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Reactions of organocobaloximes with aryldisulfonyl chlorides ☆

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Dedicated to Prof. M. Tada, Waseda University, Japan

Abstract

Photochemical reactions of benzyl, heteroaromaticmethyl and allylcobaloximes with aryldisulfonyl chlorides yield symmetrical disulfones. Allyl cobaloximes yield allyldisulfones as the major product whereas bibenzyl is the major product in benzylcobaloximes. A time dependent ^{1}H NMR studies show that bibenzyl is formed from *O*-benzyldimethylglyoxime – a predominant product in the initial stage of the reaction.

Keywords: Organocobaloximes; Disulfonyl chlorides; S_H2 reactions; Disulfone; Bibenzyl-*O*-benzyldimethylglyoxime; ^{1}H NMR studies

1. Introduction

The use of organocobalt complexes to mediate or catalyze the organic reactions has grown tremendously in the last few years [1]. There are several type of reactions where cobalt complexes have played a prominent role as stoichiometric reagents or catalysts [2–5]. In particular the application of organocobaloximes in organic synthesis is well documented in the literature [6–8].

Organocobaloximes have recently been used for the synthesis of sulfones [9], for example allyl [10–15], benzyl [16–18], heteroaromaticmethyl [17,19], allenyl [20,21], propargyl [20,21] and alicyclic phenyl sulfone [20–25] have been synthesized.

Sulfone functionality is ubiquitous in nature where it serves several important roles [26]. Recently, it has been identified as HIV-1 non-nucleoside reverse transcriptase inhibitor, which led to the idea of developing novel synthetic sulfones [27]. Several synthetic methodologies have appeared in which sulfone is involved as an activating group and its use as intermediates in total synthesis of many natural products has become a classic [26c]. Sulfonyl group is a synthetically useful functional group and has recently been reported as potential stereoinducer [28]. It has also been utilized for carbon–carbon bond formation as carbonyl group equivalents for many synthetic transformations [29]. In particular, benzyl and allyl sulfones have been used in many organic transformations [30]. Allylic aryl sulfones serve as valuable intermediates in the carbon–carbon bond formation via alkylation of sulfonyl anion [31]. Disulfones find application in polymerization reactions [32] and in natural product synthesis [33].

Since little information is known on the synthesis of disulfones, we have carried out the reaction of organocobaloximes with aryldisulfonyl chlorides, ClO_2S–Ar–SO_2Cl, having two reactive SO_2–Cl bonds. The aim of the study is (i) to gain more insight into the S_H2/S_H2' reaction with two reactive free radical centers, (ii) to understand the mechanism of the formation of bibenzyl and (iii) to develop a general method for the synthesis of symmetrical disulfones, RO_2S–Ar–SO_2R.

2. Results and discussion

Benzyl (**1**–**5**), heteroaromaticmethyl (**6**–**8**) and allyl (**9**–**11**) cobaloximes are reacted with disulfonyl chlorides, 4,4′-biphenyldisulfonyl chloride (**A**) and 2,4-mes-

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itylenedisulfonyl chloride (**B**) in 1:2 molar ratio in dichloromethane at 0 °C under anaerobic and photolytic condition. A smooth reaction takes place and is complete within 3 h to give a mixture of products, disulfone, dimer and *O*-organodimethyl glyoxime (dmgH ether). The ratio and yield of these products depends on the nature of the cobaloxime, reaction time and the reaction conditions (Schemes 1 and 2 Table 1).

Benzyl cobaloxime (**1**) on reaction with **A** forms disulfone **1a** and bibenzyl **1c** in 15% and 52% yield, respectively. A similar reaction occurs with cobaloximes **2** and **3** to yield disulfones (**2a** and **3a**) and the substituted bibenzyl (**2c** and **3c**). However no disulfone is formed with **4** and **5**, only the dimer products (**4c** and **5c**) are isolated.

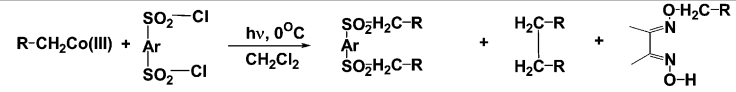
B reacts in a similar way with cobaloximes **1**–**5** to give a mixture of disulfones (**1b**–**5b**) and bibenzyl (**1c**–**5c**) in varying yields. No disulfone is formed in the reaction with **5**. The amount of bibenzyl formed is always more than the disulfone. In the reaction of **B** with **1** and **3**, dmgH ether **1d** and **3d** are also formed in low yield (<5%).

Furfuryl cobaloxime **6**, on reaction with **A** and **B** exclusively forms the disulfones **6a** and **6b** in 57% and 44% yield, respectively. No other organic product is formed (Scheme 1, Table 1). However, the reactions of the disulfonyl chlorides with cobaloximes **7** and **8** proceed differently. For example, **A** on reaction with **7** forms the disulfone **7a** exclusively whereas no disulfone is formed with **8**. The only products isolated in the latter are the dimer **8c** and the dmgH ether **8d**. On the other hand, **B** on reaction with cobaloximes **7** and **8** forms the disulfones **7b**, **8b**; dimers **7c**, **8c** and dmgH ethers **7d**, **8d**.

