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Ligand-free indium(III)-catalyzed Heck reaction

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ABSTRACT

A novel ligand-free indium(III)-catalyzed Heck reaction of various aryl iodides with olefins has been developed. As a result, a set of the corresponding *E*-internal olefins was obtained selectively in high to excellent yields. The reaction condition is tolerant to air, in accordance with the concept of modern green chemistry.

1. Introduction

The coupling between an aryl halide and a terminal alkene, widely known as the Heck reaction, has become one of the most important tools in synthetic chemistry.[1,2] As a result, many efficient and selective catalytic systems have been developed for the Heck cross-coupling reaction.[3] However, the vast majority of the existing protocols involve the use of palladium catalysts.[4] The development of improved procedures, in which less expensive, ligand-free and more sustainable catalysts are used, has remained an elusive goal. In this respect, indium catalysts stand out as valuable alternatives to those transition metals used in Heck reactions. The use of indium salts to perform established transition-metal-catalyzed reactions has gained significant attention because of their numerous advantages, namely, their relatively low cost, minimal toxicity, selectivity, and tolerance toward various functional groups, or interesting chemical properties.[5] To the best of our knowledge, an indium catalyzed C(*sp2*)–C(*sp2*) coupling reaction involving a terminal alkene and an aryl halide has not been reported so far.

In our previous research on indium(III)-catalyzed reactions of C–C triple bonds,[6] we have observed that the $InCl_3$ possess a high catalytic activity. Inspired by these findings, we envisaged that the Heck reaction could be promoted by $InCl_3$. To our delight, preliminary experiments, in which those substrates were submitted to the standard conditions used for the indium(III)-catalyzed process revealed that the target products were obtained in good yields.

2. Results and discussion

To identify the optimal conditions for the Heck reaction, a series of catalysts, bases and solvents were screened (Table 1). Initially, the coupling of styrene (**1a**) with phenyl iodide (**2a**) was selected as a model system. The effects of the additives, such as organic and inorganic bases, in the coupling reaction were investigated (Table 1, entries 10–13). When using K_2CO_3 or DMAP as base, **3aa** was obtained in good yields (Table 1, entries 10 and 11). Especially, in the presence of CH_3COONa, the yield of product **3aa** was up to 96% (Table 1, entry 1). Therefore, CH_3COONa was selected as the base for further screening reactions. When $In(OTf)_3$, CuI, or $Cu(OAc)_2$ was used, the reaction was obviously inhibited (Table 1, entries 2–4). In addition, in the presence of other metal catalysts, such as AgOTf, $FeCl_3$, $InCl_2$, and $BiCl_3$, most of the starting material **1a** was recovered (Table 1, entries 5–9). Further optimization suggested that solvents had a strong effect on this process. When this reaction was performed in CH_3NO_2 or DMA, the product **3aa** was not obtained at all (Table 1, entries 14 and 15). Moreover, in other solvents, such as DMSO, PhCl, and $PhCH_3$, the yields of **3aa** dramatically decreased to 28–50% (Table 1, entries 16–18). On the basis of the above

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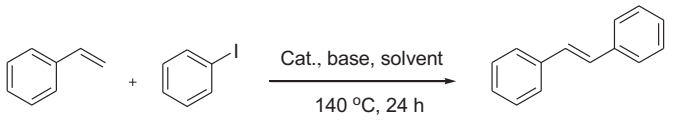
Table 1
Screening conditions for Heck reaction between styrene (**1a**) and phenyl iodide (**2a**)[a]



