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Supporting Information

for

A Cooperative Pd/Cu System for Direct C-H Bond Arylation

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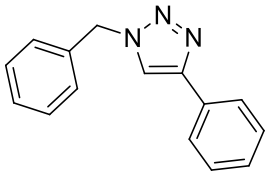
1. General information

All reactions were performed under an inert atmosphere of argon using glovebox techniques. All aryl halides were used as received. All aryl, heteroaryl reagents were used as received. Anhydrous solvents 1,4-dioxane, tetrahydrofuran (THF), 2-methyl-tetrahydrofuran, toluene, were used as received and stored in a glovebox. 1,2-dimethoxyethane (DME) was distilled on sodium/benzophenone, degassed and stored in a glovebox. [Cu(Cl)(ItBu)],[1] [Cu(Cl)(ICy)],[1] [Cu(Cl)(IPr)],[2] [Cu(Cl)(IMes)],[2] [Cu(Cl)(SIMes)],[2] [Cu(Cl)(IPr*)],[3] [Cu(IPr)(ItBu)]BF_4,[4] [Pd(allyl)(Cl)(SIPr)],[5] [Pd(allyl)(Cl)(IPr)],[5] [Pd(μ-Cl)Cl(SIPr)]$_2$,[6] and [$PdCl_2$(IPr)(PCy_3)][7] were synthesised according to reported procedures. [Pd(Cl)(cinnamyl)(SIPr)] and [Pd(allyl)(Cl)(SIMes)] are commercially available (UMICORE). Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 μm particules size. ^{1}H, ^{13}C-{^{1}H} and ^{19}F-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ADVANCE 300 MHz and Bruker ADVANCE 400 MHz spectrometer at ambient temperature (298K) using the residual solvent peak in $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm) and using TMS as internal standard. Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB. Mass Spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea University, Grove Building, Singleton Park, Swansea, SA2 8PP, Wales, UK.

2. Synthesis of *1-benzyl-4-phenyl-1*H-*1,2,3-triazole*



1-Benzyl-4-phenyl-1*H*-1,2,3-triazole was synthesised according to a reported procedure.[4]

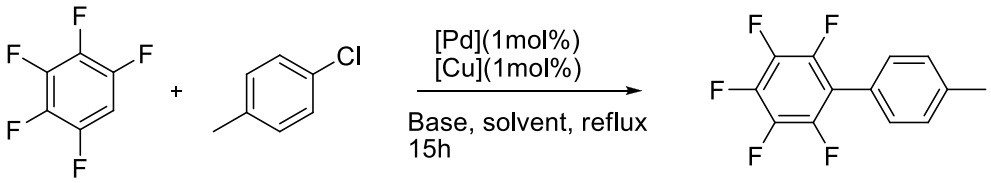
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 7.80 (d, $^3J_{HH}$ = 7.3 Hz, 2H, $C_{Ar}H$), 7.66 (s, 1H, N-C*H*), 7.43-7.28 (m, 8H, $C_{Ar}H$), 5.58 (s, 2H, NCH_2).

3. Catalysis

3.1. General procedure

In a glovebox, in a vial equipped with a stirring bar and sealed with a screw cap fitted with a septum were added the palladium catalyst (1 mol%), the copper catalyst (1 mol%), CsOH (150 mg, 0.975 mmol, 1.3 equiv.), aryl or heteroaryl (0.75 mmol, 1.0 equiv.), toluene (3 mL), and the aryl halide (0.75 mmol). The reaction mixture was stirred (900 rpm) at 110°C during 15 h. The reaction mixture was cooled down to room temperature, quenched with water (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with brine (20 mL). The organic phase was dried over $MgSO_4$, filtered and the solvents were evaporated *in vacuo*. The crude product was finally purified by flash chromatography on silica gel. The reported yields are the average of two runs.

3.2. Table S1 Optimisation of reaction conditions[a]



[Pd]	[Cu]	base	solvent	Conv. (%)[b]
[Pd(allyl)(Cl)(SIMes)]	[Cu(Cl)(ItBu)]	NaOH	toluene	31
[Pd(allyl)(Cl)(SIMes)]	[Cu(Cl)(ItBu)]	KOH	toluene	34
[Pd(allyl)(Cl)(SIMes)]	[Cu(Cl)(ItBu)]	CsOH	toluene	13
[Pd(μ-Cl)(Cl)(SIPr)]$_2$	[Cu(Cl)(ItBu)]	NaOH	toluene	19
[Pd(μ-Cl)(Cl)(SIPr)]$_2$	[Cu(Cl)(ItBu)]	KOH	toluene	31
[Pd(μ-Cl)(Cl)(SIPr)]$_2$	[Cu(Cl)(ItBu)]	CsOH	toluene	51
[Pd(allyl)(Cl)(SIPr)]	[Cu(Cl)(ItBu)]	NaOH	toluene	64
[Pd(allyl)(Cl)(SIPr)]	[Cu(Cl)(ItBu)]	KOH	toluene	67
[Pd(allyl)(Cl)(SIPr)]	[Cu(Cl)(ItBu)]	CsOH	toluene	74
[Pd(allyl)(Cl)(IPr)]	[Cu(Cl)(ItBu)]	NaOH	toluene	60
[Pd(allyl)(Cl)(IPr)]	[Cu(Cl)(ItBu)]	KOH	toluene	60
[Pd(allyl)(Cl)(IPr)]	[Cu(Cl)(ItBu)]	CsOH	toluene	75
[Pd(Cl_2)(IPr)(PPh_3)]	[Cu(Cl)(ItBu)]	NaOH	toluene	9
[Pd(Cl_2)(IPr)(PPh_3)]	[Cu(Cl)(ItBu)]	KOH	toluene	31
[Pd(Cl_2)(IPr)(PPh_3)]	[Cu(Cl)(ItBu)]	CsOH	toluene	15
[Pd(Cl_2)(IPr)(PCy_3)]	[Cu(Cl)(ItBu)]	NaOH	toluene	0
[Pd(Cl_2)(IPr)(PCy_3)]	[Cu(Cl)(ItBu)]	KOH	toluene	0
[Pd(Cl_2)(IPr)(PCy_3)]	[Cu(Cl)(ItBu)]	CsOH	toluene	0
[Pd(Cl)(cin)(IPr)]	[Cu(Cl)(ItBu)]	NaOH	toluene	67
[Pd(Cl)(cin)(IPr)]	[Cu(Cl)(ItBu)]	KOH	toluene	73
[Pd(Cl)(cin)(IPr)]	[Cu(Cl)(ItBu)]	CsOH	toluene	91
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	NaOH	toluene	66
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	KOH	toluene	67
[Pd(Cl)(cin)(SIPr)]	**[Cu(Cl)(ItBu)]**	**CsOH**	**toluene**	**93**
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ICy)]	NaOH	toluene	9
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ICy)]	KOH	toluene	18

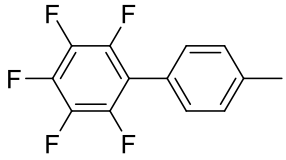
[Pd]	[Cu]	base	solvent	Conv. (%)[b]
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ICy)]	CsOH	toluene	7
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IPr)]	NaOH	toluene	13
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IPr)]	KOH	toluene	26
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IPr)]	CsOH	toluene	13
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IMes)]	NaOH	toluene	29
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IMes)]	KOH	toluene	25
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IMes)]	CsOH	toluene	23
[Pd(Cl)(cin)(SIPr)]	[Cu(IPr)(ItBu)]BF_4	NaOH	toluene	54
[Pd(Cl)(cin)(SIPr)]	[Cu(IPr)(ItBu)]BF_4	KOH	toluene	49
[Pd(Cl)(cin)(SIPr)]	[Cu(IPr)(ItBu)]BF_4	CsOH	toluene	45
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(SIMes)]	NaOH	toluene	6
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(SIMes)]	KOH	toluene	17
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(SIMes)]	CsOH	toluene	8
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IPr*)]	NaOH	toluene	16
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IPr*)]	KOH	toluene	23
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(IPr*)]	CsOH	toluene	8
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	CsOH	methyl-THF	82
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	CsOH	THF	38
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	CsOH	DME	65
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	CsOH	1,4-dioxane	84
[Pd(Cl)(cin)(SIPr)]	[Cu(Cl)(ItBu)]	K_2CO_3	Toluene	0
[Pd(Cl)(cin)(SIPr)][c]	/	K_2CO_3	Toluene	0
[Pd(Cl)(cin)(SIPr)][c]	/	CsOH	Toluene	0
[Pd(Cl)(cin)(SIPr)][d]	/	CsOH	Toluene	0

[a] Reaction conditions: 4-chlorotoluene (0.75 mmol), pentafluorobenzene (0.75 mmol), base (0.975 mmol), solvent (3 mL), [Pd] (1 mol%), [Cu] (1 mol%), 110°C, 15h. [b] Conversion to coupling product determined by GC based on aryl halide. [c] Pivalic acid (10 mol%) as additive. [d] [Pd(Cl)(cin)(SIPr)] (5 mol%).

3.3. Catalysis

2,3,4,5,6-pentafluoro-4'-methylbiphenyl (7a)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 348 mg (90 %, Cl), 352 mg (91%, Br) of the title compound as a colourless solid.

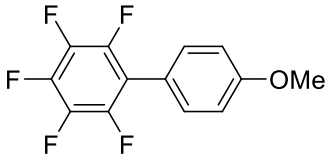


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.31 (br s, 4H, $C_{Ar}H$), 2.42 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -143.9 (dd, J_{FF} = 8.1 Hz, J_{FF} = 23.0 Hz, CF), -156.6 (t, J_{FF} = 21.0 Hz, *p*-CF), -162.8 to -163.0 (m, CF).

2,3,4,5,6-pentafluoro-4'-methoxybiphenyl (7b)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 350 mg (85%, Cl), 354 mg (86%, Br) of the title compound as a colourless solid.

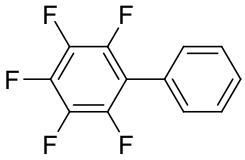


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.36 (d, $^{3}J_{HH}$ = 8.9 Hz, 2H, CH), 7.02 (d, $^{3}J_{HH}$ = 8.9 Hz, 2H, CH), 3.87 (s, 3H, OCH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -144.1 (dd, J_{FF} = 8.3 Hz, J_{FF} = 23.0 Hz, CF), -157.0 (t, J_{FF} = 21.0 Hz, *p*-CF), -162.9 to -163.2 (m, CF).

2,3,4,5,6-pentafluorobiphenyl (7c)[9]

The general procedure yielded, after flash chromatography on silica gel (pentane), 328 mg (90%, Cl), 332 mg (91%, Br) of the title compound as a colourless solid.

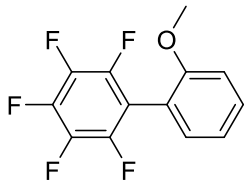


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.54-7.40 (m, 5H, $C_{Ar}H$).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -143.7 (dd, J_{FF} = 8.0 Hz, J_{FF} = 22.5 Hz, CF), -156.1 (t, J_{FF} = 21.0 Hz, *p*-CF), -162.7 (m, CF).

2,3,4,5,6-pentafluoro-2'-methoxybiphenyl (7d)[10]

The general procedure yielded, after flash chromatography on silica gel (pentane), 308 mg (75 %) of the title compound as a colourless oil.

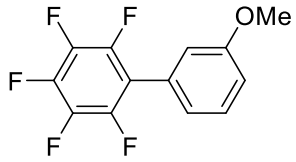


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.48-7.41 (m, 1H, CH), 7.25-7.19 (m, 1H, CH), 7.09-6.99 (m, 2H, CH), 3.80 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -140.7 to -148.8 (m, CF), -156.7 (t, J_{FF} = 21.1 Hz, *p*-CF), -163.6 to -163.9 (m, CF).

2,3,4,5,6-pentafluoro-3'-methoxybiphenyl (7e)[10]

The general procedure yielded, after flash chromatography on silica gel (pentane), 366 mg (89 %) of the title compound as a colourless oil.

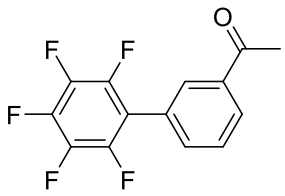


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.39 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, CH), 7.01-6.95 (m, 2H, CH), 6.95-6.94 (m, 1H, CH), 3.82 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -143.4 to -143.5 (m, CF), -156.3 (t, J_{FF} = 21.1 Hz, *p*-CF), -162.8 to -163.1 (m, CF).

3'-(2,3,4,5,6-pentafluorophenyl)acetophenone (7f)[11]

The general procedure yielded, after flash chromatography on silica gel (Ethyl acetate/pentane: 1/9), 322 mg (75 %) of the title compound as a colourless solid.

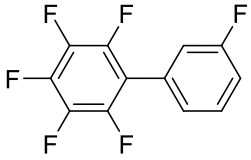


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.10-8.01 (m, 2H, CH), 7.65-7.60 (m, 2H, CH), 2.65 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -143.5 to -143.6 (m, CF), -154.9 (t, J_{FF} = 21.0 Hz, *p*-CF), -162.0 to -162.2 (m, CF).

2,3,3',4,5,6-hexafluoro-1,1'-biphenyl (7g)[12]

The general procedure yielded, after flash chromatography on silica gel (pentane), 334 mg (85 %) of the title compound as a colourless solid.

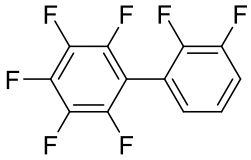


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.51-7.42 (m, 1H, CH), 7.24-7.12 (m, 3H, CH).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -112.6 (s, CF), -143.5 to -143.6 (m, CF), -155.2 (t, J_{FF} = 21.4 Hz, *p*-CF), -162.3 to -163.5 (m, CF).

2,2',3,3',4,5,6-heptafluoro-1,1'-biphenyl (7h)

The general procedure yielded, after flash chromatography on silica gel (pentane), 336 mg (80 %) of the title compound as a colourless solid.



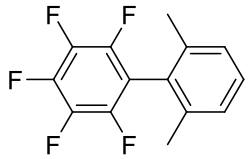
^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.39-7.30 (m, 1H, CH), 7.06-6.94 (m, 2H, CH).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -107.3 (d, J_{FF} = 9.1 Hz, CF), -108.7 (q, J_{FF} = 9.6 Hz, CF), -141.0 to -141.1 (m, CF), -154.3 (t, J_{FF} = 20.8 Hz, *p*-CF), -162.4 to -162.6 (m, CF).

HRMS calcd. For $C_{12}H_3F_7$ $(M)^+$ 280.0117, found 280.0117.

2,3,4,5,6-pentafluoro-2',6'-dimethylbiphenyl (7i)[13]

The general procedure yielded, after flash chromatography on silica gel (pentane), 168 mg (41%) of the title compound as a colourless solid.

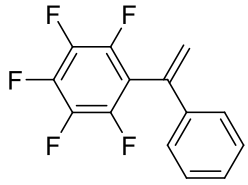


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.28 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-CH), 7.16 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-CH), 2.09 (s, 6H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -140.6 (dd, J_{FF} = 8.4 Hz, J_{FF} = 23.1 Hz, CF), -155.6 (t, J_{FF} = 21 Hz, CF), -162.2 to -162.5 (m, CF).

2,3,4,5,6-tetrafluoro-6-(1-phenylethynyl) (7j)[14]

The general procedure yielded, after flash chromatography on silica gel (pentane), 398 mg (98%) of the title compound as a colourless oil.

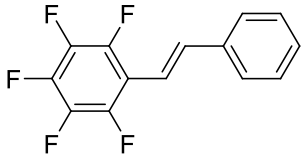


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.39-7.25 (m, 5H, CH), 6.06 (br s, 1H, CH_2), 5.45 (br s, 1H, CH_2).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -140.7 to -140.9 (m, CF), -155.7 (t, J_{FF} = 21Hz, CF), -162.4 to -162.7 (m, CF).

(E)-1,2,3,4,5-pentafluorostilbene (7k)[14]

The general procedure yielded, after flash chromatography on silica gel (pentane), 356 mg (88%) of the title compound as a colourless solid.

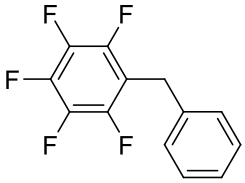


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.56-7.51 (m, 2H, $C_{Ar}H$), 7.47-7.30 (m, 4H, CH and $C_{Ar}H$), 6.98 (d, J_{HH} = 16.5 Hz, 1H, CH).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -143.1 to -143.3 (m, CF), -157.0 (t, J_{FF} = 21 Hz, CF), -163.3 to -163.5 (m, CF).

2,3,4,5,6-tetrafluoromethylbenzyl (7l)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 364 mg (94%) of the title compound as a colourless solid.

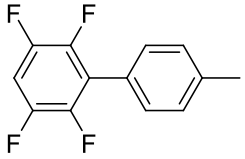


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.34-7.20 (m, 5H, CH), 4.02 (s, 2H, CH_2).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -143.7 to -143.8 (dd, J_{FF} = 8.0 Hz, J_{FF} = 20.8 Hz, CF), -157.6 (t, J_{FF} = 20.8 Hz, CF), -162.7 to -169.2 (m, CF).

2,3,5,6-tetrafluoro-4'-methylbiphenyl (7m mono-arylated)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 270 mg (75%) of the title compound as a colourless solid.

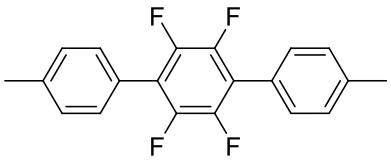


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.36 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH), 7.30 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH), 7.11-6.98 (m, 1H, CH), 2.43 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -139.8 to -139.9 (m, CF), -144.4 to -144.6 (m, CF).

1,4-di(p-tolyl)tetrafluorobenzene (7m bi-arylated)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 74 mg (15%) of the title compound as a colourless solid.

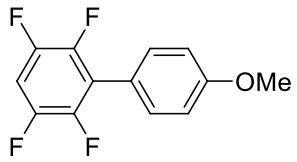


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.42 (d, $^3J_{HH}$ = 8.0 Hz, 4H, CH), 7.33 (d, $^3J_{HH}$ = 8.0 Hz, 4H, CH), 2.44 (s, 6H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -145.2 (s, CF).

2,3,5,6-tetrafluoro-4'-methoxybiphenyl (7n monoarylated)[10]

The general procedure yielded, after flash chromatography on silica gel (pentane/EtOAc: 20/1), 262 mg (68%) of the title compound as a colourless solid.

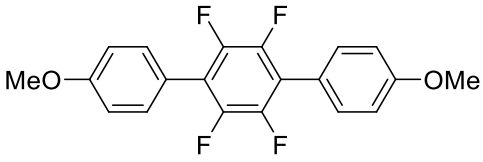


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.41 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH), 7.10-6.95 (m, 1H, CH), 7.02 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH), 3.86 (s, 3H, OCH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -139.8 to -140.0 (m, CF), -144.7 to -144.9 (m, CF).

1,4-di(p-methoxyphenyl)tetrafluorobenzene (7n diarylated)[10]

The general procedure yielded, after flash chromatography on silica gel (pentane/EtOAc: 20/1), 44 mg (8%) of the title compound as a colourless solid.

