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Note

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Synthesis of 2,3-Ring Fused Pyrroles via Cu-Catalyzed 5-*exo*-dig Annulation of Alkyne-tethered Enaminones

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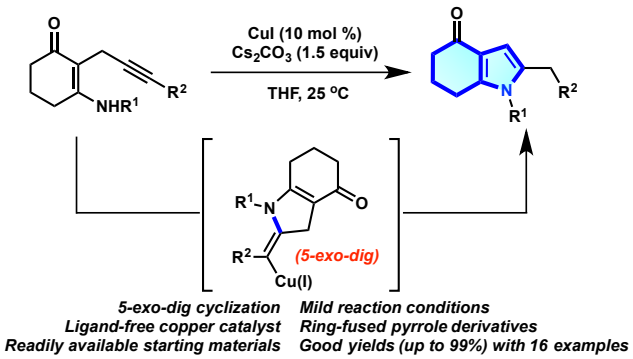
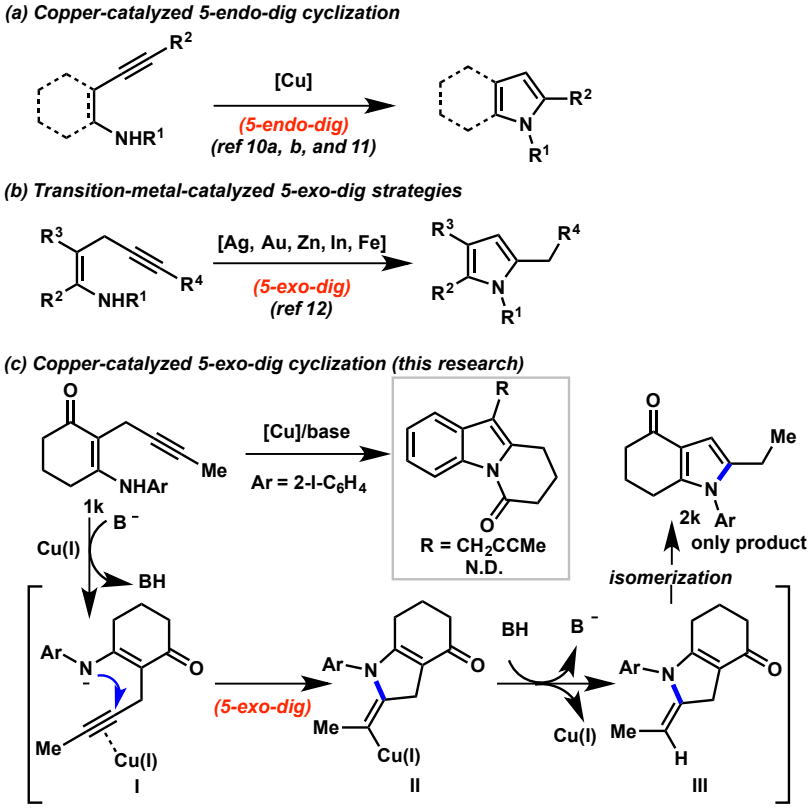


Abstract: A copper-catalyzed annulation of alkyne-tethered enaminones for the synthesis of 2,3-ring fused pyrroles is reported. The 5-*exo*-dig cyclization/olefin migration reaction delivers the multi-substituted pyrroles in 59–99% yields with 16 examples. This strategy features easily available starting materials, mild reaction conditions, and cheap ligand-free copper catalyst. The atom-economic transformation provides a simple access to a variety of synthetic useful pyrroles and their derivatives.

As one of the most abundant heterocycles, pyrroles are intensively used as building blocks in the synthesis of natural products and as pharmacophores for drug design.[1] Meanwhile, pyrrole structural cores are widely present in catalysts/ligands and photoelectric materials.[2] Correspondingly, many classical methods,[3] such as Hantzsch,[4] Paal-Knorr,[5,6] and Piloty-Robinson[7] reactions, have been developed for their syntheses. Particularly, catalytic protocols employing transition metals have made significant progress in last few decades.[8,9,10] Yet there is still room for improvement, for instance,

avoiding the use of precious metal catalysts and harsh reaction conditions, starting with more accessible materials, etc. Therefore, searching for new synthetic routes to access pyrroles, especially through novel cyclization models and with cheap metal catalyst, continues to attract the interest of the community.

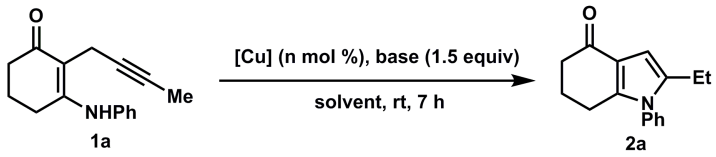
Scheme 1. Transition-Metal-Catalyzed Pyrroles Synthesis Via Cyclization of Nitrogen to Alkynes.



Copper-catalyzed 5-*endo*-dig cyclization of (*Z*)-but-1-en-3-yn-1-amines has been widely used in the synthesis of pyrroles and their derivatives (Scheme 1a), for the reason that the stability of the products increased by the formation of aromatic pyrroles.[9a,10a,b,11] In contrast, a few strategies employing (*Z*)-pent-1-en-4-yn-1-amines as the substrates to construct simple polysubstituted pyrroles through 5-*exo*-dig cyclization strategy (Scheme 1b), but mainly limited in precious silver and gold catalysis.[12a–c] Notable examples with zinc , indium, and iron as the catalysts were reported recently by the groups of Stevens[12d], Nakamura[12e], and Zhang[12f], respectively. During our studies toward DHPIs (dihydropyrido[1,2-*a*]indolones) synthesis,[13] we found that with alkyne-tethered enaminone **1k** as a substrate, intramolecular addition of nitrogen to the alkyne furnished 2,3-ring fused the pyrrole **2k** exclusively (Scheme

1c). Based on precedent reports of the pyrrole synthesis,[10,12] we proposed that the reaction is work through the coordination of alkyne of **1k** to Cu(I) to generate the π-alkyne copper intermediate **I**,[14] followed by the attack of nitrogen to the activated alkyne generates alkenyl copper intermediate **II**. Subsequently, protonolysis of **II** results intermediate **III** and the 1,3-H shift of **III** leads to the formation of the desired 2,3-fused pyrrole **2k** (Scheme 1c).[15] Given the readily accessible starting materials, cheap but efficient catalyst, and the high value of the pyrrole products, we set out to investigate the generality of this transformation. Particularly, the presence of the ketone functionality in the pyrroles provides a number of opportunities for diversity synthetic applications. Herein, we report the detail studies of this copper-catalyzed 5-*exo*-dig cyclization.

Table 1. Reaction Condition Optimizations.



