

## Electronic Supplementary Information

### A New Homogeneous Polymer Support Based on Syndiotactic Polystyrene and Its Application in Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions

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#### Materials and Characterization

1,4-Dibromobenzene, *n*-butyllithium (1.6 M in hexane), chlorodiphenylphosphine, chloro-1,5-cyclooctadiene iridium(I) dimer ([IrCl(COD)]<sub>2</sub>), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (*dtbpy*), Pd(OAc)<sub>2</sub>, 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos), tetraethylammonium hydroxide (NEt<sub>4</sub>OH, 35 wt% solution in water), 4-bromobenzene, 4-bromoacetophenone, 4-bromobenzotrifluoride, 4-bromobenzaldehyde, 4-bromotoluene, 4-bromobenzyl alcohol, 4-bromoanisole, 4-bromo-*N,N*-dimethylaniline, 4-chlorotoluene, 4-chloroacetophenone, 4-chlorobenzene, 4-chlorobenzaldehyde, phenylboronic acid, cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>), methanol, chloroform were purchased from commercial vendors (Aldrich Chemical Co., Alfa Aesar, Acros Organics, and Strem) and used without

further purification. Bis(pinacolato)diboron [ $B_2(\text{pin})_2$ ] was obtained from Frontier Scientific Co. and used after recrystallization from hexane. Anhydrous THF and toluene were obtained from EMD Chemicals (EM Recycler<sup>®</sup> Container System) and collected from the containers using a positive pressure of nitrogen. Cyclooctane was dried using sodium and benzophenone, distilled under reduced pressure, and stored in a nitrogen-filled glovebox. Syndiotactic polystyrene (sPS) was obtained from LG Chem Ltd., Daejeon, South Korea. Pinacolboronic ester-functionalized syndiotactic polystyrene [sPS-B(pin)] was synthesized according to literature method.<sup>1</sup>

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Varian NMR spectrometer (400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ ) at room temperature, and chemical shifts were referenced to tetramethylsilane (TMS).  $^{31}\text{P}$  NMR spectra were obtained using a 161.82 MHz Varian NMR spectrometer at room temperature. Chemical shifts of  $^{31}\text{P}$  NMR spectra were referenced to 85%  $\text{H}_3\text{PO}_4$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR samples were prepared at a concentration of 10 and 20 mg/mL, respectively. Polymer NMR samples were prepared by applying gentle heat to dissolve polymers in  $\text{CDCl}_3$ . GC-MS analysis was conducted using a Shimadzu QP2010S equipped with a 30 m x 0.25 mm SHR-XLB GC column and an EI ionization MS detector. The amount of palladium leached to product solution in each recycling cycle was measured by inductively coupled plasma atomic emission (ICP-AES) analysis using a Thermo Scientific iCAP 6500 Duo.

## **Product characterization data**

### **Biphenyl from Aryl Bromide (Table 2, entry 2)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 84%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.59 (d, 4H,  $J$  = 7.4 Hz), 7.44 (t, 4H,  $J$  = 7.5 Hz), 7.34 (t, 2H,  $J$  = 7.3 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 141.5, 129.0, 127.5, 127.4. Spectra agree with those reported in literature.<sup>2</sup>

#### 4-Acetylbiphenyl from Aryl Bromide (Table 2, entry 4)

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 84%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 8.04 (d, 2H,  $J$  = 8.0 Hz), 7.69 (d, 2H,  $J$  = 8.0 Hz), 7.63 (d, 2H, 7.2 Hz), 7.48 (t, 2H,  $J$  = 7.4 Hz), 7.42 (t, 1H,  $J$  = 6.8), 2.65 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.7. Spectra agree with those reported in literature.<sup>3</sup>

#### 4-Trifluoromethylbiphenyl from Aryl Bromide (Table 2, entry 6)

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 82%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.69 (s, 4H), 7.61 (m, 2H), 7.48 (m, 2H), 7.41 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 145.0, 140.0, 129.6 (q,  $J_{\text{CF}}$  = 32.2 Hz), 129.2, 128.4, 127.7, 127.5, 126.0 (q,  $J_{\text{CF}}$  = 3.7 Hz), 124.6 (q,  $J_{\text{CF}}$  = 272.3 Hz). Spectra agree with those reported in literature.<sup>4</sup>

#### 4-Formylbiphenyl from Aryl Bromide (Table 2, entry 8)

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 83%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 10.06 (s, 1H), 7.96 (d, 2H,  $J$  = 8.4 Hz), 7.76 (d, 2H,  $J$  = 8.2 Hz), 7.64 (d, 2H,  $J$  = 7.1 Hz), 7.49 (t, 2H,  $J$  = 7.2 Hz), 7.42 (t, 1H,  $J$  = 7.2 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 192.1, 147.4, 140.0, 135.4, 130.5, 129.3, 128.7, 127.9, 127.6. Spectra agree with those reported in literature.<sup>5</sup>

#### 4-Methylbiphenyl from Aryl Bromide (Table 2, entry 10)

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 82%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.58 (d, 2H,  $J$  = 7.2 Hz), 7.50 (d, 2H,  $J$  = 8.2 Hz), 7.43 (t, 2H,  $J$  = 7.4 Hz), 7.33 (t, 1H,  $J$  = 7.6 Hz), 7.25 (d, 2H,  $J$  = 8.2 Hz), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 141.1, 138.6, 137.3, 129.7, 129.0, 127.3, 127.2, 21.4. Spectra agree with those reported in literature.<sup>3</sup>

#### **4-(Hydroxymethyl)biphenyl from Aryl Bromide (Table 2, entry 12)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.59 (d, 4H, *J* = 8.2 Hz), 7.44 (t, 4H, *J* = 7.8 Hz), 7.35 (t, 1H, *J* = 7.2 Hz), 4.73 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ = 140.8, 140.6, 139.9, 128.8, 127.5, 127.3, 127.2, 127.1, 65.1. Spectra agree with those reported in literature.<sup>6</sup>

#### **4-Methoxybiphenyl from Aryl Bromide (Table 2, entry 14)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.54 (t, 4H, *J* = 7.6 Hz), 7.42 (t, 2H, *J* = 7.6 Hz), 7.30 (t, 1H, *J* = 7.2 Hz), 6.98 (d, 2H, *J* = 8.8 Hz), 3.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ = 159.4, 141.1, 134.0, 128.9, 128.4, 127.0, 126.9, 114.4, 55.6. Spectra agree with those reported in literature.<sup>2</sup>

#### **4-(*N,N*-Dimethylamino)biphenyl from Aryl Bromide (Table 2, entry 16)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 11%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.55 (d, 2H, *J* = 7.2 Hz), 7.50 (d, 2H, *J* = 9.2 Hz), 7.38 (t, 2H, *J* = 8.0 Hz), 7.26 (t, 1H, *J* = 7.6 Hz), 6.80 (d, 2H, *J* = 8.8 Hz), 2.99 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ = 150.0, 141.2, 129.3, 128.6, 127.7, 126.3, 126.0, 112.8, 40.6. Spectra agree with those reported in literature.<sup>3</sup>

#### **Biphenyl from Aryl chloride (Table 2, entry 17)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 11%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.59 (d, 4H, *J* = 7.4 Hz), 7.44 (t, 4H, *J* = 7.5 Hz), 7.34 (t, 2H, *J* = 7.3 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ = 141.5, 129.0, 127.5, 127.4. Spectra agree with those reported in literature.<sup>2</sup>

#### **4-Formylbiphenyl from Aryl chloride (Table 2, entry 18)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 28%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 10.06 (s, 1H), 7.96 (d, 2H,  $J$  = 8.4 Hz), 7.76 (d, 2H,  $J$  = 8.2 Hz), 7.64 (d, 2H,  $J$  = 7.1 Hz), 7.49 (t, 2H,  $J$  = 7.2 Hz), 7.42 (t, 1H,  $J$  = 7.2 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 192.1, 147.4, 140.0, 135.4, 130.5, 129.3, 128.7, 127.9, 127.6. Spectra agree with those reported in literature.<sup>5</sup>

