Improved One-Pot Synthesis of Styryl Tetrahydrofurans and Cyclohexanes by Radical Addition to β-Nitrostyrenes in the Presence of Benzoyl Peroxide

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Abstract: Stereoselective styryl derivatives have been prepared based on radical substitution (addition–elimination) of heterocycles or cyclohydrocarbons units to (*E*)-β-nitrostyrenes **1** using a common radical initiator benzoyl peroxide. High reactivity and selectivity with wide substrate scope were attained by using this easy methodology. The reactions using easily obtained and one-pot potential starting materials gave excellent *trans*-selectivity with medium to high yields in all cases. Synthetic utility of this approach has been demonstrated by the preparation of various *trans*-styryl derivatives.

Keywords: alkenes · heterocycles · peroxides · radical reactions

Introduction

In the last two decades carbon-carbon bonds formation has been increasingly achieved by the addition of carbon centered radicals to carbon–carbon multiple bonds. It is known from the literature that the addition of α-heterosubstituted radicals to styryl sulfimides[1] and styryl triflone[2] can give styryl heterocycles. This fact that tetrahydrofuran **2** and tetrahydropyran **5** can add to alkenes under radical-reaction conditions prompted us to investigate similar reactions with (*E*)-β-nitrostyrenes **1**, which if successful, would provide a potential one-pot route[3] and superior methodology to synthesize different styryl derivatives due to the easily and cheaply acquired starting materials (β-nitrostyrenes **1**).

Traditionally, styryl heterocycles are prepared by Horner–Emmons approach of the alkyl(diphenyl)phosphine oxide with a carbonyl compound.[4] Unfortunately, this kind of protocol is low stereoselectivity for the preparation of β-substituted styrenes due to the generation of both *erythro*- and *threo*-β-hydroxyalkyl(diphenyl)phosphine oxides. To avoid the problem of separation, some research have been done by radical-type methodology. Clark et al. have utilized benzoyl peroxide **3** or triethylborane to mediate the addition–elimination of styryl sulfimides with the tetrahydrofuranyl radical in 45 and 48% yield, respectively.[1] It also has been reported by Fuchs and co-workers that β-heterocyclostyrenes and β-cyclostyrenes can be prepared from the treatment of styryl triflone with AIBN.[2] But both of these methods are encountering the situation that the preparation of starting substrates they used are laborious and low yield.

Results and Discussion

Nitro-olefins are useful intermediates in organic synthesis and are important structural units which can be used as starting materials for many classes of compounds. Our previous study found that high yields of (*E*)-alkenes can be generated when (*E*)- or (*Z*)-β-nitrostyrenes **1** react with triethylborane in tetrahydrofuran solution at room temperature in the presence of oxygen in the air as radical initiator.[5] All these results indicate that β-nitrostyrenes **1** are good radical acceptors and can react with alkyl radicals from different source to generate alkenes under different conditions and the reaction mechanism is proposed to be free-radical addition–elimination reaction. In this paper, we wish to report a reformative and effective method, based on our previous study, to synthesize different styryl heterocycles by reaction of β-nitrostyrenes **1** with different alkyl radicals which were generated from C–H abstraction by benzoyl peroxide **3**.

In an initial experiment, (*E*)-β-nitrostyrene (**1a**) was treated with 3 equiv benzoyl peroxide **3** in tetrahydrofuran **2** and heated under reflux for 12 hours. As expected, (*E*)-styryl tetrahydrofuran **4a** was obtained as the sole product in 89% yield (Table 1, entry 1), and none of the *Z*-isomer was detected in the crude product. Similarly, the reaction of benzoyl peroxide **3** with other (*E*)-β-nitrostyrenes having

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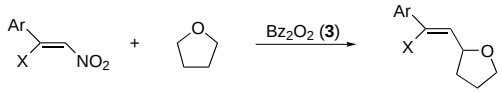
electron-withdrawing groups **1b–e** (Table 1, entries 2–5) gave the corresponding (*E*)-styryl tetrahydrofuran **4b–e**, respectively, in good to high yields. On the other hand reaction of (*E*)-*β*-nitrostyrenes having electron-donating group **1f** (Table 1, entry 6) with benzoyl peroxide **3** under identical reaction conditions led to a decrease in yield. We attributed this result to the lower reactivity of (*E*)-*p*-methoxy-*β*-nitrostyrene (**1f**) due to the well electron-donating ability of methoxy group. In the last three cases (Table 1, entries 7–9), we extended the category of our substrates to survey this reaction. Not surprisingly, medium to good yields were acquired both hetero-aromatic substrates **1g**,**h** (Table 1, entries 7 and 8) and high steric-hindrance substrate **1i** (Table 1, entry 9). Alternatively, if UV photolysis ($\lambda =$ 253.7 nm) was used to initiate the radical process instead of heating, the overall yield of the reaction of *β*-nitrostyrene **1a** with benzoyl peroxide **3** (2.25 equiv) in tetrahydrofuran **2** for 4 h would be decreased (Table 1, **4a** from 89 to 82%). Identical phenomena were observed for other *β*-nitrostyrenes when benzoyl peroxide **3** was initiated by the photochemical strategy. However, due to our ultimate aim for developing an one-pot route all further reactions were conducted under reflux reaction conditions. In all these cases, no other regio- or stereoisomers were obtained. These results (Table 1, entries 1–9) indicated that this method was widely applicable for the preparation of (*E*)-styryl tetrahydrofurans **4**. Thus an easy and convenient route to tetrahydrofuran derivatives has been developed.

