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Synthesis of Indolylquinolines, Indolylacridines, and Indolylcyclopenta[*b*]quinolines from the Baylis–Hillman Adducts: An in Situ [1,3]-Sigmatropic Rearrangement of an Indole Nucleus To Access Indolylacridines and Indolylcyclopenta[*b*]quinolines

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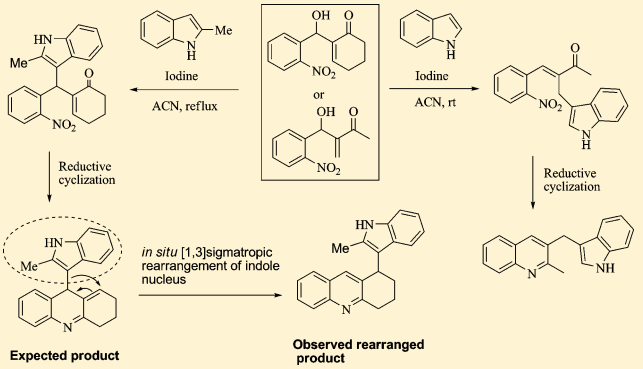
Supporting Information

ABSTRACT: A simple and easy route to the synthesis of a variety of structurally diverse indolylquinolines, indolylacridines, and indolylcyclopenta[*b*]quinoline derivatives via the reductive cyclization of C-alkylated indole derivatives, derived from acyclic as well as cyclic Baylis–Hillman adducts with indoles, is described. An unusual in situ [1,3]-sigmatropic rearrangement of the indole nucleus was observed during the reductive cyclicization of α-regioselective B–H adducts containing indoles to produce indolylacridines and indolylcyclopenta[*b*]-quinoline derivatives.



INTRODUCTION

Indole, quinoline, and acridine structures are important nitrogen heterocyclic motifs that are commonly found in a wide variety of natural products, pharmaceuticals, and synthetic compounds that are biologically active.[1] Indolylquinolines are particularly important, since they possess an array of biological activities, including potent KDR (kinase insert domain receptor) kinase inhibitors, male contraceptive activity in adult rats, antimicrobial activity, and the dual inhibition of DNA topoisomerases of *Leishmania donovani* and potent in vitro methicillin-resistant *Staphylococcus aureus*.[2] In addition, compounds bearing indole and acridine moieties are key structural components in many bioactive compounds and display interesting biological activities.[3,4] There are, however, only a few approaches available for the synthesis of indolylquinolines,[2b,c,5] and synthetic routes leading to the production of indole–acridine hybrids are rare.[3,6] Hence, the synthesis of indolylquinolines as well as indolylacridine derivatives using simple, straightforward approaches would be highly desirable.[5a]

The Baylis–Hillman (B–H) reaction is an atom-economical and versatile carbon–carbon bond-forming reaction which provides densely functionalized adducts.[7] The use of B–H adducts for the construction of various nitrogen-containing heterocyclic molecules has been reported by several research groups.[8] To the best of our knowledge, only one report by our group has appeared dealing with the synthesis of indolylquinolines from B–H adducts.[5a] There are no reports in the literature concerning the synthesis of indolylacridines and indolylcyclopenta[*b*]quinoline derivatives from B–H adducts. However, the addition of indoles to acyclic B–H adducts as well as cyclic B–H adducts has been reported.[5a,9] As part of our ongoing project on the synthesis of nitrogen-containing heterocyclic molecules via reductive cyclization,[5a,10] we report herein on a convenient procedure for the synthesis of indolylquinolines, indolylacridines, and indolylcyclopenta[*b*]-quinoline derivatives.

RESULTS AND DISCUSSION

We recently reported on the C-alkylation of Baylis–Hillman derivatives with indoles using iodine as a catalyst and the use of the resulting C-alkylated indole derivatives in the synthesis of indolylquinoline derivatives.[5a] In a continuation of this work, we now report on the synthesis of a variety of indolylquinolines, indolylacridines, and indolylcyclopenta[*b*]quinoline derivatives in this paper. The outline for the synthesis of the indolylquinolines and indolylacridine derivatives is shown in Scheme 1.

To accomplish our objectives, we initially prepared a series of B–H adducts from various *o*-nitrobenzaldehydes and methyl vinyl ketone following reported procedures.[11] The resulting B–H adducts were then reacted with various indoles to give C-

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Scheme 1. Synthetic Route to the Synthesis of Indolylquinolines, Indolylacridines, and Indolylcyclopenta[*b*]quinoline Derivatives

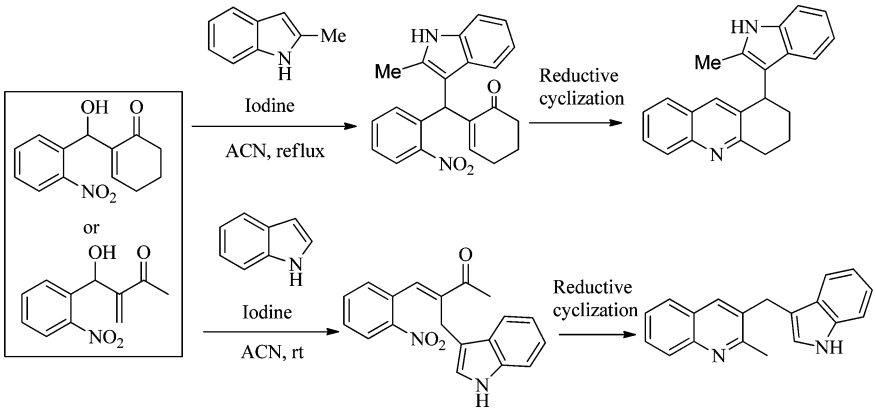
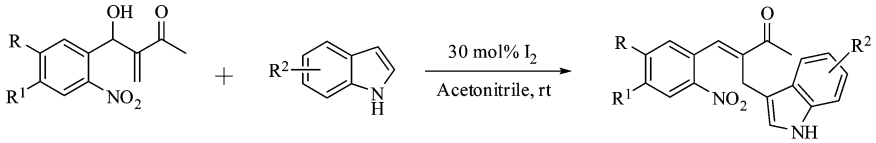
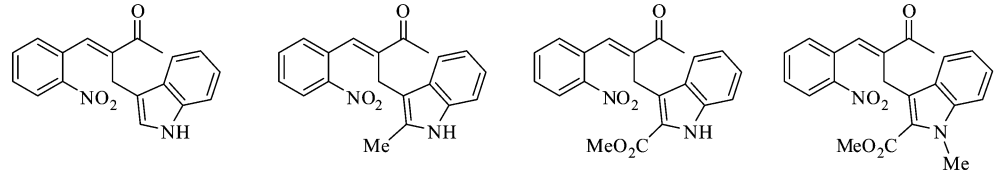


Table 1. Addition of Indoles to Acyclic Baylis–Hillman Adducts[a,b]

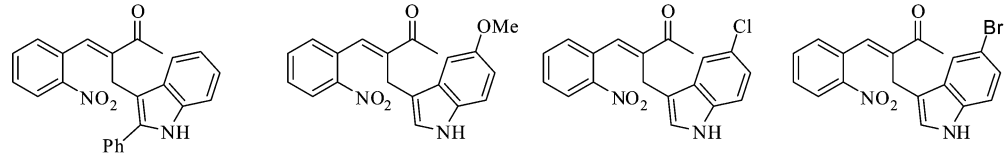


1a: R = R^1 =H
1b: R = Cl, R^1 = H
1c: R = Br, R^1 = H
1d: R = F, R^1 = H
1e: R = OMe, R^1 = H
1f: R = OMe, R^1 = OMe

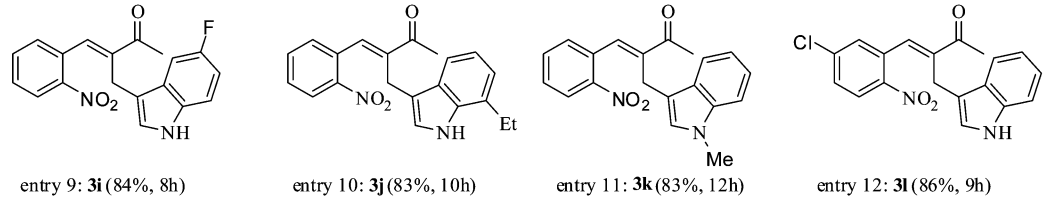
2a: R^2 = H; **2b**: R^2 = 2-Me; **2c**: R^2 = 2-CO$_2$Me;
2d: R^2 = 1-Me, 2-CO$_2$Me; **2e**: R^2 = 2-Ph;
2f: R^2 = 5-OMe; **2g**: R^2 = 5-Cl;
2h: R^2 = 5-Br;**2i**: R^2 = F; **2j**: R^2 = 7-Et;
2k: R^2 = 1-Me.



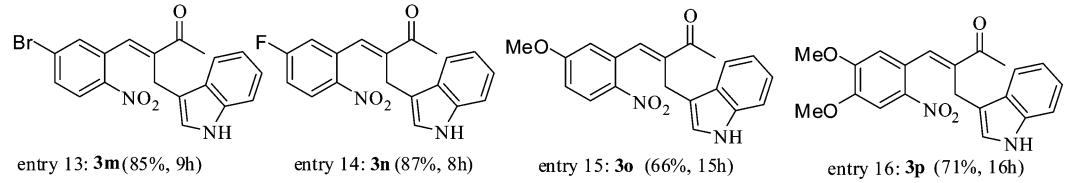
entry 1: **3a** (85%, 10h) entry 2: **3b** (85%, 4h) entry 3: **3c** (79%, 8h) entry 4: **3d** (81%, 9h)



entry 5: **3e** (84%, 4h) entry 6: **3f** (80%, 7h) entry 7: **3g** (83%, 10h) entry 8: **3h** (81%, 12h)



entry 9: **3i** (84%, 8h) entry 10: **3j** (83%, 10h) entry 11: **3k** (83%, 12h) entry 12: **3l** (86%, 9h)



entry 13: **3m** (85%, 9h) entry 14: **3n** (87%, 8h) entry 15: **3o** (66%, 15h) entry 16: **3p** (71%, 16h)

[a]All the reactions were performed on a 2.0 mmol scale. [b]Isolated yields.

alkylated indole derivatives in good yields under the previously established conditions (Table 1, entries 1–16).[5a]

To further explore the scope of the methodology, we investigated the C-alkylation of indoles with B–H alcohols derived from various substituted 2-nitrobenzaldehydes and cyclic enones (cyclohexenone and cyclopentenone). It has been reported that the reaction of cyclic B–H acetates derived from cyclic enones and indole in the presence of silver triflate resulted in the production of α-selective addition products.[9e] We therefore treated 2-methylindole with 2-(hydroxy(2-

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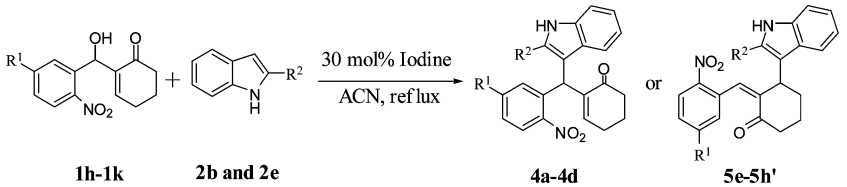
Table 2. Regioselective Addition of Indoles to Cyclic Baylis–Hillman Adducts



1h-1k 2b and 2e 4a-4d 5e-5h'

Entry	B-H alcohols	Indoles	Products	Time (h)	Yields (%)[a,b]
1	1h	2b	4a	2	87
2	1i	2b	4b	2.5	91
3	1j	2b	4c	2	88
4	1k	2b	4d	3	78[c]
5	1h	2e	5e/5e'	2.5	92(51:49)[d]
6	1i	2e	5f/5f'	3	91(60:40)[d]
7	1j	2e	5g/5g'	2.5	93(53:47)[d]
8	1k	2e	5h/5h'	3	89(55:45)[d]

[a]All the reactions were performed on a 2.0 mmol scale. [b]Isolated yields. [c]An 11% yield of γ-regioselective addition product **5d** was isolated. [d]A mixture of *E*/*Z* isomers was obtained, and the ratio of *E* to *Z* isomers was determined by ^{1}H NMR studies of the crude products.

