Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 3325

www.rsc.org/greenchem

PAPER

Convenient access to strained trisubstituted 2-azetines from enals and chloramine-T in aqueous media

Atul K. Singh, Ruchi Chawla and Lal Dhar S. Yadav*

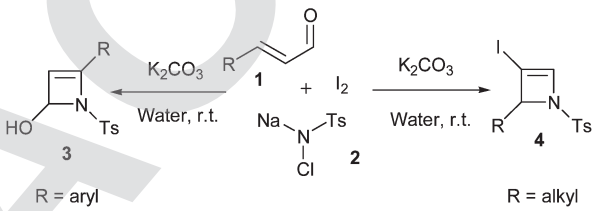
Received 22nd August 2012, Accepted 27th September 2012
DOI: 10.1039/c2gc36331c

A new, convenient and ecofriendly one-pot procedure for the synthesis of trisubstituted 2-azetines from α,β-unsaturated enals and chloramine-T using iodine and K_2CO_3 in aqueous media is reported. Easily accessible substrates, operational simplicity, wide substrate scope and ambient temperature are salient features of the present investigation.

Introduction

To design and implement new synthetic methodologies keeping in mind the alarming environmental issues are the need of the hour. Organic synthesis in aqueous media[1] is one such area of interest, which has provided chemists with exquisite alternatives to overcome the environmental hazards concerned with classical organic synthesis. The environmentally benign nature of water provides opportunities for clean processing and pollution prevention. Besides the benefits linked with carrying out an organic synthesis in water, if one can accomplish the synthesis of a scaffold which otherwise is difficult to achieve then it would definitely be a welcomed move.

2-Azetines are an enamine based ring system, the utility of which are manifested in the numerous types of reactions that they undergo, *viz.* intermolecular [2 + 2] photodimerization[2] or radical additions,[3] [4 + 2] and [2 + 2] cycloaddition reactions[4,5] and their ring-opening reaction with atmospheric oxygen.[6] The synthesis of 2-azetines has been relatively less explored owing to the highly constrained double bond present in the four-membered aza-heterocycle, which makes it highly unstable and difficult to access. However, *N*-acyl, *N*-methanesulfonyl and *N*-nitro-2-azetines are stable and the most studied 2-azetines available in the literature.[2,7,8] Most of the reports available in the literature are for the synthesis of unsubstituted 2-azetines, which are obtained from the corresponding 3-(methanesulfonyloxy)-azetidines *via* an elimination reaction in basic medium,[9] for which the results are not satisfactory in terms of yields, reaction times, synthetic steps, substrate accessibility, scope and environmental considerations. Developing a convenient route to substituted 2-azetines from easily available starting materials in an environmentally benign manner was the objective of our present investigation. We hypothesized the facile synthesis of this scaffold from enals and chloramine-T in the presence of iodine and potassium carbonate in water, as depicted in Scheme 1.



Scheme 1 The synthesis of 2-azetines **3** and **4**.

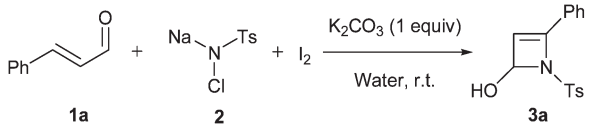
Results and discussion

Chloramine-T, which is a well known commercially available oxidising reagent, serves as a source of chloronium cations and/or nitrogen anions, and synthetic applications of chloramine-T have been developed by utilizing its reactivity towards a wide variety of functional groups.[10] Iodine catalysed transformations using chloramine-T have been carried out with different types of aromatic, aliphatic and functionalised olefins,[11] such as allylic alcohols, ethers, esters and halides, including electron-deficient olefins like nitroolefins, α,β-unsaturated ketones, esters and amides, but to the best of our knowledge, this catalytic transformation has never been studied with α,β-unsaturated enals. Taking all these aspects into consideration and in continuation of our ongoing efforts to develop new synthetic processes from easily available substrates,[12] we decided to study in detail the reaction of α,β-unsaturated enals with chloramine-T and iodine. To explore the reactivity of α,β-unsaturated enals, chloramine-T and iodine, we selected the model reaction between the cinnamaldehyde **1a** and chloramine-T **2** in the presence of iodine and potassium carbonate in water as solvent (Table 1).

