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Iodine-catalyzed disulfidation of alkenes

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ABSTRACT

The disulfidation reactions of alkenes with disulfides were thoroughly investigated in this paper. Using H_2O or DCE as the solvent, most reactions occurred smoothly to give the corresponding disulfidated products in good to high yields at room temperature within 12 h.

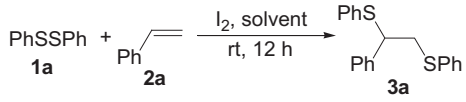
1. Introduction

The disulfidation of carbon–carbon unsaturated bonds is a useful method for the synthesis of organosulfur compounds, which can be used as good intermediates in organic synthesis.[1] Nowadays, several methods have been reported in the literature. For instance, Kitamura and Taniguchi reported the hypervalent iodine(III) reagent induced 1,2-disulphenylation of alkenes.[2] Caserio and co-workers reported boron trifluoride catalyzed addition reaction of disulfides to alkenes in 1985.[3] In 2004, Oshima and co-workers completed the gallium trichloride catalyzed disulfidation of alkenes at 0 °C to give the corresponding products in good to high yields.[4] In 2009, Yoshida and co-workers reported a catalytic amount of ArS^+ initiated disulfidation of dienes via intramolecular C–C bond formation reaction.[5] Though some progresses have been made in the disulfidation of alkenes, to develop some other simple and efficient methods for these reactions is still in demand for chemists. Herein, we wish to report the I_2-catalyzed disulfidation reactions of alkenes under mild conditions.

2. Results and discussion

Initial examinations were carried out using diphenyl disulfide **1a** (0.5 mmol) and styrene **2a** (0.6 mmol) as the substrates in the presence of I_2 (10 mol %) at room temperature for 12 h to find out the optimal solvent. The results are summarized in Table 1. The reaction took place very well in H_2O, CH_2Cl_2 or 1,2-dichloroethane (DCE) to give the corresponding disulfidation product **3a** in high yields (Table 1, entries 3–5). Almost no product was obtained when the reaction was carried out in THF or DMF (Table 1, entries 1 and 2). H_2O matches the demand of the basic principles in *Green Chemistry*[6] and it is cheap and safe enough.[7] CH_2Cl_2 is volatile at room temperature. So the optimal reaction solvents were H_2O or DCE.

Table 1
Optimization for the I_2-catalyzed disulfidation of diphenyl disulfide **1a** with styrene **2a**



Entry[a]	Solvent	Yield (%)[b]
1	THF	Trace
2	DMF	—
3	H_2O	90
4	CH_2Cl_2	94
5	DCE	96

[a] All reactions were carried out using **1a** (0.5 mmol), **2a** (0.6 mmol), and I_2 (10 mol%) in the listed solvent (2.0 mL) at rt for 12 h under air.
[b] Isolated yields.

With the optimal reaction conditions in hand, we next investigate the reactions of a variety of disulfides **1** with styrene **2a**. The results are shown in Table 2. In most cases, the corresponding disulfidation products **3** were obtained in good to high yields in both solvents of H_2O and DCE (Table 2, entries 1, 2, 4, and 5). Substituents on substrates **1** have some effect on the reactions. For instance, substrate **1d** with 4-chlorophenyl groups only gave acceptable yield in H_2O, though good yield of the corresponding

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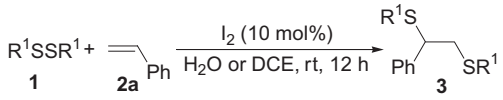
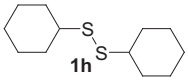
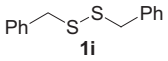
Table 2
I_2-catalyzed reactions of a variety of disulfides **1** with styrene **2a**

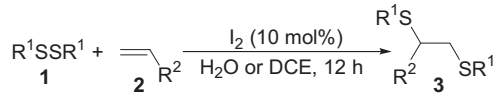


Entry[a]	**1** (R^1)	Yields (%)[b]	
		A	**B**
1	**1b** (4-MeC_6H_4)	**3b**, 94	**3b**, 96
2	**1c** (4-$MeOC_6H_4$)	**3c**, 96	**3c**, 93
3	**1d** (4-ClC_6H_4)	**3d**, 46	**3d**, 85
4	**1e** (3-FC_6H_4)	**3e**, 71	**3e**, 74
5	**1f** (4-FC_6H_4)	**3f**, 95	**3f**, 97
6	**1g** (4-$NO_2C_6H_4$)	trace	trace
7	 **1h**	trace	trace
8	 **1i**	**3g**, 73	**3g**, 56

