

# Pd(OAc)<sub>2</sub>-Catalyzed Fluoride-Free Cross-Coupling Reactions of Arylsiloxane with Aryl Bromides in Aqueous Medium

*Shengyin Shi, Yuhong Zhang\**

Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China.

E-mail: [yhzhang@zjuem.zju.edu.cn](mailto:yhzhang@zjuem.zju.edu.cn)

## Supporting Information

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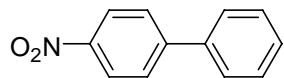
**General** Trimethoxy(4-methoxyphenyl)silane, trimethoxy(p-tolyl)silane, trimethoxy(4-(trifluoromethyl) phenyl)silane were prepared according to the method of reference 1. The other materials and solvents were purchased from common commercial sources and were used without additional purification. The gas chromatography analysis was performed on a GC instrument. <sup>1</sup>H NMR spectra were recorded at 500 MHz or 400 MHz using TMS as internal standard. Mass spectroscopy data of the product was collected on a MS-EI instrument. All of the prepared compounds are known and their CA numbers as well as the related preparation and characterization references are presented.

**General procedure for Hiyama reaction:** A mixture of NaOH (0.120 g, 3 mmol), Pd(OAc)<sub>2</sub> (4 mg, 1.8 mol%), aryl bromide (1 mmol), arylsiloxane (1.2 mmol), distilled water (3 mL) and PEG 2000 (3 g) was stirred at 60 °C for the indicated time. Afterward, the reaction solution was cooled to room temperature and extracted four times with diethyl ether (4×15 mL). GC and GC/MS analyzed the combined organic phase. The further purification of the product was achieved by flash chromatography on a silica gel column.

In the recycle experiment, the residue was subjected to a second run of the Hiyama reaction by charging with the same substrates (3-bromopyridine or 1-bromo-4-nitrobenzene, trimethoxy(phenyl)silane, NaOH) without further addition of Pd(OAc)<sub>2</sub>, PEG 2000. In the third run, fifth run and seventh run, another 0.5 ml distilled water was added to the reaction mixture.

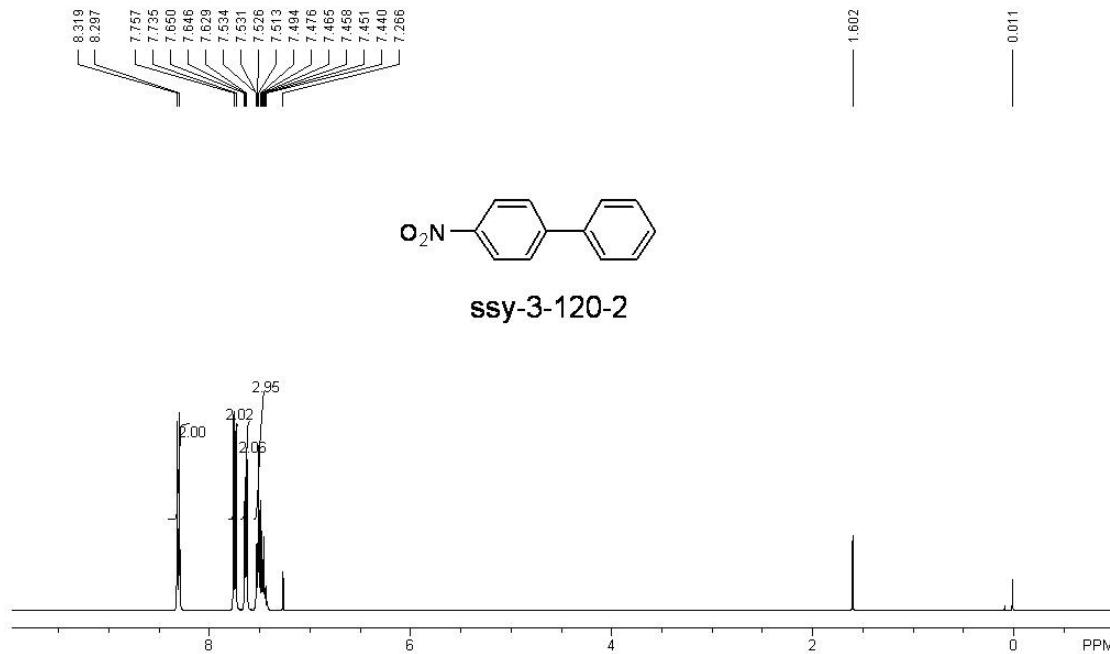
## Characterization data of the products of the Hiyama reaction

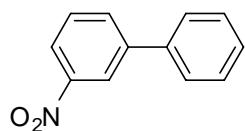
(1)



**4-Nitro-biphenyl [T2-1, 92-93-3, Ref. 2]**

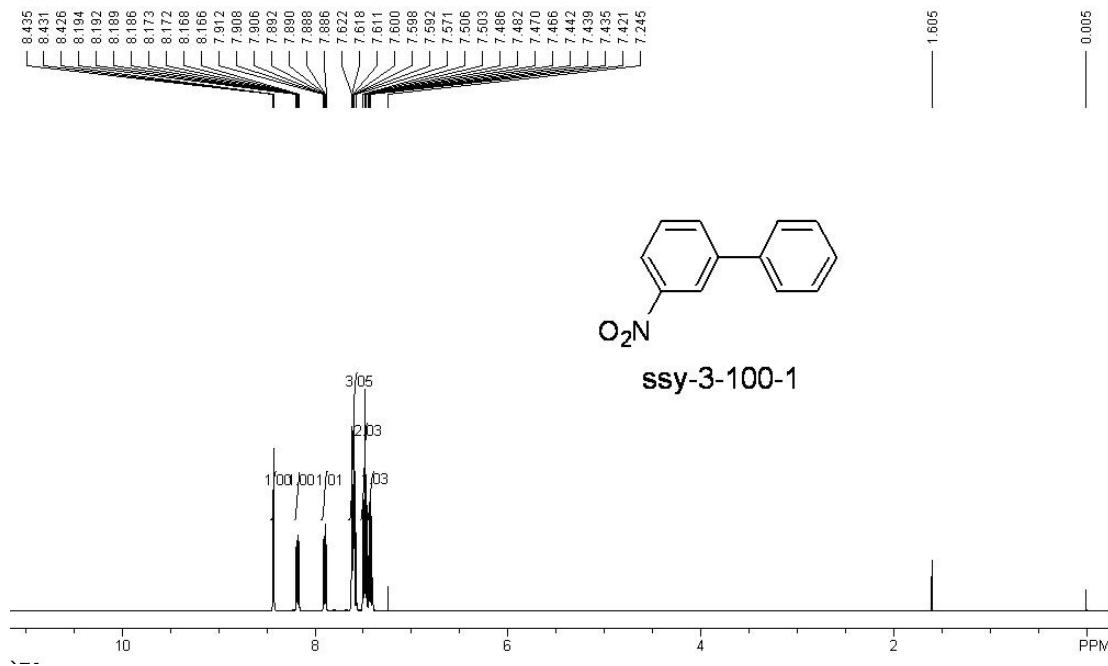
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.29-8.31 (d, 2 H, *J* = 8.8 Hz), 7.73-7.75 (d, 2 H, *J* = 8.8 Hz), 7.62-7.65 (m, 2 H), 7.44-7.53 (m, 3 H). MS (EI): m/z (%): 199 (100) [M<sup>+</sup>], 169 (37), 152 (100), 141 (24), 115 (13), 76 (13), 63 (7), 51 (6).



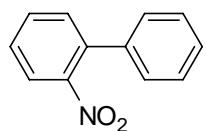


### **3-Nitro-biphenyl [T2-2, 2113-58-8, Ref. 3]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.43 (d, 1 H), 8.16-8.19 (m, 1 H), 7.88-7.91 (m, 1 H), 7.57-7.62 (m, 3 H), 7.42-7.50 (m, 3 H). MS (EI): m/z (%): 199 (100) [M<sup>+</sup>], 141 (15), 115 (25).

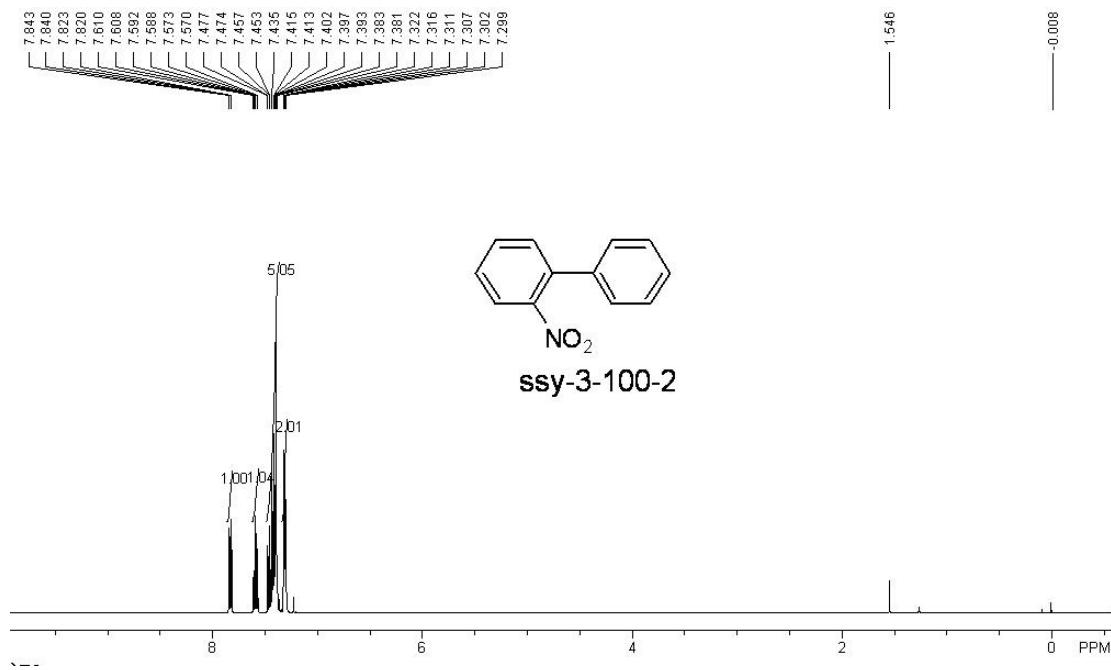


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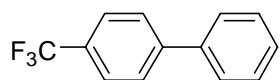


