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Alkenyl C–H insertion of a β-disulfone iodonium ylide into flavones

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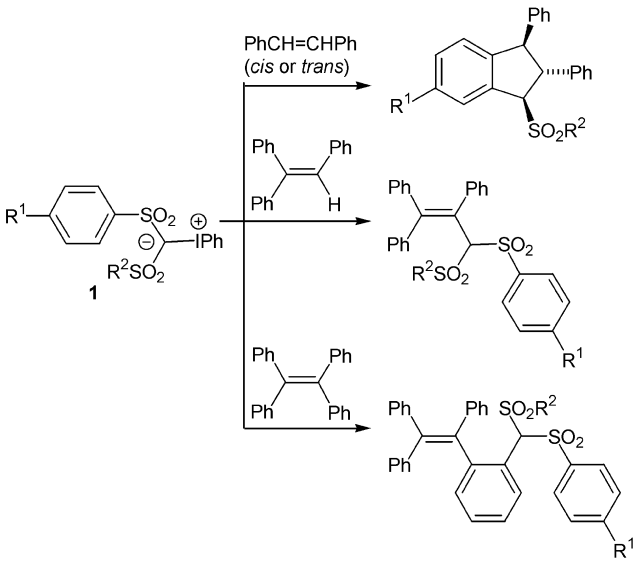
Abstract—The reaction of phenyliodonium bis(phenylsulfonyl)methylide with flavones affords insertion products into the alkenyl carbon–hydrogen bond of the flavone, presumably by an electrophilic attack of the iodonium ylide on the double bond of the flavone.

1. Introduction

The chemical behavior[1] of hypervalent iodine ylides is similar to the related diazo compounds;[2] for the latter a carbene (or carbenoid)[3] mechanism is presumably involved to account for its reactivity, although this has been questioned quite often.[4] The particular case of the phenyliodonium bis(phenylsulfonyl)methylide (**1**),[5] a rare example of an iodonium ylide, is more reactive than the analogous bis(phenylsulfonyl)diazomethane,[6] which displays thermal and photochemical persistence. Under copper(II)-catalyzed thermal activation, the ylide **1** decomposes[5] into bis(phenylsulfonyl)methylene, evidenced by the isolation[5,7] of phenyl benzene-thiosulfonate, while in the presence of alkyl-substituted alkenes, photochemical or copper(II)-catalyzed thermal activation leads to the corresponding cyclopropanes.[5] In constrast, we had shown previously that iodonium ylide **1** affords[8] with phenylated alkenes (*cis* or *trans*) at room temperature with or without catalytic amounts of $Rh_2(OAc)_4$ the *trans*,*trans*-1,2,3-trisubstituted indanes (Scheme 1), whereas, with triphenylethylene and tetraphenylethylene insertion occurs[9] into the alkenyl and phenyl C–H bonds of the substrate. Such a reactivity is unique for an iodonium ylide, since it is known[3,4] that the reaction of carbonyl-substituted iodonium ylides with *cis*-1,2-disubstituted alkenes yields cyclopropanes or dihydrofurans. With tri- and tetrasubstituted alkenes no reaction is observed, and the usual decomposition products of the ylides are formed. This perplexing diversity displayed in the reactivity pattern of the bis(sulfonyl)iodonium ylides was explained by postulating an initial electrophilic addition of the ylide on to the olefinic double bond and subsequent formation of either the [3+2] cycloadduct or the insertion product.

In the case of flavones, commonly present in nature[10] as the color-providing ingredients, only some ylide chemistry is known to date. For example, when treated with dimethylsulfoxonium methylide, flavones are converted[11] into γ-diketone derivatives. Presumably, the latter arise from the hydrolysis of the initially formed cyclopropanes during work-up; nevertheless, with isoflavones the corresponding cyclopropanes persist. Since the reaction of flavones with iodonium ylides had not been investigated previously, it was of interest to assess whether cyclopropane adducts are obtained or, analogous to phenylated ethylenes (Scheme 1), the [2+3] cycloadducts and C–H insertion products in



Scheme 1.

