

Supplementary Information

A General Carbazole Synthesis via Stitching of Indole-Ynones with Nitromethanes: Application to Total Synthesis of Carbazomycin A, Calothrixin B and Staurosporinone

Shweta Singh, Ramesh Samineni, Srihari Pabbaraja, Goverdhan Mehta

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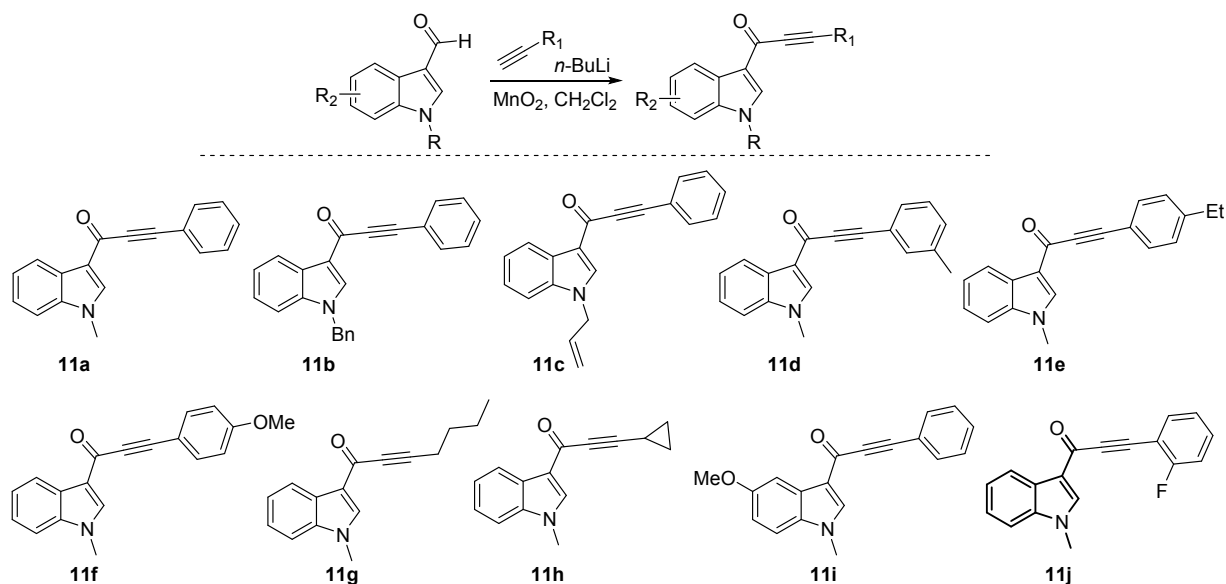
General methods: The reagents were purchased and used directly from commercial vendors. All the moisture and air sensitive reactions were performed under a flow of nitrogen or argon atmosphere using flame-dried or oven-dried glassware with magnetic stirring. The dimethylformamide (DMF) used in the reaction was commercial HPLC grade solvent and was used directly. Anhydrous tetrahydrofuran (THF) was distilled over Na, benzophenone prior to use. Anhydrous toluene used in the reactions was freshly distilled from the toluene, CaH₂ mixture. Progress of the reactions was monitored generally by thin-layer chromatography (TLC) using pre-coated silica gel plates (silica gel 60 F254, Merck) with the help of UV-light, iodine and *p*-anisaldehyde stains. Purification of the compounds was done using silica gel column chromatography (60-120 mesh or 100-200 mesh) packed in glass columns. Distilled EtOAc and petroleum ether were used for column chromatography. The ¹H NMR and ¹³C NMR spectral data was obtained by using CDCl₃ or DMSO-d₆ as solvent and using either 300 MHz or 400 MHz or 500 MHz spectrometers at ambient temperature. The coupling constant *J* is represented in Hz. The chemical shift values (δ) are shown in ppm, on scale downfield from TMS and using CDCl₃ (H: δ = 7.26 and C: δ = 77.0 ppm) or TMS (δ = 0.0) residual solvent peaks as internal standard, peak splitting patterns are designated as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q = quartet, qd = quartet of doublet, m = multiplet, br = broad, tt = triplet of triplet. Bruker Infrared spectrophotometer was used to record IR spectra and is shown as cm⁻¹. Waters-TOF spectrometer was used to record high-resolution mass spectra (HRMS).

1. General procedure for the preparation of ynones (11a-p):

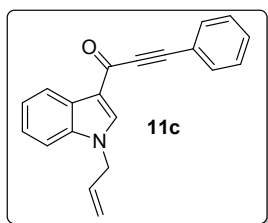
n-BuLi (1.1 mmol) was added to a stirring solution of alkyne (1.2 mmol) in anhydrous THF (5 mL) at -78 °C, and the resulting reaction mixture was stirred for another 15 min. at the same temperature. To this aldehyde (1 mmol) in THF (5 mL) was added drop-wise and allowed to warm to room temperature and the reaction was monitored by TLC. After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched by drop wise addition of saturated aq. NH₄Cl (50 mL) solution and diluted with H₂O (10 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine solution and dried over anhydrous Na₂SO₄, concentrated under reduced pressure to afford the crude propargyl alcohol, which was used for oxidation

directly. To a stirred solution of secondary alcohol (1 mmol) in CH₂Cl₂ (5 mL) at room temperature was added MnO₂ (3.0 mmol) and the reaction mixture was stirred for 6 h. After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through celite with the aid of CH₂Cl₂ and the resulting filtrate was dried over anhydrous Na₂SO₄. Volatiles were removed under reduced pressure and the obtained crude mixture was purified by silica gel column chromatography to yield the substituted ynones.

Among the ynones synthesized by us, **11a** and **11b** are known^[1] and **11c-j** are new and the corresponding spectral data for new compounds are given below.

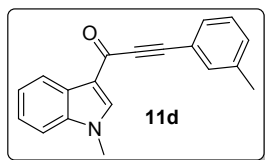


1-(1-Allyl-1H-indol-3-yl)-3-phenylprop-2-yn-1-one (11c): By following the general procedure



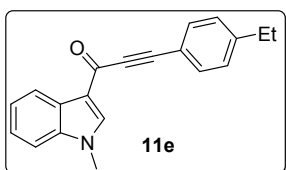
1 using 1-allyl-1H-indole-3-carbaldehyde and phenylacetylene, ynone **11c** was prepared as light brown solid (205 mg, 72%). $R_f = 0.6$ (10% EtOAc + Hexane); mp 79-81 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.38 (m, 1H), 7.99 (s, 1H), 7.64 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.48 – 7.27 (m, 6H), 6.12 – 5.93 (m, 1H), 5.31 (dd, $J = 10.3, 0.9$ Hz, 1H), 5.19 (dd, $J = 17.1, 0.8$ Hz, 1H), 4.78 (dt, $J = 5.4, 1.5$ Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 171.3, 138.0, 137.2, 132.7, 131.8, 130.1, 128.6, 126.0, 123.9, 123.1, 122.6, 120.8, 119.0, 118.8, 110.4, 88.0, 87.8, 49.7; IR (neat): ν_{max} 690, 753, 949, 1062, 1180, 1389, 1520, 1603, 2195 cm⁻¹; HRMS (ESIMS) calcd. For C₂₀H₁₆NO [M+H]⁺: calcd m/z 286.1232; found: 286.1234.

1-(1-Methyl-1H-indol-3-yl)-3-(m-tolyl)prop-2-yn-1-one (11d): By following the general



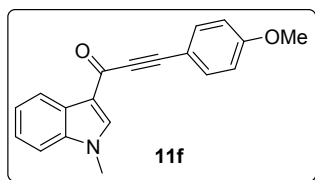
procedure **1** using 1-methyl-1H-indole-3-carbaldehyde and 3-methyl phenylacetylene, ynone **11d** was prepared as brown viscous oil (221 mg, 81%). $R_f = 0.4$ (10% EtOAc + Hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 – 8.41 (m, $J = 6.0, 3.0, 1.6$ Hz, 1H), 7.96 (s, 1H), 7.49 – 7.43 (m, 2H), 7.37 – 7.22 (m, 5H), 3.88 (s, 3H), 2.38 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.2, 138.9, 138.4, 137.8, 133.2, 131.0, 129.8, 128.5, 125.9, 123.9, 123.1, 122.5, 120.7, 118.5, 109.9, 88.0, 87.7, 33.8, 21.3; IR (neat): ν_{max} 749, 833, 949, 1084, 1251, 1463, 1517, 1598, 2186 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 274.1233; found: 274.1228.

3-(4-Ethylphenyl)-1-(1-methyl-1H-indol-3-yl)prop-2-yn-1-one (11e): By following the general



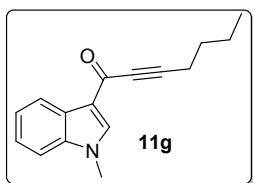
procedure **1** using 1-methyl-1H-indole-3-carbaldehyde and 4-ethyl phenylacetylene, ynone **11e** was prepared as light brown solid (215 mg, 75%). $R_f = 0.5$ (10% EtOAc + Hexane); mp 140-142 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.47 – 8.39 (m, 1H), 7.96 (s, 1H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.33 (dd, $J = 6.3, 3.4$ Hz, 3H), 7.23 (d, $J = 8.1$ Hz, 2H), 3.87 (s, 3H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.3, 146.9, 138.8, 137.8, 132.8, 128.2, 125.9, 123.8, 123.0, 122.5, 118.5, 118.0, 109.9, 88.3, 87.7, 33.8, 29.0, 15.3; IR (neat): ν_{max} 754, 835, 950, 1086, 1381, 1464, 1522, 1602, 2192, 2966 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{20}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 288.1388; found: 288.1385.