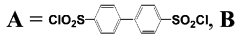
The disulfonyl chloride **A** and **B** react with allyl (**9**) and crotyl (**10**) cobaloximes **9** and **10** to yield the corresponding disulfones, **9a**, **9b**, **10a** and **10b** in 72–99% yield (Scheme 2, Table 1). No other product is formed. α-Pinenyl cobaloxime **11**, however, forms the disulfone **11a** in 37% yield with **A** and no disulfone with **B**. Dimer **11c** and dmgH ether **11d** are the only products isolated.

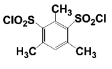
$ClCo^{III}(dmgH)_2Py$ is the main inorganic product isolated in these reactions and no attempt has been made to characterize the other water-soluble inorganic products.

Many observations are made from independent reactions. (a) The reactions do not proceed in dark. (b) All the organocobaloximes are stable in solution under inert atmosphere in the absence of aryldisulfonyl chloride. (c) The reaction of **A** with $PhCH_2Co(dmgH)_2L$ (L = 4-*t*-buPy) under photochemical condition is complete in 3 h and forms bibenzyl (79%), dmgH ether (2%) and disulfone (1%). when L is 4-cyanopyridine, the same re-

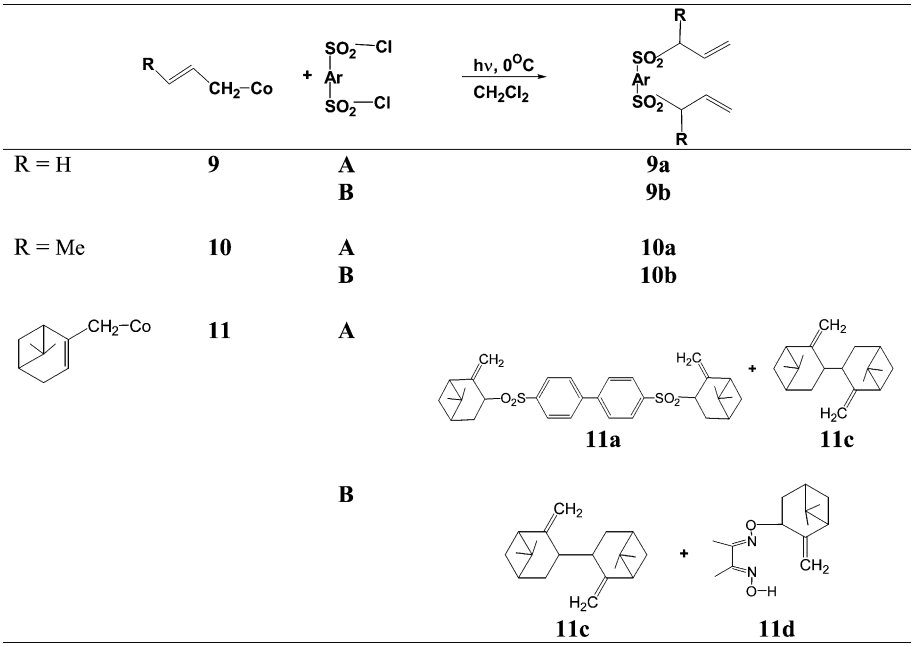


	(1-8)	(A/B)	(1a-8a)/(1b-8b)	(1c-8c)	(1d-8d)
R = C_6H_5	**1**	**A**	**1a**	**1c**	**1d**
		B	**1b**	**1c**	**1d**
R = 4-MeC_6H_4	**2**	**A**	**2a**	**2c**	**2d**
		B	**2b**	**2c**	**2d**
R = 3-$OMeC_6H_4$	**3**	**A**	**3a**	**3c**	**3d**
		B	**3b**	**3c**	**3d**
R = 4-$OMeC_6H_4$	**4**	**A**	**4a**	**4c**	**4d**
		B	**4b**	**4c**	**4d**
R = 4-CNC_6H_4	**5**	**A**	**5a**	**5c**	**5d**
		B	**5b**	**5c**	**5d**
R = 2-furyl	**6**	**A**	**6a**	**6c**	**6d**
		B	**6b**	**6c**	**6d**
R = 2-thienyl	**7**	**A**	**7a**	**7c**	**7d**
		B	**7b**	**7c**	**7d**
R = 3-thienyl	**8**	**A**	**8a**	**8c**	**8d**
		B	**8b**	**8c**	**8d**

A = 

, **B** = 

Scheme 1.



Scheme 2.

