Metal-Free Hydroarylation of Alkynes: A Very Convenient, Simple Procedure for Substituted Arylalkenes

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Received 4 July 2008; revised 27 August 2008
SYNTHESIS

Abstract: Hydroarylation of aryl-substituted alkynes with simple and substituted arenes was conducted in the presence of trifluoroacetic acid in dichloromethane without any metal catalysts or additives. Electron-rich arenes coupled with aryl-substituted alkynes to give 1,1-diarylalkenes in good to high yields.

Key words: hydroarylation, alkynes, arenes, trifluoroacetic acid

Transition-metal-catalyzed hydroarylation reactions of carbon–carbon multiple bonds are attractive methods for carbon–carbon bond formation and provide a direct synthesis of aromatic alkenes. Historically, Friedel–Crafts reactions of aromatic substrates have been employed for direct functionalization of aromatic compounds, but these reactions require more than an equimolar amount of a Lewis acid such as aluminum(III) chloride.1

Recently, direct hydroarylation of alkynes or alkenes catalyzed by transition metals or Lewis acid metals has attracted considerable attention in organic synthesis.2 Such metal-catalyzed hydroarylation reactions are, indeed, excellent and powerful methods, but in most cases they require high temperatures, strong acidic conditions, and special precautions for handling metal catalysts under an inert atmosphere. Furthermore, the contamination of pharmaceutical materials with even a trace amount of a metal in manufacturing processes causes serious problems. Thus, these drawbacks of metal-catalyzed hydroarylation reactions have attracted our attention to develop a more convenient, simple synthetic method for hydroarylation reactions without metals. In addition, a very recent paper3 reporting an efficient oxidative cleavage of double bonds as a synthetic application of arylated alkenes encouraged us to study the hydroarylation of alkynes.

Very recently, our group and Tunge et al. independently reported the hydroarylation of arylalkenes, i.e., cinnamic acid esters with phenols in trifluoroacetic acid affording dihydrocoumarins, which were catalyzed by trifluoroacetic acid.4 To the best of our knowledge, however, there are no reports on the hydroarylation of alkynes using trifluoroacetic acid as an acid catalyst. Here we wish to report a highly convenient, simple hydroarylation reaction of alkynes with electron-rich arenes without any metal catalysts.

In the present study, we confined our attention to optimizing the hydroarylation reaction of aryl-substituted alkynes with various arenes in the presence of trifluoroacetic acid. Initially, endeavors were mainly focused on the efficiency of the hydroarylation reaction of phenylacetylene (1) with arenes 2 in the presence of trifluoroacetic acid in dichloromethane at 30 °C; the results are given in Table 1. The reaction of electron-rich arenes 2 such as pentamethyldibenzene (2a), 1,2,4,5-tetramethylbenzene (2b), 1-bromo-2,4,6-trimethylbenzene (2e), 1,3,5-trimethylbenzene (2d), and 1,4-dimethylbenzene (2e) gave 1-aryl-1-phenylethenes 3 in good to high yields (entries 1–5). Sterically bulky 1,4-di-tert-butylbenzene (2f) showed low reactivity and gave 3f in 28% yield (entry 6). The reaction with toluene (2g) gave an isomeric mixture of 3g in 31% yield (entry 7). The 1H NMR spectrum showed the ratio of ortho-, meta-, and para-isomers was 41:9:50, indicating that this reaction was ortho,para-directing. The ortho para ratio (0.82) was similar to those in Friedel–Crafts alkylation of toluene with the benzyl cation,5 but higher than those in electrophilic aromatic substitution of trisubstituted arylnvinyl cations (0.3–0.4).6 This higher ortho para ratio is attributable to the lower steric hindrance of the phenylvinyl cation compared with the trisubstituted arylnvinyl cations. Benzene (2h) and naphthalene (2i) showed a very low reactivity and afforded 1,1-diaryl-1-phenylethenes 3h and 3i in 9% and 2% yields, respectively. Reaction with a lower amounts of trifluoroacetic acid or arene 2a resulted in a decrease in the yield of product 3a (entry 10 or 11).

Next, we examined the reaction of para-substituted phenylacetylens 4, 5, and 6 with arenes 2 under the same conditions as that of 1; the results are given in Table 2. In the reaction of 4-methylphenylacetylene (4) with highly electron-rich arenes 2a–d, excellent yields of products 7 were obtained (entries 1–4). However, the reaction with xylene 2e resulted in a low yield of product 7e (entry 5). Similarly, the reaction of 4-methoxynaphthalene (5) with electron-rich arenes 2a–d gave 1,1-diaryl-1-phenylethenes 8 in high yields (entries 6–9). A similar result was obtained even in the reaction of 4-fluorophenylacetylene (6) with 2a (entry 10). Furthermore, we checked the reaction of diphenylacetylene (10) with arenes 2 under the above conditions; as shown in Table 3, the desired products 11 were obtained in quite good yields (entries 1–5).
Finally, the hydroarylation reaction was applied to other alkylnyl systems without any metal catalysts. Using reactive arenes employed in the present study, the reaction of but-3-yn-2-one (12), ethyl propynoate (13) and ethyl phenylpropynoate (14) was conducted, respectively, under the conditions similar to the above reactions (Scheme 1, Table 4). Reaction of 12 with 2a and 2d ef-

