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Rauhut–Currier Reaction of Nitroalkenes with Vinyl Sulfones

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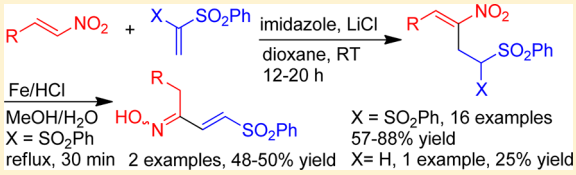
Supporting Information

ABSTRACT: The Rauhut–Currier reaction between nitroalkenes and vinyl sulfones has been successfully carried out for the first time. The reaction proceeds in the presence of an imidazole/LiCl catalyst system in dioxane to provide the adducts possessing a synthetically useful 1-bis-sulfonyl-3-nitroalkene moiety in good to excellent yield. A one-pot transformation of the products to β-sulfonyl-α,β-unsaturated ketoximes has also been demonstrated.



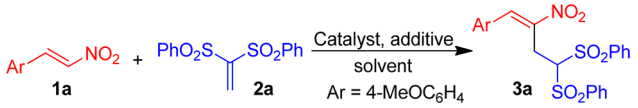
The Morita–Baylis–Hillman (MBH) reaction has emerged as an efficient method for α-functionalization of activated alkenes with various electrophiles such as aldehydes, imines, etc. in the presence of an amine or phosphine catalyst.[1] However, dimerization of the substrate in the absence of an electrophile was reported by Rauhut and Currier,[2] prior to the MBH reaction, but was overshadowed by the enormous scope and applicability of the latter. Nevertheless, the Rauhut–Currier (RC) dimerizations of activated alkenes such as acrylonitrile,[3,4] vinyl ketones,[5,6] acrylates,[4,6] and vinyl sulfone and vinyl sulfonate[6] have been reported. The scope of the reaction was further expanded by cross-coupling of different activated alkenes[7] and by developing intramolecular and asymmetric versions.[8] Applications of the RC reaction as the key step in natural product synthesis have also been investigated.[9]

In recent years, nitroalkenes have been employed as substrates in the MBH[10] and the RC[11−14] reactions.[15] The RC cross-coupling of nitroalkenes with azodicarboxylates,[11] methyl vinyl ketone,[12,13] and acrylate[12,14] afforded synthetically useful multifunctional adducts.[15] The RC dimerization of nitroalkenes and nitrodienes proceeded in low to moderate yield in the presence of imidazole and hydroquinone.[13] However, the RC cross-coupling of nitroalkenes with vinyl sulfones remained unreported hitherto.

From another perspective, organosulfones exhibit a variety of biological properties, for instance, the antiprostate cancer drug Bicalutamide and the antileprosy drug Dapsone contain a sulfonyl group. Although similar biological and synthetic applications of sulfones have been extensively investigated,[16] the reactivity of vinyl bis-sulfones, in particular, as Michael acceptors has not received sufficient attention.[17] Herein, we report a high-yielding RC coupling of nitroalkenes and nitrodienes with vinyl bis-sulfones in the presence of an imidazole/LiCl catalyst system.

Initially, we screened the classical MBH catalyst DABCO for the model reaction of nitroalkene **1a** with sulfone **2a**, which led to no conversion even after 48 h (Table 1, entry 1). While DMAP in CH_3CN gave the product **3a** in 20% yield (entry 2) after 24 h, imidazole-catalyzed reactions in different solvents were much superior, and the product **3a** was isolated in much higher yield (33–58%) in shorter reaction time (14–24 h, entries 3–7). Finally, we explored the possibility of using LiCl as a salting out agent and a weak Lewis acid.[12] This improved the yields only marginally (60–63%) in solvents such as THF and EtOAc (12–13 h, entries 8 and 9). However, complete conversion in 12 h with remarkable increase in the yield (88%) was observed when dioxane was used as the solvent (entry 10). Imidazole and LiCl in stoichiometric amounts were necessary to obtain the best yield in the shortest possible time (entry 10). While lowering the quantity of LiCl led to a drop in the yield,

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst (equiv)	additive (equiv)	solvent	time (h)	% yield[b]
1	DABCO (1)		THF	48	*c*
2	DMAP (1)		CH_3CN	24	20[d]
3	imidazole (1)		THF	16	44[d]
4	imidazole (1)		ether	15	33[d]
5	imidazole (1)		acetone	15	35[d]
6	imidazole (1)		EtOAc	14	58
7	imidazole (1)		dioxane	14	50
8	imidazole (1)	LiCl (1)	THF	12	60
9	imidazole (1)	LiCl (1)	EtOAc	13	63
10	**imidazole (1)**	**LiCl (1)**	**dioxane**	**12**	**88**
11	imidazole (1)	LiCl (0.5)	dioxane	12	81
12	imidazole (0.5)	LiCl (1)	dioxane	24	83

[a]**1a** and **2a** were used in 2:1 ratio. [b]Isolated yield after purification by silica gel chromatography. [c]No reaction. [d]Substantial quantity of **1a** was recovered and **2a** polymerized.

