Supporting Information

A Highly Active and Recyclable Homogeneous NHC-Palladium Catalyst with pH- and Light-Sensitive Tags for the Suzuki–Miyaura Coupling Reactions of Aryl Halides with Arylboronic Acids

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Content:

1. General Techniques

1.1. Materials

Unless otherwise noted, all reactions were performed under an atmosphere of dry N_2 with oven-dried glassware and anhydrous solvents. Toluene, THF, hexane, and diethyl ether were distilled from sodium benzophenone under a N_2 atmosphere. CH_2Cl_2 was dried over $CaCl_2$, and distilled prior to use. All other solvents were dried over 4-8 Å mesh molecular sieves (Aldrich). Reactions were monitored by thin layer chromatography on 0.20 mm Anhui Liangchen silica gel plates and spots were detected with UV light. Silica gel (200-300 mesh) (from Anhui Liang Chenchem Company, Ltd.) was used for flash chromatography. The (Pd(allyl)Cl)$_2$[1] and nitrobenzospiropyran (SP) [2] were prepared according to literature method. Other chemicals or reagents were obtained from commercial sources.

1.2. Spectroscopic Procedures

NMR spectra were recorded with a Bruker Avance III 400 MHz spectrometer. UV-vis spectra were recorded with a SHIMADZU UV-2700 spectrophotometer at 20 °C. Elemental analyses were determined in house using a Perkin-Elmer 2400 CHN elemental analyzer.

1.3. Synthetic Procedures

All experiments were carried out in Synthware glass round-bottom flasks, equipped with magnetic stir bars and high vacuum Teflon valves.

2. Preparation of 1
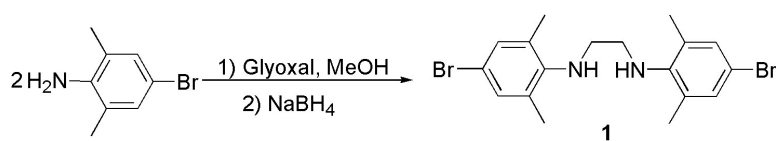
A 250-mL flask was charged with 3.73 mL 40% aqueous glyoxal and 50 mL methanol. Then 4-bromo-2,6-dimethyl phenylamine (13.5 g, 67 mmol) in 50 mL methanol was added dropwise at room temperature. After the mixture was stirred for 12 h at room temperature, the resulting yellow precipitate was collected by filtration and dried in vacuum.

A suspension of the resulting yellow precipitate (5.5 g, 13 mmol) in THF/methanol (40 mL/60 mL) was stirred at room temperature in a 250-mL round bottom flask equipped with a stir bar. Then sodium borohydride (7 g, 184 mmol) was slowly added. The mixture was refluxed for 1.5 h. After cooling to room temperature, saturated ammonium chloride aqueous solution (20 mL) was added.

The mixture was filtered and the filtrate was extracted with ether (3 x 20 mL), washed with water, dried over Na_2SO_4 and concentrated under vacuum to afford a pink solid. Yield: 69%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.05 (s, 4H), 3.07 (s, 4H), 2.19 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 144.7, 131.7, 131.4, 114.6, 48.7, 18.3. Analytical Data. Calcd (found) for $C_{18}H_{22}N_2Br_2$: C, 50.73 (50.86); H, 5.20 (4.98).

3. *Preparation of 2*
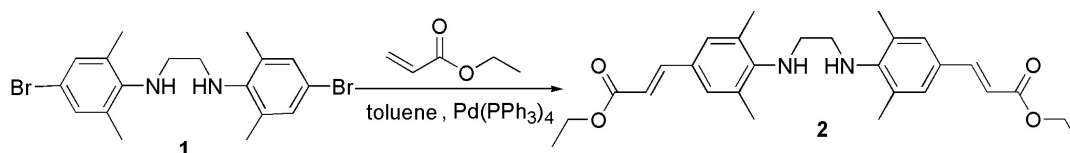
Under a N_2 atmosphere, a 50-mL flask was charged with compound **1** (1 g, 2.3 mmol), ethyl acrylate (1.9 g, 18.8 mmol), trimethylamine (TEA) (1.9 g, 18.8 mmol), tetrakis-(triphenylphosphine)-palladium (0.27 g, 0.23 mmol) and toluene (2 mL). The mixture was heated to 100 °C for 36 h. After cooling to room temperature, a quantity of water was added. The mixture was filtered and the filtrate was extracted with ether (3 x 20 mL), washed with water, dried over Na_2SO_4 and concentrated under vacuum to afford a yellow solid. The product was further purified by flash chromatography on a silica gel column using pentanes/ethyl acetate (3:1) as the eluent .Yield: 70%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (d, J = 16.0 Hz, 2H), 7.18 (s, 4H), 6.29 (d, J = 16.0 Hz, 2H), 4.23 (q, J = 7.2 Hz, 4H), 3.29 (s, 4H), 2.28 (s, 12H), 1.32 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 166.9, 147.5, 144.0, 128.6, 128.1, 127.3, 114.9, 59.7, 47.9, 18.3, 13.8. Analytical Data. Calcd (found) for $C_{29}H_{40}N_2O_4$: C, 72.47 (72.34); H, 8.39 (8.27).

4. *Preparation of 3*
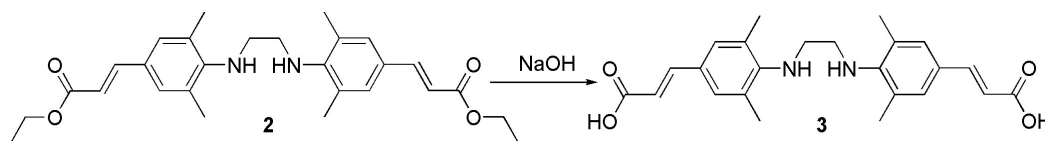
A suspension of **2** (200 mg, 0.4 mmol) in 10% NaOH (8 mL) and methanol (24 mL) was refluxed in a 100-mL round bottom flask for 1.5 h. After cooling to room temperature, the pH of the mixture was adjusted to 1.0 with 1 M HCl and then extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuum to give the resulting yellow solid. Yield: 90%. ^{1}H-NMR (400 MHz, DMSO) δ (ppm): 7.41 (d, J = 16.0 Hz, 2H), 7.23 (s, 4H), 6.26 (d, J = 16.0 Hz, 2H), 3.33 (s, 4H), 2.20 (s, 12H). ^{13}C-NMR (100 MHz, DMSO) δ (ppm): 167.9, 148.7, 144.3,

129.0, 127.8, 125.9, 115.1, 47.5, 18.7. Analytical Data. Calcd (found) for $C_{24}H_{28}N_2O_4$: C, 70.57 (70.66); H, 6.91 (6.97).

5. *Preparation of 4*
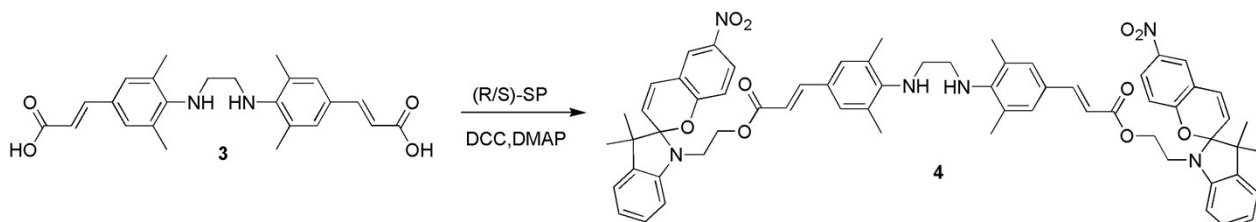
DCC (N,N'-dicyclohexylcarbodiimide) (0.206 g, 1 mmol) and DMAP (4-dimethylaminopyridine) (0.25 g, 0.2 mmol) were added to a solution of **3** (0.20 g, 0.5 mmol) and (R/S)-SP (0.35 g, 1 mmol) in 5 mL anhydrous CH_2Cl_2 at 0 °C. The reaction mixture was then slowly warmed to room temperature and stirred for another 12 h at room temperature. Then the insoluble materials were filtered out and the filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography on silica using CH_2Cl_2 as the eluent to give green product **4** as a solid. Yield: 60%. ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 8.00 (d, J = 8.0 Hz, 4H), 7.51 (d, J = 16.0 Hz, 2H), 7.22 (t, J = 7.6 Hz, 2H), 7.11-7.08 (m, 6H), 6.92-6.88 (m, 4H), 6.71 (t, J = 8.0 Hz, 4H), 6.14 (d, J = 16.0 Hz, 2H), 5.88 (d, J = 10.4 Hz, 2H), 4.33 (t, J = 5.6 Hz, 4H), 3.62-3.55 (m, 4H), 3.30 (s, 4H), 2.29 (s, 12H), 1.28 (s, 6H), 1.17 (s, 6H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ (ppm): 166.3, 158.7, 147.7, 145.9, 144.6, 140.3, 135.0, 128.4, 127.8, 127.5, 127.1, 126.5, 125.1, 121.9, 121.0, 119.1, 117.7, 114.8, 113.6, 106.0, 105.7, 61.5, 52.6, 52.1, 47.6, 41.8, 25.1, 19.1, 18.1. Analytical Data. Calcd (found) for $C_{64}H_{64}N_6O_{10}$: C, 71.36 (73.97); H, 5.99 (6.25).

6. *Preparation of 5*
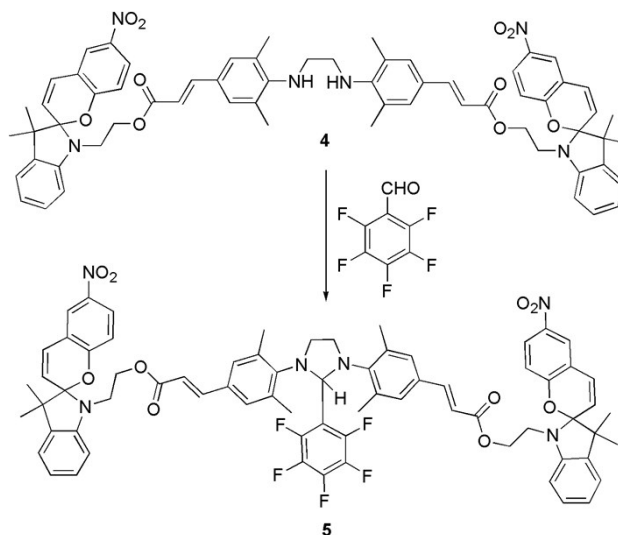
First **4** (220 mg, 0.2 mmol) and 2,3,4,5,6-pentafluorobenzaldehyde (78 mg, 0.4 mmol) were dissolved in 2 mL CH_2Cl_2. Then, 0.5 mL acetic acid was added and the mixture was stirred for 3 h at 30 °C. The solution was then extracted with CH_2Cl_2 (3 x 20 mL), washed with water, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography on a silica gel column using pentanes/CH_2Cl_2 (1:1) as the eluent to give pure product **5** as a blue solid. Yield: 37%. ^{1}H-NMR (400 MHz, CD_3CN) δ (ppm): 8.04-8.02 (m, 2H), 7.96-7.90 (m, 2H), 7.41 (d, J = 3.6 Hz, 2H), 7.21-7.17 (m, 7H), 7.13 (d, J = 7.2 Hz, 2H), 7.08-7.04 (m, 2H), 6.87 (t, J = 7.2 Hz, 2H), 6.74-6.67 (m, 4H), 6.19 (dd, J = 6.0 Hz, J = 16.0 Hz, 2H), 5.97 (d, J = 10.4 Hz, 2H), 4.36-4.27 (m, 4H), 3.65-3.50 (m, 8H), 2.39 (s, 12H), 1.25 (s, 6H), 1.11 (s, 6H). ^{19}F-NMR (376 MHz, CD_3CN) δ (ppm): -137.83 (s, 1F), -150.59 (d, J = 15 Hz, 1F), -156.85 (d, J = 19.6 Hz, 1F), -164.24 (d, J = 5.2 Hz, 1F), 164.86 (d, J = 1.8 Hz, 1F). Analytical Data. Calcd (found) for $C_{71}H_{63}F_5N_6O_{10}$: C, 67.93 (69.86); H, 5.06 (5.13).

