Sequential *Ugi* Four-Component Reaction (4-CR)/C–H Activation Using (Diacetoxyiodo)benzene for the Synthesis of 3-(Diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones

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Dedicated to Prof. *Thomas J. J. Müller* on the occasion of his 50th birthday

A sequential *Ugi* four-component reaction (4-CR)/C–H activation using (diacetoxyiodo)benzene is reported. This process is a five-component reaction of aromatic aldehydes, aniline derivatives, isocyanides, phenylpropiolic acid (3-phenylprop-2-ynoic acid), and (diacetoxyiodo)benzene for the synthesis of 3-(diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones. This procedure offers several advantages such as good yields, high bond-forming efficiency, selectivity, and short reaction times.

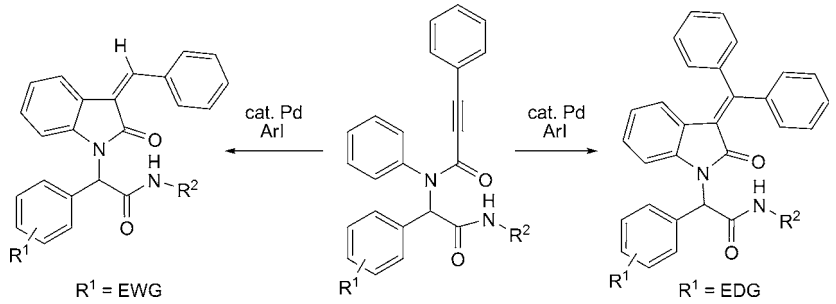
Introduction. – Transition metal-catalyzed cross-coupling has revolutionized the way chemists form C–C bonds. It has a high potential for the construction of biologically active compounds, polycyclic compounds, and complex molecules [1]. The most recently reported reactions based on metal-catalyzed cross-coupling were performed in the presence of Pd catalysts [2]. Palladium-catalyzed cross-coupling of aryl halides with organometallic reagents is now recognized to be one of the most useful methods for the construction of C–C bond. Most of the reactions using Pd catalysts need the functionalized substrate, and such starting materials require additional steps to prepare. In this way, the use of C–H bonds in the cross-coupling and its activation has more advantages, including efficiency of reactions and reducing the synthesis steps [3–6]. Most of the C–H activation reactions involve an oxidative reagent. During the recent years, hypervalent iodine compounds have been widely used as mild, environmentally benign, and inexpensive reagents in organic synthesis [7]. These types of reagents have been used not only in oxidative reaction [8–12], but also in C–C [13–15] and carbon–heteroatom [16][17] bond formation, and rearrangement reactions [18][19]. The most common hypervalent iodine compound is (diacetoxyiodo)benzene ($PhI(OAc)_2$; DIB) [20]. The excellent oxidation characteristic of DIB is related to transformation of I^{III} to I^{I} [21]. As a result of the transmutation of I^{III} to I^{I}, ArI is obtained as a product. The transition metal catalyst, especially Pd, can cause these reagents to work efficiently in oxidation reactions [22] such as activation and functionalization of C–H bonds [23][24]. The most important step in this transformation is the oxidation of Pd^{II} to Pd^{IV} species, which was isolated, and its structure was established by X-ray crystallography [25].

According to the importance of C–H activation reaction and on the other hand the biological activities of 2-oxindole (=2,3-dihydro-1*H*-indol-2-one) compounds [26], we

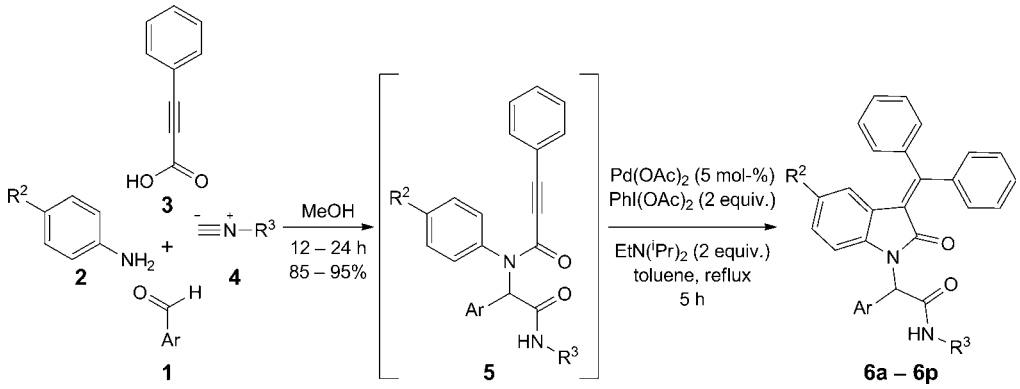
had used a sequential *Ugi* four-component reaction (4-CR)/C–H activation using Pd catalyst in the presence of PhI as source of Ph groups for the synthesis of 3-(diphenyl)methylidene)-2,3-dihydro-1*H*-indol-2-ones [27]. However, the desired 3-(phenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones as products were formed by use of benzaldehydes bearing electron-donating groups (EDGs) and with benzaldehydes which contained electron-withdrawing groups (EWGs; *Scheme 1*).

