Supporting Information for:

**Palladium Catalyzed Tandem Ring Opening- Ring Closing Reaction of
Diazabicyclic Alkenes: A Facile One Pot Strategy for
Cyclopentannulation of Heterocycles**

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General Methods

All the chemicals were of the best grade commercially available and are used without further purification. All the 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 mesh silica gel or neutral alumina and mixtures of hexane-ethyl acetate were used for elution.

Melting points was determined on a Buchi melting point apparatus and is uncorrected. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 500 spectrophotometer (CDCl_3 as solvent). Chemical shifts for ^1H 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); brs (broad singlet); 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 and FAB/LRMS at 5000 resolution using JMS600H (Jeol) mass spectrometer. IR spectra were recorded on Bomem MB series FT-IR spectrometer.

Typical Procedure for the preparation of 2,3-Diazabicyclo [2.2.1] hept-5-ene 1(a-d).

Diethyl azodicarboxylate [0.90 mL, 5.7418 mmol] was dissolved in ether and cooled to 0 °C. Cyclopentadiene [0.77 mL, 11.4837 mmol] was added to it and the reaction mixture was stirred for 12 hours. Excess cyclopentadiene was added to it if yellow color persists in the reaction mixture. Completion of the reaction was monitored by TLC and ether was evaporated off. The crude sample on purification by column chromatography (silica gel 100-200 mesh, 15% EtOAc-Hexane) afforded the product as a light yellow viscous liquid in 100% yield (1.3g).

General experimental procedure for the reaction of bicyclic hydrazine with 2-iodophenol:

Bicyclic hydrazine (1.5 equiv.), 2-iodophenol (1 equiv.), Bu₄NCl (1 equiv.), K₂CO₃ (2 equiv.) and [Pd(allyl)Cl]₂ (5 mol%) were taken in a Wheaton reactor. The mixture was dissolved in [bmim][PF₆] (2 mL) and stirred at 80 °C for 8 hours under argon atmosphere. After the completion of the reaction, the reaction mixture was extracted with ether, dried over Na₂SO₄. The solvent was evaporated in vacuo and the residue on silica gel (60-120 mesh) column chromatography using 30% ethyl acetate in hexane afforded the product in good yield.

General experimental procedure for the reaction of bicyclic hydrazine with 2-iodoaniline:

Bicyclic hydrazine (1.5 equiv.), 2-iodoaniline (1 equiv.), LiCl (1 equiv.), K₂CO₃ (2 equiv.) and Pd(OAc)₂ (5 mol%) were taken in a Wheaton reactor. The mixture was dissolved in Toluene (2 mL) and stirred at 100 °C for 36 hours under argon atmosphere. After the completion of the reaction, the solvent was evaporated in vacuo and the residue on neutral alumina column chromatography using mixtures of hexane and ethyl acetate in hexane afforded the product in good yield.

General experimental procedure for the preparation of 3,4- disubstituted cyclopentene from bicyclic hydrazine and 2-iodophenol:

Bicyclic hydrazine (1.5 equiv.), 2-iodophenol (1 equiv.), PPh₃ (10 mol%), K₂CO₃ (2 equiv.) and [Pd(allyl)Cl]₂ (5 mol%) were taken in a Wheaton reactor. The mixture was dissolved in CH₃CN (2 mL) and stirred at 60 °C for 16 hours under argon atmosphere. After the completion of the reaction, the solvent was evaporated in vacuo and the residue on silica gel (60-120 mesh) column chromatography using 20% ethyl acetate in hexane afforded the product in good yield.

General experimental procedure for the preparation of 3,4- disubstituted cyclopentene from bicyclic hydrazine and 2-iodoaniline:

Bicyclic hydrazine (1.5 equiv.), 2-iodoaniline (1 equiv.), PPh₃ (10 mol%), K₂CO₃ (2 equiv.) and Pd(OAc)₂ (5 mol%) were taken in a Wheaton reactor. The mixture was dissolved in CH₃CN (2 mL) and stirred at 60 °C for 24 hours under argon atmosphere. After the completion of the reaction, the solvent was evaporated in vacuo and the residue

on neutral alumina column chromatography using 20% ethyl acetate in hexane afforded the product in good yield.