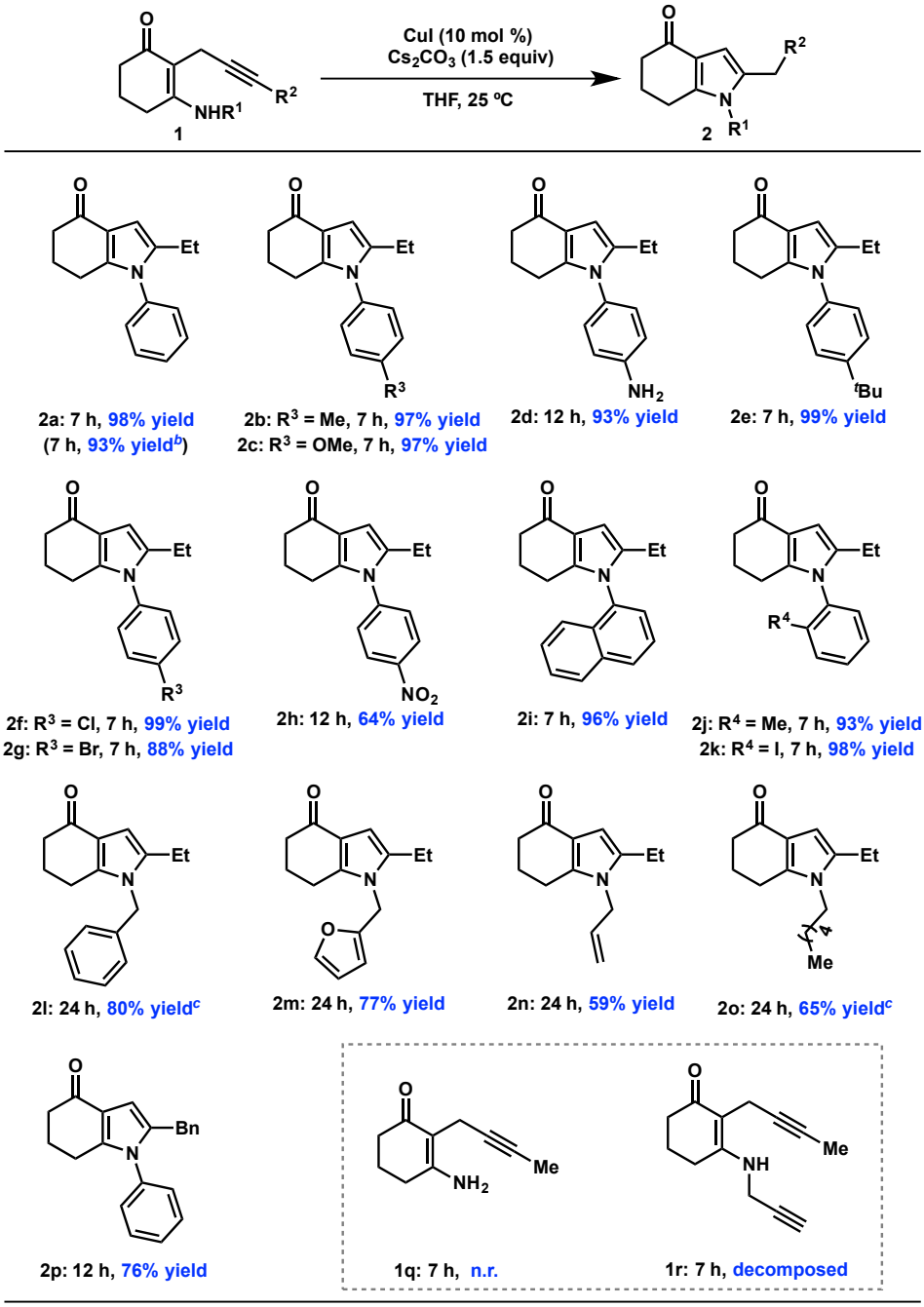
entry[a]	solvent	[Cu] (n mol %)	base	yield (%)[b]
1	THF	CuI (10)	KOAc	6[c]
2	THF	CuI (10)	K_2CO_3	32[c]
3	THF	CuI (10)	K_3PO_4	90
4	**THF**	**CuI (10)**	**Cs_2CO_3**	**98**
5	dioxane	CuI (10)	Cs_2CO_3	91
6	CH_2Cl_2	CuI (10)	Cs_2CO_3	93
7	toluene	CuI (10)	Cs_2CO_3	82
8	CH_3CN	CuI (10)	Cs_2CO_3	52
9	THF	CuBr (10)	Cs_2CO_3	80
10	THF	CuCl (10)	Cs_2CO_3	75

11	THF	$Cu(OTf)_2$ (10)	Cs_2CO_3	76[c]
12	THF	CuI (5)	Cs_2CO_3	88
13	THF	CuI (2)	Cs_2CO_3	86
14	THF	–	Cs_2CO_3	N.D.
15[d]	THF	CuI (10)	Cs_2CO_3	22

[a]Reactions conducted with 0.2 mmol of **1a** (0.2 mmol), 0.3 mmol of base (0.3 mmol) in 1 mL of solvent under Ar for 7 h. [b]Isolated yield. [c]NMR yield (1,3,5-trimethoxybenzene as an internal standard). [d]Under air. N.D. = not detected.

The optimization of the reaction conditions was initiated with butynyl phenylamino cyclohexenone **1a** as a model substrate (Table 1). With 10 mol % of CuI alone as the catalyst, KOAc as the base, and THF as the solvent, the desired pyrrole **2a** was observed in only 6% NMR yield at room temperature (entry 1). The effect of various bases was then investigated (entries 2–4). A slightly increased yield was obtained with K_2CO_3 but the use of K_3PO_4 dramatically increased the reactivity (entries 2 and 3). We were glad to find that when Cs_2CO_3 was used as a base, the yield of **2a** was increased to 98% (entry 4). Further screen of organic solvents (dioxane, CH_2Cl_2, toluene, and CH_3CN, entries 5–8) and copper sources (CuBr, CuCl, and $Cu(OTf)_2$, entries 9–11) resulted in lower yields. Control experiment revealed that the catalytic efficiency decreased as the loading of CuI reduced (entries 12–13) and no reaction occurred in the absence of CuI (entry 14). When under an air atmosphere, the desired pyrrole **2a** was obtained in 22% yield (entry 15). Thus using 10 mol % CuI, 1.5 equiv of Cs_2CO_3 in THF at room temperature (entry 4) were identified as the optimal reaction conditions.

Table 2. Scope for the Synthesis of Fused Pyrroles[a]

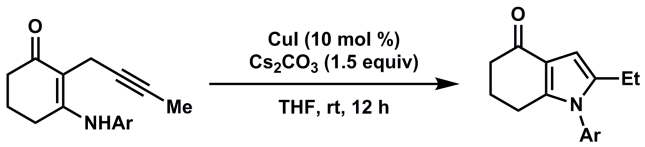


[a]Reaction conducted under the conditions of entry 5, Table 1. [b]Using the Schlenk line under argon. [c]40 °C.

Next, the efficiency of this annulation strategy was demonstrated by the construction of an array of fused pyrroles (Table 2). Substituents at the *para*-position of anilines with electron-donating (Me, OMe, NH_2, ^{t}Bu) and electron-withdrawing (Cl, Br) groups were converted into the corresponding products **2b**–**2g** smoothly in 88%–99% yields. It is noteworthy that a free amine group was also tolerated (**2d**). The reaction of **1h** was sluggish and delivered product **2h** in diminished yield (64%). Notably, the methodology

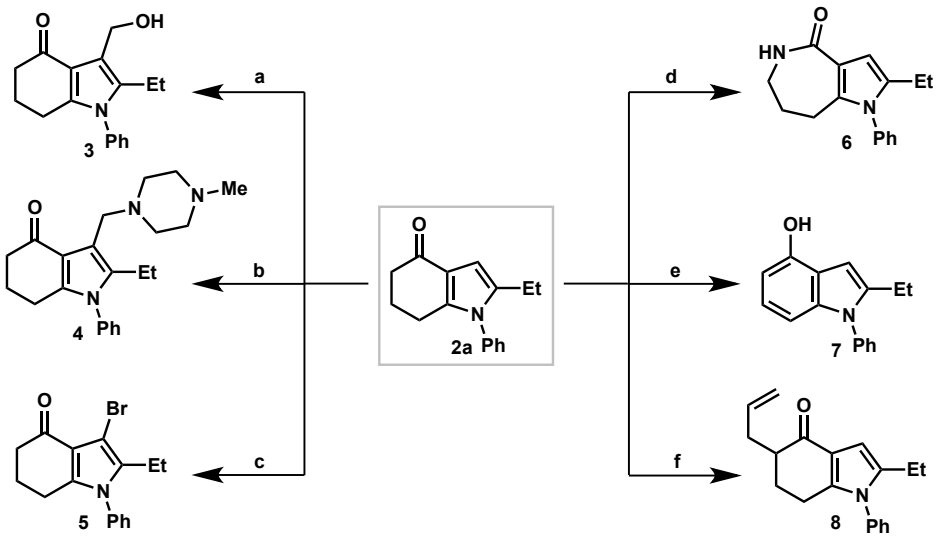
allows for the synthesis of *N*-sterically hindered pyrroles (**2i**–**2k**). Naphthalen-1-amine (**1i**), *o*-toluidine (**1j**), and 2-iodoaniline (**1k**) derived substrates all furnished the desired products **2i**–**2k** in excellent yields (93–98% yields). This reaction was not limited to access the *N*-aryl substituted pyrroles, and alkyl amine substrates are also compatible (**2l**–**2o**). The *N*-benzyl (**2l**) and *N*-furanylmethyl (**2m**) pyrroles were obtained in 80% and 77% yields, respectively. Moreover, *N*-allyl (**2n**) and *N*-alkyl (**2o**) pyrroles were also formed in moderate yields (59% and 65%). Interestingly, when phenylpropynyl substituted cyclohexenone **1p** was employed, the corresponding product **2p** was obtained in 76% yield. However, the reaction with unsubstituted enanminone **1q** synthesized from ammonia is failed to deliver the desired product. Decomposition of the starting material was obtained when treatment of a terminal alkyne bearing substrate **1r** under the standard conditions.[16]

Scheme 2. Gram-Scale Reactions.



