Electronic Supplementary Material (ESI) for ChemComm.

Selective synthesis of fluorinated biaryls by [MCl_2(PEWO)] (M = Ni, Pd) catalysed Negishi cross-coupling

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General Experimental Section

All the manipulations were performed in a dry glovebox or by means of standard Schlenk techniques under N_2 or Ar atmosphere. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents,[1] and were sparged with nitrogen gas. Solvents for experiments in an inert atmosphere were stored into flame-dried Schlenk flasks over freshly activated 3 or 4 Å molecular sieves. Commercially available chemicals were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem and Acros Organics and were used without further purification. $NiCl_2(CH_3CN)_2$,[2] PhPEWO-F,[3] $PdCl_2$(PhPEWO-F),[3] were prepared by reported methods. Flash chromatography was carried out using silica gel (230-240 mesh) and oxygen-free solvents. Chemical yields refer to pure isolated substances.

NMR spectra were recorded with Bruker Avance 400 Ultrashield and Varian 500/54 Premium Shielded instruments. Chemical shifts are reported in ppm referenced to tetramethylsilane (^1H), CCl_3F (^{19}F), and 85% H_3PO_4 (^{31}P), with positive shifts downfield, at 298 K unless otherwise stated. In the ^{19}F and ^{31}P NMR spectra registered in non-deuterated solvents, a coaxial tube containing acetone-d_6 was used to maintain the ^2H lock signal.

HRMS (EI) were performed with a MALDI Bruker Autoflex at the LTI facilities of Valladolid University (Spain).

General Procedure for Catalysis

Ni-catalysed reactions: a flame-dried screwed-capped Schlenk flask containing $NiCl_2(CH_3CN)_2$ (1.06 mg, 0.005 mmol) and PhPEWO-F (2.32 mg, 0.005 mmol) was placed in a glovebox. $Zn(C_6F_5)_2$ (60.0 mg, 0.150 mmol) was added to the flask, which was taken out of the glovebox. Aryl iodide (0.100 mmol) was added to the flask (by microsyringe when liquid) and dry and degassed dioxane was added (2 mL). For experiments employing internal standard, a known amount of 1,3,5-trifluoro-2,4,6-trichlorobenzene was added to the flask at this stage. The mixture was placed in an oil bath at 80 °C and stirred for 6 hours. Then, the flask was taken out of the bath and 3 mL of aqueous saturated NH_4Cl solution were added. The aqueous layer was extracted with Et_2O (3 x 1.5 mL). The organic fraction was dried over $MgSO_4$ and filtered through a short path of silica gel. The coloured solution was concentrated and the residue was purified by flash column chromatography.

Pd-catalysed reactions: a flame-dried screwed-capped Schlenk flask containing $PdCl_2$(PhPEWO-F) (2.01 mg, 0.003 mmol) was placed in a glovebox. $Zn(C_6F_5)_2$ (60.0 mg, 0.150 mmol) was added to the flask, which was taken out of the glovebox. Aryl iodide (0.100 mmol) was added to the flask (by microsyringe when liquid) and dry and degassed dioxane was added (2 mL). For experiments employing internal standard, a known amount of 1,3,5-trifluoro-2,4,6-trichlorobenzene was added to the flask at this stage. The mixture was placed in an oil bath at 80 °C and stirred for 6 hours. Then, the flask was taken out of the bath and 3 mL of aqueous saturated NH_4Cl solution were added. The aqueous layer was extracted with Et_2O (3 x 1.5 mL). The organic fraction was dried over $MgSO_4$ and filtered through a short path of silica gel. The coloured solution was concentrated and the residue was purified by column chromatography.

Catalysis products and isolated yields

Table ESI1. Ni-catalysed reactions.

Aryl	T (h)	ArI	ArC_6F_5	Ar_2[a]	ArH[b]	$(C_6F_5)_2$[a]	ArC_6F_5 isol. yield (%)
4-C_6H_4(Me)	6	0	99	0	0	5	96
4-C_6H_4(CN)	6	0	99	0	0	5	94
4-C_6H_4F	6	0	99	0	0	5	95
4-$C_6H_4(CF_3)$	6	0	99	0	0	5	96
3,4-$C_6H_3F_2$	6	9	89	0	2	6	83
2,4-$C_6H_3F_2$	6	1	88	8	3	9	85
3,5-$C_6H_3F_2$	6	0	92	6	2	8	88
3,5-$C_6H_3(CF_3)_2$	6	0	79	16	5	12	74
2,6-$C_6H_3F_2$	22	7	48	13	19	24	33[e]
2,4,6-$C_6Cl_2F_3$	9	0	41	10	39	28	35
C_6F_5	4	0	–	–	–[c]	>99[d]	98

[a] For Ar and C_6F_5 groups balance to 100 these molar number have to be multiplied by 2. [b] ArH comes from the Ar groups trapped as Ar–**{Zn}** at the end of the reaction and is obtained and measured after hydrolysis. [c] Cannot be measured because all the hydrolysis product of Ar–**{Zn}** is C_6F_5H in this case. [d] A total of 105 mol% could be produced. [e] The lower isolated yield is due to product volatility.

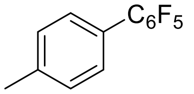
Table ESI2. Pd-catalysed reactions.

Aryl	T (h)	ArI	ArC_6F_5	Ar_2[a]	ArH[b]	$(C_6F_5)_2$[a]	ArC_6F_5 isol. yield (%)
4-C_6H_4(Me)	5	0	99	0	0	3	95
4-C_6H_4(CN)	5	0	99	0	0	3	96
4-C_6H_4F	5	0	99	0	0	3	93
4-$C_6H_4(CF_3)$	5	0	99	0	0	3	94
3,4-$C_6H_3F_2$	5	5	95	0	0	4	92
2,4-$C_6H_3F_2$	5	4	95	0	1	3	90
3,5-$C_6H_3F_2$	3	0	>99	0	0	3	96
3,5-$C_6H_3(CF_3)_2$	3	0	>99	0	0	3	92
2,6-$C_6H_3F_2$	5	8	87	0.5	4	5	71[e]
2,4,6-$C_6Cl_2F_3$	2	0	69	8	16	20	62
C_6F_5	2	0	–	–	–[c]	>99[d]	95

[a] For Ar and C_6F_5 groups balance to 100 these molar number have to be multiplied by 2. [b] ArH comes from the Ar groups trapped as Ar–**{Zn}** at the end of the reaction and is obtained and measured after hydrolysis. [c] Cannot be measured because all the hydrolysis product of Ar–**{Zn}** is C_6F_5H in this case. [d] A total of 103 mol% could be produced. [e] The lower isolated yield is due to product volatility.

Compounds Characterization

2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl



Following general procedure with 4-iodotoluene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

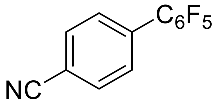
HRMS (EI) Calculated for $C_{13}H_7F_5$ $[M]^+$: 258.0468. Experimental $[M]^+$: 258.0463.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.32 (s, 4H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (100.56 MHz, Chloroform-*d*) δ 144.32 (dddt, *J* = 247.3, 11.1, 7.6, 3.9 Hz. 2C), 142.17 – 138.67 (m, *J* = 253.0 Hz, 1C), 139.57 (s, 1C), 139.49 – 136.36 (m, *J* = 250.6 Hz, 2C), 130.13 (d, *J* = 2.2 Hz, 2C), 129.60 (s, 2C), 123.52 (s, 1C), 116.12 (td, *J* = 17.2, 4.1 Hz, 1C), 21.48 (s, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -143.33 – -143.48 (m, 2F), -156.21 (t, *J* = 20.8 Hz, 1F), -162.34 – -162.86 (m, 2F).

2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-carbonitrile



Following general procedure with 4-iodobenzonitrile. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

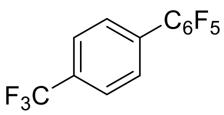
HRMS (EI) Calculated for $C_{13}H_4F_5N$ $[M]^+$: 269.0264. Experimental $[M]^+$: 269.0267.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H).

^{13}C{^{1}H} NMR (100.56 MHz, Chloroform-*d*) δ 145.75 – 142.71 (m, *J* = 248.9 Hz, 2C), 142.71 – 139.74 (m, *J* = 255.0 Hz, 1C), 139.64 – 136.43 (m, *J* = 253.5 Hz, 2C), 132.61 (s, 2C), 131.28 (s, 1C), 131.24 – 130.98 (m, 2C), 118.23 (s, 1C), 114.22 (td, *J* = 16.7, 4.1 Hz, 1C), 113.50 (s, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -142.79 (dd, *J* = 22.6, 8.1 Hz, 2F), -152.89 (t, *J* = 21.0 Hz, 1F), -160.63 – -161.09 (m, 2F).

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



Following general procedure with 4-iodobenzotrifluoride. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

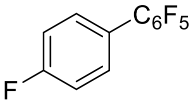
HRMS (EI) Calculated for $C_{13}H_4F_8$ $[M]^+$: 312.0185. Experimental $[M]^+$: 312.0190.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 144.30 (d, *J* = 248.9 Hz, 2C), 141.12 (d, *J* = 255.2 Hz, 1C), 138.10 (d, *J* = 253.1 Hz, 2C), 131.62 (q, *J* = 32.8 Hz, 1C), 130.80 (s, 2C), 130.27 (s, 1C), 126.02 – 125.69 (m, 2C), 123.92 (q, *J* = 271.7 Hz, 1C), 114.70 (td, *J* = 17.0, 4.1 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -62.99 (s, 3F), -142.90 – -143.02 (m, 2F), -153.78 (t, *J* = 21.0 Hz, 1F), -161.32 – -161.50 (m, 2F).

2,3,4,4',5,6-hexafluoro-1,1'-biphenyl



Following general procedure with 4-fluoroiodobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

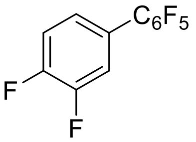
HRMS (EI) Calculated for $C_{12}H_4F_6$ $[M]^+$: 262.0217. Experimental $[M]^+$: 262.0215.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.24 – 7.15 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 163.33 (d, *J* = 249.9 Hz, 1C), 144.29 (dddt, *J* = 247.7, 11.1, 7.5, 3.9 Hz, 2C), 141.96 – 139.35 (m, *J* = 251.9 Hz, 1C), 139.34 – 136.47 (m, *J* = 248.5 Hz, 2C), 132.22 (dd, *J* = 8.5, 2.1 Hz, 2C), 122.41 (s, 1C), 116.14 (d, *J* = 21.9 Hz, 2C), 115.13 (td, *J* = 17.1, 4.1 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -111.33 (tt, *J* = 8.3, 5.4 Hz, 1F), -143.36 (m, 2F), -155.25 (t, *J* = 21.1 Hz, 1F), -161.21 – -163.05 (m, 2F).

2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl



Following general procedure with 3,4-difluoroiodobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

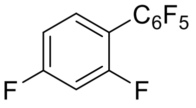
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0128.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.21 – 7.14 (m, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.08 (dd, *J* = 252.0, 12.1 Hz, 1C), 150.50 (dd, *J* = 249.7, 12.7 Hz, 1C), 145.53 – 142.79 (m, *J* =248.6 Hz, 2C), 142.34 – 139.64 (m, *J* =254.3 Hz, 1C), 139.36 – 136.47 (m, *J* = 252.9 Hz, 2C), 126.90 (dq, *J* = 5.9, 2.6 Hz, 1C), 123.10 (s, 1C), 119.67 (d, *J* = 19.0 Hz, 1C), 118.01 (d, *J* = 17.7 Hz, 1C), 114.09 (td, *J* = 17.2, 16.8, 4.5 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -135.55 – -135.69 (m, 1F), -136.26 – -136.40 (m, 1F), -143.00 – -143.11 (m, 2F), -154.10 (t, *J* = 21.0 Hz, 1F), -161.35 – -161.60 (m, 2F).

2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl



Following general procedure with 2,4-difluoroiodobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

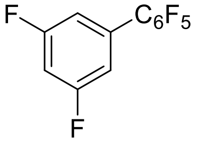
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0119.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 1H), 7.06 – 6.96 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 164.13 (dd, *J* = 252.6, 11.8 Hz, 1C), 160.43 (dd, *J* = 253.4, 12.2 Hz, 1C), 146.09 – 143.32 (m, *J* = 242.7 Hz, 2C), 142.97 – 140.08 (m, *J* = 253.0 Hz, 1C), 139.35 – 135.85 (m, *J* = 247.8 Hz, 2C), 133.04 (dd, *J* = 9.9, 3.8 Hz, 1C), 112.14 (dd, *J* = 21.6, 3.8 Hz, 1C), 110.44 (d, *J* = 16.3 Hz, 1C), 109.48 (td, *J* = 18.5, 4.1 Hz, 1C), 104.94 (t, *J* = 25.5 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -106.69 – -106.80 (m, 1F), -108.13 (h, *J* = 9.7 Hz, 1F), -140.28 – -140.42 (m, 2F), -153.63 (t, *J* = 20.8 Hz, 1F), -161.74 – -161.94 (m, 2F).

2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl



Following general procedure with 3,5-difluoroiodobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

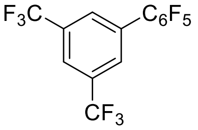
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0126.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.00 – 6.96 (m, 2H), 6.93 (tt, *J* = 8.8, 2.3 Hz, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 163.09 (dd, *J* = 249.8, 12.9 Hz, 2C), 144.22 (d, *J* = 249.7 Hz, 2C), 141.22 (d, *J* = 255.8 Hz, 1C), 138.09 (d, *J* = 251.8 Hz, 2C), 129.25 (d, *J* = 11.3 Hz, 1C), 113.98 (t, *J* = 14.8 Hz, 1C), 113.84 – 112.38 (m, 2C), 105.19 (t, *J* = 25.0 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -101.14 – -112.97 (m, 2F), -138.39 – -145.19 (m, 2F), -153.35 (t, *J* = 21.0 Hz, 1F), -156.20 – -164.29 (m, 2F).

2,3,4,5,6-pentafluoro-3',5'-bis(trifluoromethyl)-1,1'-biphenyl



Following general procedure with 3,5-bis(trifluromethyl)iodobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

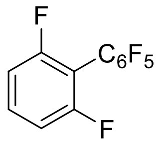
HRMS (EI) Calculated for $C_{14}H_3F_{11}$ $[M]^+$: 380.0059. Experimental $[M]^+$: 380.0065.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.91 (s, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 145.85 – 142.99 (m, *J* = 249.9 Hz, 2C), 142.99 – 140.04 (m, *J* = 257.2 Hz, 1C), 139.93 – 135.93 (m, *J* = 254.2 Hz, 2C), 132.66 (q, *J* = 33.9 Hz, 2C), 130.56 (s, 2C), 128.81 (s, 1C), 123.48 (p, *J* = 3.7 Hz, 1C), 123.06 (q, *J* = 272.9 Hz, 2C), 113.19 (td, *J* = 16.5, 4.2 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -63.12 (s, 6F), -142.81 – -142.92 (m, 2F), -152.04 (t, *J* = 20.8 Hz, 1F), -160.50 – -160.67 (m, 2F).

2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl



Following general procedure with 2,6-difluoroiodobenzene. The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent.

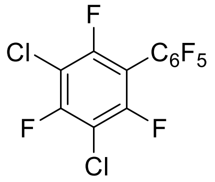
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0116.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.48 (tt, *J* = 8.5, 6.4 Hz, 1H), 7.09 – 7.04 (m, 1H).

$^{13}C\{^1H\}$ NMR (125.67 MHz, Chloroform-*d*) δ 160.30 (dd, *J* = 252.5, 5.7 Hz, 2C), 144.56 (d, *J* = 254.9 Hz, 2C), 141.66 (d, *J* = 242.6 Hz, 1C), 137.71 (d, *J* = 255.2 Hz, 2C), 132.11 (t, *J* = 10.2 Hz, 2C), 111.62 (d, *J* = 25.1 Hz, 2C). C_{ipso} not observed.

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -110.17 – -110.31 (m), -137.91 – -138.05 (m), -152.60 (tt, *J* = 20.8, 2.0 Hz), -161.74 – -161.90 (m).

3,5-dichloro-2,2',3',4,4',5',6,6'-octafluoro-1,1'-biphenyl

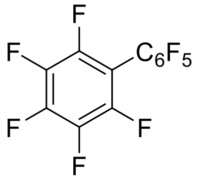


Following general procedure with 1,3-dichloro-2,4,6-trifluoro-5-iodobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

HRMS (EI) Calculated for $C_{12}Cl_2F_8$ $[M]^+$: 365.9249. Experimental $[M]^+$: 365.9255.

