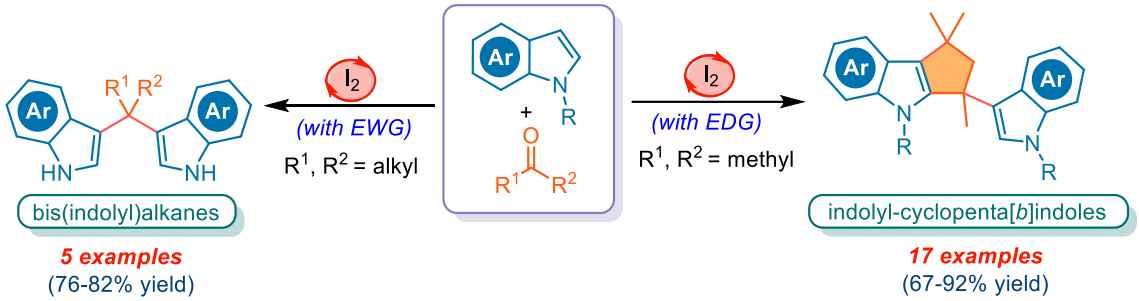
Chapter 3

Molecular Iodine Catalyzed Selective Construction of Cyclopenta[b]indoles from Indoles and Acetone



5 examples
(76-82% yield)

17 examples
(67-92% yield)

- Molecular iodine catalysis
- Substituent-guided
- Cascade addition/intramolecular cyclization
- Bis(indolyl)alkane intermediate

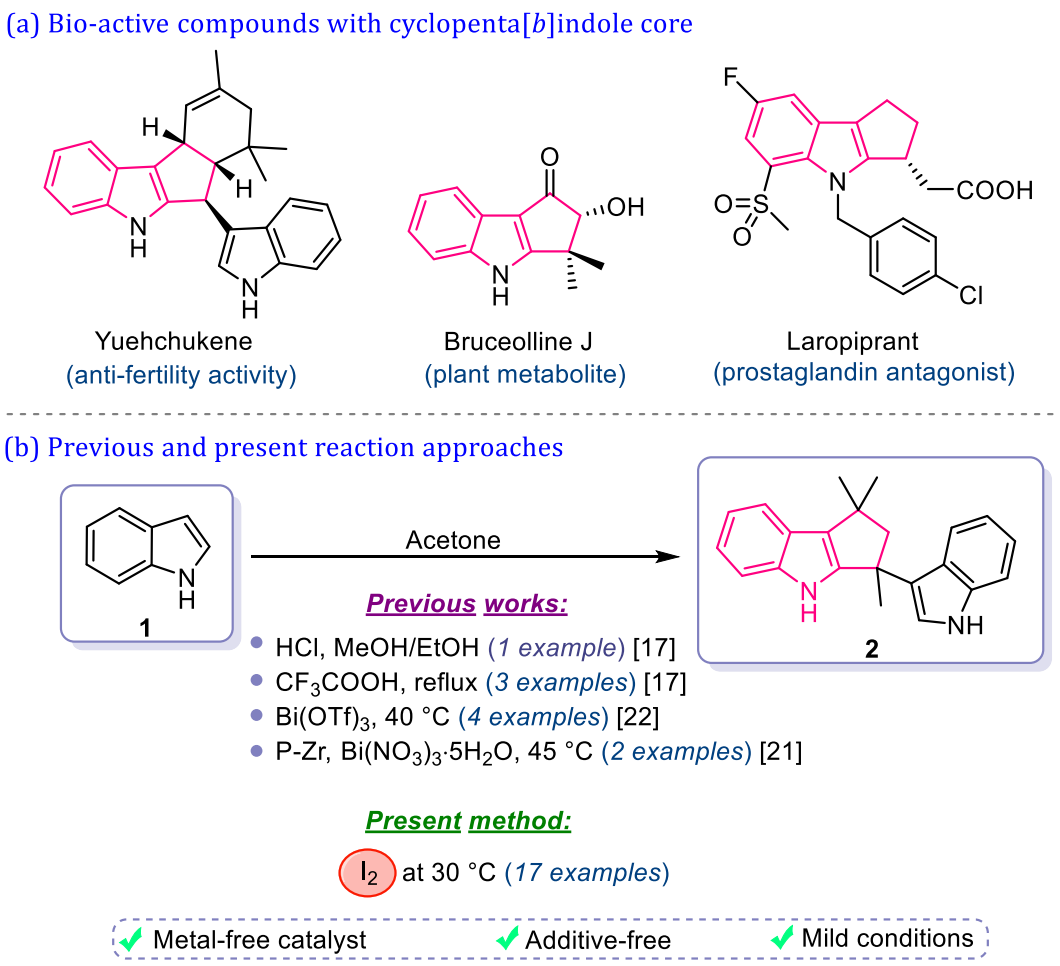
3.1 Introduction

Indole-fused annulated structures form an important class of privileged nitrogen-heterocycles due to their widespread occurrence in natural products and active pharmaceutical ingredients [1-4]. Among them, cyclopentannulated indoles are especially attractive because of their prevalence in numerous alkaloids with various pharmacological functions including cytotoxicity, anti-bacterial, insecticidal properties and as enzyme receptors (Scheme **3.1a**) [5-7]. Its enormous biological significance has prompted researchers to contribute to the design and construction of this natural product-inspired framework and drug-like molecules.

Various synthetic approaches have been developed to assemble cyclopenta[*b*]indole structural motif [8-16], however the simplest access to this class of indole derivatives can be induced from indoles and ketones as starting materials. The initial synthesis and structural determination of cyclopenta[*b*]indole was reported by Venemalm and co-workers in 1989 by reacting indole and acetone, under strong acidic conditions of ethanolic HCl or trifluoroacetic acid [17]. Following a few accounts have been disclosed using mineral and Lewis acidic conditions [18-20]. However, most of the reaction conditions are toxic and corrosive in nature, which also involves handling and disposal problems. Also, the reaction between indole and acetone in strong acidic conditions have proved to be highly complex in nature due to the possibility of formation of wide variety of products [17,20]. Recently, Nagarkar and co-workers reported $Bi(NO_3)_3{\cdot}5H_2O$-zirconia [21], and Kumar and co-workers revealed $Bi(OTf)_3$ [22], as catalysts for the transformation. However, limited substrate explorations and hygroscopic nature of the catalysts would restrict their practical utility in large scale. Thus, development of efficient catalytic systems for the reaction between ketones and substituted indoles to synthesize cyclopenta[*b*]indole is limited and deserves explorations.

In present times, molecular iodine-catalysis has emerged as an attractive choice for various organic transformations [23,24]. Shaikh and co-workers have shown an example of iodine-catalyzed reaction between indole and acetone forming bis(indolyl)methane [25]. However, no account of its catalytic feasibility towards cyclopenta[*b*]indole synthesis has been disclosed so far. The present chapter reports

a simple molecular-iodine catalyzed synthesis of cyclopenta[*b*]indoles from readily available 2,3-unfunctionalized indoles (Scheme **3.1b**).



Scheme 3.1 (a) Representative compounds having core of cyclopenta[*b*]indole, (b) synthesis of cyclopenta[*b*]indoles from indoles and acetone

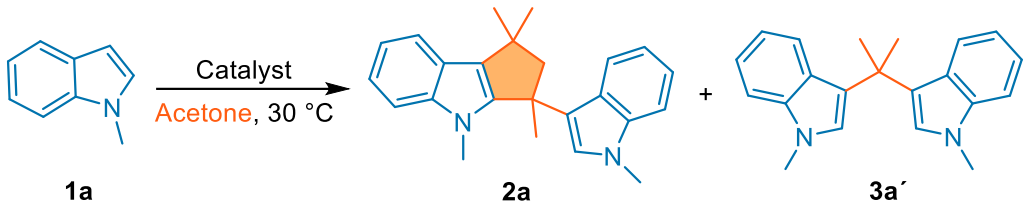
3.2 Results and Discussion

3.2.1 Optimization of Reaction Conditions

Initial study commenced with 1-methyl indole and acetone as the model substrates. In presence of molecular iodine (50 mol%), instead of the usual bis(indolyl)propane product (**3a´**), indolyl-cyclopenta[*b*]indole derivative (**2a**) was detected exclusively in 82% yield in 2 h (Table **3.1**, entry **1**). The formation of the product has been confirmed by the characteristic peaks in ^{1}H and ^{13}C NMR analysis. In order to study the activity of iodine as catalyst in the process, reactions were carried out in varying amounts. It was observed that lowering the amount to 20 mol% could display its outstanding selectivity towards cyclopenta[*b*]indole (**2a**) at 30 °C (Table **3.1**, entry

2) within 2 h. However further lowering to 15 mol% and 10 mol% leads to sequential dropping of product yield and selectivity (Table **3.1**, entries **3**-**4**). The effects of other iodine-containing additives such as HI and KI were investigated at 30 °C (Table **3.1**, entries **5**-**6**), however no considerable result could be attained, thus verifying the effectiveness of I_2 as a catalyst for the desired cyclization.

Table 3.1 Optimization of reaction conditions for synthesis of **2a**[a]



Entry	Catalyst (mol%)	Reaction medium	% Yield[b] of **2a** / **3a´**
1	I_2 (50)	Acetone	82 / 0
2	I_2 (20)	Acetone	82 / 0
3	I_2 (15)	Acetone	78 / 5
4	I_2 (10)	Acetone	60 / 20
5	HI (20)	Acetone	30 / 44
6	KI (20)	Acetone	nr
7[c]	I_2 (20)	CH_3CN	35 / 43
8[d]	I_2 (20)	CH_3CN	55 / 38
9[c]	I_2 (20)	Toluene	32 / 40
10[d]	I_2 (20)	Toluene	46 / 28
11[e]	I_2 (20)	Acetone	75 / 8
12	-	Acetone	nr

[a]Reaction conditions: **1a** (1 mmol), catalyst (20 mol%), acetone (2 mL), time (2 h), rt (30 °C); [b]isolated yield; [c]acetone (0.5 mmol); [d]acetone (1 mmol); [e]N_2 atmosphere; nr (no reaction).

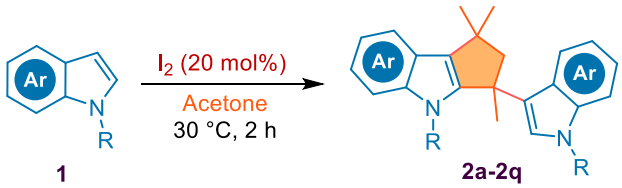
In the above examples no additional solvents were being used and acetone is playing the dual role of acting as an electrophile to the electron-rich nucleophilic indole along with serving as a reaction medium. Following, to identify any role of amount of acetone in the cyclization process, reactions were performed taking acetone as a reagent. Two sets of reactions were performed using acetone in 0.5 equiv (Table **3.1**,

entries **7**, **9**) and 1 equiv (Table **3.1**, entries **8**, **10**), under external solvent media of CH_3CN and toluene, to check the possibility of formation of (indole : acetone) 2:1 (**3a´**) and 2:2 (**2a**) addition products respectively. Although, mixture of products (**2a** and **3a´**) were detected in all the cases (Table **3.1**, entries **7**-**10**), the results clearly indicate that increasing the acetone ratio, improved the selectivity towards the generation of cyclized product (**2a**) in the reaction. Performing the reaction under N_2 atmosphere displayed comparable selectivity, revealing no major effect of aerial oxidizing environment for the cyclization process. Effect of temperature exhibited an exciting result. The synthesis proceeds at room temperature (30 °C) without the requirement of inert or anhydrous reaction conditions. However, in the absence of I_2, virtually no trace of reaction progress could be detected (Table **3.1**, entry **12**).

