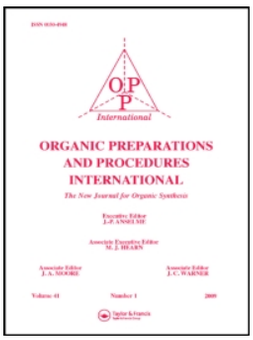

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An Improved and Efficient *N*-acetylation of Amines Using Choline Chloride Based Deep Eutectic Solvents

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Amine acetylation is one of the most widely used reactions in organic chemistry and is often used in synthesis of amides and protection of -NH group.[1] Amine acetylation is often performed using acetic anhydride[2] or acetyl chloride[1,3] in presence of acidic[2] or basic[3] catalysts in organic medium. *N*-acetylation of amines was performed in aqueous medium using sodium dodecyl sulphate with various anhydrides,[4] with acetic anhydride in acetic acid,[5] acetic anhydride in aqueous sodium bicarbonate solution,[2] in *N,N*-dimethylacetamide with *N,N*-carbonyldiimidazole,[6] with acetic anhydride in the presence of various catalysts such as $RuCl_3$,[7] $La(NO_3)_3{\cdot}6H_2O$,[8] $NbCl_5$,[9] $NaHSO_4{\cdot}SiO_2$,[10] poly(4-vinylpyridinium) perchlorate,[11] $BiFeO_3$ nanopowder,[12] iodine,[1] acylimidazoliumacetate,[13] $ZnAl_2O_4@SiO_2$nanocomposite.[14] Saikia and coworkers[15] performed *N*-acetylation of amines using acetonitrile as an acylating agent and *in situ* generated trimethylsilyl iodide as the catalyst under microwave heating conditions, while Zhang and Chen[16] treated aryl amines with dimethylacetamide in the presence of hydrochloric acid to obtain *N*-arylamide derivatives.

Many of these methods used in *N*-acetylation of amines are characterized either by use of expensive and harmful reagents, solvents or catalysts, by harsh reaction conditions or long reaction times. In our attempt to utilize choline chloride based deep eutectic solvents in organic synthesis of some heterocyclic compounds, we noticed an immediate formation of *N*-acetylated amines, which were easily isolated in very high yields, with no need for further purification. Deep eutectic solvents (DES) became interesting to our research group due to their applicability as green solvents in synthesis of heterocyclic compounds, often used without any catalysts or acting as a catalysts themselves.[17] So far DESs have been utilized in organic synthesis of various heterocyclic compounds,[18–22] alkylation of anilines[23] and thiophenic compounds,[24] as well as green solvents for extraction of various bioactive plant compounds.[25] DESs have found many useful applications in organic synthesis, which were extensively reviewed in the last few years.[17,22,26] Deep

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eutectic solvents have been described as environmentally benign mixtures of readily available, biodegradable, recyclable components with low vapor pressure.[17,22] DESs are non-toxic, formed with 100% atom economy and their high solubility in water implies a simple reaction workup.[17] Choline chloride is often used in the formation of DESs due to its low toxicity, biodegradability and low cost, in combination with urea, thiourea, glycerol, carboxylic acid, etc.[27]

The purpose of this work was to investigate the influence of various DESs on yield, reaction time and temperature applied for *N*-acetylation of various amines. We also investigated the influence of DES recycling on product yield.

An optimization on amine:acetic acid anhydride (AAA) ratio was performed on anthranilic acid in a DES made of choline chloride (ChCl) and malonic acid (*Table 1*). The best ratio was shown to be 1:2 (amine:acetic anhydride), since reaction can be performed at room temperature in only 10 minutes. If the amount of AAA is to be decreased, the reaction time should be increased. Thus, all reactions with different amines were performed at the ratio of amine:acetic anhydride (1:2) at room temperature, except for the DES derived from ChCl:adipic acid and ChCl:thiourea which were performed at higher temperatures (140°C and 110°C) due to a higher melting point of the corresponding DESs.

After the optimization of the ratio of reactants, *N*-acetylation of anthranilic acid and 4-chloroaniline amine was performed in different DESs as shown in *Table 2*. The best DES for acetylation for both compounds at room temperature, in terms of yield and reaction time, was shown to be ChCl:urea (1:2) and ChCl:malonic acid (1:1). Reactions were monitored on TLC and finished when all the reactants were consumed. Anthranilic acid was acetylated in ChCl:urea DES in 15 minutes at room temperature, with isolated yield of 68%. For acetylation of anthranilic acid in ChCl:malonic acid DES, less time (10 minutes) was required for the reaction to be completed (yield 57%). Combination of ChCl and adipic acid did not yield any products for anthranilic acid.