2a, Ar = Ph, 1.09 gram, 91% yield
2k, Ar = 2-I-C_6H_4, 1.82 gram, 99% yield

Scheme 3. Product Derivatizations.



Reaction conditions: (a) **2a** (0.2 mmol), polyformaldehyde (3 equiv), HCl (12 M), dioxane, 25 ^{o}C, 78% yield. (b) **2a** (0.2 mmol), 1-methylpiperazine (3 equiv), polyformaldehyde (3 equiv), AcOH, 25 ^{o}C, 79% yield. (c) **2a** (0.2 mmol), oxone (1.1 equiv), NH_4Br (1.1 equiv), MeOH, 35 ^{o}C, 60%

yield; (d) **2a** (0.2 mmol), NaN_3 (2 equiv), conc HCl, 0 ^oC, 57% yield. (e) i) **2a** (0.1 mmol), $CuBr_2$ (2 equiv), EtOAc, reflux; ii) LiBr (1.1 equiv), Li_2CO_3 (1.1 equiv), DMF, 150 ^oC, 52% yield of two steps; (f) **2a** (1 mmol), LDA (1 equiv), allyl bromide (4 equiv), THF, –78 – 25 ^oC, 83% yield.

The utilities of the method were demonstrated by scale-up reactions and product transformations. Gram-scale reactions with both substrates **1a** and **1k** under the standard conditions provided the desired products **2a** and **2k** in 91% (1.09 g) and 99% (1.82 g) yields, respectively (Scheme 2). The fused pyrrole products possess multiple synthetic handles for further transformations as showcasing in Scheme 3. Friedel-Crafts reactions of **2a** with polyformaldehyde and imine under acidic conditions delivered the alkylation products **3** and **4** in 78% and 79% yields, respectively.[17] Bromination reaction of **2a** with NH_4Br/oxone provided bromopyrrole **5**, a useful cross-coupling precursor, in 60% yield.[18] Moreover, subjecting **2a** to the Schmidt rearrangement conditions provided lactam **6** in 57% yield.[19] Additionally, 4-hydroxyindole **7** was readily synthesized in 52% yield by a two-step procedure.[20] Finally, an efficient α-allylation of ketone moiety of **2a** provided compound **8** in 83% yield.

Conclusions

We have reported a copper-catalyzed 5-*exo*-dig cyclization strategy for the synthesis of 2,3-ring fused pyrroles. With readily accessible alkyne-tethered enaminones as the starting materials and cheap CuI as the catalyst, the annulation reactions operate under mild reaction conditions in good to excellent yields. The diversely substituted pyrroles provide resourceful entries to valuable synthetic intermediates. Further studies on the application of the method in the synthesis of complex molecules are undergoing in our laboratory.

Experimental Section:

General Methods: Unless otherwise stated, all experiments were carried out in flame-dried glassware using argon manifolds or in a glovebox. Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using Huanghai 8±0.2 μm

precoated glass plates (0.25 mm). Huanghai silica gel (particle size 300–400 mesh) was used for chromatography. NMR spectra were recorded at room temperature on a Bruker ADVANCE III 400 MHz spectrometer. Data for ^{1}H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet, m, multiplet; br s, broad signal. Data for $^{13}C\{^{1}H\}$NMR was reported in terms of chemical shifts (δ ppm). Melting points were obtained on a RY-1G Melting point meter and were reported in range of temperature (^{o}C). High-resolution mass spectra (HRMS) were obtained by use of a Bruker Compact TOF mass spectrometer in electrospray ionization mode (ESI+). Unless otherwise noted, all reagents were purchased commercially and used without further purification. Petroleum ether (PE) (60–90 ^{o}C), ethyl acetate (EA) were used as eluent for silica gel chromatography. Dry solvents were purchased commercially or were dried by passage through an activated alumina column under argon.[21]

General Procedure for Synthesis of 2,3-Ring Fused Pyrroles (2a−2p)

To a screw capped vial equipped with a magnetic stirring bar were added CuI (3.6 mg, 0.02 mmol, 10 mol %), enaminone **1a** (47.7 mg, 0.2 mmol), Cs_2CO_3 (100.3 mg, 0.3 mmol), and 1.0 mL of THF. The vial was removed from the glovebox, and the mixture was stirred at room temperature for 7 h. The reaction was quenched with HCl aqueous solution (2 mL, 1 M in THF) and the resulted mixture was continued to stir overnight at room temperature. Then the mixture was diluted with DCM (10 mL), the organic phase was separated, and dried over anhydrous Na_2SO_4, filtered through a short pad of celite. Then the filtrate was concentrated under reduced pressure. The desired product **2a** (46.7 mg, 98% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.42 (m, 3H), 7.27–7.19 (m, 2H), 6.41 (s, 1H), 2.57–2.43(m, 4H), 2.35 (q, J = 7.2 Hz, 2H), 2.08 (quint, J = 6.3 Hz, 2H), 1.11 (t, J = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 194.6, 144.7, 138.1, 137.2, 129.6, 128.8, 127.8, 120.2, 101.9, 38.0, 24.0, 22.7, 20.0, 12.7; HRMS (ESI^{+}) calc'd for $C_{16}H_{17}NNaO$ $[M + Na]^{+}$: 262.1202, found 262.1204.

2-Ethyl-1-(*p*-tolyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2b. The general procedure was followed. The reaction was performed with CuI (3.9 mg, 10 mol %), **1b** (50.3 mg, 0.2 mmol), and Cs_2CO_3 (98.4 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2b** (48.6 mg, 97% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 2.52–2.48 (m, 4H), 2.43 (s, 3H), 2.39–2.27 (m, 2H), 2.07 (quint, *J* = 6.4 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.6, 145.1, 138.9, 138.4, 134.5, 130.2, 127.5, 120.0, 101.8, 37.9, 24.0, 22.7, 21.3, 20.0, 12.8; HRMS (ESI+) calc'd for $C_{17}H_{19}NNaO$ $[M + Na]^+$: 276.1359, found 276.1357.

2-Ethyl-1-(4-methoxyphenyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2c. The general procedure was followed. The reaction was performed with CuI (3.7 mg, 10 mol %), **1c** (53.8 mg, 0.2 mmol), and Cs_2CO_3 (97.9 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2c** (52.2 mg, 97% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 130−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.40 (s, 1H), 3.87 (s, 3H), 2.58–2.48 (m, 4H), 2.36–2.28 (m, 2H), 2.08 (quint, *J* = 6.2 Hz, 2H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.6, 159.7, 145.5, 138.6, 129.8, 128.8, 119.9, 114.7, 101.7, 55.7, 37.9, 24.0, 22.7, 20.0, 12.8; HRMS (ESI^+) calc'd for $C_{17}H_{19}NNaO_2$ $[M + Na]^+$: 292.1308, found 292.1306.

1-(4-Aminophenyl)-2-ethyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2d. The general procedure was followed. The reaction was performed with CuI (3.4 mg, 10 mol%), **1d** (50.6 mg, 0.2 mmol), and Cs_2CO_3 (97.7 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 12 h. The desired product **2d** (46.8 mg, 93% yield) was obtained as a light yellow solid after purification by silica gel chromatography (PE/EA = 3:1 to PE/EA = 1:1). mp: 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.36 (s, 1H), 3.82 (br s, 2H), 2.56–2.39 (m, 4H), 2.37–2.27 (m, 2H), 2.06 (quint, *J* = 6.3 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.6, 146.4, 145.3, 138.6, 128.6, 127.9, 119.8,

115.7, 101.3, 38.0, 24.0, 22.6, 20.0, 12.8; HRMS (ESI^+) calc'd for $C_{16}H_{19}N_2O$ $[M + H]^+$: 255.1492, found 255.1492.

1-(4-(*tert*-Butyl)phenyl)-2-ethyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2e. The general procedure was followed. The reaction was performed with CuI (3.6 mg, 10 mol %), **1e** (59.9 mg, 0.2 mmol), and Cs_2CO_3 (99.7 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2e** (59.5 mg, 99% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 202−203 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.43 (s, 1H), 2.56–2.46 (m, 4H), 2.40–2.28 (m, 2H), 2.08 (quint, J = 6.2 Hz, 2H), 1.37 (s, 9H), 1.12 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 194.5, 151.8, 144.9, 138.2, 134.4, 127.2, 126.4, 120.0, 101.6, 38.0, 34.9, 31.4, 24.0, 22.8, 20.0, 12.7; HRMS (ESI^+) calc'd for $C_{20}H_{25}NNaO$ $[M + Na]^+$: 318.1828, found 318.1832.

