Reactions of sulfonyl chlorides with silyl enol ethers catalysed by a ruthenium(II) phosphine complex: convenient synthesis of β-keto sulfones

Nobumasa Kamigata,* Kumiko Udodaira and Toshio Shimizu

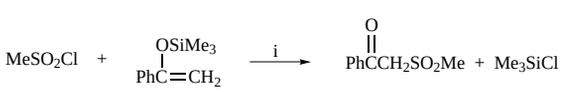
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan

The reactions of alkane- and arene-sulfonyl chlorides with silyl enol ethers in the presence of a ruthenium(II) phosphine complex are found to give β-keto sulfones in good to high yields.

Previously, we have reported that the ruthenium(II)-catalysed reactions of alkane- and arene-sulfonyl chlorides with alkenes afforded the corresponding 1:1 adducts in high yields.[1] The reaction is considered to proceed *via* a radical intermediate confined in the coordination sphere of the ruthenium complex; hence the radical is of reduced reactivity but of high selectivity and thus gives a reaction product in high yield without any accompanying side-products. Recently, Utimoto and co-workers reported a radical reaction of perfluoroalkyl iodide with 1-trimethylsilyloxycyclohexene mediated by triethylborane and base which gives perfluoroalkylated trimethylsilyl enol ethers.[2] These results prompted us to investigate the ruthenium(II)-catalysed radical reactions of some sulfonyl chlorides with various silyl enol ethers, which we found provided β-keto sulfones in good to high yields. The results are described herein.

Results and discussion

A solution of methanesulfonyl chloride **1a** (2.0 mmol), 1-trimethylsilyloxy-1-phenylethene **2a** (2.0 mmol) and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (4.0 cm^3) when degassed and heated at 120 °C for 7 h, reacted smoothly to afford methyl phenacyl sulfone **3a** in 86% isolated yield (Scheme 1). No 1:1 adduct such as 1-chloro-2-methylsulfonyl-1-trimethylsilyloxy-1-phenylethane was found in the reaction products. There was no reaction in the absence of the ruthenium(II) catalyst, unchanged **1a** and **2a** being recovered. The reaction is, therefore, truly a catalytic one.



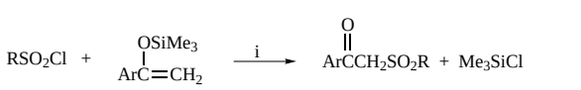
Scheme 1 *Reagent and conditions:* i, $[RuCl_2(PPh_3)_3]$, C_6H_6, 120 °C, 7 h

Product **3a** can be regarded not only as an α-substituted methylsulfonyl derivative of acetophenone, which is a starting material of silyl enol ether **2a**, but also as an active methylene compound containing carbonyl and sulfonyl groups. The present reaction seems to be a convenient and an excellent method for the synthesis of β-keto sulfones since it is known that the reactions of a metal (sodium or potassium) enolate of 3,3-dimethylbutanone with benzenesulfonyl chloride gives 1-chloro-3,3-dimethylbutanone and with benzenesulfonyl fluoride affords a mixture of 1-phenylsulfonyl-3,3-dimethylbutanone and 3,3-dimethyl-2-phenylsulfonyloxybut-1-ene.[3] Since active methylene compounds are important intermediates for reactions such as Michael addition, a number of sulfonyl chlorides were allowed to react with a variety of silyl enol ethers in order to investigate the scope and limitation of this reaction for the synthesis of β-keto sulfones (Scheme 2). The results are summarized in Table 1.

Table 1 Reaction of sulfonyl chlorides with silyl enol ethers in the presence of a ruthenium(II) phosphine complex

