Supporting Information for

Metal-Free Oxidative Cross-Coupling of Diazirines with Arylboronic Acids

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Supporting Information

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1) General
All solvents were distilled prior to use. The solvents for the reaction were distilled to remove water over Na or CaH$_2$. Column chromatograph was performed on 200-300 mesh silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded at 300 MHz (or 400 MHz) and 75 MHz (or 100 MHz) with Varian Mercury 300 spectrometer (or Bruker ARX 400 spectrometer) using CDCl$_3$ (DMSO-$d_6$) as solvent and tetramethylsilane as the internal standard. IR spectra were recorded with a Thermo Electron Corporation Nicolet AVATAR 300 FT-IR spectrometer. Mass spectra were obtained on Bruker Apex IV FTMS spectrometer.

2) Preparation and spectra data of diazirines
Diazirines used in this investigation were prepared by literature procedure.$^1$

\[
\begin{align*}
&\text{Ar} = \text{Ph} \\
&\text{R} = \text{CH}_2 \\
&\text{R'} = \text{CH}_3
\end{align*}
\]

Benzyl amine (100 mmol) and ketone (50 mmol) were mixed in toluene (150 mL). The mixture was refluxed for about 12 hours. Solvent and impurities were removed under vacuum and the benzyl imine was obtained. The benzyl imine was then dissolved in methanol (100 mL). The methanol solution was added to the liquid ammonia (50 mL) and the mixture was stirred at -60 °C for 3 hours. A solution of hydroxylamine-$O$-sulfonic acid (75 mmol) in methanol (50 mL) was subsequently added and the mixture was stirred at -60 °C for another 2 hours. The reaction mixture was allowed to warm to room temperature to evaporate the excess ammonia. Water was added to the crude residue and the mixture was extracted with diethyl ether (3 x 50 mL). The combined organic phase was concentrated to give a crude oil, which was oxidized with freshly prepared silver oxide in MeOH/H$_2$O (1:1, 150 mL) at room temperature for 2 hours. The silver salts were filtered and filtrate was extracted with diethyl ether. The combined organic phase was dried and concentrated under reduced pressure to give the crude product, which was purified by flash chromatograph on silica gel. The yields for three steps range from 20% to 30%.
3-Methyl-3-phenyl-3H-diazirine 1a. \(^2\)

Colorless oil; \(^1\)H NMR (300 MHz, \(d_6\)-DMSO) \(\delta\) 7.41-7.33 (m, 3H), 6.96-6.93 (m, 2H), 1.50 (s, 3H).

3-(4-Methoxyphenyl)-3-methyl-3H-diazirine 1b. \(^2\)

Pale yellow solid; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.85-6.81 (m, 4H), 3.79 (s, 3H), 1.49 (s, 3H).

3-Ethyl-3-phenyl-3H-diazirine 1c. \(^2\)

Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) 7.33-7.25 (m, 3H), 6.96-6.92 (m, 2H), 2.03 (q, \(J = 7.6\) Hz, 2H), 0.84 (t, \(J = 7.6\) Hz, 3H).

3-(3-Methoxyphenyl)-3-methyl-3H-diazirine 1d. \(^2\)

Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) 7.25-7.21 (m, 1H), 6.84-6.81 (m, 1H), 6.54-6.51 (m, 1H), 6.41-6.40 (m, 1H), 3.78 (s, 3H), 1.50 (s, 3H).

3-Isopropyl-3-phenyl-3H-diazirine 1e. \(^2\)

Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) 7.35-7.23 (m, 3H), 7.00-6.97 (m, 2H), 2.97-2.83 (m, 1H), 0.81 (d, \(J = 6.9\) Hz, 6H).

