Supplemental material for:

# Total Synthesis of Bicyclomahanimbine by Cu(II)-Promoted Photoredox Process

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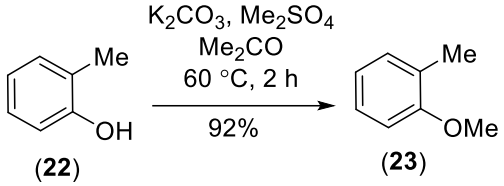
## Materials and Methods

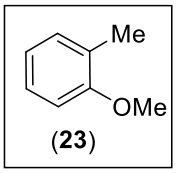
Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled over sodium/benzophenone ketyl. Dichloromethane ($CH_2Cl_2$), toluene, and benzene were distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 25 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, *p*-anisaldehyde stain, and other stains. Silica gel of particle size 100-200 mesh and 230-400 mess were used for flash column chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded 400 and 500 MHz spectrometers with $^{13}C$ operating frequencies of 100 and 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvents, $CDCl_3$ signal (δ = 7.28 for $^1H$ NMR and δ = 77.0 for $^{13}C$ NMR). Data for $^1H$ NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and a number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in the frequency of absorption ($cm^{-1}$). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

**Procedure for methylation of o-cresol:**




(**22**) (**23**)

To a solution of o-cresol (**22**) (4.14 g, 38.36 mmol, 1.00 equiv.) in acetone (42 mL), was added potassium carbonate (6.3 g, 44.03 mmol, 1.2 equiv.) followed by addition of dimethylsulphate (4.1 mL, 44.03 mmol, 1.2 equiv.) at 25 °C, and then the reaction mixture was warmed to 60 °C and vigorously stirred it for 2 h. After completion of reaction (monitored by TLC), then the reaction mixture was evaporated under lower pressure and the reaction mixture was diluted with ethyl acetate (55 mL) and water (42 mL). Then the biphasic layers were separated out and the remaining aqueous layer was further extracted with ethyl acetate (40 mL X 2). The combined organic layers were washed with brine (15 mL), dehydrated over $Na_2SO_4$, and evaporated under lowered pressure. The crude extract was purified by flash chromatography with n-hexane: EtOAc (49:1) to give 1-methoxy-2-methylbenzene (**23**).




(**23**)

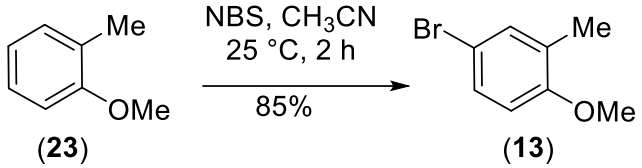
**1-Methoxy-2-methylbenzene** (**23**)**:** The compound (**23**) obtained as colorless oil (38.36 mmol; 4.3 g; 92%). $R_f$ = 0.7 (in 2.5% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 17.8, 7.8 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 3.96 (s, 3H), 2.43 (s, 3H).

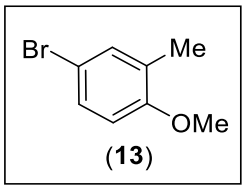
**$^{13}$C{$^1$H} NMR** (125 MHz, $CDCl_3$): δ 157.8, 130.6, 126.8, 126.6, 120.3, 109.9, 55.2, 16.2.

**IR** (film): $\nu_{max}$ 3089, 2854, 1512, 1461, 1232, 952 $cm^{-1}$.

**Procedure for bromination of compound 23:**




To a solution of 1-methoxy-2-methylbenzene (**23**) (4.1 g, 33.3 mmol, 1.00 equiv.) in acetonitrile (40 mL) was added *N*-bromo succinimide (NBS) (7.11 g, 39.96 mmol, 1.2 equiv.) at 25 °C. The reaction solution was stirred for 2 hours after it was quenched using saturated aqueous sodium thiosulfate ($Na_2S_2O_3$) (15 mL). The acetonitrile was evaporated and extracted with EtOAc (60 mL) and water (40 mL). The combined organic layers were washed with brine (15 mL), dehydrated over $Na_2SO_4$ and evaporated under lower pressure and the unrefined product was purified by flash chromatography with *n*-hexane: EtOAc (49:1) to give 4-bromo-1-methoxy-2-methylbenzene (**13**).



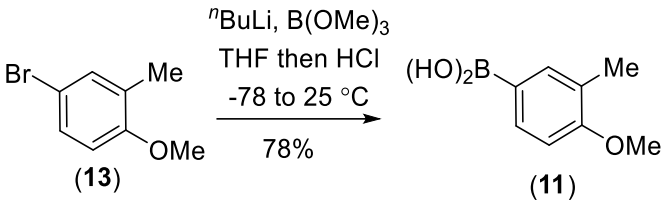

**4-Bromo-1-methoxy-2-methylbenzene** (**13**)**:** Compound **13** obtained as a white solid (33.3 mmol; 5.7 g; 85%). $R_f$ = 0.45 (in 5% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.1 Hz, 2H), 6.71 (d, *J* = 9.3 Hz, 1H), 3.83 (s, 3H), 2.23 (s, 3H).

**$^{13}$C{$^1$H} NMR** (125 MHz, $CDCl_3$): δ 156.9, 133.2, 129.4, 129.0, 112.3, 111.5, 55.5, 16.1.

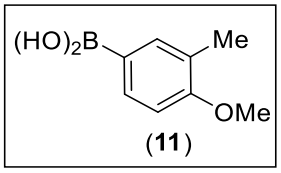
**IR** (film): $\nu_{max}$ 3412, 3025, 1345, 1127, 957 $cm^{-1}$.

**Procedure for preparation of boronic acid 11:**




(**13**) (**11**)

To a solution of 4-bromo-1-methoxy-2-methylbenzene (**13**) (5.6 g, 27.8 mmol, 1 equiv.) in dry THF (56 mL) was added $^{n}$BuLi (12 mL, 30.6 mmol, 1.1 equiv.) dropwise at −78 °C. After stirring for 30 min trimethyl borate ($B(OMe)_3$) (7.8 mL, 69.5 mmol, 2.5 equiv.) was added dropwise. Then the reaction mixture was warmed to 25 °C. The reaction solution was stirred for 10 hours before it was quenched using 4(*N*) HCl. Then the reaction mixture was stirred for 4 hours and extracted with EtOAc (60 mL) and water (45 mL). The combined organic layers were washed with brine, dehydrated over $Na_2SO_4$ and evaporated under lower pressure**.** The crude solid product was washed with hexane to give (4-methoxy-3-methylphenyl) boronic acid, (**11**).




(**11**)

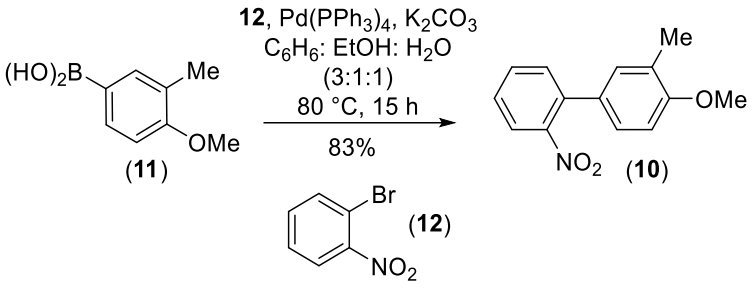
**4-Methoxy-3-methylphenyl) boronic acid (11):** Compound **11** obtained as white powder (27.8 mmol; 3.6 g; 78%). $R_f$ = 0.3 (in 5% EtOAc in *n*-hexane).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$): δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.57 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H), 2.14 (s, 3H).

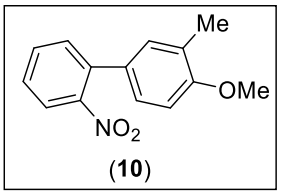
**$^{13}$C {$^{1}$H} NMR** (126 MHz, DMSO-$d_6$): δ 159.5, 137.0, 134.2, 129.8, 124.5, 109.7, 55.4, 16.5.

**IR** (film): $\nu_{max}$ 3058, 2845, 1425, 1329, 1175, 921 cm$^{-1}$.

**Procedure for Suzuki reaction between compound 12 and 11:**




To a solution of (4-methoxy-3-methylphenyl) boronic acid (**11**) (3.5 g, 21.0 mmol, 1.2 equiv.) in ethanol (14 mL) was added 2-bromonitrobenzene (3.5 g, 17.3 mmol, 1.0 equiv.) (**12**) in benzene (42 mL) followed by potassium carbonate (4.8 g, 34.6 mmol, 2.0 equiv.) dissolved in water (14 mL) and degassed the reaction mixture for 15 min. Next, tetrakis(triphenylphosphine)palladium [Pd ($PPh_3$)$_4$] (400 mg, 0.346 mmol, 0.02 equiv.) was added and the reaction mixture was warmed to 80 °C for 15 hours. When the reaction was completed (monitored by checking TLC), then the benzene was evaporated under lower pressure, and the crude product was purified by flash chromatography with *n*-hexane: EtOAc (35:1) to give **10**.




**4'-Methoxy-3'-methyl-2-nitro-1,1'-biphenyl** (**10**)**:** Compound **10** obtained as yellow crystal solid (17.30 mmol; 3.5 g; 83%). $R_f$ = 0.46 (in 2.5% EtOAc in *n*-hexane).

