Supporting Information

Dihalogen-bridged palladium(I)-NHC dimer: synthesis, characterization and application in cross-coupling reactions

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2 General Methods

All reactions were performed using standard Schlenk techniques or in a nitrogen-filled glovebox (GS Glovebox Systemtechnik). Glassware was dried in a hot oven at 120 °C overnight before use. NMR spectra were recorded at ambient temperature using $CDCl_3$ or C_6D_6 as solvent, with proton, carbon, and fluorine resonances at 400/300/250, 101/75/63 and 235 MHz, respectively. All NMR data are reported in parts per million (ppm,) and coupling constants in Hertz (Hz). The ^{1}H and ^{13}C NMR spectra were referenced to the solvent peak: $CDCl_3$ (7.27 ppm in ^{1}H and 77.0 ppm in ^{13}C), C_6D_6 (δ 7.16 ppm in ^{1}H and 128.39 ppm in ^{13}C). ^{19}F NMR spectra were externally referenced to $CFCl_3$ (0.00 ppm). Coupling constants are reported in hertz (Hz). Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. Mass spectrometric data were acquired on a GC-MS Agilent 5977B MSD. The MS ionization was achieved by EI^+. Melting points were measured on a Mettler FP 61. Infrared spectra were recorded on BrukerVertex 70 Spectrometer with Universal ATR Sampling Accessory. Bands are given in cm^{-1} with intensities (vs very strong, s strong, m medium, w weak). Melting points were measured on a Mettler Toledo MP70. GC analyses were carried out using an HP-5 capillary column (Phenyl methyl siloxane, 30 m × 320 × 0.25, 100/2.3-30-300/3, 2 min at 60 °C, heating rate 30 °C/min, 3 or 10 min at 300 °C). Column chromatography was performed on a CombiFlash Companion (Isco) or on a Reveleris X2 (BUCHI) Flash Chromatography-System using Reveleris packed columns (12 g). Solvents were dried over molecular sieves or obtained from the solvent-drying system (Braun SPS System) and stored over 3 or 4 Å molecular sieves. Molecular sieves were activated in the microwave prior to use. All solvents were degassed by bubbling argon trough the solvent. $\{(IPr)PdCl_2\}_2$ (UMICORE CX41), $[Pd(allyl)Cl]_2$ and $PdBr_2$ were donated by UMICORE. All other compounds were bought from commercial sources and used without further purification.

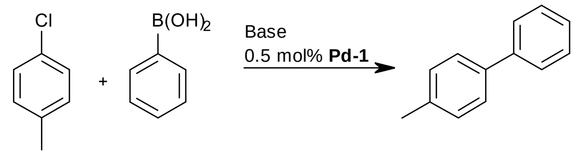
3 Screening Tables of the reaction conditions

3.1 Suzuki-Miyaura Coupling

General Procedure for the reaction screening condition of Suzuki-Miyaura Coupling of *p*-chlorotoluene with phenylboronic acid

An oven dried crimp cap vial equipped with a Teflon coated magnetic stirring bar was charged with base and phenylboronic acid. The vial was sealed, and evacuated and backfilled with argon three times. *p*-Chlorotoluene (65 mg, 0.5 mmol, 1 equiv.) was added via syringe. Degassed solvent (1 mL) and *n*-tetradecane were added to the reaction as GC internal standard. Then, a freshly prepared stock solution of **Pd-1** (0.025 M in toluene, 0.1 mL, 0.0025 mmol, 0.005 equiv.) was added via syringe and the reaction was stirred at the temperature and time reported in the table S1. Then, the reaction was analysed by GC.

Table S1. Screening of reaction conditions for the Suzuki-Miyaura cross coupling.[a]



Entry	Equiv. **2a**	Base	Equiv. base	Solvent	Temperature	Time	Yield **3aa** [%]
1	1	LiOH	1.2	EtOH	60	4	30
2	"	NaOH	"	"	"	"	47
3	"	KOH	"	"	"	"	35
4	"	LiO^{t}Bu	"	"	"	"	26
5	"	NaO^{t}Bu	"	"	"	"	62
6	"	KO^{t}Bu	"	"	"	"	86
7	"	Li_2CO_3	"	"	"	"	0
8	"	Na_2CO_3	"	"	"	"	0
9	"	K_2CO_3	"	"	"	"	40
10	"	K_3PO_4	"	"	"	"	69
11	"	Cs_2CO_3	"	MeOH	"	"	44
12	"	"	1.1	^{i}PrOH	"	"	47
13	"	"	"	^{t}BuOH	"	"	0
14	"	"	"	Toluene	"	"	0
15	"	"	"	THF	"	"	0
16	"	"	"	H_2O	"	"	18
17	"	"	"	EtOH	"	"	85
18	"	"	1.2	"	"	"	86
19	"	"	"	"	40	"	86
20	"	"	"	"	"	22	85
21	1.2	"	"	"	"	4	85
22	"	"	1.3	"	"	"	96
23	"	"	1.4	"	"	"	98

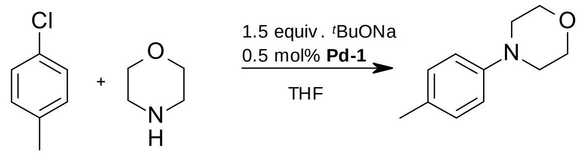
[a] Reaction conditions: *p*-chlorotoluene (0.5 mmol), phenylboronic acid (x mmol), base (x mmol), **Pd-1** (0.5 mol%), solvent (1 mL). Yield were determined by GC using *n*-tetradecane as internal standard.

3.2 Buchwald-Hartwig amination

General Procedure for the reaction screening condition of Buchwald-Hartwig Amination of *p*-chlorotoluene with morpholine

An oven dried crimp cap vial equipped with a Teflon coated magnetic stirring bar was charged sodium *tert*-butoxide (147 mg, 1.5 mmol, 1.5 equiv.). The vial was sealed, and evacuated and backfilled with argon three times. Then, a freshly prepared stock solution of **Pd-1** (0.005 M in THF, 1 mL, 0.005 mmol, 0.005 equiv.) was added via syringe followed by *p*-chlorotoluene (1 mmol, 1 equiv.), morpholine (93 µL 1.05 mmol, 1.05 equiv.) and *n*-tetradecane (100 µL). The reaction was stirred at the temperature and time reported in the table S2. Then, the reaction was analysed by GC.

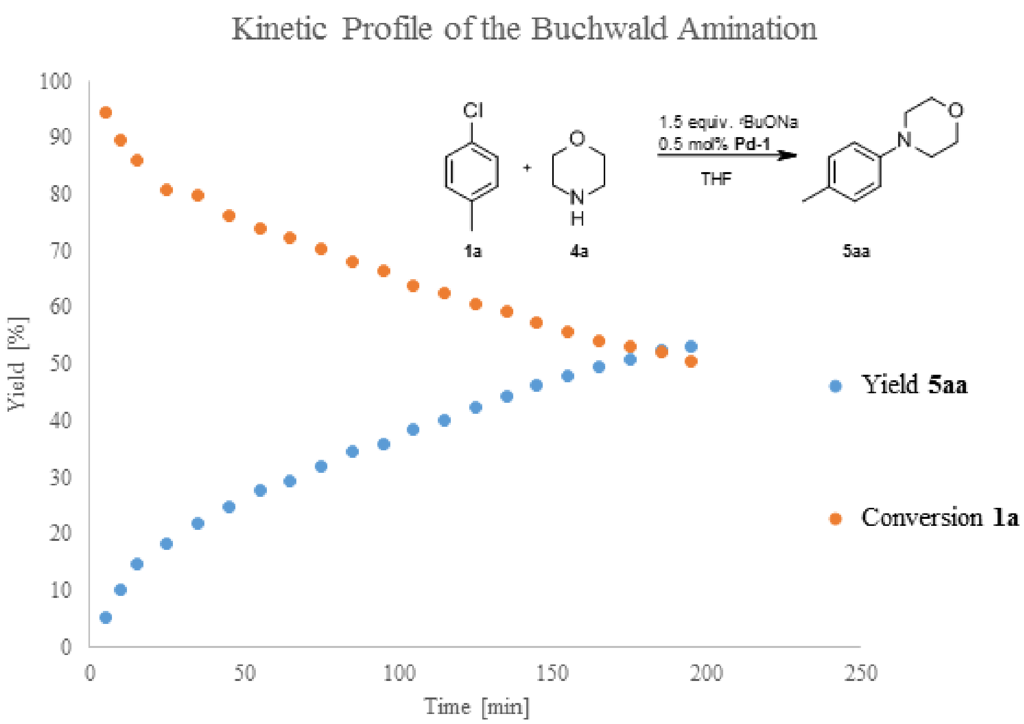
Table S2. Screening of reaction conditions for the Buchwald-Hartwig amination.[a]



1a 4a 5aa

Entry	Solvent	Time [h]	Temperature [°C]	Yield **5aa** [%]
1	THF	0.25	25	13
2	“	2	“	51
3	“	16	“	>99
4	“	0.5	40	81
5	“	1	“	97
6	“	2	“	>99
7	Toluene	2	25	17
8	“	2	60	20
9	“	2	80	30

[a] Reaction conditions: *p*-chlorotoluene (1 mmol), morpholine (1.5 mmol), ^{t}BuONa (1.5 mmol), **Pd-1** (0.005 mmol), solvent (1 mL). Yield were determined by GC using *n*-tetradecane as internal standard; average of two runs.



Graph 1. Kinetic profile of the **Pd-1** catalysed Buchwald-Hartwig amination of *p*-chlorotoluene with morpholine at 25 °C.

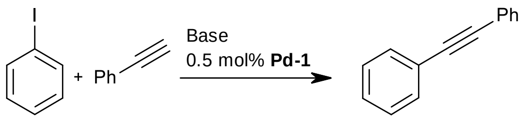
3.3 Copper-free Sonogashira coupling of aryl halides

General procedure for the reaction condition of Sonogashira coupling of aryl halides with phenyl acetylene

In a nitrogen filled glovebox, an oven dried crimp cap vial equipped with a Teflon coated magnetic stirring bar was charged with **Pd-1** (6.2 mg, 0.005 mmol, 0.005 equiv.). The vial was removed from the glovebox and the complex was dissolved in dry and degassed solvent (2 mL). After, the aryl halide (1 mmol, 1 equiv.) followed by phenylacetylene (1.2 mmol, 1.2 equiv.), base and *n*-dodecane were added. The reaction was stirred at the temperature reported in the tables S3-S4 for 16 h. Then, the reaction was analysed by GC.

3.3.1 Copper-free Sonogashira coupling of aryl iodides

Table S3. Screening of reaction conditions for the copper-free Sonogashira coupling.[a]

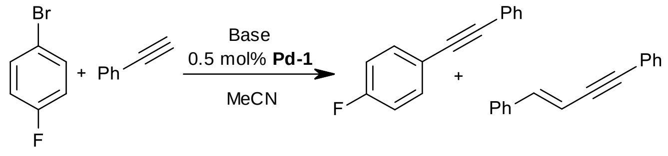


Entry	Solvent	Base	Equiv. base	Temperature [°C]	Yield **8aa** [%]
1	THF	K_2CO_3	3	65	13
2	MeCN	"	"	"	17
3	"	Et_3N	"	"	85
4	"	"	2	"	83
5	"	"	1	"	57
6	"	"	2	40	98
7	"	KOH	"	"	88
8	"	NaO^{t}Bu	"	"	0
9	"	DBU	"	"	0
10	"	IPr_2NEt	"	"	53

[a] Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.2 mmol), base (x mmol), **Pd-1** (0.5 mol%), solvent (2 mL), 16 h. Yield were determined by GC using *n*-dodecane as internal standard.

3.3.2 Copper-free Sonogashira coupling of aryl bromides

Table S4. Screening of bases, ratios and additives.[a]

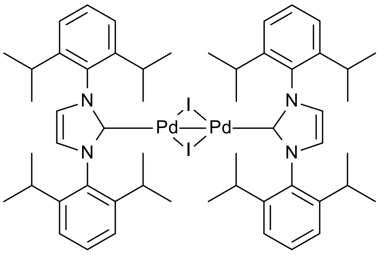


Entry	Solvent	Base	Equiv. Base	Yield **10a** [%]	Yield **11** [%]
1	MeCN	Et_3N	2	0	8
2	“	Piperidine	“	0	16
3	“	$^iPr_2NH$	“	6	13
4	“	Bu_4NOAc	“	2	17
5	“	$^iPr_2NEt$	“	0	8
6	“	K_3PO_4	“	18	34
7	“	^tBuONa	“	0	0
8	“	Cs_2CO_3	1	50	35
9	“	“	2	41	42
10	“	“	3	48	41
11	“	“	4	39	36
12	Water	“	2	19	12
13	THF	“	“	25	25
14	Toluene	“	“	10	8
15	DMF	“	“	38	43

[a] Reaction conditions: 4-bromofluorobenzene (1 mmol), phenylacetylene (1.2 mmol), base (x mmol), **Pd-1** (0.5 mol%), solvent (2 mL), 40 °C, 16 h. Yield were determined by GC using *n*-dodecane as internal standard.

4 Synthetic Procedures

*4.1 Synthesis of [(IPr)PdI]₂ (**Pd-1**)*

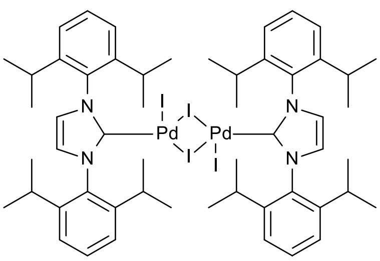


Pd-1

[(IPr)PdI$_2$]$_2$ (1.37 g, 0.91 mmol, 1 eq.) were weighted into a Schlenk flask and the air was replaced by argon. The complex was dissolved in 18 mL of dry and degassed toluene. In a 10 mL crimp cap vial, potassium hydroxide (102 mg, 1.82 mmol, 2 eq.) was dissolved in 13 mL dry and degassed methanol. This solution was added to the stirred solution of the Pd-complex and the mixture stirred for 6 h at ambient temperature. The volatiles were removed under vacuo and the remaining greenish solid was extracted with toluene (3x9 mL). The combined organic solutions were dried under vacuo to obtain [(IPr)PdI]$_2$ (678 mg, 60%) as a dark green solid. Single crystals of **Pd-1** suitable for X-ray diffraction were obtained by evaporation of toluene.

^{1}H NMR (300 MHz, C_6D_6): δ = 7.27 (t, J=7.9 Hz, 4 H), 7.10 (d, J=7.5 Hz, 4 H), 6.45 (s, 4 H), 2.77 (spt, J=6.8 Hz, 4 H), 1.41 (d, J=7.0 Hz, 24 H), 1.03 (d, J=6.8 Hz, 24 H) ppm; **^{13}C-NMR** (101 MHz, C_6D_6): δ =184.3, 146.2, 138.3, 130.2, 124.7, 122.7, 29.1, 25.2, 24.8 ppm; **EA:** Anal. Calc. For $C_{54}H_{74}I_2N_4Pd_2$: C, 52.06%; H, 5.99 %; N, 4.50%, Found: C, 52.44%; H, 5.82%; N, 4.65%.

*4.2 Synthesis of [(IPr)PdI$_2$]$_2$ [CAS 1233644-81-9] (**Pd-2**)*



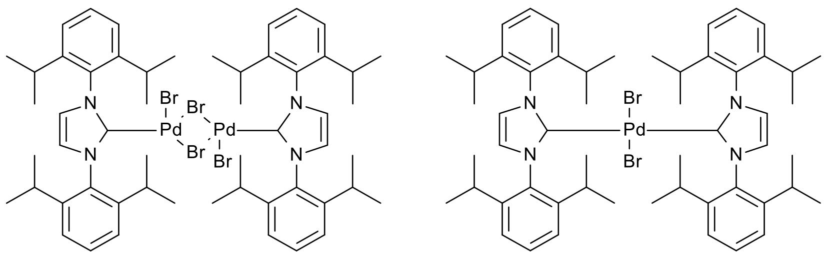
Pd-2

A 100 mL crimp cap vial was charged with [(IPr)PdCl$_2$]$_2$ (567 mg, 0.5 mmol, 1 eq.) and potassium iodide (3.35 g, 20 mmol, 40 eq.) and suspended in 50 mL acetone. The mixture was heated to 50 °C and stirred for 96 h. Then, the solution was filtered, and volatiles were removed under reduced pressure. The remaining brown solid was dissolved in 50 mL dichloromethane and washed three times with 10 mL of water. The aqueous layer was extracted three times with 20 mL dichloromethane and the combined organic layers were dried over magnesium sulfate. The removal of volatiles under vacuum yielded $[(IPr)PdI_2]_2$ (747 mg, 99%) as an orange solid.

The NMR data match with those previously reported. [1]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (t, J=7.7 Hz, 3 H), 7.22 - 7.40 (m, 8 H, overlapping with $CDCl_3$), 3.15 - 3.45 (m, 4 H), 2.60 - 2.90 (m, 4 H), 1.48 (d, J=6.6 Hz, 12 H), 1.25 (d, J=6.6 Hz, 12 H), 1.07 (d, J=6.6 Hz, 12 H), 0.94 (d, J=6.8 Hz, 12 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.5, 146.4, 146.0, 135.4, 130.3, 125.4, 124.7, 124.3, 29.1, 26.5, 24.0 ppm; **mp:** 282 °C (from chloroform) (lit.,[1] >280 °C); **IR (ATR mode):** 2966 (w), 2868 (w), 1460 (w), 1443 (w), 1402 (w), 1385 (w), 1364 (w), 1328 (w), 1264 (s), 1204 (w), 1180 (w), 1121 (w), 1057 (w), 966 (w), 941 (w), 895 (w), 801 (w), 732 (vs), 702 (vs), 636 (w), 548 (w) cm^{-1}; **EA:** Anal. Calc. For $C_{54}H_{74}I_4N_4Pd_2$: C, 43.25%; H, 4.97 %; N, 3.74%, Found: C, 43.26%; H, 4.79%; N, 3.69%.

*4.3 Synthesis of $[(IPr)PdBr_2]_2$ [1228877-10-8] (**Pd-3**) and trans-$(IPr)_2PdBr_2$*



Pd-3

Method A:

A 100 mL crimp cap vial was charged with $[(IPr)PdCl_2]_2$ (1.13 g, 1 mmol, 1 eq.) and potassium bromide (4.76 g, 40 mmol, 40 eq.) and suspended in 50 mL acetone. The mixture was heated to 50 °C and stirred for 7 days. Then, the solution was filtrated, and volatiles were removed under reduced pressure. The remaining brown solid was dissolved in 50 mL of dichloromethane and washed three times with 10 mL of water. The aqueous layer was extracted three times with 20 mL of dichloromethane and the combined organic layers were dried over magnesium sulfate. The removal of volatiles under vacuum yielded $[(IPr)PdBr_2]_2$ (1.30 g, 99%) as an orange solid.

Method B:

Under an argon atmosphere, an oven dry Schlenk tube was charged with palladium(II) bromide (226 mg, 1 mmol, 1 equiv.). To the solid, 6 mL of acetone was added and the suspension was heated to 40 °C for 15 h. After evaporating the solvent, the residual solid was heated to 120 °C for 2 h under high vacuum. Then, the solid was cooled to room temperature and 4 ml of dry THF was added. After, a solution of IPr (289 mg, 1 mmol, 1 equiv.) in 6 mL of dry THF was added. The dark red reaction mixture was stirred for 3 h at ambient temperature. After, the solution was filtered through celite and washed with several portions of THF until the filtrate was colourless. After the removal of volatiles a dark red solid afforded which was purified by flash chromatography (cyclohexane/ethyl acetate 9:1) yielding **Pd-3** (455 mg, 69%) as the orange solid and *trans*-$(IPr)_2PdBr_2$ as byproduct **(**123 mg, 6%) as orange solid. Single crystals of *trans*-$(IPr)_2PdBr_2$ suitable for X-ray diffraction were obtained by slow evaporation of ethyl acetate.

The NMR data match with those previously reported.[2]

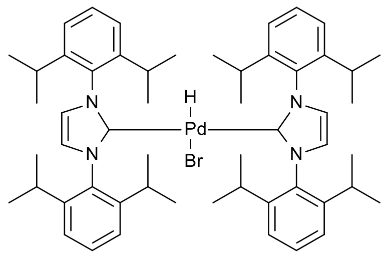
Pd-3

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (t, J=7.7 Hz, 4 H), 7.22 - 7.41 (m, 8 H overlaying with $CDCl_3$), 7.02 (s, 4 H), 2.86 - 3.39 (m, 4 H), 2.37 - 2.86 (m, 4 H), 1.42 (d, J=6.2 Hz, 11 H), 1.25 (d, J=6.4 Hz, 12 H), 1.06 (d, J=6.6 Hz, 12 H), 0.95 (d, J=6.4 Hz, 11 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 153.0, 146.6, 146.2, 134.6, 130.3, 125.4, 124.4, 124.3, 28.8, 26.4, 23.5 ppm; **mp:** 266 °C (from chloroform, decomposition) (lit.,[2] 264-267 °C, decomposition); **IR (ATR mode):** 3054 (vw), 2967 (vw), 1444 (vw), 1409(vw), 1384 (vw), 1364 (vw), 1329 (vw), 1264 (s), 1206 (vw), 1120 (vw), 1056 (vw), 971 (vw), 943 (vw), 896 (vw), 802 (vw), 732 (vs), 701 (s), 550 (vw), 459(vw) cm^{-1}; **EA:** Anal. Calc. For $C_{54}H_{74}Br_4N_4Pd_2$: C, 49.45%; H, 5.69 %; N, 4.27%, Found: C, 49.72%; H, 5.50%; N, 4.26%.

***trans*-$(IPr)_2PdBr_2$**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (t, J=7.7 Hz, 4 H), 7.08 (d, J=7.7 Hz, 8 H), 6.76 (s, 4 H), 3.04 (spt, J=6.7 Hz, 8 H), 0.96 (d, J=6.6 Hz, 24 H), 0.88 (d, J=7.0 Hz, 24 H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$): δ = 171.5, 146.5, 136.3, 129.3, 124.4, 123.8, 28.3, 26.1, 23.1 ppm; **mp:** 309 °C (from cyclohexane/ethylacetate, decomposition); **IR (ATR mode):** 3174 (vw), 3136 (vw), 3068 (vw), 2962 (s), 2927 (w), 2866 (w), 1591 (w), 1572 (w), 1463 (s), 1443 (s), 1403 (s), 1382 (s), 1361 (s), 1328 (s), 1308 (s), 1261 (s), 1204 (w), 1179 (w), 1118 (s), 1098 (s), 1080 (s), 1058 (s), 1042 (s), 1020 (s), 941 (w), 799 (vs), 754 (vs), 744 (s), 709 (vs), 637 (vw), 550 (vw), 529 (vw), 502 (vw) cm^{-1}.

*4.4 Synthesis of (IPr)$_2$PdHBr (**Pd-4**)*



Pd-4

Under an argon atmosphere, an oven dry Schlenk tube was charged with $[(IPr)PdBr_2]_2$ (262 mg, 0.2 mmol, 1 equiv.). The solid was dissolved in 4 ml of dry and degassed toluene and a solution of KOH (22.4 mg, 0.4 mmol, 2 equiv.) in 2 mL of dry and degassed MeOH was added. The mixture was stirred for 16 hours and the solvent was removed. The crude solid was extracted two times with 4 mL of toluene and the volatiles were removed under vacuum. Analysis by ^{1}H NMR of the solid in C_6D_6 showed to be mainly starting material and **Pd-4**. The solid was re-dissolved in toluene and layered with acetone to obtain brownish crystals of **Pd-4**.

^{1}H NMR (300 MHz, C_6D_6): δ = 7.26 (t, J=8.00 Hz, 2 H), 7.05 (d, J=7.54 Hz, 9 H), 6.45 (s, 4 H), 2.97 - 3.23 (m, 8 H), 1.13 (d, J=6.62 Hz, 24 H), 1.00 (d, J=6.85 Hz, 24 H), -13.97 (s, 1 H) ppm; **^{13}C NMR** (75 MHz, C_6D_6): δ = 188.1, 146.7, 137.8, 129.7, 124.5, 124.2, 28.8, 26.3, 24.0 ppm.

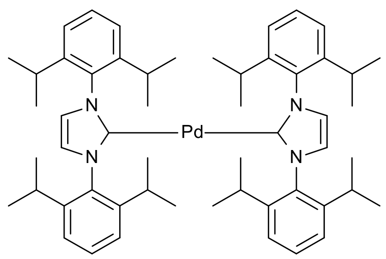
4.5 Synthesis of (η^3-allyl)(η^5-cyclopentadienyl)palladium

Under an argon atmosphere, allylpalladium chloride dimer (1.12 g, 3 mmol, 1 equiv.) was dissolved in 24 mL of dry and degassed THF and cooled to -60 °C. To the stirred solution, a solution of sodium cyclopentadienyl (2 M in THF, 3 mL, 6 mmol, 2 equiv.) was added slowly. The mixture was then allowed to warm to room temperature and stirred for an additional 30 min. After, the solvent was removed the remaining solid was extracted with 42 mL of cyclohexane and filtrated by cannula. The residual solid was washed once with 15 mL cyclohexane. The combined organic solutions were dried under vacuum yielding (η^3-allyl)(η^5-cyclopentadienyl)palladium (1.20 g, 95%) of a volatile red solid.

The NMR data match with those previously reported.[3]

^{1}H NMR (300 MHz, C_6D_6): δ = 5.86 (s, 5 H), 4.53 - 4.66 (m, 1 H), 3.42 (d, J=6.1 Hz, 2 H), 2.10 (d, J=10.6 Hz, 2 H) ppm; **^{13}C NMR** (75 MHz, C_6D_6): δ = 94.9, 94.8, 46.0 ppm.

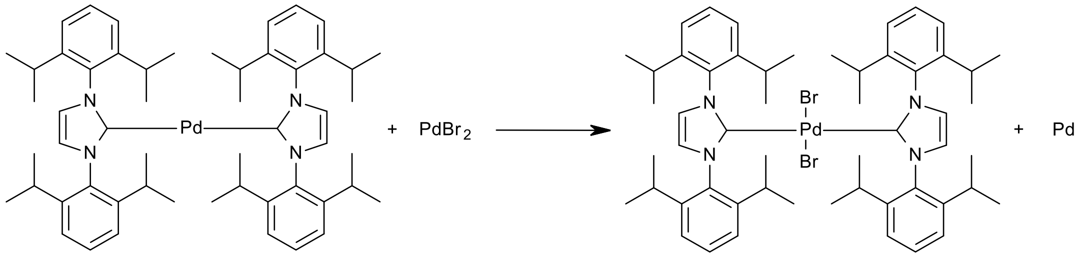
4.6 Synthesis of [(IPr)$_2$Pd]



In an oven-dried Schlenk tube, (η^3-allyl)(η^5-cyclopentadienyl)palladium (109 mg, 0.52 mmol, 1.03 equiv.) was dissolved in 2 mL of dry and degassed cyclohexane. Then a solution of IPr (606 mg, 1.56 mmol, 3.12 equiv.) in 20 mL of dry and degassed cyclohexane was added over 30 min. The resulting reaction mixture was stirred for 18 h at ambient temperature. After removal of volatiles, the residual solid was dissolved in 6 mL of dry and degassed toluene and the product was precipitated by adding 30 mL of dry and degassed MeOH. The solution was filtrated, and the orange solid was washed with dry and degassed MeOH (2x3 mL) and dried under high vacuum to afford [(IPr)$_2$Pd] (190 mg, 43%) [(IPr)$_2$Pd] as an orange solid.
The spectroscopic data match those reported in literature. [4]

^{1}H NMR (400 MHz, C_6D_6): δ = 7.30 (t, J=7.6 Hz, 3 H), 7.08 (d, J=7.8 Hz, 8 H), 6.27 (s, 4 H), 2.77 - 2.95 (m, 8 H), 1.19 (d, J=6.8 Hz, 24 H), 1.11 (d, J=7.1 Hz, 24 H) ppm; **^{13}C NMR** (75 MHz, C_6D_6): δ = 199.6, 146.4, 139.5, 128.9, 123.7, 121.6, 29.0, 25.5, 24.4 ppm; **EA:** Anal. Calc. For $C_{54}H_{72}N_4Pd$: C, 73.40%; H, 8.21%; N, 6.34%, Found: C, 73.13%; H, 8.14%; N, 6.49%.

4.7 *Comproportionation attempt between [(IPr)$_2$Pd] and PdBr$_2$*

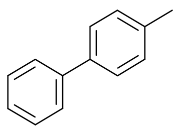


Under an argon atmosphere, an oven dry Schlenk tube was charged with palladium(II) bromide (20.6 mg, 0.077 mmol, 1.2 equiv.). To the solid, 1 mL of acetone was added and the suspension was heated to 40 °C for 16 h. After evaporating the solvent, the residual solid was heated to 120 °C for 2 h under high vacuum. Then, the solid was cooled to room temperature and 1 ml of dry and degassed toluene was added. After, a solution of [(IPr)$_2$Pd] (57 mg, 0.064 mmol, 1 equiv.) in 3 mL of dry and degassed toluene was added. The mixture was stirred for 24 h at ambient temperature. After, the solution was filtered through cannula and the remaining black solid was washed with 3 mL of dry and degassed toluene. The reunited organic solutions were dried. Isolated *trans*-(IPr)$_2$PdBr$_2$ (43 mg, 64%) as orange solid. The NMR spectra of the solid were consistent with the previously reported spectra of *trans*-(IPr)$_2$PdBr$_2$.

General Procedure for the Suzuki-Miyaura Coupling of Aryl Chlorides

An oven dried crimp cap vial equipped with a Teflon coated magnetic stirring bar was charged with caesium carbonate (253 mg, 0.77 mmol, 1.4 equiv.), phenylboronic acid (81 mg, 0.66 mmol, 1.2 equiv.) and aryl chloride (0.55 mmol, 1 equiv.) if solid. The vial was sealed, and evacuated and backfilled with argon three times. Aryl chloride (0.55 mmol, 1 equiv.) was added via syringe if liquid. Degassed EtOH (1 mL) was added and the mixture was heated to 40 °C. Then, a freshly prepared stock solution of **Pd-1** (0.0275 M in toluene, 0.1 mL, 0.00275 mmol, 0.005 equiv.) was added via syringe and the reaction was stirred for 4 h at 40 °C unless otherwise stated. The reaction solution was diluted with 10 mL ethyl acetate and washed with 10 mL water. Then the aqueous layer was extracted with ethyl acetate 2x10 mL. The combined organic layers were washed with 10 mL of brine and dried over $MgSO_4$. Afterwards the crude reaction mixture was purified by flash chromatography.

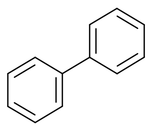
4.8 *Synthesis of 1-methyl-4-phenylbenzene (**3aa**) [CAS 644-08-6]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3aa** (85 mg, 92%) as colourless solid.
The NMR data match with those previously reported.[5]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 - 7.65 (m, 2 H), 7.50 - 7.57 (m, 2 H), 7.42 - 7.50 (m, 2 H), 7.32 - 7.40 (m, 1 H), 7.25 - 7.32 (m, 2 H), 2.44 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 127.0, 21.1 ppm (One peak is missing due to overlap); **mp:** 48 °C (from cyclohexane) (lit.,[6] 47-48 °C); **IR (ATR mode):** 3027 (w), 2920 (w); 1904 (vw), 1800 (vw), 1601 (w), 1568 (w), 1519 (s), 1487 (w) 1444 (w), 1310 (w), 1265 (s), 1188 (w), 1112 (w), 1075 (w), 1038 (w), 1008 (w), 912 (w), 821 (s), 756 (vs), 737 (s), 695 (vs), 492 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 168.05 (100) $[M]^{+}$, 167.1 (69), 165.05 (26), 153.05 (16), 152.05 (20).

4.9 *Synthesis of biphenyl (**3ba**) [CAS 92-52-4]*

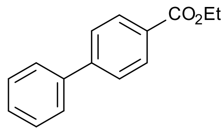


The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3ba** (80 mg, 94%) as colourless solid.
The NMR data match with those previously reported.[7]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 - 7.66 (m, 4 H), 7.43 - 7.51 (m, 4 H), 7.33 - 7.41 (m, 2 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 141.2, 128.7, 127.2, 127.2 ppm; **mp:** 70 °C (from chloroform) (lit.,[8] 69-70 °C). **IR (ATR mode):** 3033 (w), 1597 (w), 1568 (w), 1480 (w), 1430 (w), 1264 (w), 1169 (w), 1075 (w), 1042 (w), 1007 (w), 903 (w), 781 (w), 728 (s), 696 (s), 609

(w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 154.8 (12) $[M]^+$, 153.9 (100), 153.0 (31), 152.1 (20), 75.9 (12), 51.0 (11), 50.0 (14).

