Correlation of the rates of solvolysis of (arylmethyl)methylphenylsulfonium ions†

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The specific rates of solvolysis of the benzylmethylphenylsulfonium ion (prepared as the trifluoromethanesulfonate salt) and five benzylic ring-substituted derivatives can be satisfactorily correlated using N_T solvent nucleophilicity values. Addition of a secondary term, governed by the aromatic ring parameter (I), shows the sensitivities towards changes in this parameter to fall and those towards changes in N_T to rise with increasing electron-withdrawing ability of the substituent. The Hammett ρ values with electron-withdrawing substituents (based on σ^+ values) vary from -0.9 in 95% acetone to -1.8 in 97% 2,2,2-trifluoroethanol. These Grunwald–Winstein and Hammett analyses are compared to those previously reported, with essentially the same solvents and substituents, for solvolyses of arylmethyl *p*-toluenesulfonates.

Sulfonium ions have been found to be extremely useful in studies of the mechanism of solvolysis reactions which involve application of extended forms of the Grunwald–Winstein equation [eqn. (1)].

$$\log (k/k_0)_{RX} = mY_x + c \qquad (1)$$

The original Y scale, based on *tert*-butyl chloride solvolysis,[1] has now been replaced with a series of ionizing power scales, dependent upon the leaving group X, based on the solvolyses of appropriate 1- or 2-adamantyl derivatives.[2,3] In eqn. (1), m represents the sensitivity of the solvolyses of RX to changes in solvent ionizing power, c is a constant (residual) term and k and k_0 represent, respectively, the specific rates of solvolysis in a solvent of ionizing power Y_x and in the standard solvent ($Y_x = 0$), 80% ethanol.

The specific rates of solvolysis of the 1-adamantyldimethylsulfonium ion, prepared as the trifluoromethanesulfonate (triflate) salt, were found[4] to vary only little with solvent composition and the calculated Y^+ values [$\log (k/k_0)_{1\text{-AdSMe}_2^+}$] were all close to zero.[3,4] This allows one, by use of sulfonium ion solvolyses, to concentrate on aspects other than ionizing power which control the specific rates of solvolysis, such as solvent nucleophilicity[5] and perturbations introduced by the presence of aromatic rings at the α-carbon[6] or migrating from the β-carbon to the α-carbon during solvolysis.[7]

The original extension of the Grunwald–Winstein equation involved addition of a term governed by the sensitivity (l) to changes in solvent nucleophilicity (N), so as to give eqn. (2).[8] It

$$\log (k/k_0)_{RX} = lN + mY_x + c \qquad (2)$$

was a further 25 years before a solvent nucleophilicity scale was actually available. This initial scale was based on the solvolyses of methyl *p*-toluenesulfonate (tosylate).[2] If l is taken as unity for these solvolyses one can rearrange eqn. (2) to get eqn. (3). A

$$N_{OTs} = \log (k/k_0)_{MeOTs} - m_{OTs}Y_{OTs} \qquad (3)$$

major problem is that there is no independent way of assessing the magnitude of the sensitivity m_{OTs} towards changes in the Y_{OTs} solvent ionizing power scale. With the assumption that a series of aqueous ethanol and aqueous methanol solvents had approximately constant nucleophilicities, Bentley and Schleyer could estimate the m_{OTs} value as 0.3, allowing the establishment of a scale of N_{OTs} values.[2,3]

The observation that the Y^+ values vary only slightly from zero for the unimolecular solvolyses of the 1-adamantyldimethylsulfonium ion, paralleled by the observation of little specific rate variation with solvent for solvolyses of the 1-adamantylpyridinium ion,[9] supported the use of R–X$^+$-type substrates[10] for establishment of an N scale, without the need to incorporate an approximate m value within the derivation. A large range of values are available based on the specific rates of solvolysis of the *S*-methyldibenzothiophenium ion [eqn. (4)].[11] This scale

$$\log (k/k_0)_{MeDBTh^+} = N_T \qquad (4)$$

(N_T) has been found to be the best available for both initially neutral and initially positively charged substrates.[5] For R–X$^+$-type substrates it can be used in the form of eqn. (5).

