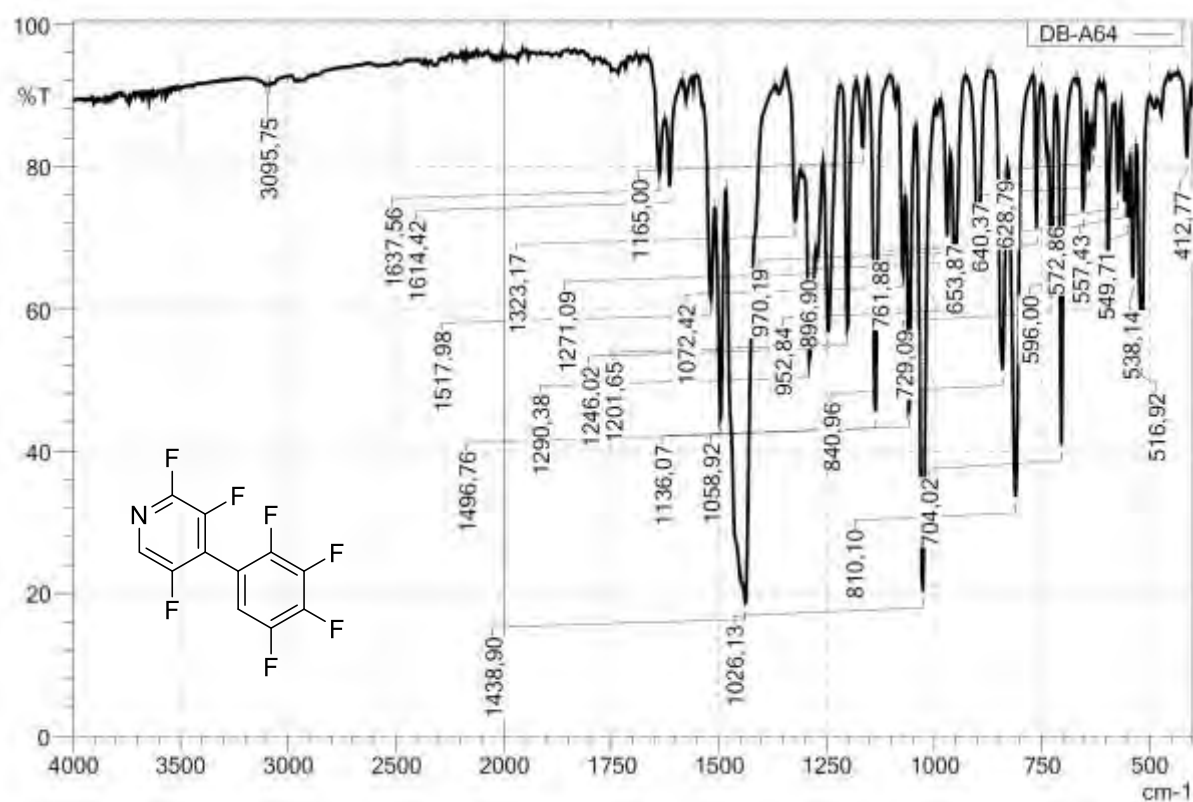
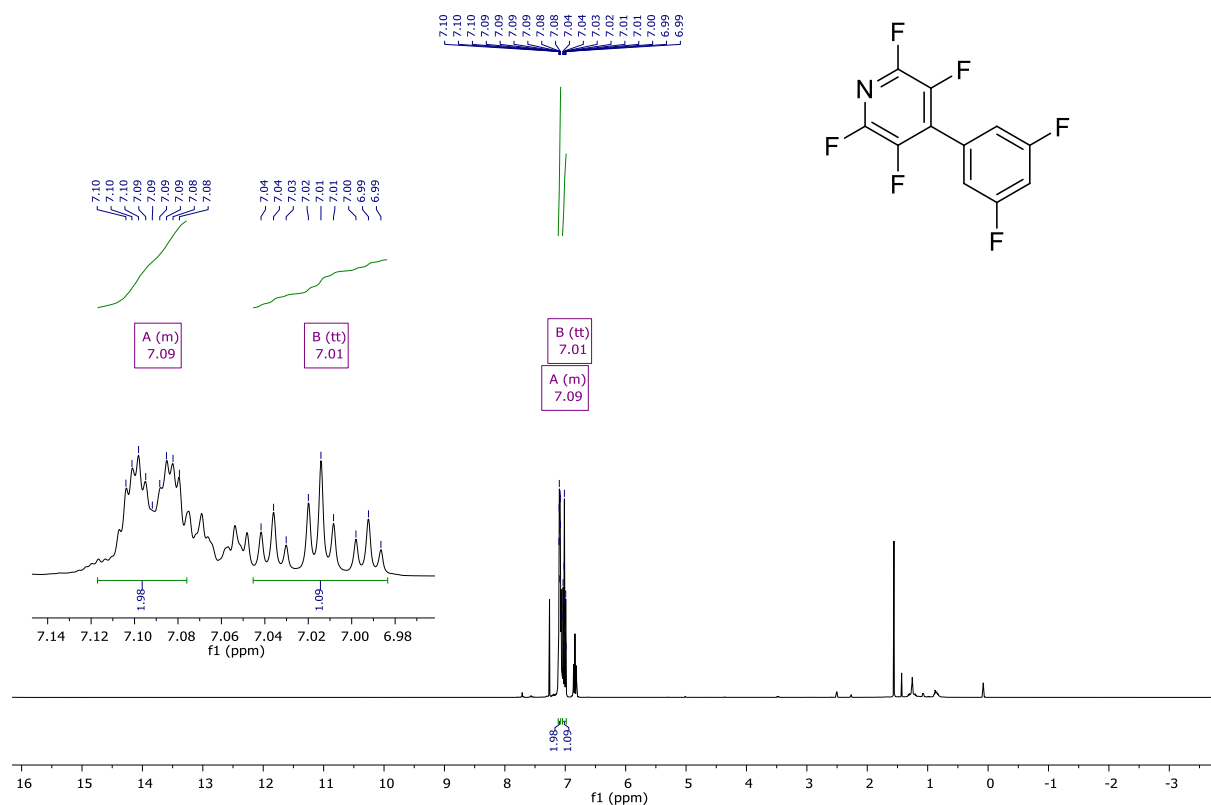
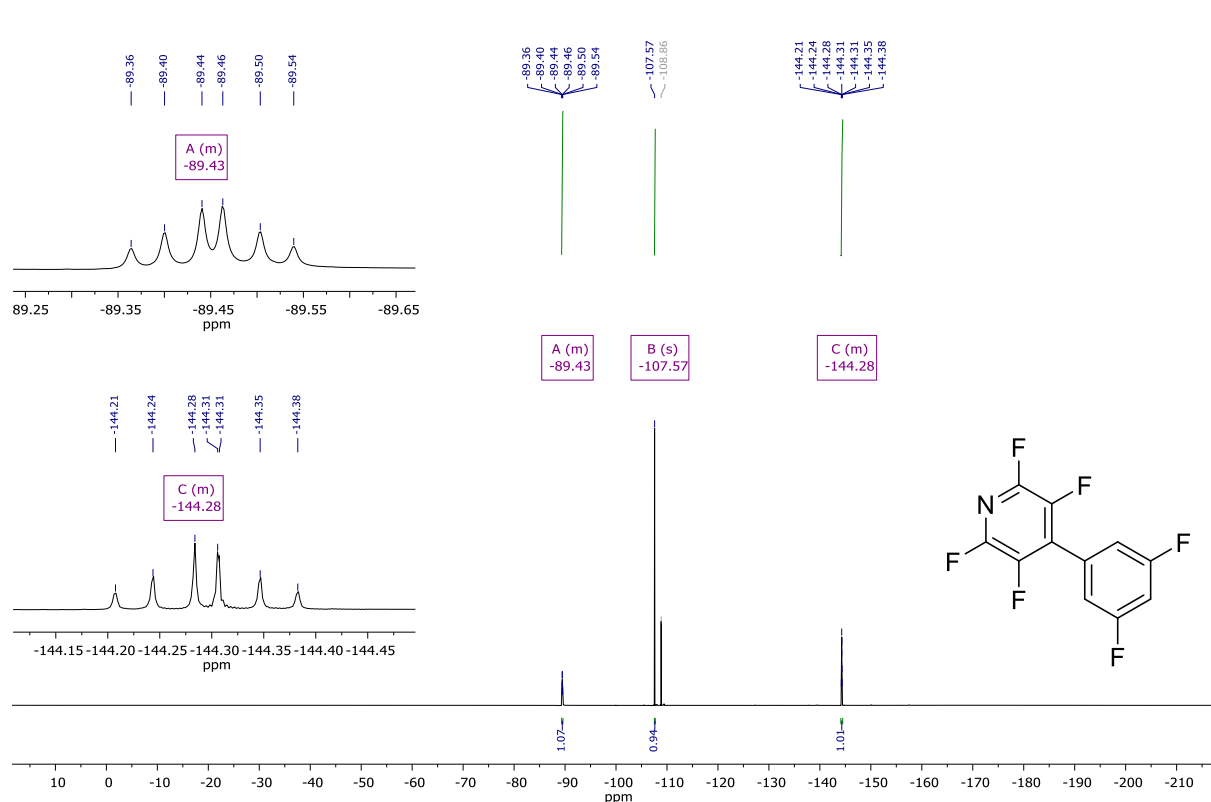
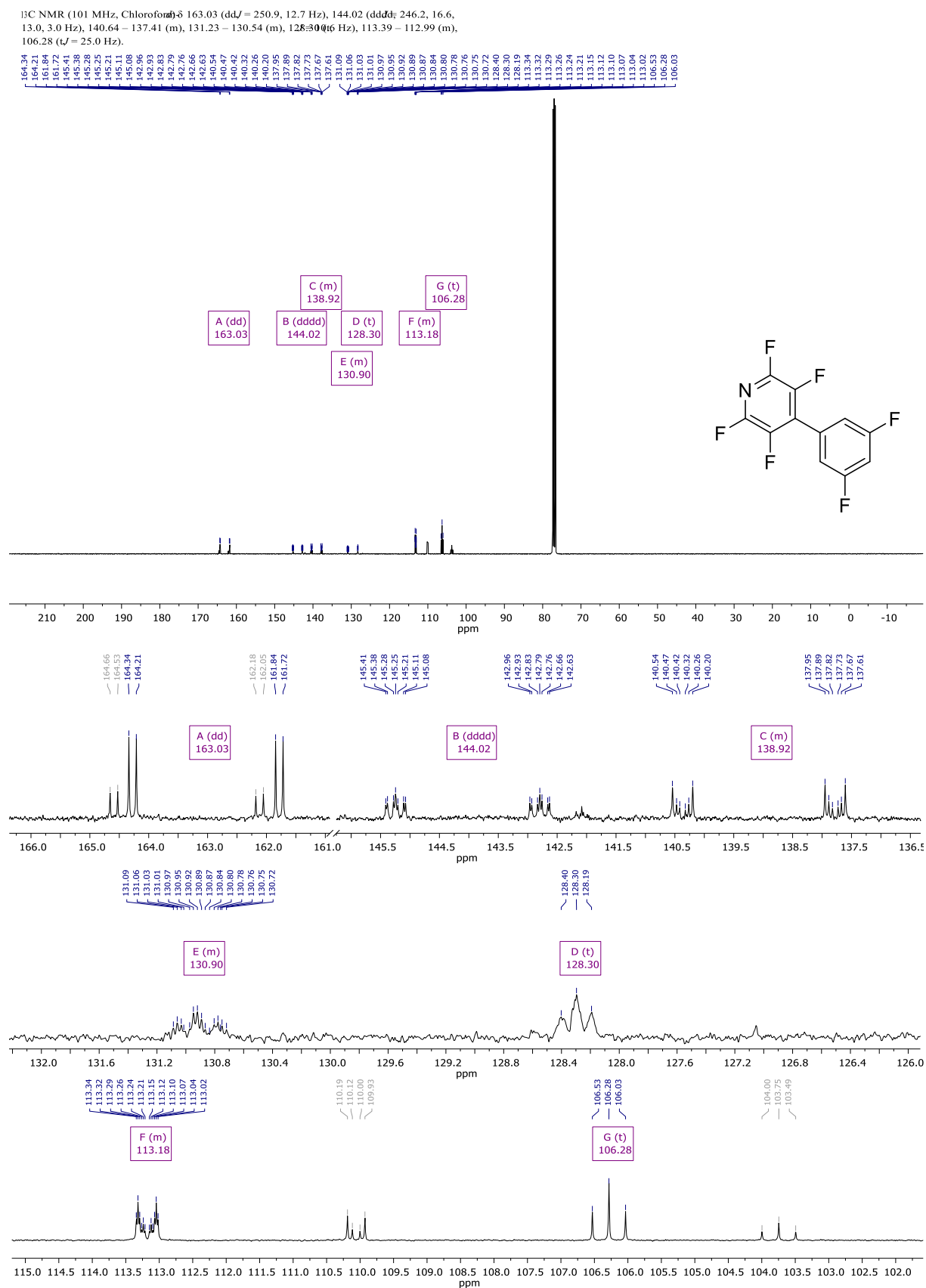
Figure S116 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

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)

 ^1H NMR (400 MHz, Chloroform- d_3) δ 7.11 – 7.08 (m, 1H), 7.01 (tt, $J = 8.7, 2.3$ Hz, 1H).Figure S118 ^1H -NMR: 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine ^{19}F NMR (377 MHz, Chloroform- d_3) δ -89.34 – -89.57 (m), -107.57, -144.18 – -144.40 (m).Figure S119 ^{19}F -NMR [^1H]: 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

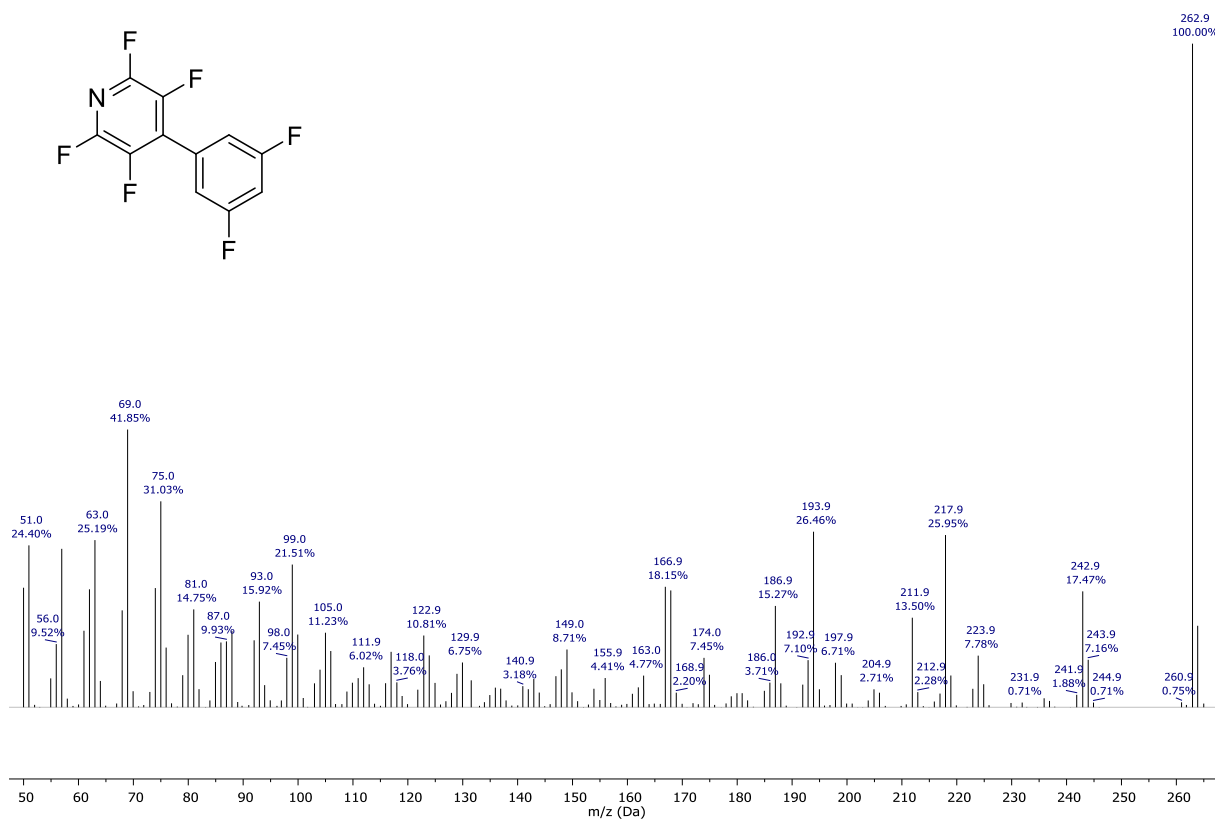
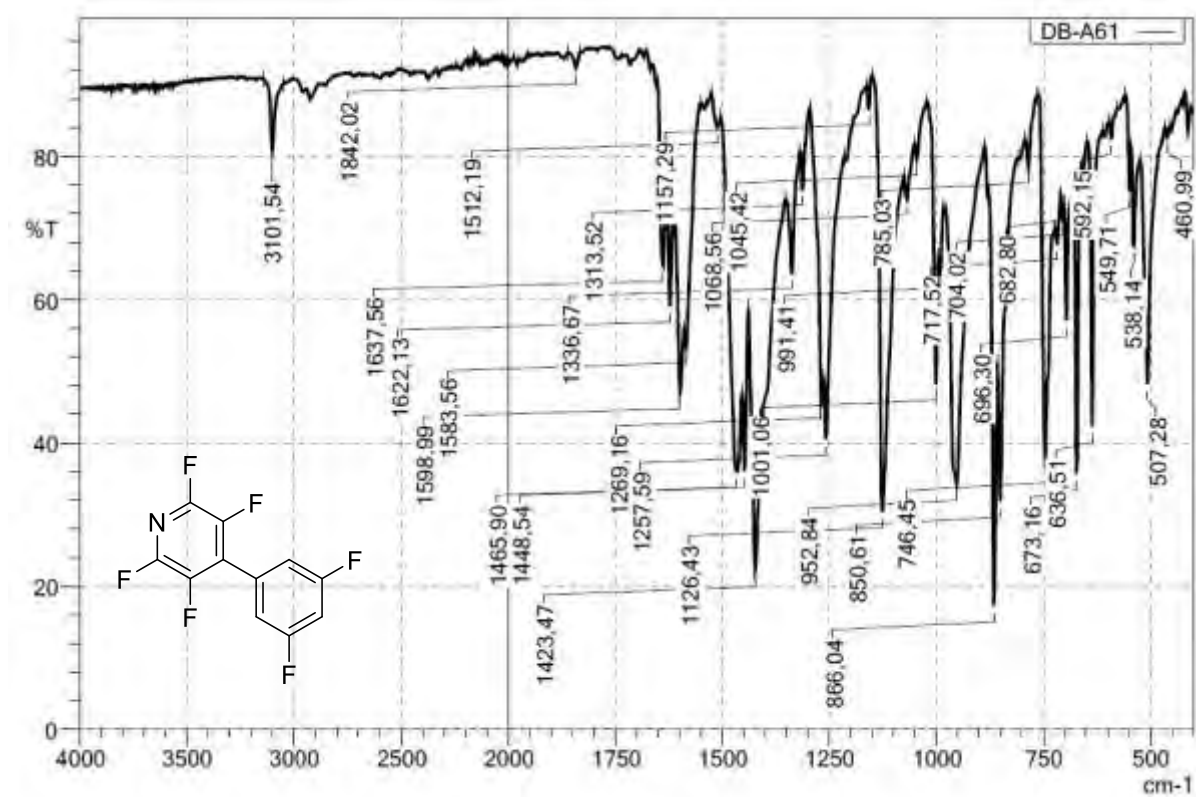
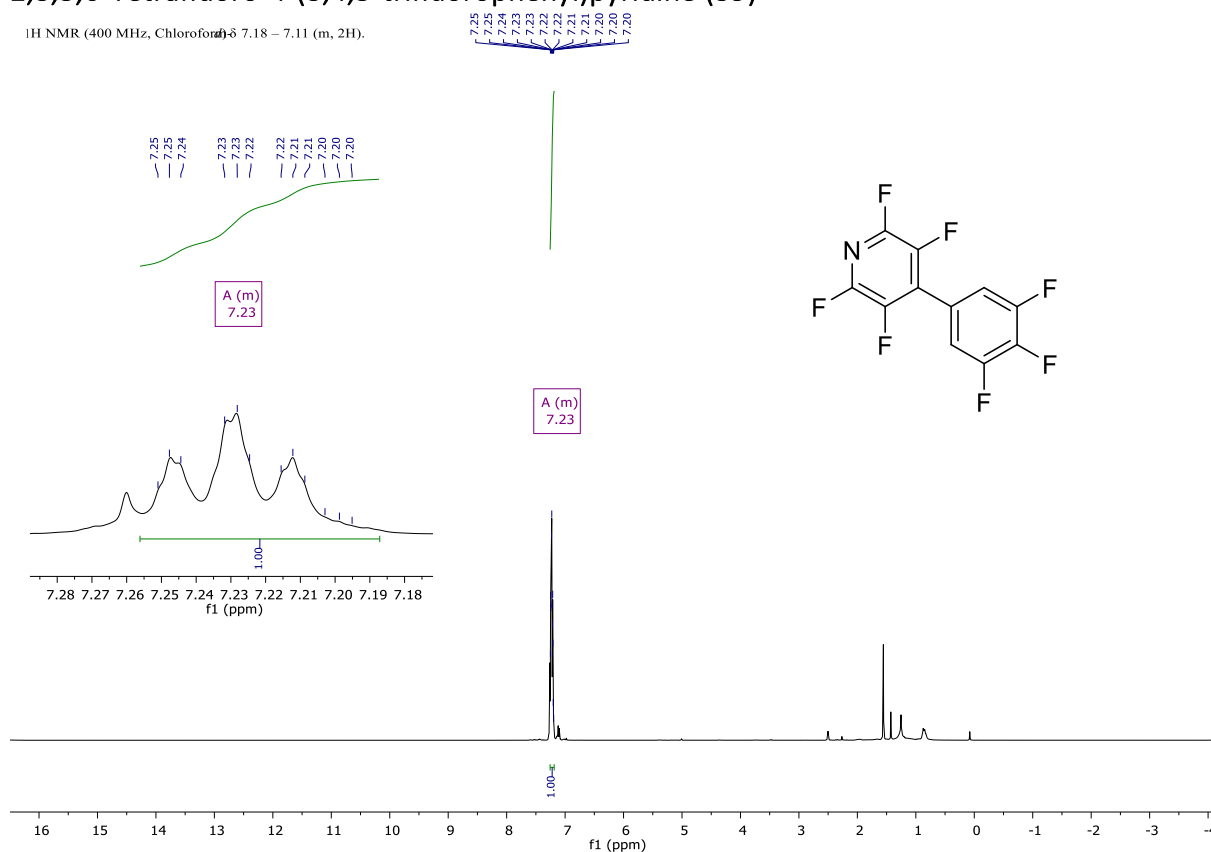
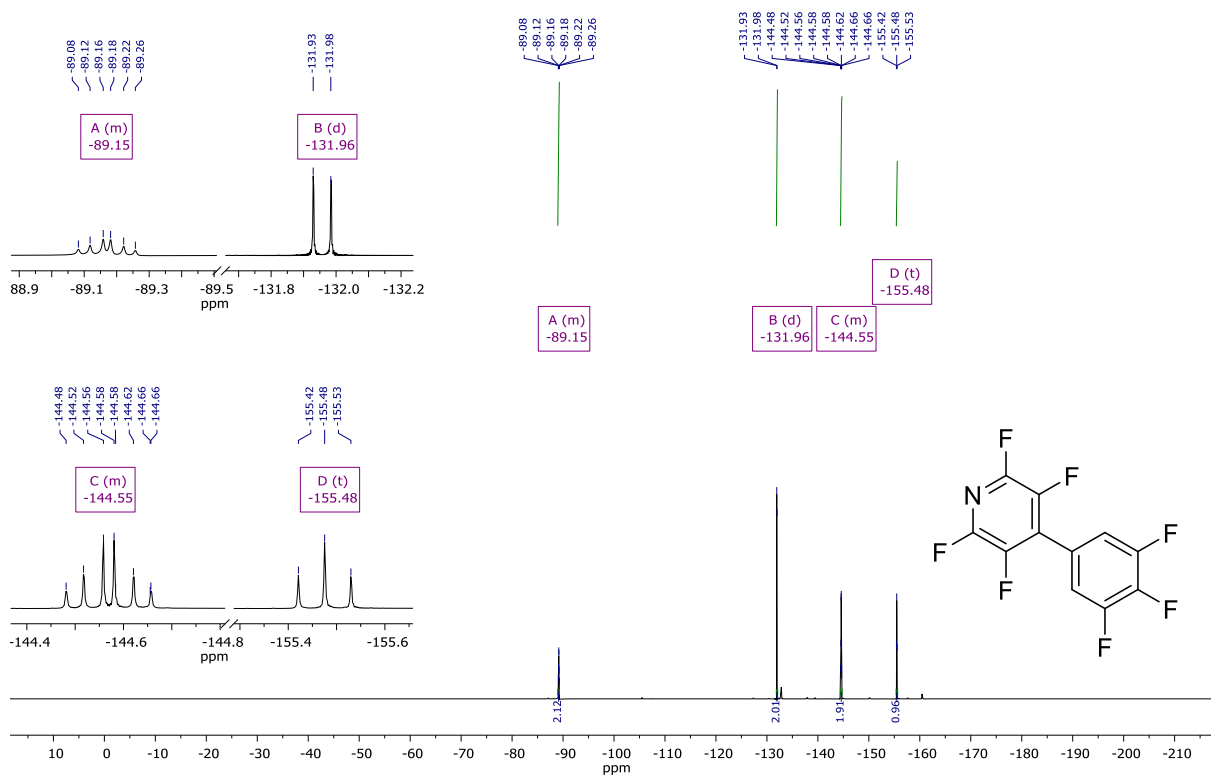
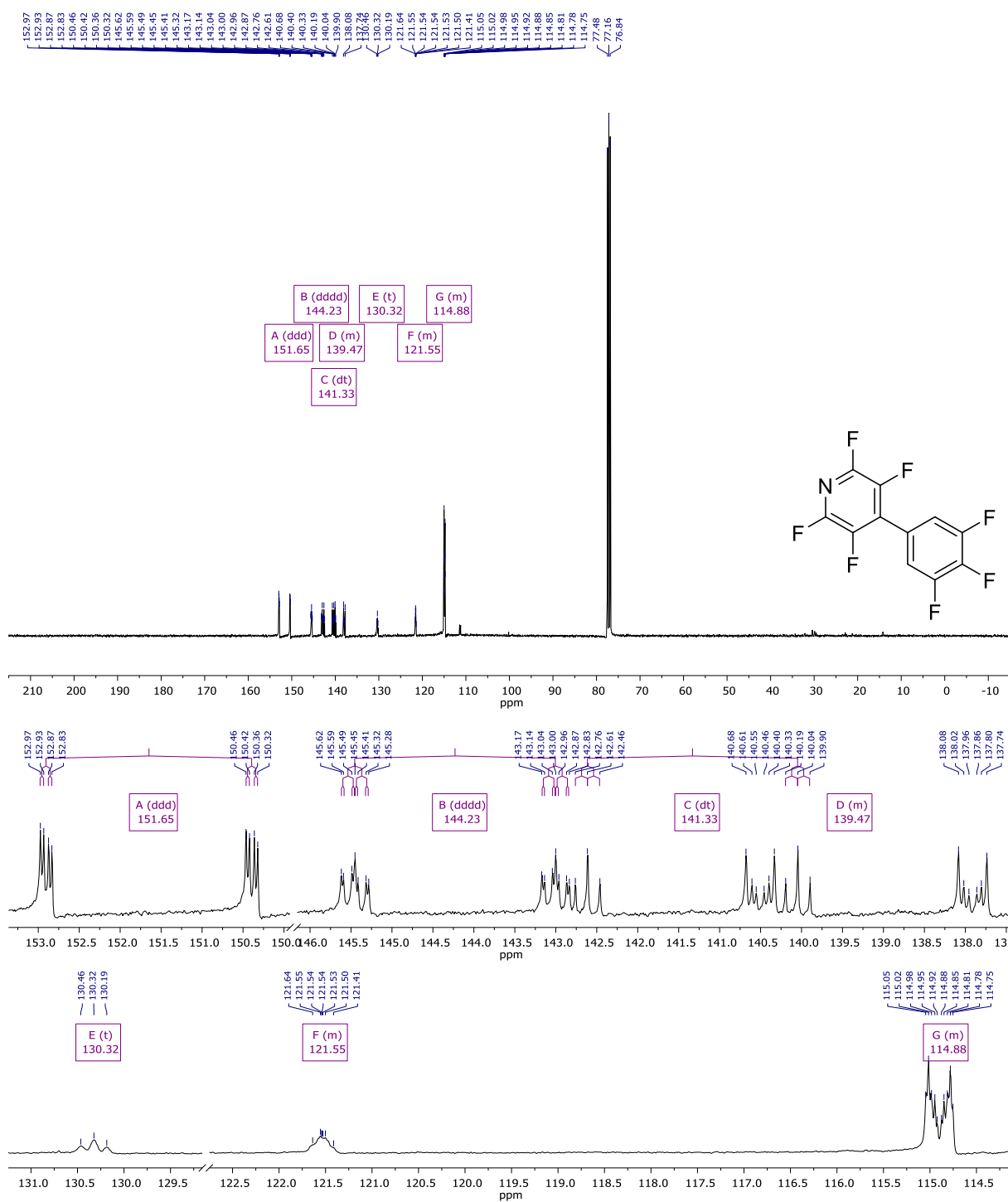
Figure S121 EI-Spectrum (EI⁺): 2,3,5-Trifluoro-4-(2,3,4,5-tetrafluorophenyl)pyridine