Searching for novel reaction condition to construct the 3-(diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones is an interesting subject in this area. Herein, we report the use of DIB in a sequential *Ugi* 4-CR/C–H activation for the aimed synthesis of 3-(diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones without 3-(phenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones as by-products (*Scheme 2*).

Scheme 1. *Synthesis of 3-(Diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones and 3-(Phenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones through C–H Activation According to [27]*

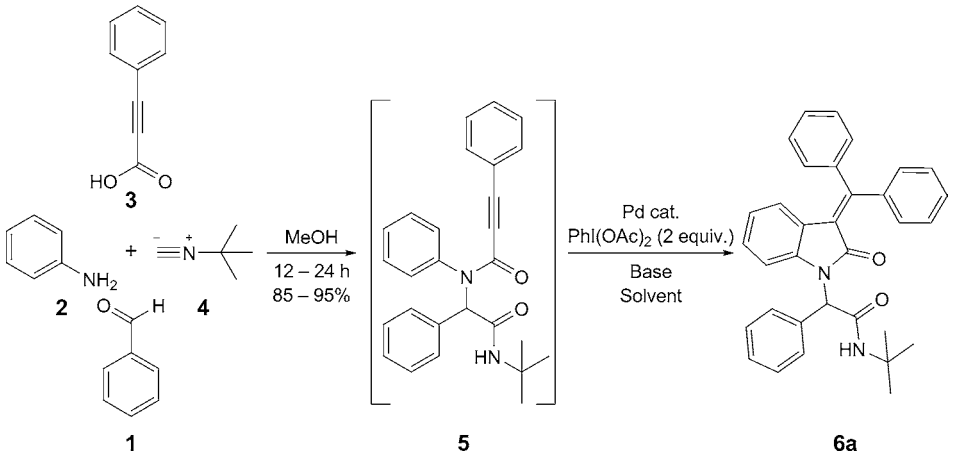


Scheme 2. *Using of DIB in Sequential* Ugi *4-CR/C–H Activation for the Synthesis of 3-(Diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones* **6a – 6p**



Results and Discussion. – In our initial study, the four-component reaction (4-CR) of benzaldehyde (Ar = Ph; **1**), aniline (**2**), phenylpropiolic acid (**3**), and *tert*-butyl isocyanide (**4**) was selected as model reaction. After formation of the desired *N*-substituted alk-2-yneamide **5** as an intermediate, the cyclization was performed under different reaction conditions using catalytic amounts of $Pd(OAc)_2$ (5%) and DIB (*Scheme 3*).

Scheme 3. *The Model Reaction for the Synthesis of* **6a** *Using Sequential* Ugi *4-CR/C–H Activation*



The effects of Pd catalyst, base, and solvent on the cyclization reaction is compiled in *Table 1*. The reaction could not be realized using $CsCO_3$ and K_2CO_3 as base. Then, we checked the reaction using amines such as morpholine, Et_3N, $EtN(^iPr)_2$, and DBU in different solvents such as MeOH, DMSO, CH_2Cl_2, and toluene. The best result was obtained with $Pd(OAc)_2$ (5 mol-%), DIB (2 equiv.), $EtN(^iPr)_2$ (2 equiv.) in toluene under reflux. Encouraged by these results, we tried to optimize the type of catalyst (*Entries 11* and *12*). The suitable Pd catalyst turned out to be $Pd(OAc)_2$.

Having established the optimum reaction conditions and in order to extend the chemical library, we proceeded to screen various benzaldehyde derivatives with EWGs and EDGs, aniline derivatives, two isocyanides, and by using of DIB to construct 3-(diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones **6a**–**6p**. In all cases, the reactions were complete within 5 h. The results are collected in *Table 2*.

Table 1. *Optimization of the Reaction Conditions for the Synthesis of Compound* **6a** (see *Scheme 3*)

Entry	Base	Catalyst (5 mol-%)	Solvent	Yield [%][a])
1	Cs_2CO_3	$Pd(OAc)_2$	MeOH	N.R.
2	K_2CO_3	$Pd(OAc)_2$	MeOH	N.R.
3	Morpholine	$Pd(OAc)_2$	MeOH	20
4	Et_3N	$Pd(OAc)_2$	MeOH	11
5	Piperidine	$Pd(OAc)_2$	MeOH	26
6	$EtN(^iPr)_2$	$Pd(OAc)_2$	MeOH	46
7	DBU[b])	$Pd(OAc)_2$	MeOH	10
8	$EtN(^iPr)_2$	$Pd(OAc)_2$	DMSO	36
9	$EtN(^iPr)_2$	$Pd(OAc)_2$	$ClCH_2CH_2Cl$	41
10	**$EtN(^iPr)_2$**	$Pd(OAc)_2$	**Toluene**	**88**
11	$EtN(^iPr)_2$	$Pd(Cl_2)_2$	Toluene	63
12	$EtN(^iPr)_2$	$Pd(Cl_2)_2(PPh_3)_2$	Toluene	42

[a]) Yield of isolated **6a**. [b]) 1,8-Diazabicyclo[5.4.0]undec-7-ene.