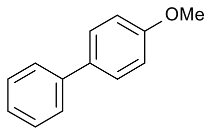
*4.10 Synthesis of ethyl 4-phenylbenzoate (**3ca**) [CAS 6301-56-0]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **3ca** (116 mg, 93%) of a colourless solid.
The NMR data match with those previously reported.[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 - 8.17 (m, 2 H), 7.60 - 7.71 (m, 4 H), 7.44 - 7.53 (m, 2 H), 7.37 - 7.44 (m, 1 H), 4.42 (q, J=7.2 Hz, 2 H), 1.43 (t, J=7.2 Hz, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 166.5, 145.5, 140.1, 130.0, 129.3, 128.9, 128.1, 127.3, 127.0, 60.9, 14.4 ppm; **mp:** 49 °C (from chloroform) (lit.,[10] 48-49 °C); **IR (ATR mode):** 2984 (w), 2903 (w), 1706 (s), 1606 (w), 1582 (w), 1473 (w), 1449 (w), 1404 (w), 1365 (w), 1313 (w), 1269 (br, s), 1201 (w), 1179 (w), 1114 (s), 1025 (w), 1005 (w), 857 (w), 745 (s), 698 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 225.9 (95) $[M]^+$, 198.1 (34), 181.1 (100), 152.0 (21).

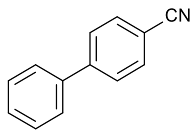
*4.11 Synthesis of 1-methoxy-4-phenylbenzene (**3da**) [CAS 613-37-6]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3da** (81 mg, 80%) as colourless solid.
The NMR data match with those previously reported.[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 - 7.60 (m, 4 H), 7.39 - 7.47 (m, 2 H), 7.33 (d, J=7.3 Hz, 1 H), 6.96 - 7.04 (m, 2 H), 3.87 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm; **mp:** 88 °C (from cyclohexane/ethyl acetate) (lit.,[11] 87-88 °C); **IR (ATR mode):** 2936 (w), 1608 (w), 1583 (w), 1519 (s), 1485 (s), 1463 (w), 1290 (s), 1265 (s), 1245 (w), 1201 (w), 1181 (s), 1112 (w), 1034 (w), 1015 (w), 895 (w), 833 (s), 803 (vs), 760 (s), 734 (w), 698 (w), 571 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 184.05 (100) $[M]^+$, 169.05 (47), 141 (40), 139 (10), 115 (26).

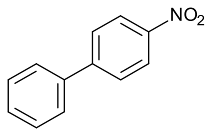
*4.12 Synthesis of 4-phenylbenzonitrile (**3ea**) [CAS 2920-38-9]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **3ea** (95 mg, 96%) as colourless solid.
The NMR data match with those previously reported.[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 - 7.78 (m, 4 H), 7.56 - 7.64 (m, 2 H), 7.39 - 7.54 (m, 3 H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 145.7, 139.2, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9 ppm; **IR (ATR mode):** 2228 (w), 1607 (w), 1845 (w), 1265 (s), 843 (s), 764 (s), 733 (s), 696 (s), 564 (s), 517 (s) cm^{-1}; **mp:** 86-87 °C (from cyclohexane/ethyl acetate) (lit.,[13] 86-87 °C); **GC-MS (EI-TOF):** m/z (%) = 179.05 (100) $[M]^+$, 178.1 (25), 151.0 (12).

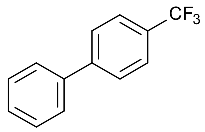
*4.13 Synthesis of 1-nitro-4-phenylbenzene (**3fa**) [CAS 92-93-3]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **3fa** (102 mg, 93%) as colourless solid.
The NMR data match with those previously reported.[14]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 - 8.35 (m, 2 H), 7.71 - 7.80 (m, 2 H), 7.60 - 7.69 (m, 2 H), 7.41 - 7.58 (m, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 147.6, 147.1, 138.8, 129.1, 128.9, 127.8, 127.4, 124.1 ppm; **mp:** 114 °C (from cyclohexane/ethyl acetate) (lit.,[15] 112-114 °C) ; **IR (ATR mode):** 2925 (w), 1733 (w), 1594 (w), 1574 (w), 1514 (w), 1478 (w), 1448 (w), 1403 (w), 1344 (s), 1264 (w), 1158 (w), 1103 (w), 1006 (w), 851 (s), 773 (s), 736 (s), 693 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 199 (66) $[M]^+$, 169.05 (100), 152 (65), 151 (12), 141 (17).

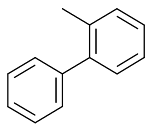
*4.14 Synthesis of 1-phenyl-4-(trifluoromethyl)benzene (**3ga**) [CAS 398-36-7]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **3ga** (117 mg, 96%) as colourless solid.
The NMR data match with those previously reported.[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (s, 4 H), 7.58 - 7.65 (m, 2 H), 7.45 - 7.53 (m, 2 H), 7.38 - 7.45 (m, 1 H) ppm; **^{19}F NMR** (235 MHz, $CDCl_3$): δ = -62.4 (s) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 144.7, 139.8, 129.4 (quart. $^2J_{C\text{-}F}$ = 32 Hz) 129.0, 128.2, 127.4, 127.3, 125.7 (quart. $^3J_{C\text{-}F}$ = 3.9 Hz), 124.3 (quart. $^1J_{C\text{-}F}$ = 272 Hz) ppm; **mp:** 70 °C (from chloroform) (lit.,[17] 70-71 ° C) ; **IR (ATR mode):** 1613 (w), 1569 (w), 1489 (w), 1403 (w), 1326 (s), 1275 (w), 1207 (w), 1161 (w), 1110 (s), 1072 (s), 1015 (w), 1005 (w), 842 (s), 766 (s), 727 (s), 690 (s), 639 (s), 599 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 221.9 (100) $[M]^+$, 152.1 (8).

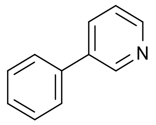
*4.15 Synthesis of 1-methyl-2-phenylbenzene (**3ha**) [CAS 643-58-3]*



The compound was synthesised according to the general procedure for a reaction time of 16 h. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3ha** (78 mg, 85%) as colourless liquid.
The NMR data match with those previously reported.[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 - 7.52 (m, 9 H), 2.34 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4 ppm; **IR (ATR mode):** 3020 (w), 1599 (w), 1478 (w), 1439 (w), 1380 (w), 1157 (w), 1119 (w), 1073 (w), 1052 (w), 1009 (w), 914 (w), 773 (s), 725 (s), 618 (w), 561 (w), 512 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 168.8 (12) $[M]^+$, 167.9 (94), 167.0 (100), 165.0 (25), 153.0 (30), 152.0 (23), 50.0 (14).

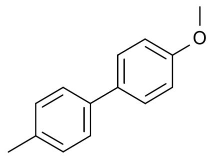
*4.16 Synthesis of 3-phenylpyridine (**3ia**) [CAS 1008-88-4]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-72%) yielding **3ia** (82 mg, 96%) as colourless liquid.
The NMR data match with those previously reported.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 - 8.92 (m, 1 H), 8.61 (d, J=4.9 Hz, 1 H), 7.93 (d, J=8.0 Hz, 1 H), 7.55 - 7.64 (m, 2 H), 7.36 - 7.54 (m, 4 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 148.4, 148.3, 137.8, 136.6, 134.3, 129.0, 128.0, 127.1, 123.5 ppm; **IR (ATR mode):** 3031 (w), 1581 (w), 1472 (w), 1450 (s), 1406 (w), 1335 (w), 1277 (w), 1188 (w), 1105 (w), 1076 (w), 1024 (w), 1005 (w), 993 (w), 912 (w), 812 (s), 751 (s), 695 (s), 638 (s), 608 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 155.8 (14) $[M]^+$, 154.8 (100), 154.0 (48), 127.0 (13), 102.0 (10), 51.0 (10), 50.0 (12).

*4.17 Synthesis of 1-methoxy-4-(4-methylphenyl)benzene (**3ab**) [CAS 53040-92-9]*

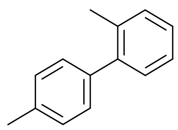


The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **3ab** (88 mg, 81%) as colourless solid.
The NMR data match with those previously reported.[20]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 - 7.58 (m, 2 H), 7.44 - 7.50 (m, 2 H), 7.21 - 7.29 (m, 2 H), 6.95 - 7.03 (m, 2 H), 3.87 (s, 3 H), 2.41 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ =

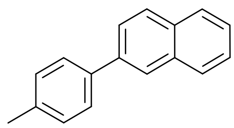
158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.6, 114.1, 55.3, 21.0 ppm; **mp:** 111 °C (from cyclohexane/ethyl acetate) (lit.,[21] 110-111 °C); **IR (ATR mode):** 2959 (w), 2914 (w), 1608 (s), 1582 (w), 1531 (w), 1501 (s), 1469 (w), 1441 (w), 1318 (w), 1289 (w), 1269 (w), 1252 (w), 1219 (w), 1197 (w), 1182 (w), 1137 (w), 1037 (w), 1013 (w), 842 (s), 807 (w), 739 (w), 659 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 198.8 (14) $[M]^+$, 197.9 (100), 184.0 (9), 183.2 (44), 155.0 (20).

*4.18 Synthesis of 1-methyl-2-(4-methylphenyl)benzene (**3ac**) [CAS 611-61-0]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3ac** (84 mg, 84%) as colourless liquid.
The NMR data match with those previously reported.[22]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 - 7.32 (m, 8 H), 2.44 (s, 3 H), 2.32 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 141.9, 139.0, 136.3, 135.4, 130.3, 129.8, 129.1, 128.8, 127.0, 125.7, 21.1, 20.5 ppm; **IR (ATR mode):** 3020 (w), 2921 (w), 1515 (w), 1482 (s), 1452 (w), 1379 (w), 1182 (w), 1109 (w), 1036 (w), 1007 (w), 941 (w), 821 (s), 787 (s), 755 (s), 727 (w), 685 (w), 581 (w), 557 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 182.8 (14) $[M]^+$, 181.8 (100), 181.1 (23), 168.0 (10), 167.1 (81), 166.2 (13), 165.2 (22).

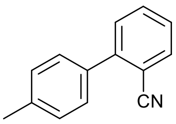
*4.19 Synthesis of 2-(4-methylphenyl)naphthalene (**3ad**) [CAS 59115-49-0]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3ad** (116 mg, 97%) as colourless liquid.
The NMR data match with those previously reported.[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, J=1.7 Hz, 1 H), 7.85 - 7.97 (m, 3 H), 7.77 (dd, J=8.4, 1.8 Hz, 1 H), 7.62 - 7.71 (m, 2 H), 7.45 - 7.58 (m, 2 H), 7.33 (d, J=7.7 Hz, 2 H), 2.46 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.5, 138.2, 137.1, 133.7, 132.5, 129.6, 128.3, 128.1, 127.6, 127.2, 126.2, 125.8, 125.5, 125.4, 21.1 ppm; **mp:** 96 °C (from cyclohexane/ethyl acetate) (lit.,[24] 95-96 °C). **IR (ATR mode):** 3053 (w), 1599 (w), 1502 (w), 1264 (s), 1189 (w), 1130 (w), 1018 (w), 948 (w), 894 (w), 857 (s), 733 (vs), 704 (s), 615 (w), 546 (w), 527 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 218.1 (100) $[M]^+$, 217.5 (31), 202.2 (8).

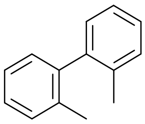
*4.20 Synthesis of 3-(4-methylphenyl)benzonitrile (**3ae**) [CAS 133909-96-3]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-20%) yielding **3ae** (56 mg, 53%) as colourless solid.
The NMR data match with those previously reported.[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 - 7.88 (m, 1 H), 7.78 - 7.83 (m, 1 H), 7.58 - 7.65 (m, 1 H), 7.54 (m, 1 H), 7.46 - 7.49 (m, 1 H), 7.44 - 7.50 (m, 2 H), 7.29 (d, J=7.7 Hz, 2 H), 2.43 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 142.3, 138.4, 135.9, 131.2, 130.4, 130.3, 129.8, 129.5, 126.9, 118.9, 112.9, 21.1 ppm; **mp:** 74 °C (from cyclohexane/ethyl acetate) (lit.,[25] 74-75 °C) **IR (ATR mode):** 3017 (w), 2921 (w), 1599 (w), 1476 (s), 1452 (w), 1378 (w), 1157 (w), 1123 (w), 1050 (w), 1007 (w), 941 (w), 866 (w), 751 (s), 727 (s), 624 (w), 569 (w), 537 cm^{-1}; **GC-MS (EI-TOF):** m/z (%) =192.8 (100) $[M]^+$, 191.8 (49), 190.0 (10), 177.9 (9), 165.0 (17).

*4.21 Synthesis of 1-methyl-2-(2-methylphenyl)benzene (**3hc**) [CAS 605-39-0]*



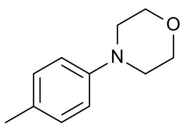
The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **3hc** (68 mg, 68%) as colourless liquid.
The NMR data match with those previously reported.[26]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 - 7.22 (m, 6 H), 6.98 - 7.06 (m, 2 H), 1.97 (s, 6 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 141.6, 135.8, 129.8, 129.3, 127.2, 125.6, 19.9 ppm; **IR (ATR mode):** 3017 (w), 2921 (w), 1599 (w), 1476 (s), 1452 (w), 1378 (w), 1157 (w), 1123 (w), 1050 (w), 1007 (w), 941 (w), 866 (w), 751 (s), 727 (s), 624 (w), 569 (w), 537 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 181.7 (64) $[M]^+$, 180.9 (16), 167.9 (13), 167.0 (100), 165.0 (27), 152.0 (14), 39.9 (16).

General procedure for the Buchwald-Hartwig amination of aryl chlorides

An oven dried crimp cap vial equipped with a Teflon coated magnetic stirring bar was charged sodium tert-butoxide (147 mg, 1.5 mmol, 1.5 equiv.). The vial was sealed, and evacuated and backfilled with argon three times. Then, a freshly prepared stock solution of **Pd-1** (0.005 M in THF, 1 mL, 0.005 mmol, 0.005 equiv.) was added via syringe followed by aryl chloride (1 mmol, 1 equiv.) and morpholine (93 µL 1.05 mmol, 1.05 equiv.). The reaction mixture was stirred for 2 h at 40 °C. The reaction solution was diluted with 10 mL ethyl acetate and washed with 10 mL water. Then the aqueous layer was extracted with ethyl acetate 2x10 mL. The combined organic layers were washed with 10 mL of brine and dried over $MgSO_4$. Afterwards the crude reaction mixture was purified by flash chromatography.

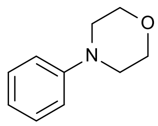
*4.22 Synthesis of 4-(4-methylphenyl)morpholine (**5aa**) [CAS 3077-16-5]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **5aa** (171 mg, 97%) as brownish solid.
The NMR data match with those previously reported. [27]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 - 7.17 (m, 2 H), 6.86 (d, J=8.6 Hz, 2 H), 3.74 - 4.05 (m, 4 H), 3.06 - 3.20 (m, 4 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.2, 129.7, 129.5, 116.0, 67.0, 49.9, 20.4 ppm; **mp:** 51 °C (from cyclohexane/ethyl acetate) (lit.,[28] 51 °C); **IR (ATR Mode):** 2962, 2856, 1612, 1514, 1449, 1378, 1329, 1301, 1260, 1236, 1119, 1068, 1050, 928, 859, 811, 734, 703, 607, 527, 498 cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 177.05 (65) $[M]^+$, 119.05 (100), 91.00 (30).

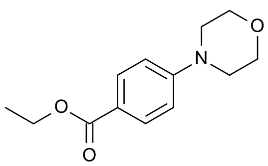
*4.23 Synthesis of 4-phenylmorpholine (**5ba**) [CAS 92-53-5]*



The compound was synthesised according to the general procedure. The crude reaction mixture was filtered over a silica plug which was washed with 70 mL of a mixture of 30% ethyl acetate in cyclohexane. The solvent was removed under reduced pressure yielding **5ba** (131 mg, 80%) as beige solid.
The NMR data match with those previously reported.[29]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 - 7.37 (m, 2 H), 6.88 - 7.00 (m, 3 H), 3.85 - 3.93 (m, 4 H), 3.13 - 3.25 (m, 4 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 151.7, 129.5, 120.4, 116.1, 67.3, 49.7 ppm; **mp:** 53 °C (from cyclohexane/ethyl acetate) (lit.,[30] 53-54 °C) ; **IR (ATR Mode):** 2962 (w), 2891 (w), 2855 (w), 1599 (s), 1494 (s), 1448 (s), 1302 (s), 1262 (s), 1230 (w), 1119 (vs), 992 (vs), 759 (vs), 734 (vs) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 163.05 (66) $[M]^+$, 105.0 (100), 104.0 (44).

*4.24 Synthesis of ethyl 4-morpholinobenzoate (**5ca**) [CAS 19614-15-4]*



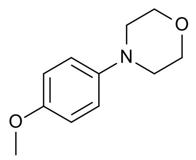
The compound was synthesised according to the general procedure and the crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-30%). The solvent was removed under reduced pressure yielding **5ca** (81 mg, 34%) as colourless solid.

The ^{1}H-NMR data with previously reported data.[29]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, J=8.8 Hz, 2 H), 6.88 (d, J=8.8 Hz, 2 H), 4.36 (q, J=7.0 Hz, 2 H), 3.88 (t, J=4.8 Hz, 4 H), 3.30 (t, J=5.1 Hz, 4 H), 1.39 (t, J=7.2 Hz, 3 H) ppm;

^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 166.6, 154.1, 131.1, 120.7, 113.5, 66.6, 60.4, 47.8, 14.4 ppm; **mp:** 85 °C (from cyclohexane/ethyl acetate) (lit.,[31] 83-85 °C) ; **IR(ATR Mode):** 2978 (w), 2859 (w), 1700 (s), 1604 (s), 1517 (w), 1449 (w), 1283 (s), 1266 (s), 1231 (s), 1187 (s), 1108 (s), 1070 (w), 1052 (w), 1021 (w), 732 (s), 699 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 235.1 (100) $[M]^+$, 190.05 (30), 177.05 (67), 149.0 (37), 132.0 (73).

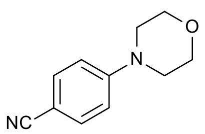
*4.25 Synthesis of 4-(4-methoxyphenyl)morpholine (**5da**) [CAS 27347-14-4]*



The compound was synthesised according to the general procedure. The crude reaction mixture was filtered over a silica plug which was washed with 70 mL of a mixture of 30% ethyl acetate in cyclohexane. The solvent was removed under reduced pressure yielding **5da** (188 mg, 97%) as beige solid.
The NMR data match with those previously reported.[19]

^{1}**H NMR** (300 MHz, $CDCl_3$): δ = 6.82 - 6.95 (m, 4 H), 3.84 - 3.90 (m, 4 H), 3.78 (s, 3 H), 3.03 - 3.10 (m, 4 H) ppm; ^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 153.9, 145.6, 117.7, 114.4, 67.0, 55.5, 50.7 ppm; **mp:** 72 °C (from cyclohexane/ethyl acetate) (lit.,[32] 72-74 °C) ; **IR (ATR Mode):** 3050 (vw), 2960 (w), 2856 (w), 2833 (vw), 1584 (vw), 1510 (vs), 1450 (s), 1378 (w), 1329 (s), 1294 (vs), 1263 (s), 1242 (s), 1227 (w), 1182 (w), 1119 (vs), 1069 cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 193.05 (89) $[M]^+$, 135.0 (100), 120.0 (55).

*4.26 Synthesis of 4-morpholinobenzonitrile (**5ea**) [CAS 10282-31-2]*

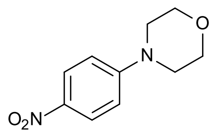


The compound was synthesised according to the general procedure. The crude reaction mixture was filtered over a silica plug which was washed with 70 mL of a mixture of 30% ethyl acetate

in cyclohexane. The solvent was removed under reduced pressure yielding **5ea** (154 mg, 82%) as colourless solid.
The NMR data match with those previously reported.[33]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, J=9.0 Hz, 2 H), 6.86 (d, J=8.8 Hz, 2 H), 3.85 (t, J=4.8 Hz, 4 H), 3.28 (t, J=4.8 Hz, 4 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 153.5, 133.5, 119.9, 114.1, 101.0 , 66.5, 47.3 ppm; **mp:** 82 °C (from cyclohexane/ethyl acetate) (lit.,[34] 82-83 °C); **IR (ATR Mode):** 2898 (w), 2857 (w), 2834 (w), 2216 (s), 1604 (vs), 1515 (s), 1450 (s), 1383 (s), 1366 (s), 1306 (w), 1266 (s), 1244 (s), 1221 (w), 1180 (s), 1115 (s), 1027 (w), 928 (s), 851 (s), 833 (s), 735 (s), 702 (w), 681 (w), 587 (w), 546 (s), 466 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 188.05 (55) $[M]^+$, 130.0 (100), 129.0 (45), 102.0(25).

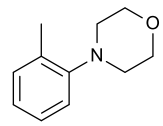
*4.27 Synthesis of 4-(4-nitrophenyl)morpholine (**5fa**) [CAS 10389-51-2]*



The compound was synthesised according to the general procedure. The crude reaction mixture purified by flash chromatography (30-50%). The solvent was removed under reduced pressure yielding **5fa** (169 mg, 81%) as yellow solid.
The NMR data match with those previously reported.[35]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.10 - 8.20 (m, 2 H), 6.79 - 6.91 (m, 2 H), 3.87 (t, J=4.9 Hz, 4 H), 3.38 (t, J=5.2 Hz, 4 H) ppm; **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 155.0, 139.0, 125.9, 112.6, 66.4, 47.2 ppm; **mp:** 149 °C (from cyclohexane/ethyl acetate) (lit.,[36] 149-150 °C) ; **IR (ATR Mode):** 3056 (vw), 2967 (vw), 2866 (vw), 1598 (s), 1507 (w), 1483 (w), 1446 (w), 1384 (w), 1327 (s), 1265 (s), 1240 (s), 1203 (w), 1119 (s), 1107 (s), 1051 (w), 996 (w), 926 (w), 825 (w), 732 (vs), 703 (s), 653 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 208.0 (84) $[M]^+$, 207.0 (19), 178.05 (28), 149.95 (100), 120.0 (65), 119.05 (24), 77.0 (24).

*4.28 Synthesis of 4-(2-methylphenyl)morpholine (**5ga**) [CAS 7178-40-7]*

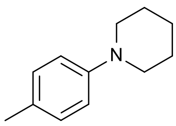


The compound was synthesised according to the general procedure. The crude reaction mixture was filtered over a silica plug which was washed with 70 mL of a mixture of 30% ethyl acetate in cyclohexane. The solvent was removed under reduced pressure yielding **5ga** (172 mg, 97%) as beige liquid.

The NMR data match with those previously reported.[29]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (t, J=7.2 Hz, 2 H), 6.86 - 7.00 (m, 2 H), 3.73 - 3.84 (m, 4 H), 2.77 - 2.94 (m, 4 H), 2.25 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 151.3, 132.7, 131.2, 126.7, 123.4, 119.0, 67.5, 52.3, 17.9 ppm; **IR (ATR Mode):** 2956 (w), 2910 (w), 2851 (w), 2814 (w), 1599 (w), 1491 (s), 1444 (s), 1295 (s), 1254 (s), 1223 (s), 1206 (w), 1194 (w), 1114 (s), 1043 (s), 932 (s), 760 (s), 721 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 177.1 (71) $[M]^+$, 119.05 (70), 118.05 (100).

*4.29 Synthesis of 1-(4-methylphenyl)piperidine (**5ab**) [CAS 31053-03-9]*

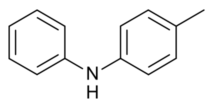


The compound was synthesised according to the general procedure and purified by flash chromatography using cyclohexane/ethyl acetate (0-20%). The solvent was removed under reduced pressure yielding **5ab** (170 mg, 97%) of a colourless oil.

The NMR data match with those previously reported.[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 - 7.16 (m, 2 H), 6.86 - 6.97 (m, 2 H), 3.14 (t, J=5.3 Hz, 4 H), 2.32 (s, 3 H), 1.69 - 1.86 (m, 4 H), 1.52 - 1.69 (m, 2 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 150.2, 129.5, 128.7, 116.9, 51.3, 25.9, 24.3, 20.4 ppm; **IR (ATR Mode):** 2932 (s), 2853 (w), 2791 (w), 1618 (w), 1574 (w), 1512 (vs), 1452 (s), 1332 (w), 1275 (vs), 1236 (vs), 1212 (s), 1042 (w), 1027 (w), 808 (vs), 732 (s), 571 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 175.1 (71) $[M]^+$, 174.1 (100).

*4.30 Synthesis of 4-methyl-N-phenylaniline (**5ac**) [CAS 620-84-8]*



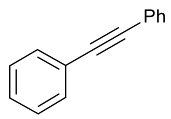
The compound was synthesised according to the general procedure and purified by flash chromatography using cyclohexane/ethyl acetate (0-20%). The solvent was removed under reduced pressure yielding **5ac** (112mg, 61%) as beige solid.
The NMR data match with those previously reported.[37]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 - 7.33 (m, 2 H), 7.11 - 7.18 (m, 2 H), 7.02 - 7.10 (m, 4 H), 6.95 (t, J=7.7 Hz, 1 H), 5.64 (br. s, 1 H), 2.36 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 143.9, 140.3, 130.9, 129.8, 129.3, 120.3, 118.9, 116.8, 20.7 ppm; **mp:** 88 °C (from cyclohexane/ethyl acetate) (lit.,[38] 87-89 °C); **IR (ATR Mode):** 3395 (s), 3013 (w), 2916 (w), 1595 (s), 1512 (vs), 1499 (vs), 1307 (vs), 874 (s), 770 (s), 745 (s), 693 (s), 505 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 183.05 (100) $[M]^{+}$.

General procedure for the Sonogashira coupling of aryl iodides

In a nitrogen filled glovebox, an oven dried crimp cap vial equipped with a Teflon coated magnetic stirring bar was charged with **Pd-1** (6.2 mg, 0.005 mmol, 0.005 equiv.). The vial was removed from the glovebox and the complex was dissolved in dry and degassed MeCN (2 mL). After, the aryl iodide (1 mmol, 1 equiv.) was added via syringe followed by triethylamine (279 µL, 2 mmol, 2 equiv.) and 134 µL phenylacetylene (1.2 mmol, 1.2 equiv.). The reaction mixture was stirred for 16 h at 40 °C. After, the reaction solution was diluted with 10 mL ethyl acetate and washed with 10 mL water. Then the aqueous layer was extracted with ethyl acetate 2x10 mL. The combined organic layers were washed with 10 mL of brine and dried over $MgSO_4$. Afterwards the crude reaction mixture was purified by flash chromatography.

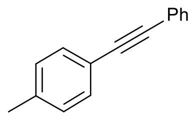
*4.31 Synthesis 1,2-diphenylethyne (**8aa**) [CAS 501-65-5]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **8aa** (166 mg, 93%) as colourless solid.
The NMR data match with those previously reported.[39]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 - 7.64 (m, 4 H), 7.31 - 7.43 (m, 6 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 131.6, 128.3, 128.2, 123.3, 89.4 ppm; **mp:** 62 °C (from cyclohexane) (lit.,[40] 62-63 °C); **IR (ATR Mode):** 3057, 1601, 1498, 1443, 1264, 1070, 755, 689 cm^{-1}; **GC-MS (EI-TOF):** m/z(%) = 179.05 (15), 178.05 (100), 176.0 (20).

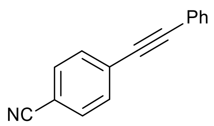
*4.32 Synthesis 1-methyl-4-(phenylethynyl)benzene (**8ba**) [CAS 3287-02-3]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **8ba** (156 mg, 81%) as colourless crystalline solid.
The NMR data match with those previously reported.[41]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 - 7.62 (m, 2 H), 7.45 - 7.52 (m, 2 H), 7.32 - 7.43 (m, 3 H), 7.16 - 7.24 (m, 2 H), 2.41 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.3, 131.5, 131.5, 129.1, 128.3, 128.0, 123.5, 120.2, 89.6, 88.7, 21.5 ppm; **mp:** 69 °C (from cyclohexane) (lit.,[42] 69-70 °C); **IR (ATR Mode):** 3081 (w), 3052 (w), 3031 (w), 2929 (w), 2857 (w), 2217 (w), 1594 (s), 1509 (s), 1486 (s), 1440 (s), 817 (vs), 754 (vs), 690 (vs), 516 (vs) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 192.05 (100), 191.05 (46), 189.0 (24).

*4.33 Synthesis 4-(phenylethynyl)benzonitrile (**8ca**) [CAS 29822-79-5]*

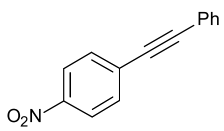


The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **8ca** (183 mg, 90%) as orange solid.

The NMR data match with those previously reported.[43]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 - 7.68 (m, 4 H), 7.51 - 7.59 (m, 2 H), 7.34 - 7.43 (m, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 132.1, 132.0, 131.8, 129.1, 128.5, 128.2, 122.2, 118.5, 111.5, 93.8 , 87.7 ppm; **mp:** 105 °C (from cyclohexane/ethyl acetate) (lit.,[44] 105-106 °C); **IR (ATR mode):** 3056 (vw), 2227 (w), 1681 (s), 1604 (s), 1503 (w), 1407 (w), 1313 (s), 896 (s), 734 (vs), 702 (vs), 691 (vs), 556 (s), 531 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 203.0 (100) $[M]^+$.

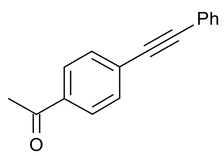
*4.34 Synthesis 1-nitro-4-(phenylethynyl)benzene (**8da**) [CAS 1942-30-9]*



The compound was synthesised according to the general procedure 5.3.3. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **8da** (215 mg, 96%) as orange solid.
The NMR data match with those previously reported.[45]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 - 8.28 (m, 2 H), 7.63 - 7.72 (m, 2 H), 7.53 - 7.62 (m, 2 H), 7.34 - 7.45 (m, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 147.0 (s), 132.2 (s), 131.8 (s), 130.2 (s), 129.3 (s), 128.5 (s), 123.6 (s), 122.1 (s), 94.7 (s), 87.5 (s) ppm; **mp:** 118 °C (from cyclohexane/ethyl acetate) (lit.,[44] 118-120 °C) ; **IR (ATR mode):** 3104 (w), 3082 (w), 2217 (s), 1592 (s), 1518 (vs), 1509 (s), 1378 (w), 1345 (s), 1310 (s), 1177 (w), 1137 (w), 921 (s), 833 (vs), 764 (s), 748 (s), 507 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 223.0 (100) $[M]^+$, 193.05 (56), 177.0 (21), 176.0 (67), 165.0 (29), 151.0 (24), 150.0 (18).

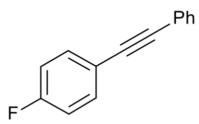
*4.35 Synthesis 1-(4-(phenylethynyl)phenyl)ethan-1-one (**8ea**) [CAS 1942-31-0]*



The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane/ethyl acetate (0-10%) yielding **8ea** (215 mg, 96%) as orange solid.
The NMR data match with those previously reported.[46]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 - 7.99 (m, 2 H), 7.59 - 7.66 (m, 2 H), 7.53 - 7.59 (m, 2 H), 7.35 - 7.42 (m, 3 H), 2.62 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 197.3 (s) 136.2 (s), 131.7 (s), 131.7 (s), 128.8 (s), 128.4 (s), 128.1 - 128.3 (m), 122.6 (s), 92.7 (s), 88.6 (s), 26.6 (s) ppm; **mp:** 98 °C (from cyclohexane/ethyl acetate) (lit.,[47] 95-98 °C); **IR (ATR mode):** 3000 (w), 1678 (vs), 1601 (s), 1552 (s), 1485 (s), 1442 (s), 1434 (s), 1423 (s), 1404 (s), 1360 (w), 1285 (s), 1180 (w), 1157 (w), 1141 (s), 1108 (w), 1070 (w), 1014 (w), 958 (s), 923 (w), 851 (vs), 760 (vs), 738 (s), 691 (vs), 640 (s), 591 (s), 568 (s), 535 (s) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 220.05 (62) $[M]^{+}$, 205.0 (100).