#### **4-Acetylbiphenyl from Aryl chloride (Table 2, entry 19)**

The crude product was purified with column chromatography (ethyl acetate:hexane = 2:98). Yield: 17%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 8.04 (d, 2H,  $J$  = 8.0 Hz), 7.69 (d, 2H,  $J$  = 8.0 Hz), 7.63 (d, 2H, 7.2 Hz), 7.48 (t, 2H,  $J$  = 7.4 Hz), 7.42 (t, 1H,  $J$  = 6.8), 2.65 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.7. Spectra agree with those reported in literature.<sup>3</sup>

#### **4-Acetylbiphenyl (Table 3, cycle 1)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 8.04 (d, 2H,  $J$  = 8.6 Hz), 7.69 (d, 2H,  $J$  = 8.4 Hz), 7.63 (d, 2H, 7.4 Hz), 7.48 (t, 2H,  $J$  = 7.2 Hz), 7.42 (t, 1H,  $J$  = 7.2), 2.64 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 198.0, 146.0, 140.1, 136.1, 129.2, 129.1, 128.5, 127.5, 127.4, 26.9. Spectra agree with those reported in literature.<sup>3</sup>

#### **Recycling Experiment of sPS-supported Catalyst Without Addition of Fresh $\text{Cs}_2\text{CO}_3$ (Table S1)**

The same reaction scale and experimental procedure of the above recycling procedure were used until the centrifugation step of methanol solution. The recovered polymer from the centrifugation (~30 mg) was dried, combined with the initially filtered base and polymer-supported palladium catalyst mixture,

and used for the next run without removing the base. Almost identical results of Table 3 were obtained (see Table S1).

**Table S1.** Recovery/Recycling of sPS-TPP-supported Palladium Catalyst in Suzuki-Miyaura Reactions and the Leaching of Palladium<sup>a</sup>

cycle <sup>b</sup>	1st	2nd	3rd	4th	5th
Conversion (%) <sup>c</sup>	99	99	99	99	60
Yield of product (%) <sup>d</sup>	97	98	98	95	— <sup>f</sup>
Leaching of Pd (%) <sup>e</sup>	1.0	0.6	0.7	0.9	0.4

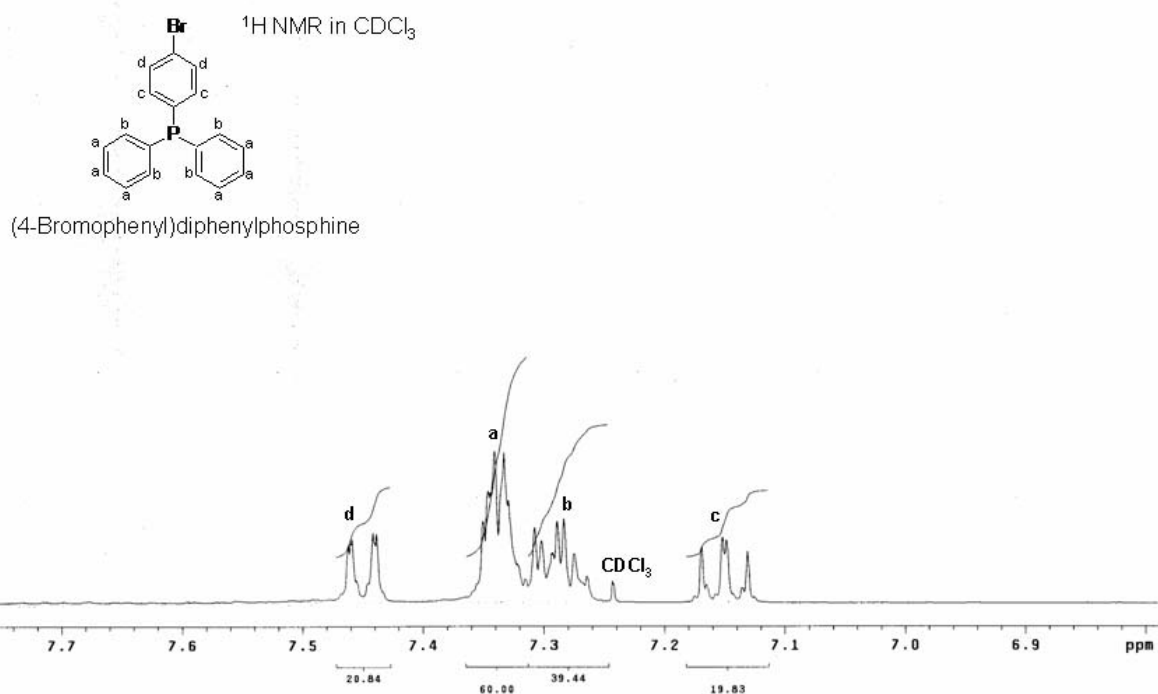
<sup>a</sup> 4-Bromoacetophenone (14.2 mmol), phenylboronic acid (21.3 mmol), sPS-TPP (1 mol%), and Pd(OAc)<sub>2</sub> (1 mol%) at 110 °C for 1 h. <sup>b</sup> No additional Pd(OAc)<sub>2</sub> and Cs<sub>2</sub>CO<sub>3</sub> were added in the recycling experiments. <sup>c</sup> Conversion to coupled product determined using GC-MS. <sup>d</sup> Isolated yield of product. <sup>e</sup> Percentage of Pd leached into the product solution. <sup>f</sup> Not measured.

## References

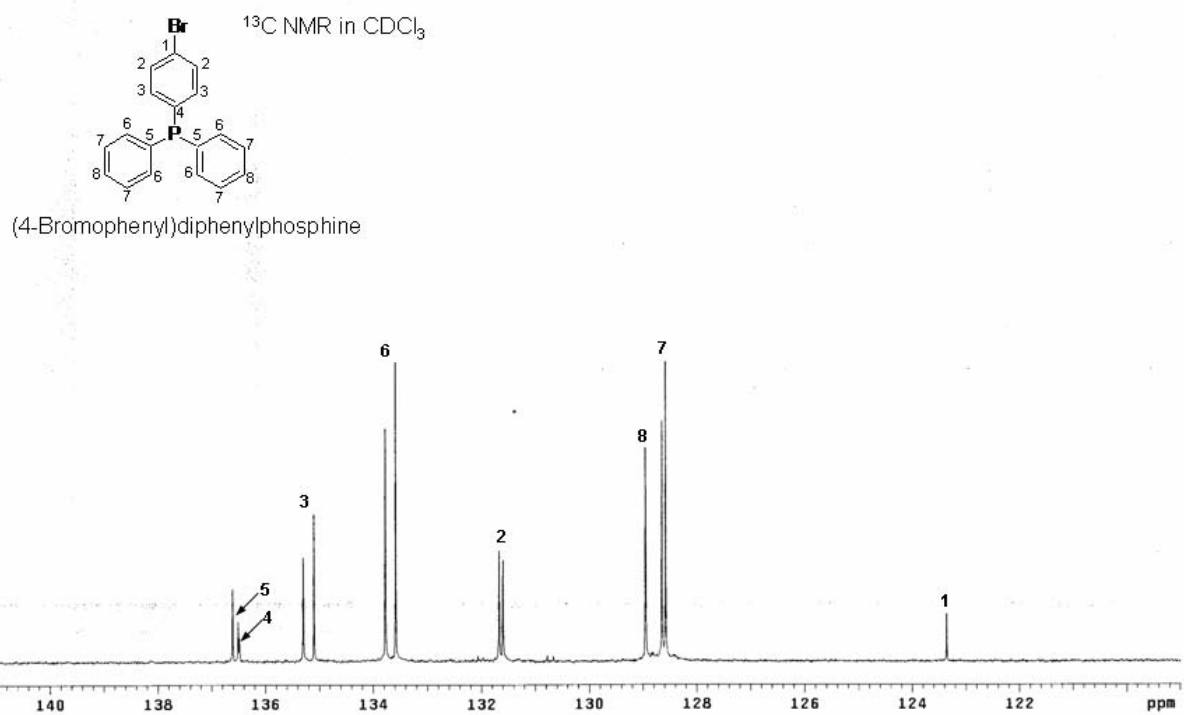
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2. C. Desmarets, R. Omar-Amrani, A. Walcarious, J. Lambert, B. Champagne, Y. Fort, R. Schneider, *Tetrahedron* **2008**, *64*, 372-381.
3. B. Mu, T. Li, W. Xu, G. Zeng, P. Liu, Y. Wu, *Tetrahedron* **2007**, *63*, 11475-11488.
4. L. Zhang, T. Meng, J. Wu, *J. Org. Chem.* **2007**, *72*, 9346-9349.
5. J. Mao, J. Guo, F. Fang, S.-J. Ji, *Tetrahedron*, **2008**, *64*, 3905-3911.