Table 2. *Sequential* Ugi *4-CR/C–H Activation for the Synthesis of Diverse 3-(Diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones* **6a**–**6p** (see *Scheme 2*)

Product	Ar	R^2	R^3	Yield [%][a])
6a	Ph	H	^{t}Bu	88
6b	4-Cl–C_6H_4	H	^{t}Bu	76
6c	3-NO_2–C_6H_4	H	^{t}Bu	68
6d	4-Me_2N–C_6H_4	H	^{t}Bu	61
6e	3,4,5-$(MeO)_3$–C_6H_2	H	^{t}Bu	78
6f	4-Me_2N–C_6H_4	H	cHex[b])	66
6g	4-Ph–C_6H_4	H	^{t}Bu	74
6h	4-Me–C_6H_4	H	^{t}Bu	65
6i	4-^{i}Pr–C_6H_4	H	^{t}Bu	75
6j	Ph	H	cHex	88
6k	Ph	Br	^{t}Bu	71
6l	4-CN–C_6H_4	H	^{t}Bu	72
6m	4-CF_3–C_6H_4	H	^{t}Bu	70
6n	4-CF_3–C_6H_4	H	cHex	85
6o	Pyridin-3-yl	H	^{t}Bu	75
6p	Ph	^{i}Pr	^{t}Bu	76

[a]) Yield of isolated products **6a**–**6p**. [b]) Cyclohexyl.

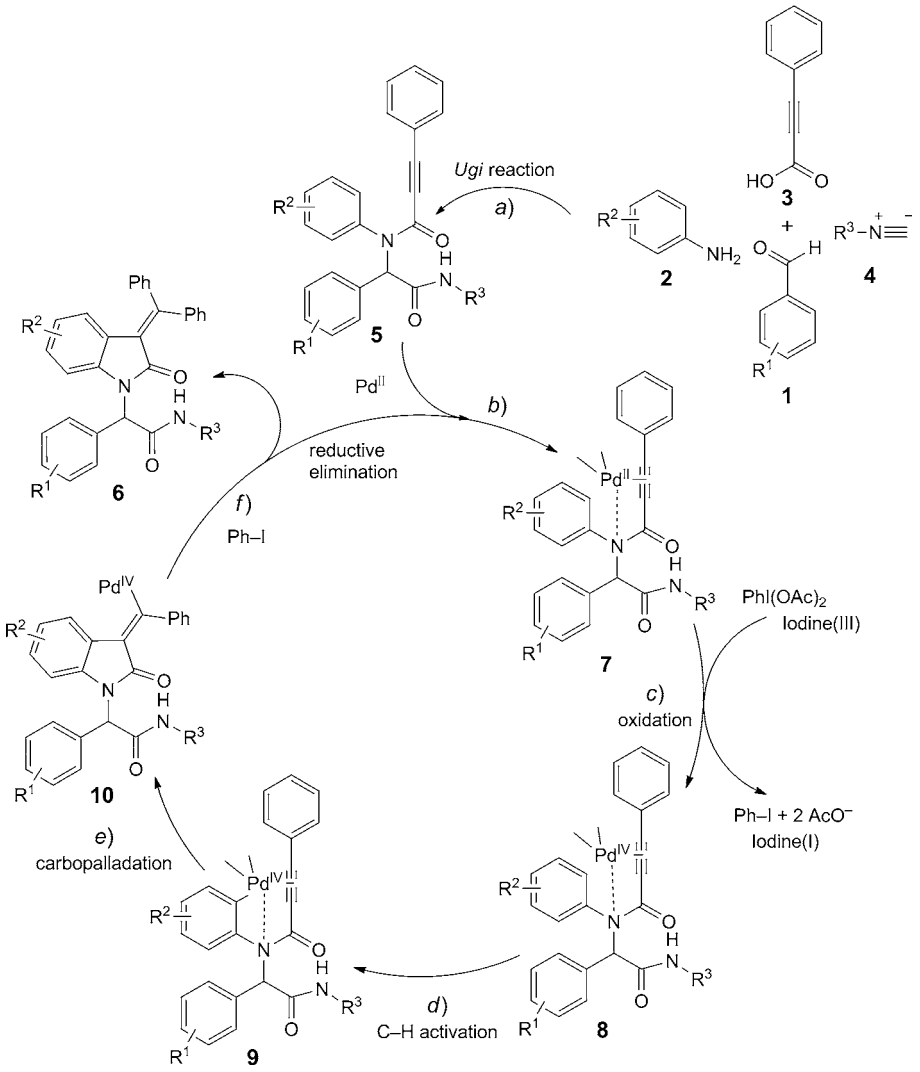
The reported method with (diacetoxyiodo)benzene [28] has two disadvantages, namely, in some cases, low yields as well as long reaction times. Meanwhile, simple *N*-substituted alkynamides were used as starting materials.