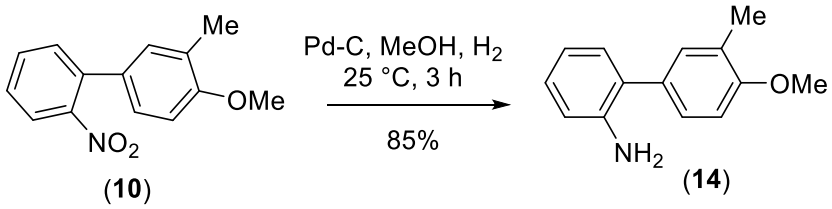
**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.83 – 7.80 (m, 1H), 7.62 – 7.58 (m, 1H), 7.45 (td, *J* = 7.4, 1.3 Hz, 2H), 7.17 – 7.13 (m, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 2.28 (s, 3H).

**$^{13}$C {$^1$H} NMR** (126 MHz, $CDCl_3$): δ 157.9, 149.5, 136.1, 132.0, 131.9, 130.2, 129.0, 127.6, 127.1, 126.4, 123.9, 110.0, 55.4, 16.3.

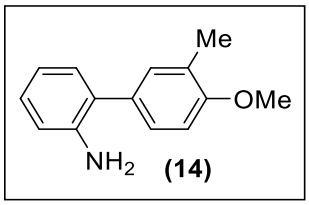
**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}NO_3$: 244.0974, found 244.0973.

**IR** (film): $\nu_{max}$ 3075, 2814, 1345, 1334, 1129, 1074, 8768 $cm^{-1}$.

**Procedure for the hydrogenation of compound 10:**




In a clean and oven-dried round bottom flask, compound **10** (3.2 g, 13.25 mmol, 1.0 equiv.) was dissolved in methanol (25 mL) and degassed the reaction mixture for 15 min. Then, Pd-C (160 mg, 5 mol% (w/w)) was added to the reaction mixture and hydrogen gas was passed through the solution for 3 h at 25 °C. Upon completion of the reaction (monitored by TLC), methanol was evaporated and the crude product was purified by flash column chromatography with *n*-hexane: EtOAc (20:1) to **14**.




**4'-Methoxy-3'-methyl -[1,1'-biphenyl]-2-amine (14):** Compound **14** obtained as colorless liquid (11.6 mmol; 2.4 g; 85%). $R_f$ = 0.25 (in 5% EtOAc in *n*-hexane).

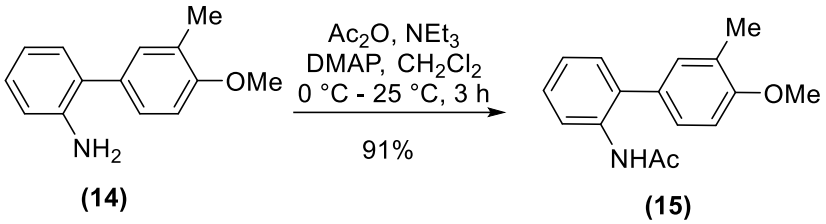
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.27 – 7.23 (m, 2H), 7.16 – 7.10 (m, 2H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.82 (td, *J* = 7.4, 1.2 Hz, 1H), 6.77 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 3.88 (s, 3H), 3.63 (d, *J* = 5.21 Hz, 2H), 2.28 (s, 3H).

**$^{13}$C {$^1$H} NMR (126 MHz, $CDCl_3$)**: δ 157.9, 149.5, 136.1, 132.0, 131.9, 130.2, 129.0, 127.6, 127.1, 126.4, 123.9, 110.0, 55.4, 16.3.

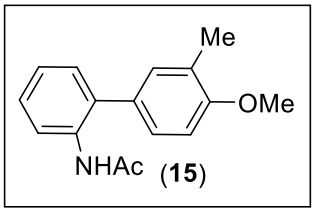
**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO$: 214.1232, found 214.1235.

**IR** (film): $\nu_{max}$ 2928, 1389, 1341, 1041, 951, 845 $cm^{-1}$.

**Procedure for the acetylation of compound 14:**




In a clean and oven-dried round bottom flask, compound **14** (2.1 g, 9.7 mmol, 1.0 equiv.) was dissolved in dichloromethane (25 mL) was added. Triethylamine (2 ml, 15.6 mmol, 1.5 equiv), acetic anhydride (1.1 mL, 11.6 mmol, 1.2 equiv) and 4-dimethylaminopyridine (237 mg, 1.94 mmol, 0.2 equiv) sequentially at 0 °C. Then, the reaction was warmed to 25 °C and stirred it for 3 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was quenched with water (15 mL) and the biphasic layers were separated and the aqueous layer was further extracted with dichloromethane (30 mL X 2). The combined organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure then the crude product was purified by flash column chromatography with *n*-hexane:EtOAc (7:1) to give **15**.




***N*-(4'-methoxy-3'-methyl-[1,1'-biphenyl]-2-yl) acetamide (15):** Compound **15** obtained as white solid (9.7 mmol; 2.3 g; 91%). $R_f$ = 0.41 (in 30% EtOAc in *n*-hexane).

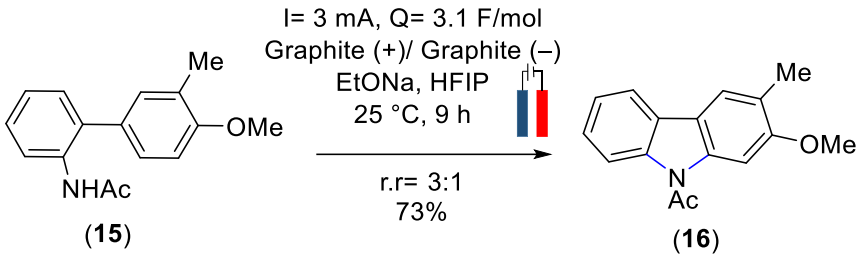
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.25 (d, *J* = 0.5 Hz, 1H), 7.20 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.13 (d, *J* = 1.9 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 2.26 (s, 3H), 2.02 (s, 3H).

**$^{13}$C {$^{1}$H} NMR** (101 MHz, $CDCl_3$): δ 172.0, 157.6, 135.0, 131.7, 130.2, 129.9, 128.1, 127.7, 124.2, 121.3, 55.5, 16.4.

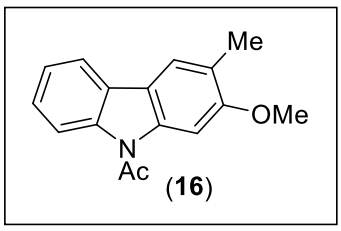
**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_2$: 256.1338, found 256.1329.

**IR** (film): $\nu_{max}$ 3025, 2845, 1625, 1212, 1189, 914, 821 $cm^{-1}$.

**Procedure for the synthesis of compound 16:**




A 10 mL glass vial was poured with biaryl acetamide **15** (500 mg, 2.0 mmol, 1.0 equiv.) to which 1,1,1,3,3,3-hexfluoroisopropanol (5 mL) followed by sodium ethoxide (100 mg, 1.5 mmol, 0.75 equiv.) were added. A lid with graphite electrodes (52 x 5 mm) was attached and electrolysis was carried out with a constant current of 3 mA until 3.1 F/mol charge was passed (~ 9 h) at room temperature. Upon completion of the reaction (monitored by TLC), the reaction mixture was transferred to a 50 mL round bottom flask to which electrodes were washed with methanol. Solvents were evaporated under reduced pressure. Then the crude product was purified by flash column chromatography with *n*-hexane: EtOAc (10:1) to give **16**.




**1-(2-Methoxy-3-methyl-9H-carbazol-9-yl) ethane-1-one (16)**: Compound **15** obtained as white solid (2.0 mmol; 277 mg; 73%). $R_f$ = 0.34 (in 10% EtOAc in *n*-hexane).

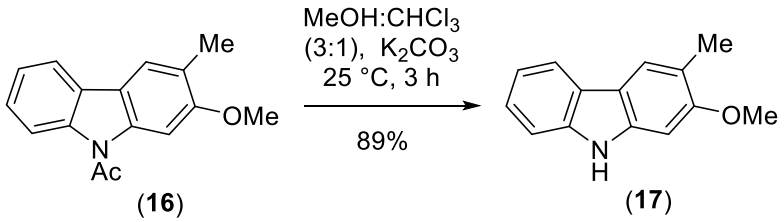
**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 12.8 Hz, 2H), 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.69 (s, 1H), 7.35 (td, *J* = 7.2, 1.5 Hz, 2H), 3.94 (s, 3H), 2.87 (s, 3H), 2.35 (s, 3H).

**$^{13}$C {$^{1}$H} NMR** (101 MHz, $CDCl_3$): δ 170.2, 158.1, 138.6, 138.1, 127.1, 125.5, 123.6, 123.6, 120.8, 119.2, 118.8, 115.5, 99.4, 55.8, 27.8, 16.7.

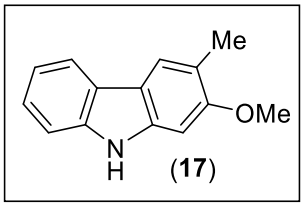
**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NO_2$ : 254.1181, found 254.1171.

