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Novel synthesis of indolylquinoline derivatives via the C-alkylation of Baylis–Hillman adducts

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ABSTRACT

A new and simple method for the C-alkylation of indoles by various Baylis–Hillman adducts and the one-pot reductive cyclization of C-alkylated indole derivatives generated from 2-nitro-Baylis–Hillman adduct to form indolylquinoline derivatives is described.

1. Introduction

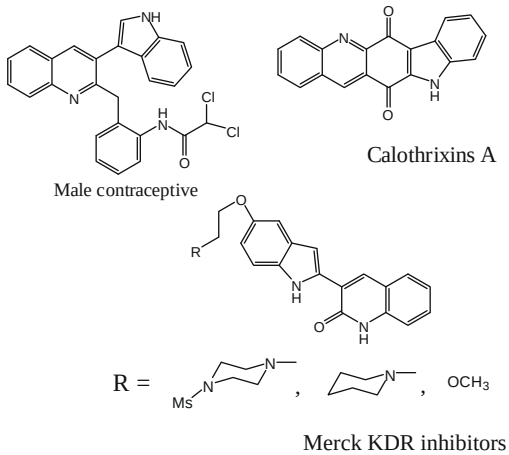
Functionalized quinoline and indole frameworks continue to play an important role in nitrogen heterocyclic chemistry, primarily due to the fact that these moieties can be found in a variety of molecules that show a wide spectrum of physiological activities and pharmaceutical applications.[1] Molecules that contain both indole and quinoline subunits possess some interesting biological activities, including male contraceptive activity in adult rats (Scheme 1),[2] the dual inhibition of DNA topoisomerases of Leishmania donovani,[3] potent in vitro methicillin-resistant *Staphylococcus* aureus[4] and antimicrobial activity.[5] Researchers at Merck recently reported on a class of potent KDR kinase inhibitors that contain an indol-2-yl quinolin-2-one structure (Scheme 1).[6] In addition, natural products that contain fused indole and quinoline rings (calothrixins) inhibit the in vitro growth of the chloroquine-resistant strain of the human parasite, *Plasmodium falciparum* in a dose-dependent manner.[7] Because of the importance of indolylquinoline and the related ones, a great deal of interest has developed regarding the development of convenient synthetic procedures for preparing such compounds.[8]

It is well known that the Baylis–Hillman (B–H) reaction constitutes a versatile and economically favorable C–C bond-forming reaction for generating multifunctional adducts. B–H adducts and their derivatives thereof act as carbon electrophiles that are capable of reacting with a variety of nucleophiles to give structurally diverse compounds, which are useful precursors for the synthesis of biologically important molecules.[9] The synthesis of substituted quinolines directly from either Baylis–Hillman adducts or derivatives thereof has attracted considerable interest after the first report by Kaye's group in 1998. Since then, several approaches have been developed for the synthesis of quinoline derivatives from B–H derivatives.[10] In the past few years, interest in iodine-catalyzed reactions has increased, due to the fact that it is inexpensive, non-toxic, and readily available. As a part of our continued interest in iodine-catalyzed reactions,[11] we wish to report a convenient procedure for the addition of indoles to Baylis–Hillman adducts catalyzed by iodine, the products of which were further subjected to the reductive cyclization to afford indolylquinoline derivatives.

2. Results and discussions

The outline for the synthesis of the indolylquinoline derivatives is shown in Scheme 2.

The B–H adducts were prepared according to known, previously published procedures.[12] The resulting B–H adduct was then reacted with various indoles in acetonitrile, catalyzed by 30 mol % of iodine to give C-alkylated derivatives of indoles in good yields.



Scheme 1. Biologically active molecules containing indole and quinoline moiety.

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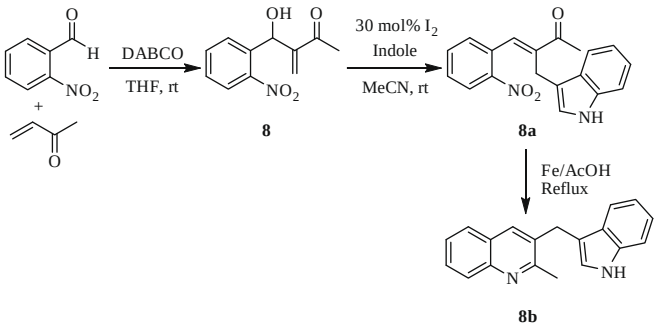


Scheme 2. Route to the synthesis of indolylquinoline derivatives.

Reduction of the nitro moiety followed by cyclization subsequently afforded indolylquinoline derivatives.

