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Molecular Iodine-Mediated Cascade Reaction of 2-Alkynylbenzaldehyde and Indole: An Easy Access to Tetracyclic Indoloazulene Derivatives

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Abstract: The synthesis of iodo-substituted tetracyclic indole fused azulene derivatives was achieved from the reaction of 2-(substituted phenylethynyl)-benzaldehydes and different indoles in the presence of molecular iodine. The reaction involves the formation of a bisindole from the corresponding 2-(substituted phenylethynyl)benzaldehyde and indole followed by iodocyclization in a one-pot cascade process. A wide range of 2-(substituted phenylethynyl)-benzaldehydes and indoles were utilized in this protocol to derive a diverse range of iodo-substituted tetracyclic indole fused azulene derivatives in moderate to good yields. Further functionalizations of the iodo-substituted tetracyclic indole fused azulenes were achieved by various palladium-catalyzed cross-coupling reactions to generate highly substituted tetracyclic indole fused azulene derivatives.

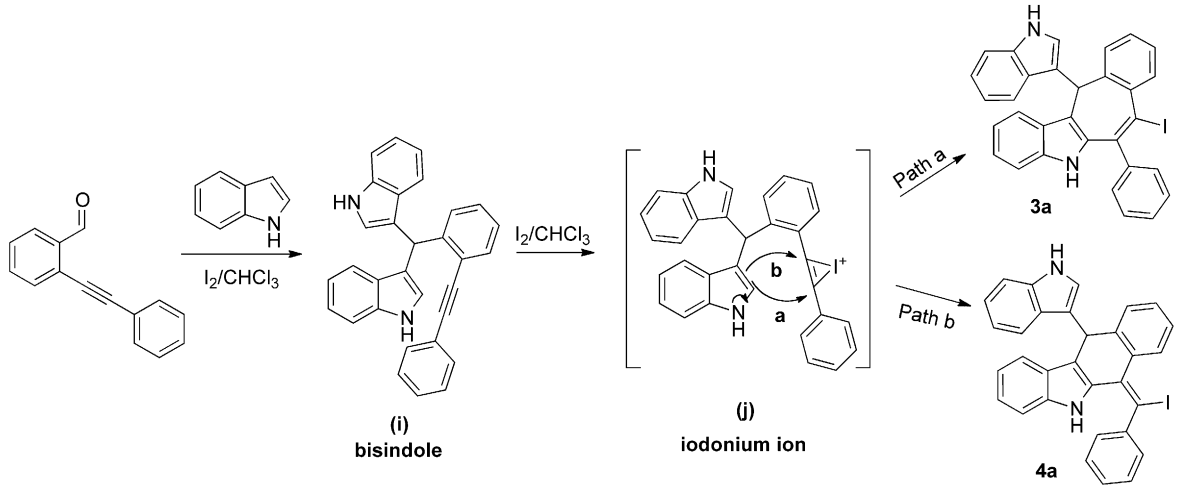
Keywords: azulenes; cascade process; cross-coupling; indoles; indoloazulenes; iodocyclization

Introduction

Medium-ring annulated indole derivatives are an important class of pharmaceutically active compounds, which exhibit a wide variety of biological activities.[1] Particularly, the seven-membered ring (azulene) annulated tetracyclic indole moiety occurs in numerous biologically active natural products and pharmaceutical intermediates, which display potent antihistaminic, antimicrobial and anticancer activities.[1,2] In general, the construction of medium sized rings is unambiguously considered to be a cumbersome task due to a combination of the transannular interactions and unfavourable entropic and enthalpic factors.[3] However, there are some reports describing the synthesis of seven-membered ring (azulene) annulated indole derivatives in the literature.[4] Most of the reported methodologies for the construction of tetracyclic indole derivatives are associated with the use of expensive metal catalysts like gold and palladium and very few of them are non-metallic protocols which require higher temperatures or having less broad substrate scopes.[5] Hence, developing an efficient and non-metallic protocol for the synthesis of azulene annulated indole tetracycle is highly desirable.

The electrophilic iodine-triggered cyclization of *ortho*-substituted arylalkynes is one of the prominent methods for the synthesis of iodine-containing fused heterocyclic derivatives.[6] A wide variety of fused heterocycles including 5-iodopyrrolo[1,2-*a*]quinolines, fused benzimidazoles, iodoisoquinoline-fused benzimidazoles, iodofuro[2,3-*b*]chromones, iodo-substituted indoloazepinones, 2-iodospiro[indene-1,10-isobenzofuran]-30-ones, dihydrocyclopenta[*b*]indole, furo[2,3-*b*]quinoline, iodopyrano[4,3-*b*]quinolines and pyrralopyridines etc. were constructed using the iodocyclization strategy.[7]

On the other hand, 2-alkynylbenzaldehyde is a handy and an interesting structural motif for the generation of functionalized polycyclic compounds and is also a very good electrophilic species for iodocyclization.[8] Our group has been interested in exploring the iodine-mediated transformations for some time.[9] In this context, we found that the reaction of aldehyde with various indoles in the presence a catalytic amount of iodine produced the corresponding bisindole in high yields. On the other hand, recently, Verma and his co-workers have reported the synthesis of indolo[1,2-*a*]quinolines *via* (6-*endo*-*dig*) iodocyclization using molecular iodine.[7d] Moreover, recently,



Scheme 1. Plausible pathway for the formation of products.

Enders and co-workers observed the formation of seven-membered (7-*endo-dig*) fused tetracyclic azulene derivatives using a gold catalyst.[4c] Based on these two observations, we envisioned that the reaction of 2-(phenylethynyl)benzaldehyde and indole in the presence of iodine could initially produce the corresponding bisindole which would further undergo iodocyclization to produce either indole fused azulene compound **3a** or benzo-fused carbazole derivative **4a** (Scheme 1).

Results and Discussion

To investigate our assumption, we choose 2-(phenylethynyl)benzaldehyde and indole as model substrates. In our initial reaction, we treated 2-(phenylethynyl)-benzaldehdye (1 equiv.) and indole (2 equiv.) in the presence of 2 equiv. of iodine (I_2) in dichloromethane at 0 °C to room temperature (Table 1, entry 1). Under these conditions, the reaction produced bisindole derivative (**i**) as a sole product. However, when 2 equiv. of sodium bicarbonate were used as base (entry 2), two products were formed. Among the two products, the major product was bisindole and the ^{1}H NMR, ^{13}C NMR, LR-MS, HR-MS, single crystal X-ray diffraction analysis revealed that the minor product was indole fused azulene compound **3a** (Figure 1). Interestingly, indole fused azulene derivatives exhibit anticancer and antineoplastic properties.[2] In fact, the syntheses of some indole fused tetracyclic azulene derivatives have reported in the literature using various metal catalysts.[4] However, to the best of our knowledge, there is no efficient, non-metallic protocol available for the construction of indole fused azulene tetracyclic derivatives. This fact prompted us to investigate the iodocyclization reaction in more detail.

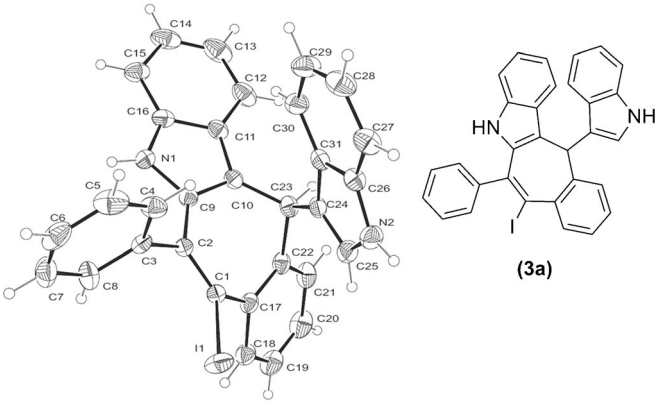
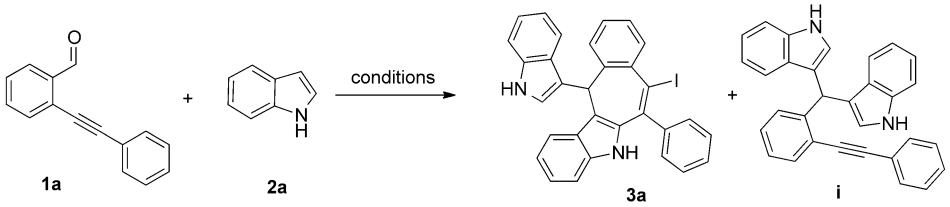


Figure 1. ORTEP diagram of single crystal X-ray diffraction structure of **3a**.[12]

To determine the best conditions for the formation of indole fused azulene (**3a**), we screened various reaction conditions. In this regard, we first evaluated the efficiency of the iodine reagent for the reaction of 2-(phenylethynyl)benzaldehdye (1 equiv.), indole (2 equiv.) and sodium bicarbonate (2 equiv.) in dichloromethane at 0 °C. The reaction results indicate that the use of molecular iodine below 3 equiv. produces the desired indole fused azulene **3a** along with bisindole as a minor product. However, the reaction with 3.2 equiv. iodine and 2 equiv. $NaHCO_3$ resulted in 66% of compound **3a** as a single product (entry 4). Next, we screened the reaction with different solvents like acetonitrile, 1,4-dioxane, THF and diethyl ether. The reaction worked in most of the solvents but did not produce high yields, however, chloroform produced the best yield of the desired product (entry 9). After solvent screening, we screened different bases such as K_2CO_3, Cs_2CO_3 and *t*-BuOK. The desired product was obtained in poor yields (entries 11, 12

Table 1. Optimization of the reaction conditions.