The mechanism of this reaction is presumably similar to our previous study in the radical addition–elimination reaction of *β*-nitrostyrenes **1** and different alkyl radicals.[5] The initial step could be the *α*-C–H abstraction of tetrahydrofuran **2** with the benzoyl or phenyl radical species generated from benzoyl peroxide **3**. The resulting tetrahydrofuran *α*-carbon radical species would react with *β*-nitrostyrenes **1** and radical attack must take place at the *β*-carbon of *β*-nitrostyrenes **1**. Finally, the benzylic radical generated by radical attack would undergo elimination to yield (*E*)-alkene due to the product stability of (*E*)-alkene is much stable than (*Z*)-alkene in energy. In addition to (*E*)-**1a**, (*Z*)-**1a** was also used to react with **2** under similar conditions as described above (Table 1, entry 1). As expected, 87% yield of the same product (*E*)-**4a** was also obtained, and this result is actually consistent with our previous report.[5]

Not only the reaction of the five-membered cyclic ether (tetrahydrofuran **2**) proceeded in good yields, but also that of six-membered cyclic ether (tetrahydropyran **5**). The reaction of *β*-nitrostyrene **1a** and tetrahydropyran **5** under analogous conditions gave the corresponding tetrahydropyran derivative isomers **6a**, **7a**, and **8a** in 41, 28, and 21% yield, respectively (Table 2, entry 1). Herein three regioisomers *α*-, *β*- and *γ*-forms were observed

Table 1. Preparation of *β*-(2-furyl)styrenes **4** from the reaction of *β*-nitrostyrenes **1**, tetrahydrofuran **2**, and benzoyl peroxide **3** (reaction mixture heated under reflux).



(1)

1a-i **2** **4a-i**

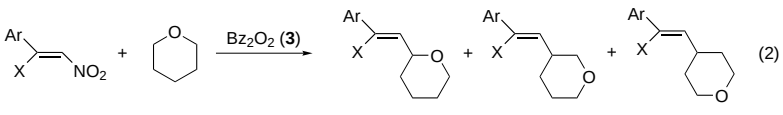
a: Ar = Ph ; X = H
b: Ar = *p*-Cl-Ph ; X = H
c: Ar = *o*-F-Ph ; X = H
d: Ar = *p*-F-Ph ; X = H
e: Ar = 2-naphthyl ; X =H
f: Ar = *p*-MeO-Ph ; X = H
g: Ar = 2-furyl ; X = H
h: Ar = 2-thienyl ; X = H
i: Ar = Ph ; X = Ph

Entry	**1**	**2** [mL]	**3** [equiv]	*t* [h]	**4**	Yield [%][a]
1	**1a**	15	3	12	**4a**	89
2	**1b**	15	3	12	**4b**	81
3	**1c**	15	3	12	**4c**	85
4	**1d**	15	3	12	**4d**	77
5	**1e**	15	3	12	**4e**	80
6	**1f**	15	3	15	**4f**	48
7	**1g**	15	3	12	**4g**	69
8	**1h**	15	3	12	**4h**	60

[a] NMR Yield.

in the reaction; the *β*- and *γ*-regioisomer which we originally did not anticipate actually exceeded half of the total yield. This special kind of regioselectivity of the C–H functionalized radical reaction of tetrahydropyran **5** has not been observed before, and we presume that this might have the following reasons: 1) the difference in the rate of abstraction of hydrogens *α* to oxygen between six-membered cyclic- and five-membered cyclic ethers; 2) the preeminent radical trapping ability of *β*-nitrostyrenes **1**. Owing mainly to the huge decrease in the reaction rate of the *α*-hydrogen abstraction of tetrahydropyran **5** compared with tetrahydrofuran **2**,[6] the *β*- and *γ*-hydrogen abstraction became noteworthy and important enough to compete with the *α*-hydrogen abstraction. At this stage, the excellent radical trapping ability of our acceptor played a conclusive role to form this regioselectivity. Once a radical formed (*α*-, *β*- or *γ*-radicals) after the hydrogen abstraction, it is added to the very reactive *β*-nitrostyrenes **1**, so that the regioselectivity of hydrogen abstraction process determines the selectivity of the reaction.

Table 2. Preparation of *β*-(2-pyranyl)styrenes **6**, *β*-(3-pyranyl)styrenes **7** and *β*-(4-pyranyl)styrenes **8** from the reaction of *β*-nitrostyrenes **1**, tetrahydropyran **5**, and benzoyl peroxide **3** (reaction mixture heated under reflux).



(2)

1 **5** **6** **7** **8**

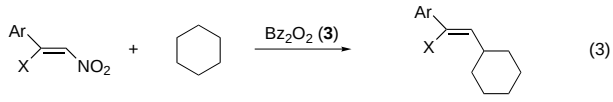
Entry	**1**	**5** [mL]	**3** [equiv]	*t* [h]	**6** [yield/%][a]	**7** [yield/%][a]	**8** [yield/%][a]
1	**1a**	10	3.25	6	**6a** [41]	**7a** [28]	**8a** [21]
2	**1b**	10	3.5	6	**6b** [39]	**7b** [26]	**8b** [22]
3	**1c**	10	2.75	6	**6c** [56]	**7c** [22]	**8c** [22]
4	**1d**	10	2.75	9	**6d** [47]	**7d** [27]	**8d** [20]

[a] NMR Yield.

On the other hand, the α-hydrogen abstraction rate factor was so huge for tetrahydrofuran **2** that we cannot observe any β-products in the crude GC-MS analysis.

Respecting the results above, we next examined the reaction of cyclohexane **9**. Treatment of β-nitrostyrene **1a** with 2.5 equiv benzoyl peroxide **3** in the presence of cyclohexane **9** gave the corresponding styryl derivative **10a** in 90% yield (Table 3, entry 1). The tendency of the reactivities of β-nitrostyrenes **1** in the reaction with cyclohexane **9** was the same as that with tetrahydrofuran **2**, although all cases were more efficient than those for the tetrahydrofuran **2** series (Table 1). After the survey of the reaction conditions for tetrahydrofuran **2**, tetrahydropyran **5**, and cyclohexane **9**, the reaction rates for β-nitrostyrenes **1** with cyclohexane **9** were much faster than those of the other two, and required the least amount of the reaction time and benzoyl peroxide **3**.