The structures of the products **6a**–**6p** were deduced from their IR, ^{1}H- and ^{13}C-NMR, and high-resolution mass-spectrometry data. For example, the ^{1}H-NMR spectrum of **6h** consisted of a *singlet* for ^{t}Bu at δ(H) 1.37, a *singlet* for NH at δ(H) 5.87, and a *singlet* for C(sp^3)–H at δ(H) 6.11, and also signals of aromatic H-atoms. The absence of alkyne signals in the ^{13}C-NMR spectra confirmed the formation of the desired products.

After formation of *Ugi* 4-CR product **5** (*Path a*, *Scheme 4*), insertion of Pd^{II} to **5** (*Path b*), oxidation of Pd^{II} to Pd^{IV}, and complexation of Pd^{IV} with the N-atom of the aniline moiety leads to intermediate **8** (*Scheme 4*). The key step for the formation of **8** is related to the conversion of DIB to PhI through reduction of I^{III} to I^{I} (*Path c*). Then, C(sp^2)–H activation leads to the formation of C–Pd bond (*Path d*). Carbopalladation of **9** results in intermediate **10** (*Path e*). Insertion of PhI (*Path f*) and, finally, reductive elimination affords the desired 3-(diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones **6a**–**6p**.

Conclusions. – We have developed a facile method for the synthesis of 3-(diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones without any 3-(benzylidene)-2,3-dihydro-1*H*-indol-2-ones by-products and introduced DIB as a source of PhI through sequential *Ugi* 4-CR/C–H activation reaction. Good yields, short reaction times (compared to other reported methods), diversity-oriented synthesis, and high bond-forming efficiencies are advantages of this method.

Scheme 4. *Proposed Mechanism for the Formation of 3-(Diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones* **6a**–**6p**



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Experimental Part

General. Commercially available materials were used without further purification. M.p.: *Electrothermal* 9100 apparatus; uncorrected. IR Spectra: *ABB FT-IR FTLA 2000* spectrometer. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX-300 AVANCE* spectrometer, at 300 and 75 MHz, resp., as well as on

Bruker DRX-500 AVANCE spectrometer, at 500 and 125 MHz, resp.; $CDCl_3$ used as solvent. HR-ESI-MS: *Mass-ESI-POS* (*Apex Qe-FT-ICR* instrument) spectrometer; in *m*/*z*.

*General Procedure for the Synthesis of 3-(Diphenylmethylidene)-2,3-dihydro-1*H*-indol-2-ones,* **6a**–**6p***, through Sequential* Ugi *4-CR/C–H Activation*. To a soln. of aldehyde **1** (1 mmol) in MeOH (5 ml) was added aniline as a primary amine **2** (1 mmol), and the mixture was stirred at r.t. (25°) for 1 h. Then, *phenylacetylenecarboxylic acid* (**3**; 1 mmol) was added, and stirring was continued for 15 min, followed by addition of isocyanide **4** (1 mmol). The mixture was stirred for 24 h. The progress of the reaction was monitored by TLC (petroleum ether/AcOEt 3:1). After completion of reaction, the solvent was removed under vacuum, then toluene (20 ml), $Pd(OAc)_2$ (11 mg, 5 mol-%), $EtN(^iPr)_2$ (258 mg, 2 mmol), and $PhI(OAc)_2$ (644 mg, 2 mmol) were simultaneously added to the mixture. The mixture was heated under reflux for 5 h. Reaction progress was monitored by TLC (hexane/AcOEt 4:1). After cooling to r.t., the mixture was diluted with brine. The aq. phase was extracted with AcOEt (2 × 30 ml). The combined org. phase was separated, dried (Na_2SO_4), filtered, concentrated *in vacuo*, and finally purified by CC (SiO_2; hexane/AcOEt 4:1) to afford the desired products with good-to-high yields (61–88%).

N-*(*tert-*Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-2-phenylacetamide* (**6a**). Yield: 428 mg (88%). Orange solid. M.p. 226–227°. IR (KBr): 3316, 1749, 1672. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.39 (*s*, ^{t}Bu); 5.90 (*s*, NH); 6.16 (*s*, CH); 6.43 (*d*, *J* = 7.7, 1 arom. H); 6.63 (*t*, *J* = 7.7, 1 arom. H); 6.79 (*d*, *J* = 8.0, 1 arom. H); 6.96 (*t*, *J* = 7.7, 1 arom. H); 7.26–7.47 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.0; 58.6; 111.7; 121.5; 123.0; 123.2; 123.6; 127.8; 128.0; 128.1; 128.5; 128.7; 128.9; 129.2; 129.3; 130.2; 134.7; 140.0; 141.2; 141.3; 155.3; 167.1; 167.2. HR-ESI-MS: 487.2380 ($[M+1]^+$, $C_{33}H_{31}N_2O_2^+$; calc. 487.2386), 509.2200 ($[M+Na]^+$, $C_{33}H_{30}N_2NaO_2^+$; calc. 509.2205).