Keywords: iodonium ylides; C–H insertion; flavone; β-disulfone.
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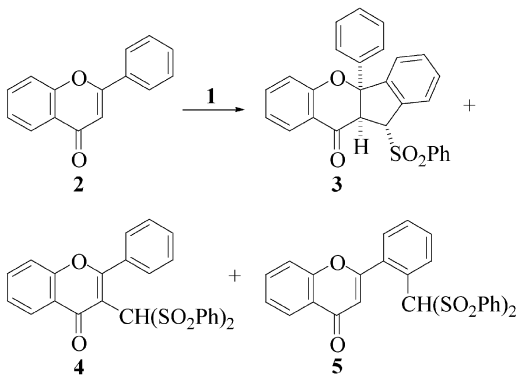
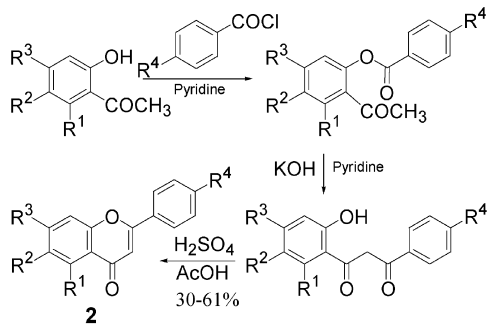
Scheme 2 are formed. We report herein that ylide **1** reacts with flavones **2** to yield only the alkenyl C–H insertion products **4** in good yield, analogous to the reaction of the ylide **1** with triphenylethylene.[9]



Scheme 2.

2. Results and discussion

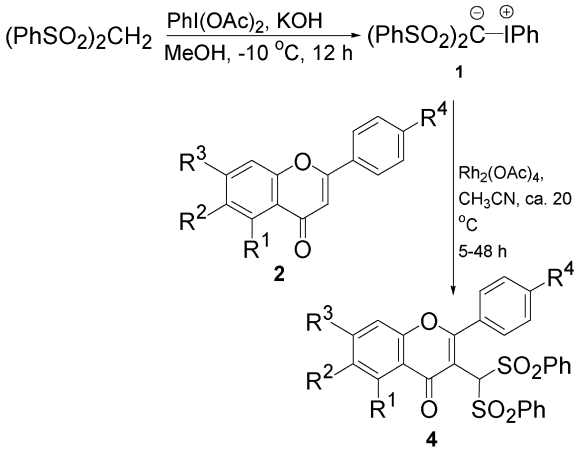
The known flavones **2** were prepared in moderate overall yields according to the known three-step sequence[12] shown in Scheme 3. For this purpose, the 2-(aroyloxy)-acetophenones were obtained from the reaction of substituted 2-hydroxyacetophenones with the corresponding aroyl chlorides. Their rearrangement into a 1,3-diketone was achieved upon treatment with hot pulverized 85% potassium hydroxide, by heating in pyridine. Finally, cyclization of the resulting 1,3-diketone with concd. sulfuric acid in glacial acetic acid afforded the desired flavones **2**.



Scheme 3.

Phenyliodonium bis(phenylsulfonyl)methylide **1** was prepared[5] from the corresponding β-disulfone by treatment with iodobenzene diacetate and KOH at −10°C (Scheme 4). This ylide is practically insoluble in common organic solvents (except DMSO); thus, the reaction of ylide **1** with the flavones **2** was conducted under heterogeneous conditions.

