Copper-Catalyzed Base-Controlled Diastereoselective Synthesis of Tetraarylethanes from 2-Benzylpyridines

Selvaraj Chandrasekar
Iyyanar Karthikeyan
Govindasamy Sekar* 0000-0003-2294-0485

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, Tamil Nadu, India
gsekar@iitm.ac.in

Dedicated to Prof. M. Periyasamy on the occasion of his 65th birthday.

Abstract
A highly efficient and base-controlled diastereoselective synthesis of tetraarylethanes through copper-catalyzed dehydrogenative homocoupling of readily available 2-benzylpyridines is reported. Various dl- and meso-tetraarylethanes were diastereoselectively synthesized by this new protocol, where base plays the role of the principle modulator: Grignard reagents selectively provide the C2 isomers, whereas KOt-Bu promotes the formation of the meso-tetraarylethanes. Interestingly, the presence of excess KOt-Bu generates the (E)-tetraarylethenes as the only product.

Key words copper, diastereoselectivity, dimerization, Grignard reaction, coupling

The synthesis of tetraarylethanes attracted chemists due to their important role in medicinal chemistry and also they can be used as ligand scaffolds in organic transformations. Recently, several groups have reported elegant syntheses of tetraarylethanes under metal-catalyzed or metal-free conditions. Among the reported reactions, Schrecken et al. described the synthesis of tetraarylethanes as a mixture of diastereomers (1:1 = dl/meso) using stoichiometric amount of copper salt (Scheme 1, a). Later, Yudin et al. reported the metal-free synthesis of tetraarylethanes as a mixture of diastereomers (Scheme 1, b). Jen et al. reported a one-pot synthesis of enantiomerically enriched tetraarylethanes [86:14 dr (dl/meso)] from the corresponding enantiomerically enriched alcohol using copper catalyst (Scheme 1, c).

However, the methods developed so far suffer from drawbacks such as poor diastereoselectivity, use of stoichiometric amount of copper catalysts, and limited substrate scope. Furthermore, these methods have worked successfully only due to the presence of either bulky substitution like bromide or methyl group at the 6-position of pyridine or electron-withdrawing group like nitro group substitution at the para-position of the aryl part of the substitution in the substrate.

As part of our ongoing research towards developing copper catalyzed coupling reactions, herein we report a copper-catalyzed dehydrogenative homodimerization of readily available 2-benzylpyridines 1 for the diastereoselective synthesis of dl-tetraarylethanes and meso-tetraarylethanes in highly diastereoselective manner (Scheme 1, d).
**Table 1** Optimization of the Reaction Conditions

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<th>Entry</th>
<th>Cu salt</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>2a + 3a/4a</th>
<th>dr dl/meso</th>
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**Scheme 1** Copper-catalyzed synthesis of dl- and meso-tetraarylethanes through diastereoselective homodimerization

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**Previous work**

a) 

\[
\begin{align*}
\text{PhLi} & (1.2 \text{ equiv}) \\
\text{CuCl} & (1 \text{ equiv}) \\
\text{THF}, 60–80^\circ \text{C}
\end{align*}
\]

- Stoichiometric amount of Cu salt
- dr 1:1 (dl/meso)

b) 

\[
\begin{align*}
\text{t-BuOK} & (2 \text{ equiv}) \\
\text{MeOH, reflux}
\end{align*}
\]

- Requirement of NO₂ group
- dr 1:1 (dl/meso)

c) 

\[
\begin{align*}
\text{X} &= \text{Br} \text{ or Me} \\
\text{CuO} & (5 \text{ mol%)} \\
\text{1,10-Phen (10 mol%)} \\
\text{MeMgBr} & (3 \text{ equiv}) \\
\text{THF}, 70^\circ \text{C}, 21 \text{ h}, \text{N}_2
\end{align*}
\]

- One-pot synthesis
- dr 86:14 (dl/meso)

d) 

\[
\begin{align*}
\text{CuO} & (5 \text{ mol%)} \\
\text{1,10-Phen (10 mol%)} \\
\text{CuCl (1 equiv)} \\
\text{MTBE, 0^\circ \text{C}}
\end{align*}
\]

