Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

for

$[Pd(\mu\text{-}Cl)Cl(IPr^*)]_2$: A highly hindered pre-catalyst for the synthesis of tetra-*ortho*-substituted biaryls *via* Grignard reagents cross-coupling

*Mathieu Lesieur, Alexandra M. Z. Slawin and Catherine S. J. Cazin**

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK.

E-mail: cc111@st-andrews.ac.uk

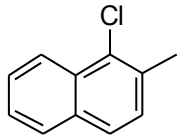
Table of contents

General information

All reactions were performed under argon using glovebox and Schlenk techniques. All aryl halides were used as received or prepared using literature procedures. All Grignard reagents were used as received. Anhydrous solvents (1,4-dioxane, tetrahydrofuran (THF), 1,2-dichloromethane (CH_2Cl_2), toluene) were used as received and stored in a glovebox. 1,2-dimethoxyethane (DME) was distilled from sodium/benzophenone, degassed and stored in a glovebox. HCl (solution in 1,4-dioxane 4M) was used as received. [PdCl(cin)(IPr*)] was synthesised according to a published procedure.[1] Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 µm particles 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 using the residual solvent peak in THF-d_8 (δ_H = 1.72 ppm, 3.58 ppm, δ_C = 67.21 ppm, 25.31 ppm) or $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm) using in some cases TMS as internal standard.

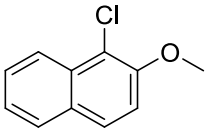
Synthesis of aryl chlorides

1-Chloro-2-methylnaphthalene[2]



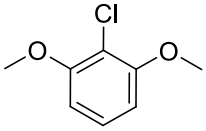
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.29 (d, ^3J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 7.81 (d, ^3J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 7.67 (d, ^3J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 7.60-7.54 (m, 1H, $C_{Ar}H$), 7.50-7.45 (m, 1H, $C_{Ar}H$), 7.35 (d, ^3J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 2.59 (s, 3H, CH_3).

1-Chloro-2-methoxynaphthalene[2]



^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.22 (d, ^3J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 7.82-7.76 (m, 2H, $C_{Ar}H$), 7.61-7.54 (m, 1H, $C_{Ar}H$), 7.44-7.37 (m, 1H, $C_{Ar}H$), 7.31 (d, ^3J(H,H) = 9.0 Hz, 1H, $C_{Ar}H$), 4.04 (s, 3H, OCH_3).

1-Chloro-2,6-dimethoxybenzene[2]



^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.18 (t, ^3J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 6.61 (d, ^3J(H,H) = 8.4 Hz, 2H, $C_{Ar}H$), 3.91 (s, 6H, OCH_3).

Catalysis

Preparation of [Pd(μ-Cl)Cl(IPr*)]$_2$ 7:

In a glovebox, a 100 mL round bottom flask equipped with a magnetic stirring bar was charged with [PdCl(cinnamyl)(IPr*)] **4** (500 mg, 0.427 mmol) in 1,4-dioxane (45 mL). The reaction was stirred during 10 minutes and a solution of HCl in 1,4-dioxane (7.5 mL, 4M) was added using a syringe. The reaction mixture was stirred 15 h at room temperature, the solvent was evaporated under reduced pressure and the product triturated with pentane and collected by filtration, leading to microanalytically pure **7** as a yellow powder (456 mg, 98%).

^{1}H NMR (400 MHz, THF-d$_8$, 298K): δ (ppm) = 7.47 (d, ^3J(H,H) = 7.2 Hz, 8H, $C_{Ar}H$), 7.23-7.10 (m, 12H, $C_{Ar}H$), 7.04-6.94 (m, 12H, $C_{Ar}H$), 6.79 (s, 4H, $C_{Ar}H$), 6.69 (d, ^3J(H,H) = 7.2 Hz, 8H, $C_{Ar}H$), 6.32 (s, 4H, PhCH), 4.76 (s, 2H, CH), 2.17 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (100 MHz, THF-d$_8$, 298K): δ (ppm) = 145.3 (s, C^{IV}), 145.0 (s, C^{IV}), 142.9 (s, C^{IV}), 138.8 (s, C^{IV}), 136.0 (s, C^{IV}), 131.3 (s, $C_{Ar}H$), 131.2 (s, $C_{Ar}H$), 130.1 (s, $C_{Ar}H$), 128.6 (s, $C_{Ar}H$), 128.2 (s, $C_{Ar}H$), 126.6 (s, $C_{Ar}H$), 126.5 (s, $C_{Ar}H$), 51.4 (s, PhCH), 21.4 (s, CH_3).

Despite several attempts, the $C_{carbene}$ atom was not observed due to a very low solubility of the complex.

Elemental Analysis Calcd (%) for $C_{138}H_{112}Cl_4N_4Pd_2$: C, 75.99; H, 5.18; N, 2.57. Found: C, 75.88; H, 5.11; N, 2.67.

Preparation of the stock solutions

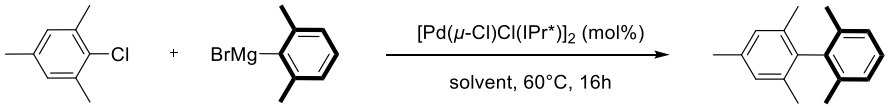
In a glovebox, 5.5 mg of the complex [Pd(μ-Cl)Cl(IPr*)]$_2$ **7** and tetrahydrofuran (1 mL) were added to a vial and closed with a screw cap fitted with a septum.

General procedure using [Pd(μ-Cl)Cl)(IPr*)]$_2$ 7

In a glovebox, a vial equipped with a stirring bar was charged with the aryl halide (0.5 mmol), 1,4-dioxane (2.5 mL), the Grignard reagent (0.55 mmol) and the pre-catalyst solution (200 μL, 0.1 mol% of dimer). The reaction mixture was then stirred (900 rpm) at 60°C during 16 h. The reaction mixture was allowed to cool 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 purified by flash chromatography on silica gel. The reported yields are the average of two reactions.

Optimisation of reaction conditions[a]

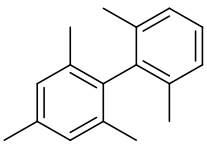


Entry	Catalyst loading (mol%)	Solvent	Conversion[b] (%)
1	0.45	toluene	72
2	0.45	DME	89
3	0.45	THF	99
4	0.45	1,4-dioxane	99
5	0.225	THF	79
6	0.225	1,4-dioxane	99
7	**0.1**	**1,4-dioxane**	**96 (91)**[c]
8	0.05	1,4-dioxane	72

[a] Reaction conditions: 2-chloromesitylene (0.5 mmol), 2,6-$Me_2C_6H_3MgBr$ (0.55 mmol), **7**, solvent (2.5 mL), 60°C, 16 h. [b] Conversion to product determined by GC based on 2-chloromesitylene. [c] Isolated yield, average of two runs.

2,2',4,6,6'-pentamethylbiphenyl (10a and 10m)[3]

The general procedure yielded, after flash chromatography on silica gel (heptane), 203 mg (91%, **10a**) and 201 mg (90%, **10m**) of the title compound as a colourless oil.

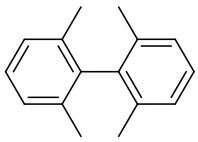


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.17-7.05 (m, 3H, $C_{Ar}H$), 6.94 (s, 2H, $C_{Ar}H$), 2.33 (s, 3H, CH_3), 1.90 (s, 6H, CH_3), 1.85 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 140.0 (s, C^{IV}), 136.9 (s, C^{IV}), 136.1 (s, C^{IV}), 135.7 (s, C^{IV}), 135.2 (s, C^{IV}), 128.2 (s, $C_{Ar}H$), 127.3 (s, $C_{Ar}H$), 126.7 (s, $C_{Ar}H$), 21.1 (s, CH_3), 19.9 (s, CH_3), 19.7 (s, CH_3).

2,2',6,6'-tetramethylbiphenyl (10b)[3]

The general procedure yielded, after flash chromatography on silica gel (pentane), 189 mg (90%) of the title compound as a colourless powder.

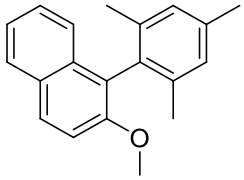


^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.22- 7.11 (m, 6H, $C_{Ar}H$), 1.91 (s, 12H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 140.1 (s, C^{IV}), 135.6 (s, C^{IV}), 127.6 (s, $C_{Ar}H$), 126.9 (s, $C_{Ar}H$), 20.0 (s, CH_3).

1-mesityl-2'-methoxynaphthalene (10c)[4]

The general procedure yielded, after flash chromatography on silica gel (pentane), 247 mg (90%, ArCl) and 240 mg (89%, ArBr) of the title compound as a colourless powder.

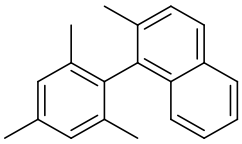


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.88 (d, ^{3}J(H,H) = 9.0 Hz, 1H, $C_{Ar}H$), 7.84-7.81 (m, 1H, $C_{Ar}H$), 7.37 (d, ^{3}J(H,H) = 9.0 Hz, 1H, $C_{Ar}H$), 7.34-7.25 (m, 2H, $C_{Ar}H$), 7.18-7.15 (m, 1H, $C_{Ar}H$), 7.00 (s, 2H, $C_{Ar}H$), 3.84 (s, 3H, OCH_3), 2. 38 (s, 3H, CH_3), 1.85 (s, 6H, CH_3).

^{13}C-{^{1}H NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 153.6 (s, C^{IV}), 137.2 (s, $C_{Ar}H$), 137.0 (s, C^{IV}), 133.1 (s, C^{IV}), 132.6 (s, C^{IV}), 129.1 (s, C^{IV}), 128.7 (s, $C_{Ar}H$), 128.1 (s, $C_{Ar}H$), 127.9 (s, $C_{Ar}H$), 126.4 (s, $C_{Ar}H$), 124.5 (s, $C_{Ar}H$), 123.4 (s, $C_{Ar}H$), 123.3 (s, C^{IV}), 113.5 (s, $C_{Ar}H$), 56.4 (s, OCH_3), 21.3 (s, CH_3), 20.0 (s, CH_3).

1-mesityl-2'-methylnaphthalene (10d and 10i)[5]

The general procedure yielded, after flash chromatography on silica gel (heptane), 240 mg (95%, ArCl, **10d**), 238 mg (94%, ArBr, **10d**) and 243 mg (96%, **10i**) of the title compound as a colourless oil.

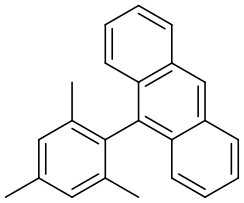


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.75 (d, ^{3}J(H,H) = 8.2Hz, 1H, $C_{Ar}H$), 7.68 (d, ^{3}J(H,H) = 8.4Hz, 1H, $C_{Ar}H$), 7.33 (d, ^{3}J(H,H) = 8.4Hz, 1H, $C_{Ar}H$), 7.32-7.28 (m, 1H, $C_{Ar}H$), 7.22-7.17 (m, 1H, $C_{Ar}H$), 7.12 (d, ^{3}J(H,H) = 8.2 Hz, $C_{Ar}H$), 6.92 (s, 2H, $C_{Ar}H$), 2,30 (s, 3H, CH_3), 2,02 (s, 3H, CH_3), 1.69 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 136.7 (s, C^{IV}), 136.6 (s, $C_{Ar}H$), 135.6 (s, C^{IV}), 133.2 (s, C^{IV}), 132.4 (s, C^{IV}), 132.3 (s, C^{IV}), 128.8 (s, $C_{Ar}H$), 128.4 (s, $C_{Ar}H$), 128.1 (s, $C_{Ar}H$), 127.0 (s, $C_{Ar}H$), 126.1 (s, $C_{Ar}H$), 125.2 (s, $C_{Ar}H$), 124.9 (s, $C_{Ar}H$), 21.3 (s, CH_3), 20.1 (s, CH_3), 20.0 (s, CH_3).

9-mesitylanthracene (10e)[4]

The general procedure yielded, after flash chromatography on silica gel (heptane), 260 mg (91%) of the title compound as a colourless powder.

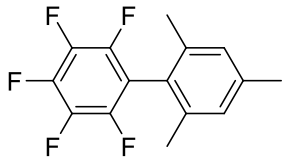


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.46 (s, 1H, $C_{Ar}H$), 8.04 (d, ^{3}J(H,H) = 8.3 Hz, 2H, $C_{Ar}H$), 7.49-7.40 (m, 4H, $C_{Ar}H$), 7.34-7.27 (m, 2H, $C_{Ar}H$), 7.08 (s, 2H, $C_{Ar}H$), 2.44 (s, 3H, CH_3), 1.70 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 137.6 (s, C^{IV}), 137.1 (s, C^{IV}), 135.7 (s, C^{IV}), 134.5 (s, C^{IV}), 131.6 (s, C^{IV}), 129.7 (s, C^{IV}), 128.6 (s, $C_{Ar}H$), 128.2 (s, $C_{Ar}H$), 126.0 (s, $C_{Ar}H$), 125.9 (s, $C_{Ar}H$), 125.5 (s, $C_{Ar}H$), 125.1 (s, $C_{Ar}H$), 21.2 (s, CH_3), 20.0 (s, CH_3).

2,3,4,5,6-pentafluoro-2',4',6'-trimethylbiphenyl (10f)[6]

The general procedure yielded, after flash chromatography on silica gel (pentane), 209 mg (73%) of the title compound as a colourless liquid.



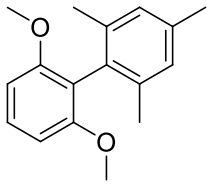
^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.00 (s, 2H, $C_{Ar}H$), 2.35 (s, 3H, CH_3), 2.06 (s, 6H, CH_3).

^{19}F-{^{1}H} NMR (282 MHz, $CDCl_3$, 298K): δ (ppm) = -140.6 (dd, *J*(F,F)= 8.4 Hz, *J*(F,F)= 23.6 Hz, CF), -155.9 (t, *J*(F,F)= 20.8 Hz, CF), -162.4 to -162.7 (m, CF).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 144.0 (d, *J*(C,F) = 243 Hz, CF), 140.6 (d, *J*(C,F) = 278 Hz, CF), 139.5 (s, C^{IV}), 138.1 (d, *J*(C,F)= 243 Hz, CF), 137.3 (s, $C_{Ar}H$), 128.7 (s, $C_{Ar}H$), 127.1 (s, C^{IV}), 122.7 (s, C^{IV}), 114.5 (m, C^{IV}), 21.3 (s, CH_3), 20.1 (s, CH_3).

2',6'-dimethoxy-2,4,6-trimethylbiphenyl (10g)[1]

The general procedure (80ºC) yielded, after flash chromatography on silica gel (pentane/Et_2O, 20:1), 244 mg (95%) of the title compound as a colourless powder.

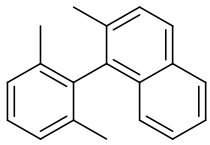


^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.31 (t, ^{3}J(H,H) = 8.3 Hz, 1H, $C_{Ar}H$), 6.95 (s, 2H, $C_{Ar}H$), 6.66 (d, ^{3}J(H,H) = 8.3 Hz, 2H, $C_{Ar}H$), 3.72 (s, 6H, OCH_3), 2.32 (s, 3H, CH_3), 1.98 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 157.7 (s, C^{IV}), 137.0 (s, C^{IV}), 136.5 (s, C^{IV}), 131.1 (s, C^{IV}), 128.6 (s, $C_{Ar}H$), 128.0 (s, $C_{Ar}H$), 117.7 (s, C^{IV}), 104.0 (s, $C_{Ar}H$), 55.9 (s, OCH_3), 21.4 (s, CH_3), 20.1 (s, CH_3).

1-(2',6'-dimethylphenyl)-2-methylnaphthalene (10h and 10o)[1]

The general procedure yielded, after flash chromatography on silica gel (pentane), 204 mg (83%, **10h**) and 231 mg (94%, **10o**) of the title compound as a colourless liquid.