Table 1
Organic products from the reaction of organocobaloximes (**1**–**11**) with aryldisulfonyl chlorides (**A** and **B**)

RCo	Disulfonyl chloride	Disulfone	Dimer	Dmg–ether
1	**A**	**1a** (15)	**1c** (52)	**1d** (–)
	B	**1b** (5)	**1c** (90)	**1d** (2)
2	**A**	**2a** (3)	**2c** (61)	**2d** (–)
	B	**2b** (4)	**2c** (60)	**2d** (–)
3	**A**	**3a** (21)	**3c** (52)	**3d** (–)
	B	**3b** (12)	**3c** (45)	**3d** (3)
4	**A**	**4a** (–)	**4c** (78)	**4d** (1)
	B	**4b** (4)	**4c** (8)	**4d** (–)
5	**A**	**5a** (–)	**5c** (86)	**5d** (–)
	B	**5b** (–)	**5c** (57)	**5d** (–)
6	**A**	**6a** (57)	**6c** (–)	**6d** (–)
	B	**6b** (44)	**6c** (–)	**6d** (–)
7	**A**	**7a** (64)	**7c** (–)	**7d** (–)
	B	**7b** (12)	**7c** (7)	**7d** (5)
8	**A**	**8a** (–)	**8c** (15)	**8d** (6)
	B	**8b** (20)	**8c** (26)	**8d** (15)
9	**A**	**9a** (72)	–	–
	B	**9b** (86)	–	–
10	**A**	**10a** (99)	–	–
	B	**10b** (85)	–	–
11	**A**	**11a** (37)	**11c** (34)	
	B	–	**11c** (35)	**11d** (7)

action takes 10 h to complete and yields bibenzyl (31%), dmgH ether (2%) and disulfone (1%). The reaction of **A** with **1** in the presence of two equivalents of pyridine yields bibenzyl (80%) in 5 h. (d) The reaction of **A** with $PhCH_2Co(dpgH)_2Py$ requires 5 h to complete and yields bibenzyl (50%) and disulfone (4%).

All the reactions are free radical in nature as inferred from the experimental observations and the nature of products formed. Since the Co–C bond in organocobaloximes is weak (17–30 kcal mol^{-1}) and photolabile, it can be cleaved even at wavelength above 360 nm [34]. Tungsten lamp and glass apparatus are, therefore, adequate for preparative photolysis experiments. Arenesulfonyl chlorides have previously been identified as chain-propagating species in many organic reactions of alkenes as well as in the reaction with organocobaloximes [35]. Cobaloxime (II), a d^7 species, formed during the homolysis of Co–C bond has been observed to be a good leaving group [35c,35d].

The general characteristics of the reaction of organocobaloximes **1**–**11** with aryldisulfonyl chloride, **A** and **B** are similar to the reaction of the same substrates with arylsulfonyl chloride described earlier by us [15–18]. We believe that a similar mechanism might be operating here.

The most surprising result in the present study is the lack of formation (or a low yield) of disulfone in the reaction of benzyl cobaloximes (**1**–**5**) with **A** or **B**. Bibenzyl is the major or the only product isolated in such cases. Since benzylcobaloxime in the absence of **A** or **B** is stable under inert conditions, the formation of such a high proportion of bibenzyl is very surprising. It suggests that simple homolysis of the Co–C bond followed by dimerisation of the benzyl radicals cannot be the only pathway for its formation. In order to rationalize the results we have studied the progress of reaction by ^{1}H NMR. The ^{1}H NMR spectra of the organic products in the reaction of **A** with benzylcobaloxime **1** has been measured at different time intervals (Fig. 1). The result shows that the disulfone **1a**, bibenzyl **1c** and dmgH ether **1d** are formed in the initial stage of the reaction with **1d** as the predominant product. As the reaction progresses, the amount of bibenzyl increases at the cost of dmgH ether and finally the peak corresponding to the dmgH

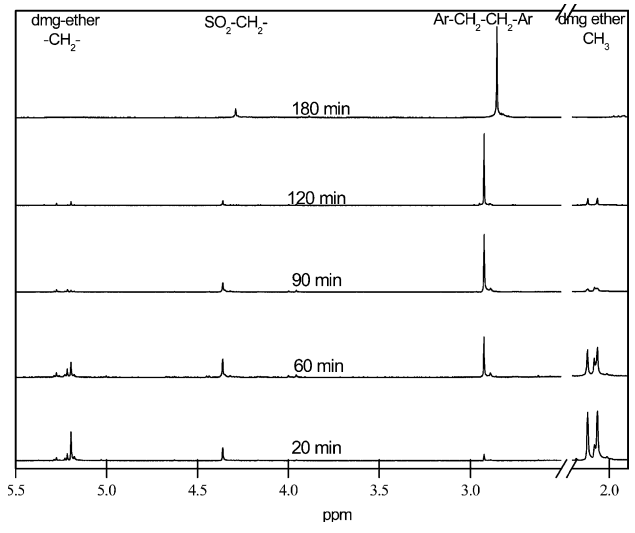


Fig. 1. Time dependent ^{1}H NMR spectra of the reaction of **1** with **A**.

