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The first ionic liquid-promoted three-component coupling strategy for an expeditious synthesis of β-nitrocarbonitriles/thiocyanates

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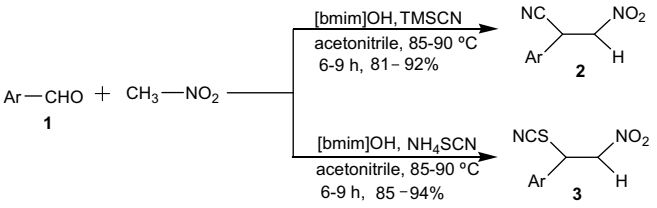
ABSTRACT

A novel and convenient three-component coupling reaction of nitromethane, aromatic aldehydes and trimethylsilyl cyanide (TMSCN) or ammonium thiocyanate has been developed for an expeditious synthesis of β-nitrocarbonitriles or β-nitrothiocyanates, respectively, via C–C and C–S bond-forming reactions. The synthetic protocol strategically involves a one-pot sequential Henry reaction and a Michael addition efficiently promoted by the same ionic liquid [bmim]OH. The main advantages of the present approach include the use of inexpensive simple substrates and an ionic liquid as an efficient reaction promoter for the mild synthesis in a one-pot procedure.

Modern synthetic design demands high efficiency in terms of minimization of synthetic steps together with maximization of complexity.[1] One of the ways to fulfil these goals is the development and use of multicomponent reactions (MCRs) which consist of several simultaneous bond-forming reactions and allow a highly efficient synthesis of complex molecules starting from simple substrates in a one-pot procedure.[2–4] Ionic liquids (ILs) have attracted increasing interest in organic synthesis owing to their great potential not only as environmentally benign reaction media but also as new catalysts and reagents, and because they are also easy to recycle.[5]

The importance of nitroalkanes in organic synthesis is tied up to their propensity to undergo facile α-alkylation reactions and interconversions to other important organic functional groups.[6] Aliphatic nitro compounds have proven to be valuable intermediates, and are powerful synthetic tools because they facilitate the carbon–carbon bond-forming processes.[7] Most importantly, the nitro group can be converted to a carbonyl compound using the Nef reaction.[8] An efficient nitroalkane-mediated cyclopropanation is a key step in the synthesis of β-amino acid analogues of Pregabalin and Gabapentin that target the α_2–δ protein.[9] Hydrocyanation or hydrothiocyanation of nitroalkenes affords straightforward access to nitroalkanes bearing a nitrile or thiocyanate functionality of considerable synthetic utility. The diverse transformations in which nitriles participate (for example, RCN→RCO_2H, $RCONH_2$. RCHO, RCH_2NH_2 and RCN_4, as well as Pinner and Ritter reactions) place them among the most versatile intermediates in organic chemistry.[10–23] Furthermore, organic thiocyanates have gained considerable importance in various areas of organosulfur chemistry[24] and are useful scaffolds for the synthesis of various heterocycles, some of which are associated with herbicidal and other important biological activity.[25,26] Moreover, the thiocyanato group occurs as an important functionality in certain anticancer natural products formed by deglycosylation of glucosinolates derived from cruciferous vegetables.[27,28]

Considering the above points along with earlier reports on hydrocyanation of alkenes[29] and our ongoing efforts to develop new one-pot synthetic processes,[30] we report herein the first ionic liquid [bmim]OH-promoted synthesis of hitherto unknown β-nitrocarbonitriles **2** and β-nitrothiocyanates **3** using a three-component coupling (**3cc**) strategy (Scheme 1). After some preliminary experimentation, it was found that β-nitrocarbonitriles **2**



Scheme 1. One-pot synthesis of β-nitrocarbonitriles **2** and β-nitrothiocyanates **3**.

