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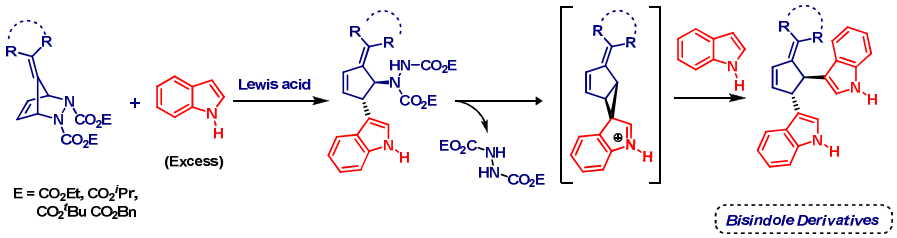
Graphical Abstract



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ARTICLE

Lewis Acid Catalyzed C-3 Alkylidenecyclopentenylation of Indoles: An Easy Access to Functionalized Indoles and Bisindoles

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A Lewis acid catalyzed C-3 alkylidenecylopentenylation of indoles through the ring opening of pentafulvene derived diazabicyclic olefins has been developed. The present protocol offers an efficient route toward the synthesis of indole and bisindole derivatives. Role of hydrazine group, as a reaction carrier in the strategy has also been demonstrated by the stepwise synthesis of functionalized bisindole.

Indole, an important nitrogen containing heterocyclic scaffold, is one of the primary building blocks of many natural products, biologically active molecules and functional materials.[1] Moreover, indole is the key component in many pharmaceutical agents such as triptan and its derivatives, a class of psychoactive drugs used in the treatment of 5HT receptor related disorders (Figure 1).[2] Owing to the great prevalence of indole nucleus, enormous research efforts have been devoted towards the synthesis and functionalization, especially at C-3 position of this privileged core.[3] Various synthetic methodologies, involving Lewis and Brønsted acids, organocatalysts or transition metal catalysts, have been developed by different research groups for the selective C-3 functionalization of indoles.[4] In 2001, Kobayashi et al. achieved the C-3 cyclopentenylation of indoles through a Lewis acid/surfactant catalyzed Friedel-Crafts type conjugate addition in aqueous medium.[5] Later, King and coworkers explored the Lewis acid catalyzed Michael addition of indoles to cyclopent-2-enone for the preparation of 3-cis-(3-aminocyclopentenyl)indoles as potent inhibitors of hSERT.[6] Among indole derivatives, bisindole moieties are present in several natural alkaloids[7] and many of these compounds show promising medicinal properties (Figure 1).[8] So the design and development of new atom economic methods for construction of bisindole derivatives remains as a highly demanding strategy in organic synthesis. Herein, we disclose a Lewis acid catalyzed ring-opening of pentafulvene derived bicyclic olefins with N-alkyl as well as free (NH) indoles toward the efficient synthesis of mono and bisindolyl functionalized alkylidenecyclopentenes.

In various cycloaddition reactions, pentafulvenes, a cyclic cross conjugated system, have been well explored as a 2π, 4π or 6π component for the construction of numerous biologically relevant molecules.[9] Additionally, desymmetrization of diazabicyclic olefins under transition metal catalysis or acid catalysis has been developed as an efficient protocol by several research groups,[10] including our laboratory for the synthesis of highly functionalized cyclopentene derivatives.[11]

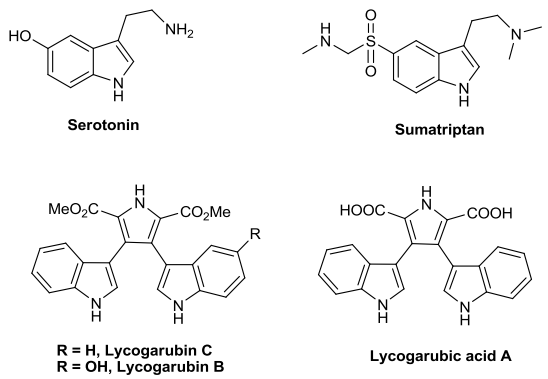
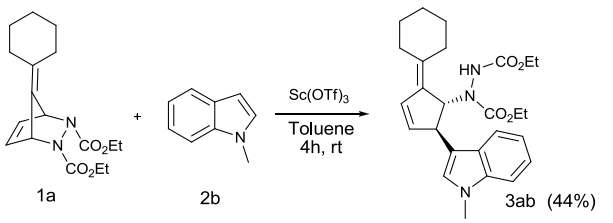


Figure 1: Bioactive compounds with indole or bisindole scaffolds

As part of our continuous interest in the chemistry of strained norbornene derivatives, we have utilized diazabicyclic olefins derived from different pentafulvenes as a simple precursor for the synthesis of substituted alkylidenecyclopentenes and complex heterocyclic scaffolds in the presence of a palladium catalyst or Lewis acid. In our previous report we have demonstrated a Lewis acid catalyzed ring-opening of pentafulvene derived diazabicyclic olefins using various ortho-functionalized aryl iodides such as 2-iodoanilines, 2-iodophenols and 2-iodobenzene thiols and aliphatic alcohols to access a variety of trans-1,2 disubstituted

alkylidenecyclopentenes.[12] In the same report, a palladium/Lewis acid mediated transformation of pentafulvene derived diazabicyclic olefins has also been described for the synthesis of novel spiropentacyclic motifs with indoline/dihydrobenzothiophene and pyrazolidine fused to the cyclopentene core. As a perpetuation of our ongoing investigations in the area of strained bicyclic olefins, we have decided to undertake the Lewis acid catalyzed desymmetrization of pentafulvene derived diazabicyclic olefins by employing biologically significant indoles as nucleophiles. The developed method successfully leads to the C-3 functionalization of indoles with alkylidenecyclopentenes, along with the formation of bisindole derivatives.

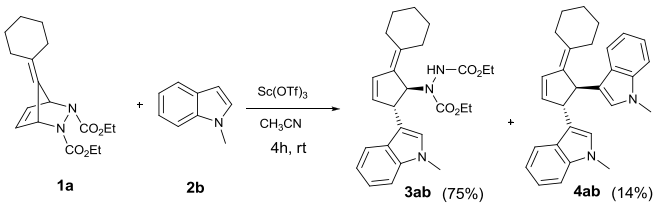
We initiated our investigation by the treatment of pentafulvene derived diazabicyclic olefin **1a** (1.2 equiv.) with *N*-methyl indole **2b** (1 equiv.) in the presence of $Sc(OTf)_3$ (2 mol%) in toluene at room temperature (Scheme 1). After 4 h, the reaction afforded the desired *trans*-1,2 disubstitutedalkylidenecyclopentene derivative **3ab** in 44% yield. The structure of **3ab** was established by the usual spectroscopic techniques and also based on comparison with our previous report.[12] Furthermore, the structure and stereochemistry of the product was confirmed by single crystal X-ray analysis of a similar derivative **3eb** (See Supporting Information, CCDC 1034718).