3.2.2 Substrate Scope Study

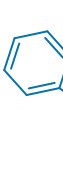
With the optimized reaction condition, the scope and limitations of this transformation was examined through wide variation of substituents on the indole core. *N*–H indole responded smoothly to the transformation affording the fused-pentacyclic compound in 78% yield in 3 h (Table **3.2**, **2b**). In the similar trend, a variety of electron-rich substituents such as methyl, methoxy produced the desired transformation in 74-92% yield, irrespective of their positions (5-, 6-, or 7-) in the carbocyclic core of indole (Table **3.2**, **2c**-**2h**). Increasing the chain length of the *N*-substituent from methyl to ethyl and further extended to *n*-butyl and *n*-hexyl chains, displayed successful conversions to the corresponding cyclopenta[*b*]indole derivatives in 70-78% yield (Table **3.2**, **2i**-**2k**). Another class of electron-rich indole derivatives containing *N*-substituted allylic and benzylic groups were also explored. To our delight, the functionalities displayed remarkable tolerance towards the catalytic system yielding the desired cyclization products in 79-88% yields (Table **3.2**, **2l**-**2o**). An example of 5-benzyloxyindole was also explored showing successful conversion to the desired transformation in 88% yield (Table **3.2**, **2p**). Formation of fused-pentacyclic structure was also confirmed from single crystal X-ray diffraction of **2d**. When a methyl group is present at 2-position of the indole nucleus, steric requirements of the moiety hinder the cyclization process, leading to a fused-six-membered ring (carbazole structure) along with dearomatization of indole core (Table **3.2**, **2q**). On the other hand, 3-methylindole failed to initiate the reaction.

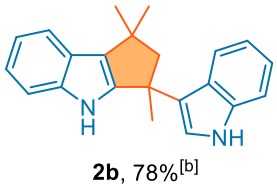
Table 3.2 Substrate scope for indolyl-cyclopenta[*b*]indole derivatives[a]



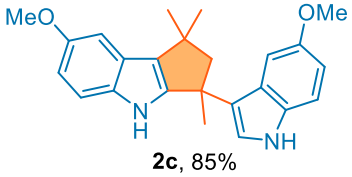
1 2a-2q

(with EDG)

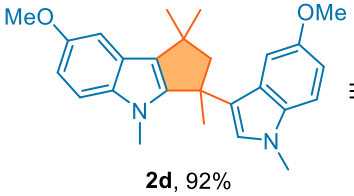

2a, 82%



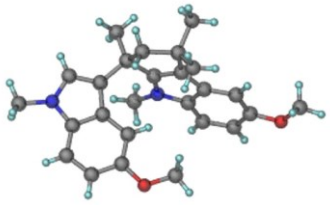
2b, 78%[b]

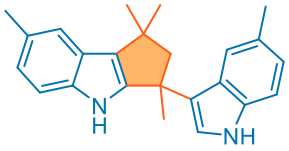


2c, 85%

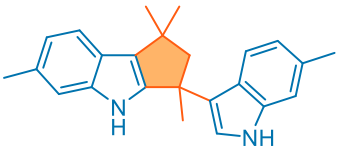


2d, 92%

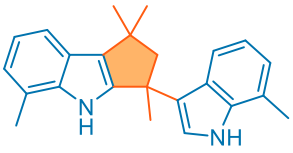




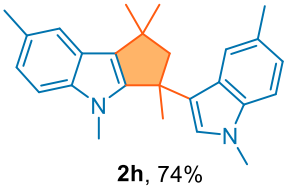
2e, 83%



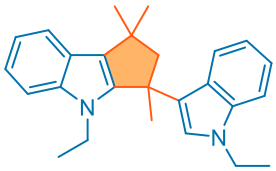
2f, 85%



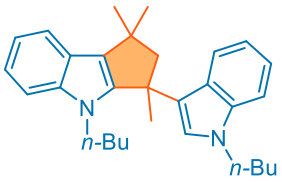
2g, 89%



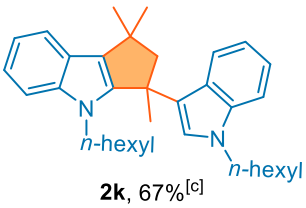
2h, 74%



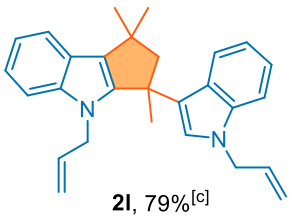
2i, 78%[c]



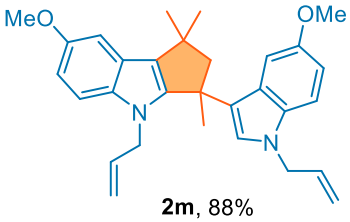
2j, 72%[c]



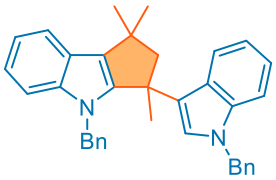
2k, 67%[c]



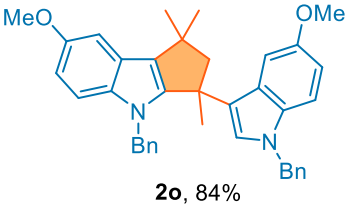
2l, 79%[c]



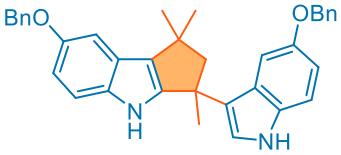
2m, 88%



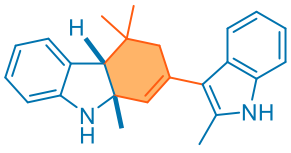
2n, 81%



2o, 84%



2p, 88%

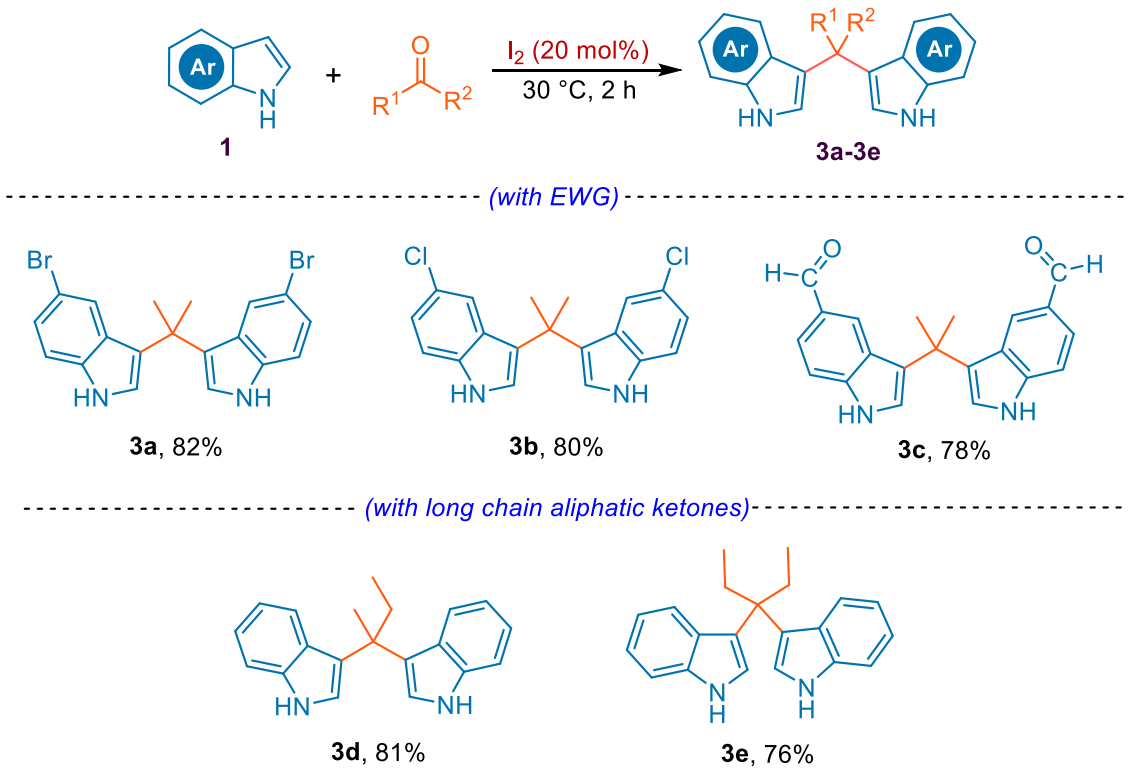


2q, 90%

[a]Reaction conditions: **1** (1 mmol), I_2 (20 mol%), acetone (2 mL), time (2 h), rt (30 °C); [b]time (3 h); [c]time (6 h); the yields reported are the isolated yields.

Furthermore, reactivity of indoles bearing electron-poor substituents were verified under the present condition. For the examination, indole ring with bromo, chloro and carbaldehyde functionalities at 5-position were tested. However, in contrary to the results obtained so far, the product formation with electron-poor indole system restricted themselves to the corresponding bis(indolyl)propane derivatives exclusively in 78-82% yield (Table **3.3**, **3a-3c**). Increasing the reaction temperature or time had no effect on the result. The results unveiled the vital electronic effect of the substituent on directing the product formation. Electron-rich core of indole systems feasibly directed the formation of corresponding cyclopenta[*b*]indoles whereas electron-poor indole rings showed no tendency towards the cyclization process thus generating the bis(indolyl)propane derivatives in good yields.

Table 3.3 Substrate scope for bis(indolyl)alkane derivatives[a]

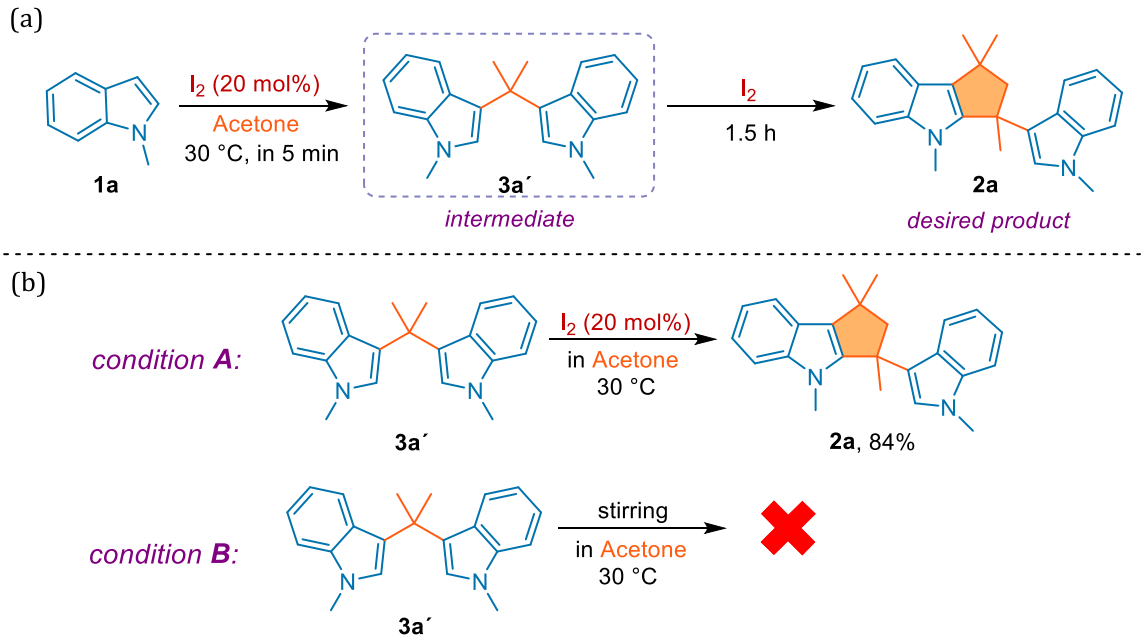


[a]Reaction conditions: **1** (1 mmol), I_2 (20 mol%), aliphatic ketone (2 mL), time (2 h), rt (30 °C); the yields reported are the isolated yields.

