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Mechanochemical Synthesis of Substituted 4*H*-3,1-Benzoxazin-4-ones, 2-Aminobenzoxazin-4-ones, and 2-Amino-4*H*-3,1-benzothiazin-4-ones Mediated by 2,4,6-Trichloro-1,3,5-triazine and Triphenylphosphine

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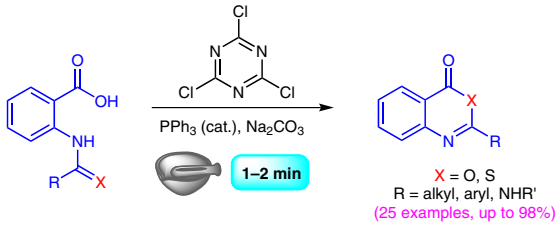

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Abstract A mild and convenient approach for the synthesis of 2-substituted 4*H*-3,1-benzoxazin-4-ones, 2-aminobenzoxazin-4-ones, and 2-amino-4*H*-3,1-benzothiazin-4-ones under solvent-assisted grinding is reported. In the presence of 2,4,6-trichloro-1,3,5-triazine and catalytic triphenylphosphine, cyclodehydration of *N*-substituted anthranilic acid derivatives proceeded rapidly within minutes at room temperature. The products were also obtained in good to excellent yields by using minimal amounts of solvent and inexpensive reagents.

Key words carboxylic acids, chemoselectivity, green chemistry, phosphorus, cyclization

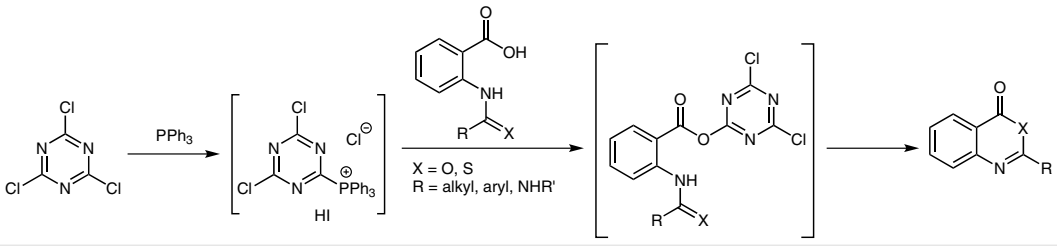
4*H*-3,1-Benzoxazin-4-ones are an important class of *N*-heterocycles that are useful precursors for the synthesis of various pharmaceutically active compounds such as dihydrobenzoxazinones,[1–3] substituted quinazolinones,[4,5] and isocoumarin derivatives.[6] A number of 2-substituted benzoxazinone derivatives have been shown to exhibit a range of useful pharmacological and biological activities such as anticonvulsant,[7] antithrombotic,[8] and inhibitors of human leukocyte elastase,[9] human cytomegalovirus protease,[10] and serine protease.[11,12] Thus, several synthetic methods have been developed for the preparation of benzoazinones. Some recent examples include TBHP/$CoCl_2$-mediated oxidative cyclization of *N*-(2-formylphenyl)amides,[13] $K_2S_2O_8$-mediated intramolecular oxidative nitrogenation/oxygenation in *N*-aryl benzylic amines,[14] palladium-catalysed carbonylation of 2-bromoanilines[15] or *N*-substituted 2-haloanilines,[16] palladium-catalysed C≡C bond cleavage of azidoalkynes,[17] and copper-catalyzed C–N bond formation/rearrangement of *N*-acyl-2-halobenzamides.[18] Nevertheless, the methods still suffer from drawbacks including the need for expensive reagents, limited availability of substrates, harsh reaction conditions, and long reaction times.

An alternative, simple and relatively straightforward approach is through cyclization of N-substituted anthranilic acids in the presence of dehydrating agents such as acetic anhydride,[4,19] di-*tert*-butyl pyrocarbonate (Boc_2O),[20] silica-bound benzoyl chloride,[21] thionyl chloride,[22] and 2,4,6-trichloro-1,3,5-triazine (TCT).[23–25] However, refluxing conditions or microwave irradiation are generally required for these methods.