3) Experimental procedure and characterizations

\[
\text{Ar}^+\text{Me} + \text{Ar}'\text{B(OH)}_2 \xrightarrow{\text{BQ, 110 °C, dioxane}} \text{Ar}^-\text{Ar}' + \text{N}_2
\]

Arylboronic acid (0.6 mmol), diazirine (1.2 mmol), \(p\)-benzoquinone (0.72 mmol) and 1, 4-dioxane (0.8 mL) were mixed in a microwave tube. The mixture was stirred at 110 °C for 2 hours. Then the crude reaction mixture was filtered through short silica
gal column. The solvent was evaporated under reduced pressure to give a crude residue, which was purified by flash chromatograph on silica gel to afford the pure products.

Ethene-1,1-diyl dibenzene 3aa.³

Yield 72%; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 - 7.29 (m, 10H), 5.44 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.1, 141.6, 128.3, 128.2, 127.8, 114.3.

1-Methyl-4-(1-phenylvinyl) benzene 3ab.³

Yield 70%; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.35 - 7.29 (m, 5H) 7.23 (d, $J$ = 8.1 Hz, 2H), 7.13 (d, $J$ = 7.9 Hz, 2H), 5.41 (dd, $J$ = 8.5, 1.3 Hz, 2H), 2.36 (s, 3H).

1-tert-Butyl-4-(1-phenylvinyl) benzene 3ac.⁴

Yield 64%; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.36 - 7.28 (m, 9H), 5.45 (d, $J$ = 1.3 Hz, 1H), 5.40 (d, $J$ = 1.3 Hz, 1H), 1.33 (s, 9H).

1-Methoxy-4-(1-phenylvinyl) benzene 3ad.³

Yield 57%; white Solid; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.34-7.32 (m, 5H), 7.27 (d, $J$= 9.2 Hz, 2H), 6.86 (d, $J$ = 8.9 Hz, 2H), 5.40 (d, $J$ = 1.3 Hz, 1H), 5.35 (d, $J$ = 1.3 Hz, 1H), 3.82 (s, 3H).

1-Bromo-4-(1-phenylvinyl) benzene 3ae.⁵

Yield 73%; Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.45 (d, $J$ = 8.6 Hz, 2H), 7.36 - 7.29 (m, 5H), 7.20 (d, $J$ = 8.5 Hz, 2H), 5.46 (d, $J$ = 1.1 Hz, 1H), 5.44 (d, $J$ = 1.0 Hz, 1H).
1-Chloro-4-(1-phenylvinyl)benzene 3af.\(^3\)

Yield 82%; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.32-7.23 (m, 9H), 5.45 (d, \(J = 1.1\) Hz, 1H), 5.43 (d, \(J = 1.1\) Hz, 1H).

1-(4-(1-Phenylvinyl)phenyl)ethanone 3ag.

Yield 27%; colorless oil; IR (film) 2918, 1683, 1605, 1358, 1267, 959.8, 904.1, 850.1, 778.8, 705.1; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.93 (d, \(J = 8.7\) Hz, 2H), 7.43 (d, \(J = 8.7\) Hz, 2H), 7.36-7.30 (m, 5H), 5.56 (d, \(J = 1.0\) Hz, 1H), 5.55 (d, \(J = 1.0\) Hz, 1H), 2.61 (s, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta \) 197.7, 149.2, 146.2, 140.7, 136.3, 128.5, 128.3, 116.0, 26.6; HRMS (ESI) \(m/e\) calcd for C\(_{16}\)H\(_{15}\)O (M+H)\(^+\) 223.1117, found 223.1118.

1-Methyl-2-(1-phenylvinyl)benzene 3ah.\(^6\)

Yield 34%; Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.28-7.19 (m, 9H), 5.77 (d, \(J = 1.4\) Hz, 1H), 5.19 (d, \(J = 1.4\) Hz, 1H), 2.05 (s, 3H).

1-Methyl-3-(1-phenylvinyl)benzene 3ai.\(^4\)

Yield 78%; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.34 -7.11 (m, 9H), 5.43 (s, 2H), 2.33 (s, 3H).

