Supporting Information

Mechanistic facets of the competition between cross-coupling and homo-coupling in supporting ligand-free iron-mediated aryl-aryl bond formations.

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# equal contributions.

1. Instrumentation and Chemicals

Gas chromatography analyses (GC) were performed on a Shimadzu Chromatograph 2010 Plus apparatus equipped with a flame ionization detector. The capillary column is a Zebron ZB-5MS (length: 10 m, I.D.: 0.10 mm, film thickness: 0.10 µm. 5% polysilarylene / 95% polydimethylsiloxane). Hydrogen was used as a carrier gas (1.14 mL/min, ratio split: 80). Standard analysis conditions: 40 °C (hold 1 min) to 200 °C (hold 3.5 min), heating rate: 30 °C/min.

Thin layer chromatography (TLC) was carried out on silica gel plates (Carlo Erba 60 F254). Spots were detected with UV light.

Flash chromatography were performed on silica gel columns (Carlo Erba, spherical, neutral, 40-60 µm).

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$) and ^{19}F NMR (282 MHz, $CDCl_3$) were recorded on a Brucker Advance 300 instrument. Chemical shifts (δ) are given in ppm from TMS (^{1}H, ^{13}C) and Trichlorofluoromethane (^{19}F). Coupling constants (*J*) are given in Hz. The following abbreviations are used: s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet, dm, doublet of multiplet.

Mass spectra were recorded on a Hewlett-Packart HP 5973 mass spectrometer via a GC/MS coupling with a Hewlett-Packart HP 6890 chromatograph equipped with a capillary column HP-5MS (50 m x 0.25 mm x 0.25 µm). Ionization was performed by electronic impact (EI, 70 eV). Mass spectra are reported as m/z (% of relative intensity).

THF (VWR, AnalaR Normapur for synthesis, 99.9%), iron(III) chloride (Acros, 99.9+%), iron(III) acetylacetonate (Sigma Aldrich, 99.9+%), magnesium turning (Acros, 99.9+%), bromobenzene (Alfa Aesar, 99%), 4-bromotoluene (Alfa Aesar, 99%), 3-bromotoluene (Alfa Aesar, 99%), 4-bromoanisole (Acros, 98%), 2-bromoanisole (Alfa Aesar, 98%), 4-fluorobromobenzene (Alfa Aesar, 99%), 4-bromo-*N*,*N*-dimethylaniline (Alfa Aesar, 98+%), 2-bromomesitylene (Alfa Aesar, 99%), 1-bromonaphthalene

(Aldrich, 98%), 2-bromonaphthalene (Alfa Aesar, 98+%), chloropentafluorobenzene (Alfa Aesar, 99.9%), 2-chloropyridine (Sigma Aldrich, 99%), ethyl 4-bromobenzoate (Alfa Aesar, 98+%), ethyl 4-chlorobenzoate (Acros, 98%), undecane (Acros, 99%) were used without purification. Iron(II) chloride was dried from iron(II) chloride tetrahydrate (Acros, 99+%) at 180 °C/ 10^{-2} Torr, *N*-methylpyrrolidone (NMP) was distilled at 78 °C/ 12 Torr.

2. Experimental Procedures

General Procedure for the Iron-catalyzed reaction of aryl Grignard reagent with C_6F_5Cl. A dry and argon flushed 100 mL four-necked flask, equipped with a mechanical stirrer, a thermometer, an argon inlet and a septum, was charged with chloropentafluorobenzene C_6F_5Cl (10 mmol, 2.03 g, 1 equiv.), $FeCl_3$ (0.3 mmol, 48.7 mg, 3 mol%) and THF (20 mL). The THF solution of aryl Grignard reagent (12 mmol, around 1 mol/L, 1.2 equiv.) was added in 30 min through a syringe-pump. The temperature can rise up to 40 °C. After 4 h at room temperature, the mixture was quenched with 50 mL of HCl 1 M. The aqueous phase was extracted with 3x50 mL of dichloromethane, and the combined organic layers were washed with brine (50 mL), dried with $MgSO_4$ and concentrated under reduced pressure at 40 °C. The product was purified by chromatography. The eluent is given in the characterization section.

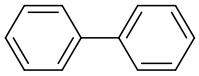
General Procedure for the Iron-catalyzed reaction of aryl Grignard reagent with 2-chloropyridine. A dry and argon flushed 100 mL four-necked flask, equipped with a mechanical stirrer, a thermometer, an argon inlet and a septum, was charged with 2-chloropyridine (10 mmol, 1.89 mL, 1 equiv.), $Fe(acac)_3$ (0.5 mmol, 35.3 mg, 5 mol%) and THF (50 mL). The THF solution of aryl Grignard reagent (12 mmol, around 1 mol/L, 1.2 equiv.) was added in 30 min through a syringe-pump. After 3 h at 0°C, the mixture was quenched with 50 mL of HCl 1 M. The aqueous phase was extracted with 3x50 mL of dichloromethane, and the combined organic layers were washed with brine (50 mL), dried with $MgSO_4$ and concentrated under reduced pressure at 40 °C. The product was purified by chromatography. The eluent is given in the characterization section.

Reduction of $FeCl_x$ by Aryl Grignard Reagents. General Procedure. A dry and argon flushed 250 mL four-necked flask, equipped with a mechanical stirrer, a thermometer, an argon inlet and a dropping funnel, was charged with $FeCl_3$ (13 mmol, 2.11 g, 1 equiv.) or $FeCl_2$ (13 mmol, 1.65 g, 1 equiv.) and THF (13 mL). The dropping funnel was charged with a THF solution of aryl Grignard reagent (130

mmol, around 1 mol/L, 10 equiv.). The THF solution of Grignard reagent was added at room temperature in 3 min. The temperature can rise up to 40 °C. The reaction was monitored by GC.

Evidence of the formation of C_6F_5MgX during the homocoupling reaction. A dry and argon flushed 500 mL four-necked flask, equipped with a mechanical stirrer, a thermometer, an argon inlet and a dropping funnel, was charged with $FeCl_3$ (3 mmol, 0.487 g, 3%), chloropentafluorobenzene C_6F_5Cl (55 mmol, 11.14 g, 1 equiv.) and THF (150 mL). A THF solution of 4-$MeOC_6H_4MgBr$ (110 mmol, 1 mol/L, 91.7 mL, 2 equiv.) was added dropwise rapidly, the temperature can rise up to 40 °C. After 4 h at room temperature, the octanoic anhydride (60 mmol, 16.22 g, 1.2 equiv.) was added. Stirring was continued for 1 h, then the reaction mixture was quenched with 250 mL of HCl 1 mol/L and the aqueous phase was extracted with 3x200 mL of dichloromethane. The combined organic layers were washed with 100 mL of water, dried with $MgSO_4$ and concentrated under reduced pressure at 40 °C. The product was purified by chromatography on silica gel. Fractions which contain the 1-(pentafluorophenyl)-octan-1-one were concentrated under reduced pressure at 40 °C, then the product was distilled with a Kugelrohr at 100 °C/10^{-2} Torr.

3. Characterization Data



1a

Biphenyl (1a).

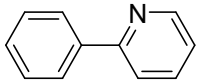
GC: t_R = 4.030 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.61 – 7.58 (m, 4H), 7.45 – 7.41 (m, 4H), 7.37 – 7.31 (m, 2H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 140.4 (2C), 127.9 (4C), 126.4 (2C), 126.3 (4C).

Spectroscopic data were in accordance with literature data.[1]



1b

2-Phenylpyridine (1b).

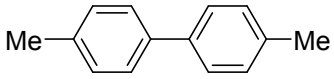
GC: t_R = 4. 380 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.77 – 8.66 (m, 1H), 8.04 – 7.96 (m, 2H), 7.80 – 7.71 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.26 – 7.22 (m, 1H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 157.5, 149.7, 139.4, 137.1, 129.2, 128.9 (2C), 127.1 (2C), 122.3, 120.8.

Spectroscopic data were in accordance with literature data.[1]



2a

4,4'-Dimethylbiphenyl (2a).

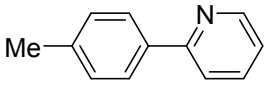
GC: t_R = 4.996 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.49 – 7.45 (m, 4H), 7.24 – 7.21 (m, 4H), 2.38 (s, 6H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 137.5 (2C), 135.8 (2C), 128.6 (4C), 126.0 (4C), 20.2 (2C).

Spectroscopic data were in accordance with literature data.[2]



2b

2-(*p*-Tolyl)pyridine (2b).

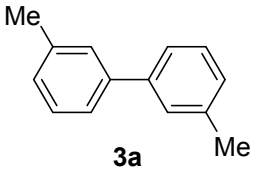
GC: t_R = 4.780 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.68 (ddd, *J* = 4.9, 1.6, 1.1 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.77 – 7.68 (m, 2H), 7.29 (dd, *J* = 8.5, 0.6 Hz, 2H), 7.21 (ddd, *J* = 6.7, 4.9, 1.8 Hz, 1H), 2.41 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 157.5, 149.6, 139.1, 137.0, 136.6, 129.6 (2C), 126.9 (2C), 122.0, 120.5, 21.4.

Spectroscopic data were in accordance with literature data.[3]



3a

3,3'-Dimethyl-1,1'-biphenyl (3a).

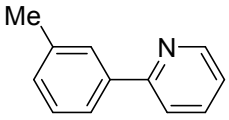
GC: t_R = 4.880 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.47 – 7.41 (m, 4H), 7.39 – 7.34 (m, 2H), 7.22 – 7.18 (m, 2H), 2.47 (s, 6H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 141.5 (2C), 138.4 (2C), 128.7 (2C), 128.1 (2C), 128.0 (2C), 124.4 (2C), 21.7 (2C).

Spectroscopic data were in accordance with literature data.[5]



3b

2-(*m*-Tolyl)pyridine (3b).

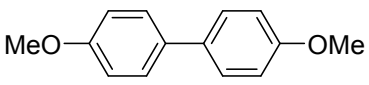
GC: t_R = 4.690 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.73 – 8.67 (m, 1H), 7.84 (s, 1H), 7.80 – 7.70 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.23 (ddd, *J* = 6.7, 4.9, 1.6 Hz, 2H), 2.44 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 157.7, 149.6, 139.3, 138.6, 137.1, 130.0, 128.8, 127.8, 124.2, 122.2, 120.9, 21.7.

Spectroscopic data were in accordance with literature data.[4]



4a

4,4'-Dimethoxybiphenyl (4a).

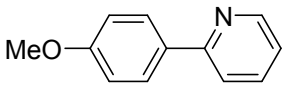
GC: t_R = 6.141 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.48 – 7.43 (m, 4H), 6.96 – 6.91 (m, 4H), 3.83 (s, 6H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 157.9 (2C), 132.7 (2C), 126.9 (4C), 113.4 (4C), 54.5 (2C).

Spectroscopic data were in accordance with literature data.[5]



4b

2-(4-Methoxyphenyl)pyridine (4b).

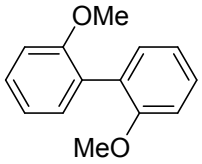
GC: t_R = 5.242 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.67 (d, *J* = 4.3 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.04 – 6.98 (m, 2H), 3.87 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 160.4, 157.1, 149.5, 136.6, 132.0, 128.1 (2C), 121.3 (2C), 119.7, 114.1, 55.3.

Spectroscopic data were in accordance with literature data.[4]



5a

2,2'-Dimethoxybiphenyl (5a).

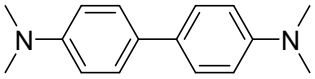
GC: t_R = 5.316 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.27 – 7.15 (m, 4H), 6.95 – 6.88 (m, 4H), 3.69 (s, 6H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 156.2 (2C), 130.6 (2C), 127.7 (2C), 127.0 (2C), 119.5 (2C), 110.3 (2C), 54.8 (2C).

Spectroscopic data were in accordance with literature data.[4]



6a

4,4'-di-*N*,*N*-Dimethylaminobiphenyl (6a).

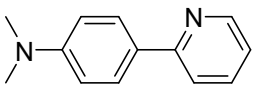
GC: t_R = 8.659 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.47 – 7.44 (m, 4H), 6.82 – 6.79 (m, 4H), 2.96 (s, 12H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 148.4 (2C), 129.1 (2C), 126.1 (4C), 112.3 (4C), 40.0 (4C).

Spectroscopic data were in accordance with literature data.[6]



6b

***N*,*N*-Dimethyl-4-(pyridin-2-yl)aniline (6b).**

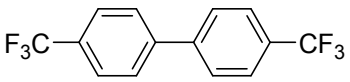
GC: t_R = 7.780 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.62 (d, *J* = 4.8 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.67 (q, *J* = 7.9 Hz, 2H), 7.16 – 7.07 (m, 1H), 6.84 – 6.76 (m, 2H), 3.02 (s, 6H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 157.5, 151.3, 149.2, 136.9, 127.9 (2C), 127.8, 120.8, 119.4, 112.4 (2C), 40.5 (2C).

Spectroscopic data were in accordance with literature data.[9]



7a

4,4'-Bis(trifluoromethyl)-1,1'-biphenyl (7a).

GC: t_R = 4.123 min.

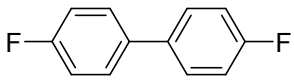
Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.75 – 7.69 (m, 8H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 143.4 (2C), 127.8 (8C), 126.1 (2C), 126.0 (2C).

^{19}F-NMR ($CDCl_3$, 282 MHz): -62.6.

Spectroscopic data were in accordance with literature data.[6]



8a

4,4'-Difluorobiphenyl (8a).

GC: t_R = 4.083 min.

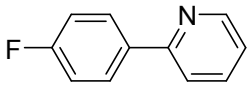
Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.50 – 7.44 (m, 4H), 7.14 – 7.05 (m, 4H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 161.6 (d, $J_{(C-F)}$ = 246.5 Hz, 2C), 135.6 (2C), 127.7 (d, $J_{(C-F)}$ = 8.0 Hz, 4C), 114.8 (d, $J_{(C-F)}$ = 21.5 Hz, 4C).

^{19}F-NMR ($CDCl_3$, 282 MHz): -116.8.

Spectroscopic data were in accordance with literature data.[2]



8b

2-(4-Fluorophenyl)pyridine (8b).

GC: t_R = 4.522 min.

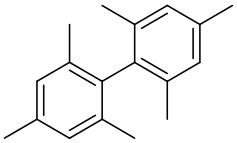
Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.69 (ddd, J = 4.9, 1.7, 0.9 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.81 – 7.74 (m, 1H), 7.70 (dt, J = 8.0, 1.0 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.12 (m, 2H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 165.0, 162.5, 156.4, 149.5, 137.4, 129.0, 128.9, 122.3, 120.6, 116.0, 115.8.

^{19}F-NMR ($CDCl_3$, 282 MHz): -112.7.

Spectroscopic data were in accordance with literature data.[10]



9a

2,2',4,4',6,6'-Hexamethylbiphenyl (9a).

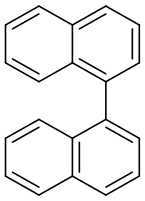
GC: t_R = 5.248 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 6.92 (s, 4H), 2.31 (s, 6H), 1.84 (s, 12H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 136.2 (2C), 135.2 (2C), 134.7 (4C), 127.3 (4C), 20.3 (2C), 18.9 (4C).

Spectroscopic data were in accordance with literature data.[7]



10a

1,1'-Binaphtyl (10a).

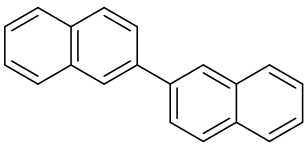
GC: t_R = 8.450 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.95 – 7.91 (m, 4H), 7.58 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 2H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 137.6 (2C), 132.7 (2C), 132.0 (2C), 127.3 (2C), 127.0 (2C), 127.0 (2C), 125.7 (2C), 125.1 (2C), 125.0 (2C), 124.5 (2C).

Spectroscopic data were in accordance with literature data.[2]



11a

2,2'-binaphtyl (11a).

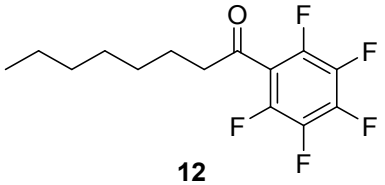
GC: t_R = 11.611 min.

Purification: Chromatography; Eluent: Petroleum ether/Ethyl acetate 15:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): 8.16 (s, 2H), 7.96 – 7.85 (m, 8H), 7.55 – 7.45 (m, 4H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 137.6 (2C), 132.9 (2C), 131.9 (2C), 127.7 (2C), 127.4 (2C), 126.8 (2C), 125.5 (2C), 125.3 (2C), 125.2 (2C), 124.9 (2C).

Spectroscopic data were in accordance with literature data.[5]



12

1-(Pentafluorophenyl)-octan-1-one (12).

Bp: 109 °C/0.11 Torr.

GC: t_R = 4.514 min.

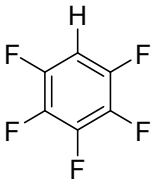
Purification: Chromatography; Eluent: Petroleum ether/Dichloromethane 90:10, then Kugelrohr distillation: 100 °C/10^{-2} Torr.

^{1}H-NMR ($CDCl_3$, 300 MHz): 2.83 (t, *J* = 7.3 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.34 – 1.26 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 193.5 (1C), 144.0 (dm, $J_{(C-F)}$ = 253.0 Hz, 2C), 142.5 (dm, $J_{(C-F)}$ = 258.4 Hz, 1C), 137.6 (dm, $J_{(C-F)}$ = 251.7 Hz, 2C), 114.5 (t, $J_{(C-F)}$ = 18.8 Hz, 1C), 44.3, 30.7, 28.1, 27.1, 22.7, 21.7, 13.1.

^{19}F-NMR ($CDCl_3$, 282 MHz): -142.4 (d, *J* = 16.5 Hz, 2F), -151.1 (t, *J* = 20.7 Hz, 1F), -161.1 (m, 2F).

Spectroscopic data were in accordance with literature data.[8]



13

Pentafluorobenzene (13).

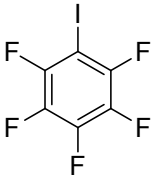
GC: t_R = 0.338 min.

^{1}H-NMR ($CDCl_3$, 300 MHz): 6.95 – 6.83 (m, 1H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 145.4 (dm, $J_{(C-F)}$ = 248.8 Hz, 2C), 141.1 (dm, $J_{(C-F)}$ = 254.1 Hz, 1C), 136.8 (dm, $J_{(C-F)}$ = 251.5 Hz, 2C), 99.9 (td, $J_{(C-F)}$ = 22.9, 3.1 Hz, 1C).

^{19}F-NMR ($CDCl_3$, 282 MHz): -139.4 – -139.6 (m, 2F), -154.4 – -154.5 (m, 1F), -162.8 – -163.0 (m, 2F).

Spectroscopic data were in accordance with literature data.[11]



14

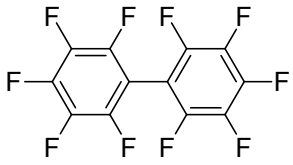
Iodopentafluorobenzene (14).

GC: t_R = 2.045 min.

^{13}C-NMR ($CDCl_3$, 75 MHz): 146.4 (dm, $J_{(C-F)}$ = 239.5 Hz, 2C), 140.8 (dm, $J_{(C-F)}$ = 255.6 Hz, 1C), 136.3 (dm, $J_{(C-F)}$ = 257.5 Hz, 2C), 65.1 (t, $J_{(C-F)}$ = 28.4 Hz, 1C).

^{19}F-NMR ($CDCl_3$, 282 MHz): -120.0 (d, J = 21.1 Hz, 2F), -153.0 (t, J = 20.0 Hz, 1F), -160.2 (m, 2F).

Spectroscopic data were in accordance with literature data.[12]



16

Decafluorobiphenyl (15).

GC: t_R = 2.733 min.

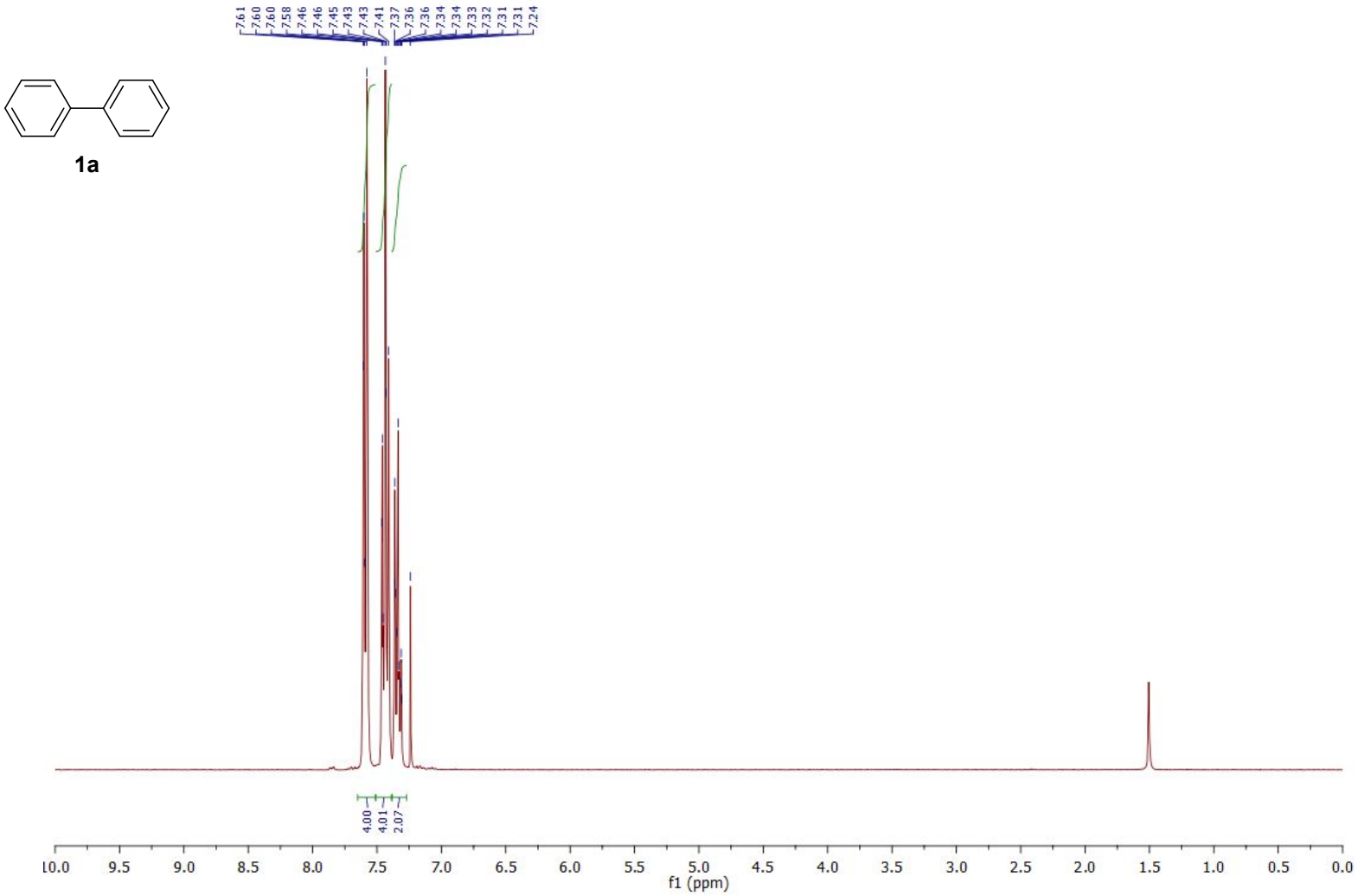
^{13}C-NMR ($CDCl_3$, 75 MHz): 143.8 (dm, $J_{(C-F)}$ = 247.2 Hz, 4C), 141.8 (dm, $J_{(C-F)}$ = 258.1 Hz, 2C), 137.2 (dm, $J_{(C-F)}$ = 253.9 Hz, 4C), 100.7 (2C).

^{19}F-NMR ($CDCl_3$, 282 MHz): -138.3 – -138.9 (m, 4F), -150.8 – -151.2 (m, 2F), -161.3 – -161.8 (m, 4F).

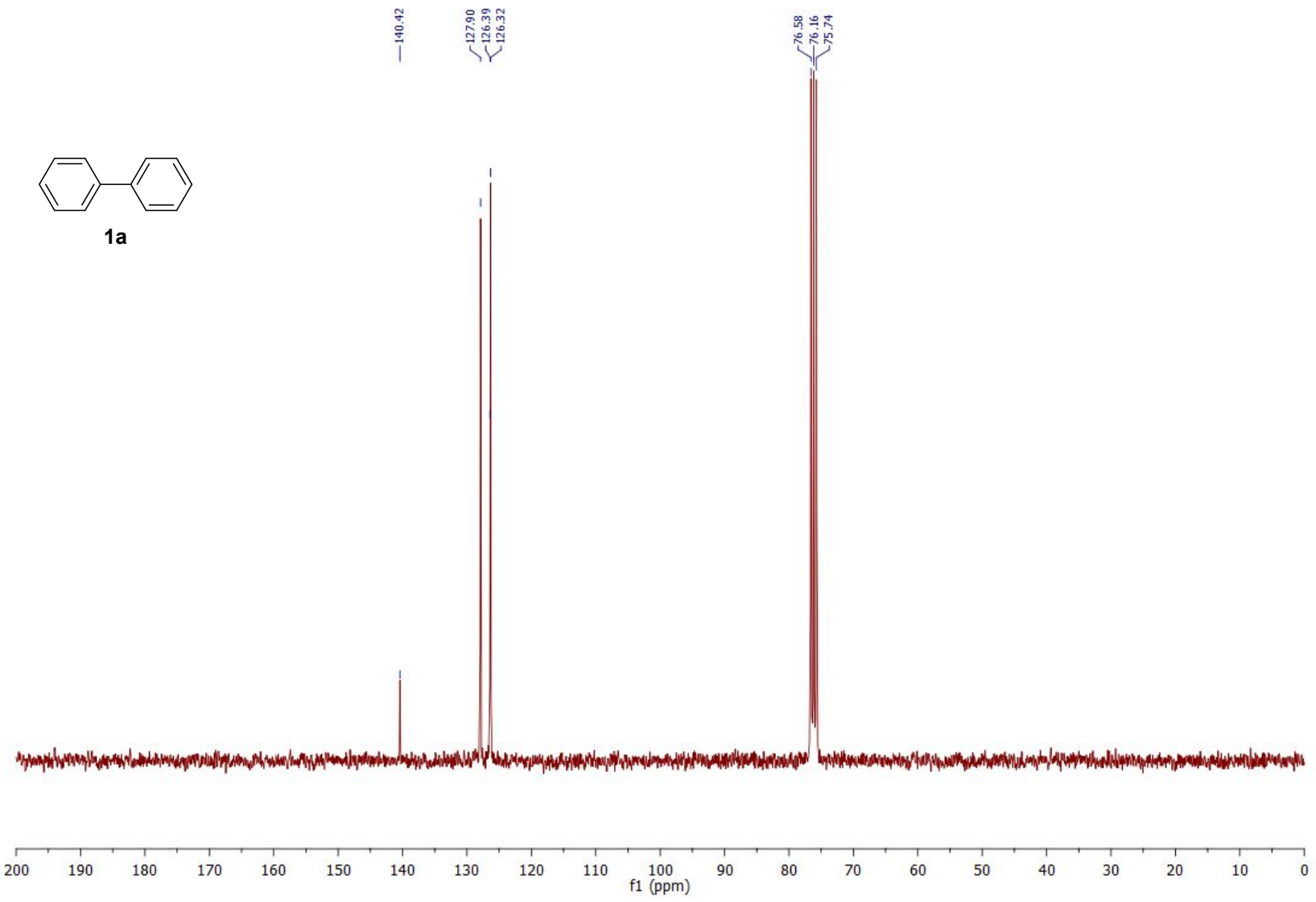
Spectroscopic data were in accordance with literature data.[13]