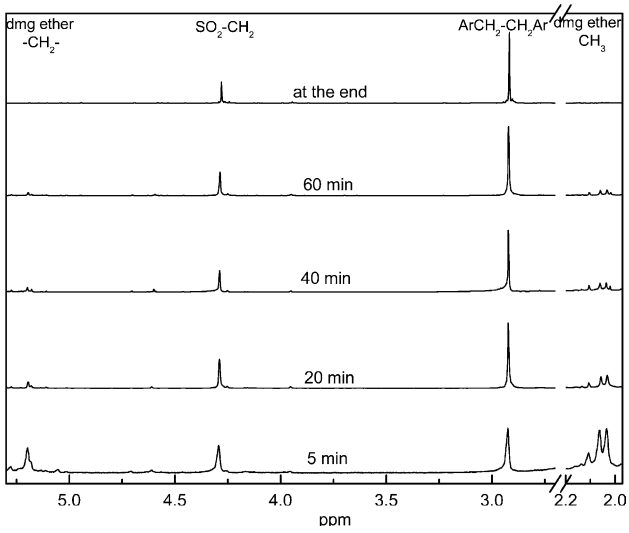


Fig. 2. Time dependent ^{1}H NMR spectra of the reaction of **1** with *p*-toluenesulfonyl chloride.

ether (**1d**) disappears. The amount of disulfone, however, remains constant during the course of the reaction (Fig. 1). So, only disulfone and bibenzyl are isolated at the end of the reaction (Table 1). The reaction of 4-methoxybenzyl cobaloxime (**4**) with **A**, monitored by ^{1}H NMR, also shows the similar result.

^{1}H NMR monitoring experiment on the previously reported reaction of benzylcobaloxime with $ArSO_2Cl$ [17] gives identical result. All the three products are formed in the initial stage and later dmgH ether product gets consumed as the reaction progresses (Fig. 2). This confirms that the formation of dmgH ether and its conversion into bibenzyl is a general phenomenon in the reaction of benzyl cobaloxime with arylsulfonyl chlorides. The extent of formation of bibenzyl and dmgH ether is a function of reaction time; if it is run longer all the dmgH ether will convert to bibenzyl.

It is difficult to pinpoint the exact mechanism of the conversion of dmgH ether to bibenzyl. The cleavage of benzyl–O bond into iminoxyl and benzyl radical occurs under the photolysis conditions. A recent report has shown that benzophenone–*O*-benzyloxime forms bibenzyl by the free radical dimerization of the benzyl radicals, produced as a result of the homolysis of the benzyl–O bond, when heated in a sealed tube at 200 °C [36]. The preferential cleavage of C–O bond (bond energy 68 kcal/mol) over N–O bond (48 kcal/mol) may be attributed to the resonance stabilization of benzyl radicals.

We have also observed that the reaction of **A** with **1** under thermal condition (refluxing dichloromethane and diffused light) is slow and remains incomplete even after 10 h. DmgH ether (**1d**, 20%) and bibenzyl (**1c**, 2%) are the only organic products isolated. No disulfone is formed. Johnson et al. [11] have also made similar observation earlier. It is, therefore, clear that dmgH ether is formed in both thermal and photochemical

conditions, but the decomposition of dmgH ether to bibenzyl occurs only under photochemical condition.

All our efforts to improve the yield of disulfone have failed. For example, the use of a stronger base than pyridine and carrying out the reaction in the presence of excess free pyridine, the modifications partially successful in increasing the yield of sulfones in the reaction of RSO_2Cl with benzyl cobaloximes [17] have failed in the present case. The distinct difference might be due to the higher stability of the disulfonyl diradical.

The use of bulky equatorial ligand, dpgH in place of dmgH, has been shown to be more selective and more reactive in exo-selective Diels–Alder reactions and in radical alkyl–alkenyl cross-coupling reactions [37,38]. This also does not improve the yield of the disulfone in the present study.

Two more factors have been considered to increase the yield of the disulfone (i) by increasing the nucleophilicity of the cobalt bound CH_2 group and hence increasing the rate of S_H2 reaction and (ii) to inhibit/retard the electron transfer process [17] responsible for the formation of dmgH ether. The introduction of a methoxy group in the *m*- or *p*-position, known to increase the reactivity of cobalt bound CH_2group towards electrophiles [39], does not make any significant improvement in the disulfone formation in the present study. The yield, however, is visibly improved in the reaction of **A** or **B** with furfuryl (**6**) and 2-thienylmethyl (**7**) cobaloximes, where the Co–CH_2 bond is more nucleophilic than the Co–benzyl bond. As observed earlier, the RCo^{III}–RCo^{IV} potential is high (compared to benzyl) that inhibits the formation of intermediate RCo^{IV} [39]. Allyl cobaloximes have always been observed to be far more reactive towards the electrophilic radicals as compared to the benzyl cobaloximes [14].

The disulfone may arise by the S_H2/S_H2' attack (concerted or stepwise) of the sulfonyl radical at the alpha carbon in benzyl cobaloxime (or γ carbon in allyl). This generates cobaloxime (II) that forms part of a chain reaction by abstracting a chlorine atom from aryldisulfonyl chloride **A** or **B** to give the sulfonyl radical [40]. Cobaloxime (II) and $ArSO_2^{\cdot}$ are known to act as propagating species [17]. We, however, can not rule out the participation of some ancillary process in which the disulfone is formed by the coupling of benzyl radical with sulfonyl radical. The absence of monosulfone product supports the concerted process.