- Catalytic amount of Cu salt
- Highly diastereoselective (> 95:5)
- ∙ Gram-scale synthesis
- ∙ 21 examples

**Present work**

THF, 70 °C, N₂

- Catalytic amount of Cu salt
- Highly diastereoselective (> 95:5)
- Gram-scale synthesis
- 21 examples
Table 1 (continued)

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<thead>
<tr>
<th>Entry</th>
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<sup>a</sup> Isolated yield.
<sup>b</sup> Diastereoselectivity was determined by ¹H NMR analysis of the crude reaction mixture.
<sup>c</sup> Reaction at 110 °C.
<sup>d</sup> Three equiv of base were used.
<sup>e</sup> Four equiv of base were used.
<sup>f</sup> Racemic product was obtained.
<sup>g</sup> Reaction at 60 °C.
<sup>h</sup> Reaction at O₂ atm.
Initially, the homodimerization reaction was started using 2-phenylpyridine (1) as a model substrate with CuI (5 mol%), 1,10-phenanthroline (10 mol%), and KOt-Bu (2 equiv) in toluene at 110 °C. After 26 hours, this reaction provided 84% isolated yield of 2a and 3a as an inseparable mixture of two diastereoisomers (Table 1, entry 1). The diastereomeric ratio 55:45 (dl/meso) of the reaction was determined by 1H NMR spectroscopy of the crude reaction mixture. In order to get high diastereoselectivity, the reaction was carried out using different bases. When the reaction was carried out using inorganic bases, the reaction gave almost a 1:1 mixture of diastereomers (entries 2–4). NaO-t-Bu was ineffective for the dimerization of 1a (entry 5). Next, the focus was shifted towards screening organic bases to increase the diastereoselectivity of this reaction. Interestingly, when the reaction was carried out using phenylmagnesium bromide as a base, the diastereoselectivity was drastically increased to ≥95:5 with 32% yield (entry 6). Screening of other bases revealed o-tolylmagnesium bromide to be the best giving 78% yield of 2a with same selectivity [≥95:5 (dl/meso)] (entries 7–12). When the reaction was carried out with 4 equivalents of base, the yield was decreased to 63% after 21 hours (entry 13). Then, the effect of various copper salts was also assessed (entries 14–20). Among them, CuO was proved to be the most efficient catalyst for this homodimerization reaction. To test the effect of ligands, the reaction was screened with several ligands (entries 21–29). 1,10-Phen (10 mol%) CuO (5 mol%) o-TolMgBr (3 equiv) was carried out using different bases. When the reaction was screened with several ligands (entries 21–29), 1,10-Phenanthroline (L₄) turned out to be the best ligand as they gave maximum yield of 78% in 21 hours with the same diastereoselectivity (entry 12). A solvent screening was then carried out, and low conversion was observed in diethyl ether and MTBE (entries 30 and 31), while the solvent mixture THF/toluene (1:1) led to a decrease in the yield as well as selectivity (entry 32). When the reaction was carried out under oxygen atmosphere, the yield decreased to 57% from 78% (entry 35).

Next, the focus was shifted towards the diastereoselective synthesis of meso-tetraarylethane using 2-phenylpyridine (1a) as a model substrate with 5 mol% of CuI, 10 mol% of 1,10-phenanthroline, and 2 equivalents of KOt-Bu in THF at 60 °C in the presence of oxygen atmosphere. After 10 hours, this homodimerization reaction afforded the product 3a in 90% isolated yield with ≥95:5 diastereoselectivity (Table 1, entry 33). The structure of 3a was confirmed by 1H NMR, HPLC, and single-crystal X-ray diffraction (Figure 1). When the reaction was carried out with 3 equivalents of KOt-Bu in THF as solvent, the reaction gave exclusively 93% of (E)-tetraarylethane 4a (entry 34). The structure and E-configured double bond of the product 4a was confirmed by single-crystal X-ray diffraction (Figure 1).

