Michael addition of thiols to α-enones in ionic liquids with and without organocatalysts

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Seventeen organocatalyts were tested for their ability to catalyst the addition of thiophenols to chalcones in [bmim]PF_6. The products were isolated in high yield after a short reaction time, but no stereoselectivity was observed. The reactions also proceeded (without any stereoselectivity) in four other ionic liquids. In contrast, 16% and 26% ee were observed when L-proline and cinchonine, respectively, were used as the catalysts in CH_2Cl_2. Addition of thiophenols is also catalysed by HCl, as well as D-mandelic and L-tartaric acids. Addition of thiophenols to chalcones also occurred in neat ionic liquids, without any additional catalyst, but the rate of the reaction depended considerably on the structure of ionic liquid. The scope of the non-catalysed reaction in ionic liquids was tested by the reactions of 5 different thiols and 3 different α-enones.

Introduction

Thiols play a very important role in organic synthesis as well as in biochemistry.[1,2] One of their most frequently studied reactions is their addition to unsaturated ketones, which is usually carried out in common solvents (acetone, THF, alcohols *etc.*) under catalysis by base (including F^-).[3] Stereoselective additions of thiols are most frequently catalysed by chiral metal complexes.[4] Recently, it was reported that zinc perchlorate hexahydrate is also a very good catalyst for this reaction, and methanol was found to be the best organic solvent.[5] Very good results have also been achieved when the reaction was catalyzed by molecular iodine and without solvent.[6]

Asymmetric reactions catalyzed by small organocatalysts have become very attractive in recent years.[7–16] L-Proline, quinine and ephedrine, as well as 2(*S*)-phenylaminomethyl-4(*S*)-hydroxypyrrolidine and 2(*S*)-(diphenylhydroxymethyl)piperidine and its 1-Boc-protected derivatives, have also been used as the catalysts for addition of thiols to unsaturated ketones, but resulting in only moderate enantioselectivity.[17–22] The Michael addition of thiophenols to chalcone in toluene at −20 °C catalyzed by cinchonine, followed by crystallisation, led to the correspondig adducts in moderate yields with high enantioselectivities (67–95%).[23] High yield and enantioselectivity up to 73% were achieved when a bifunctional molecule containing a cinchona alkaloid moiety and a thiourea moiety was used as an organocatalyst.[24] Addition of thiols to α,β-unsaturated aldehydes using optically active α,α-diarylprolinol silyl ethers was described recently. These reactions proceeded in good to high yields with excellent enantioselectivities.[25,26]

Ionic liquids are frequently used as "green" solvents for many organic reactions including transition metal and bio-catalysed reactions.[27–33] Ionic liquids have not been commonly used solvents for organocatalysed reactions. Loh[34] and ourselves[35] have found that ionic liquids are excellent solvents for L-proline-catalysed aldol reactions. Chowdari described L-proline-catalysed asymmetric Mannich reactions in ionic liquids.[36] We have also found that L-proline in ionic liquid is a very good catalytic system for the Michael addition of aliphatic aldehydes and ketones to β-nitrostyrenes,[37] giving the products in high yields with high enantioselectivity using 5 mol% of L-proline. Very recently, Rasalkar described L-proline-catalysed Michael addition of ketones to nitrostyrene. Several ionic liquids have been tested, and 1-methoxyethyl-3-methylimidazolium methanesulfonate ([MOEMIM]OMs) was found to be the best.[38] In order to achieve good yields, it was necessary to prolong the reaction time to 60 hours, and catalyst loading had to be increased to 40 mol% to achieve 75% ee. Hagiwara has described the organocatalysed addition of aliphatic aldehydes to methyl vinyl ketone in the ionic liquid [bmim]PF_6. 2(*S*)-(1-Morpholinomethyl)piperidine was found to be the best organocatalyst, but the yields of the product were moderate, with 11–51% ee.[39] Yadav *et al.*[40] disclosed the results of Michael additions of thiols to α,β-unsaturated ketones in 2 : 1 mixtures of [bmim]BF_4–H_2O and [bmim]PF_6–H_2O mixtures. Similarly, Ranu described[41] the Michael addition of thiols and thiophosphate to α,β-unsaturated carbonyl compounds in [pmim]Br ionic liquid.

The main aim of this work was to investigate the Michael addition of thiols to α-enones in ionic liquids with and without organocatalyst. The second aim was to see if the Michael addition of thiophenols to chalcones can be catalyzed by acids.