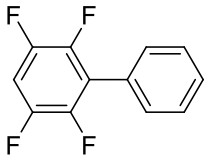


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.47 (d, $^3J_{HH}$ = 8.8 Hz, 4H, CH), 7.04 (d, $^3J_{HH}$ = 8.8 Hz, 4H, CH), 3.88 (s, 6H, OCH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -145.5 (s, CF).

2,3,5,6-tetrafluorobiphenyl (7o monoarylated)[15]

The general procedure yielded, after flash chromatography on silica gel (pentane), 238 mg (70%) of the title compound as a colourless solid.

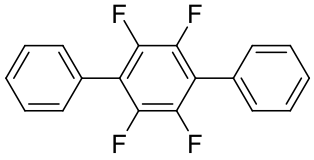


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.54-7.43 (m, 5H, CH), 7.13-7.01 (m, 1H, CH).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -139.6 to -139.7 (m, CF), -144.3 to -144.5 (m, CF).

1,4-diphenyltetrafluorobenzene (7o diarylated)[16]

The general procedure yielded, after flash chromatography on silica gel (pentane), 100 mg (22%) of the title compound as a colourless solid.

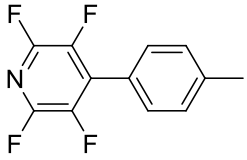


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.54-7.46 (m, 10H, CH).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -144.9 (s, CF).

2,3,5,6-tetrafluoropyridine (7p)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 354 mg (98%) of the title compound as a colourless solid.

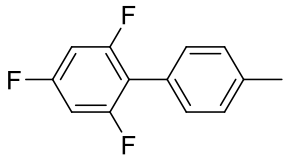


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.46-7.41 (m, 2H, C*H*), 7.38-7.33 (m, 2H, C*H*), 2.45 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -91.4 to -91.7 (m, NCF), -145.7 to -146.0 (m, CF).

2,4,6-trifluoro-4'-methylbiphenyl (7q)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane), 332 mg (50%) of the title compound as a colourless solid.

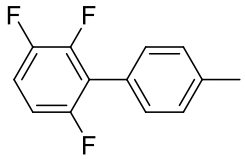


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.34-7.25 (m, 4H, CH), 6.81-6.89 (m, 2H, CH), 2.41 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -110.1 (t, J_{FF} = 6.1 Hz, *p*-CF), -111.9 (d, J_{FF} = 6.1 Hz, *o*-CF).

2,3,6-tetrafluoro-4'-*methylbiphenyl (7r)*

The general procedure yielded, after flash chromatography on silica gel (pentane), 240 mg (72%) of the title compound as a colourless solid.



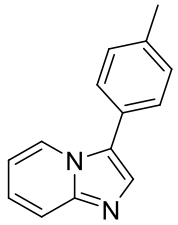
^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.37 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, CH), 7.29 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, CH), 7.17-7.04 (m, 1H, CH), 6.96-6.86 (m, 1H, CH), 2.42 (s, 3H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -120.4 (dd, J_{FF} = 3.9 Hz, J_{FF} = 15.1 Hz, CF), -138.5 (dd, J_{FF} = 3.7 Hz, J_{FF} = 21.5 Hz, CF), -142.7 (dd, J_{FF} = 15.1 Hz, J_{FF} = 21.5 Hz, CF).

HRMS calcd. For $C_{13}H_9F_3$ $(M)^+$ 222.0651, found 222.0649.

3-(p-tolyl)imidazo[1,2,a]pyridine (7s)[17]

The general procedure yielded, after flash chromatography on silica gel (CH_2Cl_2/MeOH: 99/1), 218 mg (70%) of the title compound as a pale brown solid.

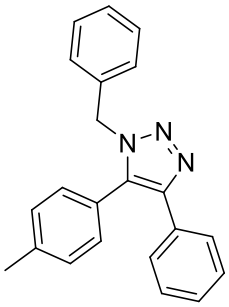


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.33 (d, $^3J_{HH}$ = 6.9 Hz, 1H, $C_{Ar}H$), 7.74-7.64 (m, 2H, $C_{Ar}H$, C*H*), 7.45 (d, $^3J_{HH}$ = 8.1 Hz, 2H, $C_{Ar}H$), 7.33 (d, $^3J_{HH}$ = 8.1 Hz, 2H, $C_{Ar}H$), 7.21 (t, $^3J_{HH}$ = 8.0 Hz, 1H, $C_{Ar}H$), 6.82 (t, $^3J_{HH}$ = 6.9 Hz, 1H, $C_{Ar}H$), 2.44 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 146.1 (s, C^{IV}), 138.2 (s, C^{IV}), 132.4 (s, C_{Ar}H), 130.0 (s, C_{Ar}H), 128.1 (s, C_{Ar}H), 126.4 (s, C^{IV}), 125.8 (s, C^{IV}), 124.1 (s, C_{Ar}H), 123.4(s, C_{Ar}H), 118.3 (s, C_{Ar}H), 112.4 (s, C_{Ar}H), 21.4 (s, CH_3).

1-benzyl-5-(4-methylphenyl)-4-phenyl-1H-1,2,3-triazole ***(7t)***

The general procedure yielded, after flash chromatography on silica gel (pentane/Et_2O: 1/1), 380 mg (78%) of the title compound as a pale yellow solid.

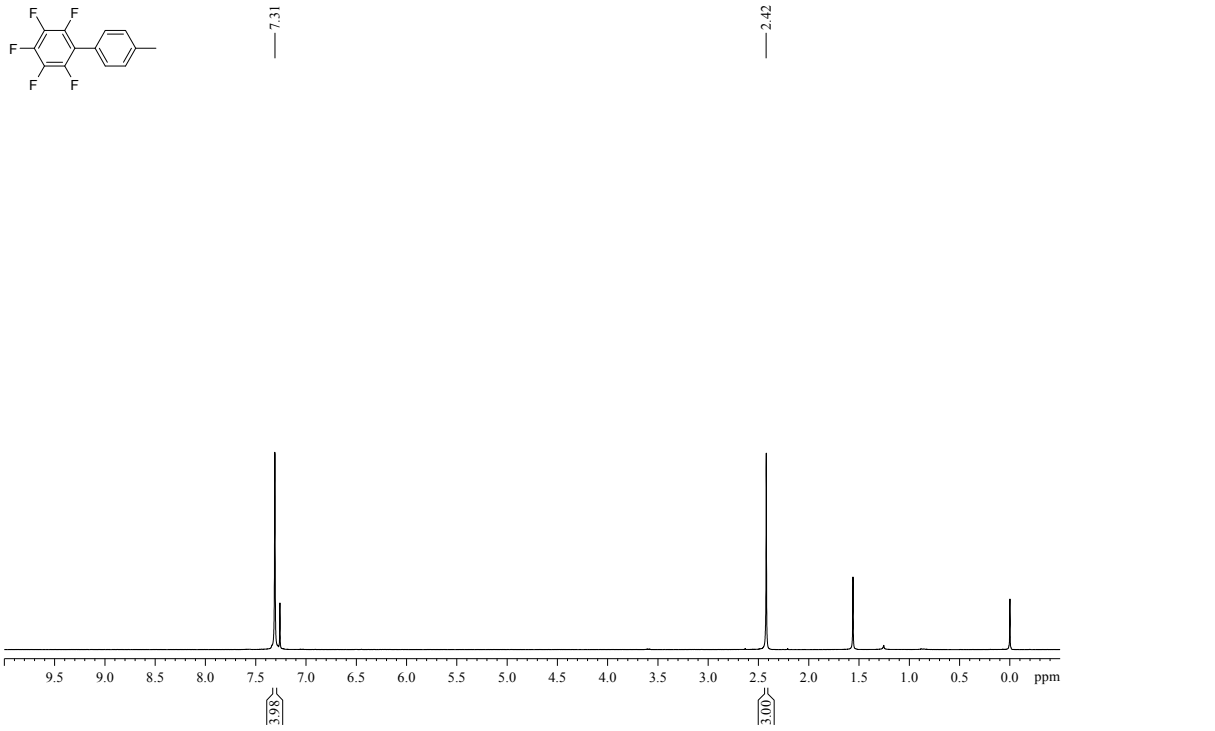


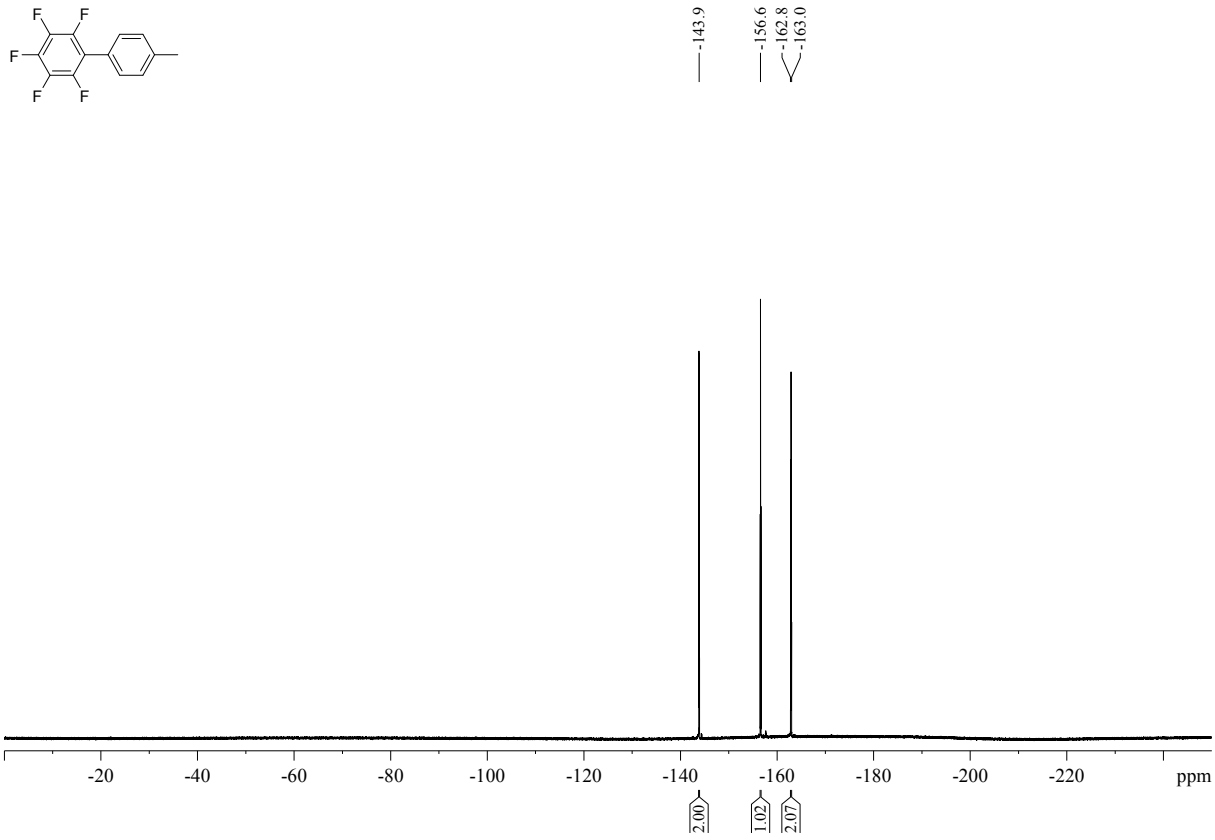
^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.60-7.54 (m, 2H, CH), 7.29-7.18 (m, 8H, CH), 7.08-7.00 (m, 4H, CH), 5.39 (s, 2H, CH_2), 2.42 (s, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 144.5 (s, C^{IV}), 139.9 (s, C^{IV}), 135.6 (s, C^{IV}), 134.1 (s, C^{IV}), 131.2 (s, C^{IV}), 130.0 (s, *C*H), 130.0 (s, *C*H), 128.8 (s, *C*H), 128.5 (s, *C*H), 128.2 (s, *C*H), 127.7 (s, *C*H), 127.6 (s, *C*H), 126.8 (s, *C*H), 124.8 (s, C^{IV}), 52.0 (s, CH_2), 21.6 (s, CH_3).

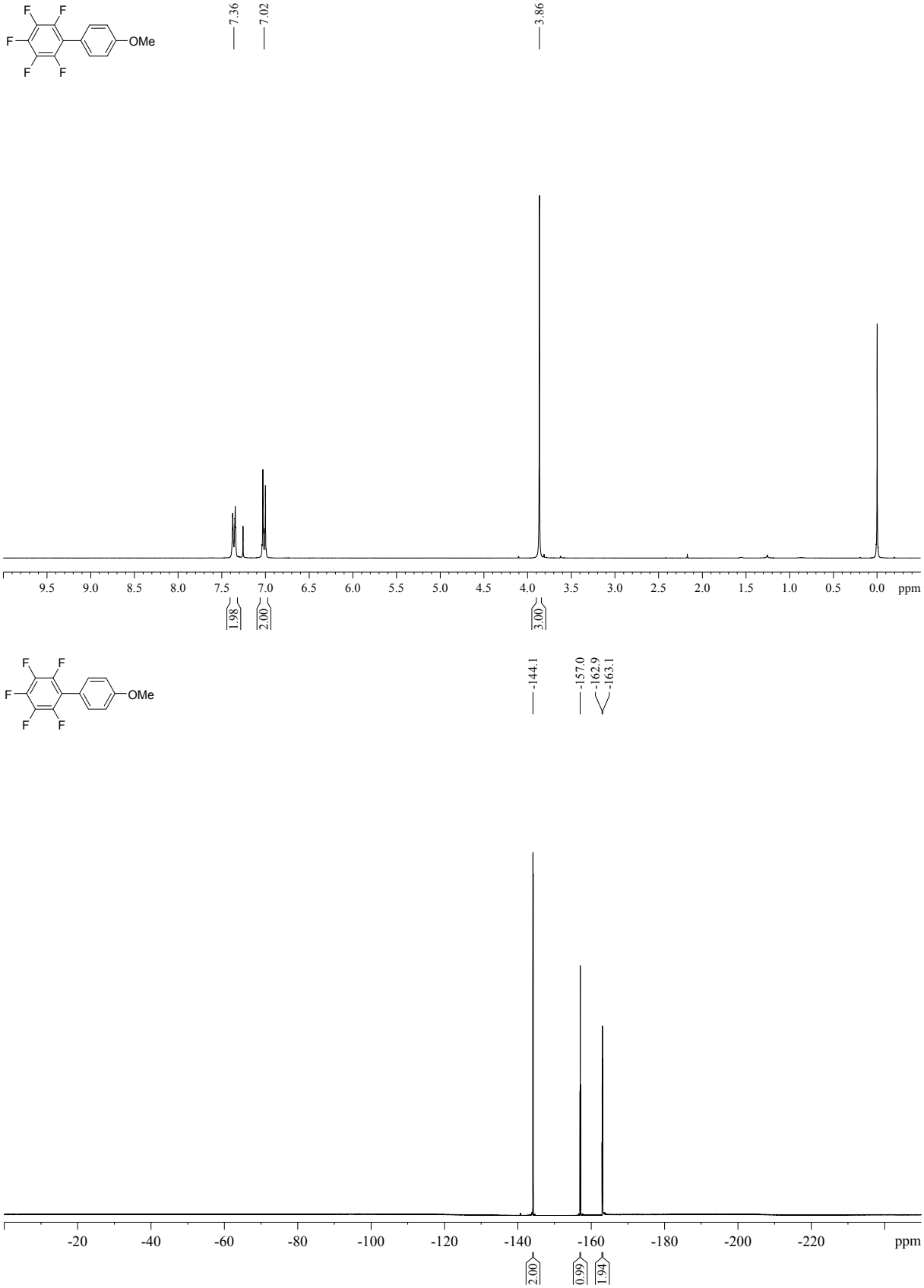
4. Spectra

^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-pentafluoro-4'-methylbiphenyl (7a)

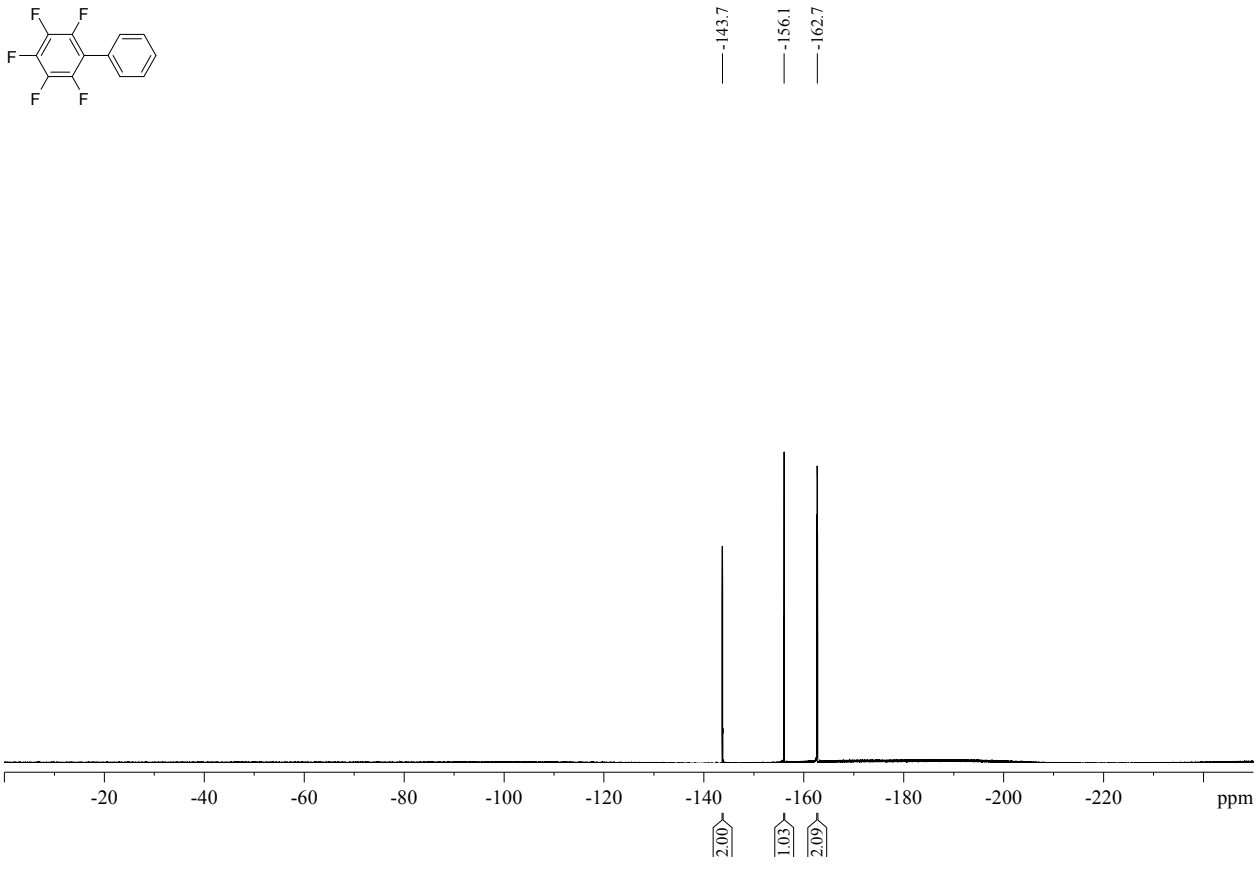




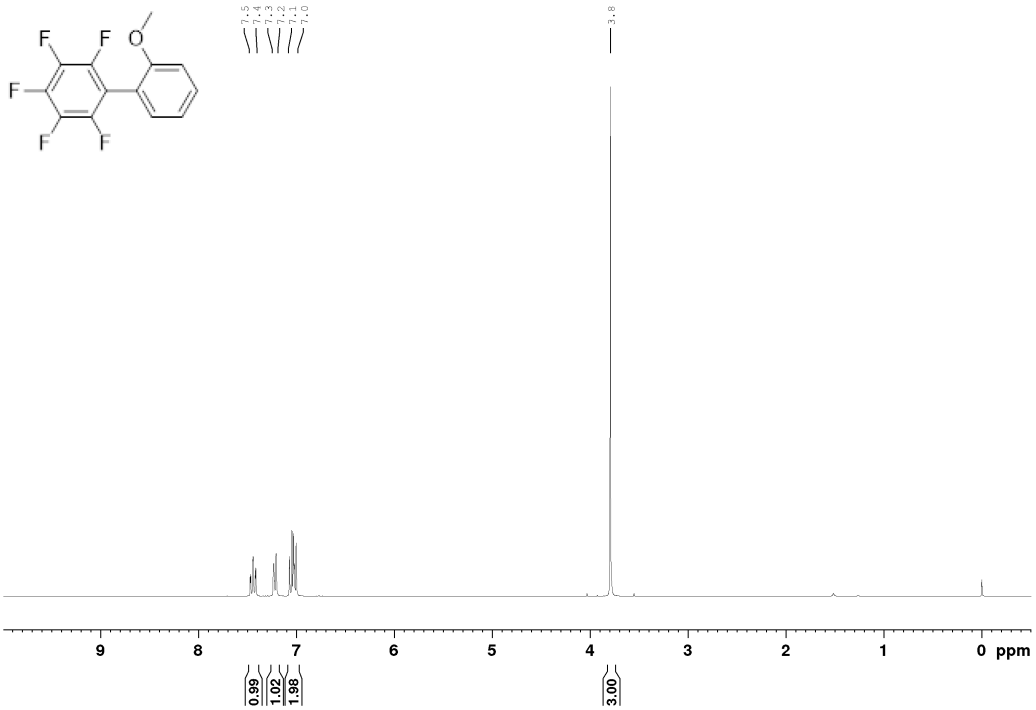
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-pentafluoro-4'-methoxybiphenyl (7b)

