Supporting Information

for

Highly Efficient Oxidative Carbon-Carbon Coupling with SBA-15-Support Iron Terpyridine Catalyst

Peng Lian, Cong-Ying Zhou, Song Xiang, Chi-Ming Che a,*

aDepartment of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, China

cmche@hku.hk
**General Experimental Section:** Reagents were obtained commercially and used without further purification unless indicated otherwise. Solvent was removed under reduced pressure and the residue obtained was chromatographed on a silica gel column (230-400 mesh) using a gradient solvent system (EtOAc / n-hexane as eluant unless specified otherwise). $^1$H and $^{13}$C NMR spectra were measured on Bruker DPX-500, DPX-400 or DPX-300 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were determined on a Finnigan MAT 95 mass spectrometer. Atomic absorption spectra were measured on Perkin Elmer 3110 atomic absorption spectrometer. Solid diffuse-reflectance UV/vis data were obtained from a Perkin Elmer Lambda 900 UV/vis/NIR integrating sphere attachment, which employs the diffuse-reflectance technique. X-ray powder diffraction (XRD) studies were performed using monochromatized Cu KR radiation and recorded over the 2 $\theta$ range from 1.5° to 30° in steps of 0.05°.

**Synthesis of SBA-15-Supported Iron Terpyridine complex 4**

Compound 1 was prepared according to published procedures. [E. C. Constable, E. L. Dunphy, C. E. Housecroft, M. Neuburger, S. Schaffner, F. Schapera, and S. R. Batten, *Dalton. Trans.*, 2007, **38**, 4323.].

Compound 1 (353 mg, 1 mmol) was dissolved in SOCl₂ (15 mL), the mixture was stirred under reflux for 1 h under N₂, then the solvent was removed by distillation under reduced pressure. To the residue was added anhydrous THF (20 mL), Et₃N (2 mL) and H₂N(CH₂)₃Si(OEt)₃ (208 mg, 1.1 mmol) subsequently. The reaction mixture was stirred under reflux for 12 h. Then the reaction mixture was extracted with CH₂Cl₂ and washed by water and brine subsequently. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give product 2 in 478 mg (86% yield).

White solid; ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 2H), 8.74 (d, J = 8.2 Hz, 2H), 8.68 (d, J = 8.2 Hz, 2H), 7.96-7.89 (m, 6H), 7.37 (m, 2H), 6.65 (t, J = 5.4 Hz, 1H), 3.81(q, J = 7.0 Hz, 6H), 3.52 (t, J = 8.0 Hz, 2H), 1.80 (m, 2H), 1.24 (t, J = 7.0 Hz, 9H), 0.75 (t, J = 8.0 Hz, 2H); ¹³C NMR (300 MHz, CDCl₃) δ 166.8, 156.0, 156.0, 149.2, 149.1, 141.2, 136.9, 135.2, 127.5, 127.4, 123.9, 121.3, 118.8, 58.5, 42.2, 18.2, 7.8, 0.9; EIMS m/z 556 (M⁺); HRMS (EI) for C₃₁H₃₆N₄O₄Si, calcd 556.2506, found 556.2496.

A mixture of compound 2 (420 mg, 0.8 mmol) and 500 mg of SBA-15 in toluene (10 mL) was...
stirred under reflux for 24 h. The precipitate was filtered and washed with CH₂Cl₂ more than five times to make sure that there was no unloaded compound 2, then was dried under reduced pressure to give a white solid (630 mg, ligand loading: 0.39 mmol/g, 18.3 wt %).

IR (cm⁻¹): 2980, 2938, 1548, 1509, 1445, 1391.

\[
\text{CONH(CH₂)₃Si} \quad \text{O} \quad \text{O} \quad \text{Fe(ClO₄)₂·6H₂O} \quad \text{CH₃CN} \quad \text{CONH(CH₂)₃Si} \quad \text{O} \quad \text{O}
\]

The mixture of Ligand 3 (500 mg) and Fe(ClO₄)₂·6H₂O (100 mg) in MeCN (5 mL) was stirred at room temperature for 1 h. A purple precipitate was filtered, washed with MeCN and then dried under reduced pressure to give a purple solid (570 mg, iron loading: 0.34 mmol/g, 1.9 wt %).

UV-Vis (CH₃CN): \(\lambda_{\text{max}}/\text{nm}: 584\); IR (cm⁻¹): 1545, 1508, 1481, 1400.