N-*(*tert-*Butyl)-2-(4-chlorophenyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-acetamide* (**6b**). Yield: 395 mg (76%). Orange solid. M.p. 243–245°. IR (KBr): 3315, 1672. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.37 (*s*, ^{t}Bu); 5.90 (*s*, NH); 6.11 (*s*, CH); 6.45 (*d*, *J* = 7.7, 1 arom. H); 6.66 (*t*, *J* = 7.7, 1 arom. H); 6.79 (*d*, *J* = 7.7, 1 arom. H); 7.01 (*t*, *J* = 7.7, 1 arom. H); 7.26–7.47 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.1; 58.0; 111.5; 121.8; 123.1; 123.2; 123.3; 127.9; 128.5; 128.8; 129.0; 129.2; 129.3; 129.4; 129.5; 130.2; 133.1; 134.0; 139.9; 140.8; 141.1; 155.9; 166.8; 167.1. HR-ESI-MS: 521.2007 ($[M+1]^+$, $C_{33}H_{30}ClN_2O_2^+$; calc. 521.1996), 543.1822 ($[M+Na]^+$, $C_{33}H_{29}ClN_2NaO_2^+$; calc. 543.1815).

N-*(*tert-*Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-2-(3-nitrophenyl)acetamide* (**6c**). Yield: 361 mg (68%). Orange solid. M.p. 210–212°. IR (KBr): 3314, 1675, 1532, 1353. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.37 (*s*, ^{t}Bu); 6.10 (*s*, NH); 6.21 (*s*, CH); 6.51 (*d*, *J* = 7.8, 1 arom. H); 6.71 (*t*, *J* = 7.8, 1 arom. H); 6.80 (*d*, *J* = 7.8, 1 arom. H); 7.05 (*t*, *J* = 7.8, 1 arom. H); 7.36–7.71 (*m*, 11 arom. H); 7.68 (*dd*, *J* = 7.4, 0.8, 1 arom. H); 8.15 (*dd*, *J* = 8.1, 1.2, 1 arom. H); 8.24 (*s*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.3; 57.7; 111.1; 122.3; 122.9; 123.0; 123.1; 123.4; 127.9; 128.7; 129.0; 129.3; 129.4; 129.5; 129.6; 130.2; 134.2; 136.7; 139.8; 140.1; 140.9; 148.3; 156.7; 166.1; 167.2. HR-ESI-MS: 532.2243 ($[M+1]^+$, $C_{33}H_{30}N_3O_4^+$; calc. 532.2236), 570.1798 ($[M+K]^+$, $C_{33}H_{29}KN_3O_4^+$; calc. 570.1795).

N-*(*tert-*Butyl)-2-[4-(dimethylamino)phenyl]-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]acetamide* (**6d**). Yield: 323 mg (61%). Orange solid. M.p. 272–274°. IR (KBr): 1670, 3318. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*s*, ^{t}Bu); 5.07 (*s*, NH); 5.82 (*s*, CH); 6.38 (*d*, *J* = 8.3, 1 arom. H); 6.59 (*t*, *J* = 7.7, 1 arom. H); 6.67 (*d*, *J* = 7.1, 2 arom. H); 7.26–7.45 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.7; 40.3; 51.8; 58.5; 111.7; 112.4; 121.2; 122.0; 122.1; 123.2; 124.0; 127.8; 128.4; 128.9; 129.0; 129.1; 129.3; 130.1; 140.2; 141.5; 141.8; 150.2; 154.5; 167.0; 167.9. HR-ESI-MS: 530.2802 ($[M+1]^+$, $C_{35}H_{36}N_3O_2^+$; calc. 530.2808), 552.2622 ($[M+Na]^+$, $C_{35}H_{35}N_3NaO_2^+$; calc. 552.2627).

N-*(*tert-*Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-2-(3,4,5-trimethoxyphenyl)acetamide* (**6e**). Yield: 449 mg (78%). Orange solid. M.p. 218–220°. IR (KBr): 1673, 1755. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.39 (*s*, ^{t}Bu); 3.79–3.83 (*m*, 3 MeO); 5.92 (*s*, NH); 6.08 (*s*, CH); 6.43 (*d*, *J* = 8.8, 1 arom. H); 6.63–6.65 (*m*, 3 arom. H); 6.86 (*d*, *J* = 7.9, 2 arom. H); 7.01 (*t*, *J* = 7.9, 1 arom. H); 7.26–7.45 (*m*, 10 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 28.6; 52.0; 56.3; 59.0; 60.8; 105.7; 111.6; 121.6; 123.0; 123.2; 123.5; 127.8; 128.5; 129.0; 129.2; 129.3; 130.1; 130.2; 138.0; 140.0; 141.2; 141.4; 153.4; 155.3; 167.2. HR-ESI-MS: 577.2697 ($[M+1]^+$, $C_{36}H_{37}N_2O_5^+$; calc. 577.2702), 599.2518 ($[M+Na]^+$, $C_{36}H_{36}N_2NaO_5^+$; calc. 599.2522), 615.2256 ($[M+K]^+$, $C_{36}H_{36}KN_2O_5^+$; calc. 615.2261).

