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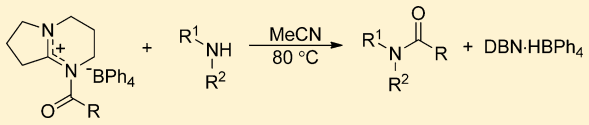
N-Acyl DBN Tetraphenylborate Salts as *N*-Acylating Agents

James E. Taylor, Matthew D. Jones, Jonathan M. J. Williams, and Steven D. Bull*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

Supporting Information

ABSTRACT: Air-stable and crystalline *N*-acyl DBN tetraphenylborate salts have been synthesized from 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and the corresponding acyl chloride in the presence of sodium tetraphenylborate. The salts have been shown to be effective *N*-acylating agents, reacting with primary amines, secondary amines, and sulfonamides to form the corresponding *N*-acylated products in good yields. The DBN hydrotetraphenylborate byproduct can be conveniently removed by filtration, providing pure *N*-acylated products without the need for further purification. The *N*-acyl DBN tetraphenylborate salts are attractive alternatives to acyl halides as they can be stored in air without decomposition, avoid the production of free acid during acylation reactions, and can be used under more forcing thermal conditions.



INTRODUCTION

Acylation reactions are one of the most significant and widely used transformations in organic chemistry. For example, the amide bond is ubiquitous throughout nature and is found in many pharmaceutically active molecules, making the *N*-acylation of amines to form amide products one of the most frequently used reactions in drug synthesis.[1,2] *N*-Acyl sulfonamides are also an important class of compounds in the medicinal and agrochemical industries, with many examples having been reported to exhibit a diverse range of pharmacological activities.[3] *N*-Acyl sulfonamides are also widely used as safety-catch linkers in solid support syntheses.[4]

Various synthetic protocols have been developed that employ different acyl sources and catalysts to increase the rate of acylation reactions.[5] Of all the potential acyl sources, acyl chlorides and acid anhydrides are currently the most widely used. For example, the Schotten−Baumann reaction, first described in 1884, between amines and acyl chlorides or acid anhydrides in the presence of aqueous base is the foundation of synthetic acylation reactions.[6] Modern variations of the original reaction can be performed in organic solvents and utilize acyl transfer catalysts such as DMAP and its derivatives or Lewis acid catalysts,[7] although uncatalyzed versions in organic solvents have also been reported.[8]

However, there are a number of problems associated with the use of acyl chlorides and acid anhydrides in *N*-acylation reactions. For example, reactions of amines with acyl chlorides can be highly exothermic, while anhydrides can form imides as side products when reacted with primary amines.[9] Many acyl chlorides are also air-sensitive and volatile and are hydrolyzed by moisture to form acids, releasing HCl in the process. This can not only render acyl chlorides practically difficult to use, but can also cause problems when acid-sensitive functionality is present within the reacting molecules. Additionally, many acyl chlorides are synthesized from their corresponding carboxylic acids, and while this is straightforward for simple substrates, problems are often encountered in preparing acyl chlorides from more complex substrates. Therefore, various alternative reagents have been developed to avoid the problems associated with using acyl chlorides and acid anhydrides for acylation reactions.

The use of carboxylic acids as potential acyl sources, in particular the coupling of amino acids for peptide synthesis, has generated much interest. Direct reaction between an acid and an amine usually results in salt formation rather than acylation, and although acid-amine salts can be condensed at high temperatures (110−180 °C),[2k,10] the conditions are impractical and often incompatible with the presence of other chemical functionality. Consequently, numerous coupling reagents have been developed that activate acids towards nucleophilic addition by amines in a one-pot procedure. Coupling reagents based on the use of carbodiimides, chloroformates, *N*-acylimidazoles, phosphonium salts, pentafluorophenol, and guanidinium salts are regularly used in peptide synthesis.[11]

Several other acyl sources have also been developed for the *N*-acylation of amines.[12] In particular, Katritzky and co-workers have extensively researched the use of *N*-acyl benzotriazoles as stoichiometric acylating agents.[9,13] Their group has prepared a large number of crystalline and stable *N*-acyl benzotriazoles by reacting benzotriazole with the appropriate acyl chlorides. Alternatively, they have developed methods of synthesizing *N*-acyl benzotriazoles directly from the corresponding acids.[14] These *N*-acyl benzotriazoles have been shown to react with a number of different nucleophiles, including amines, hydroxylamines, sulfonamides, oximes, thiols, and amino acids.

We have recently reported that the bicyclic amidine 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, **1**) can catalyze the regioselective Friedel−Crafts acylation of *N*-protected pyrroles and indoles.[15] While the mechanism of this process was being investigated, a crystalline *N*-benzoyl DBN·BPh_4 (**3a**) salt was isolated (Scheme 1) by reacting DBN (**1**) with benzoyl chloride (**2a**) in the presence of sodium tetraphenylborate, thus

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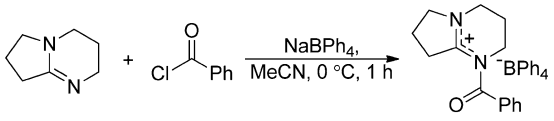
Scheme 1. Formation of *N*-Benzoyl DBN·BPh_4 (3a) from Benzoyl Chloride (2a) and DBN (1)



providing structural information on the proposed key intermediates in these acylation reactions.[16]

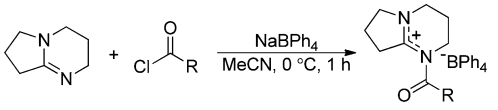
Consequently, due to the air-stable and crystalline nature of this salt, it was decided to investigate whether other *N*-acyl DBN·BPh_4 salts could be prepared and determine whether they could act as potential alternatives to acyl chlorides and acid anhydrides for the *N*-acylation of amines to form amides.

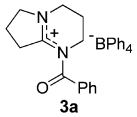
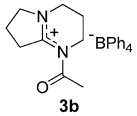
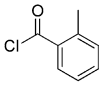
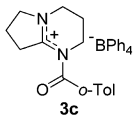
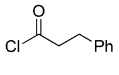
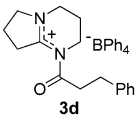
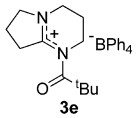
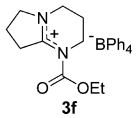
RESULTS AND DISCUSSION

Initially, we investigated whether other stable *N*-acyl DBN·BPh_4 salts (**3b–f**) could be synthesized in a similar manner to *N*-benzoyl DBN·BPh_4 (**3a**) by adding DBN (**1**) to a solution of the appropriate acyl chloride (**2b–f**) and sodium tetraphenylborate in acetonitrile (Table 1).[17] After removal of the sodium chloride precipitate by filtration, the salts were recrystallized from dichloromethane and hexane. Pleasingly, this protocol allowed for simple isolation of air-stable and crystalline *N*-acyl DBN·BPh_4 salts of acetyl chloride (**2b**), *o*-toluoyl chloride (**2c**), hydrocinnamoyl chloride (**2d**), and sterically demanding pivaloyl chloride (**2e**) in high yields (Table 1, entries 2–5). This protocol also worked well for the more reactive ethyl chloroformate (**2f**), affording *N*-ethyl carboxyl DBN·BPh_4 (**3f**) as an air-stable powder in 95% yield (Table 1, entry 6). All of the *N*-acyl DBN·BPh_4 salts (**3a–f**) were found to be bench-stable and could be stored and handled in air without decomposition.[18] This is in contrast to many of the parent acyl chlorides used, especially acetyl chloride (**2b**) and ethyl chloroformate (**2f**), which are water-sensitive and decompose rapidly to release HCl upon contact with moisture in the air. The ease of synthesis and favorable physical properties of these *N*-acyl DBN·BPh_4 salts potentially make them valuable alternatives to acyl chlorides in acylation reactions.

***N*-Acylation of Anilines.** The acylation of aniline (**4a**) using *N*-acetyl DBN·BPh_4 (**3b**) was the first acylation reaction to be investigated. An initial screen of solvents and conditions revealed that *N*-acetyl DBN·BPh_4 (**3b**) was soluble in acetonitrile, dichloromethane, and tetrahydrofuran and that its reaction with aniline (**4a**) in acetonitrile at 80 °C was optimal. Therefore, aniline (**4a**) was added to 1.3 equiv of *N*-acetyl DBN·BPh_4 (**3b**) in acetonitrile and heated at 80 °C for 24 h, before being cooled to room temperature and concentrated under reduced pressure. ^{1}H NMR spectroscopic analysis of the crude product showed that the reaction had proceeded to 100% conversion. The reaction mixture could be readily purified by dissolving the crude reaction product in ethyl acetate and filtering off the insoluble salts, which were shown to be a mixture of unreacted *N*-acetyl DBN·BPh_4 (**3b**) and DBN·$HBPh_4$. The filtrate was then concentrated under reduced pressure to give an analytically pure sample of *N*-phenylacetamide (**5a**) in 90% yield without the need for column chromatography (Table 2, entry 1). This successful acylation protocol was then applied to a range of anilines (**4b–i**), with the results summarized in Table 2. The reactions of *N*-acetyl DBN·BPh_4 (**3b**) with *p*- and *m*-toluidine (**4b** and **4c**) proceeded well, enabling the amide products (**5b** and **5c**) to be isolated in 94% and 99% yields, respectively (Table 2, entries 2 and 3). However, reaction of the more sterically demanding *o*-toluidine (**4d**) with *N*-acetyl DBN·BPh_4 (**3b**) was unsuccessful, with no amide product formed after 24 h (Table 2, entry 4). Alkyl substitution in the *para*-position was tolerated, with *p*-*tert*-butylaniline (**4e**) reacting smoothly to give the corresponding amide **5e** in 82% isolated yield (Table 2, entry 5). Halogen substitution on the aniline reduced the conversion slightly, with *p*-fluoroaniline (**4f**) reacting with *N*-acetyl DBN·BPh_4 (**3b**) to give 76% of the corresponding amide (**5f**) (Table 2, entry 6). Reaction with electron-rich *p*-methoxyaniline (**4g**) proceeded to completion, allowing *N*-(4-methoxyphenyl)acetamide (**5g**) to be isolated in 74% yield (Table 2, entry 7). However, the presence of a strongly electron-withdrawing group resulted in no amide product being observed when *p*-nitroaniline (**4h**) was used as a substrate (Table 2, entry 8). Pleasingly, the acylation protocol was successfully applied to 4-aminopyridine (**4i**), forming *N*-(pyridine-4-yl)acetamide (**5i**) in 81% yield (Table 2, entry 9).

