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Synthesis of Imidazolidin-2-ones and Imidazol-2-ones via Base-Catalyzed Intramolecular Hydroamidation of Propargylic Ureas under Ambient Conditions

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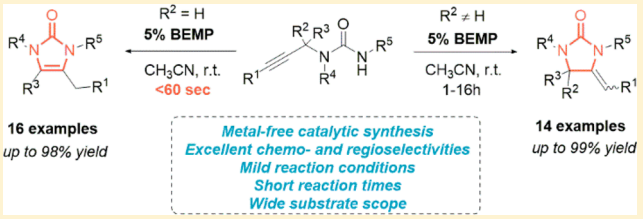
Supporting Information

ABSTRACT: The first organo-catalyzed synthesis of imidazolidin-2-ones and imidazol-2-ones via intramolecular hydroamidation of propargylic ureas is reported. The phosphazene base BEMP turned out to be the most active organo-catalyst compared with guanidine and amidine bases. Excellent chemo- and regioselectivities to five-membered cyclic ureas have been achieved under ambient conditions, with a wide substrate scope and exceptionally short reaction times (down to 1 min). A base-mediated isomerization step to an allenamide intermediate is the most feasible reaction pathway to give imidazol-2-ones, as suggested by DFT studies.



INTRODUCTION

Imidazol-2-ones and their analogues are omnipresent structural motifs of bioactive pharmaceutical compounds and natural alkaloids (Figure 1).[1] Five-membered cyclic ureas are also flexible key intermediates in synthetic transformations[2] and useful chiral auxiliaries in enantioselective syntheses.[3]

The high value of these heterocycles for synthetic and pharmaceutical chemistry has driven continuous efforts in the development of sustainable and more efficient protocols. Traditional synthetic routes to imidazolidin-2-ones are mainly based on the carbonylation of diamines,[4] which can require toxic carbonylating agents, high-pressure facilities, and harsh reaction conditions. Metal-catalyzed diamination of olefins[5] and aziridine ring expansion[6] are elegant strategies; however, the widespread application suffers from their inherent sophistication. The intramolecular hydroamidation approach[7] offers a powerful, atom- and step-economical alternative route to easily access richly decorated five-membered cyclic ureas.[4a,8,9] In this context, propargylureas have been extensively investigated as readily available precursors for the synthesis of both imidazolin-2-ones and imidazolidin-2-ones. The control of chemo- (O vs N cyclization) and regio- (exo- vs endo-) selectivity in the cyclization step is generally addressed by means of transition metal catalysts.[8a−h,8,10] As a relevant example, a Ag(I)-catalyzed one-pot protocol for the synthesis of 2-imidazolones through cycloisomerization of an *in situ* formed propargylic urea was disclosed by Van der Eycken in 2011.[8d] More recently, Reddy and co-workers have reported the synthesis of indole-fused cyclic urea derivatives through a Ag-catalyzed sequence that involves an elegant double intramolecular hydroamidation process.[8b] These interesting methods require however a high catalyst loading (up to 30 mol %) and harsh reaction conditions. More sustainable metal-free protocols to efficiently access imidazol-2-ones and imidazoli-

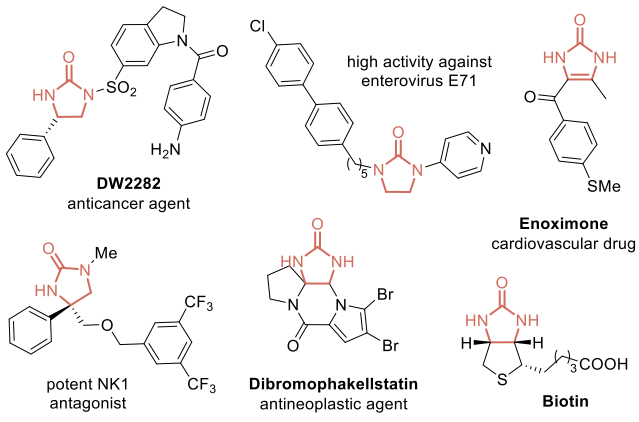


Figure 1. Selected bioactive 2-imidazol(idin)one derivatives.

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din-2-ones from propargylic ureas have been also developed by using a *stoichiometric* amount of bases or salts.[9] For instance, Dethe and Lubell have recently proposed the use of NaOH[9a] and NaH[9b] for the synthesis of imidazole-2-thione and *N*-amino-imidazolin-2-ones, respectively, under mild conditions. Despite the usefulness of these methods, a base-*catalyzed* intramolecular hydroamidation approach to imidazol-2-one derivatives is still in high demand and, to date, totally unprecedented.

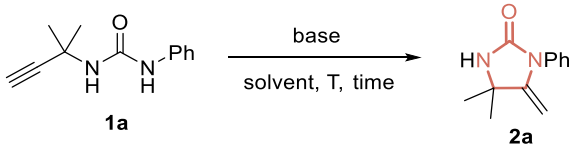
Herein, we disclose the first base-catalyzed intramolecular hydroamidation of propargylic ureas to highly substituted imidazolidin-2-ones and imidazol-2-ones. Notable features of our methodology include (i) excellent chemo- and regioselectivity to five-membered cyclic ureas, (ii) a wide substrate scope and high functional group tolerance, (iii) very mild reaction conditions, and (iv) remarkably short reaction times. Further, thanks to key mechanistic insights on the reaction pathway, we demonstrated the feasibility of a one-pot step-economical protocol starting from propargyl amines and isocyanates.

RESULTS AND DISCUSSION

Inspired by our recent studies on the base-catalyzed synthesis of imidazolidin-2-ones from propargylamines, CO_2, and primary amines,[11] we started to investigate the intramolecular hydroamidation reaction of propargylic ureas.[12] Guanidine base TBD, widely exploited in a plethora of catalytic transformations,[13] including the above-mentioned synthesis of imidazolidin-2-ones,[11] was initially employed as a catalyst for the hydroamidation of propargylic urea **1a** (Table 1) using similar reaction conditions. We found that propargylic urea **1a** in the presence of 10% of TBD at 100 °C in anhydrous acetonitrile converted quantitatively to imidazolidinone **2a** (Table 1, entry 1). Excellent results were also achieved at lower temperatures (Table 1, entries 2 and 3), and therefore, subsequent experiments were tested at rt (22−23 °C). A series of similar organic bases were then evaluated (Table 1, entries 4−7). MTBD and BTMG were found to be less effective, leading to imidazolidinone **2a** in 82% and 67% yield, respectively (Table 1, entries 4 and 5). On the contrary, DBU and TMG turned out to be totally inactive in promoting the desired cyclization (Table 1, entries 6 and 7). Notably, the catalytic activity seemed to follow the strength of the bases. We then resorted to 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), which is a stronger base that proved to be useful in other hydroamination reactions.[14] Gratifyingly, the use of 10 mol % of BEMP afforded **2a** in quantitative yield (Table 1, entry 8). Furthermore, the reaction time decreased dramatically to 30 min. This significant improvement allowed us to decrease the amount of catalyst down to 1 mol %, while still maintaining high reaction performance (Table 1, entries 9 and 10). Other solvents were then tested (Table 1, entries 11−13), and we found that MeCN was crucial to trigger an efficient reaction. Notably, the presence of water in the mixture, detrimental for other protocols,[8d,9b] did not affect the final outcome (Table 1, entry 14). Finally, no reaction took place in the control experiment in the absence of catalyst (Table 1, entry 15).

To illustrate the scope of this methodology, a series of propargyl ureas bearing a quaternary carbon α to the triple bond were then prepared. Under optimal conditions (Table 1, entry 9), propargylic ureas **1a−l** reacted smoothly to give the corresponding imidazolidin-2-ones **2a−l** in excellent yields

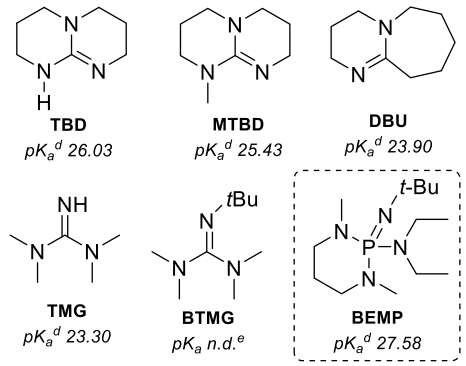
Table 1. Optimization Study[a]



1a **2a**

entry	base (mol %)	solvent	T (°C)	time (h)	yield (%)[b] **2a**
1	TBD (10)	MeCN	100	24	99
2	TBD (10)	MeCN	50	24	99
3	TBD (10)	MeCN	rt	24	99
4	MTBD (10)	MeCN	rt	24	82
5	BTMG (10)	MeCN	rt	24	67
6	DBU (10)	MeCN	rt	24	–
7	TMG (10)	MeCN	rt	24	–
8	BEMP (10)	MeCN	rt	0.5	99
9	BEMP (5)	MeCN	rt	1	99
10	BEMP (1)	MeCN	rt	7	93
11	BEMP (5)	EtOAc	rt	24	–
12	BEMP (5)	THF	rt	24	–
13	BEMP (5)	MeOH	rt	24	–
14	BEMP (5)	MeCN[c]	rt	1	99
15	–	MeCN	rt	24	–

[a]Reaction conditions: **1a** (0.4 mmol), base (1−10 mol %), solvent (4 mL). [b]Yields of **2a** were determined via ^{1}H NMR analysis using methylbenzoate as internal standard. [c]0.4 mmol (1 equiv) of H_2O was added. [d]pK_a is referred to its conjugate acid in MeCN.[13] [e]Not determined.[14]



(Table 2). Reactions reached completion within 1 to 16 h at rt. Both electron-donating (Me) and electron-withdrawing (F, CO_2Me) groups on the aryl substituent were well tolerated in this simple and robust methodology (**2b−d**, 82−98%). The reaction rate is slower increasing the hindrance on the carbon α to the triple bond (**2e** and **2f**, 3 and 16 h). However, the presence of a substituent on the nitrogen β to the triple bond caused a lower yield of the corresponding cyclic urea, as shown in the case of **2g** (R^3 = Bn, 52%). Propargylic ureas bearing an internal triple bond led to the corresponding imidazolidin-2-ones in high yield (**2h−l**, 83−97%). Aryl and alkyl groups on the triple bond were well tolerated. In all cases, the *Z* product was the preferred one,[15] although the stereocontrol was not complete. Ureas bearing an alkyl substituent in R^4, such as *n*-Bu, were unreactive under these optimized conditions. Interestingly, urea **1m** that bears an ester group in a suitable position (R^4 = CH_2CO_2Et) led to hydantoin **2m′** (72%),[9c] leaving the triple bond untouched.

We also tested the reactivity of a propargylic thiourea, which is reported to give imidazole-2-thiones under basic conditions.[9a] On the contrary, thiazolidin-2-imine **2n′** was