Results and discussion

Our work started with examination of the organocatalysed Michael addition of thiophenol (**2a**) to chalcone (**1a**), with L-Proline as the catalyst. We hoped that the reaction would proceed with some stereoselectivity either *via* activation of the chalcone carbonyl group by hydrogen bond formation with proline carboxylic acid, or by formation of an en-iminium ion. Formation of such an intermediate was suggested by King *et al.*,[42] as well as Gryko,[43] for explanation of the stereoselectivity of alkylation

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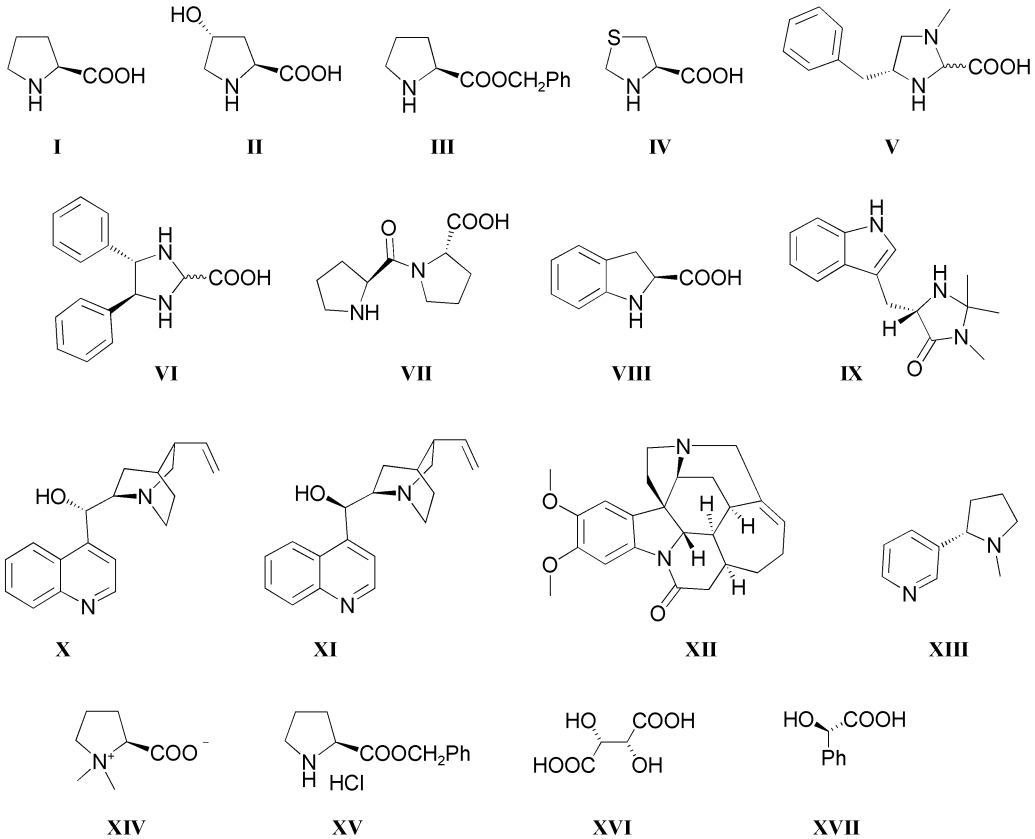

Fig. 1 Structures of the catalysts used.

of indole by enones or the Michael addition of 1,3-diketones to methyl vinyl ketone. Reaction in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) as a solvent gave high chemical yields of the product **3a**, but with practically no enantioselectivity.

We decided therefore to test several other organocatalysts with the hope of increasing the enantioselectivity (Fig. 1). The product **3a** was isolated in 76–99% yield after 10 min at room temperature, but practically no stereoselectivity (0–7%) was observed (Table 1). The best ee (7%) was achieved using (−)-cinchonidine (**XI**, entry 11) as the catalyst. Low stereoselectivity can be explained either by a rapid retro-Michael addition, or by some competitive reaction pathway in which the organocatalyst does not play any role (see later).