Table 3. Preparation of β-cyclohexylstyrenes **10** from the reaction of β-nitrostyrenes **1**, cyclohexane **9**, and benzoyl peroxide **3** (reaction mixture heated under reflux).



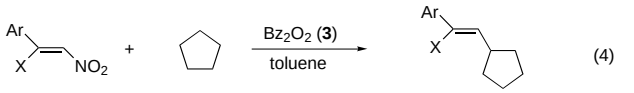
1 **9** **10**

Entry	**1**	**9** [mL]	**3** [equiv]	*t* [h]	**10**	Yield [%][a]
1	**1a**	10	2.5	4	**10a**	90
2	**1b**	10	2.5	4	**10b**	95
3	**1c**	10	2.5	4	**10c**	100
4	**1d**	10	2.5	4	**10d**	100
5	**1e**	10	2.5	4	**10e**	74
6	**1f**	10	2.5	3	**10f**	75
7	**1g**	10	2.5	4	**10g**	32
8	**1h**	10	2.5	3	**10h**	82
9	**1i**	10	2.5	6	**10i**	82

[a] NMR Yield.

Now we were interested in the reaction of β-nitrostyrenes **1** and five-, seven-, and eight-membered cyclic hydrocarbons, because of the apparent difference in reactivities between tetrahydrofuran **2**, tetrahydropyran **5** and cyclohexane **9**. First, the reaction of a cyclopentane **11** and toluene co-solvent solution of β-nitrostyrene **1a** with benzoyl peroxide **3** heated under reflux furnished the desired (*E*)-styryl cyclopentane product **12a** quantitatively as expected (Table 4, entry 1). The strategy of using toluene as co-solvent instead of radical precursor itself as the only solvent as described above was in order to elevate the temperature inside the reaction system under refluxing as a result of the low boiling point of cyclopentane **11**. Benzene was one of our first choices to increase the reaction temperature so that to initiate the cleavage of benzoyl peroxide **3**; however, some starting material (β-nitrostyrene **1a**) was always recovered under such reaction conditions. Finally, a solution with the specified ratio of toluene and cyclopentane **11** satisfied our requests and was adopted for further investigations. Applied to other β-nitrostyrenes **1b**, **1f**, **1g**, and **1h**, these conditions led in fact to the formation of cyclopentane derivatives **12b**, **12f**, **12g**, and **12h**,

Table 4. Preparation of β-cyclopentylstyrenes **12** from the reaction of β-nitrostyrenes **1**, cyclopentane **11**, and benzoyl peroxide **3** in toluene heated under reflux.

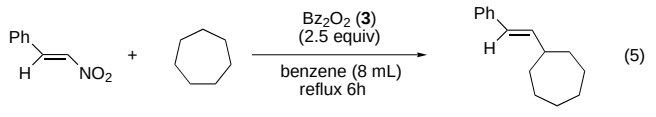


1 **11** **12**

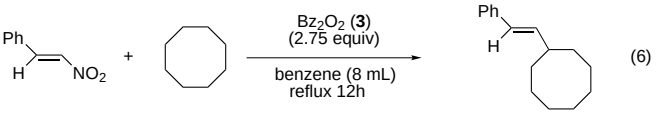
Entry	**1**	**11** [mL]	Toluene [mL]	**3** [equiv]	*t* [h]	**12**	Yield [%][a]
1	**1a**	3	12	3.25	12	**12a**	100
2	**1b**	3	12	3	12	**12b**	100
3	**1f**	3	12	2.5	6	**12f**	73
4	**1g**	3	12	2.75	10	**12g**	64
5	**1h**	3	12	2.75	9	**12h**	68

[a] NMR Yield.

respectively resulting from a conformable protocol (Table 4, entries 2–5). Then, compounds **14a** and **16a**, with a medium sized hydrocarbon ring, were obtained both in 100% yield from cycloheptane **13** and cyclooctane **15**, respectively [Eqs. (5)–(6)]. Although there is a much larger steric hindrance in medium-sized cycloalkane, the reactivity and yield were hardly reduced.



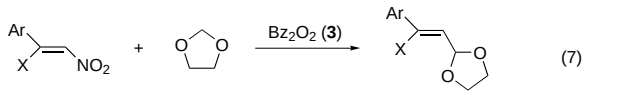
1a **13** (2 mL) **14a** (100%yield)



1a **15** (2 mL) **16a** (100% yield)

The above results prompted us to investigate the synthesis of styryl-(1,3)-dioxolane based on the present methodology. Treatment of β-nitrostyrene **1a** with benzoyl peroxide **3** in the presence of 1,3-dioxolane **17** gave the corresponding adduct **18a** in 56% yield (Table 5, entry 1). In this reaction we

Table 5. Preparation of β-(1,3-dioxolan)styrene **18** from the reaction of β-nitrostyrenes **1**, 1,3-dioxolane **17**, and benzoyl peroxide **3** (reaction mixture heated under reflux).



1 **17** **18**

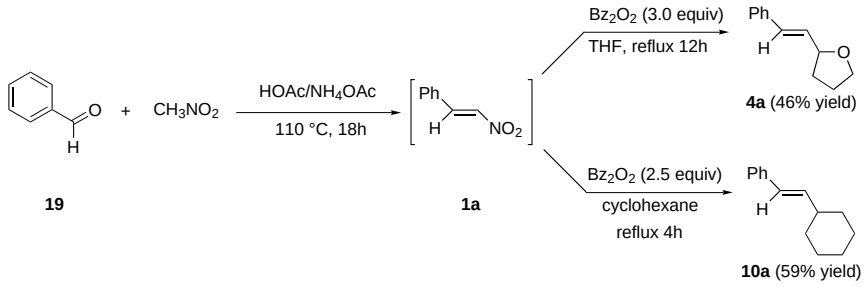
Entry	**1**	**17** [mL]	**3** [equiv]	*t* [h]	**18**	Yield [%][a]
1	**1a**	10	2.75	6	**18a**	56
2	**1b**	10	2.75	5	**18b**	60
3	**1f**	10	3	6	**18f**	57
4	**1g**	10	2.5	9	**18g**	16[b]
5	**1h**	10	2.5	6	**18h**	46

[a] NMR Yield. [b] The compound **18g** was unstable under such reaction conditions.

combined formylation and aldehyde protection in one single step and performed a key step for synthesis of conjugated aldehyde.