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)

 $^1\text{H NMR}$ (400 MHz, Chloroform- d_3) δ 7.18 – 7.11 (m, 2H).Figure S123 $^1\text{H-NMR}$: 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine $^{19}\text{F NMR}$ (377 MHz, Chloroform- d_3) δ -89.04 – -89.27 (m), -131.96 (d, 20.4 Hz), -144.43 – -144.68 (m), -155.48 (t, 20.5 Hz).Figure S124 $^{19}\text{F-NMR}$ [^1H]: 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

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

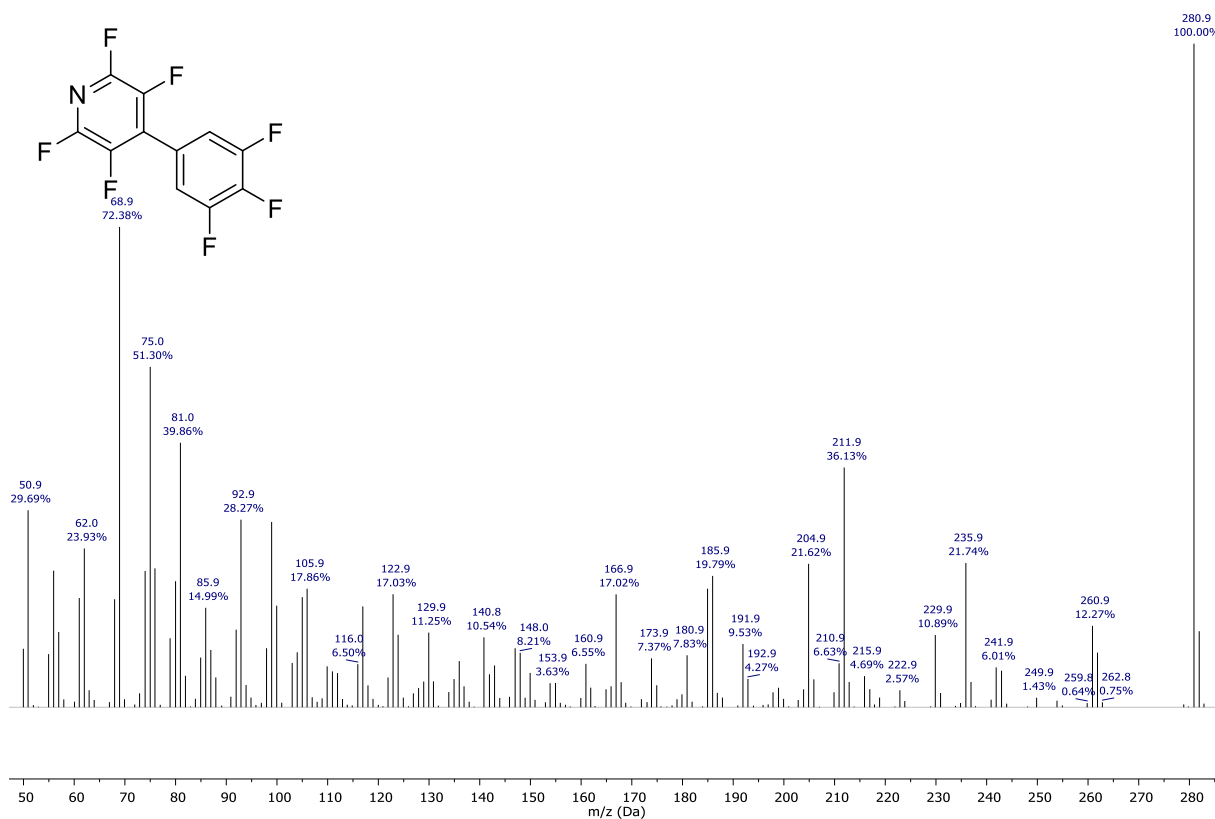
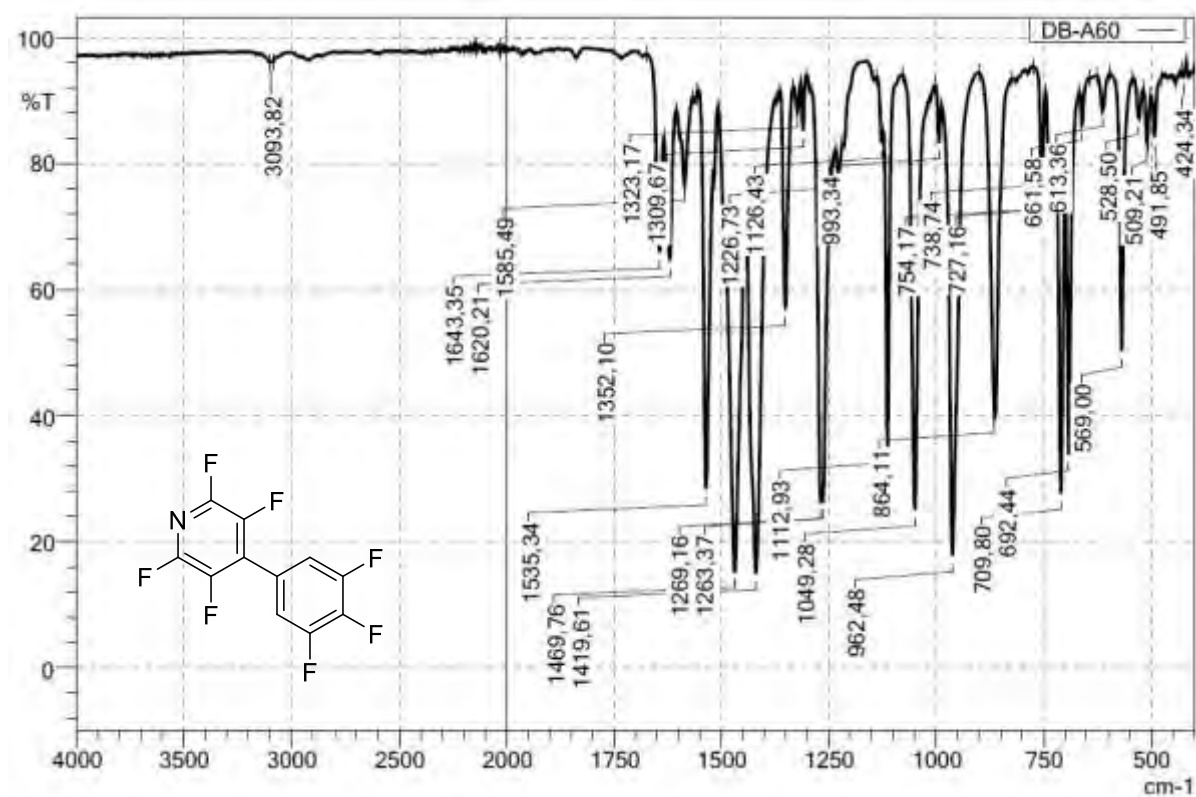
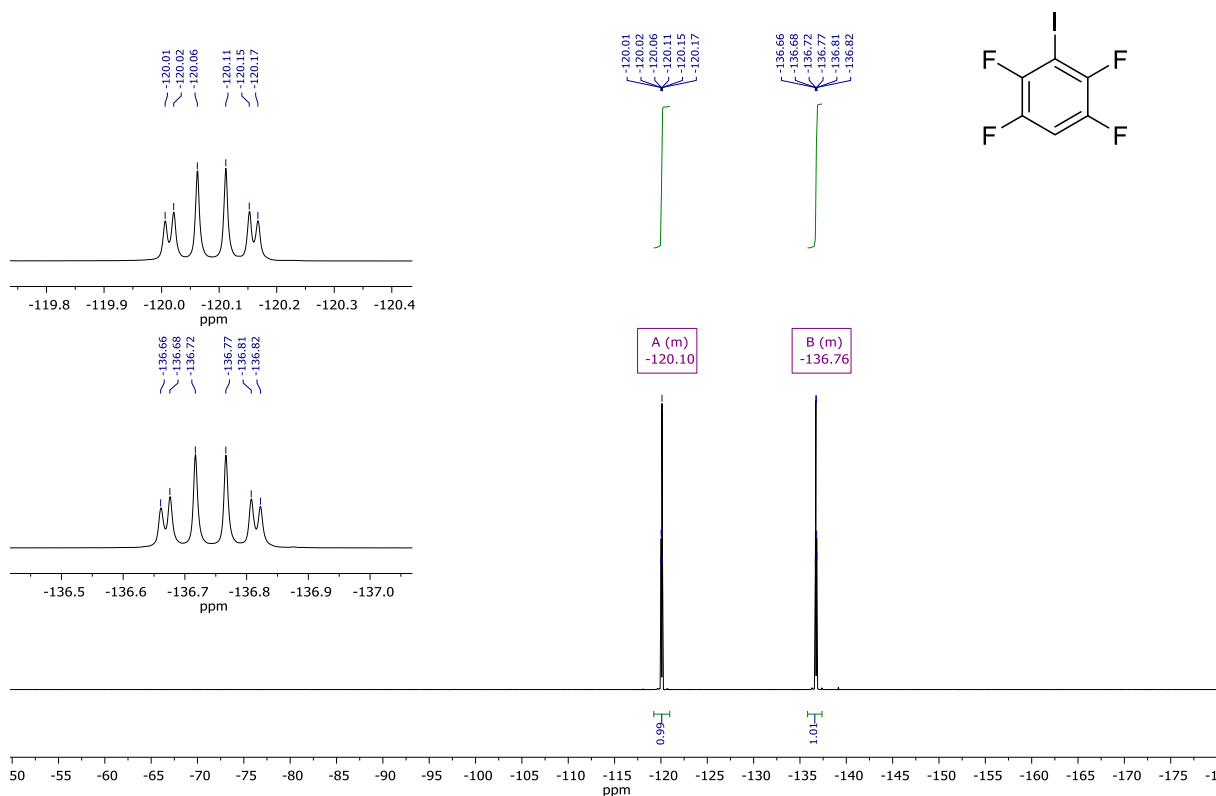
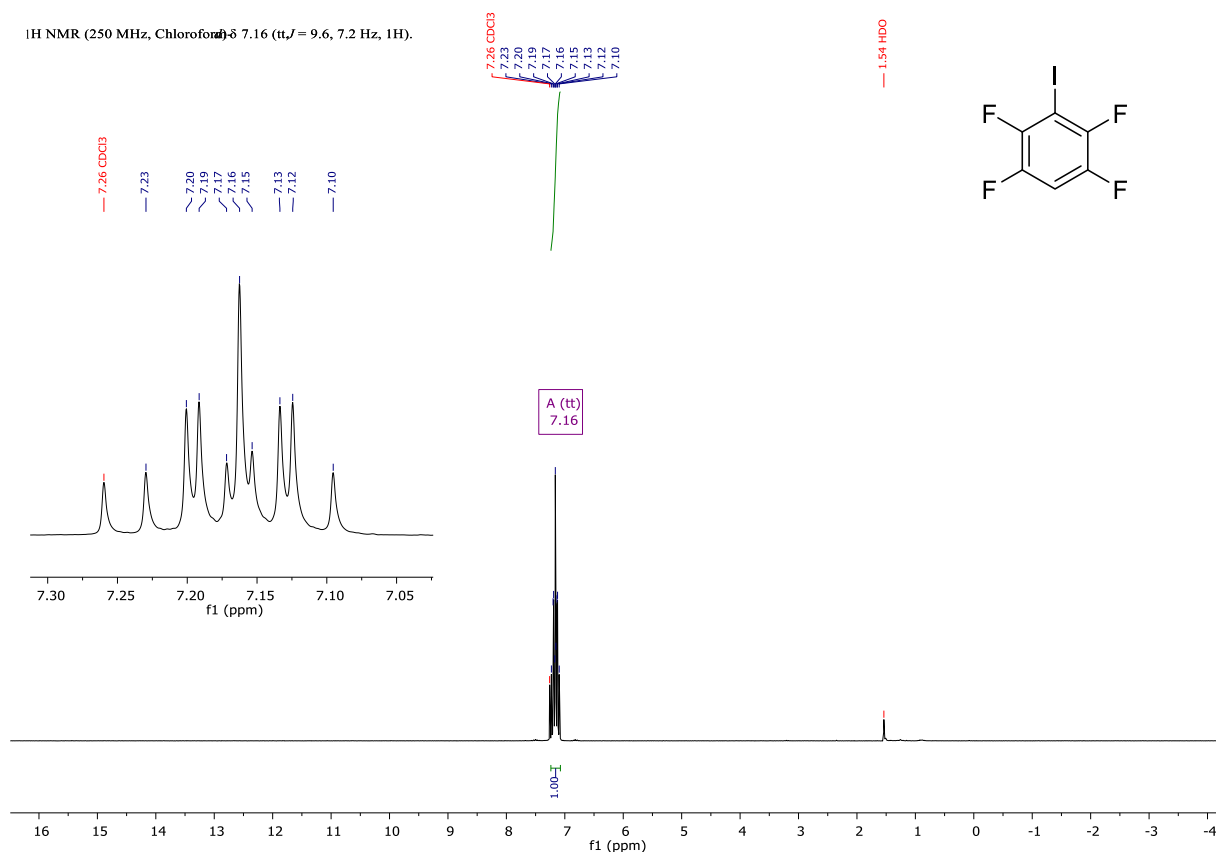
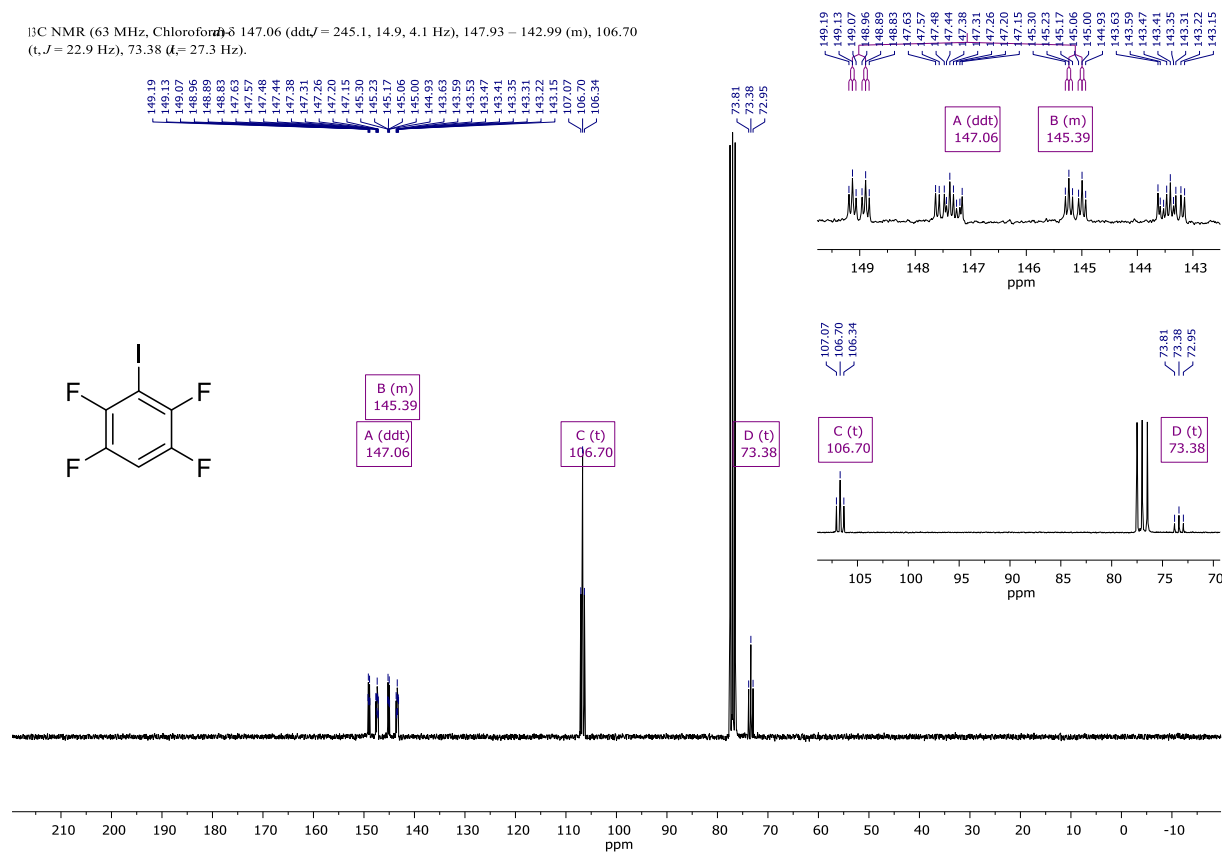
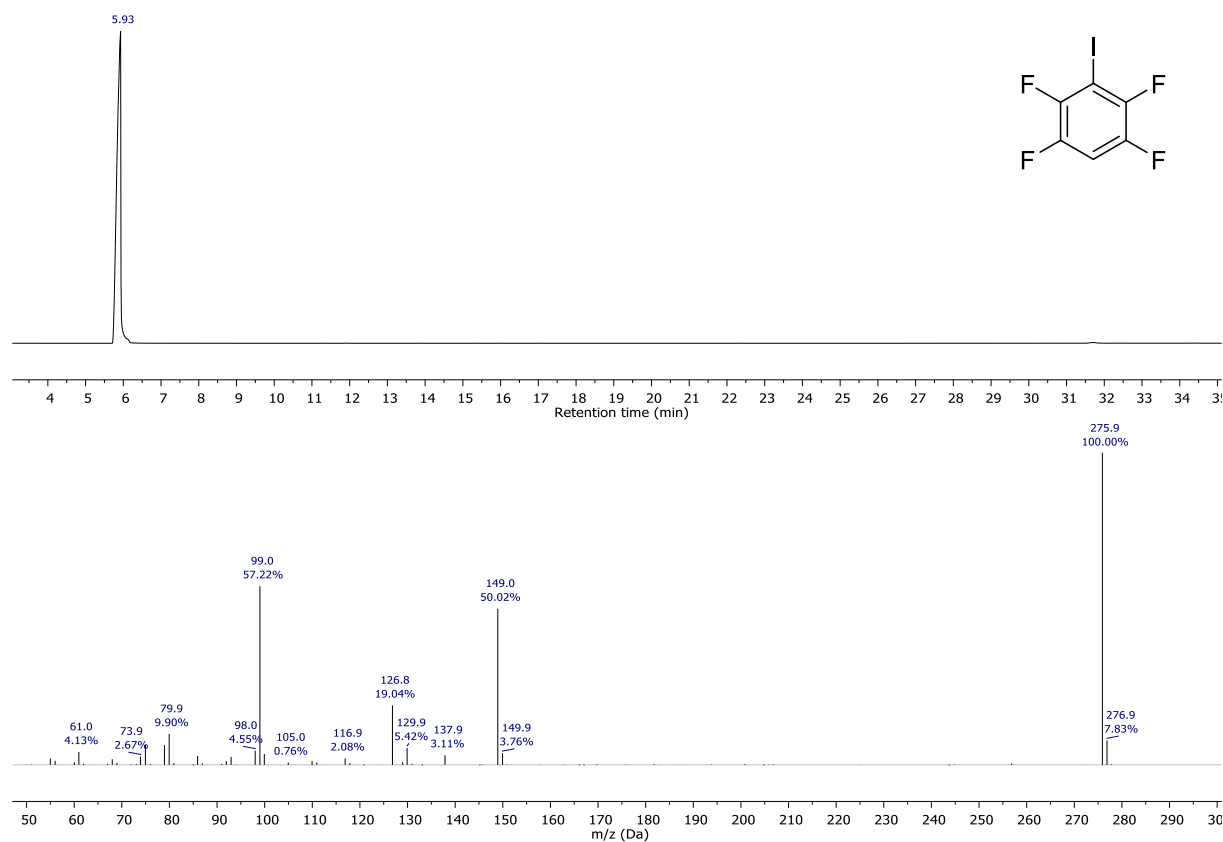
Figure S126 EI-Spectrum (EI⁺): 2,3,5,6-Tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine

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)

 ^{19}F NMR (235 MHz, Chloroform- d_3) δ -119.72 – -120.55 (m), -135.82 – -137.51 (m).Figure S128 ^{19}F -NMR $\{^1\text{H}\}$: 1,2,4,5-Tetrafluoro-3-iodobenzene ^1H NMR (250 MHz, Chloroform- d_3) δ 7.16 (tt, J = 9.6, 7.2 Hz, 1H).Figure S129 ^1H -NMR: 1,2,4,5-Tetrafluoro-3-iodobenzene

Figure S130 ^{13}C NMR: 1,2,4,5-Tetrafluoro-3-iodobenzeneFigure S131 GC/MS-Spectrum with EI-Spectrum (EI $^+$): 1,2,4,5-Tetrafluoro-3-iodobenzene

