

## Supplementary Information

# A Reusable Heterogeneous Catalyst without Palladium Leaking for High-efficient Suzuki-Miyaura Reaction in Pure Water under Air

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### Experimental Details

#### *Materials and apparatus*

Unless otherwise specified, all the solvents were of analytic grade and used without further purification.<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker AM-400 spectrometer with chemical shifts reported in ppm (in CDCl<sub>3</sub>, TMS as internal standard). Mass spectra were measured on a HP 5989A spectrometer. Melting points were determined using a Büchi Meting Point B-540 apparatus and were uncorrected. All pH values were measured with a Sartorius basic pH-Meter PB-20. Elemental analysis was performed by a GermanyElementarVario EL III. Concentration of palladium was analyzed by a Varian 710ES inductively coupled plasma atomic emission spectrometry (ICP-AES). Water was purified by a Milli-Q system.

#### *Synthetic procedures and characterization*

##### Synthesis of **Pd@FSM**

**FSM**(500 mg) and PdCl<sub>2</sub> solution in water (10 mM, 20 mL) were mixed for 3 h under magnetic stirring. Then the mixture was filtered and washed with water for three times. After that the residue was washed further with methanol under reflux for 24 h, and then filtered and washed with methanol and water for three times separately. The final product **Pd@FSM** was dried in vacuum drier. The palladium of **Pd@FSM** was 11 mg per gram analyzed by the inductively coupled plasma atomic emission spectrometry (ICP-AES)

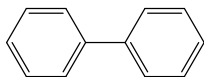
##### Procedure for Suzuki coupling reaction

###### General procedure for the reaction

Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction

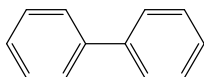
mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel and confirmed with  $^1\text{H}$  NMR and melting point.

#### Entry 1



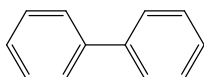
Chlorobenzene (112 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to yield biphenyl as a white solid (63.4 mg, 41% yield, m.p. 68.0-68.4 °C, reference 69-71 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.52 (d,  $J = 7.6$  Hz, 4H), 7.37 (t,  $J = 7.2$  Hz, 4H), 7.27 (t,  $J = 7.2$  Hz, 2H); MS (GC-MS)  $m/z$ , calcd. for  $\text{C}_{12}\text{H}_{10}$  154.08, found 154.1

#### Entry 2



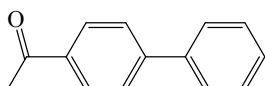
Bromobenzene (157 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to yield biphenyl as a white solid (140.6 mg, 91% yield, m.p. 68.0-68.4 °C, reference 69-71 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.52 (d,  $J = 7.6$  Hz, 4H), 7.37 (t,  $J = 7.2$  Hz, 4H), 7.27 (t,  $J = 7.2$  Hz, 2H); MS (GC-MS)  $m/z$ , calcd. for  $\text{C}_{12}\text{H}_{10}$  154.08, found 154.1

#### Entry 3



Iodobenzene (204 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to yield biphenyl as a white solid (134.3 mg, 87% yield, m.p. 68.0-68.4 °C, reference 69-71 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.52 (d,  $J = 7.6$  Hz, 4H), 7.37 (t,  $J = 7.2$  Hz, 4H), 7.27 (t,  $J = 7.2$  Hz, 2H); MS (GC-MS)  $m/z$ , calcd. for  $\text{C}_{12}\text{H}_{10}$  154.08, found 154.1

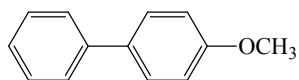
#### Entry 4



4-Bromoacetophenone (199 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column

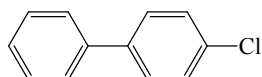
chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **4** (189.9 mg, 97% yield, m.p. 119.6-120.1°C, reference 121°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 6.8 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 1H), 2.56 (s, 3H); MS (GC-MS) *m/z*, calcd. for C<sub>14</sub>H<sub>12</sub>O 196.09, found 196.1

#### Entry 5



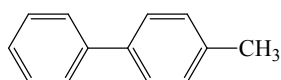
1-Bromo-4-methoxybenzene (187 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **5** (167.8 mg, 91% yield, m.p. 86.0-86.3°C, reference 90°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.47 (t, *J* = 8.2 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 3.77 (s, 3H); MS (GC-MS) *m/z*, calcd. for C<sub>13</sub>H<sub>12</sub>O 184.09, found 184.1