3-(4-Methoxyphenyl)-1-(1-methyl-1H-indol-3-yl)prop-2-yn-1-one (11f): By following the



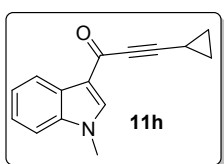
general procedure **1** using 1-methyl-1H-indole-3-carbaldehyde and 4-methoxy phenylacetylene, ynone **11f** was prepared as light brown solid (217 mg, 75%). $R_f = 0.4$ (20% EtOAc + Hexane); mp 132-134 $^{\circ}\text{C}$; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.44 – 8.42 (m, 1H), 7.94 (s, 1H), 7.64 – 7.55 (m, 2H), 7.38 – 7.30 (m, 3H), 6.94 – 6.85 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.4, 161.1, 138.7, 137.8, 134.6, 125.8, 123.8, 123.0, 122.4, 118.4, 114.3, 112.7, 109.9, 88.6, 87.5, 55.4, 33.7; IR (neat): ν_{max} 756, 832, 1088, 1256, 1382, 1465, 1519, 1601, 2190 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 290.1181; found: 290.1178.

1-(1-Methyl-1H-indol-3-yl)hept-2-yn-1-one (11g): By following the general procedure **1** using



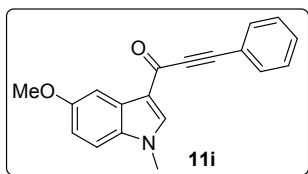
1-methyl-1H-indole-3-carbaldehyde and 1-hexyne, ynone **11g** was prepared as yellow oil (181.5 mg, 76%). $R_f = 0.4$ (10% EtOAc + Hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.38 (ddd, $J = 4.0, 2.6, 1.0$ Hz, 1H), 7.86 (s, 1H), 7.37 – 7.28 (m, 3H), 3.86 (s, 3H), 2.47 (t, $J = 7.1$ Hz, 2H), 1.70 – 1.62 (m, 2H), 1.56-1.47 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.7, 138.7, 137.7, 125.8, 123.7, 122.9, 122.5, 118.4, 109.8, 90.8, 80.6, 33.7, 30.1, 22.1, 18.8, 13.6; IR (neat): ν_{max} 748, 1108, 1220, 1374, 1464, 1524, 1603, 2211, 2933, 2958 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{16}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 240.1474; found: 240.1445.

3-Cyclopropyl-1-(1-methyl-1H-indol-3-yl)prop-2-yn-1-one (11h): By following the general



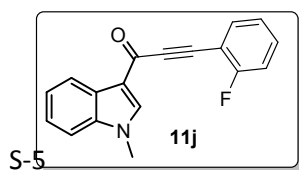
procedure **1** using 1-methyl-1H-indole-3-carbaldehyde and cyclopropyl acetylene, ynone **11h** was prepared as light brown solid (176.2 mg, 79%). $R_f = 0.5$ (10% EtOAc + Hexane); mp 78-80 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.39 – 8.33 (m, 1H), 7.83 (s, 1H), 7.35 – 7.27 (m, 3H), 3.84 (s, 3H), 1.54 – 1.45 (m, 1H), 1.01 – 0.96 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.7, 138.8, 137.8, 125.9, 123.8, 123.0, 122.6, 118.5, 109.9, 94.7, 76.3, 33.8, 9.6, 0.02; IR (neat): ν_{max} 754, 890, 1087, 1229, 1380, 1525, 1601, 2206, 2933 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{15}\text{H}_{14}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 224.1075; found: 224.1068.

1-(5-Methoxy-1-methyl-1H-indol-3-yl)-3-phenylprop-2-yn-1-one (11i): By following the



general procedure **1** using 5-methoxy-1-methyl-1H-indole-3-carbaldehyde and phenylacetylene, ynone **11i** was prepared as dark brown solid (222 mg, 77%). $R_f = 0.5$ (20% EtOAc + Hexane); mp 130-132 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.90 (d, $J = 2.5$ Hz, 1H), 7.68 – 7.62 (m, 2H), 7.48 – 7.36 (m, 3H), 7.24 (d, $J = 8.9$ Hz, 1H), 6.97 (dd, $J = 8.9, 2.5$ Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.1, 156.9, 138.9, 132.7, 132.7, 130.1, 128.6, 126.7, 120.9, 118.2, 114.3, 110.8, 103.8, 87.9, 87.6, 55.9, 34.0; IR (neat): ν_{max} 757, 1085, 1232, 1274, 1375, 1478, 1526, 1602, 2201 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 290.1240; found: 290.1234.

3-(2-Fluorophenyl)-1-(1-methyl-1H-indol-3-yl)prop-2-yn-1-one (11j): By following the



general procedure **1** using 1-methyl-1H-indole-3-carbaldehyde and 2-fluoro phenylacetylene, ynone **11j** was prepared as dark brown solid (202

mg, 73%). $R_f = 0.4$ (10% EtOAc + Hexane); mp 84-86 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 – 8.38 (m, 1H), 8.00 (s, 1H), 7.63 (td, $J = 7.3, 1.8$ Hz, 1H), 7.48 – 7.39 (m, 1H), 7.36 – 7.30 (m, 3H), 7.22 – 7.11 (m, 2H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.7, 164.9, 162.3, 139.7, 137.8, 134.6, 132.1, 125.8, 124.4, 123.9, 123.2, 122.5, 118.4, 115.9, 115.6, 109.9, 109.6, 92.6, 80.8, 33.8; IR (neat): ν_{max} 752, 836, 951, 1086, 1215, 1377, 1465, 1492, 1257, 1605, 2203 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{18}\text{H}_{13}\text{NOF}$ $[\text{M}+\text{H}]^+$: calcd m/z 278.0981; found: 278.0977.

Optimization of the reaction between ynone and nitromethane:

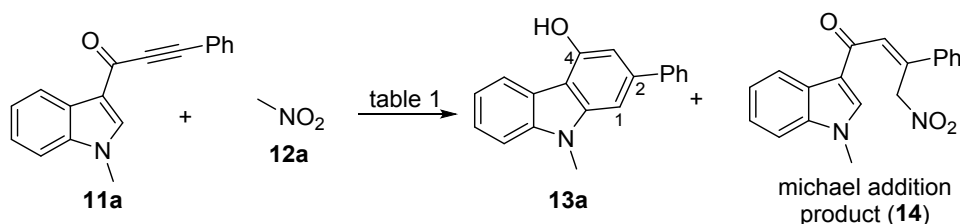


Table 1:

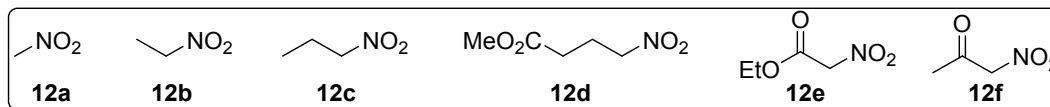
S.No	Base	Solvent, temp, time	Nitromethane 12a (eq)	Michael addition product (14)	Carbazole (13a)
1.	Cs_2CO_3 (2.0 equiv)	DMF, rt, 3 h	3eq	78%	-
2.	Cs_2CO_3 (2.0 equiv)	DMF, 70°C, 12 h	3eq	22%	61%
3.	Cs_2CO_3 (2.0 equiv)	DMF, 100 °C, 8 h	3eq	-	88%
4.	K_2CO_3 (2.0 equiv)	DMF, 100 °C, 12 h	3eq	21%	55%
5.	Na_2CO_3 (2.0 equiv)	DMF, 100 °C, 12 h	3eq	33%	46%
6.	Cs_2CO_3 (2.0 equiv)	DMSO, 100 °C, 8 h	3eq	-	75%
7.	Cs_2CO_3 (1.0 equiv)	DMF, 100 °C, 12 h	3eq	5%	68%
8.	Cs_2CO_3 (0.5equiv)	DMF, 100 °C, 12 h	3eq	24%	51%
9.	DBU (1.0 equiv)	DMF, 100 °C, 12 h	3eq	Complex mixture	Complex mixture
10.	K_2CO_3 (2.0 equiv)	DMSO, 100 °C, 12 h	3eq	11%	59%

2. General Procedure for the Preparation of Carbazoles:

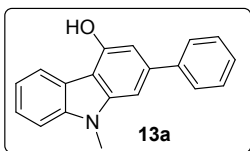
In an oven dried Ace pressure tube (15 mL), was taken indole-3- ynone (0.1 mmol, 1.0 equiv) and nitromethane* (0.3 mmol, 3.0 equiv), to this DMF (1 mL) and Cs_2CO_3 (0.2 mmol, 0.2 equiv) were added and the cap was closed tightly, it was then placed in a preheated oil bath at 100 °C and was stirred for 12h at the same temperature. The reaction mixture was cooled to room temperature, diluted with cold H_2O (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic extract

was washed with brine (10 mL) and dried over Na₂SO₄; volatiles were removed under reduced pressure to get the crude compound which was purified by silica gel flash column chromatography (EtOAc/Hexane) to give carbazoles.