Scheme 1. Lewis acid catalyzed C-3 functionalization of N-methyl indole 2b with diazabicyclic olefin 1a

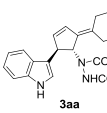
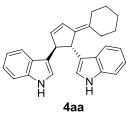
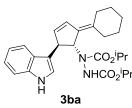
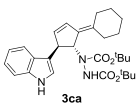
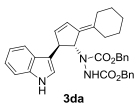
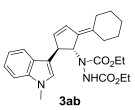
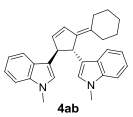
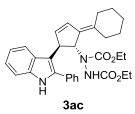
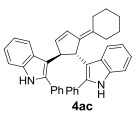
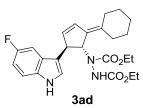
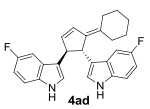
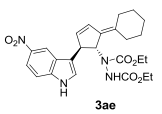
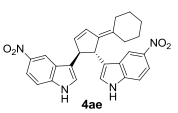
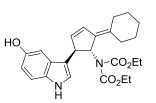
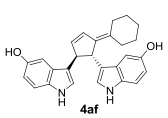
Table 1. Screening of the reactivity of various Lewis acids in different solvents

Entry	Lewis acid	Solvent	Yield %	
			3ab	**4ab**
1	$Sc(OTf)_3$	toluene	44	–
2	$Sc(OTf)_3$	DMF	38	–
3	$Sc(OTf)_3$	THF	30	–
4	$Sc(OTf)_3$	DCE	65	5
5	$Sc(OTf)_3$	DCM	58	trace
6	$Sc(OTf)_3$	CH_3CN	75	14
7	$Yb(OTf)_3$	CH_3CN	37	–
8	$Zn(OTf)_2$	CH_3CN	trace	–
9	$La(OTf)_3$	CH_3CN	35	–
10	$Cu(OTf)_2$	CH_3CN	46	–
11	$Sn(OTf)_2$	CH_3CN	70	8
12	$Fe(OTf)_3$	CH_3CN	62	6
13	AgOTf	CH_3CN	trace	–
14	$AlCl_3$	CH_3CN	53	trace
15	BF_3OEt_2	CH_3CN	36	–
16[a]	$Sc(OTf)_3$	CH_3CN	31	58



Scheme 2. Sc(OTf)3 catalyzed C-3 functionalization of N-methyl indole 2b with diazabicyclic olefin 1a in acetonitrile

Table 2. Substrate scope of indoles with various 6,6-pentamethylene fulvene derived diazabicyclic olefins

Entry	Bicyclic olefin	Indole	Product 3	Product 4	Yield (%) 3	Yield (%) 4
1	1a	2a	 3aa	 4aa	73 27[a]	16 64[a]
2	1b	2a	 3ba	4aa	72 14[a]	16 72[a]
3	1c	2a	 3ca	4aa	42 27[a]	14 28[a]
4	1d	2a	 3da	4aa	39 17[a]	12 33[a]
5	1a	2b	 3ab	 4ab	75 31[a]	14 58[a]
6	1a	2c	 3ac	 4ac	78 32[a]	11 54[a]
7	1a	2d	 3ad	 4ad	61 24[a]	14 52[a]
8	1a	2e	 3ae	 4ae	59 26[a]	12 48[a]
9	1a	2f	 3af	 4af	56 28[a]	8 39[a]

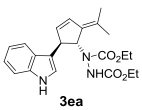
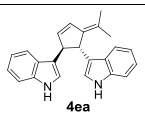
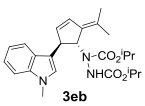
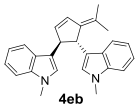
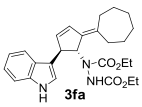
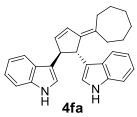
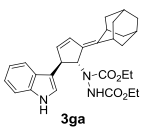
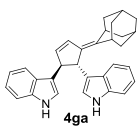
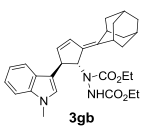
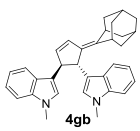
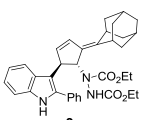
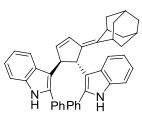
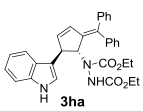
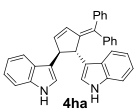
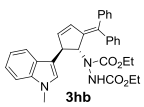
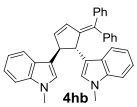
Reaction Conditons: alkene (1.2 equiv.), indole (1equiv.), catalyst (2 mol%), solvent (2 mL), at rt. for 4 h

[a] Reaction in presence of 1equiv. of alkene and 2 equiv. of indole

Further screening of solvents such as DMF, THF, 1,2-dichloroethane, DCM and CH_3CN revealed that CH_3CN was the most favorable medium for the transformation. Astonishingly, when

CH_3CN was employed as the solvent, the bisindolyl functionalized alkylidenecyclopentene **4ab** was observed along with the expected 3,4-disubstituted alkylidenecyclopentene **3ab** (Scheme 2). Various Lewis acids were also tested for the ring-opening of **1a** with **2b** in acetonitrile. Among them, $Sn(OTf)_2$ and $Fe(OTf)_3$ provided the product **3ab** in comparable yields. During optimization studies, we perceived that the change in equivalents of starting materials **1a** or **2b** played a crucial role in the outcome of the reaction. Use of 2 equiv. of *N*-methylindole **2b** resulted in the formation of bisindole product **4ab** (58% yield) in excess over **3ab** (31% yield) (Entry 16). Under optimal conditions (2 mol% $Sc(OTf)_3$ in CH_3CN), the reaction could be finely tuned towards the formation of alkylidenecyclopentenyl derivative of indole **3ab** or bisindole **4ab** by simply altering the equivalents of starting materials **1a** or **2b**.

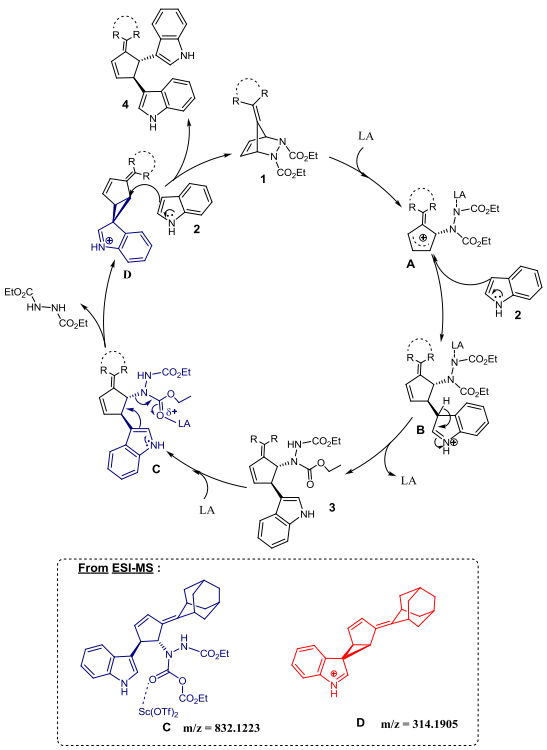
Table 3. Substrate scope of various pentafulvene derived diazabicyclic olefins for the C-3 functionalization of indole

Entry	Bicyclic olefin	Indole	Product 3	Product 4	Yield (%) 3	Yield (%) 4
1	1e	2a	 3ea	 4ea	69 24[a]	18 64[a]
2	1e	2b	 3eb	 4eb	65 27[a]	15 56[a]
3	1f	2a	 3fa	 4fa	70 25[a]	9 53[a]
4	1g	2a	 3ga	 4ga	66 30[a]	24 58[a]
5	1g	2b	 3gb	 4gb	70 32[a]	16 55[a]
6	1g	2c	 3gc	 4gc	66 13[a]	14 74[a]
7	1h	2a	 3ha	 4ha	62 8[a]	28 84[a]
8	1h	2b	 3hb	 4hb	68 10[a]	24 81[a]

Reaction Conditons: alkene (1.2 equiv.), indole (1equiv.), catalyst (2 mol%), solvent (2 mL), at rt for 4 h
[a] Reaction in presence of 1equiv. of alkene and 2 equiv. of indole

Under the optimized catalytic conditions for the preparation of alkylidenecyclopentenyl derivative of indole (Table1, Entry 6) and bisindole (Table 1, Entry 16), we examined the scope of different olefins and indoles (Table 2). Diazabicyclic alkenes **1a-d** easily underwent ring opening with 1*H*-indole **2a** and gave the corresponding indole derivatives **3aa-da** and bisindole **4aa** in good to moderate yields (Entries 1-4). To demonstrate the generality of the reaction, several C-1, C-2 and C-5 substituted indoles **2b-f** were subjected to C-3 alkylidenecyclopentenylation. Reaction was found to be compatible to a variety of indoles having substituents such as -F, -OH, $-NO_2$ etc. and yielded the C-3 functionalized indoles and bisindoles (Entries 5-9).

