Supporting Information
for DOI: 10.1055/s-0033-1338871
© Georg Thieme Verlag KG Stuttgart · New York 2013
Supplementary Material

TBHP/I$_2$-promoted oxidative coupling of azoles with benzyl compounds via cleavage of non-activated sp$^3$ C-H Bonds under solvent-free conditions

Xiang Liu, $^{a,b}$ Guiqin Yu, $^{a,b}$ Jihui Li, $^{a,b}$ Dong Wang $^{a,b}$ Yongxin Chen, $^{a,b}$ Keqin Shi, $^{a,b}$ and Baohua Chen$^{a,b}$

$^a$State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Gansu Lanzhou 730000, P. R. China
$^b$Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Lanzhou, 730000, P. R. of China
E-mail: chbh@lzu.edu.cn

Table of Contents

1. General procedure of synthesis ----------------- S2
2. Spectral data of the compounds ----------------- S3-S14
3. $^1$H and $^{13}$C NMR spectra of the compounds ----------------- S15-S39
1. General Remarks

Column chromatography was carried out on silica gel. $^1$H NMR spectra were recorded on 300 or 400 MHz in CDCl$_3$ or Dimethyl Sulfoxide-D$_6$ and $^{13}$C NMR spectra were recorded on 75 or 100 MHz in CDCl$_3$ or Dimethyl Sulfoxide-D$_6$ using TMS as internal standard. Melting points were determined on a microscopic apparatus and were uncorrected. Copies of all desired products $^1$H NMR and $^{13}$C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

The general procedure of the reaction between azoles and toluenes:

**synthesis of 3aa (1-benzyl-1H-benzo[d][1,2,3]triazole):**

All reactions were performed on a 0.50 mmol scale relative to azoles. The benzotriazole (1a) (0.50 mmol), toluene (2a) (1.50 mmol), I$_2$ (0.050 mmol) and TBHP (2 eq) were taken in a round bottom flask equipped with stirrer. The resulting mixture was stirred for 8 h at 100 °C. After cooling to room temperature, to the reaction mixture was added water (2 mL), and extracted with ester (3×10 mL). The combined organic phases were washed with brine (2×5 mL), dried over anhydrous MgSO$_4$ and concentrated in vacuo. The residue was subjected to flash column chromatography with hexanes/EtOAc (10/1) as eluent to obtain the desired 3aa a light yellow solid (90% yield). The identity and purity of the products was confirmed by $^1$H and $^{13}$C NMR spectroscopic analysis.
2. Spectral data of the compounds:

1-benzyl-1H-benzo[d][1,2,3]triazole 3aa was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as light yellow solid (yield: 90%), mp: 113-115 °C. $^1$H NMR (300 MHz, DM): $\delta$: 8.04-8.06 (d, $J=7.8$Hz, 1H), 7.25-7.38 (m, 8H), 5.82 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 146.2, 134.7, 132.7, 128.9, 128.3, 127.5, 127.3, 123.8, 119.9, 109.6, 52.1. ESI HRMS: calcd. for C$_{13}$H$_{11}$N$_3$ [M+H]$^+$: 210.1026, found: 210.1022.

1-(4-methyl-benzyl)-1H-benzo[d][1,2,3]triazole 3ab was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as light white solid (yield: 80%), mp: 102-104 °C. $^1$H NMR (300 MHz, d$_6$-DMSO): $\delta$: 8.02-8.05 (d, $J=8.4$Hz 1H), 7.28-7.37 ( m, 3H ), 7.09-7.18 (dd, $J=9.3$Hz, $J=17.4$Hz, 4H), 5.77 (s, 2H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 146.1, 138.1, 132.6, 131.6, 129.5, 127.5, 127.2, 123.7, 119.8, 109.7, 51.9, 21.0. ESI HRMS: calcd. for C$_{14}$H$_{13}$N$_3$ [M+H]$^+$: 224.1182, found: 224.1186.
1-(3-methyl-benzyl)-1H-benzo[d][1,2,3]triazole **3ac** was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as light yellow solid (yield: 75%), mp: 116-118 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 8.04-8.07 (d, J=8.4Hz, 1H), 7.06-7.39 (m, 7H), 5.79 (s, 2H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 146.2, 138.7, 134.6, 132.7, 129.1, 128.7, 128.2, 127.3, 124.6, 123.8, 119.9, 109.7, 52.1, 21.2. ESI HRMS: calcd. for C$_{14}$H$_{13}$N$_3$ [M+H]$^+$: 224.1182, found: 224.1183.

