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Palladium-catalyzed reactions of aryl iodides with trimethylsilylacetylenes and disubstituted alkynes: the synthesis of diarylacetylenes and triarylethylenes

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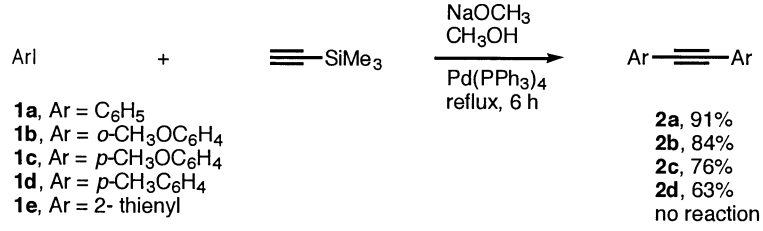
Abstract—Treatment of 2.5 equiv. of aryl iodide with trimethylsilylacetylene in the presence of 3 equiv. of sodium methoxide and 5 mol% of $Pd(PPh_3)_4$ under refluxing methanol for 6 h gave diarylacetylene in good chemical yields. When the catalyst was replaced by $Pd(dba)_2$ and 5 equiv. of aryl iodide were added under the same reaction conditions, triarylethylenes were obtained in 70–85% yields. Only the sterically hindered *o*-methoxyiodobenzene and 2-iodothiophene gave the diarylacetylene, but also in good chemical yield. Reaction of aryl iodides with disubstituted alkynes in the presence of $Pd(OAc)_2$ and sodium methoxide in methanol produced trisubstituted ethylenes in modest to good yields. The hydrogenolysis of the organopalladium is proposed through β-hydride elimination of the palladium methanolate intermediates.

In recent years, diarylacetylenes have received a great deal of attention due to their spectroscopic and electronic properties.[1,2] Triarylethylenes are also of interest because of their spectroscopic and electronic properties[3] as well as their biological activities.[4] Although numerous synthetic routes to these compounds have been reported,[5] most of the reported methods were carried out in stepwise procedure. For instance, the palladium-catalyzed coupling of aryl halides with mono-substituted acetylenes to give the disubstituted compounds and the palladium-catalyzed reaction of aryl iodides or triflates with disubstituted acetylenes to give trisubstituted alkenes.[6] Only two methods described the one-step synthesis of diarylacetylenes from acetylene gas[7] or trimethylsilylacetylene.[8] No report has described a one-step reaction to the synthesis of triarylethylene from trimethylsilylacetylene or acetylene gas. We describe herein an efficient method for the synthesis of symmetrical diarylacetylenes and triarylethylenes from aryl iodides and trimethylsilylacetylene under palladium catalysis in methanol and in the presence of sodium methoxide, as well as the unsymmetrical triarylethylenes from aryl iodides with diarylacetylenes under the same reaction conditions.

Various of aryl iodides **1a–e** reacted with trimethylsilylacetylene in the presence of 3 equiv. of sodium methoxide in methanol using $Pd(PPh_3)_4$ as a catalyst gave the diarylacetylenes in 63–91% yields. The results are summarized in Scheme 1. The reaction of *o*-methoxyphenyl iodide produced the diarylacetylene in 84% yield which indicated that steric hinderance has little effect on this coupling reaction. However, when bromobenzene was used in this reaction, only biphenyl was obtained in 20% yield, and no coupling adduct was formed. (Eq. (1)) 2-iodothiophene gave



Scheme 1.

