Supporting Information

Ionic Liquid Catalysed Reaction of Thiols with α,β-Unsaturated Carbonyl Compounds-Remarkable Influence of the C-2 Hydrogen and the Anion

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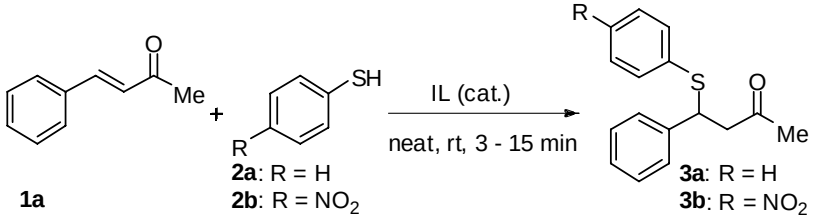
General Considerations:

General information: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 & 400 MHz NMR spectrometer in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$: 7.26/77.0) using Me_4Si as an internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. The IR spectra were recorded either as KBr pellets (for solids) or neat or CCl_4 (for liquids) on a Nicolet Impact 410 FTIR spectrometer. Mass spectra were recorded on (Shimadzu) [for EI] mass spectrometers. Optical rotations were measured on Autopol® IV Automatic Polarimeter (Rudoph Research Analytical). Melting points were measured with Gupta scientific melting point apparatus and were uncorrected. Open column chromatography, thin layer chromatography (TLC) was performed on Silica gel [CDH silica gel 60-120 mesh, F254 and Merck® silica gel respectively]. Solvent evaporation was performed at reduced pressure (Bűchi rotary evaporator). Chemicals were purchased from Aldrich, Lancaster and Fluka Chemicals and used as received.

Table 1: Reaction of 1a with 2a/2b in the presence of various ILs.[a]



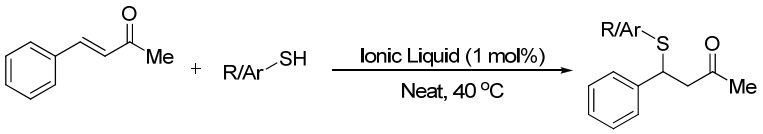
1a **2a**: R = H **2b**: R = NO_2 **3a**: R = H **3b**: R = NO_2

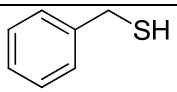
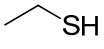
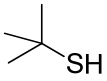
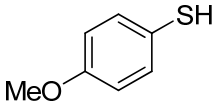
entry	IL	mol %	yield (%)[b]	
			3a	3b
1	[bmim][Br]	10	20	25
2	[bmim][BF_4]	10	15	20
3	[bmim][PF_6]	10	15	22
4	[bmim][ClO_4]	10	20	20
5	[bmim][NTf_2]	10	10	18
6	[bmim][$MeSO_4$]	10	25	28
8	[bmim][HSO_4]	10	20	26
9	[bmim][$MeSO_3$]	10	30	28
10	[bmim][N_3]	10	60	65
11	[bmim][$N(CN)_2$]	10	95	92
12	[bmim][OAc]	10	95	92
13	[bmim][N_3]	5	60	55
14	[bmim][$N(CN)_2$]	5	95	90

15	[bmim][OAc]	5	95	91
16	[bmim][N_3]	2.5	45	40
17	[bmim][$N(CN)_2$]	2.5	95	89
18	[bmim][OAc]	2.5	95	89
19	[bmim][N_3]	1	35	20
20	[bmim][$N(CN)_2$]	1	95	89
21	[bmim][OAc]	1	95	89
22	[bmim][$N(CN)_2$]	0.1	92[c]	89[c]
23	[bmim][OAc]	0.1	93[c]	89[c]
24	[bmim][$N(CN)_2$]	0.01	5[d]	15[d]
25	[bmim][OAc]	0.01	15[d]	25[d]
26	[bdmim][$N(CN)_2$]	0.1	0[c,e,f]	0[c,e,f]
27	[bdmim][OAc]	0.1	0[c,e,f]	5[c,e,f]
28	[bdmim][N_3]	5	15[e,f]	12[e,f]
29	NaN_3	5	0[e,f]	0[e,f]
30	NaOAc	1	0[e,f]	0[e,f]
31	NH_4OAc	1	0[e,f]	0[e,f]
32	$NaN(CN)_2$	1	0[e,f]	0[e,f]
33	none	---	0[e,f,g]	0[e,f,g]

[a] **1a** (2.5 mmol except for entries 23-28) was treated with **2a**/**2b** (2.75 mmol, 1.1 equiv) at rt (30-35 ^{0}C) in the presence of the IL (except for entries 29-33) for 15 min for **2a** and 3 min for **2b** under neat condition (unless otherwise mentioned). [b]Yield after column chromatographic purification (IR, NMR and MS). [c]The reaction was performed using 25 mmol of **1a**. [d]The reaction was perforned using 50 mmol of **1a**. [e]The reaction was carried out for 60 min. [f]The starting materials remained unchanged. [g]No thia-Michael addition took place when the reaction was performed using DMSO, MeCN and Et_2O as solvent in the absence of any added catalyst.

Table 2: Reaction of 1a with different thiophenol in presence of [bmim][OAc]/[bmim][N(CN)$_2$]:[a]

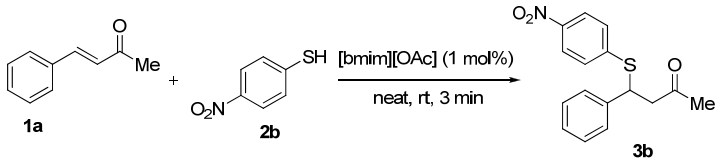


entry	thiophenol	time (min)	[bmim][OAc] yield (%)[b]	[bmim][N(CN)$_2$] yield (%)[b]
1		20	93	89
2		20	88	85
3		10	90	82[c]
4		15	91	87

[a] **1a** (2.5 mmol) was treated with thiophenol (2.75 mmol, 1.1 equiv) at rt (30-35 ^{0}C) in the presence of the IL (1 mol %) under neat condition. [b] Yield after column chromatographic purification (IR, NMR and MS). [c] The reaction was carried out at 55 ^{o}C

Experimental Procedure:

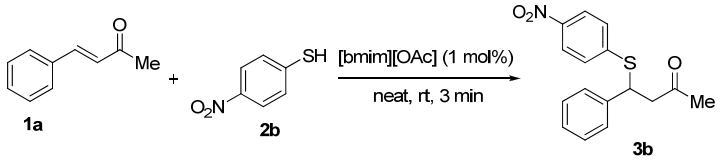
Typical procedure for thia-Michael addition for the synthesis of 4-phenyl-4-nitrothiophenyl-2-butanone 3b in presence of [bmim][OAc]:



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol) and 4-nitrothophenol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), [bmim][OAc] (0.005 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C). After complete consumption of 4-phenylbut-3-en-2-one (TLC, 3 min), the reaction mixture was diluted with EtOAc (15 mL) and water (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined EtOAc extracts were dried ($MgSO_4$) and concentrated under vacuum rotary evaporation. The residue was passed through a bed of

silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (150 mL) to afford **3b** as a light yellow solid (0.66 g, 89%).

Typical procedure for thia-Michael addition for the synthesis of 4-phenyl-4-nitrothiophenyl-2-butanone 3b in presence of [bmim][N(CN)$_2$]:



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol) and 4-nitrothophenol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), [bmim][N(CN)$_2$] (0.005 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C). After complete consumption of 4-phenylbut-3-en-2-one (TLC, 3 min), the reaction mixture was diluted with EtOAc (15 mL) and water (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined EtOAc extracts were dried ($MgSO_4$) and concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (150 mL) to afford **3b** as a light yellow solid (0.66 g, 89%).

Large Scale Reaction and Reusability of the Catalyst [bmim][OAc]:

The [bmim][OAc] (0.04 g, 0.20 mmol, 1 mol %) was added to a magnetically stirred mixture of 4-phenylbut-3-en-2-one (**1a**, 2.92 g, 20 mmol) and thophenol (**2a**, 2.42 g, 22.0 mmol, 1.1 equiv) at rt (30-35 °C). After completion of the reaction (15 min), the reaction mixture was diluted with EtOAc (30 mL) followed by addition of a 5 mL of water (to dissolved the catalyst). The EtOAc layer was separated, the EtOAc exctract was dried ($MgSO_4$) and concentrated under vacuo to obtain the crude product which on purification by column chromatography (60-120 mesh Silica gel; 10% EtOAc-Hexane as eluent) to afford **3a**. The aqueous extract/layer containing the ionic liquid was concentrated under vacuum at 80° C for 60 min to recover the IL which was found to be identical (spectral data) with an authentic sample of [bmim][OAc] (unused ionic liquid). The recovered IL (1 mol%) was reused for five consecutive fresh bathches of reactions of 4-phenylbut-3-en-2-one (**1a**) and thophenol (**2a**) (1.1 equiv) at rt to afford **3a** after usual work-up and purification (see following table).

Run	Scale (mmol)[a]	Amount of [bmim][OAc] used	Amount of [bmim][OAc] recovered (%)	Yield of **3a**[b] (Amount)
First Use	20	0.040 g	0.037 g (94%)	95% (4.86 g)
First Reuse	19	0.037 g	0.035 g (94%)	95% (4.62 g)
Second Reuse	18	0.035 g	0.033 g (93%)	94% (4.33 g)

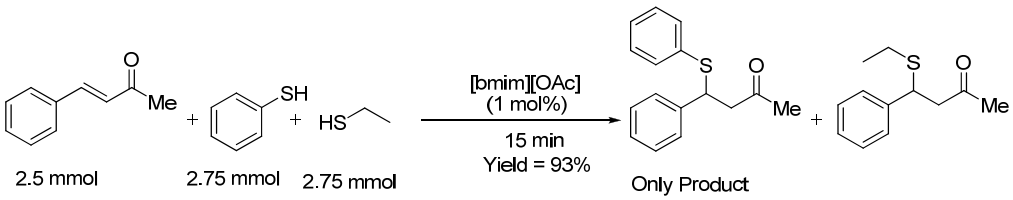
Third Reuse	16	0.031 g	0.029 g (93%)	94% (3.85 g)
Fourth Reuse	14	0.027 g	0.025 g (92%)	93% (3.33 g)
Fifth Reuse	12	0.023 g	0.022 g (91%)	90% (2.76 g)

[a]The amount of **1a** used for the reaction. [b]Yield of **3a** after purification.