Table 1. Synthesis of *N*-Acyl DBN·BPh_4 Salts (3a–f) from DBN (1) and Acyl Chlorides (2a–f)



Entry	Acyl Chloride (**2a-f**)	*N*-Acyl DBN·BPh_4 (**3a-f**)	Yield (%)[a]	mp (°C)
1	 **2a**	 **3a**	93	117-119
2	 **2b**	 **3b**	97	185[b]
3	 **2c**	 **3c**	98	173-176
4	 **2d**	 **3d**	73	167-170
5	 **2e**	 **3e**	98	157-158
6	 **2f**	 **3f**	95	156-157

[a]Yields by recrystallization from CH_2Cl_2 and hexane. [b]Decomposition observed.

Pleasingly, the acylation protocol was successfully applied to 4-aminopyridine (**4i**), forming *N*-(pyridine-4-yl)acetamide (**5i**) in 81% yield (Table 2, entry 9).

***N*-Acylation of Primary Amines.** With conditions established for the acylation of anilines and a convenient

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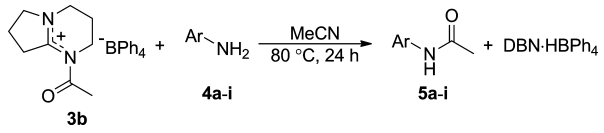
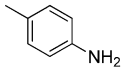
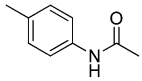
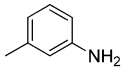
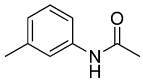
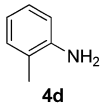
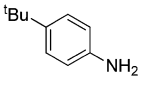
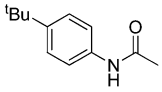
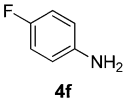
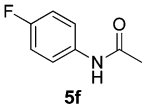
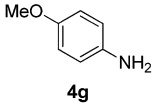
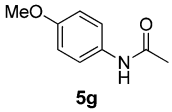
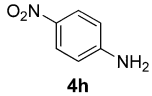
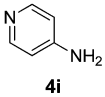
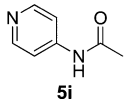
Table 2. *N*-Acylation of Anilines (4a–i) Using *N*-Acetyl DBN·BPh_4 (3b)[a]



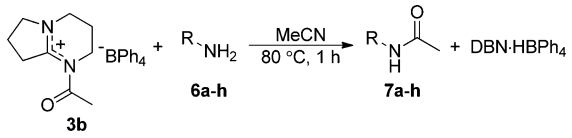
3b 4a-i 5a-i

Entry	Aniline (**4a-i**)	Amide (**5a-i**)	Conversion (%)[b,c]
1	 **4a**	 **5a**	100 (90)
2	 **4b**	 **5b**	100 (94)
3	 **4c**	 **5c**	100 (99)
4	 **4d**	-	0 (-)
5	 **4e**	 **5e**	100 (82)
6	 **4f**	 **5f**	88 (76)
7	 **4g**	 **5g**	100 (74)
8	 **4h**	-	0 (-)
9	 **4i**	 **5i**	96 (81)

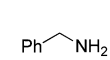
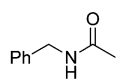
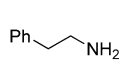
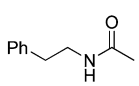
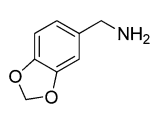
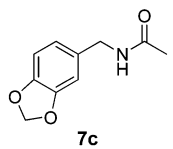
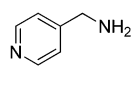
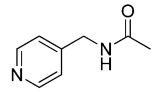
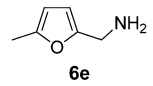
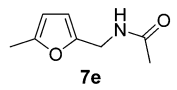
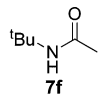
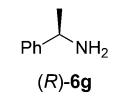
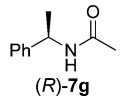
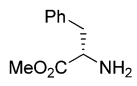
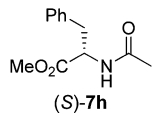
[a]Reactions performed on a 0.5 mmol scale using 0.65 mmol of *N*-acetyl DBN·BPh_4 (**3b**). [b]Determined by ^{1}H NMR spectroscopic analysis. [c]Isolated yields in parentheses.

workup procedure in hand that enabled amide products to be purified by filtration of excess DBN salts, the acylation of primary amines was then investigated. Initially, benzylamine (**6a**) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) in acetonitrile and heated at 80 °C. After only 1 h ^{1}H NMR spectroscopic analysis showed complete conversion into amide, allowing *N*-benzylacetamide (**7a**) to be isolated in 99% yield (Table 3, entry 1). This acylation protocol was then applied to a range of primary amines, the results of which are summarized in Table 3. 2-Phenethylamine (**6b**) was successfully acylated using *N*-acetyl DBN·BPh_4 (**3b**), giving 100% conversion into

Table 3. Acylation of Primary Amines (6a–h) Using *N*-Acetyl DBN·BPh_4 (3b)[a]



3b 6a-h 7a-h

Entry	Amine (**6a-h**)	Amide (**7a-h**)	Conversion (%)[b,c]
1	 **6a**	 **7a**	100 (99)
2	 **6b**	 **7b**	100 (97)
3	 **6c**	 **7c**	100 (70)
4	 **6d**	 **7d**	100 (78)
5	 **6e**	 **7e**	100 (97)
6	 **6f**	 **7f**	100 (76)
7	 (*R*)-**6g**	 (*R*)-**7g**	94 (66)
8	 (*S*)-**6h**	 (*S*)-**7h**	100 (99)

[a]Reactions performed on a 0.5 mmol scale using 0.65 mmol of *N*-acetyl DBN·BPh_4 (**3b**). [b]Determined by ^{1}H NMR spectroscopic analysis. [c]Isolated yields in parentheses.

product (**7b**) after 1 h (Table 3, entry 2). In this case it was necessary to repeat the washing and filtration isolation procedure to obtain a pure sample of *N*-phenethylacetamide (**7b**) in 97% yield. The *N*-acylation of piperonylamine (**6c**) also proceeded with complete conversion after 1 h, leading to the isolation of the corresponding amide (**7c**) in 70% yield (Table 3, entry 3). The reaction of *N*-acetyl DBN·BPh_4 (**3b**) with 4-picolylamine (**6d**) was equally successful, giving *N*-(pyridin-4-ylmethyl)acetamide (**7d**) in 78% isolated yield (Table 3, entry 4). 5-Methyl furfurylamine (**6e**) was also acylated smoothly, forming the amide **7e** in 97% yield (Table 3, entry 4). The reaction of sterically demanding *tert*-butylamine (**6f**) with *N*-acetyl DBN·BPh_4 (**3b**) proceeded smoothly, forming *N*-(*tert*-butyl)acetamide (**7f**) in 76% yield (Table 3, entry 6). The *N*-

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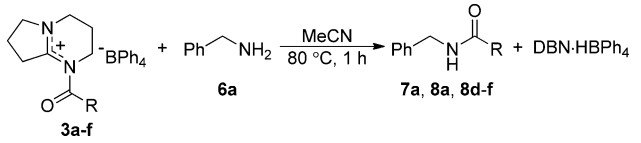
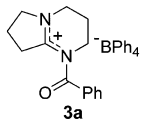
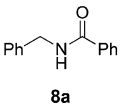
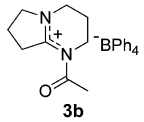
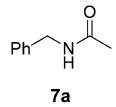
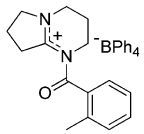
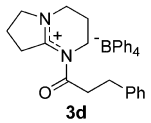
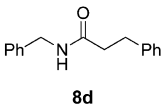
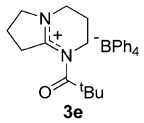
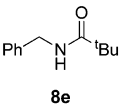
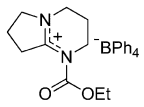
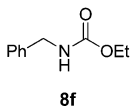
acylation methodology was then applied to enantiomerically pure (*R*)-α-methylbenzylamine ((*R*)-**6g**), to test whether the α-stereocenter would be racemized under the reaction conditions (Table 3, entry 7). (*R*)-*N*-(1-Phenethyl)acetamide ((*R*)-**7g**) was obtained in a 66% yield after 1 h with the measured specific rotation of +121 (*c* 0.97 g/100 mL in $CHCl_3$) being comparable with literature values for (*R*)-**7g** [$[\alpha]_D^{25}$ = +127, (*c* 1.0 g/100 mL in CH_2Cl_2)].[19a] *N*-Acetyl DBN·BPh_4 (**3b**) was then used to acylate (*S*)-phenylalanine methyl ester ((*S*)-**6h**), affording the corresponding amide ((*S*)-**7h**) in 99% yield (Table 3, entry 8). The specific rotation of amide (*S*)-**7h** [$[\alpha]_D^{18}$ = +90 (*c* 0.68 g/100 mL in $CHCl_3$)] was comparable with literature values for (*S*)-**7h** [$[\alpha]_D^{25}$ = +96 (*c* 1.0 g/100 mL in $CHCl_3$)][19b] thus confirming that little racemization of the α-stereocenter had occurred during the reaction.