**IR** (film): $\nu_{max}$ 2912, 1412, 1392, 1274, 1058, 1021 $cm^{-1}$.

**Procedure for the hydrolysis of compound 16:**




To a solution of compound **16** (813 mg, 3.21 mmol, 1 equiv.) in a mixed solvent system of MeOH: $CHCl_3$ (3:1) (12 mL) was added potassium carbonate (665 mg, 4.8 mmol, 1.5 eq.) at 25 °C and the reaction mixture was stirred for 3 h at the same temperature. After complete consumption of the starting material (monitored by TLC) the solution was diluted with $CH_2Cl_2$ (6 mL) and water (8 mL). The biphasic layers were separated and the aqueous layer was further extracted with dichloromethane (12 mL X 2). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residual crude product was purified by silica gel column chromatography with *n*-hexane: EtOAc (7:1) to give **17**.



**2-Methoxy-3-methyl-9H-carbazole (17):** Compound **17** obtained as yellowish powder (3.21 mmol; 603 mg; 89%). $R_f$ = 0.2 (in 10 % EtOAc in *n*-hexane).

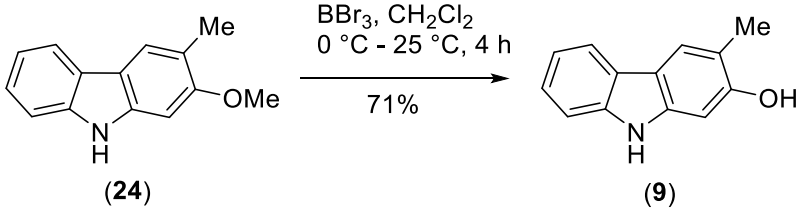
**$^1$H NMR** (500 MHz, DMSO-$d_6$): δ 10.99 (s, 1H), 7.94 (d, J = 7.4 Hz, 1H), 7.81 (d, *J* = 4.3 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.26 (dt, *J* = 6.5, 2.5 Hz, 1H), 7.09 (dt, *J* = 6.2, 3.0 Hz, 1H), 6.96 (dd, *J* = 5.9, 3.8 Hz, 1H), 3.88 (dt, *J* = 5.5, 3.3 Hz, 3H), 2.28 (dq, *J* = 7.3, 3.5 Hz, 3H).

**$^{13}$C{$^1$H} NMR** (126 MHz, DMSO-$d_6$): δ 157.2, 140.0, 139.9, 124.2, 123.1, 121.6, 119.5, 118.8, 117.8, 115.7, 111.0, 93.1, 55.8, 17.1.

**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $[C_{14}H_{14}NO+ H]^+$: 212.1075, found 212.1075.

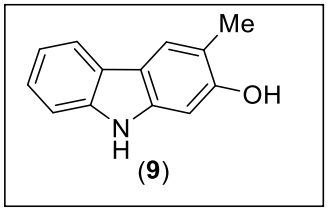
**IR** (film): $\nu_{max}$ 3421, 3042, 2841, 1632, 1245, 1056 $cm^{-1}$.

**Procedure for the demethylation of 24:**




(**24**) (**9**)

To a solution of compound **24** (538 mg, 2.55 mmol, 1.0 equiv.) in dichloromethane (8 mL) was added boron tribromide (725 µl, 7.67 mmol, 3 equiv.) in dropwise manner at 0 °C. Then the reaction mixture was warmed to 25 °C and stirred it for 4 h. Upon complete consumption of starting materials (confirmed by checking TLC), the reaction mixture was quenched with water (8 mL) and the biphasic layers were separated and the aqueous layer was further extracted with dichloromethane (12 mL X 2). The combined organic layers were washed with brine (5 mL), dried over $Na_2SO_4$, and evaporated under lower pressure**,** then the crude product was purified by flash silica gel column chromatography with *n*-hexane: EtOAc (4:1) to give **9**.



(**9**)

**2-Hydroxy-3-methylcarbazole** (**9**)**:** The compound (**9**) obtained as white solid (2.55 mmol; 357 mg; 71%). $R_f$ = 0.41 (in 30% EtOAc in *n*-hexane).

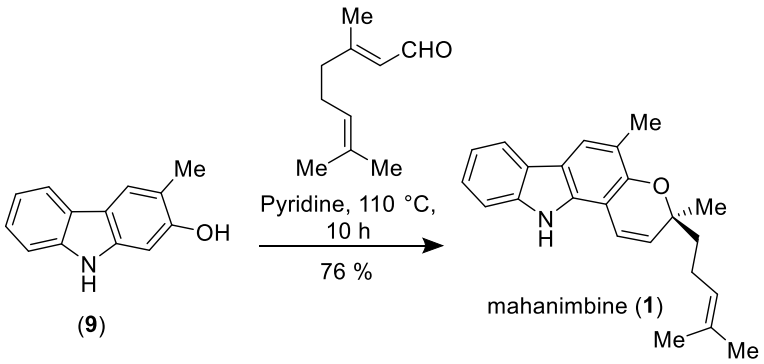
**$^1$H NMR** (400 MHz, DMSO-$D_6$): δ 10.78 (d, *J* = 2.2 Hz, 1H), 9.38 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.01 (tt, *J* = 7.5, 1.3 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 2.22 (s, 3H).

**$^{13}$C {$^1$H} NMR** (126 MHz, DMSO): δ 155.1, 140.1, 139.9, 123.9, 123.4, 121.6, 119.2, 118.6, 116.8, 115.4, 110.7, 96.5, 17.0.

**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{12}NO$: 198.0919, found 198.0920.

**IR** (film): $\nu_{max}$ 3425, 2912, 2856, 1621, 1187, 953, 824 $cm^{-1}$.

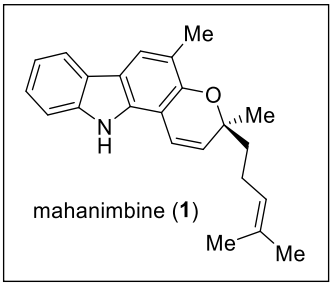
**Procedure for the synthesis of mahanimbine (1):**



(**9**) mahanimbine (**1**)

In a clean and oven-dried round bottom flask, carbazole **9** (237 mg, 1.2 mmol, 1.0 equiv.) was dissolved in pyridine (5 mL). Citral (2.0 ml, 12 mmol, 10 equiv) was added to the reaction mixture

at 25 °C. Then the reaction mixture was warmed to 110 °C and stirred it for 10 h. Upon complete consumption of starting materials (confirmed by checking TLC), then the reaction mixture was evaporated under lower pressure and diluted with ethyl acetate (7 mL) and water (5 mL). The biphasic layers were separated and the aqueous layer was further extracted with ethyl acetate (7 mL X 2). The combined organic layers were dried over $Na_2SO_4$ and evaporated under vacuum**.** The crude product was purified by silica gel column chromatography with *n*-hexane: EtOAc (20:1) to give mahanimbine (**1**)**.**




**3,5-Dimethyl-3-(4-methylpent-3-en-1-yl)-3,11-dihydropyrano[3,2-*a*]carbazole(1):** Compound (**1**) obtained as yellowish liquid (1.2 mmol; 302 mg; 76%). $R_f$ = 0.45 (in 10% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.88 (s, 1H), 7.69 (s, 1H), 7.40 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.21 (td, *J* = 7.4, 1.1 Hz, 1H), 6.67 (d, *J* = 9.8 Hz, 1H), 5.68 (d, *J* = 9.8 Hz, 1H), 5.15 (tt, *J* = 7.2, 1.5 Hz, 1H), 2.37 (s, 3H), 2.25 – 2.17 (m, 2H), 1.82 – 1.78 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.60 (s, 1H), 1.49 (s, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$): δ 150.0, 139.5, 135.0, 131.8, 128.6, 124.3, 124.3, 124.0, 121.3, 119.6, 119.4, 118.5, 117.6, 116.7, 110.5, 104.3, 78.3, 40.9, 25.9, 25.8, 22.9, 17.7, 16.2.