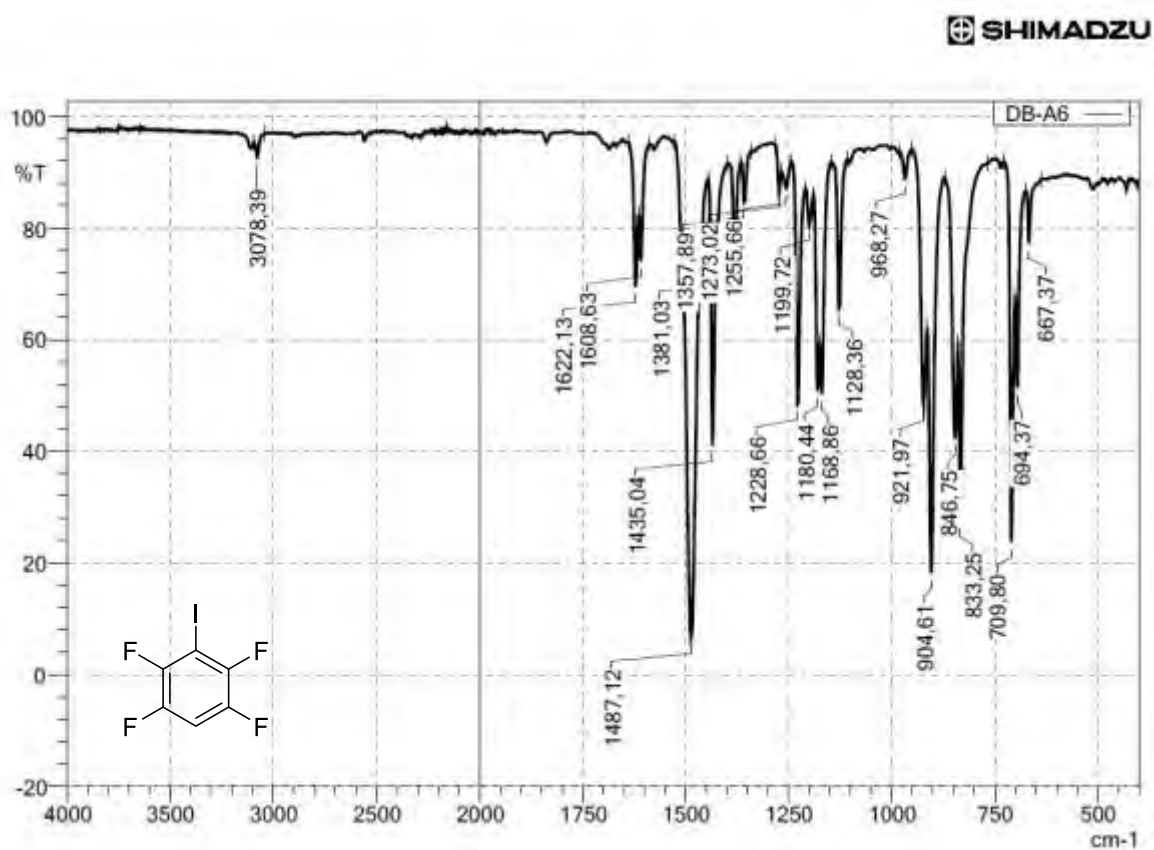
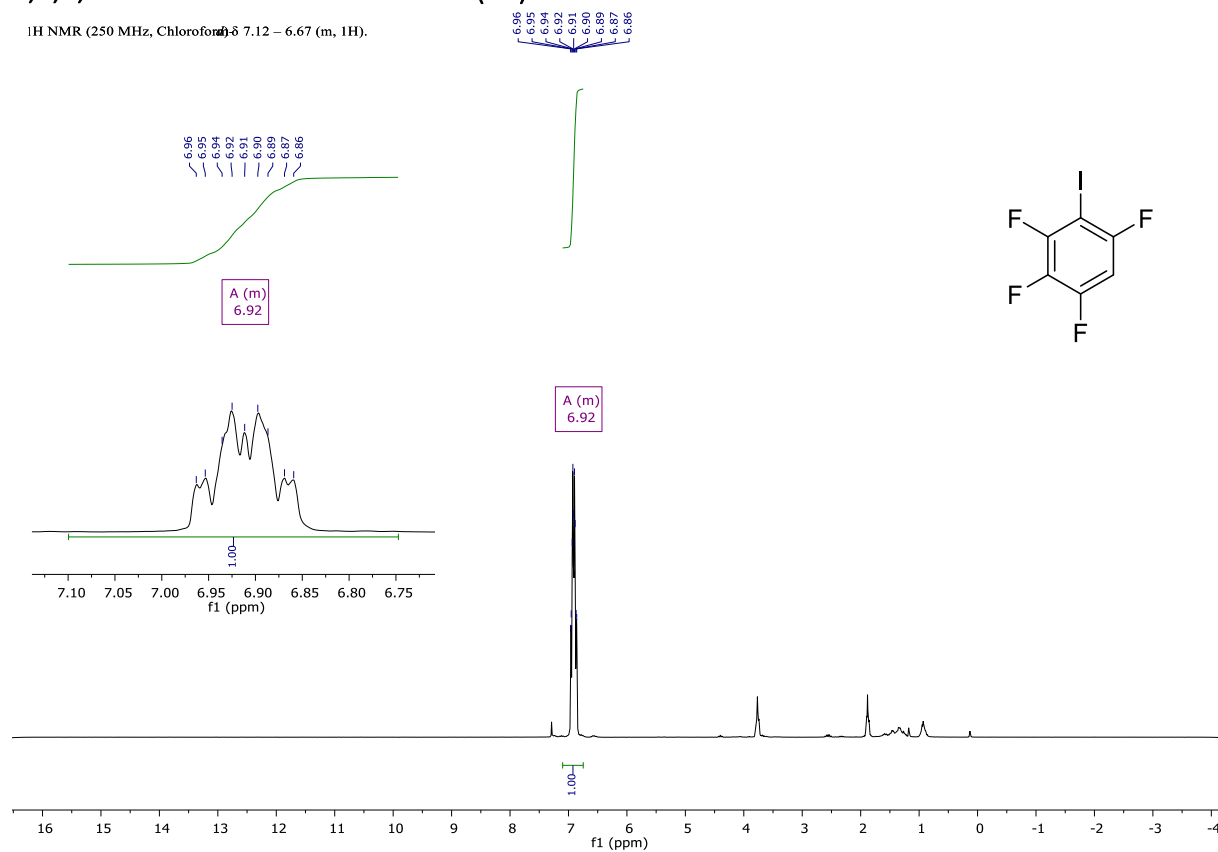
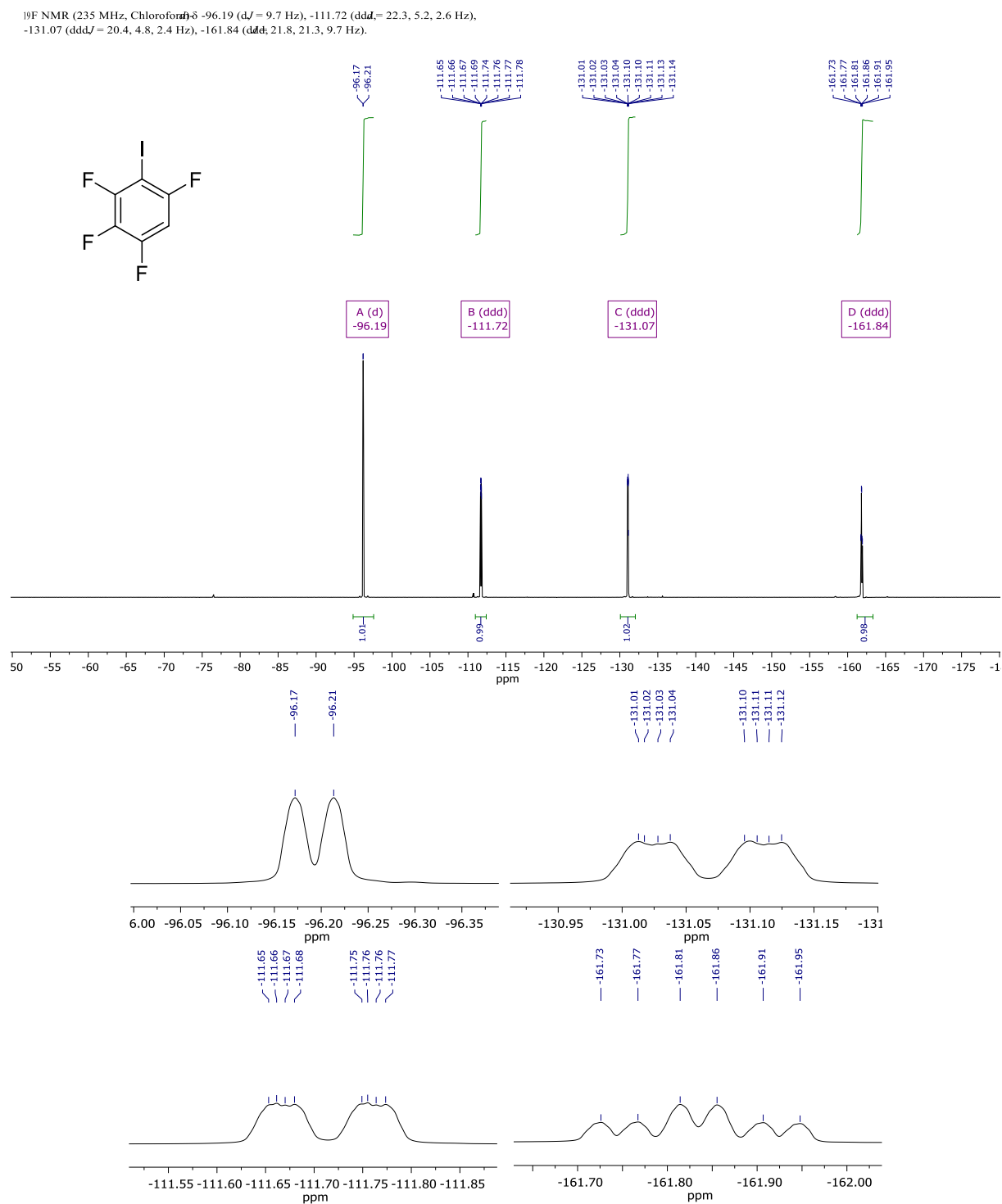
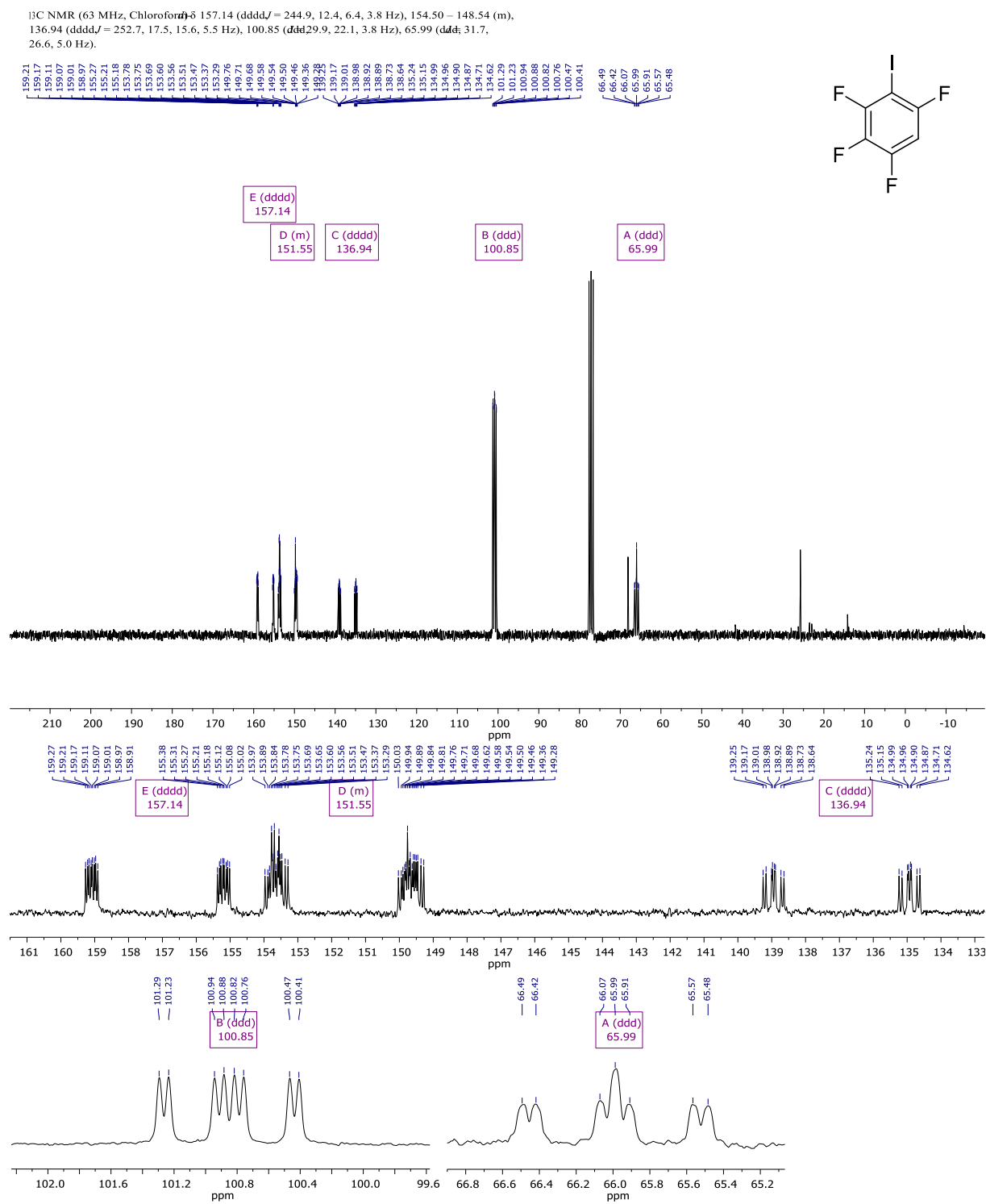


Figure S132 IR (ATR)-Spectrum: 1,2,4,5-Tetrafluoro-3-iodobenzene

1,2,3,5-Tetrafluoro-4-iodobenzene (40)¹H NMR (250 MHz, Chloroform-d) δ 7.12 – 6.67 (m, 1H).**Figure S133 ¹H-NMR: 1,2,3,5-Tetrafluoro-4-iodobenzene**

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

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

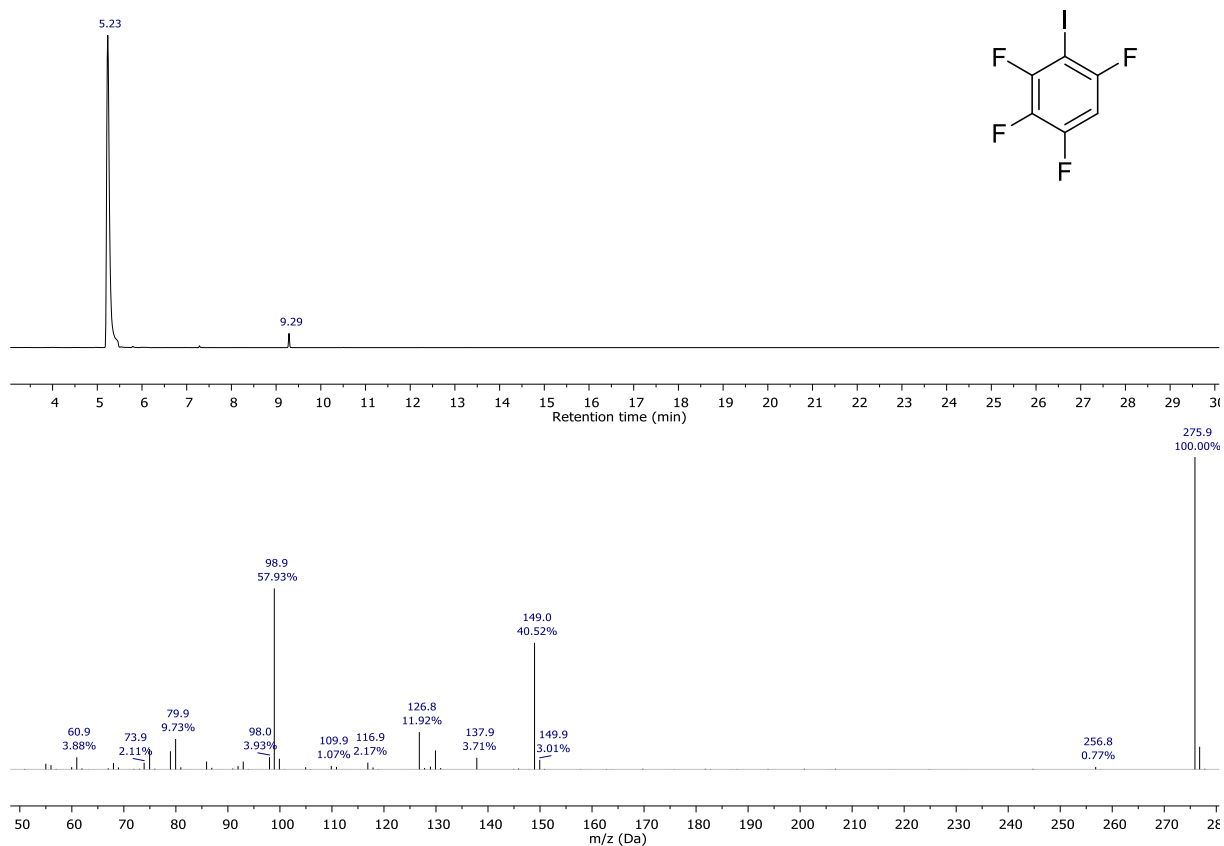
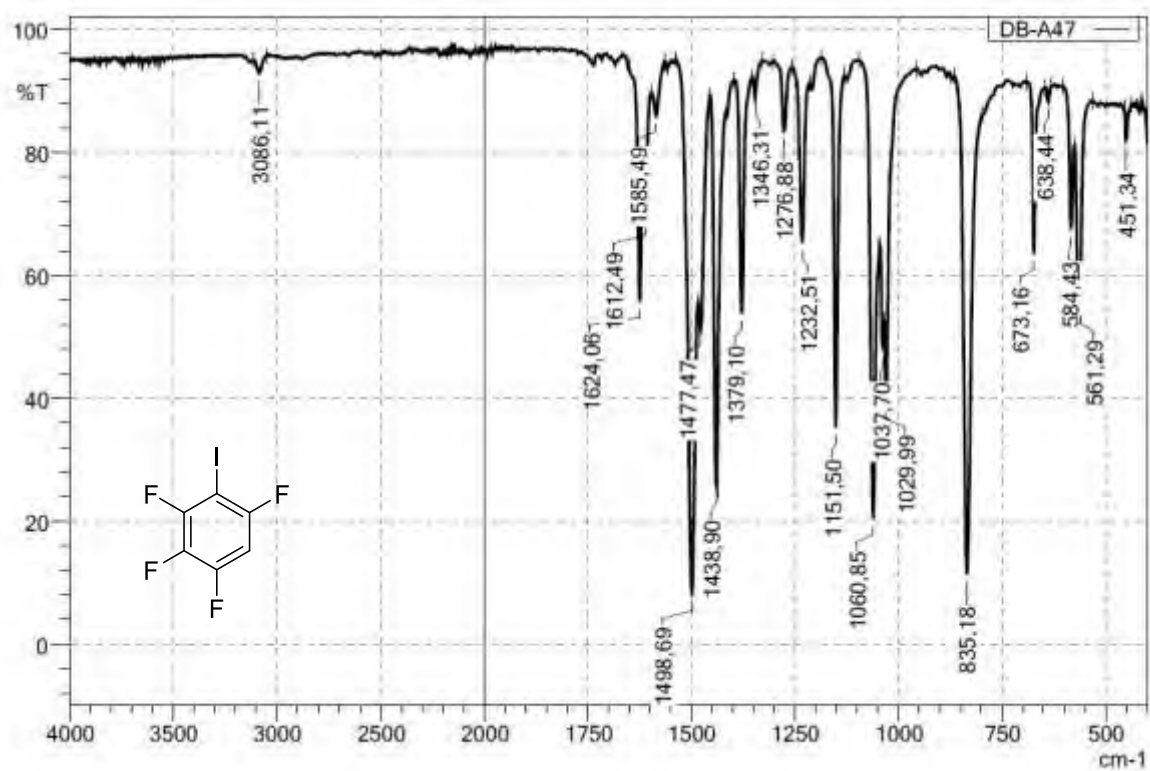
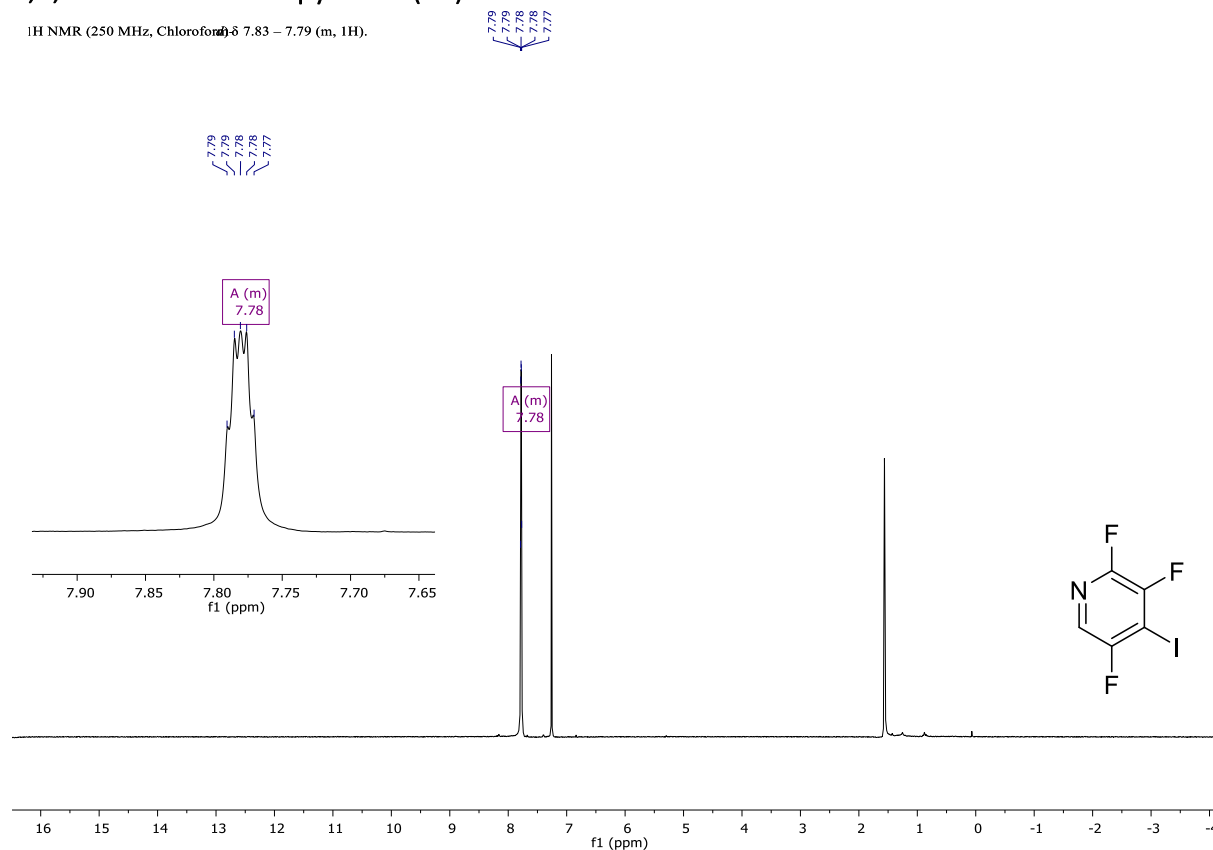
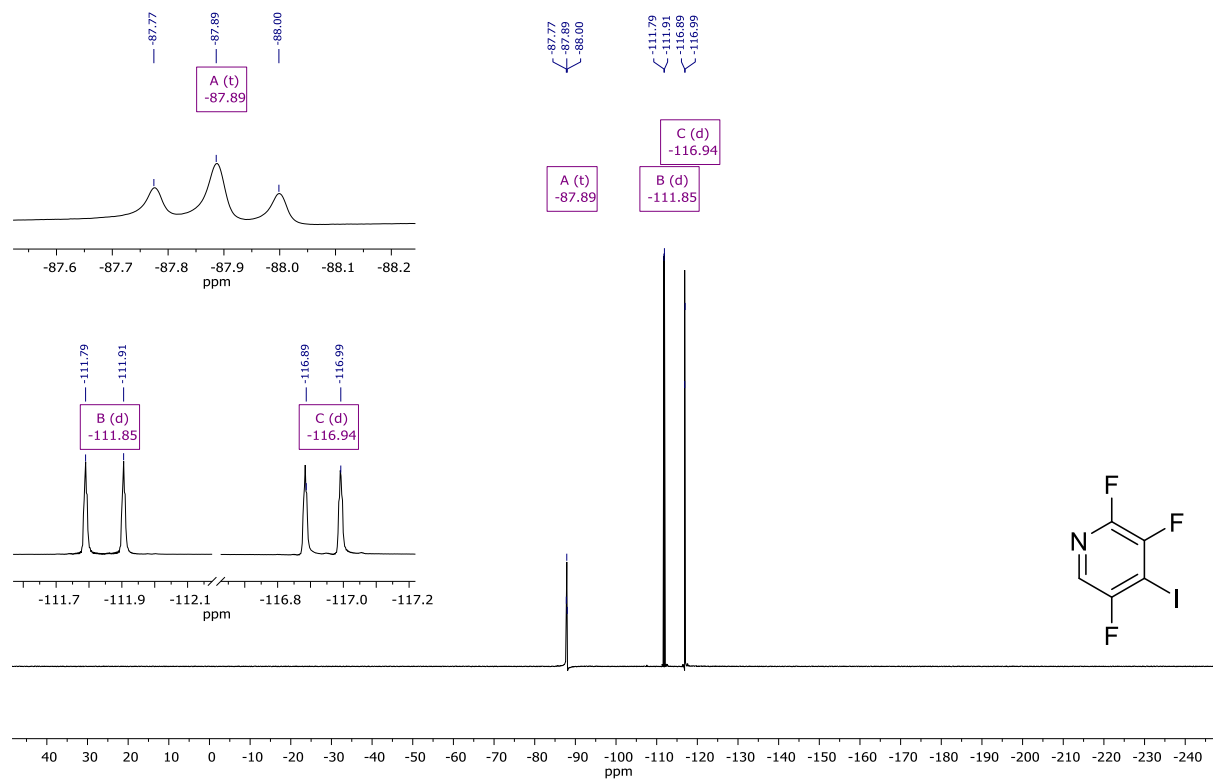
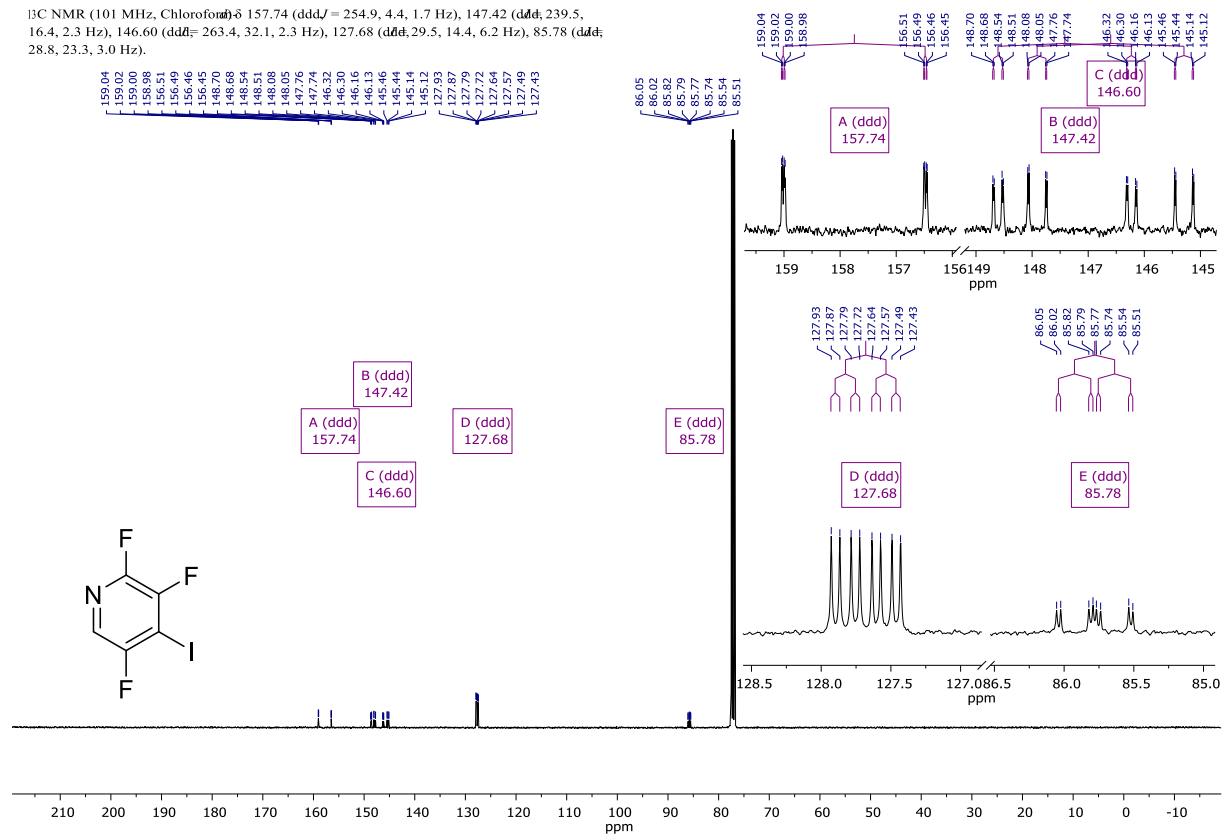
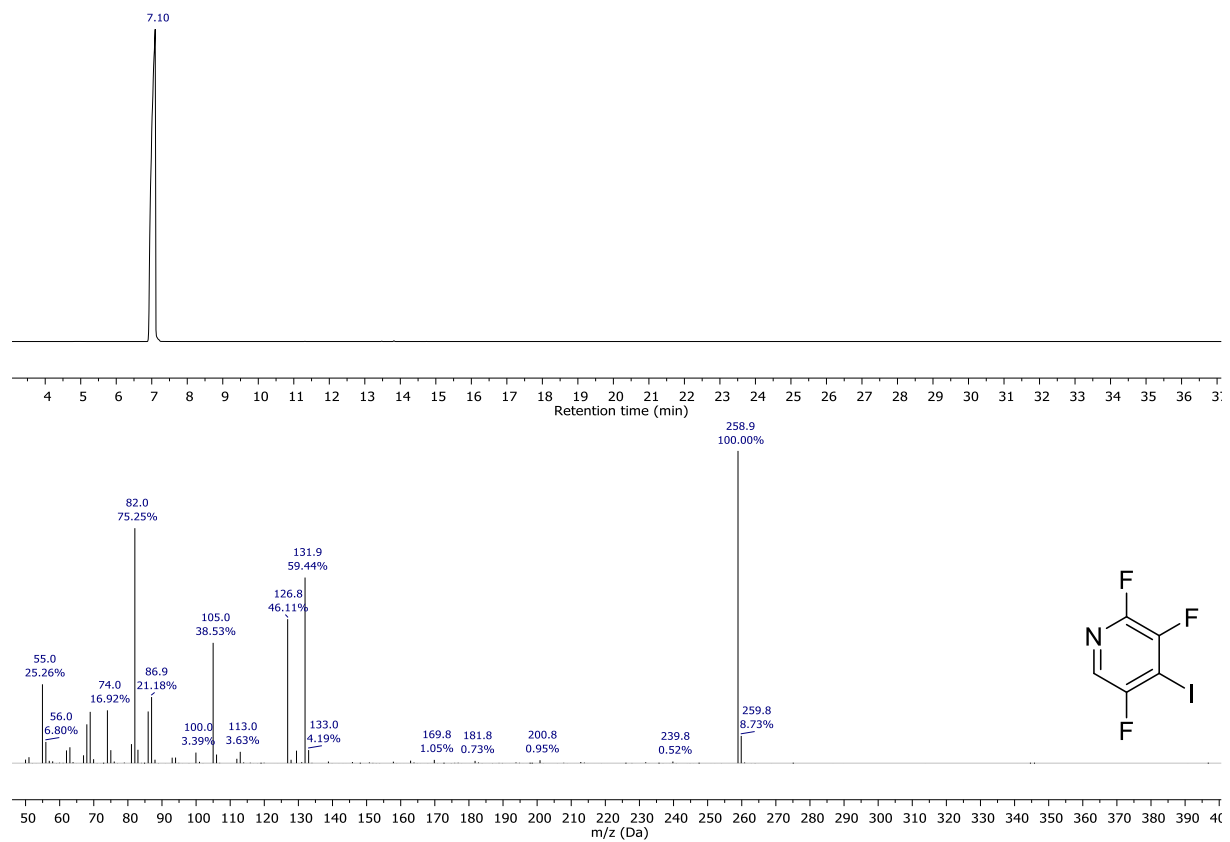
Figure S136 GC/MS-Spectrum EI-Spectrum (EI⁺): 1,2,3,5-Tetrafluoro-4-iodobenzene

