

# Iron-catalysed Mizoroki–Heck reaction using 2,2'-diamino-6,6'-dimethylbiphenyl as the ligand

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FeCl<sub>3</sub>·6H<sub>2</sub>O-catalysed Mizoroki–Heck reactions of aryl iodides with methyl acrylate have been achieved by using 2,2'-diamino-6,6'-dimethylbiphenyl as the ligand and NaHCO<sub>3</sub> as the base in DMF and H<sub>2</sub>O. It was found that an appropriate amount of H<sub>2</sub>O is essential for high yields in these reactions.

**Keywords:** Mizoroki–Heck reaction, iron catalysis, H<sub>2</sub>O, 2,2'-diamino-6,6'-dimethylbiphenyl, aryl iodides, methyl acrylate

Transition-metal catalysed cross-coupling reactions are versatile methods for carbon-carbon bond formation.<sup>1–3</sup> Among them, the Mizoroki–Heck reaction is one of the most important methods for the vinylation of aromatic compounds.<sup>4–10</sup> Traditionally, the combination of palladium and a phosphine-based ligand is a good catalyst for this reaction.<sup>11–14</sup> Because of the high cost of palladium salts and the air-sensitivity and toxicity of phosphine-based ligands, alternative metals as well as ligands have been developed.<sup>15–25</sup> In the past few years, iron salts, as one of the most inexpensive and environmentally friendly salts on the earth, have been proved to be efficient catalysts for carbon-carbon and carbon-heteroatom bond formation.<sup>26–43</sup> Recently, Shao, Lu and co-workers found that 2,2'-diamino-6,6'-dimethylbiphenyl (**L**), as a non-phosphine compound, is a good ligand in the transition metal catalysed carbon-carbon bond formation reactions.<sup>44,45</sup> An iron catalysed Mizoroki–Heck reaction using 80 mol% of proline or picolinic acid as the ligand has been reported.<sup>46</sup> In this laboratory, we have found that **L** is also a good ligand in the FeCl<sub>3</sub>·6H<sub>2</sub>O-catalysed Mizoroki–Heck reactions of aryl iodides with methyl acrylate. We now report these results in detail.

Initial investigations were carried out using 1-chloro-4-iodobenzene (**1a**, 0.5 mmol) and methyl acrylate (**2a**, 0.6 mmol) as the reactants, a combination of Fe<sub>2</sub>O<sub>3</sub> (10 mol%) and **L** (20 mol%) as the catalyst, KHCO<sub>3</sub> (2.0 equiv.) as the base and DMF (1.0 mL) as the solvent at 135 °C for 24 h (Table 1). Preliminary results showed that the amount of H<sub>2</sub>O affected the reaction dramatically. When 0–2.0 equiv. of H<sub>2</sub>O was introduced in the reaction system, none of the desired product **3a** was obtained (Table 1, entries 1–3). Careful investigations showed that 8.0 equiv. of H<sub>2</sub>O gave the best result and the corresponding coupling product **3a** was obtained in 72% yield (Table 1, entry 6). When the amount of H<sub>2</sub>O was increased to 20.0 equiv., the yield was drastically decreased to 26% (Table 1, entry 8). Next, some other iron salts as FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, Fe<sub>3</sub>O<sub>4</sub>, and FeCl<sub>3</sub> were screened and the best result was obtained in the presence of FeCl<sub>3</sub>·6H<sub>2</sub>O (Table 1, entry 9) (Note the amount of H<sub>2</sub>O added was tuned so that the total amount present was 8.0 equiv.) Finally, screening for the base showed that NaHCO<sub>3</sub> was most effective and product **3a** can be obtained in 92% yield (Table 1, entry 16).

