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A simple and efficient *thia*-Michael addition to α,β-unsaturated ketones catalyzed by $Yb(OTf)_3$ in [bmim][BF_4]

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$Yb(OTf)_3$ in an ionic liquid [bmim][BF_4] has been described as an efficient catalyst for the *thia*-Michael addition of thiols to α,β-unsaturated ketones to give β-aryl-β-mercapto ketones in 82–94% yield and the catalyst along with ionic liquid was recycled and reused.

Keywords: ionic liquid; *thia*-Michael addition; ytterbium triflate; rare-earth metal triflates; Lewis acids

1. Introduction

The development of new methods for the *thia*-Michael addition to α,β-unsaturated carbonyl compounds leading to β-mercapto carbonyl derivatives is an important area of synthetic research, because they are valuable synthetic scaffolds for biological, medicinal and synthetic organic chemists (*1*). They are used for the synthesis of various biologically active compounds such as thiochromans (*2*), thiapyrans (*3*), benzothiazapines (*4*), 4,5-dihydropyrazoles (*5*), etc. Consequently, there are several methods reported for the *thia*-Michael addition of thiols to α, β-unsaturated ketones catalyzed by different bases (*6*), Lewis acids (*7a–i*) and phase-transfer catalysts (*7j*). The potential of water (*8*) and ionic liquids (*9*) to replace environmentally harmful solvents has become an active and exciting area of research (*10*). The ionic liquids, especially those based on 1,3-dialkylimidazolium cations, have gained considerable interest as green alternative reaction media in recent years (*11*). Their non-volatile nature without any detectable vapor pressure gives them significant advantage in minimizing solvent consumption and addresses the problem of emission of volatile organic solvents in atmosphere and thus make these solvents environmentally attractive alternative to classical organic solvents (*12*). They have unique chemical and physical properties such as excellent chemical and thermal stability, and these properties of ionic liquids can be tuned by changing the alkyl chains or anions. These properties of ionic liquids have been used to modulate reactivity and selectivity of organic reactions, and their mechanistic model has been studied by mass analysis (*12e,f*). They have also been applied as solvents and catalysts for the Michael addition reaction to α,β-unsaturated carbonyl compounds and

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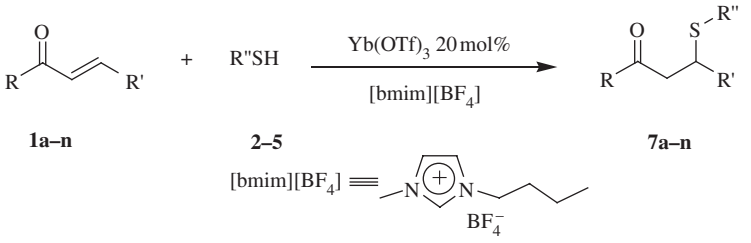


Scheme 1. *thia*-Michael addition to α,β-unsaturated ketones.

β-nitrostyrenes (*13*). Michael additions of thiols to α,β-unsaturated ketones have been studied in an ionic liquid–water mixture (*7e*) and in [pmim]Br ionic liquid (*7f*).

Recently, rare-earth metal triflates have received wide utility as Lewis acids and they have some advantages, such as low toxicity, high solubility, easy handling and reusability, associated with them when compared with conventional Lewis acids (*14*). Various reactions have been reported with metal triflates in an ionic liquid and it has been found that it increases the catalytic activity of metal triflates along with its easy reuse and recoverability (*15*). In view of environment-friendly methodologies, organic reactions employing $Yb(OTf)_3$ as Lewis acid catalyst are currently of great research interest. In our ongoing green chemistry research program, investigating the use of ionic liquid and $Yb(OTf)_3$ in an ionic liquid for various organic transformations (*16*) herein, we wish to report $Yb(OTf)_3$ in an ionic liquid as a mild, efficient and economical catalyst for the *thia*-Michael addition of thiols to α,β-unsaturated ketones (Scheme 1). To the best of our knowledge, there is no report on the *thia*-Michael addition catalyzed by $Yb(OTf)_3$ in an ionic liquid.

