Supplemental Information

Umpolung cross-coupling of polyfluoroarenes with hydrazones via activation of C−F bonds

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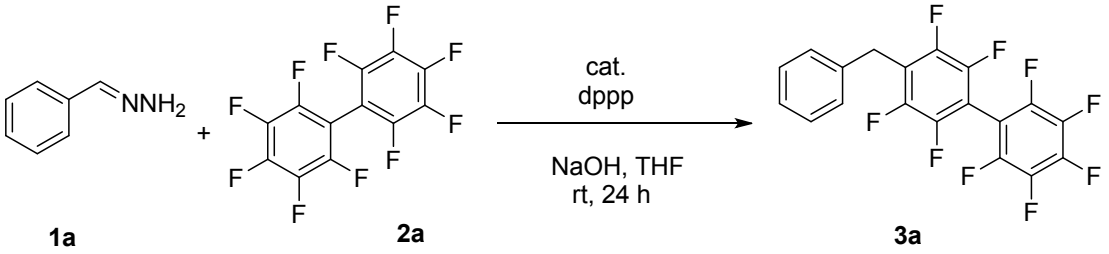
Ⅰ. General Methods

All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Alfa and Ark) and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out under argon atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents.^{1}H, ^{19}F and ^{13}C NMR spectra were taken on Bruker AV300, Bruker AV400, Varian Mercury plus 600 with TMS as an internal standard and $CDCl_3$ as solvent. Melting points were measured on micro melting point apparatus and uncorrected. GC-MS analyses were performed with a Thermo TRACE 1300 ISQ LT spectrometer. HRMS analyses were made at Lanzhou University by means of ESI.

Ⅱ. Optimization of Reaction Conditions

1) Screening catalysts

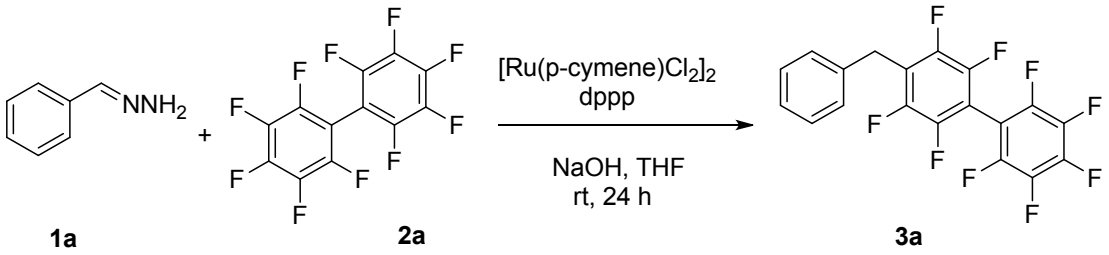


1a **2a** **3a**

Entry	Catalyst	Yield[a]/% **3a**
1	$Fe(acac)_3$	n.p.
2	$NiCl_2$	n.p.
3	CuI	n.p.
4	$RuCl_3$	trace
5	$RuCl(bpy)_3{\cdot}6H_2O$	n.p.
6	$[Ru(p\text{-cymene})Cl_2]_2$	75

General conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (5 mol%), dppp (10 mol%), KOH (1 equiv.) and THF (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

2) Control experiments

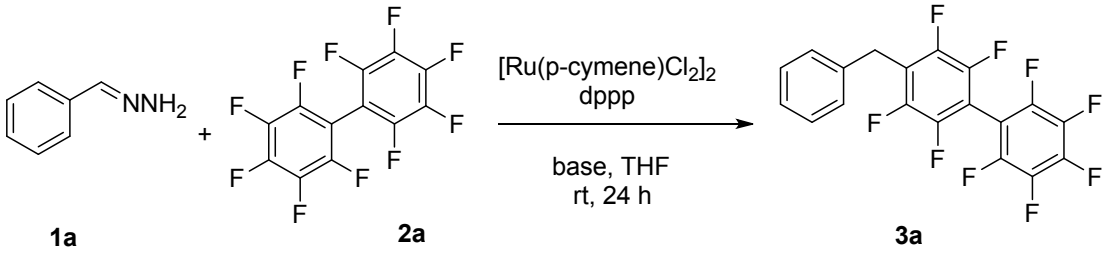


1a **2a** **3a**

Entry	Catalyst	Yield[a]/% **3a**
1	without cat.	n.p.
2	without ligand	n.p.
3	without base	n.p.
4	under air	n.p.

General conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), dppp (10 mol%), KOH (1 equiv.) and THF (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

3) Screening bases

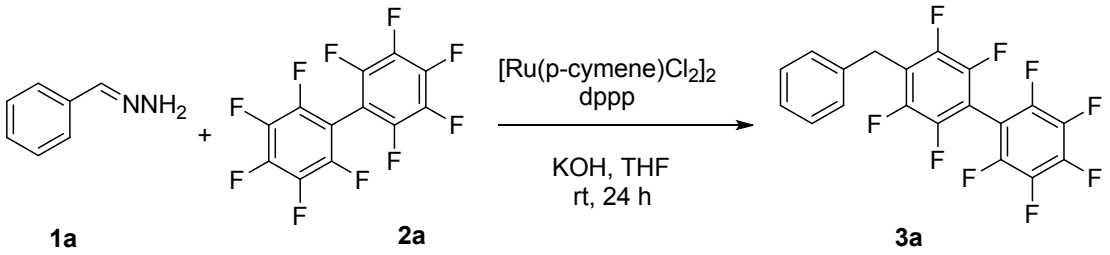


1a **2a** **3a**

Entry	base	Yield[a]/% **3a**
1	DABCO	n.p.
2	DBU	n.p.
3	NaOH	64.
4	KOH (flake)	75
5	KOH (powder)	68

General conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), dppp (10 mol%), base (1 equiv.) and THF (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

4) Screening the ratio of substrates

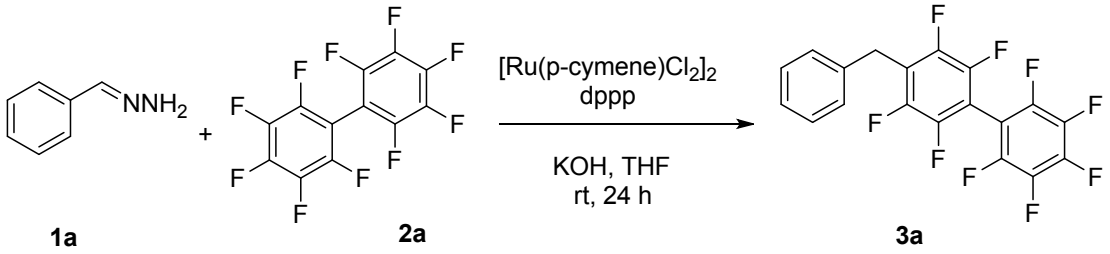


1a **2a** **3a**

Entry	**1a** or **2a**	Yield[a]/% **3a**
1	**1a** 0.2 mmol (**2a** 0.3 mmol)	80
2	**1a** 0.2 mmol (**2a** 0.4 mmol)	81
3	**1a** 0.3 mmol (**2a** 0.2 mmol)	74
4	**1a** 0.4 mmol (**2a** 0.2 mmol)	76

General conditions: **1a** (x mmol), **2a** (y mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), dppp (10 mol%), KOH (1 equiv.) and THF (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

5) Screening the amount of catalyst

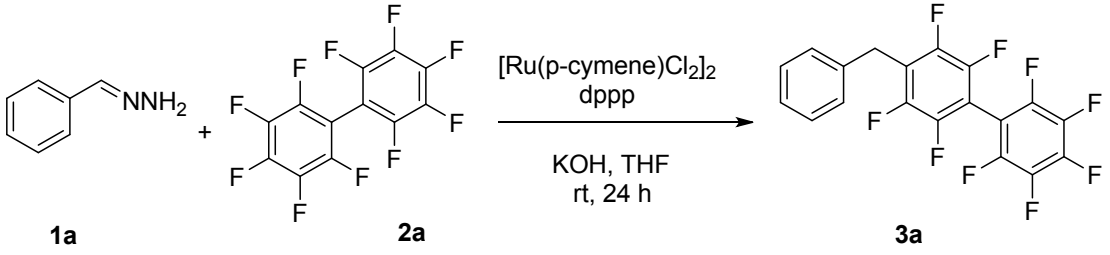


1a **2a** **3a**

Entry	$[Ru(p\text{-cymene})Cl_2]_2$	Yield[a]/% **3a**
1	4 mol%	70
2	6 mol%	81

General conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (x mol%), dppp (10 mol%), KOH (1 equiv.) and THF (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

6) Screening ligands and the amount of ligand



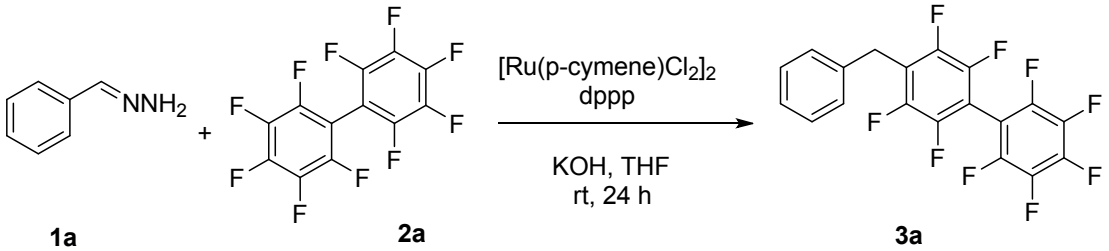
1a **2a** **3a**

Entry	ligand	Yield[a]/% **3a**

1	dppe	71
2	dppb	69
3	dppp (15 mol%)	84
4	dppp (15 mol%)	50

General conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), ligand (x mol%), KOH (1 equiv.) and THF (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

7) Screening solvents

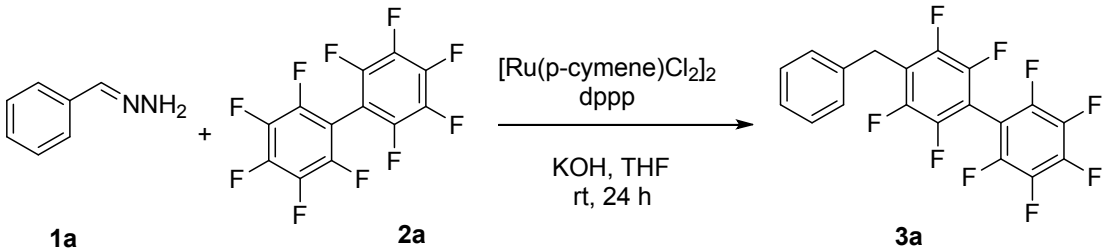


1a **2a** **3a**

Entry	solvent	Yield[a]/% **3a**
1	Et_2O	76
2	toluenee	n.p.
3	MeCN	n.p.
4	DMSO	n.p.
5	DMF	n.p.

General conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), dppp (15 mol%), base (1 equiv.) and solvent (1 mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

8) Screening the amount of THF

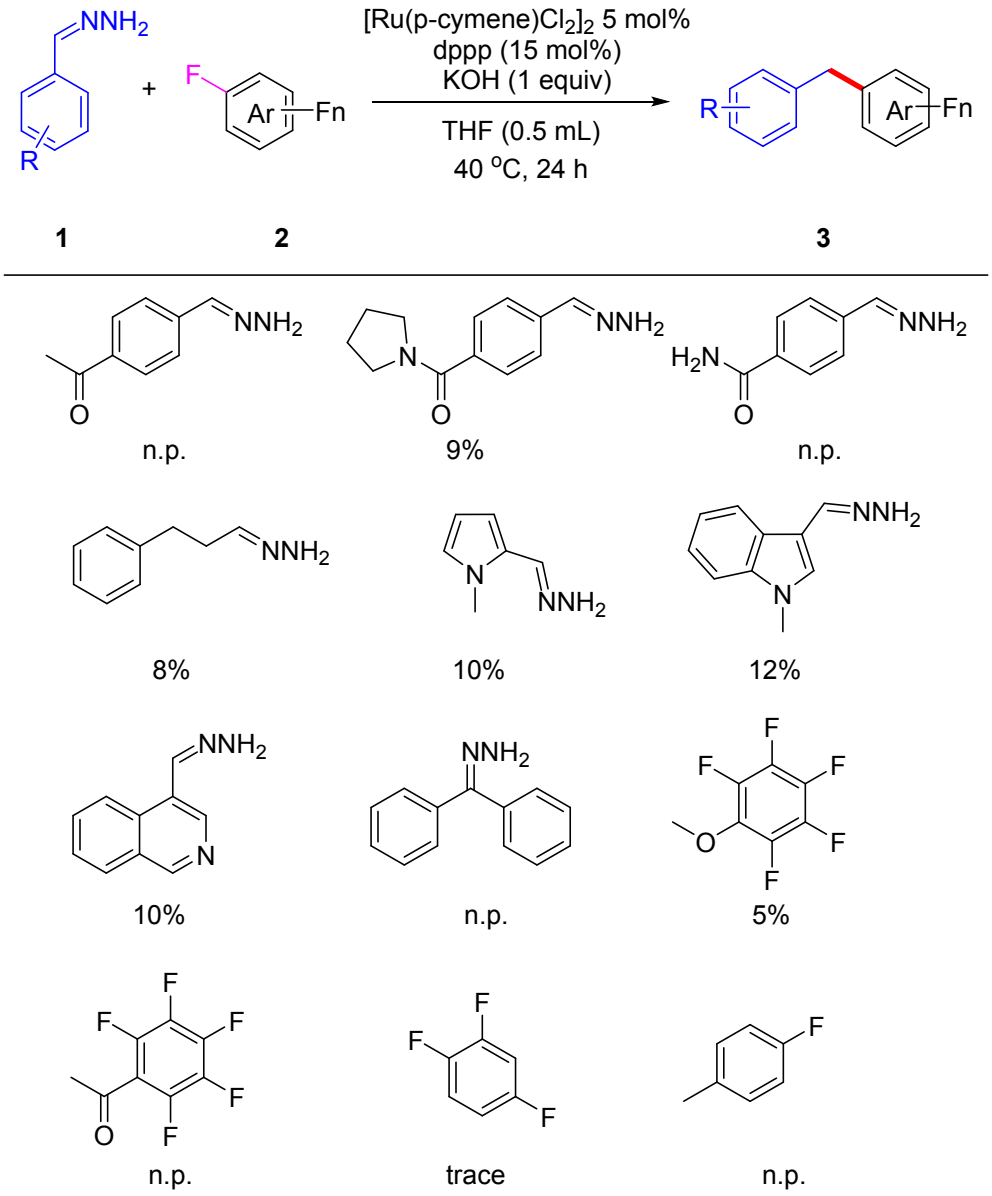


1a **2a** **3a**

Entry	THF	Yield[a]/% **3a**
1	0.5 mL	87
2	1.5 mL	62

General conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), dppp (15 mol%), KOH (1 equiv.) and THF (x mL) at rt for 24 h under an argon atmosphere. [a]Yields were determined by ^1H NMR with nitromethane as internal standard.

Ⅲ. Other Substrates[a]



[a] General conditions: **1** (0.2 mmol), **2** ((0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), dppp (15 mol%), KOH (1 equiv) and THF (0.5 mL) at 40 °C for 24 h under argon atmosphere. products were determined by GC-MS (EI).

Ⅳ. Synthesis of the Hydrazone Substrates [1]

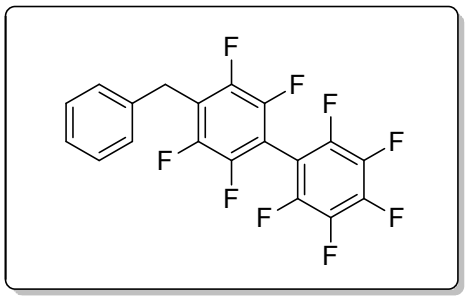
A round-bottom flask, equipped with dropping funnel, was charged with magnetic stirring bar and hydrazine hydrate (98% purity, 12 mmol, 1.2 equiv), and then the

solution of aldehyde (10 mmol) in methanol (25 mL) was added dropwise. The mixture was stirred at room temperature for 1 h. After the aldehyde was consumed completely, methanol and the extra hydrazine were removed under reduced pressure at room temperature (25 °C). Water (30 mL) was added and the mixture was extracted with dichloromethane (3×20 mL). The combined extracts were washed with brine and dried with anhydrous sodium sulfate. Solvent was removed by rotary evaporation at room temperature (25 °C) to provide the desired hydrazone (> 95%, as shown by ^{1}H NMR), which was used directly without further purification.

Ⅴ. General Procedure for the Coupling of Polyfluoroarenes with Hydrazones

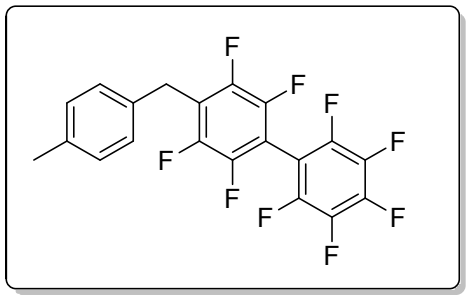
A 20 mL microwave vial was charged with a magnetic stir-bar, $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 5 mol%), dppp (11.6 mg, 15 mol%), KOH (11.2 mg, 0.2 mmol), hydrazone **1** (0.2 mmol) and polyfluoroarenes **2** (0.6 mmol). The tube was then evacuated and backfilled with argon three times. THF (0.5 mL) was added by syringe and microsyringe. The tube was placed in a preheated oil bath at 40 ^{o}C and the mixture was stirred under an argon atmosphere for 24 h. The reaction mixture was cooled to room temperatures and concentrated, and then purified by preparative TLC on silica gel eluting with hexane: EtOAc (100:1-10:1) to afford the products.

The products were characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and HRMS (ESI). However, a large mass discrepancy was observed when testing such polyfluoro-substituted products using HRMS with ESI resource. Because most of those compounds were only composed of C, F and H, which were difficult to abstract the ion from the ESI resource. This reason made the error range greater than 5ppm. The same results of such compounds were seen in the literature, and the HRMS (ESI) of polyfluoroaryl compounds were not within the 5 ppm error range (please see SI in ref. 11). In contrast, the MS (EI resource) gave better results for those compounds. Therefore, all of those compounds were analyzed by MS (EI). Polyfluoroaryl compounds were also analyzed by MS (EI) in literature (please see SI in ref. 14a).



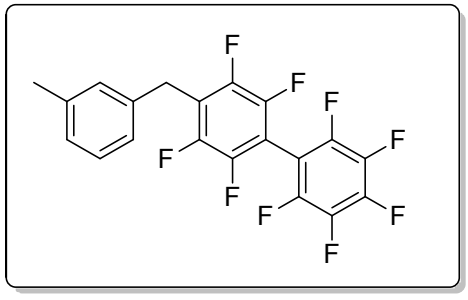
4-benzyl-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl

White solid, m.p. 65−66 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.36−7.26 (m, 5H), 4.15 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.98 to -137.94 (m, 2F), -138.72 to -139.47 (m, 2F), -142.38 (dd, *J* = 20.7, 10.9 Hz, 2F), -150.62 (tt, *J* = 21.0, 2.7 Hz, 1F), -160.65 to -160.84 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.2−143.6 (m), 145.8−142.7 (m), 144.1 (ddt, *J* = 252.5, 15.2, 5.1 Hz), 139.1−137.2 (m), 137.1, 141.0−136.6 (m), 128.9, 128.6, 127.1, 122.2 (t, *J* = 19.2 Hz), 104.4−102.5 (m), 28.9. GC-MS (EI) m/z: 406(100), 386(34), 385(38), 367(17), 219(19), 203(17), 108(17), 91(41).



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

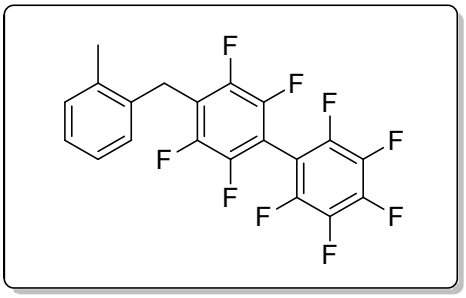
White solid, m.p. 55−56 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.23 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.10 (s, 2H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.35 to -137.66 (m, 2F), -139.07 (qd, *J* = 9.5, 4.5 Hz, 2F), -142.63 (dd, *J* = 21.2, 11.5 Hz, 2F), -150.89 (t, *J* = 20.8 Hz, 1F), -161.00 (qd, *J* = 10.4, 4.6 Hz, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.2−143.7 (m), 145.1−142.9 (m), 144.2 (ddt, *J* = 257.6, 16.2, 6.0 Hz), 139.1−137.0 (m), 136.9, 141.2−136.6 (m), 134.1, 129.6, 128.5, 122.5 (t, *J* = 18.2 Hz), 104.3−102.4 (m), 28.5, 20.9. GC-MS (EI) m/z: 420(46), 405(36), 385(24), 91(100), 77(18), 65(22).



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

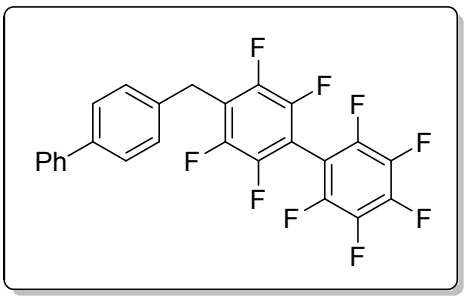
White solid, m.p. 67−68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28−7.20 (m, 1H), 7.19−7.07 (m, 3H),

4.11 (s, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.49 (dddd, *J* = 20.3, 11.6, 5.8, 2.9 Hz, 2F), -138.64 to -139.51 (m, 2F), -142.43 (dd, *J* = 19.9, 10.3 Hz, 2F), -150.68 to -151.13 (m, 1F), -160.76 to -161.31 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.3−143.5 (m), 145.2−142.8 (m), 144.2 (ddt, *J* = 252.5, 16.1, 5.8 Hz), 139.2−136.7 (m), 138. 7, 137.0, 141.5−136.2 (m), 129.4, 128.8, 127.9, 125.6, 122.3 (t, *J* = 18.3 Hz), 104.3−102.4 (m), 28.8, 21.3. GC-MS (EI) m/z: 420(44), 405(30), 385(24), 104(18), 91(100), 77(15), 65(20).



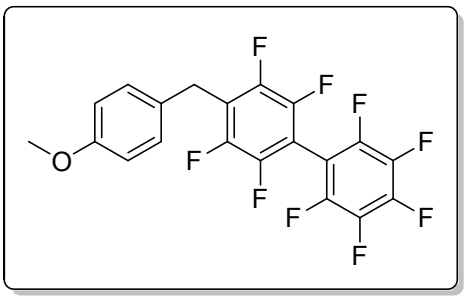
2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(2-methylbenzyl)-1,1'-biphenyl

White solid, m.p. 140−141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.24−7.14 (m, 3H), 7.08 (d, *J* = 6.6 Hz, 1H), 4.14 (s, 2H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.20 to -137.64 (m, 2F), -138.92 (qdd, *J* = 12.6, 8.4, 4.0 Hz, 2F), -141.19 to -141.50 (m, 2F), -150.59 (tt, *J* = 21.0, 2.7 Hz, 1F), -160.45 to -161.03 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.6−143.7 (m), 145.9−142.9 (m), 144.2 (ddt, *J* = 252.5, 16.0, 4.1 Hz), 139.2−136.6 (m), 141.2−136.2 (m), 136.2, 134.9, 130.5, 128.5, 127.1, 126.3, 121.5 (t, *J* = 18.2 Hz), 104.5−102.4 (m), 26.3, 19.6. GC-MS (EI) m/z: 420(55), 400(27), 385(20), 309(20), 105(32), 91(100), 77(32), 65(31).



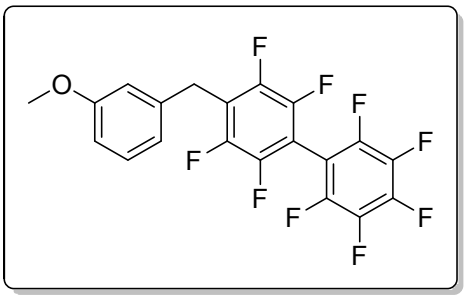
4-([1,1'-biphenyl]-4-ylmethyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl

White solid, m.p. 139−140 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.59 (dd, *J* = 8.6, 2.2 Hz, 4H), 7.48−7.40 (m, 4H), 7.39−7.33 (m, 1H), 4.20 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.15 to -137.51 (m, 2F), -138.72 (ttd, *J* = 12.6, 8.4, 4.0 Hz, 2F), -142.32 (dd, *J* = 20.9, 11.2 Hz, 2F), -150.60 (tt, *J* = 20.8, 2.7 Hz, 1F), -160.29 to -161.37 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.3−143.4 (m), 145.9−143.2 (m), 144.0 (ddt, *J* = 252.5, 15.2, 5.1 Hz), 140.6, 140.2, 139.2−136.5 (m), 141.2−136.4 (m), 136.0, 129.0, 128.8, 127.6, 127.4, 127.0, 122.1 (t, *J* = 18.2 Hz), 104.5−102.3 (m), 28.6. GC-MS (EI) m/z: 482(79), 167(60), 165(100), 152(89), 115(27), 77(18).



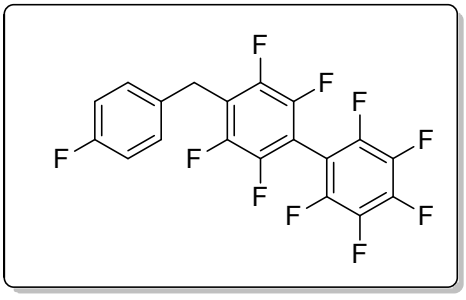
2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(4-methoxybenzyl)-1,1'-biphenyl

White solid, m.p. 107−108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.07 (s, 2H), 3.79 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.17 to -137.70 (m, 2F), -138.95 (ttd, *J* = 12.7, 8.4, 4.0 Hz, 2F), -142.78 (dd, *J* = 20.9, 11.1 Hz, 2F), -150.74 (tt, *J* = 21.0, 2.7 Hz, 1F), -160.67 to -161.08 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.3−143.6 (m), 145.7−142.6 (m), 144.0 (ddt, *J* = 252.5, 16.1, 5.1 Hz), 139.2−136.7 (m), 141.1−136.4 (m), 129.7, 129.1, 122.6 (t, *J* = 19.2 Hz), 114.2, 104.2−102.3 (m), 55.2, 28.1. GC-MS (EI) m/z: 436(56), 218(14), 206(14), 121(100), 77(69).



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

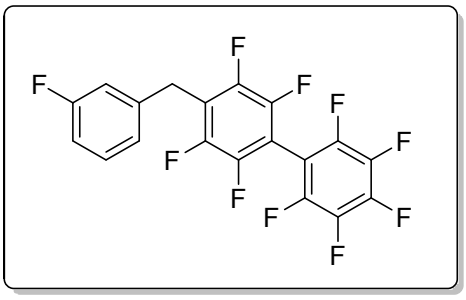
White solid, m.p. 121−122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28−7.22 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.90 (dd, *J* = 15.9, 8.0 Hz, 2H), 4.13 (s, 2H), 3.85 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.30 to -137.62 (m, 2F), -139.59 to -140.09 (m, 2F), -141.34 to -141.88 (m, 2F), -150.93 (tt, *J* = 20.9, 2.6 Hz, 1F), -160.71 to -161.25 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.2, 146.7−144.1 (m), 145.8−143.3 (m), 143.9 (ddt, *J* = 251.5, 15.2, 5.1 Hz), 139.2−136.6 (m), 141.0−136.3 (m), 129.8, 128.4, 125.1, 121.8 (t, *J* = 18.2 Hz), 120.5, 110.3, 104.1−102.5 (m), 55.3, 23.8. GC-MS (EI) m/z: 436(100), 420(27), 401(14), 385(20), 218(18), 121(30), 91(41), 77(65).



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

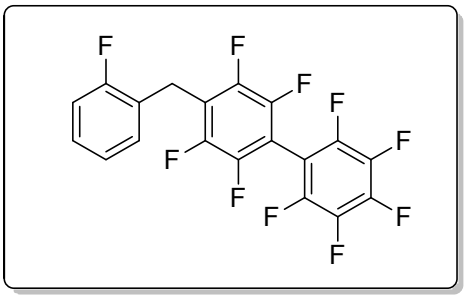
White solid, m.p. 52−53 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.36 (d, *J* = 5.3 Hz, 2H), 7.06 (td, *J* =

8.6, 1.9 Hz, 2H), 4.18 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -114.27 to -116.08 (m, 1F), -137.64 (dd, *J* = 28.7, 20.5 Hz, 2F), -138.84 (ddd, *J* = 17.9, 15.5, 9.1 Hz, 2F), -142.30 to -143.22 (m, 2F), -150.82 (dd, *J* = 54.9, 34.0 Hz, 1F), -160.99 (ddd, *J* = 49.3, 31.8, 22.3 Hz, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 161.9 (d, *J* = 244.5 Hz), 146.3−143.7 (m), 145.7−143.2 (m), 144.1 (ddt, *J* = 251.5, 15.2, 5.1 Hz), 139.3−136.6 (m), 141.1−136.4 (m), 132.8, 130.2(d, *J* = 8.1 Hz), 122.0 (t, *J* = 18.2 Hz), 115.7 (d, *J* = 21.2 Hz), 104.6−102.3 (m), 28.1. GC-MS (EI) m/z: 424(75), 403(24), 237(19), 212(18), 145(20), 126(34), 109(100), 83(30).



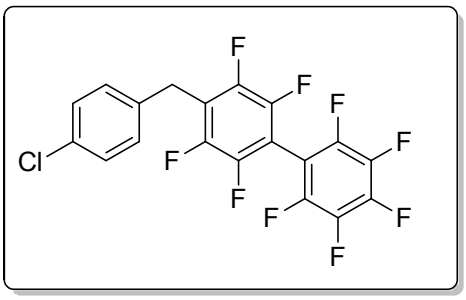
2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(3-fluorobenzyl)-1,1'-biphenyl

White solid, m.p. 81−82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.36−7.30 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 9.6 Hz, 1H), 6.99 (td, *J* = 8.4, 2.3 Hz, 1H), 4.16 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.50 (td, *J* = 9.0, 6.0 Hz, 1F), -137.09 to -137.86 (m, 2F), -137.96 to -139.09 (m, 2F), -142.34 (dd, *J* = 20.1, 10.5 Hz, 2F), -150.51 (ddd, *J* = 20.8, 11.9, 2.7 Hz, 1F), -160.08 to -161.41 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 162.9 (d, *J* = 248.2 Hz), 146.2−143.5 (m), 145.8−143.2 (m), 144.0 (ddt, *J* = 253.5, 15.2, 5.0 Hz), 139.3 (d, *J* = 7.1 Hz), 139.3−136.7 (m), 141.2−136.4 (m), 130.4 (d, *J* = 8.1 Hz), 124.2, 121.4 (t, *J* = 18.2 Hz), 115.6 (d, *J* = 22.2 Hz), 114.1 (d, *J* = 25.3 Hz), 104.8−102.2 (m), 28.6. GC-MS (EI) m/z: 424(100), 403(34), 329(22), 237(27), 167(26), 126(40), 109(92), 83(34).



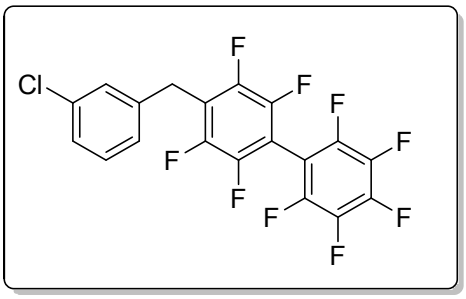
2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(2-fluorobenzyl)-1,1'-biphenyl

White solid, m.p. 90−91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28−7.26 (m, 2H), 7.15−7.04 (m, 2H), 4.19 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -116.52 to -117.84 (m, 1F), -136.21 to -138.09 (m, 2F), -138.19 to -139.86 (m, 2F), -141.77 (dd, *J* = 19.8, 9.6 Hz, 2F), -150.13 to -151.13 (m, 1F), -160.21 to -161.63 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 160.7 (d, *J* = 247.1 Hz), 146.5−143.8 (m), 145.7−143.2 (m), 144.1 (ddt, *J* = 253.5, 15.2, 5.0 Hz), 139.2−136.6 (m), 141.2−136.5 (m), 130.5 (d, *J* = 4.0 Hz), 129.0 (d, *J* = 8.1 Hz), 124.3 (d, *J* = 3.0 Hz), 123.8 (d, *J* = 8.1 Hz), 120.6 (t, *J* = 18.2 Hz), 115.6 (d, *J* = 22 Hz), 104.8−102.3 (m), 22.2. GC-MS (EI) m/z: 424(100), 403(30), 385(17), 329(20) 237(24), 145(19), 126(34), 109(85), 83(31).



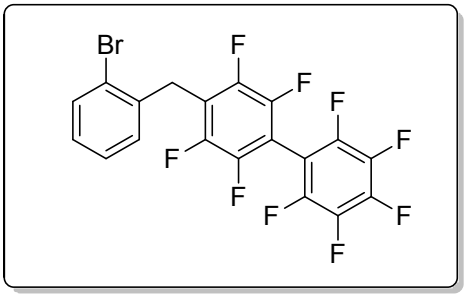
4-(4-chlorobenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl

White solid, m.p. 98−99 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31−7.25 (m, 4H), 4.10 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.15 to -137.59 (m, 2F), -138.34 to -138.79 (m, 2F), -142.47 (dd, *J* = 20.7, 11.1 Hz, 2F), -150.49 (tt, *J* = 20.9, 2.8 Hz, 1F), -160.43 to -160.96 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.2−143.6 (m), 145.7−143.1 (m), 144.1 (ddt, *J* = 252.5, 16.1, 5.1 Hz), 139.2−136.6 (m), 141.2−136.5 (m), 135.5, 133.1, 129.9, 129.0, 121.6 (t, *J* = 18.2 Hz), 114.2, 104.7−102.2 (m), 28.3. GC-MS (EI) m/z: 442 (17), 440 (49), 405(100), 385(68), 203(36), 125(26), 89(29).



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

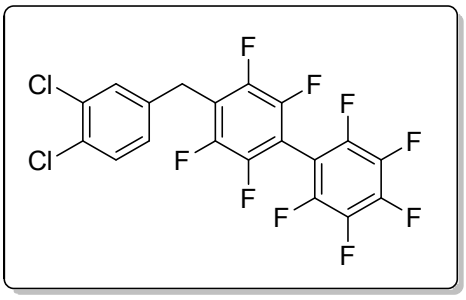
White solid, m.p. 90−91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31−7.20 (m, 4H), 4.11 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.09 to -137.61 (m, 2F), -138.06 to -138.52 (m, 2F), -142.26 (dd, *J* = 21.5, 12.4 Hz, 2F), -150.50 (t, *J* = 20.9 Hz, 1F), -160.73 (td, *J* = 20.2, 5.7 Hz, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.2−143.4 (m), 145.8−143.2 (m), 144.0 (ddt, *J* = 251.5, 15.2, 5.1 Hz), 138.8, 139.3−136.7 (m), 141.0−136.4 (m), 134.6, 130.1, 128.7, 127.4, 126.8, 121.2 (t, *J* = 18.2 Hz), 104.8−102.2 (m), 28.5. GC-MS (EI) m/z: 442 (18), 440 (56), 405(100), 385(73), 203(19), 192(28), 89(29).



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

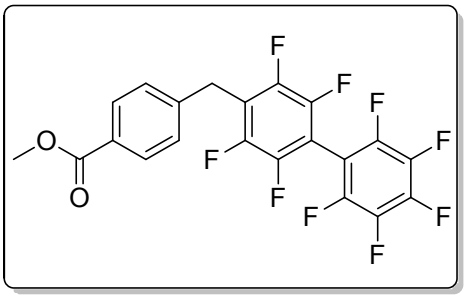
White solid, m.p. 124−125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61 (dd, *J* = 7.9, 0.8 Hz, 1H),

7.30−7.22 (m, 1H), 7.14 (td, *J* = 7.8, 1.3 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 4.28 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.99 to -137.64 (m, 2F), -138.51 to -139.19 (m, 2F), -140.41 to -140.84 (m, 2F), -150.03 to -150.91 (m, 1F), -160.69 (ddt, *J* = 21.0, 10.5, 5.2 Hz, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.6−143.7 (m), 145.9−143.2 (m), 144.1 (ddt, *J* = 251.5, 15.2, 5.1 Hz), 139.3−136.6 (m), 141.2−136.1 (m), 136.1, 133.1, 129.7, 128.7, 127.7, 124.3, 120.4 (t, *J* = 18.2 Hz), 105.0−102.2 (m), 29.5. GC-MS (EI) m/z: 486(29), 484(28), 405(97), 385(100), 237(35), 193(62), 167(34), 90(31), 89(42), 63(26).



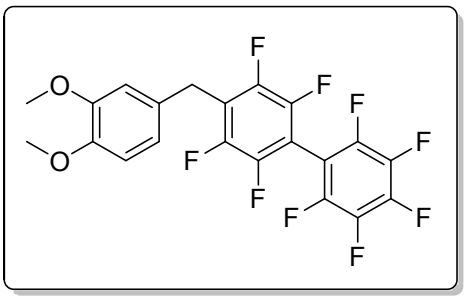
4-(3,4-dichlorobenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl

White solid, m.p. 122−123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.41 (dd, *J* = 5.1, 3.1 Hz, 2H), 7.17 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.10 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.09 to -137.64 (m, 2F), -138.12 (qdd, *J* = 12.2, 8.4, 3.7 Hz, 2F), -142.24 (dd, *J* = 20.8, 11.2 Hz, 2F), -150.30 (tt, *J* = 20.9, 2.8 Hz, 1F), -160.21 to -161.21 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.6−143.5 (m), 145.9−143.2 (m), 144.0 (ddt, *J* = 253.5, 16.2, 4.1 Hz), 137.0, 139.3−136.6 (m), 141.3−136.4 (m), 132.9, 131.4, 130.8, 130.5, 128.0, 120.8 (t, *J* = 18.2 Hz), 105.1−102.1 (m), 28.1. GC-MS (EI) m/z: 476(22), 474(58), 438(100), 403(54), 237(44), 202(59), 177(43), 167(53), 158(26), 123(58).