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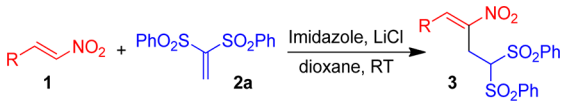
though marginal (81%, entry 11), a decrease in reaction rate with marginal decrease in the yield was observed upon lowering the quantity of imidazole (24 h, 83%, entry 12). It appears that the solvation of LiCl is minimized as the dielectric constant of the solvent decreases (ε: THF 7.52, EtOAc 6.08, dioxane 2.22) resulting in substantial improvement in the yield (entries 8–10).

The above optimized conditions were employed to investigate the scope of the reaction by screening different nitroalkenes **1** (Table 2). Thus nitroalkenes **1a–e** with

Table 2. Scope of the Reaction[a]



entry	R	3	time (h)	% yield[b]
1	4-OMeC$_6$H$_4$	**3a**	12	88
2	3,4-(OMe)$_2$C$_6$H$_3$	**3b**	13	85
3	benzo[*d*][1,3]dioxole	**3c**	15	82
4	4-NMe$_2$C$_6$H$_4$	**3d**	12	72
5	4-MeC$_6$H$_4$	**3e**	14	78
6	C$_6$H$_5$	**3f**	14	68
7	3-BrC$_6$H$_4$	**3g**	18	60
8	2-ClC$_6$H$_4$	**3h**	20	57
9	4-FC$_6$H$_4$	**3i**	12	72
10	4-NO$_2$C$_6$H$_4$	**3j**	18	61
11	2-furyl	**3k**	13	80
12	2-thienyl	**3l**	13	86
13	C$_6$H$_5$CH=CH	**3m**	15	75
14	2-NO$_2$C$_6$H$_4$CH=CH	**3n**	17	83
15	cyclohexyl	**3o**	15	61
16	CH$_3$(CH$_2$)$_3$	**3p**	15	62

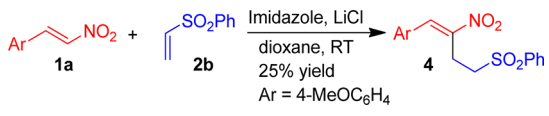
[a]Carried out at 0.5 mmol scale of sulfone **2a** with 2 equiv of nitroalkene **1** and 1 equiv each of imidazole and LiCl. [b]Isolated yield after purification by silica gel chromatography.

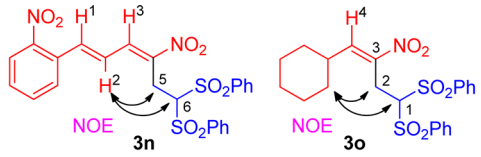
electron-donating substituents on the aromatic ring provided the RC adducts **3a–e** in high yield (72–88%, entries 1–5). The yields were lower (60–72%) with nitrostyrene **1f** and nitroalkenes **1g–j** possessing weakly and strongly deactivating substituents on the aromatic ring (entries 6–10). The RC adducts **3k–l** were isolated in excellent yield (80–86%) when heteroaromatic nitroalkenes **1k–l** were reacted with sulfone **2a** (entries 11 and 12). While the yields of RC adducts **3m–n** were high (75–83%) with nitrodienes **1m–n** (entries 13 and 14), aliphatic nitroalkenes **1o–p** afforded the products **3o–p** in lower yield (61–62%, entries 15 and 16).

Under the above conditions, the reaction of a representative nitroalkene **1a** with vinyl sulfone **2b** afforded the desired product **4** in only low yield (25%, Scheme 1).

The structure and stereochemistry of RC adducts **3** were established by extensive NMR analysis (Figure 1). Appearance of the ^{1}H β to the nitro group in the RC adducts **3a–l** and **4** in the range of 7.90–8.30 confirmed that the geometry of the double bond is *E*. The *E*,*E* geometry in the RC adducts **3m–n**

Scheme 1





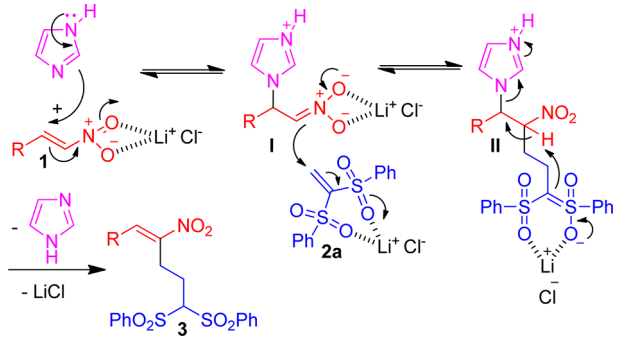
H2: δ 7.19 (dd, *J* = 15.1, 11.7 Hz) H4: δ 7.13 (d, *J* = 7.0 Hz)

Figure 1. Structure and stereochemical assignment of **3** by NMR.

was evident from the ^{1}H–^{1}H NOESY spectrum of **3n**. First of all, the three olefinic protons in **3n** were assigned by ^{1}H–^{1}H COSY experiment. While H2 appeared as a dd at δ 7.19, H1 overlapped with aromatic protons in the range δ 7.67–7.75, and H3, the ^{1}H β to the nitro group, overlapped with aromatic protons in the range δ 7.82–7.89. Since H1 and H3 are very close in terms of chemical shifts and the corresponding signals overlap with the aromatic protons, their NOE cross peaks are not very diagnostic. However, the presence of strong NOE for H2 with H5 and H6 and a *J* value of 15.1 and 11.7 Hz for H2 supported the above assignment. The double bond geometry in RC adducts **3o–p** was also determined by ^{1}H–^{1}H NOESY analysis. The absence of any NOE for H4 with H2 or H1 together with the presence of medium NOE for cyclohexyl protons with H2 and H1 confirmed the *E* geometry in **3o**. This assignment was unambiguously established by single crystal X-ray analysis of a representative compound **3n** (see the Experimental Section and the Supporting Information).