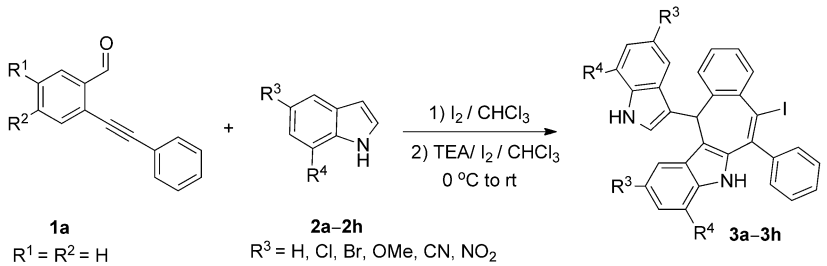


Entry	Solvent	Base (2 equiv.)	Electrophile (equiv.)	Temperature [°C]	Time [h]	Yield [%][a,b], 3a	Yield [%][a,b], i
1	CH_2Cl_2	-	I_2 (2.0)	0	1.5	-	89 (100)
2	CH_2Cl_2	$NaCH2O_3$	I_2 (2.0)	0	1.5	25 (39)	50 (65)
3	CH_2Cl_2	$NaHCO_3$	I_2 (3.0)	0	3	60 (79)	10 (15)
4	CH_2Cl_2	$NaHCO_3$	I_2 (3.2)	0	3	66 (89)	
5	CH_3CN	$NaHCO_3$	I_2 (3.2)	r.t.	1.5	35 (55)	
6	1,4-dioxane	$NaHCO_3$	I_2 (3.2)	0	2	55 (73)	
7	THF	$NaHCO_3$	I_2 (3.2)	r.t.	1.5	33 (56)	
8	diethyl ether	$NaHCO_3$	I_2 (3.2)	0	2	45 (61)	
9	$CHCl_3$	Na_2CO_3	I_2 (3.2)	0	1.5	70 (87)	
10	$CHCl_3$	Na_2CO_3	I_2 (3.2)	0	1.5	70 (89)	
11	$CHCl_3$	K_2CO_3	I_2 (3.2)	0	2	20 (35)	
12	$CHCl_3$	Cs_2CO_3	I_2 (3.2)	0	2	10 (19)	
13	$CHCl_3$	K_3PO_4	I_2 (3.2)	0	2	74 (92)	
14	$CHCl_3$	*t*-BuOK	I_2 (3.2)	0	1.5	22 (39)	
15	**$CHCl_3$**	**TEA**	**I_2 (3.2)**	**0 to r.t.**	**9**	**84 (100)**	
16	$CHCl_3$	DIPEA	I_2 (3.2)	0 to .r.t	12	60 (75)	
17	$CHCl_3$	DBU	I_2 (3.2)	0 to r.t.	15	65 (75)	
18	$CHCl_3$	DABCO	I_2 (3.2)	0 to r.t.	18	58 (77)	
19	$CHCl_3$	TEA	ICl (3.2)	0	1.5	20 (39)	
20	$CHCl_3$	TEA	NIS(3.2)	0 to r.t.	16	37 (51)	11 (18)
21	$CHCl_3$	TEA	I_2 (2.0)	0 to r.t.	17	17 (23)	67 (75)
22	$CHCl_3$	TEA	I_2 (2.5)	0 to r.t.	17	51 (60)	31 (37)
23	$CHCl_3$	TEA	I_2 (3.0)	0 to r.t.	17	72 (81)	15 (18)

[a] Reactions were performed on a 0.25-mmol scale.
[b] Yields refer to isolated and purified compound. Values in parentheses correspond to the NMR yield using CH_2Br_2 as an internal standard.

and 14). However, the reactions furnished good yields of the expected product when the mild bases such as Na_2CO_3 and K_3PO_4 were used instead (entries 10 and 13).

Table 2. Iodine-mediated tandem cyclization of 2-(phenylethynyl)benzaldehyde and various indole derivatives.



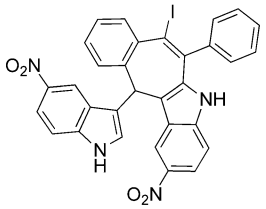
1a
$R^1 = R^2 = H$

2a–2h
R^3 = H, Cl, Br, OMe, CN, NO_2
R^4 = H, Me, Et.

3a–3h

Entry	Indole (**2**)	Product (**3**)	Time [h]	Yield [%][a,b,c,d]
1	R^3 = H, R^4 = H, **2a**	**3a**	9	84 (100)
2	R^3 = Cl, R^4 = H, **2b**	**3b**	8	77 (98)
3	R^3 = Br, R^4 = H, **2c**	**3c**	6	80 (95)
4	R^3 = H, R^4 = Me, **2d**	**3d**	10	80 (96)
5	R^3 = H, R^4 = Et, **2e**	**3e**	13	79 (99)
6	R^3 = OMe, R^4 = H, **2f**	**3f**	18	68 (81)
7	R^3 = CN, R^4 = H, **2g**	**3g**	18	77 (93)[d]

Table 2. (Continued)

Entry	Indole (**2**)	Product (**3**)	Time [h]	Yield [%][a,b,c,d]
8	$R^3 = NO_2$ $R^4 = H$ **2h**	**3h** 	18	71 (87)[d]

[a] All reactions were performed with 0.25 mmol of aldehyde **1a** and 0.5 mmol of indole **2a**–**2h**.
[b] Iodine (3.2 equiv.) and triethylamine (2.0 equiv.) in $CHCl_3$.
[c] Yields refer to isolated and purified compound. Values in parentheses correspond to the NMR yield using CH_2Br_2 as an internal standard.
[d] The reactions were carried out at 60 °C.

Moreover, we screened the reaction in the presence of organic bases. When the reaction was carried out in the presence of strong organic bases such as DIPEA (*N*,*N*-diisopropylethylamine), DBU (1,8-diazabicycloundec-7-ene) and weak base such as DABCO (1,4-diazabicyclo[2.2.2]octane), the desired product was obtained in moderate yields (entries 16, 17 and 18). To our delight, in the presence of TEA (triethylamine) the reaction gave the best result with 84% isolated yield (100% NMR yield) of the desired product in 9 h (entry 15). Furthermore, we also screened different iodine sources for this reaction. NIS (*N*-iodosuccinimide) and ICl (iodine monochloride) gave the desired product in poor yields (entries 19 and 20). Molecular iodine was found to be the best choice for this reaction. The reaction was also tested using varied quantities of iodine with TEA as base (entries 21-'-23). However, in the presence of iodine at less than 3.2 equiv., the reactions were incomplete and resulted in poor yield of the desired product.

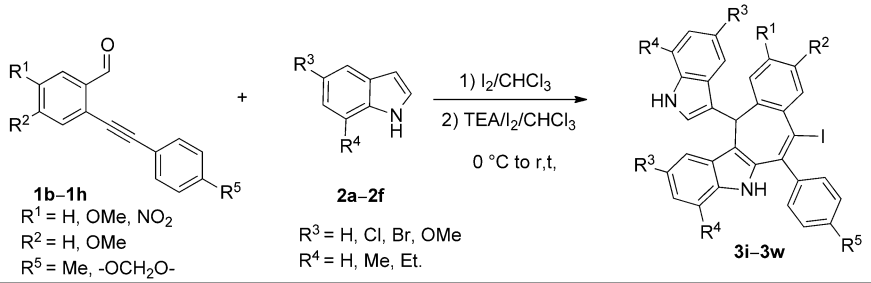
To compare the stepwise and one-pot reactions, the intermediate bisindole (**i**) was prepared by the reaction of 1 equiv. of aldehyde (**1a**) and 2 equiv. of indole (**2a**) in the presence of a catalytic amount of iodine. Then, the bisindole was treated with 2.2 equiv. of iodine and 2 equiv. of triethylamine. The reaction resulted in 100% NMR yield and 88% isolated yield of the desired product in 8 h. The stepwise and one-pot reaction produced almost similar results. Hence, the scope of reaction was examined with the one-pot reaction conditions.

After the optimization of reaction conditions, the scope and limitations of this one-pot tandem iodocyclization of the indole fused tetracyclic azulene was further investigated by using various 2-(phenylethynyl)benzaldehydes and substituted indole derivatives.

The reaction of **1a** with unsubstituted indole under the optimized reaction conditions, gave the corresponding product **3a** in excellent yield (Table 2, entry 1). However, moderately electron-withdrawing groups such as chloro and bromo on the indoles produces the corresponding compounds **3b** and **3c** in good yields in shorter reaction times (entries 2 and 3). Indoles with moderately electron-donating groups (methyl and ethyl) also provided the desired products **3d** and **3e** in good yields with longer reaction times (entries 4 and 5). On the other hand, the reaction of **1a** with indole bearing a strong electron-donating group such as methoxy gave the desired product **3f** in moderate yield (entry 6). It is worthy of note that reactions of indoles possessing electron-donating groups required longer reaction times compared to indoles with electron-withdrawing groups. Furthermore under the standard reaction conditions, those indole derivatives possessing strong electron-withdrawing groups like nitro or cyano furnished only traces of the intermediate bisindole derivatives. However, when the reactions were carried out at 60 °C, they produced thecorresponding tetracyclic derivatives **3g** and **3h** in good yields. The need for higher temperature may be due to the less nucleophilic nature of the indoles.