* In case of nitromethanes **12d**, **e**, **f** as reaction partners with ynones; only 1.5 equiv/0.15 mmol of nitromethane derivatives were used.



9-Methyl-2-phenyl-9H-carbazol-4-ol (13a): By following the general procedure **2** using ynone

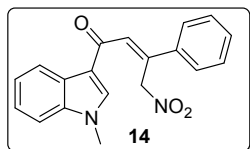


(**11a**) and nitromethane (**12a**), carbazole **13a** was prepared as pale brown

solid (24.0 mg, 88%); $R_f = 0.4$ (20% EtOAc + Hexane); mp 166-168 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, $J = 7.7$ Hz, 1H), 7.69 – 7.63 (m, 2H), 7.48 – 7.42 (m, 3H), 7.38 – 7.32 (m, 2H), 7.28 – 7.22 (m, 1H), 7.16 (d, $J = 1.2$ Hz, 1H), 6.78 (d, $J = 1.2$ Hz, 1H), 5.41 (s, 1H), 3.82 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 151.8, 143.4, 141.9, 140.9, 140.3, 128.8, 127.6, 127.3, 125.0, 122.7, 121.7, 119.4, 110.3, 108.1, 104.6, 100.3, 29.4; IR (neat): ν_{\max} 641, 699, 756, 833, 922, 1156, 1263, 1329, 1489, 1601, 1634, 3051, 3472 cm⁻¹; HRMS (ESIMS) calcd. For C₁₉H₁₆NO [M+H]⁺: calcd m/z 274.1233; found: 274.1232.

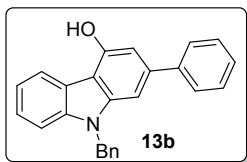
(Z)-1-(1-Methyl-1H-indol-3-yl)-4-nitro-3-phenylbut-2-en-1-one (14): In an oven dried Ace



pressure tube, was taken ynone **11a** (0.1 mmol) and nitromethane **12a** (0.3 mmol) and to this DMF (2 mL) and Cs₂CO₃ (0.1 mmol) were added and the cap was closed tightly and the reaction was stirred for 3 h at room

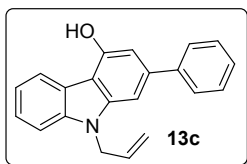
temperature, it was diluted with cold H₂O (5 mL) and was extracted with EtOAc (3 x 5 mL). The combined organic extract was washed with brine (10 mL) and dried over Na₂SO₄; volatiles were removed under reduced pressure to get the crude compound which was purified by silica gel flash column chromatography (EtOAc/Hexane) to give the Michael adduct **14** as light brown solid (25 mg, 78%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 174-176 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.45 (ddd, $J = 5.9, 4.3, 1.8$ Hz, 1H), 7.84 (s, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.32 (m, 3H), 7.28 (s, 1H), 6.18 (s, 2H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 184.5, 140.9, 138.7, 137.7, 135.9, 129.7, 129.6, 129.1, 126.6, 124.0, 123.2, 122.9, 118.3, 109.9, 74.1, 33.7; IR (neat): ν_{\max} 750, 1083, 1217, 1372, 1542, 1629 cm⁻¹; HRMS (ESIMS) calcd. For C₁₉H₁₇N₂O₃ [M+H]⁺: calcd m/z 321.1239; found: 321.1232.

9-Benzyl-2-phenyl-9H-carbazol-4-ol (13b): By following the general procedure **2** using ynone



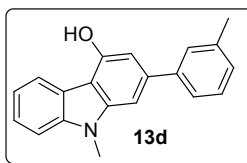
(**11b**) and nitromethane (**12a**), *N*-Bn-carbazole **13b** was prepared as pale brown solid (31.4 mg, 90%). $R_f = 0.5$ (20% EtOAc + Hexane); mp 145-147 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.32 (d, $J = 7.7$ Hz, 1H), 7.63 – 7.57 (m, 2H), 7.46 – 7.37 (m, 3H), 7.36 – 7.31 (m, 2H), 7.29 – 7.20 (m, 4H), 7.16 (dd, $J = 6.2, 1.2$ Hz, 3H), 6.84 (d, $J = 1.1$ Hz, 1H), 5.53 (s, 2H), 5.48 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.0, 143.2, 141.8, 140.6, 140.5, 137.1, 128.8, 128.8, 127.6, 127.5, 127.3, 126.4, 125.2, 122.8, 122.0, 119.8, 110.6, 108.6, 105.0, 100.6, 46.8; IR (neat): ν_{max} 698, 759, 1224, 1434, 1455, 1601, 1633, 3059, 3513 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{25}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 350.1545; found: 350.1543.

9-Allyl-2-phenyl-9H-carbazol-4-ol (13c): By following the general procedure **2** using ynone



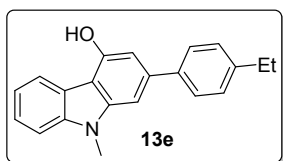
(**11c**) and nitromethane (**12a**), *N*-allyl-carbazole **13c** was prepared as off white solid (25.4 mg, 85%); $R_f = 0.5$ (20% EtOAc + Hexane); mp 105-107 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.29 (d, $J = 7.7$ Hz, 1H), 7.72 – 7.60 (m, 2H), 7.44 (ddd, $J = 8.1, 7.1, 1.4$ Hz, 3H), 7.35 (dt, $J = 7.3, 3.2$ Hz, 2H), 7.29 – 7.22 (m, 1H), 7.15 (d, $J = 1.0$ Hz, 1H), 6.81 (d, $J = 1.1$ Hz, 1H), 6.00 (ddt, $J = 17.0, 10.1, 4.9$ Hz, 1H), 5.42 (s, 1H), 5.16 (dd, $J = 10.3, 1.1$ Hz, 1H), 5.05 (dd, $J = 17.1, 1.1$ Hz, 1H), 4.91 (dd, $J = 3.0, 1.8$ Hz, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.9, 142.8, 141.9, 140.3, 132.2, 128.8, 127.6, 127.3, 125.1, 122.8, 121.9, 119.6, 116.9, 110.5, 108.4, 104.8, 100.6, 45.5; IR (neat): ν_{max} 698, 756, 993, 1155, 1224, 1434, 1456, 1601, 3058, 3511 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{21}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 300.1388; found: 300.1386.

9-Methyl-2-m-tolyl-9H-carbazol-4-ol (13d): By following the general procedure **2** using ynone



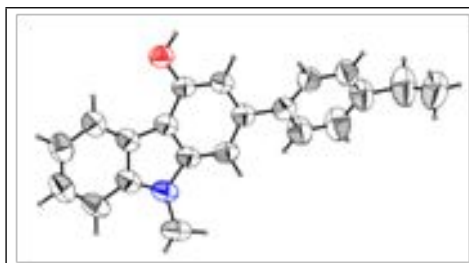
(**11d**) and nitromethane (**12a**), carbazole **13d** was prepared as light brown solid (25.0 mg, 87%); $R_f = 0.4$ (20% EtOAc + Hexane); mp 163-165 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.27 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.42 (m, 3H), 7.40 – 7.31 (m, 2H), 7.29 – 7.22 (m, 1H), 7.17 (t, $J = 4.1$ Hz, 2H), 6.81 (d, $J = 1.1$ Hz, 1H), 5.38 (s, 1H), 3.85 (s, 3H), 2.45 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.8, 143.4, 141.9, 140.9, 140.4, 138.4, 128.7, 128.3, 128.0, 125.0, 124.7, 122.6, 121.7, 119.4, 110.2, 108.0, 104.7, 100.3, 29.4, 21.6; IR (neat): ν_{max} 750, 1089, 1243, 1384, 1553, 1612, 1720, 2352, 3458 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{20}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 288.1388; found: 288.1386.

2-(4-Ethylphenyl)-9-methyl-9H-carbazol-4-ol (13e): By following the general procedure 2



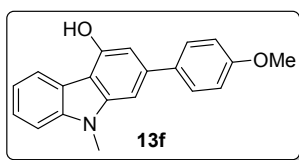
using ynone (**11e**) and nitromethane (**12a**), carbazole **13e** was prepared as a brown solid (26.8 mg, 89%). $R_f = 0.4$ (20% EtOAc + Hexane); mp 171-173 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (dd, $J = 7.7, 0.8$ Hz, 1H), 7.61 – 7.56 (m, 2H), 7.44 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.31 – 7.21 (m, 3H), 7.15 (d, $J = 0.8$ Hz, 1H), 6.78 (d, $J = 1.0$ Hz, 1H), 5.38 (s, 1H), 3.82 (s, 3H), 2.71 (q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.8, 143.4, 140.9, 140.3, 139.2, 128.3, 127.5, 124.9, 122.6, 121.7, 119.4, 110.1, 108.0, 104.5, 100.1, 29.4, 28.6, 15.7; IR (neat): ν_{max} 749, 819, 1154, 1457, 1594, 1602, 2925, 3495 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{21}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 302.1545; found: 302.1545;

X-ray Data for **13e**: (CCDC 1849825).