1-(4-Chlorophenyl)-2-ethyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2f. The general procedure was followed. The reaction was performed with CuI (3.8 mg, 10 mol %), **1f** (54.7 mg, 0.2 mmol), and Cs_2CO_3 (97.3 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2f** (54.4 mg, 99% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 96−97 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 9.3 Hz, 2H), 7.18 (d, J = 9.4 Hz, 2H), 6.42 (s, 1H), 2.55–2.45 (m, 4H), 2.40–2.28 (m, 2H), 2.09 (quint, J = 6.3 Hz, 2H), 1.11 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 194.5, 144.7, 138.0, 135.7, 134.9, 129.9, 129.1, 120.5, 102.3, 37.9, 24.0, 22.7, 20.0, 12.8; HRMS (ESI^+) calc'd for $C_{16}H_{16}ClNNaO$ $[M + Na]^+$: 296.0813, found 296.0809.

1-(4-Bromophenyl)-2-ethyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2g. The general procedure was followed. The reaction was performed with CuI (3.8 mg, 10 mol %), **1g** (63.8 mg, 0.2 mmol), and Cs_2CO_3 (97.7 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2g** (55.9 mg, 88% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 146−147 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 9.4 Hz, 2H), 7.12 (d, J = 9.4 Hz, 2H), 6.42 (s, 1H), 2.55–2.44 (q, J = 5.8 Hz, 4H), 2.39 – 2.27 (m, 2H), 2.09

(quint, J = 6.0 Hz, 2H), 1.11 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 194.5, 144.5, 138.0, 136.3, 132.9, 129.4, 122.9, 120.5, 102.3, 37.9, 24.0, 22.7, 20.0, 12.8; HRMS (ESI^+) calc'd for $C_{16}H_{16}BrNNaO$ $[M + Na]^+$: 340.0307, found 340.0306.

2-Ethyl-1-(4-nitrophenyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2h. The general procedure was followed. The reaction was performed with CuI (3.6 mg, 10 mol %), **1h** (56.2 mg, 0.2 mmol), and Cs_2CO_3 (97.7 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 12 h. The desired product **2h** (36.1 mg, 64% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 5:1 to 3:1). mp: 146−147 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 6.47 (s, 1H), 2.60–2.45 (m, 4H), 2.38 (q, J = 7.0 Hz, 2H), 2.11 (quint, J = 6.1 Hz, 2H), 1.13 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 194.4, 147.6, 144.0, 142.9, 137.7, 128.7, 125.1, 121.2, 103.4, 38.0, 24.0, 22.9, 20.2, 12.8. HRMS (ESI^+) calc'd for $C_{16}H_{17}N_2O_3$ $[M + Na]^+$: 285.1234, found 285.1227.

2-Ethyl-1-(naphthalen-1-yl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2i. The general procedure was followed. The reaction was performed with CuI (3.9 mg, 10 mol %), **1i** (57.7 mg, 0.2 mmol), and Cs_2CO_3 (98.0 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2i** (55.6 mg, 96% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 92−93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H), 7.62–7.54 (m, 2H), 7.53–7.47 (m, 1H), 7.44 (dd, J = 7.0, 1.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.53 (s, 1H), 2.53 (t, J = 6.3 Hz, 2H), 2.50–2.38 (m, 1H), 2.29–2.18 (m, 2H), 2.17–2.10 (m, 1H), 2.08–1.99 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 194.8, 146.1, 139.3, 134.4, 133.7, 131.0, 129.7, 128.5, 127.9, 127.1, 126.1, 125.5, 122.5, 120.2, 101.8, 37.9, 24.0, 22.2, 19.7, 12.8; HRMS (ESI^+) calc'd for $C_{20}H_{20}NO$ $[M + H]^+$: 290.1539, found 290.1532.

2-Ethyl-1-(*o*-tolyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2j. The general procedure was followed. The reaction was performed with CuI (3.9 mg, 10 mol %), **1j** (50.2 mg, 0.2 mmol), and Cs_2CO_3 (100.1 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2j** (46.9 mg, 93% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 93−94 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 3H), 7.16 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.43 (s, 1H), 2.55–2.45 (m, 2H), 2.44–2.39 (m, 1H), 2.36–2.15 (m, 3H), 2.13–2.01 (m, 2H), 1.97 (s, 3H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.6, 144.5, 137.8, 136.4, 136.2, 131.2, 129.4, 128.4, 127.1, 120.2, 101.7, 38.0, 24.1, 22.3, 19.8, 17.3, 12.7; HRMS (ESI$^+$) calc'd for $C_{17}H_{19}NNaO$ [M + Na]$^+$: 276.1359, found 276.1359.

2-Ethyl-1-(2-iodophenyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2k. The general procedure was followed. The reaction was performed with CuI (3.8 mg, 10 mol %), **1k** (73.3 mg, 0.2 mmol), and Cs_2CO_3 (98.0 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 7 h. The desired product **2k** (72.0 mg, 98% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.50 (td, *J* = 7.7, 1.5 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.20 (td, *J* = 8.0, 1.5 Hz, 1H), 6.43 (s, 1H), 2.57–2.47 (m, 2H), 2.46–2.33 (m, 2H), 2.25–2.15 (m, 2H), 2.14–2.04 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.7, 144.5, 140.3, 140.0, 137.5, 130.9, 129.6, 129.4, 120.6, 102.0, 99.5, 37.9, 24.0, 22.6, 20.0, 12.6; HRMS (ESI$^+$) calc'd for $C_{16}H_{16}INNaO$ [M + Na]$^+$: 388.0169, found 388.0168.

1-Benzyl-2-ethyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2l. The general procedure was followed. The reaction was performed with CuI (4.1 mg, 10 mol %), **1l** (50.6 mg, 0.2 mmol), and Cs_2CO_3 (98.5 mg, 0.3 mmol) in 1.0 mL of THF at 40 ^{o}C in a heating mantle for 24 h. The desired product **2l** (40.5 mg, 80% yield) was obtained as a brown oil after purification by silica gel chromatography (PE/EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.22 (m, 3H), 6.90 (d, *J* = 6.8 Hz 2H), 6.40 (s, 1H), 5.04 (s, 2H), 2.64 (t, *J* = 6.1 Hz, 2H), 2.55–2.37 (m, 4H), 2.11 (quint, *J* = 6.1 Hz, 2H), 1.20 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.4, 144.5, 137.4, 136.8, 129.1, 127.8, 125.7, 120.0, 102.1, 47.2, 37.7, 23.9, 22.1, 19.5, 12.4; HRMS (ESI$^+$) calc'd for $C_{17}H_{19}NNaO$ [M + Na]$^+$: 276.1359, found 276.1358.

2-Ethyl-1-(furan-2-ylmethyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2m. The general procedure was followed. The reaction was performed with CuI (3.6 mg, 10 mol %), **1m** (48.6 mg, 0.2 mmol), and Cs_2CO_3 (97.9 mg, 0.3 mmol) in 1.0 mL of THF at room

temperature in a heating mantle for 24 h. The desired product **2m** (37.6 mg, 77% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 1.0 MHz,1H), 6.38–6.25 (m, 2H), 6.10 (d, *J* = 2.4 Hz, 1H), 4.93 (s, 2H), 2.80 (t, *J* = 6.2 Hz, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 6.0 Hz, 2H), 2.14 (quint, *J* = 6.3 Hz, 2H), 1.24 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.2, 149.8, 144.1, 142.9, 137.0, 120.0, 110.6, 107.9, 101.8, 40.8, 37.7, 23.8, 22.0, 19.4, 12.3; HRMS (ESI^+) calc'd for $C_{15}H_{17}NNaO_2$ $[M + Na]^+$: 266.1151, found 266.1148.