Keywords: palladium and compounds; hydrogenolysis; β-hydride elimination; diarylacetylenes; triarylethylenes.
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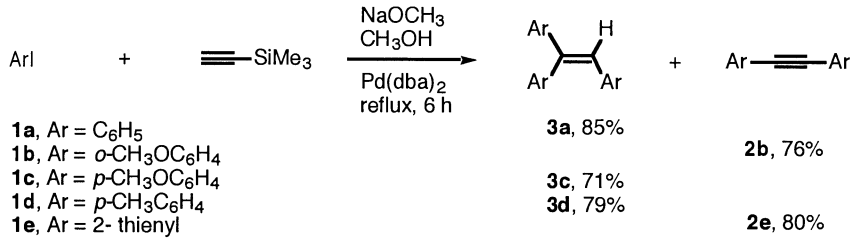
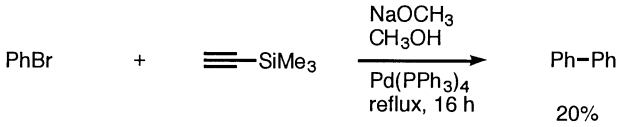


Scheme 2.

no product at all, after stirring the reaction mixture under reflux overnight.



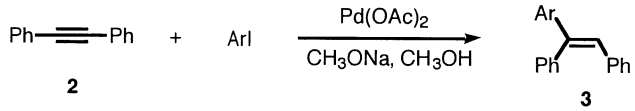
(1)

When 5 equiv. of iodobenzene was used under the same reaction conditions except for 24 h reaction times, diphenylacetylene was obtained in 32% yield and triphenylethylene was produced in 49% yield. When the catalyst was replaced by $Pd(dba)_2$, reaction of 5 equiv. of iodobenzene with 1 equiv. of trimethylsilylacetylene under the same reaction conditions for 6 h, gave triphenylethylene in 85% yield. (Scheme 2) Under the same reaction conditions, *p*-methoxyiodobenzene and *p*-iodotoluene gave the corresponding triarylethylene in 71 and 79% yields, respectively. *o*-Methoxyiodobenzene and 2-iodothiophene gave only diarylacetylenes **2b** and **2e** in 76 and 80%, respectively. This is probably due to the steric hinderance of *o*-methoxyiodobenzene and the poor reactivity of 2-iodothiophene, thus preventing the addition reaction of aryl iodides with diarylacetylenes.

Although the palladium-catalyzed addition of aryl or vinyl halides or triflates to internal alkynes has been reported,[6] all of these methods used formic acid or its salts. The use of palladium catalyst in methanol with sodium methoxide represents an alternative route to trisubstituted alkenes. This finding encouraged us to investigate this hydroarylation of aryl halides with internal alkynes. We first examined the hydroarylation of 1,2-diphenylacetylene (**2a**) with iodobenzene (1.2 equiv.) in the presence of 5 mol% of $Pd(OAc)_2$, 5 mol% of PPh_3 and 5 atom equiv. of sodium in CH_3OH. Stirring this reaction mixture at room temperature for 24 h gave, after chromatography, triphenylethylene (**3a**) in 51% yield. When $Pd(dba)_2$ was used as the catalyst without triphenylphosphine ligand, the reaction gave the same product in 49% yield. Using $Pd(PPh_3)_4$ as the catalyst provided no addition adduct and most of the starting materials were recovered. The optimal conditions were found with 2 equiv. of iodobenzene and $Pd(OAc)_2$ as the catalyst in this case, the reaction produced triphenylethylene in 64% yield. Other aryl iodides were also employed with the optimal conditions and the results are summarized in Table 1. When *p*-trifluoromethyliodobenzene was employed in this reaction, the reaction took place much slower and required refluxing to obtain the addition adduct.