Therefore, the optimised reaction conditions were established as: using the combination of FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol%) and **L** (20 mol%) as the catalyst, NaHCO<sub>3</sub> (2.0 equiv.) as the base, DMF (1.0 mL) as the solvent in the presence of 7.4 equiv. H<sub>2</sub>O at 135 °C for 24 h.<sup>47</sup>

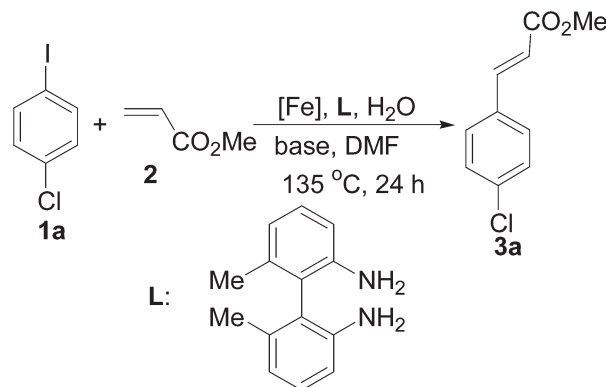
To exclude the possibility that trace copper salts were effective in this reaction, copper powder (10 mol%) and copper compounds (10 mol%) – CuI, CuO, CuCl<sub>2</sub>·2H<sub>2</sub>O, CuCl and CuBr were also investigated instead of FeCl<sub>3</sub>·6H<sub>2</sub>O, and it was found that these showed no activity for the Mizoroki–Heck

reaction of 1-chloro-4-iodobenzene **1a** with methyl acrylate **2**.

With the optimal reaction conditions in hand, we next explored the generality of the reaction with a set of aryl iodides. We were pleased to find out that all reactions proceeded smoothly to give the desired coupling products **3** in good to high yields (Table 2). It seems that substituents on the *ortho*-position on the phenyl ring of the iodides **1** have some effect on the reaction. For example, 2-iodotoluene **1e** and 1-bromo-2-iodobenzene **1h** only gave the corresponding products **3e** and **3h** in 53 and 60% yields, respectively (Table 2, entries 4 and 7). However, 2-methoxy group on the phenyl ring of iodide **1k** has less effect on the reaction and product **3k** was obtained in 85% yield (Table 2, entry 10).

In conclusion, we have found that 2,2'-diamino-6,6'-dimethylbiphenyl (**L**) is an efficient ligand in the FeCl<sub>3</sub>·6H<sub>2</sub>O-catalysed Mizoroki–Heck reaction of aryl iodides with methyl

**Table 1** Optimisation for the reaction of **1a** with **2**

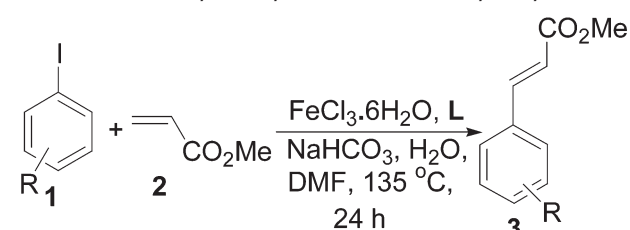


Entry <sup>a</sup>	H <sub>2</sub> O (equiv)	[Fe]	Base	Yield/% <sup>b</sup>
1	—	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	—
2	1.2	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	—
3	2.0	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	trace
4	4.0	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	15
5	6.0	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	69
6	8.0	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	72
7	10.0	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	61
8	20.0	Fe <sub>2</sub> O <sub>3</sub>	KHCO <sub>3</sub>	26
9	7.4	FeCl <sub>3</sub> ·6H <sub>2</sub> O	KHCO <sub>3</sub>	90
10	7.6	FeCl <sub>2</sub> ·4H <sub>2</sub> O	KHCO <sub>3</sub>	81
11	8.0	Fe <sub>3</sub> O <sub>4</sub>	KHCO <sub>3</sub>	74
12	8.0	FeCl <sub>3</sub>	KHCO <sub>3</sub>	79
13	7.4	FeCl <sub>3</sub> ·6H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	43
14	7.4	FeCl <sub>3</sub> ·6H <sub>2</sub> O	AcOK	72
15	7.4	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	85
16	7.4	FeCl <sub>3</sub> ·6H <sub>2</sub> O	NaHCO <sub>3</sub>	92

<sup>a</sup> All reactions were carried out using **1a** (0.5 mmol), **2** (0.6 mmol), [Fe] (10 mol%), **L** (20 mol%), base (2.0 equiv), DMF (1.0 mL), H<sub>2</sub>O (3.7 mmol), 24 h.

