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A Stereocontrolled 1,2-Addition Reaction of Tetrazoles with Alkyl Propiolates for the Synthesis of Highly Functionalized Enamines

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Abstract: A stereocontrolled 1,2-addition reaction of 1-aryl-1*H*-tetrazoles with alkyl propiolates for the synthesis of highly functionalized enamines was developed. In the presence of silver oxide (Ag_2O), the 1,2-addition reaction generated (*Z*)-*N*-cyano enamines in good yields with exclusive formation of the *Z*-isomers. Meanwhile, the 1,2-addition reaction generated (*E*)-*N*-cyano enamines in the presence of Ag_2O and potassium carbonate (K_2CO_3) with high stereoselectivity and yields.

Keywords: 1,2-addition reaction; alkyl propiolates; *N*-cyano enamines; silver catalysis; tetrazoles

Introduction

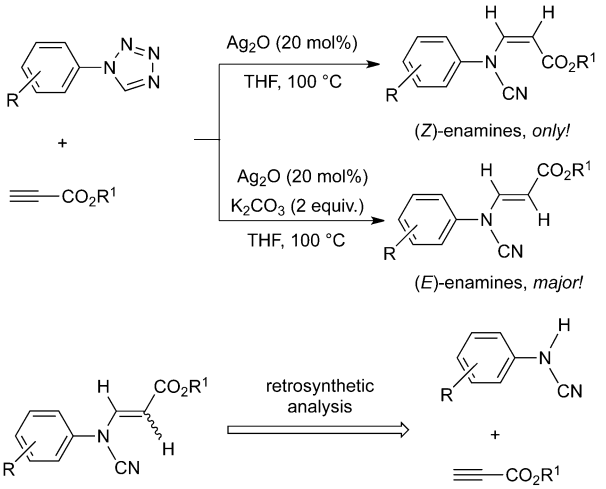
Enamines are key structural motifs in many natural products. And most importantly, functionalized enamines are pharmaceuticals with biologically relevant properties, and versatile and valuable intermediates in a variety of functional group transformations.[1] The traditional approach for enamine synthesis is derived from the reaction of an aldehyde or ketone with a secondary amine followed by loss of water.[2] However, it is difficult to prepare the enamines from aromatic amines through the above method owing to their weak nucleophilic properties.

As an alternative method, the addition of amines to alkynes is one of the most powerful methods for enamine preparation.[3] In general, N–C(sp^2) bond-forming reactions using electron-deficient alkynes as electrophilic precursors have been developed. However, only the *Z*- or the *E*-configuration addition products were obtained under the different reaction conditions without any stereocontrol.[4]

Silver salts have increasingly received interest as catalysts by virtue of their expanding reactivity patterns[5] and have covered many interesting reactions, such as cycloisomerization cycloaddition,[6] C–H activation,[7] domino reaction,[8] and alkynylation reaction,[9] etc. Remarkable progress has been made in the Ag-catalyzed reaction of alkynes in recent years because Ag could bind/activate π-systems,[10] but there are a few reports on stereoselective addition reactions controlled by an Ag catalyst.[11]

Apart from the wide applications of 1-aryltetrazoles in rocket propellants and explosives,[12a–c] they are also used for organic transformations *via* their C–H bond functionalizations.[12d] 1-Aryltetrazoles are known to decompose into *N*-arylcyanamides in the presence of a strong base.[13] However, there is no example of the application of tetrazole as a potential synthetic equivalent of cyanamide.

Herein, we wish to report a stereocontrolled 1,2-addition reaction of tetrazoles with alkyl propiolates for the synthesis of highly functionalized enamines (Scheme 1). The stereochemistry of the products depended on the choice of different reaction conditions. In the presence of Ag_2O, the 1,2-addition reaction generated (*Z*)-*N*-cyano enamines in good yields with exclusive formation of the *Z*-isomers. Meanwhile, the 1,2-addition reaction generated (*E*)-*N*-cyano enamines in the presence of Ag_2O and K_2CO_3 with high stereoselectivity and yields. Although cyanamides are highly versatile building blocks for a number of organic transformations, including the synthesis of



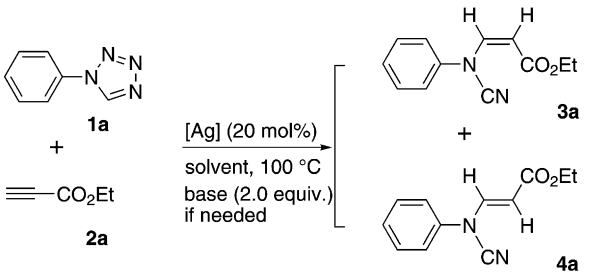
Scheme 1.

a number of heterocycles, guanidines, imidazolines and arylation of cyanamides,[14] *N*-cyano enamines have not been prepared from the reaction of cyanamides and alkyl propiolates according to retrosynthetic analysis (Scheme 1). Moreover, it is noteworthy to mention that the tetrazoles, as synthetic precursors, are more stable and less poisonous as compared with cyanamides, and *N*-cyano enamines are potiential pharmaceuticals with biological activity.

Results and Discussion

In the initial exploration of the stereocontrolled 1,2-addition reaction of tetrazoles to alkyl propiolates, 1-phenyl-1*H*-tetrazole (**1a**) and ethyl propiolate (**2a**) were chosen as the model substrates for our investigation and the results are shown in Table 1. Firstly, the effect of Ag salts on the model reaction was examined. When the model reaction was performed in the presence of $AgCO_3$ (20 mol%) in THF at 100 °C (sealed tube) for 12 h, a mixture of (*Z*)-*N*-cyano enamine **3a** (42% yield) and (*E*)-*N*-cyano enamine **4a** (35% yield) was isolated (Table 1, entry 1). To our delight, **3a** was obtained as the exclusive product and its yield could be increased to 92% when Ag_2O (20 mol%) was used as catalyst (Table 1, entry 2). With use of other Ag salts, such as AgCl, and Ag_2SO_4, the model reaction also produced a mixture of the stereoisomeric enamines **3a** and **4a** in poor stereoselectivity (Table 1, entries 3 and 4). However, no addition product was detected when $AgNO_3$ or AgOAc was used as catalyst in the reaction (Table 1, entries 5 and 6). Furthermore, when the model reaction was carried out in the presence of Ag_2O, a significant solvent effect was observed. Among the solvents tested, THF was found to be the best one. Diethyl ether, DMSO, DMF and dioxane were inferior and afforded 21–56% yields of **3a** (Table 1, entries 7–10). When the solvent was switched to CH_2Cl_2, CH_3CN or CH_3NO_2, no product was detected by TLC (Table 1, entries 11–13). In order to further investigate the stereoselectivity of this 1,2-addition, a base was added to the reaction system. Gratifyingly, when K_2CO_3 (2.0 equiv.) was added into Ag_2O-catalyzed model reaction, an 81% yield of (*E*)-enamine **4a** was obtained in good *E*-stereoselectivity, along with 3% yield of its *Z*-isomer **3a** (Table 1, entry 14). Other bases, such as K_3PO_4, KOH and NaOH, generated the *E*-configuration addition product **4a** in 36–69% yields and trace amount of **3a** (Table 1, entries 15–17). Meanwhile, when Na_2CO_3, KF, *t*-BuOLi, and Et_3N as bases were added to the reaction, mixtures of **4a** and **3a** were ob-

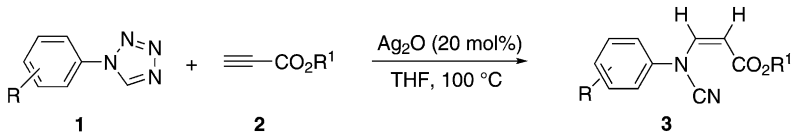
Table 1. Optimization of the reaction conditions for the model reaction.[a]



Entry	Ag salt	Base	Solvent	**3a** [%][b]	**4a** [%][b]
1	Ag_2CO_3	–	THF	42	35
2	***Ag_2O***	–	***THF***	***92***	ND
				92[c]	ND
3	AgCl	–	THF	12	23
4	Ag_2SO_4	–	THF	31	14
5	$AgNO_3$	–	THF	ND	ND
6	AgOAc	–	THF	ND	ND
7	Ag_2O	–	EtOEt	56	ND
8	Ag_2O	–	DMSO	53	ND
9	Ag_2O	–	DMF	34	ND
10	Ag_2O	–	dioxane	21	ND
11	Ag_2O	–	CH_2Cl_2	ND	ND
12	Ag_2O	–	CH_3CN	ND	ND
13	Ag_2O	–	CH_3NO_2	ND	ND
14	***Ag_2O***	***K_2CO_3***	***THF***	**(3)**[d]	***81***
				(3)[d]	***81***[c]
15	Ag_2O	K_3PO_4	THF	(5)[d]	69
16	Ag_2O	KOH	THF	(4)[d]	47
17	Ag_2O	NaOH	THF	(4)[d]	36
18	Ag_2O	Na_2CO_3	THF	21	45
19	Ag_2O	KF	THF	32	13
20	Ag_2O	*t*-BuOLi	THF	15	36
21	Ag_2O	Et_3N	THF	14	31

[a] *Reaction conditions:* **1a** (0.50 mmol), **2a** (0.60 mmol), Ag salt (0.10 mmol), base (2.0 equiv., if need), solvent (2.0 mL) at 100 °C (sealed tube) under air, 12 h.
[b] Isolated yields.
[c] Under a nitrogen atomsphere.
[d] GC yields in parentheses. ND = not detected.