nitrophenyl)methyl)cyclohex-2-enone under our previously established conditions, which were used in the case of acyclic B–H adducts.[5a] Unfortunately, the reaction failed to produce the α-regioselective product under the previously established conditions. However, when the reaction was carried out with 30 mol % iodine in acetonitrile under reflux, the corresponding product was produced in good yield. Hence, all reactions involving cyclic B–H adducts were conducted under reflux conditions. The results are summarized in Table 2. As shown in Table 2, under the reaction conditions used, the reaction of 2-methylindole with 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone, 2-((5-fluoro-2-nitrophenyl)hydroxymethyl)cyclohex-2-enone, and 2-((5-chloro-2-nitrophenyl)hydroxymethyl)-cyclohex-2-enone furnished the α-regioselective products **4a**, **4b**, and **4c** in good yields (Table 2, entries 1–3). However, the reaction of 2-((5-bromo-2-nitrophenyl)hydroxymethyl)-cyclohex-2-enone with 2-methylindole produced α-regioselective product **4d** along with traces of the γ-regioselective product **5d** (Table 2, entry 4). On the other hand, the reaction of 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone with 2-phe-

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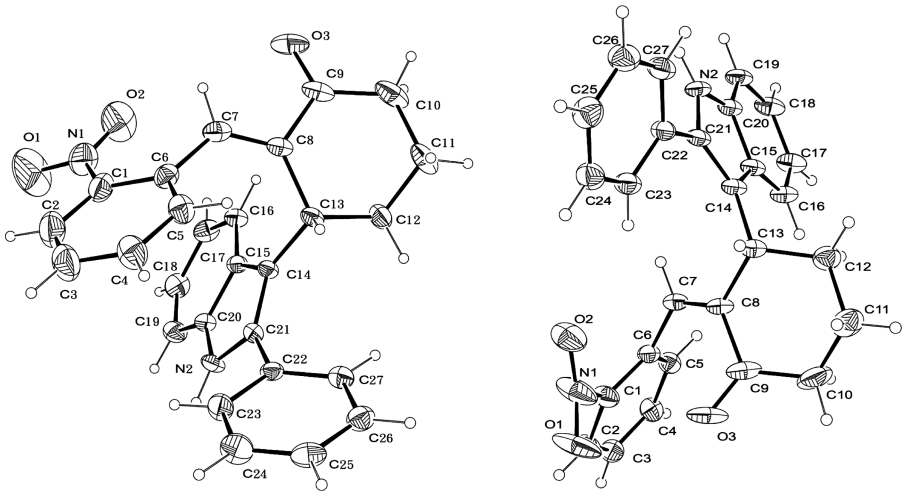
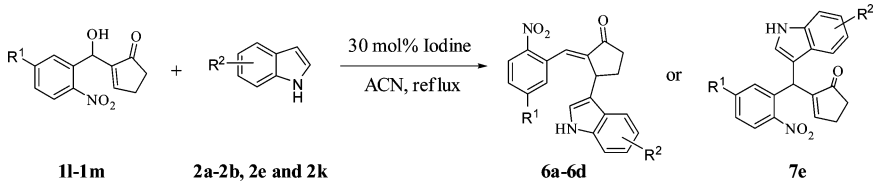
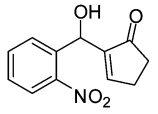
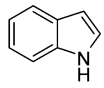
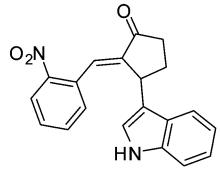
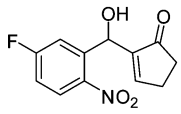
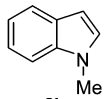
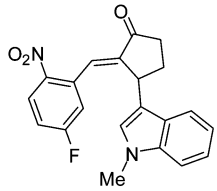
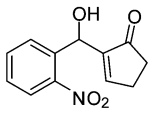
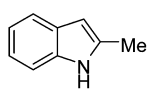
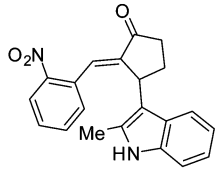
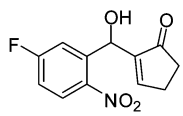
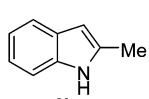
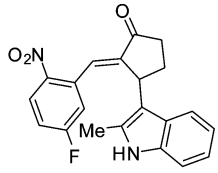
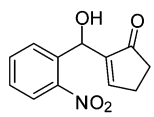
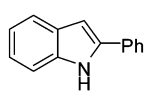
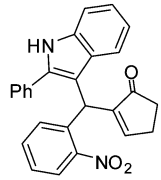


Figure 1. Crystal structures of the γ-regioselective *E* (**5e**) and *Z* (**5e′**) isomers.

Table 3. Regioselective Addition of Indoles to Cyclic Baylis–Hillman Adducts



1l-1m **2a-2b, 2e and 2k** **6a-6d** **7e**

Entry	B-H alcohols	Indoles	Product	Time (h)	Yield (%) [a,b]
1	 **1l**	 **2a**	 **6a**	2	81
2	 **1m**	 **2k**	 **6b**	8	79
3	 **1l**	 **2b**	 **6c**	2	87
4	 **1m**	 **2b**	 **6d**	2.5	91
5	 **1l**	 **2e**	 **7e**	3	88

[a]All the reactions were performed on a 2.0 mmol scale. [b]Isolated yields.

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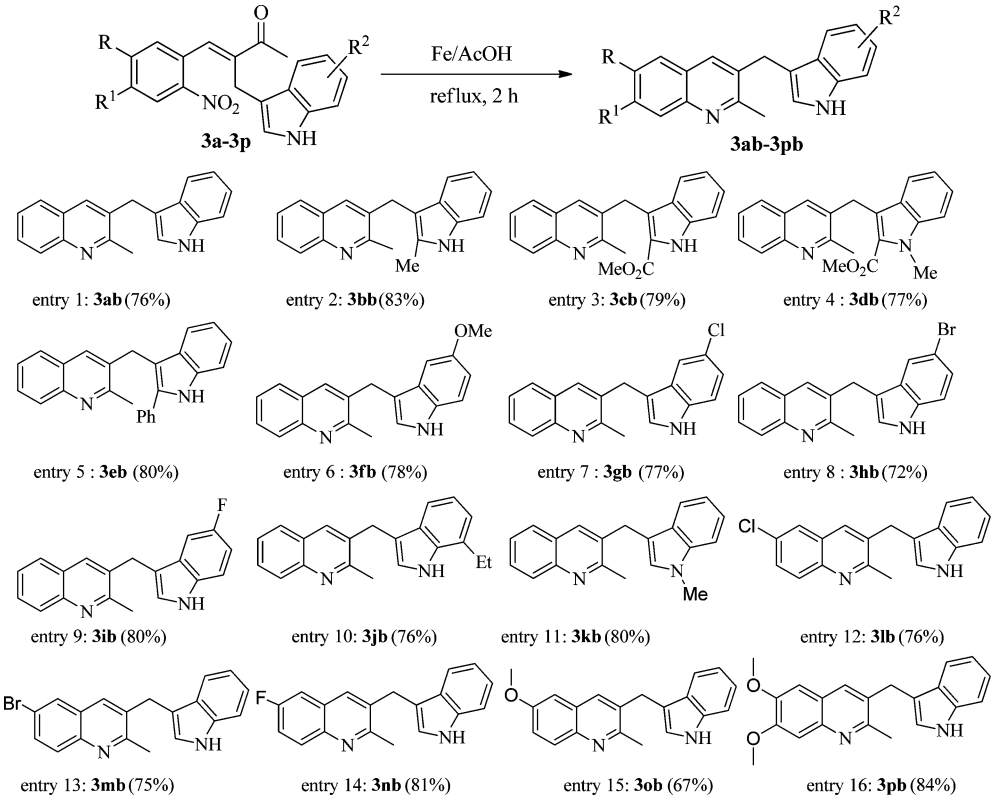
Table 4. Reductive Cyclization of C-Alkylated Indoles of Baylis–Hillman Adducts[a,b]



[a]All the reactions were performed on a 1.0 mmol scale. [b]Isolated yields.

nylindole under the same reaction conditions afforded the γ-regioselective product in a mixture of *E* and *Z* isomers **5e** and **5e′** (Table 2, entry 5), which were separated by column chromatography, the γ-regioselective *E* isomer **5e** as the major product and the γ-regioselective *Z* isomer **5e′** as a minor product, as evidenced by ^{1}H NMR, ^{13}C NMR, and HRMS analysis and single-crystal X-ray analysis (Figure 1). Even the reactions of 2-((5-fluoro-2-nitrophenyl)hydroxymethyl)cyclohex-2-enone, 2-((5-chloro-2-nitrophenyl)hydroxymethyl)cyclohex-2-enone, and 2-((5-bromo-2-nitrophenyl)hydroxymethyl)cyclohex-2-enone with 2-phenylindole resulted in the formation of γ-regioselective products in the form of a mixture of *E* and *Z* isomers (Table 2, entries 6–8), which were not separated due to the fact they eluted close to one another on the TLC plate. However, the reaction of 2-(hydroxy(2-nitrophenyl)methyl)-cyclohex-2-enone with indole and other indole derivatives did not proceed under the above reaction conditions.

Encouraged by these results, we further explored the reactions of cyclic B–H alcohols derived from various substituted 2-nitrobenzaldehyde and cyclopent-2-enone derivatives with substituted indoles in the presence of 30 mol % iodine in acetonitrile under reflux conditions. The results are summarized in Table 3. As shown in Table 3, the reaction of 2-(hydroxy(2-nitrophenyl)methyl)cyclopent-2-enone with indole and 2-methylindole afforded the γ-regioselective C-alkylated indole derivatives **6a** and **6c** in good yields (Table 3, entries 1 and 3). Interestingly, the reaction of *N*-methylindole and 2-methylindole with 2-((5-fluoro-2-nitrophenyl)hydroxymethyl)cyclopent-2-enone also produced the corresponding γ-regioselective C-alkylated indole derivatives **6b** and **6d** in 79% and 91% yields, respectively (Table 3, entries 2 and 4). Moreover, the reaction of 2-(hydroxy(2-nitrophenyl)methyl)cyclopent-2-enone with 2-phenylindole furnished the α-regioselective C-alkylated B–H adduct **7e** in good yield (Table 3, entry 5). It is noteworthy that the reaction of 2-methylindole with various 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone derivatives afforded the α-regioselective C-alkylated cyclic B–H adducts (Table 2, entries 1–4), whereas the reaction of 2-methylindole with various 2-(hydroxy(2-nitrophenyl)methyl)cyclopent-2-enone derivatives under similar reaction conditions furnished the γ-regioselective C-alkylated cyclic B–H adducts (Table 3, entries 3 and 4). However, the reaction of 2-phenylindole with various 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone derivatives afforded the γ-regioselective C-alkylated cyclic B–H adducts (Table 2, entries 5–8), and the reaction with 2-(hydroxy(2-nitrophenyl)methyl)cyclopent-2-enone under the same reaction conditions furnished the α-regioselective C-alkylated cyclic B–H adduct (Table 3, entry 5).

After synthesizing the various substituted C-alkylated indole derivatives from acyclic B–H and cyclic B–H alcohols containing a nitro group in the second position, we then subjected these C-alkylated indoles to reductive cyclization in the presence of powdered Fe in acetic acid, and the results are summarized in Table 4. As could be seen from Table 4, the substrates containing electron-withdrawing groups as well as electron-releasing groups reacted with equal ease to produce the corresponding indolylquinoline derivatives in good to excellent yields. It is interesting to note that, when 2-substituted indole derivatives were used, product yields were excellent. It is also noteworthy that chemoselective cyclization was achieved in the presence of an ester group.