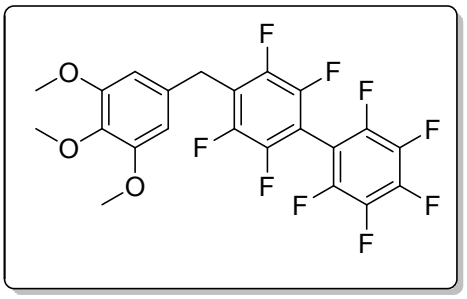
methyl 4-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)benzoate

White solid, m.p. 87−88 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 4.20 (s, 2H), 3.92 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.99 to -137.96 (m, 2F), -138.09 to -138.74 (m, 2F), -142.14 (dd, *J* = 20.8, 11.2 Hz, 2F), -150.35 (tt, *J* = 21.1, 2.8 Hz, 1F), -160.21 to -161.08 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 166.6, 146.5−143.5 (m), 145.8−143.2 (m), 144.0 (ddt, *J* = 253.5, 16.2, 4.1 Hz), 142.1, 139.3−136.6 (m), 141.2−136.4 (m), 130.2, 129.1, 128.6, 121.2 (t, *J* = 18.2 Hz), 104.9−102.2 (m), 52.1, 28.9. GC-MS (EI) m/z: 464(39), 432(100), 384(40), 216(55), 192(29), 63(13).



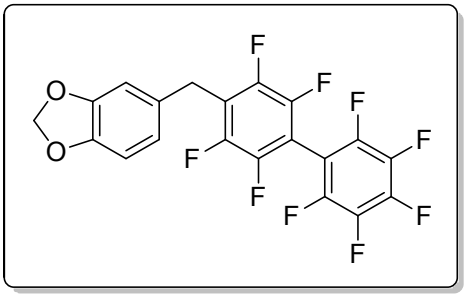
4-(3,4-dimethoxybenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl

White solid, m.p.78−79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.90 (s, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 4.10 (s, 2H), 3.93 (s, 3H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.09 to -137.76 (m, 2F), -138.82 (ttd, *J* = 12.7, 8.4, 4.0 Hz, 2F), -142.76 (dd, *J* = 20.9, 11.1 Hz, 2F), -150.63 (tt, *J* = 21.0, 2.7 Hz, 1F), -160.43 to -161.31 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 149.0, 148.0, 146.2−143.4 (m), 145.7−143.1 (m), 144.0 (ddt, *J* = 252.5, 15.2, 5.1 Hz), 139.2−136.5 (m), 141.0−136.3 (m), 129.45, 121.4 (t, *J* = 18.2 Hz), 120.6, 111.7, 111.2, 104.2−102.3 (m), 55.8 (2C), 28.5. GC-MS (EI) m/z: 466(46), 329(100), 233(14), 151(11), 77(27), 51(17).



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

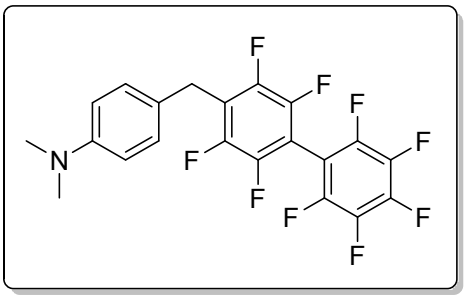
White solid, m.p. 82−83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.57 (s, 2H), 4.07 (s, 2H), 3.88 (s, 6H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.99 to -137.96 (m, 2F), -138.62 (ttd, *J* = 12.6, 8.4, 3.9 Hz, 2F), -142.54 (dd, *J* = 21.0, 11.1 Hz, 2F), -150.46 (tt, *J* = 20.9, 2.8 Hz, 1F), -160.31 to -161.21 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 153.4, 146.2−143.4 (m), 145.6−143.1 (m), 144.0 (ddt, *J* = 252.5, 16.2, 5.1 Hz), 137.1, 139.2−136.5 (m), 141.1−136.4 (m), 132.6, 122.1 (t, *J* = 18.2 Hz), 105.6, 104.4−102.1 (m), 60.7, 56.0 (2C), 29.1. GC-MS (EI) m/z: 496(43), 309(67), 208(45), 207(100), 128(29), 77(86), 55(66).



5-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)benzo[d][1,3]dioxole

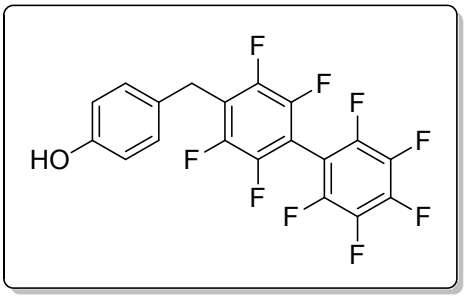
White solid, m.p. 92−93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.82−6.76 (m, 3H), 5.96 (s, 2H), 4.06

(s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.99 to -137.76 (m, 2F), -138.78 (ttd, *J* = 12.5, 8.3, 4.0 Hz, 2F), -142.65 (dd, *J* = 20.8, 11.0 Hz, 2F), -150.63 (tt, *J* = 20.9, 2.7 Hz, 1F), -160.43 to -161.41 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 147.9, 146.6, 146.1−143.4 (m), 145.7−143.1 (m), 144.0 (ddt, *J* = 252.5, 15.2, 5.1 Hz), 139.2−136.5 (m), 141.1−136.4 (m), 130.7, 122.2 (t, *J* = 18.2 Hz), 121.7, 109.0, 108.5, 104.4−102.1 (m), 101.1, 28.6. GC-MS (EI) m/z: 450(100), 449(26), 391(28), 372(22), 225(36), 135(73), 77(50), 51(28).



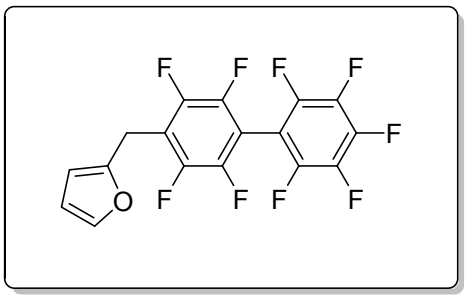
***N*,*N*-dimethyl-4-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)aniline**

White solid, m.p. 141−142 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.21 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 4.04 (s, 2H), 2.93 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.07 to -137.58 (m, 2F), -138.83 to -139.51 (m, 2F), -142.85 (dd, *J* = 21.1, 11.2 Hz, 2F), -150.88 (t, *J* = 20.9 Hz, 1F), -160.71 to -161.51 (m, 2F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 149.7, 145.6−143.2 (m), 144.9−142.9 (m), 141.4 (ddt, *J* = 257.6, 16.2, 6.0 Hz), 138.8−136.9 (m), 129.3, 124.8, 123.2 (t, *J* = 18.2 Hz), 112.8, 103.9−102.6 (m), 40.5, 28.0. GC-MS (EI) m/z: 449(100), 448(62), 385(12), 225(23), 134(73), 118(49), 91(14).



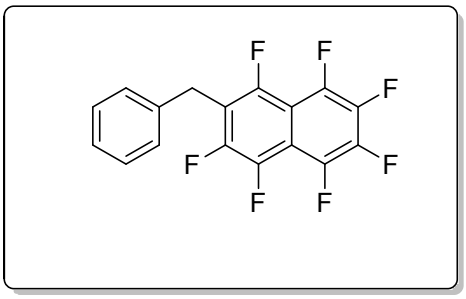
4-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)phenol

Colorless liquid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.33 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 4.14 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.16 to -137.46 (m, 2F), -137.80 to -138.06 (m, 1F), -138.52 (td, *J* = 14.8, 6.0 Hz, 1F), -142.52 (dd, *J* = 20.9, 11.2 Hz, 1F), -149.89 to -150.52 (m, 1F), -152.68 (td, *J* = 11.8, 4.6 Hz, 1F), -160.28 to -160.76 (m, 2F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 156.0, 146.0−143.4 (m), 145.0−142.8 (m), 144.1 (ddt, *J* = 257.6, 16.2, 6.0 Hz), 138.9−137.1 (m), 141.2−137.1 (m), 133.0, 130.1, 121.9 (t, *J* = 18.2 Hz), 116.3, 104.6−102.3 (m), 28.2. GC-MS (EI) m/z: 422(32), 91(100), 77(8), 65(38).



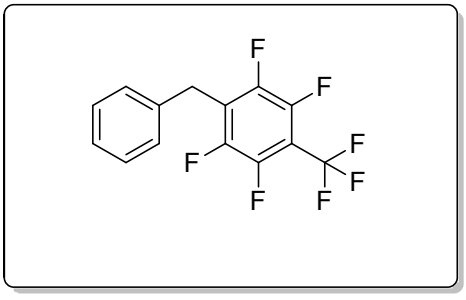
2-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)furan

White solid, m.p. 85–86 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.33 (d, *J* = 1.6 Hz, 1H), 6.31 (dd, *J* = 4.7, 2.9 Hz, 1H), 6.17 (d, *J* = 4.7 Hz, 1H), 4.16 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.25 – -137.42 (m, 2F), -138.76 (dt, J = 10.7, 7.4 Hz, 2F), -142.49 (dd, J = 21.2, 11.8 Hz, 2F), -150.48 (t, J = 20.9 Hz, 1F), -160.68 (tt, J = 10.4, 5.3 Hz, 2F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 149.7, 146.0−144.2 (m), 145.5−143.7 (m), 145.0−143.1 (m), 142.1, 138.8−137.0 (m), 119.2 (t, *J* = 18.2 Hz), 110.6, 107.0, 104.9−102.4 (m), 21.9. GC-MS (EI) m/z: 396(100), 349(65), 329(33) 299(29), 198 (21), 81(69).



2-benzyl-1,3,4,5,6,7,8-heptafluoronaphthalene

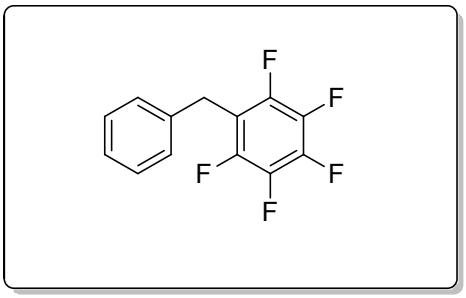
White solid, m.p. 115−116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32−7.18 (m, 5H), 4.18 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -122.05 (dd, *J* = 67.6, 18.7 Hz, 1F), -137.50 (d, *J* = 17.6 Hz, 1F), -144.54 (dt, *J* = 67.6, 16.8 Hz, 1F), -145.94 to -147.04 (m, 1F), -148.14 to -150.13 (m, 1F), -154.33 (t, *J* = 18.6 Hz, 1F), -156.00 (ddd, *J* = 13.4, 6.6, 3.3 Hz, 1F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 151.4−147.7 (m), 148.9−145.3 (m), 142.5−139.6 (m), 141.9−139.1 (m), 140.7−137.9 (m), 137.4, 128.8, 128.5, 127.0, 118.8−118.3 (m), 111.4−107.8 (m), 28.7. GC-MS (EI) m/z: 344(100), 324(37), 323(46), 305(27), 267(14), 137(27), 91(25).



1-benzyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene

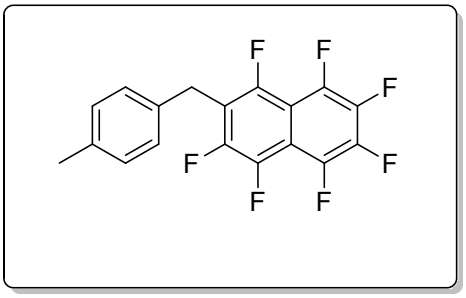
White solid, m.p. 60−61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43 -7.28 (m, 5H), 4.17 (s, 2H). ^{19}F

NMR (376 MHz, $CDCl_3$) δ: -56.32 (t, *J* = 21.5 Hz, 3F), -140.34 to -141.17 (m, 2F), -141.30 to -141.59 (m, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.4−143.7 (m), 145.6−145.5 (m), 136.5, 129.0, 128.5, 127.3, 124.4 (t, *J* = 18.2 Hz), 125.0−116.8 (m), 108.5−107.5 (m), 28.8. GC-MS (EI) m/z: 308(100), 289(29), 287(24), 237(24), 91(44).



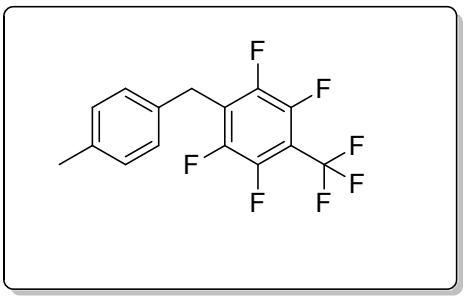
1-benzyl-2,3,4,5,6-pentafluorobenzene

White solid, m.p. 56−57 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ: ^1H NMR (400 MHz, CDCl3) δ 7.48−7.19 (m, 5H), 4.08 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -143.34 (dd, *J* = 22.4, 8.3 Hz, 2F), -157.17 (t, *J* = 20.8 Hz, 1F), -162.42 (dt, *J* = 22.3, 8.4 Hz, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 146.3−143.6 (m), 141.3−138.6 (m), 138.9−136.1 (m), 137.4, 128.8, 128.3, 127.0, 114.4 (td, *J* = 19.2, 4.0 Hz), 28.1. HRMS (ESI) calcd. for $C_{11}H_{18}N$ ($[M+H]^+$): 164.1434, found: 164.1431. MS (EI) m/z: 181, 138, 124, 110, 98, 68, GC-MS (EI) m/z: 258(100), 237(51), 219(27), 181(11), 91(23).



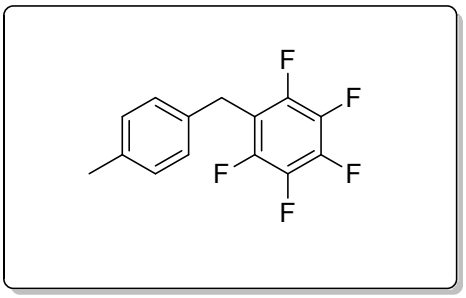
1,2,3,4,5,6,8-heptafluoro-7-(4-methylbenzyl)naphthalene

White solid, m.p. 132−133 °C. ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.19 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.15 (s, 2H), 2.30 (s, 3H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: -122.19 (dd, *J* = 67.1, 19.1 Hz, 1F), -137.54 (d, *J* = 16.9 Hz, 1F), -144.60 (dt, *J* = 67.5, 16.8 Hz, 1F), -146.30 to -146.66 (m, 1F), -149.08 (dt, *J* = 57.1, 18.3 Hz, 1F), -154.46 (t, *J* = 18.5 Hz, 1F), -156.10 (t, *J* = 16.9 Hz, 1F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 151.0−147.4 (m), 149.1−145.7 (m), 142.1−140.2 (m), 141.5−138.8 (m), 139.7−136.6 (m), 136.7, 134.4, 129.5, 128.4, 119.0−118.0 (m), 110.5−107.9 (m), 28.4, 21.0. GC-MS (EI) m/z: 358(100), 343(67), 323(71), 105(30), 91(58), 77(24), 65(19).



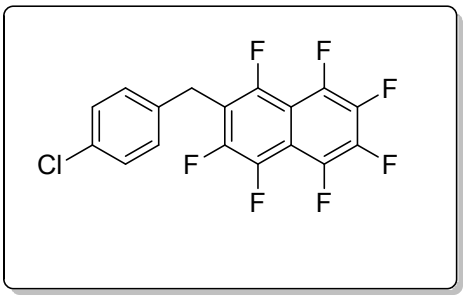
1,2,4,5-tetrafluoro-3-(4-methylbenzyl)-6-(trifluoromethyl)benzene

Colorless liquid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.20 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 4.09 (s, 2H), 2.35 (s, 3H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: -56.35 (t, J = 21.6 Hz, 3F), -140.97 to -141.24 (m, 2F), -141.48 to -141.72 (m, 2F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 145.9−144.1 (m), 145.0−143.2 (m), 137.0, 133.5, 129.6, 128.4, 124.8 (t, J = 18.2 Hz), 127.2−120.8 (m), 108.1−107.5 (m), 28.5, 20.9. GC-MS (EI) m/z: 322(62), 307(52), 287(16), 238(19), 91(100), 77(15), 65 (16).



1,2,3,4,5-pentafluoro-6-(4-methylbenzyl)benzene

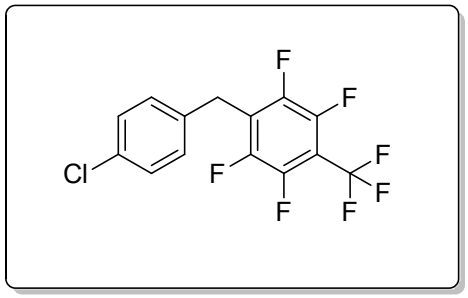
White solid, m.p. 30−32 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.18 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 4.02 (s, 2H), 2.36 (s, 3H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: -143.47 (dd, J = 22.3, 8.1 Hz, 2F), -157.42 (t, J = 20.8 Hz, 1F), -162.43 to -162.64 (m, 2F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 145.9−144.2 (m), 140.8−138.9 (m), 138.6−136.8 (m), 136.8, 134.5, 129.5, 128.2, 114.8 (td, J = 19.2, 4.0 Hz), 27.7, 20.9. GC-MS (EI) m/z: 272(100), 257(92), 237(51), 135(17), 91(76), 77(18).



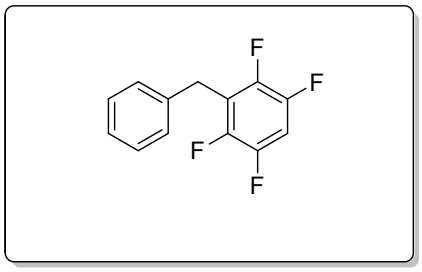
2-(4-chlorobenzyl)-1,3,4,5,6,7,8-heptafluoronaphthalene

White solid, m.p. 110−112 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.28−7.20 (m, 4H), 4.16 (s, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: -122.10 (dd, J = 67.5, 18.6 Hz, 1F), -137.84 (d, J = 17.1 Hz, 1F), -144.46 (dt, J = 67.6, 16.8 Hz, 1F), -146.09 to -146.41 (m, 1F), -148.56 to -148.90 (m, 1F), -154.03 (t, J = 18.6 Hz, 1F), -155.68 to -155.89 (m, 1F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 151.0−147.1 (m), 149.3−145.5 (m), 142.1−139.7 (m), 141.6−139.5 (m), 138.7−137.2 (m), 135.8, 133.0, 129.9, 129.0,

118.2−117.9 (m), 110.6−107.9 (m), 28.1. GC-MS (EI) m/z: 380(25), 378(87), 343(93), 323(100), 162(54), 146(66), 125(30), 89(36), 75(11).



1-(4-chlorobenzyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene
Colorless liquid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.28 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.07 (s, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: -56.38 (t, *J* = 21.6 Hz, 3F), -140.50 to -140.82 (m, 2F), -141.25 to -141.69 (m, 2F). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 145.9−144.2 (m), 145.1−143.3 (m), 134.9, 133.4, 129.8, 129.1, 123.8 (t, *J* = 18.2 Hz), 125.2−120.0 (m), 108.9−108.0 (m), 28.3. GC-MS (EI) m/z: 344(15), 342(51), 307(100), 287(31), 238(41), 125(19), 89(20), 75(12).



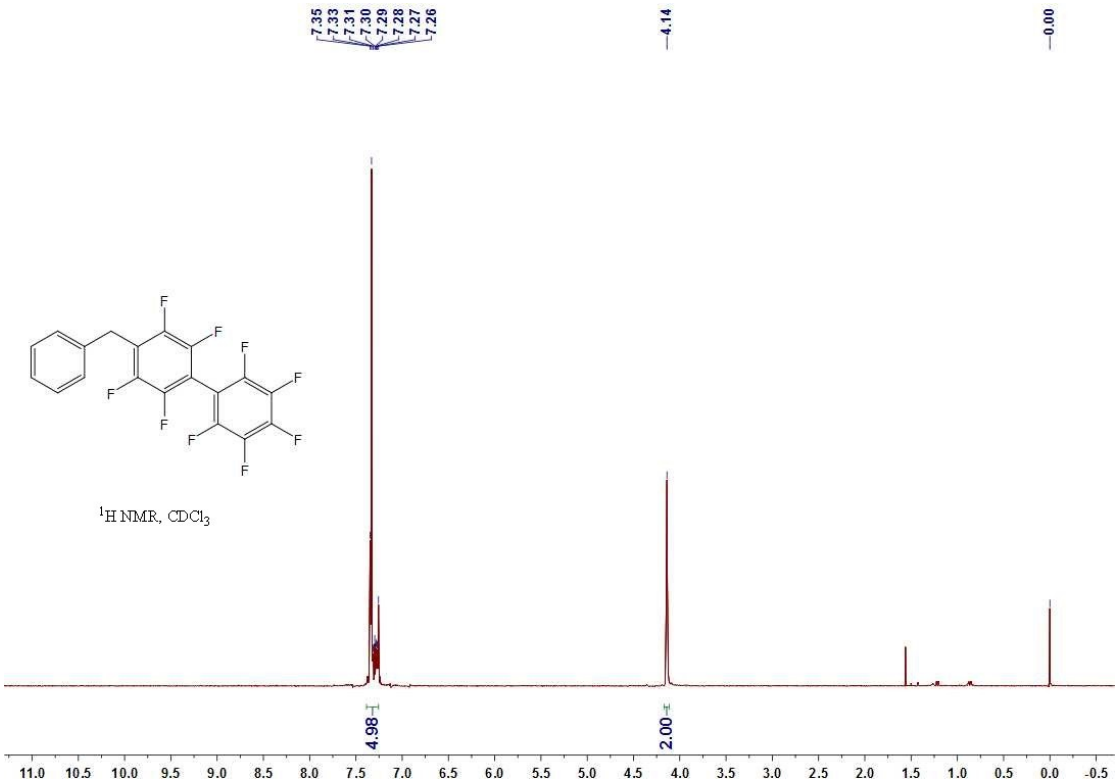
3-benzyl-1,2,4,5-tetrafluorobenzene Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.41 – 7.11 (m, 5H), 6.93 (tt, J = 9.7, 7.4 Hz, 1H), 4.06 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.70 to -140.49 (m, 2F), -143.78 (ddd, J = 20.8, 13.0, 7.4 Hz, 2F). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 145.8 (dm, J = 248.5 Hz), 144.7 (dm, J = 245.4 Hz), 137.6, 128.7, 128.4, 126.8, 120.3 (t, J = 18.2 Hz), 104.1 (t, J = 22.2 Hz), 28.7. GC-MS (EI) m/z: 240, 220, 219, 201, 189, 163, 143, 109, 91, 85, 51.

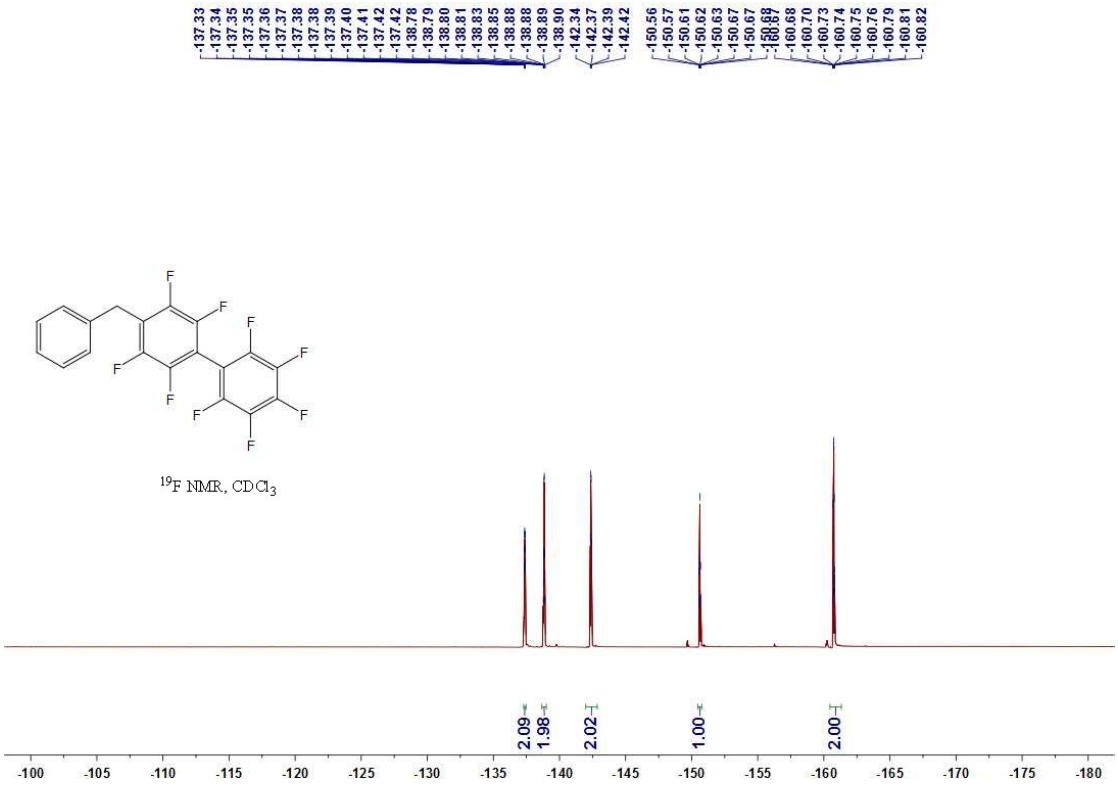
Ⅵ. References

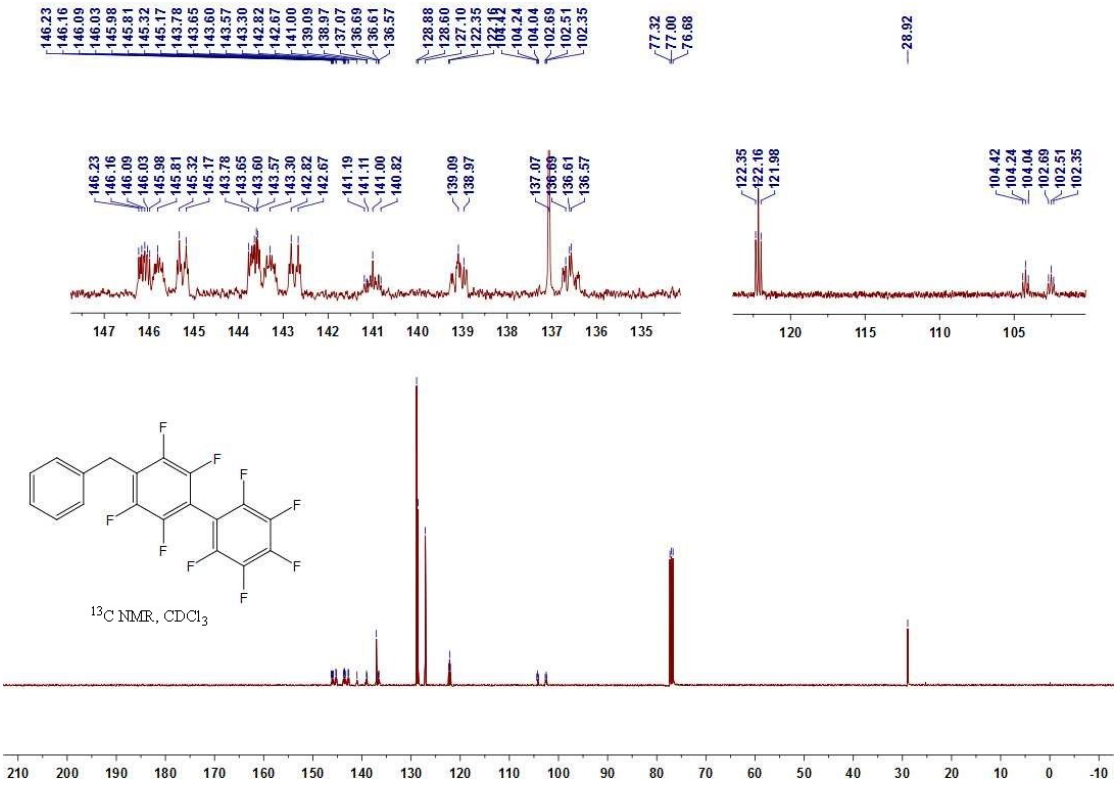
[1] (a) J.-S. Poh, D. N. Tran, C. Battilocchio, J. M. Hawkins and S. V. Ley, *Angew. Chem. Int. Ed.* 2015, **54**, 7920; (b) S.-S. Yan, L. Zhu, J.-H. Ye, Z. Zhang, H. Huang, H. Zeng, C.-J. Li, Y. Lan and D.-G. Yu, *Chem. Sci.* 2018, **9**, 4873.

Ⅶ. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR

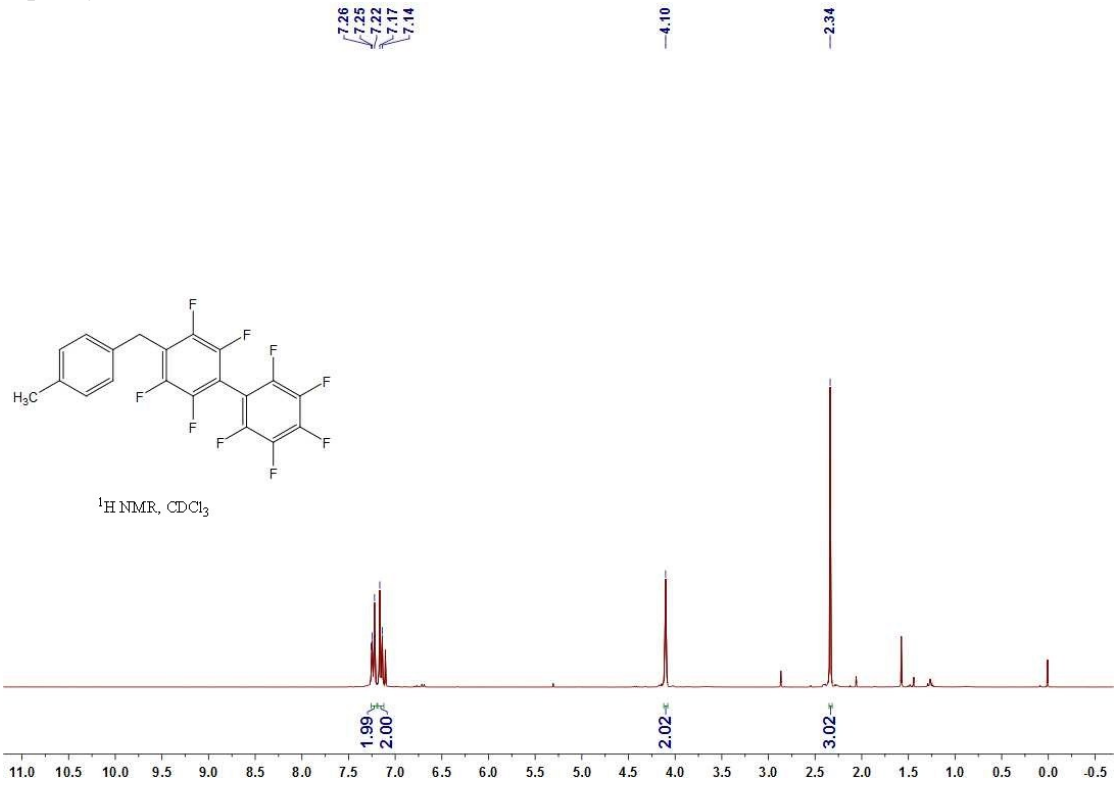
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-benzyl-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl**

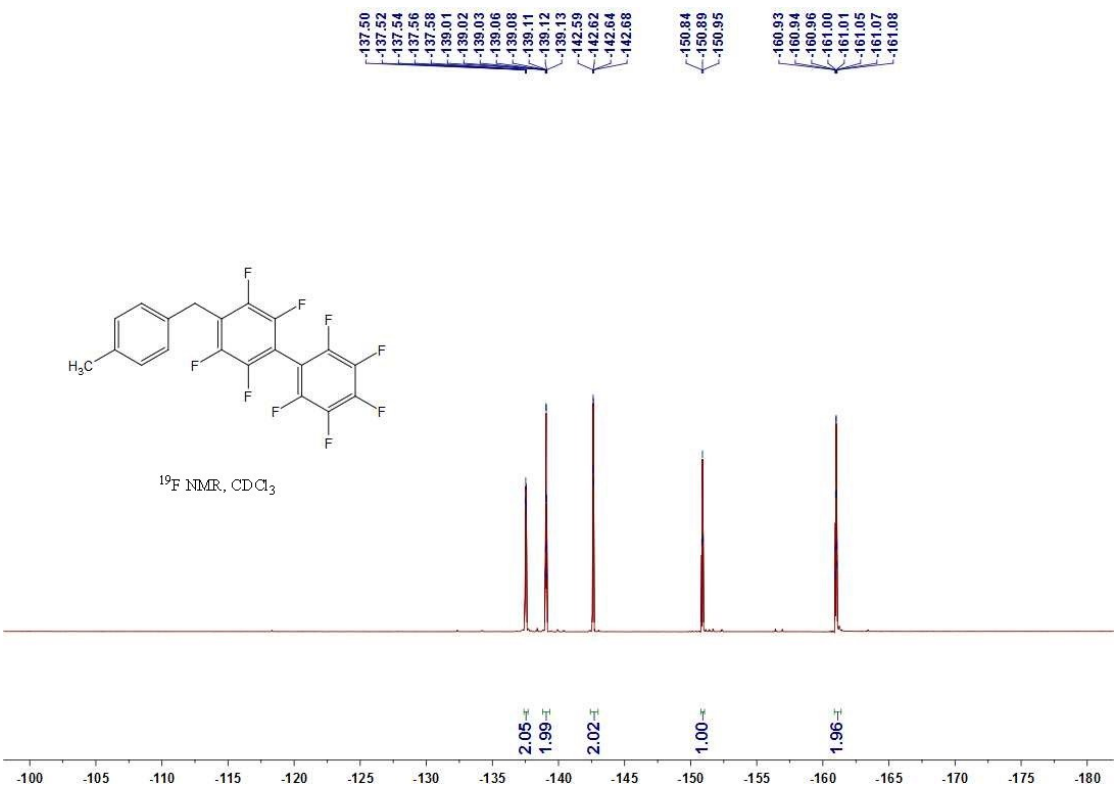


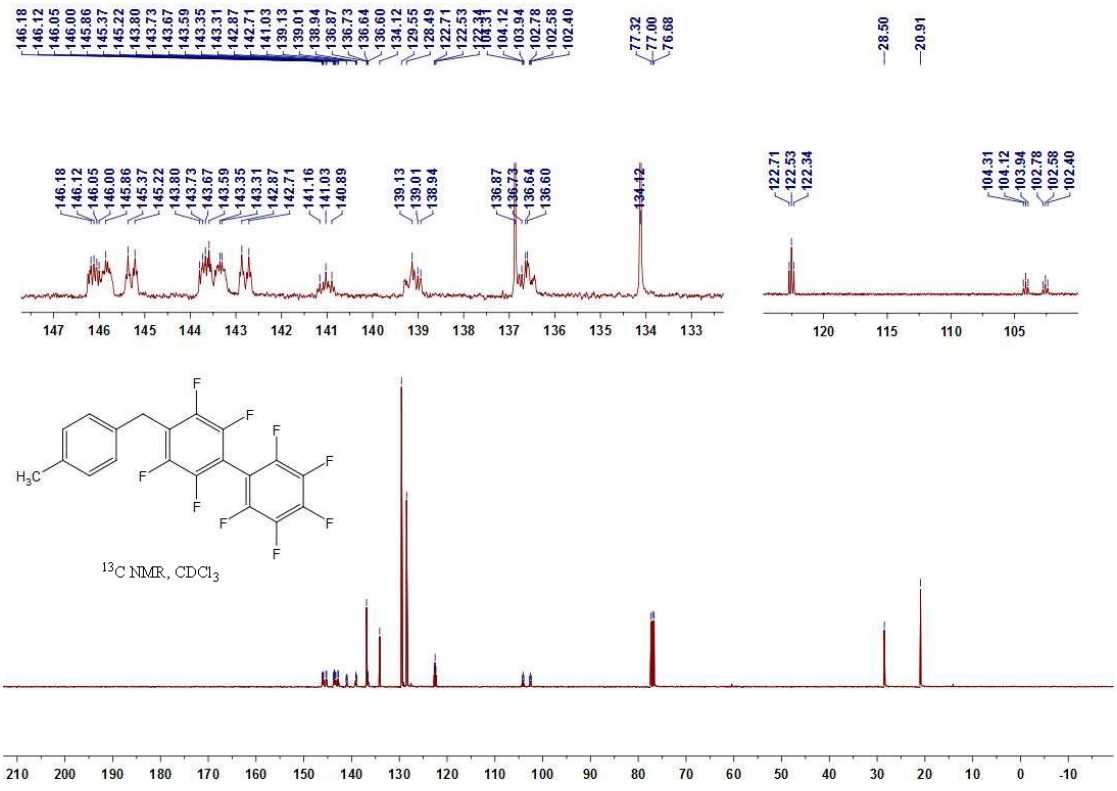




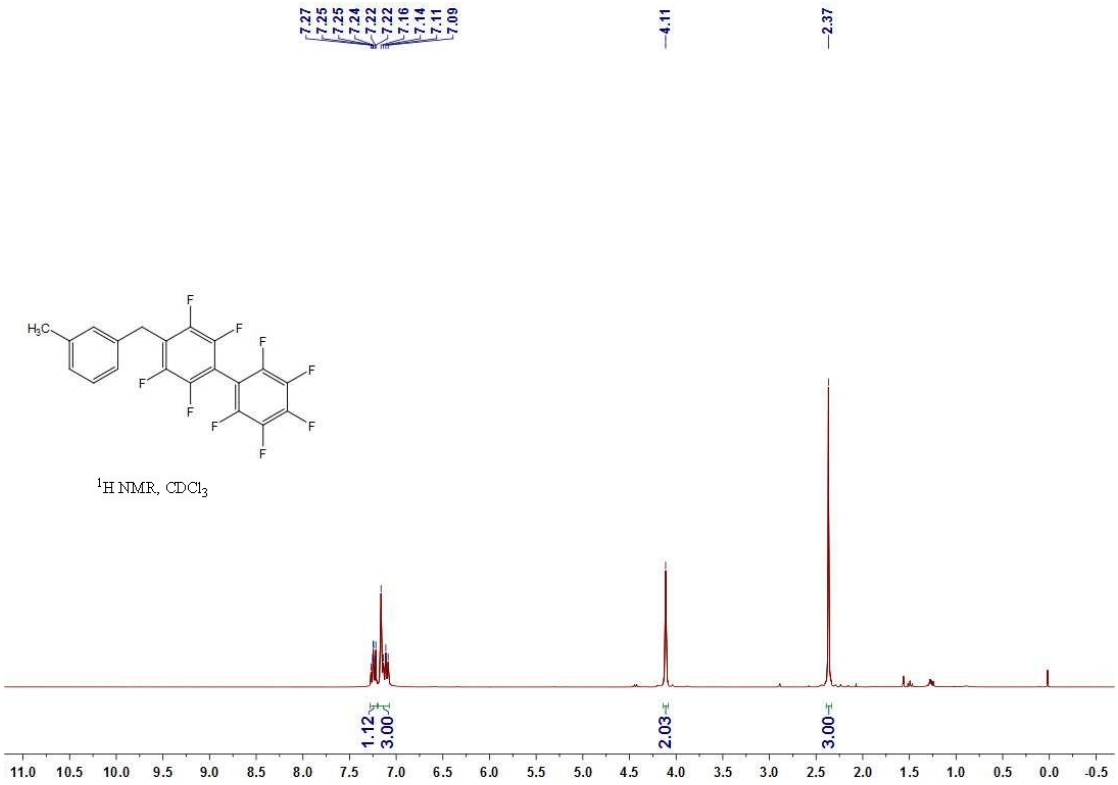
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(4-methylbenzyl)-1,1'-biphenyl**