**2-Nitro-biphenyl [T2-3, 86-00-0, Ref. 3]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ7.84 (d, 1 H), 7.57-7.61 (m, 1 H), 7.38-7.47 (m, 5 H), 7.29-7.32 (m, 2 H). MS (EI): m/z (%): 199 (98) [M<sup>+</sup>], 198 (100), 153 (59), 152 (46), 141 (8), 139 (8), 115 (14), 83 (14), 63 (6), 51 (4).

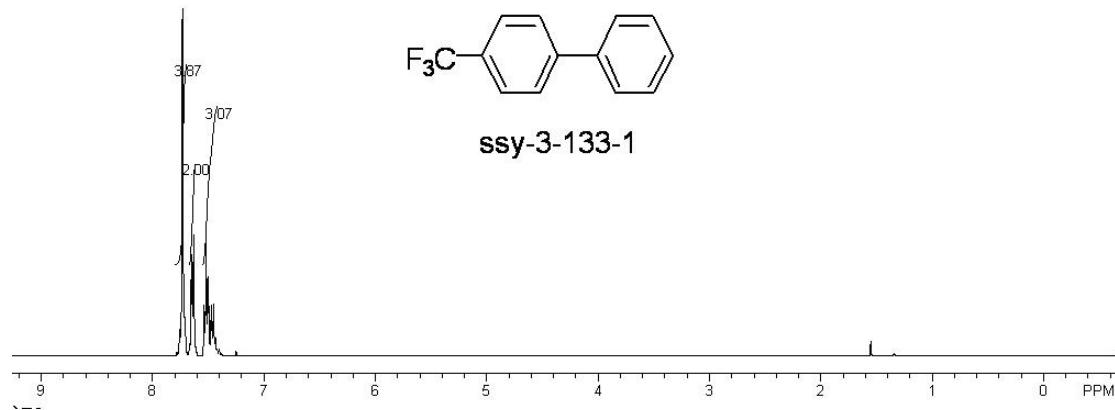
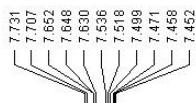


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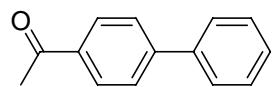


**4-Trifluoromethyl-biphenyl [T2-4, 398-36-7, Ref. 4]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.70-7.73 (d, 4 H), 7.63-7.65 (m, 2 H), 7.45-7.53 (m, 3 H). MS (EI): m/z (%): 222 (100) [M<sup>+</sup>], 201 (13), 152 (26), 86 (4).

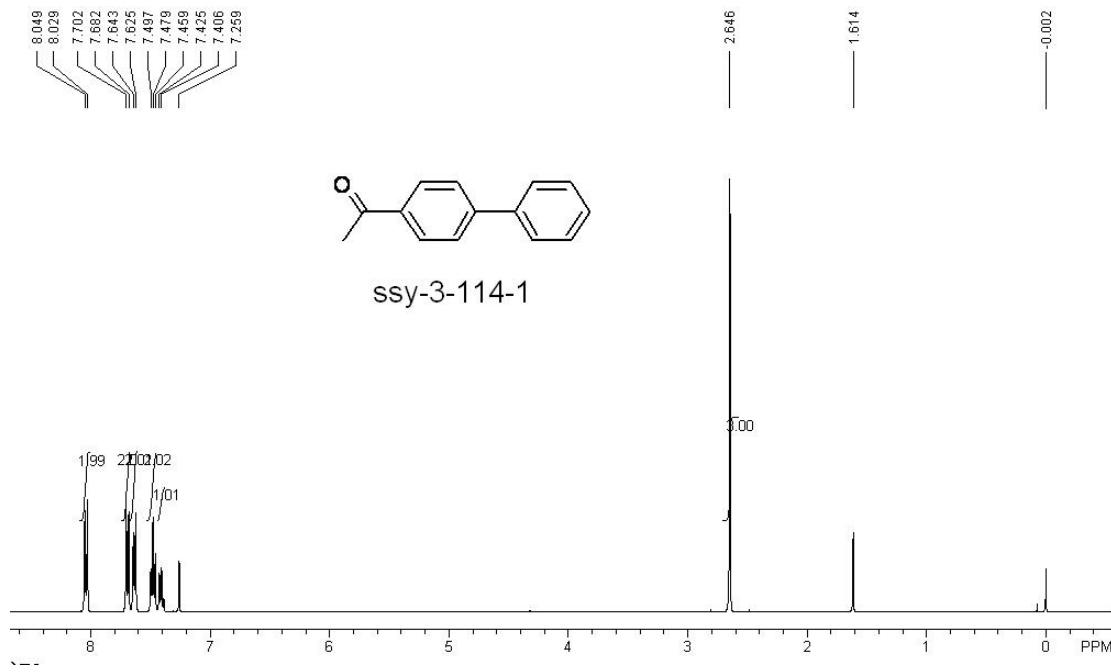


(5)

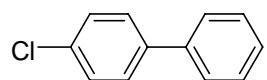


**1-Biphenyl-4-yl-ethanone [T2-5, 92-91-1, Ref. 5]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.02-8.04 (d, 2 H, *J* = 8.0 Hz), 7.68-7.70 (d, 2 H, *J* = 8.0 Hz), 7.62-7.64 (d, 2 H, *J* = 7.2 Hz), 7.45-7.49 (m, 2 H), 7.40-7.42(m, 1 H), 2.64 (s, 3 H). MS (EI): m/z (%): 196 (51) [M<sup>+</sup>], 181 (100), 153 (33), 152 (51), 76 (13), 43 (4).

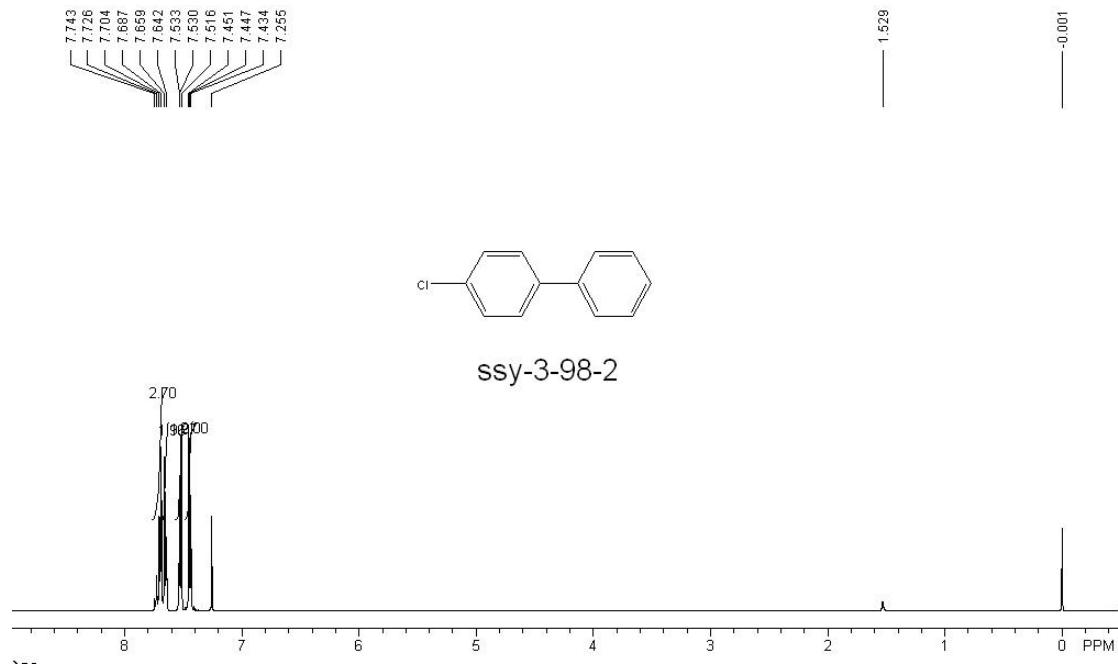


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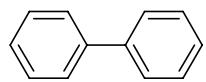


**4-Chloro-biphenyl [T2-6, 2051-62-9, Ref. 2]**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.73 (d, 1 H,  $J = 8.5$  Hz), 7.69 (d, 2 H,  $J = 8.5$  Hz), 7.65 (d, 2 H,  $J = 8.5$  Hz), 7.52 (t, 2 H,  $J = 7.0$  Hz), 7.44 (t, 2 H,  $J = 6.5$  Hz). MS (EI): m/z (%): 190 (34) [ $\text{M}^+ + 2$ ], 188 (100) [ $\text{M}^+$ ], 152 (43), 76 (15).