The proposed role of imidazole and LiCl in mediating the RC reaction of nitroalkenes **1** with vinyl sulfone **2a** is outlined in Scheme 2. The initial conjugate addition of imidazole, a

Scheme 2. Proposed Mechanism for the Imidazole/LiCl Mediated Rauhut–Currier Reaction



nucleophilic Lewis base, is facilitated and the reversibility of the reaction is minimized by co-ordination of the nitro group with LiCl, a weak Lewis acid. This stabilized nitronate **I** then adds in a Michael fashion to vinyl sulfone **2a** which is also activated by LiCl to generate intermediate **II**. The β-elimination of imidazole from **II**, triggered by the γ-hydrogen abstraction by the alkanesulfonyl group, completes the reaction to deliver the RC adduct **3**.

Having developed an efficient method for the coupling of nitroalkenes **1** with vinyl sulfones **2** under the RC conditions, we sought to investigate the possible applications of the RC adducts **3**. Thus, representative RC adducts **3e** and **3i** were subjected to metal/acid reduction under standard conditions (Scheme 3). Much to our amusement, the nitro group reduction stopped at the oxime stage, and elimination of one of the sulfonyl groups took place, all in one pot, to afford β-sulfonyl α,β-unsaturated oximes **5e** and **5i** in satisfactory yield

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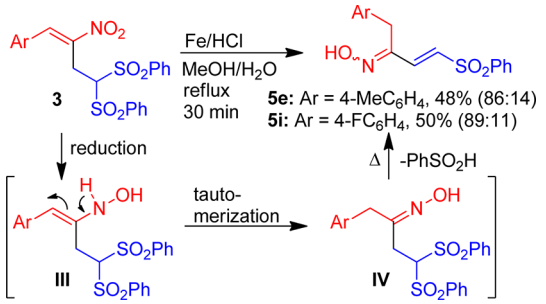
Scheme 3



(48−50%) as an inseparable mixture of *syn*/*anti* or *anti*/*syn* isomers in 86:14 to 89:11 ratio. The plausible mechanism for the transformation of the RC adduct **3** to oxime **5** involves formation of hydroxylamine **III**, its tautomerization to oxime **IV**, and elimination of benzenesulfinic acid from **IV**. The *J* values for the olefinic protons in *anti* and *syn* isomers were in the same range (15.5−15.9), as expected, indicating *E* geometry for the double bond in **5**, which was further confirmed by NOE experiment. A moderate NOE between CH_2 and the proton *β* to the oxime group confirmed this assignment.

In conclusion, cross-coupling of nitroalkenes with vinyl sulfone has been carried out for the first time under the Rauhut−Currier conditions to afford the adducts in good to excellent yield in most cases. While vinyl bis-sulfones are good coupling partners, vinyl monosulfones were less efficient. A one-pot nitro group reduction−sulfone elimination under metal-acid conditions delivered synthetically useful *β*-sulfonyl *α*,*β*-unsaturated oximes in satisfactory yield and >85:15 *anti*/*syn* selectivity.

EXPERIMENTAL SECTION

General. The melting points recorded are uncorrected. NMR spectra (^{1}H, ^{1}H decoupled ^{13}C, ^{13}C-APT, ^{1}H−^{1}H COSY, and ^{1}H−^{1}H NOESY) were recorded with TMS as the internal standard. The coupling constants (*J* values) are given in hertz. High resolution mass spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo K*α* radiation. The structure was solved by direct methods shelxs97 and refined by full-matrix least-squares against F^2 using shelxl97 software.

General Procedure for the Rauhut−Currier Reaction. To a stirred solution of nitroalkene **1** (1 mmol) and vinyl sulfone **2** (0.5 mmol) in dioxane (5 mL) were added imidazole (34 mg, 0.5 mmol) and LiCl (21 mg, 0.5 mmol), and the resulting mixture was stirred until the completion of the reaction (monitored by TLC). Then the reaction mixture was concentrated in vacuo, and the crude residue was directly subjected to silica gel column chromatography (60−120 mesh, *n*-hexane/ethyl acetate, 40:60) to afford pure products **3**.