6. B. Tao, D. W. Boykin, *J. Org. Chem.* **2004**, *69*, 4330-4335.

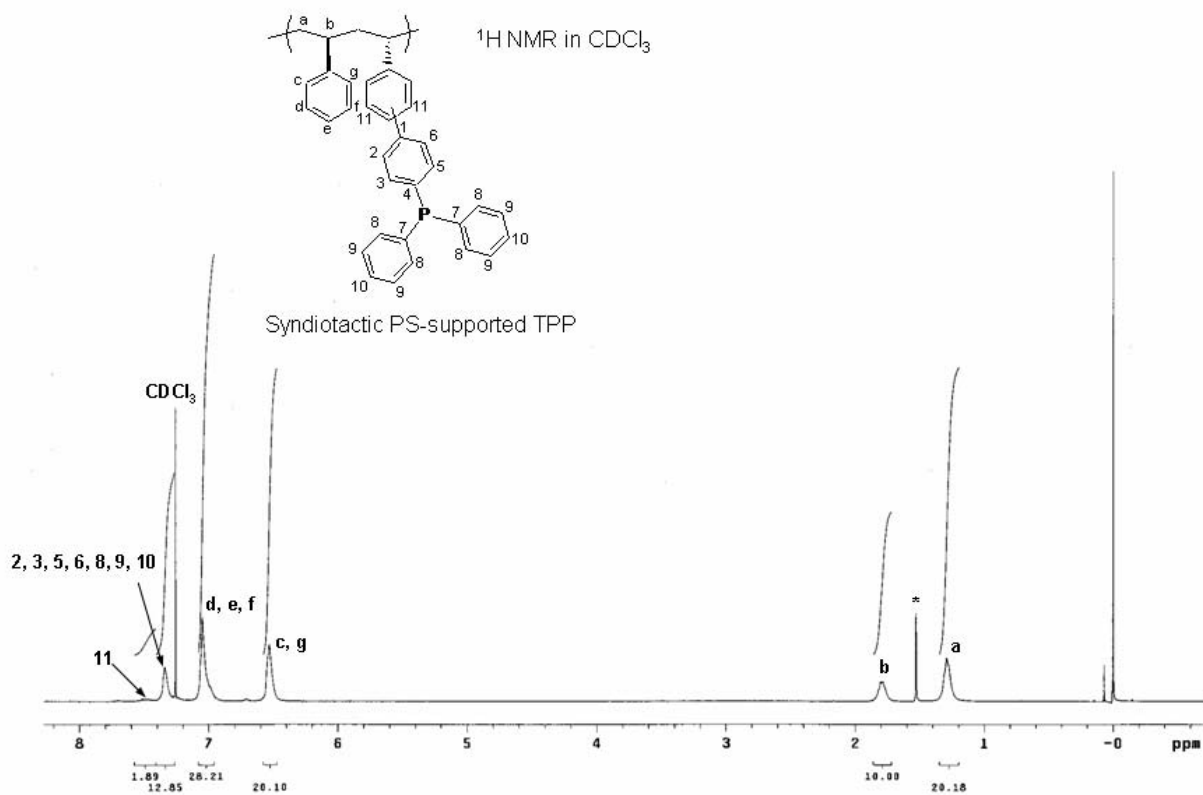
## Supporting Figures



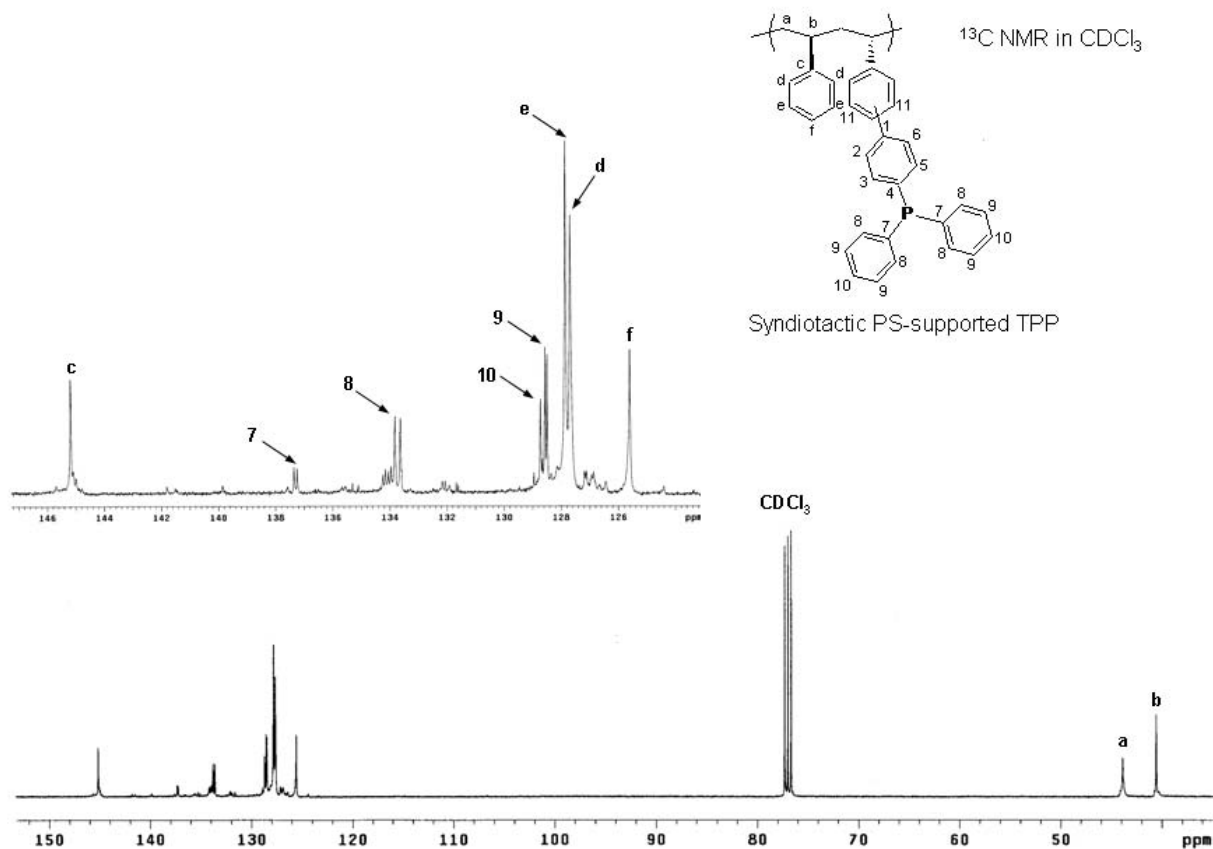
**Figure S1.**  $^1\text{H}$  NMR spectrum [delay time = 1 s, number of scans = 16] of (4-bromophenyl)diphenylphosphine [10 mg/mL  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ ].



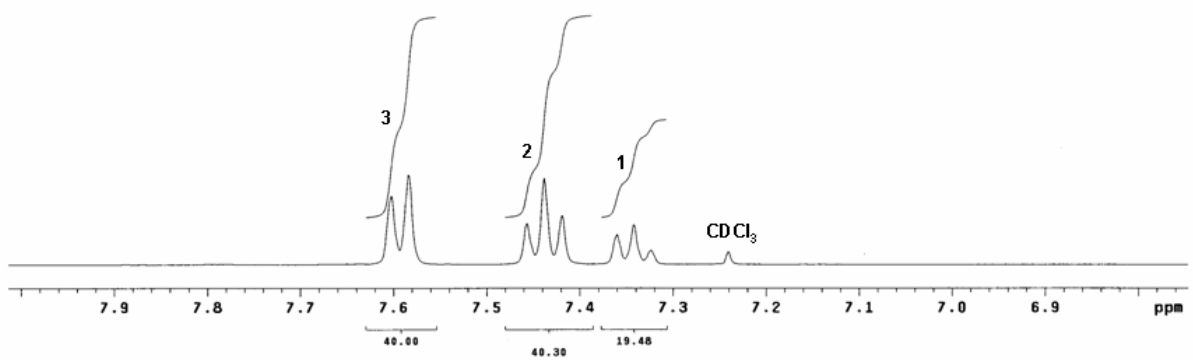
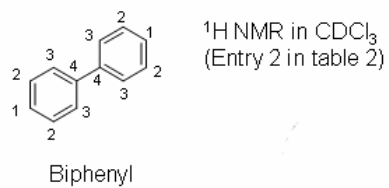
**Figure S2.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of (4-bromophenyl)diphenylphosphine [20 mg/mL CDCl<sub>3</sub> at 25 °C].



