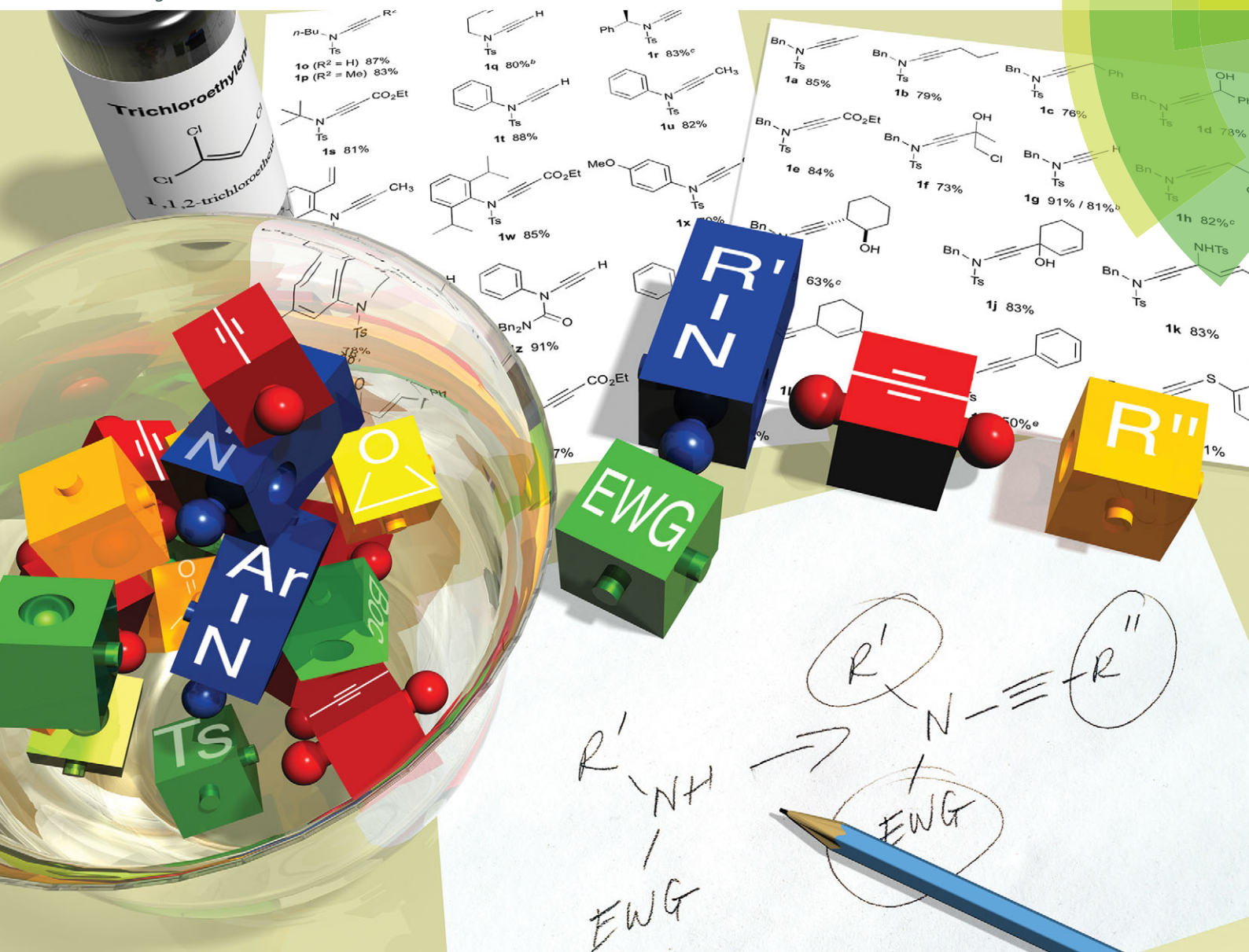


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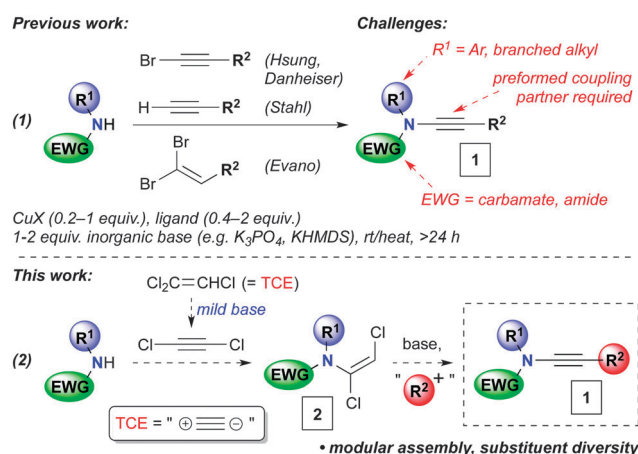
A robust and modular synthesis of ynamides†

