Tetrahedron 71 (2015) 6813–6817

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Catalysis of the acylation of aromatic derivatives by metallic tosylates

Vincent Morizur [a], Jessica Szafranek [a], Dominique Bonhomme [a], Sandra Olivero [a], Jean Roger Desmurs [b], Elisabet Duñach [a,*]

[a] Institut de Chimie de Nice, UMR 7272, Université Nice Sophia Antipolis, Faculté des Sciences, Parc Valrose, 06108 Nice cedex 2, France
[b] CDP-Innovation, G2C Business Center, 63 Rue André Bollier, 69307 Lyon, France

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form 8 July 2015
Accepted 10 July 2015
Available online 17 July 2015

Keywords:
Metal tosylate
Friedel–Crafts acylation
Lewis acid catalysis
Ultrasound activation

ABSTRACT

A series of metallic tosylates were prepared by ultrasonic metal activation and were further used as efficient catalysts for the acylation of aromatic derivatives.

1. Introduction

A large variety of intermediates and products for pharmaceuticals, agrochemicals, fragrances and fine chemistry are prepared through the selective functionalisation of aromatic compounds.[1] The acylation of aryl derivatives lies among the most important atom-economy transformations with high applicability, both at academic and industrial levels. First described by C. Friedel and J. Crafts in 1877,[2] the electrophilic aromatic substitution has been largely developed since, mainly by the use of conventional Lewis acids such as $AlCl_3$, $SnCl_4$, $TiCl_4$, $ZnCl_2$ or $BF_3 \cdot Et_2O$, in stoichiometric or over-stoichiometric amounts, as the reaction mediators.[3]

Catalytic processes have been further explored with strong protic acids such as triflic acid (HOTf), triflimide ($HNTf_2$) or solid acid catalysts.[4] Thus, for example, the acylation of *p*-xylene with heptanoic acid at 220 °C was catalysed by HOTf or $HNTf_2$ (10–20 mol %), but *p*-toluenesulfonic acid (HOTs) remained inactive.[5]

Strong Lewis acids, mainly triflate salts, have also been reported to present high catalytic activity in acylation reactions. In particular, $Bi(OTf)_3$ (1–10 mol %) has been reported as an active catalyst for the acylation of a variety of aromatic derivatives by acid chlorides.[6] The acylation by carboxylic acids was efficient with metallic triflimides, namely $Eu(NTf_2)_3$, used in 15 mol %.[5] Acylation of aromatic amines with anhydrides has been described with $Ga(OTf)_3$ (10 mol %).[7] The association $Cu(OTf)_2/LiClO_4$ has been reported for the quantitative anisole acylation by benzoyl chloride in ionic liquids.[8]

Although several superacids and various metallic triflates and triflimides have shown catalytic activity in aryl acylation reactions, strong protic acids are corrosive and the triflate-based Lewis acids might be relatively expensive. Therefore, the set-up of other catalytic systems for the Friedel–Crafts acylation processes still remains highly desirable. Herein, we report the use of metal tosylates as an efficient catalyst alternative for this reaction. Metallic tosylates and mesylates, mainly under their hydrated form, are known compounds, but their catalytic activity has not been yet explored in detail.[9] To our knowledge, no report deals with the use of these inexpensive and easily available catalysts in acylation processes.

2. Results and discussion

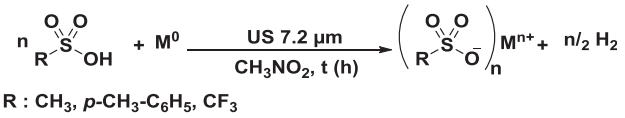
2.1. Preparation of metallic tosylate salts

The classical preparation procedure for metallic tosylates is based on the reaction of *p*-toluenesulfonic acid with metal oxides,[10] hydroxides[11] or carbonates[12] in aqueous media. This methodology allows obtaining the corresponding tosylates under their hydrated form. In order to provide more active catalysts with low amount of water-coordinated molecules, we prepared a series of metal tosylates ($M^{+}\ ^{-}OTs$) as well as some mesylates ($M^{+}\ ^{-}OMs$), by adapting

* Corresponding author. E-mail address: dunach@unice.fr (E. Duñach).

http://dx.doi.org/10.1016/j.tet.2015.07.027
0040-4020/

a redox procedure described for metal triflates under ultrasonic activation (Scheme 1).[13] These results are summarised in Table 1.