We then investigated the use of the different *N*-acyl DBN·BPh_4 salts (**3a–f**) for the acylation of benzylamine (**6a**). The reaction of *N*-benzoyl DBN·BPh_4 (**3a**) with benzylamine (**6a**) required 16 h to proceed to completion, with *N*-benzyl benzamide (**8a**) being isolated in 78% yield (Table 4, entry 1). The acylation of benzylamine (**6a**) with sterically demanding *N*-*o*-toluoyl DBN·BPh_4 (**3c**) was unsuccessful, with no evidence of any amide formation after 16 h (Table 4, entry 3). In contrast, the reactions of benzylamine (**6a**) with both *N*-hydrocinnamoyl DBN·BPh_4 (**3d**) and *N*-pivaloyl DBN·BPh_4 (**3e**) worked well, with both reactions proceeding to complete conversion within 1 h to afford *N*-benzyl-3-phenylpropanamide (**8d**) and *N*-benzylpivalamide (**8e**) in 73% and 98% yield, respectively (Table 4, entries 4 and 5). Finally, reaction of benzylamine (**6a**) with *N*-ethyl carboxyl DBN·BPh_4 (**3f**) also proceeded to completion within 1 h, enabling the corresponding carbamate (**8f**) to be isolated in 82% yield (Table 4, entry 6).

***N*-Acylation of Secondary Amines.** Next, the use of *N*-acetyl DBN·BPh_4 (**3b**) for the acylation of secondary amines (**9a–h**) to afford tertiary amides was investigated (Table 5). First, it was found that *N*-benzyl-*N*-methylamine (**9a**) reacted with *N*-acetyl DBN·BPh_4 (**3b**) to give quantitative conversion into amide product (**10a**) in 1 h (Table 5, entry 1). The *N*-acylation protocol also worked well for *N*-benzyl-*N*-phenethylamine (**9b**), giving *N*-benzyl-*N*-phenethylacetamide (**10b**) in 98% isolated yield (Table 5, entry 2). The reaction of *N*-acetyl DBN·BPh_4 (**3b**) with the more sterically demanding *N*-benzyl-*N*-isopropylamine (**9c**) gave a lower 83% conversion, with the amide product (**10c**) being isolated in 55% yield after the standard workup procedure followed by an additional acid/base wash to remove the excess amine (Table 5, entry 3). *N*,*N*-Dibenzylamine (**9d**) also reacted slowly, with a reaction time of 16 h required to give complete conversion into tertiary amide (**10d**) (Table 5, entry 4). It was found that 2 equiv of the cyclic secondary amine pyrrolidine (**9e**) was required to consume 1 equiv of *N*-acetyl DBN·BPh_4 (**3b**), allowing amide **10e** to be isolated in 88% yield (Table 5, entry 5). Next, piperazine (**9f**) was reacted with 1 equiv of *N*-acetyl DBN·BPh_4 (**3b**), forming a single amide product (**10f**), with no bis-*N*,*N*′-acylated product observed (Table 5, entry 6). As expected, morpholine (**9g**) worked well as a substrate for acylation with *N*-acetyl DBN·BPh_4 (**3b**), affording 1-morpholinoethanone (**10g**) in a 97% isolated yield (Table 5, entry 7). Finally, *N*,*O*-dimethylhydroxylamine hydrochloride (**9h**) was used as a nucleophile in an attempt to form the corresponding Weinreb amide. *N*-Hydrocinnamoyl DBN·BPh_4 (**3d**) was employed instead of *N*-acetyl DBN·BPh_4 (**3b**) in order to increase the molecular weight of the Weinreb amide formed and thus facilitate its isolation during workup. An additional 1 equiv of DBN (**1**) was also added to the reaction to liberate the nucleophile (**9h**) from its hydrochloride salt. Pleasingly, the reaction proceeded to completion in 1 h, allowing the Weinreb amide **10h** to be isolated in 80% yield after standard workup followed by an additional acid/base wash to remove residual DBN hydrochloride (Table 5, entry 8).

Table 4. Acylation of Benzylamine (6a) Using Different *N*-Acyl DBN·BPh_4 Salts (3a–f)[a]



Entry	*N*-acyl DBN·BPh_4 (**3a-f**)	Amide (**7a**, **8a**, **8d-f**)	Conversion (%)[b,c]
1[d]	 **3a**	 **8a**	95 (78)
2	 **3b**	 **7a**	100 (99)
3	 **3c**	-	0 (-)
4	 **3d**	 **8d**	100 (73)
5	 **3e**	 **8e**	100 (98)
6	 **3f**	 **8f**	100 (82)

[a]Reactions performed using 0.5 mmol of benzylamine (**6a**) and 0.65 mmol of *N*-acyl DBN·BPh_4. [b]Determined by ^1H NMR spectroscopic analysis. [c]Isolated yields in parentheses. [d]16 h reaction time.

***N*-Acyl DBN·BPh_4 Salts for the *N*-Acylation of Sulfonamides.** Because *N*-acetyl DBN·BPh_4 (**3b**) had been shown to be a highly efficient *N*-acylating agent for a wide range of amines, it was decided to investigate its use for the acylation of sulfonamides (Table 6). Initially, *N*-acetyl DBN·BPh_4 (**3b**) and benzenesulfonamide (**11a**) were heated under the previously developed conditions for 16 h; however, only 38% conversion into *N*-acetyl benzenesulfonamide (**12a**) was observed. In an attempt to improve the conversion, the reaction was repeated using 20 mol % DBN (**1**) as a catalyst. Pleasingly, this resulted in 95% conversion into *N*-acetyl

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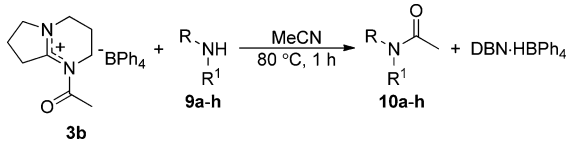
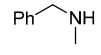
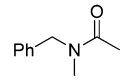
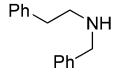
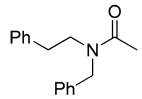
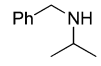
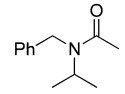
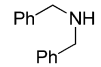
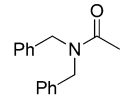
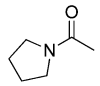
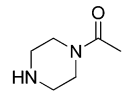
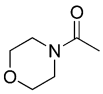
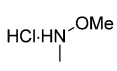
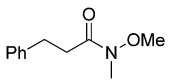
Table 5. Acylation of Secondary Amines (9a–h) Using *N*-Acetyl DBN·BPh_4 (3b)[a]



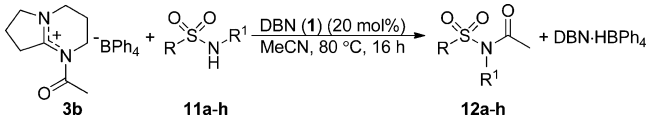
3b 9a-h 10a-h

Entry	Amine (**9a-h**)	Amide (**10a-h**)	Conversion (%)[b,c]
1	 **9a**	 **10a**	100 (99)
2	 **9b**	 **10b**	100 (98)
3	 **9c**	 **10c**	83 (55)
4[d]	 **9d**	 **10d**	100 (70)
5[e]	 **9e**	 **10e**	100 (88)
6[f]	 **9f**	 **10f**	100 (99)
7	 **9g**	 **10g**	100 (97)
8[g]	 **9h**	 **10h**	100 (80)

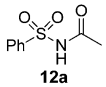
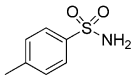
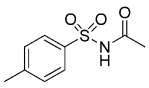
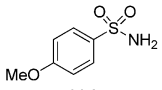
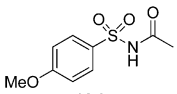
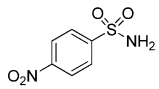
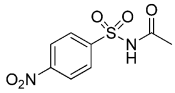
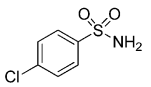
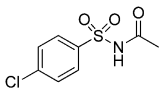
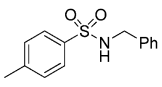
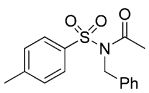
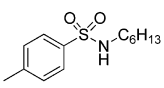
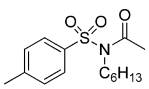
[a]Reactions performed on a 0.5 mmol scale using 0.65 mmol of *N*-acetyl DBN·BPh_4 (**3b**). [b]Determined by ^{1}H NMR spectroscopic analysis. [c]Isolated yields in parentheses. [d]16 h. [e]Reaction using 2 equiv of pyrrolidine (**9e**). [f]Reaction performed using 0.5 mmol of *N*-acetyl DBN·BPh_4 (**3b**). [g]Reaction performed using 0.65 mmol of *N*-hydrocinnamoyl DBN·BPh_4 (**3d**) and 0.6 mmol of DBN (**1**).