Table 2. Ag_2O-catalyzed synthesis of (*Z*)-enamines.[a]



1 **2** **3**

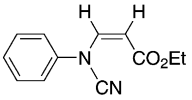
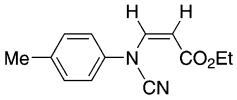
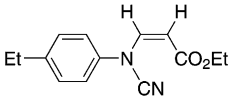
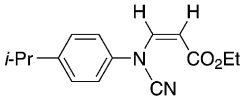
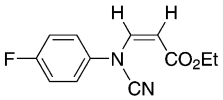
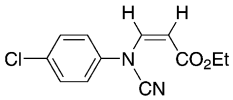
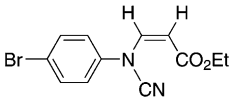
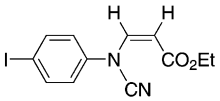
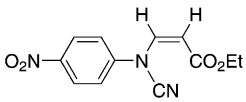
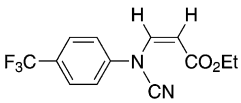
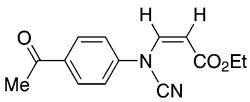
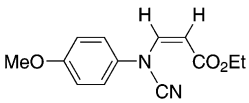
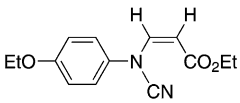
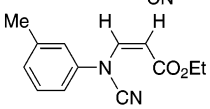
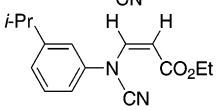
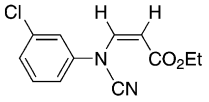
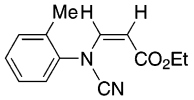
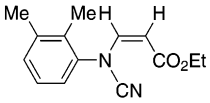
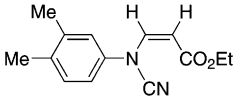
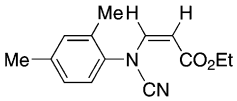
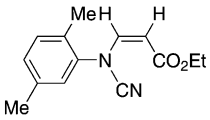
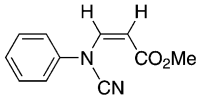
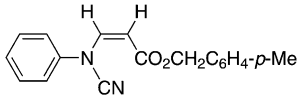
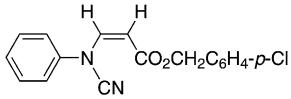
Entry	**1**, R; **2**, R^1	Product **3**		Yield [%][b]
1	**1a**, H; **2a**, Et		**3a**	92
2	**1b**, 4-Me; **2a**, Et		**3b**	93
3	**1c**, 4-Et; **2a**, Et		**3c**	94
4	**1d**, 4-(*i*-Pr); **2a**, Et		**3d**	95
5	**1e**, 4-F; **2a**, Et		**3e**	80
6	**1f**, 4-Cl; **2a**, Et		**3f**	84
7	**1g**, 4-Br; **2a**, Et		**3g**	83
8	**1h**, 4-I; **2a**, Et		**3h**	88
9	**1i**, 4-NO_2; **2a**, Et		**3i**	70
10	**1j**, 4-CF_3; **2a**, Et		**3j**	74
11	**1k**, 4-MeCO; **2a**, Et		**3k**	72
12	**1l**, 4-MeO; **2a**, Et		**3l**	70
13	**1m**, 4-EtO; **2a**, Et		**3m**	71
14	**1n**, 3-Me; **2a**, Et		**3n**	87
15	**1o**, 3-(*i*Pr); **2a**, Et		**3o**	85

Table 2. (Continued)

Entry	**1**, R; **2**, R^1	Product **3**		Yield [%][b]
16	**1p**, 3-Cl; **2a**, Et		**3p**	83
17	**1q**, 2-Me; **2a**, Et		**3q**	70
18	**1r**, 2,3-$(Me)_2$; **2a**, Et		**3r**	77
19	**1s**, 3,4-$(Me)_2$; **2a**, Et		**3s**	82
20	**1t**, 2,4-$(Me)_2$; **2a**, Et		**3t**	75
21	**1u**, 2,5-$(Me)_2$; **2a**, Et		**3u**	74
22	**1a**, H; **2b**, Me		**3v**	90
23	**1a**, H; **2c**,$CH_2C_6H_4$(*p*-Me)		**3w**	82
24	**1a**, H; **2d**, $CH_2C_6H_4$(*p*-Cl)		**3x**	87

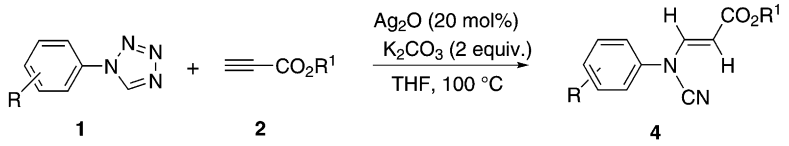
[a] *Reaction conditions:* **1** (0.50 mmol), **2** (0.60 mmol), Ag_2O (0.10 mmol), THF (2.0 mL) at 100 °C, sealed tube, air, 12 h.
[b] Isolated yields.

tained, leading to low stereoselectivity (Table 1, entries 18–21). It should be noted that the same results were obtained when the reactions were performed under an inert nitrogen atmosphere (Table 1, entries 2 and 14).

Inspired by the above observations, we first investigated the scope of the Ag_2O-catalyzed *Z*-selective 1,2-addition reaction of tetrazoles and alkyl propiolates under the optimized reaction conditions and the results are listed in Table 2. A variety of 1-aryl-1*H*-tetrazoles (**1**) was subjected to the reaction. It was found that reactions of **1** with ethyl propiolate (**2a**) gave the corresponding (*Z*)-enamines **3** in moderate to good yields with exclusive *Z*-isomers regardless of the substituted groups on the aromatic rings of **1**. Clearly, a 1-aryl-1*H*-tetrazole with an electron-donating group on the aromatic ring gave a better yield than that having an electron-withdrawing group on the aromatic ring. For example, **1** with an electron-donating group, such as Me, Et or *i*-Pr at the *para*-position of benzene ring reacted with **2a**, providing the desired products **3b–d** in excellent yields (Table 2, entries 2–4). On the other hand, the reactions of substrates **1** with F, Cl, Br, I, NO_2, CF_3 or MeCO group attached on the benzene ring with **2a** generated the corresponding products **3e–k** in 70–88% yields (Table 2, entries 5–11). However, substrates **1** with MeO or EtO group at the *para*-position of benzene ring gave **3l** and **3m** in 70% and 71% yields, respectively (Table 2, entries 12 and 13). Treatment of (3-tolyl)-, (3-isopropylphenyl)- and (3-chlorophenyl)-1*H*-tetrazoles with **2a** afforded the corresponding products **3n–p** in 83–87% yields (Table 2, entries 14–16). An *ortho*-position effect of the 1-aryl-1*H*-tetrazole was observed in the reaction of 1-(*o*-tolyl)-1*H*-tetrazole with **2** (Table 2, entry 17). Notably, multi-substituted 1-aryl-1*H*-tetrazoles with **2a** could also be converted to the anticipated products in 70–82% yields under standard conditions (Table 2, entries 18–21).