**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}NO$: 332.2004, found 332.2014.

**IR** (film): $\nu_{max}$ 3319, 2941, 2842, 1712, 1612, 1423, 1042 $cm^{-1}$.

**Comparison of $^1$H-NMR Data:**

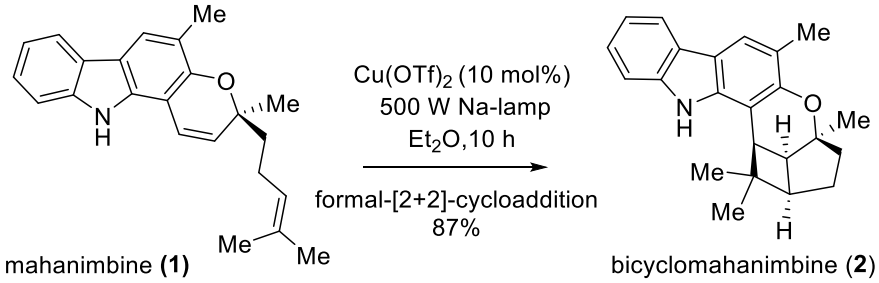
| Ali's report[23] on mahanimbine [**1**] ($^1$H NMR, 400 MHz, $CDCl_3$) | Knolker's report[10] on mahanimbine [**1**] ($^1$H NMR, 500 MHz, $CDCl_3$) | This report of mahanimbine [**1**] ($^1$H NMR, 500 MHz, $CDCl_3$) |
|---|---|---|
| 7.91 (d, *J* = 7.8 Hz, 1H) | 7.93 (d, *J* = 7.7 Hz, 1H) | 7.94 (dd, *J* = 7.7, 1.1 Hz, 1H) |
| 7.86 (s, 1H) | 7.87 (brs, 1H) | 7.88 (s, 1H) |
| 7.66 (s, 1H) | 7.68 (s, 1H) | 7.69 (s, 1H) |
| 7.37 (d, *J* = 8.0 Hz, 1H) | 7.37 (d, *J* = 7.9 Hz, 1H) | 7.40 (dt, *J* = 8.1, 0.9 Hz, 1H) |
| 7.30 (t, *J* = 7.5 Hz, 1H) | 7.32 (brt, *J* = 7.5 Hz, 1H) | 7.35 – 7.31 (m, 1H) |
| 7.17 (t, *J* = 7.4 Hz, 1H) | 7.19 (brt, *J* = 7.3 Hz, 1H) | 7.21 (td, *J* = 7.4, 1.1 Hz, 1H) |
| 6.65 (d, *J* = 9.8 Hz, 1H) | 6.63 (d, *J* = 9.8 Hz, 1H) | 6.67 (d, *J* = 9.8 Hz, 1H) |
| 5.66 (d, *J* = 9.8 Hz, 1H) | 5.66 (d, *J* = 9.8 Hz, 1H) | 5.68 (d, *J* = 9.8 Hz, 1H) |
| 5.15 (t, *J* = 7.1 Hz, 1H) | 5.14 (t, *J* = 7.1 Hz, 1H) | 5.15 (tt, *J* = 7.2, 1.5 Hz, 1H) |
| 2.33 (s, 3H) | 2.37 (s, 3H) | 2.37 (s, 3H) |
| 2.19 – 2.14 (m, 2H) | 2.19 (m, 2H) | 2.25 – 2.17 (m, 2H) |
| 1.79 – 1.74 (m, 2H) | 1.79 (t, J = 8.3 Hz, 2H) | 1.82 – 1.78 (m, 2H) |
| 1.66 (s, 3H) | 1.69 (s, 3H) | 1.70 (s, 3H) |
| 1.58 (s, 3H) | 1.61 (s, 3H) | 1.62 (s, 3H) |
| 1.56 (s, 3H) | - | 1.60 (s, 1H) |
| 1.45 (s, 3H) | 1.47 (s, 3H) | 1.49 (s, 3H) |

**Comparison of $^{13}$C-NMR Data:**

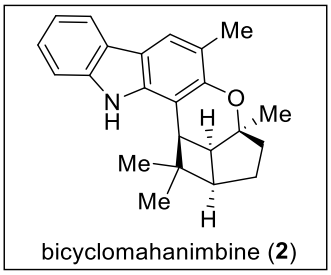
| Ali's report[23] on mahanimbine [**1**] | Knolker's report[10] on mahanimbine [**1**] | This report mahanimbine [**1**] |
|---|---|---|
| ($^{13}$C NMR, 100 MHz, $CDCl_3$) | ($^{13}$C NMR, 125 MHz, $CDCl_3$) | ($^{13}$C NMR, 100 MHz, $CDCl_3$) |
| 149.9 | 149.86 | 150.0 |
| 139.4 | 139.41 | 139.5 |
| 134.8 | 134.82 | 135.0 |

| | | |
|---|---|---|
| 131.7 | 131.65 | 131.8 |
| 128.5 | 128.44 | 128.6 |
| 124.2 | 124.16 | 124.3 |
| 124.2 | | 124.3 |
| 123.9 | 123.86 | 124.0 |
| 121.2 | 121.15 | 121.3 |
| 119.5 | 119.41 | 119.6 |
| 119.3 | 119.25 | 119.4 |
| 118.4 | 118.36 | 118.5 |
| 117.5 | 117.49 | 117.6 |
| 116.6 | 116.56 | 116.7 |
| 110.3 | 110.56 | 110.5 |
| 104.2 | 104.16 | 104.3 |
| 78.1 | 78.12 | 78.3 |
| 40.7 | 40.72 | 40.9 |
| 25.8 | 25.79 | 25.9 |
| 25.7 | 25.65 | 25.8 |
| 22.7 | 22.72 | 22.9 |
| 17.6 | 17.55 | 17.7 |
| 16.1 | 16.07 | 16.2 |

**Procedure for the synthesis of bicyclomahanimbine (2):**




To a solution of mahanimbine (**1**) (59 mg, 0.18 mmol, 1.0 equiv.) in diethyl ether (3 mL) was added copper triflate (7 mg, 0.018 mmol, 10 mol%) in presence of 500 W Na-lamp for 10 h. When the reaction was completed (confirmed by checking TLC), then the reaction mixture was extracted with EtOAc (6 mL X 3) and water (5 mL). The combined organic layers were dried over $Na_2SO_4$ and evaporated under vacuum**.** The crude product was purified by silica gel column chromatography with *n*-hexane: EtOAc (7:1) to give bicyclomahanimbine (**2**).




**Bicyclomahanimbine (2):** Compound **2** obtained as yellowish liquid (0.18 mmol; 52 mg; 87%). $R_f$ = 0.55 (in 10% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.71 (d, *J* = 0.8 Hz, 1H), 7.45 (s, 1H), 7.40 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.21 – 7.18 (m, 1H), 3.32 (d, *J* = 9.5 Hz, 1H), 2.73 (dd, *J* = 9.5, 7.7 Hz, 1H), 2.54 (td, *J* = 8.3, 7.8 Hz, 1H), 2.38 (s, 3H), 2.11 – 2.07 (m, 1H), 1.76 (ddd, *J* = 7.1, 4.4, 1.8 Hz, 1H), 1.70 – 1.66 (m, 2H), 1.59 (s, 3H), 1.47 (s, 3H), 0.78 (s, 3H).

**$^{13}$C {$^1$H} NMR** (125 MHz, $CDCl_3$): δ 150.4, 139.3, 137.8, 124.2, 123.9, 120.0, 119.3, 119.3, 119.3, 115.8, 110.3, 106.3, 83.5, 46.5, 39.3, 38.4, 37.9, 37.4, 35.1, 27.4, 25.6, 18.6, 16.7.

**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}NO$ :332.2014, found 332.2013.

**IR** (film): $\nu_{max}$ 3456, 2934, 1607, 1321, 1012, 951 $cm^{-1}$.

**Comparison of $^1$H-NMR Data:**

| Ali's report[23] of bicyclomahanimbine [**2**] ($^1$H NMR, 500 MHz, $CDCl_3$) | Knolker's report[10] of bicyclomahanimbine [**2**] ($^1$H NMR, 500 MHz, $CDCl_3$) | Nafiah's report[24] of bicyclomahanimbine [**2**] ($^1$H NMR, 500 MHz, $CDCl_3$) | This report of report of bicyclomahanimbine [**2**] ($^1$H NMR, 500 MHz, $CDCl_3$) |
|---|---|---|---|
| 7.92 (d, *J* = 7.7 Hz, 1H) | 7.94 (d, *J* = 7.7 Hz, 1H) | 7.93 (d, *J* = 8.1 Hz, 1H) | 7.96 (dd, *J* = 7.8, 1.1 Hz, 1H) |
| 7.67 (s, 1H) | 7.69 (s, 1H) | 7.66 (s, 1H) | 7.71 (d, *J* = 0.8 Hz, 1H) |
| 7.41 (s, 1H) | 7.43 (brs, 1H) | 7.44 (brs, 1H) | 7.45 (s, 1H) |
| 7.36 (d, *J* = 8.0 Hz, 1H) | 7.38 (d, *J* = 8.0 Hz, 1H) | 7.37 (d, *J* = 8.1 Hz, 1H) | 7.40 (dt, *J* = 8.0, 1.0 Hz, 1H) |
| 7.32 – 7.26 (m, 1H) | 7.30 (brt, *J* = 7.6 Hz, 1H) | 7.28 (td, *J* = 8.1, 1.0 Hz, 1H) | 7.33 – 7.31 (m, 1H) |
| 7.20 – 7.14 (m, 1H) | 7.18 (brt, *J* = 7.4 Hz, 1H) | 7.15 (td, *J* = 8.1, 1.0 Hz, 1H) | 7.21 – 7.18 (m, 1H) |
| 3.26 (d, *J* = 9.5 Hz, 1H) | 3.30 (d, *J* = 9.5 Hz, 1H) | 3.30 (d, *J* = 9.2 Hz, 1H) | 3.32 (d, *J* = 9.5 Hz, 1H) |
| 2.68 (dd, *J* = 9.3, 8.0 Hz, 1H) | 2.71 (dd, *J* = 9.3, 7.9 Hz, 1H) | 2.71 (t, *J* = 7.5 Hz, 1H) | 2.73 (dd, *J* = 9.5, 7.7 Hz, 1H) |
| 2.49 (t, *J* = 6.2 Hz, 1H) | 2.51 (brt, *J* = 6.6 Hz, 1H) | 2.50 (t, *J* = 7.4 Hz, 1H) | 2.54 (td, *J* = 8.3, 7.8 Hz, 1H) |
| 2.35 (s, 3H) | 2.36 (s, 3H) | 2.33 (s, 3H) | 2.38 (s, 3H) |
| 2.12 – 1.99 (m, 1H) | 2.06 – 2.09 (m, 1H) | 2.01 – 2.07 (m, 1H) | 2.11 – 2.07 (m, 1H) |
| 1.78-1.69 (m, 1H) | 1.64-1.76 (m, 3H) | 1.64 - 1.68 (m, 1H) | 1.76 (ddd, *J* = 7.1, 4.4, 1.8 Hz, 1H) |
| 1.69 – 1.61 (m, 2H) | | - | 1.70 – 1.66 (m, 2H) |