Selectivity Studies:

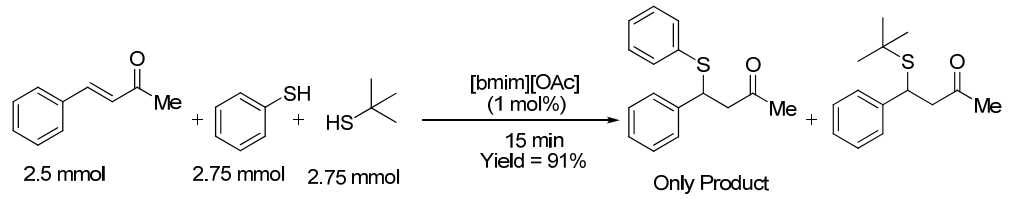
Experimental procedures for selective thia-Michael addition reaction catalysed by [bmim][OAc]:

*Scheme : Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2a** and **2d** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and marcaptoethanol (**2d**, 0.170 g, 2.75 mmol, 1.1 equiv) was added [bmim][OAc] (0.005 g, 1 mol%) and the reaction mixture was stirred magnetically at rt (30-35 °C) for 15 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-phenyl-4-(phenylthio)butan-2-one (**3a**) as only product (0.595 g, 93%).

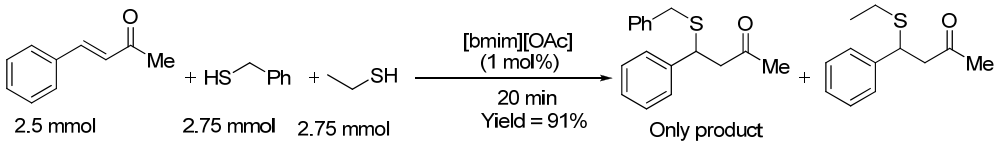
*Scheme : Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g. **2a** and **2e** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and *tert*-butylthiol (**2e**, 0.247 g, 2.75 mmol, 1.1 equiv) was added [bmim][OAc] (0.005 g, 1 mol%) and the reaction mixture was stirred magnetically at rt (30-35 °C) for 15 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed

through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-phenyl-4-(phenylthio)butan-2-one (**3a**) as only product (0.582 g, 91%).

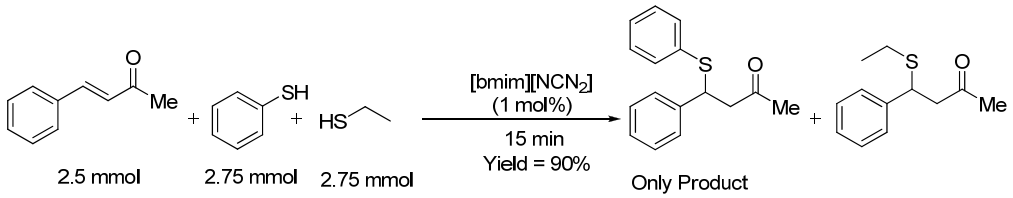
*Scheme : Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2f** and **2d** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), α-tolunethiol (**2f,** 0.341 g, 2.75 mmol, 1.1 equiv) and marcaptoethanol (**2d**, 0.170 g, 2.75 mmol, 1.1 equiv) was added [bmim][OAc] (0.005 g, 1 mol%) and the reaction mixture was stirred magnetically at rt (30-35 °C) for 20 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-(benzylthio)-4-phenylbutan-2-one as only product (0.614 g, 91%).

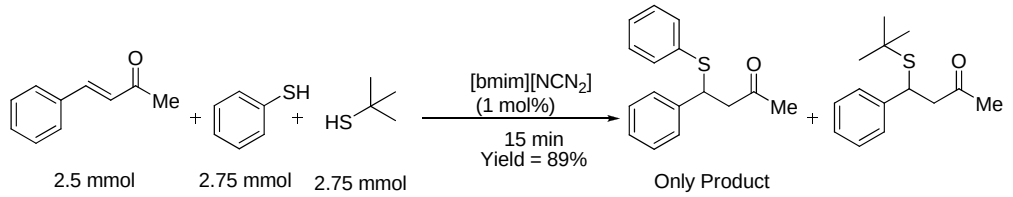
Experimental procedures for selective thia-Michael addition reaction catalysed by [bmim][N(CN)$_2$]:

*Scheme : Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2a** and **2d** with varying hydrogen bond formation ability:*



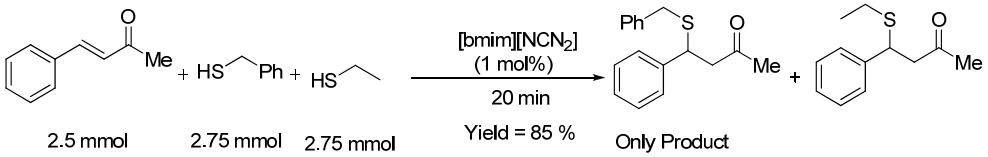
To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and marcaptoethanol (**2d**, 0.170 g, 2.75 mmol, 1.1 equiv) was added [bmim][N(CN)$_2$] (0.005 g, 1 mol%) and the reaction mixture was stirred magnetically at rt (30-35 °C) for 15 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-phenyl-4-(phenylthio)butan-2-one (**3a**) as only product (0.575 g, 90%).

*Scheme : Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g. **2a** and **2e** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and *tert*-butylthiol (**2e**, 0.247 g, 2.75 mmol, 1.1 equiv) was added [bmim][N(CN)$_2$] (0.005 g, 1 mol%) and the reaction mixture was stirred magnetically at rt (30-35 °C) for 15 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-phenyl-4-(phenylthio)butan-2-one (**3a**) as only product (0.569 g, 89%).

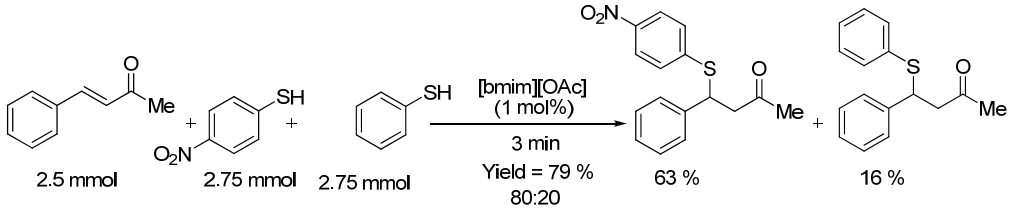
*Scheme : Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2f** and **2d** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), α-tolunethiol (**2f,** 0.341 g, 2.75 mmol, 1.1 equiv) and marcaptoethanol (**2d**, 0.170 g, 2.75 mmol, 1.1 equiv) was added [bmim][$N(CN)_2$] (0.005 g, 1 mol%) and the reaction mixture was stirred magnetically at rt (30-35 °C) for 20 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-(benzylthio)-4-phenylbutan-2-one as only product (0.573 g, 85%).

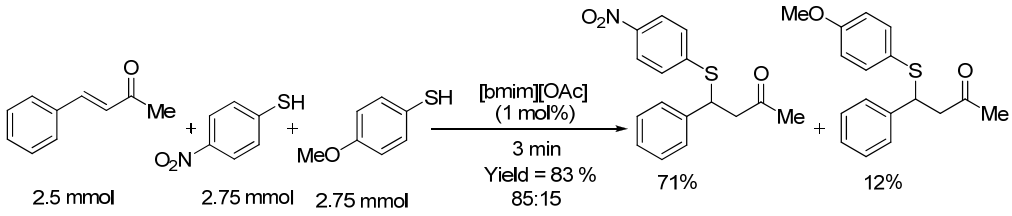
Experimental procedures for selective thia-Michael addition reaction catalysed by [bmim][OAc]:

*Scheme 2: Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2a** and **2b** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and 4-nitrobenzenethiol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), [bmim][OAc] (0.005 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C) for 3 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation to afford the thia-Miclael adducts in 79% yield. The crude thia-Michael adduct was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afforded the 4-(benzylthio)-4-phenylbutan-2-one (0.102 g, 16%). Further elution with 10% EtOAc in hexane (200 mL) affords the 4-(4-nitrophenylthio)-4-phenylbutan-2-one as major products (0.477 g, 63%). This reflected a 80:20 selectivity in favour of the thia-Michael adduct of thiophenol.

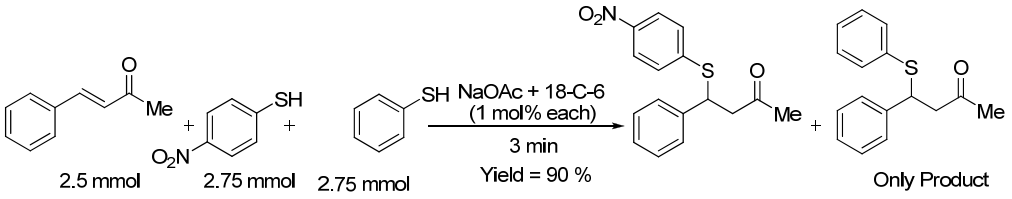
*Scheme 2: Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2b** and **2c** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), 4-methoxybenzenethiol (**2c**, 0.385 g, 2.75 mmol, 1.1 equiv) and 4-nitrobenzenethiol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), [bmim][OAc] (0.005 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C) for 3 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation to afford the thia-Miclael adducts in 83% yield. The crude thia-Michael adduct was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afforded the 3-(benzylthio)-3-methylcyclohexanone (0.086 g, 12%). Further elution with 10% EtOAc in hexane (200 mL) affords the 4-(4-nitrophenylthio)-4-phenylbutan-2-one as major products (0.534 g, 71%). This reflected 85:15 selectivity in favour of the thia-Michael adducts of thiophenol.

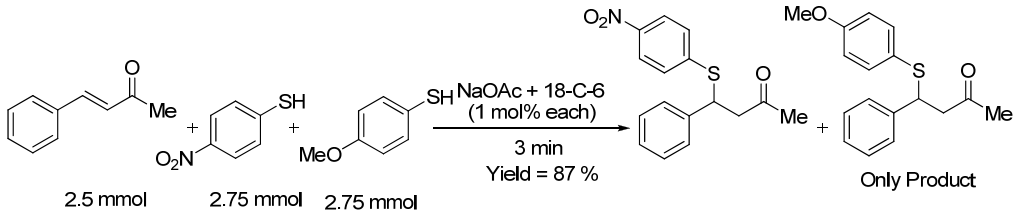
Experimental procedures for selective thia-Michael addition reaction catalysed by [NaOAc and 18-C-6]:

*Scheme 2: Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2a** and **2b** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and 4-nitrobenzenethiol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), NaOAc (0.002 g, 1 mol%) and 18-C-6 (0.007 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C) for 3 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-phenyl-4-(phenylthio)butan-2-one (**3a**) as only product (0.575 g, 90%).

