JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

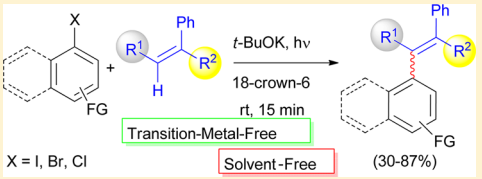
Room-Temperature and Transition-Metal-Free Mizoroki–Heck-type Reaction. Synthesis of *E*-Stilbenes by Photoinduced C–H Functionalization

Javier F. Guastavino, María E. Budén, and Roberto A. Rossi*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, X5000HUA Córdoba, Argentina

Supporting Information

ABSTRACT: We report a conceptually different approach toward *E*-stilbene syntheses by photoinduced direct C–H arylation of alkenes at rt without the addition of transition metals, with a broad range of aryl halides, including ArI, ArBr, and even ArCl. This is the first time that this reaction has been produced without extra solvent but with 18-crown-6 ether and *t*-BuOK in only 15 min of reaction.



INTRODUCTION

Stilbene-based compounds have become of particular interest to chemists because of their broad range of different biological activities.[1,2] For example, *trans*-Resveratrol[1a,3] (**1**, Figure 1) has been shown to possess antioxidative, anticarcinogenic, and antitumor properties. Piceatannol (**2**, Figure 1) is a biologically active molecule that naturally occurs in several plants. This molecule is a powerful antioxidant, and it exhibits much higher antioxidant activity than **1**.[4] Furthermore, Piceatannol can suppress proliferation of a variety of tumor cells, including leukemia, lymphoma, and melanoma.[5] Tamoxifen[6] (**3**, Figure 1) is currently being used in the treatment of several types of breast cancer.

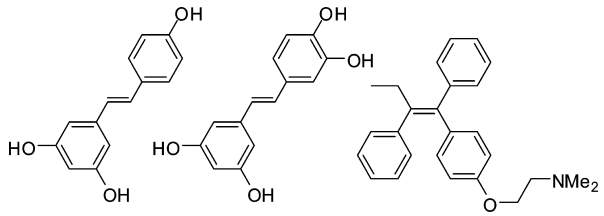
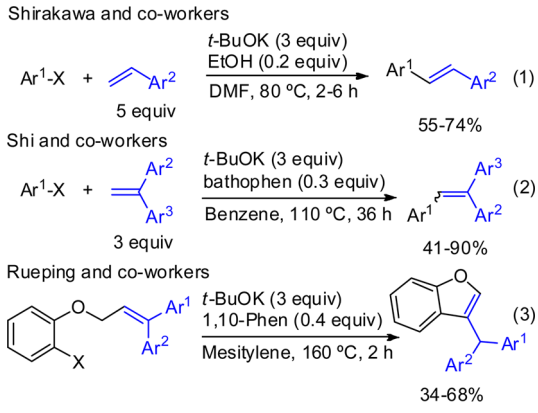


Figure 1. Structures of *trans*-Resveratrol (**1**), Piceatannol (**2**), and Tamoxifen (**3**).

Although stilbenes can be obtained by different reactions and transformations, the most commonly used are Wittig reactions,[7] metal-catalyzed cross-coupling reactions,[8] the Meerwein reaction[9] or Mc-Murry couplings,[10] and Horner–Wadsworth–Emmons (HWE reactions),[11] among others.[2] Nevertheless, the use of Mizoroki–Heck[8,12] and Heck–Matzuda reactions[13] to obtain *E*-stilbenes seems to be the most promising.

On the contrary of modern methods of synthesis, the processes that do not need transition-metal catalysis are important because the products can be directly used in pharmaceutical and other industries. Transition-metal-free coupling reactions offer an inexpensive, yet efficient, route to C–C bond formations, since transition-metal catalysts and impurities can be avoided. This area has been an important development in the past few years,[14] as examples applied to stilbene synthesis. In 2011, it was reported that the *t*-BuO$^-$ anion promoted direct arylation with ArX of different stilbenes (5 equiv) in the presence of 20 mol % of EtOH as additive in DMF at 80 °C, giving the same outcome as that of the transition-metal Mizoroki–Heck reaction (Scheme 1, eq 1).[15] In a similar sense, the olefination reaction proceeded in the presence of *t*-BuOK and a catalytic amount of bathophenanthroline in benzene as the solvent at 110 °C for 36 h (Scheme 1, eq 2).[16] This methodology was also applied to the construction of several benzofurans in an intramolecular reaction of allyl 2-halophenyl ethers in the presence of 1,10-phenanthroline in mesitylene, although a higher reaction temperature was necessary (Scheme 1, eq 3).[17]

Scheme 1. Transition-Metal-Free Mizoroki–Heck-type Reaction

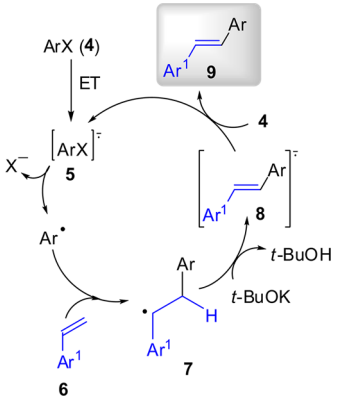


Received: July 2, 2014
Published: September 3, 2014

   dx.doi.org/10.1021/jo501474w | J. Org. Chem. 2014, 79, 9104–9111

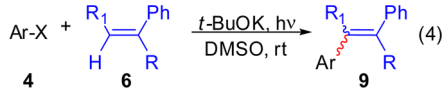
In this reaction, the ArX (**4**) is activated by electron transfer (ET) reaction to generate a radical anion **5**, which fragments to an aryl radical ($Ar^{\bullet}$) and the X^- anion. The addition of an aryl radical to styrene derivates (**6**) provides a benzylic radical intermediate **7**, which, by deprotonation by the *t*-BuO^- anion, forms the radical anion of the stilbene derivate **8**. A subsequent ET generates the *E*-stilbene derivative **9** and a new **5**, thereby continuing the chain process (Scheme 2).

Scheme 2. Mechanisms of Mizoroki−Heck-type Reaction Mediated by *t*-BuOK



Transition-metal-free coupling reactions were intensively studied and used efficiently in biaryl construction by base-promoted homolytic aromatic substitution (BHAS).[18−20] However, different from BHAS, the synthesis of stilbenes by the Mizoroki−Heck-type reaction has not been extensively investigated[15−17] and there has been no development of new synthetic protocols or applications since 2011. Given the importance of these compounds, we believe that research for the development of efficient methods is a great challenge.

Recently, we reported biaryl syntheses by photoinduced[21] direct C−H arylation of benzene and thiophene in the presence of *t*-BuOK.[22] Particularly noteworthy was the fact that this protocol worked at rt with only a base and light being necessary. Taking this into account, we speculated that this methodology could also be applicable to alkenes **6**, which would provide a very promising approach for a clean, efficient, and cheap synthesis of stilbene moieties **9** from different ArX (**4**) (eq 4).



RESULTS AND DISCUSSION

When the above hypothesis was applied, the reaction of 4-iodoanisole (**4a**) with styrene (**6a**) and 3 equiv of *t*-BuOK in DMSO under photostimulation[21] for 1.5 h gave 67% (61% of *E* isomer) of 4-methoxystilbene **9-aa** (Table 1, entry 1), with the same result being obtained in the presence of 10 equiv of **6a** (Table 1, entry 2). In contrast, a lower yield with a low conversion was observed when the reaction was carried out with only 1 equiv of *t*-BuOK (30% of **9-aa**, entry 3) or with a lower amount of DMSO (entry 4). Furthermore, the use of THF, pyridine, dioxane, and dimethoxyethane solvents did not afford any **9-aa**. However, in DMF, the reaction proceeded, but a longer reaction time was required (entries 5 and 6 for **4a**, and entries 10 and 11 for 4-iodotoluene (**4b**)). This trend was observed for different substrates, so we believe that DMSO is the most suitable solvent for this methodology, although both solvents were investigated.[23] It is worth nothing that, in contrast with thermal reaction,[15] a low yield of stilbene was observed when EtOH (20 mol %) was used, which has a lower basicity (pK_a 29.8) and is a more hydrogen-atom donor than *t*-BuOK (pK_a 32.2).[24] In this regard, when **4b** reacted with **6a** in DMF, 50% of **9-ba** was obtained, whereas, in the presence of EtOH (20 mol %), the stilbene **9-ba** was afforded in only 35% yield (entries 11 and 12).

We suggest that the formations of aryl radicals and radical anions were the key steps (Scheme 2), which was supported by the results of the experiments performed in the presence of the radical scavenger TEMPO and the good electron acceptor *m*-dinitrobenzene (*m*-DNB) that inhibited the reaction (Table 1, entries 7 and 8). In addition, this reaction occurs in very low yield in dark conditions (entry 9).