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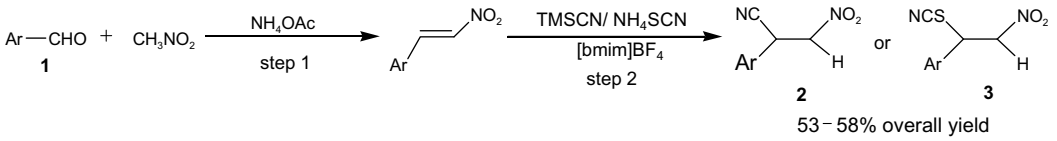
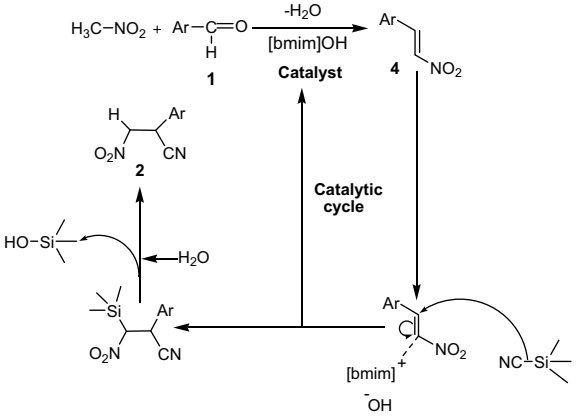


Scheme 2. Two-step synthesis of β-nitrocarbonitriles **2** and β-nitrothiocyanates **3**.

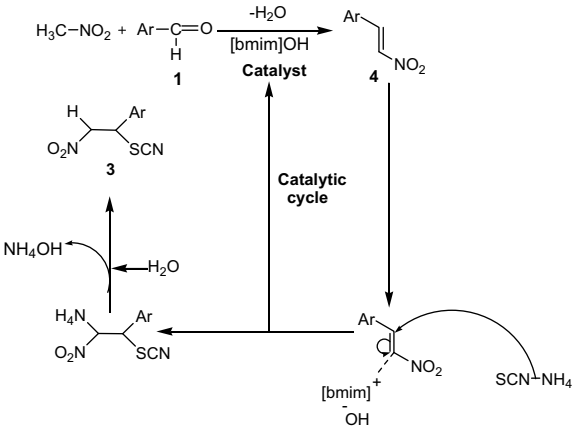
Table 1
Optimization of the catalyst for the one-pot synthesis of 2-nitro-1-(4-nitrophenyl)ethyl thiocyanate (**3d**)[a]

Entry	Catalyst	Time[b] (h)	Yield[c] (%)
1	NH_4OH (20 mol %)	9	36
2	Bu_4NF (20 mol %)	9	41
3	NH_4OAc (20 mol %)	9	48
4	[bmim]Br (20 mol %)	9	40
5	[bmim]PF_6 (20 mol %)	9	43
6	[bmim]BF_4 (20 mol %)	9	44
7	[bmim]OH (10 mol %)	9	83
8	[bmim]OH (15 mol %)	8	87
9	[bmim]OH (20 mol %)	6	94
10	[bmim]OH (25 mol %)	8	94

[a] For the experimental procedure, see Ref. 35.
[b] Time for completion of the reaction at 85–90 °C as indicated by TLC.
[c] Yield of isolated and purified product.



Scheme 3. Plausible mechanism for the formation of β-nitrocarbonitriles **2**.



Scheme 4. Plausible mechanism of the formation of β-nitrothiocyanates **3**.

and β-nitrothiocyanates **3** can be synthesized in moderate overall yields (53–58%) by following a two-step process (Scheme 2). The first step is the preparation of β-nitrostyrenes **4** by the Henry reaction[31,32], and the second step is a hitherto unreported ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4-promoted Michael addition of trimethylsilyl cyanide (TMSCN) or ammonium thiocyanate to β-nitrostyrenes **4** to afford hydrocyanated and hydrothiocyanated products **2** and **3**. In order to improve the overall yields and synthesize products **2** and **3** expeditiously from nitromethane in a one-pot procedure, we devised a novel ionic liquid [bmim]OH-promoted three-component coupling reaction of nitromethane, aromatic aldehydes **1** and TMSCN or NH_4SCN, which works well for the high yielding synthesis of β-nitrocarbonitriles **2** or β-nitrothiocyanates **3** (Scheme 1). Interestingly, no formation of the corresponding cyanohydrin trimethyl ethers (an adduct of an aldehyde and trimethylsilyl cyanide) was observed under these conditions (Scheme 2).

We set up a series of experiments to optimize the reaction conditions. Indeed, we used a very straightforward protocol and examined various basic catalysts as well as ionic liquids for the synthesis of representative compound **3d** (Tables 1 and 2). Among the catalysts tested, the best result was obtained with [bmim]OH; this evidenced the catalytic efficacy of [bmim]OH in the reaction affording **3d** in excellent yield (Table 1, entry 9). This is in accordance with the earlier observations of Ranu et al. who introduced the basic ionic liquid [bmim]OH for organic reactions for the first time.[33] The use of other ionic liquids and basic catalysts resulted in a considerable drop in yields (Table 1, entries 1–6). The optimum catalyst loading for the ionic liquid [bmim]OH was found to be 20 mol % (Table 1, entry 9). It is noteworthy that a decrease in the catalyst amount decreased the yield considerably (Table 1, entries 7 and 8). However, a catalyst loading higher than 20 mol % did not appreciably increase the yield (Table 1, entry 10).