benzenesulfonamide (**12a**), which was isolated in 83% yield after being purified by the standard workup procedure, followed by an acid wash to remove the DBN (**1**) catalyst (Table 6, entry 1). The successful acylation conditions using 20 mol % DBN (**1**) were subsequently applied to the acylation of a number of other sulfonamides. Methanesulfonamide (**11b**) was found to be more reactive than benzensulfonamide (**11a**), giving complete conversion into product (**12b**) within 16 h (Table 6, entry 2). *p*-Toluenesulfonamide (**11c**) and *p*-methoxybenzenesulfonamide (**11d**) were successfully acylated

Table 6. Acylation of Sulfonamides (11a–h) Using *N*-Acetyl DBN·BPh_4 (3b)[a]



3b 11a-h 12a-h

Entry	Sulfonamide (**11a-h**)	*N*-Acyl Sulfonamide (**12a-h**)	Conversion (%)[b,c]
1	 **11a**	 **12a**	95 (83)
2	 **11b**	 **12b**	100 (98)
3	 **11c**	 **12c**	92 (80)
4	 **11d**	 **12d**	90 (74)
5	 **11e**	 **12e**	66 (-)
6	 **11f**	 **12f**	35 (-)
7	 **11g**	 **12g**	100 (65)
8	 **11h**	 **12h**	42 (-)

[a]Reactions performed on a 0.5 mmol scale using 0.65 mmol of *N*-acetyl DBN·BPh_4 (**3b**) and 20 mol % DBN (**1**). [b]Determined by ^{1}H NMR spectroscopic analysis. [c]Isolated yields in parentheses.

using *N*-acetyl DBN·BPh_4 (**3b**) and 20 mol % DBN (**1**) to give their corresponding *N*-acetyl sulfonamides (**12c** and **12d**) in 80% and 74% yield, respectively (Table 6, entries 3 and 4). The reactions of *N*-acetyl DBN·BPh_4 (**3b**) with less nucleophilic *p*-nitrobenzenesulfonamide (**11e**) and *p*-chlorobenzenesulfonamide (**11f**) did not proceed as smoothly, with only 66% and 35% conversion into *N*-acetyl sulfonamides (**12e** and **12f**) observed, respectively (Table 6, entries 5 and 6). Acylation of the secondary sulfonamide *N*-benzyl *p*-toluenesulfonamide (**11g**) with *N*-acetyl DBN·BPh_4 (**3b**) worked well, affording *N*-acetyl *N*-benzyl *p*-toluenesulfonamide (**12g**) in 65% yield after 16 h (Table 6, entry 7). However, the reaction of the more sterically demanding *N*-hexyl *p*-toluenesulfonamide (**11h**) was less successful, with only 42% conversion into *N*-acetyl sulfonamide (**12h**) observed after 16 h (Table 6, entry 8).

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CONCLUSIONS

In conclusion, a broad range of bench-stable and highly crystalline *N*-acyl DBN·BPh_4 salts have been synthesized, which are easy to handle and do not react with moisture in air. The utility of these *N*-acyl DBN·BPh_4 salts for *N*-acylation reactions with a range of amine nucleophiles has been demonstrated, reacting with anilines, primary and secondary amines, and sulfonamides to afford their corresponding *N*-acylated products in high yields. The products can be isolated in pure form *via* a simple workup procedure without the need for purification by chromatography.

EXPERIMENTAL SECTION

General. All reactions were performed using starting materials obtained from commercial sources without further purification and using dry solvents under an atmosphere of nitrogen. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C{^{1}H} NMR spectra were recorded at 75 MHz. Chemical shifts δ are quoted in parts per million and are referenced to the residual solvent peak, and coupling constants, *J*, are reported in Hertz (Hz). NMR peak assignments were confirmed using 2D ^{1}H COSY where necessary. Infrared spectra were recorded as thin films and were recorded with internal background calibration in the range 600−4000 cm^{-1}. High resolution mass spectra were recorded in either positive or negative mode using electrospray (ES) ionization. Specific rotations were recorded with a path length of 1 dm; concentrations (*c*) are quoted in g/100 mL.

General Procedure for the Synthesis of *N*-Acyl DBN·BPh_4 Salts (3a−f). Sodium tetraphenylborate (1 equiv) is added to a round-bottom flask and purged with nitrogen. Dry acetonitrile (to make a 0.2 M solution of $NaBPh_4$) and the appropriate acyl chloride (1.04 equiv) are added, and the resulting solution is cooled to 0 °C. DBN (**1**) (1 equiv) is added dropwise, and a precipitate of sodium chloride begins to form. The reaction is left to stir for 1 h before being warmed to room temperature and filtered through a pad of Celite, washing thoroughly with acetonitrile. The filtrate is concentrated under reduced pressure, and the resulting *N*-acyl-DBN·BPh_4 salt is purified by recrystallization from dichloromethane and hexane.

1-Benzoyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine tetraphenylborate (*N*-Benzoyl DBN·BPh_4) (3a). DBN (**1**) (1.85 mL, 15 mmol) was added dropwise to a solution of sodium tetraphenylborate (5.13 g, 15 mmol) and benzoyl chloride (**2a**) (1.81 mL, 15.6 mmol) in acetonitrile (75 mL) according to the general procedure. The crude product was purified by recrystallization (CH_2Cl_2/hexane), yielding the title compound (7.62 g, 93%) as a colorless solid. Mp 117−119 °C; ^{1}H NMR (300 MHz; CD_3CN) δ_H 7.71 (3H, app d, *J* = 8.7 Hz, Ph-*H*), 7.57 (2H, app t, *J* = 7.7 Hz, Ph-*H*), 7.35−7.27 (8H, br s, BPh_4-*H*), 7.02 (8H, app t, *J* = 7.4 Hz, BPh_4-*H*), 6.87 (4H, app t, *J* = 7.1 Hz, BPh_4-*H*), 3.75 (2H, app t, *J* = 7.6 Hz, H^6), 3.65 (2H, app t, *J* = 5.5 Hz, H^2), 3.40 (2H, app t, *J* = 5.8 Hz, H^4), 3.19 (2H, app t, *J* = 7.7 Hz, H^8), 2.17−1.93 (4H, m, H^3 and H^7); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ_C 171.6, 168.8, 165.7, 165.1, 164.4, 163.8, 136.7, 136.7, 134.6, 132.8, 130.1, 130.0, 126.6, 126.6, 126.6, 126.5, 122.8, 56.1, 46.9, 45.4, 35.2, 19.9, 19.5; IR (film, cm^{-1}) ν_{max} 1714 (C═O), 1635, 1487; HRMS *m*/*z* (ES) 229.1342, $C_{14}H_{17}N_2O$ $[M]^+$ requires 229.1336.

1-Acetyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine Tetraphenylborate (*N*-Acetyl DBN·BPh_4) (3b). DBN (**1**) (1.19 mL, 10 mmol) was added dropwise to a solution of sodium tetraphenylborate (3.42 g, 10 mmol) and acetyl chloride (**2b**) (0.74 mL, 10.4 mmol) in acetonitrile (50 mL) according to the general procedure. The crude product was purified by recrystallization (CH_2Cl_2/hexane), yielding the title compound (4.72 g, 97%) as transparent crystalline plates. Mp 185 °C (dec); ^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 7.41−7.34 (8H, br s, BPh_4-*H*), 7.02 (8H, app t, *J* = 7.4 Hz, BPh_4-*H*), 6.86 (4H, app t, *J* = 7.2 Hz, BPh_4-*H*), 3.23 (2H, app t, *J* = 8.1 Hz, H^6), 3.12 (2H, app t, *J* = 7.8 Hz, H^2), 2.70 (2H, app t, *J* = 5.8 Hz, H^4), 2.49 (2H, app t, *J* = 5.9 Hz, H^8), 2.02 (3H, s, $COCH_3$), 1.87 (2H, app p, *J* = 8.0 Hz, H^7), 1.34 (2H, app p, *J* = 6.0 Hz, H^3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ_C 170.9, 166.4, 165.2, 164.5, 163.9, 163.2, 136.2, 136.1, 126.2, 126.1, 126.1, 126.0, 122.2, 55.1, 43.9, 43.5, 35.5, 24.2, 18.6, 18.3; IR (film, cm^{-1}) ν_{max} 1746 (C═O), 1640, 1479, 1428; HRMS *m*/*z* (ES) 167.1198, $C_9H_{15}N_2O$ $[M]^+$ requires 167.1179.