Figure S1, Solid diffuse-reflectance UV-vis spectrum of 4
General Procedure for Oxidative Coupling of Tertiary Amines with Nucleophiles

To a mixture of tertiary amine (0.2 mmol), nucleophile (0.24 mmol) and complex 4 (0.006 mmol, 3 mol %) in toluene (1 mL) was added TBHP (tert-butyl hydroperoxide) (0.6 mmol). The reaction mixture was stirred under reflux for 12 h. Then the reaction mixture was extracted with ethyl acetate and washed by water and brine subsequently. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent.

Epoxidation of Styrene with TBHP Catalyzed by Complex 4

To a solution of styrene (0.2 mmol) in toluene (2 mL) was added complex 4 (17 mg, 3 mol %)
and TBHP (0.3 mmol). The reaction mixture was stirred at room temperature for 3 h. The conversion of styrene and yield were determined by GC-analysis (conversion: 72%; yield: 73%).

**Oxidation of Tetrahydroisoquinoline with TBHP Catalyzed by Complex 4**

![Chemical reaction image]

To a solution of tetrahydroisoquinoline (0.2 mmol) in toluene (1 mL) was added complex 4 (17 mg, 3 mol %) and TBHP (0.3 mmol). The reaction mixture was stirred under reflux for 12 h. After cooled down, the reaction mixture was extracted with dichloromethane. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give three products (conversion: 100%; yield: a 60%, b 15%, c 12%).

**General Procedure for Recycling Silica Supported Ligand 3**

To a suspended solution of SBA-15 supported ligand 3 (0.006 mmol) in toluene (1 mL) was added Fe(ClO₄)₂·6H₂O (0.006 mmol). The mixture was stirred at room temperature for 10 min. To the mixture was added tetrahydroisoquinoline 6a (0.2 mmol) and indole 5a (0.24 mmol). The reaction mixture was stirred under reflux for 12 h. Upon completion of the reaction, the initial purple complex 4 turned white, revealing that demetalation took place. The SBA-15 supported ligand 3 could be recycled simply by filtration. The recycled ligand reacted with a new batch of Fe(ClO₄)₂·6H₂O (3 mmol%) to regenerate complex 4 in situ, which was used for consecutive reactions.
Literature References for Indoles 7a-7g and Propargylamines 13a-13e

<table>
<thead>
<tr>
<th>Structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 7g" /></td>
<td>Zhiping Li and Chao-Jun Li, <em>J. Am. Chem. Soc.</em>, 2005, <strong>127</strong>, 6968.</td>
</tr>
<tr>
<td><img src="image" alt="Structure 13a" /></td>
<td>Zhiping Li, D. Scott Bohle and Chao-Jun Li, <em>PNAS</em>, 2006, <strong>103</strong>, 8928.</td>
</tr>
</tbody>
</table>
Characterization Data

**7d**

White solid; analytical TLC (silica gel 60) (10 % EtOAc in hexane) \( R_f = 0.47; \) \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.76 (s, 1H), 7.40 (d, \( J = 8.2 \) Hz, 2H), 7.28-7.11 (m, 6H), 7.08 (s, 1H), 7.01 (d, \( J = 7.9 \) Hz, 2H), 6.84 (d, \( J = 8.2 \) Hz, 1H), 6.76 (dd, \( J = 5.2, 1.2 \) Hz, 1H), 6.53 (d, \( J = 1.2 \) Hz, 1H), 6.13 (s, 1H), 3.62-3.58 (m, 2H), 3.05 (ddd, \( J = 16.0, 7.6, 7.6 \) Hz, 1H), 2.80 (ddd, \( J = 16.0, 4.4, 4.4 \) Hz, 1H), 2.41 (s, 3H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) 149.9, 137.6, 137.1, 135.6, 132.0, 129.3, 128.8, 128.1, 126.7, 125.8, 124.4, 123.6, 121.5, 119.8, 119.1, 118.1, 115.9, 111.1, 56.8, 42.4, 26.8, 21.7; EIMS \( m/z \) 338 (M\(^+\)); HRMS (EI) for C\(_{24}\)H\(_{22}\)N\(_2\), calcd 338.1783, found 338.1763.