R in **1**	Ar in **2**	Product	Yield[a] (%)
1a Me	**2a** Ph	**3a**	86
1b *p*-Tol	**2a** Ph	**3b**	86
1c C_6F_5	**2a** Ph	**3c**	91
1a Me	**2b** *p*-$MeOC_6H_4$	**3d**	55
1b *p*-Tol	**2b** *p*-$MeOC_6H_4$	**3e**	69
1c C_6F_5	**2b** *p*-$MeOC_6H_4$	**3f**	54
1a Me	**2c** *p*-MeC_6H_4	**3g**	60
1b *p*-Tol	**2c** *p*-MeC_6H_4	**3h**	70
1c C_6F_5	**2c** *p*-MeC_6H_4	**3i**	71
1a Me	**2d** *p*-FC_6H_4	**3j**	50
1b *p*-Tol	**2d** *p*-FC_6H_4	**3k**	79
1c C_6F_5	**2d** *p*-FC_6H_4	**3l**	57
1a Me	**2e** *p*-ClC_6H_4	**3m**	68
1b *p*-Tol	**2e** *p*-ClC_6H_4	**3n**	75
1c C_6F_5	**2e** *p*-ClC_6H_4	**3o**	76
1a Me	**2f** *p*-$NO_2C_6H_4$	**3p**	65
1b *p*-Tol	**2f** *p*-$NO_2C_6H_4$	**3q**	67
1c C_6F_5	**2f** *p*-$NO_2C_6H_4$	**3r**	63

[a] Isolated yield.



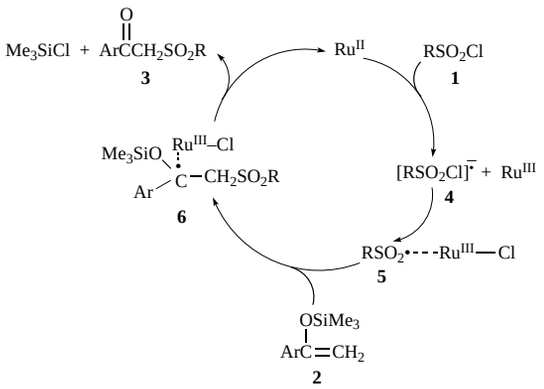
a R = Me
b R = *p*-Tol
c R = C_6F_5

Scheme 2 *Reagent and conditions:* i, $[RuCl_2(PPh_3)_3]$, C_6H_6, 120 °C, 7 h

As shown in Table 1, the ruthenium(II)-catalysed reactions of toluene-*p*-sulfonyl chloride **1b** and pentafluorobenzenesulfonyl chloride **1c** with **2a** under similar conditions afforded the corresponding β-keto sulfones **3b** and **3c**, respectively, in high yields. Similarly, the reactions of the sulfonyl chlorides **1a–c** with 1-trimethylsilyloxy-1-(4′-methoxyphenyl)ethene **2b**, 1-trimethylsilyloxy-1-(4′-tolyl)ethene **2c**, 1-trimethylsilyloxy-1-(4′-fluorophenyl)ethene **2d**, 1-trimethylsilyloxy-1-(4′-chlorophenyl)ethene **2e** and 1-trimethylsilyloxy-1-(4′-nitrophenyl)-ethene **2f** in the presence of the ruthenium(II) catalyst gave the corresponding β-keto sulfones **3d–r** in good to high yields irrespective of the substituent (an electron-donating or

-withdrawing group) on the aromatic ring of silyl enol ether. Thus, the present ruthenium(II)-catalysed reactions of sulfonyl chloride with silyl enol ether were found to be a convenient and an excellent method for the synthesis of β-keto sulfones.

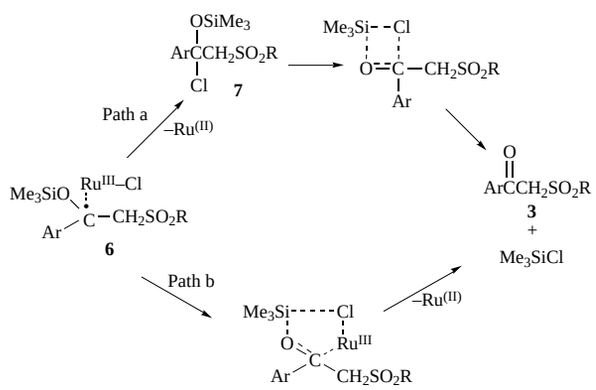
A mechanism for the ruthenium(II)-catalysed reactions of sulfonyl chloride **1** with silyl enol ethers **2** is given in Scheme 3.