$$\log (k/k_0)_{R\text{–}X^+} = lN_T + c \qquad (5)$$

Another feature of Grunwald–Winstein plots which was observed[6] very soon after the original equation was first put forward was the dispersion into separate plots for different binary solvent systems in the presence of aromatic rings on the α-carbon, with larger dispersions in the presence of two rings. Similarity models have been developed, and these have been used with some success in place of the traditional Y_x scales in correlations of the specific rates of solvolysis of benzylic derivatives. These scales must, however, be used with caution and, as one would expect,[6] new similarity model scales are needed[12,13] when two aromatic rings can enter into conjugation with the developing positive charge.

We have developed[14–16] an alternative way of treating this dispersion which avoids the need for the difficult choice of a suitable similarity model. An additional term is added to the Grunwald–Winstein equation, governed by the sensitivity h to changes in the aromatic ring parameter (I). The I values for a wide series of solvents have been obtained from a comparison of the specific rates of solvolysis of the *p*-methoxybenzyldimethylsulfonium ion and the 1-adamantyldimethylsulfonium

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Table 1 Specific rates of solvolysis of benzylmethylphenylsulfonium trifluoromethanesulfonates [$(XC_6H_4CH_2SMePh)^+OTf^-$] in pure and binary solvents at 49.2 °C, as a function of the X-substituent

	$k/10^{-3}$ s^{-1} [b]					
Solvent [a]	*p*-Me	H	*p*-Br	*m*-F	*p*-CF_3	*p*-NO_2
100% EtOH	42.7 ± 0.7	12.0 ± 0.5	8.92 ± 0.24	4.40 ± 0.05	2.46 ± 0.09	1.71 ± 0.03
80% EtOH	21.6 ± 0.9	5.10 ± 0.32	3.79 ± 0.09	1.94 ± 0.02	1.10 ± 0.04	0.752 ± 0.018
60% EtOH	14.5 ± 0.3	3.48 ± 0.16	2.31 ± 0.09	1.19 ± 0.03	0.685 ± 0.025	0.414 ± 0.007
100% MeOH	57.7 ± 1.7	15.2 ± 0.3	10.9 ± 0.3	5.38 ± 0.12	2.82 ± 0.02	1.97 ± 0.02
97% TFE	1.35 ± 0.02	0.0348 ± 0.0020	0.0212 ± 0.0014	0.005 98 ± 0.000 21	0.002 97 ± 0.000 21	0.001 56 ± 0.000 03
80% TFE	2.74 ± 0.03	0.174 ± 0.008	0.138 ± 0.008	0.0542 ± 0.0013	0.0303 ± 0.0010	0.0160 ± 0.0005
50% TFE	3.26 ± 0.10	0.386 ± 0.020	0.209 ± 0.004	0.126 ± 0.020	0.0753 ± 0.0031	0.0484 ± 0.0008
60T–40E	10.0 ± 0.2	1.83 ± 0.02	1.30 ± 0.04	0.552 ± 0.013	0.335 ± 0.005	0.170 ± 0.003
95% Acetone	4.15 ± 0.05	0.722 ± 0.013	0.632 ± 0.004	0.365 ± 0.004	0.218 ± 0.005	0.169 ± 0.006

[a] On a volume–volume basis (at 25.0 °C), except for the three aqueous–TFE solvents, which are on a weight–weight basis; T–E denotes a TFE–ethanol mixture. [b] With associated standard deviation, values are averages of all integrated rate coefficient determinations from duplicate runs.