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -106.72 (t, *J* = 3.6 Hz, 1F), -110.40 (td, *J* = 8.2, 3.5 Hz, 2F), -137.25 – -137.43 (m, 2F), -149.99 (tt, *J* = 20.9, 3.1 Hz, 1F), -160.32 – -160.50 (m, 2F).

perfluoro-1,1'-biphenyl



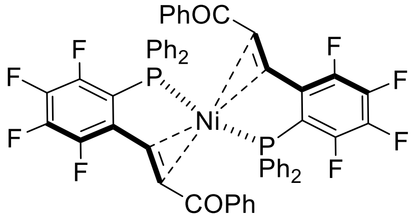
Following general procedure with iodopentafluorobenzene. The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent.

HRMS (EI) Calculated for $C_{12}F_{10}$ $[M]^+$: 333.9840. Experimental $[M]^+$: 333.9837.

$^{13}C\{^1H\}$ NMR (125.67 MHz, Chloroform-*d*) δ 144.84 (ddt, *J* = 253.2, 11.4, 3.4 Hz, 4C), 144.45 – 141.06 (m, *J* = 258.2 Hz, 2C), 139.85 – 136.49 (m, *J* = 252.1 Hz, 4C), 102.14 – 101.12 (m, 2C).

^{19}F NMR (376.21 MHz, Chloroform-*d*) δ -135.34 – -139.60 (m), -149.81 (t, *J* = 21.0 Hz), -160.23 – -160.45 (m).

Synthesis of $[Ni^0(PhPEWO\text{-}F)_2]$



To a flame-dried 10 mL Schlenk flask containing *c*-$[Ni(C_6F_5)(THF)_2]$ (58.5 mg, 0.11 mmol) and PhPEWO-F (103 mg, 0.22 mmol, 2 eq.) were added 4 mL of dry and degassed CH_2Cl_2. The mixture turned immediately deep red coloured. It was stirred for 30 min and taken to dryness. The dark red residue was washed with *n*-pentane and purified under air by chromatography column using *n*-pentane; *n*-pentane/DCM (5:1); DCM as eluent. The title compound was isolated as a red solid (90.1 mg, 83.4 % yield).

X-ray-quality crystals were grown by slow diffusion of a toluene/*n*-hexane mixture at room temperature.

HRMS (EI) Calculated for $C_{34}H_{54}F_8NiO_2P_2$ $[M]^+$: 986.1260. Experimental $[M]^+$: 986.1250.

^{1}H NMR (499.72 MHz, Methylene Chloride-*d₂*) δ 7.41 (t, *J* = 6.9 Hz, 4H), 7.29 (d, *J* = 7.7 Hz, 4H), 7.23 – 7.12 (m, 12H), 7.08 (t, *J* = 7.1 Hz, 2H), 6.79 (t, *J* = 6.7 Hz, 4H), 6.73 (t, *J* = 9.4 Hz, 4H), 5.68 – 5.60 (m, 2H), 4.84 (dt, *J* = 11.5, 3.0 Hz, 2H).

^{19}F NMR (470.17 MHz, Methylene Chloride-*d₂*) δ -125.14 – -127.17 (m, 2F), -136.78 – -139.87 (m, 2F), -150.86 (td, *J* = 22.1, 21.7, 6.3 Hz, 2F), -156.18 (t, *J* = 21.3 Hz, 2F).

^{31}P{^{1}H} NMR (202.30 MHz, Methylene Chloride-*d₂*) δ 43.59 (s).

This Ni^0 complex is air stable and can be purified by column chromatography. The stabilazing effect of electron withdrawing olefins on Ni^0 species has recently been employed in the design of new air stable Ni^0 precatalysts.[4]

The X-ray structure of $[Ni^0(PhPEWO\text{-}F)_2]$ shows a Ni atom coordinated with two PhPEWO-F ligands, both in a chelating fashion, by the phosphorous atom and the olefin moiety. The metal exhibits an intermediate geometry between a square-planar and a tetrahedral environment. The angle P-Ni-P and the one from Ni to the middle point of each olefin are close to tetrahedral, but the angle between the plane defined by P-Ni-P and the plane of Ni with the middle point of each olefin is 53.4°. It should be near 0° for square planar complexes and near 90° for tetrahedral complexes. The effect of important backdonation is observed in the large elongation of the C=C bond length (1.419 and 1.405 Å *vs* 1.314 Å in $PdCl_2(PhPEWO\text{-}F)_2$,[3] which has no olefin coordination). It is also important to note that the olefin retains its *E*-configuration.[5]

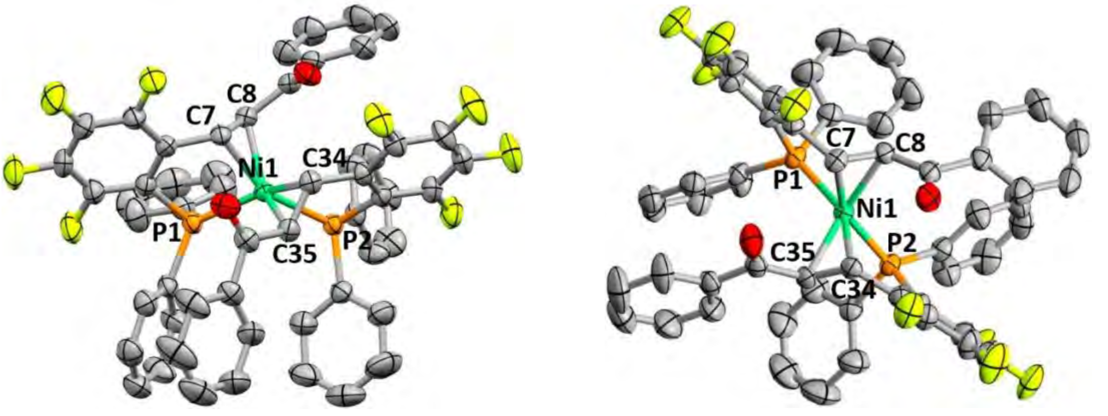


Figure ESI1. Two views of the X-ray structure of $(Ni(PhPEWO\text{-}F)_2$. Selected bond distances (Å) and angles (°) for: Ni1-C7 2.018(3); Ni1-C8 = 2.085(3); Ni-C34 = 2.035(3); Ni1-C35 = 2.086(3); Ni1-P1 = 2.2963(8); Ni1-P2 = 2.3292(8); C7-C8 = 1.419(4); C34-C35 = 1.405(4); P1-Ni1-P2 = 108.79(3); centroidC7C8-Ni1-centroidC34C35 = 109.75; centroidC7C8-Ni1-P1 = 90.12; centroidC34C35-Ni1-P2 = 86.37. Thermal ellipsoids at the 50% probability level. H atoms and *n*-hexane molecule omitted for clarity.

X-ray Crystallographic Data

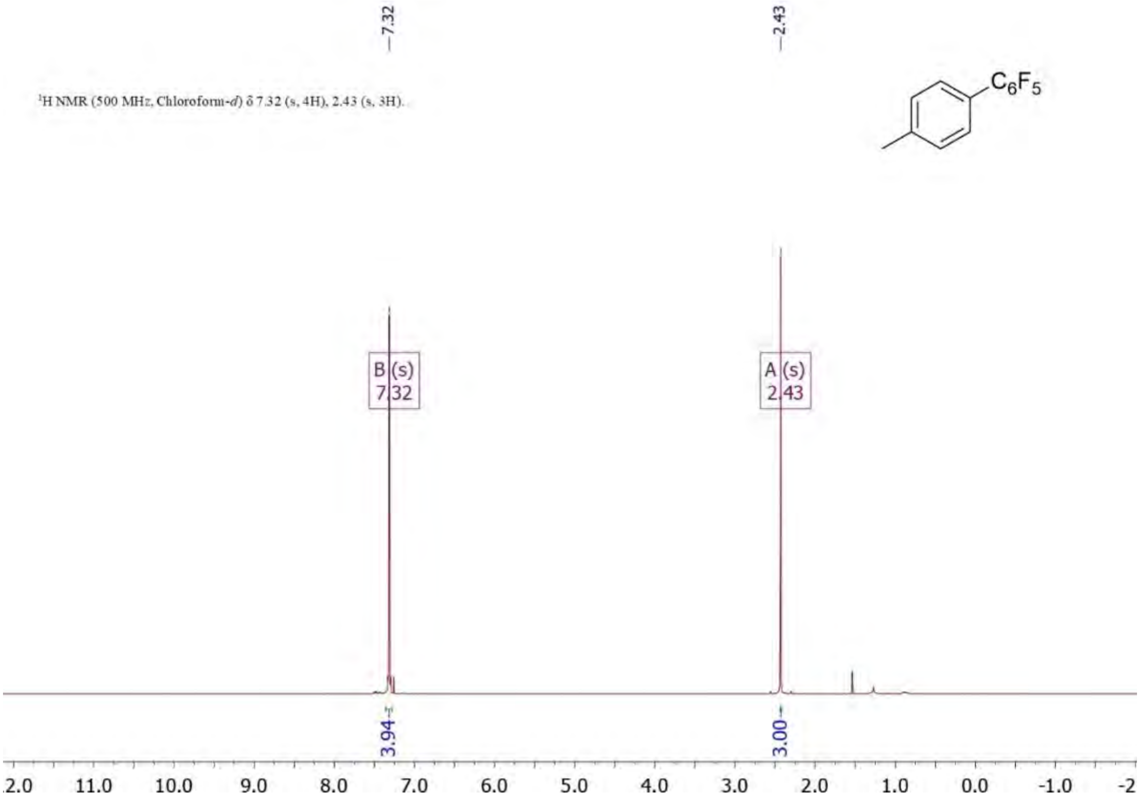
A crystal was attached to a glass fiber and transferred either to an Agilent Supernova diffractometer with an Atlas CCD area detector (Valladolid University facilities). The crystal was kept at constant temperature during data collection. Data collection was performed with Mo-Kα radiation ($\lambda = 0.71073$ Å). Data integration, scaling and empirical absorption correction were carried out using the CrysAlisPro program package.[6] Using Olex2,[7] the structure was solved with the olex2.solve[8] structure solution program and refined with ShelX program.[9] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Table ESI3. CCDC contains the supporting crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table ESI3. Crystal data and structure refinements for complex.

Identification code	Ni(PhPewo-F)$_2$·1/2 *n*-hexane
CCDC deposition N°	2105912
Empirical formula	$C_{57}H_{41}F_8NiO_2P_2$
Formula weight	1030.55
Temperature/K	294.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.2684(4)
b/Å	16.5014(5)
c/Å	21.5435(6)
α/°	90
β/°	92.706(2)
γ/°	90
Volume/Å^3	5066.7(2)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	0.517
F(000)	2116.0
Crystal size/mm^3	0.267 × 0.182 × 0.086
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.588 to 59.602
Index ranges	$-19 \le h \le 13$, $-20 \le k \le 22$, $-26 \le l \le 27$
Reflections collected	21823
Independent reflections	11837 [$R_{int} = 0.0288$, $R_{sigma} = 0.0542$]
Data/restraints/parameters	11837/5/660
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	$R_1 = 0.0540$, $wR_2 = 0.1451$
Final R indexes [all data]	$R_1 = 0.0880$, $wR_2 = 0.1751$
Largest diff. peak/hole / e Å^{-3}	0.69/-0.28

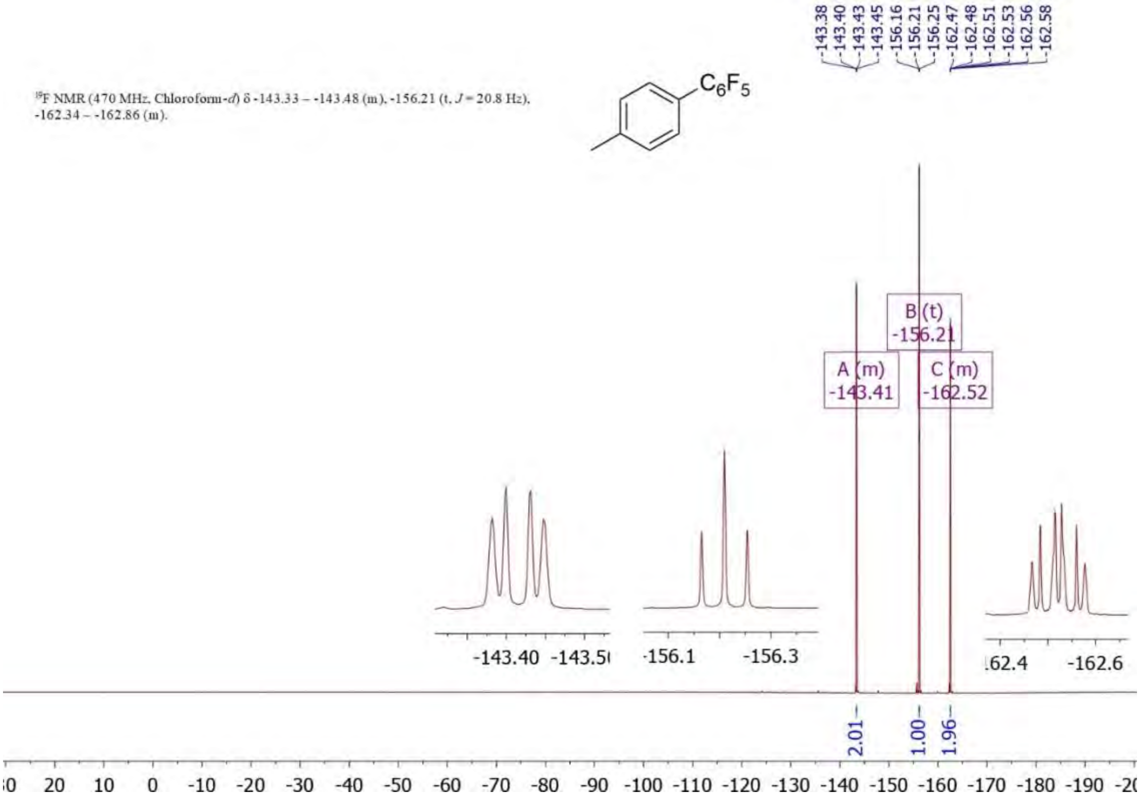
NMR Spectra

^1H NMR of 2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl in $CDCl_3$.



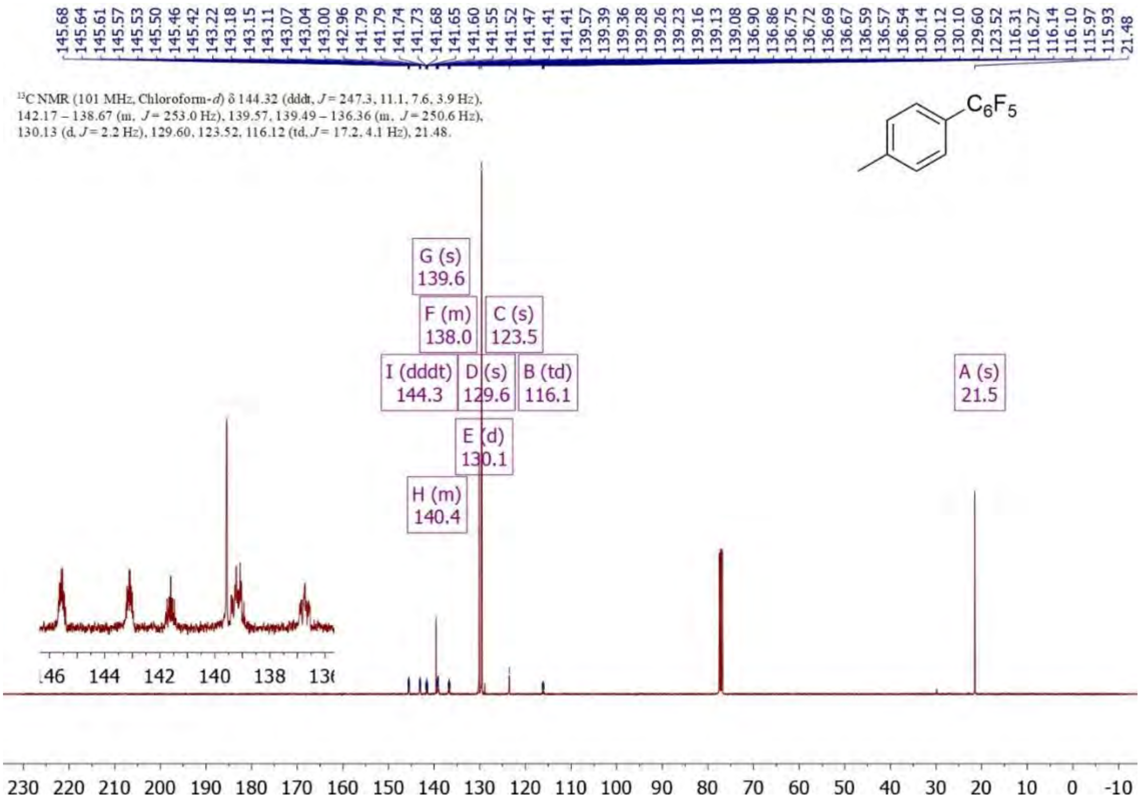
^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 (s, 4H), 2.43 (s, 3H).

