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ORIGINAL PAPER

Chemoselective synthesis of β-enaminones from ynones and aminoalkyl-, phenol- and thioanilines under metal-free conditions

Xue Cui[1] · Yu Chen[1] · Wei Wang[1] · Tingting Zeng[1] · Youbin Li[1] · Xuesong Wang[1]

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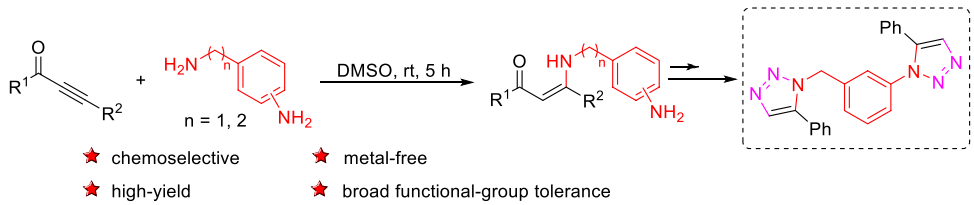
Abstract

An effective strategy for the chemoselective synthesis of β-enaminones is described by aza-Michael addition of aminoalkyl-, phenol- and thio-anilines to ynones under metal-free conditions. Diverse structural β-enaminones were obtained in up to 99% yield for 31 examples. The novel dual-1,5-disubstituted triazole scaffold was synthesized subsequently from β-enaminone. This strategy is highly efficient, highly chemoselective and metal-free.

Graphic Abstract



Keywords Chemoselective · β-enaminones · Ynones · Amines with two nucleophilic sites · Metal-free

Introduction

β-enaminones are unique scaffolds with nucleophilic and electrophilic motifs found in various *N*-containing heterocycles (Negri et al. 2004; Stanovnik et al. 2004; Elassar et al. 2003). Their specific structures and properties are present in pharmaceuticals and bioactive heterocycles such as anticonvulsant (Azzaro et al. 1981), anti-inflammatory (Dannhardt et al. 1998), antitumor agents (Boger et al. 1989), quinolone antibacterials (Wang et al. 1982) and quinoline antimalarials (Boger et al. 1989). Typical *N*-heterocyclic compounds based on β-enaminones include indole (Bernini et al. 2009; Liu et al. 2016, 2019; He et al. 2011; Sun et al. 2013; Tang et al. 2017), pyrrole (Yan et al. 2010; Cheng et al. 2018; Xu et al. 2020; Lei et al. 2016; Shen et al. 2013), pyridine (Cheng et al. 2017; Cheng et al. 2015; Yang et al. 2017; Shen et al. 2015; Kelgokmen et al. 2019), triazole (Cheng et al. 2013; Nino et al. 2019), quinolone (Xia et al. 2019, 2012), benzoxazole (Ge et al. 2020), thiazole (Wu et al. 2018), oxazole (Liu et al. 2020), quinolone (Zhang et al. 2019), quinoxaline (Ding et al. 2020) and triazine (Weng et al. 2018) (Fig. 1). Moreover, β-enaminones have also been employed as ligands for diastereoselective synthesis (Popov et al. 2003; Popov et al. 2001). Owing to their multifarious and prominent properties, the development of efficient methodologies to build such structures is still an area of very active research.

Conventionally, the most popular approaches to the construction of β-enaminones consist of: (a) the acid-catalyzed amination of 1,3-diketones (Scheme 1a) (Arcadi et al. 2003; Bartoli et al. 2004; Bhosale et al. 2006; Epifano et al. 2007; Xu et al. 2009); (b) the aza-Michael addition of amines to ynones (Scheme 1b) (Karpov et al. 2003a, b); or (c) the aza-Michael addition of ynone intermediates from α-keto acids and iodoalkynes (Scheme 1c) (Zeng et al. 2019).

✉ Xuesong Wang
wxuesong18@163.com

[1] Key Laboratory of Tropical Translational Medicine of Ministry of Education, Hainan Provincial Key Laboratory for Research and Development of Tropical Herbs, School of Pharmacy, Hainan Medical University, Haikou 571199, People's Republic of China

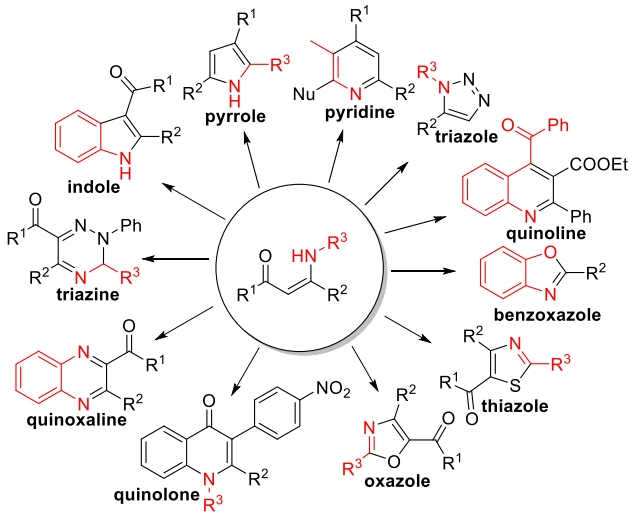


Fig. 1 Typical *N*-heterocyclic compounds based on *β*-enaminone

Nevertheless, methodologies based on the acid-catalyzed reactions limit their potential application in the pharmaceutical industry owing to low amination regioselectivity, while routes based on aza-Michael addition have higher regioselectivity (amination only on the *β*-site of ynones) and simple reaction conditions. However, if there are two nucleophilic sites in anilines (rout b and c), the desired product *β*-enaminones could be obtained as an isomeric mixture. Accordingly, the synthesis of single *β*-enaminones is still a challenging task and the development of more effective methods for such purpose is highly desirable. Herein, we designed an effective strategy for the synthesis of *β*-enaminones via the chemoselective aza-Michael addition of amines to ynones under metal-free conditions (Scheme 1d).

Results and discussion

At the outset of the study, the aza-Michael addition of 1,3-diphenylprop-2-yn-1-one **1a** and 4-(aminomethyl)aniline **2a** was chosen as a model reaction to screen the reaction parameters (Table 1). To our delight, the desired product **3aa** was obtained in 40% yield when the reaction was conducted at room temperature in DCM for 5 h (entry 1). Simultaneously, the by-product **4aa** was also provided in 15% yield. Further studies focused on screening of versatile solvent and indicated that this transformation was highly solvent dependent (entries 2–10). The yield of **3aa** was improved to 90% by switching the solvent DCM to DMF, while no obvious deviations were observed between DMF, NMP and DMSO (entries 2–4). However, other solvents, such as EtOH, toluene, 1,4-dioxane, THF, CH_3CN and H_2O led to lower yield (entries 5–10). On the basis of the above results, the optimal reaction conditions were identified as follows: DMSO as the solvent at room temperature for 5 h to give the single product **3aa** in 95% yield (Table 1, entry 4).