Table 2 Correlation of the specific rates of solvolysis, at 49.2 °C, of ring-substituted benzylmethylphenylsulfonium trifluoromethanesulfonates[a] using the Grunwald–Winstein equation, with and without addition of the aromatic ring parameter term [eqns. (5) and (6), without the mY_x term]

Substituent	*l* [b]	*h* [b]	*c* [c]	*r* [d]	*F* [e]
p-CH_3	0.42 ± 0.07		0.01 ± 0.25	0.9075	33
	0.47 ± 0.06	0.68 ± 0.28 (0.051)	−0.07 ± 0.19	0.9545	31
H	0.69 ± 0.07		0.06 ± 0.25	0.9634	90
	0.74 ± 0.06	0.65 ± 0.29 (0.067)	−0.02 ± 0.20	0.9802	74
p-Br	0.71 ± 0.06		0.05 ± 0.23	0.9722	121
	0.76 ± 0.05	0.64 ± 0.23 (0.034)	−0.02 ± 0.16	0.9878	120
m-F	0.77 ± 0.06		0.07 ± 0.19	0.9822	191
	0.81 ± 0.05	0.46 ± 0.24 (0.102)	0.01 ± 0.16	0.9890	134
p-CF_3	0.78 ± 0.05		0.07 ± 0.19	0.9836	208
	0.81 ± 0.05	0.42 ± 0.23 (0.124)	0.02 ± 0.16	0.9893	138
p-NO_2	0.81 ± 0.05		0.07 ± 0.16	0.9888	309
	0.84 ± 0.05	0.31 ± 0.21 (0.194)	0.03 ± 0.15	0.9918	180

[a] In the nine solvents listed in Table 1. [b] With associated standard error, values in parentheses are the probabilities that the *hI* term is statistically insignificant. [c] Accompanied by the standard error of the estimate. [d] Correlation coefficient. [e] *F*-test value.

ion.[14] The values have been successfully applied [eqn. (6)] to a

$$\log(k/k_0)_{RX} = lN_T + mY_X + hI + c \qquad (6)$$

wide variety of solvolyses. These have involved chloride,[14,15] bromide,[15,17] tosylate,[14–16,18] *p*-nitrobenzoate[15] and dimethyl sulfide[19] leaving groups.

The sulfonium ions which have been previously studied in terms of eqns. (5) or (6) range from the methyldiphenylsulfonium ion[20] (*l* value of 0.86 ± 0.04), to the benzyldiphenylsulfonium ion[21] (*l* value of 0.80 ± 0.05), to 1-arylethyldimethylsulfonium ions[22] (*l* values from −0.03 ± 0.06 to 0.05 ± 0.06, when the σ^+ values for the substituents are $\leqslant$0.15), to the benzhydryldimethylsulfonium ion[19] [*l* value of 0.03 ± 0.02, with $h = 0.99 \pm 0.04$ and *m* (based on Y^+ values) of 1.35 ± 0.10].

A study[23] of the specific rates of solvolysis of a series of arylmethyl tosylates in terms of Y_{OTs} values and $N_{Et_3O^+}$[10] or N_{OTs}[2] solvent nucleophilicity scales has been revisited,[18] with use of N_T values.[5,11] Also, several derivatives have been studied in an increased number of solvents,[24] and these have also been analysed[18] in terms of N_T and Y_{OTs} values or with application of the *I* parameter values,[14] using eqn. (6).

In the present paper, we report a parallel study for a series of (arylmethyl)methylphenylsulfonium ions; the specific rates of solvolysis are analysed in terms of N_T values, both with and without an accompanying *hI* term. Also, the matrix of substituent and solvent influences obtained allows a Hammett equation consideration of substituent effects for solvolyses in each pure or binary solvent.