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

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

¹H NMR (250 MHz, Chloroform-d) δ 7.83 – 7.79 (m, 1H).Figure S138 ¹H-NMR: 2,3,5-Trifluoro-4-iodopyridine¹⁹F NMR (235 MHz, Chloroform-d) δ -87.89 (J = 26.4 Hz), -111.85 (d = 27.2 Hz), -116.94 (d = 24.7 Hz).Figure S139 ¹⁹F-NMR {¹H}: 2,3,5-Trifluoro-4-iodopyridine

Figure S140 ^{13}C NMR: 2,3,5-Trifluoro-4-iodopyridineFigure S141 GC/MS-Spectrum with EI-Spectrum (EI $^+$): 2,3,5-Trifluoro-4-iodopyridine

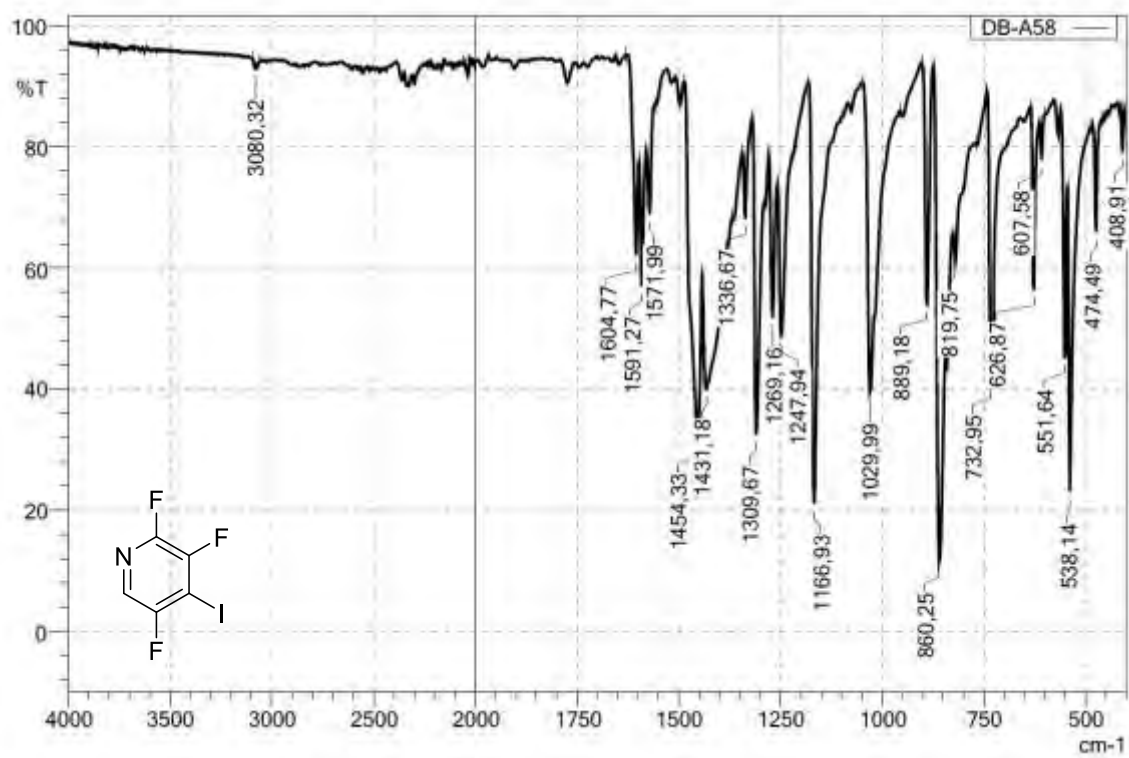
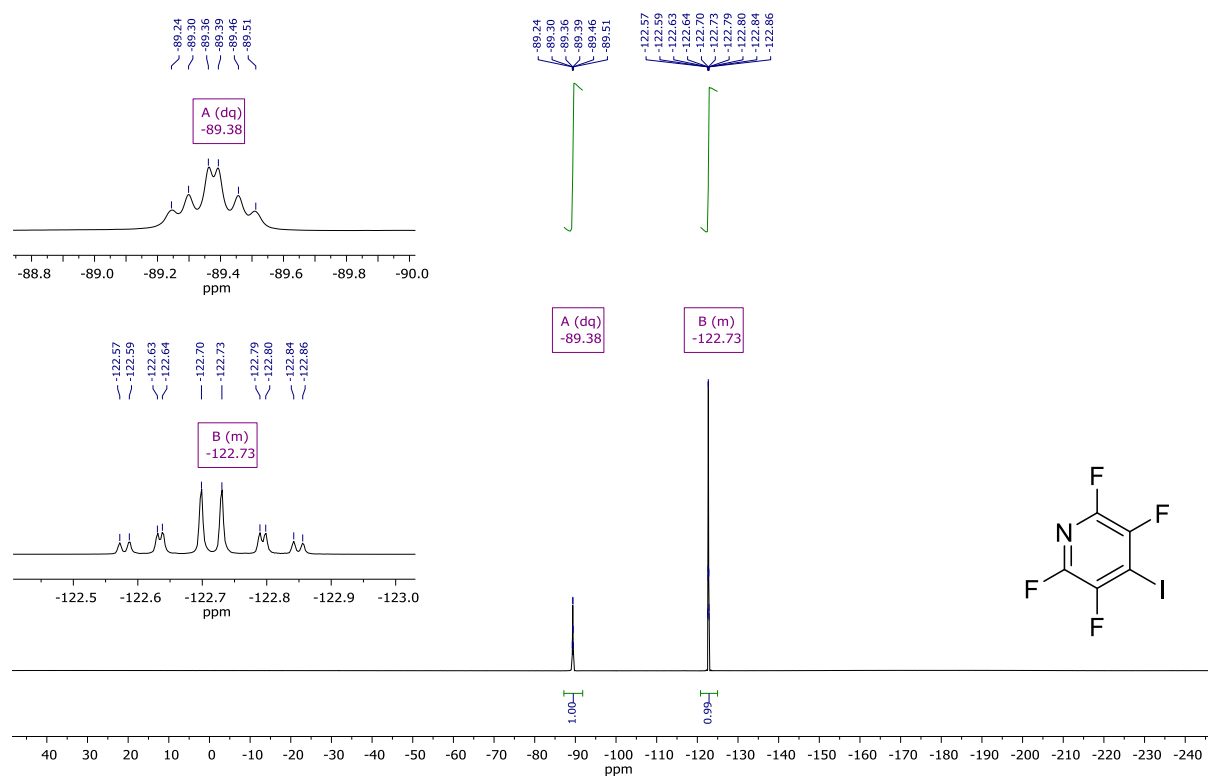
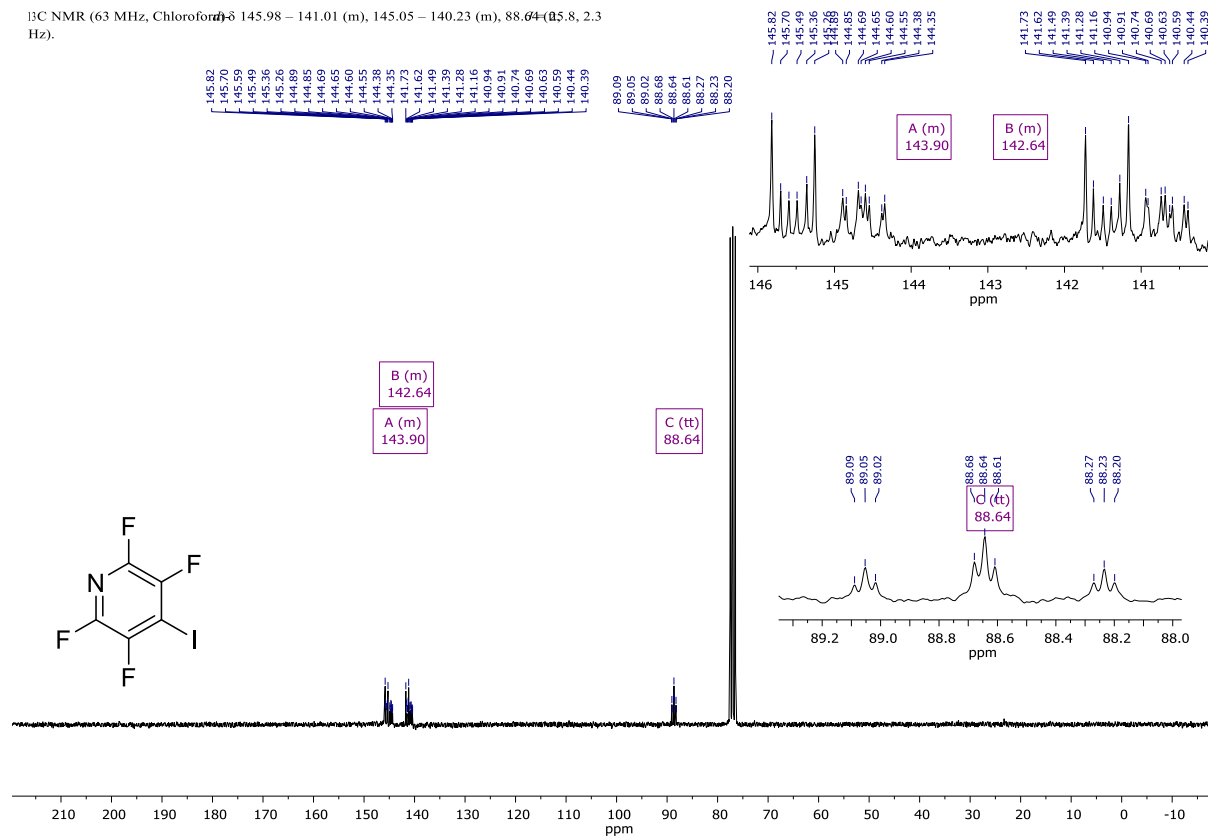


Figure S142 IR (ATR)-Spectrum: 2,3,5-Trifluoro-4-iodopyridine

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 [^1H]: 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, 2.3 Hz).Figure S144 ^{13}C NMR: 2,3,5,6-Tetrafluoro-4-iodopyridine

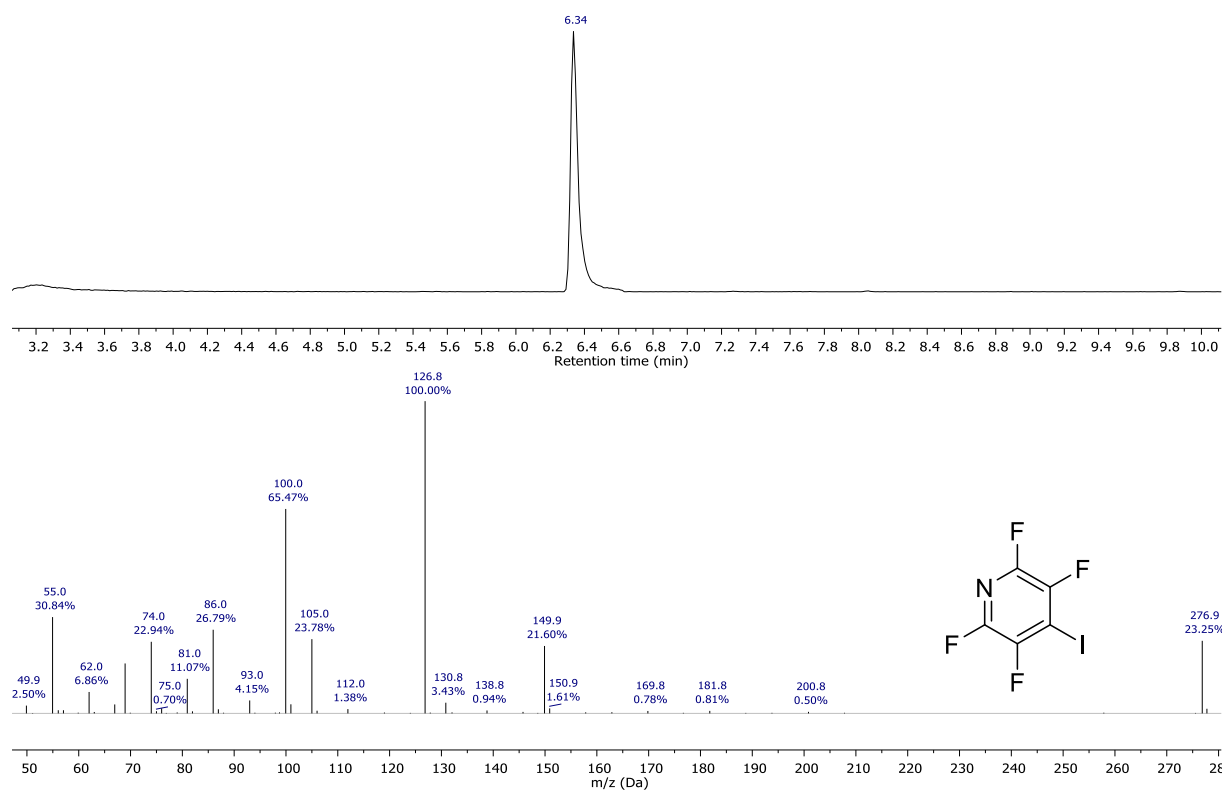
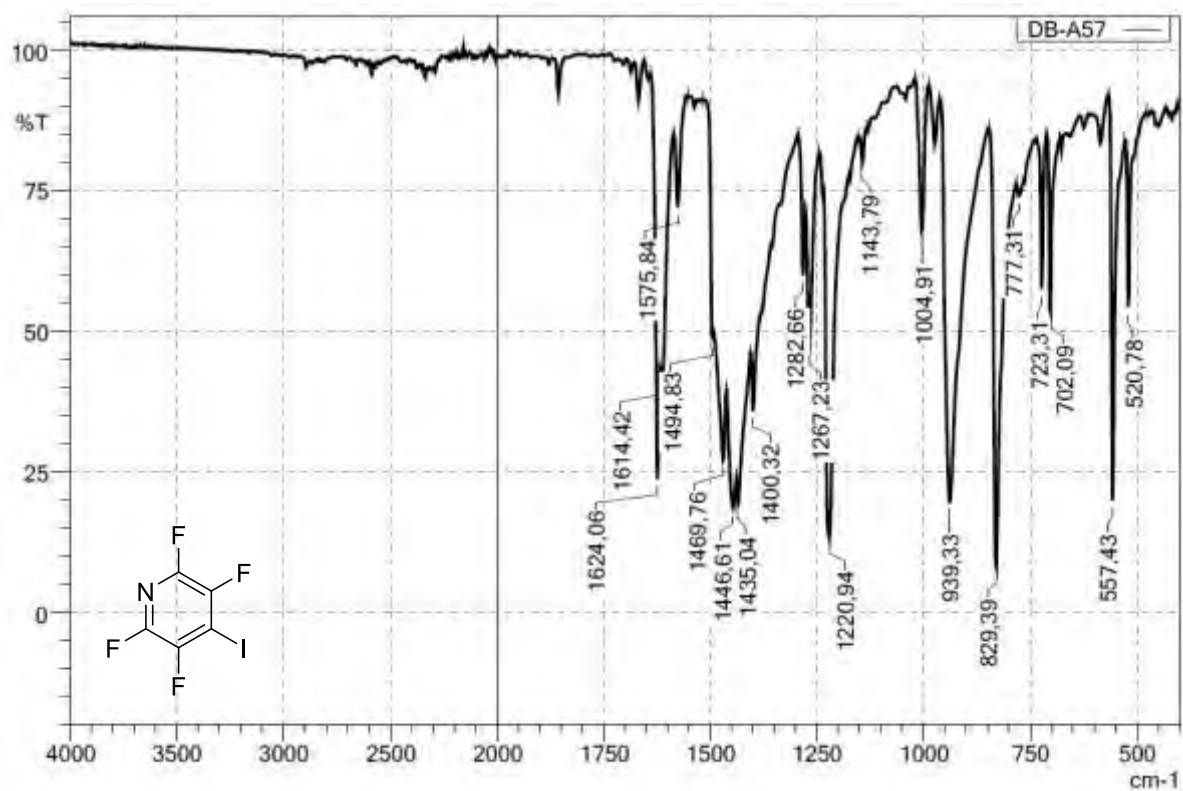
Figure S145 GC/MS-Spectrum with EI-Spectrum (EI⁺): 2,3,5,6-Tetrafluoro-4-iodopyridine

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

^{13}C NMR (63 MHz, Acetone- d_6) δ 162.55 (dd, $J = 244.7, 9.5$ Hz), 151.84 (dt, $J = 251.6, 14.2$ Hz), 147.02 (dd, $J = 243.4, 10.5$ Hz), 123.40 (dd, $J = 17.4, 10.8$ Hz), 121.14 – 114.58 (m), 105.62 (dd, $J = 32.1, 20.3$ Hz).