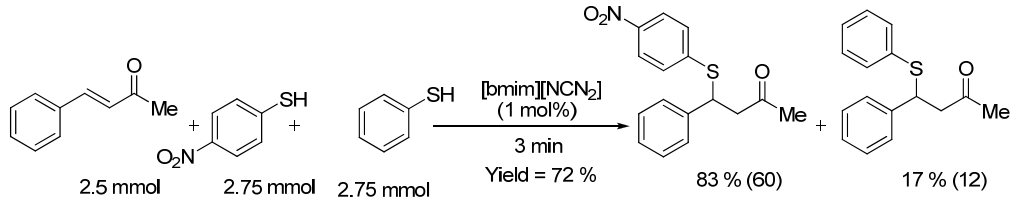
*Scheme 2: Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2b** and **2c** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), 4-methoxybenzenethiol (**2c**, 0.385 g, 2.75 mmol, 1.1 equiv) and 4-nitrobenzenethiol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), NaOAc (0.002 g, 1 mol%) and 18-C-6 (0.007 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C) for 3 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation. The residue was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afford the 4-(4-methoxyphenylthio)-4-phenylbutan-2-one (**3c**) as only product (0.62 g, 87%).

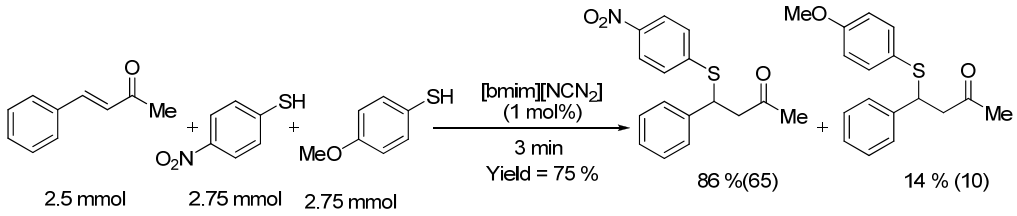
Experimental procedures for selective thia-Michael addition reaction catalysed by [bmim][$N(CN)_2$]:

*Scheme 2: Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2a** and **2b** with varying hydrogen bond formation ability:*



To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), thiophenol (**2a**, 0.302 g, 2.75 mmol, 1.1 equiv) and 4-nitrobenzenethiol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), [bmim][$N(CN)_2$] (0.005 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C) for 3 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation to afford the thia-Miclael adducts in 72% yield. The crude thia-Michael adduct was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afforded the 4-(benzylthio)-4-phenylbutan-2-one (0.077 g, 12%). Further elution with 10% EtOAc in hexane (200 mL) affords the 4-(4-nitrophenylthio)-4-phenylbutan-2-one as major products (0.454 g, 60%). This reflected a 83:17 selectivity in favour of the thia-Michael adduct of thiophenol.

*Scheme 2: Thia-Michael addition Reaction of **1a** with equimolar amounts of two different thiols e.g., **2b** and **2c** with varying hydrogen bond formation ability:*

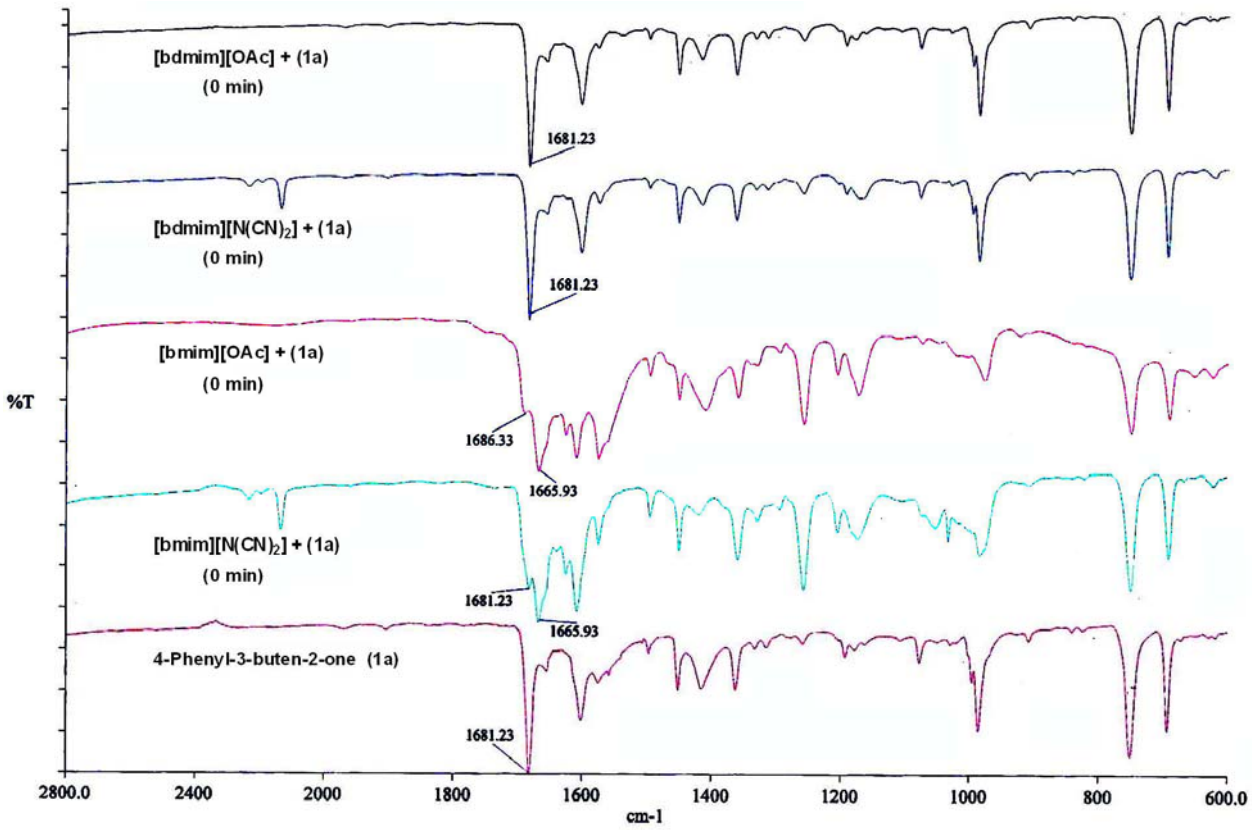


To the mixture of 4-phenylbut-3-en-2-one (**1a**, 0.365 g, 2.5 mmol), 4-methoxybenzenethiol (**2c**, 0.385 g, 2.75 mmol, 1.1 equiv) and 4-nitrobenzenethiol (**2b**, 0.426 g, 2.75 mmol, 1.1 equiv), [bmim][$N(CN)_2$] (0.005 g, 1 mol%) was added and the reaction mixture was stirred magnetically at rt (30-35 °C) for 3 min. The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined EtOAc extracts were concentrated under vacuum rotary evaporation to afford the thia-Miclael adducts in 75% yield. The crude thia-Michael adduct was passed through a bed of silica gel (10 g; #60-120) and eluted with 10% EtOAc in hexane (500 mL) to afforded the 4-(4-methoxyphenylthio)-4-phenylbutan-2-one (0.071 g, 12%). Further elution with 10% EtOAc in hexane (200 mL) affords the 4-(4-nitrophenylthio)-4-phenylbutan-2-one as major products (0.488 g, 65%). This reflected 86:14 selectivity in favour of the thia-Michael adducts of thiophenol.

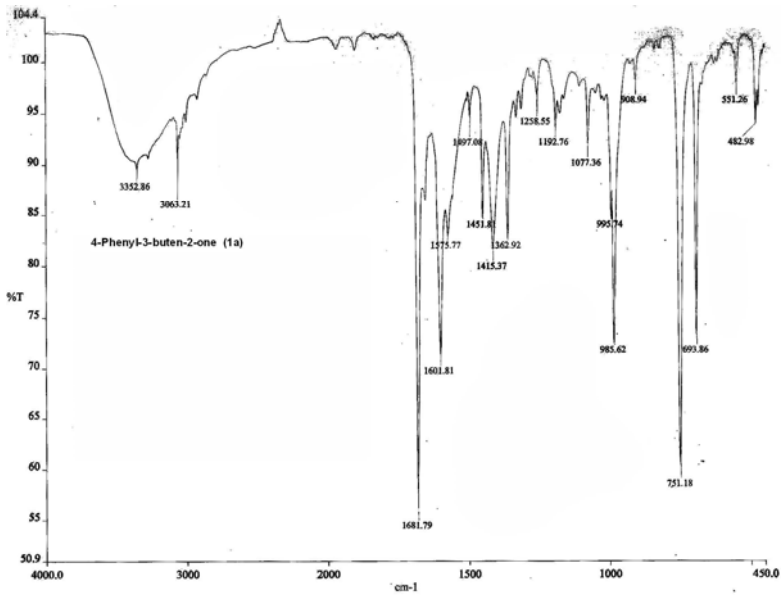
Experimental Procedure for IR Studies:

4-Phenyl-3-buten-2-one (**1a**) (0.146 g, 1 mmol) and [bmim][OAc] (0.198 g, 1 equiv, 1 mmol) was stirred magnetically at 40 °C. Aliquot portion of the reaction mixture (20μL) was taken out after 0 min, 5 min and 10 min which were subjected to record IR spectrum. Similar procedure was followed in using [bdmim][OAc], [bmim][$N(CN)_2$]and [bdmim][$N(CN)_2$] and the recorded spectra are provided below.