1-(*o*-Toluoyl)-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine Tetraphenylborate (*N*-*o*-Toluoyl DBN·BPh_4) (3c). DBN (**1**) (0.62 mL, 5 mmol) was added dropwise to a solution of sodium tetraphenylborate (1.71 g, 5 mmol) and *o*-toluoyl chloride (**2c**) (0.68 mL, 5.2 mmol) in acetonitrile (25 mL) according to the general procedure. The crude product was purified by recrystallization (CH_2Cl_2/hexane), yielding the title compound (2.75 g, 98%) as colorless crystals. Mp 173−176 °C; ^{1}H NMR (300 MHz; CD_3CN) δ_H 7.57−7.51 (1H, m, Tol-*H*), 7.44−7.35 (11H, m, 3 Tol-*H* and 8 BPh_4-*H*), 7.07 (8H, app t, *J* = 7.4 Hz, BPh_4-*H*), 6.92 (4H, app t, *J* = 7.2 Hz, BPh_4-*H*), 3.65 (2H, app t, *J* = 7.7 Hz, H^6), 3.50 (2H, app t, *J* = 5.6 Hz, H^2), 3.28 (2H, app t, *J* = 6.0 Hz, H^4), 3.15 (2H, app t, *J* = 7.9 Hz, H^8), 2.41 (3H, s, Tol-CH_3), 2.09−1.89 (4H, m, H^3 and H^7); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ_C 171.6, 168.5, 165.8, 165.1, 164.4, 163.8, 137.9, 136.8, 136.7, 136.7, 136.7, 133.2, 132.9, 132.5, 128.2, 127.2, 126.7, 126.6, 126.6, 126.6, 122.8, 56.1, 45.7, 45.4, 35.7, 19.6, 19.5, 19.3; IR (film, cm^{-1}) ν_{max} 1763 (C═O), 1653, 1478, 1427; HRMS *m*/*z* (ES) 243.1516, $C_{15}H_{19}N_2O$ $[M]^+$ requires 243.1492.

1-Hydrocinnamoyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]-pyrimidine Tetraphenylborate (*N*-Hydrocinnamoyl DBN·BPh_4) (3d). DBN (**1**) (1.19 mL, 10 mmol) was added dropwise to a solution of sodium tetraphenylborate (3.42 g, 10 mmol) and hydrocinnamoyl chloride (**2d**) (1.55 mL, 10.4 mmol) in acetonitrile (50 mL) according to the general procedure. The crude product was purified by recrystallization (CH_2Cl_2/hexane), yielding the title compound (4.23 g, 73%) as colorless crystalline plates. Mp 167−170 °C; ^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 7.41−7.34 (8H, m, BPh_4-*H*), 7.33−7.21 (5 H, m, Ph-*H*), 7.01 (8H, app t, *J* = 7.5 Hz, BPh_4-*H*), 6.86 (4H, app t, *J* = 7.2 Hz, BPh_4-*H*), 3.29 (2H, app t, *J* = 8.1 Hz, H^6), 3.19 (2H, app t, *J* = 7.8 Hz, H^2), 2.93 (2H, app t, *J* = 7.2 Hz, H^4), 2.70 (2H, app t, *J* = 5.7 Hz, H^8), 2.58−2.53 (4H, m, CH_2H_2Ph), 1.93 (2H, app p, *J* = 7.9 Hz, H^7), 1.36 (2H, app p, *J* = 5.8 Hz, H^3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ_C 173.3, 166.9, 165.7, 165.0, 164.4, 163.7, 140.2, 136.6, 129.5, 129.3, 127.5, 126.6, 126.5, 126.5, 126.5, 122.7, 55.6, 44.4, 43.2, 38.1, 36.0, 30.7, 19.0, 18.8; IR (film, cm^{-1}) ν_{max} 1742 (C═O), 1634, 1436, 1427; HRMS *m*/*z* (ES) 257.1643, $C_{16}H_{21}N_2O$ $[M]^+$ requires 257.1654.

1-Pivaloyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine Tetraphenylborate (*N*-Pivaloyl DBN·BPh_4) (3e). DBN (**1**) (0.62 mL, 5 mmol) was added dropwise to a solution of sodium tetraphenylborate (1.71 g, 5 mmol) and pivaloyl chloride (**2e**) (0.64 mL, 5.2 mmol) in acetonitrile (25 mL) according to the general procedure. The crude product was purified by recrystallization (CH_2Cl_2/hexane), yielding the title compound (2.58 g, 98%) as colorless crystals. Mp 157−158 °C; ^{1}H NMR (300 MHz; CD_3CN) δ_H 7.34−7.28 (8H, m, BPh_4-*H*), 7.02 (8H, app t, *J* = 7.4 Hz, BPh_4-*H*), 6.87 (4H, app t, *J* = 7.3 Hz, BPh_4-*H*), 3.75 (2H, app t, *J* = 5.5 Hz, H^2), 3.60 (2H, app t, *J* = 7.5 Hz, H^6), 3.25 (2H, app t, *J* = 5.9 Hz, H^4), 3.11 (2H, app t, *J* = 7.9 Hz, H^8), 2.07−1.90 4H, m, H^3 and H^7), 1.34 (9H, s, $(CH_3)_3$); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ_C 181.3, 168.2, 165.7, 165.1, 164.4, 163.8, 136.7, 136.7, 126.6, 126.6, 126.6, 126.5, 122.8, 118.3, 56.1, 45.3, 44.9, 43.0, 34.8, 28.1, 19.8, 19.3; IR (film, cm^{-1}) ν_{max} 1718 (C═O), 1642, 1470, 1426; HRMS *m*/*z* (ES) 209.1628, $C_{12}H_{21}N_2O$ $[M]^+$ requires 209.1649.

1-Ethyl Carboxyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]-pyrimidine Tetraphenylborate (*N*-Ethyl Carboxyl DBN·BPh_4) (3f). DBN (**1**) (0.62 mL, 5 mmol) was added dropwise to a solution of sodium tetraphenylborate (1.71 g, 5 mmol) and ethyl chloroformate (**2f**) (0.64 mL, 5.2 mmol) in acetonitrile (25 mL) according to the general procedure. The crude product was purified by recrystallization (CH_2Cl_2/hexane), yielding the title compound (2.45 g, 95%) as a colorless powder. Mp 156−157 °C; ^{1}H NMR (300 MHz; CD_3CN) δ_H 7.27 (8H, br s, BPh_4-*H*), 6.99 (8H, app t, *J* = 7.3 Hz, BPh_4-*H*), 6.83 (4H, app t, *J* = 7.2 Hz, BPh_4-*H*), 4.30 (2H, q, *J* = 7.1 Hz, OCH_2CH_3), 3.77−3.67 (4H, br m, H^2 and H^6), 3.41−3.30 (4H, br m, H^4 and H^8), 2.12−1.90 (4H, m, H^3 and H^7), 1.31 (3H, t, *J* = 7.1 Hz, OCH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ_C 168.7, 165.8, 165.1, 164.5,

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163.8, 152.2, 136.8, 136.7, 136.7, 136.7, 126.7, 126.6, 126.6, 126.5, 122.8, 66.2, 56.5, 45.1, 44.0, 36.1, 19.1, 18.8, 14.3; IR (film, cm^{-1}) ν_{max} 1763 (C=O), 1654, 1478; HRMS *m/z* (ES) 197.1277, $C_{10}H_{17}N_2O_2$ $[M]^+$ requires 197.1285.

General Procedure for the *N*-Acylation of Amines with *N*-Acyl DBN·BPh$_4$ Salts. The appropriate *N*-acyl-DBN·BPh$_4$ (1.3 equiv, 0.65 mmol) is added to a carousel tube and purged with nitrogen. Dry acetonitrile (2 mL) and the appropriate amine (1 equiv, 0.5 mmol) are added, and the resulting solution is heated at 80 °C for the time specified before being cooled to room temperature. The reaction mixture is filtered before being concentrated under reduced pressure. The crude product is suspended in the minimum amount of hot ethyl acetate and allowed to cool before the mixture is filtered to remove the remaining *N*-acyl-DBN salt and DBN·HBPh$_4$. If necessary, the amide can be further purified by dissolving in ethyl acetate and washing successively with 1 M HCl, 1 M NaOH, and brine before being dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

***N*-Phenylacetamide (5a).** Aniline (**4a**) (0.05 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 24 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.061 g, 90%) as a brown solid, with spectroscopic data in accordance with the literature.[19c] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.89 (1H, br s, N*H*), 7.42 (2H, d, *J* = 7.9 Hz, Ph-*H*), 7.21 (2H, t, *J* = 7.6 Hz, Ph-*H*), 7.01 (1H, t, *J* = 7.4 Hz, Ph-*H*), 2.06 (3H, s, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 169.1, 138.0, 129.0, 124.4, 120.3, 24.5; HRMS *m/z* (ES) 136.0765, $C_8H_{10}NO$ $[M + H]^+$ requires 136.0762.

***N*-(*p*-Tolyl)acetamide (5b).** *p*-Toluidine (**4b**) (0.054 g, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 24 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.070 g, 94%) as a beige solid, with spectroscopic data in accordance with the literature.[19c] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.01 (1H, br s, N*H*), 7.38 (2H, d, *J* = 8.3 Hz, Tol-*H*), 7.08 (2H, d, *J* = 8.2 Hz, Tol-*H*), 2.29 (3H, s, Tol-CH_3), 2.12 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.9, 135.6, 133.9, 129.4, 120.3, 24.4, 20.9; HRMS *m/z* (ES) 172.0761, $C_9H_{11}NNaO$ $[M + Na]^+$ requires 172.0738.

