Abstract: The [3+2] cycloaddition of phenyliodonium bis(arylsulfonyl)methylides to \(\alpha,\beta\)-enones affords exclusively trans,trans-configured 1-(arylsulfonyl)-2-aroyl-3-arylindanes. The initial electrophilic attack of the iodonium ylide on the alkenyl double bond of the chalcone, followed by cyclization of the dipolar species, and subsequent ejection of iodobenzene and sulfur dioxide, stereoselectively affords the indane cycloadduct.

Key words: iodonium ylide, chalcones, diastereoselectivity, regioselectivity, 1,2,3-trisubstituted indanes

Phenyliodonium bis(arylsulfonyl)methylides \(1\) constitute a class of compounds with unique properties among the iodonium ylides (Scheme 1). Under photochemical or Cu(acac)\(_2\)-catalyzed thermal activation, an iodonium bis(sulfonyl)methylide reacts with simple alkenes to give the corresponding cyclopropanes,\(^1\) and with various heteroatom nucleophiles to provide new ylides,\(^1,2\) presumably through a carbene (or carbenoid) pathway. At room temperature, however, an unusual [3+2] cycloaddition occurs, in which a 1,2,3-trisubstituted indane is produced. For example, various acyclic 1,2-disubstituted alkenes, either Z- or E-configured, lead to the trans,trans-indane cycloadducts,\(^3\) whereas cyclic alkenes yield the cis,cis-stereoisomers\(^4\) (Scheme 1). This reactivity is explained by postulating an initial electrophilic attack of the ylide on to the alkenyl double bond, followed by cyclization to the [3+2] cycloadduct.

This perplexing chemical behavior poses the mechanistic question, whether an iodonium bis(sulfonyl)methylide reacts initially as a nucleophile in view of its stabilized carbanionic center, as an electrophile through its positively charged iodonium center, and/or as a carbene (or carbenoid) precursor by cleavage of iodobenzene. The incentive of the present study was to distinguish between these mechanistic options by examining the reaction of the iodonium bis(sulfonyl)methylides with \(\alpha,\beta\)-enones.

In \(\alpha,\beta\)-enones, which are widely distributed in nature, the carbonyl group decreases the electron density of the olefinic double bond. Thus, while the carbonyl and the \(\beta\)-ethylenic carbon atoms are activated toward nucleophilic attack, the alkenyl double bond should be less susceptible to electrophilic attack. Nevertheless, it is well known that \(\alpha,\beta\)-enones react with a variety of stable ylides to yield cyclopropanes;\(^5\) adducts are formed as well with rather mild electrophiles\(^6\) and diazo compounds.\(^7\) If the iodonium ylide should react initially as a nucleophile, then attack at the \(\beta\)-ethylenic carbon atom of the \(\alpha,\beta\)-enone would produce an enolate, which on subsequent intramolecular ring closure with ejection of iodobenzene should afford a cyclopropane product. Such a reaction type is known as a Michael-induced ring closure,\(^5\) observed in the reaction of \(\alpha,\beta\)-enones with sulfur and phosphorus ylides. The same cyclopropane cycloadduct would also result if the iodonium bis(sulfonyl)methylide should serve as a carbene (or carbenoid) source. In contrast, if the iodonium bis(sulfonyl)methylide should react initially as an electrophile by attacking the \(\alpha\)-ethylenic carbon atom of the \(\alpha,\beta\)-enone, indane derivatives should be formed by [3+2] cycloaddition, as observed for the simple alkenes.\(^3,4\)
Indeed, we report here that the reaction of iodonium bis(sulfonyl)methylides 1 with a variety of \( \alpha, \beta \)-enones affords, in moderate yields, 1,2,3-trisubstituted indanes 4 with the trans,trans configuration. Given that the sulfonyle substituent may be reductively cleaved or appropriately modified through established carbamion methodology, the present cycloaddition constitutes a potentially valuable synthetic method for the construction of 2-arylin-dane derivatives.\(^9\)

The iodonium bis(sulfonyl)methylides 1 were prepared,\(^5\) in analytically pure form, by condensation of the corresponding disulfones 2 with iodosobenzene diacetate and potassium hydroxide as base at \(-10^\circ C\) (Scheme 2). These ylides were stored at \(-30^\circ C\) for a few weeks without significant decomposition. They are practically insoluble in common organic solvents (except DMSO), so that their reactions were conducted under heterogeneous conditions.