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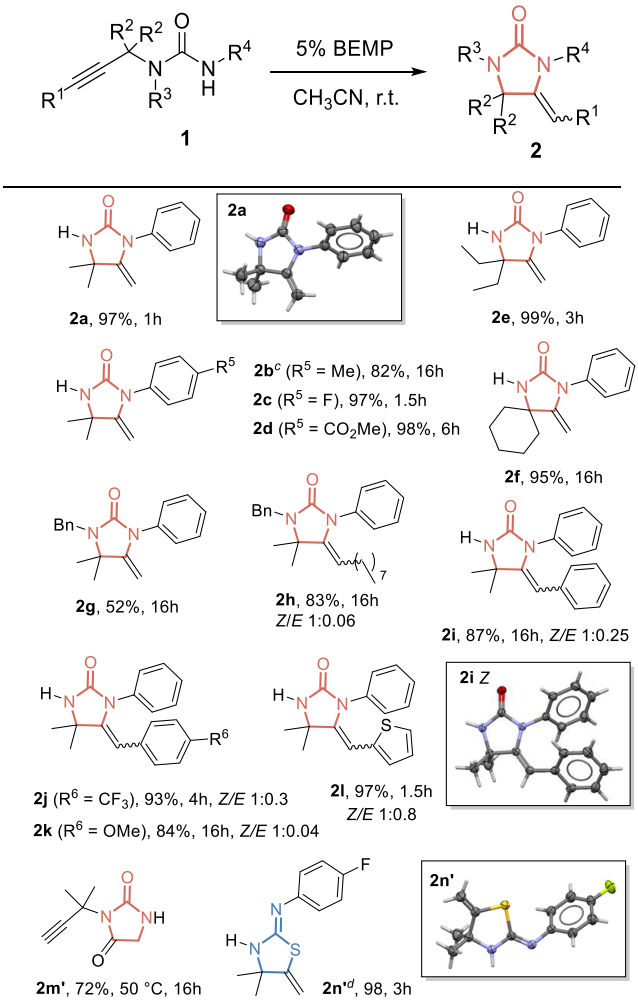
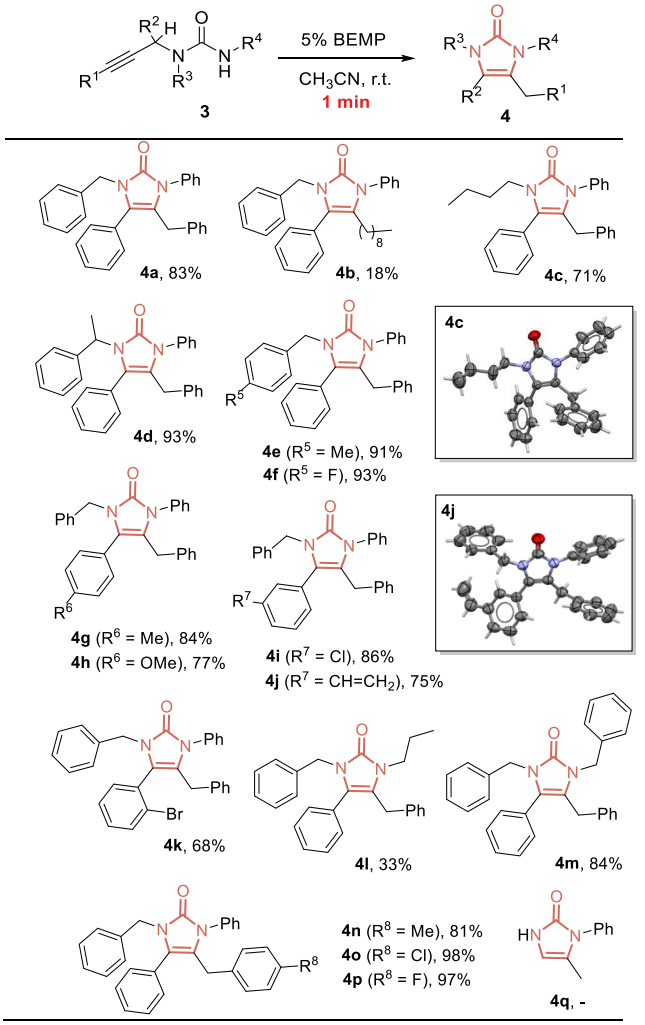
Table 2. Scope of the BEMP-Catalyzed Synthesis of Imidazolidin-2-ones 2[a,b]



[a]Reaction conditions: **1** (0.4 mmol), BEMP (5 mol %), MeCN (4 mL), room temperature. [b]Yields of **2**. [c]The reaction was performed at 40 °C. [d]Compound **2n′** was obtained directly from propargylic amine and isothiocyanate without catalyst (see SI for details).

Table 3. Scope of the BEMP-Catalyzed Synthesis of Imidazol-2-ones 4[a,b]



[a]Reaction conditions: **3** (0.4 mmol), BEMP (5 mol %), MeCN (4 mL), room temperature, 1 min. [b]Yields of **4**.

selectively obtained directly from propargylic amine and isothiocyanate precursors through intramolecular S-cyclization without a catalyst. The structure of **2n′** was undoubtedly confirmed by SC-XRD (see the Supporting Information (SI) for details).[15]

We then further explored the substrate scope of the transformation by employing a variety of propargylic ureas **3** bearing a tertiary carbon α to the triple bond (Table 3). In this case, selective formation of imidazol-2-ones **4** was observed, with a formal double bond shift from the exo- to the endocyclic position. To our delight, reaction times were impressively shortened. Upon reagent mixing, the reaction completes in about 1 min. The protocol was again characterized by a remarkable tolerance of valuable functional groups, including Cl (**4i**, 86%), Br (**4k**, 68%), F (**4f**, 93%), OMe (**4h**, 77%), or vinyl (**4j**,[15] 75%) substituents. It is worth noting that this ample tolerance ensures vast handles for further functionalizations. Alkyl substituents on the triple bond (R^1) or on terminal nitrogen (R^4) gave low yields, as shown for example for **4b** and **4l** (18% and 33% yield, respectively). Alkyl or benzyl substituents on nitrogen β to the triple bond (R^3) led to an excellent yield of product **4**, even for more sterically demanding groups, as in the case of **4d** (93% yield). This is complementary to the trend observed with products **2** (**2g**, Table 2). Electronic effects exerted by substituents in the *para* position on the aromatic ring (R_1) were also explored. Urea **3n** bearing a tolyl group on the triple bond (R^1 = 4-MeC_6H_4) led to the corresponding imidazolone **4n** in 81% yield, which is slightly less than those observed for **4a** (R^1 = C_6H_5). The best results were obtained with electron-withdrawing groups, such as Cl (**4o**, 98%) and F (**4p**, 97%). Finally, the unsubstituted propargylic urea **3q** (R^1, R^2, R^3 = H) did not provide the corresponding imidazolone **4q**, being unreactive under these conditions.

To further demonstrate the applicability of this protocol, the one-pot synthesis of imidazol-2-one derivatives starting from propargylic amines and isocyanates was performed under standard conditions. Gratifyingly, compound **2a** was quantitatively obtained in 1 h from 2-methylbut-3-yn-2-amine and phenyl isocyanate (Scheme 1a). Without further optimization, imidazolinone **4a** was synthesized directly from the propargyl-

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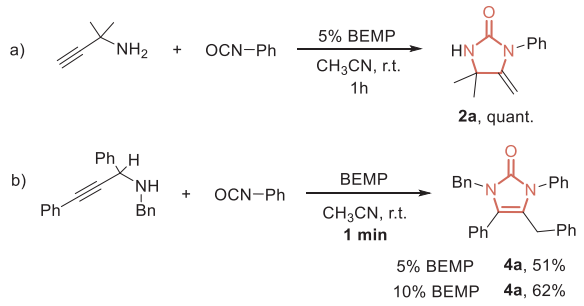
Scheme 1. Representative Examples of the One-Pot Synthesis of Imidazolidin-2-one 2a and Imidazolin-2-one 4a from Propargylic Amines and Isocyanates



amine **3a** and phenyl isocyanate in 62% yield, using 10 mol % of BEMP (Scheme 1b). Noteworthy, this intermolecular reaction was still complete within 1 min.

Intrigued by the complete chemoselectivity and site selectivity features as well as by the unexpectedly fast formation of imidazol-2-ones **4** under very mild conditions, we carried out computational studies to gain insights into the reaction mechanism. Investigation began by employing the Gaussian09 package[16] using the range separated, hybrid ωb97xd functional.[17] The possible reaction routes have been studied in terms of solvent-corrected Gibbs free energy values (see SI for details). Figure 2 shows the most feasible

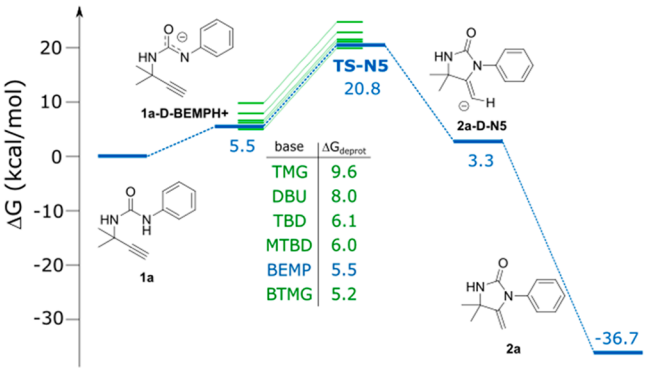


Figure 2. Gibbs free energy profile of the formation of imidazolidin-2-one **2a** (N-5-exo-dig cyclization pathway). Color code used for the effect of bases: (blue) BEMP as base; (green, from top to bottom) TMG, DBU, TBD, MTBD, BTMG as base.[21]

mechanism to generate imidazolidin-2-one **2a** from propargylic urea **1a**. The reaction starts with the abstraction of the most acidic urea proton by the base, which is a slightly endergonic process. We obtained good correlation between the pK_a of the bases and the energonicity of the deprotonation step.[18] The levels obtained with the strongest base (BEMP) are shown in blue. The deprotonation yields **1a-D-BEMPH+** (ΔG +5.5 kcal/mol). We observed that, upon this proton transfer, the conjugated acid/base pair dissociates as higher ΔG values were obtained modeling a tight ion pair. We explained this by the entropy penalty of the association of the two ions,[19] and also by the enhanced solvation of the two independent ions which together boost therefore dissociation in the polar MeCN solvent. The deprotonated urea can then react with the triple bond in four different ways depending on the cyclization fashion. *N*- or *O*-carbon bond formation occurs via either 5-exo- or 6-endo-dig cyclization modes. The formation of the anionic form of product **2a** (**2a-D-N5**) is the most favorable pathway both kinetically and thermodynamically (not shown here; see SI, Figure S1). Eventually, the cyclization is followed by the strongly exergonic protonation yielding the product **2a** (ΔG −36.7 kcal/mol). The rate-determining step is the cyclization, which requires a moderate 20.8 kcal/mol activation free energy (from **1a** to **TS-N5**) in the presence of BEMP. This is fully compatible with the observed reaction rate.[20] The calculated trend among different bases evenly correlates with the experimental results listed in Table 1. Indeed, stronger bases proved to be better catalysts, as they can more easily deprotonate the substrate (Figure 2).

Second, formation of imidazol-2-one **4a** from **3a** was investigated. The initial base-catalyzed isomerization of the triple bond to the corresponding allenamide was the most favored pathway to imidazol-2-ones **4a** (Figure 3, blue

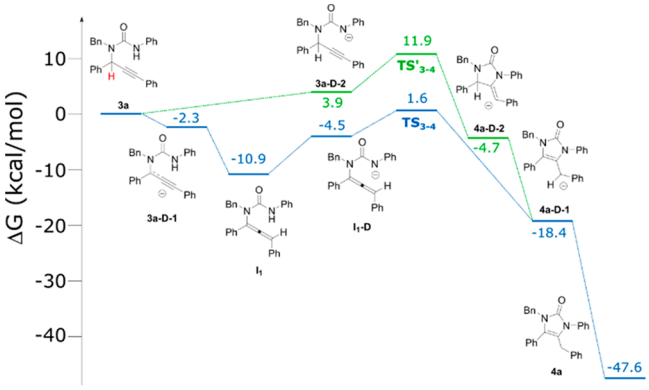


Figure 3. Gibbs free energy profile of the formation of imidazol-2-one **4a**, employing BEMP as catalyst. Blue profile: allene-route. Green profile: mechanism analogue to the one presented in Figure 2.

pathway). The proton of **3a** highlighted in red became the most acidic one. This ensures that the initial allenamide formation is preferred to urea deprotonation (Figure 3, green pathway). Hence, the resting state under the reaction conditions is allenamide $\mathbf{I_1}$. Isomerization of the propargylic arm to the corresponding allenamide is highly plausible under strongly basic conditions.[22] Then, the N−H deprotonation can occur and leads to the formation of the imidazol-2-one ring (**4a-D-1**) through a low barrier transition state. The final protonation yields the neutral product in a highly exergonic step. The calculations confirmed that the central carbon of the allene moiety is the most electron-deficient,[23] which explains the preference for the five-membered ring formation. The barrier for the cyclization step is only 12.5 kcal/mol (from $\mathbf{I_1}$ to $\mathbf{TS_{3-4}}$). This suggests a very fast reaction, in perfect agreement with the experimental observations.[24]

■ CONCLUSION

In summary, we have developed the first organo-catalyzed method to access imidazolidin-2-ones and imidazol-2-ones from propargylureas under ambient conditions. The protocol is simple, tolerates the presence of water, and provides five-membered cyclic ureas with excellent space−time yields. DFT calculations provided support for the nonassisted cyclization of deprotonated urea in the imidazolidin-2-one formation and revealed the involvement of an allene intermediate in the imidazol-2-one pathway. The one-pot protocol starting from propargylic amines and isocyanates was also demonstrated. We

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anticipate that the unique features of this method will ensure wide interest and vast application within the chemistry community at large.