We next, investigated the reductive cyclization of C-alkylated indole derivatives derived from cyclic B–H alcohols and indoles. We expected that a 9-(2-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahy-

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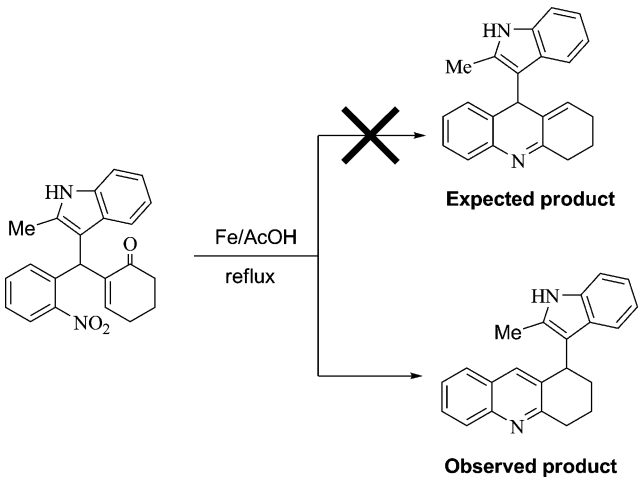
droacridine derivative would be produced from the reductive cyclization of the α-regioselective addition product **4a** derived from the reaction of 2-(hydroxy(2-nitrophenyl)methyl)-cyclohex-2-enone and 2-methylindole. Surprisingly, the expected 9-(2-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydroacridine derivative was not produced, and instead, 1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine was produced as the sole product (Scheme 2). Encouraged by this result, we further tested the

Scheme 2. Reaction of 2-((2-Methyl-1*H*-indol-3-yl)(2-nitrophenyl)methyl)cyclohex-2-enone with Fe/AcOH

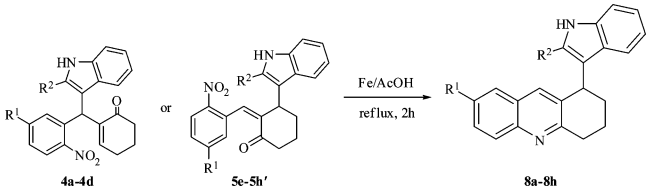


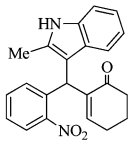
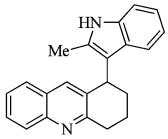
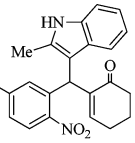
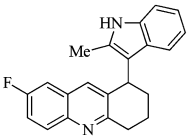
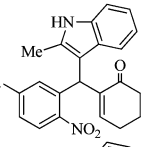
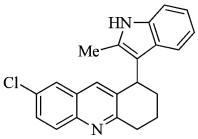
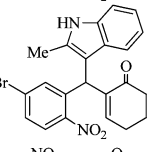
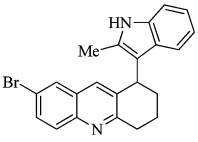
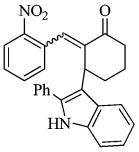
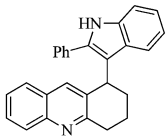
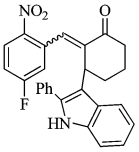
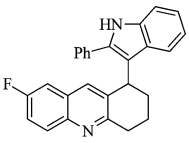
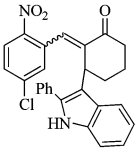
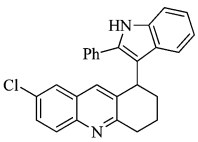
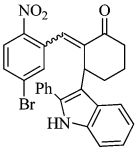
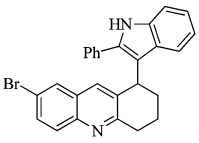
other α-regioselective addition products, derived from 2-methylindole and various 2-(hydroxy(2-nitrophenyl)methyl)-cyclohex-2-enone derivatives. In all cases, the corresponding1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine derivatives **8a**−**8d** were produced in good to excellent yields (Table 5, entries 1−4).

On the other hand, the reductive cyclization of γ-regioselective addition products (*E* and *Z* mixture) derived from various substituted 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone and 2-phenylindole derivatives resulted in the formation of the corresponding 1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine derivatives **8e**−**8h** in good yields (Table 5, entries 5−8). It is important to note that the reductive cyclization of α-regioselective addition products derived from various substituted 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone derivatives with 2-methylindole as well as γ-regioselective addition products (*E* and *Z* mixture) derived from various substituted 2-(hydroxy(2-nitrophenyl)methyl)cyclohex-2-enone derivatives with 2-phenylindole produced the same structural motif under the reaction conditions employed (Table 5, entries 1−8). The products were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS analyses. The crystal structures of representative compounds **4a** and **8a** are shown in Figure 2.

Consequently, we examined the reductive cyclization of γ-regioselective addition products derived from various 2-(hydroxy(2-nitrophenyl)methyl)cyclopent-2-enone and indole derivatives, including indole, *N*-methylindole, and 2-methylindole, in the presence of powdered Fe in acetic acid at 80 °C. Under these conditions the reactions afforded the corresponding 1-(1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline derivatives **8i**−**8l** in good yields (Table 6, entries 1−4). Even the reductive cyclization of the α-regioselective addition product derived from 2-(hydroxy(2-nitrophenyl)methyl)cyclopent-2-

Table 5. Synthesis of Indolylacridine Derivatives via Reductive Cyclization



Entry	Substrates		Products		Yield (%) [a, c]
1		**4a**		**8a**	80
2		**4b**		**8b**	83
3		**4c**		**8c**	81
4		**4d**		**8d**	82
5[b]		**5e/5e′**		**8e**	83
6[b]		**5f/5f′**		**8f**	85
7[b]		**5g/5g′**		**8g**	84
8[b]		**5h/5h′**		**8h**	83

[a]All the reactions were performed on a 1.0 mmol scale. [b]A mixture of the products was subjected to reductive cyclization. [c]Isolated yields.

enone with 2-phenylindole produced the similar structural motif **8m** in moderate yield (Table 6, entry 5).

The mechanistic pathways for the formation of indolylacridine derivatives from both the regioselective adducts are depicted in Scheme 3. As shown in Scheme 3, the formation of indolylacridine derivatives from γ-regioselective adducts **5d**−**5h**, **5e′**−**5h′**, and **6a**−**6d** involves straightforward reductive cyclization. However, formation of indolylacridine derivatives **8a**−**8d** and **8m** from the α-regioselective adducts **4a**−**4d** and **7e**

dx.doi.org/10.1021/jo301313m | *J. Org. Chem.* 2012, 77, 8451−8464

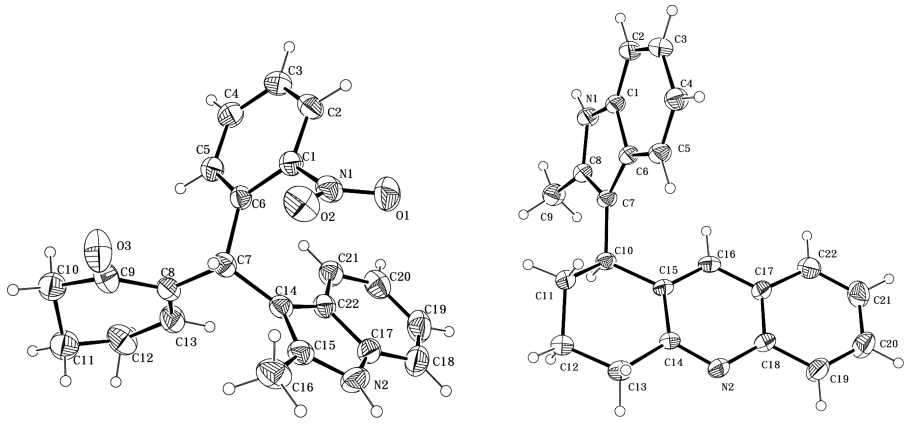
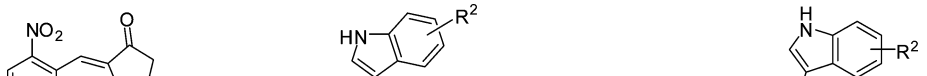
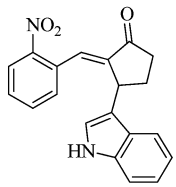
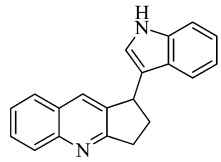
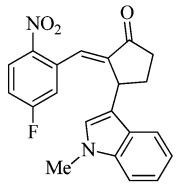
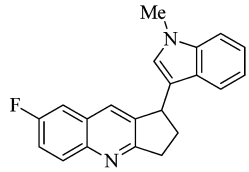
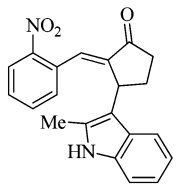
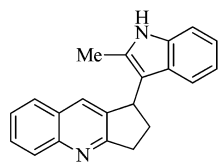
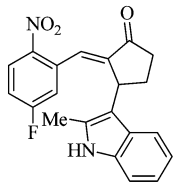
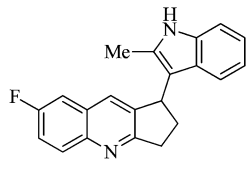
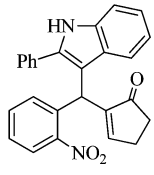
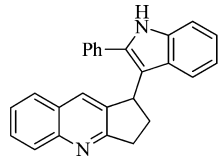


Figure 2. Crystal structures of **4a** and **8a**.

Table 6. Synthesis of Indolylcyclopenta[*b*]quinoline Derivatives via Reductive Cyclization



6a-6d **7e** **8i-8m**

Entry	Substrates		Products		Yield (%) [a, b]
1		**6a**		**8i**	69
2		**6b**		**8j**	66
3		**6c**		**8k**	75
4		**6d**		**8l**	77
5		**7e**		**8m**	53

[a]All the reactions were performed on a 1.0 mmol scale at 80 °C. [b]Isolated yields.

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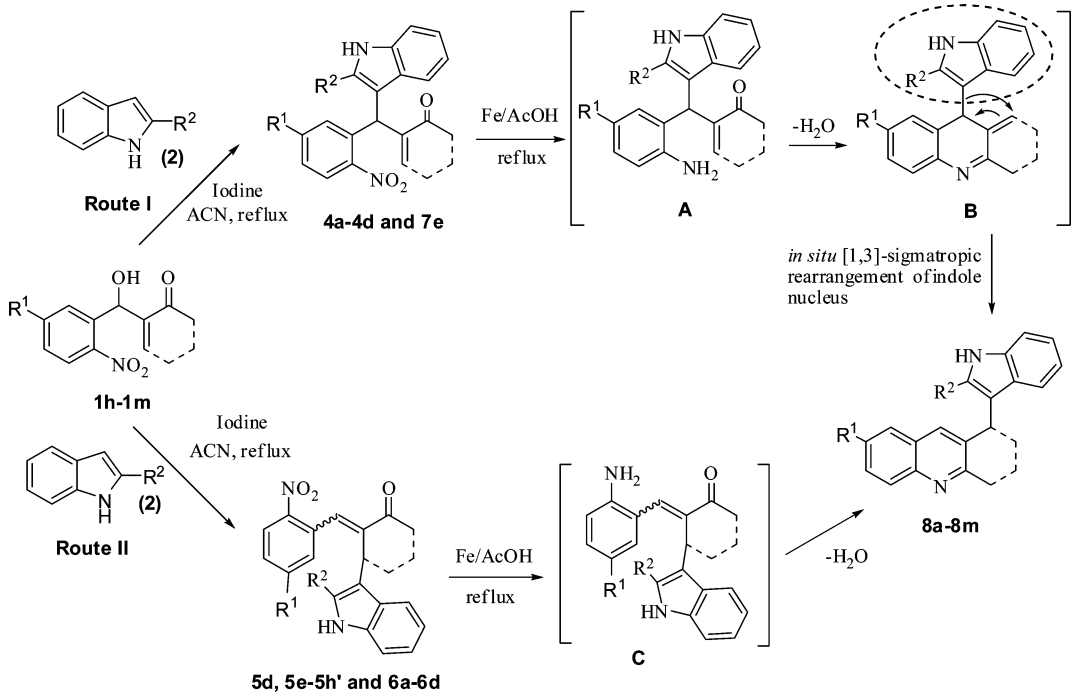
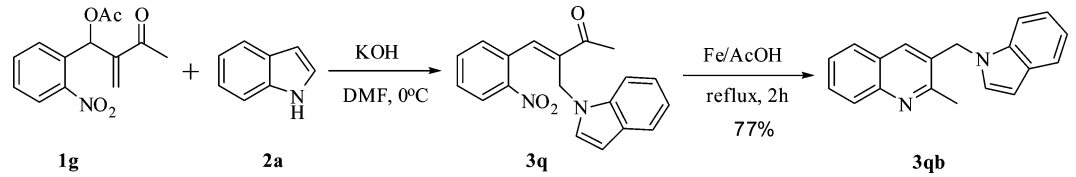
Scheme 3. Plausible Mechanism for the Formation of Indolylacridine Derivatives from the α-Regioselective and γ-Regioselective Adducts



Scheme 4. Short Route for the Synthesis of 3-((1*H*-Indol-1-yl)methyl)-2-methylquinoline (3qb)



may proceed through an unusual in situ [1,3]-sigmatropic rearrangement of the indole nucleus during the reaction. In fact, similar types of [1,3]-sigmatropic regarrangements are known in the literature. Recently, Liu et al. observed the [1,3]-sigmatropic rearrangement of an indole nucleus in the presence of a catalytic amount of iodine in trifluoroethanol under reflux conditions.[9f] In this protocol, they found that the indole moiety migrated from the γ-position to the α-position. In another protocol, Chen et. al observed an in situ [1,3]-sigmatropic rearrangement of the phenyl group during the formation of 4,10-dihydropyrimido[1,2-*a*]benzimidazoles from a base-catalyzed Povarov reaction of arylamines, aldehydes, and electron-deficient dienophiles.[12]

Baylis–Hillman acetates and the N-alkylation of an indole with B–H acetate were carried out using a previously reported procedure.[8e,9d] Subsequently, we were able to smoothly reductively cyclize the product **3q** to compound **3qb** in good yield in the presence of Fe/AcOH under reflux conditions (Scheme 4). Compound **3qb** was synthesized in a previous study, but multiple steps were involved.[13] Using our protocol, the preparation was much more efficient.