Moreover, when acetone was substituted with its long chain analogues such as 2-butanone and 3-pentanone, then reactions with *N*–H indole delivered the corresponding 3,3′-bis(indolyl)alkanes as major products in 2 h (Table **3.3**, **3d-3e**).

3.2.3 Investigations on Reaction Mechanism

To account for the distinct reactivity difference between the two electronically varied classes: electron-rich and electron-poor indole derivatives and to identify the possible reaction pathway, following control experiments were performed.



Scheme 3.2 Control experiments for investigations on reaction pathway

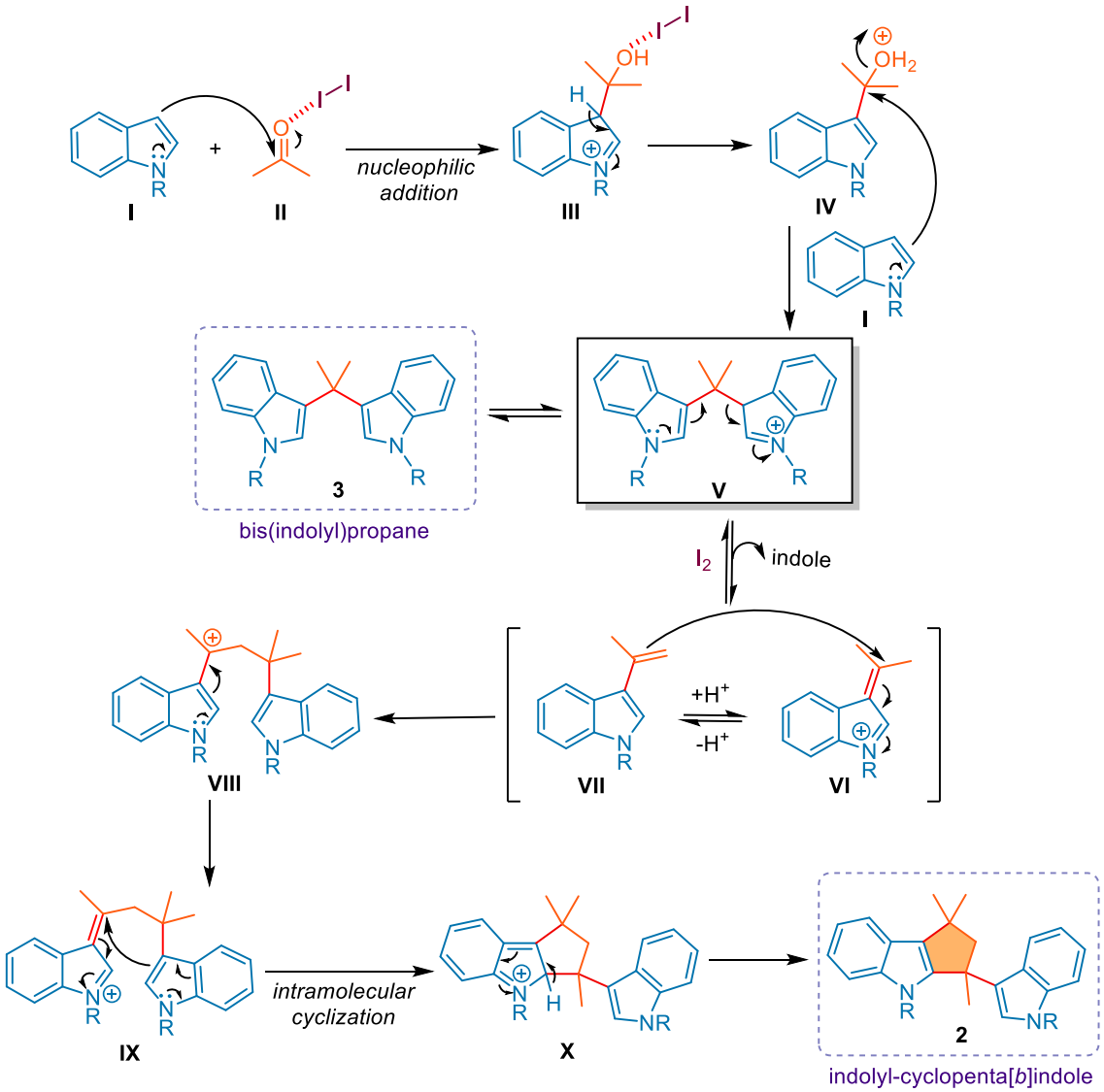
At first 1-methyl indole (**1a**) and acetone is allowed to react in presence of I_2 (20 mol%) at 30 °C (Scheme **3.2a**). TLC monitoring after 5 min of reaction, showed complete conversion of the reactant to a major polar spot (**3a´**). Monitoring the reaction further, a new non-polar spot (**2a**) is formed with increasing reaction time, along with the diminishing concentration of earlier spot (**3a´**). After 1.5 h of reaction, the polar spot (**3a´**) completely disappeared leading to the exclusive **2a** product. The intermediate **3a´** was isolated after 5 min reaction time, and further purified by column chromatography. ^{1}H and ^{13}C spectral analysis of the spot clearly confirmed the formation of bis(1-methylindolyl)-propane during the reaction. Concluding from the above experimental findings, bis(indolyl)alkane is expected to be the intermediate for this addition-cyclization reaction.

To further validate the mechanistic aspect, **3a´** was prepared following standard procedure [26,27]. The isolated product **3a´** have been charged for two different experiments (Scheme **3.2b**). In condition **A**: I_2 (20 mol%) was added; and in condition

B: no additional reagent was added. Both the systems were stirred in acetone at 30 °C for 1 h. TLC monitoring of the experiments showed complete conversion of **3a´** to **2a** in **A**, whereas no trace of reaction progress was detected in **B**. The experiments confirmed the potential intermediate actions of bis(indolyl)alkane in the process and established the fact that presence of I_2 is crucial for the subsequent intramolecular cyclization process. Thus, molecular iodine is acting as an efficient catalyst in each step of the cascade addition-intramolecular cyclization reaction.

3.2.4 Plausible Mechanism

Based on the experimental findings and literature, a plausible reaction route has been proposed as shown in **Scheme 3.3**.



Scheme 3.3 Plausible mechanism for I_2 catalyzed reaction between indole and acetone

The first step is expected to be the activation of electrophile acetone (**II**) by molecular iodine *via* halogen-bond activation [28,29], followed by addition to nucleophilic indole (**I**) through C3 position of indole ring forming species **III**. Isomerization of **III** generates **IV**. In the next step, nucleophilic attack with another molecule of indole generates the intermediate compound bis(indolyl)propane (**V**) which can readily be converted to compound **3**. In the subsequent step, I_2 is expected to activate the indole species **V**, allowing the lone pair of electrons on indole nitrogen to initiate a facile rearrangement leading to C(sp^3)−C(indolyl) bond cleavage [28], hence generating an alkene substituted indole species **VI**. Furthermore, species **VI** and **VII** undergo an addition reaction to form a carbocation intermediate **VIII**, which can be transformed into a more stable species **IX**. In the following step, intramolecular cyclization of species **IX** takes place producing the desired indolyl-cyclopenta[*b*]indole product **2**.

The mechanism unfolds some important information about the reaction. Bis(indolyl)propane intermediate (**V**) is expected to be formed during the reaction. When the indole core is electron-rich, the lone pair of electrons on indole-*N* gets involved in the subsequent rearrangement step, which is crucial for the formation of indolyl-cyclopenta[*b*]indole product (**X**). However, if an electron withdrawing group is attached to indole, the tendency of lone pair of electrons on *N* to participate in rearrangement decreases. Consequently, the reaction stops at the bis(indolyl)propane (**V**) stage, making it the major product under the reaction condition. Thus, it is the electronic nature of the nucleophile which is controlling the product formation to two different classes of indole derivatives.

The mechanism can also explain the structural difference in case of 2-methylindole where the steric hindrance in species **IX** favours the terminal carbon from acetone to involve in intramolecular cyclization step instead of the quaternary carbon atom. Thus, giving rise to an indole-fused six-membered cycle along with indole ring dearomatization (Table **3.2**, **2q**) [21].

3.3 Summary

This chapter presents a mild, simple, and greener gateway to an exciting class of bioactive indole derivative- cyclopenta[*b*]indoles using molecular iodine catalysis. Interesting substitution dependence on the product distribution to two different

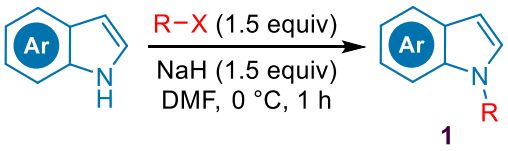
classes of indole derivatives have been realized. High electron density of indole ring favours the formation of indolyl-cyclopenta[*b*]indole derivatives, whereas electron deficiency of the core directed the reaction to bis(indolyl)propane derivatives. Mechanistic investigations *via* isolation and structure elucidation proved bis(indolyl)alkane to be the key intermediate for the cascade addition-intramolecular cyclization reaction. The findings contribute to enrich the chemistry of cyclopenta[*b*]indoles and provide greener potentials for the synthesis of ring-fused indoles.