EXPERIMENTAL SECTION

General Methods. All chemicals were purchased from commercial sources and used as received, unless otherwise noted. Solvents were dried and stored over molecular sieves previously activated in an oven (450 °C overnight). Organocatalyzed reactions were carried out under nitrogen using standard Schlenk techniques. Reactions were analyzed by thin layer chromatography (TLC) on silica gel 60 F254. GC analyses were performed with an Agilent Tenchnologies 7820A equipped with an FID detector and a 30 m capillary column. GC-MS analyses (*m*/*z*, relative intensity%) were performed with an Agilent Technologies 6890N gas chromatograph coupled to a 5973N mass selective detector (Agilent Technologies) working at 70 eV ionizing voltage. Column chromatography was performed on silica gel 60 (70−230 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 300 K on a Bruker Avance 400 or 300 MHz using the solvent as the internal standard (7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR for $CDCl_3$). The terms m, s, d, t, q, and quint represent multiplet, singlet, doublet, triplet, quadruplet, and quintuplet, respectively, and the term br means a broad signal. Exact masses were recorded on an LTQ ORBITRAP XL Thermo Mass Spectrometer (ESI source). Melting points were measured with an electrothermal apparatus and are uncorrected.

Experimental Procedures. *Synthesis of Propargylic Ureas **1a−f, 1m, 3q**.*[25] A dry round-bottom two-necked flask, containing a magnetic stir bar, was charged with the selected isocyanate (2.5 mmol), the desired propargylic amine (2.5 mmol), and dry THF (25 mL). The resulting mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. Yields were quantitative, and propargylic ureas **1a−f**, **1m**, and **3q** were employed without further purification.

*Synthesis of Propargylic Ureas **1i−l** through Sonogashira Coupling.*[26] A Schlenk-type flask equipped with a magnetic stir bar was charged with $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 2 mol %, 14 mg), CuI (0.07 mmol, 7 mol %, 13 mg), and Et_3N (5 mL) under an inert atmosphere (N_2). The aryl iodide (1 mmol, 1 equiv) and the propargylic urea (1.2 equiv) were dissolved in dry CH_2Cl_2(7 mL) and then added. The reaction mixture was stirred at room temperature overnight. The crude mixture was filtered through a fritted funnel, the solid residue was washed with CH_2Cl_2, and the combined organic solutions were concentrated under reduced pressure. Purification via flash column chromatography yielded the desired propargyl urea.

*Synthesis of Propargylic Urea **1g**.*[27] A solution of 2-methylbut-3-yn-2-amine (5 mmol, 519 μL) and benzaldehyde (5 mmol, 507 μL) in MeOH (10 mL) was stirred at room temperature overnight. Sodium borohydride (10 mmol, 378 mg) was then added to the reaction mixture at 0 °C for 1 h under stirring. Then the reaction crude was diluted with water (25 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography (Eluent: hexane/ethyl acetate 7:3) to afford *N*-benzyl-2-methylbut-3-yn-2-amine in 55% yield (476 mg).

A dry round-bottom two-necked flask, containing a magnetic stir bar, was charged with phenyl isocyanate (2.5 mmol, 297 mg), *N*-benzyl-2-methylbut-3-yn-2-amine (2.5 mmol, 432 mg), and dry THF (25 mL).[25] The resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The yield is quantitative, and propargylic urea **1g** was employed without further purification.

Synthesis of N-Benzyl-2-methyldodec-3-yn-2-amine.[28] A test tube equipped with a magnetic stirrer was charged with CuI (0.6 mmol, 30% mol, 114 mg). The test tube was sealed and flushed with N_2 and then was charged with dec-1-yne (2 mmol, 361 μL), acetone (2 mmol, 147 μL), and benzylamine (2 mmol, 219 μL). The test tube was then placed in an oil bath at 75 °C, and it was allowed to stir overnight. The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (206 mg, 31% yield) as a transparent oil.

Synthesis of α-Monosubstituted Propargylic Amines.[28] In a typical experiment, CuI (0.6 mmol, 30% mol, 114 mg) was charged in a test tube equipped with a magnetic stirrer. The test tube was sealed and flushed with N_2 and then was charged with the alkyne (2 mmol), the aldehyde (2 mmol), and the amine (2 mmol). The test tube was then placed in an oil bath at 75 °C, and it was allowed to stir overnight. The crude reaction mixture was purified by silica gel column chromatography with a mixture of hexane/ethyl acetate (from 95:5 to 80:20) to provide the desired secondary propargylic amine.

*Synthesis of Propargylic Ureas **1h** and **3a−p**.*[25] A dry round-bottom two-necked flask, containing a magnetic stir bar, was charged with the selected isocyanate (1 mmol), the desired propargylic amine (1 mmol), and dry THF (10 mL). The resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. Yields were quantitative for propargylic ureas **3a−k**, **3n−p**, which were employed without further purification. Silica gel column chromatography (Eluent: hexane/ethyl acetate) was required to isolate propargylic ureas **3l** and **3m** with 45% and 62% yield, respectively.

*General Procedure for the BEMP-Catalyzed Synthesis of Imidazolidin-2-ones **2** (Table 2).* A test tube, equipped with a magnetic stir bar, was charged with propargylic urea **1** (0.4 mmol) and CH_3CN (4 mL). BEMP (5 mol %, 6 μL) was added. The reaction mixture was stirred at room temperature and monitored by TLC. After completion, the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography with the mixture hexane/ethyl acetate.

*General Procedure for the BEMP-Catalyzed Synthesis of Imidazol-2-ones **4** (Table 3).* A test tube, equipped with a magnetic stir bar, was charged with propargylic urea **3** (0.4 mmol) and CH_3CN (4 mL). BEMP (5 mol %, 6 μL) was added. The reaction mixture was stirred at room temperature for 1 min (TLC confirmed the completion of the reaction). The solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography with the mixture hexane/ethyl acetate.

*One-Pot BEMP-Catalyzed Synthesis of **2a** from Propargylic Amine and Isocyanate (Scheme 1a).* A test tube, equipped with a magnetic stir bar, was charged with 2-methylbut-3-yn-2-amine (0.4 mmol, 33 mg), phenyl isocyanate (0.4 mmol, 48 mg), and CH_3CN (4 mL). BEMP (5 mol %, 6 μL) was added. The reaction mixture was stirred at room temperature and monitored by TLC. After completion (1 h), the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography (Eluent: hexane/ethyl acetate 1:1) to afford **2a** in quantitative yield (81 mg).

*One-Pot BEMP-Catalyzed Synthesis of **4a** from Propargylic Amine and Isocyanate (Scheme 1b).* A test tube, equipped with a magnetic stir bar, was charged with *N*-benzyl-1,3-diphenylprop-2-yn-1-amine (0.4 mmol, 119 mg), phenyl isocyanate (0.4 mmol, 48 mg), and CH_3CN (4 mL). BEMP (5 mol %, 6 μL) was added. The reaction mixture was stirred at room temperature for 1 min. Solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography (Eluent: hexane/ethyl acetate 6:4) to afford **4a** in 51% yield (85 mg). With 10% of BEMP, **4a** was isolated in 62% yield (103 mg).

*Synthesis of **2n′**.*[25] A dry two-necked flask containing a magnetic stir bar was charged with 1-fluoro-4-isothiocyanatobenzene (1 mmol, 122 μL), 2-methylbut-3-yn-2-amine (1 mmol, 105 μL), and dry THF (10 mL). The resulting mixture was stirred at room temperature and monitored by TLC. After 3 h, the solvent was removed under reduced pressure. The crude did not require purification, and product **2n′** was recovered in 98% yield (231 mg) as a yellow solid.

N-Benzyl-2-methyldodec-3-yn-2-amine. *N*-Benzyl-2-methyldodec-3-yn-2-amine was synthesized from 2 mmol of starting materials, according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (206 mg, 31% yield) as a transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.35 (m, 2H), 7.34−7.30 (m, 2H),

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7.25−7.22 (m, 1H), 3.88 (s, 2H), 2.23 (t, J = 7.0 Hz, 2H), 1.59−1.49 (m, 2H), 1.47−1.42 (m, 2H), 1.40 (s, 6H), 1.34−1.27 (m, 9H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 141.2, 128.6, 128.5, 126.9, 85.3, 82.4, 50.3, 49.2, 32.0, 30.1, 29.4, 29.2 (2C), 29.0, 22.8, 18.8, 14.2. HRMS (ESI) calcd for $C_{20}H_{32}N$ (M + H)$^+$ m/z 286.2535, found m/z 286,2533.

N-Benzyl-2-methylbut-3-yn-2-amine. *N*-Benzyl-2-methylbut-3-yn-2-amine was synthesized according to the general procedure.[27] The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give the desired amine (476 mg, 55% yield) as a white solid; mp (hexane) 44.7−45.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.33 (m, 4H), 7.31−7.26 (m, 1H), 3.91 (s, 2H), 2.39 (s, 1H), 1.46 (two overlapping signals: brs and s, 7H). Spectroscopic data were consistent with literature values.[29]

N-Benzyl-1,3-diphenylprop-2-yn-1-amine. *N*-Benzyl-1,3-diphenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (8:2) as eluent to give the desired amine (349 mg, 59% yield) as a viscous colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.4 Hz, 2H), 7.59−7.55 (m, 2H), 7.50−7.41 (m, 5H), 7.40−7.36 (m, 5H), 7.35−7.31 (m, 1H), 4.88 (s, 1H), 4.12−4.00 (m, 2H), 2.01 (bs, 1H). Spectroscopic data were consistent with literature values.[30]

N-Benzyl-1-phenylundec-2-yn-1-amine. *N*-Benzyl-1-phenylundec-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (342 mg, 53% yield) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.4 Hz, 2H), 7.48−7.41 (m, 4H), 7.40−7.37 (m, 2H), 7.36−7.29 (m, 2H), 4.65 (s, 1H), 4.04−3.94 (m, 2H), 2.37 (further split t, J = 7.0 Hz, 2H), 1.79 (bs, 1H), 1.70−1.60 (m, 2H), 1.57−1.48 (m, 2H), 1.44−1.34 (m, 8H), 0.98 (t, J = 6.9 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 141.1, 140.1, 128.5, 128.4, 128.2, 127.7, 127.5, 127.0, 86.1, 79.9, 53.3, 51.1, 31.9, 29.3, 29.2, 29.0, 28.9, 22.8, 18.9, 14.2. HRMS (ESI) calcd for $C_{24}H_{32}N$ (M + H)$^+$ m/z 334.2534, found m/z 334.2530.

N-(1,3-Diphenylprop-2-yn-1-yl)butan-1-amine. *N*-Benzyl-1,3-diphenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (8:2) as eluent to give the desired amine (315 mg, 60% yield) as a viscous yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.62−7.50 (m, 2H), 7.49−7.40 (m, 2H), 7.39−7.32 (m, 4H), 4.88 (s, 1H), 2.98−2.88 (m, 1H), 2.86−2.70 (m, 1H), 1.64−1.38 (m, 4H), 1.00 (t, J = 7.3 Hz, 3H). Spectroscopic data were consistent with literature values.[31]

1,3-Diphenyl-N-(1-phenylethyl)prop-2-yn-1-amine. 1,3-Diphenyl-*N*-(1-phenylethyl)prop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (257 mg, 42% yield) together with the corresponding imine intermediate.[32] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.31 (m, 30H), 4.71 (s, 1H), 4.50 (s, 1H), 4.40 (q, J = 6.6 Hz, 1H), 3.96 (q, J = 6.6 Hz, 1H), 1.76 (brs, 2H), 1.45 (d, J = 6.6 Hz, 3H), 1.42 (d, J = 6.6 Hz, 3H). Spectroscopic data were consistent with literature values.[32]

N-(4-Methylbenzyl)-1,3-diphenylprop-2-yn-1-amine. *N*-(4-Methylbenzyl)-1,3-diphenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (433 mg, 70% yield) as a viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.2 Hz, 2H), 7.69−7.66 (m, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.49−7.44 (m, 6H), 7.30 (d, J = 7.8 Hz, 2H), 4.96 (s, 1H), 4.12 (s, 2H), 2.49 (s, 3H), 1.98 (bs, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 140.4, 136.8, 136.6, 131.8, 129.1, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 123.2, 89.4, 85.7, 53.6, 50.9, 21.2. HRMS (ESI) calcd for $C_{23}H_{22}N$ (M + H)$^+$ m/z 312.1752, found m/z 312.1754.