[a] All reactions were carried out using **1** (0.5 mmol), **2a** (0.6 mmol) and I_2 (10 mol%) in H_2O (2.0 mL, **A**) or DCE (2.0 mL, **B**) at rt for 12 h under air.
[b] Isolated yields.

product **3d** was obtained in DCE (Table 2, entry 3). For substrate **1e** with 3-fluorophenyl groups, lower yields of product **3e** were obtained in H_2O or DCE (Table 2, entry 4). With di-(4-nitrophenyl) disulfide **1g** having strongly electron-withdrawing groups on the phenyl rings and dicyclohexyl disulfide **1h** as the substrates, respectively, almost no reactions occurred in H_2O or DCE (Table 2, entries 6 and 7). Dibenzyl disulfide **1i** also gave moderate yields in H_2O or DCE, respectively (Table 2, entry 8).

Table 3
I_2-catalyzed reactions of disulfides **1** with alkenes **2**

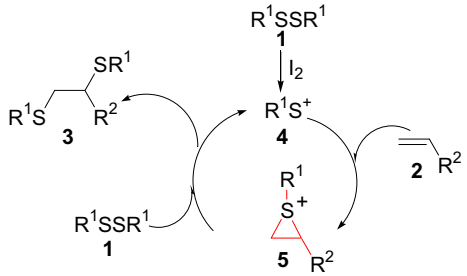


Entry[a]	**1** (R^1)	**2** (R^2)	Yields (%)[b]	
			A	B
1	**1b** (4-MeC_6H_4)	**2b** (3-$NO_2C_6H_4$)	**3h**, 98	**3h**, 58
2	**1b**	**2c** (4-FC_6H_4)	**3i**, 92	**3i**, 91
3	**1b**	**2d** (4-ClC_6H_4)	**3j**, 99	**3j**, 98
4	**1b**	**2e** (2-ClC_6H_4)	**3k**, 98	**3k**, 90
5	**1b**	**2f** (3-MeC_6H_4)	**3l**, 92	**3l**, 93
6	**1c** (4-$MeOC_6H_4$)	**2f**	**3m**, 99	**3m**, 97
7	**1d** (4-ClC_6H_4)	**2f**	**3n**, 19	**3n**, 84
8	**1d**	**2c**	**3o**, 49	**3o**, 79
9	**1a** (Ph)	**2g** (4-MeC_6H_4)	**3p**, 72	**3p**, 80
10	**1a**	**2f**	**3q**, 88	**3q**, 91
11	**1a**	**2b**	**3r**, 98	**3r**, 42
12	**1a**	**2c**	**3s**, 89	**3s**, 86
13	**1a**	**2d**	**3t**, 95	**3t**, 86
14	**1a**	**2e**	**3u**, 99	**3u**, 81
15	**1a**	**2h** (2-BrC_6H_4)	**3v**, 95	**3v**, 82
16[c]	**1a**	 **2i**	Trace	**3w**, 25

[a] Otherwize specified, all reactions were carried out using **1** (0.5 mmol), **2** (0.6 mmol) and I_2 (10 mol%) in H_2O (2.0 mL, **A**) or DCE (2.0 mL, **B**) at rt for 12 h under air.
[b] Isolated yields.
[c] The reaction was carried out at 70 °C.

Subsequently, we examined the I_2-catalyzed reactions of various disulfides **1** with alkenes **2** under the identical conditions (Table 3). As can be seen from Table 3, good to high yields of the corresponding disulfidation products **3** were achieved in H_2O or DCE in most cases with styrenes as the substrates (Table 3, entries 2–6, 9, 10, 12–15). Electron- and solvent-effect affected the reactions evidently. For example, in the reactions of substrate **1d** bearing 4-chlorophenyl groups with substrates **2f** and **2c**, very lower yields of products **3n** and **3o** were obtained in H_2O, while good yields were achieved in DCE (Table 3, entries 7 and 8). For the reactions involving substrate **2b** bearing strongly electron-withdrawing 3-nitro group on the phenyl ring, only acceptable yields of products **3h** and **3r** were obtained in DCE, which are far from that obtained in H_2O (Table 3, entries 1 and 11). Cyclohexene **2i** was not a suitable substrate in this reaction and only trace of product was formed in H_2O and 25% yield was obtained in DCE, although both reactions were carried out at 70 °C (Table 3, entry 16).