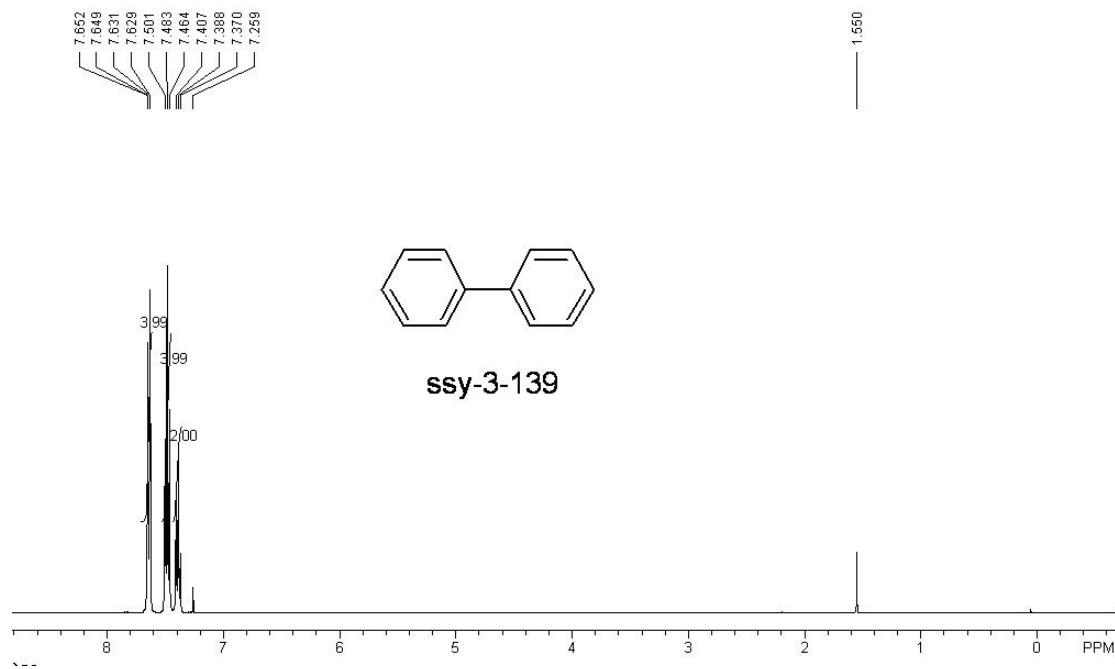


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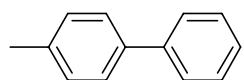


**Biphenyl [T2-7, 92-52-4, Ref. 2]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 7.62-7.65 (d, 4 H), 7.46-7.50 (t, 4 H), 7.37-7.40 (t, 2 H). MS (EI): m/z (%): 154 (100) [M<sup>+</sup>], 153 (35), 152 (20), 115 (3), 76 (13), 51 (4).

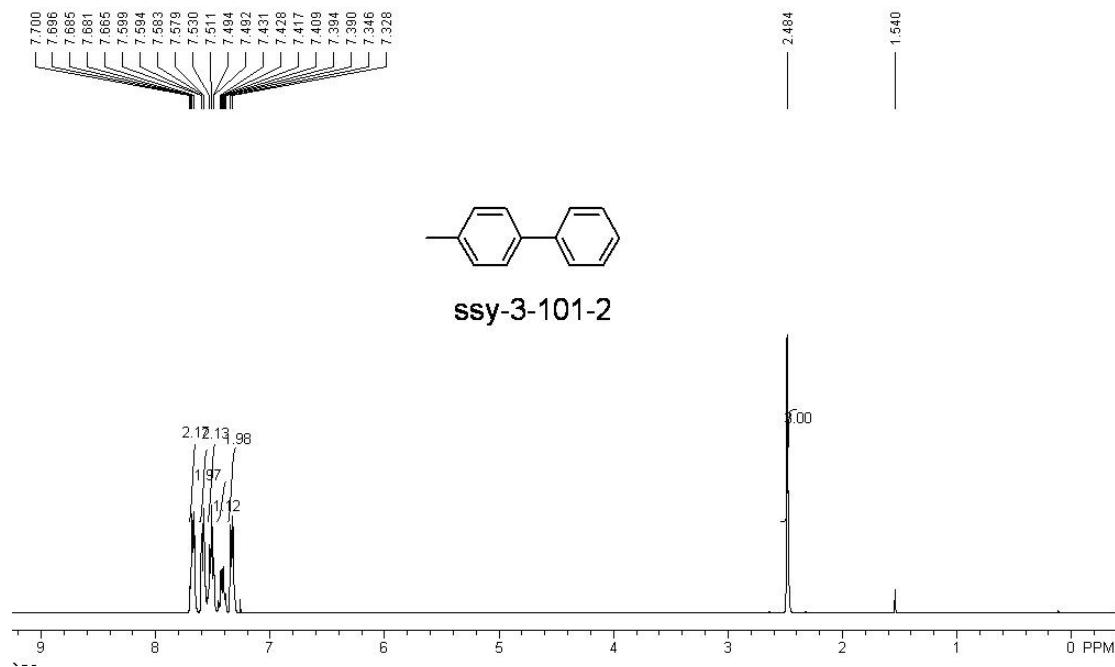


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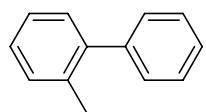


**4-Methyl-biphenyl [T2-8, 644-08-6, Ref.6]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.66-7.70 (m, 2 H), 7.57-7.59 (m, 2 H), 7.49-7.53(m, 2 H), 7.39-7.43 (m, 1 H,), 7.32-7.34 (m, 2 H). MS (EI): m/z (%): 168 (100) [M<sup>+</sup>], 167(68), 165 (22), 152 (20), 115 (6).

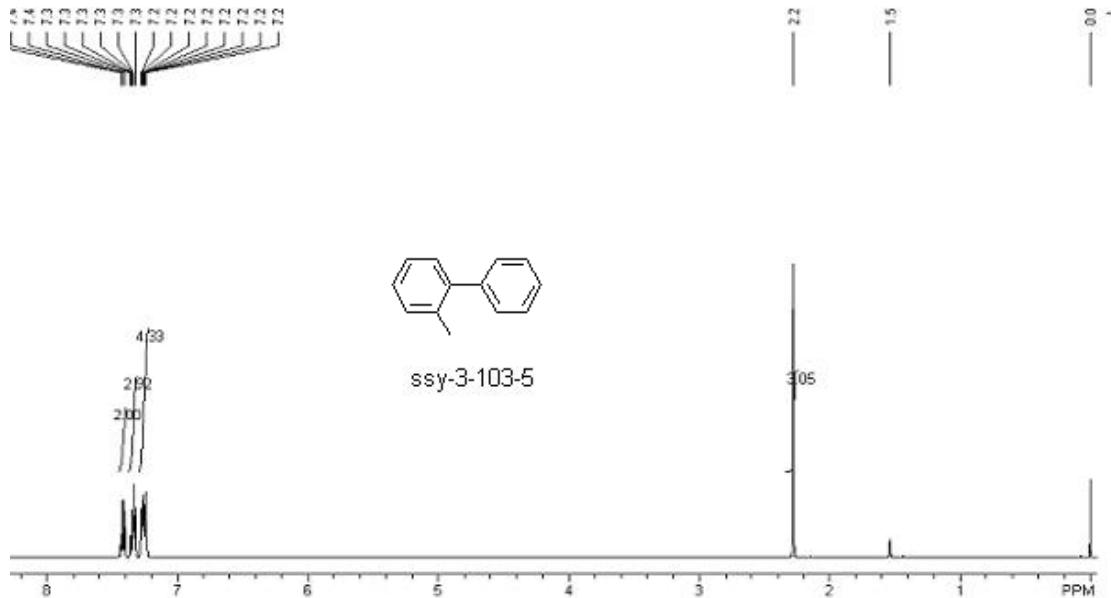


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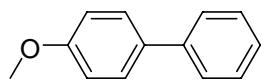


**2-Methyl-biphenyl [T2-9, 643-58-3, Ref. 4]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ 7.42 (t, 2 H, *J* = 7.5 Hz), 7.34 (m, 3 H), 7.26 (m, 4 H), 2.28 (s, 3 H).  
MS (EI): m/z (%): 168 (100) [M<sup>+</sup>], 167 (100), 165 (60), 153 (59), 152 (46), 141 (8), 139 (8), 115 (14), 83 (14), 63 (6), 51 (4).