1-Allyl-2-ethyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2n. The general procedure was followed. The reaction was performed with CuI (3.7 mg, 10 mol %), **1n** (40.3 mg, 0.2 mmol), and Cs_2CO_3 (98.2 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 24 h. The desired product **2n** (24.0 mg, 59% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 59−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1H), 5.98–5.74 (m, 1H), 5.15 (d, *J* = 10.6 Hz, 1H), 4.75 (d, *J* = 16.9 Hz, 1H), 4.46–4.33 (m, 2H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.56–2.35 (m, 4H), 2.11 (quint, *J* = 6.2 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.3, 144.1, 137.0, 132.8, 116.5, 101.6, 45.9, 37.7, 23.9, 21.8, 19.2, 12.4; HRMS (ESI^+) calc'd for $C_{13}H_{17}NNaO$ $[M + Na]^+$: 226.1202, found 226.1203.

2-Ethyl-1-(*n*-hexyl)-1,5,6,7-tetrahydro-*4H*-indol-4-one 2o. The general procedure was followed. The reaction was performed with CuI (4.0 mg, 10 mol %), **1o** (49.4 mg, 0.2 mmol), and Cs_2CO_3 (100.5 mg, 0.3 mmol) in 1.0 mL of THF at 40 ^{o}C in a heating mantle for 24 h. The desired product **2o** (31.9 mg, 65% yield) was obtained as a yellow oil after purification by silica gel chromatography (PE/EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (s, 1H), 3.73 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.52 (q, *J* = 7.4 Hz, 2H), 2.44 (t, *J* = 6.3 Hz, 2H), 2.12 (quint, *J* = 6.2 Hz, 2H), 1.68–1.50 m, 2H), 1.39–1.19 (m, 9H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.1, 143.6, 136.7, 119.6, 101.5, 44.1, 37.8, 31.5, 30.8, 26.6, 23.9, 22.6, 22.2, 19.4, 14.1, 12.4; HRMS (ESI^+) calc'd for $C_{16}H_{25}NNaO$ $[M + Na]^+$: 270.1828, found 270.1827.

2-Benzyl-1-phenyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 2p. The general procedure

was followed. The reaction was performed with CuI (3.6 mg, 10 mol %), **1p** (60.2 mg, 0.2 mmol), and Cs_2CO_3 (96.8 mg, 0.3 mmol) in 1.0 mL of THF at room temperature in a heating mantle for 12 h. The desired product **2p** (45.6 mg, 76% yield) was obtained as a light yellow solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.35 (m, 3H), 7.21–7.12 (m, 3H), 7.11–7.04 (m, 2H), 6.93 (d, *J* = 7.3 Hz, 2H), 6.38 (s, 1H), 3.71 (s, 2H), 2.55 – 2.40 (m, 4H), 2.15–1.99 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.6, 145.3, 138.5, 137.0, 135.1, 129.5, 128.9, 128.8, 128.4, 128.0, 126.4, 120.3, 104.8, 38.0, 33.2, 24.0, 22.7; HRMS (ESI$^+$) calc'd for $C_{21}H_{19}NNaO$ $[M + Na]^+$: 324.1359, found 324.1357.

Gram Scale Synthesis of 2a. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added CuI (95.7 mg, 0.5 mmol, 10 mol %), substrate **1a** (1.19 g, 5 mmol), Cs_2CO_3 (2.47 g, 7.5 mmol), and 25 mL of THF. The flask was removed from the glovebox, and the reaction was stirred at room temperature for 12 h under argon. After completion of the reaction, it was quenched with 50 mL of HCl aqueous solution (1 M in THF). The resulted mixture was continued to stir overnight at room temperature. Then the mixture was diluted with DCM (100 mL) and the organic phase was separated, dried over anhydrous Na_2SO_4, and filtered with a pad of celite. The solvents were removed under reduced pressure and the desired product **2a** (1.09 g, 91% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 3:1).

Gram Scale Synthesis of 2k. Followed the procedure of the gram scale synthesis of **2a**, the reaction was carried out with substrate **1k** (1.83 g, 5 mmol) for 12 h. The desired product **2k** (1.82 g, 99% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 1:1).

Synthesis of 2-Ethyl-3-(hydroxymethyl)-1-phenyl-1,5,6,7-tetrahydro-*4H*-indol -4-one 3. To a solution of **2a** (48.1 mg, 0.2 mmol) in 1 mL of dioxane were added polyformaldehyde (19.4 mg, 0.6 mmol) and HCl (1 mL, 12 M). The mixture was stirred at room temperature and monitored by TLC. After completion of the reaction, the solvents were removed under reduced pressure. The desired product **3** (42.1 mg, 78% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 1:1). mp: 136−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 3H),

7.25–7.19 (m, 2H), 4.62 (s, 2H), 2.52 (t, J = 5.7 Hz, 2H), 2.50–2.37 (m, 4H), 2.07 (quint, J = 6.6 Hz, 2H), 0.88 (t, J = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 196.6, 145.9, 136.9, 133.6, 129.7, 129.1, 127.9, 119.2, 119.0, 56.4, 37.9, 23.8, 22.6, 17.5, 15.4; HRMS (ESI^+) calc'd for $C_{17}H_{19}NNaO_2$ $[M + Na]^+$: 292.1308, found 292.1308.

Synthesis of 2-Ethyl-3-((4-methylpiperazin-1-yl)methyl)-1-phenyl-1,5,6,7-tetrahydro-*4H*- indol-4-one 4. Compound **2a** (47.6 mg, 0.2 mmol) and polyformaldehyde (18.8 mg, 0.6 mmol) were dissolved in acetic acid (0.4 mL), then *N*-methyl piperazine (60.5 mg, 0.6 mmol) was added to the mixture. The reaction was stirred at room temperature and monitored by TLC. After completion of the reaction, the mixture was diluted with water (5 mL), and the pH was adjusted to 8–9 by the addition of $NH_3•H_2O$ carefully. The mixture was then extracted with DCM (5 mL×3). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The desired product **4** (55.4 mg, 79% yield) was obtained as a brown oil without further purification. mp: 103−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.36 (m, 3H), 7.24–7.14 (m, 2H), 3.84 (s, 2H), 2.65 (br s, 4H), 2.54–2.44 (m, 4H), 2.45–2.33 (m, 6H), 2.23 (s, 3H), 1.97 (quint, J = 6.3 Hz, 2H), 0.77 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 194.9, 143.9, 137.3, 136.6, 129.5, 128.7, 127.8, 118.9, 113.0, 54.8, 52.0, 51.0, 45.9, 38.9, 23.6, 22.8, 17.6, 14.3; HRMS (ESI^+) calc'd for $C_{22}H_{30}N_3O$ $[M + H]^+$: 352.2383, found 352.2383.

Synthesis of 3-Bromo-2-ethyl-1-phenyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 5. Compound **2a** (47.4 mg, 0.2 mmol) and NH_4Br (22.1 mg, 0.22 mmol) were dissolved in MeOH (1 mL), then oxone (35.5 mg, 0.22 mmol) was added to the mixture. The reaction was stirred at 35 ^{o}C in a heating mantle and monitored by TLC. After completion of the reaction, saturated $Na_2S_2O_3$ aqueous solution was added to quench the reaction. The aqueous layer was extracted with EA (5 mL × 3). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The desired product **5** (38.3 mg, 60% yield) was obtained as a brown solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 120−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.58–7.46 (m, 3H), 7.25–7.18 (m, 2H), 2.59–2.40 (m, 6H), 2.06 (t, J = 6.2 Hz, 2H), 0.92 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 193.3, 144.1, 136.8, 135.5, 129.8, 129.4, 127.9, 117.2, 93.0, 38.6, 23.4, 23.1, 18.3, 13.6; HRMS (ESI^+) calc'd for $C_{16}H_{16}BrNNaO$ $[M + Na]^+$: 340.0307, found 340.0304.

Synthesis of 2-Ethyl-1-phenyl-5,6,7,8-tetrahydropyrrolo[3,2-*c*]azepin-4(*1H*)-one 6. Compound **2a** (47.4 mg, 0.2 mmol) was dissolved in concentrated HCl (0.35 mL) at 0 ^oC, and NaN_3 (25.5 mg, 0.4 mmol) was then added to the mixture carefully. The reaction was stirred at 50 ^oC in a heating mantle and monitored by TLC until the full conversion of the starting material. The mixture was poured into ice water, and the pH was adjusted to 10 by the addition of aqueous K_2CO_3 (1 M). The mixture was then extracted with DCM (5 mL×3), and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The desired product **6** (28.8 mg, 57% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1). mp: 120−121 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.41 (m, 3H), 7.24–7.16 (m, 2H), 6.34 (s, 1H), 3.81–3.73 (m, 2H), 2.57 (t, J = 6.5 Hz, 2H), 2.28 (q, J = 7.5 Hz, 2H), 1.96–1.80 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 151.5, 137.5, 136.8, 136.1, 129.7, 129.1, 128.2, 116.0, 107.7, 52.1, 29.0, 23.6, 20.0, 12.8; HRMS (ESI^+) calc'd for $C_{16}H_{19}N_2O$ $[M + H]^+$: 255.1492, found 255.1489.