Scheme 1. Ultrasonic preparation of metallic tosylates, mesylates and triflates.

Table 1
Preparation of metallic tosylates, mesylates and triflates by ultrasonic activation, in nitromethane at room temperature

Entry	R	M^{n+}	Time (h)	Yield (%)
1	*p*-$CH_3C_4H_6$–	In^{3+}	1.5	99
2	*p*-$CH_3C_4H_6$–	Bi^{3+}	3	92
3	*p*-$CH_3C_4H_6$–	Cu^{2+}	11.5	99
4	*p*-$CH_3C_4H_6$–	Zn^{2+}	9	92
5	*p*-$CH_3C_4H_6$–	Ga^{3+}	5	85
6	CH_3–	Ga^{3+}	1.5	99
7	CH_3–	Bi^{3+}	3.5	84
8	CH_3–	Sc^{3+}	40	71
9	CF_3–	In^{3+}	0.5	98

Good yields of the corresponding metal salts were generally obtained in reactions run in nitromethane. With In^{3+} and Cu^{2+}, the yields were quantitative (entries 1 and 3). The NMR spectra of the different tosylates and mesylates in DMSO-d_6 did not indicate the presence of coordinated nitromethane, as it is a low-coordinating solvent. For comparison, In^{3+} triflate (entry 9) and In^{3+} trifluoroacetate were also prepared following the same methodology and were obtained in almost quantitative yields.

2.2. Titration of indium salts

The acidity of several of the newly prepared salts was monitored by pH titration with a 1×10^{-2} M solution of sodium hydroxide. Thus, the behaviour of $In(OTf)_3$, $In(OTs)_3$, $In(OMs)_3$ and $In(O_2CCF_3)_3$ was examined. As illustrated in Fig. 1, the initial pH values ranged from 2.5 to 3.5 for the different indium salts tested.

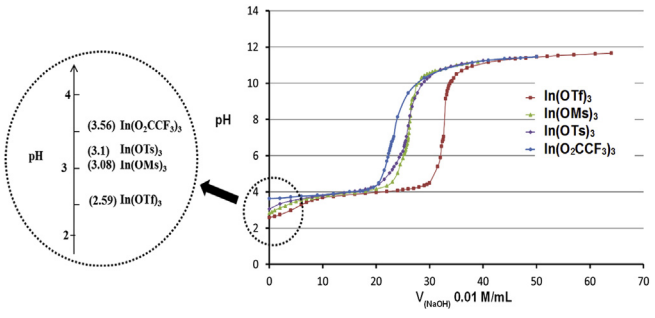


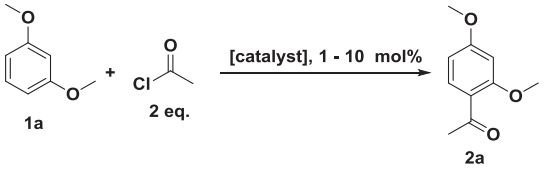
Fig. 1. Titration of In^{3+} salts by an aqueous NaOH solution.

As expected, the most acidic compound resulted to be indium triflate, followed by indium tosylate, mesylate and trifluoroacetate. The acidity of the salts is in the order: $In(OTf)_3$>$In(OTs)_3$> $In(OMs)_3$>$In(O_2CCF_3)_3$.

For all indium salts, three protons were titrated with the same acidity, indicating their equivalence in terms of their acidity in water.

2.3. Acylation reactions

The Friedel–Crafts acylation was tested with 1,3-dimethoxybenzene **1a** as the model compound, using acetyl chloride as the acylating agent (Scheme 2).



Scheme 2. Acylation of 1,3-dimethoxybenzene.

We first examined the influence of the nature of the catalyst. The catalytic activity of several metal tosylates and of indium mesylate was monitored by gas chromatography, by the quantification of the acylation product **2a**, using dodecane as internal standard. The results of the reactions run in refluxing nitromethane with 10 mol % of catalysts are shown in Fig. 2.