Next, we turned our attention to explore the scope of C-3 functionalization of indoles with diazabicyclic olefins derived from different pentafulvenes (Table 3). Alkylidenecyclopentenylation of indoles proceeds efficiently through the ring opening of diazabicyclic alkenes **1e-h** to provide the desired indole and bisindole derivatives. In the case of diphenylfulvene derived bicyclic olefin **1h** with indoles **2a** and **2b**, corresponding bisindole derivatives were formed in 84% and 81% yield respectively (Entries 7,8). Furthermore, the stereochemistry of the bisindole product **4** was unambiguously confirmed by the single crystal X-ray analysis of compound **4ha** (Figure 2, CCDC 989506).



Scheme 3: Plausible Mechanism

Based on these results we propose a plausible mechanism as shown in Scheme 3. As similar to our previous reports,[12] the catalytic cycle is initiated by coordination of the Lewis acid with the carbonyl oxygen of one of the carbamate groups of diazabicyclic olefin **1** and subsequent cleavage of the C–N bond leads to the generation of a

transient allylic cation species **A**. Regioselective nucleophilic attack of indole from the opposite side with respect to the hydrazine moiety of intermediate **A** delivers *trans*-1,2-disubstituted alkylidenecyclopentene **3**. In the next step, the Lewis acid coordinates with the carbonyl group of the hydrazine moiety, followed by the elimination of the hydrazine group through C-N bond cleavage, resulting in the formation of intermediate **D**. Attack of the second molecule of indole to intermediate **D** furnishes the bisindole product **4.** Furthermore, ESI-MS studies provided strong supporting evidence for the formation of intermediates **C** and **D** (See Supporting Information).

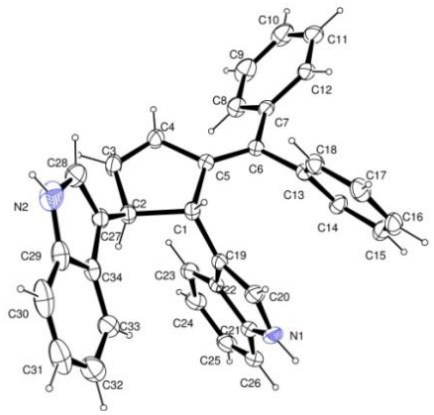
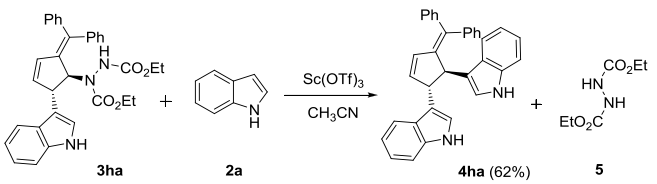


Figure 2. Single crystal X-ray structure of compound **4ha**

To confirm the Lewis acid catalyzed generation of an intermediate from **3** by the elimination of hydrazine moiety, we have carried out a reaction with 1 equiv. of 3,4-disubstituted alkylidenecyclopentene **3ha** and 1.2 equiv. of indole **2a** (Scheme 4). As expected, bisindole product **4ha** was obtained in 62% yield, supporting the role of 3,4-disubstituted alkylidenecyclopentene as an intermediate in the course of reaction. It is to be noted that the hydrazine group acts as a key functional moiety in the present atom economic strategy toward the synthesis of functionalized bisindoles. In addition, oxidation of the generated hydrazine could provide the corresponding dialkyl diazene-1,2-dicarboxylates, which can be reused in the cycloaddition reactions.



Scheme 4. Lewis acid catalyzed synthesis of bisindole derivative catalyzed synthesis of bisindole derivative

In summary, we have developed a Lewis acid catalyzed C-3 alkylideneclopentenylation of indoles through the ring opening of pentafulvene derived diazabicyclic olefins. The developed method provides an efficient synthetic route to furnish pharmaceutically valuable indole and bisindole derivatives of alkylidenecyclopentenes from easily accessible starting materials. While multiple steps are involved in conventional synthetic strategies, this protocol offers a one-pot access to cyclopentene-bisindole hybrids. Moreover, the present strategy is compatible with both *N*-alkyl and free (NH) indoles. Further investigations to elaborate the scope of the reaction on other *N*-heterocycles and also to explore the biological applications of synthesized molecules are currently underway.

Experimental Section

General Methods

All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulfate binder. Gravity column chromatography was performed using 60-120 or 100-200 mesh silica gel and mixtures of hexane-ethyl acetate were used for elution.

Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.25, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quadret); dd (double doublet); m (multiplet). Coupling constants are reported as *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, triplet). Mass spectra were recorded under EI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on Bruker FT-IR spectrometer.

General Procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines towards the synthesis of 3.

A mixture of pentafulvene derived bicyclic hydrazine (1.2 eqiuv.), indole (1.0 equiv.) and $Sc(OTf)_3$ (2 mol %) were weighed in a Schlenk tube and degassed for 10 minutes. Dry CH_3CN (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 4 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography yielded *trans*-3,4-disubstituted alkylidene cyclopentene (**3**) along with minor amount *trans*-3,4-disubstituted bisindolyl product (**4)**

General Procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines towards the synthesis of 4.

A mixture of pentafulvene derived bicyclic hydrazine (1.0 eqiuv.), indole (2.0 equiv.) and $Sc(OTf)_3$ (2 mol %) were weighed in a Schlenk tube and degassed for 10 minutes. Dry CH_3CN (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 4 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography yielded *trans*-3,4-disubstituted bisindolyl product (**4)** along with minor amount *trans*-3,4-disubstituted *trans*-3,4-disubstituted alkylidene cyclopentene.

Diethyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3aa)

Yield: 73%; pale yellow solid; M. p. 122–124^{o}C; R_f: 0.31 (hexane/ethyl acetate = 3:1). **IR (Neat) ν_{max}:** 3334, 3054, 2976, 2920, 2853, 1709, 1586, 1458, 1410, 1330, 1220, 1120, 1052, 920, 745cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.10 (brs, 1H), 7.68 (brs,.03 (m, 1H), 6.84 (s, 1H), 6.53(d, *J* = 6 Hz, 1H), 6.26 (brs, 1H), 6.04 (brs, 1H), 5.34- 5.12 (m, 1H), 4.50-4.40 (m, 1H), 4.24-4.17 (m, 4H), 2.39- 2.33 (m, 2H), 2.08- 2.07 (m, 2H), 1.66-1.53 (m, 6H), 1.30-1.29 (m, 5H), 1.02 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.6, 155.1, 136.7, 136.2, 134.0, 129.7, 126.6, 121.9, 120.0, 119.2, 118.1, 110.0, 65.4, 64.1, 62.4, 61.9, 47.4, 32.0, 31.0, 28.4, 28.1, 26.6, 14.5, 14.2. **HRMS (ESI):** Calcd for $C_{25}H_{31}N_3O_4Na$: 460.22123; Found: 460.22171.