#### Entry 6



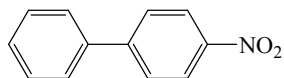
1-bromo-4-chlorobenzene (191 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **6** (152.6 mg, 81% yield, m.p. 67.2-68.1°C, reference 78.8°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.53-7.43 (m, 4H), 7.39-7.28 (m, 5H). MS (GC-MS) *m/z*, calcd. for C<sub>12</sub>H<sub>9</sub>Cl 188.04, found 188.1

#### Entry 7



1-bromo-4-methylbenzene (171 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **7** (136.5 mg, 81% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 6.4 Hz, 2H), 6.71 (t, *J* = 8.8 Hz, 1H), 2.54 (s, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>13</sub>H<sub>12</sub> 168.09, found 168.1

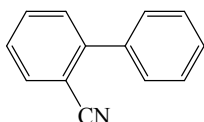
#### Entry 8



1-bromo-4-nitrobenzene (202 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic

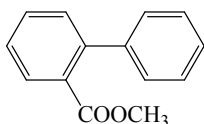
layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **8** (181.5 mg, 91% yield, m.p. 110.6-112.9°C, reference 114°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 6.8 Hz, 2H), 7.45-7.37 (m, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>12</sub>H<sub>9</sub>NO<sub>2</sub> 199.06, found 199.0

#### Entry 9



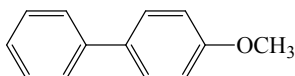
2-bromobenzonitrile (182 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **9** (168.4 mg, 94% yield, liquid, m.p. reference 41°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.45-7.35 (m, 5H). MS (GC-MS) *m/z*, calcd. for C<sub>13</sub>H<sub>9</sub>N 179.07, found 179.0

#### Entry 10



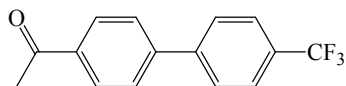
Methyl 2-iodobenzoate (262 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **10** (178.5 mg, 84% yield, liquid, m.p. reference 114-115°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.91 (td, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 7.36-7.28 (m, 5H), 7.26-7.24 (m, 2H), 3.56 (s, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub> 212.08, found 212.1

#### Entry 11



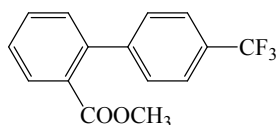
1-iodo-4-methoxybenzene (234 mg, 1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **11** (158.9 mg, 86% yield, m.p. 86.0-86.3 °C, reference 90 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.47 (t, *J* = 8.2 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 3.77 (s, 3H); MS (GC-MS) *m/z*, calcd. for C<sub>13</sub>H<sub>12</sub>O 184.09, found 184.1

#### Entry 12



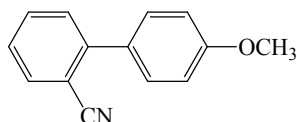
4-Bromoacetophenone (199 mg, 1.0 mmol), (4-(trifluoromethyl)phenyl)boronic acid (285 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **12** (8.0 Hz, 2H), 7.65 (s, 4H), 7.52 (d,  $J = 8.0$  Hz, 2H), 2.50 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{15}H_{11}F_3O_2$  264.08, found 264.1

#### Entry 13



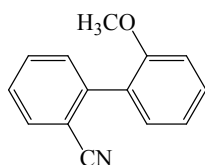
Methyl-2-iodobenzoate (262 mg, 1.0 mmol), (4-(trifluoromethyl)phenyl)boronic acid (285 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 3/1, v/v) to afford compound **13** (255.9 mg, 91% yield, liquid).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.94 (d,  $J=8.0$  Hz, 1H), 7.69 (d,  $J=8.0$  Hz, 2H), 7.59 (t,  $J=8.0$  Hz, 1H), 7.49 (t,  $J = 8.0$  Hz, 1H), 7.45 (t,  $J = 8.0$  Hz, 1H), 7.37 (d,  $J = 8.0$  Hz, 1H), 3.69 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{15}H_{11}F_3O_2$  280.07, found 280.1

#### Entry 14



2-Bromobenzonitrile (182 mg, 1.0 mmol), (4-methoxyphenyl)boronic acid (228 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **14** (198.7 mg, 95% yield, m.p. 84.4-85.1°C, reference 83-84°C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.67 (d,  $J=7.6$  Hz, 1H), 7.54 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.4$  Hz, 1H), 7.45-7.41 (m, 3H), 7.32 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.4$  Hz, 1H); 6.95 (d,  $J = 6.8$  Hz), 3.79 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{14}H_{11}NO$  209.08, found 209.1