No iodoamidated and aziridinated products were obtained under the reaction conditions. Unexpectedly, substituted 2-azetine **3a** was obtained in excellent yield (Table 1, entry 1). Encouraged by the results, we next focused our investigation towards the quantitative optimization of iodine and chloramine-T. We found that the best yield of azetine **3a** was obtained with 50 mol% of iodine (Table 1, entry 1). The yield of **3a** decreased in the presence of 30 mol% of iodine in comparison to 50 mol%

Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211 002, India. E-mail: ldsyadav@hotmail.com; Fax: (+91) 532-246-0533; Tel: (+91) 532-250-0652

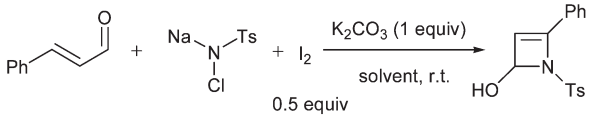
Table 1 Optimization of chloramine-T and iodine for the synthesis of 2-azetine **3a**[a]



Entry	Iodine mol%	Chloramine-T mol%	Time (h)	Yield[b] (%)
1	50	100	6	87
2	30	100	8	51
3	100	100	10	87
4	50	150	6	87
5	50	50	8	38
6	100	150	8	87

[a] For experimental procedure, see Experimental section. [b] Yield of isolated and purified product **3a**.

Table 2 Comparison of solvents in the synthesis of 2-azetine **3a**[a]



Entry	Solvent	Time (h)	Yield[b] (%)
1	H_2O	6	87
2	CH_3CN	9	10
3	EtOAc	9	30
4	CH_2Cl_2	7	80
5	THF	9	—
6	Dioxane	7	50
7	CH_3OH	9	—
8	Toluene	8	60

[a] For experimental procedure, see Experimental section. [b] Yield of isolated and purified product **3a**.

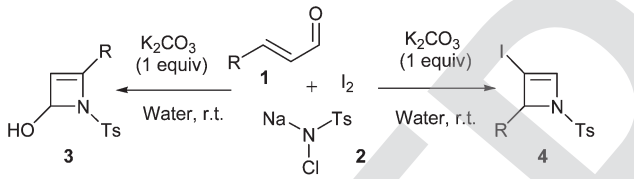
of iodine (Table 1, entry 2). In the presence of 1 equivalent of iodine the yield of azetine **3a** did not change even when the reaction time was extended up to 10 h. Next, we optimized the amount of chloramine-T and found that the use of 1.5 equivalents did not increase the yield of azetine **3a** (Table 1, entry 4), but its yield decreased on using 0.5 equivalent of chloramine-T (Table 1, entry 5).

For comparison purposes, we also performed the reaction in various solvents with 0.5 equivalent of iodine and 1 equivalent of K_2CO_3 but we obtained significantly lower yield of **3a** in relatively longer reaction times (Table 2).

Of the solvents tested, water was the best in terms of the yield and reaction time (Table 2, entry 1). This might be attributed to the greater solubility of chloramine-T in water than in organic solvents. Under the established optimized reaction conditions the process was extended to a variety of α,β-unsaturated enals and the results are summarised in Table 3.

We examined the substrate scope for different aromatic and aliphatic α,β-unsaturated enals. It can be seen from Table 3 that various aromatic α,β-unsaturated enals bearing functional groups reacted successfully to give the corresponding 1-tosylazet-2-ols

Table 3 Synthesis of azetines **3**[a] and **4**[a]

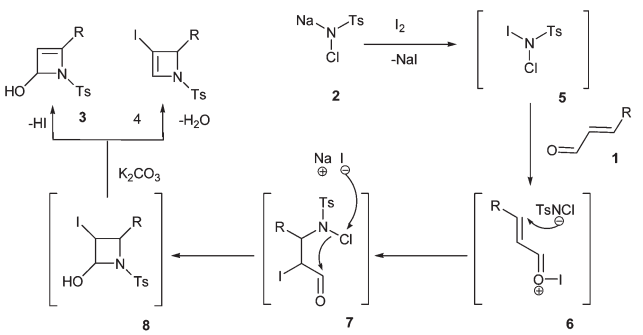


Entry	R	Product	Time (h)	Yield[b,c] (%)
1	C_6H_5	**3a**	6	87
2	4-$MeOC_6H_4$	**3b**	7	85
3	4-$CH_3C_6H_4$	**3c**	7	82
4	4-$NO_2C_6H_4$	**3d**	6	95
5	4-ClC_6H_4	**3e**	7	91
6	3-$MeOC_6H_4$	**3f**	7	83
7	3-$CH_3C_6H_4$	**3g**	7	80
8	3-$NO_2C_6H_4$	**3h**	6	92
9	CH_3	**4a**	7	85
10	C_2H_5	**4b**	7	81
11	C_3H_7	**4c**	8	77
12	C_4H_9	**4c**	9	76