When a suspension of ylide 1a in acetonitrile was heated at reflux for two hours, the formation of iodosobenzene and the disulfone 2a was observed. Under similar reaction conditions, but in the presence of a catalytic amount of Cu(acac)\(_2\), sulfur dioxide was detected, and the disulfone 2a and 5-phenyl benzenesulfonylthioate (PhSO\(_2\)SPh) were obtained in 22% and 54% yield, respectively. In the presence of Rh\(_2\)(OAc)\(_4\), however, only the disulfone 2a was produced in 58% yield. Sulfur dioxide and PhSO\(_2\)SPh are decomposition products obtained from the labile bis(phenylsulfonyl)methylene.\(^1,10\)

All the reactions of the ylides 1 with the \( \alpha, \beta \)-enones 3 were run with an excess of the \( \alpha, \beta \)-enone until complete consumption of the ylide, as indicated by the dissolution of the heterogeneous mixture to a clear solution (Scheme 2). Furthermore, all the reactions of ylide 1a with the \( \alpha, \beta \)-enones 3 were carried out in the presence of a catalytic amount of Rh\(_2\)(OAc)\(_4\) to shorten the reaction time. Without the metal catalyst, longer reaction times are required, but the same product composition is obtained. In contrast, all the reactions of ylide 1b with the chalcones ran faster and were carried out in the absence of Rh\(_2\)(OAc)\(_4\). The indanes 4 were isolated in moderate yields after flash chromatography on silica gel (Table 1).

The initial experiments were performed with the ylides 1 and chalcone 3a. Treatment of ylide 1a with chalcone 3a in acetonitrile and a catalytic amount of Rh\(_2\)(OAc)\(_4\) furnished the indane 4a in 52% yield (Table 1, entry 1). Similarly, the reaction of ylide 1b with the same chalcone 3a in dichloromethane was much faster, even without any catalytic amounts of Rh\(_2\)(OAc)\(_4\), giving the analogous indane derivative 4b as a single diastereomer in 77% yield (Table 1, entry 2). The para-methyl substituent of the arylsulfonyle moiety in ylide 1b allowed us to assess which aryl group (the ylide or the chalcone) is the source of the aryl ring in the indane cycloadduct. Also, it was possible to determine the regioselectivity of the cycloaddition process with regard to the location of the methyl group in the benzo ring of the indane product.

Replacement of the aryl functionality of the chalcone by an acetyl or an ester group lowered the reactivity of the enone toward the ylides 1. For example, the reaction of ylide 1a with \((E)-4\)-phenylbut-3-en-2-one (3b) gave indane 4c in 18% yield (Table 1, entry 3), while ylide 1b with methyl cinnamate (3c) afforded indane 4d in 33% yield (Table 1, entry 4). Introduction of an electron-donating substituent in the aryl functionality of the chalcone increases the reactivity of the enone toward the ylides 1. Thus, the reaction of ylide 1a with chalcones 3d and 3e (Table 1, entries 5, 7) gave the indanes 4e (54% yield) and 4g (49% yield), whereas ylide 1b with chalcones 3d and 3e (Table 1, entries 6, 8) afforded indanes 4f (41% yield) and 4h (33% yield). It should be noted that a clean process operates, except that a substantial amount of the ylide is diverted to the disulfone 2 through thermal decomposition. Introduction of an electron-donating substituent in the aryl functionality of the chalcone molecule results, however, in alkene byproduct, together with the desired indane 4. Evidently, reaction of iodonium ylide 1a with chalcone 3f furnishes, after the usual workup and silica gel chromatography, the Z-alkene (Z)-5 in 34% yield, along with the indane cycloadduct 4i in 10% yield (Scheme 3; Table 1, entry 9). Although the Z-alkene (Z)-5 was isolated in pure form after silica gel chromatography, it readily isomerizes in solution to a 60:40 mixture of the Z- and E-diastereomers.
Cycloaddition of Iodonium Bis(sulfonyl)methylides with \(\alpha,\beta\)-Enones

