SUPPORTING INFORMATION

A Regio- and Stereoselective Synthesis of Core Structure of Hexahydrobenzo[c]phenanthridine Alkaloids via Redox-Neutral Cp*Rh(III) Catalyzed C-H/N-H Annulation of Cyclic Alkenes with Benzamides

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**Abbreviations:** Dimethyl formamide (DMF), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), tert- butyl alcohol (tBuOH), hexafluoroisopropanol (HFIP), no reaction (nr), room temperature (rt), 2,2,2-trifluoro ethanol (TFE), 1,2-dichloro ethane (DCE), pentamethylcyclopentadiene (Cp*), equivalent (equiv), trimethylacetic anhydride [(Piv)₂O], percentage (%), molarity (M), millimole (mmol), hours (h).

**General Information:**

All reactions were carried out in a sealed tube. Chemicals were purchased from Sigma-Aldrich, Alfa-esar, Spectrochem and were used without further purification. All solvents were purified by using standard conditions from the book by Armarego and Chai, 2003, Elsevier Science (USA). Compounds were purified by Column chromatography using Merck Silica gel (230-400 mesh size), and distilled solvents. TLC was visualized by short wave (254 nm) UV light and/or submersion in acidic p-anisaldehyde solution (PPA). NMR spectra were recorded using Bruker AV-700 (\(^1H\): 700 MHz, \(^{13}C\): 175 MHz) and Bruker AV-400 (\(^1H\): 400 MHz, \(^{13}C\): 100 MHz) and Jeol ECZ-400 R (\(^1H\): 400 MHz, \(^{13}C\): 100 MHz). NMR spectra are reported as δ in units of parts per million (ppm). \(^1H\) chemical shifts were referenced in ppm with respect to TMS (0.0) and CDCl₃ (7.26, singlet) as per requirement. \(^{13}C\) chemical shifts were referenced in ppm with respect to CDCl₃ as 77 ppm (triplet). Chemical shifts were reported in parts per million (ppm) and multiplicities were indicated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and td (triplet of doublet), brs (broad singlet). Coupling constants, J, were reported in Hertz and integration were provided. High Resolution Mass Spectrometry were recorded in the School of Chemical Science, NISER, Bhubaneswar using Bruker micrOTOF Q-II.
1. Deuterium exchange study:

a) Deuterium exchange experiment without coupling partner:

To an oven dried Schlenk tube, cooled under N\textsubscript{2} atmosphere, was charged with N-\((pivaloyloxy)\) benzamide 1\textsubscript{a} (0.04 mmol, 1.0 equiv), [Cp*RhCl\textsubscript{2}]\textsubscript{2} (0.03 mmol, 0.06 equiv), NaHCO\textsubscript{3} (0.02 mmol, 0.5 equiv), anhydrous TFE (0.4 M) and deuterium oxide (3.0 equiv). The sealed tube was tightened under positive pressure of N\textsubscript{2}. The reaction mixture was stirred at room temperature for 3 hours. After 3 h, the crude mixture was passed through celite pad and excess solvent was evaporated under reduce pressure. Then, the crude mixture was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

\[ \text{Figure S1: } ^1\text{H NMR (400 MHz, CDCl}_3\text{) spectra of compound 1a'} \]
b) Deuterium exchange experiment in presence of coupling partner:

To an oven dried Schlenk tube, cooled under N\textsubscript{2} atmosphere, was charged with \textit{N}-pivaloyloxy benzamide 1\textit{a} (0.04 mmol, 1.0 equiv), 1,2-dihydronaphthalene 2\textit{a} (0.06 mmol, 1.3 equiv), [Cp*RhCl\textsubscript{2}]\textsubscript{2} (0.03 mmol, 0.06 equiv), NaHCO\textsubscript{3} (0.02 mmol, 0.5 equiv), anhydrous TFE (0.4 M) and deuterium oxide (3.0 equiv). The sealed tube was tightened under positive pressure of N\textsubscript{2}. The reaction mixture was stirred at room temperature for 3 hours. After 3 h, the crude mixture was passed through celite pad and excess solvent was evaporated under reduce pressure. Then, the crude mixture was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