With the optimized reaction conditions identified (Table 1, entry 13), we investigated the substrate scope for the synthesis of dl-tetraarylethanes (Scheme 2). The different electronic properties of meta- and para-methyl substituents on the phenyl group of the 2-phenylpyridine had little effect on the yields (68–74%) and diastereoselectivities (≥95:5 2b and 2c). Also, substrates containing an ethyl group at ortho- and para-position of benzylpyridine gave the corresponding products 2d, e in good yields. The electron-rich substrates such as para-substituted tert-butyl and 3,5-dimethyl groups contained in the aryl part gave the corresponding products 2f, g in good yields. The structure of 2g was confirmed by single-crystal X-ray crystallography analysis (Figure 1).

![Figure 1](image.png)

**Figure 1** Single-crystal X-ray structures of 2g, 3a, and 4a with 30% probability ellipsoid.

![Scheme 2](image.png)

**Scheme 2** Substrate scope for dl-tetraarylethanes. Isolated yields are shown. The diastereoselectivity was determined by 1H NMR analysis of the crude reaction mixture.
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E

Scheme 3 Substrate scope for the synthesis of meso-tetraarylethanes. Isolated yields are shown. The diastereoselectivity was determined by H NMR analysis of the crude reaction mixture.

Scheme 4 Stereoselective synthesis of (E)-tetraarylethene in manners. Isolated yields are shown. Indicated relative configuration was based on X-ray crystal structure of 4a.

Scheme 5 Gram-scale synthesis of meso-tetraarylethane 3a and (E)-tetraarylethene 4a

E

estingly, substrates having a methyl group at the 6-position of pyridine motif in benzylpyridine was converted into the corresponding homo-coupled product 2i with ≥95:5 diastereoselectivity. We also performed the reaction with ortho-substituted tert-butylbenzylpyridine under optimized conditions. This reaction gave a complex reaction mixture.

Then the focus was shifted towards the selective synthesis of meso-tetraarylethane 3a from 2-benzylpyridine (1a) under the CuI/1,10-Phen/KOt-Bu system. Gratifyingly, a variety of substituted 2-benzylpyridines reacted well under the standard conditions to afford the desired coupling products in good yields (Scheme 3). 2-Benzylpyridines bearing substituted electron-donating groups such as methoxy and ethyl groups gave the desired tetraarylethanes 3b–e in excellent yields with ≥95:5 diastereoselectivity.

We next examined the scope of the (E)-tetraarylethene reaction and the results are summarized in Scheme 4. During our investigation it was observed that the electron-rich or poor substituted 4-t-Bu and 4-Cl benzylpyridines underwent C=C bond formation in 38% and 20% yields in the reaction conditions given in Table 1 (entry 34).

When the reaction was conducted with 4 equivalents of the base, 4-tert-butyl- and 4-chloro- substituted benzylpyridine furnished the corresponding tetraarylethanes 4b and 4e in 78% and 68% yield, respectively. Similarly, 4-SMe containing benzylpyridine derivatives afforded the corresponding product 4d in 72% yield. Under the same optimized reaction conditions, the analogues of benzylpyridine such as 4-(4-methylbenzyl)pyridine (1e) and 4-(4-chlorobenzyl)pyridine (1f) were subjected to homodimerization reactions. These reactions underwent smoothly and gave corresponding tetraarylethanes 4e and 4f in excellent yields.

To find a practical utility of this copper catalyzed homocoupling of 2-benzylpyridine, the reaction was carried out under the optimized conditions on a 30 mmol scale (~5 g). The large-scale reactions gave the corresponding product 3a and 4a in excellent yields (Scheme 5).

We next investigated the copper-catalyzed synthesis of (E)-tetraarylethene (4a) from tetraarylethane (3a) using CuI (5 mol%), 1,10-Phen (10 mol%), and KOt-Bu (2 equiv) in THF, which gave the corresponding product in good yield (Scheme 6). We have also performed a reaction without the addition of copper catalyst and ligands in the presence of two equivalents KOt-Bu, which gave the corresponding tetraarylethene in 51% yield.
The reaction was monitored by TLC. After 10 h, the reaction mixture methanol derivative (1 mmol) in AcOH (3 mL) was stirred at 140 °C.