1-Methoxy-3-(1-phenylvinyl)benzene 3aj.\(^3\)

Yield 71%; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.35 - 7.26 (m, 5H), 7.24 - 7.21 (m, 1H), 6.94 - 6.83 (m, 3H), 5.45 (s, 2H), 3.77 (s, 3H).
1-(1-Phenylvinyl)-3-(trifluoromethoxy)benzene 3ak.\(^4\)

Yield 42%; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.35 - 7.19 (m, 9H), 5.48 (d, \(J = 1.0\) Hz, 1H), 5.45 (d, \(J = 0.9\) Hz, 1H).

1-Chloro-3-(1-phenylvinyl)benzene 3al.\(^3\)

Yield 50%, Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38 - 7.25 (m, 9H), 5.52 (d, \(J = 1.0\) Hz, 1H), 5.49 (d, \(J = 1.0\) Hz, 1H).

1-Bromo-3-(1-phenylvinyl)benzene 3am.

Yield 17%; colorless oil; IR (film) 3057, 2917, 1554, 1492, 1470, 1074, 904.1, 776.2, 697.2; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.46 - 7.39 (m, 2H), 7.31 - 7.27 (m, 5H), 7.23 - 7.13 (m, 2H), 5.45 (d, \(J = 1.0\) Hz, 1H), 5.42 (d, \(J = 1.0\) Hz, 1H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.8, 143.7, 140.7, 131.2, 130.7, 129.7, 128.3, 128.2, 128.0, 126.9, 122.4, 115.3. HRMS (EI) \(m/e\) calcd for C\(_{14}\)H\(_{11}\)Br (M) 258.0044, found 258.0048; C\(_{14}\)H\(_{11}\)Br (M) 260.0024, found 260.0028.

1,3-Dimethyl-5-(1-phenylvinyl)benzene 3an.\(^3\)

Yield 62%; Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.35 - 7.30 (m, 5H), 6.95 (s, 3H), 5.41 (s, 2H), 2.29 (s, 6H).

1,3-Dibromo-5-(1-phenylvinyl)benzene 3ao.

Yield 31%; colorless oil; IR (film) 3057, 3023, 1578, 1544, 907.3, 856.7, 777.2, 743.1, 696.0; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.61 (t, \(J = 1.8\) Hz, 1H), 7.40 (d, \(J = 1.8\) Hz, 2H), 7.36 - 7.25 (m, 5H), 5.51 (d, \(J = 0.8\) Hz, 1H), 5.45 (d, \(J = 0.8\) Hz, 1H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 147.7, 145.2, 140.1, 133.1, 130.0, 128.5, 128.3, 128.1, 122.8, 116.3. HRMS (ESI) \(m/e\) calcd for C\(_{14}\)H\(_{11}\)Br\(_2\) (M+H)\(^+\) 336.9222, found 336.9228.

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2-(1-Phenylvinyl)naphthalene 3ap. Yield 66%; white solid; mp: 53-55 °C; \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.85-7.78 (m, 4H), 7.50-7.45 (m, 3H), 7.37-7.34 (m, 5H), 5.59 (d, \( J = 1.2 \) Hz, 1H), 5.55 (d, \( J = 1.2 \) Hz, 1H).

3-(1-Phenylvinyl)furan 3aq. Yield 58%; colorless oil; IR (film) 3026, 2918, 2843, 1684, 1492, 1161, 1066, 1022, 873.4, 794.8, 775.8, 732.1, 698.6; \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.44–7.40 (m, 3H), 7.38–7.31 (m, 4H), 6.56–6.52 (m, 1H), 5.44 (d, \( J = 1.2 \) Hz, 1H), 5.23 (d, \( J = 1.2 \) Hz, 2H), 5.23 (d, \( J = 1.2 \) Hz, 1H). \( ^{13}C \) NMR (75 MHz, CDCl\(_3\)) \( \delta \). HRMS (ESI) \( m/e \) calcd for C\(_{12}\)H\(_{11}\)O (M+H)\(^+\) 171.0804, found 171.0805.

