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

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 paper[3] reporting an efficient oxidative cleavage of double bonds as a synthetic application of arylated alkenes encouraged us to study the hydroarylation of alkynes.

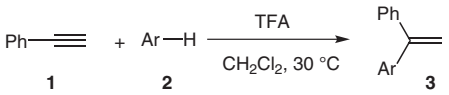
Very recently, our group and Tunge et al. independently reported the hydroarylation of arylalkenes, i.e., cinnamic acid esters with phenols in trifluoroacetic acid affording dihydrocoumarins, which were catalyzed by trifluoroacetic acid.[4] To the best of our knowledge, however, there are no reports 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.

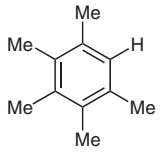
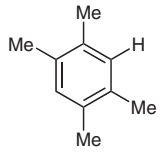
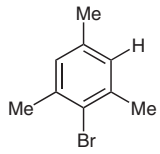
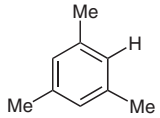
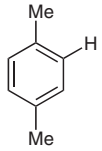
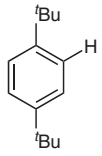
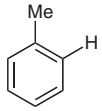
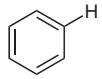
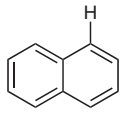
In the present study, we confined our attention to optimizing the hydroarylation reaction of aryl-substituted alkynes with various arenes in the presence of trifluoroacetic acid. Initially, endeavors were mainly focused on the efficiency of the hydroarylation reaction of phenylacetylene (**1**) with 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 pentamethylbenzene (**2a**), 1,2,4,5-tetramethylbenzene (**2b**), 1-bromo-2,4,6-trimethylbenzene (**2c**), 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 ^{1}H 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 alkylations of toluene with the benzyl cation,[5] but higher than those in electrophilic aromatic substitution of trisubstituted arylvinyl 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 arylvinyl cations. Benzene (**2h**) and naphthalene (**2i**) showed a very low reactivity and afforded 1,1-diarylethenes **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 phenylacetylenes **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-methoxyphenylacetylene (**5**) with electron-rich arenes **2a**–**d** gave 1,1-diarylethenes **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).

SYNTHESIS 2008, No. 23, pp 3755–3760
Advanced online publication: 06.11.2008
DOI: 10.1055/s-0028-1083635; Art ID: F15508SS

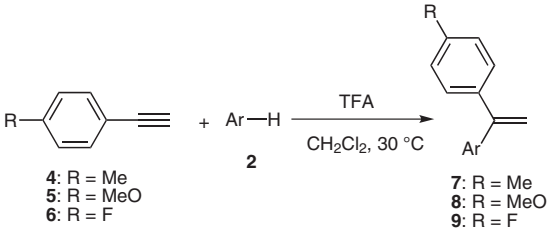
Table 1 Reaction of Alkyne **1** with Arenes **2** in the Presence of Trifluoroacetic Acid [a]



Entry	Ar-H **2** (mmol)		Time (h)	Product	Yield[b] (%)
1		**2a** (10)	48	**3a**	93
2		**2b** (3)	24	**3b**	75
3		**2c** (6)	60	**3c**	69
4		**2d** (3)	24	**3d**	71
5		**2e** (10)	24	**3e**	63
6		**2f** (10)	60	**3f**	28
7[c]		**2g** (100)	72	**3g**	31[d]
8[c]		**2h** (100)	72	**3h**	9
9		**2i** (5)	50	**3i**	2
10[e]		**2a** (10)	48	**3a**	65
11		**2a** (1)	18	**3a**	42

[a] Reaction conditions: **1** (1 mmol), **2**, TFA (1 mL), CH_2Cl_2 (2 mL), 30 °C.
[b] Isolated yields based on alkyne **1**.
[c] No CH_2Cl_2 was added.
[d] A mixture of *ortho*-, *meta*-, and *para*-isomers were formed.
[e] TFA (0.15 mL) was used.

