Electronic Supplementary Information

Pd/DNA as highly active and recyclable catalyst of Suzuki-Miyaura

General Remarks

All substrates were purchased commercially and used without further purification Fish sperm DNA (CAS:438545-06-3) was purchased from Sigma-Aldrich (price: 145 €/gram).

Spectrometer ARL model 3410 was used for the ICP measurements of the palladium content.

The XRD measurement was carried out with a DRON-1 diffractometer operating with the Cu-Kα ratiation time.

Infrared (IR) spectra were acquired in transmission mode on a Nicolet iS50 FT-IR spectrometer.

TEM measurements were performed using a FEI Tecnai G^2 20 X-TWIN electron microscope with LaB_6 catode with 0.25 nm resolution. The nanoparticle size distributions were determined by counting the size of 200 palladium nanoparticles from several TEM images obtained from different places of the TEM grids.

The SEM micrographs and EDS spectra were acquired using a Hitachi S-3400N scanning electron microscope with the Thermo Scientific Ultra Dry EDS detector.

XPS spectra were recorded on a SPECS UHV/XPS/AES system equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 100 analyzer operating in the fixed analyzer transmission (FAT) mode. High-resolution spectra were obtained with a pass energy of 8 or 10 eV; a Mg-Kα X-ray source was operated at 250 W and 10 kV.

GC-FID and GC/MS Spectra of the organic products were performed using the HP 5890 (Hewlett Packard) instrument with mass detector 5971 A. Capillary column HP 5 was used with a non-polar liquid phase containing 95% of dimethyl- and 5% of diphenylpolysiloxane.

For preparation of Pd/DNA double-distilled water and 99.8% ethanol were used.

Organic products were separated on silica gel 60 (0.040-0.063 mm, CAS: 112926-00-8).

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 500 MHz spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 125 MHz) using TMS as internal reference. Chemical shifts (δ) are reported in ppm.

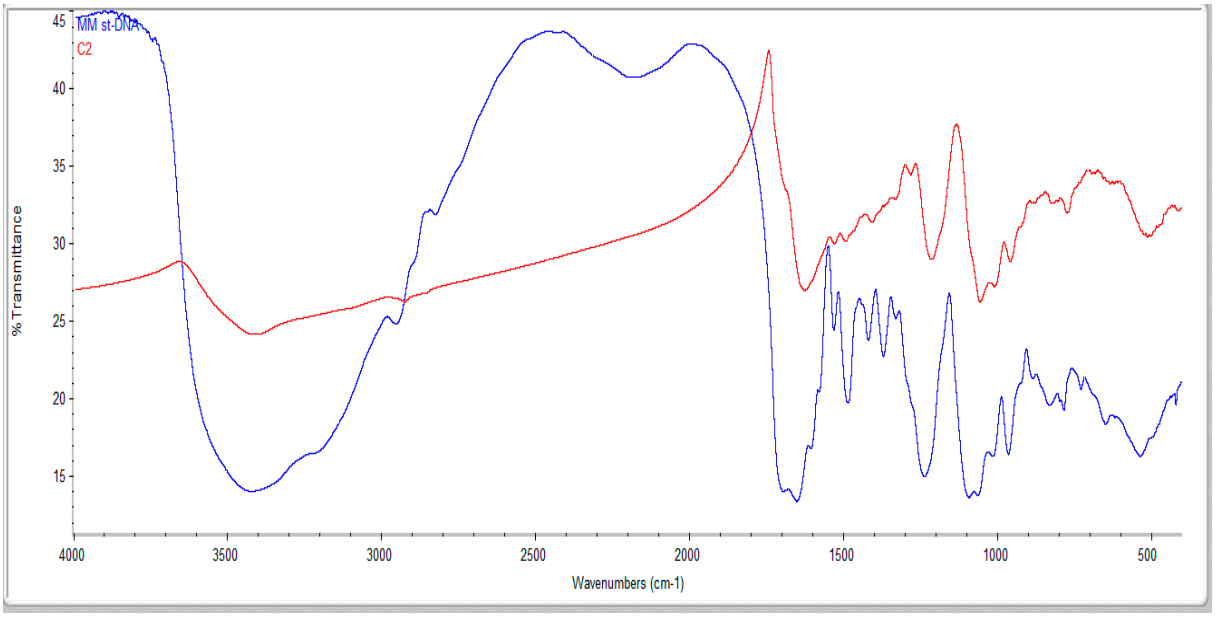


Figure S1. FT-IR (KBr) spectra of: Pd/DNA(C2) (red), pure DNA (blue)

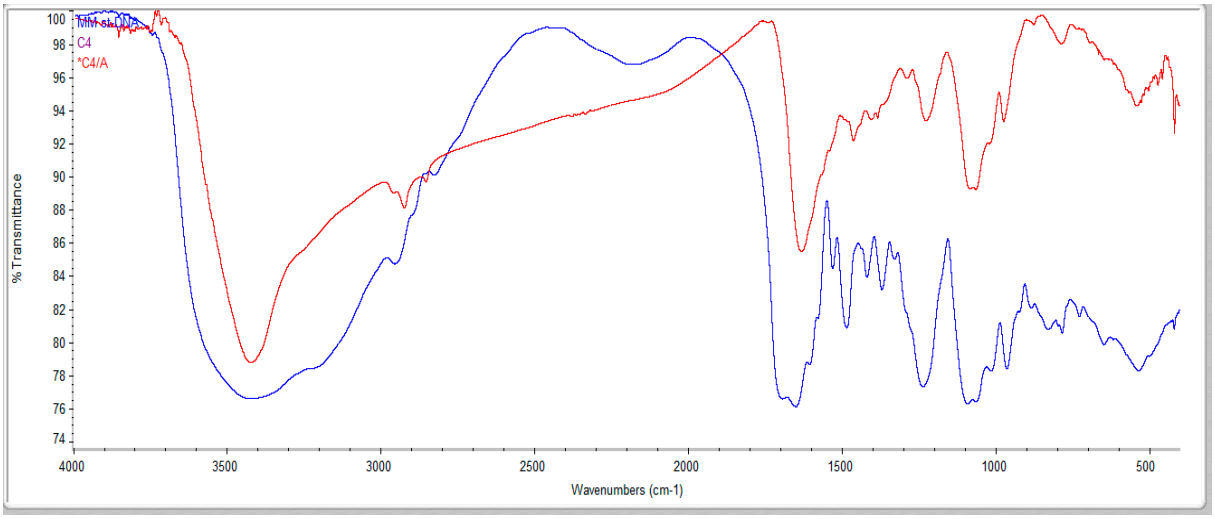


Figure S2. FT-IR (KBr) spectra of: Pd/DNA(C4) catalyst recovered after Suzuki-Miyaura reaction (red) and DNA (blue)