Several unsymmetrical disubstituted alkynes have also been examined in the palladium-catalyzed hydroarylation with aryl iodides. The results are summaried in Table 2. We first tested (*p*-methoxyphenyl)-phenylacetylene (**2f**) with *p*-iodotoluene under the optimal conditions. This reaction produced **4f** and **5f** in 42 and 18% yields, respectively. When (*o*-methoxyphenyl)phenylacetylene (**2g**) was employed in this reaction, compounds **4g** and **5g** were obtained in 24 and 37% yields, respectively. These results indicate that the steric effects or the methoxyl coordination to palladium probably overcome the electronic effects in directing the addition reactions. In the cases of compound **2h** and **2i**, the reactions favor the addition of the aryl group to the less sterically hindered site to give **4h** and **4i** as the major products, respectively. Reaction of **2j** with iodobenzene gave **5j** in 40% yield along with 10% of dimer. This result indicates that both electronic and steric effects strongly influence the regioselectivity of this addition reaction. Bromobenzene has also been employed in this reaction, but with diphenylacetylene under the optimal

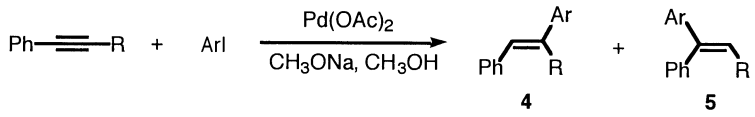
Table 1. Palladium-catalyzed addition of aryl iodides with 1,2-diphenylacetylene



Aryl iodides	Reaction time (h)	Temperature (°C)	Products[a] (yield, %)
2a Ar=C_6H_5	24	25	**3a** (64%)
2b Ar=*o*-$CH_3OC_6H_4$	24	25	**3h** (69%)
2c Ar=*p*-$CH_3OC_6H_4$	24	25	**3g** (69%)
2d Ar=*p*-$CH_3C_6H_4$	24	25	**3f** (72%)
2k Ar=*p*-$CF_3C_6H_4$	48	reflux	**3i** (52%)[b]

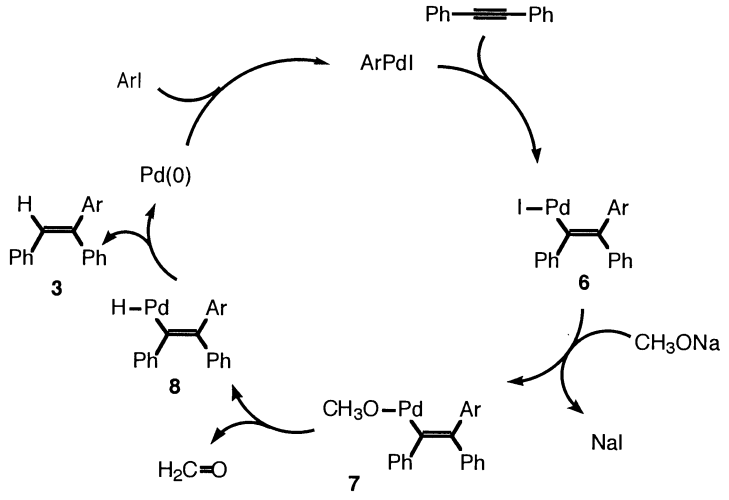
[a] Yields refer to isolated yields. All of the compounds gave satisfactory ^1H ^{13}C NMR and mass spectral data.
[b] Based on recovered starting material.

Table 2. Palladium-catalyzed addition of aryl iodides with unsymmetrical disubstituted alkynes



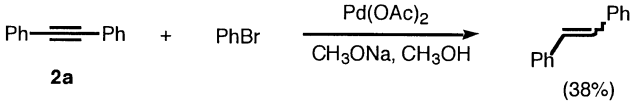
Alkynes	Ar	Temp (°C)/Time (h)	Products (yields, %)[a,b]	
2f, R=*p*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	25/24	**4f** (42%)	**5f** (18%)
2g, R=*o*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	25/48	**4g** (24%)	**5g** (37%)[c]
2h, R=CH_2OH	*p*-$CH_3C_6H_4$	reflux/24	**4h** (37%)	
2i, R=$CH_2CH_2CH_3$	*p*-$CH_3C_6H_4$	reflux/24	**4i** (37%)	**5i** (12%)
2j, R=*o*-NCC_6H_4	C_6H_5	reflux/24		**5j** (40%)[d]

[a] Yields refer to isolated yields. All of the compounds gave satisfactory ^1H ^{13}C NMR and mass spectral data.
[b] Regioisomeric ratios were calculated by GC and NMR.
[c] The structure of 5 g was unambiguously determined by X-ray crystallography.
[d] 10% yield of dimer was also obtained.