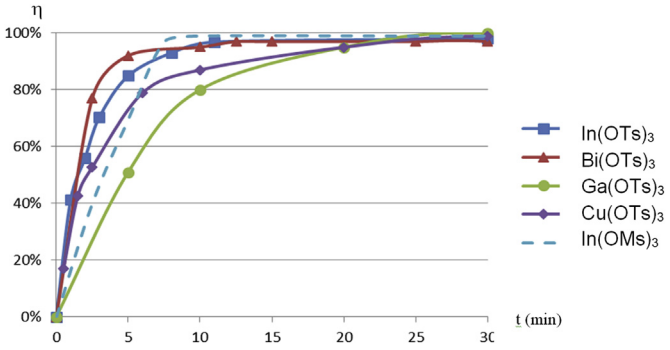


Fig. 2. Evaluation of the acylation of **1a** to **2a** catalysed by metal tosylates or mesylates (10 mol %) in refluxing nitromethane.

A good activity was obtained among all the catalysts tested and quantitative yields of **2a** were obtained after 30 min of reaction. $In(OTs)_3$ and $Bi(OTs)_3$ offered the best catalytic activity; $In(OTs)_3$ was selected for its ease and yield of preparation. These acylation reactions were also run with 1 mol % of catalyst and in this case, quantitative yields of **2a** were reached within 2 h, unless for the less active $Ga(OTs)_3$.

In order to compare the influence of the nature of the anion, the reaction rates between $In(OTf)_3$, $In(NTf_2)_3$, $In(OTs)_3$, $In(OMs)_3$ and $In(O_2CCF_3)_3$, were monitored for reactions of **1a** with acetyl chloride run in nitromethane with 10 mol % of catalyst. Fig. 3 illustrates these results.

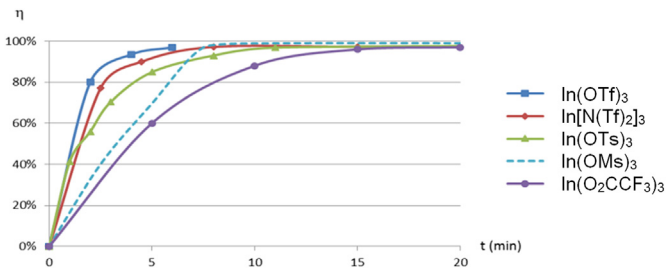


Fig. 3. Evolution of the yield of **2a** catalysed by several In(III) salts (10 mol %) in refluxing nitromethane.

As expected, $In(OTf)_3$ and $In(NTf_2)_3$ were the most active catalysts, leading to quantitative yields of **2a** in less than 10 min. The activity of $In(OTs)_3$ allowed also the complete and clean conversion of **1a** in less than 15 min.

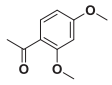
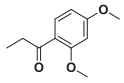
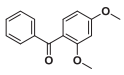
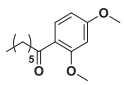
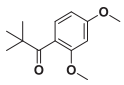
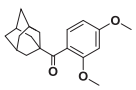
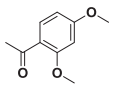
Different solvents and reaction temperatures were also tested for the acylation of **1a** with In^{3+} or Bi^{3+} tosylates and the results are summarised in Table 2. At temperatures of 80 °C and above, the acylation was almost quantitative in 8–30 min.

Table 2
Influence of the reaction conditions in the acylation of **1a**

Entry	Catalyst	Solvent	*T* (°C)	Time	Yield (%)
1	$In(OTs)_3$	CH_2Cl_2	42	60 min	60
2	$In(OTs)_3$	$C_2H_4Cl_2$	80	30 min	95
3	$In(OTs)_3$	CH_3CN	80	25 min	95
4	$In(OTs)_3$	CH_3NO_2	101	11 min	97
5	$Bi(OTs)_3$	CH_3NO_2	25	24 h	36
6	$Bi(OTs)_3$	CH_3NO_2	50	1 h	60
7	$Bi(OTs)_3$	CH_3NO_2	101	8 min	98

The results of the influence of the acylating agent on the functionalisation of **1a** are presented in Table 3.