The focus of our initial studies was on the C-alkylation of B–H adducts derived from 2-nitro benzaldehyde and methyl vinylketone, with various indole derivatives. To our knowledge, only one method is available for the C-alkylation of indoles with B–H acetates using indium tribromide,[13] direct reactions with B–H alcohols have not been reported in the literature. We therefore investigated this reaction and examined the use of various mild acidic catalysts. Iodine was found to be a suitable catalyst for this transformation.

The reaction conditions for the C-alkylation were tuned by performing a sxseries of reactions with varying proportions of indole and iodine and 1 equiv of Baylis–Hillman adduct in acetonitrile. Initially, indole (1 mmol) was reacted with B–H adduct (1 mmol) catalyzed by 30 mol % of iodine to afford C-alkylated indole in 63% yield. Upon increasing the amount of indole to 1.2 mmol, the product formation was increased to 79%. Further, with 1.4 mmol of indole the C-alkylated indole was obtained in excellent yield (98%) (Table 1). Hence, the optimum conditions involved in a reaction using 1.4 equiv of indole and 30 mol % of iodine, with 1 equiv of B–H adduct in acetonitrile as the solvent at room temperature (25 °C).

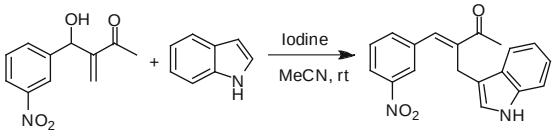
The scope of this protocol was investigated by reacting various substituted indoles with a variety of B–H adducts. The results are presented in Table 2. All the products produced in this reaction showed (*E*)-stereoselectivity.

The (*E*)-stereochemistry of the products was assigned on the basis of the ^{1}H NMR[22] chemical shifts of the vinyl and allylic protons and single crystal X-ray diffraction analysis (Fig. 1). It has been reported that the reaction of Baylis–Hillman adducts with iodine leads to the formation of allyl iodides.[14] Fortunately, no iodinated products were detected in the present reaction conditions.

The reductive cyclization of the B–H adducts derived from 2-nitro benzaldehyde and derivatives thereof to quinoline derivatives has been extensively explored using various reagents.[10r] Among the reagents available for the reductive cyclization, the Fe/AcOH reagent gained importance, due to its availability, environmental safety, and low cost. This reagent has been used in the synthesis of quinoline deriatives,[15] 2*H*-pyrrolo[3,4-*c*]quinolines,[16] double reductive cyclization reactions[17] and in the synthesis of disubstituted α-methylene-γ–butyrolactams.[18] Based on these findings, we initiated a study of the reductive cyclization of similar compounds obtained from the reaction of indoles and B–H adducts that contain a nitro moiety.

The products obtained from the reaction of B–H adduct containing a nitro group and indoles were reduced with Fe/AcOH to the corresponding amines. In the case of compounds containing a nitro group in the second position, the reaction was followed by in situ cyclization employing the same reagent. Compounds **8a–14a** were subjected to Fe/AcOH reductive cyclization, resulting in the production of indolylquinoline derivatives. Some examples are shown in Table 3. As can be seen from Table 3, the reductive cyclization was not affected by any of the substituents present on the benzene ring of the B–H adduct; the substrates containing electron-withdrawing groups as well as electron-releasing groups all reacted smoothly, giving good yields of indolylquinoline derivatives. It is interesting to note that the reaction with 2-substituted indole derivatives gave excellent product yields. It is also noteworthy that

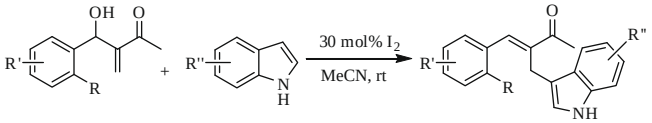
Table 1
The iodine-catalyzed C-alkylation of indole under various conditions



Entry	Indole (mmol)	Iodine (mol %)	Time (h)	Yield[a] (%)
1	1	30	10	63
2	1.2	30	10	79
3	1.4	30	10	98
4	1.4	10	24	95
5	1.4	20	18	96

[a] Yields were determined by ^{1}H NMR spectrum.

Table 2
The iodine-catalyzed C-alkylation of indoles by various Baylis–Hillman derivatives[20]



(**1a-15a**)

Entry	R	R′	R″	Product	Time (h)	Yield[a] (%)
1	H	H	H	la	10	73
2	H	3-NO_2	H	2a	10	85
3	H	3-NO_2	2-Me	3a	3	87
4	H	3-NO_2	2-Ph	4a	3	89
5	H	3-NO_2	5-OMe	5a	8	80
6	H	3-NO_2	5-Br	6a	8	81
7	H	3-NO_2	7-Et	7a	9	80
8	NO_2	H	H	8a	10	85
9	NO_2	H	2-Me	9a	4	85
10	NO_2	H	2-COOMe	10a	8	79
11	NO_2	H	2-Ph	lla	4	84
12	NO_2	H	5-OMe	l2a	7	80
13	NO_2	H	5-Br	l3a	12	81
14	NO_2	H	7-Et	l4a	10	83
15	H	4-F	H	l5a	10	74

[a] Isolated yields.