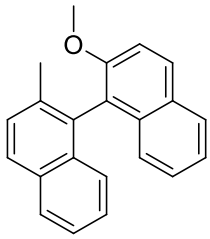


^{1}H NMR (300 MHz, $CDCl_3$, 298K,TMS): δ (ppm) = 7.85 (d, ^{3}J(H,H) = 8.3 Hz, 1H, $C_{Ar}H$), 7.78 (d, ^{3}J(H,H)= 8.3 Hz, 1H, $C_{Ar}H$), 7.45-7.37 (m, 2H, $C_{Ar}H$), 7.32-7.16 (m, 5H, $C_{Ar}H$) , 2.11 (s, 3H, CH_3), 1.82 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 138.7 (s, C^{IV}), 136.8 (s, C^{IV}), 136.6 (s, C^{IV}), 133.0 (s, C^{IV}), 132.4 (s, C^{IV}), 132.1 (s, C^{IV}), 128.9 (s, $C_{Ar}H$), 128.1 (s, $C_{Ar}H$), 127.6 (s, $C_{Ar}H$), 127.3 (s, $C_{Ar}H$), 127.1 (s, $C_{Ar}H$), 126.2 (s, $C_{Ar}H$), 125.1 (s, $C_{Ar}H$), 125.0 (s, $C_{Ar}H$), 20.0 (s, CH_3), 19.9 (s, CH_3).

2-methoxy-2'-methyl-1,1'-binaphthyl (10j)[1]

The general procedure yielded, after flash chromatography on silica gel (pentane/Et_2O, 10:1), 271 mg (91%) of the title compound as a pale yellow powder.

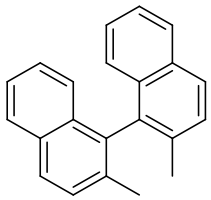


^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 8.01 (d, ^{3}J(H,H) = 9.0 Hz, 1H, $C_{Ar}H$), 7.92-7.88 (m, 3H, $C_{Ar}H$), 7.54 (d, ^{3}J(H,H) = 8.4 Hz, 1H, $C_{Ar}H$), 7.48 (d, ^{3}J(H,H) = 9.0 Hz, 1H, $C_{Ar}H$), 7.42-7.32 (m, 2H, $C_{Ar}H$), 7.25-7.20 (m, 2H, $C_{Ar}H$), 7.15 (d, ^{3}J(H,H) = 8.2 Hz, 1H, $C_{Ar}H$), 7.03 (d, ^{3}J(H,H) = 8.4 Hz,1H, $C_{Ar}H$), 3.77 (s, 3H, OCH_3), 2.12 (s, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 154.6 (s, C^{IV}), 135.1 (s, C^{IV}), 133.8 (s, C^{IV}), 133.3 (s, C^{IV}), 132.5 (s, C^{IV}), 132.3 (s, $C_{Ar}H$), 129.5 (s, $C_{Ar}H$), 129.3 (s, $C_{Ar}H$), 128.8 (s, $C_{Ar}H$), 128.1 (s, $C_{Ar}H$), 128.0 (s, $C_{Ar}H$), 127.6 (s, $C_{Ar}H$), 126.7 (s, $C_{Ar}H$), 126.0 (s, $C_{Ar}H$), 125.2 (s, $C_{Ar}H$), 124.8 (s, $C_{Ar}H$), 123.7 (s, $C_{Ar}H$), 122.2 (s, C^{IV}), 114.0 (s, $C_{Ar}H$), 56.7 (s, OCH_3), 20.4 (s, CH_3).

2,2'-dimethyl-1,1'-binaphthyl (10k)[1]

The general procedure yielded, after flash chromatography on silica gel (pentane), 276 mg (98%, ArBr) and 255 mg (91%, ArCl) of the title compound as a colourless powder.

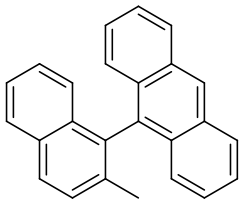


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.91 (d, ^{3}J(H,H) = 4.6 Hz, 2H, $C_{Ar}H$), 7.88 (d, ^{3}J(H,H) = 4.6 Hz, 2H, $C_{Ar}H$), 7.50 (d, ^{3}J(H,H) = 8.4 Hz, 2H, $C_{Ar}H$), 7.40 (dt, ^{3}J(H,H) = 6.8 Hz, ^{2}J(H,H) = 1.1 Hz, 2H, $C_{Ar}H$), 7.20 (dt, ^{3}J(H,H) = 6.8 Hz, ^{2}J(H,H) = 1.1 Hz, 2H, $C_{Ar}H$), 7.10 (d, ^{3}J(H,H) = 8.4 Hz, 2H, $C_{Ar}H$), 2.0 (s, 6H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 135.2 (s, C^{IV}), 134.4 (s, C^{IV}), 132.8 (s, C^{IV}), 132.3 (s, C^{IV}), 128.8 (s, $C_{Ar}H$), 128.0 (s, $C_{Ar}H$), 127.5 (s, $C_{Ar}H$), 126.2 (s, $C_{Ar}H$), 125.7 (s, $C_{Ar}H$), 125.0 (s, $C_{Ar}H$), 20.1 (s, CH_3).

9-(2'-methylnaphthalene)anthracene (10l)[7]

The general procedure yielded, after flash chromatography on silica gel (pentane), 271 mg (95%) of the title compound as a colourless powder.



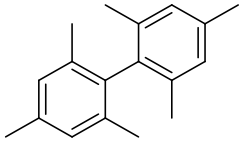
^{1}H NMR (300 MHz, $CDCl_3$, 298K,TMS): δ (ppm) = 8.58 (s, 1H, $C_{Ar}H$), 8.10 (d, ^{3}J(H,H) = 8.7 Hz, 2H, $C_{Ar}H$), 7.97 (d, ^{3}J(H,H) = 8.7 Hz, 1H, $C_{Ar}H$), 7.93 (d, ^{3}J(H,H) = 8.7 Hz, 1H, $C_{Ar}H$), 7.58 (d, ^{3}J(H,H) = 8.7 Hz, 1H, $C_{Ar}H$), 7.47-7.43 (m, 2H, $C_{Ar}H$), 7.41-7.36 (m, 1H, $C_{Ar}H$), 7.31-7.21 (m, 4H, $C_{Ar}H$), 7.13-7.08 (m, 1H, $C_{Ar}H$), 6.83 (d, ^{3}J(H,H) = 8.7 Hz, 1H, $C_{Ar}H$), 1.95 (s, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 135.7 (s, C^{IV}), 134.3 (s, C^{IV}), 133.9 (s, C^{IV}), 132.3 (s, C^{IV}), 131.8 (s, C^{IV}), 130.7 (s, C^{IV}), 128.9 (s, $C_{Ar}H$), 128.7 (s, $C_{Ar}H$), 128.1 (s,

$C_{Ar}H$), 128.0 (s, $C_{Ar}H$), 126.8 (s, $C_{Ar}H$), 126.5 (s, $C_{Ar}H$), 126.4 (s, $C_{Ar}H$), 126.3 (s, $C_{Ar}H$), 125.9 (s, $C_{Ar}H$), 125.4 (s, $C_{Ar}H$), 125.1 (s, $C_{Ar}H$), 20.4 (s, CH_3).

2,2',4,4',6,6'-hexamethylbiphenyl (10n)[4]

The general procedure yielded, after flash chromatography on silica gel (heptane), 215 mg (90%, ArCl) and 217 mg (91%, ArBr) of the title compound as a colourless powder.

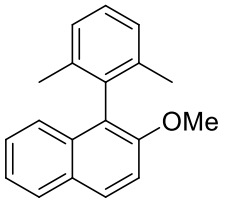


^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 6.93 (s, 4H, $C_{Ar}H$), 2.32 (s, 6H, CH_3), 1.86 (s, 12H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 137.0 (s, C^{IV}), 136.0 (s, C^{IV}), 135.5 (s, C^{IV}), 128.2 (s, $C_{Ar}H$), 21.1 (s, CH_3), 19.8 (s, CH_3).

1-(2',6'-dimethylphenyl)-2-methoxynaphthalene (10p)[8]

The general procedure yielded, after flash chromatography on silica gel (pentane/Et_2O, 10:1), 236 mg (90%) of the title compound as a colourless powder.

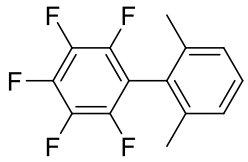


^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.90 (d, ^3J(H,H) = 9Hz, 1H, $C_{Ar}H$), 7.86-7.81 (m, 1H, $C_{Ar}H$), 7.34 (d, ^3J(H,H) = 9Hz, 1H, $C_{Ar}H$), 7.34- 7.23 (m, 3H, $C_{Ar}H$), 7.21-7.12 (m, 3H, $C_{Ar}H$), 3.85 (s, 3H, OCH_3), 1.88 (s, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 153.6 (s, C^{IV}), 137.5 (s, C^{IV}), 135.8 (s, C^{IV}), 133.0 (s, C^{IV}), 129.3 (s, C^{IV}), 129.0 (s, $C_{Ar}H$), 128.1 (s, $C_{Ar}H$), 127.5 (s, $C_{Ar}H$), 127.3 (s, $C_{Ar}H$), 126.6 (s, $C_{Ar}H$), 124.5 (s, $C_{Ar}H$), 123.6 (s, $C_{Ar}H$), 123.4 (s, C^{IV}), 113.6 (s, $C_{Ar}H$), 56.5 (s, OCH_3), 20.2 (s, CH_3).

2,3,4,5,6-pentafluoro-2',6'-dimethylbiphenyl (10q)[9]

The general procedure yielded, after flash chromatography on silica gel (pentane), 201 mg (74%) of the title compound as a colourless powder.



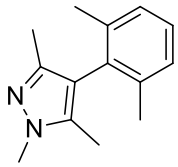
^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.29 (t, ^{3}J(H,H) = 7.6 Hz, 1H, $C_{Ar}H$), 7.17 (d, ^{3}J(H,H) = 7.6 Hz, 2H, $C_{Ar}H$), 2.09 (s, 6H, CH_3).

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

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 143.8 (d, *J*(C,F) = 246 Hz, CF), 140.9 (d, *J*(C,F) = 230 Hz, CF), 137.8 (d, *J*(C,F) = 230 Hz, CF), 137.5 (s, C^{IV}), 129.6 (s, $C_{Ar}H$), 127.9 (s, $C_{Ar}H$), 125.8 (s, C^{IV}), 114.4 (m, C^{IV}), 20.3 (s, CH_3).

4-(2',6'-dimethylphenyl)-1,3,5-trimethyl-1H-pyrazole (10r)[1]

The general procedure yielded, after flash chromatography on silica gel (pentane), 192 mg (90%) of the title compound as a white powder.



^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ (ppm) = 7.18-7.07 (m, 3H, $C_{Ar}H$), 3.79 (s, 3H, NCH_3), 2.01(s, 6H, CH_3), 1.97 (s, 6H, CH_3).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 145.3 (s, C^{IV}), 138.5 (s, C^{IV}), 136.1 (s, C^{IV}), 132.9 (s, C^{IV}), 127.3 (s, $C_{Ar}H$), 127.2 (s, $C_{Ar}H$), 117.3 (s, C^{IV}), 36.1 (s, CH_3), 20.6 (s, CH_3), 12.2 (s, CH_3), 9.9 (s, CH_3).

Crystal data and Structure refinement for [Pd(μ-Cl)Cl(IPr*)]$_2$, 7.

Crystals were obtained by slow diffusion of pentane in a 1,4-dioxane solution of the complex.

	CCDC 902044 **(7)**
Emperical formula	$C_{138}H_{112}Cl_4N_4Pd_2$
Formula Weight	2181,04 g.mol^{-1}
Crystal color, Habit	Yellow, prism
Temperature (K)	-180±1°C
Crystal system	Monoclinic
Space group	C2/c (#15)
Unit cell dim.	0.200 X 0.200 X 0.120 mm
Lattice type	C-centred
Lattice parameter a,b,c (Å)	a = 42.67(2) Å b = 14.426(6) Å c = 25.267(10) Å
α,β,γ (°)	β = 110.300(5) ^{o}
Volume (Å)^3	V = 14587(10) Å^3
Z	4
Density calculated	0.993 g/cm^3
Absorption coefficient (cm^{-1})	3.611 cm^{-1}
F(000)	4512.00
Diffractometer	Saturn 70
Radiation	MoKα (λ = 0.71075 Å)
Voltage, Current	50kV, 16mA
Theta range for data collection (°)	2θ=50.8
Reflexions collected	Total: 71864 Unique: 13441 (Rint = 0.2225)
Correction	Lorentz-polarization Absorption (trans. factors: 0.448 - 0.958)
Structure solution	Direct Methods (SHELX97)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	13441
No. variables	667
Reflection/parameter ratio	20.15
Goodness-of-fit on F^2	2.162
Final R indices [I>2sigma(I)]	0.2385
R indices (all data)	0.2495
Maximum peak in Final Diff Map (e.Å^{-3})	4.71 e$^-$/Å^3
Minimum peak in Final Diff Map (e.Å^{-3})	-1.53 e$^-$/Å^3
Max shift/error in final cycle	0.065

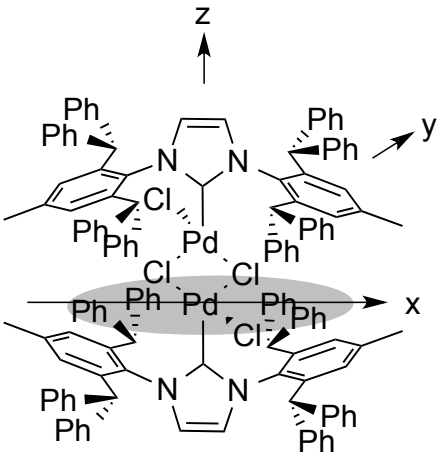
%V_{Bur} and mapping

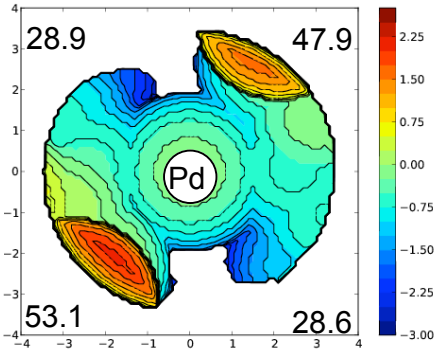
Pd-C bond distances and %V_{Bur}.

Complex	Pd-C (Å)	%V_{Bur} [a]
[Pd(μ-Cl)Cl(IPr)]$_2$	1.9553(3)	37.3
[Pd(μ-Cl)Cl(SIPr)]$_2$ **6**	1.947(5)	38.2
[Pd(μ-Cl)Cl(IPr*)]$_2$ **7**	1.974(12)	39.6
[PdCl(cin)(IPr)]	2.041(9)	36.8
[PdCl(cin)(SIPr)]	2.025(7)	37.3
[PdCl(cin)(IPr*)] **4**	2.038(6)	44.7

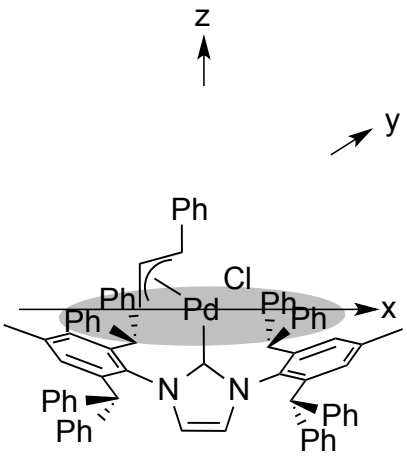
[a] Calculated for Pd-C = 2.00 Å.

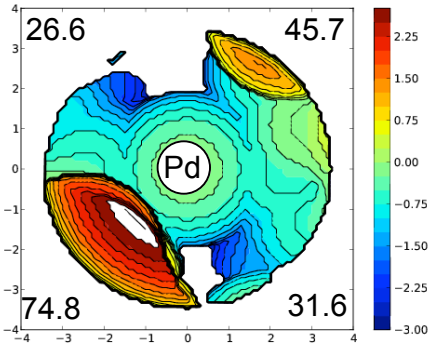
%V_{Bur} calculated from the web application Samb*V*ca. The %V_{Bur} values reported here, calculated with release 2.0 of the SambVca package, are slightly different from those reported in - A. Chartoire, M. Lesieur, L. Falivene, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 4517 - calculated with release 1.0, due to a different scheme for building the grid used in the numerical integration of the volume.