All reactions were run at room temperature (ca. 20°C) until complete consumption of the ylide (indicated by the change of the heterogeneous mixture to a clear solution), as shown in Scheme 4. To suppress the undesired oxidative cleavage of the olefin, a small excess of the flavone was employed. In some cases, mixtures of acetonitrile and dichloromethane were found to be advantageous for the solubilization of the



Scheme 4.

flavones. All reactions were carried out in the presence of catalytic amounts of $Rh_2(OAc)_4$; in the absence of this catalyst, much longer reaction times were necessary, but the same product composition was obtained.[8,9]

The reaction of iodonium ylide **1** with flavones **2** in acetonitrile afforded the 3-bis(phenylsulfonyl)methyl flavones **4** and the β-disulfone; the latter derives from the decomposition of the ylide **1** (Table 1). This alkenyl C–H insertion proceeds well when the flavone bears electron-donating substituents in the benzo ring, since the absolute yield (Table 1) is increased by ca. 15–25% compared to the parent flavone **2a** (entry 1). In contrast, when 4′-nitroflavone or the parent isoflavone were employed, only the ylide decomposition product, namely the β-disulfone, was isolated quantitatively on prolonged heating.

The C–H insertion products **4** (Table 1) were isolated in moderate yields (42–66%) by flash chromatography on silica gel. The deficit in the material balance constitutes the β-disulfone. It be should be emphasized that when referred to the amount of flavone consumed, high yields (up to ca. 100%) of C–H insertion products **4** are registered (Table 1) except for the competitive decomposition of the ylide **1** to the β-disulfone. Phenyl benzenethiosulfonate ($PhSO_2SPh$), the typical by-product of the in situ generated carbene, namely bis(phenylsulfonyl)methylene, was not detected; thus a carbene or a carbenoid are not responsible for the observed insertion products.[5,7]

The C–H insertion products **4** were characterized by IR and NMR (H–H COSY, HMBC, HMQC) spectra, and elemental analyses. In the case of the adduct **4d**, for example, the IR band at 1645 cm^{-1} corresponds to the carbonyl group, the pair of bands at 1345 and 1155 cm^{-1} to the sulfonyl groups. The ^1H NMR spectrum displays the signal of the proton attached to the carbon atom with the two phenylsulfonyl groups as a singlet at δ=5.66 ppm, which is CH-correlated with the peak at δ=87.8 ppm in the ^{13}C NMR spectrum. Furthermore, ^{13}C NMR resonances at δ=169.1 (C-2), δ=111.8 (C-3), and δ=174.3 ppm (C-4) are consistent with the assigned flavone structure. Had an aurone[13] product been formed, then the IR band for the carbonyl group should have appeared at 1690 cm^{-1} and the ^{13}C NMR peak of the carbonyl group at δ=195 ppm.

Table 1. CH insertions of bis(phenylsulfonyl)iodonium ylide **1** with the flavones **2**

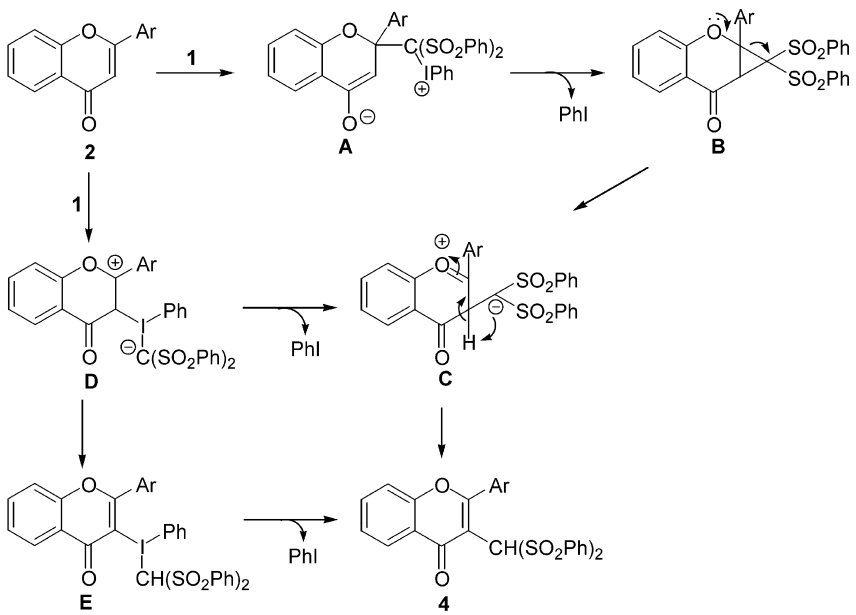
Entry	Flavone	Substituents				Reaction conditions		
		R^1	R^2	R^3	R^4	Solvent	Time[a] (h)	Yield (%)[b]
1	**2a**	H	H	H	H	CH_3CN	40	42
2	**2b**	OMe	H	H	H	CH_3CN	48	55
3	**2c**	H	H	OMe	H	CH_3CN	24	59
4	**2d**	H	H	H	Me	CH_3CN	5	66
5	**2e**	H	H	H	OMe	$CH_3CN:CH_2Cl_2$ (1:2)	24	55
6	**2f**	OMe	H	H	OMe	$CH_3CN:CH_2Cl_2$ (1:1)	12	64
7	**2g**	H	Me	H	OMe	$CH_3CN:CH_2Cl_2$ (1:3)	12	55

