

Supporting Information for

CuBr-Catalyzed Coupling of *N*-Tosylhydrazones and Terminal Alkynes: Synthesis of Benzofurans and Indoles

Lei Zhou, Yi Shi, Qing Xiao, Yizhou Liu, Fei Ye, Yan Zhang and Jianbo Wang*

Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Email: wangjb@pku.edu.cn

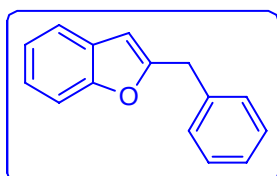
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General All reactions were performed under a nitrogen atmosphere in a 10 mL Schlenk tube. MeCN was dried over CaH₂ before use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H NMR and ¹³C NMR spectra were recorded on Varian 300 or Bruker ARX 400 spectrometer in CDCl₃ solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). *N*-Tosylhydrazones was prepared by literature procedure.¹ Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

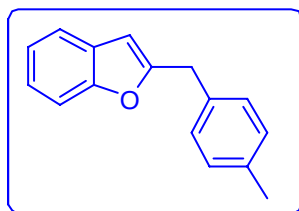
Spectral data for the products

2-Benzylbenzofuran (3a)²



¹H NMR (400 MHz, CDCl₃) δ 4.09 (s, 2H), 6.35 (s, 1H), 7.16-7.31 (m, 7H), 7.38-7.46 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 35.2, 103.5, 111.1, 120.6, 122.7, 123.6, 126.9, 128.8, 129.0, 129.1, 137.4, 155.1, 157.9;

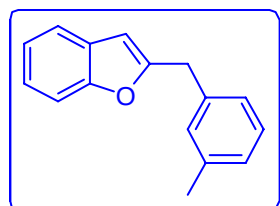
2-(4-Methylbenzyl)benzofuran (3b)



IR (film) 2917, 1454, 954, 749 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.33 (s, 3H), 4.06 (s, 2H), 6.35 (s, 1H), 7.12-7.21 (m, 6H), 7.38-7.46 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 34.7, 103.4, 111.0, 120.5, 122.6, 123.5, 128.9, 129.0, 129.4, 134.3, 136.5, 155.1, 158.3;

EI-MS (*m/z*, relative intensity): 222 (M⁺, 100), 207 (68), 178 (26), 131 (27). HRMS (ESI) calcd for C₁₆H₁₅O [(M+H)⁺] 223.1117. Found: 223.1110.

2-(3-Methylbenzyl)benzofuran (3c)

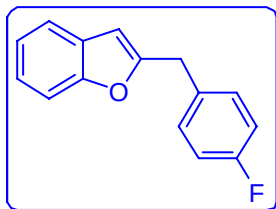


IR (film) 1454, 1252, 955, 907, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.33 (s, 3H), 4.06 (s, 2H), 6.37 (s, 1H), 7.05-7.10 (m, 3H), 7.16-7.22 (m, 3H), 7.39-7.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 35.1, 103.5, 111.1, 120.5, 122.6, 123.5, 126.1, 127.7, 128.6, 129.0,

129.8, 137.3, 138.4, 155.1, 158.1; EI-MS (*m/z*, relative intensity): 222 (M⁺, 100), 207 (60),

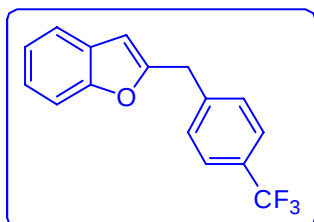
178 (28), 131 (34). HRMS (ESI) calcd for $C_{16}H_{15}O$ $[(M+H)^+]$ 223.1117. Found: 223.1109.

2-(4-Fluorobenzyl)benzofuran (3d)



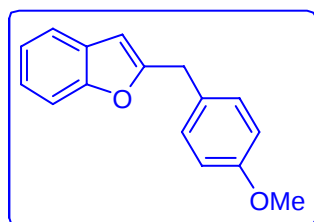
IR (film) 1603, 1509, 1455, 1224, 814, 750 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.07 (s, 2H), 6.36 (s, 1H), 6.98-7.03 (m, 2H), 7.15-7.27 (m, 4H), 7.39-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.4, 103.6, 111.1, 115.6 (d, $J = 21.3$ Hz), 120.6, 122.7, 123.7, 128.9, 130.5 (d, $J = 7.9$ Hz), 133.04 (d, $J = 3.2$ Hz), 155.1, 157.6, 161.9 (d, $J = 243.3$ Hz); EI-MS (m/z , relative intensity): 226 (M^+ , 93), 225 (100), 207 (9), 196 (14), 131 (26). HRMS (ESI) calcd for $C_{15}H_{12}FO$ $[(M+H)^+]$ 227.0866. Found: 227.0862.