1-((*E*)-4-(4-Methoxyphenyl)-3-nitro-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3a). Yellow solid; yield 88% (214 mg); mp 158−160 °C; IR (KBr, cm^{-1}) 3209 (w), 2923 (w), 1644 (m), 1603 (s), 1520 (s), 1448 (m), 1334 (s), 1309 (s), 1262 (s), 1177 (s), 1156 (s), 1079 (m), 736 (s); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.84 (d, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 5.18 (t, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.49−7.53 (m, 4H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.66−7.70 (m, 2H), 7.80−7.82 (m, 4H), 8.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 24.46, 55.66, 79.10, 115.02, 123.33, 129.36, 129.41, 132.70, 134.95, 137.78, 138.02, 142.77, 162.02; MS (ES+, Ar) *m*/*z* (rel intensity) 510 (MNa^+, 31), 505 (29), 489 ([MH + 1]$^+$, 7), 488 (MH^+, 31), 444 (13), 443 (24), 442 (100); HRMS (ES+, Ar) calcd for $C_{23}H_{22}NO_7S_2$ (MH^+) 488.0838, found 488.0827.

1-((*E*)-4-(3,4-Dimethoxyphenyl)-3-nitro-1-(phenylsulfonyl)-but-3-enylsulfonyl)benzene (3b). Yellow solid; yield 85% (220 mg); mp 176−178 °C; IR (KBr, cm^{-1}) 3225 (w), 2923 (w), 1645 (m), 1556 (w), 1520 (s), 1448 (m), 1331 (m), 1314 (m), 1268 (s), 1245 (m), 1148 (s), 1079 (w), 1021 (m), 737 (m); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.85 (d, *J* = 7.4 Hz, 2H), 3.94 (s, 3H), 3.95 (s, 3H), 5.25 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.36 (d, *J* = 1.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 4H), 7.68 (t, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 4H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 24.93, 56.19, 56.52, 78.95, 111.41, 112.41, 123.66, 125.69, 129.38 (×2), 134.97, 137.93, 138.47, 142.75, 149.65, 151.82; MS (ES +, Ar) *m*/*z* (rel intensity) 540 (MNa^+, 100), 519 ([M + 2]$^+$, 20), 518 (M^+, 50); HRMS (ES+, Ar) calcd for $C_{24}H_{24}NO_8S_2$ (MH^+) 518.0943, found 518.0942.

(*E*)-5-(2-Nitro-4,4-bis(phenylsulfonyl)but-1-enyl)benzo[*d*]-[1,3]dioxole (3c). Yellow solid; yield 82% (205 mg); mp 184−186 °C; IR (KBr, cm^{-1}) 3231 (w), 3066 (w), 2918 (w), 1643 (vs), 1504 (w), 1487 (w), 1449 (m), 1334 (s), 1311 (m), 1262 (m), 1157 (m), 1037 (m), 741 (m); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.81 (d, *J* = 7.3 Hz, 2H), 5.17 (t, *J* = 7.3 Hz, 1H), 6.08 (s, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 7.08−7.11 (m, 2H), 7.50−7.54 (m, 4H), 7.68 (tt, *J* = 6.4, 1.1 Hz, 2H), 7.82 (dd, *J* = 8.4, 1.1 Hz, 4H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 24.49, 79.20, 102.18, 109.33, 109.82, 124.96, 126.72, 129.41, 129.51, 135.02, 137.81, 138.08, 143.42, 148.80, 150.35; MS (ES+, Ar) *m*/*z* (rel intensity) 524 (MNa^+, 40), 503 ([M + 2]$^+$, 9), 502 (MH^+, 35), 496 (56), 480 (38), 458 (93), 456 (100); HRMS (ES+, Ar) calcd for $C_{23}H_{20}NO_8S_2$ (MH^+) 502.0630, found 502.0639.

(*E*)-*N*,*N*-Dimethyl-4-(2-nitro-4,4-bis(phenylsulfonyl)but-1-enyl)aniline (3d). Yellow solid; yield 72% (180 mg); mp 190−192 °C; IR (KBr, cm^{-1}) 3065 (w), 2925 (w), 1668 (w), 1598 (s), 1531 (w), 1448 (w), 1332 (s), 1311 (s), 1292 (m), 1159 (vs), 1078 (m), 749 (m), 732 (m); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.10 (s, 6H), 3.91 (d, *J* = 7.2 Hz, 2H), 5.27 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 4H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.82−7.84 (m, 4H), 8.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 24.98, 40.21, 79.11, 112.20, 117.88, 129.34, 129.41, 133.83, 134.83, 138.37, 138.80, 139.62, 152.51; MS (ES+, Ar) *m*/*z* (rel intensity) 523 (MNa^+, 15), 502 ([MH + 1]$^+$, 24), 501 (MH^+, 80), 444 (22), 379 (33), 363 (100), 341 (52); HRMS (ES+, Ar) calcd for $C_{24}H_{25}N_2O_6S_2$ (MH^+) 501.1154, found 501.1169.