1a **2a** **3aa**

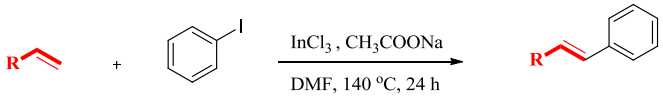
Entry	Catalyst	Solvent	Base	Yield[b] (%)
1	$InCl_3$	DMF	CH_3COONa	96
2	$In(OTf)_3$	DMF	CH_3COONa	65
3	CuI	DMF	CH_3COONa	18
4	$Cu(OAc)_2$	DMF	CH_3COONa	16
5	AgOTf	DMF	CH_3COONa	0
7	$FeCl_3$	DMF	CH_3COONa	0
8	$InCl_2$	DMF	CH_3COONa	0
9	$BiCl_3$	DMF	CH_3COONa	0
10	$InCl_3$	DMF	K_2CO_3	78
11	$InCl_3$	DMF	DMAP	68
12	$InCl_3$	DMF	Cs_2CO_3	45
13	$InCl_3$	DMF	$NaHCO_3$	62
14	$InCl_3$	DMA	CH_3COONa	0
15	$InCl_3$	CH_3NO_2	CH_3COONa	0
16	$InCl_3$	DMSO	CH_3COONa	50
17	$InCl_3$	PhCl	CH_3COONa	45
18	$InCl_3$	$PhCH_3$	CH_3COONa	28
19	—	DMF	CH_3COONa	0

[a] Reaction conditions: styrene **1a** (0.3 mmol), phenyl iodide **2a** (0.45 mmol), catalyst (5 mol % to **1a**), base (1 equiv to **1a**), solvent (2.0 mL), 140 °C, 24 h.
[b] Isolated yield of pure product based on **1a**.

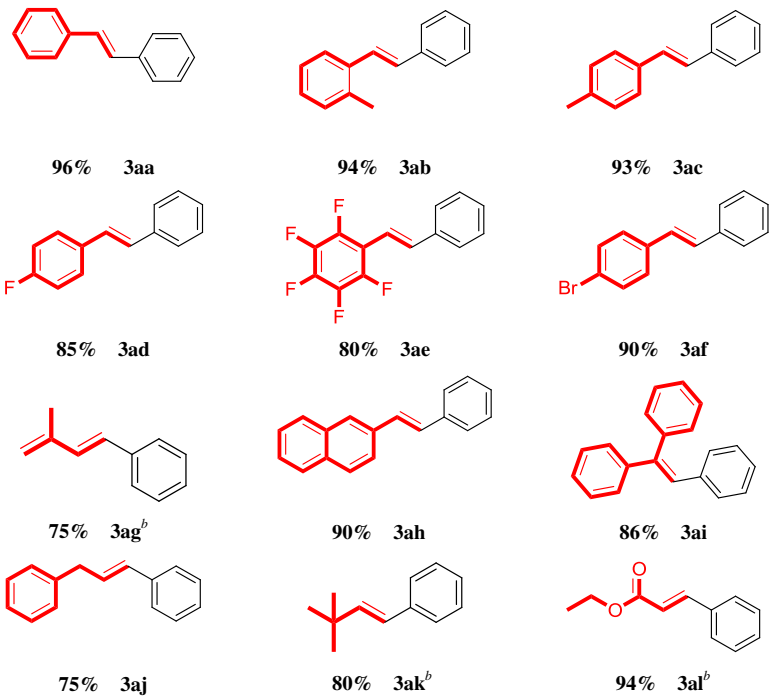
experiments, the optimized reaction conditions are summarized as follows: 5 mol % $InCl_3$, 1 equiv of CH_3COONa, and in DMF.