4. ^{1}H,^{13}C and ^{19}F NMR Spectra

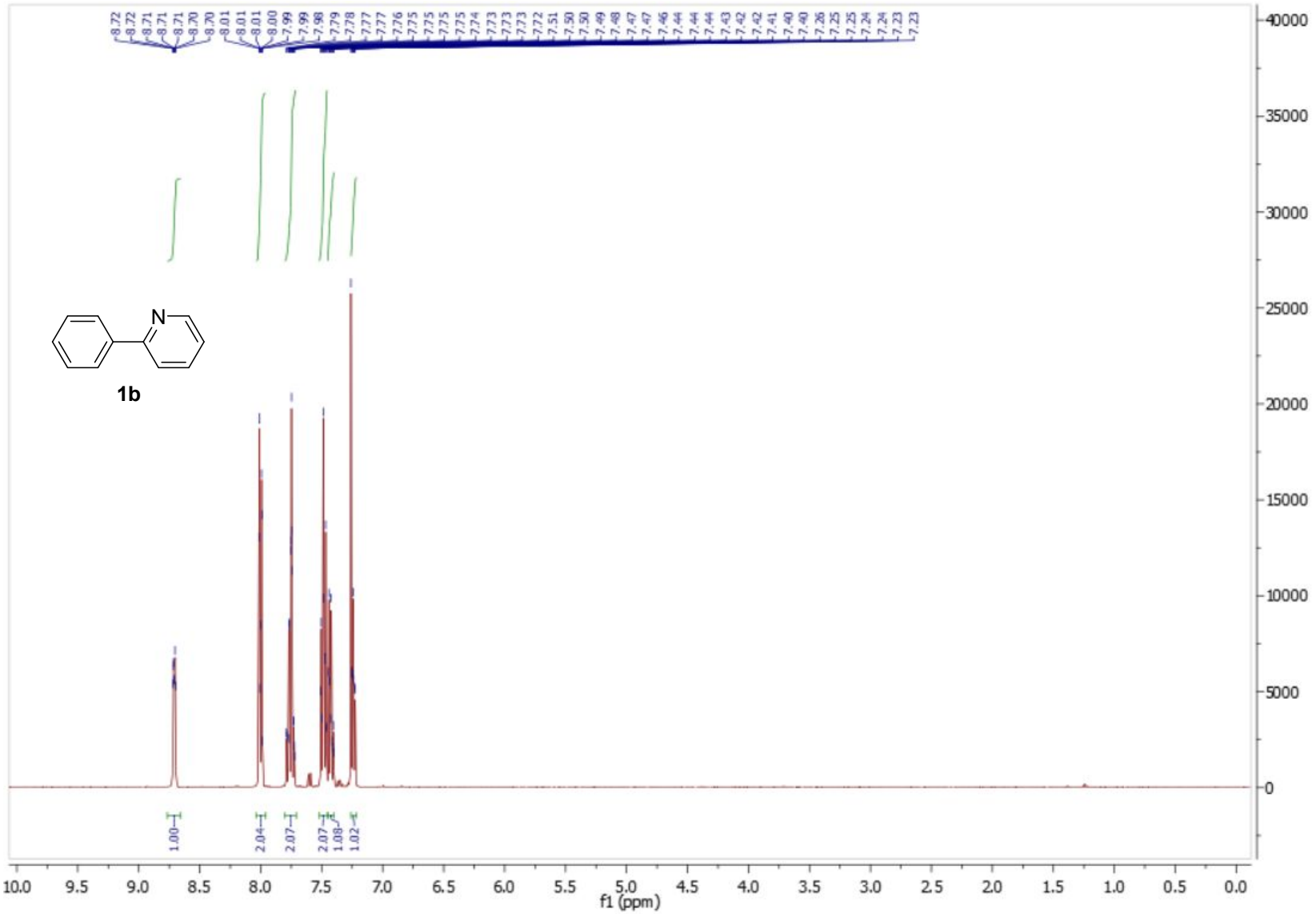
^{1}H-NMR spectrum: **Biphenyl (1a)**



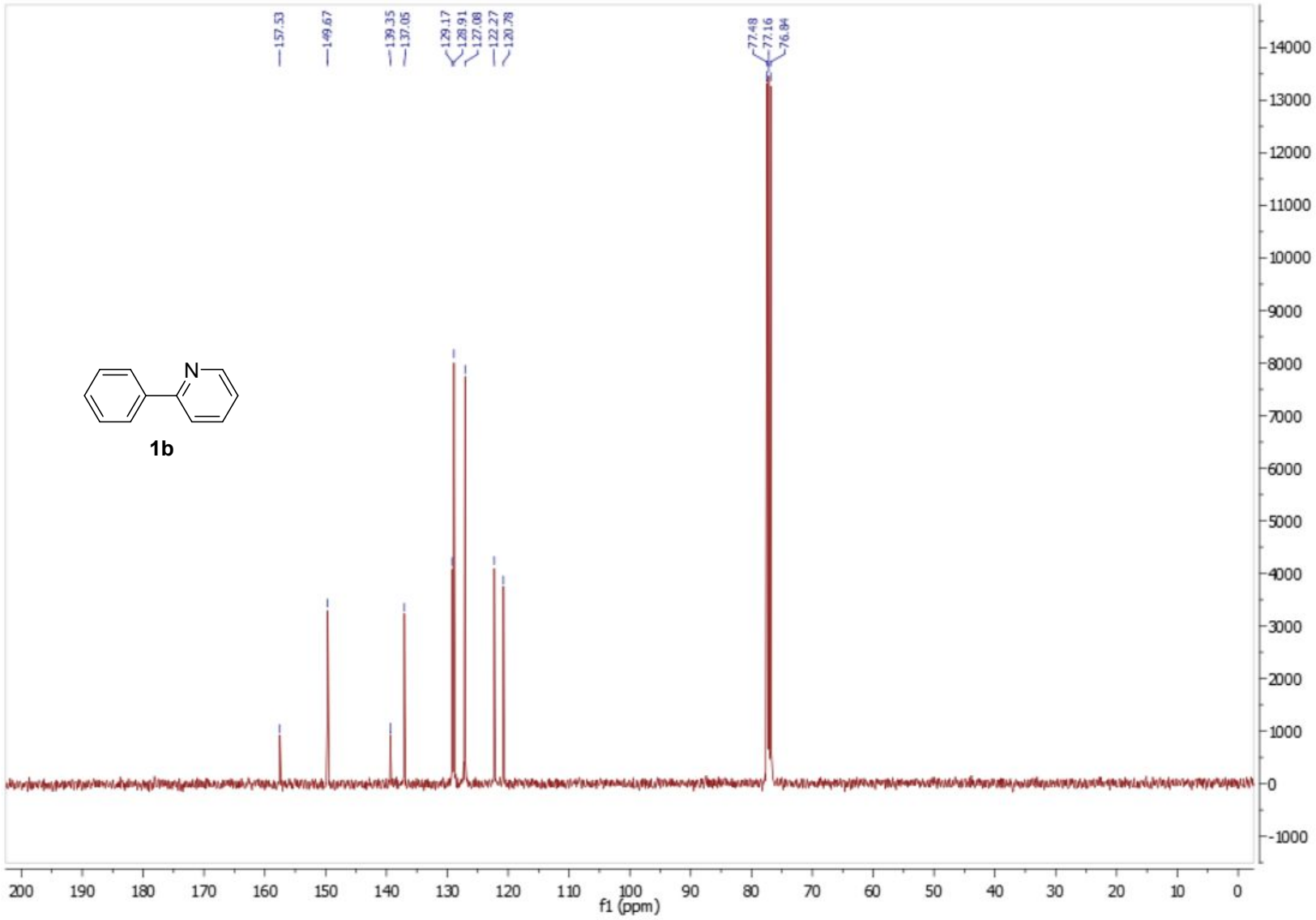
^{13}C-NMR spectrum: **Biphenyl (1a)**



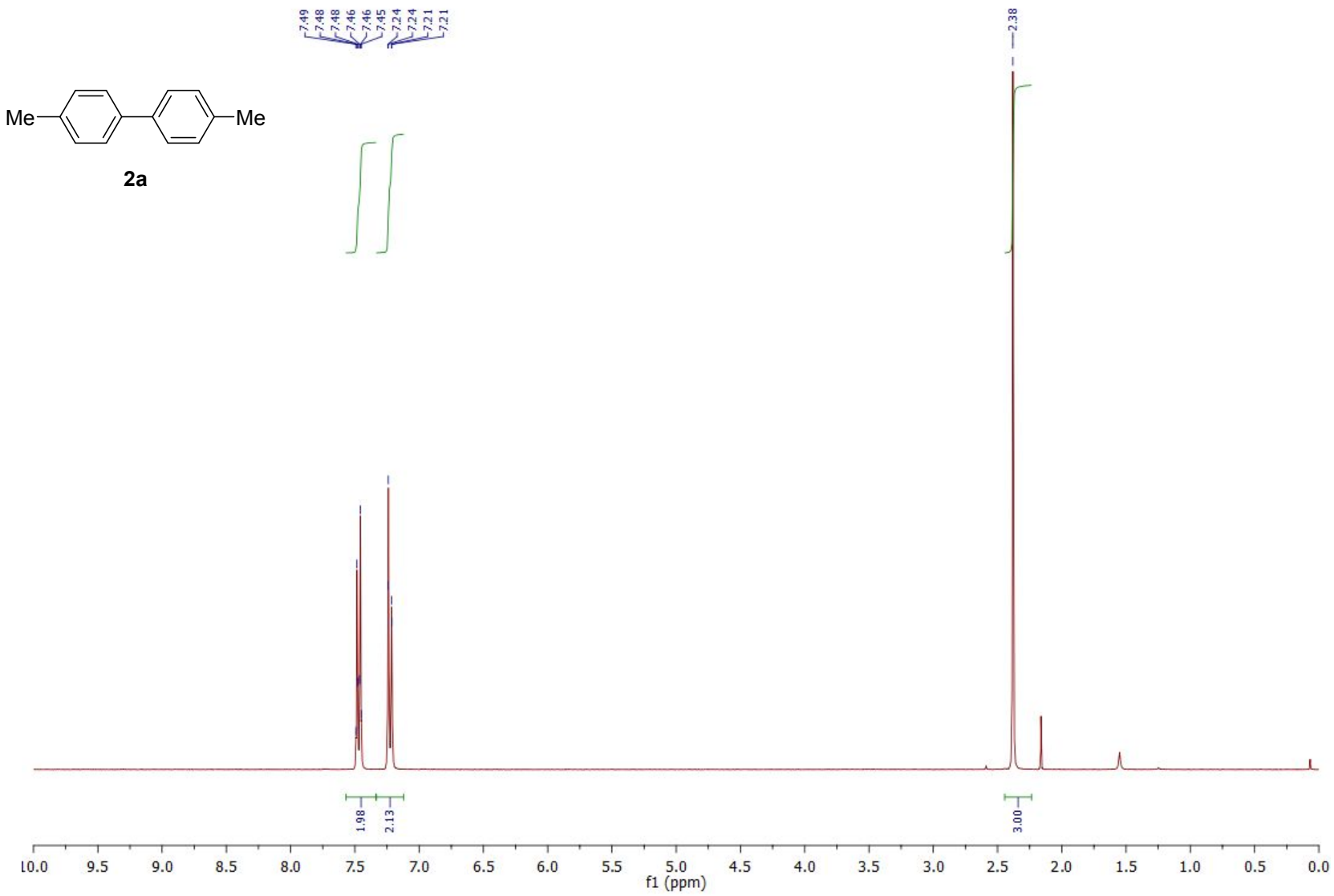
^{1}H-NMR spectrum: **2-Phenylpyridine (1b)**



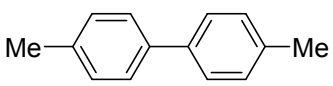
^{13}C-NMR spectrum: **2-Phenylpyridine (1b)**



^{1}H-NMR spectrum: **4,4'-Dimethylbiphenyl (2a)**

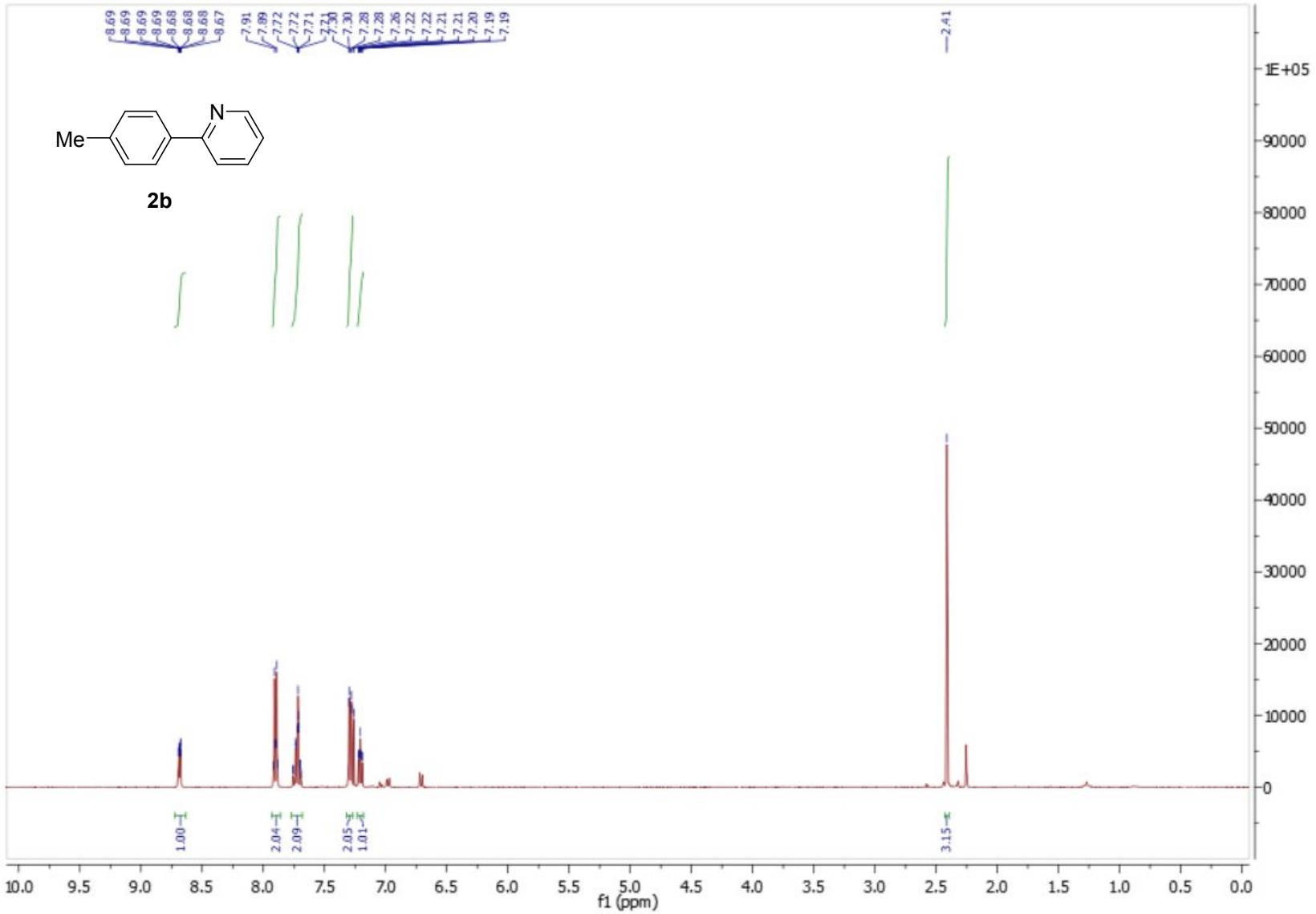


^{13}C-NMR spectrum**: 4,4'-Dimethylbiphenyl (2a)**

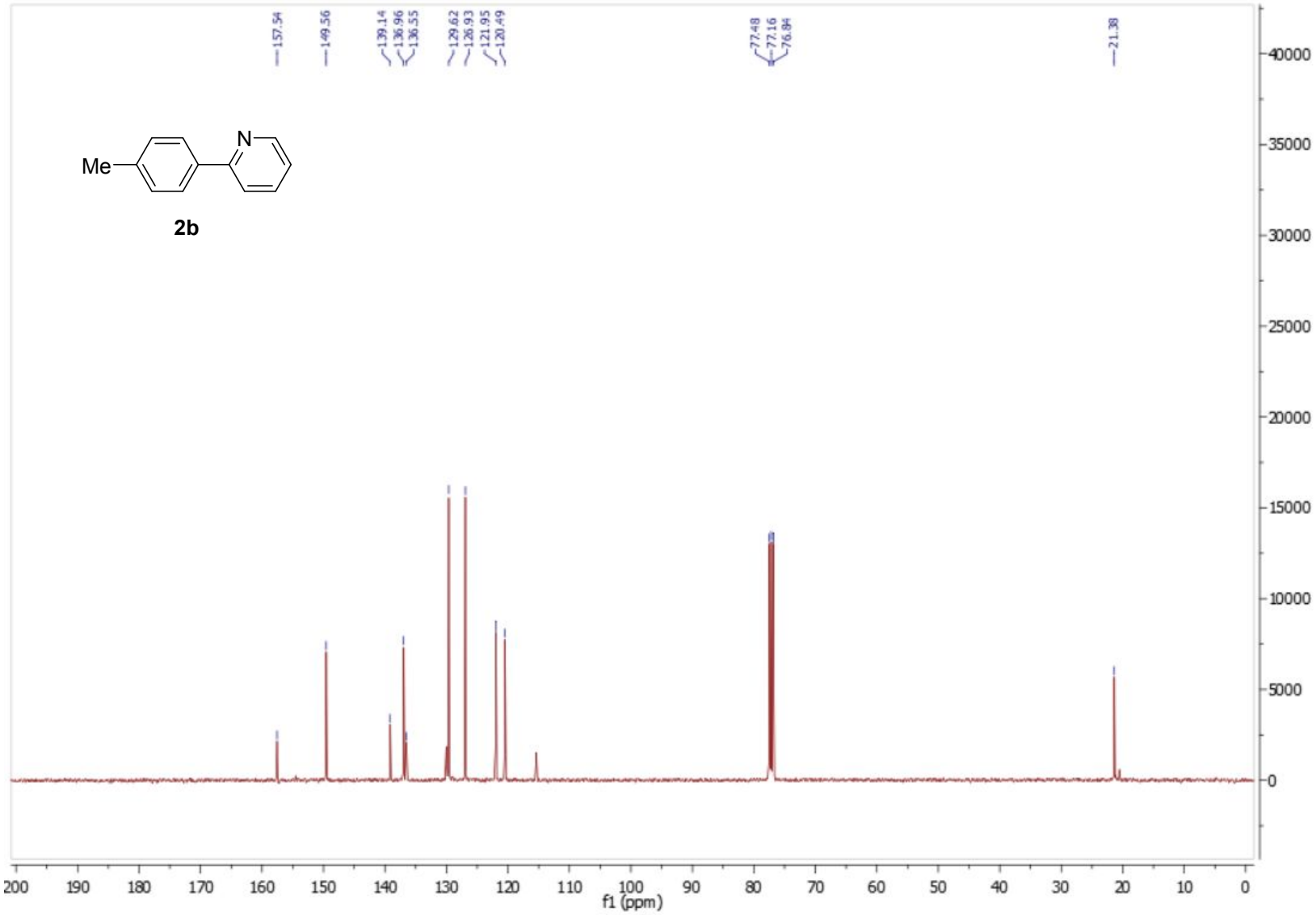


2a

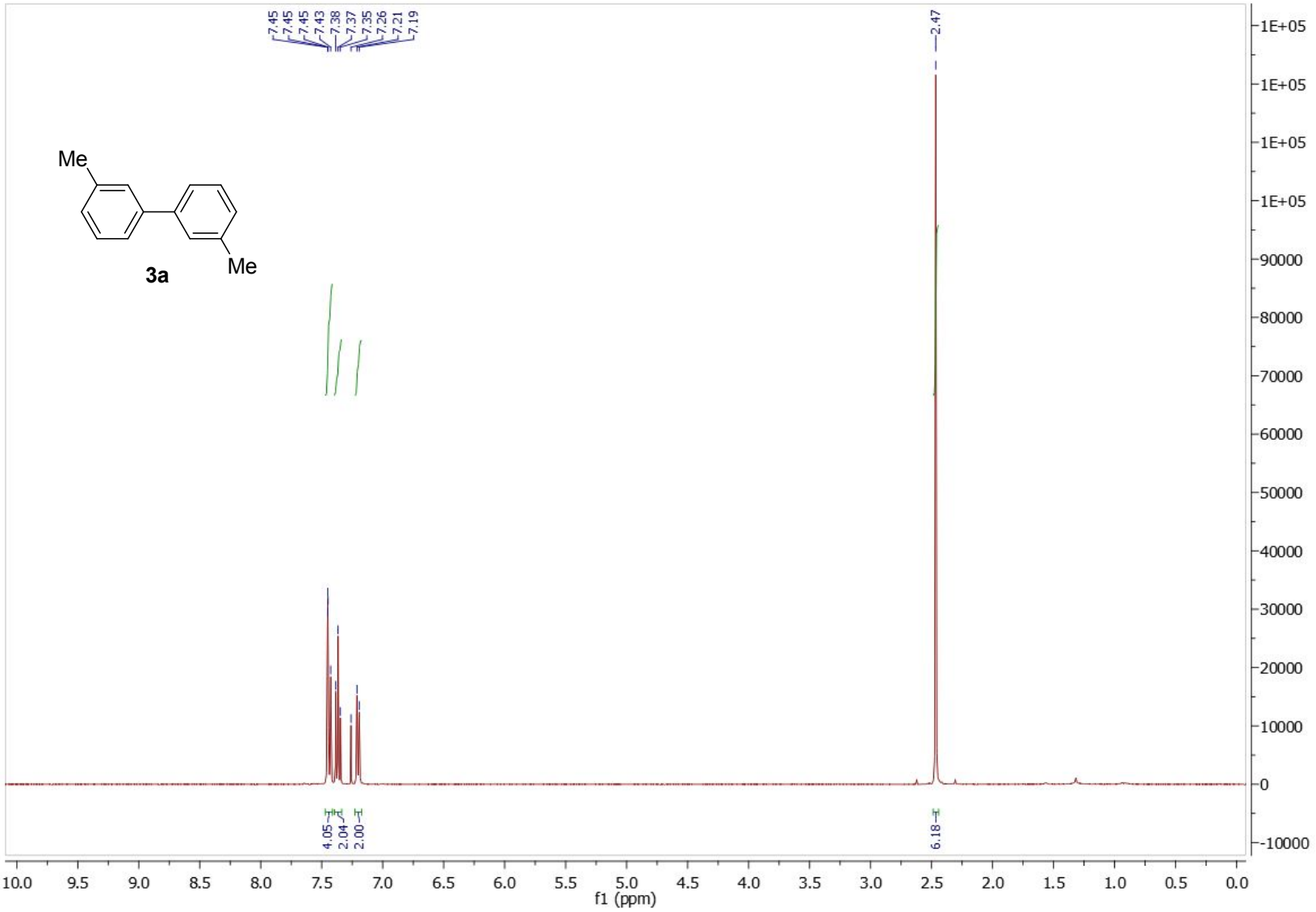
[1]H-NMR spectrum: **2-(*p*-Tolyl)pyridine (2b)**



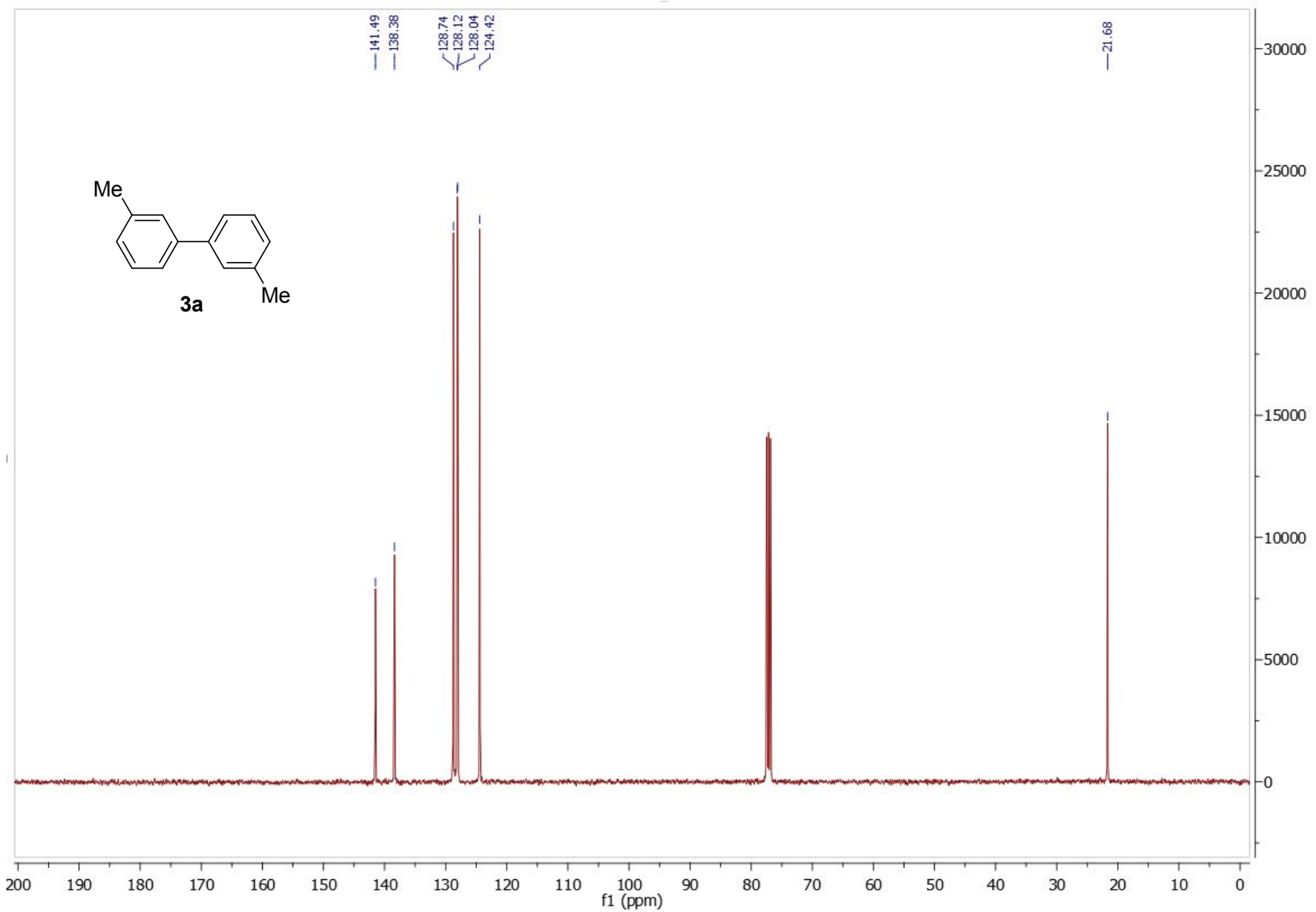
^{13}C-NMR spectrum**: 2-(*p*-Tolyl)pyridine (2b)**



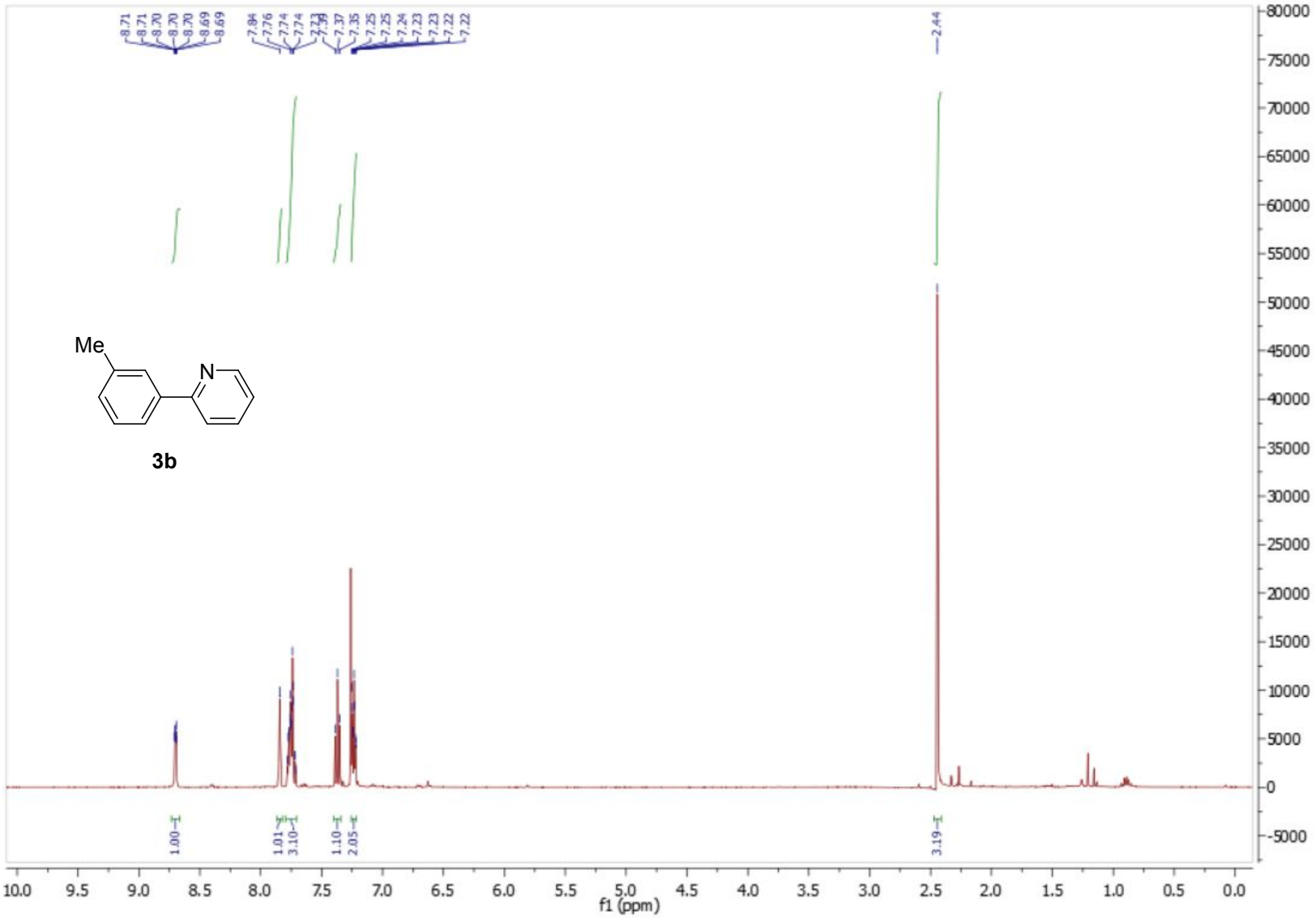
[1]H-NMR spectrum: **3,3'-Dimethyl-1,1'-biphenyl (3a)**



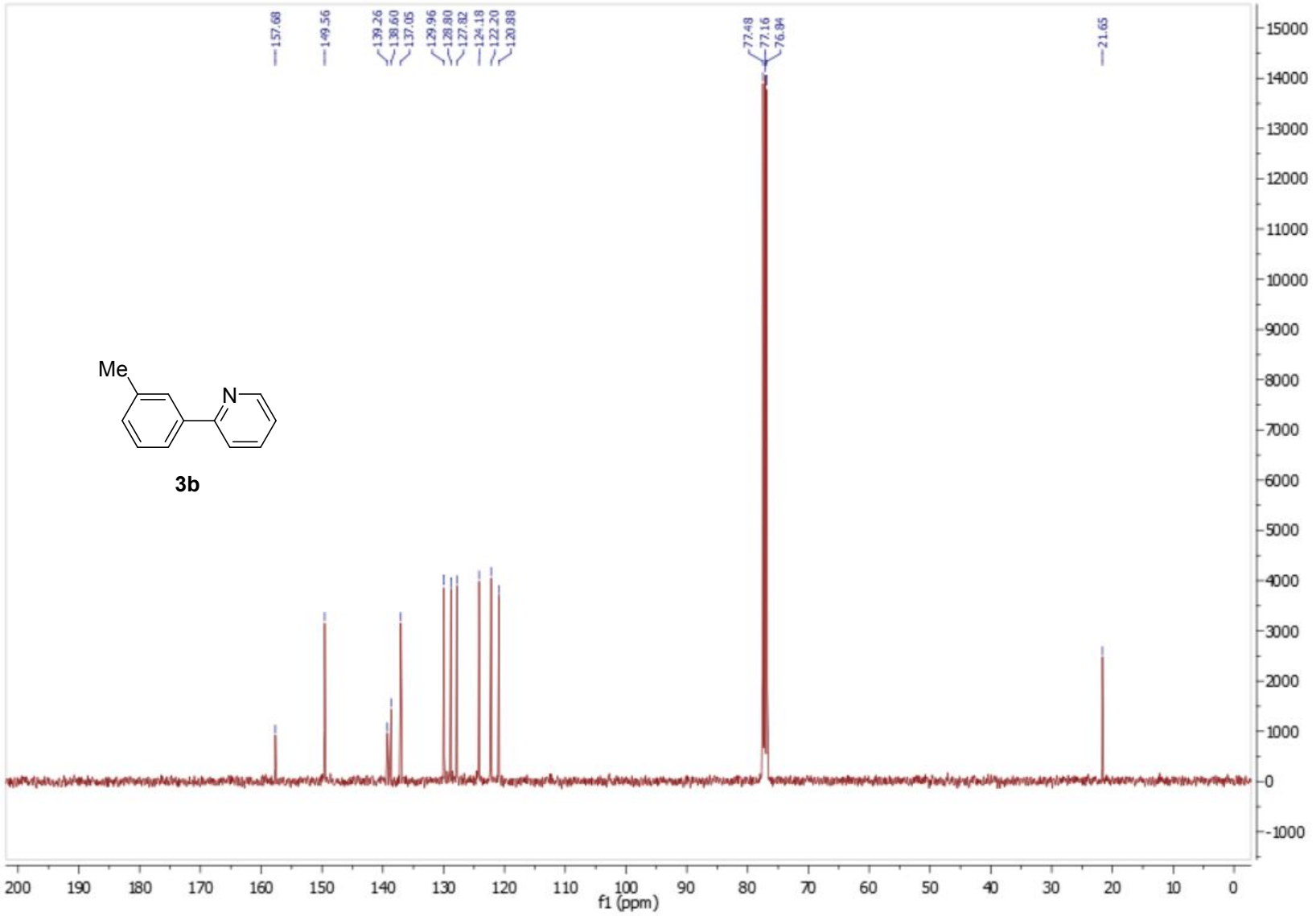
^{13}C-NMR spectrum: **3,3'-Dimethyl-1,1'-biphenyl (3a)**



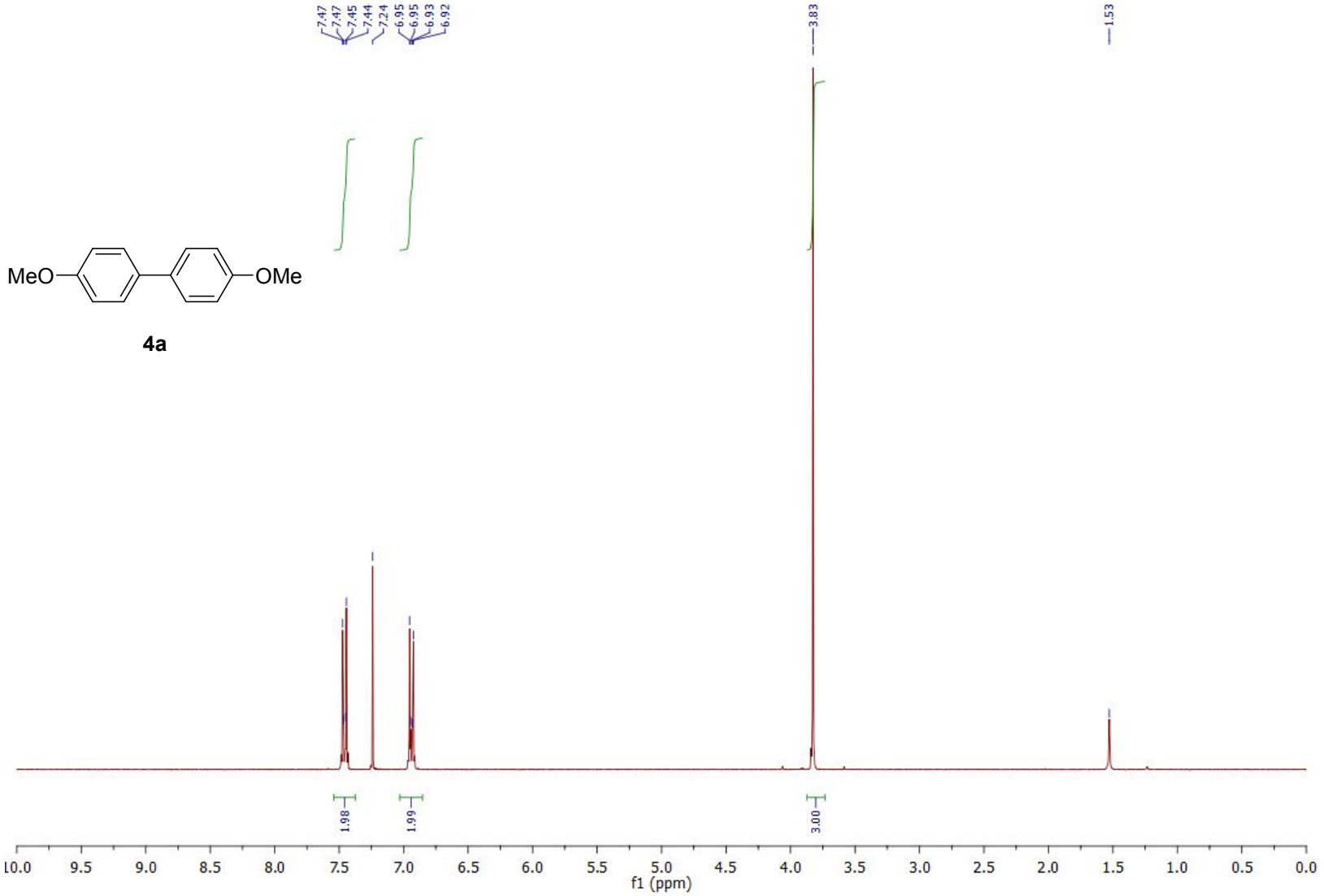
^{1}H-NMR spectrum: **2-(*m*-Tolyl)pyridine (3b)**



