Highly Stereoselective Synthesis of Trisubstituted α,β-Unsaturated Sulfoxides by Heck Reaction

Inés Alonso and Juan C. Carretero*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

juancarlos.carretero@uam.es

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During the last two decades α,β-unsaturated sulfoxides have been widely used in a variety of highly diastereoselective processes, such as Michael additions or Diels−Alder cycloadditions, because of the high stereochemical control usually exerted by the sulfinyl group.[1] Although simple α,β-unsaturated sulfoxides are easily prepared by different methods[2] (especially by Wadsworth−Emmons olefination and condensation of α-sulfinyl carbanions with carbonyl compounds and further dehydration), often *E*/*Z* mixtures of stereoisomers are obtained.[1,2] From a synthetic point of view, this problem is particularly important in the case of the stereoselective synthesis of acyclic trisubstituted α,β-unsaturated sulfoxides.

The palladium-catalyzed reaction of organic halides with alkenes (the Heck reaction[3]) is nowadays a powerful method for the stereoselective synthesis of trans disubstituted alkenes from terminal olefins. However, this reaction has been much less applied to the stereoselective synthesis of trisubstituted alkenes from disubstituted ones. In particular, several examples of synthesis of trisubstituted α,β-unsaturated esters, nitriles, aldehydes, and ketones by Heck arylation of the corresponding disubstituted conjugated olefins have been reported in recent years.[4] In connection with our previous work on the application of sulfoxides as chiral auxiliaries in asymmetric Heck reactions,[5] we describe here the first examples of synthesis of trisubstituted α,β-unsaturated sulfoxides by highly stereoselective Heck arylation of appropriately substituted vinyl sulfoxides.[6]

Results and Discussion

First, to check the reactivity of acyclic 1,2-disubstituted α,β-unsaturated sulfoxides in Heck reactions, the known 1-*p*-tolylsulfinyl-1-heptene (*E*)-**1**[7] was treated with iodobenzene or *p*-methoxyphenyl diazonium tetrafluoroborate under the optimal conditions previously found in the Heck arylation of β-sulfinyldihydrofurans and cyclopentenes:[5] $Pd(OAc)_2$ as catalyst, Ag_2CO_3 as base, a bidentate ligand (dppp or dppf), and a polar solvent (CH_3CN or DMF). However, either a sluggish transformation or no reaction at all was observed in all cases. As the best result a 40% conversion was detected after treating (*E*)-**1** with excess of iodobenzene (3 equiv) in the presence of $Pd(OAc)_2$ (10 mol %), Ag_2CO_3 (200 mol %), dppf (10 mol %) in DMF at 100 °C for 29 h[8] (Scheme 1).

To overcome the poor reactivity of disubstituted α,β-unsaturated *p*-tolyl sulfoxides in Heck reactions, we reasoned that the introduction of a palladium coordinating group, such as a Me_2N moiety, in the *ortho* position of the arylsulfinyl moiety (substrates **2**) could enhance the rate of the process due to the possible coordination of the arylpalladium intermediate species with the nitrogen atom of the Me_2N group. This previous coordination would presumably facilitate the further olefin coordination/insertion steps[9] (Scheme 2).

To test this idea, α,β-unsaturated 2-(*N*,*N*-dimethylamino)phenyl sulfoxides **2** were readily prepared by deprotonation of 2-(*N*,*N*-dimethylamino)phenyl methyl sulfoxide[10] (LDA, THF, −78 °C), addition of the corresponding aldehyde, and subsequent mesylation (MsCl, Et_3N, CH_2Cl_2) and basic elimination (DBU). The vinyl sulfoxides **2** were obtained in good yields (53−72%) as *E*/*Z* mixtures, in which the *E* isomer clearly predominated (Table 1). Both stereoisomers were readily separated by simple flash chromatography.