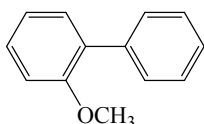
#### Entry 15



2-Bromobenzonitrile (182 mg, 1.0 mmol), (2-methoxyphenyl)boronic acid (228 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10

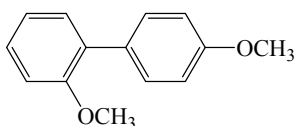
h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 5/1, v/v) to afford compound **15** (96.3 mg, 46% yield, liquid).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.65 (d,  $J=8.0$  Hz, 1H), 7.56 (td,  $J_1=8.0$  Hz,  $J_2=1.2$  Hz, 1H), 7.39-7.32 (m, 3H), 7.19 (td,  $J_1=8.0$  Hz,  $J_2=1.6$  Hz, 1H), 7.01-6.95 (m, 2H), 3.77 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $\text{C}_{14}\text{H}_{11}\text{NO}$  209.08, found 209.1

#### Entry 16



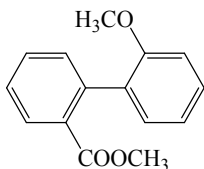
Iodobenzene (204 mg, 1.0 mmol), (2-methoxyphenyl)boronic acid (228 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 5/1, v/v) to afford compound **16** (156.9 mg, 85% yield, liquid, m.p. reference 29°C).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.45 (d,  $J=7.6$  Hz, 2H), 7.32 (t,  $J=7.2$  Hz, 2H), 7.25-7.21 (m, 3H), 6.96-6.88 (m, 2H), 3.71 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}$  184.09, found 184.1

#### Entry 17



1-iodo-4-methoxybenzene (234 mg, 1.0 mmol), (2-methoxyphenyl)boronic acid (228 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 3/1, v/v) to afford compound **17** (178.1 mg, 83% yield, m.p. 65.0-65.1 °C, reference 70°C).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.46 (d,  $J=8.0$  Hz, 2H), 7.29 (d,  $J=8.0$  Hz, 2H), 7.02-6.93 (m, 4H), 3.82 (s, 3H), 3.79 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}_2$  214.10, found 214.1

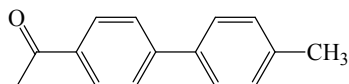
#### Entry 18



Methyl-2-iodobenzoate (262 mg, 1.0 mmol), (2-methoxyphenyl)boronic acid (228 mg, 1.5 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The remaining residue was

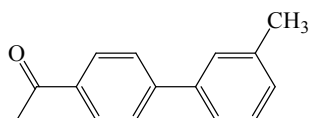
purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 3/1, v/v) to afford compound **18** (63.6 mg, 26% yield, liquid). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.41-7.34 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> 242.09, found 240.0

#### Entry 19



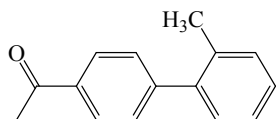
4-Bromoacetophenone (199 mg, 1.0 mmol), *p*-tolylboronic acid (204 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **19** (208.8 mg, >99% yield, m.p. 116.7-118.1 °C, reference 122 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 12.0 Hz, 2H), 7.52 (d, *J* = 12.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.62 (s, 3H), 2.40 (s, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> 210.10, found 210.1

#### Entry 20



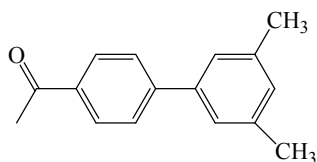
4-Bromoacetophenone (199 mg, 1.0 mmol), *m*-tolylboronic acid (204 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **20** (209.1 mg, >99% yield, m.p. 84.4-86.6 °C, reference 92 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 2.52 (s, 3H), 2.33 (s, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> 210.10, found 210.1

#### Entry 21



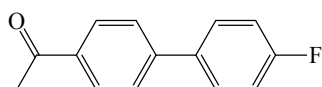
4-Bromoacetophenone (199 mg, 1.0 mmol), *o*-tolylboronic acid (204 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), Pd@FSM (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5/1, v/v) to afford compound **21** (208.7 mg, >99% yield, liquid). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 9.2 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 2.48 (s, 3H), 2.12 (s, 3H). MS (GC-MS) *m/z*, calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> 210.10, found 210.1