Next, we investigated the tandem iodocyclization of various substituted 2-(phenethynyl)benzaldehydes and substituted indoles. As depicted in Table 3, the reactions of 2-(phenylethynyl)benzaldehydes having both electron-donating (OMe) and electron-withdrawing (NO_2) substitutions with indole delivered the desired products **3i** and **3j** in good yields (entries 1 and 2). However, the nitro aldehyde forms the corresponding compound faster than the methoxy aldehyde. Moreover, the aldehydes possessing strong electron-donating groups such as **1d** and **1e** gave the expected products **3k** and **3l** in moderate yields, with longer reaction times (entries 3 and 4). On the other hand, the reactions of methyl-substituted indole (**2d**) with aldehydes **1b** and **1c** furnished the desired products **3m** and **3n** in good yields but nitro aldehyde **1c**

Table 3. Iodine-mediated tandem cyclization of 2-(phenylethynyl)benzaldehyde and various indole derivatives.



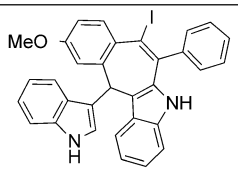
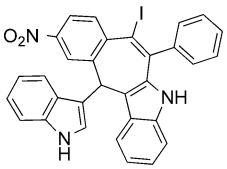
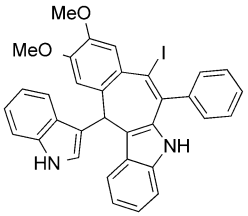
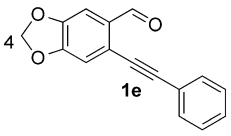
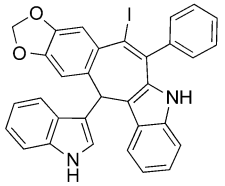
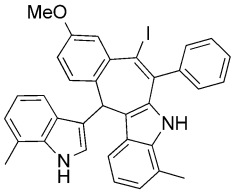
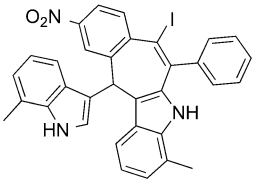
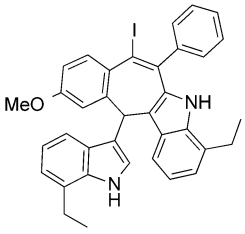
Entry	Aldehyde	Indole	Product		Time [h]	Yield [%][a,b,c]
1	R^1 = OMe, R^2 = H, **1b**	R^3 = H, R^4 = H, **2a**		**3i**	15	83 (100)
2	R^1 = NO_2, R^2 = H, **1c**	R^3 = H, R^4 = H, **2a**		**3j**	11	78 (100)
3	R^1 = OMe, R^2 = OMe, **1d**	R^3 = H, R^4 = H, **2a**		**3k**	19	61 (82)
4	 **1e**	R^3 = H, R^4 = H, **2a**		**3l**	18	69 (91)
5	R^1 = OMe, R^2 = H, **1b**	R^3 = H, R^4 = Me, **2d**		**3m**	14	75 (91)
6	R^1 = NO_2, R^2 = H, **1c**	R^3 = H, R^4 = Me, **2d**		**3n**	10	61 (79)
7	R^1 = OMe, R^2 = H, **1b**	R^3 = H, R^4 = Et, **2e**		**3o**	17	75 (100)

Table 3. (Continued)

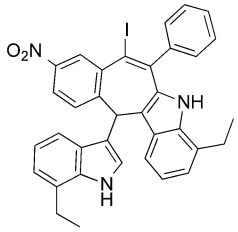
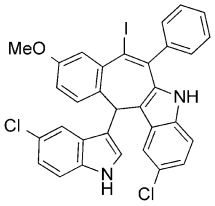
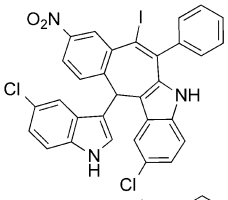
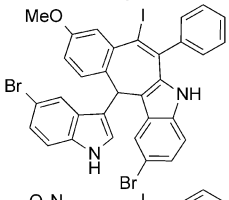
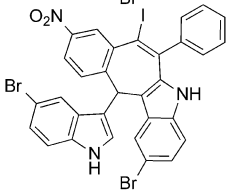
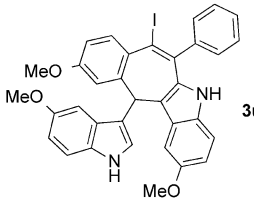
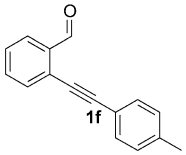
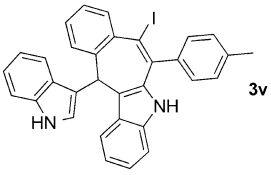
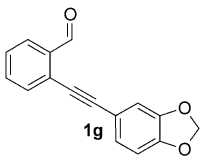
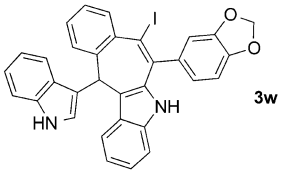
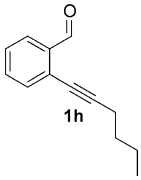
Entry	Aldehyde	Indole	Product	Time [h]	Yield [%][a,b,c]
8	$R^1 = NO_2$ $R^2 = H$ **1c**	$R^3 = H$ $R^4 = Et$ **2e**	 **3p**	12	68 (79)
9	$R^1 = OMe$ $R^2 = H$ **1b**	$R^3 = Cl$ $R^4 = H$ **2b**	 **3q**	11	73 (91)
10	$R^1 = NO_2$ $R^2 = H$ **1c**	$R^3 = Cl$ $R^4 = H$ **2b**	 **3r**	11	85 (99)
11	$R^1 = OMe$ $R^2 = H$ **1b**	$R^3 = Br$ $R^4 = H$ **2c**	 **3s**	9	77 (100)
12	$R^1 = NO_2$ $R^2 = H$ **1c**	$R^3 = Br$ $R^4 = H$ **2c**	 **3t**	5	78 (97)
13	$R^1 = OMe$ $R^2 = H$ **1b**	$R^3 = OMe$ $R^4 = H$ **2f**	 **3u**	18	62 (82)
14	 **1f**	$R^3 = H$ $R^4 = H$ **2a**	 **3v**	13	68 (89)

Table 3. (Continued)

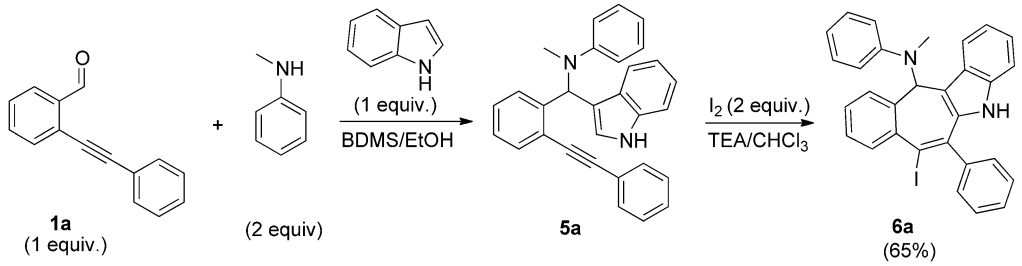
Entry	Aldehyde	Indole	Product	Time [h]	Yield [%][a,b,c]
15	 **1g**	R^3 = H R^4 = H **2a**	 **3w**	20	62 (81)
16	 **1h**	R^3= H R^4= H **2a**	-	-	–[d]

[a] All reactions were performed on a 0.25-mmol scale of aldehyde **1a–1h** and 0.5 mmol of indole **2a–2f**.
[b] Iodine (3.2 equiv.) and triethylamine (2.0 equiv.) in $CHCl_3$.
[c] Yields refer to isolated and purified compound. Values in parentheses correspond to the NMR yield using CH_2Br_2 as an internal standard.
[d] Inseparable mixture of products.

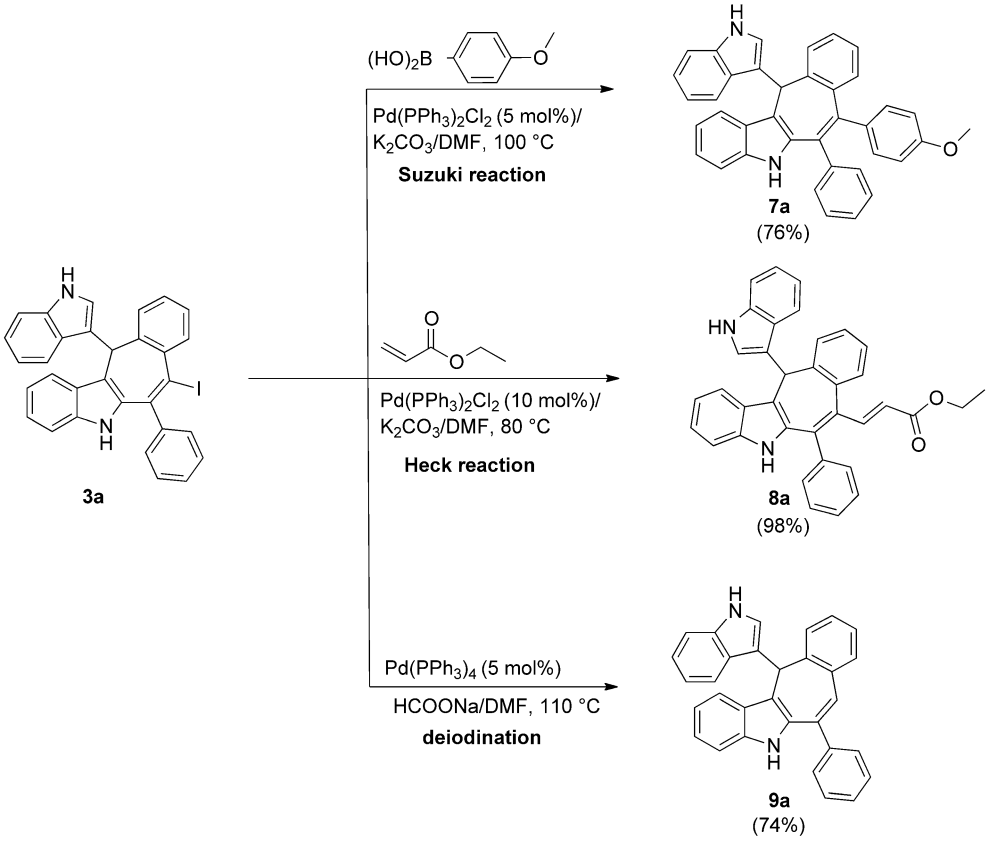
took a longer time. A similar trend was observed when ethyl-substituted indole (**2e**) was used (entries 7 and 8) to obtain the corresponding products **3o** and **3p**. The reactions of indoles containing moderate electron-withdrawing groups such as chloro and bromo gave the desired products in good yields with 5-methoxy-2-(phenylethynyl)benzaldehyde (**1b**) and 5-nitro-2-(phenylethynyl)benzaldehyde (**1c**) (entries 9–12). Furthermore, the scope of the reaction was examined with mild and strong electron-donating substitution at the aromatic alkynes. The moderately electron-donating methyl-substituted alkyne aldehyde **1f** produced the compound **3v** in better yield and shorter reaction time than compound **3w** when the strong electron-donating methyleneoxy alkyne aldehyde was used as a substrate (entries 14 and 15). This protocol failed to produce the corresponding product with aliphatic 2-(hex-1-yn-1-yl)benzaldehyde. Probably the bulky long chain alkyl group may prevent the attack of indole on the intermediate iodonium ion to form the corresponding tetracyclic compound. This may lead to decomposition or formation of several other products. (entry 16).