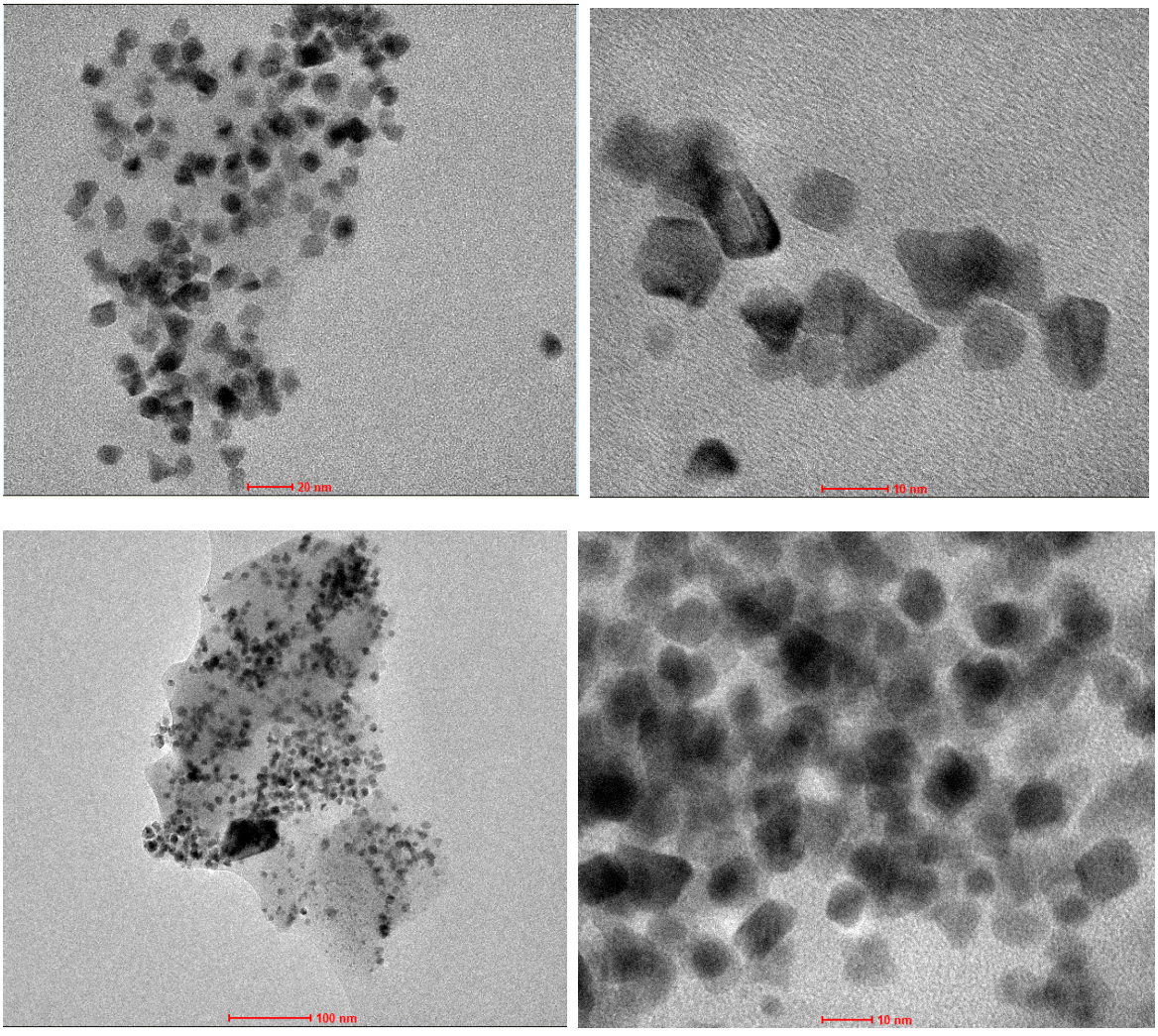


Figure S3. Morphology of Pd/DNA (C4) catalyst recovered after Suzuki-Miyaura reaction

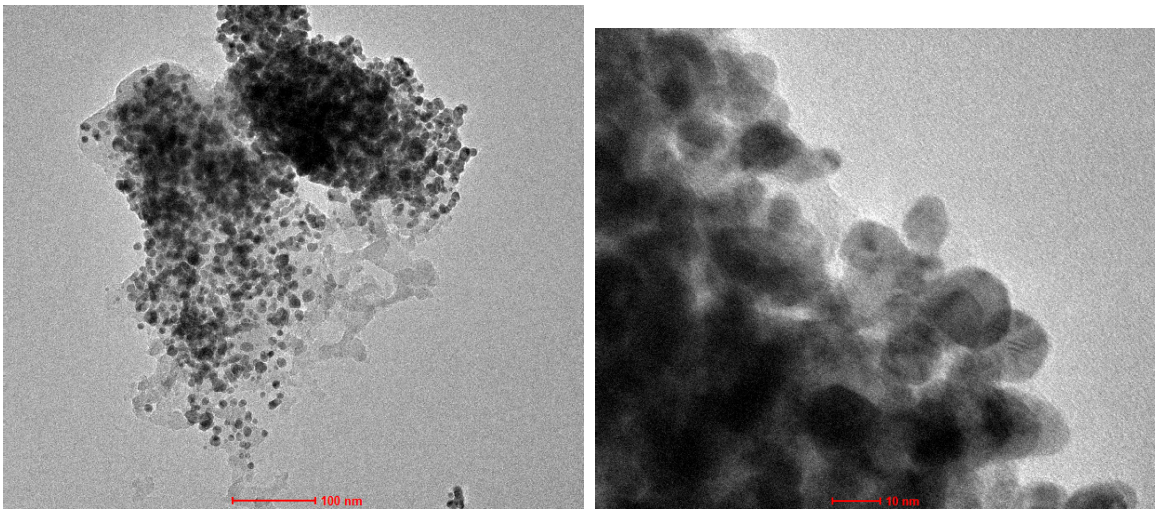


Figure S4. Morphology of Pd/DNA (C2) after seven catalytic runs

Pd-leaching Study

Pd-leaching was studied after the first run of 4-bromobenzaldehyde with phenylboronic acid. After the products had been extracted the remaining solution was filtered through celite into a 25 volumetric flask. Then 2 ml of concentrated nitric acid and 6 ml of concentrated hydrochloric acid were added. The flask was filled until 25 ml with distilled water and analysed by ICP. The palladium content of the solution was determined as 0.152 ppm.

Hot Filtration Test

Suzuki-Miyaura reaction of 2-bromotoluene with phenylboronic acid catalyzed by Pd/DNA was stopped after 30 minutes and subjected to hot filtration through celite. The rest of the liquid phase was re-heated for 3.5 h at 80 ^{o}C. After that time, the Schlenk flask was cooled down, and the organic products were extracted with 3x7 mL of diethyl ether. The extracts were GC-FID analyzed with dodecane (0,076 mL) as an internal standart.

Table S1. The Suzuki–Miyaura coupling with the catalyst C2: screening of the reaction conditions [a]

Entry	Solvent	Base	[Pd] (mol %)	Time (h)	Yield of biphenyl[b]
1	H_2O/EtOH (1:1)	Na_2CO_3	1	4	65
2	H_2O/IPA (1:1)	Na_2CO_3	1	4	81
3	H_2O/IPA (1:1)	$NaHCO_3$	1	4	48
4	H_2O/IPA (1:1)	K_2CO_3	1	4	69
5	H_2O/IPA (1:1)	K_3PO_4	1	4	74
6	H_2O/IPA (1:1)	NaOH	1	4	75
7	H_2O/Dioxane (1:1)	Na_2CO_3	1	4	85
8	H_2O/Dioxane (1:1)	$NaHCO_3$	1	4	67
9	H_2O/Dioxane (1:1)	K_3PO_4	1	4	93
10	H_2O/Dioxane (1:1)	$K_3PO_4.H_2O$	1	4	91
11	H_2O/Dioxane (1:1)	NaOH	1	4	94
12	H_2O/Dioxane (1:1)	NaOH	1	2	74
13	H_2O/Dioxane (1:1)	NaOH	0.5	4	79
14	H_2O/Dioxane (1:1)	NaOH	0.5	2	64

a[Pd] (0.5 or 1 mol%), base (1.2 mmol), solvent (5 mL), bromobenzene (1 mmol), phenylboronic acid (1.2 mmol), 80 °C,2–4 h.**b**Yield was determined by GC using dodecane as an internal standard.