***N*-(*m*-Tolyl)acetamide (5c).** *m*-Toluidine (**4c**) (0.054 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 24 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.074 g, 99%) as a beige solid, with spectroscopic data in accordance with the literature.[19c] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.11 (1H, br s, N*H*), 7.28 (1H, s, Tol-*H*), 7.21 (1H, t, *J* = 8.3 Hz, Tol-*H*), 7.07 (1H, t, *J* = 7.7 Hz, Tol-*H*), 6.81 (1H, d, *J* = 7.5 Hz, Tol-*H*), 2.20 (3H, s, Tol-CH_3), 2.04 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 169.1, 138.8, 138.1, 128.7, 125.1, 120.9, 117.3, 24.5, 21.5; HRMS *m/z* (ES) 150.0907, $C_9H_{12}NO$ $[M + H]^+$ requires 150.0914.

***N*-(4-(*tert*-Butyl)phenyl)acetamide (5e).** 4-*tert*-Butylaniline (**4e**) (0.080 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 24 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.078 g, 82%) as a beige solid, with spectroscopic data in accordance with the literature.[19d] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.81 (1H, br s, N*H*), 7.43 (2H, d, *J* = 8.5 Hz, Ar-*H*), 7.31 (2H, d, *J* = 8.6 Hz, Ar-*H*), 2.14 (3H, s, COCH_3), 1.29 (9H, s, (CH_3)$_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.8, 147.3, 135.4, 125.8, 120.0, 34.4, 31.5, 24.5; HRMS *m/z* (ES) 192.1403, $C_{12}H_{18}NO$ $[M + H]^+$ requires 192.1388.

***N*-(4-Fluorophenyl)acetamide (5f).** 4-Fluoroaniline (**4f**) (0.048 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 24 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.058 g, 76%) as a beige solid, with spectroscopic data in accordance with the literature.[19c] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.89 (1H, br s, N*H*), 7.46–7.41 (2H, m, Ar-*H*), 6.97 (2H, t, *J* = 8.6 Hz, Ar-*H*), 2.13 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.8, 159.5 (d, *J* = 242.6 Hz, FC), 134.1 (d, *J* = 2.9 Hz, FCCHCHC), 122.1 (d, *J* = 7.9 Hz, FCCHCH), 115.7 (d, *J* = 22.5 Hz, FCCH), 24.4; HRMS *m/z* (ES) 154.0685, C_8H_9FNO $[M + H]^+$ requires 154.0668.

***N*-(4-Methoxyphenyl)acetamide (5g).** 4-Methoxyaniline (**4g**) (0.062 g, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 24 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.061 g, 74%) as a brown solid, with spectroscopic data in accordance with the literature.[19c] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.60 (1H, br s, N*H*), 7.39 (2H, d, *J* = 8.9 Hz, Ar-*H*), 6.83 (2H, d, *J* = 8.9 Hz, Ar-*H*), 3.77 (3H, s, OCH_3), 2.13 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.6, 156.5, 131.2, 122.1, 114.2, 55.6, 24.4; HRMS *m/z* (ES) 188.0716, $C_9H_{11}NNaO_2$ $[M + Na]^+$ requires 188.0687.

***N*-(Pyridin-4-yl)acetamide (5i).** 4-Aminopyridine (**4i**) (0.047 g, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.055 g, 81%) as a light brown solid, with spectroscopic data in accordance with the literature.[19e] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 9.72 (1H, br s, N*H*), 8.42 (2H, d, *J* = 6.3 Hz, py-CHC*H*N), 7.58 (2H, dd, *J* = 5.1, 1.3 Hz, py-C*H*CHN), 2.18 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 170.2, 150.1, 146.3, 114.0, 24.7; HRMS *m/z* (ES) 137.0732, $C_7H_9N_2O$ $[M + H]^+$ requires 137.0710.

***N*-Benzylacetamide (7a).** Benzylamine (**6a**) (0.055 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.074 g, 99%) as a brown solid, with spectroscopic data in accordance with the literature.[2h] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.26–7.16 (5H, m, Ph-*H*), 6.08 (1H, br s, N*H*), 4.30 (2H, d, *J* = 5.8 Hz, CH_2N), 1.89 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 170.2, 138.4, 128.7, 127.9, 127.5, 43.7, 23.2; HRMS *m/z* (ES) 172.0755, $C_9H_{11}NNaO$ $[M + Na]^+$ requires 172.0738.

***N*-Phenethylacetamide (7b).** 2-Phenethylamine (**6b**) (0.063 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with brine before being dried over $MgSO_4$ and concentrated to give the title compound (0.079 g, 97%) as a brown oil, with spectroscopic data in accordance with the literature.[12f] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.26–7.09 (5H, m, Ph-*H*), 5.47 (1H, br s, N*H*), 3.39 (2H, q, *J* = 6.9 Hz, NHCH_2CH_2Ph), 2.71 (2H, t, *J* = 7.0 Hz, NHCH$_2$CH_2Ph), 1.81 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 170.3, 139.0, 128.8, 128.7, 126.6, 40.8, 35.7, 23.4; HRMS *m/z* (ES) 186.0906, $C_{10}H_{13}NNaO$ $[M + Na]^+$ requires 186.0889.

***N*-(Benzo[*d*][1,3]dioxol-5-ylmethyl)acetamide (7c).** Piperonylamine (**6c**) (0.062 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.068 g, 70%) as a light brown solid, with spectroscopic data in accordance with the literature.[19f] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 6.69–6.62 (3H, m, Ar-*H*), 6.00 (1H, br s, N*H*), 5.85 (2H, s, OCH_2O), 4.23 (2H, d, *J* = 5.6 Hz, CH_2N), 1.92 (3H, s, COCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 170.1, 148.0, 147.0, 132.3, 121.2, 108.5, 108.4, 101.2, 43.6, 23.3; HRMS *m/z* (ES) 194.0814, $C_{10}H_{12}NO_3$ $[M + H]^+$ requires 194.0817.

***N*-(Pyridin-4-ylmethyl)acetamide (7d).** 4-Picolylamine (**6d**) (0.050 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh$_4$ (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give

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the title compound (0.059 g, 78%) as a yellow oil, with spectroscopic data in accordance with the literature.[19g] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.45 (2H, d, J = 6.1 Hz, py-CHC*H*N), 7.13 (2H, d, J = 5.9 Hz, py-C*H*CHN), 6.83 (1H, br d, J = 7.0 Hz, N*H*), 4.35 (2H, d, J = 6.1 Hz, CH_2NH), 1.99 (3H, s, COCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 170.6, 149.8, 147.9, 122.4, 42.4, 23.1; HRMS m/z (ES) 173.0709, $C_8H_{10}N_2NaO$ [M + Na]$^+$ requires 173.0691.

***N*-((5-Methylfuran-2-yl)methyl)acetamide (7e).** 5-Methyl furfurylamine (**6e**) (0.056 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.074 g, 97%) as an orange oil. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 6.14 (1H, br s, N*H*), 6.00 (1H, d, J = 2.9 Hz, OCC*H*), 5.80 (1H, d, J = 2.1 Hz, OCC*H*), 4.26 (2H, d, J = 5.4 Hz, CH_2N), 2.17 (3H, s, CHCCH_3), 1.90 (3H, s, COCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 170.0, 151.9, 149.4, 108.3, 106.3, 36.7, 23.1, 13.5; HRMS m/z (ES) 154.0885, $C_8H_{12}NO_2$ [M + H]$^+$ requires 154.0868.

***N*-(*tert*-Butyl)acetamide (7f).** *tert*-Butylamine (**6f**) (0.053 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.044 g, 76%) as a brown solid, with spectroscopic data in accordance with the literature.[19h] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 5.44 (1H, br s, N*H*), 1.88 (3H, s, COCH_3), 1.31 (9H, s, (CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 169.7, 51.2, 28.8, 24.6; HRMS m/z (ES) 116.1091, $C_6H_{14}NO$ [M + H]$^+$ requires 116.1075.

(*R*)-*N*-(1-Phenylethyl)acetamide ((*R*)-7g). (*R*)-α-Methyl benzylamine ((*R*)-**6g**) (0.064 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.054 g, 66%) as a brown solid, with spectroscopic data in accordance with the literature.[19a] $[\alpha]_D^{22}$ = +121 (*c* 0.97 g/100 mL in $CHCl_3$); ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.28−7.19 (5H, m, Ph-*H*), 5.84 (1H, br s, N*H*), 5.03 (1H, p, J = 7.2 Hz, C*H*CH$_3$), 1.88 (3H, s, COCH_3), 1.39 (3H, d, J = 7.0 Hz, CHCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 169.3, 143.3, 128.8, 127.5, 126.3, 48.9, 23.5, 21.8; HRMS m/z (ES) 186.0922, $C_{10}H_{13}NNaO$ [M + Na]$^+$ requires 186.0895.