<table>
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<tr>
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<th>Yield (%)</th>
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<td>3a</td>
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<tr>
<td>2</td>
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<td>24</td>
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<td>18</td>
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Table 1 Reaction of Alkyne 1 with Arenes 2 in the Presence of Trifluoroacetic Acid

<table>
<thead>
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<th>Product</th>
<th>Yield (%)</th>
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Table 2 Reaction of Alkyne 4, 5, or 6 with Arenes 2 in the Presence of Trifluoroacetic Acid

<table>
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<th>Time (h)</th>
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<td>2a</td>
<td>48</td>
<td>11a</td>
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<tr>
<td>2</td>
<td>4</td>
<td>2b</td>
<td>24</td>
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<td>4</td>
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<td>11d</td>
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<td>11e</td>
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Table 3 Reaction of Alkyne 10 with Arenes 2 in the Presence of Trifluoroacetic Acid

<table>
<thead>
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<th>Arene</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>2a</td>
<td>48</td>
<td>11a</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
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<td>73b</td>
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<td>4</td>
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<td>24</td>
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<td>76</td>
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<tr>
<td>5</td>
<td>2e</td>
<td>24</td>
<td>11e</td>
<td>69</td>
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</tbody>
</table>

* A reaction conditions: alkyne (1 mmol), arene (10 mmol), TFA (1 mL), CH₂Cl₂ (2 mL), 30 °C.

b Isolated yields based on alkyne (1 mmol), arene (10 mmol), TFA (1 mL), CH₂Cl₂ (2 mL), 30 °C.

c A mixture of ortho-, meta-, and para-isomers were formed.

d TFA (0.15 mL) was used.

e A reaction conditions: alkyne (1 mmol), arene (10 mmol), TFA (1 mL), CH₂Cl₂ (2 mL), 30 °C.

f A mixture of E- and Z-isomers.


The present reactions are considered to proceed via α-arylvinyl cations generated by protonation of arylalkynes. The α-arylvinyl cations are stable enough to react with electron-rich aromatics and undergo electrophilic aromatic substitution. Since α-arylvinyl cations without β-substituents predominantly undergo deprotonation, the corresponding vinyl derivatives are not a good choice for the substrate. Therefore, the protonation tool using arylacetylenes is suitable for the synthesis of arylalkynes with hydroarylation.

In summary, we have demonstrated that metal-free hydroarylation of alkynes efficiently proceeds in the presence of trifluoroacetic acid when aryl-substituted alkynes and electron-rich arenes are employed. The simplicity of this procedure, along with the mildness, makes it practical as a synthetic tool for arylalkynes. Furthermore, this metal-free procedure is particularly attractive in pharmaceutical fields.

All solvents and starting materials were used as received without further purification. 'H NMR, 13C NMR and GC-MS were recorded on a Jeol JNM-AL 300 spectrometer in CDCl3 soln (TMS as internal standard) and Shimadzu GCMS-QP5050, respectively. Melting points were determined by a Yanaco melting point apparatus and are uncorrected. Column chromatographic separations were carried out using silica gel as the stationary phase. Pre-coated plates (silica gel 60 F254, Merck, on aluminum sheets) were used for TLC analysis. Elemental analysis was performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

**Hydroarylation of Alkynes; General Procedure**

A test tube with a stopper was charged with an appropriate arene (10 mmol), an alkyne (1 mmol), and CH2Cl2 (2 mL). The mixture was stirred for 5 min in an ice-water bath, and then TFA (1 mL) was gradually added with constant stirring. The mixture was stirred for ~15 min in the ice-water bath and stirred again for ~15 min at r.t. The mixture was then gradually increased to 30 °C and stirred. After completion of the reaction, CH2Cl2 (20 mL) and H2O (20 mL) were added. Solid NaHCO3 was gradually added to neutralize the TFA. The neutral aqueous mixture was extracted with CH2Cl2 (4 × 10 mL) and dried (anhdy Na2SO4). Finally, CH2Cl2 was removed under reduced pressure below 40 °C. Individual pure compounds were isolated by column chromatography (silica gel).

**Scheme 1**

The reactions are considered to proceed via α-arylvinyl cations generated by protonation of arylalkynes. The α-arylvinyl cations are stable enough to react with electron-rich aromatics and undergo electrophilic aromatic substitution. Since α-arylvinyl cations without β-substituents predominantly undergo deprotonation, the corresponding vinyl derivatives are not a good choice for the substrate. Therefore, the protonation tool using arylacetylenes is suitable for the synthesis of arylalkynes with hydroarylation.