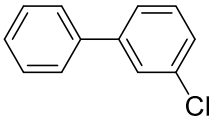
Table S2. Carbonylative Suzuki coupling catalyzed by C1: solvent, base and CO pressure testing.[a]

Entry	Solvent	Base	Conv.[b] (%)	Yield **1**[b]	Yield **2**[b]	Yield **3**[b]
1	H_2O	NEt_3	88	25	41	22
2	H_2O	NaOAc	32	5	0	27
3	H_2O	Na_2CO_3	38	4	12	22
4	H_2O	NaHC	39	5	12	22

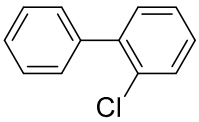
		O_3				
5	IPA/H_2O (1/1)	Na_2CO_3	100	17	71	12
6	IPA/H_2O (1/1)	Na_2CO_3	35[c]	0[c]	0[c]	35[c]
7	IPA/H_2O (1/1)	NaHC O_3	100	34	38	28
8	IPA/H_2O (1/1)	NaOAc	19	11	0	8
9	Dioxane/H_2O (1/1)	NaOH	100	10	85	5
10	Dioxane/H_2O (1/1)	NaOH	30[c]	0[c]	0[c]	30[c]
11	Dioxane/H_2O (1/1)	NaOAc	38	9	0	29
12	Dioxane/H_2O (1/1)	NaHC O_3	100	26	55	19
13	Dioxane/H_2O (1/1)	NaHC O_3	24[c]	0[c]	0[c]	24[c]
14	Dioxane/H_2O (4/1)	NaHC O_3	66	14	0	52
15	Dioxane/H_2O (4/1)	K_3PO_4	80	29	20	31
16	Dioxane/H_2O (4/1)	NaOH	76	15	41	20
17	Dioxane/H_2O (1/4)	NaHC O_3	69	12	50	7
18	Dioxane	K_3PO_4	0	0	0	0
19	Dioxane	NaHC O_3	0	0	0	0
20	Anisole	K_2CO_3	0	0	0	0
21	Anisole	K_2CO_3	0[d]	0[d]	0[d]	0[d]
22	Anisole/H_2O (9/1)	K_2CO_3	66[d]	35[d]	31[d]	0[d]

[a][Pd] (1 mol%), base (1.2 mmol), solvent (5 mL), iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), 80 °C, CO (balloon pressure), 4h. [b]Conversion and yield were determined by GC using mesitylene as an internal standard.[c]5 bar, 80 °C, 4h. [d] 100 °C, K_2CO_3 (3 mmol), phenylboronic acid (2 mmol).

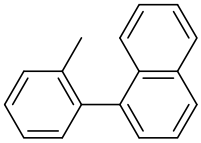
MS data for the products:



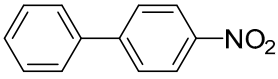
3-chloro-1,1'-biphenyl GC-MS: m/z=39 (4%), 51 (10%), 76 (34%), 94 (6%), 126 (5%), 152 (56%), 188 ([M^+]=100%).



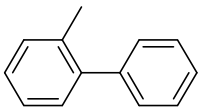
2-chloro-1,1'-biphenyl GC-MS: m/z=39 (6%), 51 (13%), 63 (19%), 76 (58%), 94 (7%), 113 (2%), 126 (5%), 152 (55%), 188 ([M^+]=100%).



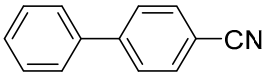
1-(o-tolyl)naphthalene GC-MS: m/z=95 (11%), 108 (17%), 189 (6%), 203 (50%), 218 ([M^+]=100%).



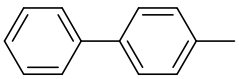
4-nitro-1,1'-biphenyl GC-MS: m/z=51 (11%), 63 (11%), 76 (17%), 102 (4%), 115 (11%), 127 (9%), 141 (21%), 152 (98%), 169 (26%), 199 ([M^+]=100%).



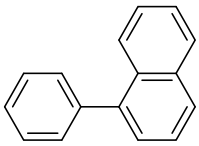
2-methyl-1,1'-biphenyl GC-MS: m/z=39 (4%), 51 (4%), 63 (6%), 70 (4%), 76 (4%), 83 (17%), 89 (4%), 115 (9%), 127 (4%), 141 (4%), 153 (36%), 165 (38%), 168 ([M^+]=100%).



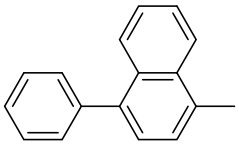
[1,1'-biphenyl]-4-carbonitrile GC-MS: m/z= 63 (4%) 76 (13%), 89 (4%), 151 (13%) 179 ([M$^+$]=100%).



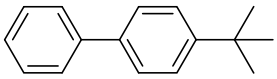
4-methyl-1,1'-biphenyl GC-MS: m/z= 51 (%4%), 63 (4%), 82 (11%), 115 (4%), 152 (21%), 168 ([M$^+$]=100%).



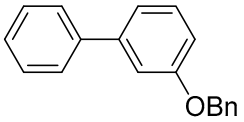
1-phenylnaphthalene GC-MS: m/z=63 (4%), 76 (7%), 88 (14%), 101 (23%), 176 (4%), 204 ([M$^+$]=100%)



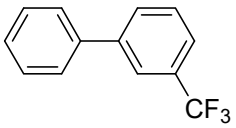
1-methyl-4-phenylnaphthalene GC-MS: m/z=51 (2%), 63 (4%), 88 (2%), 101 (19%), 115 (2%), 141 (2%), 165 (2%), 189 (2%), 203 (47%), 218 ([M$^+$]=100%)



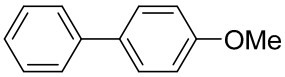
4-(tert-butyl)-1,1'-biphenyl GC-MS: m/z=84 (15%), 115 (4%), 155 (11%), 167 (26%), 178 (7%), 195 (100%), 210 ([M$^+$]=37%)



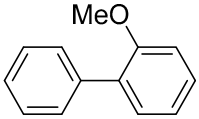
3-(benzyloxy)-1,1'-biphenyl GC-MS: m/z=65 (13%), 91 (100%), 92 (11%), 260 ([M$^+$]=28%)



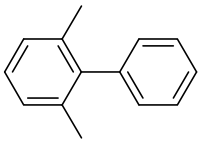
3-(trifluoromethyl)-1,1'-biphenyl GC-MS: m/z=111 (7%), 152 (29%), 201 (18%), 222 ([M$^+$]=100%)



4-methoxy-1,1'-biphenyl GC-MS: m/z=39 (4%), 51 (4%), 63 (8%), 76 (7%), 115 (26%), 141 (38%), 169 (47%), 184 ([M^+]=100%)

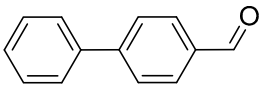


2-methoxy-1,1'-biphenyl GC-MS: m/z=39 (4%), 51 (7%), 63 (13%), 76 (9%), 91 (7%), 115 (37%), 141 (35%), 152 (9%), 169 (52%), 184 ([M^+]=100%)



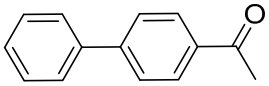
2,6-dimethyl-1,1'-biphenyl GC-MS: m/z=39 (4%), 51 (6%), 63 (6%), 76 (15%), 89 (21%), 115 (6%), 152 (19%), 167 (100%), 182 ([M^+]=96%)

Isolated Reaction Products



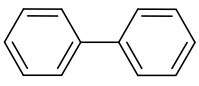
Biphenyl-4-carboxaldehyde

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.89 (d, *J*=8.2 Hz, 2H), 7.69 (d, *J*=8.2 Hz, 2H), 7.58-7.56 (m, 2H), 7.43-7.40 (m, 2H), 7.37-7.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.3. GC-MS: m/z=39 (4%), 51 (15%), 63 (11%), 76 (37%), 152 (70%), 181 (100%), 182 ([M^+]=96%). Spectral data are consistent with data reported in literature. [R1]



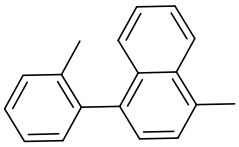
4-Acetylbiphenyl

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J*=8.3 Hz, 2H), 7.62 (d, *J*=8.3 Hz, 2H), 7.57 (d, *J*=6.1 Hz, 2H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 1H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 145.8, 139.9, 135.8, 128.9, 128.2, 127.3, 127.2, 26.6. GC-MS: m/z=39 (5%), 43 (24%), 63 (12%), 76 (38%), 91 (12%),127 (7%), 152 (62%), 181 (100%), 196 ([M^+]=58%). Spectral data are consistent with data reported in literature. [R2]



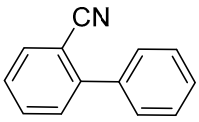
Biphenyl

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.55 (m, 4H), 7.42-7.39 (m, 4H), 7.33-7.29 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 128.8, 127.3, 127.2. GC-MS: m/z=39 (%6), 51 (15%), 63 (11%), 76 (30%),154 ([M^+]=100%). Spectral data are consistent with data reported in literature. [R1, R3]