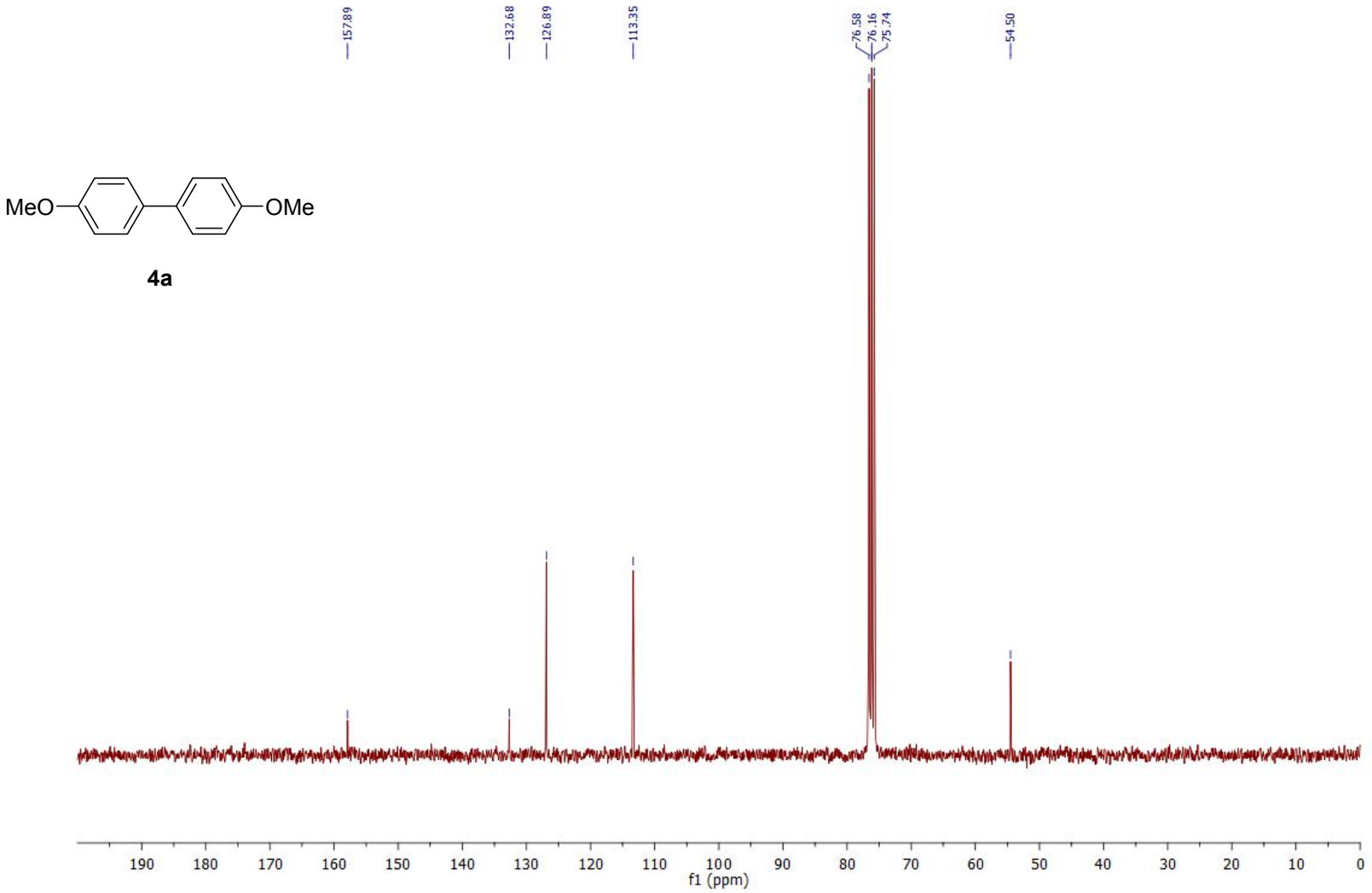
^{13}C-NMR spectrum**: 2-(*m*-Tolyl)pyridine (3b)**



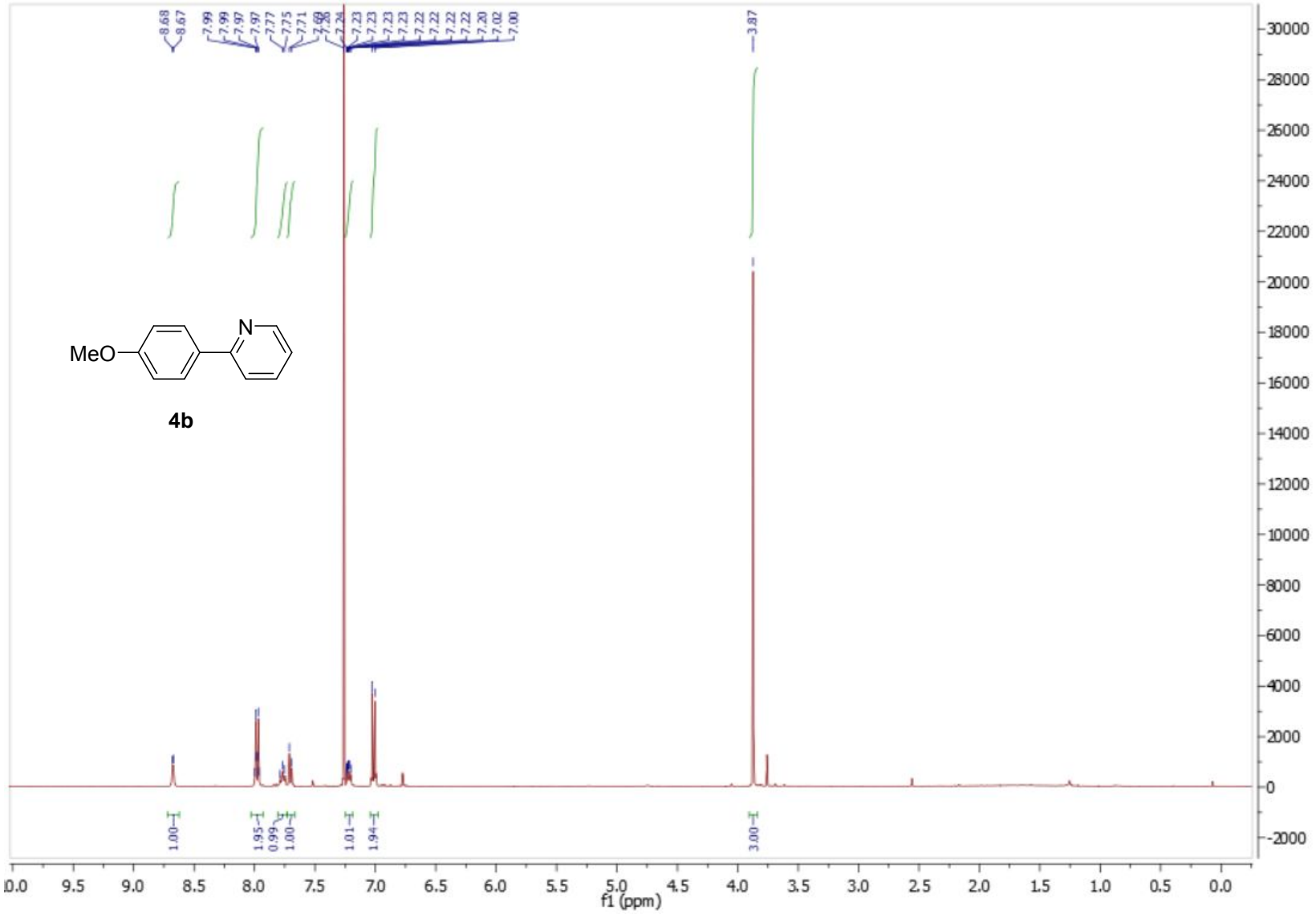
^{1}H-NMR spectrum: **4,4'-Dimethoxybiphenyl (4a)**



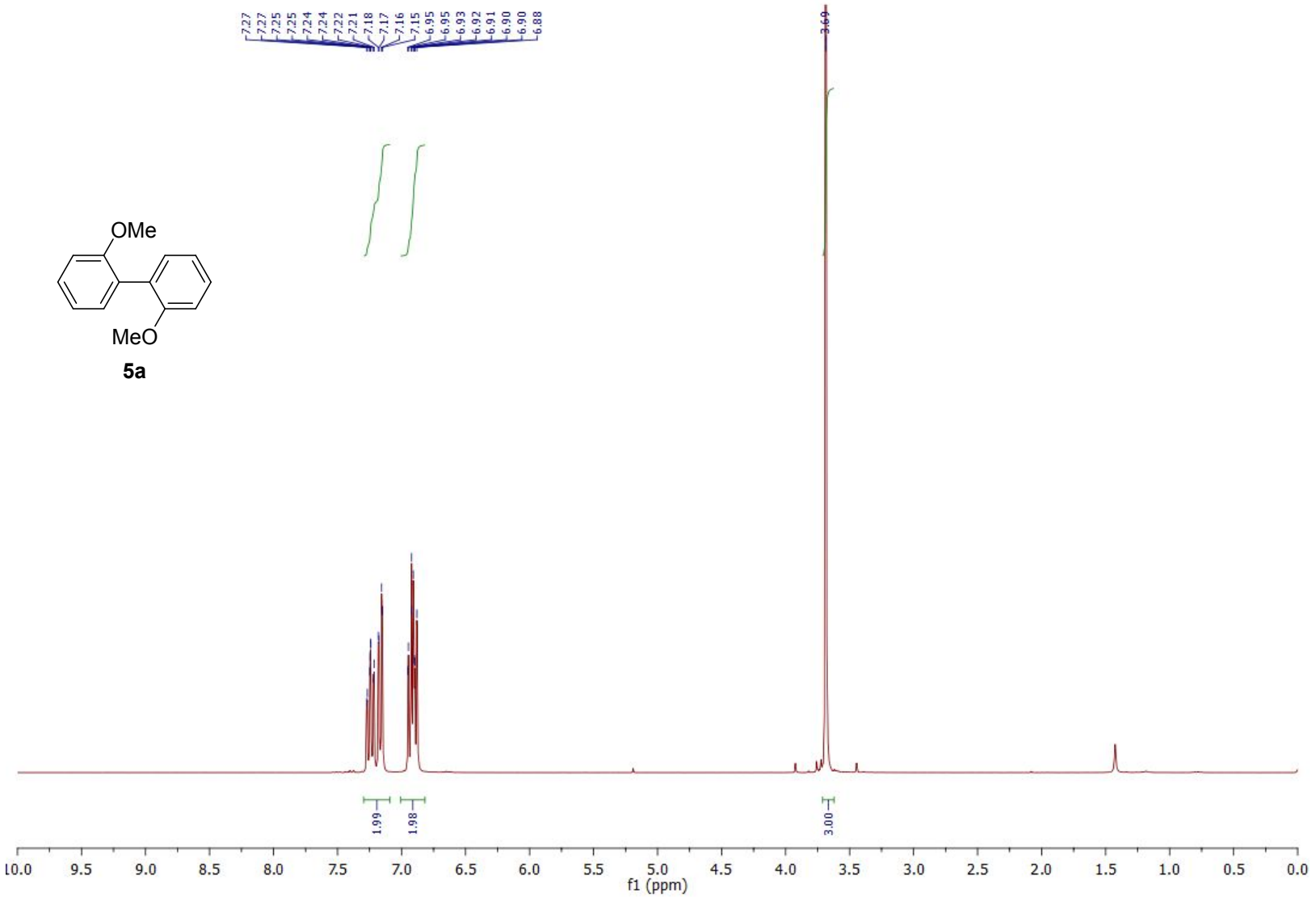
^{13}C-NMR spectrum: **4,4'-Dimethoxybiphenyl (4a)**



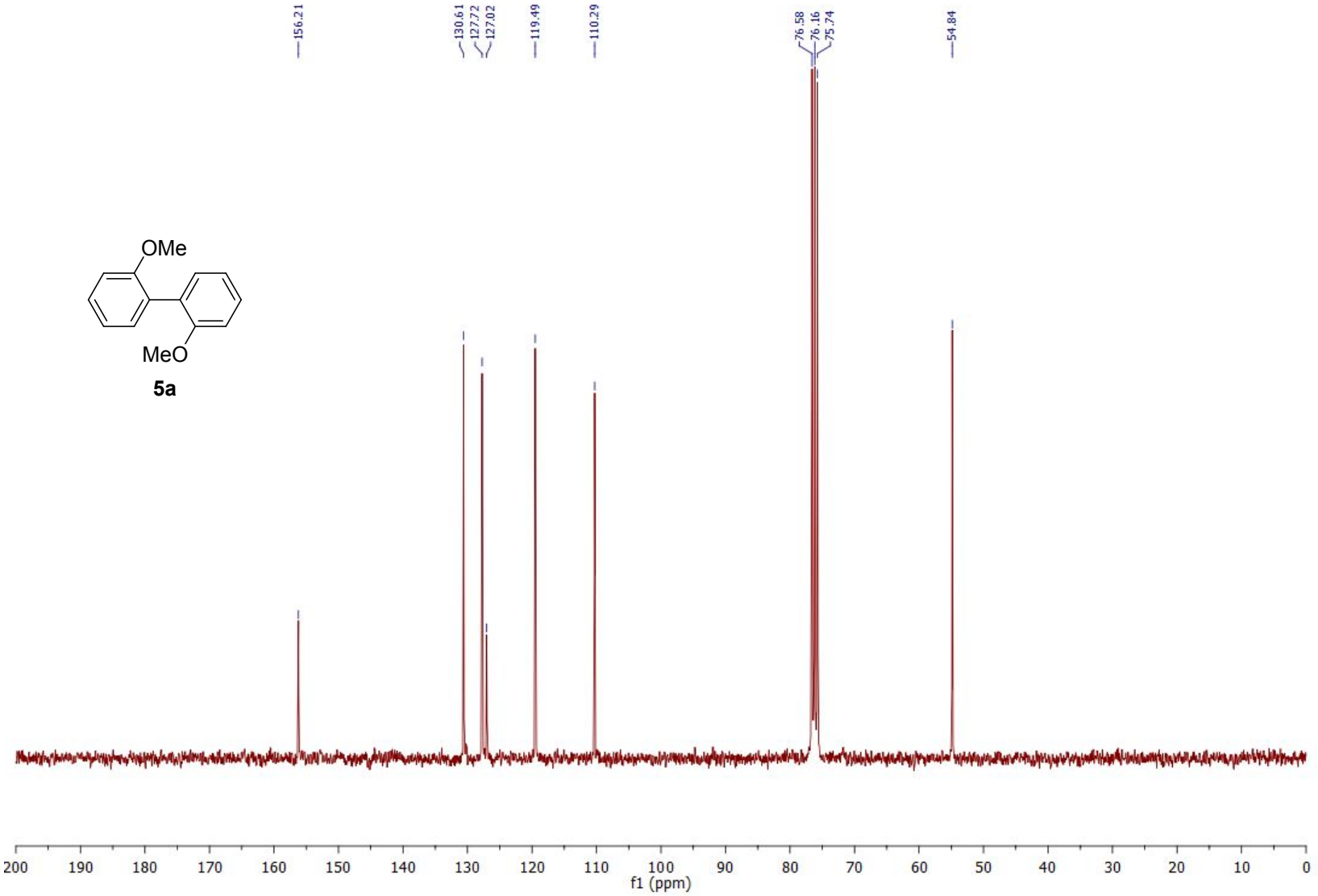
[1]H-NMR spectrum: **2-(4-Methoxyphenyl)pyridine (4b)**



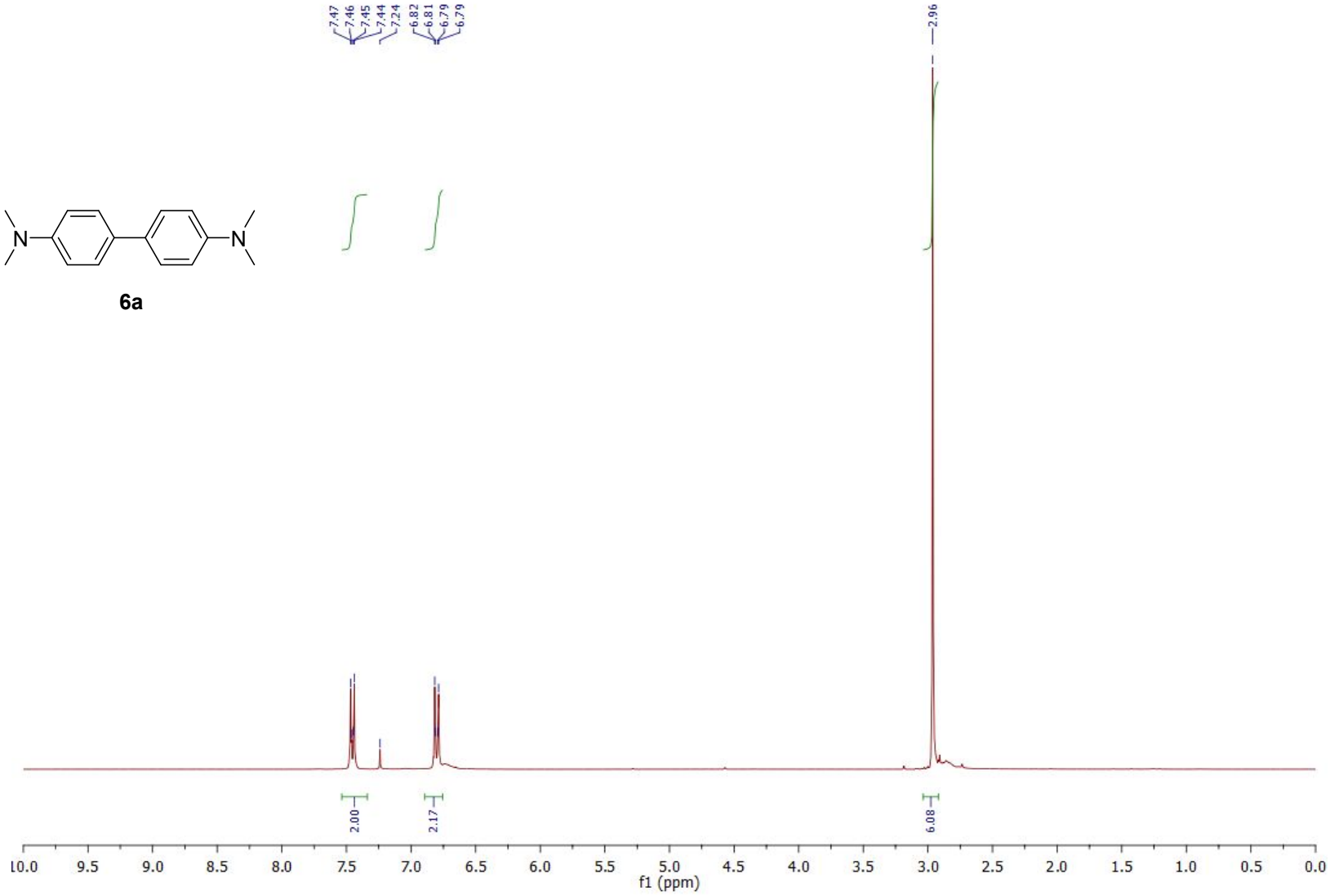
^{1}H-NMR spectrum: **2,2'-Dimethoxybiphenyl (5a)**



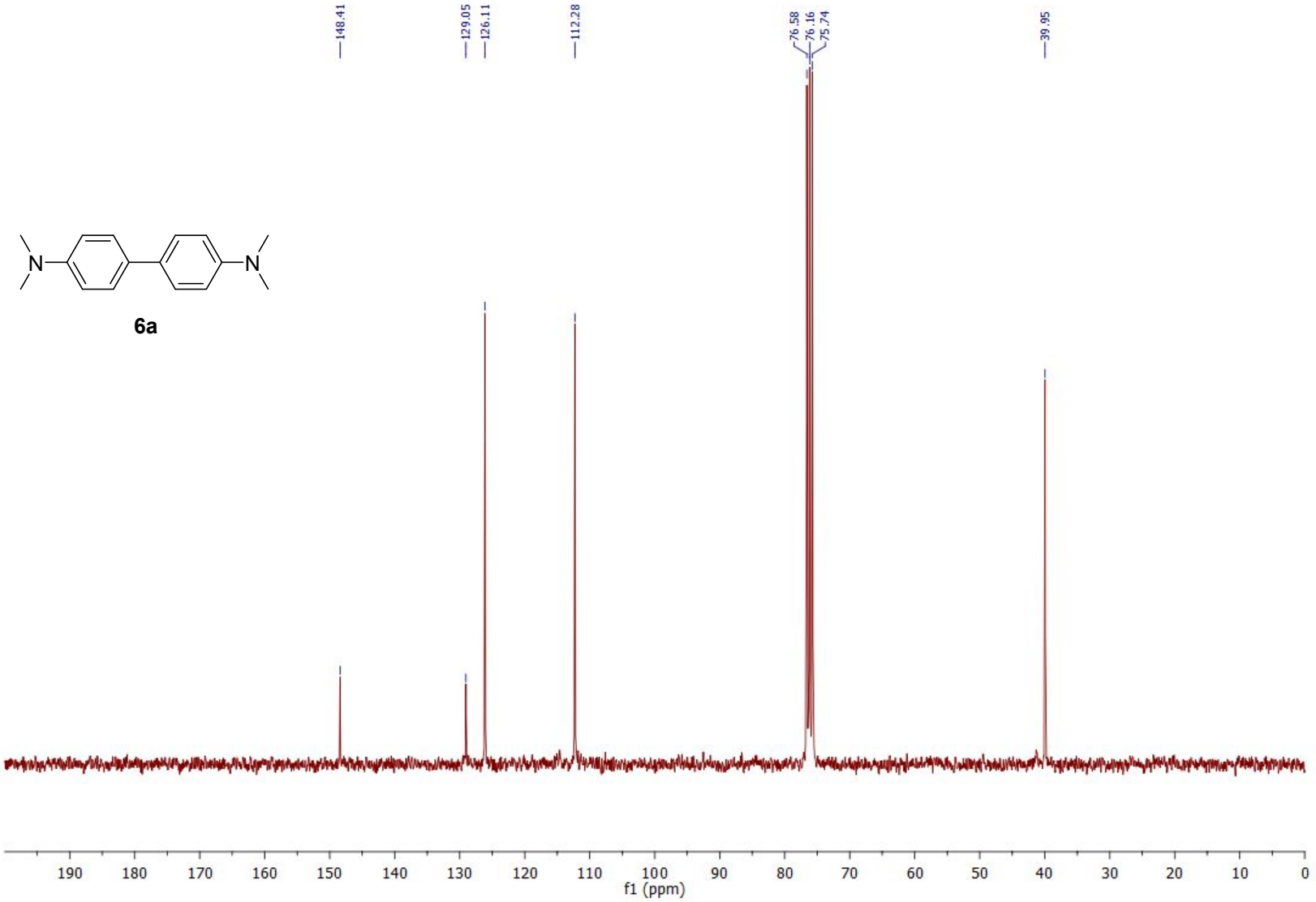
^{13}C-NMR spectrum: **2,2'-Dimethoxybiphenyl (5a)**



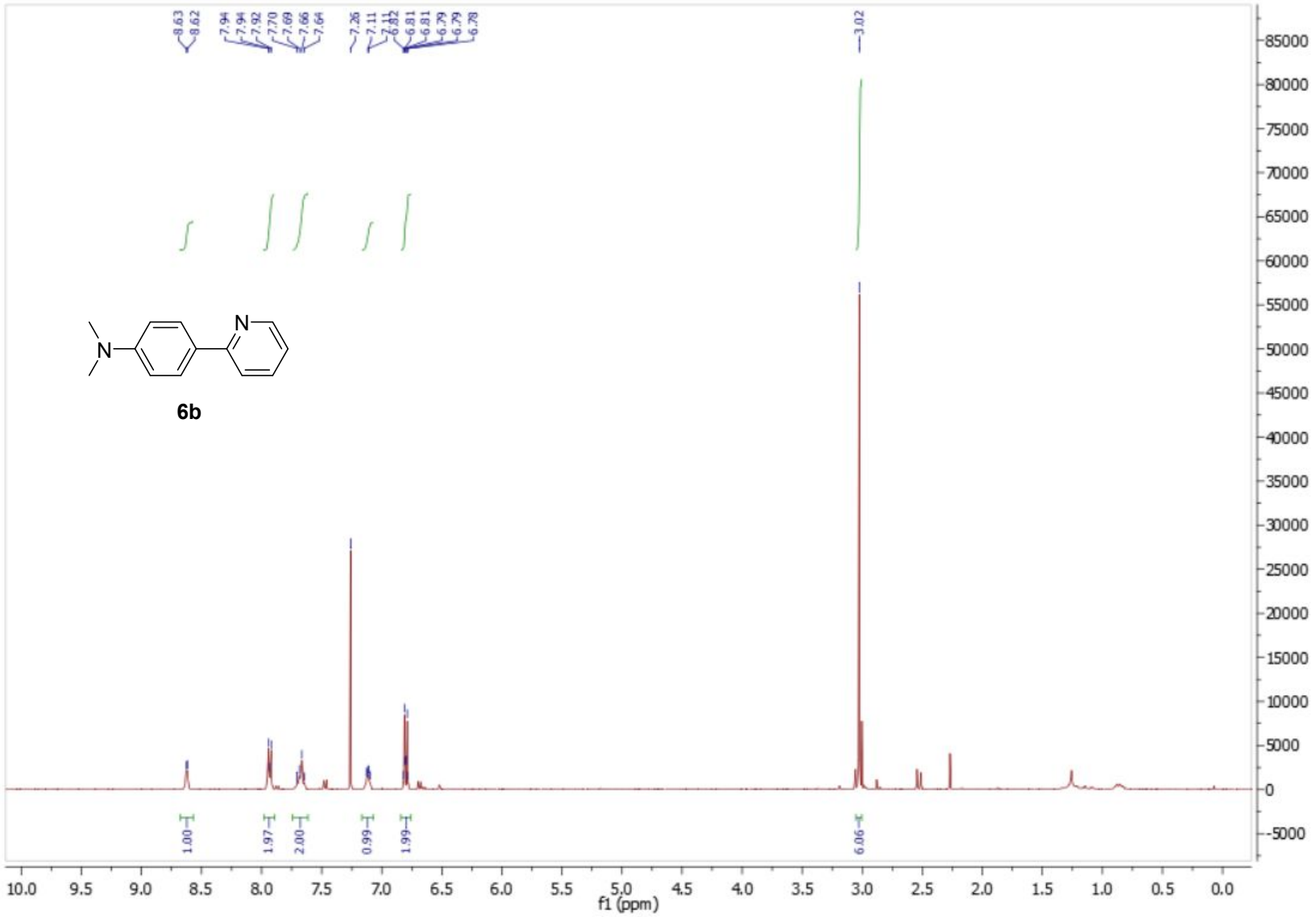
[1]H-NMR spectrum: **4,4'-di-*N*,*N*-Dimethylaminobiphenyl (6a)**



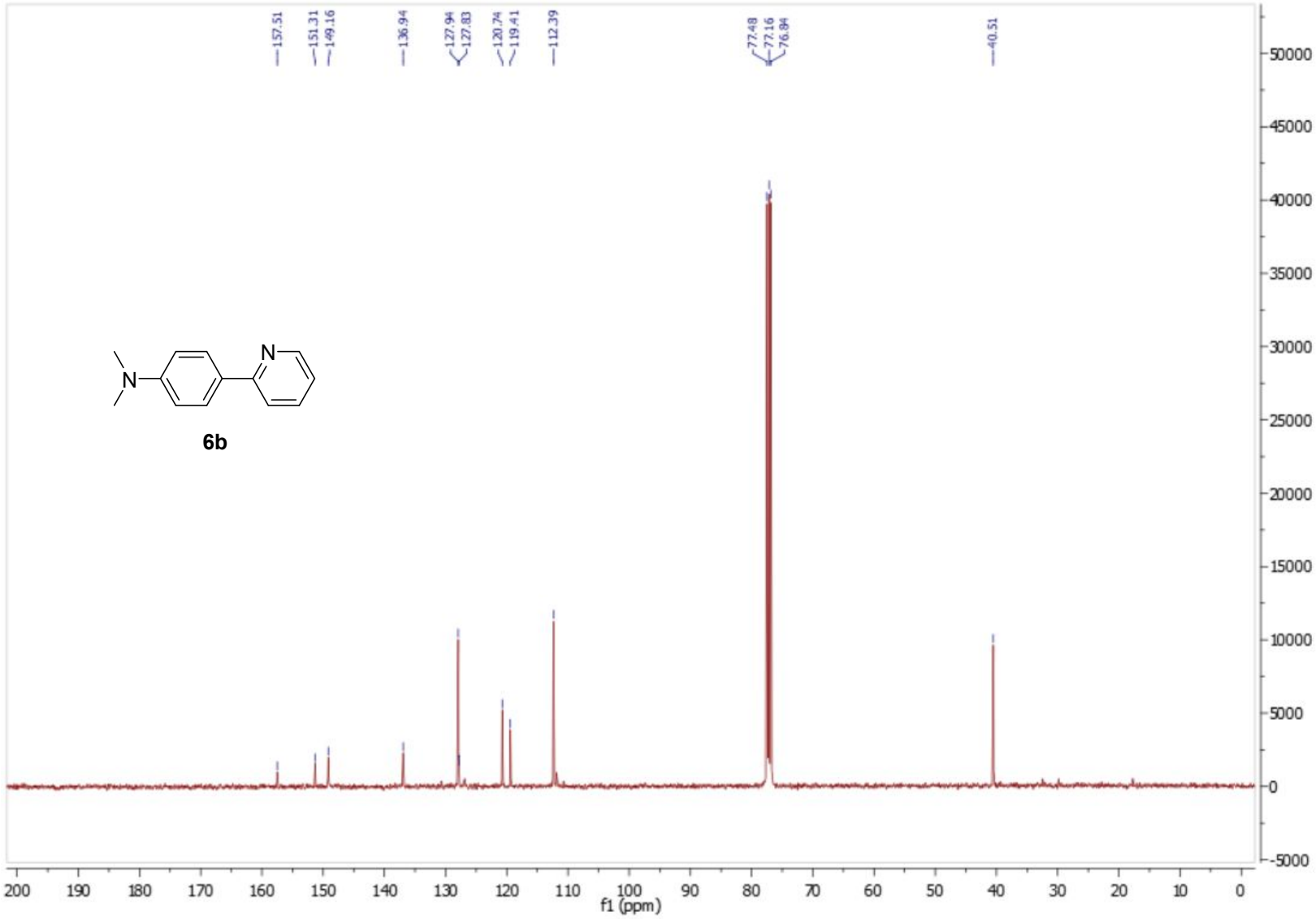
^{13}C-NMR spectrum: **4,4'-di-*N*,*N*-Dimethylaminobiphenyl (6a)**