Gratifyingly, a fast and clean evolution was observed in the palladium-catalyzed reactions of the β-alkyl-substituted vinyl sulfoxides (*E*)-**2a**,**b** with different iodoarenes under the same experimental conditions previously used with sulfoxide (*E*)-**1** [$Pd(OAc)_2$, Ag_2CO_3, dppf, DMF, 100 °C]. In most cases a complete evolution was observed in 2−4 h, affording the trisubstituted vinyl sulfoxides **3**−**5** in good yields (66−75%) and as single stereoisomers (Table 2). However, unlike the reaction of **2a** with iodobenzene and *p*-iodoanisole, its reaction with *p*-nitroiodobenzene was much slower, being observed a 67% conversion yield after 91 h. The trisubstituted olefin (*E*)-**5a** was isolated in 58% yield (87% in converted yield). The *E* stereochemistry of alkenes **3**−**5** was the expected according to the mechanism of the Heck reaction (ste-

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(4) (a) Gürtler, C.; Buchwald, S. L. *Chem. Eur. J.* **1999**, *5*, 3107. (b) König, W. A.; Stenzel, W.; Schotten, T. *Tetrahedron Lett.* **1999**, *40*, 2101. (c) Beller, M.; Riermeier, T. H.; *Eur. J. Inorg. Chem.* **1998**, 29. (d) Moreno-Mañas, M.; Pleixats, R.; Roglans, A. *Synlett* **1997**, 1157. (e) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F.; Pace, P. *Tetrahedron* **1996**, *52*, 6983. (f) Cacchi, S.; Ciattini, P. G.; Morena, E.; Pace, P. *Synlett* **1996**, 545. (g) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F.; Pace, P. *Synlett* **1996**, 568.

(5) (a) Priego, J.; Carretero, J. C. *Synlett* **1999**, 1603. (b) Díaz Buezo, N.; Alonso, I.; Carretero, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 7129.

(6) For the synthesis of a disubstituted α,β-unsaturated sulfoxide by a Heck reaction on *p*-tolyl vinyl sulfoxide, see: Somei, M.; Yamada, F.; Ohnishi, H.; Makita, Y.; Kuriki, M. *Heterocycles* **1987**, *26*, 2823.

(7) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078. (*E*)-**1** was prepared from methyl *p*-tolyl sulfoxide following the same experimental procedure used for the synthesis of sulfoxides **2**.

(8) A very low reactivity was observed in the reaction of (*E*)-**1** with diazonium salts. On the other hand, the stereoisomer (*Z*)-**1** was even less reactive giving rise the corresponding Heck product in 5% yield after 29 h at 100 °C.

(9) For the participation of Pd−N coordinated complexes in the Heck reaction of amino olefins, see: Larhed, M, Andersson, C.; Hallberg, A. *Tetrahedron* **1994**, *50*, 285 (and references therein).

(10) 2-(*N*,*N*-Dimethylamino)phenyl methyl sulfoxide was readily prepared by methylation of *o*-aminothiophenol (NaH, MeI, DMF, 0 °C to room temperature) and oxidation (MCPBA, CH_2Cl_2, −78 °C).

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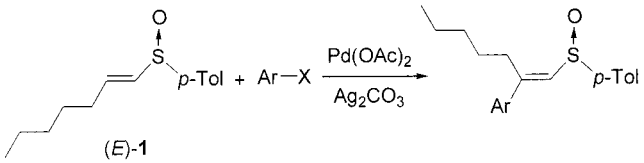
Scheme 1



Scheme 2

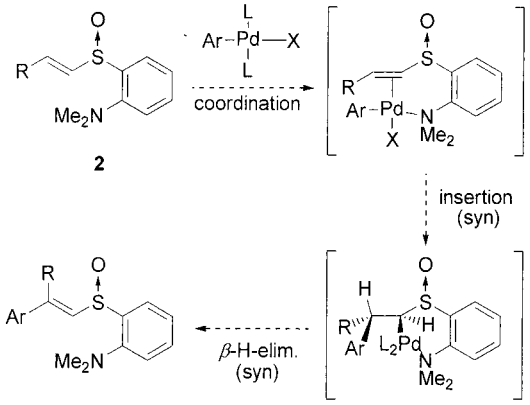
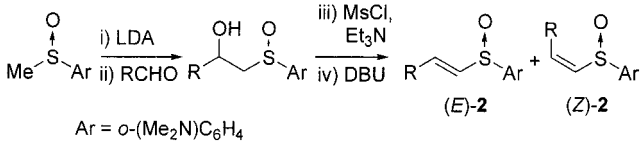