2. Results and discussion

First, the reaction between chalcone (**1a**) and thiophenol (**2**) in $[bmim][BF_4]$ was chosen as the model reaction (Scheme 1) to detect whether the use of Lewis acids was efficient. The results are summarized in Table 1. It was found that Lewis acids such as $BF_3 \cdot Et_2O$, $TiCl_4$, $SnCl_2$, MgO, $CoCl_2$, Montmorilonite K10 (Mont. K10), Amberlyst-15 as well as the condition of no catalyst gave low yields of **7a**, whereas $Zn(OTf)_2$ and $Yb(OTf)_3$ exhibited good catalytic effect with a good yield in a short reaction time. Considering the higher activity of $Yb(OTf)_3$, it was chosen as the catalyst of choice. The reaction of **1a** with **2** in the presence of 20 mol% of $Yb(OTf)_3$ in $[bmim][BF_4]$ gave **7c** in 94% yield. Formation of **7a** was indicated by a characteristic peak shift for carbonyl group in infrared (IR) from 1650 to 1665 cm^{-1} due to the disappearance of conjugation of carbonyl group with double bond. In ^1H NMR, α- and β-protons disappeared and two new peaks appeared at δ 5.10–4.97 and 3.90–3.85 for ArSCH– and $ArCOCH_2$– protons, respectively.

Establishing the higher catalytic activity of $Yb(OTf)_3$ among the tested acid catalysts in $[bmim][BF_4]$, optimization of reaction conditions using various solvents was undertaken. The model reaction was carried out in solvents such as DCM, toluene, 1,2-dichloroethane, DMF, DMSO, [bmim][Br] and $[bmim][PF_6]$ in order to determine whether the ionic liquid, $[bmim][BF_4]$, was an essential factor to promote the reaction of thiols with α,β-unsaturated ketones catalyzed by $Yb(OTf)_3$. The results are summarized in Table 2.

The investigation of reaction medium for the process revealed that reaction solvents played a significant role in the model reaction. Ionic liquid was a type of feasible reaction medium for this addition reaction. After screening a variety of reaction media, $[bmim][BF_4]$ was found

Table 1. *thia*-Michael addition of **2** to chalcone **1a** catalyzed by different acid catalysts in [bmim][BF_4].[a]

Entry	Catalyst	Time (min)	Yield[b] (%)
1	–	240	40
2	$Yb(OTf)_3$	30	94
3	$Zn(OTf)_2$	30	76
4	$SnCl_2$	30	60
5	$BF_3{\cdot}Et_2O$	30	65
6	$TiCl_4$	30	55
7	MgO	30	50
8	$CoCl_2$	30	5
9	Mont. K10	90	34 (80)[c]
10	Amberlyst-15	30	8

Notes: [a]All reactions were carried out in [bmim][BF_4] at room temperature using 20 mol% catalyst. [b]Isolated yields. [c]Yield reported in refluxing methanol for 1,3-diphenylpropenone (**1a**) after 5 h (*7d*).

Table 2. *thia*-Michael addition of **2** to chalcone **1a** catalyzed by $Yb(OTf)_3$ in different solvents.[a]

Entry	Solvent	Time (h)	Yield[b] (%)
1	[bmim][BF_4]	0.5	94
2	[bmim][Br]	1	40
3	[bmim][PF_6]	1	65
4	CH_2Cl_2	14	–[c]
5	Benzene	14	–[c]
6	THF	14	–[c]
7	DMSO	14	50
8	DMF	14	44
9	EtOH	14	54
10	PEG-400	14	47
11	H_2O	3	57

Notes: [a]Reaction conditions: 1,3-diphenylpropenone (**1a**; 340 mg, 1.4 mmol), **2** (253 mg, 2.3 mmol, 1.2 equiv.) and $Yb(OTf)_3$ (178 mg, 20 mol%) at room temperature. [b]Isolated yield. [c]No product formation was observed.

to be the most effective medium for the generation of desired product in 94% yield (Table 2, Entry 2). The reaction in polar organic solvents resulted in poor yield of product along with unchanged starting material, whereas in ionic liquids [bmim][Br] and [bmim][PF_6], it resulted in moderate yields (Table 2, Entries 2 and 3). It is noteworthy to mention that there was no product formation with $Yb(OTf)_3$ in non-polar organic solvents even after 14 h at room temperature. With further optimization of the reaction conditions, the effect of catalyst loading was also examined in [bmim][BF_4], when $Yb(OTf)_3$ was used as a catalyst, and 20 mol% was enough to complete the reaction in 30 min. Increasing the catalyst loading in model reaction did not significantly affect the yield of **7a** (Table 3, Entry 1).