**7h**

Yellow oil; analytical TLC (silica gel 60) (5 % EtOAc in hexane) \( R_f = 0.51; \) \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.62 (d, \( J = 7.9 \) Hz, 1H), 7.55 (d, \( J = 8.2 \) Hz, 1H), 7.51-7.41 (m, 4H), 7.31-7.29 (m, 1H), 7.26-7.22 (m, 3H), 7.20-7.18 (m, 2H), 6.88 (d, \( J = 7.9 \) Hz, 2H), 6.73 (t, \( J = 7.2 \) Hz, 1H), 4.73 (s, 2H), 3.03 (s, 3H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) 140.1, 136.8, 130.4, 130.0, 129.6, 128.6, 126.5, 124.6, 124.5, 123.9, 123.1, 120.6, 119.8, 114.3, 113.7, 110.1, 49.4, 30.1; EIMS \( m/z \) 312 (M\(^+\)); HRMS (EI) for C\(_{22}\)H\(_{20}\)N\(_2\), calcd 312.1626, found 312.1621.
Yellow oil; analytical TLC (silica gel 60) (5 % EtOAc in hexane) \( R_f = 0.52 \); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.54 (d, \( J = 7.8 \) Hz, 1H), 7.47 (d, \( J = 8.1 \) Hz, 1H), 7.47-7.45 (m, 4H), 7.24-7.15 (m, 4H), 7.04 (d, \( J = 8.4 \) Hz, 2H), 6.81 (d, \( J = 8.6 \) Hz, 2H), 4.67 (s, 2H), 2.97 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) 148.2, 139.7, 136.3, 129.7, 129.5, 128.3, 126.2, 126.0, 124.2, 122.6, 120.1, 119.5, 118.2, 114.5, 113.5, 110.6, 49.1, 38.2, 20.3; EIMS m/z 326 (M\(^+\)); HRMS (EI) for C\(_{23}\)H\(_{22}\)N\(_2\), calcd 326.1783, found 326.1786.

White solid; analytical TLC (silica gel 60) (10 % EtOAc in hexane) \( R_f = 0.52 \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.60-7.55 (m, 2H), 7.51-7.44 (m, 4H), 7.31-7.24 (m, 5H), 7.13 (s, 1H), 6.97 (d, \( J = 8.1 \) Hz, 2H), 4.69 (s, 2H), 3.00 (s, 3H); 13C NMR (400 MHz, CDCl\(_3\)) \( \delta \) 149.1, 136.5, 131.9, 129.7, 128.1, 126.5, 126.2, 124.4, 122.9, 120.4, 119.4, 114.6, 114.1, 113.9, 110.8, 108.6, 48.8, 38.3; EIMS m/z 390 (M\(^+\)); HRMS (EI) for C\(_{22}\)H\(_{19}\)N\(_2\)Br, calcd 390.0732, found 390.0735.

White solid; analytical TLC (silica gel 60) (10 % EtOAc in hexane) \( R_f = 0.57 \); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.66 (d, \( J = 7.8 \) Hz, 1H), 7.55 (d, \( J = 8.2 \) Hz, 1H), 7.23-7.38 (m, 7H), 7.21-7.18
(m, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 4.75 (s, 2H), 3.05 (s, 3H), 2.35 (s, 3H);

$^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 150.3, 136.6, 135.3, 130.2, 129.3, 128.2, 126.4, 124.4, 124.2, 122.6, 120.1, 119.5, 116.8, 114.1, 113.2, 110.8, 48.8, 38.1, 21.2; EIMS $m/z$ 326 (M$^+$); HRMS (EI) for C$_{23}$H$_{22}$N$_2$, calcd 326.1783, found 326.1781.

![11a](mixture of diastereomers)

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) $R_f$ = 0.43; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.79 (s, 1H), 7.24-7.18 (m, 10H), 7.09 (d, J = 6.4 Hz, 2H), 6.90-6.85 (m, 4H), 6.78 (d, J = 7.2 Hz, 2H), 5.76 (s, 1H), 5.74 (s, 0.8 H), 5.48 (d, J = 2.6 Hz, 0.8 H), 5.42 (d, J = 2.6 Hz, 1H), 3.48-3.42 (m, 2H), 3.31-3.23 (m, 2H), 2.93-2.87 (m, 2H), 2.70-2.62 (m, 2H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 150.2, 150.2, 135.9, 135.9, 135.2, 135.2, 132.8, 132.7, 129.5, 129.4, 128.8, 128.8, 127.9, 127.1, 125.9, 125.9, 119.3, 119.2, 116.5, 116.4, 107.8, 107.7, 58.1, 58.0, 42.9, 42.6, 27.4(2), 27.4(0); EIMS $m/z$ 481 (M$^+$); HRMS (EI) for C$_{34}$H$_{31}$N$_3$, calcd 481.2518, found 481.2511.