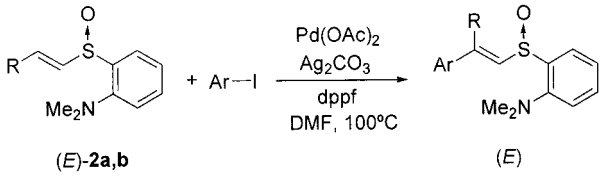
Table 1. Synthesis of α,β-Unsaturated *o*-(*N*,*N*-Dimethylamino)phenylsulfoxides



R	product	*E*/*Z*[a]	yield[b] (%) [*E* (%)][c]
nC_5H_{11}	**2a**	85/15	72 (57)
*i*Pr	**2b**	95/5	56 (53)
Ph	**2c**	76/24	53 (40)
p-MeO(C_6H_4)	**2d**	77/23	65 (48)

[a] Determined by ^{1}H NMR on the crude mixtures. [b] Overall yields from the starting methyl sulfoxide after flash chromatography. [c] In brackets overall yield in pure *E* isomer.

Table 2. Heck Arylation of α,β-Unsaturated *o*-(*N*,*N*-Dimethylamino)phenyl Sulfoxides (*E*)-2a,b



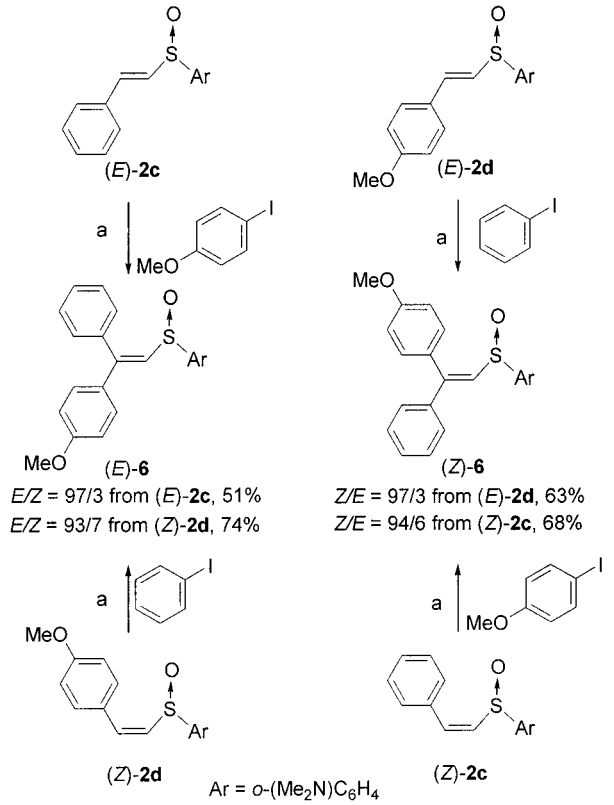
2	R	Ar	product	*E*/*Z*[a]	yield[b] (%)
2a	nC_5H_{11}	Ph	**3a**	>98/<2	75
2a	nC_5H_{11}	*p*-MeO(C_6H_4)	**4a**	98/2	70
2a	nC_5H_{11}	*p*-NO_2(C_6H_4)	**5a**	95/5	58 (87)[c]
2b	*i*Pr	Ph	**3b**	>98/<2	75
2b	*i*Pr	*p*-MeO(C_6H_4)	**4b**	>98/<2	66

[a] Determined by ^{1}H NMR on the crude mixtures. [b] In pure compound after flash chromatography. [c] Conversion yield.

reospecific syn Pd−C insertion and syn β-H elimination steps) and was unequivocally proved by NOESY experiments in **3a** and **4a**.[11]

This methodology has also been applied to the highly stereoselective preparation of β,β′-diaryl-substituted α,β-unsaturated sulfoxides. Thus, the Heck reactions of

Scheme 3



(a) $Pd(OAc)_2$ 10 mol %, Ag_2CO_3 200 mol %, dppf 10 mol %, DMF, 100°C.