Next, optimization of the solvent for the synthesis of **3d** was investigated and it was found that among methanol, ethanol, 1,4-dioxane and acetonitrile, the best solvent in terms of yield was acetonitrile. In view of the above findings, stirring the reaction mixture in acetonitrile with catalyst [bmim]OH (20 mol %) at 85–90 °C configures the optimized reaction condition. In order to investigate the substrate scope of the reaction, a wide range of substituted aldehydes were subjected to this procedure. The results are summarized in Table 2. Both electron-donating and electron-withdrawing substituents are tolerated to afford the corresponding products **2** and **3** in consistently good yields. After isolation of the product, the catalyst could be easily recycled and reused without loss of efficiency.[34,35]

The **3cc** approach reported herein for the envisaged synthesis of β-nitrocarbonitriles **2** or β-nitrothiocyanates **3** was successfully realized by stirring an equimolar mixture of an aldehyde, nitromethane and cyanating/thiocyanating agents, that is, TMSCN/NH_4SCN with 20 mol % of ionic liquid [bmim]OH as catalyst in acetonitrile at 85–90 °C for the time specified in Table 2. Isolation and purification afforded analytically pure compounds **2**[34] and **3**[35] in 81–94% yields. The requisite ionic liquids were prepared employing known methods.[33a,36–38] Plausible mechanisms for the formation of **2** and **3** are depicted in Schemes 3 and 4.

In conclusion, we have demonstrated a novel, convenient and expeditious method for the synthesis of β-nitrocarbonitriles and β-nitrothiocyanates in excellent yields via a one-pot three-compo-

Table 2
One-pot [bmim]OH-promoted reaction of nitromethane with aldehydes and nucleophiles to afford products **2** and **3**

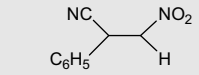
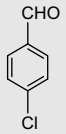
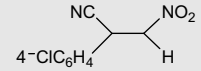
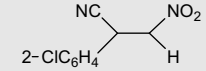
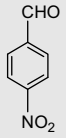
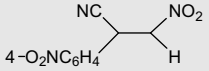
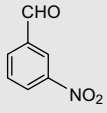
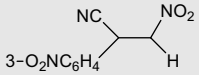
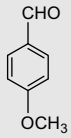
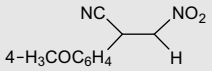
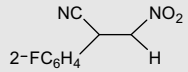
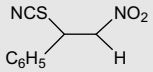
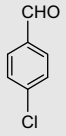
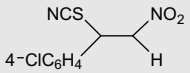
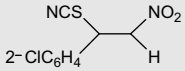
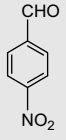
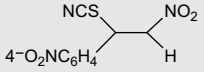
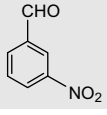
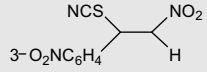
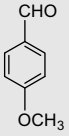
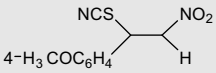
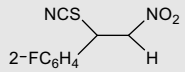
Entry	Aldehyde **1**	Nucleophile (TMSCN/NH_4SCN)	Product **2** or **3**	Time[a] (h)	Yield[b,c] (%)
1		TMSCN	 **2a**	8	83
2		TMSCN	 **2b**	7	89
3		TMSCN	 **2c**	8	84
4		TMSCN	 **2d**	6	92
5		TMSCN	 **2e**	8	85
6		TMSCN	 **2f**	9	81
7		TMSCN	 **2g**	7	85
8		NH_4SCN	 **3a**	8	86
9		NH_4SCN	 **3b**	6	91
10		NH_4SCN	 **3c**	7	87
11		NH_4SCN	 **3d**	6	94
12		NH_4SCN	 **3e**	8	88

Table 2 (*continued*)

Entry	Aldehyde **1**	Nucleophile (TMSCN/NH_4SCN)	Product **2** or **3**	Time[a] (h)	Yield[b,c] (%)
13		NH_4SCN	 **3f**	9	85
14		NH_4SCN	 **3g**	7	90

[a] Stirring time at 85–90 °C.
[b] Yield of isolated and purified products.
[c] All compounds gave C, H and N analyses within ±0.37% and satisfactory spectral (IR, ^{1}H NMR, ^{13}C NMR and EIMS) data.

nent coupling of aldehydes, nitromethane and TMSCN/NH_4SCN using ionic liquid as an efficient promoter. The present protocol for the synthesis of various functionalized nitroalkanes has high potential for its application in organic chemistry.