The substrate scope for this reaction was examined, with the best results obtained with Method A being shown in Scheme 3.[23] PhI and ArI with electron-donating groups (EDG) in the *para* position (OMe, Me, Ph) underwent the coupling with **6a** in good or very good yields (see **9-aa**, **9-ba**, **9-ca**, and **9-fa**). However, a slight prolonged reaction time was necessary for *ortho*-substituted ArI (**9-da** and **9-ea**). In addition, the reaction of the ArI with electron-withdrawing groups (EWGs) (F and CF_3) gave the stilbenes **9-ga** and **9-ha** in regular yields. When the aryl radical had an EWG, it was converted into arene, probably through further reduction to aryl anions or by H-abstraction from the solvent. Similar results were obtained for the 1- and 2-naphthyl system to afford **9-ia** and **9-ja** stilbenes. In contrast, the addition of a dimsyl anion to alkene was observed when 1,1-diphenylethylene **6b**, *cis*-stilbene **6c**, and α-methylstyrene **6d** were employed, and stilbenes **9-cb**, **9-bc**, **9-bd**, and **9-ad** were obtained in regular yields. It should be noted that, in these cases, a high conversion was found, despite the product yields being moderated. To investigate if these problems could be overcome, we decided to study this reaction without any solvent.

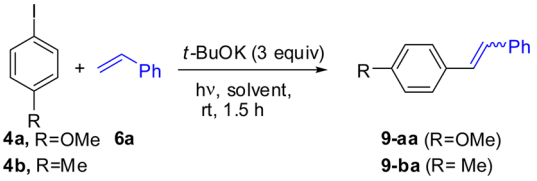
When the reaction without solvent was carried out (entry 1, Table 2), the product **9-aa** was not found, probably due to the insolubility of the base in the reaction media. To overcome this, we explored the reaction in the presence of different ligands such as diglyme and 1,10-phenathroline (entries 2 and 3), but unlike the reported methodology (Scheme 1, eqs 2 and 3), no reaction took place under this condition. The breakthrough came when we used 18-crown-6 ether (18-C-6) (3 equiv) for coordinating the potassium cation. In this case, the reaction provided stilbene **9-aa** in 76% yield (entry 4, Table 2). It is proposed that 18-C-6 coordinated the potassium cation, which suppresses ion-pairing in *t*-BuOK salt. In this condition, the free *t*-BuO^- anion could act as an electron donor. It is known that *t*-BuOK can form the radical anion type **5** by ET in photostimulated $S_{RN}1$ reactions, which can start the chain process.[25]

Then, a screening of equivalents of *t*-BuOK, 18-C-6, and alkene and the reaction time was carried out (entries 5−8, Table 2),[26] with the best result being obtained in the photostimulated reaction of **4a** (1 equiv) with **6a** (10 equiv), *t*-BuOK (3 equiv), and 18-C-6 (3 equiv), which, after 15 min, gave a 90% yield of **9-aa** (87% of *E* isomer **9-aa**, entry 8, Table 2). It is noteworthy that the amount of alkene or base can be lowered, but the yields of **9-aa** were slightly lower.

In the reaction of **4a** with **6a** in the dark (entry 9, Table 2), the product **9-aa** was surprisingly obtained in 59% yield.

dx.doi.org/10.1021/jo501474w | J. Org. Chem. 2014, 79, 9104−9111

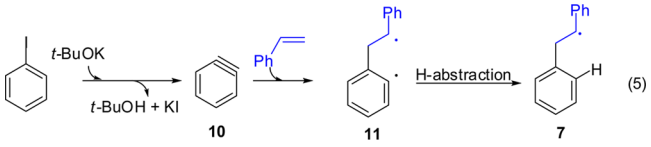
Table 1. Photostimulated Reaction of 4a−4b and 6a[a]



entry	recovered yield of **4a−4b**[b] (%)	conditions	yield of **9aa-9ba**[c] (yield of *E*)[d] (%)	I^- (%)[e]
1	**4a** (4)	**DMSO**	**67 (61)**	**86**
2[f]		DMSO	66 (57)	90
3		DMSO, 1 equiv *t*-BuOK	30 (21)	52
4[fg]	(39)	DMSO	33 (30)	58
5		DMF	(30)	44
6		DMF, 5 h	64 (51)	81
7		DMSO, 30 mol % TEMPO	4	8
8	(62)	DMSO, 30 mol % *m*-DNB	8 (7)	36
9[f]		DMSO, dark	17 (16)	27
10	**4b**	DMSO, 1 h	(74)	89
11		DMF, 5 h	(50)	92
12		DMF, 5 h, 20 mol % EtOH	(35)	83

[a]The photostimulated reaction was carried out under a N_2 atmosphere using **4a−4b** (1 equiv, 0.5 mmol), *t*-BuOK (3 equiv), and **6a** (5 equiv) with 1 mL of solvent in a sealed tube for 1.5 h. [b]Yields of recovered **4a−4b** were determined by GC (internal standard method). [c]Yields of **9-aa** or **9-ba** were determined by GC and correspond to *Z* and *E* isomers. [d]Yields were determined by GC. [e]I^- anions were determined potentiometrically. [f]With 10 equiv of **6a**. [g]0.5 mL of DMSO was used.

The conversion under this reaction condition was not complete (66% of I^- ions being found) even at long reaction times (48 h; results not tabulated). One possibility is that the initiation step is



via a benzyne intermediate.[27] It is known that *t*-BuOK can react with PhI to form benzyne **10** (eq 5).[28] This intermediate undergoes reactions with alkenes to yield a diradical **11**,[29] which then, by hydrogen atom abstractions, gives a benzylic radical intermediate **7**, which continues the chain process (Scheme 2). Radicals and radical anions were intermediates for this mechanism, due to the dark reaction being inhibited in the presence of TEMPO and *m*-DNB (entries 10 and 11, Table 2). On the other hand, in dark conditions, spontaneous or thermal ET from *t*-BuOK to ArI[25,30] cannot be ruled out as initiation steps.

To investigate if the arylation of alkenes could effectively be promoted in the absence of the photostimulation, we decided to study the reaction at 50 °C (entry 12). For these conditions, although the conversion was complete (96% of I^- ion being found), the yields of **9-aa** remained unchanged with the two regioisomers 3- and 4-methoxy-1-(*tert*-butoxy)benzene products, being observed at similar ratios, which were probably formed by the benzyne intermediate. These outcomes show that the light catalyzed the reaction, thereby allowing it to be completed in only 15 min, probably due to that the light is favoring the ET process over benzyne intermediate formation, which increased the yields of stilbene. However, the generation of stilbene under this thermal condition opens up possibilities for further investigation to develop the stilbene synthesis from ArX and alkenes in metal-free conditions at rt (entry 9).[31]

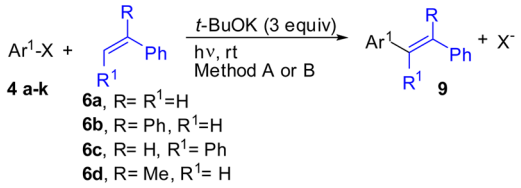
To explore further this strategy in the presence of 18-C-6 ether, several ArX were subjected to the optimized conditions to afford the *E*-stilbene products, with the best results obtained being shown in Scheme 3 (Method B, without solvent at rt). Using this methodology, *ortho*- and *para*-substituted ArI with EDG reacted with **6a** in good to very good yields (55−87% yields). Once again, the reaction of ArI with EWGs gave the *E*-stilbene products in regular yields (46% for **9-ga** and 30% for **9-ha**). It should also be noted that strong EWGs in the ArI (e.g., associated CF_3 group) were ineffective substrates in the Shirakawa protocol.[15] Moreover, not only ArI but also ArBr and even ArCl underwent coupling when the organic moiety had an extended π-system, as a biphenyl, quinolyl, or 1- or 2-naphthyl group, providing good to very good yields (53−75% of stilbenes **9-fa**, **9-ka**, **9-ia**, and **9-ja**). Finally, when other alkenes were tested, the trisubstituted *E*-stilbenes **9-cb**, **9-bc**, **9-bd**, and **9-ad** were obtained in good to very good yields (45−82%).