For an initial mechanistic consideration, it seems as if a radical route is involved in this I_2-triggered disulfidation reaction of alkenes. The reaction of disulfide **1a** with styrene **2a** was tested under the optimized conditions **B** in the presence of 2,6-di-*tert*-butyl-4-methyl-phenol, a classical radical trap. Unexpectedly, the reaction proceeded smoothly to give product **2a** as the sole product in 99% yield, which, to some extent, may be a proof to rule out the radical pathway. Based on this result, a plausible mechanism for this I_2-catalyzed disulfidation reaction is shown in Scheme 1. The sulfonium ion **4**, which is formed by oxidation of disulfide **1** with I_2, adds to alkenes **2** to form intermediate **5**. Intermediate **5** reacts with another disulfide molecule to afford product **3** with regeneration of the sulfonium ion **4** to furnish the catalytic cycle.



Scheme 1. Proposed mechanism.

3. Conclusion

In summary, I_2 was found to be an efficient catalyst in the disulfidation reactions of aromatic alkenes in H_2O and DCE, respectively. This strategy will be useful synthetic methods for the disulfidation of aromatic alkenes, complementary to the reported Lewis acid catalyzed addition reactions of disulfides to alkenes.

4. Experimental section

4.1. General methods

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or 500 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in hertz. THF was distilled from sodium (Na) under nitrogen (N_2) atmosphere. DMF, CH_2Cl_2, and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen (N_2) atmosphere. Commercially obtained reagents were used without further purification. Flash column chromatography was carried out using Huanghai 300–400 mesh silica gel at increased pressure.

4.2. Experimental procedures

General Procedure for the I_2-catalyzed disulfidation of alkenes: into a reaction tube were added disulfide **1** (0.5 mmol), I_2 (10 mol %), H_2O or DCE (2.0 mL), and alkenes **2** (0.6 mmol) successively. The mixture was stirred at room temperature for 12 h. Then the reaction was quenched with saturated aqueous Na_2SO_3. The mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4, filtered, and purified by flash column chromatography to give the pure products.

*4.2.1. Compound **3a**[8].* A colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.29–7.16 (m, 15H, Ar), 4.25 (dd, J=9.9, 5.1 Hz, 1H), 3.49 (dd, J=13.5, 5.1 Hz, 1H), 3.35 (dd, J=13.5, 9.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 139.6, 135.5, 134.1, 132.8, 129.9, 128.89, 128.87, 128.5, 128.0, 127.7, 127.6, 126.4, 52.4, 39.7.

*4.2.2. Compound **3b**[9].* A white solid, Mp: 67–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.29–7.21 (m, 5H, Ar), 7.16 (d, J=8.0 Hz, 2H, Ar), 7.06 (d, J=8.0 Hz, 2H, Ar), 7.02 (d, J=7.0 Hz, 2H, Ar), 7.01 (d, J=7.0 Hz, 2H, Ar), 4.17 (dd, J=10.0, 5.0 Hz, 1H), 3.44 (dd, J=13.5, 5.0 Hz, 1H), 3.29 (dd, J=13.5, 10.0 Hz, 1H), 2.30 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 139.8, 137.8, 136.4, 133.4, 131.7, 130.5, 130.4, 129.63, 129.60, 128.4, 128.1, 127.6, 52.6, 40.0, 21.1, 21.0.

*4.2.3. Compound **3c**.* A white solid, Mp: 56–57 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.26–7.18 (m, 3H, Ar), 7.17–7.14 (m, 6H, Ar), 6.77–6.72 (m, 4H, Ar), 4.05 (dd, J=10.0, 5.0 Hz, 1H), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.36 (dd, J=13.5, 5.0 Hz, 1H), 3.25 (dd, J=13.5, 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 159.7, 159.0, 139.9, 135.9, 133.5, 128.3, 128.1, 127.5, 125.6, 124.1, 114.5, 114.3, 55.3, 55.2, 53.3, 41.0. IR (CH_2Cl_2) ν 3049, 2953, 2914, 2834, 1589, 1491, 1284, 1265, 1241, 1171, 1027, 906, 825, 738, 698 cm^{-1}. MS (%) m/z 382 (M^+, 1), 139 (100). HRMS (EI) calcd for $C_{22}H_{22}O_2S_2$: 382.1061, found: 382.1058.