When ylide 1a was allowed to react with chalcone 3g, after the usual workup and silica gel chromatography, indane 4j was isolated in 28% yield, along with propanone 6 (36%) and significant amounts of 4-methylbenzaldehyde (Scheme 4; Table 1, entry 10). Presumably, propanone 6 and 4-methylbenzaldehyde result from the oxidative cleavage of either the corresponding Z-alkene or its labile precursor intermediate.

**Scheme 3**  Cycloadduct 4i and insertion product (Z)-5 in the reaction of enone 3f with methylide 1a

**Scheme 4**  Cycloadduct 4j and oxidative cleavage product 6 in the reaction of enone 3g with methylide 1a

The introduction of a hydroxy substituent in the aroyl group of the chalcone molecule leads to the corresponding flavanone, together with the desired indane cycloadduct, but in a much lower yield. Thus, the reaction of iodonium ylide 1a with 2-hydroxychalcone 3h in the presence of a catalytic amount of Rh\(_2\)(OAc)\(_4\) gave, after the usual work-up and silica gel chromatography, the flavanone 7 (67% yield) and the indane derivative 4k in only 22% yield (Scheme 5; Table 1, entry 11).

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**Table 1**  Reactions of Iodonium Bis(arylsulfonyl)methylides 1 with \(\alpha,\beta\)-Enones 3

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ylide</th>
<th>(\alpha,\beta)-Enone</th>
<th>R</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>Time(^b) (h)</th>
<th>Product(s) [Yield(^c) (%)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>3a</td>
<td>H</td>
<td>Ph</td>
<td>Ph</td>
<td>62</td>
<td>4a (52)</td>
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<tr>
<td>2</td>
<td>1b</td>
<td>3a</td>
<td>Me</td>
<td>Ph</td>
<td>Ph</td>
<td>12</td>
<td>4b (77)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>3b</td>
<td>H</td>
<td>Me</td>
<td>Ph</td>
<td>84</td>
<td>4c (18)</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>3c</td>
<td>Me</td>
<td>MeO</td>
<td>Ph</td>
<td>48</td>
<td>4d (34)</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>3d</td>
<td>H</td>
<td>4-MeC(_6)(_4)</td>
<td>Ph</td>
<td>18</td>
<td>4e (54)</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>3d</td>
<td>Me</td>
<td>4-MeC(_6)(_4)</td>
<td>Ph</td>
<td>12</td>
<td>4f (41)</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>3e</td>
<td>H</td>
<td>4-MeOC(_6)(_4)</td>
<td>Ph</td>
<td>132</td>
<td>4g (49)</td>
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<tr>
<td>8</td>
<td>1b</td>
<td>3e</td>
<td>Me</td>
<td>4-MeOC(_6)(_4)</td>
<td>Ph</td>
<td>12</td>
<td>4h (33)</td>
</tr>
<tr>
<td>9</td>
<td>1a</td>
<td>3f</td>
<td>H</td>
<td>4-MeOC(_6)(_4)</td>
<td>4-MeOC(_6)(_4)</td>
<td>84</td>
<td>4i (10), (Z)-5 (34)</td>
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<tr>
<td>10</td>
<td>1a</td>
<td>3g</td>
<td>H</td>
<td>4-MeC(_6)(_4)</td>
<td>4-MeC(_6)(_4)</td>
<td>72</td>
<td>4j (28), 6 (36)</td>
</tr>
<tr>
<td>11</td>
<td>1a</td>
<td>3h</td>
<td>H</td>
<td>2-HO-5-CIC(_6)(_4)</td>
<td>Ph</td>
<td>16</td>
<td>4k (22), 7 (67)</td>
</tr>
</tbody>
</table>

\(^a\) All reactions were carried out by stirring a suspension of the ylide 1 (0.37–1.00 mmol) and the \(\alpha,\beta\)-enone 3 (0.90–6.20 mmol) in CH\(_2\)Cl\(_2\) or MeCN (5–10 mL) in the presence of a catalytic amount of Rh\(_2\)(OAc)\(_4\) (only for ylide 1a) at room temperature (ca. 25 °C).