The best reaction time and yield (at room temperature) for 4-chloroaniline was in the DES made of ChCl and malonic acid (88% yield in 15 minutes), as well as urea (98% yield in 30 minutes), but for choline chloride/urea DES it took more time for the reactants to be completely consumed. Thiourea in combination with ChCl was also proven to be very efficient, but higher temperature was required. This suggests that the effect will be highly dependent on the combination of compounds mixed to produce the DES.

Table 1
Optimization of Anthranilic Acid:Acetic Acid Anhydride Ratio for *N*-acetylation

Anthranilic acid in DES ChCl:malonic acid (1:1)		
Ratio anthranilic acid: acetic anhydride	reaction time (min)	yield (%)
1: 3	1–3	57
1: 2	10	57
1: 1.5	60	52
1: 1.2	120	49
1: 1	180	15

Table 2
Optimization of Conditions for *N*-acetylation of Anthranilic Acid and 4-chloroaniline

Anthranilic acid			
Solvent	T(°C)	Yield (%)	Reaction time (min)
ChCl:urea (1:2)	r.t.	68	15
ChCl:malonic acid (1:1)	r.t.	57	10
ChCl:oxalic acid (1:1)	r.t.	56	60
ChCl:thiourea (1:2)	109	52	60
ChCl:adipic acid (1:1)	140	—	—
4-chloroaniline			
Solvent	T(°C)	Yield (%)	Reaction time (min)
ChCl:urea (1:2)	r.t.	98	30
ChCl:malonic acid (1:1)	r.t.	88	15
ChCl:oxalic acid (1:1)	r.t.	62	30
ChCl:thiourea (1:2)	109	87	15
ChCl:adipic acid (1:1)	140	64	30

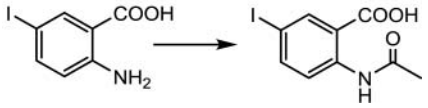
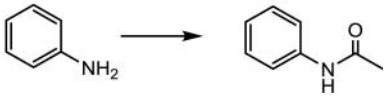
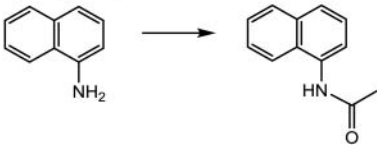
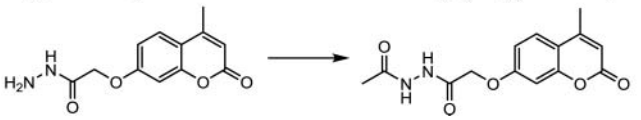
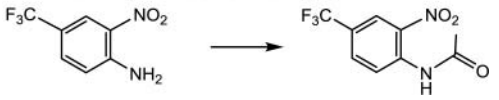
All of the above indicated that the best choice for *N*-acetylation of amines are two DESs, ChCl:urea and ChCl:malonic acid. Therefore, the rest of amines were acetylated in these two DESs and the results are shown in *Table 3*. All the reactions were monitored on TLC and finished when all the reactants were consumed or after 60 minutes.

When aniline was acetylated, TLC showed full consumption of aniline, but isolation required an extraction with dichloromethane (DCM) after water was added to the mixture. ChCl:urea DES yielded 91% of acetanilide in only 30 minutes. 1-Naphthylamine was acetylated in the highest yield (86%) and in the shortest time (15 min) in ChCl:urea DES. The same procedure was also applied on 2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetohydrazide and the same results were achieved for ChCl:urea (52%) and ChCl:malonic acid (54%) DESs. Acetylation of 2-nitro-4-(trifluoromethyl)aniline yielded no acetylated product, while acetylation of 4-nitro-3-(trifluoromethyl)aniline yielded acetylated product; but after 60 minutes, some of the reactant was still in the mixture. This indicates the significance of the nitro group position. 4-(Trifluoromethyl)aniline was easily acetylated in both solvents in 60 minutes in 88% and 87% yields. Combination of ChCl:urea or malonic acid was also suitable for 2,3,4-trifluoroaniline (58% and 31%) and cyclopropylamine (36% and 44%). 2-Aminothiophenol was successfully acetylated by obtaining diacetylated product *S*-(2-acetamidophenyl)ethanethioate.