the β-aryl-substituted vinyl sulfoxides (*E*)-**2c** with *p*-iodoanisole afforded (*E*)-**6** with almost complete stereoselectivity (*E*/*Z* = 97/3, 51%[12] yield), while the reaction of (*E*)-**2d** with iodobenzene gave the corresponding stereoisomer (*Z*)-**6** (*Z*/*E* = 94/6, 63% yield). Interestingly, in agreement with the usual stereospecificity of the Heck reaction, the corresponding stereoisomers (*Z*)-**2c** and (*Z*)-**2d** reacted under the same palladium-catalyzed conditions with *p*-iodoanisole and iodobenzene, respectively, to provide also with very high stereoselectivity (*Z*)-**6** and (*E*)-**6**, respectively[13] (68% and 74% yields) (Scheme 3).

In summary, β,β′-disubstituted α,β-unsaturated sulfoxides can be prepared in a highly stereoselective manner by Heck arylation of the readily available (*E*) and (*Z*) β-substituted α,β-unsaturated sulfoxides. This procedure relies on the use of 2-(*N*,*N*-dimethylamino)phenyl sulfoxides, in which the Me_2N group would facilitate the Heck reaction likely due to its capability of acting as ligand in the palladium-catalyzed pathway.

(11) The NOESY spectrum of (*E*)-**3a** shows a strong cross-peak between the olefinic proton and the *ortho* hydrogens of the phenyl group. Similarly, in the case of **4a** the same strong NOE effect was present in (*E*)-**4a** but absent in (*Z*)-**4a**.

(12) In this case the regioisomer 1-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-1-(4-methoxyphenyl)-2-phenylethene was isolated as a minor compound (14% yield).

(13) The stereochemical assignment of isomers **6** was unambiguously established by NOESY experiments. Thus, in a mixture *Z*/*E* (ratio 88/12), the major product (*Z*)-**6** showed a strong cross-peak between the olefinic proton and those of the *ortho* position to the phenyl group [this correlation is not present in (*E*)-**6**]. Similarly, a strong correlation is observed between the olefinic proton and those of the *ortho* position of the *p*-methoxyphenyl substituent in (*E*)-**6**, but not in (*Z*)-**6**.

Experimental Section

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ at room temperature. Chemical shifts (ppm) and coupling constants (Hz) were obtained by first-order analysis of spin patterns. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded by using FAB technique. Mass data are reported in mass units (*m*/*z*), and values in brackets show the relative intensity from the base peak (as 100%). All reagents were obtained from commercial suppliers and were used without further purification except for aldehydes, which were used freshly distilled. DMF was distilled from CaH_2. THF was distilled from sodium/benzophenone. CH_2Cl_2 was distilled from P_2O_5. All reactions involving the use of LDA and $Pd(OAc)_2$ were carried out in flame- and oven-dried glassware under inert argon atmosphere. Chromatography was carried out using Merck 60 230−400 mesh silica gel.

General Procedure for the Preparation of Vinyl Sulfoxides 2. To a solution of *o*-(*N*,*N*-dimethylamino)phenyl methyl sulfoxide (500 mg, 2.7 mmol) in THF (4 mL) was added LDA (0.5M THF solution, 6.2 mL, 3.1 mmol, 1.1 equiv) dropwise at −78 °C under argon atmosphere. The mixture was stirred at −78 °C for 10 min, and the corresponding aldehyde (5.4 mmol, 2 equiv) was added. Stirring was continued for 3 h while the mixture was warmed to room temperature. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and evaporated. The residue was dissolved in dried CH_2Cl_2 (9 mL) and stirred under argon atmosphere at 0 °C. Then MsCl (314 μL, 4.05 mmol, 1.5 equiv) and Et_3N (3.7 mL, 27 mmol, 10 equiv) were added. The mixture was stirred at room temperature until the intermediate mesylate disappeared by TLC (4−5 h). The reaction was quenched with NH_4Cl, and the product was extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-1-heptene [(*E*)-2a]. ^{1}H NMR δ: 7.74 (dd, 1H, J = 1.6 and 7.8 Hz), 7.36 (dt, 1H, J = 1.7 and 7.7 Hz), 7.20 (dt, 1H, J = 1.2 and 7.5 Hz), 7.11 (dd, 1H, J = 1.2 and 7.9 Hz), 6.45 (dt, 1H, J = 6.6 and 15.1 Hz), 6.32 (dt, 1H, J = 1.2 and 15.1 Hz), 2.69 (s, 6H), 2.16−2.08 (m, 2H), 1.42−1.18 (m, 6H), 0.81 (bt, 3H, J = 6.9 Hz). ^{13}C NMR δ: 150.9, 139.0, 138.0, 133.1, 131.1, 124.6, 124.1, 119.9, 44.8, 31.7, 31.0, 27.8, 22.2, 13.8. MS: 266 (100, $M^+ + 1$), 248 (34.8, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{15}H_{24}NOS$ ($M^+ + 1$) 266.1579, found 266.1576.