In conclusion, for the first time, the copper-catalyzed homocoupling of 2-benzylpyridine derivatives has been developed for the diastereoselective synthesis of tetraarylethane under mild reaction conditions. The dl- and meso-tetraarylethane were obtained by two different approaches: The Grignard reagents gave the C2 isomers and KOt-Bu promotes the formation of meso-isomers of tetraarylethane. On the other hand, (E)-tetraarylethane was obtained using an excess of KOt-Bu as the base. In this catalytic system, 1,10-phenanthroline as a ligand played a vital role to bring down copper system from stoichiometric amount to catalytic quantity for homodimerization.

Copper salt and 1,10-phenanthroline were purchased from Aldrich and THF (AR grade) from RANKEM chemical company. Solvents used for extraction and purification were technical grade and distilled before use. Reactions were monitored by TLC on precoated aluminum-packed plates (0.25 mm, Merck Kieselgel 60 with fluorescent indicator UV254) and visualized by fluorescence quenching. Column chromatography was performed with silica gel (particle size 100–120 mesh, RANKEM). IR spectra were recorded on a FTIR 4000 Series spectrophotometer using anhydrous KBr pellets. The wavenumbers of recorded IR signals are quoted in cm⁻¹. Silica gel for column chromatography (particle size 100–200 mesh) was purchased from SRL India.

The 2-benzylpyridine derivatives 1a-i prepared are known compounds and showed analytical and spectral data in accordance with the literature.

**dl-Tetraarylethanes 2a–i; General Procedure**

In a reaction tube, CuO (4 mg, 0.05 mmol), 1,10-phenanthroline (10 mg, 0.010 mmol), and 2-benzylpyridine 1 (159 mg, 160 μL, 1 mmol) were added under N2 atmosphere and the tube was closed with a rubber septum. Then the reaction tube was evacuated and refilled with N2. Freshly prepared Grignard reagent (144 mg, 3 equiv; prepared from 1.2 mmol of Mg with 540 mg (0.6 mL, 1 mmol) of 2-bromo-toluenone in 3 mL of THF) in THF was added dropwise to the reaction mixture at 0 °C. The reaction tube containing the resulting mixture was closed by a glass stopper under an inert atmosphere and the contents were stirred at 70 °C for 24 h. The mixture was quenched with sat. aq NH4Cl (6 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried (anhyd Na2SO4) and concentrated.

The dr was determined by 1H NMR analysis of the crude reaction mixture and the mixture was subsequently purified by silica gel column separation using hexanes and EtOAc mixture to give the respective pure product dl-1,2-diaryl-1,2-di(pyridin-2-yl)ethane 2a–i.

### 1.2-Bis(phenyl)-1,2-di(pyridin-2-yl)ethane (2a)

Yield: 130 mg (78%); white solid; mp 164–166 °C; Rf = 0.57 (hexanes/EtOAc 70:30 v/v).

IR (neat): 2956, 2952, 2857, 1587, 1469, 1431, 747, 703 cm⁻¹.

1H NMR (400 MHz, CDCl3): δ = 7.81 (d, J = 7.2 Hz, 4 H), 7.01 (t, J = 7.2 Hz, 2 H), 6.90 (dd, J = 6.6, 5.2 Hz, 2 H), 5.28 (s, 2 H).

13C NMR (100 MHz, CDCl3): δ = 162.6, 149.0, 142.1, 136.2, 128.9, 126.3, 124.4, 121.0, 57.7.

HRMS: m/z [M + H]+ calcd for C24H21N2: 337.1075; found: 337.1712.

### 1,2-Bis(phenyl)-1,2-di(pyridin-2-yl)ethane (2b)

Yield: 127 mg (68%); white solid; mp 160–162 °C; Rf = 0.52 (hexanes/EtOAc 70:30 v/v).

IR (neat): 2956, 2952, 2857, 1587, 1469, 1431, 747, 703 cm⁻¹.