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A flexible, modular ynamide synthesis is reported that uses trichloroethene as an inexpensive two carbon synthon. A wide range of amides and electrophiles can be converted to the corresponding ynamides, importantly including acyclic carbamates, hindered amides, and aryl amides. This method thus overcomes many of the limitations of other approaches to this useful functionality.

Ynamides (**1**, Scheme 1) are versatile functionalities that are finding use in an increasing array of transformations.^{1,2} Their popularity can be attributed to the high regioselectivity of reactions of the polarized and nucleophilic alkyne, and also to the advent of several methods for their synthesis over the last decade. At the forefront of these are copper-catalyzed couplings of amides with alkynes³ or their derivatives,⁴ or dibromoalkenes (Scheme 1, eqn (1)).⁵ Despite these important advances, limitations remain for the preparation of certain ynamide derivatives. For instance, whilst oxazolidinones are excellent substrates for copper-catalyzed ynamide synthesis, acyclic carbamates and amides typically are not.⁶ Furthermore, these reactions are usually ineffective for poorly nucleophilic amides, including those with branched substituents adjacent to the nitrogen centre, and aniline derivatives. Here we report a solution to these problems, in the form of a modular and flexible ynamide synthesis that proceeds in short reaction times and displays extensive substituent diversity, and thus opens up new possibilities for the wider use of ynamides in organic synthesis.

We hypothesized that dichloroacetylene, generated from inexpensive trichloroethene (TCE) under mildly basic reaction conditions, could serve as an excellent two carbon synthon for ynamide synthesis (eqn (2), Scheme 1).^{7,8} Addition of an amide



Scheme 1 Copper-catalyzed ynamide formations, and the planned modular approach to ynamides **1** via dichloroenamides **2**.

to dichloroacetylene would lead to a dichloroenamide **2**, a direct precursor to an ynamide *via* elimination. This route would benefit from a late-stage diversifying introduction of the alkyne substituent (R^2) in the course of ynamide synthesis, using readily available electrophiles (*i.e.* **2** \rightarrow **1**). Notably, this obviates the need for a preformed (halo)alkyne or dihaloalkene, as required in most ynamide synthesis methodology, which can restrict product scope.

Investigations into dichloroenamide synthesis began with sulfonamides **3a** and **3b**, the latter of which is a challenging substrate for ynamide formation using other methods (Table 1). An initial screen of inorganic bases afforded good results with a slight excess of LiOH and TCE in DMF at 70 °C (entries 1 and 2), albeit after extended reaction times; other base-solvent combinations proved less effective (entries 3 and 4) or inconsistent (entries 5 and 6). The reaction time was significantly shortened by increasing the concentration, and the amount of base and TCE, which gave excellent yields of dichloroenamide (entries 7 and 8).⁹ Pleasingly, these conditions were further improved by using just 1.1 equiv. of TCE with Cs_2CO_3 (1.5 equiv.) in DMF at 50 °C, which effected rapid and high yielding formation of both enamides **2a**

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† Electronic supplementary information (ESI) available: Experimental procedures and characterisation data, copies of 1H and ^{13}C NMR spectra for dichloroenamides and ynamides, and X-ray crystallographic data. CCDC 1022574 and 1022575. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc07876d