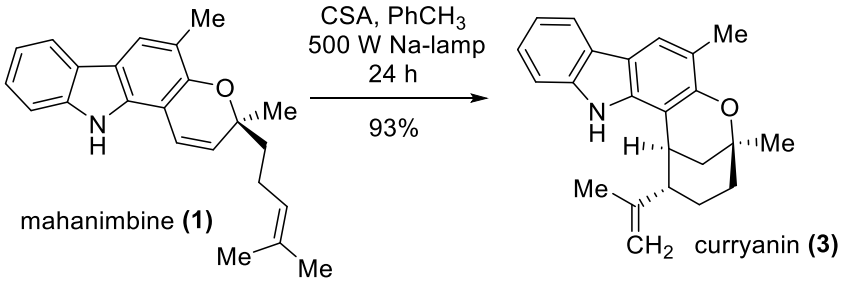
| | | | |
|---|---|---|---|
| 1.54 (s, 3H) | 1.57 (s, 3H) | 1.57 (s, 3H) | 1.59 (s, 3H) |
| - | - | 1.55 - 1.57 (m, 1H) | - |
| - | - | 1.53 - 1.57 (m, 1H) | - |
| 1.44 (s, 3H) | 1.45 (s, 3H) | 1.43 (s, 3H) | 1.47 (s, 3H) |
| 0.74 (s, 3H) | 0.75 (s, 3H) | 0.74 (s, 3H) | 0.78 (s, 3H) |

**Comparison of $^{13}$C-NMR Data:**

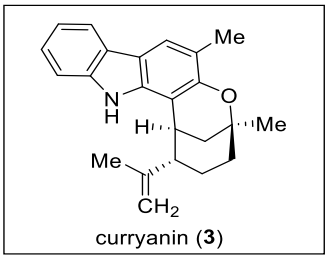
| Ali's report[23] of bicyclomahanimbine [**2**] | Knolker's report[10] of bicyclomahanimbine [**2**] | Nafiah's report[24] of bicyclomahanimbine [**2**] | This report bicyclomahanimbine [**2**] |
|---|---|---|---|
| ($^{13}$C NMR, 126 MHz, $CDCl_3$) | ($^{13}$C NMR, 125 MHz, $CDCl_3$) | ($^{13}$C NMR, 125 MHz, $CDCl_3$) | ($^{13}$C NMR, 100 MHz, $CDCl_3$) |
| 150.33 | 150.35 | 150.2 | 150.4 |
| 139.20 | 139.21 | 139.3 | 139.3 |
| 137.74 | 137.75 | 137.8 | 137.8 |
| 124.17 | 124.16 | 124.2 | 124.2 |
| 123.86 | 123.87 | 124.0 | 123.9 |
| 119.98 | 120.00 | 120.1 | 120.0 |
| 119.30 | 119.31 | 119.4 | 119.3 |
| 119.28 | 119.28 | 119.4 | 119.3 |
| 119.24 | 119.26 | 119.2 | 119.3 |
| 115.73 | 115.74 | 115.8 | 115.8 |
| 110.26 | 110.25 | 110.4 | 110.3 |
| 106.30 | 106.30 | 106.5 | 106.3 |
| 83.49 | 83.51 | 83.5 | 83.5 |

| | | | |
|---|---|---|---|
| 46.38 | 46.40 | 46.5 | 46.5 |
| 39.24 | 39.27 | 39.5 | 39.3 |
| 39.29 | 38.31 | 38.4 | 38.4 |
| 37.75 | 37.78 | 37.9 | 37.9 |
| 37.30 | 37.34 | 37.5 | 37.4 |
| 35.03 | 35.07 | 35.2 | 35.1 |
| 27.40 | 27.41 | 27.5 | 27.4 |
| 25.58 | 25.60 | 25.7 | 25.6 |
| 18.56 | 18.58 | 18.6 | 18.6 |
| 16.70 | 16.70 | 16.8 | 16.7 |

**Synthesis of Curruyanin (3):**




In a clean and oven-dried round bottom flask, mahanimbine (**1**) (166 mg, 0.50 mmol, 1.0 equiv.) dissolved in toluene (5 mL). Camphor sulphonic acid (CSA) (174 mg, 0.75 mmol, 1.5 equiv) was added to the reaction mixture and was irradiated with light using a 500W Na-lamp for 24 h. Upon complete consumption of starting materials (monitored by TLC), volatiles were evaporated under lower pressure and extracted with ethyl acetate (7 mL X 3) and water (5 mL). The combined organic layers were dried over $Na_2SO_4$ and evaporated under vacuum**.** The crude product was purified by flash chromatography with *n*-hexane: EtOAc (50:1) to give curruyanin (**3**)**.**



curryanin (**3**)

**Curruyanin (3):** Compound (**3**) obtained as white solid (0.50 mmol; 154 mg; 93%). $R_f$ = 0.65 (in 10% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.91 (dq, *J* = 7.7, 0.9 Hz, 1H), 7.74 (s, 1H), 7.66 (t, *J* = 0.9 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.30 (d, *J* = 1.2 Hz, 1H), 7.17 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 4.84 (s, 1H), 4.76 (s, 1H), 3.44 (d, *J* = 3.1 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.36 (s, 3H), 2.12 (dt, *J* = 9.2, 2.4 Hz, 1H), 2.06 (dd, *J* = 12.9, 2.7 Hz, 1H), 1.94 – 1.90 (m, 1H), 1.68 – 1.63 (m, 2H), 1.53 (s, 3H), 1.46 (s, 3H).

**$^{13}$C {$^1$H} NMR** (100 MHz, $CDCl_3$): δ 153.7, 150.2, 139.5, 138.4, 124.4, 123.6, 119.6, 119.2, 119.1, 117.7, 114.7, 112.1, 110.3, 105.3, 77.3, 74.0, 48.8, 40.0, 37.5, 36.3, 29.1, 23.2, 21.7, 16.8.

**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}NO$ :332.2007, found 332.2014.

**IR** (film): $\nu_{max}$ 3421, 2912, 2815, 1458, 1378, 1229, 1105 $cm^{-1}$.

**Comparison of $^1$H-NMR Data:**

| Ali's report[23] of curruyanin [**3**] ($^1$H NMR, 500 MHz, $CDCl_3$) | Knolker's report[10] of curruyanin [**3**] ($^1$H NMR, 500 MHz, $CDCl_3$) | This report of curruyanin [**3**] ($^1$H NMR, 500 MHz, $CDCl_3$) |
|---|---|---|
| 7.88 (d, *J* = 7.7 Hz, 1H) | 7.90 (d, *J* = 7.7 Hz, 1H) | 7.91 (dq, *J* = 7.7, 0.9 Hz, 1H) |

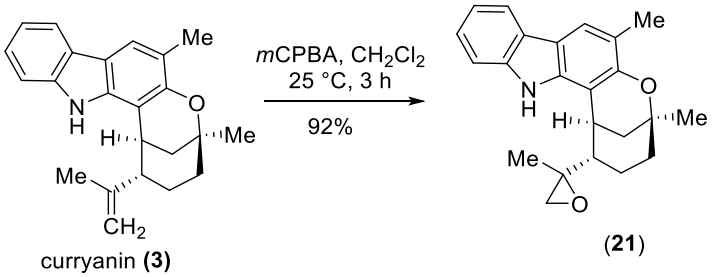
| | | |
|---|---|---|
| 7.68 (s, 1H) | 7.73 (brs, 1H) | 7.74 (s, 1H) |
| 7.62 (s, 1H) | 7.65 (s, 1H) | 7.66 (t, *J* = 0.9 Hz, 1H) |
| 7.29 (d, *J* = 8.0 Hz, 1H) | 7.32 (d, *J* = 8.0 Hz, 1H) | 7.34 (d, J = 7.9 Hz, 1H) |
| 7.25 (t, *J* = 7.3 Hz, 1H) | 7.27 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H) | 7.30 (d, *J* = 1.2 Hz, 1H) |
| 7.13 (t, J = 7.3Hz, 1H) | 7.15 (brt, J = 7.4 Hz, 1H) | 7.17 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H) |
| 4.77 (s, 1H) | 4.82 (s, *J* = 1.6 Hz, 1H) | 4.84 (s, 1H) |
| 4.69 (s, 1H) | 4.75 (s, 1H) | 4.76 (s, 1H) |
| 3.32 (s, 1H) | 3.42 (d, *J* = 2.6 Hz, 1H) | 3.44 (d, *J* = 3.1 Hz, 1H) |
| 2.56 – 2.45 (m, 1H) | 2.59 (m, 1H) | 2.65 – 2.57 (m, 1H) |
| 2.33 (s, 3H) | 2.34 (s, 3H) | 2.36 (s, 3H) |
| 2.05 (d, *J* = 9.1 Hz, 1H) | 2.10 (dt, *J* = 9.1, 2.1 Hz, 1H) | 2.12 (dt, *J* = 9.2, 2.4 Hz, 1H) |
| - | 2.03 (dd, *J* = 12.8, 2.6 Hz, 1H) | 2.06 (dd, *J* = 12.9, 2.7 Hz, 1H) |
| 1.99 – 1.89 (m, 1H) | 1.90 (dt, *J* = 12.8, 3.1 Hz, 1H) | 1.94 – 1.90 (m, 1H) |
| 1.87 – 1.77 (m, 1H) | - | - |
| 1.65 – 1.51 (m, 1H) | 1.59 – 1.68 (m, 2H) | 1.68 – 1.63 (m, 2H) |
| 1.45 (s, 3H) | 1.51 (s, 3H) | 1.53 (s, 3H) |
| 1.40 (s, 3H). | 1.44 (s, 3H). | 1.46 (s, 3H). |