All reactions were carried out by stirring a suspension of ylide **1** (1 equiv.) and flavone **2** (2.4 equiv.), in the presence of a catalytic amount of $Rh_2(OAc)_4$.
[a] Time required for complete consumption of the ylide **1**, indicated by the generation of a clear solution.
[b] Yield of isolated product (relative to 100% consumption of the ylide) after silica-gel chromatography.

Such carbon–hydrogen bond insertions are characteristic for carbene or carbenoid reactivity; however, in constrast to the formation of carbenes reported[5] for the $Cu(acac)_2$-catalyzed thermal decomposition or photolysis, in the present case, it is unlikely that the ylide **1** generates bis(phenylsulfonyl)methylene under the mild (Rh^{II}-catalyzed) reaction conditions that have been employed. Had a carbene or a carbenoid intervened, analogous to the $Cu(acac)_2$-catalyzed decomposition of the ylide **1**, phenyl benzenethiosulfonate should have been observed as the typical by-product[5,7] of the bis(phenylsulfonyl)methylene. As already mentioned, a control experiment established the absence of this indicative product in the $Rh_2(OAc)_4$-catalysed decomposition of ylide **1**.

The results presented here, are consistent with either nucleophilic or electrophilic attack by the ylide on the flavone, as illustrated in Scheme 5. In the first case, it is assumed that the iodonium ylide behaves as a reactive nucleophile, equipped with a potential leaving group (PhI), such that the initial nucleophilic attack of the ylide **1** at the C-2 position of the flavone yields the intermediate enolate anion **A**. This enolate anion collapses to the cyclopropane **B** with direct displacement of iodobenzene. Such a highly substituted cyclopropane (one electron-donating and three electron-accepting substituents) should be rather labile[14] and ring opening is expected to generate the dipolar species **C**. Subsequent hydrogen-atom migration would yield the C–H insertion product **4**. In the second case, it is assumed that the iodonium ylide expresses its electrophilic character, such that electrophilic addition to the flavone generates the dipolar species **D**, elimination of iodobenzene affords again the dipole **C**, and finally leads to the insertion product **4** by hydrogen atom migration. Moreover, if the hydrogen atom transposes first, then the trivalent iodine compound **E** would be formed, which by elimination of PhI would also afford the C–H insertion product **4**.

Although there is no definitive evidence which of these mechanisms operates, we favor the reaction between the flavone and the ylide **1** to proceed by electrophilic attack of the latter. Our speculation rests on the facts that flavones, although reluctantly, may engage in electrophilic attack (i.e. epoxidation by dioxiranes[15]), but they are inert towards nucleophiles.[16] Moreover, the nucleophilic reactivity of the iodonium ylide should be rather low, because its negatively charged site is sterically rather congested[17] and electronically deactivated[18] by the electron-withdrawing sulfonyl groups.



Scheme 5.

3. Conclusions

Irrespective of the mechanistic complexities, we have developed a convenient one-step synthesis of substituted flavones **4** through an unusual alkenyl C–H insertion of phenyliodonium bis(phenylsulfonyl)methylide **1**. This direct method offers preparative advantages over the established synthesis[19] of such substituted flavones.