(*S*)-Methyl 2-Acetamido-3-phenylpropanoate ((*S*)-7h). (*S*)-Phenylalanine methyl ester ((*S*)-**6h**) (0.090 g, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.110 g, 99%) as a beige solid, with spectroscopic data in accordance with the literature.[19b] $[\alpha]_D^{18}$ = +90 (*c* 0.68 g/100 mL in $CHCl_3$); ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.24−7.16 (3H, m, Ph-*H*), 7.02 (2H, app d, J = 7.1 Hz, Ph-*H*), 6.04 (1H, br d, J = 7.3 Hz, N*H*), 4.80 (1H, dd, J = 13.6, 5.9 Hz, C*H*CH$_A$H$_B$), 3.64 (3H, s, OCH_3), 3.07 (1H, dd, J = 13.9, 5.9 Hz, CHCH_AH$_B$), 2.99 (1H, dd, J = 13.9, 5.9 Hz, CHCH_AH$_B$), 1.90 (3H, s, COCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 172.2, 169.8, 135.9, 129.3, 128.6, 127.2, 53.2, 52.4, 37.9, 23.1; HRMS m/z (ES) 222.1132, $C_{12}H_{16}NO_3$ [M + H]$^+$ requires 222.1130.

***N*-Benzyl Benzamide (8a).** Benzylamine (**6a**) (0.055 mL, 0.5 mmol) was added to a solution of *N*-benzoyl DBN·BPh_4 (**3a**) (0.356 g, 0.65 mmol) in acetonitrile (2 mL), and the resulting solution was heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.077 g, 78%) as a beige solid, with spectroscopic data in accordance with the literature.[2h] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.73−7.70 (2H, m, Ph*H*), 7.43−7.18 (8H, m, Ph*H*), 6.36 (1H, br s, N*H*), 4.58 (2H, d, J = 5.7 Hz, CH_2N); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 167.4, 138.2, 134.4, 131.6, 128.8, 128.6, 128.0, 126.7, 126.1, 44.2; HRMS m/z (ES) 212.1067, $C_{14}H_{14}NO$ [M + H]$^+$ requires 212.1075.

***N*-Benzyl-3-phenylpropanamide (8d).** Benzylamine (**6a**) (0.055 mL, 0.5 mmol) was added to a solution of *N*-hydrocinnamoyl DBN·BPh_4 (**3d**) (0.375 g, 0.65 mmol) in acetonitrile (2 mL), and the resulting solution was heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with 1 M HCl, 1 M NaOH, and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.087 g, 73%) as a colorless solid, with spectroscopic data in accordance with the literature.[2h] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.23−7.03 (10H, m, Ph-*H*), 5.78 (1H, br s, N*H*), 4.28 (2H, d, J = 5.7 Hz, HNCH_2Ph), 2.89 (2H, t, J = 7.6 Hz, COCH_2CH_2Ph), 2.41 (2H, t, J = 7.6 Hz, COCH_2CH$_2$Ph); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 172.1, 140.9, 138.3, 128.7, 128.6, 128.5, 127.8, 127.5, 126.3, 43.6, 38.5, 31.8; HRMS m/z (ES) 240.1375, $C_{16}H_{18}NO$ [M + H]$^+$ requires 240.1388.

***N*-Benzylpivalamide (8e).** Benzylamine (**6a**) (0.055 mL, 0.5 mmol) was added to a solution of *N*-pivaloyl DBN·BPh_4 (**3e**) (0.343 g, 0.65 mmol) in acetonitrile (2 mL), and the resulting solution was heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with 1 M HCl, 1 M NaOH, and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.094 g, 98%) as a pale yellow oil, with spectroscopic data in accordance with the literature.[19i] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.27−7.15 (5H, m, Ph-*H*), 6.01 (1H, br s, N*H*), 4.34 (2H, d, J = 5.6 Hz, HNCH_2Ph), 1.14 (9H, s, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 178.4, 138.7, 128.7, 127.6, 127.4, 43.6, 38.7, 27.7; HRMS m/z (ES) 214.1194, $C_{12}H_{17}NNaO$ [M + Na]$^+$ requires 214.1203.

Ethyl Benzylcarbamate (8f). Benzylamine (**6a**) (0.055 mL, 0.5 mmol) was added to a solution of *N*-ethyl carboxyl DBN·BPh_4 (**3f**) (0.336 g, 0.65 mmol) in acetonitrile (2 mL), and the resulting solution was heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with 1 M HCl, 1 M NaOH, and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.073 g, 82%) as a pale yellow oil, with spectroscopic data in accordance with the literature.[19j] ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.45−7.20 (5H, m, Ph-*H*), 5.95 (1H, br s, N*H*), 4.29 (2H, d, J = 5.9 Hz, NCH_2Ph), 4.08 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.18 (3H, t, J = 7.1 Hz, OCH$_2$CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 157.2, 134.9, 128.8, 128.1, 127.6, 61.2, 45.2, 14.8.

***N*-Benzyl-*N*-methylacetamide (10a).** *N*-Benzyl-*N*-methylamine (**9a**) (0.065 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.081 g, 99%) as a dark brown oil, with spectroscopic data in accordance with the literature.[12f] The product was analyzed as a 4:3 mixture of rotamers (25 °C). *major* ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.31−7.08 (5H, m, Ph-*H*), 4.50 (2H, s, NCH_2Ph), 2.83 (3H, s, NCH_3), 2.07 (3H, s, COCH_3); *minor* ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.31−7.08 (5H, m, Ph-*H*), 4.44 (2H, s, NCH_2Ph), 2.86 (3H, s, NCH_3), 2.07 (3H, s, COCH_3); *major and minor* ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 171.1, 170.8, 137.3, 136.5, 128.9, 128.6, 128.0, 127.6, 127.3, 126.3, 54.2, 50.6, 35.5, 33.7, 21.9, 21.5; HRMS m/z (ES) 186.0921, $C_{10}H_{13}NNaO$ [M + Na]$^+$ requires 186.0894.

***N*-Benzyl-*N*-phenethylacetamide (10b).** *N*-Benzyl-*N*-phenethylamine (**9b**) (0.10 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.124 g, 98%) as a dark brown oil, with spectroscopic data in accordance with the literature.[19k] The product was analyzed as a 1:1 mixture of rotamers (25 °C). ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.28−7.02 (20H, m, 4 Ph-*H*), 4.53 (2H, s, NCH_2Ph), 4.27 (2H, s, NCH_2Ph), 3.49 (2H, t, J = 7.5 Hz, NCH_2CH$_2$Ph), 3.34 (2H, t, J = 7.5 Hz, NCH_2CH$_2$Ph), 2.80−2.69 (4H, m, 2 NCH$_2$CH_2Ph), 2.04 (3H, s, COCH_3), 1.93 (3H, s,

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$COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 171.0, 170.8, 139.3, 138.2, 137.7, 136.8, 129.0, 128. 9, 128.8, 128.8, 128.7, 128.6, 128.2, 127.7, 127.5, 126.8, 126.4, 126.4, 52.7, 49.5, 48.3, 48.1, 34.9, 34.0, 21.9, 21.3; HRMS *m/z* (ES) 254.1545, $C_{17}H_{20}NO$ $[M + H]^+$ requires 254.1540.

***N*-Benzyl-*N*-isopropylacetamide (10c).** *N*-Benzyl-*N*-isopropylamine (**9c**) (0.080 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with 1 M HCl, 1 M NaOH, and brine before being dried over $MgSO_4$ and concentrated to give the title compound (0.053 g, 55%) as a pale yellow oil. The product was analyzed as a 4:3 mixture of rotamers (25 °C). *major* ^1H NMR (300 MHz; $CDCl_3$) δ_H 7.29−7.10 (5H, m, Ph-*H*), 4.79 (1H, h, *J* = 6.8 Hz, $CH(CH_3)_2$), 4.38 (2H, s, CH_2Ph), 1.93 (3H, s, $COCH_3$), 1.01 (6H, d, *J* = 6.8 Hz, $CH(CH_3)_2$); *minor* ^1H NMR (300 MHz; $CDCl_3$) δ_H 7.29−7.10 (5H, m, Ph-*H*), 4.46 (2H, s, CH_2Ph), 4.04 (1H, h, *J* = 6.7 Hz, $CH(CH_3)_2$), 2.15 (3H, s, $COCH_3$), 1.06 (6H, d, *J* = 6.7 Hz, $CH(CH_3)_2$); *major and minor* $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 171.5, 170.7, 139.7, 138.6, 128.8, 128.3, 127.2, 127.0, 126.6, 125.8, 49.8, 47.0, 45.5, 43.7, 22.7, 22.1, 21.5, 20.4; HRMS *m/z* (ES) 214.1221, $C_{12}H_{17}NNaO$ $[M + Na]^+$ requires 214.1203.

***N*,*N*-Dibenzylacetamide (10d).** Dibenzylamine (**9d**) (0.10 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.084 g, 70%) as a pale yellow oil, with spectroscopic data in accordance with the literature.[19l] ^1H NMR (300 MHz; $CDCl_3$) δ_H 7.32−7.06 (10H, m, Ph*H*), 4.51 (2H, s, NCH_2Ph), 4.35 (2H, s, NCH_2Ph), 2.13 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 171.3, 137.3, 136.4, 129.0, 128.7, 128.5, 128.5, 128.3, 127.7, 127.5, 126.4, 50.8, 48.0, 21.8; HRMS *m/z* (ES) 262.1213, $C_{16}H_{17}NNaO$ $[M + Na]^+$ requires 262.1208.