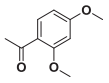
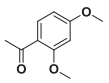
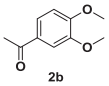
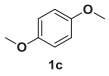
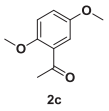
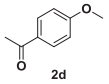
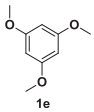
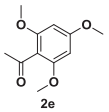
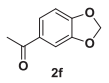
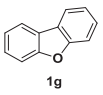
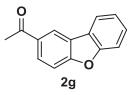
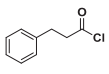
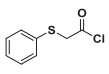
Table 3
Acylation of **1a** with several acylating agents with 10 mol % of $In(OTs)_3$ in refluxing nitromethane

Entry	Acylating agent	Time (min)	Product	Yield of **2** and **3** (%)
1		11	 **2a**	97
2		15	 **3a**	98
3		120	 **3b**	70
4		60	 **3c**	90
5		120	 **3d**	85
6		20	 **3e**	75
7		180	 **3f**	63

Good yields of **2a** and **3a**–**3e** were obtained with differently substituted aromatic or aliphatic acyl chlorides (Table 3, entries 1–6). Interestingly, the catalysis became less efficient when acetic anhydride was used as the acylating agent (entry 7).

The extension of the $In(OTs)_3$-catalysed reaction to several electron-rich aromatic derivatives is presented in Table 4.

Table 4
Acylation of aromatic derivatives with acetyl chloride catalysed by 1–10 mol % of $In(OTs)_3$ in refluxing nitromethane

Entry	Starting compound	% Catalyst	Time	Product	Yield of **2** (%)
1	 **1a**	1	2 h	 **2a**	99
2	 **1a**	10	11 min	 **2a**	97
3	 **1b**	10	1 h	 **2b**	99
4	 **1c**	10	17 h	 **2c**	9
5	 **1d**	10	1 h	 **2d**	99
6	 **1e**	1	2 h	 **2e**	76
7	 **1f**	10	2 h 30	 **2f**	94
8	 **1g**	10	1 h	 **2g**	21
9	 **1h**	10	2 h	 **2h**	62
10	 **1i**	10	2 h	 **2i**	63

The acylation of 1,2-, 1,3- and 1,4-dimethoxybenzenes revealed different kinetics. The 1,3-derivative afforded quantitative yields using either 1 or 10 mol % of $In(OTs)_3$ in short times (entries 1 and 2). *ortho*-Substituted **1b** gave quantitatively **2b** after 1 h with 10 mol % of catalyst, whereas the *para*-substituted analogue **1c** afforded only 9% of **2c** after 17 h under the same conditions (entries 3 and 4). Anisole afforded **2d** quantitatively after 1 h reaction (entry 5) and more activated 1,3,5-trimethoxybenzene **1e** could be acylated with 1 mol % of $In(OTs)_3$ (entry 6). 1,3-Benzodioxole **1f** (entry 7) reacted quantitatively to **2f**, similarly as **1b**. Dibenzofuran **1g** afforded the acylated derivative in 21% yield after 1 h reaction (entry 8). Intramolecular acylation occurred also efficiently with **1h** and **1i** (entries 9 and 10).

Interestingly, indium(III) tosylate allowed the efficient and catalytic acylation of electron-rich aromatic compounds, without need to use the corresponding more active metal triflates as the catalysts.

3. Conclusions

In conclusion, we prepared a series of metal tosylates using a redox procedure by ultrasonic activation, under non-aqueous

conditions. These metal salts have been shown to be active and efficient catalysts, in particular for the Friedel–Crafts acylation of aromatic derivatives. Thus, a series of electron-rich aromatic compounds could be acylated using 1–10 mol % of $In(OTs)_3$, both inter- and intramolecularly. The possibility to use metal tosylates replacing metal triflates, generally used as catalysts in these Friedel–Crafts reactions, allows to widen the family of active Lewis acid catalysts and to provide less expensive available materials for catalysis.

4. Experimental section

4.1. Preparation of metal tosylates, general procedure

p-Toluenesulfonic acid (1 g) was introduced in 30 mL nitromethane (0.193 M). The metal (0.32 equiv for a trivalent metal and 0.48 equiv for a divalent metal) was added to the solution. The mixture was placed under ultrasonic activation (35 KHz, 70 W, Sonometre UIP1000hd, Hielsher) at room temperature. At the end of the reaction, the solution was filtered-off and the precipitate was washed with 3×10 mL of nitromethane and dried under vacuum overnight (1×10^{-2} mbar).