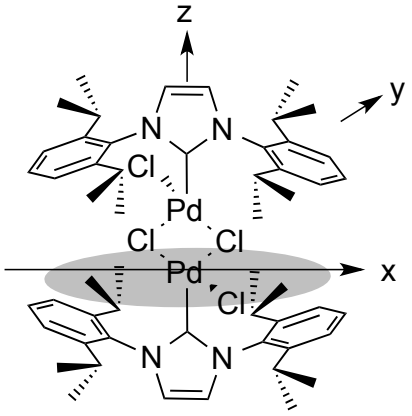


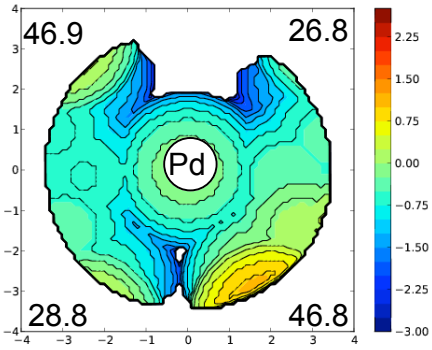
[Pd(μ-Cl)Cl(IPr*)]$_2$, 7



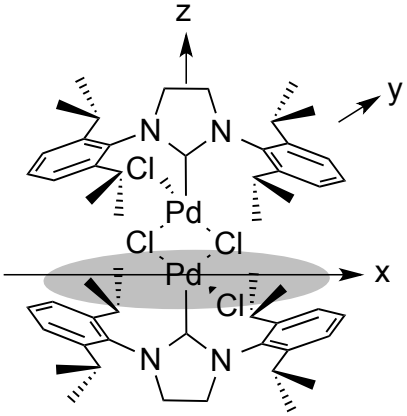


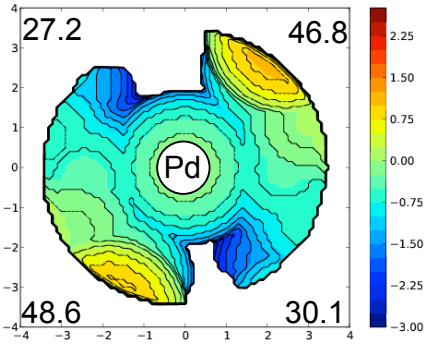
[PdCl(cin)(IPr*)], 4





[Pd(μ-Cl)Cl(IPr)]$_2$





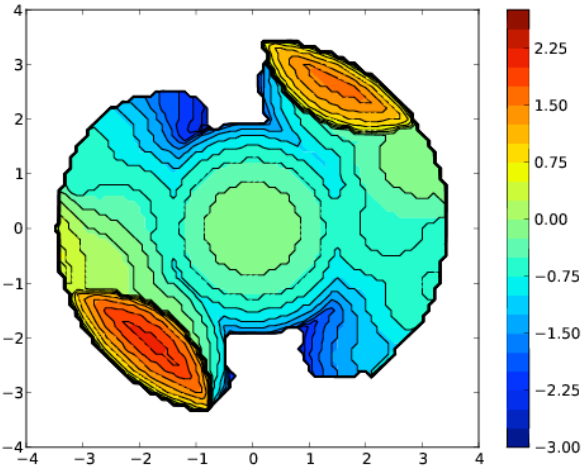
[Pd(μ-Cl)Cl(SIPr)]$_2$, 6

%V_{Bur} and mapping of [Pd(μ-Cl)Cl(IPr*)]$_2$ 7

V Free	V Buried	V Total	V Exact
108.4	71.1	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
60.369	**39.6**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	21.05	23.82	44.87	46.91	**53.09**
-+	31.90	12.96	44.86	71.11	**28.89**
++	23.36	21.49	44.85	52.09	**47.91**
+-	32.02	12.83	44.86	71.39	**28.61**

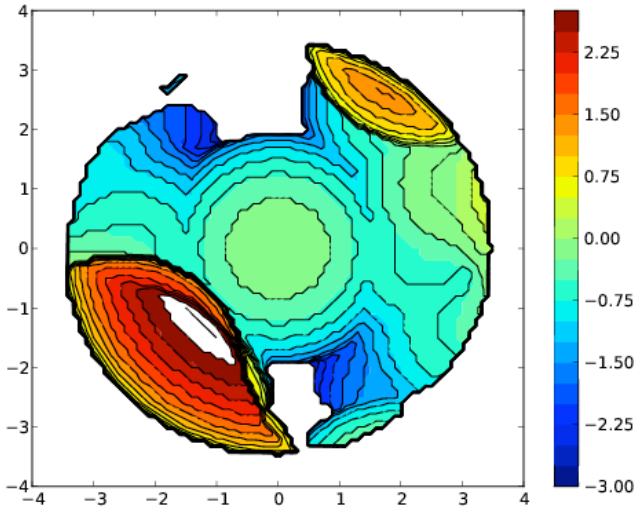


$\%V_{Bur}$ and mapping of [Pd(cin)Cl(IPr*)] 4

V Free	V Buried	V Total	V Exact
99.3	80.2	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
55.328	**44.7**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	11.30	33.57	44.87	25.19	**74.81**
-+	32.93	11.93	44.86	73.41	**26.59**
++	24.36	20.49	44.85	54.31	**45.69**
+-	30.69	14.17	44.86	68.42	**31.58**



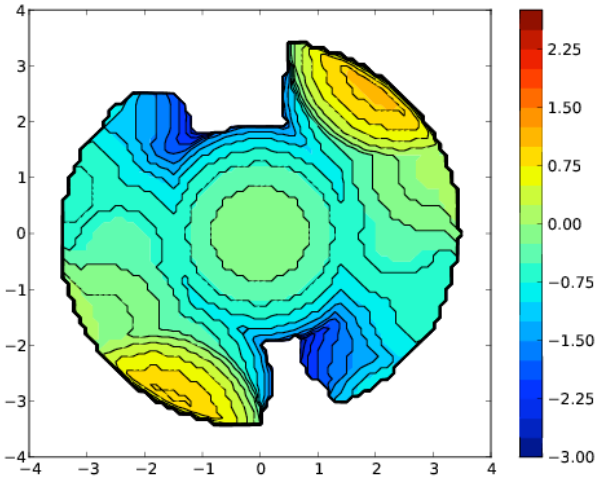
%V_{Bur} and mapping of [Pd(μ-Cl)Cl(SIPr)]$_2$ 6

V Free	V Buried	V Total	V Exact
111.0	68.5	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
61.847	**38.2**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	23.08	21.79	44.87	51.43	**48.57**
-+	32.66	12.20	44.86	72.81	**27.19**
++	23.88	20.96	44.85	53.25	**46.75**
+-	31.36	13.50	44.86	69.91	**30.09**

Steric Map

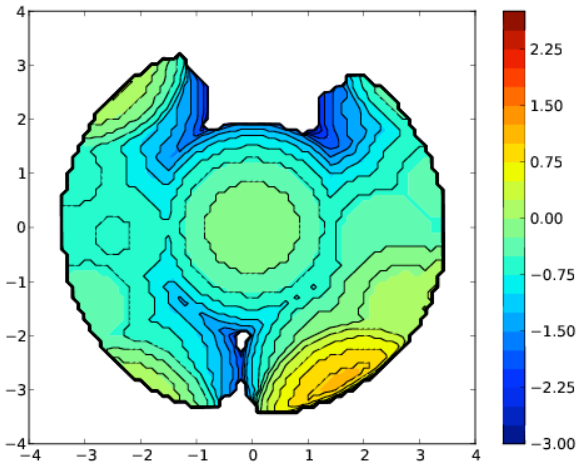


%V_{Bur} and mapping of [Pd(cin)Cl(SIPr)]

V Free	V Buried	V Total	V Exact
112.6	66.9	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
62.735	**37.3**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	28.17	16.70	44.87	62.77	**37.23**
-+	30.34	14.52	44.86	67.64	**32.36**
++	31.60	13.25	44.85	70.46	**29.54**
+-	22.47	22.39	44.86	50.09	**49.91**

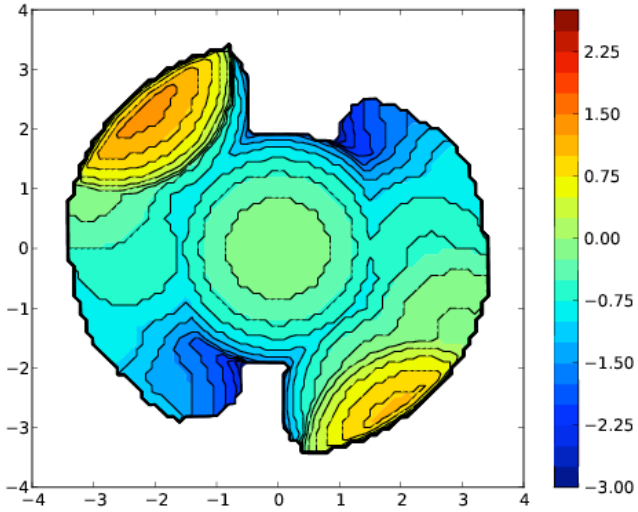


%V_{Bur} and mapping of [Pd(μ-Cl)Cl(IPr)]$_2$

V Free	V Buried	V Total	V Exact
112.5	67.0	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
62.671	**37.3**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	31.97	12.90	44.87	71.25	**28.75**
-+	23.82	21.03	44.86	53.11	**46.89**
++	32.82	12.02	44.85	73.19	**26.81**
+-	23.84	21.01	44.86	53.16	**46.84**

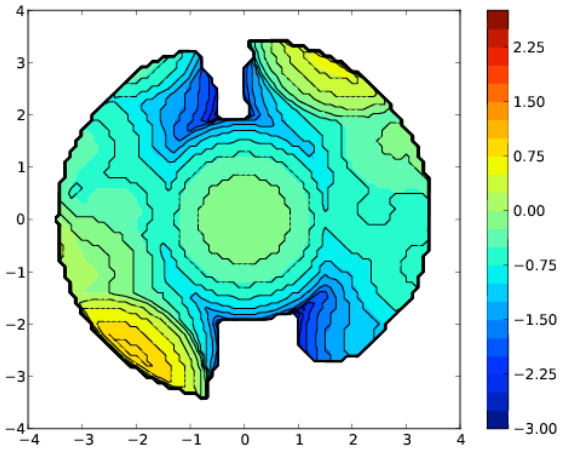


%V_{Bur} and mapping of [Pd(cin)Cl(IPr)]

V Free	V Buried	V Total	V Exact
113.5	66.0	179.5	179.6

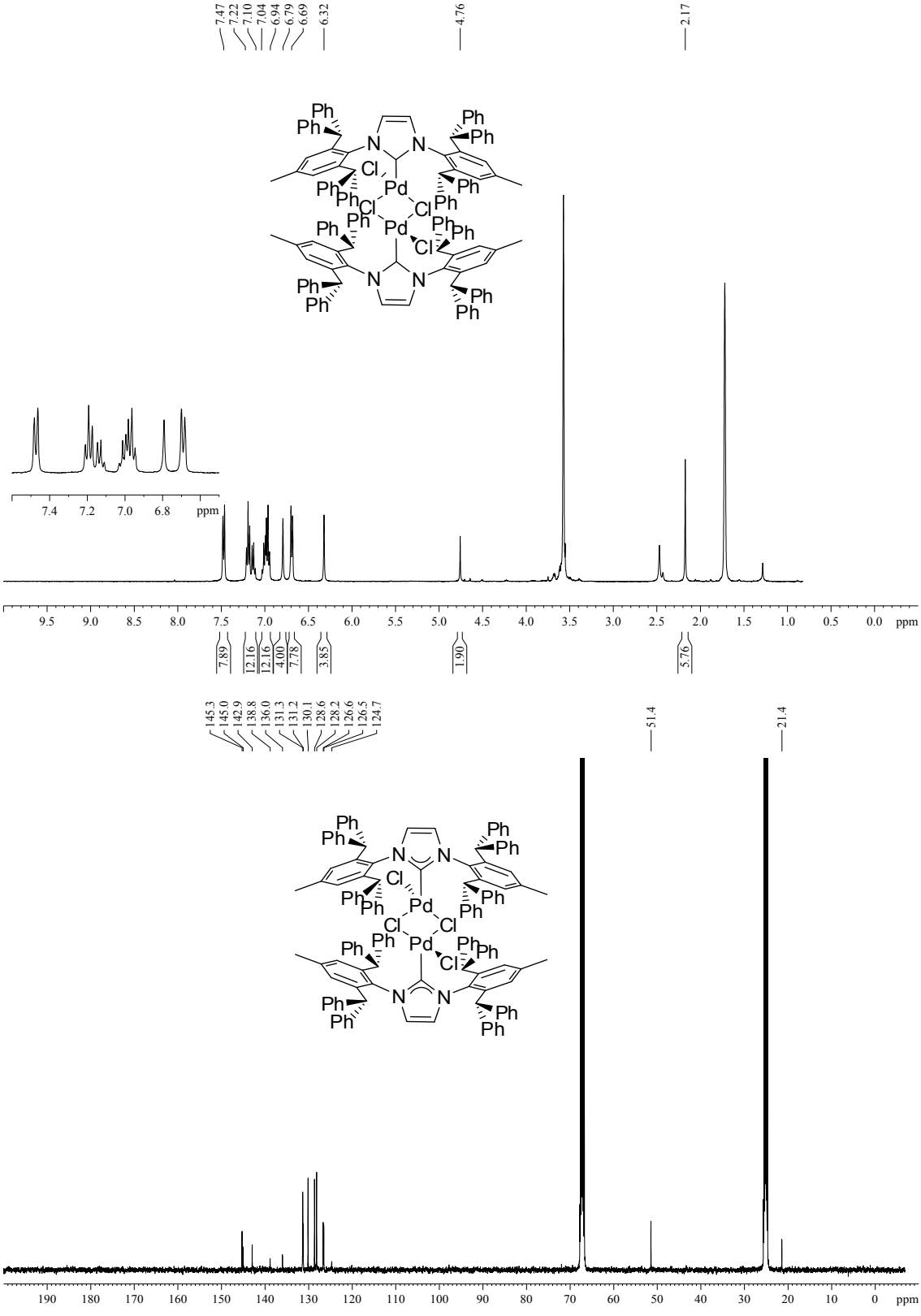
%V_Free	**%V_Bur**	% Tot/Ex
63.220	**36.8**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	24.79	20.08	44.87	55.25	**44.75**
-+	30.33	14.52	44.86	67.62	**32.38**
++	25.94	18.91	44.85	57.84	**42.16**
+-	32.38	12.48	44.86	72.19	**27.81**