The reactions of 1-phenyl-1*H*-tetrazole (**1a**) with methyl propiolate (**2b**), 4-methylbenzyl propiolate (**2c**), and 4-chlorobenzyl propiolate (**2d**) generated

Table 3. Ag_2O-catalyzed synthesis of (*E*)-enamines in the presence of K_2CO_3.[a]



1 **2** **4**

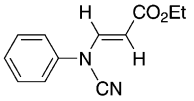
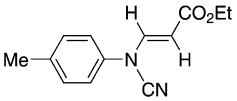
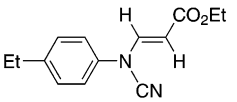
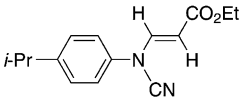
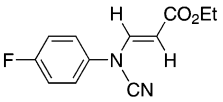
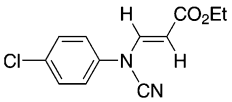
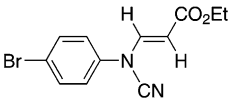
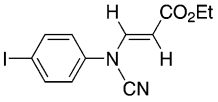
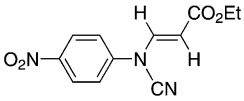
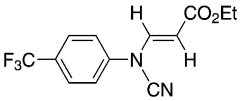
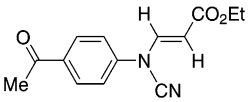
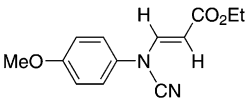
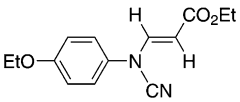
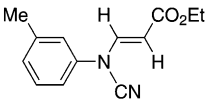
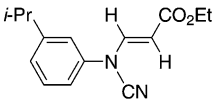
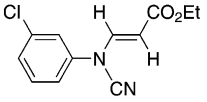
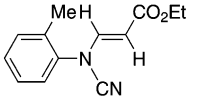
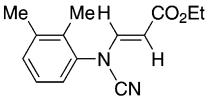
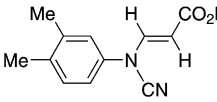
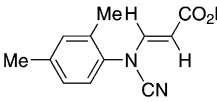
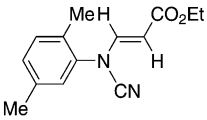
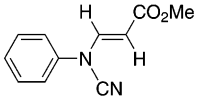
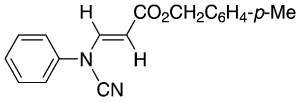
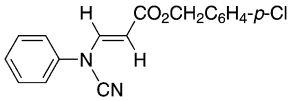
Entry	**1**, R; **2**, R^1	Product **4**		Yield [%][b]
1	**1a**, H; **2a**, Et		**4a**	81
2	**1b**, 4-Me; **2a**, Et		**4b**	92
3	**1c**, 4-Et; **2a**, Et		**4c**	90
4	**1d**, 4-(*i*-Pr); **2a**, Et		**4d**	93
5	**1e**, 4-F; **2a**, Et		**4e**	78
6	**1f**, 4-Cl; **2a**, Et		**4f**	80
7	**1g**, 4-Br; **2a**, Et		**4g**	76
8	**1h**, 4-I; **2a**, Et		**4h**	74
9	**1i**, 4-NO_2; **2a**, Et		**4i**	63
10	**1j**, 4-CF_3; **2a**, Et		**4j**	72
11	**1k**, 4-MeCO; **2a**, Et		**4k**	73
12	**1l**, 4-MeO; **2a**, Et		**4l**	89
13	**1m**, 4-EtO; **2a**, Et		**4m**	90
14	**1n**, 3-Me; **2a**, Et		**4n**	83
15	**1o**, 3-(*i*-Pr); **2a**, Et		**4o**	81

Table 3. (Continued)

Entry	**1**, R; **2**, R[1]	Product **4**		Yield [%][b]
16	**1p**, 3-Cl; **2a**, Et		**4p**	80
17	**1q**, 2-Me; **2a**, Et		**4q**	64
18	**1r**, 2,3-$(Me)_2$; **2a**, Et		**4r**	71
19	**1s**, 3,4-$(Me)_2$; **2a**, Et		**4s**	77
20	**1t**, 2,4-$(Me)_2$; **2a**, Et		**4t**	73
21	**1u**, 2,5-$(Me)_2$; **2a**, Et		**4u**	70
22	**1a**, H; **2b**, Me		**4v**	72
23	**1a**, H; **2c**, $CH_2C_6H_4$(*p*-Me)		**4w**	74
24	**1a**, H; **2d**, $CH_2C_6H_4$(*p*-Cl)		**4x**	77

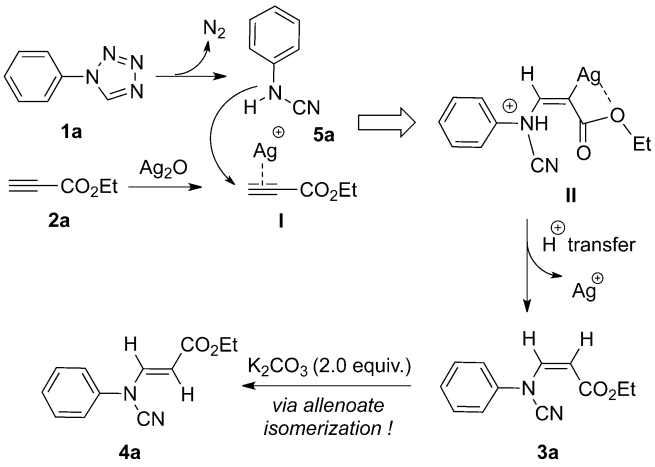
[a] *Reaction conditions:* **1** (0.50 mmol), **2** (0.60 mmol), Ag_2O (0.10 mmol), K_2CO_3 (1.0 mmol), THF (2.0 mL) at 100 °C, sealed tube, air, 12 h.
[b] Isolated yield.

the corresponding products **3v–x** in 82–90% yields (Table 2, entries 22–24).

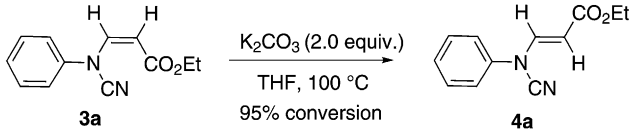
Next, we investigated Ag_2O-catalyzed 1,2-addition reaction of 1-aryl-1*H*-tetrazoles with alkyl propiolates in the presence of K_2CO_3 (2 equiv.), leading to (*E*)-*N*-cyano enamines in good yields and high stereoselectivity. As can be seen from Table 3, a similar electron effect was also observed as compared with Table 2. The reactivity of the 1-aryl-1*H*-tetrazoles with an electron-donating substitute, such as Me, Et, *i*-Pr, MeO or EtO at the *para*-position of benzene ring, was more than that of the tetrazoles with an electron-withdrawing substitutes, including F, Cl, Br, I, NO_2, CF_3 or MeCO at the *para*-position (Table 3, entries 2–6, 12 and 13 *vs.* 7–11). The substituent groups occupying the *meta*-position of the substrates **1n–p** gave the desired products **4n–p** in 80–83% yields, and the *ortho*-position effect was also observed when **1q** was used as substrate (Table 3, entries 14–17). As expected, the multi-substituted 1-aryl-1*H*-tetrazoles **1r–u** reacted with **2a** smoothly to give the corresponding products **4r–u** in 70–77% yields (Table 3, entries 18–21).

The reactions of **1a** with methyl propiolate (**2b**), 4-methylbenzyl propiolate (**2c**), and 4-chlorobenzyl propiolate (**2d**) afforded the desired products **4v–x** in 72–77% yields (Table 3, entries 22–24). It should be noted that a only trace amount of (*Z*)-*N*-cyano enamines (<5%) was observed in the presence of Ag_2O and K_2CO_3.

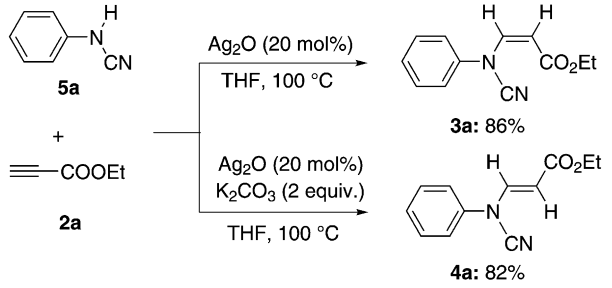
On the basis of our experiment results, a plausible mechanism for the stereocontrolled 1,2-addition reaction was proposed, as shown in Scheme 2. Firstly, 1-phenyl-1*H*-tetrazole (**1a**) was transformed into *N*-phenylcyanamide (**5a**) with loss of N_2, and the C≡C bond of ethyl propiolate (**2a**) was activated by Ag(I) to form intermediate **I**.[15] In the case of Ag_2O as the only catalyst in the reaction system, **5a** underwent a 1,2-*trans* addition of N and Ag^+ to **I**, affording intermediate **II** through a coordination effect, then fol-



Scheme 2. Proposed reaction mechanism.



Scheme 3. Conversion of **3a** to **4a** in the presence of K_2CO_3.



Scheme 4. The reactions of cyanamide with ethyl propiolate.

lowed by a proton transfer process and regeneration of Ag(I) to produce (*Z*)-enamine (**3a**) exclusively. On the other hand, in the case of Ag_2O and K_2CO_3 (2 equiv.) in the reaction system, the obtained (*Z*)-enamine (**3a**) could be transformed into the more stable (*E*)-enamine (**4a**) *via* an allenoate isomerization process. To verify this process, when the prepared (*Z*)-enamine (**3a**) was performed in THF at 100 °C in a sealed tube in the presence of K_2CO_3 for 12 h, 95% conversion of **3a** to **4a** was obtained (Scheme 3).