With the optimal conditions in hand, the scope of the substrates was investigated. Typical results are shown in Table 2. Promoted by $InCl_3$, almost all of the alkyl- and aryl-substituted alkenes processed smoothly under the optimal conditions. The terminal aryl alkenes **1b** and **1c** possessing an electron-donating group at the aryl ring (R=2-MeC_6H_4, 4-MeC_6H_4) reacted with-out a hitch and afforded the desired products **3ab** and **3ac** in 94% and 93% yields, respectively (Table 2, entries **3ab** and **3ac**). Substrates **1d** and **1f**, possessing an electron-withdrawing group (R=4-FC_6H_4, 4-BrC_6H_4) at the benzene ring, also reacted smoothly and afforded the desired products **3ad** and **3af** in 85% and 90% yields, respectively (Table 2, entries **3ad** and **3af**). It was noted that aryl-substituted alkenes bearing a strong electron-withdrawing group on the benzene ring (R=C_6F_5) treated with phenyl iodide **2a** afford the desired product **3ae** in high yield (Table 2, entry **3ae**). Obviously, electron-rich terminal alkenes provided the desired products in higher yields than electron-poor terminal alkenes did. To our delight, the terminal alkyl alkenes **1j** and **1k** in the presence of $InCl_3$ also gave the products **3aj** and **3ak** in 75% and 80% yields, respectively (Table 2, entries **3aj** and **3ak**). Very interestingly, the reaction of substrate 2-methyl-3-butene-2-ol **1g** and phenyl iodide afforded the unexpected product **3ag** (Table 2, entry **3ag**). Additionally, alkenes bearing polycyclic aromatic substituents, such as 2-vinylnaphthalene **1h** were found to give the corresponding products **3ah** in excellent yield (Table 2, entry **3ah**). A mono-substitution on the *ortho*- and *para*-position of aryl olefins had no

Table 2
Ligand-free indium-catalyzed Heck reaction with alkenes **1** and **2a**[a]



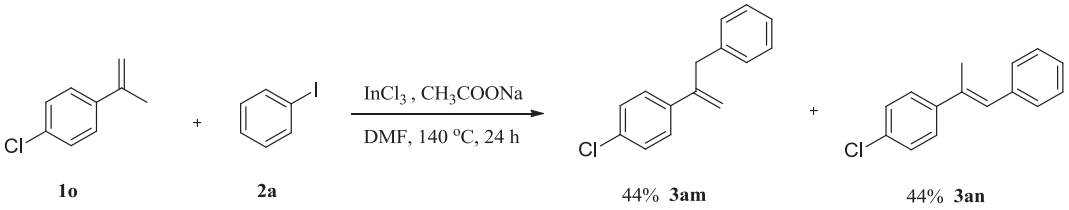
1 **2a** **3** [c]



[a] Reaction conditions: alkenes **1** (0.3 mmol), phenyl iodide **2a** (0.45 mmol), $InCl_3$ (5 mol % to **1a**), CH_3COONa (1 equiv to **1a**), DMF (2.0 mL), 140 °C, 24 h. Isolated yield of pure product based on **1a**. [b] The reactions were carried out in sealed tubes. [c] Only *E* isomer was observed by ^1H NMR.

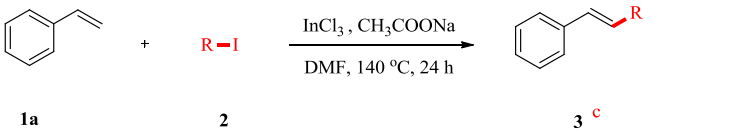
effect on the yields of the reaction (Table 2, entries **3ab** and **3ac**). This method was also successful with ethyl acrylate to afford the corresponding *E*-internal olefin **3al** in 94% yield (Table 2, entry **3al**). The steric effect in our system was then examined. 1,1-Diphenylethylene **1i** was found to give the corresponding product **3ai** in excellent yield (Table 2, entry **3ai**).