^{19}F NMR of 2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl in $CDCl_3$.



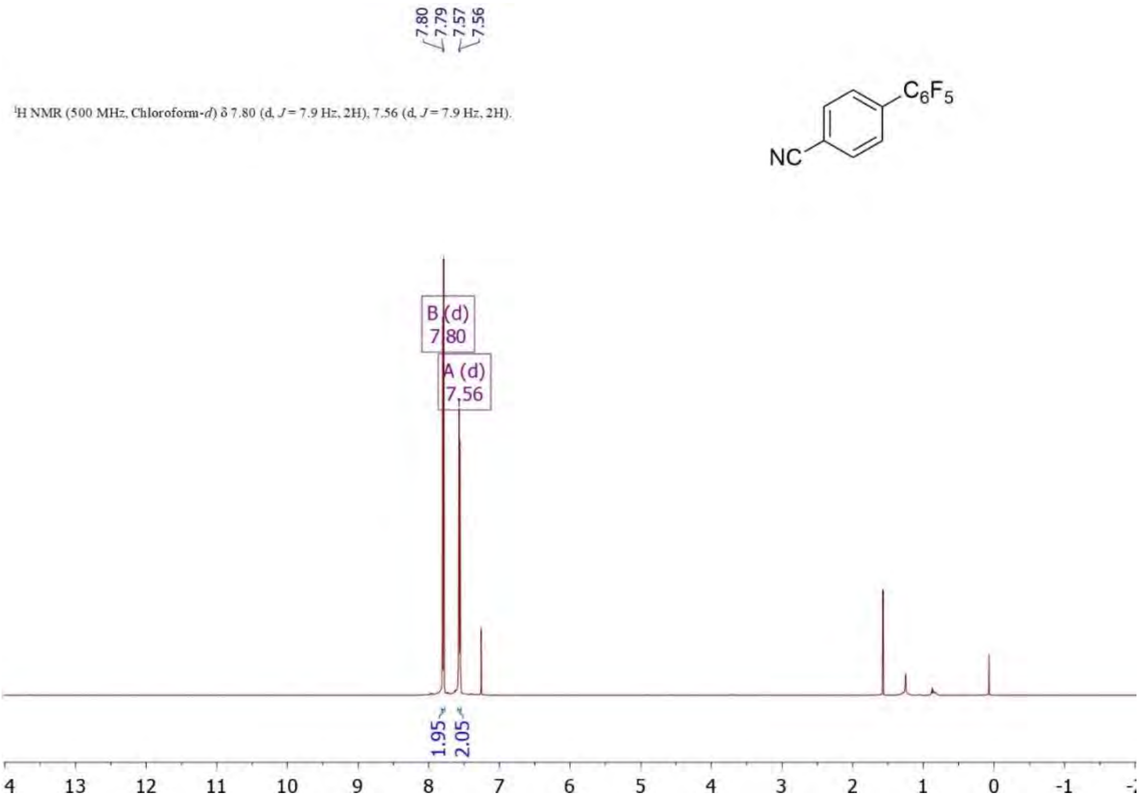
^{19}F NMR (470 MHz, Chloroform-*d*) δ -143.33 – -143.48 (m), -156.21 (t, *J* = 20.8 Hz), -162.34 – -162.86 (m).

$^{13}C\{^1H\}$ NMR of 2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl in $CDCl_3$.



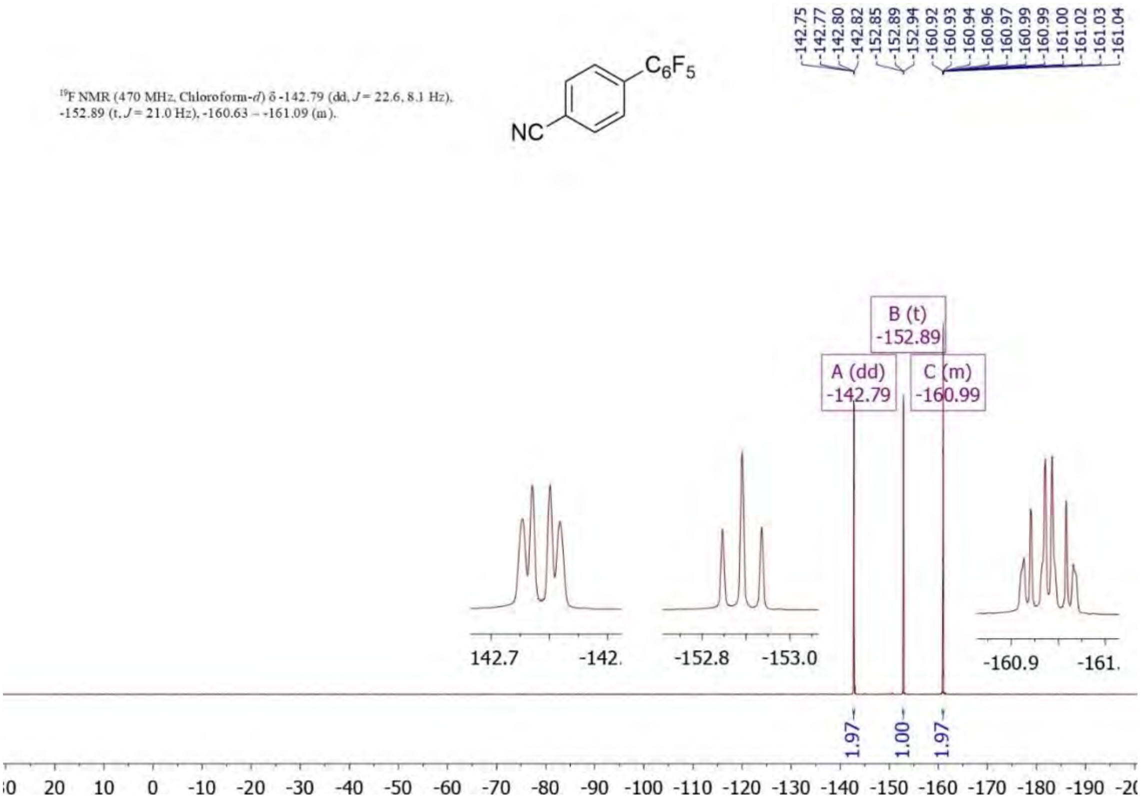
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.32 (dddt, *J* = 247.3, 11.1, 7.6, 3.9 Hz), 142.17 – 138.67 (m, *J* = 253.0 Hz), 139.57, 139.49 – 136.36 (m, *J* = 250.6 Hz), 130.13 (d, *J* = 2.2 Hz), 129.60, 123.52, 116.12 (td, *J* = 17.2, 4.1 Hz), 21.48.

^1H NMR of 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-carbonitrile in $CDCl_3$.



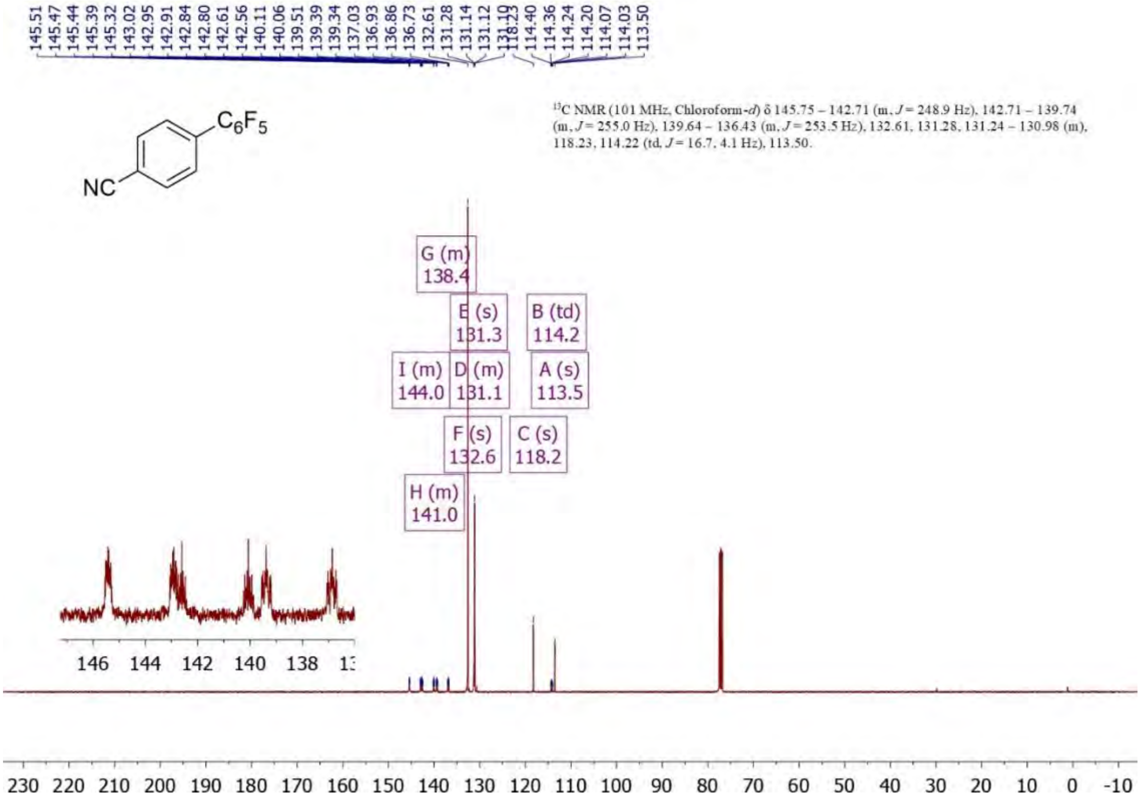
^1H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H).

^{19}F NMR of 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-carbonitrile in $CDCl_3$.



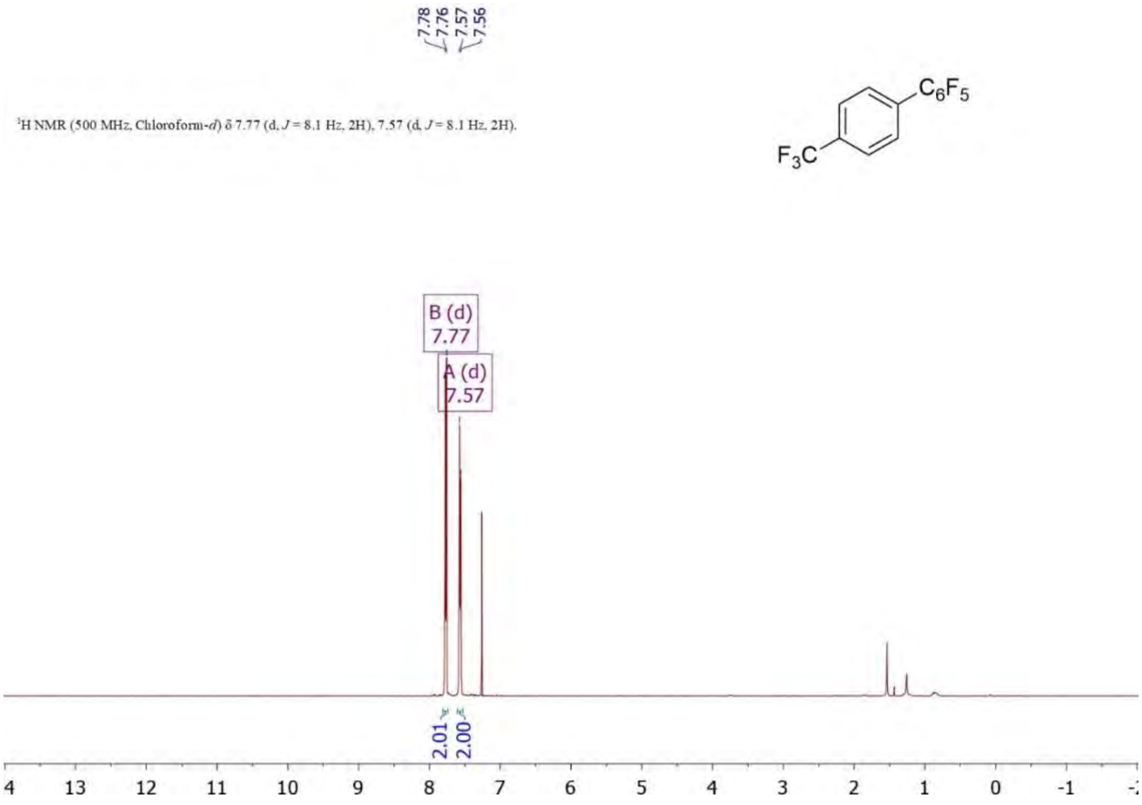
^{19}F NMR (470 MHz, Chloroform-*d*) δ -142.79 (dd, J = 22.6, 8.1 Hz), -152.89 (t, J = 21.0 Hz), -160.63 – -161.09 (m).

$^{13}C\{^1H\}$ NMR of 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-carbonitrile in $CDCl_3$.



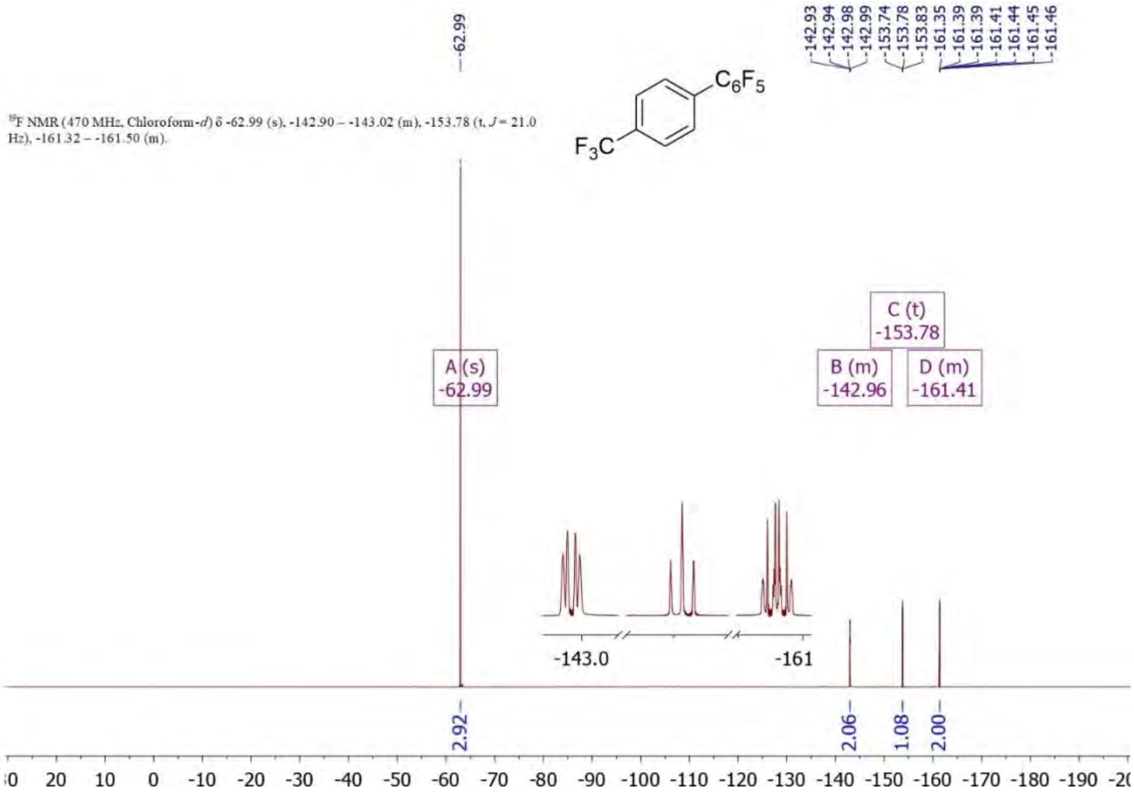
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.75 – 142.71 (m, J = 248.9 Hz), 142.71 – 139.74 (m, J = 255.0 Hz), 139.64 – 136.43 (m, J = 253.5 Hz), 132.61, 131.28, 131.24 – 130.98 (m), 118.23, 114.22 (td, J = 16.7, 4.1 Hz), 113.50.