Single crystal X-ray data was collected on Bruker smart Apex CCD diffractometer, equipped with a Mo- K_α radiation ($\lambda = 0.7103$ Å) source at 298 K. Data reduction was carried out with *saint* software. Structure solution and refinements were performed with the help of *SHELX-2014/7* program available in the WinGX package;³ $\text{C}_{21}\text{H}_{19}\text{NO}$, $M = 301.37$, triclinic, $P - 1$, $a = 8.19(7)$ Å, $b = 12.61(11)$ Å, $c = 16.43(15)$ Å, $\alpha = 87.85(4)^\circ$, $\beta = 80.15(4)^\circ$, $\gamma = 77.76(4)^\circ$, $V = 1636.5(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.223$ g/cm³, $R1 = 0.0587$ and $wR2 = 0.1746$.

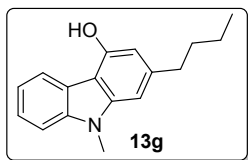
2-(4-Methoxyphenyl)-9-methyl-9H-carbazol-4-ol (13f): By following the general procedure 2



using ynone (**11f**) and nitromethane (**12a**), carbazole **13f** was prepared as pale brown solid (24.8 mg, 82%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 217-219 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, $J = 7.7$ Hz, 1H), 7.66 – 7.58 (m, 2H), 7.49 – 7.42 (m, 1H), 7.38 (d, $J = 8.1$ Hz, 1H), 7.30 – 7.21 (m, 4H), 7.14 (d, $J = 1.0$ Hz, 1H), 7.04 – 6.96 (m, 2H), 6.79 (d, $J = 1.1$ Hz, 1H), 5.39 (s, 1H), 3.88, (s, 3H), 3.87 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.2, 151.8, 143.5, 140.9, 140.0, 134.4, 128.5, 124.9, 122.5, 121.7, 119.3, 114.2, 109.8, 108.0, 104.4, 99.8, 55.4, 29.4; IR

(neat): ν_{\max} 722, 747, 807, 1021, 1155, 1329, 1457, 1604, 3388 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{20}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 304.1338; found: 304.1336.

2-Butyl-9-methyl-9H-carbazol-4-ol (13g): By following the general procedure 2 using ynone



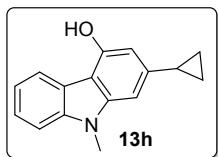
(**11g**) and nitromethane (**12a**), carbazole **13g** was prepared as light brown

solid (19.7 mg, 78%); $R_f = 0.5$ (20% EtOAc + Hexane); mp 111-113 $^\circ\text{C}$;

^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 7.7$ Hz, 1H), 7.41 (ddd, $J = 8.2$, 7.1, 1.2 Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.24 – 7.18 (m, 1H), 6.79 (s,

1H), 6.42 (d, $J = 0.7$ Hz, 1H), 5.20 (s, 1H), 3.79 (s, 3H), 2.78 – 2.67 (m, 2H), 1.74 – 1.63 (m, 2H), 1.46 – 1.34 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.5, 143.3, 142.4, 140.5, 124.4, 122.2, 121.9, 119.07, 109.0, 107.9, 105.7, 101.0, 36.4, 34.1, 29.3, 22.5, 14.0; IR (neat): ν_{\max} 740, 826, 1099, 1334, 1464, 1597, 1639, 2932, 3488 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{17}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 254.1545; found: 254.1544.

2-Cyclopropyl-9-methyl-9H-carbazol-4-ol (13h): By following the general procedure 2 using

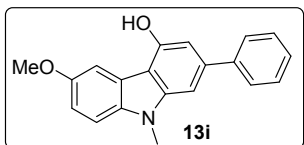


ynone (**11h**) and nitromethane (**12a**), cyclopropane-carbazole **13h** was prepared as off white solid (19.7 mg, 83%). $R_f = 0.3$ (20% EtOAc + Hexane);

mp 149-151 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 7.7$ Hz, 1H), 7.44

– 7.36 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.26 – 7.16 (m, 1H), 6.71 (s, 1H), 6.27 (s, 1H), 5.21 (s, 1H), 3.76 (s, 3H), 2.05-1.98 (m, 1H), 1.04 – 0.96 (m, 2H), 0.80 – 0.74 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.6, 143.5, 143., 140.6, 124.4, 122.1, 121.9, 119.1, 109.1, 107.9, 103.0, 98.6, 29.3, 16.3, 9.6; IR (neat): ν_{\max} 7533, 818, 959, 1222, 1332, 1465, 1597, 1638, 3489 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{16}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 238.1232; found: 238.1230.

6-Methoxy-9-methyl-2-phenyl-9H-carbazol-4-ol (13i): By following the general procedure 2

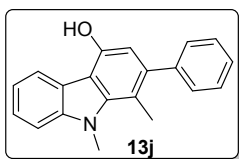


using ynone (**11i**) and nitromethane (**12a**), carbazole **13i** was prepared as light brown solid (25.7 mg, 85%). $R_f = 0.3$ (20% EtOAc + Hexane);

mp 164-166 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 2.5$ Hz,

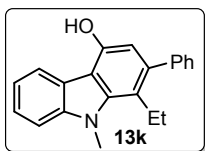
1H), 7.68 – 7.63 (m, 2H), 7.47 – 7.40 (m, 2H), 7.37 – 7.31 (m, 1H), 7.26 (d, $J = 8.8$ Hz, 1H), 7.12 (s, 1H), 7.10 (dd, $J = 8.8, 2.6$ Hz, 1H), 6.75 (s, 1H), 3.94 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 151.9, 143.9, 141.9, 140.2, 136.0, 128.8, 127.5, 127.2, 122.1, 114.10, 110.3, 108.6, 105.9, 104.0, 100.2, 56.3, 29.5; IR (neat): ν_{\max} 759, 1032, 1167, 1206, 1295, 1419, 1483, 1580, 1632, 3415 cm^{-1} ; HRMS (ESIMS) calcd. for $\text{C}_{20}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 304.1336; found 304.1331.

1,9-Dimethyl-2-phenyl-9H-carbazol-4-ol (13j): By following the general procedure **2** using



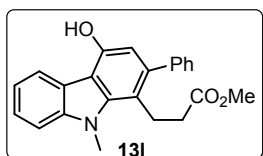
ynone (**11a**) and (**12b**), carbazole **13j** was prepared as off white solid (25.3 mg, 88%); mp 158-160 °C; $R_f = 0.4$ (20% EtOAc + Hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (d, $J = 7.7$ Hz, 1H), 7.48 – 7.32 (m, 7H), 7.28 – 7.22 (m, 1H), 6.50 (s, 1H), 5.17 (s, 1H), 4.13 (s, 3H), 2.62 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.29, 142.56, 142.20, 141.91, 141.42, 129.88, 127.99, 126.72, 124.89, 122.70, 121.87, 119.40, 111.37, 110.55, 108.30, 107.58, 33.06, 16.74; IR (neat): ν_{max} 756, 832, 1088, 1256, 1382, 1465, 1519, 1601, 2190, 3049, 3468 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{20}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 288.1389; found: 288.1384.

1-Ethyl-9-methyl-2-phenyl-9H-carbazol-4-ol (13k): By following the general procedure **2** using



ynone (**11a**) and (**12c**), carbazole **13k** was prepared as pale yellow solid (27.1 mg, 90%). $R_f = 0.4$ (20% EtOAc + Hexane); mp: 127-129 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.31 (m, 7H), 7.25 (dd, $J = 10.7, 3.8$ Hz, 1H), 6.41 (s, 1H), 5.22 (s, 1H), 4.07 (s, 3H), 2.96 (q, $J = 7.4$ Hz, 2H), 1.12 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.1, 142.8, 141.8, 141.3, 140.9, 129.6, 127.9, 126.7, 124.9, 122.7, 122.0, 119.4, 117.7, 111.8, 108.29, 107.8, 32.3, 21.2, 17.2; IR (neat): ν_{max} 756, 1160, 1325, 1398, 1463, 1598, 2973, 3513 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{21}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 302.1545; found: 302.1539.

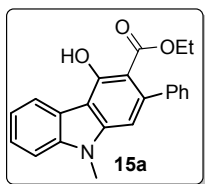
Methyl 3-(4-hydroxy-9-methyl-2-phenyl-9H-carbazol-1-yl)propanoate (13l): By following



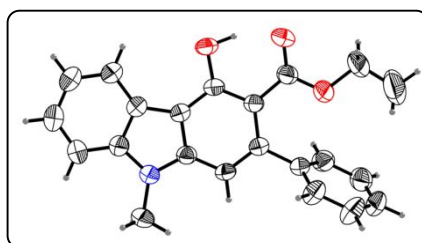
the general procedure **2** using ynone (**11a**) and **12d** (1.5 equiv), carbazole **13l** was prepared as off white solid (30.5 mg, 85%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 169-171 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 (d, $J = 7.7$ Hz, 1H), 7.53 – 7.15 (m, 8H), 6.43 (s, 1H), 5.51 (s, 1H), 4.06 (s, 3H), 3.60 (s, 3H), 3.43 – 3.21 (m, 2H), 2.51 – 2.36 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.2, 149.7, 142.2, 142.0, 141.8, 141.0, 129.4, 128.1, 127.0, 125.1, 122.8, 122.0, 119.6, 113.6, 112.1, 108.4, 108.0, 51.7, 36.1, 32.6, 23.6; IR (neat): ν_{max} 706, 750, 1109, 1166, 1199, 1402, 1441, 1461, 1582, 1709, 3389 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{23}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 360.1600; found: 360.1596.