The reaction of a 1:1 mixture of allyl (**9**) and benzyl (**1**) cobaloximes or a 1:1 mixture of allyl (**9**) and furfuryl (**6**) cobaloximes with **A**, does not form any cross-coupling-organic product. The only products formed are the corresponding disulfones and bibenzyl. The ^1H NMR monitoring of this reaction shows that these are the only products formed from the beginning itself. The extent of allyl disulfone formation, however, is more in the beginning. The absence of any cross-coupling product supports the concerted mechanism.

3. Conclusions

Symmetrical disulfones are formed in the reaction of organocobaloximes with aryldisulfonyl chlorides. The reactions are more complicated as compared to the reactions of the same organocobaloximes with monosulfonyl chlorides. Allyl cobaloximes yield disulfones in good yield whereas bibenzyl is the major product in benzyl cases. ^1H NMR studies have confirmed that bibenzyl is formed from *O*-benzyldimethylglyoxime, a product in the initial stage of the reaction. The conversion of *O*-benzyldimethylglyoxime to bibenzyl has been reported for the first time.

4. Experimental

4.1. General instrumental and experimental techniques used

The synthesis of all the organocobaloximes has been reported earlier [10,14,17,41]. Silica gel (ACME, 100–200 mesh size) was used in the column chromatography. All solvents were distilled and dried prior to use. Melting points were recorded on a FISHER-JOHNS apparatus and all the values were uncorrected. UV–vis spectra were recorded on a Shimadzu 160-A Spectrophotometer. ^1H NMR spectra were recorded on JEOL PMX-60 instrument and in JEOL-JNM LAMBDA 400 model spectrometer in $CDCl_3$ using TMS as internal reference. $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL-JNM LAMBDA 400 model spectrometer in $CDCl_3$. IR spectra were recorded from 4000–400 cm^{-1} on a Bruker FT-IR-Vector 22 model. They were recorded in solid state as KBr pellets. Elemental analysis was carried out using a Thermoquest CE instruments CHNS-O elemental analyzer.

4.2. General procedure for the photochemical reaction

A solution of aryldisulfonyl chloride (1 mmol in 30 ml of dichloromethane) was degassed for 30 min, and organocobaloxime (2 mmol) was added to it. The reaction mixture was cooled to 0 °C and irradiated using 2×200 W tungsten lamps. The progress of the reaction was monitored using TLC in ethyl acetate. On completion, the mixture was concentrated and the organic compounds were separated by flash chromatography. The organic products were further separated by column chromatography. In some cases, a white solid product insoluble in chloroform was formed.

4.3. General procedure for the cross-reaction

The same procedure as outlined above, except that a 1:1 mixture of allyl cobaloxime and benzyl cobaloxime or allyl cobaloxime and furfuryl cobaloxime was used.

4.4. ^1H NMR monitoring: general procedure

A 3.0 ml aliquot of the reaction mixture was taken out at regular time interval. The total organic product in each fraction was separated by flash chromatography and was analyzed further by ^1H NMR spectroscopy.

Disulfones were characterized by ^1H, $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis. UV and IR spectra were recorded for representative examples. The dimers and dmgH ether were characterized by ^1H NMR spectroscopy and were compared with the known samples from another study. The characteristics of disulfones obtained are given below.

Disulfone 1a: White solid; m.p. 202–204 °C; ^1H NMR (400 MHz) δ: 4.37 (s, 4H, $-CH_2SO_2$), 7.14 (d, $J = 7.2$ Hz, 4H, Ar), 7.26–7.36 (m, 6H, Ar), 7.69 (d, $J = 8.8$ Hz, 4H, Ar), 7.75 (d, $J = 8.0$ Hz, 4H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 62.9 (CH_2SO_2), 127.8 (Ar), 127.9 (Ar), 128.6 (Ar), 128.7 (Ar), 129.6 (Ar), 130.9 (Ar), 138.4 (Ar), 143.7 (Ar), 144.1 (Ar), 146.0 (Ar); Anal. Calc. for $C_{26}H_{22}O_4S_2$: C, 67.53; H, 4.76; S, 13.85. Found: C, 67.49; H, 4.78; S, 13.80%.

Disulfone 2a: White solid; m.p. 200–202 °C; ^1H NMR (400 MHz) δ: 2.34 (s, 6H, CH_3), 4.32 (s, 4H, CH_2SO_2), 7.02 (d, $J = 8.4$ Hz, 4H, Ar), 7.09 (d, $J = 8.0$ Hz, 4H, Ar), 7.67 (d, $J = 8.0$ Hz, 4H, Ar), 7.74 (d, $J = 8.0$ Hz, 4H, Ar); $^{13}C\{^1H\}$NMR (100.6 MHz) δ: 21.2(CH_3), 62.6 (CH_2SO_2), 124.8 (Ar), 127.8 (Ar), 129.4 (Ar), 129.5 (Ar), 130.7 (Ar), 138.1 (Ar), 138.9 (Ar), 144.3 (Ar); Anal. Calc. for $C_{28}H_{26}O_4S_2$: C, 68.57; H, 5.31; S, 13.06. Found: C, 68.50; H, 5.30; S, 12.98%.