4.1.1. Indium(III) tosylate. ^{1}H NMR (200 MHz, DMSO) δ 7.51 (d, J=8.0 Hz, 2H), 7.15 (d, J=7.9 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ 144.3, 138.5, 128.3, 125.5, 20.8; IR ν (cm^{-1}): 3064, 1497, 1196, 1153, 1119, 1094, 1033, 1007, 815, 677.

4.1.2. Bismuth(III) tosylate. ^{1}H NMR (200 MHz, DMSO) δ 7.48 (d, J=8.0 Hz, 2H), 7.12 (d, J=8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ 145.1, 137.9, 128.1, 125.5, 20.7; IR ν (cm^{-1}): 3080, 1497, 1156, 1112, 1032, 1007, 815, 677.

4.1.3. Copper(II) tosylate. ^{1}H NMR (200 MHz, DMSO) δ 7.48 (d, J=6.6 Hz, 2H), 7.12 (d, J=5.8 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ 137.6, 128.1, 125.7, 20.7; IR ν (cm^{-1}): 1637, 1496, 1169, 1125, 1037, 1010, 812, 680.

4.1.4. Zinc(II) tosylate. ^{1}H NMR (200 MHz, DMSO) δ 7.48 (d, J=8.0 Hz, 2H), 7.12 (d, J=8.1 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ 145.7, 137.5, 128.0, 125.4, 20.7; IR ν (cm^{-1}): 1641, 1179, 1124, 1036, 812, 676.

4.1.5. Galium(III) mesylate. ^{1}H NMR (200 MHz, DMSO) δ 7.52 (d, J=8.1 Hz, 2H), 7.12 (d, J=8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ 144.8, 138.1, 128.2, 125.5, 20.7; IR ν (cm^{-1}): 1644, 1183, 1152, 1125, 1037, 1012, 812, 681.

4.1.6. Indium(III) mesylate. ^{1}H NMR (200 MHz, D_2O) δ 2.66 (s, 3H); ^{13}C NMR (50 MHz, D_2O) δ 38.4; IR ν (cm^{-1}): 1650, 1166, 1054.

4.1.7. Bismuth(III) tosylate. ^{1}H NMR (200 MHz, D_2O) 2.66 (s, 3H); ^{13}C NMR^{13}C NMR (50 MHz, D_2O) δ 38.4; IR ν (cm^{-1}): 1260, 1145, 1054.

4.1.8. Scandium(III) mesylate. ^{1}H NMR (200 MHz, D_2O) δ 2.64 (s, 3H); ^{13}C NMR (50 MHz, D_2O) δ 38.4; IR ν (cm^{-1}): 1178, 1099, 1021.

4.2. Acylation reactions, general procedure

Into a Schlenk flask were introduced 20 mL of nitromethane, 2 mmol of 1,3-dimethoxybenzene, 10 mol % of catalyst and 4 mmol of acetyl chloride, with 0.5 mmol of dodecane for GC monitoring. The solutions were heated at reflux. The reactions were followed by gas chromatography, by analysis of aliquots. The products were obtained after extraction by diethyl ether and purification by column chromatography. All products are known compounds.

*4.2.1. 1-(2,4-Dimethoxyphenyl)-ethanone (**2a**).* MS (EI, 70 eV m/z): $[M]^+$ 180 (20); 165 (100); 150 (7); 122 (19); 104 (16); 92 (7); 77 (18); 63 (10); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.83 (d, J=8.7 Hz, 1H), 6.52 (dd, J=8.7, 2.3 Hz, 1H), 6.45 (d, J=2.3 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.8, 164.5, 161.1, 132.7, 121.2, 105.0, 98.3, 55.5, 55.4, 31.8.

*4.2.2. 1-(3,4-Dimethoxyphenyl)-ethanone (**2b**).* MS (EI, 70 eV m/z): $[M]^+$ 180 (48); 165 (100); 137 (22); 122 (13); 79 (32); 77 (27); 43 (33); 51 (21); 43 (33); ^{1}H NMR (200 MHz, DMSO) δ 7.63 (d, J=8.4 Hz, 1H), 7.44 (s, 1H), 7.06 (d, J=8.4 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ 196.3, 153.0, 148.5, 129.8, 123.0, 110.7, 110.1, 55.7, 55.4, 26.2.