#### Entry 22



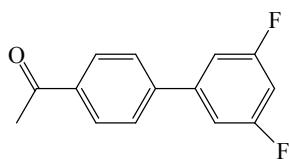
4-Bromoacetophenone (199 mg, 1.0 mmol), (3,5-dimethylphenyl)boronic acid (225 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **22** (222.5 mg, >99% yield, m.p. 84.5-85.5 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.90 (d,  $J = 8.4$  Hz, 2H), 7.55 (d,  $J = 8.4$  Hz, 2H), 7.13 (s, 2H), 6.93 (s, 1H), 2.51 (s, 3H), 2.28 (s, 6H). MS (GC-MS)  $m/z$ , calcd. for  $C_{16}H_{16}O$  224.12, found 224.1

### Entry 23



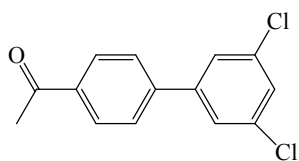
4-Bromoacetophenone (199 mg, 1.0 mmol), (4-fluorophenyl)boronic acid (210 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **23** (200.7 mg, 94% yield, m.p. 103.2-103.4 °C, reference 102-103 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.93 (d,  $J = 8.4$  Hz, 2H), 7.55-7.48 (m, 4H), 7.06 (t,  $J = 8.4$  Hz, 2H), 2.54 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{14}H_{11}FO$  214.08, found 214.1

### Entry 24

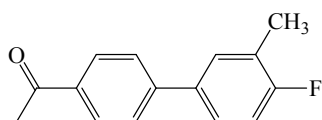


4-Bromoacetophenone (199 mg, 1.0 mmol), (3,5-difluorophenyl)boronic acid (237 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **24** (231.1 mg, >99% yield, m.p. 68.2-69.1 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.93 (d,  $J = 8.2$  Hz, 2H), 7.52 (d,  $J = 8.2$  Hz, 2H); 7.01 (d,  $J = 6.4$  Hz, 2H), 6.71 (t,  $J = 8.8$  Hz, 1H), 2.54 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{14}H_{10}F_2O$  232.07, found 232.1

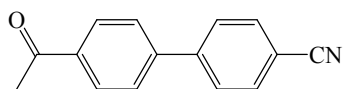


**Entry 25**

4-Bromoacetophenone (199 mg, 1.0 mmol), (3,5-dichlorophenyl)boronic acid (285 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **25** (261.6 mg, 99% yield, m.p. 63.2-63.6 °C, reference 64-66 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.04 (d,  $J=8.2$  Hz, 2H); 7.63 (d,  $J=8.2$  Hz, 2H); 7.48 (s, 2H), 7.38 (s, 1H), 2.65 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{14}H_{10}Cl_2O$  264.01, found 264.0

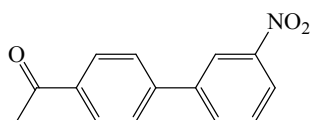
**Entry 26**

4-Bromoacetophenone (199 mg, 1.0 mmol), (4-fluoro-3-methylphenyl)boronic acid (231 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **26** (219.1 mg, 96% yield, m.p. 79.7-79.9 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.01 (d,  $J=8.4$  Hz, 2H), 7.62 (d,  $J=8.4$  Hz, 2H), 7.44-7.39 (m, 2H), 7.09 (t,  $J=8.4$  Hz, 1H), 2.63 (s, 3H), 2.35 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{15}H_{13}NO$  228.10, found 228.1

**Entry 27**

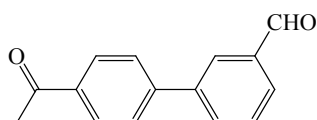
4-Bromoacetophenone (199 mg, 1.0 mmol), (4-cyanophenyl)boronic acid (220 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **27** (201.9 mg, 91% yield, m.p. 116.3-116.8 °C, reference 115-116 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.00 (d,  $J=8.4$  Hz, 2H), 7.71-7.61 (m, 6H), 2.59 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{15}H_{11}NO$  221.08, found 221.1

### Entry 28



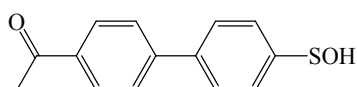
4-Bromoacetophenone (199 mg, 1.0 mmol), (3-nitrophenyl)boronic acid (250 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **28** (78.1 mg, 32% yield, m.p. 106.8-108.4 °C, reference 109-110°C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.50 (s, 1H), 8.27 (d,  $J = 8.4$  Hz, 1H), 8.09 (d,  $J = 8.4$  Hz, 2H), 7.96 (t,  $J = 8.4$  Hz, 1H), 7.74 (d,  $J = 8.4$  Hz, 2H), 7.67 (t,  $J = 8.4$  Hz, 1H), 2.67 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{14}H_{11}NO_3$  241.07, found 241.1