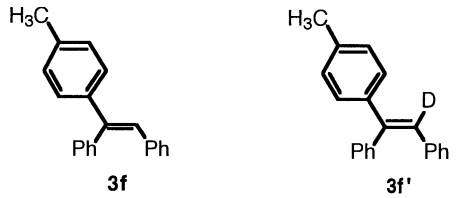
Scheme 3.

reaction conditions, only the reduction adduct, stilbene, was obtained in 38% yield. (Eq. (2))



(2)

To investigate the mechanism of this addition reaction, two reactions were carried out. Treatment of *p*-iodotoluene with diphenylacetylene under the optimal conditions using CH_3OD as the solvent gave the product **3f** in 48% yield. No deuterium incorporation was found in this product. However, when CD_3OD was used as the solvent, the deutero adduct **3f′** was obtained in 50% yield.



According to the results, we proposed a mechanism for this hydroarylation reaction as shown in Scheme 3. This mechanism involves the addition of arylpalladium complex to the alkyne to give the vinylpalladium adduct **6**. Replacement of iodide with methoxide gives **7**,[9] followed by β-hydride elimination[10] to give the hydridpalladium **8**. Reductive elimination of **8** affords the product **3**. The isotope study supported the proposed mechanism which demonstrated that the hydrogen source for hydrogenolysis was the α-hydrogen of methanol.

In conclusion, we have developed efficient synthetic methods for the synthesis of diarylacetylenes and triarylethylenes, and good chemical yields were obtained in most cases. For the directed synthesis of triarylethylenes from trimethylsilylacetylene, $Pd(dba)_2$ is found to be a more efficient catalyst than $Pd(PPh_3)_4$. We have also demonstrated that reaction of aryl iodides with disubstituted alkynes in the presence of $Pd(OAc)_2$ and sodium methoxide in methanol gave trisubstituted ethylenes in reasonable yields. A mechanism of the hydroarylation reaction is proposed through a β-hydride elimination of palladium methanolate which provides an alternative route for hydrogenolysis of organopalladiums.

1. Experimental

Method A. To a stirred solution of trimethylsilylacetylene (1 mmol) in dry methanol (7 mL) was added sequentially the aryl iodide (2.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol) and sodium metal (3 mmol). The resulting solution was heated under reflux and stirred at this temperature for 6 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was diluted with saturated aqueous NaCl solution and extracted with EtOAc (3×10 mL). The extracts were dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by flash column chromatography to give the products.

Method B. Same as method A except 5 equiv. of aryl iodide was used.

1.1. General procedure for hydroarylation of disubstituted acetylenes (Method C)

To a stirred solution of diarylacetylene (1 mmol) and aryl iodide (1.2 mmol) in methanol (5 mL) in the presence of $Pd(OAc)_2$ (5 mol%) and PPh_3 (5 mol%) was added a freshly cut sodium (5 atom equiv.). The reaction mixture was stirred at room temperature for 24 h. Solvent was then removed in vacuo. The residue was treated with saturated aqueous ammonium chloride solution (10 mL) and extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by column chromatography (silica gel) to give the products.

1.1.1. Diphenylacetylene (2a). Obtained by method A in 91% yield as a white solid. mp 60–61°C (lit.,[11] 59–61°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57–7.62 (m, 4H), 7.31–7.42 (m, 6H); MS(EI) *m/z* 178 (M^+, 92%).

1.1.2. 1,2-Bis(2-methoxyphenyl)acetylene (2b). Obtained by method A in 84% yield as a white solid. mp 124–125°C (lit.,[12] 127–128°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (dd, 2H, *J*=7.6, 1.6 Hz), 7.26–7.31 (m, 2H), 6.88–6.95 (m, 4H), 3.92 (s, 6H); MS(EI) *m/z* 238 (M^+, 94%).