Scheme 3

The redox-transfer reaction between the sulfonyl chloride **1** and the ruthenium(II) catalyst affords the anion radical **4** of compound **1**, which is cleaved homolytically to give the sulfonyl radical **5** and Ru^{III}–Cl. The sulfonyl radical **5** adds to the carbon–carbon double bond of the silyl enol ether **2** to give the carbon radical **6** which affords the β-keto sulfone **3** and trimethylchlorosilane, the ruthenium(II) catalyst being regenerated. The radicals **5** and **6** are considered to be confined in the coordination sphere of the ruthenium catalyst.[4]

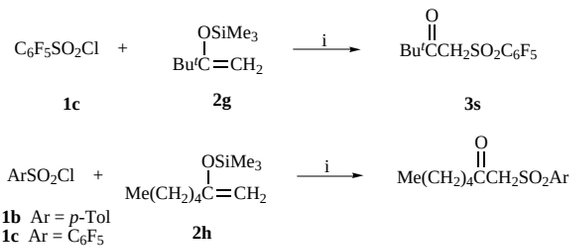
Two pathways are plausible for the formation of the β-keto sulfone and trimethylchlorosilane from the radical intermediate **6** (see Scheme 4). One is abstraction of the chlorine which is



Scheme 4

bonded to the ruthenium by the carbon radical to give a 1:1 adduct **7** and ruthenium(II) complex. Adduct **7** will rapidly degrade to the β-keto sulfone **3** and trimethylchlorosilane probably *via* a four-centre type reaction, the affinity between silicon and chlorine being strong and the reaction occurring very easily (path a). The other mechanism is direct reaction between silicon and chlorine atoms in the radical intermediate **6** *via* a five-membered ring (path b); since **6** is thought to be confined to the coordination sphere of the ruthenium complex, such a transition state will easily form. The fact that no adduct **7** (Ar = Ph, R = *p*-tolyl) was found in the reaction mixture in the ruthenium(II)-catalysed reaction of **1b** with **2a** suggests that either adduct **7** will eliminate trimethylchlorosilane very rapidly under the reaction conditions (path a) or **3** is formed directly from **6** *via* the 5-centre transition state (path b).

If we suppose that **7** is initially formed when **1b** and **2a** react in the presence of a base, this adduct is expected to give 1-aryl-



Scheme 5 *Reagent and conditions:* i, $[RuCl_2(PPh_3)_3]$, C_6H_6, 120 °C, 7 h

1-trimethylsilyloxy-2-(*p*-tolylsulfonyl)ethene (R = tosyl) by base-catalysed β-elimination reaction competing with the elimination of trimethylchlorosilane to give **3**. However, since no 1-trimethylsilyloxy-1-phenyl-2-(*p*-tolylsulfonyl)ethene was obtained in the ruthenium(II)-catalysed reaction of **1b** with **2a** in the presence of 2,6-di-*tert*-butylpyridine, **3b** and trimethylsilane being formed instead, path b is the more plausible mechanism.

The ruthenium(II)-catalysed reactions of sulfonyl chloride with 1-alkyl-1-trimethylsilyloxyethene were investigated under similar conditions. The ruthenium(II)-catalysed reaction of **1c** with 3,3-dimethyl-2-trimethylsilyloxybut-1-ene **2g** gave 1-pentafluorophenylsulfonyl-3,3-dimethylbutan-2-one **3s** in low yield (12%) contrary to our expectation. Moreover, only a trace amount of the corresponding β-keto sulfone was obtained in the reactions of **1b** and **1c** with 2 trimethylsilyloxyhept-1-ene **2h** in the presence of a ruthenium(II) complex. These results suggest that the carbon radical formed by the addition of a sulfonyl radical to the carbon–carbon double-bond of the silyl enol ether **2g** or **2h** is unstable since the carbon radical cannot be resonance stabilized with any neighbouring substituent. Thus, it is considered that the addition of a sulfonyl radical to the carbon–carbon double bond of silyl enol ethers possessing only an alkyl group such as **2h** is a difficult process. This may be a limitation of the ruthenium(II)-catalysed reaction.

In conclusion, we have found that the reactions of sulfonyl chlorides with silyl enol ethers, prepared from acetophenone derivatives, in the presence of a ruthenium(II) complex gave the corresponding β-keto sulfones in good to high yield. This is therefore an excellent method for conveniently synthesising active methylene compounds.