Diethyl 1-(2-cyclohexylidene-5-(1-methyl-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ab)

Yield: 75%; pale yellow solid; M. p. 120–122^{o}C, R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3323, 3055, 2981, 2932, 2855, 1710, 1619, 1583, 1513, 1458, 1415, 1339, 1302, 1227, 1096, 1061, 920, 743cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.68 (brs, 1H), 7.25-7.23 (m, 2H), 7.05 (t, *J* = 7Hz,1H), 6.73 (s, 1H), 6.53(d, J=5.5, 1H), 6.23 (brs, 1H), 6.04 (s, 1H), 5.31-5.09 (m, 1H), 4.49-4.39 (m, 1H), 4.24-4.18 (m, 4H), 3.72 (s, 3H), 2.38-2.34 (m, 2H), 2.07-2.03 (m, 2H), 1.61-1.53 (m, 6H), 1.31-1.26 (m, 5H), 1.05-1.04 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.4, 155.1, 137.4, 133.7, 129.6, 127.0, 125.7, 121.5, 120.1, 118.7, 109.1, 108.8, 65.5, 62.3, 61.8, 47.5, 32.5, 31.9, 28.3, 28.0, 26.5, 14.5. **HRMS (ESI):** Calcd for $C_{26}H_{33}N_3O_4Na$: 474.23688; Found: 474.23764.

Diethyl 1-(2-cyclohexylidene-5-(2-phenyl-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ac)

Yield: 78%; yellow viscous liquid; R_f: 0.36 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3324, 2980, 2930, 2854, 1701, 1519, 1472, 1420, 1382, 1332, 1261, 1233, 1097, 1060 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.16 (brs, 1H), 7.60-7.25 (m, 6H), 7.19-7.03 (m, 2H), 7.03 (d, *J* = 7Hz, 1H), 6.55 (brs, 1H), 6.20-6.03 (m, 1H), 5.91 (brs, 1H), 5.59-5.45 (m, 1H), 4.68-4.53 (m, 1H), 4.16-4.12 (m, 4H), 2.58 (brs, 1H), 2.39-2.12 (m, 3H), 1.75-1.59 (m,6H), 1.29-0.88 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.2, 155.4, 137.7, 136.3, 134.7, 132.8, 129.0, 128.6, 128.2, 127.6, 125.3, 121.9, 120.3, 119.4, 110.9, 62.4, 61.7, 60.3, 48.3, 34.6, 32.1, 26.9, 26.7, 21.5, 14.5, 14.2. **HRMS (ESI):** Calcd for $C_{31}H_{35}N_3O_4Na$: 536.25253; Found: 536.25289.

Diethyl 1-(2-cyclohexylidene-5-(5-fluoro-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ad)

Yield: 61%; colourless viscous liquid; R_f: 0.26 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3363, 3277, 3054, 2984, 2931, 2854, 1711, 1582, 1500, 1149, 1411, 1330, 1120, 1050, 1010, 919, 744cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.26 (s, 1H), 7.34 (brs, 1H), 7.27-7.22 (m, 1H), 6.96-6.92 (brs, 1H), 6.65-6.56 (m, 2H), 6.40-6.31 (m, 1H), 6.02 (d, J = 3.5Hz,1H), 5.32-5.11 (m, 1H), 4.46-4.18 (m, 5H), 2.41- 2.33 (m, 2H), 2.07-2.05 (m, 2H), 1.62-1.45 (m, 6H), 1.35-1.07 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 158.5, 156.8, 155.3, 136.9, 133.3, 130.0, 126.9, 123.1, 118.1, 111.5, 110.3, 104.9, 65.4, 62.6, 62.3, 47.5, 32.0, 31.1, 28.3, 28.0, 26.5, 14.4.

HRMS (ESI): Calcd for $C_{25}H_{30}FN_3O_4Na$: 478.21180; Found: 478.21223.

Diethyl 1-(-2-cyclohexylidene-5-(5-nitro-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ae)

Yield: 59%; pale yellow solid; M. p. 132–134^{o}C. R_f: 0.22 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3365, 3071, 2960, 2852, 1712, 1623, 1582, 1469, 1410, 1380, 1318, 1245, 1173, 1115, 1058, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 9.22 (brs, 1H), 8.56(s, 1H), 7.92 (brs, 1H), 7.17-7.13 (m, 1H), 6.92-6.82 (m, 1H), 6.61 (d, 1H, *J* = 4.5Hz), 6.34 (brs, 1H), 5.98 (brs, 1H), 5.39-5.17 (m, 1H), 4.49-4.23 (m, 5H), 2.56-2.06 (m, 4H), 1.76-1.22 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.3, 155.6, 141.3, 139.8, 137.7, 130.1, 129.0, 128.2, 125.5, 125.3, 124.2, 117.6, 117.2, 111.0, 64.3, 62.9, 62.2, 47.5, 32.1, 31.3, 28.2, 26.6, 21.5, 14.5, 14.2.

HRMS (ESI): Calcd for $C_{25}H_{30}N_4O_6Na$: 505.20630; Found: 505.20668.

Diethyl 1-(2-cyclohexylidene-5-(5-hydroxy-1H-indol-3-yl) cyclopent-3-enyl) hydrazine-1,2-dicarboxylate. (3af)

Yield: 56%; pale yellow viscous liquid; R_f: 0.17 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3380, 3280, 3054, 2976, 2928, 2853, 1709, 1586, 1499, 1149, 1410, 1330, 1220, 1120, 1052, 1011, 920, 745cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.89 (brs, 1H), 7.23-7.15 (m, 2H), 6.79-6.77 (m, 1H), 6.56-6.28 (m, 2H), 6.05 (brs, 1H), 5.32-5.09 (m,1H), 4.45-4.11 (m, 5H), 2.37-2.33 (m, 2H), 2.07-2.06 (m, 2H), 1.60-1.38 (m, 6H), 1.29-1.13 (m, 5H), 0.99 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 155.2, 154.5, 147.5, 135.8, 135.0, 134.3, 127.2, 126.8, 125.3, 111.9, 111.8, 108.5, 104.5, 64.9, 62.8, 62.2, 41.9, 32.0, 28.2, 26.5, 19.4, 19.2, 14.5. **HRMS (ESI)**: Calcd for $C_{25}H_{31}N_3O_5Na$: 476.21614; Found: 476.21658.

Diisopropyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ba)

Yield: 72%; pale yellow viscous liquid; R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3331, 3068, 2981, 2932, 2857, 1688, 1621, 1583, 1514, 1462, 1380, 1304, 1238, 1108, 1042, 957, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.16 (brs, 1H), 7.75-7.71 (m, 1H), 7.31-7.23 (m, 1H), 7.18-7.05 (m, 2H), 6.88 (brs, 1H), 6.56-6.27 (m, 2H), 6.07 (brs, 1H), 5.34-5.14 (m, 1H), 5.00-4.95 (m, 2H), 4.53-4.43 (m, 1H), 2.36 (brs, 2H), 2.09-1.81 (m, 2H), 1.61-1.51 (m, 6H), 1.44-1.22 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.5, 154.7, 136.8, 133.8, 129.8, 129.0, 128.2, 126.7, 125.3, 121.7, 119.1, 110.9, 69.9, 69.5, 63.9, 47.2, 31.6, 30.8, 29.7, 28.3, 26.9, 22.7, 22.4, 22.1. **HRMS (ESI)**: Calcd for $C_{27}H_{35}N_3O_5Na$: 488.25253; Found: 488.25286.