1-Methoxy-4-(1-p-tolylvinyl)benzene 3bb. Yield 71%; white solid; mp: 72-74 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.29-7.13 (m, 4H), 6.86 (dd, \( J = 2.2, 6.7 \) Hz, 2H), 5.34 (dd, \( J = 1.4, 6.1 \) Hz, 2H), 5.34 (d, \( J = 1.3 \) Hz, 1H), 5.33 (d, \( J = 1.4 \) Hz, 1H), 3.83 (s, 3H), 2.37 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 159.5, 149.4, 139.0, 137.4, 134.2, 129.4, 128.8, 128.2, 55.3, 21.2.

1-Chloro-4-(1-(4-methoxyphenyl)vinyl)benzene 3bf. Yield 88%; white solid; mp: 66-68 °C; \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.31-7.24 (m, 6H), 6.88 (dd, \( J = 2.1, 6.7 \) Hz, 2H), 5.41 (d, \( J = 1.1 \) Hz, 1H), 5.35 (d, \( J = 1.1 \) Hz, 1H).

1-(4-(1-(4-Methoxyphenyl)vinyl)phenyl)ethanone 3bg. Yield 85%; white solid; mp: 96 °C; IR (film) 2958, 2837, 1686, 1604, 1510, 1250, 1180, 1026, 902.6, 842.0, 732.0; \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.92 (dd, \( J = 1.7, 6.5 \) Hz, 2H), 7.45-7.42 (m, 2H), 7.26-7.23 (m, 2H), 6.88 (dd, \( J = 2.0, 6.6 \) Hz, 2H), 5.49 (d, \( J = 1.0 \) Hz, 1H), 5.44 (d, \( J = 1.0 \) Hz, 1H), 3.83 (s, 3H), 2.62.
(s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 197.7, 159.5, 148.7, 146.6, 136.3, 133.2, 129.3, 128.5, 128.3, 114.6, 113.7, 55.3, 26.6; HRMS (ESI) m/e calcd for C\(_{17}\)H\(_{15}\)O\(_2\) (M+H)\(^+\) 253.1223, found 253.1225.

1, 3-Difluoro-5-(1-(4-methoxyphenyl)vinyl)benzene 3br.

Yield 96%; white solid; mp: 46-47 °C; IR (film) 3091, 2958, 2834, 1620, 1586, 1511, 1346, 1247, 1178, 1117, 1034, 987.0, 866.6, 835.5; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26 - 7.22 (m, 2H), 6.90 - 6.84 (m, 4H), 6.78 - 6.73 (m, 1H), 5.44 (s, 1H), 5.39 (d, \(J = 0.8\) Hz, 1H), 3.83 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.8 (dd, \(J = 12.9, 247.9\) Hz, 2C), 159.6, 147.7, 145.2 (t, \(J = 9.3\) Hz, 1C), 132.7, 129.4, 114.5, 113.8, 111.1 (dd, \(J = 6.7, 18.5\), 2C), 102.9 (t, \(J = 25.5\) Hz, 1C), 55.3. HRMS (ESI) m/e calcd for C\(_{15}\)H\(_{13}\)F\(_2\)O (M+H)\(^+\) 247.0929, found 247.0932.

Prop-1-ene-1,1-diylidibenzenes 3ca.

Yield 54%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 - 7.17 (m, 10H), 6.17 (q, \(J = 7.0\) Hz, 1H), 1.76 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.0, 142.4, 140.0, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 124.1, 15.7.

1-Methyl-4-(1-phenylprop-1-enyl)benzene 3cb.

Yield 55%; colorless oil; IR (film) 3026, 2911, 2856, 1511, 1441, 809.8, 759.0, 702.3; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.06 (m, 9H), 6.13 (q, \(J = 7.0\) Hz, 1H), 2.38 (s, 1.25H), 2.32 (s, 1.75H), 1.76 (d, \(J = 7.0\) Hz, 1.20H), 1.74 (d, \(J = 7.0\) Hz, 1.80H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.2, 142.3, 142.2, 140.2, 137.0, 136.4, 130.0, 129.9, 128.8, 128.7, 128.1, 128.0, 127.2, 127.1, 126.7, 126.6, 123.9, 123.2, 21.2, 21.0, 15.7, 15.6. HRMS (ESI) m/e calcd for C\(_{16}\)H\(_{17}\) (M+H)\(^+\) 209.1325, found 209.1326.