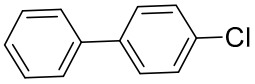
1-methyl-4-(o-tolyl)naphthalene

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J*=8.4 Hz, 1H), 7.49-7.43 (m, 2H), 7.35-7.18 (m, 7H), 2.71 (s, 3H),
1.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 138.1, 136.9, 133.6, 132.6, 132.0, 130.5, 129.8, 127.4, 126.7, 126.3, 126.1, 125.6, 125.5, 124.3, 20.1, 19.5. GC-MS: m/z=95 (%13), 108 (19%), 114 (15%), 189 (%6), 202 (32%), 217 (83%), 232 ([M^+]=100%)



2-cyanobiphenyl

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J*=7.7 Hz, 0.9 Hz, 1H), 7.58 (td, *J*=7.7 Hz, 1.3 Hz, 1H), 7.52-7.49 (m, 2H), 7.46-7.36 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 138.1, 133.7, 132.8, 130.1, 128.8, 128.7, 128.6, 118.7, 111.3. GC-MS: m/z=51 (4%), 76 (13%), 151 (15%), 179 ([M^+]=100%). Spectral data are consistent with data reported in literature. [R4]



4-chlorobiphenyl

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.46 (m, 4H), 7.41-7.35 (m, 4H), 7.33-7.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 139.7, 133.4, 128.9, 128.4, 127.6, 127.0. GC-MS: m/z=39 (5%), 51 (12%), 76 (36%), 94 (8%), 126 (5%), 152 (51%), 188 ([M^+]=100%). Spectral data are consistent with data reported in literature. [R1,R5]

References

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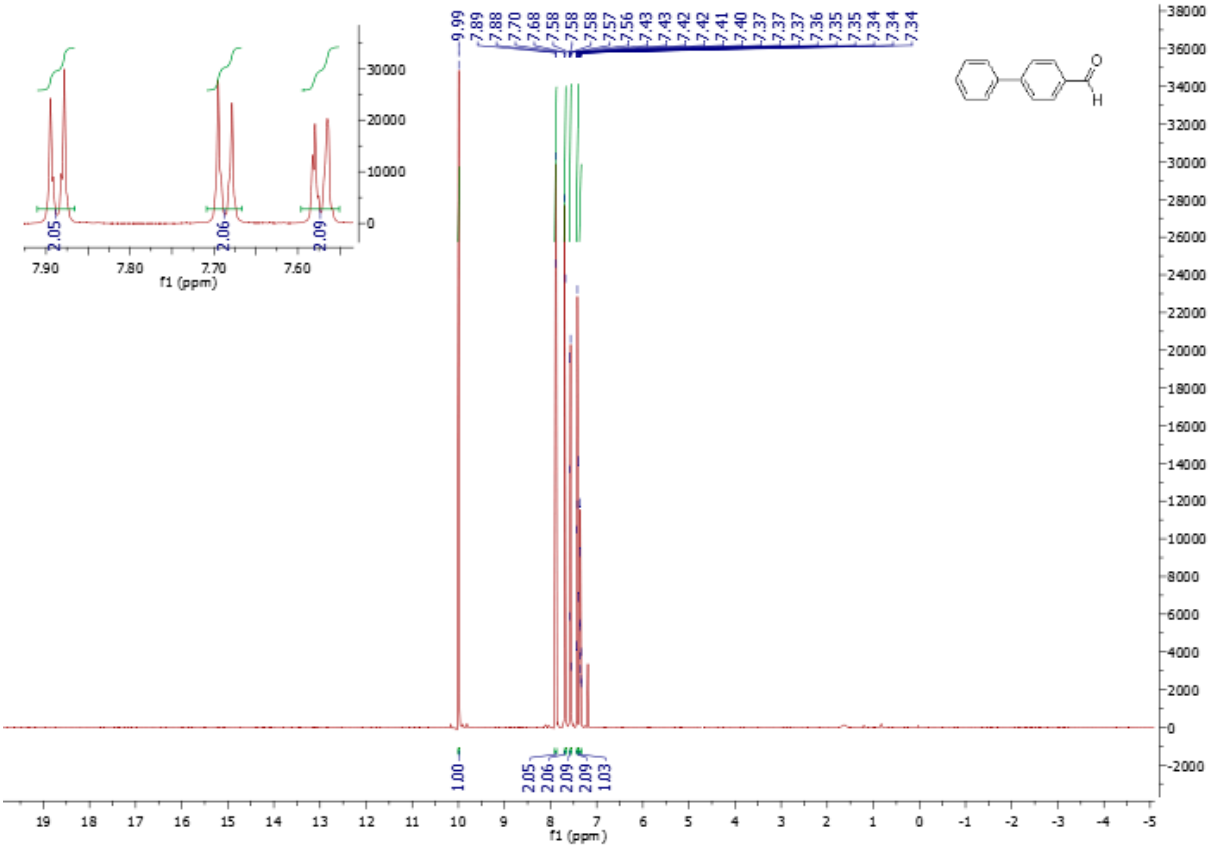
R2 Min, H.; Miyamura, H.; Kobayashi, S., Chem. Lett. 2016, 45, 837–839.

R3 Yanga J.; Wang, L.; Dalton Trans., 2012, 41, 12031–12037.

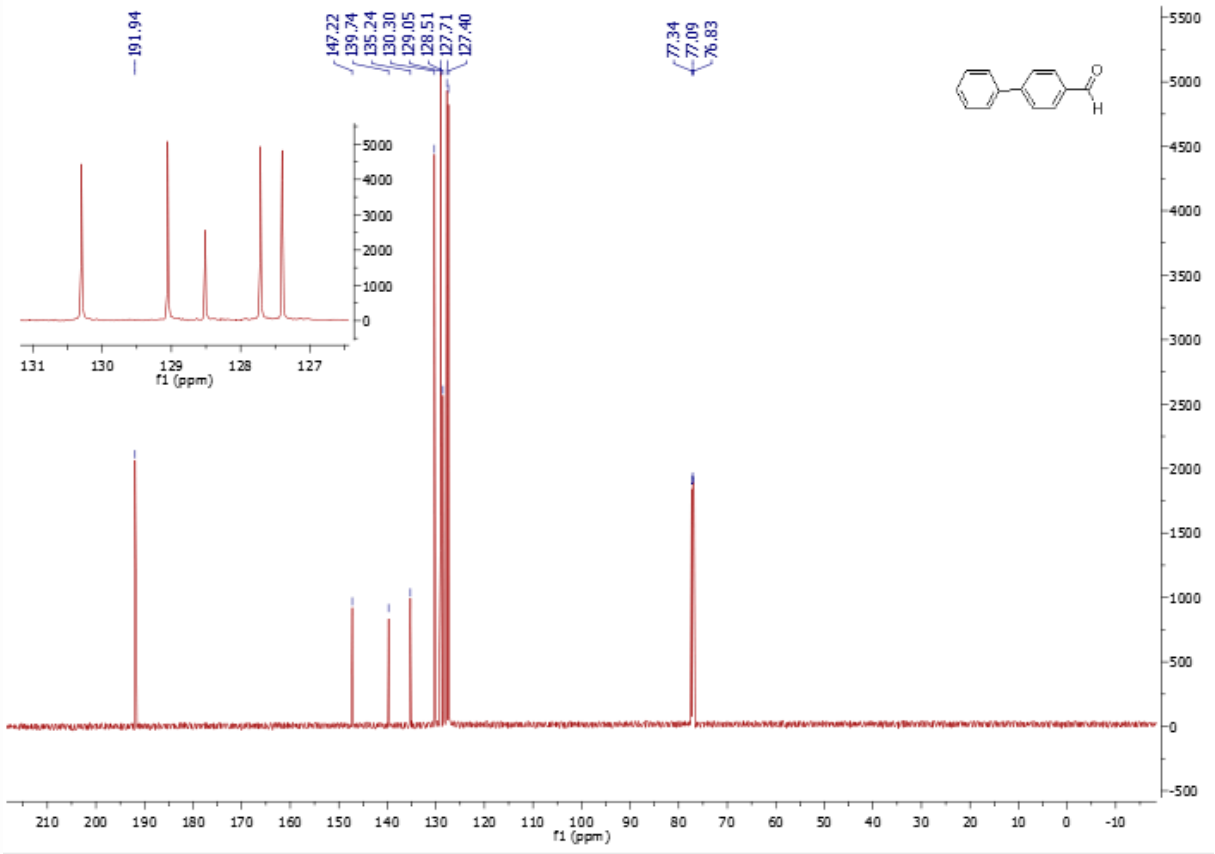
R4 Lan, X.B.; Chen, F.M.; Ma, B.B.; Shen, D.S.; Liu, F.S., Organometallics, 2016, 35, 3852−3860.