<sup>b</sup> Isolated yields.

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**Table 2** Iron catalysed aryl iodides with methyl acrylate

Entry <sup>a</sup>	1 (R)	Yield/% <sup>b</sup>
1	<b>1b</b> (4-MeO)	<b>3b</b> , 96
2	<b>1c</b> (H)	<b>3c</b> , 94
3	<b>1d</b> (4-Me)	<b>3d</b> , 97
4	<b>1e</b> (2-Me)	<b>3e</b> , 53
5	<b>1f</b> (3-Me)	<b>3f</b> , 92
6	<b>1g</b> (4-CO <sub>2</sub> Et)	<b>3g</b> , 83
7	<b>1h</b> (2-Br)	<b>3h</b> , 60
8	<b>1i</b> (4-F)	<b>3i</b> , 81
9	<b>1j</b> (3,5-Me <sub>2</sub> )	<b>3j</b> , 94
10	<b>1k</b> (2-MeO)	<b>3k</b> , 85
11	<b>1l</b> (4-Ac)	<b>3l</b> , 93

<sup>a</sup> All reactions were carried out using **1** (0.5 mmol), **2** (0.6 mmol), FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol %), **L** (20 mol %), NaHCO<sub>3</sub> (2.0 equiv), H<sub>2</sub>O (7.4 equiv), DMF (1.0 mL) at 135 °C for 24 h.

<sup>b</sup> Isolated yields.

acrylate in DMF at 135 °C. Though the mechanism for this reaction is not clear at this stage, it was found that an appropriate amount of H<sub>2</sub>O plays an important role in this reaction. Efforts are underway to elucidate the reaction mechanism and to find more applications for this catalytic system in organic synthesis.

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-300 or 500 MHz spectrometer for solution in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Flash column chromatography was carried out using Huanghai 300–400 mesh silica gel at increased pressure.

### Iron-catalysed Mizoroki–Heck reaction of aryl iodides with methyl acrylate; general procedure

Under a N<sub>2</sub> atmosphere, in a dry Schlenk tube were placed the corresponding iodide **1** (0.5 mmol), FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol%), NaHCO<sub>3</sub> (2.0 equiv), **L** (20 mol%), degassed DMF (1.0 mL) and methyl acrylate **2** (0.6 mmol). Finally, H<sub>2</sub>O (3.7 mmol) was added. Then, the septum was replaced by a sealed condenser pipe, and the reaction vessel was placed in an oil bath at 135 °C for 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (20 mL), and washed with saturated brine (15 mL). The organic phase was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the pure products.

**3-(4-Chlorophenyl)acrylic acid methyl ester (3a):**<sup>47</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H, Ar), 7.35 (d, *J* = 8.5 Hz, 2H, Ar), 6.40 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H, OMe). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.1, 143.3, 136.1, 132.8, 129.2, 129.1, 118.3, 51.7.

**3-(4-Methoxyphenyl)acrylic acid methyl ester (3b):**<sup>47</sup> Rf = 0.4 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 50/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H, Ar), 6.90 (d, *J* = 8.6 Hz, 2H, Ar), 6.31 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H, OMe), 3.79 (s, 3H, OMe). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.6, 161.3, 144.4, 129.6, 127.0, 115.2, 114.2, 55.3, 51.5.

**3-Phenylacrylic acid methyl ester (3c):**<sup>47</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.70 (d,

*J* = 16.0 Hz, 1H), 7.54–7.51 (m, 2H, Ar), 7.39–7.37 (m, 3H, Ar), 6.45 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H, OMe). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.3, 144.8, 134.3, 130.2, 128.8, 128.0, 117.8, 51.6.

**3-(4-Methylphenyl)acrylic acid methyl ester (3d):**<sup>47</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H, Ar), 7.17 (d, *J* = 8.0 Hz, 2H, Ar), 6.39 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H, OMe), 2.35 (s, 3H, Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.5, 144.8, 140.59, 131.5, 129.5, 128.0, 116.5, 51.5, 21.3.