Ethyl 4-hydroxy-9-methyl-2-phenyl-9H-carbazole-3-carboxylate (15a): By following the general procedure **2** using ynone (**11a**) and ethylnitroacetate **12e** (1.5 equiv), carbazole **15a** was prepared as light brown solid (31.4 mg, 91%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 152-154 °C;

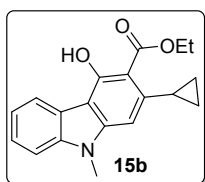
¹H NMR (400 MHz, CDCl₃) δ 12.25 (s, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.41 – 7.29 (m, 7H), 6.78 (s, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.9, 160.0, 144.6, 143.9, 143.1, 140.6, 128.5, 127.5, 126.5, 125.2, 123.2, 122.6, 120.6, 109.9, 108.4, 104.1, 102.7, 60.5, 29.3, 13.1; IR (neat): ν_{max} 704, 750, 1058, 1172, 1255, 1319, 1371, 1602, 1650, 3057 cm⁻¹; HRMS (ESIMS) calcd. For C₂₂H₂₀NO₃ [M+H]⁺: calcd *m/z* 346.1443; found: 346.1441.



X-Ray data for **15a**: (CCDC 1841112).



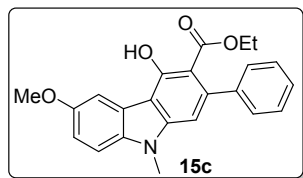
Single crystal X-ray data was collected on a Bruker AXS SMART APEX CCD diffractometer at 298 K using graphite monochromated MoK_α radiation (λ = 0.7107 Å). The data were reduced by *SAINTPLUS*; an empirical absorption correction was applied using the package *SADABS* and *XPREP* was used to determine the space group. The crystal structure was solved by direct methods using *SIR92* and refined by the full-matrix least-squares method on *F*² using *SHELXL-14*;³ C₂₂H₁₉N₁O₃, *M* = 345.38, Monoclinic, *P* 21/*c*, *a* = 11.624(3) Å, *b* = 16.171(3) Å, *c* = 9.500(2) Å, α = γ = 90°, β = 95.215(8)°, *V* = 1778.3(7) Å³, *Z* = 4, ρ_{calcd} = 1.290 Mg/m³, 56813 reflections measured, 4086 unique (*R*(int) = 0.0368), *R*1 = 0.0390 and *wR*2 = 0.1615.



Ethyl 2-cyclopropyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (15b): By following the general procedure **2** using ynone (**11h**) and ethylnitroacetate **12e** (1.5 equiv), carbazole **15b** was prepared as pale yellow viscous oil (25.9 mg, 84%). *R*_f = 0.3 (20% EtOAc + Hexane); ¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.25 (s, 1H), 5.54 (s, 1H), 4.50 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.18 (tt, *J* = 8.5, 5.3 Hz, 1H), 1.45 (t, *J* = 7.2 Hz, 3H), 0.99 – 0.91 (m, 2H), 0.77 – 0.69 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 169.9, 152.4, 141.3, 140.3, 139.5, 125.0, 122.3, 121.3, 119.7, 111.1, 110.4, 108.3,

103.23, 61.4, 31.2, 14.4, 14.0, 8.0; IR (neat): ν_{\max} 751, 1099, 1202, 1250, 1410, 1450, 1629, 1692, 3314 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 310.1443; found: 310.1438.

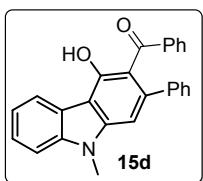
Ethyl 4-hydroxy-6-methoxy-9-methyl-2-phenyl-9H-carbazole-3-carboxylate (15c): By



following the general procedure **2** using ynone (**11i**) and **12e** (1.5 equiv), carbazole **15c** was prepared as off white solid (30.4 mg, 81%). R_f = 0.2 (20% EtOAc + Hexane); mp 135-137 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.31 (s, 1H), 7.91 (d, J = 2.5 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.23 –

7.18 (m, 1H), 7.06 (dd, J = 8.8, 2.6 Hz, 1H), 6.69 (s, 1H), 3.98 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 3.69 (s, 3H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.0, 160.2, 154.7, 144.6, 144.1, 142.9, 135.5, 128.5, 127.4, 126.5, 123.0, 114.4, 109.7, 109.1, 105.8, 104.2, 102.1, 60.5, 56.1, 29.3, 13.1; IR (neat): ν_{\max} 760, 1054, 1173, 1206, 1300, 1370, 1484, 1648, 2937, 3021 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{23}\text{H}_{22}\text{NO}_4$ $[\text{M}+\text{H}]^+$: calcd m/z 376.1549; found: 376.1551.

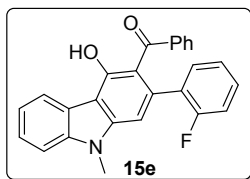
(4-Hydroxy-9-methyl-2-phenyl-9H-carbazol-3-yl)(phenyl)methanone (15d): By following the



general procedure **2** using ynone (**11a**) and benzoylnitromethane **12f** (1.5 equiv), carbazole **15d** was prepared as pale yellow solid (30.9 mg, 82%). R_f = 0.4 (20% EtOAc + Hexane); mp 214-216 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.12 (s, 1H), 8.46 (d, J = 7.7 Hz, 1H), 7.50 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H),

7.43 (d, J = 8.1 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.26 – 7.20 (m, 2H), 7.16 – 7.10 (m, 1H), 7.09 – 6.95 (m, 5H), 6.94 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.6, 159.8, 144.5, 142.4, 140.9, 131.0, 130.1, 129.4, 128.0, 127.4, 126.9, 125.4, 123.3, 120.8, 108.6, 103.8, 29.5; IR (neat): ν_{\max} 701, 750, 770, 1286, 1326, 1602, 1634, 2854, 2927 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{26}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 378.1494; found: 378.1488.

(2-(2-Fluorophenyl)-4-hydroxy-9-methyl-9H-carbazol-3-yl)(phenyl)methanone (15e): By

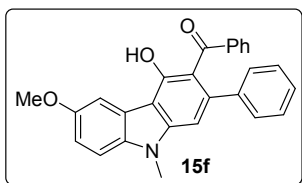


following the general procedure **2** using ynone (**11j**) and benzoylnitromethane **12f** (1.5 equiv), carbazole **15e** was prepared as yellow solid (33.6 mg, 85%); R_f = 0.4 (30% EtOAc + Hexane); mp 201-203 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.44 (s, 1H), 8.47 (d, J = 7.7 Hz,

1H), 7.51 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.19-7.13 (m, 2H), 7.08 – 7.04 (m, 2H), 7.00 – 6.92 (m, 2H), 6.88 (ddd, J = 7.5, 6.1, 1.2 Hz, 1H), 6.67 (ddd, J = 10.1, 8.2, 1.1 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.5, 160.0, 159.9, 157.5, 144.3, 140.8, 140.6, 136.2, 132.2, 131.0, 129.3, 129.2, 129.0, 127.4, 125.6, 123.7, 123.4, 120.9,

115.5, 115.3, 112.4, 110.3, 108.6, 104.8, 29.5; IR (neat): ν_{\max} 753, 1288, 1327, 1345, 1604, 1633, 2355, 3445 cm^{-1} ; HRMS (ESIMS) calcd. for $\text{C}_{26}\text{H}_{19}\text{FNO}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 396.1402; found: 396.1395.

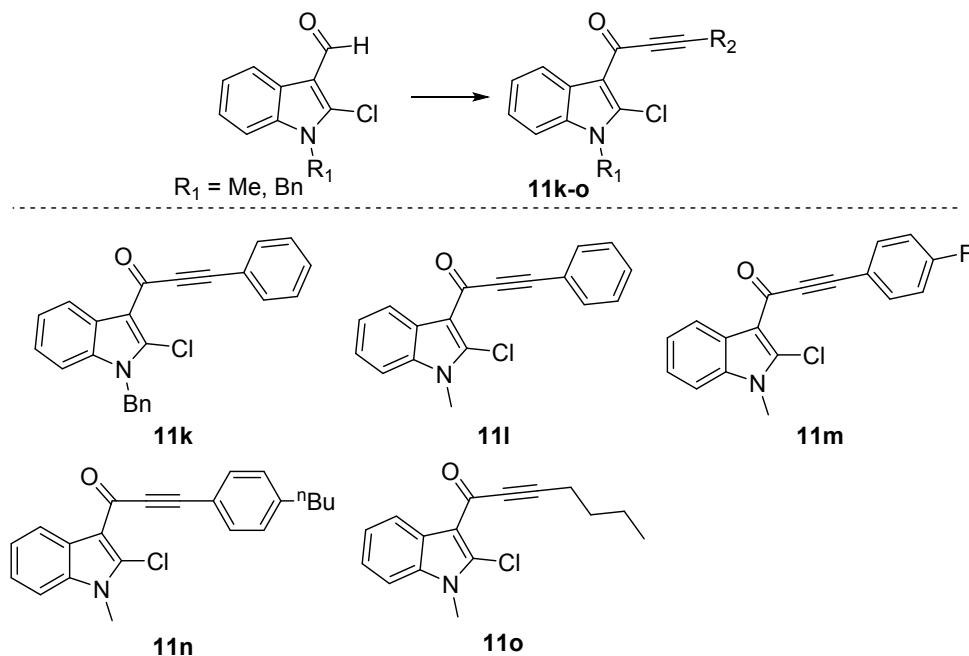
(4-Hydroxy-6-methoxy-9-methyl-2-phenyl-9H-carbazol-3-yl)(phenyl)methanone (15f): By



following the general procedure **2** using ynone (**11i**) and benzoyl nitromethane **12f** (1.5 equiv), carbazole **15f** was prepared as pale yellow solid (32.1 mg, 79%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 236-238 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.31 (s, 1H), 7.97 (d, $J =$

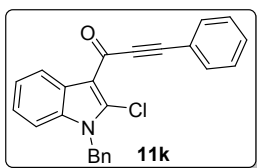
2.5 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.23-7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 7.08 – 6.95 (m, 5H), 6.90 (s, 1H), 3.98 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.5, 160.1, 154.9, 144.7, 143.3, 142.4, 140.9, 135.6, 130.9, 130.1, 129.4, 127.9, 127.4, 126.9, 123.2, 114.8, 111.9, 109.6, 109.3, 105.8, 104.0, 56.1, 29.6; IR (neat): ν_{\max} 761, 1062, 1206, 1306, 1612, 1683, 2340, 3366 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{27}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 408.1600; found: 408.1600.