\textbf{Figure S2:} \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}) spectra of compound 1\textit{a}'}
Figure S3: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3aa’

c) Intermolecular Kinetic isotope (KIE) effect:

To an oven dried Schlenk tube, cooled under N$_2$ atmosphere, was charged with N-(pivaloyloxy) benzamide 1a (0.04 mmol, 0.5 equiv) and N-(pivaloyloxy) benzamide-d$_5$ 1a-d$_5$ (0.04 mmol, 0.5 equiv), 1,2-dihydronaphthalene 2a (0.06 mmol, 1.3 equiv), [Cp*RhCl$_2$]$_2$ (0.003 mmol, 0.06 equiv), NaHCO$_3$ (0.02 mmol, 0.5 equiv), anhydrous TFE (0.4 M). The sealed tube was tightened under positive pressure of N$_2$. The reaction mixture was stirred at room temperature for 3 hours. After 3 h, the crude mixture was passed through celite pad and excess solvent was evaporated under
reduced pressure. Then, the crude mixture was purified by silica gel column chromatography using ethyl acetate/hexane as eluent to yield a mixture of 3aa and 3aa-\textit{d}_4 (14% yield) with 80% of starting material (1a/1a-\textit{d}_5) recovered. $K_{\text{h}}/K_{\text{D}}$ was calculated from doublet at $\delta$ 8.12 and was found to be 1.8.

$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3aa
Figure S4: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3aa/3aa-$d_5$
2. $^1$H and $^{13}$C NMR Spectra of Products:

**Figure S5**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3aa

**Figure S6**: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3aa
Figure S7: $^1$H NMR (700 MHz, CDCl$_3$) spectra of compound 3ba

Figure S8: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ba
**Figure S9**: $^1$H NMR (700 MHz, CDCl$_3$) spectra of compound 3ca

**Figure S10**: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ca
Figure S11: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3da

Figure S12: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3da
Figure S13: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ea

Figure S14: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ea
Figure S15: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3fa

Figure S16: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3fa
**Figure S17:** $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ga

**Figure S18:** $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ga
Figure S19: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ha

Figure S20: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ha
**Figure S21:** $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ia

**Figure 22:** $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ia
Figure S23: $^1$H NMR (700 MHz, CDCl$_3$) spectra of compound 3ja

Figure S24: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ja
**Figure S25**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ka

**Figure S26**: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ka
Figure S27: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 31a

Figure S28: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 31a
Figure S29: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ma

Figure S30: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ma
Figure S31: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ae

Figure S32: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ae
Figure S33: $^1$H NMR (700 MHz, CDCl$_3$) spectra of compound 3ab

Figure S34: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ab
Figure S35: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3bb

Figure S36: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3bb
Figure S37: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3cb

Figure S38: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3cb
Figure S39: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3db

Figure S40: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3db
**Figure S41**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3eb

**Figure S42**: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3eb
Figure S43: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3fb

Figure S44: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3fb
Figure S45: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3gb

Figure S46: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3gb
**Figure S47**: $^1$H NMR (700 MHz, CDCl$_3$) spectra of compound 3hb

**Figure S48**: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3hb
Figure S49: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ib

Figure S50: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ib
Figure S51: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3jb

Figure S52: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3jb
**Figure S53**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3kb

**Figure S54**: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3kb
Figure S55: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3lb

Figure S56: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3lb
Figure S57: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3af

Figure S58: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3af
Figure S59: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3af’

Figure S60: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3af’
Figure S61: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ac

Figure S62: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ac
Figure S63: $^1$H NMR (700 MHz, CDCl$_3$) spectra of compound 3bc

Figure S64: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3bc
Figure S65: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3cc

Figure S66: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3cc
Figure S67: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3dc

Figure S68: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3dc
Figure S69: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ec

Figure S70: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3ec
Figure S71: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3fc

Figure S72: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3fc
Figure S73: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3gc

Figure S74: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3gc
Figure S75: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3hc

Figure S76: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3hc
Figure S77: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ic

Figure S78: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3ic
**Figure S79**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3jc