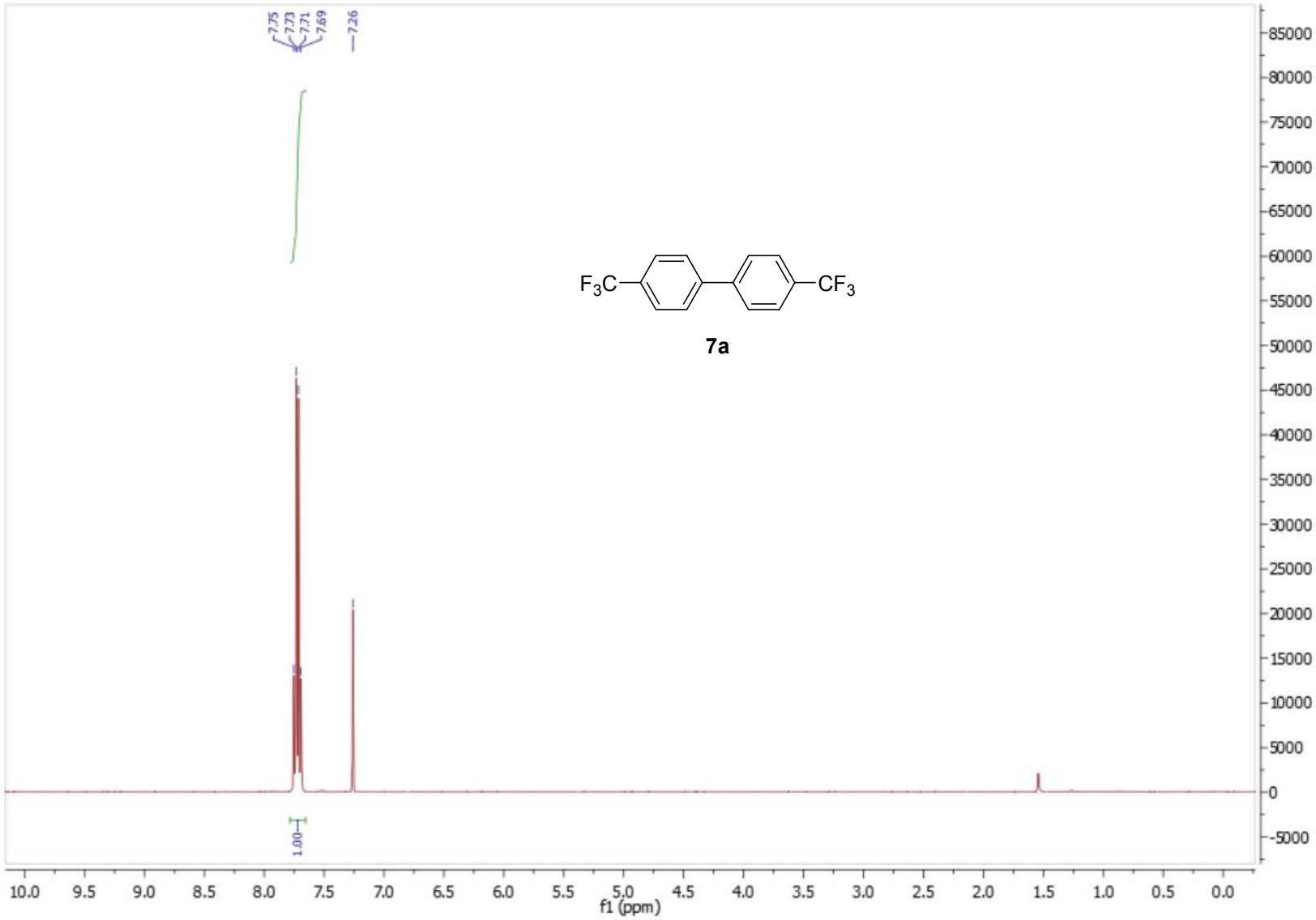
^{1}H-NMR spectrum: ***N,N*-Dimethyl-4-(pyridin-2-yl)aniline (6b)**



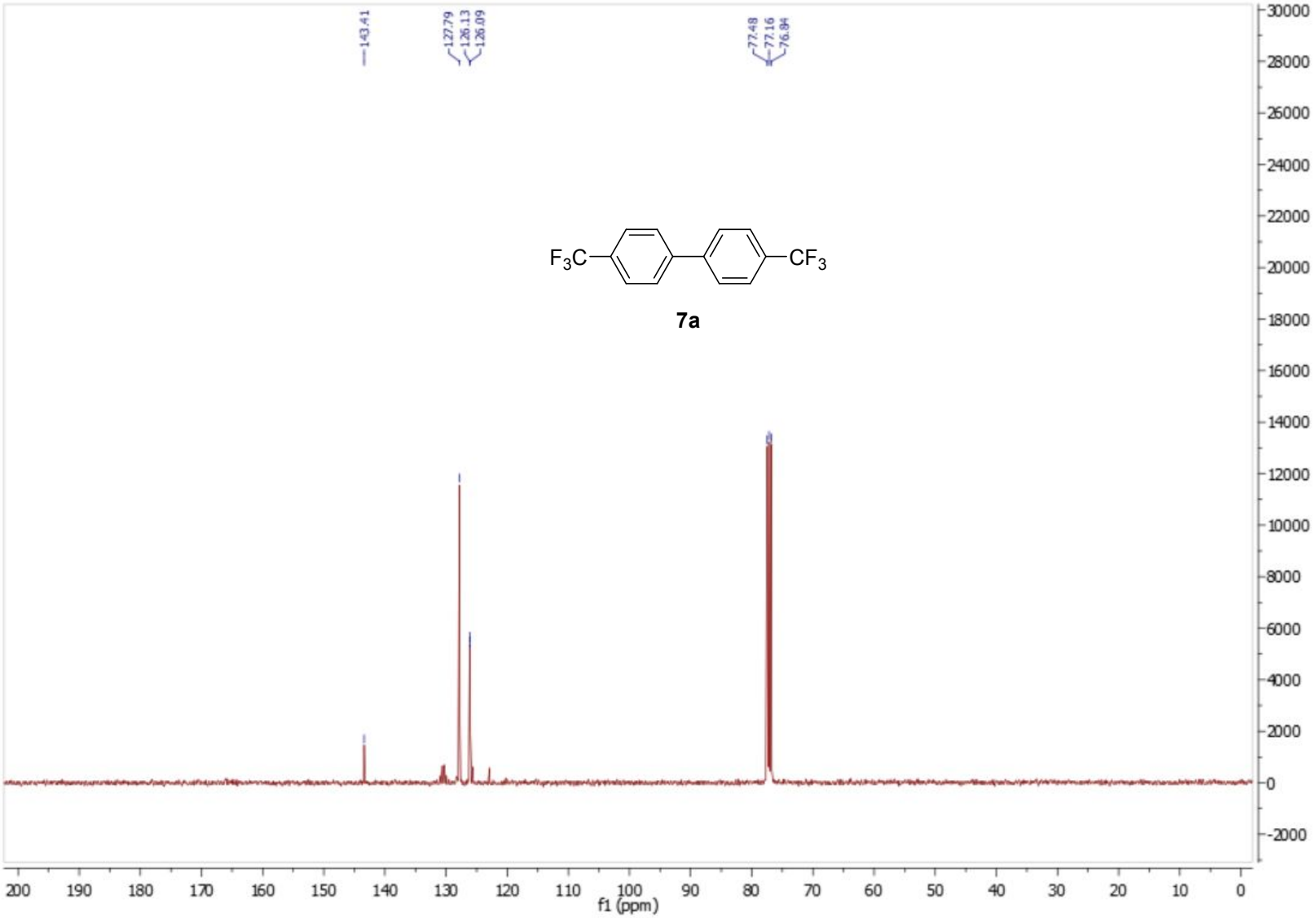
^{13}C-NMR spectrum: ***N*,*N*-Dimethyl-4-(pyridin-2-yl)aniline (6b)**



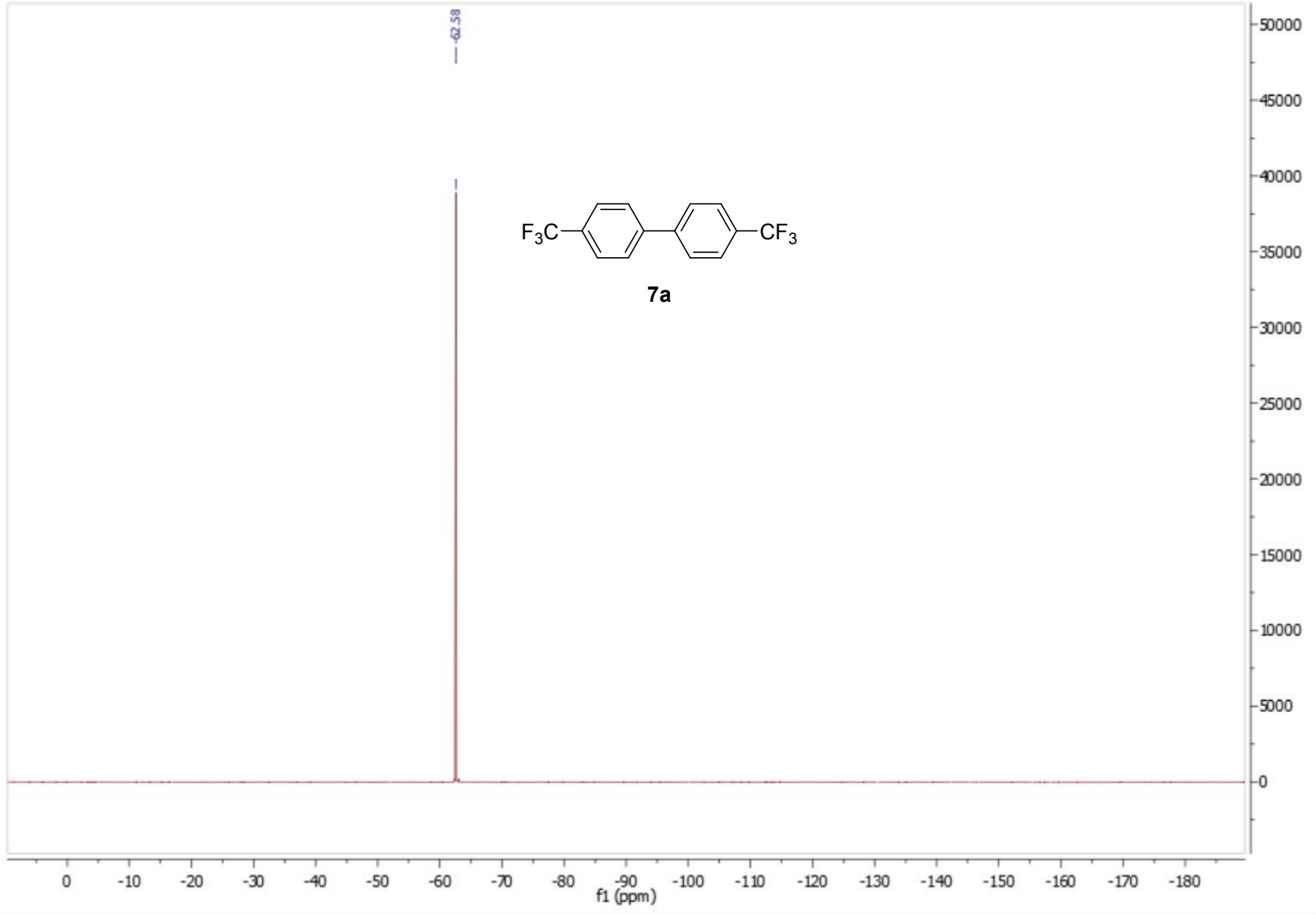
^{1}H-NMR spectrum: **4,4'-Bis(trifluoromethyl)-1,1'-biphenyl (7a)**



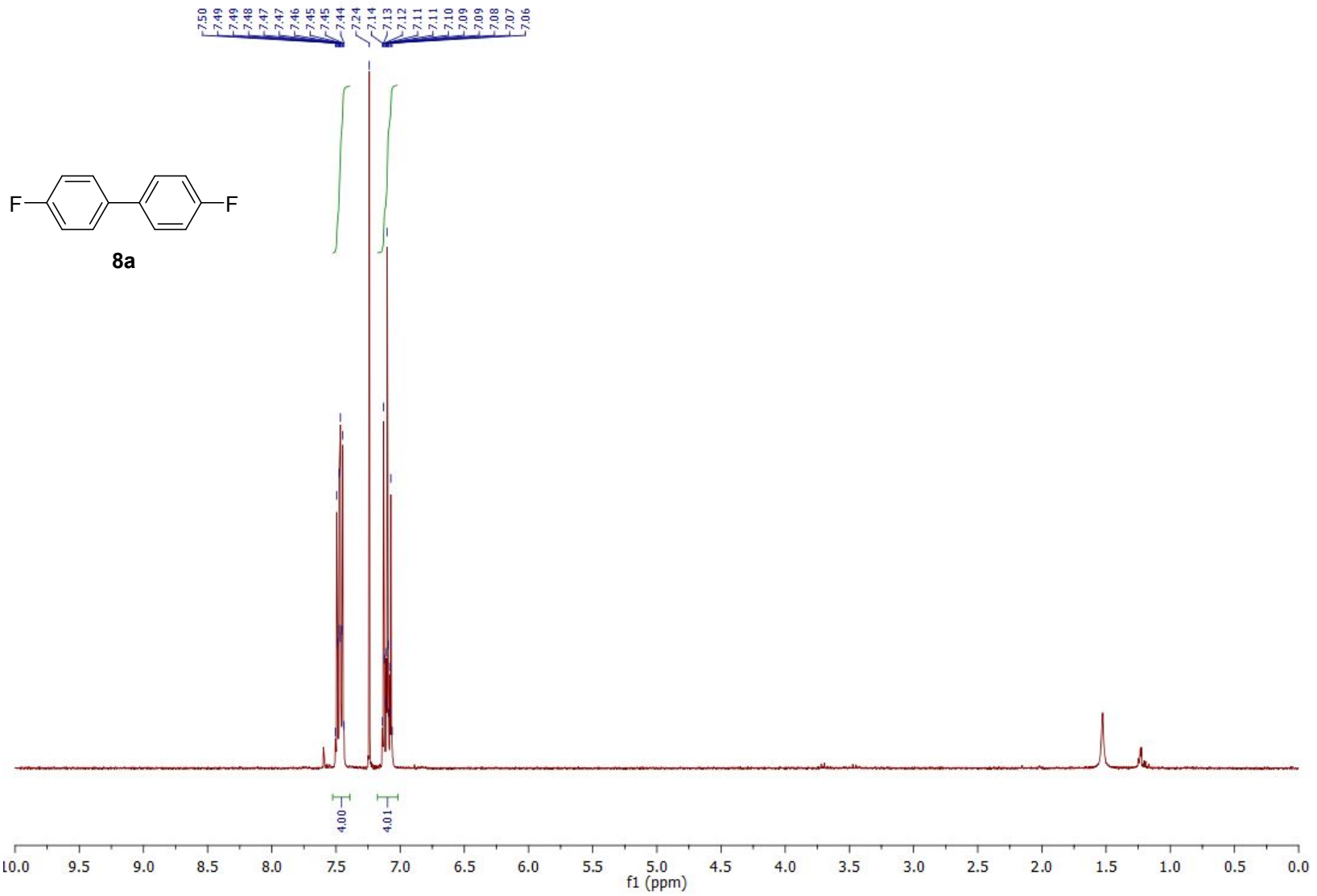
^{13}C-NMR spectrum: **4,4'-Bis(trifluoromethyl)-1,1'-biphenyl (7a)**



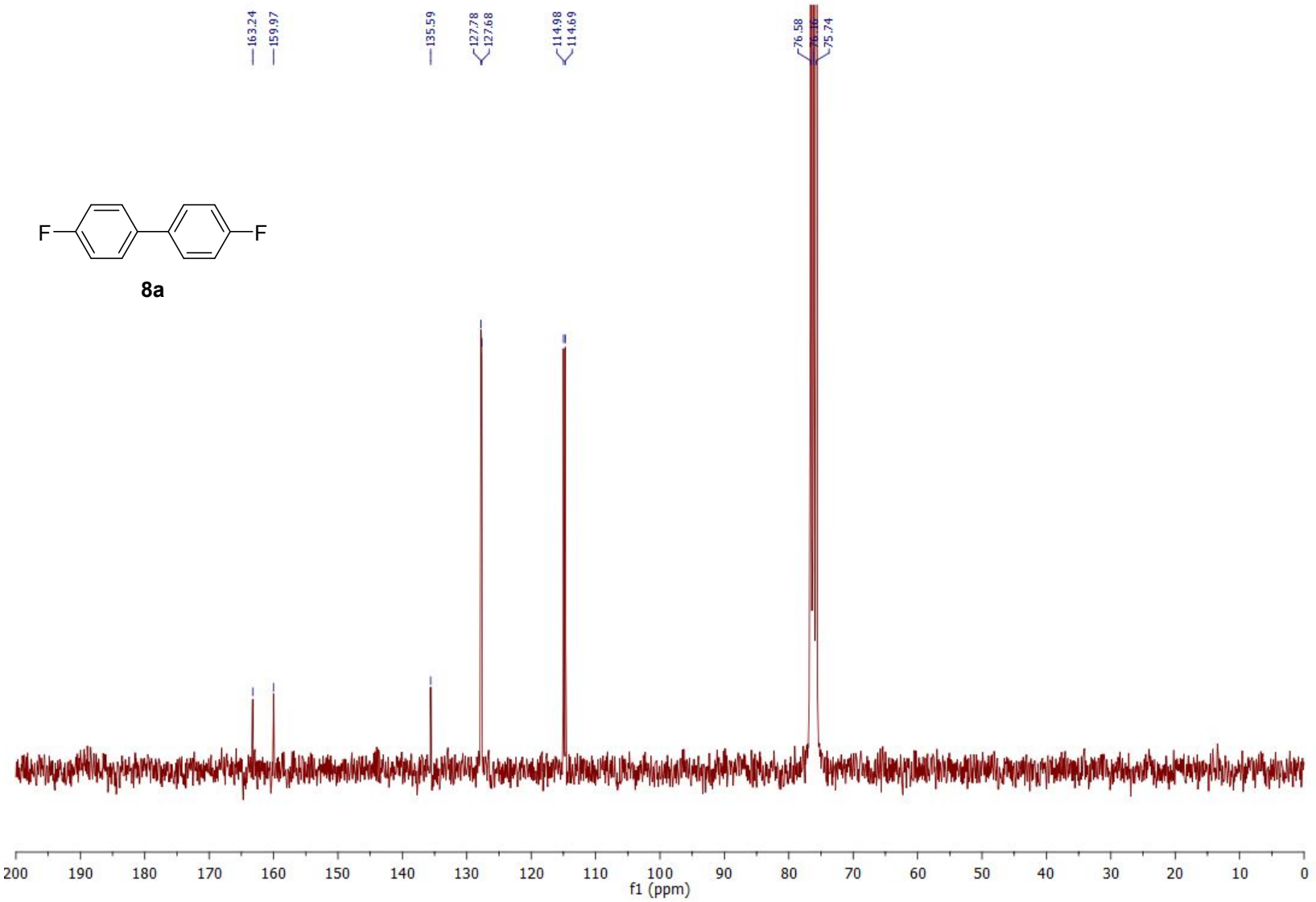
^{19}F-NMR spectrum: **4,4'-Bis(trifluoromethyl)-1,1'-biphenyl (7a)**



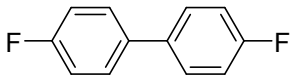
^{1}H-NMR spectrum: **4,4'-Difluorobiphenyl (8a)**



^{13}C-NMR spectrum: **4,4'-Difluorobiphenyl (8a)**

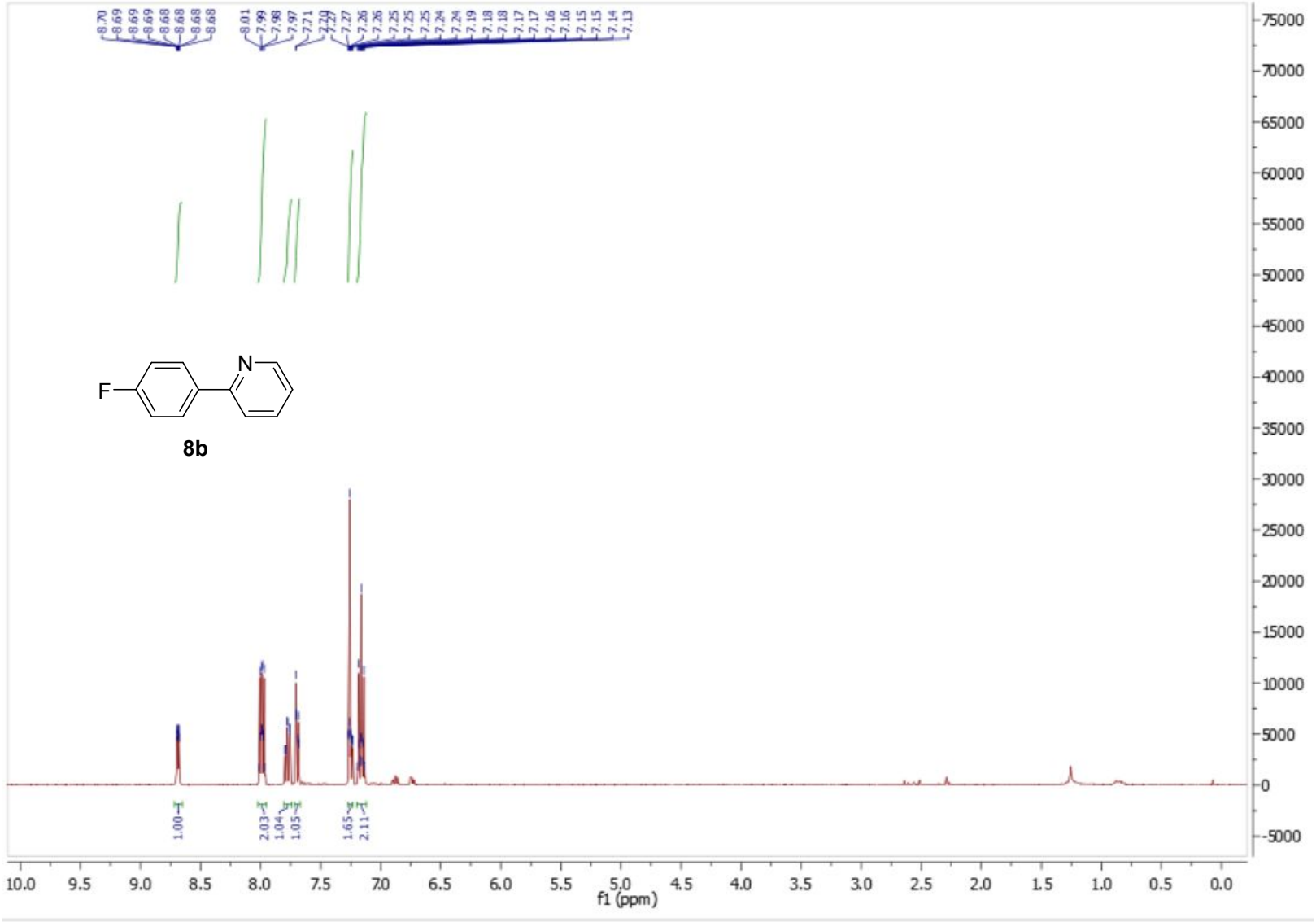


^{19}F-NMR spectrum: **4,4'-Difluorobiphenyl (8a)**

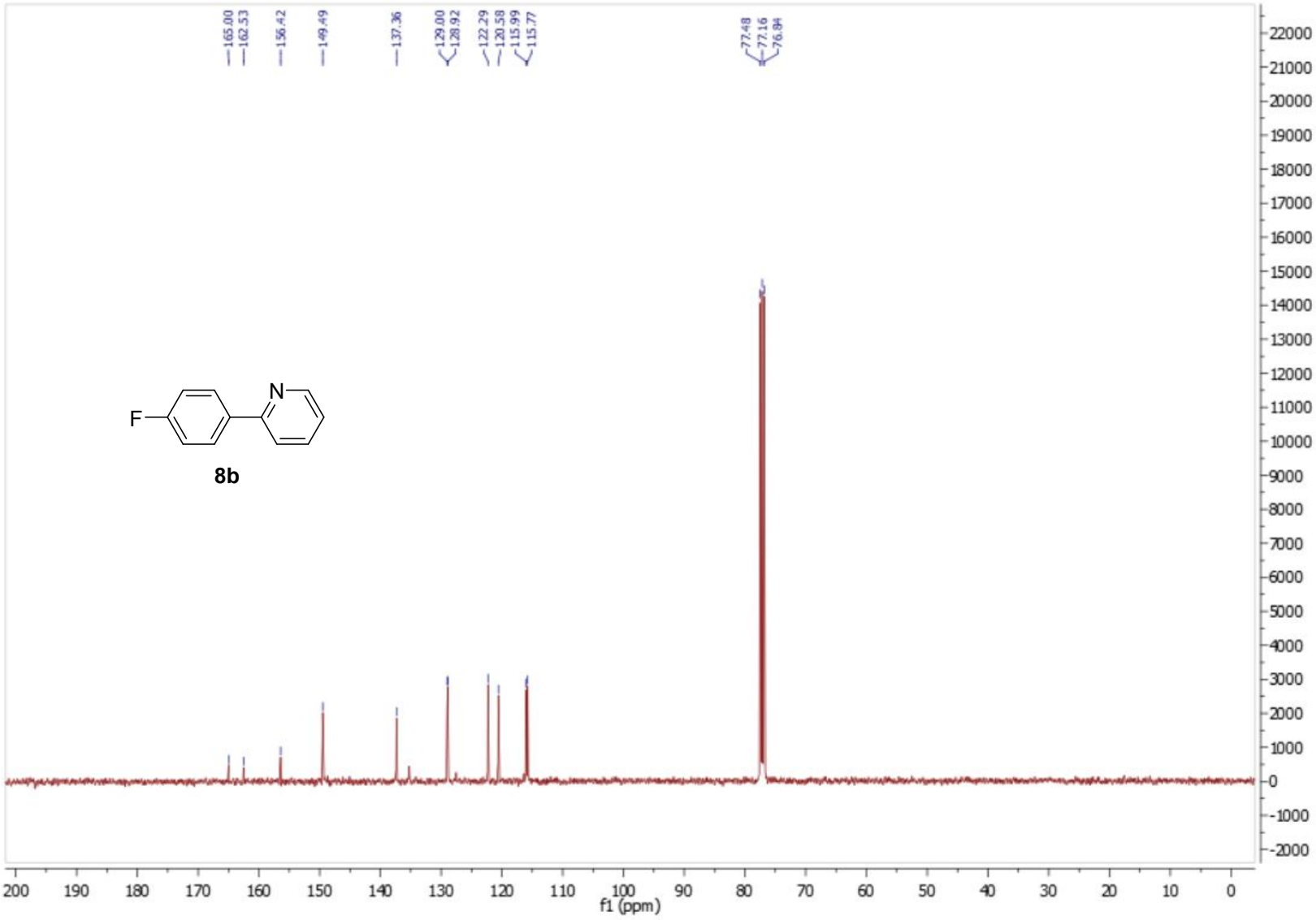


8a

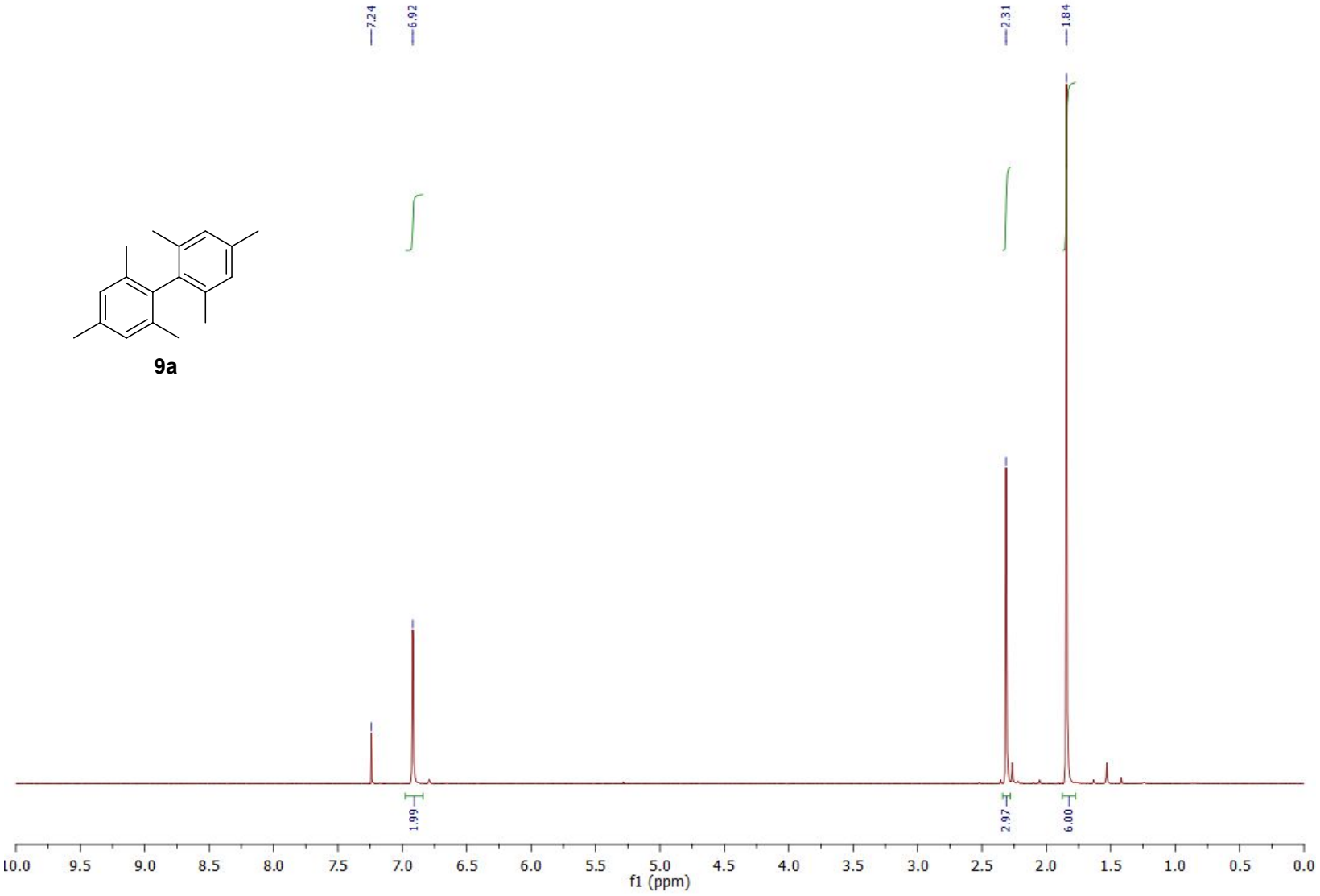
^{1}H-NMR spectrum: **2-(4-Fluorophenyl)pyridine (8b)**