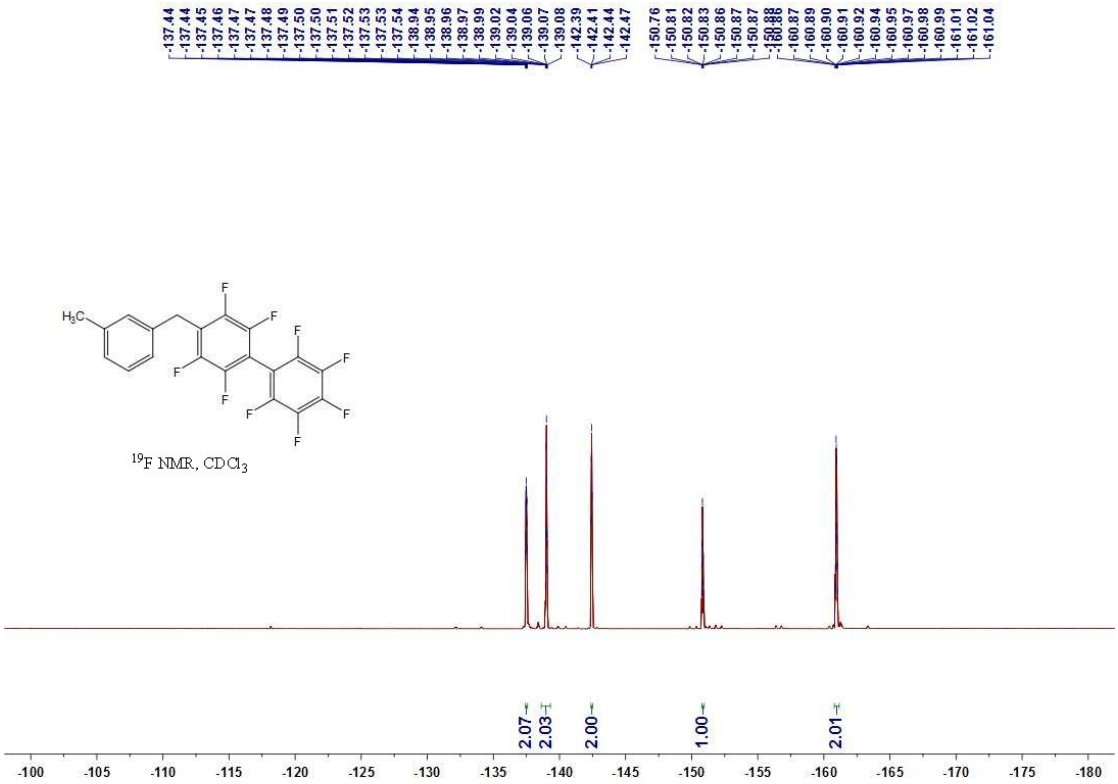


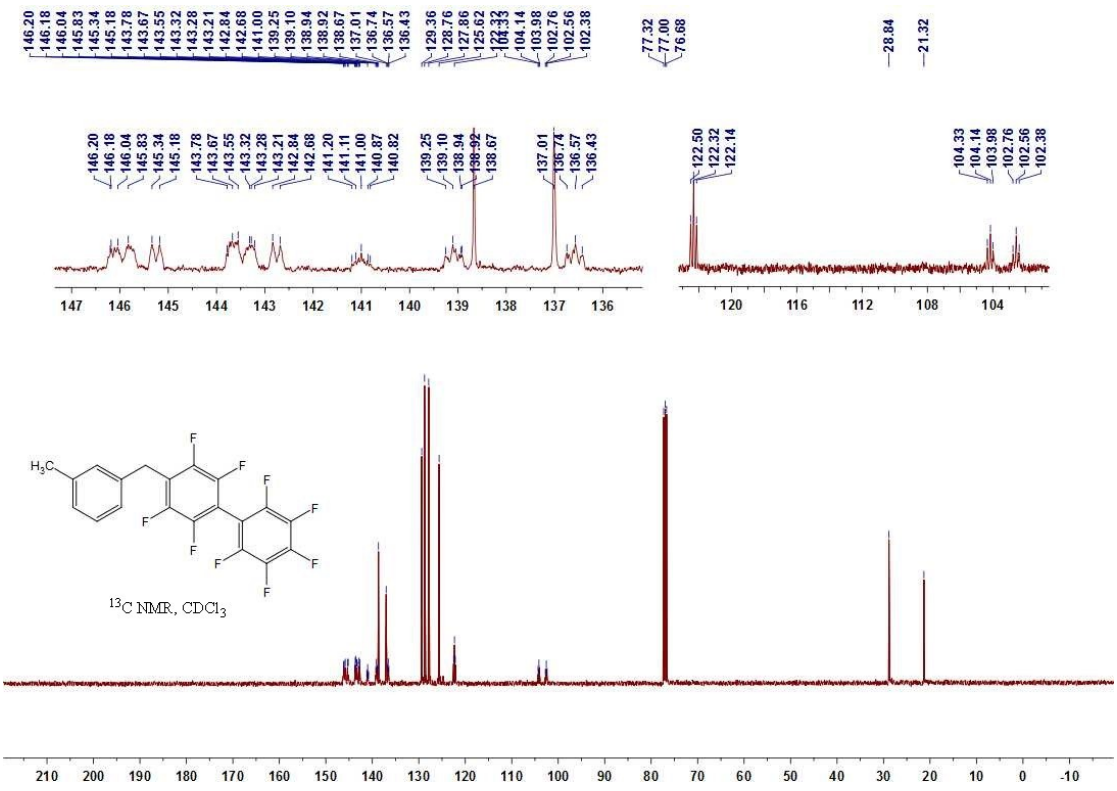

^{19}F NMR, $CDCl_3$


^{13}C NMR, $CDCl_3$

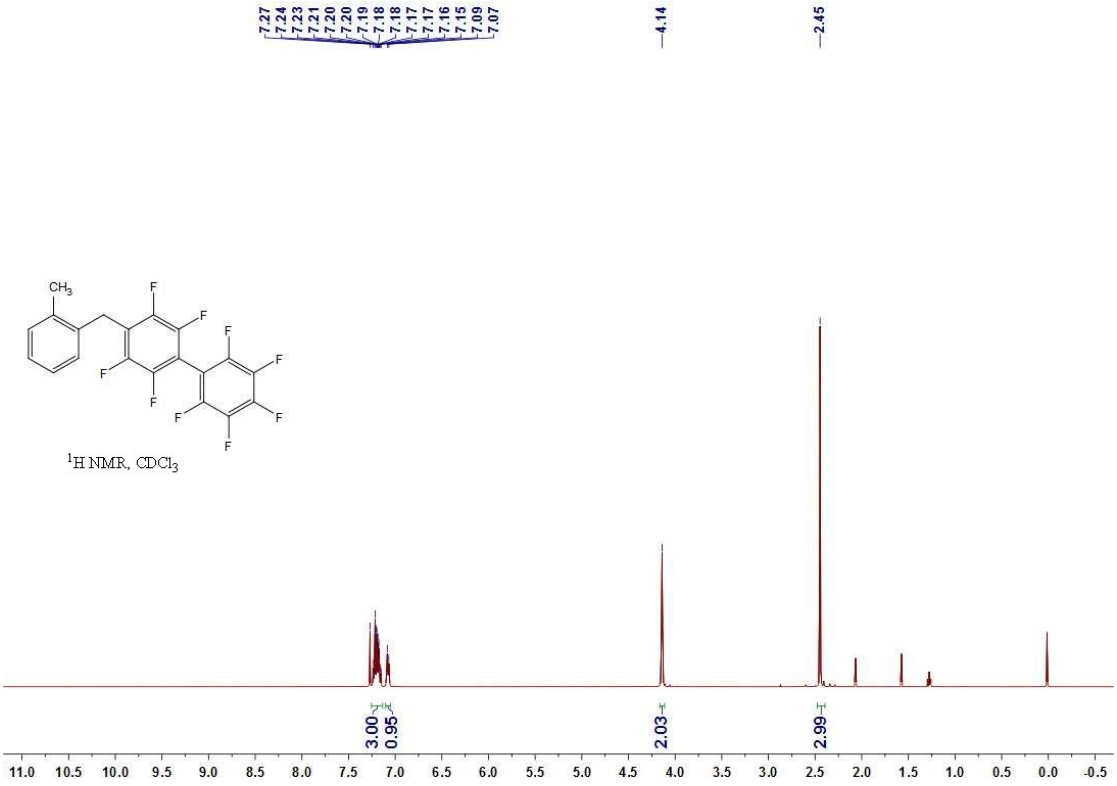
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(3-methylbenzyl)-1,1'-biphenyl**

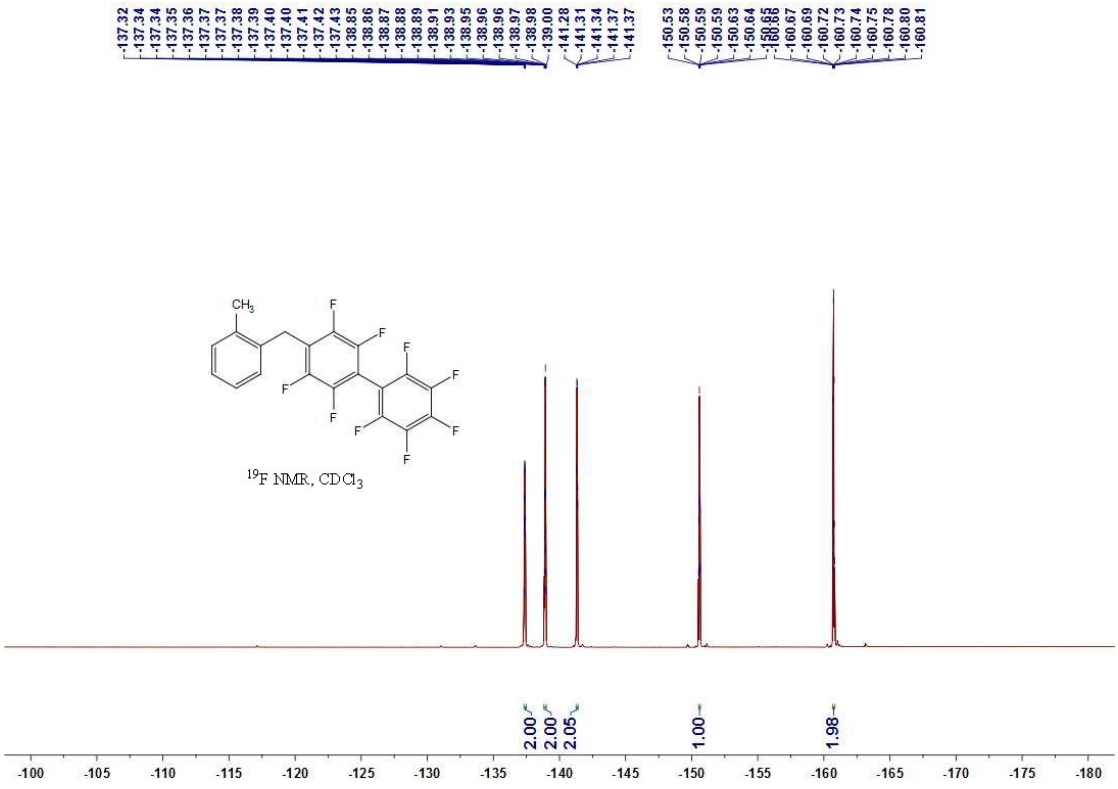


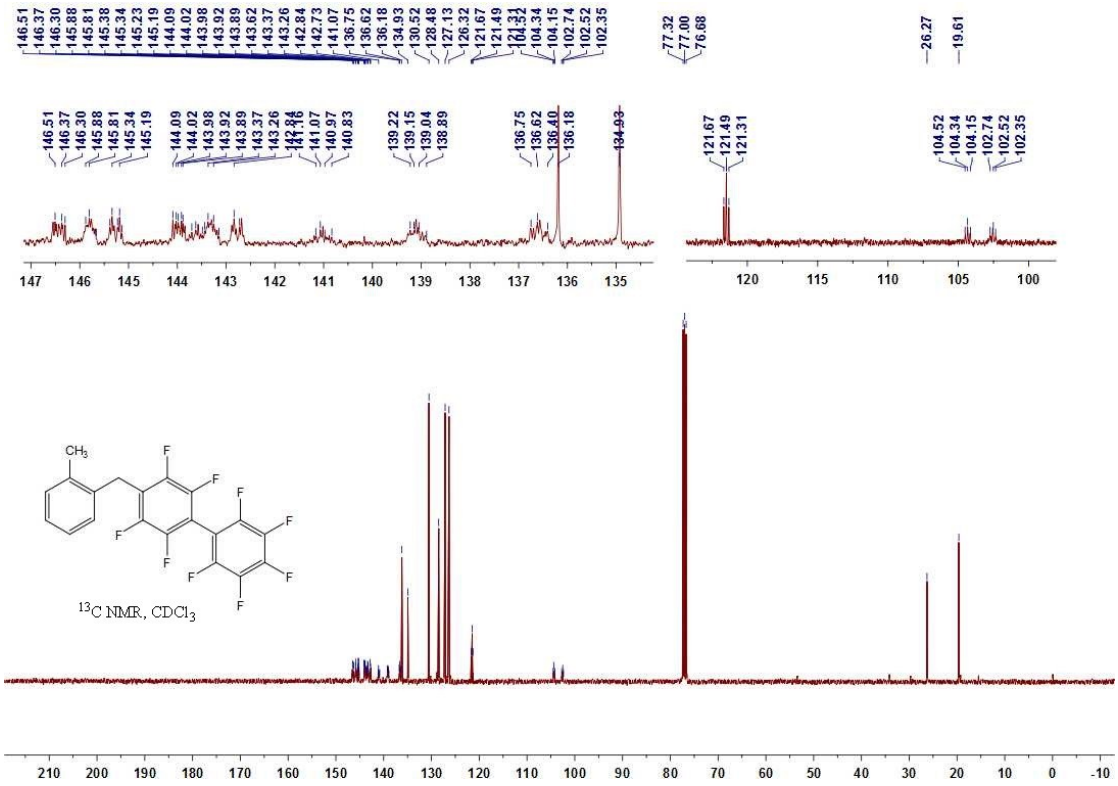




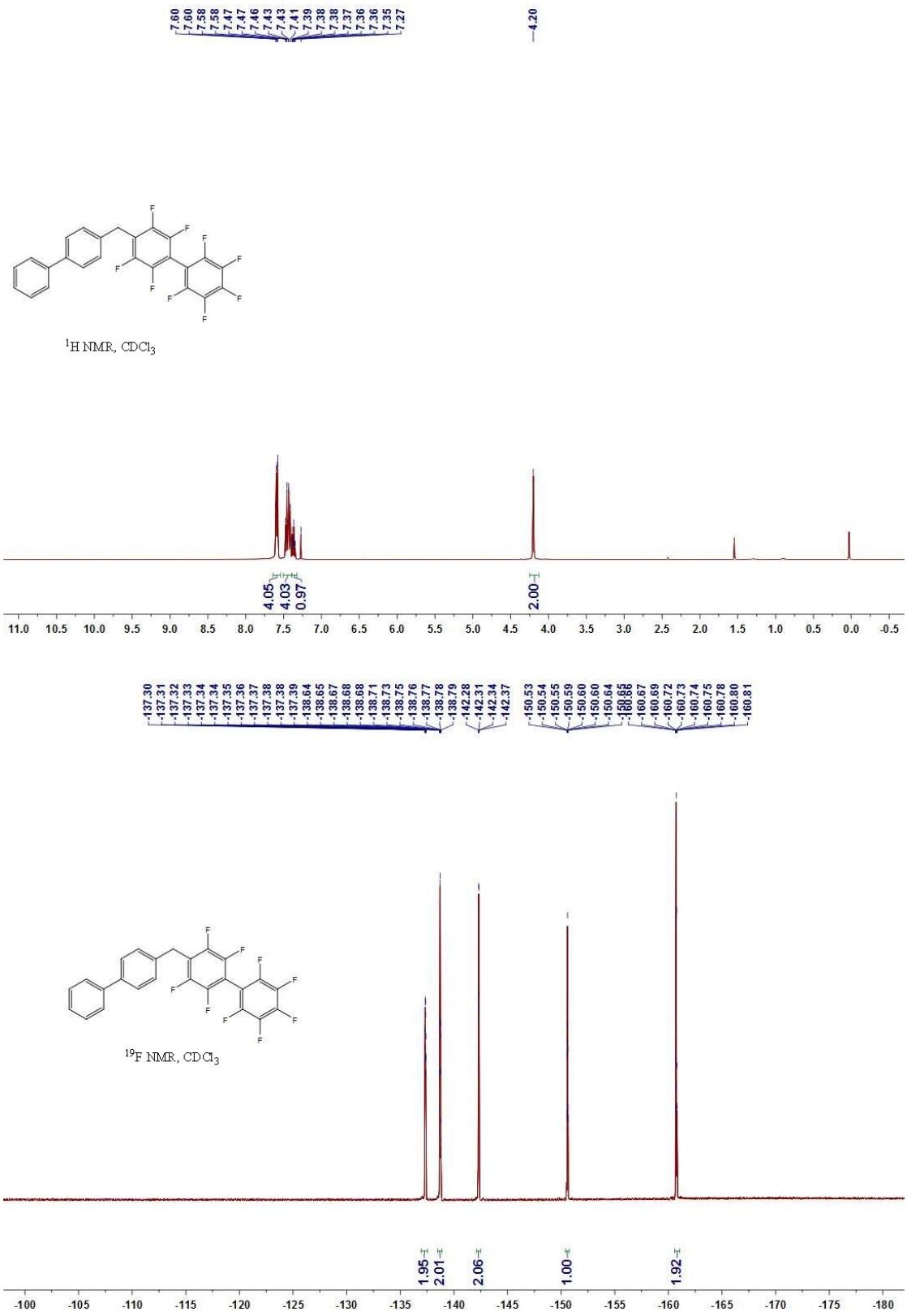
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(2-methylbenzyl)-1,1'-biphenyl**

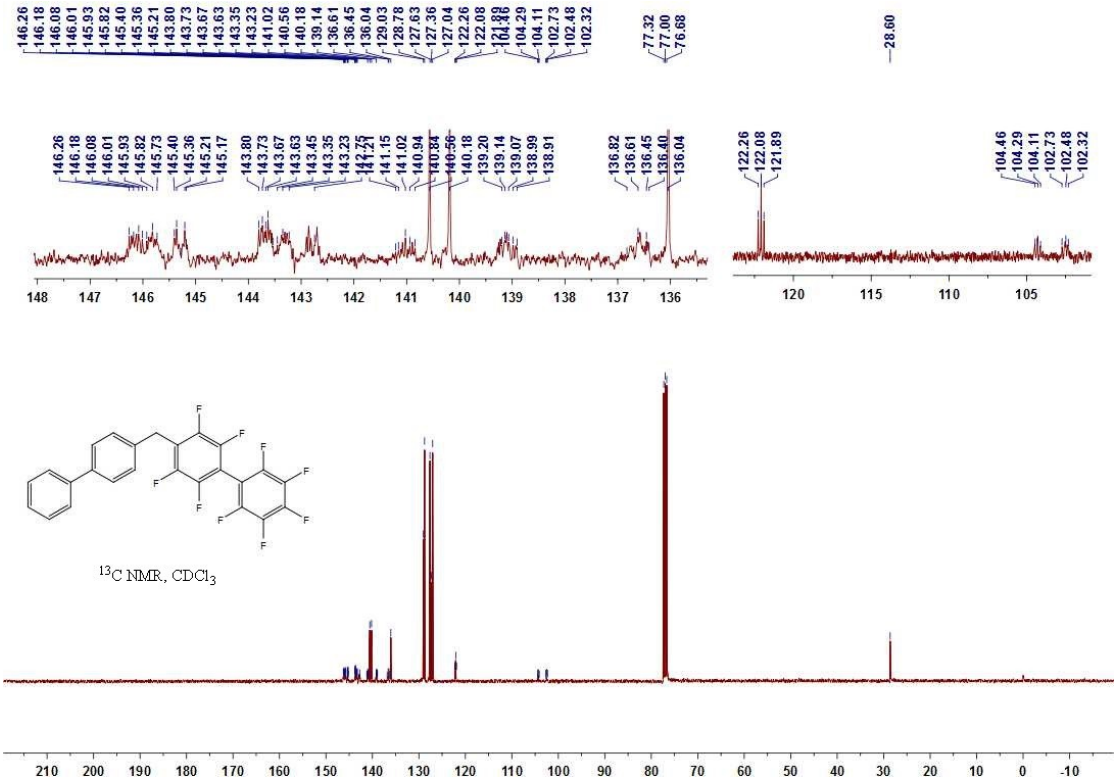



CH3
F
19F NMR, CDCl3
2.00
2.00
2.05
1.00
1.98

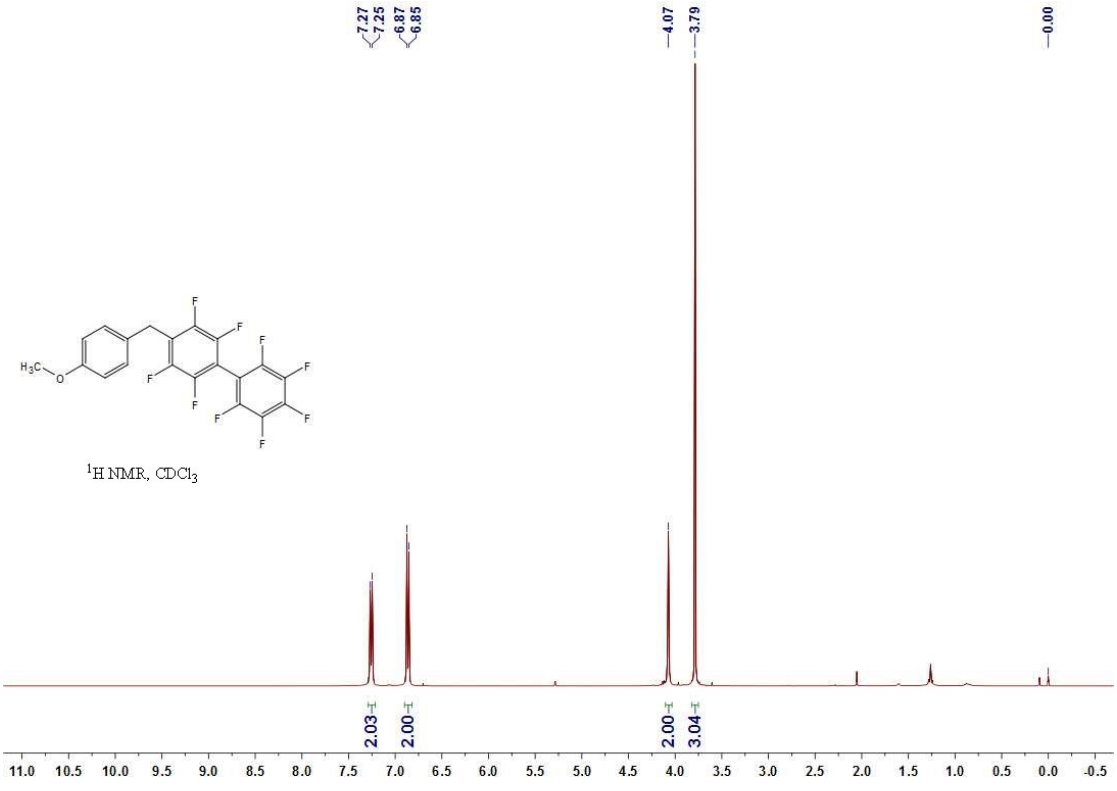

CH3
F
13C NMR, CDCl3

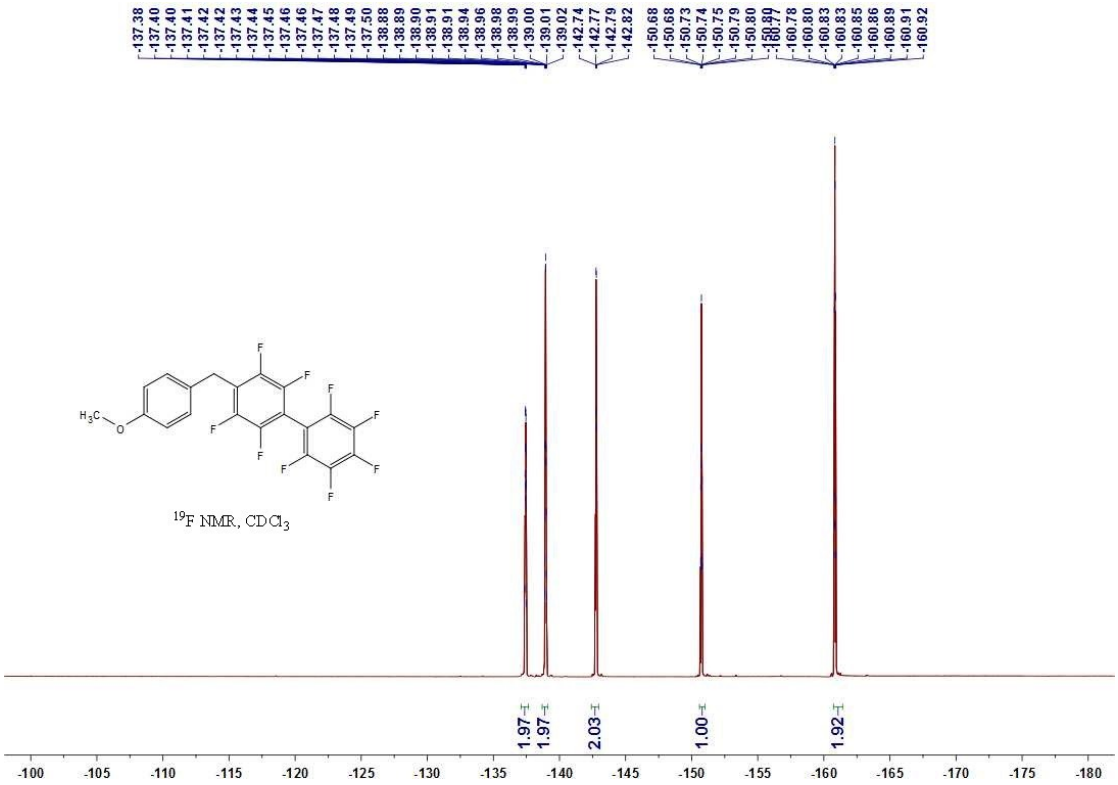
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-([1,1'-biphenyl]-4-ylmethyl)-2,2',3,3',4',5,5',6,6'- nonafluoro-1,1'-biphenyl**





^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(4-methoxybenzyl)-1,1'-biphenyl**




-137.38
-137.40
-137.40
-137.41
-137.42
-137.42
-137.43
-137.44
-137.45
-137.46
-137.46
-137.47
-137.48
-137.49
-137.50
-138.88
-138.89
-138.90
-138.91
-138.91
-138.94
-138.96
-138.98
-138.99
-139.00
-139.01
-139.02
-142.74
-142.77
-142.79
-142.82
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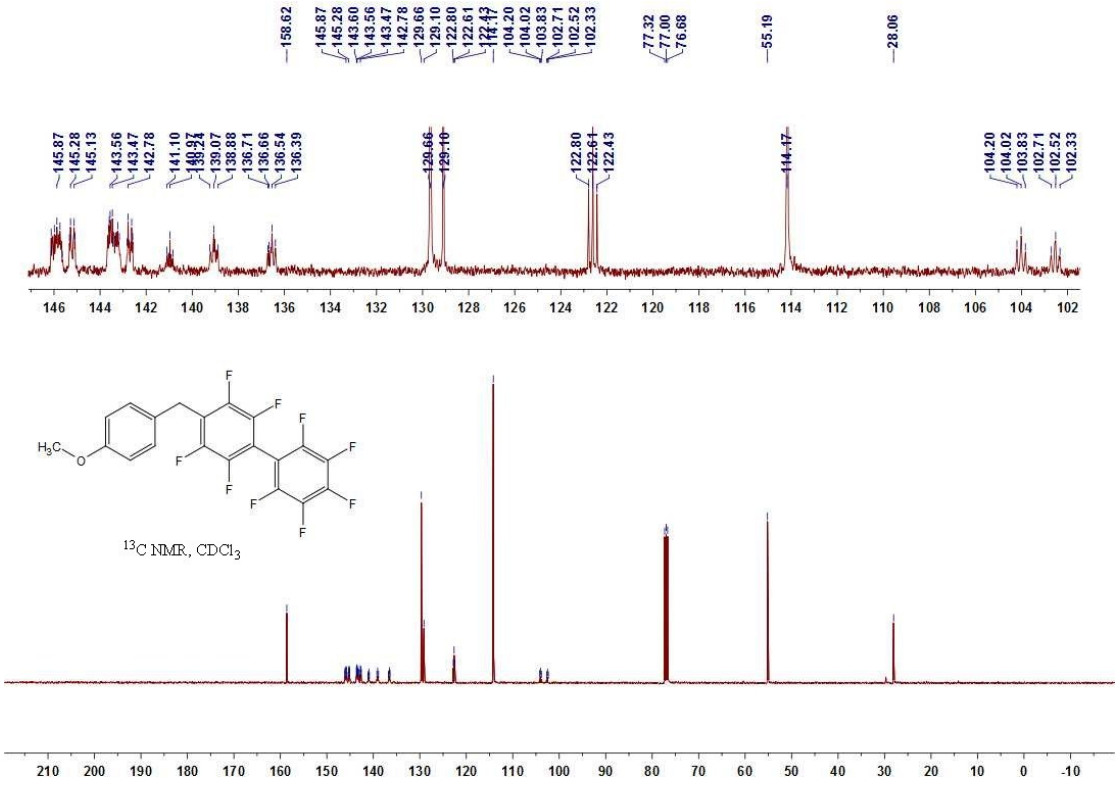
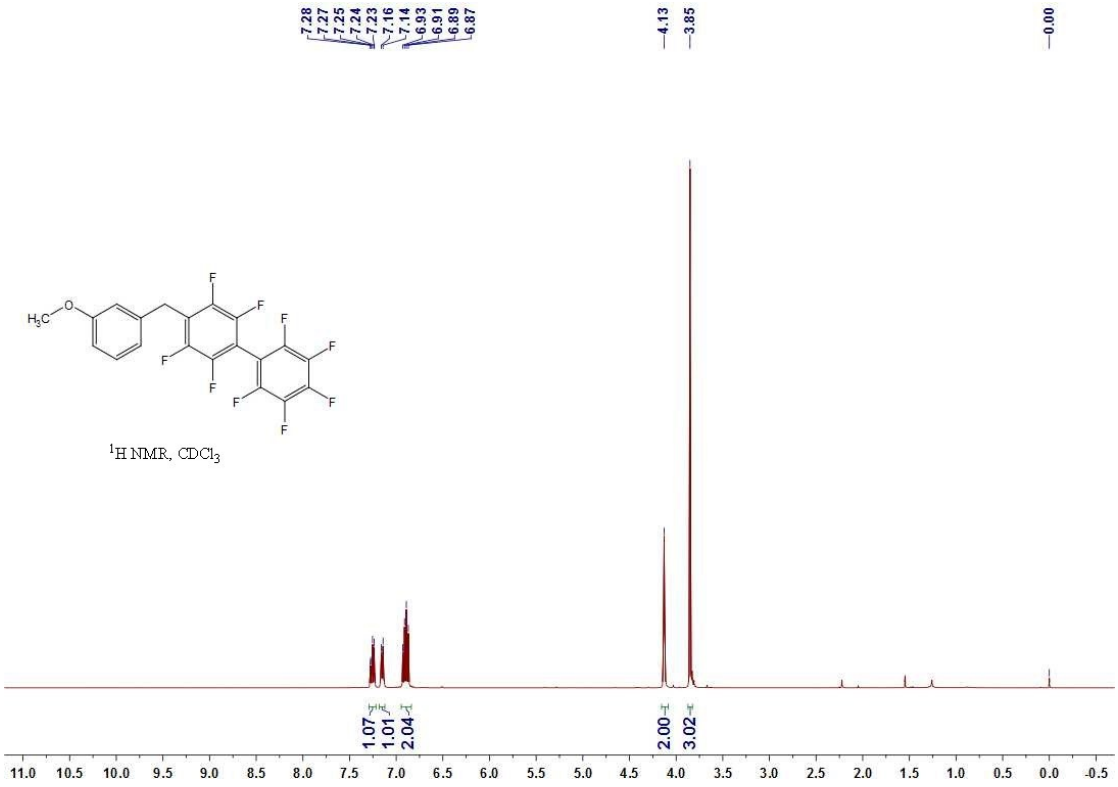
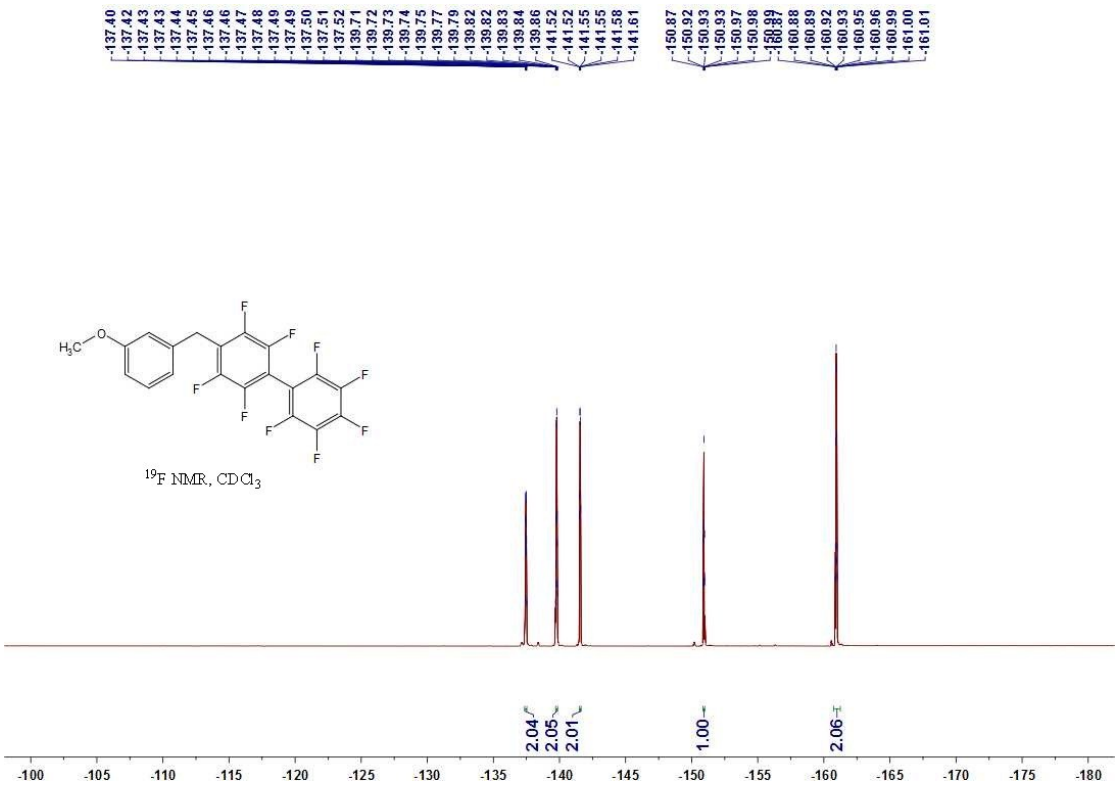
-150.68
-150.73
-150.74
-150.75
-150.79
-150.80
-160.78
-160.80
-160.83
-160.83
-160.85
-160.86
-160.89
-160.91
-160.92
^{19}F NMR, CDCl$_3$
1.97
1.97
2.03
1.00
1.92
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180


158.62
145.87
145.28
143.60
143.56
143.47
142.78
129.66
129.10
122.80
122.61
104.20
104.02
103.83
102.71
102.52
102.33
77.32
77.00
76.68
55.19
28.06
114.17
^{13}C NMR, CDCl$_3$
146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