1-((*E*)-3-Nitro-1-(phenylsulfonyl)-4-*p*-tolylbut-3-enylsulfonyl)benzene (3e). Yellow solid; yield 78% (184 mg); mp 156−158 °C; IR (KBr, cm^{-1}) 3225 (w), 3055 (w), 1650 (vs), 1604 (s), 1517 (w), 1505 (w), 1443 (w), 1328 (s), 1310 (vs), 1279 (m), 1156 (m), 1080 (w), 742 (m); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.44 (s, 3H), 3.81 (d, *J* = 7.2 Hz, 2H), 5.14 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.47−7.51 (m, 4H), 7.65−7.69 (m, 2H), 7.78 (dd, *J* = 8.4, 1.1 Hz, 4H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.72, 24.26, 79.23, 128.31, 129.34, 129.47, 130.21, 130.34, 134.95, 137.65, 138.09, 141.69, 144.33; MS (ES+, Ar) *m*/*z* (rel intensity) 494 (MNa^+, 10), 489 (16), 474 ([MH + 2]$^+$, 13), 473 ([MH + 1]$^+$, 29), 472 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{23}H_{22}NO_6S_2$ (MH^+) 472.0889, found 472.0887.

1-((*E*)-3-Nitro-4-phenyl-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3f). Yellow solid; yield 68% (156 mg); mp 174−176 °C; IR (KBr, cm^{-1}) 3065 (w), 2930 (w), 1648 (m), 1558 (m), 1525 (s), 1448 (m), 1333 (vs), 1264 (m), 1157 (vs), 1079 (m), 737 (s); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.78 (d, *J* = 7.2 Hz, 2H), 5.13 (t, *J* = 7.2 Hz, 1H), 7.47−7.54 (m, 9H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.77 (dd, *J* = 8.4, 1.1 Hz, 4H), 8.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 24.21, 79.32, 129.38, 129.49, 129.53, 130.08, 130.84, 131.32, 135.00, 137.55, 137.86, 145.32; MS (ES+, Ar) *m*/*z* (rel intensity) 480 (MNa^+, 7), 475 (12), 460 ([MH + 2]$^+$, 14), 459 ([MH + 1]$^+$, 29), 458 (MH^+, 100); HRMS (ES+, Ar) calcd for $C_{22}H_{20}NO_6S_2$ (MH^+) 458.0732, found 458.0746.

1-(*E*)-4-(3-Bromophenyl)-3-nitro-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3g). Yellow solid; yield 60% (161 mg); mp 122−124 °C; IR (KBr, cm^{-1}) 3065 (w), 2927 (w), 1653 (m), 1525 (s), 1448 (m), 1334 (vs), 1287 (m), 1156 (s), 1078 (s), 737 (s), 685 (s); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.72 (d, *J* = 7.2 Hz, 2H), 5.12 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.48−7.52 (m, 5H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 0.8 Hz, 1H), 7.67 (td, *J* = 8.3, 0.8, 2H),

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7.77 (dd, J = 8.3, 0.8 Hz, 4H), 8.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.22, 79.22, 123.33, 128.14, 129.41, 129.47, 130.94, 132.66, 133.33, 133.57, 135.08, 136.10, 137.39, 146.36; MS (ES+, Ar) m/z (rel intensity) 538 ([MH + 2]$^+$, 23), 537 ([MH + 1]$^+$, 100), 536 (MH$^+$, 65); HRMS (ES+, Ar) calcd for $C_{22}H_{19}NO_6S_2Br$ (MH$^+$) 535.9837, found 535.9855.

1-((*E*)-4-(2-Chlorophenyl)-3-nitro-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3h). Yellow liquid; yield 57% (140 mg); IR (neat, cm^{-1}) 3063 (w), 2929 (w), 1657 (m), 1559 (w), 1528 (s), 1473 (w), 1447 (w), 1340 (vs), 1266 (w), 1157 (s), 1078 (m), 753 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (d, J = 7.3 Hz, 2H), 5.14 (t, J = 7.3 Hz, 1H), 7.49−7.55 (m, 4H), 7.66−7.75 (m, 4H), 7.75−7.80 (m, 4H), 8.30 (s, 1H), 8.31 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.13, 79.30, 127.59, 129.36, 129.42, 129.51, 129.71, 130.19, 130.25, 131.64, 134.85, 134.99, 137.43, 146.83; MS (ES+, Ar) m/z (rel intensity) 494 ([MH + 2]$^+$, 40), 493 ([MH + 1]$^+$, 25), 492 (MH$^+$, 100), 297 (17); HRMS (ES+, Ar) calcd for $C_{22}H_{19}NO_6S_2Cl$ 492.0342, found 492.0337.

1-((*E*)-4-(4-Fluorophenyl)-3-nitro-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3i). Yellow solid; yield 72% (171 mg); mp 116−118 °C; IR (KBr, cm^{-1}) 3056 (m), 2987 (w), 1655 (w), 1603 (w), 1564 (w), 1527 (m), 1510 (m), 1422 (w), 1336 (m), 1266 (s), 1161 (m), 745 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (d, J = 7.3 Hz, 2H), 5.16 (t, J = 7.3 Hz, 1H), 7.16 (t, J = 8.6 Hz, 2H), 7.50 (t, J = 7.7 Hz, 4H), 7.56 (dd, J = 8.6, 5.3 Hz, 2H), 7.67 (t, J = 7.7 Hz, 2H), 7.78 (dd, J = 7.7, 0.8 Hz, 4H), 8.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.27, 79.06, 116.73 (d, J_{C-F} = 22.0 Hz), 127.37 (d, J_{C-F} = 5.0 Hz), 129.41 (d, J_{C-F} = 2.0 Hz), 132.40 (d, J_{C-F} = 8.0 Hz), 135.04, 136.82, 137.54, 145.01, 162.72, 165.24; MS (ES+, Ar) m/z (rel intensity) 476 (MH$^+$, 100); HRMS (ES+, Ar) calcd for $C_{22}H_{19}NO_6S_2F$ 476.0638, found 476.0627.