### Entry 29



4-Bromoacetophenone (199 mg, 1.0 mmol), (3-formylphenyl)boronic acid (225 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 3/1, v/v) to afford compound **29** (155.2 mg, 69% yield, m.p. 69.1-69.2 °C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  10.11 (s, 1H), 8.14 (s, 1H), 8.07 (d,  $J = 8.2$  Hz, 2H), 7.91 (t,  $J = 7.6$  Hz, 2H), 7.73 (d,  $J = 8.2$  Hz, 2H), 7.66 (t,  $J = 7.8$  Hz, 1H), 2.66 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{15}H_{12}O_2$  224.08, found 224.1

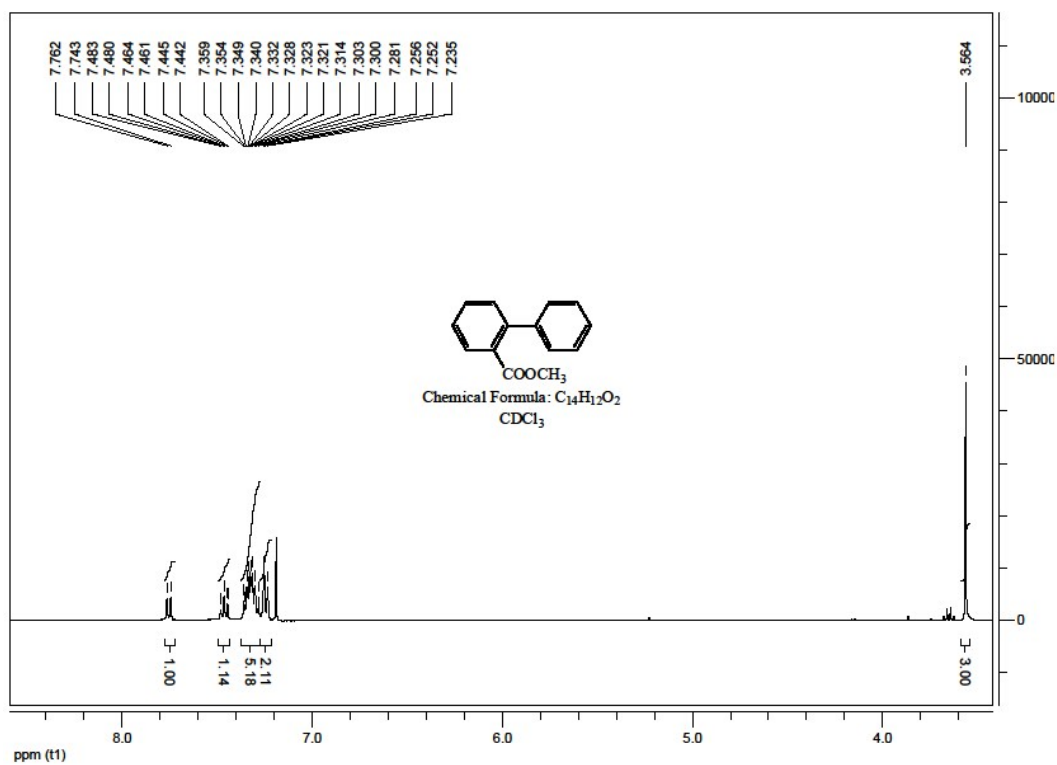
### Entry 30



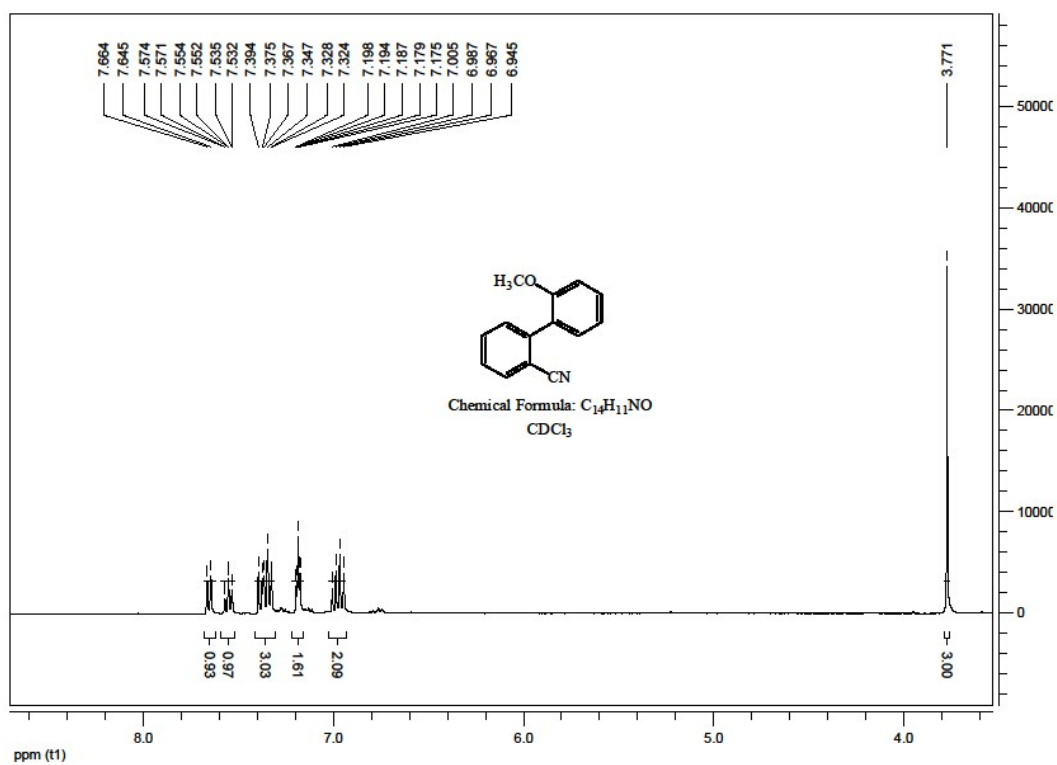
4-Bromoacetophenone (199 mg, 1.0 mmol), (4-(hydroxythio)phenyl)boronic acid (255 mg, 1.5 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol), **Pd@FSM** (5.0 mg, 0.05 mol %) and water (5 mL) were mixed and stirred at 80 °C for 10 h. After the reaction completed, the reaction mixture was extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $MgSO_4$  and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2$ , 5/1, v/v) to afford compound **30** (117.6 mg, 48% yield, m.p. 99.7°C).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.02 (d,  $J = 8.4$  Hz, 2H), 7.66 (d,  $J = 8.4$  Hz, 2H), 7.56 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H), 2.53 (s, 3H). MS (GC-MS)  $m/z$ , calcd. for  $C_{14}H_{12}O_2S$  244.06, found 244.1