3.4 Experimental Section

3.4.1 General Information

Reactions were carried out in Tarsons spinot digital magnetic stirrer under standard conditions. Analytical TLC was carried out on Merck silica gel $60F_{254}$ plates using short wave (254 nm) UV light. Column chromatography purifications were performed over silica gel (100-200 mesh) and ethyl acetate/hexane as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM 400ECS NMR spectrometer (400 and 100 MHz respectively). The raw data of NMR were processed by MestReNova software. Chemical shifts for both ^{1}H and ^{13}C NMR are assigned in ppm using TMS (0 ppm) as the internal reference, and $CDCl_3$ and DMSO-d_6 as solvent ($CDCl_3$: ^{1}H NMR, δ = 7.25 ppm, δ = 1.56 ($CDCl_3$-water), and ^{13}C NMR, δ = 77.0 ppm; DMSO-d_6: ^{1}H NMR, δ = 2.50 ppm, δ = 3.33 ppm (DMSO-d_6 absorbed water), and ^{13}C NMR, δ = 39.5 ppm). Multiplicities are indicated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), dq (doublet of quartets) and br (broad). Coupling constants (*J* values) are given in Hz. A PerkinElmer 2400 Series II CHNS/O analyzer was utilized for the elemental analysis of all compounds. HRMS data were recorded *via* electron spray ionization with a Q-TOF mass analyzer. Single crystal X-ray diffractions were collected on a Bruker SMART APEX-II CCD diffractometer using Mo Kα (λ = 0.71073 Å) radiation. Melting points were determined with a Buchi-535 apparatus and were not corrected. All chemicals used were purchased commercially from either Sigma Aldrich, Merck or Alfa Aesar and used without further purification. Solvents used for extraction and chromatographic separations were distilled prior to use.

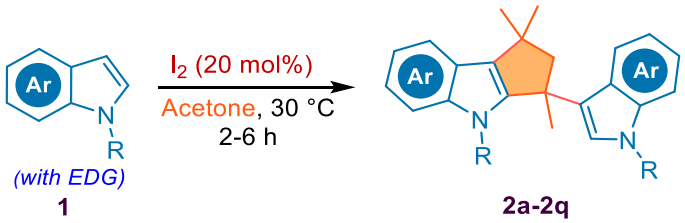
3.4.2 Synthesis of *N*-Substituted Indoles



1

In a round-bottom flask placed in ice-bath, *N*–H indole (2 mmol) was dissolved in 5 mL DMF. To the mixture NaH (3 mmol) was added slowly by stirring. Following, alkyl/benzyl/allyl halide (3 mmol) was added and stirred for 1 h. After the completion of reaction, the reaction mixture was extracted with ethyl acetate and water (3 times the organic layer). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was passed over a short column to give the corresponding *N*-substituted indoles (**1**).

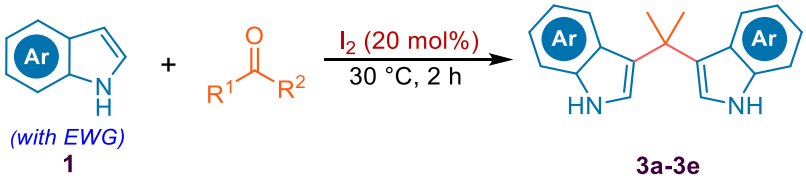
3.4.3 General Procedure for the Synthesis of Indolyl-cyclopenta[*b*]indole Derivatives



1 **2a-2q**

A round-bottom flask was charged with indole **1** (1 mmol) in acetone (2 mL) in the presence of 20 mol% (0.2 mmol, 0.051 g) molecular iodine (I_2) at rt (30 °C) for 2 h. After completion of reaction (confirmed by TLC), the reaction mixture was quenched with saturated solution of $Na_2S_2O_3{\cdot}5H_2O$ and extracted with ethyl acetate and water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to give the desired products **2a-2q**.

3.4.4 General Procedure for the Synthesis of Bis(indolyl)alkane Derivatives

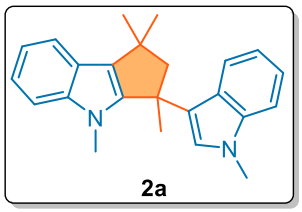


1 **3a-3e**

Following the general procedure **3.4.3**, bis(indolyl)alkane derivatives **3a-3e** were obtained from the respective electron-poor indole derivatives or aliphatic ketones.

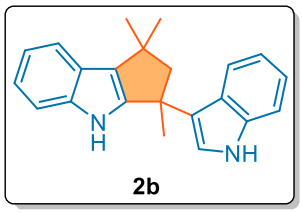
3.5 Characterization Data of the Products

1,1,3,4-Tetramethyl-3-(1-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole



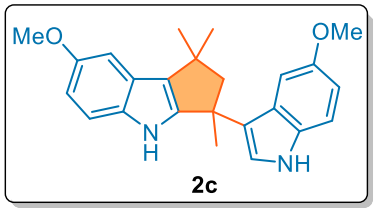
Obtained as white solid, 280 mg, 82% yield; mp 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.62 (d, J = 6.3 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.23-7.19 (m, 1H), 7.18-7.06 (m, 4H), 6.89-6.85 (m, 1H), 6.84 (s, 1H), 3.74 (s, 3H), 3.30 (s, 3H), 2.89 (d, J = 12.9 Hz, 1H), 2.43 (d, J = 13.1 Hz, 1H), 1.88 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 148.0, 141.5, 137.8, 126.1, 125.3, 124.9, 123.0, 122.1, 121.4, 120.5, 120.0, 118.9, 118.7, 118.4, 109.5, 109.0, 64.1, 42.1, 38.5, 32.7, 30.9, 30.3, 29.6, 28.0. Anal. calculated for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18; found: C, 84.23; H, 7.66; N, 8.19.

3-(1H-Indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



Obtained as brown solid, 245 mg, 78% yield; mp 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.91 (br s, 1H), 7.62-7.60 (m, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.25-7.22 (m, 2H), 7.16-7.10 (m, 3H), 6.99 (d, J = 2.5 Hz, 1H), 6.95-6.91 (m, 1H), 2.93 (d, J = 13.1 Hz, 1H), 2.49 (d, J = 12.9 Hz, 1H), 1.85 (s, 3H), 1.55 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 147.3, 140.9, 137.0, 126.1, 125.7, 123.8, 123.8, 121.9, 120.6, 120.2, 119.4, 119.1, 118.5, 118.0, 111.9, 111.1, 62.7, 42.2, 39.1, 30.7, 30.1, 28.6. Anal. calculated for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91; found: C, 84.35; H, 7.08; N, 8.87.

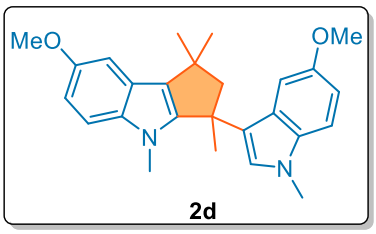
7-Methoxy-3-(5-methoxy-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



Obtained as brown gum, 318 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.84 (br s, 1H), 7.49 (br s, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 2.5 Hz, 1H), 6.99 (d, J = 2.5 Hz, 1H), 6.77 (td, J = 8.9, 2.5 Hz, 2H), 6.49 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H), 3.45 (s, 3H), 2.88 (d, J = 13.1 Hz, 1H), 2.48 (d, J = 13.1 Hz, 1H), 1.84 (s, 3H), 1.55 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 153.8, 153.5, 148.4, 136.1, 132.0, 126.1, 124.1, 123.5, 121.3, 112.3, 112.1, 111.8, 111.7, 109.8, 101.9, 101.4, 62.7, 56.1, 55.4, 42.0, 38.9, 30.8, 29.9,

28.3. HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ calculated for $C_{24}H_{26}N_2O_2$ is 375.2073; found 375.2078. Anal. calculated for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48; found: C, 77.15; H, 7.04; N, 7.44.

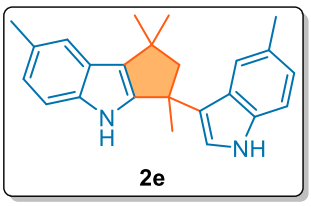
7-Methoxy-3-(5-methoxy-1-methyl-1H-indol-3-yl)-1,1,3,4-tetramethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



2d

Obtained as white solid, 370 mg, 92% yield; mp 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.13 (d, J = 8.9 Hz, 1H), 7.10-7.05 (m, 2H), 6.83 (s, 1H), 6.80-6.77 (m, 2H), 6.29 (d, J = 2.4 Hz, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.35 (s, 3H), 3.24 (s, 3H), 2.84 (d, J = 13.1 Hz, 1H), 2.44 (d, J = 13.1 Hz, 1H), 1.87 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 153.5, 153.3, 148.8, 136.9, 133.0, 126.3, 125.6, 124.6, 123.0, 121.7, 111.7, 110.1, 109.8, 109.3, 101.8, 101.3, 64.2, 56.1, 55.3, 41.9, 38.3, 32.9, 31.0, 30.0, 29.6, 27.8. HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ calculated for $C_{26}H_{30}N_2O_2$ is 403.2386; found 403.2385. Anal. calculated for $C_{26}H_{30}N_2O_2$: C, 77.58; H, 7.51; N, 6.96; found: C, 77.87; H, 7.55; N, 6.91.

1,1,3,7-Tetramethyl-3-(5-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole

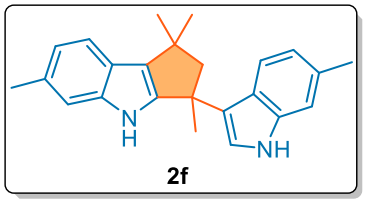


2e

Obtained as brown gum, 284 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.79 (br s, 1H), 7.54 (br s, 1H), 7.38 (s, 1H), 7.23 (d, J = 8.3 Hz, 1H), 7.18-7.14 (m, 2H), 6.98 (dd, J = 8.3, 1.8 Hz, 1H), 6.94 (dd, J = 8.3, 1.9 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 2.93 (d, J = 12.9 Hz, 1H), 2.50-2.47 (m, 4H), 2.33 (s, 3H), 1.82 (s, 3H), 1.53 (s, 3H), 1.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 147.5, 139.1, 135.4, 128.41, 128.36, 125.8, 125.5, 124.0, 123.4, 121.9, 120.8, 120.1, 120.0, 118.3, 111.5, 110.9, 62.1, 42.2, 39.0, 30.6, 30.1, 28.7, 21.6, 21.5. Anal. calculated for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18; found: C, 83.85; H, 7.69; N, 8.22.

1,1,3,6-Tetramethyl-3-(6-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole

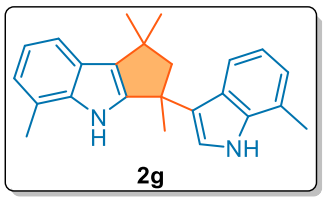
Obtained as colorless liquid, 291 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.74 (br s, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.41 (br s, 1H), 7.12-7.09 (m, 2H), 6.98-6.96



2f

(m, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 2.89 (d, *J* = 12.9 Hz, 1H), 2.47-2.44 (m, 4H), 2.41 (s, 3H), 1.82 (s, 3H), 1.54 (s, 3H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), δ (ppm): 146.7, 141.3, 137.4, 131.7, 130.3, 125.8, 123.7, 123.5, 121.5, 121.1, 120.8, 120.1, 119.9, 117.9, 112.0, 111.1, 62.7, 42.1, 39.0, 30.6, 30.2, 28.4, 21.63, 21.57. Anal. calculated for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18; found: C, 83.97; H, 7.62; N, 8.20.