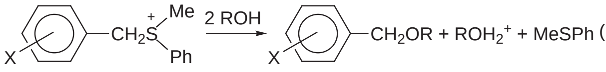
Results

The specific rates of solvolysis at 49.2 °C of six (arylmethyl)methylphenylsulfonium triflates are reported in Table 1 for solvolyses in ethanol, methanol, two aqueous ethanol compositions, three aqueous 2,2,2-trifluoroethanol (TFE) compositions, 95% acetone and a 60% TFE–40% ethanol mixture. These specific rates have been analysed both in terms of solvent variation for a given substituent (Grunwald–Winstein equation) and in terms of substituent variation for a given solvent (Hammett equation). The analyses were carried out using the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado, USA).

Analyses using the Grunwald–Winstein equation have been carried out in terms of eqns. (5) and (6), with omission of the mY^+ term, and the results of these analyses are reported in Table 2. The required N_T values[5,11] and *I* values[14] were available. Analyses using the Hammett equation have employed σ^+ values[25] and they have been carried out with and without the *p*-methyl derivative.

Discussion

The specific rates of solvolysis of the unsubstituted benzylmethylphenylsulfonium ion and the benzylic ring-substituted *p*-Me, *p*-Br, *m*-F, *p*-CF_3 and *p*-NO_2 derivatives [eqn. (7)] vary



(7)

appreciably with solvent, consistent with a contribution to the linear free energy relationship from the solvent nucleophilicity term. These variations are largest in the presence of the stronger electron-withdrawing substituents, which also show slower rates of reaction in each solvent (Table 1).

The data have been analysed in terms of eqn. (5), and these results are presented in Table 2. Reasonably good correlations are obtained for five of the six substrates, with correlation coefficients in the range of 0.963–0.989. The *p*-Me derivative has the lowest *l* value of 0.42 ± 0.07 and also the lowest (0.908) correlation coefficient. Also in Table 2 are reported analyses within which the *hI* term is also incorporated [eqn. (6) without the mY_x term]. The improvements in the correlation coefficient range from appreciable to slight as one goes to increasingly electron-withdrawing substituents. The *F*-test values are all slightly reduced. The *h* values range from 0.68 for the *p*-Me derivative to 0.31 for the *p*-NO_2 derivative. The *l* and *h* values

Table 3 Comparison of the l and h values obtained from studies of the solvolyses of (arylmethyl)methylphenylsulfonium ions and arylmethyl tosylates in the nine solvents of this study

	$ArCH_2S^+MePh$ at 49.2 °C[a]		$ArCH_2OTs$ at 50.0 °C[b]	
Substituent	l	h	l	h
p-CH_3	0.47 ± 0.06	0.68 ± 0.28	0.29 ± 0.14[c]	0.69 ± 0.45[c]
H	0.74 ± 0.06	0.65 ± 0.29	0.60 ± 0.12	0.61 ± 0.39
			0.43 ± 0.07[d]	0.64 ± 0.18[d]
p-Cl			0.58 ± 0.13	0.59 ± 0.41
p-Br	0.76 ± 0.05	0.64 ± 0.23	0.56 ± 0.12	0.46 ± 0.38
m-F	0.81 ± 0.05	0.46 ± 0.24	0.76 ± 0.10	0.36 ± 0.32
p-CF_3	0.81 ± 0.05	0.42 ± 0.23	0.88 ± 0.07	0.29 ± 0.21
p-NO_2	0.84 ± 0.05	0.31 ± 0.21	0.98 ± 0.06	0.05 ± 0.20
			1.06 ± 0.05[e]	0.25 ± 0.11[e]

[a] From Table 2. [b] From Table 3 of ref. 18. [c] At 0.0 °C. [d] In 35 solvents at 25.0 °C, specific rates from ref. 24(*a*). [e] In 28 solvents at 45.0 °C, specific rates from ref. 24(*b*).

are compared in Table 3 with those obtained using the same nine solvents in measurements of the specific rates of solvolysis of arylmethyl tosylates.[18]

Both sets of l values within Table 3 show increases with increasing electron-withdrawing ability of the substituent. For the sulfonium ions, there is a relatively large increase in going from the p-CH_3 substituent to the unsubstituted compound and then only a slight rise from 0.74 to 0.84 as one continues to the p-NO_2 substituent. With the series of tosylates, there is a fairly steady rise from 0.29 to 0.98 over the same range of substituents. The standard errors associated with the h values are rather large, reflecting the relatively small contribution that the hI term makes towards these linear free energy relationships. A consistent trend can be seen, however, of lower h values being associated with higher degrees of nucleophilic participation by the solvent, and the h values for a given substituent are only slightly dependent on the leaving group.