In order to further understand the reaction process, **5a** was synthesized from the reaction of 1-phenyl-1*H*-tetrazole (**1a**) with NaOH (aq.) at the room temperature. Upon treatment of **5a** and **2a** under the above reaction conditions, expected products **3a** and **4a** were isolated in 86% and 82% yields, respectively, as shown in Scheme 4.

Conclusions

In conclusion, a stereocontrolled 1,2-addition reaction of tetrazoles with alkyl propiolates for the preparation of highly functionalized enamines has been developed. Depending on the presence or absence of K_2CO_3 in the Ag_2O-catalyzed reaction, synthesis of either (*Z*)- or (*E*)-*N*-cyano enamines could be achieved in good to excellent yields with high selectivity. (*Z*)-*N*-Cyano enamines were obtained exclusively when Ag_2O was used as catalyst, whereas the use of Ag_2O catalyst in the presence of K_2CO_3 gave predominantly (*E*)-*N*-cyano enamines. It is important to note that 1-aryl-1*H*-tetrazoles could represent the synthetic equivalents of cyanamides for the synthesis of the *N*-cyano enamines, which are the potiential pharmaceuticals with biological activity.

Experimental Section

General Remarks

All the stereocontrolled 1,2-addition reaction of tetrazoles with alkyl propiolates were carried out under an air atmosphere. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument using EI (70 eV) or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

The starting materials tetrazoles were prepared in our laboratory according to the literature method.[16] The identity and purity of known products, **1a**,[17] **1b**,[17] **1d**,[18] **1e**,[19] **1f**,[17] **1g**,[17] **1h**,[20] **1i**,[17] **1j**,[19] **1k**,[17] **1l**,[17] **1m**,[21] **1n**,[17] **1p**,[22] **1q**,[17] **1r**,[23] and **1t**[17] were confirmed by ^1H and ^{13}C NMR spectroscopic analysis, and new products, **1c**, **1o**, **1s**, and **1u** were fully characterized.

Silver oxide (Ag_2O, AR) was commercially available from Aladdin Chem. Co. Ltd. (Shanghai, batch number: 30284; item number: 1125429) and used in the reactions directly. General chemicals and solvents were purchased from commercial suppliers and used without further purification.

Representative Procedure for the Synthesis of 1-Phenyl-1*H*-tetrazole

A 100-mL reaction flask equipped with a magnetic stirrer bar was charged with aniline (10.0 mmol, 930 mg), NaN_3 (11.0 mmol, 715 mg), triethyl orthoformate (30.0 mmol, 3018 mg) and AcOH (80.0 mmol, 4800 mg). The mixture was stirred at 80 °C for 4 h, cooled to room temperature, diluted with brine water (100 mL), and finally an appropriate amount of sodium carbonate was added until the gas evolution ceased. The precipitate was separated by filtration, washed with water and dried under vacuum at 50 °C to give 1-phenyl-1*H*-tetrazole (**1a**).

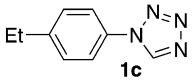
General Procedure for Ag_2O-Catalyzed 1,2-Addition Reaction of Tetrazole with Alkyl Propiolate

A sealable reaction tube equipped with a magnetic stirrer bar was charged with tetrazole (0.50 mmol), alkyl propiolate (0.60 mmol), Ag_2O (0.10 mmol) and THF (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel was placed in an oil bath at 100 °C [An Ace pressure tube is highly recommended to be employed for safety considerations]. After stirring of the mixture at this temperature for 12 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water and brine, dried over $MgSO_4$. After the solvent had been removed under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the desired product (*Z*)-*N*-cyano enamine.

General Procedure for Ag_2O-Catalyzed 1,2-Addition Reaction of Tetrazole with Alkyl Propiolate in the Presence of K_2CO_3

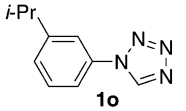
A sealable reaction tube equipped with a magnetic stirrer bar was charged with tetrazole (0.50 mmol), alkyl propiolate (0.60 mmol), Ag_2O (0.10 mmol), K_2CO_3 (1.0 mmol) and THF (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel was placed in an oil bath at 100 °C [An Ace pressure tube is highly recommended to be employed for safety considerations]. After stirring of the mixture at this temperature for 12 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water and brine, dried over $MgSO_4$. After the solvent had been removed under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the desired product (*E*)-*N*-cyano enamine.

Characterization Data for New Starting Material Tetrazoles and All Products



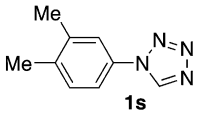
1c

1-(4-Ethylphenyl)-1*H*-tetrazole (1c): Yellow solid, mp 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 (s, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 140.5, 131.4, 129.3, 121.0, 28.3, 15.1; HR-MS (ESI): m/z = 175.0979 $[M+H]^+$, calcd. for $C_9H_{10}N_4$: 175.0984.



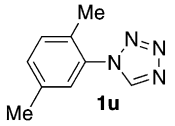
1o

1-(3-Isopropylphenyl)-1*H*-tetrazole (1o): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 (s, 1H), 7.57 (s, 1H), 7.49–7.46 (m, 2H), 7.39–7.38 (m, 1H), 3.05–2.98 (m, 1H), 1.29 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 140.6, 133.7, 130.0, 128.2, 119.4, 118.5, 34.0, 23.7; HR-MS (ESI): m/z = 189.1144 $[M+H]^+$, calcd. for $C_{10}H_{12}N_4$: 189.1140.



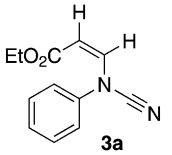
1s

1-(3,4-Dimethylphenyl)-1*H*-tetrazole (1s): Yellow solid, mp 61–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04 (s, 1H), 7.45 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 138.8, 138.7, 131.4, 130.8, 121.9, 118.2, 19.7, 19.3; HR-MS (ESI): m/z = 175.0981 $[M+H]^+$, calcd. for $C_9H_{10}N_4$: 175.0984.



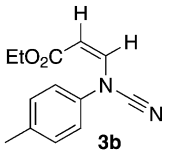
1u

1-(2,5-Dimethylphenyl)-1*H*-tetrazole (1u): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 1H), 7.28–7.27 (m, 2H), 7.12 (s, 1H), 2.38 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 137.3, 132.6, 131.6, 131.5, 130.3, 126.2, 20.6, 17.2; HR-MS (ESI): m/z = 175.0984 $[M+H]^+$, calcd. for $C_9H_{10}N_4$: 175.0984.



3a

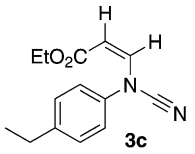
(*Z*)-Ethyl 3-(*N*-phenylcyanamido)acrylate (3a): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2H), 7.28–7.23 (m, 3H), 6.44 (d, J = 8.9 Hz, 1H), 5.67 (d, J = 8.8 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3, 139.3, 135.6, 129.8, 126.3, 118.4, 109.6, 108.4, 60.7, 14.1; IR (KBr): ν = 2234 (C≡N), 1716 cm^{-1} (C=O); HR-MS (ESI): m/z = 217.0972, $[M+H]^+$, calcd. for $C_{12}H_{13}N_2O_2$: 217.0977.



3b

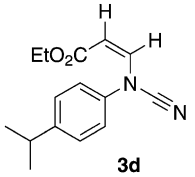
(*Z*)-Ethyl 3-(*N*-*p*-tolylcyanamido)acrylate (3b): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.40 (d, J = 8.9 Hz, 1H), 5.63 (d, J = 9.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 137.1, 136.5, 136.1, 130.3, 118.7, 108.8, 108.7, 60.8, 20.7, 14.2; IR (KBr): ν = 2232 (C≡N), 1711 cm^{-1}) (C=O);

HR-MS (ESI): $m/z = 231.1130$ $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_2$: 231.1134.



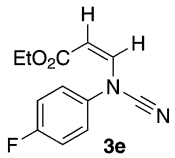
3c

(*Z*)-Ethyl 3-[*N*-(4-ethylphenyl)cyanamido]acrylate (3c): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.24$ (d, $J = 8.3$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.40 (d, $J = 8.9$ Hz, 1H), 5.61 (d, $J = 8.9$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.64 (q, $J = 7.6$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.4$, 142.7, 137.1, 136.0, 129.1, 118.7, 108.7, 108.6, 60.6, 28.0, 15.3, 14.1; IR (KBr): $\nu = 2233$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 245.1288$, $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



3d

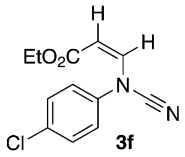
(*Z*)-Ethyl 3-[*N*-(4-isopropylphenyl)cyanamido]acrylate (3d): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.27$ (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.9$ Hz, 2H), 6.40 (d, $J = 8.9$ Hz, 1H), 5.61 (d, $J = 8.9$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 2.95–2.88 (m, 1H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.23 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.4$, 147.4, 137.2, 135.9, 127.7, 118.7, 108.8, 108.7, 60.6, 33.4, 23.8, 14.1; IR (KBr): $\nu = 2233$ (C≡N), 1717 cm^{-1} (C=O); HR-MS (ESI): $m/z = 259.1449$ $[M+H]^+$, calcd. for $C_{15}H_{19}N_2O_2$: 259.1447.