1-Chloro-4-(1-phenylprop-1-enyl)benzene 3cf.

Yield 58%; colorless oil; IR (film) 3029, 2911, 2849, 1489, 1442, 1091, 1014, 894.9, 816.5, 759.4, 701.0; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.11 (m, 9H), 6.20-6.13 (m, 1H), 1.76 (s, 1.5H), 1.74 (s, 1.5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.5, 141.4, 141.4, 141.3, 139.5, 138.4, 132.7, 132.5, 131.4,
129.9, 128.4, 128.4, 128.2, 128.1, 127.1, 127.0, 126.9, 124.7, 124.7, 15.7, 15.7. HRMS (ESI) m/e calcd for C\textsubscript{15}H\textsubscript{14}Cl (M+H)	extsuperscript{+} 229.0779, found 229.0781.

1-Methoxy-3-[(1-4-methoxyphenyl)vinyl]benzene 3dd. Yield 72%; colorless oil; IR (film) 3011, 2958, 2831, 1606, 1510, 1247, 1178, 1035, 885.6, 836.7, 786.6, 715.5; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.29-7.23 (m, 3H), 6.94-6.85 (m, 5H), 5.39 (d, J = 1.2 Hz, 1H), 5.36 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 159.4, 159.3, 149.3, 143.3, 133.8, 129.4, 129.0, 120.9, 113.9, 113.4, 113.1, 113.0, 55.3, 55.2. HRMS (ESI) m/e calcd for C\textsubscript{16}H\textsubscript{17}O\textsubscript{2} (M+H)	extsuperscript{+} 241.1123, found 241.1124.

1-Methoxy-3-(1-m-tolylvinyl)benzene 3di. Yield 71%; colorless oil; IR (film) 2948, 2834, 1598, 1577, 1486, 1247, 1047, 882.6, 791.5, 706.1; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.24-7.20 (m, 2H), 7.16-7.11 (m, 3H), 6.93-6.85 (m, 3H), 5.43 (s, 2H), 3.78 (s, 3H), 2.34 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 159.4, 150.0, 143.1, 141.3, 137.7, 129.0, 128.9, 128.5, 128.0, 125.4, 120.9, 114.2, 113.9, 113.1, 55.2, 21.4. HRMS (ESI) m/e calcd for C\textsubscript{16}H\textsubscript{17}O (M+H)	extsuperscript{+} 225.1274, found 225.1276.

2-(1-(3-Methoxyphenyl)vinyl)naphthalene 3dp. Yield 56%; white Solid; mp: 79-81 °C; IR (film) 3054, 2914, 2849, 1600, 1577, 1489, 1248, 1046, 896.5, 859.8, 822.1, 785.9, 752.5, 700.0; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.85-7.79 (m, 4H), 7.50-7.46 (m, 3H), 6.99-6.89 (m, 3H), 5.59 (d, J = 1.2 Hz, 1H), 5.55 (d, J = 1.2 Hz, 1H), 3.79 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 159.5, 149.9, 143.0, 138.7, 133.3, 132.9, 129.2, 128.2, 127.7, 127.6, 127.3, 126.4, 126.1, 126.0, 121.0, 114.9, 114.0, 113.4, 55.2. HRMS (ESI) m/e calcd for C\textsubscript{19}H\textsubscript{17}O (M+H)	extsuperscript{+} 261.1274, found 261.1276.

(2-Methylprop-1-ene-1,1-diyl)dibenzene 3ea. Yield 10 %; colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.29-7.12 (m, 10H), 1.80 (s, 6H).
4) References


For imide synthesis: (c) S. Shirai, H. Nara, Y. Kayaki, T. Ikariya, *Organometallics* 2009, **28**, 802.


5) $^1$H NMR and $^{13}$C NMR spectra

[Chemical structures and spectra images]

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