1-((*E*)-3-Nitro-4-(4-nitrophenyl)-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3j). Yellow solid; yield 61% (153 mg); mp 158−160 °C; IR (KBr, cm^{-1}) 3066 (w), 2926 (w), 1657 (w), 1525 (s), 1448 (w), 1345 (vs), 1264 (w), 1157 (m), 1079 (w), 749 (m), 737 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (d, J = 7.5 Hz, 2H), 5.14 (t, J = 7.5 Hz, 1H), 7.49−7.53 (m, 4H), 7.67−7.73 (m, 3H), 7.76−7.78 (m, 4H), 8.21 (s, 1H), 8.31 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.41, 78.96, 124.45, 129.46, 129.52, 130.63, 135.22, 135.24, 137.43, 137.84, 147.77, 148.62; MS (ES+, Ar) m/z (rel intensity) 526 (MNa$^+$, 8), 525 (29), 520 (38), 505 ([MH + 1]$^+$, 16), 504 (MH$^+$, 32), 503 (M$^+$, 100), 297 (17); HRMS (ES+, Ar) calcd for $C_{22}H_{19}N_2O_8S_2Na$ 526.0481, found 526.0459.

(*E*)-2-(2-Nitro-4,4-bis(phenylsulfonyl)but-1-enyl)furan (3k). Yellow solid; yield 80% (179 mg); mp 126−128 °C; IR (KBr, cm^{-1}) 3152 (w), 3064 (m), 2927 (w), 1648 (s), 1560 (m), 1513 (s), 1448 (w), 1314 (vs), 1158 (vs), 1080 (m), 1024 (m), 928 (m), 753 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (d, J = 7.3 Hz, 2H), 5.18 (t, J = 7.3 Hz, 1H), 6.58 (dd, J = 3.5, 1.8 Hz, 1H), 6.96 (d, J = 3.5 Hz, 1H), 7.50−7.55 (m, 5H), 7.67 (t, J = 7.5 Hz, 2H), 7.86−7.87 (m, 4H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.70, 80.17, 113.48, 122.64, 123.79, 129.31, 129.50, 134.87, 138.01, 141.01, 146.82, 147.73; MS (ES+, Ar) m/z (rel intensity) 449 ([MH + 1]$^+$, 32), 448 (MH$^+$, 100), 447 (12), 402 (44), 398 (16); HRMS (ES+, Ar) calcd for $C_{20}H_{18}NO_7S_2$ (MH$^+$) 448.0525, found 448.0533.

(*E*)-2-(2-Nitro-4,4-bis(phenylsulfonyl)but-1-enyl)thiophene (3l). Yellow solid; yield 86% (200 mg); mp 134−136 °C; IR (KBr, cm^{-1}) 3225 (w), 3060 (w), 2944 (w), 1642 (s), 1583 (w), 1503 (m), 1495 (m), 1449 (w), 1402 (w), 1325 (s), 1303 (vs), 1154 (s), 1082 (m), 732 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (d, J = 7.3 Hz, 2H), 5.27 (t, J = 7.3 Hz, 1H), 7.19 (dd, J = 5.0, 3.7 Hz, 1H), 7.52 (td, J = 8.1, 1.0 Hz, 4H), 7.57 (d, J = 3.7 Hz, 1H), 7.66−7.70 (m, 3H), 7.86 (dd, J = 8.1, 1.0 Hz, 4H), 8.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.26, 79.10, 128.65, 129.20, 129.39, 131.26, 133.62, 133.69, 134.97, 136.62, 137.87, 141.12; MS (ES+, Ar) m/z (rel intensity) 466 ([MH + 2]$^+$, 18), 465 ([MH + 1]$^+$, 26), 464 (MH$^+$, 100), 418 (22); HRMS (ES+, Ar) calcd for $C_{20}H_{18}NO_6S_3$ (MH$^+$) 464.0296, found 464.0285.

1-((1*E*,3*E*)-4-Nitro-6,6-bis(phenylsulfonyl)hexa-1,3-dienyl)benzene (3m). Yellow solid; yield 75% (181 mg); mp 206−208 °C; IR (KBr, cm^{-1}) 3055 (w), 2923 (w), 1629 (vs), 1496 (m), 1445 (w), 1328 (s), 1306 (s), 1163 (s), 1148 (vs), 1079 (m), 754 (s), 733 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (d, J = 6.9 Hz, 2H), 5.12 (t, J = 6.9 Hz, 1H), 7.18 (ABq, J = 15.2 Hz, 2H), 7.40−7.45 (m, 3H), 7.52−7.56 (m, 4H), 7.57−7.60 (m, 2H), 7.69 (tt, J = 6.9, 1.1 Hz, 2H), 7.84 (dd, J = 8.5, 2.5 Hz, 1H), 7.87 (dd, J = 8.4, 1.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.17, 79.48, 121.21, 128.37, 129.25, 129.37, 129.47, 130.78, 135.02, 135.49, 138.13, 138.90, 142.59, 147.45; MS (ES+, Ar) m/z (rel intensity) 486 ([MH + 2]$^+$, 13), 485 ([MH + 1]$^+$, 27), 484 (MH$^+$, 100), 296 (15); HRMS (ES+, Ar) calcd for $C_{24}H_{22}NO_6S_2$ (MH$^+$) 484.0889, found 484.0874.