3e

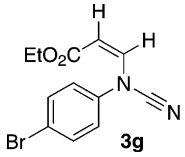
(*Z*)-Ethyl 3-[*N*-(4-fluorophenyl)cyanamido]acrylate (3e): White solid, mp 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.25–7.22 (m, 2H), 7.15–7.10 (m, 2H), 6.37 (d, $J = 8.9$ Hz, 1H), 5.65 (d, $J = 8.9$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.3$, 160.8 (d, $J_{C,F} = 245.8$ Hz), 135.7, 135.6 (d, $J_{C,F} = 2.7$ Hz), 120.7 (d, $J_{C,F} = 8.5$ Hz), 116.7 (d, $J_{C,F} = 23.3$ Hz), 109.5, 108.6, 60.8, 14.1; IR (KBr): $\nu = 2234$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 235.0878$ $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2F$: 235.0883.

(*Z*)-Ethyl 3-[*N*-(4-chlorophenyl)cyanamido]acrylate (3f): Yellow solid, mp 61–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.39 (d, $J = 7.2$ Hz, 2H), 7.18 (d, $J = 7.4$ Hz, 2H), 6.40 (d, $J =$ 8.8 Hz, 1H), 5.70 (d, $J = 8.8$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 1.31 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):



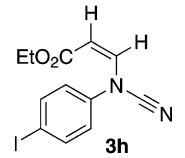
3f

$\delta = 163.2$, 137.9, 135.1, 131.9, 129.9, 119.6, 110.4, 108.1, 60.9, 14.1; IR (KBr): $\nu = 2236$ (C≡N), 1713 cm^{-1} (C=O); HR-MS (ESI): $m/z = 251.0587$ $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2Cl$: 251.0587.



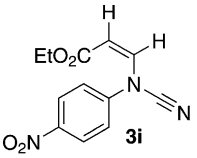
3g

(*Z*)-Ethyl 3-[*N*-(4-bromophenyl)cyanamido]acrylate (3g): White solid, mp 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.55 (d, $J = 8.9$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.40 (d, $J =$ 8.8 Hz, 1H), 5.71 (d, $J = 8.8$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.2$, 138.4, 135.0, 132.8, 119.9, 119.5, 110.6, 108.0, 60.9, 14.1; IR (KBr): $\nu = 2235$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 295.0081$ $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2Br$: 295.0082.



3h

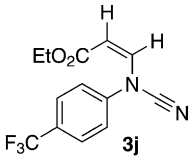
(*Z*)-Ethyl 3-[*N*-(4-iodophenyl)cyanamido]acrylate (3h): White solid, mp 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.73 (d, $J = 8.6$ Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 6.40 (d, $J =$ 8.8 Hz, 1H), 5.71 (d, $J = 8.8$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.2$, 139.2, 138.8, 134.8, 120.1, 110.8, 108.0, 90.2, 60.9, 14.1; IR (KBr): $\nu = 2234$ (C≡N), 1711 cm^{-1} (C=O); HR-MS (ESI): $m/z = 342.9942$ $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2I$: 342.9943.



3i

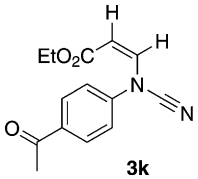
(*Z*)-Ethyl 3-[*N*-(4-nitrophenyl)cyanamido]acrylate (3i): Yellow solid, mp 94–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.29 (d, $J = 9.0$ Hz, 2H), 7.35 (d, $J = 9.0$ Hz, 2H), 6.57 (d, $J =$ 8.6 Hz, 1H), 5.90 (d, $J = 8.6$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 162.7$, 145.0, 144.1, 133.5, 125.5, 117.4, 113.9, 107.1, 61.2, 14.0; IR (KBr): $\nu = 2236$ (C≡N), 1719 cm^{-1} (C=O); HR-MS

(ESI): $m/z = 262.0823$ $[M+H]^+$, calcd. for $C_{12}H_{12}N_3O_4$: 262.0828.



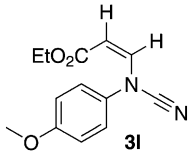
3j

(*Z*)-Ethyl 3-{*N*-[4-(trifluoromethyl)phenyl]cyanamido}-acrylate (3j): White solid, mp 89–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.50 (d, $J = 8.7$ Hz, 1H), 5.81 (d, $J = 8.7$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.0$, 142.0, 134.2, 128.1 (q, $J_{C,F} = 33.0$ Hz), 127.1 (q, $J_{C,F} = 3.7$ Hz), 123.5 (q, $J_{C,F} = 270.3$ Hz), 117.8, 112.2, 107.7, 61.0, 14.0; IR (KB): $\nu = 2238$ (C≡N), 1712 cm^{-1} (C=O); HR-MS (ESI) ($[M+H]^+$): calcd. for $C_{13}H_{12}N_2O_2F_3$: 285.0851. Found 285.0849.



3k

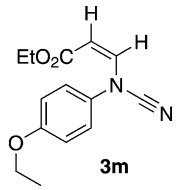
(*Z*)-Ethyl 3-(*N*-(4-acetylphenyl)cyanamido)acrylate (3k): White liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 8.6$ Hz, 2H), 6.52 (d, $J = 8.7$ Hz, 1H), 5.82 (d, $J = 8.7$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 2.60 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.2$, 163.1, 142.8, 134.6, 134.3, 130.2, 117.3, 112.2, 107.6, 61.1, 26.5, 14.1; IR (KBr): $\nu = 2236$ (C≡N), 1716 (C=O), 1707 cm^{-1} (C=O); HR-MS (ESI): $m/z = 259.1079$ $[M+H]^+$, calcd. for $C_{14}H_{15}N_2O_3$: 259.1083.



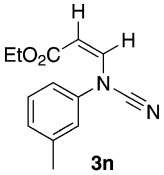
3l

(*Z*)-Ethyl 3-(*N*-(4-methoxyphenyl)cyanamido)acrylate (3l): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$ (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 9.0$ Hz, 2H), 6.33 (d, $J = 9.0$ Hz, 1H), 5.57 (d, $J = 9.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.6$, 158.4, 136.6, 132.8, 121.0, 115.0, 109.1, 107.9, 60.7, 55.6, 14.2; IR (KBr): $\nu = 2231$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 247.1078$ $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_3$: 247.1083.

(*Z*)-Ethyl 3-[*N*-(4-ethoxyphenyl)cyanamido]acrylate (3m): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.16$ (d, $J = 8.9$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 6.32 (d, $J = 9.0$ Hz, 1H), 5.55 (d, $J = 9.0$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 4.01 (q, $J = 7.0$ Hz, 2H), 1.39 (t, $J = 7.0$ Hz, 3H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.5$, 157.6, 136.6, 132.5, 120.9, 115.4, 109.1, 107.7, 63.8, 60.6, 14.6, 14.1; IR (KBr): $\nu = 2232$ (C≡N), 1711 cm^{-1} (C=O); HR-MS (ESI): $m/z = 261.1240$ $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_3$: 261.1239.

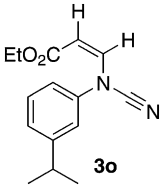


3m



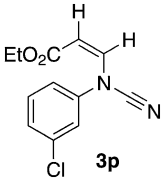
3n

(*Z*)-Ethyl 3-(*N*-*m*-tolylcyanamido)acrylate (3n): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.31$–7.27 (m, 1H), 7.06–7.01 (m, 3H), 6.42 (d, $J = 8.9$ Hz, 1H), 5.64 (d, $J = 8.9$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.36 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.3$, 140.0, 139.2, 135.7, 129.5, 127.0, 118.9, 115.4, 109.2, 108.5, 60.6, 21.2, 14.1; IR (KBr): $\nu = 2234$ (C≡N), 1716 cm^{-1} (C=O); HR-MS (ESI): $m/z = 231.1131$ $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_2$: 231.1134.



3o

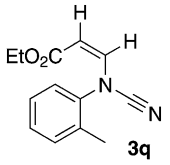
(*Z*)-Ethyl 3-[*N*-(3-isopropylphenyl)cyanamido]acrylate (3o): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$–7.31 (m, 1H), 7.14–7.12 (m, 1H), 7.10 (s, 1H), 7.05–7.03 (m, 1H), 6.44 (d, $J = 8.9$ Hz, 1H), 5.65 (d, $J = 8.9$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 2.96–2.89 (m, 1H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.24 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.4$, 151.1, 139.3, 135.8, 129.7, 124.5, 116.6, 116.0, 109.2, 108.6, 60.7, 34.0, 23.6, 14.1; IR (KBr): $\nu = 2234$ (C≡N), 1717 cm^{-1} (C=O); HR-MS (ESI): $m/z = 259.1449$ $[M+H]^+$, calcd. for $C_{15}H_{19}N_2O_2$: 259.1447.