In conclusion, we report on the successful development of a simple and facile protocol for the synthesis of indolylquinolines, indolylacridines, and indolylcyclopenta[*b*]quinoline derivatives from Baylis–Hillman adducts. The protocol involves two steps. The first step involves the addition of indoles to acyclic and cyclic Baylis–Hillman adducts, and in the second step, the resulting products are subjected to reductive cyclization, with the production of indolylquinolines, indolylacridines, and indolylcyclopenta[*b*]quinoline derivatives. During the reductive cyclization of α-regioselective cyclic B–H adducts containing indoles, we observed an unusual in situ [1,3]-sigmatropic rearrangement of the indole nucleus with the production of more stable indolylacridines and indolylcyclopenta[*b*]quinoline derivatives.

■ EXPERIMENTAL SECTION

Reagents and solvents were purchased from various commercial sources and used directly without any further purification unless otherwise stated. Column chromatography was performed on 63–200 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were made in reference to NMR solvent signals ($CDCl_3$ or DMSO-d_6), and coupling constants are expressed in hertz. Mass spectra were recorded using the EI^+ mode, and data are reported as the mass/charge (m/z) ratio with the percent relative abundance. High-resolution mass spectrometry (HRMS) was performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer. Melting points were recorded using a capillary melting point apparatus and are uncorrected.

General Procedure for the Synthesis of 3a–3p. To a stirred solution of the Baylis–Hillman alcohol (2.0 mmol, 1.0 equiv) in acetonitrile (10.0 mL) were added indole (2.8 mmol, 1.4 equiv) and iodine (0.3 equiv), and the mixture was stirred until the reaction was complete, as monitored by TLC. The reaction mixture was quenched with a saturated solution of sodium thiosulfate and extracted with ethyl acetate (2.0 × 10.0 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated to give the crude

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product. All of the crude products were purified by passing them through a short silica gel column (ethyl acetate/hexane).

*Data for 3-((1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (**3a**):* yield 544 mg (85%); yellow solid; mp 135−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.1, 1.0 Hz, 1H), 7.99 (br s, 1H), 7.94 (s, 1H), 7.53−7.47 (m, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.34−7.28 (m, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 6.75 (s, 1H), 3.79 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 147.6, 141.3, 136.7, 136.4, 133.8, 131.9, 131.0, 129.4, 127.0, 125.1, 122.0, 119.5, 118.7, 114.8, 113.9, 111.2, 26.7, 22.6; MS (EI) m/z (relative intensity) 320 (M^+, 18), 276 (31), 261 (50), 260 (100), 230 (33), 202 (16); HRMS (EI) m/z calcd for $C_{19}H_{16}N_2O_3$ (M^+) 320.1155, found 320.1153.

*Data for 3-((2-methyl-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)-but-3-en-2-one (**3b**):* yield 568 mg (85%); yellow solid; mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.1, 0.9 Hz, 1H), 7.83 (s, 1H), 7.60 (br s, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.37−7.32 (m, 2H), 7.12−7.10 (m, 2H), 7.10−7.01 (m, 1H), 6.93−6.91 (m, 1H) 3.77 (s, 2H), 2.45 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 147.0, 142.0, 136.1, 135.1, 133.3, 131.9, 131.8, 131.0, 128.9, 128.3, 124.8, 120.8, 119.1, 118.0, 110.1, 108.1, 26.6, 21.8, 11.7; MS (EI) 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 (EI) m/z calcd for $C_{20}H_{18}N_2O_3$ (M^+) 334.1312, found 334.1317.

*Data for methyl 3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate (**3c**):* yield 597 mg (79%); colorless solid; mp 149−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (br s, 1H), 7.87 (s, 1H), 7.81 (dd, J = 8.2, 1.0 Hz, 1H), 7.35−7.31 (m, 2H), 7.21−7.18 (m, 4H), 7.15−6.97 (m, 1H), 4.21 (s, 2H), 3.82 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 162.0, 146.3, 141.5, 137.7, 135.7, 133.0, 131.9, 130.5, 128.6, 127.4, 125.7, 124.3, 123.2, 121.3, 121.2, 120.2, 111.6, 51.7, 26.3, 22.3; MS (EI) 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 (EI) m/z calcd for $C_{21}H_{18}N_2O_5$ (M^+) 378.1210, found 378.1210.

*Data for (E)-methyl 1-methyl-3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate (**3d**):* yield 635 mg (81%); pale brown solid; mp 99−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.30−7.28 (m, 1H), 7.25−7.23 (m, 1H), 7.22−7.14 (m, 2H), 7.12−7.08 (m, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.95 (t, 7.4 Hz, 1H), 4.15 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 162.5, 142.1, 138.3, 137.4, 132.7, 131.9, 130.2, 128.0, 126.2, 125.2, 124.8, 123.9, 121.7, 120.9, 119.9, 114.7, 109.8, 51.4, 31.9, 26.3, 22.9; MS (EI) m/z (relative intensity) 392 (M^+, 32), 333 (100), 332 (83), 273 (30), 202 (98), 189 (39); HRMS (EI) m/z calcd for $C_{22}H_{20}N_2O_5$ (M^+) 392.1367, found 392.1384.

*Data for 4-(2-nitrophenyl)-3-((2-phenyl-1H-indol-3-yl)methyl)-but-3-en-2-one (**3e**):* yield 665 mg (84%); red solid; mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.85 (m, 2H), 7.76 (s, 1H), 7.41−7.38 (m, 4H), 7.36−7.28 (m, 3H), 7.25−7.19 (m, 2H), 7.14−7.07 (m, 2H), 6.98 (t, J = 7.5 Hz, 1H), 4.05 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 146.5, 142.0, 136.7, 135.8, 134.8, 133.0, 132.9, 131.7, 130.5, 128.8, 128.7, 128.3, 127.8, 124.6, 122.3, 119.7, 119.5, 110.7, 110.7, 109.8, 26.4, 22.4; MS (EI) 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 (EI) m/z calcd for $C_{25}H_{20}N_2O_3$ (M^+) 396.1468, found 396.1461.

*Data for 3-((5-methoxy-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)-but-3-en-2-one (**3f**):* yield 560 mg (80%); 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 200.0, 154.1, 147.6, 141.4, 136.6, 133.8, 131.9, 131.5, 131.1, 129.4, 127.4, 125.1, 122.8, 113.6, 112.6, 112.0, 100.6, 56.0, 26.7, 22.7; MS (EI) 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 (EI) m/z calcd for $C_{20}H_{18}N_2O_4$ (M^+) 350.1261, found 350.1254.

*Data for (E)-3-((5-chloro-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)-but-3-en-2-one (**3g**):* yield 587 mg (83%); yellow solid; mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 7.99 (br s, 1H), 7.93 (s, 1H), 7.61−7.57 (m, 1H), 7.54−7.50 (m, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 7.11−7.06 (m, 2H), 6.81 (s, 1H), 3.70 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 147.4, 141.1, 137.4, 134.5, 133.9, 131.7, 130.9, 129.6, 128.0, 125.2, 125.1, 123.6, 122.4, 118.1, 113.4, 112.2, 26.5, 22.1; MS (EI) m/z (relative intensity) 354 (M^+, 20), 311 (23), 295 (100), 294 (16); HRMS (EI) m/z calcd for $C_{19}H_{15}ClN_2O_3$ (M^+) 354.0771, found 354.0775.

*Data for 3-((5-bromo-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)-but-3-en-2-one (**3h**):* yield 644 mg (81%); 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 199.7, 147.5, 141.2, 137.3, 134.8, 133.9, 131.8, 130.9, 129.6, 128.7, 125.2, 125.0, 123.5, 121.3, 113.5, 112.7, 112.7, 26.5, 22.0; MS (EI) m/z (relative intensity) 400 (M^+ + 2, 9), 398 (M^+, 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 (EI) m/z calcd for $C_{19}H_{15}{}^{79}BrN_2O_3$ (M^+) 398.0261, found 398.0258; HRMS (EI) m/z calcd for $C_{19}H_{15}{}^{81}BrN_2O_3$ (M^+) 400.0240, found 400.0242.

*Data for (E)-3-((5-fluoro-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)-but-3-en-2-one (**3i**):* yield 568 mg (84%); red solid; mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.94 (s, 1H), 7.57−7.46 (m, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.17−7.14 (m, 1H), 6.89−6.83 (m, 2H), 6.76 (s, 1H), 3.70 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 157.7 (d, J = 233.0 Hz), 147.4, 141.1, 137.2, 133.8, 132.7, 131.7, 130.9, 129.5, 127.2 (d, J = 10.0 Hz), 125.1, 124.0, 113.8 (d, J = 5.0 Hz), 111.9 (d, J = 10.0 Hz), 110.4 (d, J = 26.0 Hz), 103.5 (d, J = 23.0 Hz), 26.5, 22.3; MS (EI) m/z (relative intensity) 338 (M^+, 53), 294 (21), 279 (100); HRMS (EI) m/z calcd for $C_{19}H_{15}FN_2O_3$ (M^+) 338.1067, found 338.1075.

*Data for 3-((7-ethyl-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (**3j**):* yield 577 mg (83%); 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), 7.01−7.00 (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 200.1, 147.5, 141.2, 136.5, 135.2, 133.8, 131.8, 131.0, 129.3, 126.7, 126.6, 125.0, 121.7, 120.7, 119.7, 116.4, 114.1, 26.7, 24.0, 22.8, 13.9; MS (EI) 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 (EI) m/z calcd for $C_{21}H_{20}N_2O_3$ (M^+) 348.1468, found 348.1480.

*Data for (E)-3-((1-methyl-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (**3k**):* yield 554 mg (83%); red solid; mp 240−242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.0, 0.9 Hz,1H), 7.95 (s, 1H), 7.56−7.50 (m, 2H), 7.43 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 4.8 Hz, 1H), 7.23−7.19 (m, 1H), 7.07−7.04 (m, 1H), 6.66 (s, 1H), 3.80 (s, 2H), 3.71 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 147.7, 141.6, 137.1, 136.4, 133.7, 131.9, 131.1, 129.3, 127.4, 126.9, 125.0, 121.8, 118.9, 118.8, 112.2, 109.3, 32.8, 26.7, 22.6; MS (EI) m/z (relative intensity) 335 (M^+, 30), 334 (90), 291 (58), 275 (100), 274 (39), 247 (17), 131 (19); HRMS (EI) m/z calcd for$C_{20}H_{18}N_2O_3$ (M^+) 334.1317, found 334.1325.

*Data for (E)-3-((1H-indol-3-yl)methyl)-4-(5-chloro-2-nitrophenyl)-but-3-en-2-one (**3l**):* yield 609 mg (86%); yellow solid; mp 165−167 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (br s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.92 (s, 1H), 7.67 (dd, J = 8.8, 1.7 Hz, 1H), 7.55 (s, 1H), 7.28−7.24 (m, 2H), 7.04−7.01 (m, 1H), 6.91−6.87 (m, 1H), 6.78 (s, 1H), 3.66 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 145.6, 142.0, 140.2, 136.2, 135.4, 133.7, 130.8, 129.3, 126.8, 126.4, 122.3, 122.1, 119.6, 118.6, 113.4, 111.2, 26.6, 22.5; MS (EI) m/z (relative intensity) 354 (M^+, 29), 311 (36), 295 (100), 294 (52), 116 (13); HRMS (EI) m/z calcd for$C_{19}H_{15}ClN_2O_3$ (M^+) 354.0771, found 354.0769.