Experimental

Mps were determined on a Yamato MP21 apparatus and are uncorrected. IR Spectra were determined on a JASCO A-100 IR spectrophotometer with samples as either neat liquids or KBr disks. ^1H and ^{13}C NMR spectra were determined on a JEOL JNM-EX 400 FT NMR spectrometer at 400 and 100 MHz, respectively, using Me_4Si as an internal standard. ^{19}F NMR Spectra were taken on a JEOL JNM-EX 400 FT NMR spectrometer at 376 MHz using $CFCl_3$ as an external standard; *J* values are given in Hz. Mass spectra were measured on a JEOL JMS-AX 500 spectrometer by electron impact (EI) at 70 eV. Gas-liquid chromatography (GLC) were performed using a Hitachi G-3000 gas chromatograph with OV-1 (10%) 25 m capillary column. Gel-permeation chromatography (GPC) was performed using a JAI LC-08 and JAI LC-908 liquid chromatograph with two JAIGEL-1H columns (20 × 600 mm) with chloroform as eluent.

All solvents were distilled and stored under nitrogen. *p*-Methoxyacetophenone and *p*-fluoroacetophenone were from Wako Chemicals, *p*-methylacetophenone, *p*-nitroacetophenone and 3,3-dimethylbutan-2-one were from Nakarai Chemicals, heptan-2-one and *p*-chloroacetophenone were from Tokyo Kasei Chemicals and trimethylchlorosilane was obtained from

the Shinetsu Chemical Industry. All were used without further purification for the preparation of the corresponding silyl enol ethers. 1-Trimethylsilyloxy-1-phenylethene **2a** from Aldrich Chemicals was used without further purification. Methanesulfonyl chloride from Wako Chemicals and pentafluorobenzenesulfonyl chloride from Hydrus Chemicals were used without further purification. Toluene-*p*-sulfonyl chloride from Wako Chemicals was recrystallized from hexane prior to use. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared by the method described in the literature, mp 123 °C.[5]

General procedures for the preparation of silyl enol ethers[6] 2b–f

To a solution of aryl methyl ketone (80 mmol) in DMF (32 ml) under nitrogen was added triethylamine (19.5 g, 192 mmol) followed by trimethylchlorosilane (10.4 g, 96 mmol). After the solution had been refluxed and stirred for 48 h, it was extracted with pentane (80 cm^3) and the extract was washed with a saturated aqueous potassium hydrogen carbonate (× 3), water (80 cm^3 × 3), 1.5 M hydrochloric acid (80 cm^3 × 2), water (80 cm^3), saturated aqueous potassium hydrogen carbonate (80 cm^3 × 2), water (80 cm^3 × 2) and brine (80 cm^3). The solvent then evaporated under reduced pressure and the residual oily silyl enol ether was distilled. Yields and boiling points of silyl enol ethers are as follows: 1-trimethylsilyloxy-1-(4′-methoxyphenyl)ethene **2b** (50%), bp 88 °C/0.50 mmHg; 1-trimethylsilyloxy-1-(4′-tolyl)ethene **2c** (67%), bp 59–60 °C/0.45 mmHg; 1-trimethylsilyloxy-1-(4′-fluorophenyl)ethene **2d** (59%), bp 43–46 °C/0.50 mmHg; 1-trimethylsilyloxy-1-(4′-chlorophenyl)ethene **2e** (42%), bp 54–56 °C/0.8 mmHg; 1-trimethylsilyloxy-1-(4′-nitrophenyl)-ethene **2f** (34%), bp 95–97 °C/0.45 mmHg.

Preparation of the silyl enol ethers 2g and 2h

3,3-Dimethyl-2-trimethylsilyloxybut-1-ene **2g** was prepared from 3,3-dimethylbutan-2-one by the method reported in the literature;[6] yield 33%. 2-Trimethylsilyloxyhept-1-ene **2h** was prepared according to the literature by treating heptan-2-one with LDA in THF at − 78 °C and then adding trimethylchlorosilane to the resultant lithium enolate of heptan-2-one.[7]

General procedure for the reaction of sulfonyl chlorides with silyl enol ethers

A solution containing the sulfonyl chloride **1** (2.0 mmol), silyl enol ether **2** (2.0 mmol) and dichlorotris(triphenylphosphine)-ruthenium(II) (0.02 mmol) in dry benzene (4.0 cm^3) was degassed by a freeze–pump–thaw cycle, sealed in an ampoule and heated at 120 °C for 7 h.The reaction mixture was subjected to column chromatography on Merck 7734 silica gel 60 with hexane–ethyl acetate (5:1) as eluent. The product was further purified by recrystallization from dichloromethane–hexane and identified by IR, NMR and MS spectroscopy. The physical and spectral data for the compounds obtained are as follows.