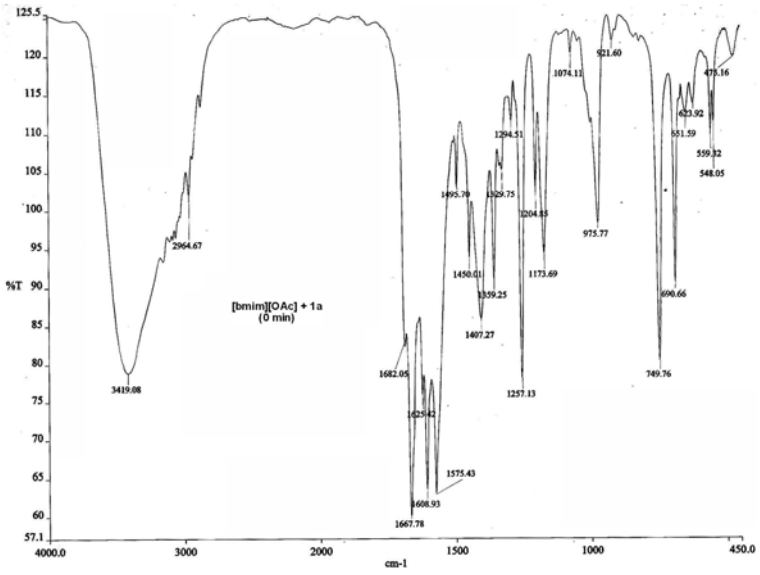
Effect on $\upsilon_{c=o}$ of the carbonyl substrate: Overlay of IR spectra after 0 min of treatment/mixing of 1a with [bmim][OAc], [bdmim][OAc], [bmim[[N(CN)$_2$], [bdmim][N(CN)$_2$].



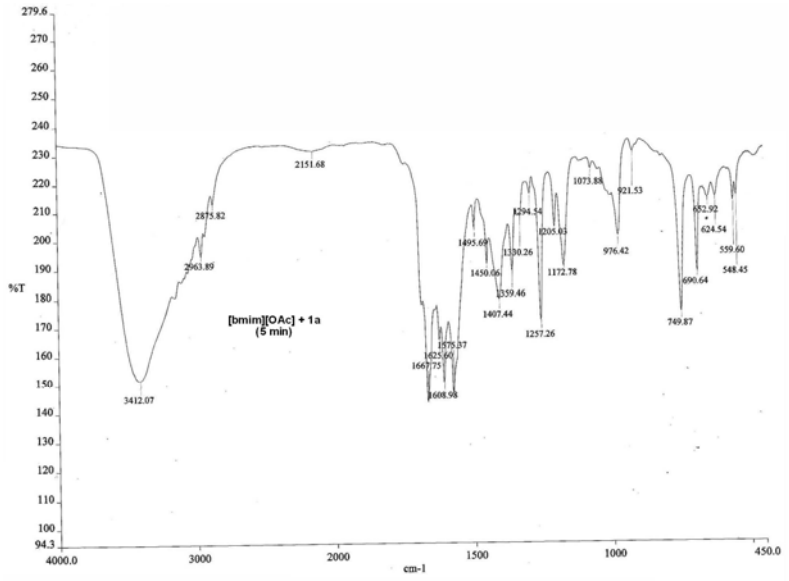
IR spectrum 4-phenyl-3-buten-2-one (1a):



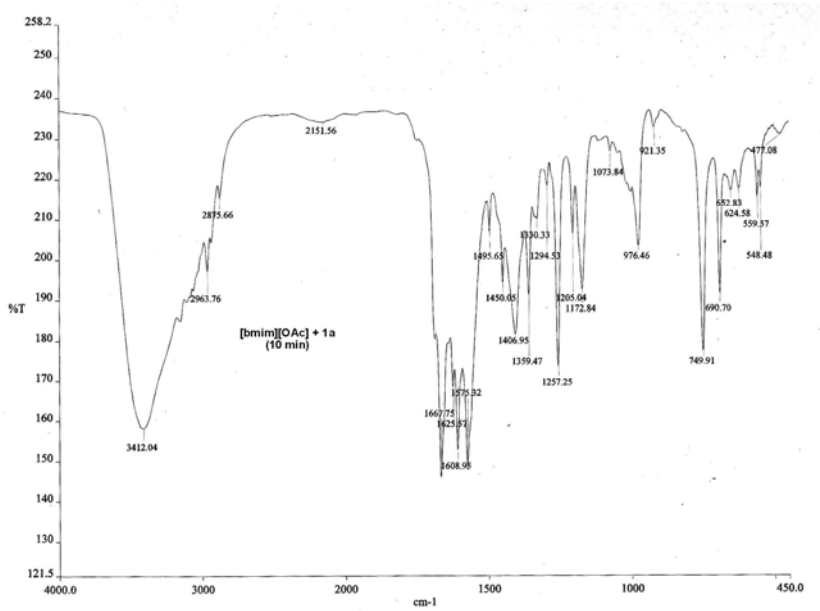
IR spectrum of sample after 0 min of treatment/mixing of 1a with [bmim][OAc]



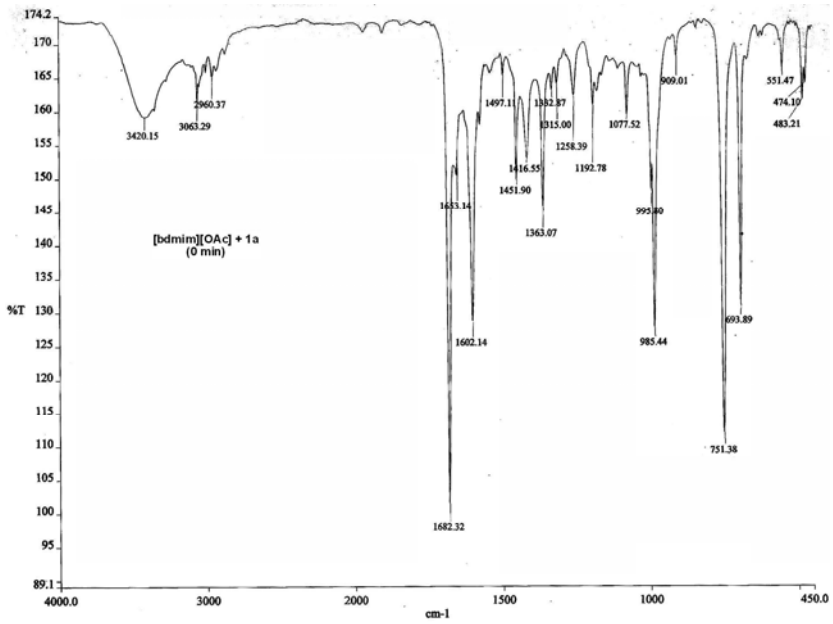
IR spectrum of sample after 5 min of treatment/mixing of 1a with [bmim][OAc]



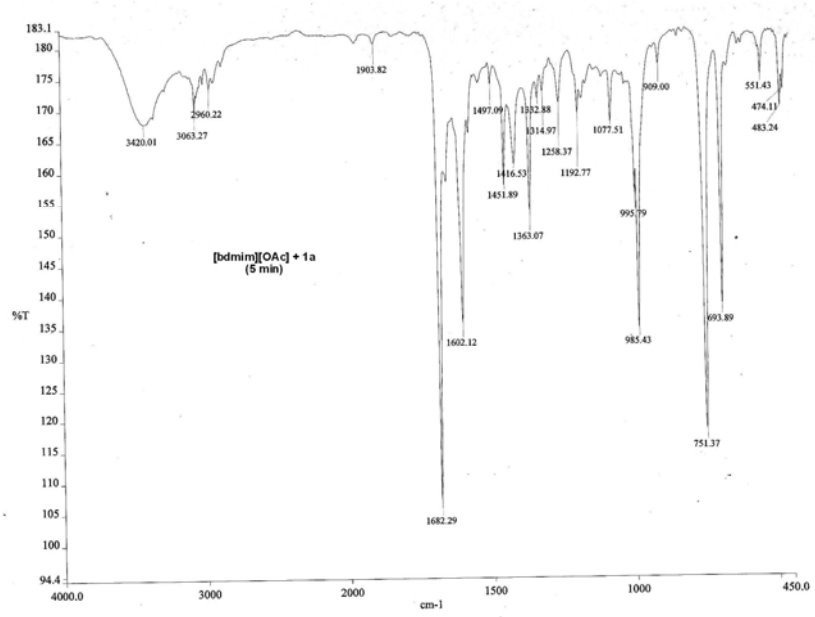
IR spectrum of sample after 10 min of treatment/mixing of 1a with [bmim][OAc]



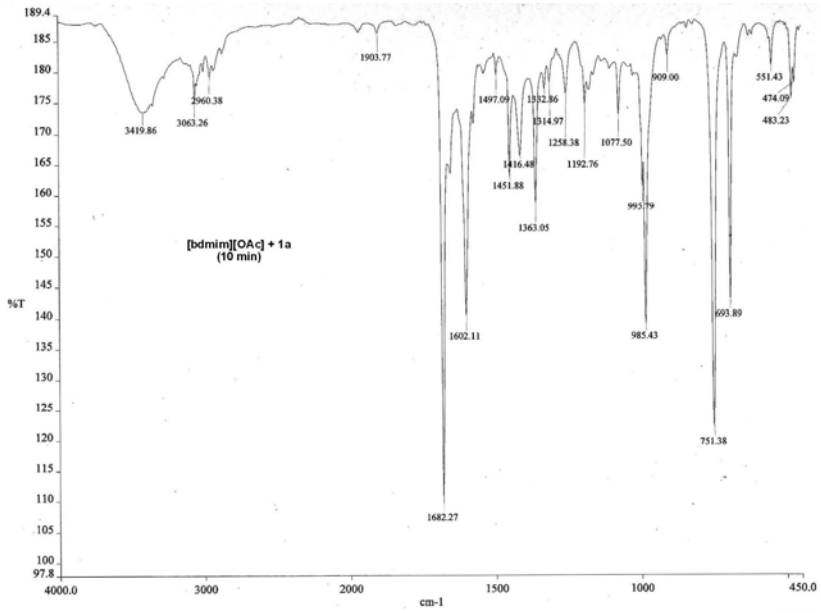
IR spectrum of sample after 0 min of treatment/mixing of 1a with [bdmim][OAc]