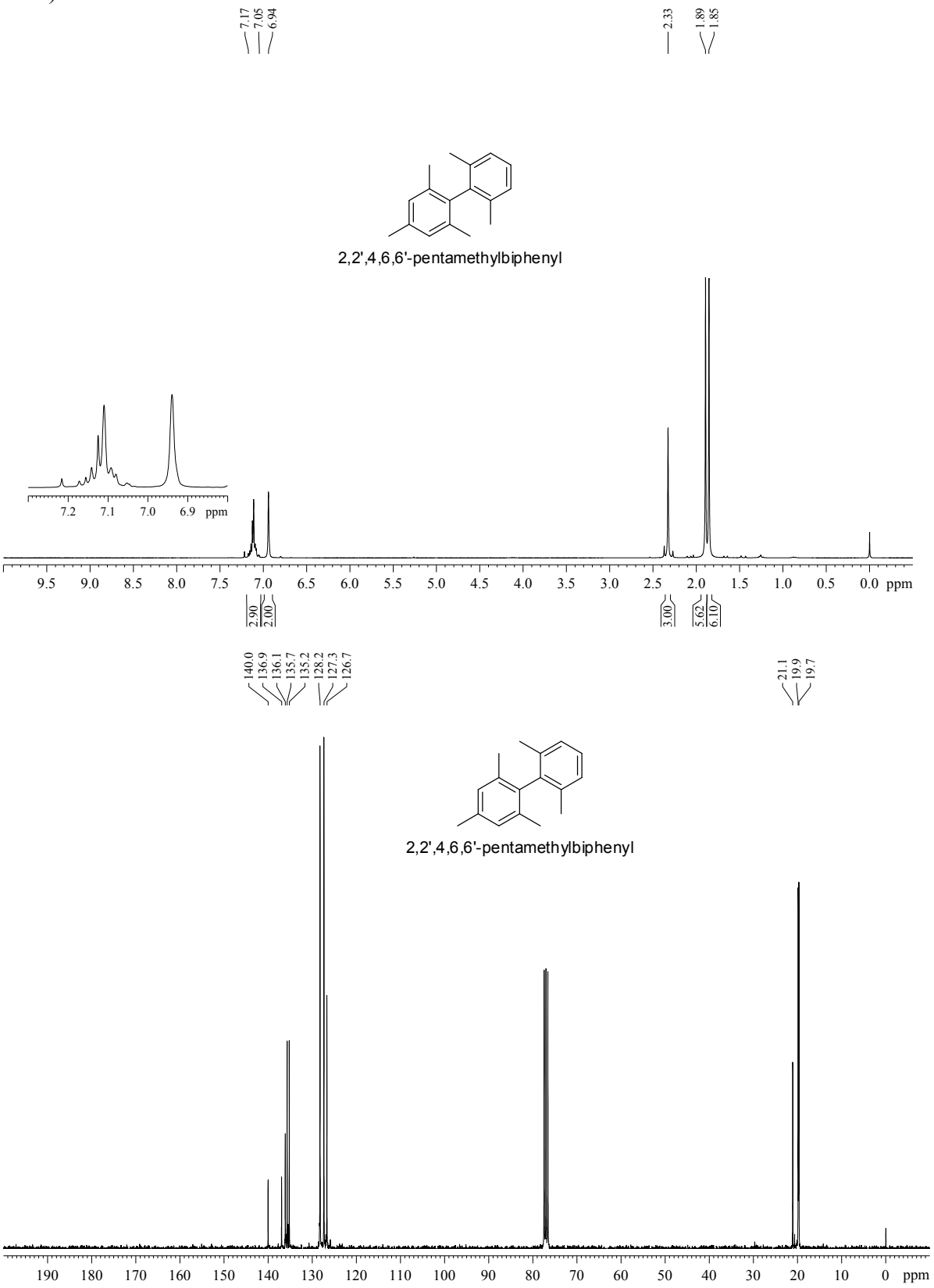
Spectra

Spectra ^{1}H (THF-d_8) and ^{13}C-{^{1}H} (THF-d_8) of complex [Pd(μ-Cl)Cl(IPr*)]$_2$ 7

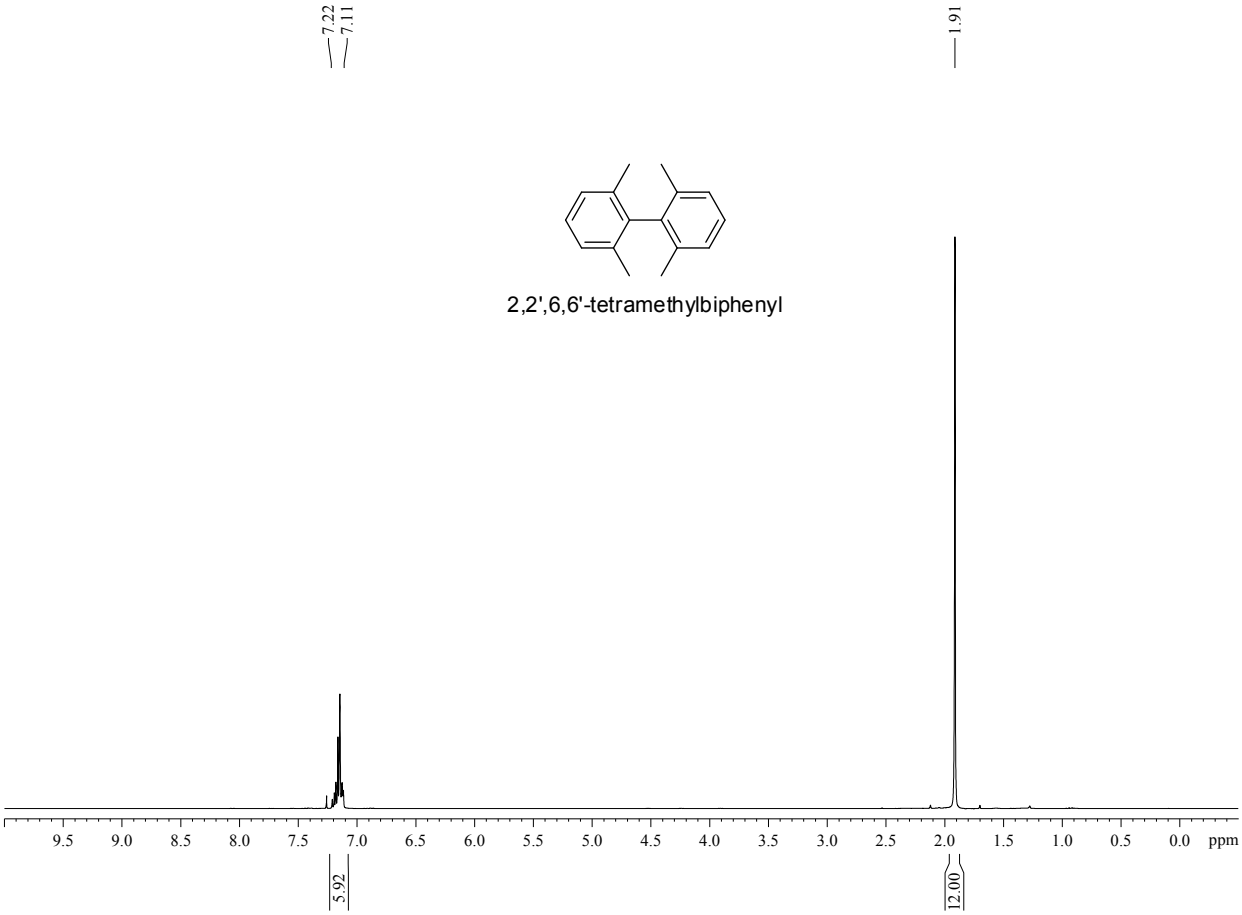


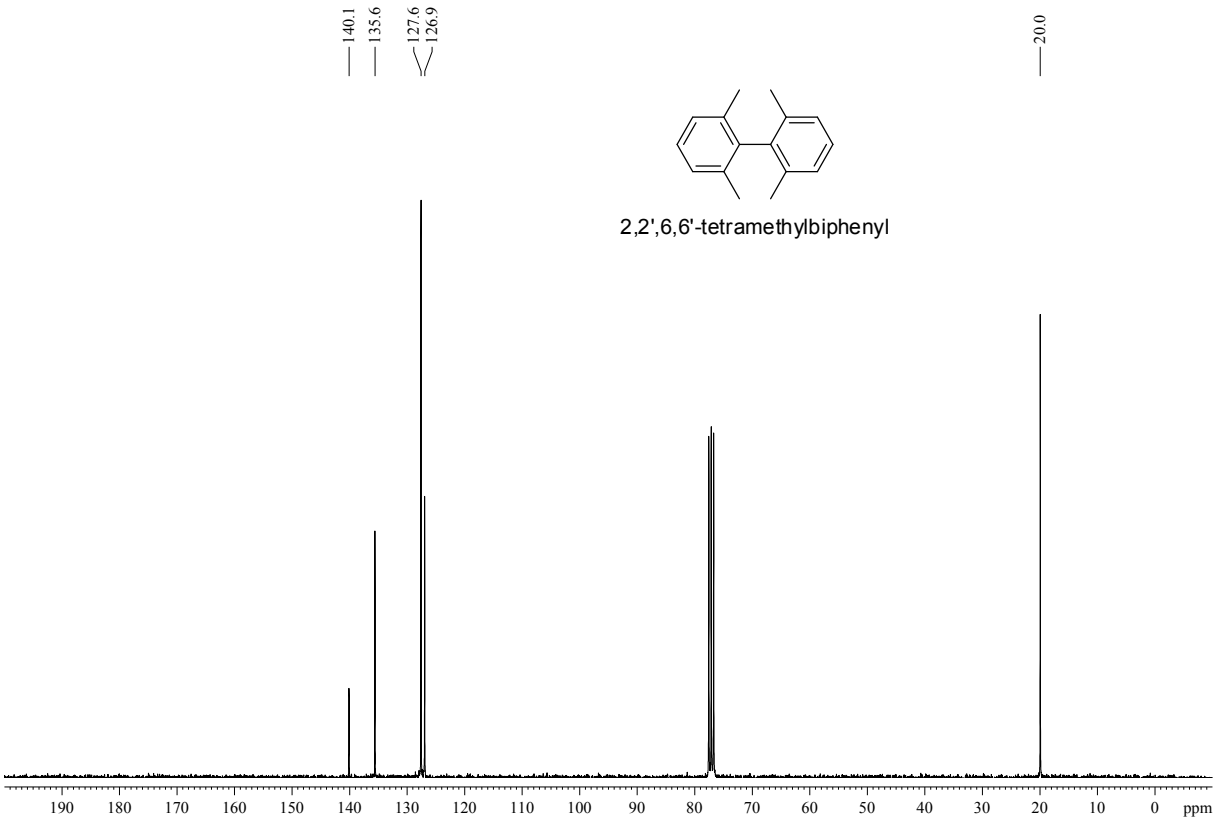
Spectra of catalysis product

^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 2,2',4,6,6'-pentamethylbiphenyl (**10a** and **10m**)

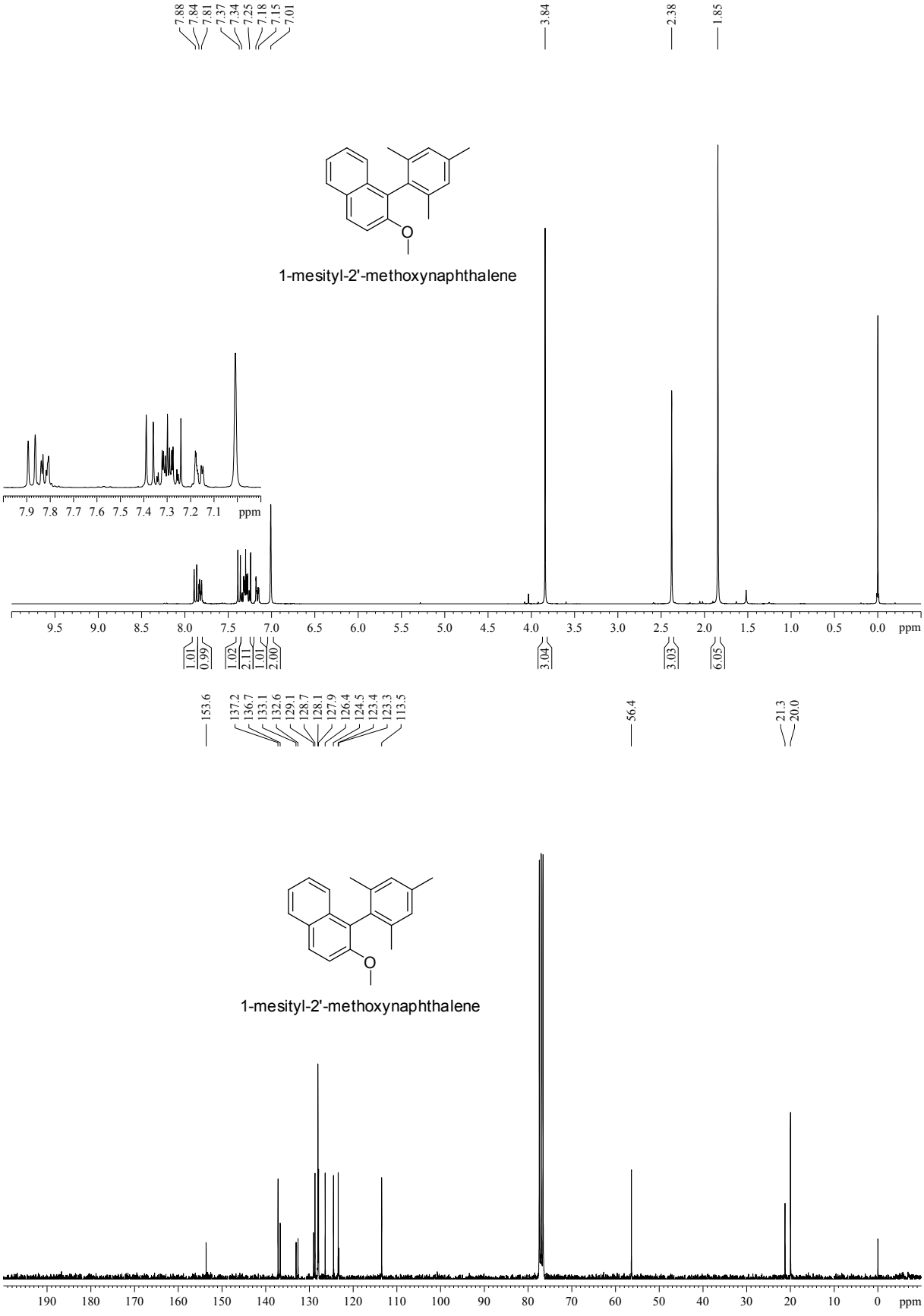


^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 2,2',6,6'-tetramethylbiphenyl (**10b**)