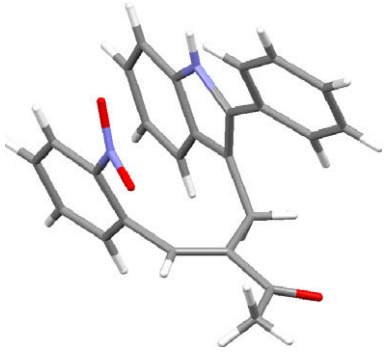
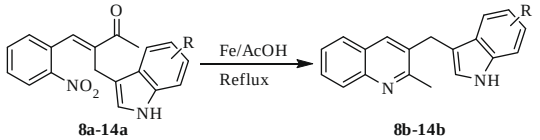
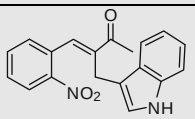
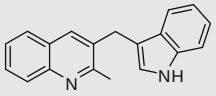
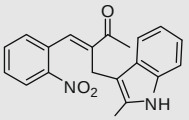
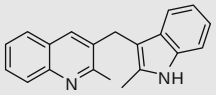
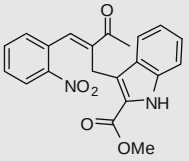
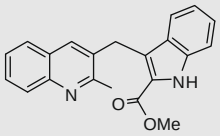
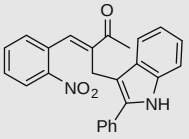
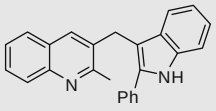
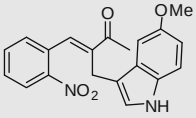
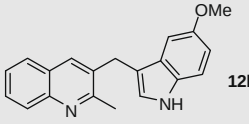
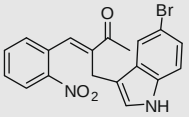
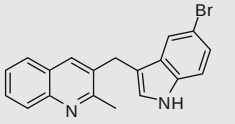
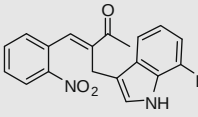
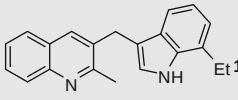


Figure 1. Crystal structure of compound **11a**.[19]

Table 3
Reductive cyclization of C-alkylated indole derivatives (**8a**–**14a**) using Fe/acetic acid[21]



8a-14a **8b-14b**

Entry	Substrate	Product	Time	Yield[a] (%)
1		**8a**  **8b**	2	76
2		**9a**  **9b**	2	83
3		**10a**  **10b**	2	79
4		**11a**  **11b**	2	80
5		**12a**  **12b**	2	78
6		**13a**  **13b**	2	72
7		**14a**  **14b**	2	76

[a] Isolated yields.

chemoselective cyclization was achieved in the presence of an ester group, and all the reactions proceeded smoothly in high yield without any detectable side products. The obtained products were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopic analyses.[22] The crystal structure of a representative compound is shown in Figure 2.

In conclusion, we report on the development of a new and simple method for the C-alkylation of indoles by various Baylis–Hillman adducts and the one-pot reductive cyclization of C-alkylated indole derivatives generated from 2-nitro-Baylis–Hillman adducts to form indolylquinoline derivatives. The overall reactions involved the use of mild reaction conditions, an environmentally acceptable catalyst (iodine) in the first step and a conventional reducing reagent (Fe/acetic acid) in the second step. The fact that the reactions were clean, devoid of side reaction products constitutes additional

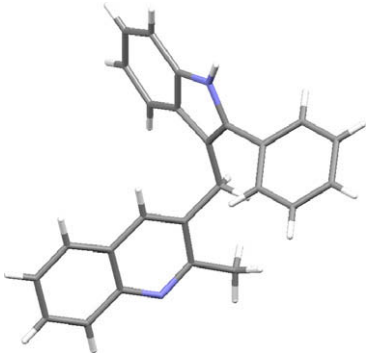


Figure 2. Crystal structure of compound **11b**.[19]

attractive features of this method. Extensions of the reactions are currently under way in our laboratory.