1-Nitro-2-((1*E*,3*E*)-4-nitro-6,6-bis(phenylsulfonyl)hexa-1,3-dienyl)benzene (3n). Yellow solid; yield 83% (219 mg); mp 120−122 °C; IR (KBr, cm^{-1}) 3155 (m), 2988 (m), 1727 (w), 1618 (w), 1528 (s), 1446 (m), 1350 (s), 1244 (s), 1023 (vs), 982 (s), 785 (m), 737 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (d, J = 6.9 Hz, 2H), 5.10 (t, J = 6.9 Hz, 1H), 7.19 (dd, J = 15.1, 11.7 Hz, 1H), 7.52−7.58 (m, 5H), 7.67−7.75 (m, 4H), 7.82−7.89 (m, 6H), 8.06 (dd, J = 8.2, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.25, 79.23, 125.23, 125.99, 129.27, 129.57, 129.90, 130.53, 131.33, 134.04, 135.12, 137.72, 138.19, 141.25, 144.45, 148.17; MS (ES+, Ar) m/z (rel intensity) 531 ([MH + 2]$^+$, 15), 530 ([MH + 1]$^+$, 28), 529 (MH$^+$, 100); HRMS (ES+, Ar) calcd for $C_{24}H_{21}N_2O_8S_2$ (MH$^+$) 529.0739, found 529.0765; $C_{52}H_{48}N_4O_{18}S_4$, M = 1145.18, Orthorhombic, space group $Pna21$, a = 13.2930 (3) Å, b = 11.5155 (3) Å, c = 34.5292 (9) Å, α = 90°, β = 90°, γ = 90°, V = 5285.6 (2) Å^3, D_c = 1.439 Mg/m^3, Z = 4, F(000) = 2384, λ = 0.71073 Å, μ = 0.259 mm^{-1}, total/unique reflections = 46996/9252 [R(int) = 0.0497], T = 150(2) K, θ range = 3.12−24.98°, final R [$I > 2\sigma(I)$]: R1= 0.0486, wR2 = 0.1185; R (all data): R1 = 0.0576, wR2 = 0.1270 (two molecules in the unit cell + EtOAc). Confirmed by ^{1}H−^{1}H COSY and NOESY experiments as well as single crystal X-ray analysis.

1-((*E*)-4-Cyclohexyl-3-nitro-1-(phenylsulfonyl)but-3-enylsulfonyl)benzene (3o). White solid; yield 61% (141 mg); mp 122−124 °C; IR (KBr, cm^{-1}) 2923 (m), 2846 (w), 1645 (vs), 1509 (m), 1446 (w), 1315 (vs), 1149 (s), 738 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15−1.28 (m, 3H), 1.32−1.42 (m, 2H), 1.70−1.78 (m, 5H), 2.57 (qt, J = 10.9, 3.8 Hz, 1H), 3.50 (d, J = 7.0 Hz, 2H), 5.04 (t, J = 7.0 Hz, 1H), 7.13 (d, J = 7.0 Hz, 1H), 7.52 (td, J = 7.9, 1.1 Hz, 4H), 7.67 (tt, J = 7.9, 1.1 Hz, 2H), 7.82 (dd, J = 7.9, 1.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.62, 25.07, 25.67, 31.56, 38.17, 79.51, 129.33, 129.44, 134.93, 138.10, 143.62, 146.87; MS (ES+, Ar) m/z (rel intensity) 466 ([MH + 2]$^+$, 16), 465 ([MH + 1]$^+$, 30), 464 (MH$^+$, 100); HRMS (ES+, Ar) calcd for $C_{22}H_{26}NO_6S_2$ (MH$^+$) 464.1202, found 464.1182. Confirmed by ^{1}H−^{1}H COSY and NOESY experiments.

1-((*Z*)-3-Nitro-1-(phenylsulfonyl)oct-3-enylsulfonyl)benzene (3p). White solid; yield 62% (135 mg); mp 102−104 °C; IR (KBr, cm^{-1}) 3066 (w), 2959 (m), 2934 (m), 1657 (m), 1657 (s), 1646 (s), 1520 (s), 1448 (m), 1334 (vs), 1311 (s), 1157 (vs), 1079 (m), 737 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (t, J = 7.4 Hz, 3H), 1.39 (sextet, J = 7.4 Hz, 2H), 1.51 (q, J = 7.4 Hz, 2H), 2.43 (q, J = 7.4 Hz, 2H), 3.49 (d, J = 7.0 Hz, 2H), 5.03 (t, J = 7.0 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 4H), 7.68 (t, J = 7.6 Hz, 2H), 7.81−7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94, 22.62, 23.62, 28.59, 30.31, 79.26, 129.32, 129.44, 134.96, 138.06, 143.16, 144.87; MS (ES+, Ar) m/z (rel intensity) 440 ([MH + 2]$^+$, 15), 439 ([MH + 1]$^+$, 27), 438 (MH$^+$, 100), 420 (15), 278 (54); HRMS (ES+, Ar) calcd for $C_{20}H_{24}NO_6S_2$ (MH$^+$) 438.1045, found 438.1049.