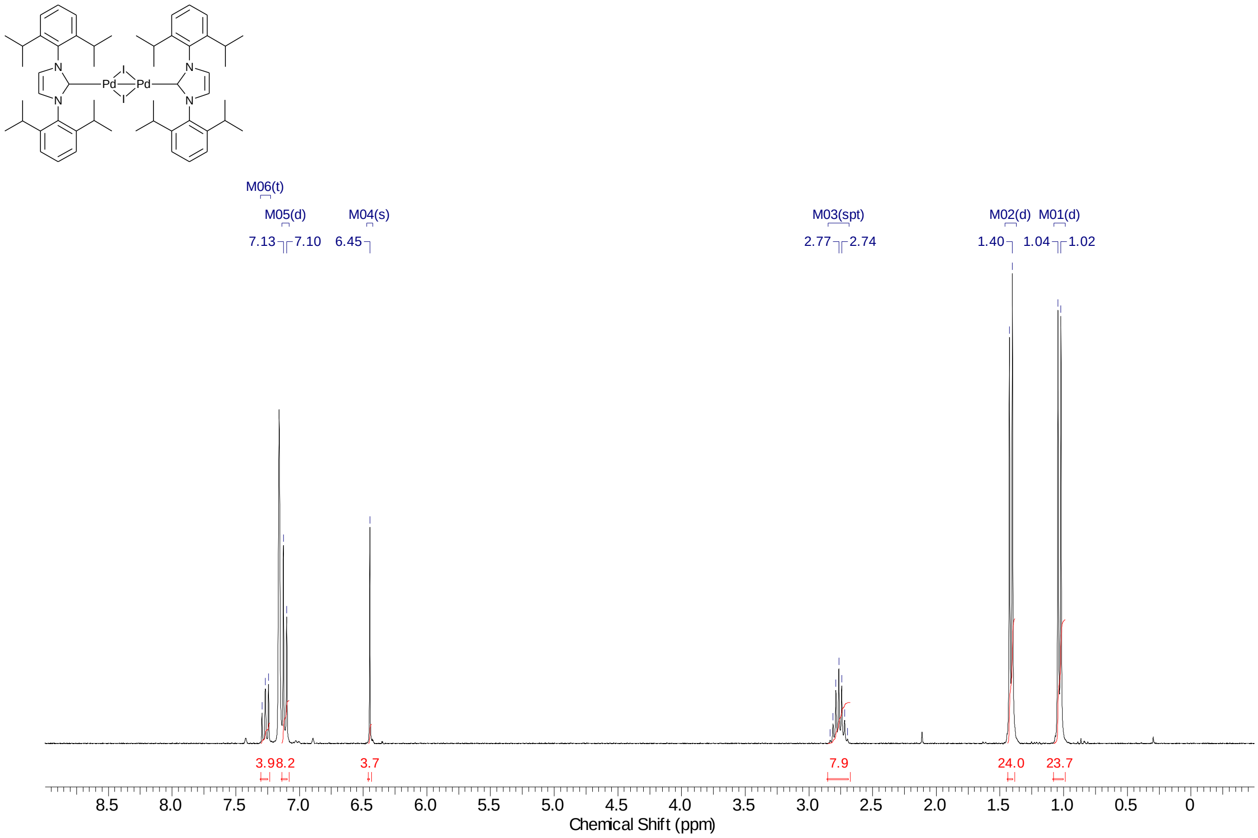
*4.36 Synthesis 1-fluoro-4-(2-phenylethynyl)benzene (**8fa**) [CAS 1942-30-9]*



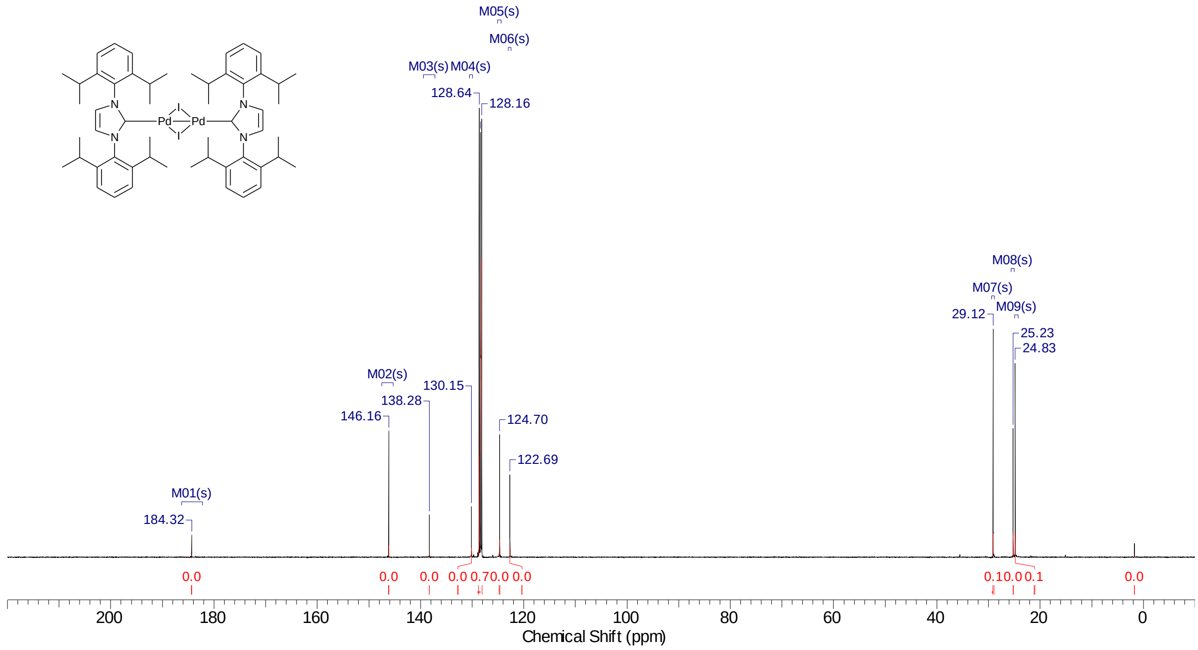
The compound was synthesised according to the general procedure. The crude reaction mixture was purified by flash chromatography using cyclohexane yielding **8fa** (183 mg, 93%) as colourless solid.
The NMR data match with those previously reported.[48]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45 - 7.62 (m, 4 H), 7.29 - 7.43 (m, 3 H), 6.99 - 7.14 (m, 2 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.5 (d, *J*=250.4 Hz), 133.5 (d, *J*=8.3 Hz), 131.6, 128.4, 128.3, 123.1, 119.4 (d, *J*=3.3 Hz), 115.6 (d, *J*=23.2 Hz), 89.0, 88.3 ppm; **^{19}F NMR** (235 MHz, $CDCl_3$): δ = -111.29 - -110.82 (m) ppm; **mp:** 111 °C (from cyclohexane/ethyl acetate) (lit.,[49] 108-111 °C); **IR (ATR mode):** 1508 (w), 1217 (w), 841 (w), 755 (w), 687 (w), 515 (w), 493 (w) cm^{-1}; **GC-MS (EI-TOF):** m/z (%) = 197.1 (15), 196.1 (100), 194.1 (12), 170.05 (8), 98.05 (8).

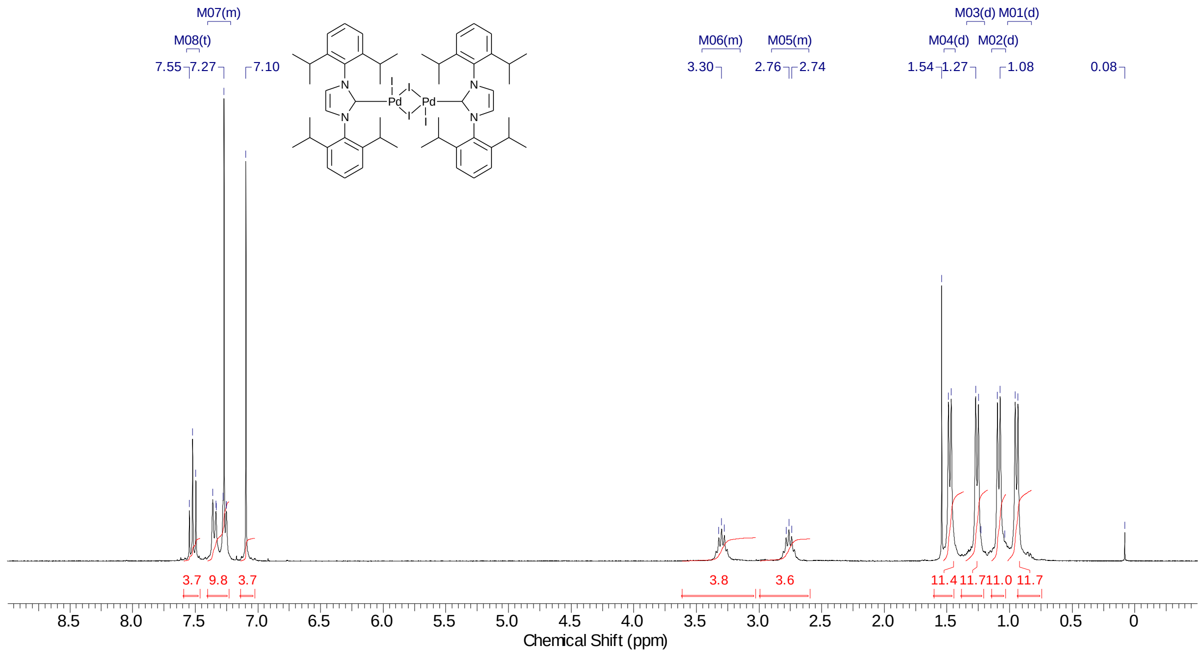
5 NMR Data



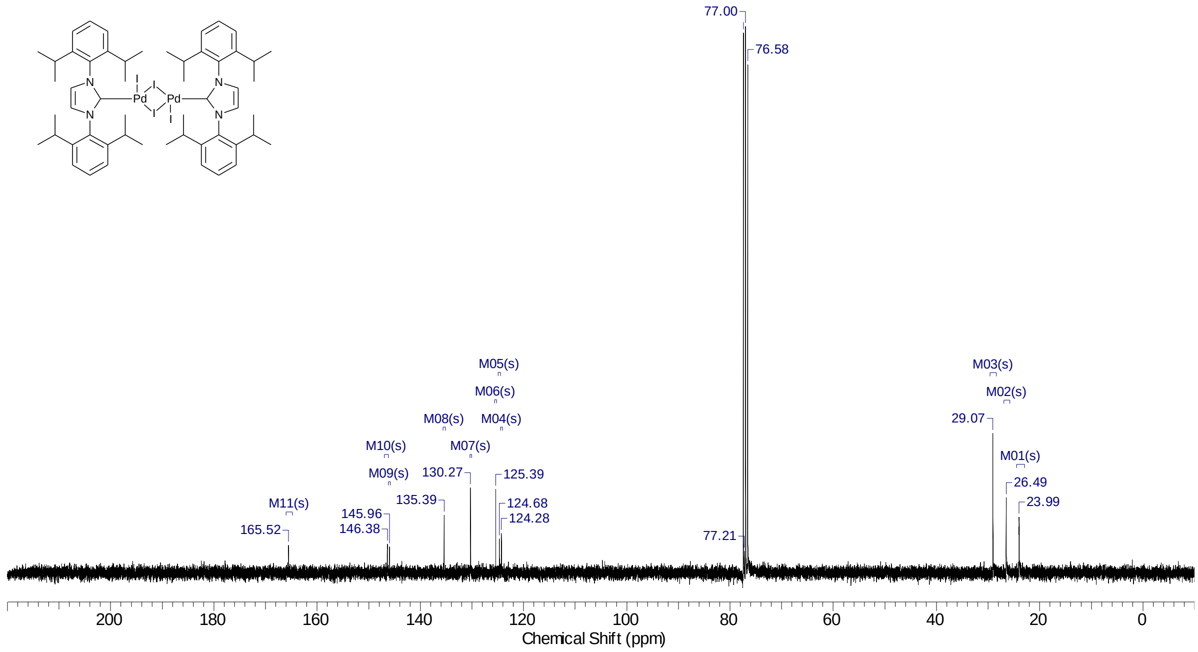
[1]H-NMR of $[(IPr)PdI]_2$ (**Pd-1**).



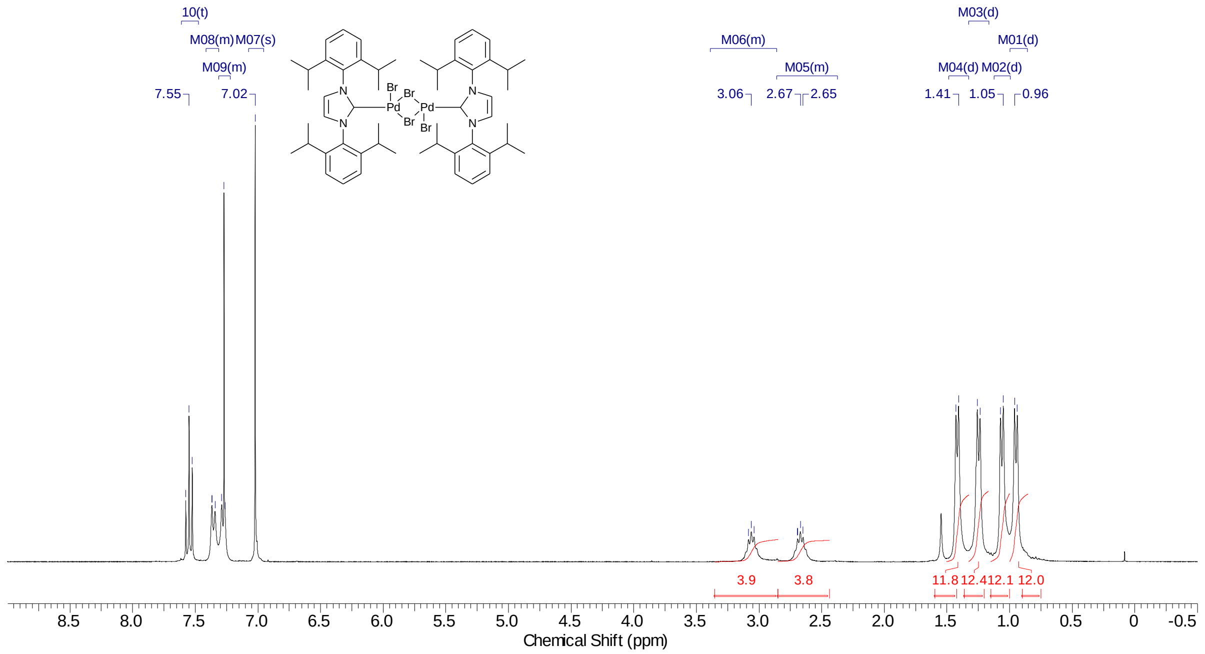
[13]C-NMR of $[(IPr)PdI]_2$ (**Pd-1**).



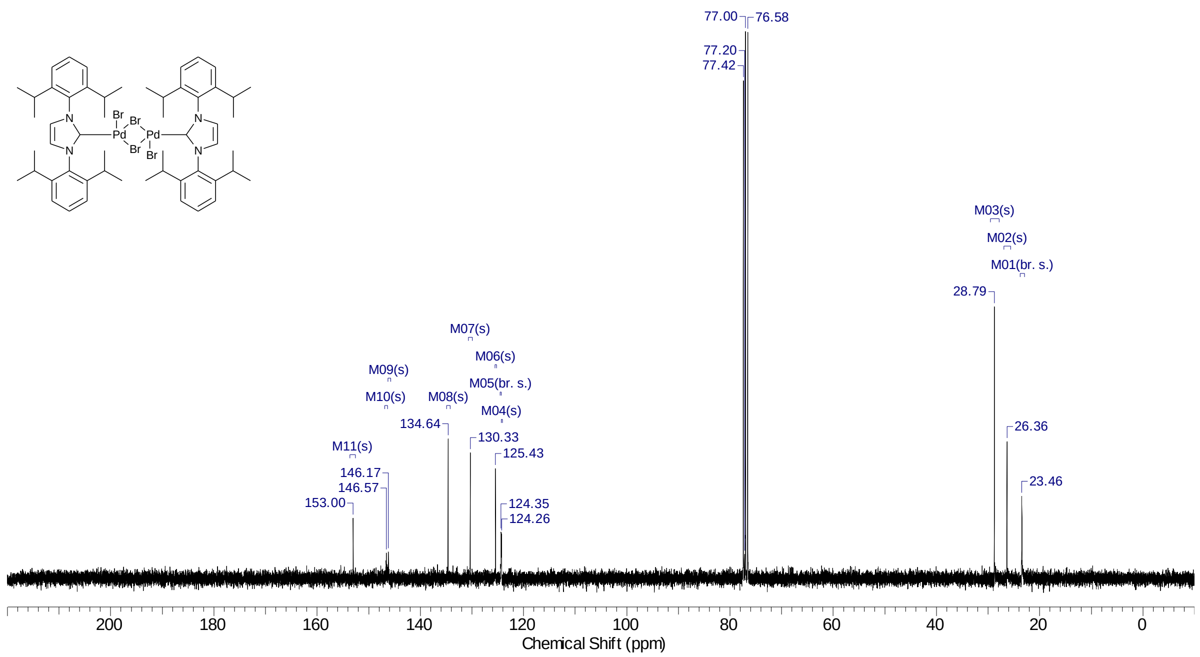
[1]H-NMR of $[(IPr)PdI_2]_2$ (**Pd-2**)



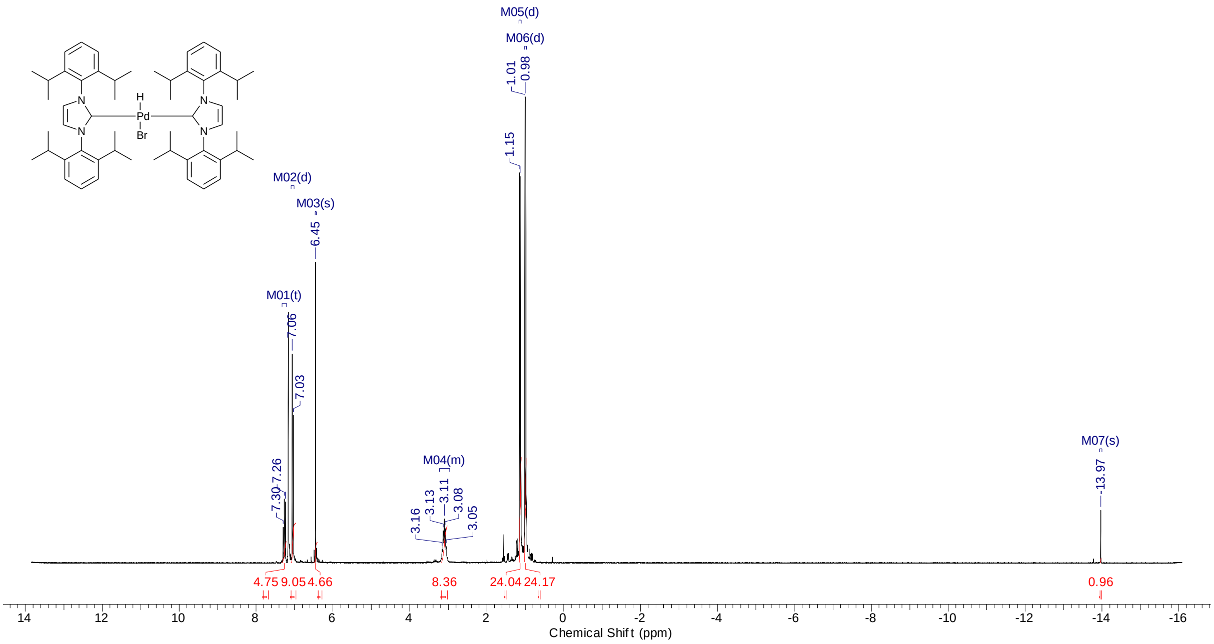
[13]C NMR of $[(IPr)PdI_2]_2$ (**Pd-2**).



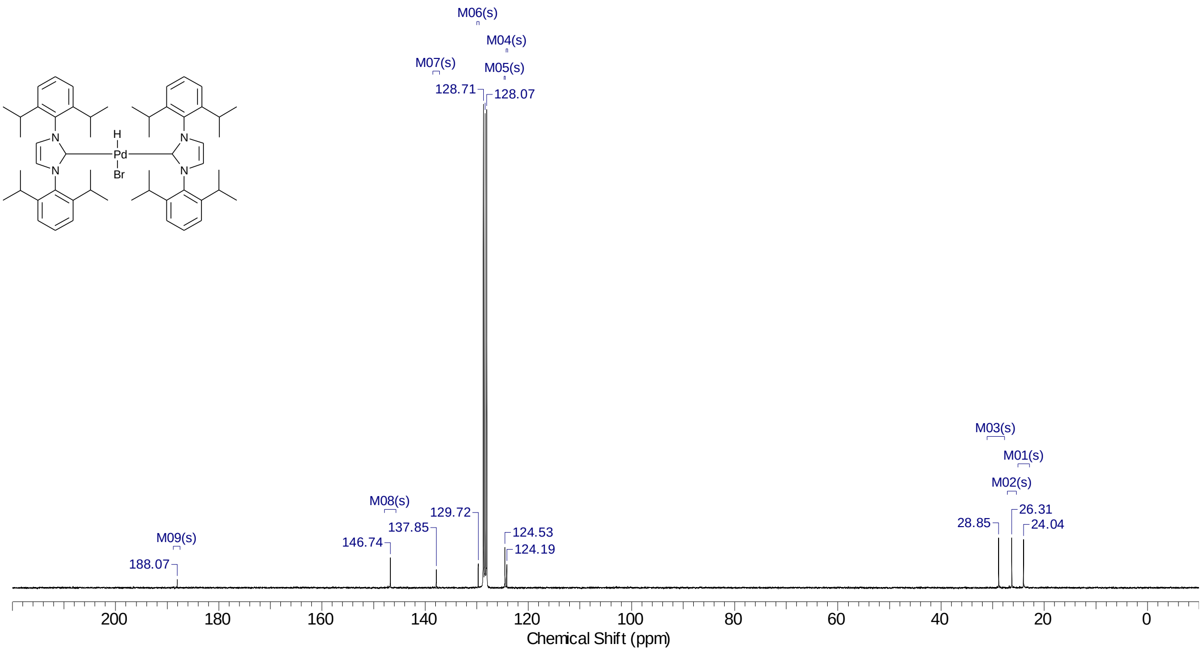
[1]H-NMR of [{(IPr)PdBr$_2$}$_2$] (**Pd-3**).



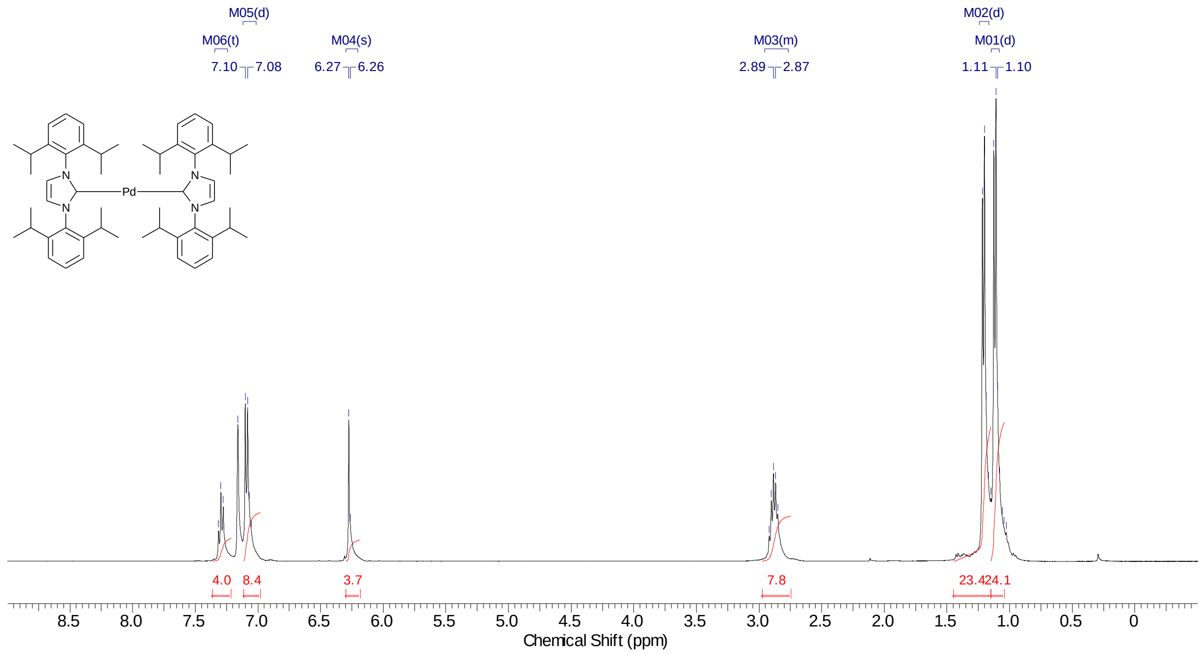
[13]C NMR of [{(IPr)PdBr$_2$}$_2$] (**Pd-3**).



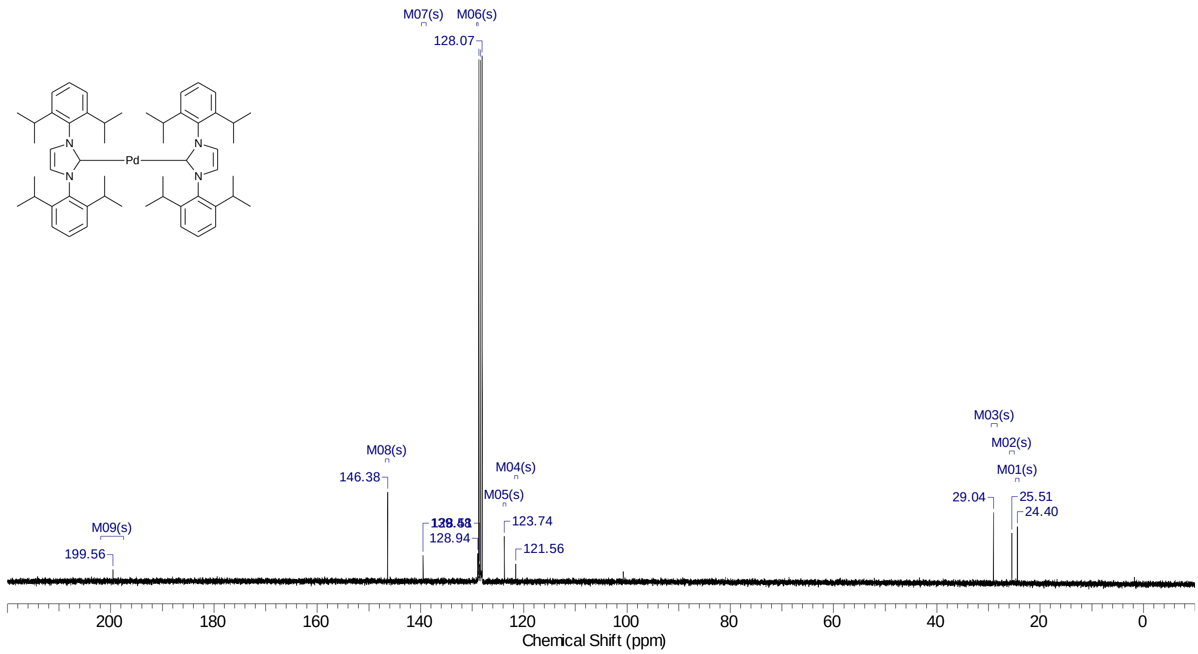
[1]H-NMR of [(IPr)$_2$PdHBr] (**Pd-4**).



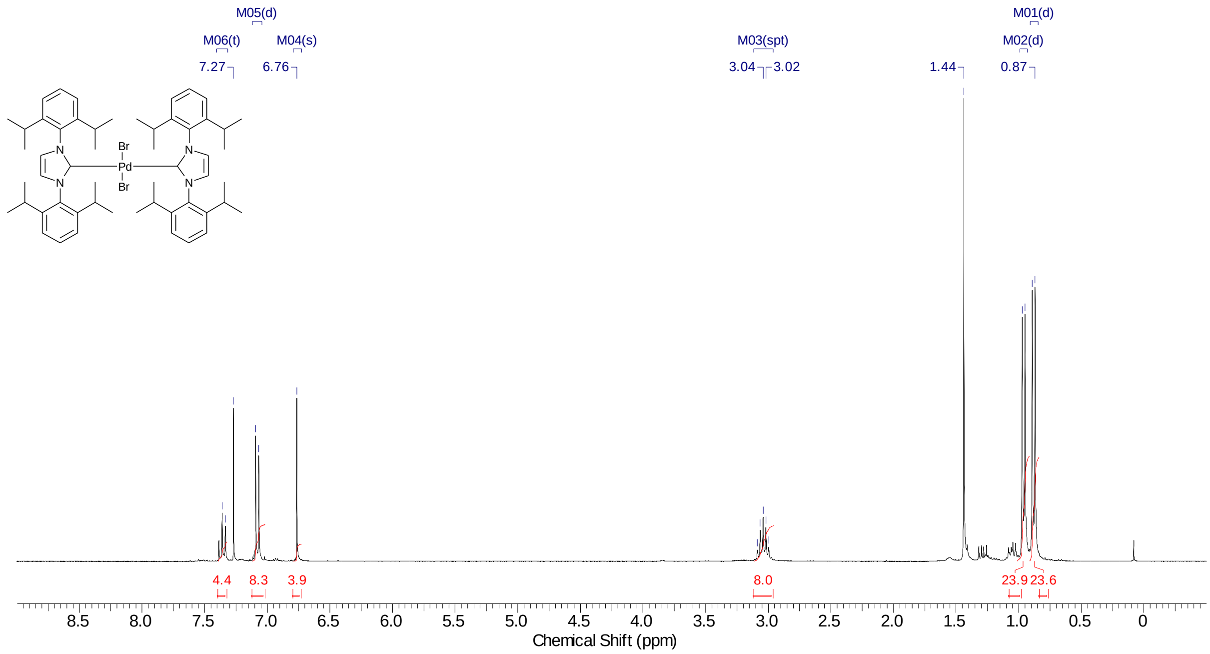
[13]C-NMR of [(IPr)$_2$PdHBr] (**Pd-4**).



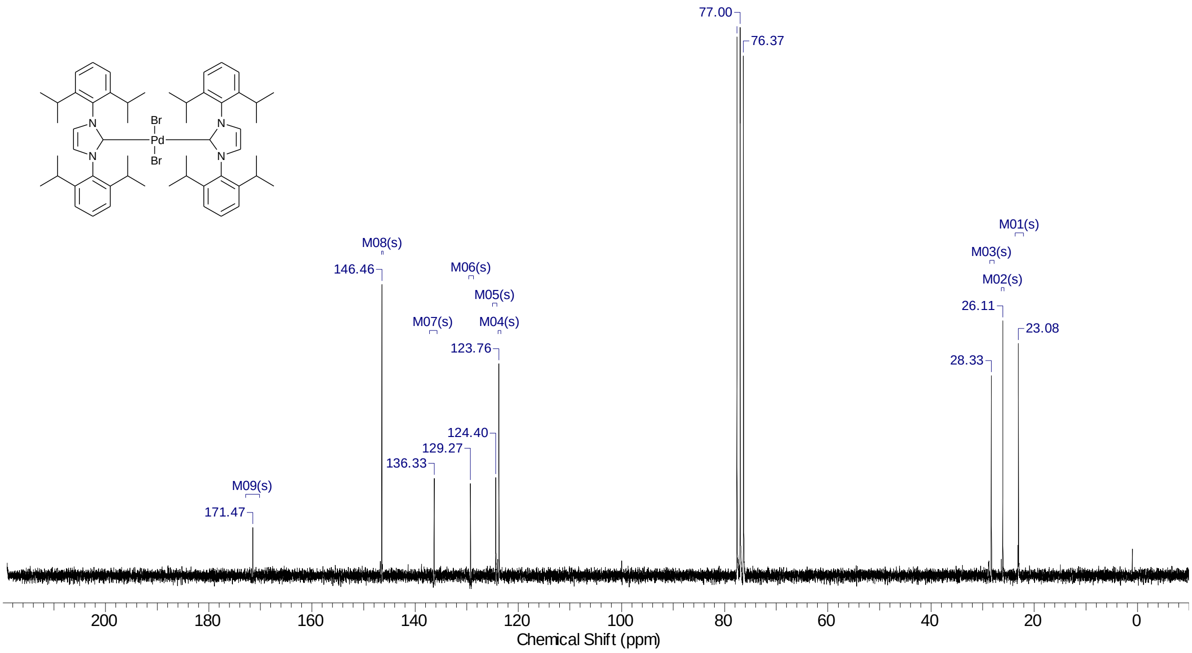
[1]H-NMR of [$(IPr)_2Pd$].



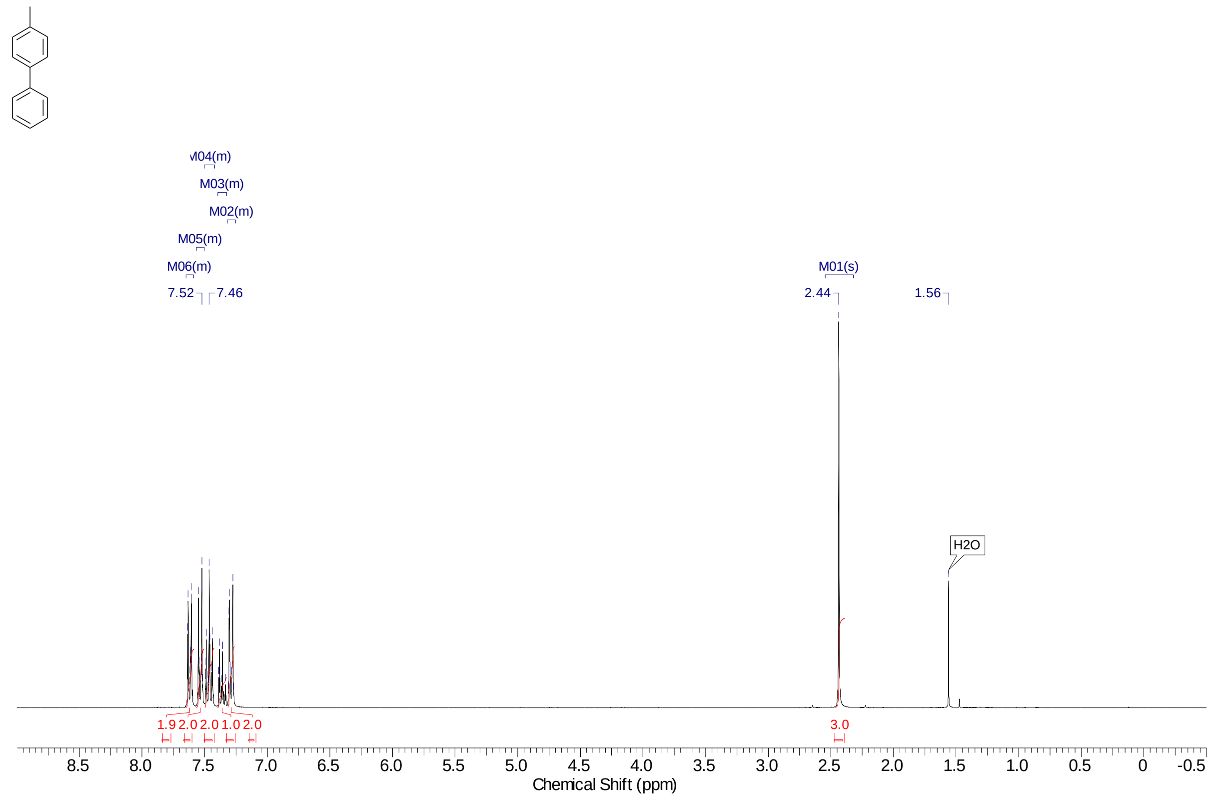
[13]C NMR of [$(IPr)_2Pd$].