Methyl phenacyl sulfone 3a. Colourless needles; mp 106.7–107.0 °C (from CH_2Cl_2–hexane; lit.,[8] 106–107 °C); ν_{max}(KBr)/cm^{-1} 3000, 2950, 1680, 1300 and 1150; δ_H(400 MHz, $CDCl_3$) 3.16 (3 H, s), 4.61 (2 H, s), 7.54 (2 H, dd, *J* 8.0 and 7.4), 7.67 (1 H, t, *J* 7.4) and 8.01 (2 H, d, *J* 8.0); δ_C(100 MHz, $CDCl_3$) 41.8, 61.3, 129.1, 129.3, 134.8, 135.6 and 189.2; *m/z* 198 (M^+), 105 and 77.

Phenacyl 4′-tolyl sulfone 3b. Colourless needles; mp 106.4–106.8 °C (from CH_2Cl_2–hexane; lit.,[9] 108 °C); ν_{max}(KBr)/cm^{-1} 3000, 1680, 1320 and 1150; δ_H(400 MHz, $CDCl_3$) 2.44 (3 H, s), 4.71 (2 H, s), 7.33 (2 H, d, *J* 8.3), 7.48 (1 H, dd, *J* 8.3 and 7.3), 7.61 (1 H, t, *J* 7.3), 7.76 (2 H, d, *J* 8.3) and 7.94 (2 H, d, *J* 8.3); δ_C(100 MHz, $CDCl_3$) 21.6, 63.5, 128.5, 128.8, 129.3, 129.8, 134.3, 135.7, 136.0, 145.3 and 188.1; *m/z* 274 (M^+) and 211.

Pentafluorophenyl phenacyl sulfone 3c. Colourless needles; mp 141.4–142.5 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 3000, 2950, 1700, 1490, 1350, 1270, 1160 and 990; δ_H(400 MHz, $CDCl_3$) 4.29 (2 H, s), 7.52 (2 H, dd, *J* 8.3 and 7.3), 7.68 (1 H, t, *J* 7.3) and 7.93 (2 H, d, *J* 8.3); δ_C(100 MHz, $CDCl_3$) 63.1, 129.0, 129.2, 135.0, 135.1 and 187.8; δ_F(376 MHz, $CDCl_3$) 135.88–136.01 (2 F, m), 142.84 (1 F, tt, *J* 21.3 and 7.8) and 158.27–158.43 (2 F, m); *m/z* 350 (M^+), 287, 183 and 167 (Found: C, 48.00; H, 1.81. Calc. for $C_{14}H_7F_5O_3S$: C, 48.01; H, 2.01%).

4-Methoxyphenacyl methyl sulfone 3d. Colourless needles; mp 136.0–136.9 °C (from CH_2Cl_2–hexane; lit.,[10] 136–137 °C); ν_{max}(KBr)/cm^{-1} 3150, 2960, 1670, 1600, 1330, 1310, 1270, 1190 and 1160; δ_H(400 MHz, $CDCl_3$) 3.13 (3 H, s), 3.90 (3 H, s), 4.54 (2 H, s), 6.98 (2 H, d, *J* 8.8) and 7.98 (2 H, d, *J* 8.8); δ_C(100 MHz, $CDCl_3$) 41.7, 55.6, 61.1, 114.2, 128.6, 131.9, 164.8 and 187.3; *m/z* 229 (M^+ + 1), 150, 136 and 107.

4-Methoxyphenacyl 4′-tolyl sulfone[11] 3e. Colourless needles; mp 124.0–124.4 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 2950, 2900, 1675, 1600, 1570, 1310, 1260, 1180 and 1140; δ_H(400 MHz, $CDCl_3$) 2.44 (3 H, s), 3.89 (3 H, s), 4.66 (2 H, s), 6.95 (2 H, d, *J* 8.8), 7.33 (2 H, d, *J* 8.1), 7.75 (2 H, d, *J* 8.1) and 7.94 (2 H, d, *J* 8.8); δ_C(100 MHz, $CDCl_3$) 22.0, 55.9, 63.9, 114.3, 128.9, 129.2, 130.1, 132.2, 136.0, 145.6, 164.8 and 186.6; *m/z* 304 (M^+), 240 and 135.