Di-tert-butyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ca)

Yield: 42%; pale yellow viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3375, 3078, 2992, 2943, 2836, 1690, 1610, 1583, 1565, 1468, 1462, 1400, 1316, 1238, 1152, 1123, 969, 938, 746 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.00 (d, *J* = 11Hz,1H), 7.99-7.79 (m, 1H), 7.32-7.28 (m, 1H), 7.20-7.06 (m, 2H), 6.87 (s, 1H), 6.55 (d, *J* = 5.5Hz, 1H), 6.15-6.00 (m, 2H), 5.30-5.08 (m, 1H), 4.54-4.44 (m, 1H), 2.37 (brs, 2H), 2.12 (brs, 2H), 1.63-1.53 (m, 24H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 155.7, 154.0, 136.7, 136.5, 126.7, 122.1, 121.8, 119.2, 118.2, 111.1, 110.9, 110.7, 81.3, 80.7, 65.5, 44.3, 32.0, 31.1, 28.3, 28.2, 28.0, 26.6. **HRMS (ESI)**: Calcd for $C_{29}H_{39}N_3O_4Na$: 516.28383; Found: 516.28414.

Dibenzyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3da)

Yield: 39%; yellow viscous liquid; R_f: 0.31 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3358, 3059, 3027, 2920, 2858, 1702, 1580, 1489, 1449, 1400, 1311, 1281, 1050, 1000, 743cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.28 (brs, 1H),7.66 (brs, 1H), 7.39-6.90 (m, 13H), 6.75 (brs, 2H), 6.46 (s, 1H), 5.98-5.86 (m, 1H), 5.36 -5.05 (m, 5H), 4.52-4.29 (m, 1H), 2.36-2.32 (m, 2H), 2.02-1.94 (m, 2H), 1.56-1.26 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.4, 154.8, 136.7, 135.8, 133.4, 128.6, 128.5, 128.3, 128.2, 127.9, 126.6, 122.0, 121.2, 119.9, 119.4, 117.5, 110.9, 68.1, 67.6, 47.5, 32.0, 31.0, 28.3, 28.0, 26.5. **HRMS (ESI)**: Calcd for $C_{35}H_{35}N_3O_4Na$: 584.25253; Found: 584.25288.

Diethyl 1-(2-(1H-indol-3-yl)-5-(propan-2-ylidene) cyclopent-3-enyl) hydrazine-1,2-dicarboxylate. (3ea)

Yield: 69%; colourless viscous liquid; R_f: 0.29 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3317, 3056, 2982, 2931, 1719, 1620, 1582, 1512, 1415, 1382, 1229, 1096, 1062, 744 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.30 (s, 1H), 7.71 (brs, 1H), 7.34-7.27 (m, 1H), 7.19-7.08 (m, 2H), 6.86-6.78 (m, 2H), 6.52 (d, 1H, *J* = 5Hz), 6.05 (s, 1H), 5.35-5.14 (m, 1H), 4.53-4.18 (m, 5H), 1.89 (s, 3H), 1.67 (brs, 3H), 1.29-1.26 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.9, 155.8, 136.8, 136.6, 135.5, 129.0, 126.7, 125.3, 121.7, 119.9, 119.1, 119.0, 117.9, 111.3, 66.0, 62.6, 62.2, 47.6, 21.5, 14.4. **HRMS (ESI)**: Calcd for $C_{22}H_{27}N_3O_4Na$: 420.18993; Found: 420.18866.

Diethyl 1-(2-(1-methyl-1H-indol-3-yl)-5-(propan-2-ylidene) cyclopent-3-enyl) hydrazine -1,2-dicarboxylate. (3eb)

Yield: 65%; colourless solid; M. p. 124–126^{o}C, R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3385, 3055, 2981, 2924, 1707, 1611, 1474, 1413, 1379, 1321, 1265, 1219, 1163, 1122, 1061, 1021, 933, 739 cm-1. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.73 (s, 1H), 7.29-7.23 (m, 2H), 7.10 (t, *J* = 7Hz, 1H), 6.77 (brs, 1H), 6.53 (d, *J* = 5Hz, 1H), 6.39 (brs, 1H), 6.07 (s, 1H), 5.36-5.14 (m, 1H), 4.53-4.20 (m, 5H), 3.73 (s, 3H), 1.90 (s, 3H), 1.69 (s, 3H), 1.31-1.05 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.7, 155.6, 137.5, 136.7, 135.6, 130.5, 128.3, 127.1, 125.9, 121.6, 120.1, 118.8, 116.7, 109.0, 66.2, 62.5, 61.9, 47.5, 32.6, 21.5, 13.8. **HRMS (ESI)**: Calcd for $C_{23}H_{29}N_3O_4Na$: 434.20588; Found: 434.20615.

Diethyl 1-(2-cycloheptylidene-5-(1H-indol-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3fa)

Yield: 70%; colourless viscous liquid; R_f: 0.31 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3348, 3056, 2924, 2853, 1708, 1617, 1458, 1414, 1380, 1226, 1177, 1121, 1061, 741cm-1. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.09 (brs, 1H), 7.66 (brs, 1H),7.28 (brs, 1H), 7.16-7.04(m 2H), 6.84 (brs, 1H), 6.51 (d, *J* = 5.5Hz, 1H), 6.25-6.21 (m, 1H), 6.04 (brs, 1H), 5.33-5.11 (m, 1H), 4.50-4.18 (m, 5H), 2.50-2.41 (m, 2H), 2.20-2.16 (brs, 2H), 1.71-1.03 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.3, 155.5, 136.8, 129.0, 128.2, 126.6, 125.3, 121.7, 119.0, 119.0, 111.1, 62.4, 61.9, 47.6, 32.7, 32.3, 29.1, 28.2, 27.6, 14.5, 14.2. **HRMS (ESI)**: Calcd for $C_{26}H_{33}N_3O_4Na$: 474.23688; Found: 474.23714.

Compound 3ga

Yield: 66%; colourless viscous liquid; R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3323, 3057, 2920, 2848, 1713, 1620, 1475, 1413, 1381, 1305, 1294, 1216, 1116, 1085, 1065, 1025, 742 cm-^{1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.21 (brs, 1H), 7.70 (brs, 1H), 7.32-7.25 (m, 2H), 7.20-7.05 (m, 3H), 6.86 (brs, 1H), 6.56 (d, *J* =5.5Hz, 1H), 6.29 (brs, 1H), 6.05 (brs, 1H), 5.39-5.16 (m, 1H), 4.53-4.41 (m, 1H), 4.30-4.13(m, 4H), 3.06 (brs,1H), 2.59 (brs,1H), 2.08-1.64 (m, 12H), 1.35-1.08 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.7, 155.2, 144.4, 136.5, 130.2, 129.0, 128.3, 126.6, 125.3, 121.4, 121.1, 119.9, 119.0, 117.1, 111.1, 63.8, 62.5, 62.0, 47.6, 39.9, 39.5, 39.1, 37.0, 35.1, 34.4, 28.1, 28.0, 21.5, 14.6. **HRMS (ESI)**: Calcd for $C_{29}H_{35}N_3O_4$: 512.25253; Found: 515.25290.