N-*Cyclohexyl-2-[4-(dimethylamino)phenyl]-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]acetamide* (**6f**). Yield: 366 mg (66%). Orange solid. M.p. 204–206°. IR (KBr): 1675, 1742, 3328. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.09–2.00 (*m*, 5 CH_2); 2.92 (*s*, Me_2N); 3.87 (*m*, CH(cHex)); 5.89 (*d*, *J* = 7.8, NH); 6.14 (*s*, CH); 6.40 (*d*, *J* = 7.7, 1 arom. H); 6.60 (*t*, *J* = 7.6, 1 arom. H); 6.67 (*d*, *J* = 8.7, 2 arom. H); 6.84 (*d*, *J* = 7.9, 1 arom. H); 6.99 (*t*, *J* = 7.8, 1 arom. H); 7.27 (*d*, *J* = 8.8, 2 arom. H); 7.26–7.45 (*m*, 7 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 24.8; 25.5; 32.8; 33.0; 40.4; 48.7; 58.0; 111.6; 112.4; 121.3; 121.8; 122.9; 123.3; 123.9; 127.8; 128.4; 128.9; 129.1; 129.2; 129.3; 129.4; 130.2; 140.1; 141.4; 141.7; 150.2; 154.7; 167.0; 167.5. HR-ESI-MS: 556.2956 ($[M+1]^+$, $C_{37}H_{38}N_3O_2^+$; calc. 556.2964), 578.2778 ($[M+Na]^+$, $C_{37}H_{37}N_3NaO_2^+$; calc. 578.2783), 594.2517 ($[M+K]^+$, $C_{37}H_{37}KN_3O_2^+$; calc. 594.2517).

2-(1,1′-Biphenyl-4-yl)-N-*(*tert-*butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]acetamide* (**6g**). Yield: 416 mg (74%). Red solid. M.p. 173–175°. IR (KBr): 1667, 3317. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.40 (*s*, ^{t}Bu); 5.97 (*s*, NH); 6.20 (*s*, CH); 6.46 (*d*, *J* = 7.7, 1 arom. H); 6.63 (*t*, *J* = 7.6, 1 arom. H); 6.80 (*d*, *J* = 7.9, 1 arom. H); 6.99 (*t*, *J* = 7.5, 1 arom. H); 7.26–7.59 (*m*, 22 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 28.7; 52.0; 58.5; 111.7; 121.6; 123.0; 123.3; 123.6; 127.1; 127.4; 127.5; 127.9; 128.6; 128.8; 129.3; 129.3; 130.2; 133.7; 140.0; 140.4; 140.9; 141.3; 155.4; 167.2. HR-ESI-MS: 563.2693 ($[M+1]^+$, $C_{39}H_{35}N_2O_2^+$; calc. 563.2693), 585.2513 ($[M+Na]^+$, $C_{39}H_{34}N_2NaO_2^+$; calc. 585.2518).

N-*(*tert-*Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]-2-(4-methylphenyl)-acetamide* (**6h**). Yield: 325 mg (65%). Orange solid. M.p. 259–261°. IR (KBr): 1673, 3414. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.37 (*s*, Me_3C); 2.33 (*s*, Me); 5.87 (*s*, NH); 6.11 (*s*, CH); 6.42 (*d*, *J* = 9.9, 1 arom. H); 6.62 (*t*, *J* = 8.2, 1 arom. H); 6.81 (*d*, *J* = 8.3, 1 arom. H); 6.99 (*t*, *J* = 8.3, 1 arom. H); 7.14 (*d*, *J* = 8.0, 2 arom. H); 7.28 (*d*, *J* = 8.0, 2 arom. H); 7.26–7.45 (*m*, 10 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.1; 28.6; 51.9; 58.6; 111.7; 121.5; 122.9; 123.2; 123.7; 127.8; 28.1; 128.4; 128.9; 129.1; 129.2; 129.3; 129.4; 130.1; 131.7; 137.8; 140.0; 141.3; 141.4; 155.1; 167.1; 167.3. HR-ESI-MS: 501.2537 ($[M+1]^+$, $C_{34}H_{33}N_2O_2^+$; calc. 501.2542), 523.2356 ($[M+Na]^+$, $C_{34}H_{32}N_2NaO_2^+$; calc. 523.2361), 539.2095 ($[M+K]^+$, $C_{34}H_{32}KN_2O_2^+$; calc. 539.2101).

N-*(*tert-*Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]-2-[4-(propan-2-yl)-phenyl]acetamide* (**6i**). Yield: 396 mg (75%). Orange solid. M.p. 262–264°. IR (KBr):1675, 3328. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.24 (*dd*, *J* = 6.9, 1.2, 2 Me); 1.38 (*s*, ^{t}Bu); 2.89 (*m*, Me_2CH); 5.89 (*s*, NH); 6.14 (*s*, CH); 6.42 (*d*, *J* = 7.7, 1 arom. H); 6.63 (*t*, *J* = 7.6, 1 arom. H); 6.83 (*d*, *J* = 7.9, 1 arom. H); 7.00 (*t*, *J* = 8.1, 1 arom. H); 7.20 (*d*, *J* = 8.2, 2 arom. H); 7.32 (*d*, *J* = 8.2, 2 arom. H); 7.35–7.45 (*m*, 10 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.8; 23.8; 23.9; 28.6; 33.8; 51.9; 58.7; 111.7; 121.4; 122.9; 123.2; 123.7; 126.8; 127.8; 128.2; 128.4; 128.9; 129.2; 129.2; 129.3; 130.2; 132.0; 140.0; 141.3; 141.5; 148.7; 155.1; 167.1; 167.4. HR-ESI-MS: 529.2850 ($[M+1]^+$, $C_{36}H_{37}N_2O_2^+$; calc. 529.2855), 551.2669 ($[M+Na]^+$, $C_{36}H_{36}N_2NaO_2^+$; calc. 551.2674), 567.2408 ($[M+K]^+$, $C_{36}H_{36}KN_2O_2^+$; calc. 567.2414).