1.1.3. 1,2-Bis(4-methoxyphenyl)acetylene (2c). Obtained by method A in 76% yield as a white solid. mp 146–147°C (lit.,[13] 142°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, 4H, *J*=8.4 Hz), 6.86 (d, 4H, *J*=8.4 Hz), 3.82 (s, 6H); MS(EI) *m/z* 238 (M^+, 100%).

1.1.4. 1,2-Bis(4-methylphenyl)acetylene (2d). Obtained by method A in 63% yield as a white solid. mp 138–139°C (lit.,[14] 134–135°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (d, 4H, *J*=8.4 Hz), 7.14 (d, 4H, *J*=8.4 Hz), 2.36 (s, 6H); MS(EI) *m/z* 206 (M^+, 100%).

1.1.5. 1,2-Bis(2-thienyl)acetylene (2e). Obtained by method B in 63% yield as a white solid. mp 101–102°C (lit.,[8] 93–95°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26–7.32 (m, 4H), 7.01 (dd, 2H, *J*=5.2, 3.0 Hz); MS(EI) *m/z* 190 (M^+, 100%).

1.1.6. 1,1,2-Trisphenylethylene (3a). Obtained by method B in 85% yield as a white solid. mp 73–74°C (lit.,[15] 73°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.01–7.35 (m, 15H), 6.97 (s, 1H); MS(EI) *m/z* 256 (M^+, 95%).

1.1.7. 1,1,2-Tris(4-methoxyphenyl)ethylene (3c). Obtained by method B in 71% yield as a white solid. mp 71–72°C (lit.,[16] 69–70°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, 2H, *J*=8.4 Hz), 7.12 (d, 2H, *J*=8.4 Hz), 6.96 (d, 2H, *J*=8.4 Hz), 6.87 (d, 2H, *J*=8.4 Hz), 6.83 (d, 2H, *J*=8.4 Hz), 6.78 (s, 1H), 6.67 (d, 2H, *J*=8.4 Hz), 3.84 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H); MS(EI) *m/z* 346 (M^+, 92%).

1.1.8. 1,1,2-Tris(4-methylphenyl)ethylene (3d). Obtained by method B in 79% yield as a white solid. mp 84–85°C (lit.,[17] 82–84°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09–7.26 (m, 8H), 6.95 (s, 4H), 6.89 (s, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H); MS(EI) *m/z* 298 (M^+, 98%).

1.1.9. (*E*)-1-(4-Methylphenyl)-1,2-diphenylethylene (3f). Obtained by the reaction of *p*-methyliodobenzene with diphenylacetylene (method C) in 72% yield as a white solid. mp 74–75°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12–7.34 (m, 12H), 7.03 (d, 2H, *J*=7.7 Hz), 6.95 (s, 1H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.5, 140.6, 140.5, 137.5, 137.4, 130.4, 129.5, 128.9, 128.6, 127.9, 127.5, 127.3, 126.6, 112.3, 21.1. Anal. Calcd for $C_{21}H_{18}$: C, 93.28; H, 6.72. Found: C, 93.23; H, 6.77.

1.1.10. (*E*)-1-(4-Methoxyphenyl)-1,2-diphenylethylene (3g). Obtained by the reaction of *p*-methoxyiodobenzene with diphenylacetylene (method C) in 69% yield as an oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.23–7.36 (m, 7H), 7.04–7.15 (m, 5H), 6.92 (s, 1H), 6.87 (d, 2H, *J*=8.9 Hz), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 159.2, 142.1, 140.5, 137.6, 136.0, 130.4, 129.4, 128.7, 128.6, 127.9, 127.3, 126.5, 126.4, 113.6, 55.3; EI(MS) *m/z* (rel. intensity) 286 (M^+, 100); HRMS (EI) calcd for $C_{21}H_{18}O$ 286.1358, found 286.1359.