With the optimized conditions in hand, the scope and generality of the aza-Michael addition reactions were investigated (Table 2). Interestingly, a wide range of substituents was well tolerated under the reaction conditions, affording the corresponding *β*-enaminones (**3aa–3af**) in 80–99% yields. First, the substituents R^1 of ynones **1** were examined, and the substituents with electron-donating groups (–Me, –*n*Bu, –OMe) (**3ba–3ea**) provided the corresponding products in higher yields than those bearing electron-withdrawing substituents (–F, –Cl, –Br, –CN) (**3fa–3 ka**). Compared to the yield of **3fa** with the yield of **3 ha** (88% *vs.* 85%), we found that the steric hindrance did not influence this reaction obviously. Moreover, either electron-donating groups (such as –Me, –OMe) (**3la–3oa and 3ta**) or electron-withdrawing groups (such as –F, –Cl, –Br, –I) (**3pa–3sa and 3ua**) in the R^2 substituent of ynones **1** could react smoothly with

Scheme 1 Strategies for the synthesis of *β*-enaminones

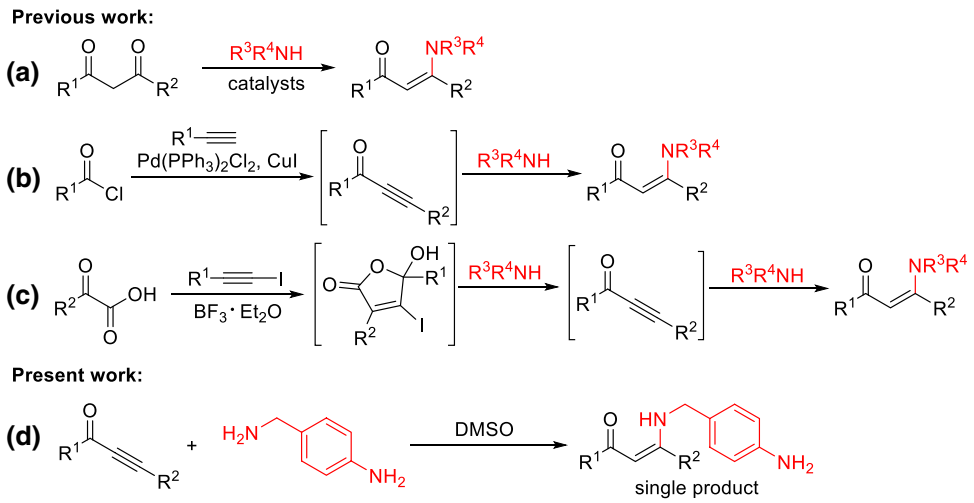
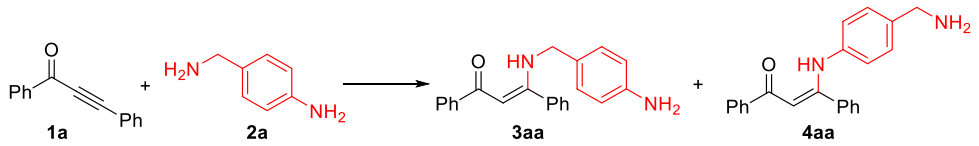


Table 1 Optimization of the reaction conditions



Entry	Solvent	Yield (%)[a]	
		3aa	**4aa**
1	DCM	40	15
2	DMF	90	6
3	NMP	88	9
4	**DMSO**	**95 (93)**[b]	**0**
5	EtOH	65	25
6	toluene	25	8
7	1,4-Dioxane	35	10
8	THF	50	16
9	CH_3CN	45	14
10	H_2O	5	0

General conditions are **1a** (0.5 mmol), **2a** (0.6 mmol) in 2 mL of solvent at room temperature for 5 h under air

Bold values indicate the optimal reaction conditions

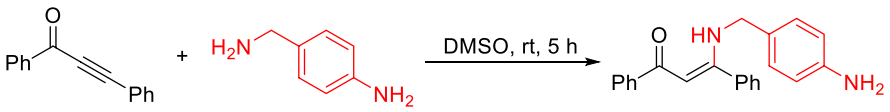
DMF N,N-dimethylformamide, *DMSO* dimethylsulfoxide, *NMP* 1-methylpyrrolidin-2-one, *THF* tetrahydrofuran.

[a]Yield was determined by GC base on **1a**

[b]Isolated yield

4-(aminomethyl)aniline **2a**, affording the corresponding *β*-enaminones in excellent yields. A significant influence of steric hindrance on this reaction was observed. For instance, the *ortho*-substituted substrate led to lower yield than the *para*-substituted substrate (**3la** *vs.* **3na**). Other representative aromatic and aliphatic substrates, such as naphthyl, thienyl and aliphatic groups, were also tolerated (**3va**–**3za**).

To prove the practicality of this aza-Michael addition reaction, a gram-scale synthesis of *β*-enaminone **3aa** was performed. When 2.06 g of 1,3-diphenylprop-2-yn-1-one **1a** (10 mmol) and 1.47 g of 4-(aminomethyl)aniline **2a** (12 mmol) were loaded, 3.05 g of *β*-enaminone **3aa** was obtained in 93% yield (Eq. 1).

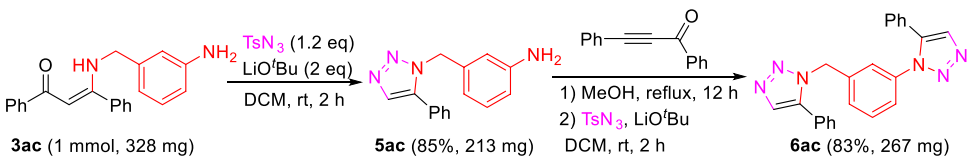


1a (10 mmol, 2.06 g) **2a** (12 mmol, 1.47 g) **3aa** (3.05 g, 93%) (1)

Additionally, 4-(2-aminoethyl)aniline **2b**, 3-(aminomethyl) aniline **2c** and 2-(aminomethyl)aniline **2d** were also tested and furnished the desired products in 98%, 92% and 85% yields, respectively (**3ab**, **3ac**, **and 3ad**). Finally, 4-(aminomethyl)phenol and 2-aminoethane-1-thiol were also investigated under the standard reaction conditions and good yields of the target products were obtained (**3ae** and **3af**).