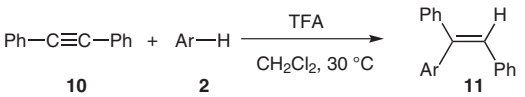
Table 2 Reaction of Alkyne **4**, **5**, or **6** with Arenes **2** in the Presence of Trifluoroacetic Acid[a]



Entry	Alkyne	Arene	Time (h)	Product	Yield[b] (%)
1	**4**	**2a**	48	**7a**	100
2	**4**	**2b**	24	**7b**	89
3	**4**	**2c**	60	**7c**	85
4	**4**	**2d**	24	**7d**	100
5	**4**	**2e**	24	**7e**	40
6	**5**	**2a**	48	**8a**	94
7	**5**	**2b**	24	**8b**	78
8	**5**	**2c**	60	**8c**	73
9	**5**	**2d**	24	**8d**	92
10	**6**	**2a**	48	**9**	92

[a] Reaction conditions: alkyne **4**, **5**, or **6** (1 mmol), arene **2** (10 mmol), TFA (1 mL), CH_2Cl_2 (2 mL), 30 °C.
[b] Isolated yields based on alkyne **4**, **5**, or **6**.

Table 3 Reaction of Alkyne **10** with Arenes **2** in the Presence of Trifluoroacetic Acid[a]



Entry	Arene	Time (h)	Product	Yield (%)
1	**2a**	48	**11a**	68
2	**2b**	24	**11b**	65
3	**2c**	60	**11c**	73[b]
4	**2d**	24	**11d**	76
5	**2e**	24	**11e**	69

[a] Reaction conditions: **10** (1 mmol), **2** (10 mmol), TFA (1 mL), CH_2Cl_2 (2 mL), 30 °C.
[b] A mixture of *E*- and *Z*-isomers.

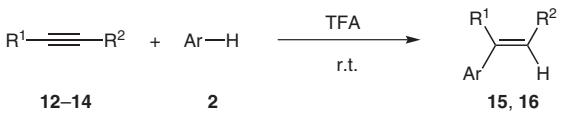
Finally, the hydroarylation reaction was applied to other alkynyl systems without any metal catalysts. Using reactive arenes **2a** and **2d** employed in the present study, the reaction of but-3-yn-2-one (**12**), ethyl propynoate (**13**) and ethyl phenylpropynoate (**14**) was conducted, respectively, under the conditions similar to the above reactions (Scheme 1, Table 4). Reaction of **12** with **2a** and **2d** effi-

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

Entry	Alkyne (mmol)		Arene (mmol)		Time (h)	Product	Yield[b] (%)
1	H—≡—COMe **12**	3	**2a**	2	3	Ar, COMe **15**	96
2[c]	**12**	3	**2d**	2	3	Ar, COMe **16**	97
3[d]	H—≡—CO_2Et **13**	1.5	**2a**	2.4	4	–[e]	–
4[f]	Ph—≡—CO_2Et **14**	1.25	**2a**	2.4	5	–[e]	–

[a] Reaction conditions: alkyne, arene, TFA (1 mL), r.t.
[b] Isolated yields based on alkyne.
[c] CH_2Cl_2 (0.1 mL) was added.
[d] TFA (1.5 mL) and CH_2Cl_2 (0.5 mL) were used.
[e] No hydroarylation products were formed.
[f] CH_2Cl_2 (0.25 mL) was added.

ciently proceeded to give hydroarylation products **15** and **16** in 96% and 97% yields, respectively. However, in the cases of **13** and **14**, the reaction with **2a** did not afford any hydroarylation products at all. This result suggests that ethyl propynoates are less reactive than arylalkynes and but-3-yn-2-one, and their reactions require metal catalysts such as palladium or platinum to activate them.[2b,c]



Scheme 1

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.[6] 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 arylalkenes 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 arylalkenes. Furthermore, this metal-free procedure is particularly attractive in pharmaceutical fields.

All solvents and starting materials were used as received without further purification. ^{1}H NMR, ^{13}C NMR and GC-MS were recorded on a Jeol JNM-AL 300 spectrometer in $CDCl_3$ 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 F_{254}, 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 CH_2Cl_2 (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, CH_2Cl_2 (20 mL) and H_2O (20 mL) were added. Solid $NaHCO_3$ was gradually added to neutralize the TFA. The neutral aqueous mixture was extracted with CH_2Cl_2 (4 × 10 mL) and dried (anhyd Na_2SO_4). Finally, CH_2Cl_2 was removed under reduced pressure below 40 °C. Individual pure compounds were isolated by column chromatography (silica gel).

1-(Pentamethylphenyl)-1-phenylethene (3a)[7]

Yield: 0.2541 g (93%); mp 71.9–73.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.31 (m, 5 H_{Ph}), 5.97 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.07 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.29 (s, 3 H, Me), 2.24 (s, 6 H, 2 Me), 2.10 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.65, 140.03, 138.71, 133.71, 132.33, 131.57, 128.35, 127.41, 126.01, 114.29, 17.84, 16.77, 16.56.

MS (EI): *m*/*z* = 250 (M^+).