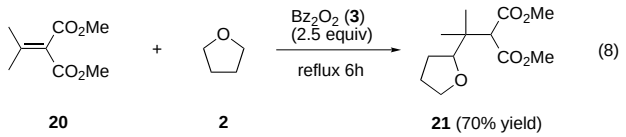
The development of substrates for use in radical chemistry that can form carbon–carbon bonds while at the same time introducing additional functionality are of great importance. Advantages of the radical acceptors in our current work include their greater variety and convenience, and now we wish to report the first examples of one-pot synthesis of styryl tetrahydrofurans **4** and cyclohexanes **10** by the radical reaction by combining our previous study and literature methodology.[3]

The radical precursors chosen for this study were tetrahydrofuran **2** and cyclohexane **9** because of their good behavior in radical reactions to β-nitrostyrenes **1**. The strategy was to react β-nitrostyrene **1a** (prepared in situ from aromatic aldehyde **19** with nitromethane in acetic acid with a catalytic amount of ammonium acetate at 110 °C for 18 h) with benzoyl peroxide **3** and tetrahydrofuran **2** or cyclohexane **9** as radical precursor at the radical reaction conditions described above. When the reaction was carried out in tetrahydrofuran **2**, 46% of (*E*)-styryl tetrahydrofuran **4a** was observed (Scheme 1). Similarly, when cyclohexane **9** was used, 59% of **10a** was also observed. A simple one-pot procedure has been developed in which styryl tetrahydrofurans **4** and cyclohexanes **10** were synthesized from cheap and easily accessible materials in medium yields.



Scheme 1.

Finally we turned our attention to the radical addition reaction mediated by benzoyl peroxide **3**. Thus, when using the radical initiation system benzoyl peroxide **3** (2.5 equiv) in tetrahydrofuran **2** heated under reflux, the tetrahydrofuran α-carbon radical species reacted with the acceptor **20** by a 1,4-addition process to adduct **21** over 6 h in 70% yield.



In conclusion, we have succeeded in the stereoselective substitution of β-nitrostyrenes **1** leading to (*E*)-alkenes exclusively. Further studies on the application of this methodology to synthesize other compounds is under investigation.

Experimental Section

All reactions were performed under nitrogen in oven-dried glassware. Radical precursors such as tetrahydrofuran, tetrahydropyran, cyclopentane, cyclohexane, cycloheptane, cyclooctane and 1,3-dioxolane were freshly distilled before use. Analytical thin-layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography with E. Merck silica gel 60 (230–400 mesh). MS or HRMS were measured by JEOL JMS-D300 or JEOL JMS-HX110 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-200. All NMR data were obtained in $CDCl_3$ solution and chemical shifts (δ) were given in ppm relative to TMS.

General procedure for the reaction of radical precursors with β-nitrostyrene

Preparation of (*E*)-4a: β-Nitrostyrene **1a** (149.2 mg, 1.0 mmol) and benzoyl peroxide **3** (726.7 mg, 3.0 mmol) were added to THF (15 mL). The mixture was heated for 12 h under reflux and then concentrated in vacuo. After the solvent (radical precursor) was evaporated, the residue was purified by column chromatography on silica gel and yielded the desired product **(*E*)-4a** as a colourless oil.

Compound (4a): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 1.61–1.78 (m, 1H), 1.87–2.19 (m, 3H), 3.77–4.02 (m, 2H), 4.41–4.51 (m, 1H), 6.20 (dd, $J = 16$, 6.6 Hz, 1H), 6.58 (d, $J = 16$ Hz, 1H), 7.17–7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.84$, 32.32, 68.12, 79.64, 126.49, 127.51, 128.54, 130.47, 130.57, 136.92.

Compound (4b): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.62$–1.79 (m, 1H), 1.81–2.21 (m, 3H), 3.79–4.03 (m, 2H), 4.41–4.52 (m, 1H), 6.18 (dd, $J =$ 15.8, 6.4 Hz, 1H), 6.54 (d, $J = 15.8$ Hz, 1H), 7.24–7.40 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.79$, 32.26, 68.16, 79.41, 127.68, 128.68, 129.15, 131.33, 133.11, 135.46; MS: *m*/*z* (%): 208 (26) $[M]^+$, 206 (72), 171 (90), 165 (100); HRMS: calcd for $C_{12}H_{13}OCl$: 208.0655; found: 208.0634 $[M]^+$.

Compound (4c): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.64$–1.80 (m, 1H), 1.89–2.22 (m, 3H), 3.79–4.03 (m, 2H), 4.44–4.54 (m, 1H), 6.29 (dd, $J = 16.2$, 6.6 Hz, 1H), 6.74 (d, $J = 16.2$ Hz, 1H), 6.97–7.25 (m, 3H), 7.41–7.49 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.81$, 32.27, 68.17, 79.72, 115.46, 115.90, 122.82, 122.90, 124.00, 124.08, 124.57, 124.81, 127.54, 127.61, 128.66, 128.83, 133.21, 133.32, 157.88, 162.84; MS: *m*/*z* (%): 192 (100) $[M]^+$, 149 (65), 133 (35), 122 (80).

Compound (4d): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.62$–1.78 (m, 1H), 1.89–2.21 (m, 3H), 3.78–4.02 (m, 2H), 4.40–4.51 (m, 1H), 6.12 (dd, $J = 15.8$, 6.6 Hz, 1H), 6.55 (d, $J = 15.8$ Hz, 1H), 6.93–7.05 (m, 2H), 7.29–7.39 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.84$, 32.32, 68.16, 79.56, 115.20, 115.64, 127.92, 128.07, 128.40, 129.34, 130.35, 130.39, 133.08, 133.14, 159.92, 164.82; MS: *m*/*z* (%): 192 (100) $[M]^+$, 149 (74), 122 (75), 109 (38).