^{1}H NMR of 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl in $CDCl_3$.



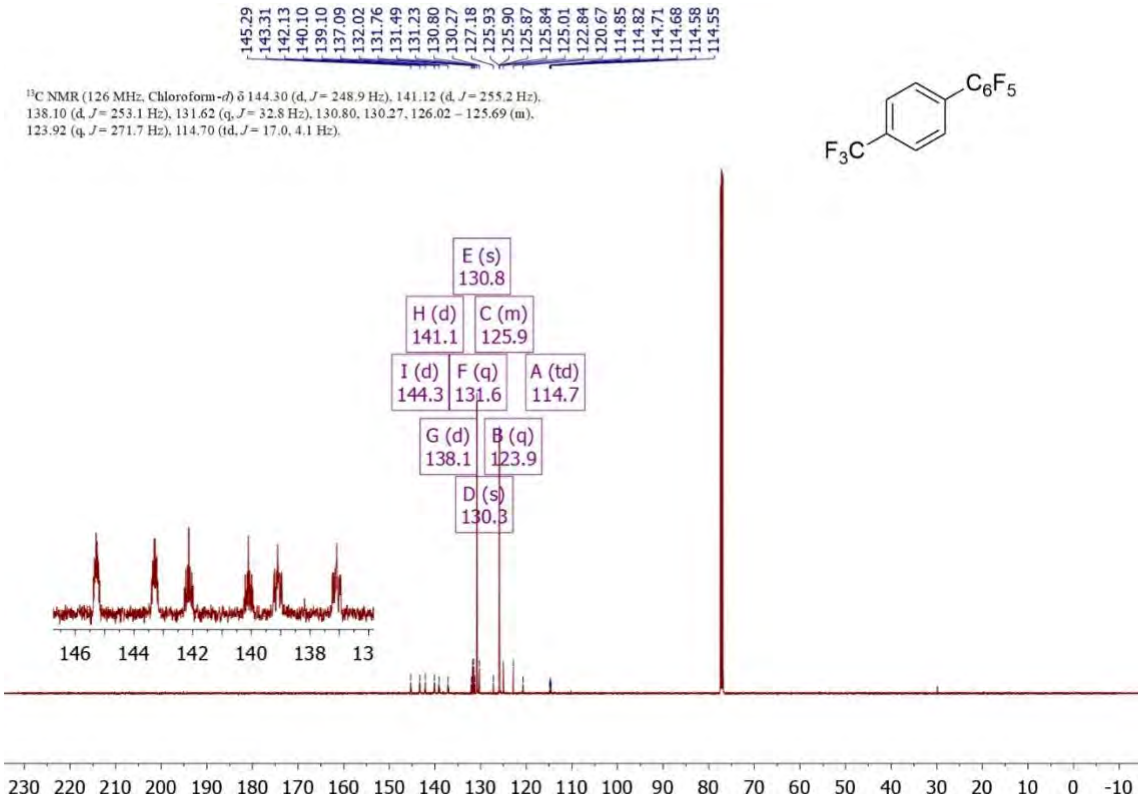
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H).

^{19}F NMR of 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl in $CDCl_3$.



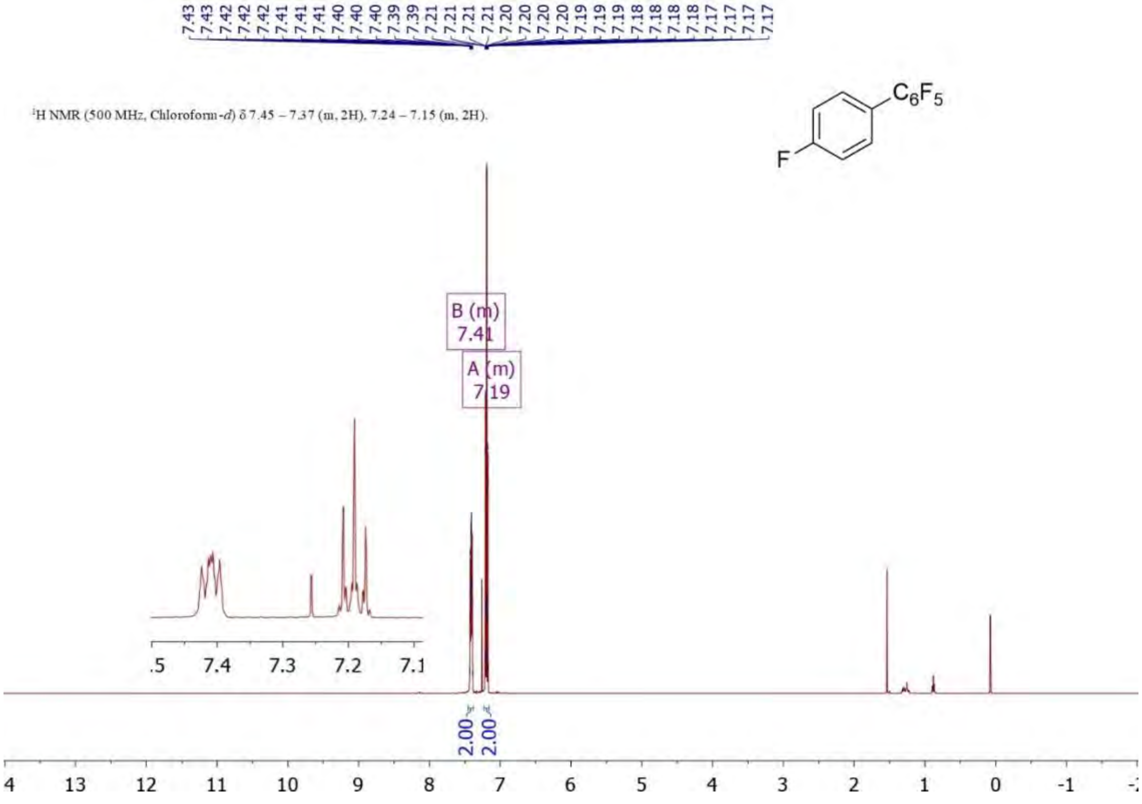
^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.99 (s), -142.90 – -143.02 (m), -153.78 (t, J = 21.0 Hz), -161.32 – -161.50 (m).

$^{13}C\{^1H\}$ NMR of 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl in $CDCl_3$.



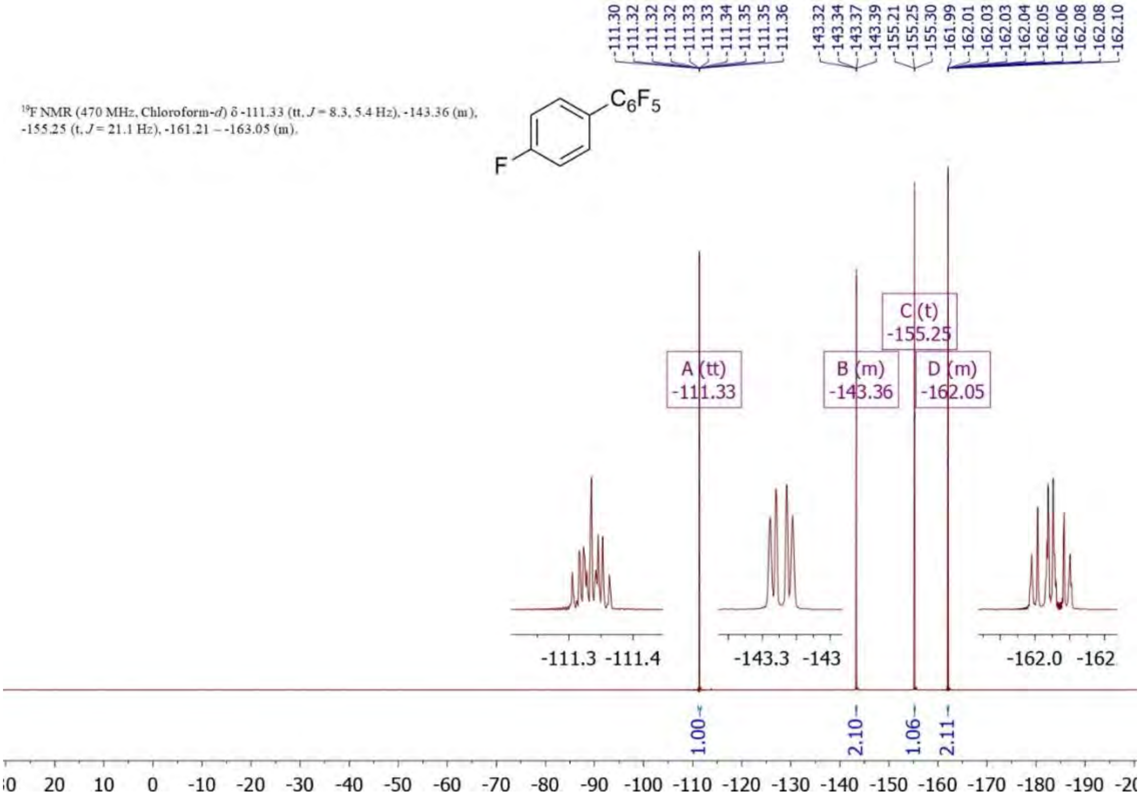
^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.30 (d, *J* = 248.9 Hz), 141.12 (d, *J* = 255.2 Hz), 138.10 (d, *J* = 253.1 Hz), 131.62 (q, *J* = 32.8 Hz), 130.80, 130.27, 126.02 – 125.69 (m), 123.92 (q, *J* = 271.7 Hz), 114.70 (td, *J* = 17.0, 4.1 Hz).

^1H NMR of 2,3,4,4',5,6-hexafluoro-1,1'-biphenyl in $CDCl_3$.



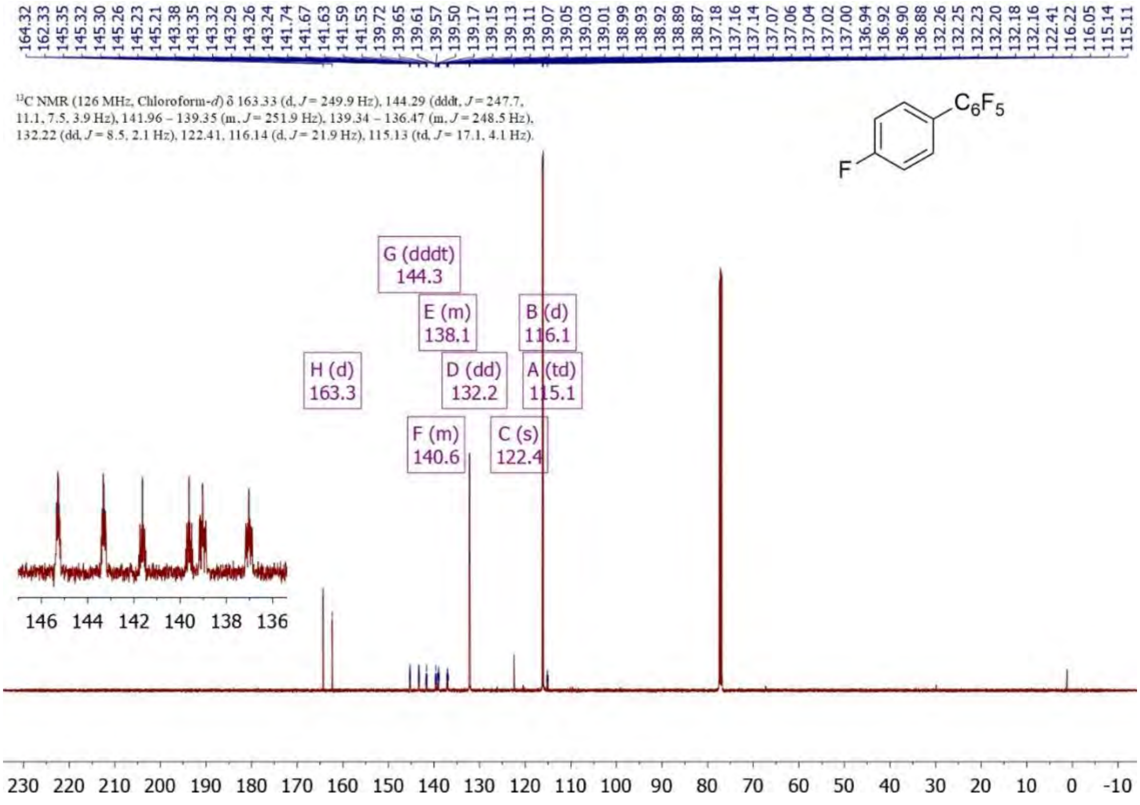
^1H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.24 – 7.15 (m, 2H).

^{19}F NMR of 2,3,4,4',5,6-hexafluoro-1,1'-biphenyl in $CDCl_3$.



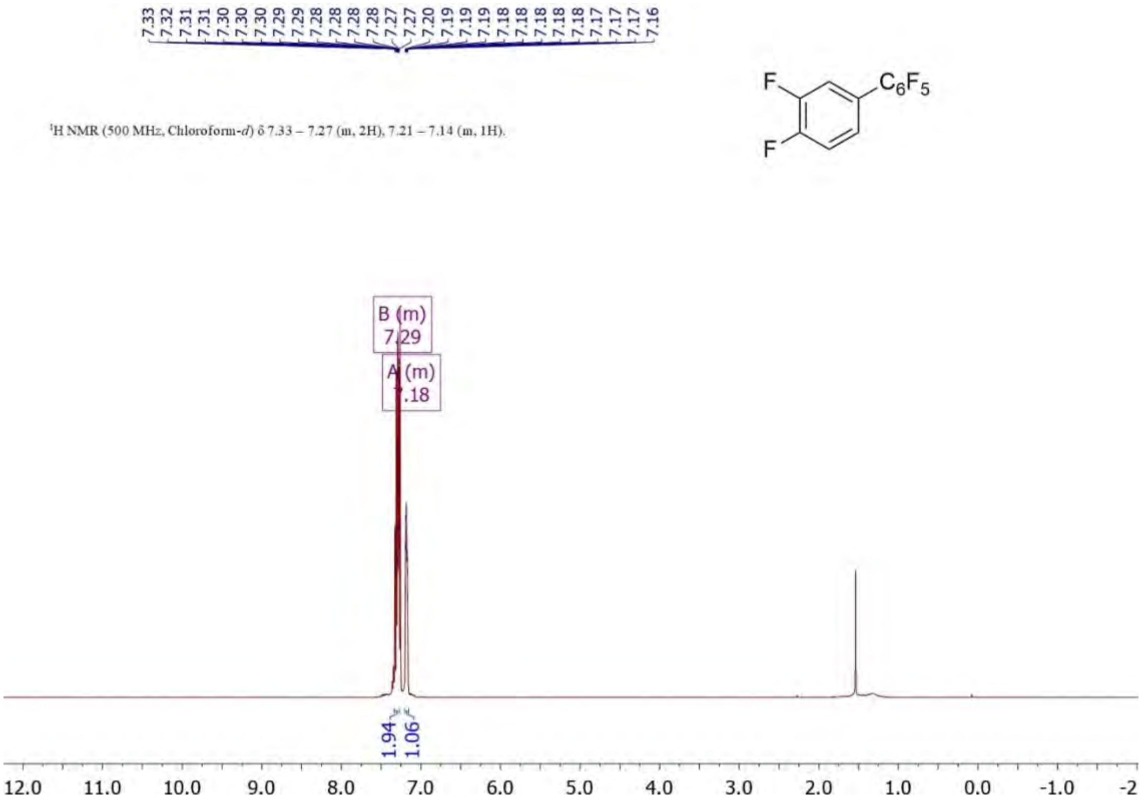
^{19}F NMR (470 MHz, Chloroform-*d*) δ -111.33 (tt, *J* = 8.3, 5.4 Hz), -143.36 (m), -155.25 (t, *J* = 21.1 Hz), -161.21 – -163.05 (m).

^{13}C{^{1}H} NMR of 2,3,4,4',5,6-hexafluoro-1,1'-biphenyl in $CDCl_3$.