*4.2.4. Compound **3d**.* A white solid, Mp: 61–62 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.29–7.23 (m, 3H, Ar), 7.20–7.17 (m, 8H, Ar), 7.15–7.09 (m, 2H, Ar), 4.17 (dd, J=9.5, 5.5 Hz, 1H), 3.40 (dd, J=13.5, 5.5 Hz, 1H), 3.32 (dd, J=13.5, 9.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 139.1, 134.3, 134.0, 133.8, 132.6, 132.3, 131.5, 129.05, 129.04, 128.6, 128.0, 127.9, 52.8, 40.0. IR (CH_2Cl_2) ν 3049, 2360, 1509, 1475, 1388, 1265, 1226, 1159, 1094, 1013, 816, 742, 697 cm^{-1}. MS (%) m/z 247 [(M−C_6H_4ClS)$^+$, 53], 169 (100), 143 (72), 108 (64), 104 (54). HRMS (EI) calcd for $C_{20}H_{16}Cl_2S_2$: 390.0070, found: 390.0068.

*4.2.5. Compound **3e**.* A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.30–7.26 (m, 5H, Ar), 7.21–7.15 (m, 2H, Ar), 7.05 (d, J=7.5 Hz, 1H, Ar), 6.99–6.90 (m, 3H, Ar), 6.87–6.86 (m, 2H, Ar), 4.29 (dd, J=9.0, 4.5 Hz, 1H), 3.46 (dd, J=13.5, 4.5 Hz, 1H), 3.36 (dd, J=13.5, 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 162.7 (d, J_{C-F}=247.1 Hz), 162.5 (d, J_{C-F}=247.8 Hz), 139.0, 137.7 (d, J_{C-F}=7.6 Hz), 136.3 (d, J_{C-F}=7.6 Hz), 130.2 (d, J_{C-F}=2.0 Hz), 130.1 (d, J_{C-F}=1.9 Hz), 128.6, 128.0, 127.9, 127.8 (d, J_{C-F}=3.0 Hz), 125.1 (d, J_{C-F}=2.9 Hz), 119.0 (d, J_{C-F}=22.0 Hz), 116.3 (d, J_{C-F}=22.6 Hz), 114.6 (d, J_{C-F}=21.0 Hz), 113.4 (d, J_{C-F}=21.0 Hz), 52.3, 39.5. IR (CH_2Cl_2) ν 3061, 2953, 1598, 1577, 1490, 1474, 1453, 1426, 1264, 1217, 1157, 1066, 878, 816, 775, 741, 698 cm^{-1}. MS (%) m/z 358 (M^+, 4), 231 (96), 217 (50), 153 (100). HRMS (EI) calcd for $C_{20}H_{16}F_2S_2$: 358.0662, found: 358.0666.

*4.2.6. Compound **3f**.* A white solid, Mp: 65–66 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.28–7.15 (m, 9H, Ar), 6.94–6.89 (m, 4H, Ar), 4.10 (dd, J=10.0, 5.0 Hz, 1H), 3.38 (dd, J=13.5, 5.0 Hz, 1H), 3.31 (dd, J=13.5, 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 162.7 (d, J_{C-F}=247.1 Hz), 162.0 (d, J_{C-F}=245.8 Hz), 139.4, 135.9 (d, J_{C-F}=8.3 Hz), 133.1 (d, J_{C-F}=8.0 Hz), 130.2 (d, J_{C-F}=3.3 Hz), 128.8 (d, J_{C-F}=3.3 Hz), 128.5, 128.0, 127.8, 116.02 (d, J_{C-F}=21.8 Hz), 115.95 (d, J_{C-F}=21.6 Hz), 53.4, 40.7. IR (CH_2Cl_2) ν 3052, 2917, 2847, 1588, 1488, 1265, 1224, 1155, 1013, 828, 739, 698 cm^{-1}. MS (%) m/z 358 (M^+, 1), 153 (100), 231 (87), 153 (100), 127 (66). HRMS (EI) calcd for $C_{20}H_{16}F_2S_2$: 358.0662, found: 358.0646.