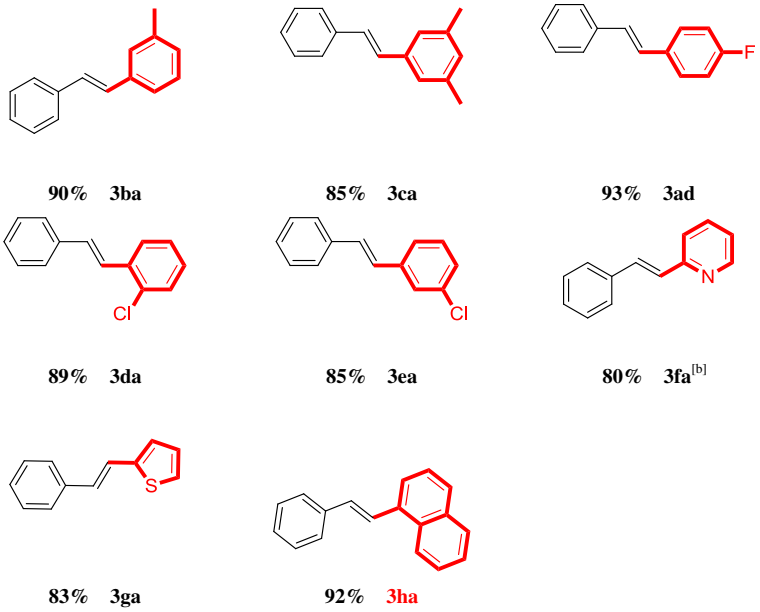
Interestingly, the reaction of 4-chloro-alpha-methylstyrene with **2a** resulted in a mixture of the two regioisomeric products **3am** and **3an** (ratio=1:1) in 44% and 44% yields, respectively (Scheme 1).



Scheme 1. Heck reaction of 4-chloro-alpha-methylstyrene **1o** with phenyl iodide **2a**.

Table 3
Ligand-free indium-catalyzed Heck reaction with styrene **1a** and aryl iodides **2**[a]



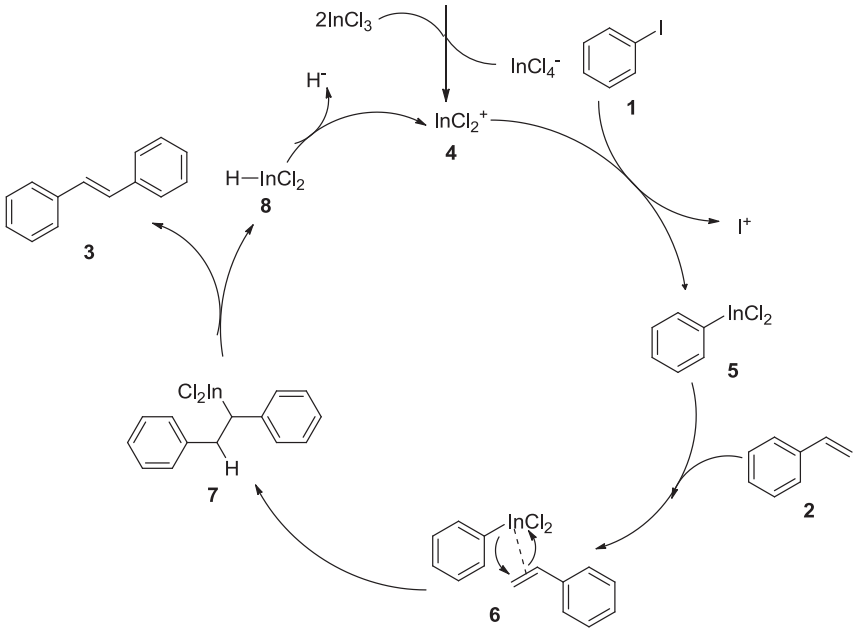


90% 3ba | 85% 3ca | 93% 3ad
89% 3da | 85% 3ea | 80% 3fa[b]
83% 3ga | 92% 3ha

[a] Reaction conditions: styrene **1** (0.3 mmol), aryl iodides **2a** (0.45 mmol), $InCl_3$ (5 mol % to **1a**), CH_3COONa (1 equiv to **1a**), DMF (2.0 mL), 140 °C, 24 h. Isolated yield of pure product based on **1a.** [b] The reactions were carried out in sealed tubes. [c] Only *E* isomer was observed by ^1H NMR.