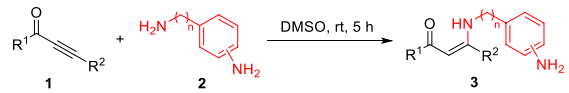
Yield of isolated product based on ynones **1** was reported.

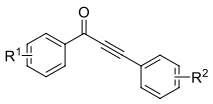
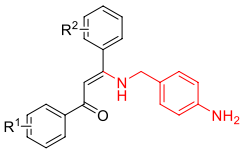
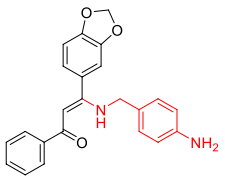
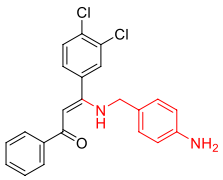
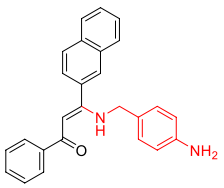
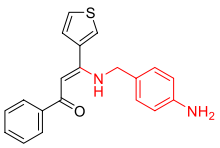
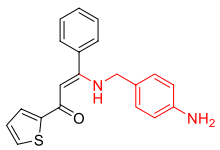
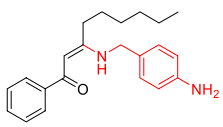
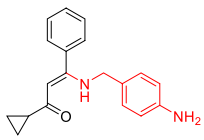
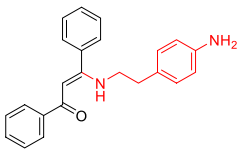
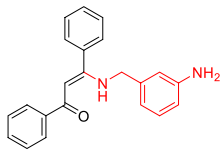
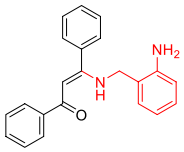
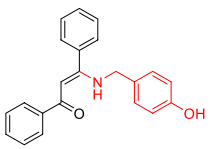
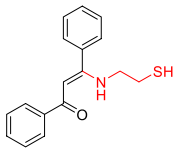
To further demonstrate the application of *β*-enaminones in the synthesis of complicated molecules, *β*-enaminone **3ac** was employed with tosyl azide in the presence of $LiOBu^t$ to furnish the 1,2,3-triazole **5ac** in 85% yield (Cheng et al. 2013). Subsequently, the novel dual(triazole) structure **6ac** containing two 1,5-disubstituted triazoles scaffold could be generated in 83% yield from **5ac** and ynone **1a** (Eq. 2).



3ac (1 mmol, 328 mg) **5ac** (85%, 213 mg) **6ac** (83%, 267 mg) (2)

Table 2 Scope of Substrates



Entry	Substrate	Product	Yield (%)
			
1	R^1 = H, R^2 = H, **1a**	**3aa**	93
2	R^1 = 4-Me, R^2 = H, **1b**	**3ba**	97
3	R^1 = 4-*n*-Bu, R^2 = H, **1c**	**3ca**	98
4	R^1 = 3-Me, R^2 = H, **1d**	**3da**	91
5	R^1 = 3-OMe, R^2 = H, **1e**	**3ea**	99
6	R^1 = 4-F, R^2 = H, **1f**	**3fa**	88
7	R^1 = 3-F, R^2 = H, **1g**	**3ga**	90
8	R^1 = 2-F, R^2 = H, **1h**	**3ha**	85
9	R^1 = 4-Cl, R^2 = H, **1i**	**3ia**	89
10	R^1 = 4-Br, R^2 = H, **1j**	**3ja**	91
11	R^1 = 4-CN, R^2 = H, **1k**	**3ka**	86
12	R^1 = H, R^2 = 4-Me, **1l**	**3la**	96
13	R^1 = H, R^2 = 3-Me, **1m**	**3ma**	88
14	R^1 = H, R^2 = 2-Me, **1n**	**3na**	78
15	R^1 = H, R^2 = 4-OMe, **1o**	**3oa**	98
16	R^1 = H, R^2 = 4-F, **1p**	**3pa**	87
17	R^1 = H, R^2 = 4-Cl, **1q**	**3qa**	89
18	R^1 = H, R^2 = 4-Br, **1r**	**3ra**	86
19	R^1 = H, R^2 = 4-I, **1s**	**3sa**	85
20		**3ta**, 93%	
21		**3ua**, 82%	
22		**3va**, 84%	
23		**3wa**, 80%	
24		**3xa**, 85%	
25		**3ya**, 81%	
26		**3za**, 79%	
27		**3ab**, 98%	
28		**3ac**, 92%	
29		**3ad**, 85%	
30		**3ae**, 92%	
31		**3af**, 88%	

Conclusions

In conclusion, an effective strategy for the chemoselective synthesis of β-enaminones was developed. This reaction tolerated a wide range of functional groups in moderate-to-excellent yields under metal-free conditions. Due to the importance of β-enaminones, this protocol could be further expanded to find wide applications in synthetic chemistry. This strategy is highly efficient, high chemoselective and metal-free.

Experimental section

General information

Unless otherwise stated, all reagents were used directly without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400 MHz, ^{13}C100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. HRMS-ESI spectra were equipped with an ESI source and a TOF detector. PE is petroleum ether (60–90 °C).

Typical procedure for the preparation of (*Z*)-3-((4-aminobenzyl) amino)-1,3-diphenylprop-2-en-1-one (3aa)

A suspension of 1,3-diphenylprop-2-yn-1-one **1a** (0.5 mmol, 103.0 mg) and 4-(aminomethyl)aniline **2a** (0.6 mmol, 73.2 mg) in DMSO (2 mL) was stirred at rt for 5 h. After 1,3-diphenylprop-2-yn-1-one exhausted completely (monitored by TLC), saturated aqueous brine (20 mL) was added. The mixture was stirred for 10 min and then was extracted by EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4. Removal of the solvent gave a residue, which was purified by a column chromatography (silica gel, PE/EtOAc/TEA = 100/15/1) to afford **3aa** as light yellow solid; mp 95–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (*s*, 1H), 7.90 (*d*, *J* = 8.0 Hz, 2H), 7.44–7.39 (*m*, 8H), 7.00 (*d*, *J* = 8.0 Hz, 2H), 6.62 (*d*, *J* = 8.0 Hz, 2H), 5.81 (*s*, 1H), 4.30 (*d*, *J* = 4.0 Hz, 2H), 3.66 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 166.6, 145.7, 140.2, 135.6, 130.6, 129.4, 128.5 (2C), 128.2 (2C), 128.1 (2C), 128.0, 127.7 (2C), 127.0 (2C), 115.2 (2C), 93.6, 48.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{20}N_2O$, $(M+Na)^+$ 351.1468; found, 351.1469.