^{13}C-NMR spectrum: **2-(4-Fluorophenyl)pyridine (8b)**

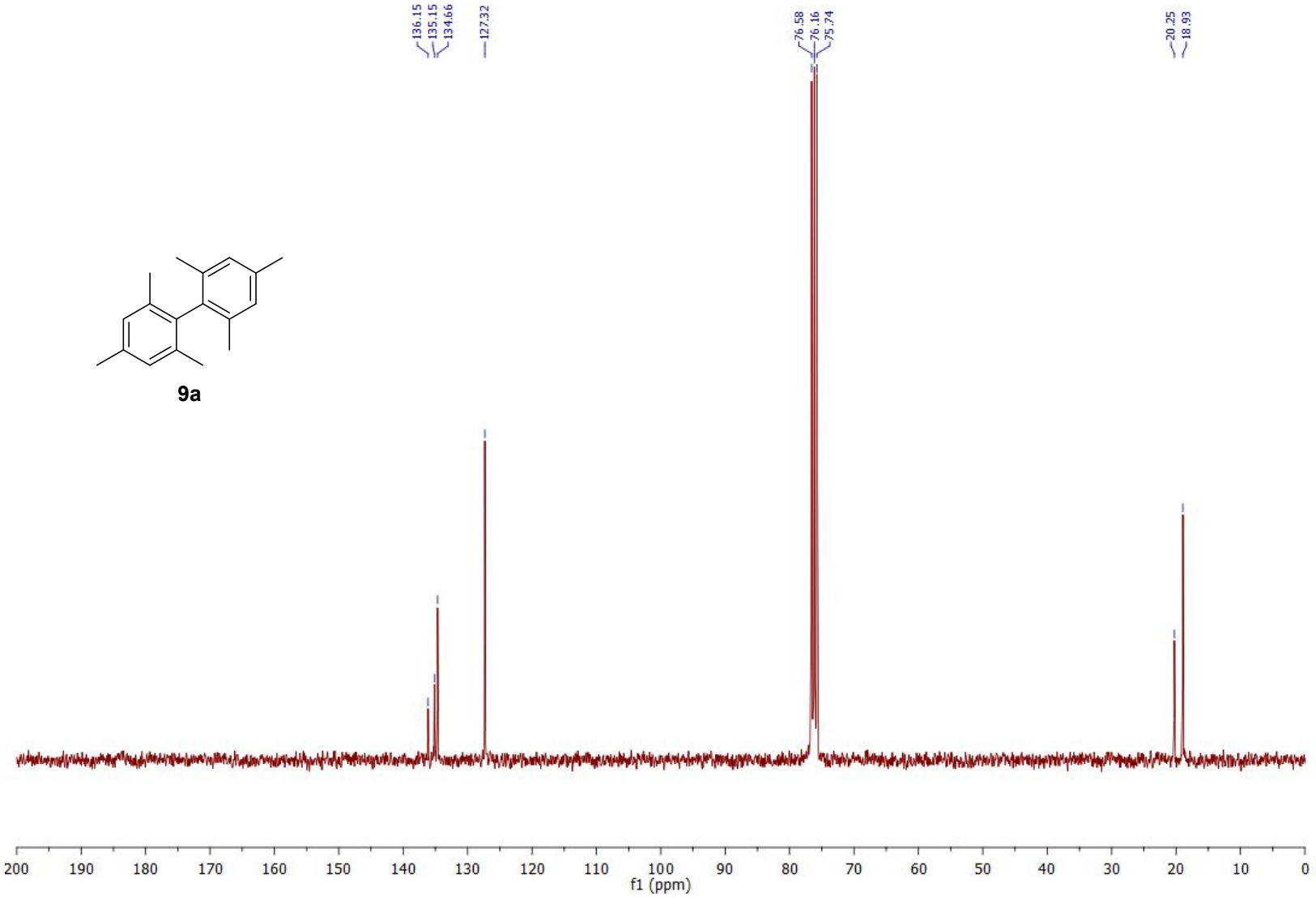


^{1}H-NMR spectrum: **2,2',4,4',6,6'-Hexamethylbiphenyl (9a)**

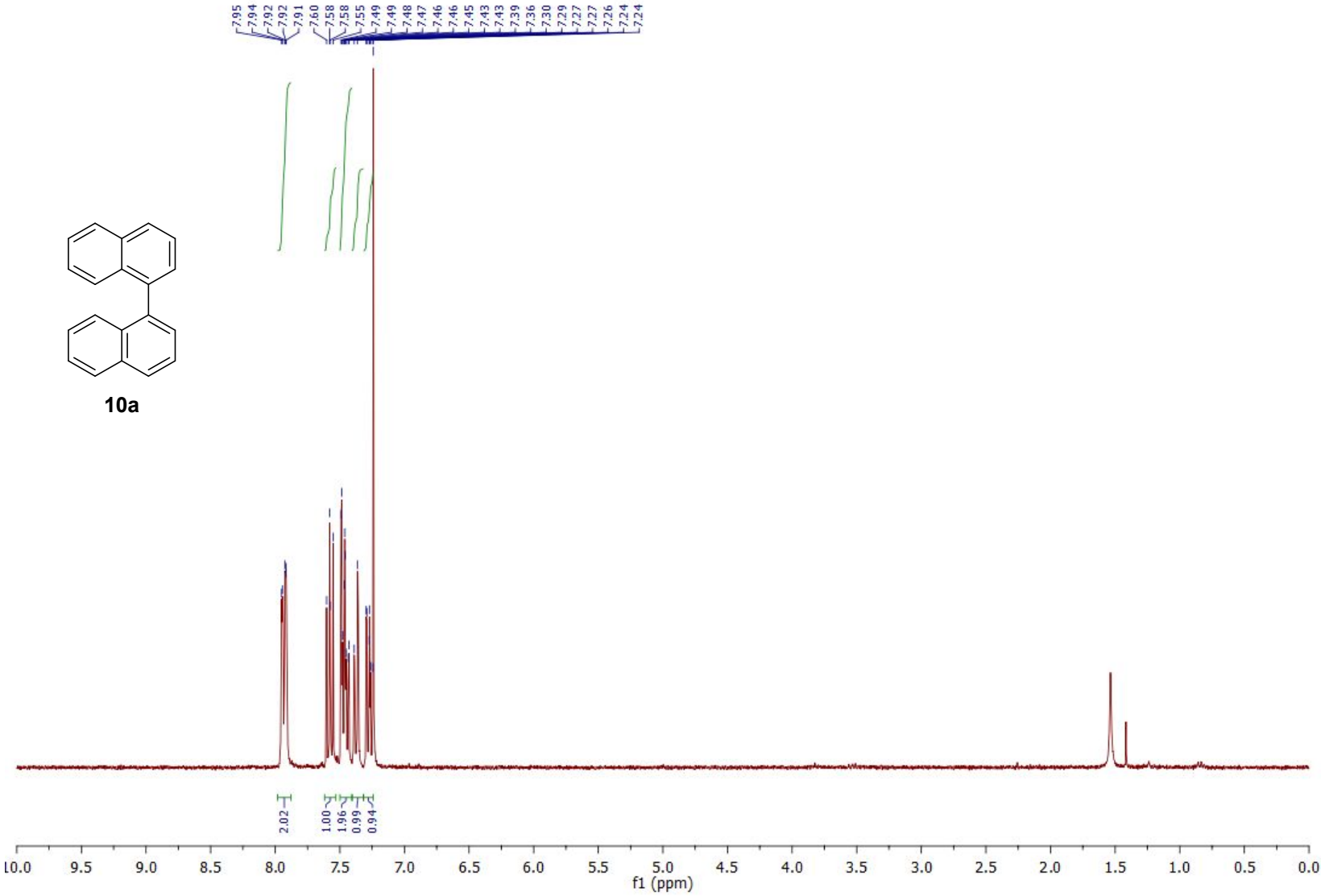


9a

^{13}C-NMR spectrum: **2,2',4,4',6,6'-Hexamethylbiphenyl (9a)**

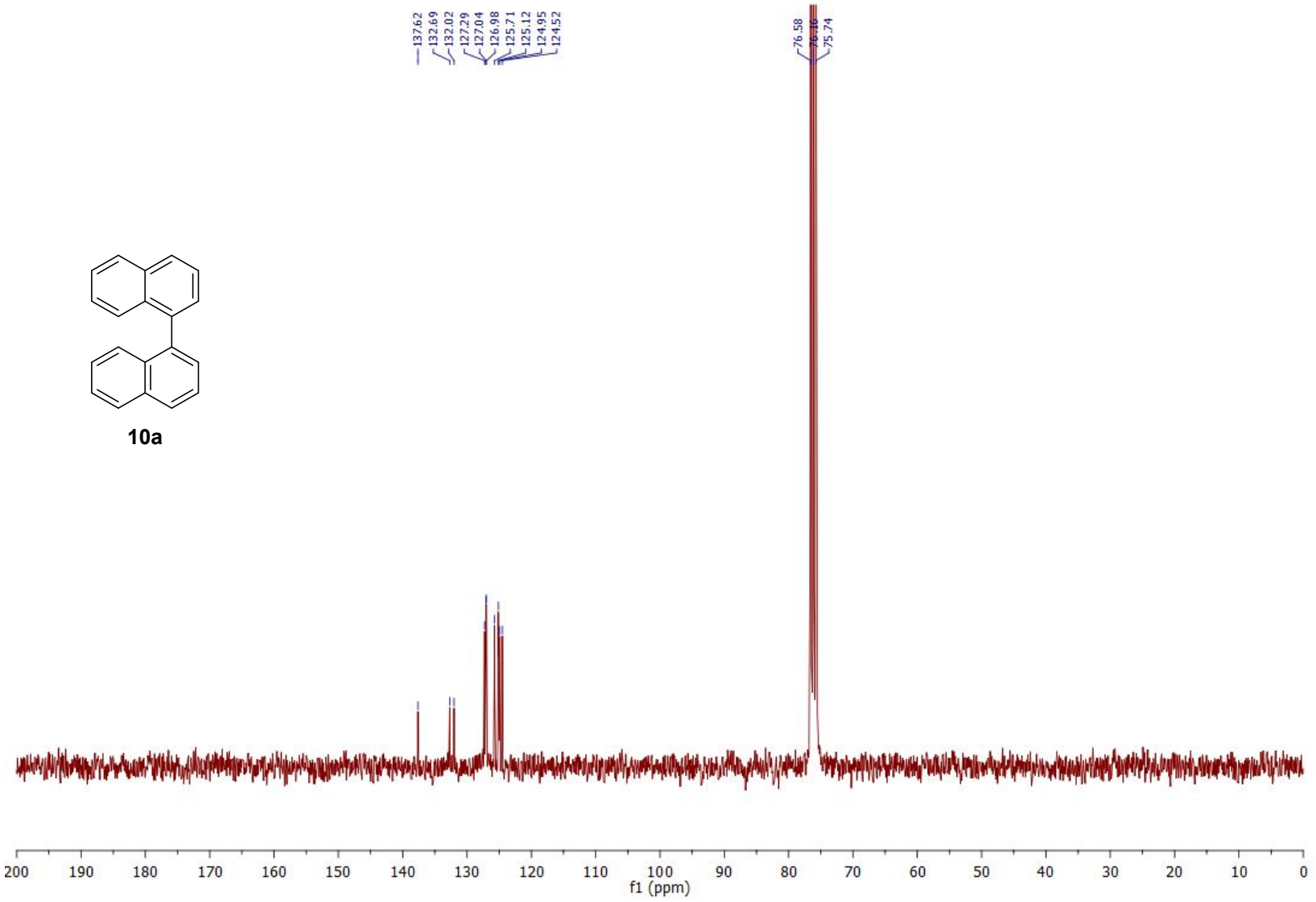


^{1}H-NMR spectrum: **1,1'-Binaphtyl (10a)**



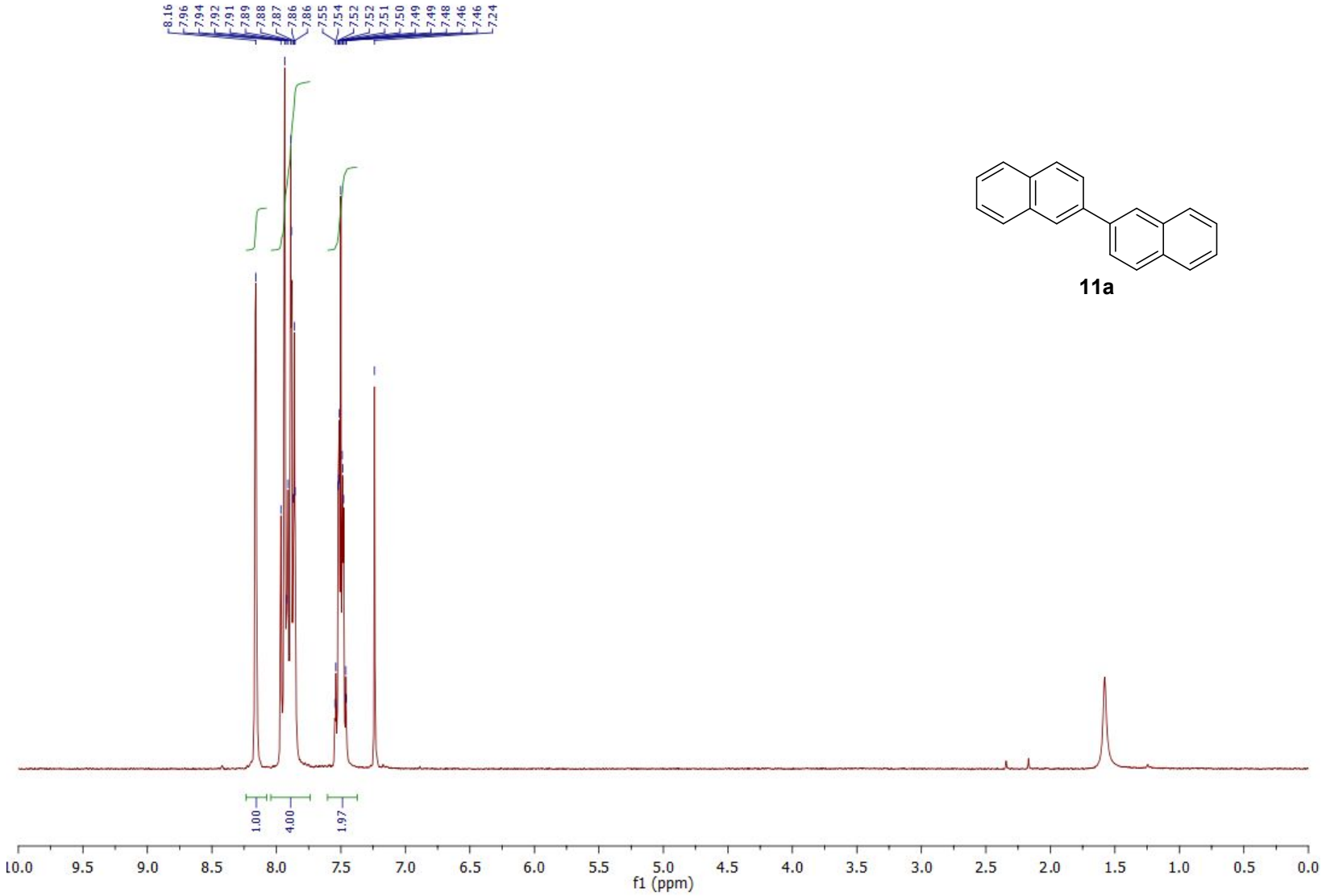
10a

^{13}C-NMR spectrum: **1,1'-Binaphtyl (10a)**



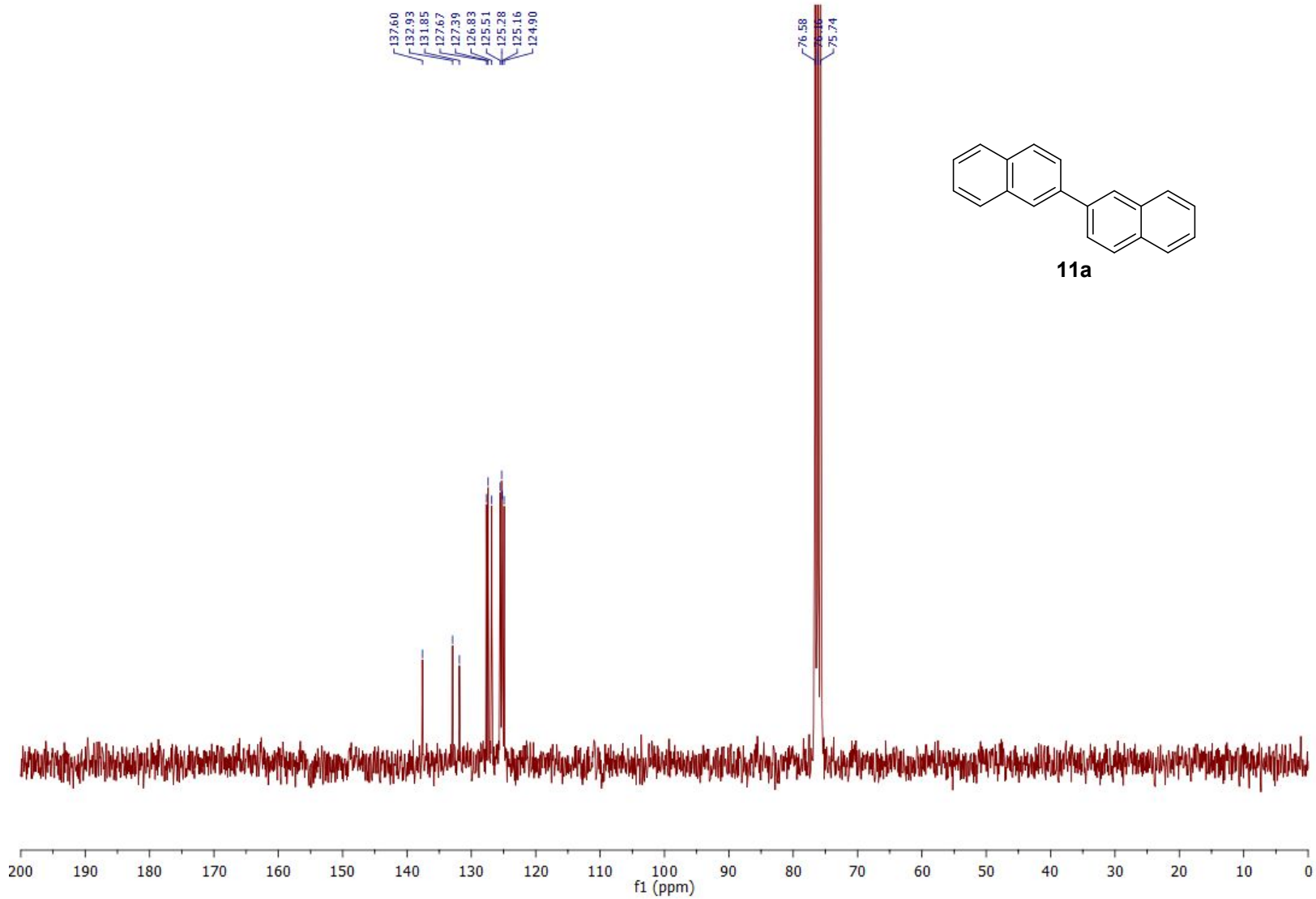
10a

^{1}H-NMR spectrum: **2,2'-binaphtyl (11a)**

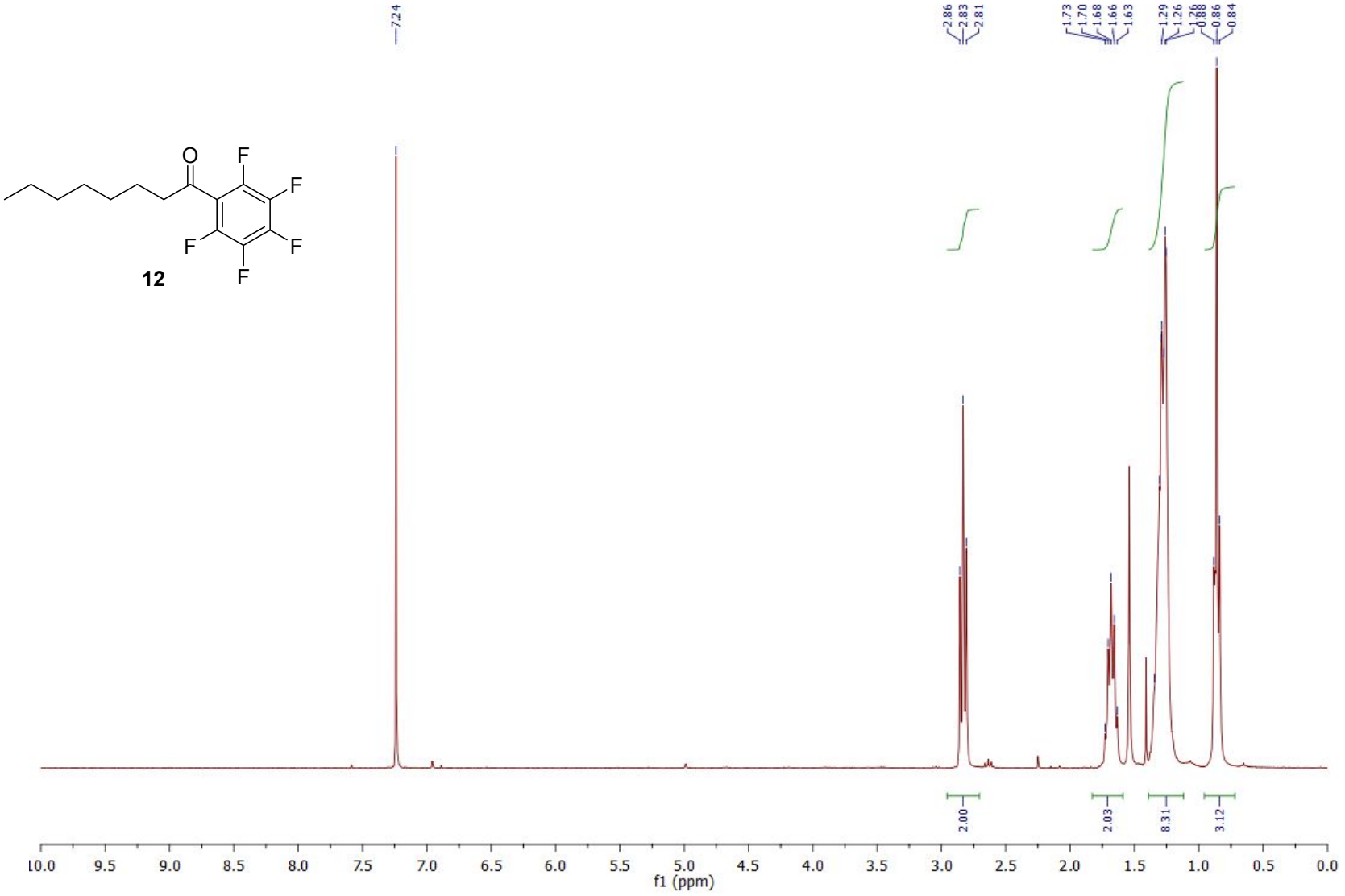


11a

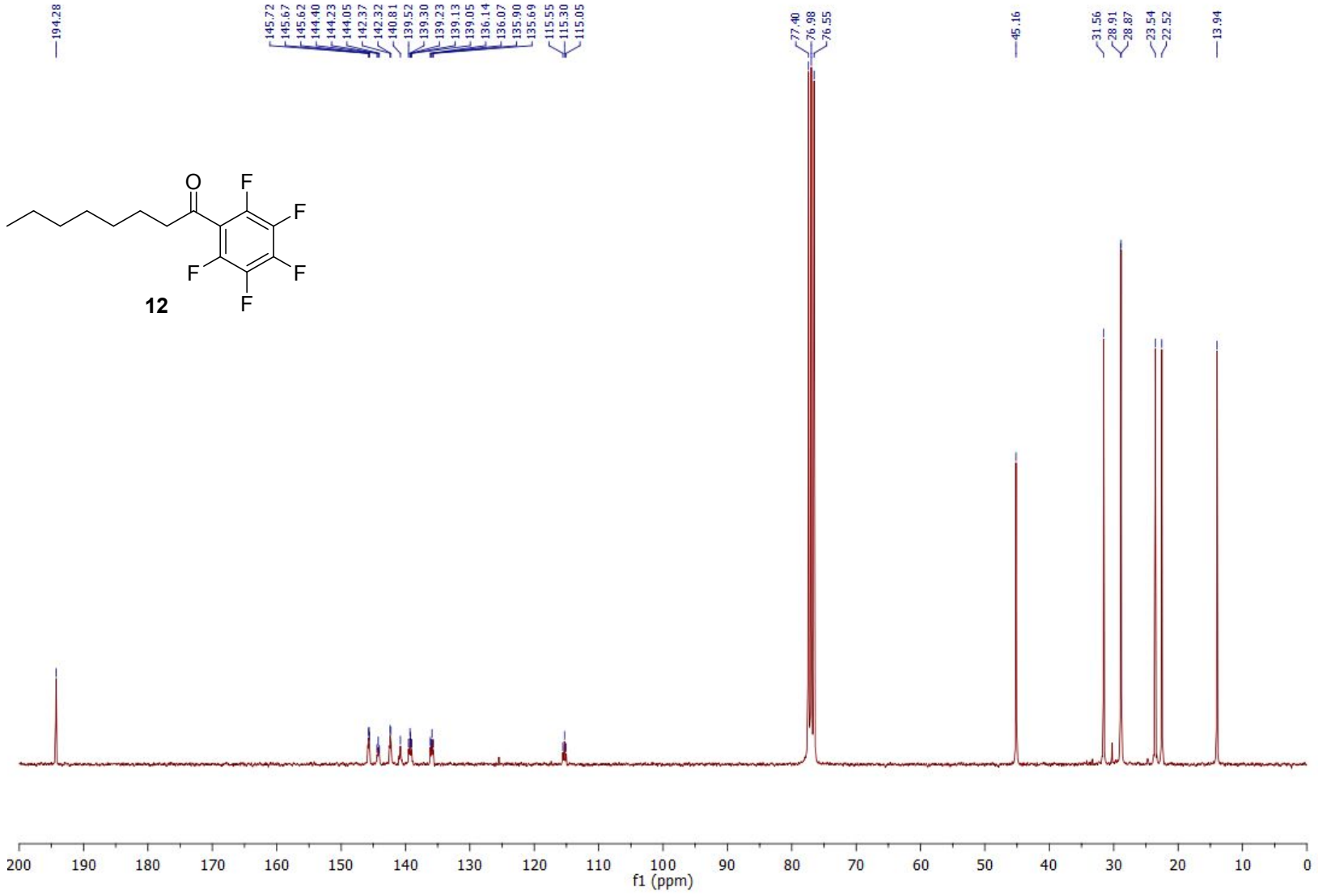
^{13}C-NMR spectrum: **2,2'-binaphtyl (11a)**



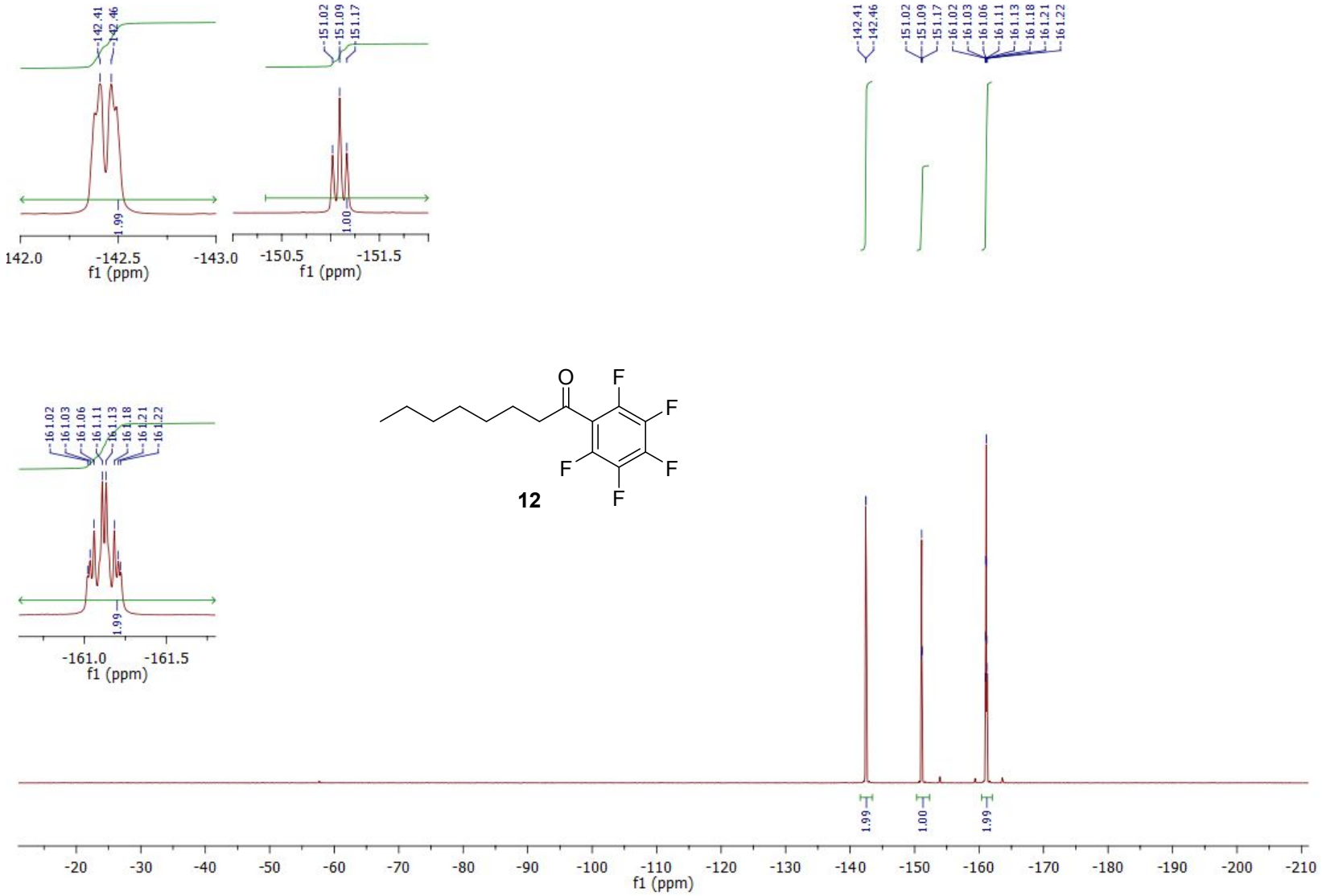
^{1}H-NMR spectrum: **1-(Pentafluorophenyl)-octan-1-one (12)**



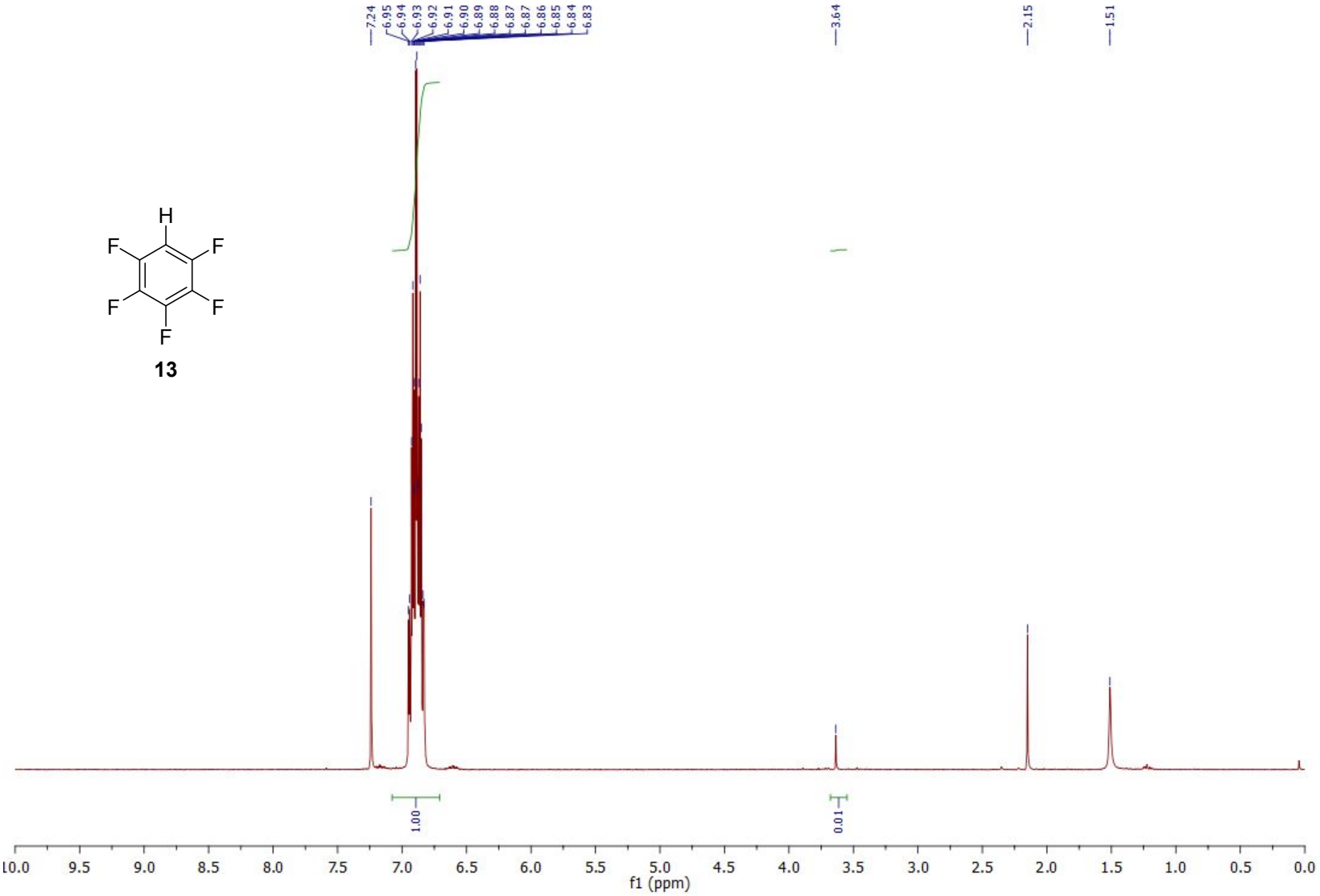
^{13}C-NMR spectrum: **1-(Pentafluorophenyl)-octan-1-one (12)**