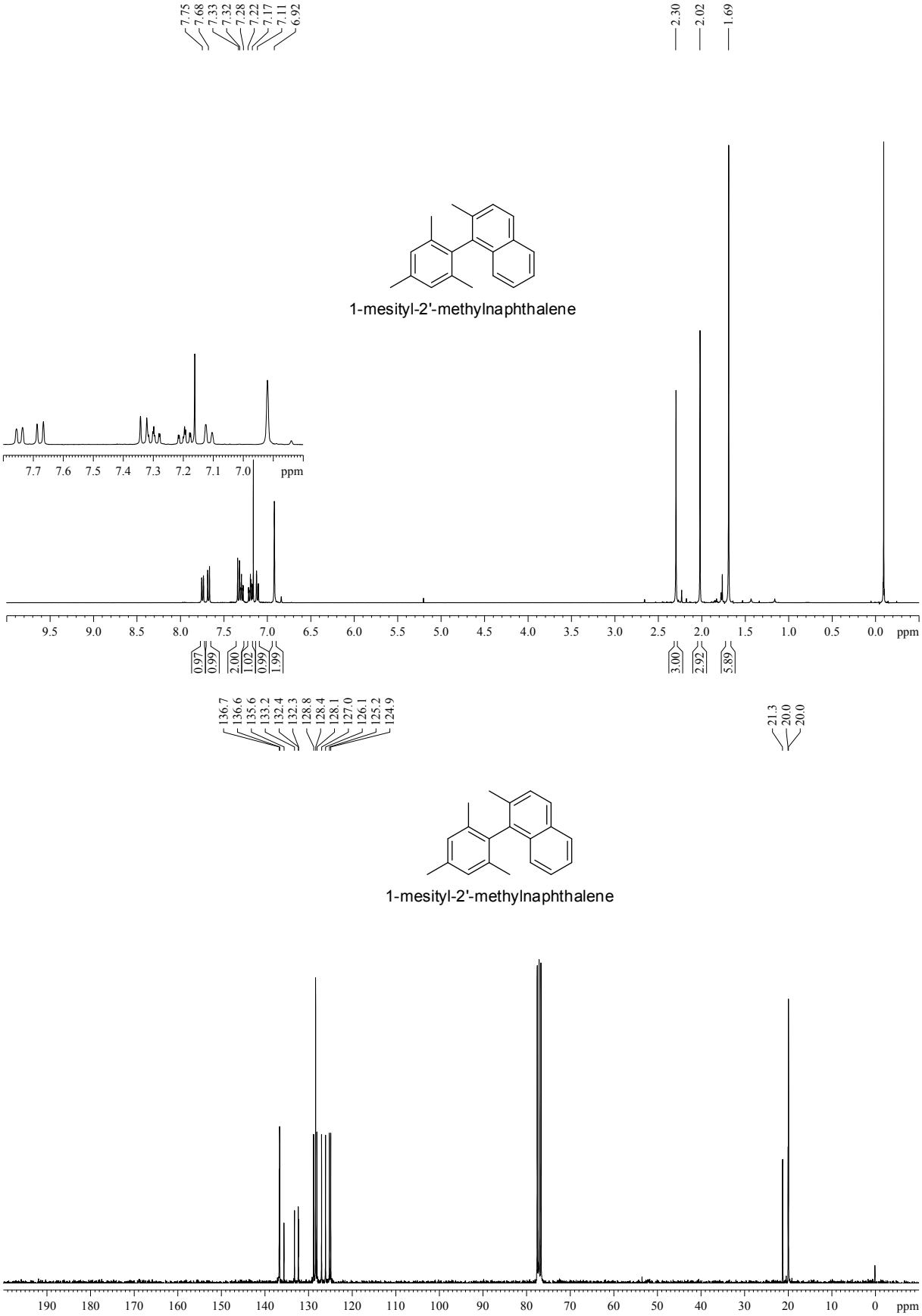




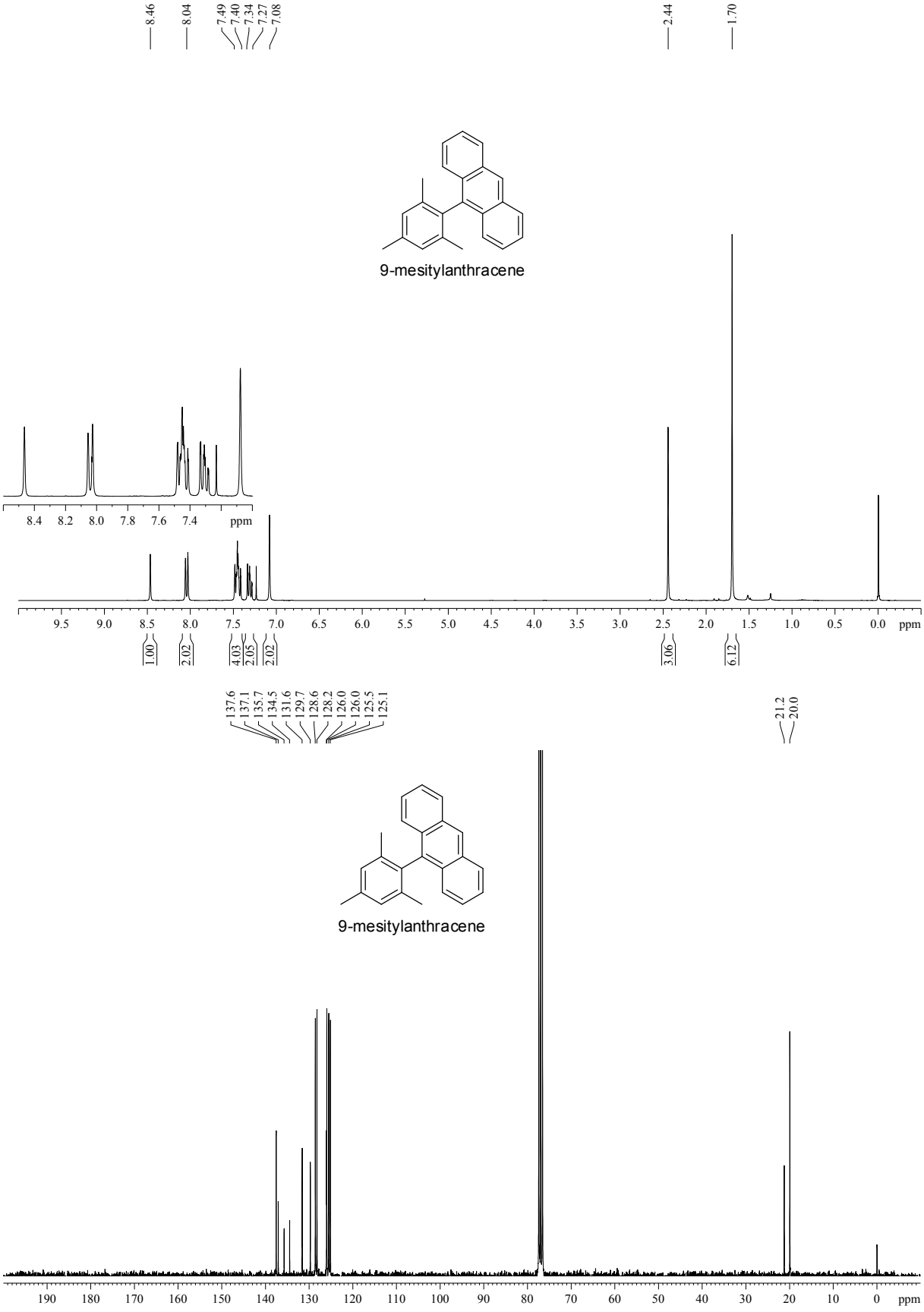
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 1-mesityl-2’-methoxynaphthalene (**10c**)



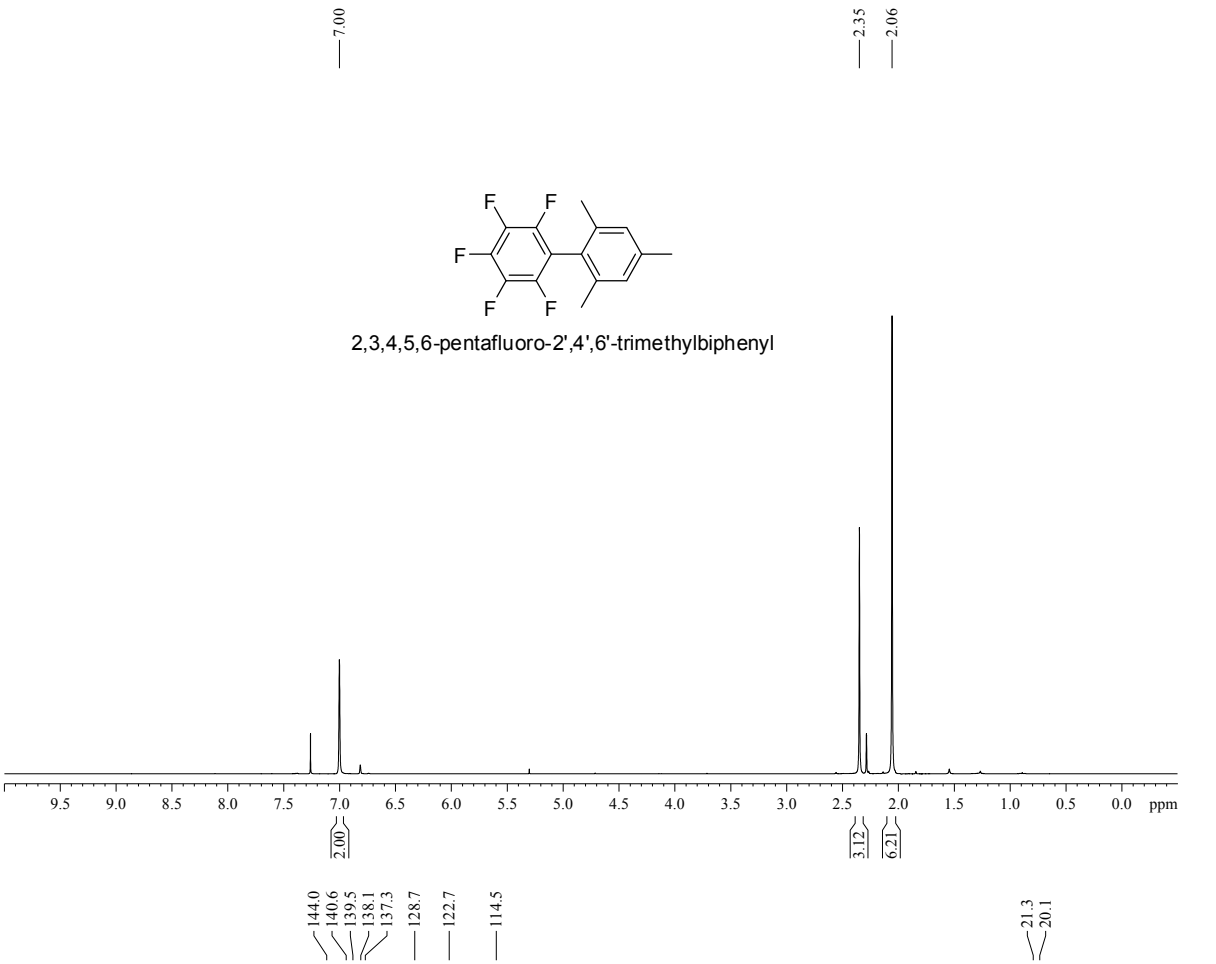
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 1-mesityl-2'-methylnaphthalene (**10d**)

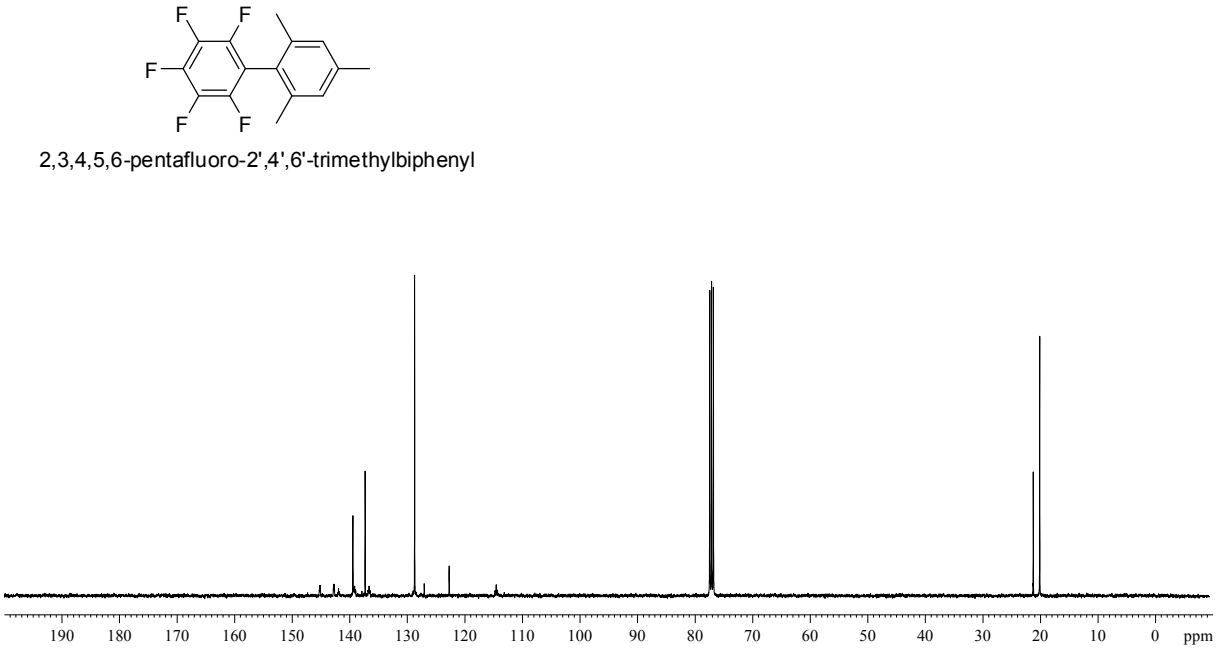


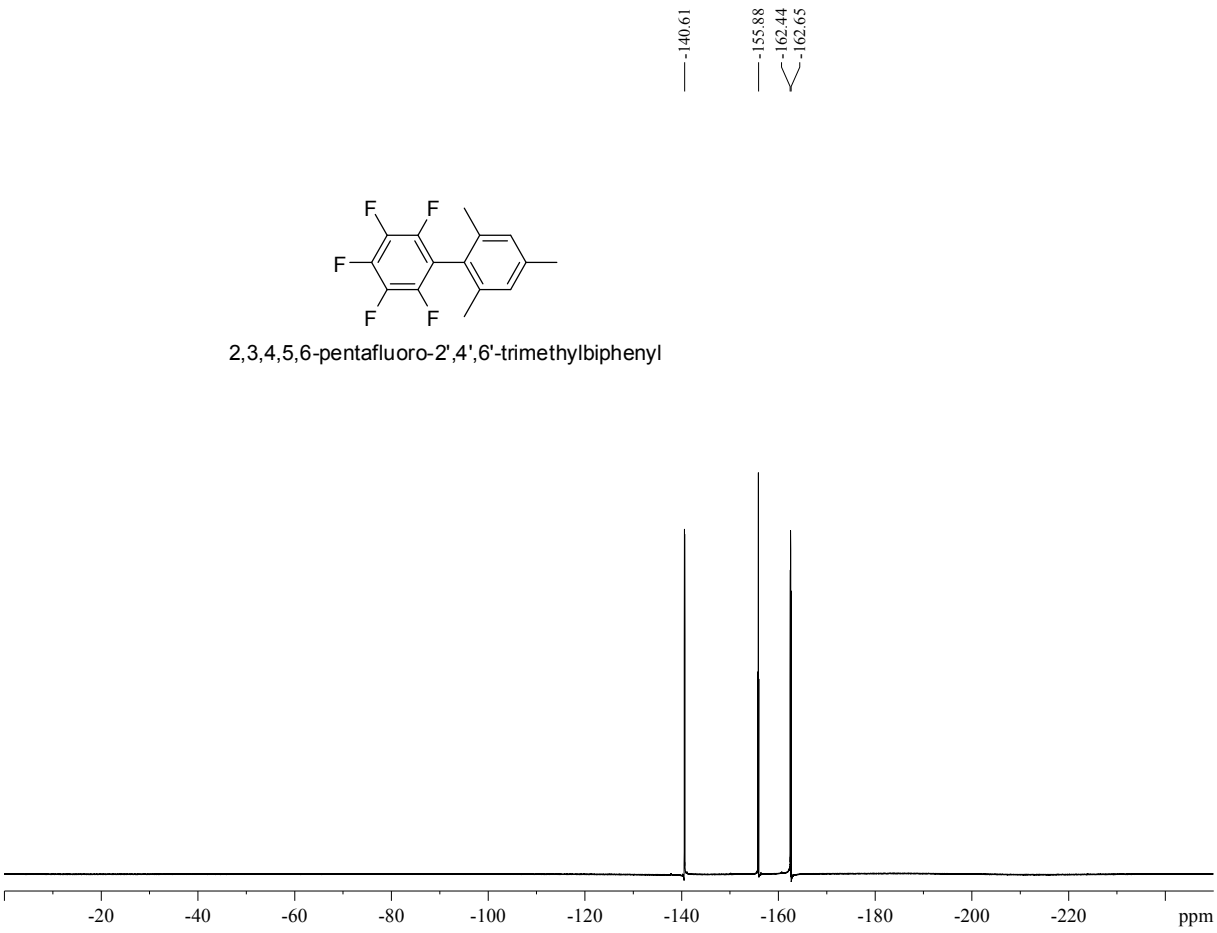
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 9-mesitylanthracene (**10e**)