**Table 4** Reaction of Alkynes 12–14 with Arenes 2a and 2d

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne (mmol)</th>
<th>Arene (mmol)</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
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<tr>
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<td>2</td>
<td>Ar=COMe</td>
<td>96</td>
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<tr>
<td>2</td>
<td>H=CO2Et</td>
<td>2a</td>
<td>2</td>
<td>Ar=CO2Et</td>
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<td>2</td>
<td>Ar=CO2Et</td>
<td>97</td>
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<tr>
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<td>Ph=CO2Et</td>
<td>2a</td>
<td>2</td>
<td>Ar=CO2Et</td>
<td>97</td>
</tr>
</tbody>
</table>

**Notes:**
- a Reaction conditions: alkyne, arene, TFA (1 mL), r.t.
- b Isolated yields based on alkyne.
- c CH2Cl2 (0.1 mL) was added.
- d TFA (1.5 mL) and CH2Cl2 (0.5 mL) were used.
- e No hydroarylation products were formed.
- f CH2Cl2 (0.25 mL) was added.

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,3,5,6-tetramethylphenyl)ethene (3b)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(Pentamethylphenyl)-1-phenylethene (3a)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(2,5-Dimethylphenyl)-1-phenylethene (3e)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,3,5,6-tetramethylphenyl)ethene (3b)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.

**1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)**

Yield: 0.2241 g (75%); mp 68.2–69.4 °C.
13C NMR (75 MHz, CDCl3): δ = 149.58, 141.47, 140.68, 135.03, 132.93, 130.65, 129.96, 128.29, 128.17, 127.49, 126.50, 114.62, 120.89, 19.58.

1-(2,5-Di-tert-butylphenyl)-1-phenylethene (3f)
Yield: 0.2272 g (89%); mp 117.4–117.9 °C.

1-(4-Methylphenyl)-1-(2,3,5,6-tetramethylphenyl)ethene (7a)
Yield: 0.0208 g (9%).

1-(3-Bromo-2,4,6-trimethylphenyl)-1-(4-methylphenyl)ethene (7c)
Colorless viscous liquid; yield: 0.2710 g (85%).

1H NMR (300 MHz, CDCl3): δ = 7.13 (d, J = 8.1 Hz, 2 HAr), 7.06 (d, J = 8.1 Hz, 2 HAr), 6.99 (s, 1 HAr), 5.93 (d, J = 1.2 Hz, 1 Hvinyl), 5.00 (d, J = 1.2 Hz, 1 Hvinyl), 2.42 (s, 3 H, Me), 2.32 (s, 3 H, Me), 2.26 (s, 3 H, Me), 2.06 (s, 3 H, Me).

13C NMR (75 MHz, CDCl3): δ = 146.80, 140.12, 137.64, 136.69, 136.11, 136.09, 134.90, 129.55, 129.21 125.68, 125.40, 113.82, 23.96, 21.39, 21.12, 19.89.

1-(4-Methylphenyl)-1-(2,4,6-trimethylphenyl)ethene (7d)
Colorless viscous liquid; yield: 0.2434 g (100%).

1H NMR (300 MHz, CDCl3): δ = 7.15 (d, J = 8.4 Hz, 2 HAr), 7.06 (d, J = 8.4 Hz, 2 HAr), 6.91 (s, 2 HAr), 5.91 (d, J = 1.5 Hz, 1 Hvinyl), 5.03 (d, J = 1.5 Hz, 1 Hvinyl), 2.32 (s, 6 H, 2 Me), 2.11 (s, 6 H, 2 Me).

13C NMR (75 MHz, CDCl3): δ = 145.58, 138.31, 137.33, 136.65, 136.30, 136.10, 129.10, 128.02, 125.69, 113.54, 21.11, 21.03, 20.04.

1-(2,5-Dimethylphenyl)-1-(4-methylphenyl)ethene (7e)

1H NMR (300 MHz, CDCl3): δ = 7.14–7.20 (m, 2 HAr), 7.03–7.10 (m, 5 HAr), 5.72 (d, J = 1.5 Hz, 1 Hvinyl), 5.12 (d, J = 1.5 Hz, 1 Hvinyl), 2.33 (s, 6 H, 2 Me), 2.01 (s, 3 H, Me).


1-(4-Methoxycarbonylphenyl)-1- (pentamethylphenyl)ethene (8a)

Yield: 0.2687 g (94%); mp 102.2–103.7 °C.