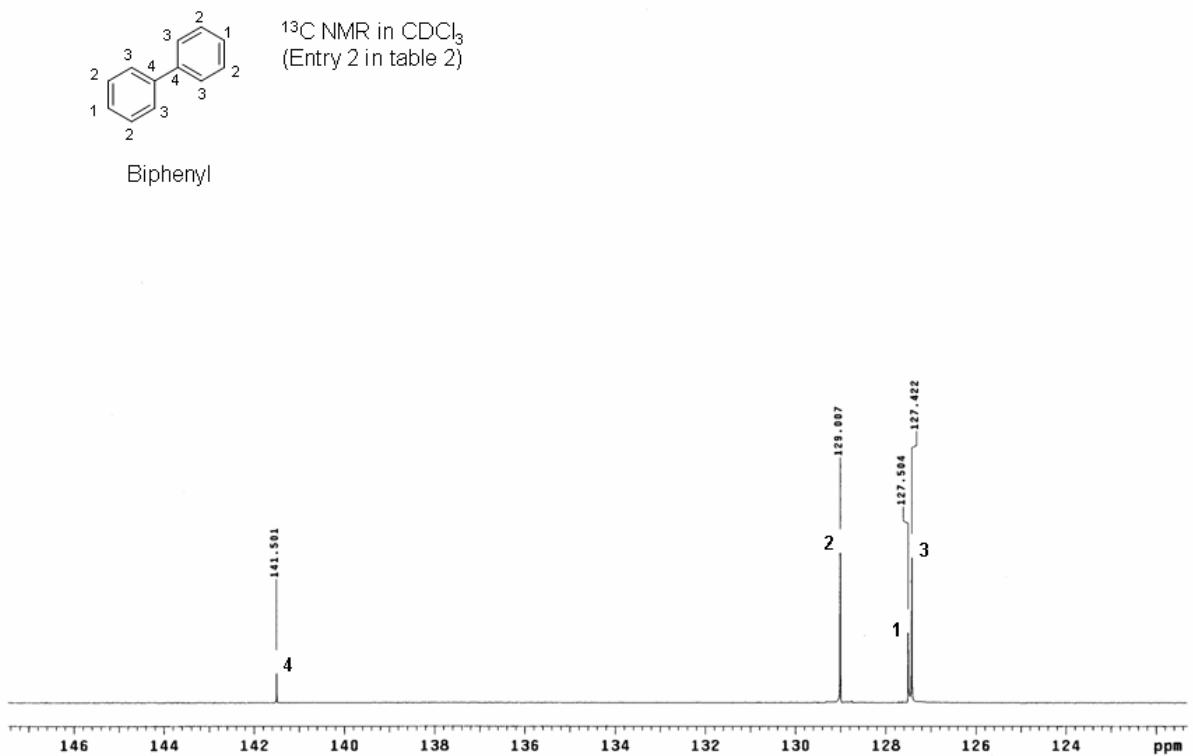
**Figure S3.**  $^1\text{H NMR}$  spectrum [delay time = 1 s, number of scans = 16] of syndiotactic polystyrene-supported triphenylphosphine [10 mg/mL  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ ] (An asterisk indicates  $\text{H}_2\text{O}$  from  $\text{CDCl}_3$ ).



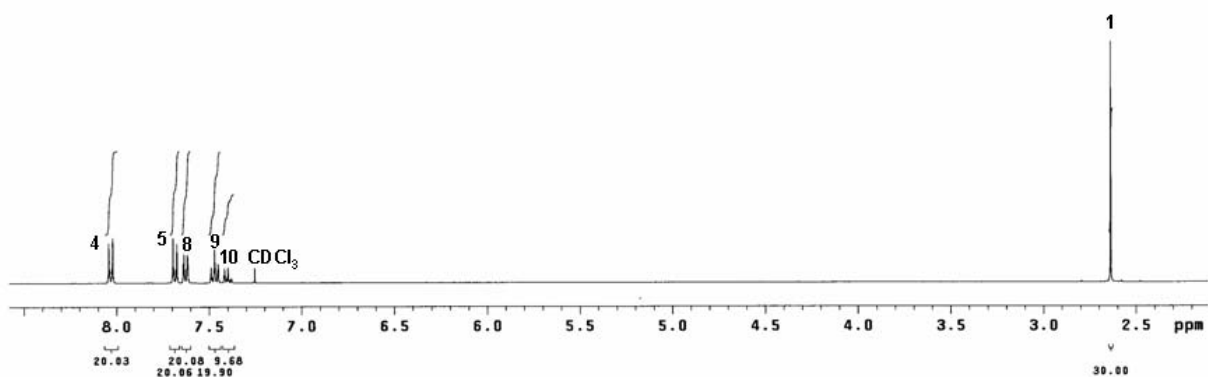
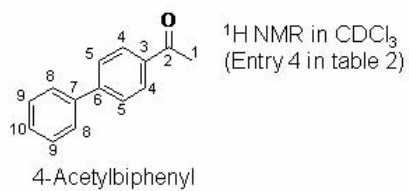
**Figure S4.**  $^{13}\text{C}$  NMR spectrum [delay time = 4 s, number of scans = 9000] of syndiotactic polystyrene-supported triphenylphosphine [20 mg/mL  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ ].



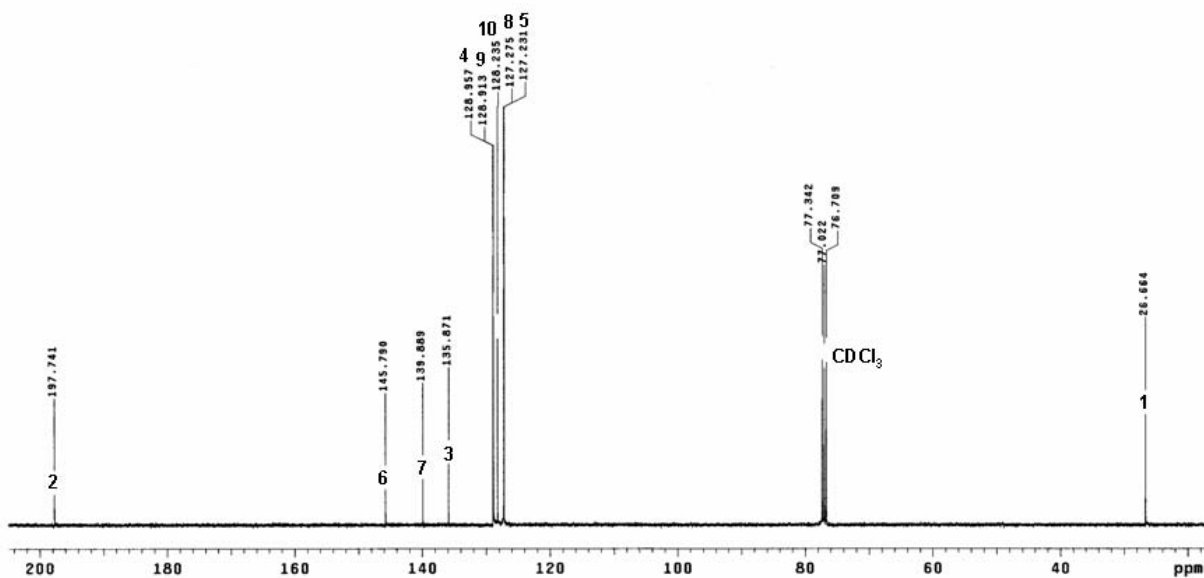
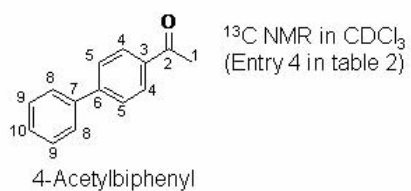
**Figure S5.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of biphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 2 in table 2).