**Figure S80**: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3jc
Figure S81: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3kc

Figure S82: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3kc
Figure S83: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3lc

Figure S84: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of compound 3lc
**Figure S85**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3mc

**Figure S86**: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3mc
3. $^1$H and $^{13}$C NMR Spectra of Starting Materials:

**Figure S87**: $^1$H NMR (400 MHz, CDCl$_3$) spectra of 4-ethyl-N-(pivaloyloxy)benzamide 1c

**Figure S88**: $^{13}$C NMR (175 MHz, CDCl$_3$) spectra of 4-ethyl-N-(pivaloyloxy)benzamide 1c
Figure S89: $^1$H NMR (400 MHz, CDCl$_3$) spectra of 4-isopropyl-N-(pivaloyloxy)benzamide 1d

Figure S90: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 4-isopropyl-N-(pivaloyloxy)benzamide 1d
Figure S91: $^1$H NMR (400 MHz, CDCl$_3$) spectra of 4-butyl-N-(pivaloyloxy)benzamide 1e

Figure S92: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 4-butyl-N-(pivaloyloxy)benzamide 1e
Figure S93: $^1$H NMR (400 MHz, CDCl$_3$) spectra of N-(pivaloyloxy)-trifluoromethoxy)benzamide 1k

Figure S94: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of N-(pivaloyloxy)-4-(trifluoromethoxy)benzamide 1k
Figure S95: $^1$H NMR (400 MHz, CDCl$_3$) spectra of (E:Z, 1:1)-1,2-dimethoxy-4-(2-methoxyvinyl)-5-vinylbenzene 7

Figure S96: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of (E:Z, 1:1)-1,2-dimethoxy-4-(2-methoxyvinyl)-5-vinylbenzene 7
Figure S97: $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1-(2-bromo-4,5-dimethoxyphenyl)but-3-en-2-ol 14

Figure S98: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 1-(2-bromo-4,5-dimethoxyphenyl)but-3-en-2-ol 14
Figure S99: $^1$H NMR (400 MHz, CDCl$_3$) spectra of {1-(4,5-dimethoxy-2-vinylphenyl)but-3-en-1-yl)oxy}triisopropylsilane 17

Figure S100: $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of {1-(4,5-dimethoxy-2-vinylphenyl)but-3-en-1-yl)oxy}triisopropylsilane 17
4. Approach Towards Total Synthesis:-

After successfully demonstrating the methodology for the regio- and stereo-selective synthesis of hexahydrobenzo[c]phenanthridine skeleton, we decided to attempt the total synthesis of Chelidonine alkaloid \textbf{3nd} (scheme S1). We envisioned that annulation of benzamide \textbf{1n} and 6,7-dimethoxy-1,2-dihydronaphthalene-2-ol \textbf{2d} would give the advanced tetracyclic intermediate \textbf{3nd}$'$ (scheme S1) with \textit{cis} ring junction as required in the natural product.

\textbf{Scheme S1. Retrosynthetic Plan for the Synthesis of Chelidonine 3nd:}

We presumed that functional group maneuvering of tetracyclic intermediate \textbf{3nd}$'$ would give the natural product Chelidonine \textbf{3nd} (scheme S1). We also thought that, the coupling partner 6,7-dimethoxy-1,2-dihydronaphthalene-2-ol \textbf{2d} for the key annulation reaction, could be prepared from 3,4-dimethoxybenzaldehyde \textbf{c} via tin mediated vinylation of aromatic bromide and ring closing metathesis reactions. Accordingly, we performed bromination reaction of 3,4-dimethoxybenzaldehyde \textbf{4} (scheme S2) in methanol at room temperature. It gave us 2-bromo-4,5-dimethoxybenzaldehyde \textbf{5} (also available commercially) as colorless crystalline solid in 75\% yield. Stille coupling of 2-bromo-4,5-dimethoxybenzaldehyde \textbf{5} with vinyltributylstannane and \textit{Pd(PPh$_3$)$_4$} gave 4,5-dimethoxy-2-vinylbenzaldehyde \textbf{6} as colourless liquid in 80\% yield. Wittig olefination of the aldehyde \textbf{6} using potassium tert-butoxide and
Scheme S2. Synthetic Approach for the Synthesis of 6,7-Dimethoxy-1,2-dihydronapthalene-2-ol:

methoxymethyltriphenylphosphonium bromide in THF at room temperature gave us a mixture of (Z)-1,2-dimethoxy-4-(2-methoxyvinyl)-5-vinylbenzene and (E)-1,2-dimethoxy-4-(2-methoxyvinyl)-5-vinylbenzene 7 (E:Z;1:1) as a colorless liquid in 72% yield. The enol ether 7 was then subjected to acid catalyzed hydrolysis reaction. However, the reaction did not give us the expected homologated aldehyde 9, instead we got aromatized product 8. Formation of aromatic product 8 can be explained by the fact that, protonation of the electron rich olefin followed by the interception of carbocation by the pendant vinyl group leads to cyclization and aromatization. Several attempts to optimize this reaction with different acidic conditions did not give any fruitful result forcing us to search for alternative approaches. As the vinyl group was interfering with the acid catalysed hydrolysis step, we decided to install the vinyl group after the homologation step. Accordingly, treatment of 2-bromo-4,5-dimethoxybenzaldehyde 5 with methoxymethyltriphenyl phosphonium
bromide and potassium tert-butoxide in THF at room temperature gave us a mixture of (Z)-1-bromo-4,5-dimethoxy-2-(2-methoxyvinyl)benzene and (E)-1-bromo-4,5-dimethoxy-2-(2-methoxyvinyl)benzene 12 (E:Z; 1:1) in 70% yield. The E:Z mixture of enol ether 12 was then treated with aqueous hydrochloric acid. Gratifyingly, this time we got 2-(2-bromo-4,5-dimethoxyphenyl)acetaldehyde 13 as colorless liquid in 71% yield. The pure compound 13 was then subjected to Stille coupling reaction using catalytic amount of Pd(PPh₃)₄ and vinyl tributylstannane. Surprisingly, even after several trials we could not obtain the vinylated product 9. The TLC of this reaction was not very clean and presence of multiple spots indicated several side products. Silica gel chromatographic purification of the crude mixture did not yield any characterizable product. Therefore, we decided to postpone installation of vinyl group. Hence the pure compound 13 was subjected to Grignard reaction using vinyl magnesium bromide to obtain the allyl alcohol 14 in 68% yield. Left with limited options, we optimistically explored Still e protocol on the tricky allyl alcohol 14. Unfortunately, we could not get the desired product 10. Having failed to synthesize the desired coupling partner 6,7-dimethoxy-1,2-dihydronaphthalene-2-ol 11 through multiple approaches, we decided to adopt different coupling partner 6,7-dimethoxy-1,2-dihydronaphthalene-1-ol 16 (scheme S3) which differs only in the position of hydroxy group.

Scheme S3. Synthetic Approach for the Synthesis of 6,7-Dimethoxy-1,2-dihydronaphthalene-1-ol:

Although the hydroxy group in coupling partner 6,7-dimethoxy-1,2-dihydronaphthalene-1-ol 16 is on the wrong carbon in comparison to natural product, we still thought of
using it as coupling partner. As we could address this issue later through late stage functional group modification. Accordingly, we set ourselves to explore the synthesis of 6,7-dimethoxy-1,2-dihydronaphthalene-1-ol 16.