Next, the scope of this indium-catalyzed Heck reaction was explored by treating styrene **1a** with an array of aryl iodides under the aforementioned optimized conditions. The reaction was readily extended to a variety of aryl iodides in high yields, as long as aryl iodides were used as the arylating agents. Unfortunately, phenyl bromide and phenyl tosylate were not suitable for the reaction under the current conditions. The coupling reactions of both electron-rich and electron-deficient aryl iodides provided corresponding products in high yields. In general, the presence of the *ortho*-, *meta*-, and *para*-position substituents in the electrophilic reagent did not hamper the reaction, which proceeded smoothly in those cases, and afforded the corresponding products **3** in 85–90% yields (Table 3, entries **3ba**, **3ca**, **3ad**, **3da** and **3ea**). In addition, iodide bearing polycyclic aromatic substituent, such as 1-iodonaphthalene led to the corresponding *E*-internal olefin **3ah** in 92% yield (Table 3, entry **3ah**). Alkynes bearing a heterocyclic aromatic substituent, such as 2-thienyl iodide, and 3-pyridinyl iodide were also found to afford the desired products **3ga** and **3fa** in 83% and 80% yields, respectively (Table 3, entries **3fa** and **3ga**).

On the basis of the mechanism of previous reports[7] and our results, a possible catalytic cycle for this indium-catalyzed the reaction of aryl iodides with olefins was proposed in Scheme 2. An immediate $InCl_2^+$ **4** was formed firstly and subsequently the reaction of immediate **4** with phenyl iodide **1** afforded an organoindium intermediate **5**. Then, the intermediate **5** could easily react



Scheme 2. Possible reaction mechanism.

with styrene **2** to give intermediate **7**. β-H elimination of the intermediate **7** occurred to give the desired products **3** and indium species **8**. Finally, indium species **8** could be deprotonated to the active intermediate $InCl_2^+$ **4** to finish the catalytic cycle.

3. Conclusion

In summary, we have developed an effective Heck reaction of alkenes to aryl iodides, which was catalyzed by the commercially available indium catalyst in the presence of CH_3COONa. The alkyl- and aryl-substituted alkenes with aryl iodides are readily available. This reaction system can be carried out under mild conditions that give a rapid access to a variety of *E*-internal olefin and will be appealing for industries.

4. Experimental section

4.1. General methods and materials

All manipulations were performed under an air atmosphere unless otherwise statement. Column chromatography was performed on silica gel (300–400 mesh). NMR spectra were obtained using a Bruker Avance 500 spectrometer (^1H at 500 MHz and ^{13}C at 125 MHz). Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with APCI ionization source.

4.2. General procedure for the *E*-internal olefin 3aa–3an and 3ba–3ga

The reaction mixture of alkenes **1** (0.3 mmol), aryl iodides **2** (0.45 mmol), $InCl_3$ (5 mol %), CH_3COONa (1 equiv) and DMF (2 mL) in a 10 mL dried flask was stirred at 140 °C, and monitored periodically by TLC. Upon completion, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum. The residue was purified by flash column chromatography to afford *E*-internal olefins **3**.

4.3. Characterization of the compounds

*4.3.1. (E)-Stilbenze (**3aa**).*[8] White solid; mp 123–124 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J=7.7 Hz, 4H), 7.43–7.40 (m, 4H), 7.33–7.30 (m, 2H), 7.17 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 128.7, 127.6, 126.5; APCI HRMS exact mass calcd for $(C_{14}H_{13})^+$ requires m/z 181.10173, found m/z 181.10029.

*4.3.2. (E)-2-Methylstilbene (**3ab**).*[8] White solid; mp 158–159 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J=7.4 Hz, 1H), 7.55 (d, J=7.6 Hz, 2H), 7.40–7.34 (m, 3H), 7.31–7.20 (m, 4H), 7.02 (d, J=16.2 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 136.4, 135.8, 130.4, 130.0, 128.7, 128.1, 127.6, 127.5, 126.5, 126.2, 125.3, 19.9. APCI HRMS exact mass calcd for $(C_{15}H_{15})^+$ requires m/z 195.11738, found m/z 195.11545.