R5 Witzel, S.; Xie, J.; Rudolph, M.; Hashmi, A.S.K., Adv. Synth. Catal. 2017, 359, 1522-1528.

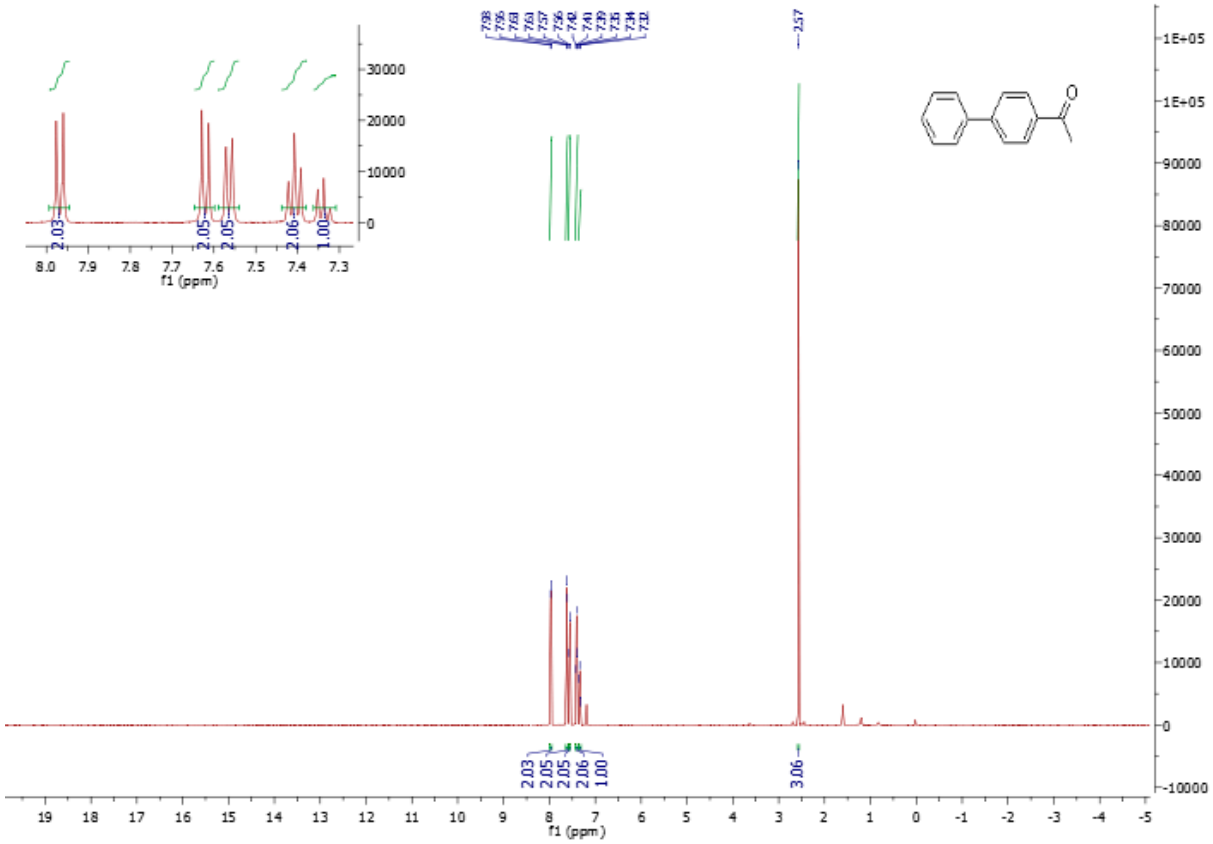
^{1}H NMR of Biphenyl-4-carboxaldehyde



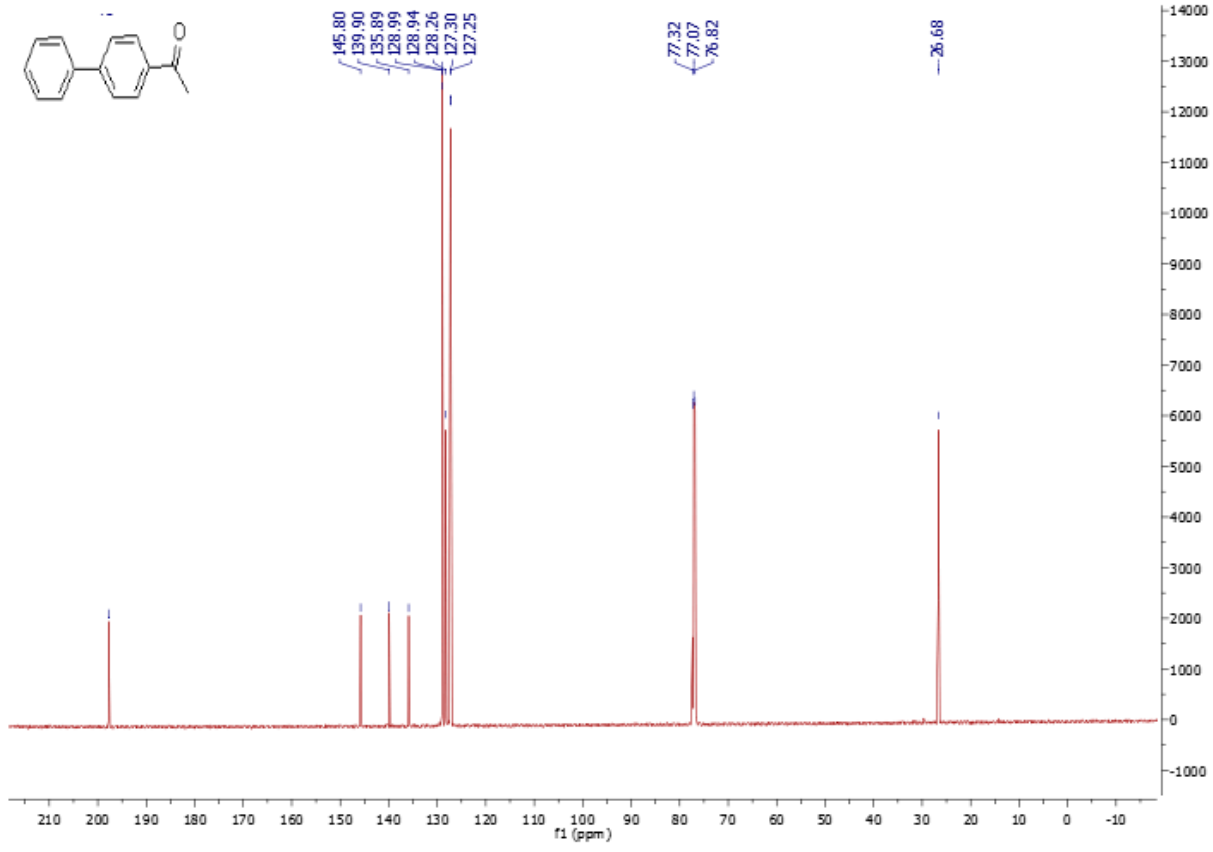