1H NMR (400 MHz, CDCl3): δ = 8.32 (m, 2 H), 7.30 (td, J = 7.6, 1.6 Hz, 2 H), 7.16 (d, J = 7.6 Hz, 2 H), 7.08 (s, 2 H), 7.05 (d, J = 7.6 Hz, 2 H), 6.91 (t, J = 7.6 Hz, 2 H), 6.80 (ddd, J = 7.5, 2.6, 1.2 Hz, 2 H), 6.75 (d, J = 7.6 Hz, 2 H), 5.15 (s, 2 H), 2.12 (s, 6 H).

13C NMR (100 MHz, CDCl3): δ = 162.9, 148.9, 142.0, 137.5, 136.1, 129.7, 128.0, 127.0, 126.0, 124.0, 121.0, 57.5.


### 1,2-Bis(pyridin-2-yl)-1,2-di(phenyl)ethane (2c)

Yield: 136 mg (74%); white solid; mp 179–181 °C; Rf = 0.50 (hexanes/EtOAc 70:30 v/v).

IR (neat): 2922, 2857, 1512, 1471, 1431, 790, 746 cm⁻¹.

1H NMR (400 MHz, CDCl3): δ = 8.31 (m, 2 H), 7.28 (td, J = 7.6, 1.6 Hz, 2 H), 7.12–7.20 (m, 6 H), 6.78 (ddd, J = 7.6, 4.8, 1.2 Hz, 2 H), 6.84 (d, J = 7.6 Hz, 4 H), 5.17 (s, 2 H), 2.10 (s, 6 H).

13C NMR (100 MHz, CDCl3): δ = 163.0, 148.9, 139.1, 136.1, 135.6, 129.0, 128.7, 124.2, 120.9, 57.1, 21.1.


1,2-Bis(2-ethylphenyl)-1,2-di(pyridin-2-yl)ethane (2d)
Yield: 145 mg (74%); white solid; mp 186–188 °C; \( R_f = 0.53 \) (hexanes/EtOAc 70:30 v/v).
IR (neat): 2925, 1643, 1640, 630, 413 cm\(^{-1}\).
\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 8.33–8.38 \) (m, 2 H), 7.72 (d, \( J = 7.6 \) Hz, 2 H), 5.62 (s, 2 H), 2.68–2.92 (m, 4 H), 1.13 (t, \( J = 6.8 \) Hz, 6 H).
\(^1^3\)C NMR (100 MHz, DMSO-\(d_6\)): \( \delta = 161.2, 148.9, 141.2, 136.2, 130.5, 128.0, 123.8, 121.3, 55.4 \).
HRMS: \( m/z \) [M + H\(^+\)] calcd for \( C_{24}H_{24}N_2: 353.1789 \); found: 353.1772.

\( \text{meso-Tetraarylethanes 3a–e; General Procedure} \)
In a reaction tube, Cul (4 mg, 0.05 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), KOH-Bu (224.42 mg, 2 mmol, 2 equiv), and 2-benzylpyridine (159 mg, 160 \( \mu \)L, 1 mmol) in THF (3 mL) were added under \( O_2 \) atmosphere, then closed with a rubber septum. The reaction tube was evacuated and refilled with \( O_2 \). The reaction tube containing the resulting reaction mixture was closed and the contents were stirred at 60 °C for 24 h. The mixture was quenched with \( H_2O \) (3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried (anhyd \( Na_2SO_4 \)). The dr was determined by \(^1\)H NMR analysis of the crude reaction mixture and the mixture was subsequently purified by silica gel column chromatography using hexanes and EtOAc to give the pure respective meso-1,2-diaryl-1,2-di(pyridin-2-yl)ethane 3–e.