4-Methoxyphenacyl pentafluorophenyl sulfone 3f. Colourless needles; mp 112.9–113.3 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 3020, 2980, 2900, 1690, 1600, 1500, 1340, 1260 and 1170; δ_H(400 MHz, $CDCl_3$) 3.91 (3 H, s), 4.86 (2 H, s), 6.99 (2 H, d, *J* 6.8) and 7.92 (2 H, d, *J* 6.8); δ_C(100 MHz, $CDCl_3$) 55.7, 63.1, 114.4, 128.2, 131.6, 165.1 and 185.8; δ_F(376 MHz, $CDCl_3$) 136.67–136.80 (2 F, m), 143.77 (1 F, tt, *J* 21.4 and 7.5) and 159.11–159.28 (2 F, m); *m/z* 381 (M^+ + 1), 317, 231, 167 and 134 (Found: C, 47.60; H, 2.30. Calc. for $C_{15}H_9F_5O_4S$: C, 47.38; H, 2.39%).

Methyl 4-methylphenacyl sulfone 3g. Colourless needles; mp 114.0–114.7 °C (from CH_2Cl_2–hexane; lit.,[12] 114–117 °C); ν_{max}-(KBr)/cm^{-1} 3000, 2940, 1660, 1600, 1420, 1320 and 1160; δ_H(400 MHz, $CDCl_3$) 2.44 (3 H, s), 3.14 (3 H, s), 4.58 (2 H, s), 7.32 (2 H, d, *J* 8.3) and 7.90 (2 H, d, *J* 8.3); δ_C(100 MHz, $CDCl_3$) 21.8, 41.7, 61.2, 129.4, 129.7, 133.1, 146.0 and 188.7; *m/z* 212 (M^+), 119 and 91.

4-Methylphenacyl 4′-tolyl sulfone 3h. Colourless needles; mp 112.1–112.4 °C (from CH_2Cl_2–hexane; lit.,[9] 112 °C); ν_{max}(KBr)/cm^{-1} 2960, 1670, 1610, 1310 and 1150; δ_H(400 MHz, $CDCl_3$) 2.33 (3 H, s), 2.43 (3 H, s), 4.68 (2 H, s), 7.28 (2 H, d, *J* 8.3), 7.33 (2 H, d, *J* 8.3), 7.75 (2 H, d, *J* 8.3) and 7.85 (2 H, d, *J* 8.3); δ_C(100 MHz, $CDCl_3$) 22.0, 22.1, 63.9, 128.9, 129.80, 129.83, 130.1, 133.7, 136.1, 145.6, 145.8 and 187.9; *m/z* 288 (M^+), 225 and 120.

4-Methylphenacyl pentafluorophenyl sulfone 3i. Colourless needles; mp 151.8–152.1 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 2980, 2910, 1690, 1610, 1500, 1350 and 1150; δ_H(400 MHz, $CDCl_3$) 2.45 (3 H, s), 4.89 (2 H, s), 7.32 (2 H, d, *J* 8.3) and 7.83 (2 H, d, *J* 8.3); δ_C(100 MHz, $CDCl_3$) 22.1, 63.5, 129.5, 130.2, 133.0, 146.8 and 187.5; δ_F(376 MHz, $CDCl_3$) 136.66–136.79 (2 F, m), 144.0 (1 F, tt, *J* 22.0 and 7.1) and 159.03–159.22 (2 F, m); *m/z* 364 (M^+), 344, 300, 168 and 119 (Found: C, 49.27; H, 2.29. Calc. for $C_{15}H_9F_5O_3S$: C, 49.46; H, 2.49%).