*4.2.3. 1-(2,5-Dimethoxyphenyl)-ethanone (**2c**).* MS (EI, 70 eV m/z): $[M]^+$ 180 (54); 165 (100); 150 (12); 137 (12); 122 (19); 109 (18); 107 (34); 92 (11); 79 (27); 77 (36); 63 (14); 51 (17); 43 (54); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29 (d, J=3.2 Hz, 1H), 7.03 (dd, J=9.0, 3.2 Hz, 1H), 6.91 (d, J=9.0 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.4, 153.5, 153.4, 128.3, 120.4, 113.7, 113.2, 56.0, 55.8, 31.8.

*4.2.4. 1-(4-Methoxyphenyl)-ethanone (**2d**).* MS (EI, 70 eV m/z): $[M]^+$ 150.15 (29); 135.15 (100); 107.10 (41); 92.10 (19); 77.10 (41); 51.10 (7); 43.05 (13); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.87 (d, J=8.8 Hz, 2H), 6.87 (d, J=8.8 Hz, 2H), 3.80 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.8, 163.5, 130.4, 113.7, 55.4, 26.3.

*4.2.5. 1-(2,4,6-Trimethoxyphenyl)-ethanone (**2e**).* MS (EI, 70 eV m/z): $[M]^+$ 210 (11); 180 (33); 165 (100); 137 (7); 109 (22); 107 (32); 92 (10); 79 (30); 77 (39); 63 (18); 51 (18); 43 (12); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.08 (s, 2H), 3.81 (s, 3H), 3.77 (s, 6H), 2.44 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.0, 162.3, 158.8, 158.3, 118.4, 113.7, 91.0, 90.5, 64.2, 55.8, 55.4.

*4.2.6. 1-(1,3-Benzodioxol-5-yl)-ethanone (**2f**).* MS (EI, 70 eV m/z): $[M]^+$ 164 (48); 149 (100); 121 (49); 91 (13); 77 (5); 65 (40); 63 (32); 51 (12); 43 (27); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (dd, J=8.1, 1.7 Hz, 1H), 7.37 (d, J=1.7 Hz, 1H), 6.78 (d, J=8.1 Hz, 1H), 5.98 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.2, 151.7, 148.1, 132.1, 124.7, 107.9, 107.8, 101.8, 26.4.

*4.2.7. 1-(2-Dibenzofuranyl)-ethanone (**2g**).* MS (EI, 70 eV m/z): $[M]^+$ 210 (52); 195 (100); 167 (37); 139 (72); 113 (10); 69 (19); 63 (13); 43 (13); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.59 (d, J=1.8 Hz, 1H), 8.11 (dd, J=8.7, 1.8 Hz, 1H), 8.00 (d, J=6.9 Hz, 1H), 7.60 (d, J=8.6 Hz, 2H), 7.45 (dtd, J=22.2, 7.1, 1.3 Hz, 2H), 2.71 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.3, 158.9, 156.9, 132.5, 128.0, 124.6, 123.7, 123.4, 121.6, 120.9, 111.9, 111.6, 26.8.

*4.2.8. 2,3-Dihydro-1H-inden-1-one (**2h**).* MS (EI, 70 eV m/z): $[M]^+$ 132 (100); 131 (24); 104 (86); 103 (34); 78 (27); 77 (24); 63 (10); 51 (28); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41–7.00 (m, 4H), 2.94 (t, J=7.7 Hz, 2H), 2.61 (t, J=7.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.9, 140.6, 128.5, 128.3, 126.2, 35.9, 31.0.

*4.2.9. Benzothiophen-3-2H-one (**2i**).* MS (EI, 70 eV m/z): $[M]^+$. 150 (78); 132 (100); 131 (29); 120 (78); 78 (24); 77 (19); 63 (11); 51

(32); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43–7.22 (m, 4H), 3.67 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.7, 130.0, 129.0, 126.9, 36.7.

Supplementary data

^{1}H NMR and ^{13}C NMR, spectra of all compounds and acid–base titration. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.07.027.

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