Table 1 Optimization of 1,2-dichloroenamide synthesis

		Conditions (see Table) 70 °C		Yield ^a [%] (conversion [%])	
Entry	Substrate	TCE equiv.	Base (equiv.), solvent ([M])	t (h)	
1	3a R = Bn	1.5	LiOH (1.2), DMF (0.8)	48	79 (100)
2	3b R = Ph	1.5	LiOH (1.2), DMF (0.8)	48	63 (100)
3	3a	1.5	KOH (1.2), DMSO (0.8)	72	n.d. ^b (<10)
4	3a	1.5	K ₂ CO ₃ (1.2), DMF (0.8)	48	n.d. ^b (<60)
5	3a	1.5	KOH (1.2), MeCN (0.8)	48	90 (100)
6	3b	1.5	KOH (1.2), MeCN (0.8)	48	n.d. ^b (<10)
7 ^c	3a	3.0	K ₂ CO ₃ (3.0), DMF (1.33)	5	93 (100)
8 ^c	3b	3.0	K ₂ CO ₃ (3.0), DMF (1.33)	7	92 (100)
9 ^d	3a	1.1	Cs ₂ CO ₃ (1.5), DMF (1.33)	0.75	90 (100)
10 ^d	3b	1.1	Cs ₂ CO ₃ (1.5), DMF (1.33)	2	90 (100)
11 ^{d,e}	3a	1.1	Cs ₂ CO ₃ (1.5), DMF (1.33)	1.5	95 (100)

^a Isolated yield; conversion determined by ¹H NMR spectroscopic analysis of the crude reaction mixture. ^b Not determined. ^c Anhydrous DMF used.

^d Reaction conducted at 50 °C. ^e Conducted with 4.1 g (15.7 mmol) of **3a**.

and **2b** (entries 9 and 10). The reaction remained efficient on multigram scale (4.1 g of **3a**, 95% yield, entry 11).

With optimized conditions in hand, we investigated the scope of dichloroenamide formation (Table 2). We were delighted to find that both unhindered and hindered *N*-alkyl sulfonamides were highly competent substrates, affording dichloroenamides **2c–h** in excellent yields. Similarly, sulfonamides of electron-rich, electron-poor, and sterically hindered anilines also proved to be outstanding substrates (**2i–m**), including the particularly challenging but highly efficient reaction of 2,6-diisopropylaniline sulfonamide (**2m**). The *N*-vinylation of a range of aromatic azacycles was also successful, with indoles **2n–2q**, benzotriazole **2r** and imidazole **2s** all obtained in good yields; for **2q**, the decreased acidity of this indole starting material necessitated the use of NaH as base.

This latter example suggested that a subtle balance of p*K*_a and nucleophilicity determines the reactivity of the substrate towards dichlorovinilation. This indeed turned out to be the case for the reactions of other amide derivatives: where unhindered carbamate derivatives such as oxazolidinone **2t** and methoxycarbamate **2u** were readily obtained using Cs₂CO₃-promoted vinylation conditions, substrates that are both less nucleophilic and weakly acidic (such as ureas, hydrazides and *tert*-butyl carbamates) required the use of either phase-transfer conditions,¹⁰ or NaH as base for formation of the desired dichloroenamides (**2w–2bb**), with all obtained in good to excellent yields. In virtually all cases, only the (*E*)-stereoisomer of these bench-stable dichloroenamide products was obtained (see Table 2), as determined through X-ray crystallographic analysis of products **2a** (Fig. 1) and **2t**, with others assigned by analogy.¹¹

Having established mild, general and high yielding routes to 1,2-dichloroenamides, we next surveyed conditions to effect their conversion to functionalised ynamides (Table 3).¹² After some optimisation,¹³ we found either *n*-butyllithium or phenyllithium

Table 2 Synthesis of 1,2-dichloroenamides: reaction scope^a

		Conditions (see Table)		Yield [%]	
Entry	Substrate	TCE equiv.	Base (equiv.), solvent ([M])	t (h)	
2c	<i>n</i> -Bu-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	79%
2d	CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	93%
2e	CH ₂ =CH-CH ₂ -CH ₂ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	92%
2f	CH ₂ =CH-CH ₂ -CH ₂ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	79%
2g	CH ₂ =CH-CH ₂ -CH ₂ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	72% ^b
2h	CH ₂ =CH-CH ₂ -CH ₂ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	84%
2i	4-MeO-C ₆ H ₄ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	94%
2j	4-F ₃ C-C ₆ H ₄ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	88%
2k	4-Br-C ₆ H ₄ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	86%
2l	4-Cl-C ₆ H ₄ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	82% ^b
2m	2,6-diisopropyl-C ₆ H ₃ -NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	99%
2n	Indole-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	79%
2o	Indole-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	79%
2p	Indole-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	68% ^c
2q	Indole-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	9%, 80% ^{c,d}
2r	Indole-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	80%
2s	Imidazole-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	83%
2t	Oxazolidinone-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	85%
2u	Methoxycarbamate-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	87%
2v	Urea-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	84%
2w	Hydrazide-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	0%, 67% ^d , 0% ^e
2x	tert-butyl carbamate-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	0%, 58% ^{d,f} , 0% ^e
2y	Hydrazide-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	0%, 68% ^d , 95% ^e
2z	Hydrazide-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	0%, 88% ^e
2aa	Hydrazide-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	0%, 76% ^e
2bb	Hydrazide-NH-Ts	1.5	LiOH (1.2), DMF (0.8)	48	82% ^e