CONCLUSIONS

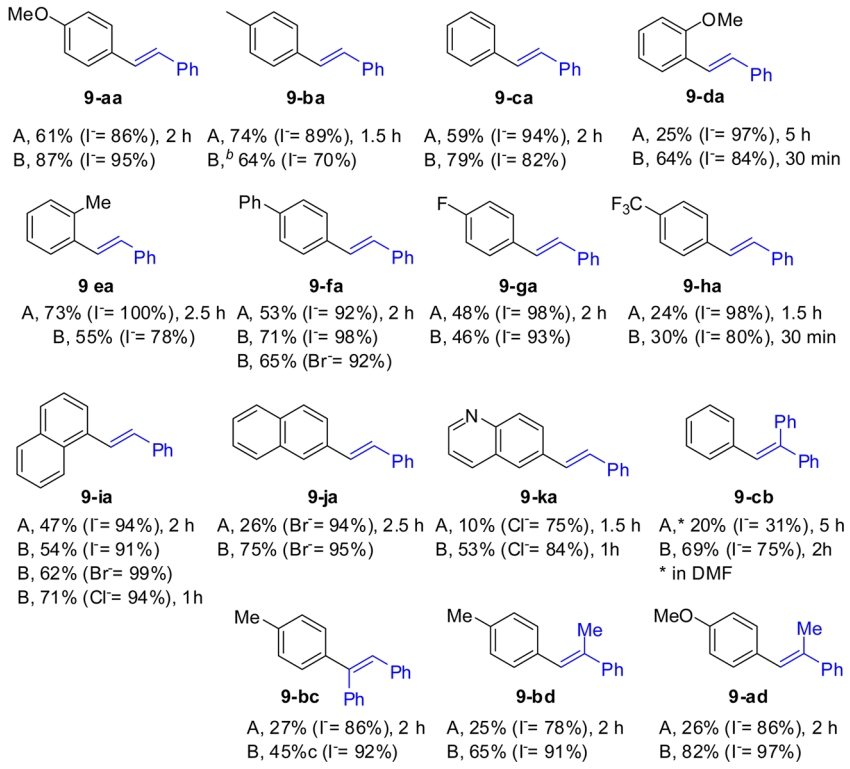
In summary, we have developed a novel approach toward the stilbene syntheses, solvent- and metal-free photoinduced direct C−H functionalization at rt. This environmentally friendly methodology effectively promoted the arylation of the unactivated alkenes, such as **6a−d**, using a broad range of ArI. Both, ArBr and ArCl, react when the organic moiety had an extended π-system. In all cases, a high regioselectivity was found with *E*-stilbenes being formed as the main products. On the basis of these results, a plausible chain mechanism via ET with radicals and radical anions as intermediates for this photoinduced reaction is proposed. However, in dark conditions, possibly, species generated from the benzyne intermediate could be operating in the initiation step. Further investigations to expand this novel method to a broad number of substrates are currently underway in our laboratory.

dx.doi.org/10.1021/jo501474w | J. Org. Chem. 2014, 79, 9104−9111

Scheme 3. Direct Arylation of 4a–k with Alkenes 6a–d[a,b,c]



Method A: 1 equiv of Ar^1X, 5 equiv of **6**, 3 equiv of *t*-BuOK in DMSO (1 mL)
Method B: 1 equiv of Ar^1X, 10 equiv of **6**, 3 equiv of t-BuOK and 3 equiv of 18-crown-6 ether (15 min)



[a]These reactions were carried out under a N_2 atmosphere of **4** in the presence of alkene **6** and *t*-BuOK under photostimulation in a sealed Schlenk tube. Yields of *E* isomer were determined by GC (internal standard method). *Z* isomer was detected (low yield) in all reactions but was not quantified. [b]In 1 mL of benzene as the solvent. [c]Yield of *E* + *Z* isomers.

Table 2. Photostimulated Reaction of 4a and 6a in the Presence of 18-C-6 Ether[a]

entry	equiv **6a**	equiv 18-C-6	reaction time	conditions	yield **9-aa** (yield *E*)[b] (%)	I^- (%)[c]
1	5		2 h			6
2	10		15 min	diglyme, 3 equiv		<4
3	10		15 min	1,10-phenantroline, 3 equiv		<4
4	5	3	2 h		76 (72)	94
5[d]	5	1.5	2 h		64 (51)	76
6	5	3	45 min		76 (73)	79
7	5	3	15 min		73 (71)	80
8	10	3	15 min		90 (87)	95
9	10	3	15 min	dark	(59)	66
10	10	3	15 min	dark, 30 mol % TEMPO		24
11	10	3	15 min	dark, 30 mol % *m*-DNB		11
12	10	3	15 min	dark, 50 °C	(52)	96

[a]The photostimulated reaction was carried out under a N_2 atmosphere using **4a** (1 equiv, 0.5 mmol), *t*-BuOK (3 equiv), 18-C-6 (3 equiv), and **6a** without solvent in a sealed tube. [b]Yields were determined by GC (internal standard method). [c]I^- ions were determined potentiometrically. [d]With 1.5 equiv of *t*-BuOK.

EXPERIMENTAL SECTION

General Methods. Gas chromatographic analyses were performed using a gas chromatograph with a flame ionization detector, and equipped with the following columns: HP1 25 m × 0.20 mm × 0.25 μm column and VF-1 ms, 15 m × 0.25 mm × 0.25 μm column. ^1H NMR (400.16 MHz) and ^{13}C NMR (100.63 MHz) spectra were obtained in

dx.doi.org/10.1021/jo501474w | J. Org. Chem. 2014, 79, 9104–9111

$CDCl_3$ as solvent. Coupling constants are given in Hz, and chemical shifts are reported in δ values in parts per million (ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. Gas chromatographic/mass spectrometer analyses were carried out with a VF-5 ms, 30 m × 0.25 mm × 0.25 μm column. Irradiation was conducted in a reactor equipped with two Philips HPI-T 400-W lamps (cooled with water). Potentiometric titration of halide ions was performed in a pH meter using a Ag/Ag^+ electrode.

Materials. 4-Iodoanisole (**4a**), 4-iodotoluene (**4b**), iodobenzene (**4c**), 2-iodoanisole (**4d**), 2-iodotoluene (**4e**), 4-iodobiphenyl (**4f-1**), 4-bromobiphenyl (**4f-2**), 1-fluoro-4-iodobenzene (**4g**), 1-iodo-4-(trifluoromethyl)benzene (**4h**), 1-iodonaphthalene (**4i-1**), 1-bromonaphthalene (**4i-2**), 1-chloronaphthalene (**4i-3**), 2-bromonaphthalene (**4j**), 6-chloroquinoline (**4k**), 1,1-diphenylethylene (**6b**), *cis*-stilbene (**6c**), and α-methylstyrene (**6d**) were commercially available and used as received from the supplier. DMSO was stored under molecular sieves (4 Å). Styrene (**6a**) was distillated before used. All solvents were analytical-grade and used as received from the supplier. Silica gel (0.063−0.200 mm) was used in column chromatography, and 1, 2, and 4 mm silica gel (60 PF 254) plates where employed in radial thin-layer chromatography purification.

Experimental Procedures. *Method A: Photostimulated Reaction of 4-Iodoanisole (**4a**) with Styrene (**6a**) in DMSO.* The reaction was carried out in a 20 mL flame-dried Schlenk tube, equipped with a nitrogen inlet and magnetic stirrer at rt. DMSO (1 mL) was dried and deoxygenated; then, styrene (**6a**, 5 equiv, 0.290 mL), substrate **4a** (1.0 equiv, 0.117 g, 0.5 mmol), and *t*-BuOK (3.0 equiv, 0.168 g, 1.5 mmol) were added and the reaction mixture was irradiated for 1.5 h. The reaction was quenched with water and ammonium nitrate in excess. The residue was extracted with ethyl acetate (3 × 20 mL), and the organic extract was washed with water, dried with anhydrous Na_2SO_4, and filtered. The solvent was removed to leave the crude product. The product **9-aa** was purified by radial thin-layer chromatography on silica gel, eluting with pentane, and was isolated as a white solid.

*Method B: Photostimulated Reaction of 4-Iodoanisole (**4a**) with Styrene (**6a**) and 18-Crown-6 Ether (18-C-6).* The reaction was carried out in a 5 mL flame-dried Schlenk tube, equipped with a nitrogen inlet and magnetic stirrer at room temperature. Styrene (**6a**, 10 equiv, 0.580 mL, 5 mmol), 18-C-6 (3 equiv, 396.5 mg, 1.5 mmol), substrate **4a** (1.0 equiv, 0.117 g, 0.5 mmol), and *t*-BuOK (3.0 equiv, 0.168 g, 1.5 mmol) were added, and the reaction mixture was irradiated for 15 min. The reaction was quenched with water and ammonium nitrate in excess. The residue was extracted with ethyl acetate (3 × 20 mL), and the organic extract was washed with water, dried with anhydrous Na_2SO_4, and filtered. The solvent was removed to leave the crude product. The product **9-aa** was purified by radial thin-layer chromatography on silica gel, eluting with pentane, and was isolated as a white solid.

*Method C: Reaction of 4-Iodoanisole (**4a**), Styrene, and 18-Crown-6 Ether with Conventional Heating.* The reaction was carried out in a 5 mL flame-dried Schlenk tube, equipped with a nitrogen inlet and magnetic stirrer at 50 °C. Styrene (**6a**, 10 equiv, 0.580 mL, 5 mmol), 18-crown-6 ether (3 equiv, 396.5 mg, 1.5 mmol), substrate **4a** (1.0 equiv, 0.117 g, 0.5 mmol), and *t*-BuOK (3.0 equiv, 0.168 g, 1.5 mmol) were added, and the reaction mixture was heated at 50 °C for 15 min. The reaction was quenched with water and ammonium nitrate in excess. The residue was extracted with ethyl acetate (3 × 20 mL), and the organic extract was washed with water, dried with anhydrous Na_2SO_4, and filtered. The solvent was removed to leave the crude product. The product **9-aa** was purified by radial thin-layer chromatography on silica gel, eluting with pentane, and was isolated as a white solid.