4. Experimental

4.1. General remarks

Melting points (uncorrected) were determinated on a Büchi B-545 apparatus. TLC analysis was conducted on precoated silica-gel foils 60 F_{254} (20×20 cm) from Merck, Darmstadt, Germany. The spots were visualized either by UV irradiation (254 nm) or with a 5% polymolybdic acid solution in ethanol. Silica gel (32–62 mm) from Woelm, Erlangen, Germany, was used for column chromatography. For the IR spectra, a Perkin–Elmer 1420 ratio-recording infrared spectrophotometer was used. H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (^{1}H: 200 MHz; ^{13}C: 50 MHz) or a Bruker Avance 400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. All commercial reagents were used without further purification. Solvents were dried by standard methods and purified by distillation before use. Ylide **1**[5] and flavones **2**[12] were synthesized by following literature procedures.

4.2. General procedure for the reaction of ylide 1 with the flavones 2

To a suspension of the ylide **1** (1.0 equiv.) and the particular flavone **2** (2.4 equiv.) in acetonitrile (10 mL) or in a mixture of acetonitrile/dichloromethane (5–10 mL) were added catalytic amounts (0.1–0.2 mol%) of $Rh_2(OAc)_4$ and the mixture was stirred at ca. 20°C until a clear solution was produced (complete consumption of the ylide). The solvent was removed (20°C at 10 Torr) and the residue was chromatographed on silica gel with mixtures of dichloromethane and ethyl acetate as eluent to yield the adducts **4**.

4.2.1. Reaction with the flavone 2a. A suspension of ylide **1** (343 mg, 0.69 mmol) and flavone **2a** (400 mg, 1.8 mmol) in acetonitrile (10 mL) was stirred for 40 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 150 mg (42%) of the insertion product **4a** at a flavone conversion of 18%; colorless plates, mp 214–215°C.

IR (KBr): ν=1680, 1640, 1580, 1480, 1465, 1400, 1365, 1355, 1325, 1245, 1230, 1200, 1180, 1160, 1130, 1090, 920 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ=5.61 (s, 1H), 7.38–7.76 (m, 14H), 7.87–7.91 (m, 4H), 8.00 (dd, J=1.4, 8.0 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ=87.7 (d), 112.2 (s), 118.1 (d), 123.4 (s), 126.2 (d), 126.6 (d), 129.0 (d), 129.4 (d), 130.0 (d), 131.5 (s), 131.7 (d), 134.6 (d), 134.8 (d), 140.4 (s), 156.0 (s), 169.4 (s), 175.0 (s).

Anal. calcd for $C_{28}H_{20}O_6S_2$ (516.6): C, 65.10; H, 3.90; S, 12.41. Found: C, 65.06; H, 4.25; S, 11.91.

4.2.2. Reaction with the flavone 2b. A suspension of the ylide **1** (220 mg, 0.44 mmol) and flavone **2b** (290 mg, 1.15 mmol) in acetonitrile (10 mL) was stirred for 48 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 132 mg (55%) of the insertion product **4b** at a flavone conversion of 24%; colorless powder, mp 232–233°C.

IR (KBr): ν=1695, 1650, 1635, 1605, 1500, 1485, 1470, 1455, 1405, 1370, 1355, 1345, 1330, 1300, 1285, 1250, 1215, 1175, 1160, 1140, 1105, 1090, 945, 815, 805 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ=3.85 (s, 3H), 5.53 (s, 1H), 6.80 (d, J=8.2 Hz, 1H), 6.97 (d, J=8.2 Hz, 1H), 7.40–7.61 (m, 12H), 7.87 (d, J=7.5 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=56.2 (q), 87.5 (d), 107.2 (d), 109.4 (d), 113.1 (s), 113.8 (s), 128.6 (d), 128.7 (d), 129.0 (d), 129.6 (d), 131.1 (d), 131.2 (d), 133.9 (d), 134.4 (d), 140.4 (s), 157.4 (s), 160.0 (s), 166.8 (s), 173.4 (s).