2-(4-(Trifluoromethyl)benzyl)benzofuran (3e)



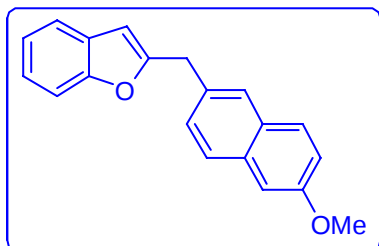
IR (film) 1323, 1164, 1122, 1067, 750 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 2H), 6.40 (s, 1H), 7.16-7.24 (m, 2H), 7.38-7.40 (m, 3H), 7.47-7.49 (m, 1H), 7.56-7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.9, 104.0, 111.1, 120.7, 122.9, 123.0, 123.9, 125.7 (q, $J = 3.7$ Hz), 128.7, 129.3 (d, $J = 32.2$ Hz), 129.4, 141.5, 155.2, 156.5; EI-MS (m/z , relative intensity): 276 (M^+ , 100), 257 (7), 207 (15), 178 (13), 131 (41). HRMS (ESI) calcd for $C_{16}H_{12}F_3O$ $[(M+H)^+]$ 277.0834. Found: 277.0833.

2-(4-Methoxybenzyl)benzofuran (3f)³



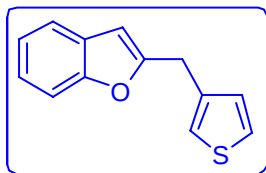
1H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.04 (s, 2H), 6.34 (s, 1H), 6.86 (m, 2H), 7.16-7.24 (m, 4H), 7.38-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3, 55.4, 103.3, 111.0, 114.2, 120.5, 122.6, 123.5, 129.0, 129.4, 130.1, 155.1, 158.4, 158.6; EI-MS (m/z , relative intensity): 220 (M^+ , 100), 205 (81), 177 (40), 161 (72), 128 (69).

2-((6-Methoxynaphthalen-2-yl)methyl)benzofuran (3g)



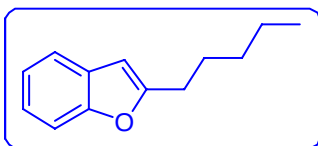
IR (film) 2923, 2852, 2089, 1607, 1263, 1030 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 3H), 4.22 (s, 2H), 6.38 (s, 1H), 7.11-7.23 (m, 4H), 7.37-7.47 (m, 3H), 7.66-7.70 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 35.1, 55.4, 103.6, 105.8, 111.1, 119.1, 120.6, 122.7, 123.6, 127.3, 127.4, 127.9, 129.0, 129.2, 129.3, 132.5, 133.6, 155.1, 157.7, 158.1; EI-MS (m/z , relative intensity): 288 (M^+ , 100), 273 (10), 257 (11), 215 (8); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{O}_2$ [$\text{M}+\text{H}$] $^+$ 289.1223. Found: 289.1217.

2-(Thiophen-3-ylmethyl)benzofuran (3h)⁴



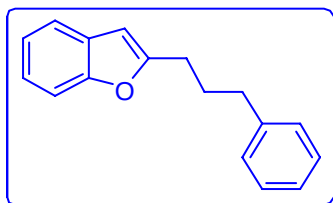
IR (film) 2916, 1454, 1254, 908, 730 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.10 (s, 2H), 6.37 (s, 1H), 7.01-7.27 (m, 5H), 7.40-7.47 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.8, 103.2, 111.0, 120.6, 122.2, 122.7, 123.6, 125.9, 128.5, 128.9, 137.3, 155.0, 157.4; EI-MS (m/z , relative intensity): 214 (M^+ , 97), 213 (100), 184 (11), 131 (10).

2-Pentylbenzofuran (3i)⁵



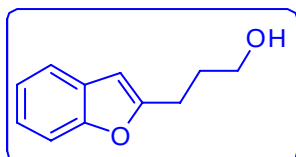
^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, J = 6.4 Hz, 3H), 1.36-1.39 (m, 4H), 1.73-1.76 (m, 2H), 2.76 (t, J = 7.6 Hz, 2H), 6.37 (s, 1H), 7.14-7.21 (m, 2H), 7.39-7.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 22.6, 27.5, 28.6, 31.5, 101.9, 110.8, 120.3, 122.5, 123.1, 129.2, 154.8, 159.9.