N-(4-Fluorobenzyl)-1,3-diphenylprop-2-yn-1-amine. *N*-(4-Fluorobenzyl)-1,3-diphenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (490 mg, 78% yield) as a viscous yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.68 (m, 2H), 7.62−7.57 (m, 2H), 7.49−7.42 (m, 4H), 7.42−7.36 (m, 4H), 7.13−7.07 (m, 2H), 4.87 (s, 1H), 4.04 (s, 2H), 1.89 (bs, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.1 (d, $J_{C,F}$ = 244.8 Hz), 135.6 (d, $J_{C,F}$ = 3.1 Hz), 140.3, 131.8, 130.0 (d, $J_{C,F}$ = 7.9 Hz), 128.6, 128.4, 128.3, 127.9, 127.7, 123.1, 115.2 (d, $J_{C,F}$ = 21.2 Hz), 89.2, 85.9, 53.6, 50.4. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −115.56. HRMS (ESI) calcd for $C_{22}H_{18}FN$ (M + H)$^+$ m/z 316.1501, found m/z 316.1498.

N-Benzyl-3-phenyl-1-(p-tolyl)prop-2-yn-1-amine. *N*-Benzyl-3-phenyl-1-(p-tolyl)prop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (533 mg, 86% yield) as a viscous colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.65 (m, 2H), 7.61−7.56 (m, 4H), 7.53−7.40 (m, 7H), 7.27 (d, J = 7.8 Hz, 1H), 4.94 (s, 1H), 4.21−4.12 (m, 2H), 2.53 (s, 3H), 2.11 (bs, 1H). Spectroscopic data were consistent with literature values.[33]

N-Benzyl-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-amine. *N*-Benzyl-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (8:2) as eluent to give the desired amine (376 mg, 58% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.59 (m, 4H), 7.54−7.49 (m, 2H), 7.46−7.39 (m, 5H), 7.38−7.33 (m, 1H), 7.04−6.98 (m, 2H), 4.88 (s, 1H), 4.12−4.03 (m, 2H), 3.88 (s, 3H), 1.94 (bs, 1H). Spectroscopic data were consistent with literature values.[30]

N-Benzyl-1-(3-chlorophenyl)-3-phenylprop-2-yn-1-amine. *N*-Benzyl-1-(3-chlorophenyl)-3-phenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (342 mg, 52% yield) as dark yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75−7.72 (m, 1H), 7.63−7.58 (m, 3H), 7.53−7.48 (m, 2H), 7.47−7.40 (m, 5H), 7.39−7.34 (m, 3H), 4.87 (s, 1H), 4.07 (s, 2H), 2.03 (bs, 1H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 142.4, 139.6, 134.4, 131.8, 129.8, 128.6, 128.5, 128.4 (2C), 128.0, 127.9, 127.2, 125.9, 122.9, 88.5, 86.3, 53.2, 51.1.HRMS (ESI) calcd for $C_{22}H_{18}ClN$ (M + H)$^+$ m/z 332.1206, found m/z 332.1203.

N-Benzyl-3-phenyl-1-(3-vinylphenyl)prop-2-yn-1-amine. *N*-Benzyl-3-phenyl-1-(3-vinylphenyl)prop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (504 mg, 78% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.71−7.63 (m, 3H), 7.57 (d, J = 7.1 Hz, 2H), 7.53−7.39 (m, 8H), 6.90 (dd, J = 17.6, 10.9 Hz, 1H), 5.94 (d, J = 17.6, 1H), 5.42 (d, J = 10.9 Hz, 1H), 4.97 (s, 1H), 4.19−4.11 (m, 2H), 2.11 (bs, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 140.6, 139.8, 137.8, 136.8, 131.8, 128.7, 128.4 (2C), 128.3, 128.2, 127.2, 127.1, 125.7, 125.6, 123.1, 114.1, 89.2, 85.8, 53.6, 51.1. HRMS (ESI) calcd for $C_{24}H_{22}N$ (M + H)$^+$ m/z 324.1752, found m/z 324.1755.

N-Benzyl-1-(2-bromophenyl)-3-phenylprop-2-yn-1-amine. *N*-Benzyl-1-(2-bromophenyl)-3-phenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (558 mg, 74% yield) as a viscous pale orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.7, 1.7 Hz, 1H), 7.64 (dd, J = 8.0, 1.2 Hz, 1H), 7.61−7.56 (m, 2H), 7.50 (d, J = 6.9 Hz, 2H), 7.42−7.37 (m, 6H), 7.36−7.31 (m, 1H), 7.24−7.19 (m, 1H), 5.28 (s, 1H), 4.12−4.02 (m, 2H), 2.03 (bs, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 139.5, 139.4, 133.2, 131.8, 129.6, 129.4, 128.7, 128.4, 128.3 (2C), 127.8, 127.2, 123.8, 123.0, 88.4, 85.8, 53.7, 51.7. HRMS (ESI) calcd for $C_{22}H_{19}BrN$ (M + H)$^+$ m/z 376.0700, found m/z 376.0703.

N-Benzyl-1-phenyl-3-(p-tolyl)prop-2-yn-1-amine. *N*-Benzyl-1-phenyl-3-(*p*-tolyl)prop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (9:1) as eluent to give the desired amine (280 mg, 45% yield) as a viscous yellow oil. ^{1}H NMR

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(400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.3 Hz, 2H), 7.48−7.41 (m, 5H), 7.40−7.35 (m, 3H), 7.35−7.26 (m, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.84 (s, 1H), 4.08−3.98 (m, 2H), 2.40 (s, 3H), 1.91 (bs, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.5, 139.9, 138.4, 131.8, 129.2, 128.61 (2C), 128.56, 127.9, 127.8, 127.2, 120.2, 88.5, 86.0, 53.8, 51.2, 21.6. HRMS (ESI) calcd for $C_{23}H_{22}N$ $(M + H)^+$ m/z 312.1752, found m/z 312.1751.

N-Benzyl-3-(4-chlorophenyl)-1-phenylprop-2-yn-1-amine. *N*-Benzyl-3-(4-chlorophenyl)-1-phenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (8:2) as eluent to give the desired amine (358 mg, 54% yield) as a viscous dark yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.3 Hz, 2H), 7.47−7.38 (m,7H), 7.38−7.27 (m, 5H), 4.84 (s, 1H), 4.09−3.94 (m, 2H), 2.01 (bs, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.2, 139.8, 134.3, 133.1, 128.8, 128.7, 128.6, 128.5, 128.0, 127.7, 127.2, 121.6, 90.5, 84.7, 53.8, 51.3. HRMS (ESI) calcd for $C_{22}H_{19}ClN$ $(M + H)^+$ m/z 332.1206, found m/z 332.1207.

N-Benzyl-3-(4-fluorophenyl)-1-phenylprop-2-yn-1-amine. *N*-Benzyl-3-(4-fluorophenyl)-1-phenylprop-2-yn-1-amine was synthesized according to the general procedure.[28] The crude was purified by flash column chromatography using hexane/ethyl acetate (8:2) as eluent to give the desired amine (265 mg, 42% yield) as a viscous yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.62 (m, 2H), 7.54−7.48 (m, 2H), 7.48−7.34 (m, 7H), 7.33−7.28 (m, 1H), 7.10−7.01 (m, 2H), 4.84 (s, 1H), 4.11−3.96 (m, 2H), 1.89 (s, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.51 (d, $J_{C,F}$ = 249.2 Hz), 140.35, 139.84, 133.67 (d, $J_{C,F}$ = 8.3 Hz), 128.64, 128.55, 128.51, 127.93, 127.73, 127.23, 119.27 (d, $J_{C,F}$ = 3.5 Hz), 115.62 (d, $J_{C,F}$ = 22.0 Hz), 89.05, 84.72, 53.73, 51.26. $^{19}F\{1H\}$ NMR (376 MHz, $CDCl_3$) δ −111.03. HRMS (ESI) calcd for $C_{22}H_{19}FN$ $(M + H)^+$ m/z 316.1501, found m/z 332.1498.

*1-(2-Methylbut-3-yn-2-yl)-3-phenylurea (**1a**).* Compound **1a** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1a** was obtained as a white solid; mp (hexane) 116.3−117.6 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.28 (bs, 1H), 7.36 (d further split, 2H), 7.26−7.17 (m, 2H), 6.95−6.83 (m, 1H), 6.38 (bs, 1H), 3.10 (s, 1H), 1.54 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 153.8, 140.2, 128.6, 121.1, 117.5, 88.5, 70.7, 46.0, 29.3. HRMS (ESI) calcd for $C_{12}H_{14}N_2NaO$ $(M + Na)^+$ m/z 225.1004, found m/z 225.1008.

*1-(2-Methylbut-3-yn-2-yl)-3-(p-tolyl)urea (**1b**).* Compound **1b** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1b** was obtained as a white solid; mp (hexane) 144.4−146.1 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.19 (bs, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 6.34 (bs, 1H), 3.11 (s, 1H), 2.22 (s, 3H), 1.54 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 153.9, 137.7, 129.8, 129.0, 117.6, 88.7, 70.7, 46.0, 29.4, 20.3. HRMS (ESI) calcd for $C_{13}H_{16}N_2NaO$ $(M + Na)^+$ m/z 239.1160, found m/z 239.1158.

*1-(4-Fluorophenyl)-3-(2-methylbut-3-yn-2-yl)urea (**1c**).* Compound **1c** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1c** was obtained as a light purple solid; mp (hexane) 174.1−174.8 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.33 (bs, 1H), 7.41−7.30 (m, 2H), 7.09−7.01 (m, 2H), 6.38 (bs, 1H), 3.11 (s, 1H), 1.53 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 156.9 (d, $J_{C,F}$ = 237.2 Hz), 153.9, 136.6 (d, $J_{C,F}$ = 2.3 Hz), 119.1 (d, $J_{C,F}$ = 7.5 Hz), 115.1 (d, $J_{C,F}$ = 22.0 Hz), 88.6, 70.8, 46.0, 29.4. $^{19}F\{1H\}$ NMR (376 MHz, DMSO-d_6) δ −122.40. HRMS (ESI) calcd for $C_{12}H_{13}FN_2NaO$ $(M + Na)^+$ m/z 243.0910, found m/z 243.0912.

*Methyl 4-(3-(2-Methylbut-3-yn-2-yl)ureido)benzoate (**1d**).* Compound **1d** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1d** was obtained as a white solid; mp (hexane) 189.6−190.9 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.73 (bs, 1H), 7.86−7.81 (m, 2H), 7.52−7.48 (m, 2H), 6.58 (bs, 1H), 3.79 (s, 3H), 3.10 (s, 1H), 1.55 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 166.0, 153.4, 144.9, 130.4, 121.9, 116.7, 88.3, 70.8, 51.6, 46.2, 29.2. HRMS (ESI) calcd for $C_{14}H_{16}N_2NaO_3$ $(M + Na)^+$ m/z 283.1059, found m/z 283.1057.

*1-(3-Ethylpent-1-yn-3-yl)-3-phenylurea (**1e**).* Compound **1e** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1e** was obtained as a white solid; mp (hexane) 122.3−123.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (bs, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.21 (t, J = 7.9 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 5.85 (bs, 1H), 2.32 (s, 1H), 2.01−1.78 (m, 2H), 1.76−1.53 (m, 2H), 0.99 (t, J = 7.4 Hz, 6H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.5, 139.2, 128.9, 122.8, 119.8, 85.8, 71.8, 55.6, 31.4, 8.5. HRMS (ESI) calcd for $C_{14}H_{18}N_2NaO$ $(M + Na)^+$ m/z 253.1317, found m/z 253.1320.

*1-(1-Ethynylcyclohexyl)-3-phenylurea (**1f**).* Compound **1f** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1f** was obtained as a white solid; mp (hexane) 157.2−157.8 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.32 (bs, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.22 (t, J = 7.9 Hz, 2H), 6.89 (t, J = 7.3 Hz, 1H), 6.29 (bs, 1H), 3.15 (s, 1H), 2.08−1.92 (m, 2H), 1.81−1.69 (m, 2H), 1.62−1.43 (m, 5H), 1.34−1.22 (m, 1H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 154.2, 140.8, 129.1, 121.5, 117.9, 87.6, 73.3, 50.6, 37.3, 25.3, 22.4. HRMS (ESI) calcd for $C_{15}H_{18}N_2NaO$ $(M + Na)^+$ m/z 265.1317, found m/z 265.1319.

*1-Benzyl-1-(2-methylbut-3-yn-2-yl)-3-phenylurea (**1g**).* Compound **1g** was synthesized according to the general procedure.[27] Compound **1g** was obtained as colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47−7.41 (m, 4H), 7.37−7.31 (m, 2H), 7.29−7.23 (m, 4H), 6.95 (bs, 1H), 4.85 (s, 2H), 2.56 (s, 1H), 1.88 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.2, 139.3, 139.2, 129.2, 128.9, 127.6, 126.5, 123.1, 119.8, 88.1, 72.8, 54.8, 50.1, 29.2. HRMS (ESI) calcd for $C_{19}H_{20}N_2NaO$ $(M + Na)^+$ m/z 315.1473, found m/z 315.1476.