Compound (4e): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.68$–1.93 (m, 1H), 1.94–2.28 (m, 3H), 3.82–4.08 (m, 2H), 4.55–4.65 (m, 1H), 6.23 (dd, $J =$ 15.8, 6.4 Hz, 1H), 7.30–7.61 (m, 3H), 7.74–7.85 (m, 2H), 8.10–8.16 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.82$, 32.39, 68.19, 79.76, 123.91, 125.60, 125.73, 125.96, 127.57, 127.84, 128.49, 131.24, 133.65, 133.90, 134.72; MS: *m*/*z* (%): 224 (72) $[M]^+$, 181 (55), 165 (100), 153 (100); HRMS: calcd for $C_{16}H_{16}O$: 224.1201; found: 224.1202 $[M]^+$.

Compound (4f): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.62$–1.78 (m, 1H), 1.86–2.19 (m, 3H), 3.80 (s, 3H), 3.82–4.03 (m, 2H), 4.40–4.50 (m, 1H), 6.07 (dd, $J = 15.8$, 6.8 Hz, 1H), 6.53 (d, $J = 15.8$ Hz, 1H), 6.80–6.89 (m, 2H), 7.28–7.35 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.86$, 32.35, 55.21, 68.03, 79.90, 113.94, 127.68, 128.25, 130.22, 133.59, 159.23; MS: *m*/*z* (%): 204 (79) $[M]^+$, 161 (94), 147 (100), 134 (89).

Compound (4g): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.62$–1.78 (m, 1H), 1.81–2.19 (m, 3H), 3.77–4.01 (m, 2H), 4.41–4.51 (m, 1H), 6.09–6.46 (m, 4H), 7.33–7.40 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.75$, 32.32,

68.16, 79.11, 107.77, 111.24, 118.59, 129.42, 141.91, 152.69; MS: *m/z* (%): 164 (100) $[M]^+$, 107 (36), 94 (93), 42 (63).

Compound (4h): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.62-1.78$ (m, 1H), 1.85–2.19 (m, 3H), 3.77–4.01 (m, 2H), 4.39–4.49 (m, 1H), 6.05 (dd, $J =$ 15.6, 6.6 Hz, 1H), 6.71 (d, $J = 15.6$ Hz, 1H), 6.92–7.01 (m, 2H), 7.12–7.15 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.79$, 32.27, 68.16, 79.26, 123.56, 124.17, 125.66, 127.33, 130.32, 142.12; MS: *m/z* (%): 180 (100) $[M]^+$, 137 (53), 123 (37), 110 (88); HRMS: calcd for $C_{10}H_{12}OS$: 180.0609; found: 180.0610 $[M]^+$.

Compound (4i): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.63-2.09$ (m, 4H), 3.67–3.78 (m, 1H), 3.88–3.99 (m, 1H), 4.24–4.35 (m, 1H), 6.06 (d, $J =$ 9 Hz, 1H), 7.17–7.41 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 26.33$, 32.99, 68.03, 76.62, 127.36, 127.45, 127.63, 128.12, 129.78, 129.98, 139.49, 142.04, 143.74; MS: *m/z* (%): 250 (100) $[M]^+$, 178 (67), 173 (100), 165 (74); HRMS: calcd for $C_{18}H_{18}O$: 250.1357; found: 250.1355 $[M]^+$.

Synthesis of styryl-tetrahydropyran [(*E*)-6, 7, 8]: The procedure given above was used with the precursor of radical **5** (10 mL), and the starting materials **1a–d** (1 mmol) under the specified conditions shown in Table 2.

Compound (6a): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.39-1.92$ (m, 6H), 3.47–3.60 (m, 1H), 3.93–4.11 (m, 2H), 6.21 (dd, $J = 15.9$, 5.8 Hz, 1H), 6.59 (dd, $J = 15.9$, 1 Hz, 1H), 7.16–7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 23.32$, 25.76, 32.14, 68.35, 77.99, 126.42, 127.43, 128.49, 129.75, 130.86, 137.05; MS: *m/z* (%): 188 (83) $[M]^+$, 131 (75), 104 (100); HRMS: calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1194 $[M]^+$.

Compound (6b): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.41-1.93$ (m, 6H), 3.48–3.60 (m, 1H), 3.93–4.11 (m, 2H), 6.18 (dd, $J = 16$, 5.6 Hz, 1H), 6.54 (dd, $J = 16$, 1.2 Hz, 1H), 7.23–7.33 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 23.34$, 25.76, 32.11, 68.43, 77.82, 127.66, 128.54, 128.71, 131.57, 133.09, 135.61; MS: *m/z* (%): 222 (100) $[M]^+$, 187 (97), 138 (91), 131 (87); HRMS: calcd for $C_{13}H_{15}OCl$: 222.0812; found: 222.0820 $[M]^+$.

Compound (6c): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.39-1.97$ (m, 6H), 3.47–3.60 (m, 1H), 3.95–4.11 (m, 2H), 6.29 (dd, $J = 16.2$, 5.6 Hz, 1H), 6.74 (d, $J = 16.2$ Hz, 1H), 6.95–7.26 (m, 3H), 7.40–7.49 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 23.29$, 25.73, 32.05, 68.35, 78.08, 115.42, 115.86, 122.21, 122.27, 123.99, 124.05, 124.66, 124.90, 127.39, 127.46, 128.60, 128.77, 133.41, 133.50, 157.87, 162.83.

Compound (6d): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.38-1.93$ (m, 6H), 3.47–3.60 (m, 1H), 3.92–4.10 (m, 2H), 6.12 (dd, $J = 16.2$, 5.6 Hz, 1H), 6.55 (d, $J = 16.2$ Hz, 1H), 6.92–7.04 (m, 2H), 7.28–7.38 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 23.32$, 25.75, 32.14, 68.38, 77.88, 115.16, 115.60, 127.83, 127.99, 128.65, 130.62, 130.65, 133.18, 133.24, 159.86, 164.76.