N-*Cyclohexyl-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]-2-phenylacetamide* (**6j**). Yield: 450 mg (88%). Orange solid. M.p. 202–204°. IR (KBr): 3308, 1700, 1655. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09–2.06 (*m*, 5 CH_2); 3.87–3.89 (*m*, CH(cHex)); 6.08 (*d*, *J* = 7.7, NH); 6.25 (*s*, CH); 6.45 (*d*, *J* = 7.7, 1 arom. H); 6.65 (*t*, *J* = 7.7, 1 arom. H); 6.82 (*d*, *J* = 7.7, 1 arom. H); 7.00 (*t*, *J* = 7.7, 1 arom. H); 7.27–7.47 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.7; 24.8; 25.5; 32.7; 32.8; 48.8; 58.2; 111.7; 121.6; 123.0; 123.3; 123.5; 127.9; 128.1; 128.5; 128.7; 129.0; 129.3; 129.4; 130.2; 134.5; 139.9; 141.2; 141.3; 155.4; 166.9; 167.1. HR-ESI-MS: 513.2537 ($[M+1]^+$, $C_{35}H_{33}N_2O_2^+$; calc. 513.2542), 535.2356 ($[M+Na]^+$, $C_{35}H_{32}N_2NaO_2^+$; calc. 535.2361).

*2-[5-Bromo-3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]*-N-*(*tert-*butyl)-2-phenylacetamide* (**6k**). Yield: 401 mg (71%). Orange solid. M.p. 304–306°. IR (KBr): 3324, 1679, 1596. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.40 (*s*, ^{t}Bu); 6.00 (*s*, NH); 6.20 (*s*, CH); 6.48 (*d*, *J* = 1.8, 1 arom. H); 6.68 (*d*, *J* = 8.5, 1 arom. H); 7.07 (*dd*, *J* = 8.5, 1.8, 1 arom. H); 7.35–7.50 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.1; 58.5; 113.5; 114.4; 122.6; 125.2; 125.8; 127.9; 128.0; 128.3; 128.5; 128.9; 129.1; 129.3; 129.7; 129.8; 130.4; 130.8; 134.4; 139.5; 140.1; 140.7; 157.1; 166.6; 167.1. HR-ESI-MS: 565.1506 ($[M+1]^+$, $C_{33}H_{30}{}^{79}BrN_2O_2^+$; calc. 565.1491), 587.1328 ($[M+Na]^+$, $C_{33}H_{29}{}^{79}BrN_2NaO_2^+$; calc. 587.1310).

N-*(*tert-*Butyl)-2-(4-cyanophenyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H-*indol-1-yl]-acetamide* (**6l**). Yield: 368 mg (72%). Orange solid. M.p. 334–336°. IR (KBr): 3313, 1671, 1600. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*s*, ^{t}Bu); 6.04 (*s*, NH); 6.18 (*s*, CH); 6.50 (*d*, *J* = 7.8, 1 arom. H); 6.71 (*t*, *J* = 7.8, 1 arom. H); 6.77 (*d*, *J* = 7.8, 1 arom. H); 7.04 (*t*, *J* = 7.8, 1 arom. H); 7.36–7.40 (*m*, 6 arom. H); 7.45–7.48

(*m*, 6 arom. H); 7.61 (*d*, *J* = 8.2, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.2; 58.0; 111.2; 111.8; 118.5; 122.2; 122.9; 123.3; 127.9; 128.7; 128.8; 129.0; 129.3; 129.5; 129.6; 130.1; 132.2; 139.7; 139.9; 140.2; 140.9; 156.6; 166.1; 167.1. HR-ESI-MS: 512.2346 ($[M+1]^+$, $C_{34}H_{30}N_3O_2^+$; calc. 512.2338), 550.1906 ($[M+K]^+$, $C_{34}H_{29}KN_3O_2^+$; calc. 550.1897).