**Comparison of $^{13}$C-NMR Data:**

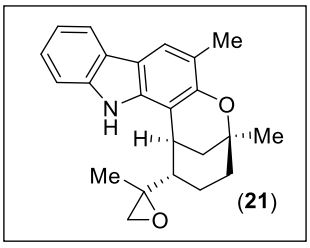
| Ali's report[23] of curruyanin [**3**] | Knolker's report[10]of curruyanin [**3**] | This report of curruyanin [**3**] |
|---|---|---|
| ($^{13}$C NMR, 126 MHz, $CDCl_3$) | ($^{13}$C NMR, 126 MHz, $CDCl_3$) | ($^{13}$C NMR, 100 MHz, $CDCl_3$) |

| | | |
|---|---|---|
| 153.59 | 153.61 | 153.7 |
| 149.97 | 150.06 | 150.2 |
| 139.39 | 139.34 | 139.5 |
| 138.29 | 138.38 | 138.4 |
| 124.21 | 124.24 | 124.4 |
| 123.46 | 123.47 | 123.6 |
| 119.45 | 119.47 | 119.6 |
| 119.07 | 119.08 | 119.2 |
| 119.00 | 119.02 | 119.1 |
| 117.52 | 117.58 | 117.7 |
| 114.54 | 114.57 | 114.7 |
| 111.97 | 112.02 | 112.1 |
| 110.15 | 110.15 | 110.3 |
| 105.17 | 105.19 | 105.3 |
| 73.87 | 73.91 | 74.0 |
| 48.60 | 48.69 | 48.8 |
| 39.84 | 39.90 | 40.0 |
| 37.27 | 37.35 | 37.5 |
| 36.12 | 36.22 | 36.3 |
| 28.95 | 28.98 | 29.1 |
| 23.03 | 23.08 | 23.2 |
| 21.54 | 21.59 | 21.7 |
| 16.78 | 16.76 | 16.8 |

**Procedure for epoxidation of curryanin (3):**




To a solution of curruyanin (**3**) (132 mg, 0.40 mmol, 1.0 equiv.) in dichloromethane (4 mL) was added meta-chloroperoxybenzoic acid (83 mg, 0.48 mmol, 1.2 equiv.) at 25 °C for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with saturated aqueous solution of sodium bicarbonate (3 mL) and the biphasic layers were separated and the aqueous layer was further extracted with dichloromethane (5 mL X 2). The combined organic layers were washed with brine (3 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with *n*-hexane: EtOAc (7:1) to give **21**.



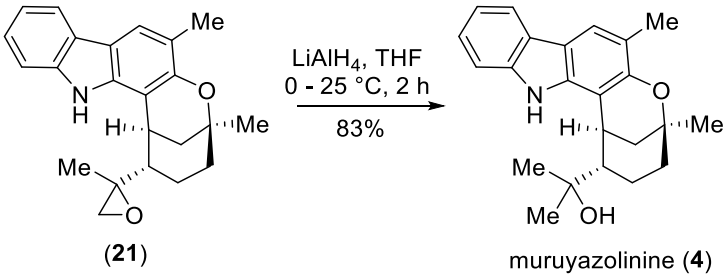

**(5,7-Dimethyl-2-2-methyloxiran-2-yl)-1,2,3,4,5,13-hexahydro-1,5-methanooxocino[3,2-a] carbazole** (**21**)**:** Compound **21** obtained as yellow solid (0.40 mmol; 128 mg; 92%). $R_f$ = 0.4 (in 10% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.91 (dt, *J* = 7.8, 0.7 Hz, 1H), 7.68 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.16 – 7.12 (m, 1H), 3.58 (d, *J* = 3.1 Hz, 1H), 2.71 (dd, *J* = 5.2, 0.8 Hz, 1H), 2.64 (d, *J* = 5.1 Hz, 1H), 2.34 (s, 3H), 2.11 – 2.07 (m, 1H), 1.85 – 1.83 (m, 2H), 1.73 (dt, *J* = 12.4, 3.2 Hz, 2H), 1.59 – 1.56 (m, 2H), 1.43 (s, 3H), 0.66 (s, 3H).

**$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$): δ 153.6, 139.6, 138.1, 124.1, 123.6, 119.7, 119.0, 118.9, 117.5, 114.8, 110.6, 104.9, 74.2, 59.3, 58.5, 47.0, 39.7, 37.1, 30.7, 29.0, 22.6, 18.5, 16.8.

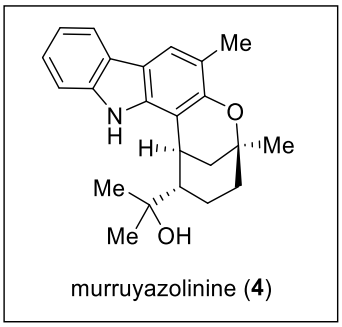
**HRMS** (ESI) m/z: $[M + H]^+$calcd for $C_{23}H_{26}NO_2$: 348.1964, found 348.1964.
**IR** (film): $\nu_{max}$ 3121, 2932, 2842, 1523, 1234, 925 $cm^{-1}$.

**Procedure for the Synthesis of Muruyazolinine (4):**




(**21**) muruyazolinine (**4**)

In a clean and oven-dried round bottom flask, **21** (121 mg, 0.35 mmol, 1.0 equiv.) was dissolved in THF (4 mL). $LiAlH_4$ (33 mg, 0.88 mmol, 2.5 equiv.) was added portion wise over the period of 5 min at 0 °C and the reaction mixture was then warmed to 25 ºC and stirred it for 18 h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of ammonium chloride (2 mL) and the solution was extracted with ethyl acetate (5 mL X 3). The combined organic layers were washed with brine (3 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residual crude product was purified by silica gel column chromatography with *n*-hexane: EtOAc (16:1) to give murruyazolinine (**4**)




murruyazolinine (**4**)

**5,7-Dimethyl-1,2,3,4,5,13-hexahydro-1,5-methanooxocino[3,2-a]carbazol-2-yl)propan-2-ol** (**4**)**:** Compound **4** obtained as white solid (0.35 mmol; 101 mg; 83%). $R_f$ = 0.25 (in 10% EtOAc in *n*-hexane).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.8 Hz, 1H), 7.65 (d, *J* = 0.9 Hz, 1H), 7.37 (d, *J* = 8.0, 0.9 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.13 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 3.78 (q, *J* = 3.0 Hz, 1H), 2.33 (s, 3H), 2.13 – 2.07 (m, 1H), 1.92 – 1.87 (m, 1H), 1.87 – 1.83 (m, 2H), 1.65 – 1.57 (m, 1H), 1.44 (t, *J* = 3.6 Hz, 1H), 1.42 (s, 3H), 1.42 – 1.37 (m, 1H), 1.30 (s, 3H), 1.26 (d, *J* = 1.5 Hz, 1H), 0.54 (s, 3H).

**$^{13}$C {$^1$H} NMR** (100 MHz, $CDCl_3$): δ 153.8, 139.8, 139.0, 124.5, 123.4, 119.5, 119.1, 118.8, 117.5, 114.8, 110.6, 105.9, 74.4, 74.4, 52.8, 40.5, 38.4, 33.4, 29.3, 29.0, 23.3, 23.0, 16.9.

**HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{28}NO_2$: 350.2120, found 350.2111.

**IR** (film): $\nu_{max}$ 3513, 3012, 2946, 1605, 1456, 1208, 1124 $cm^{-1}$.

**Comparison of $^1$H-NMR data:**

| Ali's report[23] of muruyazolinine (**4**) ($^1$H NMR, 400 MHz, $CDCl_3$) | Knolker's report[10] of muruyazolinine (**4**) ($^1$H NMR, 600 MHz, $CDCl_3$) | Sarpong's report[22] of muruyazolinine (**4**) ($^1$H NMR, 600 MHz, $CDCl_3$) | This report of muruyazolinine (**4**) ($^1$H NMR, 400 MHz, $CDCl_3$) |
|---|---|---|---|
| 7.90 (d, *J* = 7.7 Hz, 1H) | 7.91 (d, *J* = 7.7 Hz, 1H) | 7.90 (d, *J* = 7.7Hz, 1H) | 7.90 (d, *J* = 7.8 Hz, 1H) |
| 7.64 (s, 1H) | 7.66 (d, *J* = 0.5 Hz, 1H) | 7.66 (s, 1H) | 7.65 (d, *J* = 0.9 Hz, 1H) |
| 7.37 (d, *J* = 8.0 Hz, 1H) | 7.37 (d, *J* = 8.0 Hz, 1H) | 7.37 (d, *J* = 7.9 Hz, 1H) | 7.37 (d, *J* = 8.0 Hz, 1H) |

| | | | |
|---|---|---|---|
| 7.27 (dd, *J* = 11.1, 4.0 Hz, 1H) | 7.26 (brt, *J* = 7.5 Hz, 1H) | 7.26 (d, *J* = 15.3 Hz 1H) | 7.28 – 7.25 (m, 1H) |
| 7.13 (t, *J* = 7.4 Hz, 1H) | 7.13 (brt, *J* = 7.4 Hz, 1H) | 7.13 (t, *J* = 7.4 Hz, 1H) | 7.13 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H) |
| 3.66 (d, *J* = 2.4 Hz, 1H) | 3.80 (brd, *J* = 2.7 Hz, 1H) | 3.81 (d, *J* = 3.2 Hz, 1H) | 3.78 (q, *J* = 3.0 Hz, 1H) |
| 2.33 (s, 3H) | 2.34 (s, 3H) | 2.33 (s, 3H) | 2.33 (s, 3H) |
| 2.04 (d, *J* = 13.3 Hz, 1H) | 2.10 (m, 1H) | 2.10 (d, *J* = 13.5 Hz, 1H) | 2.13 – 2.07 (m, 1H) |
| 1.77 (d, J = 7.8 Hz, 2H) | 1.90 – 1.94 (m, 1H) | 2.01 (d, *J*= 6.6 Hz, 1H) | 1.92 – 1.87 (m, 1H) |
| | 1.88 (dd, *J* = 12.9, 2.8 Hz 1H) | 1.86 (dd, *J*= 8.2, 3.6 Hz, 2H) | 1.87 – 1.83 (m, 2H) |
| | 1.88 (dt, *J* = 12.9, 2.3 Hz 1H) | 1.71 (s, 1H) | |
| 1.54 (m, 2H) | 1.60 – 1.65 (m, 1H) | 1.65 – 1.59 (m, 1H) | 1.65 – 1.57 (m, 1H) |
| 1.42 -1.34 (m, 5H) | 1.41 – 1.45 (m, 1H) | 1.46 – 1.42 (m, 1H) | 1.44 (t, *J* = 3.6 Hz, 1H) |
| | 1.43 (s, 3H) | 1.43 (s, 3H) | 1.42 (s, 3H) |
| | - | - | 1.42 – 1.37 (m, 1H), |
| 1.19 (s, 3H) | 1.32 (s, 3H) | 1.33 (s, 3H) | 1.30 (s, 3H) |
| - | 1.28 – 1.31 (m, 1H) | 1.31 – 1.28 (m, 1H) | 1.26 (d, *J* = 1.5 Hz, 1H) |
| 0.45 (s, 3H) | 0.55 (s, 3H) | 0.55 (s, 3H) | 0.54 (s, 3H) |

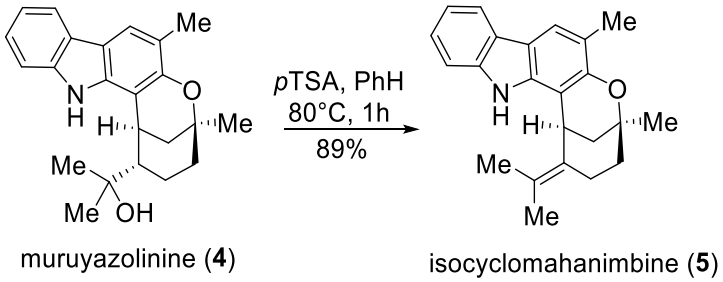
**Comparison of $^{13}$C-NMR Data:**

| Ali's report[23] on muruyazolinine (**4**) | Knolker's report[10] of muruyazolinine (**4**) | This report muruyazolinine (**4**) |
|---|---|---|

| ($^{13}$C NMR, 126 MHz, $CDCl_3$) | ($^{13}$C NMR, 150 MHz, $CDCl_3$) | ($^{13}$C NMR, 100 MHz, $CDCl_3$) |
|---|---|---|
| 153.79 | 153.64 | 153.8 |
| 139.83 | 139.69 | 139.8 |
| 139.08 | 138.91 | 139.0 |
| 124.47 | 124.35 | 124.5 |
| 123.46 | 123.30 | 123.4 |
| 119.51 | 119.41 | 119.5 |
| 119.14 | 118.99 | 119.1 |
| 118.80 | 118.65 | 118.8 |
| 117.52 | 117.40 | 117.5 |
| 114.76 | 114.71 | 114.8 |
| 110.76 | 110.51 | 110.6 |
| 106.04 | 105.82 | 105.9 |
| 74.41 | 74.32 | 74.4 |
| - | 74.26 | 74.4 |
| 52.70 | 52.76 | 52.8 |
| 40.43 | 40.41 | 40.5 |
| 38.28 | 38.28 | 38.4 |
| 33.20 | 33.36 | 33.4 |
| 29.25 | 29.21 | 29.3 |
| 28.99 | 28.87 | 29.0 |
| 23.19 | 23.22 | 23.3 |
| 22.91 | 22.86 | 23.0 |

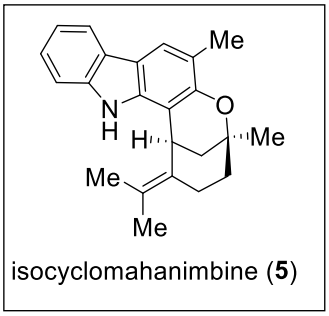
| | | |
|---|---|---|
| 17.01 | 16.80 | 16.9 |

**Procedure for synthesis of isocyclomahanimbine (5):**




muruyazolinine (**4**) isocyclomahanimbine (**5**)

To a solution of muruyazolinine (**4**) (72 mg, 0.21 mmol, 1.0 equiv.) in benzene (3 mL) was added *para*-toluene sulfuric acid (*p*-TSA) (43 mg, 0.25 mmol, 1.2 equiv) at 25 °C. Then the reaction mixture was warmed to 80 °C and stirred for 2 h. After complete consumption of starting materials (monitored by TLC), then the volatile was evaporated under reduced pressure and extracted with EtOAc (6 mL) and water (4 mL). The combined organic layers were dried over $Na_2SO_4$ and evaporated under vacuum**.** The crude product was purified by silica gel column chromatography with *n*-hexane: EtOAc (20:1) to give isocyclomahanimbine (**5**)**.**




isocyclomahanimbine (**5**)

**Isocyclomahanimbine (5**): Compound **5** obtained as white crystal solid (0.21 mmol; 61 mg; 89%). $R_f$ = 0.5 (in 10% EtOAc in *n*-hexane).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 0.9 Hz, 1H), 7.47 (s, 1H), 7.37 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.19 – 7.15 (m, 1H), 4.29 (s, 1H), 2.43 (d, *J* = 8.8 Hz, 1H), 2.37 (s, 3H), 2.16 (d, *J* = 2.0 Hz, 3H), 2.10 – 2.07 (m, 1H), 2.04 – 2.01 (m, 1H), 1.95 (dd, *J* = 12.6, 2.7 Hz, 1H), 1.90 (s, 1H), 1.69 (d, *J* = 1.3 Hz, 3H), 1.63 (s, 1H), 1.46 (s, 3H).

**$^{13}$C {$^1$H} NMR** (100 MHz, $CDCl_3$): δ 153.3, 139.3, 136.9, 132.4, 124.5, 123.6, 120.8, 119.3, 119.2, 119.1, 117.9, 114.9, 110.4, 107.1, 74.2, 40.8, 36.9, 32.1, 29.0, 23.4, 20.5, 20.4, 16.7.