1.1.11. (*E*)-1-(2-Methoxyphenyl)-1,2-diphenylethylene (3h). Obtained by the reaction of *o*-methoxyiodobenzene with diphenylacetylene (method C) in 69% yield as a white solid. mp 71–72°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.27–7.32 (m, 7H), 7.10–7.23 (m, 5H), 7.00 (d, 1H, *J*=6.2 Hz), 6.90 (d, 1H, *J*=8.5 Hz), 6.82 (s, 1H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.3, 141.1, 140.4, 137.5, 133.7, 131.0, 130.2, 129.6, 129.5, 128.7, 127.9, 127.8, 126.7, 126.5, 120.5, 111.9, 55.6; Anal. Calcd for $C_{21}H_{18}O$: C, 88.07; H, 6.34. Found: C, 88.12; H, 6.41.

1.1.12. (*E*)-1-(4-Trifluoromethylphenyl)-1,2-diphenylethylene (3i). Obtained by the reaction of *p*-trifluoromethyliodobenzene with diphenylacetylene (method C) in 52% yield as an oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.56 (d, 2H, *J*=8.1 Hz), 7.42 (d, 2H, *J*=8.1 Hz), 7.05–7.38 (m, 10H), 7.02 (s, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 146.9, 141.3, 139.6, 136.8, 131.6, 130.9, 130.3, 130.0, 129.6, 128.7, 128.1, 127.8, 127.3, 125.2, 125.1; EI(MS) *m/z* (rel. intensity) 324 (M^+, 100); HRMS (EI) calcd for $C_{21}H_{15}F_3$ 324.1126, found 324.1126.

1.1.13. 1-(4-Methylphenyl)-1-(4-methoxyphenyl)-2-phenylethylene (4f) and 1-(4-methylphenyl)-1-phenyl-2-(4-methoxyphenyl)ethylene (5f). Obtained by the reaction of

p-methyliodobenzene with phenyl(4-methoxyphenyl)-acetylene (method C) in 60% yield as a 7:3 ratio as an oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.46–7.51 (m, 0.9H), 7.07–7.36 (m, 8.1H), 6.66–6.98 (m, 5H), 3.84 (s, 2.1H), 3.75 (s, 0.9H), 2.40 (s, 0.9H), 2.37 (s, 2.1H); EI(MS) *m/z* (rel. intensity) 300 (M^+, 100); HRMS (EI) calcd for $C_{22}H_{20}O$ 300.1514, found 300.1520.

1.1.14. 1-(4-Methylphenyl)-1-(2-methoxyphenyl)-2-phenylethylene (4g) and 1-(4-methylphenyl)-1-phenyl-2-(2-methoxyphenyl)ethylene (5g). Reaction of *p*-methyliodobenzene with phenyl(2-methoxyphenyl)acetylene (method C) gave **4g** in 24% yield as an oil and **5g** in 37% yield as a white solid.-Chromatography solvent system uses ethyl acetate–hexane: 1:400. Spectra data for **4g**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (td, 1H, *J*=7.6, 1.0 Hz), 7.25 (dd, 2H, *J*=8.0, 1.0 Hz), 7.08–7.14 (m, 6H), 7.05 (s, 1H), 6.93–7.05 (m, 4H), 3.59 (s, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 157.5, 139.9, 138.8, 137.7, 137.0, 131.6, 129.4, 129.1, 128.9,128.9, 127.9, 127.8, 126.5, 126.4, 121.1, 111.6, 55.6, 21.1; HRMS (EI) calcd for $C_{22}H_{20}O$ 300.1514, found 300.1517. Spectra data for **5g**: mp 75–76°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.11–7.29 (m, 10H), 7.08 (s, 1H), 6.84 (d, 1H, *J*=8.0 Hz), 6.77 (dd, 1H, *J*=7.2, 1.2 Hz), 6.60 (td, 1H, *J*=8.0, 0.8 Hz), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.9, 142.4, 141.0, 140.8, 137.1, 130.6, 130.4, 130.2, 128.8, 128.2, 128.0, 127.8, 127.0, 122.5, 119.8, 110.3, 55.4, 21.1; EI(MS) *m/z* (rel. intensity) 300 (M^+, 100); HRMS (EI) calcd for $C_{22}H_{20}O$ 300.1514, found 300.1515.