1H NMR (300 MHz, CDCl3): δ = 7.25–7.20 (m, 2 HAr), 6.82–6.77 (m, 2 HAr), 5.85 (d, J = 1.2 Hz, 1 Hvinyl), 4.95 (d, J = 1.2 Hz, 1 Hvinyl), 3.78 (s, 3 H, OMe), 2.28 (s, 3 H, Me), 2.23 (s, 6 H, 2 Me), 2.10 (s, 6 H, 2 Me).

13C NMR (75 MHz, CDCl3): δ = 159.40, 147.93, 138.91, 133.58, 132.67, 132.29, 131.51, 127.20, 113.66, 112.23, 17.78, 16.75, 16.55.

1-(4-Methylphenyl)-1-(2,3,5,6-tetramethylphenyl)ethene (8b)

Yield: 0.2149 g (78%); mp 124.3–126.3 °C.

1H NMR (300 MHz, CDCl3): δ = 7.23–7.18 (m, 2 HAr), 6.96 (br s, 1 HAr), 6.82–6.77 (m, 2 HAr), 5.86 (d, J = 1.2 Hz, 1 Hvinyl), 4.94 (d, J = 1.2 Hz, 1 Hvinyl), 3.78 (s, 3 H, OMe), 2.24 (s, 6 H, 2 Me), 2.04 (s, 6 H, 2 Me).

13C NMR (75 MHz, CDCl3): δ = 159.09, 147.38, 138.93, 133.58, 132.67, 132.29, 131.51, 127.20, 113.66, 112.23, 55.19, 17.78, 16.75, 16.55.
(Z)-1-(2,4,6-Trimethylphenyl)-1,2-diphenylethene (11c)\(^\text{ii}\)

Colorless semi-solid; yield: 0.2784 g (73%); mixture of isomers (44:56).

\(1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.91–7.35\) (m, 11 H\(_{\text{Ar}}\) and H\(_{\text{vinyl}}\)), 2.31 (s, 3 H, Me), 2.21 (s, 6 H, 2 Me), 2.01 (s, 6 H, 2 Me).

\(1^C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 142.18, 141.67, 137.60, 136.24, 133.90, 132.72, 131.08, 128.59, 128.35, 128.13, 127.82, 127.09, 126.71, 126.18, 17.20, 16.89, 16.65.


Z-1,2-Diphenyl-1-(2,3,5,6-tetramethylphenyl)ethene (11b)

Yield: 0.2023 g (68%); mp 112.8–115.5 °C.

\(1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.90–7.34\) (m, 12 H\(_{\text{Ar}}\) and H\(_{\text{vinyl}}\)), 2.23 (s, 6 H, 2 Me), 1.95 (s, 6 H, 2 Me).

\(1^C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 141.78, 140.95, 138.85, 137.48, 134.00, 131.72, 130.69, 128.55, 128.40, 128.17, 127.83, 127.20, 126.83, 126.11, 20.22, 16.09.


1-(3-Bromo-2,4,6-trimethylphenyl)-1,2-diphenylethene (11c)\(^\text{ii}\)

Colorless semi-solid; yield: 0.2784 g (73%); mixture of E- and Z-isomers (44:56).

\(1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.92–7.30\) (m, 23 H\(_{\text{Ar}}\) and H\(_{\text{vinyl}}\)), 6.48 (s, 1 H\(_{\text{vinyl}}\)), 2.45 (s, 3 H, Me), 2.43 (s, 3 H, Me), 2.40 (s, 3 H, Me), 2.20 (s, 6 H, 2 Me), 1.95 (s, 3 H, 3 Me).

\(1^C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 142.43, 140.43, 139.55, 138.66, 137.87, 137.25, 137.00, 136.87, 136.19, 135.00, 134.89, 130.65, 130.28, 129.76, 129.54, 129.21, 128.71, 128.54, 128.44, 128.31, 128.16, 128.05, 127.47, 127.23, 127.21, 126.96, 125.96, 125.84, 125.63, 24.10, 23.97, 21.72, 20.90, 20.22, 19.61.

MS (EI): \(m/z = 376\) (M\(^+\))/378 (M\(^+\) + 2).

Anal. Calcd for C\(_{32}\)H\(_{22}\)Br: C, 73.21; H, 5.61. Found: C, 73.09; H, 5.57.

(Z)-1,2-Diphenyl-1-(2,4,6-trimethylphenyl)ethene (11d)\(^\text{ii}\)

Yield: 0.2300 g (76%); mp 138.8–140.9 °C.

\(1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.92–7.34\) (m, 13 H\(_{\text{Ar}}\) and H\(_{\text{vinyl}}\)), 2.35 (s, 3 H, Me), 2.00 (s, 6 H, 2 Me).

\(1^C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 141.51, 139.79, 137.47, 136.86, 136.03, 135.89, 128.70, 128.44, 128.21, 128.05, 127.27, 126.94, 125.99, 21.19, 19.80.

References


(9) Identified by comparison with a commercial sample from Tokyo Chemical Industry Co.