1-(2-methyl-benzyl)-1H-benzo[d][1,2,3]triazole **3ad** was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as white solid (yield: 82%), mp: 80-82 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 8.03-8.06 (d, J=9Hz, 1H), 7.02-7.36 (m, 6H), 5.82 (s, 2H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 146.1, 136.4, 132.8, 132.4, 130.8, 128.5, 128.4, 127.2, 126.3, 123.7, 119.9, 109.8, 50.6, 19.1. ESI HRMS: calcd. for C$_{14}$H$_{13}$N$_3$ [M+H]$^+$: 224.1182, found: 224.1181.
1-(3,5-dimethyl-benzyl)-1H-benzo[d][1,2,3]triazole 3ae was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as white solid (yield: 93%), mp: 96-98 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ: 8.04-8.07 (d, J=9Hz, 1H), 7.31-7.40 (m, 3H), 6.89-6.92 (d, J=9Hz, 3H), 5.74 (s, 2H), 2.23 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 146.2, 138.5, 134.6, 132.7, 129.9, 127.2, 125.2, 123.8, 119.8, 109.8, 52.1, 21.1. ESI HRMS: calcd. for C$_{15}$H$_{15}$N$_3$ [M+H]$^+$: 238.1339, found: 238.1337.

1-(4-bromobenzyl)-1H-benzo[d][1,2,3]triazole 3af was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as light brown solid (yield: 81%), mp: 120-122 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ: 8.05-8.08 (d, J=9Hz, 1H), 7.28-7.45 (m, 5H), 7.12-7.15 (t, J=5.6Hz, 2H), 5.78 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 146.1, 133.6, 132.5, 132.0, 129.1, 127.5, 124.0, 122.4, 119.9, 109.4, 51.4. ESI HRMS: calcd. for C$_{13}$H$_{10}$BrN$_3$ [M+H]$^+$: 288.0131, found: 288.0135.
1-(4-chlorobenzyl)-1H-benzo[d][1,2,3]triazole 3ag was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as light brown solid (yield: 74%), mp: 92-94°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 8.06-8.08 (dd, J=0.9Hz, J=4.8Hz, 1H), 7.18-7.44 (m, 7H), 5.80 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 146.1, 134.3, 133.1, 132.5, 129.1, 128.8, 127.5, 124.0, 120.0, 109.4, 51.3. ESI HRMS: calcd. for C$_{13}$H$_{10}$ClN$_3$ [M+H]$^+$: 244.0636, found: 244.0633.

1-(2-chlorobenzyl)-1H-benzo[d][1,2,3]triazole 3ah was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as white solid (yield: 77%). mp: 85-87°C $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 8.07-8.10 (d, J=9Hz, 1H), 7.18-7.45 (m, 6H), 6.94-7.18 (m, 1H), 5.97 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 145.9, 132.8, 132.77, 132.4, 129.7, 129.6, 127.5, 127.2, 123.9, 119.9, 109.5, 49.0. ESI HRMS: calcd. for C$_{13}$H$_{10}$ClN$_3$ [M+H]$^+$: 244.0636, found: 244.0637.
1-benzhydryl-1H-benzo[d][1,2,3]triazole **3ai** was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as white solid (yield: 97%), mp: 71-73°C. $^1$H NMR (300 MHz, CDCl₃): δ: 8.05-8.08 (d, J=9.0Hz, 1H), 7.11-7.39 (m, 13H), 7.08-7.11 (m, 1H). $^{13}$C NMR (100 MHz, CDCl₃): δ: 146.2, 137.6, 132.9, 128.7, 128.3, 128.2, 127.2, 123.8, 110.5, 67.0. ESI HRMS: calcd. for C₁₉H₁₅N₃ [M+H]$^+$: 286.1339, found: 286.1337.