(*Z*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-1-heptene [(*Z*)-2a]. ^{1}H NMR δ: 7.91 (dd, 1H, J = 1.7 and 7.7 Hz), 7.41 (dt, 1H, J = 1.7 and 7.6 Hz), 7.29 (dt, 1H, J = 1.2 and 7.6 Hz), 7.15 (dd, 1H, J = 1.2 and 7.7 Hz), 6.15−6.07 (m, 1H), 5.97 (dt, 1H, J = 1.3 and 9.4 Hz), 2.72−2.62 (m, 1H), 2.68 (s, 6H), 2.50−2.40 (m, 1H), 1.55−1.28 (m, 6H), 0.95−0.88 (m, 3H). ^{13}C NMR δ: 151.3, 141.1, 139.8, 136.5, 131.4, 125.1, 124.8, 120.4, 44.9, 31.5, 29.4, 28.7, 22.5, 14.0. MS: 266 (100, $M^+ + 1$), 248 (34.2, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{15}H_{24}NOS$ ($M^+ + 1$) 266.1579, found 266.1574.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-3-methyl-1-butene [(*E*)-2b]. ^{1}H NMR δ: 7.74 (dd, 1H, J = 1.6 and 7.7 Hz), 7.36 (dt, 1H, J = 1.6 and 7.3 Hz), 7.21 (dt, 1H, J = 1.2 and 7.7 Hz), 7.11 (dd, 1H, J = 1.2 and 7.6 Hz), 6.43 (dd, 1H, J = 6.5 and 15.0 Hz), 6.25 (dd, 1H, J = 1.2 and 15.0 Hz), 2.68 (s, 6H), 2.45−2.34 (m, 1H), 0.98 (d, 6H, J = 6.9 Hz. ^{13}C NMR δ: 151.1, 144.6, 139.2, 131.3, 131.2, 124.9, 124.3, 120.2, 44.9, 30.8, 21.5, 21.3.

(*E*)-2-Phenyl-1-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-ethene [(*E*)-2c]. ^{1}H NMR δ: 7.79 (dd, 1H, J = 1.6 and 7.7 Hz), 7.38−7.33 (m, 4H), 7.29−7.18 (m, 3H), 7.24 (d, 1H, J = 15.5 Hz), 7.12 (dd, 1H, J = 1.1 and 7.9 Hz), 7.07 (d, 1H, J = 15.5 Hz), 2.73 (s, 6H). ^{13}C NMR δ: 150.9, 138.7, 134.1, 133.7, 131.9, 131.4, 129.0, 128.6, 127.3, 125.0, 124.1, 120.2, 44.9. MS: 272 (100, $M^+ + 1$), 254 (30.0, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{16}H_{18}NOS$ ($M^+ + 1$) 272.1109, found 272.1107.