Compound 3gb

Yield: 70%; pale yellow viscous liquid; R_f: 0.36 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3315, 3054, 2910, 2852, 1711, 1612, 1472, 1413, 1379, 1305, 1221, 1124, 1061, 1019, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.71 (brs, 1H), 7.7-7.21 (m, 2H), 7.07 (t, *J* = 7Hz, 1H), 6.80 (brs, 1H), 6.55 (d, *J* = 5.5Hz, 1H), 6.25 (brs, 1H), 6.05 (s, 1H), 5.35-5.12 (m, 1H), 4.53-4.28 (m, 1H), 4.23-4.13 (m, 4H), 3.75 (s, 3H), 3.05 (s, 1H), 2.58 (brs, 1H), 2.02-1.63 (m, 12H), 1.37-1.09 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.6, 154.9, 137.4, 130.2, 127.1, 125.8, 121.5, 120.2, 118.7, 108.9, 62.3, 61.9, 47.2, 39.6, 37.0, 35.1, 34.7, 32.6, 28.1, 26.9, 25.3, 22.9, 20.8, 14.9. **HRMS (ESI)**: Calcd for $C_{30}H_{37}N_3O_4Na$: 526.26818; Found: 526.26862.

Compound 3gc

Yield: 66%; pale yellow viscous liquid; R_f: 0.38 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3378, 3058, 2978, 2908, 2848, 1756, 1704, 1467, 1445, 1409, 1379, 1364, 1338, 1308, 1277, 1248, 1218, 1172, 1157, 1097, 1062, 1022cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.58- 7.44 (m, 6H), 7.33-7.19 (m, 3H), 7.04 (brs,1H), 6.50-6.42 (m, 1H), 6.12-5.81 (m, 2H), 5.45 (brs, 1H), 4.25-4.15 (m, 4H), 3.58 (s, 3H), 3.06 (brs, 1H), 2.65-2.61 (m, 1H), 2.03-1.85 (m, 10H), 1.59-1.25 (m, 2H), 1.01-0.87 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.4, 155.3, 137.4, 131.3, 130.6, 128.1, 128.0, 121.5, 120.2, 119.0, 113.5, 109.3, 65.9, 62.3, 61.7, 47.8, 39.5, 39.4 37.0, 35.1, 34.6, 30.8, 28.2, 28.1, 14.7. **HRMS (ESI)**: Calcd for $C_{36}H_{41}N_3O_4Na$: 602.29948; Found: 602.29977

Diethyl 1-(2-(diphenylmethylene)-5-(1-methyl-1H-indol-3-yl)cyclopent-3-enyl)hydrazine -1,2-dicarboxylate. (3ha)

Yield: 62%; pale yellow solid, M. p. 182–184^{o}C; R_f: 0.24 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3362, 3051, 2968, 2911, 2852, 1736, 1710, 1552, 1514, 1467, 1454, 1411, 1384, 1364, 1308, 1287, 1243, 1231, 1168, 1157, 1069, 1063, 1022, 742cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.85-7.79 (m, 1H), 7.42-7.03 (m, 12H), 6.90-6.59 (m, 3H), 6.32-6.22 (brs, 1H), 6.04-5.91 (m, 2H),

5.08 (brs, 1H), 4.23-4.13 (m, 4H), 3.92-3.73 (m, 1H), 1.35-1.01 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.0, 154.7, 142.5, 142.4, 141.3, 140.8, 137.4, 130.0, 129.9, 128.6, 128.2, 127.7, 127.4, 126.8, 121.6, 120.2, 119.1, 116.9, 115.5, 110.2, 65.6, 62.0, 61.8, 47.9, 14.8. **HRMS (ESI)**: Calcd for $C_{32}H_{31}N_3O_4Na$: 544.22123; Found: 544.22151.

Diethyl 1-(2-(diphenylmethylene)-5-(1-methyl-1H-indol-3-yl)cyclopent-3-enyl)hydrazine -1,2-dicarboxylate. (3hb)

Yield: 68%; yellow viscous liquid; R_f: 0.29 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3340, 3068, 2981, 2932, 2857, 1688, 1621, 1602, 1583, 1555, 1514, 1462, 1380, 1315, 1238, 1108, 1042, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.79 (brs, 1H), 7.34-7.19 (m, 14H), 7.09-6.97 (m, 2H), 6.61-6.55 (m, 1H), 6.32 (brs, 1H), 5.82-5.56 (m, 2H), 4.70-4.65 (m, 1H), 4.25-4.15 (m, 4H), 3.76 (brs, 3H), 1.32- 1.29 (m, 4H), 1.03 (brs, 1H), 0.69 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.9, 154.9, 142.6, 142.3, 141.3, 140.7, 137.4, 130.0, 129.9, 128.5, 128.1, 127.4, 127.3, 127.1, 126.6, 121.4, 120.2, 118.8, 116.0, 115.3, 108.9, 65.5, 62.0, 61.8, 47.6, 32.6, 14.5,13.8. **HRMS (ESI)**: Calcd for $C_{33}H_{33}N_3O_4Na$: 558.23688; Found: 558.23721.

3, 3'-(5-Cyclohexylidenecyclopent-3-ene-1, 2-diyl)bis(1H-indole) (4aa)

Yield: 64%; pale yellow coloured solid, M. p. 152–156^{o}C; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3405, 2922, 2851, 2362, 2349, 1590, 1459, 1421, 1364, 1120, 1033 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.93 (s, 1H), 7.85 (s, 1H), 7.61-7.57 (m, 2H), 7.38-7.34 (m, 2H), 7.22-7.17 (m, 2H), 7.09-6.94 (m, 4H), 6.78 (d, J = 5.5Hz, 1H), 6.04 (dd, J_1 = 5.5Hz, J_2 = 2.5Hz, 1H), 4.32 (brs, 1H), 4.19 (brs, 1H), 2.46 (t, J = 6 Hz, 2H), 2.04-1.97 (m, 2H), 1.67-1.29 (m, 6H).**^{13}C NMR**(125MHz,$CDCl_3$, TMS): δ139.1, 136.9, 135.9, 133.0, 129.9, 129.1, 128.3, 126.7, 126.6 , 125.4, 121.9, 121.8, 121.0, 120.9, 120.2, 120.1, 119.6, 118.9, 111.2, 111.0, 52.3, 45.8, 32.1, 31.8, 28.6, 27.7, 26.9. **HRMS (ESI)**: Calcd for $C_{27}H_{26}N_2Na$: 401.19937; Found: 401.19968.

3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(1-methyl-1H-indole) (4ab)

Yield: 58%; pale yellow viscous liquid; R_f: 0.48 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 2935, 2855, 2358, 2353, 1680, 1595, 1449, 1431, 1358, 1156, 1120, 1033 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.56-7.52 (m, 2H), 7.28-7.16 (m, 4H), 7.14-6.99 (m, 2H), 6.83 (s, 1H), 6.75 (s, 1H), 6.71 (dd, J1 = 5.5Hz, J2 = 1Hz, 1H), 5.97 (dd, J1 = 5.5Hz, J2= 2.5Hz, 1H), 4.26 (s, 1H), 4.11 (s, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.45-2.41 (m, 2H), 2.02-2.00 (m, 1H), 1.94-1.92 (m, 1H), 1.63-1.45 (m, 4H), 1.34-1.31 (m, 1H), 1.18-1.17 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 139.2, 137.5, 137.4, 136.1, 132.8, 129.6, 129.0, 128.2, 127.1, 126.9, 125.6, 125.3, 121.5, 121.3, 120.4, 120.3, 120.2, 118.8, 118.6, 118.3, 109.1, 108.9, 52.3, 45.7, 32.6, 32.5, 32.0, 31.9, 28.6, 27.7, 26.9. **HRMS (ESI)**: Calcd for $C_{29}H_{30}N_2Na$: 429.23067; Found: 429.23102.