1-(bis(4-butylphenyl)methyl)-1H-benzo[d][1,2,3]triazole **3aj** was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as white solid (yield: 92%), mp: 218-220°C. $^1$H NMR (300 MHz, CDCl₃): δ: 8.02-8.05 (d, J=9.0Hz, 1H), 7.14-7.33 (m, 12H), 1.26 (s, 18H). $^{13}$C NMR (100 MHz, CDCl₃): δ: 151.1, 146.1, 134.8, 132.9, 127.9, 127.0, 125.5, 123.6, 119.9, 110.6, 66.5, 34.4, 31.1. ESI HRMS: calcd. for C₂₇H₃₁N₃ [M+H]$^+$: 398.2591, found: 398.2588.
1-((4-phenyl-phenyl)(phenyl)methyl)-1H-benzo[d] triazole 3ak was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as white solid (yield: 85%), mp: 187-189°C. $^1$H NMR (300 MHz, d$_6$-DMSO): δ: 8.09-8.12 (d, J=9Hz, 1H), 7.32-7.78 (m, 18H). $^3$C NMR (100 MHz, d$_6$-DMSO): δ: 144.7, 139.4, 138.9, 137.9, 137.2, 132.6, 128.4, 128.3, 128.2, 127.7, 126.2, 118.8, 110.3, 64.0. ESI HRMS: calcd. for C$_{25}$H$_{19}$N$_3$ [M+H]$^+$: 362.1652, found: 362.1655.

1-benzyl-1H-benzo[d]imidazole 3al was purified by flash chromatography (Hexane-EtOAc, v/v=10/1) as white solid (yield: 53%), mp: 153-155°C. $^1$H NMR (300 MHz, CDCl$_3$): δ: 7.95 (s, 1H), 7.82-7.85 (d, J=7.2, 1H), 7.16-7.35 (m, 8H), 5.34 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 143.8, 143.1, 135.4, 133.9, 129.0, 128.2, 127.0, 123.0, 122.2, 120.3, 109.9, 48.8. ESI HRMS: calcd. for C$_{14}$H$_{12}$N$_2$ [M+H]$^+$: 209.1073, found: 209.1074.
1-(1-phenylethyl)-1H-benzo[d][1,2,3]triazole **3am** was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow liquid (yield: 80%); 

$^1$H NMR (300 MHz, CDCl$_3$): δ: 8.01-8.04 (d, J=9Hz, 1H), 7.22-7.37 (m, 8H), 5.09-6.06 (dd, J=6Hz, J=15Hz, 1H), 2.14-2.17 (d, J=9Hz, 3Hz). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 146.2, 140.0, 128.8, 128.3, 128.1, 127.2, 126.9, 126.2, 119.8, 110.0, 58.3, 21.0. ESI HRMS: calcd. for C$_{14}$H$_{13}$N$_3$ [M+H]$^+$: 224.1182, found: 224.1187.

1-benzhydryl-6-chloro-1H-benzo[d][1,2,3]triazole **3ba** was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:94%), mp: 146-148°C. $^1$H NMR (300 MHz, CDCl$_3$): δ: 8.04-8.05 (m, 1H), 7.02-7.38 (m, 7H), 7.17-7.19 (m, 5H), 6.95-6.98 (d, J=9.0Hz 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 146.9, 137.2, 131.7, 129.7, 128.8, 128.6, 128.3, 128.2, 119.4, 111.5, 67.4. ESI HRMS: calcd. for C$_{19}$H$_{14}$ClN$_3$ [M+H]$^+$: 320.0949, found: 320.0944.
1-benzhydryl-5-chloro-1H-benzo[d][1,2,3]triazole **4ba** was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:94%), mp: 130-132°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.98-8.01 (d, J=9Hz, 1H), 7.30-7.37 (m, 8H), 7.18-7.27 (m, 4H), 7.09 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 151.5, 148.2, 137.2, 133.8, 128.9, 128.6, 128.2, 125.1, 121.0, 110.2, 67.3. ESI HRMS: calcd. for C$_{19}$H$_{14}$ClN$_3$ [M+H]$^+$: 320.0949, found: 320.0945.