Recently, our group reported a convenient mechanochemical synthesis of 4-arylidene-2-phenyl-5(4*H*)-oxazolones from hippuric acid by using TCT in combination with a catalytic amount of triphenylphosphine (PPh_3).[26] We envisaged that a similar strategy could be applied to the preparation of 2-substituted benzoxazin-4-ones and other related derivatives. In a continuation of our ongoing research involving TCT, we wish to report a mild and rapid synthesis of substituted 4*H*-3,1-benzoxazin-4-ones, 2-aminobenzoxazin-4-ones, and 2-amino-4*H*-3,1-benzothiazin-4-ones under solvent-assisted grinding (Scheme 1).

To optimize the reaction conditions, a solvent-assisted grinding technique was used to promote the cyclization of *N*-benzoylanthranilic acid. Typically, equimolar amounts of *N*-benzoylanthranilic acid and TCT were ground together in a mortar in the presence of two equivalents of base and a few drops of tetrahydrofuran (THF), either with or without addition of PPh_3. After one minute (the time at which the starting acid completely disappeared), the cyclized product was isolated by filtration through a short pad of silica.

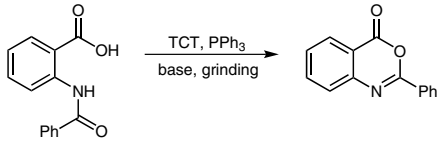
According to Table 1, reaction in the presence of an organic base such as NMM (entry1) gave a low yield of the cyclized product, possibly due to decomposition of the qua-



Scheme 1 TCT/PPh_3 mediated cyclodehydration of *N*-substituted anthranilic acids

ternary *N*-triazinylammonium intermediates.[27] A slightly improved yield was observed when using weak inorganic bases such as sodium bicarbonate or sodium carbonate (entries 2 and 3). However, the best yield was obtained with the latter base (entry 3). In the absence of PPh_3, the reaction was incomplete, leading to a lower yield of product (entry 4). This result suggested that the reactive triazinylphosphonium chloride (**I**)[28] was formed which rapidly activated *N*-benzoylanthranilic acid toward cyclization. It should be noted that when the best conditions were applied under conventional stirring or using ultrasound (entries 5 and 6), the product yield decreased significantly, indicating that the grinding process leads to reaction rate acceleration; presumably due to an increase in the contact surface area of the solid reactants.[29]

Table 1 Optimization of Reaction Conditions[a]

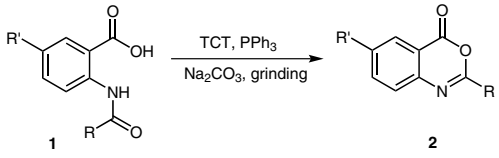


Entry	Base	Method	Yield (%)
1	NMM	grinding	55
2	$NaHCO_3$	grinding	61
3	Na_2CO_3	grinding	91
4	Na_2CO_3	grinding	57[b]
5	Na_2CO_3	stirring[c]	trace
6	Na_2CO_3	sonication[c]	32

[a] Reaction conditions: *N*-benzoylanthranilic acid (0.542 mmol), TCT (0.542 mmol), PPh_3 (0.0542 mmol), base (1.084 mmol), a few drops of THF, 1 min.
[b] Reaction without PPh_3.
[c] Reaction performed in THF (2 mL).

With the optimized reaction conditions established (Table 1, entry 3), we turned our attention to the scope and generality of this methodology. As summarized in Table 2, the reaction proceeded well with a variety of N-substituted anthranilic acid derivatives.[30] 2-Arylbenzoxazinones containing electron-donating or electron-withdrawing substituents could be prepared in good to excellent yields within 1–2 minutes grinding (entries 1–9). Consistent with other studies,[15,17] the presence of an electron-withdrawing group on the *N*-benzoylanthranilic acid decreased the yield of the corresponding products (entries 2–4). Considering steric and electronic effects, it was found that steric hindrance by the OMe moiety at the *ortho*-position did not significantly affect either the yield or the rate of the reaction (entry 5). Whereas no obvious electronic effect was observed when the R group contained a strongly electron-donating OMe or weak electron-withdrawing Cl substituent (entries 6 and 7), significantly lower yields were obtained with electron-deficient substrates bearing a strongly electron-withdrawing nitro group on R (entries 8 and 9).