![11b](Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) $R_f$ = 0.41; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (s, 1H), 7.30-7.27 (m, 2H), 7.26-7.24 (m, 3H), 7.15 (m, 1H), 6.98 (d, J = 7.8 Hz, 2H), 6.82 (t, J = 7.6 Hz, 1H), 6.65 (d, J = 1.6 Hz, 1H), 6.06 (m, 1H), 5.89 (s, 1H), 5.69 (d, J = 1.6 Hz, 1H), 3.59-3.53 (m, 1H), 3.49-3.47 (m, 1H), 2.96 (ddd, J = 16.0, 7.6, 7.6 Hz, 1H), 2.77 (ddd, J = 16.0, 4.4, 4.4 Hz, 1H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 150.0, 150.2, 135.9, 135.9, 135.2, 135.2, 129.5, 129.4, 128.8, 128.9, 127.9, 127.3, 126.1, 118.9, 117.2, 115.7, 108.4, 107.7, 57.8, 43.1, 27.3; EIMS $m/z$ 274 (M$^+$); HRMS (EI) for C$_{19}$H$_{18}$N$_2$, calcd 274.1470, found 274.1463.
Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.46; ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.21 (m, 5H), 7.07 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H), 6.82 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 1.8 Hz, 1H), 5.94 (m, 1H), 5.77 (s, 1H), 5.42 (d, J = 1.8 Hz, 1H), 3.62-3.58 (m, 2H), 3.56 (s, 3H), 2.92 (ddd, J = 16.0, 7.6, 7.6 Hz, 1H), 2.59 (ddd, J = 16.0, 4.4, 4.4 Hz, 1H); ¹³C NMR (300 MHz, CDCl₃) δ 149.8, 135.8, 135.6, 134.1, 129.4, 129.2, 128.7, 126.9, 125.7, 123.0, 119.7, 117.8, 111.2, 106.0, 55.8, 43.0, 34.4, 25.3; EIMS m/z 288 (M⁺); HRMS (EI) for C₂₀H₂₀N₂, calcd 288.3862, found 288.3868.

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.41; ¹H NMR (300 MHz, CDCl₃) δ 7.63 (s, 1H), 7.23-7.17 (m, 6H), 6.93 (d, J = 7.8 Hz, 2H), 6.82 (t, J = 7.4 Hz, 1H), 6.50 (m, 1H), 5.93 (m, 1H), 5.79 (s, 1H), 3.56-3.52 (m, 2H), 3.06-2.87 (m, 2H), 1.89 (s, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 150.4, 136.6, 135.6, 129.4, 129.3, 129.0, 128.9, 128.2, 127.1, 126.4, 119.7, 117.4, 115.9, 110.9, 57.6, 44.9, 28.1, 11.5; EIMS m/z 288 (M⁺); HRMS (EI) for C₂₀H₂₀N₂, calcd 288.3862, found 288.3864.

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.41; ¹H NMR (300 MHz,
CDCl3) δ 7.82 (s, 1H), 7.28-7.20 (m, 5H), 7.15 (m, 1H), 6.97 (d, J = 7.8 Hz, 2H), 6.80 (t, J = 7.3 Hz, 1H), 6.40 (s, 1H), 5.85 (s, 1H), 5.53 (s, 1H), 3.58-3.48 (m, 2H), 2.94 (ddd, J = 16.0, 7.6, 7.6 Hz, 1H), 2.77 (ddd, J = 16.0, 4.4, 4.4 Hz, 1H), 2.00 (s, 3H); 13C NMR (300 MHz, CDCl3) δ 150.0, 136.2, 135.5, 133.5, 131.0, 129.5, 128.8, 127.9, 127.2, 126.0, 118.7, 115.5, 114.9, 109.2, 57.7, 43.0, 27.3, 12.1; EIMS m/z 288 (M+); HRMS (EI) for C20H20N2, calcd 288.3862, found 288.3858.