\(^b\) Time required for the complete consumption of the ylide 1.

\(^c\) Yield of isolated pure product after column chromatography on silica gel.
The structural assignment of the indanes is exemplified for the 4b derivative. Its $^1$H NMR spectrum displays a doublet signal at $\delta = 4.15$ with $J = 7.8$ Hz for the proton at C-3, a triplet at $\delta = 4.48$ with $J = 7.6$ Hz for the proton at C-2, and a doublet at $\delta = 5.65$ with $J = 7.2$ Hz for the proton at the sulfonyl-bearing C-1 position. The lack of a ROESY signal between the protons at the C-1 and C-2 positions and the protons at the C-2 and C-3 positions, as well as the values of the coupling constants, indicate the $trans,trans$ configuration of the three substituents in the five-membered ring. 2-D NMR studies of this cycloadduct reveal that the methyl group of the fused aryl ring and the sulfonyl-bearing C-1 position of the five-membered ring are located $meta$ to one another in the indane product, although originally this methyl substituent occupied the $para$-position in the $p$-tolylsulfonyl group of the iodonium ylide.

In regard to the mechanism for this [3+2] cycloaddition, the exact role of the Rh$_2$(OAc)$_4$ catalyst is unclear; palladium complexes have the same effect of enhancing the rate of the cycloaddition. The formation of bis(phenylsulfonyl)methylene is evidenced by the isolation of $S$-phenyl benzenesulfonothioate (PhSO$_2$SPh) and the detection of sulfur dioxide. This is corroborated by the independent Cu(acac)$_2$-catalyzed thermal decomposition of iodonium ylide 1a, which yields disulfone 2a and bis(phenylsulfonyl)methylene, the latter again indicated by the $S$-phenyl benzenesulfonothioate and sulfur dioxide products. The analogous Rh$_2$(OAc)$_4$-catalyzed thermal decomposition affords, however, exclusively the disulfone 2a. Besides, a cyclopropane product been generated by carbone (or carbenoid) addition to the $\alpha,\beta$-enone, it should have been sufficiently persistent for isolation. Such a cyclopropane cycloadduct, instead of rearranging into the isolated indane derivative, would be expected to undergo dipolar ring opening, reclosure and aromatization to afford a 2-benzoyl-1,1-bis(sulfonyl)indane. The benzo ring would
stem from the alkene partner and not, as observed, from the ylide.

As for a Michael-type nucleophilic addition of the carbanionic carbon atom of the iodonium bis(sulfonyl)methyldie to the enone partner, this negatively charged center is only weakly nucleophilic due to the electron-withdrawing sulfonyl and the phenyldiiodonio groups. Moreover, the severe steric hindrance of this site should render the nucleophilic addition of the iodonium ylide to the chalcone as unlikely. The fact that the reaction of phenyliodonium bis(phenylsulfonyl)methylide \(1a\) with triethyl phosphite gives a persistent triethoxyphosphonium ylide\(^{25}\) (Scheme 1) indicates that these ylides are electrophilic rather than nucleophilic in their chemical behavior.

In accord with our previously proposed mechanism for the \([3+2]\) cycloaddition with simple alkenes,\(^{3,4}\) the current results support the mechanistic scenario displayed in Scheme 6 for the reaction between ylide \(1b\) and chalcones 3. The dipolar species \(A\) may be generated directly by electrophilic attack of the iodonium ylide on the chalcone. This dipolar intermediate is expected\(^{11}\) to have a T-shaped geometry for the trivalent iodine functionality, which prevents the ring closure to a four-membered cyclic iodinane. Instead, nucleophilic attack by the bis(sulfonyl)-substituted carbanion on the ortho-position of the phenylsulfonyl ring and closure of the resulting dipole leads to iodonane \(B\). Such a nucleophilic attack constitutes the initial step of the Truce–Smiles rearrangement,\(^{12}\) observed in carbanions of diaryl sulfones with an ortho-methyl group. Elimination of iodobenzene from the iodonane \(B\), followed by sulfur dioxide extrusion, or vice versa, and subsequent aromatization by a hydrogen atom shift affords the observed indane products 4.