Table 1 Michael addition of thiophenol **2a** to chalcone **1a** at room temperature in **IL1** catalyzed by different catalysts, reaction time 10 min

Entry	Catalyst	Yield of **3a** (%)	ee of **3a** (%)
1	**I**	99	2
2	**II**	81	1
3	**III**	87	1
4	**IV**	94	0
5	**V**	92	1
6	**VI**	79	2
7	**VII**	76	1
8	**VIII**	83	0
9	**IX**	94	2
10	**X**	81	1
11	**XI**	86	7
12	**XII**	83	4
13	**XIII**	92	1
14	**XIV**	87	4

Our next aim was to see whether the rapid reaction of thiophenol with chalcone in 2 : 1 mixtures of [bmim]BF_4–H_2O and [bmim]PF_6–H_2O , observed by Yadav,[40] was being caused by acid catalysis by HF, which could be present due to the hydrolysis of BF_4^- or PF_6^- anions. Hydrolysis of these anions in water was proved by Swatlovski *et al.*[44] For this reason we performed several experiments in dichloromethane. No reaction was observed in pure dichloromethane even after 8 h (Table 2, entry 1). On the other hand, a reasonably rapid Michael addition providing 88% yield of the product **3a** (Table 2, entry 2) was observed after addition of a few (3–4) drops of hydrochloric acid (35%) into the reaction mixture.

It was of interest to check if the acid catalysis is more general, and therefore some additional L-proline benzyl ester (**III**) was tested as a catalyst. Experiments with L-tartaric acid (**XVI**) and D-mandelic acid (**XVII**) as catalysts were included with the hope that some enantioselectivity could be observed. From the results given in Table 2, it follows that acid catalysis is more general. With the catalyst **III**, product **3a** was isolated in 87% and 96% yield when the reaction was carried out in **IL1** and **IL3**, respectively. Reactions with L-tartaric acid and L-mandelic acid in **IL3** were slower, but **3a** was isolated in 97% and 96% yield after 1 hour. As the organocatalyst-catalyzed reactions with α-enones described in the literature[36,37] were perfomed in CH_2Cl_2–*i*-PrOH or NMP, we decided to perform some selected reactions in CH_2Cl_2. However, reactions were much slower, providing adduct **3a** in 47% and 36%

Table 2 Effect of acid catalysis and solvent effect on the thiophenol **2a** adition to chalcone **1a**

Entry	Solvent	Catalyst[a]	Time	Yield of **3a** (%)	ee of **3a** (%)
1	CH_2Cl_2	—	8 h	Trace	—
2	CH_2Cl_2	HCl[b]	2 h	88	0
3	**IL1**	**III**	15 min	87	0
4	**IL3**	**XV**	15 min	96	1
5	**IL3**	**XVI**	1 h	97	1
6	**IL3**	**XVII**	1 h	96	0
7	CH_2Cl_2	**XVI**	8 h	47	2
8	CH_2Cl_2	**XVII**	8 h	36	4
9	CH_2Cl_2	**I**	8 h	62	16
10	CH_2Cl_2	**X**	10 min	91	26
11	CH_2Cl_2	**XIII**	10 min	93	2
12	Toluene	**I**	2.5 h	44	1
13	Toluene	—	2.5 h	Trace	—
14	**IL3**	**I**	1.5 h[c]	69	1

[a] 5 mol% of **I**, **III**, **X**, **XIII**, **XV** and 10 mol% of **XVI** and **XVII** were used. [b] 3–4 Drops of HCl. [c] The reaction was performed at −4 °C.

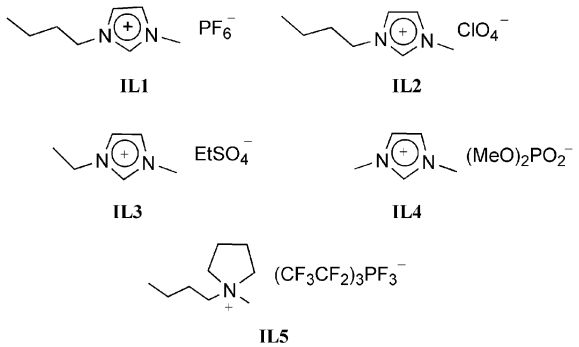

Fig. 2 Structures of the ionic liquids used. **IL1** = 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6); **IL2** = 1-butyl-3-methylimidazolium perchlorate; **IL3** = 1-butyl-3-methylimidazolium ethylsulfate ([emim]SO_4Et, ECOENGTM212); **IL4** = 1,3-dimethylimidazolium dimethylphosphate (ECOENGTM1111P); **IL5** = 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate.

yield after 8 h at room temperature with L-tartaric acid and D-mandelic acid, respectively, with 2–4% ee. Reaction in CH_2Cl_2 catalyzed by L-proline was also slow, 62% (16% ee) of the product **3a** being isolated after 8 h. This result prompted us to perform the reaction in CH_2Cl_2 using catalyst **X** (cinchonine), which gave 7% ee when carried out in [bmim]PF_6. Reaction in dichloromethane was quite rapid, and after 10 min, **3a** was isolated in 91% yield and 26% ee. The reaction catalyzed by **XIII** (nicotine) proceeded, to our surprise, practically without any enantioselectivity. No enantioselectivity was observed, either when the reaction was carried out using L-proline as the catalyst at room temperature in toluene (Table 2, entry 12), or in **IL3** at −4 °C (Table 2, entry 14).