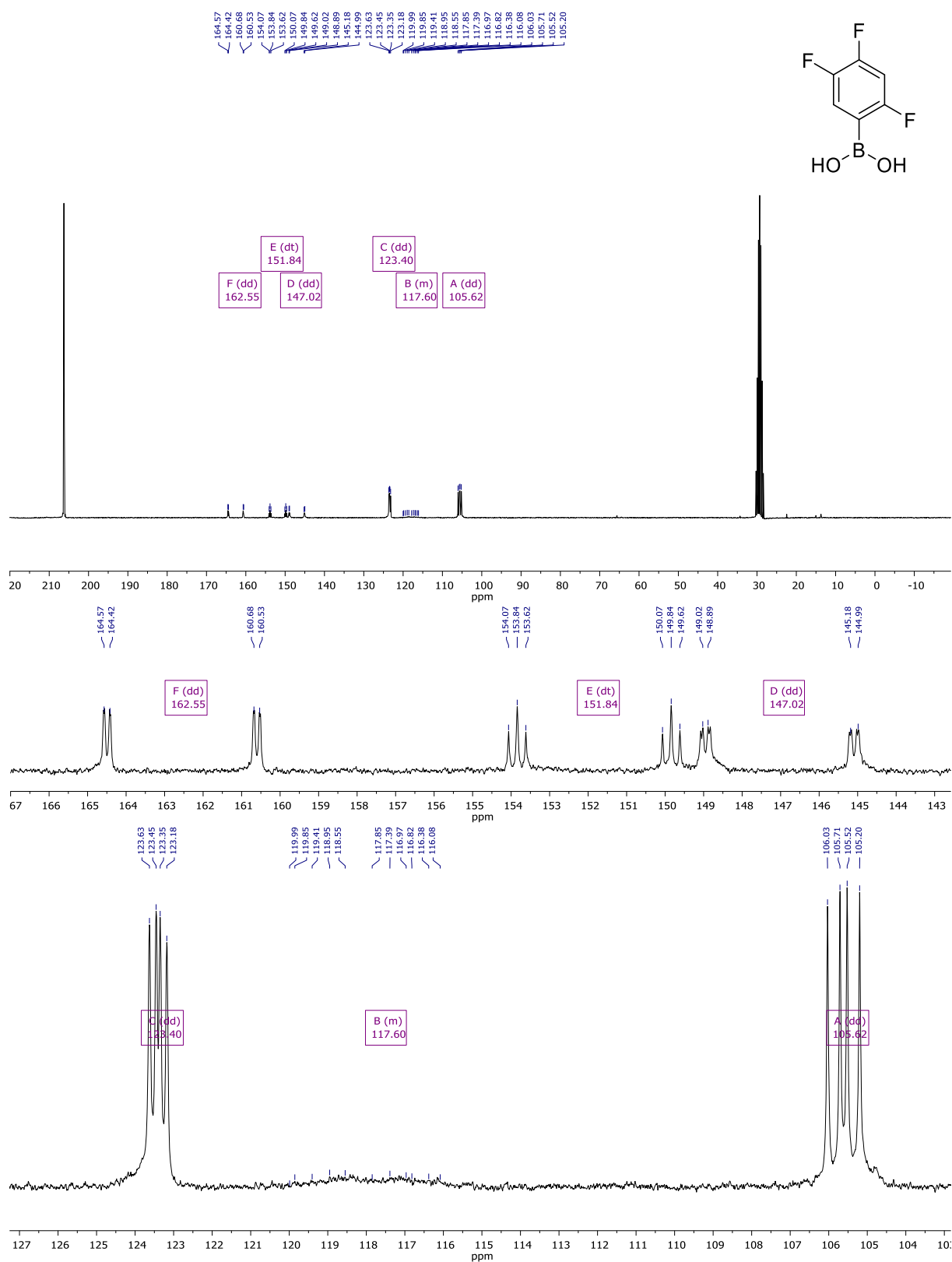


Figure S149 ^{13}C NMR: (2,4,5-Trifluorophenyl)boronic acid

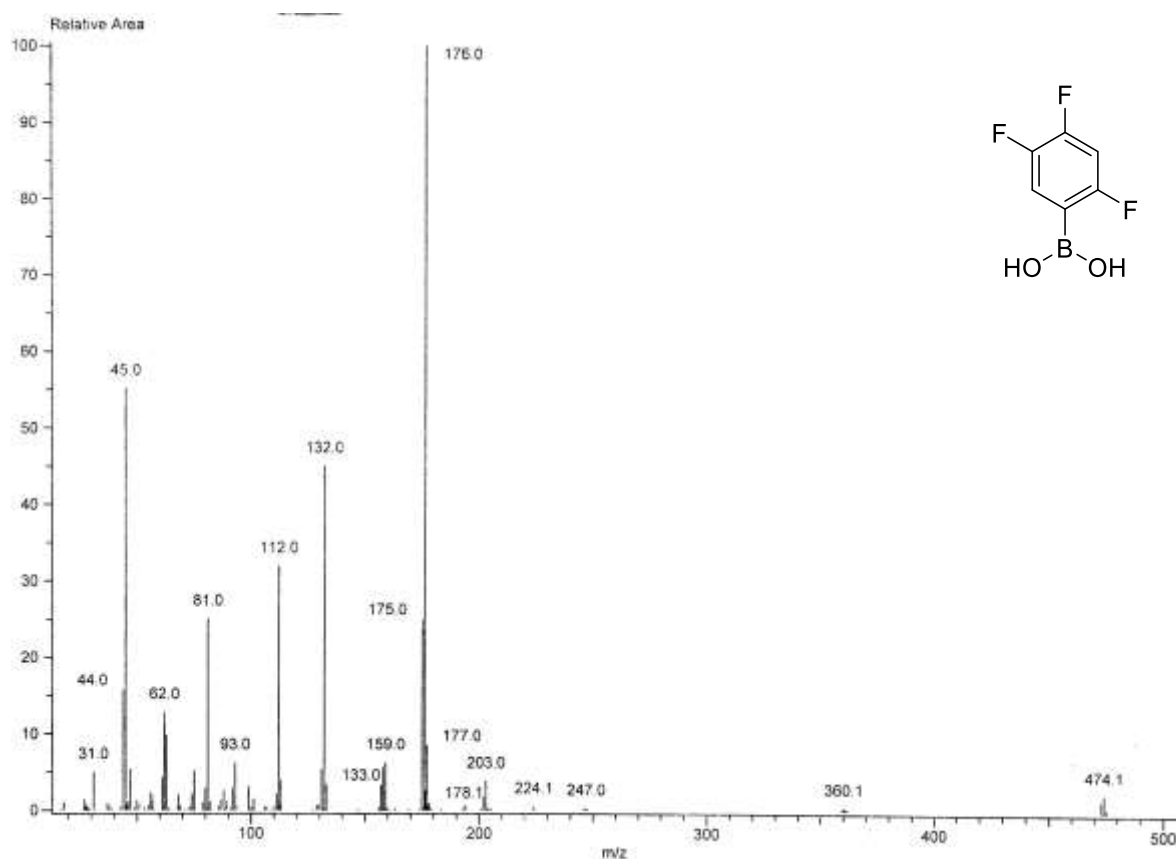


Figure S150 EI-Spectrum (EI⁺): (2,4,5-Trifluorophenyl)boronic acid

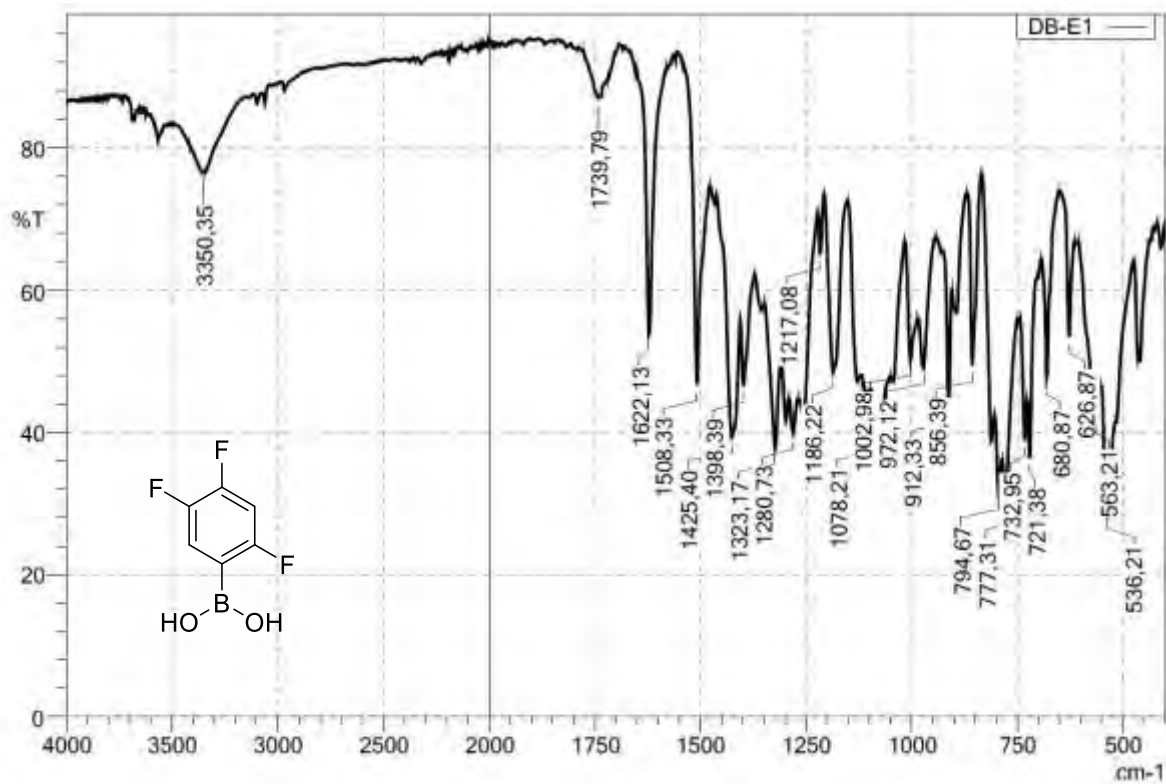
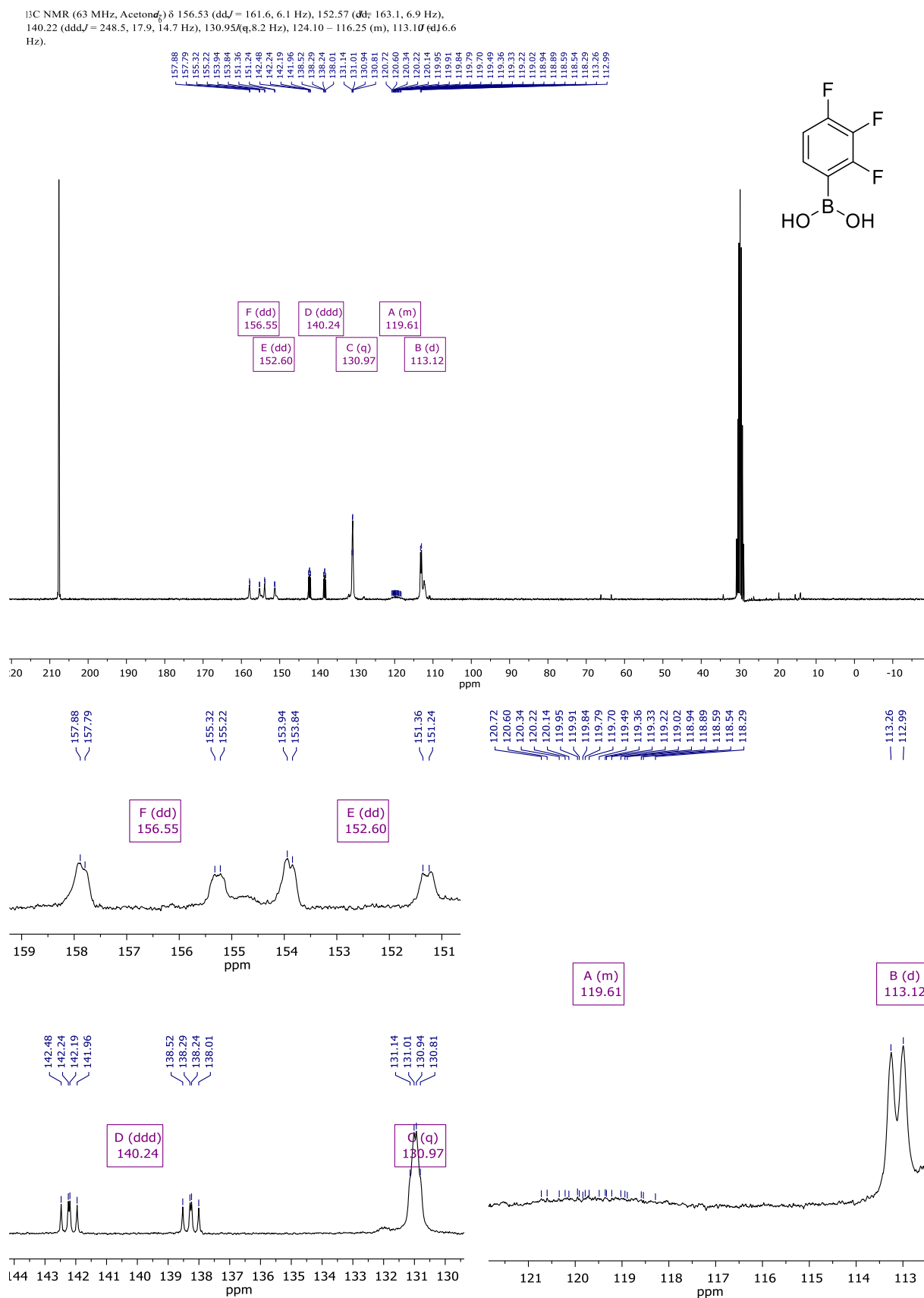
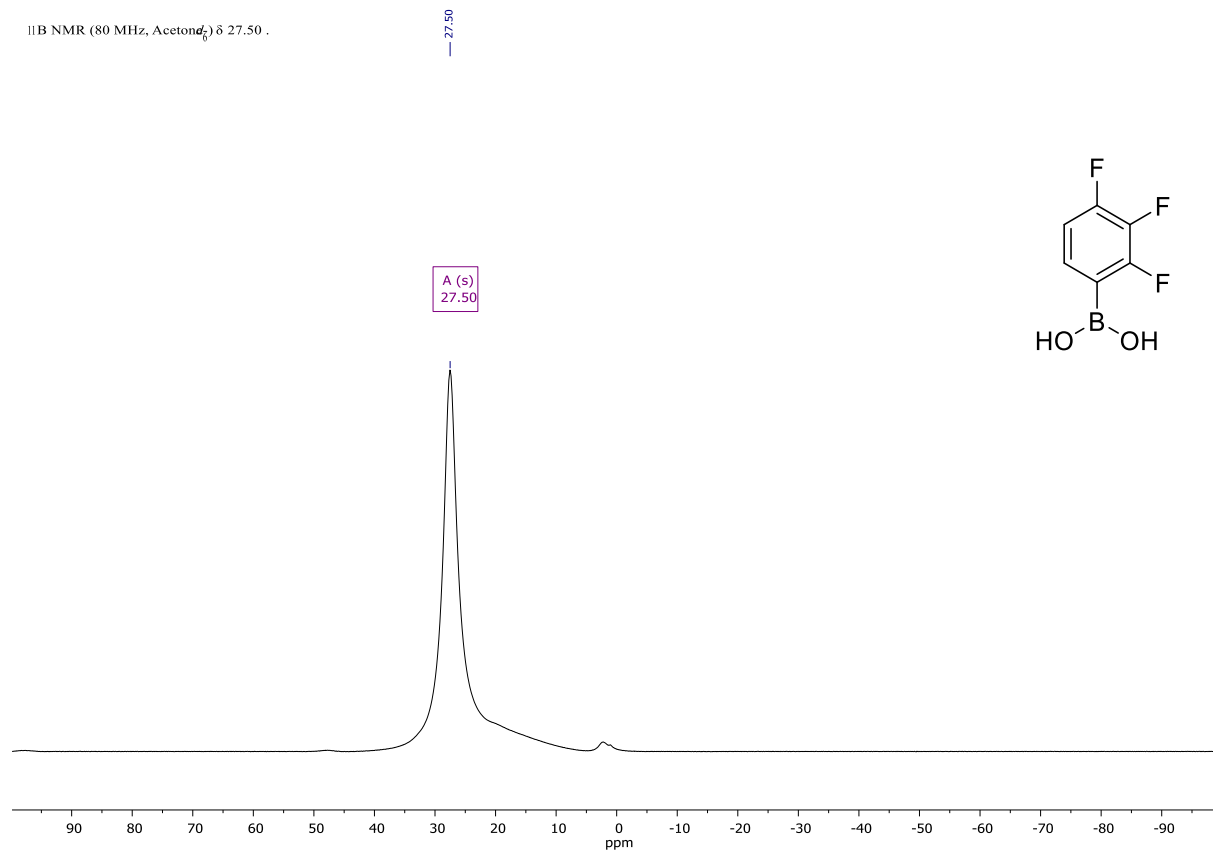
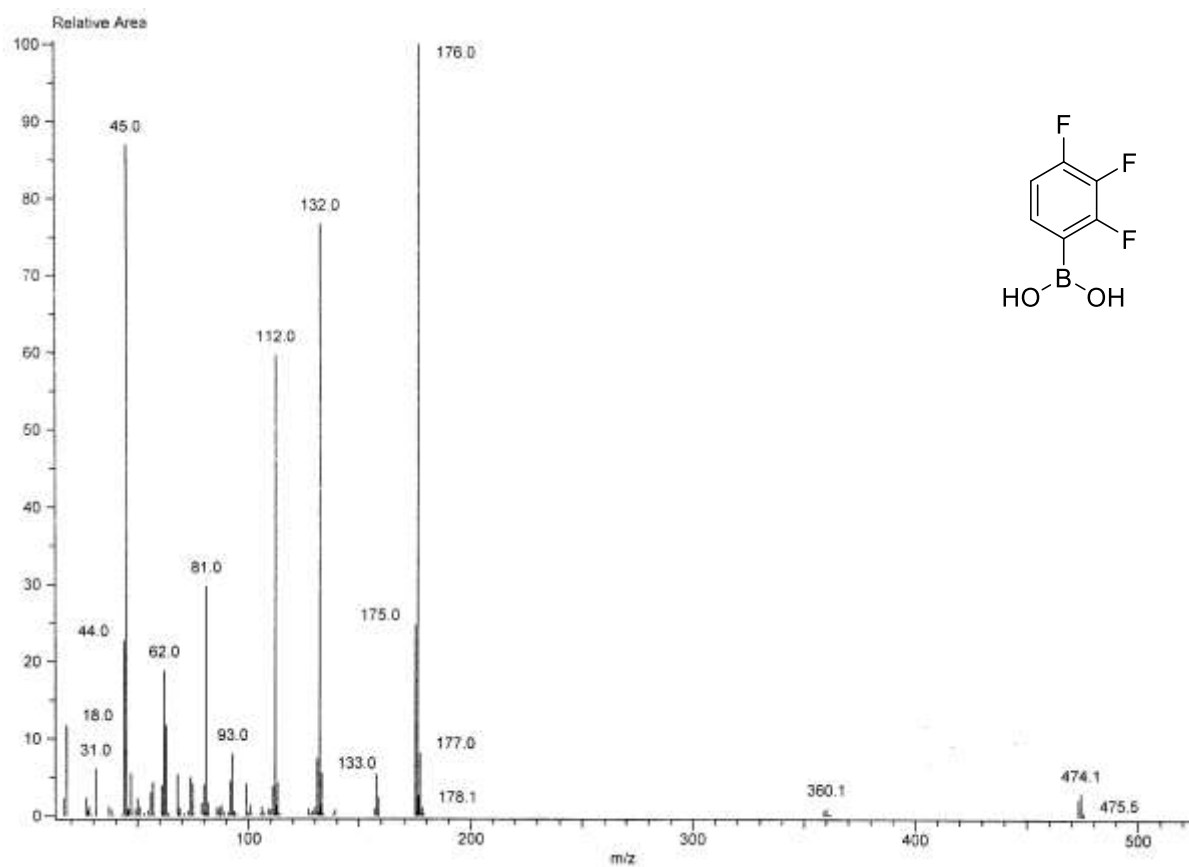


Figure S151 IR (ATR)-Spectrum: (2,4,5-Trifluorophenyl)boronic acid

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

Figure S155 ^{11}B -NMR: (2,3,4-Trifluorophenyl)boronic acidFigure S156 EI-Spectrum (EI⁺): (2,3,4-Trifluorophenyl)boronic acid

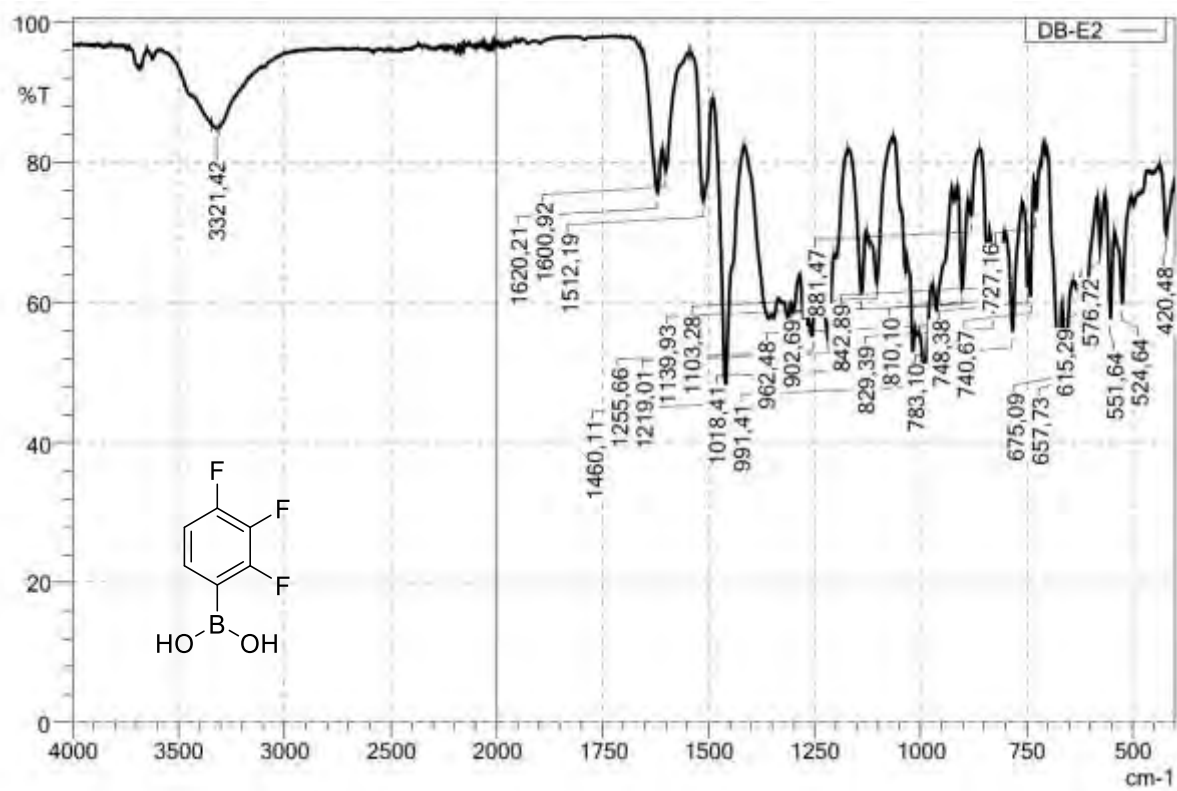
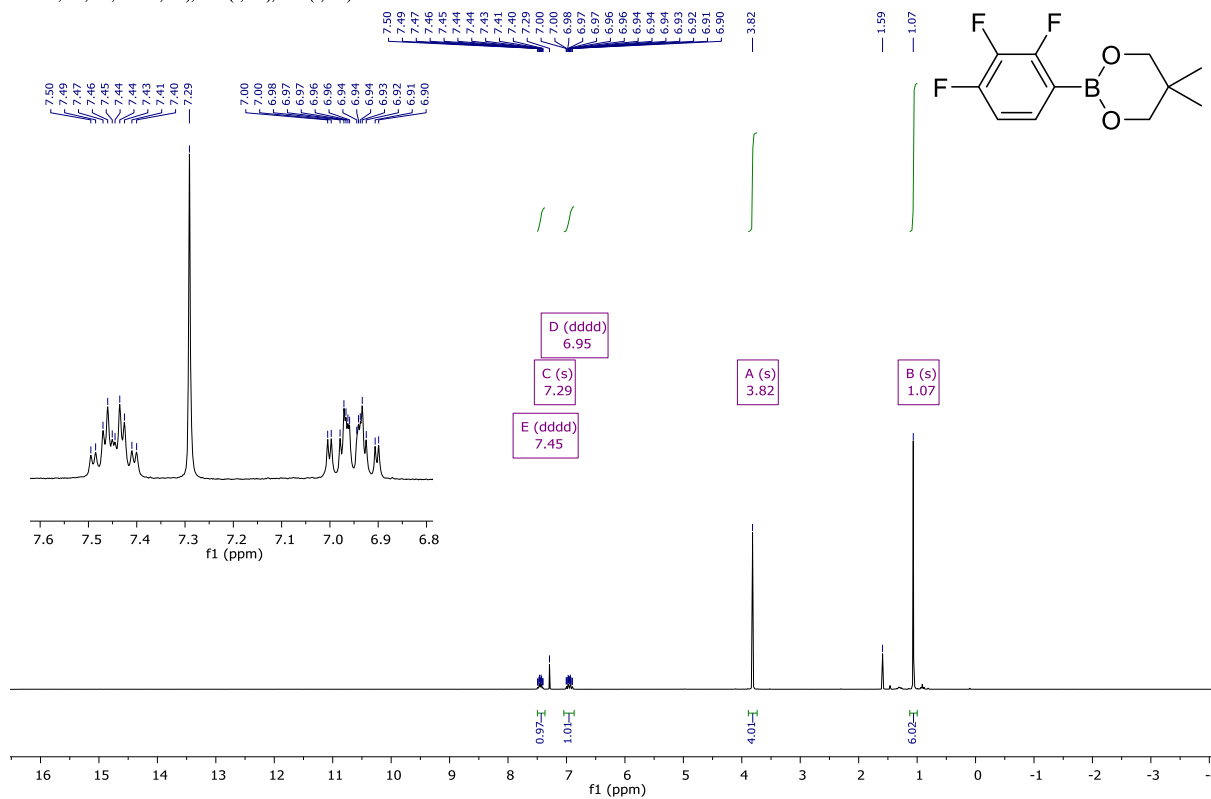