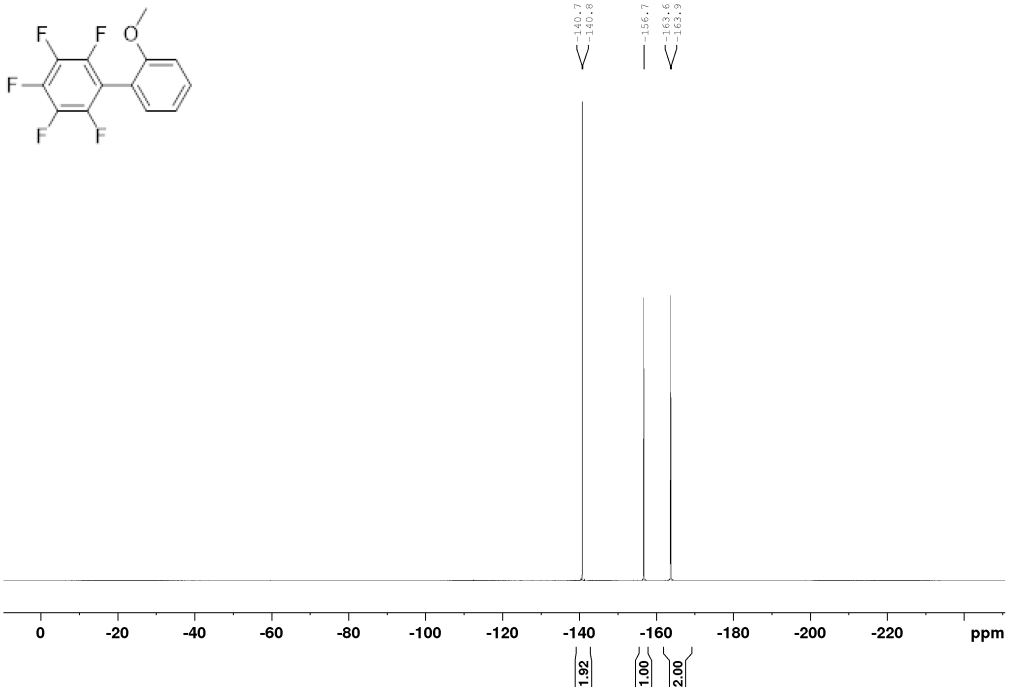


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-pentafluorobiphenyl (7c)

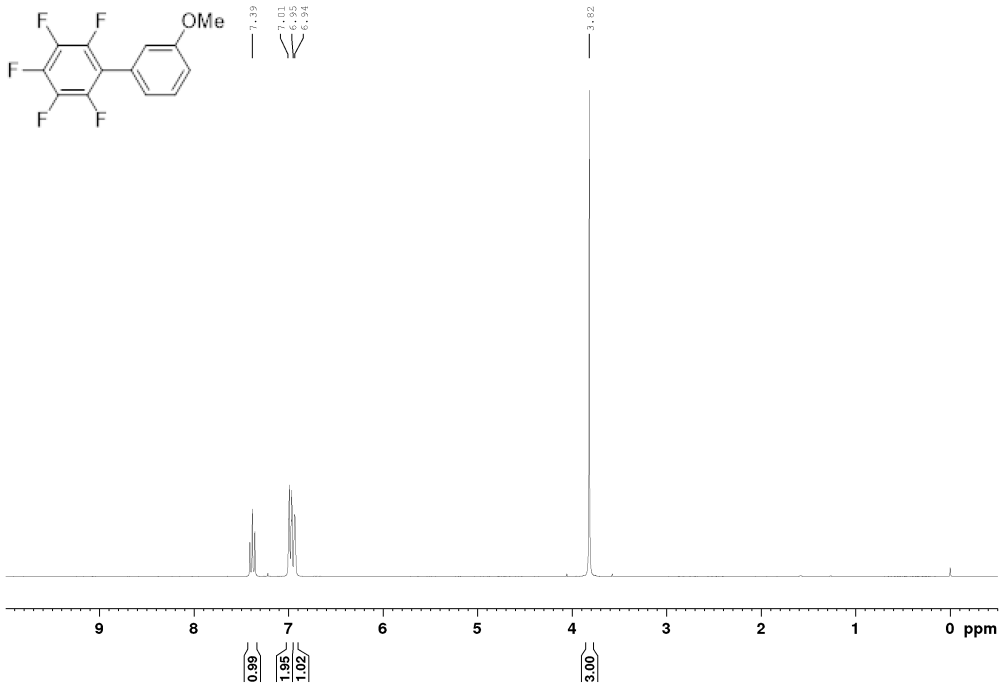


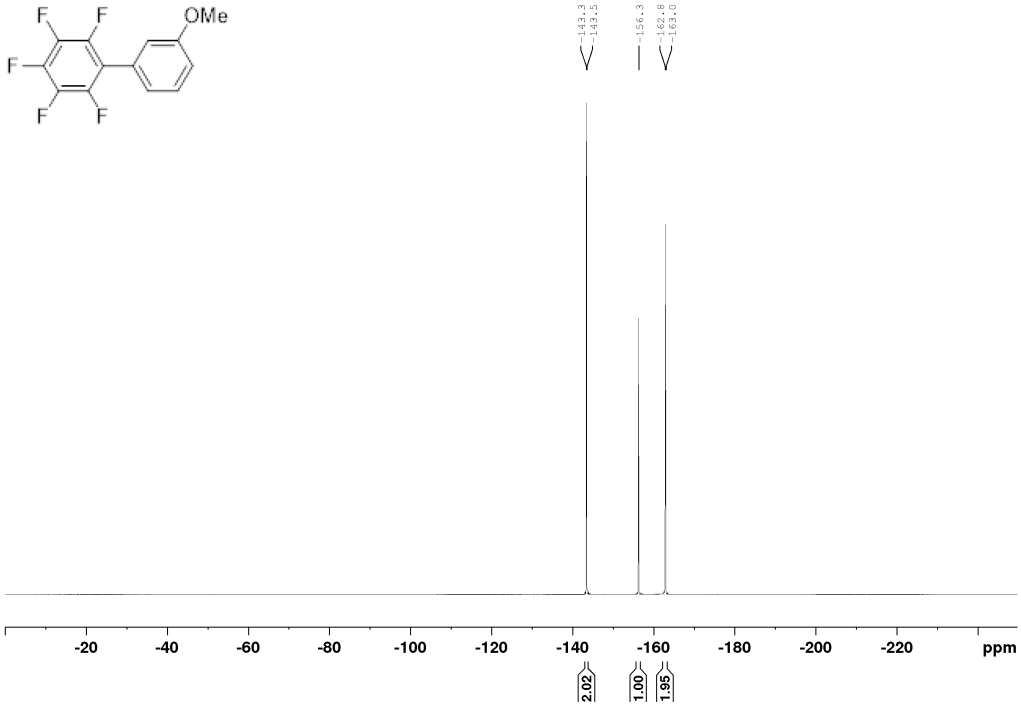
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-pentafluoro-2'-methoxybiphenyl (7d)



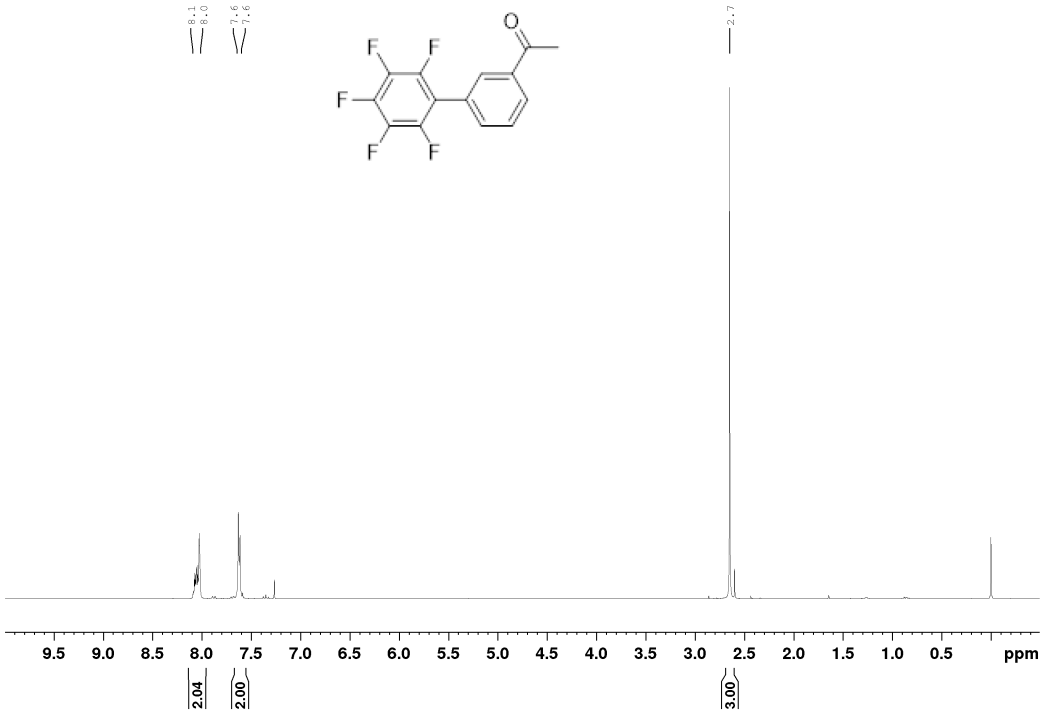


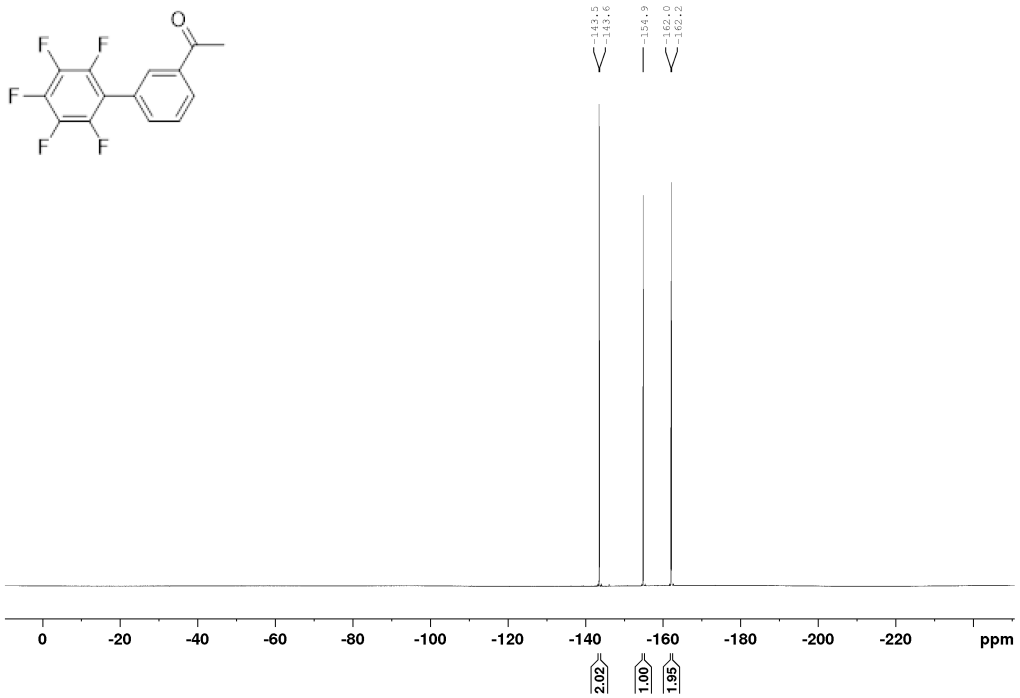
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-pentafluoro-3'-methoxybiphenyl (7e)



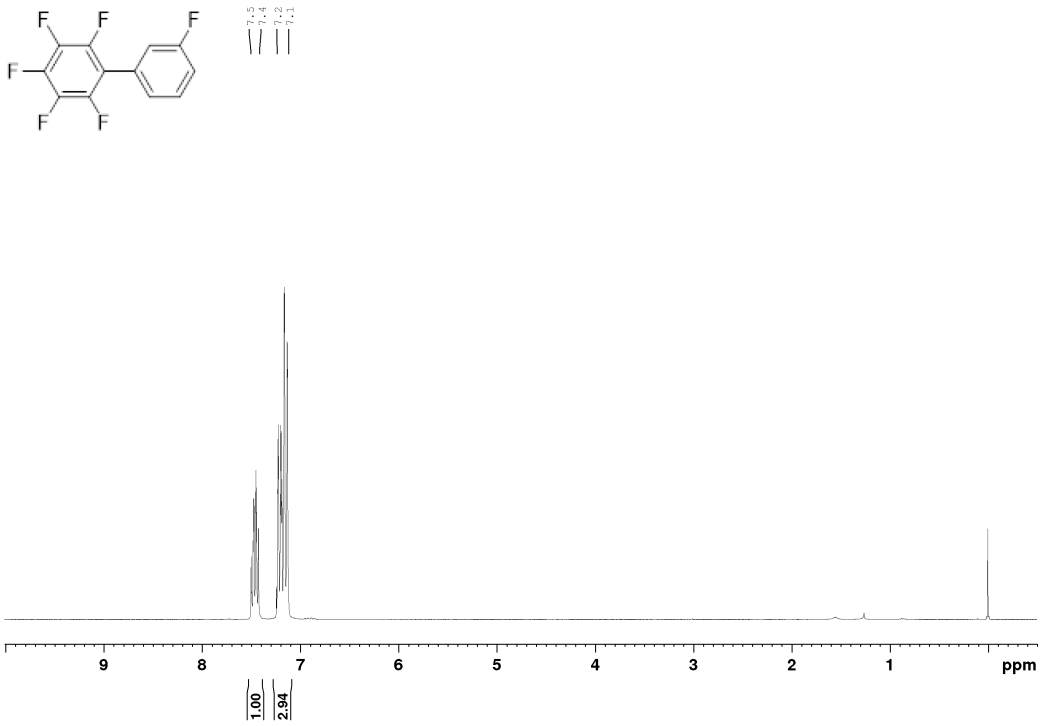


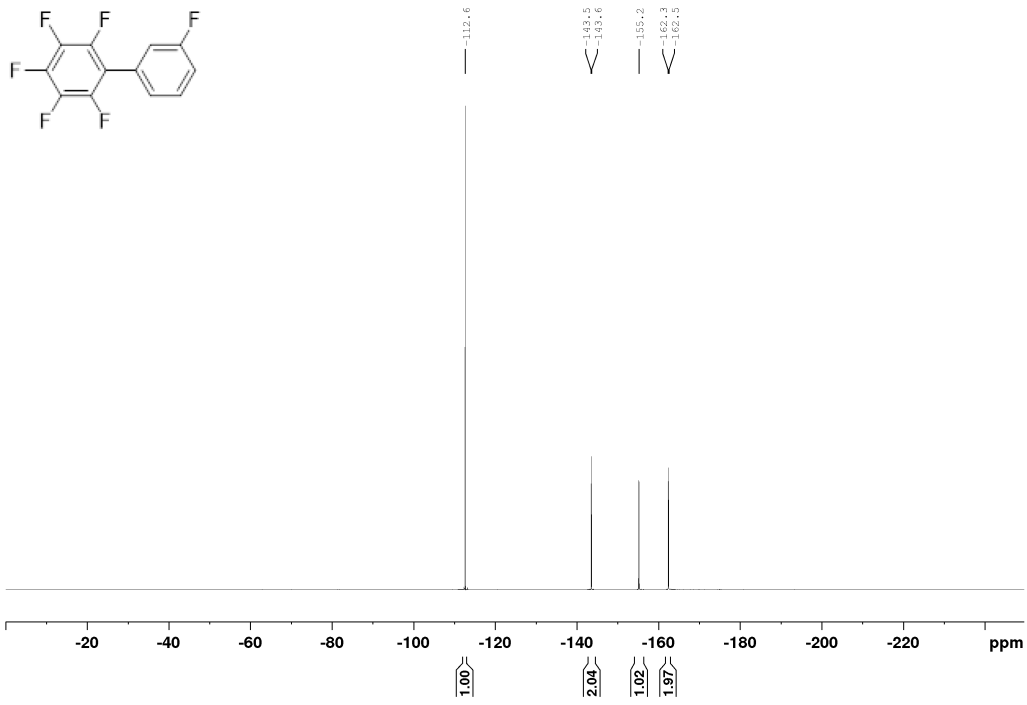
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 3'-(2,3,4,5,6-pentafluorophenyl)acetophenone (7f)