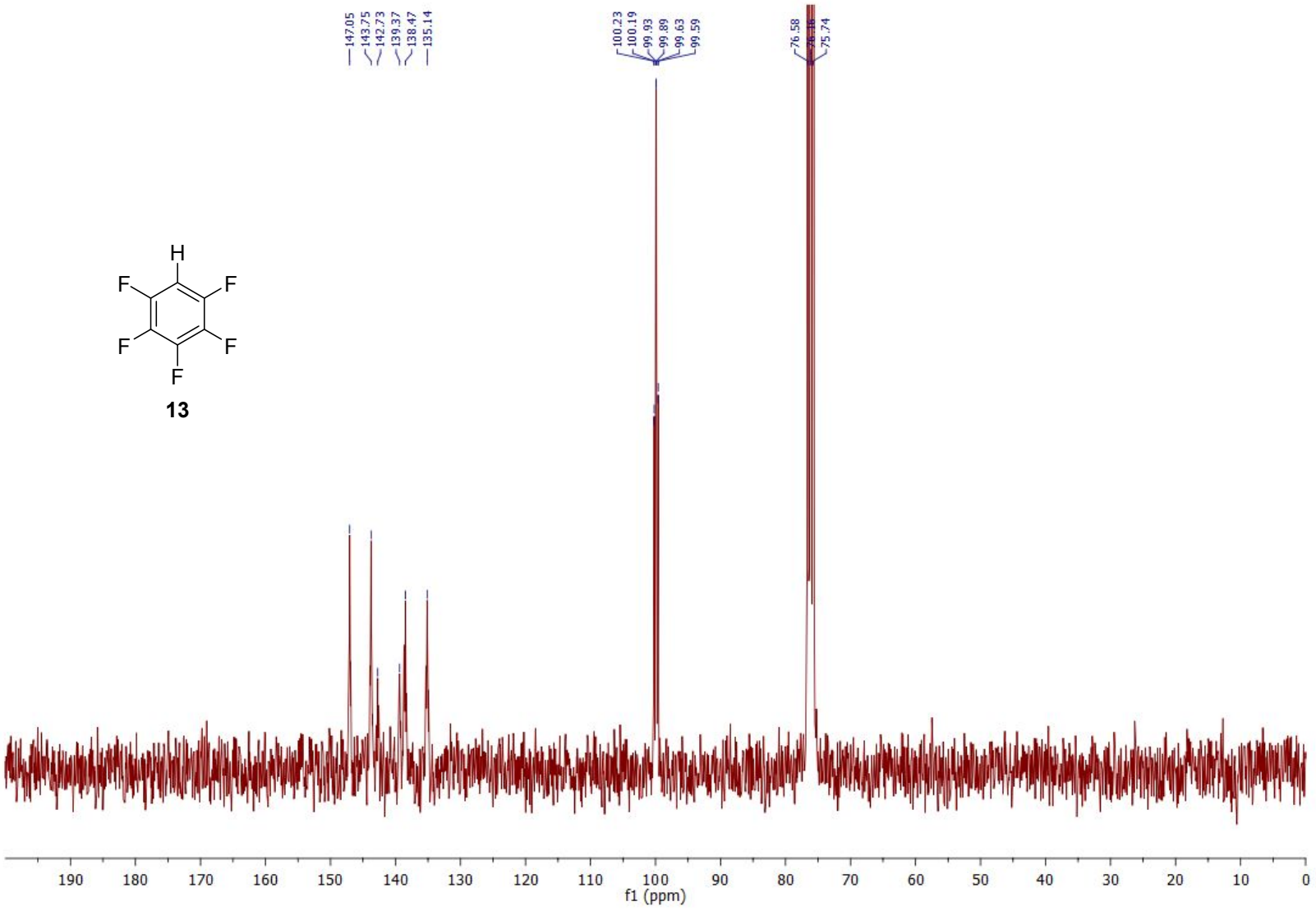
^{19}F-NMR spectrum: **1-(Pentafluorophenyl)-octan-1-one (12)**



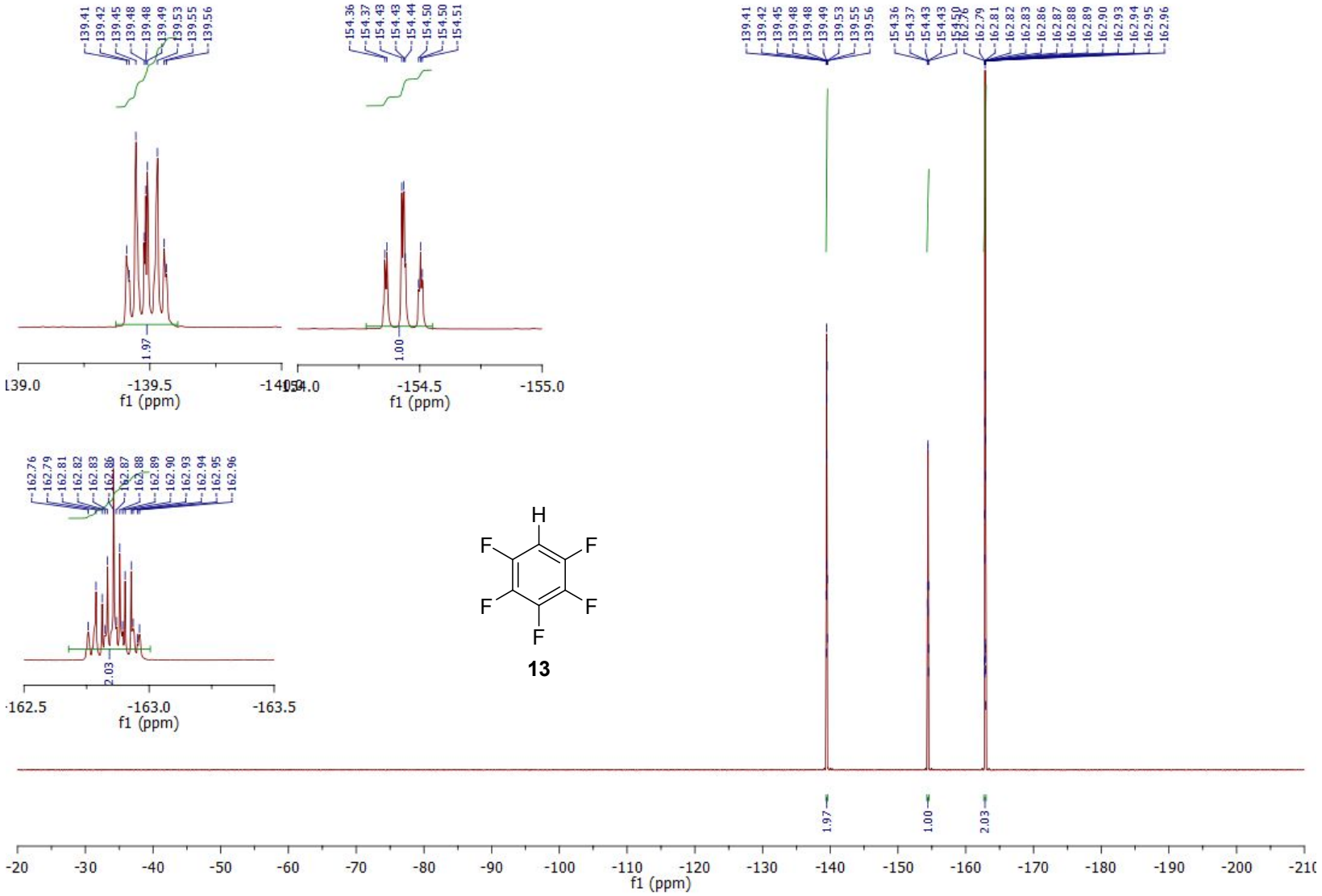
^{1}H-NMR spectrum: **Pentafluorobenzene (13)**



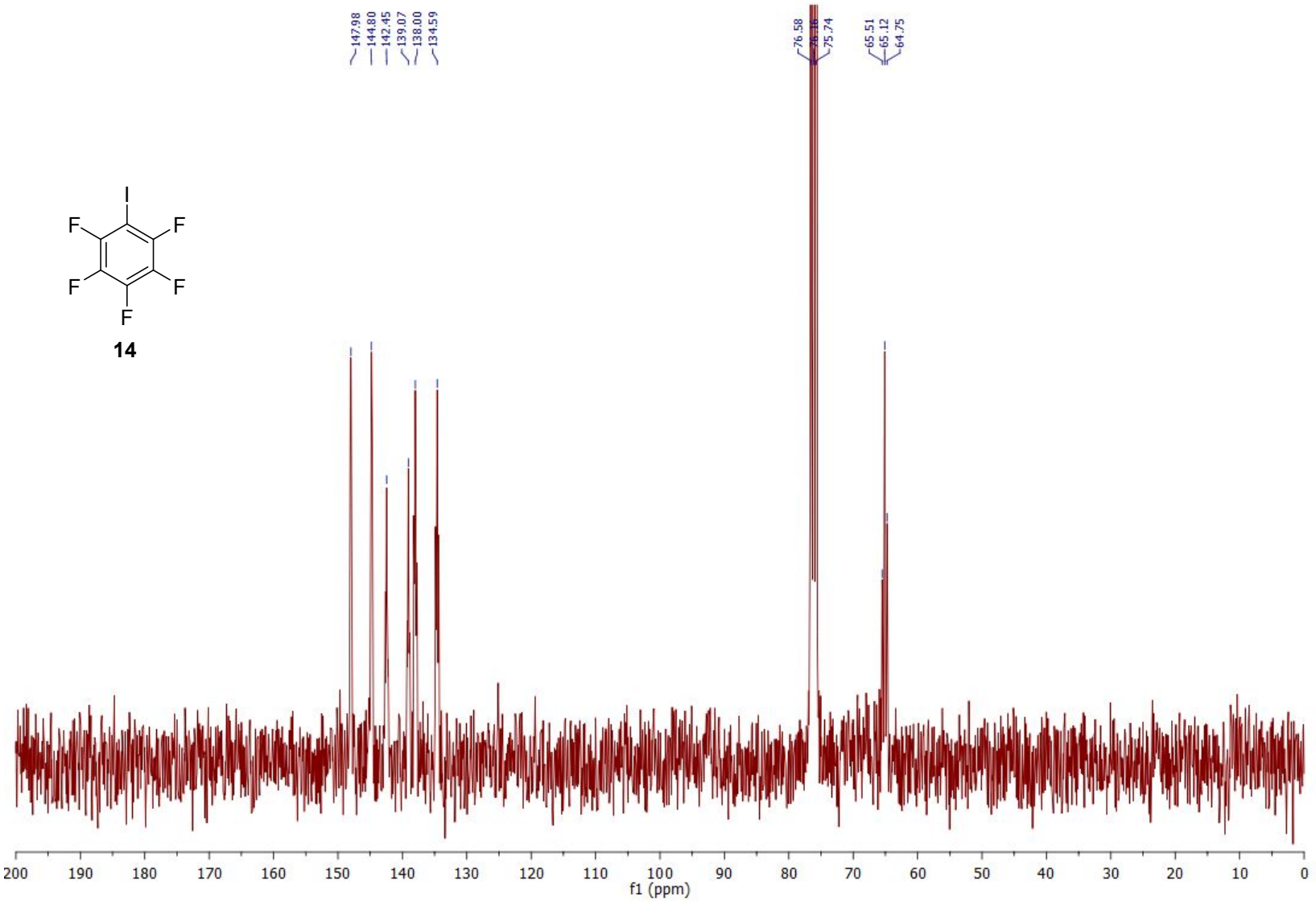
^{13}C-NMR spectrum: **Pentafluorobenzene (13)**



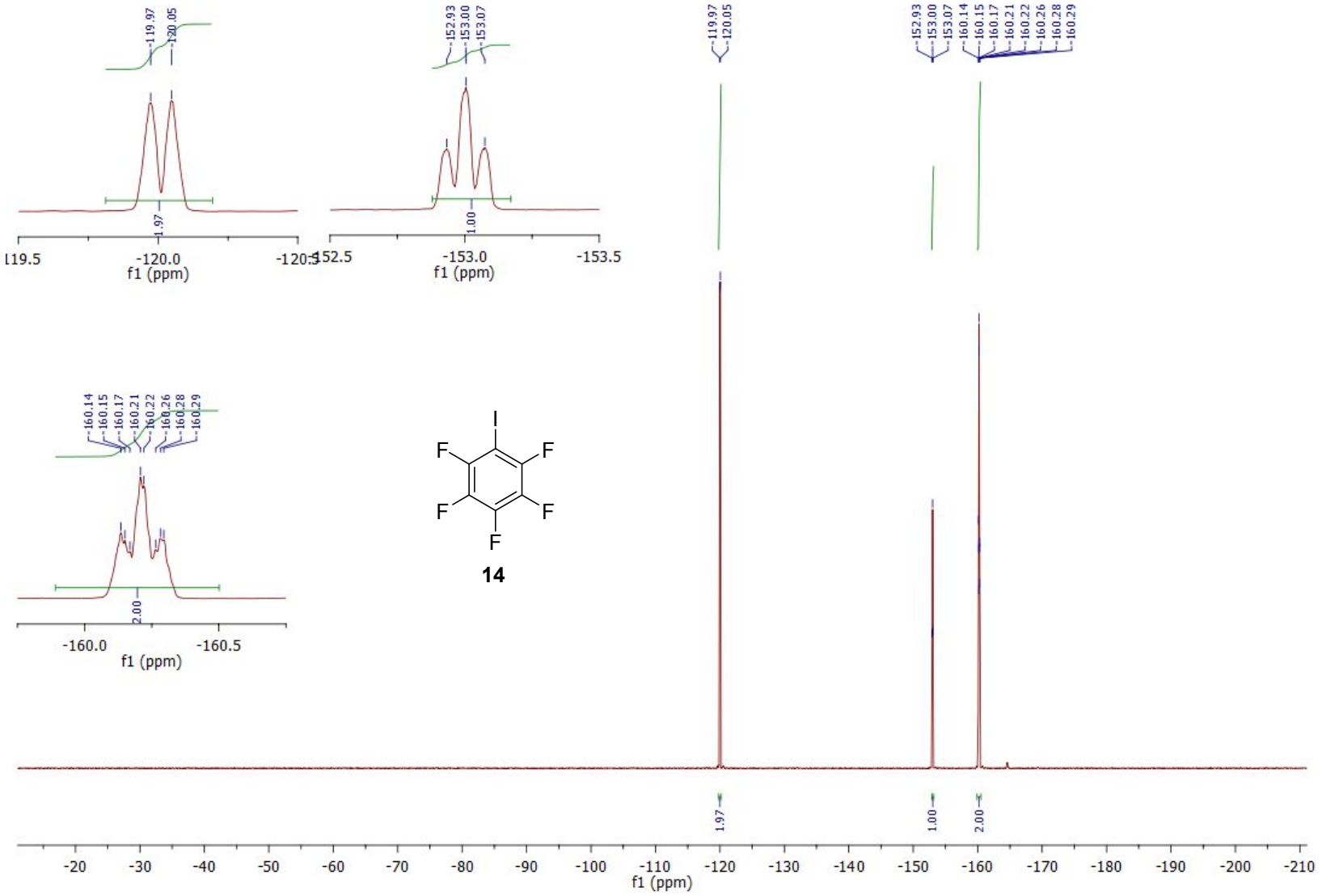
^{19}F-NMR spectrum: **Pentafluorobenzene (13)**



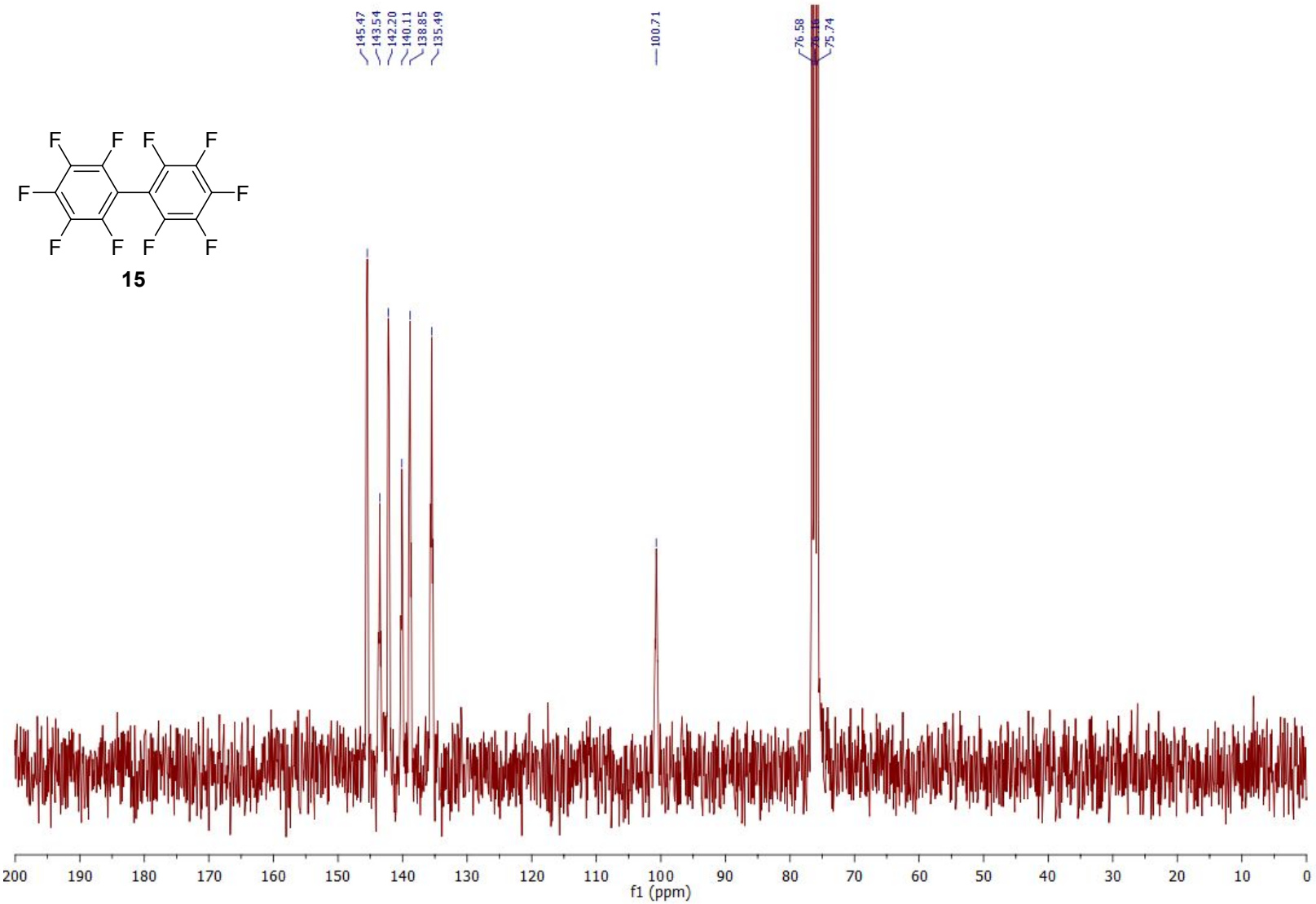
^{13}C-NMR spectrum: **Iodopentafluorobenzene (14)**



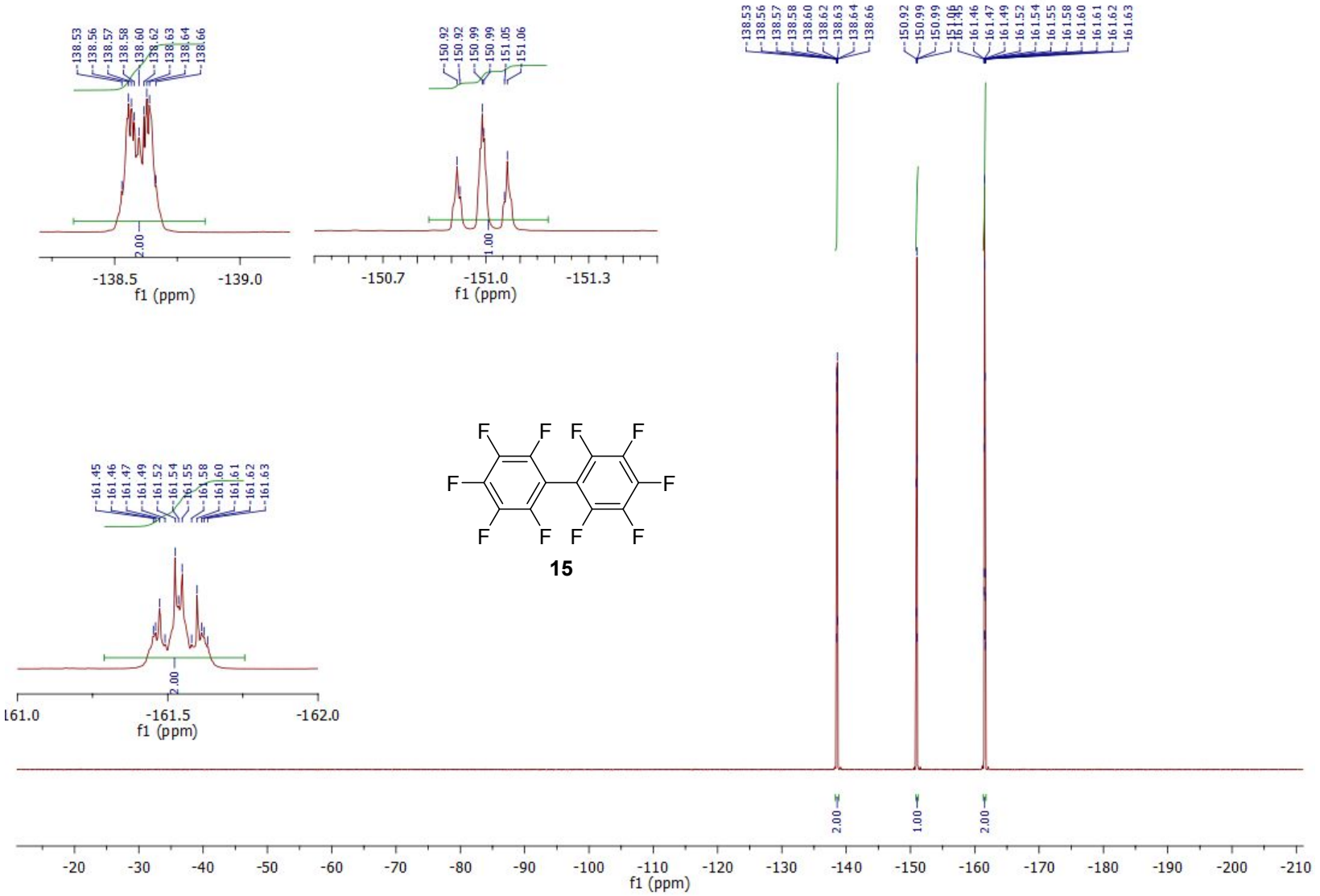
^{19}F-NMR spectrum: **Iodopentafluorobenzene (14)**



^{13}C-NMR spectrum: **Decafluorobiphenyl (15)**



^{19}F-NMR spectrum: **Decafluorobiphenyl (15)**



5. DFT calculations.

This computational work was carried out using the Gaussian09 code,[14] and OPBE functional was chosen, since it proved to efficiently reproduce both electronic and thermic properties of iron complexes, regardless of their oxidation and spin states.[15-17] Implicit PCM solvation model[18,19] was associated with explicit solvation of the magnesium adducts by THF molecules. Unless specified otherwise, all energies and cartesian coordinates discussed in this section were computed using SDD basis set and pseudo-potential for Fe.

Full surface for the reductive elimination of Ph-(2-Py) from $[Ph_2(2\text{-}Py)Fe^{II}]^-$

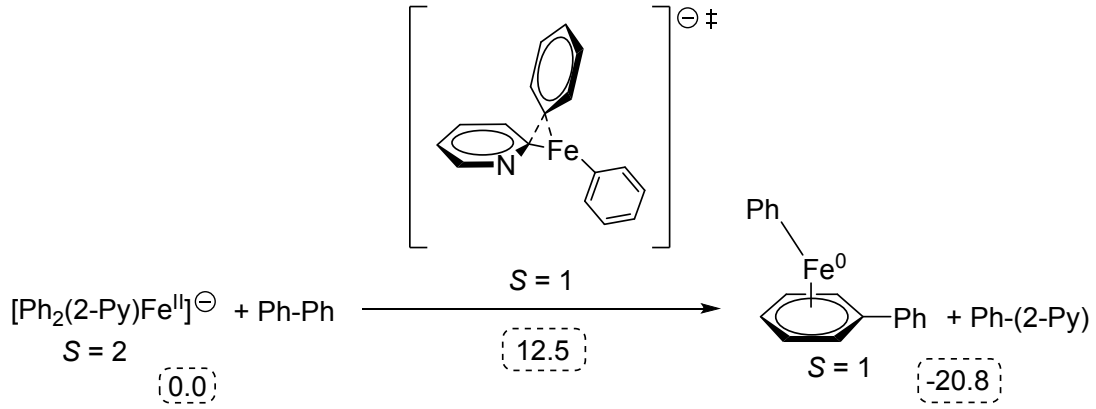


Figure S1: DFT-computed surface for the reductive elimination of Ph-(2-Py) starting from *ate* complex $[Ph_2(2\text{-}Py)Fe^{II}]^-$; thermal energies given in kcal.mol^{-1} (dashed squares)

Full surface for the reductive elimination of Ph-(2-Py) from $Ph_3(2\text{-}Py)Fe^{II}Mg(THF)$

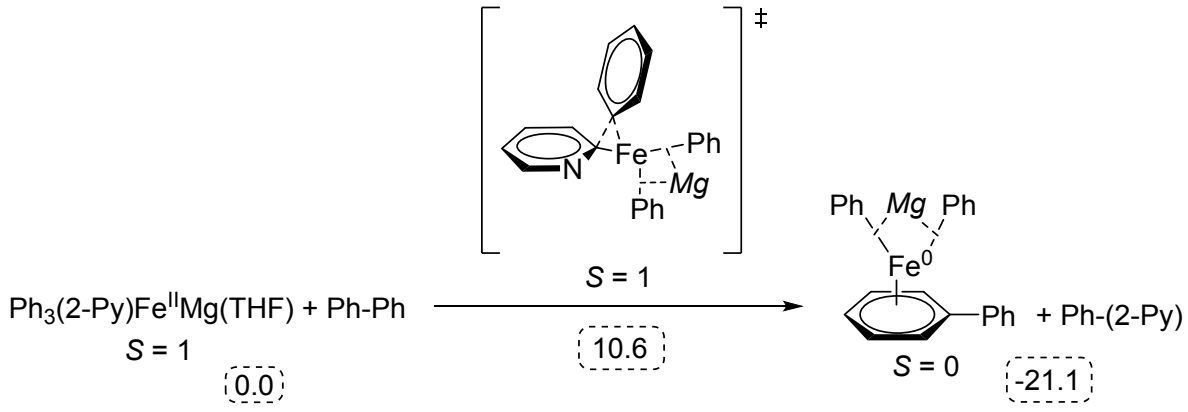


Figure S2: DFT-computed surface for the reductive elimination of Ph-(2-Py) starting from quaternized complex $Ph_3(2\text{-}Py)Fe^{II}Mg(THF)$; thermal energies given in kcal.mol^{-1} (dashed squares)

Table S1: Thermal activation energies of the cross- and homocoupling paths discussed in Scheme 5 of the article (def2TZVPP[20,21] was used as basis set and pseudo-potential for Fe)

	Path i	Path ii	Path iii	Path iv	Path v
	$\Delta E_{cc,t}^{\ddagger}$	$\Delta E_{hc,t}^{\ddagger}$	$\Delta E_{cc,q}^{\ddagger}$	$\Delta E_{hc,q}^{\ddagger}$	$\Delta E_{hc,t'}^{\ddagger}$
Ar = Ph Ar' = C_6F_5	27.7	15.9	19.4	12.5	15.9
Ar = Ph Ar' = 2-Py	10.8	15.2	14.6	8.4	

Computed structures:

$[Ph_2Ar'Fe^{II}]^-$ (S = 2)

Ar' = 2-Py

Fe	0.803271000	-0.014616000	-0.093964000
C	-0.168478000	-1.714757000	0.554594000
C	-1.529398000	-2.009619000	0.280080000
C	0.519183000	-2.715772000	1.290042000
C	-2.155589000	-3.197268000	0.694202000
H	-2.135013000	-1.287912000	-0.278775000
C	-0.088391000	-3.906040000	1.718849000
H	1.575554000	-2.567030000	1.540751000
C	-1.436076000	-4.155331000	1.420532000
H	-3.208595000	-3.375115000	0.452445000
H	0.489027000	-4.643518000	2.285991000
C	-0.056942000	1.712508000	-0.758839000
N	-1.399225000	1.935500000	-0.572455000
C	0.710484000	2.730406000	-1.397549000
C	-1.946266000	3.090562000	-0.991083000
C	0.131772000	3.924625000	-1.830371000
H	1.781606000	2.570867000	-1.550884000
C	-1.242222000	4.119837000	-1.624159000
H	-3.023173000	3.201462000	-0.808385000
H	0.734680000	4.695266000	-2.321332000
C	2.878195000	-0.068282000	-0.081323000
C	3.643418000	0.422987000	1.005099000
C	3.631156000	-0.598864000	-1.157542000
C	5.047115000	0.387170000	1.027382000
C	5.034797000	-0.642079000	-1.158583000
C	5.751732000	-0.147769000	-0.060052000
H	3.111318000	-1.000570000	-2.036556000
H	5.594116000	0.776889000	1.891940000
H	5.571962000	-1.063014000	-2.014612000
H	6.844440000	-0.178981000	-0.051448000
H	-1.749359000	5.033897000	-1.941430000
H	-1.916498000	-5.080657000	1.749537000
H	3.133817000	0.853538000	1.876428000

Sum of electronic and thermal Energies= -834.671638
Sum of electronic and thermal Enthalpies= -834.670694
Sum of electronic and thermal Free Energies= -834.742138
Lowest vibration frequencies (/cm^-1): 15.4032 27.3835 33.4799

Ar' = C_6F_5

Fe	1.148491000	-0.169099000	-0.033863000
C	0.003696000	-1.850658000	0.270983000
C	-0.456599000	-2.656345000	-0.798457000
C	-0.363725000	-2.286149000	1.567019000
C	-1.227844000	-3.812282000	-0.598012000
H	-0.210958000	-2.381507000	-1.831387000
C	-1.134389000	-3.438632000	1.788283000
H	-0.042075000	-1.712826000	2.444892000
C	-1.571565000	-4.208431000	0.701642000
H	-1.562950000	-4.404987000	-1.454869000
H	-1.395880000	-3.737646000	2.808048000
C	0.121941000	1.649862000	-0.289572000
C	-0.194067000	2.486382000	0.775371000
C	-0.327431000	2.092158000	-1.528895000
C	-0.910782000	3.679647000	0.652443000
F	0.205883000	2.150828000	2.040329000
C	-1.048573000	3.272439000	-1.728443000
F	-0.066057000	1.348920000	-2.647590000
C	-1.341767000	4.072462000	-0.619030000
F	-1.201281000	4.461520000	1.716242000
F	-1.471036000	3.663495000	-2.951662000
C	3.186080000	-0.223830000	-0.066496000
C	3.991804000	0.939526000	-0.167870000
C	3.902571000	-1.446086000	0.013951000
C	5.395760000	0.896213000	-0.186590000
C	5.303837000	-1.509884000	-0.004054000
C	6.061740000	-0.333580000	-0.104121000
H	3.350570000	-2.389588000	0.092594000
H	5.971997000	1.823662000	-0.265682000
H	5.809140000	-2.478883000	0.060091000
H	7.153910000	-0.376311000	-0.118630000
F	-2.035394000	5.215003000	-0.774001000
H	-2.172222000	-5.106826000	0.865751000
H	3.513187000	1.923335000	-0.235957000

Sum of electronic and thermal Energies= -1314.614420
Sum of electronic and thermal Enthalpies= -1314.613476
Sum of electronic and thermal Free Energies= -1314.696273
Lowest vibration frequencies (/cm^-1): 15.4410 16.7344 19.9636

Ar' = Ph

Fe	1.024722000	-0.097225000	-0.114251000
C	-0.083176000	-1.798804000	0.261728000

C	-1.243762000	-2.165881000	-0.467997000
C	0.226041000	-2.651672000	1.353831000
C	-2.028493000	-3.284871000	-0.147451000
H	-1.556152000	-1.556470000	-1.324453000
C	-0.548574000	-3.771843000	1.697354000
H	1.110056000	-2.443013000	1.968704000
C	-1.683946000	-4.096918000	0.943097000
H	-2.912280000	-3.525938000	-0.747241000
H	-0.265852000	-4.395034000	2.552107000
C	0.052243000	1.697672000	-0.465486000
C	-0.601539000	2.420183000	0.563020000
C	0.007573000	2.299882000	-1.747254000
C	-1.246116000	3.647935000	0.341050000
H	-0.615574000	2.017113000	1.583345000
C	-0.636507000	3.523222000	-1.993562000
H	0.495963000	1.804579000	-2.595819000
C	-1.266992000	4.206516000	-0.944540000
H	-1.735718000	4.170020000	1.169404000
H	-0.644923000	3.947586000	-3.002693000
C	3.077148000	-0.105498000	-0.046477000
C	3.835811000	1.091229000	0.056621000
C	3.854497000	-1.290839000	-0.139803000
C	5.238763000	1.111867000	0.077484000
C	5.259315000	-1.292803000	-0.124143000
C	5.963329000	-0.086304000	-0.012332000
H	3.349886000	-2.260531000	-0.224746000
H	5.771811000	2.064453000	0.164974000
H	5.807276000	-2.238120000	-0.197680000
H	7.056412000	-0.078594000	0.005018000
H	-1.767896000	5.161045000	-1.126321000
H	-2.290287000	-4.969966000	1.198760000
H	3.313786000	2.052455000	0.127626000

Sum of electronic and thermal Energies= -818.625934
Sum of electronic and thermal Enthalpies= -818.624990
Sum of electronic and thermal Free Energies= -818.695921
Lowest vibration frequencies (/cm^-1): 22.4152 27.0592 36.7050

[Ph_3Ar'Fe^{II}Mg(THF)] (*S* = 1)