Synthesis of 2-Ethyl-1-phenyl-*1H*-indol-4-ol 7. To a Schlenk flask were added prrrole **2a** (24.0 mg, 0.1 mmol), $CuBr_2$ (44.5 mg, 0.2 mmol) and EA (1 mL) under argon. The flask was then connected with a condenser and the mixture was reflux in a heating mantle until the completion of the starting material as monitored by TLC. Then the mixture was filtered while it was hot. The filtrate was diluted with DCM, and washed with brine and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulted crude product was directly carried out into the next step without further purification.

To a solution of above prepared crude product in DMF (1 mL), LiBr (9.3 mg, 0.1 mmol), and Li_2CO_3 (9.0 mg) were added. The mixture was stirred at 150 ^oC in a heating mantle under argon for 1.5 h. Then the mixture was poured into saturated NH_4Cl aqueous

solution and the aqueous phase was extracted with DCM (5 mL × 3). The combined organic phase was washed with water, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The desired product **7** (12.3 mg, 52% yield of two steps) was obtained as a yellow oil after purification by silica gel chromatography (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.58–7.50 (m, 2H), 7.49–7.42 (m, 1H), 7.39–7.31 (m, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.47 (br s, 1H), 2.62 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 148.2, 142.5, 140.3, 138.1, 129.6, 128.3, 128.0, 122.0, 117.4, 104.6, 103.5, 95.4, 20.7, 13.0; HRMS (ESI$^+$) calc'd for $C_{16}H_{16}NO$ $[M + H]^+$: 238.1226, found 238.1220.

Synthesis of 5-Allyl-2-ethyl-1-phenyl-1,5,6,7-tetrahydro-*4H*-indol-4-one 8. To a solution of **2a** (239.5 mg, 1 mmol) in THF (5 mL) was added LDA (5 mL, 1 mmol, 0.2 M in THF) dropwise at –78 ^{o}C under argon. After the mixture was stirred at –78 ^{o}C for 2 h, a solution of allyl bromide (476.9 mg, 4 mmol) in THF (5 mL) was added slowly by syringe. The reaction was stirred at room temperature until the completion of **2a**. Then saturated NH_4Cl aqueous solution was added to quench the reaction. THF was removed under reduced pressure, and the aqueous layer was extracted with DCM (5 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The desired product **8** (231.0 mg, 83% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 69−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.41 (m, 3H), 7.25–7.21 (m, 2H), 6.41 (t, *J* = 1.1 Hz, 1H), 5.93–5.73 (m, 1H), 5.11–4.98 (m, 2H), 2.79–2.66 (m, 1H), 2.55–2.49 (m, 2H), 2.49–2.40 (m, 1H), 2.39–2.30 (m, 2H), 2.30–2.19 (m, 1H), 2.16–2.09 (m, 1H), 1.92–1.79 (m, 1H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 195.5, 144.0, 138.3, 137.2, 137.1, 129.6, 128.8, 127.8, 119.8, 116.6, 102.2, 45.9, 34.2, 28.4, 21.5, 20.1, 12.8; HRMS (ESI$^+$) calc'd for $C_{19}H_{21}NNaO$ $[M + Na]^+$: 302.1515, found 302.1514.

General Procedure for the Synthesis of Enaminones 1 (see Table S1 in SI for structures). To a 100 mL two-neck round-bottomed flask equipped with a Dean-Stark apparatus were added aniline (1.49 g, 15 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-

dione (1.65 g, 10 mmol), *p*-TsOH•H_2O (125.5 mg, 0.66 mmol) and 50 mL of toluene. The mixture was refluxed and monitored by TLC. After completion of the reaction, it was cooled to room temperature and neutralized with solid K_2CO_3. The mixture was diluted with DCM (100 mL), washed with brine and dried over anhydrous Na_2SO_4. The desired product 2-(but-2-yn-1-yl)-3-(phenylamino)cyclohex-2-en-1-one **1a** (1.73 g, 72% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 10:1 to PE/EA = 1:1). mp: 127−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.33 (br s, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.38 (q, *J* = 2.8 Hz, 2H), 2.51 (t, *J* = 6.1 Hz, 2H), 2.39 (t, *J* = 6.5 Hz, 2H), 1.92 (quint, *J* = 6.3 Hz, 2H), 1.83 (t, *J* = 2.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.3, 160.1, 138.8, 129.4, 125.6, 124.9, 107.8, 77.4, 76.5, 36.5, 27.2, 22.0, 12.3, 3.8; HRMS (ESI^+) calc'd for $C_{16}H_{17}NNaO$ $[M + Na]^+$: 262.1202, found 262.1202.

2-(But-2-yn-1-yl)-3-(*p*-tolylamino)cyclohex-2-en-1-one 1b. The general procedure was followed. The reaction was conducted with 4-methylaniline (322.6 mg, 3.0 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (332.2 mg, 2.0 mmol), *p*-TsOH•H_2O (21.6 mg, 0.11 mmol) in toluene (20 mL). The desired product **1b** (386.2 mg, 76% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1 to PE/EA = 1:1). mp: 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (br s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.37 (q, *J* = 2.7 Hz, 2H), 2.45 (t, *J* = 6.2 Hz, 2H), 2.38 (t, *J* = 5.9 Hz, 2H), 2.36 (s, 3H), 1.89 (quint, *J* = 6.4 Hz, 2H), 1.81 (t, *J* = 2.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.1, 160.6, 136.1, 135.8, 130.0, 125.2, 107.2, 77.2, 76.6, 36.5, 27.2, 21.9, 21.1, 12.2, 3.8; HRMS (ESI^+) calc'd for $C_{17}H_{19}NNaO$ $[M + Na]^+$: 276.1359, found 276.1358.

2-(But-2-yn-1-yl)-3-((4-methoxyphenyl)amino)cyclohex-2-en-1-one 1c. The general procedure was followed. The reaction was conducted with 4-methoxyaniline (930.4 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (820.4 mg, 5.0 mmol), *p*-TsOH•H_2O (58.6 mg, 0.31 mmol) in toluene (30 mL). The desired product **1c** (953.8 mg, 71% yield) was obtained as a light yellow solid after purification by silica gel chromatography (PE/EA = 10:1 to PE/EA = 1:1). mp: 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (br s, 1H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 3.82 (s,

3H), 3.36 (q, J = 2.7 Hz, 2H), 2.43–2.31 (m, 4H), 1.88 (quint, J = 6.4 Hz, 2H), 1.80 (t, J = 2.6 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 194.0, 161.1, 158.0, 131.5, 127.3, 114.6, 106.7, 77.1, 76.6, 55.7, 36.4, 27.1, 21.7, 12.2, 3.8; HRMS (ESI^+) calc'd for $C_{17}H_{20}NO_2$ $[M + H]^+$: 270.1489, found 270.1496.

3-((4-Aminophenyl)amino)-2-(but-2-yn-1-yl)cyclohex-2-en-1-one 1d. The general procedure was followed. The reaction was conducted with benzene-1,4-diamine (435.4 mg, 4.0 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (824.7 mg, 5.0 mmol), *p*-TsOH•H_2O (59.5 mg, 0.31 mmol) in toluene (30 mL). The desired product **1d** (947.2 mg, 93% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 1:1 to PE/EA = 1:2). mp: 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (br s, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 3.72 (br s, 2H), 3.35 (q, J = 2.7 Hz, 2H), 2.49–2.22 (m, 4H), 1.87 (quint, J = 6.3 Hz, 2H), 1.79 (t, J = 2.7 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 193.9, 161.6, 144.7, 129.6, 127.5, 115.7, 106.3, 76.9, 76.7, 36.4, 27.0, 21.7, 12.2, 3.8; HRMS (ESI^+) calc'd for $C_{16}H_{19}N_2O$ $[M + H]^+$: 255.1492, found 255.1488.