7. *Preparation of Catalyst 6*
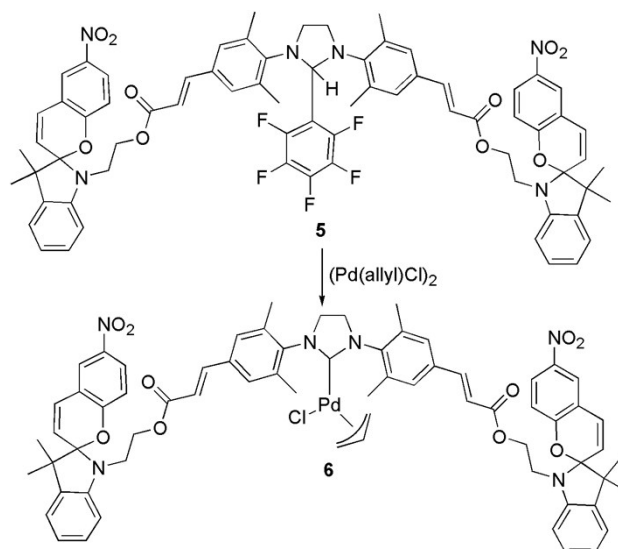
A suspension of (Pd(allyl)Cl)$_2$ (0.04 mg, 0.03 mmol) and **5** (0.022 mg, 0.06 mmol) in toluene (1 mL) was heated at 80 °C for 1.5 h under a N_2 atmosphere. After cooling to room temperature, petroleum ether was added. The mixture was filtered and the resulting solid was washed with petroleum ether. The product was dried under vacuum to give **6** as a light blue solid. Yield: 95%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99-7.97 (m, 4H), 7.61-7.48 (m, 2H), 7.28-7.19 (m, 6H), 7.09 (d, J = 7.2 Hz, 2H), 6.94-6.89 (m, 4H), 6.75-6.69 (m, 4H), 6.41 (d, J = 8.0 Hz, 1H), 6.22 (d, J = 8.0 Hz, 2H), 5.89 (d, J = 10.4 Hz, 2H), 4.38-4.23 (m, 4H), 3.88 (d, J = 7.2 Hz, 1H), 3.65-3.45 (m, 4H), 3.19-
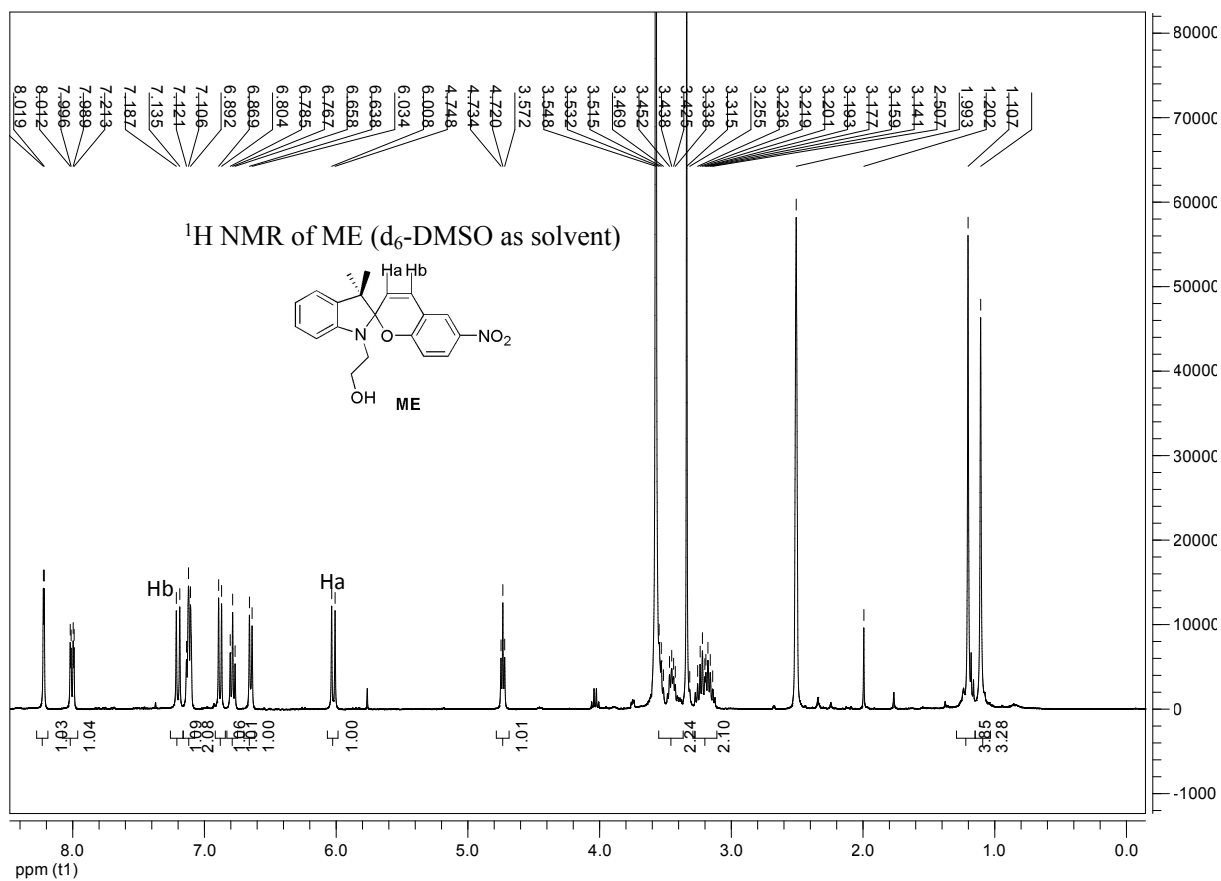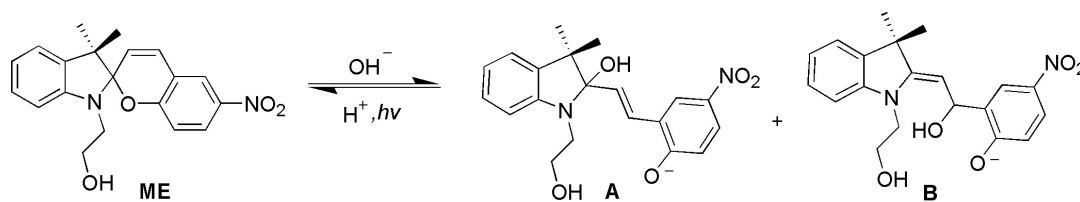
3.13 (m, 4H), 3.03 (d, J = 12.0 Hz, 1H), 2.70 (d, J = 13.6 Hz, 1H), 2.49 (s, 12H), 1.81 (d, J = 12.0 Hz, 1H), 1.28 (s, 6H), 1.17 (s, 6H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ (ppm): 211.4, 166.7, 166.4, 159.4, 146.5, 144.3, 143.5, 141.0, 140.0, 139.8, 137.2, 135.7, 134.5, 131.1, 128.4, 127.8, 125.9, 122.7, 121.8, 121.8, 119.9, 119.1, 118.5, 118.2, 115.6, 114.4, 106.6, 106.4, 72.7, 62.6, 60.5, 52.9, 51.0, 46.0, 42.4, 29.6, 25.8, 19.8, 18.8. Analytical Data. Calcd (found) for C$_{68}$H$_{67}$ClN$_6$O$_{10}$Pd: C, 64.30 (64.66); H, 5.32 (5.87). High-resolution MS analysis (ESI) m/z: [M-Cl]$^+$ calcd 1233.3953, found 1233.3958.
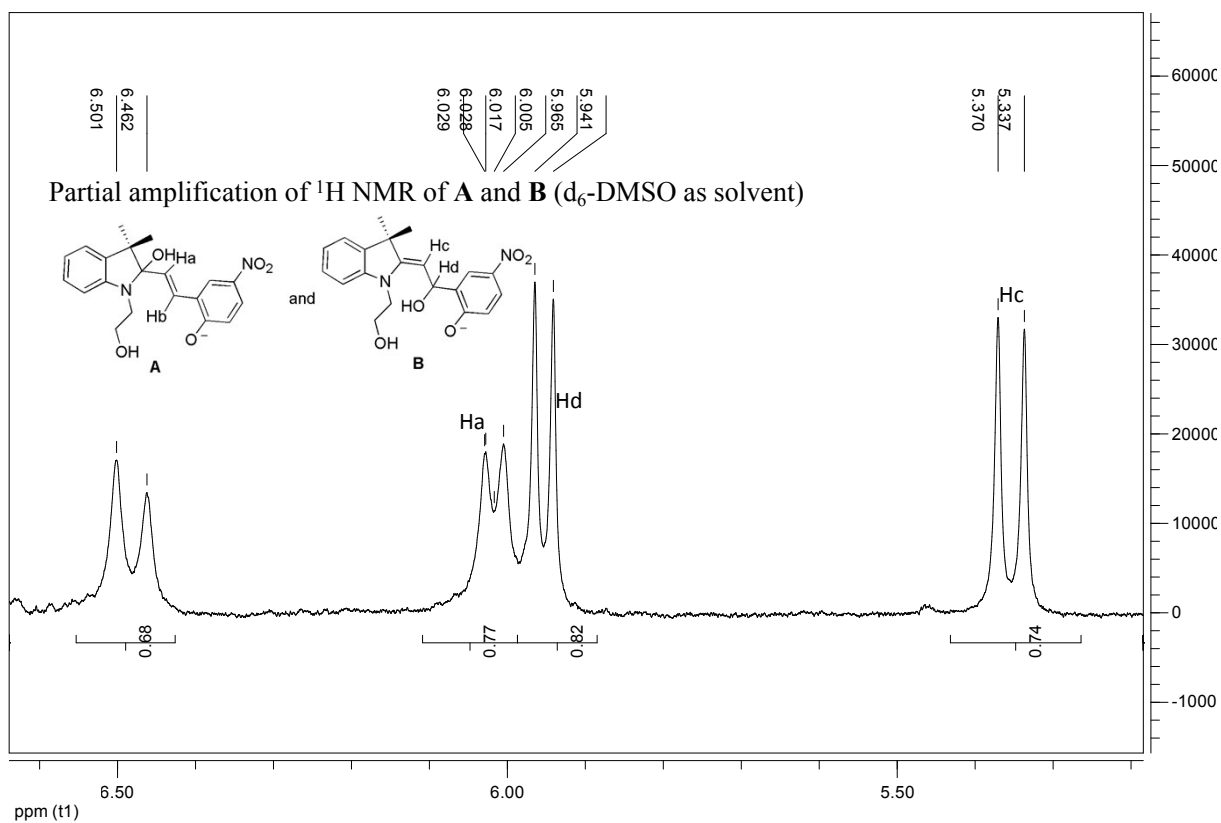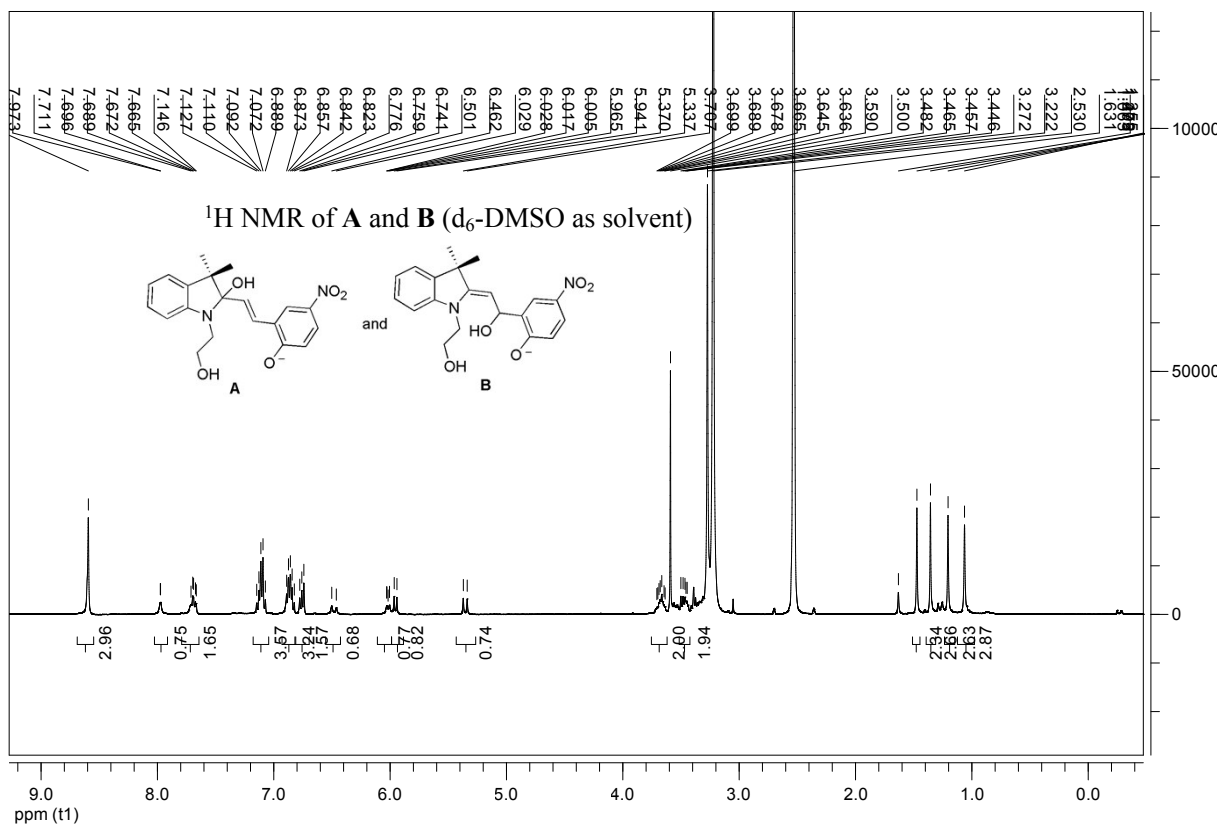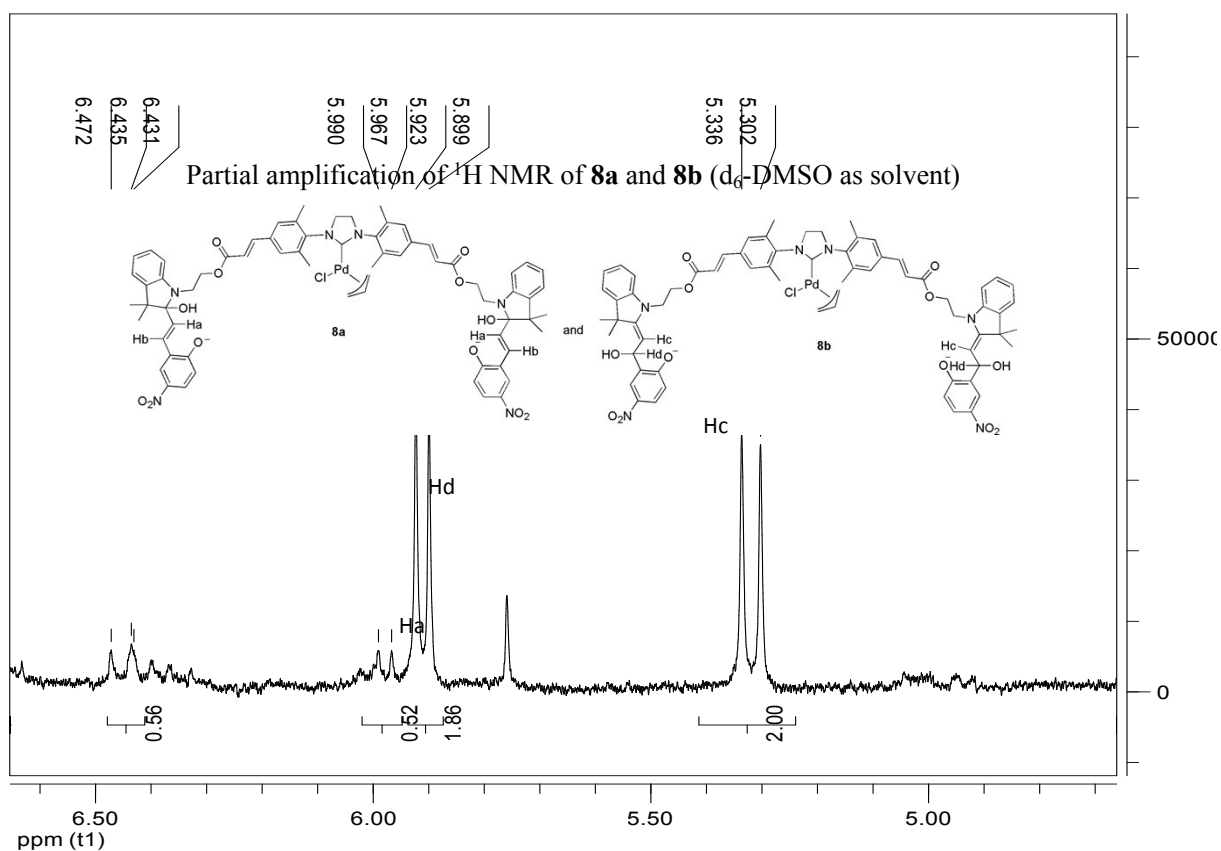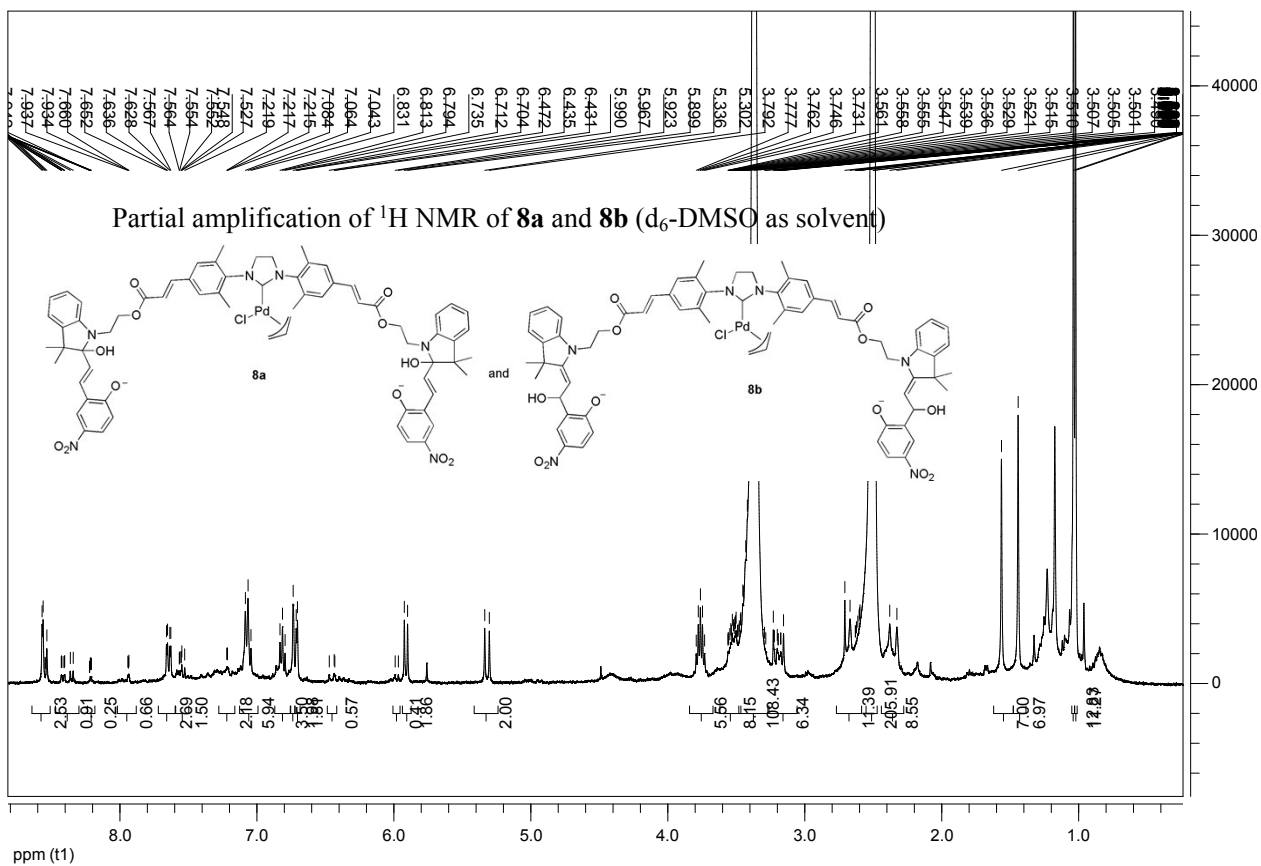
8. *Characterization of Complex 8*
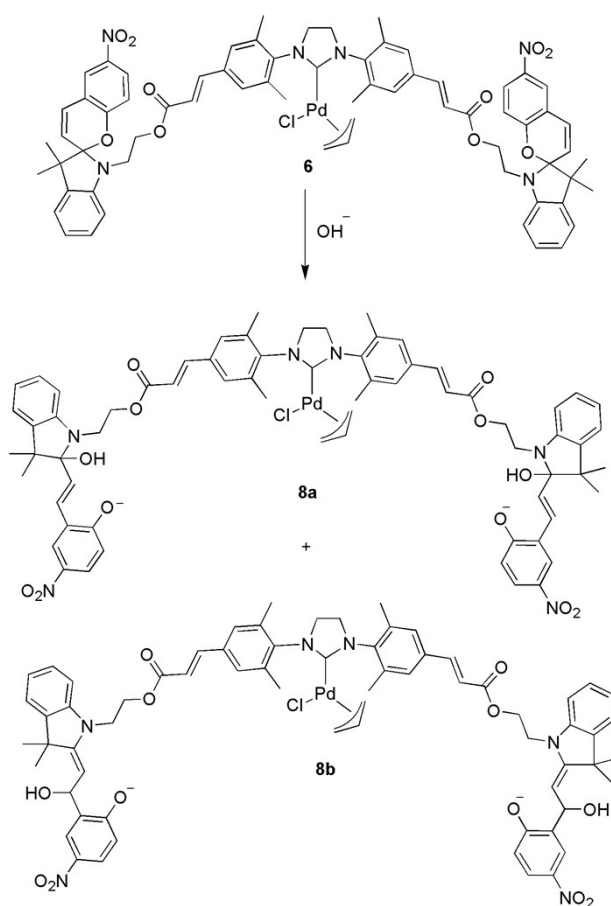
According to Ref (Org. Biomol. Chem. 2013, 11, 6047-6055.), the compound **ME** was converted to compound **A** and **B** in the presence of KOH in *i*-PrOH/H$_2$O. We characterized them by ^{1}H NMR and the spectra are shown as follows. Judging from the spectra (base on the chemistry shift from 6.50 to 5.00 ppm), the products are a mixture and the ratio of **A** and **B** is 1:1. By this way, we also