Optimization Studies for Palladium- catalyzed reaction of Azabicyclic Olefins with 2-Iodophenol (Table 1)

1a + 2a $\xrightarrow[\text{additive, base, solvent, 80 } ^\circ\text{C, time}]{\text{catalyst}}$ 3a

Entry	Catalyst	Solvent	Base	Additive	Yield (%) ^a
1	Pd(OAc) ₂	DMF	K ₂ CO ₃	Bu ₄ NCl	63
2	Pd(OAc) ₂	"	"	Bu ₄ NBr	No Reaction
3	Pd(OAc) ₂	"	"	Bu ₄ NI	No Reaction
4	Pd(OAc) ₂	"	"	-	No Reaction
5	Pd(OAc) ₂	"	Na ₂ CO ₃	Bu ₄ NCl	22
6	Pd(OAc) ₂	"	Cs ₂ CO ₃	"	Trace
7	Pd[(allyl)Cl] ₂	"	K ₂ CO ₃	"	91
8	PdCl ₂	"	"	"	32
9	Pd(PPh ₃) ₄	"	"	"	33
10	[Pd(allyl)Cl] ₂	CH ₃ CN	"	"	93
11	[Pd(allyl)Cl] ₂	THF	"	"	37
12	[Pd(allyl)Cl] ₂	Toluene	"	"	26
13	[Pd(allyl)Cl] ₂	[bmim][PF ₆]	"	"	94 ^b
14	[Pd(allyl)Cl] ₂	[bmim][PF ₆]	"	"	Trace ^c

Reaction Conditions: alkene (1.5 equiv.), 2- iodophenol (1 equiv.), catalyst (5 mol%), base (2 equiv.), additive (1 equiv.), solvent (2 mL), 80 °C, 24 h.

^a Isolated yield, ^b Reaction time 8 h, ^c rt, 2 days.

Table 1 describes our efforts towards optimizing various reaction parameters. Among the additives that were examined Bu₄NBr and Bu₄NI were found to be ineffective (Table 1, entry 2 and 3). However the reaction was not working in the absence of Bu₄NCl (Table 1, entry 4). We went on optimizing other parameters such as base, catalyst and solvent. A base screen revealed that K₂CO₃ was more effective than Na₂CO₃ and Cs₂CO₃ (Table 1, entry 1, 5 and 6). Various catalysts such as Pd(OAc)₂, [Pd(allyl)Cl]₂, PdCl₂, Pd(PPh₃)₄ were screened from which [Pd(allyl)Cl]₂ gave the highest yield (Table 1, entry 1, 7- 9). We then turned our attention to solvent effects. An increase in reaction efficiency

was observed with DMF, CH₃CN and ionic liquid [bmim][PF₆] (Table 1, entry 7, 10 and 13). The rate of reaction was found to be accelerated in [bmim][PF₆] as observed earlier in our studies with bicyclic hydrazines.^{6a, b} Lowering the temperature resulted in sluggish reaction (Table 1, entry 14).

Optimization Studies for Palladium- catalyzed reaction of Azabicyclic Olefins with 2-Iodoaniline (Table 2)

Entry	Catalyst/Additive	Solvent	Yield of 7a (%)	Yield of 6 (%)
1	Pd(OAc) ₂ /Bu ₄ NCl	DMF	40	21
2	Pd(OAc) ₂ /LiCl	DMF	65	34
3	Pd(OAc) ₂ /LiCl	CH ₃ CN	54	7
4	Pd(OAc) ₂ /LiCl	Toluene	91	6
5	Pd(OAc) ₂ /LiCl	THF	49	12
6	[Pd(allyl)Cl] ₂ /LiCl	[bmim][PF ₆]	No reaction	
7	PdCl ₂ /LiCl	Toluene	31	7
8	[Pd(allyl)Cl] ₂ /LiCl	"	14	7
9	Pd(PPh ₃) ₂ Cl ₂ /LiCl	"	63	36
10	Pd(PPh ₃) ₄ /LiCl	"	53	46
11	Pd ₂ (dba) ₃ .CHCl ₃ /LiCl	"	13	67
12 ^a	Pd(OAc) ₂ /LiCl	Toluene	93	Trace
13 ^b	Pd(OAc) ₂ /PPh ₃	Toluene	-	60

Reaction Conditions: alkene (1.5 equiv.), 2- iodoaniline (1 equiv.), catalyst (5 mol%), K₂CO₃ (2 equiv.), LiCl (1 equiv.), solvent (2 mL), 80 °C, 24 h.