In order to extend the scope of our protocol, we synthesized *N*-{(1*H*-indol-3-yl)[2-(phenylethynyl)phenyl]methyl}-*N*-methylaniline (**5a**) using *N*-methylaniline (2 equiv.), 2-(phenylethynyl)benzaldehyde (1 equiv.) and indole (1 equiv.) in ethanol with bromodimethylsulfonium bromide (BDMS, 10 mol%) to obtain crude compound **5a**.[11] Then, the crude compound (**5a**) was treated with iodine (2 equiv.) and triethylamine (2 equiv.) to yield compound (**6a**) in 65% yield together with 10% unreacted starting material (Scheme 2). The unreacted starting material was not consumed even after the addition of extra iodine to the reaction mixture.

The presence of an iodo group in the tetracyclic system gave us the opportunity to generate diverse functionalized indole fused tetracyclic azulene derivatives by various palladium-catalyzed C–C bond coupling reactions (Scheme 3).[11] In this regard, compound **3a** was treated with 4-methoxyphenylboronic



Scheme 2. Synthesis of amino-substituted tetracyclic indole fused azulene (**6a**).



Scheme 3. Functionalization of indolotetracyclic azulene (**3a**).

acid under Suzuki reaction conditions to afford compound **7a** in 76% yield.[11a] Next, **3a** was treated with ethyl acrylate in the presence of bis(triphenylphosphine)palladium(II) dichloride and K_2CO_3 as a base in DMF to afford the Heck-type product **8a** in excellent yield (98%).[11b] Finally, compound **3a** was deiodinated by tetrakis(triphenylphosphine)palladium(0) and sodium formate to furnish the product **9a** in moderate yield (74%).[11c]

Conclusions

In conclusion, we have developed an easy, efficient and non-metallic protocol for the construction of tetracyclic indoloazulene derivatives by the sequential iodocyclization of 2-(phenylethynyl)benzaldehyde and indole *via* bisindole in the presence of molecular iodine and base. Wide ranges of 2-(substituted phenylethynyl)benzaldehydes and indoles were utilized in this reaction to derive a diverse array of iodo-substituted tetracyclic indole fused azulene derivatives in good to moderate yields. Interestingly, the reaction is completely regioselective and only iodo-substituted tetracyclic indole fused azulene derivatives were obtained. The present method was applied to synthesize the amino-substituted tetracyclic indole fused azulene derivative (**6a**). Finally, the iodo compound (**3a**) was successfully utilized for further functionalization with C–C bond coupling reactions such as Suzuki, Heck and deiodination to furnish a diverse array of functionalized tetracyclic indole fused azulene derivatives.

Experimental Section

General Information

All chemicals were purchased from various sources and were used directly without further purification. Analytical thin-layer chromatography was performed using silica gel 60F glass plates and silica gel 60 (230–400 mesh) was used in flash chromatographic separations. NMR spectra were recorded in DMSO-d_6 with DMSO and $CDCl_3$ with $CHCl_3$ as the internal standards for ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz). Coupling constants were expressed in Hertz. HR-mass spectra were recorded using the MALDI, ESI^- or ESI^+ mode. Melting points were recorded using an electrothermal capillary melting point apparatus and are uncorrected.

2-(1*H*-Indol-3-yl)-9-iodo-10-phenyl-12-azatetracyclo-[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13(18),14,16-octaene (3a); Typical Procedure for the Synthesis of 3a–3w

To an ice-cold solution of **1a** (0.25 mmol) and indole (0.5 mmol) in $CHCl_3$ (5 mL) was added a solution of I_2 (1.1 equiv.) in $CHCl_3$ (5 mL) dropwise. After stirring of the reaction mixture for 10 min, triethylamine (2 equiv.) was added dropwise. To this resulting mixture, an additional solution of I_2 (2.1 equiv.) in $CHCl_3$ was added followed by stirring at room temperature. The progress of the reaction was monitored by TLC. After the completion of the reaction, saturated aqueous $Na_2S_2O_3$ (5 mL) was added to the mixture, which was further stirred for 2 min. The resulting mixture was then extracted with $CHCl_3$ (2×20 mL). The organic layer washed with water and brine. The organic layer was dried over $MgSO_4$, filtered and then concentrated under reduced pressure to obtain the crude product. The crude compound was then purified by column chromatography using hexane-ethyl acetate as the eluent to yield compound **3a**.

Synthesis of 9-Iodo-*N*-methyl-*N*,10-diphenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaen-2-amine (6a)

To a stirred solution of **1a** (0.5 mmol) and *N*-methylaniline (1 mmol) in EtOH (2 mL) was added BDMS (10 mol%). The mixture was then stirred at room temperature for 20 min followed by the addition of indole (0.5 mmol). The reaction mixture was then stirred at room temperature for 15 h. The progress of reaction was monitored by TLC. After completion of the reaction, the solution was diluted with water (25 mL) and then extracted with ethyl acetate (3× 30 mL). The organic layer washed with water and brine. The organic layer was dried over $MgSO_4$, filtered and then concentrated under reduced pressure to obtain the crude product **5a**. The crude compound was directly used for next step due to its poor stability.

To an ice-cold solution of **5a** in $CHCl_3$ (10 mL) was added a solution of I_2 (2 equiv.) in $CHCl_3$ (20 mL) dropwise. Then to this was added TEA (2 equiv.) dropwise. The reaction mixture was then stirred at room temperature. The progress of reaction was monitored by TLC. After the completion of the reaction, $CHCl_3$ (20 mL) was added. The excess of iodine was removed by washing with saturated aqueous $Na_2S_2O_3$, water and brine successively. The organic layer was dried over $MgSO_4$, filtered and then concentrated under reduced pressure to yield crude product. The crude compound was then purified by column chromatography using hexane-ethyl acetate as the eluent to afford compound **6a** as a white solid.

2-(1*H*-Indol-3-yl)-9-(4-methoxyphenyl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (7a)

To a solution of **3a** (1 equiv.) and 4-methoxyphenylboronic acid (1.2 equiv.) in DMF (10 mL) was added $PdCl_2(PPh_3)_2$ (10 mol%). The mixture was then stirred at room temperature for 15 min followed by the addition of K_2CO_3 (2 equiv.). The reaction mixture was the stirred at 110 °C for 8 h. The progress of reaction was monitored by TLC. After the completion of the reaction, the solution was allowed to cool, was diluted with ice/water (25 mL) and then extracted with ethyl acetate (3×40 mL). The organic layer washed with water and brine. The organic layer was dried over $MgSO_4$, filtered and then concentrated under reduced pressure to obtain the crude product. The crude compound was then purified by column chromatography using hexane-ethyl acetate as the eluent to yield compound **7a** as a light pink solid.

Ethyl (2*E*)-3-{2-(1*H*-Indol-3-yl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaen-9-yl}prop-2-enoate (8a)

To a stirred solution of **3a** (1 mmol) in 5 mL DMF in a 10-mL flask was added $PdCl_2(PPh_3)_2$ (10 mol%) and the mixture stirred for 15 min under an argon atmosphere. Then ethyl acrylate (2.5 equiv.) was added to the reaction mixture. After 15 min, K_2CO_3 (2.5 equiv.) was added. The reaction mixture was then stirred at 100 °C for 7 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature, dilued with ice/water (50 mL) and extracted with ethyl acetate (3×50 mL). The organic layer was washed with cold water (100 mL) and finally with brine (50 mL). The ethyl acetate later was dried over $MgSO_4$, filtered and then concentrated under reduced pressure. The crude compound was then purified by column chromatography using hexane-ethyl acetate as the eluent to afford compound **8a** as a white solid.