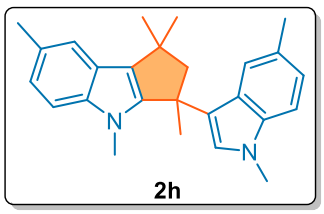
1,1,3,5-Tetramethyl-3-(7-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole



2g

Obtained as colorless liquid, 304 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.88 (br s, 1H), 7.55 (br s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.08-7.01 (m, 2H), 6.94 (dd, *J* = 10.8, 7.0 Hz, 2H), 6.90-6.84 (m, 1H), 2.92 (d, *J* = 13.1 Hz, 1H), 2.50-2.45 (m, 4H), 2.37 (s, 3H), 1.86 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), δ (ppm): 147.0, 140.4, 136.5, 126.7, 125.2, 124.4, 123.3, 122.5, 121.4, 121.0, 120.4, 120.3, 119.7, 119.5, 118.3, 116.1, 62.8, 42.3, 39.0, 30.6, 30.2, 28.7, 16.8, 16.6. Anal. calculated for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18; found: C, 83.51; H, 7.68; N, 8.14.

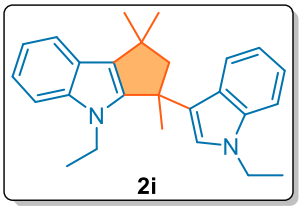
3-(1,5-Dimethyl-1H-indol-3-yl)-1,1,3,4,7-pentamethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



2h

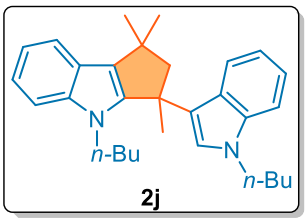
Obtained as colorless gum, 274 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.39 (s, 1H), 7.14 (dd, *J* = 14.3, 8.2 Hz, 2H), 7.08 (s, 1H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 3.68 (s, 3H), 3.36 (s, 3H), 2.90 (d, *J* = 12.9 Hz, 1H), 2.48 (s, 3H), 2.42 (d, *J* = 12.8 Hz, 1H), 2.30 (s, 3H), 1.86 (s, 3H), 1.51 (s, 3H), 1.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), δ (ppm): 148.2, 140.0, 136.3, 127.8, 127.7, 126.2, 125.5, 124.3, 123.2, 123.0, 121.6, 121.3, 120.2, 118.2, 109.2, 108.8, 63.4, 42.3, 38.5, 32.7, 30.8, 30.3, 29.8, 28.1, 21.6, 21.5. Anal. calculated for $C_{26}H_{30}N_2$: C, 84.28; H, 8.16; N, 7.56; found: C, 84.55; H, 8.19; N, 7.50.

4-Ethyl-3-(1-ethyl-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



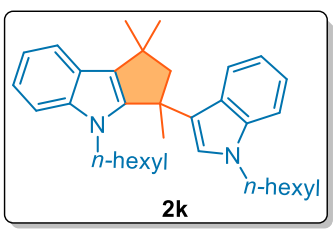
Obtained as white solid, 289 mg, 78% yield; mp 87-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.64 (dd, J = 6.6, 2.4 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.26-7.24 (m, 1H), 7.19-7.09 (m, 4H), 6.92-6.85 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.78 (q, J = 7.2 Hz, 2H), 2.96 (d, J = 13.1 Hz, 1H), 2.44 (d, J = 13.1 Hz, 1H), 1.92 (s, 3H), 1.54 (s, 3H), 1.51 (s, 3H), 1.45 (t, J = 7.3 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 147.6, 140.2, 136.7, 126.4, 124.6, 123.6, 123.2, 122.1, 121.3, 120.9, 119.8, 118.7, 118.6, 118.5, 110.0, 109.1, 63.8, 42.4, 40.8, 38.4, 30.9, 30.2, 29.7, 28.2, 15.5, 14.8. Anal. calculated for $C_{26}H_{30}N_2$: C, 84.28; H, 8.16; N, 7.56; found: C, 84.59; H, 8.17; N, 7.54.

4-Butyl-3-(1-butyl-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



Obtained as white solid, 307 mg, 72% yield; mp 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.66-7.57 (m, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.23-7.06 (m, 5H), 6.90-6.82 (m, 2H), 4.16-3.99 (m, 2H), 3.64 (t, J = 8.0 Hz, 2H), 2.98 (d, J = 13.1 Hz, 1H), 2.41 (d, J = 12.9 Hz, 1H), 1.89 (s, 3H), 1.85-1.74 (m, 2H), 1.52 (d, J = 6.0 Hz, 6H), 1.41-1.28 (m, 3H), 1.19-0.96 (m, 3H), 0.94 (t, J = 7.3 Hz, 3H), 0.59 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 147.7, 140.8, 138.6, 137.1, 126.4, 124.6, 124.3, 123.2, 121.9, 121.3, 120.9, 119.8, 118.7, 118.3, 110.1, 109.1, 63.7, 46.0, 43.7, 42.4, 38.4, 32.4, 31.7, 30.2, 29.7, 28.2, 20.2, 20.1, 13.7, 13.4. Anal. calculated for $C_{30}H_{38}N_2$: C, 84.46; H, 8.98; N, 6.57; found: C, 84.61; H, 9.02; N, 6.55.

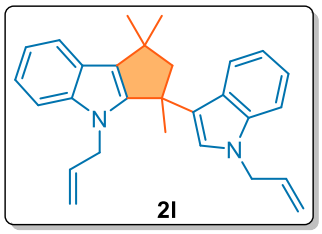
4-Hexyl-3-(1-hexyl-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



Obtained as white solid, 322 mg, 67% yield; mp 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.67 (d, J = 7.3 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.28-7.23 (m, 2H), 7.19-7.14 (m, 3H), 6.93-6.89 (m, 2H), 4.15-4.07 (m, 2H), 3.70 (t, J = 8.1 Hz, 2H), 3.03 (d, J = 13.0 Hz, 1H), 2.46 (d, J = 14.5 Hz, 1H), 1.94 (s, 3H), 1.90-1.83 (m, 2H), 1.58 (d, J = 5.9 Hz, 6H), 1.50-1.45 (m, 1H), 1.37

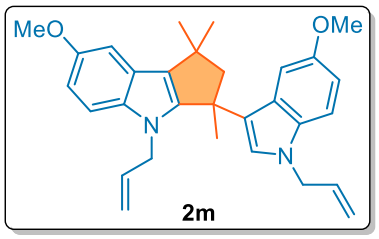
(s, 6H), 1.25-0.92 (m, 10H), 0.82 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 147.7, 140.8, 137.1, 126.4, 124.7, 124.2, 123.2, 121.9, 121.3, 120.9, 119.8, 118.7, 118.5, 118.4, 110.1, 109.2, 63.8, 46.2, 44.0, 42.4, 38.4, 31.4, 31.2, 30.9, 30.24, 30.21, 29.7, 28.3, 26.70, 26.67, 22.6, 22.4, 14.0, 13.9. Anal. calculated for $C_{34}H_{46}N_2$: C, 84.59; H, 9.60; N, 5.80; found: C, 83.27; H, 9.64; N, 5.79.

4-Allyl-3-(1-allyl-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



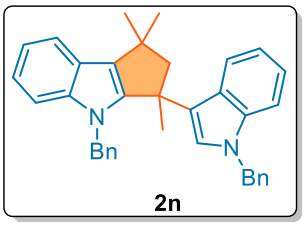
Obtained as white solid, 311 mg, 79% yield; mp 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$), *δ* (ppm): 7.67-7.59 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21-7.08 (m, 5H), 6.92-6.83 (m, 2H), 6.05-5.92 (m, 1H), 5.60-5.47 (m, 1H), 5.18 (dq, *J* = 10.3, 1.5 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.92 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.84 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.69 (dt, *J* = 5.3, 1.7 Hz, 2H), 4.37-4.19 (m, 2H), 2.94 (d, *J* = 13.1 Hz, 1H), 2.42 (d, *J* = 13.1 Hz, 1H), 1.86 (s, 3H), 1.54 (s, 3H), 1.52 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 147.6, 141.0, 137.2, 133.8, 133.6, 126.3, 125.0, 124.4, 123.3, 122.2, 121.5, 120.8, 120.0, 119.0, 118.9, 118.4, 117.0, 116.2, 110.5, 109.4, 63.9, 48.6, 46.1, 42.3, 38.4, 30.9, 30.2, 28.3. Anal. calculated for $C_{28}H_{30}N_2$: C, 85.24; H, 7.66; N, 7.10; found: C, 86.47; H, 7.64; N, 7.35.

4-Allyl-3-(1-allyl-5-methoxy-1H-indol-3-yl)-7-methoxy-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



Obtained as colorless liquid, 400 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$), *δ* (ppm): 7.12 (d, *J* = 8.8 Hz, 1H), 7.08-7.03 (m, 2H), 6.88 (s, 1H), 6.78-6.74 (m, 2H), 6.37 (d, *J* = 2.5 Hz, 1H), 6.02-5.91 (m, 1H), 5.60-5.49 (m, 1H), 5.17 (dq, *J* = 10.3, 1.6 Hz, 1H), 5.01 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.93 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.84 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.64 (dt, *J* = 5.3, 1.7 Hz, 2H), 4.29-4.14 (m, 2H), 3.87 (s, 3H), 3.36 (s, 3H), 2.90 (d, *J* = 13.1 Hz, 1H), 2.43 (d, *J* = 13.1 Hz, 1H), 1.84 (s, 3H), 1.54 (s, 3H), 1.52 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 153.5, 153.3, 148.3, 136.2, 133.9, 133.8, 132.4, 126.6, 124.72, 124.67, 123.3, 121.7, 116.9, 116.0, 111.8, 110.9, 110.2, 109.2, 102.0, 101.2, 63.9, 56.1, 55.3, 48.8, 46.1, 42.0, 38.3, 31.0, 30.0, 28.1. Anal. calculated for $C_{30}H_{34}N_2O_2$: C, 79.26; H, 7.54; N, 6.16; found: C, 79.48; H, 7.52; N, 6.14.

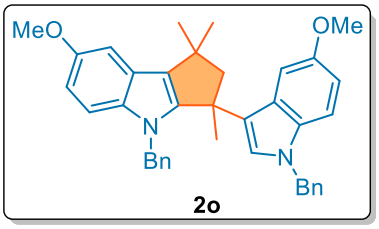
4-Benzyl-3-(1-benzyl-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



2n

Obtained as colorless liquid, 400 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.66 (d, J = 7.8 Hz, 1H), 7.25-7.19 (m, 5H), 7.13-7.07 (m, 5H), 7.04-6.99 (m, 4H), 6.91-6.88 (m, 2H), 6.75 (dd, J = 7.5, 2.1 Hz, 2H), 5.29 (d, J = 16.1 Hz, 1H), 5.22 (d, J = 16.1 Hz, 1H), 4.94 (d, J = 16.6 Hz, 1H), 4.74 (d, J = 16.8 Hz, 1H), 3.03 (d, J = 13.1 Hz, 1H), 2.43 (d, J = 13.0 Hz, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 147.9, 141.4, 138.1, 137.8, 137.5, 128.7, 128.2, 127.5, 126.8, 126.5, 126.4, 126.1, 125.3, 124.9, 123.4, 122.3, 121.8, 120.8, 120.2, 119.2, 119.0, 118.4, 110.6, 109.6, 63.8, 49.8, 47.0, 42.3, 38.5, 31.0, 30.2, 28.2. Anal. calculated For $C_{36}H_{34}N_2$: C, 87.41; H, 6.93; N, 5.66; found: C, 87.56; H, 6.96; N, 5.68.