^a 100 °C, 36 h. ^b 60 °C

Table 2 describes our efforts towards optimizing various reaction parameters. Among the additives scanned LiCl was found to be more effective (Table 2, entry 1 and 2). From the solvents tested, toluene was found to be the best for the formation of cyclopentannulated product (Table 2, entry 4). The reaction did not work in ionic liquid [bmim][PF₆] (Table 2, entry 6). The catalysts screened were Pd(OAc)₂, [Pd(allyl)Cl]₂, PdCl₂, PdCl₂(PPh₃)₂, Pd₂dba₃.CHCl₃ and Pd(PPh₃)₄, from which Pd(OAc)₂ gave the

highest yield (Table 2, entry 4, 7- 11). An increase in the reaction temperature and time lead to the decrease in the formation of 3,4-disubstituted cyclopentene (Table 2, entry 12). When the reaction was repeated by replacing the chloride salt by PPh_3 , the exclusive formation of 3,4-disubstituted cyclopentene **6** was observed (Table 2, entry 13).

Characterization of the products:

Diethyl 1-((1R,3aR,8bS)-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3a).

Yield : 94% as colorless viscous liquid.

R_f : 0.42 (hexane/ethyl acetate = 6:4).

IR (KBr) $\nu_{\max}$: 3396, 2987, 2927, 2854, 1749, 1710, 1595, 1481, 1307, 1253, 1132, 914, 813 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ 7.36 (brs, 1H), 7.12 (t, 1H, J = 7.50 Hz), 6.87 (t, 1H, J = 7.40 Hz), 6.74-6.71 (d, 1H, J = 7.95 Hz), 6.29 (s, 1H), 6.09 (m, 1H), 5.86-5.81 (m, 2H), 5.34 (s, 1H), 4.27-4.16 (m, 4H), 4.11 (s, 1H), 1.34-1.26 (m, 6H).

¹³C NMR (125 MHz, CDCl₃): δ 158.1, 156.6, 155.6, 135.3, 132.3, 128.9, 128.2, 125.3, 120.8, 110.1, 90.8, 71.8, 62.8, 62.4, 50.2, 14.6, 14.4.

HRMS (EI): Calcd for C₁₇H₂₀N₂O₅, M⁺: 332.1372; Found: 332.1383.

Diisopropyl 1-((1R,3aR,8bS)-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3b).

Yield : 88% as colorless viscous liquid.

R_f : 0.50 (hexane/ethyl acetate = 6:4).

IR (KBr) $\nu_{\max}$: 3310, 3067, 2981, 2935, 1739, 1708, 1595, 1479, 1311, 1257, 1146, 1107, 976, 751 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ 7.31 (brs, 1H), 7.05 (t, 1H, J = 7.40 Hz), 6.79 (t, 1H, J = 7.30 Hz), 6.67-6.64 (d, 1H, J = 7.91 Hz), 6.23 (s, 1H), 6.00 (s, 1H), 5.79-5.73 (m, 2H), 5.26 (s, 1H), 4.96-4.87 (m, 2H), 4.03 (s, 1H), 1.25-1.19 (m, 12H).

¹³C NMR (125 MHz, CDCl₃): δ 157.9, 156.1, 155.1, 132.6, 128.8, 128.2, 125.3, 120.7, 110.0, 90.8, 71.3, 70.4, 69.9, 50.1, 22.1, 21.9.

HRMS (EI): Calcd for $C_{19}H_{24}N_2O_5$, M^+ : 360.1685; Found: 360.1695.

Di-tert-butyl 1-((1R,3aR,8bS)-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3c).

Yield : 86% as white solid

R_f : 0.52 (hexane/ethyl acetate = 6:4).

Mp : 142-144 °C

IR (KBr) ν_{max} : 3396, 2981, 2935, 1737, 1703, 1595, 1477, 1332, 1240, 1149, 1107, 966, 856, 751 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.39 (brs, 1H), 7.11 (t, 1H, J = 7.40 Hz), 6.86 (t, 1H, J = 7.30 Hz), 6.74-6.71 (d, 1H, J = 7.90 Hz), 6.07 (s, 2H), 5.81 (m, 2H), 5.31 (s, 1H), 4.12 (s, 1H), 1.52 (s, 9H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 155.7, 154.6, 132.7, 128.9, 125.6, 125.1, 120.8, 110.1, 90.0, 81.2, 71.2, 70.9, 50.3, 28.2.

HRMS (EI): Calcd for $C_{21}H_{28}N_2O_5$, M^+ : 388.1998; Found: 388.1995.

Dibenzyl 1-((1R,3aR,8bS)-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3d).

Yield : 87% as colorless viscous liquid.