With these results in mind, we considered why no enantioselectivity was observed in the Michael additions of thiophenol to chalcone in [bmim]PF_6. Our working hypothesis was that the addition reaction of thiophenol in ionic liquid is for some reason so rapid that formation of the en-iminium intermediate from the chalcone and L-proline can not compete. To prove this hypothesis, it was necessary to perform reactions in [bmim]PF_6 with and without L-proline. It was also of interest to examine if the structure of ionic liquid had some influence on the reaction. The structures of the ionic liquids used are depicted in Fig. 2; results are given in Table 3.

From the data given in Table 3, it follows that the rate of the L-proline-catalysed reaction is highest in **IL2** and **IL4**, with the rate of reaction in **IL3** being comparable with that in **IL1**, and the reaction rate in **IL5** being much slower. It should be noted that reactions were stopped after full conversion of chalcone (by TLC), so that the reaction time gives therefore some information about the reaction rate. Negligible enantioselectivity was observed in all cases.

Table 3 Solvent and catalyst effect on the Michael addition of thiophenol **2a** to chalcone **1a**

Entry	Solvent	Catalyst[a]	Time	Yield of **3a** (%)
1	**IL1**	**I**	10 min	99
2	**IL1**	—	10 min	90
3	**IL2**	**I**	30 s	94
4	**IL2**	—	2 min	92
5	**IL3**	**I**	15 min	91
6	**IL3**	—	15 min	94
7	**IL4**	**I**	30 s	91
8	**IL4**	—	2 min	94
9	**IL5**	**I**	1 h	87
10	**IL5**	—	3 h	91

[a] 5 mol% of L-proline was used.

It is of interest to note that addition of thiophenol (**2a**) to chalcone (**1a**) proceeded *without* addition of L-proline, although it was slightly slower (Table 3, entries 2, 4, 6, 8, 10). Since **IL2** (pH = 8.5) and **IL4** (pH = 8.0) are basic ionic liquids, and **IL3** and **IL5** are neutral, these reactions could not be catalysed by any residual acidity of the ionic liquid. In order to exclude ClO_4^- being a catalyst, an experiment using $LiClO_4$ in CH_2Cl_2 was carried out, but no reaction was observed. We do not have any explanation for the very high reaction rate in **IL2** and **IL4**.

The above-mentioned results prove that Michael addition of thiophenol in ionic liquids proceeds well without any catalyst. A question therefore arose: Why do these reactions proceed in neat ionic liquids?

There are several reports on the higher nucleophilicity of halide anions,[45–47] water,[48] and amines[49] in ionic liquids compared to their nucleophilicity in organic solvents. We can speculate therefore that the nucleophilicity of thiophenol could also be higher in ionic liquids. However, this explanation is questionable based upon results published very recently. Landini proved that the nucleophilicity of halide ions and the azide ion in [hexmim]PF_6 is comparable with their nucleophilicity in methanol, and slightly lower than in DMSO.[50] Lancaster reported that amines had higher nucleophilicity in ionic liquids, but found that the nucleophilicity of halide anions is lower in ionic liquids than in dichloromethane, and that the nucleophilicity order of different halides depends strongly depend on the stucture of the ionic liquid.[51]

Another explanation of high reactivity of thiophenol in ionic liquids, especially neutral ionic liquids (**IL3** and **IL5**), could be that the dissociation constant of thiophenol is higher in ionic liquids than in organic solvents. Slightly basic **IL2** and **IL4** can assist in the formation of the $PhS^{(-)}$ anion from PhSH, which results in an increase of the reaction rate. A possible explanation for the observed results is depicted in Scheme 1. Direct addition (routes a and b) of thiols to α-enones is much faster than the formation of an en-iminium ion (route c).