(*E*)-1-Methoxy-4-(2-nitro-4-(phenylsulfonyl)but-1-enyl)-benzene (4a). Yellow solid; yield 25% (44 mg); mp 116−118 °C; IR (KBr, cm^{-1}) 3060 (w), 2934 (w), 1645 (w), 1603 (s), 1519 (s), 1506 (s), 1446 (m), 1317 (m), 1262 (m), 1179 (s), 1143 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28−3.31 (m, 2H), 3.43−3.47 (m, 2H), 3.87 (s, 3H), 6.95 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.61 (td, J = 7.6, 1.4 Hz, 2H), 7.71 (tt, J = 7.6, 1.4 Hz, 1H), 7.94−7.96 (m, 2H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.00, 53.30, 55.71, 115.17, 123.40, 128.35, 129.73, 132.57, 134.34, 136.63, 138.55, 144.65, 162.15; MS (ES+, Ar) m/z (rel intensity) 370 (MNa$^+$, 100); HRMS (ES+, Ar) calcd for $C_{17}H_{18}NO_5SNa$ 371.0803, found 371.0800.

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One-Pot Metal/Acid Reduction−Sulfone Elimination of RC Adducts 3. To a stirred solution of RC adduct **3** (0.2 mmol) in a mixture of MeOH (1.5 mL), water (0.5 mL), and conc HCl (0.2 mL) was added iron dust (35 mg, 0.6 mmol). The resulting reaction mixture was heated to reflux on a water bath. After completion of reaction (monitored by TLC, ∼30 min), the mixture was cooled to ambient temperature and filtered through a Celite pad. The filtrate was concentrated *in vacuo*, and the residue was diluted with water (5 mL), basified with 30% NaOH (10 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (5 mL) and concentrated *in vacuo*, and the residue was purified by silica gel column chromatography by eluting with 20% EtOAC-pet ether.

(2*E*,3*E*)-4-(Phenylsulfonyl)-1-*p*-tolylbut-3-en-2-one Oxime (5a). White solid; yield 48% (30 mg, ∼86:14, inseparable); mp 126−128 °C; IR (KBr, cm^{-1}) 3391 (m), 3060 (w), 2924 (m), 2854 (w), 1608 (w), 1515 (w), 1448 (m), 1309 (vs), 1150 (vs), 1085 (s), 998 (m), 831 (m), 800 (m), 754 (m); ^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 2.28 (s, 3H), 3.83 (s, 2H), 6.65 (d, J = 15.6 Hz, 1H), 7.01 (ABq, J = 16.5 Hz, 4H), 7.45 (d, J = 15.6 Hz, 1H), 7.50−7.53 (m, 2H), 7.60−7.64 (m, 1H), 7.79−7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 21.16, 30.33, 127.84, 128.33, 129.53, 129.64, 132.10, 132.37, 133.80, 136.57, 139.41, 140.06, 155.60; MS (ES+) m/z (rel intensity) 338 (MNa^+, 27), 325 (100), 186 (21), 132 (10); HRMS (ES+) calcd for $C_{17}H_{17}NO_3SNa$ (MNa^+) 338.0821, found 338.0821.

(2*E*,3*E*)-1-(4-Fluorophenyl)-4-(phenylsulfonyl)but-3-en-2-one Oxime (5b). White solid; yield 50% (32 mg, ∼89:11, inseparable); mp 156−158 °C; IR (KBr, cm^{-1}) 3509 (s), 3064 (w), 2924 (w), 1604 (m), 1583 (m), 1510 (s), 1324 (s), 1226 (m), 1151 (vs), 1085 (m), 826 (m), 754 (m); ^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 3.83 (s, 2H), 6.64 (d, J = 15.6 Hz, 1H), 6.88−6.94 (m, 2H), 7.05−7.09 (m, 2H), 7.50−7.55 (m, 3H), 7.62−7.66 (m, 1H), 7.82−7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 29.94, 115.83 (d, J_{C-F} = 22.0 Hz), 127.83, 129.62, 130.02 (d, J_{C-F} = 8.0 Hz), 130.89 (d, J_{C-F} = 4.0 Hz), 132.38, 133.98, 139.26, 139.91, 155.24, 161.86 (d, J_{C-F} = 244.0 Hz); MS (ES+) m/z (rel intensity) 320 (MH^+, 100), 295 (24), 245 (31), 231 (33); HRMS (ES+) calcd for $C_{16}H_{15}FNO_3S$ (MH^+) 320.0751, found 320.0739.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file for **3n** and copies of NMR spectra for all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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