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

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

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.29 (m, 5 H_{Ph}), 6.97 (s, 1 H_{Ar}), 5.98 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.07 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.25 (s, 6 H, 2 Me), 2.04 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.04, 141.08, 139.78, 133.53, 131.97, 130.29, 128.37, 127.48, 125.95, 114.19, 20.14, 16.65.

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.41; H, 8.59.

1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene (3c)[2e]

Liquid; yield: 0.2198 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.31 (m, 5 H_{Ph}), 7.00 (s, 1 H_{Ar}), 5.98 (d, *J* = 1.4 Hz, 1 H_{vinyl}), 5.07 (d, *J* = 1.4 Hz, 1 H_{vinyl}), 2.42 (s, 3 H, Me), 2.27 (s, 3 H, Me), 2.07 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.07, 139.97, 138.97, 136.83, 136.14, 134.91, 129.61, 128.50, 127.78, 125.81, 125.45, 114.81, 23.95, 21.42, 19.91.

1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (3d)[2e]

Liquid; yield: 0.1705 g (71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.28 (m, 5 H_{Ph}), 6.91 (s, 2 H_{Ar}), 2.11 (s, 6 H, 2 Me), 2.32 (s, 3 H, Me), 5.96 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.10 (d, *J* = 1.5 Hz, 1 H_{vinyl}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.89, 139.57, 138.17, 136.41, 136.12, 128.39, 128.10, 127.51, 125.82, 114.50, 21.02, 20.06.

1-(2,5-Dimethylphenyl)-1-phenylethene (3e)[2e]

Liquid; yield: 0.1376 g (63%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.28 (m, 5 H_{Ph}), 7.065–7.068 (m, 2 H_{Ar}), 7.02–7.04 (m, 1 H_{Ar}), 5.18 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.75 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.34 (s, 3 H, Me), 2.01 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): 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, 20.89, 19.58.

1-(2,5-Di-*tert*-butylphenyl)-1-phenylethene (3f)
Yield: 0.1010 g (28%); mp 76.2–78.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9 H, *t*-Bu), 1.32 (s, 9 H, *t*-Bu), 5.22 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.90 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 7.05 (d, *J* = 2.4 Hz, 1 H_{Ar}), 7.21–7.33 (m, 6 H_{Ar}), 7.43 (d, *J* = 8.4 Hz, 1 H_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.67, 147.80, 144.80, 141.58, 139.64, 130.24, 128.17, 127.32, 126.89, 126.48, 123.98, 114.93, 36.19, 34.05, 32.26, 31.31.

Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.47; H, 9.67.

1-Phenyl-1-tolylethenes 3g[8]
Liquid; yield: 0.0650 g (31%); mixture of *ortho*-, *meta*- and *para*-isomers (41:9:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13–7.34 (m, H_{Ar}), 5.20 (d, *J* = 1.2 Hz, H_{vinyl}), 5.41 (d, *J* = 1.2 Hz, H_{vinyl}), 5.44 (d, *J* = 1.2 Hz, H_{vinyl}), 5.77 (d, *J* = 1.2 Hz, H_{vinyl}), 2.05 (s, *ortho*-Me), 2.34 (s, *meta*-Me), 2.37 (s, *para*-Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.92, 149.47, 141.69, 141.62, 140.58, 138.61, 137.44, 136.08, 130.05, 129.99, 128.92, 128.84, 128.44, 128.30, 128.27, 128.13, 128.09, 127.60, 127.53, 127.51, 126.46, 125.65, 125.43, 114.79, 114.07, 113.57, 21.39, 21.13, 20.07.

MS (EI): *m*/*z* = 194 (M^+).

1,1-Diphenylethene (3h)[9]
Liquid; yield: 0.0208 g (9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.36 (m, 10 H, 2 Ph), 5.46 (s, 2 H_{vinyl}).

1-(1-Naphthyl)-1-phenylethene (3i)[8c]
Yield: 0.0067 g (2%); mp 46.5–48.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.91 (m, 12 H_{Ar}), 5.98 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.39 (d, *J* = 1.5 Hz, 1 H_{vinyl}).

1-(4-Methylphenyl)-1-(pentamethylphenyl)ethene (7a)
Yield: 0.2696 g (100%); mp 86.4–86.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.4 Hz, 2 H_{Ar}), 7.06 (d, *J* = 8.4 Hz, 2 H_{Ar}), 5.93 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.00 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.32 (s, 3 H, Me), 2.29 (s, 3 H, Me), 2.23 (s, 6 H, 2 Me), 2.10 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.38, 138.85, 137.22, 137.16, 133.60, 132.29, 131.55, 129.07, 125.89, 113.33, 21.11, 17.83, 16.76, 16.55.