^{13}C NMR of Biphenyl-4-carboxaldehyde



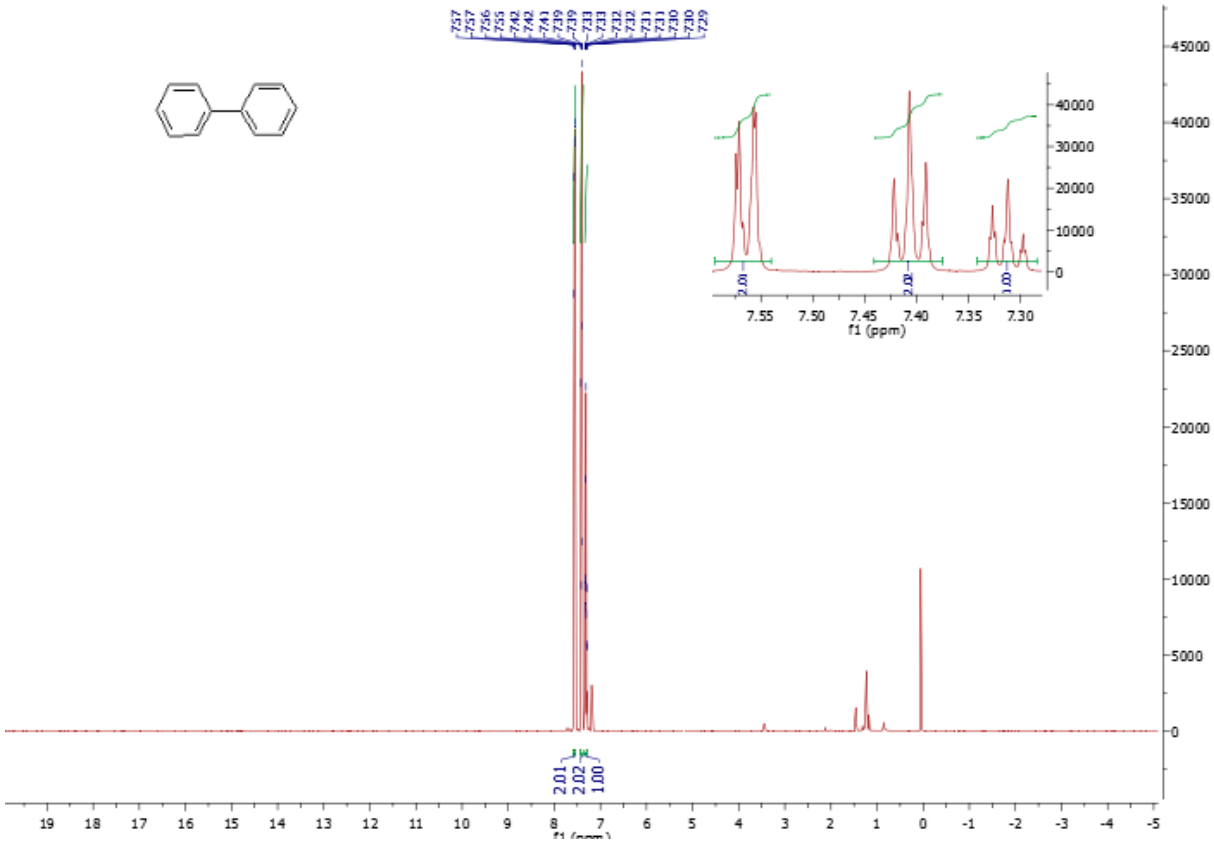
^{1}H NMR of 4-Acetylbiphenyl



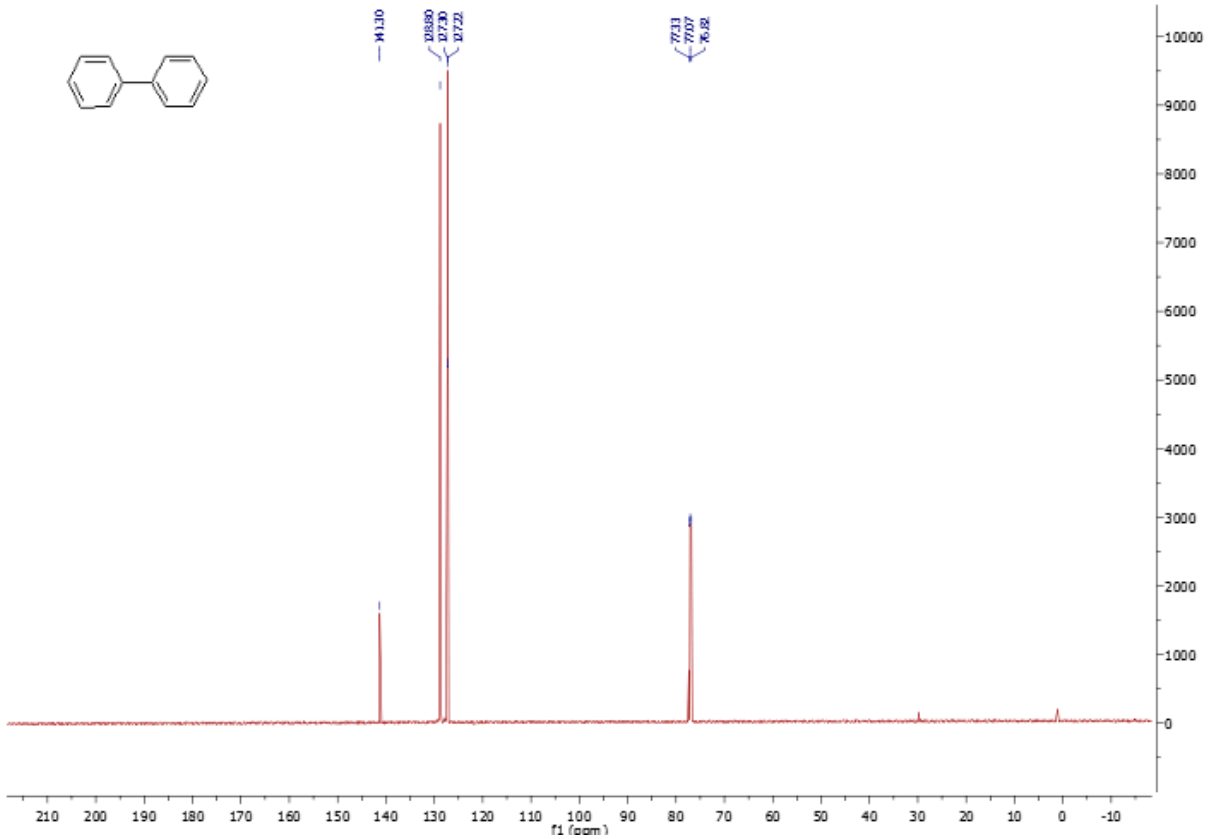
^{13}C NMR of 4-Acetylbiphenyl