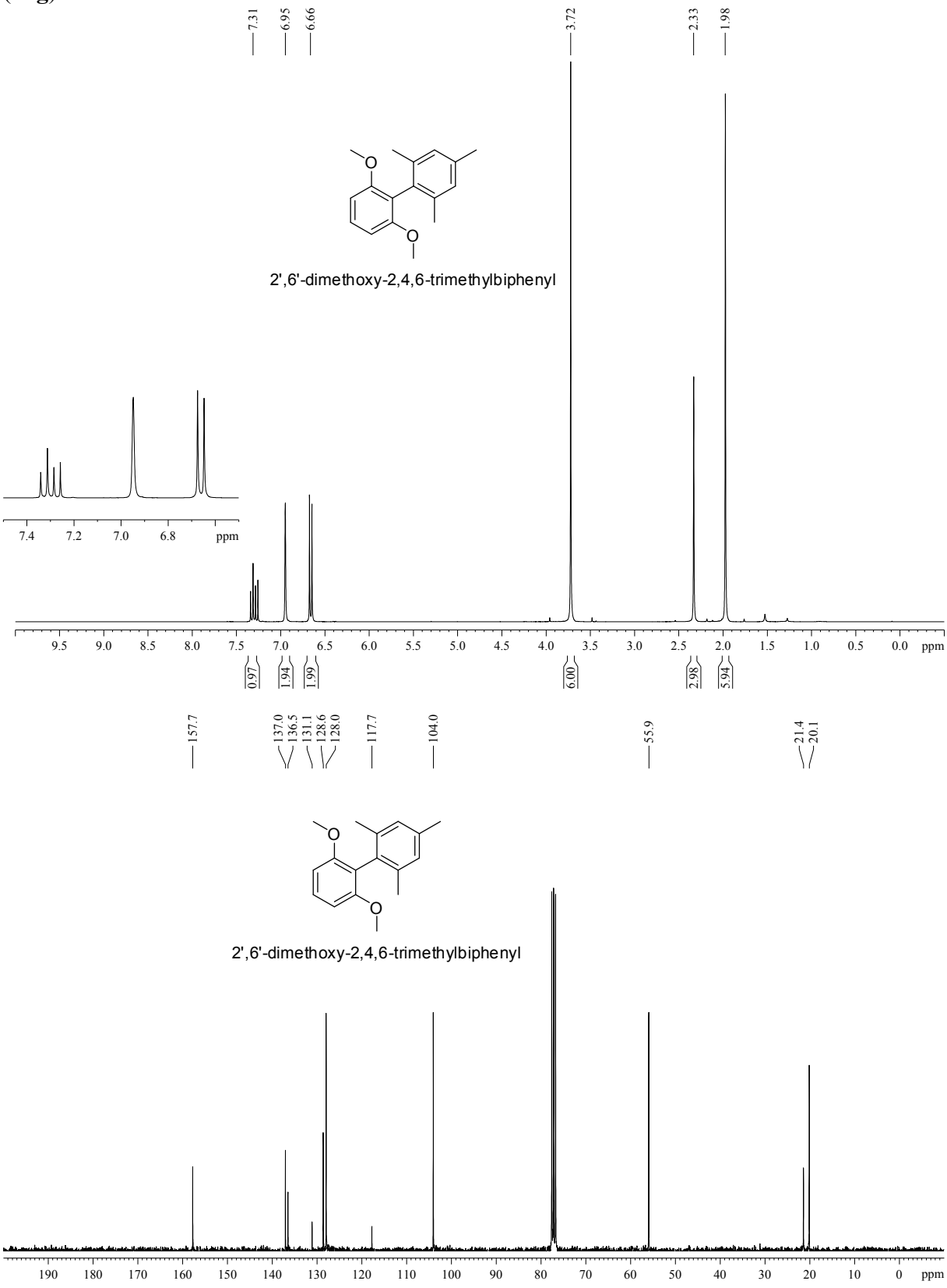
^{1}H NMR ($CDCl_3$), ^{13}C-{^{1}H} NMR ($CDCl_3$) and ^{19}F-{^{1}H} ($CDCl_3$) of 2,3,4,5,6-pentafluoro-2',4',6'-trimethylbiphenyl (**10f**)



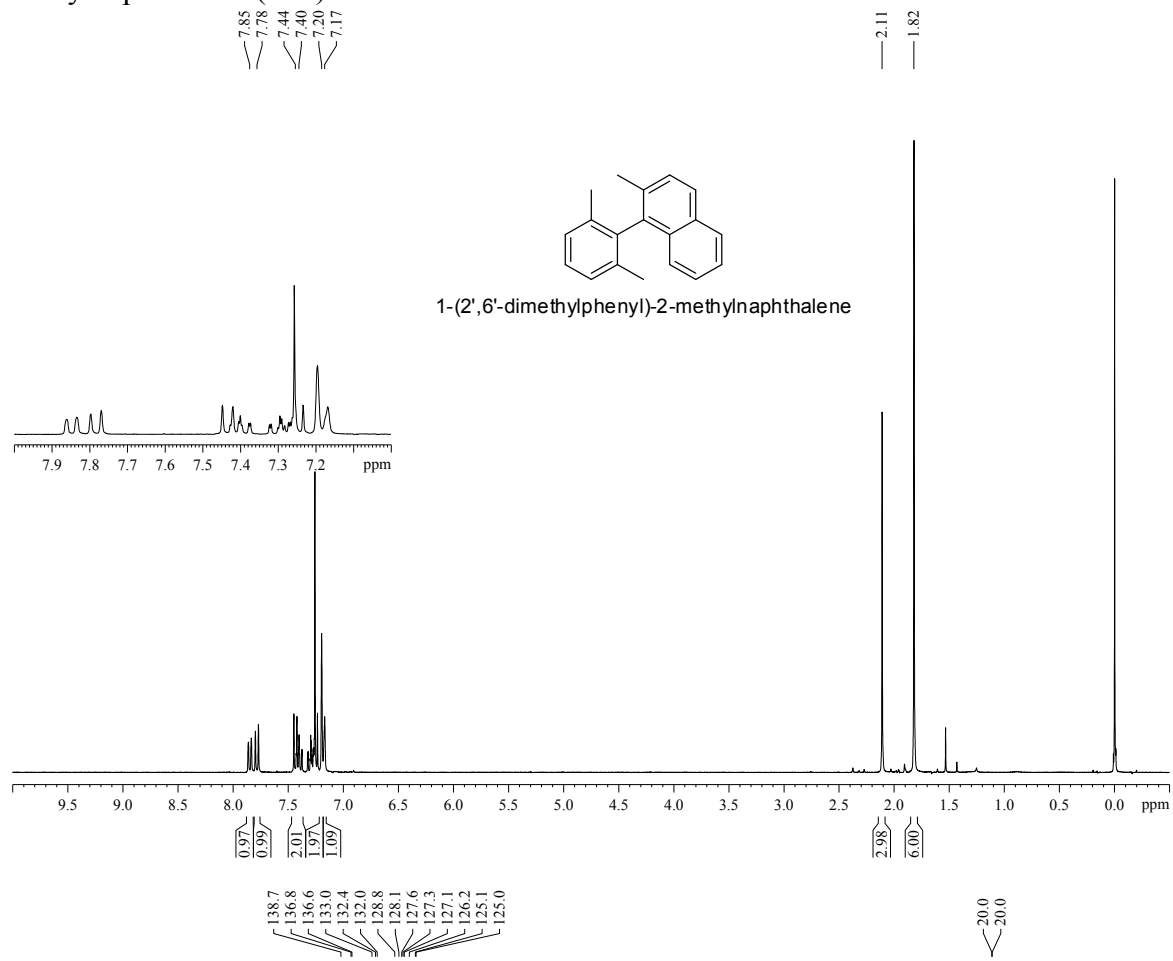


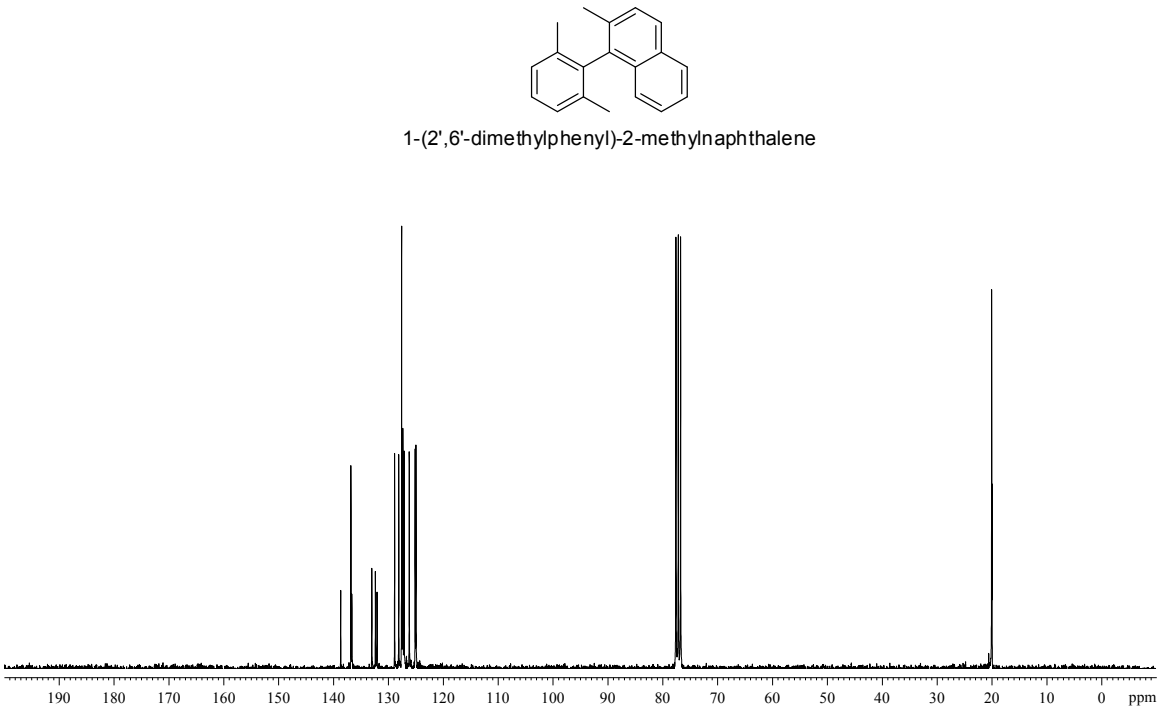

-140.61
-155.88
-162.44
-162.65
F
F
F
F
F
2,3,4,5,6-pentafluoro-2',4',6'-trimethylbiphenyl
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm

^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 2',6'-dimethoxy-2,4,6-trimethylbiphenyl (**10g**)

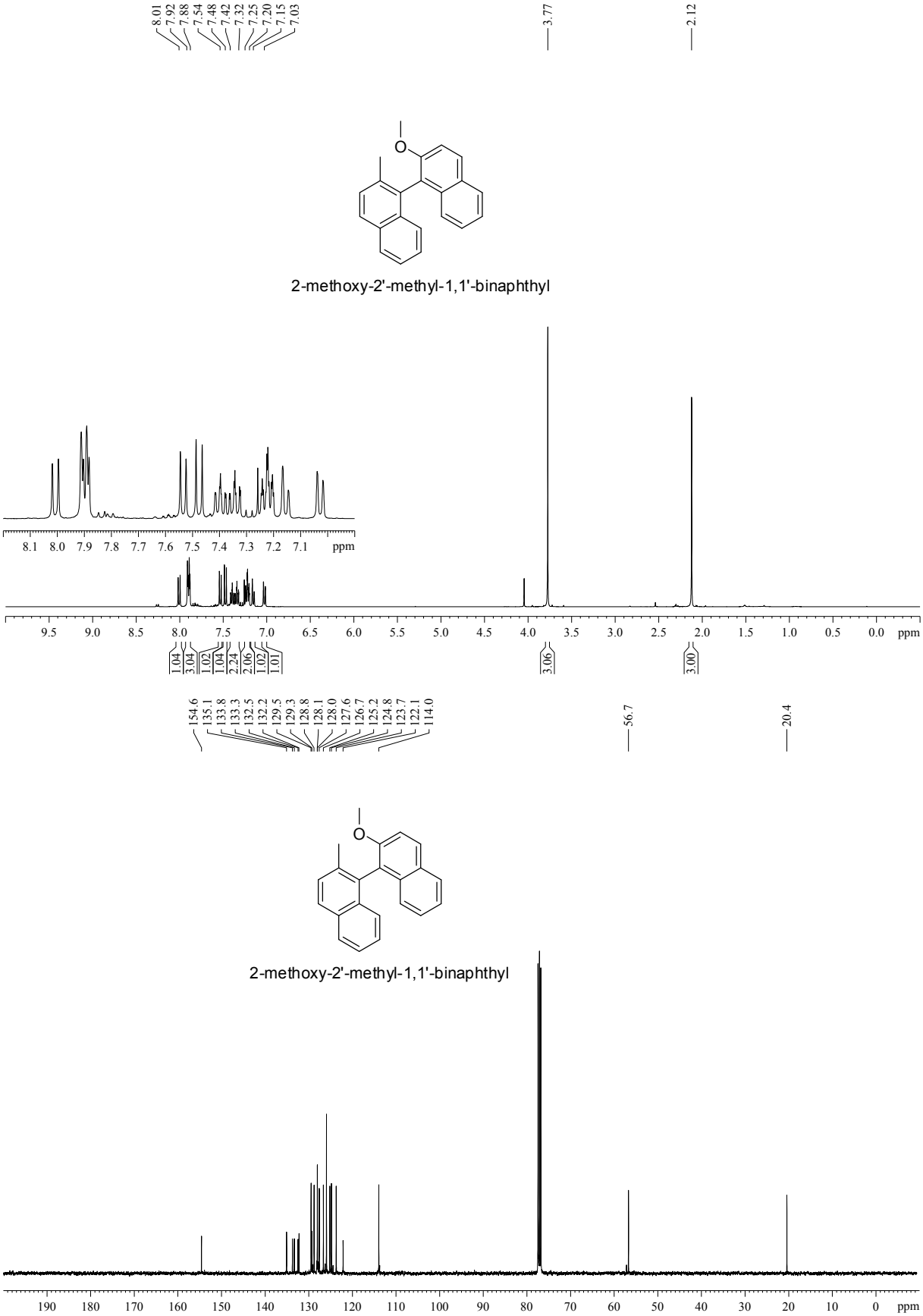


^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 1-(2’,6’-dimethylphenyl)-2-methylnaphthalene (**10h**)