We planned a Barbier reaction on 4,5-dimethoxy-2-vinylbenzaldehyde 6, accordingly the aldehyde 6 was sonicated at room temperature with allyl bromide and zinc dust in anhydrous THF. We obtained allyl alcohol 15 in good yield without any difficulty. The allyl alcohol 15 was then treated with Grubbs’ catalyst to get the desired compound 16. But unfortunately, we got aromatized product 8. Even after several trial by lowering temperature, catalysts etc, we could not get favourable result. The aromatization process seems very rapid under these conditions. We then thought that protecting the hydroxy group of compound 15 with bulky protecting group such as triisopropylsilylether might solve the problem. Accordingly, the free hydroxy group in compound 15 was efficiently protected as its TIPS ether using triisopropylsilyl chloride (TIPSCI) and potassium tert-butoxide condition in anhydrous THF at room temperature. To our despair, even the TIPS protected compound 17 also underwent rapid aromatization with Grubbs’ catalyst after ring closing metathesis. Even after several attempts by lowering temperature, varying concentration and varying catalyst loading, we did not observe any sign of improvement. While this manuscript was under review (previous submission) a closely similar work was published by Jeganmohan’s group, wherein they have described a three-step approach for the synthesis of core skeleton of aromatic natural products. 1 Whereas our approach is a one-step approach, moreover the required cis ring junction and regioselectivity were achieved exclusively. Due to competitive nature of this area and huge loss of time due to multiple attempted synthesis, we decided to conclude our journey with this.

**Experimental Procedures and References:**

Compound 5, 6, 8, 12, 13, 15 are reported earlier. Compound 7, 14 and 17 are new compound, whose detailed preparation procedure were given below.

(E:Z:1:1)-1,2-dimethoxy-4-(2-methoxyvinyl)-5-vinylbenzene (7). To the stirred solution of methoxy triphenylphosphoranimide (801 mg, 2.3 mmol, 3 equiv) in anhydrous THF (3 ml) was added potassium tert-butoxide (350 mg, 3.1 mmol, 4 equiv) under nitrogen atmosphere. The reaction mixture became deep red in colour, which indicates the formation of methoxy ylide. The deep red colour solution was heated to room
temperature and stirred for 20 minutes. Thereafter 4,5-dimethoxy-2-vinylbenzaldehyde 6 (150 mg, 0.8 mmol, 1 equiv) in anhydrous THF (2 ml) was added drop wisely to red color solution of ylide at room temperature. The solution became brownish color. The reaction mixture was stirred at room temperature for 12 hours. After completion of reaction as indicated by TLC, the reaction was quenched by saturated NH₄Cl. The combined organic layer was extracted by dichloromethane and dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by column chromatography (5% EtOAc in Hexane) to afford pure colourless liquid 7 (124 mg, Z:E:1:1, 72%).

1-(2-bromo-4,5-dimethoxyphenyl)but-3-en-2-ol (14). To the stirred solution of 2-(2-bromo-4,5-dimethoxyphenyl)acetaldehyde 13 (50 mg, 0.2 mmol, 1 equiv) in THF (1 ml) was added vinyl magnesium bromide (1 ml, 0.6 mmol, 3 equiv) at room temperature and stirred for 2 hours. Upon completion of starting material as confirmed from TLC, the reaction mixture was quenched by saturated NH₄Cl. The combined organic layer was extracted by dichloromethane and dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by column chromatography (40% EtOAc in Hexane) to afford pure colourless liquid (38 mg, 68%).

{(1-(4,5-dimethoxy-2-vinylphenyl)but-3-en-1-yl)oxy}triisopropylsilane (17). To the stirred solution of 1-(4,5-dimethoxy-2-vinylphenyl)but-3-en-1-ol 15 (30 mg, 0.1 mmol, 1 equiv) in anhydrous THF (1 ml) was added potassium tert-butoxide (36 mg, 0.3 mmol, 2.5 equiv) at ice cold temperature. The reaction mixture was heated to room temperature and stirred for 10 minutes. Thereafter triisopropylsilyl chloride (30 mg, 0.1 mmol, 1.2 equiv) in anhydrous THF (2 ml) was added drop wisely at room temperature. The reaction mixture was stirred at room temperature for 12 hours. After completion of reaction as indicated by TLC, the reaction was quenched by saturated NH₄Cl. The combined organic layer was extracted by dichloromethane and dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by column chromatography (5% EtOAc in Hexane) to afford pure colourless liquid 17 (41 mg, Z:E:1:1, 82%).