*4.3.3. (E)-4-Methylstilbene (**3ac**).*[8] White solid; mp 120–121 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J=7.5 Hz, 2H), 7.46 (d, J=8.0 Hz, 2H), 7.40 (t, J=7.6 Hz, 2H), 7.29 (t, J=7.3 Hz, 1H), 7.21 (d, J=7.9 Hz, 2H), 7.13 (d, J=3.8 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 134.5, 130.4, 129.4, 128.6, 127.7, 127.4, 126.4, 126.4, 21.2; APCI HRMS exact mass calcd for $(C_{15}H_{15})^+$ requires m/z 195.11738, found m/z 195.11586.

*4.3.4. (E)-4-Fluorostilbene (**3ad**).*[8] White solid; mp 123–124 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54–7.49 (m, 4H), 7.41–7.38 (m, 2H), 7.32–7.29 (m, 1H), 7.12–7.03 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 and 161.3, 137.1, 133.5, 128.7, 128.4 and 128.0, 127.9, 127.6, 127.4, 126.4, 115.7 and 115.5; APCI HRMS exact mass calcd for $(C_{14}H_{12}F)^+$ requires m/z 199.09230, found m/z 199.09111.

*4.3.5. (E)-1,2,3,4,5-Pentafluoro-6-styrylbenzene (**3ae**).*[9] White solid; mp 135–136 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J=7.4 Hz, 2H), 7.46–7.33 (m, 4H), 6.99 (d, J=16.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 138.8, 137.3, 136.5, 129.0, 128.9, 126.9, 124.6, 112.7;

APCI HRMS exact mass calcd for $(C_{14}H_8F_5)^+$ requires *m*/*z* 271.05462, found *m*/*z* 271.05481.

*4.3.6. (E)-4-Bromostilbene (**3af**).*[8] Yellow solid; mp 137–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.48 (m, 4H), 7.41–7.34 (m, 4H), 7.31–7.28 (m, 1H), 7.11 (d, *J*=16.3 Hz, 1H), 7.04 (d, *J*=16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 136.2, 131.7, 129.4, 128.7, 127.9, 127.9, 127.4, 126.5, 121.3; APCI HRMS exact mass calcd for $(C_{14}H_{12}Br)^+$ requires *m*/*z* 259.01224; 261.01019, found *m*/*z* 259.01227; 261.01019.

*4.3.7. (E)-(3-Methylbuta-1,3-dienyl)benzene (**3ag**).*[13] Colourless solid; mp 58–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J*=7.5 Hz, 2H), 7.36 (t, *J*=7.7 Hz, 2H), 7.29–7.25 (m, 1H), 6.92 (d, *J*=16.1 Hz, 1H), 6.57 (d, *J*=16.1 Hz, 1H), 5.15 (s, 1H), 5.11 (s, 1H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 137.4, 131.7, 128.7, 128.6, 127.4, 126.5, 117.3, 18.6; APCI HRMS exact mass calcd for $(C_{11}H_{13})^+$ requires *m*/*z* 145.10173, found *m*/*z* 145.10117.

*4.3.8. 2-[(E)-2-Phenyl-1-ethenyl]naphthalene (**3ah**).*[10] White solid; mp 147–149 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.87–7.85 (m, 3H), 7.79 (d, *J*=8.4 Hz, 1H), 7.61 (d, *J*=7.6 Hz, 2H), 7.50 (s, 1H), 7.43 (t, *J*=7.5 Hz, 2H), 7.37–7.26 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 134.8, 133.7, 133.0, 129.0, 128.8, 128.7, 128.3, 128.0, 127.8, 127.7, 126.6, 126.5, 126.3, 125.9, 123.5; APCI HRMS exact mass calcd for $(C_{18}H_{15})^+$ requires *m*/*z* 231.11738, found *m*/*z* 231.11583.