R_f : 0.48 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3394, 3031, 2981, 2927, 1753, 1714, 1598, 1460, 1330, 1255, 1130, 1103, 968 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.32 (m, 11H), 7.09 (t, 1H, J = 7.30 Hz), 6.71-6.68 (d, 2H, J = 7.90 Hz), 6.67 (brs, 1H), 6.03 (s, 1H), 5.82-5.73 (m, 2H), 5.34 (s, 1H), 5.20-5.12 (m, 4H), 4.09-4.05 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 156.0, 154.5, 135.1, 133.5, 131.5, 128.5, 128.2, 128.1, 127.8, 120.4,

114.3, 113.9, 109.6, 90.3, 71.4, 67.5, 55.0, 49.9.

HRMS (EI): Calcd for $C_{27}H_{24}N_2O_5$, M^+ : 456.1685;

Found: 456.1615.

Diethyl 1-((1R,3aR,8bS)-7-phenyl-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3e)

Yield : 78% as colorless viscous liquid.

R_f : 0.40 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3297, 3058, 3025, 2972, 2932, 1750, 1718, 1606, 1474, 1314, 1255, 970, 758 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.61-7.28 (m, 7H), 6.84-6.81 (d, 1H, J = 8.18 Hz), 6.45 (s, 1H), 6.14 (s, 1H), 5.91 (s, 2H), 5.42 (s, 1H), 4.29-4.20 (m, 5H), 1.35-1.29 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 156.6, 155.6, 141.2, 134.5, 132.3, 128.9, 128.6, 128.1, 126.8, 126.5, 124.1, 110.3, 91.4, 71.8, 62.8, 62.2, 50.3, 14.6, 14.5.

HRMS (EI): Calcd for $C_{23}H_{24}N_2O_5$, M^+ : 408.1685;

Found: 408.1693.

Diisopropyl 1-((1R,3aR,8bS)-7-phenyl-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3f).

Yield : 81% as colorless viscous liquid.

R_f : 0.46 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3303, 3065, 3025, 2979, 2919, 1706, 1600, 1474, 1374, 1248, 1102, 956, 758 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.60-7.25 (m, 7H), 6.81-6.78 (d, 1H, J = 8.29 Hz), 6.26 (s, 1H), 6.11 (s, 1H), 5.88 (s, 2H), 5.39 (s, 1H), 5.04-4.93 (m, 2H), 4.17 (s, 1H), 1.32-1.27 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 156.2, 155.1, 141.2, 134.5, 132.5, 128.9, 128.6, 128.0, 126.8, 126.4, 124.1, 110.2, 91.4, 70.3, 69.9, 50.2, 22.1, 21.9.

HRMS (EI): Calcd for $C_{25}H_{28}N_2O_5$, M^+ : 436.1998;
Found: 436.2030.

Di-tert-butyl

1-((1R,3aR,8bS)-7-phenyl-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3g).

Yield : 80% as colorless viscous liquid.

R_f : 0.44 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3330, 3051, 2976, 2927, 1745, 1706, 1613, 1470, 1327, 1253, 1160, 966, 751 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$) : δ 7.59-7.28 (m, 7H), 6.81-6.78 (d, 1H, J = 8.22 Hz), 6.09 (s, 2H), 5.87 (s, 2H), 5.36 (s, 1H), 4.16 (s, 1H), 1.52 (s, 9H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 155.6, 154.4, 141.2, 134.4, 129.1, 128.5, 127.9, 126.8, 126.4, 124.1, 110.1, 91.4, 81.2, 50.0, 28.3, 28.1.

HRMS (EI): Calcd for $C_{27}H_{32}N_2O_5$, M^+ : 464.2311;
Found: 464.2310.

Dibenzyl 1-((1R,3aR,8bS)-7-phenyl-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3h).

Yield : 75% as colorless viscous liquid.

R_f : 0.42 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3297, 3065, 3032, 2952, 2919, 1719, 1600, 1474, 1248, 1314, 1129, 970, 751 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.70-7.31 (m, 17H), 6.78-6.76 (d, 1H, J = 8.31 Hz), 6.65 (brs, 1H), 6.04 (s, 1H), 5.84-5.79 (m, 2H), 5.42 (s, 1H), 5.26-5.12 (m, 4H), 4.21-4.07 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 156.4, 155.4, 141.2, 135.5, 134.5, 132.2, 128.6, 128.5, 128.2, 126.9, 124.1, 110.3, 91.3, 71.7, 67.9, 50.2.