2-(1*H*-Indol-3-yl)-10-phenyl-12-azatetracyclo-[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (9a)

To a stirred solution of compound **3a** (0.5 mmol) and sodium formate (3 equiv.) in DMF (5 mL) was added $Pd(PPh_3)_4$ (5 mol%) and the mixture heated at 110 °C for 6 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature. The solution was diluted with water (25 mL) and then extracted with ethyl acetate (3× 30 mL). The organic layer washed with water and brine. The organic layer was dried over $MgSO_4$, filtered and then concentrated under reduced pressure to obtain the crude product. The crude compound was the purified by column chromatography using ethyl acetate-hexane for afford pure compound **9a** as a white solid.

Spectral Data of New Compounds

3,3′-{[2-(Phenylethynyl)phenyl]methylene}bis(1*H*-indole) (i): Yield: 89%; white solid; mp 250–252 °C; FT-IR (KBr): ν= 3431, 1635, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.86 (brs, 2H), 7.57 (d, J=7.16 Hz, 1H), 7.38 (m, 2H), 7.35 (m, 8H), 7.24–7.31 (m, 2H), 7.05 (t, J=7.44 Hz, 2H), 6.85 −6.90 (m, 4H), 6.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 147.2, 137.1, 132.4, 131.6, 129.1, 129.0, 128.9, 127.2, 126.6, 124.3, 122.9, 122.0, 121.5, 119.1, 118.8, 117.9, 112.0, 93.9, 88.9, 37.9; LR-MS (ESI): m/z (relative intensity)=421 (80) [M−H]$^-$, 127 (20); HR-MS (ESI): m/z=421.1704, calcd. for $C_{31}H_{22}N_2$ [M−H]$^-$: 421.1705.

2-(1*H*-Indol-3-yl)-9-iodo-10-phenyl-12-azatetracyclo-[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13(18),14,16-octaene (3a): Yield: 84%; white solid; mp 209–211 °C; FT-IR (KBr): ν = 3468, 3431, 1635, 704 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.74 (brs, 1H), 10.25 (brs, 1H), 8.08–8.09 (m, 1H), 7.89 (d, *J* = 7.56 Hz, 1H), 7.60–7.62 (m, 2H), 7.36–7.40 (m, 2H), 7.28–7.33 (m, 5H), 7.13–7.15 (m, 3H), 6.96–6.99 (m, 2H), 6.71 (t, *J* = 7.48 Hz, 1H), 6.62 (s, 1H), 6.06 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.7, 144.1, 139.5, 138.8, 136.8, 134.9, 130.3, 129.2, 128.9, 128.0, 127.7, 127.4, 126.4, 126.4, 125.5, 123.0, 122.3, 121.2, 120.5, 119.1, 118.9, 117.9, 117.8, 113.5, 111,7, 111.2, 105.3, 38.8; LR-MS (EI): *m/z* (relative intensity) = 549 (90) [M + H]$^+$, 307 (40); HR-MS: *m/z* = 549.0826, calcd. for $C_{31}H_{21}IN_2$ [M + H]$^+$: 549.0828.

16-Chloro-2-(5-chloro-1*H*-indol-3-yl)-9-iodo-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3b): Yield: 77%; yellow solid; mp 213–215 °C; FT-IR (KBr): ν = 360, 3400, 580 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.99 (brs, 1H), 10.49 (brs, 1H), 8.22 (s, 1H), 7.88 (d, *J* = 7.72 Hz, 1H), 7.67 (d, *J* = 7.60 Hz, 2H), 7.39–7.42 (m, 2H), 7.31- 7.34 (m, 4H), 7.29 (s, 1H), 7.14–7.16(m, 2H), 6.99 (dd, *J* = 1.19 Hz, 8.52 Hz, 1H), 6.89 (d, *J* = 1.96 Hz, 1H), 6.70 (s, 1H), 6.11 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.5, 143.4, 139.2, 138.8, 135.1, 135.0, 134.9, 131.9, 129.4, 128.9, 128.2, 127.9, 127.4, 127.4, 126.5, 125.6, 124.8, 123.8, 122.5, 122.4, 120.5, 120.3, 118.1, 117.1, 113.4, 113.3, 112.8, 106.5, 38.1; LR-MS (ESI): *m/z* (relative intensity) = 615 (100) [M − H]$^-$, 553 (60); HR-MS: *m/z* = 614.9898, calcd. for $C_{32}H_{21}Br_2IN_2O$ [M − H]$^-$: 614.9892.

16-Bromo-2-(5-bromo-1*H*-indol-3-yl)-9-iodo-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3c): Yield: 80%; light yellow solid; mp 245–246 °C; FT-IR (KBr): ν = 3808, 3372, 1447, 585 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.0 (brs, 1H), 10.50 (brs, 1H), 8.36 (s, 1H), 7.87 (d, *J* = 7.68 Hz, 1H), 7.67 (d, *J* = 6.92 Hz, 1H), 7.39–7.42 (m, 3H), 7.31–7.34 (m, 2H), 7.28 (m, 1H), 7.25- 7.26 (m, 3H), 7.10–7.11 (m, 1H), 7.07–7.08 (m, 2H), 6.68 (s, 1H), 6.11 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.4, 143.6, 139.1, 138.8, 135.3, 135.0, 131.6, 129.4, 128.9, 128.2, 128.1, 127.9, 127.4, 127.2, 125.6, 124.9, 124.5, 122.9, 121.2, 120.3, 120.2, 117.4, 113.7, 113.3, 113.2, 111.8, 110.5, 106.4, 38.8; LR-MS (ESI): *m/z* (relative intensity) = 703 (65) [M − H]$^-$, 643 (80); HR-MS: *m/z* = 702.8878, calcd. for $C_{31}H_{19}Br_2IN_2$ [M − H]$^-$: 702.8881.

9-Iodo-14-methyl-2-(7-methyl-1*H*-indol-3-yl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3d): Yield: 80%; white solid; mp 246–248 °C; FT-IR (KBr): ν = 3446, 3422, 1620, 745 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.69 (brs, 1H), 9.93 (brs, 1H), 7.89 (dd, *J* = 15.08 Hz, 7.96 Hz, 2H), 7.56–7.59 (m, 2H), 7.32–7.37 (m, 2H), 7.29–7.30 (m, 3H), 7.04–7.08 (m, 2H), 6.92–6.97 (m, 2H), 6.79 (d, *J* = 6.84 Hz, 1H), 6.64–6.67 (m, 2H), 6.00 (s, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.4, 144.4, 139.6, 139.2, 136.3, 135.9, 134.9, 130.2, 129.5, 129.1, 127.7, 127.6, 127.3, 126.1, 125.5, 125.3, 123.2, 122.7, 121.1, 120.8, 119.9, 119.4, 118.0, 116.5, 115.5, 114.6, 113.7, 105, 39.0, 16.9, 16.6; LR-MS (EI): *m/z* (relative intensity) = 577 (100) [M + H]$^+$, 578 (60); HR-MS: *m/z* = 577.1135, calcd. for $C_{33}H_{25}IN_2$ [M + H]$^+$: 577.1141.

14-Ethyl-2-(7-ethyl-1*H*-indol-3-yl)-9-iodo-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3e): Yield: 79%; yellow solid; mp 216–218 °C; FT-IR (KBr): ν = 3489, 3469, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.68 Hz, 1H), 7.96 (d, *J* = 7.92 Hz, 1H), 7.85 (brs, 1H), 7.49–7.51 (m, 3H), 7.34–7.41 (m, 3H), 7.25–7.32 (m, 3H), 7.12–7.14 (m, 2H), 6.96–7.02 (m, 2H), 6.85 (t, *J* = 7.44 Hz, 1H), 6.72 (brs, 1H), 6.03 (s, 1H), 2.83 (q, *J* = 7.48 Hz, 15.0 Hz, 2H), 2.67 (q, *J* = 7.28 Hz, 14.80 Hz, 2H), 1.35 (t, *J* = 7.52 Hz, 3H) 1.25 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.8, 143.7, 139.3, 139.1, 135.6, 135.5, 130.2, 129.6, 129.3, 128.8, 128.6, 128.2, 127,7, 126.6, 126.4, 126.2, 125.7, 122.9. 122.6, 121.8, 120.5, 120.5, 119.6, 117.6, 116.1, 115.6, 105.4, 40.3, 23.9, 23.6, 13.9, 13.4; LR-MS (EI): *m/z* (relative intensity) = 604 (100) [M]$^+$, 603 (40); HR-MS: *m/z* = 604.1372, calcd. for $C_{35}H_{29}IN_2$ [M]$^+$: 604.1376.

9-Iodo-16-methoxy-2-(5-methoxy-1*H*-indol-3-yl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3f): Yield: 68%; grey solid; mp 220–222 °C; FT-IR (KBr): ν = 3500, 3450, 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.56 Hz, 1H), 7.79 (s, 1H), 7.52 (m, 3H), 7.38–7.47 (m, 2H), 7.29–7.36 (m, 3H), 7.06–7.15 (m, 3H), 6.90 (d, *J* = 7.92 Hz, 1H), 6.74 (d, *J* = 7.32 Hz, 1H), 6.62 (s, 1H), 6.40 (s, 1H), 5.92 (s, 2H), 3.96 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 153.6, 152.2, 144.9, 143.9, 139.6, 138.9, 135.1, 132.2, 131.5, 130.9, 129.3, 129.1, 128,0, 127.6, 126,7, 125.9, 125.3, 123.5, 121.0, 113.5, 112.9, 112.5, 111.6, 110.3, 105.1, 101.3, 99.5, 55.5, 54.6, 38.8; LR-MS (EI): *m/z* (relative intensity) = 608 (100) [M]$^+$, 607 (95); HR-MS; *m/z* = 608.0959, calcd. for $C_{33}H_{25}IN_2O_2$ [M]$^+$: 608.0961.