4-Fluorophenacyl methyl sulfone 3j. Colourless needles; mp 112.5–113.4 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 3020, 1670, 1590, 1420, 1300, 1230 and 1140; δ_H(400 MHz, $CDCl_3$) 3.15 (3 H, s), 4.57 (2 H, s), 7.21 (2 H, dd, *J* 7.8 and 7.8) and 8.06 (2 H, dd, *J* 7.8 and 5.4); δ_C(100 MHz, $CDCl_3$) 41.7, 61.5, 116.3, 132.1, 132.3, 166.7 and 187.6; *m/z* 216 (M^+), 201, 138 and 96; δ_F(376 MHz, $CDCl_3$) 102.80–102.88 (1 F, m) (Found: C, 50.04; H, 4.11. Calc. for $C_9H_9FO_3S$: C, 49.99; H, 4.20%).

4-Fluorophenacyl 4′-tolyl sulfone 3k. Colourless needles; mp 134.0–134.4 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 3010, 1680, 1600, 1420, 1290, 1230 and 1150; δ_H(400 MHz, $CDCl_3$) 2.45 (3 H, s), 4.68 (2 H, s), 7.16 (2 H, dd, *J* 8.6 and 8.6), 7.34 (2 H, d, *J* 8.3), 7.75 (2 H, d, *J* 8.3) and 8.01 (2 H, dd, *J* 8.6 and 5.4); δ_C(100 MHz, $CDCl_3$) 21.7, 63.7, 116.1, 128.5, 129.9, 131.5, 132.2, 135.6, 145.5, 166.4 and 186.5; δ_F(376 MHz, $CDCl_3$) 103.52–103.60 (1 F, m); *m/z* 292 (M^+), 226, 155, 123 and 95 (Found: C, 61.51; H, 4.35. Calc. for $C_{15}H_{13}FO_3S$: C, 61.63; H, 4.48%).

4-Fluorophenacyl pentafluorophenyl sulfone 3l. Colourless needles; mp 127.4–128.0 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 2950, 1700, 1600, 1500, 1320, 1220 and 1160; δ_H(400 MHz, $CDCl_3$) 4.89 (2 H, s), 7.21 (2 H, dd, *J* 8.6 and 8.6) and 7.99 (2 H, dd, *J* 8.6 and 5.4); δ_C(100 MHz, $CDCl_3$) 63.2, 116.5, 131.6, 132.0, 166.9 and 186.2; δ_F(376 MHz, $CDCl_3$) 101.91–101.97 (1 F, m), 136.55–136.68 (2 F, m), 143.19 (1 F, tt, *J* 21.1 and 8.2) and 158.82–158.99 (2 F, m); *m/z* 368 (M^+), 304, 168 and 123 (Found: C, 45.64; H, 1.46. Calc. for $C_{14}H_6F_6O_3S$: C, 45.66; H, 1.64%).

4-Chlorophenacyl methyl sulfone 3m. Colourless needles; mp 142.3–143.1 °C (from CH_2Cl_2–hexane; lit.,[11] 147–148 °C); ν_{max}(KBr)/cm^{-1} 3050, 2950, 1680, 1590, 1410, 1300 and 1120; δ_H(400 MHz, $CDCl_3$) 3.14 (3 H, s), 4.57 (2 H, s), 7.50 (2 H, d, *J* 8.8) and 7.95 (2 H, d, *J* 8.8); δ_C(100 MHz, $CDCl_3$) 41.7, 61.3, 129.4, 130.6, 133.9, 141.5 and 188.0; *m/z* 232 (M^+), 154, 141 and 111.

4-Chlorophenacyl 4′-tolyl sulfone 3n. Colourless needles; mp 134.4–134.9 °C (from CH_2Cl_2–hexane; lit.,[9] 137 °C); ν_{max}(KBr)/cm^{-1} 3000, 1680, 1590, 1310 and 1150; δ_H(400 MHz, $CDCl_3$) 2.45 (3 H, s), 4.58 (2 H, s), 7.34 (2 H, d, *J* 8.3), 7.46 (2 H, d, *J* 8.3), 7.74 (2 H, d, *J* 8.3) and 7.91 (2 H, d, *J* 8.3); δ_C(100 MHz, $CDCl_3$) 22.0, 64.1, 128.9, 129.5, 130.2, 131.1, 134.4, 135.9, 141.4, 145.9 and 187.3; *m/z* 308 (M^+), 244, 139 and 91.