An influence of DES recycling on final yield of the product was also investigated. An acetylation of 4-chloroaniline was performed in two eutectic solvents CC/U and CC/malonic acid and results are shown in *Table 4*. It is evident that recycling of DES up to five times does not influence the yield of the final product.

The overall data shows that the best DES for *N*-acetylation of amines is ChCl:urea (1:2) in terms of reaction time, temperature, yield and purity of final compounds. This solvent is easily prepared from biodegradable components and final

Table 3
N-Acetylation of Different Amines in Choline Chloride:urea and Choline Chloride: malonic Acid DESs

Solvent	T(°C)	Yield (%)	Reaction time (min)
5-iodoanthranilic acid			
			
ChCl:urea	r.t.	34	60
ChCl:malonic acid	r.t.	69	60
aniline			
			
ChCl:urea	r.t.	91	30
ChCl:malonic acid	r.t.	60	30
1-naphthylamine			
			
ChCl:urea	r.t.	86	15
ChCl:malonic acid	r.t.	53	60
2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetohydrazide			
			
ChCl:urea	r.t.	52	30
ChCl:malonic acid	r.t.	54	30
2-nitro-4-(trifluoromethyl)aniline			
			
ChCl:urea	r.t.	–	–
ChCl:malonic acid	r.t.	–	–

(*Continued on next page*)

Table 3
N-Acetylation of Different Amines in Choline Chloride:urea and Choline Chloride: malonic Acid DESs *(Continued)*

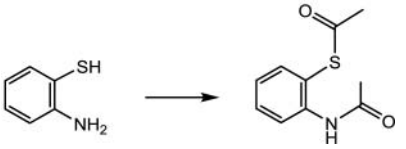
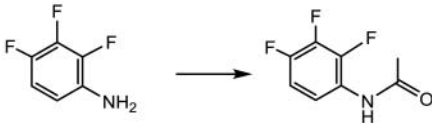
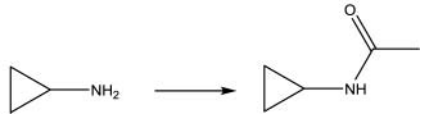
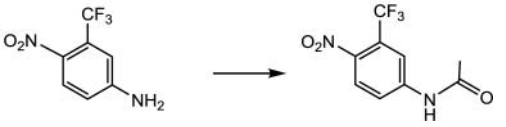
Solvent	T(°C)	Yield (%)	Reaction time (min)
4-(trifluoromethyl)aniline			
			
ChCl:urea	r.t.	88	60
ChCl:malonic acid	r.t.	87	60
2-aminothiophenol			
			
ChCl:urea	r.t.	65	60
ChCl:malonic acid	r.t.	57	60
2,3,4-trifluoroaniline			
			
ChCl:urea	r.t.	58	15
ChCl:malonic acid	r.t.	31	15
cyclopropylamine			
			
ChCl:urea	r.t.	36	60
ChCl:malonic acid	r.t.	44	60
4-nitro-3-(trifluoromethyl)aniline			
			
ChCl:urea	r.t.	74	60
ChCl:malonic acid	r.t.	69	60

Table 4
Influence of DES Recycle on Final Product Yield Shown for Acetylation of 4-chloroaniline

Solvent	Yield (%)
Choline chloride:urea	98
1st recycle	94
2nd recycle	97
3rd recycle	97
4th recycle	97
5th recycle	96
Choline chloride:malonic acid	88
1st recycle	88
2nd recycle	87
3rd recycle	87
4th recycle	86
5th recycle	87

products are easily isolated by addition of water or extraction with suitable solvents. Apart from being effective, this procedure is also environmentally friendly.

Experimental Section

Melting points were determined on a capillary melting point apparatus (Electrothermal, Rochford, UK) and are uncorrected. Thin-layer chromatography was performed with fluorescent silica gel plates F254 (Merck, Darmstadt, Germany), which were checked under UV (254 and 365 nm) light, using benzene: acetone: acetic acid (8: 1: 1) as a solvent. The MS spectra were recorded on LC/MS/MS API 2000 (Applied Biosystems/MDS SCIEX, CA, USA). 1 H NMR spectra were recorded on a Bruker Avance 600 MHz NMR Spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany) at 293 K in DMSO-d6. The elemental analysis for C, H and N was done on a Perkin-Elmer Analyzer 2400 Series II (Perkin–Elmer, Boston, MA, USA). Infrared spectra (νmax-cm-1) were recorded on a Beckmann FT-IR 3303, using KBr disks. All solvents and reagents were supplied by commercial suppliers.