Disulfone 3a: White solid; m.p. 178–180 °C; ^1H NMR (400 MHz) δ: 3.72 (s, 6H, OCH_3), 4.33 (s, 4H, CH_2SO_2), 6.69 (s, 4H, Ar), 6.87 (d, $J = 8.0$ Hz, 2H, Ar), 7.18 (t, $J = 8.0$ Hz, 2H, Ar), 7.66 (d, $J = 8.4$ Hz, 4H, Ar), 7.75 (d, $J = 8.4$ Hz, 4H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 55.2 (OCH_3), 62.9 (CH_2SO_2), 114.8 (Ar), 116.1 (Ar), 123.2 (Ar), 127.8 (Ar), 129.2 (Ar), 129.5 (Ar), 129.6 (Ar), 137.9 (Ar), 144.4 (Ar), 159.6 (Ar); UV λ_{max} 269.2 nm ($\log\varepsilon$ 4.43). Anal. Calc. for $C_{28}H_{26}O_6S_2$: C, 68.57; H, 5.31; S, 13.06. Found: C, 68.50; H, 5.28; S, 13.00%.

Disulfone 6a: White solid; m.p. 188–190 °C; ^1H NMR (400 MHz) δ: 4.48 (s, 4H, CH_2SO_2), 6.35–6.37 (m, 4H, Ar), 7.33 (s, 2H, Ar), 7.73 (d, $J = 8.4$ Hz, 4H, Ar), 7.83 (d, $J = 8.4$ Hz, 4H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 56.0 (CH_2SO_2), 111.28 (Ar), 112.4 (Ar), 128.0 (Ar), 129.3 (Ar), 138.2 (Ar), 142.2 (Ar), 143.9 (Ar), 144.5 (Ar); UV λ_{max} 269.4 nm ($\log\varepsilon$ 4.33); IR (KBr) ν 1314 and 1156 cm^{-1}; Anal. Calc. for $C_{22}H_{18}O_6S_2$: C, 59.73; H, 4.07; S, 14.48. Found: C, 59.70; H, 4.00; S, 14.40%.

Disulfone 7a: White solid; m.p. 218–220 °C; ^1H NMR (400 MHz) δ: 4.58 (s, 4H, CH_2SO_2), 6.92–6.95 (m, 2H, Ar), 7.27–7.30 (m, 4H, Ar), 7.68–7.81 (m, 8H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 57.3 (CH_2SO_2), 127.3 (Ar), 127.7 (Ar), 127.9 (Ar), 128.3 (Ar), 129.5 (Ar), 130.4 (Ar), 137.2 (Ar), 144.5 (Ar); UV λ_{max} 250.6 nm ($\log\varepsilon$ 4.46), 269.2 nm ($\log\varepsilon$ 4.51); IR ν 1313 and 1151 cm^{-1}; Anal. Calc. for $C_{22}H_{18}O_4S_4$: C, 55.70; H, 3.80; S, 27.00. Found: C, 55.73; H, 3.82; S, 27.09%.

Disulfone 9a: White solid; m.p. 146 °C; ^1H NMR (400 MHz) δ: 3.88 (d, $J = 4.6$ Hz, 4H, CH_2SO_2), 5.21 (d, $J = 16.8$ Hz, 2H, CH_2=C), 5.38 (d, $J = 9.6$ Hz, 2H, CH_2=C), 5.83–5.85 (m, 2H, =CH–C), 7.80 (d, $J = 6.8$ Hz, 4H, Ar) 7.99 (d, $J = 6.4$ Hz, 4H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 60.9 (CH_2SO_2), 124.5 (Ar), 125.0 (Ar), 128.0 (Ar), 129.3 (Ar), 138.2 (Ar), 144.4 (Ar); UV λ_{max} 266.4 nm ($\log\varepsilon$ 4.56); Anal. Calc. for $C_{18}H_{18}O_4S_2$: C, 55.70; H, 3.80; S, 27.00. Found: C, 55.70; H, 3.82; S, 27.08%.

Disulfone 10a: White solid; m.p. 107 °C; ^1H NMR (400 MHz) δ: 1.49 (d, $J = 6.8$ Hz, 6H, CH_3) 3.76–3.80 (m, 2H, CH–SO_2), 5.15 (d, $J = 17.2$ Hz, 2H, CH_2=C), 5.32 (d, $J = 10.4$ Hz, 2H, CH_2=C), 5.82–5.91 (m, 2H, =CH–C), 7.79 (d, $J = 8.0$ Hz, 4H, Ar), 7.96 (d, $J = 8.0$ Hz, 4H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 12.9 (CH_3), 60.9 ($CHSO_2$), 122.1 (Ar), 127.8 (Ar), 130.1 (Ar), 131.0 (Ar), 136.7 (Ar), 144.3 (Ar); UV λ_{max} 267.4 nm ($\log\varepsilon$ 4.50); Anal. Calc. for $C_{20}H_{22}O_4S_2$: C, 61.54; H, 5.64; S, 16.41. Found: C, 61.49; H, 5.60; S, 16.42%.