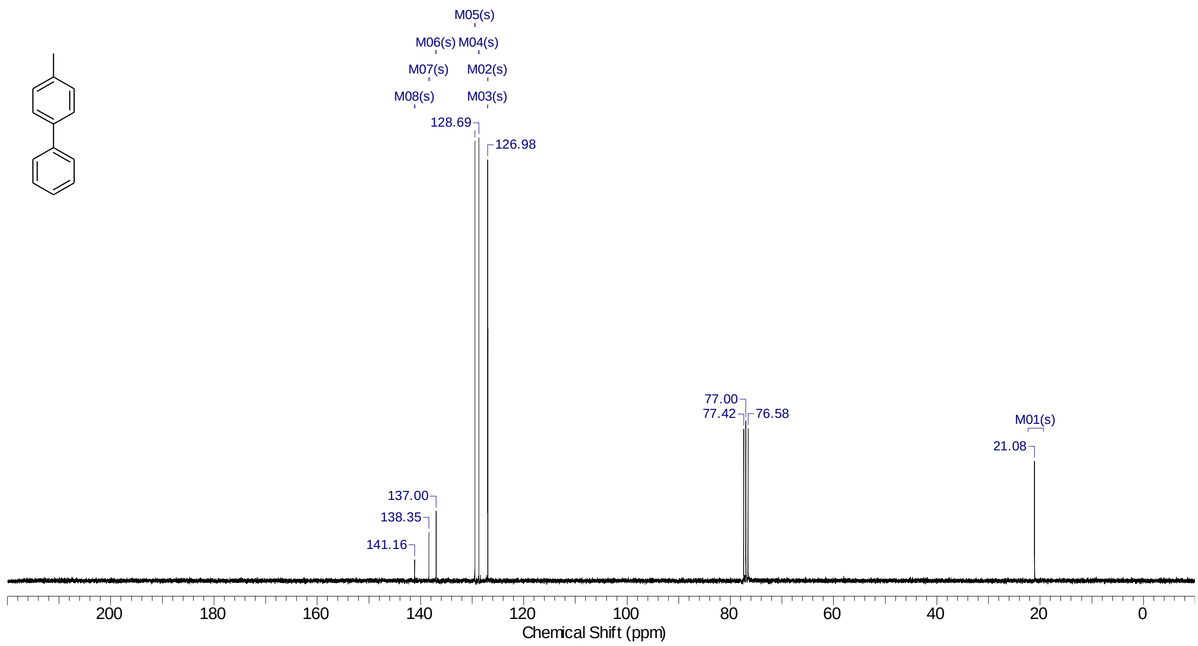
[1]H-NMR of [(IPr)$_2$PdBr$_2$].



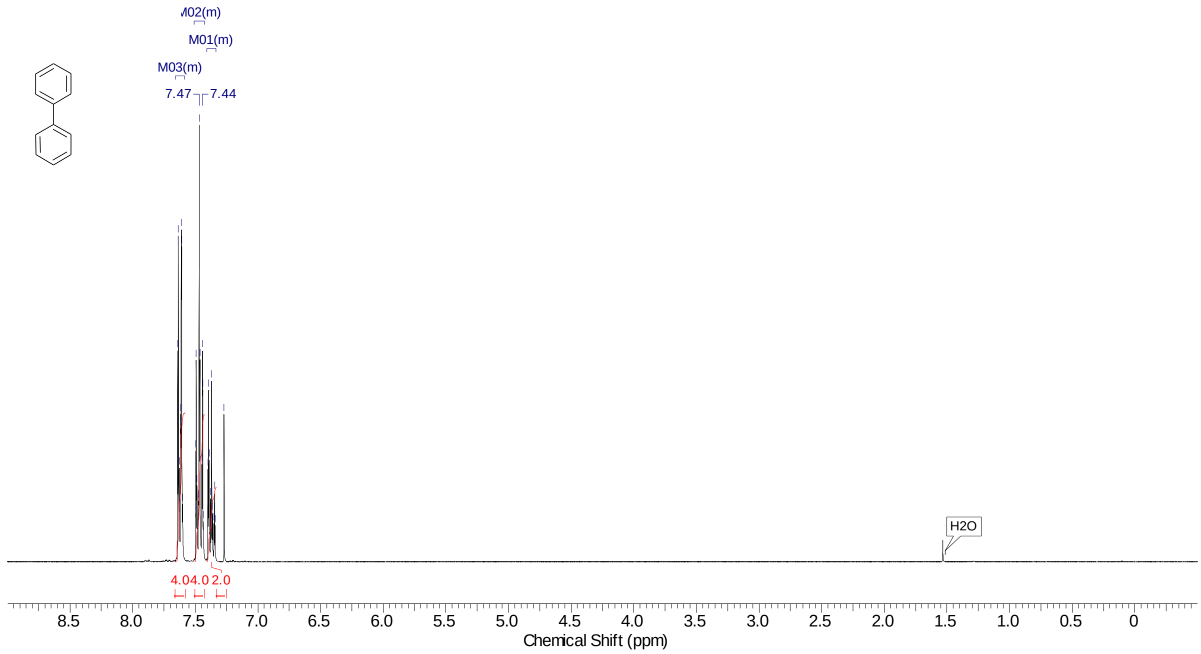
[13]C NMR of [(IPr)$_2$PdBr$_2$].



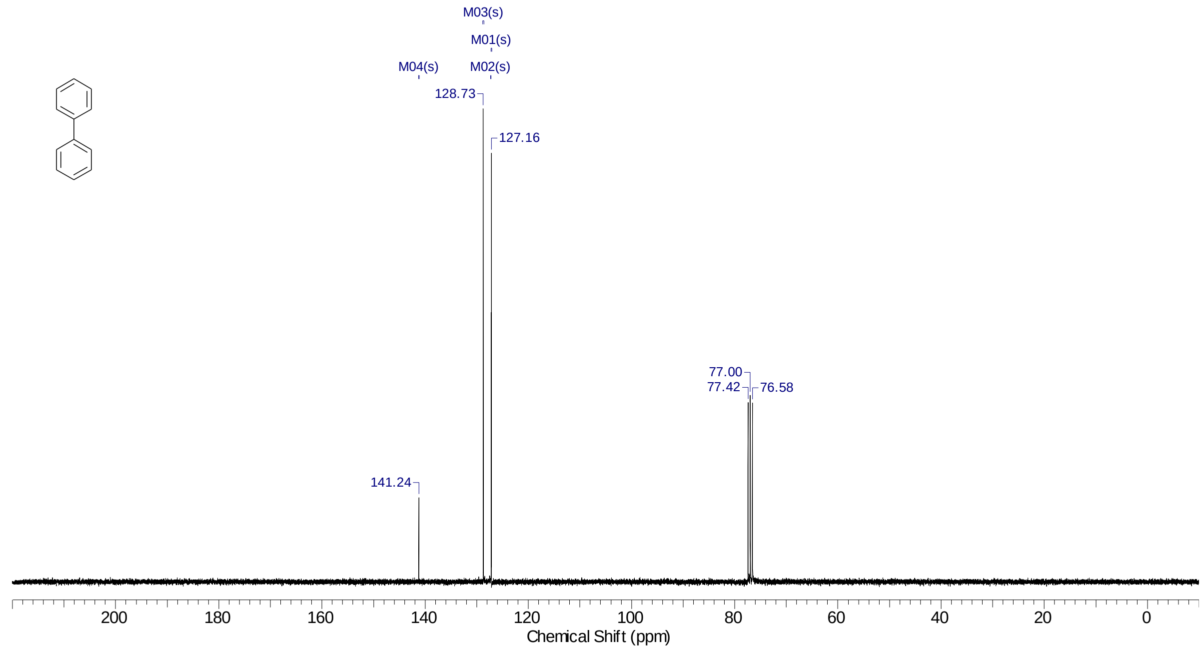
^{1}H-NMR of 1-methyl-4-phenyl-benzene (**3aa**).



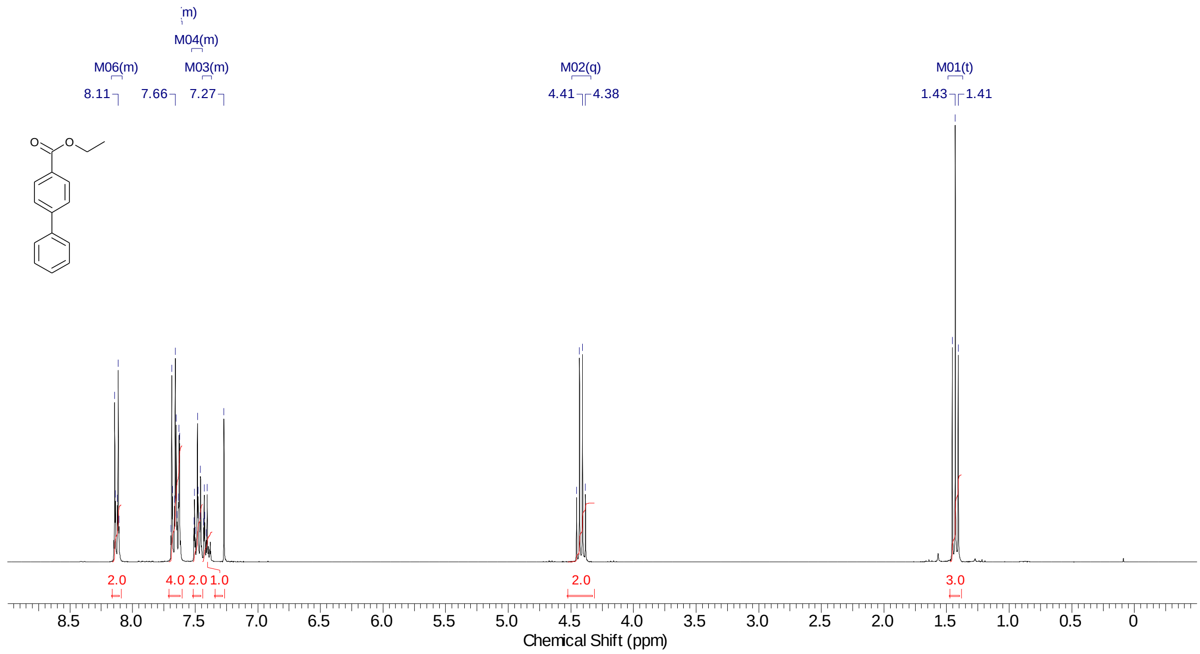
^{13}C NMR of 1-methyl-4-phenyl-benzene (**3aa**).



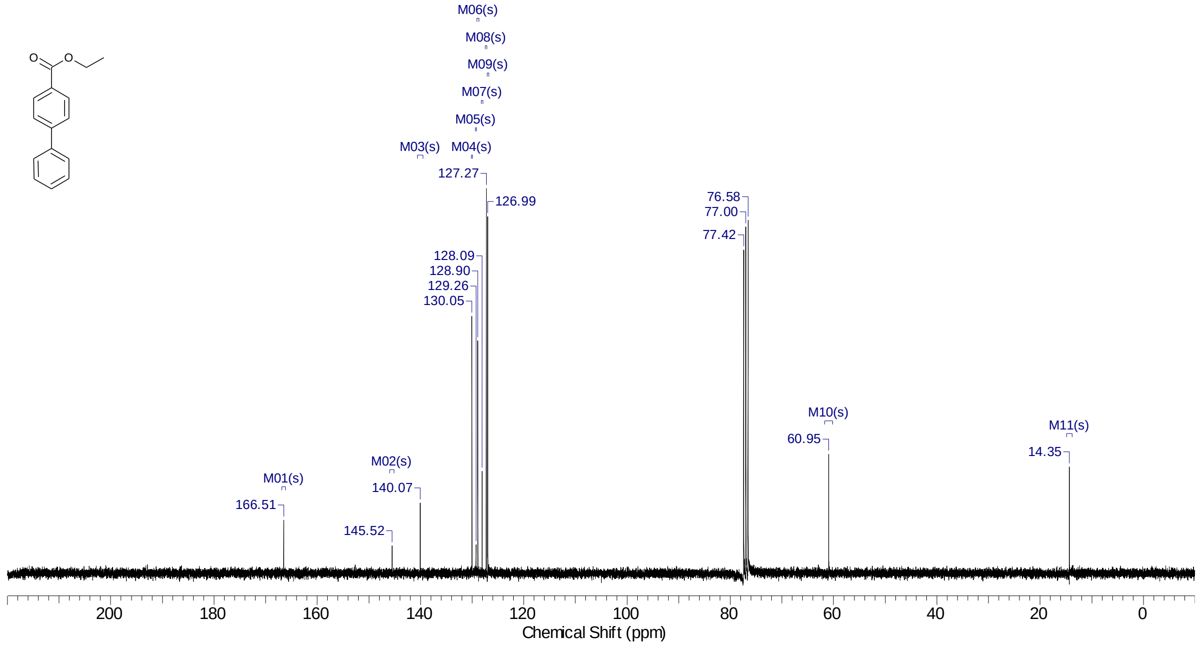
[1]H-NMR of biphenyl (**3ba**).



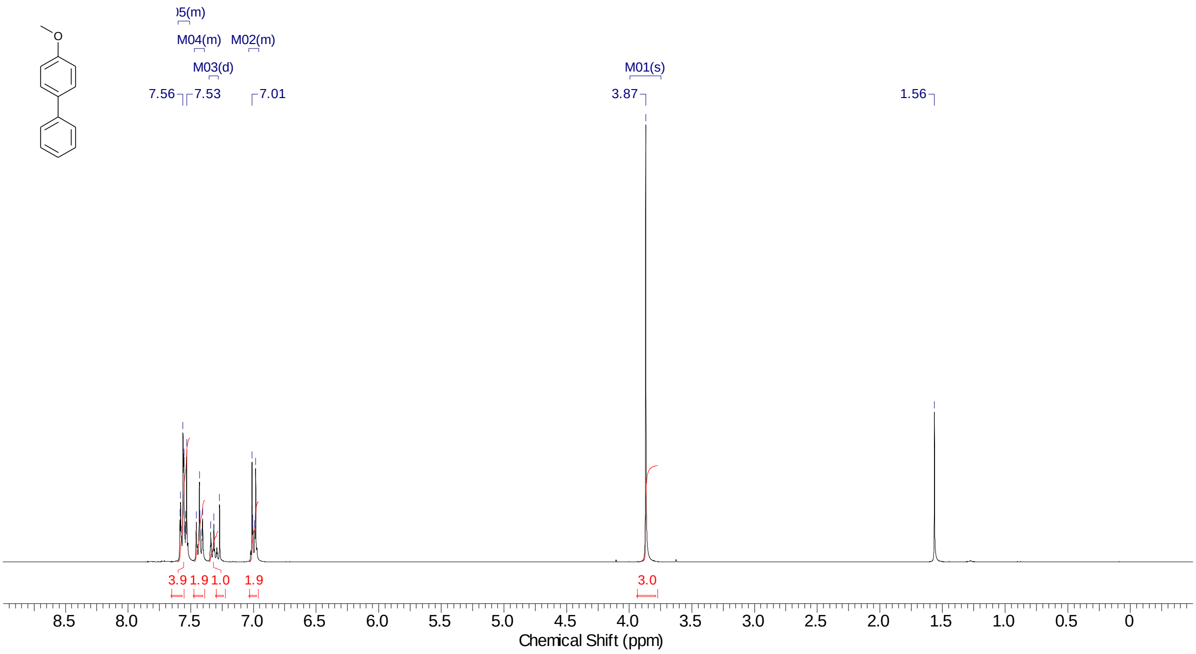
[13]C NMR of biphenyl (**3ba**).



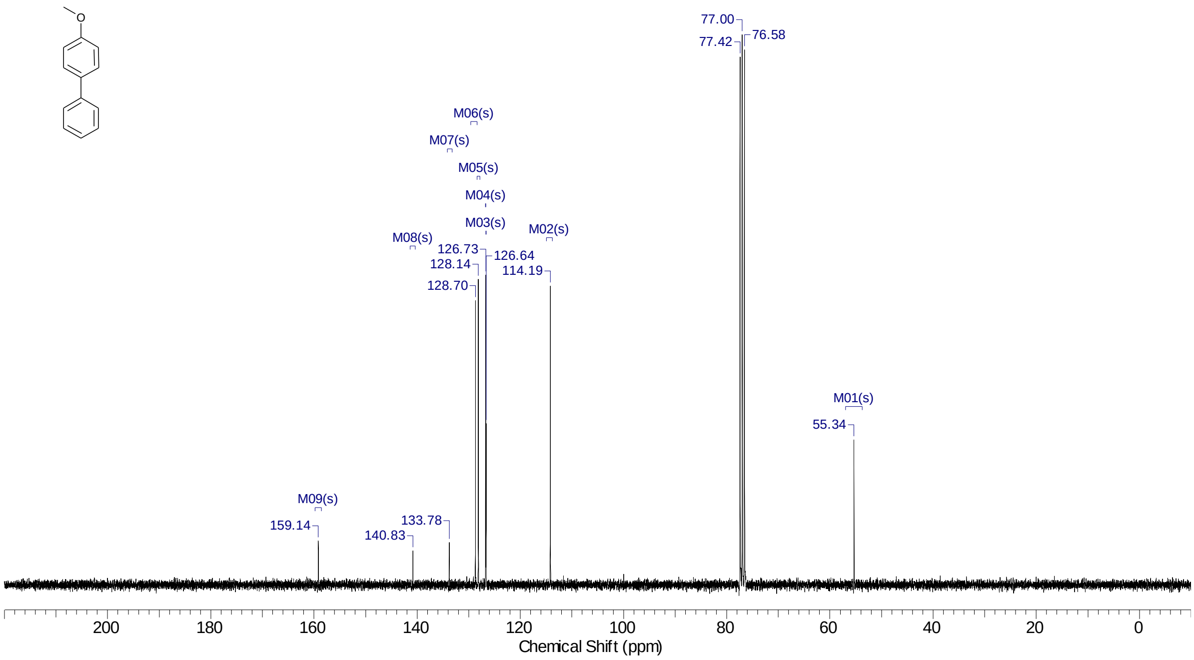
[1]H-NMR of ethyl 4-phenylbenzoate (**3ca**).



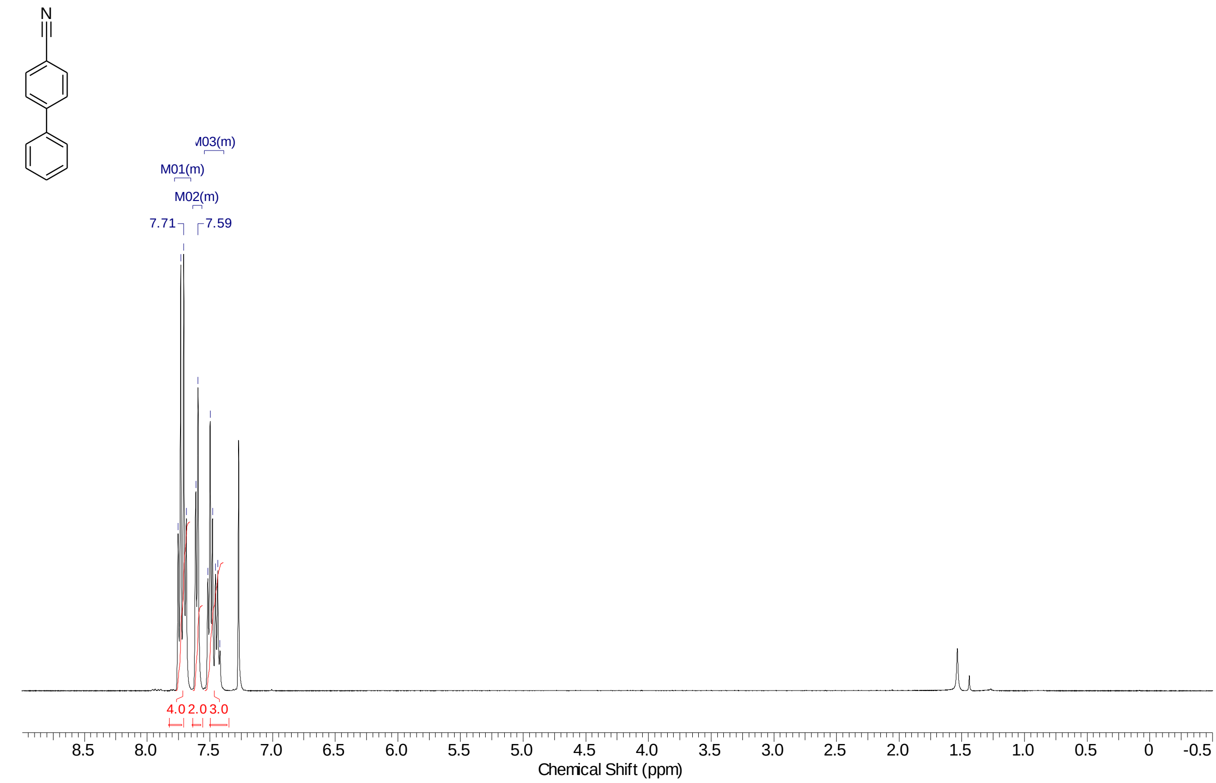
[13]C NMR of ethyl 4-phenylbenzoate (**3ca**).



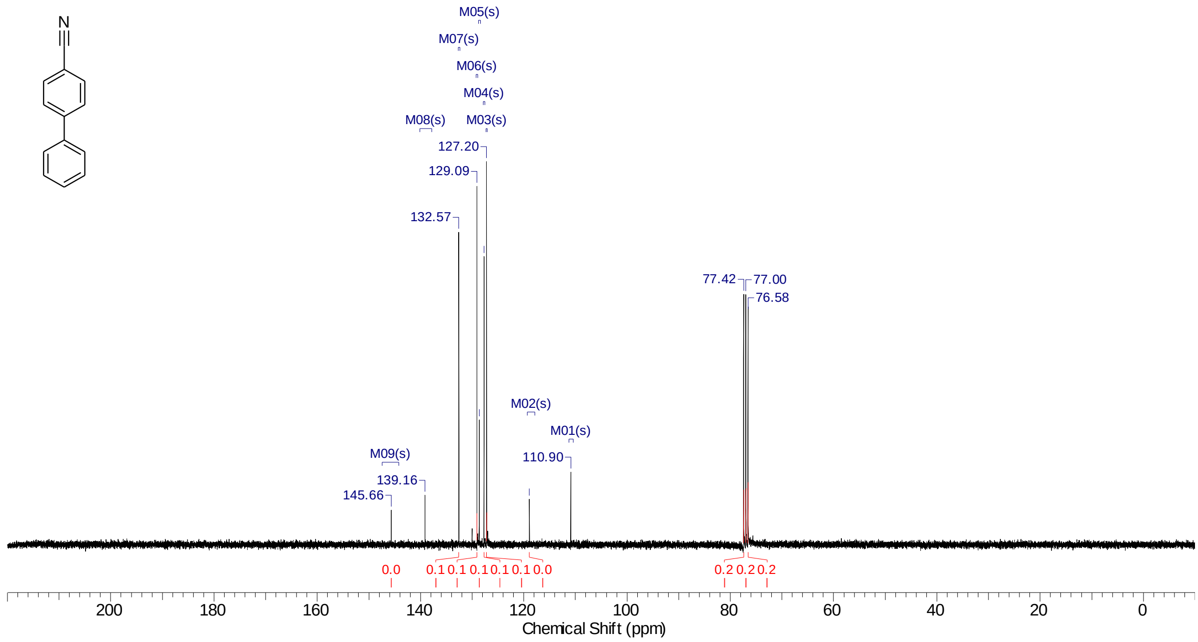
[1]H-NMR of 1-methoxy-4-phenyl-benzene (**3da**).



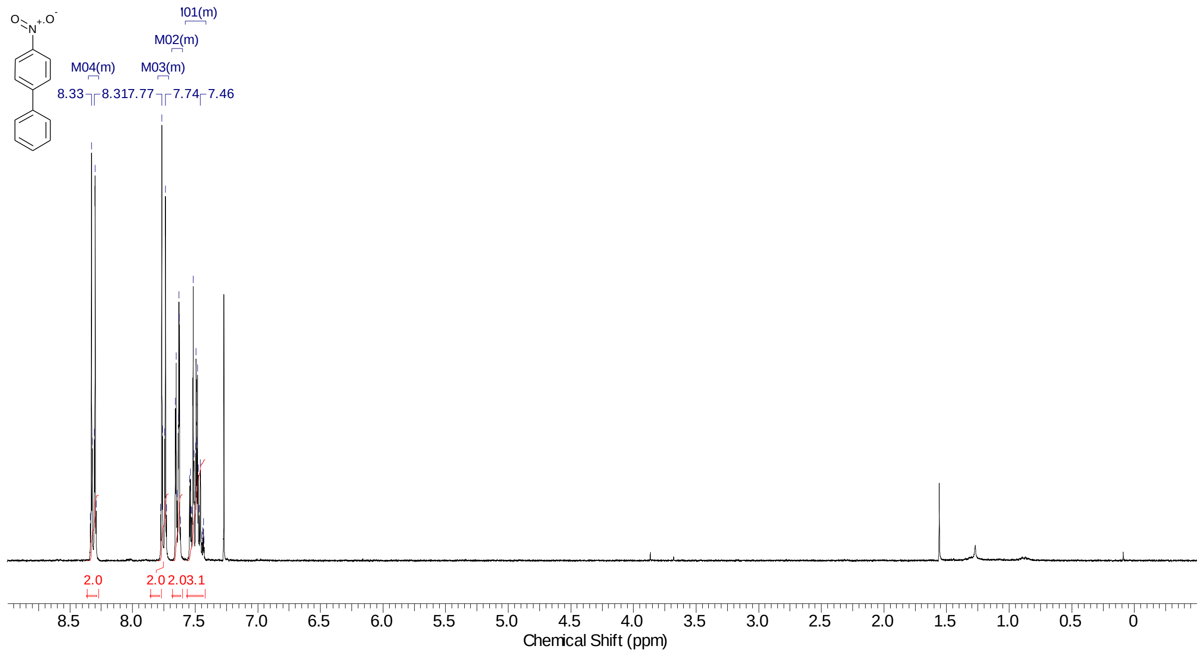
[13]C NMR of 1-methoxy-4-phenyl-benzene (**3da**).



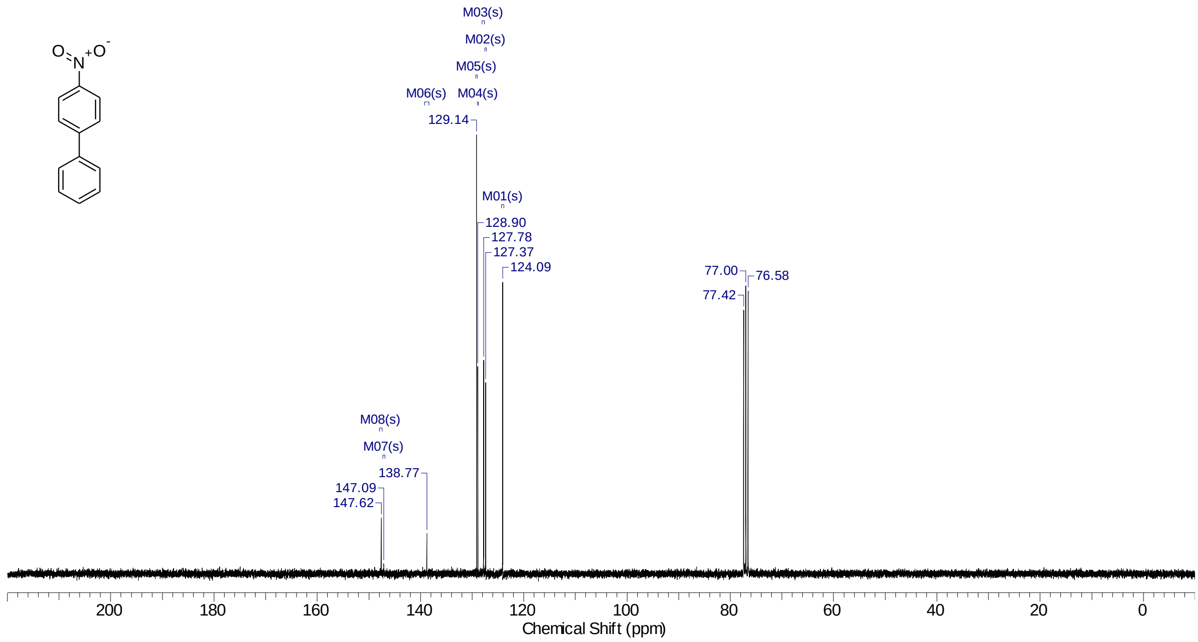
[1]H-NMR of 4-phenylbenzonitrile (**3ea**).



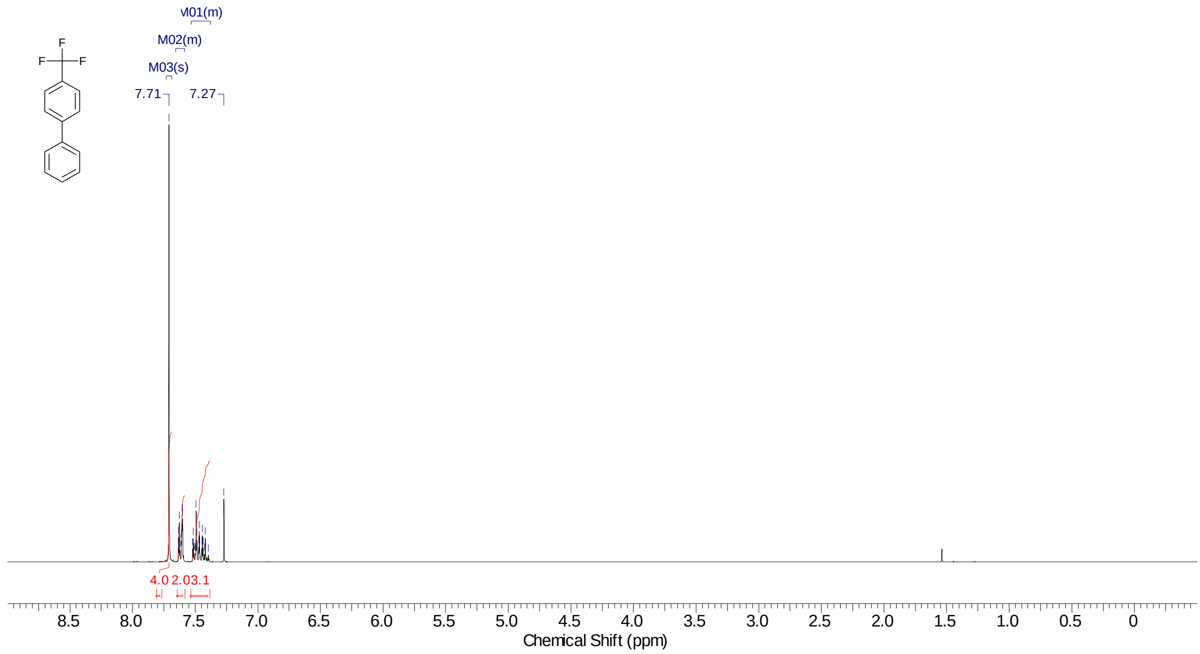
[13]C-NMR of 4-phenylbenzonitrile (**3ea**).