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**Spectral data of starting materials used in total synthesis approach:**

(E:Z;1:1)-1,2-dimethoxy-4-(2-methoxyvinyl)-5-vinylbenzene (7). Colourless liquid; yield: (124 mg, 72%). *Rf*: 0.40 (in 5% EtOAc/Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 (s, 1H), 6.99–6.93 (m, 3H), 6.90 (d, $J = 10.8$ Hz, 1H), 6.76 (d, $J = 12.8$ Hz, 1H), 6.73 (s, 1H), 6.13 (d, $J = 7.2$ Hz, 1H), 5.98 (d, $J = 12.8$ Hz, 1H), 5.56–5.49 (m, 2H), 5.39 (d, $J = 7.2$ Hz, 1H), 5.22 (dd, $J = 2.8$, 1.2 Hz, 1H), 5.19 (dd, $J = 2.8$, 1.2 Hz, 1H), 3.89 (s, 6H), 3.88 (s, 6H), 3.74 (s, 3H), 3.69 (s, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 149.3, 148.9, 148.3, 147.7, 147.3, 146.9, 134.7, 134.6, 128.4, 127.9, 127.1, 126.2, 113.6, 113.4, 112.1, 109.1, 108.7, 108.4, 102.6, 102.1, 60.5, 56.5, 55.9, 55.84, 55.76, 55.7. HRMS (ESI) m/z calcd for C$_{13}$H$_{17}$O$_3$ [M+H]$^+$: 221.1172; found: 221.1171.

1-(2-bromo-4,5-dimethoxyphenyl)but-3-en-2-ol (14). Colourless liquid; yield: (38 mg, 68%). *Rf*: 0.40 (in 5% EtOAc/Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.02 (s, 1H), 6.78 (s, 1H), 6.00–5.92 (m, 1H), 5.27 (dt, $J = 17.2$, 1.2 Hz, 1H), 5.14 (dt, $J = 10.2$, 1.2 Hz, 1H), 4.45–4.40 (m, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.85 (s, 3H), 2.97 (dd, $J = 13.6$, 4.8 Hz, 1H), 2.83
(dd, J = 14.0, 8.4 Hz, 1H), 3.85 (brs, 1H). $^1$H NMR (100 MHz, CDCl$_3$): $\delta$ 148.3, 148.2, 140.0, 129.3, 115.6, 116.0, 114.6, 114.4, 72.4, 56.1, 56.0, 43.3. HRMS (ESI) m/z calcd for C$_{12}$H$_{15}$BrO$_3$ [M+Na]$^+$: 309.0097; found: 309.0071.

{(1-(4,5-dimethoxy-2-vinylphenyl)but-3-en-1-yl)oxy}triisopropylsilane (17). Colourless liquid; yield: 41 mg, 82%). $R_f$: 0.40 (in 5% EtOAc/Hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.06 (s, 1H), 6.96–6.89 (m, 2H), 5.78–5.68 (m, 1H), 5.50 (dd, J = 17.2, 1.2 Hz, 1H), 5.20 (dd, J = 10.8, 1.2 Hz, 1H), 5.14 (t, J = 6.0 Hz, 1H), 4.99–4.98 (m, 1H), 4.95 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.46 (t, J = 7.2 Hz, 2H), 1.06–1.01 (m, 3H), 1.10 (d, J = 18.8 Hz, 9H), 0.99 (d, J = 20.0 Hz, 9H). $^{13}$C$[^1]$H NMR (100 MHz, CDCl$_3$): $\delta$ 148.6, 147.7, 135.3, 134.6, 133.7, 126.8, 117.1, 114.0, 109.5, 107.9, 70.6, 55.7, 45.0, 18.0, 17.9, 12.3. HRMS (ESI) m/z calcd for C$_{23}$H$_{38}$O$_3$Si [M+Na]$^+$: 413.2482; found: 413.2464.
5. **Crystal Data:**

a) **X-ray data of (4bS,10bR)-4b,10b,11,12-tetrahydrobenzo[c]phenanthridin-6(5H)-one (3aa):** This compound was crystallised from methanol as solvent. Thermal ellipsoid is at 50%. Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART software packages and corrected for absorption with SADABS. The structure was solved by direct methods and refined on F2 with SHELXL-97 using Olex-2 software.