*Data for (E)-3-((1H-indol-3-yl)methyl)-4-(5-bromo-2-nitrophenyl)but-3-en-2-one (**3m**):* yield 676 mg (85%); yellow solid; mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.7 Hz,

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1H), 7.90 (br s, 1H), 7.82 (s, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.48−7.46 (m, 1H), 7.30−7.27 (m, 2H), 7.16−7.12 (m, 1H), 7.06−7.02 (m, 1H), 6.74 (s, 1H), 3.78 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 145.3, 136.7, 134.3, 134.2, 132.2, 130.2, 129.3, 128.7, 127.4, 122.9, 122.6, 119.9, 119.5, 119.0, 113.4, 111.5, 29.2, 23.5; MS (EI) m/z (relative intensity) 398 (M^+, 36), 355 (30), 339 (100), 117 (25); HRMS (EI) m/z calcd for $C_{19}H_{15}{}^{79}BrN_2O_3$ (M^+) 398.0266, found 398.0273; HRMS (EI) m/z calcd for $C_{19}H_{15}{}^{81}BrN_2O_3$ (M^+) 400.0246, found 400.0263.

*Data for (E)-3-((1H-indol-3-yl)methyl)-4-(5-fluoro-2-nitrophenyl)-but-3-en-2-one (**3n**):* yield 588 mg (87%); yellow solid; mp 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.13 (m, 1H), 7.92 (br s, 1H), 7.86 (s, 1H), 7.33−7.26 (m, 2H), 7.17−7.04 (m, 4H), 6.76−6.75 (m, 1H), 3.79 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 164.8 (d, J = 258.0 Hz), 143.6, 141.7, 136.3, 135.6, 135.1 (d, J = 10.0 Hz), 128.0 (d, J = 10.0 Hz), 126.8, 122.4, 122.0, 119.6, 118.6, 117.9 (d, J = 24.0 Hz), 116.3 (d, J = 23.0 Hz), 113.4, 111.2, 26.6, 22.6; MS (EI) m/z (relative intensity) 338 (M^+, 53), 295 (38), 279 (100), 117 (10); HRMS (EI) m/z calcd for $C_{19}H_{15}FN_2O_3$ (M^+) 338.1067, found 338.1063.

*Data for (E)-3-((1H-indol-3-yl)methyl)-4-(5-methoxy-2-nitrophenyl)but-3-en-2-one (**3o**):* yield 462 mg (66%); yellow solid; mp 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.06 (br s, 1H), 7.93 (s, 1H), 7.32−7.27 (m, 3H), 7.20−7.16 (m, 1H), 7.09−7.05 (m, 1H), 6.86 (s, 1H), 6.77 (s, 1H), 3.77 (s, 2H), 3.21 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 155.9, 142.4, 138.9, 138.3, 137.7, 136.2, 135.6, 126.4, 123.6, 122.9, 122.0, 120.1, 118.4, 115.3, 114.2, 111.4, 56.7, 26.6, 23.2; LRMS (FAB) m/z (relative intensity) 350 (M^+, 12), 245 (100), 154 (100), 136 (57), 107 (28); HRMS (FAB) m/z calcd for $C_{20}H_{18}N_2O_4$ (M^+) 350.1267, found 350.1261.

*Data for (E)-3-((1H-indol-3-yl)methyl)-4-(4,5-dimethoxy-2-nitrophenyl)but-3-en-2-one (**3p**):* yield 539 mg (71%); yellow solid; mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 8.01 (s, 1H), 7.72 (s, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.17−7.14 (m, 1H), 7.07−7.04 (m, 1H), 6.79 (d, J = 1.0 Hz, 1H), 6.71 (s, 1H), 3.94 (s, 3H), 3.78 (s, 2H), 3.14 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 153.2, 148.9, 140.3, 140.1, 138.2, 136.3, 126.8, 126.4, 122.5, 121.9, 119.7, 118.7, 114.8, 112.0, 111.2, 107.9, 56.5, 55.7, 26.6, 23.1; LRMS (FAB) m/z (relative intensity) 381 (M^+ + 1, 100), 337 (52), 321 (72); HRMS (FAB) m/z calcd for $C_{21}H_{20}N_2O_5$ (M + H)$^+$ 381.1450, found 381.1451.

*Data for (E)-3-((1H-indol-1-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (**3q**):* yield 505 mg (79%); brown gummy liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12−8.10 (m, 1H), 8.07 (s, 1H), 7.48−7.43 (m, 3H), 7.09−7.00 (m, 3H), 6.89 (d, J = 7.8 Hz, 1H), 6.83−6.82 (m, 1H), 6.32−6.31 (m, 1H), 4.97 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 146.7, 140.7, 137.6, 136.0, 133.8, 130.5, 130.4, 129.8, 128.5, 127.4, 125.2, 121.6, 120.9, 119.6, 109.3, 102.2, 41.3, 26.4; MS (EI) m/z (relative intensity) 320 (M^+, 100) 117 (26); HRMS (EI) m/z calcd for $C_{19}H_{16}N_2O_3$ (M^+) 320.1155, found 320.1157.

General Procedure for the Synthesis of 3ab−3qb. To a stirred solution of C-alkylated acyclic Baylis−Hillman adducts containing indole moieties (1.0 mmol) in acetic acid (5.0 mL) was added powdered Fe (6.0 mmol, 6.0 equiv), and the reaction mixture was then refluxed for 2 h. The mixture was cooled to room temperature, the acetic acid was removed under reduced pressure, and EtOAc (10.0 mL) was added. The resulting mixture was stirred for 2 min and the solution filtered to remove any iron impurities. The insoluble iron residue was washed with EtOAc (10.0 mL). The filtrate and washings were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and all of the crude products were purified by passing them through a short silica gel column (ethyl acetate/hexane).

*Data for 3-((1H-indol-3-yl)methyl)-2-methylquinoline (**3ab**):* yield 206 mg (76%); colorless solid; mp 180−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.83 (s, 1H), 7.66−7.60 (m, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.44−7.38 (m, 2H), 7.24−7.21 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.80 (s, 1H), 4.25 (s, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 146.7, 136.7, 135.4, 133.1, 128.8, 128.3, 127.6, 127.5, 127.3, 125.8, 122.9, 122.4, 119.7, 119.0, 113.8, 111.5, 29.2, 23.5; MS (EI) m/z (relative intensity) 271 (M^+, 100), 257 (22), 232 (8), 154 (9), 153 (14), 129 (26), 114 (8); HRMS (EI) m/z calcd for $C_{19}H_{16}N_2$ (M^+) 272.1308, found 272.1302.

*Data for 2-methyl-3-((2-methyl-1H-indol-3-yl)methyl)quinoline (**3bb**):* yield 237 mg (83%); colorless solid; mp 210−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1H), 7.97 (br s, 1H), 7.61−7.54 (m, 3H), 7.39−7.34 (m, 2H), 7.28 (d, J = 7.9 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 7.01 (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, 145.7, 135.4, 133.5, 132.9, 128.3, 127.7, 127.1, 126.8, 125.5, 120.0, 118.2, 117.5, 110.5, 106.3, 27.1, 23.2, 11.4; MS (EI) m/z (relative intensity) 285 (M^+, 100), 270 (48), 267 (9), 154 (9), 153 (11), 143 (52), 129 (14), 115 (6); HRMS (EI) m/z calcd for $C_{20}H_{18}N_2$ (M^+) 286.1465, found 286.1465.

*Data for methyl 3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate (**3cb**):* yield 260 mg (79%); yellow solid; mp 224−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (br s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.51−7.42 (m, 4H), 7.37−7.33 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 4.63 (s, 2H), 3.86 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 158.6, 146.4, 136.3, 134.2, 133.0, 128.7, 128.3, 128.2, 127.5, 127.3, 126.1, 125.7, 124.3, 121.2, 120.8, 120.5, 112.2, 52.1, 28.0, 23.8; MS(EI) m/z (relative intensity) 330 (M^+, 100), 298 (24), 271 (85), 256 (25), 227 (8), 156 (8), 149 (16), 134 (20), 101 (18); HRMS (EI) m/z calcd for $C_{21}H_{18}N_2O_2$ (M^+) 330.1363, found 330.1361.

*Data for methyl 1-methyl-3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate (**3db**):* yield 264 mg (77%); white solid; mp 191−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.59−7.55 (m, 1H), 7.49−7.45 (m, 3H), 7.42−7.32 (m, 3H), 7.10 (t, J = 7.0 Hz, 1H), 4.57 (s, 2H), 4.12 (s, 3H), 3.77 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 158.4, 146.4, 139.1, 133.7, 133.4, 128.6, 128.3, 127.5, 127.3, 127.0, 125.9, 125.7, 125.6, 120.9, 120.7, 120.6, 110.5, 51.7, 32.5, 28.5, 23.9; MS (EI) m/z (relative intensity) 344 (M^+, 100), 285 (30); HRMS (EI) m/z calcd for $C_{22}H_{20}N_2O_2$ (M^+) 344.1519, found 344.1528.

*Data for 2-methyl-3-((2-phenyl-1H-indol-3-yl)methyl)quinoline (**3eb**):* yield 278 mg (80%); 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 158.8, 146.5, 136.4, 136.2, 134.4, 133.3, 132.8, 129.5, 129.2, 128.8, 128.3, 128.1, 127.7, 127.6, 127.5, 125.7, 122.8, 120.2, 119.5, 111.2, 109.1, 28.2, 23.7; MS (EI) m/z (relative intensity) 348 (M^+, 62), 347 (100), 333 (7), 270 (6), 206 (79), 192 (35), 173 (17), 151 (11); HRMS (EI) m/z calcd for $C_{25}H_{20}N_2$ (M^+) 348.1621, found 348.1625.

*Data for 3-((5-methoxy-1H-indol-3-yl)methyl)-2-methylquinoline (**3fb**):* yield 235 mg (78%); brown solid; mp 185−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (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), 6.96−6.95 (m, 1H), 6.89 (dd, J = 8.7, 2.3 Hz, 1H), 6.79−6.78 (m, 1H), 4.20 (s, 2H), 3.80 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 154.3, 146.7, 135.4, 133.0, 131.9, 128.8, 128.3, 127.9, 127.6, 127.3, 125.8, 123.7, 113.5, 112.6, 112.2, 100.9, 56.1, 29.2, 23.5; MS (EI) m/z (relative intensity) 301 (M^+ −1, 100), 300 (45), 286 (24), 257 (7), 159 (19), 127 (6); HRMS (EI) m/z calcd for $C_{20}H_{18}N_2O$ (M^+) 302.1414, found 302.1419.

*Data for 3-((5-chloro-1H-indol-3-yl)methyl)-2-methylquinoline (**3gb**):* yield 235 mg (77%); yellow solid; mp 217−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (br s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.67−7.62 (m, 2H), 7.51 (d, J = 1.8 Hz, 1H), 7.46−7.42 (m, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.18 (dd, J = 8.6, 1.9 Hz, 1H), 6.82 (d, J = 1.9 Hz, 1H), 4.20 (s, 2H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.6, 145.8, 134.8, 134.1, 133.3, 128.4, 128.1, 127.8, 127.1, 126.8, 125.7, 125.6, 123.1, 121.0, 117.6, 113.0, 111.5, 28.0, 23.0; MS (EI) m/z (relative intensity) 308 (M^+, 56), 306 (100); HRMS (EI) m/z calcd for$C_{19}H_{15}ClN_2$ (M^+) 306.0924, found 306.0917.

*Data for 3-((5-bromo-1H-indol-3-yl)methyl)-2-methylquinoline (**3hb**):* yield 252 mg (72%); 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), 6.80−6.79 (m, 1H), 4.19 (s, 2H), 2.73 (s, 3H); ^{13}C NMR (100 MHz,

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$CDCl_3$) δ 158.9, 146.7, 135.5, 135.3, 132.6, 129.3, 129.0, 128.2, 127.5, 127.3, 126.0, 125.3, 124.2, 121.6, 113.5, 113.0, 113.0, 29.0, 23.4; MS (EI) 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 (EI) m/z calcd for $C_{19}H_{15}{}^{79}BrN_2$ (M^+) 350.0413, found 350.0408; HRMS (EI) m/z calcd for $C_{19}H_{15}{}^{81}BrN_2$ (M^+) 352.0393, found 352.0392.