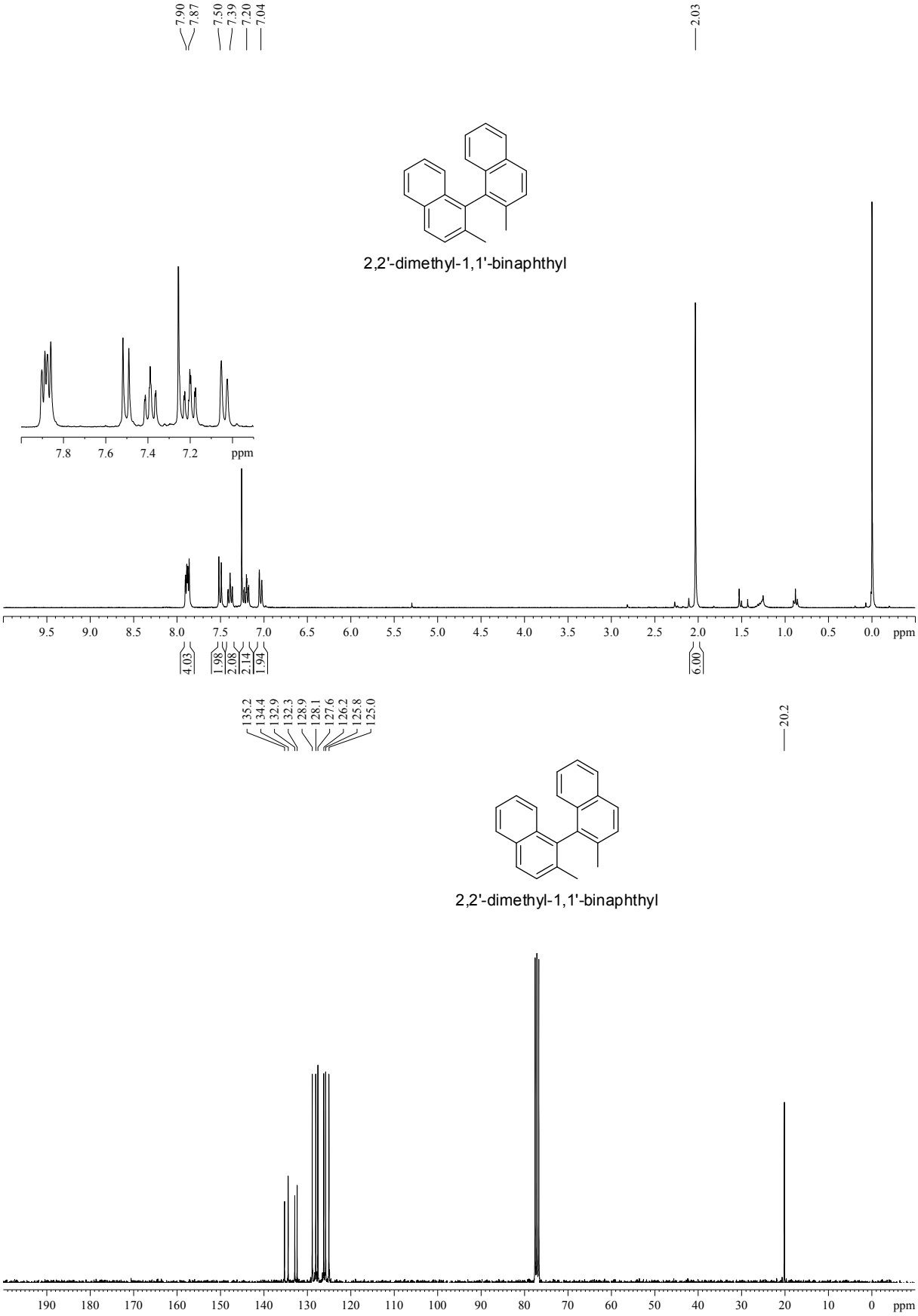




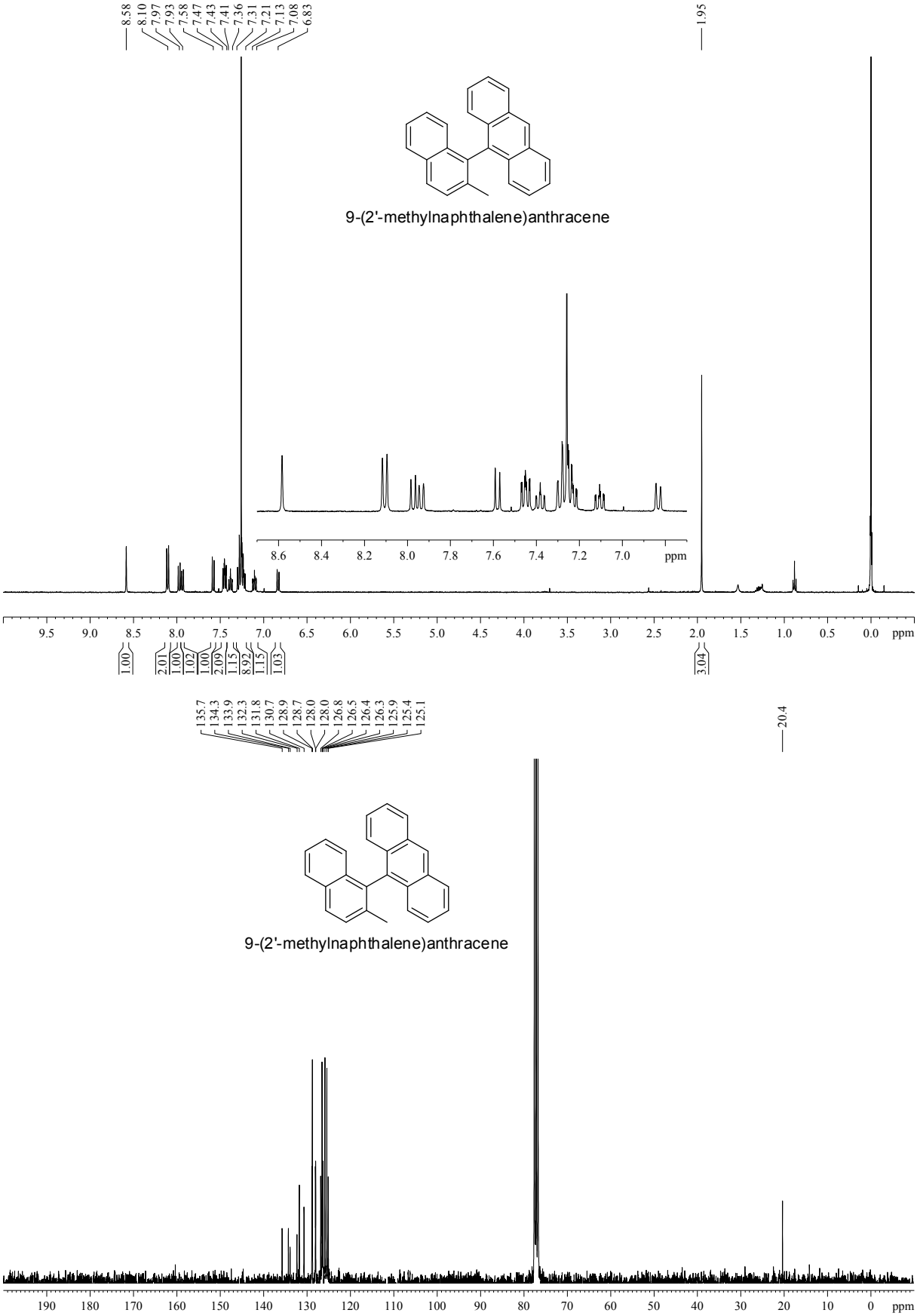
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 2-methoxy-2'-methyl-1,1'-binaphthyl (**10j**)



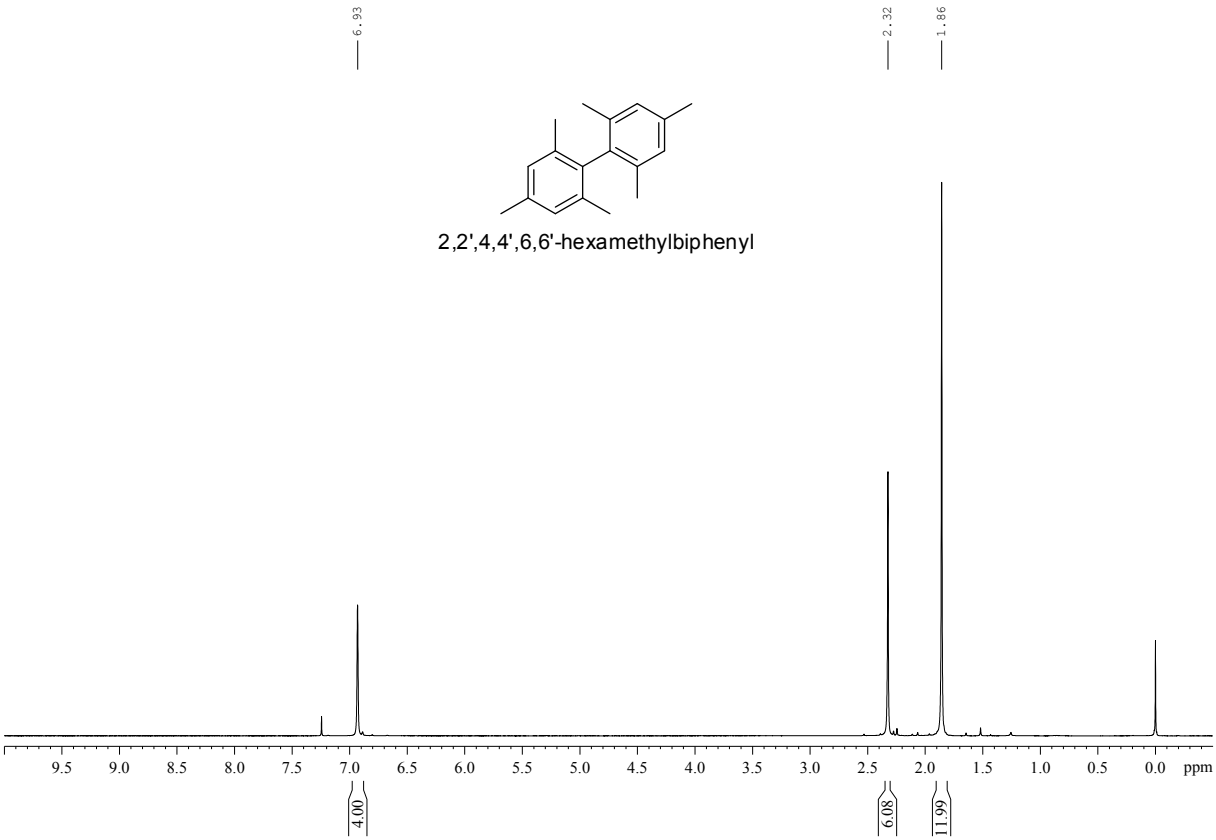
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 2,2'-dimethyl-1,1'-binaphthyl (**10k**)

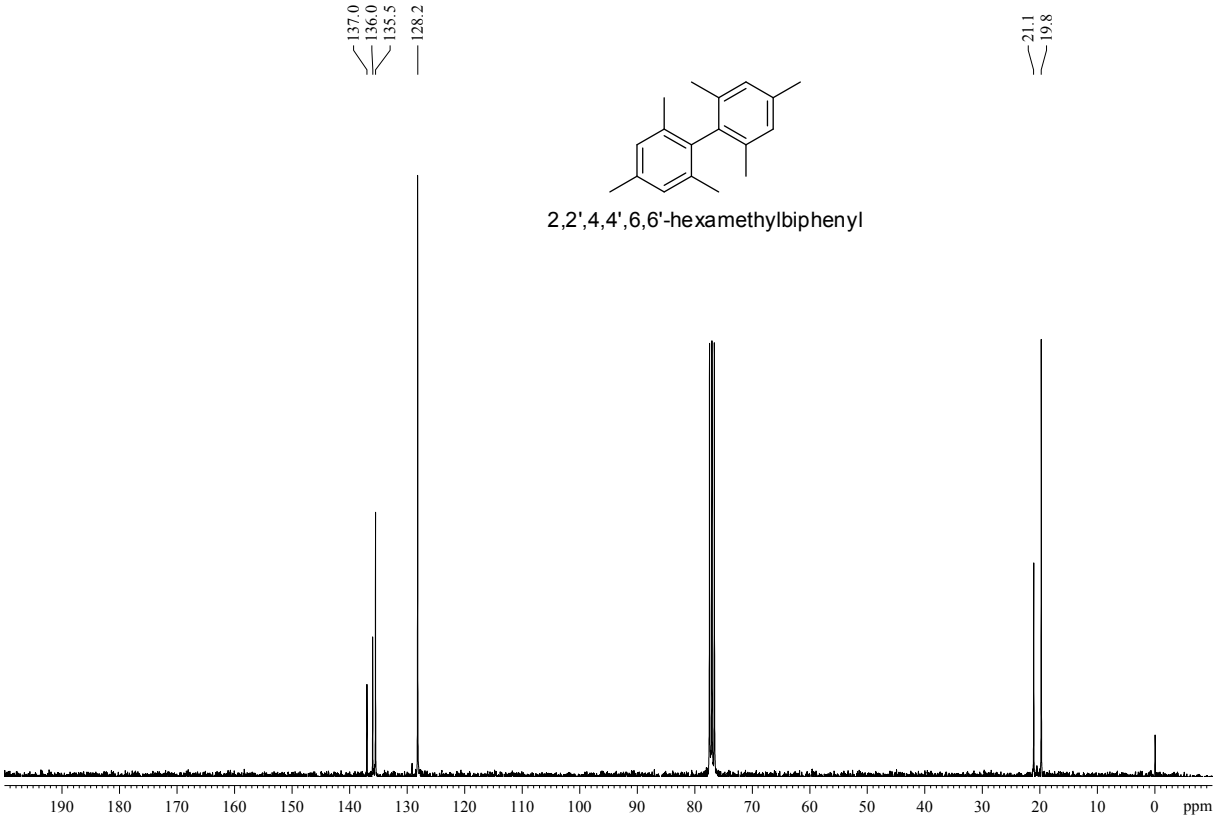


^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 9-(2'-methylnaphthalene)anthracene (**10l**)

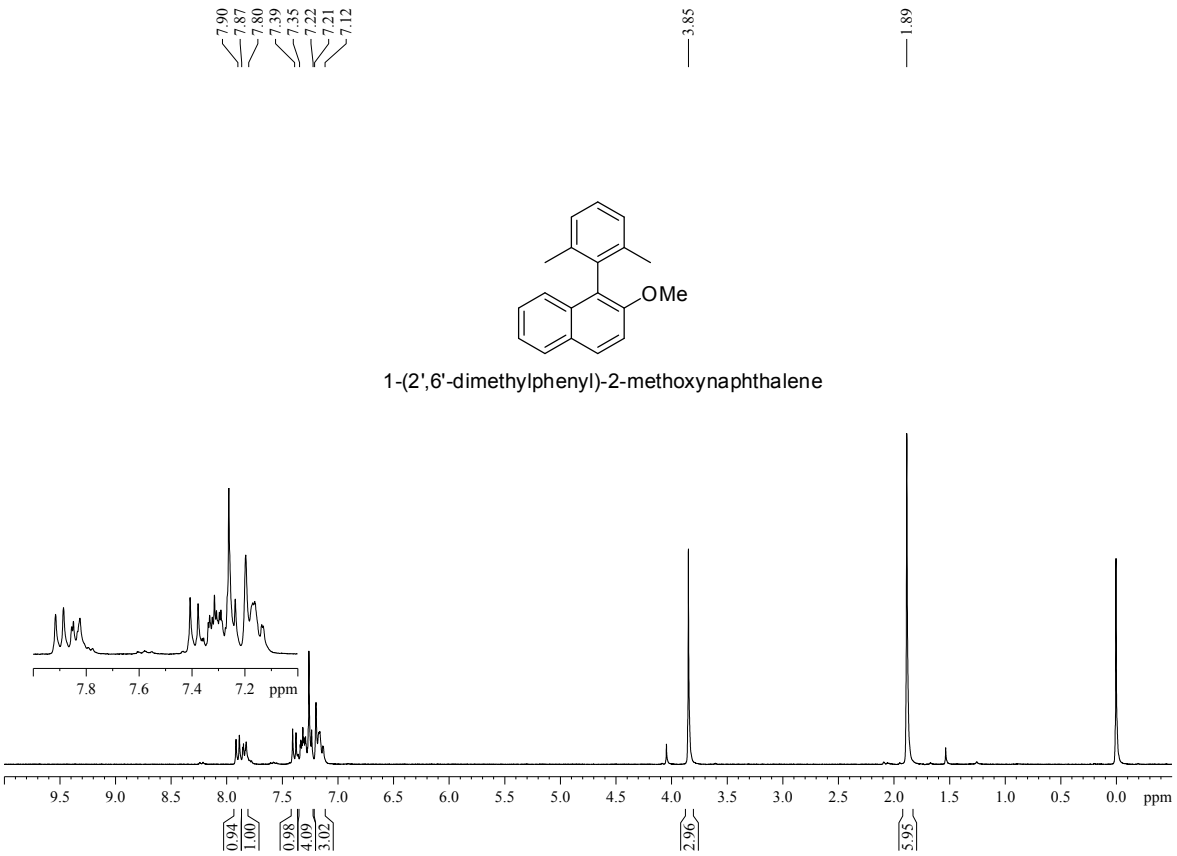


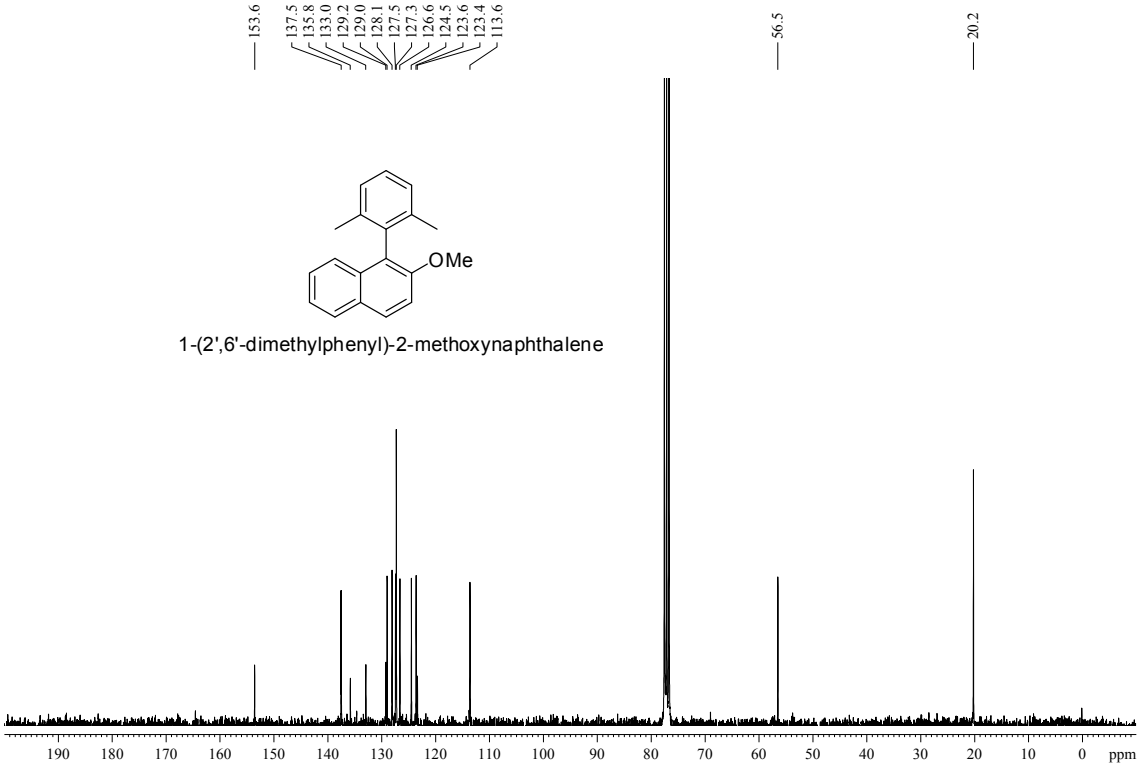
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 2,2',4,4',6,6'-hexamethylbiphenyl (**10n**)