**HRMS (ESI) *m/z*:** $[M+H]^+$ Calcd for $C_{23}H_{26}NO$: 332.2014; Found 332.2012.

**IR** (film): $\nu_{max}$ 3125, 1364, 1302, 1125, 1089, 921 $cm^{-1}$.

**Comparison of $^1$H-NMR Data:**

| Ali's report[23] of isocyclomahanimbine [**5**] ($^1$H NMR, 500 MHz, $CDCl_3$) | Knolker's report[10] of isocyclomahanimbine [**5**] ($^1$H NMR, 500 MHz, $CDCl_3$) | This report of isocyclomahanimbine [**5**] ($^1$H NMR, 500 MHz, $CDCl_3$) |
|---|---|---|
| 7.86 (d, *J* = 7.6 Hz, 1H) | 7.89 (d, *J* = 7.7 Hz, 1H) | 7.91 (d, *J* = 7.7 Hz, 1H) |
| 7.60 (s, 1H) | 7.63 (s, 1H) | 7.65 (d, *J* = 0.9 Hz, 1H) |
| 7.30 (m, 2H) | 7.45 (brs, 1H) | 7.47 (s, 1H) |
| | 7.35 (d, *J* = 8.0 Hz, 1H) | 7.37 (dt, *J* = 8.0, 0.9 Hz, 1H) |
| 7.28 – 7.20 (m, 1H) | 7.27 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H) | 7.30 – 7.29 (m, 1H) |
| 7.12 (m, 1H) | 7.17 (brt, *J* = 7.4 Hz 1H) | 7.19 – 7.15 (m, 1H) |
| 3.99 (s, 1H) | 4.27 (brs, 1H) | 4.29 (s, 1H) |

| | | |
|---|---|---|
| - | 2.40 (dd, *J* = 14.5, 5.6 Hz, 1H) | 2.43 (d, *J* = 8.8 Hz, 1H) |
| 2.34 (s, 3H) | 2.35 (d, *J* = 0.6 Hz, 3H) | 2.37 (s, 3H) |
| 2.31 (m, 1H) | 2.14 (d, *J* = 2.0 Hz, 3H) | 2.16 (d, *J* = 2.0 Hz, 3H) |
| - | 2.05 – 2.09 (m, 1H) | 2.10 – 2.07 (m, 1H) |
| 1.99 (m, 1H) | 2.01 (dt, *J* = 12.6, 3.2 Hz, 1H) | 2.04 – 2.01 (m, 1H) |
| 1.96 (s, 3H) | 1.93 (dd, *J* = 12.6, 2.6 Hz, 1H) | 1.95 (dd, *J* = 12.6, 2.7 Hz, 1H) |
| 1.79 (m, 2H) | 1.88 (m, 1H) | 1.90 (s, 1H) |
| 1.61 (s, 3H) | 1.67 (d, *J* = 0.9 Hz, 3H) | 1.69 (d, *J* = 1.3 Hz, 3H) |
| 1.50 (m, 1H) | 1.60 (td, *J* = 13.6, 5.7 Hz 1H) | 1.63 (s, 1H) |
| 1.38 (s, 3H). | 1.44 (s, 3H). | 1.46 (s, 3H). |

**Comparison of $^{13}$C-NMR Data:**

| Ali's report[23] of isocyclomahanimbine [**5**] | Knolker's report[10] of isocyclomahanimbine [**5**] | This report of isocyclomahanimbine [**5**] |
|---|---|---|
| ($^{13}$C NMR, 126 MHz, $CDCl_3$) | ($^{13}$C NMR, 125 MHz, $CDCl_3$) | ($^{13}$C NMR, 100 MHz, $CDCl_3$) |
| 153.36 | 153.23 | 153.3 |
| 139.36 | 139.26 | 139.3 |
| 136.93 | 136.78 | 136.9 |
| 132.36 | 132.33 | 132.4 |
| 124.52 | 124.38 | 124.5 |

| | | |
|---|---|---|
| 123.74 | 123.59 | 123.6 |
| 120.86 | 120.78 | 120.8 |
| 119.45 | 119.29 | 119.3 |
| 119.27 | 119.15 | 119.2 |
| 119.24 | 119.10 | 119.1 |
| 117.96 | 117.88 | 117.9 |
| 114.95 | 114.84 | 114.9 |
| 110.49 | 110.32 | 110.4 |
| 107.24 | 107.06 | 107.1 |
| 74.23 | 74.12 | 74.2 |
| 40.86 | 40.77 | 40.8 |
| 36.82 | 36.82 | 36.9 |
| 32.08 | 32.08 | 32.1 |
| 29.05 | 28.93 | 29.0 |
| 23.40 | 23.30 | 23.4 |
| 20.57 | 20.48 | 20.5 |
| 20.33 | 20.40 | 20.4 |
| 16.85 | 16.64 | 16.7 |

**Crystal Data and Structure Refinement of 5**

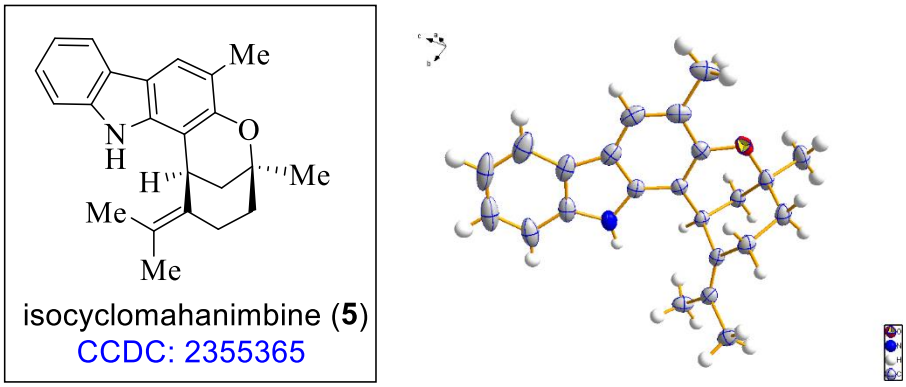



**Figure** . Single crystal XRD structure of **5** ORTEP drawn at 50% probability level.

**Solvent System for growing X-Ray Single Crystal:**

Single crystals as Clear Colorless, Block and Crystal size/mm3: 0.4 × 0.4 × 0.4 of **5**, were obtained by slow evaporation from methanol solvent after 11 days.

**Instrument used for X-Ray Crystallography:**

The X-ray data of **5** was collected at 300 K with Rigaku XtaLAB Synergy, Dual flex four-circle diffractometer with HyPix3000 detector and CuKα radiation (λ = 1.54184 Å). For **5**, the data was collected, reduced, and cell refinement was done in CrysAlis PRO (41_64.115a) software. The structure was solved by intrinsic phasing using SHELXT and implemented in the program system Olex2. All non-H atoms for **5**, were refined anisotropically against F2 for all reflections. The nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated positions and treated as riding throughout the refinement.

**CCDC Information for X-Ray Structure:**

The cif file was deposited with the Cambridge Crystallographic Data Centre, and the following code was allocated: CCDC-2355365 for **5**.

| **Table 1 Crystal data and structure refinement for AB_DGJ_08SCM_auto.** | |
|---|---|
| Identification code | 2355365 |
| Empirical formula | $C_{46}H_{50}N_2O_2$ |
| Formula weight | 662.88 |
| Temperature/K | 100.00(13) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.8359(2) |
| b/Å | 13.2198(3) |
| c/Å | 15.2566(2) |
| α/° | 85.4510(10) |
| β/° | 82.6730(10) |
| γ/° | 69.423(2) |
| Volume/Å$^3$ | 1840.79(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.196 |
| μ/mm$^{-1}$ | 0.557 |
| F(000) | 712.0 |
| Crystal size/mm$^3$ | 0.4 × 0.4 × 0.4 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.844 to 136.41 |
| Index ranges | $-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-18 \leq l \leq 17$ |

| | |
|---|---|
| Reflections collected | 35510 |
| Independent reflections | 6683 [$R_{int}$ = 0.0463, $R_{sigma}$ = 0.0290] |
| Data/restraints/parameters | 6683/0/459 |
| Goodness-of-fit on $F^2$ | 1.057 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0415, $wR_2$ = 0.1112 |
| Final R indexes [all data] | $R_1$ = 0.0480, $wR_2$ = 0.1164 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.26/-0.19 |

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ab_dgj_08scm_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: ab_dgj_08scm_auto

---

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Bond precision:   C-C = 0.0020 A           Wavelength=1.54184

Cell:           a=9.8359(2)        b=13.2198(3)      c=15.2566(2)
                alpha=85.451(1)    beta=82.673(1)    gamma=69.423(2)
Temperature:    100 K

                 Calculated                 Reported
Volume           1840.79(7)                 1840.79(7)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C23 H25 N O                2(C23 H25 N O)
Sum formula      C23 H25 N O                C46 H50 N2 O2
Mr               331.44                     662.88
Dx,g cm-3        1.196                      1.196
Z                4                          2
Mu (mm-1)        0.557                      0.557
F000             712.0                      712.0
F000'            713.88
h,k,lmax         11,15,18                   11,15,18
Nref             6731                       6683
Tmin,Tmax                                   0.565,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.565 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.993           Theta(max)= 68.205

R(reflections)= 0.0415( 5712)                wR2(reflections)=
                                             0.1164( 6683)
S = 1.058                  Npar= 459
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---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

**Alert level C**

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PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings  Differ     Please Check
             Calc: C23 H25 N O
             Rep.: 2(C23 H25 N O)
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C29      --C30      .        5.7 s.u.
PLAT250_ALERT_2_C Large U3/U1 Ratio for <U(i,j)> Tensor(Resd    2)        2.1 Note
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N003     --H003     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N004     --H004     .     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         21 Report
               -7-15  1,  -2-14  7,   8 -6  7,   9 13  7,  11  3  8,  -2-13  9,
               -7 -5 13,  -3  8 13,  -3  7 14,   3 11 14,   2 -7 15,   6 -2 15,
                3 10 15,   3 -5 16,   4 -4 16,   5 -2 16,   7  4 16,   4 -2 17,
                2 -1 18,   0  2 18,   2  4 18,
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**Alert level G**

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PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
             H003  H004
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...          2 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          6 Note
             O001    O002    N003    H003    N004    H004
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         27 Note
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........       2.68 Note
             Predicted wR2: Based on SigI**2  4.35 or SHELX Weight 11.40
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         16 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          3 Check
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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**PLATON version of 06/01/2024; check.def file version of 05/01/2024**

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**Datablock ab_dgj_08scm_auto** - ellipsoid plot