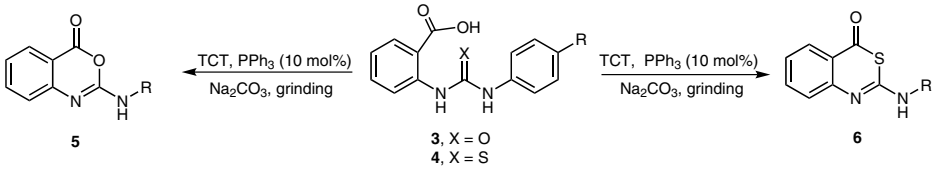
Table 2 TCT-Mediated Synthesis of 2-Substituted 4*H*-3,1-Benzoxazin-4-ones **2**[a]



1 **2**

Entry	R′	R	**2**	Yield (%)	Ref
1	H	Ph	**2a**	91	31a
2	I	Ph	**2b**	87	31b
3	Cl	Ph	**2c**	88	31c
4	NO_2	Ph	**2d**	75	31d
5	H	2-$MeOC_6H_4$	**2e**	81	31e
6	H	4-$MeOC_6H_4$	**2f**	83	31e
7	H	4-ClC_6H_4	**2g**	86	31e
8	H	3-$NO_2C_6H_4$	**2h**	75	31f
9	H	4-$NO_2C_6H_4$	**2i**	56	31e
10	H	$C_6H_5CH_2$	**2j**	90	31g
11	H	4-$FC_6H_4CH_2$	**2k**	85	
12	H	4-$MeOC_6H_4CH_2$	**2l**	87	16b
13	H	2,6-$Cl_2C_6H_3CH_2$	**2m**	81	
14	H	4-$HOC_6H_4CH_2$	**2n**	71	
15	H	1-naphthylacetyl	**2o**	90	31h

[a] Reaction conditions: *N*-acylanthranilic acid (0.542 mmol), TCT (0.542 mmol), PPh_3 (0.0542 mmol), Na_2CO_3 (1.084 mmol), 1–2 min.



5

5a, R = C_6H_5 (1 min, 94%)[32a]
5b, R = 4-MeC_6H_4 (2 min, 88%)[32a]
5c, R = 2-MeC_6H_4 (2 min, 66%)[32a]
5d, R = 4-BrC_6H_4 (1 min, 77%)
5e, R = 1-naphthyl (2 min, 86%)[32b]
5f, R = Bn (3 min, 55%)[9]

3, X = O
4, X = S

6

6a, R = C_6H_5 (1 min, 98%)[33a]
6b, R = 4-MeC_6H_4 (2 min, 92%)[33b]
6c, R = 4-ClC_6H_4 (2 min, 84%)[33b]
6d, R = 1-naphthyl (2 min, 82%)

Scheme 2 TCT/PPh_3-mediated synthesis of 2-amino-4*H*-3,1-benzoxazin-4-ones **5** and 2-amino-4*H*-3,1-benzothiazin-4-ones **6**

2-Alkyl substituted benzoxazinones are known to be highly hygroscopic and readily undergo hydrolysis to 2-acetaminobenzoic acids during aqueous work-up.[23] Since no aqueous workup was necessary, we were able to synthesize a series of 2-alkyl substituted benzoxazinone derivatives in high yields (entries 10–15). Notably, no significant interference from bulky groups or the free hydroxy function could be observed (entries 13–15).

Notably, by using our method, all the cyclized products were obtained within 1–2 minutes at ambient temperature. However, the reaction mediated by TCT in the presence of triethylamine required heating to reflux overnight in anhydrous toluene to afford **2a** in 83% yield.[23] A reaction mediated by the iminium cation generated from a mixture of TCT and *N*,*N*-dimethylformamide (DMF) required 4 hours in chloroform/DMF to provide **2a** in 86% yield.[25]

Encouraged by these results, the scope of the reaction was further extended toward cyclization of 1-aryl-3-(1-benzene carboxylic acid)carbamides **3** as well as thiocarbamides **4**. According to Scheme 2, cyclization of **3** proceeded rapidly to afford 2-aminobenzoxazin-4-ones **5** in good to excellent yields. Likewise, the thiocarbamide derivatives **4** also underwent rapid cyclization to provide 2-amino-4*H*-3,1-benzothiazin-4-ones **6** in comparable yields.

The conditions were applicable to substrates containing various functional groups, although sterically hindered substrate **3c** gave a lower yield of the product **5c**. Remarkably, no product from cyclodesulfurization (to 2-amino-4*H*-3,1-benzoxazin-4-one) or cyclization with the NH of the thiourea moiety (to 3-phenyl-quinazoline-2-thion-4-one) was observed, indicating that the reaction was highly chemoselective.