3p

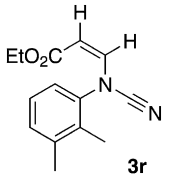
(*Z*)-Ethyl 3-[*N*-(3-chlorophenyl)cyanamido]acrylate (3p): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$–7.30 (m, 1H), 7.19–7.18 (m, 2H), 7.11–7.09 (m, 1H), 6.42 (d, $J = 8.8$ Hz, 1H), 5.70 (d, $J = 8.8$ Hz, 1H), 4.22 (q, $J = 7.0$ Hz,

2H), 1.27 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.0, 140.2, 135.5, 134.7, 130.7, 126.1, 118.2, 116.1, 110.9, 107.7, 60.7, 14.0; IR (KBr): ν=2237 (C≡N), 1717 cm^{-1} (C=O); HR-MS (ESI): m/z=251.0584 $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2Cl$: 251.0587.



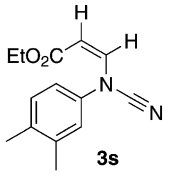
3q

(*Z*)-Ethyl 3-(*N*-*o*-tolylcyanamido)acrylate (3q): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.26 (m, 4H), 6.14 (d, J=9.2 Hz, 1H), 5.40 (d, J=9.2 Hz, 1H), 4.19 (q, J=7.1 Hz, 2H), 2.39 (s, 3H), 1.28 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.6, 138.4, 138.2, 134.6, 131.9, 129.2, 127.5, 125.4, 110.0, 105.0, 60.5, 17.4, 14.1; IR (KBr): ν=2229 (C≡N), 1714 cm^{-1} (C=O); HR-MS (ESI): m/z=231.1134 $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_2$: 231.1134.



3r

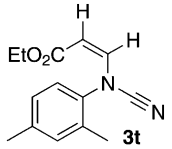
(*Z*)-Ethyl 3-[*N*-(2,3-dimethylphenyl)cyanamido]acrylate (3r): Yellow solid, mp 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.15–7.09 (m, 3H), 6.09 (d, J=9.2 Hz, 1H), 5.34 (d, J=9.2 Hz, 1H), 4.17 (q, J=7.0 Hz, 2H), 2.26 (d, J=10.1 Hz, 6H), 1.26 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.5, 139.1, 138.5, 133.2, 130.5, 126.6, 123.0, 110.0, 104.3, 60.2, 20.0, 13.9, 13.6; IR (KBr): ν=2229 (C≡N), 1714 cm^{-1} (C=O); HR-MS (ESI): m/z=245.1285 $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



3s

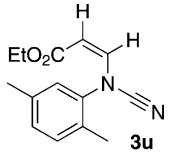
(*Z*)-Ethyl 3-[*N*-(3,4-dimethylphenyl)cyanamido]acrylate (3s): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.13–7.11 (m, 1H), 6.99 (s, 1H), 6.93–6.91 (m, 1H), 6.37 (d, J=8.9 Hz, 1H), 5.58 (d, J=8.9 Hz, 1H), 4.22 (q, J=7.0 Hz, 2H), 2.22 (d, J=10.8 Hz, 6H), 1.28 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.3, 138.2, 137.0, 136.0, 134.8, 130.5, 119.6, 115.8, 108.6, 108.3, 60.4, 19.6, 18.8, 14.0; IR (KBr): ν=2234 (C≡N), 1716 cm^{-1} (C=O); HR-MS (ESI): m/z=245.1295 $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.

(*Z*)-Ethyl 3-[*N*-(2,4-dimethylphenyl)cyanamido]acrylate (3t): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.21–7.19 (m, 1H), 7.09 (s, 1H), 7.06–7.04 (m, 1H), 6.10 (d, J=



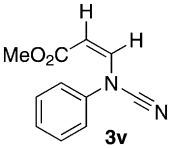
3t

9.2 Hz, 1H), 5.36 (d, J=9.2 Hz, 1H), 4.20 (q, J=7.1 Hz, 2H), 2.33 (d, J=11.2 Hz, 6H), 1.29 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.7, 139.3, 138.5, 136.0, 134.2, 132.3, 128.0, 125.3, 110.1, 104.5, 60.4, 20.8, 17.2, 14.1; IR (KBr): ν=2228 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): m/z=245.1287 $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



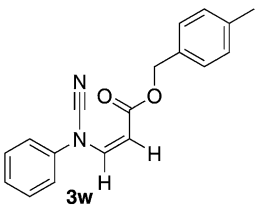
3u

(*Z*)-Ethyl 3-[*N*-(2,5-dimethylphenyl)cyanamido]acrylate (3u): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.18–7.16 (m, 2H), 7.13–7.11 (m, 1H), 6.13 (d, J=9.2 Hz, 1H), 5.40 (d, J=9.2 Hz, 1H), 4.23 (q, J=7.2 Hz, 2H), 2.35 (d, J=6.5 Hz, 6H), 1.32 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.8, 138.4, 138.3, 137.7, 131.7, 131.3, 130.1, 126.0, 104.9, 60.6, 20.7, 17.0, 14.2; IR (KBr): ν=2228 (C≡N), 1713 cm^{-1} (C=O); HR-MS (ESI): m/z=245.1288 $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



3v

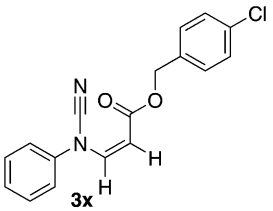
(*Z*)-Methyl 3-(*N*-phenylcyanamido)acrylate (3v): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.44–7.40 (m, 2H), 7.28–7.22 (m, 3H), 6.45 (d, J=8.9 Hz, 1H), 5.68 (d, J=8.9 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.7, 139.2, 135.9, 129.8, 126.4, 118.4, 115.2, 108.9, 51.5; IR (KBr): ν=2231 (C≡N), 1716 cm^{-1} (C=O); HR-MS (ESI): m/z=203.0826 $[M+H]^+$, calcd. for $C_{17}H_{11}N_2O_2$: 203.0821.



3w

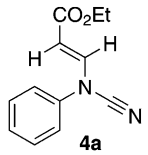
(*Z*)-4-Methylbenzyl 3-(*N*-phenylcyanamido)acrylate (3w): Yellow solid, mp 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.47–7.43 (m, 2H), 7.32 (d, J=7.8 Hz, 2H), 7.29–7.26 (m, 3H), 7.19 (d, J=7.8 Hz, 2H), 6.46 (d, J=8.9 Hz, 1H), 5.71 (d, J=8.9 Hz, 1H), 5.23 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.2, 139.5, 138.2, 136.2, 132.6, 129.9, 129.2, 128.8, 126.5, 118.6, 109.2, 108.4, 66.5, 21.2; IR

(KBr): ν = 2229 (C≡N), 1718 cm^{-1} (C=O): HR-MS (EI): *m/z* = 292.1209 [M$^+$], calcd. for $C_{18}H_{16}N_2O_2$: 292.1212.



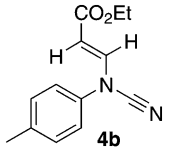
3x

(*Z*)-4-Chlorobenzyl 3-(*N*-phenylcyanamido)acrylate (3x): White solid, mp 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 2H), 7.37–7.30 (m, 5H), 7.27–7.25 (m, 2H), 6.48 (d, *J* = 8.9 Hz, 1H), 5.71 (d, *J* = 8.9 Hz, 1H), 5.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 139.3, 136.5, 134.2, 134.0, 129.9, 129.9, 128.7, 126.6, 118.6, 115.3, 108.6, 65.7; IR (KBr): ν = 2230 (C≡N), 1712 cm^{-1} (C=O); HRMS (EI): *m/z* = 312.0665 [M$^+$], calcd. for $C_{17}H_{13}N_2O_2Cl$: 312.0666.



4a

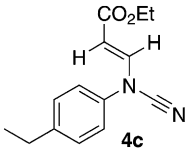
(*E*)-Ethyl 3-(*N*-phenylcyanamido)acrylate (4a): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 13.6 Hz, 1H), 7.50–7.46 (m, 2H), 7.36–7.31 (m, 3H), 5.91 (d, *J* = 13.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 140.7, 137.8, 130.2, 127.4, 119.9, 108.6, 105.1, 60.7, 14.2; IR (KBr): ν = 2232 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): *m/z* = 217.0972 [M+H]$^+$, calcd. for $C_{12}H_{13}N_2O_2$: 217.0977.