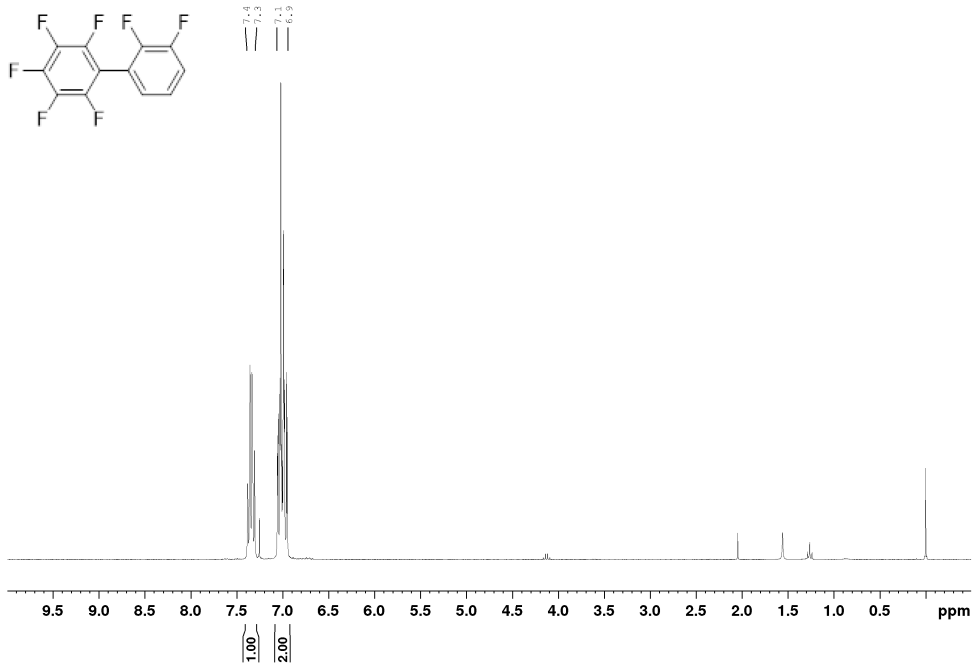


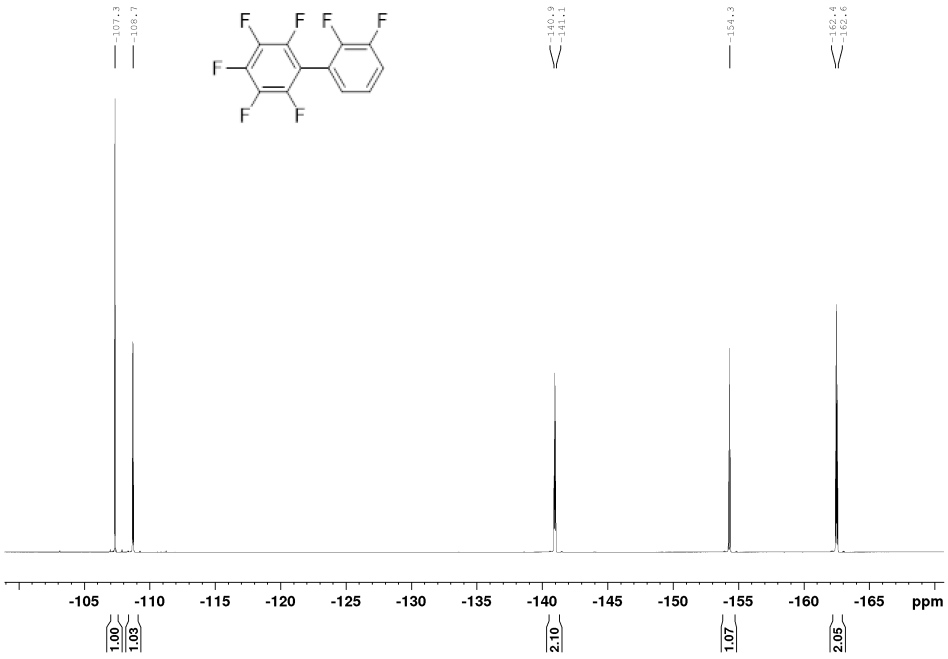
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,3',4,5,6-hexafluoro-1,1'-biphenyl (7g)



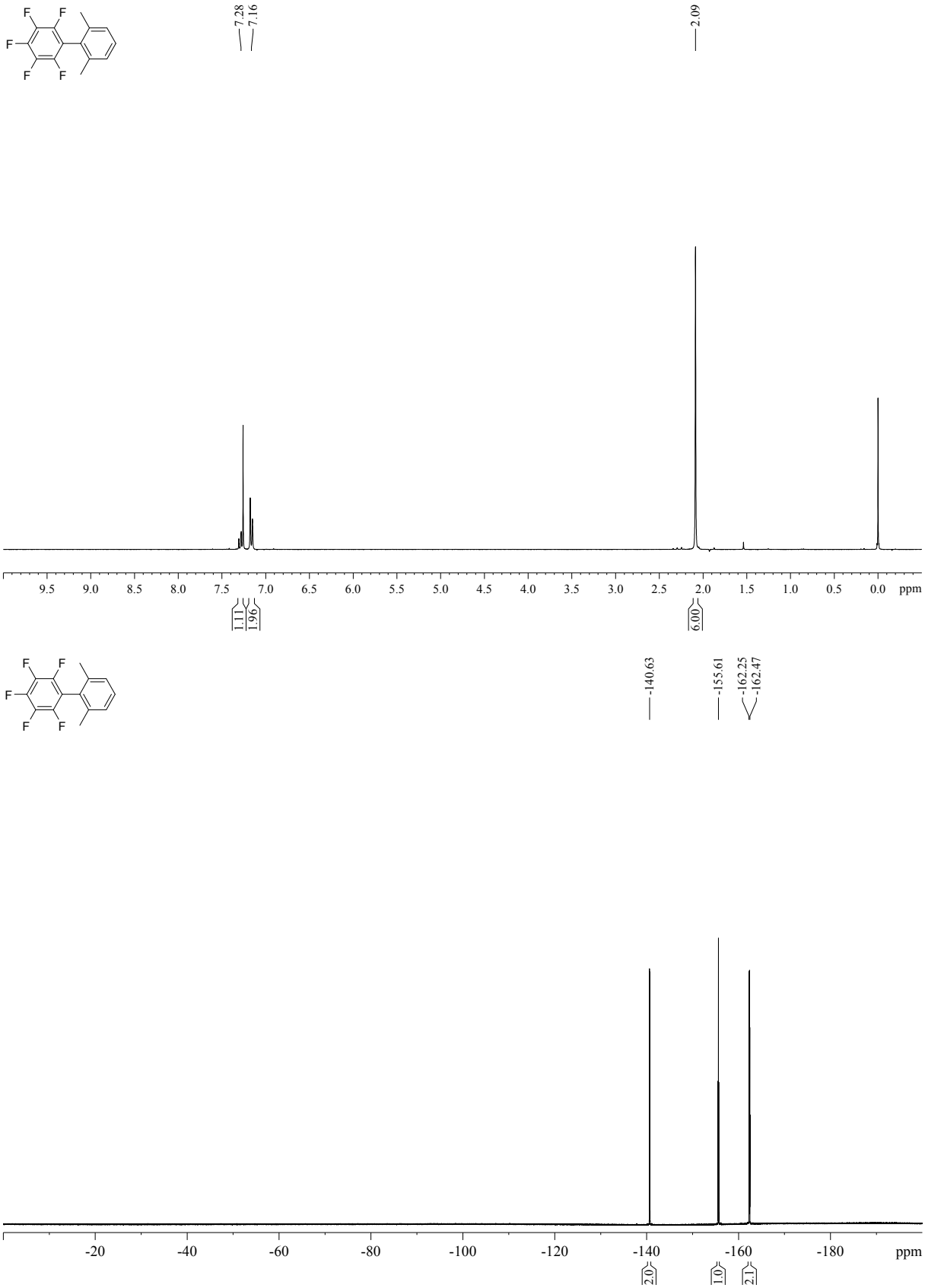


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,2',3,3',4,5,6-heptafluoro-1,1'-biphenyl (7h)

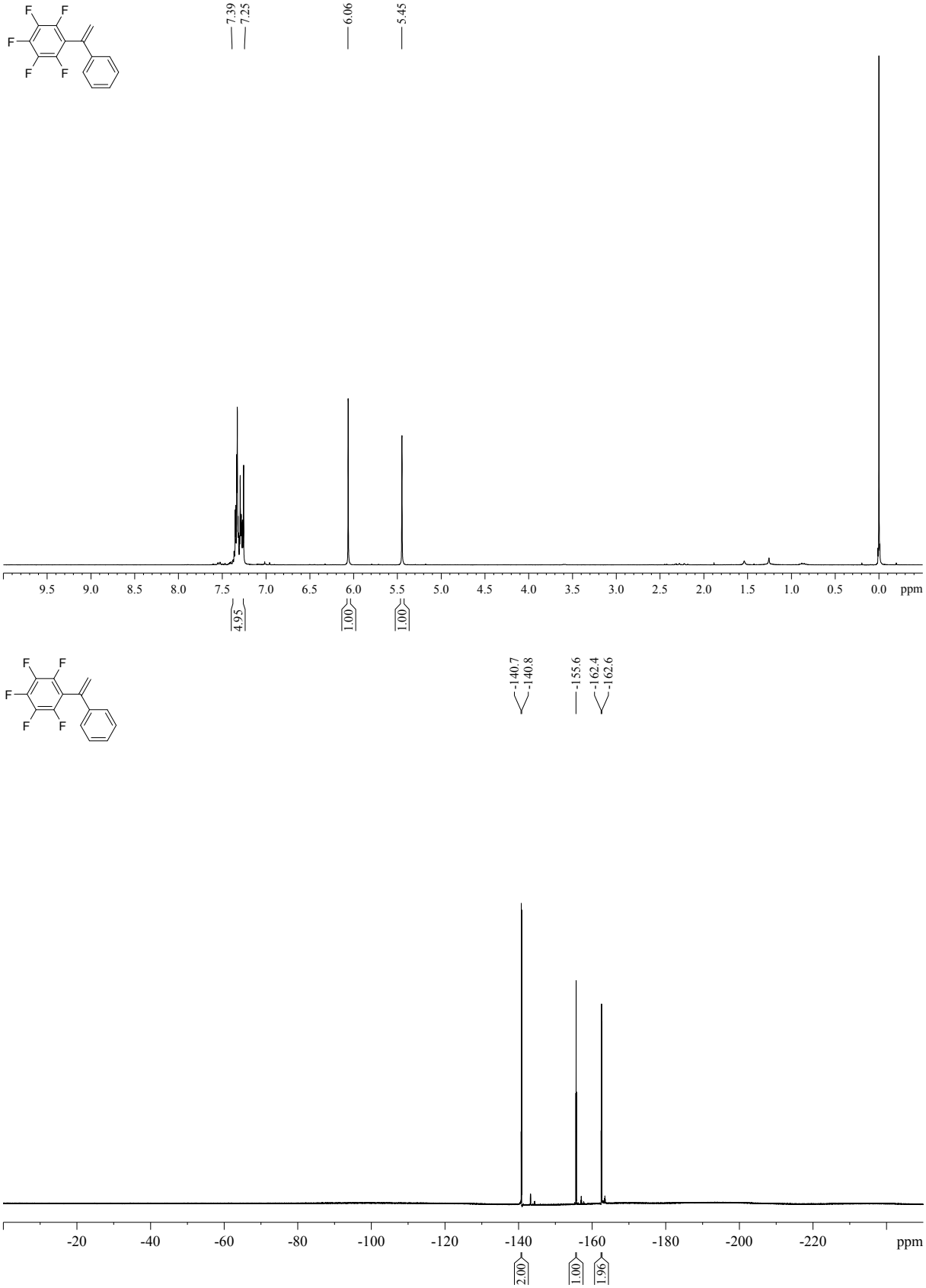




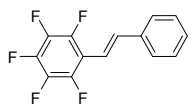
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-pentafluoro-2',6'-dimethylbiphenyl (7i)

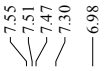


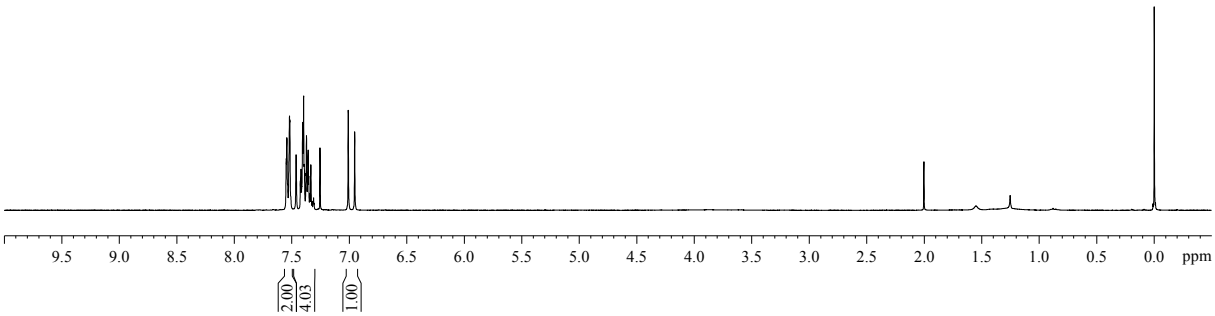
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-tetrafluoro-6-(1-phenylethynyl) (7j)

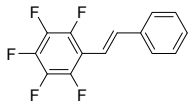


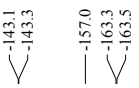
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of (E)-1,2,3,4,5-pentafluorostilbene (7k)