### NMR spectrum for partial Suzuki coupling reaction products

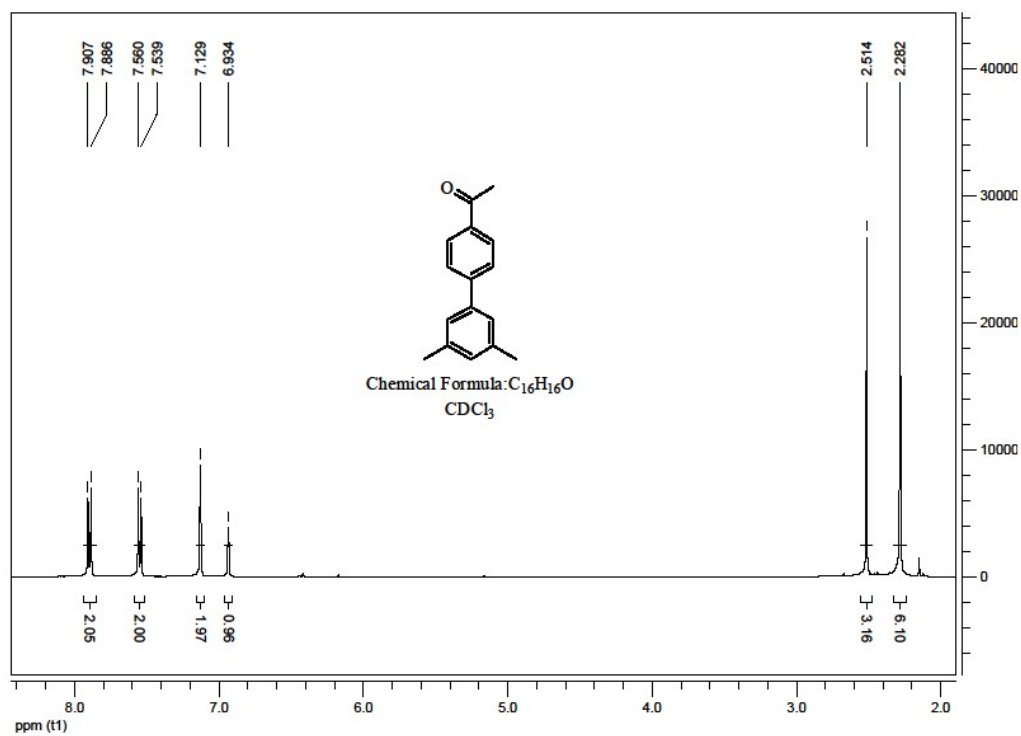
Entry 10



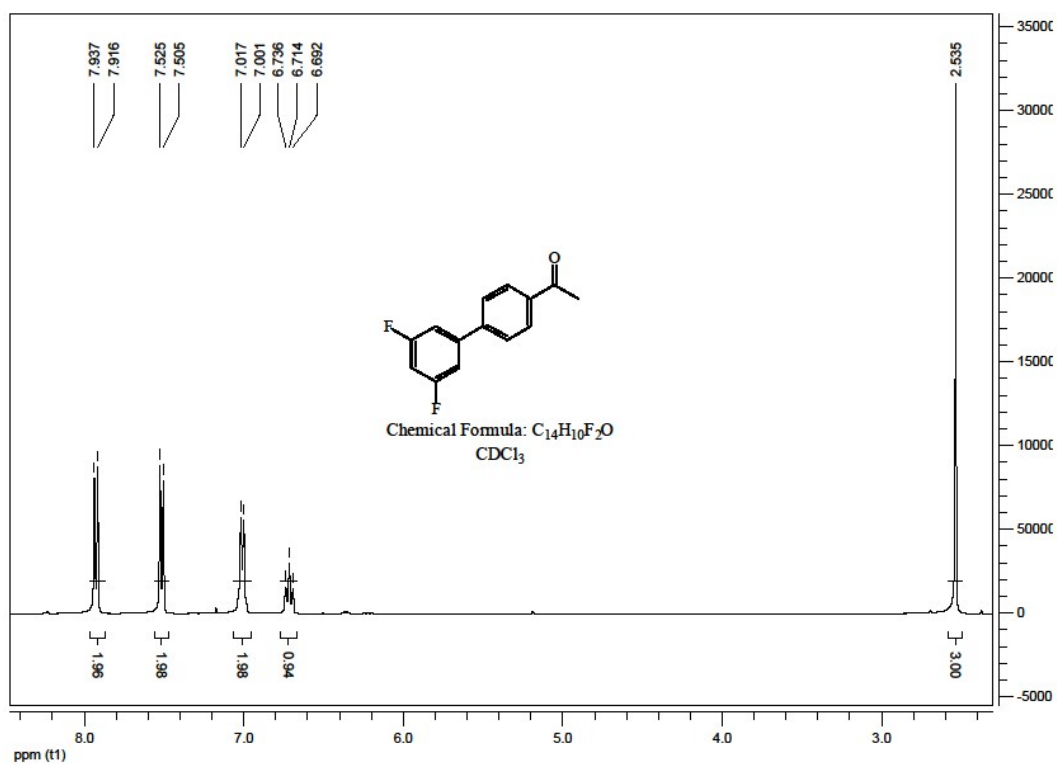