1-benzhydryl-6-chloro-1H-benzo[d]imidazole **3ca** was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as white solid (yield:97%), mp: 190-192°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.80 (s, 1H), 7.61 (s, 1H), 7.36-7.38 (m, 6H), 7.13-7.15 (m, 5H), 7.00-7.03 (d, J=9Hz, 1H), 6.72 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 167.9, 144.9, 144.6, 143.7, 137.6, 129.1, 128.7, 128.1, 123.5, 120.1, 111.6, 63.9. ESI HRMS: calcd. for C$_{20}$H$_{15}$ClN$_2$ [M+H]$^+$: 319.0997, found: 319.0993.
1-benzhydryl-5-chloro-1H-benzo[d]imidazole 4ca was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as white solid (yield:97%), mp: 200-202°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.72-7.75 (d, $J$=9Hz, 1H), 7.61 (s, 1H), 7.36-7.38 (m, 6H), 7.24-7.25 (m, 1H), 7.12-7.14 (t, $J$=3Hz, 5H), 6.69 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 164.7, 147.9, 144.6, 144.1, 137.6, 129.1, 128.7, 128.1, 123.2, 121.3, 110.8, 63.7. ESI HRMS: calcd. for C$_{20}$H$_{15}$ClN$_2$ [M+H]$^+$: 319.0997, found: 319.0998.

1-benzhydryl-6-nitro-1H-benzo[d]imidazole 3da was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:96%), mp: 108-110°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 8.73 (s, 1H), 8.09-8.12 (d, $J$=9Hz, 1H), 7.81 (s, 1H), 7.39-7.41 (m, 6H), 7.15-7.27 (m, 5H), 6.82 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 148.2, 146.1, 143.8, 137.1, 132.1, 129.2, 128.9, 128.0, 118.7, 117.1, 110.9, 64.3. ESI HRMS: calcd. for C$_{20}$H$_{15}$N$_3$O$_2$ [M+H]$^+$: 330.1237, found: 330.1234.
1-benzhydryl-5-nitro-1H-benzo[d]imidazole 4da was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:96%), mp: 146-148°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 8.20-8.21 (d, J=1.2Hz, 1H), 8.17-8.19 (d, J=3.6Hz, 1H), 7.85-7.90 (m, 2H), 7.38-7.43 (m, 6H), 7.15-7.27 (m, 4H), 6.86 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 148.4, 147.0, 143.8, 137.1, 133.0, 129.3, 129.0, 128.1, 120.6, 118.3, 107.7, 64.1. ESI HRMS: calcd. for C$_{20}$H$_{15}$N$_3$O$_2$ [M+H]$^+$: 330.1237, found: 330.1239.

1-benzhydryl-1H-benzo[d]imidazole 3ea was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as white solid (yield:90%), mp: 160-162°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.82-7.85 (d, J=9.0Hz, 1H), 7.61 (s, 1H), 7.26-7.37 (m, 6H), 7.13-7.25 (m, 7H), 6.74 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 144.1, 142.5, 138.1, 134.1, 128.9, 128.5, 128.2, 122.9, 122.4, 120.4, 110.7, 63.6. ESI HRMS: calcd. for C$_{20}$H$_{16}$N$_2$ [M+H]$^+$: 285.1386, found: 285.1382.
1-benzhydryl-2-(trifluoromethyl)-1H-benzo[d]imidazole 3fa was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:73%), mp: 127-129°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.87-7.90 (d, J=9.0Hz, 1H), 7.25-7.36 (m, 6H), 7.06-7.17 (m, 7H), 6.75-6.77 (d, J=6Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 152.9, 141.5, 137.2, 135.1, 128.8, 128.5, 127.9, 125.1, 123.4, 121.7, 117.9, 113.9, 63.8. ESI HRMS: calcd. for C$_{21}$H$_{15}$F$_3$N$_2$ [M+H]$^+$: 353.1260, found: 353.1263.