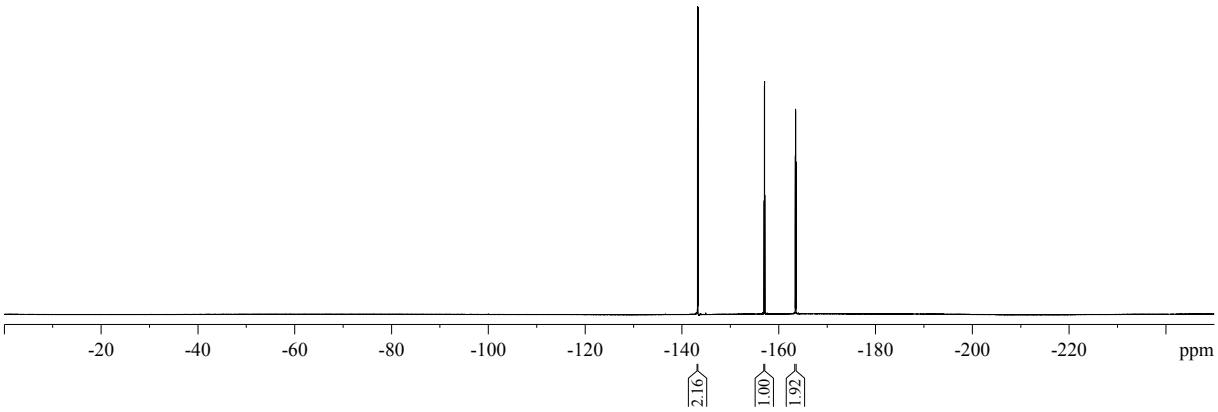




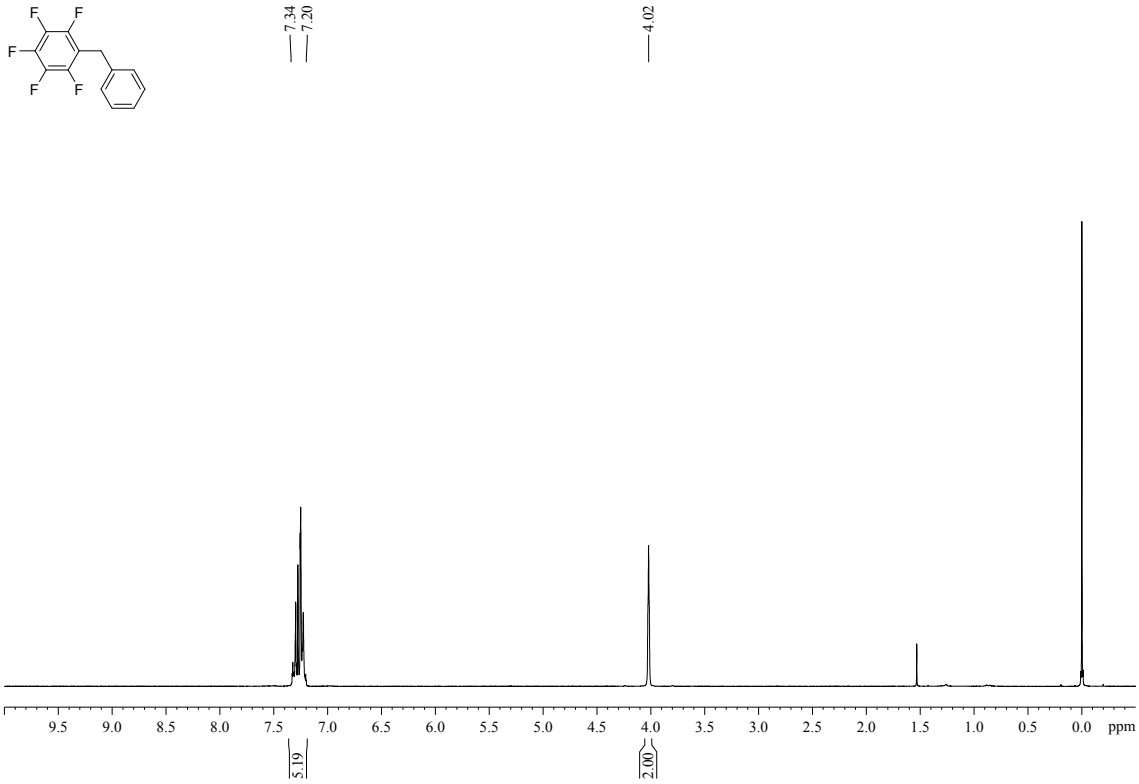


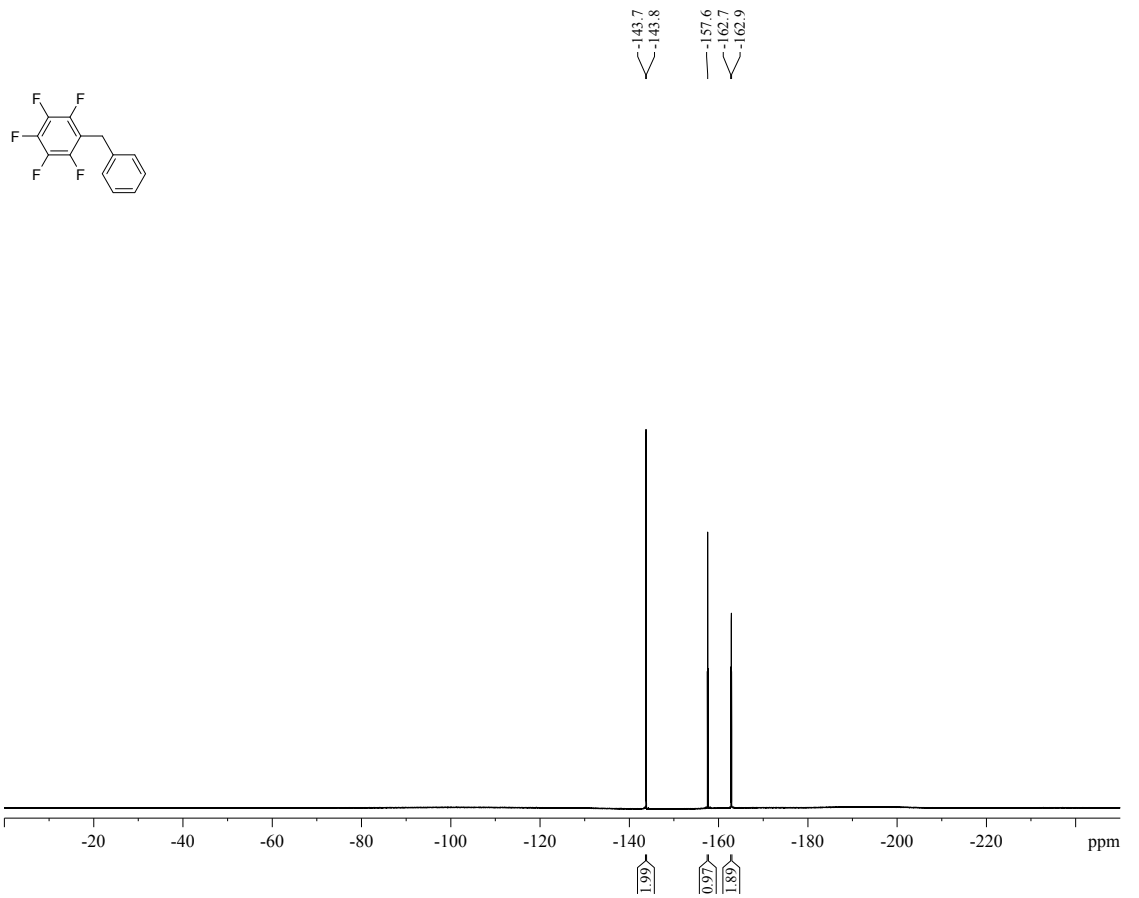




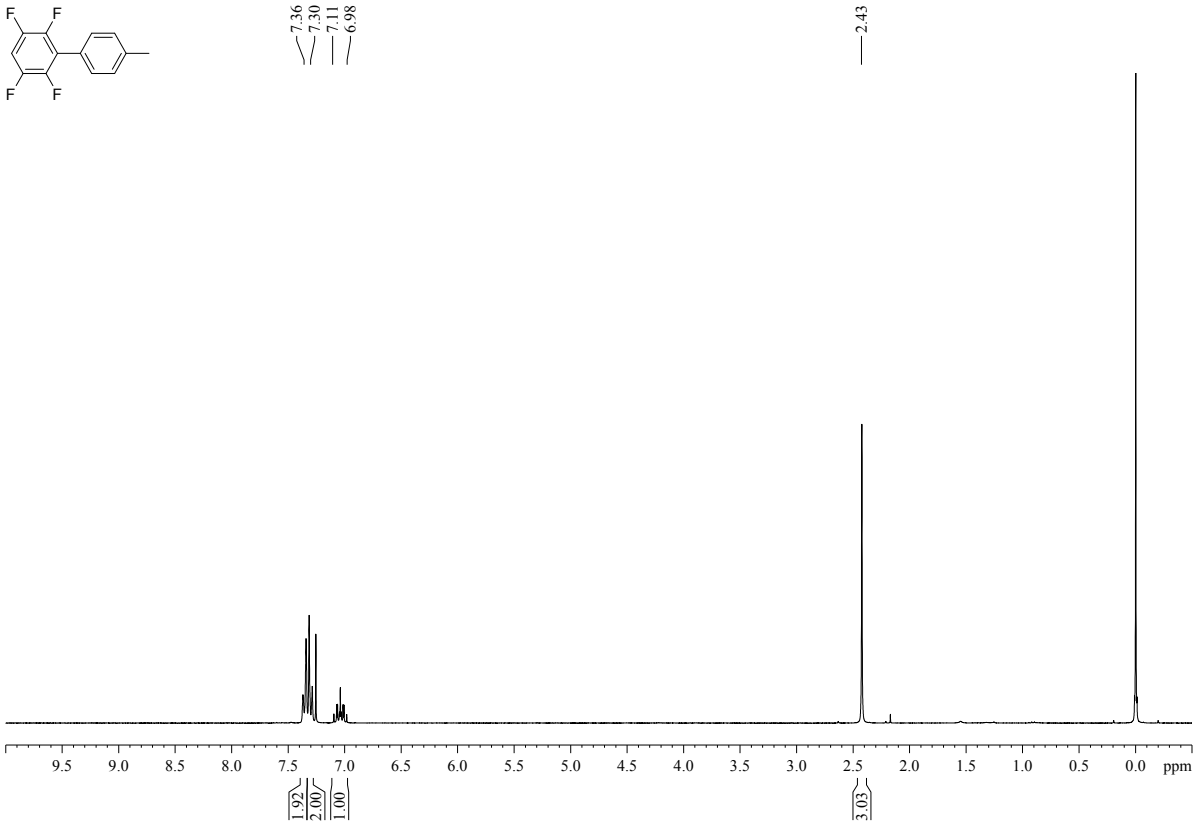


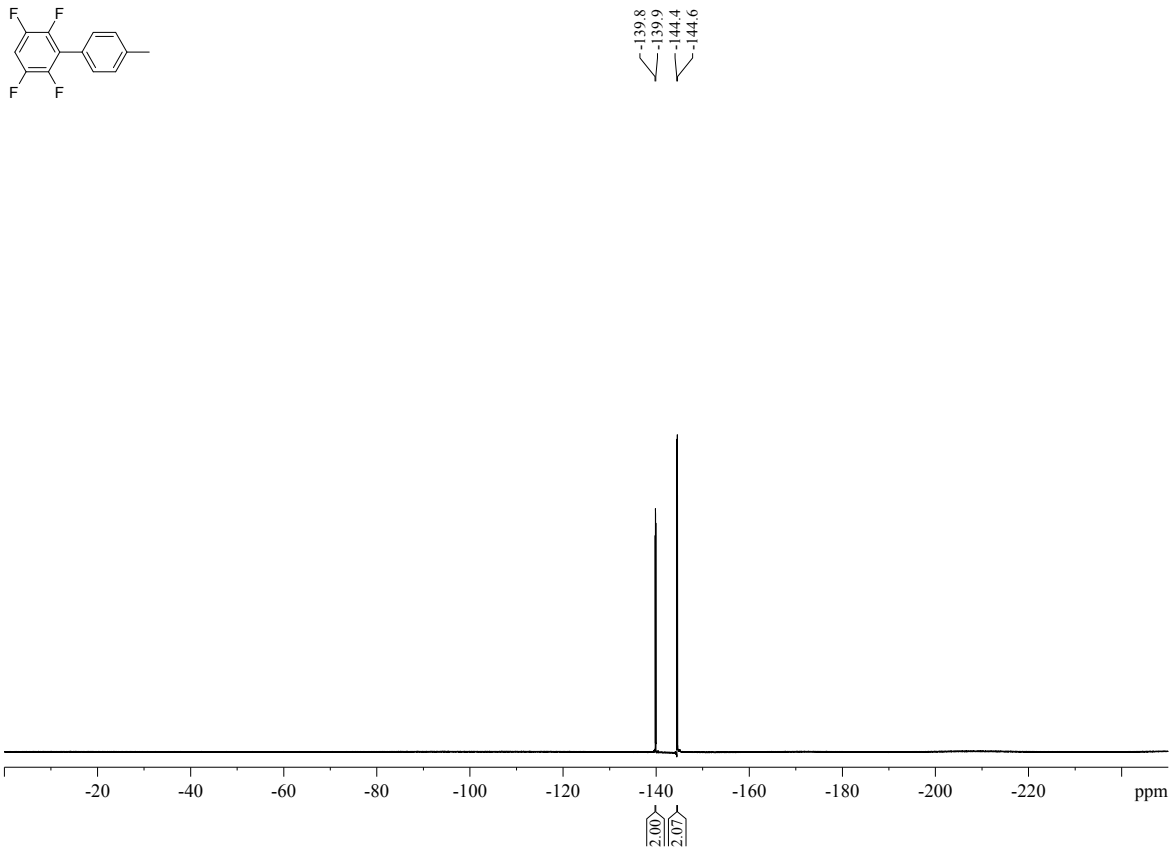
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,4,5,6-tetrafluoromethylbenzyl (7l)



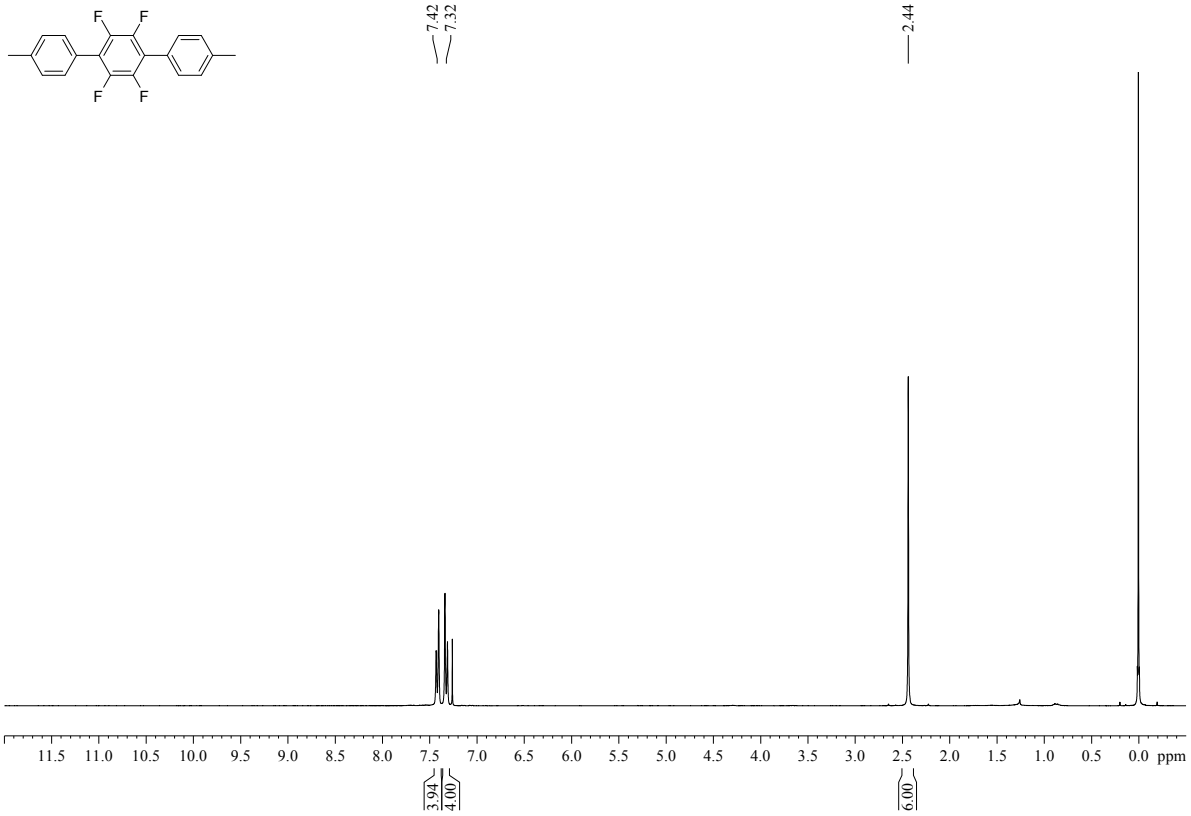


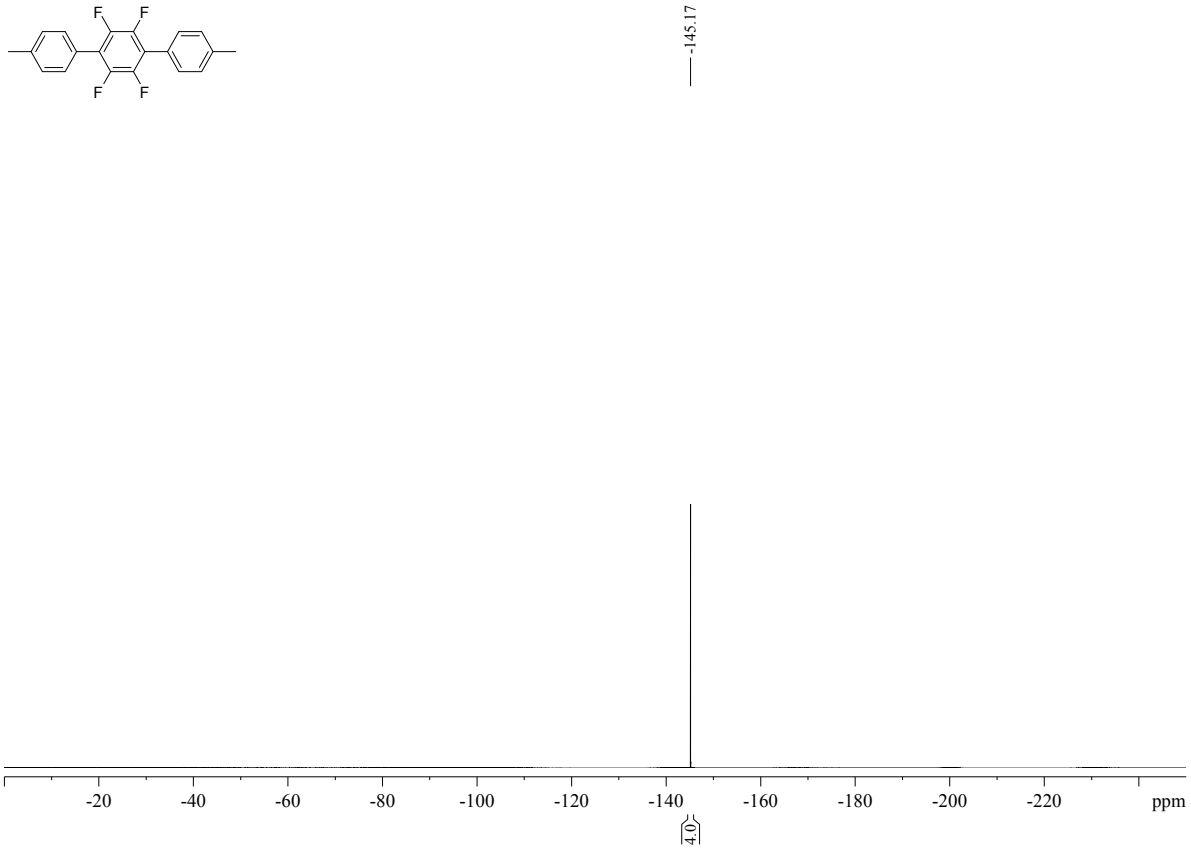
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,5,6-tetrafluoro-4'-methylbiphenyl (7m monoarylated)



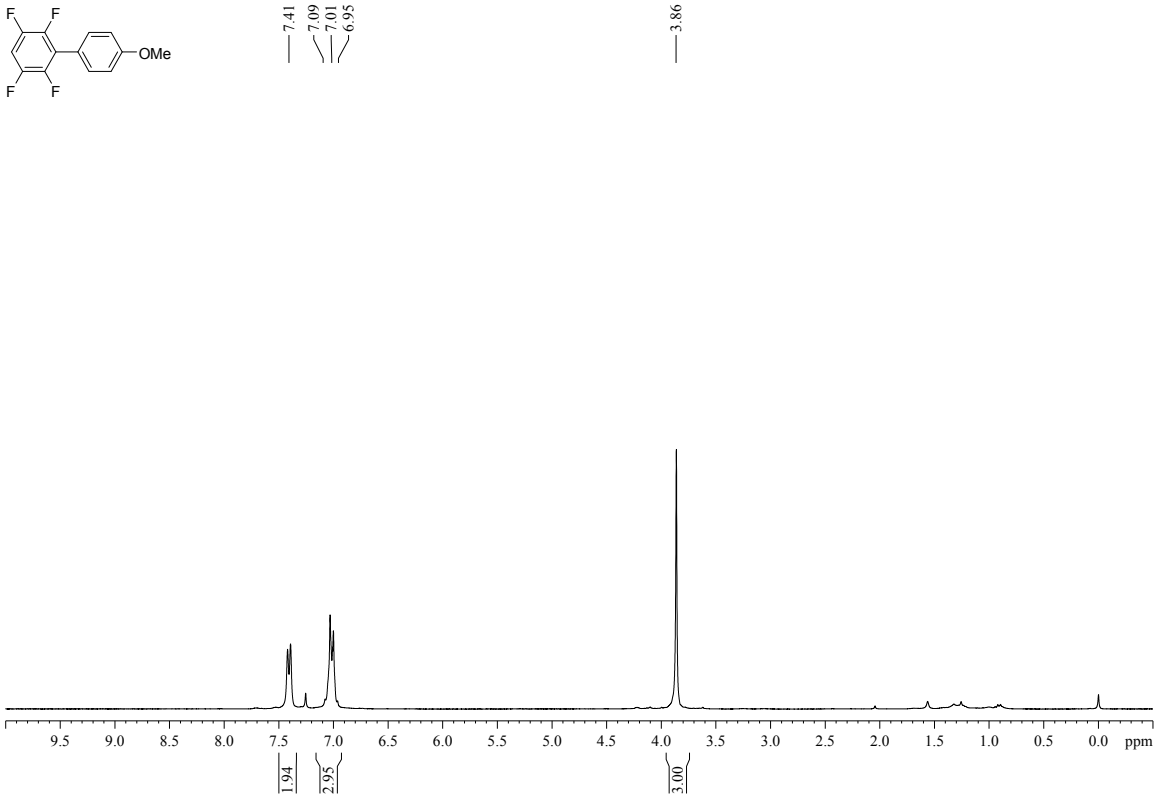


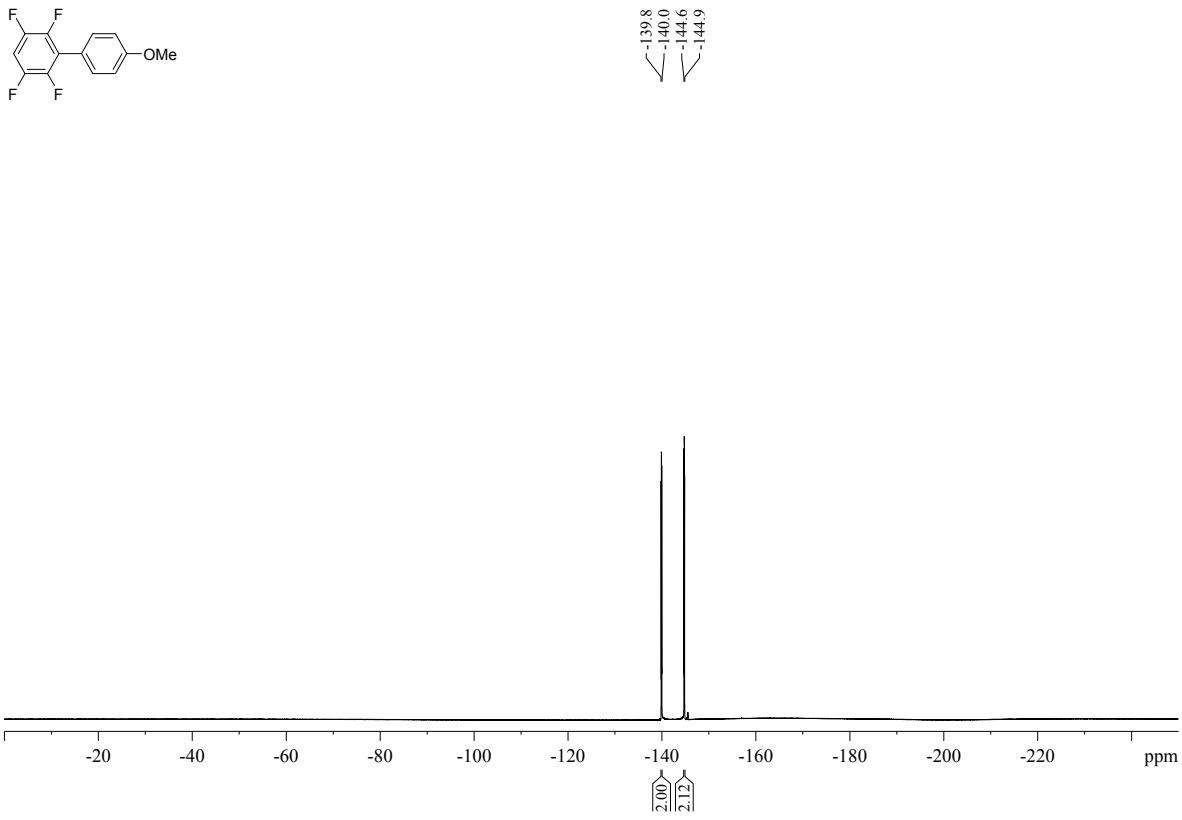
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 1,4-di(p-tolyl)tetrafluorobenzene (7m diarylated)