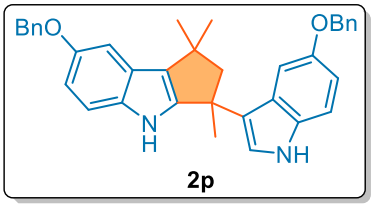
4-Benzyl-3-(1-benzyl-5-methoxy-1H-indol-3-yl)-7-methoxy-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole



2o

Obtained as colorless liquid, 465 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.26-7.21 (m, 4H), 7.11-7.07 (m, 4H), 7.02-6.97 (m, 2H), 6.86 (d, J = 9.2 Hz, 2H), 6.79-6.74 (m, 2H), 6.73 (dd, J = 8.9, 2.5 Hz, 1H), 6.67 (dd, J = 8.9, 2.5 Hz, 1H), 6.45 (d, J = 2.5 Hz, 1H), 5.24 (d, J = 16.1 Hz, 1H), 5.18 (d, J = 16.0 Hz, 1H), 4.86 (d, J = 16.7 Hz, 1H), 4.70 (d, J = 16.8 Hz, 1H), 3.86 (s, 3H), 3.38 (s, 3H), 2.97 (d, J = 13.2 Hz, 1H), 2.42 (d, J = 13.2 Hz, 1H), 1.66 (s, 3H), 1.58 (s, 3H), 1.57 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 153.6, 153.4, 148.7, 138.3, 137.9, 136.6, 132.6, 128.7, 128.3, 127.5, 127.0, 126.6, 126.4, 126.0, 125.2, 125.0, 123.4, 121.8, 112.0, 110.9, 110.4, 109.4, 102.0, 101.1, 63.7, 56.0, 55.3, 50.0, 46.9, 42.0, 38.3, 31.1, 29.7, 28.0. Anal. calculated for $C_{38}H_{38}N_2O_2$: C, 82.28; H, 6.90; N, 5.05; found: C, 82.55; H, 6.93; N, 5.03.

7-(Benzyloxy)-3-(5-(benzyloxy)-1H-indol-3-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydrocyclopenta[b]indole

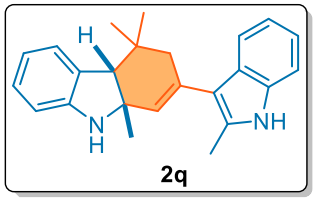


2p

Obtained as colorless liquid, 463 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.79 (s, 1H), 7.48 (d, J = 7.9 Hz, 3H), 7.39-7.15 (m, 10H), 7.11 (d, J = 8.9 Hz, 1H), 6.93 (d, J = 2.5 Hz, 1H), 6.85 (dt, J = 8.8, 2.2 Hz, 2H),

6.50 (d, *J* = 2.5 Hz, 1H), 5.10 (s, 2H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 2.82 (d, *J* = 13.0 Hz, 1H), 2.46 (d, *J* = 13.0 Hz, 1H), 1.81 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 153.2, 152.7, 148.4, 137.8, 137.5, 136.3, 132.1, 128.5, 128.3, 127.7, 127.6, 127.5, 127.3, 126.3, 126.0, 124.1, 123.7, 121.2, 113.1, 112.2, 111.8, 110.7, 103.2, 103.1, 71.2, 70.2, 62.9, 42.0, 38.9, 30.8, 29.8, 28.4. Anal. calculated for $C_{36}H_{34}N_2O_2$: C, 82.10; H, 6.51; N, 5.32; found: C, 82.38; H, 6.52; N, 5.29.

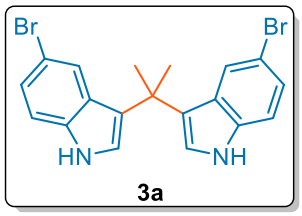
4,4,9a-Trimethyl-2-(2-methyl-1H-indol-3-yl)-4,4a,9,9a-tetrahydro-3H-carbazole



2q

Obtained as colorless liquid, 308 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$), *δ* (ppm): 7.80 (br s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.28-7.22 (m, 2H), 7.16-7.04 (m, 3H), 6.76 (t, *J* = 6.9 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 5.77 (d, *J* = 2.6 Hz, 1H), 2.78 (s, 1H), 2.48-2.44 (m, 4H), 2.23 (d, *J* = 16.1 Hz, 1H), 1.34 (s, 3H), 1.19 (s, 3H), 0.82 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 149.9, 135.1, 130.9, 130.1, 130.0, 128.9, 128.8, 127.7, 126.6, 121.2, 119.5, 119.2, 118.3, 115.7, 110.2, 109.9, 62.6, 57.6, 44.3, 34.8, 30.8, 29.2, 20.6, 12.7. Anal. calculated for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18; found: C, 84.25; H, 7.67; N, 8.20.

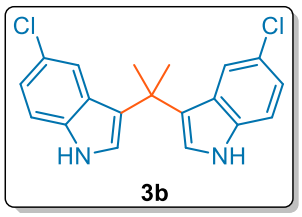
3,3'-(Propane-2,2-diyl)bis(5-bromo-1H-indole)



3a

Obtained as colorless liquid, 354 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$), *δ* (ppm): 7.96 (br s, 2H), 7.44 (s, 2H), 7.19-7.13 (m, 4H), 7.08 (d, *J* = 2.5 Hz, 2H), 1.84 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 135.7, 127.8, 124.6, 124.4, 123.3, 121.6, 112.6, 112.0, 34.5, 29.8.

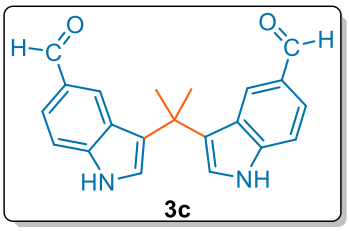
3,3'-(Propane-2,2-diyl)bis(5-chloro-1H-indole)



3b

Obtained as colorless liquid, 274 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$), *δ* (ppm): 7.92 (br s, 2H), 7.26 (d, *J* = 2.9 Hz, 2H), 7.19 (s, 1H), 7.17 (s, 1H), 7.09 (d, *J* = 2.5 Hz, 2H), 7.02 (d, *J* = 1.9 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 1.83 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$), *δ* (ppm): 135.4, 127.1, 124.7, 124.2, 121.8, 121.7, 120.2, 112.2, 34.4, 29.7.

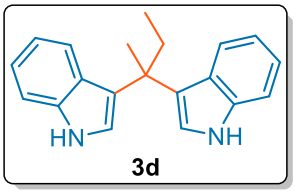
3,3'-(Propane-2,2-diyl)bis(1H-indole-5-carbaldehyde)



3c

Obtained as colorless liquid, 257 mg, 78% yield; ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 11.39 (br s, 2H), 9.72 (s, 2H), 7.76 (s, 2H), 7.50-7.48 (m, 4H), 7.44 (d, J = 8.5 Hz, 2H), 1.88 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6), δ (ppm): 192.3, 140.6, 127.7, 125.6, 124.9, 123.4, 123.3, 121.0, 112.2, 34.3, 30.2. Anal. calculated for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48; found: C, 76.45; H, 5.51; N, 8.51.

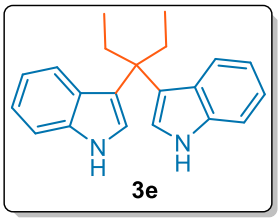
3,3'-(Butane-2,2-diyl)bis(1H-indole)



3d

Obtained as colorless liquid, 233 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.88 (br s, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.09-7.04 (m, 4H), 6.88-6.84 (m, 2H), 2.43 (q, J = 7.4 Hz, 2H), 1.82 (s, 3H), 0.78 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 137.0, 126.4, 124.2, 121.3, 121.2, 118.5, 111.0, 110.9, 38.6, 32.7, 26.2, 9.0.

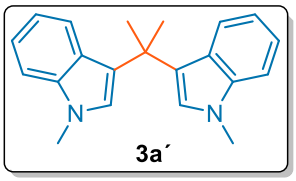
3,3'-(Pentane-3,3-diyl)bis(1H-indole)



3e

Obtained as colorless liquid, 229 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.89 (br s, 2H), 7.25 (d, J = 7.2 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 2.4 Hz, 2H), 7.02-6.98 (m, 2H), 6.76-6.72 (m, 2H), 2.29 (q, J = 7.4 Hz, 4H), 0.66 (t, J = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 136.9, 126.6, 122.7, 121.8, 121.2, 118.4, 110.8, 110.7, 42.0, 27.9, 8.3.

3,3'-(Propane-2,2-diyl)bis(1-methyl-1H-indole)



3a´

Reaction intermediate is isolated as yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.44 (d, J = 8.0 Hz, 2H), 7.25-7.23 (m, 2H), 7.13-7.09 (m, 2H), 6.91-6.87 (m, 4H), 3.72 (s, 6H), 1.90 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ (ppm): 137.7, 126.7, 125.5, 124.1, 121.4, 120.9, 118.0, 109.0, 34.9, 32.6, 30.3.

3.6 X-Ray Crystallography Details

Methods to cultivate the crystals of 2d: Solid **2d** (~10 mg) was dissolved in 2mL ethyl acetate in a small glass vial. Slow evaporation of this solution at rt produced the crystals after two days that were analyzed by X-ray crystallography.

Single crystal X-ray diffraction: Bruker SAINT software has been employed for reducing the data and SADABS for correcting the intensities of absorption. Structure was solved and refined using SHELXL with anisotropic displacement parameters for non-H atoms. C–H atoms were fixed geometrically using the HFIX command in SHELX-TL. No any missed symmetry observed in the final check of CIF file using PLATON. Crystallographic parameters for the structure are furnished in Table **3.4**.