characterized **8a/8b** by ^{1}H NMR and the products are also a mixture of **8a** and **8b**. The ratio of **8a** and **8b** is 1:4.

^{1}H NMR of ME (d$_6$-DMSO as solvent)

^{1}H NMR of **A** and **B** (d$_6$-DMSO as solvent)

Partial amplification of ^{1}H NMR of **A** and **B** (d$_6$-DMSO as solvent)

Partial amplification of ^{1}H NMR of **8a** and **8b** (d$_6$-DMSO as solvent)

Partial amplification of ^{1}H NMR of **8a** and **8b** (d$_6$-DMSO as solvent)

9. Absorption Spectrum of Complex 6, 7 and 8
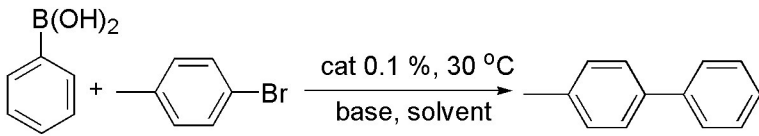
Catalyst **6** (1 x 10^{-3} mmol) was dissolved in 10 mL i-PrOH–H$_2$O (1:1 v/v) (C=1.0 x 10^{-4} M). The

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absorption spectrum of the resulting solution was then measured and the results are shown in Figure 1 (black line). Then, KOH (2 x 10^{-3} mmol) was added and the solution was shaken by hand. The absorption spectrum of the resulting solution is shown in Figure 1 (red line). Then, the pH of the above solution was adjusted to 7.0 with 1 M HCl. The absorption spectrum of that solution is shown in Figure 1 (blue line). The solution was then irradiated with light ($\lambda > 380$ nm) at room temperature for 2 min. The results are shown in Figure 1 (green line).

10. Optimization of the Reaction Conditions

A mixture of phenylboronic acid (0.25 mmol), 4-bromotoluene (0.25 mmol), and base (0.5 mmol) was dissolved in different solvent (1 mL) and heated to 30 °C. Then catalyst **6** (0.1 mol %) was added and the reaction mixture was stirred for 4-12 h. After completion of the reaction, the mixture was extracted three times with n-hexane (3 x 1 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The products were further purified by flash chromatography on a silica gel column. The results are presented in Table S1.

Table S1 Optimizing reaction conditions for the reaction of 4-bromotoluene with phenylboronic acid.[a]

entry	base	solvent	time	yield (%)[b]
1	KOH	i-PrOH/ H$_2$O (1:1)	4h	99
2	KOH	DMF/ H$_2$O (1:1)	12h	0
3	KOH	THF/ H$_2$O (1:1)	12h	0
4	KOH	MeOH/ H$_2$O (1:1)	12h	60
5	KOH	i-PrOH	12h	0
6	KOH	DMF	12h	0
7	KOH	THF	12h	0
8	KOH	toluene	12h	0
9	KOH	H$_2$O	12h	0
10	KOH	MeOH	12h	70
11	K$_2$CO$_3$	i-PrOH/ H$_2$O (1:1)	4h	50

[a] Reactions were carried out using 4-bromotoluene (0.25 mmol, 1 equiv), PhB(OH)$_2$ (0.25 mmol, 1 equiv), solvent (1 mL) and base (1 mmol, 2 equiv) at 30 °C. [b] Isolated yields.

11. Photo of Homogeneous catalyst system for Suzuki-Miyaura coupling reactions of aryl halides with arylboronic acids.
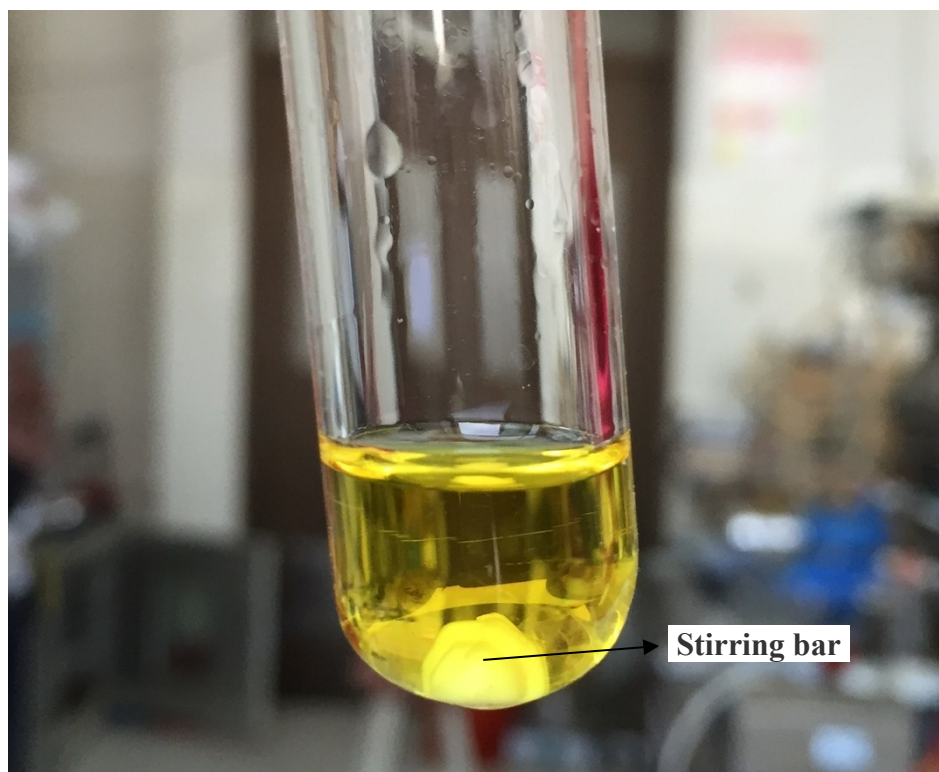
Fig.S1 Homogeneous catalyst system for Suzuki-Miyaura coupling reactions of aryl halides with arylboronic acids.