*4.2.7. Compound **3g**.* A colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.35–7.13 (m, 15H, Ar), 3.72 (dd, J=8.7, 6.6 Hz, 1H), 3.56–3.39 (m, 4H), 2.89–2.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 140.9, 138.01, 137.95, 128.92, 128.87, 128.5, 128.43, 128.41, 128.2, 127.6, 127.0, 49.1, 37.3, 36.7, 35.8. IR (CH_2Cl_2) ν 3051, 1583, 1532, 1490, 1477, 1439, 1353, 1265, 1225, 1157, 816, 741, 698 cm^{-1}. MS (%) m/z 350 (M^+, 1), 91 (100). HRMS (EI) calcd for $C_{22}H_{22}S_2$: 350.1163, found: 350.1171.

*4.2.8. Compound **3h**.* A white solid, Mp: 79–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.06 (d, J=8.0 Hz, 1H, Ar), 7.96 (s, 1H, Ar), 7.49 (d, J=7.5 Hz, 1H, Ar), 7.40 (t, J=7.5 Hz, 1H, Ar), 7.14 (d, J=7.0 Hz, 2H, Ar), 7.07–7.01 (m, 6H, Ar), 4.23 (dd, J=10.5, 4.0 Hz, 1H), 3.50 (dd, J=13.5, 4.0 Hz, 1H), 3.28 (dd, J=13.5, 10.5 Hz, 1H), 2.31 (s, 3H, Me) 2.30 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 148.0, 142.1, 138.6, 137.0, 134.4, 133.9, 131.0, 130.8, 129.81, 129.77, 129.1, 128.9, 123.1, 122.4, 52.3, 39.6, 21.1, 20.9. IR (CH_2Cl_2) ν 3050, 2919, 2851, 1528, 1477, 1439, 1349, 1265, 1210, 1158, 1096, 1014, 808, 739, 704 cm^{-1}. MS (%) m/z 395 (M^+, 3), 272 (76), 149 (47), 139 (44), 123 (100). HRMS (EI) calcd for $C_{22}H_{21}NO_2S_2$: 395.1014, found: 395.1014.

*4.2.9. Compound **3i**.* A white solid, Mp: 79–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.17–7.14 (m, 4H, Ar), 7.07–7.02 (m, 6H, Ar), 6.95 (t, J=8.5 Hz, 2H, Ar), 4.15 (dd, J=10.5, 4.5 Hz, 1H), 3.43 (dd, J=13.5, 4.5 Hz, 1H), 3.23 (dd, J=13.5, 10.5 Hz, 1H), 2.32 (s, 3H, Me), 2.31 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 162.1 (d, J_{C-F}=244.8 Hz), 138.0, 136.6, 135.6 (d, J_{C-F}=3.1 Hz), 133.5, 131.5, 130.6, 130.0, 129.674, 129.667 (d, J_{C-F}=8.0 Hz), 115.3 (d, J_{C-F}=21.4 Hz), 51.9, 40.1, 21.1, 21.0. IR (CH_2Cl_2) ν 3021, 2954, 2919, 2849, 1604, 1508, 1491, 1477, 1439, 1264, 1227, 1158, 1095, 1068, 1015, 909, 839, 808, 739, 693 cm^{-1}. MS (%) m/z 368 (M^+, 1), 245 (52), 149 (100), 123 (97). HRMS (EI) calcd for $C_{22}H_{21}FS_2$: 368.1069, found: 368.1068.

*4.2.10. Compound **3j**.* A white solid, Mp: 76–77 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.24–7.21 (m, 2H, Ar), 7.14 (d, J=8.0 Hz, 2H, Ar), 7.11 (d, J=8.5 Hz, 2H, Ar), 7.07–7.01 (m, 6H, Ar), 4.13 (dd, J=10.5, 5.0 Hz, 1H), 3.43 (dd, J=13.5, 5.0 Hz, 1H), 3.22 (dd, J=13.5, 10.5 Hz, 1H), 2.31 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 138.4, 138.0, 136.6, 133.5, 133.2, 131.4, 130.7, 129.8, 129.7, 129.4, 128.5, 52.0, 39.9, 21.1, 21.0. IR (CH_2Cl_2) ν 3022, 2917, 2849, 1583, 1514, 1490, 1439, 1407, 1265, 1090, 1014, 909, 806, 739, 693 cm^{-1}. MS (%) m/z 384 (M^+, 1), 261 (33), 149 (100), 123 (97). HRMS (EI) calcd for $C_{22}H_{21}ClS_2$: 384.0773, found: 384.0772.