![Crystal Structure Diagram](image-url)
Figure S101. ORTEP view of compound (3aa)
Table S1:

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | PCR-GKD-23-8-18                            |
| Empirical formula                             | C_{68}H_{60}N_{4}O_{4}                      |
| Formula weight                                | 997.20                                     |
| Temperature/K                                 | 293(2)                                    |
| Crystal system                                | triclinic                                  |
| Space group                                   | P-1                                        |
| a/Å                                          | 9.3640(4)                                  |
| b/Å                                          | 12.4629(4)                                 |
| c/Å                                          | 12.6747(3)                                 |
| α/°                                          | 105.516(2)                                 |
| β/°                                          | 102.852(3)                                 |
| γ/°                                          | 102.045(3)                                 |
| Volume/Å³                                     | 1331.73(8)                                 |
| Z                                            | 1                                          |
| $\rho_{\text{calc}}$/g/cm³                    | 1.243                                      |
| $\mu$/mm⁻¹                                    | 0.605                                      |
| F(000)                                        | 528.0                                      |
| Crystal size/Å³                               | 0.25 × 0.25 × 0.24                        |
| Radiation                                     | CuKα ($\lambda = 1.54184$)                |
| 2θ range for data collection/°                | 7.576 to 134                               |
| Index ranges                                  | -11 ≤ h ≤ 10, -14 ≤ k ≤ 14, -13 ≤ l ≤ 15  |
| Reflections collected                         | 24012                                      |
| Independent reflections                       | 4749 [R_{int} = 0.1609, R_{sigma} = 0.0835] |
| Data/restraints/parameters                    | 4749/0/343                                 |
| Goodness-of-fit on F²                          | 1.082                                      |
| Final R indexes [I>=2σ (I)]                   | R_1 = 0.1000, wR_2 = 0.2623                |
| Final R indexes [all data]                    | R_1 = 0.1124, wR_2 = 0.2688                |
| Largest diff. peak/hole / e Å⁻³               | 0.41/-0.26                                 |
b) X-ray data of (6aS,11aR)-2-isopropyl-6,6a,11,11a-tetrahydro-5H-indeno[1,2-c]isoquinolin-5-one (3db):- This compound was crystallised from methanol as solvent. Thermal ellipsoid is at 50%. Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART software packages and corrected for absorption with SADABS. The structure was solved by direct methods and refined on F2 with SHELXL-97 using Olex-2 software.
Figure S102. ORTEP view of compound (3db)
### Table S2:

| Property                        | Value                           |
|---------------------------------|---------------------------------|
| Identification code             | PCR-GKD-IPR                     |
| Empirical formula               | C$_{38}$H$_{38}$N$_2$O$_2$       |
| Formula weight                  | 554.70                          |
| Temperature/K                   | 293(2)                          |
| Crystal system                  | triclinic                       |
| Space group                     | P-1                             |
| a/Å                             | 9.1117(4)                       |
| b/Å                             | 9.1126(3)                       |
| c/Å                             | 9.5279(4)                       |
| α/°                             | 73.971(3)                       |
| β/°                             | 81.252(4)                       |
| γ/°                             | 86.515(3)                       |
| Volume/Å$^3$                    | 751.36(5)                       |
| Z                               | 1                               |
| ρ$_{calc}$/cm$^3$                | 1.226                           |
| μ/mm$^{-1}$                     | 0.075                           |
| F(000)                          | 296.0                           |
| Crystal size/mm$^3$             | $0.25 \times 0.25 \times 0.25$ |
| Radiation                       | MoKα ($\lambda = 0.71073$)     |
| 2Θ range for data collection/$^\circ$ | 6.554 to 62.018    |
| Index ranges                    | $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-12 \leq l \leq 12$ |
| Reflections collected           | 14692                           |
| Independent reflections         | 3872 [R$_{int} = 0.0455$, R$_{sigma} = 0.0337$] |
| Data/restraints/parameters      | 3872/0/192                      |
| Goodness-of-fit on F$^2$        | 1.111                           |
| Final R indexes [I>=2σ (I)]    | R$_1 = 0.0650$, wR$_2 = 0.1924$ |
| Final R indexes [all data]     | R$_1 = 0.0855$, wR$_2 = 0.2076$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.42/-0.21                   |