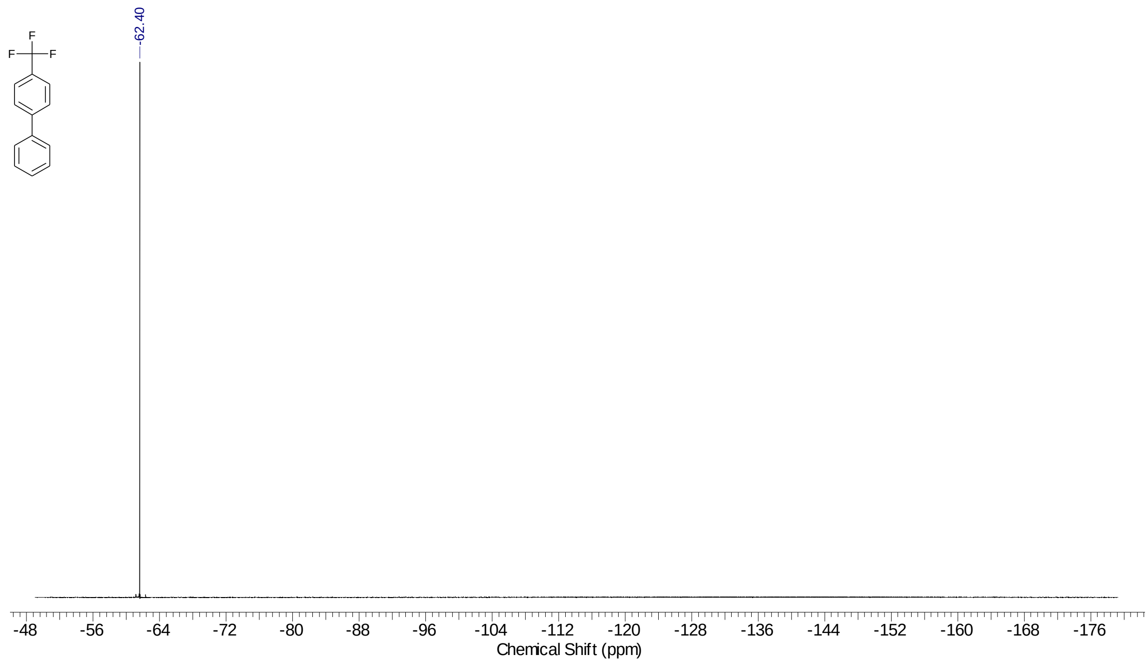
[1]H-NMR of 1-nitro-4-phenyl-benzene (**3fa**).



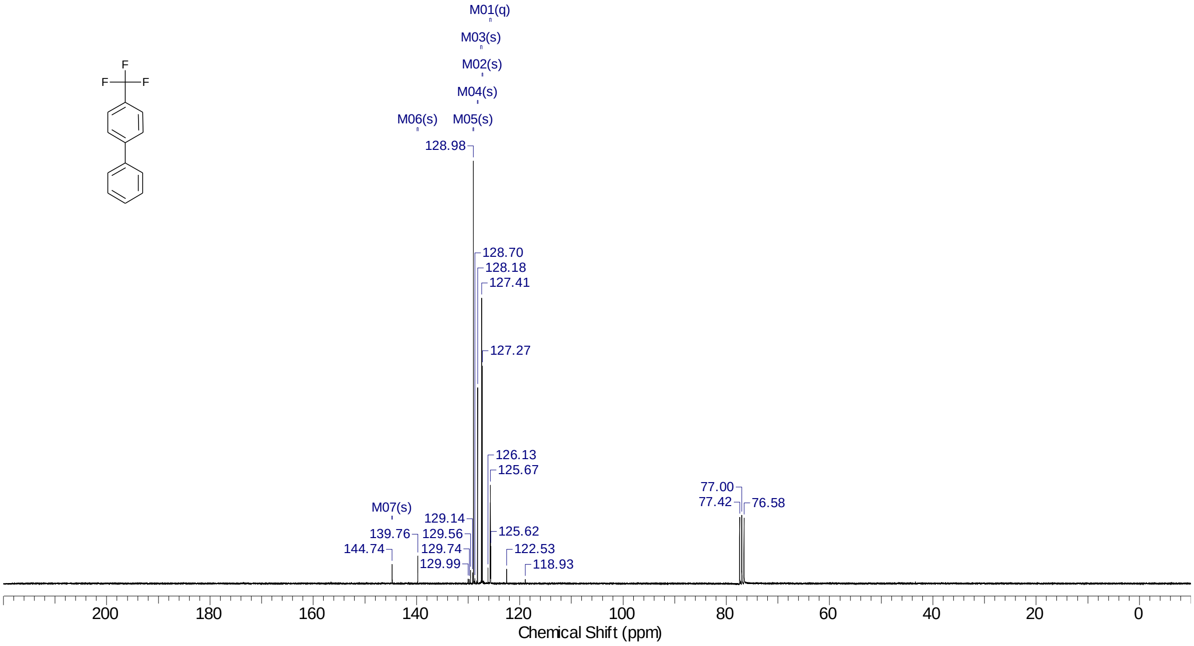
[13]C NMR of 1-nitro-4-phenyl-benzene (**3fa**).



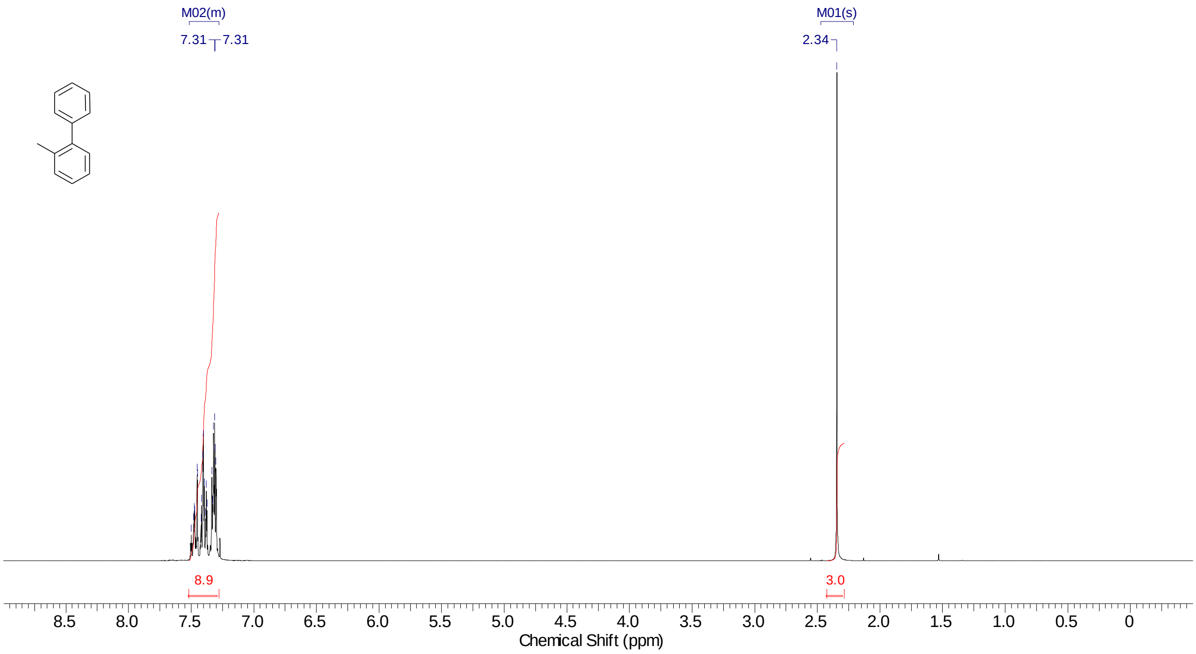
[1]H-NMR of 1-phenyl-4-(trifluoromethyl)benzene (**3ga**).



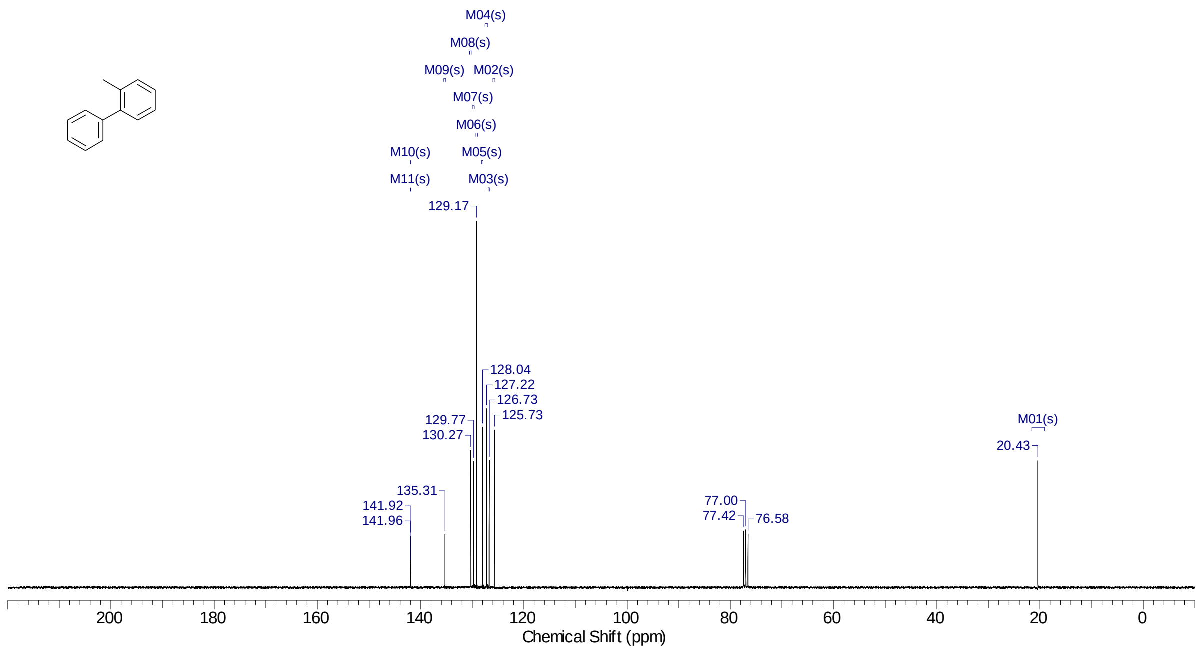
[19]F NMR of 1-phenyl-4-(trifluoromethyl)benzene (**3ga**).



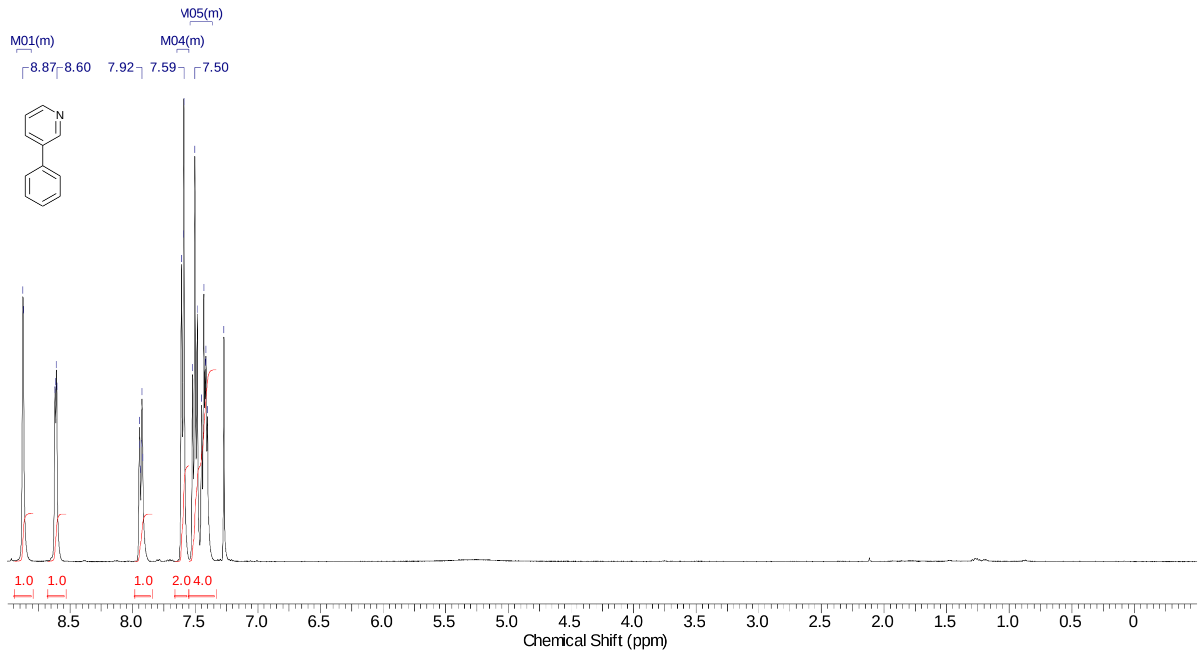
[13]C NMR of 1-phenyl-4-(trifluoromethyl)benzene (**3ga**).



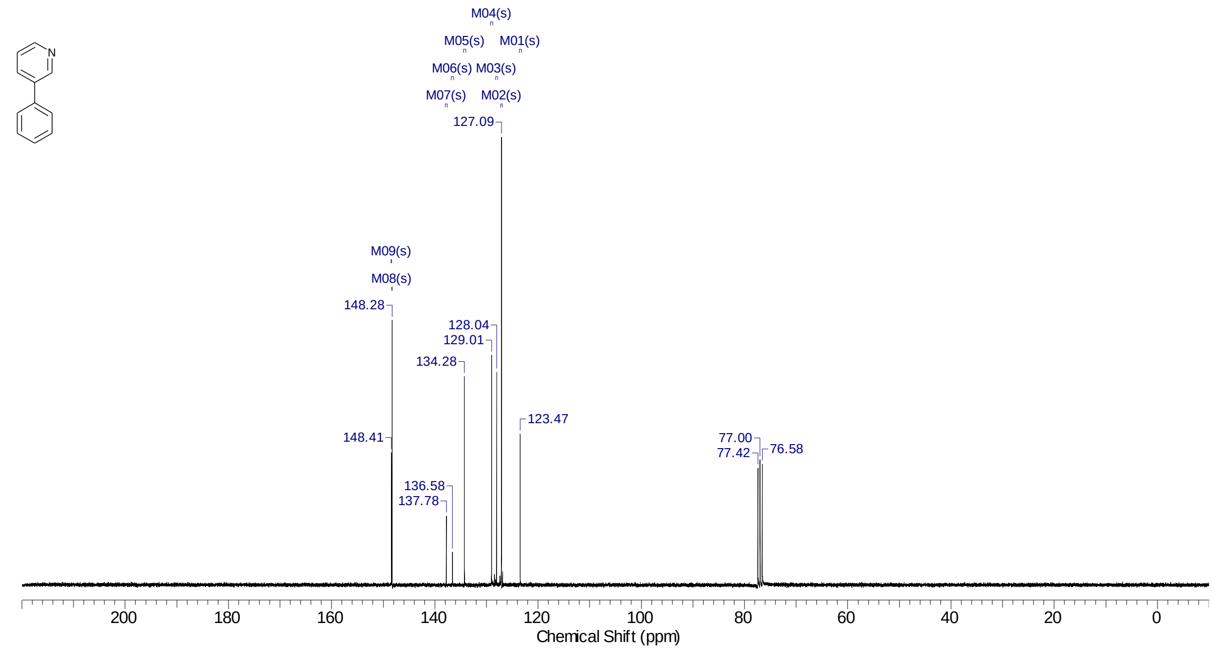
[1]H-NMR of 1-methyl-2-phenyl-benzene (**3ha**).



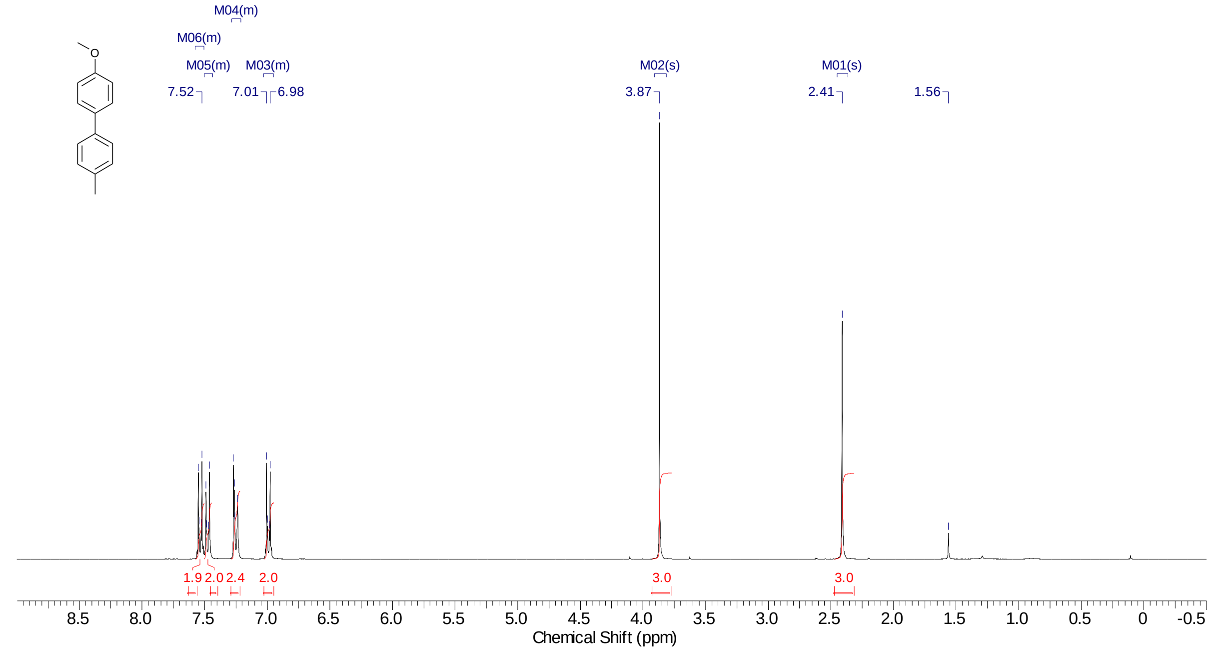
[13]C NMR of 1-methyl-2-phenyl-benzene (**3ha**).



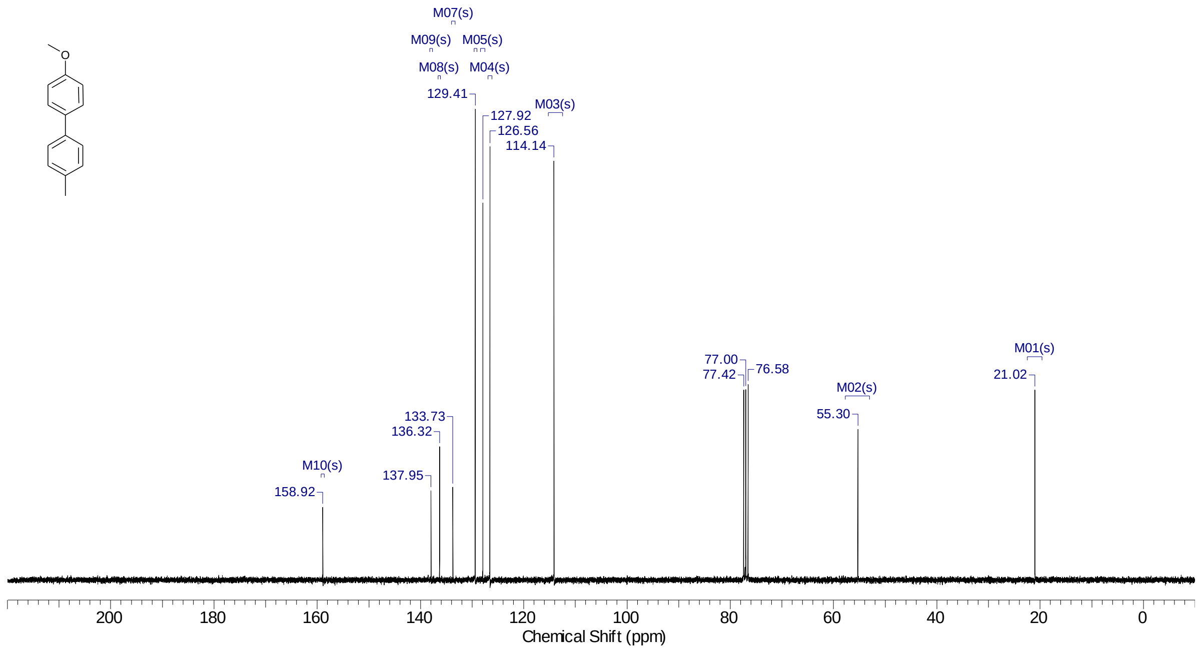
[1]H NMR of 3-phenylpyridine (**3ia**).



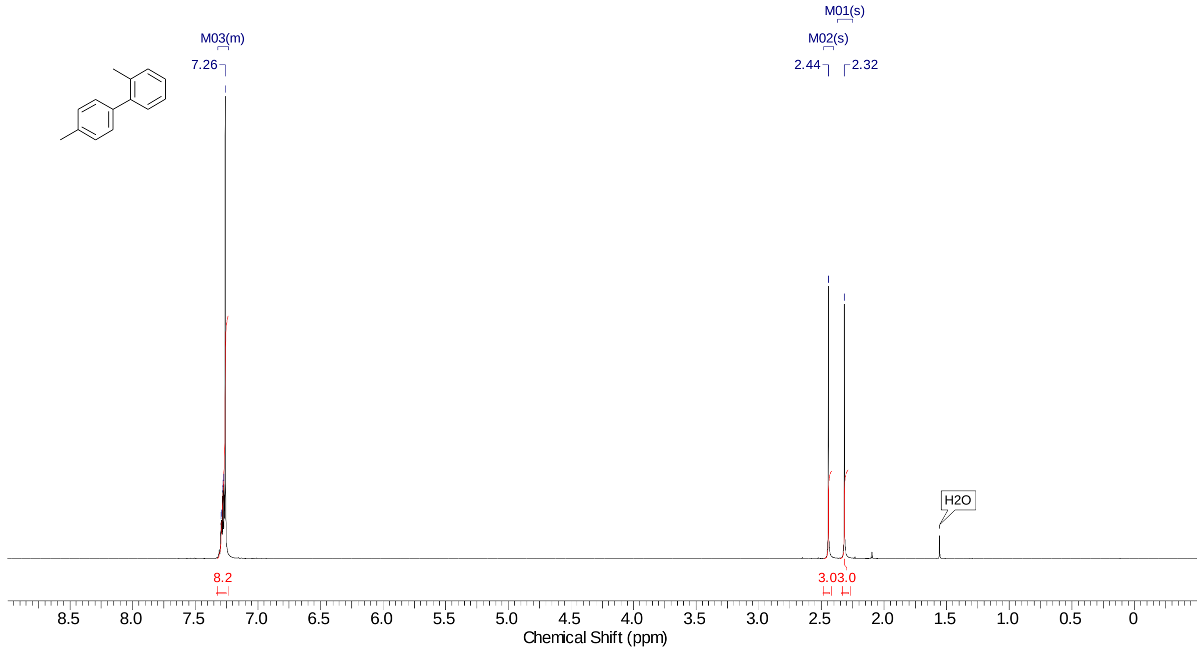
^{13}C NMR of 3-phenylpyridine (**3ia**).



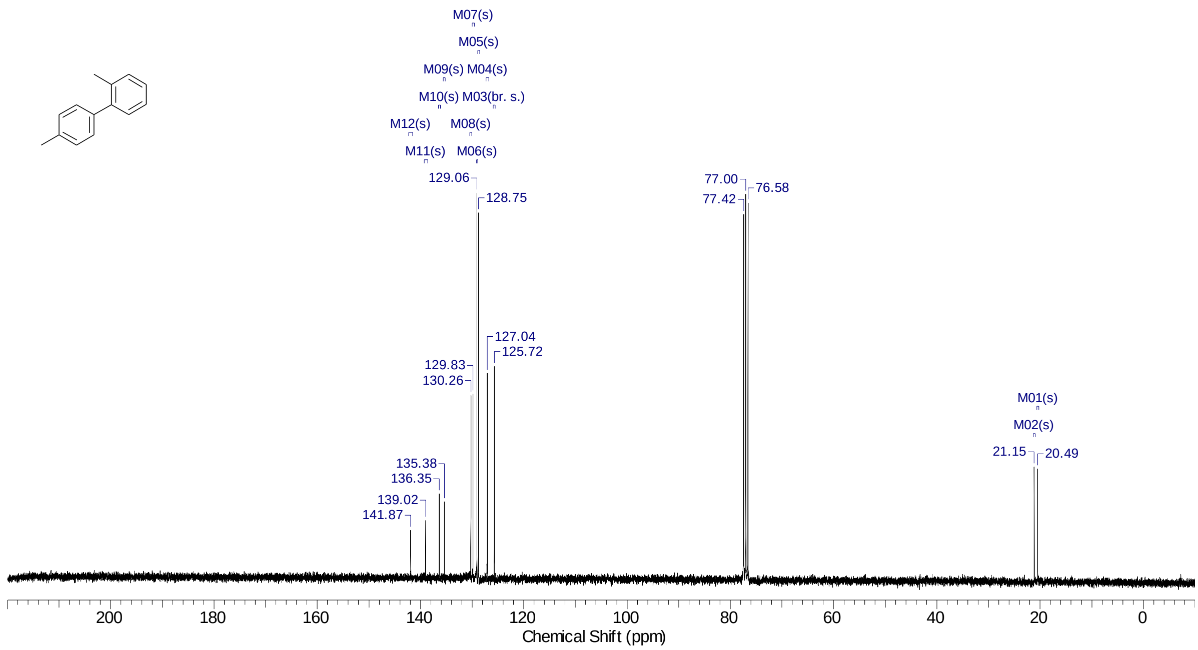
^{1}H-NMR of 1-methoxy-4-(p-tolyl)benzene (**3ab**).



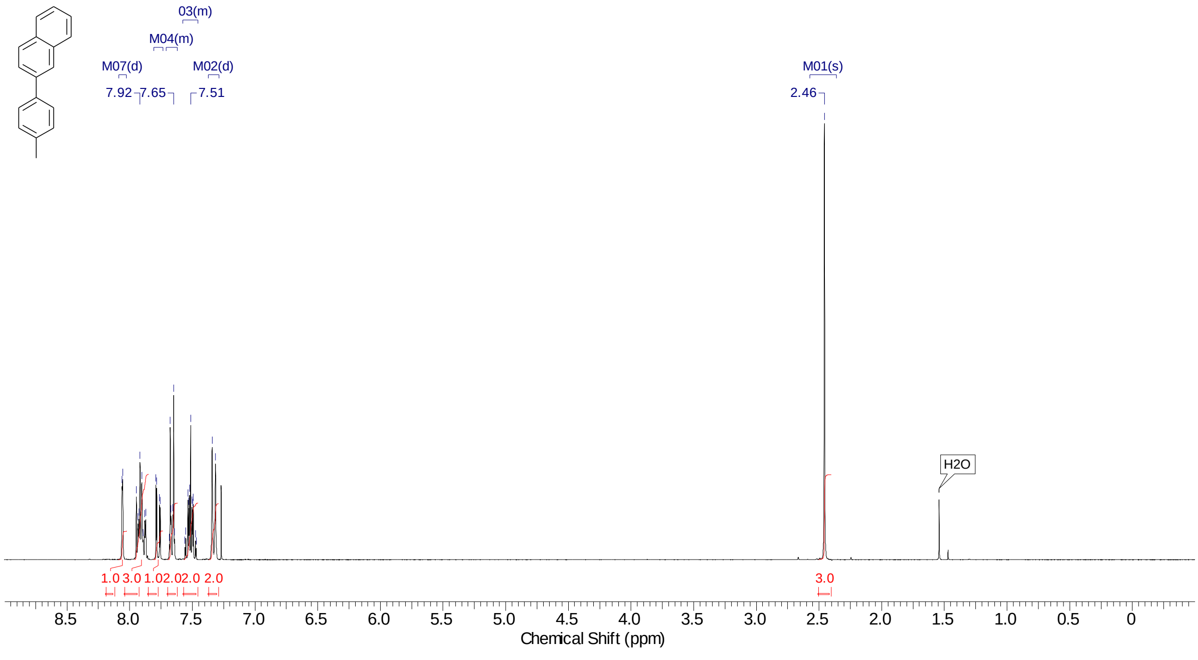
^{13}C-NMR of 1-methoxy-4-(p-tolyl)benzene (**3ab**).



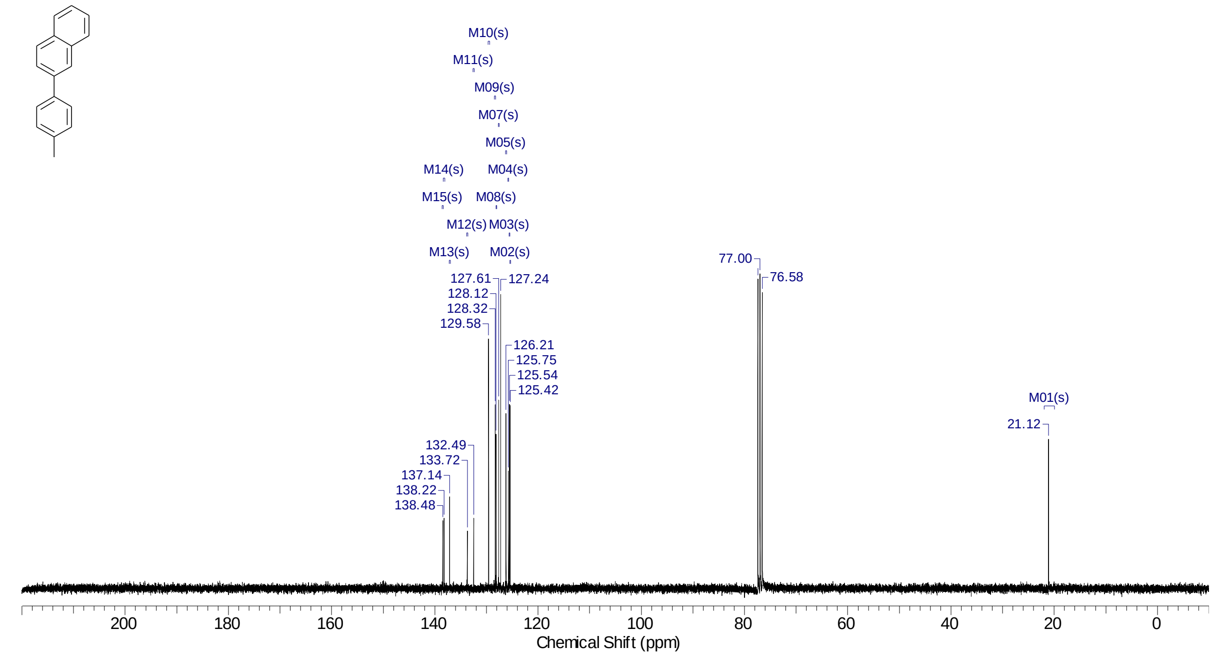
^{1}H-NMR of 1-methyl-2-(p-tolyl)benzene (**3ac**).



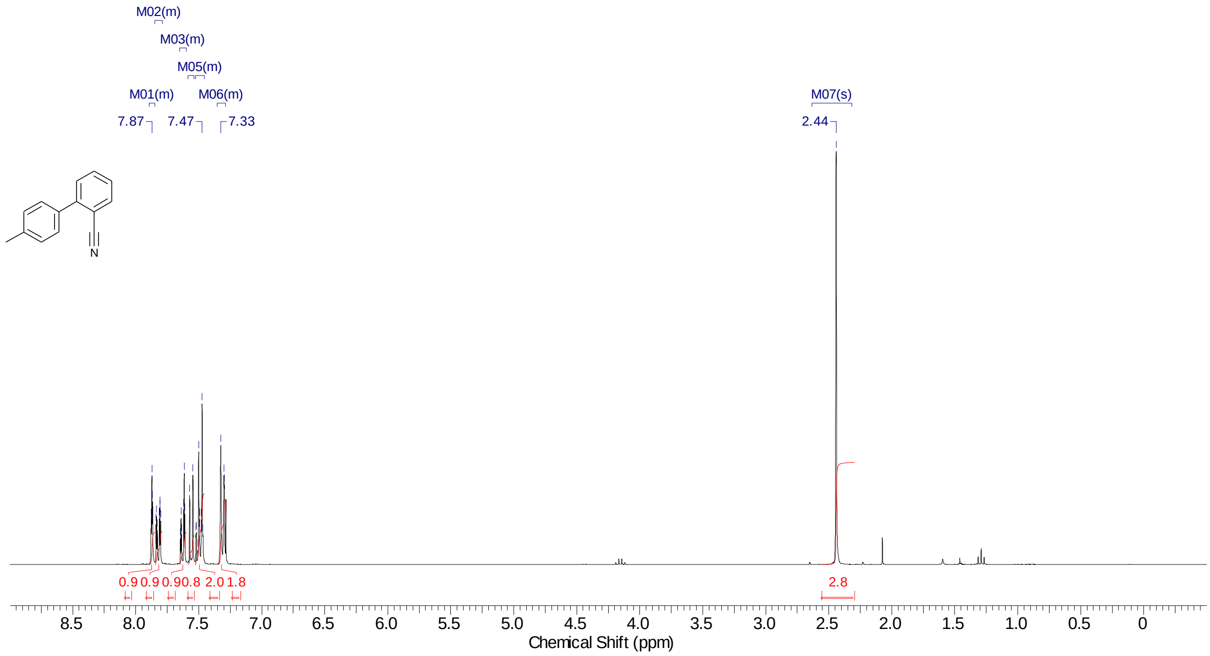
[13]C-NMR of 1-methyl-2-(p-tolyl)benzene (**3ac)**.