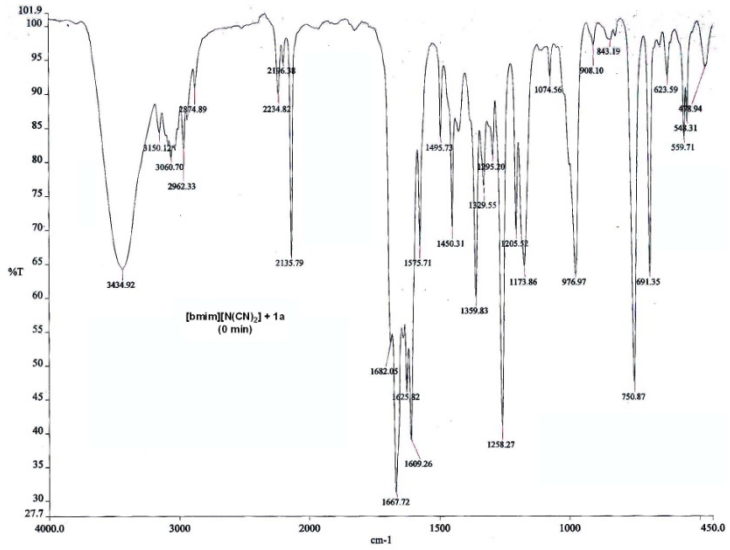
IR spectrum of sample after 5 min of treatment/mixing of 1a with [bdmim][OAc]



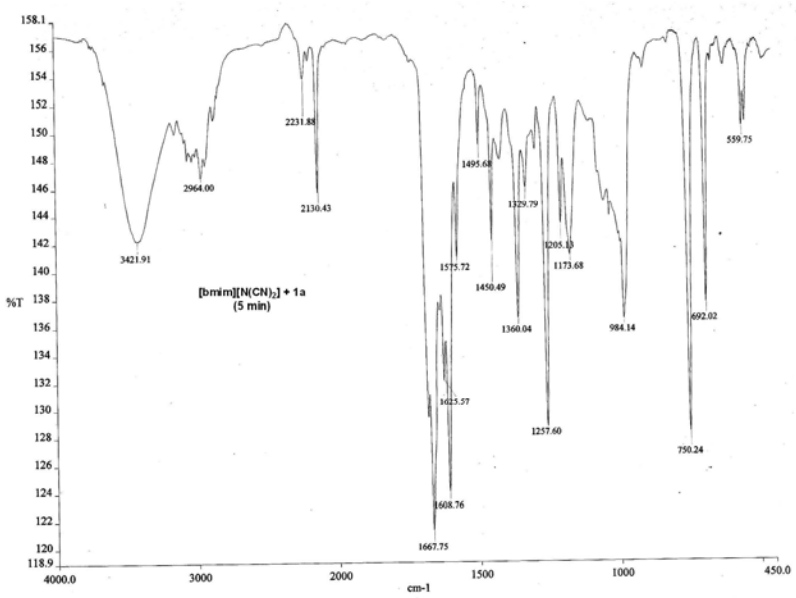
IR spectrum of sample after 10 min of treatment/mixing of 1a with [bdmim][OAc]



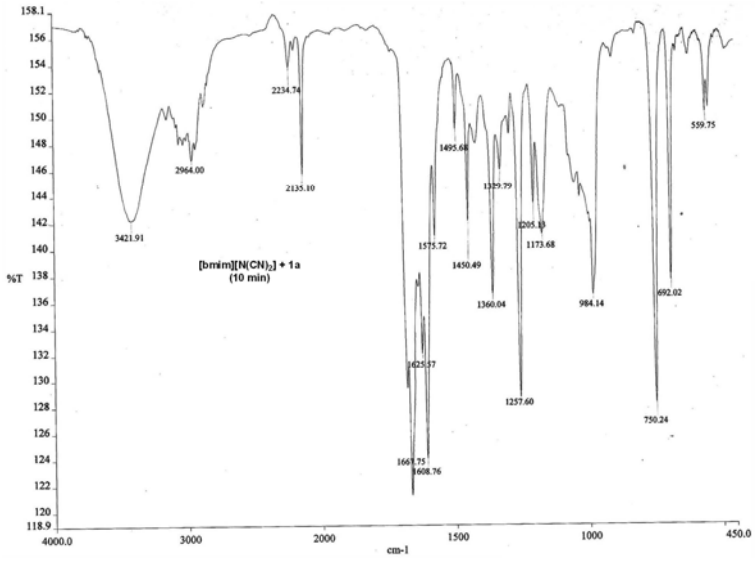
IR spectrum of sample after 0 min of treatment/mixing of 1a with [bmim][N(CN)$_2$]



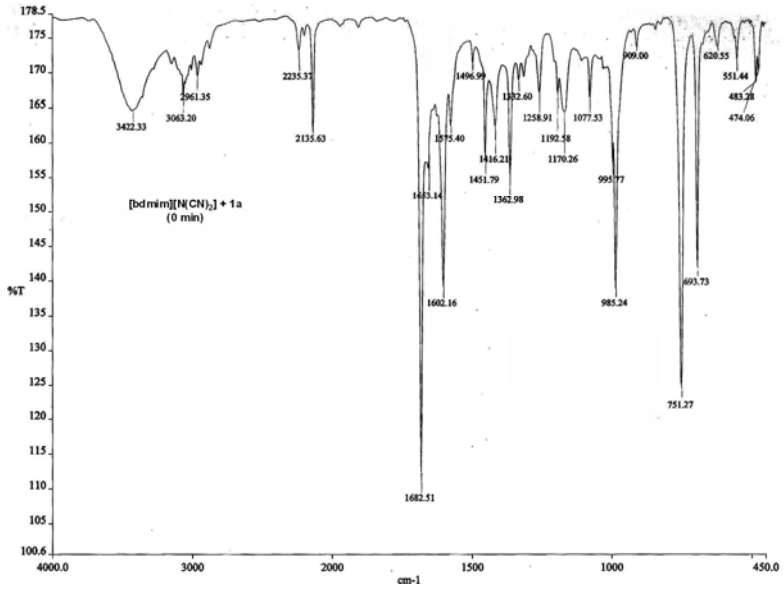
IR spectrum of sample after 5 min of treatment/mixing of 1a with [bmim][N(CN)$_2$]



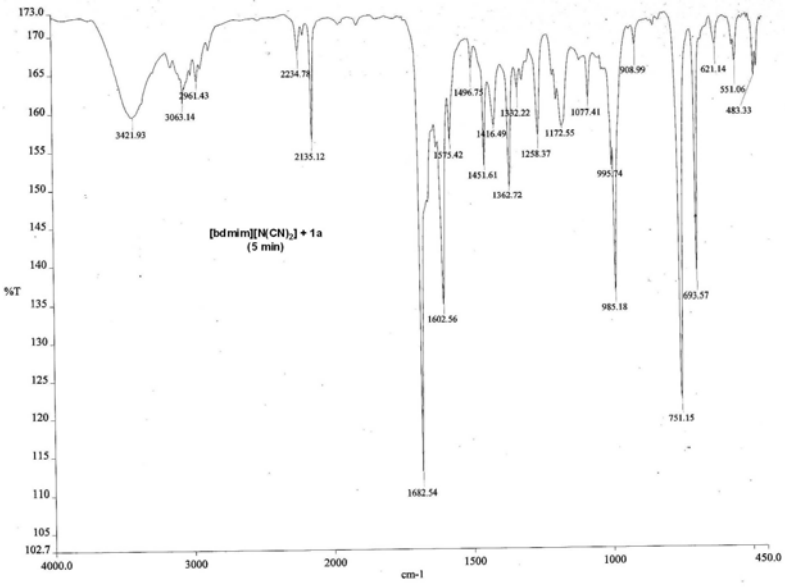
IR spectrum of sample after 10 min of treatment/mixing of 1a with [bmim][N(CN)$_2$]



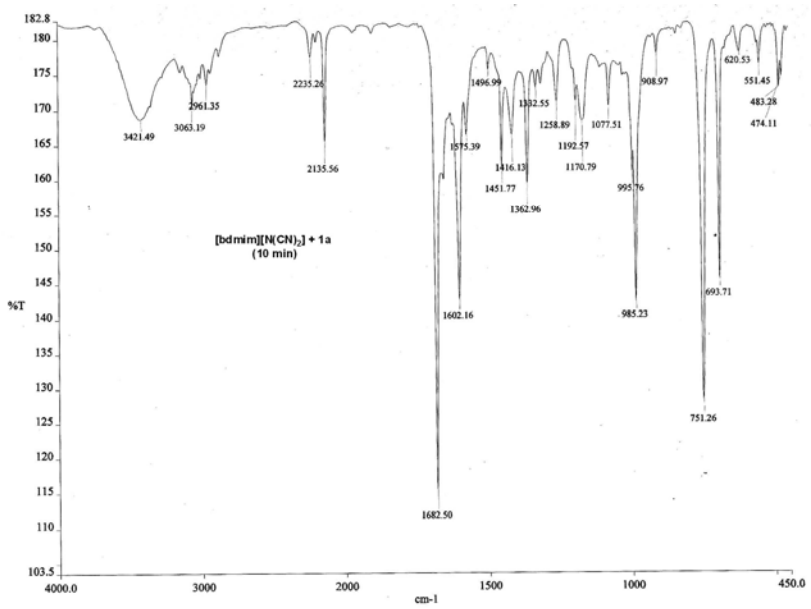
IR spectrum sample after 0 min of treatment/mixing of 1a with [bdmim][N(CN)$_2$]



IR spectrum of sample after 5 min of treatment/mixing of 1a with [bdmim][N(CN)$_2$]



IR spectrum of sample after 10 min of treatment/mixing of 1a with [bdmim][N(CN)$_2$]



Rationalisation of thia-Michael Reaction in DMSO, MeCN, Et_2O and DCM and Comparison with [bmim][OAc] and [bmim][$N(CN)_2$] catalysed Reactions:

Thia-Michael reaction of chalcone, cyclohexenone and benzylideneacetone with thiophenol and benzylthiol is reported to take place in common organic solvents such as DMSO, MeCN, Et_2O in the absence of any addendum (catalyst) [*Lett. Org. Chem*. 2006, *3*, 794-797]. However, the outcome of these reactions can be adequately and more appropriately accounted for as a general base-catalysed process. Herein the solvents such as DMSO, MeCN, Et_2O, DCM or PhMe do not merely act as a solvent either to create a homogenius environment or to provide polarity to the reaction condition. If providing a homogenious environment is the reason then all of these should have been equally effective but this is not what happens as no appreciable thia-Michael addition has been observed after 8 h using DCM or PhMe as solvent. On the other hand, if polarity is the criteria then DCM (a more polar solvent with $\varepsilon = 8.93$) should not have been ineffective (trace yield after 6 h) but Et_2O (a less polar solvent $\varepsilon = 4.20$) would have afforded 69 and 95% yields after 30 and 60 min, respectively. The common organic solvents are Lewis bases [*Angew. Chem. Int Ed.* 2008, 47, 1560-1638] and their relative basicity is determined by the Gutmann donicity number (DN). The DN values of DMSO, MeCN, Et_2O and DCM are 29.8, 14.1, 19.2 and 0, respectively. Thus, DMSO acts as a Lewis base towards a proton donor (in this case thiol) and would be as effective as pyridine (DN value is 33.1). The negligible DN value of DCM accounts for its ineffectiveness in promoting the thia-Michael reaction. Therefore the thia-Michael reaction of chalcone with thiophenol **2a** in DMSO, MeCN and Et_2O [*Lett. Org. Chem*. 2006, 3, 794-797] proceeds through a base catalysis mode wherein the solvent itself acts as the base. In this context we reasoned that it would be difficult to perform thia-michael reaction with electron deficient thiols (e.g. 4-nitrothiophenol) as in that case the negative charge of the generated 4-nitrothiophenolate anion would be stabilised/delocalised by the nitro group due to polarity of these solvents. It is due to this reason that we performed the reaction of **1a** with **2a** and **2b** in DMSO, MeCN and Et_2O (table 1, entry 33, footnote h of the manuscript). Similarly the reactions of alkyl thiols such as *tert*-butyl thiol would not proceed efficiently as it is less acidic that would not permit generation of the corresponding thiolate anion with these solvents.