Entry 15



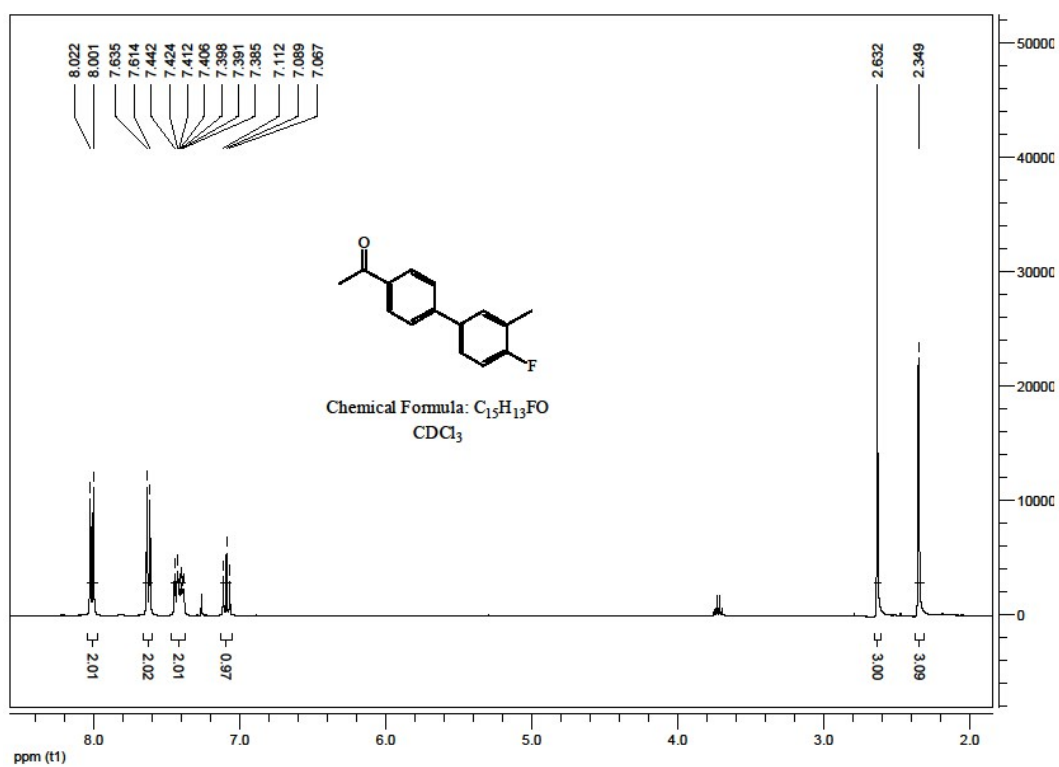
Entry 22



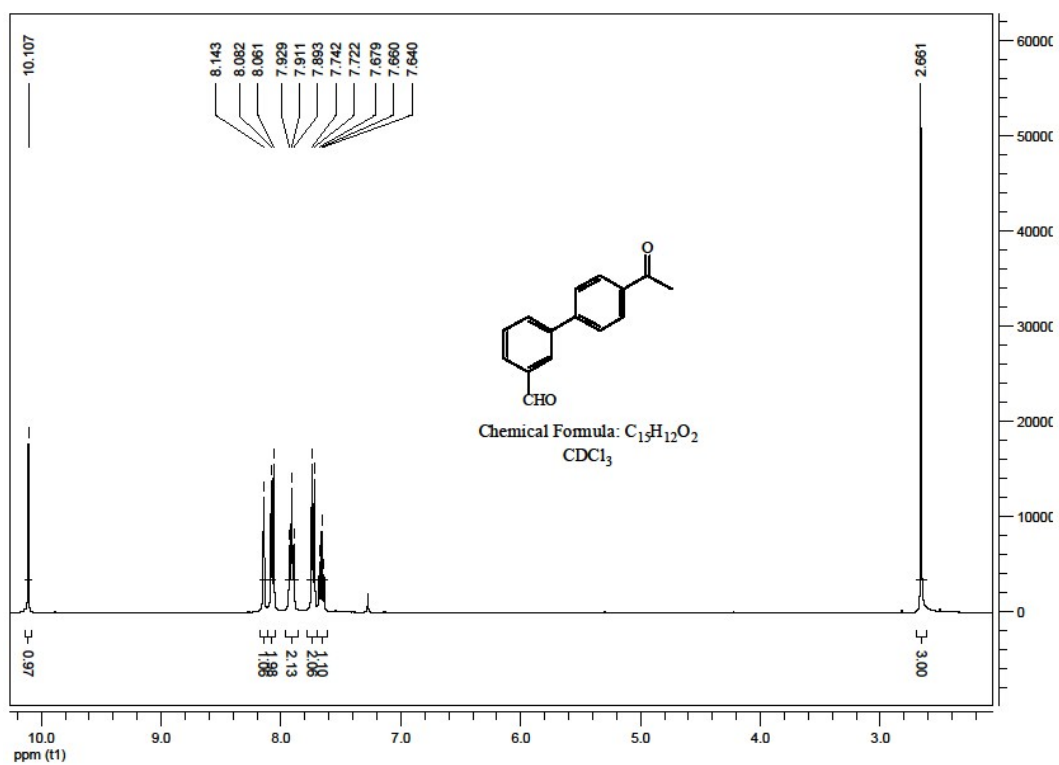
Entry 24



Entry 26



Entry 29



Entry 30