3. Cl-substituted indole-3-ynones:



1-(1-Benzyl-2-chloro-1H-indol-3-yl)-3-phenylprop-2-yn-1-one (11k): By following the general procedure **1** using 1-benzyl-2-chloro-1*H*-indole-3-carbaldehyde² and phenylacetylene, ynone **11k** was prepared as brownish yellow solid (277 mg, 75%). $R_f = 0.5$ (10% EtOAc + Hexane); mp 80-82 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.56 – 8.50 (m, 1H), 7.67 (dd, $J = 8.2, 1.4$ Hz, 2H), 7.48 –

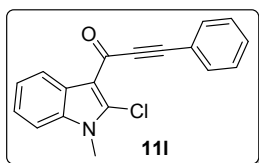
7.37 (m, 3H), 7.35 – 7.26 (m, 6H), 7.16 – 7.10 (m, 2H), 5.48 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3)



δ 170.6, 135.3, 135.2, 133.7, 132.8, 130.4, 129.1, 128.6, 128.1, 126.5, 125.8, 124.3, 123.6, 122.1, 120.9, 114.0, 110.1, 91.3, 89.1, 47.4; IR (neat): ν_{max} 753, 949, 1069, 1387, 1457, 1492, 1596, 2200 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{24}\text{H}_{17}\text{NOCl}$ $[\text{M}+\text{H}]^+$: calcd m/z 370.0999; found:

370.1003.

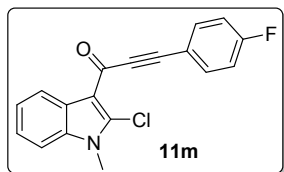
1-(2-Chloro-1-methyl-1H-indol-3-yl)-3-phenylprop-2-yn-1-one (11l): By following the general



procedure **1** using 2-chloro-1-methyl-1*H*-indole-3-carbaldehyde² and phenylacetylene, ynone **11l** was prepared as light orange solid (211 mg, 72%). R_f = 0.4 (10% EtOAc + Hexane); mp 99-101 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.53 – 8.41 (m, 1H), 7.71 – 7.63 (m, 2H), 7.49 – 7.37 (m,

3H), 7.35 – 7.28 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 135.5, 134.1, 132.8, 130.3, 128.7, 125.6, 124.0, 123.5, 121.9, 121.0, 113.6, 109.5, 91.0, 89.1, 30.4; IR (neat): ν_{max} 753, 1070, 1372, 1479, 1588, 2197 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{18}\text{H}_{13}\text{NOCl}$ $[\text{M}+\text{H}]^+$: calcd m/z 294.0686; found: 294.0683.

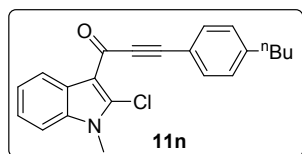
1-(2-Chloro-1-methyl-1H-indol-3-yl)-3-(4-fluorophenyl)prop-2-yn-1-one (11m): By



following the general procedure **1** using 2-chloro-1-methyl-1*H*-indole-3-carbaldehyde and 4-fluoro phenylacetylene, ynone **11m** was prepared as light brown solid (221 mg, 71%). R_f = 0.3 (10% EtOAc + Hexane); mp 102-104 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.52 – 8.44 (m, 1H), 7.72 –

7.62 (m, 2H), 7.38 – 7.31 (m, 3H), 7.16 – 7.06 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.3, 165.0, 162.5, 135.5, 135.0, 134.9, 133.9, 125.6, 124.1, 123.6, 121.9, 117.2, 116.3, 116.0, 113.6, 109.5, 89.9, 88.9, 30.4; IR (neat): ν_{max} 750, 801, 1092, 1220, 1420, 1727, 2925 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{18}\text{H}_{12}\text{NOClF}$ $[\text{M}+\text{H}]^+$: calcd m/z 312.0591; found: 312.0589.

3-(4-butylphenyl)-1-(2-chloro-1-methyl-1H-indol-3-yl)prop-2-yn-1-one (11n): By following

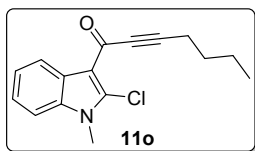


the general procedure **1** using 2-chloro-1-methyl-1*H*-indole-3-carbaldehyde and 4-*n*-butyl phenylacetylene, ynone **11n** was prepared as dark brown oil (238 mg, 68%). R_f = 0.6 (20% EtOAc + Hexane); ^1H

NMR (400 MHz, CDCl_3) δ 8.54 – 8.46 (m, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.23 (d, J = 8.2 Hz, 2H), 3.85 (s, 3H), 2.72 – 2.55 (m, 2H), 1.66-1.58 (m, 2H), 1.41-1.32 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.7, 145.9, 135.5, 133.9, 132.8, 128.8,

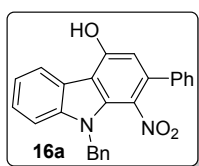
125.7, 123.9, 123.4, 121.9, 118.1, 113.7, 109.4, 91.7, 88.9, 35.8, 33.3, 30.38, 22.3, 13.9; IR (neat): ν_{\max} 753, 1073, 1373, 1479, 1594, 2195, 2926 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{22}\text{H}_{21}\text{NOCl}$ $[\text{M}+\text{H}]^+$: calcd m/z 350.1312; found: 350.1311.

1-(2-Chloro-1-methyl-1H-indol-3-yl)hept-2-yn-1-one (11o): By following the general



procedure **1** using 2-chloro-1-methyl-1H-indole-3-carbaldehyde and 1-hexyne, ynone **11o** was prepared as pale yellowish oil (202 mg, 74%). $R_f = 0.5$ (20% EtOAc + Hexane); ^1H NMR (400 MHz, CDCl_3) δ 8.48 – 8.41 (m, 1H), 7.38 – 7.28 (m, 3H), 3.81 (s, 3H), 2.51 (t, $J = 7.1$ Hz, 2H), 1.67 (dq, $J = 12.5, 7.1$ Hz, 2H), 1.51 (ddd, $J = 14.4, 8.6, 6.3$ Hz, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 135.4, 133.7, 125.6, 123.8, 123.3, 121.8, 113.4, 109.4, 94.9, 81.7, 30.3, 29.8, 22.2, 19.1, 13.6; IR (neat): ν_{\max} 756, 832, 1088, 1256, 1382, 1465, 1519, 1601, 2190 cm^{-1} ; HRMS (ESIMS) calcd. for $\text{C}_{16}\text{H}_{17}\text{NOCl}$ $[\text{M}+\text{H}]^+$: calcd m/z 274.0999; found: 274.0997.

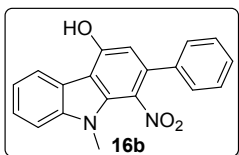
9-Benzyl-1-nitro-2-phenyl-9H-carbazol-4-ol (16a): By following the general procedure **2** using



Cl-ynone (**11k**) and nitromethane (**12a**), nitro-carbazole **16a** was prepared as pale brown solid (34.3 mg, 87%). $R_f = 0.4$ (30% EtOAc + Hexane); mp 147–149 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.39 (d, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.43 – 7.31 (m, 7H), 7.23 – 7.15 (m, $J = 10.2, 5.2$ Hz, 3H), 7.03 – 6.96 (m, 2H), 6.52 (s, 1H), 6.19 (s, 1H), 5.46 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.7, 141.8, 137.7, 136.6, 134.9, 132.7, 130.2, 128.7, 128.5, 128.2, 128.1, 127.6, 126.5, 126.1, 123.2, 121.2, 113.4, 109.5, 107.7, 47.8; IR (neat): ν_{\max} 700, 752, 1161, 1226, 1322, 1519, 1602, 3062, 3496 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{25}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 395.1396; found: 395.1397.