4-Chlorophenacyl pentafluorophenyl sulfone 3o. Colourless needles; mp 152.5–153.1 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 3000, 2950, 1690, 1590, 1500, 1360, 1310, 1220, 1160 and 950; δ_H(400 MHz, $CDCl_3$) 4.88 (2 H, s), 7.52 (2 H, d, *J* 8.8) and 7.89 (2 H, d, *J* 8.8); δ_C(100 MHz, $CDCl_3$) 63.1, 129.6, 130.4, 133.4, 141.9 and 186.6; δ_F(376 MHz, $CDCl_3$) 136.50–136.64 (2 F, m), 143.06 (1 F, tt, *J* 22.4 and 7.5) and 158.74–158.91 (2 F, m); *m/z* 384 (M^+), 320, 141 and 111 (Found: C, 43.67; H, 1.47. Calc. for $C_{14}H_6F_5ClO_3S$: C, 43.71; H, 1.57%).

Methyl 4-nitrophenacyl sulfone[13] 3p. Pale yellow needles; mp 148.9–149.4 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1}) 3100, 3030, 2950, 1680, 1600, 1520, 1310, 1150 and 1120; δ_H(400 MHz, $CDCl_3$) 3.17 (3 H, s), 4.65 (2 H, s), 7.90 (2 H, d, *J* 7.1) and 8.20 (2 H, d, *J* 7.1); δ_C(100 MHz, $CDCl_3$) 41.8, 61.7, 124.2, 130.5, 139.9, 150.8 and 188.2; *m/z* 244 (M^+ + 1), 227, 180, 164 and 151.

4-Nitrophenacyl 4′-tolyl sulfone 3q. Pale yellow needles; mp 142.2–142.9 °C (from CH_2Cl_2–hexane; lit.,[8] 145 °C); ν_{max}(KBr)/cm^{-1} 3000, 1690, 1600, 1530, 1350, 1310 and 1150; δ_H(400 MHz, $CDCl_3$) 2.46 (3 H, s), 4.77 (2 H, s), 7.37 (2 H, d, *J* 8.1), 7.75 (2 H, d, *J* 8.1), 8.15 (2 H, d, *J* 9.0) and 8.33 (2 H, d, *J* 9.0); δ_C(100 MHz, $CDCl_3$) 21.4, 64.0, 123.9, 128.5, 130.0, 130.5, 135.3, 139.9, 145.9, 150.7 and 187.0; *m/z* 319 (M^+), 255, 240, 150 and 91.

4-Nitrophenacyl pentafluorophenyl sulfone 3r. Pale yellow needles; mp 184.3–185.0 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 2950, 1700, 1530, 1500, 1350, 1170, 1140 and 950; δ_H(400 MHz, $CDCl_3$) 4.95 (2 H, s), 8.16 (2 H, d, *J* 8.8) and 8.40 (2 H, d, *J* 8.8); δ_C(100 MHz, $CDCl_3$) 63.2, 124.3, 130.4, 139.6, 150.7 and 187.2; δ_F(376 MHz, $CDCl_3$) 136.29–136.43 (2 F, m), 142.26 (1 F, tt, *J* 21.0 and 8.3) and 158.33–158.50 (2 F, m); *m/z* 395 (M^+), 331, 167 and 151 (Found: C, 42.92; H, 1.40; N, 3.55. Calc. for $C_{14}H_6NF_5O_5S$: C, 42.54; H, 1.53; N, 3.54%).

1-Pentafluorophenylsulfonyl-3,3-dimethylbutanone 3s. Colourless plates; mp 137.9–138.4 °C (from CH_2Cl_2–hexane); ν_{max}(KBr)/cm^{-1} 3000, 1720, 1500, 1360, 1310, 1170 and 1100; δ_H(400 MHz, $CDCl_3$) 1.19 (9 H, s) and 4.49 (2 H, s); δ_C(100 MHz, $CDCl_3$) 25.4, 45.5, 61.3 and 203.5; δ_F(376 MHz, $CDCl_3$) 137.36–137.49 (2 F, m), 144.18 (1 F, tt, *J* 21.8 and 7.1) and 159.26–159.36 (2 F, m); *m/z* 331 (M^+ + 1), 266, 231 and 99 (Found: C, 43.64; H, 3.36. Calc. for $C_{12}H_{11}F_5O_3S$: C, 43.46; H, 3.20%).

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