Benzylideneacetone [i.e., 4-phenyl-3-butene-2-one **1a**] has not been used as a substrate in performing thia-michael reaction in DMSO, MeCN and Et_2O [*Lett. Org. Chem*. **2006**, *3*, 794-797] and 4-nitrothiophenol, benzylthiol and *tert*-butyl thiols were not used as the reacting thiols. We performed the following reactions to put more insight on this mater:

Table A. Reaction of Chalcone (1,3-diphenyl-3-butene-2-one) with Thiophenol, 4-Nitrothiophenol and *tert*-Butyl thiol in different Solvents at Room Temperature (rt).[a]

Entry	thiol	catalyst (mol%)	solvent	time (min)	yield (%)[b]
1	PhSH	none	DMSO	20	80
2	PhSH	none	MeCN	15	93
3	PhSH	none	Et_2O	60	95
4	**PhSH**	**[bmim][OAc] (0.1)**	**neat**	**2**	**93**
5	**PhSH**	**[bmim][$N(CN)_2$] (0.1)**	**neat**	**2**	**92**
6	**PhSH**	**none**	**neat**	**2**	**Nil**
7	4-NO_2-C_6H_4SH	none	DMSO	60	Nil
8	4-NO_2-C_6H_4SH	none	MeCN	60	Nil
9	4-NO_2-C_6H_4SH	none	Et_2O	60	Nil
10	**4-NO_2-C_6H_4SH**	**[bmim][OAc] (1)**	**neat**	**1**	**92**
11	^{t}BuSH	none	DMSO	60	Nil
12	^{t}BuSH	none	MeCN	60	Nil
13	^{t}BuSH	none	Et_2O	60	Nil
14	**^{t}BuSH**	**[bmim][OAc] (1)**	**neat**	**7**	**92**

[a]Entries 1-3 were performed to reproduce the reported data [*Lett. Org. Chem.* 2006, **3**, 794-797]. [b]Refers to the corresponding thia-Michael adduct.

Table B. Reaction of 4-Phenyl-3-butene-2-one (1a) with Thiophenol (2a), 4-Nitrothiophenol (2b) and *tert*-Butyl thiol (2e) in different Solvents.

Entry	thiol	catalyst (mol%)	solv	temp (°C)	time (min)	yield (%)[a]
1	PhSH	none	DMSO	rt	60	Nil
2	PhSH	none	MeCN	rt	60	Nil
3	PhSH	none	Et_2O	rt	60	Nil

4	**PhSH**	**[bmim][OAc] (1)**	**neat**	**rt**	**15**	**95**
5	**PhSH**	**[bmim][$N(CN)_2$] (1)**	**neat**	**rt**	**15**	**95**
6	4-NO_2-C_6H_4SH	none	DMSO	rt	60	Nil
7	4-NO_2-C_6H_4SH	none	MeCN	rt	60	Nil
8	4-NO_2-C_6H_4SH	none	Et_2O	rt	60	Nil
9	**4-NO_2-C_6H_4SH**	**[bmim][OAc] (1)**	**neat**	**rt**	**3**	**89**
10	**4-NO_2-C_6H_4SH**	**[bmim][$N(CN)_2$] (1)**	**neat**	**rt**	**3**	**89**
11	^{t}BuSH	none	DMSO	55	60	Nil
12	^{t}BuSH	none	MeCN	55	60	Nil
13	^{t}BuSH	none	Et_2O	55	60	Nil
14	**^{t}BuSH**	**[bmim][OAc] (1)**	**neat**	**55**	**10**	**90**
15	**^{t}BuSH**	**[bmim][$N(CN)_2$] (1)**	**neat**	**55**	**10**	**82**

[a]Refers to the corresponding thia-Michael adduct.

Characterization of the compounds:

4-Phenyl-4-phenylsulfanyl-butan-2-one (3a):[1]

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 2.08 (s, 3 H), 3.03 (dd, *J* = 4 Hz, 16 Hz, 1H), 3.09 (dd, *J* = 8 Hz, 16 Hz, 1H), 4.71 (q, *J* = 4 Hz, 1H), 7.19-7.31 (m, 10 H); MS (ESI): *m/z* 258 (M + 1).

4-(4-Nitro-phenylsulfanyl)-4-phenyl-butan-2-one (3b):[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 2.12 (s, 3 H), 3.06 (dd, *J* = 4 Hz, 16 Hz, 1H), 3.13 (dd, *J* = 4 Hz, 12 Hz, 1H), 4.71 (t, *J* = 8 Hz, 1H), 7.22-7.61 (m, 7 H), 7.62-7.63 (m, 2 H); MS (ESI): *m/z* 302 (M + 1).

4-(4-Methoxy-phenylsulfanyl)-4-phenyl-butan-2-one (3c):

IR (DCM) ν: 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 2.06 (s, 3 H), 3.02 (dd, *J* = 1.72 Hz, 7 Hz, 2H), 3.76 (s, 3H), 4.53 (t, *J* = 7.40 Hz, 1H), 6.73-6.83 (m, 2H), 7.16-7.38 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 30.67, 49.12, 55.27, 55.37, 114.34, 114.62, 124.02, 127.30, 127.72, 128.26, 128.39, 128.98, 132.67, 136.27, 141.27, 159.89, 205.67; HRMS: *m/z* 287.1061 (M + 1).

[1] Gaurav Sharma, Raj Kumar, Asit K. Chakraborti, Tetrahedron Letters 49, 4272–4275, 2008
[2] Gopal L. Khatik, Gaurav Sharma, Raj Kumar and Asit K. Chakraborti, Tetrahedron 63, 1200–1210, 2007

4-Ethylsulfanyl-4-phenyl-butan-2-one (3d):[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 1.15 (t, *J* = 8 Hz, 3H), 2.08 (s, 3H), 2.08-2.36 (m, 2H), 2.96 (d, *J* = 4 Hz, 2H), 4.34 (t, *J* = 8 Hz, 1H), 7.20-7.35 (m, 5H); MS (ESI): *m/z* 209 (M + 1).

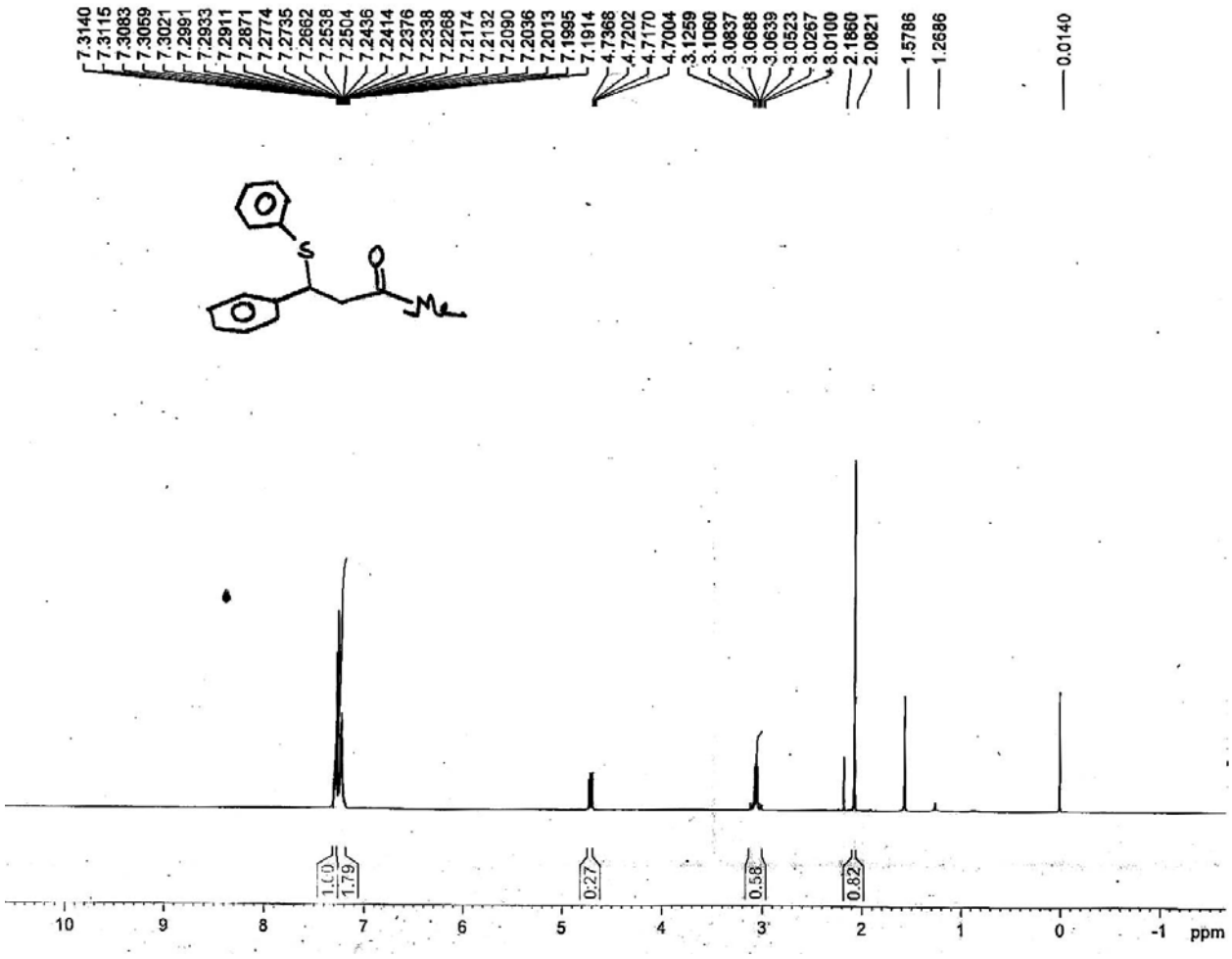
4-*tert*-Butylsulfanyl-4-phenyl-butan-2-one (3e):[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 1.19 (s, 9H), 2.05 (s, 3H), 2.89 (dd, *J* = 8 Hz, 16 Hz, 2H), 4.41 (t, *J* = 8 Hz, 1H), 7.19-7.20 (m, 1H), 7.26-7.29 (m, 2H), 7.37-7.40 (m, 2H); MS (ESI): *m/z* 237 (M + 1).