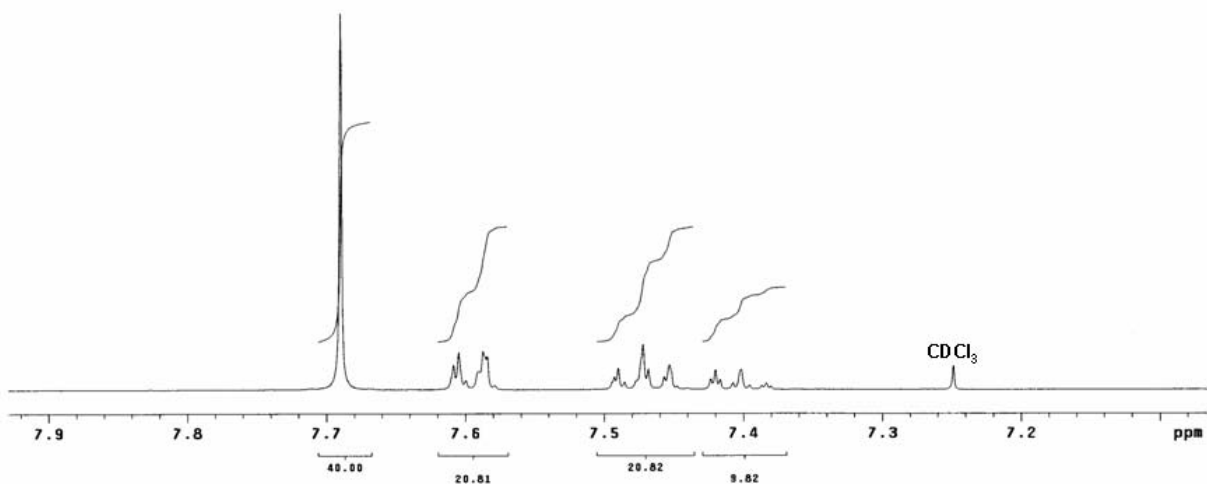
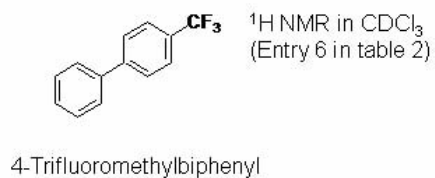
**Figure S6.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of biphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 2 in table 2).



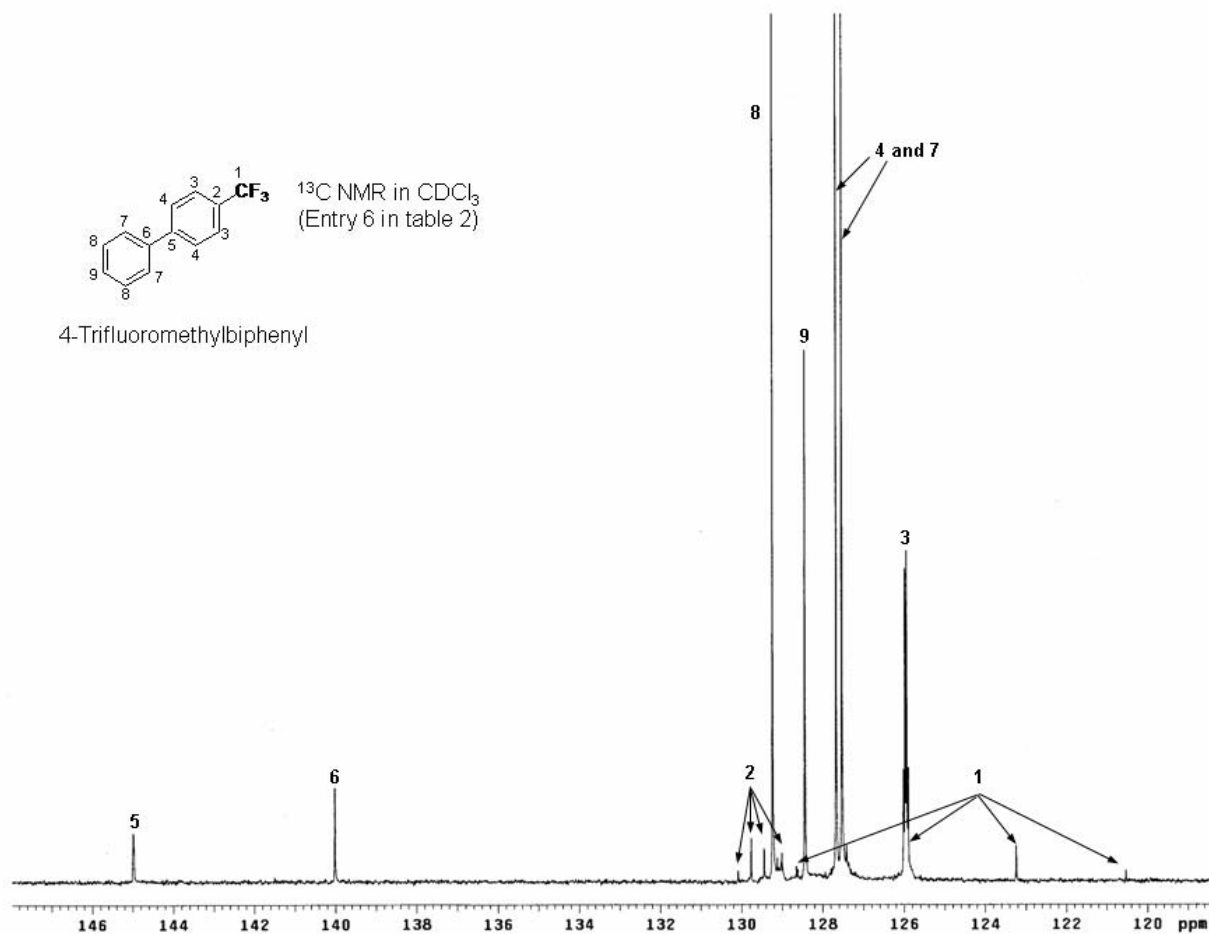
**Figure S7.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of 4-acetylbiphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 4 in table 2).



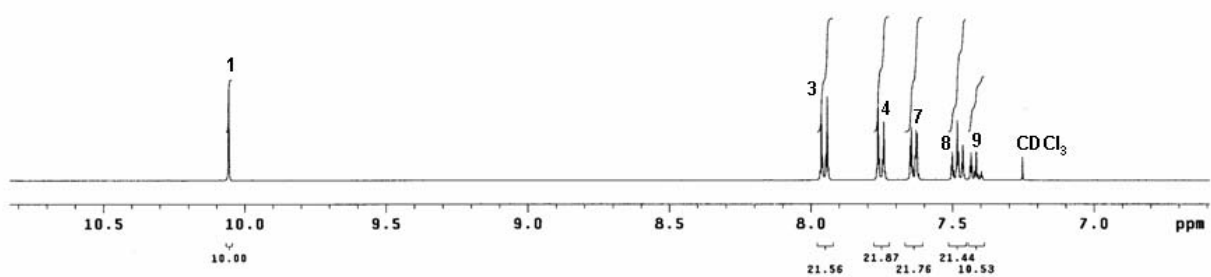
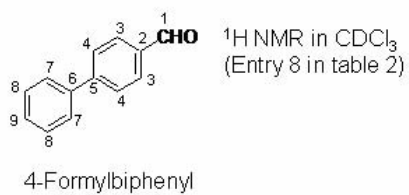
**Figure S8.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-acetylbiphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 4 in table 2).