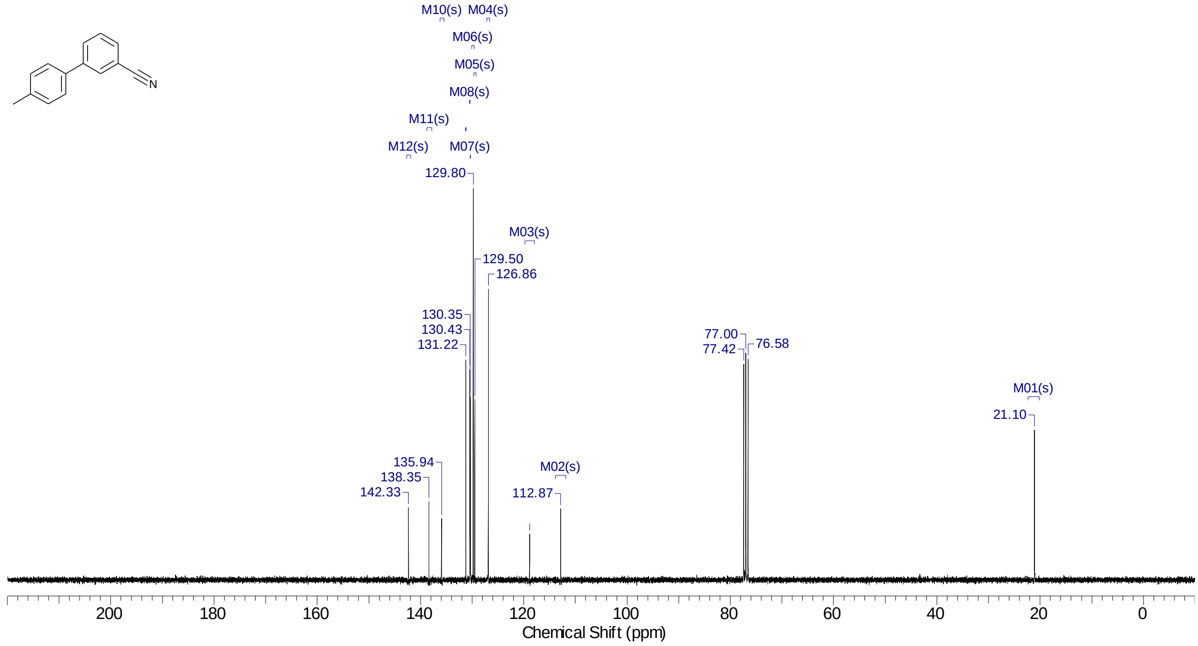
[1]H-NMR of 2-(p-tolyl)naphthalene (**3ad)**.



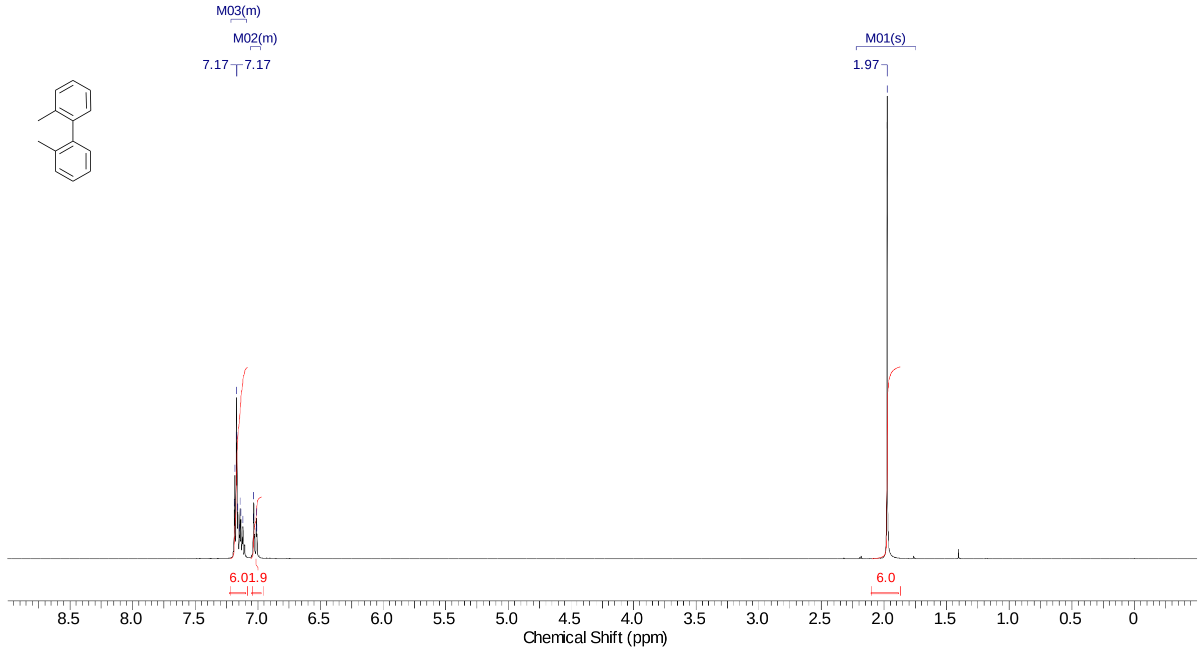
^{13}C NMR of 2-(p-tolyl)naphthalene (**3ad**).



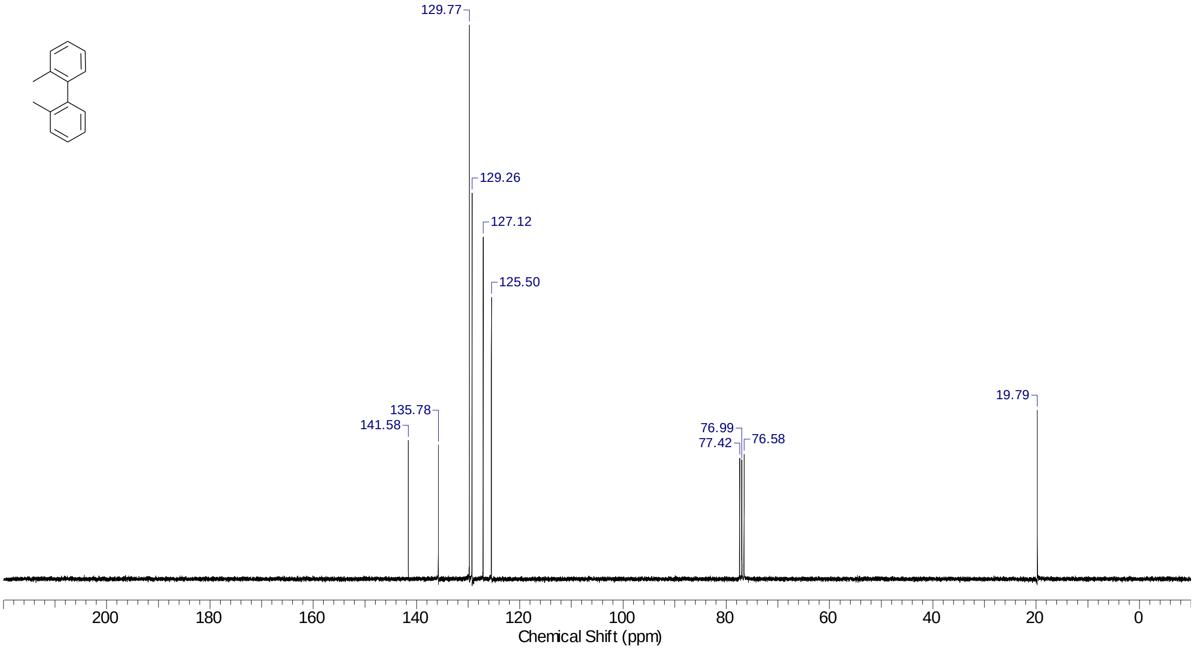
^{1}H NMR of 3-(p-tolyl)benzonitrile (**3ae**).



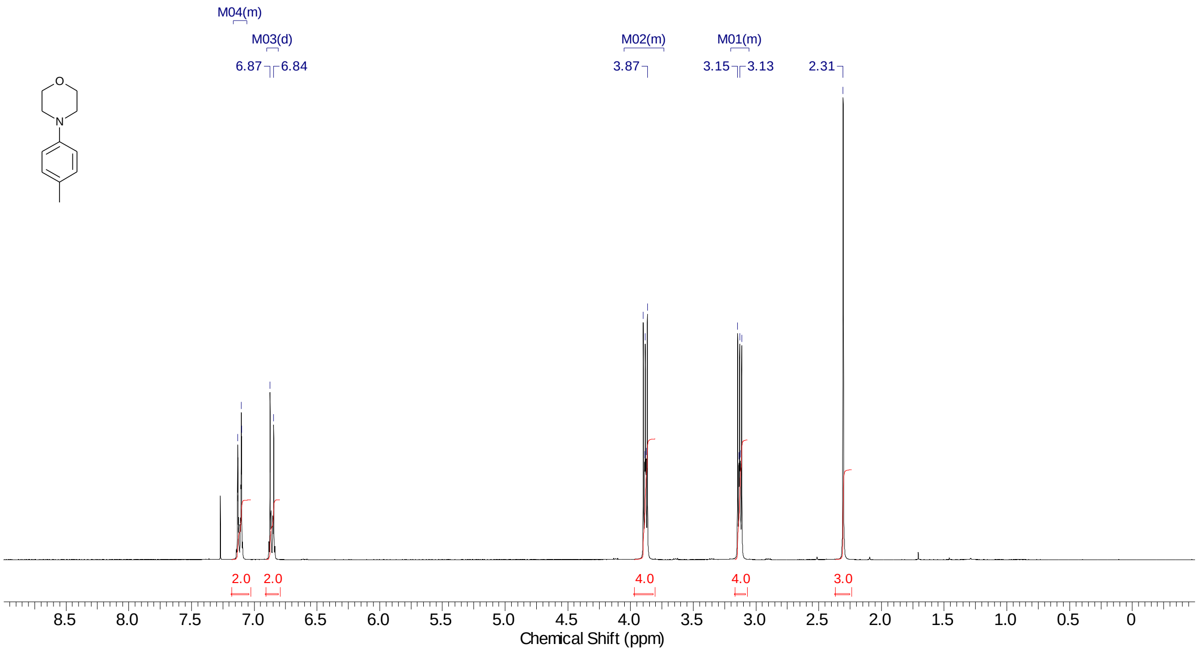
^{13}C NMR of 3-(p-tolyl)benzonitrile (**3ae**).



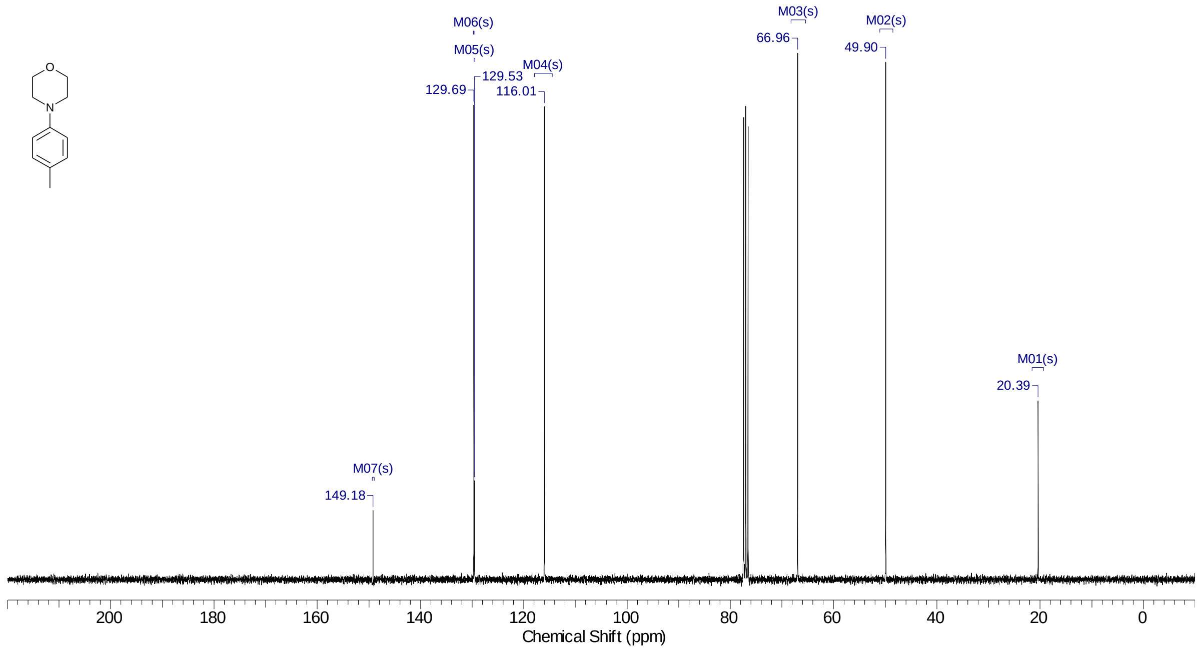
^{1}H-NMR of 1-methyl-2-(o-tolyl)benzene (**3hc**).



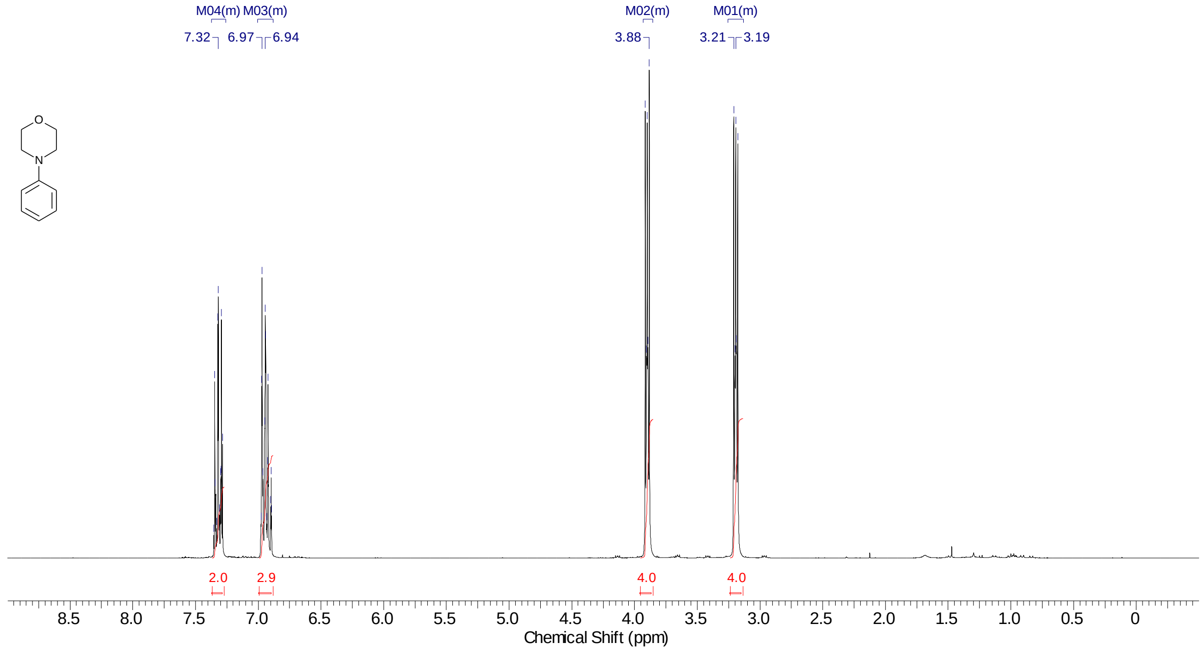
^{13}C-NMR of 1-methyl-2-(o-tolyl)benzene (**3hc**).



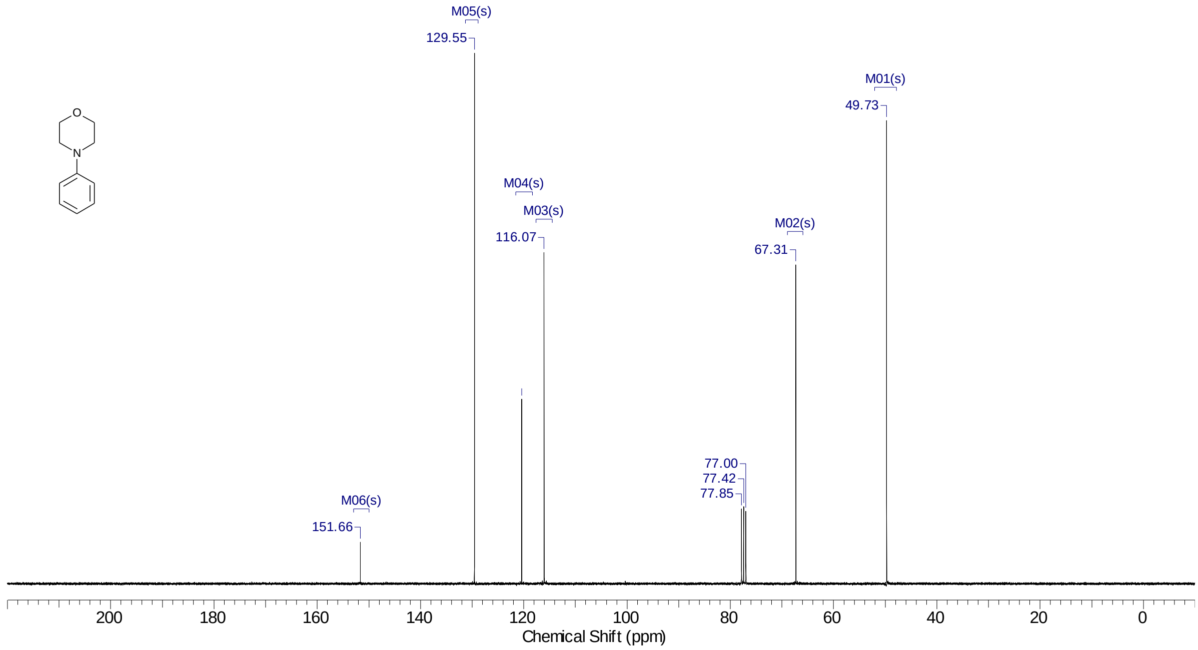
^{1}H-NMR of 4-(p-tolyl)morpholine (**5aa**).



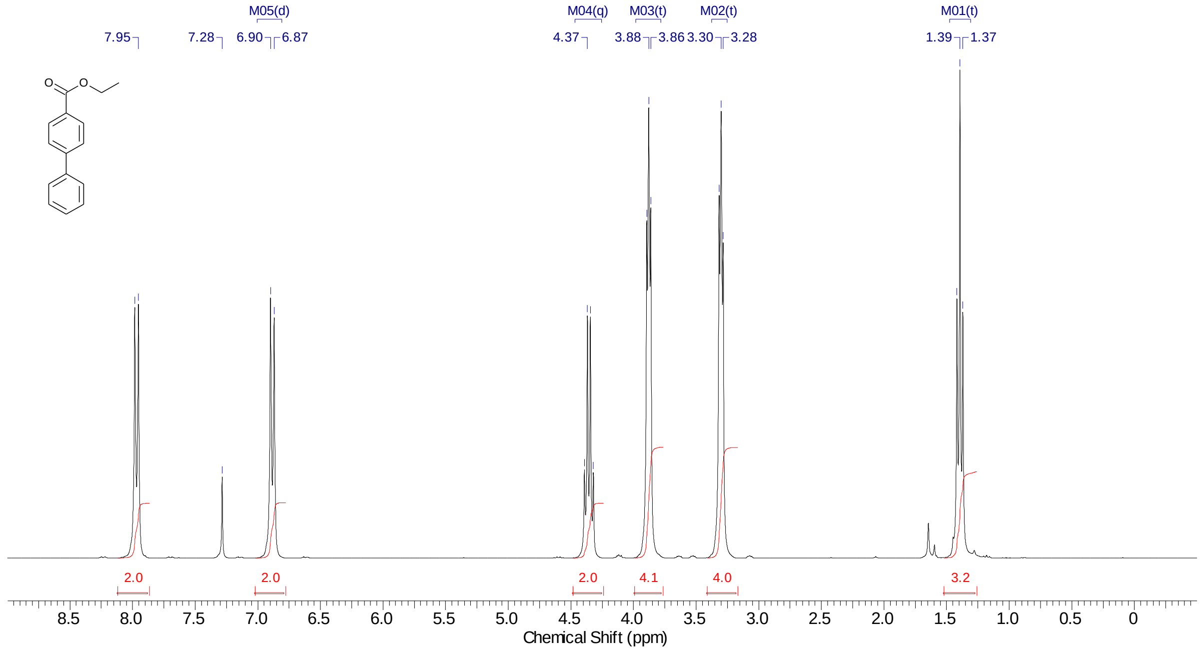
^{13}C NMR of 4-(p-tolyl)morpholine (**5aa**).



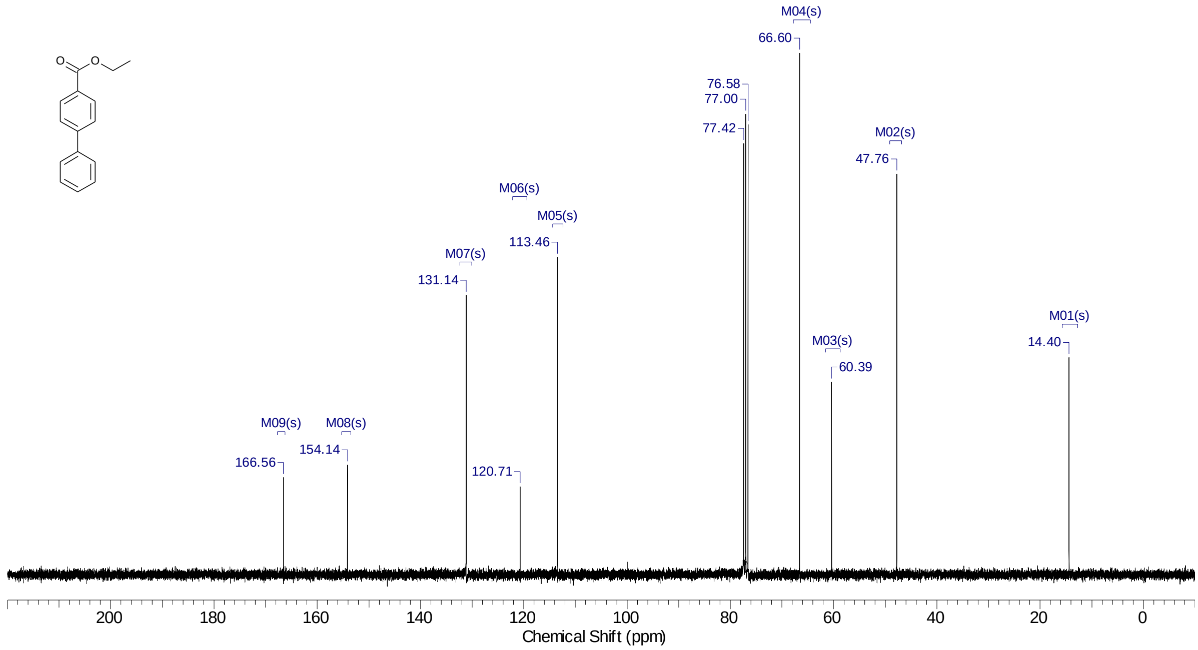
^{1}H-NMR of 4-phenylmorpholine (**5ba**).



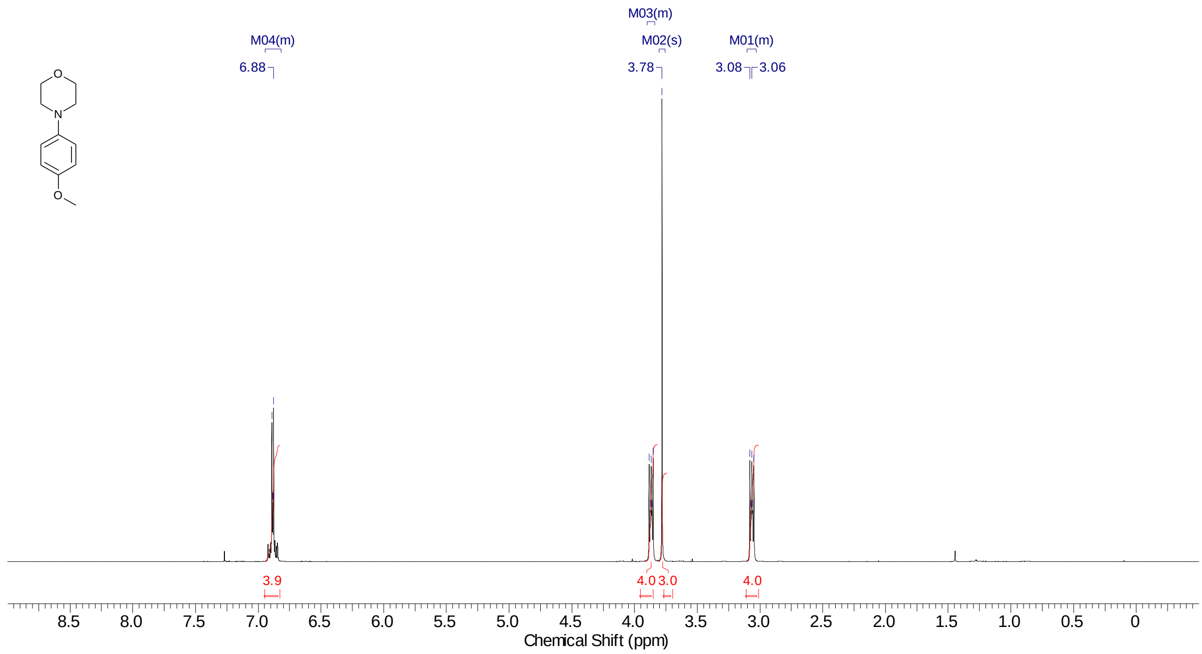
^{13}C NMR of 4-phenylmorpholine (**5ba**).



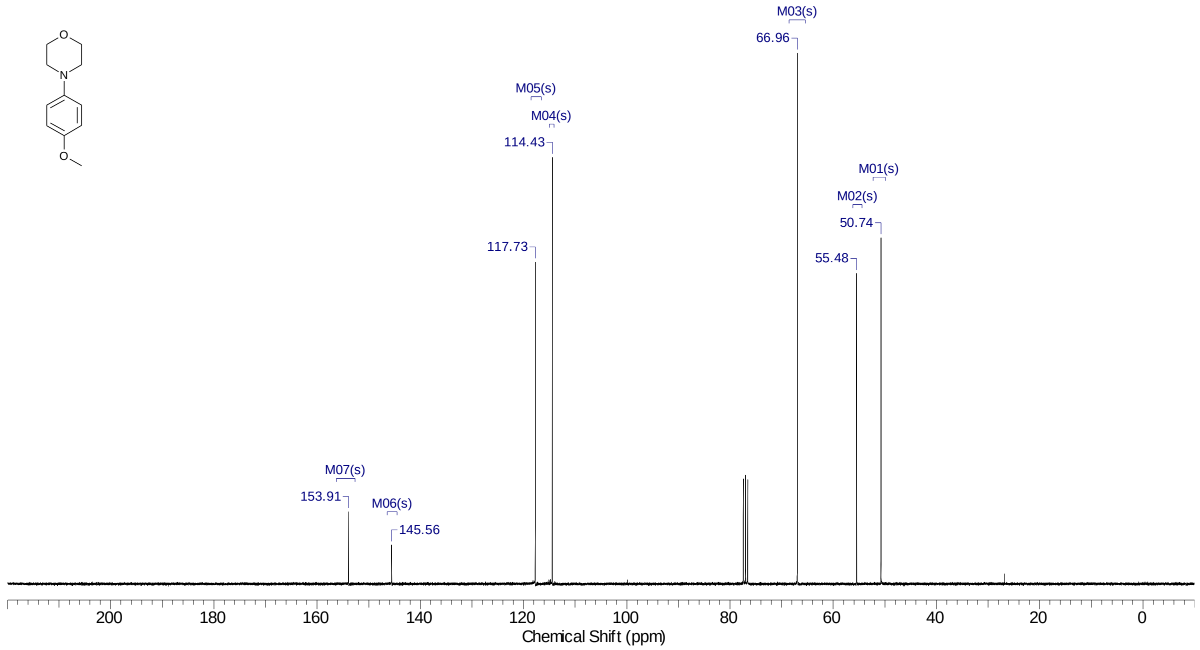
^{1}H-NMR of ethyl 4-morpholinobenzoate (**5ca**).



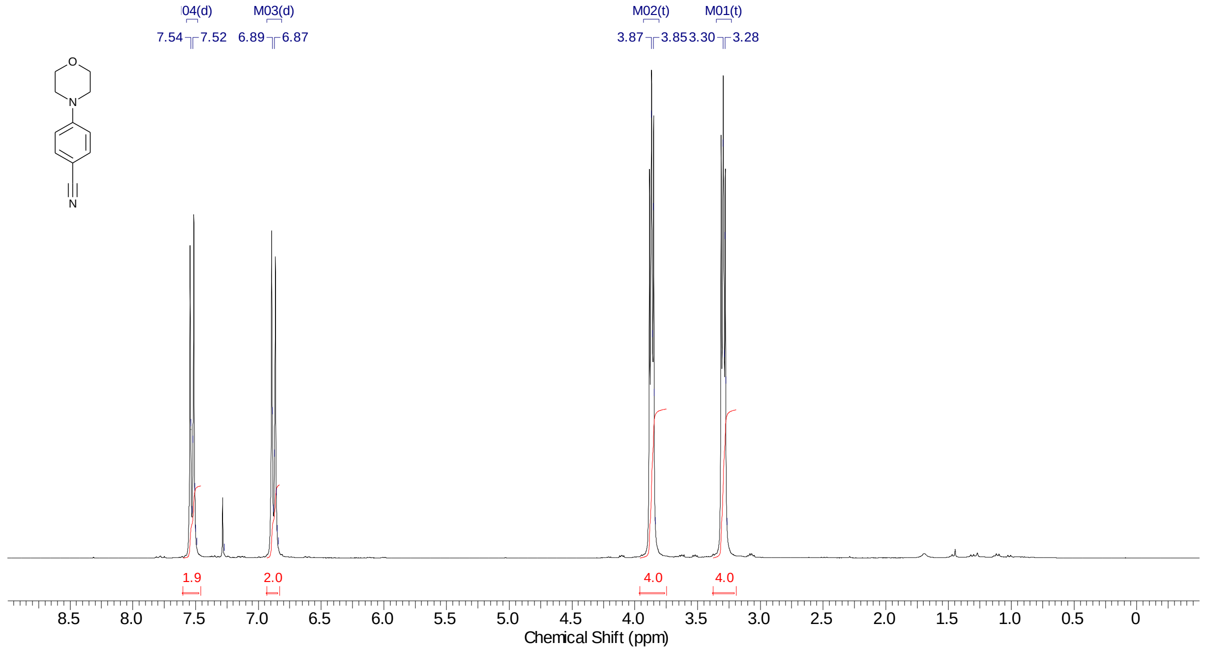
^{13}C NMR of ethyl 4-morpholinobenzoate (**5ca**).



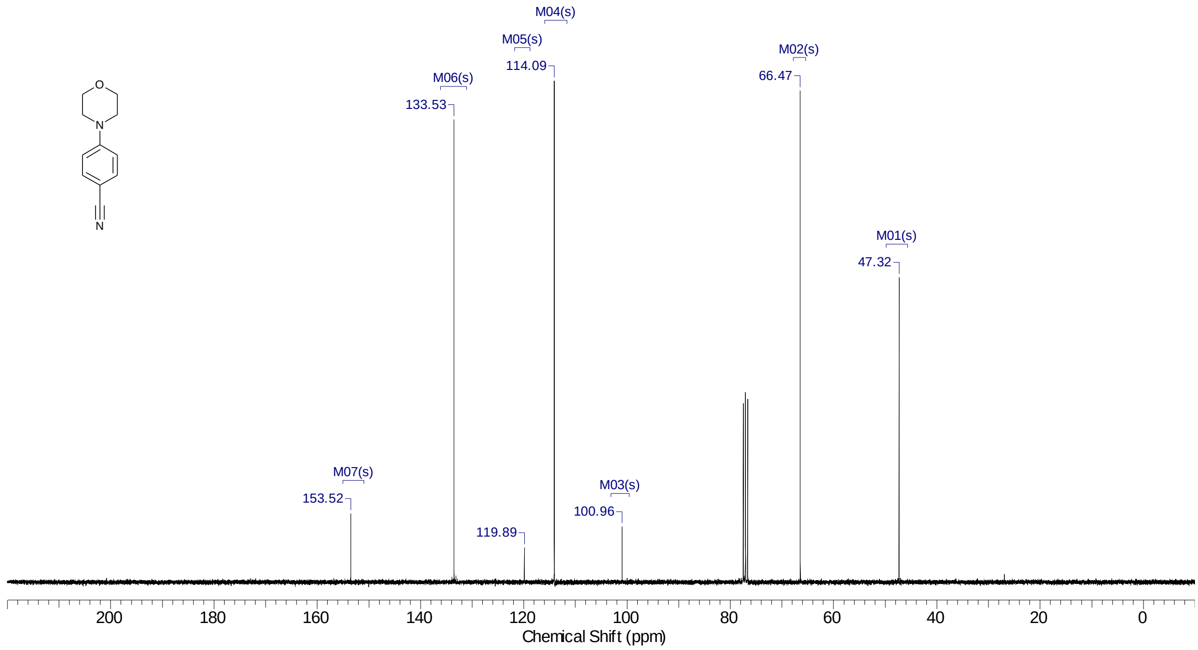
^{1}H-NMR of 4-(4-methoxyphenyl)morpholine (**5da**).