To examine the scope of the method, a series of α,β-unsaturated ketones with thiophenol were investigated and the results are summarized in Table 3. The starting α,β-unsaturated ketones (chalcones) were prepared by the Claisen–Schmidt condensation between various substituted arylmethyl ketones with aryl aldehyde following the reported procedure (*17*). The reaction of various chalcones with thiophenols afforded the corresponding β-aryl-β-mercapto ketones in 82–94% yield. As shown in Table 3, an array of ketones bearing either electron-donating or -withdrawing groups on the aromatic ring was investigated. The electron-withdrawing groups on the phenyl ring of ketonic side required longer time for completion of the reaction (Entries 3, 6, 10 and 15 in Table 3). The work-up procedure is very straightforward, *i.e.* the product was extracted by diethyl ether leaving behind $Yb(OTf)_3$ in an ionic liquid. The diethyl ether layer was dried and concentrated. The compound was purified by passing through a bed of silica gel using

Table 3. Synthesis of β-aryl-β-mercapto ketones (**7a**–**7q**).[a]

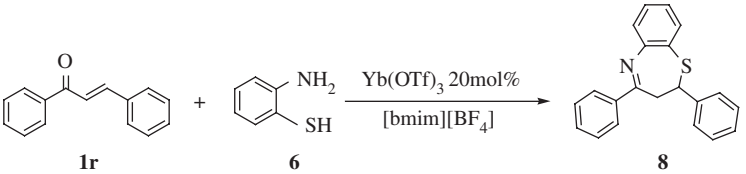
Entry	R	R′	R″	Product	Time (min)	Yield[b] (%)
1	H	4-Cl	Ph	**7a**	30	94[c]
2	4-CH_3	H	Ph	**7b**	30	84
3	4-Cl	H	Ph	**7c**	60	82
4	4-OCH_3	3-NO_2	Ph	**7d**	30	86
5	4-CH_3	4-Cl	Ph	**7e**	30	84
6	4-Cl	4-OCH_3	Ph	**7f**	60	83
7	H	4-OCH_3	Ph	**7g**	30	82
8	4-CH_3	4-OCH_3	Ph	**7h**	30	88
9	4-OCH_3	4-OCH_3	Ph	**7i**	30	91
10	4-Cl	4-Cl	Ph	**7j**	60	90
11	4-CH_3	3-NO_2	Ph	**7k**	30	85
12	H	3-NO_2	Ph	**7l**	30	90
13	4-OCH_3	H	Ph	**7m**	30	93
14	4-NO_2	H	Ph	**7n**	240	88
15	4-Cl	H	4-MeOPh	**7o**	45	92
16	4-Cl	H	CH_2CH_2OH	**7p**	45	91
17	4-Cl	H	2-Napth	**7q**	45	90

Notes: [a]All reactions were carried out in the presence of chalcone (1.4 mmol), thiol (1.2 equiv., 1.73 mmol), $Yb(OTf)_3$ (20 mol%) in [bmim][BF_4] (3.0 ml) at room temperature. [b]Isolated pure product yields. [c]Yields were 57, 78, 94, 93 and 95% when $Yb(OTf)_3$ was used in 5, 10 20, 50 and 100 mol%, respectively.

ethyl acetate:hexane as an eluent. All of the β-aryl-β-mercapto ketones have been characterized by IR, ^1H and ^{13}C NMR spectra.

After the success of the *thia*-Michael addition and to extend the scope of the catalyst for the Michael addition reaction, we next studied the reaction of anilines and phenols with chalcone (**1a**). Anilines and phenols did not result in product formation even at 100 °C. The non-reactivity of phenols and anilines relative to thiophenols could be rationalized based on the relative nucleophilicity of oxygen and nitrogen versus sulfur. This difference in reactivity of thiols versus anilines and phenols under the reaction conditions can be used as a tool to generate selectivity in the *thia*-Michael versus *aza*-Michael addition. An example for this selectivity is presented by the reaction of 2-aminothiophenol (**6**) with chalcone (**1r**) to give 1,5-benzothiazepines (**8**) in 84% yield through chemoselective formation of the *thia*-Michael addition product (Scheme 2). The method thus can be used to synthesize 1,5-benzothiazepine derivatives that show various biological activities such as calcium channel antagonist, free-radical scavengers and as inhibitors of cholinesterases and α-glucosidase (*18*). The IR spectra of the final compound did not show the characteristic absorptions for C=O and NH_2 in the regions 1690–1650 and 3445–3200 cm^{-1}. Similarly, the reaction of 2-mercaptoethanol (**4**) with **1a** gave selectively **7p** in 91% yield (Table 3, Entry 16) by the chemoselective addition of a thiol group.