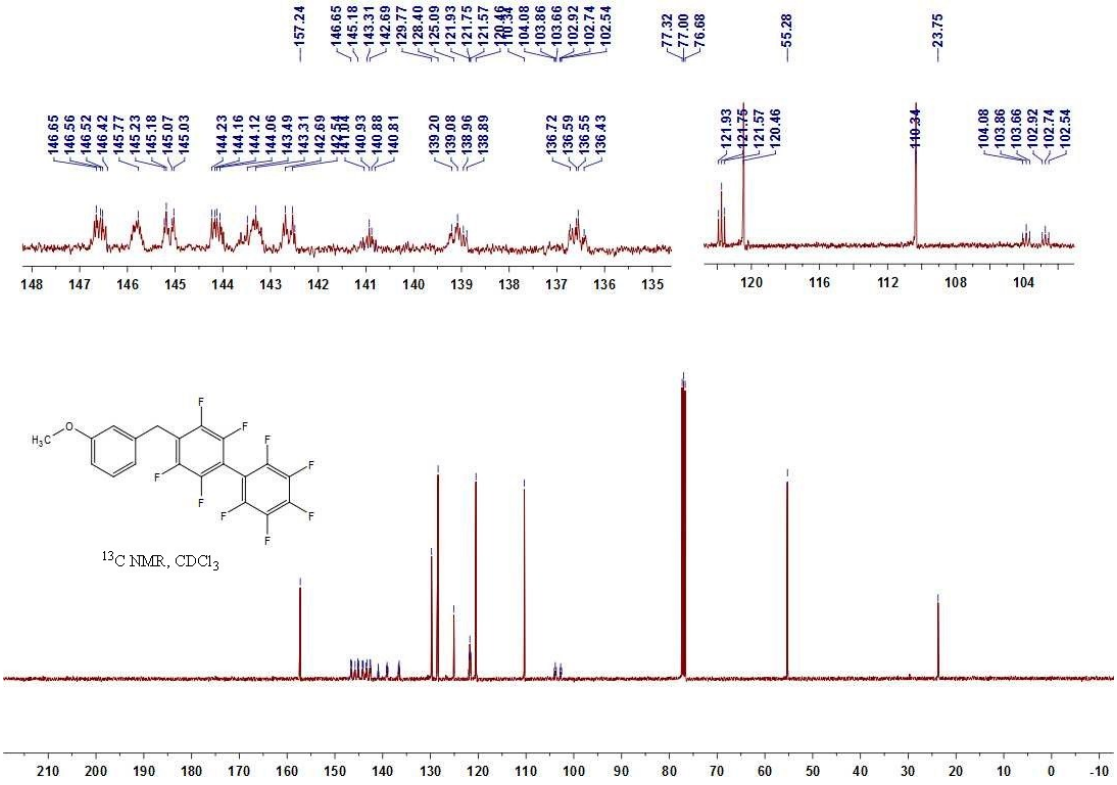
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(3-methoxybenzyl)-1,1'-biphenyl**



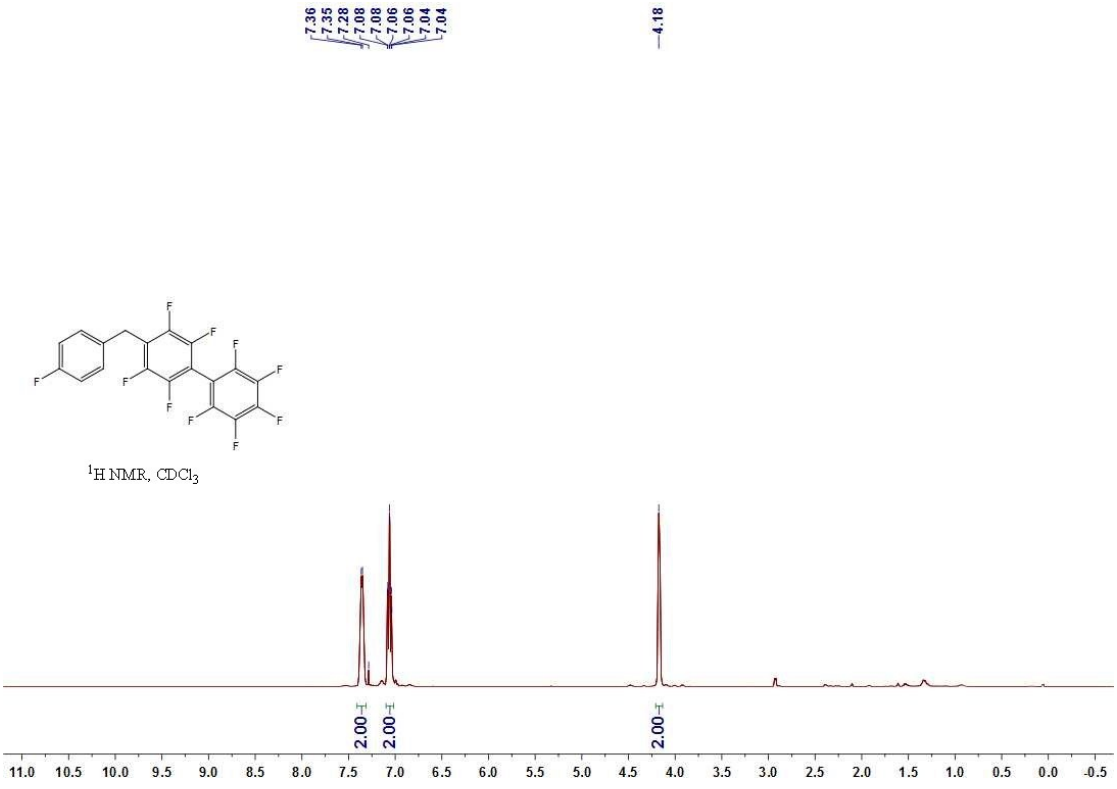
^{1}H NMR, $CDCl_3$

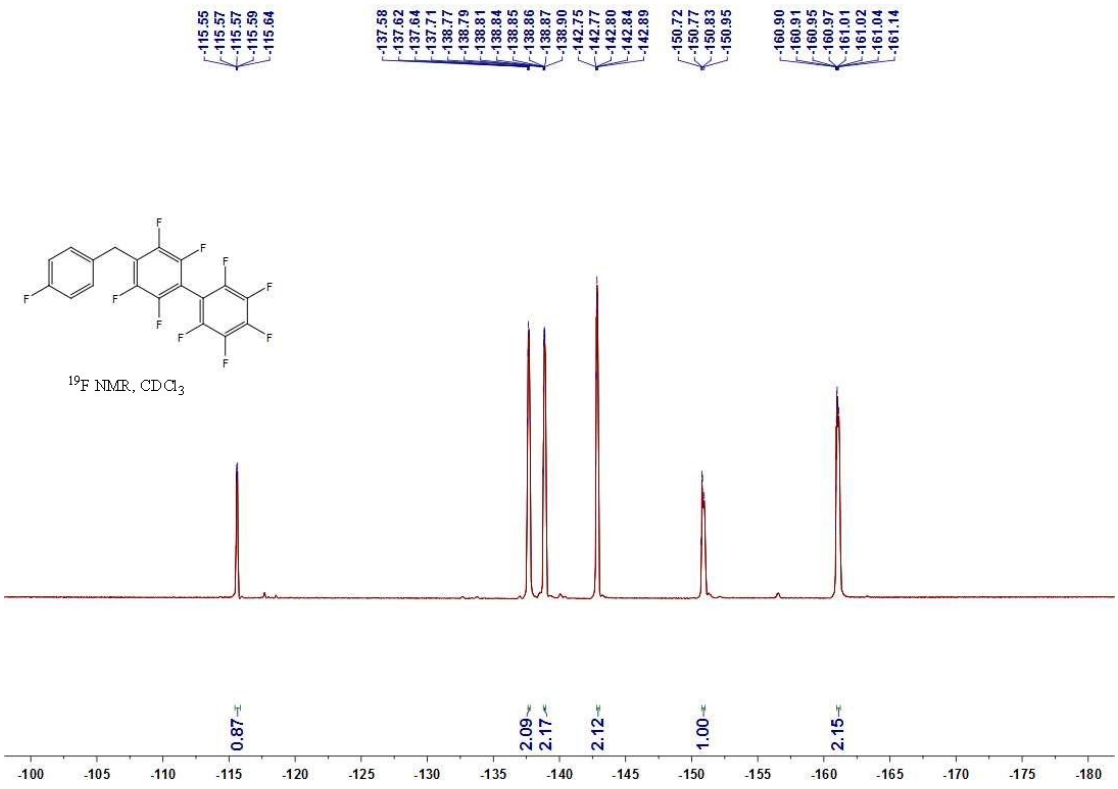


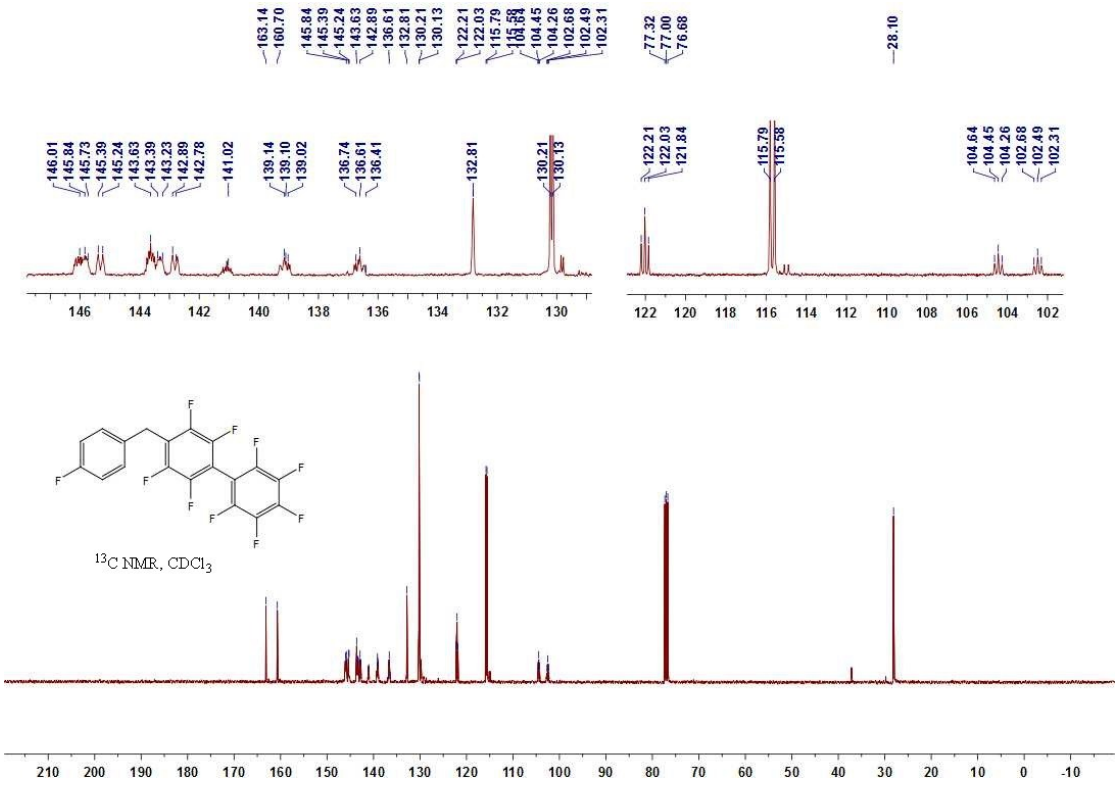
^{19}F NMR, $CDCl_3$



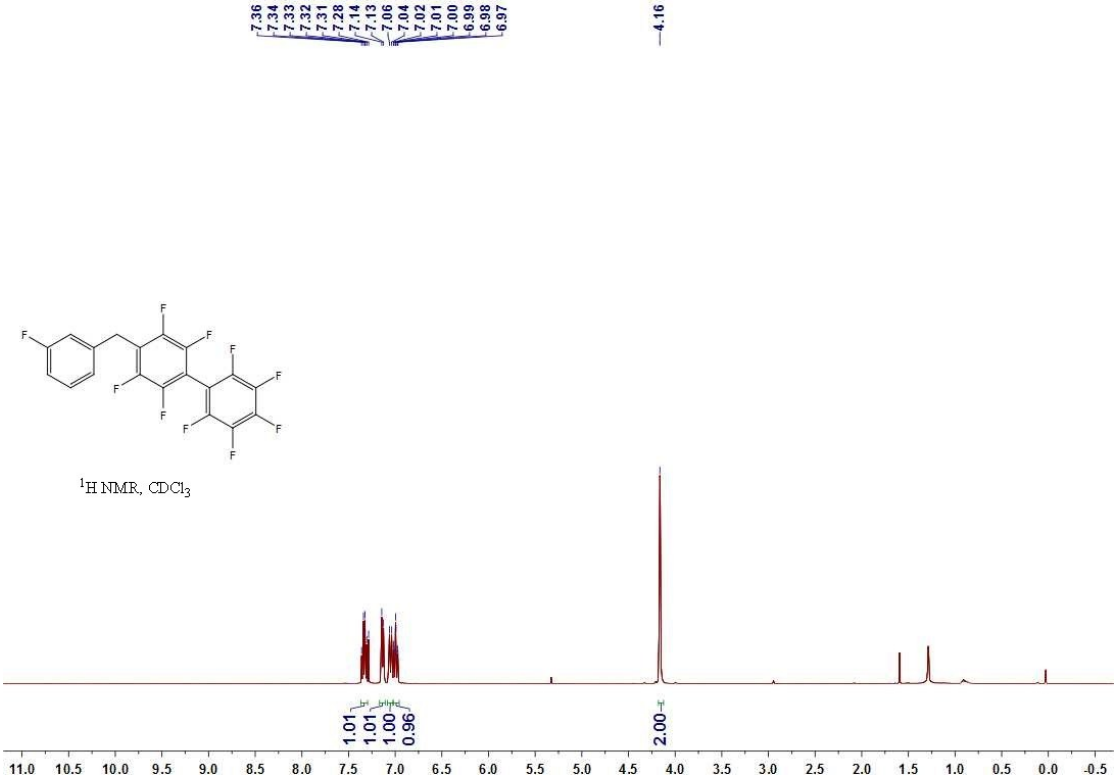
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(4-fluorobenzyl)-1,1'-biphenyl**

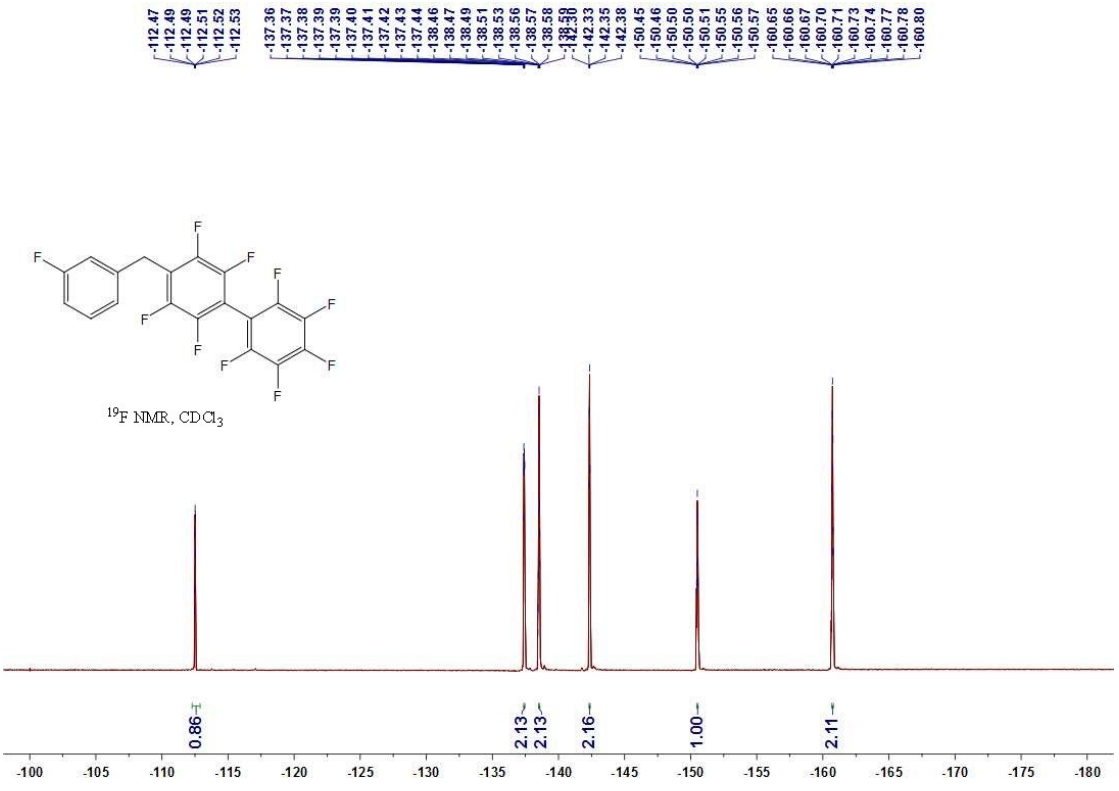


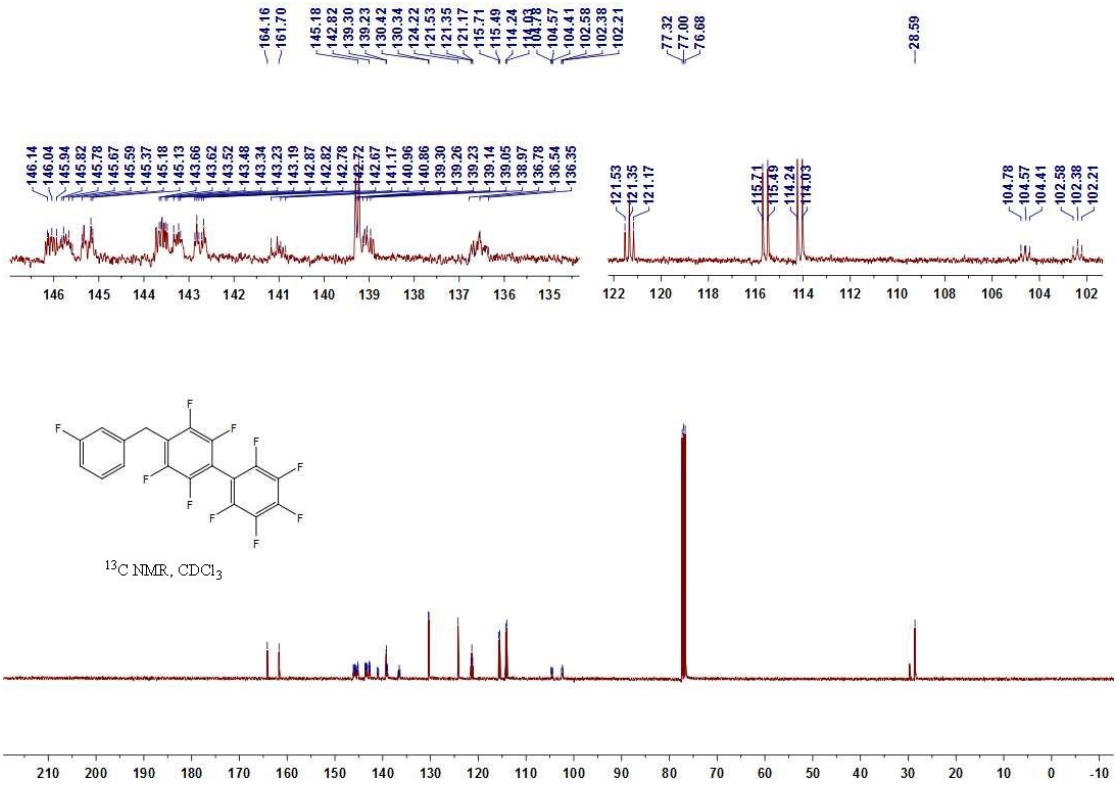

-115.55
-115.57
-115.57
-115.59
-115.64
-137.58
-137.62
-137.64
-137.71
-138.77
-138.79
-138.81
-138.84
-138.85
-138.86
-138.87
-138.90
-142.75
-142.77
-142.80
-142.84
-142.89
-150.72
-150.77
-150.83
-150.95
-160.90
-160.91
-160.95
-160.97
-161.01
-161.02
-161.04
-161.14
19F NMR, CDCl3
0.87
2.09
2.17
2.12
1.00
2.15
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180


163.14
160.70
145.84
145.39
145.24
143.63
142.89
136.61
132.81
130.21
130.13
122.21
122.03
115.79
104.45
104.26
102.68
102.49
102.31
77.32
77.00
76.68
28.10
146.01
145.84
145.73
145.39
145.24
143.63
143.39
143.23
142.89
142.78
141.02
139.14
139.10
139.02
136.74
136.61
136.41
132.81
130.21
130.13
122.21
122.03
121.84
115.79
115.58
104.64
104.45
104.26
102.68
102.49
102.31
13C NMR, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

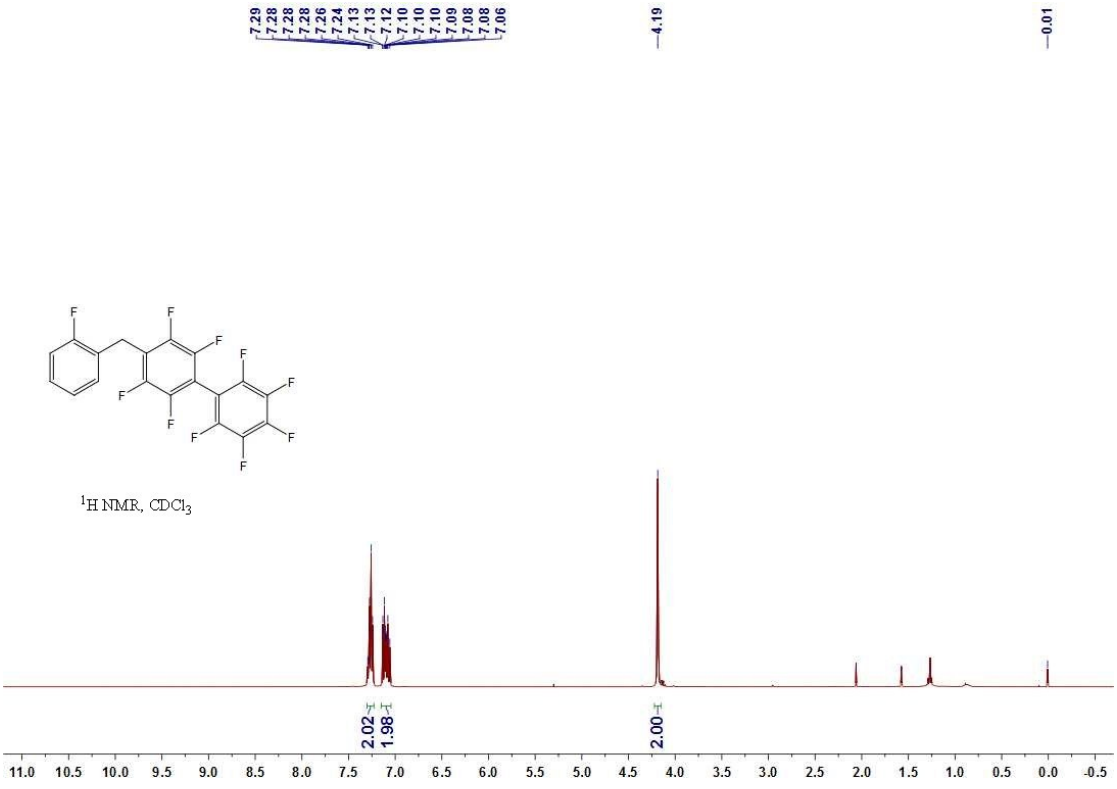
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(3-fluorobenzyl)-1,1'-biphenyl**

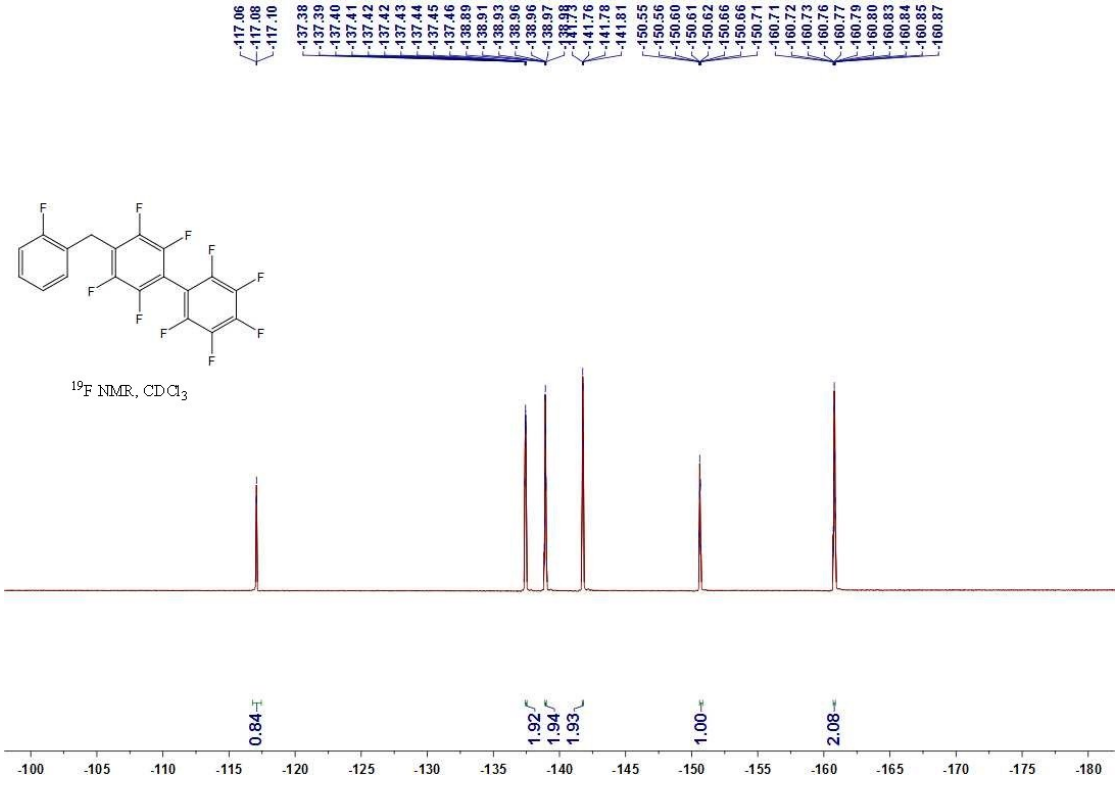


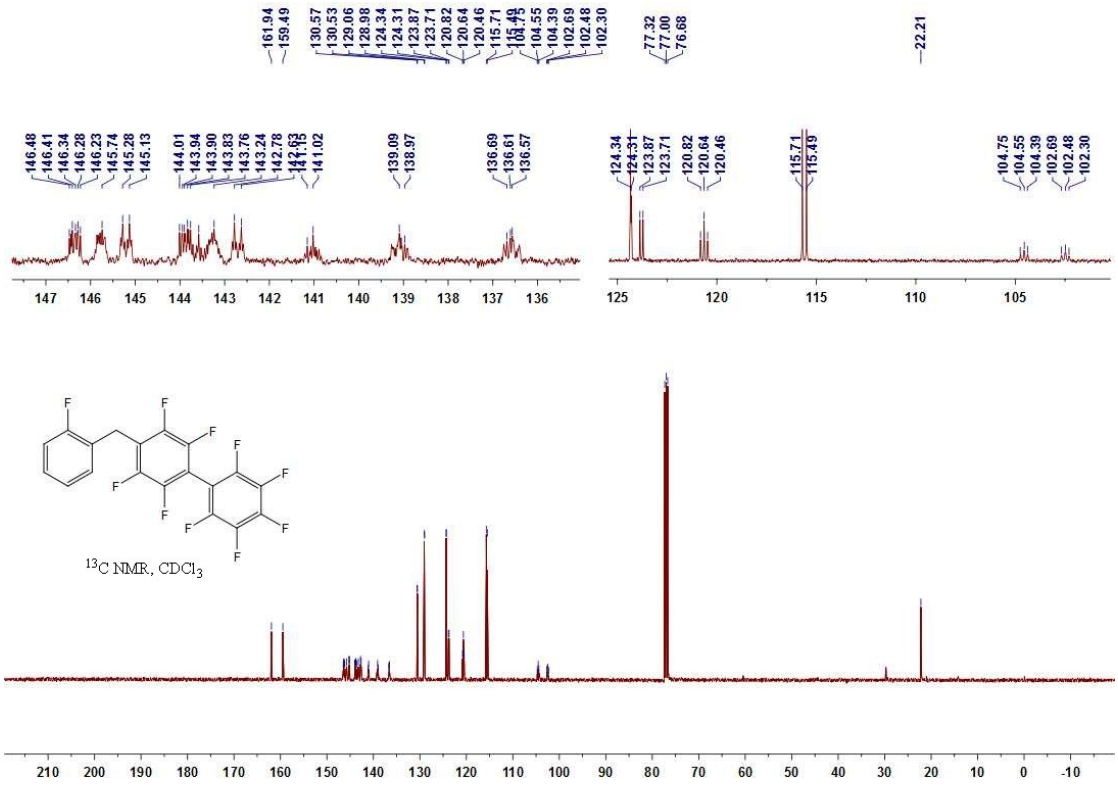




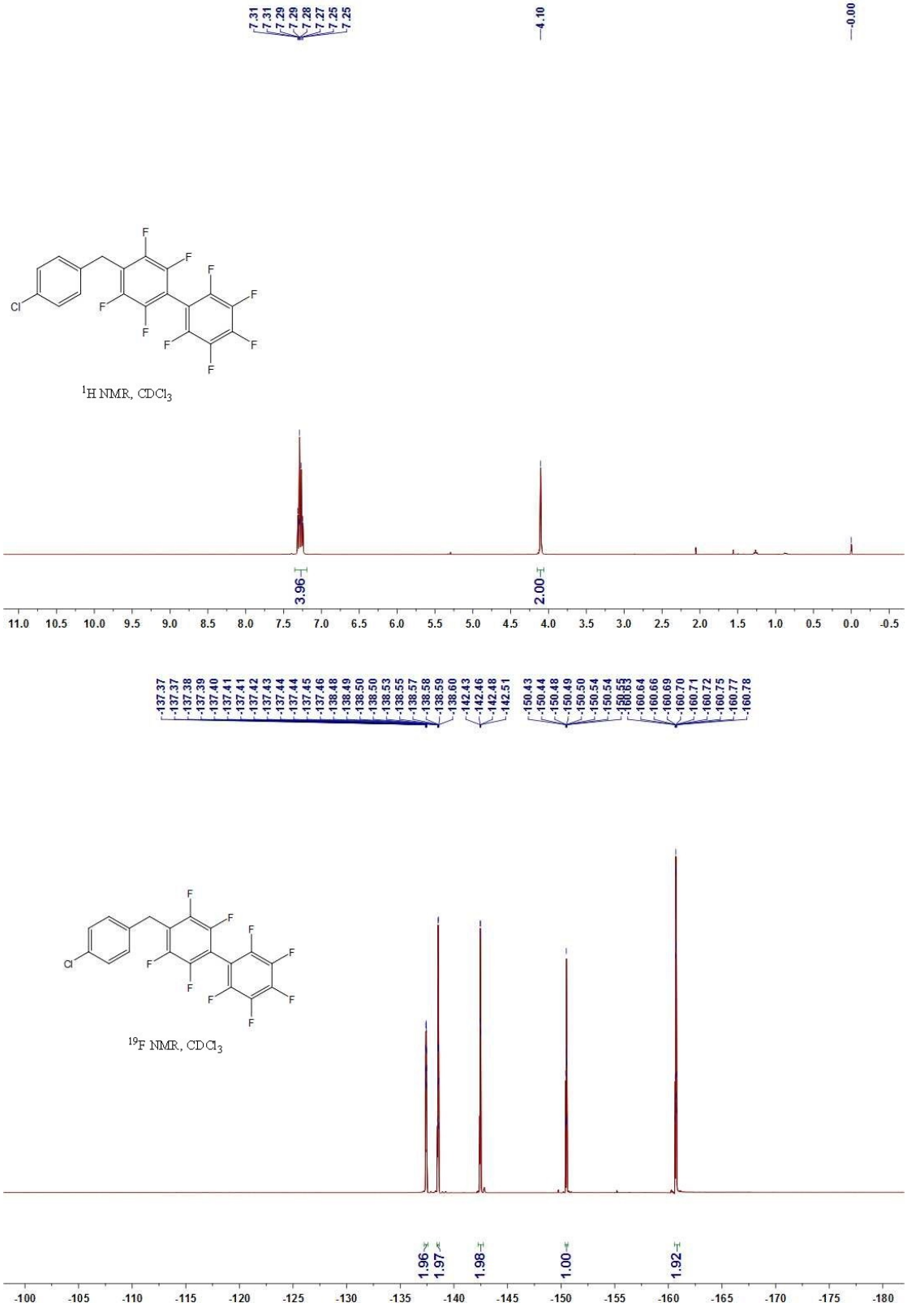
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(2-fluorobenzyl)-1,1'-biphenyl**

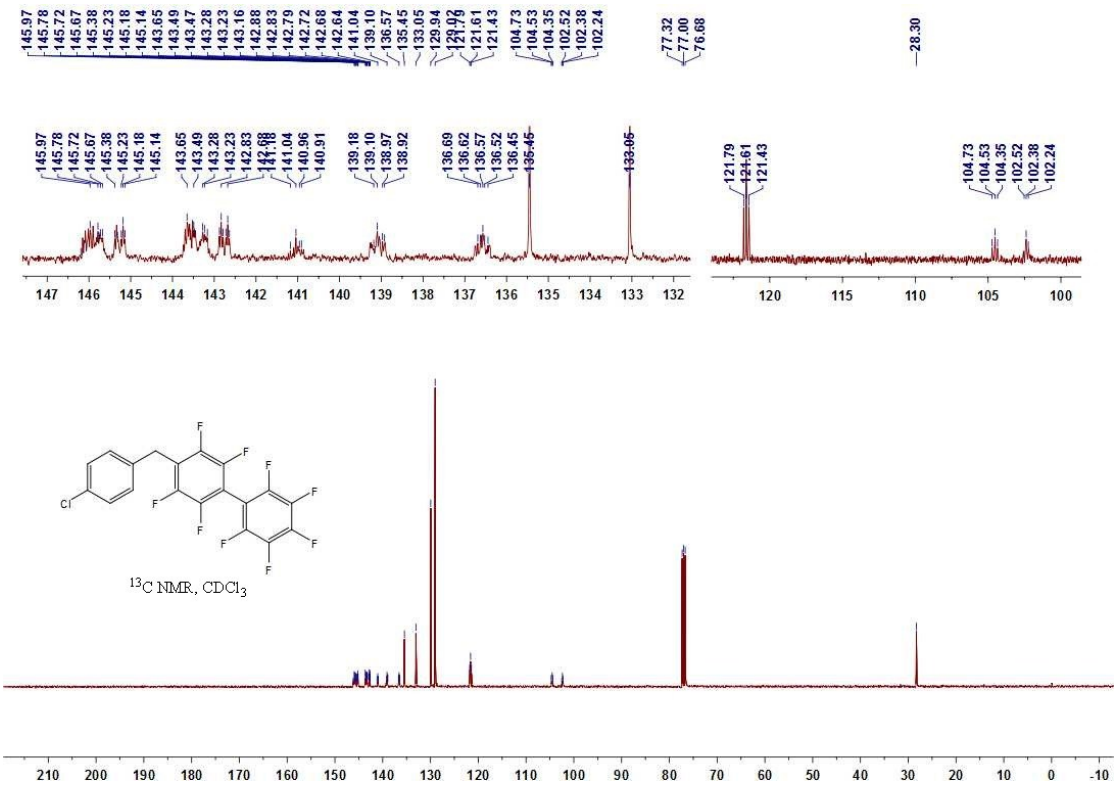



-117.06
-117.08
-117.10
-137.38
-137.39
-137.40
-137.41
-137.42
-137.42
-137.43
-137.44
-137.45
-137.46
-138.89
-138.91
-138.93
-138.96
-138.96
-138.97
-141.76
-141.78
-141.81
-150.55
-150.56
-150.60
-150.61
-150.62
-150.66
-150.66
-150.71
-160.71
-160.72
-160.73
-160.76
-160.77
-160.79
-160.80
-160.83
-160.84
-160.85
-160.87
^{19}F NMR, CDCl$_3$
0.84
1.92
1.94
1.93
1.00
2.08
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180

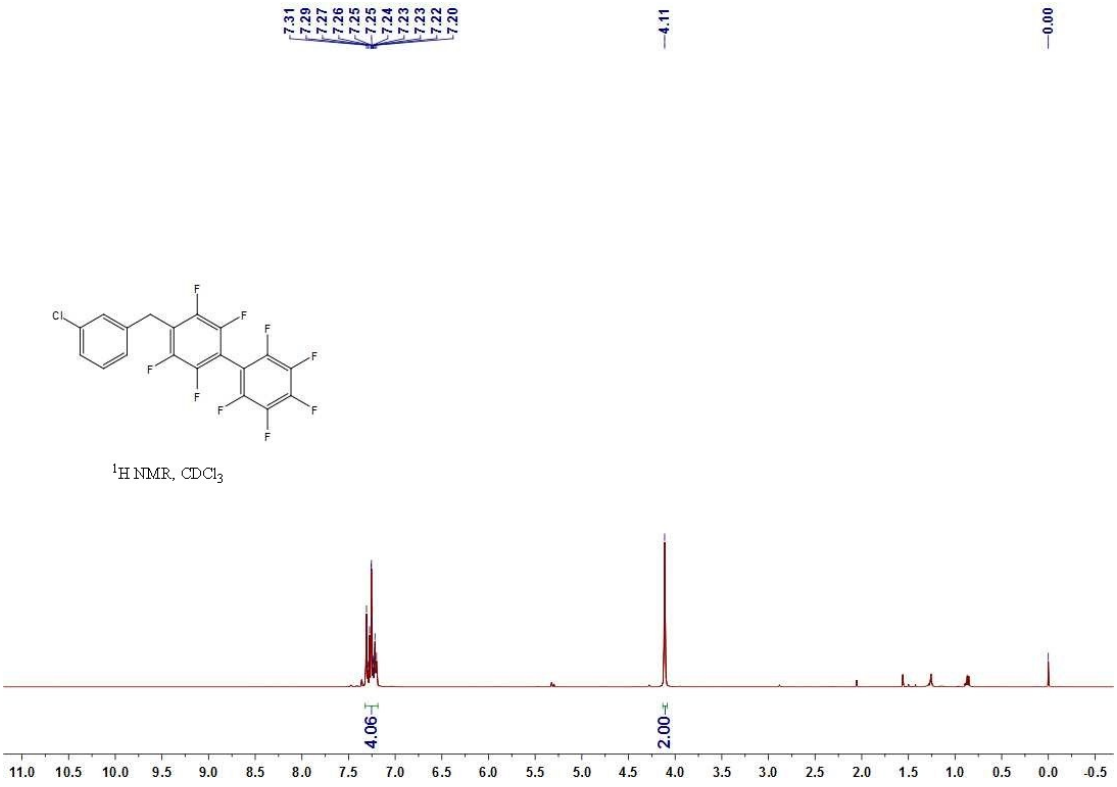

161.94
159.49
130.57
130.53
129.06
128.98
124.34
124.31
123.87
123.71
120.82
120.64
120.46
115.71
104.55
104.39
102.69
102.48
102.30
77.32
77.00
76.68
22.21
146.48
146.41
146.34
146.28
146.23
145.74
145.28
145.13
144.01
143.94
143.90
143.83
143.76
143.24
142.78
141.02
139.09
138.97
136.69
136.61
136.57
124.34
124.31
123.87
123.71
120.82
120.64
120.46
115.71
115.49
104.75
104.55
104.39
102.69
102.48
102.30
147 146 145 144 143 142 141 140 139 138 137 136
125 120 115 110 105
^{13}C NMR, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