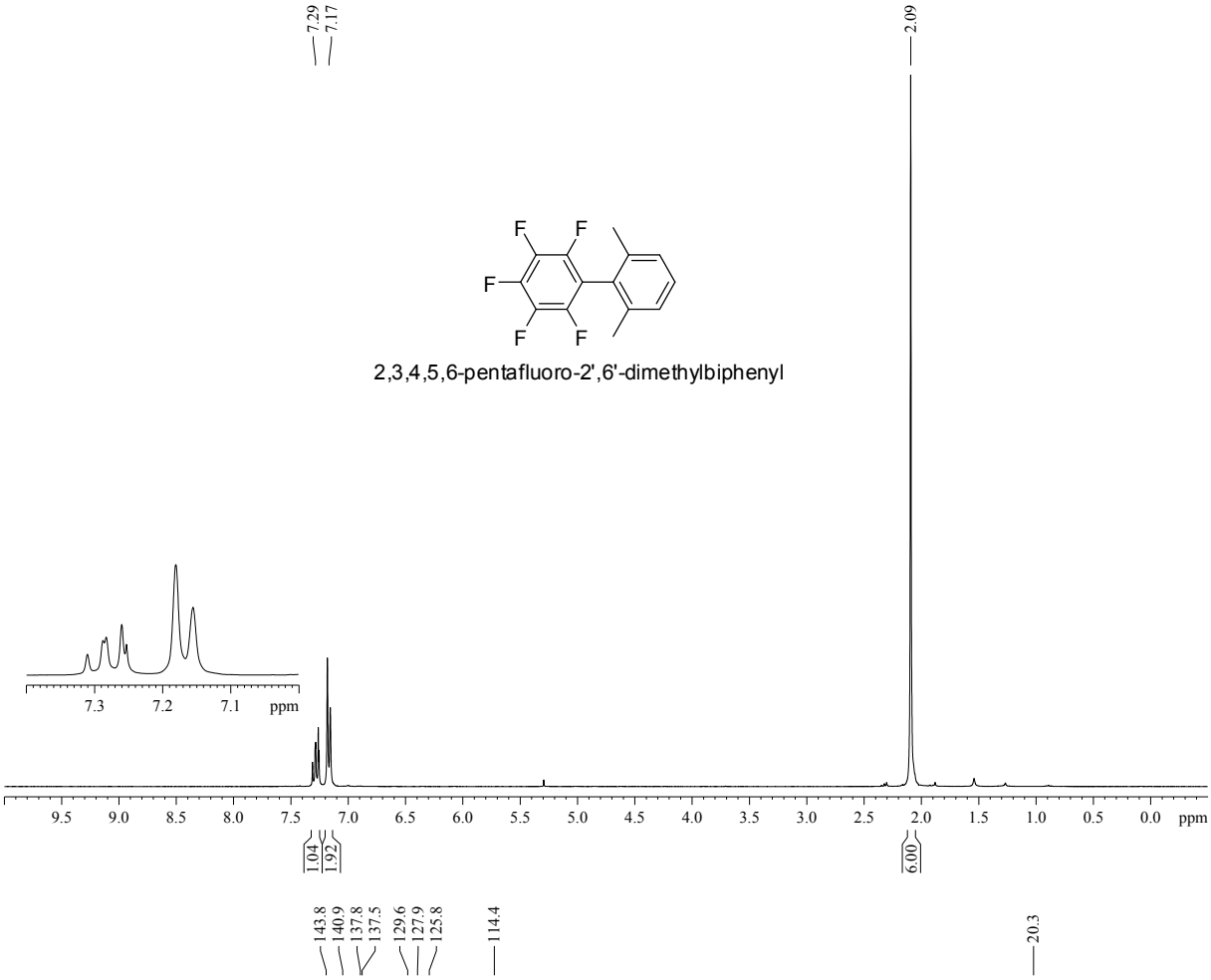


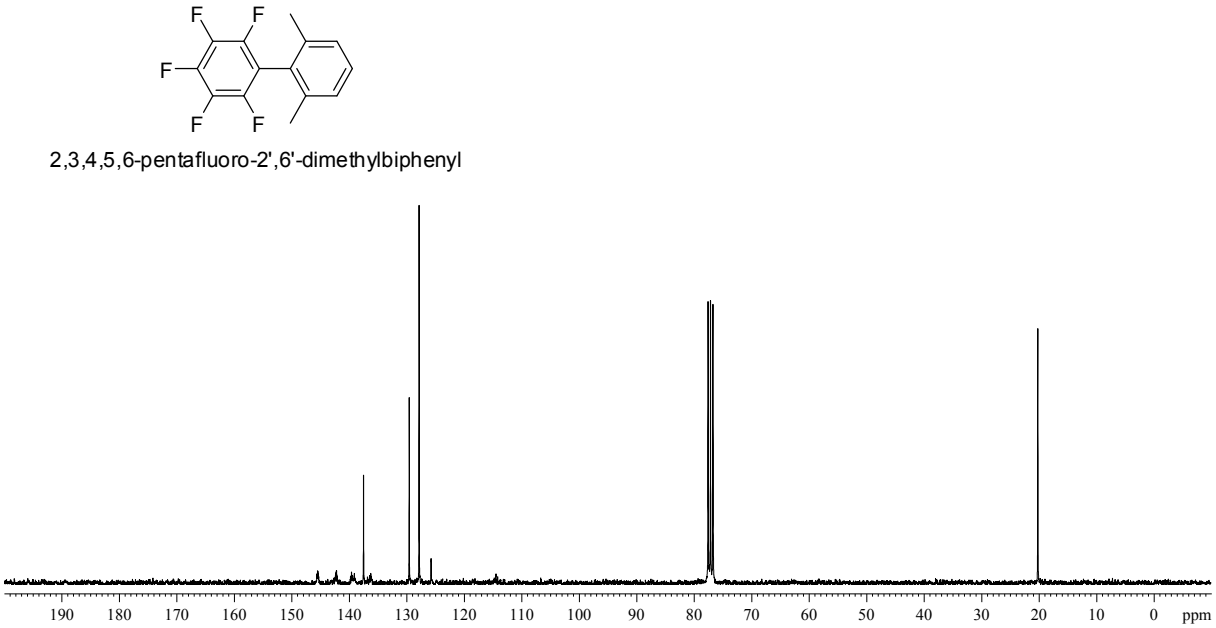
^{1}H NMR ($CDCl_3$) and ^{13}C-{^{1}H} NMR ($CDCl_3$) of 1-(2',6'-dimethylphenyl)-2-methoxynaphthalene (**10p**)

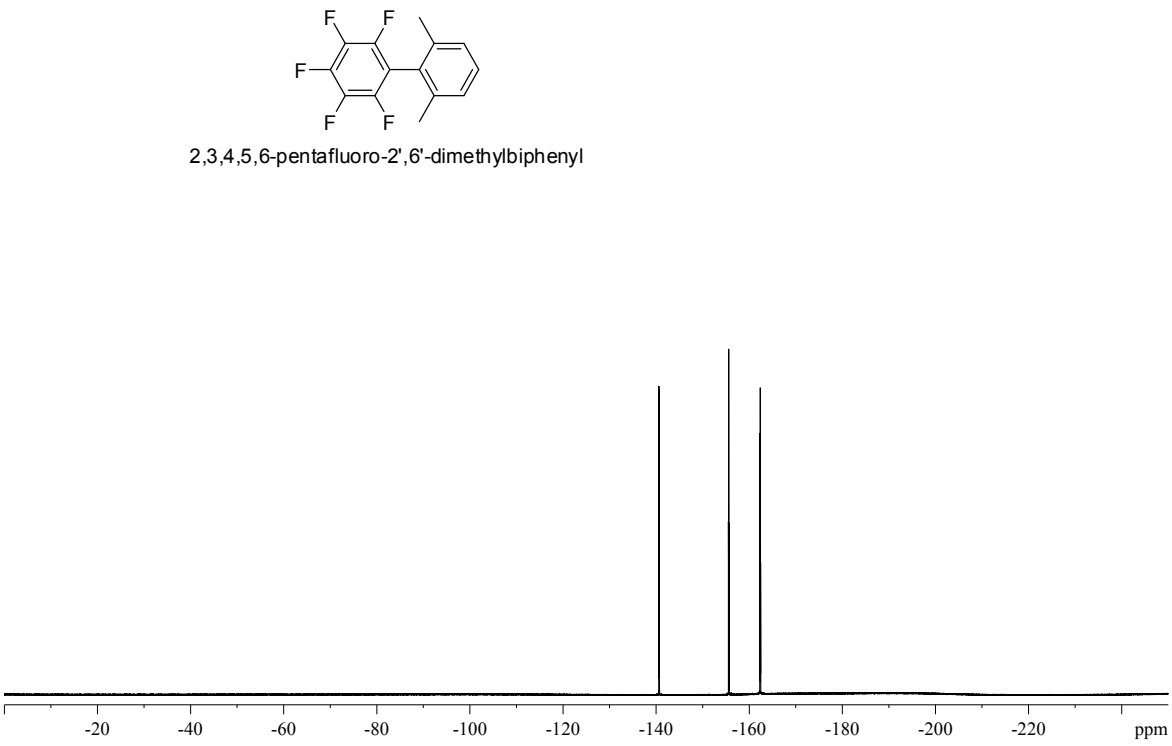




^{1}H NMR ($CDCl_3$), ^{13}C-{^{1}H} NMR ($CDCl_3$) and ^{19}F-{^{1}H} ($CDCl_3$) of 2,3,4,5,6-pentafluoro-2',6'-dimethylbiphenyl (**10q**)

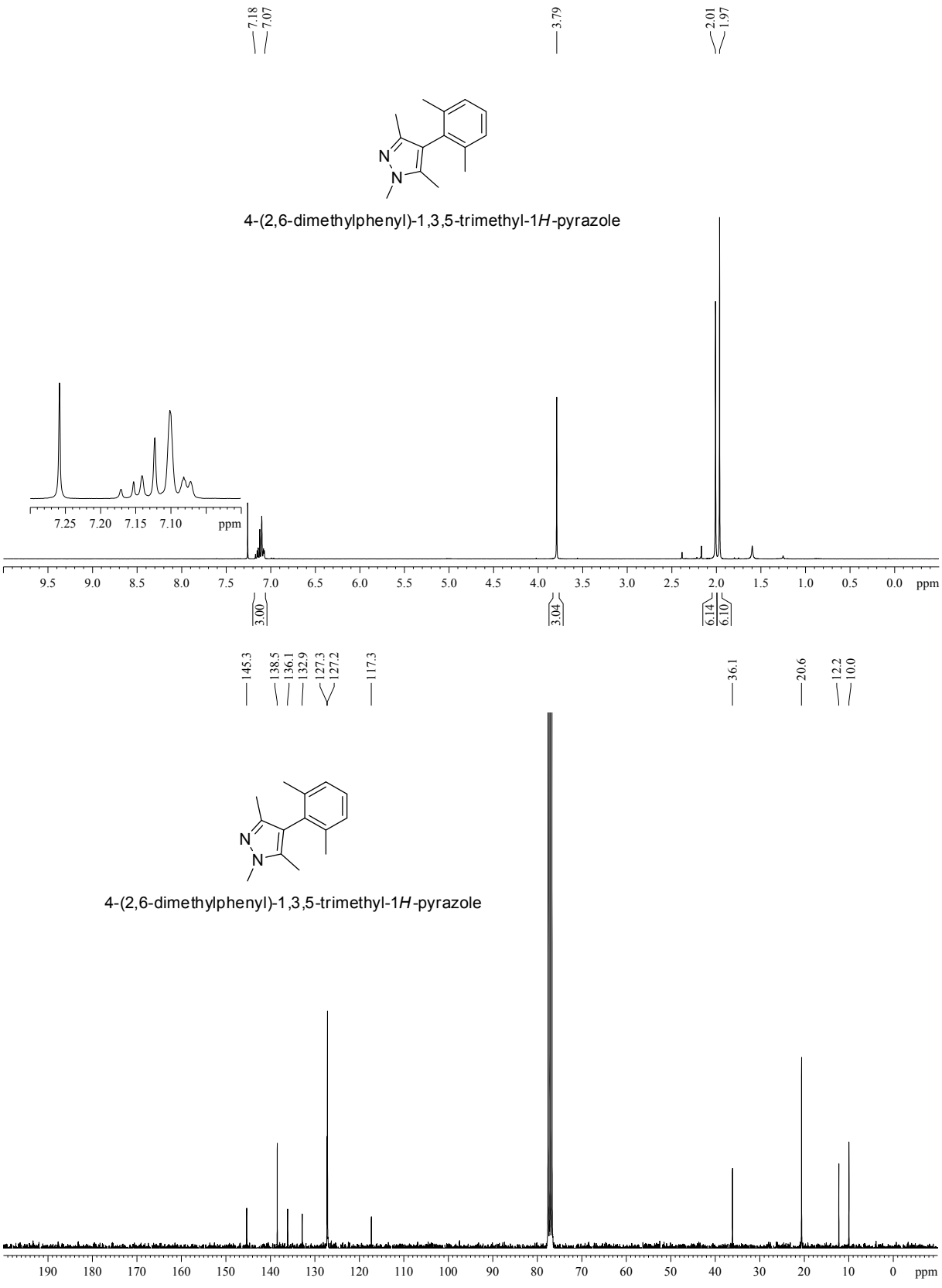






2,3,4,5,6-pentafluoro-2',6'-dimethylbiphenyl

^{1}H NMR ($CDCl_3$), ^{13}C-{^{1}H} NMR ($CDCl_3$) of 4-(2',6'-dimethylphenyl)-1,3,5-trimethyl-1*H*-pyrazole (**10r**)



References

[1] A. Chartoire, M. Lesieur, L. Falivene, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin and S. P. Nolan, *Chem. – Eur. J.* **2012**, *18*, 4517.
[2] L. Wu, E. Drinkel, F. Gaggia, S. Capolicchio, A. Linden, L. Falivene, L. Cavallo and R. Dorta, *Chem.-Eur. J.* **2011**, *17*, 12886.
[3] C. E. Hartmann, S. P. Nolan and C. S. J. Cazin, *Organomet.* **2009**, *28*, 2915.
[4] G.-Q. Li, Y. Yamamoto and N. Miyaura, *Synlett* **2011**, *2011*, 1769.
[5] W. Su, S. Urgaonkar, P. A. McLaughlin and J. G. Verkade, *J. Am. Chem. Soc.* **2004**, *126*, 16433.
[6] H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128.
[7] M. G. Organ, S. Çalimsiz, M. Sayah, K. H. Hoi and A. J. Lough, *Angew. Chem. Int. Ed.* **2009**, *48*, 2383.
[8] J. Yin, M. P. Rainka, X.-X. Zhang and S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 1162.
[9] G. Altenhoff, R. Goddard, C. W. Lehmann and F. Glorius, *J. Am. Chem. Soc.* **2004**, *126*, 15195.