Figure S157 IR (ATR)-Spectrum: (2,3,4-Trifluorophenyl)boronic acid

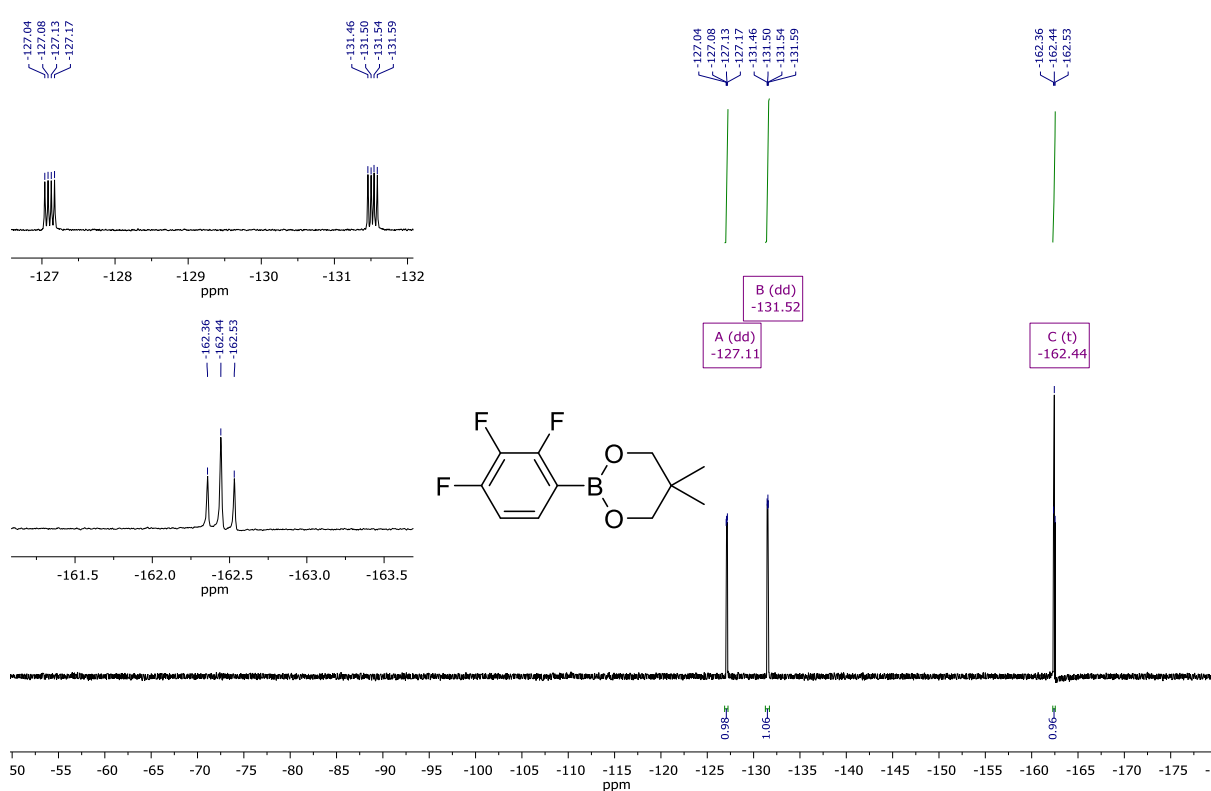
Boronic acid esters

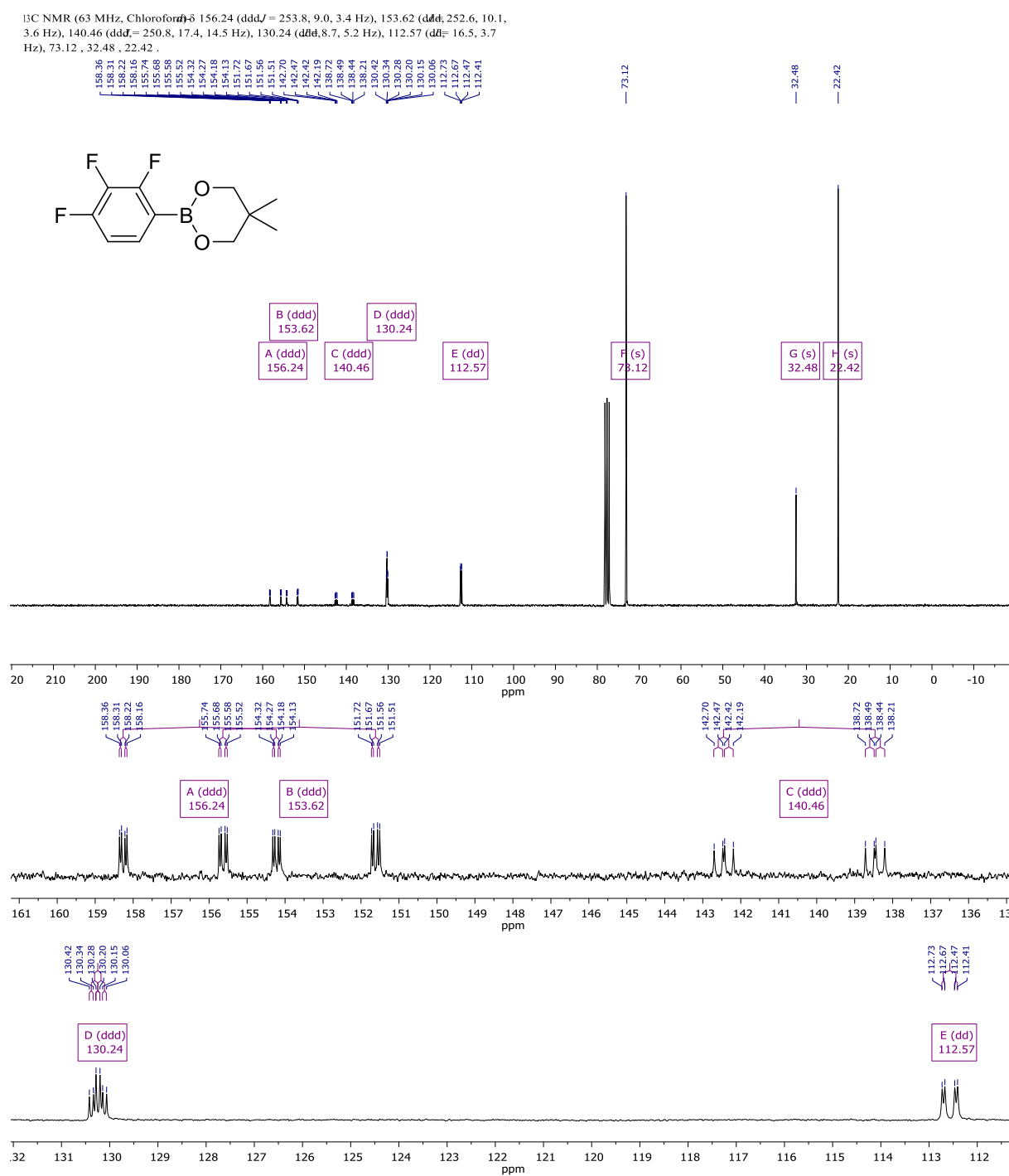
5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane (15)

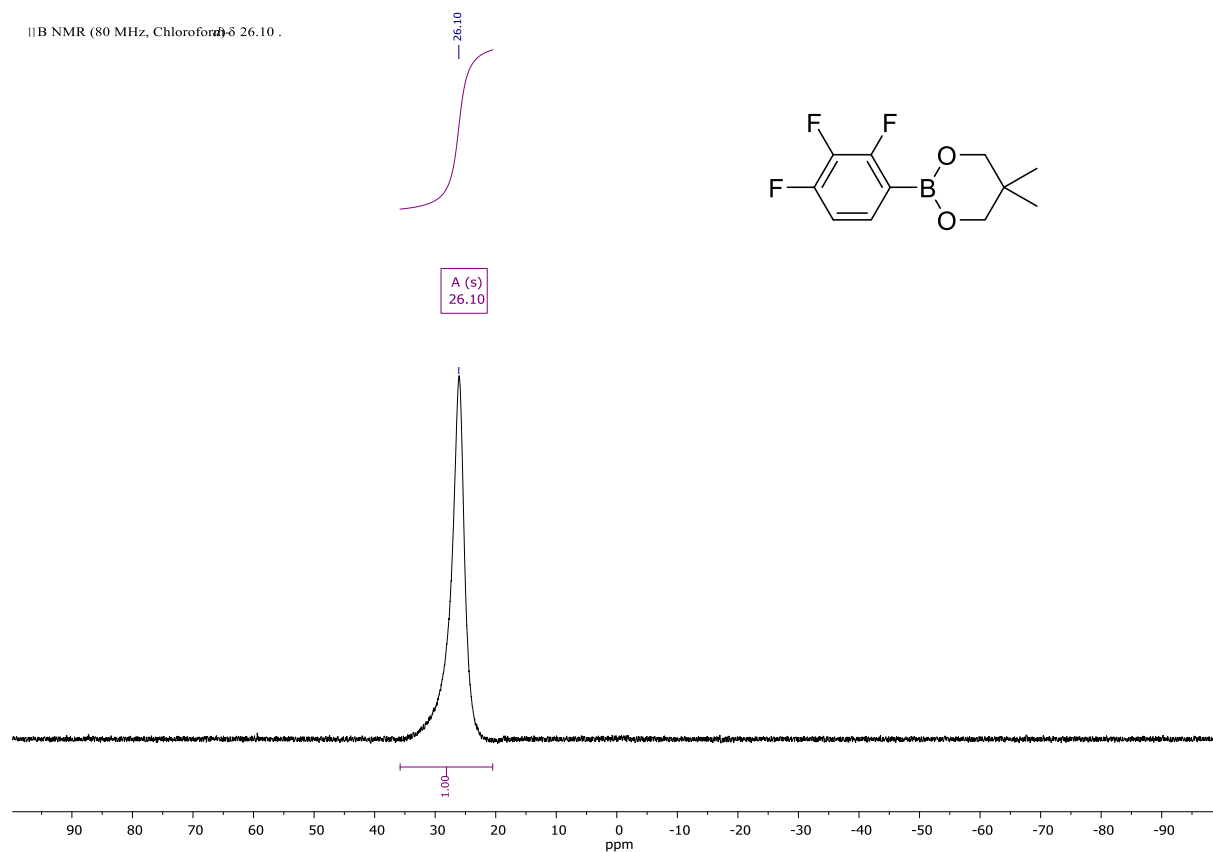
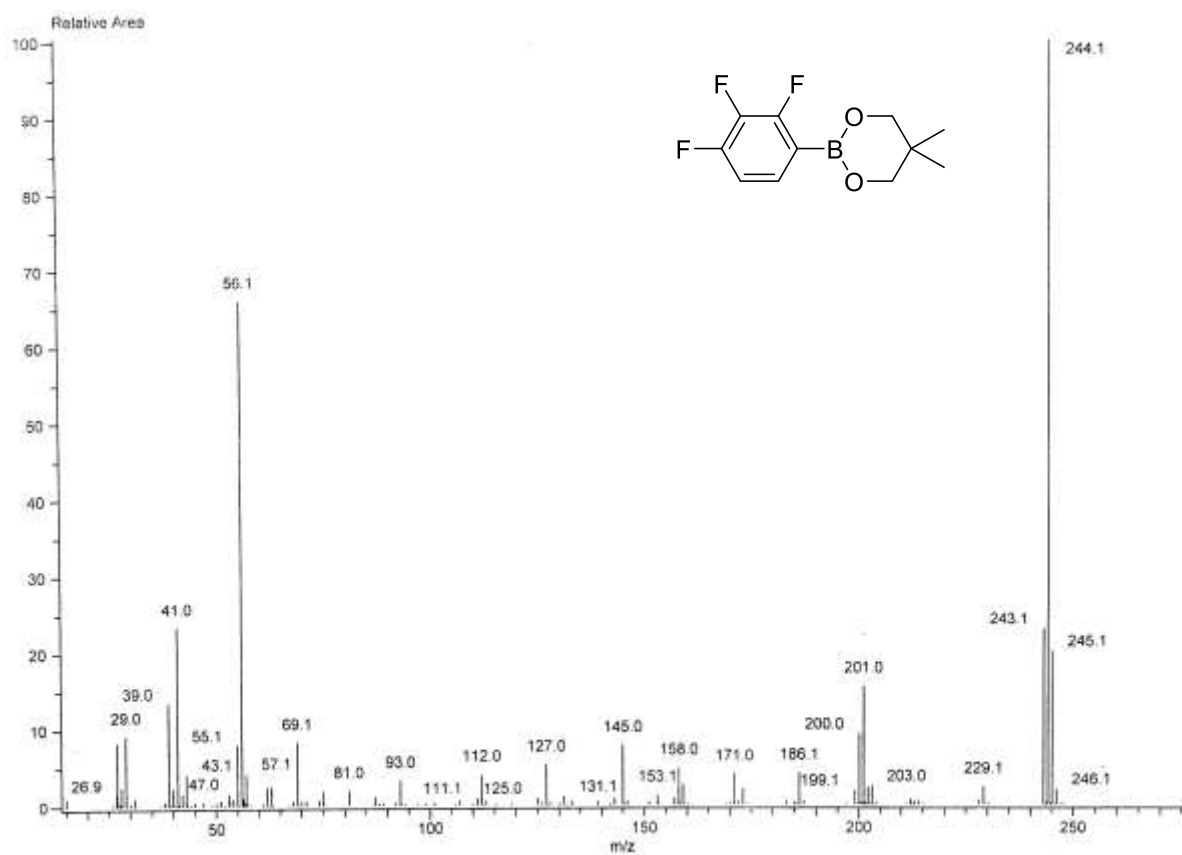
$^1\text{H NMR}$ (250 MHz, Chloroform- d_3) δ 7.45 (dddd, $J = 8.7, 6.3, 2.5$ Hz, 0H), 7.29 (s, 0H), 6.95 (dddd, $J = 9.5, 8.5, 6.4, 1.8$ Hz, 0H), 3.82 (s, 1H), 1.07 (s, 1H).

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

$^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) δ -127.11 (dd, $J = 20.9, 10.5$ Hz), -131.52 (dd, $J = 19.9, 10.4$ Hz), -162.44 ($J = 20.4$ Hz).

Figure S159 $^{19}\text{F-NMR}$ { ^1H }: 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-dioxaborinaneFigure S162 EI-Spectrum (E^+): 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

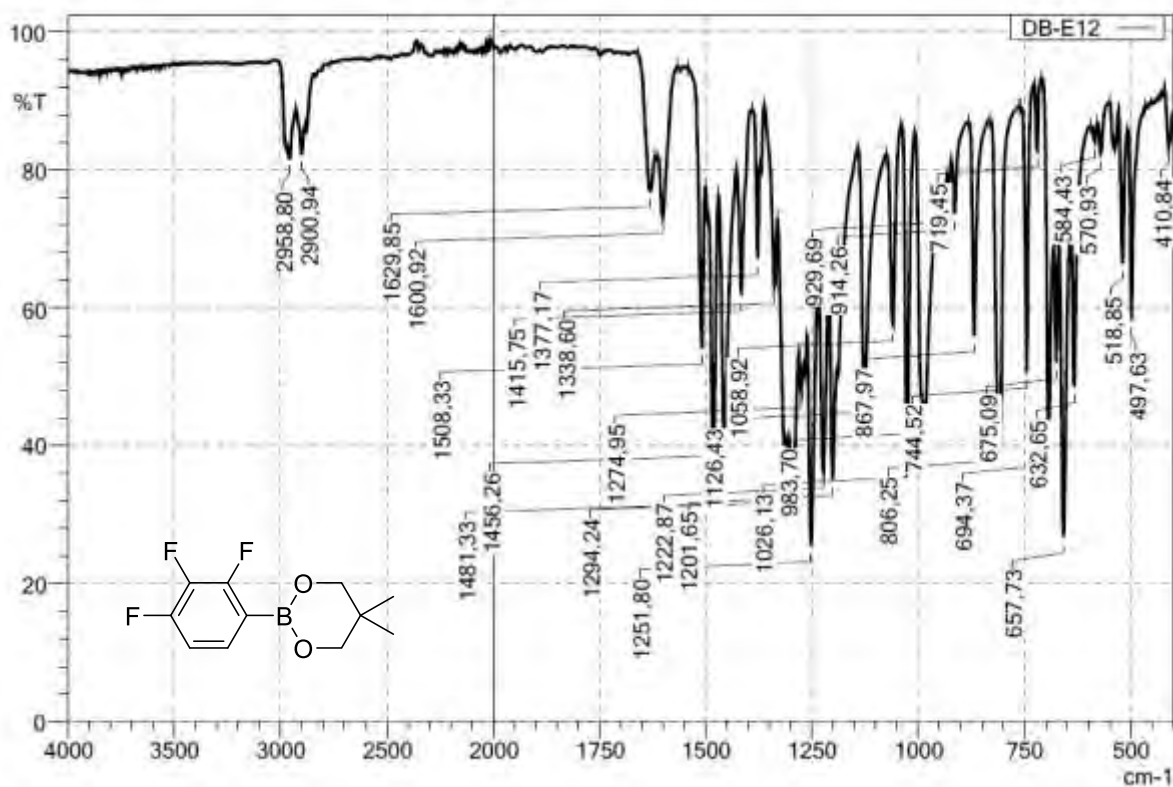
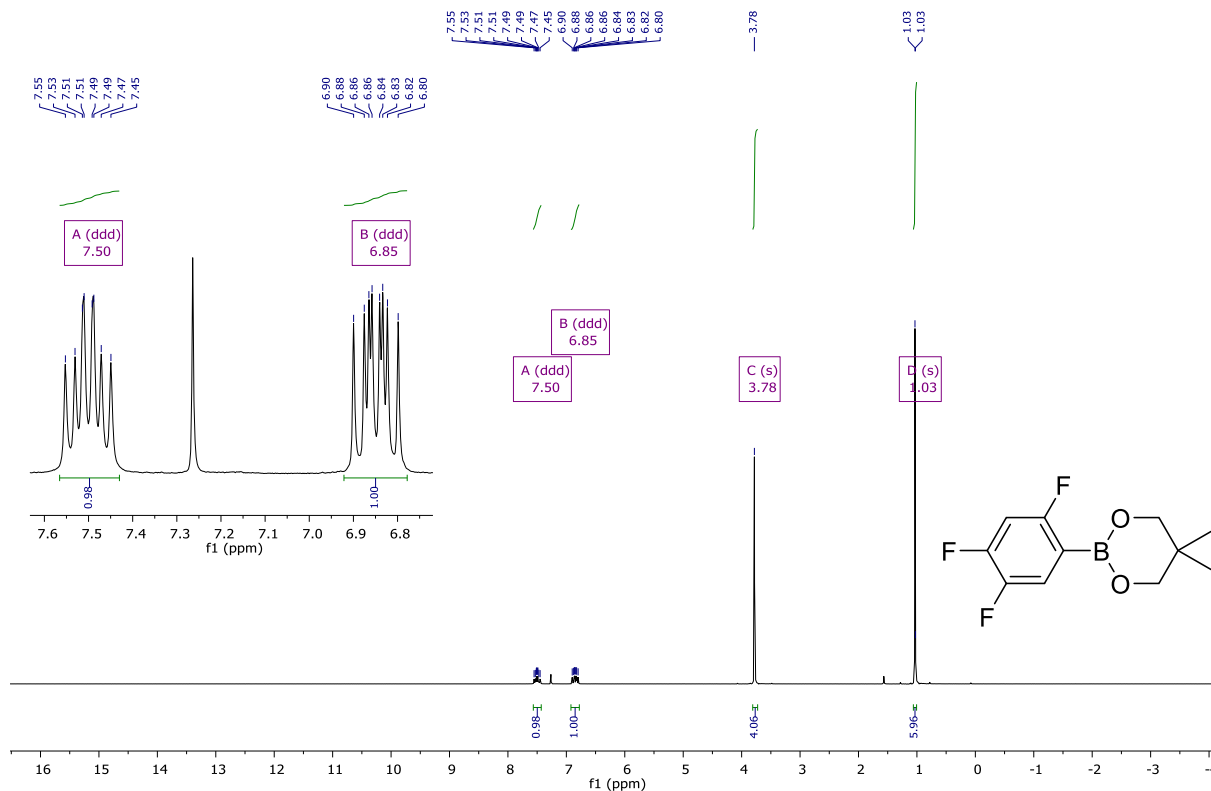


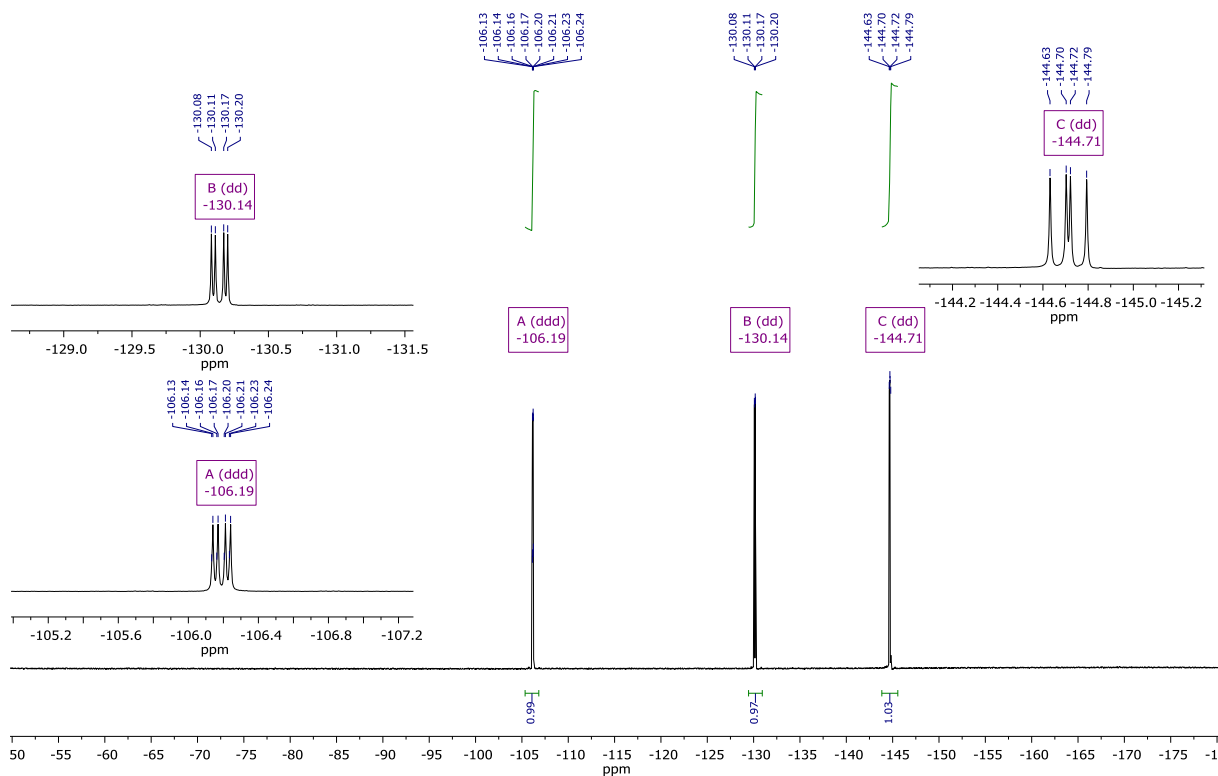
Figure S163 IR (ATR)-Spectrum: 5,5-Dimethyl-2-(2,3,4-trifluorophenyl)-1,3,2-dioxaborinane

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

$^1\text{H NMR}$ (250 MHz, Chloroform- d_3) δ 7.50 (ddd, $J = 10.7, 9.7, 5.5$ Hz, 1H), 6.85 (ddd, 10.5, 8.7, 6.1 Hz, 1H), 3.78 (s, 4H), 1.03 (s, 6H).

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

$^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) δ -106.19 (ddd, $J = 16.8, 6.9, 1.6$ Hz), -130.14 (dd, 21.3, 6.9 Hz), -144.71 (dd, 21.3, 16.8 Hz).

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

^{13}C NMR (75 MHz, Chloroform- d_3) δ 162.52 (ddd, $J = 249.6, 9.4, 2.1$ Hz), 152.10 (ddd, 254.0, 14.5, 13.2 Hz), 146.88 (ddd, $J = 244.1, 11.9, 3.6$ Hz), 123.37 (ddd, 17.6, 10.3, 1.9 Hz), 105.61 (dd, 31.1, 19.9 Hz), 72.64, 31.98, 21.95.