N-*(*tert*-Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-2-[4-(trifluoromethyl)-phenyl]acetamide* (**6m**). Yield: 381 mg (70%). Orange solid. M.p. 302–304°. IR (KBr): 3314, 1668, 1596. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.37 (*s*, ^{t}Bu); 6.10 (*s*, NH); 6.21 (*s*, CH); 6.49 (*d*, *J* = 7.6, 1 arom. H); 6.69 (*t*, *J* = 7.3, 1 arom. H); 6.83 (*d*, *J* = 7.5, 1 arom. H); 7.04 (*t*, *J* = 7.3, 1 arom. H); 7.38–7.51 (*m*, 12 arom. H); 7.59 (*d*, *J* = 7.5, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.2; 58.2; 111.4; 122.0; 123.1; 123.2; 123.3; 125.3; 125.4; 125.5; 125.6 (CF_3); 127.9; 128.4; 128.6; 129.0; 129.3; 129.5; 129.6; 129.9; 130.2; 138.6; 139.8; 140.6; 141.0; 156.3. HR-MS-ESI: 555.2275 ($[M+1]^+$, $C_{34}H_{30}F_3N_2O_2^+$; calc. 555.2259), 593.1832 ($[M+K]^+$, $C_{34}H_{29}F_3KN_2O_2^+$; calc. 593.1818).

N-*Cyclohexyl-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-2-[4-(trifluoromethyl)-phenyl]acetamide* (**6n**). Yield: 493 mg (85%). Orange solid. M.p. 291–293°. IR (KBr): 3313, 1666, 1601. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08–1.37 (*m*, 5 CH_2); 3.82–3.91 (*m*, CH(cHex)); 6.24 (*d*, NH); 6.28 (*s*, CH); 6.49 (*d*, *J* = 7.7, 1 arom. H); 6.70 (*t*, *J* = 7.7, 1 arom. H); 6.82 (*d*, *J* = 7.7, 1 arom. H); 7.04 (*t*, *J* = 7.7, 1 arom. H); 7.35–7.39 (*m*, 7 arom. H); 7.43–7.51 (*m*, 6 arom. H); 7.59 (*d*, *J* = 8.2, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.6; 24.7; 25.4; 32.7; 32.6; 32.8; 48.9; 57.7; 76.6; 111.4; 122.1; 123.1; 123.2; 123.3; 125.4; 125.5 (CF_3); 127.9; 128.3; 128.7; 129.0; 129.3; 129.5; 129.6; 129.9; 130.2; 138.4; 139.8; 140.5; 141.0; 156.4; 166.4; 167.2. HR-ESI-MS: 581.2422 ($[M+1]^+$, $C_{36}H_{32}F_3N_2O_2^+$; calc. 581.2416), 603.2239 ($[M+Na]^+$, $C_{36}H_{31}F_3N_2NaO_2^+$; calc. 603.2235).

N-*(*tert*-Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-1*H*-indol-1-yl]-2-(pyridin-3-yl)acetamide* (**6o**). Yield: 422 mg (75%). Orange solid. M.p. 210–212°. IR (KBr): 3316, 1673, 1597. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*s*, ^{t}Bu); 6.10 (*s*, NH); 6.20 (*s*, CH); 6.47 (*d*, *J* = 7.7, 1 arom. H); 6.67 (*t*, *J* = 7.7, 1 arom. H); 6.82 (*d*, *J* = 7.8, 1 arom. H); 7.03 (*t*, *J* = 7.7, 1 arom. H); 7.20–7.46 (*m*, 10 arom. H, 1 pyridine H); 7.73 (*d*, *J* = 7.1, 1 pyridine H); 8.52 (*d*, *J* = 4.2, 1 pyridine H); 8.54 (*s*, 1 pyridine H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 52.1; 56.4; 111.3; 113.9; 122.1; 123.1; 123.2; 123.3; 127.9; 128.4; 128.7; 129.0; 129.3; 129.4; 129.5; 130.1; 130.5; 136.1; 139.8; 140.3; 141.0; 149.1; 156.3; 166.2; 167.1. HR-ESI-MS: 488.2320 ($[M+1]^+$, $C_{32}H_{30}N_3O_2^+$; calc. 488.2338).

N-*(*tert*-Butyl)-2-[3-(diphenylmethylidene)-2,3-dihydro-2-oxo-5-(propan-2-yl)-1*H*-indol-1-yl]-2-phenylacetamide* (**6p**). Yield: 401 mg (76%). Red solid. M.p. 244–246°. IR (KBr): 3328, 1677, 1607. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.93 (*d*, *J* = 6.9, Me); 0.95 (*d*, *J* = 6.9, Me); 1.39 (*s*, ^{t}Bu); 2.54 (*m*, CH); 5.98 (*s*, NH); 6.15 (*s*, CH); 6.25 (*d*, *J* = 1.5, 1 arom. H); 6.70 (*d*, *J* = 8.2, 1 arom. H); 6.85 (*dd*, *J* = 8.2, 1.6, 1 arom. H); 7.24–7.48 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.7; 28.6; 33.4; 51.9; 58.7; 111.3; 121.1; 123.1; 124.0; 127.0; 127.8; 128.0; 128.2; 128.6; 128.9; 129.0; 129.1; 129.3; 130.2; 134.9; 139.3; 139.8; 141.4; 141.8; 154.7; 167.2; 167.3. HR-ESI-MS: 529.2851 ($[M+1]^+$, $C_{36}H_{37}N_2O_2^+$; calc. 529.2855), 551.2671 ($[M+Na]^+$, $C_{36}H_{36}N_2NaO_2^+$; calc. 551.2674).

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