MS (FAB): Calcd for $C_{33}H_{28}N_2O_5$, (M+1): 533.1998;
Found: 533.2007.

Diethyl 1-((1R,3aR,8bS)-7-acetyl-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3i).

Yield : 60% as colorless viscous liquid.

R_f : 0.15 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3299, 2987, 2912, 2839, 1734, 1706, 1679, 1604, 1487, 1261, 1116, 950, 764 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.86-7.83 (d, 1H, J = 8.40 Hz), 6.80-6.77 (d, 1H, J = 8.40 Hz), 6.36 (s, 1H), 6.13 (m, 1H), 5.97-5.94 (m, 2H), 5.35 (s, 1H), 4.33-4.19 (m, 5H), 2.58 (s, 3H), 1.39-1.27 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 196.0, 162.3, 156.8, 155.6, 134.8, 131.1, 129.0, 126.1, 109.8, 92.4, 71.9, 62.3, 49.7, 14.6, 14.4.

MS (FAB): Calcd for $C_{19}H_{22}N_2O_6$, (M+1): 375.1478;
Found: 375.1500.

Diisopropyl 1-((1R,3aR,8bS)-7-acetyl-3a,8b-dihydro-1H-benzo[b]cyclopenta[d]furan-1-yl)hydrazine-1,2-dicarboxylate (3j).

Yield : 55% as colorless viscous liquid.

R_f : 0.19 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3297, 3058, 2979, 2925, 1743, 1712, 1650, 1601, 1487, 1261, 1109, 970, 771 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.79-7.77 (d, 1H, J = 8.50 Hz), 6.66 (m, 1H), 6.22 (s, 1H), 6.03 (s, 1H), 5.84-5.81 (m, 2H), 5.23 (s, 1H), 4.95-4.86 (m, 2H), 4.09 (s, 1H), 2.49 (s, 3H), 1.21-1.20 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4, 161.9, 156.2, 154.9, 143.9, 133.8, 130.8, 127.9, 120.8, 109.6, 92.6, 72.1, 69.7, 49.9, 22.1, 21.9.

MS (FAB): Calcd for $C_{21}H_{26}N_2O_6$, (M+1): 403.1791;
Found: 403.1752.

Diethyl 1-((1S,2S)-2-(2-hydroxyphenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (4).

Yield : 80% as colorless viscous liquid.

R_f : 0.40 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3443, 3290, 3051, 2959, 2919, 2846, 1744, 1719, 1600, 1454, 1235, 1155, 1049, 950, 751 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 7.31-7.17 (m, 5H), 6.37 (s, 1H), 5.87-5.85 (m, 1H), 5.72-5.69 (m, 1H), 4.75-4.72 (m, 1H), 4.26-4.19 (m, 2H), 4.00 (s, 3H), 2.68-2.58 (m, 2H), 1.33-1.25 (m, 3H), 1.06 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 155.9, 143.2, 132.7, 129.6, 128.4, 127.4, 126.5, 67.2, 62.2, 62.1, 53.8, 35.1, 14.4, 14.2.

HRMS (FAB): Calcd for $C_{17}H_{22}N_2O_5$, (M+1): 335.1529; Found: 335.1502.

Diethyl 1-((1S,2S)-2-(2-aminophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (6).

Yield : 60% as colorless viscous liquid.

R_f : 0.23 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3363, 2959, 2919, 2846, 1738, 1714, 1604, 1462, 1259, 1023, 869, 798 cm^{-1} .

1H NMR (500 MHz, $CDCl_3$): δ 7.59-7.58 (m, 1H), 7.41-7.39 (m, 1H), 6.94-6.86 (m, 2H), 6.59-6.56 (m, 3H), 5.84 (s, 1H), 5.66 (s, 1H), 4.68-4.66 (m, 1H), 4.16-4.13 (m, 2H), 4.05-4.02 (m, 3H), 2.67 (m, 1H), 2.42-2.40 (m, 1H), (1.24-1.22 (m, 3H), 1.08-1.02 (m, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 155.6, 154.1, 132.7, 132.1, 131.9, 128.5, 128.4, 127.4, 62.5, 62.3, 49.4, 36.1, 14.5.

HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_4$, M^+ : 333.1689; Found: 333.1680.

Diethyl 1-((1R,3aR,8bR)-1,3a,4,8b-tetrahydrocyclopenta[b]indol-1-yl)hydrazine-1,2-dicarboxylate (7a).

Yield : 93% as colorless viscous liquid.