Characterization Data. *(E)-1-Methoxy-4-styrylbenzene (**9-aa**):*.[15,32−34] [1142-15-0] Compound **9-aa** was obtained according to the general procedure. The product was purified by column chromatography on silica gel, eluting with a pentane/diethyl ether gradient (100:0 → 80:20), and was isolated as a white solid (Method B, 91.5 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50−7.48 (m, 2H, CH), 7.47−7.44 (m, 2H, CH) 7.36−7.32 (m, 2H, CH), 7.26−7.21 (m, 1H, CH), 7.07 (d, J = 16.3 Hz, 1H, CH), 6.97 (d, J = 16.3 Hz, 1H, CH), 6.90 (m, 2H, CH), 3.83 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (C), 137.8 (C), 130.3 (C), 128.8 (CH), 128.4 (CH), 127.9 (CH), 127.4 (CH), 126.8 (CH), 126.4 (CH), 114.3 (CH), 55.5 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.49/7.34, 7.49/7.23, 7.49/6.97, 7.45/7.07, 7.45/6.90, 7.34/7.23, 7.34/6.97, 7.07/6.97. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.49/126.4, 7.45/127.9, 7.34/128.8, 7.23/127.4, 7.07/128.4, 6.97/126.8, 6.90/114.3, 3.83/55.5. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.49/127.4, 7.45/159.5, 7.45/128.4, 7.34/137.8, 7.23/126.4, 7.07/137.8, 6.97/137.8, 6.97/130.3, 6.97/128.4, 6.97/126.4, 6.90/159.5, 6.90/130.3, 3.83/159.5. GC−MS (70 eV): m/z (%): 211 (M^+ +1, 16), 210 (M^+, 100), 209 (18), 195 (20), 179 (14), 178 (9), 167 (32), 166 (12), 165 (37), 152 (24), 115 (7), 89 (11), 82 (11).

*(E)-1-Methyl-4-styrylbenzene (**9-ba**):*.[32−35] [1860-17-9] Compound **9-ba** was obtained according to the general procedure. The product was purified by column chromatography on silica gel, eluting with petroleum ether, and was isolated as a white solid (Method A, 71.9 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37 (d, J = 7.5 Hz, 2H, CH), 7.28 (d, J = 8.0 Hz, 2H, CH), 7.21 (t, J = 7.5 Hz, 2H, CH), 7.11 (t, J = 7.3 Hz, 1H, CH), 7.03 (d, J = 8.0 Hz, 2H, CH), 6.99−6.90 (m, 2H, CH), 2.22 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6 (C), 137.5 (C), 134.7 (C), 129.5 (CH), 128.7 (CH), 127.8 (CH), 127.5 (CH), 126.6 (CH), 126.5 (CH), 21.3 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.37/7.21, 7.28/7.03, 7.28/2.22, 7.21/7.11, 7.03/2.22. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.37/126.5, 7.28/126.6, 7.21/128.7, 7.11/127.5, 7.03/129.5, 6.98/128.7, 6.98/127.8, 2.22/21.3. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.37/127.5, 7.37/126.5, 7.28/137.5, 7.28/128.7, 7.28/126.6, 7.21/137.6, 7.21/128.7, 7.11/128.7, 7.11/127.8, 7.11/126.6, 7.03/134.7, 7.03/129.5, 7.03/21.3, 6.98/137.5, 6.98/134.7, 6.98/128.7, 6.98/127.8, 6.98/126.6, 2.22/137.5, 2.22/129.5. GC−MS (70 eV): m/z (%): 195 (M^+ + 1, 15), 194 (M^+, 91), 193 (25), 180 (16), 179 (100), 178 (90), 165 (10), 115 (11), 96 (16), 89 (13), 82 (15).

*(E)-1,2-Diphenylethene (**9-ca**):*.[15,32−35] [103-30-0] Compound **9-ca** was obtained according to the general procedure and was isolated as a white solid (Method B, 71.2 mg, 79% yield). GC−MS (70 eV): m/z (%): 181 (M^+ + 1, 12), 180 (M^+, 100), 179 (84), 178 (62), 177 (10), 176 (11), 165 (45), 152 (11), 102 (9), 90 (11), 89 (26), 77 (9), 76 (21), 63 (8), 51 (9).

*(E)-1-Methoxy-2-styrylbenzene (**9-da**):*[36] [52805-92-2] The product **9-da** was separated by radial thin-layer chromatography (4 mm) on silica gel, eluting with petroleum ether, and was isolated as a white solid (Method B, 67.3 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (dd, J = 7.7, 1.6 Hz, 1H, CH), 7.54−7.51 (m, 2H, CH), 7.48 (d, J = 16.5 Hz, 1H, CH), 7.36−7.32 (m, 2H, CH), 7.26−7.21 (m, 2H, CH), 7.11 (d, J = 16.5 Hz, 1H), 6.98−6.94 (m, 1H, CH), 6.89 (dd, J = 8.3, 0.8 Hz, 1H, CH), 3.88 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (C), 138.1 (C), 129.3 (CH), 128.8 (CH), 128.7 (2 CH), 127.5 (CH), 126.7 (2 CH), 126.6 (C), 126.5 (CH), 123.7 (CH), 120.9 (CH), 111.1 (CH), 55.7 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.59/7.48, 7.59/7.23, 7.59/6.94, 7.53/7.34, 7.53/7.23, 7.53/7.11, 7.48/7.11, 7.48/6.94, 7.34/7.23, 7.23/6.94, 7.23/6.89, 6.94/6.89, 6.89/3.88. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59/126.5, 7.53/126.7, 7.48/123.7, 7.34/128.7, 7.23/128.8, 7.23/127.5, 7.11/129.3, 6.94/120.9, 6.89/111.1, 3.88/55.7. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59/157.1, 7.59/128.8, 7.59/123.7, 7.59/111.1, 7.53/129.3, 7.53/127.5, 7.53/126.7, 7.48/157.1, 7.48/138.1, 7.48/126.7, 7.48/126.6, 7.34/138.1, 7.34/128.7, 7.23/157.1, 7.23/126.6, 7.11/126.7, 7.11/126.6, 7.11/111.1, 6.94/126.6, 6.94/111.1, 6.89/157.1, 6.89/126.6, 6.89/120.9, 3.88/157.1. GC−MS (70 eV): m/z (%): 211 (M^+ + 1, 14), 210 (M^+, 100), 179 (15), 178 (11), 167 (24), 166 (13), 165 (47), 152 (28), 119 (23), 104 (25), 91 (36), 89 (16), 82 (23), 76 (7).

*(E)-1-Methyl-2-styrylbenzene (**9-ea**):*.[15,34,37] [74685-42-0] Compound **9-ea** was obtained according to the general procedure. The product was purified by column chromatography on silica gel, eluting with pentane/CH_2Cl_2 (100:0 → 80:20), and was isolated as a yellow oil (Method A, 70.9 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, J = 7.0 Hz, 1H, CH), 7.55−7.49 (m, 2H, CH), 7.38−7.31 (m, 3H, CH), 7.28−7.24 (m, 1H, CH), 7.23−7.20 (m, 1H, CH), 7.19−7.17

dx.doi.org/10.1021/jo501474w | J. Org. Chem. 2014, 79, 9104−9111

(m, 2H, CH), 7.00 (d, J = 16.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (C), 136.5 (C), 135.9 (C), 130.5 (CH), 130.1 (CH), 128.8 (2 CH), 127.8 (CH), 127.7 (CH), 126.7 (3 CH), 126.3 (CH), 125.5 (CH), 20.1 (CH_3).^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H δ 7.59/7.22, 7.59/2.43, 7.52/7.34, 7.52/7.26, 7.52/6.98, 7.34/7.26, 7.34/2.43, 7.22/6.98. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59/125.5, 7.52/126.7, 7.34/128.8, 7.34/126.7, 7.26/127.8, 7.22/126.3, 7.18/130.5, 7.18/127.7, 7.00/130.1, 2.43/20.1. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59/135.9, 7.59/127.7, 7.52/130.1, 7.52/127.7, 7.52/126.7, 7.34/137.7, 7.34/135.9, 7.34/128.8, 7.34/125.5, 7.26/126.7, 7.22/130.5, 7.22/125.5, 7.18/136.5, 7.18/130.5, 7.18/126.3, 7.18/20.1, 2.43/135.9, 2.43/130.5. GC−MS (70 eV): m/z (%): 195 (M^+ + 1, 12), 194 (M^+, 85), 193 (13), 180 (13), 179 (100), 178 (72), 165 (12), 152 (9), 116 (20), 115 (30), 96 (24), 91 (10), 89 (17), 82 (13).