*Data for 3-((5-fluoro-1H-indol-3-yl)methyl)-2-methylquinoline (**3ib**):* yield 232 mg (80%); red solid; mp 209−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (br s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.67−7.61 (m, 2H), 7.46−7.42 (m, 1H), 7.32−7.29 (m, 1H), 7.17 (d, J = 6.9 Hz, 1H), 6.99−6.95 (m, 1H), 6.86 (s, 1H), 4.19 (s, 2H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.6, 156.6 (d, J = 230.0 Hz), 145.8, 134.2, 133.1 (d, J = 22.0 Hz), 128.4, 127.8, 127.2, 127.1, 126.9, 125.8, 125.5, 112.4 (d, J = 10.0 Hz), 111.9, 111.8, 109.1 (d, J = 26.0 Hz), 103.3 (d, J = 23.0 Hz), 28.2, 23.0; MS (EI) m/z (relative intensity) 290 (M^+, 100), 275 (5), 148 (5); HRMS (EI) m/z calcd for $C_{19}H_{15}FN_2$ (M^+) 290.1219 found 290.1220.

*Data for 3-((7-ethyl-1H-indol-3-yl)methyl)-2-methylquinoline (**3jb**):* yield 228 mg (76%); colorless solid; mp 179−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 8.01 (s, 1H), 7.84 (br s, 1H), 7.67−7.60 (m, 2H), 7.45−7.39 (m, 2H), 7.08−7.07 (m, 2H), 6.81−6.80 (m, 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 159.1, 146.7, 135.5, 135.4, 133.1, 128.8, 128.3, 127.5, 127.3, 127.2, 126.9, 125.8, 122.5, 120.9, 120.0, 116.7, 114.2, 29.3, 24.1, 23.4, 13.9; MS (EI) m/z (relative intensity) 301 (M^+ + 1, 3), 299 (100), 269 (20), 267 (9), 157 (31), 142 (15), 134 (7); HRMS (EI) m/z calcd for $C_{21}H_{20}N_2$ (M^+) 300.1621, found 300.1628.

*Data for 2-methyl-3-((1-methyl-1H-indol-3-yl)methyl)quinoline (**3kb**):* yield 228 mg (80%); yellow solid; mp 142−144 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.65−7.61 (m, 1H), 7.51−7.44 (m, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.16−7.12 (m, 1H), 7.01−6.97 (m, 2H), 4.21 (s, 2H), 3.72 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 146.6, 137.4, 135.4, 133.2, 128.8, 128.3, 127.8, 127.6, 127.5, 127.2, 125.8, 122.0, 119.2, 119.1, 112.3, 109.4, 32.8, 29.0, 23.4; MS (EI) m/z (relative intensity) 286 (M^+, 100), 271 (8), 144 (9); HRMS (EI) m/z calcd for $C_{20}H_{18}N_2$ (M^+) 286.1470, found 286.1464.

*Data for 3-((1H-indol-3-yl)methyl)-6-chloro-2-methylquinoline (**3lb**):* yield 232 mg (76%); yellow solid; mp 200−202 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.94 (br s, 1H), 7.97−7.89 (m, 3H), 7.62 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.07−7.05 (m, 2H), 6.95−6.92 (m,1H), 4.22 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 145.6, 136.7, 134.3, 134.2, 131.4, 130.0, 129.6, 128.2, 127.4, 126.0, 122.9, 122.5, 119.8, 119.0, 113.4, 111.5, 29.1, 23.5; MS (EI) m/z (relative intensity) 308 (M^+, 55), 306 (100), 130 (9); HRMS (EI) m/z calcd for$C_{19}H_{15}ClN_2$ (M^+) 306.0924, found 306.0921.

*Data for 3-((1H-indol-3-yl)methyl)-6-bromo-2-methylquinoline (**3mb**):* yield 262 mg (75%); yellow solid; mp 200−202 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (br s, 1H), 8.08 (s, 1H), 7.97 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.07−7.05 (m, 2H), 6.95−6.92 (m, 1H), 4.21 (s, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 145.3, 136.7, 134.3, 134.2, 132.2, 130.2, 129.3, 128.7, 127.4, 122.9, 122.6, 119.9, 119.5, 119.0, 113.5, 111.5, 29.2, 23.5; MS (EI) m/z (relative intensity) 350 (M^+, 100), 349 (29), 130 (10); HRMS m/z calcd for $C_{19}H_{15}{}^{79}BrN_2$ (M^+) 350.0419, found 350.0421; HRMS (EI) m/z calcd for $C_{19}H_{15}{}^{81}BrN_2$ (M^+) 352.0398, found 352.0409.

*Data for 3-((1H-indol-3-yl)methyl)-6-fluoro-2-methylquinoline (**3nb**):* yield 234 mg (81%); yellow solid; mp 189−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (br s, 1H,), 8.01 (dd, J = 9.0, 5.3 Hz, 1H), 7.76 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.41−7.35 (m, 2H), 7.25−7.22 (m, 2H), 7.14−7.10 (m, 1H), 6.83 (s, 1H), 4.23 (s, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (d, J = 245.0 Hz), 158.4, 143.7, 136.7, 134.7 (d, J = 5.0 Hz), 134.1, 130.6 (d, J = 9.0 Hz), 128.1 (d, J = 10.0 Hz), 127.4, 122.9, 122.5, 119.8, 119.0, 118.7, 113.4, 111.5, 110.3 (d, J = 21.0 Hz), 29.1, 23.3; MS (EI) m/z (relative intensity) 290 (M^+, 100), 275 (7), 130 (9); HRMS (EI) m/z calcd for $C_{19}H_{15}FN_2$ (M^+) 290.1219, found 290.1218.

*Data for 3-((1H-indol-3-yl)methyl)-6-methoxy-2-methylquinoline (**3ob**):* yield 202 mg (67%); yellow solid; mp 184−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.63 (s, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.27−7.21 (m, 3H), 7.13−7.10 (m, 1H), 6.81−6.80 (m, 2H), 4.16 (s, 2H), 3.90 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 148.2,143.3 140.1, 136.7, 134.8, 129.4, 127.6, 122.9, 122.3, 121.8, 119.7, 119.2, 114.4, 111.4, 108.0, 104.1, 55.8, 28.8, 22.5; LRMS (FAB) m/z (relative intensity) 302 (M^+, 5), 318 (100), 154 (15), 136 (14); HRMS (FAB) m/z calcd for $C_{20}H_{18}N_2O_1$ (M^+) 302.1419, found 302.1418.

*Data for 3-((1H-indol-3-yl)methyl)-6,7-dimethoxy-2-methylquinoline (**3pb**):* yield 279 mg (84%); yellow solid; mp 229−231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 7.67 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.41−7.38 (m, 2H), 7.25−7.21 (m, 1H), 7.14−7.10 (m, 1H), 6.89 (s, 1H), 6.82 (d, J = 1.2 Hz, 1H), 4.21 (s, 2H), 3.99 (s, 3H), 3.93 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 151.9, 149.2, 143.4, 136.7, 134.0, 131.1, 127.6, 122.9, 122.8, 122.4, 119.7, 119.1, 114.2, 111.4, 107.3, 105.1, 56.2, 56.1, 29.0, 23.1; LRMS (FAB) m/z (relative intensity) 333 (M^+ + 1, 100), 281 (35), 149 (100), 147 (81); HRMS (FAB) m/z calcd for $C_{21}H_{20}N_2O_2$ $(M + H)^+$ 333.1603, found 333.1601.

*Data for 3-((1H-indol-1-yl)methyl)-2-methylquinoline (**3qb**):* yield 209 mg (77%); pale white solid; mp 151−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.71−7.69 (m, 1H), 7.66−7.62 (m, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.33 (s, 1H), 7.25−7.23 (m, 1H), 7.20−7.13 (m, 2H), 7.08−7.07 (m, 1H), 6.63−6.62 (s, 1H), 5.43 (s, 2H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 147.3, 136.4, 133.8, 129.6, 129.4, 128.9, 128.1, 127.6, 127.0, 126.2, 122.2, 121.4, 120.0, 109.6, 102.5, 47.8, 23.2; MS (EI) m/z (relative intensity) 272 (M^+, 100), 156 (25); HRMS (EI) m/z calcd for $C_{19}H_{16}N_2$ (M^+) 272.1308, found 272.1316.

General Procedure for the Synthesis of 4a−4d, 5d−5h, 5e′−5h′, 6a−6d, and 7e. To a stirred solution of cyclic Baylis−Hillman alcohol (2.0 mmol) in acetonitrile (10.0 mL) were added 2-methylindole or 2 phenylindole (2.4 mmol, 1.2 equiv) and iodine (0.3 equiv), and the reaction mixture was refluxed until the reaction was complete, as monitered by TLC. The resulting reaction mixture was quenched with a saturated solution of sodium thiosulfate and extracted with ethyl acetate (2.0 × 10.0 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated to give the crude products. The crude products were purified by passing them through a short silica gel column (ethyl acetate/hexane).

*Data for 2-((2-methyl-1H-indol-3-yl)(2-nitrophenyl)methyl)-cyclohex-2-enone (**4a**):* yield 626 mg (87%); yellow solid; mp 209−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (br s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.44−7.32 (m, 3H), 7.24 (s, 1H), 7.10−7.03 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.59−6.57 (m, 1H), 6.30 (s, 1H), 2.48−2.39 (m, 4H), 2.34 (s, 3H), 2.04−1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 149.8, 146.5, 140.4, 137.5, 135.6, 134.0, 132.3, 131.1, 128.3, 127.3, 124.9, 120.7, 119.3, 118.9, 110.8, 108.8, 38.6, 37.2, 26.1, 23.0, 12.1; MS (EI) m/z (relative intensity) 360 (M^+, 100), 343 (19), 270 (22), 247 (12); HRMS (EI) m/z calcd for $C_{22}H_{20}N_2O_3$ (M^+) 360.1468, found 360.1481.

*Data for 2-((5-fluoro-2-nitrophenyl)(2-methyl-1H-indol-3-yl)-methyl)cyclohex-2-enone (**4b**):* yield 688 mg (91%); yelow solid; mp 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br s, 1H), 7.88 (dd, J = 8.6, 5.1 Hz, 1H), 7.23 (s, 1H), 7.08−6.98 (m, 4H), 6.92 (t, J = 7.4 Hz, 1H), 6.61−6.58 (m, 1H), 6.33 (s, 1H), 2.49−2.35 (m, 4H), 2.32 (s, 3H), 2.04−1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 164.4 (d, J = 254.0 Hz), 146.9, 145.6, 141.8 (d, J = 7.0 Hz), 140.0, 135.5, 134.1, 128.0, 127.8 (d, J = 10.0 Hz), 120.9, 119.6, 118.6, 118.1 (d, J = 24.0 Hz), 114.2 (d, J = 23.0 Hz) 110.9, 108.0, 38.5, 37.6, 26.1, 22.9, 12.1; MS (EI) m/z (relative intensity) 378 (M^+, 100), 361 (50), 266 (33); HRMS (EI) m/z calcd for $C_{22}H_{19}FN_2O_3$ (M^+) 378.1374, found 378.1388.

*Data for 2-((5-chloro-2-nitrophenyl)(2-methyl-1H-indol-3-yl)-methyl)cyclohex-2-enone (**4c**):* yield 693 mg (88%); light yellow solid; mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br s, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.34−7.30 (m, 2H), 7.24 (s, 1H), 7.08−7.04 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.61−6.59 (m, 1H), 6.29 (s, 1H), 2.50−2.35 (m, 4H), 2.33 (s, 3H), 2.04−1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 148.0, 147.0, 140.0, 139.9, 138.7, 135.5, 134.0,

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130.9, 128.0, 127.5, 126.5, 121.0, 119.7, 118.6, 110.8, 108.1, 38.5, 37.3, 26.2, 22.9, 12.2; MS (EI) m/z (relative intensity) 394 (M^+, 100), 377 (65), 299 (34), 282 (41); HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{35}ClN_2O_3$ (M^+) 394.1079, found 394.1085; HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{37}ClN_2O_3$($M^+$) 396.1049, found 396.1070.