**3-(2-methylphenyl)acrylic acid methyl ester (3e):**<sup>47</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.98 (d, *J* = 15.9 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H, Ar), 7.30–7.18 (m, 3H, Ar), 6.36 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H, OMe), 2.44 (s, 3H, Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.5, 142.5, 137.6, 133.3, 130.7, 130.0, 126.3, 126.3, 118.7, 51.7, 19.8.

**3-(3-Methylphenyl)acrylic acid methyl ester (3f):**<sup>47</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.32–7.19 (m, 4H, Ar), 6.42 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H, OMe), 2.36 (s, 3H, Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.4, 145.0, 138.4, 134.2, 131.1, 128.7, 128.6, 125.2, 117.4, 51.6, 21.2.

**4-(2-Methoxycarbonylvinyl)benzoic acid ethyl ester (3g):**<sup>48</sup> Rf = 0.4 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 50/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 8.05 (d, *J* = 8.3 Hz, 2H, Ar), 7.71 (d, *J* = 16.1 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H, Ar), 6.52 (d, *J* = 16.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H, OMe), 1.40 (t, *J* = 7.1 Hz, 3H, Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.9, 165.9, 143.4, 138.4, 131.7, 130.0, 127.8, 120.0, 61.1, 51.8, 14.2.

**3-(2-Bromophenyl)acrylic acid methyl ester (3h):**<sup>49</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 8.05 (d, *J* = 16.0 Hz, 1H), 7.62–7.58 (m, 2H, Ar), 7.32–7.22 (m, 2H, Ar), 6.39 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H, OMe). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.74, 143.10, 134.39, 133.36, 131.15, 127.69, 127.65, 125.25, 120.59, 51.79.

**3-(4-Fluorophenyl)acrylic acid methyl ester (3i):**<sup>48</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.54–7.49 (m, 2H, Ar), 7.08 (t, *J* = 8.6 Hz, 2H, Ar), 6.37 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H, OMe). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.2, 163.9 (d, *J*<sub>C-F</sub> = 249.8 Hz), 143.5, 130.6 (d, *J*<sub>C-F</sub> = 3.3 Hz), 129.9 (d, *J*<sub>C-F</sub> = 8.4 Hz), 117.5 (d, *J*<sub>C-F</sub> = 2.3 Hz), 116.0 (d, *J*<sub>C-F</sub> = 21.8 Hz), 51.7.

**3-(3,5-Dimethylphenyl)acrylic acid methyl ester (3j):**<sup>48</sup> Rf = 0.6 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 100/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.14 (s, 2H, Ar), 7.02 (s, 1H, Ar), 6.41 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H, OMe), 2.32 (s, 6H, 2Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.5, 145.2, 138.3, 134.3, 132.0, 125.9, 117.3, 51.6, 21.1.

**3-(2-Methoxyphenyl)acrylic acid methyl ester (3k):**<sup>50</sup> Rf = 0.4 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 50/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 8.01 (d, *J* = 16.2 Hz, 1H), 7.52–7.49 (m, 1H, Ar), 7.37–7.32 (m, 1H, Ar), 6.98–6.89 (m, 2H, Ar), 6.53 (d, *J* = 16.2 Hz, 1H), 3.87 (s, 3H, OMe), 3.80 (s, 3H, OMe). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.8, 158.3, 140.2, 131.41, 128.82, 123.3, 120.6, 118.2, 111.1, 55.4, 51.5.

**3-(4-Acetylphenyl)acrylic acid methyl ester (3l):**<sup>48</sup> Rf = 0.2 (petroleum ether/ethyl acetate = 20:1, v/v). Chromatography solvent: petroleum ether/ethyl acetate = 30/1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.98 (d, *J* = 8.3 Hz, 2H, Ar), 7.72 (d, *J* = 16.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H, Ar), 6.54 (d, *J* = 16.1 Hz, 1H), 3.83 (s, 3H, OMe), 2.63 (s, 3H, Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.2, 166.9, 143.3, 138.7, 138.0, 128.82, 128.1, 120.3, 51.9, 26.6.

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