Ar' = 2-Py

Fe	-0.785007000	0.024401000	-1.218429000
C	0.346485000	1.303966000	-0.235661000
C	1.717073000	1.054626000	0.050648000
C	-0.120137000	2.590553000	0.147354000
C	2.544040000	1.994207000	0.681826000
H	2.168179000	0.104385000	-0.245857000
C	0.702428000	3.544640000	0.764588000
H	-1.161189000	2.864709000	-0.045367000

C	2.043845000	3.252452000	1.047675000
H	3.592410000	1.746812000	0.876756000
H	0.290633000	4.524477000	1.027027000
H	2.687622000	3.990987000	1.531388000
C	-0.467959000	-2.120533000	-0.958987000
C	-1.353410000	-2.999407000	-1.649471000
C	0.739196000	-2.740649000	-0.520953000
C	-1.048317000	-4.337834000	-1.923325000
H	-2.312560000	-2.613384000	-2.008039000
C	1.055607000	-4.085954000	-0.771082000
H	1.482646000	-2.151905000	0.028806000
C	0.163298000	-4.894278000	-1.483752000
H	-1.758906000	-4.955836000	-2.480575000
H	2.002680000	-4.500009000	-0.412008000
H	0.402821000	-5.939886000	-1.691073000
C	0.179418000	0.309119000	-2.900725000
C	-0.271411000	1.333336000	-3.769991000
C	1.292982000	-0.434885000	-3.355373000
C	0.338585000	1.594607000	-5.006341000
H	-1.127013000	1.953401000	-3.482435000
C	1.914240000	-0.182856000	-4.587980000
H	1.687392000	-1.245964000	-2.738883000
C	1.440735000	0.835931000	-5.425539000
H	-0.047601000	2.395131000	-5.645254000
H	2.770984000	-0.789656000	-4.898584000
H	1.919975000	1.034479000	-6.387525000
C	-2.513589000	0.358496000	-0.283154000
N	-2.785526000	0.155694000	-1.596858000
C	-3.514236000	0.940656000	0.535083000
C	-3.949390000	0.483479000	-2.157111000
C	-4.763277000	1.246719000	-0.026884000
H	-3.329704000	1.145511000	1.592960000
C	-4.999040000	1.015464000	-1.386947000
H	-4.053254000	0.308625000	-3.231905000
H	-5.553505000	1.671074000	0.598238000
H	-5.961817000	1.240745000	-1.846849000
Mg	-1.131424000	-1.083710000	0.937839000
C	-0.858526000	-1.696321000	4.027484000
C	-2.628468000	-2.937791000	3.017165000
C	-1.340108000	-2.760604000	4.999100000
H	-1.119709000	-0.680581000	4.361192000
H	0.217239000	-1.744369000	3.812919000
C	-2.772555000	-3.009815000	4.526808000
H	-2.302661000	-3.895835000	2.584442000
H	-3.530495000	-2.589914000	2.497158000
H	-0.735764000	-3.673889000	4.904131000
H	-1.284677000	-2.416374000	6.039544000
H	-3.168917000	-3.979899000	4.852391000

H	-3.446839000	-2.220848000	4.890201000
O	-1.576766000	-1.957582000	2.787143000

Sum of electronic and thermal Energies= -1498.315158
Sum of electronic and thermal Enthalpies= -1498.314214
Sum of electronic and thermal Free Energies= -1498.414656
Lowest vibration frequencies (/cm^-1): 15.3722 24.3933 29.0190

Ar' = C_6F_5

Fe	-0.589856000	-0.178389000	-0.870901000
C	0.617011000	0.757778000	0.570471000
C	2.042041000	0.850386000	0.533436000
C	-0.009435000	1.664049000	1.479651000
C	2.765163000	1.786584000	1.283933000
H	2.606726000	0.187613000	-0.129719000
C	0.702440000	2.610385000	2.229350000
H	-1.100055000	1.651033000	1.585209000
C	2.098751000	2.679481000	2.134319000
H	3.855177000	1.822886000	1.202126000
H	0.165618000	3.295573000	2.891372000
H	2.659274000	3.412565000	2.718460000
C	-1.099272000	-2.052856000	-0.227041000
C	-2.327505000	-2.417717000	0.406291000
C	-0.307445000	-3.162172000	-0.660601000
C	-2.751010000	-3.745968000	0.539900000
H	-2.993584000	-1.631863000	0.776800000
C	-0.727345000	-4.494047000	-0.541803000
H	0.659478000	-2.975869000	-1.142947000
C	-1.956841000	-4.796347000	0.058605000
H	-3.711254000	-3.963364000	1.016122000
H	-0.091289000	-5.299389000	-0.919729000
H	-2.287878000	-5.832461000	0.155709000
C	-0.090994000	1.389698000	-2.021420000
C	-0.710095000	2.638871000	-2.055790000
C	0.997139000	1.271929000	-2.885531000
C	-0.306102000	3.692704000	-2.880895000
F	-1.775686000	2.892827000	-1.242716000
C	1.453075000	2.284321000	-3.732619000
F	1.693171000	0.092033000	-2.925142000
C	0.789055000	3.514568000	-3.731252000
F	-0.945686000	4.883630000	-2.871749000
F	2.516424000	2.105455000	-4.547996000
F	1.200155000	4.514751000	-4.535362000
C	-1.902413000	-0.560104000	-2.310401000
C	-1.621982000	-1.247388000	-3.513320000
C	-3.241200000	-0.133855000	-2.143171000
C	-2.604978000	-1.493884000	-4.483210000
H	-0.607186000	-1.604060000	-3.712997000
C	-4.234211000	-0.374853000	-3.104202000

H	-3.534053000	0.413238000	-1.240761000
C	-3.922784000	-1.058732000	-4.287041000
H	-2.338530000	-2.027327000	-5.401160000
H	-5.254995000	-0.019670000	-2.930813000
H	-4.690114000	-1.244241000	-5.042661000
Mg	0.161793000	-1.250302000	1.426297000
C	2.369317000	-2.741436000	3.131013000
C	0.316245000	-2.522267000	4.326434000
C	2.381451000	-3.684767000	4.321919000
H	3.075614000	-1.907218000	3.253996000
H	2.555372000	-3.241033000	2.171458000
C	1.391135000	-3.018193000	5.276707000
H	-0.421742000	-3.304804000	4.093194000
H	-0.203872000	-1.618908000	4.671523000
H	2.027304000	-4.683706000	4.029414000
H	3.387017000	-3.786684000	4.749048000
H	0.984606000	-3.710428000	6.024810000
H	1.862518000	-2.176270000	5.803613000
O	1.023253000	-2.184600000	3.098954000

Sum of electronic and thermal Energies= -1978.245032
Sum of electronic and thermal Enthalpies= -1978.244088
Sum of electronic and thermal Free Energies= -1978.353090
Lowest vibration frequencies (/cm^-1): 21.9669 26.6189 31.8547

Transition states for the reductive elimination of Ar-(2-Py) in $[Ar_2(2\text{-}Py)Fe^{II}]^-$ (*S* = 1)

Ar = *p*-Me_2N-C_6H_4

Fe	0.466198000	0.157087000	0.088322000
C	-1.162261000	-0.755143000	-0.053345000
C	-1.731027000	-1.317677000	-1.252168000
N	-1.402624000	-1.371687000	1.164834000
C	-2.376021000	-2.543231000	-1.204221000
H	-1.616384000	-0.799238000	-2.205571000
C	-2.017384000	-2.560321000	1.169002000
C	-2.517084000	-3.213159000	0.034458000
H	-2.766406000	-2.992214000	-2.122795000
H	-2.133163000	-3.026853000	2.156960000
H	-3.020893000	-4.177759000	0.116345000
C	-1.251780000	1.065654000	0.059742000
C	-1.919350000	1.546307000	1.224619000
C	-1.514458000	1.826427000	-1.121169000
C	-2.671097000	2.720601000	1.239059000
H	-1.844688000	0.968373000	2.147960000
C	-2.260210000	3.005608000	-1.115384000
H	-1.099464000	1.501940000	-2.079806000
C	-2.845562000	3.513713000	0.074060000
H	-3.134542000	3.013440000	2.181173000
H	-2.384118000	3.531131000	-2.062208000

C	2.447147000	0.002738000	0.063549000
C	3.320396000	1.126841000	0.051214000
C	3.155035000	-1.228637000	-0.013712000
C	4.718514000	1.050129000	-0.030069000
C	4.550625000	-1.342395000	-0.101830000
C	5.383495000	-0.197146000	-0.129611000
H	2.594425000	-2.171702000	0.003248000
H	5.286769000	1.981204000	-0.021016000
H	4.982552000	-2.342974000	-0.147545000
H	2.898540000	2.138190000	0.117574000
N	6.778602000	-0.289595000	-0.286490000
N	-3.539780000	4.732903000	0.100070000
C	7.407326000	-1.572573000	-0.052238000
H	7.272307000	-1.946964000	0.983038000
H	7.017641000	-2.333302000	-0.742905000
H	8.483355000	-1.484714000	-0.245510000
C	7.583090000	0.863572000	0.059776000
H	7.496218000	1.156369000	1.126080000
H	8.636715000	0.641106000	-0.148481000
H	7.311430000	1.732823000	-0.554904000
C	-4.391493000	5.015293000	1.236645000
H	-5.221771000	4.289725000	1.352941000
H	-3.811975000	5.023890000	2.170175000
H	-4.825342000	6.015470000	1.119281000
C	-3.968322000	5.307633000	-1.157940000
H	-3.108267000	5.511186000	-1.810911000
H	-4.679106000	4.663932000	-1.714746000
H	-4.458121000	6.269228000	-0.963746000

Sum of electronic and thermal Energies= -1102.304744
Sum of electronic and thermal Enthalpies= -1102.303800
Sum of electronic and thermal Free Energies= -1102.391162
Lowest vibration frequencies (/cm^-1) : -248.1878 12.3179 18.5260

Ar = *p*-Me

Fe	0.398248000	0.064067000	0.040110000
C	-1.236768000	-0.862396000	-0.079283000
C	-1.804545000	-1.435900000	-1.270336000
N	-1.461948000	-1.467340000	1.143596000
C	-2.450352000	-2.660909000	-1.206269000
H	-1.696604000	-0.925919000	-2.228847000
C	-2.077781000	-2.654760000	1.164843000
C	-2.585829000	-3.316277000	0.038996000
H	-2.847876000	-3.117900000	-2.117451000
H	-2.187475000	-3.110916000	2.157757000
H	-3.092156000	-4.278242000	0.133395000
C	-1.314448000	0.957861000	0.018870000
C	-1.952225000	1.452810000	1.199043000
C	-1.573213000	1.705490000	-1.175732000

C	-2.689274000	2.636275000	1.198223000
H	-1.848264000	0.888184000	2.127606000
C	-2.309619000	2.890992000	-1.160034000
H	-1.153650000	1.370232000	-2.128562000
C	-2.886390000	3.396138000	0.024199000
H	-3.131457000	2.983376000	2.138321000
H	-2.442227000	3.443244000	-2.096474000
C	2.376508000	-0.017235000	0.043430000
C	3.205140000	1.136640000	0.153558000
C	3.112873000	-1.228223000	-0.114615000
C	4.607331000	1.091968000	0.114817000
C	4.512747000	-1.285776000	-0.158976000
C	5.299422000	-0.122745000	-0.045065000
H	2.570820000	-2.177884000	-0.204165000
H	5.178525000	2.022631000	0.210287000
H	5.007816000	-2.256163000	-0.281831000
H	2.741590000	2.123194000	0.280787000
C	-3.720893000	4.649937000	0.026649000
H	-3.456249000	5.314052000	-0.809304000
H	-4.798687000	4.429252000	-0.068161000
H	-3.595820000	5.220091000	0.959721000
C	6.805172000	-0.180612000	-0.109516000
H	7.258302000	0.779458000	0.176645000
H	7.214348000	-0.954166000	0.559199000
H	7.162924000	-0.420114000	-1.125086000

Sum of electronic and thermal Energies= -913.193280
Sum of electronic and thermal Enthalpies= -913.192336
Sum of electronic and thermal Free Energies= -913.269418
Lowest vibration frequencies (/cm^-1) : -256.8203 14.2851 21.9708

Ar = Ph

Fe	0.393660000	0.050798000	0.033453000
C	-1.245720000	-0.875420000	-0.077446000
C	-1.817118000	-1.460641000	-1.260095000
N	-1.463957000	-1.467311000	1.151983000
C	-2.464884000	-2.683891000	-1.179646000
H	-1.712355000	-0.961738000	-2.224683000
C	-2.080953000	-2.653580000	1.189421000
C	-2.595946000	-3.325247000	0.072842000
H	-2.867591000	-3.149801000	-2.083889000
H	-2.185885000	-3.099012000	2.187519000
H	-3.103889000	-4.284996000	0.179687000
C	-1.315113000	0.945365000	0.004544000
C	-1.952988000	1.446877000	1.184015000
C	-1.566535000	1.679600000	-1.202689000
C	-2.685485000	2.633722000	1.174279000
H	-1.854616000	0.881596000	2.112562000
C	-2.296762000	2.868928000	-1.200965000

H	-1.149697000	1.325718000	-2.149715000
C	-2.861213000	3.368938000	-0.013176000
H	-3.133758000	2.993329000	2.105762000
H	-2.431421000	3.416015000	-2.139217000
H	-3.442366000	4.293473000	-0.017590000
C	2.369985000	-0.017945000	0.045390000
C	3.186413000	1.147039000	0.157084000
C	3.107241000	-1.229533000	-0.108416000
C	4.588259000	1.114017000	0.123593000
C	4.508589000	-1.281676000	-0.147797000
C	5.265966000	-0.105832000	-0.030886000
H	2.564939000	-2.178588000	-0.200460000
H	5.158748000	2.044438000	0.216491000
H	5.015881000	-2.244910000	-0.268616000
H	6.358278000	-0.138914000	-0.059442000
H	2.709295000	2.127716000	0.277580000

Sum of electronic and thermal Energies= -834.651697
Sum of electronic and thermal Enthalpies= -834.650752
Sum of electronic and thermal Free Energies= -834.717895
Lowest vibration frequencies (/cm^-1) : -260.8678 17.0968 25.2079

Ar = *p*-CF_3-C_6H_4

Fe	0.414949000	0.013373000	0.009904000
C	-1.252892000	-0.890973000	-0.099675000
C	-1.821234000	-1.448363000	-1.291186000
N	-1.490191000	-1.476771000	1.119853000
C	-2.517267000	-2.646993000	-1.219772000
H	-1.684668000	-0.952790000	-2.253207000
C	-2.155921000	-2.636928000	1.152689000
C	-2.688325000	-3.280651000	0.028401000
H	-2.928379000	-3.095357000	-2.128518000
H	-2.285306000	-3.079639000	2.148120000
H	-3.236804000	-4.218429000	0.127390000
C	-1.250260000	0.954375000	-0.002497000
C	-1.864103000	1.453360000	1.192078000
C	-1.529632000	1.696375000	-1.199890000
C	-2.593806000	2.634368000	1.208448000
H	-1.749285000	0.887618000	2.117829000
C	-2.256663000	2.879702000	-1.182102000
H	-1.133605000	1.352957000	-2.158677000
C	-2.788577000	3.384341000	0.025972000
H	-3.017707000	2.985062000	2.151420000
H	-2.408065000	3.425880000	-2.115250000
C	2.382156000	-0.028221000	0.041632000
C	3.189356000	1.143488000	0.151654000
C	3.131656000	-1.235800000	-0.083600000
C	4.586117000	1.124863000	0.141213000
C	4.527958000	-1.282615000	-0.099266000

C	5.277606000	-0.096687000	0.021659000
H	2.602928000	-2.191666000	-0.171497000
H	5.141879000	2.061267000	0.229523000
H	5.037568000	-2.243423000	-0.199151000
H	2.707390000	2.122434000	0.253108000
C	-3.627427000	4.611552000	0.030178000
F	-3.249964000	5.525928000	-0.912205000
F	-4.963136000	4.363302000	-0.231965000
F	-3.618513000	5.265772000	1.227451000
C	6.767594000	-0.120603000	-0.060888000
F	7.364352000	0.849743000	0.691352000
F	7.310351000	-1.305177000	0.339845000
F	7.236096000	0.079185000	-1.342555000

Sum of electronic and thermal Energies= -1508.427268
Sum of electronic and thermal Enthalpies= -1508.426324
Sum of electronic and thermal Free Energies= -1508.513890
Lowest vibration frequencies (/cm^-1): -261.0878 11.2733 11.6503

Ar = *p*-CN

Fe	0.414514000	-0.038869000	-0.029920000
C	-1.261240000	-0.952942000	-0.106979000
C	-1.856059000	-1.506662000	-1.282329000
N	-1.482299000	-1.517042000	1.118683000
C	-2.588666000	-2.682812000	-1.182546000
H	-1.718169000	-1.028436000	-2.252805000
C	-2.184985000	-2.654645000	1.182556000
C	-2.759804000	-3.291127000	0.075817000
H	-3.028764000	-3.130428000	-2.077669000
H	-2.306976000	-3.080755000	2.185472000
H	-3.337022000	-4.208828000	0.196230000
C	-1.222254000	0.932111000	-0.028514000
C	-1.813537000	1.436567000	1.175668000
C	-1.526253000	1.656532000	-1.230750000
C	-2.551042000	2.608306000	1.198058000
H	-1.674420000	0.879854000	2.103662000
C	-2.260794000	2.831060000	-1.216544000
H	-1.144042000	1.303211000	-2.191390000
C	-2.785450000	3.343010000	0.002131000
H	-2.961780000	2.975389000	2.140951000
H	-2.438029000	3.374243000	-2.147050000
C	2.377143000	-0.034149000	0.002859000
C	3.147926000	1.164275000	0.105963000
C	3.157471000	-1.226676000	-0.100255000
C	4.540712000	1.188100000	0.108207000
C	4.550370000	-1.239435000	-0.103281000
C	5.270157000	-0.022667000	0.001919000
H	2.652481000	-2.195580000	-0.181655000
H	5.080615000	2.134388000	0.190342000

H	5.097901000	-2.181430000	-0.184540000
H	2.634712000	2.128497000	0.189733000
C	-3.539603000	4.539503000	0.019870000
N	-4.168813000	5.541141000	0.034228000
C	6.689627000	-0.016972000	-0.000418000
N	7.870705000	-0.012450000	-0.003315000

Sum of electronic and thermal Energies= -1019.092480
Sum of electronic and thermal Enthalpies= -1019.091536
Sum of electronic and thermal Free Energies= -1019.167522
Lowest vibration frequencies (/cm^-1): -247.9158 15.8359 21.5699

Transition states for the reductive elimination of Ar-Ar in $[Ar_2(2\text{-}Py)Fe^{II}]^-$ (*S* = 1)

Ar = *p*-Me_2N-C_6H_4

Fe	0.442836000	0.022716000	-0.006203000
C	-1.271318000	-0.834404000	-0.033479000
C	-1.884190000	-1.373862000	-1.206387000
C	-1.545813000	-1.577768000	1.159344000
C	-2.613875000	-2.562373000	-1.205230000
H	-1.765402000	-0.862099000	-2.164215000
C	-2.266899000	-2.772675000	1.163613000
H	-1.147313000	-1.232677000	2.117579000
C	-2.838840000	-3.308524000	-0.018663000
H	-3.015912000	-2.905643000	-2.158588000
H	-2.383321000	-3.286860000	2.117816000
C	-1.214580000	0.992100000	0.085399000
C	-1.759046000	1.561096000	1.276387000
C	-1.484768000	1.750373000	-1.097401000
C	-2.411962000	2.793385000	1.300949000
H	-1.666486000	1.026073000	2.224193000
C	-2.129844000	2.987821000	-1.078305000
H	-1.163745000	1.371038000	-2.071398000
C	-2.598278000	3.569902000	0.127348000
H	-2.779710000	3.149002000	2.263407000
H	-2.266718000	3.499992000	-2.030702000
C	2.389143000	-0.091640000	-0.059301000
N	3.141045000	1.067815000	0.088333000
C	3.111161000	-1.318468000	-0.249407000
C	4.480940000	1.002161000	0.050572000
C	4.502678000	-1.366310000	-0.290393000
C	5.227667000	-0.168698000	-0.135032000
H	2.546956000	-2.250377000	-0.367299000
H	5.006043000	1.959787000	0.177147000
H	5.026728000	-2.316677000	-0.439413000
H	6.319721000	-0.143771000	-0.156989000
N	-3.188460000	4.844994000	0.162449000
N	-3.637544000	-4.467998000	-0.005509000
C	-3.547701000	-5.339008000	1.148346000

H	-3.846273000	-4.810728000	2.064301000
H	-4.244873000	-6.175759000	1.019597000
H	-2.532209000	-5.756453000	1.306901000
C	-3.626014000	5.430694000	-1.087067000
H	-2.783871000	5.541988000	-1.784020000
H	-4.418991000	4.844346000	-1.594937000
H	-4.016858000	6.436821000	-0.893015000
C	-3.979416000	5.202001000	1.322008000
H	-4.858579000	4.543072000	1.472979000
H	-3.371986000	5.176315000	2.237119000
H	-4.339581000	6.231353000	1.206384000
C	-3.865978000	-5.147798000	-1.264257000
H	-2.933718000	-5.510719000	-1.743523000
H	-4.519648000	-6.011203000	-1.090735000
H	-4.384199000	-4.492984000	-1.978111000

Sum of electronic and thermal Energies= -1102.296080
Sum of electronic and thermal Enthalpies= -1102.295136
Sum of electronic and thermal Free Energies= -1102.383202
Lowest vibration frequencies (/cm^-1): -253.5750 15.6690 19.9718

Ar = *p*-Me

Fe	0.447768000	0.009935000	-0.028372000
C	-1.268642000	-0.835666000	-0.030134000
C	-1.881356000	-1.369516000	-1.210491000
C	-1.545203000	-1.563374000	1.175993000
C	-2.612521000	-2.556552000	-1.193223000
H	-1.758740000	-0.853980000	-2.165325000
C	-2.272918000	-2.753725000	1.173658000
H	-1.147613000	-1.205566000	2.129409000
C	-2.829112000	-3.290371000	-0.006595000
H	-3.031608000	-2.928295000	-2.134449000
H	-2.417032000	-3.284176000	2.121102000
C	-1.201028000	0.986958000	0.079085000
C	-1.690759000	1.564894000	1.293556000
C	-1.491920000	1.735554000	-1.109075000
C	-2.331470000	2.803597000	1.318261000
H	-1.547386000	1.039801000	2.240346000
C	-2.126835000	2.976963000	-1.066500000
H	-1.181519000	1.349744000	-2.083788000
C	-2.567131000	3.551059000	0.144504000
H	-2.659913000	3.206342000	2.282323000
H	-2.287176000	3.519325000	-2.004446000
C	2.398508000	-0.106440000	-0.092125000
N	3.135374000	1.057619000	0.053095000
C	3.124822000	-1.328096000	-0.279516000
C	4.476365000	1.005012000	0.015658000
C	4.517419000	-1.363818000	-0.319327000
C	5.230679000	-0.160840000	-0.166773000

H	2.567345000	-2.263884000	-0.395807000
H	4.992627000	1.967128000	0.139880000
H	5.049710000	-2.309657000	-0.465774000
H	6.322402000	-0.127523000	-0.188506000
C	-3.660372000	-4.546105000	0.006398000
H	-3.537891000	-5.124627000	-0.921901000
H	-3.389452000	-5.202219000	0.846897000
H	-4.738876000	-4.329416000	0.105153000
C	-3.301232000	4.865491000	0.176293000
H	-2.990506000	5.523096000	-0.649290000
H	-4.393719000	4.732680000	0.084109000
H	-3.125724000	5.406290000	1.118373000

Sum of electronic and thermal Energies= -913.185996
Sum of electronic and thermal Enthalpies= -913.185052
Sum of electronic and thermal Free Energies= -913.261843
Lowest vibration frequencies (/cm^-1): -261.8072 20.8509 27.7444

Ar = Ph

Fe	0.444323000	0.005895000	-0.030353000
C	-1.271624000	-0.837829000	-0.033076000
C	-1.895742000	-1.362705000	-1.213612000
C	-1.535405000	-1.564560000	1.179382000
C	-2.626113000	-2.550582000	-1.195431000
H	-1.784838000	-0.836626000	-2.163701000
C	-2.261401000	-2.755663000	1.183574000
H	-1.131657000	-1.200995000	2.127828000
C	-2.815737000	-3.272220000	-0.002014000
H	-3.059860000	-2.922225000	-2.129008000
H	-2.402442000	-3.290792000	2.127851000
C	-1.202553000	0.983385000	0.079041000
C	-1.700116000	1.554036000	1.295878000
C	-1.480693000	1.731268000	-1.115224000
C	-2.333968000	2.796376000	1.321714000
H	-1.570192000	1.017882000	2.237973000
C	-2.108564000	2.976536000	-1.077067000
H	-1.168575000	1.338006000	-2.086208000
C	-2.542398000	3.531632000	0.140268000
H	-2.673771000	3.201121000	2.279996000
H	-2.264906000	3.524823000	-2.011218000
C	2.396135000	-0.109894000	-0.093166000
N	3.126835000	1.055647000	0.057598000
C	3.125089000	-1.328440000	-0.284125000
C	4.468223000	1.008656000	0.021937000
C	4.518083000	-1.358708000	-0.322173000
C	5.226287000	-0.154029000	-0.164030000
H	2.570785000	-2.265448000	-0.404644000
H	4.980580000	1.972086000	0.150623000
H	5.054115000	-2.301896000	-0.471386000

H	6.317878000	-0.116886000	-0.184154000
H	-3.045940000	4.500183000	0.165545000
H	-3.397729000	-4.195988000	0.007697000

Sum of electronic and thermal Energies= -834.644636
Sum of electronic and thermal Enthalpies= -834.643692
Sum of electronic and thermal Free Energies= -834.710474
Lowest vibration frequencies (/cm^-1): -276.7247 24.8885 29.8627

Ar = *p*-CF_3-C_6H_4

Fe	0.497107000	-0.047607000	-0.016809000
C	-1.211753000	-0.892953000	-0.019498000
C	-1.735689000	-1.441275000	-1.238922000
C	-1.642573000	-1.554390000	1.181166000
C	-2.526446000	-2.582688000	-1.260610000
H	-1.489832000	-0.976518000	-2.195304000
C	-2.430397000	-2.696573000	1.157900000
H	-1.318998000	-1.180166000	2.154211000
C	-2.879119000	-3.246252000	-0.064730000
H	-2.869813000	-2.970414000	-2.221344000
H	-2.696881000	-3.175920000	2.102120000
C	-1.120268000	0.964931000	0.058245000
C	-1.521948000	1.564416000	1.297498000
C	-1.525877000	1.669918000	-1.124080000
C	-2.181422000	2.786304000	1.351155000
H	-1.285299000	1.073635000	2.243078000
C	-2.182032000	2.892093000	-1.070099000
H	-1.289492000	1.262724000	-2.108861000
C	-2.513654000	3.483615000	0.169708000
H	-2.434695000	3.209621000	2.324581000
H	-2.435192000	3.400332000	-2.002754000
C	2.460787000	-0.150939000	-0.067025000
N	3.122665000	1.054898000	-0.013560000
C	3.238838000	-1.344147000	-0.160907000
C	4.465305000	1.077270000	-0.051371000
C	4.632927000	-1.305533000	-0.199658000
C	5.276995000	-0.059314000	-0.143567000
H	2.729987000	-2.312550000	-0.204649000
H	4.926685000	2.072405000	-0.005013000
H	5.216781000	-2.228517000	-0.272546000
H	6.365271000	0.029316000	-0.170769000
C	-3.273184000	4.761647000	0.212367000
F	-2.870699000	5.656700000	-0.741154000
F	-4.627999000	4.599554000	-0.007854000
F	-3.178514000	5.405715000	1.408837000
C	-3.778553000	-4.428878000	-0.073928000
F	-5.104249000	-4.111911000	0.160931000
F	-3.777374000	-5.098806000	-1.261091000
F	-3.466314000	-5.349644000	0.888900000

Sum of electronic and thermal Energies= -1508.421994
Sum of electronic and thermal Enthalpies= -1508.421050
Sum of electronic and thermal Free Energies= -1508.504728
Lowest vibration frequencies (/cm^-1): -273.2768 -12.0608 19.8791

Ar = *p*-CN

Fe	0.483200000	-0.049706000	-0.034170000
C	-1.204031000	-0.922713000	-0.020686000
C	-1.744785000	-1.454339000	-1.239977000
C	-1.648311000	-1.563230000	1.185320000
C	-2.580156000	-2.558819000	-1.260127000
H	-1.477461000	-1.002261000	-2.196826000
C	-2.482271000	-2.668781000	1.173727000
H	-1.302263000	-1.198245000	2.154124000
C	-2.968530000	-3.199943000	-0.052114000
H	-2.943808000	-2.946533000	-2.213875000
H	-2.768475000	-3.142596000	2.114882000
C	-1.109090000	0.992218000	0.057083000
C	-1.493462000	1.578822000	1.307417000
C	-1.554549000	1.681832000	-1.118236000
C	-2.185214000	2.777422000	1.380397000
H	-1.217251000	1.093706000	2.245337000
C	-2.246609000	2.880718000	-1.055578000
H	-1.325093000	1.278677000	-2.106309000
C	-2.577154000	3.461444000	0.198323000
H	-2.430480000	3.205297000	2.354441000
H	-2.539444000	3.388531000	-1.976606000
C	2.451608000	-0.173581000	-0.098015000
N	3.099448000	1.035776000	-0.053651000
C	3.231970000	-1.362141000	-0.191578000
C	4.441942000	1.070851000	-0.100206000
C	4.626022000	-1.311899000	-0.239509000
C	5.259535000	-0.061015000	-0.193134000
H	2.729197000	-2.333647000	-0.227953000
H	4.895089000	2.069538000	-0.061024000
H	5.216881000	-2.230106000	-0.312454000
H	6.346833000	0.035167000	-0.228164000
C	-3.822280000	-4.327541000	-0.068204000
N	-4.533069000	-5.272842000	-0.081064000
C	-3.287049000	4.684061000	0.268080000
N	-3.878035000	5.706391000	0.325881000

Sum of electronic and thermal Energies= -1019.087113
Sum of electronic and thermal Enthalpies= -1019.086169
Sum of electronic and thermal Free Energies= -1019.162566
Lowest vibration frequencies (/cm^-1): -269.9425 23.4734 25.6288

Transition state for the reductive elimination of Ph-C_6F_5 in $[Ph_2(C_6F_5)Fe^{II}]^-$ (*S* = 1)

Fe	0.465107000	-0.028878000	-0.000282000
C	-1.240533000	-0.986411000	-0.020506000
C	-1.704717000	-1.628043000	-1.218431000
C	-1.671816000	-1.695619000	1.151361000
C	-2.616652000	-2.667754000	-1.251791000
F	-1.112841000	-1.291815000	-2.409070000
C	-2.581572000	-2.737439000	1.151724000
C	-3.101862000	-3.221735000	-0.057884000
F	-3.008655000	-3.209483000	-2.436590000
F	-2.937076000	-3.349414000	2.313652000
F	-4.191120000	-4.037568000	-0.065638000
C	-1.327848000	0.754795000	0.028653000
C	-1.713571000	1.376336000	1.262169000
C	-1.690107000	1.452508000	-1.171016000
C	-2.317216000	2.633376000	1.285443000
H	-1.515100000	0.876217000	2.209024000
C	-2.292449000	2.709813000	-1.127240000
H	-1.474142000	1.012762000	-2.143773000
C	-2.606738000	3.324566000	0.096563000
H	-2.569306000	3.081401000	2.250867000
H	-2.524697000	3.218141000	-2.067434000
H	-3.082695000	4.306587000	0.122855000
C	2.445694000	0.044230000	-0.012021000
C	3.149398000	1.280930000	-0.072323000
C	3.280943000	-1.106889000	0.036180000
C	4.549271000	1.367642000	-0.084114000
C	4.682745000	-1.039289000	0.024696000
C	5.330334000	0.203010000	-0.035863000
H	2.822356000	-2.101700000	0.083942000
H	5.035751000	2.347343000	-0.132304000
H	5.274302000	-1.959816000	0.062766000
H	6.421694000	0.263036000	-0.045884000
H	2.586016000	2.221403000	-0.112944000
F	-1.046568000	-1.424080000	2.342151000

Sum of electronic and thermal Energies= -1314.568982
Sum of electronic and thermal Enthalpies= -1314.568038
Sum of electronic and thermal Free Energies= -1314.643774
Lowest vibration frequencies (/cm^-1): -288.9180 -23.0470 19.0476

Transition state for the reductive elimination of Ph-Ph in $[Ph_2(C_6F_5)Fe^{II}]^-$ (*S* = 1)