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References and notes

1. Trost, B. M.. *Science* **1991**, *254*, 1471.
2. Bienayme, H.; Hulme, C.; Oddon, G.; Schmidt, P. *Chem. Eur. J.* **2000**, *6*, 3321.
3. von Wangelin, A. J.; Neumann, H.; Gördes, D.; Klaus, S.; Strubing, D.; Beller, M. *Chem. Eur. J.* **2003**, *9*, 4286.
4. Orru, R. V. A.; de Greef, M. *Synthesis* **2003**, 1471.
5. (a) Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363; (b) Bao, W.; Wang, Z. *Green Chem.* **2006**, *8*, 1028; (c) Zhao, D.; Wu, M.; Kou, Y.; Min, E. *Catal. Today* **2002**, *74*, 157; (d) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667; (e) Qiao, K.; Yakoyama, C. *Chem. Lett.* **2004**, *33*, 472; (f) Sun, W.; Xia, C.-G.; Wang, H.-W. *Tetrahedron Lett.* **2003**, *44*, 2409; (g) Kamal, A.; Chouhan, G. *Tetrahedron Lett.* **2005**, *46*, 1489; (h) Earle, M. J.; Katdare, S. P.; Seddon, K. R. *Org. Lett.* **2004**, *6*, 707.
6. Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: New York, 2001.
7. (a) Ballini, R.; Rosini, G. *Synthesis* **1988**, 833; (b) Rosini, G.; Ballini, R.; Petrini, M.; Marotta, E.; Righi, P. *Org. Prep. Proc. Int.* **1990**, *22*, 707; (c) Ballini, R.; Marziali, P.; Mozzicafreddo, A. *J. Org. Chem.* **1996**, *61*, 3209; (d) Ballini, R.; Bosica, G. *Tetrahedron Lett.* **1996**, *37*, 8027; (e) Ballini, R.; Bosica, G. *J. Org. Chem.* **1997**, *62*, 425; (f) Ballini, R.; Petrini, M. *Tetrahedron* **2004**, *60*, 1017; (g) Amantini, D.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Vaccaro, C. *J. Org. Chem.* **2003**, *68*, 9263; (h) Marotta, E.; Righi, P.; Rosini, G. *Tetrahedron Lett.* **1998**, *39*, 1041; (i) Areces, P.; Gil, M. V.; Higes, F. J.; Romàn, E.; Serrano, J. A. *Tetrahedron Lett.* **1998**, *39*, 8557.
8. Pinnick, H. W. *Org. React.* **1990**, *38*, 655.
9. Schwartz, J. B. et al *J. Med. Chem.* **2005**, *48*, 3026.
10. Xi, F.; Kamal, F.; Schenerman, M. A. *Tetrahedron Lett.* **2002**, *43*, 1395.
11. Demko, Z. P.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2113.
12. Davis, B.; Brandstetter, T. W.; Smith, C.; Hackett, L.; Winchester, B. G.; Fleet, G. W. J. *Tetrahedron Lett.* **1995**, *36*, 7507.
13. Gaspar, B.; Carreira, E. M. *Angew. Chem., Int. Ed* **2007**, *46*, 4519.
14. Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.
15. Collier, S. J.; Langer, P.. In *Science of Synthesis*; Georg Thieme: Stuttgart, 2004; Vol. 19, p 403.
16. Kukushkin, V. Y.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2005**, *358*, 1.
17. Wang, M.-X. *Top. Catal.* **2005**, *35*, 117.
18. Brown, H. C.; Choi, Y. M.; Narasimhan, S. *Synthesis* **1981**, 605.
19. Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299.
20. Yadav, V. K.; Babu, K. G. *Eur. J. Org. Chem.* **2005**, 452.
21. Sharifi, A.; Mohsenzadeh, F.; Mojtahedi, M. M.; Saidi, M. R.; Balalaie, S. *Synth. Commun.* **2001**, *31*, 431.