*1-Benzyl-1-(2-methyldodec-3-yn-2-yl)-3-phenylurea (**1h**).* Compound **1h** was synthesized according to the general procedure.[26] The crude was purified by silica gel column chromatography to obtain **1h** with a 78% yield (352 mg) as a yellowish oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (bs, 1H), 7.44−7.34 (m, 4H), 7.33−7.24 (m, 5H), 7.05−6.98 (m, 1H), 4.87 (s, 2H), 2.21 (t, J = 7.0 Hz, 2H), 1.80 (s, 6H), 1.49−1.39 (m, 2H), 1.37−1.19 (m, 10H), 0.91 (t, J = 7.0 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.4, 140.1, 139.5, 128.9, 128.8, 127.2, 126.6, 122.8, 119.6, 85.9, 84.6, 54.6, 49.4, 31.9, 29.8, 29.3, 29.2, 29.0, 28.6, 22.8, 18.8, 14.2. HRMS (ESI) calcd for $C_{27}H_{37}N_2O$ $(M + H)^+$ m/z 405.2906, found m/z 405.2908.

*1-(2-Methyl-4-phenylbut-3-yn-2-yl)-3-phenylurea (**1i**).* Compound **1i** was synthesized according to the general procedure.[26] The crude was purified by silica gel column chromatography to obtain **1i** with a 78% yield (217 mg) as a yellowish solid; mp (hexane) 182.3−183.7 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.36 (bs, 1H), 7.45−7.30 (m, 7H), 7.23 (t, J = 7.9 Hz, 2H), 6.90 (t, J = 7.3 Hz, 1H), 6.53 (bs, 1H), 1.66 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 153.8, 140.2, 131.2, 128.6, 128.4, 128.1, 122.6, 121.0, 117.5, 94.5, 79.6, 46.6, 29.4. HRMS (ESI) calcd for $C_{18}H_{18}N_2NaO$ $(M + Na)^+$ m/z 301.1317, found m/z 301.1313.

*1-(2-Methyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)-3-phenylurea (**1j**).* Compound **1j** was synthesized according to the general procedure.[26] The crude was purified by silica gel column chromatography to obtain **1j** with a 91% yield (315 mg) as a white solid; mp (hexane) 183.9−185.2 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.38 (bs, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.23 (t, J = 7.9 Hz, 2H), 6.90 (t, J = 7.3 Hz, 1H), 6.58 (bs, 1H), 1.68 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, DMSO-d_6) δ 153.9, 140.2, 132.0, 128.6, 128.3 (q, $J_{C,F}$ = 32.1 Hz), 127.1 (q, $J_{C,F}$ = 1.2 Hz), 125.4 (q, $J_{C,F}$ = 3.6 Hz), 124.0 (q, $J_{C,F}$ = 271.9 Hz), 121.2, 117.7, 97.4, 78.5, 46.6, 29.3. $^{19}F\{1H\}$ NMR (376 MHz, DMSO-d_6) δ −61.47. HRMS (ESI) calcd for $C_{19}H_{17}F_3N_2NaO$ $(M + Na)^+$ m/z 369.1191, found m/z 369.1194.

*1-(4-(4-Methoxyphenyl)-2-methylbut-3-yn-2-yl)-3-phenylurea (**1k**).* Compound **1k** was synthesized according to the general procedure.[26] The crude was purified by silica gel column chromatography to obtain **1k** with 57% yield (176 mg) as pale yellow solid; mp (hexane) 178.2−178.6 °C. ^1H NMR (400 MHz,

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DMSO-d_6) δ 8.35 (bs, 1H), 7.41 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.23 (t, J = 7.8 Hz, 2H), 6.95−6.86 (m, 3H), 6.51 (bs, 1H), 3.74 (s, 3H), 1.66 (s, 6H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ 159.1, 153.9, 140.3, 132.8, 128.7, 121.1, 117.6, 114.7, 114.1, 93.0, 79.6, 55.1, 46.8, 29.6. HRMS (ESI) calcd for $C_{19}H_{20}N_2NaO_2$ (M +Na)$^+$ m/z 331.1422, found m/z 331.1424.

*1-(2-Methyl-4-(thiophen-2-yl)but-3-yn-2-yl)-3-phenylurea (**1l**).* Compound **1l** was synthesized according to the general procedure.[26] The crude was purified by silica gel column chromatography to obtain **1l** with 94% yield (267 mg) as a yellowish solid; mp (hexane) 210.3-211.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (bs, 1H), 7.51 (d, J = 4.9 Hz, 1H), 7.41 (d, J = 7.9 Hz, 2H), 7.26−7.18 (m, 3H), 7.04−6.99 (m, 1H), 6.91 (t, J = 7.3 Hz, 1H), 6.55 (bs, 1H), 1.65 (s, 6H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ 153.9, 140.2, 131.8, 128.7, 127.7, 127.4, 122.4, 121.2, 117.6, 98.3, 73.1, 46.8, 29.4. HRMS (ESI) calcd for $C_{16}H_{16}N_2NaOS$ (M+Na)$^+$ m/z 307.0881, found m/z 307.0883.

*Ethyl 2-(3-(2-Methylbut-3-yn-2-yl)ureido)acetate (**1m**).* Compound **1m** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **1m** was obtained as a white solid; mp (hexane) 83.2−84.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, J = 7.1 Hz, 2H), 4.01 (s, 2H), 2.42 (s, 1H), 1.59 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 171.3, 157.2, 87.5, 70.4, 61.4, 46.9, 42.2, 30.1, 14.3. HRMS (ESI) calcd for $C_{10}H_{16}N_2NaO_3$ (M +Na)$^+$ m/z 235.1059, found m/z 235.1058.

*1-Benzyl-1-(1,3-diphenylprop-2-yn-1-yl)-3-phenylurea (**3a**).* Compound **3a** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **3a** was obtained as a yellow solid; mp (hexane) 96.2−97.7 °C. The spectroscopic data of **3a** were consistent with literature values.[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.81 (m, 2H), 7.54−7.37 (m, 13H), 7.33−7.25 (m, 4H), 7.15 (s, 1H), 7.12−7.03 (m, 1H), 6.59 (bs, 1H), 4.76 (d, J = 17.1 Hz, 1H), 4.57 (d, J = 17.1 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.5, 138.7, 138.0, 137.1, 131.6, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.0, 123.1, 122.3, 119.7, 86.9, 86.0, 51.3, 48.5. HRMS (ESI) calcd for $C_{29}H_{25}N_2O$ (M + H)$^+$ m/z 417.1967, found m/z 417.1970.

*1-Benzyl-3-phenyl-1-(1-phenylundec-2-yn-1-yl)urea (**3b**).* Compound **3b** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **3b** was obtained as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.5 Hz, 2H), 7.48−7.35 (m, 8H), 7.33−7.12 (m, 4H), 7.03 (t, J = 7.1 Hz, 1H), 6.75 (s, 1H), 6.52 (s, 1H), 4.68 (d, J = 16.8 Hz, 1H), 4.48 (d, J = 16.9 Hz, 1H), 2.35 (t, J = 6.7 Hz, 2H), 1.63−1.52 (m, 2H), 1.51−1.25 (m, 10H), 0.99 (t, J = 6.8 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.5, 138.8, 138.6, 137.4, 128.9, 128.7, 128.6, 128.0, 127.9, 127.6, 127.2, 123.0, 119.7, 87.8, 76.7, 51.1, 48.6, 31.8, 29.2, 29.1, 28.9, 28.5, 22.6, 18.7, 14.1. HRMS (ESI) calcd for $C_{31}H_{37}N_2O$ (M + H)$^+$ m/z 453.2906, found m/z 453.2909.

*1-Butyl-1-(1,3-diphenylprop-2-yn-1-yl)-3-phenylurea (**3c**).* Compound **3c** was synthesized according to the general procedure.[25] The crude was dried under vacuum and used without purification. Compound **3c** was obtained as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.64 (m, 2H), 7.55−7.50 (m, 2H), 7.44−7.33 (m, 8H), 7.32−7.27 (m, 2H), 7.08−7.02 (m, 1H), 6.67 (s, 1H), 6.58 (s, 1H), 3.48−3.30 (m, 2H), 1.87−1.73 (m, 1H), 1.61−1.43 (m, 1H), 1.42−1.26 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 154.9, 139.0, 138.1, 131.8, 129.0, 128.8, 128.7, 128.5, 128.2, 127.5, 123.2, 122.6, 120.0, 86.8, 86.1, 51.3, 45.5, 31.5, 20.4, 13.9. HRMS (ESI) calcd for $C_{26}H_{27}N_2O$ (M + H)$^+$ m/z 383.2123, found m/z 383.2120.

*1-(1,3-Diphenylprop-2-yn-1-yl)-3-phenyl-1-(1-phenylethyl)urea (**3d**).* Compound **3d** was synthesized according to the general procedure.[25] Compound **3d** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.55−7.45 (m, 4H), 7.45−7.30 (m, 6H), 7.29−7.22 (m, 3H), 7.14 (t, J = 7.8 Hz, 2H), 7.03 (t, J = 7.3 Hz, 1H), 6.92 (bs, 1H), 6.36 (s, 1H), 5.52−5.48 (m, 1H), 1.44 (d, J = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 154.6, 140.9, 138.8, 138.2, 131.6, 129.0, 128.7 (2C), 128.6, 128.45, 128.36, 128.3, 128.1, 127.7, 127.2, 122.9, 119.4, 86.9, 86.5, 52.0, 50.7, 17.2. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ (M + H)$^+$ m/z 431.2123, found m/z 431.2121.

*1-(1,3-Diphenylprop-2-yn-1-yl)-1-(4-methylbenzyl)-3-phenylurea (**3e**).* Compound **3e** was synthesized according to the general procedure.[25] Compound **3e** was obtained as an orange solid; mp (hexane) 109.8−111.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 2H), 7.55−7.48 (m, 4H), 7.45 (d, J = 7.2 Hz, 1H), 7.41−7.35 (m, 5H), 7.32−7.29 (m, 4H), 7.26 (d, J = 7.9 Hz, 2H), 7.18 (s, 1H), 7.10−7.04 (m, 1H), 6.67 (bs, 1H), 4.72 (d, J = 16.9 Hz, 1H), 4.52 (d, J = 16.9 Hz, 1H), 2.43 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.5, 138.8, 138.0, 137.6, 134.0, 131.6, 129.7, 128.7, 128.6, 128.5, 128.2, 128.1, 127.6, 127.0, 123.0, 122.3, 119.6, 86.8, 86.1, 51.2, 48.1, 21.0. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ (M + H)$^+$ m/z 431.2123, found m/z 431.2119.

*1-(1,3-Diphenylprop-2-yn-1-yl)-1-(4-fluorobenzyl)-3-phenylurea (**3f**).* Compound **3f** was synthesized according to the general procedure.[25] Compound **3f** was obtained as a light orange solid; mp (hexane) 125.6−126.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 2H), 7.51−7.45 (m, 4H), 7.44−7.36 (m, 6H), 7.32−7.23 (m, 4H), 7.13−7.04 (m, 3H), 7.00 (s, 1H), 6.53 (bs, 1H), 4.70 (d, J = 17.0 Hz, 1H), 4.54 (d, J = 17.0 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.4 (d, J = 246.7 Hz), 155.4, 138.7, 137.9, 133.0 (d, J = 3.1 Hz), 131.7, 128.9 (d, J = 7.8 Hz), 128.8 (2C), 128.7, 128.4, 127.7, 123.4, 122.3, 119.9, 116.0 (d, J = 21.5 Hz), 87.1, 85.9, 51.5, 48.0. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −113.93. HRMS (ESI) calcd for $C_{29}H_{24}FN_2O$ (M + H)$^+$ m/z 435.1873, found m/z 435.1875.

*1-Benzyl-3-phenyl-1-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)urea (**3g**).* Compound **3g** was synthesized according to the general procedure.[25] Compound **3g** was obtained as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.61 (m, 2H), 7.54−7.46 (m, 6H), 7.45−7.37 (m, 5H), 7.33−7.25 (m, 5H), 7.12−7.05 (m, 2H), 6.60 (bs, 1H), 4.78 (d, J = 17.0 Hz, 1H), 4.59 (d, J = 17.1 Hz, 1H), 2.49 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.4, 138.8, 138.4, 137.9, 137.2, 131.6, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.1, 124.8, 123.1, 122.4, 119.7, 86.8, 86.2, 51.3, 48.5, 21.5. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ (M + H)$^+$ m/z 431.2123, found m/z 431.2121.