Anal. calcd for $C_{29}H_{22}O_7S_2$ (546.6): C, 63.72; H, 4.06; S, 11.73. Found: C, 63.62; H, 3.99; S, 12.03.

4.2.3. Reaction with the flavone 2c. A suspension of the ylide **1** (395 mg, 0.8 mmol) and flavone **2c** (500 mg, 2.0 mmol) in acetonitrile (10 mL) was stirred for 24 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 256 mg (59%) of the insertion product **4c** at a flavone conversion of 24%; colorless powder, mp 251–252°C.

IR (KBr): ν=3140, 3000, 1685, 1655, 1635, 1595, 1530, 1520, 1470, 1460, 1410, 1380, 1370, 1355, 1300, 1280, 1255, 1215, 1200, 1175, 1165, 1135, 1110, 1090, 1025, 990, 970, 960, 920, 880, 800 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ=3.89 (s, 3H), 5.58 (s, 1H), 6.84 (d, J=2.3 Hz, 1H), 6.97 (dd, J=2.3, 8.9 Hz, 1H), 7.42–7.56 (m, 7H), 7.59–7.63 (m, 4H), 7.88–7.90 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=55.9(q), 87.8(d), 100.2(d), 112.0(s), 115.1(d), 117.0(s), 127.7(d), 128.6(d), 128.7(d), 129.0(d), 129.8(d), 131.3(d), 134.1(d), 140.2(s), 157.3(s), 164.6(s), 168.4(s), 173.6(s).

Anal. calcd for $C_{29}H_{22}O_7S_2$ (546.6): C, 63.72; H, 4.06; S, 11.73. Found: C, 63.92; H, 3.96; S, 12.01.

4.2.4. Reaction with the flavone 2d. A suspension of the ylide **1** (260 mg, 0.5 mmol) and flavone **2d** (295 mg, 1.25 mmol) in acetonitrile (10 mL) was stirred for 5 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 183 mg (66%) of the insertion product **4d** at a flavone conversion of 28%; colorless needles, mp 233–234°C.

IR (KBr): ν=3070, 2920, 1645, 1615, 1595, 1585, 1565, 1505, 1465, 1445, 1385, 1345, 1335, 1320, 1310, 1230, 1190, 1155, 1135, 1110, 1075, 1025, 910, 855, 825 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ=2.42 (s, 3H), 5.66 (s, 1H), 7.28 (d, J=7.8 Hz, 2H), 7.37–7.49 (m, 8H), 7.61 (t, J=7.5 Hz, 2H), 7.66–7.70 (m, 1H), 7.88–7.91 (m, 4H), 7.88 (dd, J=1.4, 7.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=21.5 (q), 87.8 (d), 111.8 (s), 117.8 (d), 123.0 (s), 125.8 (d), 126.2 (d), 128.3 (d), 128.5 (d), 128.6 (d), 129.6 (d), 129.7 (d), 134.1 (d), 134.3 (s), 140.0 (s), 141.9 (s), 155.4 (s), 169.1 (s), 174.3 (s).

Anal. calcd for $C_{29}H_{22}O_6S_2$ (530.6): C, 65.65; H, 4.18; S, 12.08. Found: C, 65.31; H, 4.30; S, 11.93.

4.2.5. Reaction with the flavone 2e. A suspension of the ylide **1** (395 mg, 0.8 mmol) and flavone **2e** (500 mg, 2.0 mmol) in acetonitrile (5 mL) and dichloromethane (10 mL) was stirred for 24 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 237 mg (55%) of the adduct **4e** at a flavone conversion of 27%; colorless powder, mp 254–255°C.