3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(2-phenyl-1H-indole) (4ac)

Yield: 54%; Pale yellow solid, M. p. 160–164^{o}C; R_f: 0.52 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3342, 3075, 2953, 2912, 2857, 1695, 1611, 1514, 1462, 1380, 1238, 1100, 1030, 931, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.98 (s, 1H), 7.88 (s, 1H), 7.68 (d, J = 8Hz, 1H), 7.59 (d, J = 8Hz, 1H), 7.42-7.37 (m, 4H), 7.28-6.80 (m, 13H), 6.14 (m, 1H), 4.76 (brs, 1H), 4.71 (brs, 1H), 2.51-2.49 (m, 1H), 2.38-2.18(m, 1H), 1.83-1.07 (m, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 138.4, 136.5, 136.4, 136.3, 135.1, 134.5, 133.4, 132.6, 132.5, 130.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.4, 127.3, 122.3, 122.2, 121.3, 120.9, 119.6, 119.2, 117.3, 114.7, 110.5, 110.3, 50.6, 44.8, 32.5, 30.8, 28.6, 27.1, 26.8. **HRMS (ESI)**: Calcd for $C_{39}H_{34}N_2Na$: 553.26197; Found: 553.26233.

3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(5-fluoro-1H-indole). (4ad)

Yield: 52%; pale yellow viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3356, 3052, 2978, 2939, 2849, 1689, 1619, 1583, 1514, 1462, 1415, 1402, 1380, 1304, 1238, 1111, 1047, 942, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.03 (s, 1H), 7.94 (s, 1H), 7.31-7.20 (m, 4H), 7.07 (s, 1H), 7.00-6.77 (m, 4H), 6.00 (t, 1H, J = 3Hz), 4.22 (s, 1H), 4.09 (s, 1H), 2.46- 2.42 (m, 2H), 2.06-2.04 (m, 1H), 1.96- 1.94 (m, 1H), 1.67- 1.44 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 158.5, 156.7, 138.5, 135.3, 133.8, 133.5, 130.3, 126.9, 122.9, 122.7, 121.9, 120.3, 111.7, 111.6, 110.5, 110.3, 110.2, 105.2, 105.0, 45.6, 32.0, 31.8, 28.5, 27.6, 26.8. **HRMS (ESI)**: Calcd for $C_{27}H_{24}F_2N_2Na$: 437.18052; Found: 437.18088.

3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(5-nitro-1H-indole) . (4ae)

Yield: 48%; orange red viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3326, 3056, 2955, 2932, 2850, 1675, 1629, 1583, 1457, 1385, 1300, 1238, 1100, 1040, 931, 7445 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.91 (s, 1H), 8.74 (s, 1H), 8.53-8.52 (m, 2H), 8.12- 8.09 (m, 2H), 7.45-7.41 (m, 2H), 7.26 (d, J = 10.5Hz, 1H), 7.14 (s, 1H), 6.86 (d, J = 5.5Hz, 1H), 5.99 (d, J = 4.5Hz, 1H), 4.33 (s, 1H), 4.22 (brs, 1H), 2.61-2.58 (m, 1H), 2.44-2.42 (m, 1H), 2.07-2.04 (m, 1H), 1.93-1.90 (m, 1H), 1.89-1.37 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 141.4, 141.2, 140.1, 140.0, 137.6, 135.1, 134.6, 130.9, 125.9, 125.7, 124.1, 124.0, 123.8, 122.2, 117.7, 117.6, 117.5, 112.9, 111.3, 52.3, 45.7, 32.1, 32.0, 28.2, 27.7, 26.7. **HRMS (ESI)**: Calcd for $C_{27}H_{24}N_2O_4Na$: 491.16952; Found: 491.16993.

3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(1H-indol-5-ol). (4af)

Yield: 39%; pale yellow viscous liquid; R_f: 0.19 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3339, 3061, 2990, 2940, 2842, 1680, 1623, 1580, 1514, 1380, 1302, 1240, 1110, 1042, 931, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.87 (brs, 1H), 7.78 (brs, 1H), 7.27-7.22 (m, 2H), 7.03-6.98 (m, 3H), 6.92 (d J = 2Hz, 1H), 6.81-6.74 (m 3H) ,6.01-6.00 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1H), 4.82 (d, J = 6.5Hz, 2H), 4.16 (s, 1H), 4.07(s, 1H), 2.45-2.39 (m, 2H), 1.99-1.94 (m, 2H),1.50-1.44 (m 3H), 1.33-0.87 (m 5H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 149.1, 148.9, 138.8, 135.6, 133.1, 132.1, 130.0, 127.3, 122.2, 121.3, 119.8, 111.8, 111.7, 111.6, 111.6, 104.8, 104.7, 51.7, 45.8, 32.0, 31.8, 28.6, 27.6, 26.8. **HRMS (ESI)**: Calcd for $C_{27}H_{26}N_2O_2Na$: 433.18920; Found: 433.18954.

3,3'-(5-(Propan-2-ylidene)cyclopent-3-ene-1,2-diyl)bis(1H-indole). (4ea)

Yield: 64%; colourless viscous liquid; R_f: 0.45 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3315, 2920, 2857, 2377, 1648, 1590, 1520, 1468, 1367, 1160, 1119, 1037cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$,

TMS): **δ** 7.99 (s, 1H), 7.92 (s, 1H), 7.60-7.56 (m, 2H), 7.40- 7.37 (m, 2H), 7.23-7.18 (m, 3H), 7.09-7.05 (m, 3H), 7.00 (s, 1H), 6.94 (s, 1H), 6.74 (dd, 1H, J_1 = 5.5Hz, J_2 = 2Hz), 6.05 (dd, 1H, J_1 = 5.5Hz, J_2 = 2.5Hz), 4.28 (s, 1H), 4.22 (s, 1H), 1.93 (s, 3H), 1.61 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 141.9, 137.1, 136.9, 135.8, 130.4, 127.3, 126.8, 125.8,125.7, 124.4, 121.5, 121.3, 120.5, 120.3, 120.0, 118.4, 118.2, 117.9, 110.8, 110.7, 52.4, 46.4, 21.3. **HRMS (ESI)**: Calcd for $C_{24}H_{22}N_2Na$: 361.16807; Found: 361.16848.

3,3'-(5-(Propan-2-ylidene)cyclopent-3-ene-1,2-diyl)bis(1-methyl-1H-indole). (4eb)

Yield: 56%; pale yellow solid, M. p. 162–164^{o}C; R_f: 0.50 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 2925, 2852, 2371, 1649, 1586, 1523, 1465, 1364, 1254, 1167, 1122, 1042cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.66-7.61 (m, 2H), 7.38-7.31 (m, 2H), 7.29- 7.27 (m, 2H), 7.14-7.09 (m, 2H), 6.90 (s, 1H), 6.83 (s, 1H), 6.78 (dd, 1H, J_1= 5.5Hz, J_2= 2Hz,) 6.09 (dd, H, J_1 = 5.5Hz, J_2 = 2.5Hz), 4.32 (s, 1H), 4.25 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.99 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 142.2, 137.6, 137.5, 135.9, 130.5, 127.1, 127.0, 125.9, 125.7, 124.4, 121.5, 121.3, 120.3, 120.2, 119.9, 118.8, 118.7, 118.4, 109.2, 109.1, 52.6, 46.6, 31.7, 21.4. **HRMS (ESI)**: Calcd for $C_{26}H_{26}N_2Na$: 389.19937; Found: 389.19969.