A similar procedure was used for the preparation of products **3ba**–**3af**.

(*Z*)-3-((4-aminobenzyl)amino)-3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (**3ba**) yellow solid, mp 93–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (*s*, 1H), 7.79 (*d*, *J* = 8.0 Hz, 2H), 7.44–7.40 (*m*, 5H), 7.19 (*d*, *J* = 8.0 Hz, 2H), 6.99 (*d*, *J* = 8.0 Hz, 2H), 6.61 (*d*, *J* = 8.0 Hz, 2H), 5.78 (*s*, 1H), 4.27 (*d*, *J* = 8.0 Hz, 2H), 3.62 (*s*, 2H), 2.37 (*s*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 166.3, 145.7, 141.0, 137.5, 135.6, 129.4, 128.9 (2C), 128.4 (2C), 128.2 (3C), 127.8 (2C), 127.1 (2C), 115.3 (2C), 93.5, 48.1, 21.4. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O$, $(M+Na)^+$ 365.1624; found, 365.1627.

(*Z*)-3-((4-aminobenzyl)amino)-1-(4-butylphenyl)-3-phenylprop-2-en-1-one (**3ca**) yellow solid, mp 79–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (*t*, *J* = 8.0 Hz, 1H), 7.81 (*d*, *J* = 8.0 Hz, 2H), 7.44–7.40 (*m*, 5H), 7.19 (*d*, *J* = 8.0 Hz, 2H), 6.99 (*d*, *J* = 8.0 Hz, 2H), 6.61 (*d*, *J* = 8.0 Hz, 2H), 5.78 (*s*, 1H), 4.28 (*d*, *J* = 4.0 Hz, 2H), 3.66 (*s*, 2H), 2.63 (*t*, *J* = 8.0 Hz, 2H), 1.60 (*m*, 2H), 1.34 (*m*, 2H), 0.91 (*t*, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 166.3, 146.0, 145.7, 137.7, 135.7, 129.4, 128.4 (2C), 128.24, 128.21 (3C), 128.18 (2C), 127.8 (2C), 127.1 (2C), 115.3 (2C), 93.6, 48.1, 35.5, 33.4, 22.3, 13.9. HRMS *m/z* (ESI) calcd for $C_{26}H_{28}N_2O$, $(M+Na)^+$ 407.2094; found, 407.2096.

(*Z*)-3-((4-aminobenzyl)amino)-3-phenyl-1-(*m*-tolyl) prop-2-en-1-one (**3da**) yellow solid, mp 87–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (*t*, *J* = 8.0 Hz, 1H), 7.71 (*s*, 1H), 7.68 (*d*, *J* = 4.0 Hz, 1H), 7.44–7.40 (*m*, 5H), 7.29–7.20 (*m*, 3H), 6.99 (*d*, *J* = 8.0 Hz, 2H), 6.61 (*d*, *J* = 8.0 Hz, 2H), 5.78 (*s*, 1H), 4.28 (*d*, *J* = 4.0 Hz, 2H), 3.60 (*s*, 2H), 2.37 (*s*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 166.4, 145.7, 140.2, 137.8, 135.6, 131.4, 129.4, 128.4 (2C), 128.2 (2C), 128.1, 128.0, 127.73 (2C), 127.68, 124.2, 115.2 (2C), 93.7, 48.1, 21.4. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O$, $(M+Na)^+$ 365.1624; found, 365.1625.

(*Z*)-3-((4-aminobenzyl)amino)-3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (**3ea**) yellow solid, mp 103–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.59 (*t*, *J* = 8.0 Hz, 1H), 7.47–7.40 (*m*, 7H), 7.28 (*d*, *J* = 8.0 Hz, 2H), 6.98 (*m*, 3H), 6.62 (*d*, *J* = 8.0 Hz, 2H), 5.78 (*s*, 1H), 4.29 (*d*, *J* = 4.0 Hz, 2H), 3.83 (*s*, 3H), 3.65 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 166.6, 159.6, 145.7, 141.7, 135.5, 129.5, 129.1, 128.5 (2C), 128.2 (2C), 128.0, 127.7 (2C), 119.5, 117.2, 115.3 (2C), 111.5, 93.7, 55.3, 48.2. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O_2$, $(M+Na)^+$ 381.1573; found, 381.1575.

(*Z*)-3-((4-aminobenzyl)amino)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (**3fa**) yellow solid, mp 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (*s*, 1H), 7.89 (*t*, *J* = 8.0 Hz, 2H), 7.46–7.36 (*m*, 5H), 7.05 (*t*, *J* = 8.0 Hz, 2H), 6.98 (*d*, *J* = 8.0 Hz, 2H), 6.61 (*d*, *J* = 8.0 Hz, 2H), 5.73 (*s*, 1H), 4.28 (*d*, *J* = 8.0 Hz, 2H), 3.62 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 166.7, 164.4 (*d*, *J* = 249.0 Hz), 145.8, 136.4 (*d*, *J* = 3.0 Hz), 135.4, 129.5, 129.2 (*d*, *J* = 8.0 Hz, 2C), 128.5 (2C), 128.2 (2C), 127.9, 127.7 (2C), 115.3 (2C), 115.0 (*d*,

J = 21.0 Hz, 2C), 93.2, 48.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}FN_2O$, $(M+Na)^+$ 369.1374; found, 369.1378.

(*Z*)-3-((4-aminobenzyl)amino)-1-(3-fluorophenyl)-3-phenylprop-2-en-1-one (**3ga**) yellow solid, mp 98–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (*s*, 1H), 7.65 (*d*, J = 8.0 Hz, 1H), 7.58 (*d*, J = 8.0 Hz, 1H), 7.48–7.39 (*m*, 5H), 7.36–7.31 (*m*, 1H), 7.10 (*t*, J = 8.0 Hz, 1H), 6.99 (*d*, J = 8.0 Hz, 2H), 6.62 (*d*, J = 8.0 Hz, 2H), 5.74 (*s*, 1H), 4.30 (*d*, J = 4.0 Hz, 2H), 3.64 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.56 (*d*, J = 2.0 Hz), 167.1, 162.8 (*d*, J = 245.0 Hz), 145.8, 142.6 (*d*, J = 7.0 Hz), 135.3, 129.7, 129.6, 128.5 (2C), 128.2 (2C), 127.8, 127.7 (2C), 122.6 (*d*, J = 2.0 Hz), 117.4 (*d*, J = 21.0 Hz), 115.3 (2C), 113.9 (*d*, J = 22.0 Hz), 93.4, 48.2. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}FN_2O$, $(M+Na)^+$ 369.1374; found, 369.1375.