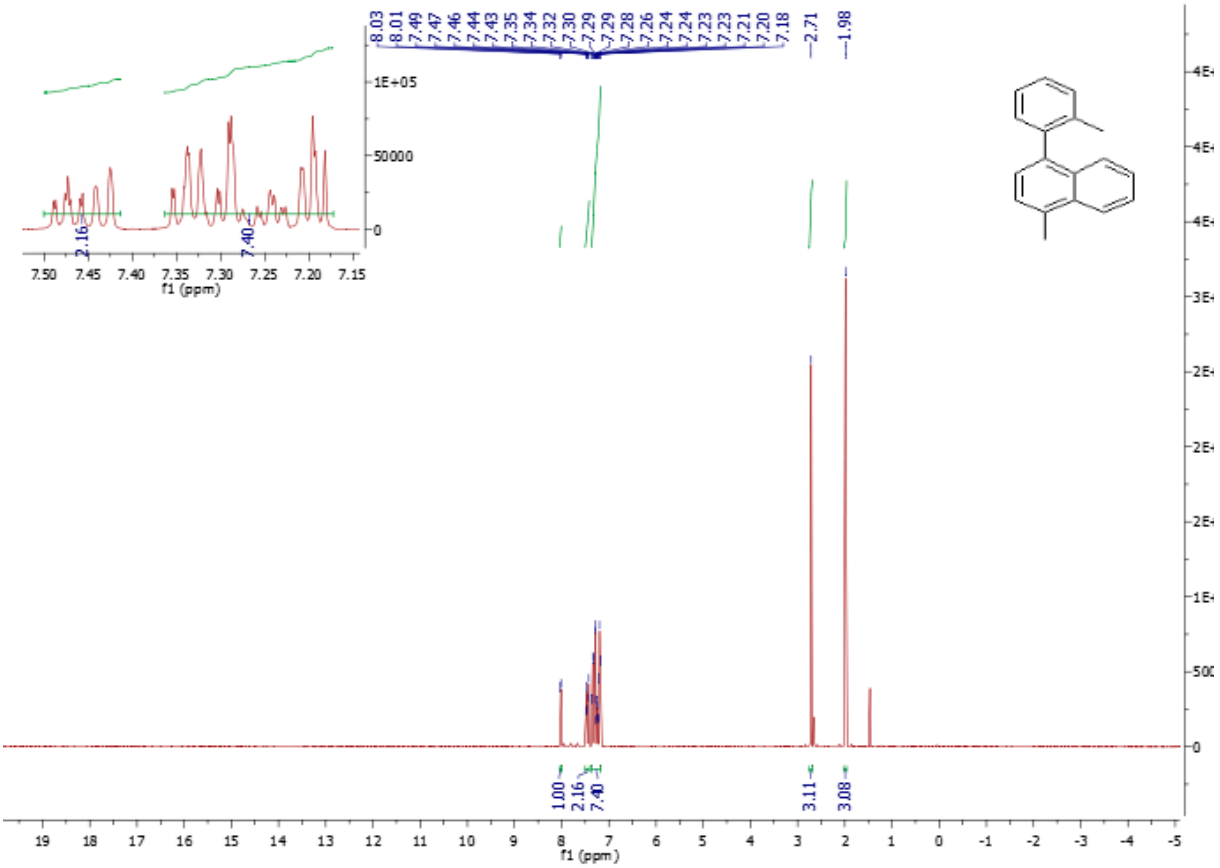
^{1}H NMR of Biphenyl



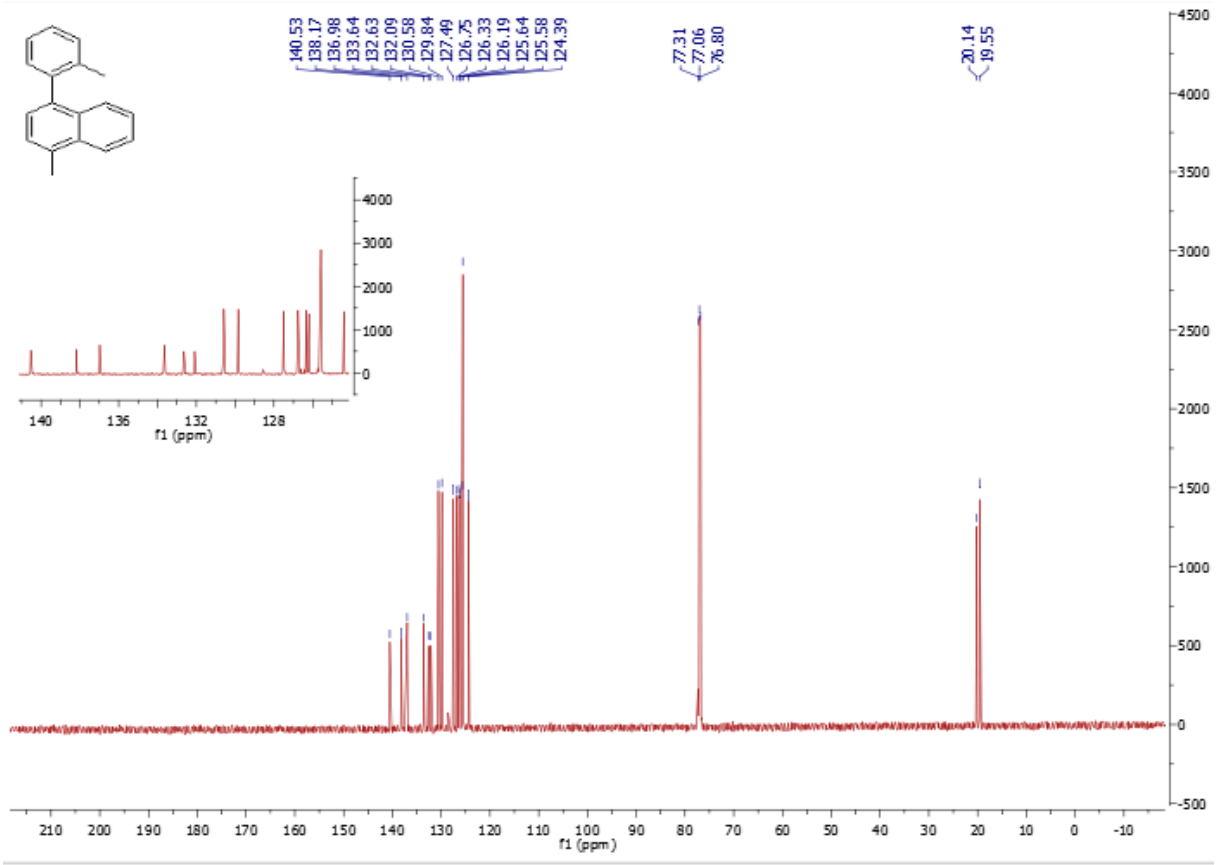
^{13}C NMR of Biphenyl



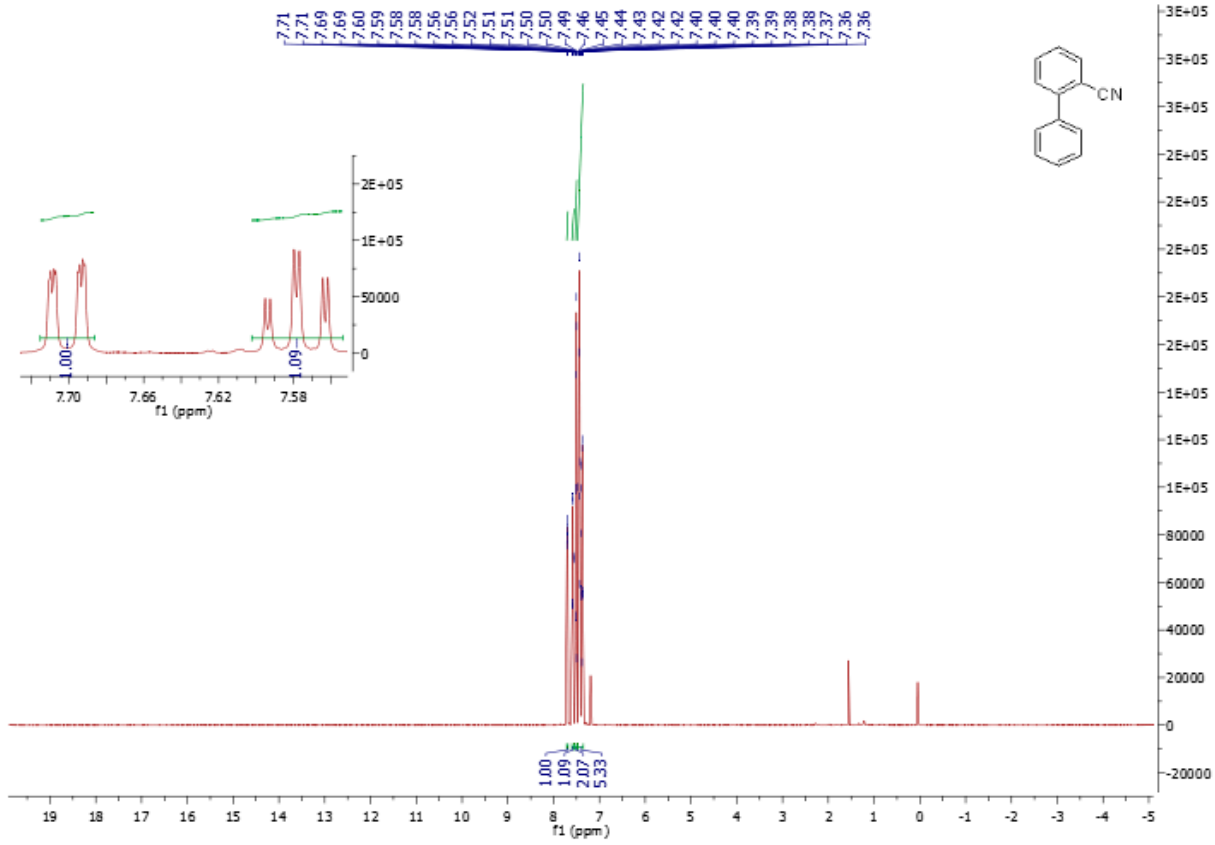
^{1}H NMR of 1-methyl-4-(o-tolyl)naphthalene