The very similar behaviour observed for the series of sulfonium ions and the series of tosylate esters strongly supports the belief that the N_T and I scales can be usefully applied to solvolyses of both $R–X^+$ (neutral leaving group) and R–X (anionic leaving group) substrates. The large l values for solvolyses of all but the p-Me derivatives suggest an S_N2 mechanism, and the significant hI contributions suggest that, at the transition state, bond-breaking is somewhat ahead of bond making, so that positive charge develops on the α-carbon but this is reduced, and the h values falls, as one moves towards the p-NO_2 substituent. The l value of 0.47 for the p-Me derivative is only slightly higher than values which have been observed in solvolyses of the *tert*-butyldimethylsulfonium ion[26] and *tert*-butyl chloride,[27] and the solvolyses of this substrate can best be considered as involving an ionization (S_N1 process) with appreciable nucleophilic solvation of the developing carbocation.[28]

It has also been possible to analyse the effect of variation of substituent for solvolyses in each solvent using the Hammett equation. This has been done using the σ^+ scale of values[25] and ρ values are reported in Table 4, as calculated both with and without inclusion of the p-Me substituent data. In ethanol, aqueous ethanol, methanol and TFE–ethanol, a higher correlation coefficient and higher F-test value are obtained with all six substituents, but in aqueous–TFE solvents and aqueous acetone the situation is reversed. In all cases, a slightly higher (more negative) ρ value is obtained with all six substituents. The ρ values with five substituents (no p-Me) can be compared with those reported[23] for solvolyses of the benzylic tosylates with a similar set of substituents in the same series of solvents. The earlier study[23] used σ values but, for the unsubstituted compound and derivatives with electron-withdrawing substituents, the σ and σ^+ scales are very similar in value.[25]

In the previous study[23] of the specific rates of solvolysis of a series of arylmethyl tosylates, the ρ values varied over quite a large range from -1.3 in 95% acetone to -5.0 in 97% TFE. These are also the extreme solvents in the present study, but the range is now only from -0.9 to -1.8. It has been indicated above that the sensitivities to changes in solvent nucleophilicity varied over a wider range for the tosylates than for the sulfonium ions, and we now see that substituent effects follow a similar pattern. These observations suggest that for the S_N2 transition states the variation of the structure with either substituent or solvent is greater for the tosylates than the sulfonium ions. This is probably related to the push–pull nature of the process for solvolyses of the tosylates, indicated by an appreciable sensitivity to changes in Y_{OTs} values,[18,23] as opposed to only a significant push for the solvolyses of the sulfonium ions.

Table 4 Variation of the Hammett equation ρ value, calculated using σ^+ values,[a] with solvent at 49.2 °C