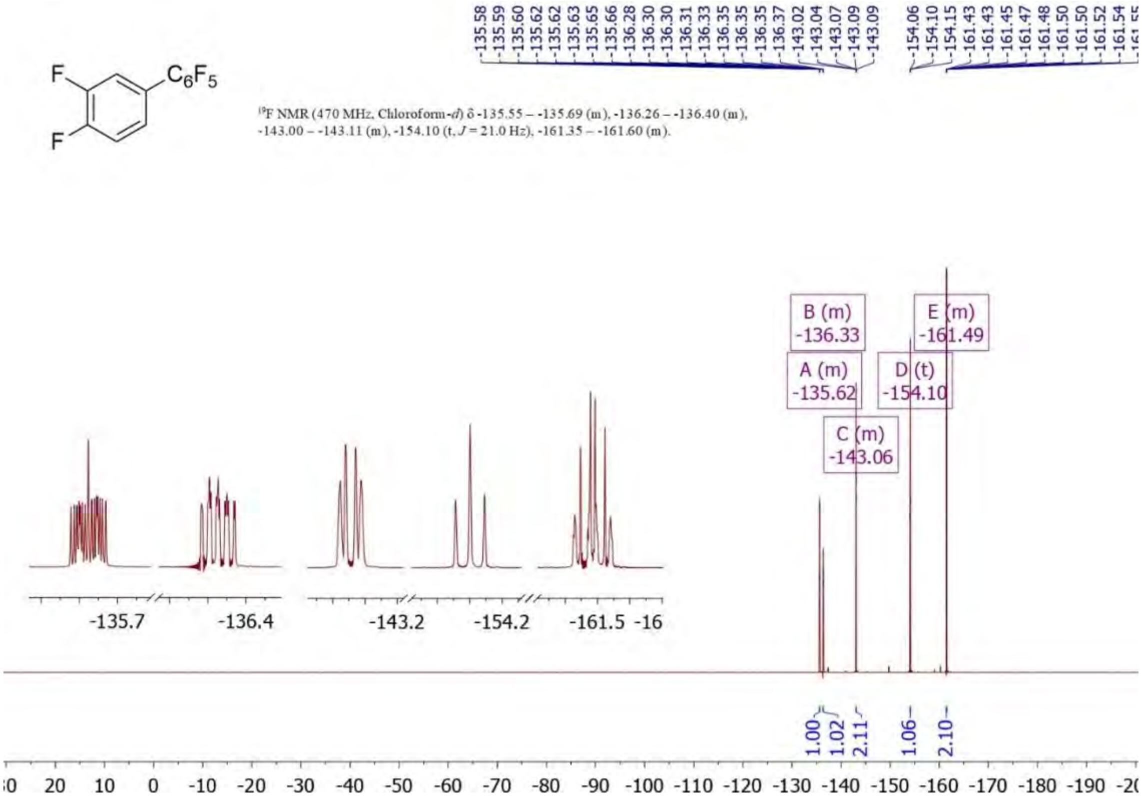
^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.33 (d, *J* = 249.9 Hz), 144.29 (dddt, *J* = 247.7, 11.1, 7.5, 3.9 Hz), 141.96 – 139.35 (m, *J* = 251.9 Hz), 139.34 – 136.47 (m, *J* = 248.5 Hz), 132.22 (dd, *J* = 8.5, 2.1 Hz), 122.41, 116.14 (d, *J* = 21.9 Hz), 115.13 (td, *J* = 17.1, 4.1 Hz).

^{1}H NMR of 2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl in $CDCl_3$.



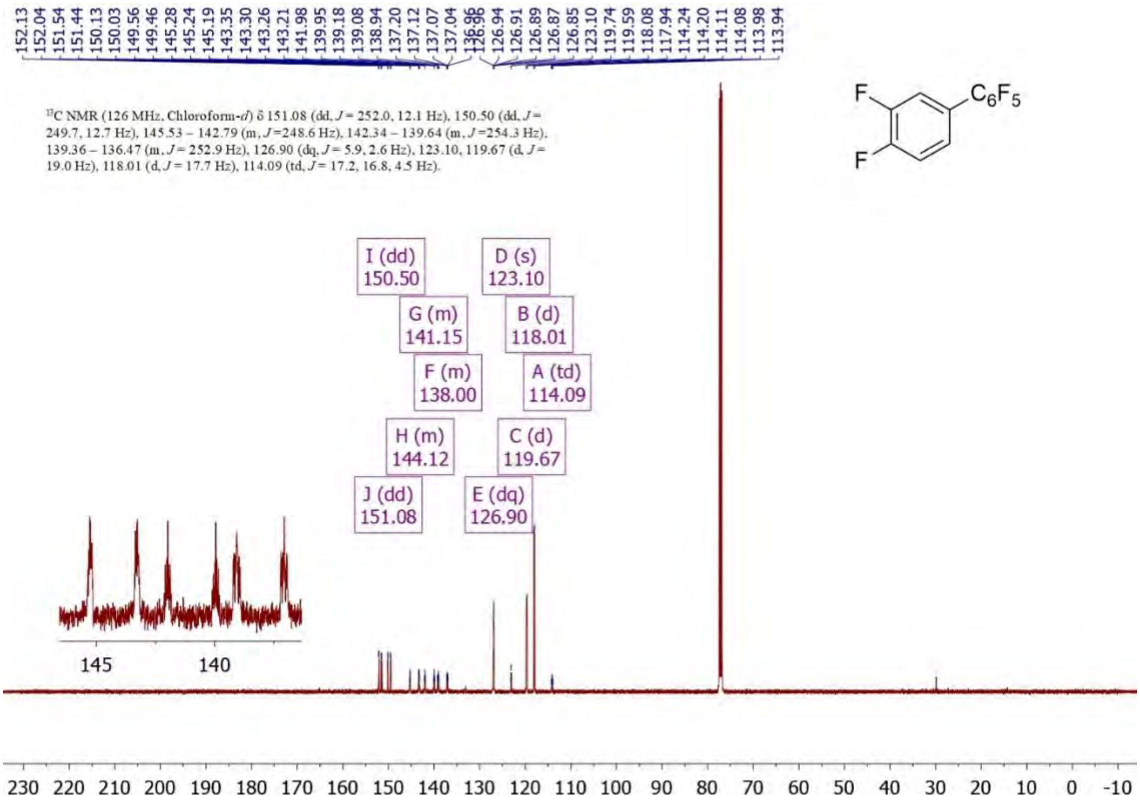
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.21 – 7.14 (m, 1H).

^{19}F NMR of 2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl in $CDCl_3$.



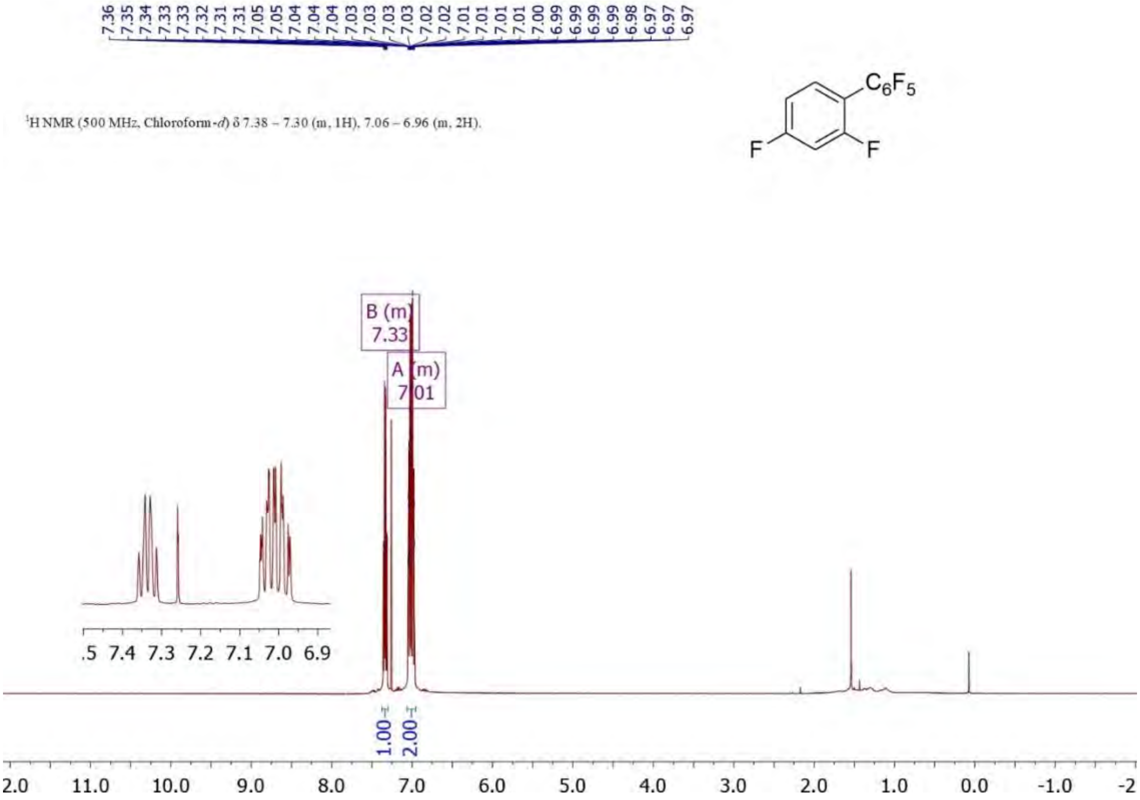
^{19}F NMR (470 MHz, Chloroform-*d*) δ -135.55 – -135.69 (m), -136.26 – -136.40 (m), -143.00 – -143.11 (m), -154.10 (t, J = 21.0 Hz), -161.35 – -161.60 (m).

^{13}C{^{1}H} NMR of 2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl in CDCl$_3$.



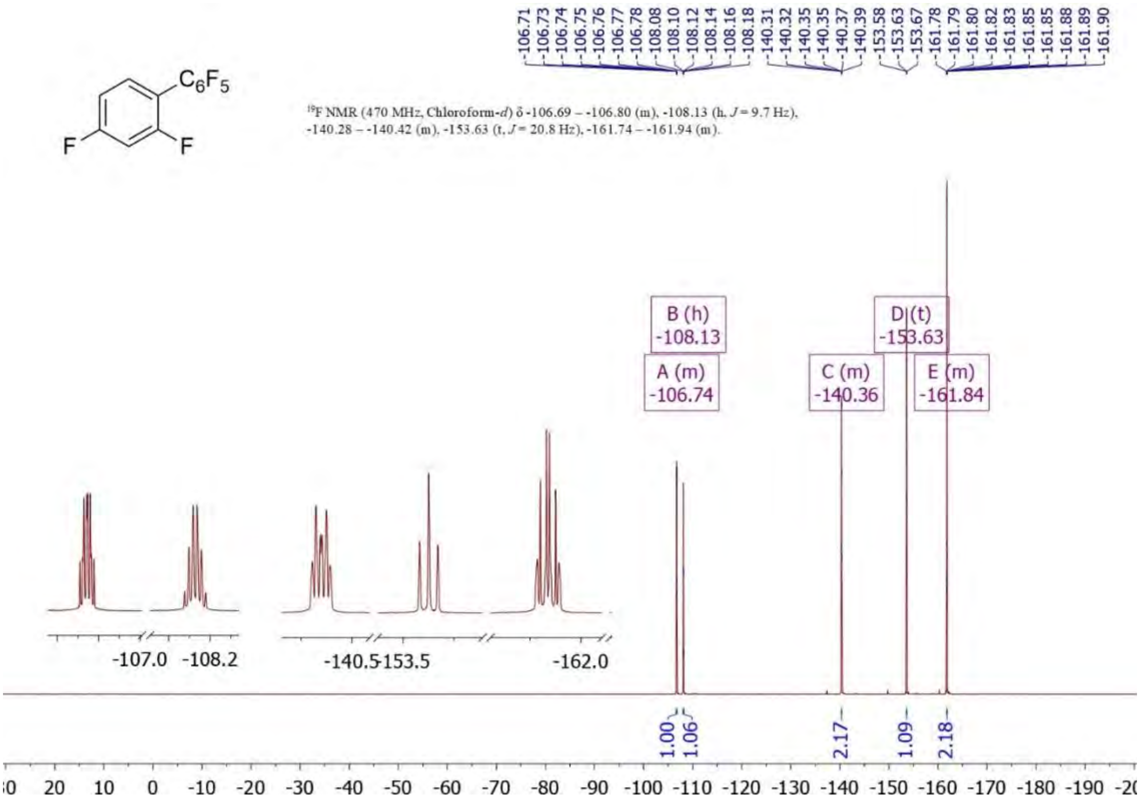
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.08 (dd, J = 252.0, 12.1 Hz), 150.50 (dd, J = 249.7, 12.7 Hz), 145.53 – 142.79 (m, J =248.6 Hz), 142.34 – 139.64 (m, J =254.3 Hz), 139.36 – 136.47 (m, J = 252.9 Hz), 126.90 (dq, J = 5.9, 2.6 Hz), 123.10, 119.67 (d, J = 19.0 Hz), 118.01 (d, J = 17.7 Hz), 114.09 (td, J = 17.2, 16.8, 4.5 Hz).

^{1}H NMR of 2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl in CDCl$_3$.



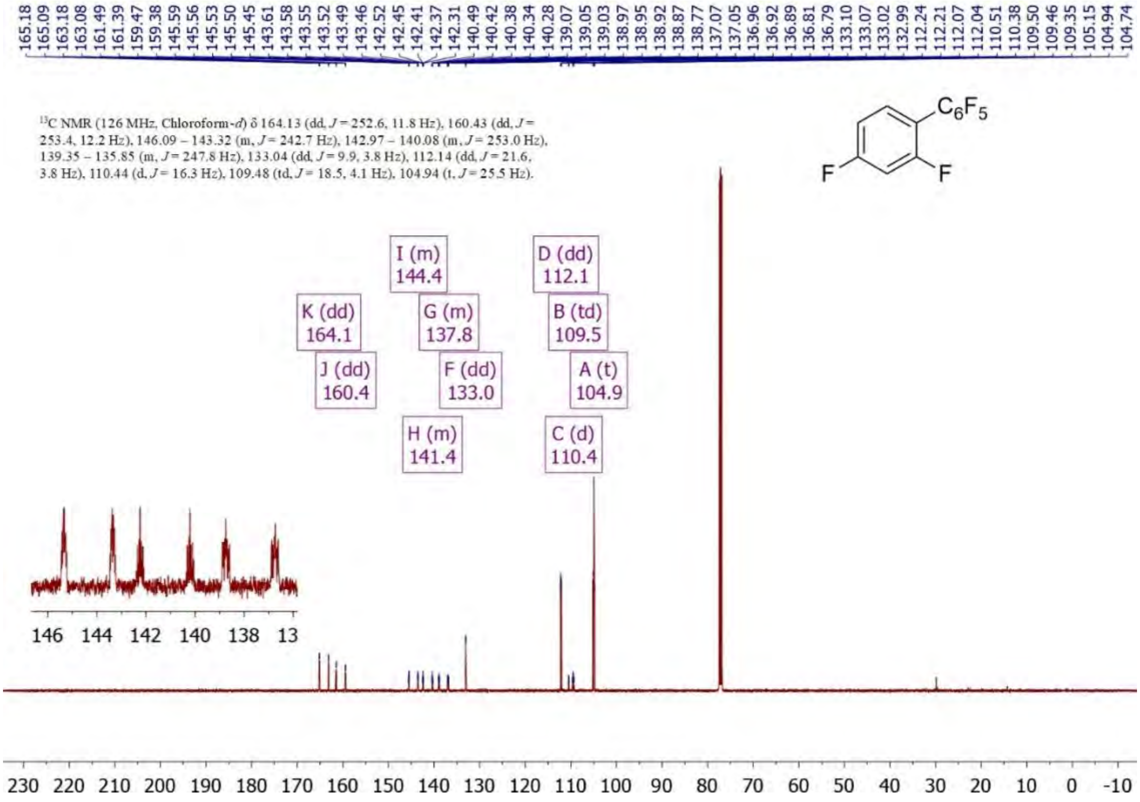
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 1H), 7.06 – 6.96 (m, 2H).

^{19}F NMR of 2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl in $CDCl_3$.