^a All yields are isolated yields. ^b 3.0 equiv. K₂CO₃, 3.0 equiv. TCE, anhydrous DMF, 70 °C. ^c *E/Z* = 94:6. ^d 2.1 equiv. NaH, 1.0 equiv. TCE, anhydrous DMF, rt. ^e 0.2 equiv. (*n*-Bu)₄NHSO₄, 3.0 equiv. TCE, toluene, 25% aq. NaOH, rt. ^f *E/Z* = 88:12.

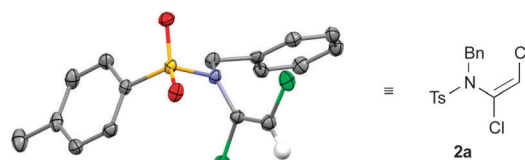
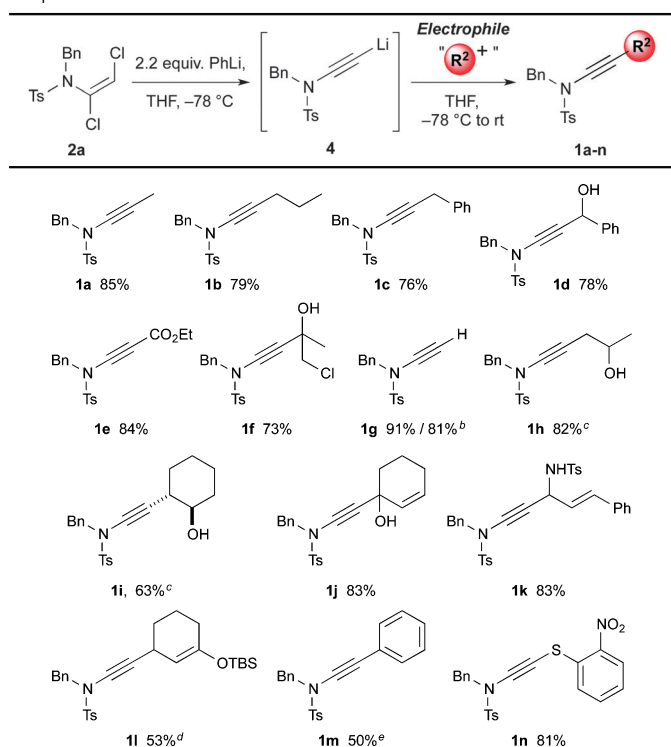


Fig. 1 ORTEP diagram for (*E*)-dichloroenamide **2a** (the alkene hydrogen is retained for clarity).

to be efficient bases for this elimination process, with the former of these requiring a more controlled addition of the base at −78 °C to avoid side-reactions. Following trapping of the alkynyllithium intermediate **4** with iodomethane, ynamide **1a** was isolated in 85% yield.

This lithiated ynamide proved to be an extremely competent nucleophile, giving high yields of a wide range of ynamides. Products arising from reaction with primary alkyl iodides/bromides