Fe	0.362473000	-0.000864000	0.010432000
C	-1.318890000	-0.907432000	-0.000689000
C	-1.616192000	-1.562310000	-1.243540000
C	-1.825613000	-1.549782000	1.176662000
C	-2.270768000	-2.793497000	-1.288366000
H	-1.299659000	-1.109636000	-2.186197000
C	-2.484885000	-2.777375000	1.118538000

H	-1.681061000	-1.084513000	2.153434000
C	-2.712817000	-3.422520000	-0.110807000
H	-2.442436000	-3.271543000	-2.257541000
H	-2.829491000	-3.241415000	2.047564000
H	-3.237806000	-4.378951000	-0.151466000
C	-1.319091000	0.905065000	0.010368000
C	-1.626988000	1.560092000	1.250530000
C	-1.815896000	1.547069000	-1.171429000
C	-2.281853000	2.791375000	1.289405000
H	-1.318569000	1.107550000	2.195927000
C	-2.475269000	2.774841000	-1.119300000
H	-1.663129000	1.081484000	-2.146801000
C	-2.713500000	3.420299000	0.107937000
H	-2.461960000	3.269654000	2.256934000
H	-2.811745000	3.238748000	-2.051370000
H	-3.238579000	4.376872000	0.143859000
C	2.362125000	-0.000978000	0.000055000
C	3.133349000	1.167568000	-0.057137000
C	3.133828000	-1.170083000	0.034952000
C	4.527956000	1.203085000	-0.081957000
C	4.528452000	-1.206800000	0.013291000
C	5.239656000	-0.002184000	-0.046362000
F	2.505797000	-2.387428000	0.094776000
F	5.213568000	2.369388000	-0.139817000
F	5.214613000	-2.373727000	0.047536000
F	6.589370000	-0.002840000	-0.069459000
F	2.504806000	2.385607000	-0.092541000

Sum of electronic and thermal Energies= -1314.587819
Sum of electronic and thermal Enthalpies= -1314.586875
Sum of electronic and thermal Free Energies= -1314.659594
Lowest vibration frequencies (/cm^-1): -266.2792 -54.8177 -2.1625

Transition state for the reductive elimination of Ph-Ar' in [$Ph_3Ar'Fe^{II}Mg(THF)$] (*S* = 1)

Ar' = 2-Py

Fe	-0.806748000	-0.331536000	-1.165533000
C	-0.200722000	0.859430000	0.401232000
C	1.215747000	1.064102000	0.532302000
C	-0.979686000	1.790479000	1.162679000
C	1.783571000	2.113555000	1.265500000
H	1.904791000	0.385700000	0.014656000
C	-0.425068000	2.833783000	1.913211000
H	-2.071649000	1.711868000	1.134789000
C	0.966018000	3.014342000	1.966215000
H	2.871679000	2.228042000	1.295610000
H	-1.082585000	3.519559000	2.457126000
H	1.402623000	3.831012000	2.545656000
C	-0.683578000	-2.376838000	-0.810624000

C	-1.783312000	-3.290402000	-0.864217000
C	0.589746000	-2.979451000	-1.066914000
C	-1.638480000	-4.645730000	-1.186357000
H	-2.795947000	-2.920093000	-0.674461000
C	0.746534000	-4.330054000	-1.403358000
H	1.494311000	-2.361285000	-1.030835000
C	-0.370411000	-5.177645000	-1.465259000
H	-2.520656000	-5.291772000	-1.230853000
H	1.743784000	-4.726734000	-1.616140000
H	-0.254146000	-6.233255000	-1.721608000
C	-0.465249000	0.275717000	-3.036659000
C	0.641699000	1.147296000	-3.219247000
C	-0.834442000	-0.532472000	-4.143014000
C	1.374506000	1.157039000	-4.409933000
H	0.942884000	1.817182000	-2.410909000
C	-0.095032000	-0.528865000	-5.329295000
H	-1.717328000	-1.170392000	-4.061810000
C	1.019274000	0.312452000	-5.473293000
H	2.232608000	1.828113000	-4.510132000
H	-0.394630000	-1.182099000	-6.153998000
H	1.590656000	0.322192000	-6.404077000
C	-1.946078000	0.888970000	-2.031337000
N	-3.005090000	0.026916000	-2.124842000
C	-2.156387000	2.299562000	-2.167921000
C	-4.245433000	0.515677000	-2.240426000
C	-3.447593000	2.777028000	-2.327890000
H	-1.312593000	2.987968000	-2.121982000
C	-4.538200000	1.879787000	-2.358347000
H	-5.052486000	-0.227428000	-2.262526000
H	-3.620697000	3.853369000	-2.421070000
H	-5.563932000	2.224271000	-2.496664000
Mg	-0.638268000	-1.255646000	1.193372000
C	-0.851646000	-1.096418000	4.344315000
C	-1.022889000	-3.338535000	3.545456000
C	-1.347969000	-1.987471000	5.468721000
H	-1.492412000	-0.228731000	4.144344000
H	0.181727000	-0.756197000	4.510487000
C	-0.820289000	-3.359779000	5.050355000
H	-0.287185000	-3.930436000	2.985898000
H	-2.037827000	-3.652946000	3.259909000
H	-0.967923000	-1.660513000	6.444880000
H	-2.446866000	-1.987233000	5.507959000
H	0.246357000	-3.458912000	5.298160000
H	-1.361980000	-4.189761000	5.521423000
O	-0.862429000	-1.941619000	3.157601000

Sum of electronic and thermal Energies= -1498.298206
Sum of electronic and thermal Enthalpies= -1498.297262
Sum of electronic and thermal Free Energies= -1498.395454

Lowest vibration frequencies (/cm^-1) : -271.2634 15.8238 21.1921

Ar' = C_6F_5

Fe	-0.630065000	-0.088123000	-1.044347000
C	0.469099000	0.913965000	0.366434000
C	1.887624000	1.102721000	0.341865000
C	-0.222050000	1.804006000	1.250451000
C	2.540172000	2.097876000	1.079908000
H	2.503544000	0.464348000	-0.299623000
C	0.419256000	2.810640000	1.982296000
H	-1.309666000	1.718199000	1.356408000
C	1.810917000	2.967213000	1.903750000
H	3.627114000	2.199367000	1.008754000
H	-0.169239000	3.475301000	2.621469000
H	2.316963000	3.746160000	2.478242000
C	-1.219083000	-2.041963000	-0.593821000
C	-2.487698000	-2.383106000	-0.030791000
C	-0.540638000	-3.137496000	-1.212132000
C	-3.045280000	-3.665750000	-0.115836000
H	-3.077881000	-1.608379000	0.472620000
C	-1.088271000	-4.422457000	-1.310356000
H	0.448693000	-2.974470000	-1.656298000
C	-2.349314000	-4.697663000	-0.760863000
H	-4.028550000	-3.862725000	0.321539000
H	-0.529952000	-5.215222000	-1.816973000
H	-2.778656000	-5.699753000	-0.829153000
C	-0.480095000	1.232014000	-2.529099000
C	-0.876808000	2.613306000	-2.557685000
C	0.767980000	1.050063000	-3.221727000
C	-0.262870000	3.594931000	-3.315103000
F	-1.878719000	3.025553000	-1.723234000
C	1.418580000	2.008159000	-3.970936000
F	1.435317000	-0.138685000	-3.008204000
C	0.889254000	3.305344000	-4.060766000
F	-0.737782000	4.869563000	-3.312950000
F	2.596360000	1.730519000	-4.592414000
F	1.341959000	4.174664000	-5.002637000
C	-1.700673000	0.116004000	-2.878287000
C	-1.535988000	-0.709142000	-4.022567000
C	-3.039195000	0.387940000	-2.483696000
C	-2.626242000	-1.249636000	-4.701993000
H	-0.532617000	-0.922216000	-4.394215000
C	-4.131938000	-0.155478000	-3.163323000
H	-3.232824000	1.032197000	-1.624902000
C	-3.937509000	-0.978922000	-4.279936000
H	-2.454264000	-1.887077000	-5.573380000
H	-5.144592000	0.065489000	-2.815796000
H	-4.790840000	-1.396067000	-4.818403000

Mg	0.079206000	-1.233800000	1.101267000
C	2.282398000	-2.676814000	2.832062000
C	0.305093000	-2.267083000	4.102571000
C	2.386994000	-3.396862000	4.166237000
H	2.987104000	-1.835172000	2.757648000
H	2.405765000	-3.335556000	1.961991000
C	1.445382000	-2.581877000	5.053457000
H	-0.427928000	-3.086747000	4.047795000
H	-0.214941000	-1.325419000	4.323033000
H	2.034294000	-4.434144000	4.075752000
H	3.418994000	-3.414438000	4.538618000
H	1.100296000	-3.136697000	5.934992000
H	1.932540000	-1.656984000	5.394005000
O	0.931024000	-2.132705000	2.795965000

Sum of electronic and thermal Energies= -1978.215812
Sum of electronic and thermal Enthalpies= -1978.214868
Sum of electronic and thermal Free Energies= -1978.322479
Lowest vibration frequencies (/cm^-1) : -253.7097 19.3277 23.9729

Transition state for the reductive elimination of Ph-Ph in [$Ph_3Ar'Fe^{II}Mg(THF)$] (*S* = 1)

Ar' = 2-Py

Fe	-0.537946000	-0.168696000	-1.160746000
C	0.128359000	0.670772000	0.573849000
C	1.538164000	0.541584000	0.811609000
C	-0.455277000	1.853641000	1.131588000
C	2.294162000	1.516797000	1.475473000
H	2.064139000	-0.342069000	0.433406000
C	0.292710000	2.833125000	1.791766000
H	-1.530572000	2.022665000	1.019173000
C	1.678209000	2.675989000	1.968813000
H	3.370774000	1.373121000	1.607647000
H	-0.205057000	3.728807000	2.175889000
H	2.262570000	3.439723000	2.486998000
C	0.116165000	-2.106695000	-1.193849000
N	0.156777000	-2.807422000	0.012290000
C	0.602708000	-2.831512000	-2.321486000
C	0.609915000	-4.075574000	0.109104000
C	1.076912000	-4.137754000	-2.231336000
H	0.607651000	-2.334054000	-3.291483000
C	1.081973000	-4.790970000	-0.983448000
H	0.588726000	-4.521225000	1.109078000
H	1.450496000	-4.654765000	-3.120526000
H	1.444528000	-5.813094000	-0.866046000
C	-0.523870000	0.172396000	-3.092222000
C	0.465488000	1.189120000	-3.286212000
C	-0.919961000	-0.528261000	-4.268537000
C	1.083058000	1.400432000	-4.521172000

H	0.770380000	1.816700000	-2.441425000
C	-0.325646000	-0.290704000	-5.510016000
H	-1.713890000	-1.275867000	-4.204595000
C	0.693713000	0.665050000	-5.653479000
H	1.865192000	2.160870000	-4.606444000
H	-0.660201000	-0.863407000	-6.380621000
H	1.154875000	0.849544000	-6.625983000
C	-2.038934000	0.660166000	-2.048629000
C	-3.093840000	-0.299646000	-1.985222000
C	-2.422456000	2.025645000	-2.133240000
C	-4.435999000	0.090588000	-1.926552000
C	-3.764827000	2.407843000	-2.093424000
H	-1.653149000	2.794459000	-2.234295000
C	-4.785942000	1.448283000	-1.979544000
H	-5.217402000	-0.672609000	-1.863041000
H	-4.022517000	3.469417000	-2.152312000
H	-5.834366000	1.753198000	-1.961296000
Mg	-0.723679000	-1.337283000	1.183099000
C	-0.587734000	-2.108792000	4.283179000
C	-2.806290000	-2.212470000	3.425977000
C	-1.565674000	-2.170619000	5.444636000
H	0.094589000	-1.249496000	4.322910000
H	-0.001013000	-3.035102000	4.185292000
C	-2.783648000	-2.841100000	4.808538000
H	-3.231896000	-2.859920000	2.647587000
H	-3.332412000	-1.244974000	3.422528000
H	-1.157587000	-2.735955000	6.292051000
H	-1.817153000	-1.158810000	5.793964000
H	-2.637507000	-3.928619000	4.738132000
H	-3.714257000	-2.652595000	5.358790000
O	-1.412262000	-1.974751000	3.092053000
H	-2.852603000	-1.367255000	-1.994524000

Sum of electronic and thermal Energies= -1498.307825
Sum of electronic and thermal Enthalpies= -1498.306880
Sum of electronic and thermal Free Energies= -1498.404688
Lowest vibration frequencies (/cm^-1) : -255.4885 17.4630 26.4944

Ar' = C_6F_5

Fe	-0.944778000	-0.040499000	-1.024677000
C	-0.511251000	1.121903000	0.628425000
C	0.837900000	1.536272000	0.879453000
C	-1.501289000	1.956187000	1.240055000
C	1.163447000	2.693522000	1.598432000
H	1.666092000	0.949119000	0.466756000
C	-1.186927000	3.116517000	1.957167000
H	-2.560975000	1.708956000	1.116440000
C	0.151128000	3.498657000	2.141095000
H	2.212771000	2.973205000	1.731199000

H	-1.989825000	3.730520000	2.375870000
H	0.399707000	4.403027000	2.700938000
C	-0.701115000	-2.113131000	-0.758304000
C	-1.751211000	-3.051517000	-0.771415000
C	0.557088000	-2.714414000	-0.971383000
C	-1.613419000	-4.412372000	-1.041656000
F	-3.022563000	-2.627490000	-0.485263000
C	0.765119000	-4.064750000	-1.244036000
F	1.675169000	-1.933139000	-0.919693000
C	-0.336674000	-4.929406000	-1.290201000
F	-2.677119000	-5.244601000	-1.058238000
F	2.000199000	-4.562866000	-1.466012000
F	-0.167064000	-6.239010000	-1.545627000
C	-0.497720000	-0.000761000	-2.924391000
C	0.643536000	0.838460000	-3.077175000
C	-0.742234000	-0.932206000	-3.968711000
C	1.524917000	0.690737000	-4.153499000
H	0.858162000	1.614327000	-2.336774000
C	0.129355000	-1.062804000	-5.051039000
H	-1.625898000	-1.571558000	-3.927131000
C	1.278387000	-0.260564000	-5.153411000
H	2.405457000	1.336414000	-4.218061000
H	-0.088721000	-1.802271000	-5.827221000
H	1.954109000	-0.362846000	-6.005055000
C	-2.113352000	0.874207000	-2.280192000
C	-3.350403000	0.200671000	-2.485538000
C	-2.112027000	2.279891000	-2.495496000
C	-4.521521000	0.900688000	-2.800559000
C	-3.280308000	2.970396000	-2.819920000
H	-1.182301000	2.843049000	-2.400790000
C	-4.501856000	2.291759000	-2.967833000
H	-5.455843000	0.347242000	-2.932258000
H	-3.238051000	4.053872000	-2.963177000
H	-5.412006000	2.834692000	-3.230834000
Mg	-0.735268000	-1.039135000	1.343279000
C	0.500279000	-2.025048000	4.086765000
C	-1.646679000	-2.986107000	3.675134000
C	-0.010714000	-2.666779000	5.364294000
H	0.780799000	-0.969928000	4.199909000
H	1.341616000	-2.583747000	3.649217000
C	-0.987774000	-3.715681000	4.833098000
H	-1.967740000	-3.642489000	2.856003000
H	-2.495932000	-2.368222000	4.004485000
H	0.805153000	-3.101269000	5.955672000
H	-0.533242000	-1.926771000	5.987406000
H	-0.448884000	-4.604505000	4.475033000
H	-1.722075000	-4.035785000	5.582902000
O	-0.618291000	-2.094350000	3.155258000

H -3.403220000 -0.885373000 -2.404239000
Sum of electronic and thermal Energies= -1978.226018
Sum of electronic and thermal Enthalpies= -1978.225074
Sum of electronic and thermal Free Energies= -1978.330188
Lowest vibration frequencies (/cm^-1) : -307.7219 -10.7402 17.4625

Transition state for the reductive elimination of Ph-Ph in $[Ph_3Fe^{II}]^-$ (S = 1)

Fe	0.392922000	0.005251000	-0.002010000
C	-1.295081000	-0.897295000	-0.031324000
C	-1.851222000	-1.485154000	-1.217652000
C	-1.570354000	-1.603982000	1.191789000
C	-2.522997000	-2.706812000	-1.191511000
H	-1.731647000	-0.980015000	-2.178074000
C	-2.236651000	-2.829339000	1.204322000
C	-2.720347000	-3.405388000	0.014934000
H	-2.902295000	-3.125339000	-2.128996000
H	-2.384584000	-3.346259000	2.157736000
H	-3.254631000	-4.357499000	0.030422000
C	-1.294631000	0.908433000	0.029616000
C	-1.849070000	1.496682000	1.216544000
C	-1.571079000	1.615093000	-1.193258000
C	-2.520445000	2.718579000	1.191039000
H	-1.728507000	0.991631000	2.176890000
C	-2.236939000	2.840679000	-1.205157000
H	-1.222631000	1.205983000	-2.145112000
C	-2.719002000	3.417058000	-0.015263000
H	-2.898453000	3.137382000	2.128922000
H	-2.385811000	3.357536000	-2.158460000
H	-3.252958000	4.369361000	-0.030236000
C	2.365780000	0.005405000	-0.004305000
C	3.145995000	1.199180000	0.074319000
C	3.146359000	-1.187982000	-0.085108000
C	4.548423000	1.209177000	0.074444000
C	4.548788000	-1.197263000	-0.089386000
C	5.267959000	0.006137000	-0.008535000
H	2.636874000	-2.157812000	-0.148207000
H	5.087217000	2.160878000	0.138037000
H	5.087875000	-2.148696000	-0.154509000
H	6.361135000	0.006414000	-0.010156000
H	2.636203000	2.168750000	0.138918000
H	-1.220663000	-1.195111000	2.143286000

Sum of electronic and thermal Energies= -818.598779
Sum of electronic and thermal Enthalpies= -818.597834
Sum of electronic and thermal Free Energies= -818.663330
Lowest vibration frequencies (/cm^-1) : -284.7438 -19.0560 17.4641

Ph-Ph

C	0.000000000	0.000000000	-0.742635000
C	-0.452791000	-1.120649000	-1.468187000
C	0.452791000	1.120649000	-1.468187000
C	-0.453435000	-1.120620000	-2.866712000
C	0.453435000	1.120620000	-2.866712000
C	0.000000000	0.000000000	-3.573257000
H	-0.830537000	-1.993017000	-0.931794000
H	0.830537000	1.993017000	-0.931794000
H	-0.817863000	-1.997618000	-3.405788000
H	0.817863000	1.997618000	-3.405788000
H	0.000000000	0.000000000	-4.664972000
C	0.000000000	0.000000000	0.742635000
C	-0.452791000	1.120649000	1.468187000
C	0.452791000	-1.120649000	1.468187000
C	-0.453435000	1.120620000	2.866712000
C	0.453435000	-1.120620000	2.866712000
C	0.000000000	0.000000000	3.573257000
H	-0.830537000	1.993017000	0.931794000
H	0.830537000	-1.993017000	0.931794000
H	-0.817863000	1.997618000	3.405788000
H	0.817863000	-1.997618000	3.405788000
H	0.000000000	0.000000000	4.664972000

Sum of electronic and thermal Energies= -462.934463
Sum of electronic and thermal Enthalpies= -462.933519
Sum of electronic and thermal Free Energies= -462.977202
Lowest vibration frequencies (/cm^-1) : 67.5411 89.1712 115.7508

Ph-(2-Py)

C	0.765480000	0.018071000	-0.002748000
N	1.373145000	-1.137522000	-0.349995000
C	1.501144000	1.163075000	0.364130000
C	2.711967000	-1.167187000	-0.358457000
C	2.895744000	1.113354000	0.344673000
C	3.525008000	-0.076724000	-0.030533000
H	0.991894000	2.072226000	0.683676000
H	3.162303000	-2.121710000	-0.648722000
H	3.481226000	1.989689000	0.629518000
H	4.611820000	-0.163993000	-0.061519000
C	-0.721916000	0.016595000	-0.004521000
C	-1.459864000	1.170463000	-0.334352000
C	-1.427889000	-1.158037000	0.322465000
C	-2.858299000	1.151738000	-0.329821000
C	-2.825019000	-1.174045000	0.334387000
C	-3.547431000	-0.018978000	0.008395000
H	-0.942610000	2.085710000	-0.626148000
H	-0.868421000	-2.058488000	0.576904000
H	-3.410419000	2.053921000	-0.600644000
H	-3.352293000	-2.092312000	0.601179000

H	-4.639076000	-0.032319000	0.014017000

Sum of electronic and thermal Energies= -478.980263
Sum of electronic and thermal Enthalpies= -478.979319
Sum of electronic and thermal Free Energies= -479.024397
Lowest vibration frequencies (/cm^-1) : 49.7017 88.2158 126.2633

[PhFe^0(η^6-PhPh)]$^-$ (*S* = 1)

Fe	0.866809000	1.290114000	-0.181823000
C	-1.267371000	1.010996000	0.185328000
C	-0.584212000	1.477413000	1.360793000
C	-1.002012000	1.695321000	-1.052357000
C	0.251888000	2.631110000	1.324644000
H	-0.719691000	0.953112000	2.309229000
C	-0.179518000	2.862593000	-1.092201000
H	-1.422031000	1.310862000	-1.984182000
C	0.448579000	3.335019000	0.098257000
H	0.758491000	2.962477000	2.234927000
H	0.024360000	3.350064000	-2.048702000
H	1.135233000	4.183987000	0.056181000
C	-2.157048000	-0.165088000	0.230505000
C	-1.929057000	-1.250362000	1.111004000
C	-3.296553000	-0.248064000	-0.605532000
C	-2.794179000	-2.346100000	1.158951000
H	-1.040485000	-1.248884000	1.743313000
C	-4.155408000	-1.351253000	-0.567600000
H	-3.526312000	0.579203000	-1.279625000
C	-3.915608000	-2.409887000	0.318377000
H	-2.580556000	-3.167894000	1.847162000
H	-5.026892000	-1.376400000	-1.226900000
H	-4.587288000	-3.270316000	0.352102000
C	2.005576000	-0.356793000	-0.173584000
C	3.053250000	-0.571097000	0.771729000
C	1.953925000	-1.350319000	-1.196108000
C	3.949960000	-1.649656000	0.714042000
C	2.838529000	-2.437373000	-1.274137000
C	3.850569000	-2.598113000	-0.315329000
H	3.173854000	0.134319000	1.603425000
H	1.177870000	-1.281028000	-1.967784000
H	4.728968000	-1.755381000	1.477354000
H	2.737422000	-3.167825000	-2.084557000
H	4.540878000	-3.444677000	-0.365829000

Sum of electronic and thermal Energies= -818.659080
Sum of electronic and thermal Enthalpies= -818.658135
Sum of electronic and thermal Free Energies= -818.722053
Lowest vibration frequencies (/cm^-1) : 27.3367 48.2356 52.0223

Ph$_2$Fe^0(η^6-PhPh)•(Mg(THF)) (*S* = 0)

Fe	-0.532101000	0.458813000	-1.104845000

C	0.289671000	1.411905000	0.478561000
C	1.459021000	0.971865000	1.179741000
C	-0.167619000	2.696111000	0.931941000
C	2.126775000	1.731885000	2.151828000
H	1.883497000	-0.004747000	0.946592000
C	0.489766000	3.469896000	1.895749000
H	-1.082131000	3.112041000	0.502905000
C	1.657525000	3.000213000	2.516357000
H	3.029937000	1.328426000	2.621100000
H	0.081672000	4.448040000	2.169922000
H	2.176709000	3.599989000	3.267481000
C	-0.061384000	-1.397550000	-0.564560000
C	-0.992927000	-2.469285000	-0.376279000
C	1.298176000	-1.839423000	-0.588743000
C	-0.622966000	-3.815146000	-0.199819000
H	-2.069366000	-2.252253000	-0.409087000
C	1.682655000	-3.175722000	-0.437407000
H	2.086546000	-1.111443000	-0.789815000
C	0.725186000	-4.181448000	-0.224070000
H	-1.397384000	-4.575113000	-0.058084000
H	2.743246000	-3.440133000	-0.494254000
H	1.026644000	-5.223526000	-0.095017000
C	0.479931000	0.819594000	-2.993269000
C	-0.461459000	-0.259379000	-3.054353000
C	-0.021465000	2.017105000	-2.388875000
C	-1.812611000	-0.147231000	-2.627084000
H	-0.114298000	-1.245921000	-3.365088000
C	-1.381522000	2.168219000	-2.006621000
H	0.645420000	2.865626000	-2.227254000
C	-2.273510000	1.061421000	-2.034828000
H	-2.447715000	-1.034488000	-2.645086000
H	-1.697422000	3.110059000	-1.556812000
H	-3.314204000	1.173808000	-1.719583000
Mg	-1.282211000	-0.174911000	1.090623000
C	1.847489000	0.699361000	-3.527843000
C	2.130650000	-0.164805000	-4.613709000
C	2.934078000	1.435353000	-2.995198000
C	3.424582000	-0.295673000	-5.127312000
H	1.319185000	-0.725319000	-5.080822000
C	4.223838000	1.310802000	-3.514379000
H	2.772821000	2.092372000	-2.139971000
C	4.484850000	0.441173000	-4.584621000
H	3.601321000	-0.970280000	-5.968796000
H	5.037474000	1.890010000	-3.070709000
H	5.494961000	0.342157000	-4.987112000
O	-2.526153000	-0.571721000	2.795566000
C	-2.508357000	0.192262000	4.034247000
C	-3.534613000	-1.615626000	2.872979000

C	-3.769004000	-0.218379000	4.775460000
C	-3.942025000	-1.672112000	4.335576000
H	-4.374211000	-1.327629000	2.221474000
H	-2.471780000	1.257879000	3.773487000
H	-4.625174000	0.390772000	4.451313000
H	-1.596068000	-0.077211000	4.588489000
H	-3.658518000	-0.107391000	5.861713000
H	-4.968649000	-2.039588000	4.459903000
H	-3.268110000	-2.332195000	4.900685000
H	-3.088298000	-2.545817000	2.499476000

Sum of electronic and thermal Energies= -1482.303057
Sum of electronic and thermal Enthalpies= -1482.302113
Sum of electronic and thermal Free Energies= -1482.395358
Lowest vibration frequencies (/cm^-1) : 19.0179 22.4478 30.3120

6. EPR spectroscopy

X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with a Bruker ER 4116DM X band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC 503 temperature control system.

Speciation of iron(I) (S = 1/2) has been performed by double integration of the 250-370 mT area and was performed against a methanol solution of $CuSO_4$ whose signal was double-integrated on the same field area.

EPR analysis of solutions of $Fe(acac)_3$ reduced with ArMgBr (Ar = *p*-F-C_6F_4 or *p*-MeO-C_6H_4) followed by addition of C_6F_5Cl or 2-PyCl:

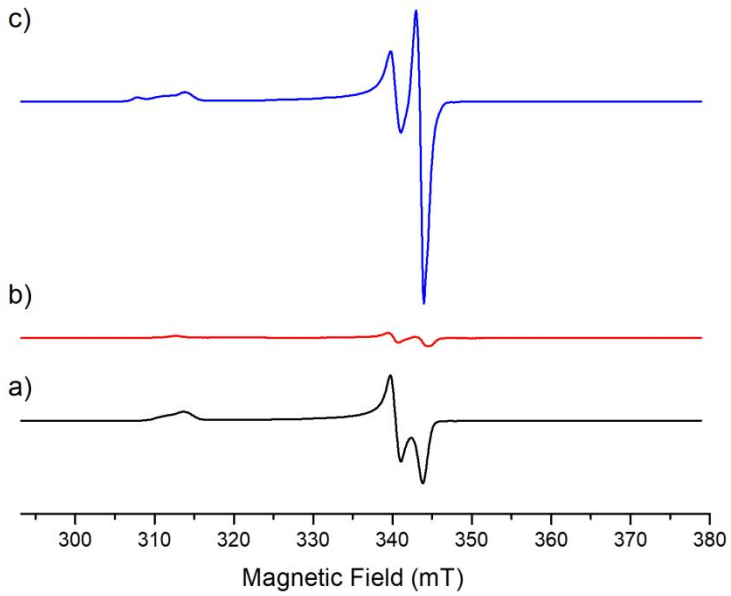


Figure S3 : X-band EPR analysis (T = 90 K) of a solution of a) $Fe(acac)_3$ (9 mM in a 98:2 THF:2-MeTHF mixture) treated by 15 equiv. *p*-F-C_6H_4MgBr (g = 2.194; 2.022; 2.002); b), c): the same, after addition of resp. C_6F_5Cl or 2-PyCl (10 equiv. *vs* Fe); samples frozen after a 10 min reaction time at room temperature.

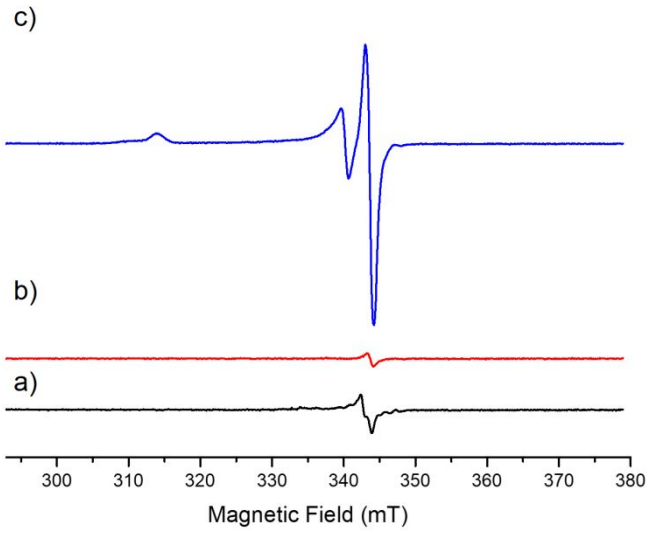


Figure S4 : X-band EPR analysis (T = 90 K) of a solution of a) $Fe(acac)_3$ (9 mM in a 98:2 THF:2-MeTHF mixture) treated by 15 equiv. *p*-MeO-C_6H_4MgBr; b), c): the same, after addition of resp. C_6F_5Cl or 2-PyCl (10 equiv. *vs* Fe); samples frozen after a 10 min reaction time at room temperature.

Speciation of the low-spin iron(I) oxidation state with respect to the overall iron quantity in the spectra displayed in Figures S3 and S4:

Figure S3: a) 9.6%; b) 2.3%; c) 14%

Figure S4: a) 0.2%; b) 0.1%; c) 1.5%

7. Experimental Hammett plots

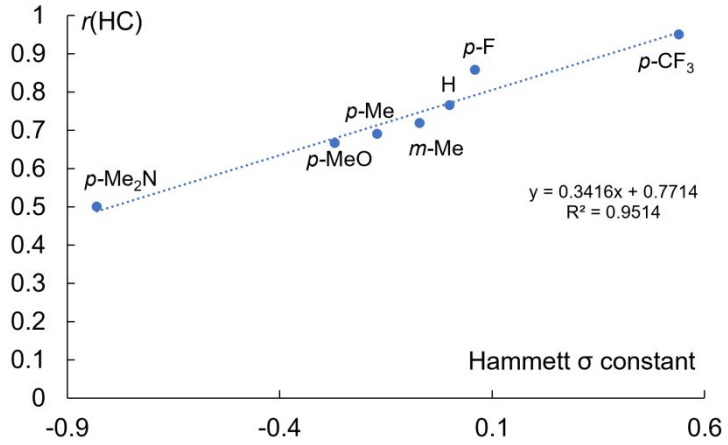


Figure S5: experimental evolution of the homo-coupling (hc) *versus* cross-coupling (cc) ratio r_{hc} for ArMgBr / 2-PyCl coupling systems reported in Table 1.

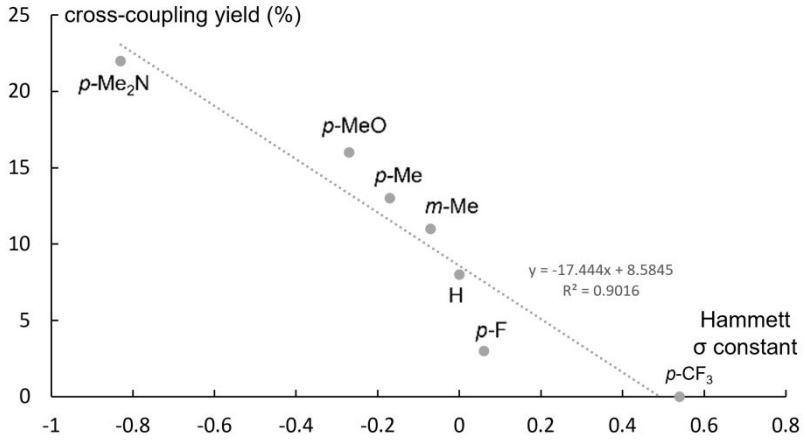


Figure S6: Experimental Hammett plot for the cross-coupling between ArMgBr and 2-PyCl (conditions of Table 1) as a function of the Hammett constant of the Ar substituents.

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