Disulfone 11a: White solid; m.p. 96 °C; ^1H NMR (400 MHz) δ: 0.72 (s, 6H, CH_3), 1.21 (s, 6H, CH_3), 1.34 (d, $J = 10.4$, 2H), 1.79–1.86 (m, 2H), 2.02 (q, $J = 5.2$, 2H), 2.133 (dd, $J = 13.6$, 9.6 Hz, 2H), 2.30–2.35 (m, 2H), 2.56 (t, $J = 5.6$, 2H) 4.33–4.37 (m, 2H) 5.09 (d, $J = 2.8$, 2H), 5.90 (d, $J = 2.4$, 2H) 7.80 (dd, $J = 8.0$,2.0 Hz, 4H), 8.08 (dd, $J = 6.8$,1.6 Hz, 4H); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 20.6 (CH_3), 26.2, 26.5, 27.6, 39.6, 41.5, 52.7, 58.6 ($CHSO_2$), 113.5, 128.8, 129.8, 139.1, 141.9, 144.4; UV λ_{max} 269.2 nm ($\log\varepsilon$ 4.48); IR ν 1314 and 1146 cm^{-1}; Anal. Calc. for $C_{32}H_{38}O_4S_2$: C, 69.82; H, 6.91; S, 11.64. Found: C, 69.78; H, 6.92; S, 11.62%.

Disulfone 1b: White solid; m.p. 172–174 °C; ^1H NMR (400 MHz) δ: 2.27 (s, 6H, CH_3), 2.87 (s, 3H, CH_3), 4.39 (s, 4H, CH_2SO_2), 6.88 (s, 1H, Ar), 7.11 (d, $J = 7.2$ Hz, 4H, Ar), 7.26–7.36 (m, 6H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.3 (CH_3), 23.7 (CH_3), 62.7 (CH_2SO_2), 127.4 (Ar), 128.7 (Ar), 129.1 (Ar), 131.0 (Ar), 136.1 (Ar), 136.3 (Ar), 143.3 (Ar), 146.3 (Ar); UV λ_{max} 245.0 nm ($\log\varepsilon$ 3.88), 284.0 nm ($\log\varepsilon$ 3.19), 291.8 nm ($\log\varepsilon$ 3.19); Anal. Calc. for $C_{23}H_{24}O_4S_2$: C, 64.49; H, 5.61; S, 14.95. Found: C, 64.51; H, 5.52; S, 14.92%.

Disulfone 2b: White solid; m.p. 168–170 °C; ^1H NMR (400 MHz) δ: 2.29 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 2.88 (s, 3H, CH_3), 4.35 (s, 4H) 6.89 (s, 1H, Ar), 6.99 (d, $J = 8.4$ Hz, 4H, Ar), 7.09 (d, $J = 7.6$ Hz, 4H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.4 (CH_3), 21.2 (CH_3),

23.7 (CH_3), 62.5 (CH_2SO_2), 124.3 (Ar), 128.3 (Ar), 128.9 (Ar), 129.5 (Ar), 130.9 (Ar), 136.3 (Ar), 139.2 (Ar), 146.2 (Ar); Anal. Calc. for $C_{25}H_{28}O_4S_2$: C, 65.79; H, 6.14; S, 14.04. Found: C, 65.77; H, 6.10; S, 14.00%.

Disulfone 3b: White solid; m.p. 156–158 °C; ^{1}H NMR (400 MHz) δ: 2.32 (s, 6H, CH_3), 2.85 (s, 3H, CH_3), 3.71 (s, 6H, OCH_3), 4.35 (s, 4H, CH_2SO_2), 6.62–6.67 (m, 4H, Ar), 6.85–6.88 (m, 2H, Ar), 6.91 (s, 1H, Ar), 7.12–7.20 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.4, 23.6 (CH_3), 55.2 (OCH_3), 62.7 (CH_2SO_2), 114.8 (Ar), 116.4 (Ar), 121.1 (Ar), 123.2 (Ar), 128.6 (Ar), 129.7 (Ar), 136.2 (Ar), 143.4 (Ar), 146.2 (Ar), 159.6 (Ar); Anal. Calc. for $C_{25}H_{28}O_6S_2$: C, 61.48; H, 5.74; S, 13.11. Found: C, 61.52; H, 5.70; S, 13.15%.

Disulfone 4b: White solid; m.p. 80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H, CH_3), 2.87 (s, 3H, CH_3), 3.79 (s, 6H, OCH_3), 4.36 (s, 4H, CH_2SO_2), 6.78–6.81 (m, 4H, Ar), 6.93–7.05 (m, 5H Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.7 (CH_3), 23.4 (CH_3), 55.3 (OCH_3), 62.1 (CH_2SO_2), 114.1 (Ar), 114.2 (Ar), 119.1 (Ar), 121.2 (Ar), 131.4 (Ar), 132.3 (Ar), 136.0 (Ar), 142.0 (Ar); Anal. Calc. for $C_{25}H_{28}O_6S_2$: C, 61.48; H, 5.74; S, 13.11. Found: C, 61.45; H, 5.72; S, 13.10%.