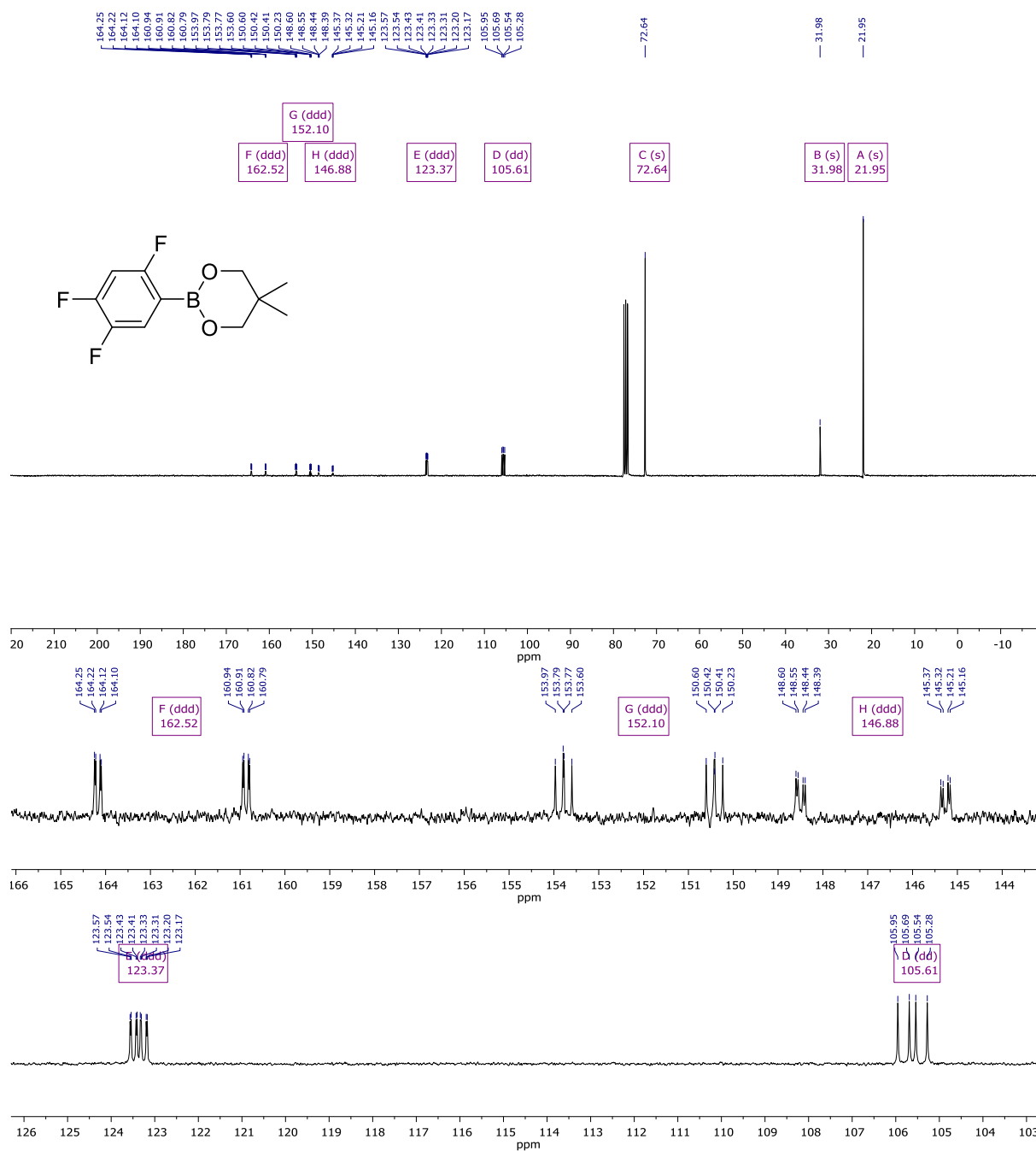


Figure S166 ^{13}C NMR: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

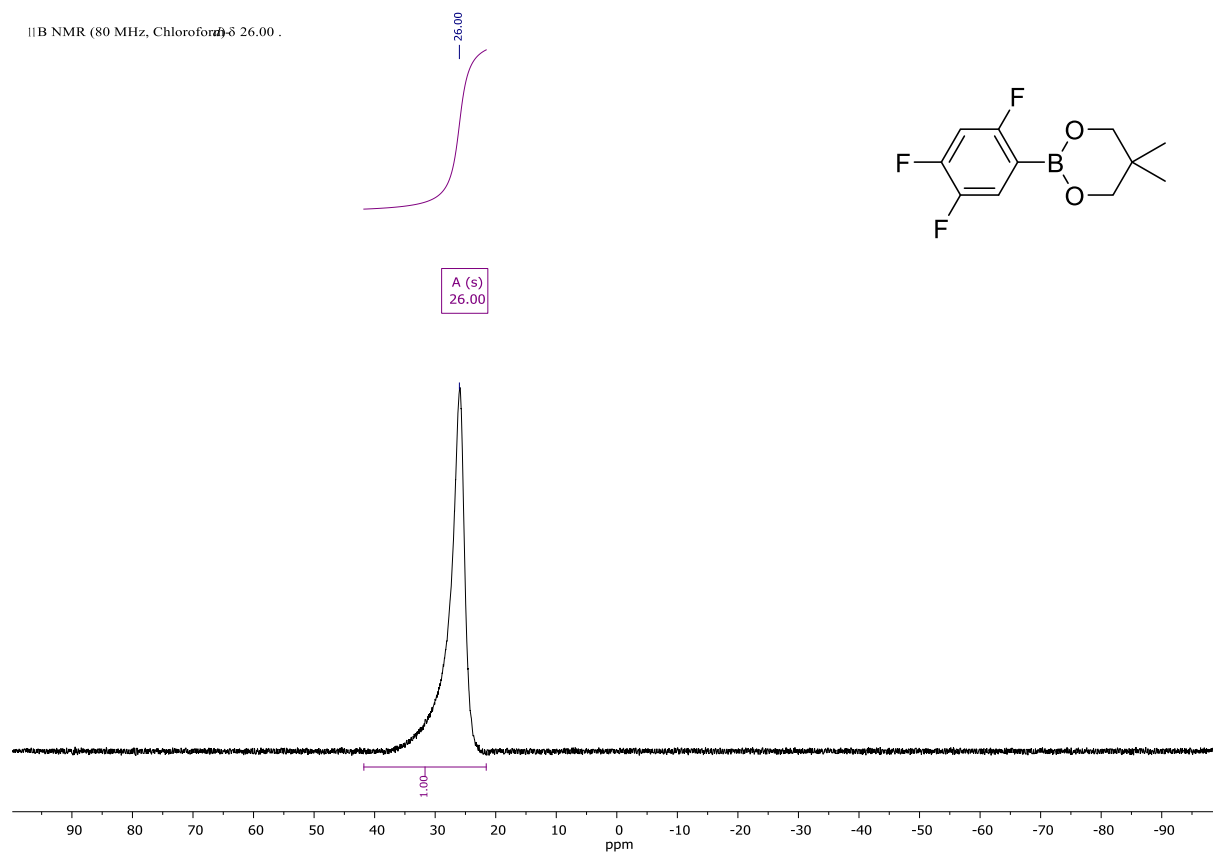


Figure S167 ^{11}B -NMR: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

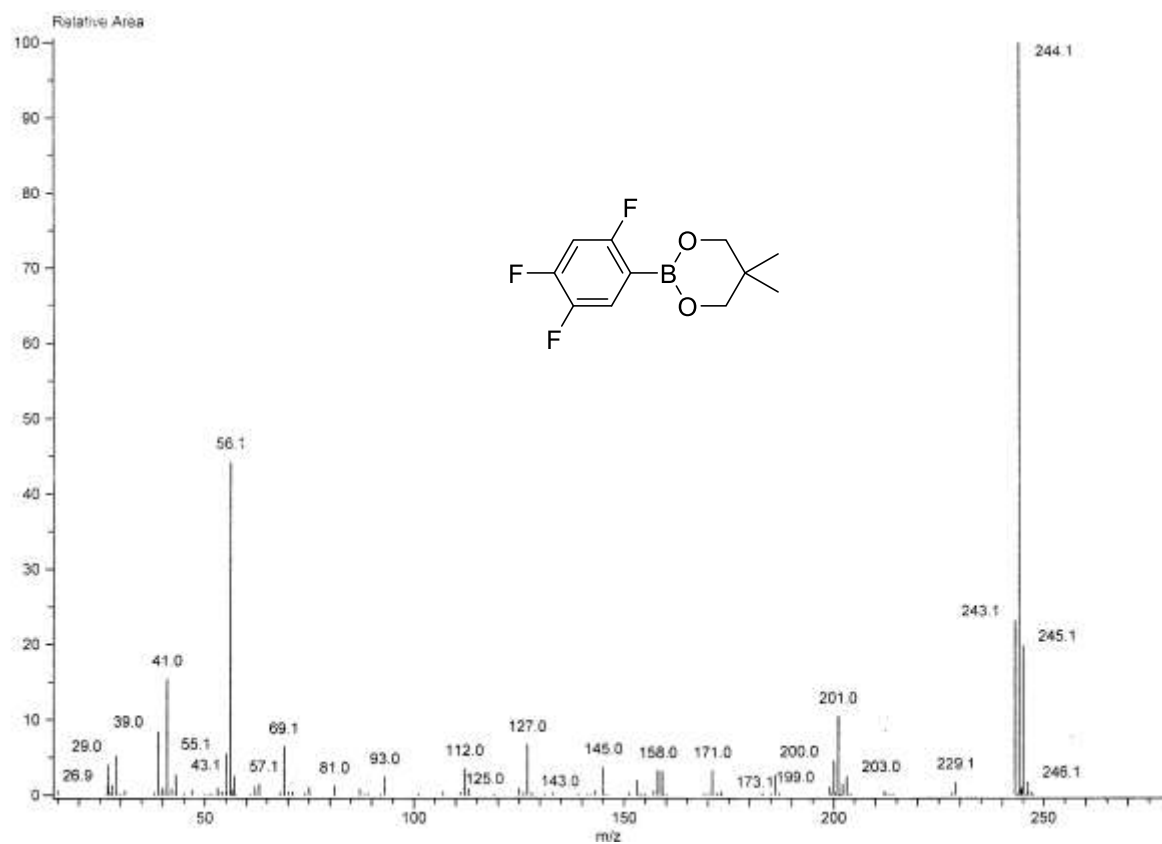


Figure S168 EI-Spectrum (E^+): 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

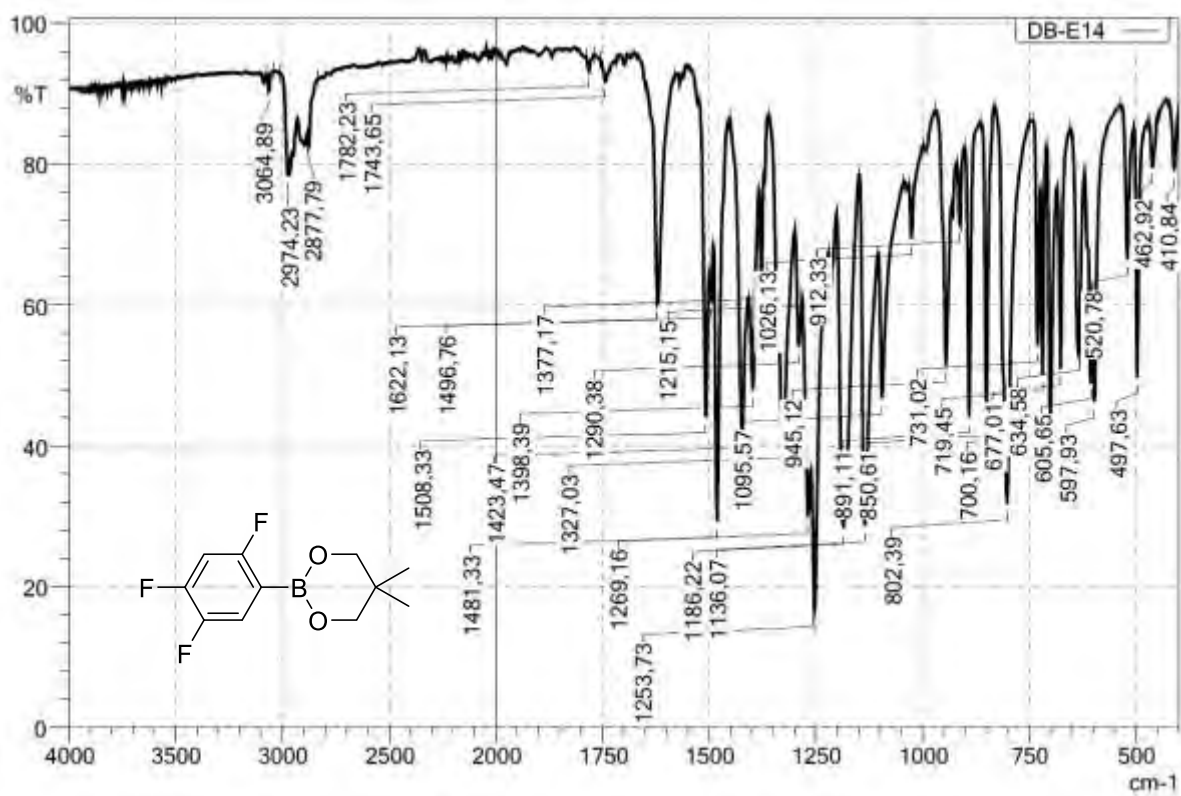
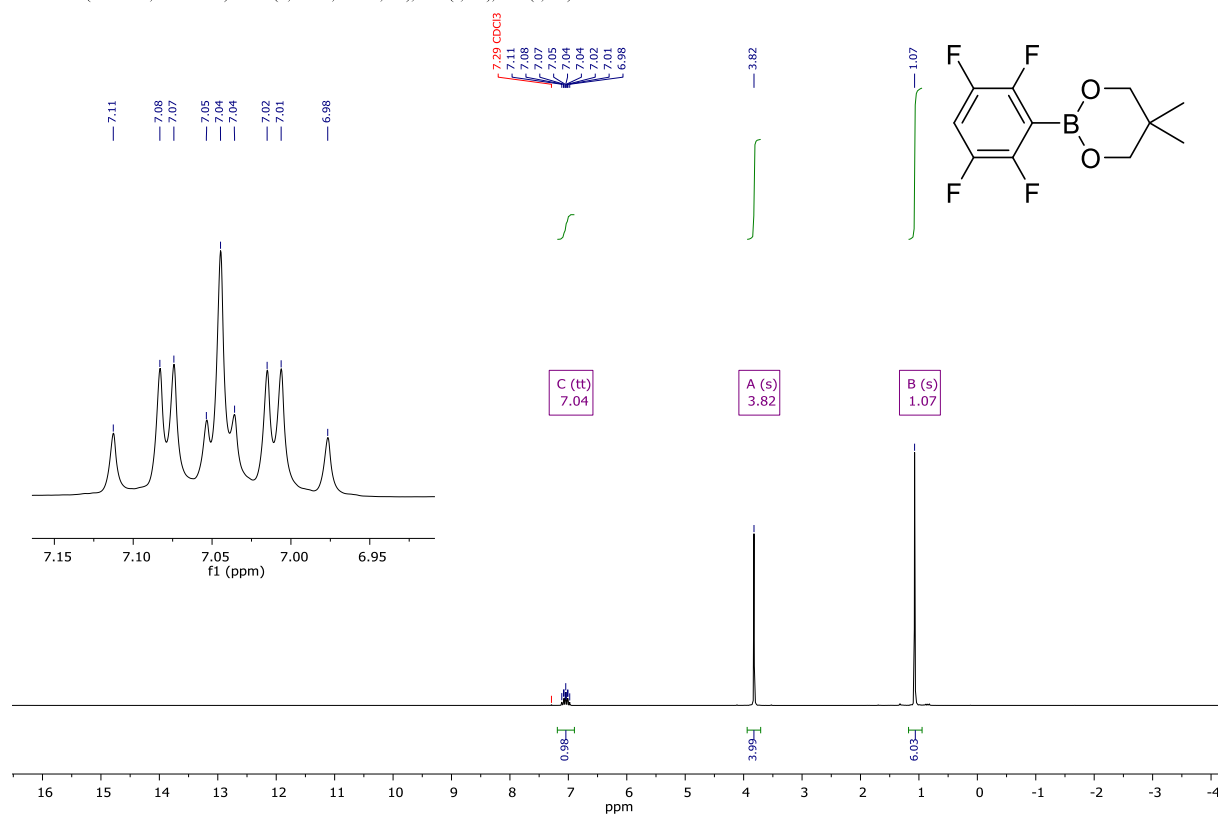
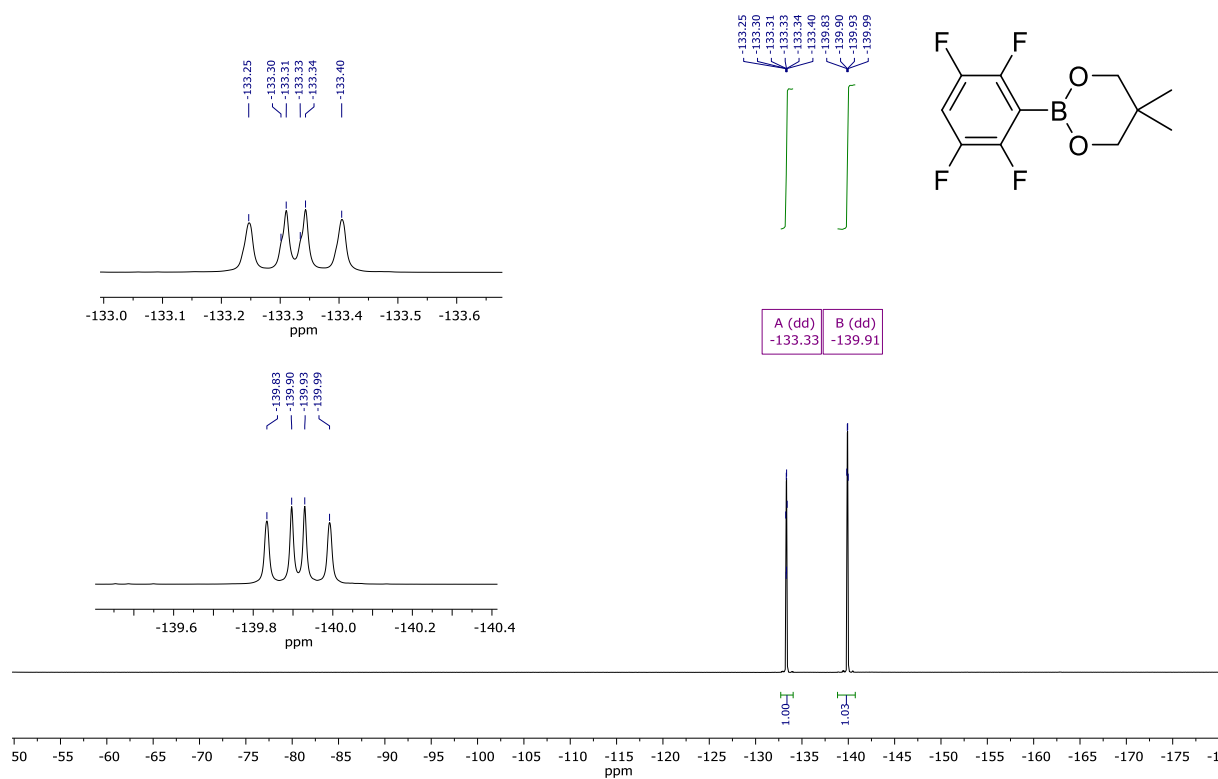


Figure S169 IR (ATR)-Spectrum: 5,5-Dimethyl-2-(2,4,5-trifluorophenyl)-1,3,2-dioxaborinane

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

 $^1\text{H NMR}$ (250 MHz, Chloroform- d_3) δ 7.04 (tt, $J = 9.6, 7.4$ Hz, 1H), 3.82 (s, 4H), 1.07 (s, 6H).Figure S170 $^1\text{H-NMR}$: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane $^{19}\text{F NMR}$ (235 MHz, Chloroform- d_3) δ -133.33 (dd, $J = 22.5, 14.7$ Hz), -139.91 (dd, $J = 22.4, 14.7$ Hz).Figure S171 $^{19}\text{F-NMR}$ { ^1H }: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

^{13}C NMR (75 MHz, Chloroform- d_3) δ 147.91 (dddd, $J = 245.8, 13.0, 11.1, 3.6$ Hz), 145.64 (dddd, 248.3, 16.5, 8.8, 3.8 Hz), 114.94 – 110.71 (m), 107.18 (t, 1.6 Hz), 72.72, 31.77, 21.38.

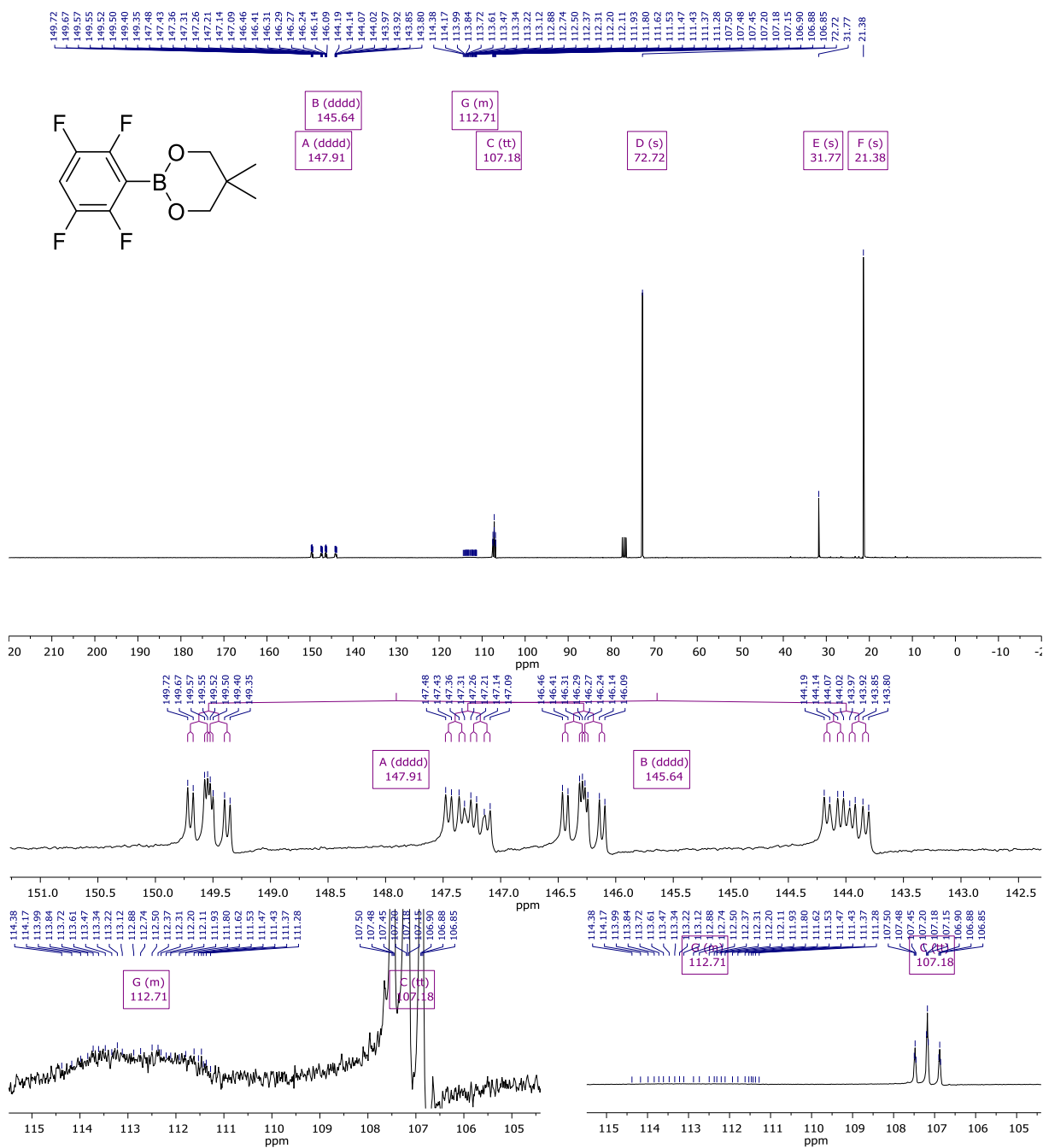
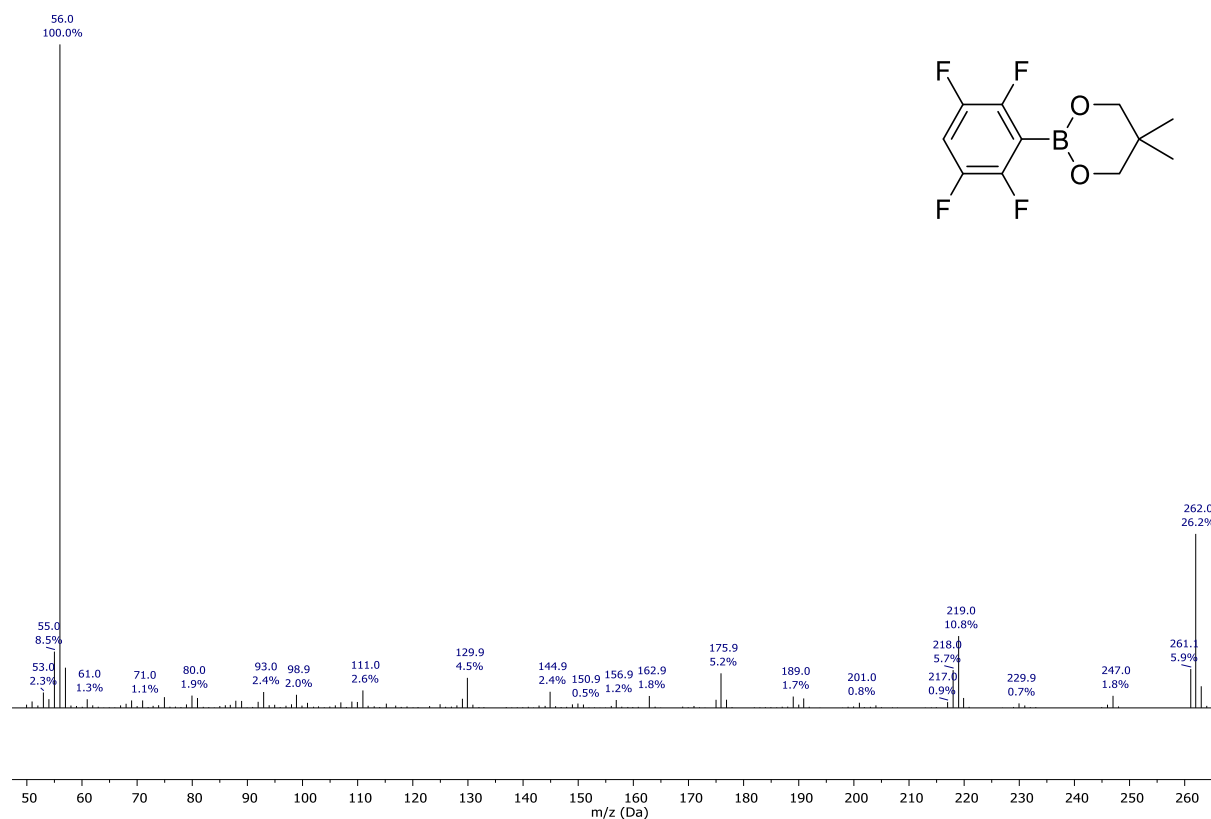
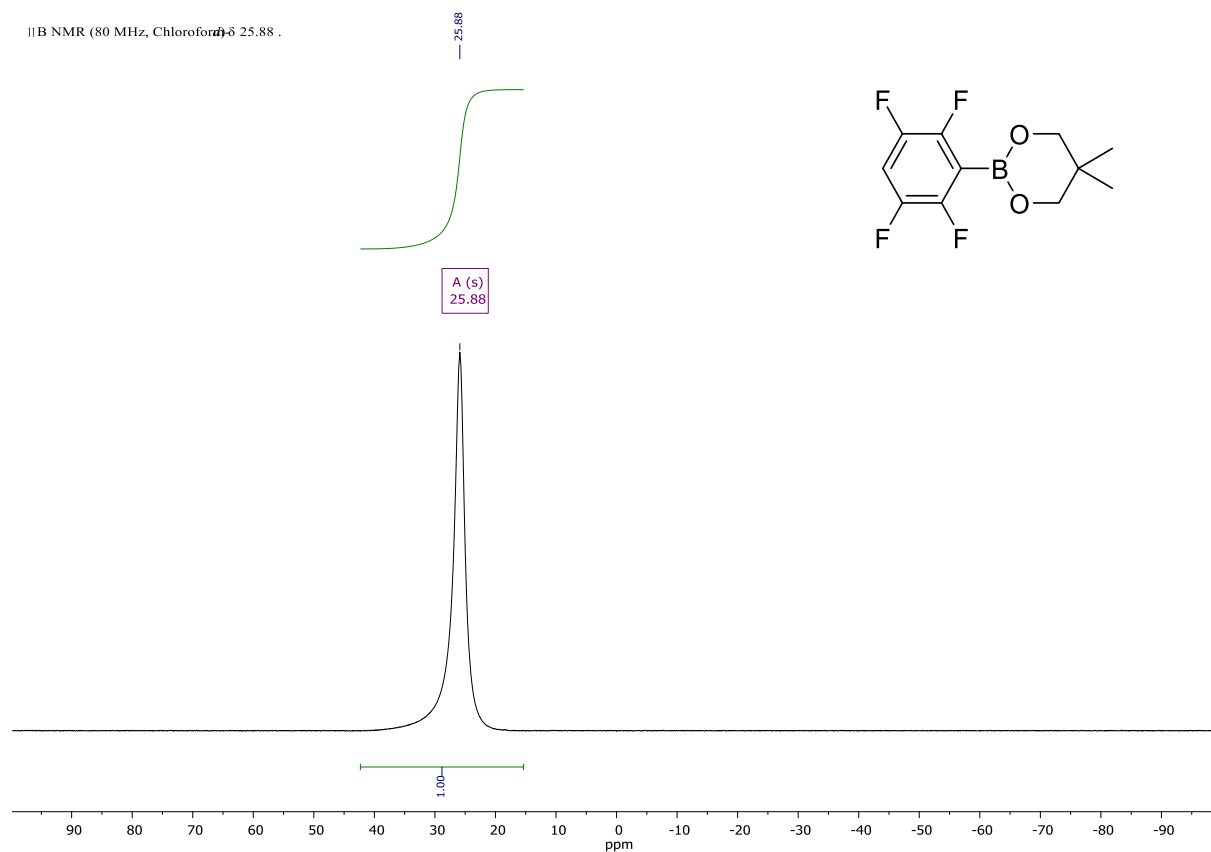