When an electron-donating substituent, i.e. a methyl or a methoxy group, exists in the aryl moiety of the chalcone, then the positive charge in the intermediate \(A\) is delocalized into the ary ring, which reduces the electrophilic character at the benzyl carbon. Presumably, the cycloaddition proceeds slower and side reactions may compete, e.g. hydrogen abstraction and iodobenzene elimination to afford the alkene \(Z\)-5 as insertion product (Scheme 3), or oxidative degradation of intermediate \(A\) to generate propacone 6 and 4-methylbenzaldehyde (Scheme 4).

In summary, we have demonstrated that the unprecedented diastereoselective formation of functionalized 1,2,3-trisubstituted indanes is quite general, by extending the \([3+2]\) cycloaddition of iodonium bis(aryl sulfonfonyl)methylides also to the electron-deficient \(\alpha,\beta\)-enones. Although the yields are moderate for this direct process, to prepare such \(trans,trans\)-configured 1,2,3-trisubstituted indanes 4 would be considerably more cumbersome by alternative existing synthetic methodology.

Melting points (uncorrected) were determined on a Buchi B-510 apparatus. For the IR spectra, a Perkin–Elmer 257 ratio recording IR spectrophotometer was used. \(^1H\) and \(^{13}C\) NMR spectra were recorded on Bruker AMX 250 and Bruker Avance 400 instruments. Mass spectra were carried out on a Finnigan MAT 8200 spectrometer; exact masses were determined on a Finnigan MAT 90 spectrometer. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. TLC analysis was conducted on precoated silica gel glass plates from Merck, Darmstadt, Germany. The spots were visualized either by UV irradiation (254 nm) or with a 5% polyoxymethylene acid solution in EtOH. Silica gel (0.040–0.063 \(\mu m\)) from Merck, Darmstadt, Germany was used for flash column chromatography. All commercial reagents were used without further purification. Solvents were dried by standard methods and purified by distillation before use. Iodonium ylides \(1a\) and chalcones \(3^\alpha\) were synthesized following the literature procedures.

**Thermal Decomposition of Ylide 1a Catalyzed by Cu(acac)\(_2\)**

A suspension of phenyliodonium bis(phenylsulfonyl)methylide \(1a\) (0.50 g, 1.0 mmol) and a catalytic amount of Cu(acac)\(_2\) (1.0 mg) in MeCN (10 mL) was refluxed for 12 min (clear soln). The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH\(_2\)Cl\(_2\)) to afford 5-phenyl benzenesulfonothioate\(^{14}\) (135 mg, 54%) as a colorless oil, and bis(phenylsulfonyl)methane\(^{15}\) (2a; 65.0 mg, 22%) as colorless needles.

**Thermal Decomposition of Ylide 1a Catalyzed by Rh\(_2\)(OAc)\(_4\)**

A suspension of phenyliodonium bis(phenylsulfonyl)methylide \(1a\) (0.50 g, 1.0 mmol) and a catalytic amount of Rh\(_2\)(OAc)\(_4\) (1.0 mg) in MeCN (10 mL) was refluxed for 8 h. The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH\(_2\)Cl\(_2\)) to afford bis(phenylsulfonyl)methane (2a; 172 mg, 58%) as colorless needles.

**Reaction of the Ylides 1 with the Enones 3; General Procedure**

A suspension of an iodonium ylide \(1d\) (0.37–1.0 mmol) and an \(\alpha,\beta\)-enone \(3\) (0.90–6.2 mmol) in MeCN or CH\(_2\)Cl\(_2\) (5–10 mL) in the presence of a catalytic amount of Rh\(_2\)(OAc)\(_4\) (0.1–0.2 mol%) was stirred for 12–13 h. The solvent was evaporated (20 °C/15 Torr) and the residue was flash-chromatographed on silica gel to afford the indane derivative 4, and in some cases the side products 5, 6, and 7.