Compound (7a): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.36-1.82$ (m, 3H), 1.93–2.01 (m, 1H), 2.38–2.56 (m, 1H), 3.20–3.46 (m, 2H), 3.89–3.96 (m, 2H), 6.05 (dd, $J = 16$, 7.2 Hz, 1H), 6.43 (d, $J = 16$ Hz, 1H), 7.17–7.38 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.37$, 29.71, 39.87, 68.12, 72.52, 126.08, 127.27, 128.57, 130.24, 130.86, 137.43; MS: *m/z* (%): 188 (32) $[M]^+$, 129 (72), 104 (100); HRMS: calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1204 $[M]^+$.

Compound (7b): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.36-1.82$ (m, 3H), 1.92–2.00 (m, 1H), 2.37–2.55 (m, 1H), 3.20–3.47 (m, 2H), 3.88–3.94 (m, 2H), 6.03 (dd, $J = 16$, 7.4 Hz, 1H), 6.38 (d, $J = 16$ Hz, 1H), 7.13–7.47 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.29$, 29.62, 39.83, 68.12, 72.39, 127.31, 128.71, 129.09, 131.61, 132.83, 135.96; MS: *m/z* (%): 222 (30) $[M]^+$, 138 (100), 129 (78); HRMS: calcd for $C_{13}H_{15}OCl$: 222.0811; found: 222.0805 $[M]^+$.

Compound (7c): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.38-1.82$ (m, 3H), 1.92–2.04 (m, 1H), 2.41–2.58 (m, 1H), 3.21–3.50 (m, 2H), 3.89–3.98 (m, 2H), 6.13 (dd, $J = 16$, 7.2 Hz, 1H), 6.59 (d, $J = 16$ Hz, 1H), 6.96–7.23 (m, 3H), 7.37–7.46 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.31$, 29.57, 40.24, 68.11, 72.39, 115.46, 115.90, 122.62, 122.70, 124.02, 124.08, 125.04, 125.28, 127.02, 127.10, 128.37, 128.54, 133.44, 133.53, 157.64, 162.59.

Compound (7d): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.35-1.90$ (m, 3H), 1.92–2.01 (m, 1H), 2.37–2.54 (m, 1H), 3.19–3.46 (m, 2H), 3.87–3.95 (m, 2H), 5.96 (dd, $J = 16$, 7.6 Hz, 1H), 6.39 (d, $J = 16$ Hz, 1H), 6.92–7.04 (m, 2H), 7.19–7.35 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.32$, 29.68, 39.80, 68.11, 72.48, 115.19, 115.61, 127.45, 127.61, 129.09, 130.59, 130.63, 133.56, 133.62, 159.73, 164.63.

Compound (8a): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.46-1.74$ (m, 4H), 2.29–2.48 (m, 1H), 3.40–3.53 (m, 2H), 3.98–4.05 (m, 2H), 6.16 (dd, $J = 16$, 6.6 Hz, 1H), 6.39 (d, $J = 16$ Hz, 1H), 7.17–7.38 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.55$, 38.30, 67.70, 126.05, 127.13, 128.30, 128.56, 134.64, 137.57; MS: *m/z* (%): 188 (100) $[M]^+$, 143 (37), 91 (52); HRMS: calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1198 $[M]^+$.

Compound (8b): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.45-1.74$ (m, 4H), 2.29–2.45 (m, 1H), 3.40–3.61 (m, 2H), 3.98–4.04 (m, 2H), 6.13 (dd, $J =$ 15.8, 6.6 Hz, 1H), 6.34 (dd, $J = 15.8$, 1 Hz, 1H), 7.16–7.39 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.46$, 38.28, 67.65, 127.17, 127.28, 128.68, 128.84, 135.34, 136.10; MS: *m/z* (%): 222 (34) $[M]^+$, 139 (51), 125 (51), 83 (100); HRMS: calcd for $C_{13}H_{15}OCl$: 222.0812; found: 222.0814 $[M]^+$.

Compound (8c): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.47-1.75$ (m, 4H), 2.32–2.51 (m, 1H), 3.40–3.53 (m, 2H), 3.97–4.06 (m, 2H), 6.23 (dd, $J = 16$, 6.8 Hz, 1H), 6.55 (d, $J = 16$ Hz, 1H), 6.96–7.25 (m, 3H), 7.40–7.50 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.44$, 38.69, 67.65, 115.45, 115.89, 120.71, 120.79, 124.02, 124.08, 125.17, 125.41, 126.98, 127.05, 128.24, 128.40, 137.13, 137.20, 157.66, 162.60.

Compound (8d): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.39-1.73$ (m, 4H), 2.28–2.46 (m, 1H), 3.34–3.53 (m, 2H), 3.97–4.05 (m, 2H), 6.07 (dd, $J = 16$, 6.6 Hz, 1H), 6.35 (d, $J = 16$ Hz, 1H), 6.93–7.18 (m, 2H), 7.21–7.36 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.55$, 38.25, 67.67, 115.17, 115.61, 127.16, 127.42, 127.58, 133.70, 133.76, 134.38, 134.41, 159.67, 164.57.

Synthesis of styryl-cyclohexane [(*E*)-10]: The procedure given above was used with the precursor of radical **9** (10 mL), and the starting materials **1a–i** (1 mmol) under the specified conditions shown in Table 3.

Compound (10c): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.08-1.44$ (m, 5H), 1.66–2.08 (m, 5H), 2.10–2.28 (m, 1H), 6.23 (dd, $J = 16.2$, 6.8 Hz, 1H), 6.51 (d, $J = 16.2$ Hz, 1H), 6.94–7.20 (m, 3H), 7.39–7.47 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.95$, 26.10, 32.80, 41.48, 115.37, 115.81, 119.62, 119.71, 123.93, 124.0, 125.72, 125.96, 126.90, 126.98, 127.83, 127.99, 139.39, 139.46, 157.64, 162.57; MS: *m/z* (%): 204 (32) $[M]^+$, 122 (100), 109 (23); HRMS; calcd for $C_{14}H_{17}F$: 204.1269; found: 204.1291 $[M]^+$.