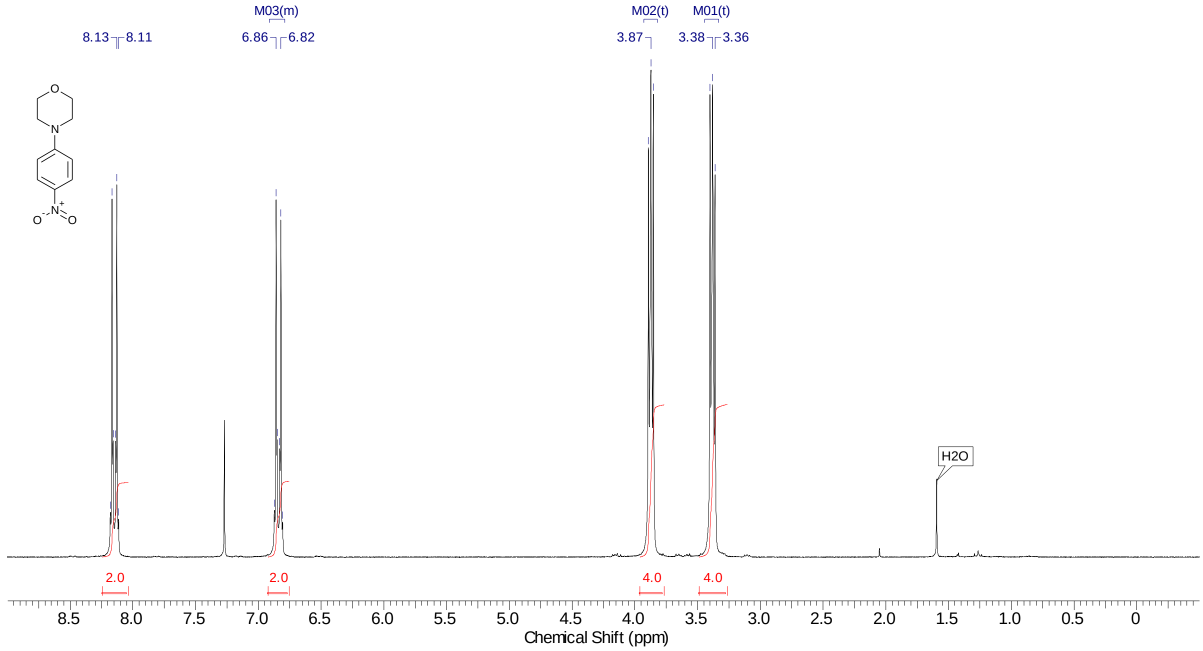
[13]C NMR of 4-(4-methoxyphenyl)morpholine (**5da**).



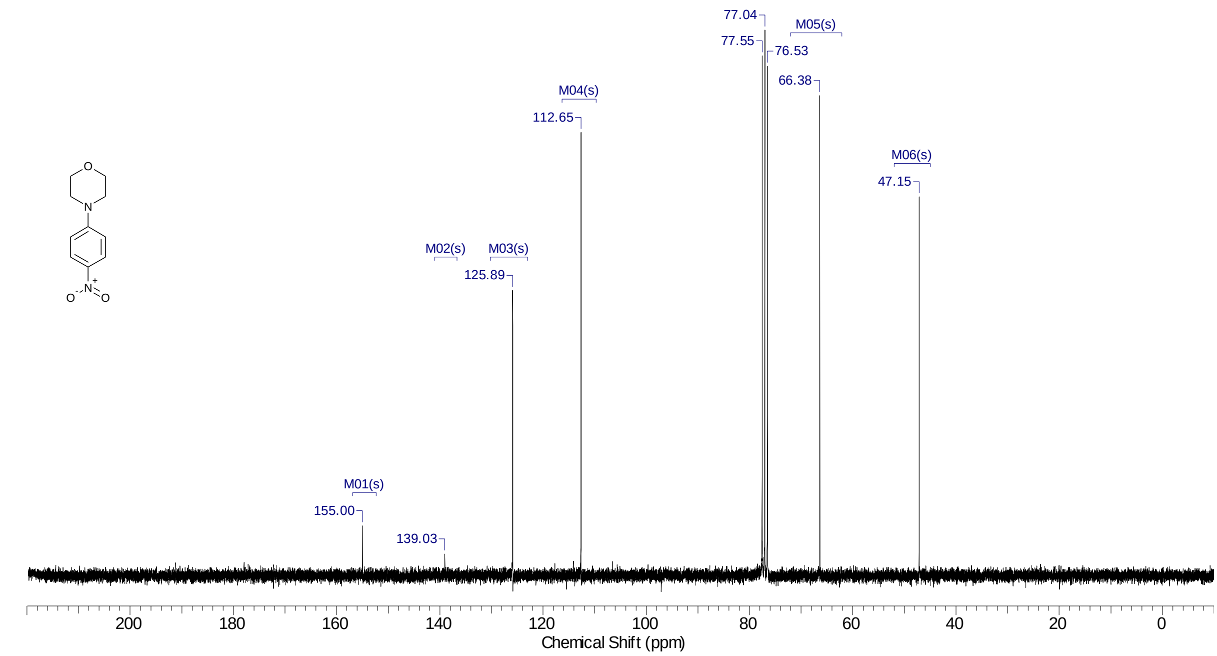
[1]H-NMR of 4-morpholinobenzonitrile (**5ea**).



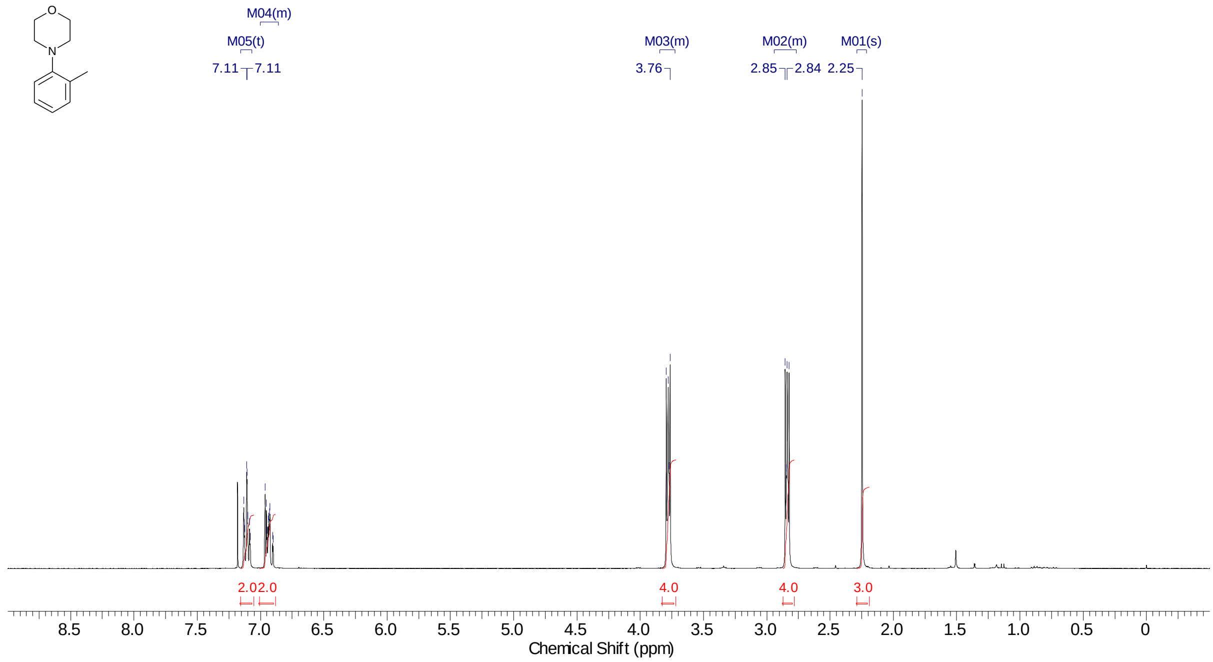
^{13}C NMR of 4-morpholinobenzonitrile (**5ea**).



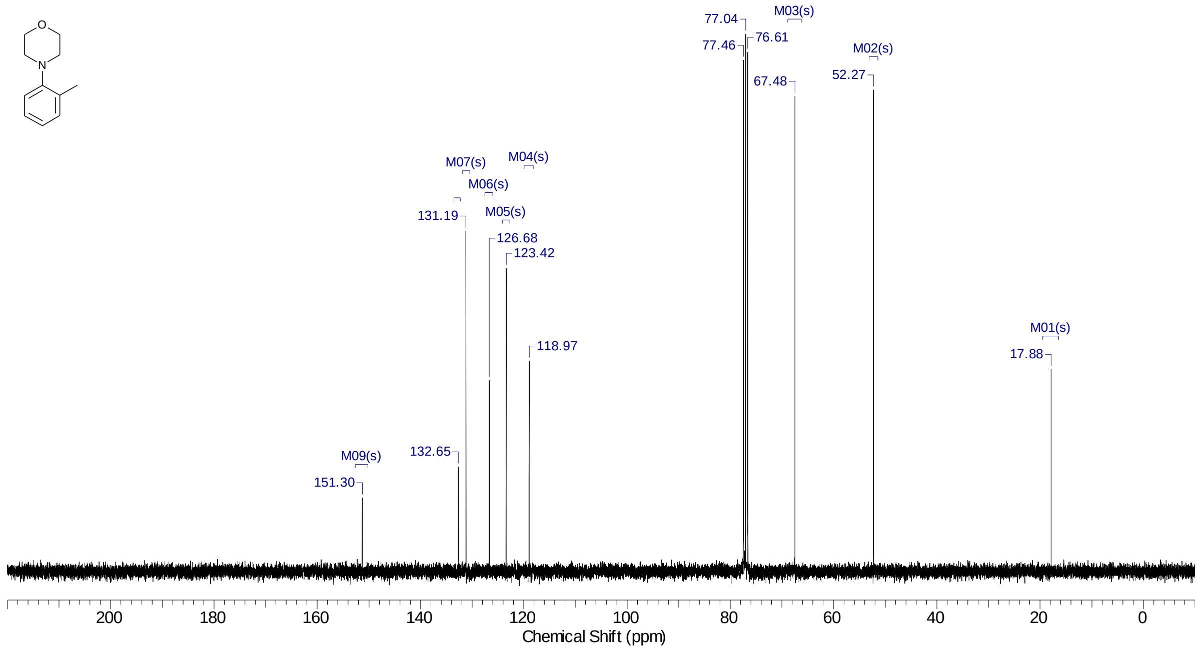
^{1}H-NMR of 4-(4-nitrophenyl)morpholine (**5fa**).



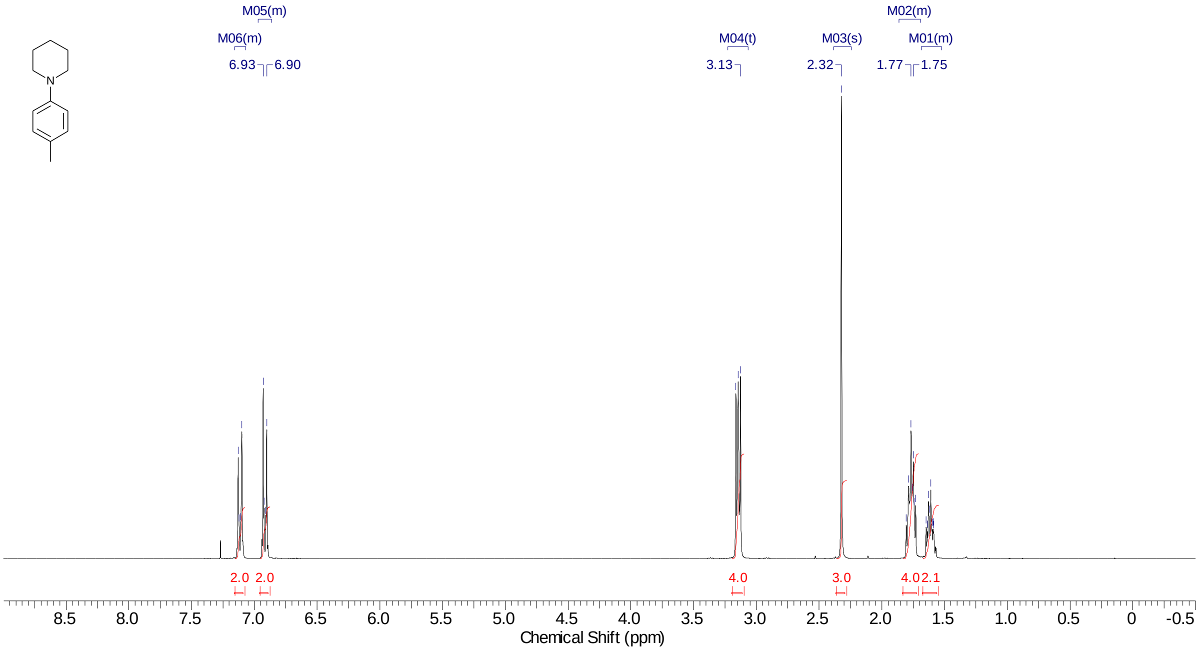
^{13}C NMR of 4-(4-nitrophenyl)morpholine (**5fa**).



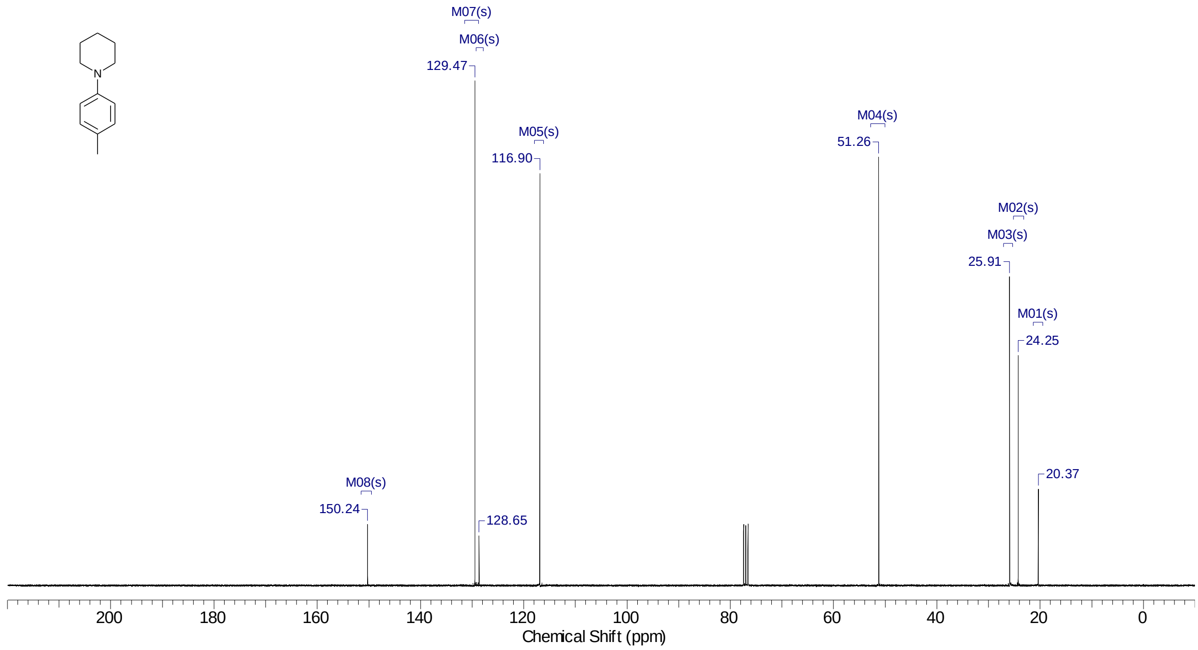
^{1}H-NMR of 4-(o-tolyl)morpholine (**5ga**).



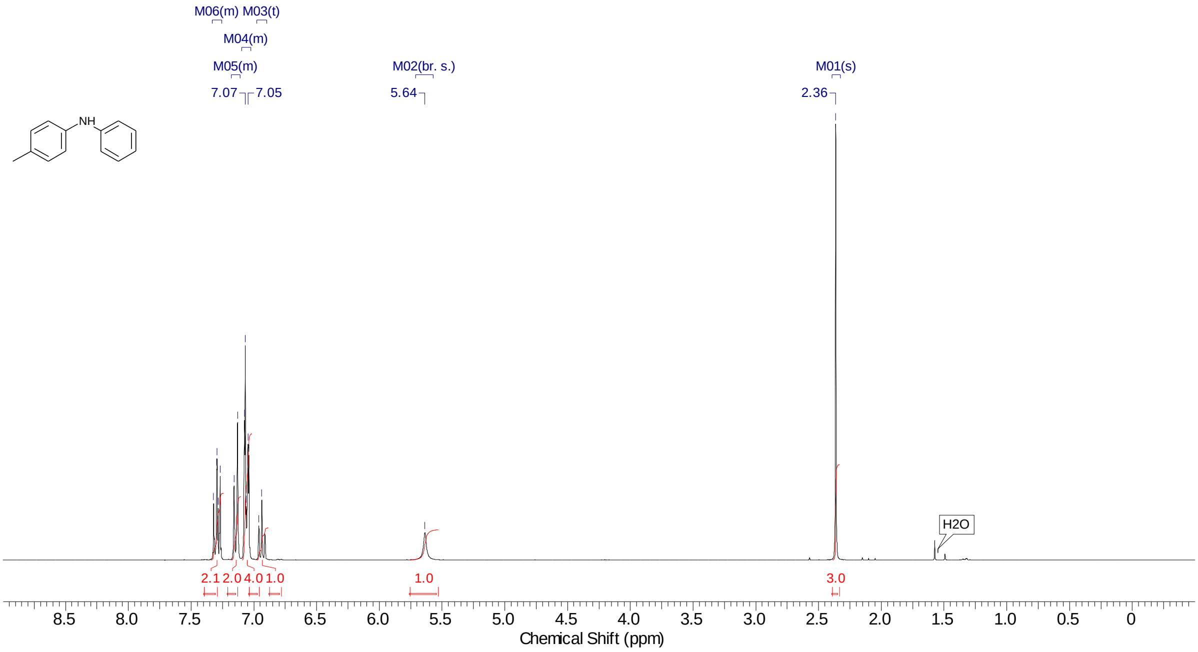
^{13}C NMR of 4-(o-tolyl)morpholine (**5ga)**.



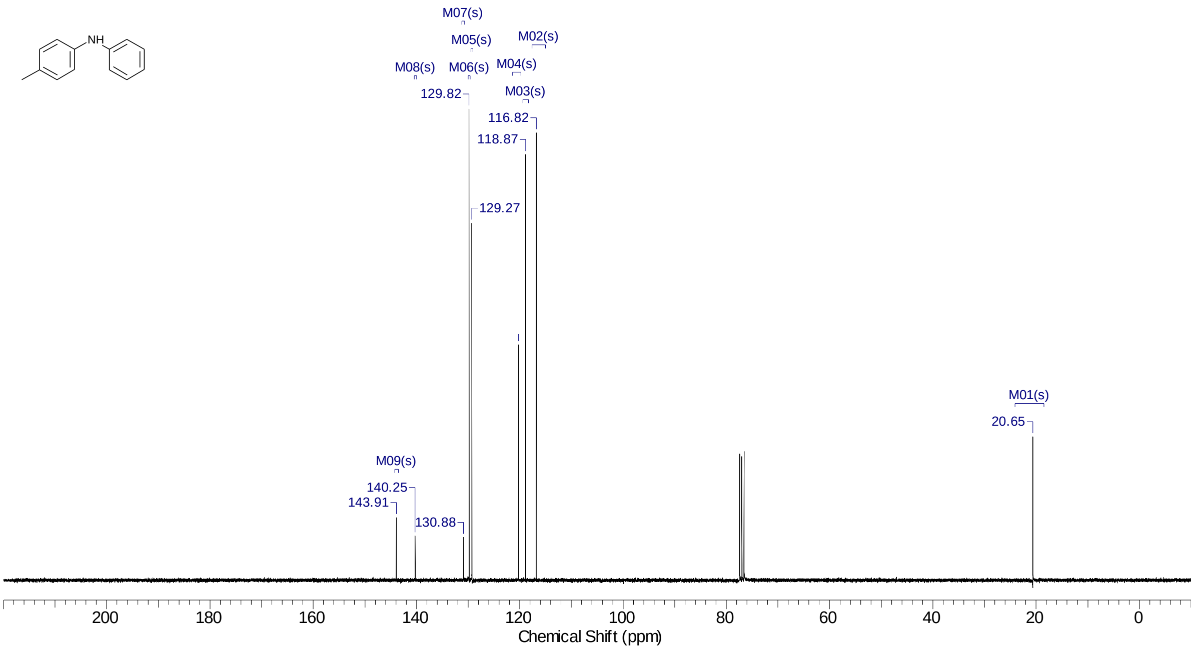
^{1}H-NMR of 1-(p-tolyl)piperidine (**5ab)**.



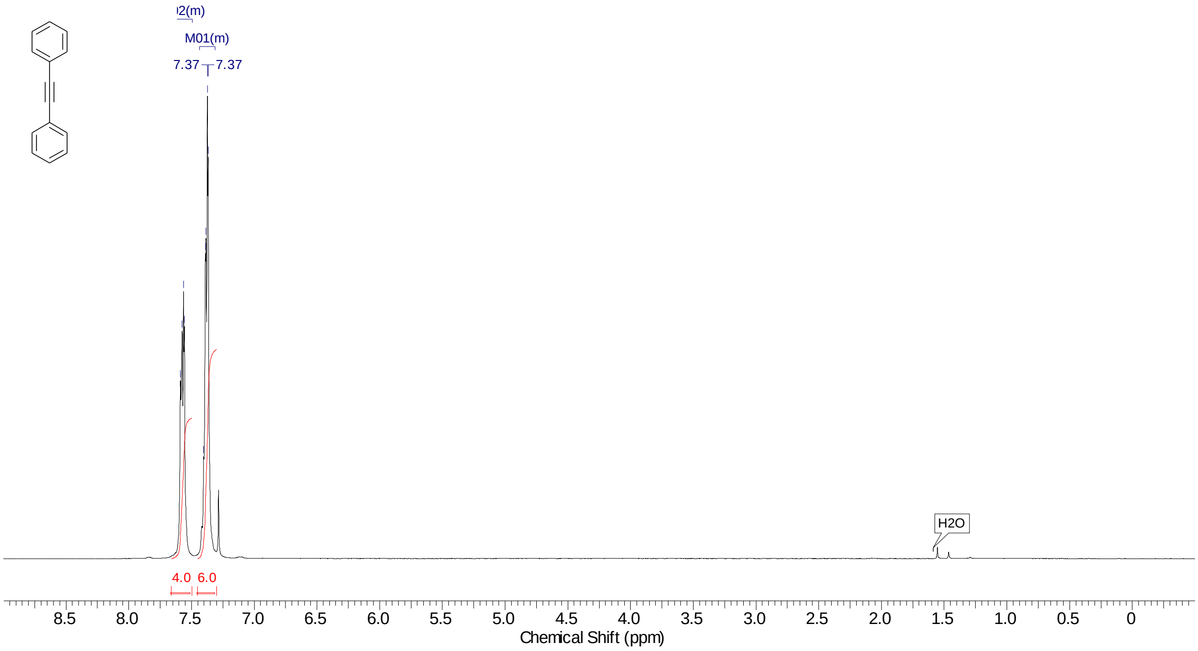
^{13}C NMR of 1-(p-tolyl)piperidine (**5ab**).



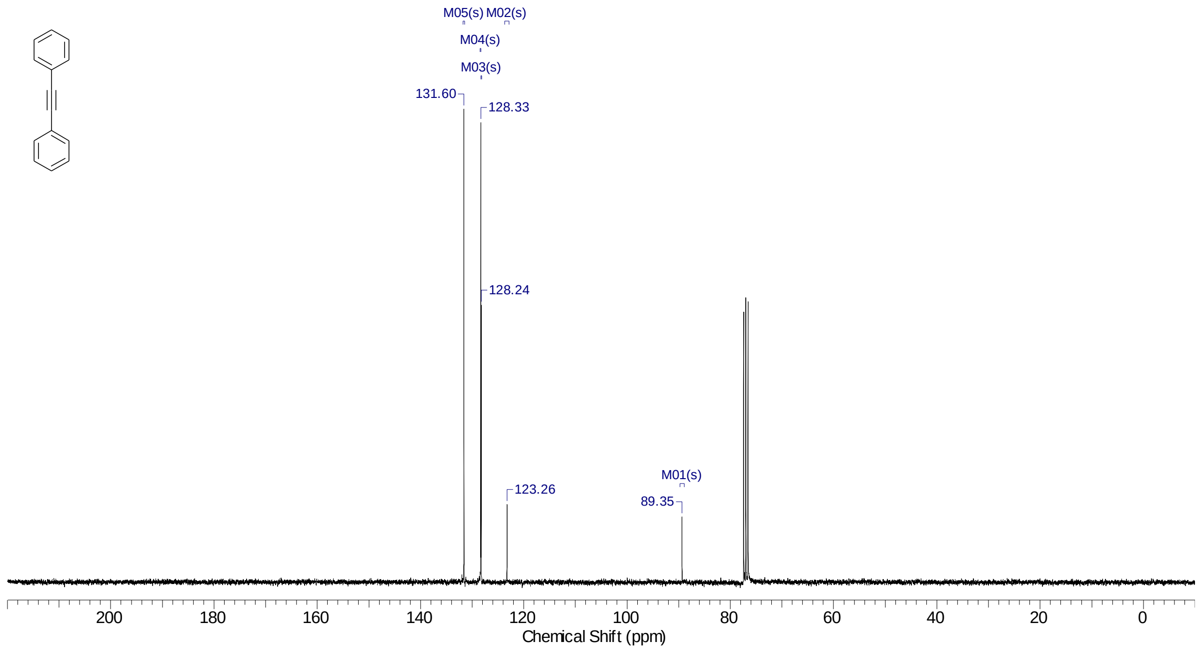
^{1}H-NMR of 4-methyl-*N*-phenylaniline (**5ac**).



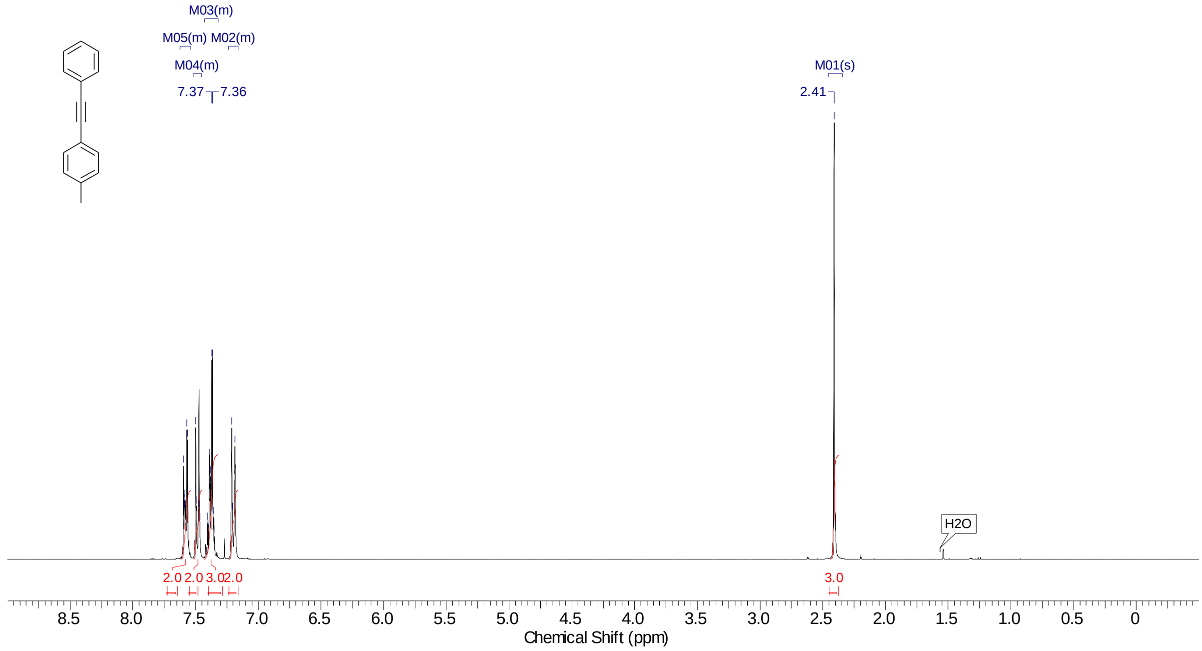
[13]C NMR of 4-methyl-*N*-phenylaniline (**5ac**).



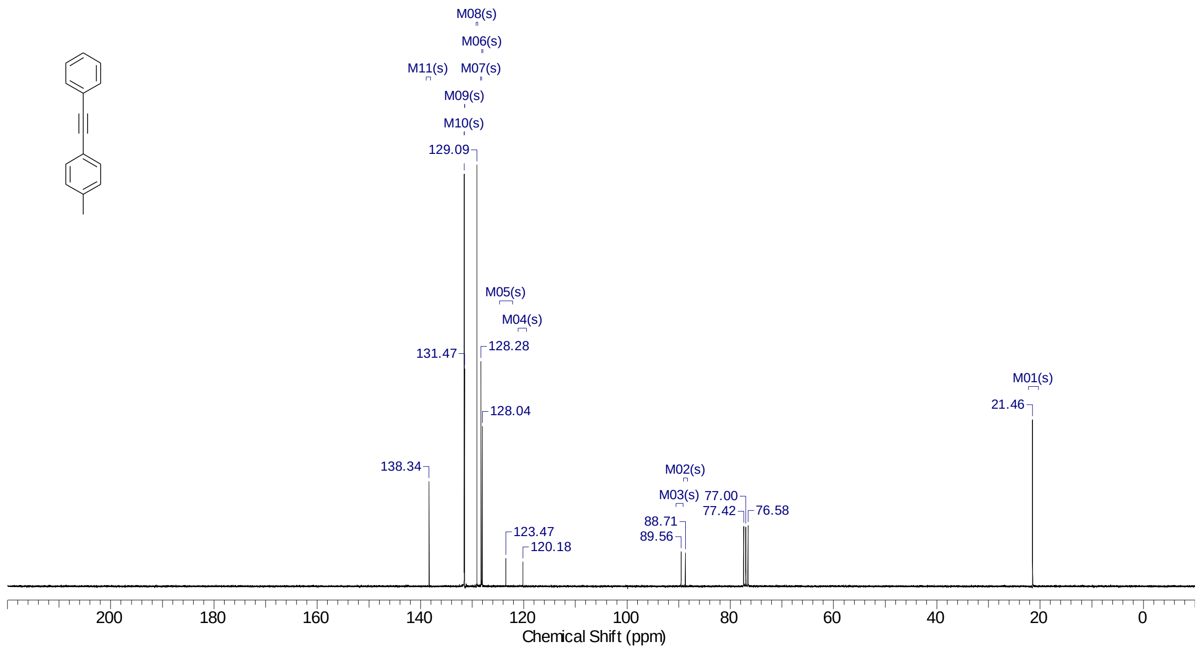
[1]H-NMR of 1,2-diphenylethyne (**8aa**).



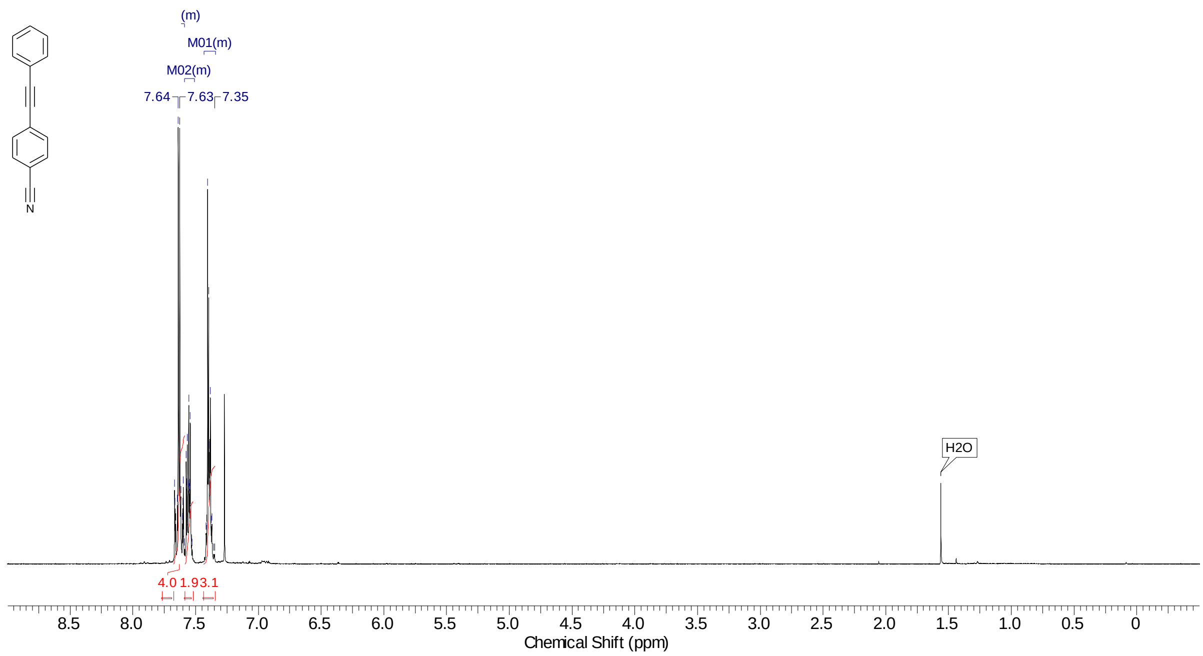
[13]C NMR of 1,2-diphenylethyne (**8aa**).