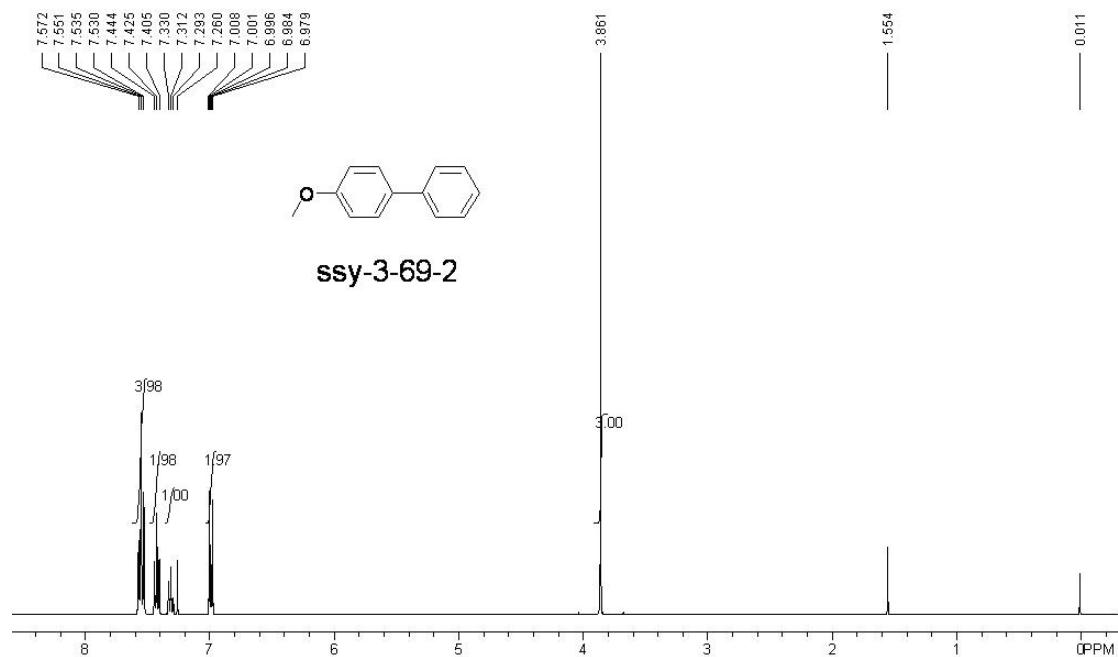


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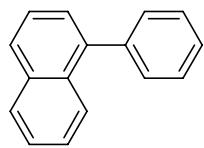


**4-Methoxy-biphenyl [T2-10, 613-37-6, Ref. 5]**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.53-7.57 (q, 4 H), 7.40-7.44 (t, 2 H), 7.29-7.33 (t, 1 H), 6.97-7.00 (m, 2 H), 3.86 (s, 3 H). MS (EI): m/z (%): 184 (100) [ $\text{M}^+$ ], 169 (44), 141 (38), 115 (26), 63 (4).

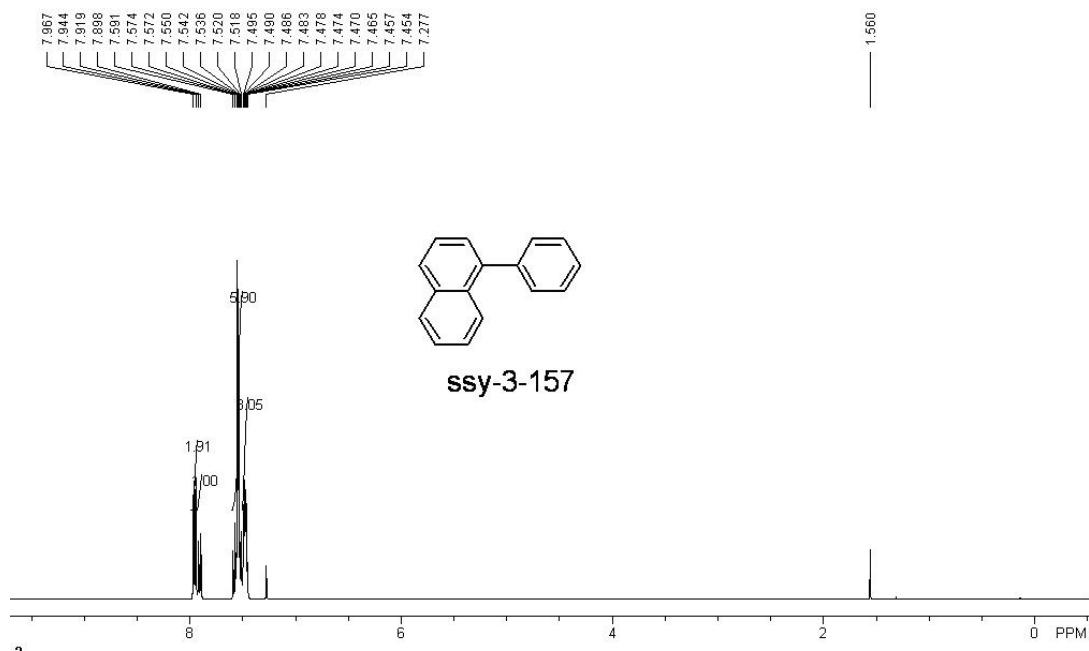


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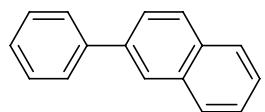


**1-phenylnaphthalene [T2-11, 605-02-7, Ref. 2]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 7.94-7.96 (d, 2 H □ J = 9.2 Hz), 7.89-7.91 (d, 1 H, J = 8.4 Hz), 7.51-7.59 (m, 6 H), 7.45-7.49 (m, 3 H). MS (EI): m/z (%): 204 (100) [M<sup>+</sup>], 203 (97), 101 (21).

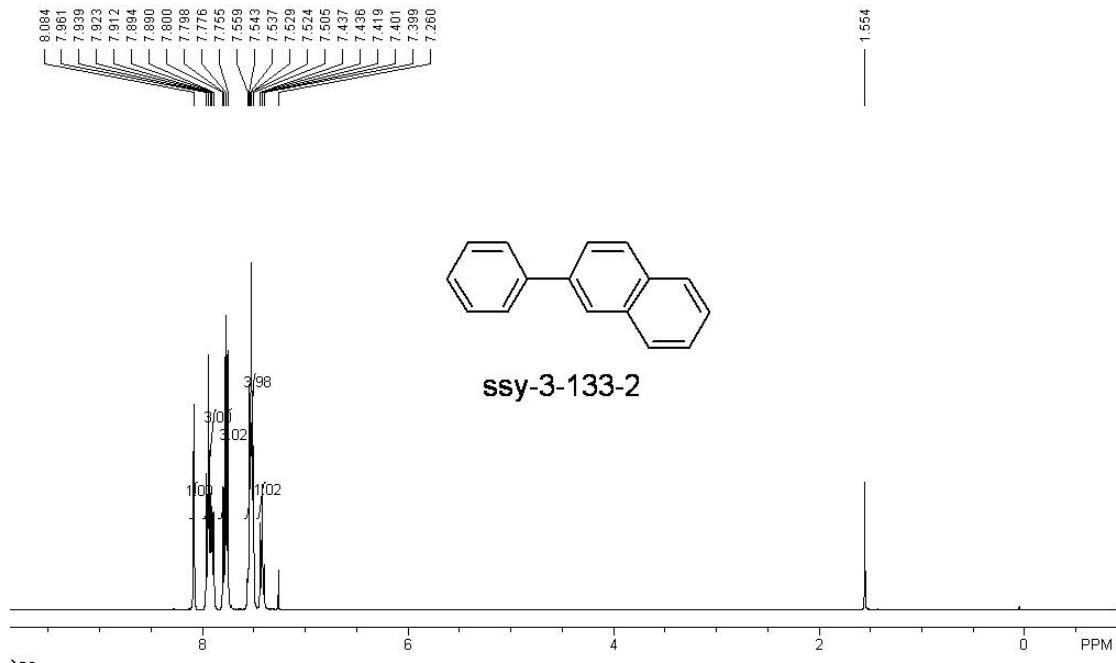


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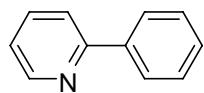


**2-phenylnaphthalene [T2-12, 612-94-2, Ref. 6]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.08 (s, 1 H), 7.89-7.96 (m, 3 H), 7.75-7.80 (m, 3 H, *J* = 8.4 Hz), 7.50-7.55 (m, 4 H), 7.39-7.43 (m, 1 H). MS (EI): m/z (%): 204 (100) [M<sup>+</sup>], 101 (11).

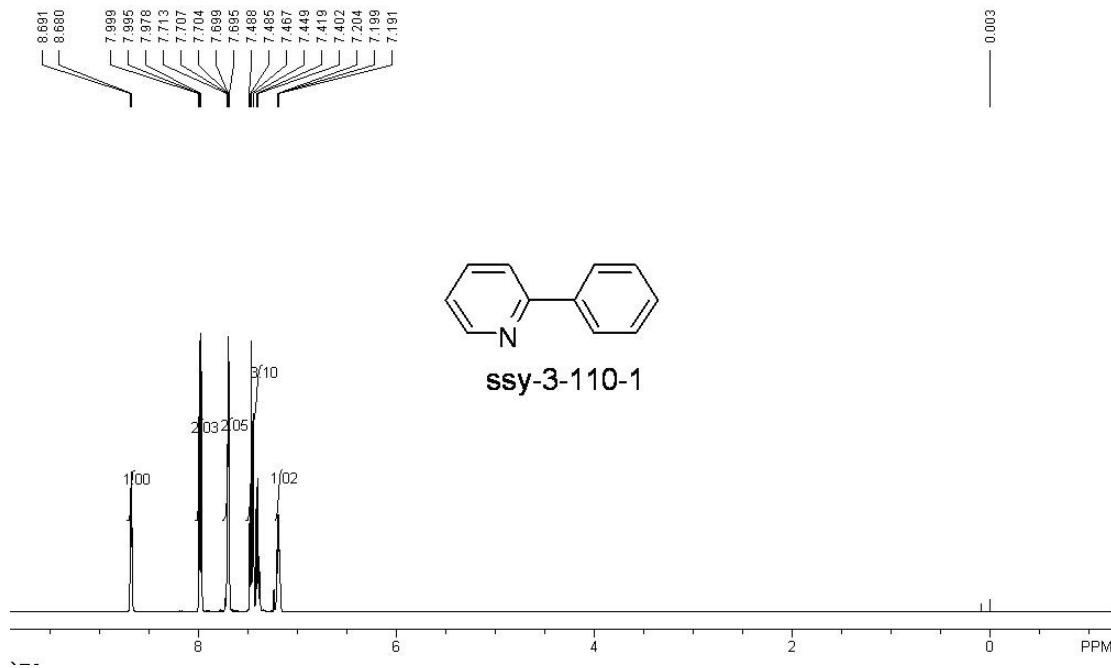


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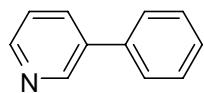