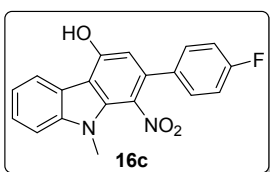
Reaction at 1 mmol scale: In an oven dried Ace pressure tube (15 mL) was taken Cl-indole ynone **11k** (1 mmol, 1.0 equiv) and nitromethane (3 mmol, 3.0 equiv) and to this DMF (5 mL) and Cs_2CO_3 (2 mmol, 2 equiv) were added and the cap was closed tightly, placed in a preheated oil bath at 100 $^{\circ}\text{C}$ and stirred for 12 h at the same temperature. The reaction mixture was cooled to room temperature and diluted with cold H_2O (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic extract was washed with brine (10 mL) and dried over Na_2SO_4 ; volatiles were removed under reduced pressure to get the crude compound which was purified by silica gel flash column chromatography (EtOAc/Hexane) to afford carbazole **16a** (315 mg, 80%).

9-Methyl-1-nitro-2-phenyl-9H-carbazol-4-ol (16b): By following the general procedure **2** using



Cl-ynone (**11l**) and nitromethane (**12a**), nitro-carbazole **16b** was prepared as dark orange solid (26.1 mg, 82%). $R_f = 0.4$ (30% EtOAc + Hexane); mp 197-199 °C; $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.33 (s, 1H), 8.29 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.57 – 7.43 (m, 4H), 7.40 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 6.60 (s, 1H), 3.69 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 155.5, 141.7, 138.3, 134.7, 133.5, 129.1, 128.6, 128.4, 128.3, 126.5, 122.9, 121.1, 112.6, 110.0, 107.4, 31.0; IR (neat): ν_{max} 706, 750, 1158, 1386, 1462, 1516, 2925, 3498 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 319.1083; found: 319.1081.

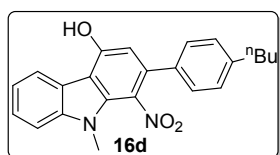
2-(4-Fluorophenyl)-9-methyl-1-nitro-9H-carbazol-4-ol (16c): By following the general



procedure **2** using Cl-ynone (**11m**) and nitromethane (**12a**), nitro-carbazole **16c** was prepared as dark orange solid (28.5 mg, 85%). $R_f = 0.6$ (30% EtOAc + Hexane); mp 191-193 °C; $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.36 (s, 1H), 8.29 (d, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 8.3$ Hz,

1H), 7.55 – 7.51 (m, 1H), 7.44 – 7.41 (m, 2H), 7.34 – 7.30 (m, 3H), 6.58 (s, 1H), 3.68 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 163.7, 161.3, 155.5, 141.7, 134.6, 133.7, 133.5, 130.5, 128.4, 126.5, 122.9, 121.1, 116.2, 115.9, 112.7, 110.0, 107.4, 31.1; IR (neat): ν_{max} 758, 1230, 1315, 1461, 1517, 2505, 3624 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{14}\text{FN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 337.0988; found: 337.0978.

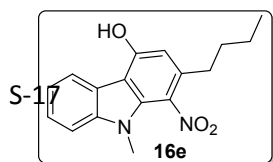
2-(4-Butylphenyl)-9-methyl-1-nitro-9H-carbazol-4-ol (16d): By following the general



procedure **2** using Cl-ynone (**11n**) and nitromethane (**12a**), nitro-carbazole **16d** was prepared as orange solid (30.3 mg, 81%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 187-189 °C; $^1\text{H NMR}$ (500 MHz, DMSO-

d_6) δ 11.28 (s, 1H), 8.28 (d, $J = 7.7$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 1H), 7.58 – 7.46 (m, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.26 (s, 4H), 6.59 (s, 1H), 3.68 (s, 3H), 2.70 – 2.59 (m, 2H), 1.66 – 1.54 (m, 2H), 1.35 (dd, $J = 14.9, 7.4$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, DMSO- d_6) δ 155.4, 142.8, 141.7, 135.5, 134.6, 133.4, 129.0, 128.4, 128.2, 126.4, 122.8, 121.1, 121.0, 112.4, 110.0, 107.4, 35.0, 33.5, 30.9, 22.4, 14.3; IR (neat): ν_{max} 748, 833, 1258, 1311, 1464, 1503, 3369 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 375.1709; found: 375.1699.

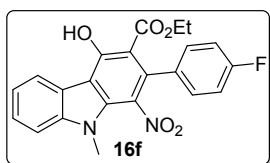
2-Butyl-9-methyl-1-nitro-9H-carbazol-4-ol (16e): By following the general procedure **2** using



Cl-ynone (**11p**) and nitromethane (**12a**), nitro-carbazole **16e** was prepared

as orange solid (23.2 mg, 78%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 137-139 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.27 – 8.21 (m, 1H), 7.48 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.39 (d, $J = 8.3$ Hz, 1H), 7.32 – 7.27 (m, 1H), 6.41 (s, 1H), 5.88 (s, 1H), 3.68 (s, 3H), 2.72 (dd, $J = 9.0, 6.7$ Hz, 2H), 1.69 – 1.61 (m, 2H), 1.40 (dq, $J = 14.6, 7.4$ Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.9, 141.4, 135.3, 134.1, 130.3, 125.9, 122.6, 120.9, 120.6, 111.8, 108.7, 106.4, 33.5, 32.1, 30.8, 22.6, 13.9; IR (neat): ν_{max} 748, 833, 1258, 1311, 1464, 1503, 3369 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd m/z 299.1396; found: 299.1395.

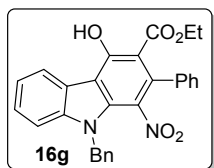
Ethyl 2-(4-fluorophenyl)-4-hydroxy-9-methyl-1-nitro-9H-carbazole-3-carboxylate (16f): By



following the general procedure **2** using Cl-ynone (**11m**) and ethylnitroacetate (**12e**), nitro-carbazole **16f** was prepared as a light yellow solid (33.5 mg, 82%). $R_f = 0.4$ (20% EtOAc + Hexane); mp 176-178 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.67 (s, 1H), 8.45 (d, $J = 7.8$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.40 (dd, $J = 16.5, 8.5$ Hz, 2H), 7.28 – 7.21 (m, 2H), 7.08 (ddd, $J = 8.7, 5.8, 2.4$ Hz, 2H), 4.00 (q, $J = 7.1$ Hz, 2H), 3.69 (s, 3H), 0.79 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.9, 163.9, 161.5, 160.2, 141.2, 133.6, 133.3, 132.3, 132.2, 131.1, 130.8, 130.8, 126.6, 123.5, 121.8, 121.6, 114.7, 114.5, 113.0, 109.0, 102.7, 61.4, 29.8, 13.1; IR (neat): ν_{max} 758, 1255, 1324, 1373, 1524, 1660, 2383, 3330 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_5\text{F}$ $[\text{M}+\text{H}]^+$: calcd m/z 409.1200; found: 409.1193.

Ethyl 9-benzyl-4-hydroxy-1-nitro-2-phenyl-9H-carbazole-3-carboxylate (16g): By following



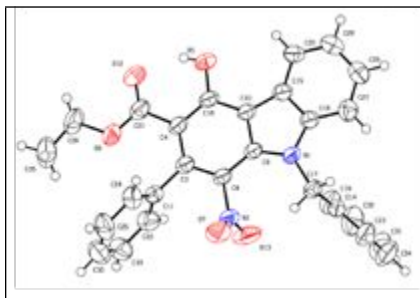
the general procedure **2** using Cl-ynone (**11k**) and ethyl nitroacetate (**12e**), nitro-carbazole **16g** was prepared as pale yellow solid (39.1 mg, 84%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 179-181 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 12.64 (s, 1H), 8.69 – 8.37 (m, 1H), 7.49 (ddd, $J = 8.4, 7.3, 1.3$ Hz, 1H), 7.41 (td, $J = 7.7, 0.9$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.34 – 7.27 (m, 3H), 7.24 – 7.19 (m, 5H), 7.01 – 6.97 (m, 2H), 5.38 – 5.35 (m, 2H), 3.95 (q, $J = 7.2$ Hz, 2H), 0.69 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.0, 160.1, 141.4, 136.4, 136.1, 134.9, 133.2, 131.3, 129.0, 128.7, 127.9, 127.7, 127.5, 126.8, 125.9, 123.6, 122.1, 122.0, 113.3, 109.8, 103.2, 61.3, 47.4, 12.9; IR (neat): ν_{max} 698, 751, 1228, 1324, 1371, 1446, 1528, 2979, 3445 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: calcd m/z 465.1450; found: 465.1448.

Reaction at 1 mmol scale: In an oven dried Ace pressure tube (15 mL) was taken Cl-indole ynone **11k** (1 mmol, 1.0 equiv) and nitromethane (1.5 mmol, 1.5 equiv) and to this DMF (5 mL) and

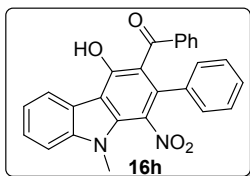
Cs₂CO₃ (2 mmol, 2 equiv) were added and the cap was closed tightly, placed in a preheated oil bath at 100 °C and stirred for 12 h at the same temperature. The reaction mixture was cooled to room temperature and diluted with cold H₂O (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic extract was washed with brine (10 mL) and dried over Na₂SO₄; volatiles were removed under reduced pressure to get the crude compound which was purified by silica gel flash column chromatography (EtOAc/Hexane) to afford carbazole **16g** (368 mg, 79%).

X-ray Data of **16g**: CCDC 1891723.