[a] For experimental procedure, see Experimental section. [b] Yield of isolated and purified product. [c] All compounds gave C, H and N analyses within ±0.37% and satisfactory spectral (IR, ^1H NMR, ^{13}C NMR and EIMS) data.

in high yield within a short time period (Table 3, entries 1–8). α,β-Unsaturated enals bearing an electron-withdrawing group gave higher yield in comparison to α,β-unsaturated enals bearing an electron-donating group (Table 3, entries 4, 5, 8). After being successful in the case of aromatic α,β-unsaturated enals, we extended the procedure to various kinds of aliphatic α,β-unsaturated enals. Interestingly, it was observed that aliphatic α,β-unsaturated enals gave the corresponding 3-iodo-1-tosylazete instead of 1-tosylazet-2-ol (Table 3, entries 9–12).

This is understandable if we look at the mechanism of reaction as depicted in Scheme 2. In the case of aromatic α,β-unsaturated enals, elimination of the more acidic benzylic hydrogen and iodide ion takes place from the intermediate **8** to form the more stable product **3** (Table 3, entries 1–8), which is stabilised by extended conjugation, whereas in the case of aliphatic α,β-unsaturated enals, dehydration takes place by removal of the more acidic 3-H, an α-H of the aza-hemiacetal system, to form product **4** (Table 3, entries 9–12).



Scheme 2 A plausible mechanism for the synthesis of azetines **3** and **4**.

Initially, chloramine-T **2** reacts readily with iodine to form the active species *N*-chloro-*N*-iodo-*p*-toluenesulfonamide **5**, which acts as a source of iodonium ions and activates the carbonyl group of enals **1** to induce the 1,4-addition of the nitrogen nucleophile to form intermediate **6**. The liberated NaI reduces the intermediate **7** and the resulting species undergoes cyclization to afford **8**. Intermediate **8** undergoes elimination of HI or dehydration to afford products **3** or **4**, respectively. The proposed mechanism is in accordance with the earlier observations.[11]

Conclusions

In conclusion, we have developed a novel, highly efficient and ecofriendly one-pot procedure for the synthesis of 2-azetines from α,β-unsaturated enals using chloramine-T as the nitrogen source in the presence of iodine and K_2CO_3 in aqueous media. Importantly, aromatic enals afforded azetinols, while aliphatic enals furnished iodoazetes under the same reaction conditions. Easily accessible substrates, operational simplicity, wide substrate scope and ambient temperature are salient features of the present investigation, which make it one of the most convenient and efficient green methodologies for the synthesis of this relatively inaccessible class of compounds.

Experimental

General

IR spectra in KBr were recorded on a Perkin-Elmer 993 IR spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker Avance II (400 MHz) FT spectrometer in $CDCl_3$ using TMS as an internal reference. ^{13}C NMR spectra were recorded on the same instrument at 100 MHz in $CDCl_3$ and TMS was used as an internal reference. Mass (EI) spectra were recorded on JEOL D-300 mass spectrometer. Elemental analyses were carried out in a Coleman automatic carbon, hydrogen and nitrogen analyser. All chemicals used were reagent grade and were used as received without further purification. All reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates.

General procedure for the synthesis of azetines 3 and 4. A mixture of α,β-unsaturated aldehyde **1** (1 mmol), chloramine-T **2** (1 mmol) and iodine (0.5 mmol) in water was stirred at room temperature for 2 h with subsequent addition of K_2CO_3 (1 mmol). The reaction mixture was then stirred for another 4–7 h (Table 3). After completion of the reaction (monitored by TLC), aqueous $Na_2S_2O_3$ (0.2 M, 5 mL) was added to the reaction mixture and the resulting solution was extracted with EtOAc (3 × 5 mL). The combined organic phase was dried over anhyd. Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using a mixture of EtOAc–hexane (1 : 9) as eluent to afford an analytically pure sample of **3** or **4**.