Figure S172 ^{13}C NMR: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane



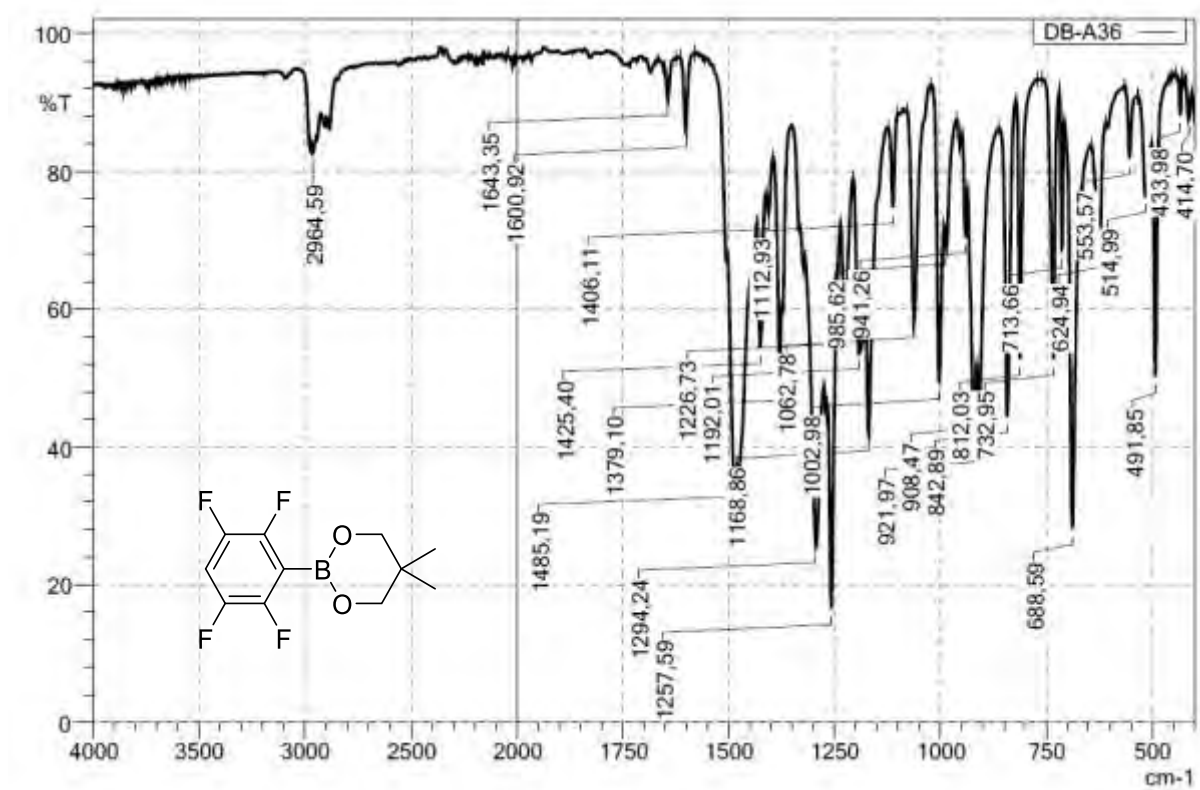
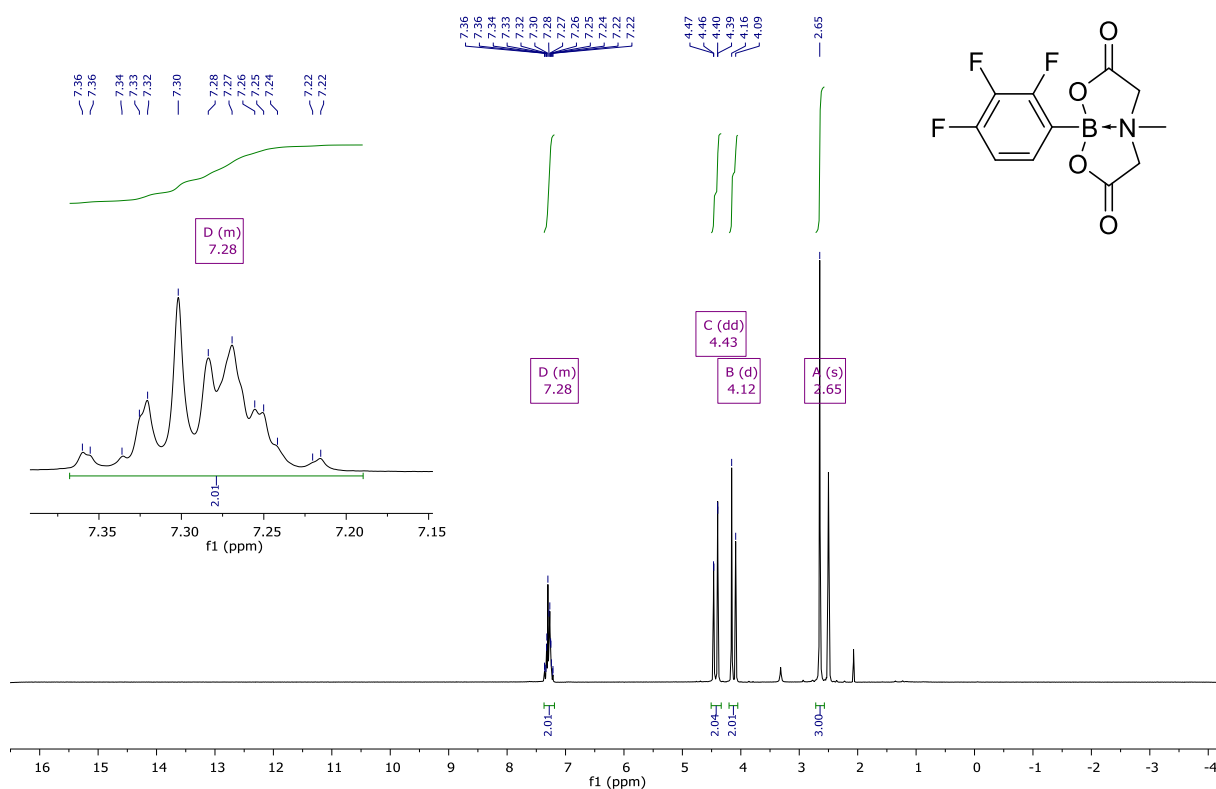


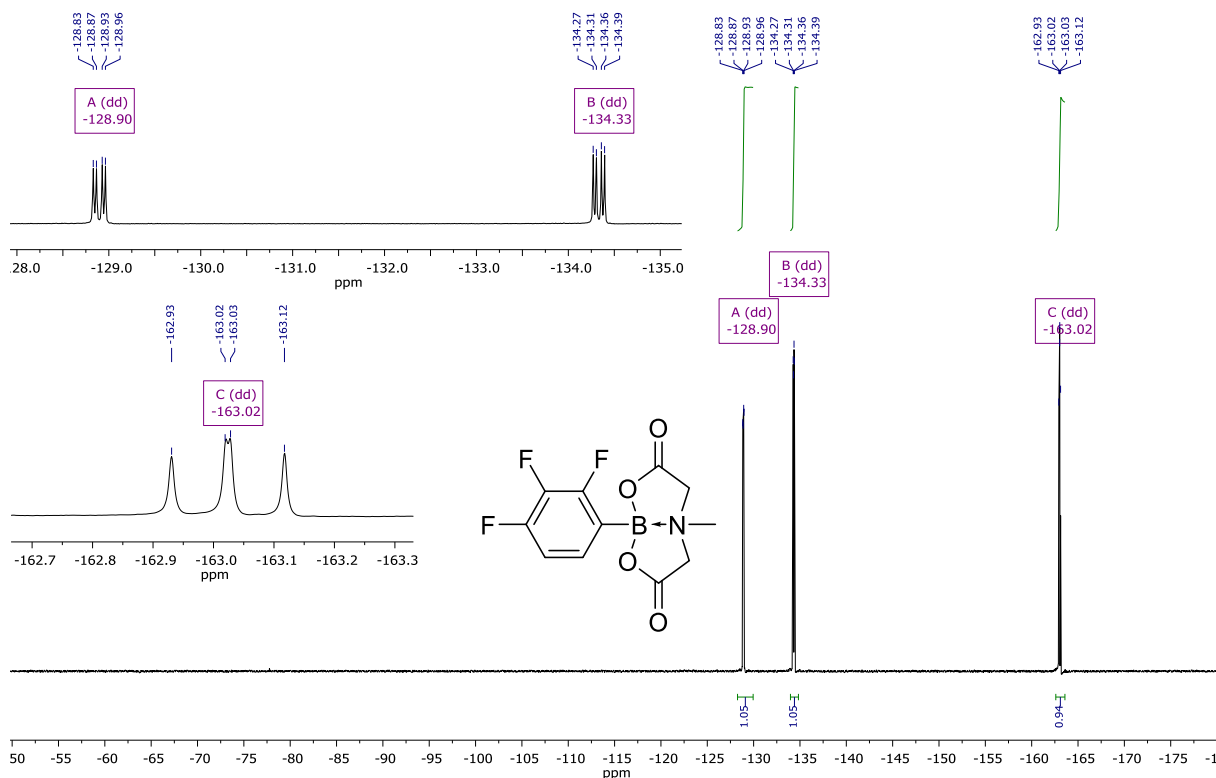
Figure S175 IR (ATR)-Spectrum: 5,5-Dimethyl-2-(2,3,5,6-tetrafluorophenyl)-1,3,2-dioxaborinane

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

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

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

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

^{13}C NMR (63 MHz, DMSO-d_6) δ 169.26, 153.76 (ddd, = 244.6, 8.7, 3.1 Hz), 151.61 (ddd, 248.5, 9.8, 3.6 Hz), 139.27 (ddd, = 249.0, 18.1, 14.7 Hz), 129.54 – 128.96 (m), 113.21 (dd, 2, 3.3 Hz), 62.76 (d, $J = 1.5$ Hz), 47.97.

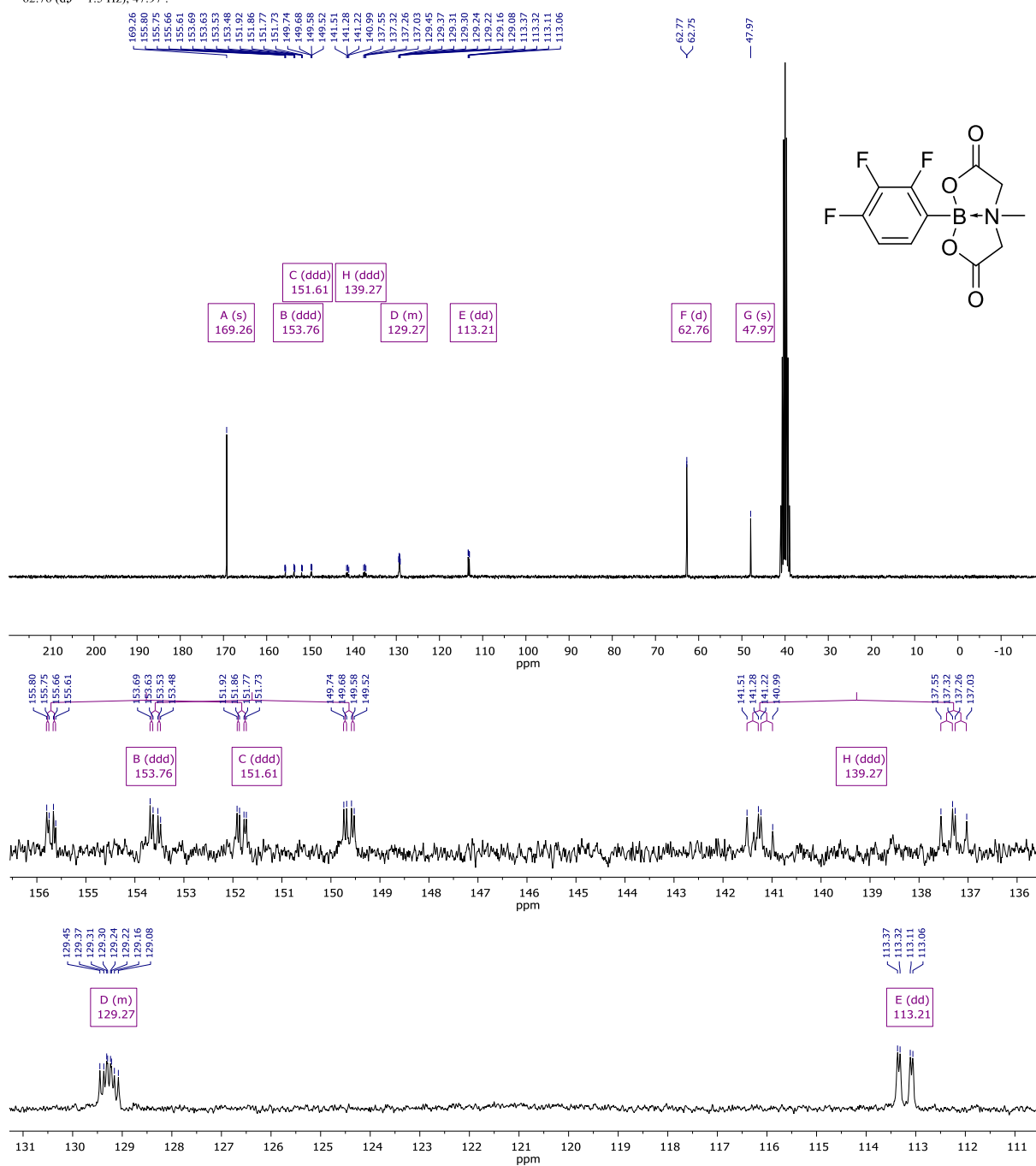


Figure S178 ^{13}C NMR: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

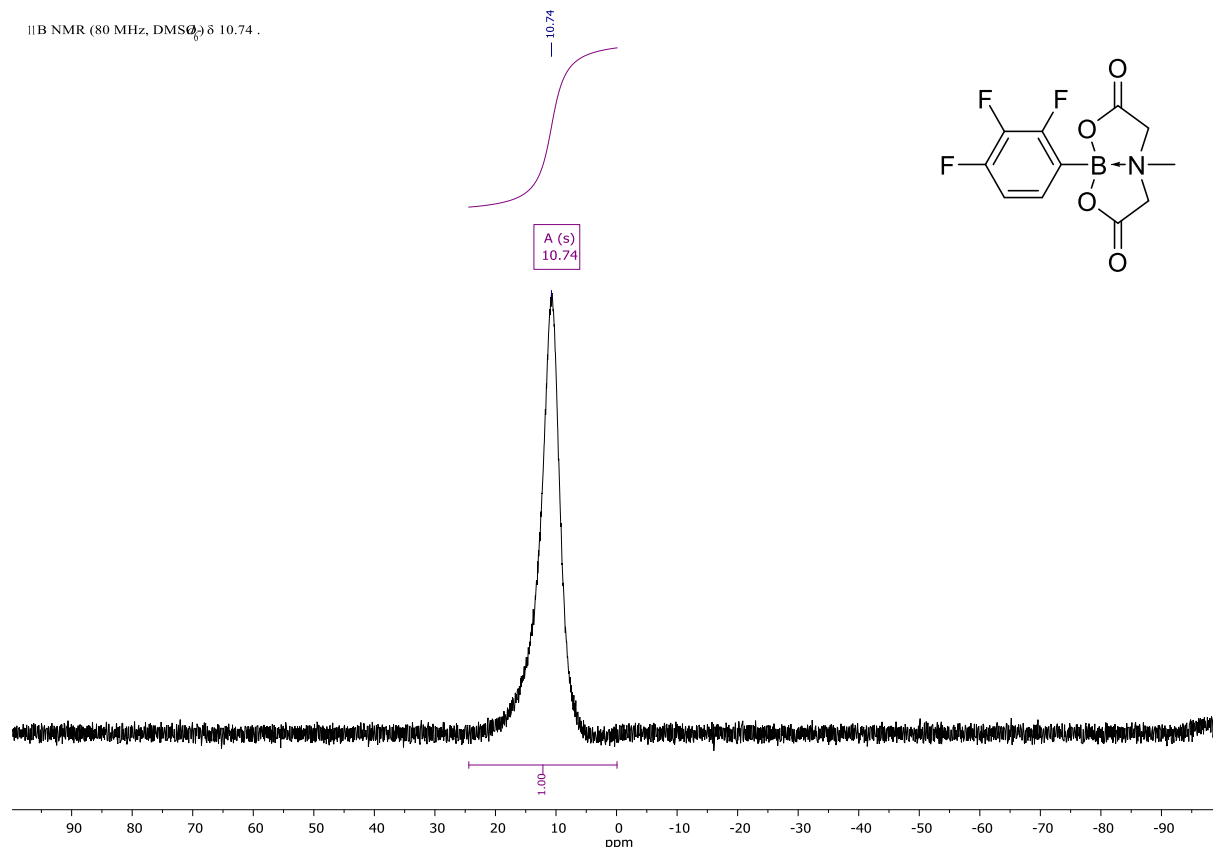


Figure S179 ^{11}B -NMR: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

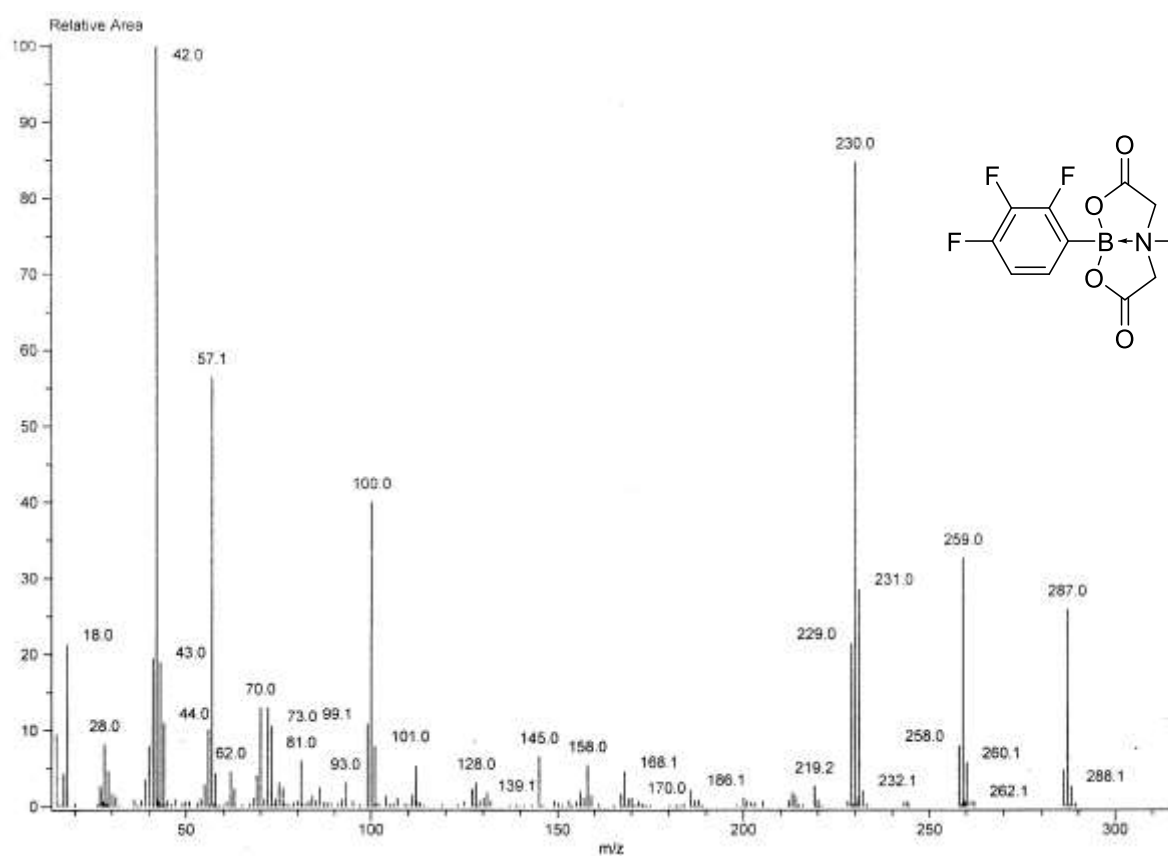


Figure S180 EI-Spectrum (EI^+): 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione

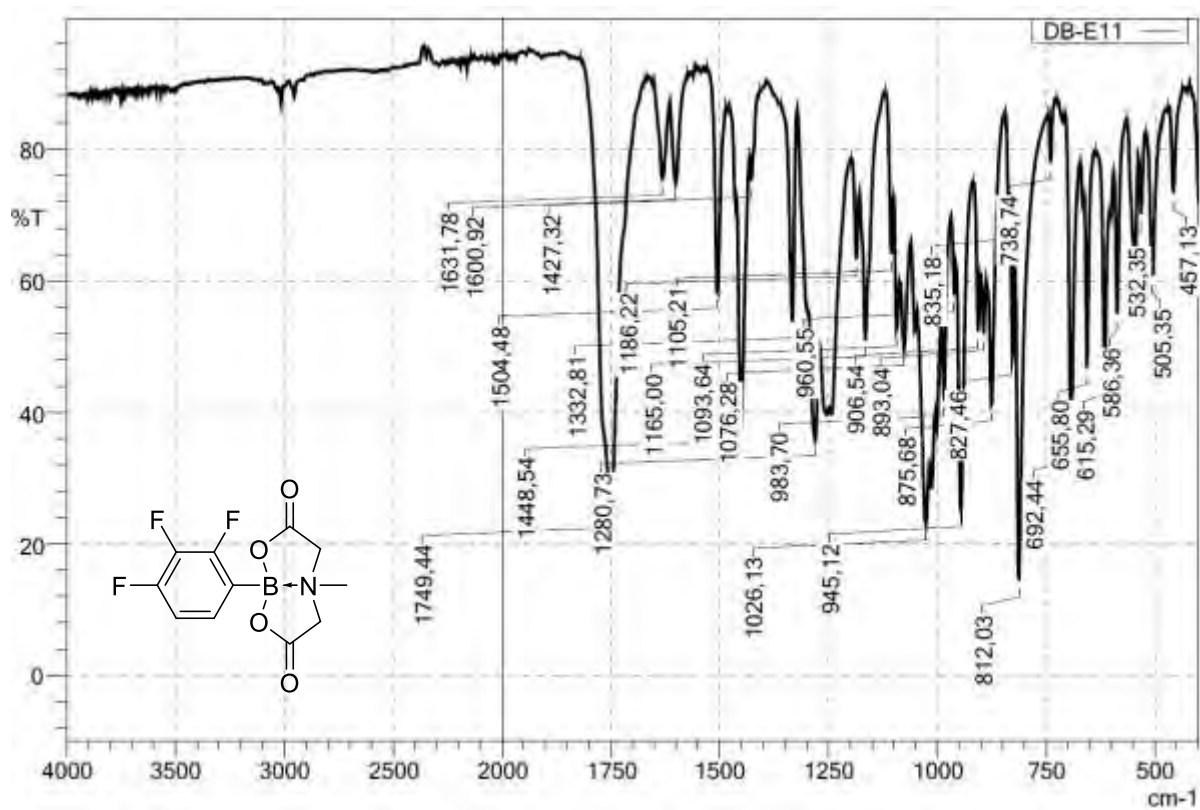


Figure S181 IR (ATR)-Spectrum: 6-Methyl-2-(2,3,4-trifluorophenyl)-1,3,6,2-dioxazaborocane-4,8-dione