*4.2.11. Compound **3k**.* A colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.33 (dd, J=7.0, 1.5 Hz, 1H, Ar), 7.27–7.25 (m, 1H, Ar), 7.18–7.11 (m, 6H, Ar), 7.09–6.99 (m, 4H, Ar), 4.79 (dd, J=10.0, 5.5 Hz, 1H), 3.42 (dd, J=13.5, 5.5 Hz, 1H), 3.36 (dd, J=13.5, 10.5 Hz, 1H), 2.30 (s, 3H, Me), 2.29 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 137.9, 137.2, 136.6, 134.3, 133.4, 131.4, 131.0, 129.8, 129.7, 129.59, 129.57, 128.6, 128.5, 126.8, 48.2, 39.6, 21.1, 21.0. IR (CH_2Cl_2) ν 3022, 2953, 2918, 1509, 1490, 1476, 1439, 1265, 1158, 1121, 1016, 909, 809, 740, 704, 679 cm^{-1}. MS (%) m/z 384 (M^+, 9), 263 (41), 261 (100), 149 (99), 123 (53). HRMS (EI) calcd for $C_{22}H_{21}ClS_2$: 384.0773, found: 384.0770.

*4.2.12. Compound **3l**.* A pale yellow solid, Mp: 49–50 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.18–7.15 (m, 3H, Ar), 7.06–7.00 (m, 9H, Ar), 4.15 (dd, J=10.0, 5.0 Hz, 1H), 3.42 (dd, J=13.5, 5.0 Hz, 1H), 3.30

(dd, J=13.5, 10.5 Hz, 1H), 2.31 (s, 3H, Me), 2.30 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 139.5, 138.0, 137.7, 136.3, 133.3, 131.8, 130.53, 130.46, 129.6, 128.7, 128.4, 128.3, 125.1, 52.5, 40.0, 21.4, 21.1, 21.0. IR (CH_2Cl_2) ν 3051, 2953, 2917, 1532, 1490, 1438, 1353, 1265, 1226, 1159, 1016, 800, 738, 703 cm^{-1}. MS (%) m/z 364 (M^+, 1), 241 (22), 149 (100), 123 (39). HRMS (EI) calcd for $C_{23}H_{24}S_2$: 364.1319, found: 364.1315.

4.2.13. Compound ***3m***. A colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.21–7.12 (m, 5H, Ar), 7.04 (d, J=8.0 Hz, 1H, Ar), 6.96 (d, J=6.0 Hz, 2H, Ar), 6.77–6.73 (m, 4H, Ar), 4.02 (dd, J=10.0, 5.0 Hz, 1H), 3.77 (s, 6H, 2OMe), 3.34 (dd, J=13.5, 5.0 Hz, 1H), 3.25 (dd, J=13.5, 10.5 Hz, 1H), 2.29 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 159.7, 158.9, 139.6, 137.9, 135.9, 133.4, 128.7, 128.3, 128.2, 125.7, 125.2, 124.3, 114.4, 114.3, 55.2, 53.3, 40.9, 21.4. IR (CH_2Cl_2) ν 3051, 2954, 1590, 1532, 1492, 1439, 1353, 1265, 1243, 1172, 1070, 1026, 825, 738, 704 cm^{-1}. MS (%) m/z 257 [($M-C_7H_7OS)^+$, 15], 165 (22), 139 (100). HRMS (EI) calcd for $C_{23}H_{24}O_2S_2$: 396.1218, found: 396.22.12.

4.2.14. Compound ***3n***. A colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.20–7.16 (m, 7H, Ar), 7.10–7.06 (m, 3H, Ar), 7.00 (d, J=5.5 Hz, 2H, Ar), 4.14 (dd, J=9.5, 5.5 Hz, 1H), 3.38 (dd, J=13.5, 5.5 Hz, 1H), 3.33 (dd, J=13.5, 9.5 Hz, 1H), 2.30 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 138.9, 138.2, 134.1, 133.8, 132.5, 131.4, 129.0, 128.9, 128.7, 128.5, 128.4, 125.0, 52.8, 39.9, 21.3. IR (CH_2Cl_2) ν 3004, 2952, 1606, 1573, 1514, 1475, 1439, 1388, 1265, 1093, 1012, 818, 739, 702 cm^{-1}. MS (%) m/z 261 [($M-C_6H_4ClS)^+$, 29], 171 (37), 169 (100), 143 (38), 118 (36), 108 (34). HRMS (EI) calcd for $C_{21}H_{18}Cl_2S_2$: 404.0227, found: 404.0226.