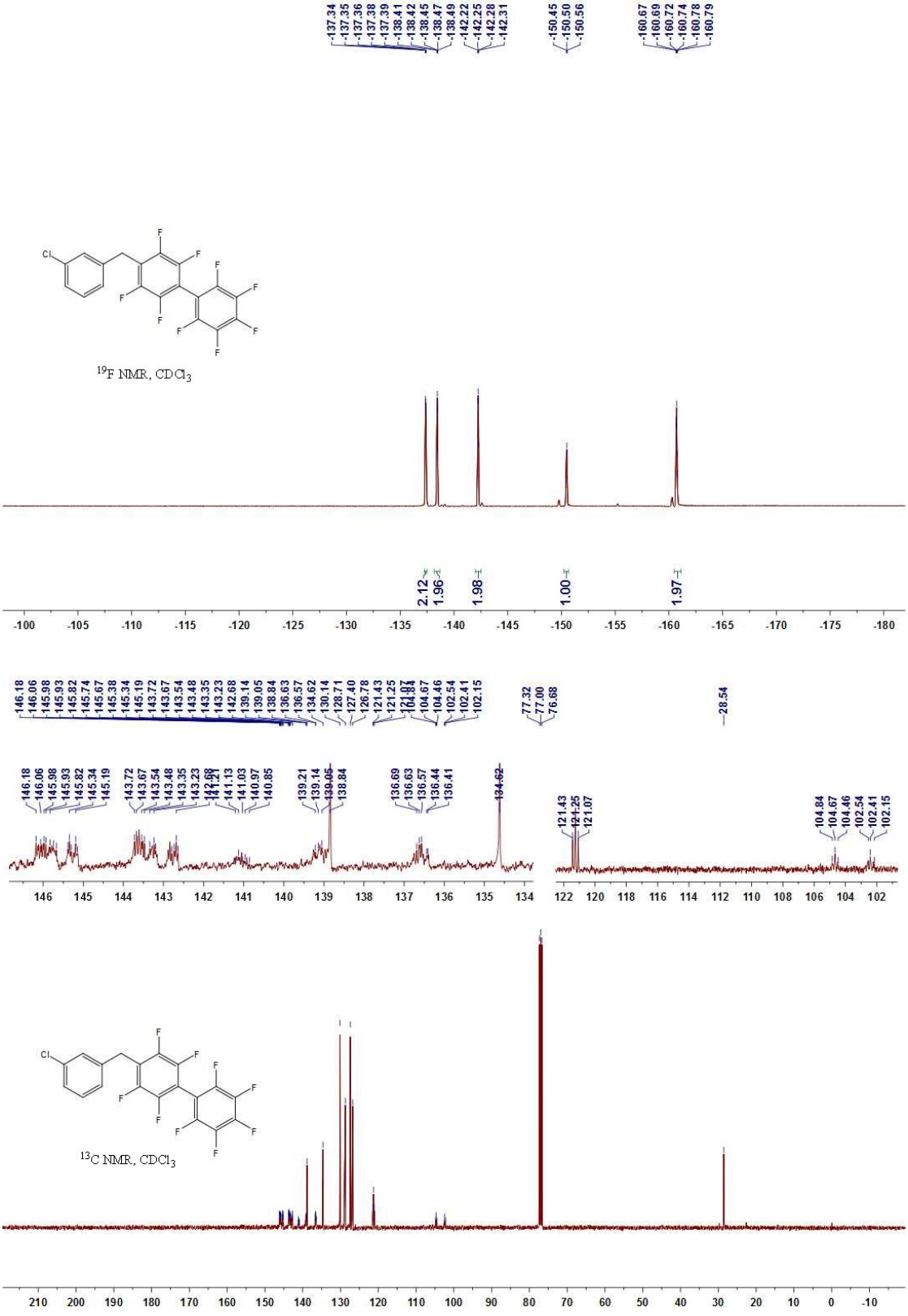
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-(4-chlorobenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl**



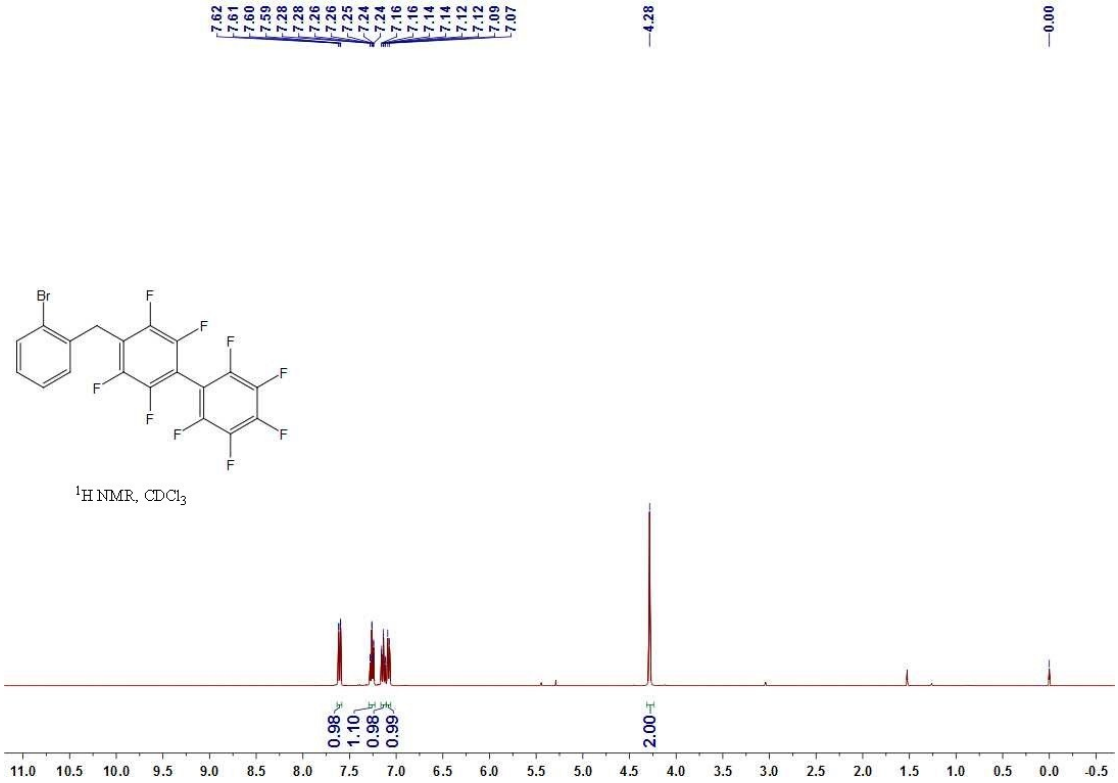


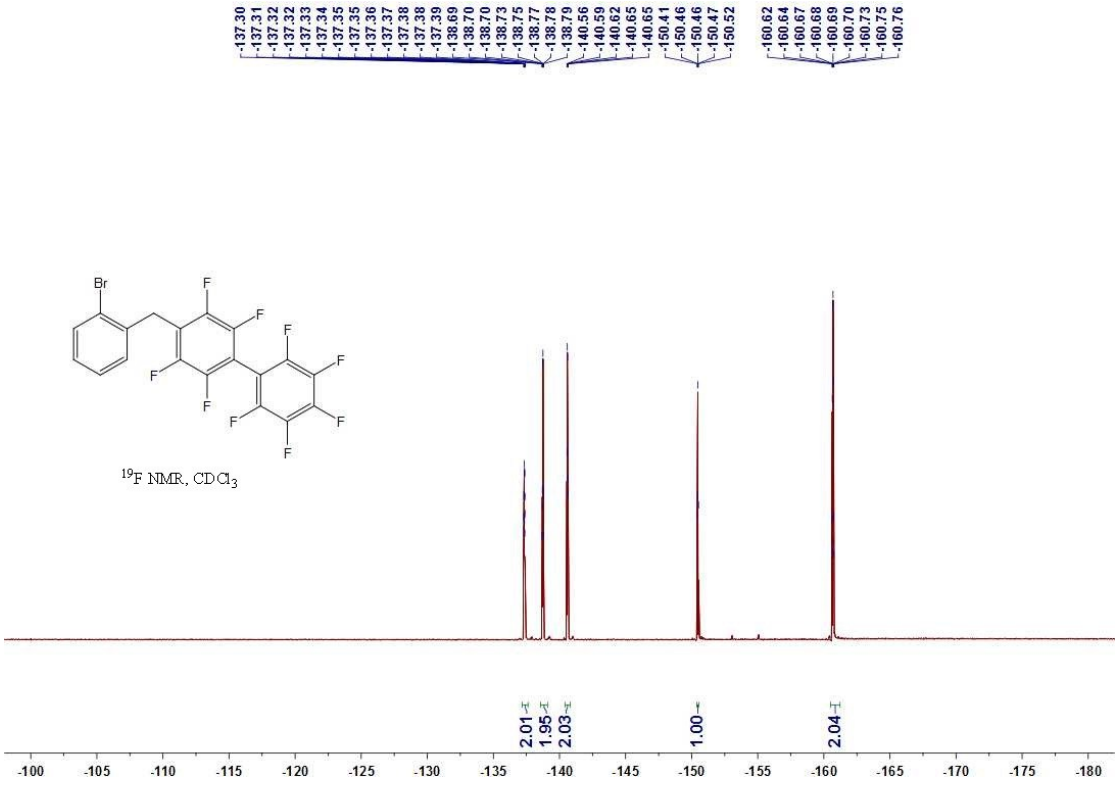
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-(3-chlorobenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl**

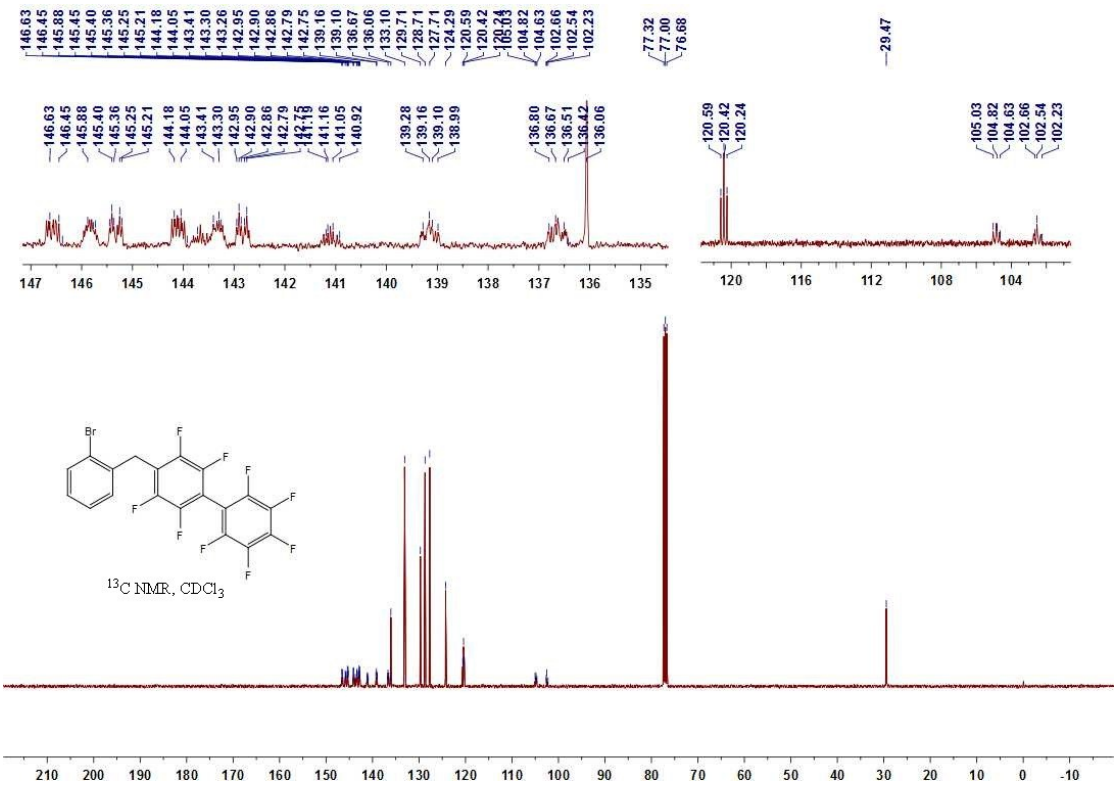



19F NMR, CDCl3
13C NMR, CDCl3

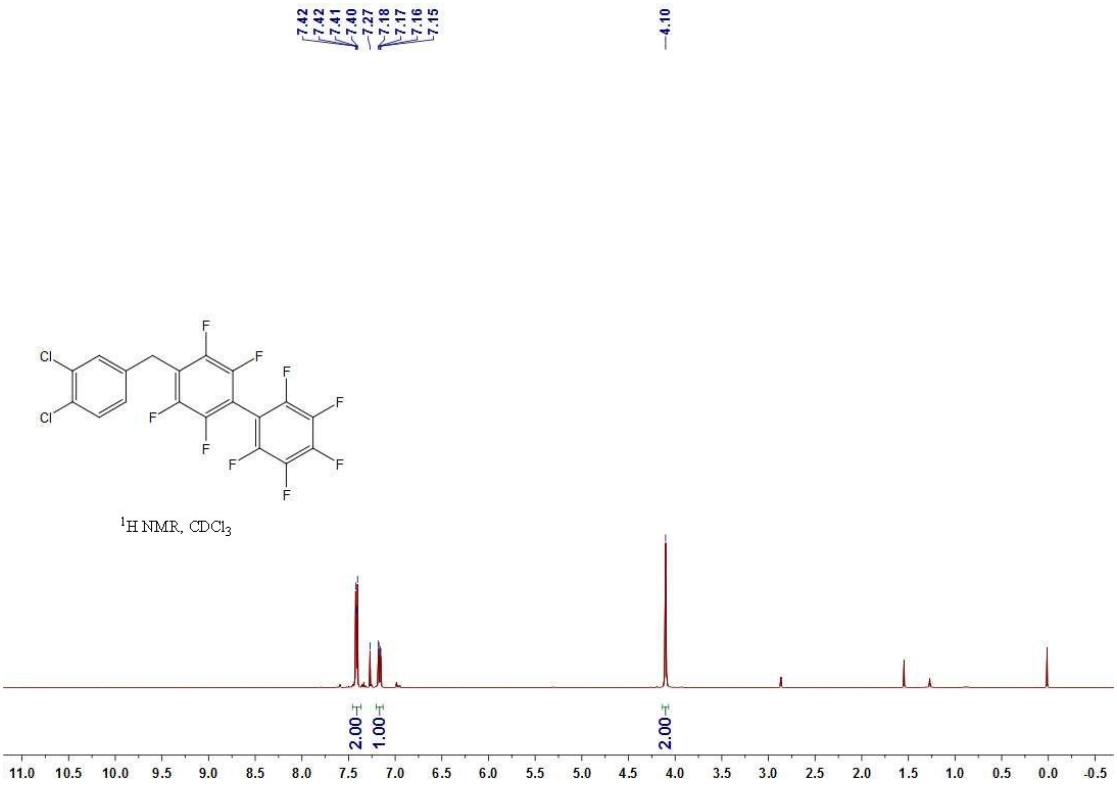
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-(2-bromobenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl**

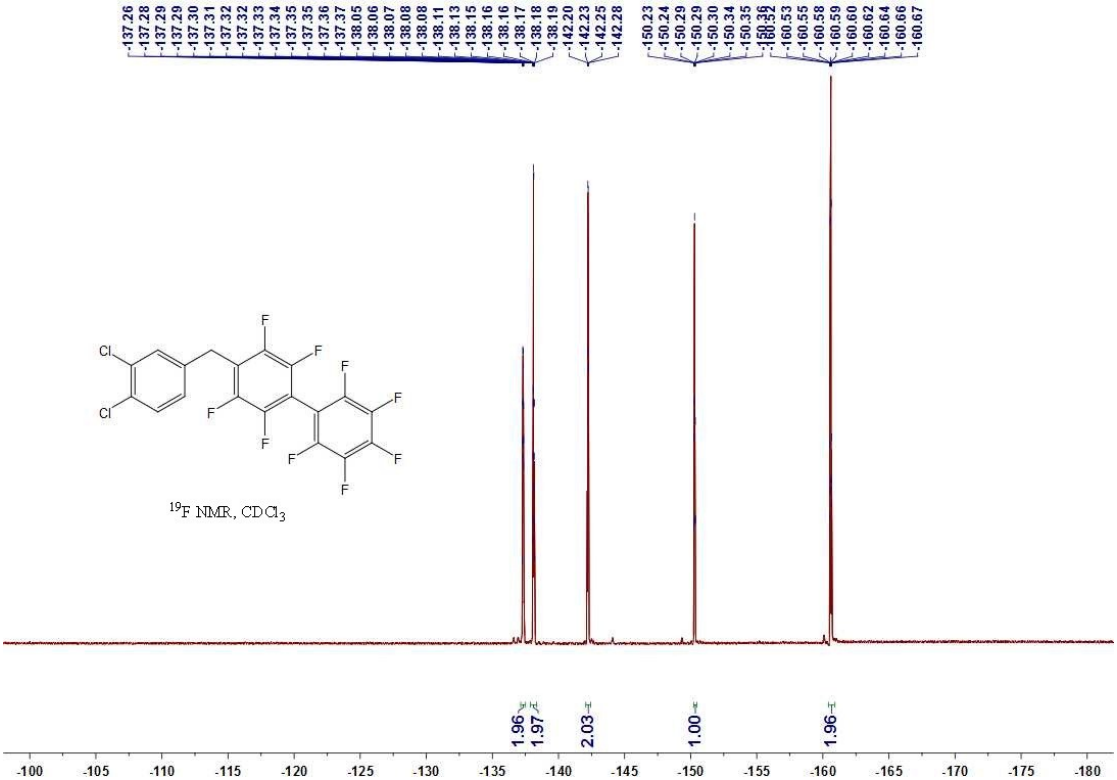


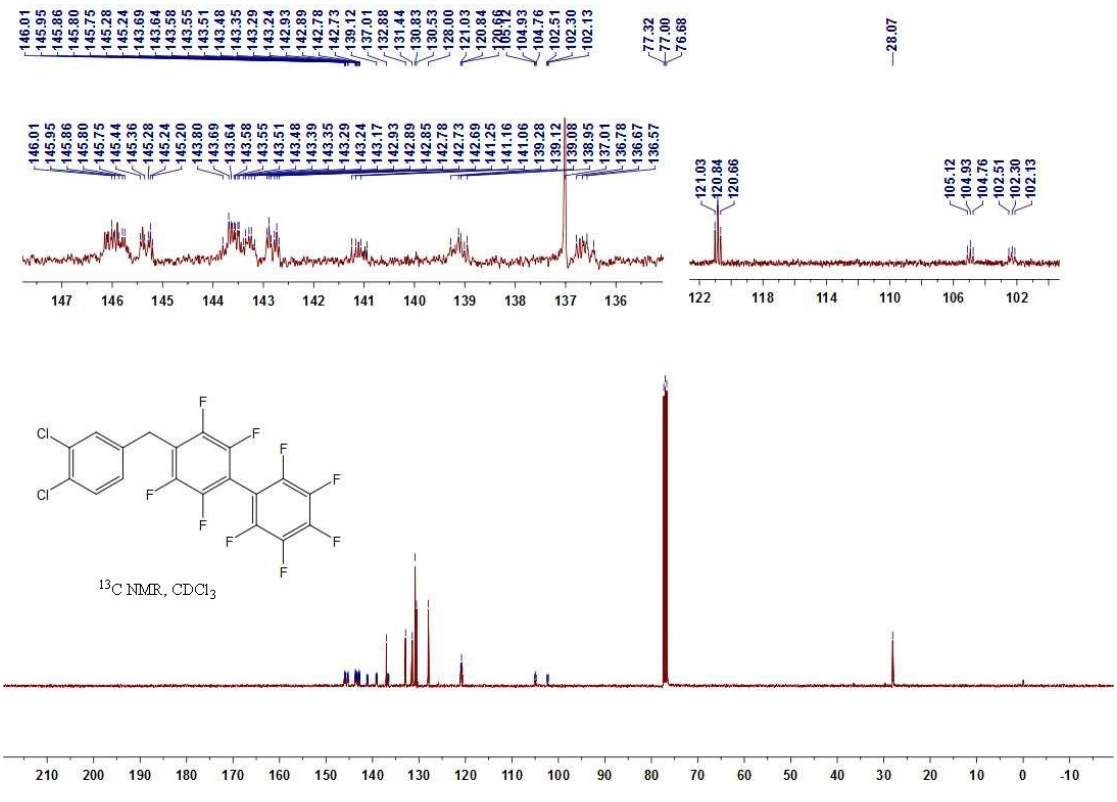




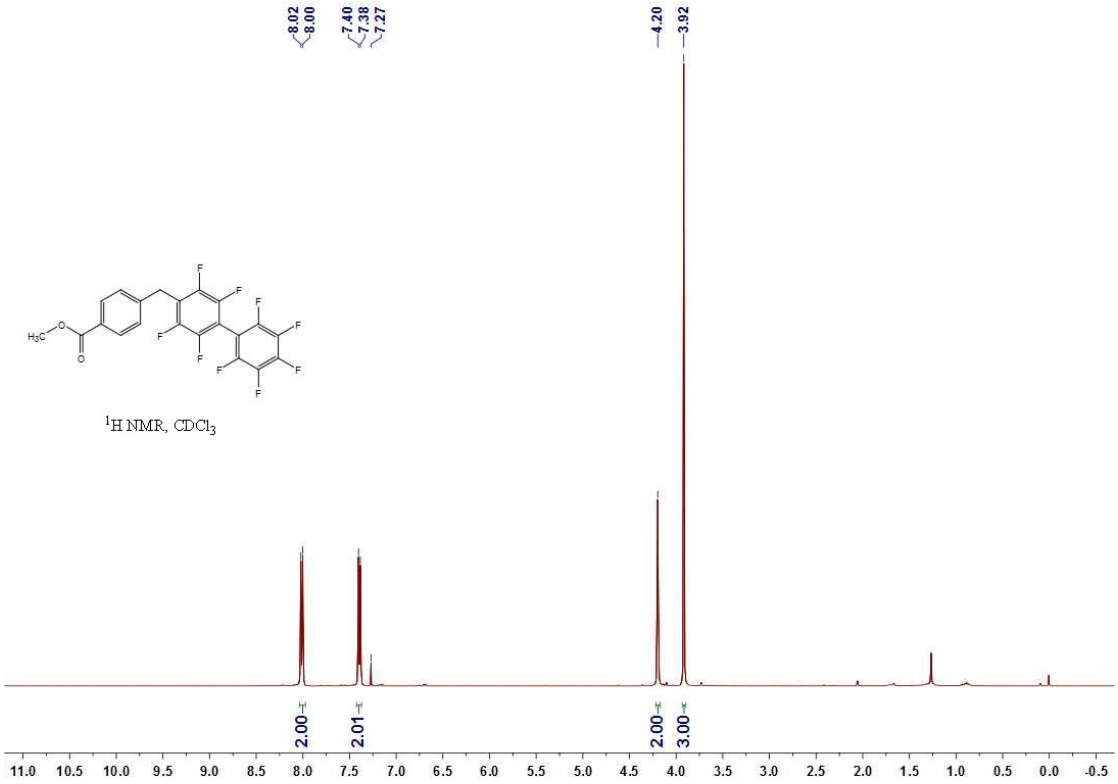
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-(3,4-dichlorobenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro -1,1'-biphenyl**



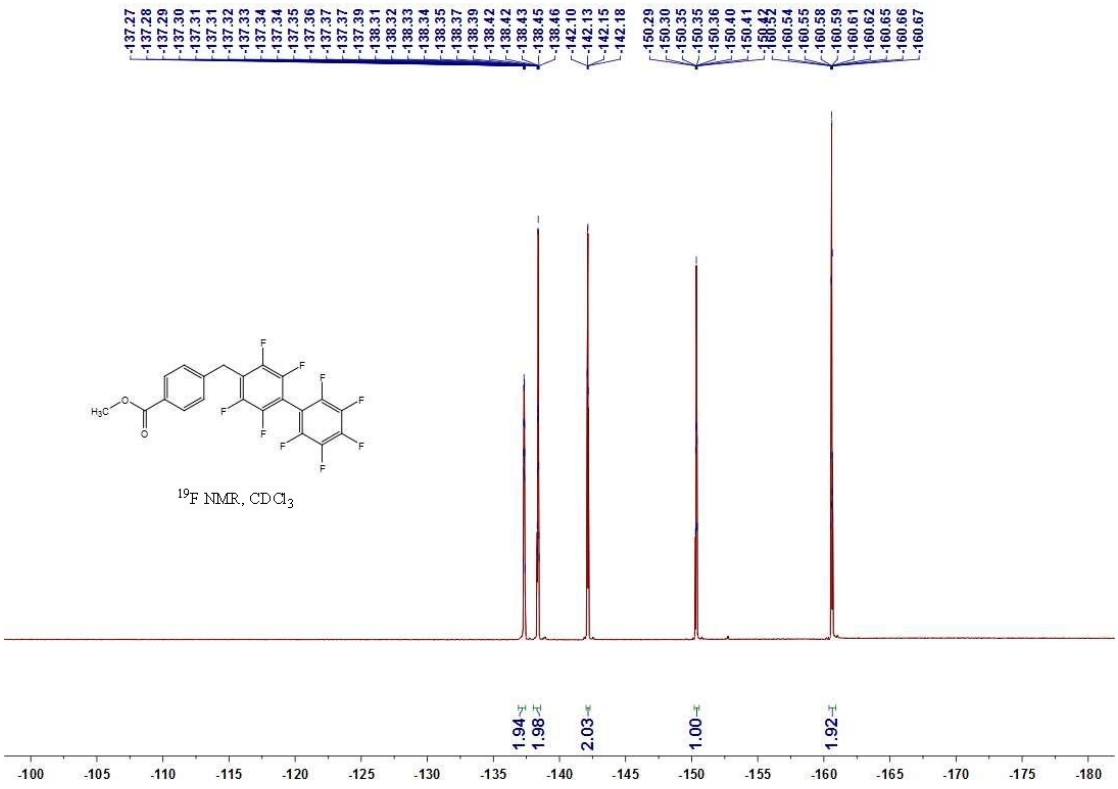

137.26
137.28
137.29
137.29
137.30
137.31
137.32
137.32
137.33
137.34
137.35
137.35
137.36
137.37
138.05
138.06
138.07
138.08
138.08
138.11
138.13
138.15
138.16
138.16
138.17
138.18
138.19
142.20
142.23
142.25
142.28
150.23
150.24
150.29
150.29
150.30
150.34
150.35
160.53
160.55
160.58
160.59
160.60
160.62
160.64
160.66
160.67
Cl
Cl
F
F
F
F
F
F
F
F
F
^{19}F NMR, $CDCl_3$
1.96
1.97
2.03
1.00
1.96
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180


146.01
145.95
145.86
145.80
145.75
145.28
145.24
143.69
143.64
143.58
143.55
143.51
143.48
143.35
143.29
143.24
142.93
142.89
142.78
142.73
139.12
137.01
132.88
131.44
130.83
130.53
128.00
121.03
120.84
105.12
104.93
104.76
102.51
102.30
102.13
77.32
77.00
76.68
28.07
146.01
145.95
145.86
145.80
145.75
145.44
145.36
145.28
145.24
145.20
143.80
143.69
143.64
143.58
143.55
143.51
143.48
143.39
143.35
143.29
143.24
143.17
142.93
142.89
142.85
142.78
142.73
142.69
141.25
141.16
141.06
139.28
139.12
139.08
138.95
137.01
136.78
136.67
136.57
121.03
120.84
120.66
105.12
104.93
104.76
102.51
102.30
102.13
147
146
145
144
143
142
141
140
139
138
137
136
122
118
114
110
106
102
Cl
Cl
F
F
F
F
F
F
F
F
F
^{13}C NMR, $CDCl_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

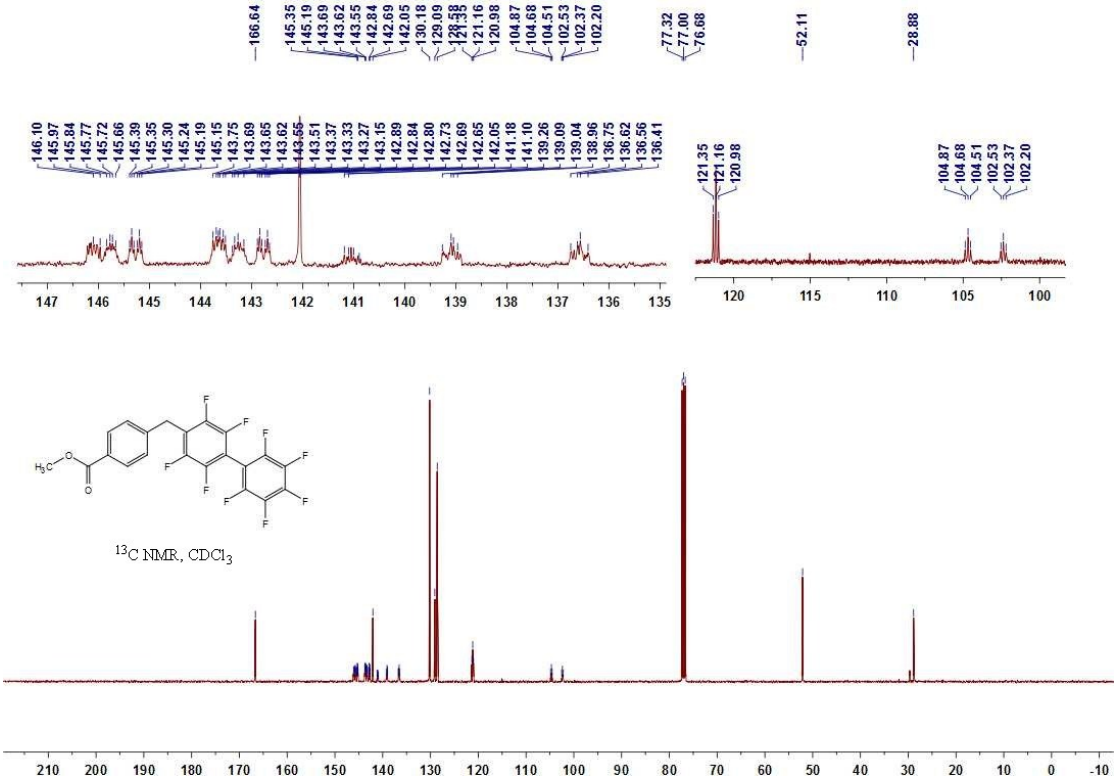
^{1}H, ^{19}F and ^{13}C NMR spectra of **methyl 4-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)benzoate**



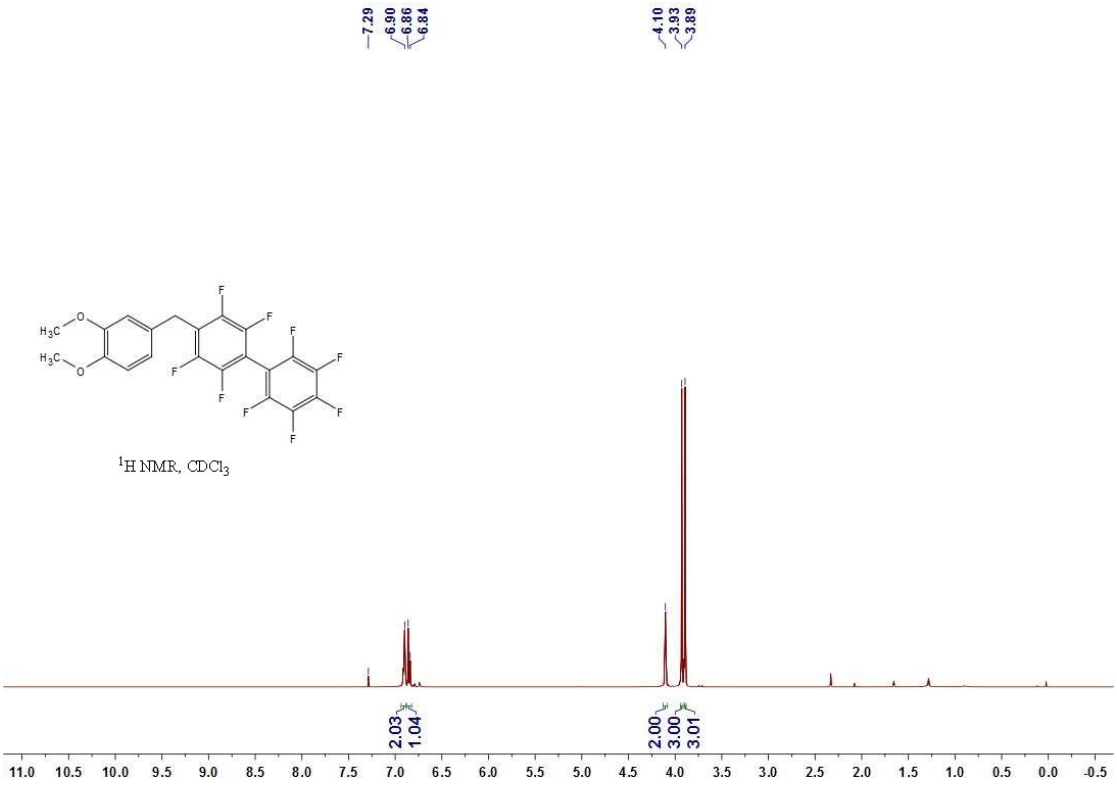
^{1}H NMR, $CDCl_3$

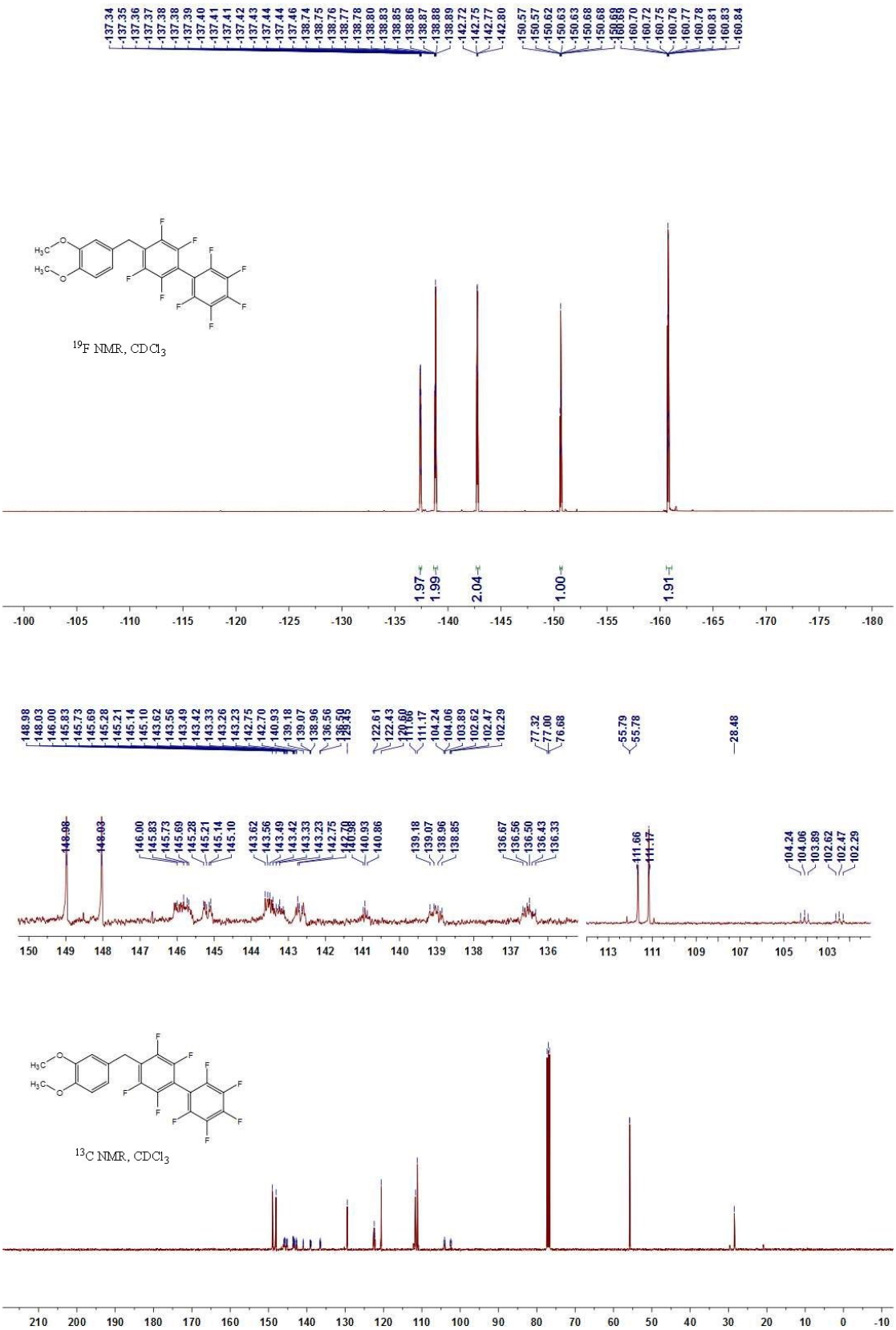


^{19}F NMR, $CDCl_3$

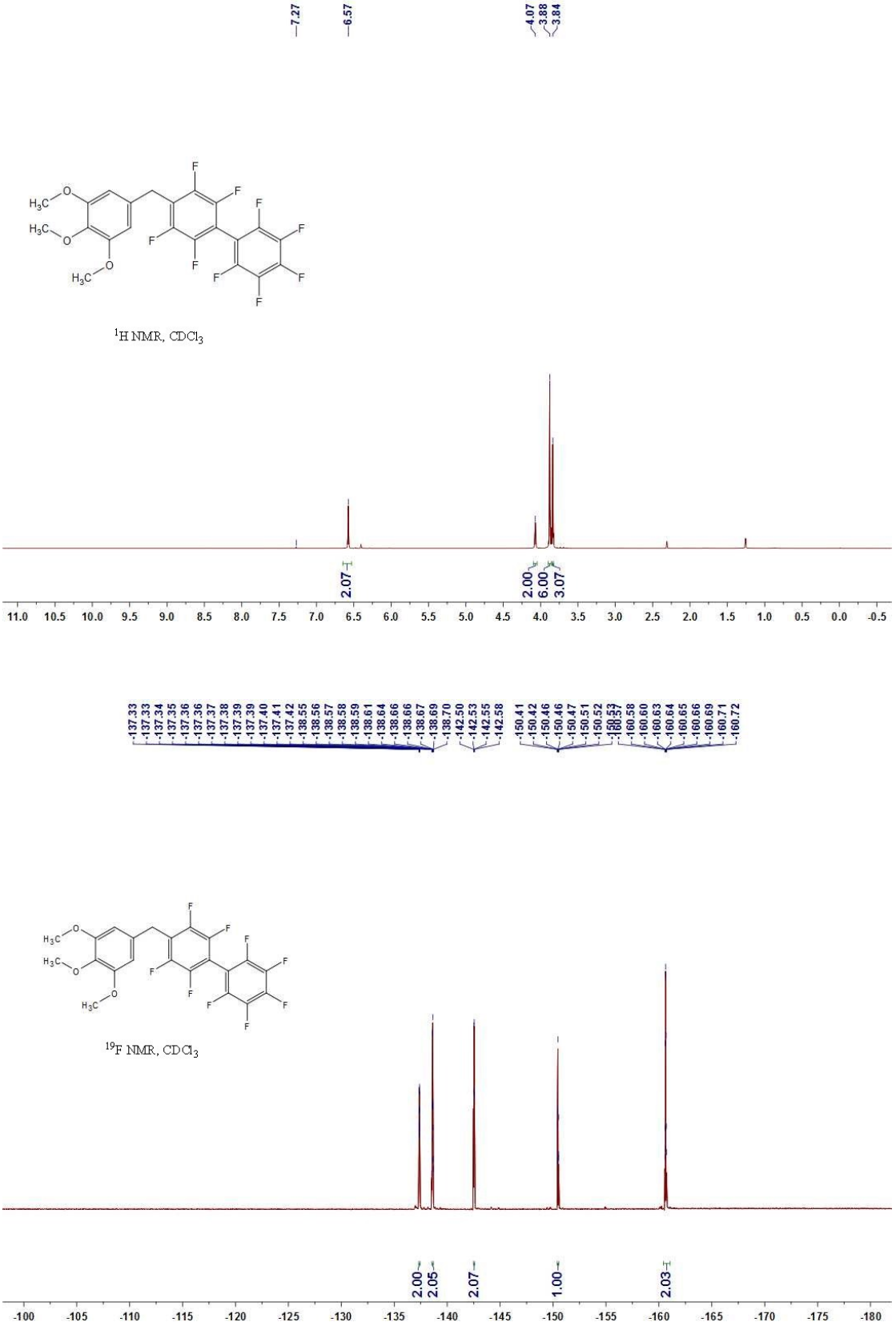


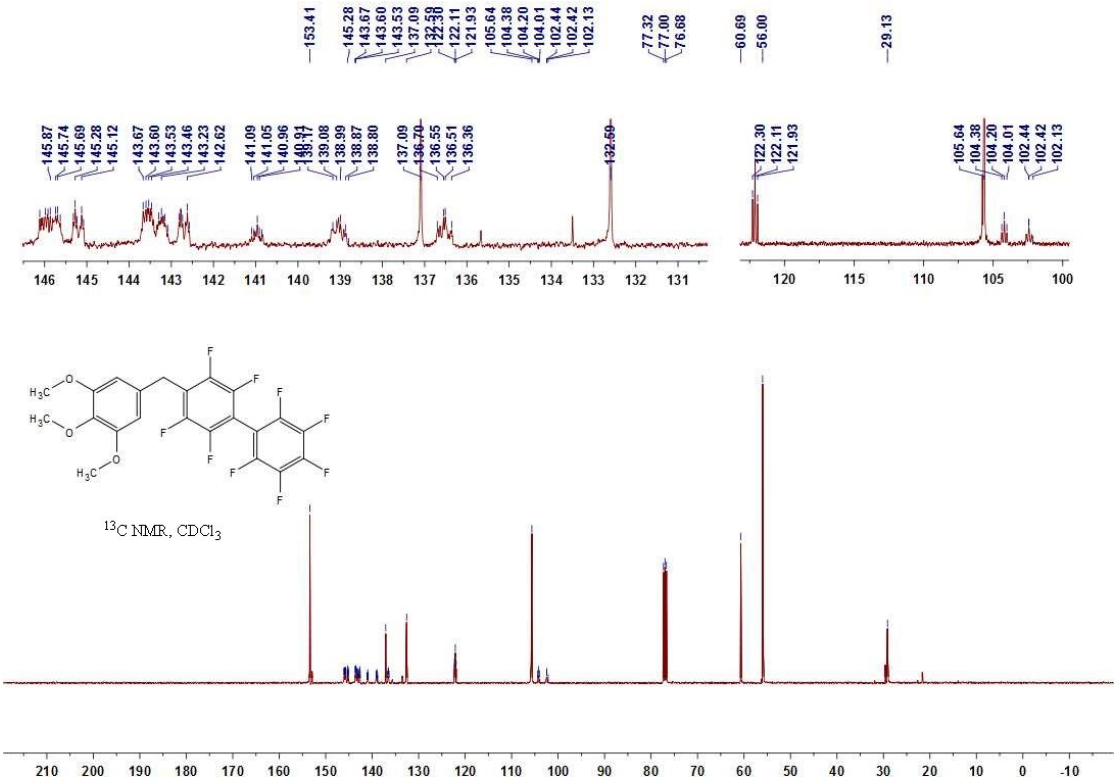
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-(3,4-dimethoxybenzyl)-2,2',3,3',4',5,5',6,6'-nonafluoro -1,1'-biphenyl**