(*Z*)-3-((4-aminobenzyl)amino)-1-(2-fluorophenyl)-3-phenylprop-2-en-1-one (**3 ha**) yellow solid, mp 115–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (*s*, 1H), 7.83 (*t*, J = 8.0 Hz, 1H), 7.44–7.32 (m, 6H), 7.17 (*t*, J = 8.0 Hz, 1H), 7.05 (*d*, J = 8.0 Hz, 1H), 7.00 (*d*, J = 8.0 Hz, 2H), 6.62 (*d*, J = 8.0 Hz, 2H), 5.76 (*s*, 1H), 4.30 (*d*, J = 8.0 Hz, 2H), 3.66 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.95 (*d*, J = 3.0 Hz), 166.7, 160.3 (*d*, J = 250.0 Hz), 145.8, 135.2, 131.7 (*d*, J = 9.0 Hz), 130.3 (*d*, J = 3.0 Hz), 129.5, 128.8 (*d*, J = 13.0 Hz), 128.5 (2C), 128.2 (2C), 127.83, 127.76 (2C), 124.0 (*d*, J = 4.0 Hz), 116.1 (*d*, J = 24.0 Hz), 115.3 (2C), 97.9 (*d*, J = 9.0 Hz), 48.2. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}FN_2O$, $(M+Na)^+$ 369.1374; found, 369.1376.

(*Z*)-3-((4-aminobenzyl)amino)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**3ia**) yellow solid, mp 101–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (*t*, J = 4.0 Hz, 1H), 7.82 (*d*, J = 8.0 Hz, 2H), 7.45–7.33 (*m*, 7H), 6.98 (*d*, J = 8.0 Hz, 2H), 6.61 (*d*, J = 8.0 Hz, 2H), 5.73 (*s*, 1H), 4.28 (*d*, J = 8.0 Hz, 2H), 3.65 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 166.9, 145.8, 138.6, 136.7, 135.3, 129.6, 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.8, 127.7 (2C), 115.3 (2C), 93.2, 48.2. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}ClN_2O$, $(M+Na)^+$ 385.1078; found, 385.1080.

(*Z*)-3-((4-aminobenzyl)amino)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (**3ja**) yellow solid, mp 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (*t*, J = 4.0 Hz, 1H), 7.75 (*d*, J = 12.0 Hz, 2H), 7.51–7.38 (*m*, 7H), 6.98 (*d*, J = 12.0 Hz, 2H), 6.60 (*d*, J = 8.0 Hz, 2H), 5.73 (*s*, 1H), 4.28 (*d*, J = 4.0 Hz, 2H), 3.66 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 166.9, 145.8, 139.0, 135.3, 131.3 (2C), 129.5, 128.6 (2C), 128.5 (2C), 128.2 (2C), 127.7, 127.6 (2C), 125.2, 115.2 (2C), 93.2, 48.2. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}BrN_2O$, $(M+Na)^+$ 429.0573; found, 429.0576.

(*Z*)-4-(3-((4-aminobenzyl)amino)-3-phenylacryloyl) benzonitrile (**3 ka**) yellow solid, mp 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (*t*, J = 4.0 Hz, 1H), 7.95 (*d*, J = 12.0 Hz, 2H), 7.66 (*d*, J = 8.0 Hz, 2H), 7.49–7.39 (*m*, 5H), 6.99 (*d*, J = 12.0 Hz, 2H), 6.63 (*d*, J = 8.0 Hz, 2H), 5.75 (*s*, 1H), 4.32 (*d*, J = 4.0 Hz, 2H), 3.28 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 167.6, 145.9, 144.0, 134.9, 132.0 (2C), 129.8, 128.6 (2C), 128.2 (2C), 127.5 (2C), 127.4, 127.3 (2C), 118.6, 115.2 (2C), 113.6, 93.5, 48.3. HRMS *m/z* (ESI) calcd for $C_{23}H_{19}N_3O$, $(M+Na)^+$ 354.1601; found, 354.1600.

(*Z*)-3-((4-aminobenzyl)amino)-1-phenyl-3-(*p*-tolyl)prop-2-en-1-one (**3la**) yellow solid, mp 108–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (*s*, 1H), 7.89 (*d*, J = 8.0 Hz, 2H), 7.44–7.36 (*m*, 3H), 7.31 (*d*, J = 8.0 Hz, 2H), 7.23 (*d*, J = 8.0 Hz, 2H), 7.01 (*d*, J = 8.0 Hz, 2H), 6.62 (*d*, J = 8.0 Hz, 2H), 5.79 (*s*, 1H), 4.30 (*d*, J = 4.0 Hz, 2H), 3.58 (*s*, 2H), 2.40 (*s*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 166.8, 145.7, 140.3, 139.6, 132.7, 130.6, 129.1 (2C), 128.20, 128.18 (2C), 128.13 (2C), 127.7 (2C), 127.0 (2C), 115.3 (2C), 93.6, 48.1, 21.3. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O$, $(M+Na)^+$ 365.1624; found, 365.1627.

(*Z*)-3-((4-aminobenzyl)amino)-1-phenyl-3-(*m*-tolyl)prop-2-en-1-one (**3ma**) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (*t*, J = 8.0 Hz, 1H), 7.81 (*d*, J = 8.0 Hz, 2H), 7.36–7.12 (*m*, 7H), 6.92 (*d*, J = 8.0 Hz, 2H), 6.54 (*d*, J = 8.0 Hz, 2H), 5.71 (*s*, 1H), 4.21 (*d*, J = 4.0 Hz, 2H), 3.33 (*s*, 2H), 2.31 (*s*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 166.8, 145.7, 140.3, 138.3, 135.5, 130.6, 130.2, 128.3 (2C), 128.2 (2C), 128.14, 128.12 (2C), 127.0 (2C), 124.8, 115.2 (2C), 93.5, 48.2, 21.4. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O$, $(M+Na)^+$ 365.1624; found, 365.1626.