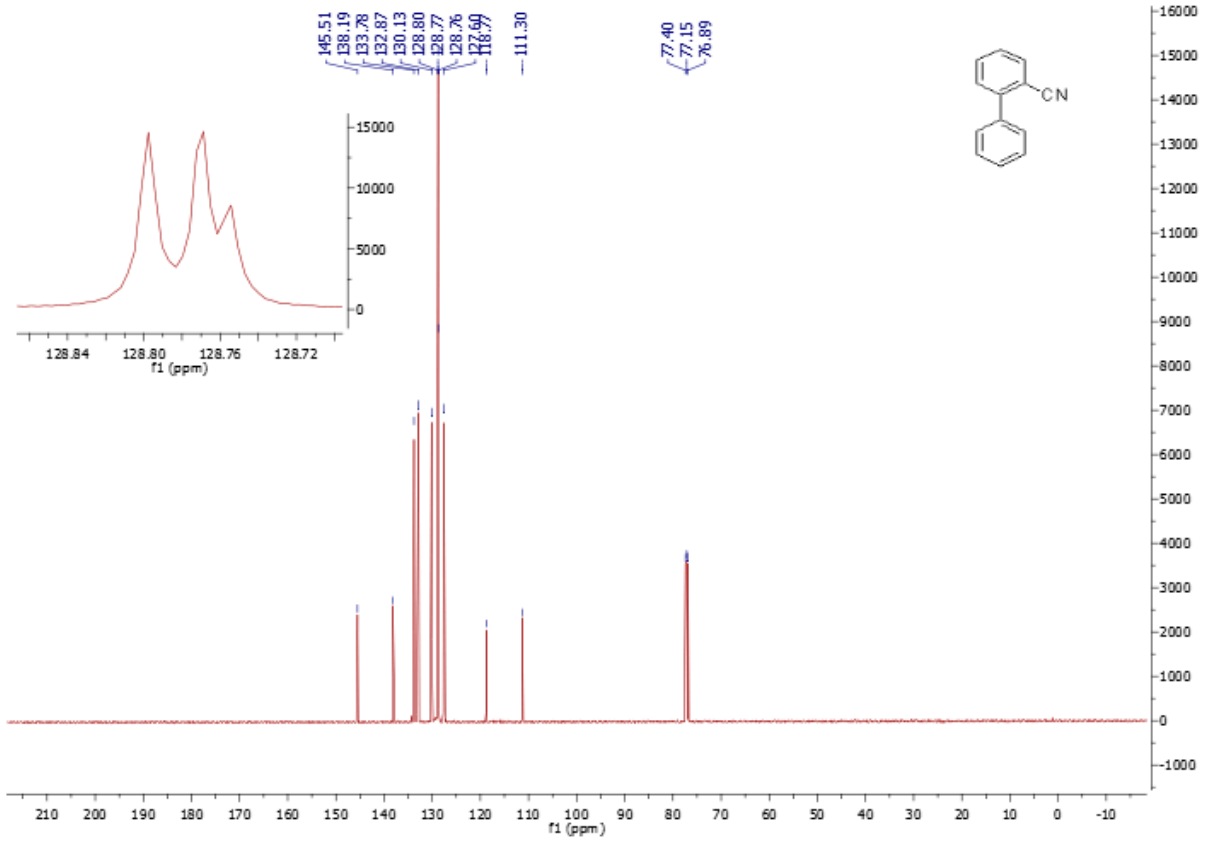
^{13}C NMR of 1-methyl-4-(o-tolyl)naphthalene



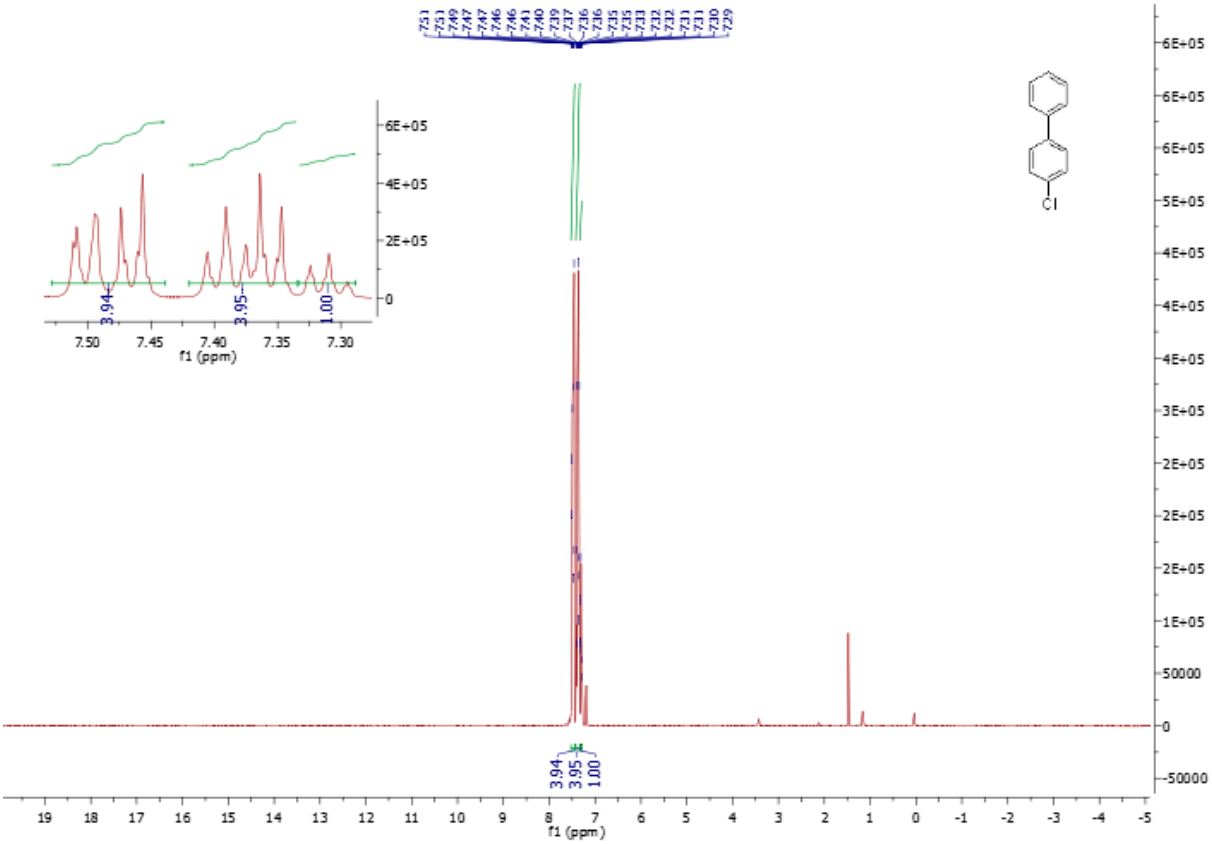
^{1}H NMR of 2-cyanobiphenyl



^{13}C NMR of 2-cyanobiphenyl



^{1}H NMR of 4-chlorobiphenyl



^{13}C NMR of 4-chlorobiphenyl