4b

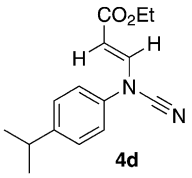
(*E*)-Ethyl 3-(*N*-*p*-tolylcyanamido)acrylate (4b): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 13.6 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 5.82 (d, *J* = 13.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 141.2, 137.5, 135.2, 130.6, 120.0, 108.8, 104.3, 60.5, 20.7, 14.1; IR (KBr): ν = 2230 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): *m/z* = 231.1130 [M+H]$^+$, calcd. for $C_{13}H_{15}N_2O_2$: 231.1134.

(*E*)-Ethyl 3-[*N*-(4-ethylphenyl)cyanamido]acrylate (4c): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 13.6 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.84 (d, *J* = 13.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 144.0, 141.3, 135.4, 129.5, 120.3, 108.9, 104.5, 60.5, 28.2, 15.3, 14.2;



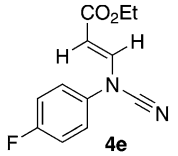
4c

IR (KBr): ν = 2231 (C≡N), 1714 cm^{-1} (C=O); HR-MS (ESI): *m/z* = 245.1288 [M+H]$^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



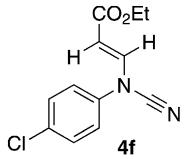
4d

(*E*)-Ethyl 3-[*N*-(4-isopropylphenyl)cyanamido]acrylate (4d): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 13.6 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.82 (d, *J* = 13.6 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 2.95–2.88 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 148.4, 141.2, 135.3, 128.0, 120.1, 108.7, 104.3, 60.4, 33.5, 23.7, 14.1; IR (KBr): ν = 2230 (C≡N), 1719 cm^{-1} (C=O); HR-MS (ESI): *m/z* = 259.1449 [M+H]$^+$, calcd. for $C_{15}H_{19}N_2O_2$: 259.1447.



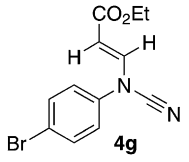
4e

(*E*)-Ethyl 3-[*N*-(4-fluorophenyl)cyanamido]acrylate (4e): White solid, mp 59–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 13.6 Hz, 1H), 7.30–7.27 (m, 2H), 7.16–7.12 (m, 2H), 5.79 (d, *J* = 13.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 161.3 (d, $J_{C,F}$ = 247.3 Hz), 141.1, 133.7 (d, $J_{C,F}$ = 3.0 Hz), 122.5 (d, $J_{C,F}$ = 8.6 Hz), 117.1 (d, $J_{C,F}$ = 23.3 Hz), 108.6, 104.8, 60.5, 14.1; IR (KBr): ν = 2231 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): *m/z* = 235.0878 [M+H]$^+$, calcd. for $C_{12}H_{12}N_2O_2F$: 235.0883.



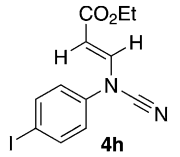
4f

(*E*)-Ethyl 3-[*N*-(4-chlorophenyl)cyanamido]acrylate (4f): Yellow solid, mp 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 13.6 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 5.90 (d, *J* = 13.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 140.0, 136.2, 132.9, 130.2, 121.0, 108.0, 105.4, 60.6, 14.1; IR (KBr): ν = 2233 (C≡N), 1716 cm^{-1} (C=O); HR-MS (ESI): *m/z* = 251.0587 [M+H]$^+$, calcd. for $C_{12}H_{12}N_2O_2Cl$: 251.0587.



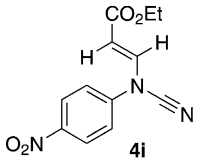
4g

(*E*)-Ethyl 3-[*N*-(4-bromophenyl)cyanamido]acrylate (4g): White solid, mp 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 13.6 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 5.89 (d, J = 13.5 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 139.9, 136.8, 133.2, 121.2, 120.6, 108.0, 105.6, 60.7, 14.1; IR (KBr): ν = 2231 (C≡N), 1714 cm^{-1} (C=O); HR-MS (ESI): m/z = 295.0081 $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2Br$: 295.0082.



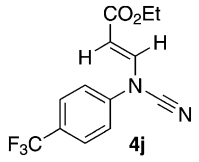
4h

(*E*)-Ethyl 3-[*N*-(4-iodophenyl)cyanamido]acrylate (4h): White solid, mp 95–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 13.6 Hz, 1H), 7.08 (d, J = 8.6 Hz, 2H), 5.93 (d, J = 13.6 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 139.8, 139.2, 137.6, 121.3, 108.0, 105.8, 91.4, 60.7, 14.2; IR (KBr): ν = 2232 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): m/z = 342.9942 $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2I$: 342.9943.



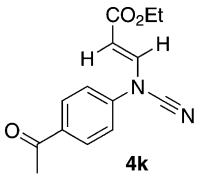
4i

(*E*)-Ethyl 3-[*N*-(4-nitrophenyl)cyanamido]acrylate (4i): Yellow solid, mp 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, J = 9.1 Hz, 2H), 7.65 (d, J = 13.5 Hz, 1H), 7.49 (d, J = 9.1 Hz, 2H), 6.10 (d, J = 13.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 145.7, 142.6, 137.8, 125.9, 118.5, 108.0, 106.9, 61.1, 14.2; IR (KBr): ν = 2241 (C≡N), 1723 cm^{-1} (C=O); HR-MS (ESI): m/z = 262.0823 $[M+H]^+$, calcd. for $C_{12}H_{12}N_3O_4$: 262.0828.



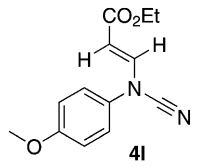
4j

(*E*)-Ethyl 3-{*N*-[4-(trifluoromethyl)phenyl]cyanamido}-acrylate (4j): White solid, mp 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 13.5 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H), 6.01 (d, J = 13.5 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 140.6, 138.9, 129.1 (q, $J_{C,F}$ = 33.2 Hz), 127.5 (q, $J_{C,F}$ = 3.8 Hz), 123.4 (q, $J_{C,F}$ = 270.5 Hz), 119.0, 107.5, 106.7, 60.8, 14.1; IR (KBr): ν = 2238 (C≡N), 1714 cm^{-1} (C=O); HR-MS (ESI): m/z = 285.0849 $[M+H]^+$, calcd. for $C_{13}H_{12}N_2O_2F_3$: 285.0851.



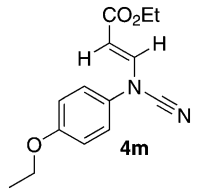
4k

(*E*)-Ethyl 3-[*N*-(4-acetylphenyl)cyanamido]acrylate (4k): White solid, mp 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 13.6 Hz, 1H), 7.38 (d, J = 8.6 Hz, 2H), 6.00 (d, J = 13.5 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.60 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 165.5, 141.2, 138.7, 135.3, 130.4, 118.3, 107.4, 106.6, 60.8, 26.4, 14.2; IR (KBr): ν = 2242 (C≡N), 1714 (C=O), 1701 cm^{-1} (C=O); HR-MS (ESI): m/z = 259.1079 $[M+H]^+$, calcd. for $C_{14}H_{15}N_2O_3$: 259.1083.



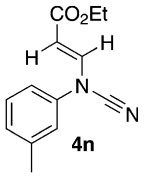
4l

(*E*)-Ethyl 3-[*N*-(4-methoxyphenyl)cyanamido]acrylate (4l): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 13.6 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 5.69 (d, J = 13.4 Hz, 1H), 4.17 (q, J = 7.0 Hz, 2H), 3.78 (s, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 159.0, 142.1, 130.3, 122.7, 115.1, 109.2, 103.7, 60.3, 55.4, 14.1; IR (KBr): ν = 2229 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): m/z = 247.1078 $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_3$: 247.1083.

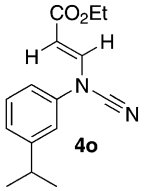


4m

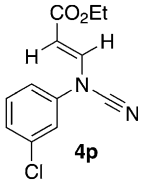
(*E*)-Ethyl 3-[*N*-(4-ethoxyphenyl)cyanamido]acrylate (4m): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 13.6 Hz, 1H), 7.20 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.71 (d, J = 13.6 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 4.02 (q, J = 6.9 Hz, 2H), 1.40 (t, J = 6.9 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 158.4, 142.2, 130.2, 122.8, 115.7, 109.3, 103.7, 63.8, 60.4, 14.5, 14.1; IR (KBr): ν = 2229 (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): m/z = 261.1240 $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_3$: 261.1239.