*(E)-4-Styryl-1,1′-biphenyl (**9-fa**)*:.[15,38] [21175-18-8] Compound **9-fa** was obtained according to the general procedure. The product was recrystallized from CH_2Cl_2 as a white solid (Method B, 91.0 mg, 71% yield from **4f-1**). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63−7.56 (m, 6H, CH), 7.54−7.52 (m, 2H, CH), 7.44 (t, J = 7.6 Hz, 2H, CH), 7.38−7.32 (m, 3H, CH), 7.28−7.24 (m, 1H, CH), 7.15 (s, 2H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 (C), 140.5 (C), 137.5 (C), 136.6 (C), 129.0 (CH), 128.9 (CH), 128.4 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 127.1 (CH), 127.0 (CH), 126.7 (CH). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.59/7.44, 7.59/7.35, 7.59/127.0, 7.53/7.35, 7.53/7.26, 7.53/7.15, 7.44/7.35, 7.35/7.26, 7.35/7.15. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59/127.5, 7.59/127.1, 7.53/126.7, 7.44/129.0, 7.35/128.9, 7.35/127.4, 7.26/127.8, 7.15/129.0, 7.15/128.4. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.59/140.9, 7.59/140.5, 7.59/136.6, 7.59/128.4, 7.59/127.5, 7.53/129.0, 7.53/127.8, 7.53/126.7, 7.44/140.9, 7.44/129.0, 7.35/137.5, 7.35/128.9, 7.35/127.1, 7.26/126.7, 7.15/137.5, 7.15/136.6, 7.15/129.0, 7.15/128.4, 7.15/127.1, 7.15/126.7. GC−MS (70 eV): m/z (%): 257 (M^+ + 1, 23), 256 (M^+, 100), 255 (26), 254 (9), 253 (13), 252 (13), 241 (15), 240 (15), 239 (16), 179 (16), 178 (22), 165 (19), 113 (9), 91 (9).

*(E)-1-Fluoro-4-styrylbenzene (**9-ga**)*:.[33,35] [718-25-2] The product **9-ga** was separated by radial thin-layer chromatography (4 mm) on silica gel, eluting with pentane, and was isolated as a white solid (Method B, 45.6 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50−7.44 (m, 4H, CH), 7.37−7.33 (m, 2H, CH), 7.27−7.23 (m, 1H, CH), 7.08−6.98 (m, 4H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162,5 (d, J = 247.3 Hz, C), 137.4 (C), 133.7 (d, J = 3.3 Hz, C), 128.9 (2 CH), 128.7 (d, J = 2.2 Hz, CH), 128.1 (d, J = 7.9 Hz, 2 CH), 127.8 (CH), 127.7 (CH) 126.6 (2 CH), 115.8 (d, J = 21.6 Hz, 2 CH). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.47/7.35, 7.47/7.25, 7.47/7.03, 7.35/7.25, 7.35/7.03. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.47/128.1, 7.47/126.6, 7.35/128.9, 7.25/127.8, 7.03/128.7, 7.03/127.7, 7.03/115.8. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.47/162.5, 7.47/127.8, 7.47/126.6, 7.35/137.4, 7.35/128.9, 7.25/126.6, 7.03/162.5, 7.03/137.4, 7.03/133.7, 7.03/128.1, 7.03/127.7, 7.03/126.6. GC−MS (70 eV): m/z (%): 199 (M^+ + 1, 13), 198 (M^+, 100), 197 (66), 196 (44), 183 (39), 178 (11), 177 (28), 176 (11), 170 (10), 98 (17), 85 (11).

*(E)-1-Styryl-4-(trifluoromethyl)benzene (**9-ha**)*:[33] The product **9-ha** was separated by radial thin-layer chromatography (4 mm) on silica gel, eluting with pentane, and was isolated as a white solid (Method B, 37.2 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60 (br s, 4H, CH), 7.54−7.52 (m, 2H, CH), 7.40−7.36 (m, 2H, CH), 7.32−7.28 (m, 1H, CH), 7.19 (d, J = 16.4 Hz, 1H, CH), 7.11 (d, J = 16.3 Hz, 1H, CH). ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.47. ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0 (C), 136.8 (C), 131.4 (CH), 129.5 (q, J = 32.3 Hz, C), 128.9 (2 CH), 128.4 (CH), 127.3 (CH), 126.9 (2 CH), 126.7 (2 CH), 125.8 (q, J = 3.7 Hz, 2 CH), 123.0 (CF_3).^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.54/7.38, 7.54/7.30, 7.54/7.19, 7.38/7.30, 7.19/7.11. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.60/126.7, 7.60/125.8, 7.53/126.9, 7.38/128.9, 7.30/128.4, 7.19/131.4, 7.11/127.3. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.60/141.0, 7.60/129.5, 7.60/127.3, 7.60/125.8, 7.60/123.0, 7.53/131.4, 7.53/128.4, 7.53/127.3, 7.38/136.8, 7.38/128.9, 7.19/141.0, 7.19/126.9, 7.11/136.8, 7.11/131.5, 7.11/126.7. GC−MS (70 eV): m/z (%): 249 (M^+ + 1, 12), 248 (M^+, 100), 233 (13), 229 (7), 227 (16), 180 (10), 179 (86), 178 (78), 176 (9), 89 (12), 76 (9).

*(E)-1-Styrylnaphthalene (**9-ia**)*:.[15,33,34] [2840-87-1] Compound **9-ia** was obtained according to the general procedure. The product was purified by column chromatography on silica gel, eluting with pentane/CH_2Cl_2 (100:0 → 90:10), and was isolated as a colorless oil (Method B, 71.4 mg, 62% yield from 1-bromonaphthalene). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.21 (d, J = 8.1 Hz, 1H, CH), 7.90−7.85 (m, 2H, CH), 7.79 (d, J = 8.2 Hz, 1H, CH), 7.74 (d, J = 7.2 Hz, 1H, CH), 7.61−7.59 (m, 2H, CH), 7.53−7.48 (m, 3H, CH), 7.41−7.37 (m, 2H, CH), 7.31−7.29 (m, 1H, CH), 7.14 (d, J = 16.0 Hz, 1H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (C), 135.2 (C), 133.9 (C), 131.9 (CH), 131.6 (C), 128.9 (2 CH), 128.8 (CH), 128.2 (CH), 127.9 (CH), 126.8 (2 CH), 126.2 (CH), 126.0 (2 CH), 125.8 (CH), 123.9 (CH), 123.8 (CH). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 8.21/7.51, 7.87/7.51, 7.87/7.14, 7.79/7.51, 7.74/7.51, 7.60/7.39, 7.60/7.30, 7.39/7.30. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.21/123.9, 7.87/128.8, 7.87/126.0, 7.79/128.2, 7.74/123.8, 7.60/126.8, 7.51/126.2, 7.51/126.0, 7.51/125.8, 7.39/128.9, 7.30/127.9, 7.14/131.9. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.21/135.2, 8.21/133.9, 8.21/126.0, 8.21/125.8, 7.87/137.8, 7.87/131.9, 7.87/131.6, 7.87/128.2, 7.87/126.2, 7.87/123.8, 7.87/123.9, 7.79/131.6, 7.79/128.8, 7.79/123.8, 7.74/13.6, 7.74/128.2, 7.74/126.0, 7.60/131.9, 7.60/128.9, 7.60/127.9, 7.60/126.8, 7.51/135.2, 7.51/133.9, 7.51/131.6, 7.51/128.8, 7.51/123.9, 7.51/123.8, 7.39/137.8, 7.39/128.9, 7.39/126.8, 7.30/126.8, 7.14/137.8, 7.14/135.2, 7.14/126.8. GC−MS (70 eV): m/z (%): 231 (M^+ + 1, 17), 230 (M^+, 94), 229 (100), 228 (33), 227 (14), 226 (16), 215 (24), 202 (11), 153 (12), 152 (28), 115 (11), 114 (27), 113 (16), 101 (18).