Preparation of Deep Eutectic Solvents

All deep eutectic solvents were prepared according to the procedures described in the literature.[20]

Synthetic Procedures for N-acetylation of Amines

0.0025 Moles of the respective amine was added to DES and stirred at different temperatures (depending on the solvent) until dissolved. 0.005 Moles of acetic anhydride was added to the mixture and stirred until the completion of reaction, which was monitored by TLC. Upon completion, water was added to the reaction mixture; separated solid was

filtered off and dried. DES was recycled by evaporation of water. Water soluble acetylated amines were extracted with a suitable organic solvent.

***N*-Acetylanthranilic acid**. White-yellow solid (68%, 0.30 g, 1.7 mmol); Mp = 180°C (*lit*.[28,29] 184°C); Rf = 0.67; ^{1}H NMR (300 MHz, DMSO-d6) δ: 11.08 (s, 1 H), 8.49–8.46 (d, 1 H, J = 8.29), 8.00–7.97 (dd, 1 H), 7.59 (t, 1 H, J = 7.91, J = 1.51), 7.16 (t, 1 H), 2.16 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 170.0, 168.9, 141.3, 134.4, 131.5, 122.9, 120.4, 117.0, 25.4; MS (ESI): m/z = 177.90 [M-H$^+$].

***N*-(4-Chlorophenyl)acetamide**. White solid (98%, 0.42 g, 2.5 mmol); Mp = 179°C–181°C (*lit*.[29] 178°C); Rf = 0.59; ^{1}H NMR (600 MHz, DMSO-d6) δ: 10.09 (br.s, 1 H), 7.62–7.60 (d, J = 8.80, 1 H), 7.34–7.35 (d, J = 8.80, 1 H), 2.05 (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d6) δ: 168.4, 138.2, 128.5, 126.7, 120.4, 24.0; MS (ESI): m/z = 167.80 [M-H+].

5-Iodo-*N*-acetylanthranilic acid. Off white solid (69%, 0.53 g, 1.7 mmol); Mp = 155°C (*lit*.[28] 160°C); Rf = 0.68; ^{1}H NMR (300 MHz, DMSO-d6) δ: 11.07 (br.s., 1 H), 8.29–8.22 (d, 1 H), 7.95–7.90 (d, 1 H), 1.25 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 169.0, 151.4, 142.5, 141.9, 139.4, 122.6, 119.5, 74.6, 25.5; MS (ESI): m/z = 304.00 [M-H$^+$].

***N*-Phenylacetamide**. Off white solid (91%, 0.31 g, 2.3 mmol); Mp = 114°C–115°C (*lit*.[29] 114°C); Rf = 0.41; ^{1}H NMR (300 MHz, DMSO-d6) δ: 11.06 (br.s., 1 H), 8.47–8.44 (d, J = 8.29, 1 H), 7.98–7.95 (d, J = 7.91, J = 1.51, 1 H), 7.56 (t, 1 H), 7.13 (t, 1 H), 2.13 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 169.9, 141.3, 134.4, 131.5, 123.0, 120.4, 116.9, 25.4; MS (ESI): m/z = 133.90 [M-H$^+$].

***N*-(Naphthalen-1-yl)acetamide**. Pale purple solid (86%, 0.40 g, 2.2 mmol); Mp = 157°C (*lit*.[29] 158–160°C); Rf = 0.67; ^{1}H NMR (300 MHz, DMSO-d6) δ: 9.94 (br.s., 1 H), 8.13–7.46 (m, J = 9.42, J = 9.04, 7 H), 2.21 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 169.4, 134.3, 134.2, 128.6, 126.4, 126.2, 126.0, 125.5, 123.2, 122.0, 24.0; MS (ESI): m/z = 184.00 [M-H$^+$].