2-(5-Cyano-1*H*-indol-3-yl)-10-iodo-9-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene-16-carbonitrile (3g): Yield: 77%; white solid; mp 216–218 °C; FT-IR (KBr): ν = 3480, 3494, 2280, 650 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.46 (bs, 1H), 10.97 (bs, 1H), 8.79 (s, 1H), 7.88 (d, *J* = 7.61 Hz, 1H), 7.68–7.70 (m, 2H), 7.46–7.52 (m, 5H), 7.35 (m, 4H), 7.22 (m, 2H), 6.87 (s, 1H), 6.27(s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.1, 143.3, 138.9, 138.8, 138.3, 135.2, 132.7, 129.8, 128.5, 128.3, 127.5, 127.4, 126.2, 126.0, 125.8, 125.8, 125.3, 125.1, 124.4, 124.1, 123.4, 121.2, 120.8, 120.7, 114.6, 113.1, 112.9, 107.5, 101.5, 100.1, 37.8; LR-MS (EI): *m/z* (relative intensity) = 598 (100) [M]$^+$; HR-MS: *m/z* = 598.0654, calcd. for $C_{35}H_{19}IN_4$ [M]$^+$: 598.0650.

10-Iodo-16-nitro-2-(5-nitro-1*H*-indol-3-yl)-9-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3h): Yield: 71%; yellow solid; mp 220–222 °C; FT-IR (KBr): ν = 3500, 3455, 1650 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.62 (bs, 1H), 11.13 (bs, 1H), 9.29 (s, 1H), 8.07 (dd, *J* = 1.76 Hz, 7.28 Hz, 1H), 7.89–7.91 (m, 2H), 7.82–7.87 (m, 2H), 7.80(s, 1H), 7.49–7.44(m, 4H), 7.38–7.35 (m, 4H), 6.92(s, 1H), 6.46 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144, 143.1, 141.2, 139.9, 139.9, 139.7, 138.9, 138.8, 135.2, 133.8, 129.9, 128.5, 128.3, 127.6, 126.9, 126.1, 125.6, 124.9, 122.5, 117.9, 116.3, 116.2, 116.1, 115.8, 112.3, 112.3, 111.9, 107.9, 37.8; LR-MS (EI): *m/z* (relative intensity) = 638 (100) [M]$^+$, 637 (95); HR-MS: *m/z* = 638.0459, calcd. for $C_{31}H_{19}IN_4O_4$ [M]$^+$: 638.0451.

2-(1*H*-Indol-3-yl)-9-iodo-5-methoxy-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3i): Yield: 83%; yellow solid; mp 180–181 °C; FT-IR (KBr): ν = 3468, 1636, 339 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.73 (brs, 1H), 10.19 (brs, 1H), 8.09 (s,

1H), 7.81 (d, J=8.64 Hz, 1H), 7.27–7.29 (m, 5H), 7.13–7.20 (m, 4H), 6.95–7.00 (m, 2H), 6.88–6.90 (d, J=8.24 Hz, 1H), 6.69 (t, J=7.32 Hz, 1H), 6.63 (s, 1H), 6.01 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=160.0, 145.5, 144.9, 138.3, 136.7, 136.6, 136.4, 131.7, 130.5, 129.0, 127.9, 127.6, 126.4, 125.7, 122.2, 120.6, 120.5, 119.0, 118.9, 117.9, 117.8, 113.6, 112.0, 111.7, 111.3, 111.1, 105.6, 55.3, 38.9; LR-MS: m/z (relative intensity)=579 (100) $[M+H]^+$, 541 (80), 527 (30); HR-MS: m/z=579.0934, calcd. for $C_{32}H_{23}IN_2O$ $[M+H]^+$: 579.0933.

2-(1*H*-Indol-3-yl)-9-iodo-5-nitro-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3j); Yield: 78%; yellow solid; mp 223–225 °C; FT-IR (KBr): ν=3450, 1530, 1365, 600 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.81 (brs, 1H), 10.40 (brs, 1H), 8.65 (s, 1H), 8.19–8.22 (s, 1H), 8.12–8.13 (m, 2H), 7.31–7.34 (m, 4H), 7.28–7.29 (m, 2H), 7.15–7.19 (m, 3H), 6.98 (t, J=7.32 Hz, 1H), 6.86–6.88 (m, 1H), 6.70 (t, J=7.40 Hz, 1H), 6.62 (s, 1H), 6.39 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=147.3, 145.1, 144.9, 144.1, 141.6, 137.1, 136.5, 136.2, 130.2, 128.8, 128.1, 127.9, 126.2, 125.4, 123.8, 122.8, 121.9, 120.9, 120.6, 119.9, 119.3, 118.8, 118.5, 117.9, 112.3, 111.8, 111.3, 101.8, 38.3; LR-MS (EI): m/z (relative intensity)=593 (100) $[M]^+$, 547 (55); HR-MS: m/z=593.0591, calcd. for $C_{31}H_{20}IN_3O_2$ $[M]^+$: 593.0600.

2-(1*H*-Indol-3-yl)-9-iodo-5,6-dimethoxy-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3k): Yield: 61%; white solid; mp 230–232 °C; FT-IR (KBr): ν=3461, 3444, 1636, 551 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.72 (brs, 1H), 10.17 (brs, 1H), 8.09 (s, 1H), 7.41 (m, 3H), 7.25–7.29 (m, 5H), 7.12–7.15 (m, 3H), 7.04 (d, J=7.88 Hz, 1H), 6.97 (t, J=7.40 Hz, 1H), 6.71 (t, J=7.52 Hz, 1H), 6.65 (s, 1H), 5.99 (s, 1H), 3.87 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=149.7, 145.7, 145.0, 138.6, 137.4, 136.8, 136.4, 130.9, 130.8, 130.4, 128.8, 128.0, 127.6, 126.4, 125.5, 122.9, 122.2, 121.2, 120.4, 119.1, 118.8, 118.0, 117.8, 114.1, 111.6, 111.1, 110.9, 105.9, 55.7, 55.6, 38.2; LR-MS (EI): m/z (relative intensity)=608 (100) $[M]^+$, 481 (80); HR-MS (ESI): m/z=609.1038, calcd. for $C_{33}H_{25}IN_2O_2$ $[M+H]^+$: 609.1039.

2-(1*H*-Indol-3-yl)-13-iodo-12-phenyl-17,19-dioxa-10-azapentacyclo[12.7.0.0^{3,11}.0^{4,9}.0^{16,20}]henicosa-1(14),3(11),4,6,8,12,15,20-octaene (3l): Yield: 69%; pink solid; mp 238–240 °C; FT-IR (KBr): ν=3550, 3480, 590 cm^{-1}; ^{1}H NMR (400 MHz, DMSO): δ=10.71 (brs, 1H), 10.31 (brs, 1H), 8.05 (d, J=7.12 Hz, 1H), 7.86 (d, J=7.64 Hz, 1H), 7.56 (d, J=7.40 Hz, 1H), 7.35 (t, J=7.24 Hz, 1H), 7.26–7.29 (m, 3H), 7.11–7.17 (m, 3H), 6.95–6.98 (m, 3H), 6.65–6.69 (m, 2H), 6.57 (s, 1H), 5.99 (s, 1H), 5.96 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=147.1, 147.0, 144.5, 139.3, 139.1, 138.9, 137.1, 136.8, 135.4, 130.8, 128.7, 127.7, 126.6, 125.9, 125.8, 123.5, 122.9, 121.4, 121.0, 119.6, 119.2, 118.3, 113.9, 112.1, 111.7, 108.4, 105.9, 101.3, 38.9; LR-MS (EI): m/z (relative intensity)=591 (100) $[M+H]^+$, 535 (20); HR-MS: m/z=591.0933, calcd. for $C_{32}H_{21}IN_2O_2$ $[M+H]^+$: 591.0933.

9-Iodo-5-methoxy-14-methyl-2-(7-methyl-1*H*-indol-3-yl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3m): Yield: 75%; white solid; mp 219–212 °C; FT-IR (KBr): ν=3445, 1650, 700 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6); δ=10.73 (brs, 1H), 9.92 (brs, 1H), 7.95 (d, J=7.88 Hz, 1H), 7.82 (d, J=8.76 Hz, 1H), 7.27 (m, 3H), 7.19–7.20 (m, 2H), 7.06–7.09 (m, 2H), 6.96–6.98 (m, 2H), 6.90 (dd, J=2.44 Hz, 8.76 Hz, 1H), 6.80 (d, J=6.88 Hz, 1H), 6.65–6.69 (m, 2H), 5.99 (s, 1H), 3.83 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=159.9, 145.8, 144.6, 138.5, 13.5, 13.2, 135.9, 131.9, 130.4, 129.6, 127.6, 127.5, 126.1, 123.1, 122.6, 122.1, 121.1, 120.8, 119.9, 119.3, 118.1, 116.5, 115.5, 113.8, 111.9, 111.2, 105.6, 55.3,39.09, 17.0, 16.3; LR-MS (EI): m/z (relative intensity)=606 (60) $[M]^+$, 605 (100); HR-MS: m/z=606.1161, calcd. for $C_{34}H_{27}IN_2O$ $[M]^+$: 606.1168.