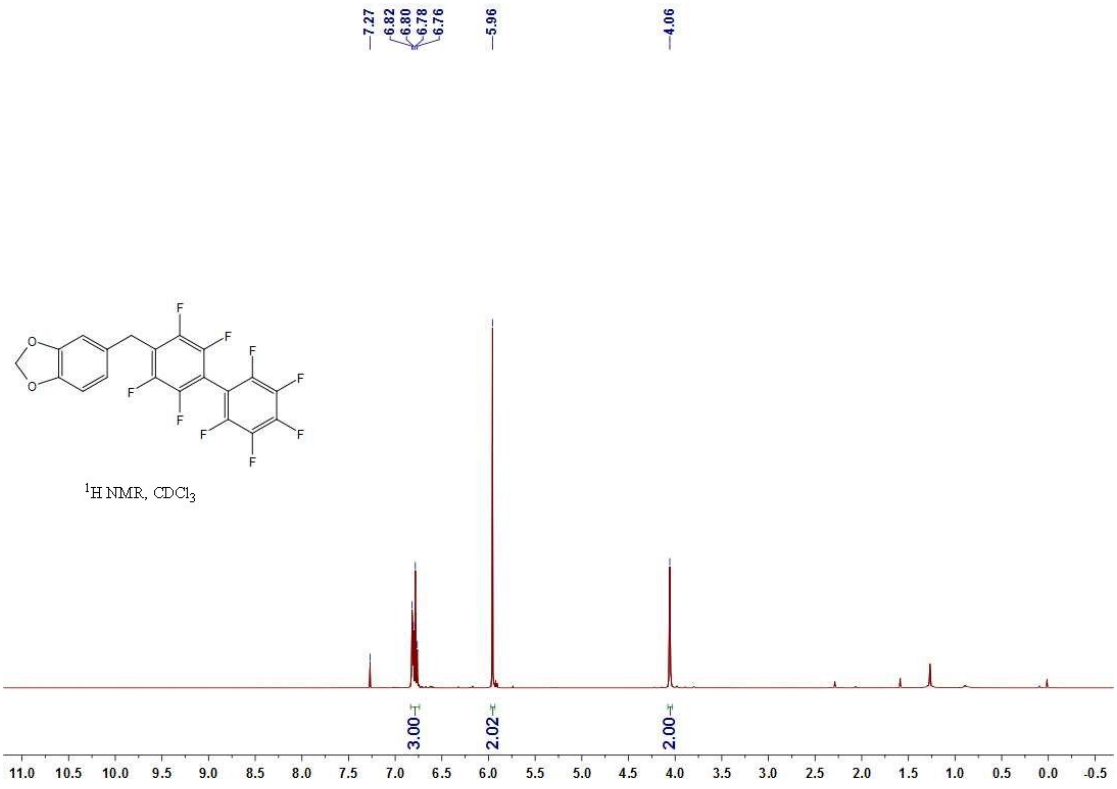

^{19}F NMR, $CDCl_3$
^{13}C NMR, $CDCl_3$

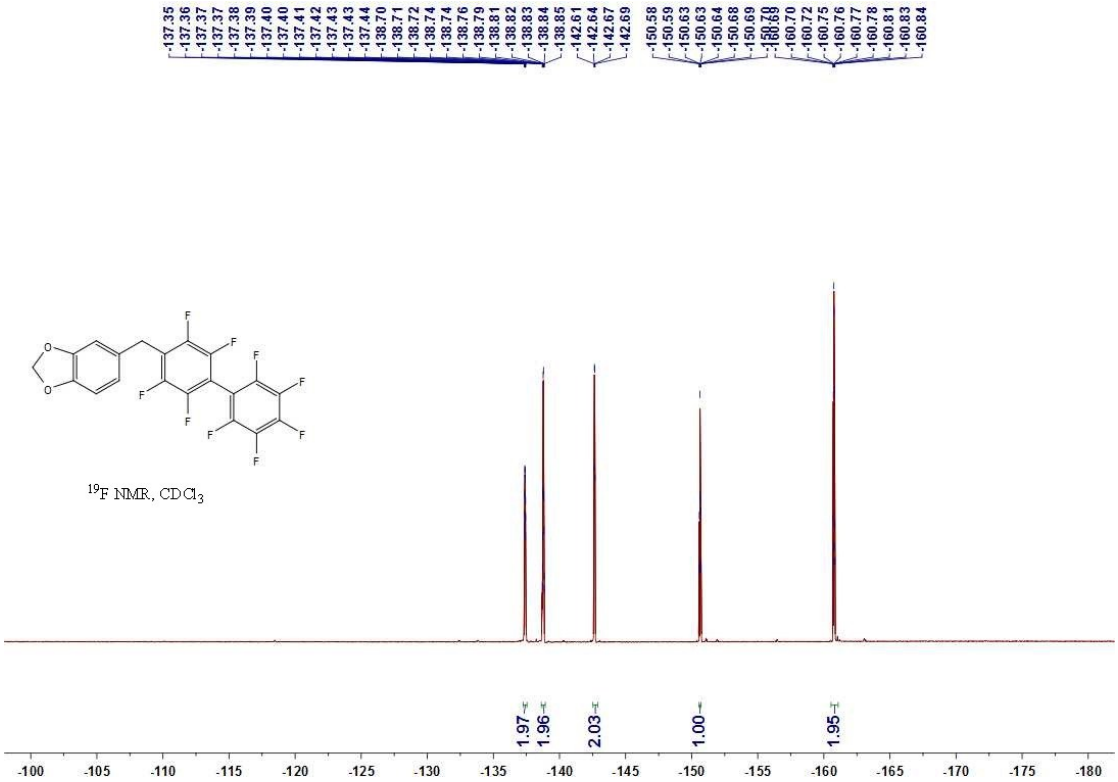
^{1}H, ^{19}F and ^{13}C NMR spectra of **2,2',3,3',4,5,5',6,6'-nonafluoro-4'-(3,4,5-trimethoxybenzyl) -1,1'-biphenyl**

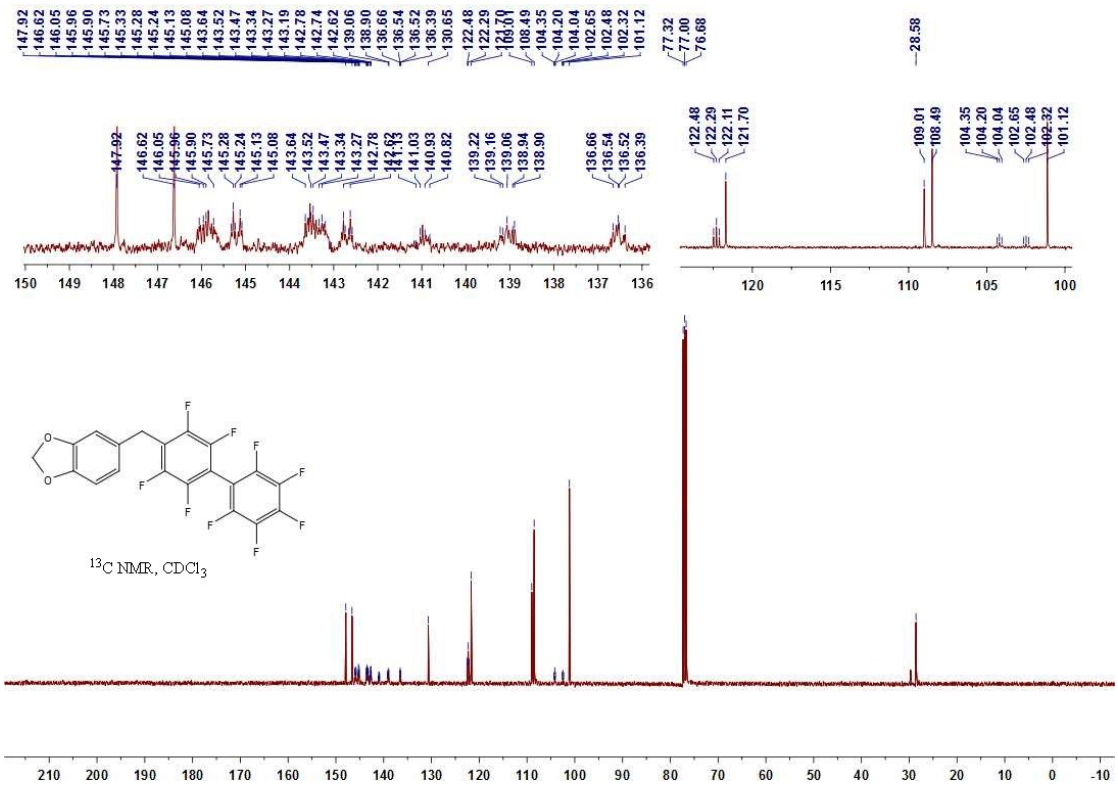




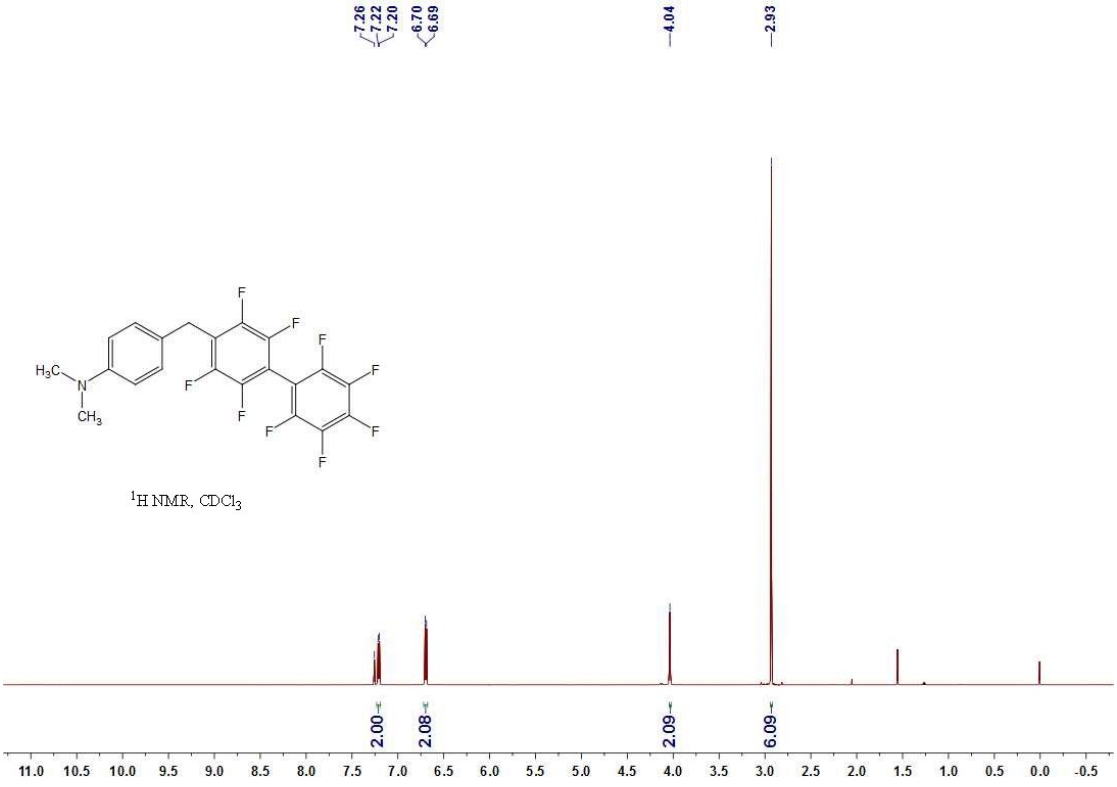
^{1}H, ^{19}F and ^{13}C NMR spectra of **5-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)benzo[d][1,3] dioxole**



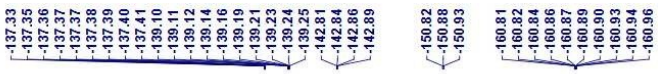

^{19}F NMR, $CDCl_3$
1.97
1.96
2.03
1.00
1.95

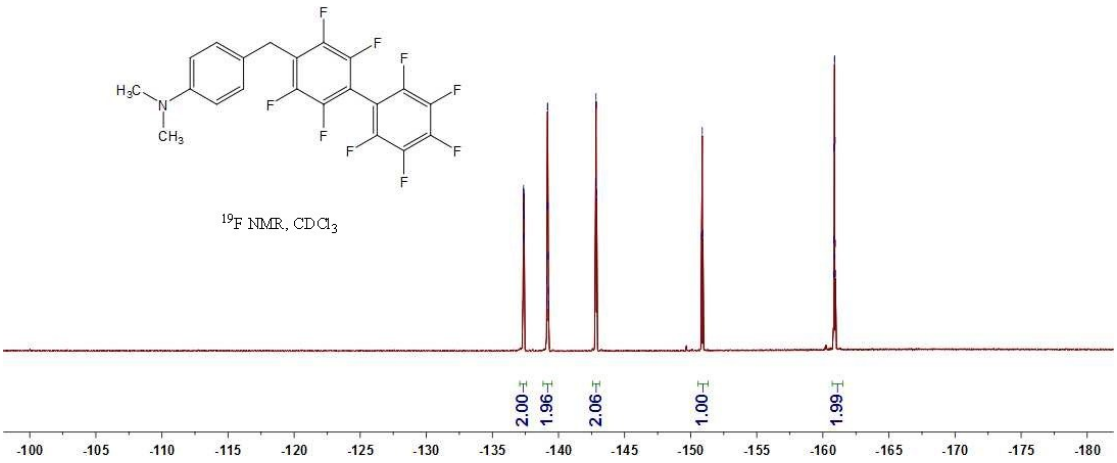

^{13}C NMR, $CDCl_3$

^{1}H, ^{19}F and ^{13}C NMR spectra of ***N,N*-dimethyl-4-((perfluoro-[1,1'-biphenyl]-4-yl)methyl) aniline**

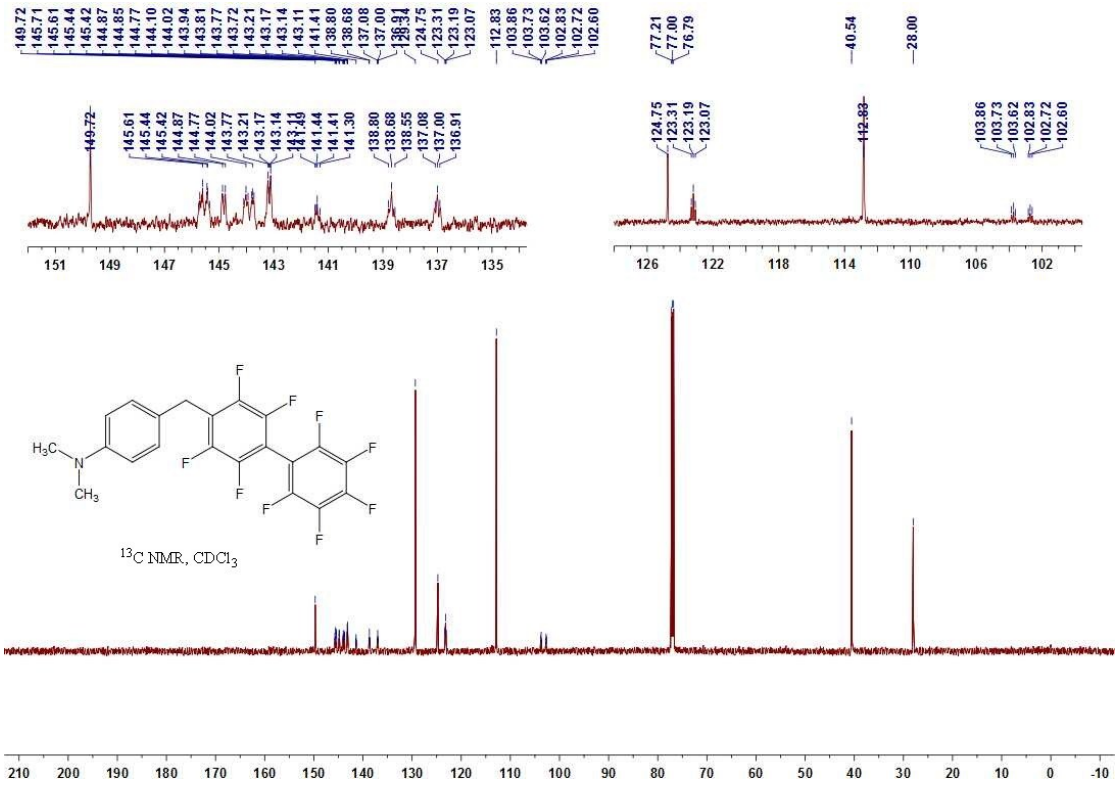


^{1}H NMR, $CDCl_3$

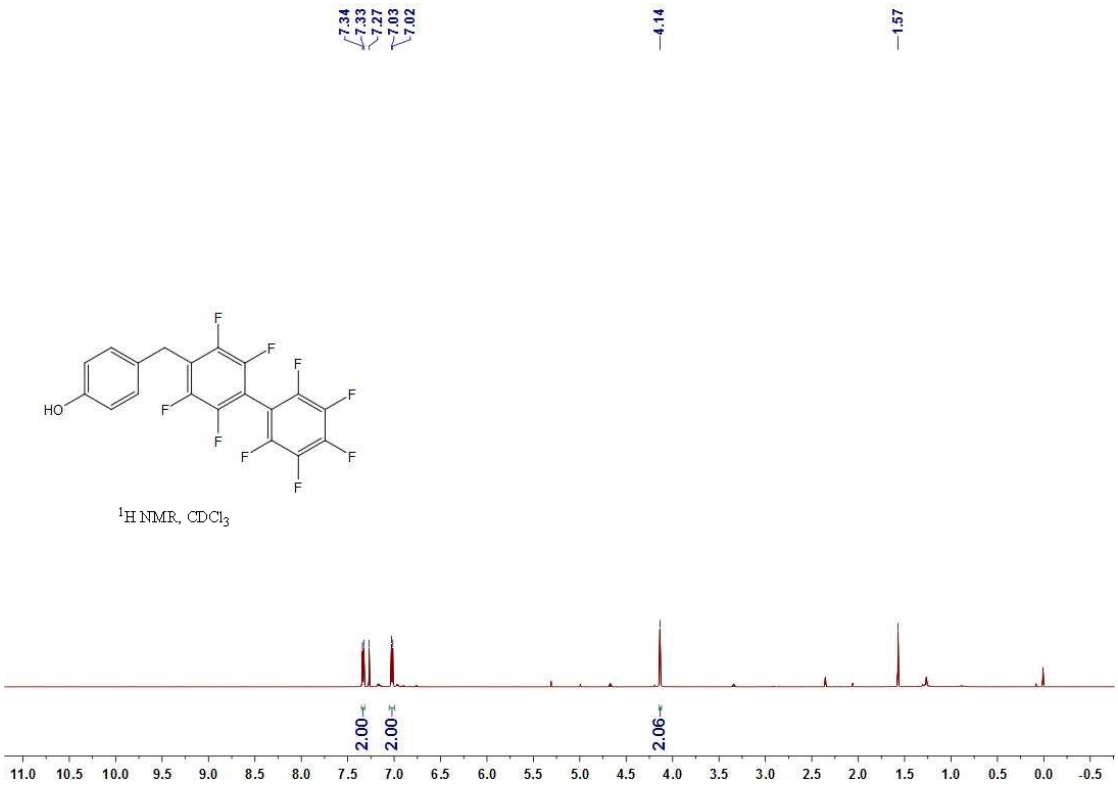


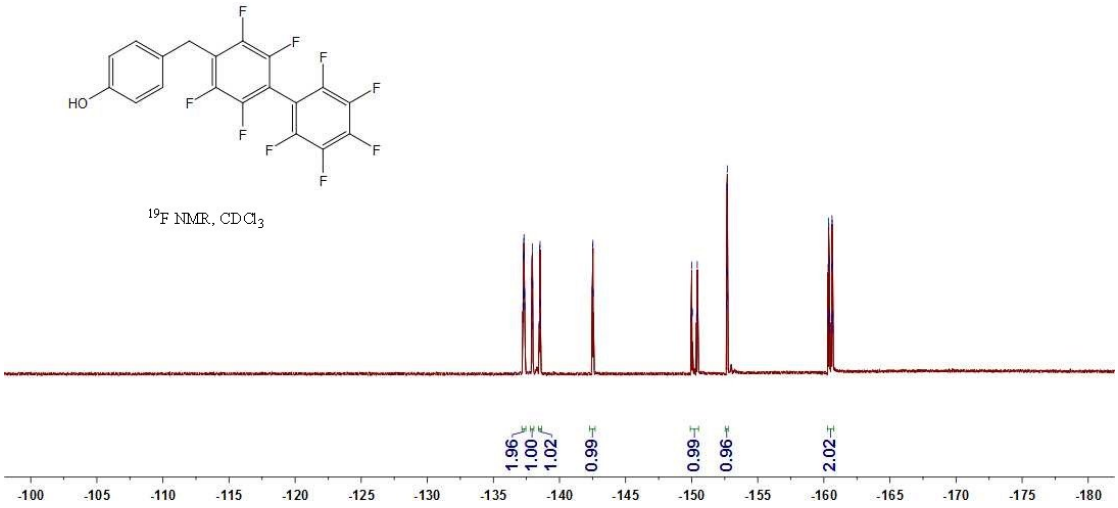


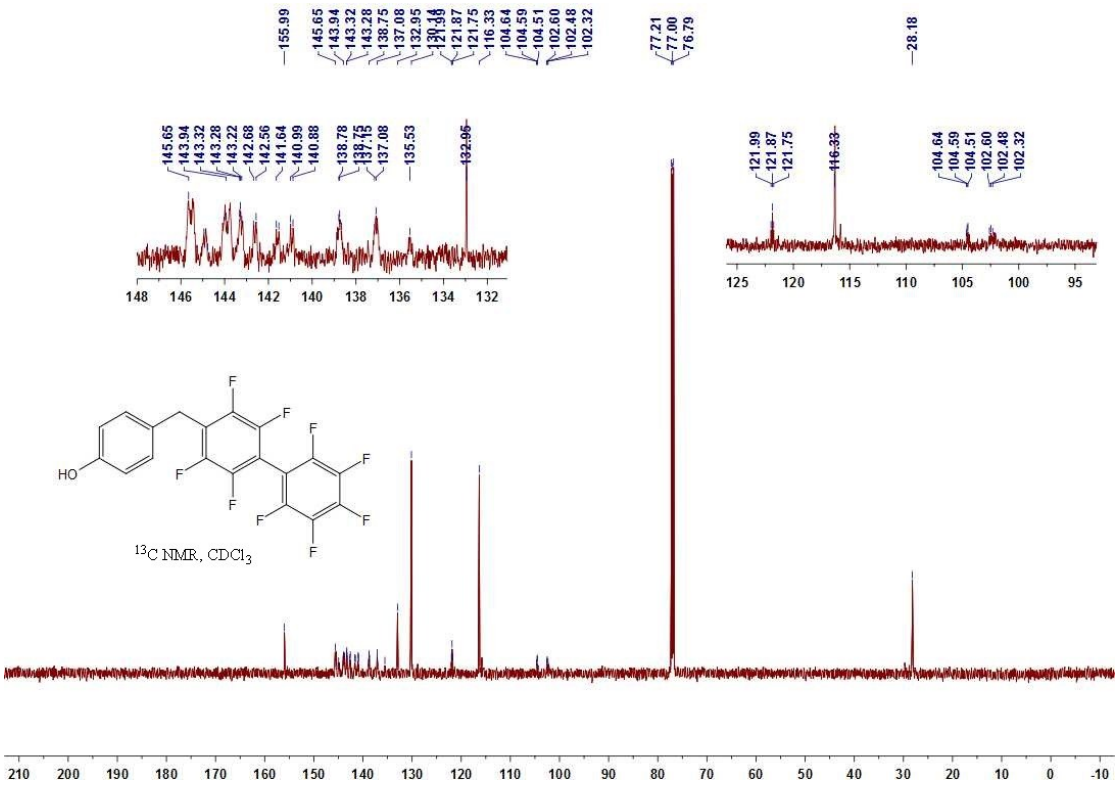
^{19}F NMR, $CDCl_3$



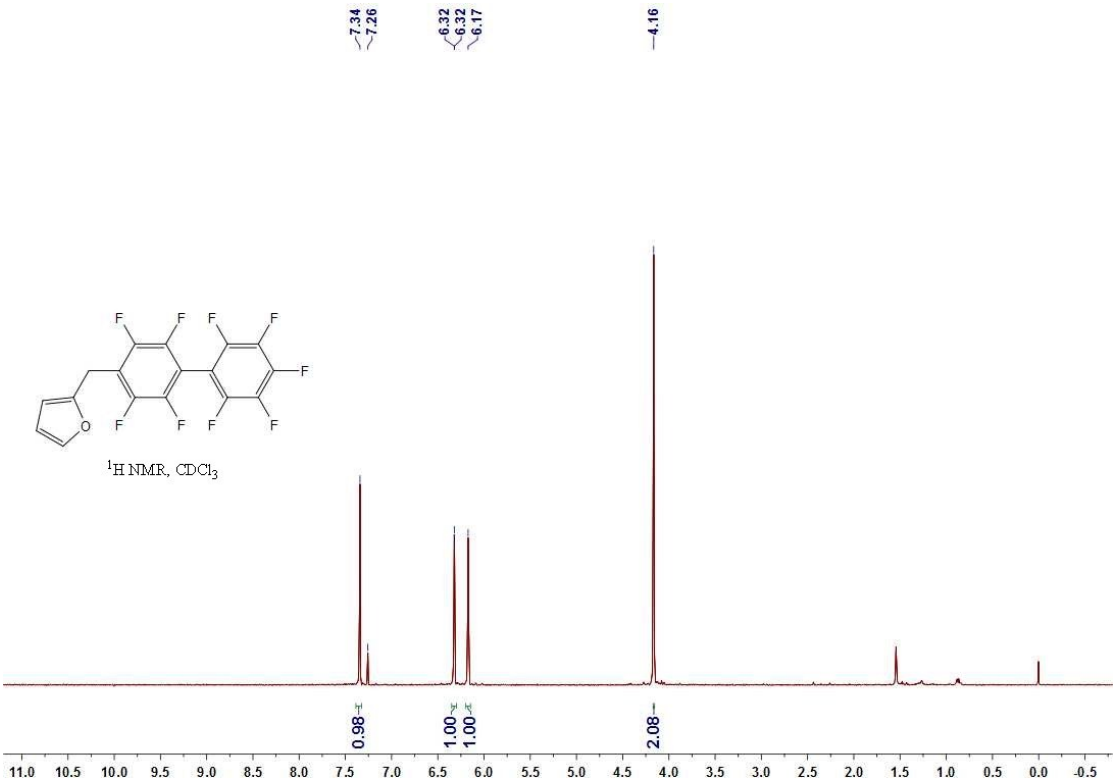
^{1}H, ^{19}F and ^{13}C NMR spectra of **4-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)phenol**

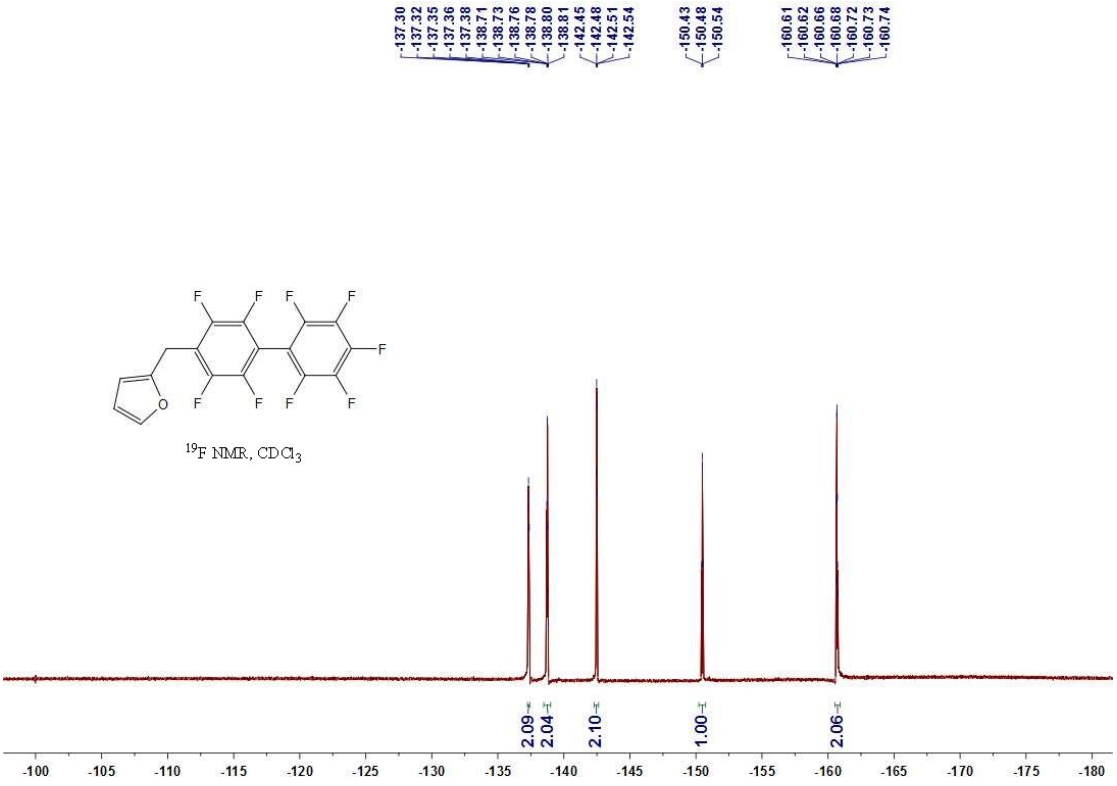


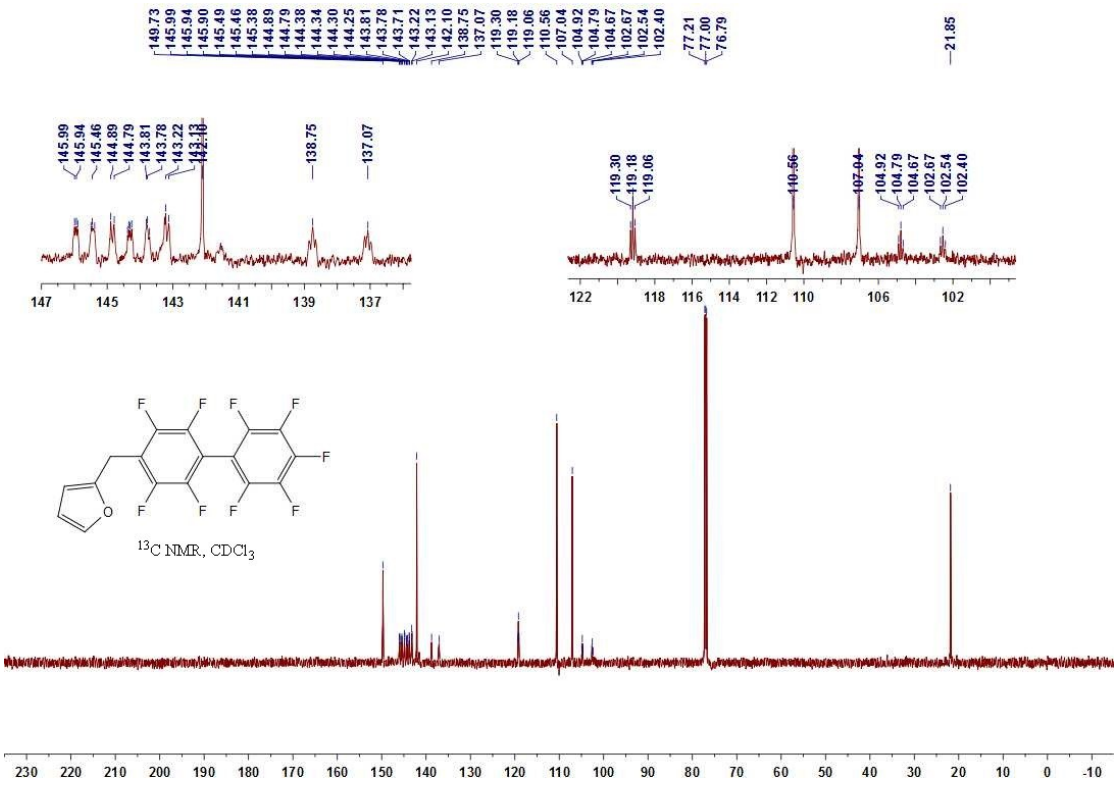

HO
F
^{19}F NMR, $CDCl_3$
1.96
1.00
1.02
0.99
0.99
0.96
2.02


HO
F
^{13}C NMR, $CDCl_3$

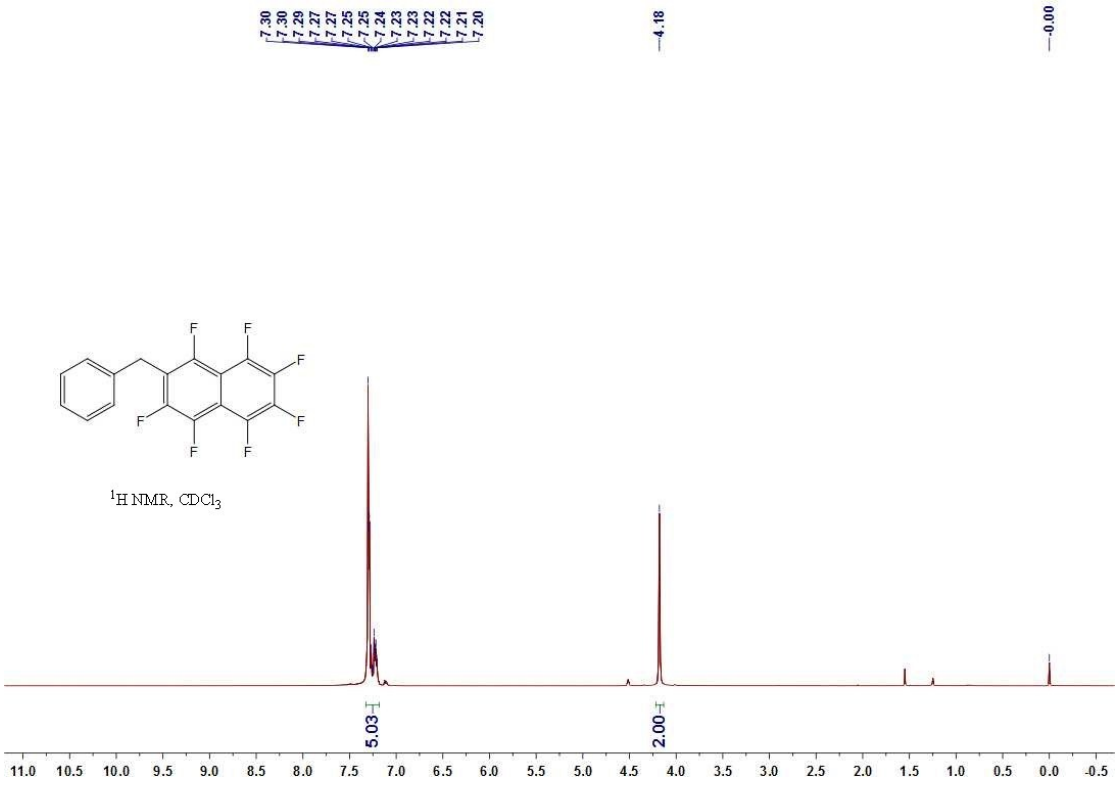
^{1}H, ^{19}F and ^{13}C NMR spectra of **2-((perfluoro-[1,1'-biphenyl]-4-yl)methyl)furan**