4.2.15. Compound ***3o***. A white solid, Mp: 55–56 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.19–7.13 (m, 8H, Ar), 7.09 (d, J=8.5 Hz, 2H, Ar), 6.95 (t, J=8.5 Hz, 2H, Ar), 4.15 (dd, J=10.0, 5.0 Hz, 1H), 3.39 (dd, J=13.5, 5.0 Hz, 1H), 3.26 (dd, J=13.5, 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 162.1 (d, J_{C-F}=245.6 Hz), 134.9 (d, J_{C-F}=3.3 Hz), 134.4, 134.2, 133.6, 132.7, 131.9, 131.5, 129.6 (d, J_{C-F}=8.1 Hz), 129.08, 129.06, 115.4 (d, J_{C-F}=21.4 Hz), 52.0, 40.0. IR (CH_2Cl_2) ν 3023, 2952, 1604, 1574, 1508, 1476, 1438, 1389, 1265, 1228, 1159, 1095, 1013, 910, 820, 741, 692 cm^{-1}. MS (%) m/z 265 [($M-C_6H_4ClS)^+$, 57], 169 (93), 143 (100), 122 (61), 108 (80). HRMS (EI) calcd for $C_{20}H_{15}Cl_2FS_2$: 407.9976, found: 407.9971.

4.2.16. Compound ***3p***. A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.29–7.08 (m, 14H, Ar), 4.24 (dd, J=10.0, 5.0 Hz, 1H), 3.47 (dd, J=13.5, 5.0 Hz, 1H), 3.32 (dd, J=13.5, 10.0 Hz, 1H), 2.30 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 137.4, 136.4, 135.5, 134.3, 132.6, 129.8, 129.2, 128.8, 127.9, 127.4, 126.3, 51.9, 39.6, 21.1. IR (CH_2Cl_2) ν 3050, 2920, 2846, 1582, 1513, 1480, 1438, 1265, 1086, 1068, 1024, 908, 818, 736, 690 cm^{-1}. MS (%) m/z 336 (M^+, 2), 227 (63), 135 (100), 117 (64), 109 (46). HRMS (EI) calcd for $C_{21}H_{20}S_2$: 336.1006, found: 336.1008.

4.2.17. Compound ***3q***. A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.30–7.28 (m, 2H, Ar), 7.23–7.14 (m, 9H, Ar), 7.05 (s, 3H, Ar), 4.22 (dd, J=10.0, 4.5 Hz, 1H), 3.47 (dd, J=13.5, 4.5 Hz, 1H), 3.35 (dd, J=13.5, 10.0 Hz, 1H), 2.30 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 139.3, 138.1, 135.5, 134.3, 132.7, 129.9, 128.9, 128.8, 128.7, 128.6, 128.3, 127.5, 126.3, 125.1, 52.3, 39.5, 21.4. IR (CH_2Cl_2) ν 3017, 2952, 2920, 1606, 1583, 1512, 1478, 1264, 1158, 1096, 1067, 1014, 854, 823, 737, 690 cm^{-1}. MS (%) m/z 336 (M^+, 3), 227 (76), 213 (30), 135 (100). HRMS (EI) calcd for $C_{21}H_{20}S_2$: 336.1006, found: 336.1001.

4.2.18. Compound ***3r***. A white solid, Mp: 67–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.08–8.02 (m, 2H, Ar), 7.52 (d, J=7.5 Hz, 1H, Ar), 7.41 (t, J=8.0 Hz, 1H, Ar), 7.27–7.15 (m, 10H, Ar), 4.31 (dd, J=10.5, 4.5 Hz, 1H), 3.55 (dd, J=14.0, 4.5 Hz, 1H), 3.33 (dd, J=14.0, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 148.1, 141.9, 134.5, 134.3, 133.4, 132.7, 130.4, 129.3, 129.13, 129.07, 128.3, 126.9, 123.2, 122.6, 52.1, 39.3. IR (CH_2Cl_2) ν 3049, 1581, 1527, 1479, 1438, 1350, 1265, 1227, 1156, 1024, 890, 736, 690 cm^{-1}. MS (%) m/z 367 (M^+, 1), 258 (41), 135 (54), 109 (100). HRMS (EI) calcd for $C_{20}H_{17}NO_2S_2$: 367.0701, found: 367.0704.