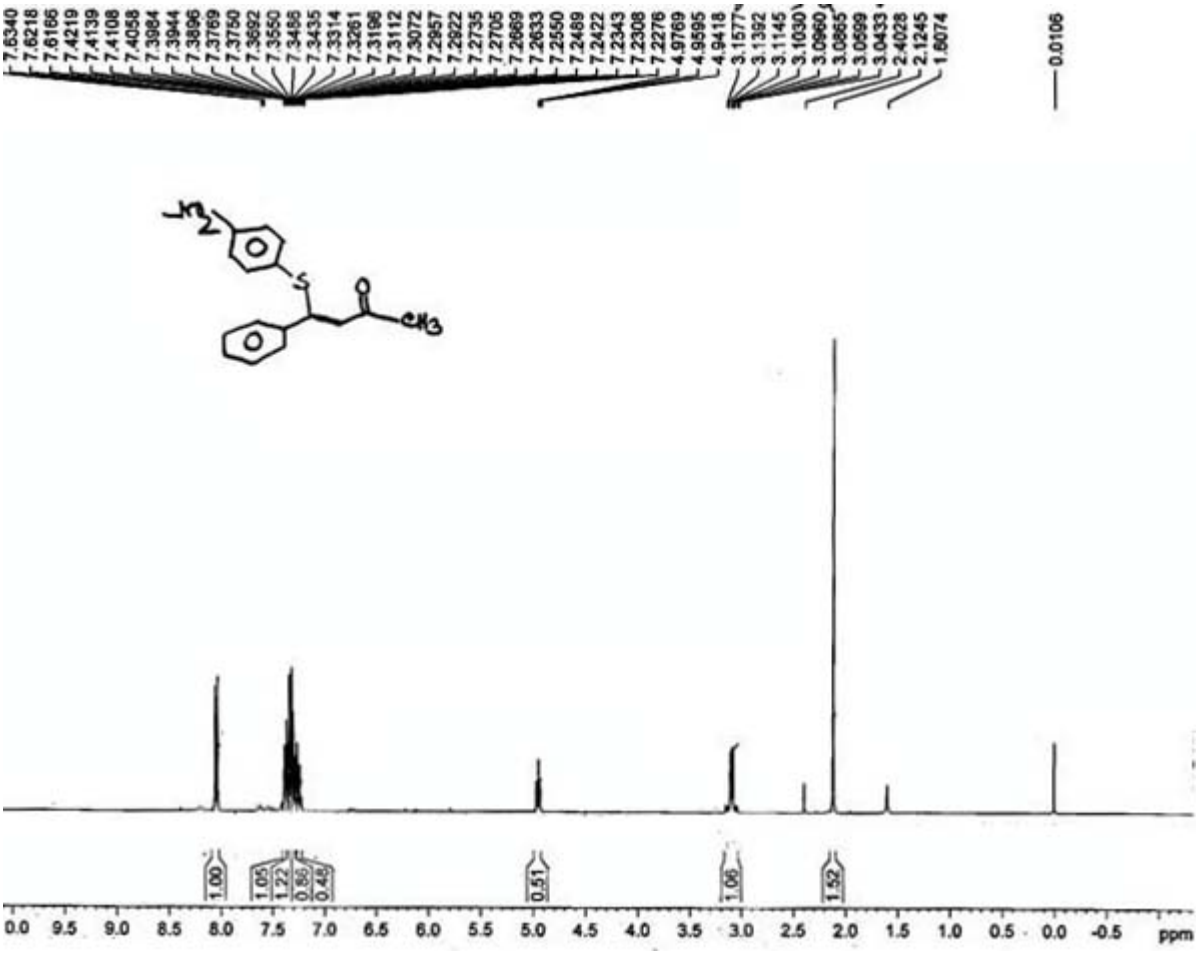
4-Benzylsulfanyl-4-phenyl-butan-2-one (3f):[1]

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 2.00 (s, 3H), 2.92 (dd, *J* = 2.88 Hz, 8 Hz, 2H), 3.44 (d, *J* = 16 Hz, 1H), 3.52 (d, *J* = 16 Hz, 1H), 4.20 (t, *J* = 8 Hz, 1H), 7.19-7.32 (m, 10H); MS (ESI): *m/z* 271 (M + 1).

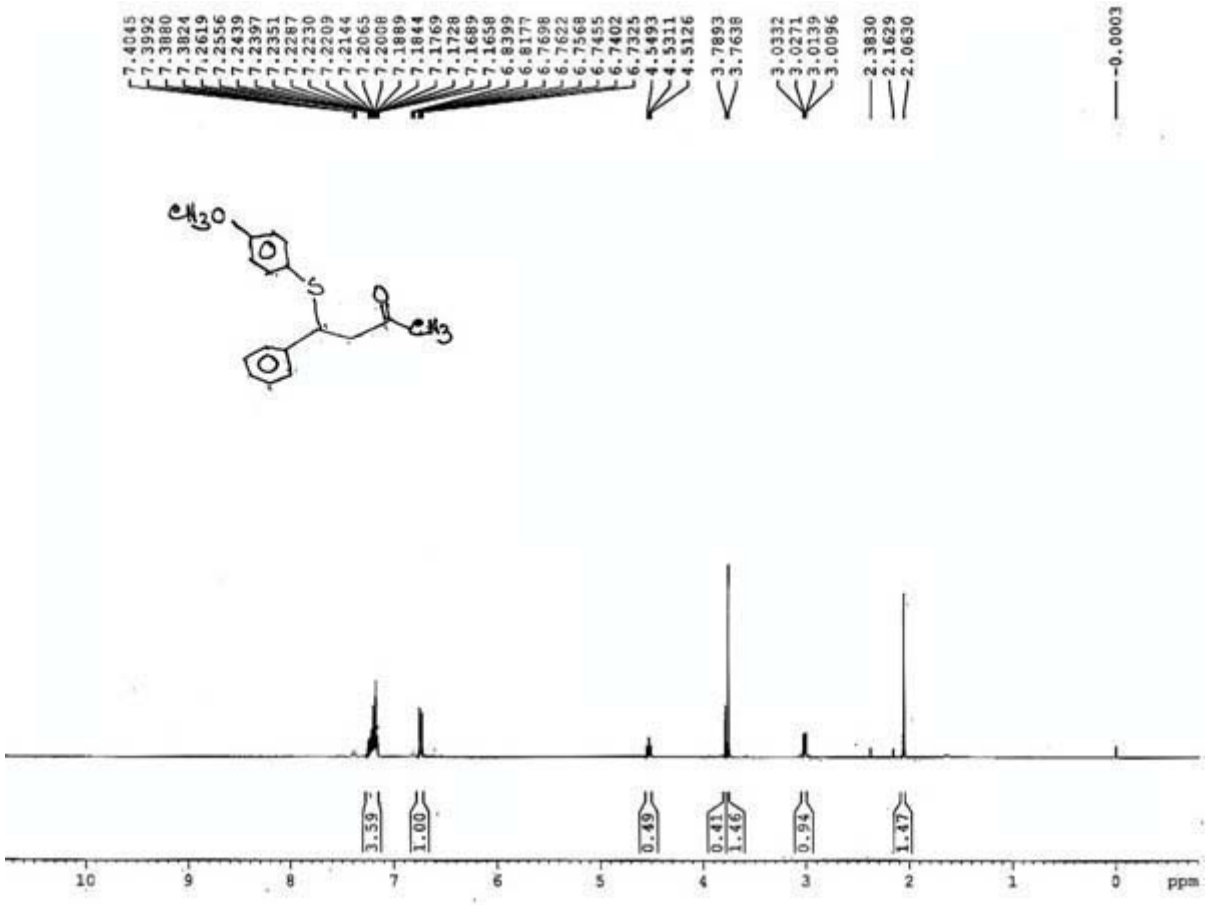
4-Phenyl-4-phenylsulfanyl-butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 27°C, TMS)