1,2-Bis(phenyl)-1,2-di(pyridin-2-yl)ethane (3a)
Yield: 155 mg (92%); white solid; mp 187–189 °C; \( R_f = 0.57 \) (hexanes/EtOAc 70:30 v/v).
IR (neat): 1584, 1464, 1428, 747, 696, 613 cm\(^{-1}\).
\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 8.35 \) (s, 2 H), 7.40–7.53 (m, 6 H), 7.31–7.39 (m, 2 H), 7.08 (t, \( J = 7.2 \) Hz, 4 H), 6.86–7.01 (m, 2 H), 5.18 (s, 2 H).
\(^1^3\)C NMR (100 MHz, DMSO-\(d_6\)): \( \delta = 162.4, 148.7, 142.3, 136.1, 128.7, 127.9, 125.9, 123.8, 121.0, 56.3 \).
HRMS: \( m/z \) [M + H\(^+\)] calcd for \( C_{24}H_{24}N_2: 337.1705 \); found: 337.1697.

1,2-Bis(3-methoxyphenyl)-1,2-di(pyridin-2-yl)ethane (3b)
Yield: 170 mg (80%); white solid; mp 184–186 °C; \( R_f = 0.54 \) (hexanes/EtOAc 70:30 v/v).
IR (neat): 2961, 2927, 1639, 1595, 749 cm\(^{-1}\).
\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 8.35 \) (d, \( J = 3.6 \) Hz, 2 H), 7.49 (t, \( J = 7.6 \) Hz, 2 H), 7.37 (d, \( J = 7.6 \) Hz, 2 H), 6.93–7.07 (m, 8 H), 6.50–6.60 (m, 2 H), 5.36 (s, 2 H), 3.63 (s, 6 H).
\(^1^3\)C NMR (100 MHz, DMSO-\(d_6\)): \( \delta = 149.1, 144.4, 136.6, 129.3, 124.3, 121.6, 115.2, 111.4, 56.3, 55.3 \).
HRMS: \( m/z \) [M + Na\(^+\)] calcd for \( C_{24}H_{24}N_2O_2Na: 419.1735 \); found: 419.1874.

1,2-Bis(4-methoxyphenyl)-1,2-di(pyridin-2-yl)ethane (3c)
Yield: 146 mg (74%); white solid; mp 171–173 °C; \( R_f = 0.46 \) (hexanes/EtOAc 60:40 v/v).
IR (neat): 2957, 2927, 1591, 1511, 1252, 1037, 912, 743 cm\(^{-1}\).
\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 8.34 \) (d, \( J = 4.0 \) Hz, 2 H), 7.46 (t, \( J = 7.6 \) Hz, 2 H), 7.30–7.40 (m, 6 H), 6.91–6.98 (m, 2 H), 6.66 (d, \( J = 8.8 \) Hz, 4 H), 5.29 (s, 2 H), 3.60 (s, 6 H).
In a reaction tube, CuI (4 mg, 0.05 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol) in THF (3 mL) were added un-
spective product (Rf = 0.66 (hex-
anes/EtOAc 70:30 v/v)).

IR (neat): 3435, 3236, 2924, 2857, 1802, 1698, 1591, 1473, 1347, 1318, 1151, 780 cm–1.


1.2-Bis(2-ethylphenyl)-1,2-di(pyridin-2-yl)ethane (3d)
Yield: 137 mg (68%); white solid; mp 160–161 °C; Rf = 0.50 (hex-
anes/EtOAc 70:30 v/v).

IR (neat): 2924, 2858, 1638, 1596, 1460 cm–1.

HRMS: m/z [M + H] + calcd for C24H19N2: 335.1548; found: 335.1548.

(E)-Tetraarylethenes 4a-f; General Procedure
In a reaction tube, Cul (4 mg, 0.05 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), KOt-Bu (448.84 mg, 4 mmol, 4 equiv), and 2-benz-
zylypyridine I (159 mg, 160 µL, 1 mmol) in THF (3 mL) were added un-
der O2 atmosphere, then closed with a rubber septum. The reaction tube was evacuated and refilled with O2. The reaction tube containing
the resulting reaction mixture was closed and the contents were stirred at 60 °C for 24 h. The mixture was quenched with H2O (3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were evaporated in vacuo and the resulting residue was purified by flash column chromatography (eluent: hexanes) to give the pure
respective product (E)-1,2-diaryl-1,2-di(pyridin-2-yl)ethene 4a-f.