*Data for 2-((5-bromo-2-nitrophenyl)(2-methyl-1H-indol-3-yl)-methyl)cyclohex-2-enone (**4d**):* yield 683 mg (78%); yellow solid; mp 180−182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.50−7.47 (m, 2H), 7.24 (s, 1H), 7.08−7.05 (m, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.61−6.59 (m, 1H), 6.29 (s, 1H), 2.50−2.35 (m, 4H), 2.32 (s, 3H), 2.04−1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 148.5, 147.2, 139.9, 139.8, 135.5, 134.0, 133.8, 130.5, 127.9, 127.2, 126.5, 120.9, 119.6, 118.5, 110.9, 108.0, 38.5, 37.3, 26.1, 22.9, 12.1; MS (EI) m/z (relative intensity) 439 (M^+ +1, 80), 438 (M^+, 100), 421 (73), 345(34), 326(41), 218(30), 146(41); HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{79}BrN_2O_3$ (M^+) 438.0574 found 438.056; HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{81}BrN_2O_3$ (M^+) 440.0553, found 440. 0562.

*Data for (E)-2-(5-bromo-2-nitrobenzylidene)-3-(2-methyl-1H-indol-3-yl)cyclohexanone (**5d**):* yield 96 mg (11%); red solid; mp 205−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (br s, 1H), 7.54−7.52 (m, 2H), 7.18−7.11 (m, 3H), 7.03 (t, J = 7.5 Hz, 1H), 6.98 (s, 1H), 6.93 (t, J = 7.4 Hz, 1H), 4.13 (t, J = 6.0 Hz, 1H), 2.75−2.71 (m, 2H), 2.15 (s, 3H), 2.08−1.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 145.2, 140.8, 135.0, 134.6, 134.5, 132.8, 131.0, 130.6, 127.4, 126.9, 125.3, 121.5, 119.5, 118.5, 114.6, 110.2, 40.4, 35.9, 31.9, 21.6, 12.5; MS (EI) m/z (relative intensity) 440 (M^+ + 2, 93), 438 (M^+, 100), 394 (47), 349 (15); HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{79}BrN_2O_3$ (M^+) 438.0574, found 438.0566; HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{81}BrN_2O_3$ (M^+) 440.0553, found 440.0551.

*Data for (E)-2-(2-nitrobenzylidene)-3-(2-phenyl-1H-indol-3-yl)-cyclohexanone (**5e**):* yield 658 mg (78%); yellow solid; mp 219−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.72 (br s, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.42−7.31 (m, 4H), 7.21−7.09 (m, 5H), 7.03−6.99 (m, 2H), 6.60 (d, J = 7.6 Hz, 1H), 4.37 (t, J = 6.0 Hz, 1H), 2.74−2.72 (m, 2H), 2.16−2.13 (m, 3H), 1.97−1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 146.1, 139.7, 136.7, 136.0, 134.0, 132.6, 132.5, 132.2, 129.6, 128.8, 128.2, 128.1, 128.0, 126.9, 124.0, 122.5, 120.5, 119.8, 115.7, 110.8, 40.2, 35.8, 32.6, 21.6; MS (EI) m/z (relative intensity) 422 (M^+, 100), 375 (33), 182 (30); HRMS (EI) m/z calcd for $C_{27}H_{22}N_2O_3$ (M^+) 422.1625, found 422.1628.

*Data for (Z)-2-(2-nitrobenzylidene)-3-(2-phenyl-1H-indol-3-yl)-cyclohexanone (**5e′**):* yield 109 mg (13%); yellow solid; mp 199−200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.63−7.61 (m, 2H), 7.54−7.41 (m, 5H), 7.34 (t, J = 7.6 Hz, 1H), 7.24−7.13 (m, 3H), 6.71 (d, J = 1.8 Hz, 1H), 4.24−4.21 (m, 1H), 2.66−2.60 (m, 3H), 2.14−2.04 (m, 2H), 1.86−1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 147.5, 142.4, 136.8, 136.7, 134.9, 133.1, 132.7, 132.5, 130.5, 129.3, 128.6, 128.5, 127.9, 127.0, 124.5, 122.4, 121.2, 111.6, 119.8, 112.4, 43.5, 43.0, 32.0, 24.5; MS (EI) m/z (relative intensity) 422 (M^+, 100), 375 (33), 182 (30); HRMS (EI) m/z calcd for $C_{27}H_{22}N_2O_3$ (M^+) 422.1625, found 422.1628.

*Data for (E)-3-(1H-indol-3-yl)-2-(2-nitrobenzylidene)-cyclopentanone (**6a**):* yield 538 mg (81%); yellow solid; mp 151−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.89−7.87 (m, 1H), 7.84 (d, J = 1.8 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.36−7.31 (m, 2H), 7.29−7.27 (m, 2H), 7.22−7.18 (m, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 1.4 Hz, 1H), 4.54−4.56 (m, 1H), 2.51−2.38 (m, 2H), 2.37−2.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 148.5, 142.1, 136.9, 133.0, 131.0, 130.7, 129.5, 129.2, 125.9, 124.5, 122.6, 122.0, 119.7, 119.1, 117.1, 111.5, 37.4, 35.9, 28.5; MS (EI) m/z (relative intensity) 332 (M^+, 100); HRMS (EI) m/z calcd for $C_{20}H_{16}N_2O_3$ (M^+) 332.1155, found 332.1157.

*Data for (E)-2-(5-fluoro-2-nitrobenzylidene)-3-(1-methyl-1H-indol-3-yl)cyclopentanone (**6b**):* yield 575 mg (79%); yellow solid; mp 150−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 9.0, 5.1 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.19−7.18 (m, 2H), 7.06−7.02 (m, 1H), 7.83 (dd, J = 8.7, 2.7 Hz, 1H), 6.86−6.81 (m, 1H), 6.65 (s, 1H), 4.48−4.47 (m, 1H), 3.62 (s, 3H), 2.55−2.42 (m, 2H), 2.41−2.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 164.1 (d, J = 256.0 Hz), 144.1, 143.1, 137.4, 134.5 (d, J = 10.0 Hz), 129.0, 127.0 (d, J = 10.0 Hz), 126.6, 126.1, 122.2, 119.1 (d, J = 21.0 Hz), 117.7, 117.5, 115.5 (d, J = 23.0 Hz), 115.3, 109.4, 37.5, 36.5, 32.6, 28.8; MS (EI) m/z (relative intensity) 364 (M^+, 100); HRMS (EI) m/z calcd for $C_{21}H_{17}FN_2O_3$ (M^+) 364.1218, found 364.1222.

*Data for (E)-3-(2-methyl-1H-indol-3-yl)-2-(2-nitrobenzylidene)-cyclopentanone (**6c**):* yield 602 mg (87%); dark red solid; mp 206−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.88 (m, 1H), 7.68−7.66 (m, 1H), 7.42 (br s, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.07- 7.01 (m, 3H), 7.00−6.89 (m, 3H), 4.37−4.33 (m, 1H), 2.67−2.64 (m, 1H), 2.59−2.52 (m, 1H), 2.39−2.37 (m, 1H), 2.36−2.17 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ and DMSO-d_6) δ 206.8, 146.2, 140.8, 135.0, 131.3, 131.1, 130.1, 130.0, 129.6, 128.1, 126.0, 123.2, 119.8, 117.9, 117.6, 109.9, 109.9, 37.4, 37.3, 28.3, 11.3; MS (EI) m/z (relative intensity) 346 (M^+, 100), 285 (15); HRMS (EI) m/z calcd for $C_{21}H_{18}N_2O_3$ (M^+) 346.1312, found 346.1326.

*Data for (E)-2-(5-fluoro-2-nitrobenzylidene)-3-(2-methyl-1H-indol-3-yl)cyclopentanone (**6d**):* yield 662 mg (91%); red solid; mp 185−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.85 (m, 1H), 7.64 (dd, J = 9.0, 5.1 Hz, 1H), 7.49 (br s, 1H), 7.13 (d, J = 7.9 Hz, 1H), 7.03−6.96 (m, 2H), 6.86 (t, J = 7.3 Hz, 1H), 6.71−6.62 (m, 2H), 4.34 (t, J = 7.3 Hz, 1H), 2.70−2.68 (m, 1H), 2.67−2.55 (m, 1H), 2.40−2.38 (m, 1H), 2.28 (s, 3H), 2.26−2.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 163.5 (d, J = 255.0 Hz), 142.9, 141.6, 135.3, 134.1 (d, J = 10.0 Hz), 131.2, 129.9, 126.4, 126.3 (d, J = 4.0 Hz), 121.5, 119.5, 118.7, 117.3 (d, J = 24.0 Hz), 115.1 (d, J = 23.0 Hz), 111.1, 110.0, 38.1, 37.9, 28.5, 11.8; MS (EI) m/z (relative intensity) 364 (M^+, 100), 318 (15); HRMS (EI) m/z calcd for $C_{21}H_{17}FN_2O_3$ (M^+) 364.1218, found 364.1233.

*Data for 2-((2-nitrophenyl)(2-phenyl-1H-indol-3-yl)methyl)-cyclopent-2-enone (**7e**):* yield 718 mg (88%); yellow solid; mp 231−233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.48−7.43 (m, 4H), 7.42−7.33 (m, 5H), 7.23 (d, J = 8.2 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.09 (s, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.21 (s, 1H), 2.53−2.46 (m, 1H), 2.43−2.37 (m, 2H), 2.29−2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 159.0, 149.5, 147.1, 137.3, 136.8, 136.1, 132.7, 132.7, 131.1, 129.0, 128.8, 128.5, 128.4, 127.7, 125.0, 122.2, 120.1, 119.9, 111.4, 109.3, 35.6, 34.7, 26.5; MS (EI) m/z (relative intensity) 408 (M^+, 80), 310 (50), 281(34), 207 (100); HRMS (EI) m/z calcd for $C_{26}H_{20}N_2O_3$ (M^+) 408.1468, found 408.1483.

General Procedure for the Synthesis of 8a−8h. To a stirred solution of C-alkylated cyclic Baylis−Hillman adducts containing indoles (1.0 mmol) in acetic acid (5.0 mL) was added powdered Fe (6.0 mmol, 6.0 equiv), and the reaction mixture was then refluxed for 2 h. The mixture was cooled to room temperature, the acetic acid was removed under reduced pressure, and EtOAc (10.0 mL) was added. The resulting mixture was stirred for 2 min, and iron impurities were removed by filtration. The insoluble iron residue was washed with EtOAc (10.0 mL). The filtrate and washings were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and all of the crude products were purified by passing them through a short silica gel column (ethyl acetate/hexane).

*Data for 1-(2-Methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8a**):* yield 249 mg (80%); white solid; mp 244−246 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (br s, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.61−7.57 (m, 3H), 7.35 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 6.89 (d, J = 7.4 Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 6.67 (t, J = 7.3 Hz, 1H), 4.49 (t, J = 7.4 Hz, 1H), 3.20−3.21 (m, 2H), 2.34 (s, 3H), 2.13−1.97 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.8, 145.9, 135.6, 134.7, 134.4, 132.3, 128.5, 127.7, 127.3, 126.9, 126.5, 125.3, 119.7, 118.2, 118.0, 113.5, 110.6, 35.8, 33.7, 30.8, 22.4, 11.6; MS (EI) m/z (relative intensity) 312 (M^+, 100), 181 (54); HRMS (EI) m/z calcd for $C_{22}H_{20}N_2$ (M^+) 312.1621, found 312.1632.

*Data for 7-fluoro-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8b**):* yield 274 mg (83%); pale gray solid; mp 245−247 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (br s, 1H), 7.96−7.92 (m, 1H), 7.62 (s, 1H), 7.51−7.47 (m, 2H), 7.25 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 4.49 (t, J = 7.6 Hz, 1H), 3.20−3.21 (m, 2H), 2.34 (s, 3H), 2.14−1.98 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.0 (d, J = 242.0 Hz), 158.3, 143.1, 135.6, 135.4, 134.4 (d, J = 20.0 Hz), 132.4, 130.4 (d, J = 10.0 Hz), 127.4 (d, J = 10.0 Hz), 126.4, 119.8, 118.5 (d, J = 26.0 Hz), 118.2, 118.0, 113.3,

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110.6, 110.1 (d, J = 22 Hz), 35.8, 33.5, 30.7, 22.4, 11.6; MS (EI) m/z (relative intensity) 330 (M^+, 100), 199 (40); HRMS (EI) m/z calcd for $C_{22}H_{19}FN_2$ (M^+) 330.1527, found 330.1528.