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.78; H, 9.25.

1-(4-Methylphenyl)-1-(2,3,5,6-tetramethylphenyl)ethene (7b)
Yield: 0.2272 g (89%); mp 117.4–117.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.1 Hz, 2 H_{Ar}), 7.06 (d, *J* = 8.1 Hz, 2 H_{Ar}), 6.96 (s, 1 H_{Ar}), 5.94 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.00 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.32 (s, 3 H, Me), 2.24 (s, 6 H, 2 Me), 2.04 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.77, 141.21, 137.30, 136.90, 133.47, 131.96, 130.18, 129.09, 125.82, 113.22, 21.11, 20.15, 16.64.

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.08; H, 8.90.

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

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8.1 Hz, 2 H_{Ar}), 7.06 (d, *J* = 8.1 Hz, 2 H_{Ar}), 6.99 (s, 1 H_{Ar}), 5.93 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 5.00 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 2.42 (s, 3 H, Me), 2.32 (s, 3 H, Me), 2.26 (s, 3 H, Me), 2.06 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): 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)[2e]
Colorless viscous liquid; yield: 0.2434 g (100%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 8.4 Hz, 2 H_{Ar}), 7.06 (d, *J* = 8.4 Hz, 2 H_{Ar}), 6.91 (s, 2 H_{Ar}), 5.91 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.03 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.32 (s, 6 H, 2 Me), 2.11 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.58, 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)[2e]
Colorless viscous liquid; yield: 0.0895 g (40%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14–7.20 (m, 2 H_{Ar}), 7.03–7.10 (m, 5 H_{Ar}), 5.72 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 5.12 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 2.33 (s, 6 H, 2 Me), 2.01 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.30, 141.62, 137.79, 137.28, 134.96, 132.91, 130.60, 129.89, 128.99, 128.07, 126.36, 113.72, 21.11, 20.89, 19.57.

1-(4-Methoxyphenyl)-1-(pentamethylphenyl)ethene (8a)[10]
Yield: 0.2687 g (94%); mp 102.2–103.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.20 (m, 2 H_{Ar},), 6.82–6.77 (m, 2 H_{Ar},), 5.85 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 4.95 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 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).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.09, 147.93, 138.91, 133.58, 132.67, 132.29, 131.51, 127.20, 113.66, 112.23, 55.19, 17.78, 16.75, 16.55.

1-(4-Methoxyphenyl)-1-(2,3,5,6-tetramethylphenyl)ethene (8b)
Yield: 0.2149 g (78%); mp 124.3–126.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.18 (m, 2 H_{Ar}), 6.96 (br s, 1 H_{Ar}), 6.82–6.77 (m, 2 H_{Ar}), 5.86 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 4.94 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 3.78 (s, 3 H, OMe), 2.24 (s, 6 H, 2 Me), 2.04 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.15, 147.35, 141.29, 133.48, 132.43, 131.91, 130.16, 127.14, 113.70, 112.10, 55.21, 20.13, 16.58.

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.57; H, 8.43.

1-(2-Bromo-2,4,6-trimethylphenyl)-1-(4-methoxyphenyl)ethene (8c)[2e]
Colorless viscous liquid; yield: 0.2434 g (73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.16 (m, 2 H_{Ar}), 6.99 (br s, 1 H_{Ar}), 6.82–6.77 (m, 2 H_{Ar}), 2.41 (s, 3 H, Me), 2.27 (s, 3 H, Me), 2.07 (s, 3 H, Me), 5.85 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 4.95 (d, *J* = 1.5 Hz, 1 H_{vinyl}), 3.78 (s, 3 H, OMe).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.36, 146.39, 140.22, 136.68, 136.08, 134.87, 131.59, 129.57, 127.03, 125.41, 113.83, 112.69, 55.23, 23.93, 21.34, 19.84.

1-(4-Methoxyphenyl)-1-(2,4,6-trimethylphenyl)ethene (8d)[2e]
Colorless viscous liquid; yield: 0.2424 g (92%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.17 (m, 2 H_{Ar}), 6.90 (br s, 2 H_{Ar}), 6.82–6.77 (m, 2 H_{Ar}), 5.84 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 4.98 (d, *J* = 1.2 Hz, 1 H_{vinyl}), 3.78 (s, 3 H, OMe), 2.31 (s, 3 H, Me), 2.11 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.17, 146.16, 138.38, 136.28, 136.06, 132.17, 128.03, 127.00, 113.71, 112.42, 55.21, 21.02, 19.99.