2-(3-Phenylpropyl)benzofuran (3j)⁶



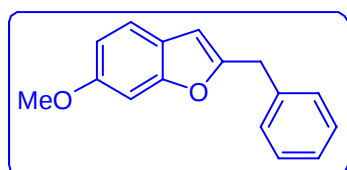
^1H NMR (400 MHz, CDCl_3) δ 2.04-2.12 (m, 2H), 2.71 (t, J = 8.0 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H), 6.38 (s, 1H), 7.17-7.22 (m, 5H), 7.27-7.31 (m, 2H), 7.39-7.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.0, 29.4, 35.4, 102.3, 110.9, 120.4, 122.6, 123.3, 126.1, 128.5, 128.7, 141.9, 154.8, 159.3.

3-(Benzofuran-2-yl)propan-1-ol (3k)⁷



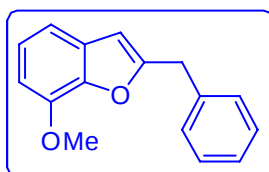
¹H NMR (400 MHz, CDCl₃) δ 1.50 (s, 1H), 2.00-2.05 (m, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 3.74, (t, *J* = 6.0 Hz, 2H), 6.41 (s, 1H), 7.18-7.26 (m, 2H), 7.40-7.49 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 24.9, 30.8, 62.1, 102.4, 110.9, 120.4, 122.6, 123.4, 129.0, 154.8, 158.8.

2-Benzyl-6-methoxybenzofuran (3l)



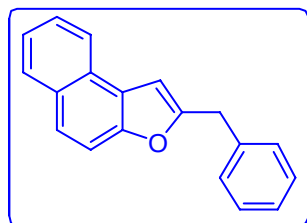
IR (film) 2918, 1629, 1492, 1149, 1106, 704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.81 (s, 3H), 4.07 (s, 2H), 6.29 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 1H), 7.24-7.33 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 35.1, 55.9, 96.1, 103.2, 111.4, 120.6, 122.2, 126.8, 128.7, 129.0, 137.6, 156.0, 156.9, 157.5; EI-MS (*m/z*, relative intensity): 238 (M⁺, 100), 223 (12), 207 (7), 195 (8), 161 (36). HRMS (ESI) calcd for C₁₆H₁₅O₂ [(M+H)⁺] 239.1066. Found: 239.1062.

2-Benzyl-7-methoxybenzofuran (3m)⁸



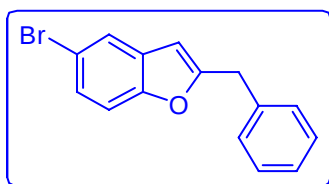
¹H NMR (400 MHz, CDCl₃) δ 3.97 (s, 3H), 4.12 (s, 2H), 6.30 (s, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 7.04-7.09 (m, 2H), 7.23-7.31 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 35.1, 56.1, 103.9, 105.9, 113.0, 123.3, 126.9, 128.7, 129.1, 130.6, 137.3, 144.1, 145.1, 158.3.

2-Benzyl-1-naphtho[2,1-b]furan (3n)



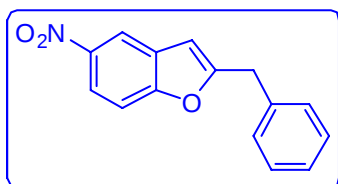
IR (film) 2919, 1575, 1384, 800, 773, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.20 (s, 2H), 6.86 (s, 1H), 7.24-7.29 (m, 1H), 7.34-7.35 (m, 4H), 7.42-7.46 (m, 1H), 7.50-7.54 (m, 1H), 7.57-7.59 (m, 1H), 7.63-7.66 (m, 1H), 7.90 (m, 1H), 8.04 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 35.3, 102.7, 112.4, 123.6, 124.0, 124.4, 124.4, 126.1, 126.9, 128.8, 129.1, 130.4, 137.6, 152.4, 157.2; EI-MS (*m/z*, relative intensity): 258 (M⁺, 100), 228 (10), 181 (46), 152 (20). HRMS (ESI) calcd. for C₁₉H₁₅O [(M+H)⁺] 259.1117. Found: 259.1120.