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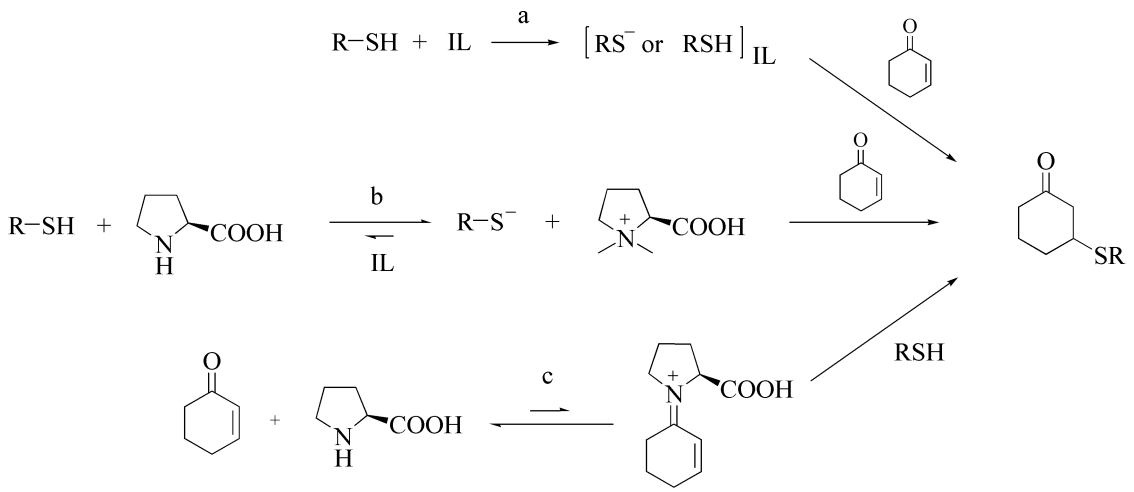
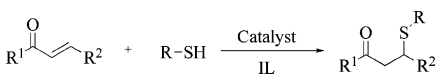


Scheme 1 The possible reaction routes of Michael addition of thiols to enones; b > a ≫ c.

Our next aim was to explore if the catalyst-free addition of thiols is a more general phenomenon. For that reason, additions of different thiols to several enones were tested (Scheme 2). The results are given in Table 4.



1a-c **2a-e** **3a-g**

1a, R^1 = Ph, R^2 = Ph
1b, R^1, R^2 = -$(CH_2)_3$-
1c, R^1 = CH_3, R^2 = Ph

2a, R = Ph
2b, R = 4-$MeOC_6H_4$
2c, R = 4-FC_6H_4
2d, R = 4-^{t}$BuOC_6H_4$
2e, R = $PhCH_2$

3a, R^1 = Ph, R^2 = Ph, R = Ph
3b, R^1 = Ph, R^2 = Ph, R = 4-$MeOC_6H_4$
3c, R^1 = Ph, R^2 = Ph, R = 4-FC_6H_4
3d, R^1 = Ph, R^2 = Ph, R = 4-^{t}$BuOC_6H_4$
3e, R^1 = Ph, R^2 = Ph, R = $PhCH_2$
3f, R^1, R^2 = -$(CH_2)_3$-, R = Ph
3g, R^1 = CH_3, R^2 = Ph, R = Ph

Scheme 2 The Michael addition of thiols to α-enones.

The results in Table 4 show that Michael addition of various thiophenols (**2a–d**) to α-enones (**1a–c**) proceeded smoothly in **IL3**. The yields of the products when the reactions were performed without any catalyst (Table 4, entries 2, 4, 6, 8, 12 and 14) were the same or only slightly lower than when 5mol% of L-proline was used (Table 4, entries 1, 3, 5, 7, 11 and 13). Experiments with $PhCH_2SH$ (**2e**) proved that this finding is more general and can be also applied to alkylthiols (Table 4, entries 9 and 10).

Table 4 Michael additions of thiols to α-enones in **IL3**

Entry	α-Enone	Thiol	Catalyst[a]	Time/min	Product (yield, %)
1	**1a**	**2a**	**I**	15	**3a** (91)
2	**1a**	**2a**	—	15	**3a** (94)
3	**1a**	**2b**	**I**	15	**3b** (77)
4	**1a**	**2b**	—	15	**3b** (75)
5	**1a**	**2c**	**I**	15	**3c** (77)
6	**1a**	**2c**	—	15	**3c** (74)
7	**1a**	**2d**	**I**	15	**3d** (75)
8	**1a**	**2d**	—	15	**3d** (60)
9	**1a**	**2e**	**I**	60	**3e** (66)
10	**1a**	**2e**	—	60	**3e** (60)
11	**1b**	**2a**	**I**	30	**3f** (87)
12	**1b**	**2a**	—	30	**3f** (73)
13	**1c**	**2a**	**I**	150	**3g** (66)
14	**1c**	**2a**	—	150	**3g** (55)

[a] 5 mol% of L-proline was used.