2-(But-2-yn-1-yl)-3-((4-(*tert*-butyl)phenyl)amino)cyclohex-2-en-1-one 1e. The general procedure was followed. The reaction was conducted with 4-*tert*-butylaniline (448.3 mg, 3.0 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (329.3 mg, 2.0 mmol), *p*-TsOH•H_2O (21.4 mg, 0.11 mmol) in toluene (20 mL). The desired product **1e** (469.2 mg, 80% yield) was obtained as an orange solid after purification by silica gel chromatography (PE/EA = 3:1 to PE/EA = 1:1). mp: 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.29 (br s, 1H), 7.02 (d, J = 8.6 Hz, 2H), 3.37 (q, J = 2.7 Hz, 2H), 2.49 (t, J = 6.1 Hz, 2H), 2.38 (t, J = 6.1 Hz, 2H), 1.90 (quint, J = 6.0 Hz, 2H), 1.81 (t, J = 2.7 Hz, 3H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 194.1, 160.6, 149.0, 136.1, 126.3, 124.8, 107.1, 77.2, 76.6, 36.5, 34.6, 31.5, 27.2, 21.9, 12.2, 3.8. HRMS (ESI^+) calc'd for $C_{20}H_{25}NNaO$ $[M + Na]^+$: 318.1828, found 318.1829.

2-(But-2-yn-1-yl)-3-((4-chlorophenyl)amino)cyclohex-2-en-1-one 1f. The general procedure was followed. The reaction was conducted with 4-chloroaniline (384.9 mg, 3.0 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (328.7 mg, 2.0 mmol), *p*-TsOH•H_2O (21.4 mg, 0.11 mmol) in toluene (20 mL). The desired product **1f** (337.3

mg, 62% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 3:1 to PE/EA = 1:1). mp: 130−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.31 (br s, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.36 (q, *J* = 2.7 Hz, 2H), 2.47 (t, *J* = 6.1 Hz, 2H), 2.40 (t, *J* = 6.1 Hz, 2H), 1.92 (quint, *J* = 6.3 Hz, 2H), 1.82 (t, *J* = 2.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.3, 159.7, 137.4, 131.2, 129.6, 126.0, 108.4, 77.5, 76.3, 36.4, 27.2, 21.9, 12.3, 3.8; HRMS (ESI^+) calc'd for $C_{16}H_{16}ClNNaO$ $[M + Na]^+$: 296.0813, found 296.0814.

3-((4-Bromophenyl)amino)-2-(but-2-yn-1-yl)cyclohex-2-en-1-one 1g. The general procedure was followed. The reaction was conducted with 4-bromoaniline (516.3 mg, 3.0 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (329.9 mg, 2.0 mmol), *p*-TsOH•H_2O (22.4 mg, 0.12 mmol) in toluene (20 mL). The desired product **1g** (470.9 mg, 74% yield) was obtained as a light yellow solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.27 (br s, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.34 (q, *J* = 2.7 Hz, 2H), 2.47 (t, *J* = 6.1 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 1.92 (quint, *J* = 6.3 Hz, 2H), 1.81 (t, *J* = 2.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.3, 159.3, 138.0, 132.5, 126.2, 118.7, 108.6, 77.5, 76.3, 36.5, 27.2, 21.9, 12.3, 3.8; HRMS (ESI^+) calc'd for $C_{16}H_{16}BrNNaO$ $[M + Na]^+$: 340.0307, found 340.0304.

2-(But-2-yn-1-yl)-3-((4-nitrophenyl)amino)cyclohex-2-en-1-one 1h. The general procedure was followed. The reaction was conducted with 4-nitroaniline (1.0530 g, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (818.0 mg, 5.0 mmol), *p*-TsOH•H_2O (51.3 mg, 0.27 mmol) in toluene (30 mL). The desired product **1h** (847.4 mg, 60% yield) was obtained as a dark yellow solid after purification by silica gel chromatography (PE/EA = 10:1 to PE/EA = 1:1). mp: 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.80 (br s, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.35 (q, *J* = 2.7 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.45 (t, *J* = 6.6 Hz, 2H), 2.02 (quint, *J* = 6.3 Hz, 2H), 1.84 (t, *J* = 2.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.9, 157.0, 145.3, 143.2, 125.5, 121.2, 112.6, 78.3, 75.8, 36.6, 27.8, 22.4, 12.6, 3.8; HRMS (ESI^+) calc'd for $C_{16}H_{17}N_2O_3$ $[M + H]^+$: 285.1234, found 285.1233.

2-(But-2-yn-1-yl)-3-(naphthalen-1-ylamino)cyclohex-2-en-1-one 1i. The general

procedure was followed. The reaction was conducted with naphthalen-1-amine (2.1527 g, 15 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (1.6485 g, 10.0 mmol), *p*-TsOH•H_2O (53.8 mg, 0.28 mmol) in toluene (50 mL). The desired product **1i** (2.11 g, 70% yield) was obtained as a brown solid after purification by silica gel chromatography (PE/EA = 10:1 to PE/EA = 1:1). mp: 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.03 (m, 1H), 7.96–7.89 (m, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.60–7.53 (m, 2H), 7.52–7.46 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 3.51 (q, *J* = 2.7 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.31 (t, *J* = 6.2 Hz, 2H), 1.92–1.80 (m, 5H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.2, 162.1, 134.6, 134.5, 130.8, 128.7, 127.6, 127.2, 126.8, 125.6, 124.6, 122.5, 107.4, 77.6, 77.4, 36.3, 26.9, 21.7, 12.3, 3.9; HRMS (ESI$^+$) calc'd for $C_{20}H_{19}NONa$ $[M + Na]^+$: 312.1359, found 312.1364.

2-(But-2-yn-1-yl)-3-(*o*-tolylamino)cyclohex-2-en-1-one 1j. The general procedure was followed. The reaction was conducted with *o*-toluidine (804.4 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (839.5 mg, 5.0 mmol), *p*-TsOH•H_2O (54.2 mg, 0.28 mmol) in toluene (30 mL). The desired product **1j** (896.8 mg, 71% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 5:1 to PE/EA = 1:1). mp: 82−84°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.24 (m, 3H), 7.18 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.09 (br s, 1H), 3.49 (q, *J* = 2.7 Hz, 2H), 2.47 (t, *J* = 6.5 Hz, 2H), 2.44–2.35 (m, 2H), 2.41 (s, 3H), 1.98 (quint, *J* = 6.4 Hz, 2H), 1.88 (t, *J* = 2.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.0, 161.0, 137.4, 134.2, 131.1, 127.0, 126.8, 107.4, 77.4, 77.0, 36.5, 27.0, 21.8, 18.1, 12.2, 3.9; HRMS (ESI$^+$) calc'd for $C_{17}H_{20}NO$ $[M + H]^+$: 254.1539, found 254.1543.

2-(But-2-yn-1-yl)-3-((2-iodophenyl)amino)cyclohex-2-en-1-one 1k. The general procedure was followed. The reaction was conducted with 2-iodoaniline (3.3052 g, 15 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (1.6450 g, 10.0 mmol), *p*-TsOH•H_2O (51.7 mg, 0.27 mmol) in toluene (50 mL). The desired product **1k** (2.2152 g, 61% yield) was obtained as a brown solid after purification by silica gel chromatography (PE/EA = 10:1 to PE/EA = 1:1). mp: 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.09 (br s, 1H), 6.95 (t, *J* = 7.8, 1.5 Hz, 1H), 3.38 (q, *J* = 2.8 Hz, 2H), 2.39 (t, *J* = 6.5 Hz, 2H), 2.33 (t, *J* = 6.1

Hz, 2H), 1.91 (quint, J = 6.3 Hz, 2H), 1.79 (t, J = 2.6 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 194.6, 159.6, 140.7, 139.7, 129.2, 127.8, 126.9, 109.4, 97.4, 77.5, 76.4, 36.6, 27.3, 21.7, 12.5, 4.4; HRMS (ESI^+) calc'd for $C_{16}H_{17}INO$ $[M + H]^+$: 366.0349, found 366.0347.