Table 3.4 Crystallographic parameters of structures **2d**

Crystal data	**2d**
Formula unit	$C_{26}H_{30}N_2O_2$
Formula weight (g mol^{-1})	402.52
Crystal system	orthorhombic
T [K]	100 K
a [Å]	8.0818(7)
b [Å]	16.4868(15)
c [Å]	32.475(3)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	4327.1(7)
Space group	*Pbca*
Z	8
D_{cal} [g/cm^3]	1.236
R_1, wR_2	0.0429, 0.0941
Instrument	Bruker CCD Apex II
CCDC Number	2254620

ORTEP for compound 2d: Figure **3.1** shows the Oak Ridge Thermal Ellipsoid Plot (ORTEP) with 50% probability ellipsoid for compound **2d.**

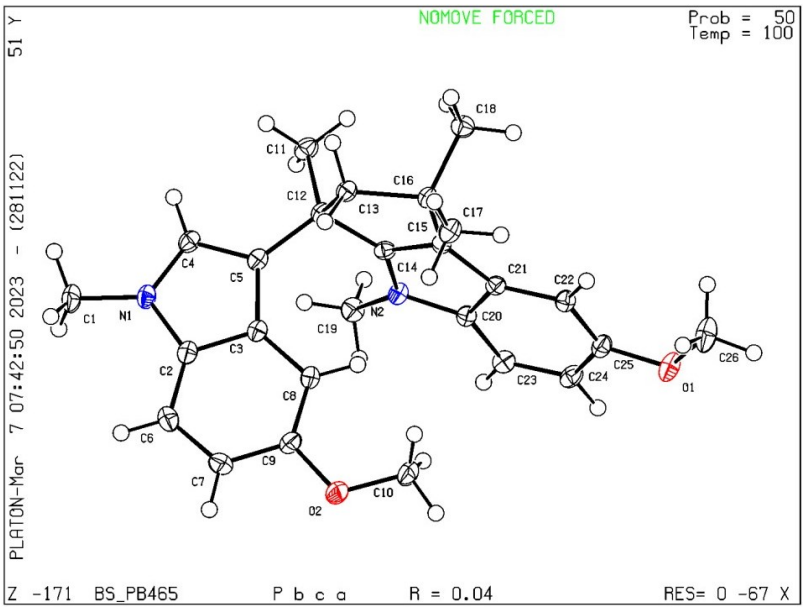


Figure 3.1 ORTEP of **2d** with 50% probability ellipsoids

3.7 Representative HRMS spectra

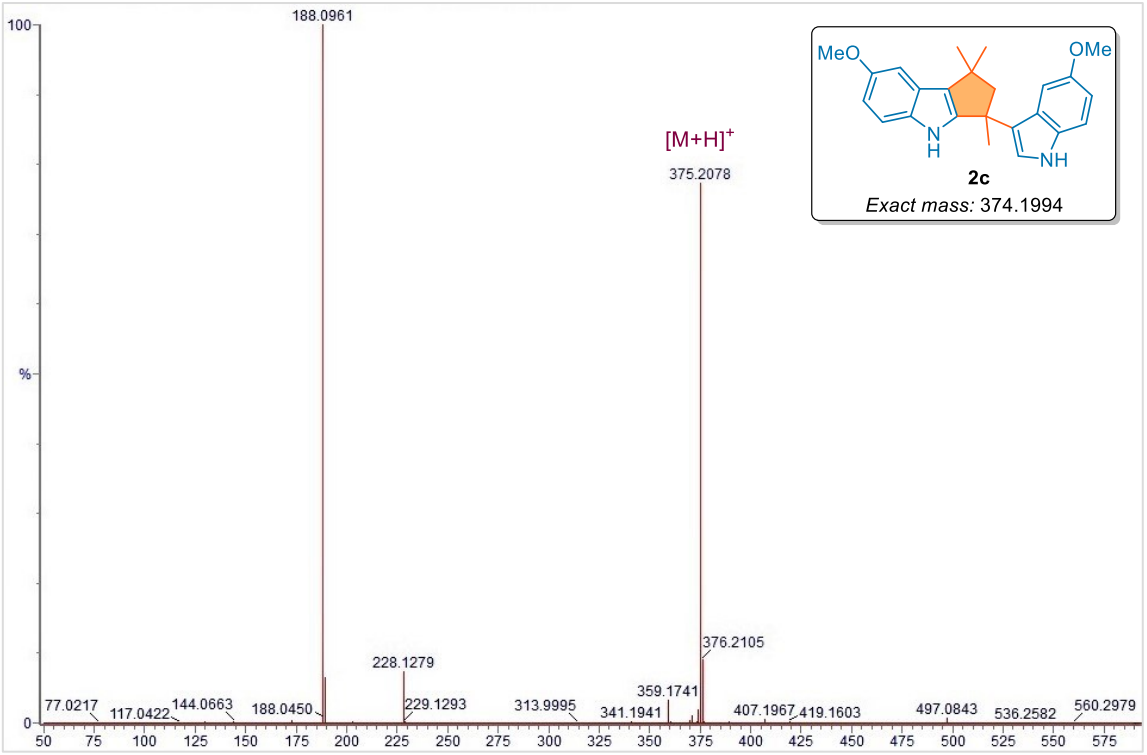


Figure 3.2 HRMS spectrum of **2c**

3.8 Representative ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra

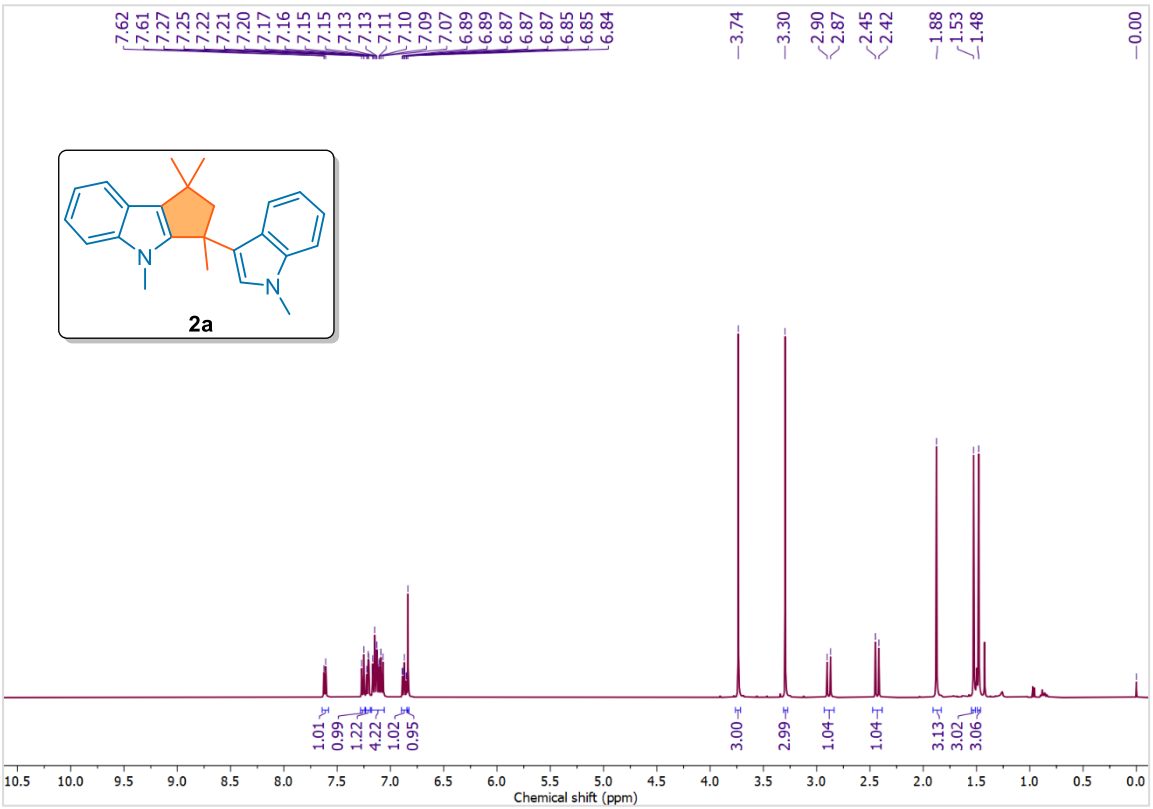


Figure 3.3 ^{1}H NMR (400 MHz) spectrum of **2a** in $CDCl_3$

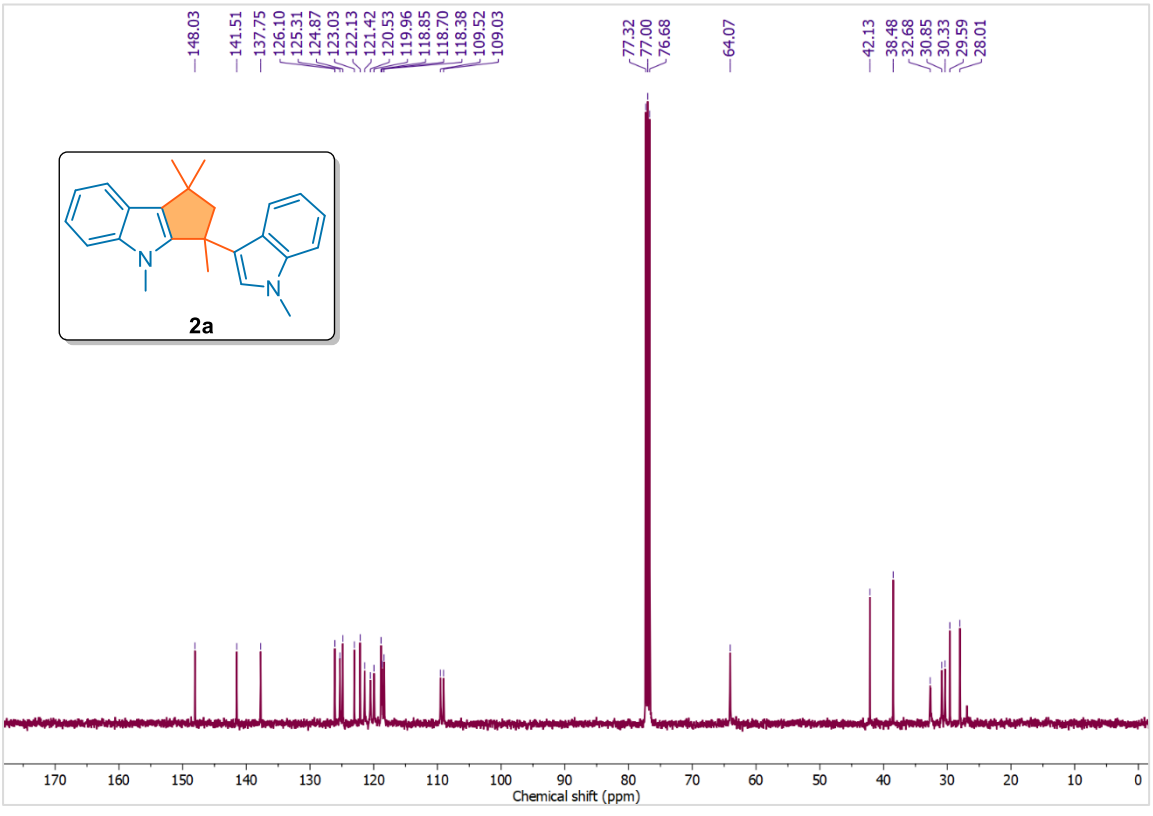


Figure 3.4 $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **2a** in $CDCl_3$