Compound 3a. Brown greasy solid, yield 87%. IR (KBr) ν_{max} 3362, 3046, 2923, 1623, 1570, 1362, 1314, 1151, 1083, 859, 770 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ = 2.45 (s, 3H), 6.98 (dd, J = 11.8, 9.4 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.41–7.45 (m, 3H), 7.49 (d, J = 11.8 Hz, 1H), 7.54–7.56 (m, 2H), 7.85 (d, J = 8.1 Hz, 2H), 8.77 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.7, 77.4, 124.7, 128.0, 128.8, 129.2, 129.8, 131.2, 135.3, 144.6, 159.0, 171.0. EIMS (m/z): 301 (M^+). Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65; Found: C, 63.52; H, 5.14; N, 4.35.

Compound 3b. Yellow greasy solid, yield 85%. IR (KBr) ν_{max} 3365, 3058, 2940, 1625, 1576, 1350, 1320, 1250, 1154, 1082, 977, 850, 765 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ = 2.43 (s, 3H), 3.85 (s, 3H), 6.86 (dd, J = 15.6, 9.5 Hz, 1H), 6.91–6.96 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 15.6 Hz, 1H), 7.49–7.53 (m, 2H), 7.84 (d, J = 8.1 Hz, 2H), 8.73 (d, J = 9.5 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.7, 55.8, 77.3, 115.1, 124.5, 126.3, 127.1, 128.1, 129.7, 143.8, 153.7, 159.2, 171.2. EIMS (m/z): 331 (M^+). Anal. Calcd for $C_{17}H_{17}NO_4S$: C, 61.61; H, 5.17; N, 4.23; Found: C, 61.58; H, 5.19; N, 4.41.

Compound 3c. Brown greasy solid, yield 82%. IR (KBr) ν_{max} 3367, 3070, 2932, 1623, 1572, 1348, 1328, 1148, 842, 764 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ = 2.37 (s, 3H), 2.44 (s, 3H), 6.87 (dd, J = 15.7, 9.6 Hz, 1H), 7.21–7.25 (m, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 15.7 Hz, 1H), 7.47–7.49 (m, 2H), 7.86 (d, J = 8.2 Hz, 2H), 8.76 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.6, 23.8, 77.2, 124.3, 126.8, 128.1, 129.0, 129.9, 133.5, 136.5, 145.1, 154.3, 169.9. EIMS (m/z): 315 (M^+). Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44; Found: C, 64.86; H, 5.17; N, 4.76.

Compound 3d. Yellow greasy solid, yield 95%. IR (KBr) ν_{max} 3360, 3062, 2960, 1628, 1580, 1520, 1347, 1332, 1318, 1150, 1094, 838, 759 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ = 2.45 (s, 3H), 7.02 (dd, J = 12.3, 9.8 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 12.3 Hz, 1H), 7.76–7.71 (m, 2H), 7.85 (d, J = 8.2 Hz, 2H), 8.23–8.28 (m, 2H), 8.80 (d, J = 9.8 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.8, 77.5, 122.3, 124.4, 127.8, 129.7, 136.4, 141.4, 144.2, 148.6, 154.2, 169.7. EIMS (m/z): 346 (M^+). Anal. Calcd for $C_{16}H_{14}N_2O_5S$: C, 55.48; H, 4.07; N, 8.09; Found: C, 55.22; H, 4.28; N, 7.95.

Compound 3e. Yellow greasy solid, yield 91%. IR (KBr) ν_{max} 3358, 3071, 2952, 1624, 1578, 1338, 1320, 1153, 1089, 856, 766 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ = 2.43 (s, 3H), 6.97 (dd, J = 11.7, 9.4 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.39–7.43 (m, 2H), 7.46 (d, J = 11.7 Hz, 1H), 7.54–7.57 (m, 2H), 7.82 (d, J = 8.3 Hz, 2H), 8.75 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.8, 77.3, 124.7, 127.0, 127.9, 128.8, 129.9, 132.8, 134.2, 144.0, 153.9, 170.2. EIMS (m/z): 335 (M^+). Anal. Calcd for $C_{16}H_{14}ClNO_3S$: C, 57.23; H, 4.20; N, 4.17; Found: C, 57.41; H, 4.57; N, 4.08.