(*Z*)-3-((4-aminobenzyl)amino)-1-phenyl-3-(*o*-tolyl)prop-2-en-1-one (**3na**) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (*t*, J = 8.0 Hz, 1H), 7.87 (*d*, J = 8.0 Hz, 2H), 7.42–7.19 (*m*, 7H), 6.93 (*d*, J = 8.0 Hz, 2H), 6.59 (*d*, J = 8.0 Hz, 2H), 5.70 (*s*, 1H), 4.08 (*d*, J = 4.0 Hz, 2H), 3.65 (*s*, 2H), 2.30 (*s*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 166.0, 145.8, 140.1, 135.2, 135.1, 130.6, 130.2, 129.0, 128.5 (2C), 128.1 (2C), 127.7, 127.6, 127.0 (2C), 125.8, 115.2 (2C), 92.8, 47.7, 19.3. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O$, $(M+Na)^+$ 365.1624; found, 365.1624.

(*Z*)-3-((4-aminobenzyl)amino)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**3oa**) yellow solid, mp 125–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (*t*, J = 8.0 Hz, 1H), 7.89 (*d*, J = 8.0 Hz, 2H), 7.43–7.35 (*m*, 5H), 7.01 (*d*, J = 8.0 Hz, 2H), 6.94 (*d*, J = 8.0 Hz, 2H), 6.61 (*d*, J = 8.0 Hz, 2H), 5.79 (*s*, 1H), 4.32 (*d*, J = 4.0 Hz, 2H), 3.83 (*s*, 3H), 3.48 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 166.6, 160.5, 145.7, 140.3, 130.5, 129.3 (2C), 128.2, 128.1 (3C), 127.8, 127.0 (2C), 115.2 (2C), 113.8 (2C), 93.6, 55.3, 48.1. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O_2$, $(M+Na)^+$ 381.1573; found, 381.1574.

(*Z*)-3-((4-aminobenzyl)amino)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (**3pa**) yellow solid, mp 135–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.58 (*t*, J = 8.0 Hz, 1H), 7.88 (*t*, J = 8.0 Hz, 2H), 7.44–7.37 (*m*, 6H), 7.11 (*t*, J = 8.0 Hz, 2H), 6.98 (*d*, J = 8.0 Hz, 2H), 6.62 (*d*, J = 8.0 Hz, 2H), 5.77

(*s*, 1H), 4.27 (*d*, *J* = 8.0 Hz, 2H), 3.65 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 165.5, 163.3 (*d*, *J* = 248.0 Hz), 145.8, 140.1, 131.6 (*d*, *J* = 4.0 Hz), 130.8, 129.8 (*d*, *J* = 8.0 Hz, 2C), 128.2 (2C), 128.1 (2C), 128.0, 127.0 (2C), 115.6 (*d*, *J* = 21.0 Hz, 2C), 115.3 (2C), 93.8, 48.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}FN_2O$, $(M + Na)^+$ 369.1374; found, 369.1375.

(*Z*)-3-((4-aminobenzyl)amino)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (**3qa**) yellow solid, mp 150–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (*t*, *J* = 4.0 Hz, 1H), 7.88 (*d*, *J* = 8.0 Hz, 2H), 7.45–7.33 (m, 7H), 6.98 (*d*, *J* = 8.0 Hz, 2H), 6.62 (*d*, *J* = 8.0 Hz, 2H), 5.76 (*s*, 1H), 4.26 (*d*, *J* = 8.0 Hz, 2H), 3.67 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 165.3, 145.8, 140.0, 135.6, 134.0, 130.8, 129.2 (2C), 128.8 (2C), 128.2 (2C), 128.1 (2C), 128.0, 127.1 (2C), 115.3 (2C), 93.7, 48.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}ClN_2O$, $(M + Na)^+$ 385.1078; found, 385.1079.

(*Z*)-3-((4-aminobenzyl)amino)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one (**3ra**) yellow solid, mp 145–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (*t*, *J* = 8.0 Hz, 1H), 7.88 (*d*, *J* = 8.0 Hz, 2H), 7.56 (*d*, *J* = 8.0 Hz, 2H), 7.45–7.37 (*m*, 3H), 7.27 (*d*, *J* = 8.0 Hz, 2H), 6.97 (*d*, *J* = 8.0 Hz, 2H), 6.62 (*d*, *J* = 8.0 Hz, 2H), 5.75 (*s*, 1H), 4.25 (*d*, *J* = 8.0 Hz, 2H), 3.65 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 165.2, 145.8, 140.0, 134.4, 131.7 (2C), 130.8, 129.4 (2C), 128.2 (2C), 128.1 (2C), 127.9, 127.0 (2C), 123.8, 115.3 (2C), 93.7, 48.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}BrN_2O$, $(M + Na)^+$ 429.0573; found, 429.0574.

(*Z*)-3-((4-aminobenzyl)amino)-3-(4-iodophenyl)-1-phenylprop-2-en-1-one (**3sa**) yellow solid, mp 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (*t*, *J* = 8.0 Hz, 1H), 7.87 (*d*, *J* = 8.0 Hz, 2H), 7.77 (*d*, *J* = 8.0 Hz, 2H), 7.45–7.37 (*m*, 3H), 7.14 (*d*, *J* = 8.0 Hz, 2H), 6.98 (*d*, *J* = 8.0 Hz, 2H), 6.62 (*d*, *J* = 8.0 Hz, 2H), 5.75 (*s*, 1H), 4.26 (*d*, *J* = 8.0 Hz, 2H), 3.66 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 165.3, 145.8, 140.0, 137.7 (2C), 135.0, 130.9, 129.5 (2C), 128.2 (2C), 128.1 (2C), 127.9, 127.0 (2C), 115.3 (2C), 95.6, 93.6, 48.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}IN_2O$, $(M + Na)^+$ 477.0434; found, 477.0435.

(*Z*)-3-((4-aminobenzyl)amino)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylprop-2-en-1-one (**3ta**) yellow solid, mp 116–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (*t*, *J* = 8.0 Hz, 1H), 7.88 (*d*, *J* = 8.0 Hz, 2H), 7.44–7.36 (*m*, 3H), 7.02 (*d*, *J* = 8.0 Hz, 2H), 6.93–6.84 (*m*, 3H), 6.63 (*d*, *J* = 8.0 Hz, 2H), 6.02 (*s*, 2H), 5.78 (*s*, 1H), 4.33 (*d*, *J* = 4.0 Hz, 2H), 3.64 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 166.2, 148.6, 147.7, 145.7, 140.3, 130.7, 129.3, 128.17 (2C), 128.16 (3C), 127.0 (2C), 121.9, 115.3 (2C), 108.38, 108.35, 101.5, 93.6, 48.2. HRMS *m/z* (ESI) calcd for $C_{23}H_{20}N_2O_3$, $(M + Na)^+$ 395.1366; found, 395.1369.