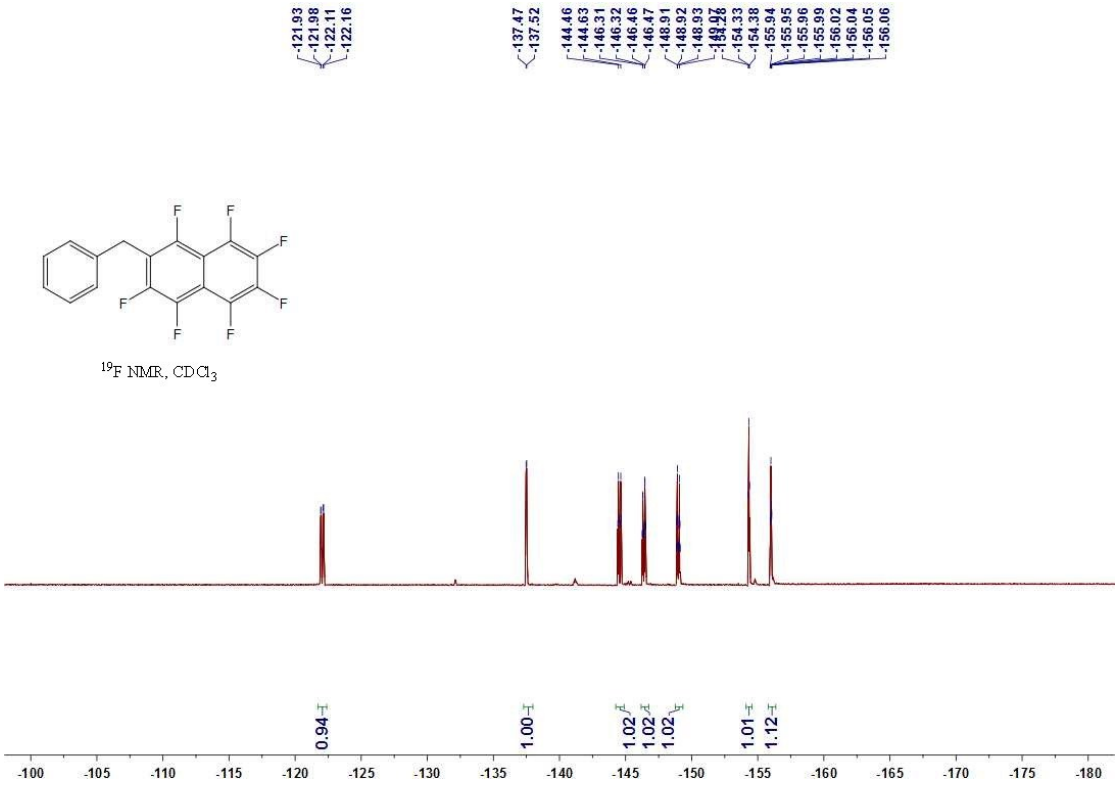






^{1}H, ^{19}F and ^{13}C NMR spectra of **2-benzyl-1,3,4,5,6,7,8-heptafluoronaphthalene**

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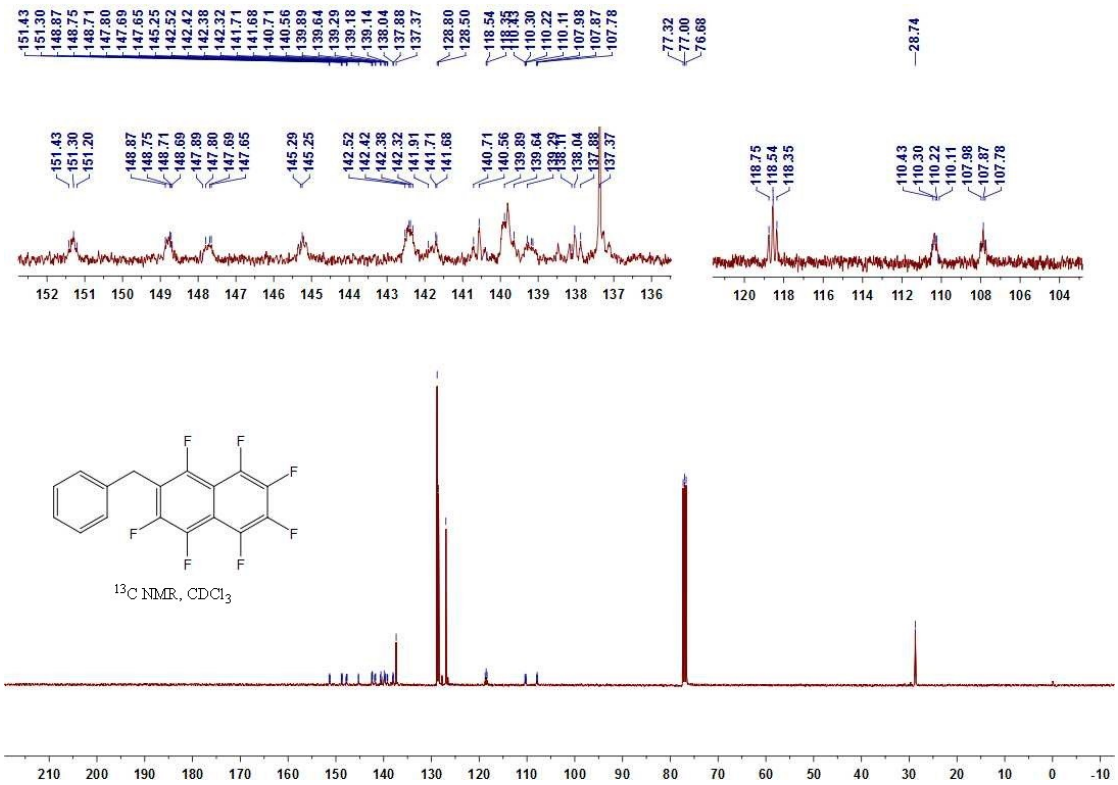
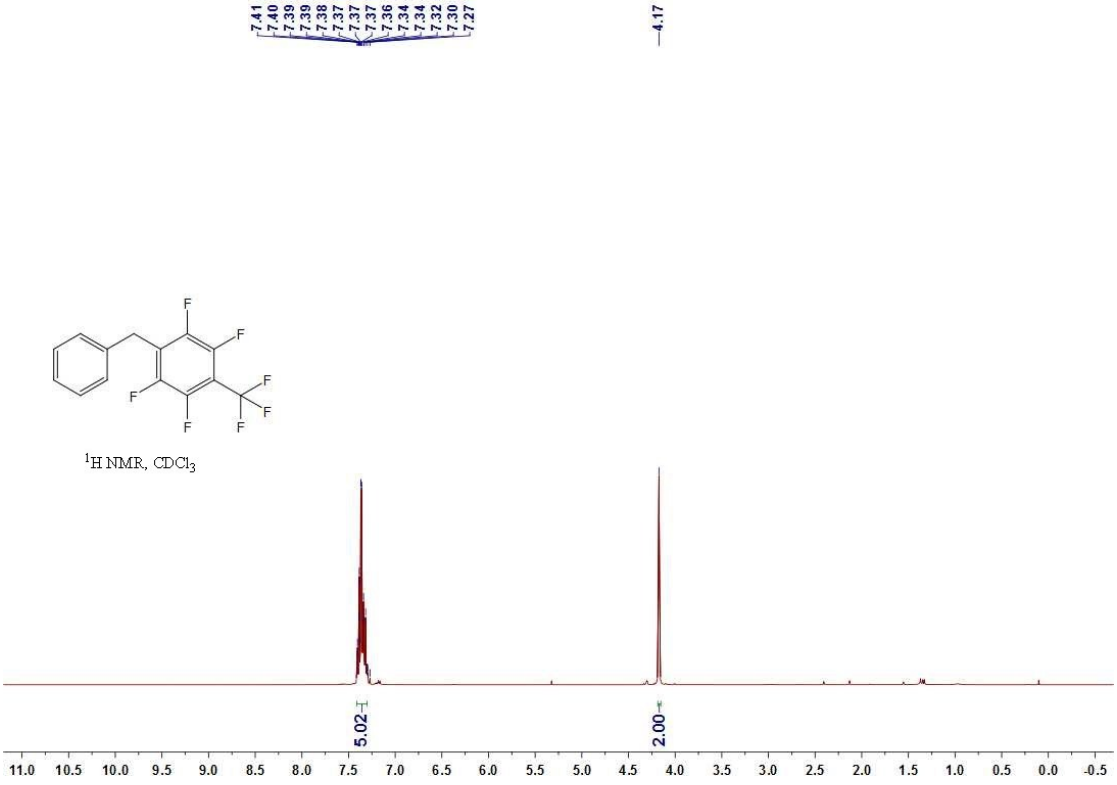
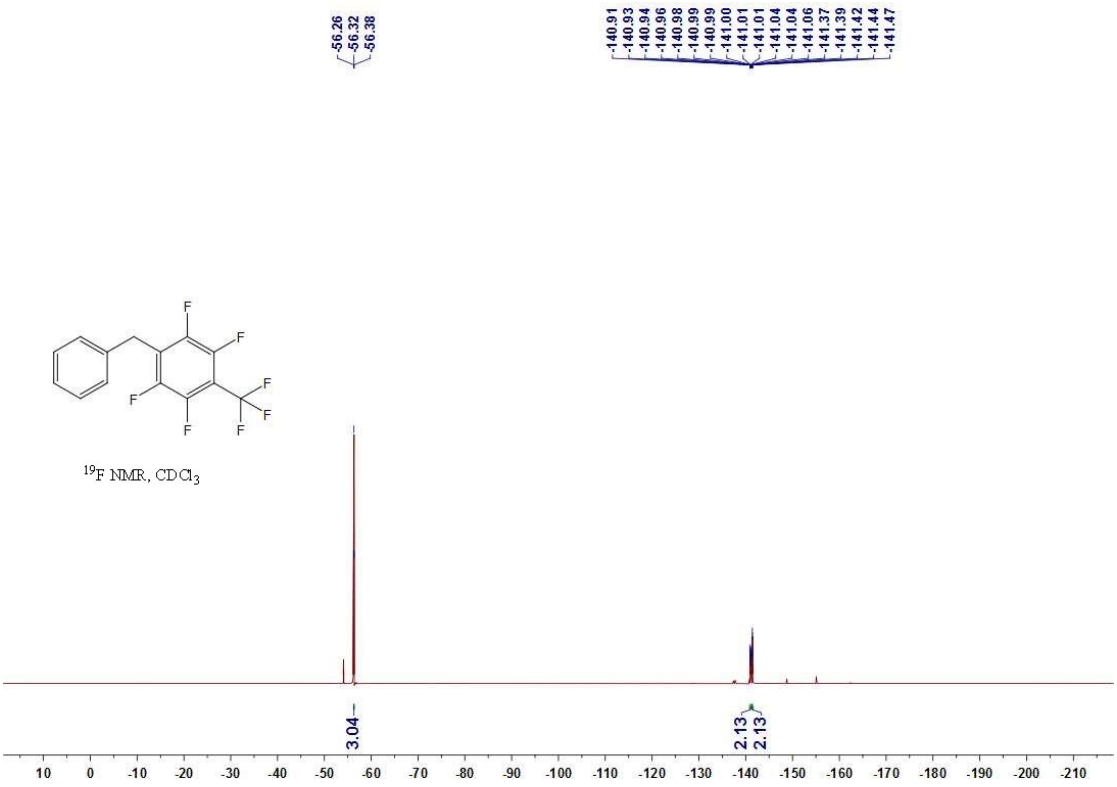
-121.98
-122.11
-122.16
-137.47
-137.52
-144.46
-144.63
-146.31
-146.32
-146.46
-146.47
-148.91
-148.92
-148.93
-154.33
-154.38
-155.94
-155.95
-155.96
-155.99
-156.02
-156.04
-156.05
-156.06
F
F
F
F
F
F
F
F
19F NMR, CDCl3
0.94
1.00
1.02
1.02
1.02
1.01
1.12
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180

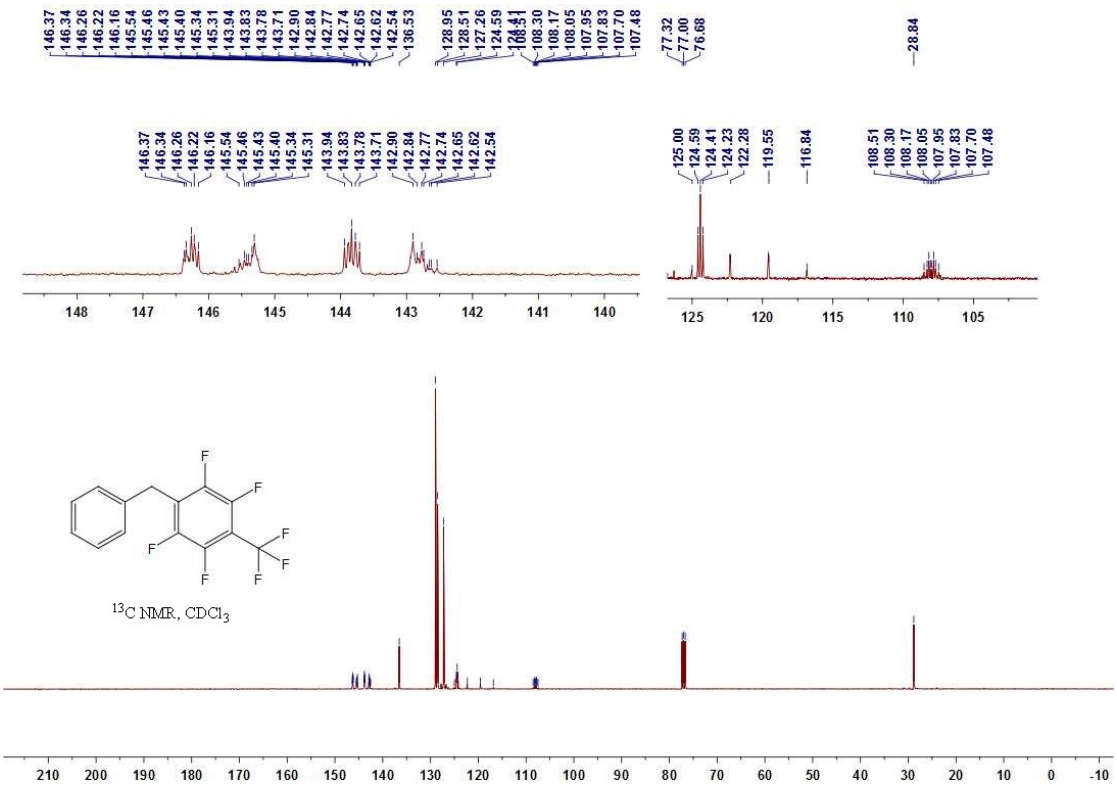

151.43
151.30
148.87
148.75
148.71
147.80
147.69
147.65
145.25
142.52
142.42
142.38
142.32
141.71
141.68
140.71
140.56
139.89
139.64
139.29
139.18
139.14
138.04
137.88
137.37
128.80
128.50
118.54
118.35
118.33
110.30
110.22
110.11
107.98
107.87
107.78
77.32
77.00
76.68
28.74
152
151
150
149
148
147
146
145
144
143
142
141
140
139
138
137
136
120
118
116
114
112
110
108
106
104

F
F
F
F
F
F
F
F
13C NMR, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

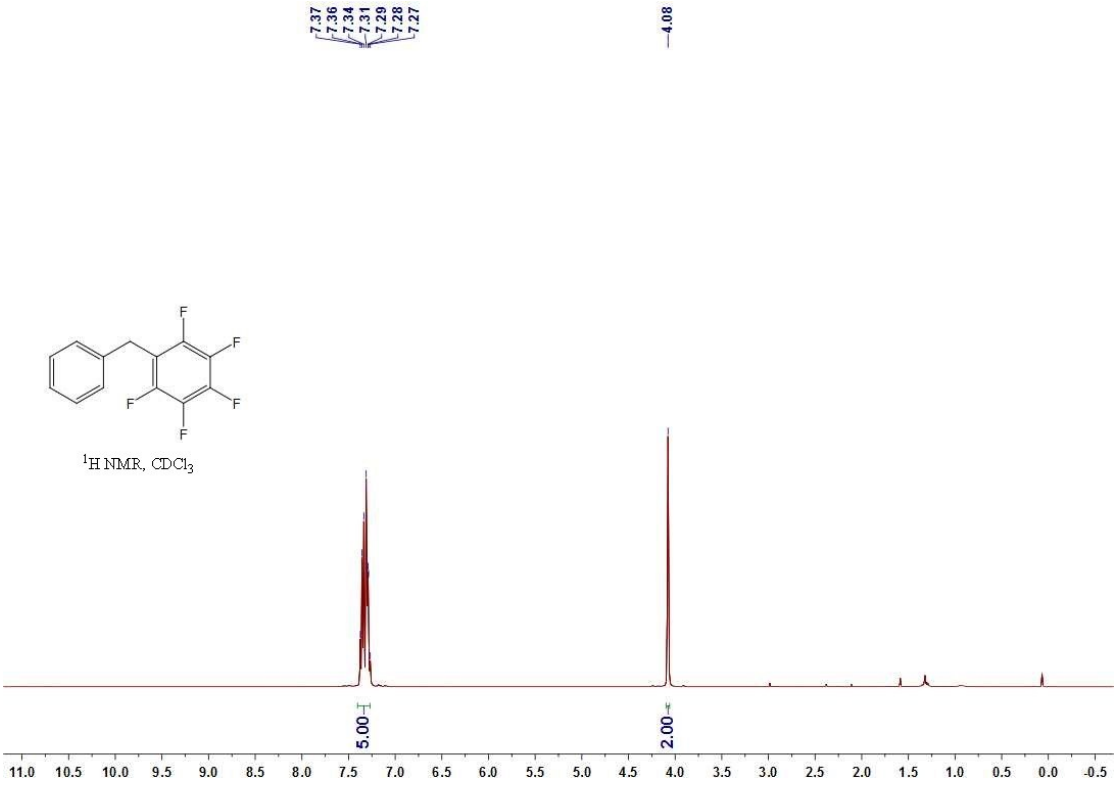
^{1}H, ^{19}F and ^{13}C NMR spectra of **1-benzyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene**

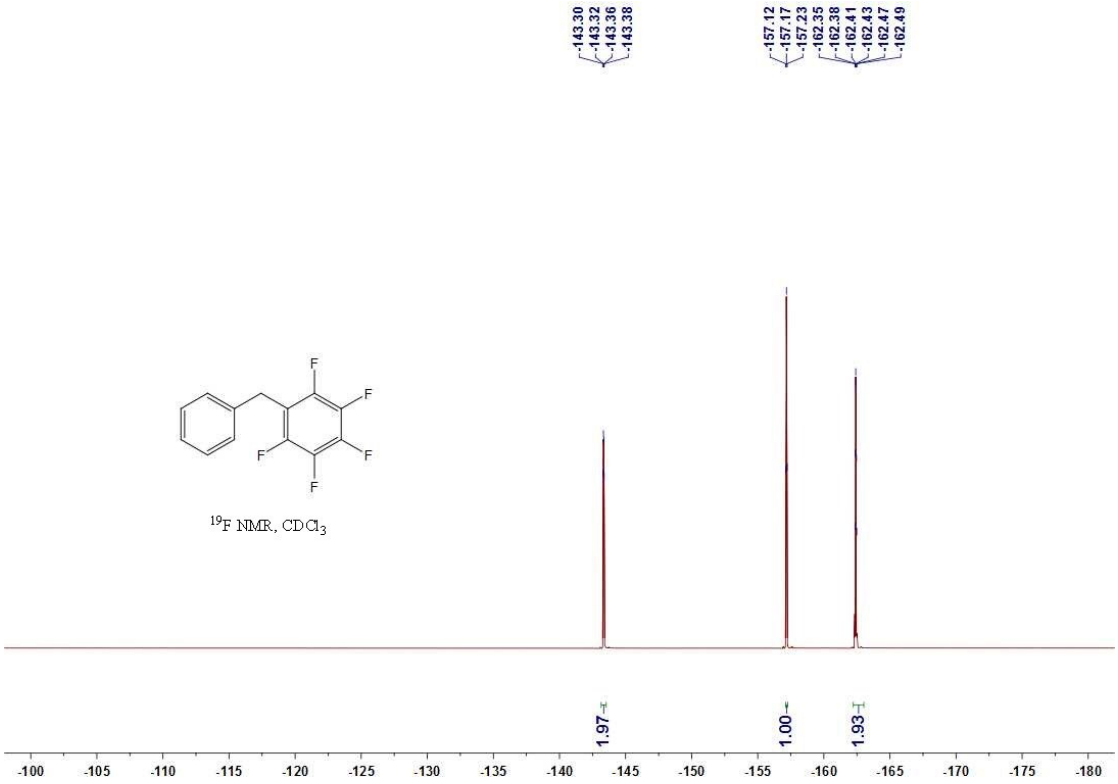


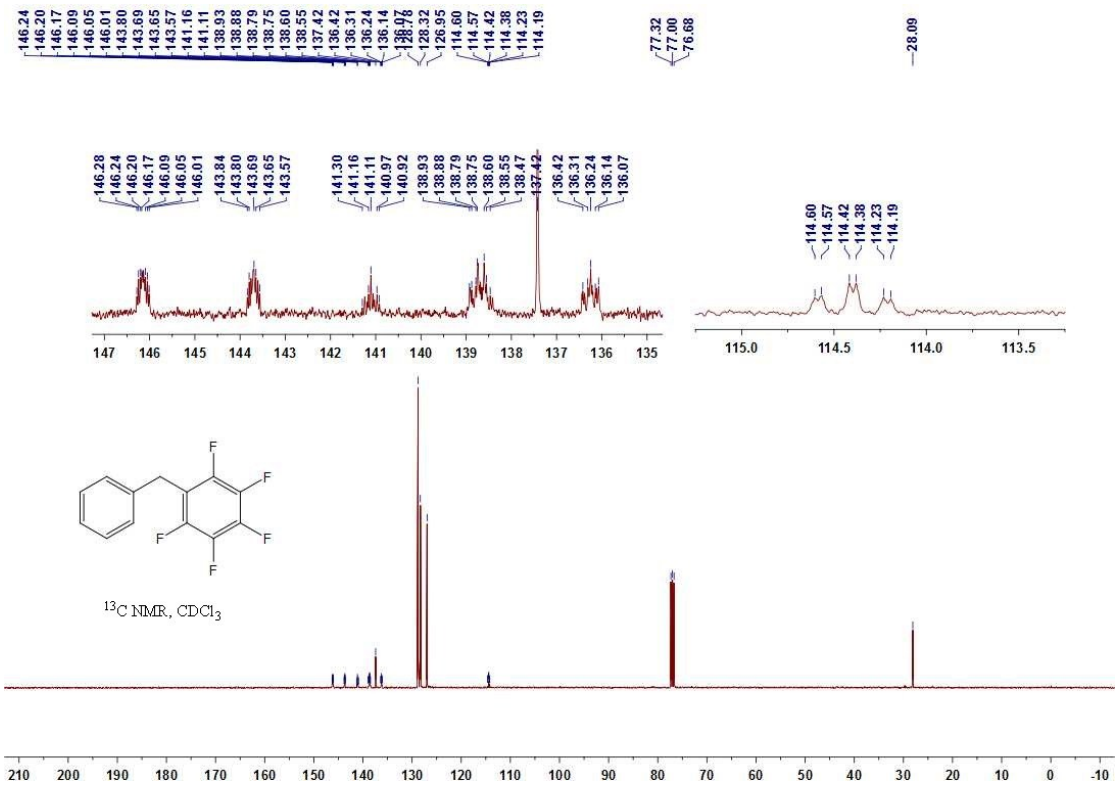




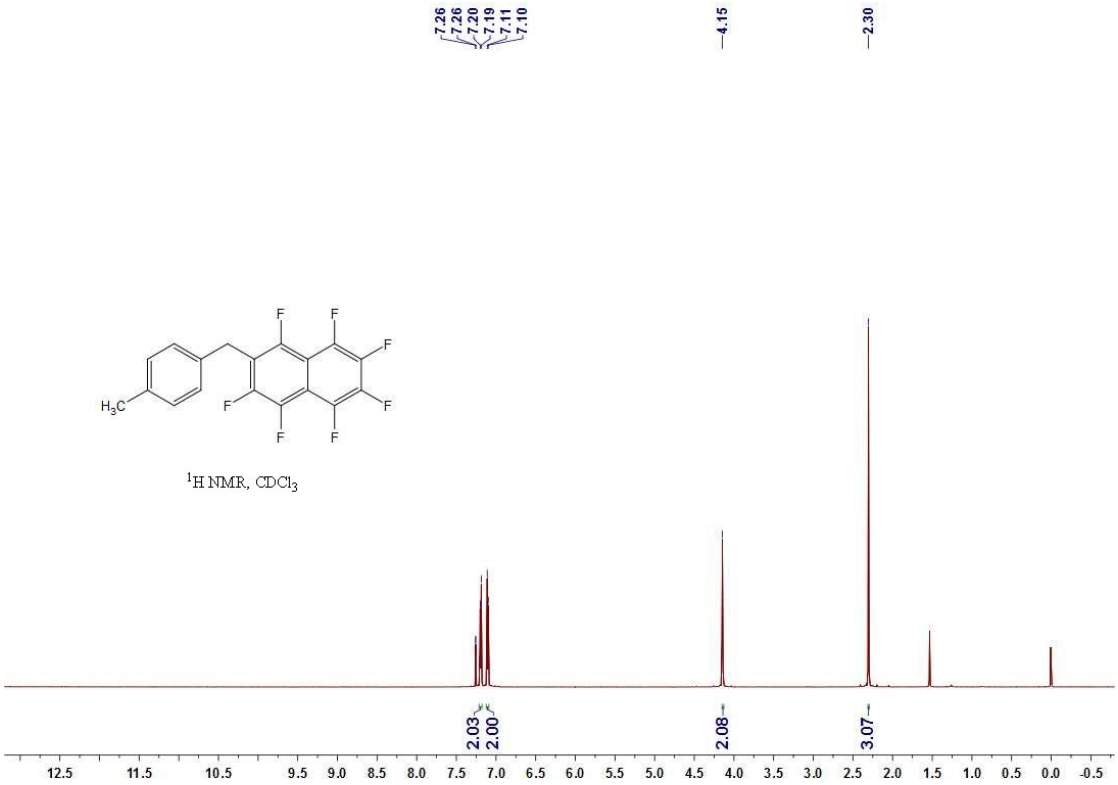
^{1}H, ^{19}F and ^{13}C NMR spectra of **1-benzyl-2,3,4,5,6-pentafluorobenzene**

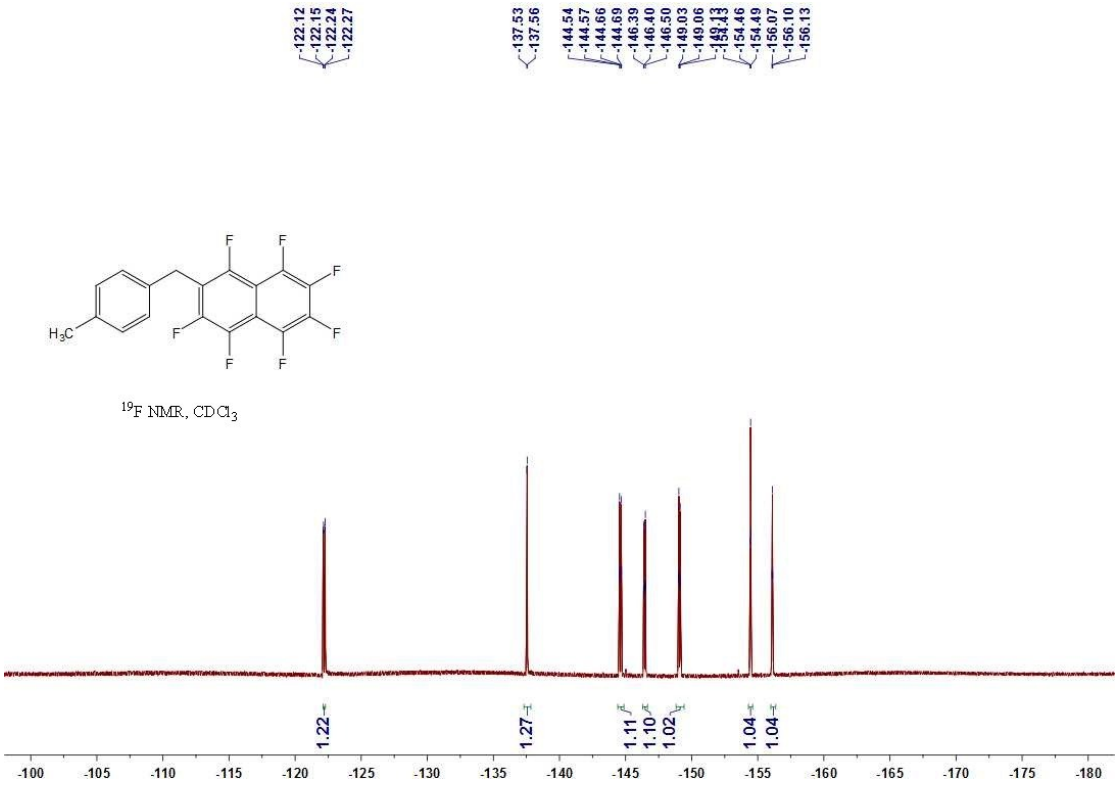


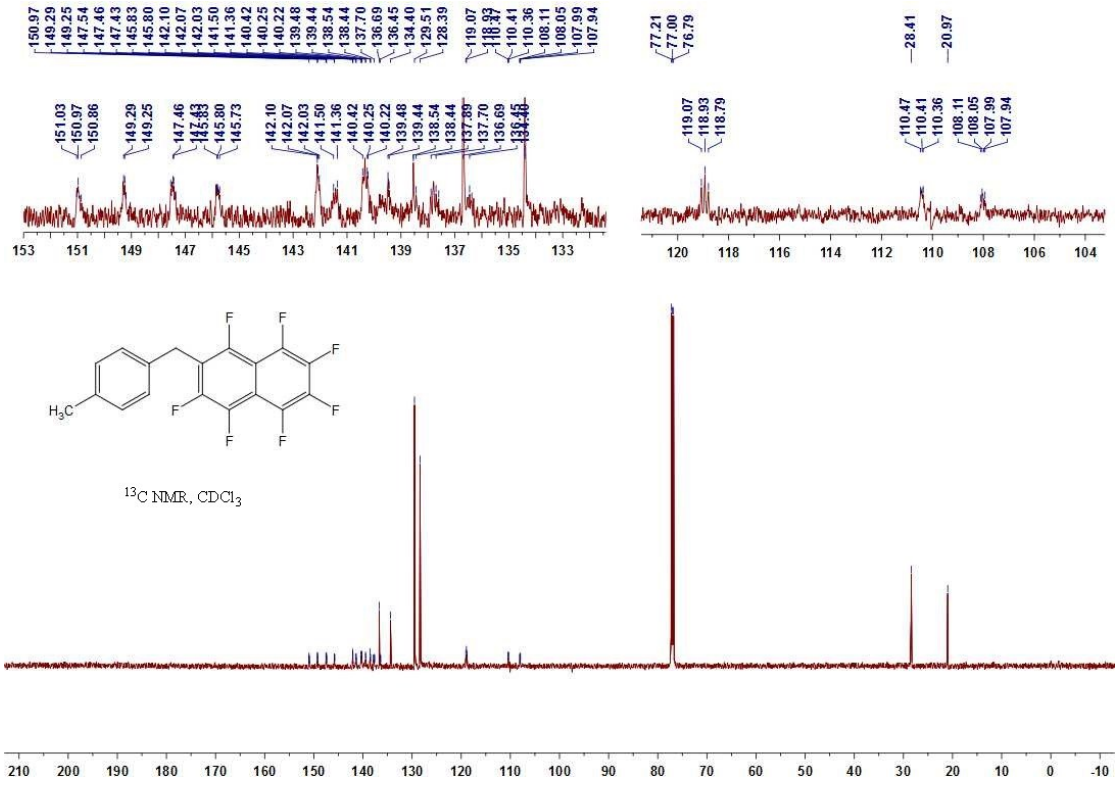

-143.30
-143.32
-143.36
-143.38
-157.12
-157.17
-157.23
-162.35
-162.38
-162.41
-162.43
-162.47
-162.49
F
F
F
F
F
19F NMR, CDCl3
1.97
1.00
1.93
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180


146.24
146.20
146.17
146.09
146.05
146.01
143.80
143.69
143.65
143.57
141.16
141.11
138.93
138.88
138.79
138.75
138.60
138.55
137.42
136.42
136.31
136.24
136.14
128.32
126.95
114.60
114.57
114.42
114.38
114.23
114.19
77.32
77.00
76.68
28.09
146.28
146.24
146.20
146.17
146.09
146.05
146.01
143.84
143.80
143.69
143.65
143.57
141.30
141.16
141.11
140.97
140.92
138.93
138.88
138.79
138.75
138.60
138.55
138.47
137.42
136.42
136.31
136.24
136.14
136.07
114.60
114.57
114.42
114.38
114.23
114.19
147 146 145 144 143 142 141 140 139 138 137 136 135
115.0 114.5 114.0 113.5
F
F
F
F
F
13C NMR, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

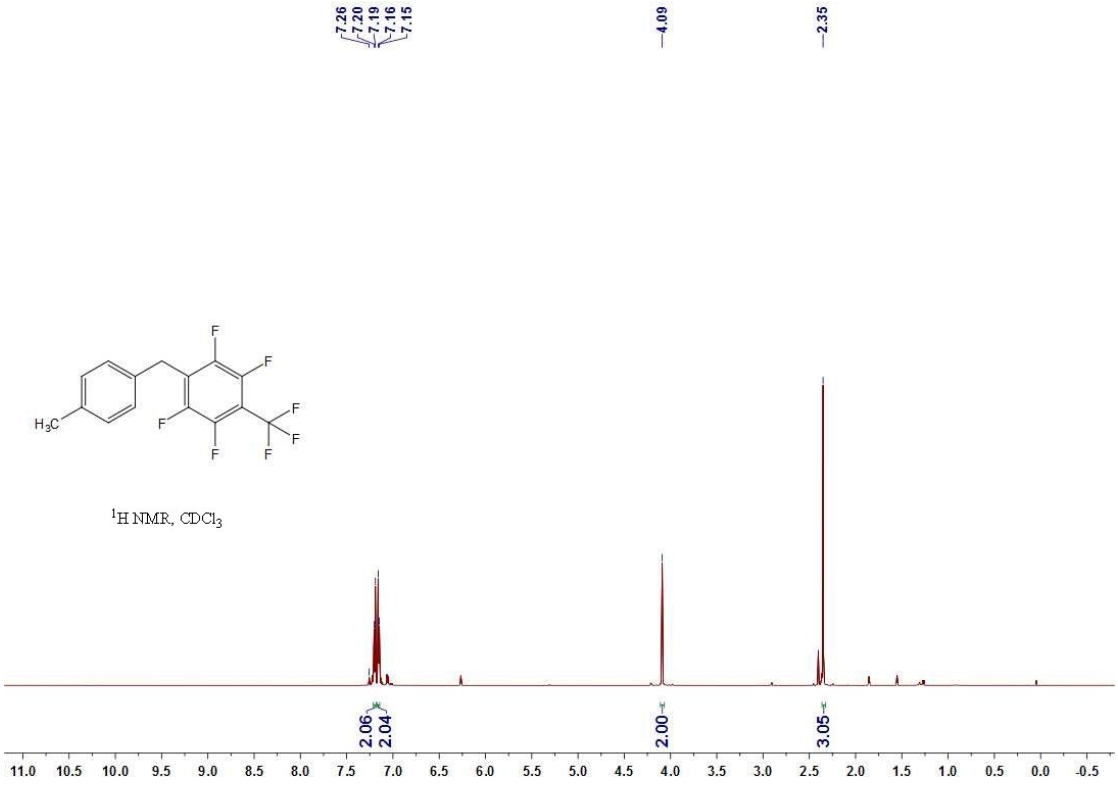
^{1}H, ^{19}F and ^{13}C NMR spectra of **1,2,3,4,5,6,8-heptafluoro-7-(4-methylbenzyl)naphthalene**