Conclusion

Organocatalysed addition of thiophenols to chalcones in ionic liquids proceeded with excellent chemical yields, although with very low enantioselectivity due to the fact that L-proline and other organocatalysts can act only as weak bases in these solvents. The addition of thiophenols to chalcones also proceeded very well in neat ionic liquids, which proved that its nucleophilicity, and possibly also dissociation constant, is higher in ionic liquids than in organic solvents. It was proved that this is a more general phenomenon by addition of various thiols to several α-enones. It was also shown that acids (including chiral carboxylic acids) can be used as the catalyst.

Experimental

NMR spectra were measured on a Varian Gemini 2000 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR); tetramethylsilane was used as an internal standard. Elemental analysis were performed on Carlo Erba instrument. Enantioselectivities were determined by HPLC (Krüss P3002RS instrument) of the product on a chiral column (Chiralcel OD–H) using *n*-hexane–2-propanol (90 : 10 v/v) as an eluent, and cellulose tris(3,5-dimethylphenylcarbamate) coated on 5 μm silica gel as the solid phase. MS data were obtained on a Hewlett–Packard Agilent 1100 Series MSD HPLC-MS instrument. Reagent-grade organocatalysts and starting materials were purchased (Aldrich, Acros, Fluka, Merck) and used without further purification. Ionic liquids were purchased from Solvent Innovation and from Merck.

General experimental procedure

Ionic liquid (1 ml) was degassed by stirring under reduced pressure (oil pump). The enone (**1a–c**) (1 mmol) and a catalyst (5 mol%) were added and the mixture was stirred for 10 min at room temperature. The thiol (**2a–e**) (1.1 mmol) was added and the

reaction mixture was stirred vigorously for a specified time (see Tables 1–4) at room temperature. The product was extracted with several portions of diethyl ether and the combined organic extracts were evaporated *in vacuo*. The residue was purified by column chromatography on SiO_2 (hexane–ethyl acetate 9 : 1). The product was isolated as a pure material and its structure was proved by ^{1}H NMR spectra. The spectroscopic characteristics of known products **3a**,[52] **3b**,[53] **3e**,[53] **3f**[54] and **3g**[55] were in agreement with published data.

1,3-Diphenyl-3-(4-fluorophenylsulfanyl)propan-1-one (3c). White solid, mp 83–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (2H, d, J = 8.4 Hz, ArH), 7.49–7.61 (2H, m, ArH), 7.45 (2H, t, J = 6.6 Hz, ArH), 7.12–7.28 (6H, m, ArH), 6.90 (2H, t, J = 8.7 Hz, ArH), 4.36 (1H, t, J = 7.2 Hz, SCH), 3.66 (1H, dd, J = 8.1 Hz, 17.1 Hz, C*H*H), 3.56 (1H, dd, J = 6.0 Hz, 17.1 Hz, CH*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 162.9 (d, J = 246.6 Hz), 141.3, 136.9, 136.2 (d, J = 8.3 Hz), 133.5, 129.2, 128.9, 128.7, 128.3, 128.0, 127.6, 116.1 (d, J = 21.5 Hz), 49.3, 44.5; ESMS 359.2 $[M + Na]^+$.

1,3-Diphenyl-3-(4-*tert*-butylphenylsulfanyl)propan-1-one (3d). White solid, mp 99–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 8.1 Hz, ArH), 7.19–7.58 (12H, m, ArH), 4.91 (1H, dd, J = 6 Hz, 8.1 Hz), 3.64 (1H, dd, J = 7.5 Hz, 15.2 Hz, C*H*H), 3.56 (1H, dd, J = 6.9 Hz, 15.2 Hz, CH*H*), 1.27 (9H, s, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 151.1, 141.5, 136.9, 133.4, 132.9, 130.9, 128.8, 128.7, 128.3, 128.0, 127.5, 126.1, 48.6, 45.0, 34.7, 31.4. Elemental analysis: calcd. for $C_{25}H_{26}OS$: C 80.18%, H 7.00%, S 8.55%; found: C 80.27%, H 7.01%, S 8.53%.

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