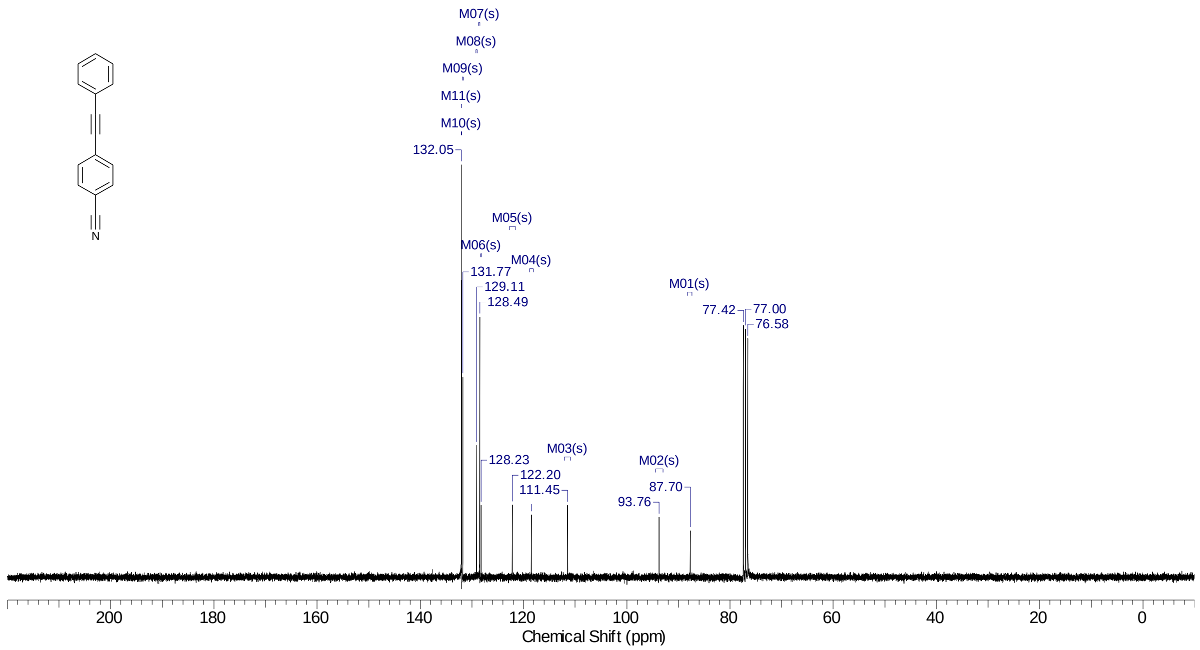
[1]H-NMR of 1-methyl-4-(phenylethynyl)benzene (**8ba**).



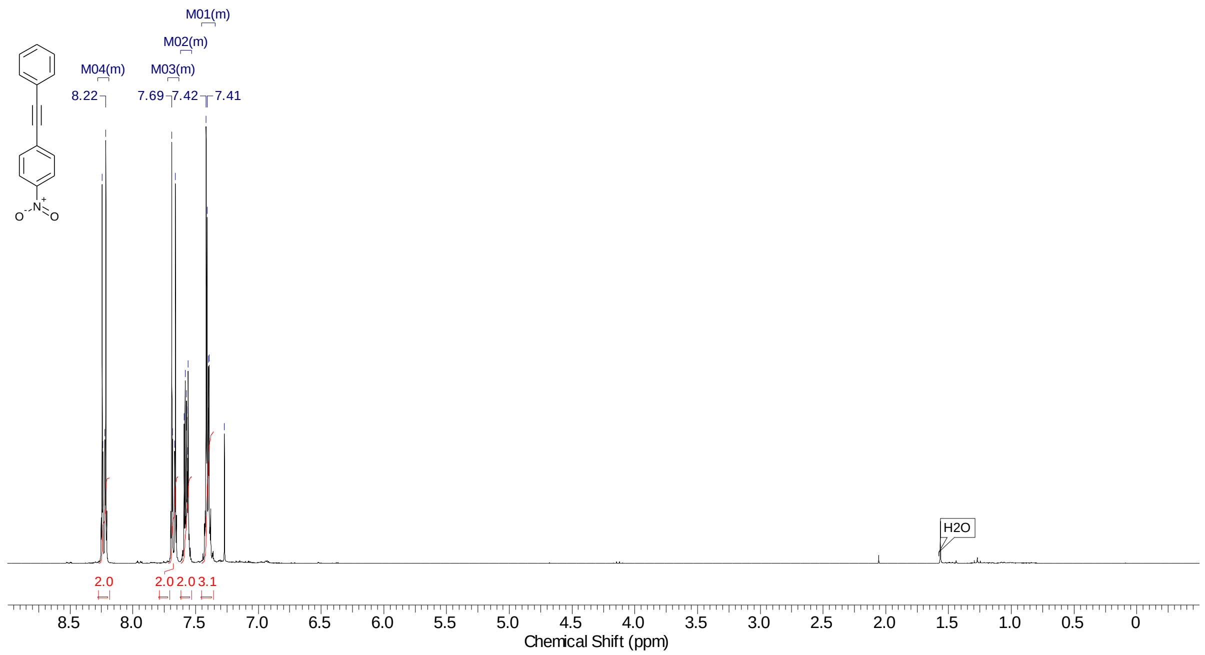
^{13}C NMR of 1-methyl-4-(phenylethynyl)benzene (**8ba**).



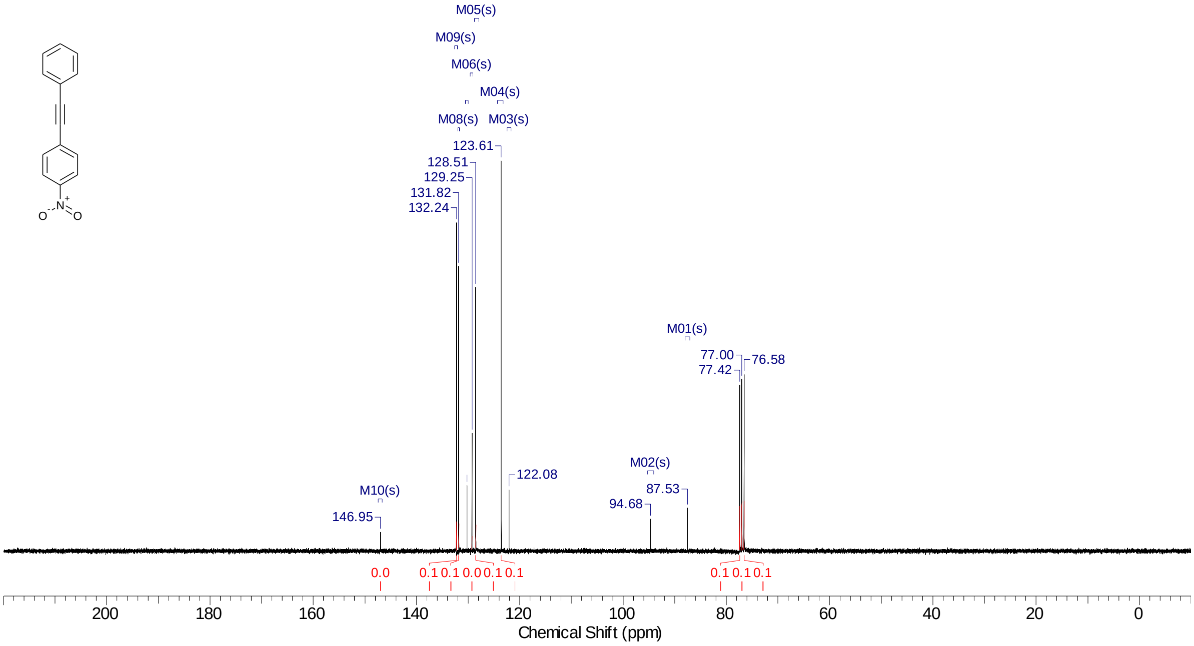
^{1}H-NMR of 4-(phenylethynyl)benzonitrile (**8ca**).



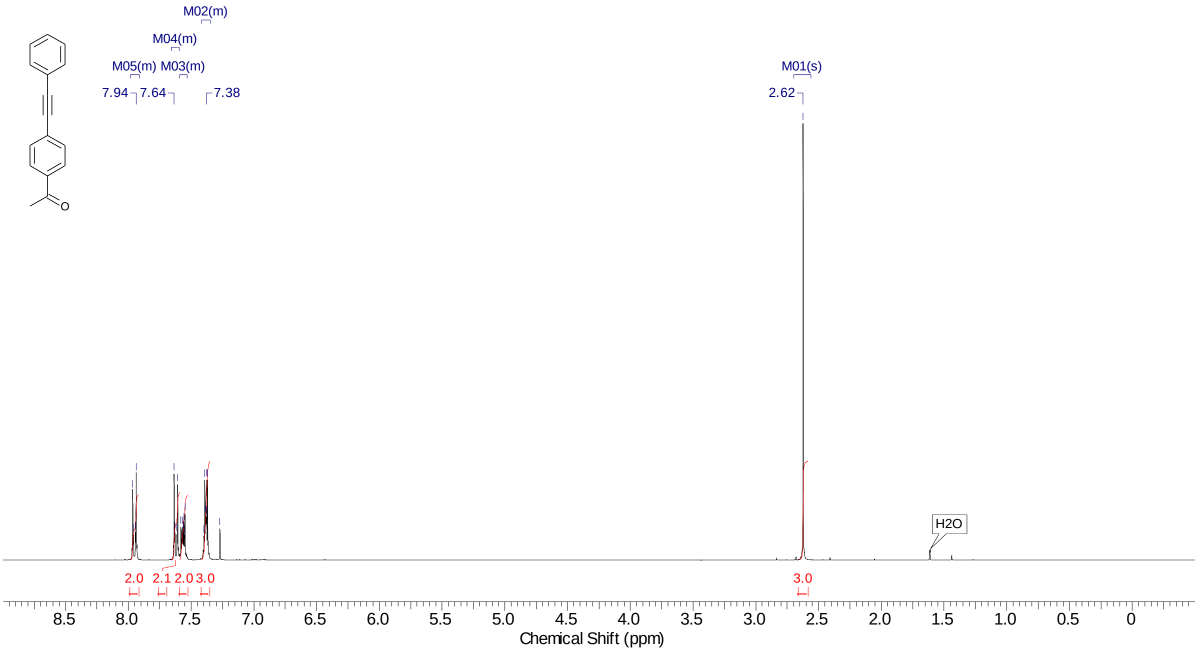
^{13}C NMR of 4-(phenylethynyl)benzonitrile (**8ca**).



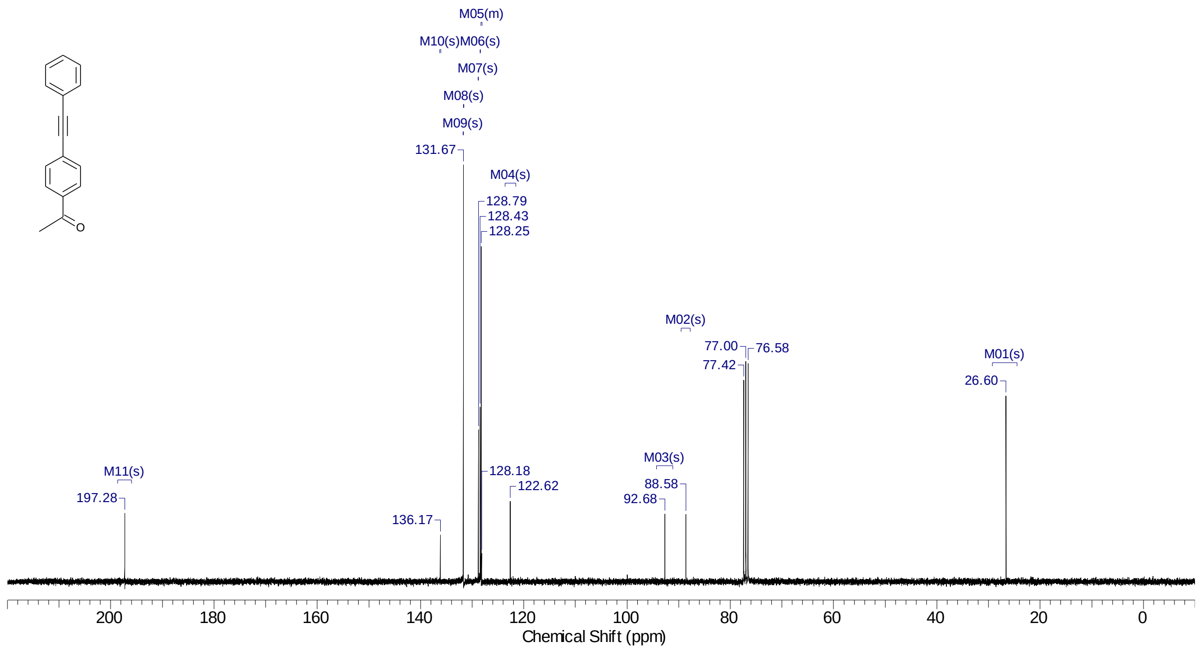
^{1}H-NMR of 1-nitro-4-(phenylethynyl)benzene (**8da**).



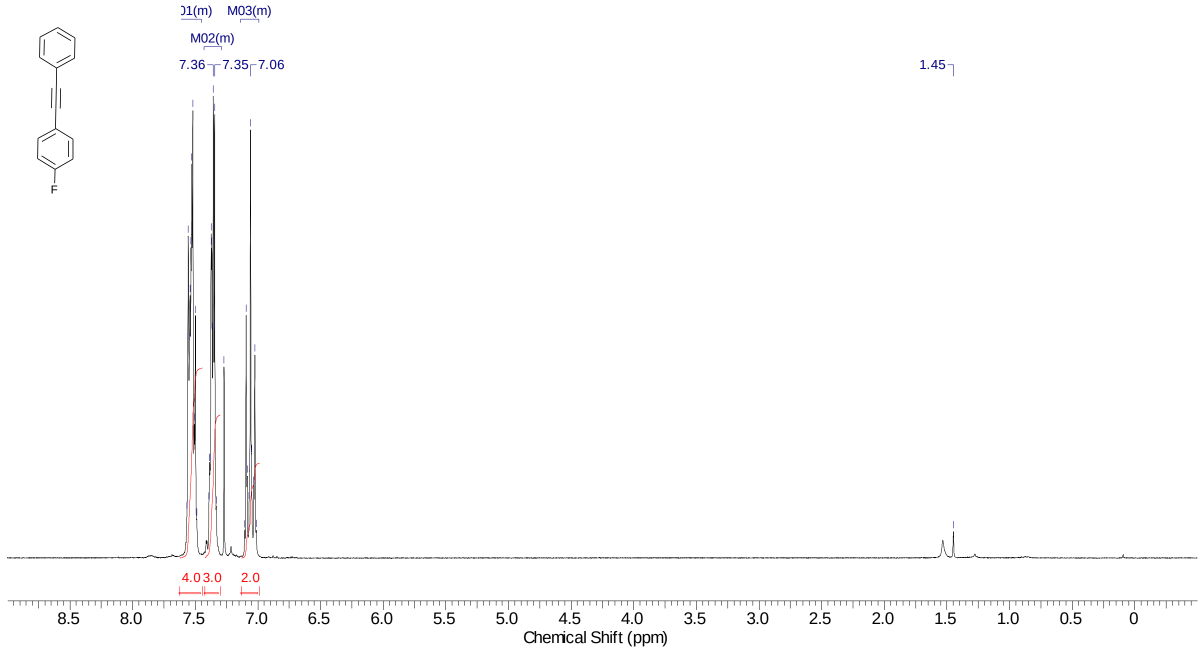
[13]C NMR of 1-nitro-4-(phenylethynyl)benzene (**8da**).



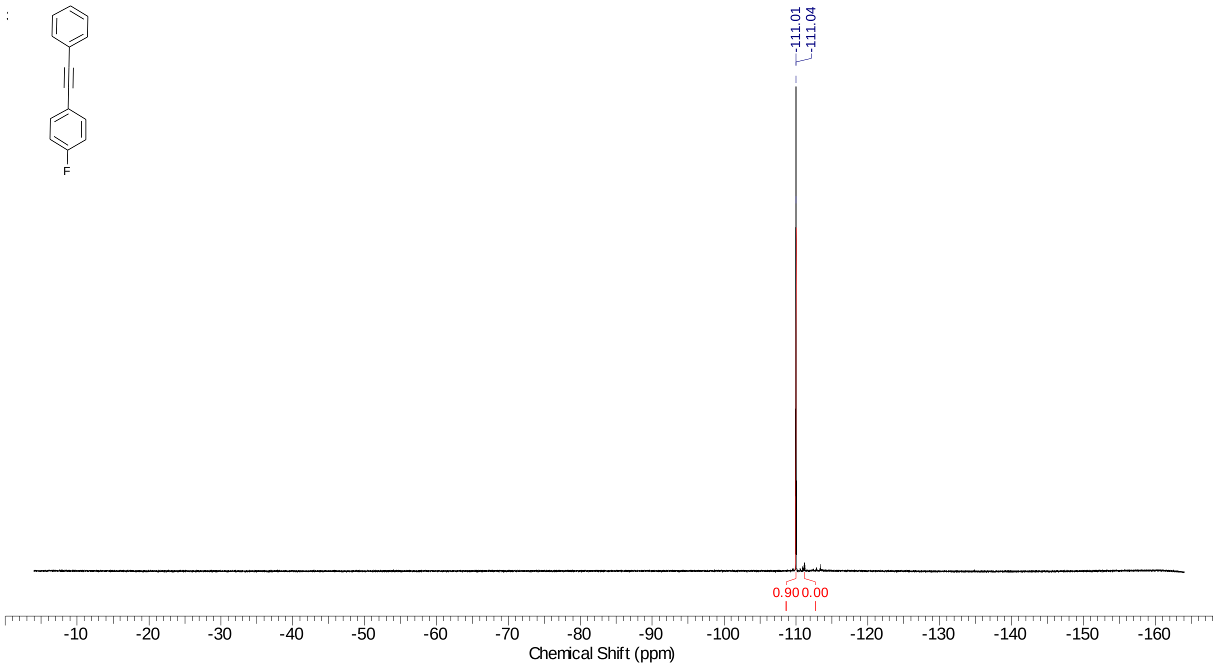
[1]H-NMR of 1-(4-(phenylethynyl)phenyl)ethan-1-one (**8ea**).



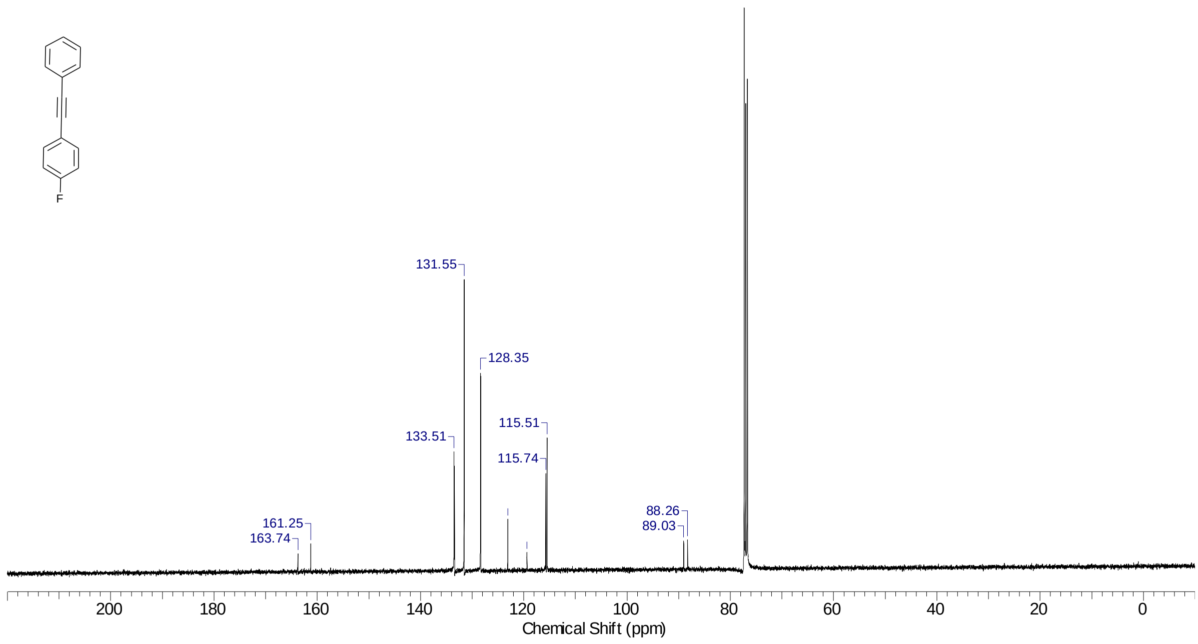
^{13}C NMR of 1-(4-(phenylethynyl)phenyl)ethan-1-one (**8ea**).



^{1}H-NMR of 1-fluoro-4-(2-phenylethynyl)benzene (**8fa**).



[19]F-NMR of 1-fluoro-4-(2-phenylethynyl)benzene (**8fa**).



[13]C NMR of 1-fluoro-4-(2-phenylethynyl)benzene (**8fa**).

6 Crystallographic Data

Experimental: A suitable crystal was selected and mounted on a SuperNova, Single source at offset, Atlas diffractometer. The crystal was kept at 100 K during data collection. Using Olex2,[50] the structure was solved with the ShelXT[51] structure solution program using Intrinsic Phasing and refined with the ShelXL[52] refinement package using Least Squares minimisation.

*6.1 Crystal Data for **Pd-1***

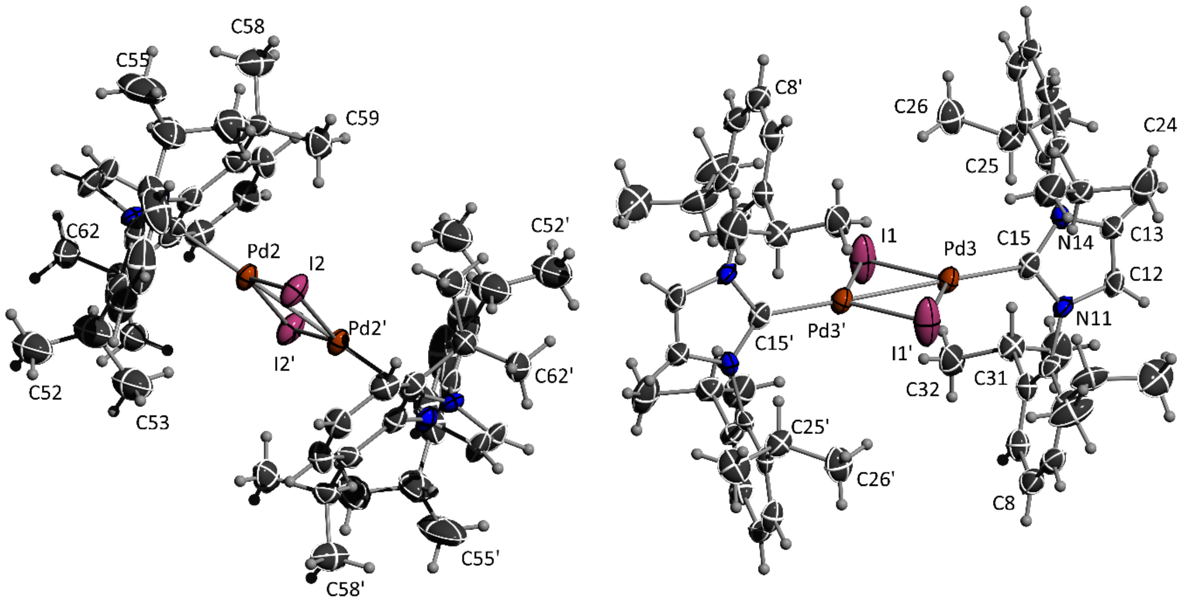


Table 12. Crystal data and structure refinement for **Pd-1**.

CCDC Number	1895948
Empirical formula	$C_{54}H_{72}N_4Pd_2I_2$
Formula weight	1243.75
Temperature/K	99.9(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	26.6817(12)
b/Å	10.4999(7)
c/Å	20.3690(12)
α/°	90
β/°	107.883(6)
γ/°	90
Volume/$Å^3$	5430.8(6)
Z	4
$\rho_{calc}g/cm^3$	1.521
μ/mm^{-1}	14.539
F(000)	2488.0
Crystal size/mm^3	0.069 × 0.037 × 0.032
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.962 to 136
Index ranges	$-15 \leq h \leq 32, -11 \leq k \leq 9, -21 \leq l \leq 22$
Reflections collected	13006
Independent reflections	7419 [R_{int} = 0.0349, R_{sigma} = 0.0558]
Data/restraints/parameters	7419/1/568
Goodness-of-fit on F^2	1.021

Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1483
Final R indexes [all data]	R_1 = 0.0848, wR_2 = 0.1679
Largest diff. peak/hole / e $Å^{-3}$	2.45/-1.95

*6.2 Crystal data for **Pd-6***

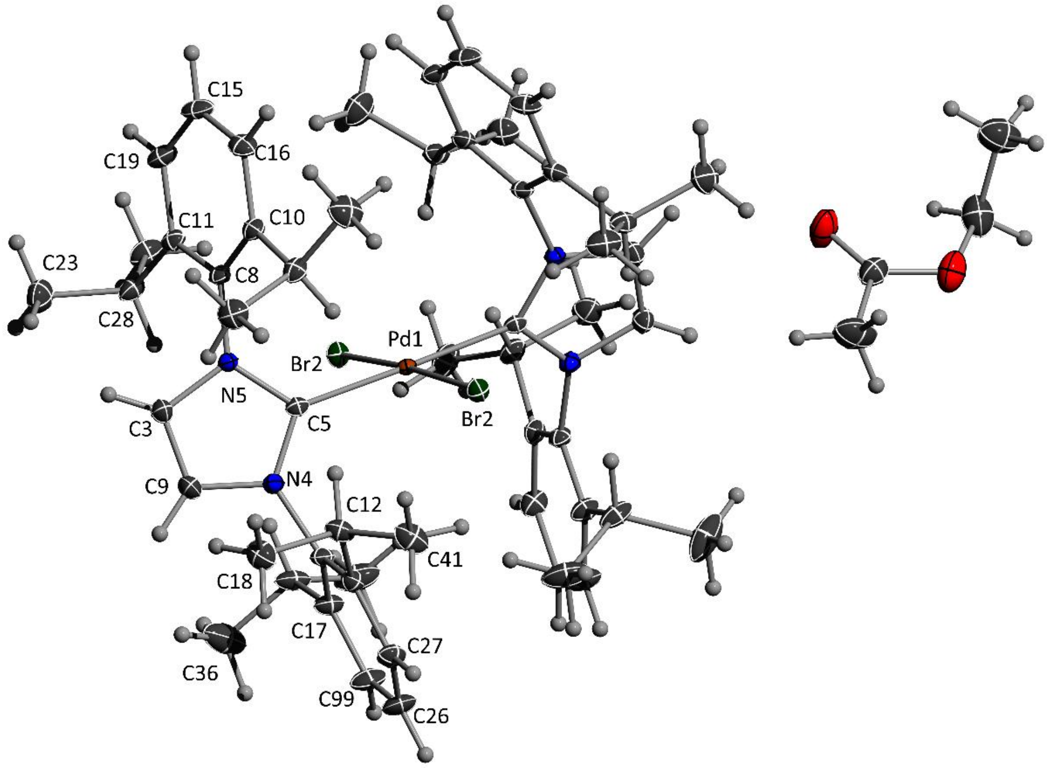


Table 13. Crystal data and structure refinement for **Pd-6**.

CCDC Number	1895949
Empirical formula	$C_{54}H_{72}Br_2N_4Pd_1(C_4H_8O_2)$
Formula weight	1219.58
Temperature/K	108(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	20.6001(5)
b/Å	13.1062(3)
c/Å	22.5609(5)
α/°	90
β/°	101.910(2)
γ/°	90
Volume/Å^3	5960.1(2)
Z	4
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	4.452
F(000)	2544.0
Crystal size/mm^3	0.329 × 0.19 × 0.116
Radiation	CuK$_\alpha$ (λ = 1.54184)
2Θ range for data collection/°	8.046 to 152.498
Index ranges	$-25 \le h \le 24$, $-16 \le k \le 15$, $-19 \le l \le 28$
Reflections collected	14530
Independent reflections	6112 [R_{int} = 0.0214, R_{sigma} = 0.0217]

Data/restraints/parameters	6112/0/340
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0771
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0780
Largest diff. peak/hole / e $Å^{-3}$	0.97/-0.58

6.3 Crystal data for ***Pd-4***

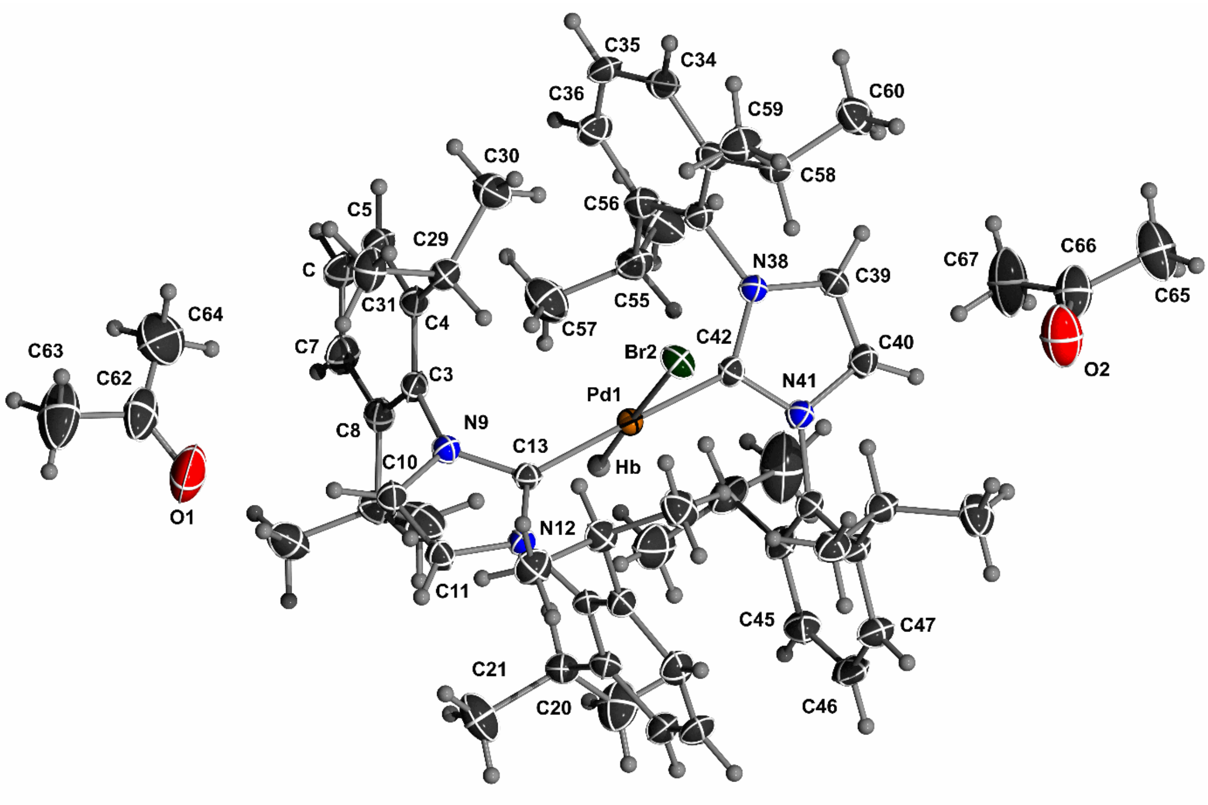


Table 14. Crystal data and structure refinement for **Pd-4**.

CCDC Number	1895950
Empirical formula	$C_{54}H_{73}Br_1N_4Pd(C_3H_6O_1)$
Formula weight	1080.62
Temperature/K	102.7(9)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.3520(2)
b/Å	21.7347(4)
c/Å	21.4568(4)
α/°	90
β/°	91.0258(15)
γ/°	90
Volume/Å^3	5759.49(17)
Z	4
ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	3.733
F(000)	2280.0
Crystal size/mm^3	0.113 × 0.089 × 0.087
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.136 to 135.99
Index ranges	$-14 \leq h \leq 14$, $-26 \leq k \leq 26$, $-25 \leq l \leq 25$
Reflections collected	33081

Independent reflections	10492 [R_{int} = 0.0455, R_{sigma} = 0.0493]
Data/restraints/parameters	10492/5/649
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0769
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.0830
Largest diff. peak/hole / e $Å^{-3}$	0.83/-0.44

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