*1-Benzyl-1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)-3-phenylurea (**3h**).* Compound **3h** was synthesized according to the general procedure.[25] Compound **3h** was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.67 (m, 2H), 7.47−7.40 (m, 6H), 7.39−7.32 (m, 4H), 7.29−7.24 (m, 2H), 7.22−7.18 (m, 2H), 7.07−6.97 (m, 4H), 6.48 (bs, 1H), 4.71 (d, J = 17.0 Hz, 1H), 4.52 (d, J = 17.0 Hz, 1H), 3.86 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 159.6, 155.6, 138.8, 137.3, 131.7, 130.2, 129.2, 129.1, 128.8, 128.6, 128.4, 128.1, 127.2, 123.2, 122.5, 119.8, 114.1, 86.8, 86.4, 55.3, 50.8, 48.5. HRMS (ESI) calcd for $C_{30}H_{27}N_2O_2$ (M + H)$^+$ m/z 447.2072, found m/z 447.2075.

*1-Benzyl-1-(1-(3-chlorophenyl)-3-phenylprop-2-yn-1-yl)-3-phenylurea (**3i**).* Compound **3i** was synthesized according to the general procedure.[25] Compound **3i** was obtained as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.72−7.67 (m, 1H), 7.51−7.44 (m, 6H), 7.42−7.35 (m, 6H), 7.32−7.23 (m, 4H), 7.13 (s, 1H), 7.10−7.05 (m, 1H), 6.62 (bs, 1H), 4.73 (d, J = 17.2 Hz, 1H), 4.53 (d, J = 17.2 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.5, 140.2, 138.5, 136.8, 134.6, 131.6, 130.0, 129.1, 128.8, 128.7, 128.4, 128.3, 128.1, 127.8, 126.9, 125.9, 123.4, 122.0, 120.0, 87.4, 85.2, 50.8, 48.3. HRMS (ESI) calcd for $C_{29}H_{24}ClN_2O$ (M + H)$^+$ m/z 451.1577, found m/z 451.1578.

*1-Benzyl-3-phenyl-1-(3-phenyl-1-(3-vinylphenyl)prop-2-yn-1-yl)-urea (**3j**).* Compound **3j** was synthesized according to the general procedure.[25] Compound **3j** was obtained as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.50−7.35 (m, 12H), 7.30−7.25 (m, 2H), 7.24−7.21 (m, 2H), 7.09 (brs, 1H), 7.08−7.03 (m, 1H), 6.83 (dd, J = 17.6, 10.9 Hz, 1H), 6.53 (bs, 1H), 5.87 (d, J = 17.6 Hz, 1H), 5.36 (d, J = 11.2 Hz, 1H), 4.73 (d, J = 17.0 Hz, 1H), 4.54 (d, J = 17.1 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.6, 138.7, 138.4, 138.1, 137.1, 136.5, 131.7, 129.2, 129.0,

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128.8, 128.6, 128.4, 128.1, 127.2, 127.1, 126.0, 125.8, 123.3, 122.4, 119.8, 114.6, 87.1, 85.9, 51.3, 48.6. HRMS (ESI) calcd for $C_{31}H_{27}N_2O$ $(M + H)^+$ m/z 443.2123, found m/z 443.2127.

*1-Benzyl-1-(1-(2-bromophenyl)-3-phenylprop-2-yn-1-yl)-3-phenylurea (**3k**).* Compound **3k** was synthesized according to the general procedure.[25] Compound **3k** was obtained as a yellow solid; mp (hexane) 124.7−126.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.7, 1.6 Hz, 1H), 7.68 (dd, J = 7.9, 1.2 Hz, 1H), 7.55−7.51 (m, 2H), 7.41−7.34 (m, 6H), 7.33−7.24 (m, 8H), 7.09 (s, 1H), 7.06−7.01 (m, 1H), 6.59 (bs, 1H), 4.62 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.5, 138.8, 137.2, 136.6, 133.6, 131.8, 130.8, 130.1, 129.1, 128.8, 128.7, 128.4, 127.9, 127.6, 126.9, 124.6, 123.1, 122.3, 119.7, 87.0, 85.8, 52.2, 48.3. HRMS (ESI) calcd for $C_{29}H_{24}BrN_2O$ $(M + H)^+$ m/z 495.1072, found m/z 495.1074.

*1-Benzyl-1-(1,3-diphenylprop-2-yn-1-yl)-3-propylurea (**3l**).* Compound **3l** was synthesized according to the general procedure.[25] Compound **3l** was isolated as a yellow oil in 45% yield (172 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.64 (m, 2H), 7.44−7.24 (m, 13H), 6.98 (bs, 1H), 4.54 (d, J = 17.1 Hz, 1H), 4.41−4.34 (m, 1H), 4.31 (d, J = 17.1 Hz, 1H), 3.26−3.04 (m, 2H), 1.40−1.25 (m, 2H), 0.69 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 158.2, 138.6, 137.9, 131.7, 128.9, 128.7, 128.5, 128.4, 128.1, 127.8, 127.7, 126.9, 122.7, 86.7, 86.56, 51.4, 48.3, 42.8, 23.2, 11.1. HRMS (ESI) calcd for $C_{26}H_{27}N_2O$ $(M + H)^+$ m/z 383.2123, found m/z 383.2126.

*1,3-Dibenzyl-1-(1,3-diphenylprop-2-yn-1-yl)urea (**3m**).* Compound **3m** was synthesized according to the general procedure.[25] Compound **3m** was isolated as a yellow oil in 62% yield (267 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77−7.70 (m, 2H), 7.48−7.30 (m, 12H), 7.28−7.22 (m, 3H), 7.06−7.00 (m, 3H), 4.84 (t, J = 5.5 Hz, 1H), 4.63 (d, J = 17.2 Hz, 1H), 4.54−4.35 (m, 3H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 157.9, 139.1, 138.4, 137.6, 131.7, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 127.1, 127.0, 126.9, 122.6, 86.8, 86.3, 51.5, 48.3, 44.9. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2121.

*1-Benzyl-3-phenyl-1-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)urea (**3n**).* Compound **3n** was synthesized according to the general procedure.[25] Compound **3n** was obtained as a yellowish solid; mp (hexane) 53.6−54.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.72 (m, 2H), 7.49−7.32 (m, 10H), 7.28−7.23 (m, 2H), 7.21−7.13 (m, 4H), 7.06−6.99 (m, 2H), 6.45 (bs, 1H), 4.71 (d, J = 17.0 Hz, 1H), 4.50 (d, J = 17.0 Hz, 1H), 2.40 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.6, 138.9, 138.8, 138.3, 137.3, 131.7, 129.3, 129.2, 128.9, 128.8, 128.3, 128.2, 127.8, 127.2, 123.2, 119.8, 119.4, 87.2, 85.4, 51.5, 48.7, 21.6. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2124.

*1-Benzyl-1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)-3-phenylurea (**3o**).* Compound **3o** was synthesized according to the general procedure.[25] Compound **3o** was obtained as a yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.50−7.29 (m, 12H), 7.28−7.22 (m, 2H), 7.21−7.15 (m, 2H), 7.10−7.00 (m, 2H), 6.44 (bs, 1H), 4.68 (d, J = 17.1 Hz, 1H), 4.51 (d, J = 17.1 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 155.6, 138.8, 137.9, 137.2, 134.7, 133.0, 129.3, 128.9, 128.8, 128.4, 128.2, 127.8, 127.1, 123.3, 121.0, 119.9, 87.2, 85.9, 51.4, 48.6. HRMS (ESI) calcd for $C_{29}H_{24}ClN_2O$ $(M + H)^+$ m/z 451.1577, found m/z 451.1579.

*1-Benzyl-1-(3-(4-fluorophenyl)-1-phenylprop-2-yn-1-yl)-3-phenylurea (**3p**).* Compound **3p** was synthesized according to the general procedure.[25] Compound **3p** was obtained as a viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.56−7.35 (m, 10H), 7.33−7.22 (m, 4H), 7.13 (s, 1H), 7.10−7.00 (m, 3H), 6.60 (bs, 1H), 4.74 (d, J = 17.1 Hz, 1H), 4.58 (d, J = 17.1 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.6 (d, $J_{C,F}$ = 249.9 Hz), 155.5, 138.8, 137.9, 137.2, 133.6 (d, $J_{C,F}$ = 8.4 Hz), 129.1, 128.7 (2C), 128.2, 127.9, 127.7, 127.0, 123.2, 119.8, 118.5 (d, $J_{C,F}$ = 3.5 Hz), 115.6 (d, $J_{C,F}$ = 22.1 Hz), 85.8 (2C), 51.2, 48.4. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −110.00. HRMS (ESI) calcd for $C_{29}H_{24}FN_2O$ $(M + H)^+$ m/z 435.1873, found m/z 435.1872.

*4,4-Dimethyl-5-methylene-1-phenylimidazolidin-2-one (**2a**).* Compound **2a** was obtained from **1a** in 1 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2a** (78 mg, 97% yield) as a white solid; mp (hexane) 127.5−130.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.42 (m, 2H), 7.35−7.30 (m, 3H), 6.23 (bs, 1H), 4.03, 3.97 (2 partly overlapping bs, 2H), 1.46 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.2, 154.68, 135.2, 129.4, 127.7, 127.6, 79.6, 56.7, 29.9. HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $(M + H)^+$ m/z 203.1184, found m/z 203.1182.

*4,4-Dimethyl-5-methylene-1-(p-tolyl)imidazolidin-2-one (**2b**).* Compound **2b** was obtained from **1b** in 16 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2b** (69 mg, 82% yield) as a pale orange solid; mp (hexane) 195.2−197.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 5.83 (bs, 1H), 4.02 (d, J = 2.1 Hz, 1H), 3.97 (d, J = 2.3 Hz, 1H), 2.39 (s, 3H), 1.48 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.3, 154.9, 137.6, 132.5, 130.1, 127.6, 79.5, 56.7, 29.9, 21.3. HRMS (ESI) calcd for $C_{13}H_{17}N_2O$ $(M + H)^+$ m/z 217.1341, found m/z 217.1344.

*1-(4-Fluorophenyl)-4,4-dimethyl-5-methyleneimidazolidin-2-one (**2c**).* Compound **2c** was obtained from **1c** in 1 h and 30 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2c** (86 mg, 97% yield) as an orange solid; mp (hexane) 165.6−167.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.25 (m, 2H), 7.17−7.08 (m, 2H), 5.89 (bs, 1H), 4.03, 3.97 (2 bs, 2H), 1.46 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{C,F}$= 247.1 Hz), 157.1, 154.7, 131.1 (d, $J_{C,F}$ = 3.1 Hz), 129.6 (d, $J_{C,F}$ = 8.6 Hz), 116.4 (d, $J_{C,F}$ = 22.8 Hz), 79.9, 56.8, 29.9. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −113.93. HRMS (ESI) calcd for $C_{12}H_{14}FN_2O$ $(M + H)^+$ m/z 221.1090, found m/z 221.1086.

*Methyl 4-(4,4-Dimethyl-5-methylene-2-oxoimidazolidin-1-yl)-benzoate (**2d**).* Compound **2d** was obtained from **1d** in 6 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2d** (102 mg, 98% yield) as a yellowish solid; mp (hexane) 218.0−220.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.07 (m, 2H), 7.48−7.40 (m, 2H), 6.34 (bs, 1H), 4.17 (dd, J = 2.6, 0.8 Hz, 1H), 4.04 (d, J = 2.6 Hz, 1H), 3.91 (s, 3H), 1.45 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.5, 156.6, 153.5, 139.6, 130.7, 128.6, 127.0, 80.6, 56.8, 52.3, 29.8. HRMS (ESI) calcd for $C_{14}H_{17}N_2O_3$ $(M + H)^+$ m/z 261.1240, found m/z 261.1242.

*4,4-Diethyl-5-methylene-1-phenylimidazolidin-2-one (**2e**).* Compound **2e** was obtained from **1e** in 3 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2e** (92 mg, 99% yield) as a pale orange solid; mp (hexane) 120.5−122.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.42 (m, 2H), 7.36−7.31 (m, 1H), 7.30−7.27 (m, 2H), 5.32 (bs, 1H), 4.13 (dd, J = 2.3, 0.8 Hz, 1H), 3.87 (d, J = 2.3 Hz, 1H), 1.75−1.57 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.9, 150.9, 135.2, 129.5, 127.8, 127.7, 80.2, 63.6, 34.1, 7.8. HRMS (ESI) calcd for $C_{14}H_{19}N_2O$ $(M + H)^+$ m/z 231.1497, found m/z 231.1499.