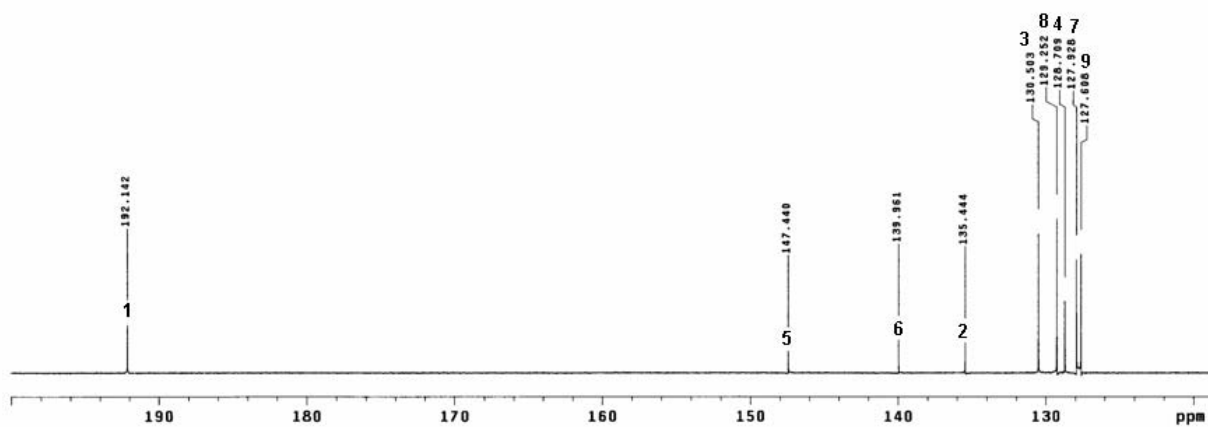
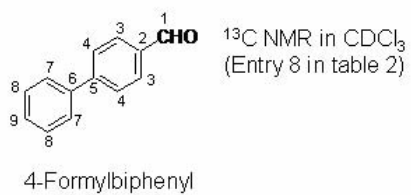
**Figure S9.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of 4-trifluoromethylbiphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 6 in table 2).



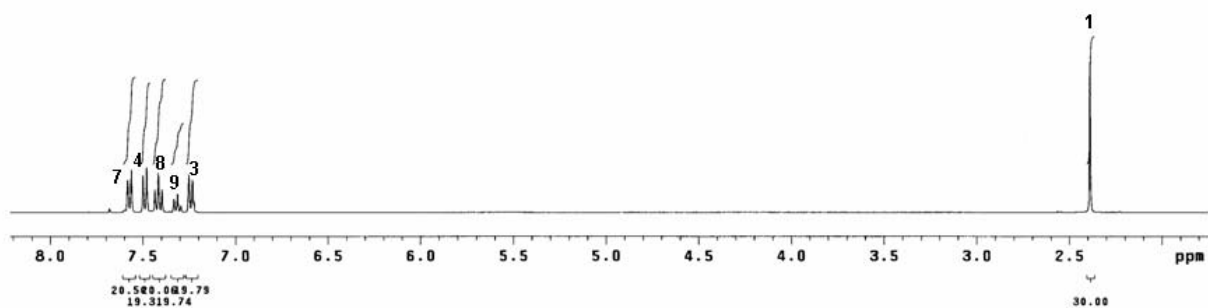
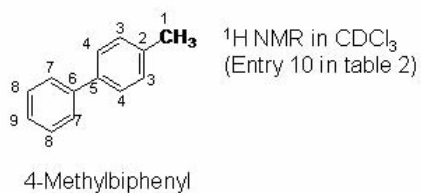
**Figure S10.**  $^{13}\text{C}$  NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-trifluoromethylbiphenyl [20 mg/mL  $\text{CDCl}_3$  at 25 °C] (entry 6 in table 2).



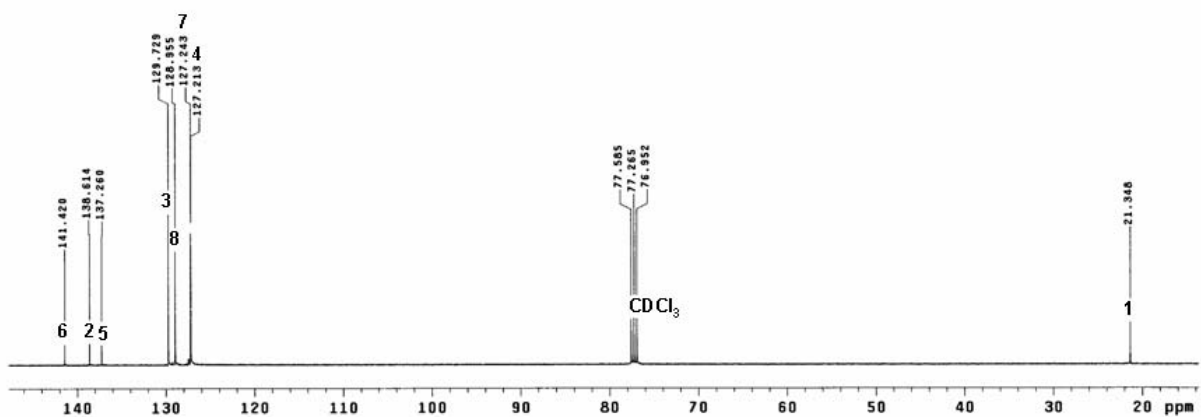
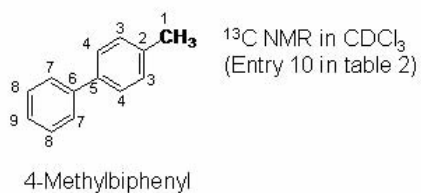
**Figure S11.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of 4-formylbiphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C (entry 8 in table 2).



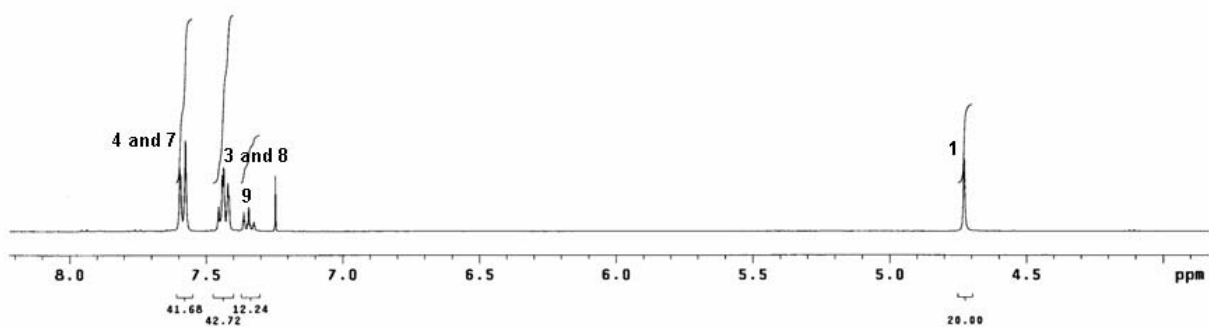
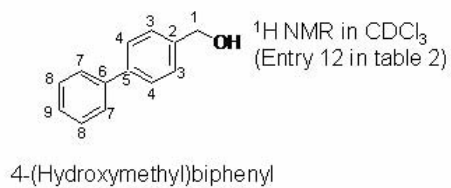
**Figure S12.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-formylbiphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 8 in table 2).