**Reaction of Ylide 1a with Chalcone 3a**

A suspension of ylide \(1a\) (0.50 g, 1.0 mmol) and \((E)-1,3\)-diphenylprop-2-en-1-one \(3a\) (0.58 g, 2.78 mmol) in MeCN (10 mL) was stirred for 62 h according to the above general procedure. The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH\(_2\)Cl\(_2\)–PE) to yield phenyl[1-phenyl-3-(phenylsulfonfonyl)]indan-2-yl)methanone\(^{1}\) (4a; 220 mg, 52%) as colorless needles; mp 150–151 °C (CHCl\(_3\)–PE).

Indane 4a was also isolated (210 mg, 48%) as colorless needles by following the above general procedure, in which a mixture of the ylide \(1a\) (0.5 g, 1.0 mmol) and \((E)-1,3\)-diphenylprop-2-en-1-one \(3a\) (0.58 g, 2.78 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was stirred for 162 h.

**Reaction of Ylide 1b with Chalcone 3a**

A suspension of ylide \(1b\) (0.53 g, 1.0 mmol) and \((E)-1,3\)-diphenylprop-2-en-1-one \(3a\) (1.0 g, 4.8 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was stirred for 12 h according to the above general procedure. The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH\(_2\)Cl\(_2\)–PE) to yield \([5\text{-methyl-1-phenyl-3-(phenylsulfonfonyl)}\text{]indan-2-yl}]\text{methylene}\ (4b; 360 mg, 77%) as colorless needles; mp 187–189 °C (EtOH).

IR (KBr): 3053, 1678, 1595, 1491, 1450, 1362, 1316, 1300, 1240, 1220, 1179, 1148, 1085, 1000, 976, 935, 910, 886, 810, 781, 751, 718 cm\(^{-1}\).

\(^1H\) NMR (250 MHz, CDCl\(_3\)): \(\delta = 2.24 (s, 3 H), 2.38 (s, 3 H), 4.15 (d, \(J = 7.8\) Hz, 1 H), 4.48 (t, \(J = 7.6\) Hz, 1 H), 5.65 (d, \(J = 7.2\) Hz, 1 H).
A suspension of ylide 1a (0.5 g, 1.0 mmol) and (E)-4-phenylbut-3-en-2-one (3b; 0.35 g, 2.4 mmol) in the presence of a catalytic amount of Rh2(OAc)4 in MeCN (10 mL) was stirred for 84 h according to the above general procedure. The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH2Cl2–PE) to yield 1-{1-[1-phenyl-3-(phenylsulfonyl)indan-2-yl]ethanone (4e; 67.0 mg, 18%) as colorless needles; mp 112–114 °C (CHCl3–PE).

IR (KBr): 1700, 1640, 1595, 1505, 1470, 1430, 1370, 1330, 1290, 1240, 1210, 1165, 1100, 1015, 935, 840, 775 cm−1.

HRMS [CI (NH3)]: [M + NH4]+ calcd for C23H20O3S·NH4+; 394.1477; found: 394.1481.

Reaction of Ylide 1b with Chalcone 3d

A suspension of ylide 1b (0.53 g, 1.0 mmol) and (E)-3-phenyl-1-(4-tolyl)prop-2-en-1-one (3d; 0.68 g, 3.1 mmol) in CH2Cl2 (10 mL) was stirred for 12 h according to the above general procedure. The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH2Cl2–PE) to yield [5-methyl-1-phenyl-3-(4-tolylsulfonyl)indan-2-yl](4-tolyl)methanone (4f; 200 mg, 41%) as colorless needles; mp 196–199 °C (EtOH).

IR (KBr): 3066, 3032, 1735, 1596, 1493, 1440, 1378, 1340, 1299, 1240, 1130, 1083, 1041, 1008, 979, 889, 854, 830, 813 cm−1.