(*Z*)-2-Phenyl-1-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-ethene [(*Z*)-2c]. ^{1}H NMR δ: 7.94 (dd, 1H, J = 1.6 and 7.5 Hz), 7.74−7.69 (m, 1H), 7.47−7.28 (m, 6H), 7.17 (dd, 1H, J = 1.6 and 7.5 Hz), 6.92 (d, 1H, J = 10.2 Hz), 6.15 (d, 1H, J = 10.2 Hz), 2.48 (s, 6H). ^{13}C NMR δ: 151.5, 140.4, 136.6, 136.4, 134.3, 131.5, 129.7, 129.0, 128.2, 125.5, 124.8, 121.0, 44.7.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)ethene [(*E*)-2d]. ^{1}H NMR δ: 7.80 (dd, 1H, J = 1.3 and 7.8 Hz), 7.40−7.12 (m, 3H), 7.32 (bd, 2H, J = 8.8 Hz), 7.20 (d, 1H, J = 15.4 Hz), 6.90 (d, 1H, J = 15.4 Hz), 6.81 (bd, 2H, J = 8.8 Hz), 3.74 (s, 3H), 2.73 (s, 6H). ^{13}C NMR δ: 160.3, 151.0, 139.0, 133.8, 131.3, 129.3, 128.8, 126.9, 124.9, 124.2, 120.2, 114.0, 55.1, 44.9.

(*Z*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)ethene [(*Z*)-2d]. ^{1}H NMR δ: 7.92 (dd, 1H, J = 1.7 and 7.7 Hz), 7.68 (bd, 2H, J = 8.8 Hz), 7.41 (dt, 1H, J = 1.7 and 7.6 Hz), 7.32 (dt, 1H, J = 1.2 and 7.6 Hz), 7.18 (dd, 1H, J = 1.2 and 7.8 Hz), 6.90 (bd, 2H, J = 8.8 Hz), 6.82 (d, 1H, J = 10.6 Hz), 6.03 (d, 1H, J = 10.6 Hz), 3.82 (s, 3H), 2.50 (s, 6H). ^{13}C NMR δ: 160.3, 151.5, 140.8, 136.0, 134.3, 131.6, 131.4, 126.9, 125.7, 124.8, 121.1, 113.6, 55.2, 44.8. MS: 302 (100, $M^+ + 1$), 284 (33.0, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{17}H_{20}NO_2S$ ($M^+ + 1$) 302.1215, found 302.1212.

General Procedure for the Heck Reaction of Sulfoxides 2: Synthesis of Trisubstituted Sulfoxides 3−6. A mixture of the α,β-unsaturated sulfoxide **2** (0.4 mmol), silver carbonate (0.8 mmol, 200 mol %), $Pd(OAc)_2$ (0.04 mmol, 10 mol %), dppf (0.04 mmol, 10 mol %), aryl iodide (1.2 mmol, 300 mol %), and DMF (8 mL) was heated at 100 °C under argon atmosphere. When the sulfoxide **2** disappeared by TLC (eluent hexanes−ethyl acetate = 1:1) the mixture was allowed to cool to room temperature, diluted with Et_2O (20 mL), filtered through Celite, washed with water (20 mL), dried ($MgSO_4$), and evaporated. The residue was analyzed by ^{1}H NMR to determine the *E*/*Z* ratio and was purified by flash chromatography (the reaction time, the *E*/*Z* ratio, the eluent for the silica gel chromatography, and the yield was indicated below for each case).