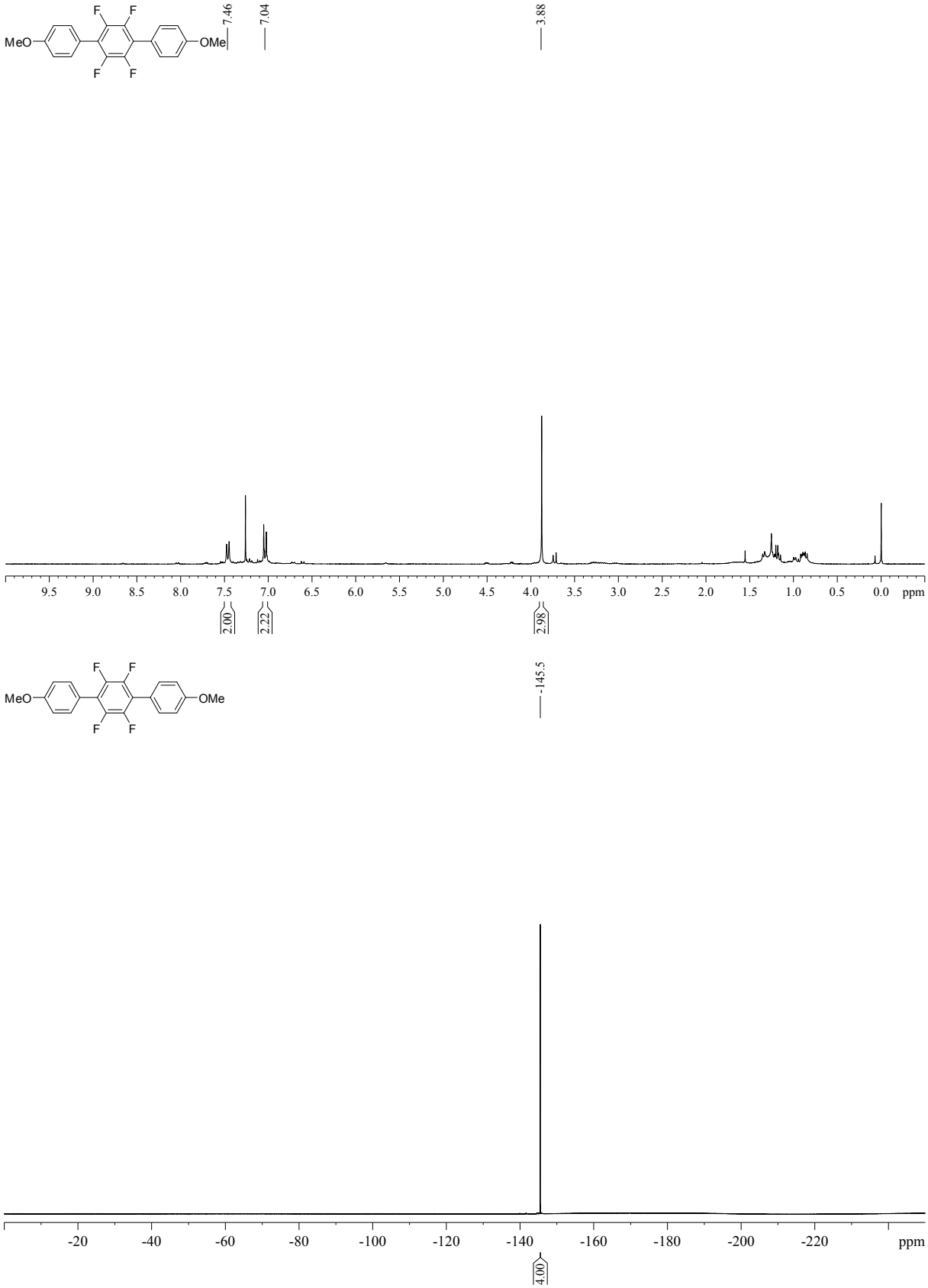


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,5,6-tetrafluoro-4'-methoxybiphenyl (7n monoarylated)

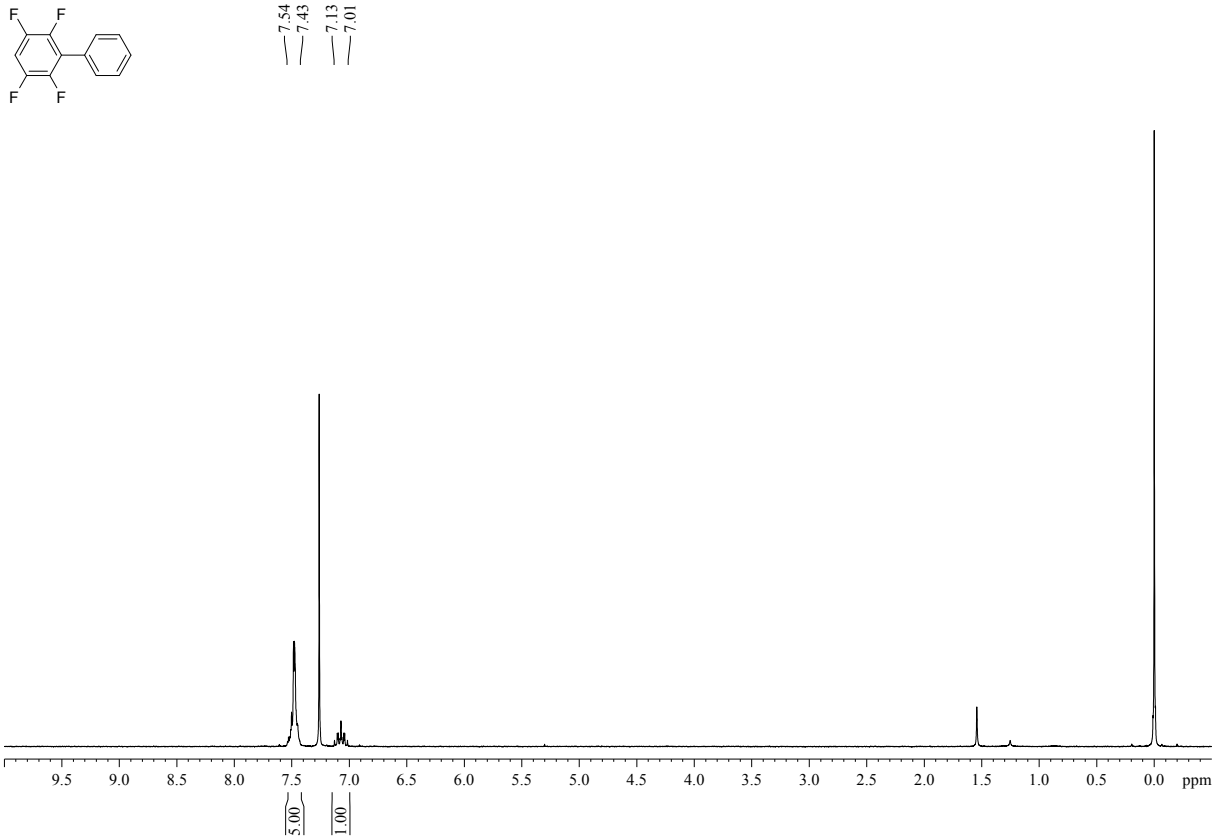


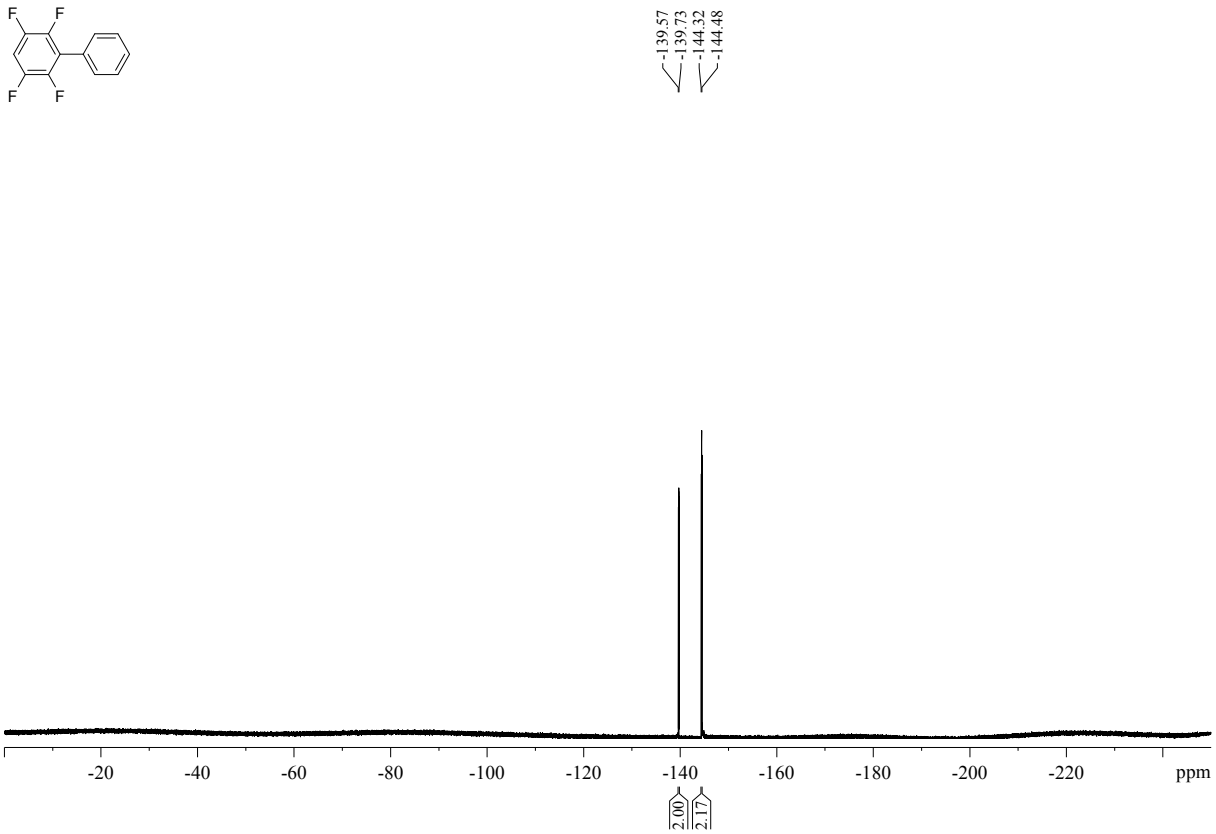


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 1,4-di(p-methoxyphenyl)tetrafluorobenzene (7n diarylated)

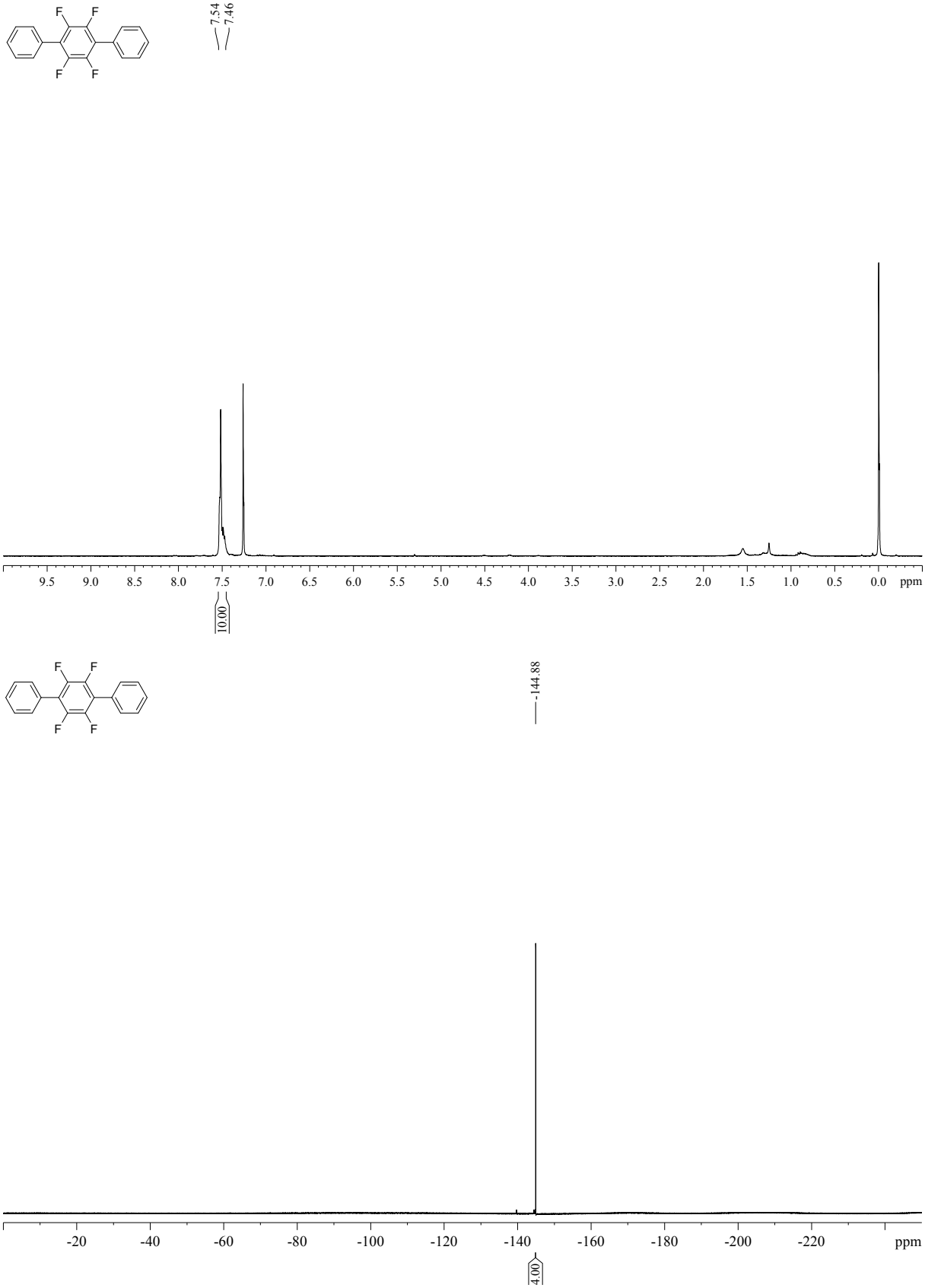


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,5,6-tetrafluorobiphenyl (7o monoarylated)