Solvent	No. of compounds[b]	ρ[c]	c[d]	r[e]	F[f]
EtOH	6	−1.26 ± 0.09	0.09 ± 0.08	0.9888	176
	5	−1.17 ± 0.15	0.03 ± 0.08	0.9832	87
80% EtOH	6	−1.29 ± 0.11	0.12 ± 0.10	0.9852	133
	5	−1.11 ± 0.11	0.03 ± 0.07	0.9850	98
60% EtOH	6	−1.37 ± 0.10	0.10 ± 0.09	0.9895	188
	5	−1.20 ± 0.10	0.02 ± 0.06	0.9904	153
MeOH	6	−1.32 ± 0.10	0.10 ± 0.09	0.9895	187
	5	−1.19 ± 0.12	0.03 ± 0.07	0.9850	98
97% TFE	6	−2.52 ± 0.38	0.40 ± 0.34	0.9568	43
	5	−1.78 ± 0.22	0.02 ± 0.14	0.9770	63
80% TFE	6	−1.89 ± 0.27	0.33 ± 0.24	0.9608	48
	5	−1.37 ± 0.17	0.06 ± 0.11	0.9765	61
50% TFE	6	−1.57 ± 0.22	0.20 ± 0.19	0.9646	54
	5	−1.14 ± 0.07	−0.02 ± 0.04	0.9945	273
60T–40E	6	−1.54 ± 0.14	0.15 ± 0.12	0.9849	129
	5	−1.33 ± 0.15	0.04 ± 0.09	0.9816	79
95% Acetone	6	−1.20 ± 0.17	0.21 ± 0.15	0.9611	48
	5	−0.87 ± 0.11	0.04 ± 0.07	0.9767	62

[a] $\log (k/k_0) = \rho\sigma^+ + c$ (σ^+ values from ref. 25). [b] Using log k values for the unsubstituted compound (log k_0) together with all five derivatives or with four derivatives (excluding p-Me). [c] With associated standard error. [d] Reported together with the standard error of the estimate. [e] Correlation coefficient. [f] F-test value.

The data point for the p-methyl substituent lies somewhat above the plots, as indicated by the larger ρ values obtained when it is included in the analyses. This parallels the behaviour observed for the tosylate esters in acetic acid[23] and aqueous acetone.[23,29] Since our original communication concerning the tosylate esters, a very thorough study in terms of the LArSR equation,[30] with a large number of substituents, has been reported by Fujio, Tsuno and coworkers for solvolyses in 80% acetone[31] and acetic acid.[32] Their conclusions as regards a duality of mechanism are in accord both with our studies[18,23] and with earlier conclusions based on the use of σ^+ values.[33]

Conclusions

Application of either the Grunwald–Winstein equation to the effect of solvent variation with a given substituent or the Hammett equation to the effect of substituent variation with a given solvent indicates that for the substrates considered in this study there is a variation in solvolysis mechanism. The (p-methylbenzyl)methylphenylsulfonium ion solvolyses predominantly by an ionization mechanism but with an appreciable nucleophilic solvation of the developing carbocation, and the unsubstituted compound and derivatives with electron-withdrawing substituents by an S_N2 mechanism. Within the S_N2 range, the appreciably negative Hammett ρ values (-0.9 to -1.8) suggest that bond breaking is running ahead of bond making, such that positive charge is developed at the α-carbon of the transition state.

Within the S_N2 range, the sensitivities to changes in solvent nucleophilicities (l values) and the sensitivities to changes in the substituent (ρ values) vary over a narrower range than with the previously studied tosylates.[18,23] These observations both suggest that there is a much more limited variation in the structure of the S_N2 transition state for solvolyses of the benzylsulfonium ions than for the solvolyses of the benzyl tosylates. This is consistent with the major influence of solvent variation being only in the nucleophilic push for solvolyses of the sulfonium ions but with this effect being accompanied by appreciable variations in the electrophilic pull for solvolyses of the tosylate esters.

Experimental

Solvents were purified and kinetic runs carried out as previously described.[11]

(Arylmethyl)methylphenylsulfonium triflates

The procedure followed that previously reported for the preparation of (p-methoxybenzyl)dimethylsulfonium triflate,[14] but with an equivalent amount of methyl phenyl sulfide substituted for dimethyl sulfide. The benzyl bromide and five ring-substituted derivatives were used in the syntheses as received (Aldrich, 95–99%). The products were all obtained as white crystals. The ^{1}H NMR spectra contain a pair of doublets for the benzylic hydrogens, due to these hydrogens being prochiral within a monochiral sulfonium ion.