(*Z*)-3-((4-aminobenzyl)amino)-3-(3,4-dichlorophenyl)-1-phenylprop-2-en-1-one (**3ua**) yellow solid, mp 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (*t*, *J* = 4.0 Hz, 1H), 7.88 (*d*, *J* = 4.0 Hz, 2H), 7.51–7.38 (*m*, 5H), 7.23 (*d*, *J* = 8.0 Hz, 2H), 6.97 (*d*, *J* = 8.0 Hz, 2H), 6.63 (*d*, *J* = 8.0 Hz, 2H), 5.75 (*s*, 1H), 4.25 (*d*, *J* = 8.0 Hz, 2H), 3.47 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 163.7, 145.9, 139.8, 135.4, 133.8, 132.9, 131.0, 130.6, 129.8, 128.3 (2C), 128.1 (2C), 127.8, 127.12, 127.08 (2C), 115.3 (2C), 93.8, 48.2. HRMS *m/z* (ESI) calcd for $C_{22}H_{18}Cl_2N_2O$, $(M + Na)^+$ 419.0688; found, 419.0690.

(*Z*)-3-((4-aminobenzyl)amino)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (**3va**) yellow solid, mp 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (*t*, *J* = 8.0 Hz, 1H), 7.95–7.87 (*m*, 6H), 7.59–7.38 (*m*, 6H), 7.02 (*d*, *J* = 8.0 Hz, 2H), 6.63 (*d*, *J* = 8.0 Hz, 2H), 5.92 (*s*, 1H), 4.35 (*d*, *J* = 4.0 Hz, 2H), 3.66 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 166.5, 145.7, 140.2, 133.5 (2C), 133.0, 132.8, 130.7, 128.3, 128.19 (2C), 128.16 (2C), 128.0, 127.8, 127.4, 127.0 (3C), 126.7, 125.1, 115.3 (2C), 93.9, 48.3. HRMS *m/z* (ESI) calcd for $C_{26}H_{22}N_2O$, $(M + Na)^+$ 401.1624; found, 401.1626.

(*Z*)-3-((4-aminobenzyl)amino)-1-phenyl-3-(thiophen-3-yl)prop-2-en-1-one (**3wa**) yellow solid, mp 170–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (*t*, *J* = 8.0 Hz, 1H), 7.91 (*d*, *J* = 12.0 Hz, 2H), 7.48–7.37 (*m*, 5H), 7.18 (*d*, *J* = 4.0 Hz, 1H), 7.03 (*d*, *J* = 12.0 Hz, 2H), 6.64 (*d*, *J* = 8.0 Hz, 2H), 5.90 (*s*, 1H), 4.39 (*d*, *J* = 8.0 Hz, 2H), 3.68 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 161.4, 145.7, 140.2, 136.1, 130.7, 128.1 (2C), 128.04, 127.97 (2C), 127.3, 127.0 (2C), 126.2, 125.8, 115.3 (2C), 93.3, 48.1. HRMS *m/z* (ESI) calcd for $C_{20}H_{18}N_2OS$, $(M + Na)^+$ 357.1032; found, 357.1033.

(*Z*)-3-((4-aminobenzyl)amino)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (**3xa**) yellow solid, mp 136–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (*t*, *J* = 8.0 Hz, 1H), 7.54 (*d*, *J* = 4.0 Hz, 1H), 7.45–7.39 (*m*, 6H), 7.04 (*t*, *J* = 4.0 Hz, 1H), 6.98 (*d*, *J* = 12.0 Hz, 2H), 6.60 (*d*, *J* = 8.0 Hz, 2H), 5.69 (*s*, 1H), 4.26 (*d*, *J* = 4.0 Hz, 2H), 3.69 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 166.2, 147.0, 145.8, 135.2, 129.9, 129.4, 128.4 (2C), 128.1 (2C), 127.63, 127.60 (3C), 127.5, 115.1 (2C), 93.1, 48.1. HRMS *m/z* (ESI) calcd for $C_{20}H_{18}N_2OS$, $(M + Na)^+$ 357.1032; found, 357.1035.

(*Z*)-3-((4-aminobenzyl)amino)-1-phenylnon-2-en-1-one (**3ya**) yellow solid, mp 78–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (*t*, *J* = 8.0 Hz, 1H), 7.88 (*d*, *J* = 8.0 Hz, 2H), 7.42–7.37 (*m*, 3H), 7.08 (*d*, *J* = 8.0 Hz, 2H), 6.63 (*d*, *J* = 12.0 Hz, 2H), 5.73 (*s*, 1H), 4.41 (*d*, *J* = 8.0 Hz, 2H), 3.72 (*s*, 2H), 2.34 (*t*, *J* = 8.0 Hz, 2H), 1.61 (*m*, 2H), 1.43–1.26 (*m*, 6H), 0.91 (*t*, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 168.8, 145.9, 140.5, 130.2, 128.1 (2C), 128.0 (2C), 127.1, 126.7 (2C), 115.2 (2C), 91.1, 46.3, 32.3, 31.4, 29.0, 28.0, 22.4, 13.9. HRMS *m/z* (ESI) calcd for $C_{22}H_{28}N_2O$, $(M + Na)^+$ 359.2094; found, 359.2096.

(*Z*)-3-((4-aminobenzyl)amino)-1-cyclopropyl-3-phenylprop-2-en-1-one (**3za**) yellow solid, mp 128–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (*t*, *J* = 8.0 Hz, 1H), 7.41–7.35 (*m*, 5H), 6.93 (*d*, *J* = 8.0 Hz, 2H), 6.57 (*d*,

J = 8.0 Hz, 2H), 5.25 (*s*, 1H), 4.18 (*d*, 2H), 3.66 (*s*, 2H), 1.72 (*m*, 1H), 1.01 (*m*, 2H), 0.75 (*m*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 163.9, 145.6, 135.3, 129.1 (2C), 128.3 (2C), 128.04 (2C), 128.01, 127.6 (2C), 115.1 (2C), 96.5, 47.8, 20.2, 9.0 (2C). HRMS *m/z* (ESI) calcd for $C_{19}H_{20}N_2O$, $(M+Na)^+$ 315.1468; found, 315.1470.