12. General Procedure for NHC-Pd(II) Catalyzed Suzuki-Miyaura Coupling Reaction of Aryl halides with Arylboronic acids

A mixture of arylboronic acids (0.25 mmol), aryl halides (0.25 mmol), and KOH (0.5 mmol) was dissolved in i-PrOH/H$_2$O (0.5 mL / 0.5 mL) and heated to 30 °C. Then catalyst **6** (0.1 mol %) was added and the reaction mixture was stirred for 4 h. After completion of the reaction, the mixture was extracted three times with n-hexane (3 x 1 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum. The products were further purified by flash chromatography on a silica gel column.

## 13. General Procedure for Recycling the NHC-Pd(II) Catalyst

A mixture of PhB(OH)$_2$ (0.25 mmol), 4-bromotoluene (0.25 mmol), and KOH (0.5 mmol) was dissolved in i-PrOH/H$_2$O (0.5 mL/ 0.5 mL) and heated to 30 °C. Then catalyst **6** (0.5 mol %) was added and the mixture was stirred. After completion of the reaction, the products were separated from the reaction mixture by adding cyclohexane (2 x 1 mL) as the extraction media. Then, the pH of the solution was adjusted to 7.0 with 1 M HCl and extracted with CH$_2$Cl$_2$ (2 x 1 mL). The CH$_2$Cl$_2$

solution was irradiated with visible light (λ > 380 nm). After the color of the purple solution disappeared, the solution was dried over magnesium sulfate, filtered and concentrated by vacuum to give the original catalyst **6**, which was then used in another reaction cycle.
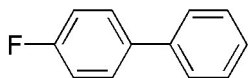
## 14. Characterization Data of the Products in Table 2 and Table 3:
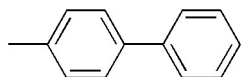
4-Methyl-biphenyl (11a) [3]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.61-7.57 (m, 2H), 7.51-7.41 (m, 4H), 7.37-7.30 (m, 1H), 7.26-7.24 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 141.2, 138.4, 137.0, 129.5, 128.8, 127.3, 127.2, 127.0, 21.1.
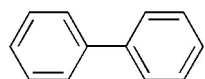

Biphenyl (11b): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.70-7.68 (m, 4H), 7.55-7.51 (m, 4H), 7.45-7.42 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 141.3, 128.8, 127.7, 127.2.
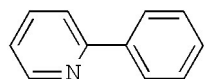

4-Fluoro-biphenyl (11c) [4]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.59 (d, J = 8.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.46-7.41 (m, 3H), 7.34 (t, J = 7.6 Hz, 3H), 7.12 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.4 (d, J = 245.7 Hz, 1C), 140.3, 137.3, 128.8, 128.7, 128.6, 127.2, 127.0, 115.6 (d, J = 21.2 Hz, 1C).
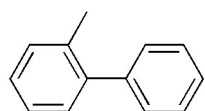
2-Methyl-biphenyl (11d) [5]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.40-7.33 (m, 2H), 7.32-7.26 (m, 3H), 7.25-7.18 (m, 4H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 142.0, 142.0, 135.3, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5.
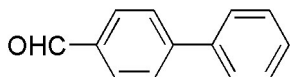

Biphenyl-4-carbaldehyde (11e) [3]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 10.06 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.66-7.63 (m, 2H), 7.51-7.40 (m, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 191.9, 147.1, 139.7, 135.2, 130.2, 129.0, 128.5, 127.6, 127.3.


**2-Phenyl-pyridine (11f)**: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.72-8.71 (m, 1H), 8.01-7.99 (m,

2H), 7.81-7.40 (m, 2H), 7.51-7.42 (m, 3H), 7.28-7.24 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 157.1, 149.4, 139.1, 136.5, 128.7, 128.5, 126.7, 121.8, 120.3.

O$_2$N—⟨benzene⟩—⟨benzene⟩
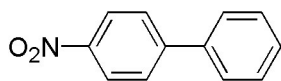
4-Nitro-biphenyl (11g) [4]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.32-8.28 (m, 2H), 7.76-7.72 (m, 2H), 7.64-7.61 (m, 2H), 7.52-7.43 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 147.6, 147.0, 138.7, 129.1, 128.9, 127.8, 127.4, 124.1

H$_3$CO—⟨benzene⟩—⟨benzene⟩—
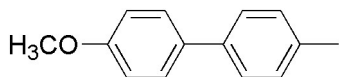
4-Methoxy-4'-methyl-biphenyl (12a) [6]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.51 (d, J = 8.8 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 158.9, 138.0, 136.3, 133.7, 129.4, 127.9, 126.6, 114.2, 55.3, 21.0.

Cl—⟨benzene⟩—⟨benzene⟩—
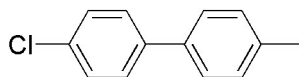
4-Chloro-4'-methyl-biphenyl (12b) [4]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.51-7.49 (m, 2H), 7.47-7.46 (m, 2H), 7.44-7.41 (m, 2H), 7.40-7.37 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 139.6, 137.4, 137.1, 133.0, 129.6, 128.8, 128.1, 126.8, 21.1.

—⟨benzene⟩—⟨benzene⟩—
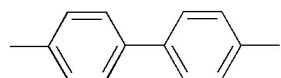
4,4'-Dimethyl-biphenyl (12c) [7]*:* ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.47 (d, *J* = 8.0 Hz, 4H) 7.23 (d, *J* = 8.0 Hz, 4H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 138.4, 136.7, 129.5, 126.9, 21.1.