Compound 3f. Yellow greasy solid, yield 83%. IR (KBr) ν_{max} 3366, 3038, 2930, 1621, 1576, 1363, 1324, 1274, 1153, 1089, 1045, 767 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ = 2.44 (s, 3H), 3.87 (s, 3H), 6.87 (dd, J = 15.5, 9.3 Hz, 1H), 6.99–7.04 (m, 1H), 7.10–7.13 (m, 1H), 7.17–7.21 (m, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.34–7.42 (m, 1H), 7.45 (d, J = 15.5 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 8.75 (d, J = 9.5 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.6, 55.4, 77.0, 111.5, 116.2, 121.3, 124.8, 126.8,

129.4, 130.2, 136.1, 144.2, 154.0, 161.2, 170.7. EIMS (*m*/*z*): 331 (M^+). Anal. Calcd for $C_{17}H_{17}NO_4S$: C, 61.61; H, 5.17; N, 4.23; Found: C, 61.33; H, 5.26; N, 4.40.

Compound 3g. Brown greasy solid, yield 80%. IR (KBr) ν_{max} 3372, 3062, 2935, 1627, 1569, 1340, 1326, 1146, 761 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 2.42 (s, 3H), 2.45 (s, 3H), 6.88 (dd, J = 15.6, 9.5 Hz, 1H), 7.26–7.30 (m, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.36–7.41 (m, 3H), 7.45 (d, J = 15.6 Hz, 1H), 7.88 (d, J = 8.3 Hz, 2H), 8.78 (d, J = 9.5 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.6, 23.7, 76.9, 122.6, 124.7, 125.8, 127.1, 128.0, 128.9, 129.8, 133.7, 136.9, 144.1, 153.9, 171.1. EIMS (*m*/*z*): 315 (M^+). Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44; Found: C, 64.98; H, 5.30; N, 4.11.

Compound 3h. Yellow greasy solid, yield 92%. IR (KBr) ν_{max} 3370, 3064, 2959, 1623, 1573, 1347, 1342, 1326, 1153, 1092, 851, 762 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 2.44 (s, 3H), 7.04 (dd, J = 12.5, 9.9 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 12.5 Hz, 1H), 7.72–7.74 (m, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.92–7.96 (m, 1H), 8.27–8.35 (m, 1H), 8.43–8.45 (m, 1H), 8.83 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 21.6, 77.4, 121.3, 122.8, 124.6, 127.6, 129.2, 130.1, 132.2, 136.1, 144.0, 149.1, 154.2, 171.2. EIMS (*m*/*z*): 346 (M^+). Anal. Calcd for $C_{16}H_{14}N_2O_5S$: C, 55.48; H, 4.07; N, 8.09; Found: C, 55.13; H, 4.23; N, 8.40.

Compound 4a. Brown greasy solid, yield 85%. IR (KBr) ν_{max} 3052, 2925, 1630, 1580, 1460, 1378, 1363, 1152, 869 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 1.40 (d, J = 5.5 Hz, 3H), 2.40 (s, 3H), 3.22 (q, J = 5.5 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 8.47 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 19.7, 21.5, 57.2, 97.8, 127.6, 129.0, 144.1, 151.7, 154.2. EIMS (*m*/*z*): 349 (M^+). Anal. Calcd for $C_{11}H_{12}INO_2S$: C, 37.84; H, 3.46; N, 4.01; Found: C, 37.55; H, 3.32; N, 4.37.

Compound 4b. Brown greasy solid, yield 82%. IR (KBr) ν_{max} 3067, 2930, 1632, 1583, 1474, 1383, 1365, 1157, 878 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 0.90 (t, J = 7.2 Hz, 3H), 1.70–1.93 (m, 2H), 2.42 (s, 3H), 3.11 (t, J = 5.2 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 8.46 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 11.2, 21.6, 25.7, 59.1, 98.6, 127.4, 129.2, 143.9, 151.3, 154.3. EIMS (*m*/*z*): 363 (M^+). Anal. Calcd for $C_{12}H_{14}INO_2S$: C, 39.68; H, 3.89; N, 3.86; Found: C, 39.99; H, 3.64; N, 3.78.

Compound 4c. Brown greasy solid, yield 78%. IR (KBr) ν_{max} 3058, 2932, 1637, 1585, 1469, 1380, 1364, 1154, 884 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 0.91 (t, J = 7.1 Hz, 3H), 1.19–1.78 (m, 4H), 2.41 (s, 3H), 3.15 (t, J = 5.3 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 8.45 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 13.5, 15.7, 21.7, 34.8, 58.1, 99.9, 127.5, 129.1, 144.2, 151.2, 154.1. EIMS (*m*/*z*): 377 (M^+). Anal. Calcd for $C_{13}H_{16}INO_2S$: C, 41.39; H, 4.27; N, 3.71; Found: C, 41.26; H, 4.55; N, 4.03.