22. Caddick, S.; Judd, D. B.; Lewis, A. K. deK.; Reich, M. T.; Williams, M. R. V. *Tetrahedron* **2003**, *59*, 5417.
23. Jayachitra, G.; Yasmeen, N.; Rao, K. S.; Ralte, S. L.; Srinivasan, R.; Singh, A. K. *Synth. Commun.* **2003**, *33*, 3461.
24. Guy, R. G. In *The Chemistry of the Cyanates and Their Thio Derivatives*; Patai, S., Ed.; Wiley-Interscience: New York, 1977; p 819.
25. *Comprehensive Heterocyclic Chemistry*; Metzer, J. B., Katritzky, A., Eds.; Pergamon: Oxford, 1984; Vol. 6, p 235.
26. Kawamura, S.; Izumi, K.; Satoh, J.; Sanemitsu, Y.; Hamada, T.; Shibata, H.; Satoh, R. Eur. Pat. 1991, Appl E.P. 446802; *Chem. Abstr.* **1992**, *116*, 59360j.
27. Shahidi, F. In *Sulphur Compounds in Foods*; Mussinan, C. J., Keelan, M. E., Eds.; American Chemical Society: Washington, DC, 1994; p 106. Chapter 9.
28. Mehta, R. G.; Liu, J.; Constantinou, A.; Thomas, C. F.; Hawthorne, M.; You, M.; Gerhaeuser, C.; Pezzuto, J. M.; Moon, R. C.; Moriarty, R. M. *Carcinogenesis* **1995**, *16*, 399.
29. (a) Gross, Z.; Hoz, S. *J. Am. Chem. Soc.* **1988**, *110*, 7489; (b) Russell, G. A.; Dedolph, D. *J. Org. Chem.* **1985**, *50*, 3878.
30. (a) Yadav, L. D. S.; Yadav, S.; Rai, V. K. *Tetrahedron* **2006**, *62*, 5464; (b) Yadav, L. D. S.; Yadav, S.; Rai, V. K. *Green Chem.* **2006**, *8*, 455; (c) Yadav, L. D. S.; Rai, A.; Rai, V. K.; Awasthi, C. *Synlett* **2007**, 1905; (d) Yadav, L. D. S.; Awasthi, C.; Rai, V. K.; Rai, A. *Tetrahedron Lett.* **2007**, *48*, 4899; (e) Yadav, L. D. S.; Rai, A.; Rai, V. K.; Awasthi, C. *Tetrahedron* **2008**, *64*, 1420; (f) Yadav, L. D. S.; Patel, R.; Srivastava, V. P. *Synlett* **2008**, 0583; (g) Yadav, L. D. S.; Rai, A. *Tetrahedron Lett.* **2008**, *49*, 5751.
31. Yan, S.; Gao, Y.; Xing, R.; Shen, Y.; Liu, Y.; Wu, P.; Wu, H. *Tetrahedron* **2008**, *64*, 6294.
32. Jang, Y.-J.; Lin, W.-W.; Shih, Y.-K.; Liu, J.-T.; Hwang, M.-H.; Yao, C. -F. *Tetrahedron* **2003**, *59*, 4979.
33. (a) Ranu, B. C.; Banerjee, S. *Org. Lett.* **2005**, *7*, 3049; (b) Ranu, B. C.; Jana, R.; Sowniah, S. *J. Org. Chem.* **2007**, *72*, 3152.
34. *General procedure for the synthesis of* β-nitrocarbonitriles **2**: A mixture of an aromatic aldehyde (1 mmol), nitromethane (1 mmol), TMSCN (1 mmol) and [bmim]OH (20 mol %) in acetonitrile (5 ml) was stirred at 85–90 °C for an appropriate time of 6–9 h (Table 2). After completion of the reaction (monitored by TLC), water (10 mL) was added and the product was extracted with diethyl ether (3 × 15 mL). The combined extract was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the crude product thus obtained was purified by silica gel column chromatography using ethyl acetate–*n*-hexane (1:9) as eluate to afford an analytically pure sample of **2**. The remaining ionic liquid was rinsed with ether (2 ml), dried under vacuum at 90 °C for 2 h to eliminate any water trapped and reused for subsequent runs.