⟨benzene with methyl⟩—⟨benzene⟩—
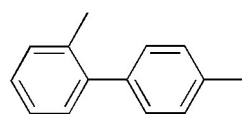
2,4'-Dimethyl-biphenyl (12d) [8]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.30-7.27 (m, 8H), 2.44 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 141.9, 139.1, 136.4, 135.4, 130.3, 129.9, 129.1, 128.8, 127.1, 125.8, 21.2, 20.6.
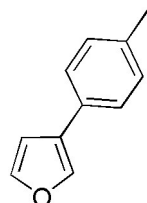
HO—⟨benzene⟩—⟨benzene⟩—
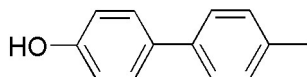
4'-Methyl-biphenyl-4-ol (12e) [9]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.44 (d, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.75 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 154.8, 137.9, 136.4, 134.0, 129.4, 128.1, 126.5, 115.5, 21.0.
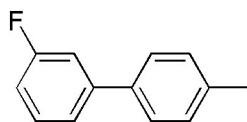
3-Fluoro-4'-methyl-biphenyl (12f) [10]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.49-7.46 (m, 2H), 7.42-7.34 (m, 2H), 7.29-7.25 (m, 3H), 7.09-6.99 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 163.2 (d, J＝243.9 Hz), 143.4 (d, J＝7.8 Hz), 137.7, 137.3, 130.2 (d, J＝8.2 Hz), 129.6, 126.9, 122.7 (d, J＝19.8 Hz), 113.8 (t, J＝5.3 Hz), 113.7 (d, J＝4.7 Hz), 21.0.
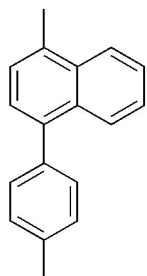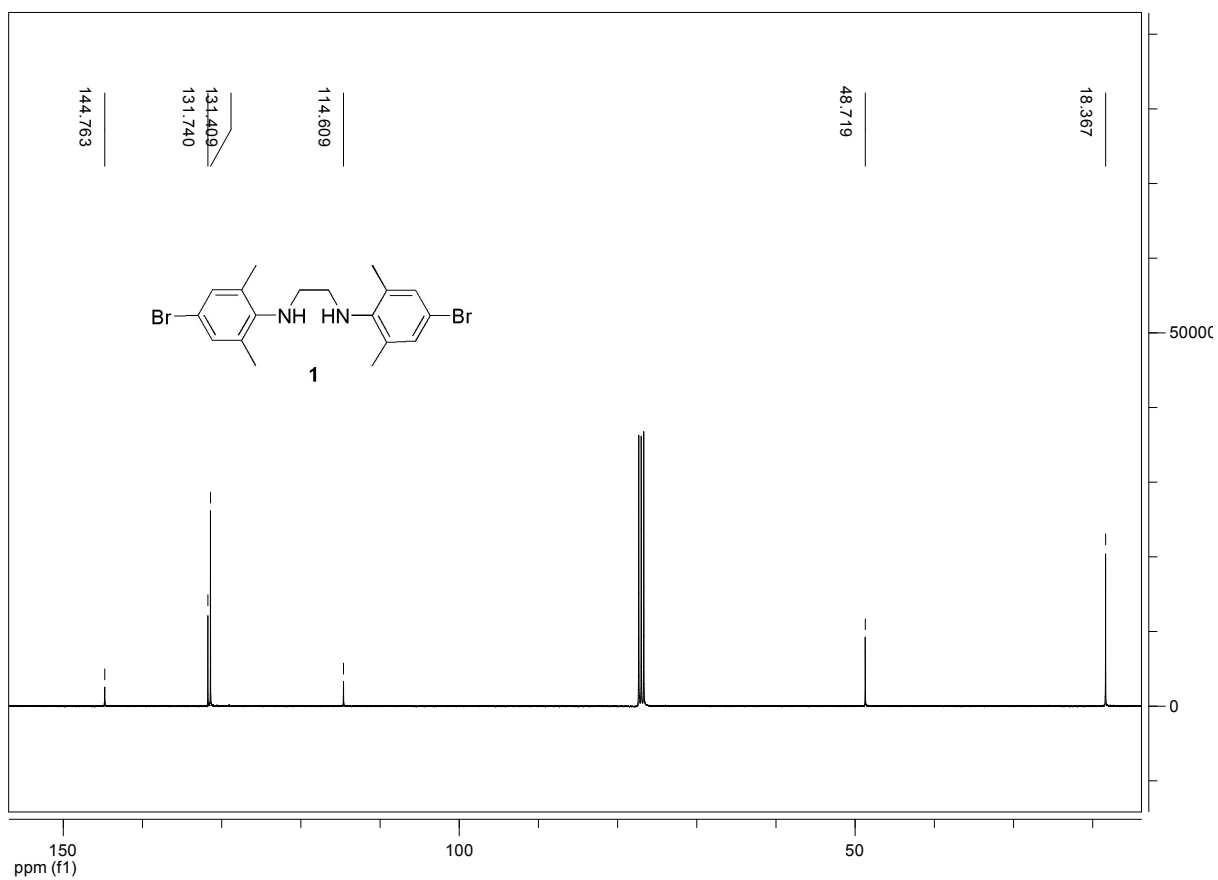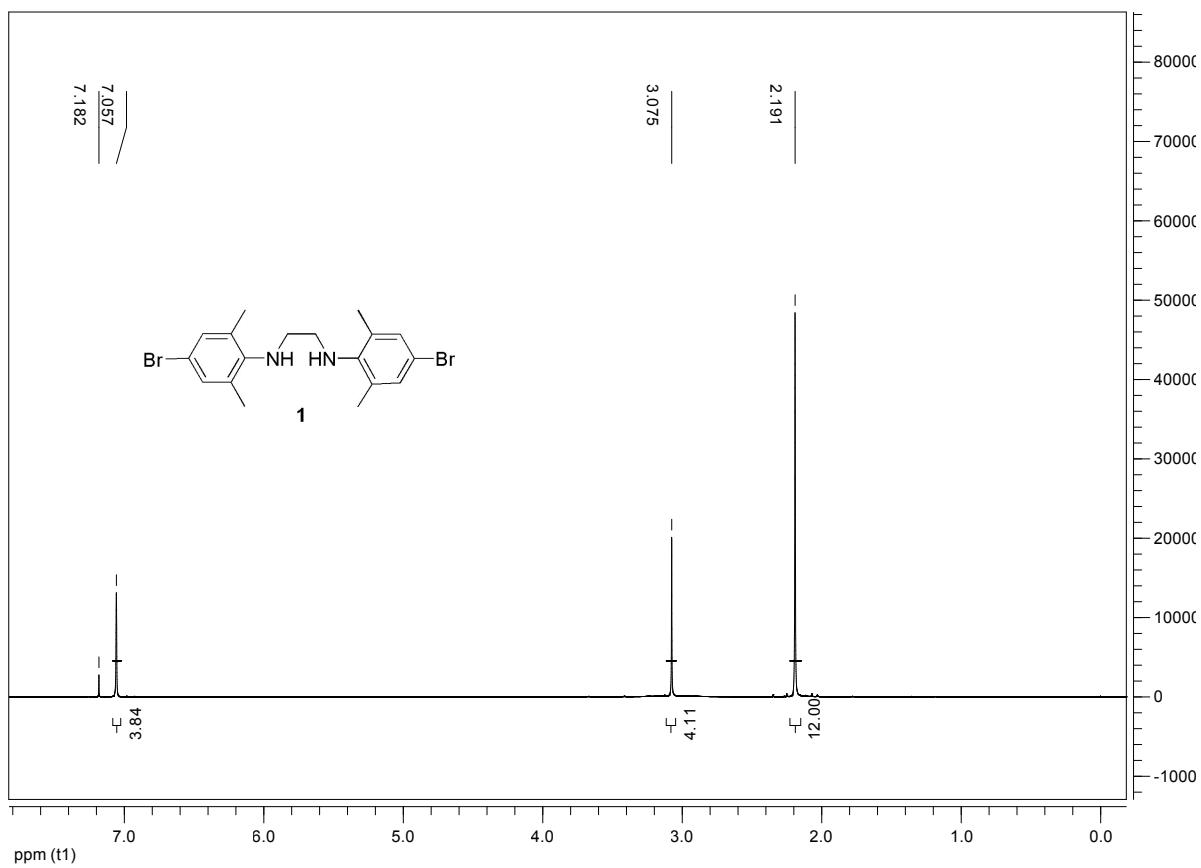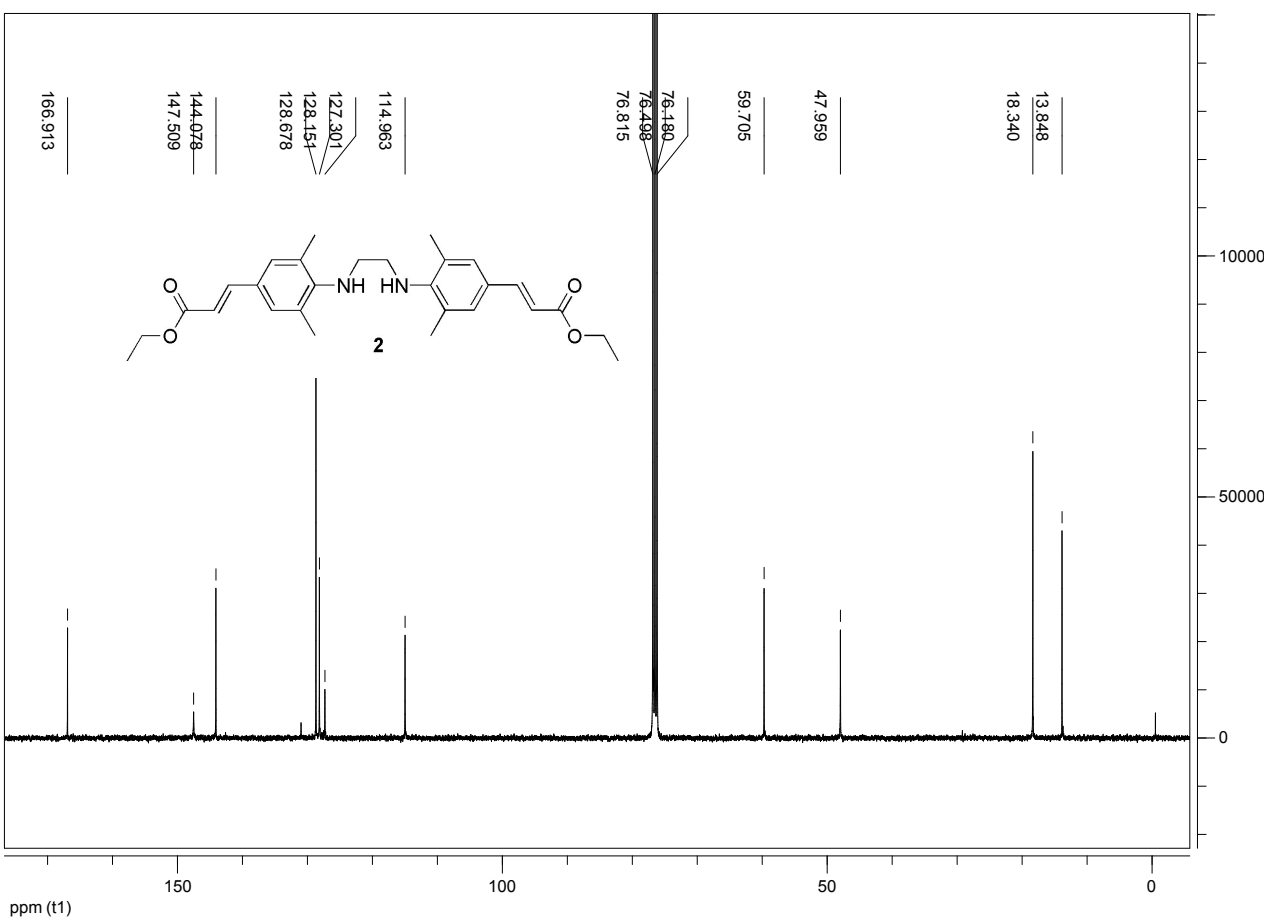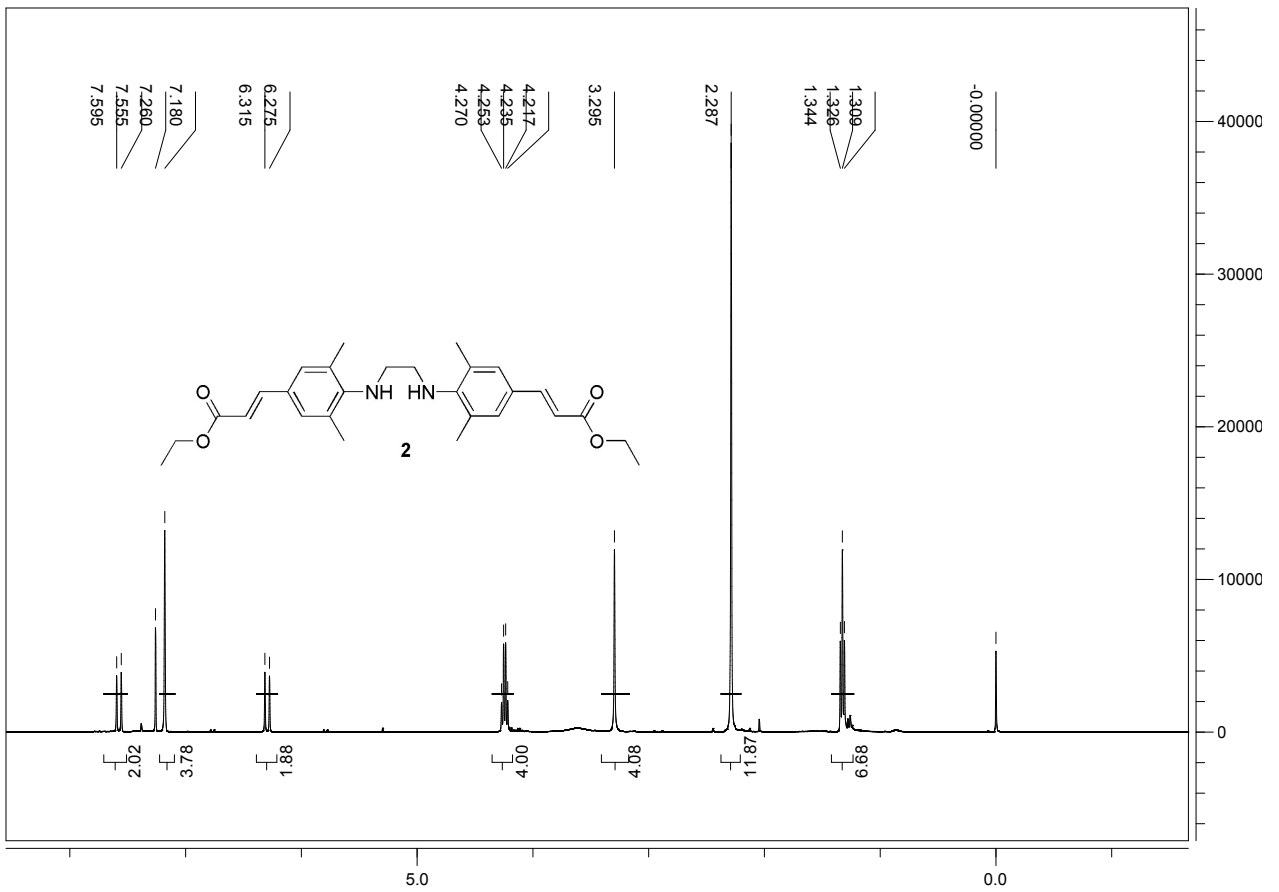