From an environmental point of view, it is desirable to minimize the amount of waste for each organic transformation. In this context, we recycled the catalyst solution for subsequent runs. To study the reusability, the recovered $Yb(OTf)_3$ dissolved in an ionic liquid [bmim][BF_4] after



1r **6** **8**

Scheme 2. Chemoselective addition of 2-aminothiophenol to 1,3-diphenylpropenone (chalcone).

extraction of the product with diethyl ether was reused for the reaction of **1a** with **2** to give **7a**. The catalyst solution was recycled for subsequent cycles. The recovered catalyst, $Yb(OTf)_3$ in an ionic liquid, showed a good catalytic activity without a noticeable decrease in yield up to five runs (yield of **7a** in five cycles were 94, 92, 90, 88 and 89%, respectively).

3. Conclusion

In conclusion, we have developed a novel, simple, effective, convenient and economical environment-friendly method for the *thia*-Michael addition to α,β-unsaturated ketones. The yields of the products are good and the catalyst could be recovered easily after reaction and reused without evident loss of activity. The combination of simple experimental procedures, mild reaction conditions, good yields, ease of recovery and reuse of catalyst in an ionic liquid is expected to contribute to the development of a green strategy. Because of its numerous benefits, this method should find utility in the synthesis of biologically active compounds such as 1,5-benzothiazepines by the reaction of 1,3-diaryl-2-propenones with 2-aminothiophenols. Currently, investigation on the reaction of anilines and phenols with unsaturated ketones catalyzed by different metal triflates in an ionic liquid is in progress in our laboratory.

4. Experimental

4.1. *General experimental procedure*

To a 10 ml round-bottom flask containing ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (3.0 ml) were added **1a** (340 mg, 1.4 mmol), thiophenol (**2**) (190 mg, 1.73 mmol, 1.2 equiv.) and $Yb(OTf)_3$ (178 mg, 20 mol%). The reaction mixture was stirred at room temperature for 30 min. After completion of the reaction as indicated by thin layer chromatography (TLC), the reaction mixture was extracted with diethyl ether (2×5 ml). The combined organic layer was dried and evaporated under reduced pressure. The residue was percolated through a bed of silica gel 60–120-mesh using hexane-ethyl acetate (95:5, v/v) as an eluent to give a pure **7a** in 94% yield. Similarly, other α,β-unsaturated ketones (**1b**–**1n**) reacted with **2** to give **7b**–**7n** and **1a** with **3**–**5** to give **7o**–**7q**. All the products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopic data.

4.2. *^{1}H NMR and ^{13}C NMR data for 7a–7q*

7a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, $J = 7.3$ Hz), 7.59–7.55 (1H, m), 7.46 (2H, d, $J = 7.5$ Hz), 7.38–7.16 (9H, m), 4.94–4.90 (1H, m), 3.67–3.55 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.50, 139.62, 136.31, 133.47, 133.24, 132.78, 128.97, 128.77, 128.49, 128.38, 127.85, 127.63, 47.41, 44.27. ν_{max} (KBr) 1682 cm^{-1}.

7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, $J = 7.4$ Hz), 7.33–7.22 (12H, m), 4.95 (1H, t, $J = 7.0$ Hz), 3.63–3.50 (2H, m), 2.39 (3H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.63, 132.50, 129.09, 128.63, 128.23, 128.00, 127.60, 127.28, 127.13, 48.01, 44.27, 21.46. ν_{max} (KBr) 1684 cm^{-1}.

7c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, d, $J = 7.6$ Hz), 7.42–2.24 (12H, m), 4.94 (1H, t, $J = 7.8$ Hz), 3.66–3.52 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.69, 140.77, 139.55, 134.78, 133.86, 132.60, 129.29, 128.74, 128.71, 128.32, 127.57, 127.44, 127.28, 48.02, 44.44. ν_{max} (KBr) 1680 cm^{-1}.

7d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, s), 8.04 (1H, d, $J = 6.5$ Hz), 7.88 (2H, $J = 7.5$ Hz), 7.62 (1H, d, $J = 6.7$ Hz), 7.48–7.35 (1H, m), 7.31–7.23 (5H, m), 6.93 (2H, $J = 7.5$ Hz), 5.01 (1H, t, $J = 6.0$ Hz), 3.86 (3H, s), 3.63 (2H, d, $J = 6.8$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.46, 163.68, 143.64, 134.13, 133.19, 130.20, 129.14, 129.01, 128.88, 128.04, 122.42, 122.09, 113.69, 55.34, 47.64, 43.46. ν_{max} (KBr) 1685, 1576, 1347 cm^{-1}.