**2-Phenyl-pyridine [T2-13, 1008-89-5, Ref. 5]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ8.68-8.69 (d, 1 H, *J*=4.4 Hz), 7.97-7.99 (t, 2 H), 7.69-7.71 (m, 2 H), 7.40-7.48 (m, 3 H), 7.19-7.20 (m, 1 H). MS (EI): m/z (%): 155 (100) [M<sup>+</sup>], 154 (21), 153 (7), 115 (7), 76 (9).

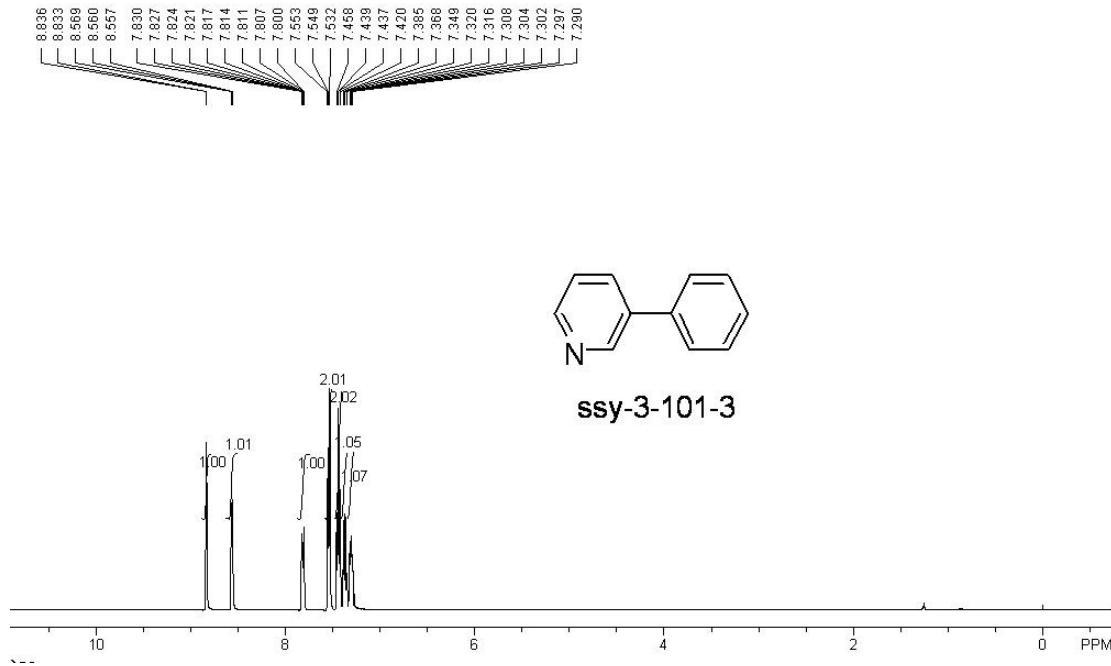


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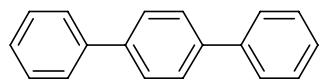


**3-Phenyl-pyridine [T2-14, 1008-88-4, Ref. 5]**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.83 (d, 1 H), 8.55-8.56 (m, 1 H), 7.80-7.83 (m, 1 H), 7.53-7.55 (m, 2 H), 7.42-7.45 (m, 2 H), 7.29-7.38 (m, 2 H). MS (EI): m/z (%): 155 (100) [ $\text{M}^+$ ], 154 (22), 153 (15), 76 (9)

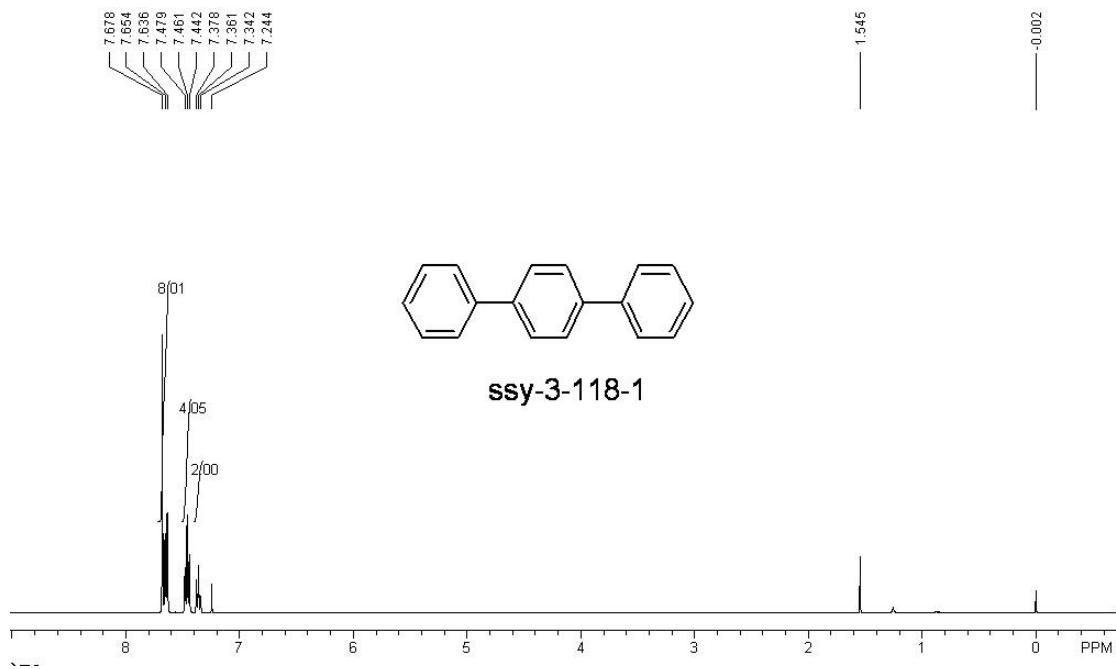


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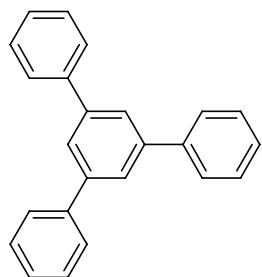


**1, 4-Diphenylbenzene [T2-15, 92-94-4, Ref. 7]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.63-7.67 (m, 8 H), 7.44-7.47 (t, 4 H, *J* = 7.2 Hz), 7.34-7.37 (t, 2 H, *J* = 7.2 Hz). MS (EI): m/z (%): 230 (100) [M<sup>+</sup>], 215 (8), 202 (10), 152 (8), 115 (12).

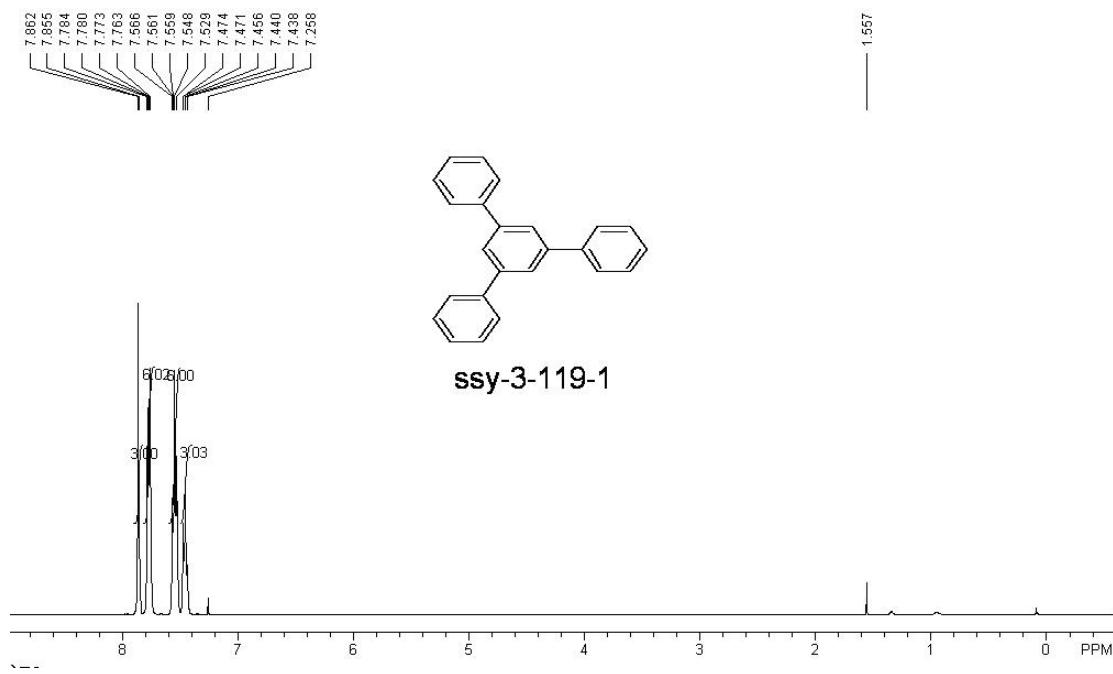


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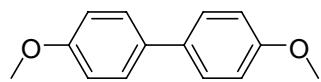


**1, 3, 5-Triphenylbenzene [T2-16, 612-71-5, Ref. 8]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.85-7.86 (d, 3 H), 7.76-7.78 (m, 6 H), 7.52-7.56 (m, 6 H), 7.43-7.47 (m, 3 H). MS (EI): m/z (%): 307(81) [M<sup>+</sup>+1], 306 (100) [M<sup>+</sup>], 289 (33), 276 (9), 228 (26), 202 (10), 153 (9), 77 (8).