*4-Methylene-3-phenyl-1,3-diazaspiro[4.5]decan-2-one (**2f**).* Compound **2f** was obtained from **1f** in 16 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2f** (92 mg, 95% yield) as a white solid; mp (hexane) 175.2−176.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.41 (m, 2H), 7.34−7.29 (m, 3H), 6.07 (bs, 1H), 4.07 (d, J = 2.3 Hz, 1H), 3.96 (d, J = 2.3 Hz, 1H), 1.92−1.83 (m, 2H), 1.81−1.70 (m, 2H), 1.63−1.53 (m, 2H), 1.49−1.35 (m, 2H), 1.35−1.21 (m, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.2, 154.5, 135.1, 129.4, 127.7, 127.6, 80.2, 59.5, 38.6, 25.0, 22.4. HRMS (ESI) calcd for $C_{15}H_{19}N_2O$ $(M + H)^+$ m/z 243.1497, found m/z 243.1500.

*3-Benzyl-4,4-dimethyl-5-methylene-1-phenylimidazolidin-2-one (**2g**).* Compound **2g** was obtained from **1g** in 16 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give **2g** (61 mg, 52% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.2 Hz, 2H), 7.39−7.25 (m, 5H), 7.20−7.16 (m, 2H),

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7.06−7.00 (m, 1H), 4.64 (d, J = 3.3 Hz, 1H), 4.63 (s, 2H), 4.20 (d, J = 3.3 Hz, 1H), 1.36 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.8, 149.2, 147.0, 139.0, 128.6, 128.5, 127.8, 127.3, 123.8, 122.3, 83.3, 61.1, 44.4, 27.6. HRMS (ESI) calcd for $C_{19}H_{21}N_2O$ $(M + H)^+$ m/z 293.1654, found m/z 293.1652.

*3-Benzyl-4,4-dimethyl-5-nonylidene-1-phenylimidazolidin-2-one (**2h**).* Compound **2h** was obtained from **1h** in 16 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give a mixture of E and Z (150 mg, 83%) in a ca. 1:0.06 molar ratio. The major Z isomer was characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.40 (m, 4H), 7.38−7.30 (m, 5H), 7.30−7.26 (m, 1H), 4.54 (s, 2H), 4.34 (t, J = 7.3 Hz, 1H), 1.47−1.41 (m, 2H), 1.35 (s, 6H), 1.32−1.27 (m, 2H), 1.25−1.04 (m, 10H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.4, 143.3, 139.6, 138.1, 128.7, 128.5, 127.9, 127.7, 127.2, 126.9, 99.4, 61.1, 43.4, 31.9, 30.0, 29.3, 29.2, 29.0, 27.9, 26.1, 22.7, 14.1.HRMS (ESI) calcd for $C_{27}H_{37}N_2O$ $(M + H)^+$ m/z 405.2906, found m/z 405.2904.

*5-Benzylidene-4,4-dimethyl-1-phenylimidazolidin-2-one (**2i**).* Compound **2i** was obtained from **1i** in 16 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give two fractions, one containing the pure **2i** Z isomer (62 mg), the other containing a mixture of E and Z (35 mg; see ^{1}H NMR spectrum of the mixture in the SI). The overall yield of Z and E isomers of **2i** amounted to 87% (97 mg) with Z/E isomers in a 1:0.25 molar ratio. The major isomer Z was isolated as a yellowish solid (mp from hexane: 216.5−217.8 °C) and characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06−6.95 (m, 5H), 6.88−6.80 (m, 3H), 6.68 (dd, J = 7.2, 1.9 Hz, 2H), 5.81 (bs, 1H), 5.59 (s, 1H), 1.57 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.8, 145.0, 135.9, 134.6, 128.3, 128.1, 127.0, 126.2, 126.1, 125.2, 99.0, 57.6, 30.1. HRMS (ESI) calcd for $C_{18}H_{19}N_2O$ $(M + H)^+$ m/z 279.1497, found m/z 279.1498.

*4,4-Dimethyl-1-phenyl-5-(4-(trifluoromethyl)benzylidene)-imidazolidin-2-one (**2j**).* Compound **2j** was obtained from **1j** in 4 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give two fractions, one containing the pure **2j** Z isomer (85 mg), the other containing a mixture of E and Z (43 mg; see ^{1}H NMR spectrum of the mixture in the SI). The overall yield of Z and E isomers of **2j** amounted to 93% (128 mg) with Z/E isomers in a 1:0.3 molar ratio. The major isomer Z was isolated as a white solid (mp from hexane: 208.5−211.4 °C) and characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.47 (m, 4H), 7.41−7.34 (m, 3H), 7.29 (d, J = 8.6 Hz, 2H), 5.61 (s, 1H), 5.49 (bs, 1H), 1.42 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 156.7, 149.5, 140.1 (q, $J_{C,F}$ = 0.9 Hz),134.9, 130.3, 129.8, 128.6 (q, $J_{C,F}$ = 29.5 Hz), 128.5, 128.3, 125.0 (q, $J_{C,F}$ = 3.8 Hz), 124.3 (q, $J_{C,F}$ = 271.8 Hz), 99.9, 57.8, 29.2. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −62.44. HRMS (ESI) calcd for $C_{19}H_{18}F_3N_2O$ $(M + H)^+$ m/z 347.1371, found m/z 347.1369.

*5-(4-Methoxybenzylidene)-4,4-dimethyl-1-phenylimidazolidin-2-one (**2k**).* Compound **2k** was obtained from **1k** in 16 h, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give two fractions, one containing the pure **2k** Z isomer (32 mg), the other containing a mixture of E and Z (71 mg; see ^{1}H NMR spectrum of the mixture in the SI). The overall yield of Z and E isomers of **2k** amounted to 84% (103 mg) with Z/E isomers in a 1:0.04 molar ratio. The major isomer Z was isolated as a white solid (mp from hexane: 182.4−184.7 °C) and characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08−6.96 (m, 5H), 6.59 (d, J = 8.7 Hz, 2H), 6.39 (d, J = 8.7 Hz, 2H), 5.92 (bs, 1H), 5.54 (s, 1H), 3.65 (s, 3H), 1.55 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.9, 157.3, 143.9, 135.9, 129.3, 128.0, 127.2, 126.1, 126.0, 112.6, 98.7, 57.5, 55.3, 30.1. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_2$ $(M + H)^+$ m/z 309.1603, found m/z 309.1607.

*4,4-Dimethyl-1-phenyl-5-(thiophen-2-ylmethylene)imidazolidin-2-one (**2l**).* Compound **2l** was obtained from **1l** in 1 h and 30 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give a mixture of E and Z (110 mg, 97%) in a 1:0.8 molar ratio. E and Z isomers were characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.46 (m, 1H(Z) + 1H(E)), 7.43−7.31 (m, 3H), 7.19−7.06 (m, 6H), 6.96−6.85 (m, 1H(Z) + 1H(E)), 6.77 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 5.0, 3.7 Hz, 1H), 6.13 (bs, 1H), 6.01 (bs, 1H), 5.98 (d, J = 3.5 Hz, 1H), 5.57 (s, 1H(E)), 5.51 (s, 1H(Z)), 1.57 (s, 6H(Z)), 1.55 (s, 6H(E)). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 157.6, 156.8, 150.1, 145.6, 137.5, 136.8, 135.7, 134.9, 129.7, 128.7, 128.2, 127.3, 126.8, 126.6, 126.5, 126.5, 126.3, 124.8, 123.8, 93.1, 91.5, 57.9, 57.7, 29.9, 28.4. HRMS (ESI) calcd for $C_{16}H_{17}N_2OS$ $(M + H)^+$ m/z 285.1061, found m/z 285.1063.

*3-(2-Methylbut-3-yn-2-yl)imidazolidine-2,4-dione (**2m′**).* Compound **2m′** was obtained from **1m** in 16 h at 50 °C, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (1:1) as eluent to give **2m′** (48 mg, 72% yield) as a white solid; mp (hexane) 81.1−82.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (bs, 1H), 3.88 (d, J = 1.2 Hz, 2H), 2.47 (s, 1H), 1.89 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 170.9, 158.1, 85.5, 71.2, 52.3, 46.2, 29.0. HRMS (ESI) calcd for $C_8H_{11}N_2O_2$ $(M + H)^+$ m/z 167.0820, found m/z 167.0817.

*(Z)-N-(4,4-Dimethyl-5-methylenethiazolidin-2-ylidene)-4-fluoroaniline (**2n′**).* Compound **2n′** was synthesized as reported above, in the absence of catalyst.[25] Expected acyclic thiourea **1i** was not detected, and (*Z*)-*N*-(4,4-dimethyl-5-methylenethiazolidin-2-ylidene)-4-fluoroaniline (**2n′**) was instead isolated. Product **2n′** was recovered without purification in 98% yield (1 mmol, 231 mg) as a yellow solid; mp (hexane) 223.3−224.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6, recorded at 80 °C) δ 8.73 (bs, 1H), 7.54−7.32 (m, 2H), 7.16−6.88 (m, 2H), 5.21 (d, J = 1.4 Hz, 1H), 5.14 (d, J = 1.4 Hz, 1H), 1.42 (s, 6H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6, recorded at 80 °C) δ 157.0 (d, $J_{C,F}$ = 238.3 Hz), 154.7, 149.5, 139. 8, 120.0 (d, $J_{C,F}$ = 7.1 Hz), 114.6 (d, $J_{C,F}$ = 22.2 Hz), 101.6, 74.4, 29.5. ^{19}F{1H} NMR (376 MHz, DMSO-d_6) δ −121.82. HRMS (ESI) calcd for $C_{12}H_{13}FN_2NaS$ $(M + Na)^+$ m/z 259.0681, found m/z 259.0683.

*1,4-Dibenzyl-3,5-diphenyl-1H-imidazol-2(3H)-one (**4a**).* Compound **4a** was obtained from **3a** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4a** (139 mg, 83% yield) as a pale yellow oil. The spectroscopic data of **4a** were consistent with literature values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.36 (m, 3H), 7.35−7.23 (m, 8H), 7.20−7.15 (m, 2H), 7.14−7.08 (m, 5H), 6.81−6.72 (m, 2H), 4.92 (s, 2H), 3.71 (s, 2H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 153.6, 138.2, 137.9, 135.2, 130.4, 129.1, 129.0, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.8, 127.3, 126.3, 122.3, 119.1, 45.5, 29.8. HRMS (ESI) calcd for $C_{29}H_{25}N_2O$ $(M + H)^+$ m/z 417.1967, found m/z 417.1970.

*1-Benzyl-4-nonyl-3,5-diphenyl-1H-imidazol-2(3H)-one (**4b**).* Compound **4b** was obtained from **3b** in 1 min, according to the general procedure. After 16 h, the yield of **4b** did not improve and most of the starting material was recovered (70%). The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give **4b** (33 mg, 18% yield) as a pale orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.45 (m, 2H), 7.42−7.40 (m, 1H), 7.40−7.38 (m, 1H), 7.38−7.34 (m, 4H), 7.23−7.15 (m, 5H), 7.06−7.02 (m, 2H), 4.81 (s, 2H), 2.35−2.31 (m, 2H), 1.27−0.90 (m, 14H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.5, 138.0, 135.7, 130.6, 129.5, 129.3, 128.6, 128.4, 128.4, 127.9, 127.8 (2C), 127.3, 121.1, 120.8, 45.4, 31.9, 29.3, 29.2, 28.9, 28.7, 28.4, 23.5, 22.7, 14.2. HRMS (ESI) calcd for $C_{31}H_{37}N_2O$ $(M + H)^+$ m/z 453.2906, found m/z 453.2902.

*4-Benzyl-1-butyl-3,5-diphenyl-1H-imidazol-2(3H)-one (**4c**).* Compound **4c** was obtained from **3c** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give **4c** (108 mg, 71% yield) as a white solid; mp (hexane) 112.6−113.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.36 (m, 5H), 7.31−7.23 (m, 3H), 7.14−7.05 (m, 5H), 6.73 (dd, J = 6.6, 2.8 Hz, 2H), 3.75−3.70 (m, 2H), 3.68 (s, 2H), 1.56−1.47 (m, 2H), 1.28−1.17 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.2, 138.3, 135.2, 130.0, 129.4, 128.9, 128.8, 128.5, 128.2, 128.0, 127.9,

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127.7, 126.2, 122.2, 118.7, 41.5, 31.3, 29.7, 19.8, 13.6. HRMS (ESI) calcd for $C_{26}H_{27}N_2O$ $(M + H)^+$ m/z 383.2123, found m/z 383.2126.