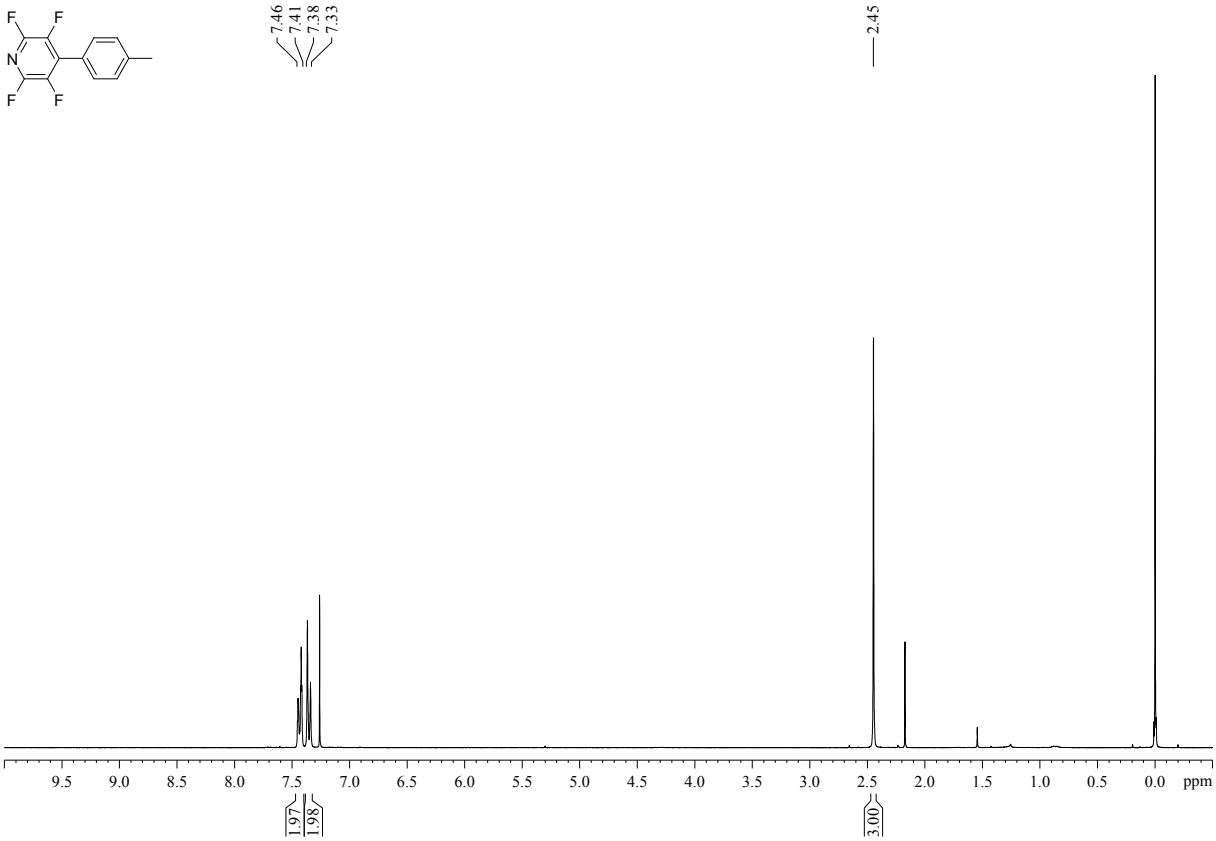


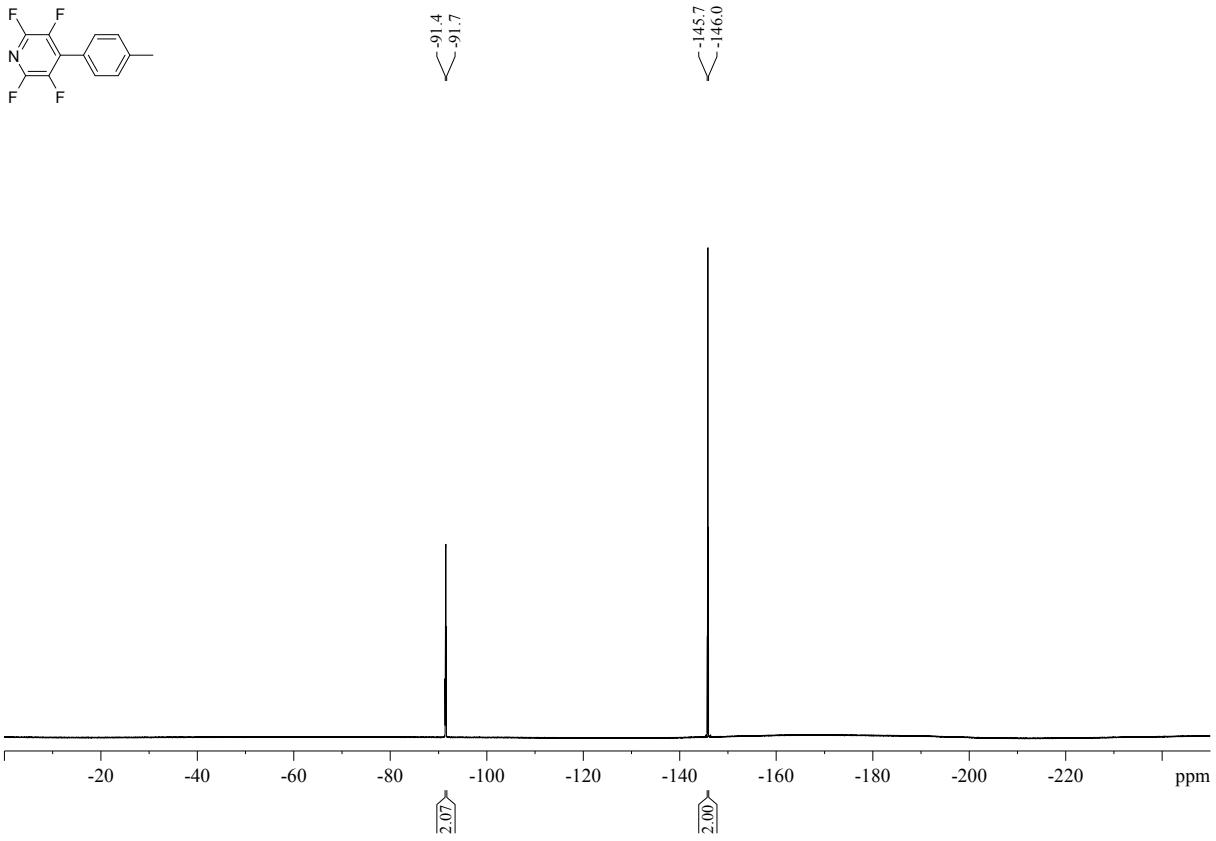


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 1,4-diphenyltetrafluorobenzene(7o diarylated)

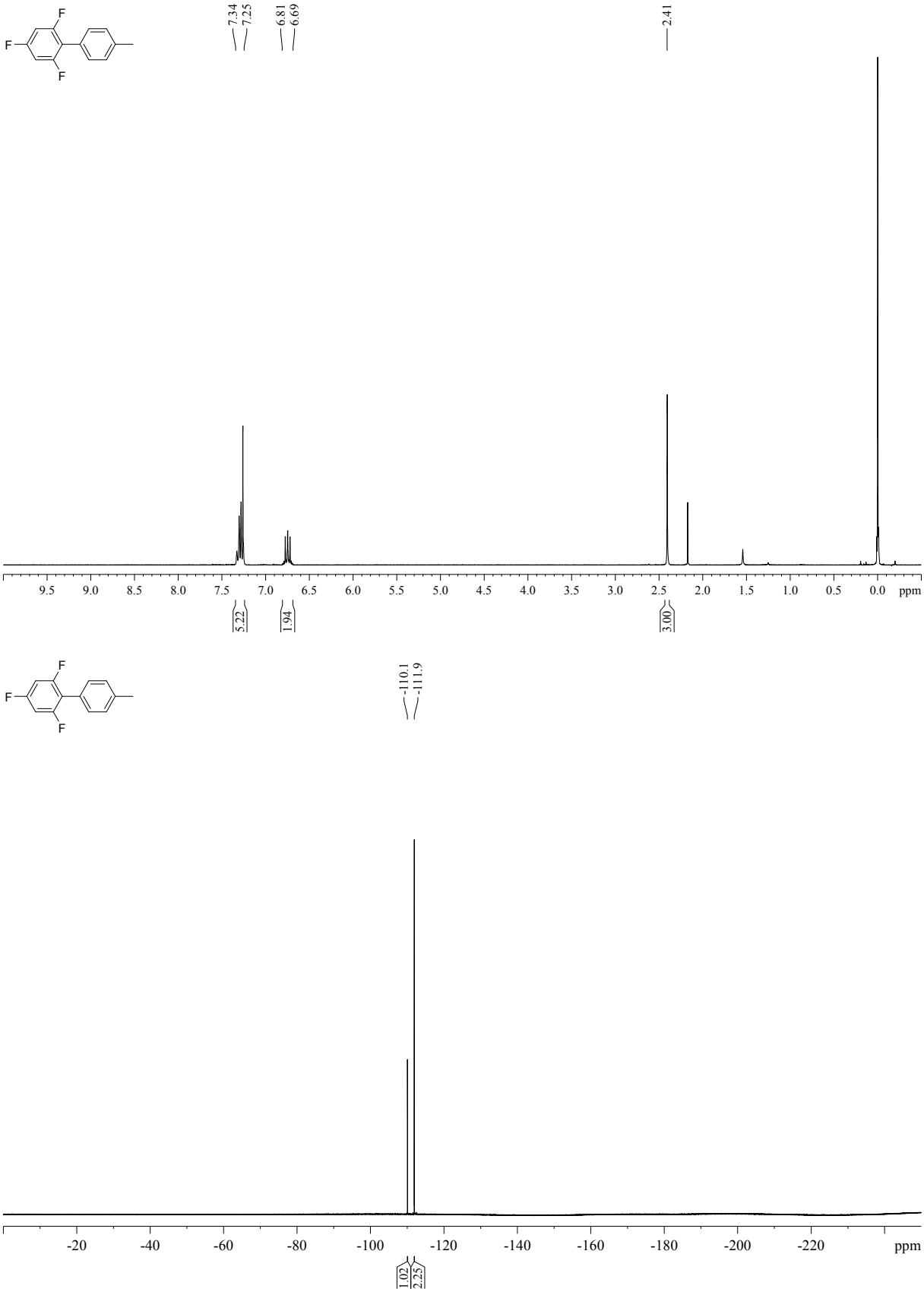


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,5,6-tetrafluoropyridine (7p)

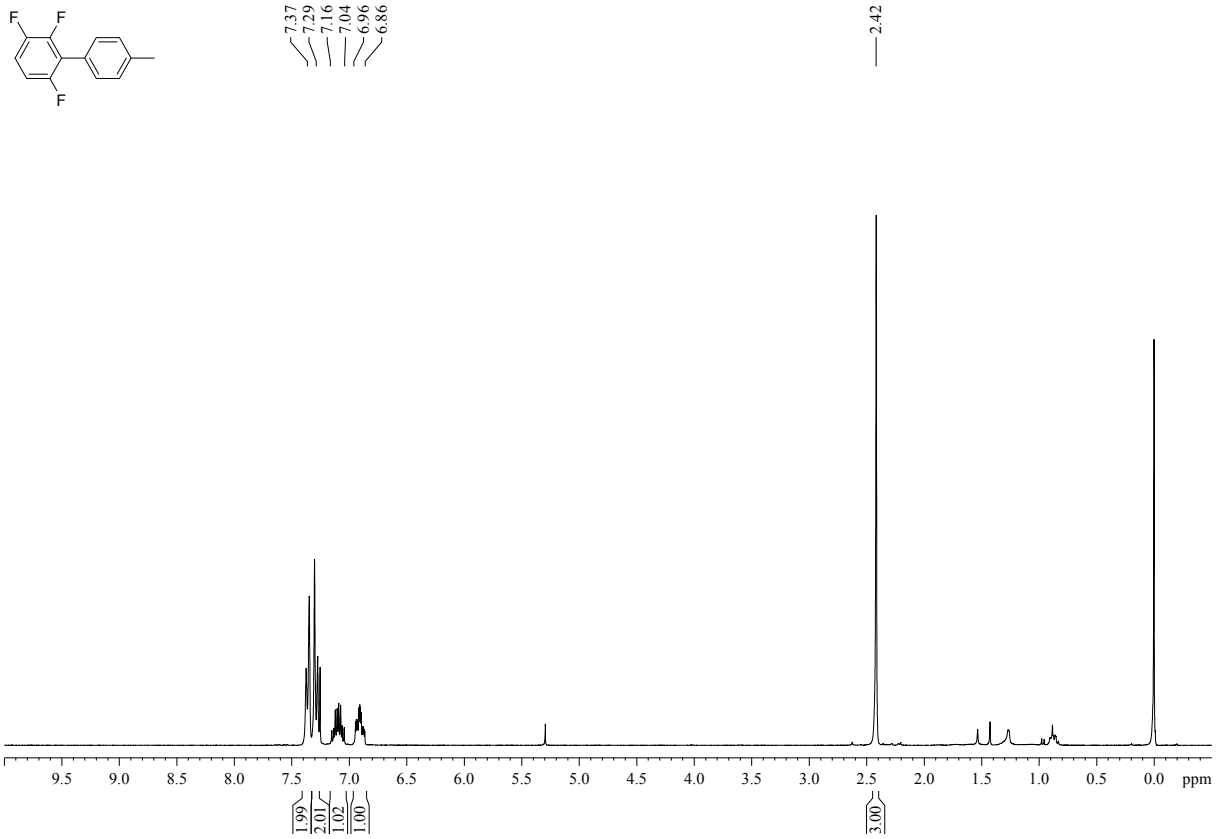


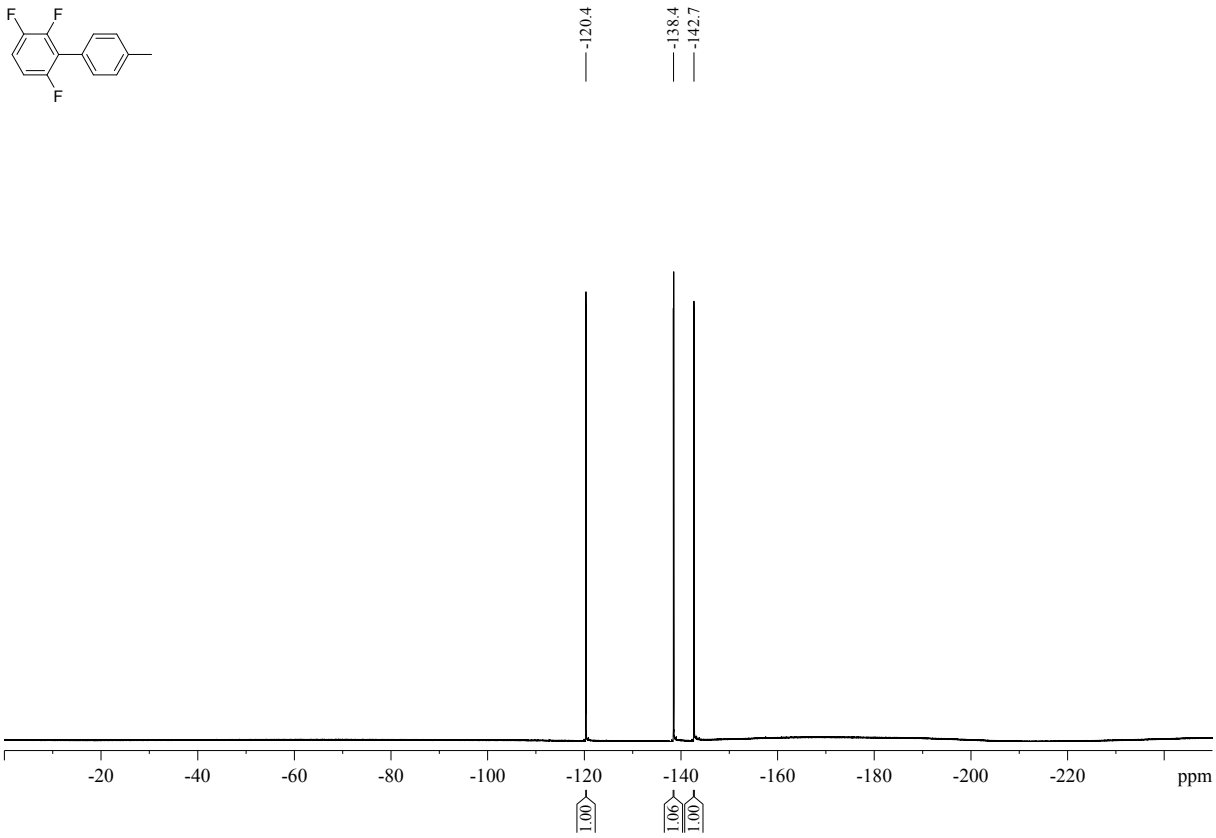


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,4,6-trifluoro-4'-methylbiphenyl (7q)

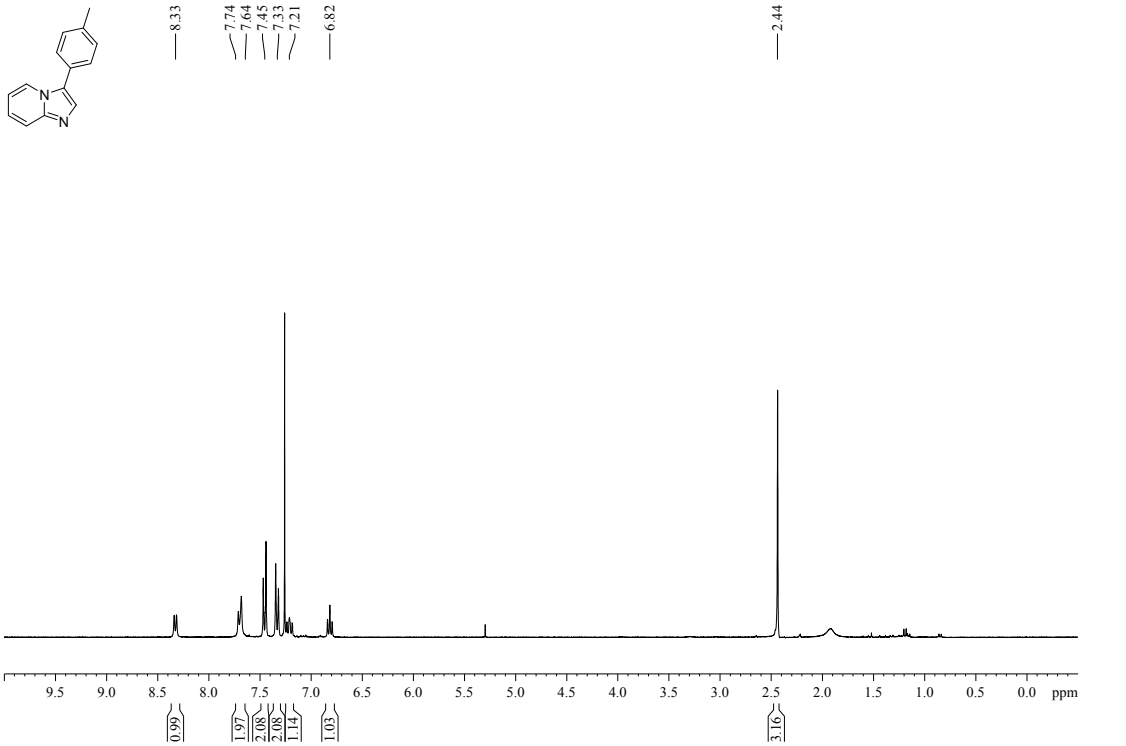


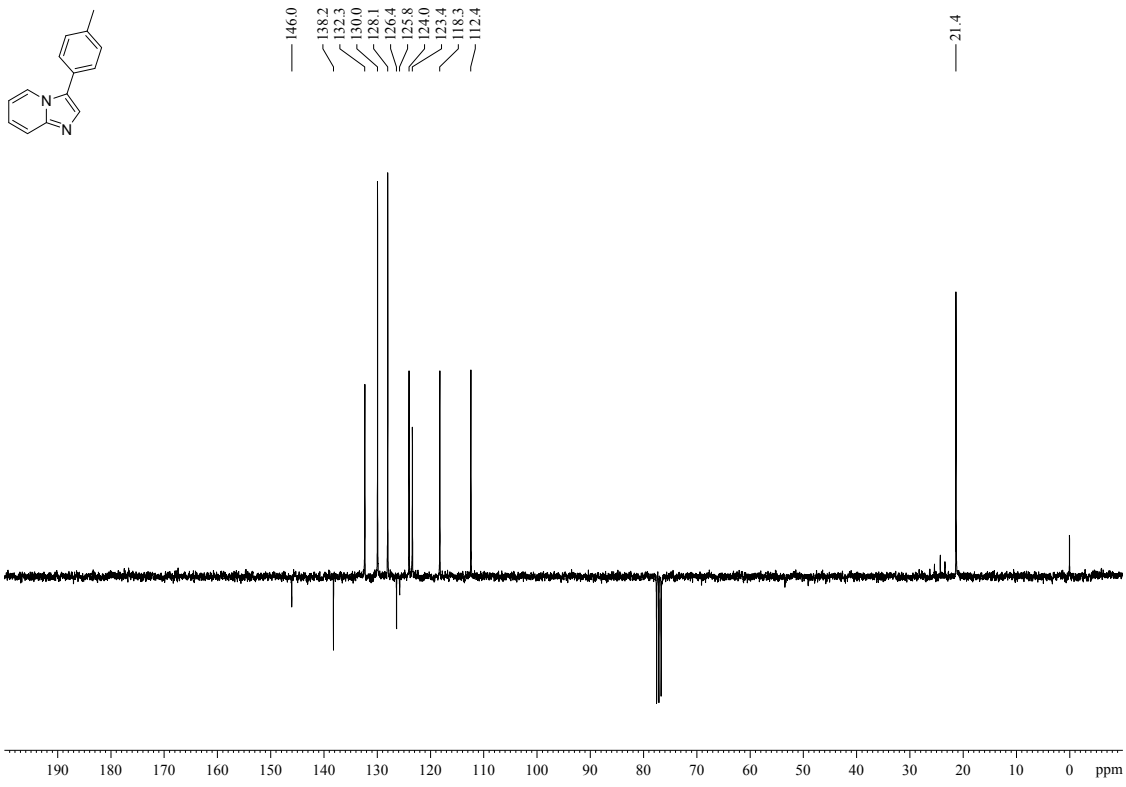
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of 2,3,6-tetrafluoro-4'-methylbiphenyl (7r)