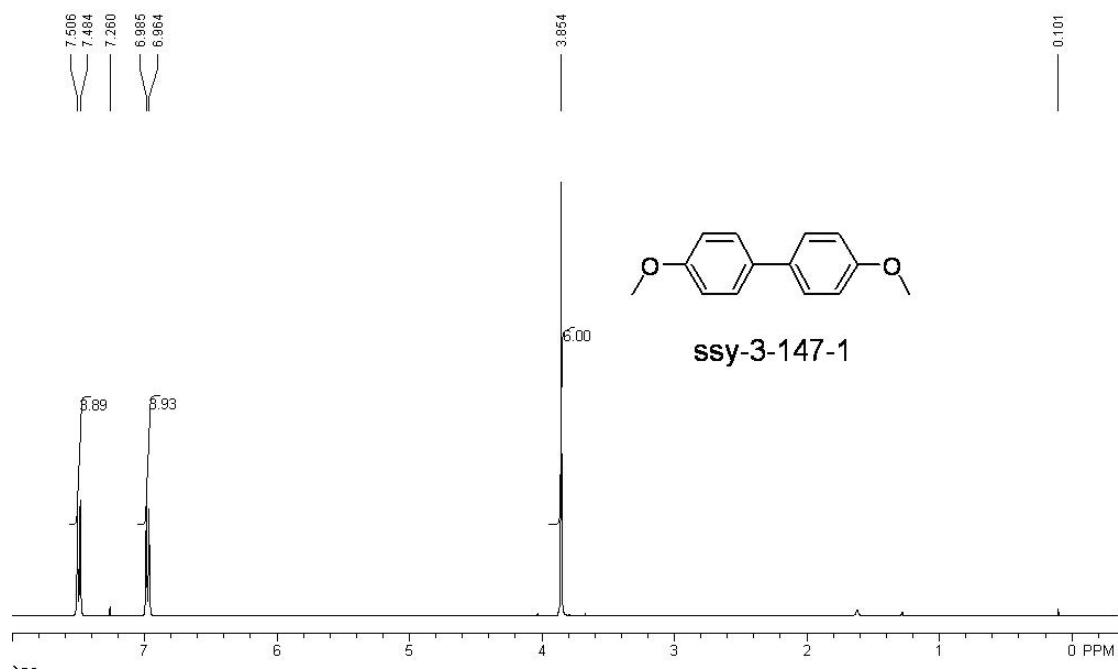


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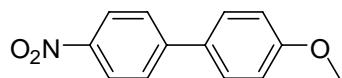


**4,4'-dimethoxy-biphenyl [T3-1, 2132-80-1, Ref. 9]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 7.48-7.50 (d, 4 H, *J* = 8.8 Hz), 6.96-6.98 (d, 4 H, *J* = 8.4 Hz), 3.85 (s, 6 H). MS (EI): m/z (%): 182 (100) [M<sup>+</sup>], 167 (55), 152 (12), 89 (11), 76 (3).

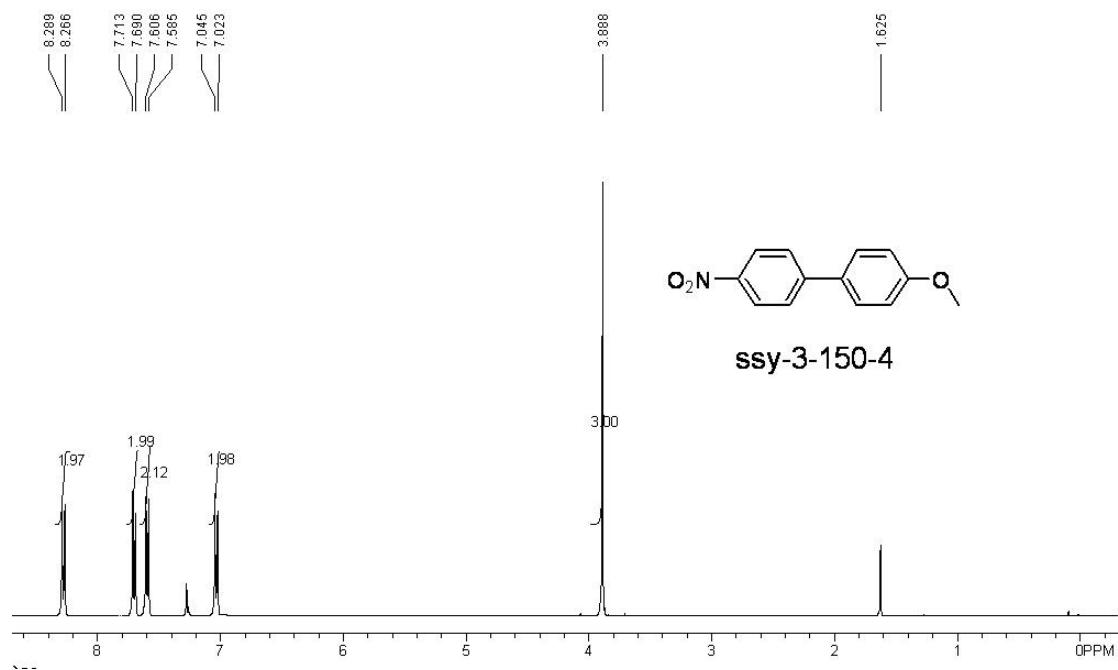


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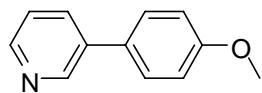


**4'-Methoxy-4-nitro-biphenyl [T3-3, 2143-90-0, Ref. 10]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.26-8.28 (d, 2 H, *J* = 9.2 Hz), 7.69-7.71 (d, 2 H, *J* = 9.2 Hz), 7.58-7.60 (d, 2 H, *J* = 8.4 Hz), 7.02-7.04 (d, 2 H, *J* = 8.8 Hz), 3.88 (s, 3 H). MS (EI): m/z (%): 229 (100) [M<sup>+</sup>], 199 (17), 183 (12), 152 (13), 139 (35), 128 (6), 63 (4).

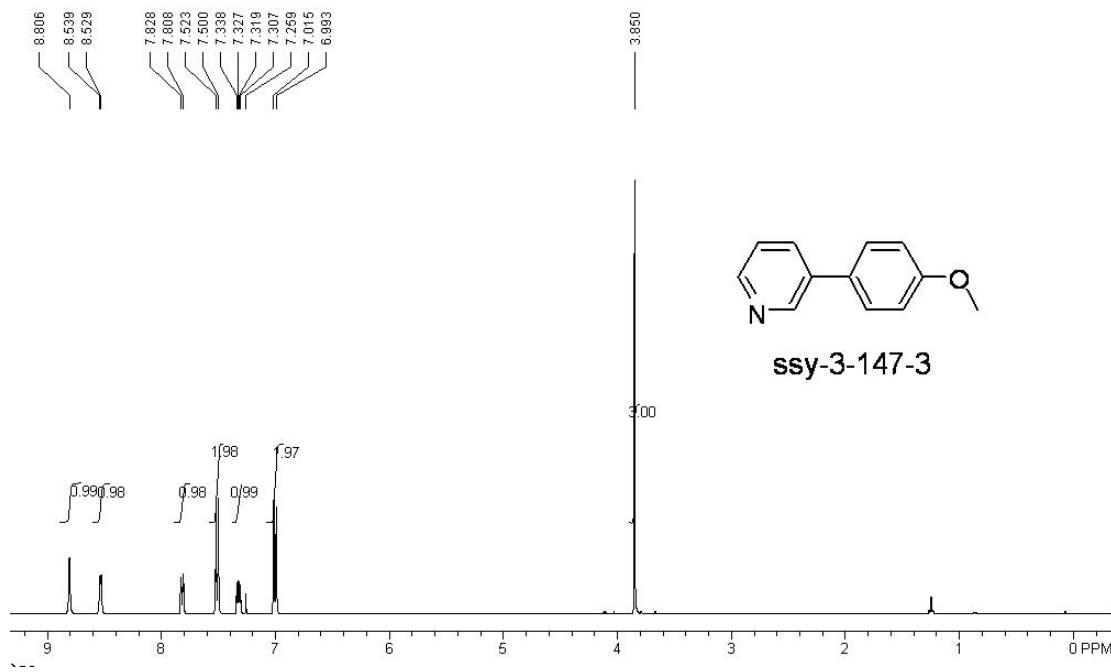


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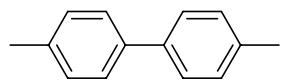


**3-(4-methoxyphenyl)pyridine [T3-4, 5958-02-1 , Ref. 5]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.80 (s, 1 H), 8.52-8.54 (d, 1 H, *J* = 4.4 Hz), 7.80-7.82 (d, 1 H, *J* = 7.6 Hz), 7.50-7.52 (d, 2 H, *J* = 8.8 Hz), 7.30-7.33 (q, 1 H), 6.99-7.01 (d, 2 H, *J* = 5.2 Hz), 3.85 (s, 3 H). MS (EI): m/z (%): 186 (16) [M<sup>+</sup>+1], 185 (100) [M<sup>+</sup>], 170 (50), 142 (37), 115 (16), 89 (7), 63 (5).