1-Methyl-4-p-tolyl-naphthalene (12g): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.06 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.56-7.52 (m, 1H), 7.45-7.41 (m, 1H), 7.39-7.36 (m, 3H), 7.32-7.29 (m, 3H), 2.75 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 138.6, 138.1, 136.7, 133.5, 132.8, 131.8, 130.0, 128.9, 126.7, 126.5, 126.1, 125.5, 124.3, 21.2, 19.5. Analytical Data. Calcd (found) for C$_{18}$H$_{16}$: C, 93.06 (93.12); H, 6.94 (6.88).
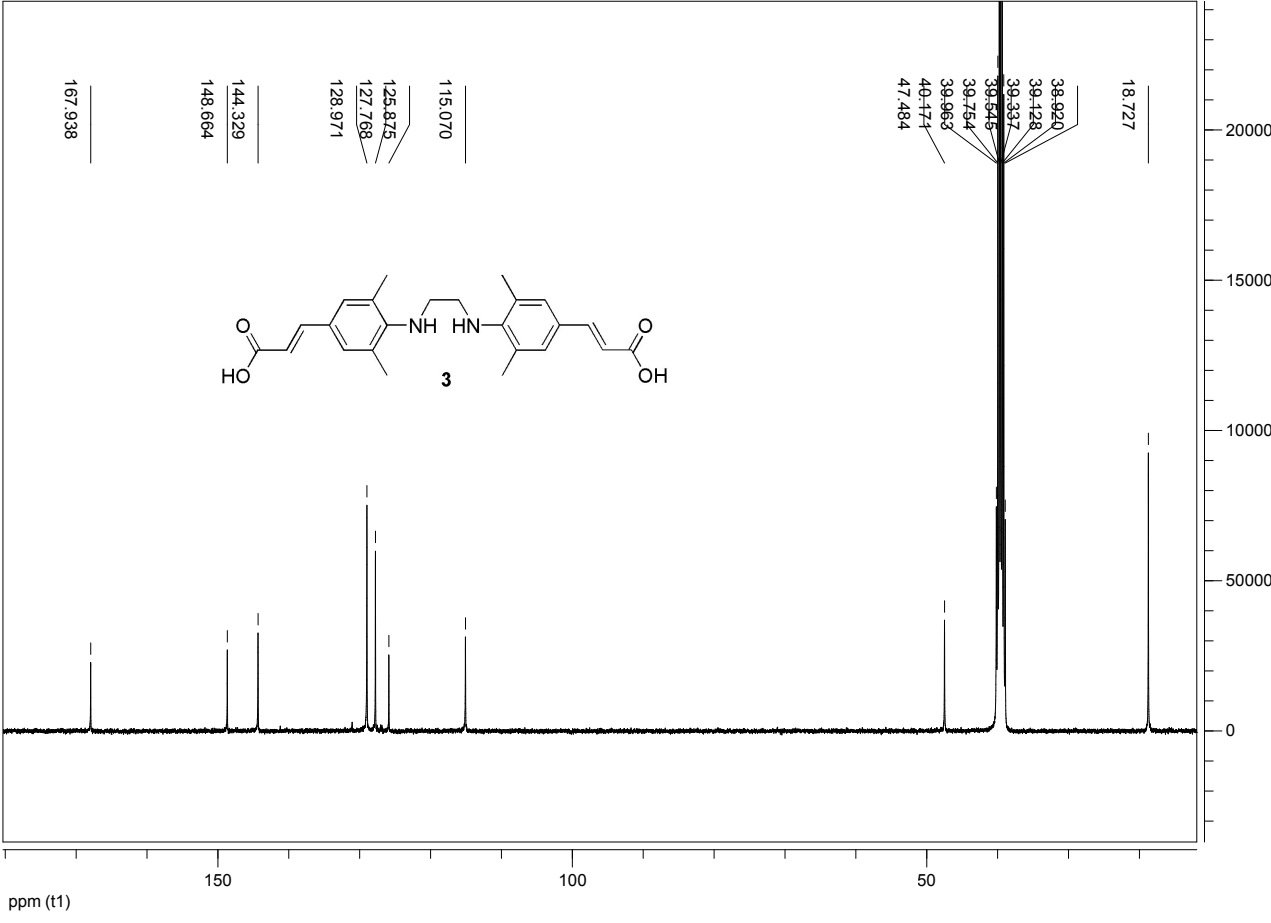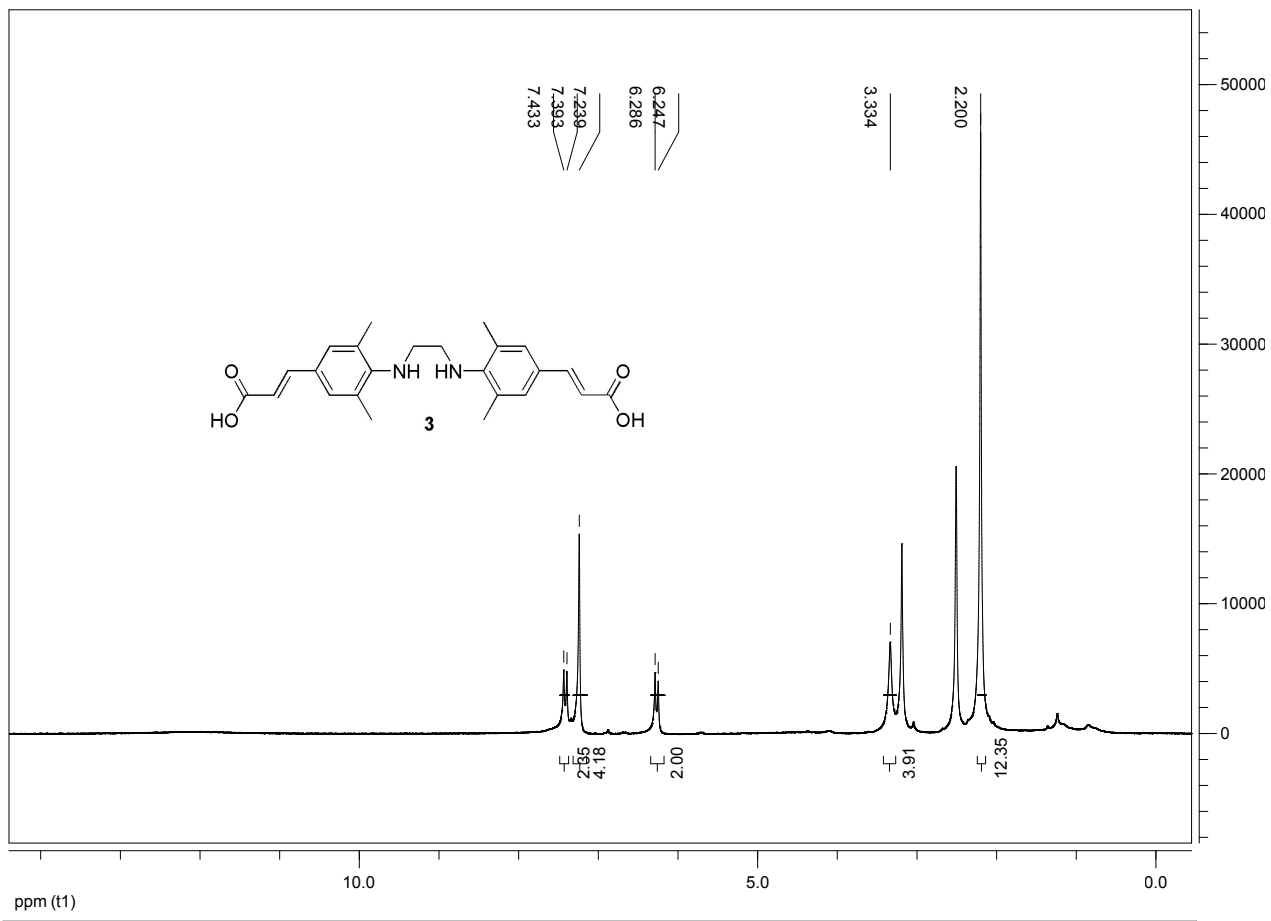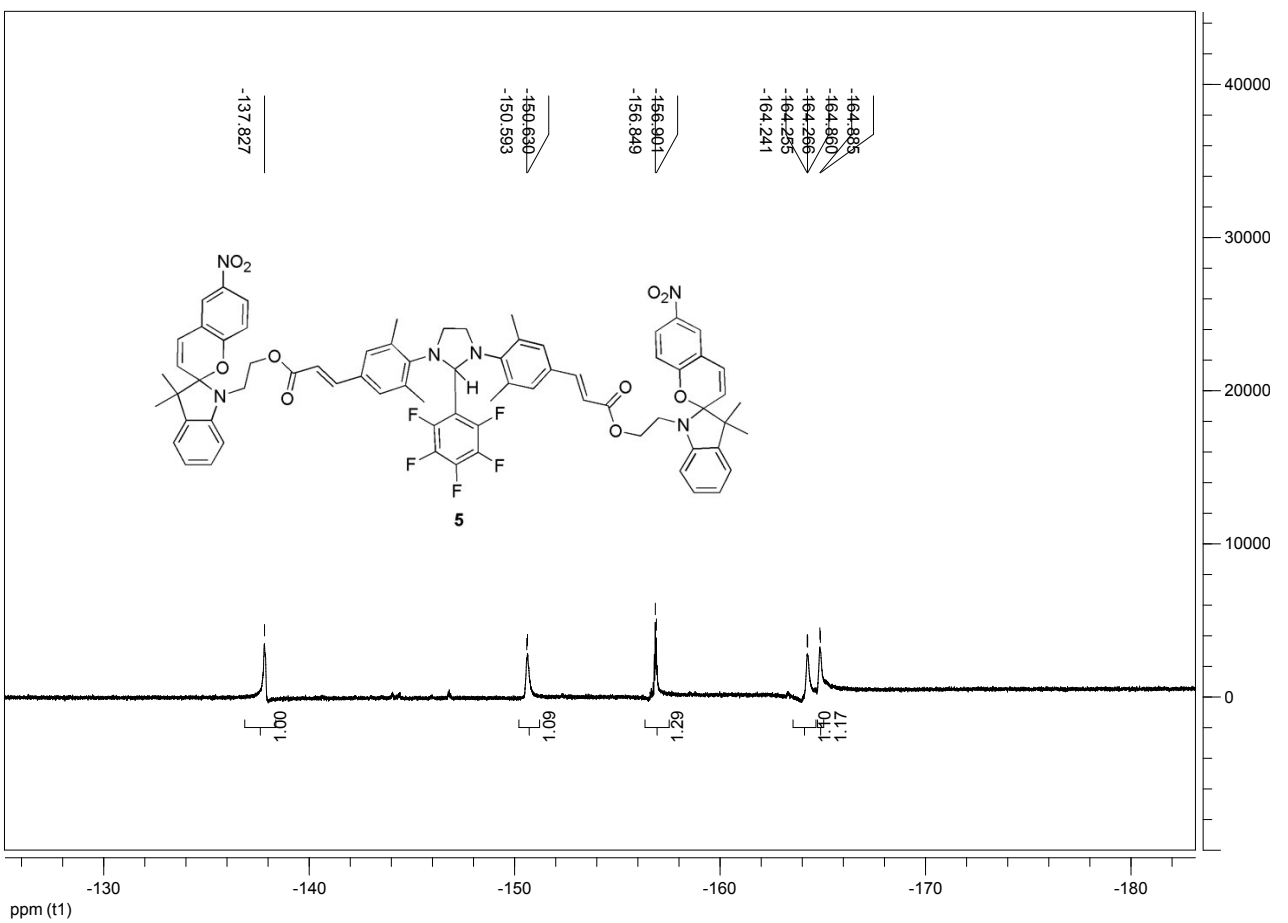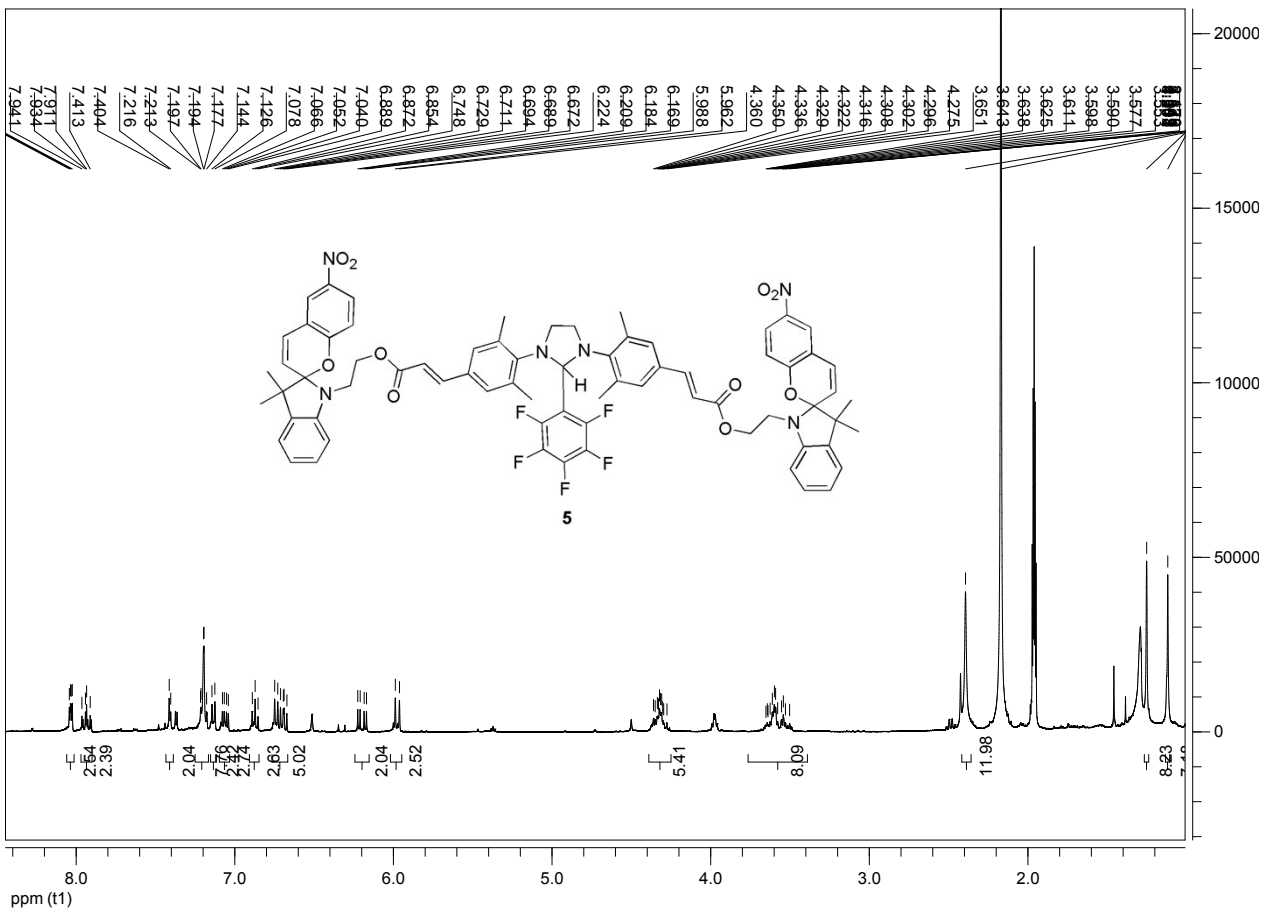