9-Iodo-14-methyl-2-(7-methyl-1*H*-indol-3-yl)-5-nitro-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3n): Yield: 61%; red solid; mp 208–210 °C; FT-IR (KBr): ν=3445, 1580, 1385 cm^{-1}; ^{1}H NMR (400 MHz, [DMSO-d_6): δ=10.77 (brs, 1H), 10.13 (brs, 1H), 8.61 (d, J=2.04 Hz, 1H), 8.08–8.12 (m, 2H), 8.03 (d, J=7.88 Hz, 1H), 7.31 (m, 4H), 7.08 (t, J=7.78 Hz, 1H), 6.98 (d, J=7.04 Hz, 1H), 6.78–6.83 (m, 3H), 6.63–6.67 (m, 2H), 6.34 (s, 1H), 2.39 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=147.2, 145.6, 145.4, 143.8, 141.7, 136.6, 136.2, 136.0, 130.2, 129.5, 128.0, 127.8, 125.9, 125.4, 123.7, 122.9, 122.4, 121.8, 121.2, 120.9, 120.1, 119.9, 119.6, 118.2, 116.5, 116.1, 112.5, 101.7, 38.4, 17.0, 16.6; LR-MS (EI): m/z (relative intensity)=621(100) $[M^+]$, 595.2 (70); HR-MS: m/z=621.0909, calcd. for $C_{33}H_{24}IN_3O_2$ $[M^+]$: 621.0913.

14-Ethyl-2-(7-ethyl-1*H*-indol-3-yl)-9-iodo-5-methoxy-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3o): Yield: 75%; yellow solid; mp 167–169 °C; FT-IR (KBr): ν=3520, 3489, 670 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ=10.71 (brs, 1H), 9.87 (brs, 1H), 7.91 (d, J=7.92 Hz, 1H), 7.78 (d, J=8.76 Hz, 1H), 7.24–7.27 (m, 4H), 7.15–7.16 (m, 2H), 7.09 (t, J=7.52 Hz, 1H), 6.97–6.99 (m, 3H), 6.88 (dd, J=2.60 Hz, 8.80 Hz, 1H), 6.79–6.81 (m, 1H), 6.68 (d, J=7.62 Hz, 1H), 6.65 (s, 1H), 5.95 (s, 1H), 3.81 (s, 3H), 2.78 (q, J=11.4 Hz, 7.4 Hz, 2H), 2.69 (m, 2H) 1.19 (t, J=7.48 Hz, 3H), 1.09 (t, J=7.48 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=145.9, 144.7, 138.6, 136.6, 135.4, 135.1, 132.0, 130.3, 129.6, 128.0, 127.6, 127.5, 127.0, 126.6, 126.4, 125.8, 122.5, 122.3, 121.1, 119.5, 119.3, 118.2, 116.6, 115.5, 113.8, 111.9, 111.2, 105.7, 55.3, 39.1, 23.5, 23.1, 14.4, 14.1; LR-MS (EI): m/z (relative intensity)=634 (80) $[M^+]$, 508 (45); HR-MS: m/z=634.1475, calcd. for: $C_{36}H_{31}IN_2O$ (M^+): 634.1481.

14-Ethyl-2-(7-ethyl-1*H*-indol-3-yl)-9-iodo-5-nitro-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3p): Yield: 68%; yellow solid; mp 199–201 °C; FT-IR (KBr): ν=3472, 3431, 1590, 1379 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.79 (brs, 1H), 10.12 (brs, 1H), 8.16 (d, J=0.2 Hz, 1H), 8.07–8.14 (m, 2H), 8.03 (d, J=7.92 Hz, 1H), 7.29–7.31 (m, 4H), 7.01–7.13 (m, 3H), 6.88 (d, J=7.84 Hz, 1H), 6.81 (d, J=6.96 Hz, 1H), 6.69 (d, J=7.60 Hz, 1H), 6.64–6.66 (m, 1H), 6.34 (s, 1H), 2.69–2.81 (m, 4H), 1.19 (t, J=7.48 Hz, 3H), 1.10 (t, J=7.44 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=147.2, 145.6, 145.5, 143.8, 141.7, 136.2, 135.8, 135.1, 130.0, 129.6, 127.9, 127.7, 127.3, 126.6, 126.1, 125.5, 122.8, 122.5, 121.7, 121.6, 119.9, 119.7, 119.3, 118.3, 116.5, 116.1, 112.4, 101.7, 38.9, 23.4, 23.1, 14.3, 14.1; LR-MS (EI): m/z (relative intensity)=649 (100) $[M]^+$, 603 (50); HR-MS: m/z=649.1224, calcd. for $C_{35}H_{28}IN_3O_2$ $[M]^+$: 649.1226.

16-Chloro-2-(5-chloro-1*H*-indol-3-yl)-9-iodo-5-methoxy-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3q): Yield: 73%; pink solid; mp

188–190 °C; FT-IR (KBr): ν = 3530, 3470, 1635, 540 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.99 (brs, 1H), 10.44 (brs, 1H), 8.22 (s, 1H), 7.81 (d, *J* = 8.76 Hz, 1H), 7.28–7.34 (m, 7H), 7.13–7.15 (m, 2H), 6.89–7.00 (m, 3H), 6.73 (s, 1H), 6.06 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.2, 145.1, 144.7, 138.0, 136.7, 135.1, 134.9, 132.1, 131.6, 128.9, 128.2, 127.9, 127.4, 126.7, 124.8, 123.9, 122.6, 122.3, 120.5, 119.8, 118.1, 117.3, 113.5, 113.3, 112.8, 112.1, 111.6, 106.8, 55.4, 38.2; LR-MS (EI): *m/z* (relative intensity) = 647 (95) $[M+H]^+$, 521 (80); HR-MS: *m/z* = 647.0150, calcd. for $C_{32}H_{22}Cl_2IN_2O$ $[M+H]^+$: 647.0154.

16-Chloro-2-(5-chloro-1*H*-indol-3-yl)-9-iodo-5-nitro-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3r): Yield: 85%; light red solid; mp 193–195 °C; FT-IR (KBr): ν = 3490, 1580, 1360 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 11.08 (brs, 1H), 10.66 (brs, 1H), 8.72 (s, 1H), 8.35 (s, 1H), 8.09–8.14 (m, 2H), 7.36–7.38 (m, 3H), 7.31–7.34 (m, 3H), 7.17–7.19 (m, 2H), 7.00 (dd, *J* = 8.56 Hz, 1.80 Hz, 1H), 6.80 (d, *J* = 1.52 Hz, 1H), 6.74 (s, 1H), 6.43 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ = 147.4, 145.1, 144.6, 143.9, 141.2, 136.4, 135.7, 134.9, 131.8, 128.8, 128.3, 128.2, 127.2, 126.4, 125.2, 124.2, 122.9, 122.7, 122.0, 120.6, 120.3, 119.8, 118.0, 117.8, 113.6, 112.1, 103.2, 37.5; LR-MS (EI): *m/z* (relative intensity) = 662 (100) $[M+H]^+$; HR-MS: *m/z* = 661.9891, calcd. for $C_{31}H_{18}Cl_2IN_3O_2$ $[M+H]^+$: 661.9899.

16-Bromo-2-(5-bromo-1*H*-indol-3-yl)-9-iodo-5-methoxy-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3s): Yield: 77%; white solid; mp 236–238 °C; FT-IR (KBr): ν = 3525, 3425, 1635, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ = 11.0 (brs, 1H), 10.44 (brs, 1H), 8.35 (s, 1H), 7.79 (d, *J* = 8.68 Hz, 1H), 7.31 (m, 5H), 7.28 (m, 1H), 7.26 (m, 1H), 7.24 (m, 2H), 7.13 (s, 1H), 7.09 (d, *J* = 8.52 Hz, 1H), 6.91 (d, *J* = 8.24 Hz, 1H), 6.70 (s, 1H), 6.06 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.2, 145.0, 144.7, 137.9, 136.7,135.3, 135.0, 131.9, 131.6, 129.1, 128.3, 128.1, 127.9, 127.4, 124.8, 124.5, 123.0, 121.3, 120.4, 119.0, 113.7, 113.4, 112.0, 111.8, 111.6, 110.6, 106.9, 55.4, 38.1; LR-MS (EI): *m/z* (relative intensity) = 736 (100) $[M+H]^+$, 734 (80); HR-MS: *m/z* = 733.9062, calcd. for $C_{30}H_{18}N_2Br_2I$ $[M+H]^+$: 733.9065.

16-Bromo-2-(5-bromo-1*H*-indol-3-yl)-9-iodo-5-nitro-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3t): Yield: 78%; red solid; mp 223–225 °C; FT-IR (KBr): ν = 3439, 3400, 1530, 1360 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 11.08 (brs, 1H), 10.66 (brs, 1H), 8.72 (s, 1H), 8.48 (s, 1H), 8.09–8.15 (m, 2H), 7.34–7.38 (m, 3H), 7.26–7.29 (m, 4H), 7.09–7.12 (m, 2H), 6.97 (s, 1H), 6.72 (s, 1H), 6.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.4, 145.1, 144.7, 143.9, 141.3, 136.4, 135.7, 135.1, 131.6, 128.9, 128.4, 128.3, 127.9, 127.1, 125.4, 124.9, 123.2, 122.2, 121.2, 120.9, 120.3, 119.9, 113.9, 113.4, 112.1, 110.7, 103.2, 37.4; LR-MS (EI): *m/z* (relative intensity) = 750 (100) $[M+H]^+$; HR-MS: *m/z* = 749.8894, calcd. for $C_{31}H_{18}Br_2IN_3O_2$ $[M+H]^+$: 749.8889.