1-benzhydryl-2-methyl-1H-benzo[d]imidazole 3ga was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:62%), mp: 139-141°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.69-7.72 (d, J=9.0Hz, 1H), 7.19-7.35 (m, 6H), 7.13-7.16 (m, 5H), 6.88-6.98 (dd, J=9.0Hz, J=15Hz, 1H), 6.86-6.88 (m, 1H), 6.58-6.60 (d, J=6Hz, 1H), 2.54 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 153.0, 142.8, 137.8, 135.7, 128.8, 128.3, 128.26, 122.1, 121.8, 119.1, 111.8, 63.2, 15.1. ESI HRMS: calcd. for C$_{21}$H$_{18}$N$_2$ [M+H]$^+$: 299.1543, found: 299.1546.
1-benzhydryl-2-phenyl-1H-benzo[d]imidazole 3ha was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:57%), mp: 159-161°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.81-7.84 (d, J=9.0Hz, 1H), 7.50-7.61 (m, 2H), 7.44-7.47 (m, 3H), 7.26-7.33 (m, 7H), 7.13-7.23 (m, 4H), 6.84-6.99 (m, 2H), 6.81 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 154.9, 143.4, 141.8, 138.2, 134.7, 130.5, 129.9, 129.6, 128.7, 128.1, 128.0, 122.6, 122.3, 119.9, 113.4, 63.8. ESI HRMS: calcd. for C$_{26}$H$_{20}$N$_2$ [M+H]$^+$: 361.1699, found: 361.1697.

1-benzhydryl-2-(4-chlorophenyl)-1H-benzo[d]imidazole 3ia was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as yellow solid (yield:62%), mp: 194-196°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.80-7.83 (d, J=8.4Hz, 1H), 7.52-7.55 (d, J=9.0Hz, 2H), 7.41-7.43 (d, J=8.4Hz, 2H), 7.22-7.33 (m, 6H), 7.11-7.18 (m, 1H), 6.92-7.02 (m, 6H), 6.79-6.82 (d,
J=9.0Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 153.6, 143.3, 138.0, 136.3, 134.7, 130.9, 128.9, 128.8, 128.7, 128.2, 128.1, 122.8, 122.4, 120.0, 113.4, 63.9. ESI HRMS: calcd. for C$_{26}$H$_{19}$ClN$_2$ [M+H]$^+$: 395.1310, found: 395.1313.

1-benzhydryl-2-(4-methoxyphenyl)-1H-benzo[d]imidazole 3ja was purified by flash chromatography (Hexane-EtOAc, v/v=5/1) as white solid (yield:63%), mp: 159-161°C. $^1$H NMR (300 MHz, CDCl$_3$): δ: 7.79-7.82 (d, J=9.0Hz, 1H), 7.53-7.56 (dd, J=6.6Hz, J=2.1Hz, 2H), 7.16-7.32 (m, 6H), 7.12-7.15 (m, 5H), 6.95-6.99 (m, 4H), 6.80-6.81 (d, J=3Hz, 1H), 3.86 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ: 160.9, 154.4, 143.3, 138.3, 134.7, 131.0, 128.7, 128.1, 128.0, 122.6, 122.4, 122.1, 119.7, 114. 1, 113.3, 63.7, 55.3. ESI HRMS: calcd. for C$_{27}$H$_{22}$N$_2$O [M+H]$^+$: 391.1805, found: 391.1807.
3. $^1$H and $^{13}$C NMR spectra of the compounds

![NMR Spectra Image]
3ah