2-Benzyl-5-bromobenzofuran (3o)



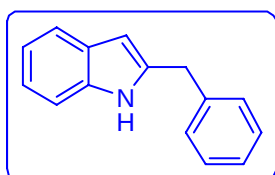
IR (film) 1596, 1444, 1259, 953, 794, 705 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.07 (s, 2H), 6.28 (s, 1H), 7.23-7.34 (m, 7H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 35.1, 103.0, 112.5, 115.7, 123.2, 126.4, 127.1, 128.8, 129.0, 130.9, 136.9, 153.8, 159.4; EI-MS (m/z , relative intensity): 288 [$(\text{M}^+(\text{Br}^{81})$), 98], 286 [$(\text{M}^+(\text{Br}^{79})$), 98], 209 (33), 178 (54), 152 (20). HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{Br}^{81}\text{O}$ [$(\text{M}+\text{H})^+$] 284.9909. Found: 284.9905.

2-Benzyl-5-nitrobenzofuran (3p)



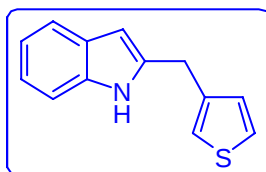
IR (film) 2917, 1523, 1263, 753, 707 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.14 (s, 2H), 6.50 (s, 1H), 7.30-7.37 (m, 5H), 7.45 (d, J = 9.2 Hz, 1H), 8.12-8.15 (m, 1H), 8.37-8.38 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 35.1, 104.2, 111.3, 117.0, 119.6, 127.3, 128.9, 129.1, 129.3, 136.3, 144.2, 157.9, 161.7; EI-MS (m/z , relative intensity): 253 (M^+ , 100), 206 (21), 178 (36), 152 (12). HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{12}\text{NO}_3$ [$(\text{M}+\text{H})^+$] 254.0811. Found: 254.0808.

2-Benzyl-1H-indole (3q)⁹



^1H NMR (400 MHz, CDCl_3) δ 4.12 (s, 2H), 6.32 (s, 1H), 7.04-7.12 (m, 2H), 7.22-7.26 (m, 4H), 7.30-7.34 (m, 2H), 7.53-7.55 (m, 1H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 34.9, 101.3, 110.6, 119.9, 120.1, 121.5, 126.9, 128.8, 129.0, 136.4, 137.9, 138.7.

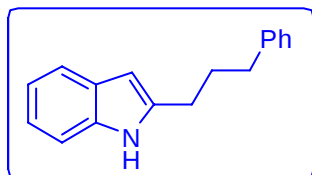
2-(Thiophen-3-ylmethyl)-1H-indole (3r)



IR (film) 3403, 2922, 1456, 1296, 907, 730 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.12 (s, 2H), 6.32 (s, 1H), 6.85 (d, J = 4.8 Hz, 1H), 7.04-7.13 (m, 3H), 7.23-7.29 (m, 2H), 7.536 (m, 1H), 7.77 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.5, 100.9, 110.6, 119.9, 120.2, 121.5, 122.0, 126.3, 128.5, 128.8, 136.3, 137.5, 139.0; EI-MS (m/z , relative intensity): 213 (M^+ , 100), 212 (85), 180 (9), 167 (11), 130 (30); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{NS}$ [$(\text{M}+\text{H})^+$] 214.0685.

Found: 214.0678.

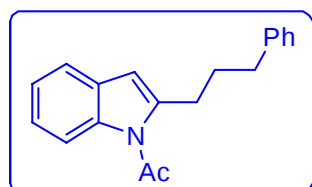
2-(3-Phenylpropyl)-1H-indole (3s)¹⁰



¹H NMR (400 MHz, CDCl₃) δ 2.03-2.10 (m, 2H), 2.70-2.80 (m, 4H), 6.26 (s, 1H), 7.05-7.13 (m, 2H), 7.18-7.32 (m, 6H), 7.52-7.54 (m, 1H), 7.81 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 27.8, 30.8, 35.4, 99.9, 110.4, 119.8, 119.9, 121.2, 126.1, 128.7, 129.0, 136.0,

139.5, 141.9.

1-(2-(3-Phenylpropyl)-1H-indol-1-yl)ethanone (3t)¹¹



¹H NMR (400 MHz, CDCl₃) δ 2.01-2.09 (m, 2H), 2.73-2.77 (m, 5H), 3.05 (t, *J* = 7.2 Hz, 2H), 6.42 (s, 1H), 7.19-7.31 (m, 7H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 27.8, 30.2, 30.6, 35.7, 108.5, 114.8, 120.4, 123.1, 123.6,

126.0, 128.53, 128.59, 128.62, 128.68, 142.1, 142.6, 170.4.

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