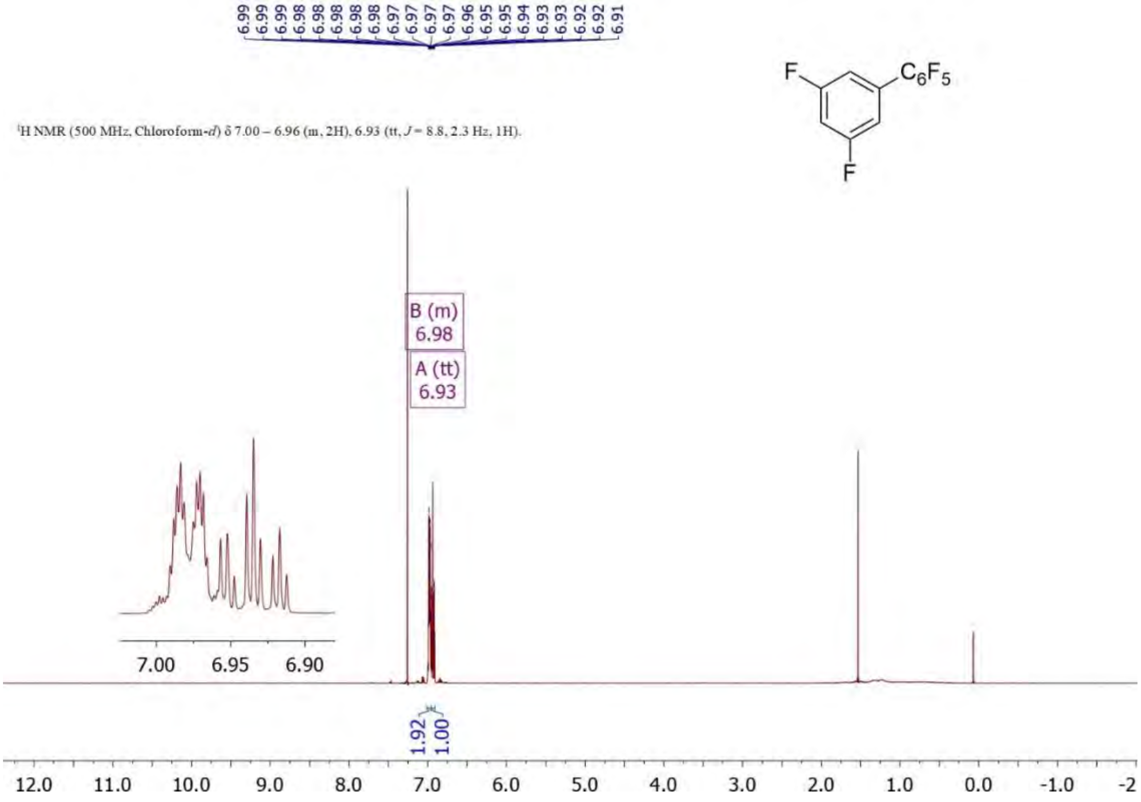
^{19}F NMR (470 MHz, Chloroform-*d*) δ -106.69 – -106.80 (m), -108.13 (h, J = 9.7 Hz), -140.28 – -140.42 (m), -153.63 (t, J = 20.8 Hz), -161.74 – -161.94 (m).

^{13}C{^{1}H} NMR of 2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl in $CDCl_3$.

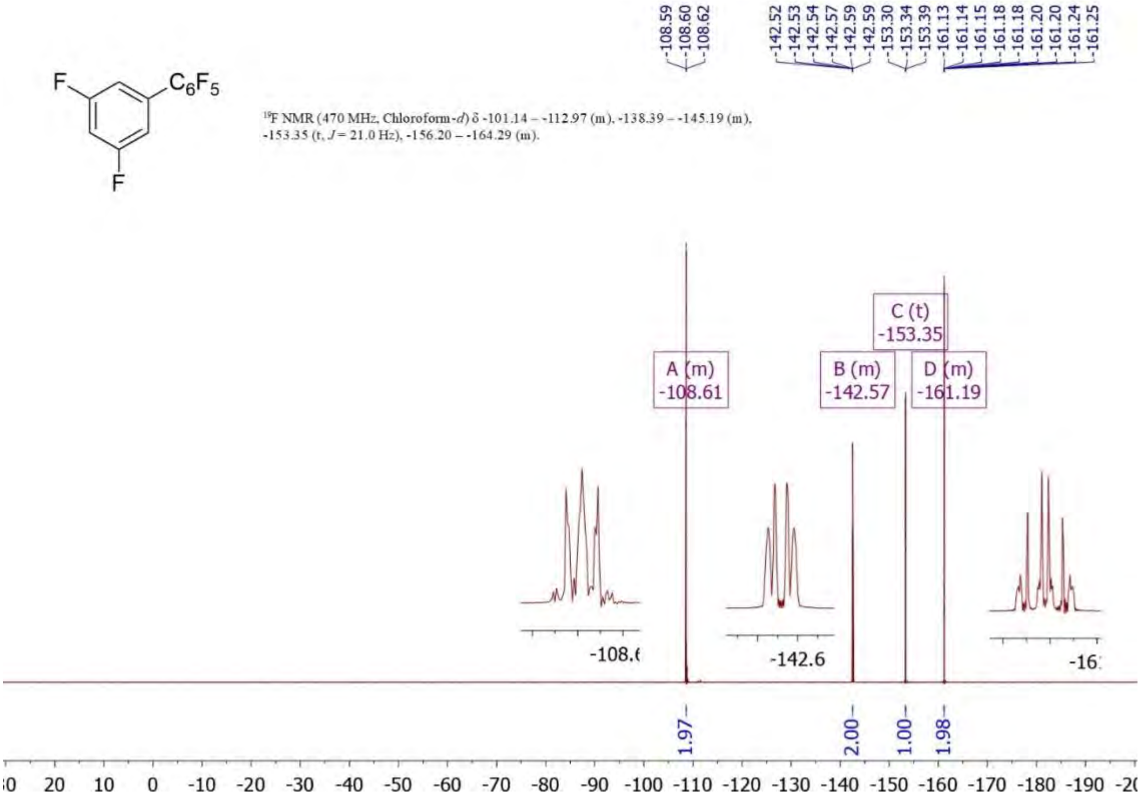


^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.13 (dd, J = 252.6, 11.8 Hz), 160.43 (dd, J = 253.4, 12.2 Hz), 146.09 – 143.32 (m, J = 242.7 Hz), 142.97 – 140.08 (m, J = 253.0 Hz), 139.35 – 135.85 (m, J = 247.8 Hz), 133.04 (dd, J = 9.9, 3.8 Hz), 112.14 (dd, J = 21.6, 3.8 Hz), 110.44 (d, J = 16.3 Hz), 109.48 (td, J = 18.5, 4.1 Hz), 104.94 (t, J = 25.5 Hz).

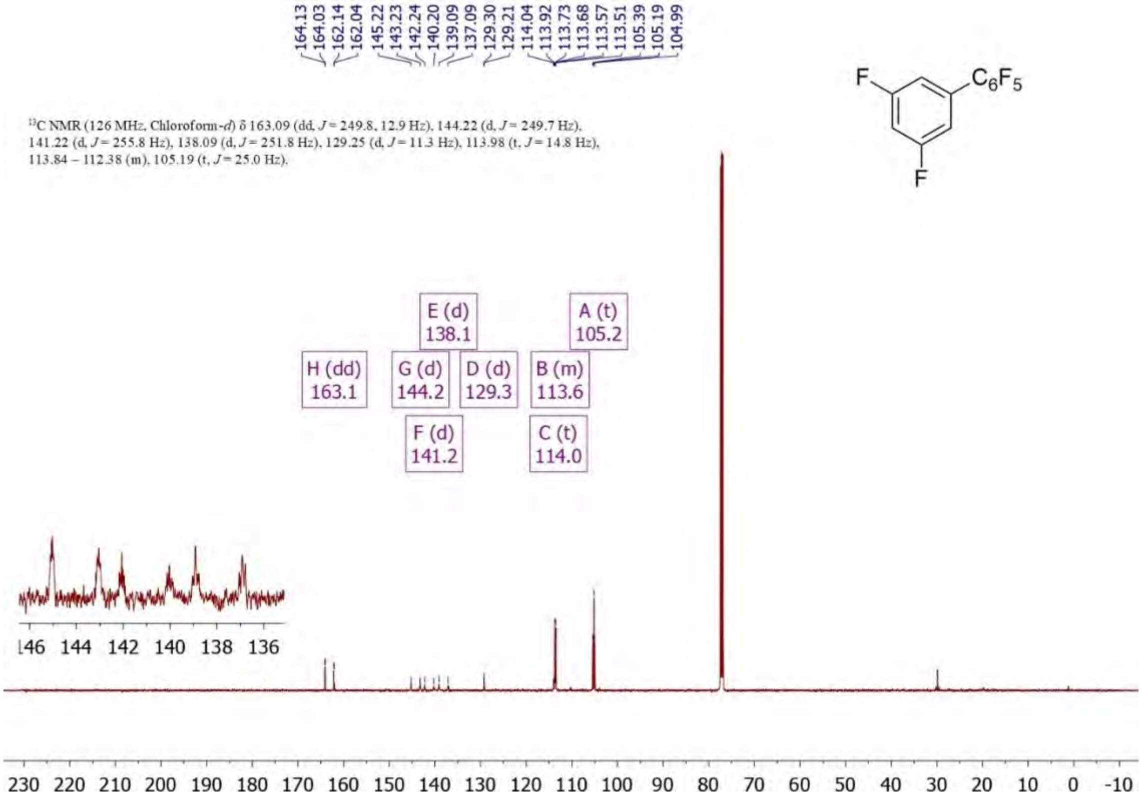
^{1}H NMR of 2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl in $CDCl_3$.


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.00 – 6.96 (m, 2H), 6.93 (tt, *J* = 8.8, 2.3 Hz, 1H).

^{19}F NMR of 2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl in $CDCl_3$.

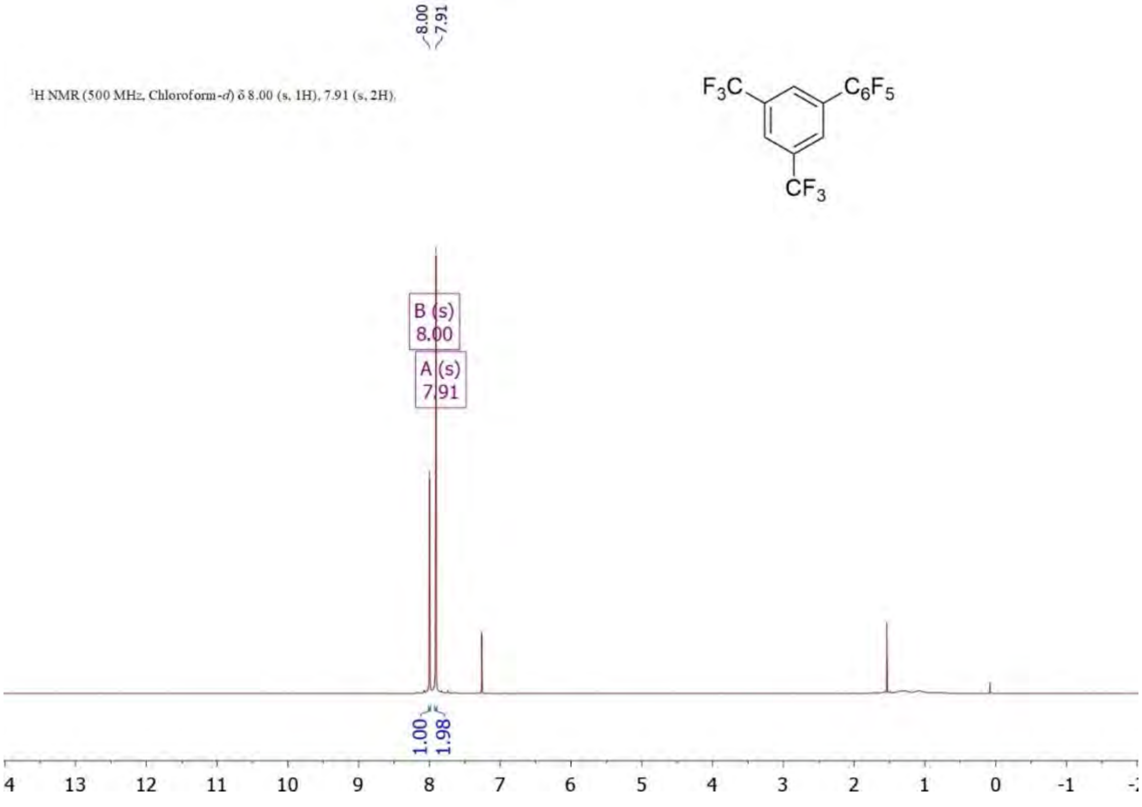

^{19}F NMR (470 MHz, Chloroform-*d*) δ -101.14 – -112.97 (m), -138.39 – -145.19 (m), -153.35 (t, *J* = 21.0 Hz), -156.20 – -164.29 (m).

$^{13}C\{^1H\}$ NMR of 2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl in $CDCl_3$.



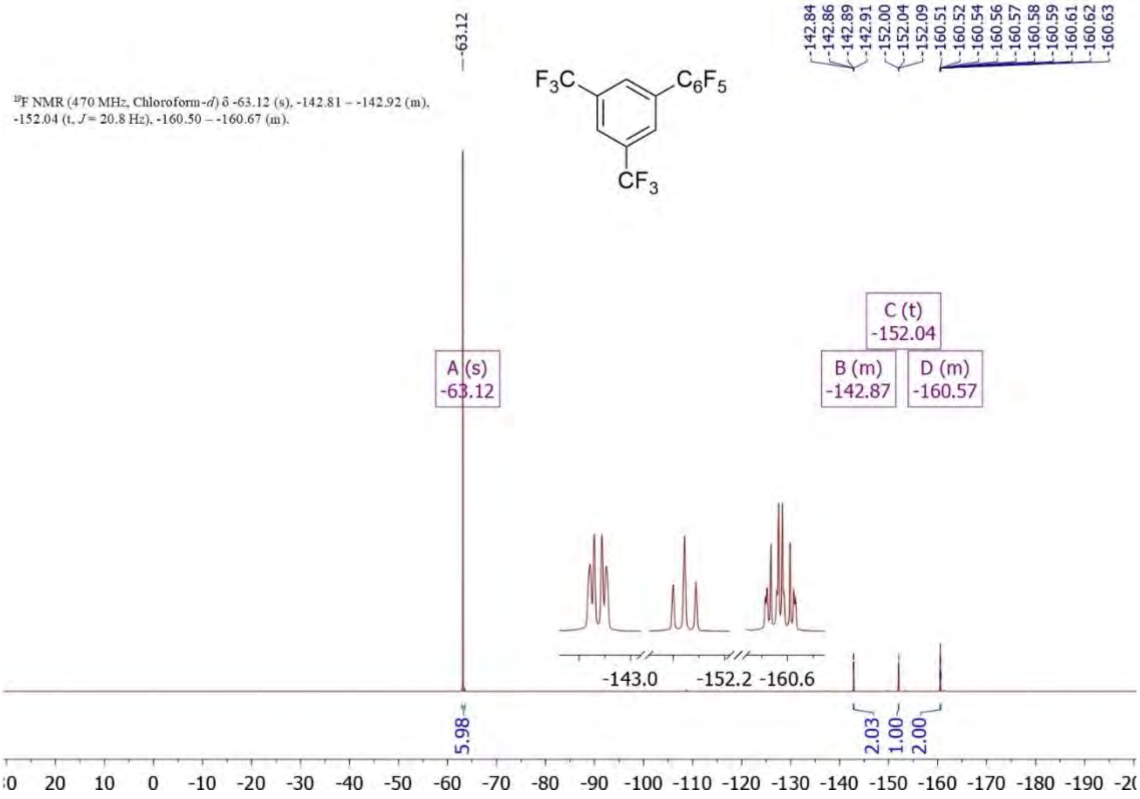
^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.09 (dd, *J* = 249.8, 12.9 Hz), 144.22 (d, *J* = 249.7 Hz), 141.22 (d, *J* = 255.8 Hz), 138.09 (d, *J* = 251.8 Hz), 129.25 (d, *J* = 11.3 Hz), 113.98 (t, *J* = 14.8 Hz), 113.84 – 112.38 (m), 105.19 (t, *J* = 25.0 Hz).

^1H NMR of 2,3,4,5,6-pentafluoro-3',5'-bis(trifluoromethyl)-1,1'-biphenyl in $CDCl_3$.