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19. CCDC numbers of **12a, 12b** are 714386, 714387, respectively. These data can be obtained free of charge from Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif.
20. *Experimental procedures: The C-alkylation of indoles with Baylis–Hillman adducts*: To a stirred solution of Baylis–Hillman adduct (**8**) (2 mmol) in acetonitrile were added indole (2.8 mmol) and iodine (30 mol %) and the mixture was stirred to completion, as monitored by TLC. After completion of the reaction, the reaction mixture was quenched with saturated solution of sodium thiosulfate and extracted with ethyl acetate (2 × 10 mL). The organic layer was separated, dried over anhydrous magnesium sulfate and concentrated to give the crude product. The crude product obtained **8a** was purified by passing through a short silica gel column.
21. *Reductive cyclization*: To a stirred solution of **8a** (1 mmol) in acetic acid (5 mL), powdered Fe (6 mmol) was added and the reaction mixture was then refluxed for 2 h. The mixture was cooled to room temperature and the acetic acid was removed under reduced pressure, EtOAc (10 mL) was added, then the mixture was stirred for 2 min and then filtered to remove any iron impurities. The insoluble iron residue was washed with EtOAc (10 mL). The filtrate and washings were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography (silica gel).
22. *Spectral data: 3-((1H-indol-3-yl)methyl)-4-phenylbut-3-en-2-one* (**1a**): Gummy liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (br s, 1H), 7.70 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.43–7.41 (m, 2H), 7.31–7.29 (m, 4H), 7.22–7.15 (m, 1H), 7.11–7.07 (m, 1H), 6.78 (s, 1H), 3.99 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 140.1, 139.4, 136.2, 134.1, 129.3, 128.6, 128.3, 126.7, 121.7, 121.6, 118.8, 118.4, 112.9, 111.1, 26.0, 22.7.MS (*m/z*) (relative intensity) 275 (M^+, 66), 274 (100), 232 (30), 201 (7), 153 (6), 114 (24), 102 (5). HRMS calcd for $C_{19}H_{17}NO$ (M^+) 275.1305, found 275.1307. Anal. Calcd for $C_{19}H_{17}NO$: C, 80.60; H, 6.94; N, 4.72. Found: C, 80.21; H, 6.78; N, 4.79. *3-((1H-Indol-3-yl)methyl)-4-(3-nitrophenyl)but-3-en-2-one* (**2a**): Brown gummy liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 8.20 (s, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 4.8 Hz, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.38–7.33 (m, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.16–7.12 (m, 1H), 7.10–7.04 (m, 1H), 6.74 (s, 1H), 3.93 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 148.0, 142.0, 136.9, 136.8, 136.4, 134.7, 129.5, 126.6, 124.1, 123.1, 122.1, 121.8, 119.3, 118.4, 112.7, 111.2, 26.3, 22.9. MS (*m/z*) (relative intensity) 319 (M^+, 100), 302 (36), 277 (28), 260 (14), 230 (47), 202 (18), 200 (14), 159 (8), 129 (31), 116 (18), 76 (8). HRMS calcd for $C_{19}H_{16}N_2O_3$ (M^+) 320.1155, found 320.1162. Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 69.45; H, 4.70; N, 8.37. *3-((2-Methyl-1H-indol-3-yl)methyl)-4-(3-nitrophenyl)but-3-en-2-one* (**3a**): Red solid, mp: 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.12 (dd, J = 8.1, 1.6 Hz, 1H), 7.74 (br s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.55 (s, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.16 (m, 2H), 7.03 (t, J = 7.0 Hz, 1H), 6.95–6.92 (m, 1H), 3.95 (s, 2H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 148.0, 143.5, 137.4, 135.4, 135.0, 134.8, 131.8, 129.3, 128.1, 123.9, 122.8, 120.8, 119.1, 117.9, 110.2, 107.5, 26.6, 22.4, 11.9. MS (*m/z*) (relative intensity) 335 (M+1, 16), 333 (100), 318 (36), 290 (10), 244 (18), 201 (10), 183 (15), 143 (80), 130 (70), 126 (7). HRMS calcd for $C_{20}H_{18}N_2O_3$ (M^+) 334.1312, found 334.1320. Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 72.11; H, 5.12; N, 8.39. *4-(3-Nitrophenyl)-3-((2-phenyl-1H-indol-3-yl)methyl)but-3-en-2-one* (**4a**): Red solid; mp: 109–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 3H), 7.43–7.33 (m, 8H), 7.27–7.23 (m, 2H), 7.14–7.10 (m, 1H), 7.05–7.01 (m, 1H), 4.19 (s, 2H), 2.29 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 147.7, 143.5, 137.0, 136.3, 135.7, 134.9, 134.2, 132.8, 128.8, 128.6, 128.4, 128.2, 127.8, 123.4, 122.5, 122.1, 119.6, 119.1, 110.8, 109.1, 26.3, 22.4. MS (*m/z*) (relative intensity) 396 (M^+, 56), 394 (46), 353 (18), 318 (8), 305 (15), 229 (19), 217 (68), 206 (100), 192 (72), 178 (18), 151 (8). HRMS calcd for $C_{25}H_{20}N_2O_3$ (M^+) 396.1468, found 396.1466. Anal. Calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.08; N, 7.07. Found: C, 75.63; H, 5.36; N, 7.09. *3-((5-Methoxy-1H-indol-3-yl)methyl)-4-(3-nitrophenyl)but-3-en-2-one* (**5a**): Yellow solid; mp: 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.16–8.14 (m, 1H), 7.93 (br s, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.67 (s, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 6.90–6.82 (m, 3H), 3.93 (s, 2H), 3.81 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 154.0, 148.3, 142.3, 137.1, 136.5, 134.8, 131.6, 129.6, 127.2, 124.3, 123.2, 122.6, 112.7, 112.5, 111.9, 100.5, 55.8, 26.4, 23.0. MS (*m/z*) (relative intensity) 349 (M^+, 100), 333 (26), 306 (33), 290 (16), 260 (18), 228 (21), 189 (11), 160 (35), 147 (24), 116 (12). HRMS calcd for $C_{20}H_{18}N_2O_4$ (M^+) 350.1261, found 350.1264. Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 67.80; H, 4.93; N, 7.66. *3-((5-Bromo-1H-indol-3-yl)methyl)-4-(3-nitrophenyl) but-3-en-2-one* (**6a**): Yellow solid; mp: 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 8.18–8.16 (m, 2H), 7.67 (d, J = 6.2 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.25–7.17 (m, 2H), 6.84 (s, 1H), 3.88 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 148.3, 142.2, 137.1, 136.9, 134.9, 134.6, 129.7, 128.5, 125.1, 124.1, 123.4, 123.2, 121.3, 112.8, 112.7, 112.6, 26.3, 22.6. MS (*m/z*) (relative intensity) 400 (M+2, 69), 399 (M^+, 55), 382 (53), 381 (37), 301 (19), 275 (75), 274 (58), 208 (70), 207 (51), 195 (39), 153 (18), 128 (38), 114 (22), 101 (14). HRMS calcd for $C_{19}H_{15}BrN_2O_3$ (M^+) 398.0261, found 398.0248 and HRMS calcd for $C_{19}H_{15}{}^{81}BrN_2O_3$ (M^+) 400.0240, found 400.0240. Anal. Calcd for $C_{19}H_{15}BrN_2O_3$: C, 57.16; H, 3.79; N, 7.02. Found: C, 56.96; H, 3.89; N, 6.69. *3-((7-Ethyl-1H-indol-3-yl)methyl)-4-(3-nitro phenyl) but-3-en-2-one* (**7a**): Brown gummy liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.14 (dd, J = 8.2, 1.4 Hz, 1H), 7.99 (br s, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.67 (s, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.34–7.32 (m, 1H), 7.10–7.05 (m, 2H), 6.85 (s, 1H), 3.97 (s, 2H), 2.84 (q, J = 7.5 Hz, 2H), 2.46 (s, 3H), 1.35 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 147.8, 141.9, 136.7, 136.6, 135.0, 134.6, 129.3, 126.5, 126.3, 123.9, 122.8, 121.5, 120.3, 119.3, 115.9, 112.7, 26.1, 23.5, 22.8, 13.5. MS (*m/z*) (relative intensity) 348 (M^+, 100), 304 (51), 275 (23), 258 (36), 228 (32), 227 (23), 202 (14), 157 (48), 144 (38), 129 (24), 114 (9). HRMS calcd for $C_{21}H_{20}N_2O_3$ (M^+) 348.1468, found 348.1472. Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 67.58; H, 5.70; N, 7.16. *3-((1H-Indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one* (**8a**): Yellow solid; mp: 135–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 9.6 Hz, 1H,), 7.98 (br s, 1H), 7.93 (s, 1H), 7.54–7.44 (m, 2H), 7.39 (d, J = 7.6 Hz, 1H,), 7.33–7.25 (m, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H), 6.7 (s, 1H), 3.7 (s, 2H), 2.4 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 147.4, 141.1, 136.4, 136.2, 133.6, 131.7, 130.8, 129.2, 126.8, 124.9, 122.1, 121.9, 119.2, 118.5, 113.7, 111.0, 26.5, 22.4. MS (*m/z*) (relative intensity): 320 (M^+, 18), 276 (31), 261 (50), 260 (100), 230 (33), 202 (16). HRMS calcd for $C_{19}H_{16}N_2O_3$ (M^+) 320.1155, found 320.1153. Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.02; N, 8.74. Found: C, 71.31; H, 5.26; N, 8.53. *3-((2-Methyl-1H-indol-3-yl) methyl)-4-(2-nitrophenyl)but-3-en-2-one* (**9a**): Brown gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.4 Hz, 1H), 7.8 (s, 1H), 7.59 (br s, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.38–7.31 (m, 2H), 7.12–7.07 (m, 2H), 7.02–6.99 (m, 1H), 6.92 (m, 1H) 3.76 (s, 2H), 2.44 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 146.8, 141.8, 135.9, 134.9, 133.1, 131.7, 131.6, 130.8, 128.7, 128.1, 124.6, 120.6, 118.9, 117.8, 109.9, 107.9, 26.4, 21.6, 11.5. MS (*m/z*) (relative intensity) 335 (M+1, 15), 333 (81), 290 (33), 275 (72), 274 (80), 244 (20), 183 (15), 158 (46), 143 (100), 129 (79), 126 (15). HRMS calcd for $C_{20}H_{18}N_2O_3$ (M^+) 334.1312, found 334.1317. Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 70.99; H, 5.55; N, 7.99. *Methyl 3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate* (**10a**): Yellow solid; mp: 149–150 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (br s, 1H), 7.88 (s, 1H), 7.82 (dd, J = 8.2, 1.0 Hz, 1H), 7.36–7.30 (m, 2H), 7.22–7.14 (m, 4H), 7.00–6.97 (m, 1H), 4.22 (s, 2H), 3.83 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 161.8, 146.0, 141.3, 137.5, 135.5, 132.8, 131.7, 130.3, 128.4, 127.2, 125.5, 124.0, 122.9, 121.1, 121.0, 120.0, 111.4, 51.6, 26.1, 22.1. MS (*m/z*) (relative intensity) 378 (M^+, 60), 361 (27), 318 (59), 286 (57), 258 (62), 228 (32), 188 (100), 187 (80), 155 (53), 127 (40), 101 (15). HRMS calcd for $C_{21}H_{18}N_2O_5$ (M^+) 378.1210, found 378.1210. Anal. Calcd for $C_{21}H_{18}N_2O_5$: C, 72.40; H, 5.79; N, 8.04. Found: C, 66.30; H, 4.95; N, 7.22. *4-(2-Nitrophenyl)-3-((2-phenyl-1H-indol-3-yl)methyl)but-3-en-2-one* (**11a**): Red solid; mp: 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.0, 1.1 Hz, 2H), 7.76 (s, 1H), 7.42–7.38 (m, 4H), 7.36–7.28 (m, 3H), 7.26–7.20 (m, 2H), 7.15–7.08 (m, 2H), 6.99 (t, J = 7.5 Hz, 1H) 4.06 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 146.3, 141.9, 136.5, 135.6, 134.6, 132.8, 132.7, 131.5, 130.3, 128.6, 128.5, 128.1, 127.6, 124.4, 122.1, 119.5, 119.3, 110.5, 110.4, 109.6, 26.2, 22.2. MS (*m/z*) (relative intensity) 396 (M^+, 23), 362 (10), 353 (30), 336 (51), 318 (42), 305 (12), 229 (13), 216 (22), 203 (100), 193 (85), 178 (22), 151 (7). HRMS calcd for $C_{25}H_{20}N_2O_3$ (M^+) 396.1468, found 396.1461. Anal. Calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.08; N, 7.07. Found: C, 75.84; H, 5.14; N, 6.98. *3-((5-Methoxy-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one* (**12a**): Yellow solid; mp: 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.1, 1.2 Hz, 1H), 7.93 (s, 1H), 7.86 (br s, 1H), 7.54–7.52 (m, 1H), 7.49–7.47 (m, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 6.83–6.78 (m, 2H), 6.73 (s, 1H), 3.79 (s, 3H), 3.74 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 153.8, 147.4, 141.1, 136.4, 133.6, 131.7, 131.3, 130.9, 129.2, 127.1, 124.9, 122.6, 113.4, 112.4, 111.8, 100.4, 55.8, 26.5, 22.6. MS (*m/z*) (relative intensity) 350 (M^+, 47), 315 (8), 306 (33), 290 (100), 248 (23), 247 (29), 217 (25), 188 (19), 159 (48), 147 (35), 132 (22), 117 (11), 89 (6). HRMS calcd for $C_{20}H_{18}N_2O_4$ (M^+) 350.1261, found 350.1254. Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.78; H, 5.15; N, 7.83. *3-((5-Bromo-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one* (**13a**): Yellow solid; mp: 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.1, 1.0 Hz, 1H), 8.0 (br s, 1H), 7.93 (s, 1H), 7.61–7.57 (m, 1H), 7.54–7.50 (m,