*(E)-2-Styrylnaphthalene (**9-ja**)*:.[15,35] Compound **9-ja** was obtained according to the general procedure. The product was purified by column chromatography on silica gel, eluting with a pentane, and was isolated as a white solid (Method B, 86.3 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.84−7.79 (m, 4H, CH), 7.73 (dd, J = 8.6, 1.6 Hz, 1H, CH), 7.58−7.52 (m, 2H, CH), 7.48−7.41 (m, 2H, CH), 7.39−7.35 (m, 2H, CH), 7.29−7.19 (m, 3H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4 (C), 134.9 (C), 133.8 (C), 133.1 (C), 129.1 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 126.7 (CH), 126.6 (CH), 126.4 (CH), 125.9 (CH), 123.6 (CH). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.81/7.73, 7.81/7.45, 7.81/7.24, 7.73/7.24, 7.55/7.37, 7.55/7.24, 7.37/7.24. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.81/126.7, 7.8/128.0, 7.81/128.3, 7.81/127.8, 7.73/123.6, 7.55/126.6, 7.45/126.4, 7.45/125.9, 7.37/128.7, 7.24/129.1, 7.24/128.8, 7.24/127.7. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.81/134.9, 7.81/133.8, 7.81/133.1, 7.81/128.8, 7.81/128.0, 7.81/127.7, 7.81/126.4, 7.81/125.9, 7.81/123.6, 7.73/133.1, 7.73/128.8, 7.73/128.7, 7.73/126.7, 7.55/129.1, 7.55/127.8, 7.55/126.7, 7.45/133.8, 7.45/133.1, 7.45/128.0, 7.45/127.8, 7.37/137.4, 7.37/128.7, 7.37/126.6, 7.24/137.4, 7.24/134.9, 7.24/129.1, 7.24/128.8, 7.24/126.7, 7.24/126.6, 7.24/123.6. GC−MS (70 eV): m/z (%): 231 (M^+ + 1, 17), 230 (M^+, 100), 229 (96), 228 (55), 227 (15), 226 (21), 215 (27), 202 (14), 152 (9), 115 (16), 114 (31), 113 (13), 108 (10), 102 (6), 101 (22).

*(E)-6-Styrylquinoline (**9-ka**)*:[39] [121611-55-0] Compound **9-ka** was obtained according to the general procedure. The product was recrystallized from diethyl ether as yellow crystals (Method B, 61.3 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.85 (dd, J = 4.2, 1.7 Hz, 1H, CH), 8.08 (m, 2H, CH), 7.95 (dd, J = 8.8, 2.0 Hz, 1H, CH), 7.78 (d, J = 1.9 Hz, 1H, CH), 7.56−7.54 (m, 2H, CH), 7.41−7.33 (m, 3H, CH), 7.31−7.26 (m, 1H, CH), 7.24 (s, 2H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2 (CH), 148.2 (C), 137.1 (C), 136.0 (CH), 135.7 (C), 130.3 (CH), 129.9 (CH), 128.9 (CH), 128.7 (C), 128.1 (CH), 127.9 (CH), 127.3 (CH), 126.8 (CH), 126.0 (CH), 121.6 (CH). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 8.85/8.08, 8.85/7.37, 8.08/7.95, 8.08/7.78, 8.08/7.37, 8.08/7.24, 7.95/7.78, 7.95/7.24, 7.78/7.24, 7.55/7.37, 7.55/7.28, 7.55/7.24, 7.37/7.28. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.85/150.2, 8.08/135.7, 8.08/129.9, 7.95/127.3, 7.78/126.0, 7.55/126.8, 7.37/128.9, 7.37/121.6, 7.28/128.1, 7.24/130.3, 7.24/127.9. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.85/148.2, 8.85/136.0, 8.85/121.6, 8.08/150.2, 8.08/148.2,

dx.doi.org/10.1021/jo501474w | J. Org. Chem. 2014, 79, 9104−9111

8.08/135.7, 8.08/128.7, 8.08/126.0, 7.95/148.2, 7.95/127.9, 7.95/126.0, 7.78/148.2, 7.78/136.0, 7.78/129.9, 7.78/127.9, 7.78/123.7, 7.55/130.3, 7.55/128.1, 755/126.8, 7.37/150.2, 7.37/137.1, 7.37/128.9, 7.37/128.7, 7.37/126.8, 7.28/126.8, 7.24/137.1, 7.24/135.7, 7.24/130.3, 7.24/127.3, 7.24/126.8, 7.24/126.0. GC−MS (70 eV): *m*/*z* (%): 232 (M^+ + 1, 13), 231 (M^+, 81), 230 (100), 228 (11), 216 (12), 202 (17), 115 (41), 102 (11), 101 (11).

*1,1,2-Triphenylethylene (**9-cb**):*[16] [58-72-0] Compound **9-cb** was obtained according to the general procedure. The 1,1-diphenylethene was distilled under reduced pressure using a Kügelrohr apparatus. The product was purified by column chromatography on silica gel, eluting with petroleum ether/CH_2Cl_2 (100:0 → 80:20), and was isolated as a colorless oil (Method B, 88.4 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32−7.27 (m, 8H, CH), 7.22−7.19 (m, 2H, CH), 7.15−7.07 (m, 3H, CH), 7.04−7.02 (m, 2H, CH), 6.97 (s, 1H, CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (C), 142.8 (C), 140.5 (C), 137.5 (C), 130.5 (2 CH), 129.7 (2 CH), 128.8 (2 CH), 128.4 (2 CH), 128.3 (CH), 128.1 (2 CH), 127.8 (2 CH), 127.6 (CH), 127.5 (CH), 126.9 (CH). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.29/7.20, 7.11/7.03, 7.03/6.97. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.29/128.8, 7.29/128.4, 7.29/127.8, 7.29/127.6, 7.29/127.5, 7.20/130.5, 7.11/128.1, 7.11/126.9, 7.03/129.7, 6.97/128.3. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.29/143.6, 7.29/140.5, 7.29/130.5, 7.29/128.8, 7.29/127.6, 7.20/127.5, 7.11/129.7, 7.11/127.8, 7.03/126.9, 6.97/143.6, 6.97/140.5, 6.97/129.7. GC−MS (70 eV): *m*/*z* (%): 257 (M^+ + 1, 21), 256 (M^+, 100), 255 (26), 254 (9), 253 (17), 252 (16), 241 (23), 240 (15), 239 (16), 179 (33), 178 (55), 176 (13), 165 (21), 152 (9), 126 (19), 120 (24), 113 (15).

*(Z, E) (1-(p-Tolyl)ethene-1,2-diyl)dibenzene (**9-bc**):*[40] [70603-14-4] Compound **9-bc** was obtained according to the general procedure. The *cis*-stilbene was distilled under reduced pressure using a Kügelrohr apparatus. The product was purified by column chromatography on silica gel, eluting with petroleum ether/CH_2Cl_2 (100:0 → 80:20), and was isolated as a white solid as a mixture of *Z*, *E* isomers (Method B, 60.8 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33−7.25 (m, 4H, CH), 7.22−7.18 (m, 2H, CH), 7.14−7.00 (m, 8H, CH), 6.93, 6.92 (s, s, sum = 1H), 2.37, 2.34 (s, s, sum = 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9 (C), 142.7 (C), 142.6 (C), 140.8 (C), 140.7 (C), 137.7 (C), 137.6 (C), 137.5 (C), 137.4 (C), 137.2 (C), 130.5 (CH), 130.4 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.1 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 126.7 (CH), 21.5 (CH_3), 21.3 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.29/7.20, 7.20/7.11, 7.11/2.37, 7.11/2.34. ^{1}H−^{13}C HMBC (400 MHz, $CDCl_3$) δ 7.29/128.1, 7.29/127.5, 7.20/130.5, 7.20/127.8, 7.07/130.6, 7.07/129.7, 7.07/129.6; 7.07/129.5, 7.07/128.1, 7.07/126.8, 6.93/127.6, 6.92/128.3, 2.37/21.5, 2.34/21.3. GC−MS (70 eV): *m*/*z* (%): 271 (M^+ + 1, 23), 270 (M^+, 100), 269 (10), 255 (48), 254 (23), 253 (28), 252 (20), 240 (14), 239 (10), 193 (12), 192 (12), 179 (19), 178 (41), 176 (10), 165 (11), 126 (26), 120 (10), 119 (14), 113 (14).

*(E)-1-Methyl-4-(2-phenylprop-1-en-1-yl)benzene (**9-bd**):*[41] Compound **9-bd** was obtained according to the general procedure. The α-methylstyrene was distilled under reduced pressure using a Kügelrohr apparatus. The product was purified by column chromatography on silica gel, eluting with petroleum ether/diethyl ether (100:0 → 80:20), and was isolated as a white solid (Method B, 67.7 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52−7.50 (m, 2H, CH), 7.37−7.33 (m, 2H, CH), 7.28−7.25 (m, 3H, CH), 7.18 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H, CH), 2.36 (s, 3H, CH_3), 2.27 (d, *J* = 1.3 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (C), 136.7 (C), 136.1 (C), 135.4 (C), 129.1 (CH), 128.9 (CH), 128.3 (CH), 127.6 (CH), 127.0 (CH), 125.9 (CH), 21.2 (CH_3), 17.4 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_C δ 7.57/7.41, 7.41/7.33, 7.33/7.23, 7.33/2.42, 7.23/2.42, 6.87/2.33. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.57/125.9, 7.41/128.3, 7.33/129.1, 7.33/127.0, 7.23/128.9, 6.87/127.6, 2.42/21.2, 2.33/17.4. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.57/136.7, 7.57/127.0, 7.57/125.9, 7.41/144.1, 7.41/128.3, 7.33/136.1, 7.33/129.1, 7.33/127.6, 7.33/125.9, 7.23/135.4, 7.23/128.9, 7.23/21.2, 6.87/144.1, 6.87/129.1, 6.87/17.45, 2.42/136.1, 2.42/128.9, 2.33/144.1, 2.33/136.7, 2.33/127.6. GC−MS (70 eV): *m*/*z* (%): 209 (M^+ + 1, 15), 208 (M^+, 100), 194 (14), 193 (88), 192 (21), 191 (14), 189 (10), 179 (13), 178 (66), 165 (14), 115 (32), 103 (11), 95 (14), 91 (13), 89 (19), 82 (11), 77 (11).