***p*-Methyl derivative.** Mp 111–112 °C; ^{1}H NMR ([$^2H_3$]CH_3-CN): 2.32 (s, 3H), 3.21 (s, 3H), 4.68 (d, $J = 12.7$ Hz, 1H), 4.85 (d, $J = 12.7$ Hz, 1H), 7.07 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 7.6–7.9 (m, 5H); IR (KBr) includes 3109, 3036, 2947, 2930, 1613, 1516, 1432, 1267, 1030, 820, 637 cm^{-1}; Calc. for $C_{16}H_{17}O_3S_2F_3$: C, 50.78; H, 4.53; S, 16.94. Found: C, 50.79; H, 4.50; S, 17.23%.

Unsubstituted compound. Mp 60–62 °C; ^{1}H NMR ([$^2H_3$]CH_3-CN): 3.18 (s, 3H), 4.72 (d, $J = 12.6$ Hz, 1H), 4.88 (d, $J = 12.6$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.3–7.5 (m, 3H), 7.6–7.9 (m, 5H); IR (KBr) includes 3129, 2950, 1657, 1448, 1279, 1246, 1030, 748, 698 cm^{-1}; Calc. for $C_{15}H_{15}O_3S_2F_3$: C, 49.44; H, 4.15; S, 17.60. Found: C, 49.50; H, 4.00; S, 17.81%.

***p*-Bromo derivative.** Mp 120–122 °C; ^{1}H NMR ([$^2H_3$]CH_3-CN): 3.19 (s, 3H), 4.69 (d, $J = 12.7$ Hz, 1H), 4.86 (d, $J = 12.7$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.5–7.9 (m, 5H); IR (KBr) includes 3075, 3032, 2934, 1593, 1489, 1449, 1271, 1071, 1030, 839, 637, 571 cm^{-1}; Calc. for $C_{15}H_{14}O_3S_2F_3Br$: C, 40.64; H, 3.18; S, 14.46. Found: C, 41.10; H, 3.36; S, 14.92.

***m*-Fluoro derivative.** Mp 54–55 °C; ^{1}H NMR ([$^2H_3$]CH_3CN): 3.20 (s, 3H), 4.71 (d, $J = 12.7$ Hz, 1H), 4.89 (d, $J = 12.7$ Hz, 1H), 6.9–7.9 (m, 9H); IR (KBr) includes 3020, 2920, 1590, 1450, 1260, 1030, 760, 690 cm^{-1}; Calc. for $C_{15}H_{14}O_3S_2F_4$: C, 47.13; H, 3.66; S, 16.77. Found: C, 47.00; H, 3.87; S, 17.21%.

***p*-Trifluoromethyl derivative.** Mp 83–85 °C; ^{1}H NMR ([$^2H_3$]CH_3CN): 3.21 (s, 3H), 4.77 (d, $J = 12.9$ Hz, 1H), 4.95 (d, $J = 12.9$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.5–7.9 (m, 7H); IR (KBr) includes 3020, 2950, 1620, 1440, 1325, 1270, 1150, 1030, 855, 750, 690 cm^{-1}; Calc. for $C_{16}H_{14}O_3S_2F_6$: C, 44.44; H, 3.26; S, 14.83. Found: C, 44.43; H, 3.22; S, 14.76%.

***p*-Nitro derivative.** Mp 91–93 °C; ^{1}H NMR ([$^2H_3$]CH_3CN): 3.23 (s, 3H), 4.80 (d, $J = 12.8$ Hz, 1H), 4.97 (d, $J = 12.8$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.5–7.9 (m, 5H), 8.16 (d, $J = 8.8$ Hz, 2H); IR (KBr) includes 3027, 2992, 2940, 1607, 1526, 1422, 1356, 1275, 1028, 860 cm^{-1}; Calc. for $C_{15}H_{14}O_5NS_2F_3$: C, 44.01; H, 3.45; N, 3.42; S, 15.66. Found: C, 44.13; H, 3.45; N, 3.41; S, 16.19%.

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