1-(Pyrrolidin-1-yl)ethanone (10e). Pyrrolidine (**9e**) (0.083 g, 1.0 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.243 g, 0.5 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.05 g, 88%) as a yellow oil, with spectroscopic data in accordance with the literature.[19m] ^1H NMR (300 MHz; $CDCl_3$) δ_H 3.34 (4H, app q, *J* = 6.7 Hz, CH_2NCH_2), 1.95 (3H, s, $COCH_3$), 1.90−1.75 (4H, m, $NCH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 169.4, 47.5, 45.6, 26.2, 24.7, 22.6; HRMS *m/z* (ES) 136.0729 $C_6H_{11}NNaO$ $[M + Na]^+$ requires 136.0733.

1-(Piperazin-1-yl)ethanone (10f). Piperazine (**9f**) (0.043 g, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.243 g, 0.5 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.063 g, 99%) as a orange oil, with spectroscopic data in accordance with the literature.[19n] ^1H NMR (300 MHz; $CDCl_3$) δ_H 3.55−3.51 (2H, m, CH_2NCOCH_3), 3.40−3.37 (2H, m, CH_2NCOCH_3), 2.83−2.76 (4H, m, CH_2NHCH_2), 2.12 (1H, br s, N*H*), 2.04 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 169.1, 47.5, 46.3, 45.8, 42.5, 21.4; HRMS *m/z* (ES) 151.0868, $C_6H_{12}N_2NaO$ $[M + Na]^+$ requires 151.0847.

1-Morpholinoethanone (10g). Morpholine (**9g**) (0.044 mL, 0.5 mmol) was added to a solution of *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off to give the title compound (0.063 g, 97%) as a brown oil, with spectroscopic data in accordance with the literature.[19o] ^1H NMR (300 MHz; $CDCl_3$) δ_H 3.65−3.60 (4H, m, CH_2OCH_2), 3.57−3.54 (2H, m, CH_2NCOCH_3), 3.41 (2H, t, *J* = 4.8 Hz, CH_2NCOCH_3), 2.05 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 169.2, 66.9, 66.6, 46.7, 41.8, 21.2; HRMS *m/z* (ES) 152.0692, $C_6H_{11}NNaO_2$ $[M + Na]^+$ requires 152.0687.

***N*-Methoxy-*N*-methyl-3-phenylpropanamide (10h).** *N*,*O*-Dimethylhydroxylamine hydrochloride (**9h**) (0.049 g, 0.5 mmol) was added to a solution of *N*-hydrocinnamoyl DBN·BPh_4 (**3d**) (0.375 g, 0.65 mmol) and DBN (**1**) (0.070 mL, 0.6 mmol) in acetonitrile (2 mL) and heated at 80 °C for 1 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with 1 M HCl, 1 M NaOH, and brine before being dried over $MgSO_4$ and concentrated to give the title compound (0.077 g, 80%) as a pale orange oil, with spectroscopic data in accordance with the literature.[19p] ^1H NMR (300 MHz; $CDCl_3$) δ_H 7.25−7.10 (5H, m, Ph-*H*), 3.53 (3H, s, OCH_3), 3.11 (3H, s, NCH_3), 2.89 (2H, t, *J* = 7.8 Hz, CH_2CH_2Ph), 2.67 (2H, t, *J* = 7.8 Hz, CH_2CH_2Ph); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 173.9 141.5, 128.6, 128.6, 126.2, 61.3, 34.0, 30.8; HRMS *m/z* (ES) 194.1209, $C_{11}H_{16}NO_2$ $[M + H]^+$ requires 194.1181.

General Procedure for the *N*-Acylation of Sulfonamides with *N*-Acetyl DBN·BPh_4. *N*-Acetyl DBN·BPh_4 (**3b**) (1.3 equiv, 0.65 mmol) and the appropriate sulfonamide (1 equiv, 0.5 mmol) are added to a carousel tube and purged with nitrogen. Dry acetonitrile (2 mL) and DBN (**1**) (20 mol %, 0.1 mmol) are added, and the resulting solution is heated at 80 °C for 16 h before being cooled to room temperature. The crude product is suspended in the minimum amount of hot ethyl acetate and allowed to cool before the mixture is filtered to remove the remaining *N*-acetyl-DBN salt and DBN·$HBPh_4$.The filtrate is then washed with NH_4Cl and brine before being dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

***N*-(Phenylsulfonyl)acetamide (12a).** DBN (**1**) (0.01 mL, 0.1 mmol) and acetonitrile (2 mL) were added to the *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) and benzenesulfonamide (**11a**) (0.079 g, 0.5 mmol), and the resulting solution was heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with NH_4Cl and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.083 g, 83%) as a light brown solid, with spectroscopic data in accordance with the literature.[19q] ^1H NMR (300 MHz; $CDCl_3$) δ_H 9.05 (1H, br s, N*H*), 7.99 (2H, d, *J* = 7.7 Hz, Ph-*H*), 7.59 (1H, t, *J* = 7.3 Hz, Ph-*H*), 7.49 (2H, t, *J* = 7.6 Hz, Ph-*H*), 2.00 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.5, 138.6, 134.2, 129.2, 128.4, 23.7; HRMS *m/z* (ES) 200.0384, $C_8H_{10}NO_3S$ $[M + H]^+$ requires 200.0381.

***N*-(Methylsulfonyl)acetamide (12b).** DBN (**1**) (0.01 mL, 0.1 mmol) and acetonitrile (2 mL) were added to the *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) and methanesulfonamide (**11b**) (0.048 g, 0.5 mmol), and the resulting solution was heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with NH_4Cl and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.067 g, 98%) as a deep purple oil. ^1H NMR (300 MHz; $CDCl_3$) δ_H 6.00 (1H, br s, N*H*), 3.23 (3H, s, SO_2CH_3), 2.13 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 171.4, 41.3, 24.1; HRMS *m/z* (ES) 160.0029, $C_3H_7NNaO_3S$ $[M + Na]^+$ requires 160.0044.

***N*-Tosylacetamide (12c).** DBN (**1**) (0.01 mL, 0.1 mmol) and acetonitrile (2 mL) were added to the *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) and *p*-toluenesulfonamide (**11c**) (0.086 g, 0.5 mmol), and the resulting solution was heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with NH_4Cl and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.085 g, 80%) as a brown solid, with spectroscopic data in accordance with the literature.[19q] ^1H NMR (300 MHz; $CDCl_3$) δ_H 9.15 (1H, br s, N*H*), 7.86 (2H, d, *J* = 8.3 Hz, Tol-*H*), 7.27 (2H, d, *J* = 8.1 Hz, Tol-*H*), 2.37 (3H, s, Tol-CH_3), 1.99 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.7, 145.4, 135.6, 129.8, 128.4, 23.6, 21.8; HRMS *m/z* (ES) 214.0539, $C_9H_{12}NO_3S$ $[M + H]^+$ requires 214.0533.

***N*-((4-Methoxyphenyl)sulfonyl)acetamide (12d).** DBN (**1**) (0.01 mL, 0.1 mmol) and acetonitrile (2 mL) were added to the *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) and 4-methoxybenzenesulfonamide (**11d**) (0.094 g, 0.5 mmol), and the resulting solution

was heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with NH_4Cl and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.085 g, 74%) as a brown solid, with spectroscopic data in accordance with the literature.[19q] ^1H NMR (300 MHz; $CDCl_3$) δ_H 9.01 (1H, br s, NH), 7.92 (2H, d, J = 9.0 Hz, Ar-H), 6.93 (2H, d, J = 9.0 Hz, Ar-H), 3.81 (3H, s, OCH_3), 1.99 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 168.6, 164.1, 130.8, 129.9, 114.3, 55.9, 23.6; HRMS m/z (ES) 230.0472, $C_9H_{12}NO_4S$ $[M + H]^+$ requires 230.0487.

***N*-Benzyl-*N*-tosylacetamide (12g).** DBN (**1**) (0.01 mL, 0.1 mmol) and acetonitrile (2 mL) were added to the *N*-acetyl DBN·BPh_4 (**3b**) (0.316 g, 0.65 mmol) and *N*-benzyl-*p*-toluenesulfonamide (**11g**) (0.131 g, 0.5 mmol), and the resulting solution was heated at 80 °C for 16 h according to the general procedure. The crude product was dissolved in ethyl acetate, and the excess salts were filtered off. The solution was washed with NH_4Cl and brine before being dried over $MgSO_4$, filtered, and concentrated to give the title compound (0.099 g, 65%) as a beige solid, with spectroscopic data in accordance with the literature.[19r] ^1H NMR (300 MHz; $CDCl_3$) δ_H 7.53 (2H, d, J = 8.4 Hz, Tol-H), 7.31−7.17 (7H, m, Ar-H), 5.00 (2H, s, NCH_2Ph), 2.34 (3H, s, Tol-CH_3), 2.20 (3H, s, $COCH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 170.5, 145.1, 136.8, 136.6, 129.9, 128.7, 128.1, 127.9, 49.6, 25.0, 21.7; HRMS m/z (ES) 304.1012, $C_{16}H_{18}NO_3S$ $[M + H]^+$ requires 304.1007.

■ ASSOCIATED CONTENT

Supporting Information

^1H and $^{13}C\{^1H\}$ NMR spectra of all *N*-acyl DBN·BPh_4 salts (**3a**−**f**); X-ray crystal structures and CIF files for *N*-benzoyl DBN·BPh_4 (**3a**) and *N*-hydrocinnamoyl DBN·BPh_4 (**3d**). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: S.D.Bull@bath.ac.uk

Notes

The authors declare no competing financial interest.

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