1,2-Bis(phenyl)-1,2-di(pyridin-2-yl)ethene (4a)
Yield: 155 mg (93%); white solid; mp 150–152 °C; Rf = 0.57 (hex-
anes/EtOAc 70:30 v/v).

IR (neat): 1427, 1462, 1582, 2922, 3047 cm–1.


1.2-Bis(4-chlorophenyl)-1,2-di(pyridin-2-yl)ethene (4e)
Yield: 137 mg (68%); white solid; mp 160–161 °C; Rf = 0.50 (hex-
anes/EtOAc 70:30 v/v).

IR (neat): 2924, 2858, 1638, 1596, 1460 cm–1.

1H NMR (400 MHz, CDCl3): δ = 8.67 (dd, J = 4.8 Hz, 4 H), 7.57 (td, J = 2.0 Hz, 4 H), 7.33–7.49 (m, 8 H).

HRMS: m/z [M + H] + calcd for C18H15N2Cl2: 363.1835; found: 363.1835.

1H NMR (400 MHz, CDCl3): δ = 8.40–8.43 (m, 2 H), 7.42 (td, J = 7.6, 1.6 Hz, 2 H), 7.12 (dt, J = 8.4, 1.6 Hz, 4 H), 7.08 (dd, J = 7.8, 1.2 Hz, 2 H), 6.94–7.01 (m, 6 H), 1.13 (s, 18 H).

1C NMR (100 MHz, CDCl3): δ = 160.2, 149.9, 148.9, 142.3, 138.6, 135.8, 130.7, 126.6, 124.8, 121.4, 34.6, 31.4.

HRMS: m/z [M + Na] + calcd for C26H23N2Na: 469.2620; found: 469.2613.

1.2-Bis(4-chlorophenyl)-1,2-di(pyridin-2-yl)ethene (4d)
Yield: 155 mg (72%); white solid; mp 179–181 °C; Rf = 0.50 (hex-
anes/EtOAc 70:30 v/v).

IR (neat): 2924, 2858, 1591, 1318, 1151, 802 cm–1.

HRMS: m/z [M + H] + calcd for C24H17Cl2N2: 403.0769; found: 403.0774.

1H NMR (400 MHz, CDCl3): δ = 8.48–8.39 (m, 2 H), 7.42 (td, J = 8.0, 1.6 Hz, 2 H), 7.13 (t, J = 2.0 Hz, 2 H ), 7.04 (dd, J = 3.6, 2.0 Hz, 2 H), 6.98 (t, J = 2.4 Hz, 2 H), 7.02 (dd, J = 5.6, 1.6 Hz, 2 H), 6.99 (d, J = 2.0 Hz, 2 H).

1C NMR (100 MHz, CDCl3): δ = 161.1, 149.4, 142.1, 139.8, 136.0, 133.5, 132.5, 128.7, 126.4, 122.0.


1H NMR (400 MHz, CDCl3): δ = 8.51–8.53 (d, J = 4.0 Hz, 2 H), 8.39 (d, J = 4.0 Hz, 2 H), 7.65–7.75 (m, 10 H), 6.93–7.00 (m, 4 H).

13C NMR (100 MHz, CDCl3): δ = 161.7, 149.5, 142.8, 141.8, 135.7, 131.1, 128.1, 127.2, 126.6, 121.6.

HRMS: m/z [M + H] + calcd for C23H15N2: 335.1548; found: 335.1548.

12-Bis(4-tert-butylphenyl)-1,2-di(pyridin-2-yl)ethene (4b)
Yield: 181 mg (78%); White solid; mp 164–166 °C; Rf = 0.66 (hex-
anes/EtOAc 70:30 v/v).

IR (neat): 2924, 2855, 1637, 1599, 1093, 1019 cm–1.
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References


(10) With 4 equiv of o-TolMgBr, 4a was obtained in 18%.

(11) CCDC 1486840 (2g), 1486841 (3a), and 1486842 (4a) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.