Compound (10d): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.06-1.43$ (m, 5H), 1.60–1.90 (m, 5H), 2.07–2.19 (m, 1H), 6.07 (dd, $J = 16$, 6.8 Hz, 1H), 6.30 (d, $J = 16$ Hz, 1H), 6.90–7.05 (m, 2H), 7.24–7.32 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.96$, 26.10, 32.90, 41.04, 115.07, 115.49, 126.16, 127.28, 127.45, 134.24, 134.31, 136.61, 136.66, 159.51, 164.39; MS: *m/z* (%): 204 (31) $[M]^+$, 122 (100), 109 (26); HRMS: calcd for $C_{14}H_{17}F$: 204.1314; found: 204.1311 $[M]^+$.

Compound (10e): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.12-1.45$ (m, 5H), 1.68–1.92 (m, 5H), 2.12–2.35 (m, 1H), 6.18 (dd, $J = 15.8$, 7.0 Hz, 1H), 7.07 (d, $J = 15.8$ Hz, 1H), 7.36–7.56 (m, 4H), 7.69–7.73 (m, 1H), 7.79–7.84 (m, 1H), 8.09–8.14 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 26.01$, 26.16, 32.99, 41.47, 123.47, 124.0, 124.44, 125.61, 125.69, 125.73, 127.17, 128.49, 131.29, 133.70, 135.97, 140.24; MS: *m/z* (%): 236 (88) $[M]^+$, 179 (58), 165 (64), 154 (100); HRMS: calcd for $C_{18}H_{20}$: 236.1565; found: 236.1567 $[M]^+$.

Compound (10i): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.05-1.34$ (m, 5H), 1.52–1.78 (m, 5H), 2.02–2.24 (m, 1H), 5.90 (d, $J = 9.8$ Hz, 1H), 7.12–7.42 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.52$, 25.92, 33.27, 38.24, 126.73, 126.80, 127.24, 128.05, 128.16, 129.81, 135.97, 139.72, 140.66, 143.0; MS: *m/z* (%): 262 (78) $[M]^+$, 205 (50), 180 (100), 165 (53); HRMS: calcd for $C_{20}H_{22}$: 262.1722; found: 262.1725 $[M]^+$.

Synthesis of styryl-cyclopentane [(*E*)-12]: The procedure given above was used with toluene and the precursor of radical **11** (3 mL, volume ratio of **11**/toluene 1:4) as co-solvent, and the starting materials **1a**,**b**, **f–h** (1 mmol) under the specified conditions shown in Table 4.

Compound (12a): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.30-1.93$ (m, 8H), 2.50–2.69 (m, 1H), 6.20 (dd, $J = 16$, 7.6 Hz, 1H), 6.37 (d, $J = 16$ Hz, 1H), 7.13–7.37 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.16$, 33.15, 43.77, 125.96, 126.75, 127.89, 128.49, 135.76, 137.99; MS: *m/z* (%): 172 (32) $[M]^+$, 104 (89), 84 (75), 66 (100); HRMS: calcd for $C_{13}H_{16}$: 172.1252; found: 172.1244 $[M]^+$.

Compound (12b): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.29-1.92$ (m, 8H), 2.48–2.67 (m, 1H), 6.16 (dd, $J = 16$, 7.4 Hz, 1H), 6.31 (d, $J = 16$ Hz, 1H), 7.07–7.43 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.22$, 33.15, 43.77, 126.70, 127.10, 128.53, 132.18, 136.40, 136.43; MS: *m/z* (%): 206 (44) $[M]^+$, 171 (45), 138 (100), 129 (79); HRMS: calcd for $C_{13}H_{15}Cl$: 206.0862; found: 206.0854 $[M]^+$.

Compound (12f): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.28-1.91$ (m, 8H), 2.46–2.66 (m, 1H), 3.78 (s, 3H), 6.05 (dd, $J = 15.8$, 7.6 Hz, 1H), 6.31 (d, $J =$

15.8 Hz, 1H), 6.79–6.86 (m, 2H), 7.24–7.31 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.13, 33.21, 43.74, 55.20, 113.90, 126.99, 127.22, 130.80, 133.61, 158.64; MS: *m*/*z* (%): 202 (84) $[M]^+$, 159 (52), 134 (87), 121 (100); HRMS: calcd for $C_{14}H_{18}O$: 202.1358; found: 202.1361 $[M]^+$.

Compound (12g): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20–2.10 (m, 8H), 2.42–2.64 (m, 1H), 6. 07–6.39 (m, 4H), 7.19–7.41 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.11, 33.08, 43.52, 105.92, 111.11, 116.74, 134.76, 141.19, 153.48; MS: *m*/*z* (%): 162 (12) $[M]^+$, 85 (67), 71 (85), 57 (100); HRMS: calcd for $C_{11}H_{14}O$: 162.1044; found: 162.1049 $[M]^+$.

Compound (12h): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28–2.00 (m, 8H), 2.45–2.65 (m, 1H), 6.05 (dd, *J* = 15.8, 7.8 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.84–6.98 (m, 2H), 7.00–7.23 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.11, 33.03, 43.56, 121.24, 122.99, 124.14, 127.21, 135.70, 143.30; MS: *m*/*z* (%): 178 (28) $[M]^+$, 110 (70), 84 (75), 66 (100); HRMS: calcd for $C_{11}H_{14}S$: 178.0817; found 178.0814 $[M]^+$.

Synthesis of styryl-cycloheptane and -cyclooctane [(*E*)-14a, (*E*)-16a]: The procedure given above was used with benzene and the precursor of radical **13** or **15** (2 mL, volume ratio of **13** or **15**/benzene 1:4) as co-solvent, and the starting material **1a** (1 mmol) under the specified conditions shown in Equations (5)–(6).