1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.25 (s, 1H), 7.19 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 6.79 (s, 1H), 3.69 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 147.2, 140.9, 137.2, 134.6, 133.7, 131.5, 130.7, 129.4, 128.4, 125.0, 124.7, 123.3, 121.0, 113.2, 112.5, 112.4, 26.3, 21.8. MS (*m/z*) (relative intensity) 400 (M+2, 9), 398 ($M^{+\cdot}$ 8), 354 (24), 340 (100), 310 (13), 297 (2), 259 (49) 228 (32), 208 (50), 207 (33), 195 (17), 187 (6), 128 (30), 101 (131), 74 (2). HRMS calcd for $C_{19}H_{15}BrN_2O_3$ (M^+) 398.0261, found 398.0258; HRMS calcd for $C_{19}H_{15}{}^{81}BrN_2O_3$ (M^+) 400.0240, found 400.0242. Anal. Calcd for $C_{19}H_{15}BrN_2O_3$: C, 57.16; H, 3.79; N, 7.02. Found: C, 57.22; H, 3.79; N, 6.98. *3-((7-Ethyl-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one* **(14a)**: Brown gummy liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.94 (s, 1H), 7.92 (br s, 1H), 7.53–7.51 (m, 1H), 7.49–7.46 (m, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.21–7.19 (m, 1H), 7.0 (m, 2H), 6.77 (s, 1H), 3.79 (s, 2H), 2.81 (q, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 1.33 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 147.3, 141.0, 136.3, 135.0, 133.6, 131.6, 130.8, 129.1, 126.5, 126.4, 124.8, 121.5, 120.5, 119.5, 116.2, 113.9, 26.5, 23.8, 22.6, 13.7. MS (*m/z*) (relative intensity) 348 (M^+, 38), 304 (39), 288 (100), 287 (56), 259 (39), 243 (18), 240 (112), 187 (10), 157 (30), 142 (19), 129 (13), 115 (8). HRMS calcd for $C_{21}H_{20}N_2O_3$ (M^+) 348.1468, found 348.1480. Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.77; H, 5.56; N, 7.83. *3-((1H-Indol-3-yl)methyl)-4-(4-fluorophenyl)but-3-en-2-one* **(15a)**: Brown gummy liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (br s, 1H), 7.68 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.43–7.39 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.03–6.98 (m, 2H), 6.8 (s, 1H), 3.98 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 162.7 (d, *J* = 248.0 Hz), 139.1 (d, *J* = 48.0 Hz), 136.5, 131.5, 131.4, 131.36, 131.33, 126.9, 121.4 (d, *J* = 34.0 Hz), 119.2, 118.6, 115.6 (d, *J* = 21.0 Hz), 113.3, 111.20, 26.3, 22.9. MS (*m/z*) (relative intensity) 292 (M-1, 100), 250 (62), 247 (12), 183 (10), 129 (42), 117 (19), 102 (6). HRMS calcd for $C_{19}H_{16}FNO$ (M^+) 293.1210, found 293.1213. Anal. Calcd for $C_{19}H_{16}FNO$: C, 77.80; H, 5.50; N, 4.77. Found: C, 75.63; H, 5.68; N, 4.07. *3-((1H-Indol-3-yl)methyl)-2-methylquinoline* **(8b)**: Colorless solid; mp: 180–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.83 (s, 1H), 7.65–7.59 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.44–7.38 (m, 2H), 7.25–7.20 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 4.24 (s, 2H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 146.5, 136.5, 135.2, 132.9, 128.6, 128.1, 127.4, 127.3, 127.1, 125.6, 122.7, 122.2, 119.5, 118.8, 113.6, 111.2, 29.0, 23.3. MS (*m/z*) (relative intensity) 271 (M^+, 100), 257 (22), 232 (8), 154 (9), 153 (14), 129 (26), 114 (8). HRMS calcd for $C_{19}H_{16}N_2$ (M^+) 272.1308, found 272.1302. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.82; H, 5.92; N, 10.21. *2-Methyl-3-((2-methyl-1H-indol-3-yl)methyl) quinoline* **(9b)**: Colorless solid; mp: 210–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (br s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.60–7.53 (m, 3H), 7.40–7.33 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 4.16 (s, 2H), 2.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.3, 135.4, 134.3, 132.9, 132.3, 128.8, 128.5, 128.1, 127.4, 127.2, 125.5, 121.2, 119.5, 118.2, 110.3, 107.9, 27.5, 23.5, 11.8. MS (*m/z*) (relative intensity) 285 (M^+, 100), 270 (48), 267 (9), 154 (9), 153 (11), 143 (52), 129 (14), 115 (6). HRMS calcd for $C_{20}H_{18}N_2$ (M^+) 286.1465, found 286.1465. Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.24; N, 9.78. Found: C, 83.90; H, 6.16; N, 9.80. *Methyl 3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate* **(10b)**: Colorless solid; mp: 224–225 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (br s, 1H), 8.0 (d, *J* = 8.4 Hz, 1H), 7.58–7.42 (m, 5H), 7.38 -7.34 (m, 2H), 7.07 (s, 1H), 4.63 (s, 2H), 3.87 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 158.4, 146.2, 136.1, 133.1, 132.8, 128.5, 128.1, 128.0, 127.3, 127.1, 125.9, 125.5, 124.1, 121.0, 120.6, 120.3, 112.0, 51.9, 27.8, 23.6. MS (*m/z*) (relative intensity) 330 (M^+, 100), 298 (24), 271 (85), 256 (25), 227 (8), 156 (8), 149 (16), 134 (20), 101 (18). HRMS calcd for $C_{21}H_{18}N_2O_2$ (M^+) 330.1363, found 330.1361. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.08; H, 5.68; N, 8.38. *2-Methyl-3-((2-phenyl-1H-indol-3-yl)methyl)quinoline* **(11b)**: Brown solid; mp: 254–255 °C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (br s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.63–7.59 (m, 1H), 7.54–7.43 (m, 2H), 7.40–7.34 (m, 7H), 7.27–7.24 (m, 1H), 7.10–7.06 (m, 1H), 4.32 (s, 2H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.3, 136.2, 136.1, 134.2, 133.1, 132.6, 129.4, 129.0, 128.6, 128.1, 127.9, 127.5, 127.4, 127.3, 125.5, 122.6, 120.0, 119.3, 111.0, 108.9, 28.0, 23.5. MS (*m/z*) (relative intensity) 348 (M^+, 62), 347 (100), 333 (7), 270 (6), 206 (79), 192 (35), 173 (17), 151 (11). HRMS calcd for $C_{25}H_{20}N_2$ (M^+) 348.1621, found 348.1625. Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 85.75; H, 5.88; N, 7.69. *3-((5-methoxy-1H-indol-3-yl)methyl)-2-methylquinoline* **(12b)**: Brown solid; mp: 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (br s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.66–7.60 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 1H), 6.88 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.78 (s, 1H), 4.20 (s, 2H), 3.79 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 154.1, 146.5, 135.2, 132.8, 131.7, 128.6, 128.1, 127.7, 127.4, 127.1, 125.6, 123.5, 113.3, 112.4, 111.1, 110.7, 55.9, 29.0, 23.3. MS (*m/z*) (relative intensity) 301 (M-1, 100), 300 (45), 286 (24), 257 (7), 159 (19), 127 (6). HRMS calcd for $C_{20}H_{18}N_2O$ (M^+) 302.1414, found 302.1419. Anal. Calcd for $C_{20}H_{18}N_2O$: C, 64.97; H, 4.30; N, 7.98. Found: C, 64.41; H, 4.42; N, 8.04. *3-((5-Bromo-1H-indol-3-yl)methyl)-2-methyl quinoline* **(13b)**: Brown solid; mp: 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br s, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.79 (s, 1H), 7.68–7.62 (m, 3H), 7.46–7.42 (m, 1H), 7.32–7.28 (m, 2H), 6.79 (s, 1H), 4.19 (s, 2H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 146.6, 135.2, 135.1, 132.4, 129.1, 128.8, 128.1, 127.3, 127.1, 125.8, 125.1, 123.9, 121.4, 113.5, 112.9, 112.7, 28.8, 23.2. MS (*m/z*) (relative intensity) 352 (M+2, 68), 350 (M^+, 100), 347 (13), 334 (12), 269 (3), 267 (20), 227 (13), 208 (25), 200 (10), 154 (23), 153 (35), 134 (55), 114 (20), 101 (12). HRMS calcd for $C_{19}H_{15}BrN_2$ (M^+) 350.0413, found 350.0408; HRMS calcd for $C_{19}H_{15}{}^{81}BrN_2$ (M^+) 352.0393, found 352.0392. Anal. Calcd for $C_{19}H_{15}BrN_2$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.49; H, 5.86; N, 8.83. *3-((7-Ethyl-1H-indol-3-yl)methyl)-2-methylquinoline* **(14b)**: Colorless solid. mp: 179–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.85 (s, 1H), 7.67–7.61 (m, 2H), 7.44–7.39 (m, 2H), 7.10–7.07 (m, 2H), 6.79 (s, 1H), 4.24 (s, 2H), 2.88 (q, *J* = 7.6 Hz, 2H), 2.76 (s, 3H), 1.38 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 146.5, 135.3, 135.2, 132.9, 128.6, 128.1, 127.3, 127.1, 127.0, 126.7, 125.6, 122.3, 120.7, 119.8, 116.5, 114.0, 29.1, 23.9, 23.2, 13.7. MS (*m/z*) (relative intensity) 301 (M+1, 3), 299 (100), 269 (20), 267 (9), 157 (31), 142 (15), 134 (7). HRMS calcd for $C_{21}H_{20}N_2$ (M^+) 300.1621, found 300.1628. Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.73; H, 6.63; N, 8.98.