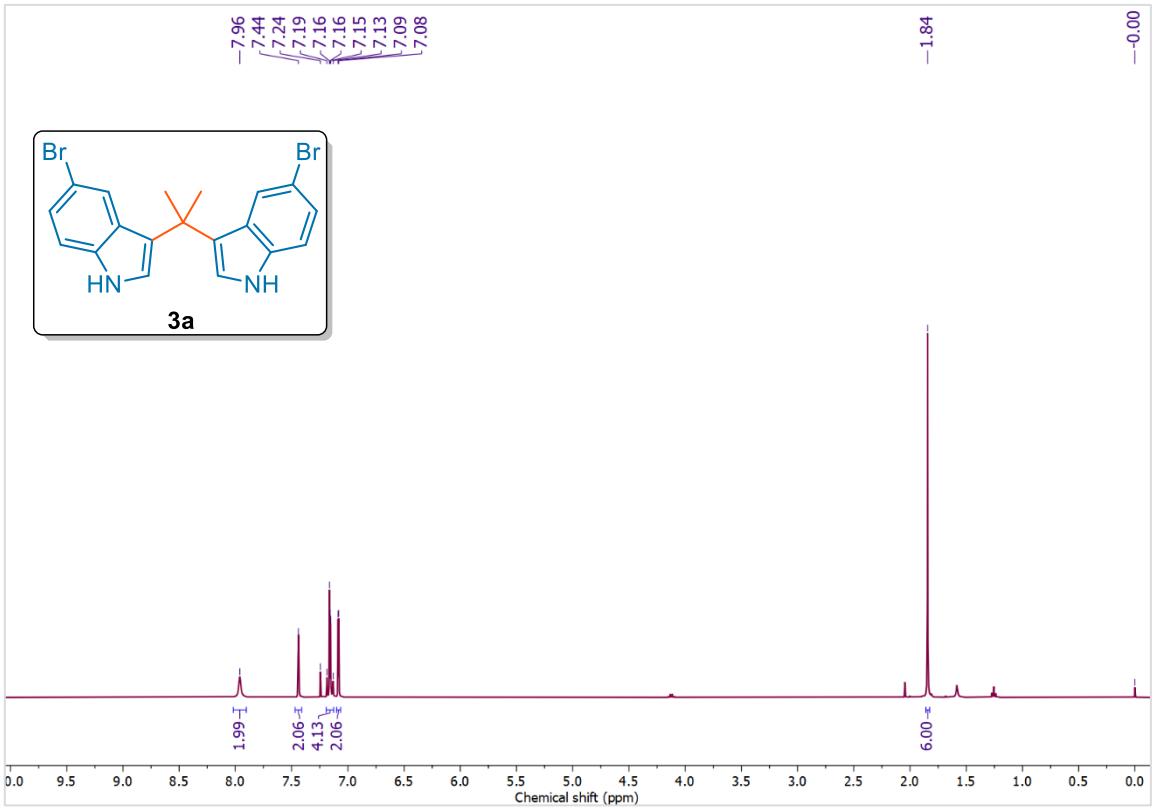


Figure 3.5 ^{1}H NMR (400 MHz) spectrum of **3a** in $CDCl_3$

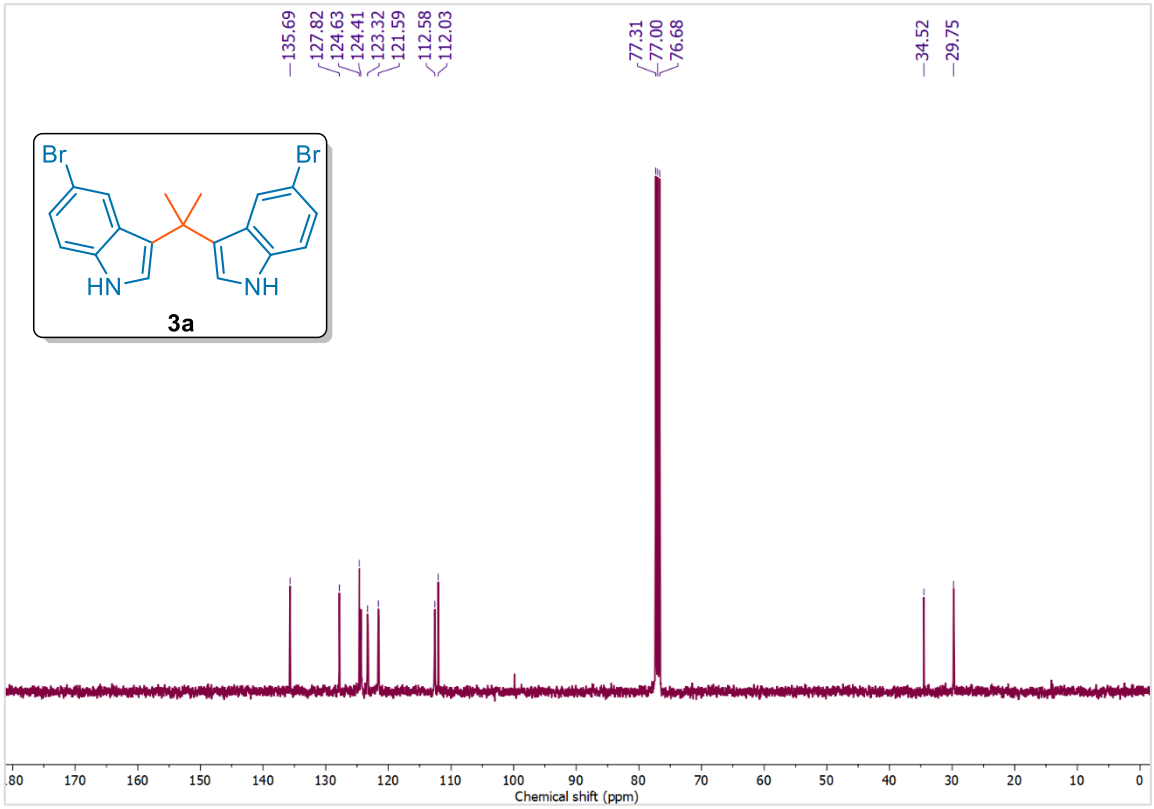


Figure 3.6 $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **3a** in $CDCl_3$

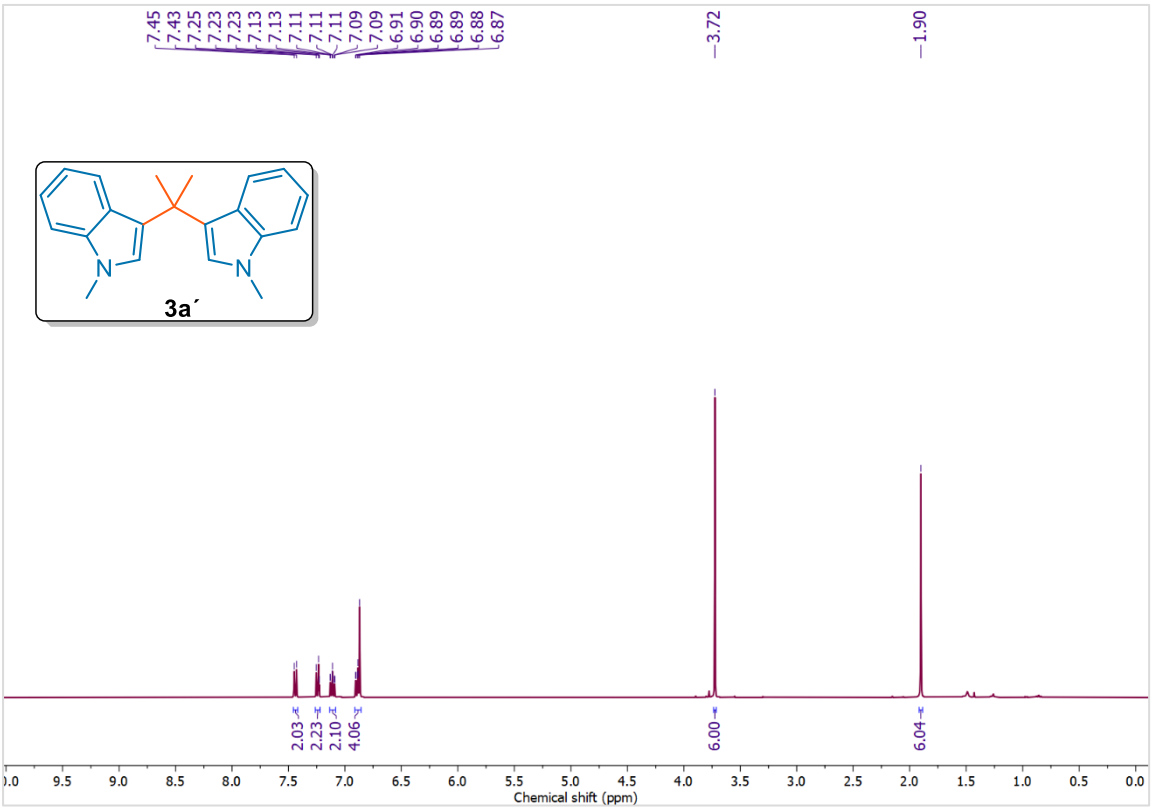


Figure 3.7 ^{1}H NMR (400 MHz) spectrum of **3a´** in $CDCl_3$

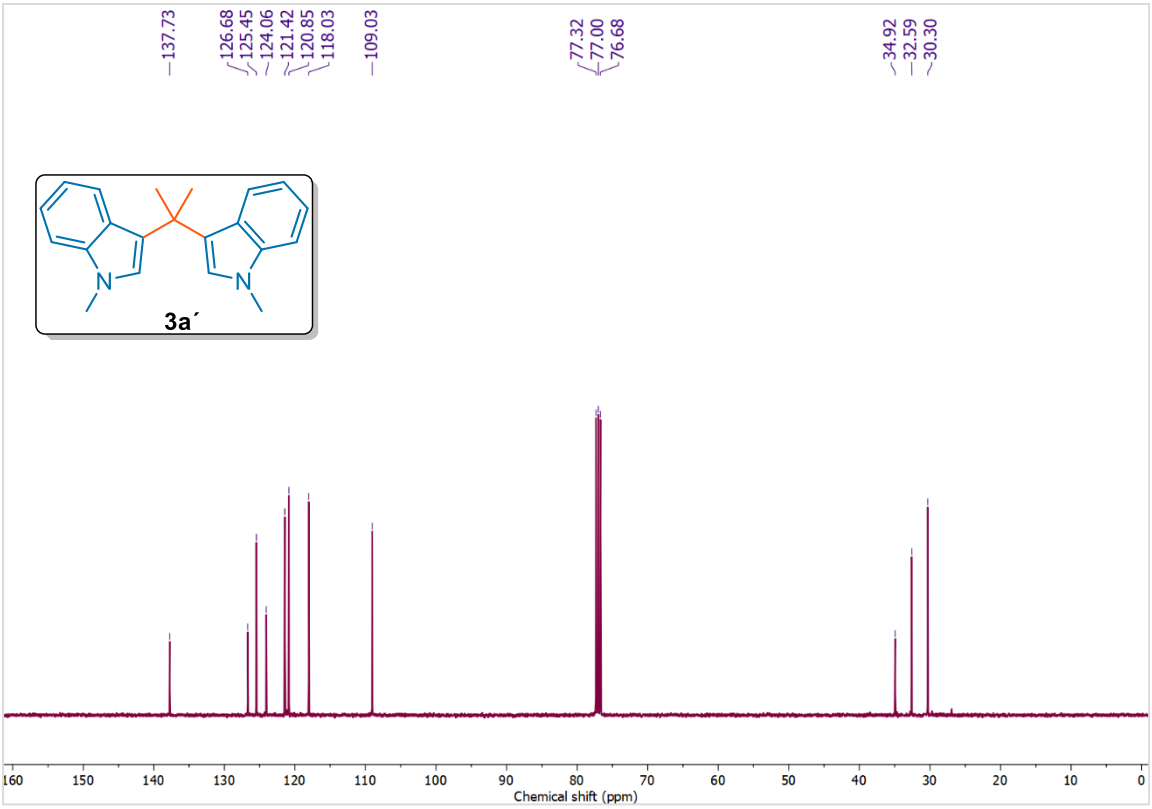


Figure 3.8 $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **3a´** in $CDCl_3$

3.9 Bibliography

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