*Data for 7-chloro-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8c**):* yield 280 mg (81%); white solid. mp 246−247 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (br s, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.81 (s, 1H), 7.64 (s, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 6.90 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H), 4.50 (t, J = 7.1 Hz, 1H), 3.20−3.22 (m, 2H), 2.33 (s, 3H), 2.09−1.98 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.5, 144.0, 135.6, 135.5, 134.2, 132.4, 129.7, 129.6, 129.1, 127.6, 126.4, 125.9, 119.7, 118.1, 118.0, 113.2, 110.6, 35.8, 33.5, 30.7, 22.2, 11.6; MS (EI) m/z (relative intensity) 346 (M^+, 100), 215 (63); HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{35}ClN_2$ (M^+) 346.1231, found 346.1240; HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{37}ClN_2$ (M^+) 348.1202, found 348.1219.

*Data for 7-bromo-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8d**):* yield 319 mg (82%); light yellow solid; mp 259−261 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (br s, 1H), 7.95 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.70−7.68 (m, 1H), 7.61 (s, 1H), 7.25 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H), 4.50 (t, J = 7.4 Hz, 1H), 3.21−3.20 (m, 2H), 2.33 (s, 3H), 2.13−1.98 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.8, 144.4, 135.7, 135.6, 134.1, 132.5, 131.6, 130.0, 129.3, 128.3, 126.5, 119.8, 118.3, 118.2, 118.1, 113.4, 110.7, 35.9, 33.7, 30.7, 22.3, 11.6; MS (EI) m/z (relative intensity) 392 (M^+ + 2, 100), 390 (M^+, 77); HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{79}BrN_2$ (M^+) 390.0726, found 390.0725; HRMS (EI) m/z calcd for $C_{22}H_{19}{}^{81}BrN_2$ (M^+) 392.0706, found 392.0714.

*Data for 1-(2-phenyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8e**):* yield 310 mg (83%); white solid; mp 272−273 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (br s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.67−7.57 (m, 5H), 7.54−7.50 (m, 2H), 7.43−7.32 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 4.61 (dd, J = 11.2, 4.7 Hz, 1H), 3.28−3.24 (m, 2H), 2.32−2.29 (m, 1H), 2.17−2.14 (m, 2H), 1.98−1.96 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.6, 145.9, 136.6, 135.9, 134.5, 134.3, 132.8, 128.8, 128.6, 128.3, 127.8, 127.7, 127.3, 126.8, 126.0, 125.3, 121.2, 119.8, 118.5, 114.3, 111.5, 36.5, 33.6, 30.8, 22.8; MS (EI) m/z (relative intensity) 374 (M^+, 100), 181 (8); HRMS (EI) m/z calcd for $C_{27}H_{22}N_2$ (M^+) 374.1778, found 374.1783.

*Data for 7-fluoro-1-(2-phenyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8f**):* yield 333 mg (85%); white solid; mp 265−266 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.33 (br s, 1H), 7.94 (dd, J = 9.9, 5.3 Hz, 1H), 7.68−7.64 (m, 3H), 7.54−7.47 (m, 4H), 7.43−7.37 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 4.59 (dd, J = 11.2, 4.7 Hz, 1H), 3.27−3.18 (m, 2H), 2.31−2.28 (m, 1H), 2.16−2.14 (m, 2H), 1.98−1.94 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.2 (d, J = 245.0 Hz), 158.1, 143.1, 136.6, 135.9, 135.2, 134.1 (d, J = 5.0 Hz), 132.8, 130.4 (d, J = 9.0 Hz), 128.8, 128.3, 127.7, 127.4 (d, J = 10.0 Hz), 126.0, 121.2, 119.7, 118.7, 118.5, 118.4, 114.1, 111.5, 110.2 (d, J = 22 Hz), 36.5, 33.5, 30.8, 22.7; MS (EI) m/z (relative intensity) 392 (M^+, 100), 199 (8); HRMS (EI) m/z calcd for $C_{27}H_{21}FN_2$ (M^+) 392.1683, found 392.1690.

*Data for 7-chloro-1-(2-phenyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8g**):* yield 342 mg (84%); yellow solid; mp 281−282 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (br s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 1.7 Hz, 1H), 7.68−7.60 (m, 3H), 7.60−7.57 (m, 1H), 7.54−7.50 (m, 2H), 7.43−7.37 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 4.59 (dd, J = 11.9, 4.7 Hz, 1H), 3.28−3.23 (m, 2H), 2.31−2.28 (m, 1H), 2.16−2.14 (m, 2H), 1.98−1.94 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.3, 144.2, 136.6, 136.0, 135.5, 134.0, 132.8, 129.8, 129.7, 129.1, 128.8, 128.3, 127.8, 127.6, 126.0, 125.9, 121.2, 119.7, 118.5, 114.0, 111.5, 36.5, 33.5, 30.7, 22.6; MS (EI) m/z (relative intensity) 408 (M^+, 100), 214 (7); HRMS (EI) m/z calcd for $C_{27}H_{21}{}^{35}ClN_2$ (M^+) 408.1388, found 408.1389; HRMS (EI) m/z calcd for $C_{27}H_{21}{}^{37}ClN_2$ (M^+) 410.1358, found 410.1375.

*Data for 7-bromo-1-(2-phenyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (**8h**):* yield 375 mg (83%); yellow solid; mp 269−270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.33 (br s, 1H), 7.97 (s, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.70−7.64 (m, 4H), 7.54−7.50 (m, 2H), 7.43−7.37 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 4.59 (dd, J = 11.0, 4.7 Hz, 1H), 3.27−3.17 (m, 2H), 2.28−2.25 (m, 1H), 2.16−2.14 (m, 2H), 1.98−1.95 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.5, 144.3, 136.6, 136.0, 135.5, 133.9, 132.8, 131.6, 129.8, 129.3, 128.8, 128.4, 128.1, 127.8, 125.9, 121.2, 119.7, 118.5, 118.2, 114.0, 111.5, 36.5, 33.6, 30.7, 22.6; MS (EI) m/z (relative intensity) 454 (M^+ + 2, 100), 452 (M^+, 90), 261 (9); HRMS (EI) m/z calcd for $C_{27}H_{21}{}^{79}BrN_2$ (M^+) 452.0883, found 452.0878; HRMS (EI) m/z calcd for $C_{27}H_{21}{}^{81}BrN_2$ (M^+) 454.0862, found 454.0870.

General Procedure for the Synthesis of 8i−8m. To a stirred solution of C-alkylated cyclic Baylis−Hillman adducts containing indoles (1.0 mmol) in acetic acid (5.0 mL) was added powdered Fe (6.0 mmol, 6.0 equiv), and the reaction mixture was heated at 80 °C for 2 h. The mixture was cooled to room temperature, the acetic acid was removed under reduced pressure, and EtOAc (10.0 mL) was added. The resulting mixture was stirred for 2 min, and iron impurities were removed by filtration. The insoluble iron residue was washed with EtOAc (10.0 mL). The filtrate and washings were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and all of the crude products were purified by passing them through a short silica gel column (ethyl acetate/hexane).

*Data for 1-(1H-indol-3-yl)-2,3-dihydro-1H-cyclopenta[b]-quinoline (**8i**):* yield 196 mg (69%); pale brown solid; mp 235−237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (br s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.67−7.63 (m, 2H), 7.46−7.41 (m, 3H), 7.23−7.19 (m, 1H), 7.08−7.04 (m, 1H), 7.00 (d, J = 2.2 Hz, 1H), 4.81 (t, J = 8.3 Hz, 1H), 3.39−3.26 (m, 2H), 2.76−2.68 (m, 1H), 2.47−2.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 146.8, 139.2, 137.0, 132.1, 129.2, 128.0, 128.0, 127.7, 126.6, 126.1, 122.4, 121.9, 119.7, 119.5, 118.2, 111.6, 40.6, 33.7, 33.1; MS (EI) m/z (relative intensity) 284 (M^+, 100), HRMS (EI) m/z calcd for $C_{20}H_{16}N_2$ (M^+), 284.1308, found 284.1300.

*Data for 7-fluoro-1-(1-methyl-1H-indol-3-yl)-2,3-dihydro-1H-cyclopenta[b]quinoline (**8j**):* yield 208 mg (66%); yellow solid; mp 239−241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 9.0, 5.1 Hz, 1H), 7.74 (br s, 1H), 7.43−7.34 (m, 4H), 7.27 (s, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.85 (s, 1H), 4.78 (t, J = 8.3 Hz, 1H), 3.76 (s, 3H), 3.35−3.24 (m, 2H), 2.74−2.68 (m, 1H), 2.43−2.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 160.2 (d, J = 245.0 Hz), 144.1, 140.2, 137.7, 131.1 (d, J = 5.0 Hz), 130.4 (d, J = 9.0 Hz), 128.4 (d, J = 10.0 Hz), 126.9, 126.5, 122.1, 119.5, 119.2, 118.9 (d, J = 26.0 Hz), 116.6, 111.1 (d, J = 22.0 Hz), 109.7, 40.6, 33.6, 33.3, 32.9. MS (EI) m/z (relative intensity) 316 (M^+, 100); HRMS (EI) m/z calcd for $C_{21}H_{17}FN_2$ (M^+) 316.1370, found 316.1370.

*Data for 1-(2-methyl-1H-indol-3-yl)-2,3-dihydro-1H-cyclopenta-[b]quinoline (**8k**):* yield 223 mg (75%); brown solid; mp 232−233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.95 (br s, 1H), 7.65−7.58 (m, 3H), 7.40 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 4.74 (t, J = 9.0 Hz, 1H), 3.39−3.30 (m, 2H), 2.62−2.57 (m, 1H), 2.48−2.45 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 147.8, 138.6, 135.8, 132.0, 131.2, 128.7, 128.6, 128.0, 127.7, 127.1, 125.7, 121.1, 119.4, 119.2, 112.5, 110.6, 40.4, 34.2, 32.7, 12.3; MS (EI) m/z (relative intensity) 298 (M^+, 100), 282 (78); HRMS (EI) m/z calcd for $C_{21}H_{18}N_2$ (M^+) 298.1465, found 298.1467.

*Data for 7-fluoro-1-(2-methyl-1H-indol-3-yl)-2,3-dihydro-1H-cyclopenta[b]quinoline (**8l**):* yield 243 mg (77%); pale yellow solid; mp 247−249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 9.1, 5.3 Hz, 1H), 7.96 (br s, 1H), 7.55 (s, 1H), 7.40−7.33 (m, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.21−7.18 (m, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.85 (t, J = 7.3 Hz, 1H), 4.73 (t, J = 9.3 Hz, 1H), 3.36−3.29 (m, 2H), 2.63−2.58 (m, 1H), 2.49−2.46 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 159.1 (d, J = 242.0 Hz), 144.2, 139.6, 135.7, 132.6, 130.6 (d, J = 9.0 Hz), 129.4 (d, J = 5.0 Hz), 127.8 (d, J = 11.0 Hz), 126.4, 119.8, 118.1, 118.0 (d, J = 4.0 Hz), 117.8, 111.0, 110.8, 110.8 (d, J = 11.0 Hz), 33.2, 32.0, 11.7, 11.6; MS (EI) m/z (relative intensity) 316 (M^+, 100), 301 (26); HRMS (EI) m/z calcd for $C_{21}H_{17}FN_2$ (M^+) 316.1370, found 316.1375.

*Data for 1-(2-phenyl-1H-indol-3-yl)-2,3-dihydro-1H-cyclopenta-[b]quinoline (**8m**):* yield 190 mg (53%); pale brown solid; mp 267−269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.64−7.58 (m, 5H), 7.52−7.48 (m, 2H), 7.43−7.38 (m, 3H),

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7.16−7.12 (m, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.85 (t, J = 7.3 Hz, 1H), 4.95−4.90 (m, 1H), 3.42−3.36 (m, 1H), 3.36−3.27 (m, 1H), 2.69−2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 147.8, 138.7, 136.7, 136.6, 133.1, 131.1, 129.2, 128.9, 128.7, 128.6, 128.4, 128.0, 127.7, 126.9, 125.7, 122.3, 120.9, 119.6, 113.5, 111.3, 40.7, 34.1, 32.8; MS (EI) m/z (relative intensity) 360 (M^+, 100); HRMS (EI) m/z calcd for $C_{26}H_{20}N_2$ (M^+) 360.1621, found 360.1626.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data of compound 4a, 5e, 5e' and 8a and 1H and 13C NMR copies of all the compounds are available in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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