*4-Benzyl-3,5-diphenyl-1-(1-phenylethyl)-1H-imidazol-2(3H)-one (**4d**).* Compound **4d** was obtained from **3d** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4d** (160 mg, 93% yield) as pale orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.35 (m, 3H), 7.35−7.26 (m, 8H), 7.24−7.20 (m, 2H), 7.15 (dd, J = 7.9, 1.4 Hz, 2H), 7.13−7.08 (m, 3H), 6.74 (dd, J = 6.4, 2.6 Hz, 2H), 5.29 (q, J = 7.2 Hz, 1H), 3.72−3.56 (m, 2H), 1.86 (d, J = 7.2 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.1, 141.7, 138.2, 135.0, 131.0, 129.3, 128.8, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.6, 127.1, 127.0, 126.2, 122.3, 119.0, 53.0, 29.8, 18.6. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2120.

*4-Benzyl-1-(4-methylbenzyl)-3,5-diphenyl-1H-imidazol-2(3H)-one (**4e**).* Compound **4e** was obtained from **3e** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4e** (156 mg, 91% yield) as an orange solid; mp (hexane) 146.3−148.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.36 (m, 3H), 7.35−7.27 (m, 5H), 7.18−7.14 (m, 2H), 7.12−7.04 (m, 5H), 7.01 (d, J = 8.1 Hz, 2H), 6.75 (dd, J = 6.3, 2.7 Hz, 2H), 4.88 (s, 2H), 3.70 (s, 2H), 2.32 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.5, 138.2, 136.8, 135.1, 134.9, 130.4, 129.1 (2C), 128.9, 128.7, 128.5, 128.2, 128.0, 127.9, 127.8, 127.7, 126.2, 122.3, 119.0, 45.2, 29.7, 21.1. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2121.

*4-Benzyl-1-(4-fluorobenzyl)-3,5-diphenyl-1H-imidazol-2(3H)-one (**4f**).* Compound **4f** was obtained from **3f** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4f** (161 mg, 93% yield) as a dark yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.38 (m, 3H), 7.35−7.24 (m, 5H), 7.15 (dd, J = 7.7, 1.4 Hz, 2H), 7.12−7.03 (m, 5H), 6.93 (t, J = 8.7 Hz, 2H), 6.72 (dd, J = 6.2, 2.7 Hz, 2H), 4.86 (s, 2H), 3.69 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.05 (d, $J_{C,F}$ = 245.5 Hz), 153.4, 138.0, 135.0, 133.6 (d, $J_{C,F}$ = 3.2 Hz), 130.3, 129.6 (d, $J_{C,F}$ = 8.1 Hz), 128.9, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 126.2, 122.0, 119.2, 115.20 (d, $J_{C,F}$ = 21.4 Hz), 44.7, 29.7. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −115.09. HRMS (ESI) calcd for $C_{29}H_{24}FN_2O$ $(M + H)^+$ m/z 435.1873, found m/z 435.1875.

*1,4-Bibenzyl-3-phenyl-5-(p-tolyl)-1H-imidazol-2(3H)-one (**4g**).* Compound **4g** was obtained from **3g** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4g** (144 mg, 84% yield) as a dark yellow solid; mp (hexane) 125.8−127.3 °C. The spectroscopic data of **4g** were consistent with literature values.[35] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.26 (m, 7H), 7.23−7.15 (m, 5H), 7.15−7.10 (m, 4H), 7.07 (s, 1H), 6.79 (dd, J = 6.7, 2.3 Hz, 2H), 4.93 (s, 2H), 3.74 (s, 2H), 2.34 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.5, 138.2, 138.0, 135.2, 131.1, 129.3, 128.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 127.2, 126.2, 122.5, 118.8, 45.5, 29.7, 21.3. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2120.

*1,4-Dibenzyl-5-(4-methoxyphenyl)-3-phenyl-1H-imidazol-2(3H)-one (**4h**).* Compound **4h** was obtained from **3h** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4h** (137 mg, 77% yield) as a white solid; mp (hexane) 166.6−168.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.24 (m, 6H), 7.24−7.15 (m, 6H), 7.15−7.09 (m, 3H), 6.95−6.89 (m, 2H), 6.79 (dd, J = 7.1, 2.2 Hz, 2H), 4.91 (s, 2H), 3.82 (s, 3H), 3.71 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 159.7, 153.3, 138.2, 137.9, 135.1, 131.7, 128.8, 128.3, 128.1, 127.9, 127.8, 127.6 (2C), 127.1, 126.1, 121.9, 121.0, 118.6, 114.0, 55.2, 45.3, 29.6. HRMS (ESI) calcd for $C_{30}H_{27}N_2O_2$ $(M + H)^+$ m/z 447.2072, found m/z 447.2074.

*1,4-Dibenzyl-5-(3-chlorophenyl)-3-phenyl-1H-imidazol-2(3H)-one (**4i**).* Compound **4i** was obtained from **3i** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4i** (155 mg, 86% yield) as an orange solid; mp (hexane) 130.5−132.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.25 (m, 8H), 7.22 (t, J = 1.4 Hz, 1H), 7.18−7.09 (m, 8H), 6.73 (dd, J = 6.5, 2.4 Hz, 2H), 4.89 (s, 2H), 3.69 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.4, 137.6, 137.5, 134.8, 134.4, 130.7, 130.2, 129.9, 128.9, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.3, 126.3, 120.9, 119.7, 45.5, 29.6. HRMS (ESI) calcd for $C_{29}H_{24}ClN_2O$ $(M + H)^+$ m/z 451.1577, found m/z 451.1581.

*1,4-Dibenzyl-3-phenyl-5-(3-vinylphenyl)-1H-imidazol-2(3H)-one (**4j**).* Compound **4j** was obtained from **3j** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4j** (133 mg, 75% yield) as a pale yellow solid; mp (hexane) 143.8−145.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.8 Hz, 1H), 7.38−7.32 (m, 4H), 7.32−7.26 (m, 4H), 7.23−7.16 (m, 5H), 7.15−7.11 (m, 3H), 6.80 (dd, J = 6.8, 2.2 Hz, 2H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.62 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H), 4.93 (s, 2H), 3.74 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.6, 138.2, 138.02, 137.97, 136.1, 135.1, 129.6, 129.3, 129.0, 128.9, 128.5, 128.3, 128.14, 128.08, 127.97, 127.85, 127.77, 127.3, 126.5, 126.3, 122.2, 119.1, 114.8, 45.7, 29.8. HRMS (ESI) calcd for $C_{31}H_{27}N_2O$ $(M + H)^+$ m/z 443.2123, found m/z 443.2120.

*1,4-Dibenzyl-5-(2-bromophenyl)-3-phenyl-1H-imidazol-2(3H)-one (**4k**).* Compound **4k** was obtained from **3k** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give **4k** (134 mg, 68% yield) as a dark yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.3, 1.8 Hz, 1H), 7.39−7.31 (m, 3H), 7.30−7.19 (m, 7H), 7.14 (dd, J = 6.7, 2.5 Hz, 1H), 7.10−7.06 (m, 3H), 7.05−7.01 (m, 2H), 6.79 (dd, J = 6.4, 2.7 Hz, 2H), 5.12 (d, J = 15.2 Hz, 1H), 4.60 (d, J = 15.2 Hz, 1H), 3.71−3.52 (m, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.1, 137.5, 137.4, 135.0, 133.8, 132.9, 130.7, 130.1, 128.9, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.3, 127.2, 126.4, 126.1, 120.4, 119.7, 45.6, 30.0. HRMS (ESI) calcd for $C_{29}H_{24}BrN_2O$ $(M + H)^+$ m/z 495.1072, found m/z 495.1071.

*1,4-Dibenzyl-5-phenyl-3-propyl-1H-imidazol-2(3H)-one (**4l**).* Compound **4l** was obtained from **3l** in 1 min, according to the general procedure. After 16 h, the yield remain unchanged and 42% of the starting material was recovered. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4l** (50 mg, 33% yield) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.28 (m, 5H), 7.27−7.21 (m, 4H), 7.20−7.16 (m, 2H), 7.15−7.11 (m, 2H), 7.05 (dd, J = 7.8, 1.6 Hz, 2H), 4.87 (s, 2H), 3.81 (s, 2H), 3.48−3.43 (m, 2H), 1.60−1.49 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 154.0, 138.4, 138.2, 130.2, 129.2, 128.8, 128.6, 128.4, 128.3, 127.8, 127.4, 127.2, 126.8, 121.7, 118.1, 45.4, 43.45, 29.6, 22.8, 11.3. HRMS (ESI) calcd for $C_{26}H_{27}N_2O$ $(M + H)^+$ m/z 383.2123, found m/z 383.2127.

*1,3,4-tribenzyl-5-phenyl-1H-imidazol-2(3H)-one (**4m**).* Compound **4m** was obtained from **3m** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4m** (144 mg, 84% yield) as a yellow oil. Spectroscopic data of **4m** were consistent with literature values.[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.25 (m, 12H), 7.24−7.18 (m, 4H), 7.14−7.07 (m, 4H), 4.96 (s, 2H), 4.72 (s, 2H), 3.65 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 154.4, 138.1, 138.0, 137.9, 130.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 127.8, 127.4, 127.3, 127.2, 127.1, 126.8, 122.2, 118.0, 45.6, 44.9, 29.5. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2125.

*1-Benzyl-4-(4-methylbenzyl)-3,5-diphenyl-1H-imidazol-2(3H)-one (**4n**).* Compound **4n** was obtained from **3n** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (6:4) as eluent to give **4n** (139 mg, 81% yield) as a yellow solid; mp (hexane) 128.4−129.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.33 (m, 6H), 7.32−7.25 (m, 5H), 7.24−7.18 (m, 2H), 7.18−7.11 (m, 2H), 6.94 (d, J = 7.9 Hz, 2H), 6.66 (d, J = 7.9 Hz, 2H), 4.93 (s, 2H), 3.68 (s, 2H), 2.28 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.6, 137.9, 135.7, 135.1, 130.3, 129.1, 129.0, 128.9, 128.7, 128.5, 128.4, 128.1, 127.8 (2C),

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127.7, 127.3, 122.1, 119.2, 45.5, 29.2, 21.0. HRMS (ESI) calcd for $C_{30}H_{27}N_2O$ $(M + H)^+$ m/z 431.2123, found m/z 431.2122.

*1-Benzyl-4-(4-chlorobenzyl)-3,5-diphenyl-1H-imidazol-2(3H)-one (**4o**).* Compound **4o** was obtained from **3o** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give **4o** (176 mg, 98% yield) as a viscous light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.30 (m, 6H), 7.29−7.22 (m, 5H), 7.19 (d, J = 7.3 Hz, 2H), 7.14−7.03 (m, 4H), 6.66 (d, J = 8.3 Hz, 2H), 4.91 (s, 2H), 3.67 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 153.5, 137.8, 136.7, 135.1, 132.0, 130.3, 129.3, 129.1, 128.9, 128.8, 128.7, 128.4, 128.3, 128.0, 127.9, 127.8, 127.3, 122.5, 118.5, 45.5, 29.2. HRMS (ESI) calcd for $C_{29}H_{24}ClN_2O$ $(M + H)^+$ m/z 451.1577, found m/z 451.1576.

*1-Benzyl-4-(4-fluorobenzyl)-3,5-diphenyl-1H-imidazol-2(3H)-one (**4p**).* Compound **4p** was obtained from **3p** in 1 min, according to the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (7:3) as eluent to give **4p** (168 mg, 97% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.23 (m, 11H), 7.22−7.17 (m, 2H), 7.15−7.10 (m, 2H), 6.82−6.75 (m, 2H), 6.72−6.65 (m, 2H), 4.93 (s, 2H), 3.69 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 161.3 (d, $J_{C,F}$ = 244.6 Hz), 153.4, 137.8, 135.1, 133.7 (d, $J_{C,F}$ = 3.2 Hz), 130.3, 129.3 (d, $J_{C,F}$ = 7.9 Hz), 129.0, 128.9, 128.7, 128.6, 128.3, 127.9, 127.8, 127.7, 127.2, 122.3, 118.9, 114.9 (d, $J_{C,F}$ = 21.3 Hz), 45.4, 28.9. ^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ −116.60. HRMS (ESI) calcd for $C_{29}H_{24}FN_2O$ $(M + H)^+$ m/z 435.1873, found m/z 435.1874.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00064.

Copy of NMR spectra, computational details and single crystal X-ray diffraction data for **2a**, **2i** (Z), **2n′**, **4c**, and **4j** (PDF)

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Notes

The authors declare no competing financial interest.

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