9-Iodo-5,16-dimethoxy-2-(5-methoxy-1*H*-indol-3-yl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3u): Yield: 62%; white solid; mp 218–220 °C; FT-IR (KBr): ν = 3490, 3410 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = (ppm) 10.56 (brs, 1H), 9.99 (brs, 1H), 7.83 (d, *J* = 8.80 Hz, 1H), 7.66–7.67 (m, 1H), 7.30 (m, 2H), 7.25–7.29 (m, 3H), 7.16–7.19 (m, 3H), 6.91 (dd, *J* = 2.60 Hz, 8.80 Hz, 1H), 6.79 (dd, *J* = 2.52 Hz, 8.76 Hz, 1H), 6.62- 6.64 (m, 2H), 6.57 (d, *J* = 2.12 Hz, 1H), 5.98 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.37(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.9, 153.6, 152.2, 145.3, 145.2, 138.5, 136.7, 132.1, 131.7, 131.5, 131.2, 128.9, 128.0, 127.5, 126.7, 126.1, 123.4, 120.4, 113.5, 112.7, 112.4, 112.2, 111.6, 111.2, 110.3, 105.4, 101.3, 99.6, 55.5, 55.3, 54.6, 38.9; LR-MS (EI): *m/z* (relative intensity) = 638 (100) $[M]^+$, 637 (55); HR-MS (ESI): *m/z* = 639.1152, calcd. for $C_{34}H_{27}IN_2O_3$ $[M+H]^+$: 639.1145.

2-(1*H*-Indol-3-yl)-9-iodo-10-(4-methylphenyl)-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3v): Yield: 68%; yellow solid; mp 210–212 °C; FT-IR (KBr): ν = 3477, 3410, 599 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.74 (brs, 1H), 10.23 (brs, 1H), 8.07–8.09 (m, 1H), 7.88 (d, *J* = 7.76 Hz, 1H), 7.59–7.61 (m, 2H), 7.37 (t, *J* = 7.16 Hz, 1H), 7.28–7.31 (m, 4H), 7.13–7.15 (m, 4H), 6.96–7.00 (m, 2H), 6.71 (t, *J* = 7.38 Hz, 1H), 6.62 (s, 1H), 6.05 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.2, 141.9, 139.5, 138.9, 136.9, 136.8, 136.4, 135.1, 130.5, 129.5, 129.2, 128.7, 127.4, 126.4, 125.6, 125.4, 123.0, 122.3, 121.1, 120.5, 119.1, 118.9, 117.9, 117.8, 113.6, 111.8, 111.2, 105.2, 38.9, 20.8; LR-MS (EI): *m/z* (relative intensity) = 563 (100) $[M+H]^+$, 562 (80); HR-MS: *m/z* = 563.0982, calcd. for $C_{32}H_{23}IN_2$ $[M+H]^+$: 563.0984.

10-(2*H*-1,3-Benzodioxol-5-yl)-2-(1*H*-indol-3-yl)-9-iodo-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (3w): Yield: 62%; yellow solid; mp 225–227 °C; FT-IR (KBr): ν = 3590, 3450, 1630, 558 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.74 (brs, 1H), 10.22 (brs, 1H), 8.07 (d, *J* = 5.09 Hz, 1H), 7.34 (m, 3H), 7.26–7.29 (m, 3H), 7.24 (m, 2H), 7.12–7.14 (m, 3H), 6.95–6.99 (m, 2H), 6.67–6.72 (m, 2H), 6.09 (s, 1H), 5.98 (d, *J* = 11.69 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ = 148.2, 144.8, 144.8, 139.0, 138.9, 136.9, 136.5, 132.5, 130.5, 128.9, 128.0, 127.7, 126.4, 125.5, 123.0, 122.3, 121.2, 120.5, 119.1, 118.9, 117.9, 117.8, 114.3, 113.7, 111.7, 111.2, 107.1, 105.3, 101.5, 38.4; LR-MS (EI): *m/z* (relative intensity) = 592 (100) $[M]^+$; HR-MS: *m/z* = 592.0639, calcd, for $C_{32}H_{21}IN_2O_2$: 592.0648.

9-Iodo-*N*-methyl-*N*,10-diphenyl-12-azatetracyclo-[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaen-2-amine (6a): Yield: 65%; light yellow solid; mp 238–240 °C; FT-IR (KBr): ν = 3490, 550 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.28 (brs, 1H), 7.91 (d, *J* = 7.72 Hz, 1H), 7.85 (d, *J* = 7.63 Hz, 1H), 7.45–7.47 (m, 2H), 7.33–7.37 (m, 3H), 7.27–7.31 (m, 2H), 7.24 (m, 1H), 7.11 (t, *J* = 7.04 Hz, 1H), 7.03–7.07 (m, 2H), 6.58 (d, *J* = 8.28 Hz, 2H), 6.36 (d, *J* = 8.40 Hz, 2H), 5.76 (s, 1H), 5.37 (brs, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.9, 144.9, 144.0, 139.9, 138.9, 136.9, 134.9, 130.1, 129.1, 128.9, 128.7, 128.2, 128.2, 127.8, 127.3, 126.3, 125.4, 122.4, 121.9, 119.1, 117.1, 111.7, 110.9, 104.6, 44.3, 29.9; LR-MS (EI): *m/z* (relative intensity) = 538 (100) $[M]^+$, 537 (40); HR-MS: m/z = 538.0904, calcd. for $C_{30}H_{23}IN_2$ $[M]^+$: 538.0906.

2-(1*H*-Indol-3-yl)-9-(4-methoxyphenyl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (7a): Yield: 76%; light pink solid; mp 189–191 °C; FT-IR (KBr): ν = 3490, 3410, 1700 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.77 (brs, 1H), 10.22 (brs, 1H), 7.96 (d, *J* = 7.36 Hz, 1H), 8.00 (d, *J* = 7.28 Hz, 1H), 7.37–7.40 (m, 2H), 7.33 (d, *J* = 8.08 Hz, 1H), 7.11 (m, 6H), 6.96–6.99 (m, 2H), 6.84–6.88 (m, 3H), 6.69 (t, *J* = 7.12 Hz, 1H), 6.58 (s, 1H),

6.42 (d, $J=8.36$ Hz, 2H), 6.36 (d, $J=8.08$ Hz, 2H), 6.08 (s, 1H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta=$ 156.9, 144.3, 140.1, 139.8, 138.1, 137.3, 136.6, 134.9, 132.5, 131.6, 131.4, 131.4, 129.6, 127.9, 126.8, 126.2, 126.0, 124.8, 123.2, 121.8, 120.5, 119.4, 118.9, 118.8, 117.9, 117.8, 115.4, 112.3, 111.7, 111.4, 54.7, 38.9; LR-MS (EI): *m/z* (relative intensity) = 528 (100) $[M]^+$, 412 (65); HR-MS: *m/z* = 528.2208, calcd. for $C_{38}H_{28}N_2O$ $[M]^+$: 528.2202.

Ethyl (2*E*)-3-[2-(1*H*-Indol-3-yl)-10-phenyl-12-azatetracyclo[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaen-9-yl]prop-2-enoate (8a): Yield: 98%; white solid; mp 177–179 °C; FT-IR (KBr): $\nu=3490$, 3410, 2899, 1735 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta=10.57$ (brs, 1H), 10.43 (brs, 1H), 8.06 (d, $J=7.40$ Hz, 1H), 7.43 (d, $J=7.60$ Hz, 1H), 7.56–7.57 (m, 1H), 7.39–7.45 (m, 4H), 7.25–7.31 (m, 4H), 7.11–7.19 (m, 3H), 6.86–6.94 (m, 3H), 6.67 (t, $J=$ 7.24 Hz, 1H), 6.50 (s, 1H), 6.04 (s, 1H), 5.58 (d, $J=15.6$ Hz, 1H), 3.94–3.97 (m, 2H), 1.09 (t, $J=7.08$ Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta=166.3$, 146.2, 144.6, 138.4, 137.9, 137.6, 136.4, 135.2, 133.9, 132.4, 131.6, 130.2, 128.5, 128.4, 128.4, 128.1, 126.3, 125.8, 124.6, 123.8, 123.0, 122.7, 120.5, 119.3, 118.9, 118.4, 117.8, 113.9, 111.9, 59.7, 39.9, 14.0; LR-MS (EI): *m/z* (relative intensity) = 520 (100) $[M]^+$, 404 (60); HR-MS: *m/z* = 520.2148, calcd. for $C_{36}H_{28}N_2O_2$ $[M]^+$: 520.2151.

2-(1*H*-Indol-3-yl)-10-phenyl-12-azatetracyclo-[9.7.0.0^{3,8}.0^{13,18}]octadeca-1(11),3(8),4,6,9,13,15,17-octaene (9a): Yield: 74%; white solid; mp 250–252 °C; FT-IR (KBr): $\nu=3490$, 3410 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta=$ 10.74 (brs, 1H), 10.54 (brs, 1H), 7.99 (d, $J=7.52$ Hz, 1H), 7.82 (d, $J=7.48$ Hz, 1H), 7.52–7.58 (m, 3H), 7.37–7.49 (m, 5H), 7.25–7.32 (m, 2H), 7.10–7.20 (m, 3H), 7.06 (s, 1H), 6.94 (t, $J=7.12$ Hz, 1H), 6.80 (t, $J=7.05$ Hz, 1H), 6.54 (s, 1H), 6.11 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta=$ 141.6, 140.3, 137.2, 136.4, 134.7, 133.6, 131.5, 131.0, 129.6, 129.1, 128.6, 128.5, 128.3, 127.9, 126.4, 126.2, 125.5, 122.4, 121.9, 120.5, 118.9, 118.8, 117.9, 117.9, 117.8, 114.8, 111.7, 111.2, 38.8; LR-MS (ESI): *m/z* (relative intensity) = 421 (80) $[M-H]^-$, 467 (100); HR-MS: *m/z* = 422.1779, calcd. for $C_{31}H_{22}N_2$ $[M]^+$: 422.1783.

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[12] CCDC 930945 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.