***N'*-Acetyl-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetohydrazide**. Off-white solid (54%, 0.39 g, 1.35 mmol); Mp = 237°C–239°C; Rf = 0.14; ^{1}H NMR (300 MHz, DMSO-d6) δ: 10.1 (br.s., 1 H), 9.85 (br.s., 1 H), 7.72–7.69 (d, J = 9.04, 1 H), 7.04–6.98 (m, 2 H), 6.23 (s, 1 H), 4.74 (s, 2 H), 2.40 (s, 3 H), 1.88 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 168.6, 166.4, 161.1, 160.5, 154.9, 153.7, 127.0, 126.9, 114.1, 113.0, 111.9, 102.1, 66.7, 20.9, 18.6; IR (KBr): 3173 (amide -NH stretching), 1724 (ketone –C = O),1610 (-NH banding), 1263 (-C-N stretching) cm^{-1}; MS (ESI): m/z = 289.10 [M-H+].

Anal. Calcd. for $C_{14}H_{14}N_2O_5$ (290.2): C, 59.93; H, 4.86; N, 9.65. Found: C, 60.19; H, 4.74; N, 9.81.

***N*-(4-(Trifluoromethyl)phenyl)acetamide**. White solid (88%, 0.45 g, 2.20 mmol); Rf = 0.61; ^{1}H NMR (600 MHz, DMSO-d6) δ: 10.33 (br.s, 1 H), 7.80–7.64 (d, J = 8.80 Hz, 4 H), 2.09 (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d6) δ: 168.66, 142.8, 125.9, 125.8, 123.0, 122.9, 118.7, 24.0; MS (ESI): m/z = 209.90 [M-H$^+$].

Commercially available (Matrix Scientific, USA) under CAS number: 349–97-3 and characterized by Mp = 152°C–153°C.

***S*-(2-Acetamidophenyl)ethanethioate**. Yellowish oil (65%, 0.34 g, 1.63 mmol); Rf = 0.63; ^{1}H NMR (300 MHz, DMSO-d6) δ: 9.35 (br.s., 1 H), 7.73–7.70 (m, 1 H), 7.48–7.46 (m, 1 H), 7.44–7.41 (m, 1 H), 7.19–7.25 (m, 1 H), 2.40 (s, 3 H), 2.06 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 193.6, 140.2, 137.0, 130.9, 125.8, 125.6, 30.7, 23.9; MS (ESI): *m/z* = 210.20 [M+H$^+$].

Commercially available (CheMall Corporation, USA) under CAS number: 1204–55-3.

***N*-(2,3,4-Trifluorophenyl)acetamide**. White solid (58%, 0.27 g, 1.45 mmol); Mp = 89°C–91°C (*lit.*[30] 92°C); Rf = 0.58; ^{1}H NMR (300 MHz, DMSO-d6) δ: 9.91 (br.s, 1 H), 7.59–7.28 (m, 1 H), 7.27–7.25 (m, 1 H), 2.09 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 169.3, 145.5, 141.3, 138.0, 124.5, 119.3, 112.1, 23.6; MS (ESI): *m/z* = 187.90 [M-H$^+$].

***N*-Cyclopropylacetamide**. Yellowish liquid (44%, 0.11 g, 1.1 mmol); Rf = 0.84 (DCM:ethyl acetate 20:1); ^{1}H NMR (300 MHz, DMSO-d6) δ: 7.83 (br.s, 1 H), 2.64–2.53 (m, 1 H), 1.91–1.74 (s, 3 H), 0.59–0.56 (m, 2 H), 0.36–0.34 (m, 2 H)[31]; ^{13}C NMR (75 MHz, DMSO-d6) δ: 170.67, 23.0, 22.7, 21.5, 6.0; MS (ESI): *m/z* = 100.1 [M+H$^+$].

***N*-(4-Nitro-3-(trifluoromethyl)phenyl)acetamide**. Yellow solid (74%, 0.46 g, 1.85 mmol); Mp = 95–97°C; Rf = 0.48; ^{1}H NMR (400 MHz, DMSO-d6) δ: 10.93 (br.s., 1 H), 8.28–8.04 (m, *J* = 9.54, *J* = 8.80, 3 H), 2.15 (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d6) δ: 169.7, 143.9, 129.7, 127.7, 121.8, 116.9, 114.4, 53.1, 24.2; MS (ESI): *m/z* = 247.00 [M-H$^+$].

Commercially available (Matrix Scientific, USA) under CAS number: 393–12-4 and characterized by Mp = 108°C–109°C as pale yellow solid.

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