IR (KBr): ν=1680, 1635, 1625, 1600, 1580, 1525, 1485, 1465, 1440, 1400, 1350, 1325, 1275, 1240, 1230, 1190, 1170, 1155, 1120, 1090, 1030, 1005, 930 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ=3.87 (s, 3H), 5.70 (s, 1H), 6.97 (d, J=8.8 Hz, 2H), 7.37–7.46 (m, 6H), 7.55 (d, J=8.7 Hz, 2H), 7.62 (t, J=7.4 Hz, 2H), 7.66–7.70 (m, 1H), 7.90 (d, J=7.3 Hz, 4H), 7.98 (dd, J=1.5, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=55.5 (q), 88.0 (d), 111.6 (s), 114.4 (d), 117.7 (d), 123.0 (s), 123.3 (s), 125.7 (d), 126.2 (d), 128.6 (d), 129.7 (d), 130.4 (d), 134.1 (d), 134.2 (d), 140.1 (s), 155.4 (s), 161.9 (s), 168.9 (s), 174.4 (s).

Anal. calcd for $C_{29}H_{22}O_7S_2$ (546.6): C, 63.72; H, 4.06; S, 11.73. Found: C, 63.39; H, 4.01; S, 11.97.

4.2.6. Reaction with the flavone 2f. A suspension of the ylide **1** (373 mg, 0.75 mmol) and flavone **2f** (550 mg, 1.95 mmol) in acetonitrile (5 mL) and dichloromethane (5 mL) was stirred for 12 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 274 mg (64%) of the insertion product **2f** at a flavone conversion of 27%; pale yellow powder, mp 93–94°C.

IR (KBr): ν=1685, 1640, 1630, 1600, 1540, 1495, 1465, 1405, 1365, 1340, 1300, 1270, 1250, 1190, 1175, 1160, 1140, 1090, 1025, 950, 855, 810, 805 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ=3.85 (s, 3H), 3.86 (s, 3H), 5.61 (s, 1H), 6.78 (d, J=8.2 Hz, 1H), 6.95 (d, J=8.6 Hz, 3H), 7.42 (t, J=7.7 Hz, 4H), 7.51–7.61 (m, 5H), 7.89 (d, J=7.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ=55.3 (q), 56.2 (q), 87.8 (d), 107.1 (d), 109.4 (d), 113.7 (s), 114.4 (d), 123.3 (s), 128.6 (d), 129.7 (d), 130.3 (d), 133.9 (d), 134.3 (d), 140.4 (s), 157.4 (s), 159.9 (s), 161.8 (s), 166.8 (s), 173.5 (s).

Anal. calcd $C_{30}H_{24}O_8S_2$ (576.6): C, 62.49; H, 4.20; S, 11.12. Found: C, 62.71; H, 4.15; S, 11.53.

4.2.7. Reaction with flavone 2g. A suspension of the ylide **1** (360 mg, 0.72 mmol) and flavone **2g** (500 mg, 1.88 mmol) in acetonitrile (5 mL) and dichloromethane (15 mL) was stirred for 12 h. The solvent was evaporated (20°C at 10 Torr) and the residue was chromatographed on silica gel to yield 222 mg (55%) of the insertion product **4g** at a flavone conversion of 21%; pale yellow powder, mp 255–256°C.

IR (KBr): ν=1690, 1650, 1640, 1605, 1590, 1530, 1510, 1470, 1390, 1355, 1325, 1305, 1275, 1260, 1240, 1225, 1195, 1175, 1160, 1120, 1090, 1030, 1010, 855, 830, 820 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ=2.43 (s, 3H), 3.87 (s, 3H), 5.70 (s, 1H), 6.97 (d, J=8.8 Hz, 2H), 7.33 (d, J=8.5 Hz, 1H), 7.41–7.66 (m, 9H), 7.77–7.78 (m, 1H), 7.87–7.91 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$): δ=20.6 (q), 55.4 (q), 88.2 (d), 111.6 (d), 114.6 (s), 117.8 (d), 123.0 (s), 123.7 (d), 125.8 (d), 128.9 (d), 130.1 (d), 130.8 (d), 134.5 (s), 135.9 (d), 136.2 (s), 140.5 (s), 154.3 (s), 162.3 (s), 169.3 (s), 175.2 (s).

Anal. calcd $C_{30}H_{24}O_7S_2$ (560.6): C, 64.27; H, 4.31; S, 11.44. Found: C, 63.82; H, 4.51; S, 11.19.

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