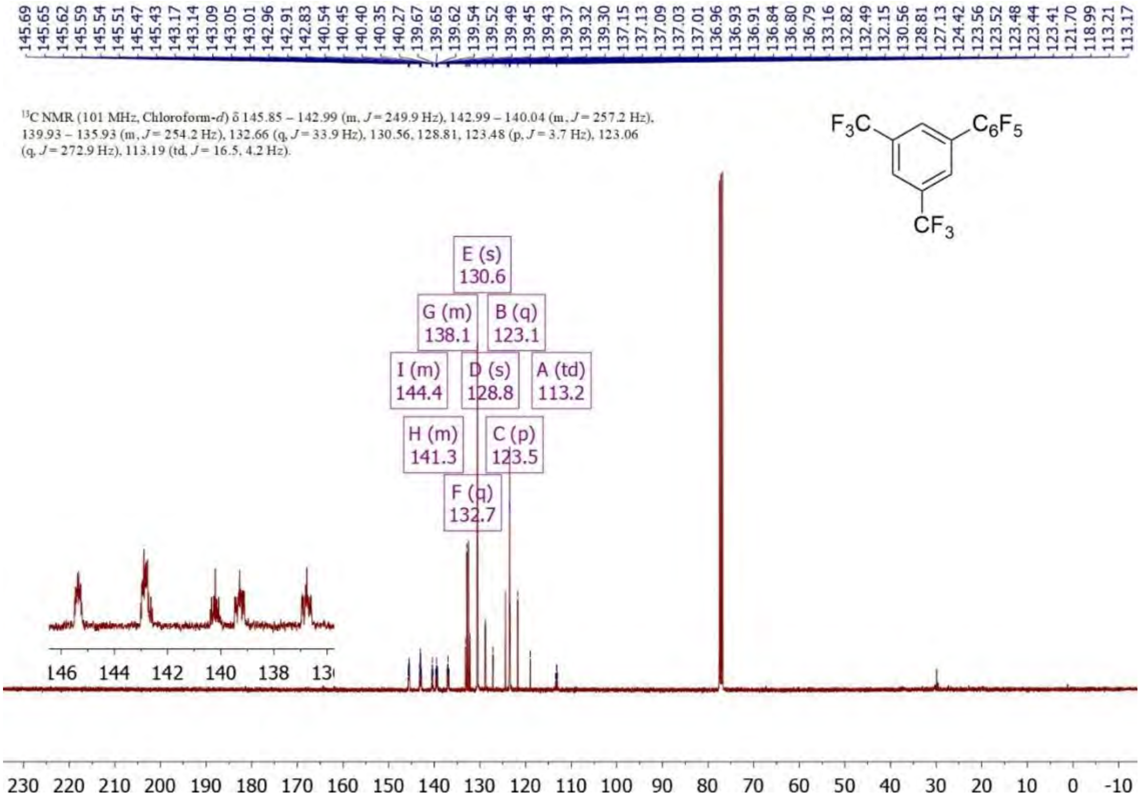
^1H NMR (500 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.91 (s, 2H).

^{19}F NMR of 2,3,4,5,6-pentafluoro-3',5'-bis(trifluoromethyl)-1,1'-biphenyl in $CDCl_3$.



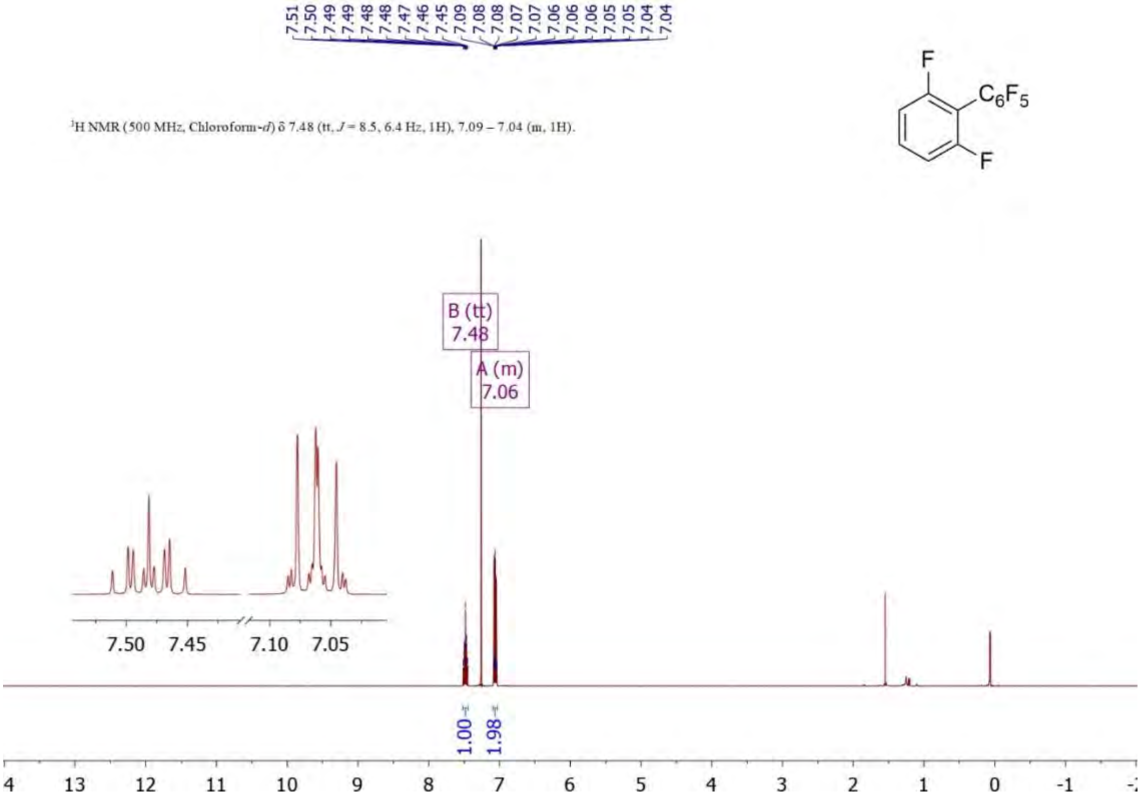
^{19}F NMR (470 MHz, Chloroform-*d*) δ -63.12 (s), -142.81 – -142.92 (m), -152.04 (t, *J* = 20.8 Hz), -160.50 – -160.67 (m).

$^{13}C\{^{1}H\}$ NMR of 2,3,4,5,6-pentafluoro-3',5'-bis(trifluoromethyl)-1,1'-biphenyl in $CDCl_3$.



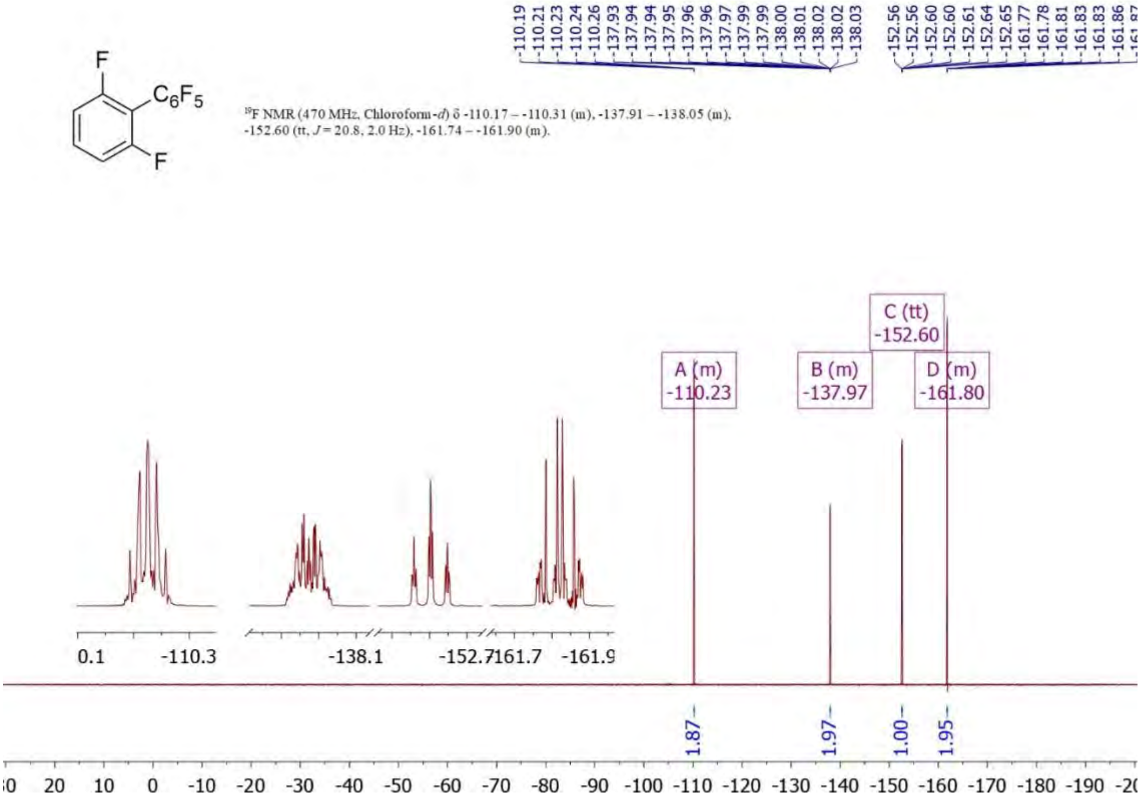
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.85 – 142.99 (m, *J* = 249.9 Hz), 142.99 – 140.04 (m, *J* = 257.2 Hz), 139.93 – 135.93 (m, *J* = 254.2 Hz), 132.66 (q, *J* = 33.9 Hz), 130.56, 128.81, 123.48 (p, *J* = 3.7 Hz), 123.06 (q, *J* = 272.9 Hz), 113.19 (td, *J* = 16.5, 4.2 Hz).

^{1}H NMR of 2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl in $CDCl_3$.



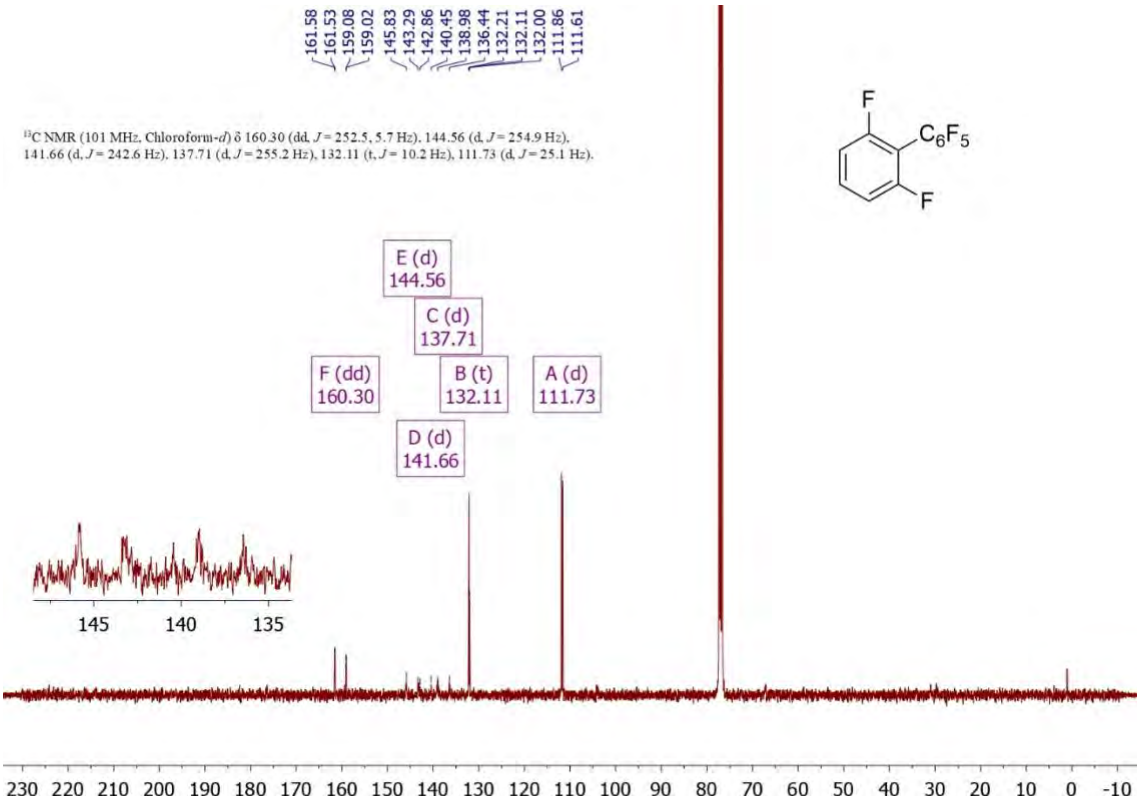
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (tt, J = 8.5, 6.4 Hz, 1H), 7.09 – 7.04 (m, 1H).

^{19}F NMR of 2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl in $CDCl_3$.



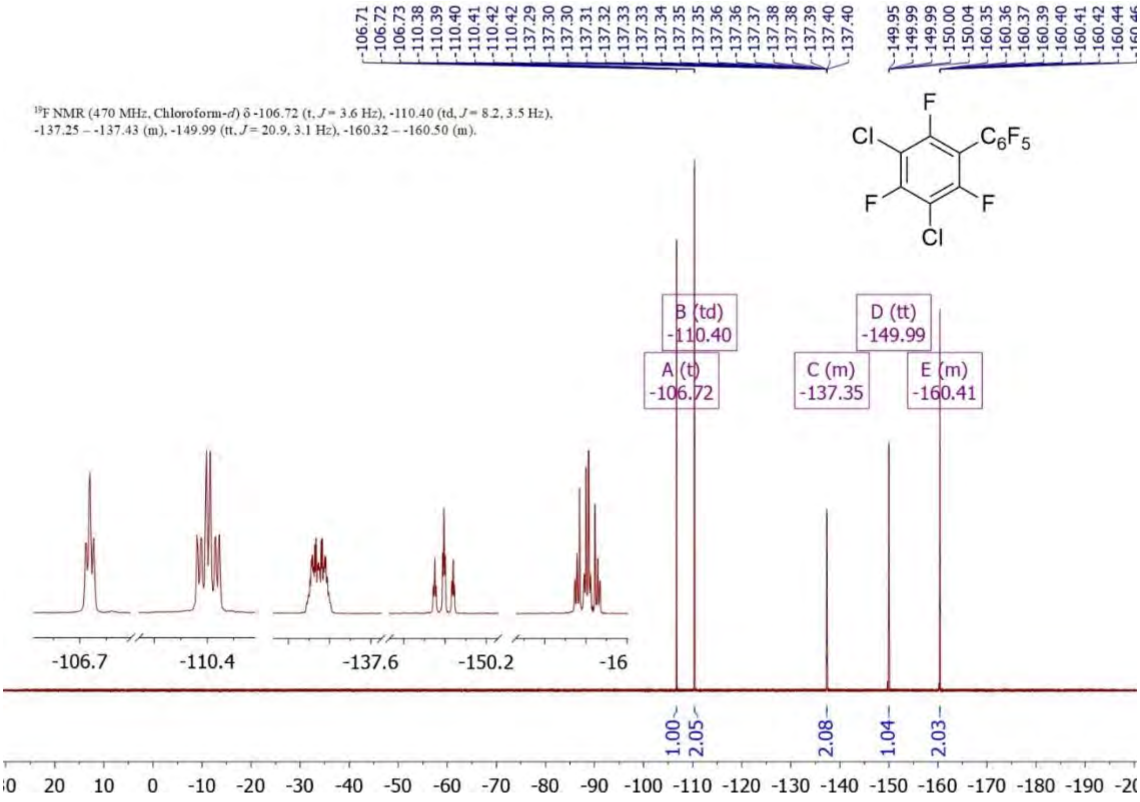
^{19}F NMR (470 MHz, Chloroform-*d*) δ -110.17 – -110.31 (m), -137.91 – -138.05 (m), -152.60 (tt, J = 20.8, 2.0 Hz), -161.74 – -161.90 (m).

$^{13}C\{^1H\}$ NMR of 2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl in $CDCl_3$.