*(E)-1-Methoxy-4-(2-phenylprop-1-en-1-yl)benzene (**9-ad**):*[42] [83832-04-6] Compound **9-ad** was obtained according to the general procedure. The α-methylstyrene was distilled under reduced pressure using a Kügelrohr apparatus. The product was purified by column chromatography on silica gel, eluting with petroleum ether/diethyl ether (100:0 → 80:20), and was isolated as a white solid (Method B, 91.9 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51−7.48 (m, 2H, CH), 7.37−7.23 (m, 5H, CH), 6.92−6.89 (m, 2H, CH), 6.77 (s, 1H, CH), 3.81 (s, 3H, CH_3), 2.27 (d, *J* = 1.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (C), 144.3 (C), 136.0 (C), 131.1 (C), 130.5 (CH), 128.4 (CH), 127.4 (CH), 127.1 (CH), 126.1 (CH), 113.8 (CH), 55.4 (CH_3), 17.6 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.49/7.30, 7.30/6.90, 7.30/6.77, 7.30/2.27, 6.78/2.27. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.49/128.4, 7.49/126.1, 7.30/130.5, 7.30/128.4, 7.30/127.1, 7.30/113.8, 6.90/130.5, 6.90/113.8, 6.77/127.4, 3.81/55.5, 2.27/17.6. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.49/136.0, 7.49/127.1, 7.49/126.1, 7.30/158.3, 7.30/144.3, 7.30/130.5, 7.30/128.4, 7.30/127.4, 7.30/126.1, 7.30/113.8, 6.90/158.3, 6.90/131.1, 6.90/113.8, 6.77/144.3, 6.77/130.5, 6.77/17.6. GC−MS (70 eV): *m*/*z* (%): 225 (M^+ + 1, 14), 224 (M^+, 100), 223 (14), 209 (26), 208 (10), 194 (12), 193 (12), 181 (12), 178 (17), 166 (19), 165 (29), 121 (14), 115 (22), 103 (9), 91 (10), 89 (8), 82 (6), 77 (12).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete tables of reactions and copies of ^{1}H, ^{13}C, COSY, HSQC, and HMBC NMR spectra of all compounds are available in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rossi@fcq.unc.edu.ar (R.A.R.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported, in part, by Agencia Córdoba Ciencia, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Secretaría de Ciencia y Tecnología, Universidad Nacional de Córdoba, and Fondo para la Investigación Científica y Tecnológica Argentina.

■ REFERENCES

(1) (a) Burns, J.; Yokota, T.; Ashihara, H.; Lean, M. E. J.; Crozier, A. *J. Agr. Food Chem.* **2002**, *50*, 3337−3340. (b) Hart, J. H. *Annu. Rev. Phytopathol.* **1981**, *19*, 437−458.

(2) Likhtenshtein, G. *Stilbenes: Applications in Chemistry, Life Sciences and Materials Science*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2010.

(3) (a) Le Corre, L.; Chalabi, N.; Delort, L.; Bignon, Y.-J.; Bernard-Gallon, D. J. *Mol. Nutr. Food Res.* **2005**, *49*, 462−471. (b) Larrosa, M.; Tomás-Barberán, F. A.; Espin, J. C. *Eur. J. Nutr.* **2004**, *43*, 275−284.

(4) Murias, M.; Jäger, W.; Handler, N.; Erker, T.; Horvath, Z.; Szekeres, T.; Nohl, H.; Gille, L. *Biochem. Pharmacol.* **2005**, *69*, 903−912.

(5) (a) Niles, R. M.; Cook, C. P.; Meadows, G. G.; Fu, Y. M.; McLaughlin, J. L.; Rankin, G. O. *J. Nutr.* **2006**, *136*, 2542−2546. (b) Tolomeo, M.; Grimaudo, S.; Di Cristina, A.; Roberti, M.; Pizzirani, D.; Meli, M.; Dusonchet, L.; Gebbia, N.; Abbadessa, V.; Crosta, L.; Barucchello, R.; Grisolia, G.; Invidiata, F.; Simoni, D. *Int. J. Biochem. Cell Biol.* **2005**, *37*, 1709−1726.

(6) (a) Jordan, V. C. *Nat. Rev. Drug Discovery* **2003**, *2*, 205−213. (b) Jordan, V. C. *J. Med. Chem.* **2003**, *46*, 883−908. (c) Jordan, V. C. *J.*