Compound 4d. Brown greasy solid, yield 77%. IR (KBr) ν_{max} 3063, 2935, 1634, 1590, 1465, 1379, 1362, 1150, 866 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 0.90 (t, J = 7.2 Hz, 3H), 1.32–1.54 (m, 4H), 1.71–1.95 (m, 2H), 2.40 (s, 3H), 3.16 (t, J = 5.0 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 8.46 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ = 13.8, 21.6, 22.5, 25.6, 30.4, 58.4, 99.8, 127.2, 129.0, 144.2, 151.6, 154.0. EIMS (*m*/*z*): 391 (M^+). Anal. Calcd for $C_{14}H_{18}INO_2S$: C, 42.98; H, 4.64; N, 3.58; Found: C, 42.88; H, 4.47; N, 3.75.

Acknowledgements

We sincerely thank SAIF, Punjab University, Chandigarh, for providing microanalyses and spectra.

References

1 (*a*) C.-J. Li and T.-H. Chan, *Organic Reactions in Aqueous Media*, John Wiley and sons, New York, 1997; (*b*) *Organic Synthesis in Water*, ed. P. A. Grieco, Blackie Academic and Professional, London, England, 1998.
2 P. R. Dave, R. Duddu, J. Li, R. Surapaneni and R. Gilardi, *Tetrahedron Lett.*, 1998, **39**, 5481.
3 N. Legrand, B. Quiclet-Sire and S. Z. Zard, *Tetrahedron Lett.*, 2000, **41**, 9815.
4 (*a*) P. R. Dave, R. Duddu, J. Li, R. Surapaneni and R. Gilardi, *Tetrahedron Lett.*, 1999, **40**, 443; (*b*) D. Osborne and P. J. Stevenson, *Tetrahedron Lett.*, 2002, **43**, 5469; (*c*) P. J. Stevenson, M. Nieuwenhuyzen and D. Osborne, *Chem. Commun.*, 2002, 444; (*d*) P. J. Stevenson, M. Nieuwenhuyzen and D. Osborne, *ARKIVOC*, 2007, **xi**, 129.
5 A. C. B. Burtoloso and C. R. D. Correia, *Tetrahedron Lett.*, 2006, **47**, 6377.
6 R. Bartnik, R. Faure and K. J. Gebicki, *J. Chem. Crystallogr.*, 1998, **28**, 119.
7 M. E. Jung and Y. M. Choi, *J. Org. Chem.*, 1991, **56**, 6729.
8 A. P. Marchand, R. Duddu, S. G. Bott and T. G. Archibald, *J. Org. Chem.*, 1994, **59**, 1608.
9 N. De Kimpe, in *Comprehensive Heterocyclic Chemistry II*, ed. A. Padwa, Elsevier, Oxford, 1996, vol. 1, ch. 1.21. Three- and four-membered rings, with all fused systems containing three- and four-membered rings.
10 (*a*) M. M. Campbell and G. Johnson, *Chem. Rev.*, 1978, **78**, 65; (*b*) D. H. Bremner, in *Synthetic Reagents*, ed. J. S. Pizey, Wiley, New York, 1985, vol. 6, p. 9.
11 (*a*) S. Minakata, *Acc. Chem. Res.*, 2009, **42**, 1172; (*b*) S. Minakata and J. Hayakawa, *Chem. Commun.*, 2011, **47**, 1905.
12 (*a*) A. K. Singh, R. Chawla, A. Rai and L. D. S. Yadav, *Chem. Commun.*, 2012, **48**, 3766; (*b*) R. Chawla, R. Kapoor, A. K. Singh and L. D. S. Yadav, *Green Chem.*, 2012, **14**, 1308; (*c*) A. K. Singh and L. D. S. Yadav, *Synthesis*, 2012, 591; (*d*) R. Chawla, A. K. Singh and L. D. S. Yadav, *Tetrahedron Lett.*, 2012, **53**, 3382; (*e*) A. K. Singh, R. Chawla and L. D. S. Yadav, *Synthesis*, 2012, 2353.