3-p-Tolyl-furan (12h) [11]: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.70 (s, 1H), 7.48-7.46 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.68 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 143.5, 138.1, 136.7, 129.4, 129.4, 126.8, 125.7, 108.8, 21.1.
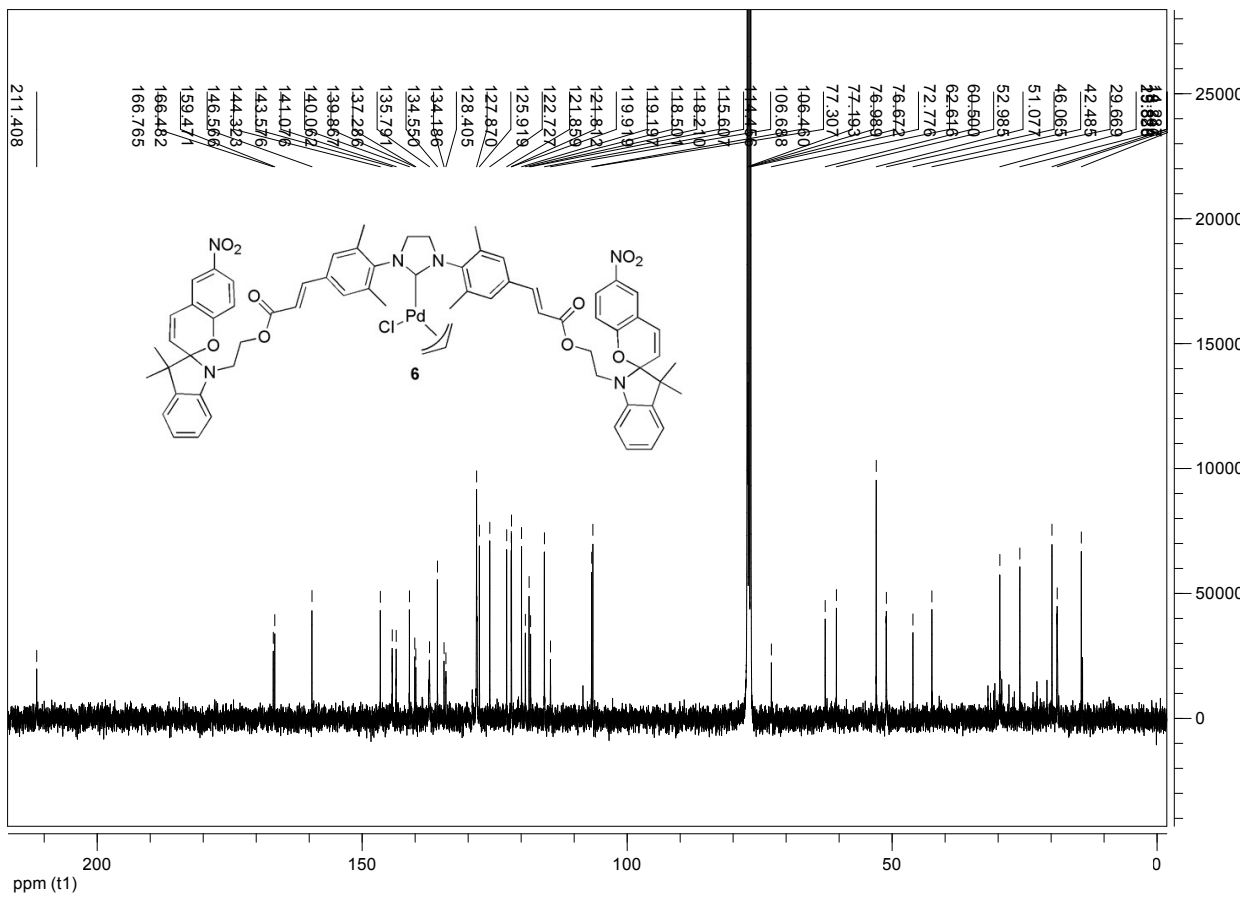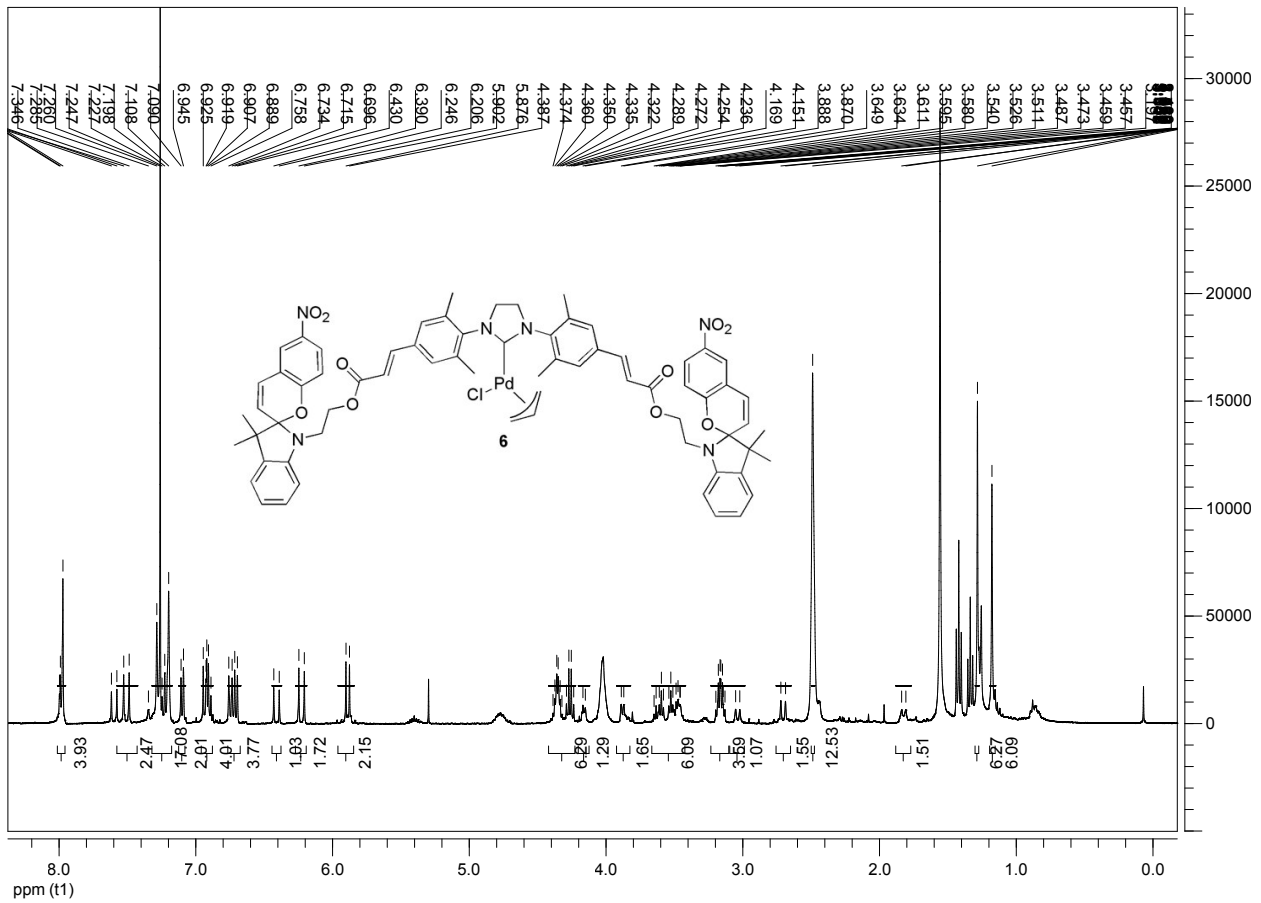
15. NMR Spectra of Compounds

1H NMR spectrum:

7.595, 7.555, 7.260, 7.180, 6.315, 6.275, 4.270, 4.253, 4.235, 4.217, 3.295, 2.287, 1.344, 1.326, 1.309, -0.00000

Integrations: 2.02, 2.0, 3.7, 1.88, 4.00, 4.08, 11.87, 6.9, 6.8

ppm (t1)

13C NMR spectrum:

166.913, 147.509, 144.078, 128.678, 128.154, 127.301, 114.963, 76.815, 76.498, 76.180, 59.705, 47.959, 18.340, 13.848

ppm (t1)

18

Varian ProMALDI
File: S-1268_MALDI.trans

Mode: Positive   Date: 11-JAN-2016
Scans: 1   Time: 15:55:29
                Scale: 10.8846

1087.4617

1085.4511
1071.4678
1059.4348
1057.4890
1043.4381
1027.4450
1101.4793
1111.5000
1127.4936
1146.3685
1163.4990
1175.3682
1192.3615
1195.3644
1198.3691
1204.6850
1217.4041
1233.3952
1235.3962
1237.3980

Mass/Charge

7.614
7.611
7.606
7.592
7.574
7.510
7.489
7.462
7.467
7.448
7.430
7.410
7.371
7.352
7.348
7.345
7.331
7.326
7.311
7.308
7.266
7.260
7.246

2.402

11a

2.52
4.42
1.54
2.80

3.00

9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0

ppm (t1)

11b

13C NMR peaks: 141.349, 128.864, 127.724, 127.273, 77.467, 77.148, 76.826

1H NMR peaks: 7.595, 7.588, 7.582, 7.573, 7.560, 7.569, 7.491, 7.473, 7.454, 7.402, 7.384, 7.365, 7.260, 7.184, 7.162, 7.140

11c

Integrations: 3.93, 1.97, 1.00, 2.04

11d

13C NMR peaks:
142.037, 142.006, 135.389, 130.358, 129.854, 129.250, 128.117, 127.302, 126.813, 125.816

76.770, 77.088, 77.405

20.517

1H NMR peaks:
10.063

7.970, 7.949, 7.770, 7.749, 7.656, 7.652, 7.638, 7.635, 7.632, 7.510, 7.507, 7.489, 7.485, 7.474, 7.470, 7.444, 7.441, 7.438, 7.429, 7.423, 7.417, 7.408, 7.405

OHC— (biphenyl-4-carbaldehyde structure)

11e

Integration: 1.00, 2.03, 2.07, 3.14

ppm (t1)

11f

11g

200 150 100 50 0
ppm (t1)

157.185
149.420
139.156
136.532
128.757
128.645
126.709
121.890
120.329
77.318
77.000
76.682

8.0 7.0 6.0 5.0 4.0 3.0 2.0
ppm (t1)

8.304
8.288
7.764
7.760
7.754
7.749
7.737
7.732
7.726
7.644
7.640
7.635
7.626
7.622
7.620
7.614
7.527
7.523
7.518
7.505
7.501
7.490
7.487
7.472
7.468
7.467
7.465
7.457
7.450
7.432
7.260

2.00
2.06
2.04
3.15

29

13C NMR peaks: 147.634, 147.098, 138.774, 129.179, 128.944, 127.808, 127.401, 124.116, 77.386, 77.069, 76.751

1H NMR peaks: 7.525, 7.509, 7.503, 7.463, 7.443, 7.260, 7.240, 7.220, 6.981, 6.976, 6.959, 3.851, 2.388

H3CO—[biphenyl]—CH3

12a

¹³C NMR

158.992
138.017
136.37
133.791
129.485
127.990
126.623
114.212
77.398
77.080
76.762
55.359
21.090

40000
30000
20000
10000
0

ppm (t1)

200   150   100   50   0

¹H NMR

7.506
7.495
7.490
7.486
7.473
7.468
7.462
7.441
7.418
7.413
7.402
7.397
7.376
7.260
7.240
2.395

25000
20000
15000
10000
50000
0

Cl—⟨ ⟩—⟨ ⟩—CH₃

12b

2.11
2.03
6.38
3.00

ppm (t1)

7.0   6.0   5.0   4.0   3.0

13C NMR spectrum peaks: 139.614, 137.443, 137.123, 133.044, 129.602, 128.854, 128.190, 126.819, 77.340, 77.022, 76.705, 21.102

1H NMR spectrum peaks: 7.487, 7.466, 7.260, 7.245, 7.225, 2.388

12c

3.89, 13.80, 6.00

13C NMR spectrum peaks: 138.411, 136.769, 129.555, 126.919, 77.476, 77.159, 76.844, 21.187

ppm (t1)

1H NMR spectrum peaks: 7.305, 7.296, 7.290, 7.286, 7.279, 7.270, 7.260, 2.315, 2.442

12d

ppm (t1)

13C NMR spectrum peaks: 141.984, 139.145, 136.440, 135.467, 130.376, 129.949, 129.172, 128.870, 127.162, 125.842, 77.446, 77.129, 76.811, 21.261, 20.604

ppm (t1): 200, 150, 100, 50, 0

1H NMR spectrum peaks: 7.473, 7.471, 7.449, 7.428, 7.260, 7.236, 7.217, 6.904, 6.883, 4.759, 2.383

12e

HO—(aryl)—(aryl)—CH3

Integrations: 4.93, 3.09, 1.96, 0.74, 3.00

ppm (t1): 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0, 0.0

34

12f

13C NMR peaks (ppm):

164.512, 162.073, 143.558, 143.480, 137.768, 137.307, 130.247, 130.165, 129.670, 126.985, 122.804, 122.606, 113.939, 113.886, 113.722, 113.675, 77.429, 77.112, 76.794, 21.164

ppm (t1)

1H NMR peaks (ppm):

7.992, 7.971, 7.872, 7.851, 7.476, 7.472, 7.464, 7.458, 7.451, 7.437, 7.434, 7.373, 7.369, 7.356, 7.352, 7.348, 7.334, 7.331, 7.311, 7.295, 7.290, 7.282, 7.243, 7.226, 7.207, 7.174