Compound (14a): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.33–1.88 (m, 12H), 2.21–2.37 (m, 1H), 6.19 (dd, *J* = 15.8, 6.6 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 7.12–7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.19, 28.33, 34.66, 43.17, 125.96, 126.67, 126.72, 128.46, 137.66, 138.16; MS: *m*/*z* (%): 200 (1) $[M]^+$, 96 (100), 91 (61), 81 (77); HRMS: calcd for $C_{15}H_{20}$: 200.1565; found: 200.1540 $[M]^+$.

Compound (16a): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.38–1.83 (m, 14H), 2.25–2.50 (m, 1H), 6.20 (dd, *J* = 16, 6.6 Hz, 1H), 6.33 (d, *J* = 16 Hz, 1H), 7.12–7.37 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.01, 25.93, 27.37, 31.80, 41.27, 125.98, 126.69, 126.87, 128.49, 137.89, 138.20; MS: *m*/*z* (%): 214 (4) $[M]^+$, 120 (45), 105 (100), 91 (40).

Synthesis of styryl-(1,3)-dioxolane [(*E*)-18]: The procedure given above was used with the precursor of radical **17** (10 mL), and the starting materials **1a**,**b**, **f**–**h** (1 mmol) under the specified conditions shown in Table 5.

Compound (18a): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.92–3.95 (m, 2H), 4.02–4.06 (m, 2H), 5.42 (d, *J* = 6.4 Hz, 1H), 6.16 (dd, *J* = 16, 6.0 Hz, 1H),6.77 (d, *J* = 16 Hz, 1H), 7.25–7.42 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 64.95, 103.76, 125.12, 126.85, 128.25, 128.49, 134.70, 135.77; MS: *m*/*z* (%): 176 (3.6) $[M]^+$, 131 (100), 103 (65), 77 (56); HRMS: calcd for $C_{11}H_{12}O_2$: 176.0838; found: 176.0865 $[M]^+$.

Compound (18b): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.89–3.98 (m, 2H), 3.98–4.08 (m, 2H), 5.40 (d, *J* = 5.8 Hz, 1H), 6.13 (dd, *J* = 16, 5.8 Hz, 1H),6.71 (d, *J* = 16 Hz, 1H), 7.25–7.35 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 64.94, 103.49, 125.84, 128.07, 128.72, 133.38, 133.96, 134.29; MS: *m*/*z* (%): 210 (1) $[M]^+$, 182 (64), 139 (100), 102 (58); HRMS: calcd for $C_{11}H_{11}O_2Cl$: 210.0448, found 210.0422 $[M]^+$.

Compound (18f): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 3.90–3.99 (m, 2H), 4.02–4.10 (m, 2H), 5.40 (d, *J* = 6.2 Hz, 1H), 6.03 (dd, *J* = 16, 6.2 Hz, 1H), 6.72 (d, *J* = 16 Hz, 1H), 6.82–6.89 (m, 2H), 7.32–7.39 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.23, 65.00, 104.23, 114.01, 122.79, 128.28, 130.41, 134.64, 159.87; MS: *m*/*z* (%): 206 (25) $[M]^+$, 147 (40), 134 (100), 119 (35); HRMS: calcd for $C_{12}H_{14}O_3$: 206.0943; found: 206.0954 $[M]^+$.

Compound (18g): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.90–3.98 (m, 2H), 4.01–4.08 (m, 2H), 5.42 (d, *J* = 5.6 Hz, 1H), 6.10 (dd, *J* = 15.8, 5.6 Hz, 1H), 6.34–6.39 (m, 2H), 6.58 (d, *J* = 16.4 Hz, 1H), 7.25–7.37 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 64.97, 103.40, 109.68, 111.38, 122.44, 123.56, 142.73, 151.74; MS: *m*/*z* (%): 166 (5) $[M]^+$, 85 (71), 71 (84), 57 (100); HRMS: calcd for $C_9H_{10}O_3$: 166.0630; found: 166.0608 $[M]^+$.

Compound (18h): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.88–3.98 (m, 2H), 4.00–4.10 (m, 2H), 5.40 (d, *J* = 6.0 Hz, 1H), 5.99 (dd, *J* = 15.8, 6.0 Hz, 1H), 6.85–7.04 (m, 3H), 7.19–7.22 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 65.00, 103.52, 124.52, 125.46, 127.14, 127.43, 127.66, 140.91; MS: *m*/*z* (%): 182 (47) $[M]^+$, 123 (25), 110 (100); HRMS: calcd for $C_9H_{10}O_2S$: 182.0402; found: 182.0402 $[M]^+$.

One-pot synthesis of 4a or 10a: Benzaldehyde **19** (1 mmol) reacted with nitromethane **2** (1 mL) in acetic acid (1 mL) with ammonium acetate (0.1 mmol) at 110 °C for 18 h to generate (*E*)-β-nitrostyrene **1a**. After the reaction cooled down, benzoyl peroxide and radical precursor **2** or **9** were added to the reaction system then this mixture was hetaed under reflux to yield the desired products **(*E*)-4a** or **10a** shown in Scheme 1 according to the procedure mentioned above.

Synthesis of compound 21: The procedure given above was used with the precursor of radical **2** (15 mL), and the starting material **20** (1 mmol) under the specified conditions shown in Equation (8).

Compound (21): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.04 (s, 3H), 1.13 (s, 3H), 1.61–1.78 (m, 1H), 1.81–1.98 (m, 3H), 3.63–3.93 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.87, 20.51, 25.93, 26.03, 39.97, 51.80, 57.37, 68.29, 83.75, 168.47, 168.84; MS: *m*/*z* (%): 244 (0.3) $[M]^+$, 149 (47), 105 (35), 71 (100); HRMS: calcd for $C_{12}H_{20}O_5$: 244.1311, found 244.1292 $[M]^+$.

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