Med. Chem. **2003**, *46*, 1081−1111. (d) Salih, A. K.; Fentiman, I. S. *Cancer Treat. Rev.* **2001**, *27*, 261−273.
(7) (a) Hilt, G.; Hengst, C. *J. Org. Chem.* **2007**, *72*, 7337−7342. (b) Mc Nulty, J.; Mc Leod, D. *Tetrahedron Lett.* **2013**, *54*, 6303−6306. (c) Saiyed, A. S.; Patel, K. N.; Kamath, B. V.; Bedekar, A. V. *Tetrahedron Lett.* **2012**, *53*, 4692−4696.
(8) de Meijere, A., Diederich, F., Eds. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Weinheim, 2004.
(9) (a) Meerwein, H.; Buchner, E.; van Emster, K. *J. Prakt. Chem.* **1939**, *152*, 237−266. (b) Rondestvedt, C. S., Jr. *Org. React.* **1976**, *24*, 225−259. (c) Hari, D. P.; König, B. *Angew. Chem., Int. Ed.* **2013**, *52*, 2−12.
(10) (a) Mc Murry, J. E. *Chem. Rev.* **1989**, *89*, 1513−1524. (b) Ephritikhine, M. *Chem. Commun.* **1998**, 2549−2554.
(11) Orelli, L. R.; Bisceglia, J. Á. *Curr. Org. Chem.* **2012**, *16*, 2206−2230.
(12) Johansson Seechurn, C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062−5085.
(13) (a) Felpin, F.-X.; Miqueu, K.; Sotiropoulos, J.-M.; Fouquet, E.; Ibarguren, O.; Laudien, J. *Chem.—Eur. J.* **2010**, *16*, 5191−5204. (b) Mo, F.; Dong, G.; Zhang, Y.; Wang. *J. Org. Biomol. Chem.* **2013**, *11*, 1582−1593.
(14) (a) Chang, T. L.; Wu, Y.; Choy, P. Y.; Kwong, F. Y. *Chem.—Eur. J.* **2013**, *19*, 15802−15814. (b) Mehta, V. P.; Punji, B. *RSC Adv.* **2013**, *3*, 11957−11986. (c) Shirakawa, E.; Hayashi, T. *Chem. Lett.* **2012**, *41*, 130−134.
(15) Shirakawa, E.; Zhang, X.; Hayashi, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 4671−4674.
(16) Sun, C.-L.; Gu, Y.-F.; Wang, B.; Shi, Z.-L. *Chem.—Eur. J.* **2011**, *17*, 10844−10847.
(17) Rueping, M.; Leiendecker, M.; Das, A.; Poisson, T.; Bui, L. *Chem. Commun.* **2011**, *47*, 10629−10631.
(18) (a) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 5018−5022. (b) Yanagisawa, S.; Ueda, K.; Taniguchi, T.; Itami, K. *Org. Lett.* **2008**, *10*, 4673−4676. (c) Liu, W.; Cao, H.; Zhang, H.; Chung, K. H.; He, C.; Wang, H.; Kwong, F. Y.; Lei, A. *J. Am. Chem. Soc.* **2010**, *132*, 16737−16740. (d) Shirakawa, E.; Itoh, K.; Higashino, T.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 15537−15539. (e) Sun, C. L.; Li, H.; Yu, D. G.; Yu, M.; Zhou, X.; Lu, X. Y.; Huang, K.; Zheng, S. F.; Li, B. J.; Shi, Z. *J. Nat. Chem.* **2010**, *2*, 1044−1049. (f) Ng, Y. S.; Chan, C. S.; Chan, K. S. *Tetrahedron Lett.* **2012**, *53*, 3911−3914. (g) Vakuliuk, O.; Koszarna, B.; Gryko, D. T. *Adv. Synth. Catal.* **2011**, *353*, 925−930. (h) Zhao, H.; Shen, J.; Guo, J.; Ye, R.; Zeng, H. *Chem. Commun.* **2013**, *49*, 2323−2325. (i) Liu, W.; Tian, F.; Wang, X.; Yu, H.; Bi, Y. *Chem. Commun.* **2013**, *49*, 2983−2985. (j) Qiu, Y.; Liu, Y.; Yang, K.; Hong, W.; Li, Z.; Wang, Z.; Yao, Z.; Jiang, S. *Org. Lett.* **2011**, *13*, 3556−3559. (k) Yong, G. P.; She, W. L.; Zhang, Y. M.; Li, Y. Z. *Chem. Commun.* **2011**, *47*, 11766−11768. (l) Chen, W. C.; Hsu, Y. C.; Shih, W. C.; Lee, C. Y.; Chuang, W. H.; Tsai, Y. F.; Chen, P. P.; Ong, T. G. *Chem. Commun.* **2012**, *48*, 6702−6704. (m) Liu, H.; Yin, B.; Gao, Z.; Li, Y.; Jiang, H. *Chem. Commun.* **2012**, *48*, 2033−2035. (n) Tanimoro, K.; Ueno, M.; Takeda, K.; Kirihata, M.; Tanimori, S. *J. Org. Chem.* **2012**, *77*, 7844−7849.
(19) (a) Zheng, X.; Yang, L.; Du, W.; Ding, A.; Guo, H. *Chem.—Asian J.* **2014**, *9*, 439−442. (b) Bhakuni, B. S.; Yadav, A.; Kumar, S.; Kumar, S. *New J. Chem.* **2014**, *38*, 827−836. (c) Xia, Z.; Huang, J.; He, Y.; Zhao, J.; Lei, J.; Zhu, Q. *Org. Lett.* **2014**, *16*, 2546−2549. (d) Crisóstomo, F. P.; Martín, T.; Carrillo, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 2181−2185. (e) Kawamoto, T.; Sato, A.; Ryu, I. *Org. Lett.* **2014**, *16*, 2111−2113. (f) Zhu, Y.-W.; Yi, W.-B.; Qian, J.-L.; Cai, C. H. *ChemCatChem* **2014**, *6*, 733−735. (g) Ghosh, D.; Lee, J.-Y.; Liu, Ch.-Y.; Chiang, Y.-H.; Lee, H. M. *Adv. Synth. Catal.* **2014**, *356*, 406−410. (h) Hofmann, J.; Jasch, H.; Heinrich, M. R. *J. Org. Chem.* **2014**, *79*, 2314−2320. (i) Cao, J.-J.; Zhu, T.-H.; Wang, S.-Y.; Gu, Z.-Y.; Wang, X.; Ji, S.-J. *Chem. Commun.* **2014**, *50*, 6439−6442. (j) Yanagisawa, S.; Itami, K. *ChemCatChem* **2011**, *3*, 827−829. (k) Sharma, S.; Kumar, M.; Kumar, V.; Kumar, N. *Tetrahedron Lett.* **2013**, *54*, 4868−4871. (l) A, S.; Liu, X.; Li, H.; He, C.; Mu, Y. *Asian J. Org. Chem.* **2013**, *2*, 857−861. (m) Cuthbertson, J.; Gray, V.; Wilden, J. D. *Chem. Commun.* **2014**, *50*, 2575−2578.
(20) For intramolecular HAS, see: (a) Roman, D. S.; Takahashi, Y.; Charette, A. B. *Org. Lett.* **2011**, *13*, 3242−3245. (b) Sun, C.-L.; Gu, Y.-F.; Huanga, W.-P.; Shi, Z.-J. *Chem. Commun.* **2011**, *47*, 9813−9815. (c) Bhakuni, B. S.; Kumar, A.; Balkrishna, S. J.; Sheikh, J. A.; Konar, S.; Kumar, S. *Org. Lett.* **2012**, *14*, 2838−2841. (d) De, S.; Ghosh, S.; Bhunia, S.; Sheikh, J. A.; Bisai, A. *Org. Lett.* **2012**, *14*, 4466−4469. (e) De, S.; Mishra, S.; Kakde, B. N.; Dey, D.; Bisai, A. *J. Org. Chem.* **2013**, *78*, 7823−7844. (f) De, S.; Mishra, S.; Kakde, B. N.; Dey, D.; Bisai, A. *J. Org. Chem.* **2013**, *78*, 7823−7844. (g) Wu, Y.; Wong, S. M.; Mao, F.; Chan, T. L.; Kwong, F. Q. *Org. Lett.* **2012**, *14*, 5306−5309. (h) Masters, K. S.; Bräse, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 866−869. (i) Masters, K. S.; Bihlmeier, A.; Klopper, W.; Bräse, S. *Chem.—Eur. J.* **2013**, *19*, 17827−17835. (j) Bhakuni, B. S.; Yadav, A.; Kumar, S.; Patel, S.; Sharma, S.; Kumar, S. *J. Org. Chem.* **2014**, *79*, 2944−2954.
(21) Irradiation was conducted in a photochemical reactor equipped with two Master HPI-T Plus 400 W lamps (cooled with water). *Guide to Uplamping for High Intensity Discharge Lamps*; Philips Electronics UK Ltd.: Surrey, U. K., 2010; pp 100 and 112. http://www.ribaproductselector.com/Docs/9/05799/external/COL605799.pdf.
(22) Budén, M. E.; Guastavino, J. F.; Rossi, R. A. *Org. Lett.* **2013**, *15*, 1174−1177.
(23) Most of these reactions were carried out also in DMF as a solvent. The yield of product was similar, but a longer time was required in all cases; see S-Table 1 in the Supporting Information.
(24) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295−3299.
(25) (a) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. *Chem. Rev.* **2003**, *103*, 71−167. (b) Schmidt, L. C.; Argüello, J. E.; Peñéñory, A. B. *J. Org. Chem.* **2007**, *72*, 2936−2944.
(26) For full optimization reaction, see the Supporting Information, in S-Table 2.
(27) Zhou, S.; Anderson, G. M.; Mondal, B.; Doni, E.; Ironmonger, V.; Kranz, M.; Tuttle, T.; Murphy, J. A. *Chem. Sci.* **2014**, *5*, 476−482.
(28) (a) Bajracharya, G. B.; Daugulis, O. *Org. Lett.* **2008**, *10*, 4625−4628. (b) Kumar, A.; Bhakuni, B. S.; Prasad, Ch. D.; Kumar, S. *Tetrahedron* **2013**, *69*, 5383−5392.
(29) (a) Gassman, P. G.; Benecke, H. P. *Tetrahedron Lett.* **1969**, *10*, 1089−1092. (b) Bowne, A. T.; Christopher, T. A.; Levin, R. H. *Tetrahedron Lett.* **1976**, *17*, 4111−4114. (c) Maurin, P.; Ibrahim-Ouali, M.; Parrain, J.-L.; Santelli, M. *J. Mol. Struct.: THEOCHEM* **2003**, *637*, 91−100.
(30) The spontaneous or thermal ET depends on the relationship between the electron affinity of the substrate (ArX) and the oxidation potential of the donor, in this case: the anion *t*-BuO$^-$.
(31) See the Supporting Information, in S-Table 3.
(32) Srinivas, P.; Likhar, P. R.; Maheswaran, H.; Sridhar, B.; Ravikumar, K.; Kantam, M. L. *Chem.—Eur. J.* **2009**, *15*, 1578−1581.
(33) Kamal, A.; Srinivasulu, V.; Seshadri, B. N.; Markandeya, N.; Alarifi, A.; Shankaraiah, N. *Green Chem.* **2012**, *14*, 2513−2522.
(34) Ren, G.; Cui, X.; Yang, E.; Yang, F.; Wu, Y. *Tetrahedron* **2010**, *66*, 4022−4028.
(35) Wu, S.; Ma, H.; Jia, X.; Zhong, Y.; Lei, Z. *Tetrahedron* **2011**, *67*, 250−256.
(36) (a) Song, S.; Ma, Y.; Chai, Q.; Ma, C.; Jiang, W.; Andrus, M. B. *Tetrahedron* **2005**, *61*, 7438−7446. (b) Srinivas, P.; Srinivas, K.; Likhar, P. R.; Sridhar, B.; Mohan, K. V.; Bhargava, S.; Kantam, M. L. *J. Organomet. Chem.* **2011**, *696*, 795−801.
(37) Yao, Q.; Zabawa, M.; Woo, J.; Zheng, C. *J. Am. Chem. Soc.* **2007**, *129*, 3088−3089.
(38) Cui, X.; Li, Z.; Tao, C. Z.; Xu, Y.; Li, J.; Liu, L.; Guo, Q. X. *Org. Lett.* **2006**, *8*, 2467−2470.
(39) Gennari, G.; Bortolus, P.; Galiazzo, G. *J. Mol. Struct.* **1991**, *249*, 189−202.
(40) Levent, A.; Melih, K.; Ozge, A.-A.; Fatma Nurcan, D.; Fatma Yelda, O. *Tetrahedron* **2009**, *65*, 9125−9133.
(41) Liu, H.; Cao, L.; Sun, J.; Fossey, J. S.; Deng, W.-P. *Chem. Commun.* **2012**, *48*, 2674−2676.
(42) Werner, R. W.; Sigman, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 9692−9695.