[33] Physical data of representative compounds: Compound **2a**: yellowish solid, yield 83%, mp 89 °C. IR (KBr) ν_{max} 3005, 2988, 2240, 1600, 1582, 1565, 1451, 753, 705 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ: 3.92 (dd, 1H, *J* = 8.5, 4.7 Hz, CHCN), 4.60 (dd, 1H, *J* = 12.8, 4.7 Hz, CH_aNO_2), 4.97 (dd, 1H, *J* = 12.8, 8.5 Hz, CH_bNO_2), 7.25–7.49 (m, $5H_{arom}$). ^{13}C NMR (100 MHz; $CDCl_3$) δ: 26.9, 77.2, 121.2, 127.3, 128.4, 129.2, 130.9. EIMS (*m/z*) 176 (M^+). Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.05; H, 4.72; N, 15.65.Compound **2d**: Yellowish solid, yield 92%, mp 91 °C. IR (KBr) ν_{max} 3008, 2983, 2245, 1602, 1581, 1563, 1454, 752, 703 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ: 3.98 (dd, 1H, *J* = 8.7, 4.8 Hz, CHCN), 4.64 (dd, 1H, *J* = 12.9, 4.8 Hz, CH_aNO_2), 4.99 (dd, 1H, *J* = 12.9, 8.7 Hz, CH_bNO_2), 7.21–7.25 (m, $2H_{arom}$), 7.33–7.46 (m, $2H_{arom.}$). ^{13}C NMR (100 MHz; $CDCl_3$) δ: 25.7, 78.1, 120.8, 12.7, 129.1, 140.1, 148.3. EIMS (*m/z*) 221 (M^+). Anal. Calcd for $C_9H_7N_3O_4$: C, 48.87; H, 3.19; N, 19.00. Found: C, 49.24; H, 3.04; N, 19.27.
35. *General procedure for the synthesis of* β-nitrothiocyanates **3**: The procedure followed was the same as described above for the synthesis of **2** (Ref. 34) except that NH_4SCN (1 mmol) was used instead of TMSCN (1 mmol). The crude product thus obtained was purified by silica gel column chromatography using ethyl acetate–*n*-hexane (2:8) as eluate to afford an analytically pure sample of **3**. The remaining ionic liquid was recycled for subsequent runs as described above.[33] Physical data of representative compounds: Compound **3a**: pale yellow oil, yield 86%. IR (KBr) ν_{max} 3010, 2985, 2143, 1605, 1585, 1562, 1450, 748, 708 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ: 3.85 (dd, 1H, *J* = 8.4, 4.3 Hz, CHCN), 4.63 (dd, 1H, *J* = 12.7, 4.3 Hz, CH_aNO_2), 4.96 (dd, 1H, *J* = 12.7, 8.4 Hz, CH_bNO_2), 7.25–7.49 (m, $5H_{arom}$). ^{13}C NMR (100 MHz; $CDCl_3$) δ: 39.5, 85.7, 112.8, 126.5, 128.2, 129.6, 148.3. EIMS (*m/z*) 208 (M^+). Anal. Calcd for $C_9H_8N_2O_2S$: C, 51.91; H, 3.87; N, 13.45. Found: C, 51.72; H,3.98; N, 13.78.Compound **3d**: Pale yellow oil, yield 94%. IR (KBr) ν_{max} 3012, 2987, 2148, 1603, 1589, 1559, 1453, 751, 710 cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$) δ: 3.89 (t, 1H, *J* = 8.9, 4.5 Hz, CHCN), 4.66 (dd, 1H, *J* = 12.8, 4.5 Hz, CH_aNO_2), 4.81 (dd, 1H, *J* = 12.8, 8.95 Hz, CH_bNO_2), 7.19–7.23 (m, $2H_{arom}$), 7.32–7.48 (m, $2H_{arom}$). ^{13}C NMR (100 MHz; $CDCl_3$) δ: 42.6, 84.2, 112.4, 120.7, 12.9, 128.5, 146.8. EIMS (*m/z*) 253 (M^+). Anal. Calcd for $C_9H_7N_3O_4S$: C, 42.69; H, 2.79; N, 16.59. Found: C, 42.40; H, 2.98; N, 16.44.
36. Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, *67*, 8855.
37. Creary, X.; Willis, E. D. *Org. Synth.* **2005**, *82*, 166.
38. Duport, J.; Consorti, C. S.; Swarez, P. A. Z.; de Souza, R. F. *Org. Synth.* **2004**, *10*, 184; . *Org. Synth.* **2002**, *79*, 236.