1.1.15. 2-(4-Methylphenyl)-3-phenyl-2-propen-1-ol (4h). Obtained by the reaction of *p*-methyliodobenzene with 3-phenyl-2-propyn-1-ol (method C) in 37% yield as a white solid. mp 78–79°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.50 (d, 2H, *J*=7.8 Hz), 7.34–7.43 (m, 5H), 7.24 (d, 2H, *J*=7.8 Hz), 6.97 (s, 1H), 4.71 (s, 2H), 2.40 (s, 3H), 1.70 (s, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 140.0, 137.5, 137.0, 130.4, 130.4, 129.4, 128.9, 128.3, 127.2, 126.4, 60.3, 21.1; Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.02; H, 7.11.

1.1.16. 1-Phenyl-2-(4-methylphenyl)-1-pentene (4i) and 1-phenyl-1-(4-methylphenyl)-1-pentene (5i). Reaction of *p*-methyliodobenzene with 1-phenyl-1-pentyne (method C) gave **4i** in 37% yield as a white solid and **5i** in 12% yield as an oil. Chromatography solvent system uses hexane. Spectra data for **4i**: mp 39–40°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.32–7.41 (m, 7H), 7.20 (d, 2H, *J*=8.2 Hz), 6.71 (s, 1H), 2.68 (t, 2H, *J*=7.7 Hz), 2.40 (s, 3H), 1.43–1.56 (m, 2H), 0.92 (t, 3H, *J*=7.4 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.1, 140.2, 138.5, 136.8, 129.0, 128.8, 128.2, 127.6, 126.5, 126.4, 32.1, 22.0, 21.1, 14.1; Anal. Calcd for $C_{18}H_{20}$: C, 91.46; H, 8.54. Found: C, 91.41; H, 8.58. Spectra data for **5i**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.35 (dd, 2H, *J*=7.8, 1.8 Hz), 7.17 (dd, 2H, *J*=7.8, 1.8 Hz), 7.04–7.12 (m, 5H), 6.05 (t, 1H, *J*=7.5 Hz), 2.32 (s, 3H), 2.08 (q, 2H, *J*=7.6 Hz), 1.40–1.55 (m, 2H), 0.90 (t, 3H, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 141.4, 140.5, 140.1, 136.4, 129.9, 129.2, 128.7, 128.0, 127.1, 126.7, 31.8, 23.2, 21.0, 13.8; EI(MS) *m/z* (rel. intensity) 236 (M^+, 68), 207 (100); HRMS (EI) calcd for $C_{18}H_{20}$ 236.1565, found 236.1567.

1.1.17. 2-(2,2-Diphenylethenyl)benzonitrile (5j). Obtained by the reaction of iodobenzene with 2-(2-phenylethynyl)benzonitrile (method C) in 40% yield as a white solid. mp 124–125°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.60–7.64 (m, 1H), 7.30–7.64 (m, 7H), 7.15–7.28 (m, 6H), 6.90–6.95 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.3, 142.2, 141.3, 139.3, 132.7, 131.7, 130.4, 129.8, 129.2, 128.6, 128.4, 128.3, 128.2, 128.1, 126.8, 123.5, 118.2; Anal. Calcd for $C_{21}H_{15}N$: C, 89.64; H, 5.38; N, 4.98. Found: C, 89.66; H, 5.38; N, 5.03.

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