1-(4-Fluorophenyl)-1-(pentamethylphenyl)ethene (9)
Yield: 0.2905 g (92%); mp 77.6–78.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 [dd, *J* = 5.1 (F-H^{meta}) and 9.0 Hz, 2 H_{Ar}], 6.93 [dd, *J* = 9.0 (F-H^{ortho}) and 9.0 Hz, 2 H_{Ar}], 5.89 (s, 1 H_{vinyl}), 5.03 (s, 1 H_{vinyl}), 2.28 (s, 3 H, Me), 2.23 (s, 6 H, 2 Me), 2.09 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.36 (d, $^1J_{C\text{-}F}$ = 246 Hz), 147.61, 138.48, 136.15 (d, $^4J_{C\text{-}F}$ = 3 Hz), 133.86, 132.43, 131.44, 127.65 (d, $^3J_{C\text{-}F}$ = 8 Hz), 115.16 (d, $^2J_{C\text{-}F}$ = 21 Hz), 113.95, 17.77, 16.75, 16.54.

Anal. Calcd for $C_{19}H_{21}F$: C, 85.03; H, 7.89. Found: C, 85.29; H, 7.97.

(*Z*)-1-(Pentamethylphenyl)-1,2-diphenylethene (11a)[7]
Yield: 0.2234 g (68%); mp 112.8–115.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.91–7.35 (m, 11 H_{Ar} and H_{vinyl}), 2.31 (s, 3 H, Me), 2.21 (s, 6 H, 2 Me), 2.01 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 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 (65%); mp 87.9–90.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90–7.34 (m, 12 H_{Ar} and H_{vinyl}), 2.23 (s, 6 H, 2 Me), 1.95 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 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.

Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.80.

1-(3-Bromo-2,4,6-trimethylphenyl)-1,2-diphenylethene (11c)
Colorless semi-solid; yield: 0.2784 g (73%); mixture of *E*- and *Z*-isomers (44:56).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–7.30 (m, 23 H_{Ar} and H_{vinyl}), 6.48 (s, 1 H_{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, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.43, 140.99, 140.81, 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 $C_{23}H_{21}Br$: C, 73.21; H, 5.61. Found: C, 73.09; H, 5.57.

(*Z*)-1,2-Diphenyl-1-(2,4,6-trimethylphenyl)ethene (11d)[2j]
Yield: 0.2300 g (76%); mp 138.8–140.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–7.34 (m, 13 H_{Ar} and H_{vinyl}), 2.35 (s, 3 H, Me), 2.00 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.51, 139.79, 137.47, 136.86, 136.03, 135.89, 128.70, 128.44, 128.42, 128.21, 128.05, 127.27, 126.94, 125.99, 21.19, 19.80.

(*Z*)-1-(2,5-Dimethylphenyl)-1,2-diphenylethene (11e)[2i]
Colorless viscous liquid; yield: 0.1967 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94–7.34 (m, 14 H_{Ar} and H_{vinyl}), 2.27 (s, 3 H, Me), 1.99 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.45, 141.36, 139.45, 137.35, 135.76, 133.27, 130.46, 130.36, 128.96, 128.36, 128.30, 128.08, 127.97, 127.28, 126.83, 126.60, 20.97, 19.09.

(*E*)-4-(Pentamethylphenyl)but-3-en-2-one (15)[7]
Yield: 0.4153 g (96%); mp 79.4–81.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 16.5 Hz, 1 H_{vinyl}), 6.15 (d, *J* = 16.5 Hz, 1 H_{vinyl}), 2.40 (s, 3 H, Me), 2.26 (s, 3 H, Me), 2.23 (s, 6 H, 2 Me), 2.22 (s, 6 H, 2 Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.31, 145.07, 135.30, 133.82, 132.81, 132.57, 131.05, 27.34, 17.90, 16.87, 16.44.

(*E*)-4-(2,4,6-Trimethylphenyl)but-3-en-2-one (16)[7]
Yield: 0.3652 g (97%); mp 65.3–66.0 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 16.8 Hz, 1 H_{vinyl}), 6.90 (s, 2 H_{Ar}), 6.33 (d, *J* = 16.8 Hz, 1 H_{vinyl}), 2.38 (s, 3 H, Me), 2.32 (s, 6 H, 2 Me), 2.28 (s, 3 H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.41, 141.95, 138.50, 136.75, 132.38, 130.88, 129.22, 27.40, 21.03, 21.02.

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