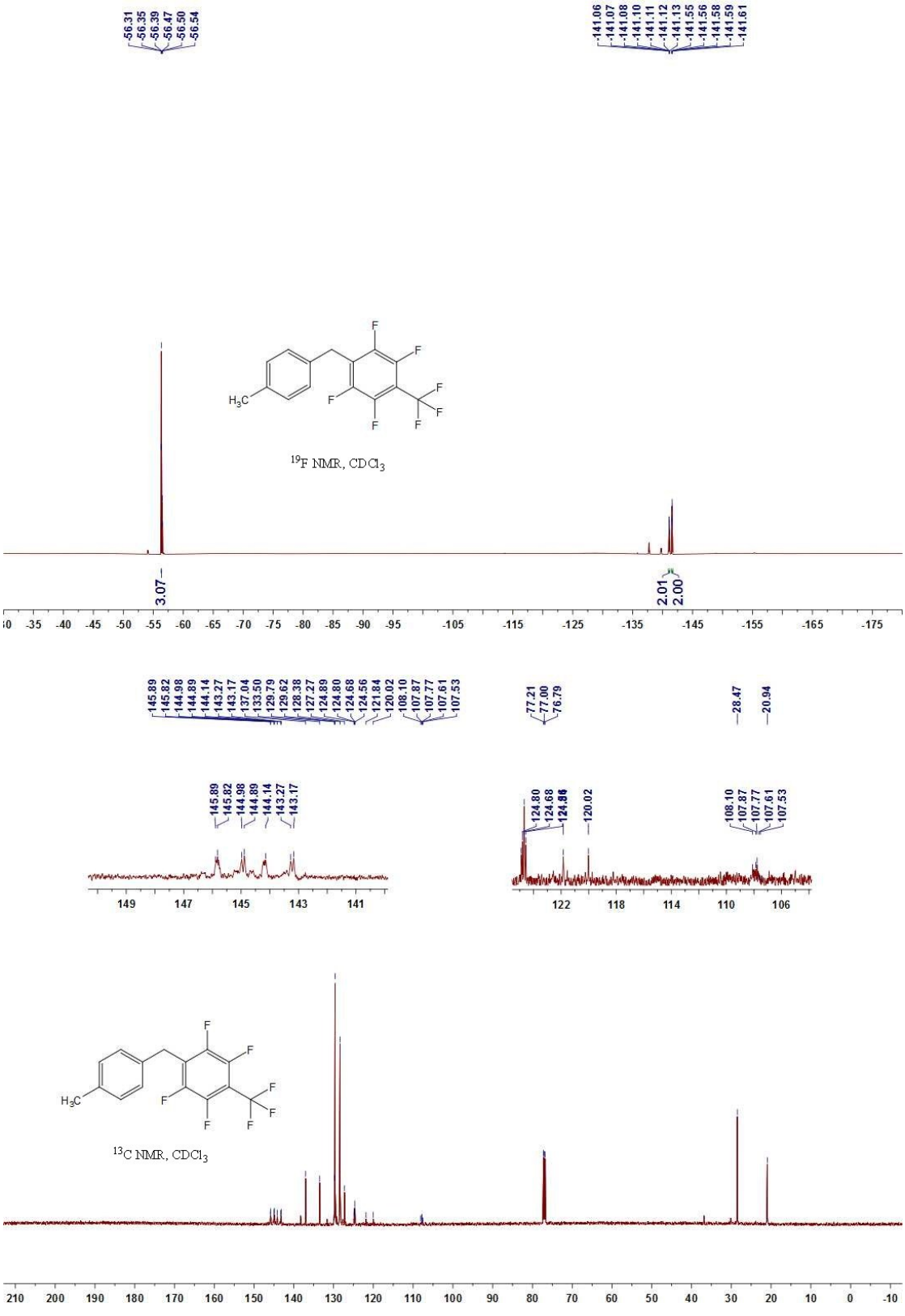




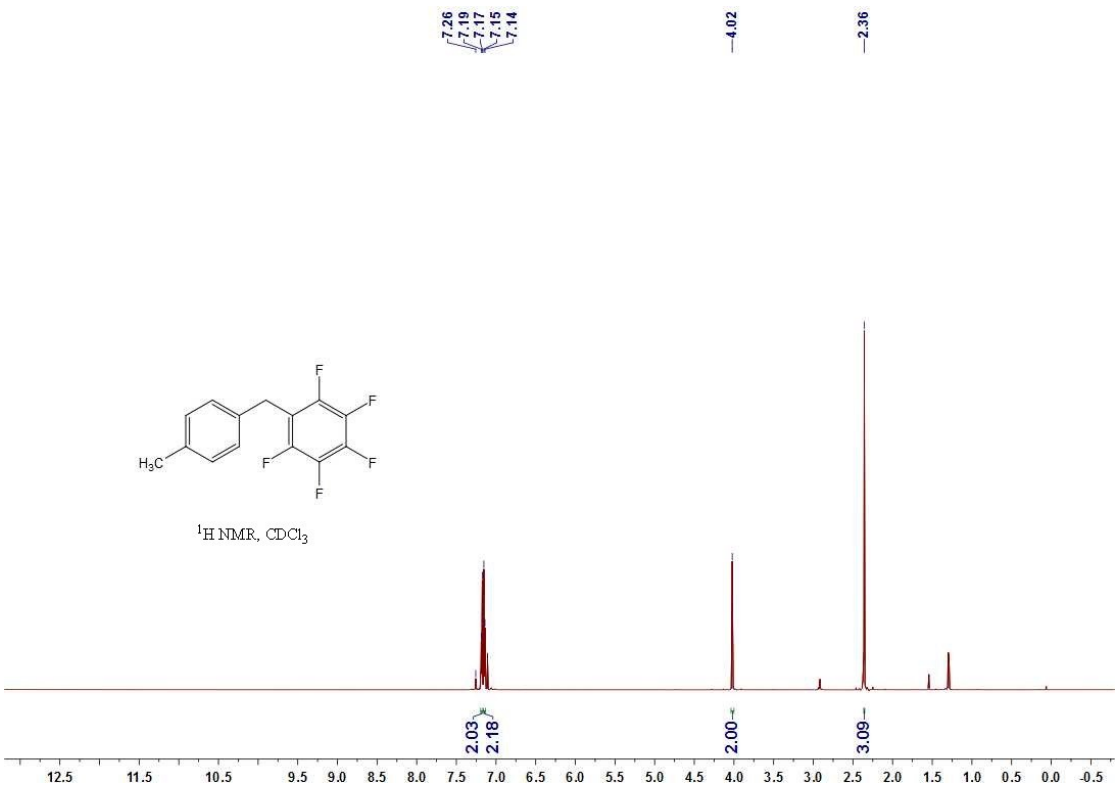


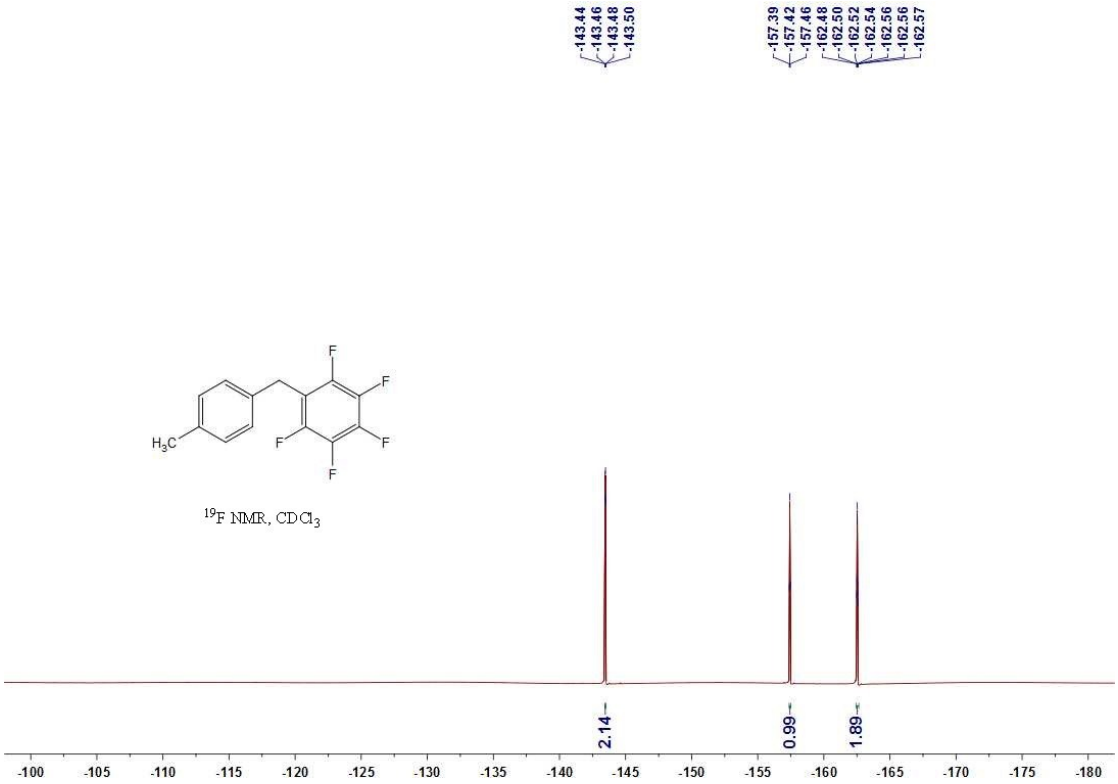
^{1}H, ^{19}F and ^{13}C NMR spectra of **1,2,4,5-tetrafluoro-3-(4-methylbenzyl)-6-(trifluoromethyl) benzene**

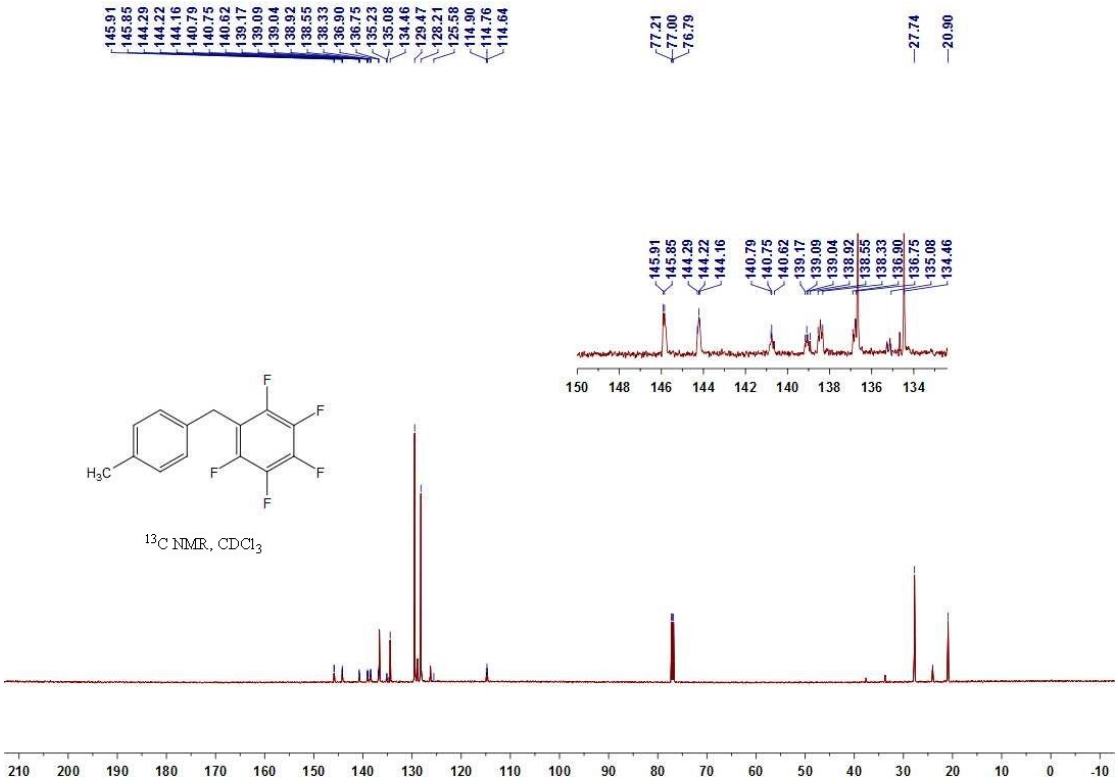



-56.31
-56.35
-56.39
-56.47
-56.50
-56.54
-141.06
-141.07
-141.08
-141.10
-141.11
-141.12
-141.13
-141.55
-141.56
-141.58
-141.59
-141.61
F
F
F
F
F
F
F
H3C
19F NMR, CDCl3
3.07
2.01
2.00
0 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
145.89
145.82
144.98
144.89
144.14
143.27
143.17
137.04
133.50
129.79
129.62
128.38
127.27
124.89
124.80
124.68
124.56
121.84
120.02
108.10
107.87
107.77
107.61
107.53
77.21
77.00
76.79
28.47
20.94
149 147 145 143 141
122 118 114 110 106
F
F
F
F
F
F
F
H3C
13C NMR, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

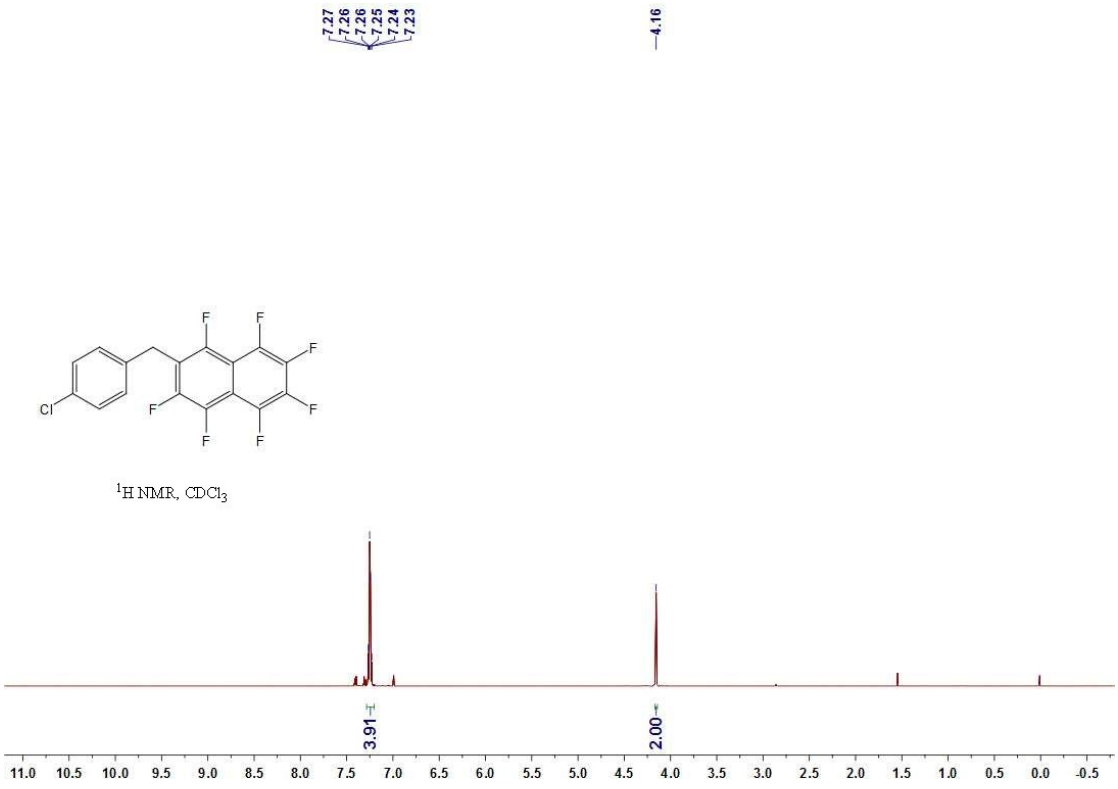
^{1}H, ^{19}F and ^{13}C NMR spectra of **1,2,3,4,5-pentafluoro-6-(4-methylbenzyl)benzene**

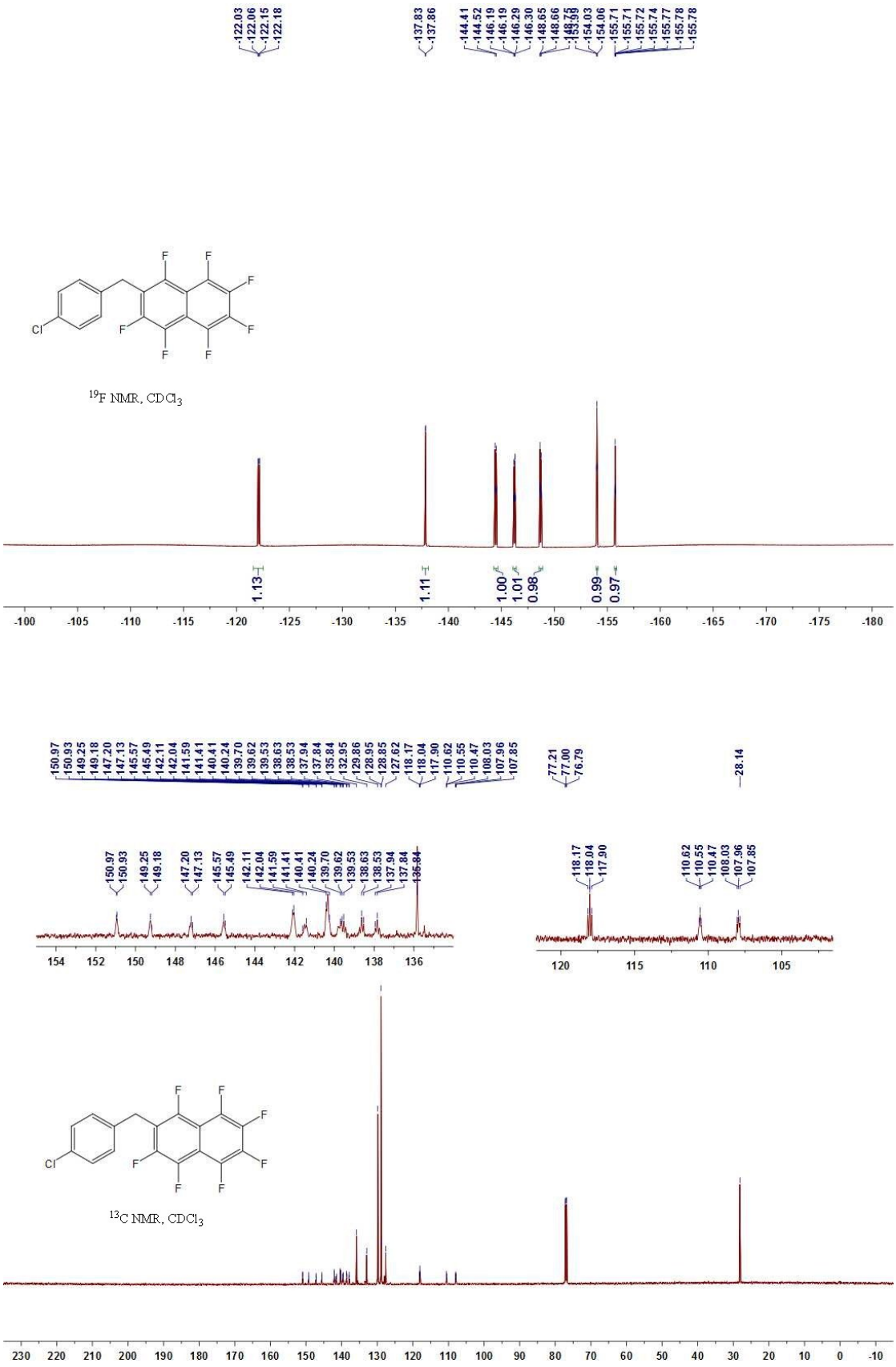




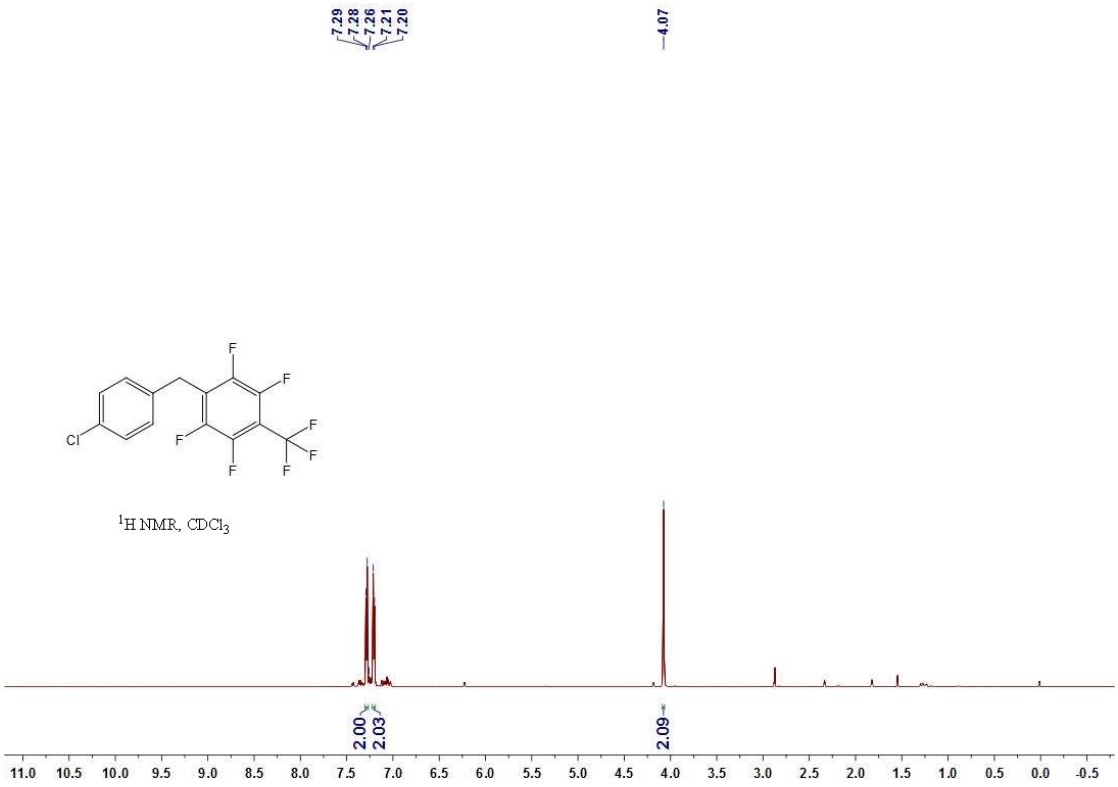


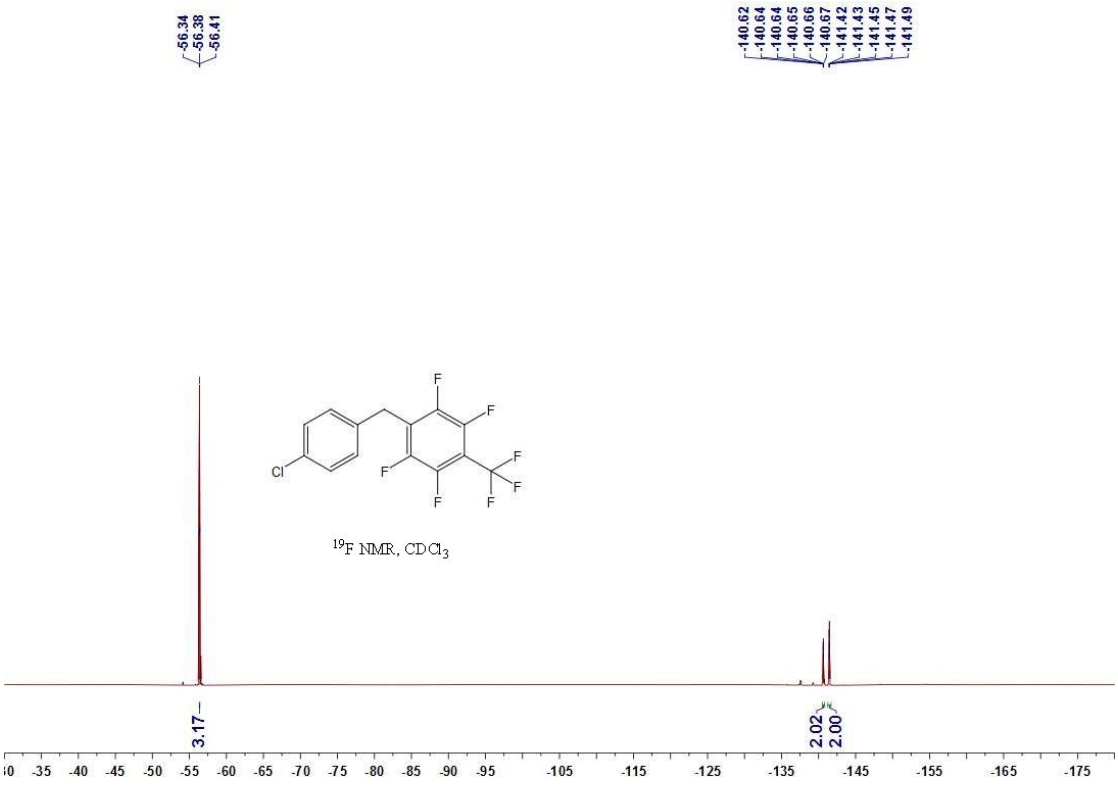
^{1}H, ^{19}F and ^{13}C NMR spectra of **2-(4-chlorobenzyl)-1,3,4,5,6,7,8-heptafluoronaphthalene**

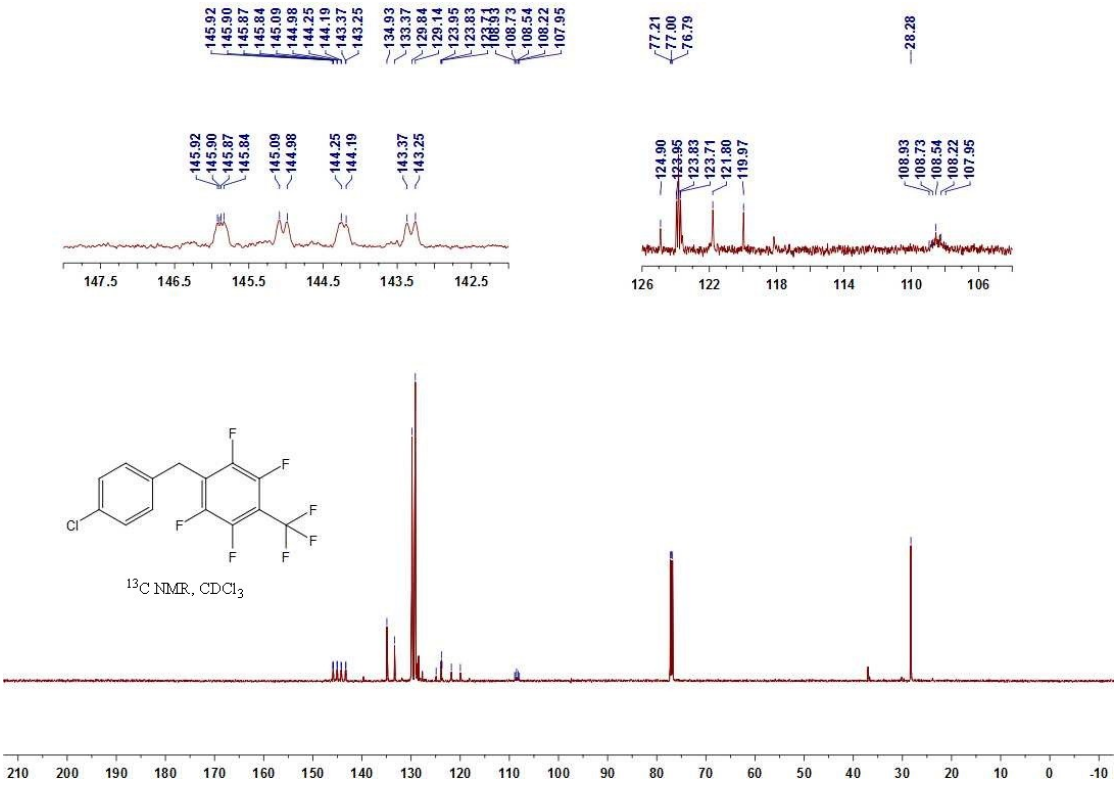



-122.03
-122.06
-122.15
-122.18
-137.83
-137.86
-144.41
-144.52
-146.19
-146.19
-146.29
-146.30
-148.65
-148.66
-153.99
-154.03
-154.06
-155.71
-155.71
-155.72
-155.74
-155.77
-155.78
-155.78
F
F
F
F
F
F
F
Cl
19F NMR, CDCl3
1.13
1.11
1.00
1.01
0.98
0.99
0.97
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
150.97
150.93
149.25
149.18
147.20
147.13
145.57
145.49
142.11
142.04
141.59
141.41
140.41
140.24
139.70
139.62
139.53
138.63
138.53
137.94
137.84
135.84
132.95
129.86
128.95
128.85
127.62
118.17
118.04
117.90
110.62
110.55
110.47
108.03
107.96
107.85
77.21
77.00
76.79
28.14
154
152
150
148
146
144
142
140
138
136
120
115
110
105
13C NMR, CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

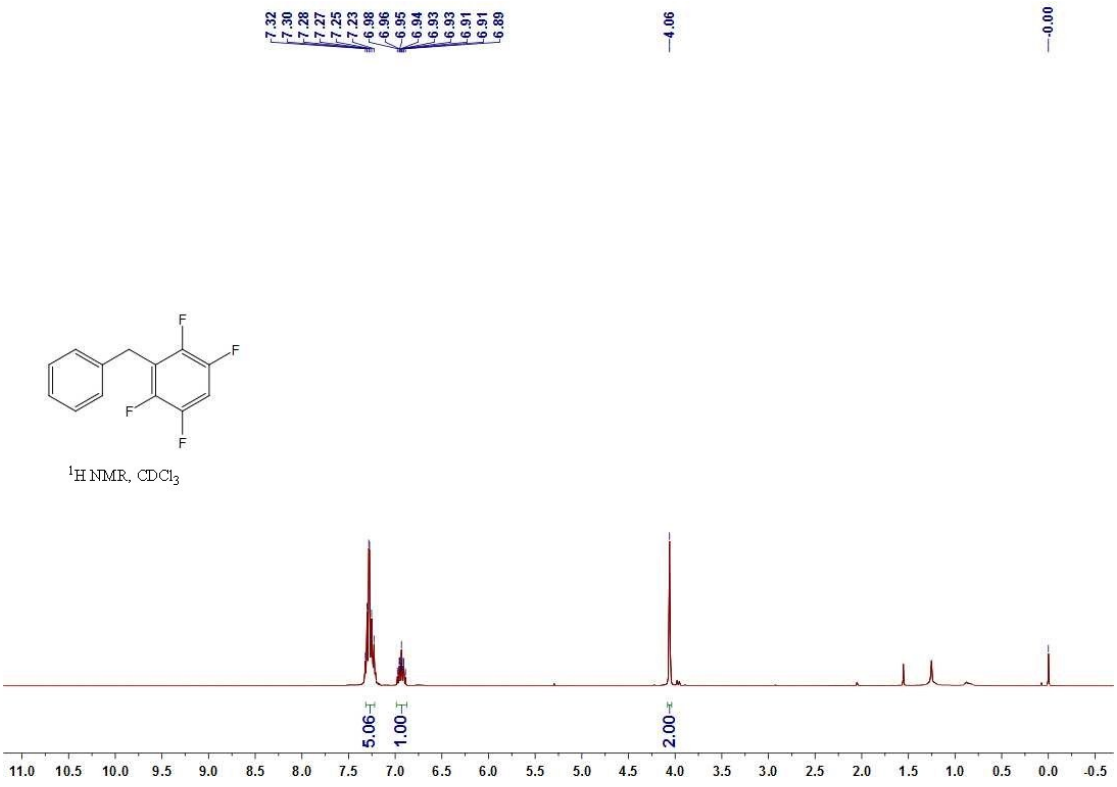
^{1}H, ^{19}F and ^{13}C NMR spectra of **1-(4-chlorobenzyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl) benzene**

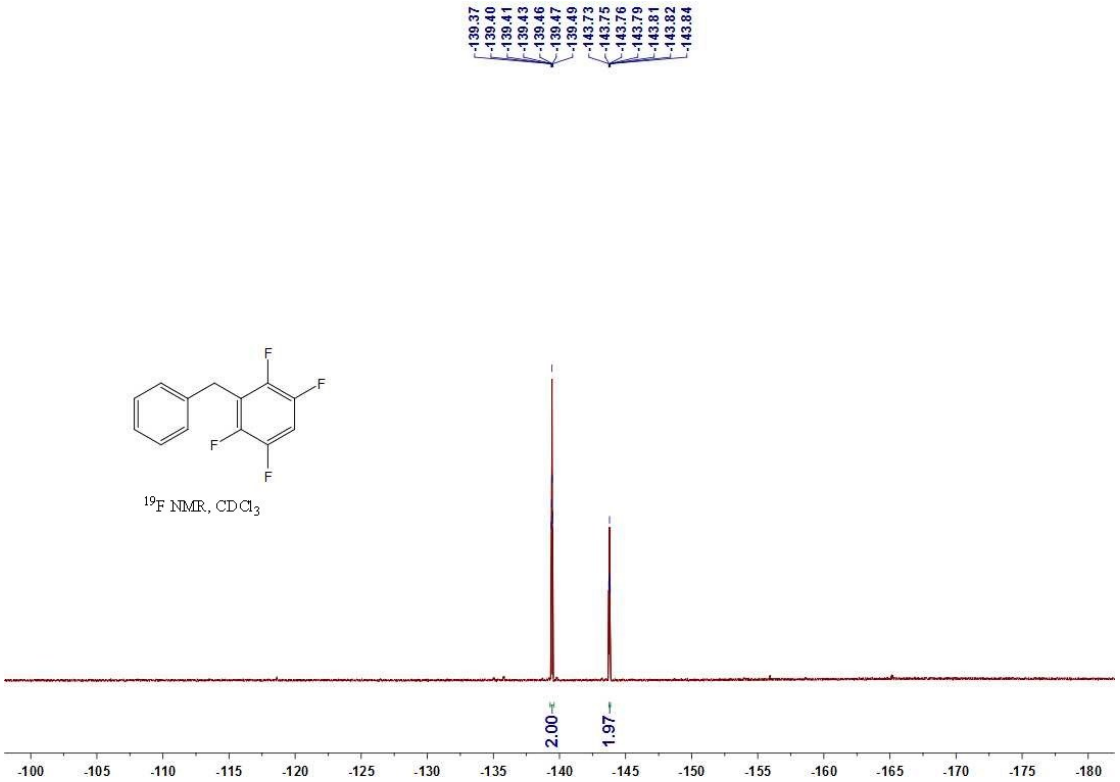


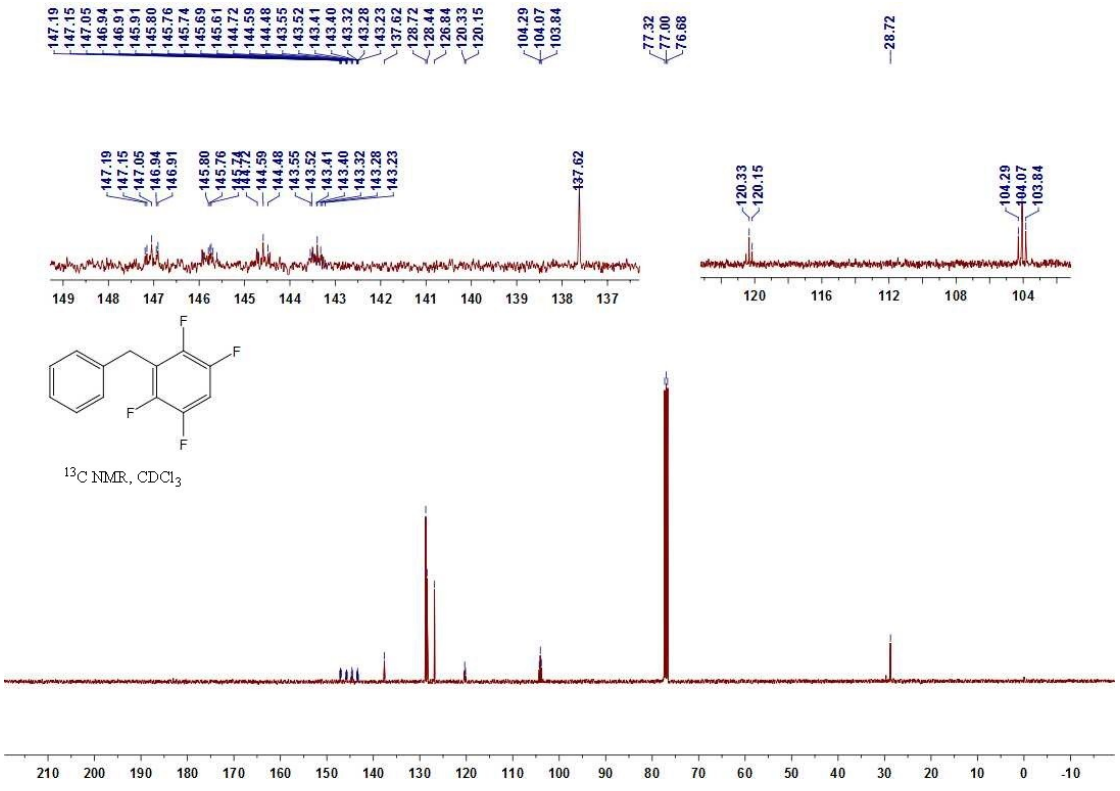




^{1}H, ^{19}F and ^{13}C NMR spectra of **3-benzyl-1,2,4,5-tetrafluorobenzene**




-139.37
-139.40
-139.41
-139.43
-139.46
-139.47
-139.49
-143.73
-143.75
-143.76
-143.79
-143.81
-143.82
-143.84
F
F
F
F
^{19}F NMR, $CDCl_3$
2.00
1.97
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180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146.91
145.91
145.80
145.76
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145.69
145.61
144.72
144.59
144.48
143.55
143.52
143.41
143.40
143.32
143.28
143.23
137.62
128.72
128.44
126.84
120.33
120.15
104.29
104.07
103.84
77.32
77.00
76.68
28.72
149 148 147 146 145 144 143 142 141 140 139 138 137
120 116 112 108 104
F
F
F
F
^{13}C NMR, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10