R_f : 0.15 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3297, 2979, 2919, 2859, 1712, 1606, 1414, 1228, 1056, 943, 758 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ 7.26 (brs, 1H), 7.03 (t, 1H, $J = 7.50$ Hz), 6.75 (t, 1H, $J = 7.40$ Hz), 6.60-6.58 (d, 1H, $J = 7.90$ Hz), 6.49 (s, 1H), 6.39 (s, 1H), 5.88 (m, 1H), 5.75 (m, 1H), 5.35 (s, 1H), 4.90-4.88 (m, 1H), 4.26-4.10 (m, 4H), 4.01 (m, 1H), 1.34-1.26 (m, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ 155.6, 154.6, 148.5, 139.2, 130.6, 129.3, 128.3, 125.5, 119.7, 110.7, 70.7, 67.6, 51.1, 14.2.

HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_4$, M^+ : 331.1532; Found: 331.1500.

Diisopropyl 1-((1R,3aR,8bR)-1,3a,4,8b-tetrahydrocyclopenta[b]indol-1-yl)hydrazine-1,2-dicarboxylate (7b).

Yield : 85% as colorless viscous liquid.

R_f : 0.17 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3297, 3051, 2972, 2925, 1741, 1705, 1600, 1487, 1374, 1255, 1102, 956, 758 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ 7.26 (s, 1H), 7.03 (t, 1H, $J = 7.30$ Hz), 6.76 (t, 1H, $J = 7.30$ Hz), 6.61-6.58

(d, 1H, $J = 7.80$ Hz), 6.18 (s, 1H), 5.88 (s, 1H), 5.75 (s, 1H), 5.34 (m, 1H), 5.03-4.91 (m, 3H), 4.02 (m, 1H), 1.28-1.26 (d, 12H, $J = 6.20$ Hz).

^{13}C NMR (125 MHz, CDCl_3): δ 156.3, 155.3, 148.5, 130.3, 128.4, 125.6, 119.9, 110.9, 70.4, 69.8, 67.5, 51.3, 22.3, 22.0.

HRMS (EI): Calcd for $\text{C}_{19}\text{H}_{25}\text{N}_3\text{O}_4$, M^+ : 359.1845; Found: 359.1838.

Di-tert-butyl

1-((1R,3aR,8bR)-1,3a,4,8b-tetrahydrocyclopenta[b]indol-1-yl)hydrazine-1,2-dicarboxylate (7c).

Yield : 75% as white solid

R_f : 0.19 (hexane/ethyl acetate = 6:4).

IR (KBr) ν_{max} : 3310, 2959, 2912, 2851, 1732, 1704, 1606, 1467, 1248, 1155, 950, 758 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ 7.26 (m, 1H), 7.02 (t, 1H, $J = 7.50$ Hz), 6.75 (t, 1H, $J = 7.30$ Hz), 6.59-6.57 (d, 1H, $J = 7.60$ Hz), 6.08 (s, 1H), 5.85 (m, 1H), 5.76 (m, 1H), 5.32 (s, 1H), 4.89 (m, 1H), 4.09-4.04 (m, 1H), 1.52 (s, 9H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 155.2, 154.2, 148.2, 134.3, 129.9, 127.7, 119.4, 110.2, 81.3, 80.4, 66.9, 52.7, 29.2, 27.7.

MS (FAB): Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_4$, ($M+1$): 388.2158; Found: 388.2190.

ORTEP drawing: **3c**

Empirical formula	C ₂₁ H ₂₈ N ₂ O ₅
Formula weight	388.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.853(4) Å alpha = 90 deg. b = 19.502(7) Å beta = 106.351(7) deg. c = 9.979(3) Å gamma = 90 deg.
Volume	2213.5(13) Å ³
Z	4
Density (calculated)	1.166 Mg/m ³
Absorption coefficient	0.083 mm ⁻¹
F(000)	832
Crystal size	0.46 x 0.31 x 0.05 mm
Theta range for data collection	1.79 to 25.00 deg.
Index ranges	-11 ≤ h ≤ 14, -23 ≤ k ≤ 21, -11 ≤ l ≤ 10

Reflections collected	10991
Independent reflections	3888 [R(int) = 0.0623]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9958 and 0.9627
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3888 / 0 / 263
Goodness-of-fit on F ²	1.235
Final R indices [I>2sigma(I)]	R1 = 0.1168, wR2 = 0.2187
R indices (all data)	R1 = 0.1741, wR2 = 0.2431
Largest diff. peak and hole	0.217 and -0.179 e.Å ⁻³