7e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, $J = 8.0$ Hz), 7.42–7.14 (11H, m), 4.91 (1H, dd, $J = 6.1$, 7.8 Hz), 3.69–3.46 (2H, m), 2.41 (3H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.11, 144.13, 139.69, 133.87, 133.53, 132.74, 129.16, 128.97, 128.74, 128.35, 127.98, 127.57, 47.47, 44.10, 21.48. ν_{max} (KBr) 1683 cm^{-1}.

7f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (2H, d, $J = 8.1$ Hz), 7.48–7.17 (9H, m), 6.79 (2H, d, $J = 8.1$ Hz), 4.98–4.82 (1H, m), 3.76 (3H, s), 3.63–3.48 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.85, 158.57, 139.52, 132.65, 132.52, 129.28, 128.72, 128.69, 128.63, 127.35, 113.65, 55.01, 47.44, 44.58. ν_{max} (KBr) 1681 cm^{-1}.

7g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, $J = 5.2$ Hz), 7.44–7.24 (10H, m), 6.80 (2H, d, $J = 4.9$ Hz), 4.95 (1H, m), 3.76 (3H, s), 3.65–3.52 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.02, 158.52, 136.50, 134.20, 133.06, 132.86, 132.46, 128.68, 128.42, 127.87, 127.26, 113.62, 55.01, 47.40, 44.61. ν_{max} (KBr) 1682 cm^{-1}.

7h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, $J = 8.1$ Hz), 7.33–7.22 (9H, m), 6.79 (2H, d, $J = 8.6$ Hz), 4.94 (1H, dd, $J = 5.6$, 8.4 Hz), 3.76 (3H, s), 3.65–3.49 (2H, m), 2.40 (3H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.61, 158.48, 143.90, 134.06, 132.94, 132.41, 129.08, 128.67, 128.64, 128.00, 127.20, 113.59, 55.00, 47.45, 44.42, 21.46. ν_{max} (KBr) 1684 cm^{-1}.

7i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (2H, d, $J = 8.0$ Hz), 7.32–7.13 (7H, m), 6.90 (2H, d, $J = 7.9$ Hz), 6.79 (2H, d, $J = 6.4$ Hz), 4.94 (1H, m), 3.85 (3H, s), 3.75 (3H, s), 3.63–3.50 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.49, 176.44, 163.37, 158.47, 132.98, 132.36, 130.19, 128.66, 127.17, 113.58, 113.52, 55.28, 55.00, 47.52, 44.16. ν_{max} (KBr) 1686 cm^{-1}.

7j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, d, $J = 7.9$ Hz), 7.43–7.23 (11H, m), 4.89 (1H, t, $J = 6.1$ Hz), 3.56 (2H, d, $J = 6.0$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.33, 139.73, 139.45, 134.61, 133.32, 132.83, 129.72, 129.26, 129.10, 128.93, 128.81, 128.43, 127.72, 47.42, 44.25. ν_{max} (KBr) 1680 cm^{-1}.

7k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, s), 8.04 (1H, d, $J = 6.1$ Hz), 7.90–7.74 (2H, m), 7.62 (1H, d, $J = 6.3$ Hz), 7.42–7.35 (1H, m), 7.32–7.25 (7H, m), 5.09–4.90 (1H, m), 3.67–3.56 (2H, m), 2.41 (3H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.62, 147.98, 144.42, 143.59, 134.11, 133.59, 133.22, 132.65, 129.24, 129.02, 128.89, 128.07, 127.99, 122.44, 122.11, 47.58, 43.72, 21.49. ν_{max} (KBr) 1683, 1581, 1352 cm^{-1}.

7l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, s), 8.05 (1H, d, $J = 7.1$ Hz), 7.91 (2H, d, $J = 7.0$ Hz), 7.71–7.54 (2H, m), 7.54–7.36 (3H, m), 7.36–7.17 (5H, m), 5.01 (1H, t, $J = 6.7$ Hz), 3.69 (2H, d, $J = 6.7$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.00, 143.51, 136.03, 134.10, 133.46, 133.26, 129.05, 128.91, 128.58, 128.12, 127.86, 122.44, 122.15, 47.51, 43.90. ν_{max} (KBr) 1681, 1580, 1353 cm^{-1}.