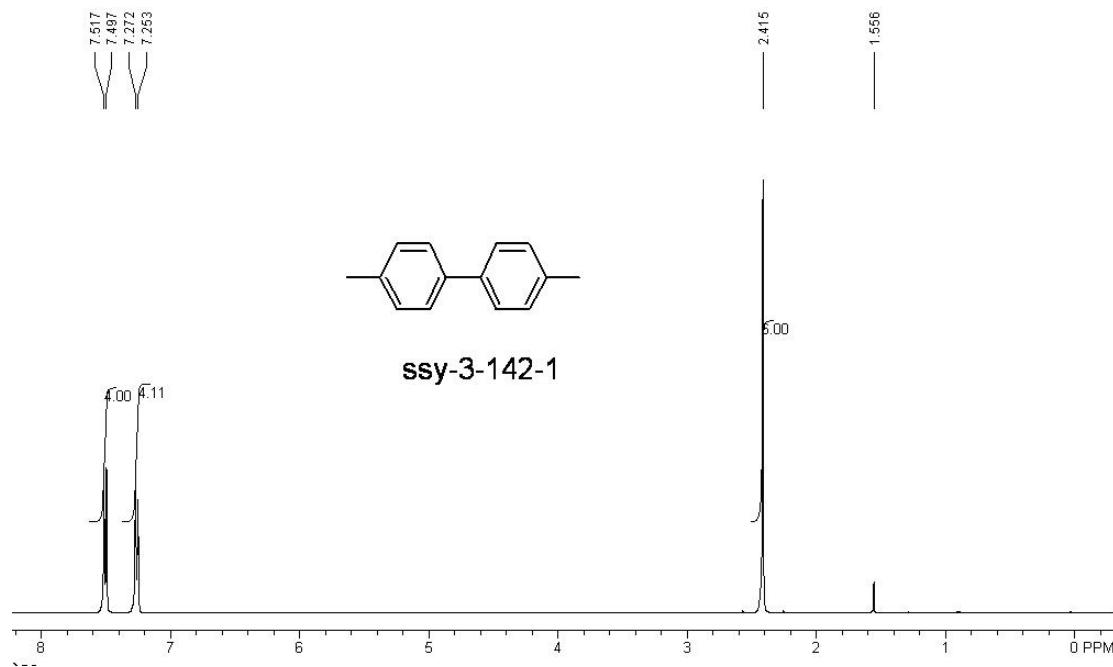


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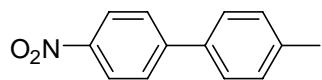


**4,4'-dimethyl-biphenyl [T3-5, 613-33-2, ref 5]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 7.49-7.51 (d, 4 H, *J* = 8.0 Hz), 7.25-7.27 (d, 4 H, *J* = 7.6 Hz), 2.41 (s, 6 H). MS (EI): m/z (%): 182 (100) [M<sup>+</sup>], 167 (55), 152 (12), 89 (11), 76 (3).

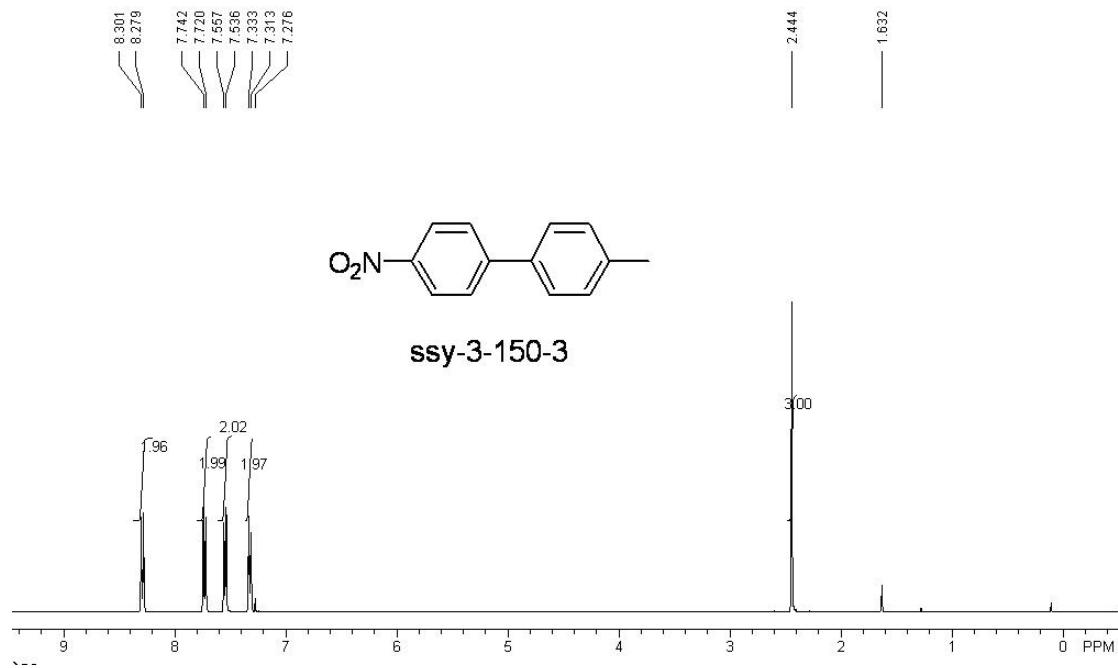


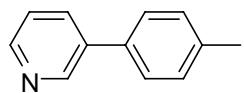
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**4-methyl-4'-nitrobiphenyl [T3-7, 2143-88-6, Ref. 11]**

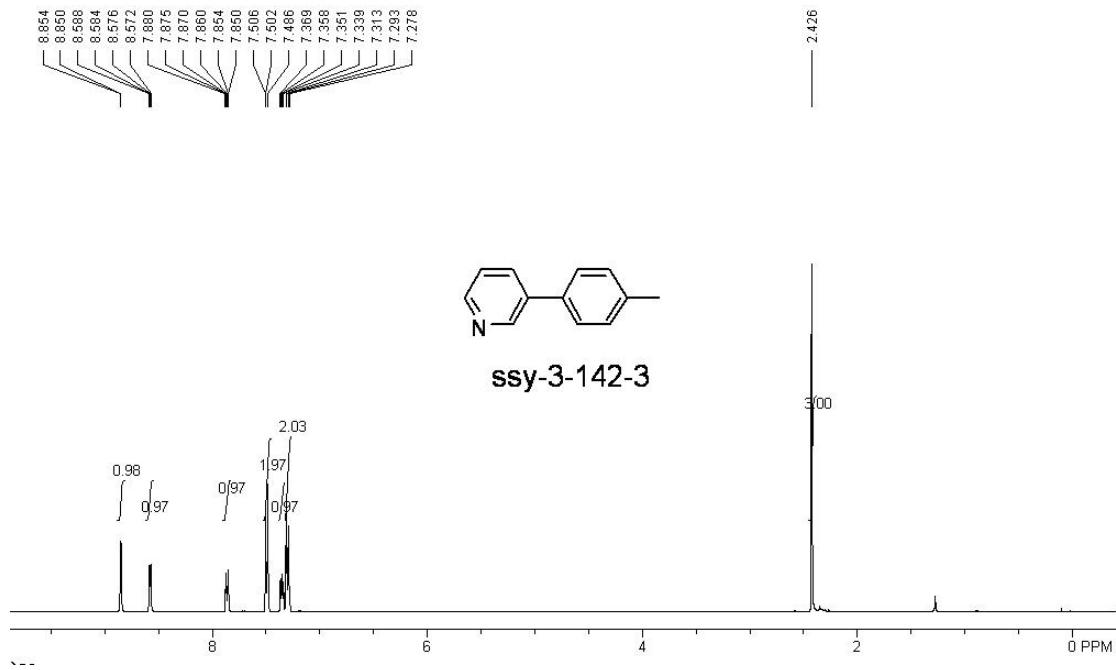
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ8.27-8.30 (d, 2 H, *J* = 8.8 Hz), 7.72-7.74 (d, 2 H, *J* = 8.8 Hz), 7.53-7.55 (d, 2 H, *J* = 8.4 Hz), 7.31-7.33 (d, 2 H, *J* = 8.0 Hz), 2.44 (s, 3 H). MS (EI): m/z (%): 214 (15) [M<sup>+</sup>+1], 213 (100) [M<sup>+</sup>], 183 (21), 165 (38), 152 (51), 115 (8).