3-(Benzylamino)-2-(but-2-yn-1-yl)cyclohex-2-en-1-one 1l. The general procedure was followed. The reaction was conducted with phenylmethanamine (857.4 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (821.6 mg, 5.0 mmol), *p*-TsOH•H_2O (31.0 mg, 0.16 mmol) in toluene (30 mL). The desired product **1l** (987.1 mg, 78% yield) was obtained as a light brown solid after purification by silica gel chromatography (PE/EA = 1:1). mp: 105−106 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 2H), 7.34–7.28 (m, 3H), 5.84 (br s, 1H), 4.51 (d, J = 6.0 Hz, 2H), 3.30 (q, J = 2.7 Hz, 2H), 2.47 (t, J = 6.2 Hz, 2H), 2.33 (t, J = 6.5 Hz, 2H), 1.91 (quint, J = 6.3 Hz, 2H), 1.68 (t, J = 2.6 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 193.2, 162.4, 138.1, 129.1, 127.9, 126.8, 76.84, 76.81, 47.3, 35.9, 25.6, 21.2, 12.0, 3.7; HRMS (ESI^+) calc'd for $C_{17}H_{19}NNaO$ $[M + Na]^+$: 276.1359, found 276.1363.

2-(But-2-yn-1-yl)-3-((furan-2-ylmethyl)amino)cyclohex-2-en-1-one 1m. The general procedure was followed. The reaction was conducted with furan-2-ylmethanamine (729.4 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (823.6 mg, 5.0 mmol), *p*-TsOH•H_2O (53.7 mg, 0.28 mmol) in toluene (30 mL). The desired product **1m** (701.8 mg, 58% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 1:1). mp: 137−138 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 1.8, 0.8 Hz, 1H), 6.33 (dd, J = 3.3, 1.8 Hz, 1H), 6.24 (dd, J = 3.3, 0.9 Hz, 1H), 5.75 (br s, 1H), 4.44 (d, J = 6.1 Hz, 2H), 3.24 (q, J = 2.7 Hz, 2H), 2.53 (t, J = 6.2 Hz, 2H), 2.31 (t, J = 6.1 Hz, 2H), 1.93 (quint, J = 6.5 Hz, 2H), 1.68 (t, J = 2.7 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 193.3, 161.7, 151.4, 142.7, 110.6, 107.3, 106.0, 76.8, 76.6, 40.5, 36.0, 25.4, 21.1, 11.9, 3.6; HRMS (ESI^+) calc'd for $C_{15}H_{18}NO_2$ $[M + H]^+$: 244.1332, found 244.1330.

3-(Allylamino)-2-(but-2-yn-1-yl)cyclohex-2-en-1-one 1n. The general procedure was followed. The reaction was conducted with prop-2-en-1-amine (424.8 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (821.2 mg, 5.0 mmol), *p*-TsOH•H_2O (97.3 mg,

0.51 mmol) in toluene (30 mL). The desired product **1n** (616.6 mg, 61% yield) was obtained as a light yellow solid after purification by silica gel chromatography (PE/EA = 1:1). mp: 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99–5.78 (m, 1H), 5.52 (br s, 1H), 5.31–5.214 (m, 1H), 5.246–5.17 (m, 1H), 3.99–3.81 (m, 2H), 3.26 (q, *J* = 2.7 Hz, 2H), 2.45 (t, *J* = 6.2 Hz, 2H), 2.31 (t, *J* = 6.0 Hz, 2H), 1.91 (quint, *J* = 6.4 Hz, 2H), 1.72 (t, *J* = 2.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 193.1, 162.4, 134.5, 116.4, 105.4, 76.7, 76.5, 45.4, 36.0, 25.2, 21.2, 11.9, 3.7; HRMS (ESI$^+$) calc'd for $C_{13}H_{18}NO$ $[M + H]^+$: 204.1383, found 204.1383.

2-(But-2-yn-1-yl)-3-(*n*-nexylamino)cyclohex-2-en-1-one 1o. The general procedure was followed. The reaction was conducted with hexan-1-amine (795.7 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (824.6 mg, 5.0 mmol), *p*-TsOH•H_2O (59.3 mg, 0.31 mmol) in toluene (30 mL). The desired product **1o** (781.8 mg, 63% yield) was obtained as a light yellow oil after purification by silica gel chromatography (PE/EA = 5:1 to PE/EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (br s, 1H), 3.34–3.16 (m, 4H), 2.47 (t, *J* = 6.2 Hz, 2H), 2.32 (t, *J* = 6.5 Hz, 2H), 1.93 (quint, *J* = 6.4 Hz, 2H), 1.75 (t, *J* = 2.7 Hz, 3H), 1.60 (quint, *J* = 7.2 Hz, 2H), 1.46–1.36 (m, 2H), 1.36–1.26 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 192.8, 162.5, 104.5, 77.0, 76.3, 43.4, 36.0, 31.6, 30.5, 26.6, 25.7, 22.7, 21.2, 14.1, 11.9, 3.8; HRMS (ESI$^+$) calc'd for $C_{16}H_{26}NO$ $[M + H]^+$: 248.2009, found 248.2015.

3-(Phenylamino)-2-(3-phenylprop-2-yn-1-yl)cyclohex-2-en-1-one 1p. The general procedure was followed. The reaction was conducted with aniline (118.6 mg, 1.26 mmol), 2-(3-phenylprop-2-yn-1-yl)cyclohexane-1,3-dione (190.2 mg, 0.84 mmol), *p*-TsOH•H_2O (13.9 mg, 0.07 mmol) in toluene (10 mL). The desired product **1p** (166.9 mg, 66% yield) was obtained as a yellow solid after purification by silica gel chromatography (PE/EA = 3:1). mp: 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.37 (m, 2H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.32–7.27 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 3.68 (s, 2H), 2.53 (t, *J* = 6.1 Hz, 2H), 2.43 (t, *J* = 6.4 Hz, 2H), 1.95 (quint, *J* = 6.2 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.3, 160.4, 138.6, 131.7, 129.5, 128.4, 128.1, 125.9, 125.0, 123.4, 107.2, 87.2, 81.9, 36.5, 27.3, 21.9, 13.0; HRMS (ESI+) calc'd for $C_{21}H_{20}NO$ $[M + H]^+$: 302.1539, found 302.1538.

2-(But-2-yn-1-yl)-3-(prop-2-yn-1-ylamino)cyclohex-2-en-1-one 1r. The general procedure was followed. The reaction was conducted with prop-2-yn-1-amine (416.9 mg, 7.5 mmol), 2-(but-2-yn-1-yl)cyclohexane-1,3-dione (822.9 mg, 5.0 mmol), *p*-TsOH•H_2O (67.7 mg, 0.36 mmol) in toluene (30 mL). The desired product **1r** (574.6 mg, 57% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 1:1). mp: 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (br s, 1H), 4.04 (dd, *J* = 5.9, 2.5 Hz, 2H), 3.23 (q, *J* = 2.7 Hz, 2H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.38–2.28 (m, 3H), 1.96 (quint, *J* = 6.5 Hz, 2H), 1.75 (t, *J* = 2.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 193.6, 161.4, 106.8, 79.5, 76.9, 76.4, 72.7, 36.0, 33.0, 25.4, 21.1, 12.0, 3.8; HRMS (ESI^+) calc'd for $C_{13}H_{16}NO$ $[M + H]^+$: 202.1226, found 202.1229.

3-Amino-2-(but-2-yn-1-yl)cyclohex-2-en-1-one 1q. To a 50 mL two-neck round-bottomed flask equipped with a Dean-Stark apparatus were added NH_4OAc (2.05 g, 25 mmol) and 2-(prop-2-yn-1-yl)cyclohexane-1,3-dione (820.2 mg, 5.0 mmol) in toluene (30 mL). The mixture was refluxed and monitored by TLC. After completion of the starting materials, it was cooled to room temperature and diluted with DCM (100 mL), dried over anhydrous Na_2SO_4. The desired product 3-amino-2-(but-2-yn-1-yl)cyclohex-2-en-1-one **1q** (750.8 mg, 87% yield) was obtained as a white solid after purification by silica gel chromatography (PE/EA = 1:1 to EA). mp: 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (br s, 2H), 3.22 (q, *J* = 2.7 Hz, 2H), 2.43 (t, *J* = 6.2 Hz, 2H), 2.33 (t, *J* = 6.5 Hz, 2H), 1.93 (quint, *J* = 6.4 Hz, 2H), 1.75 (t, *J* = 2.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 194.3, 161.3 , 106.0 , 76.6, 76.2, 36.2, 30.0, 21.3, 12.0, 3.7; HRMS (ESI+) calc'd for $C_{10}H_{14}NO$ $[M + H]^+$: 164.1070, found 164.1068.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

^{1}H NMR and ^{13}C NMR spectra of new compounds (PDF).

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Notes

The authors declare no competing financial interest.

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