7m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.79 (2H, m), 7.34–7.24 (10H, m), 6.98–6.84 (2H, m), 4.97 (1H, m), 3.85 (3H, s), 3.61–3.51 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.32, 163.40, 141.08, 132.45, 130.20, 129.60, 128.64, 128.24, 127.61, 127.26, 127.12, 113.54, 55.29, 48.10, 44.02. ν_{max} (KBr) 1687 cm^{-1}.

7n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (2H, d, $J = 8.80$ Hz), 8.00 (2H, d, $J = 8.74$ Hz), 7.37–7.17 (10H, m), 4.90 (1H, dd, $J = 7.60$, 6.0 Hz), 3.70–3.57 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.45 141.18, 139.45, 134.96, 133.98, 132.60, 129.64, 128.84, 128.61, 128.46, 127.12, 127.44, 127.28, 48.10, 44.42. ν_{max} (KBr) 1676, 1578, 1349 cm^{-1}.

7o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, $J = 8.56$ Hz), 7.38 (2H, d, $J = 8.56$ Hz), 7.29–7.17 (7H, m), 6.74 (2H, d, $J = 8.72$ Hz), 4.70 (1H, m), 3.75 (3H, s), 3.53–3.57 (2H, m). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 195.99, 159.92, 141.19, 139.69, 136.28, 135.11, 129.50, 128.93, 128.43, 127.80, 127.35, 124.06, 123.51, 121.93, 114.41, 55.29, 49.40, 44.26. ν_{max} (KBr) 1682 cm^{-1}.

7p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (2H, dd, J = 8.56, 1.72 Hz), 7.32–7.29 (4H, m), 7.22 (2H, t, J = 7.28 Hz), 7.13 (1H, t, J = 7.32 Hz), 5.10 (1H, s), 4.47 (1H, m), 3.61–3.50 (2H, m), 3.48–3.33 (2H, m), 2.46 (2H, t, J = 5.92 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.87, 141.91, 139.88, 134.93, 129.56, 128.99, 128.74, 127.79, 127.56, 60.69, 45.38, 43.87, 34.50. ν_{max} (KBr) 1680 cm^{-1}.

7q: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.75 (4H, m), 7.70–7.65 (2H, m), 7.46–7.43 (2H, m), 7.39 (1H, dd, J = 8.52, 1.76 Hz), 7.37–7.34 (4H, m), 7.25 (2H, t, J = 7.60 Hz), 7.18 (1H, tt, J = 7.52, 1.36 Hz), 7.27–5.04 (1H, m), 3.66–3.54 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.90, 140.98, 139.76, 135.02, 133.54, 132.49, 131.75, 131.49, 129.90, 129.48, 128.92, 128.59, 128.46, 127.81, 127.66, 127.56, 127.50, 126.48, 126.34, 49.69, 48.22. ν_{max} (KBr) 1682 cm^{-1}.

8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (2H, dd, J = 7.66, 1.63 Hz), 7.58 (1H, J = 7.87, 1.33 Hz), 7.48–7.57 (4H, m), 7.27–7.34 (4H, m), 7.25 (2H, dd, J = 7.62, 1.32 Hz), 7.16 (1H, dt, J = 7.60, 1.34 Hz), 5.05 (1H, dd, J = 12.64, 4.82 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 154.62, 141.54, 133.98, 133.36, 131.23, 129.41, 129.35, 128.78, 128.72, 128.69, 128.61, 128.13, 127.83, 127.74, 127.43, 127.23, 125.96, 123.65, 49.76, 42.34. ν_{max} (KBr) 1634, 1568, 1479, 1231 cm^{-1}.

4.3. *General experimental procedure for recycle of catalyst*

To the recovered ionic liquid [bmim][BF_4] containing Yb(OTf)$_3$ were added **1a** (340 mg, 1.4 mmol) and thiophenol (**2**) (190 mg, 1.73 mmol, 1.2 equiv.), and the reaction mixture was stirred at room temperature for 30 min. After completion of the reaction as indicated by TLC, the reaction mixture was extracted with diethyl ether (2 × 5 ml). The combined organic layer was dried and evaporated under reduced pressure. The residue was percolated through a bed of silica gel 60–120-mesh using hexane-ethyl acetate (95:5, v/v) as an eluent to give a pure **7a** in 92% yield. This procedure was repeated three more times to give **7a** in 90, 88 and 89% yield, respectively.

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