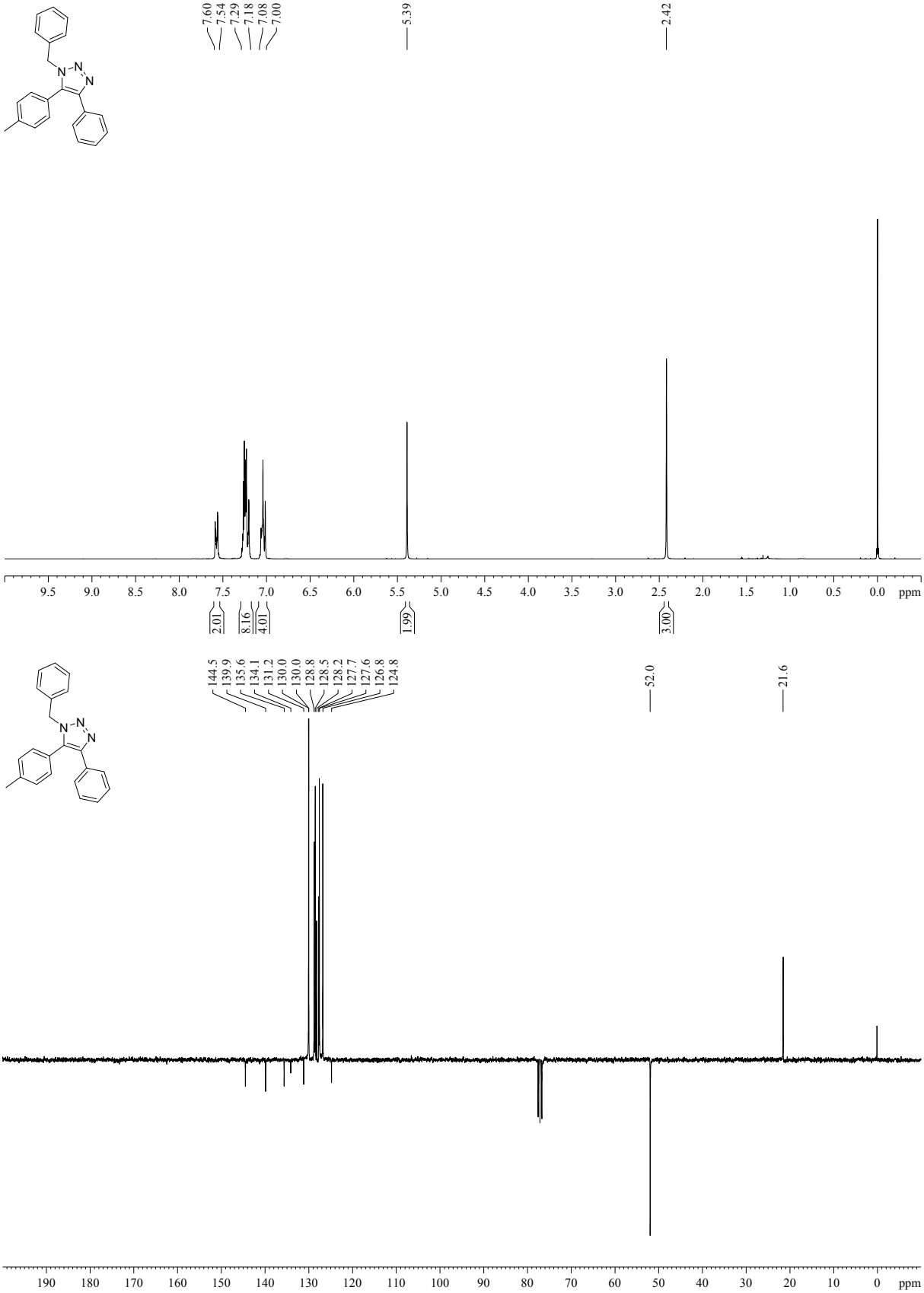


^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 3-(p-tolyl)imidazo[1,2,a]pyridine (7s)



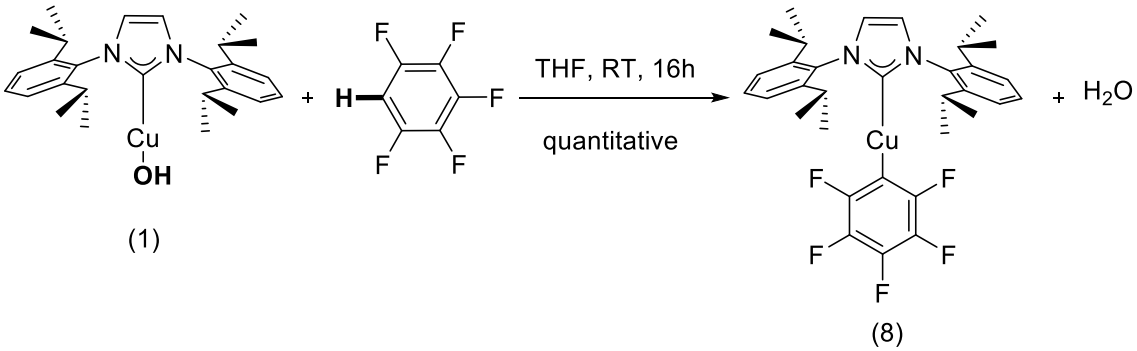


^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 1-Benzyl-5-(4-methylphenyl)-4-phenyl-1H-1,2,3-triazole (7t)



5. Mechanistic studies

5.1. C-H activation step



In a glovebox, a mixture of [Cu(OH)(IPr)] (50 mg, 0.11mmol) and pentafluorobenzene (11.8 µl, 0.11 mmol) in THF (2 ml) was stirred during 16h at room temperature under inert atmosphere. The solvent was concentrated to 1ml and pentane (10 ml) was added. The precipitate was filtered and the desired complex [Cu(C_6F_5)(IPr)] was collected as an off-white solid (63 mg, 95%).

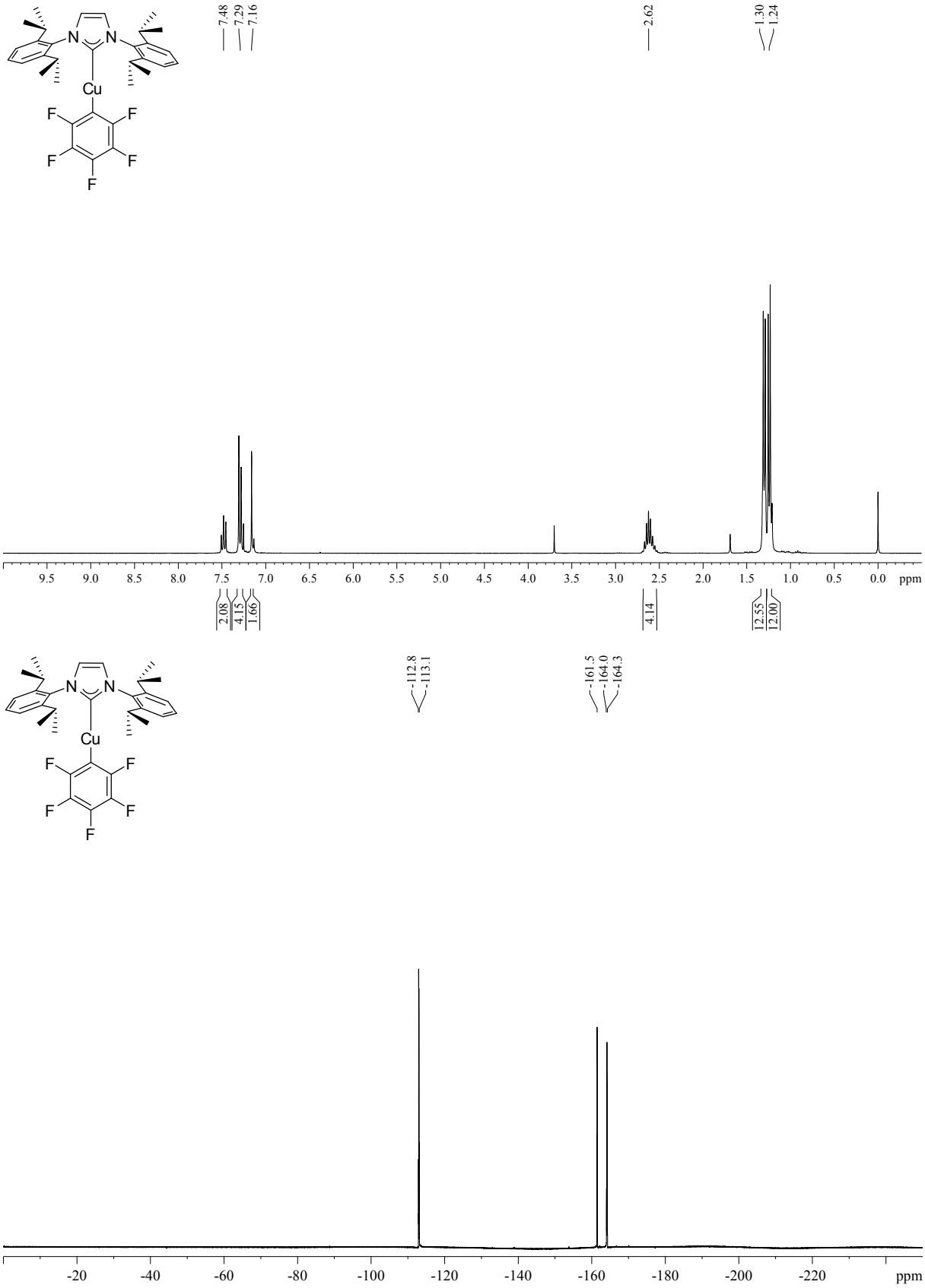
^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.48 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *p*-$C_{Ar}H$), 7.29 (d, $^3J_{HH}$ = 7.7 Hz, 4H, *m*-$C_{Ar}H$), 7.16 (s, 2H, H^4 and H^5), 2.62 (septet, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.30 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$).

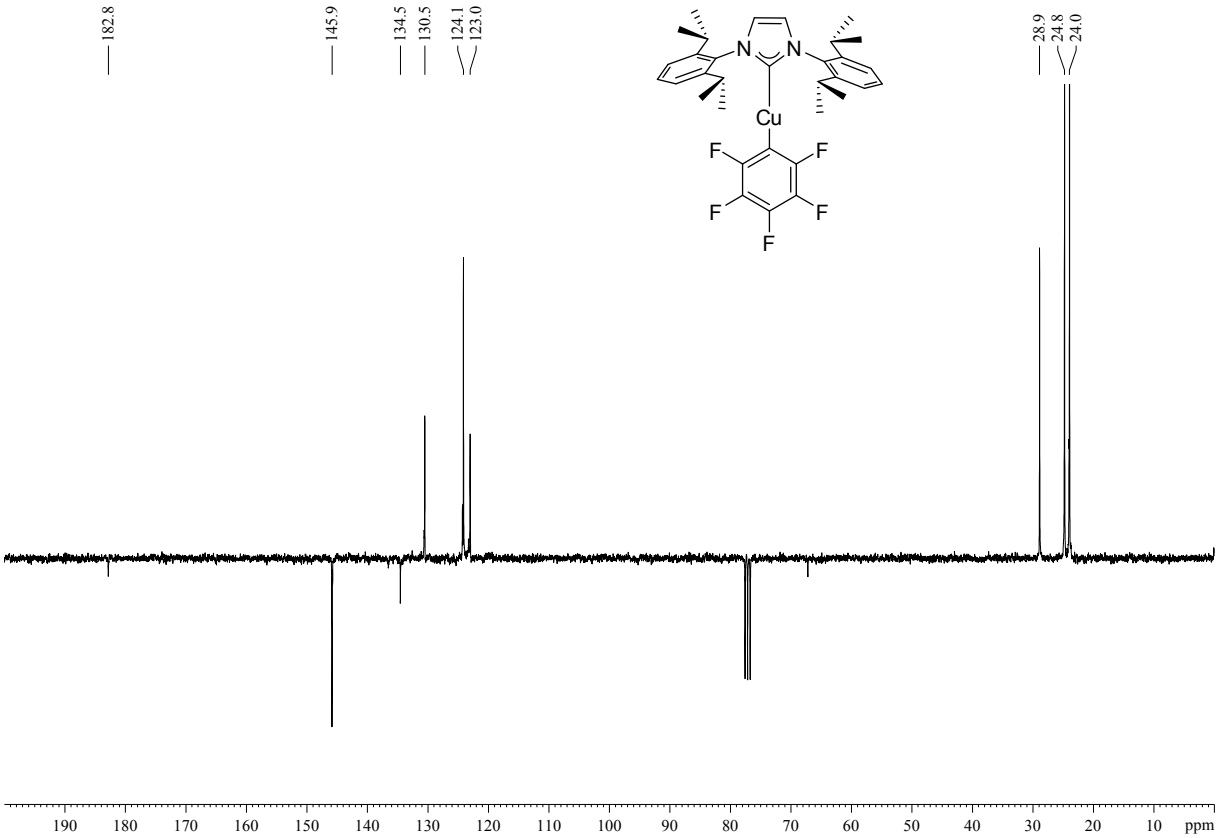
^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -118.8 to -113.1 (m, CF), -161.5 (t, $^3J_{FF}$ = 20 Hz, *p*-CF), -164.0 to -164.3 (m, CF).

^{13}C NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 182.8 (s, $C_{carbene}$), 145.9 (s, C^{IV}), 134.6 (s, C^{IV}), 130.5 (s, C^4 and C^5), 124.1 (s, $C_{Ar}H$), 123.0 (s, $C_{Ar}H$), 28.9 (s, CH), 24.8 (s, CH_3), 24.0 (s, CH_3).

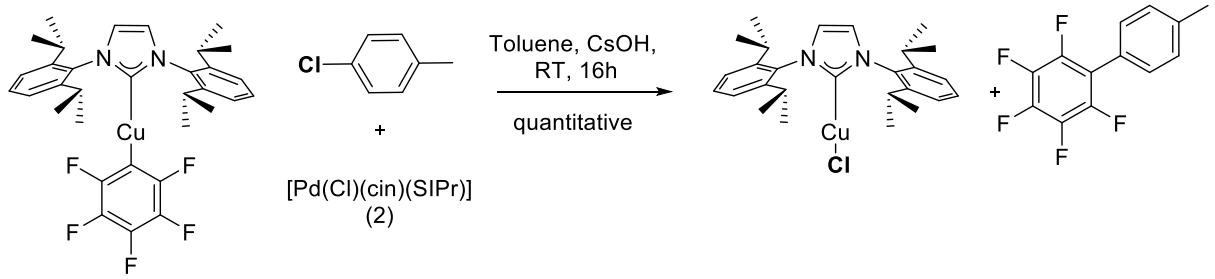
Elemental analysis calcd (%) for $C_{33}H_{36}F_5N_2Cu$: C 64.01, H 5.86, N 4.52; found C 63.79, H 6.09, N 4.57.

^{1}H NMR ($CDCl_3$), ^{19}F-{^{1}H} and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (pentafluorobenzene) copper 8



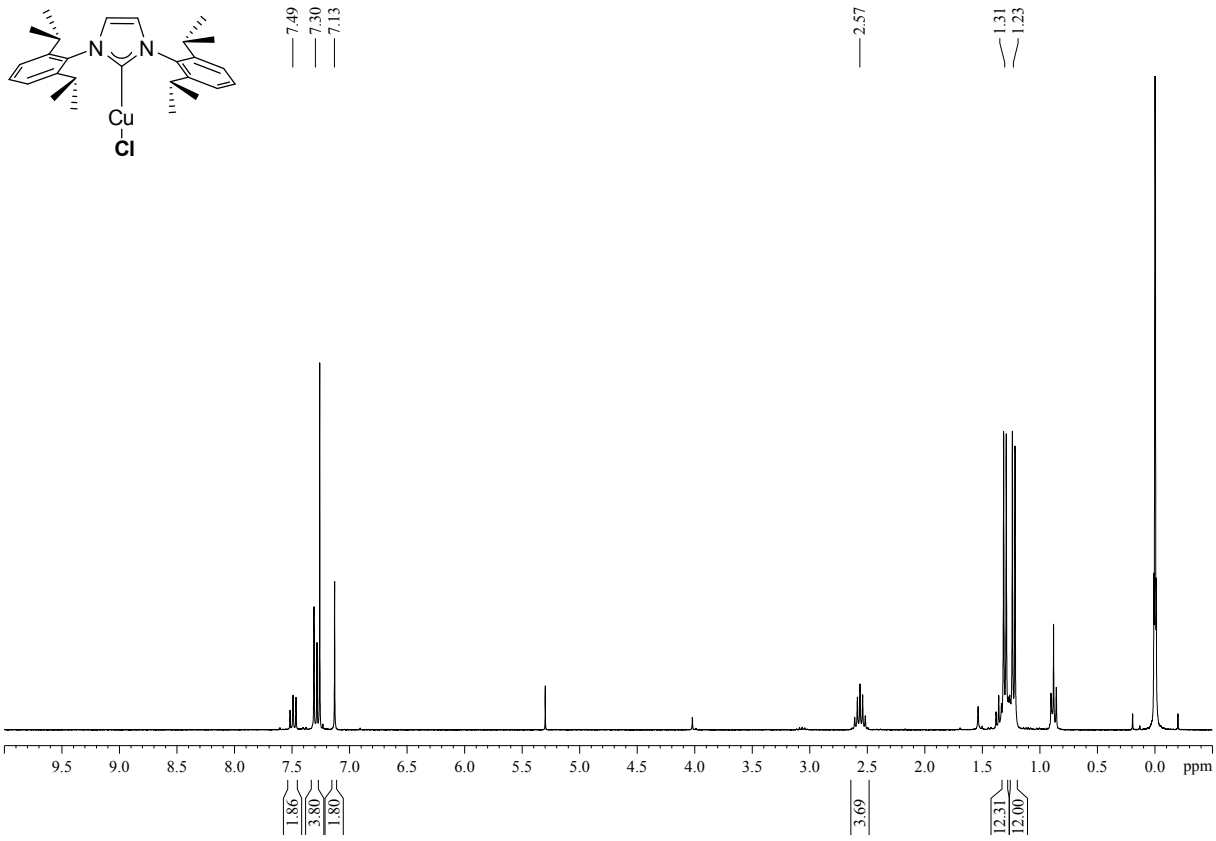


5.2. Transmetallation step



(8) (3)

In a Young tube, a mixture of [Cu(C_6F_5)(IPr)] (50 mg, 0.08 mmol), [Pd(Cl)(cin)(SIPr)] (52 mg, 0.08 mmol), chlorotoluene (9.6 µl, 0.08 mmol) and CsOH (12 mg, 0.08 mmol) in Toluene (1 ml) was stirred during 16h at room temperature under inert atmosphere. The reaction mixture was filtered on a pad of celite to remove palladium black. The solvent was concentrated to 1 ml and pentane (10 ml) was added. The precipitate was filtered and [Cu(Cl)(IPr)] was collected as a off-white solid (36 mg, 92%). The supernatant was concentrated and filtered on a pad of silica with pentane to give the desired coupling product (18 mg, 87%).


Cu
Cl
7.49
7.30
7.13
2.57
1.31
1.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.86
3.80
1.80
3.69
12.31
12.00

6. References

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