It should be noted that products such as **6** have previously been prepared by heating **4** to reflux in ethanol for 1 hours without reported yields.[33b] Acetic anhydride-mediated cyclization of **4** to **6** also required long reaction times (8–24 h) at room temperature.[34] Additionally, only 2-amino-4*H*-3,1-benzoxazin-4-ones were obtained when potassium salts of **4** were treated with mercury(II) oxide in DMF at room temperature.[32a]

In summary, we have developed a simple and economic solvent-assisted grinding method that enables convenient access to heterocycles including 2-substituted 4*H*-3,1-benzoxazin-4-ones, 2-aminobenzoxazin-4-ones, and 2-amino-4*H*-3,1-benzothiazin-4-ones from readily available N-substituted anthranilic acids. Both O- and S-containing substrates underwent rapid cyclization under mild reaction conditions with high chemoselectivity and wide functional-group tolerance.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588125.

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(30) **General Procedure:** N-Substituted anthranilic acid (0.542 mmol), TCT (0.542 mmol), PPh_3 (0.054 mmol), and Na_2CO_3 (1.084 mmol) were mixed and ground together for 1 min, during which a few drops of THF were added to aid homogeneous mixing. Upon completion of the reaction as indicated by TLC, dichloromethane (2 mL) was added and the resulting mixture was filtered through a short pad of silica, followed by solvent evaporation under reduced pressure.
2-Phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (**2a; Table 2, entry 1**): Yield: 0.1103 g (0.494 mmol, 91%); white solid; mp 120–122 °C; R_f 0.38 (EtOAc/hexanes, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.2 Hz, 2 H), 8.22 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.80 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.49 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 157.2, 147.0, 136.6, 132.7, 130.3, 128.8, 128.7, 128.4, 128.3, 127.3, 117.1.
2-(4-Fluorobenzyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2k; Table 2, entry 11): Yield: 0.1181 g (0.462 mmol, 85%); white solid; mp 125–127 °C; R_f 0.42 (EtOAc/hexanes, 10%). FTIR (neat): 1766, 1642, 1605, 1513 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.78 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.48 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.38 (dd, *J* = 8.6, 5.2 Hz, 2 H), 7.03 (t, *J* = 8.6 Hz, 2 H), 3.95 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 161.1, 161.0, 159.6, 146.4, 136.6, 131.0. 130.9, 129.9 (d, *J* = 12.4 Hz), 128.6, 126.9, 116.9, 115.9, 115.7, 40.8. HRMS (ESI-TOF): *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{11}FNO_2$: 256.0774; found: 256.0776.
2-(4-Hydroxybenzyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2n; Table 2, entry 14): Yield: 0.0978 g (0.386 mmol, 71%); white solid; mp 154.4–155.3 °C; R_f 0.26 (EtOAc/hexanes, 30%). FTIR (neat): 3427, 1761, 1647, 1597, 1518 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.78 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.49 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.50 (s, 1 H), 3.90 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 160.0, 155.6, 146.4, 136.9, 130.6, 128.65, 128.63, 126.7, 125.8, 116.8, 115.9, 40.8. HRMS (ESI-TOF): *m*/*z* [M+Na]$^+$ calcd for $C_{15}H_{11}NO_3Na$: 276.0637; found: 276.0641.
2-(Naphthalen-1-ylamino)-4*H*-benzo[*d*][1,3]oxazin-4-one (**5e**)**:** Yield: 0.1348 g (0.468 mmol, 86%); white solid; mp 182–184 °C; R_f 0.42 (EtOAc/hexanes, 20%). ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD 3 drops): δ = 8.51 (d, *J* = 8.0 Hz, 1 H), 8.07–8.04 (m, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.87–7.84 (m, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.67–7.64 (m, 1 H), 7.51–7.44 (m, 4 H), 6.95 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD 3 drops): δ = 163.4, 153.3, 150.0, 142.2, 134.50, 134.46, 130.9, 128.5, 126.88, 126.83, 126.5, 126.3, 125.8, 123.6, 122.1, 121.4, 120.05, 120.00.
2-(Phenylamino)-4*H*-benzo[*d*][1,3]thiazin-4-one (**6a**); Yield: 0.1353 g (0.532 mmol, 98%); orange solid; mp 161–162 °C; R_f 0.30 (EtOAc/hexanes, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.65 (td, *J* = 8.0, 1.6 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H, 2 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.34–7.26 (td, *J* = 8.0, 1.6 Hz, 1 H), 7.20 (t, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.5, 153.3, 149.8, 138.0, 136.1, 129.4, 128.4, 125.4, 125.3, 125.0, 122.3, 118.2.
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