1H NMR (400 MHz, CDCl3); δ = 2.21 (s, 3 H), 4.10 (d, J = 7.7 Hz, 1 H), 4.41–4.45 (m, 1 H), 5.65 (d, J = 7.1 Hz, 1 H), 6.71 (d, J = 7.6 Hz, 1 H), 6.76 and 6.88 (AA’BB’ system, 4 H), 7.07–7.26 (m, 10 H), 7.66–7.72 (m, 2 H).

13C NMR (100 MHz, CDCl3); δ = 21.5 (q), 56.3 (d), 56.9 (d), 71.5 (d), 125.5 (d), 126.0 (d), 127.4 (d), 128.0 (d), 128.6 (d), 128.7 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.2 (d), 130.5 (d), 133.0 (s), 143.0 (s), 142.5 (s), 142.6 (s), 144.4 (s), 145.2 (s), 197.8 (s).

HRMS (CI (NH3)); [M + NH4]⁺ calcd for C25H24O4S·NH4⁺; 470.1790; found: 470.1787.

Reaction of Ylide 1c with Chalcone 3e

A suspension of ylide 1c (0.436 g, 0.87 mmol) and (E)-4-tolyloxyphenyl)-3-phenylprop-2-en-1-one (3e; 0.53 g, 2.1 mmol) in the presence of a catalytic amount of Rh2(OAc)4 in MeCN (10 mL) was stirred for 132 h according to the above general procedure. The solvent was evaporated (20 °C/15 Torr) and the residue was chromatographed on silica gel (CH2Cl2–PE) to yield (4-methoxyphenyl)-3-phenylprop-2-en-1-one (4g; 201 mg, 49%) as colorless plates; mp 149–150 °C (CHCl3–PE).

IR (KBr): 3094, 1760, 1635, 1515, 1475, 1440, 1465, 1330, 1275, 1260, 1235, 1195, 1160, 1130, 1030, 1005, 890, 860, 845, 775 cm−1.

1H NMR (250 MHz, CDCl3); δ = 2.80 (s, 3 H), 3.51 (t, J = 7.2 Hz, 2 H), 7.10–7.27 (m, 6 H), 7.65–7.71 (m, 3 H).

13C NMR (63 MHz, CDCl3); δ = 12.2 (q), 21.5 (+), 52.2 (+), 54.4 (+), 55.1 (+), 71.4 (+), 125.0 (+), 126.4 (+), 127.1 (+), 128.0 (+), 128.5 (+), 129.5 (+), 130.6 (+), 133.6, 133.7, 137.8, 142.6, 142.7, 144.8, 172.6.


HRMS (EI); [M + H]⁺ calcd for C30H26O3S·H⁺; 478.1398; found: 478.1397.

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anone (4h; 170 mg, 33%) as colorless needles; mp 195–197 °C (EtOH).

IR (KBr): 3063, 3027, 1665, 1596, 1572, 1494, 1453, 1361, 1295, 1264, 1214, 1171, 1094, 1027, 898, 881, 820, 767, 707 cm⁻¹.

1H NMR (250 MHz, CDCl₃): δ = 2.27 (s, 3 H), 2.40 (s, 3 H), 3.80 (s, 3 H), 4.17 (d, J = 7.5 Hz, 1 H), 4.44 (t, J = 7.5 Hz, 1 H), 5.67 (d, J = 7.5 Hz, 1 H), 6.62–6.72 (m, 3 H), 6.86–6.92 (m, 2 H), 7.05–7.23 (m, 8 H), 7.60–7.66 (m, 6 H), 8.07 (d, J = 8.8 Hz, 1 H).

13C NMR (63 MHz, CDCl₃): δ = 21.4 (+), 21.5 (+), 55.4 (+), 56.2 (+), 71.7 (+), 113.2 (+), 125.1 (+), 126.5 (+), 127.3 (+), 128.69 (+), 128.71 (+), 128.8 (+), 129.1 (+), 129.6 (+), 130.7 (+), 131.2 (+), 134.3, 134.5, 137.9, 142.9, 143.3, 144.7, 167.3, 196.9.