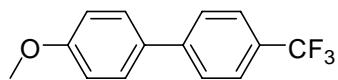


**3-(4-Methyl-phenyl)-pyridine [T3-8, 1008-88-4, Ref. 5]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.85 (d, 1 H), 8.57-8.58 (q, 1 H), 7.85-7.88 (m, 1 H), 7.48-7.50 (t, 2 H), 7.33-7.36 (m, 1 H), 7.27-7.31 (t, 2 H), 2.42 (s, 3 H). MS (EI): m/z (%): 169 (100) [M<sup>+</sup>], 154 (22), 153 (15), 76 (9).

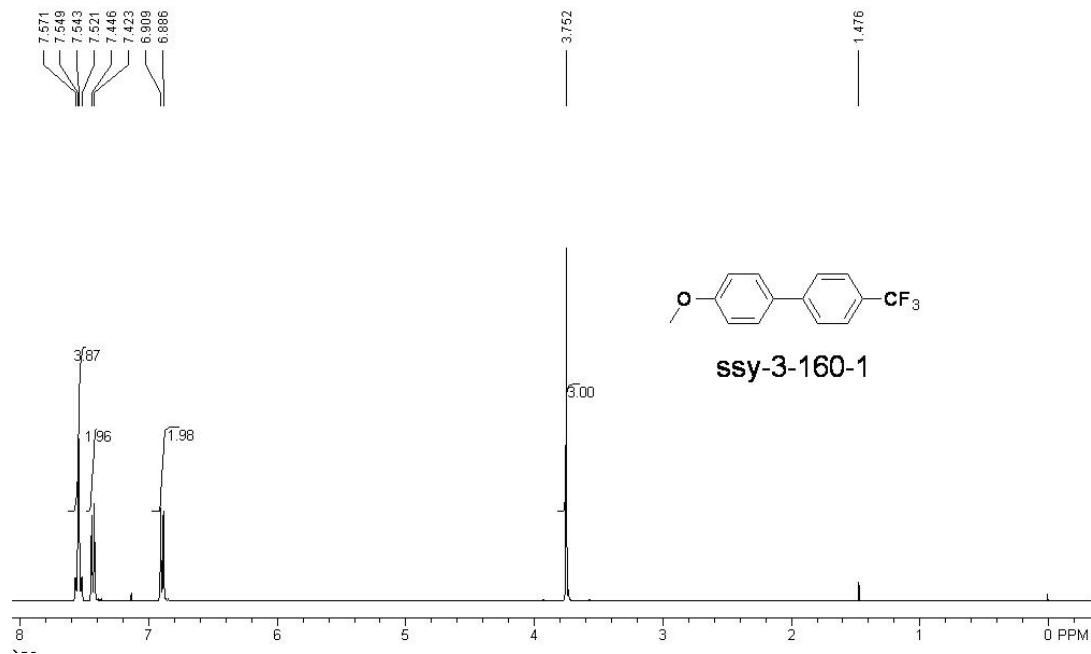


(23)

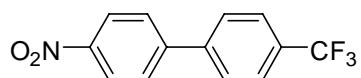


**4-Methoxy-4'-trifluoromethyl-biphenyl [T3-9, 10355-12-1, Ref. 12]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.52-7.57 (q, 4 H, *J* = 8.8 Hz), 7.42-7.44 (d, 2 H, *J* = 9.2 Hz), 6.88-6.90 (d, 2 H, *J* = 9.2 Hz), 3.75 (s, 3 H). MS (EI): m/z (%): 252 (100) [M<sup>+</sup>], 237 (26), 209 (42), 183 (8), 139 (6).

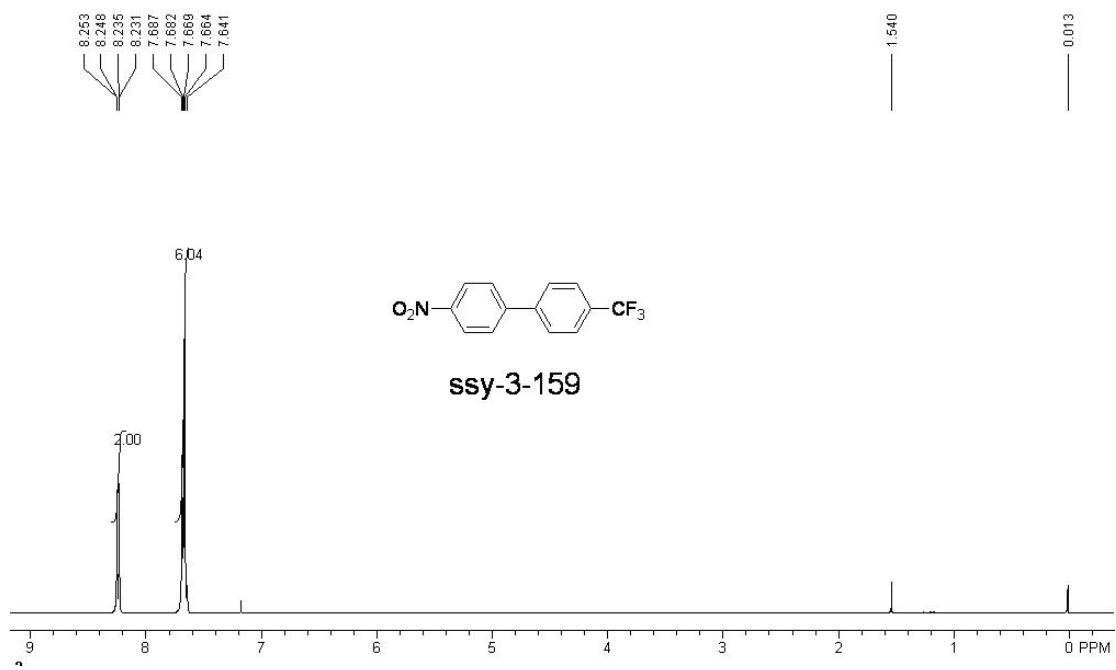


(24)

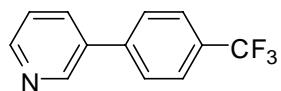


**4-nitro-4'-(trifluoromethyl)biphenyl [T3-11,80245-34-7 , Ref. 13]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.23-8.25 (q, 2 H), 7.64-7.68 (m, 6 H). MS (EI): m/z (%): 267 (100) [M<sup>+</sup>], 248 (10), 237 (40), 209 (33), 201 (50), 170 (7), 152 (51) ,75 (4).

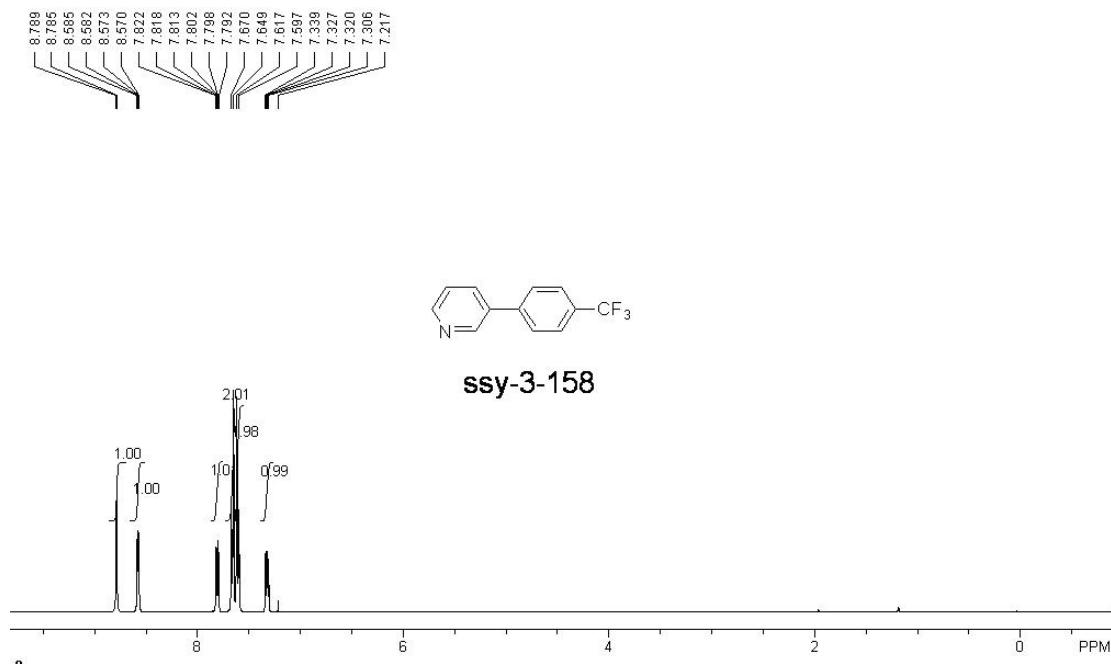


(25)



**3-(4-(trifluoromethyl)phenyl)pyridine [T3-12, 426823-25-8 , Ref. 5]**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.78 (d, 1 H), 8.57-8.58 (q, 1 H, *J* = 1.2 Hz), 7.79-7.82 (m, 1 H), 7.64-7.67 (d, 2 H, *J* = 8.4 Hz), 7.59-7.61 (d, 2 H, *J* = 8.0 Hz), 7.30-7.33 (m, 1 H). MS (EI): m/z (%): 224 (17) [M<sup>+</sup>+1], 223 (100) [M<sup>+</sup>], 204 (10), 191 (26), 154 (19), 127 (8).



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