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-phenyl-1-heptene [(*E*)-3a]. Reaction time: 2 h. Eluent: hexanes−ethyl acetate = 5:2, yield: 75%. mp: 70−72 °C. ^{1}H NMR δ: 7.93 (dd, 1H, J = 1.7 and 7.7 Hz), 7.39 (dt, 1H, J = 1.7 and 7.6 Hz), 7.31−7.24 (m, 6H), 7.15 (dd, 1H, J = 1.3 and 7.8 Hz), 6.14 (s, 1H), 3.20−3.10 (m, 1H), 2.89−2.80 (m, 1H), 2.68 (s, 6H), 1.52−1.22 (m, 6H), 0.85 (bt, 3H, J = 7.1 Hz). ^{13}C NMR δ: 152.1, 151.3, 140.4, 139.2, 133.6, 131.3, 128.6, 128.4, 126.5, 125.3, 124.7, 120.8, 45.0, 31.7, 31.4, 28.3, 22.3, 13.9. Anal. Calcd for $C_{21}H_{27}NOS$: C, 73.86%; H, 7.97%; N, 4.10%; S, 9.39%. Found: C, 73.81%; H, 7.60%; N, 4.31%; S, 9.39%.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)-1-heptene [(*E*)-4a]. Reaction time: 3 h. *E*/*Z* ratio: 98/2. Eluent: hexanes−ethyl acetate = 4:1, yield: 70%. ^{1}H NMR δ: 7.95 (dd, 1H, J = 1.7 and 7.7 Hz), 7.40 (dt, 1H, J = 1.8 and 7.7 Hz), 7.33−7.27 (m, 1H), 7.29 (bd, 2H, J = 8.8 Hz), 7.17 (dd, 1H, J = 1.3 and 7.7 Hz), 6.83 (bd, 2H, J = 8.8 Hz), 6.13 (s, 1H), 3.77 (s, 3H), 3.18−3.08 (m, 1H), 2.90−2.80 (m, 1H), 2.68 (s, 6H), 1.53−1.25 (m, 6H), 0.88 (bt, 3H, J = 7.1 Hz). ^{13}C NMR δ: 160.1, 151.7, 151.4, 140.7, 132.1, 131.3, 129.6, 127.9, 125.3, 124.8, 120.8, 113.9, 55.3, 45.1, 31.8, 31.3, 28.6, 22.5, 14.0. Anal. Calcd for $C_{22}H_{29}NO_2S$: C, 71.12%; H, 7.87%; N, 3.77%; S, 8.63%. Found: C, 70.79%; H, 7.46%; N, 3.29%; S, 8.29%.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-nitrophenyl)-1-heptene [(*E*)-5a]. Reaction time: 91 h. Conversion rate: 67%. *E*/*Z* ratio: 95/5. Eluent: hexanes−ethyl acetate = 4:1, yield: 58%. ^{1}H NMR δ: 8.18 (bd, 2H, J = 8.9 Hz), 7.94 (dd, 1H, J = 1.6 and 7.7 Hz), 7.49−7.43 (m, 1H), 7.48 (bd, 2H, J = 8.9 Hz), 7.35 (dt, 1H, J = 1.3 and 7.7 Hz), 7.22 (dd, 1H, J = 1.2 and 7.9 Hz), 6.25 (s, 1H), 3.24−3.15 (m, 1H), 2.93−2.84 (m, 1H), 2.71 (s, 6H), 1.49−1.25 (m, 6H), 0.88 (bt, 3H, J = 7.3 Hz). ^{13}C NMR δ: 151.3, 149.7, 147.8, 145.8, 139.9, 136.7, 131.7, 127.6, 125.7, 124.9, 123.9, 121.0, 45.2, 31.6, 31.5, 28.2, 22.4, 13.9. MS: 387 (100, $M^+ + 1$), 369 (30.2, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{21}H_{27}N_2O_3S$ ($M^+ + 1$) 387.1742, found 387.1757.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-3-methyl-2-phenyl-1-butene [(*E*)-3b]. Reaction time: 4 h. *E*/*Z* ratio: >98/<2. Eluent: hexanes−ethyl acetate = 4:1, yield: 75%. ^{1}H NMR δ: 7.92 (dd, 1H, J = 1.6 and 8.1 Hz), 7.39 (dt, 1H, J = 1.6 and 7.7 Hz), 7.29−7.23 (m, 4H), 7.16 (dd, 1H, J = 1.2 and 7.7 Hz), 7.13−7.07 (m, 2H), 5.88 (s, 1H), 3.84−3.75 (m, 1H), 2.74 (s, 6H), 1.22 (d, 3H, J = 6.9 Hz), 1.14 (d, 3H, J = 6.9 Hz). ^{13}C NMR δ: 158.7, 151.3, 139.8, 138.7, 134.3, 131.4, 127.9, 127.8, 127.7, 125.0, 124.9, 120.3, 45.1, 31.6, 21.9, 21.3. MS: 314 (100, $M^+ + 1$), 296 (14.7, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{19}H_{24}NOS$ ($M^+ + 1$) 314.1579, found 314.1587.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)-3-methyl-1-butene [(*E*)-4b]. Reaction time: 4 h. *E*/*Z* ratio: >98/<2. Eluent: hexanes−ethyl acetate = 4:1, yield: 66%. ^{1}H NMR *δ*: 7.93 (dd, 1H, *J* = 1.6 and 7.7 Hz), 7.40 (dt, 1H, *J* = 1.6 and 7.7 Hz), 7.27 (dt, 1H, *J* = 1.2 and 7.7 Hz), 7.16 (dd, 1H, *J* = 1.2 and 8.1 Hz), 7.07 (bd, 2H, *J* = 8.9 Hz), 6.79 (bd, 2H, *J* = 8.9 Hz), 5.87 (s, 1H), 3.83−3.74 (m, 1H), 3.76 (s, 3H), 2.73 (s, 6H), 1.24 (d, 3H, *J* = 6.9 Hz), 1.16 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR *δ*: 159.1, 158.3, 151.2, 139.8, 133.8, 131.3, 131.0, 129.0, 124.9, 124.7, 120.2, 113.1, 55.1, 45.0, 31.6, 21.9, 21.3. MS: 344 (100, $M^+ + 1$), 326 (33.2, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{20}H_{26}NO_2S$ ($M^+ + 1$) 344.1684, found 344.1681.