*4.3.9. 1,1′,1″-Ethene-1,1,2-triyltribenzene (**3ai**).*[11] White solid; mp 72–73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.04 (m, 15H), 6.99 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 142.57, 140.3, 137.4, 130.4, 129.5, 128.6, 128.2, 128.2, 127.9, 127.6, 127.5, 127.4, 126.7; APCI HRMS exact mass calcd for $(C_{20}H_{17})^+$ requires *m*/*z* 257.13303, found *m*/*z* 257.13107.

*4.3.10. (E)-1,3-Diphenylpropene (**3aj**).*[12] Yellowish oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.32–7.28 (m, 4H), 7.25–7.18 (m, 4H), 6.47 (d, *J*=15.8 Hz, 1H), 6.40–6.34 (m, 1H), 3.56 (d, *J*=6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 137.5, 131.1, 129.2, 128.7, 128.5, 128.3, 127.1, 126.2, 126.1, 39.3; APCI HRMS exact mass calcd for $(C_{15}H_{15})^+$ requires *m*/*z* 195.11738, found *m*/*z* 195.11552.

*4.3.11. (E)-1-(3,3-Dimethylbut-1-enyl)benzene (**3ak**).*[14] White solid; mp 84–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J*=7.3 Hz, 2H), 7.29 (t, *J*=7.7 Hz, 2H), 7.19 (t, *J*=7.3 Hz, 1H), 6.32–6.24 (m, 2H), 1.12 (s, 9H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 138.1, 128.5, 126.7, 126.0, 124.6, 33.3, 29.6; APCI HRMS exact mass calcd for $(C_{12}H_{17})^+$ requires *m*/*z* 161.13303, found *m*/*z* 161.13156.

*4.3.12. Ethyl(E)-cinnamate (**3ai**).*[8] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J*=16.0 Hz, 1H), 7.52–7.50 (m, 2H), 7.38–7.36 (m, 3H), 6.43 (d, *J*=16.1 Hz, 1H), 4.28–4.24 (m, 2H), 1.35–1.31 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 144.5, 134.4, 130.1, 128.8, 128.0, 118.2, 60.4, 14.2; APCI HRMS exact mass calcd for $(C_{11}H_{13}O_2)^+$ requires *m*/*z* 177.09155, found *m*/*z* 177.09096.

*4.3.13. (E)-1-Chloro-4-(1-phenylprop-1-en-2-yl)benzene (**3am**) and 1-chloro-4-(3-phenylprop-1-en-2-yl)benzene (**3an**).* White solid; mp 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J*=8.3 Hz, 2H), 7.41–7.35 (m, 8H), 7.31–7.28 (m, 5H), 7.24–7.21 (m, 3H), 6.85 (s, 1H), 5.50 (s, 1H), 5.09 (s, 1H), 3.83 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 142.4, 138.0, 136.3, 133.3, 132.9, 129.7, 129.1, 128.8, 128.4, 128.4, 127.5, 127.3, 126.7, 126.2, 115.0, 41.6, 29.7, 17.4; APCI HRMS exact mass calcd for $(C_{15}H_{14}Cl)^+$ requires *m*/*z* 229.07840, found *m*/*z* 229.07664.

*4.3.14. (E)-3-Methylstilbene (**3ba**).*[8] White solid; mp 48–49 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J*=7.3 Hz, 2H), 7.41–7.36 (m, 4H), 7.31–7.28 (m, 2H), 7.13–7.10 (m, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.4, 137.2, 128.8, 128.6, 128.6, 128.4, 127.5, 127.2, 126.5, 123.7, 21.42; APCI HRMS exact mass calcd for $(C_{15}H_{15})^+$ requires *m*/*z* 195.11738, found *m*/*z* 195.11630.