(*Z*)-3-((4-aminophenethyl)amino)-1,3-diphenylprop-2-en-1-one (**3ab**) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (*t*, J = 8.0 Hz, 1H), 7.88 (*d*, J = 8.0 Hz, 2H), 7.42–7.34 (*m*, 6H), 7.25–7.22 (*m*, 2H), 6.85 (*d*, J = 8.0 Hz, 2H), 6.56 (*d*, J = 8.0 Hz, 2H), 5.71 (s, 1H), 3.51 (s, 2H), 3.34 (*q*, J = 4.0 Hz, J = 4.0 Hz, 2H), 2.72 (*t*, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 166.7, 144.9, 140.2, 135.5, 130.5, 129.5 (2C), 129.2, 128.3 (2C), 128.1 (2C), 127.9, 127.5 (2C), 126.9 (2C), 115.1 (2C), 93.3, 48.6, 36.5. HRMS *m/z* (ESI) calcd for $C_{23}H_{22}N_2O$, $(M+Na)^+$ 365.1624; found, 365.1626.

(*Z*)-3-((3-aminobenzyl)amino)-1,3-diphenylprop-2-en-1-one (**3ac**) yellow solid, mp 117–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (*s*, 1H), 7.90 (*d*, J = 8.0 Hz, 2H), 7.46–7.37 (*m*, 8H), 7.08 (*t*, J = 8.0 Hz, 1H), 6.57 (*t*, J = 8.0 Hz, 3H), 5.83 (*s*, 1H), 4.32 (*d*, J = 8.0 Hz, 2H), 3.69 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 166.8, 146.8, 140.1, 139.6, 135.4, 130.7, 129.6, 129.5, 128.5 (2C), 128.2 (2C), 127.7 (2C), 127.1 (2C), 116.9, 114.1, 113.2, 93.8, 48.3. HRMS *m/z* (ESI) calcd for $C_{22}H_{20}N_2O$, $(M+Na)^+$ 351.1468; found, 351.1470.

(*Z*)-3-((2-aminobenzyl)amino)-1,3-diphenylprop-2-en-1-one (**3ad**) yellow solid, mp 145–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.50 (*s*, 1H), 7.89 (*d*, J = 8.0 Hz, 2H), 7.47–7.36 (*m*, 8H), 7.09 (*m*, 2H), 6.76–6.66 (*m*, 2H),, 5.85 (*s*, 1H), 4.29 (*d*, J = 4.0 Hz, 2H), 3.61 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 166.8, 144.1, 140.0, 135.4, 130.8, 129.7, 128.9, 128.8, 128.7 (2C), 128.2 (2C), 127.7 (2C), 127.1 (2C), 122.6, 119.1, 116.4, 94.1, 45.8. HRMS *m/z* (ESI) calcd for $C_{22}H_{20}N_2O$, $(M+Na)^+$ 351.1468; found, 351.1471.

(*Z*)-3-((4-hydroxybenzyl)amino)-1,3-diphenylprop-2-en-1-one (**3ae**) yellow solid, mp 167–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (*t*, J = 8.0 Hz, 1H), 9.19 (*s*, 1H), 7.91 (*d*, J = 8.0 Hz, 2H), 7.50–7.39 (m, 8H), 7.05 (*d*, J = 8.0 Hz, 2H), 6.84 (*d*, J = 8.0 Hz, 2H), 5.86 (*s*, 1H), 4.36 (*d*, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 167.6, 156.8, 139.7, 135.0, 131.0, 129.8, 128.6 (2C), 128.4 (2C), 128.3 (2C), 128.0, 127.6 (2C), 127.1 (2C), 115.8 (2C), 94.1, 48.5. HRMS *m/z* (ESI) calcd for $C_{22}H_{19}NO_2$, $(M+Na)^+$ 352.1308; found, 352.1309.

(*Z*)-3-((2-mercaptoethyl)amino)-1,3-diphenylprop-2-en-1-one (**3af**) (Štefane et al. 2002) yellow solid, mp 138–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (*t*, J = 4.0 Hz, 1H), 7.89 (*d*, J = 8.0 Hz, 2H), 7.46–7.37 (*m*, 8H), 5.80 (*s*, 1H), 3.49 (*q*, J = 8.0 Hz, J = 8.0 Hz, 2H), 2.66 (*t*, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 166.3, 139.9, 135.2, 130.8, 129.5, 128.6 (2C), 128.1 (2C), 127.7 (2C), 127.0 (2C), 94.0, 43.2, 38.5. HRMS *m/z* (ESI) calcd for $C_{17}H_{17}NOS$, $(M+Na)^+$ 306.0923; found, 306.0925.

3-((5-phenyl-1H-1,2,3-triazol-1-yl)methyl)aniline (**5ac**) yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (*s*, 1H), 7.43–7.37 (*m*, 3H), 7.28–7.26 (*m*, 2H), 7.02 (*t*, J = 8.0 Hz, 1H), 6.55 (*d*, J = 8.0 Hz, 1H), 6.39 (*t*, J = 4.0 Hz, 2H), 5.42 (*s*, 2H), 3.54 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 138.0, 136.5, 132.9, 129.5, 129.3, 128.7 (2C), 128.6 (2C), 126.6, 116.5, 114.5, 113.1, 51.5. HRMS *m/z* (ESI) calcd for $C_{15}H_{14}N_4$, $(M+Na)^+$ 273.1111; found, 273.1114.

5-phenyl-1-(3-(5-phenyl-1H-1,2,3-triazol-1-yl) benzyl)-1H-1,2,3-triazole (**6ac**) white solid, mp 159–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (*s*, 1H), 7.70 (*s*, 1H), 7.44–7.27 (*m*, 8H), 7.21–7.09 (*m*, 6H), 5.55 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.6, 137.1, 136.8, 133.3, 133.1, 129.8, 129.6, 129.2, 128.9 (2C), 128.8 (2C), 128.6 (2C), 128.3 (2C), 127.7, 126.3, 126.2, 124.7, 123.7, 50.9. HRMS *m/z* (ESI) calcd for $C_{23}H_{18}N_6$, $(M+Na)^+$ 401.1485; found, 401.1488.

Supporting information

Full experimental details, ^{1}H and ^{13}C NMR spectra. This material can be found via the Supporting information.

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Declarations

Conflict of interest The authors declare no competing financial interest.

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