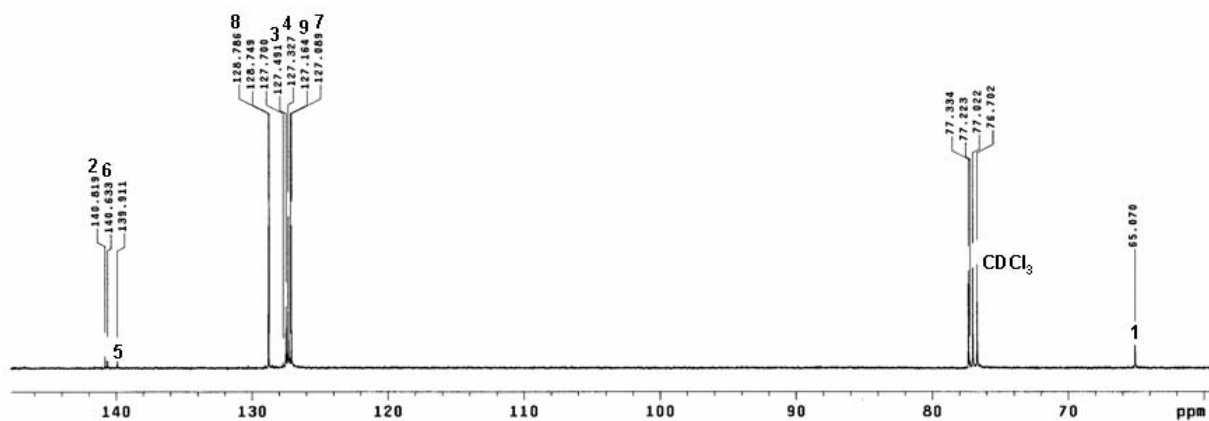
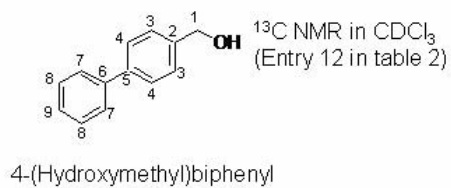
**Figure S13.**  $^1\text{H NMR}$  spectrum [delay time = 1 s, number of scans = 16] of 4-methylbiphenyl [10 mg/mL  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ ] (entry 10 in table 2).



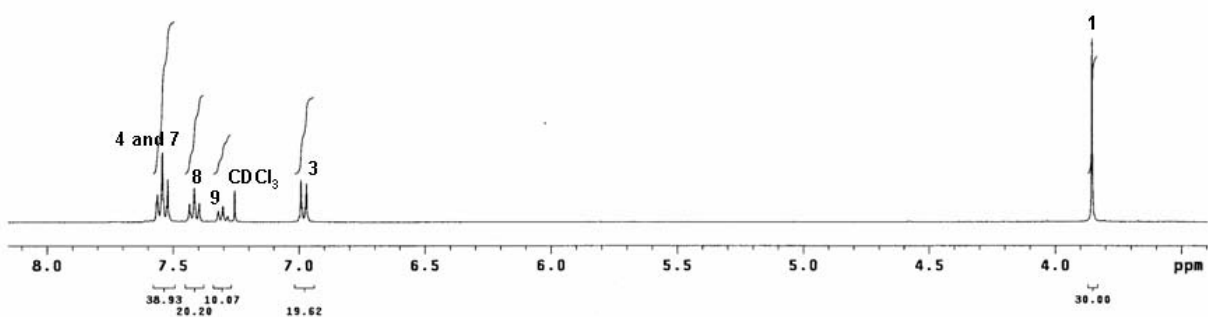
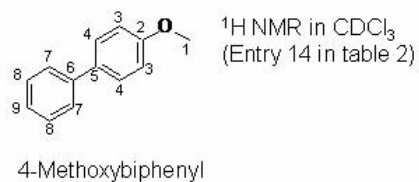
**Figure S14.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-methylbiphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 10 in table 2).



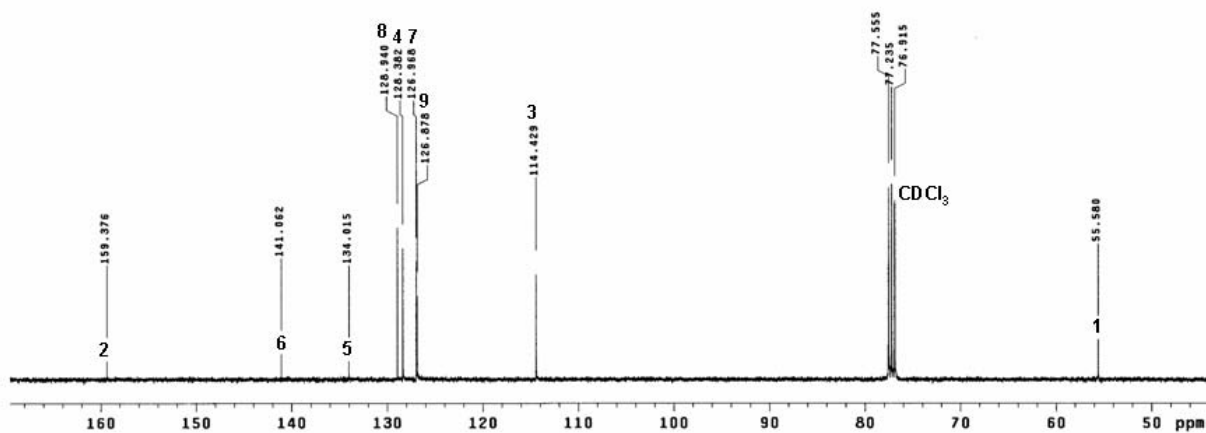
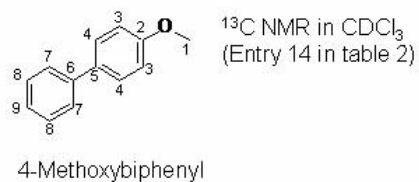
**Figure S15.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of 4-(hydroxymethyl)biphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 12 in table 2).



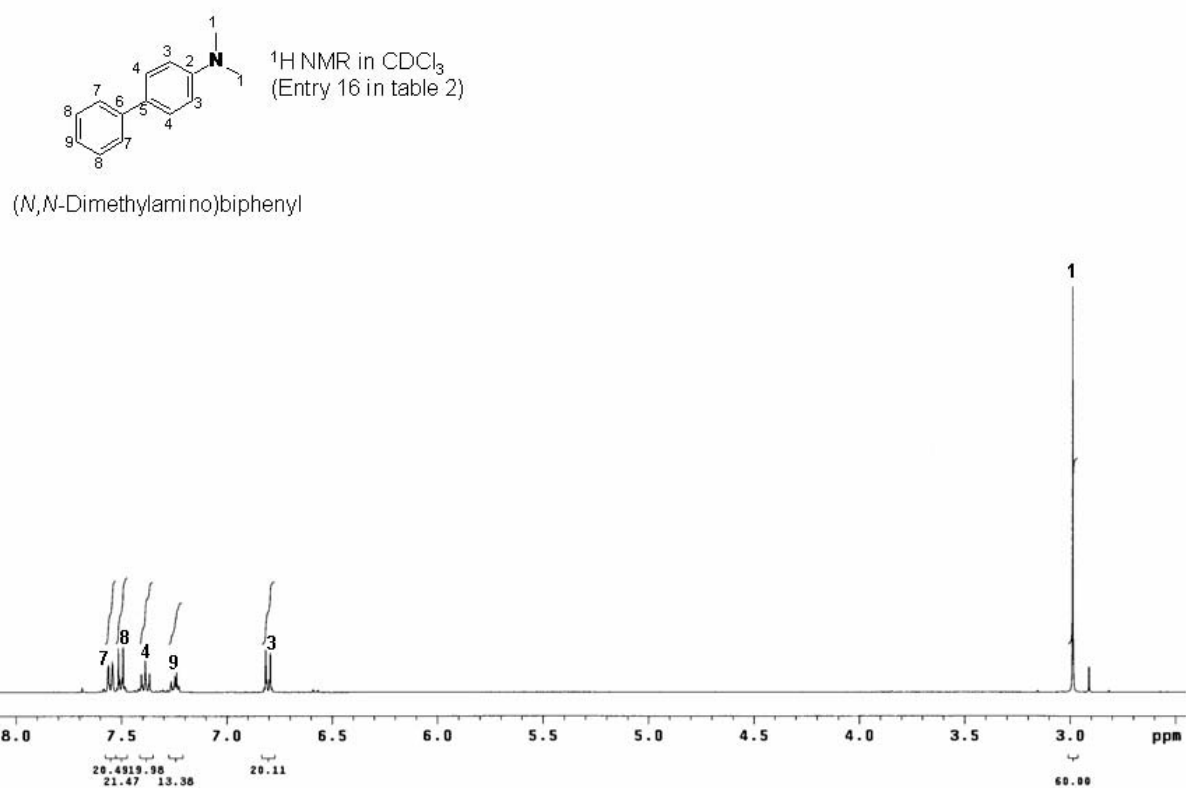
**Figure S16.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-(hydroxymethyl)biphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 12 in table 2).