*4.3.15. (E)-1,3-Dimethyl-5-styrylbenzene (**3ca**).* White solid; mp 145–146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J*=7.4 Hz, 2H), 7.42–7.39 (m, 2H), 7.31–7.28 (m, 1H), 7.20 (s, 2H), 7.11 (d, *J*=6.8 Hz, 2H), 6.96 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.6, 137.3, 129.5, 129.0, 128.7, 128.4, 127.5, 126.5, 124.5, 21.38; APCI HRMS exact mass calcd for $(C_{16}H_{17})^+$ requires *m*/*z* 209.13303, found *m*/*z* 209.13174.

*4.3.16. (E)-2-Chlorostilbene (**3da**).*[8] White solid; mp 38–39 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J*=7.8, 1.4 Hz, 1H), 7.58–7.53 (m, 3H), 7.42–7.38 (m, 3H), 7.32–7.27 (m, 2H), 7.21 (td, *J*=7.7, 1.5 Hz, 1H), 7.10 (d, *J*=16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.0, 135.4, 133.4, 131.2, 129.8, 128.7, 128.5, 128.0, 126.9, 126.8, 126.4, 124.7; APCI HRMS exact mass calcd for $(C_{14}H_{12}Cl)^+$ requires *m*/*z* 215.06275, found *m*/*z* 215.06152.

*4.3.17. (E)-3-Chlorostilbene (**3ea**).*[8] White solid; mp 72–73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.50 (m, 3H), 7.38–7.35 (m, 3H), 7.30–7.27 (m, 2H), 7.23 (t, *J*=6.2 Hz, 1H), 7.11 (d, *J*=16.3 Hz, 1H), 7.02 (d, *J*=16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 136.8, 134.6, 130.1, 129.8, 128.7, 128.0, 127.5, 127.2, 126.6, 126.3, 124.7; APCI HRMS exact mass calcd for $(C_{14}H_{12}Cl)^+$ requires *m*/*z* 215.06275, found *m*/*z* 215.06168.

*4.3.18. (E)-2-Styrylpyridine (**3fa**).*[15] White solid; mp 92–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J*=4.7 Hz, 1H), 7.68–7.65 (m, 1H), 7.63–7.55 (m, 3H), 7.41–7.36 (m, 3H), 7.31–7.28 (m, 1H), 7.20–7.14 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 149.6, 136.6, 135.7, 132.8, 128.7, 128.3, 127.9, 127.1, 122.1, 121.8; APCI HRMS exact mass calcd for $(C_{13}H_{12}N)^+$ requires *m*/*z* 182.09697, found *m*/*z* 182.09583.

*4.3.19. (E)-2-Styrylthiophene (**3ga**).*[8] Yellow solid; mp 112–113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J*=7.6 Hz, 2H), 7.39 (t, *J*=7.7 Hz, 2H), 7.31–7.26 (m, 2H), 7.23 (t, *J*=6.2 Hz, 1H), 7.11 (d, *J*=3.4 Hz, 1H), 7.06–7.02 (m, 1H), 6.98 (d, *J*=16.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 137.0, 128.7, 128.3, 127.6, 126.3, 126.1, 124.3, 121.8; APCI HRMS exact mass calcd for $(C_{12}H_{11}S)^+$ requires *m*/*z* 187.05815, found *m*/*z* 187.05727.

*4.3.20. (E)-1-Styrylnaphthalene (**3ha**).*[8] White solid; mp 68–69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J*=8.3 Hz, 1H), 7.95–7.76 (m, 4H), 7.65 (d, *J*=7.6 Hz, 2H), 7.60–7.51 (m, 3H), 7.45 (t, *J*=7.6 Hz, 2H), 7.35 (t, *J*=7.4 Hz, 1H), 7.20 (d, *J*=16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 135.0, 133.7, 131.7, 131.4, 128.7, 128.6, 128.0, 127.8, 126.7, 126.1, 125.8, 125.8, 125.7, 123.8, 123.6; APCI HRMS exact mass calcd for $(C_{18}H_{15})^+$ requires *m*/*z* 231.11738, found *m*/*z* 231.11543.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.019.

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