(*E*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)-2-phenylethene [(*E*)-6]. From (*E*)-**2c**: reaction time: 24 h, conversion rate: 85%. *E*/*Z* ratio: 97/3, yield: 51%. From (*Z*)-**2d**: reaction time: 3.5 h, conversion rate: 100%. *E*/*Z* ratio: 93/7, yield: 74%. Eluent: hexanes−ethyl acetate = 4:1. ^{1}H NMR *δ*: 7.99 (dd, 1H, *J* = 1.6 and 7.7 Hz), 7.51−7.38 (m, 6H), 7.27 (dt, 1H, *J* = 1.2 and 7.7 Hz), 7.14 (bd, 2H, *J* = 8.9 Hz), 7.10 (dd, 1H, *J* = 1.2 and 8.1 Hz), 6.78 (bd, 2H, *J* = 8.9 Hz), 6.46 (s, 1H), 3.76 (s, 3H), 2.50 (s, 6H). ^{13}C NMR *δ*: 160.6, 151.6, 151.2, 139.8, 137.5, 132.0, 131.5, 131.4, 130.2, 129.7, 128.7, 127.9, 124.8, 124.3, 119.8, 113.7, 55.2, 44.5. MS: 378 (100, $M^+ + 1$), 360 (27.5, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{23}H_{24}NO_2S$ ($M^+ + 1$) 378.1528, found 378.1538.

(*Z*)-1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)-2-phenylethene [(*Z*)-6]. From (*Z*)-**2c**: reaction time: 3.5 h, conversion rate: 100%. *Z*/*E* ratio: 94/6, yield: 68%. From (*E*)-**2d**: reaction time: 24 h, conversion rate: 95%. *Z*/*E* ratio: 97/3, yield: 63%. Eluent: hexanes−ethyl acetate = 4:1. ^{1}H NMR *δ*: 8.00 (bd, 1H, *J* = 7.7 Hz), 7.46 (bd, 2H, *J* = 8.5 Hz), 7.45−7.40 (m, 1H), 7.32−7.20 (m, 6H), 7.13 (bd, 1H, *J* = 7.3 Hz), 6.97 (bd, 2H, *J* = 8.5 Hz), 6.45 (s, 1H), 3.87 (s, 3H), 2.56 (s, 6H). ^{13}C NMR *δ*: 160.1, 151.9, 151.2, 140.3, 139.8, 132.7, 131.7, 131.4, 129.8, 129.2, 128.5, 128.3, 124.9, 124.4, 120.0, 113.4, 55.3, 44.6. MS: 378 (100, $M^+ + 1$), 360 (29.4, $M^+ + 1 - 18$). HRMS: exact mass calcd for $C_{23}H_{24}NO_2S$ ($M^+ + 1$) 378.1528, found 378.1518.

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Supporting Information Available: ^{13}C NMR spectra of all new compounds and NOESY spectra of (*E*)-**6** and (*Z*)-**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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