(*E*)-Ethyl 3-(*N*-*m*-tolylcyanamido)acrylate (4n): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.54$ (d, $J = 13.6$ Hz, 1H), 7.36–7.32 (m, 1H), 7.14–7.09 (m, 3H), 5.88 (d, $J = 13.6$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.40 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.0$, 140.8, 140.6, 137.7, 129.9, 128.1, 120.4, 116.8, 108.6, 104.8, 60.6, 21.3, 14.2; IR (KBr): $\nu = 2234$ (C≡N), 1716 cm^{-1} (C=O); HR-MS (ESI): $m/z = 231.1131$ $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_2$: 231.1134..

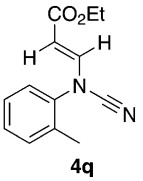


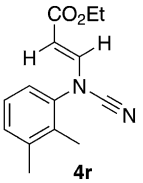
(*E*)-Ethyl 3-[*N*-(3-isopropylphenyl)cyanamido]acrylate (4o): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (d, $J = 13.6$ Hz, 1H), 7.38–7.34 (m, 1H), 7.19–7.17 (m, 1H), 7.14 (s, 1H), 7.11–7.09 (m, 1H), 5.88 (d, $J = 13.6$ Hz, 1H), 4.22 (q, $J = 7.0$ Hz, 2H), 2.97–2.90 (m, 1H), 1.29 (t, $J = 7.7$ Hz, 3H), 1.25 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.9$, 151.5, 140.9, 137.7, 130.0, 125.5, 118.0, 117.2, 108.6, 104.6, 60.5, 34.0, 23.6, 14.1; IR (KBr): $\nu = 2233$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 259.1449$ $[M+H]^+$, calcd. for $C_{15}H_{19}N_2O_2$: 259.1447.



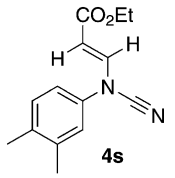
(*E*)-Ethyl 3-[*N*-(3-chlorophenyl)cyanamido]acrylate (4p): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.51$ (d, $J = 13.5$ Hz, 1H), 7.42–7.38 (m, 1H), 7.32–7.29 (m, 2H), 7.23–7.21 (m, 1H), 5.93 (d, $J = 13.6$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.6$, 139.6, 138.8, 136.0, 131.1, 127.4, 119.8, 117.5, 107.8, 105.9, 60.8, 14.2; IR (KBr): $\nu = 2235$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 251.0584$ $[M+H]^+$, calcd. for $C_{12}H_{12}N_2O_2Cl$: 251.0587.

(*E*)-Ethyl 3-(*N*-*o*-tolylcyanamido)acrylate (4q): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (d, $J = 13.6$ Hz, 1H),7.35–7.32 (m, 2H), 7.30–7.25 (m, 2H), 5.41 (d, $J = 13.6$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 2.36 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.8$, 143.8, 135.4, 134.7, 132.0, 130.0, 127.9, 126.4, 109.9, 102.8, 60.4, 17.2, 14.1; IR (KBr): $\nu = 2229$ (C≡N), 1714 cm^{-1} (C=O); HR-MS (ESI): $m/z = 231.1134$ $[M+H]^+$, calcd. for $C_{13}H_{15}N_2O_2$: 231.1134.

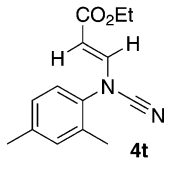




(*E*)-Ethyl 3-[*N*-(2,3-dimethylphenyl)cyanamido]acrylate (4r): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$ (d, $J = 13.6$ Hz, 1H), 7.22–7.21 (m, 1H), 7.18–7.14 (m, 1H), 7.10–7.08 (m, 1H), 5.34 (d, $J = 13.6$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 2.29 (s, 3H), 2.20 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.7$, 144.0, 139.4, 135.3, 133.3, 131.3, 127.0, 123.9, 110.1, 102.4, 60.2, 20.0, 14.0, 13.6; IR (KBr): $\nu = 2230$ (C≡N), 1715 cm^{-1}) (C=O); HR-MS (ESI): $m/z = 245.1285$ $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.

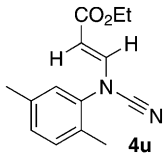


(*E*)-Ethyl 3-[*N*-(3,4-dimethylphenyl)cyanamido]acrylate (4s): Yellow solid, mp 62–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.51$ (d, $J = 13.6$ Hz, 1H), 7.21–7.19 (m, 1H), 7.08 (s, 1H), 7.04–7.01 (m, 1H), 5.83 (d, $J = 13.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.29 (d, $J = 10.3$ Hz, 6H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.0$, 141.3, 138.9, 136.2, 135.4, 131.0, 121.3, 117.5, 108.9, 104.2, 60.5, 19.8, 19.1, 14.2; IR (KBr): $\nu = 2233$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 245.1295$ $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



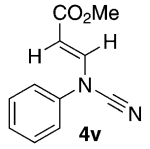
(*E*)-Ethyl 3-[*N*-(2,4-dimethylphenyl)cyanamido]acrylate (4t): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$ (d, $J = 13.6$ Hz, 1H), 7.14–7.08 (m, 3H), 5.37 (d, $J = 13.6$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 2.33 (d, $J = 16.1$ Hz, 6H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.9$,

144.1, 140.3, 134.4, 132.8, 132.6, 128.5, 126.2, 110.2, 102.5, 60.4, 21.0, 17.1, 14.1; IR (KBr): $\nu = 2228$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 245.1287$ $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



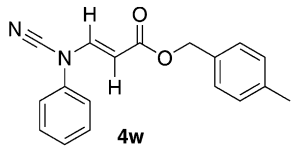
4u

(*E*)-Ethyl 3-[*N*-(2,5-dimethylphenyl)cyanamido]acrylate (4u): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$ (d, $J = 13.6$ Hz, 1H), 7.21–7.15 (m, 2H), 7.07 (s, 1H), 5.41 (d, $J = 13.6$ Hz, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.32 (d, $J = 15.4$ Hz, 6H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.9$, 143.9, 138.0, 135.2, 131.8, 131.4, 130.8, 126.7, 110.1, 102.7, 60.4, 20.6, 16.7, 14.2; IR (KBr): $\nu = 2231$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 245.1288$ $[M+H]^+$, calcd. for $C_{14}H_{17}N_2O_2$: 245.1290.



4v

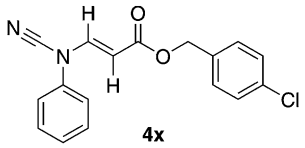
(*E*)-Methyl 3-(*N*-phenylcyanamido)acrylate (4v): Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (d, $J = 13.6$ Hz, 1H), 7.47–7.44 (m, 2H), 7.33–7.29 (m, 3H), 5.88 (d, $J = 13.6$ Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.2$, 140.8, 137.7, 130.1, 127.3, 119.7, 108.4, 104.4, 51.6; IR (KBr): $\nu = 2234$ (C≡N), 1715 cm^{-1} (C=O); HR-MS (ESI): $m/z = 203.0826$ $[M+H]^+$, calcd. for $C_{17}H_{11}N_2O_2$: 203.0821.



4w

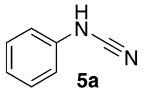
(*E*)-4-Methylbenzyl 3-(*N*-phenylcyanamido)acrylate (4w): Yellow solid, mp 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (d, $J = 13.6$ Hz, 1H), 7.50–7.46 (m, 2H), 7.36–7.28 (m, 5H), 7.21–7.19 (m, 2H), 5.94 (d, $J = 13.6$ Hz, 1H), 5.19 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.9$, 141.1, 138.2, 137.8, 132.8, 130.2, 129.3, 128.4, 127.5, 120.0, 108.5, 104.8, 66.4, 21.2; IR (KBr): $\nu = 2232$ (C≡N), 1712 cm^{-1} (C=O); HR-MS (EI): $m/z = 292.1209$ $[M^+$, calcd. for $C_{18}H_{16}N_2O_2$: 292.1212.

(*E*)-4-Chlorobenzyl 3-(*N*-phenylcyanamido)acrylate (4x): Yellow solid, mp 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (d, $J = 13.6$ Hz, 1H), 7.50–7.46 (m, 2H), 7.37–7.35 (m, 3H), 7.33–7.31 (m, 4H), 5.94 (d, $J = 13.6$ Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.7$, 141.5, 137.7, 134.3, 134.3, 130.2, 129.6, 128.8, 127.6, 120.0, 108.5, 104.4, 65.6; IR (KBr): $\nu = 2233$ (C≡N), 1716 cm^{-1} (C=O); HRMS



4x

(EI): $m/z = 312.0665$ $[M]^+$, calcd. for $C_{17}H_{13}N_2O_2Cl$: 312.0666.



5a

***N*-Phenylcyanamide (5a):**[13b] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (s, 1H), 7.38–7.34 (m, 2H), 7.12–7.09 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.2$, 129.6, 123.4, 115.4, 111.9; IR (KBr): $\nu = 2233$ cm^{-1} (C≡N).

Acknowledgements

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