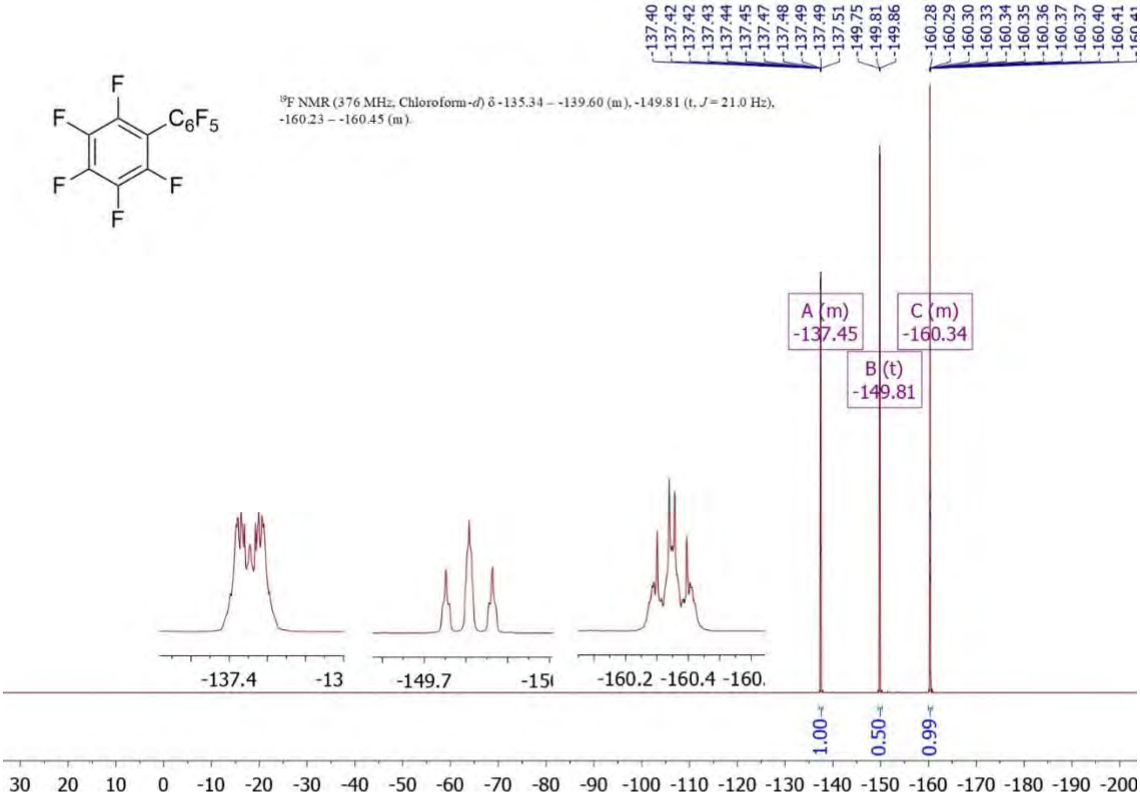
^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.30 (dd, *J* = 252.5, 5.7 Hz), 144.56 (d, *J* = 254.9 Hz), 141.66 (d, *J* = 242.6 Hz), 137.71 (d, *J* = 255.2 Hz), 132.11 (t, *J* = 10.2 Hz), 111.73 (d, *J* = 25.1 Hz).

^{19}F NMR of 3,5-dichloro-2,2',3',4,4',5',6,6'-octafluoro-1,1'-biphenyl in $CDCl_3$.



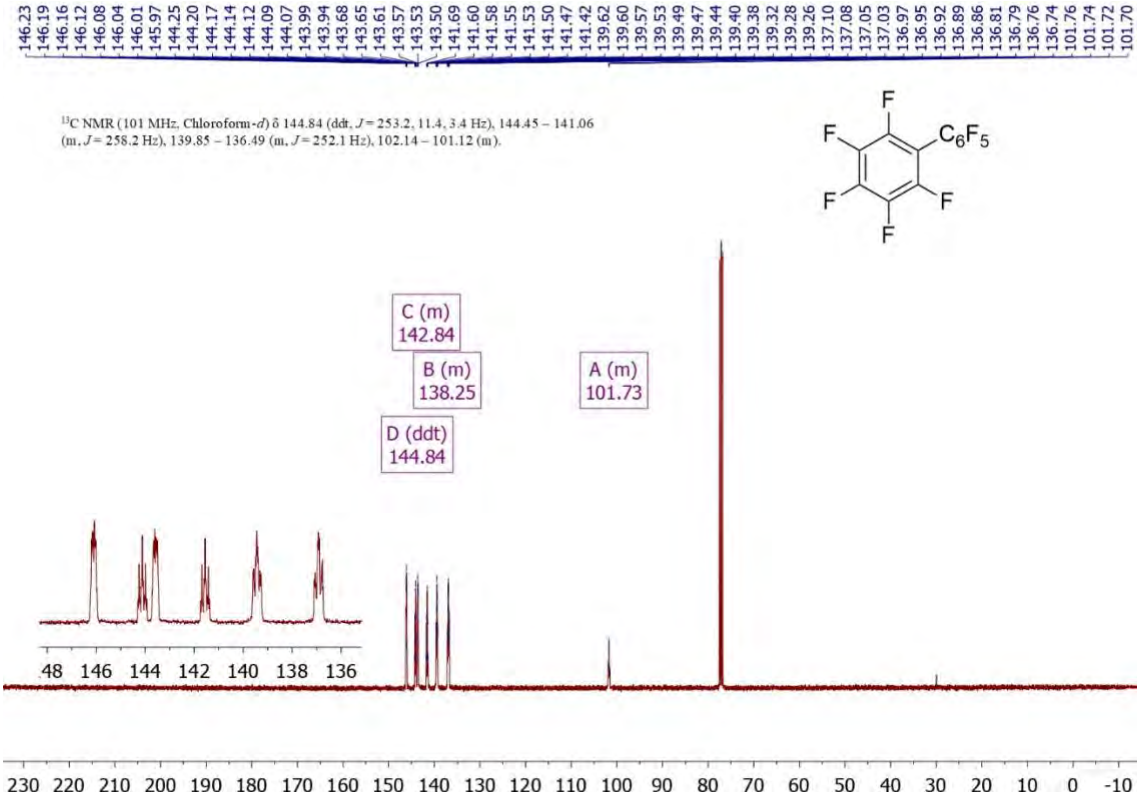
^{19}F NMR (470 MHz, Chloroform-*d*) δ -106.72 (t, *J* = 3.6 Hz), -110.40 (td, *J* = 8.2, 3.5 Hz), -137.25 – -137.43 (m), -149.99 (tt, *J* = 20.9, 3.1 Hz), -160.32 – -160.50 (m).

^{19}F NMR of perfluoro-1,1'-biphenyl in $CDCl_3$.



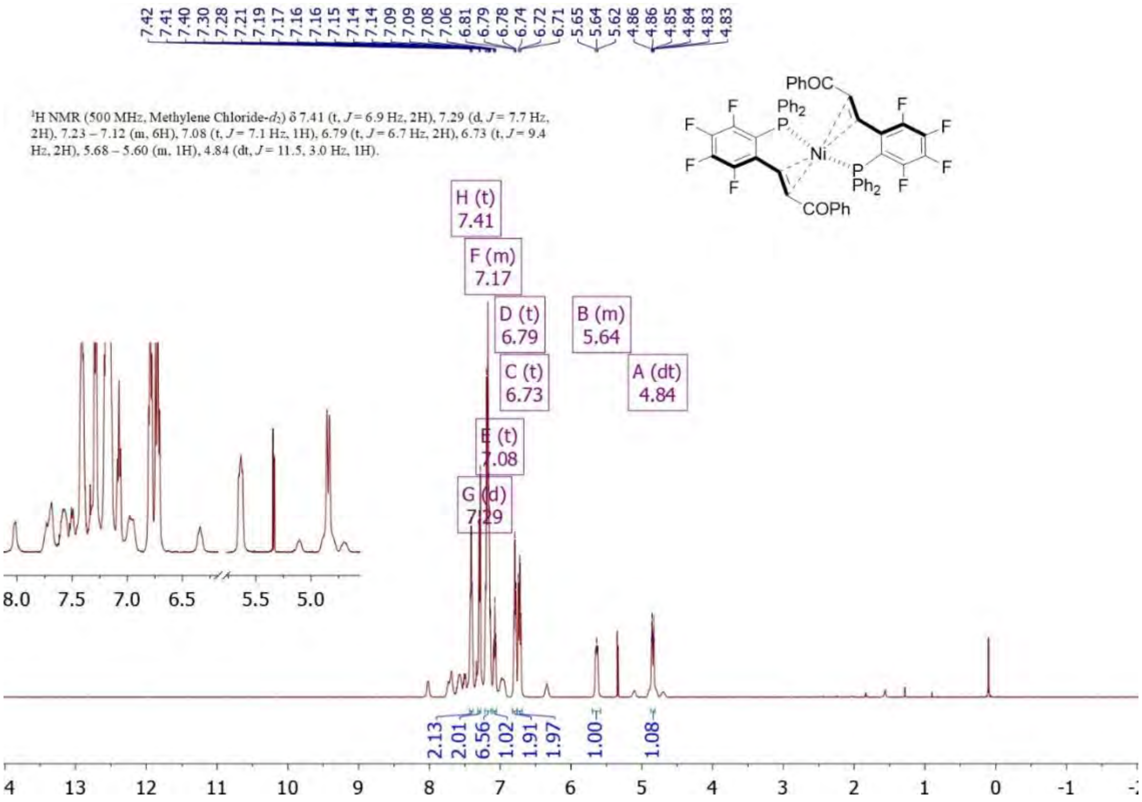
^{19}F NMR (376 MHz, Chloroform-*d*) δ -135.34 – -139.60 (m), -149.81 (t, *J* = 21.0 Hz), -160.23 – -160.45 (m).

$^{13}C\{^1H\}$ NMR of perfluoro-1,1'-biphenyl in $CDCl_3$.



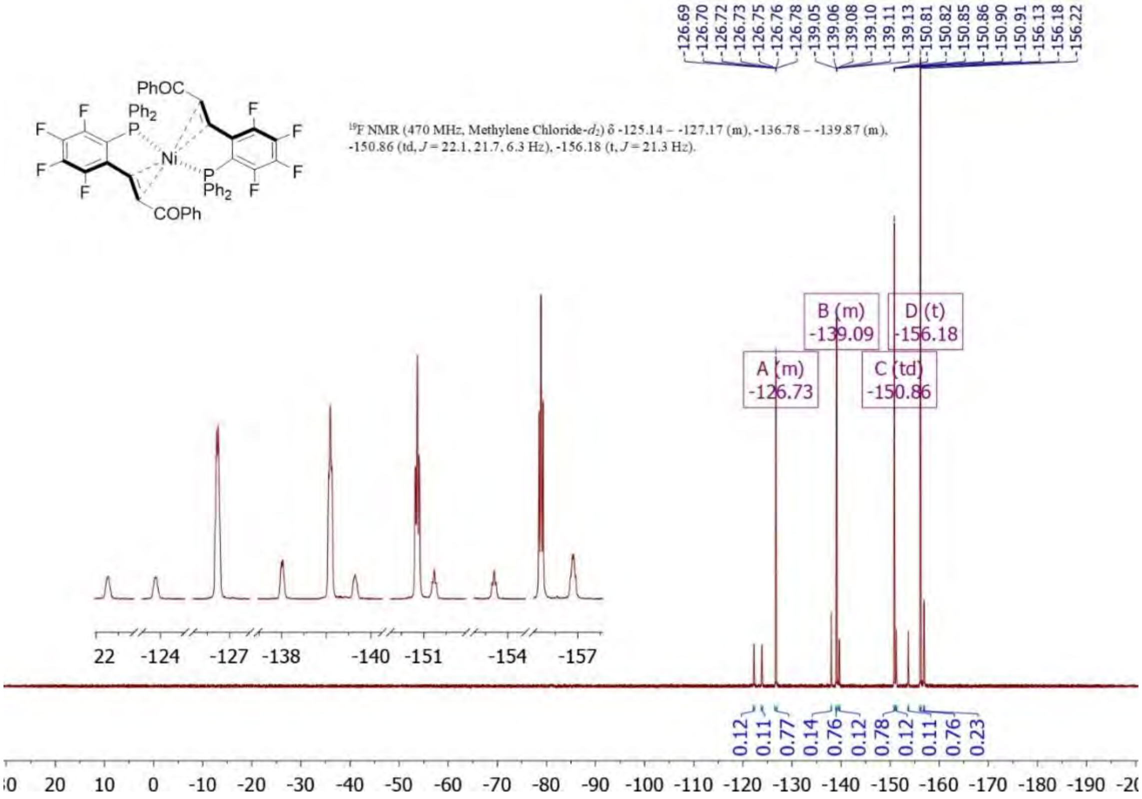
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.84 (ddt, *J* = 253.2, 11.4, 3.4 Hz), 144.45 – 141.06 (m, *J* = 258.2 Hz), 139.85 – 136.49 (m, *J* = 252.1 Hz), 102.14 – 101.12 (m).

^{1}H NMR of [Ni^0(PhPEWO-F)$_2$] in CD_2Cl_2.



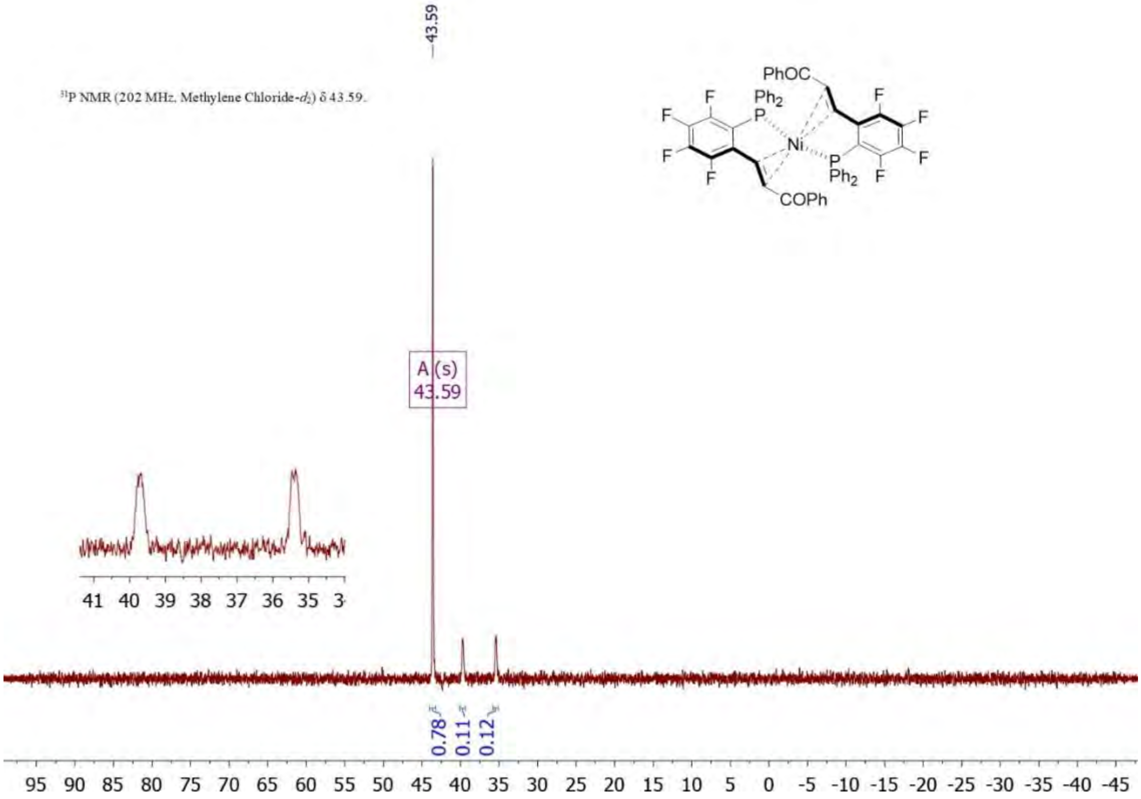
^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.41 (t, J = 6.9 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 7.23 – 7.12 (m, 6H), 7.08 (t, J = 7.1 Hz, 1H), 6.79 (t, J = 6.7 Hz, 2H), 6.73 (t, J = 9.4 Hz, 2H), 5.68 – 5.60 (m, 1H), 4.84 (dt, J = 11.5, 3.0 Hz, 1H).

^{19}F NMR of [Ni^0(PhPEWO-F)$_2$] in CD_2Cl_2.



^{19}F NMR (470 MHz, Methylene Chloride-d_2) δ -125.14 – -127.17 (m), -136.78 – -139.87 (m), -150.86 (td, J = 22.1, 21.7, 6.3 Hz), -156.18 (t, J = 21.3 Hz).

$^{31}P\{^1H\}$ NMR of [Ni^0(PhPEWO-F)$_2$] in CD_2Cl_2.



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