2.378, 2.666

12g

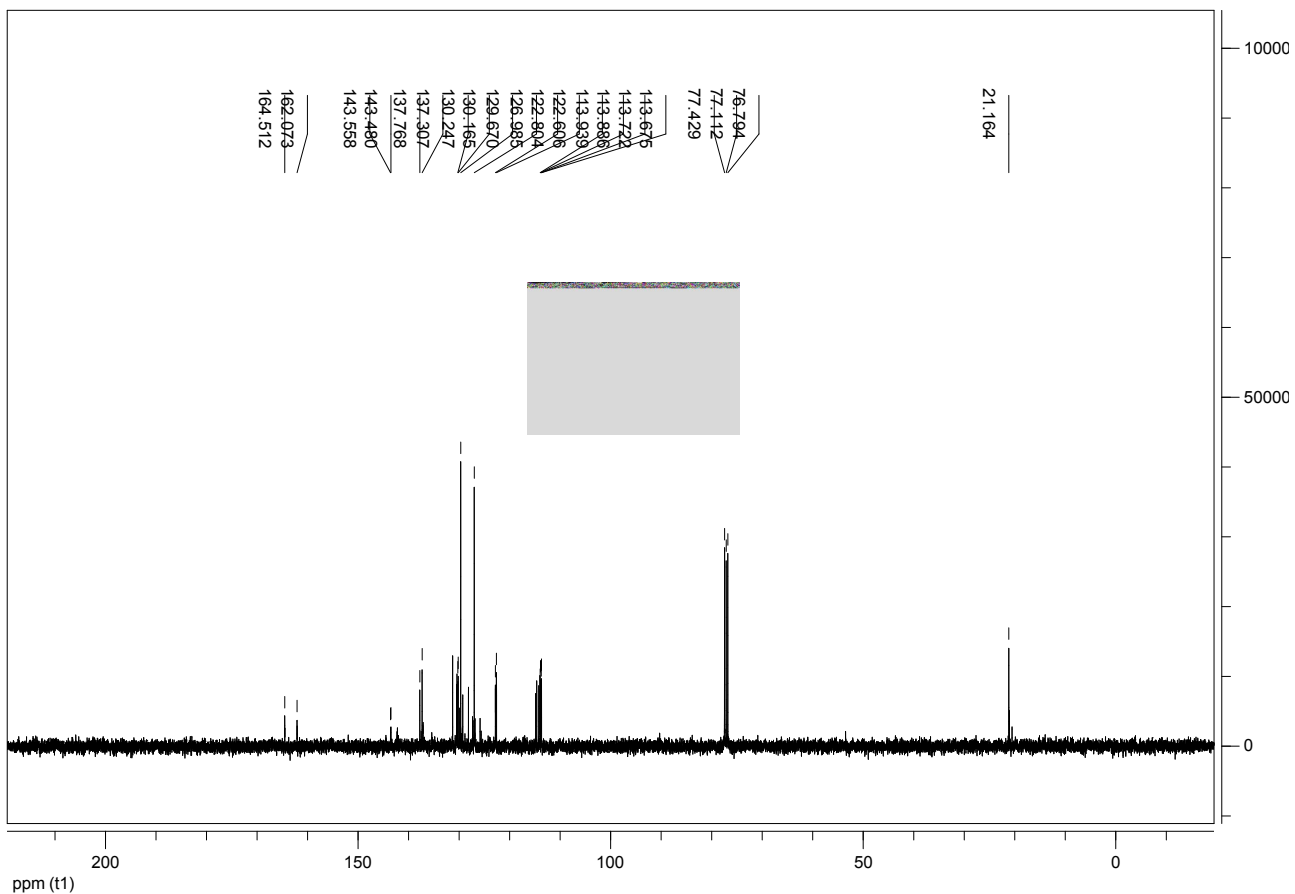Integrations: 1, 2.63, 3.6 (aromatic region), 1, 2.87, 3.00
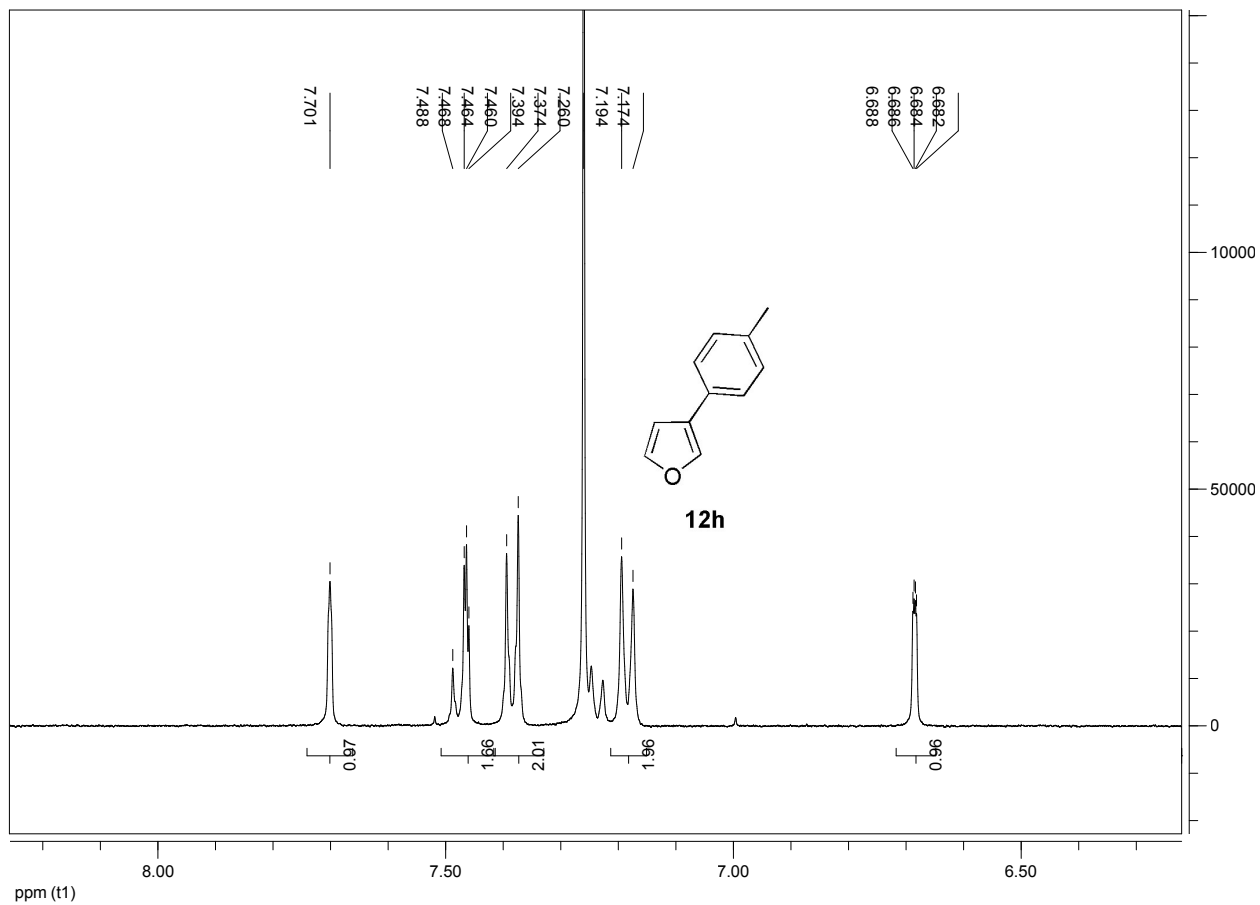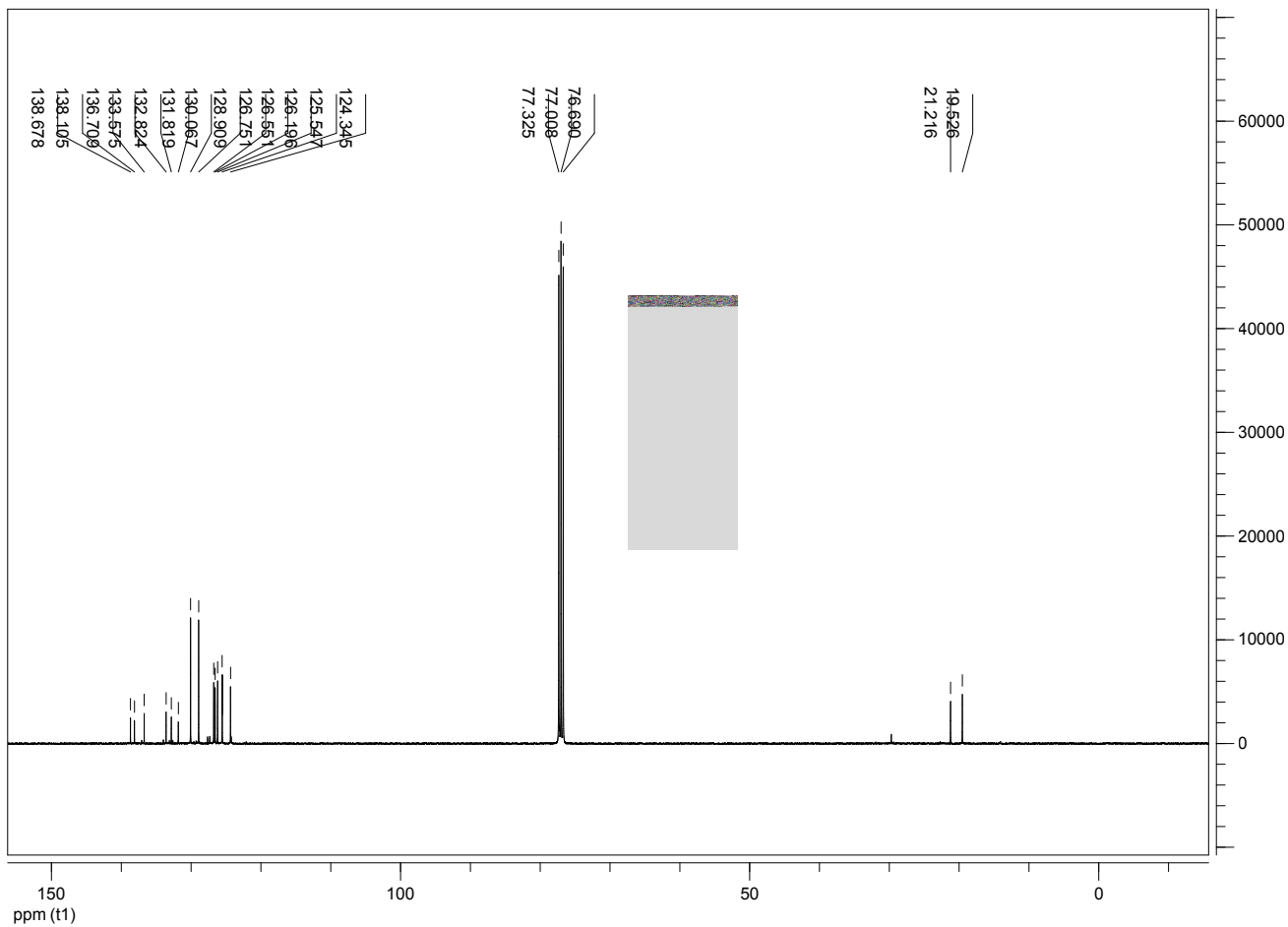
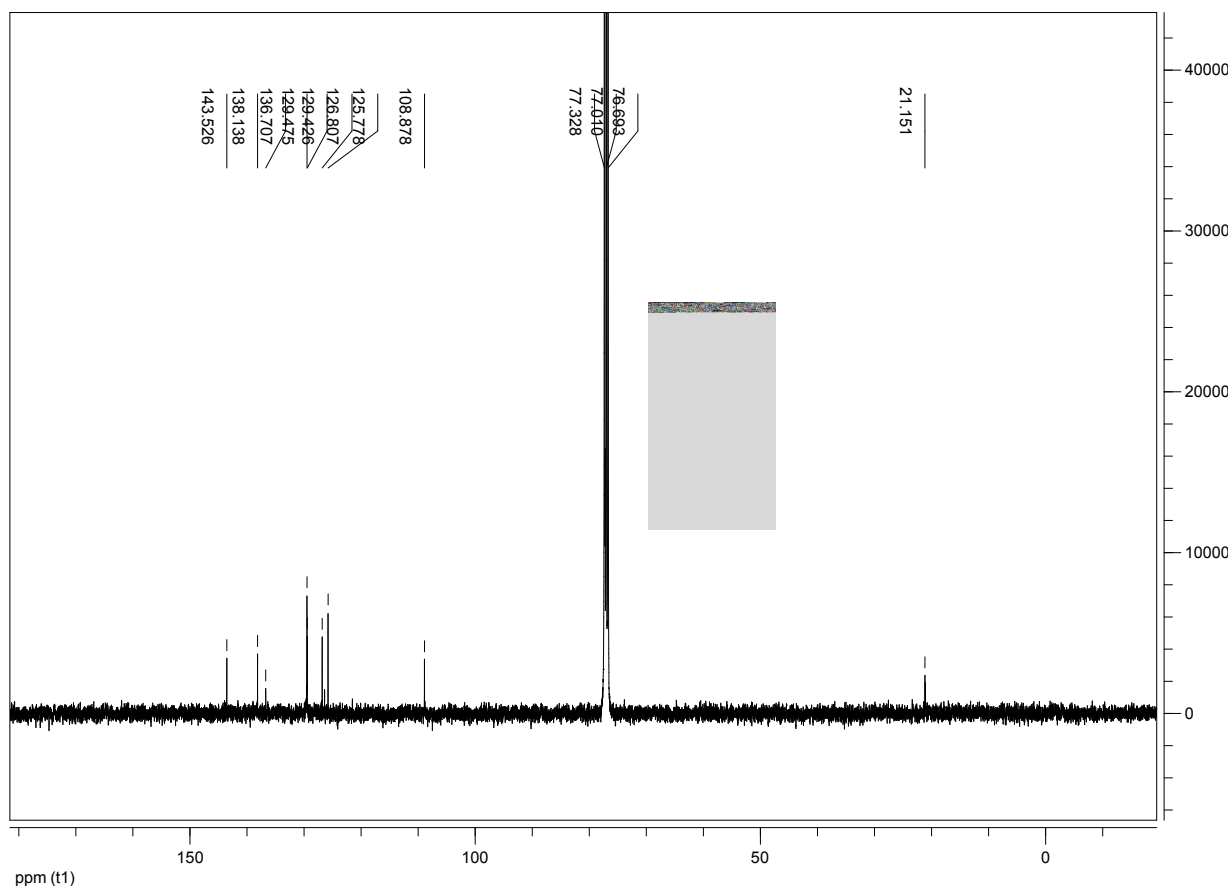ppm (t1)

10.0   5.0   0.0

12h

References

1. Y. Zhang, Z. Yuan and R. J. Puddephatt, *Chem. Mater.* 1998, **10**, 2293.

2. F. M. Raymo, S. Giordani, A. J. P. White and D. J. Williams, *J. Org. Chem.* 2003, **68**, 4158.

3. R. Mamidala, V. Mukundam, K. Dhanunjayarao and K. Venkatasubbaiah, *Dalton Trans.* 2015, **44**, 5805.

4. W. J. Zhou, K. H. Wang and J. X. Wang, *J. Org. Chem*. 2009, **74**, 5599.

5. I. Hoffmann, B. Blumenröder, S. Onodi neé. Thumann, S. Dommer and J. Schatz, *Green Chem.* 2015, **17**, 3844.

6. B. Mu, J. Li, Z. Han and Y. Wu, *Journal of Organometallic Chemistry.* 2012, **700**, 117.

7. A. R. Kapdi, G. Dhangar, J. L. Serrano, J. A. De Haro, P. Lozanod and Ian J. S. Fairlamb, *RSC Adv.* 2014, **4**, 55305.

8. L. R. Moore, E. C. Western, R. Craciun, J. M. Spruell, D. A. Dixon, K. P. O'Halloran and K. H. Shaughnessy, *Organometallics.* 2008, **27**, 576.

9. G. A. Edwards, M. A. Trafford, A. E. Hamilton, A. M. Buxton, M. C. Bardeaux and J. M. Chalker, *J. Org. Chem.* 2014, **79**, 2094.

10. K. Cheng, C. Wang, Y. Ding, Q. Song, C. Qi and X. M. Zhang, *J. Org. Chem.* 2011, **76**, 9261.

11. P. Nanayakkara and H. Alper, *Adv. Synth. Catal*, 2006, **348**, 545.