Disulfone 6b: White solid; m.p. 158–160 °C; ^{1}H NMR (400 MHz) δ: 2.46 (s, 6H, CH_3), 2.88 (s, 3H, CH_3), 4.51 (s, 4H, CH_2SO_2), 6.32–6.35 (m, 4H, Ar), 7.01 (s, 1H, Ar), 7.33 (d, $J = 0.8$ Hz, 2H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.2 (CH_3), 23.7 (CH_3), 55.9 (CH_2SO_2), 111.4 (Ar), 112.7 (Ar), 136.5 (Ar), 136.6 (Ar), 141.9 (Ar), 144.1 (Ar), 146.1 (Ar); UV λ_{max} 244.8 nm ($\log\varepsilon$ 3.84); Anal. Calc. for $C_{19}H_{20}O_6S_2$: C, 55.88; H, 4.90; S, 15.69. Found: C, 55.80; H, 4.88; S, 15.70%.

Disulfone 7b: White solid; m.p. 160–162 °C; ^{1}H NMR (400 MHz) δ: 2.40 (s, 6H, CH_3), 2.88 (s, 3H, CH_3), 4.61 (s, 4H, CH_2SO_2), 6.91 (d, $J = 2.8$ Hz, 2H, Ar), 6.94 (s, 1H, Ar), 6.96–6.98 (m, 2H, Ar), 7.30 (d, $J = 0.8$ Hz, 1H, Ar), 7.31 (d, $J = 0.8$ Hz, 1H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.4 (CH_3), 23.8 (CH_3), 57.2 (CH_2SO_2), 127.5 (Ar), 127.8 (Ar), 128.0 (Ar), 130.6 (Ar), 135.7 (Ar), 136.4 (Ar), 143.6 (Ar), 146.6 (Ar); Anal. Calc. for $C_{19}H_{20}O_4S_4$: C, 51.82; H, 4.55; S, 29.09. Found: C, 51.80; H, 4.52; S, 29.02%.

Disulfone 8b: White solid; m.p. 162–164 °C; ^{1}H NMR (400 MHz) δ: 2.35 (s, 6H, CH_3), 2.89 (s, 3H, CH_3), 4.47 (s, 4H, CH_2SO_2), 6.88 (d, $J = 4.8$ Hz, 2H, Ar), 6.94 (s, 1H, Ar), 7.09 (d, $J = 2.4$ Hz, 2H, Ar), 7.25 (s, 2H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.2 (CH_3), 23.6 (CH_3), 57.3 (CH_2SO_2), 126.5 (Ar), 127.2 (Ar), 129.1 (Ar), 136.1 (Ar), 136.4 (Ar), 143.1 (Ar), 146.2 (Ar); UV λ_{max} 245.6 nm; Anal. Calc. for $C_{19}H_{20}O_4S_4$: C, 51.82; H, 4.55; S, 29.09. Found: C, 51.78; H, 4.50; S, 29.02%.

Disulfone 9b: White solid; m.p. 156 °C; ^{1}H NMR (400 MHz) δ: 2.71 (s, 6H, CH_3), 3.10 (s, 3H, CH_3), 3.94 (d, $J = 7.6$ Hz, 4H, CH_2SO_2), 5.27 (d, $J = 17.2$ Hz, 2H, CH_2=C), 5.38 (d, $J = 10.4$ Hz, 2H, CH_2=C), 5.77–5.86 (m, 2H, =CH–C), 7.13 (s, 1H Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 19.6 (CH_3), 24.1 (CH_3), 61.0 (CH_2SO_2), 123.8, 125.4, 136.7, 142.5, 145.6; UV λ_{max} 243.0 nm ($\log\varepsilon$ 3.67), 282.8 ($\log\varepsilon$ 3.04), 291.0 ($\log\varepsilon$ 3.05); Anal. Calc. for $C_{15}H_{20}O_4S_2$: C, 54.88; H, 6.10; S, 19.51. Found: C, 54.90; H, 6.14; S, 19.50%.

Disulfone 10b: White solid; m.p. 94 °C; ^{1}H NMR (400 MHz) δ: 1.52–1.55 (m, 6H, CH_3), 2.70 (s, 6H, CH_3), 3.10 (s, 3H, CH_3) 3.87–3.91 (m, 2H, $CHSO_2$), 5.07–5.14 (m, 2H, CH_2=C), 5.28 (t, $J = 9.2$ Hz, 2H, CH_2=C), 5.76–5.87 (m, 2H, =CH–C), 7.12 (s, 1H, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz) δ: 12.0, 12.2, 19.5, 19.6, 24.2, 64.3($CHSO_2$), 122.5, 122.6, 130.74, 130.9, 136.0, 136.7, 136.8, 142.7, 142.9, 145.8, 145.9; UV λ_{max} 244.6 nm ($\log\varepsilon$ 3.72), 283.0 ($\log\varepsilon$ 3.17), 291.2 ($\log\varepsilon$ 3.18); Anal. Calc. for $C_{17}H_{24}O_4S_2$: C, 57.30; H, 6.74; S, 17.98. Found: C, 57.22; H, 6.70; S, 18.02%.

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