4.2.19. Compound ***3s***. A white solid, Mp: 52–53 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.28–7.14 (m, 12H, Ar), 6.98–6.95 (m, 2H, Ar), 4.23 (dd, J=10.5, 4.5 Hz, 1H), 3.49 (dd, J=13.5, 4.5 Hz, 1H), 3.29 (dd, J=13.5, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 162.1 (d, J_{C-F}=245.0 Hz), 135.3 (d, J_{C-F}=3.1 Hz), 135.2, 133.7, 133.0, 130.0, 129.7 (d, J_{C-F}=8.1 Hz), 128.9, 127.8, 126.5, 115.3 (d, J_{C-F}=21.5 Hz), 51.7, 39.7. IR (CH_2Cl_2) ν 3049, 1603, 1582, 1508, 1479, 1438, 1265, 1223, 1158, 1024, 1012, 906, 838, 738, 689 cm^{-1}. MS (%) m/z 340 (M^+, 1), 231 (84), 217 (31), 135 (100), 109 (76). HRMS (EI) calcd for $C_{20}H_{17}FS_2$: 340.0756, found: 340.0750.

4.2.20. Compound ***3t***. A white solid, Mp: 61–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.25–7.13 (m, 14H, Ar), 4.21 (dd, J=10.5, 4.8 Hz, 1H), 3.49 (dd, J=13.5, 4.8 Hz, 1H), 3.28 (dd, J=13.5, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 138.2, 135.1, 133.6, 133.4, 133.1, 130.1, 129.4, 128.995, 128.982, 128.6, 127.9, 126.6, 51.8, 39.6. IR (CH_2Cl_2) ν 3057, 1582, 1532, 1490, 1479, 1438, 1353, 1265, 1224, 1156, 1090, 1024, 1013, 906, 837, 740, 690 cm^{-1}. MS (%) m/z 356 (M^+, 1), 247 (44), 135 (100), 109 (69). HRMS (EI) calcd for $C_{20}H_{17}ClS_2$: 356.0460, found: 356.0461.

4.2.21. Compound ***3u***. A pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.35–7.28 (m, 4H, Ar), 7.23–7.15 (m, 10H, Ar), 4.88 (dd, J=9.3, 6.0 Hz, 1H), 3.48 (dd, J=13.8, 6.0 Hz, 1H), 3.41 (dd, J=13.8, 9.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 137.1, 135.1, 134.3, 133.7, 132.8, 130.4, 129.7, 128.90, 128.86, 128.7, 128.6, 127.7, 127.0, 126.6, 48.1, 39.2. IR (CH_2Cl_2) ν 3052, 1582, 1472, 1438, 1265, 1157, 1123, 1068, 1024, 908, 815, 739, 690 cm^{-1}. MS (%) m/z 356 (M^+, 4), 249 (32), 247 (83), 135 (100), 109 (46). HRMS (EI) calcd for $C_{20}H_{17}ClS_2$: 356.0460, found: 356.0453.

4.2.22. Compound ***3v***. A colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.52 (d, J=8.0 Hz, 1H, Ar), 7.34–7.30 (m, 3H, Ar), 7.23–7.16 (m, 9H, Ar), 7.08 (t, J=7.5 Hz, 1H, Ar), 4.87 (dd, J=8.0, 6.5 Hz, 1H), 3.39–3.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 138.6, 135.1, 133.7, 133.0, 132.9, 130.5, 129.0, 128.92, 128.87, 128.7, 127.7, 127.6, 126.6, 125.2, 50.7, 39.3. IR (CH_2Cl_2) ν 3049, 1583, 1508, 1478, 1438, 1265, 1226, 1157, 1023, 816, 741, 691 cm^{-1}. MS (%) m/z 400 (M^+, 1), 293 (19), 291 (20), 135 (100), 109 (84). HRMS (EI) calcd for $C_{20}H_{17}BrS_2$: 399.9955, found: 399.9948.

4.2.23. Compound ***3w***[10]. A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.32–7.30 (m, 4H, Ar), 7.26–7.23 (m, 6H, Ar), 3.28 (s, 2H), 2.28–2.24 (m, 2H), 1.67–1.62 (m, 4H), 1.43–1.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 134.7, 132.3, 128.9, 127.0, 49.6, 29.7, 23.4.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.04.081. These data include MOL files and InChiKeys of the most important compounds described in this article.

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