3,3'-(5-Cycloheptylidenecyclopent-3-ene-1,2-diyl)bis(1H-indole). (4fa)

Yield: 53%; colourless viscous liquid; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3408, 3056, 2923, 2853, 1703, 1619, 1583, 1517, 1485, 1455, 1338, 1227, 1095, 1012, 741cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.97 (s, 1H), 7.89 (s, 1H),7.59-7.57 (d, J= 8Hz, 2H), 7.37-7.34 (m, 2H), 7.21-7.16 (m, 2H), 7.07-7.05 (m, 2H), 6.98-6.93 (m, 2H), 6.76 (dd, J_1 = 5.5Hz, J_2 = 2.5Hz, 1H), 6.04 (dd, J_1 = 5.5Hz, J_2 = 3 Hz, 1H), 4.27 (s, 1H), 4.18 (brs, 1H), 2.57-2.51 (m, 2H), 2.25-2.19 (m, 1H), 2.07-2.06 (m, 1H), 1.72-1.29 (m, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 142.1, 136.9, 136.7, 135.9, 134.3, 130.4, 129.0, 128.2, 126.7, 126.6, 121.9, 121.5,120.8, 120.7,120.2, 120.1, 119.2,119.0, 111.0, 110.9, 52.5, 46.1, 32.8, 32.5, 29.8, 28.8, 27.2, 26.9. **HRMS (ESI)**: Calcd for $C_{28}H_{28}N_2Na$: 415.21502; Found: 415.21538.

Compound 4ga

Yield: 58%; colourless viscous liquid; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3289, 3066, 2931, 2857, 1668, 1620, 1582, 1520, 1455, 1304, 1238, 933, 744 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.88 (s, 1H), 7.79 (s, 1H), 7.62 (d, J = 8Hz, 1H), 7.55 (d, J = 8Hz, 1H), 7.54-7.21 (m, 2H), 7.19-7.13 (m, 2H), 7.05-6.93 (m, 4H), 6.72-6.71 (m, 1H), 5.94 (dd, J_1 = 5.5Hz, J_2 = 3Hz, 1H), 4.30 (s, 1H), 4.11 (brs, 1H), 3.12 (brs, 1H), 2.49 (brs, 1H), 2.04-1.68 (m, 9H), 1.53-1.43 (m, 2H), 0.88-0.84 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 140.8, 137.8, 137.0, 136.9, 135.4, 135.2, 129.5, 129.1, 128.3, 126.8, 126.5, 125.4, 122.0, 121.8, 120.9, 120.4, 119.2, 118.9, 111.2, 111.1, 52.4, 45.2, 39.8, 39.4, 38.2, 37.3, 35.1, 34.8, 28.4, 21.6. **HRMS (ESI)**: Calcd for $C_{31}H_{30}N_2Na$: 453.23067; Found: 453.23101.

Compound 4gb

Yield: 55%; colourless viscous liquid; R_f: 0.48 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3090, 2950, 2932, 2857, 1688, 1621, 1583, 1514, 1462, 1380, 1304, 1238, 1108, 1042, 957, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.65 (d, J = 8Hz, 1H), 7.58 (d, J = 8Hz, 1H), 7.33-7.20 (m, 6H), 7.08-7.02 (m, 2H), 6.89 (s, 1H), 6.83 (s, 1H), 6.73 (d, J = 5.5Hz, 1H), 5.95 (t, J = 2.5Hz, 1H), 4.32 (s, 1H), 4.13 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.17 (s, 1H), 2.53 (s, 1H), 2.01-1.58 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 140.6, 137.6, 135.6, 135.2, 129.2, 127.2, 127.0, 125.6, 125.5, 121.5, 120.5, 120.3, 118.8, 118.8, 118.6, 109.1, 108.9, 52.5, 45.2, 39.8, 39.3, 38.2, 37.3, 35.0, 34.4, 32.6, 32.5, 28.4, 28.3. **HRMS (ESI)**: Calcd for $C_{33}H_{34}N_2Na$: 481.26197; Found: 481.26141.

Compound 4gc

Yield: 74%; colourless viscous liquid; R_f: 0.55 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 2981, 2915, 2833, 1671, 1621, 1586, 1542, 1380, 1300, 1238, 1042, 957, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.62-7.47 (m, 6H), 7.38-6.96 (m, 12H), 6.66 (dd, J_1=5.5 Hz, J_2=2.5 Hz, 1H), 6.04 (dd, J_1=5.5 Hz, J_2= 2.5 Hz, 1H), 4.41 (brs, 1H), 4.22 (brs, 1H), 3.61 (s, 3H), 3.57 (s, 3H), 2.98 (brs, 1H), 2.32 (brs, 1H), 1.83-1.50 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 140.2, 137.9, 137.4, 136.2, 135.8, 134.6, 133.9, 133.4, 131.3, 130.5, 129.7, 128.7, 128.2, 127.7, 127.5, 126.6, 125.3, 122.3, 121.4, 120.3, 119.5, 119.1, 119.0, 117.5, 115.2, 108.9, 108.7, 51.0, 45.3, 39.3, 38.9, 37.8, 37.4, 34.9, 33.1, 30.9, 28.1.

HRMS (ESI): Calcd for $C_{45}H_{42}N_2Na$: 633.32457; Found: 633.32486.

3,3'-(5-(Diphenylmethylene)cyclopent-3-ene-1,2-diyl)bis(1H-indole). 4ha

Yield: 84%; pale yellow solid, M. p. 154-156^{o}C; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3294, 2857, 2366, 2335, 1647, 1590, 1369, 1120, 1037, 702 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.90 (s, 1H), 7.67-7.51 (m, 3H), 7.37-7.06 (m, 9H), 6.98-6.78 (m, 9H), 6.40 (d, J = 4 Hz, 1H), 6.24 (brs, 1H), 4.51-4.49 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 148.1, 143.2, 142.6, 140.4, 136.8, 136.5, 135.0, 133.1, 129.8, 129.3, 127.9, 127.4, 126.7, 126.5, 126.2, 125.9, 122.0, 121.5, 120.8, 120.1, 119.8, 119.5, 119.3, 119.0, 118.9, 111.1, 110.9, 57.7, 48.5. **HRMS (ESI)**: Calcd for $C_{34}H_{26}N_2Na$: 485.19937; Found: 485.19969.

3,3'-(5-(Diphenylmethylene)cyclopent-3-ene-1,2-diyl)bis(1-methyl-1H-indole). (4hb)

Yield: 81%; yellow solid, M. p. 160-162^{o}C; R_f: 0.48 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3053, 2927, 1709, 1688, 1613, 1513, 1469, 1427, 1372, 1328, 1242, 1156, 1130, 1013, 740cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.78-7.76 (m,2H), 7.72-7.30 (m, 9H), 7.20-6.99 (m, 6H), 6.87 (brs, 3H), 6.52 (t, J = 3Hz, 1H), 6.09 (dd, J_1= 4 Hz, J_2= 2.5 Hz, 1H), 4.66 (brs, 1H), 4.57-4.54 (m, 1H), 3.81 (s, 3H), 3.58 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 148.8, 143.3, 143.0, 140.8, 137.6, 137.3, 134.9, 132.9, 129.9, 129.3,129.2, 128.4, 128.0, 127.4, 127.2, 127.2, 126.8, 126.5, 125.8, 125.7, 121.7, 121.1, 120.3, 120.0, 118.9, 118.4, 118.1, 117.6, 109.3, 109.1, 51.8, 48.9, 32.6, 32.2. **MS (ESI)**: Calcd for $C_{36}H_{30}N_2Na$: 513.23067; Found: 513.23098.

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