Anal. Calc’d for C₁₃H₁₂O₅S: C, 64.04; H, 4.66; S, 11.40.

Found: C, 68.91; H, 4.48; S, 6.18.

Reaction of Ylide 1a with Chalcone 3f

A suspension of ylide 1a (0.40 g, 0.8 mmol) and (E)-1,3-bis(4-methoxyphenyl)prop-2-en-1-one (3f; 0.50 g, 1.87 mmol) in the presence of a catalytic amount of Rh₂(OAc)₄ in MeCN (10 mL) was stirred for 16 h according to the above general procedure. The residue was chromatographed on silica gel (CH₂Cl₂–PE) to yield 6-chloro-1,3-bis(4-methoxyphenyl)prop-2-en-1-one [(+), 134.2, 137.4, 137.7, 140.0, 144.8, 146.9, 198.8. HRMS [CI (NH₃)]: m/z [M + NH₄]⁺ calc’d for C₁₃H₁₂O₅S·NH₄⁺: 484.1946; found: 484.1941.

Also obtained was 3,3-bis(phenylsulfonyl)-1-(4-tolyl)propan-1-one (6; 154 mg, 36%) as colorless needles; mp 173–174 °C (CHCl₃–PE).

IR (KBr): 1715, 1630, 1600, 1495, 1450, 1420, 1405, 1375, 1340, 1295, 1240, 1230, 1200, 1150, 1080, 1000, 930, 915, 880, 840, 780, 775 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 2.91 (dd, J = 3.0, 17.0 Hz, 1 H), 3.08 (dd, J = 13.2, 17.0 Hz, 1 H), 5.47 (dd, J = 3.0, 13.2 Hz, 1 H), 7.02 (d, J = 8.8 Hz, 1 H), 7.38–7.49 (m, 6 H), 7.89 (d, J = 2.6 Hz, 1 H).

13C NMR (100 MHz, CDCl₃): δ = 44.2 (+), 79.8 (+), 119.5 (+), 121.7 (+), 126.1 (+), 126.3 (+), 127.1 (+), 128.8 (+), 128.9 (+), 135.9 (+), 138.2 (+), 159.9 (+), 190.7 (+).

Anal. Calc’d for C₁₃H₁₂ClO₂ (258.7): C, 69.64; H, 4.29. Found: C, 69.50; H, 4.61.

Also obtained was (5-chloro-2-hydroxyphenyl)[1-phenyl-3-(phenylsulfonyl)inden-2-yl](4h; 60 mg, 22%) as colorless needles; mp 176–177 °C (CHCl₃–PE).

IR (KBr): 3063, 3027, 1665, 1596, 1572, 1494, 1453, 1361, 1295, 1264, 1214, 1171, 1094, 1027, 898, 881, 820, 767, 707 cm⁻¹.

1H NMR (200 MHz, CDCl₃): δ = 4.24 (d, J = 8.0 Hz, 1 H), 4.40 (t, J = 8.0 Hz, 1 H), 5.75 (d, J = 8.0 Hz, 1 H), 6.68 (d, J = 2.4 Hz, 1 H), 6.79–6.92 (m, 4 H), 7.27–7.55 (m, 9 H), 7.78 (d, J = 7.2 Hz, 2 H), 7.88 (d, J = 7.2 Hz, 1 H).

13C NMR (50 MHz, CDCl₃): δ = 56.6 (+), 57.4 (+), 71.0 (+), 119.2 (+), 123.8, 125.9 (+), 126.3 (+), 128.5 (+), 128.7 (+), 128.8 (+), 129.5 (+), 130.3 (+), 130.4 (+), 134.0, 134.4 (+), 137.2 (+), 137.3, 141.8, 145.8, 161.9, 203.6.

Anal. Calc’d for C₁₃H₁₄ClO₂S (488.08): C, 68.78; H, 4.33; S, 6.56. Found: C, 68.91; H, 4.48; S, 6.18.

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