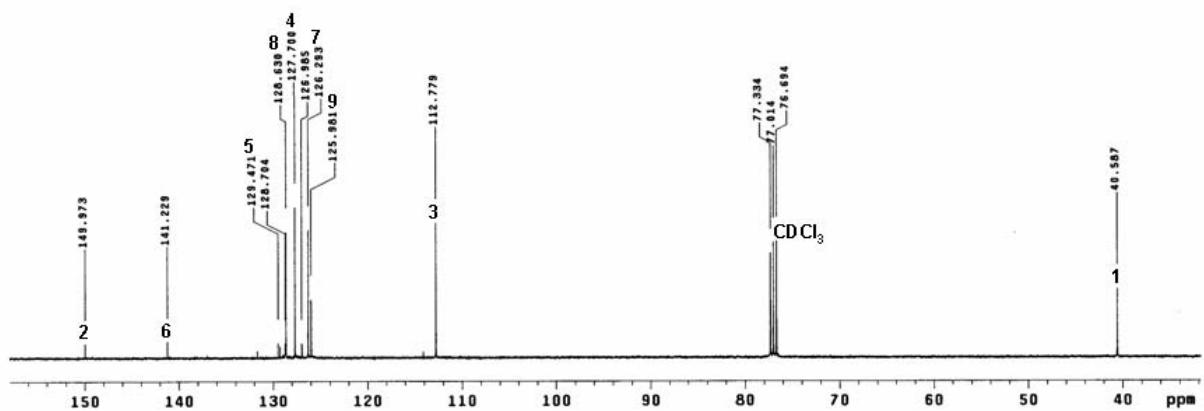
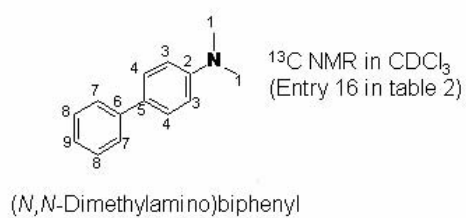
**Figure S17.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of 4-methoxybiphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 14 in table 2).



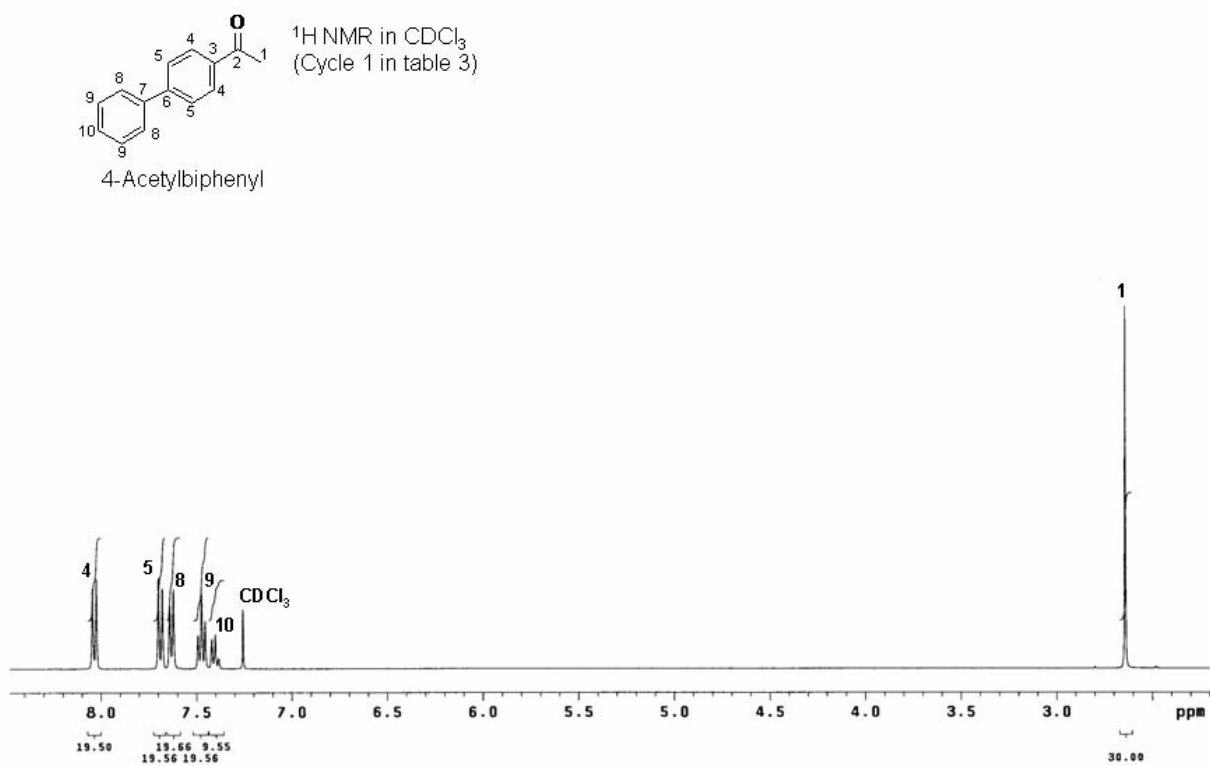
**Figure S18.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-methoxybiphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 14 in table 2).



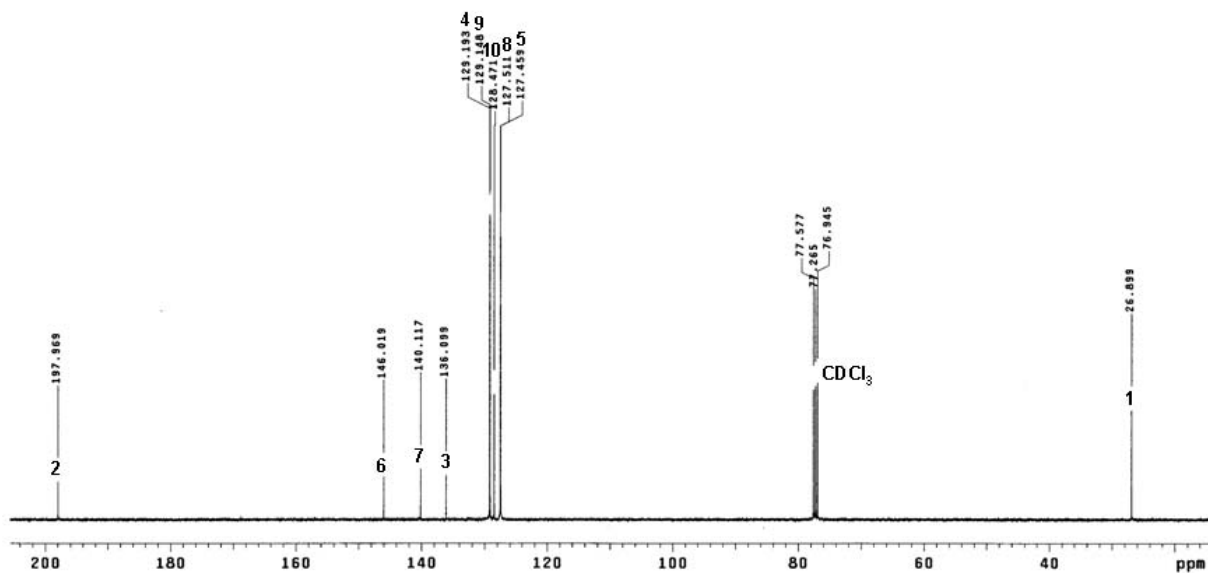
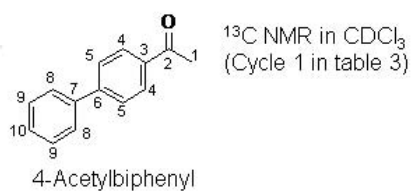
**Figure S19.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of (*N,N*-dimethylamino)biphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 16 in table 2).



**Figure S20.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of (*N,N*-dimethylamino)biphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (entry 16 in table 2).



**Figure S21.** <sup>1</sup>H NMR spectrum [delay time = 1 s, number of scans = 16] of 4-acetylbiphenyl [10 mg/mL CDCl<sub>3</sub> at 25 °C] (cycle 1 in table 3).



**Figure S22.** <sup>13</sup>C NMR spectrum [delay time = 4 s, number of scans = 1000] of 4-acetylbiphenyl [20 mg/mL CDCl<sub>3</sub> at 25 °C] (cycle 1 in table 3).