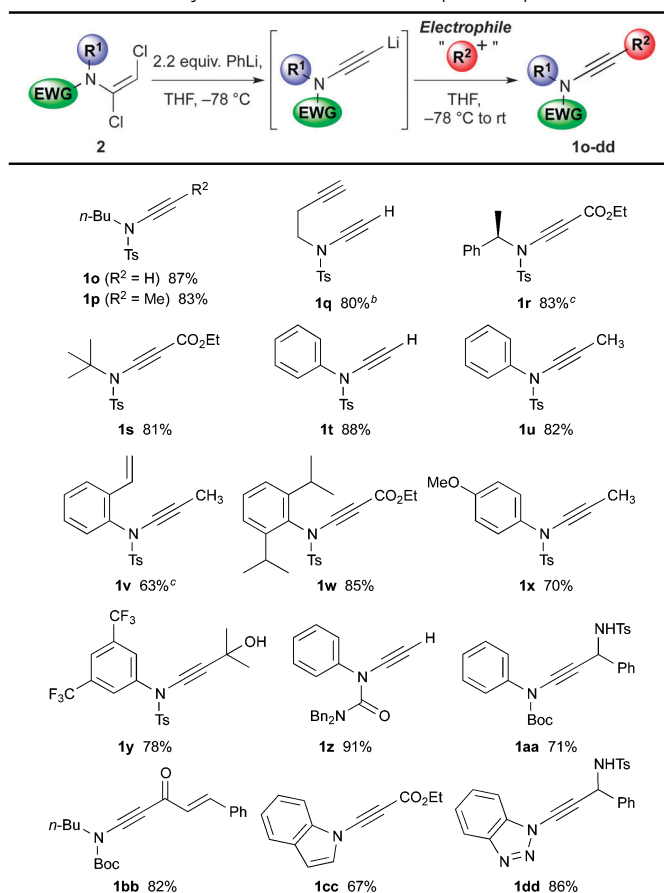


Table 3 Ynamide synthesis from dichloroenamide **2a**: electrophile scope^a

^a All yields are isolated yields. ^b 1.0 g scale. ^c 1.2 equiv. $BF_3 \cdot OEt_2$ required. ^d Transmetalation with $ZnCl_2 \cdot OEt_2$; then TBSOTf. ^e Transmetalation with $ZnCl_2 \cdot OEt_2$; then PhI, $Pd_2(dba)_3$ (3 mol%), PPh_3 (6 mol%).

(**1a-c**), and various carbonyl derivatives including aldehydes, ketones and chloroformates (**1d-f**), were all formed successfully.¹⁴ The terminal ynamide **1g** was obtained in excellent yield, including on gram scale, *via* direct protonation of **4**. The use of epoxides as electrophiles offers a convenient entry to β -hydroxy ynamides, with products **1h** and **1i** isolated in good yield. We also investigated the selectivity of 1,2- *versus* 1,4-addition of the amidoacetylide anion to α,β -unsaturated carbonyl derivatives; exclusive 1,2-addition was observed with α,β -unsaturated ketones and aldimines (**1j,k**), whereas clean 1,4-addition was accomplished following transmetalation to zinc (**1l**).¹⁵ This transmetalation also enabled acetylenic arylation to be achieved in a single step from the dichloroenamide by *in situ* Negishi coupling (**1m**).¹⁶ Finally, we were gratified to observe smooth formation of thioynamide **1n**, a markedly stable double heteroatom-substituted alkyne, upon trapping with a disulfide.

Following the success of this strategy, the generality of the process was explored, with a particular focus on the formation of ynamides inaccessible by other means. Most pleasingly, the protocol met with wide success, providing access to an array of ynamides (Table 4). Whilst these reactions could all be performed using PhLi, in a few instances (**1r**, **1v**) *n*-BuLi gave superior results. Thus, *N*-alkyl ensulfonamides were smoothly converted to various ynamides **1o-s**, including the efficient syntheses of the *N*-*tert*-butyl ynamide **1s**, for which no other method has been reported. *N*-Aryl ynamides **1t-y** were formed in excellent yields, with a wide tolerance of electronic and steric effects, the latter

Table 4 Ynamide synthesis: amide and electrophile scope^a

^a All yields are isolated yields. ^b 3.2 equiv. PhLi was used. ^c 2.2 equiv. *n*-BuLi was used.

emphasised by the high yield of the 2,6-diisopropylphenyl ynamide **1w** (85%). In addition to sulfonyl ynamides, the chemistry is equally effective with other electron-withdrawing functionalities: *N*-aryl urea ynamide **1z**, and the Boc-protected *N*-aryl and *N*-alkyl ynamides **1aa** and **1bb**, were all produced in high yields. The successful application of this chemistry extended to the formation of azacyclic ynamines, as illustrated by indole **1cc** and benzotriazole **1dd**, which further underlines the broad scope of the methodology.

In conclusion, a rapid, economic and modular route to ynamides has been developed that overcomes limitations encountered with other ynamide-forming procedures, and offers a reliable means to prepare a diverse range of ynamides with extensive variation of all substituents. The reaction is tolerant of a wide range of functionality on the amide component, including successful reactions of carbamates, hindered amides, and aryl amides. Combined with a veritable diversity of electrophile partners, this strategy can access previously challenging or unattainable ynamides, without requiring preformed alkyne or alkene coupling partners.

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