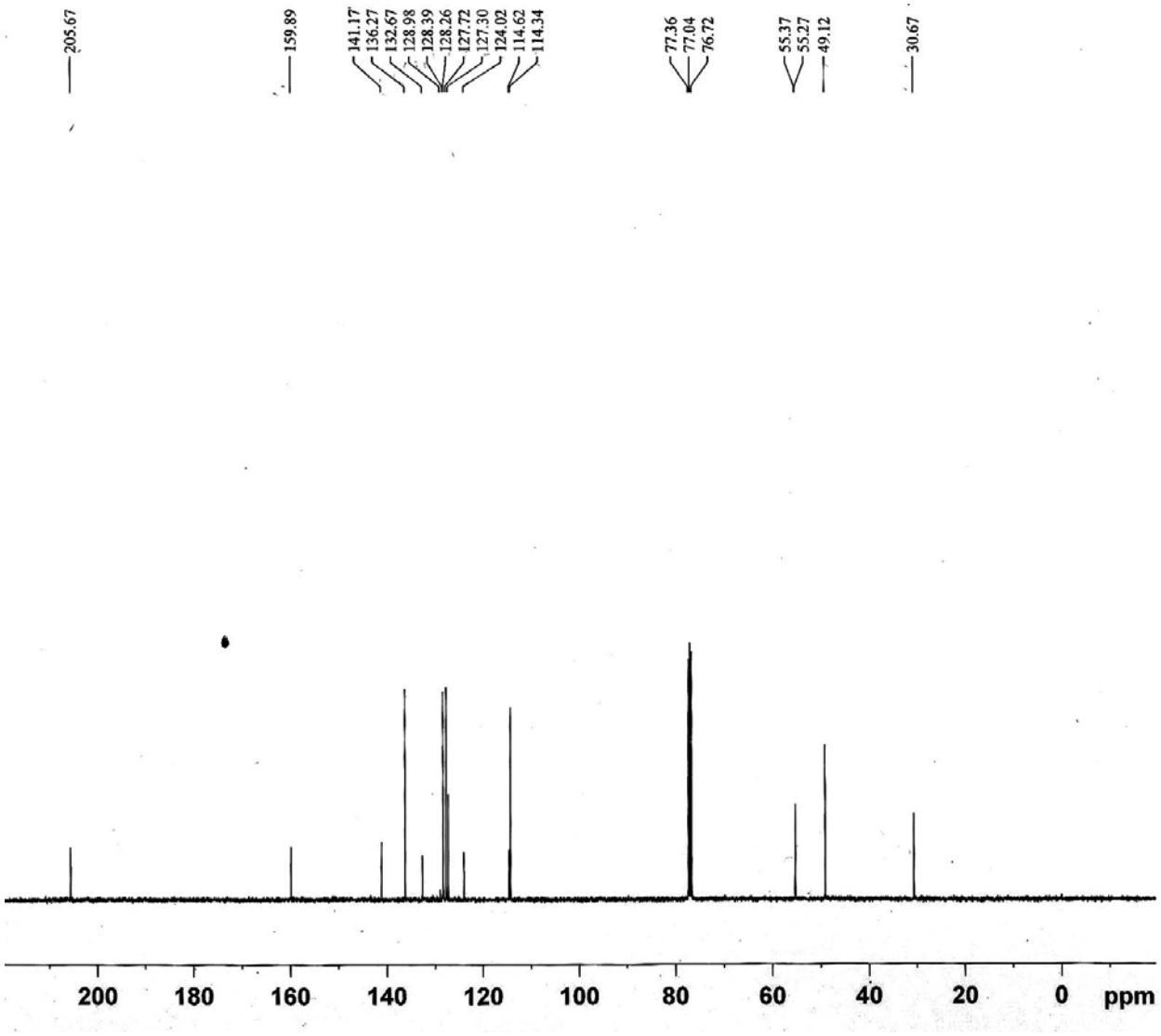
4-(4-Nitro-phenylsulfanyl)-4-phenyl-butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 27°C, TMS)



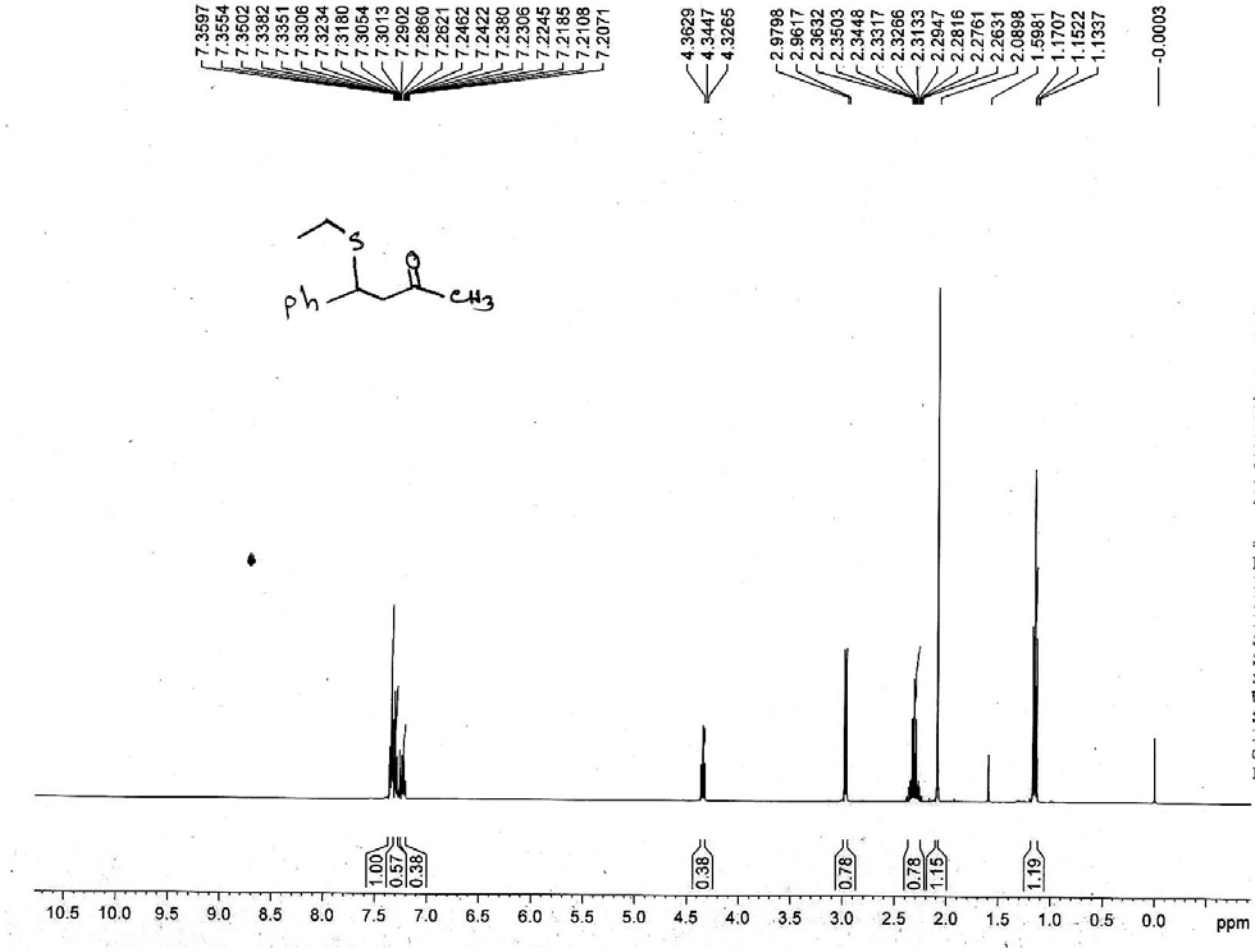
4-(4-Methoxy-phenylsulfanyl)-4-phenyl-butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 27°C, TMS)



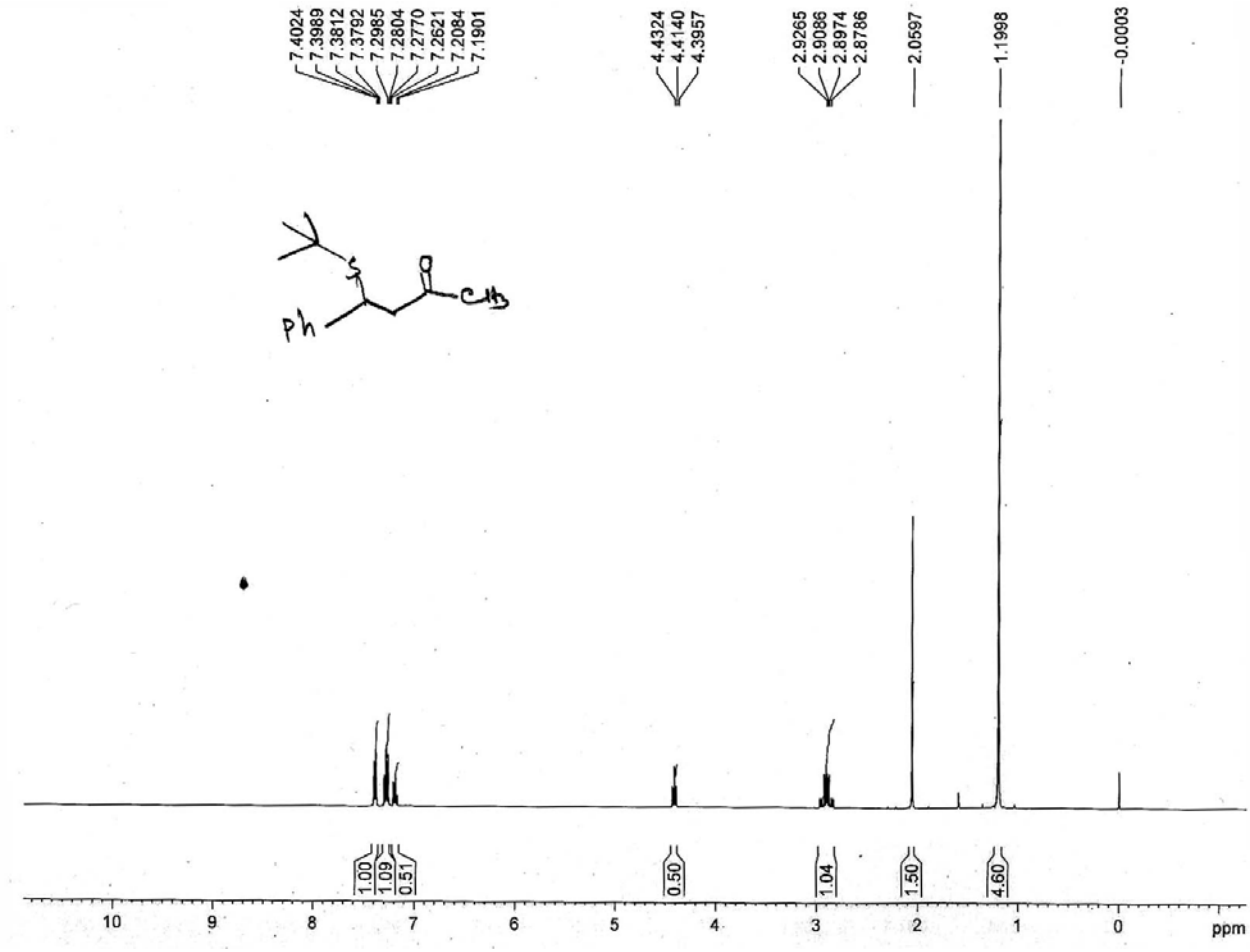
4-(4-Methoxy-phenylsulfanyl)-4-phenyl-butan-2-one: ^{13}C NMR (100 MHz, $CDCl_3$, 27°C, TMS)



4-Ethylsulfanyl-4-phenyl-butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 27°C, TMS)



4-tert-Butylsulfanyl-4-phenyl-butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 27°C, TMS)



4-Benzylsulfanyl-4-phenyl-butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 27°C, TMS)