Single crystal X-ray data was collected on a Bruker AXS SMART APEX CCD diffractometer at 298 K using graphite monochromated MoK_α radiation ($\lambda = 0.7107 \text{ \AA}$). The data were reduced by *SAINTPLUS*; an empirical absorption correction was applied using the package *SADABS* and *XPREP* was used to determine the space group. The crystal structure was solved by direct methods using *SIR92* and refined by the full-matrix least-squares method on F^2 using *SHELXL-14*; All the atomic positions were obtained by Direct Methods. However, few solvent accessible voids which cannot be modeled were revealed by PLATON.³ Therefore, a new data-set corresponding to omission of the missing solvent was generated by using the SQUEEZE algorithm and the structure was refined to convergence⁴. All the non-hydrogen atoms were anisotropically refined while; the hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 Ueq of their parent atoms. C₂₈H₂₂N₂O₅, M = 466.48, P -1, $a = 9.718 (2) \text{ \AA}$, $b = 10.3117 (19) \text{ \AA}$, $c = 13.966 (3) \text{ \AA}$, $\alpha = 71.693 (7)^\circ$, $\beta = 85.368 (8)^\circ$, $\gamma = 86.340 (7)^\circ$, $V = 1323.2(5) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.171 \text{ Mg/m}^3$, $R1 = 0.0856$ and $wR2 = 0.3275$.

(4-Hydroxy-9-methyl-1-nitro-2-phenyl-9H-carbazol-3-yl)(phenyl)methanone (16h): By

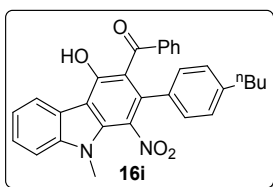


following the general procedure **2** using Cl-ynone (**11i**) and benzoylnitromethane (**12f**), nitro-carbazole **16h** was prepared as a light yellow solid (33.7 mg, 80%). $R_f = 0.4$ (20% EtOAc + Hexane); mp 183-185 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.32 (s, 1H), 8.49 (d, $J = 7.8 \text{ Hz}$,

1H), 7.59 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 7.45 – 7.40 (m, 1H), 7.24 – 7.17 (m, 3H), 7.12 – 6.98 (m, 7H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.7, 158.1, 141.5, 140.5, 134.9, 134.4, 134.0, 131.5, 130.7, 130.4, 128.6, 128.4, 127.9, 127.6, 126.8, 123.6, 121.9, 121.71, 113.5, 112.8, 109.2, 30.0; IR (neat): ν_{max} 753, 1328, 1461, 1528, 1610, 3515 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{26}\text{H}_{19}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: calcd m/z 423.1345; found: 423.1338.

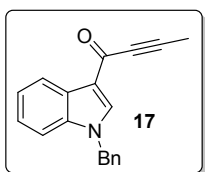
(2-(4-Butylphenyl)-4-hydroxy-9-methyl-1-nitro-9H-carbazol-3-yl)(phenyl)methanone (16i):

By following the general procedure **2** using Cl-ynone(**11n**) and benzoylnitromethane (**12f**), nitro-carbazole **16i** was prepared as yellow solid (37.3 mg, 78%). $R_f = 0.4$ (20% EtOAc + Hexane); mp



147-149 °C; ^1H NMR (500 MHz, CDCl_3) δ 11.37 (s, 1H), 8.49 (d, $J = 7.8$ Hz, 1H), 7.62 – 7.55 (m, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.23 – 7.14 (m, 3H), 7.04 (t, $J = 7.7$ Hz, 2H), 7.02 – 6.96 (m, 2H), 6.80 (d, $J = 8.1$ Hz, 2H), 3.79 (s, 3H), 2.40 (t, $J = 7.5$ Hz, 2H), 1.44 – 1.35 (m, 2H), 1.18 (dq, $J = 14.6, 7.3$ Hz, 2H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 201.8, 158.2, 143.2, 141.5, 140.5, 134.6, 134.0, 132.1, 131.2, 130.6, 130.4, 128.7, 128.1, 127.5, 126.7, 123.5, 121.9, 121.8, 113.6, 112.7, 109.1, 35.2, 33.3, 29.9, 22.0, 14.0; IR (neat): ν_{max} 746, 821, 1199, 1322, 1459, 1522, 1602, 2940 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: calcd m/z 479.1971; found: 479.1979.

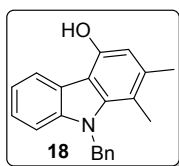
1-(1-Benzyl-1H-indol-3-yl)but-2-yn-1-one (17): To a stirred solution of 1-benzyl indole-3-carbaldehyde (235 mg, 1 mmol) at -20 °C was added 1-propynyl magnesium bromide (2.2 mL, 1.1



mmol, 0.5 M in THF) drop wise and the reaction mixture was stirred for a period of 1 h. After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched by drop wise addition of saturated aq. NH_4Cl (10 mL) solution and it was diluted with H_2O (30 mL) and EtOAc (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4 , concentrated under reduced pressure to afford the crude alcohol, which was directly used for next reaction. To a stirred solution of secondary alcohol (275 mg, 1 mmol) in CH_2Cl_2 (5 mL) at room temperature was added MnO_2 (261 mg, 3.0 mmol) and the reaction mixture was stirred for 2 h. After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through celite with the aid of CH_2Cl_2 and the resulting filtrate was dried over anhydrous Na_2SO_4 . Volatiles were removed under reduced pressure and the obtained crude mixture was

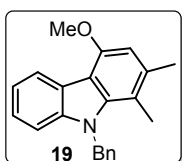
purified by silica gel column chromatography to yield the substituted ynone (**17**) as pale yellowish viscous oil (240 mg, 88%). $R_f = 0.6$ (10% EtOAc + Hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.40 (dt, $J = 7.7, 1.1$ Hz, 1H), 7.95 (s, 1H), 7.36 – 7.23 (m, 6H), 7.17 – 7.11 (m, 2H), 5.35 (s, 2H), 2.08 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.8, 138.4, 137.3, 135.6, 129.1, 128.3, 126.9, 126.1, 123.9, 123.1, 122.6, 118.8, 110.4, 86.8, 80.0, 51.0, 4.2; IR (neat): ν_{max} 749, 856, 1183, 1390, 1524, 1605, 2229 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 274.1232; found: 274.1230.

9-Benzyl-1,2-dimethyl-9H-carbazol-4-ol (18): By following the general procedure **2** using ynone



17 (200 mg, 0.73 mmol), nitroethane **12b** (165 mg, 2.2 mmol), Cs_2CO_3 (475 mg, 1.46 mmol) in DMF (6.0 mL) at 100 °C, carbazole **18** was prepared as white solid (195.6 mg, 89%). $R_f = 0.5$ (20% EtOAc + Hexane); mp 101-103 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.29 (d, $J = 7.6$ Hz, 1H), 7.35 – 7.15 (m, 6H), 7.06 (d, $J = 6.8$ Hz, 2H), 6.43 (s, 1H), 5.68 (s, 2H), 5.23 (s, 1H), 2.39 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.4, 141.7, 141.6, 138.9, 135.7, 128.9, 127.2, 125.6, 124.7, 122.5, 122.3, 119.7, 111.1, 110.8, 108.5, 108.2, 48.8, 21.0, 14.1; IR (neat): ν_{max} 751, 987, 1158, 1456, 1597, 3029, 3389, 3445 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{21}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 302.1545; found: 302.1545.

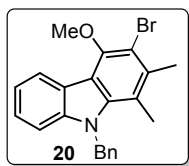
9-Benzyl-4-methoxy-1,2-dimethyl-9H-carbazole (19): To a stirring solution of carbazole **18**



(151.0 mg, 0.5 mmol) in anhydrous acetone (5.0 mL) were added K_2CO_3 (104.0 mg, 0.75 mmol) and Me_2SO_4 (76 mg, 0.6 mmol). The resulting reaction mixture was heated at 80 °C for 3 h. After completion of the reaction, it was filtered through a short plug of celite and the filtrate was concentrated in rotavapour and purified by silica gel column chromatography to afford the methoxy protected carbazole **19** as pale yellow solid (151.0 mg, 96%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 148-150 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.36 – 8.32 (m, 1H), 7.34 – 7.16 (m, 6H), 7.09 – 7.02 (m, 2H), 6.55 (s, 1H), 5.70 (s, 2H), 4.05 (s, 3H), 2.41 (s, 3H), 2.41 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.8, 141.4, 141.3, 139.0, 135.5, 128.9, 127.1, 125.7, 124.6, 122.8, 122.6, 119.6, 111.7, 111.1, 108.4, 103.7, 55.4, 48.8, 21.6, 14.2; IR (neat): ν_{max} 730, 996, 1165, 1223, 1327, 1456, 1591, 2841, 2959 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{22}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: calcd m/z 316.1701; found: 316.1699.

9-Benzyl-3-bromo-4-methoxy-1,2-dimethyl-9H-carbazole (20): To a stirring solution of carbazole **19** (100.0 mg, 0.32 mmol) in CHCl_3 (10 mL) at room temperature was added NBS (57.0

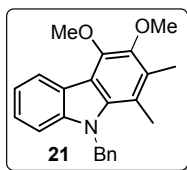
mg, 0.32 mmol) and stirred for 5 min, after completion of the reaction (monitored by TLC), the



mixture was diluted with CH₂Cl₂ (10 mL) and H₂O (10 mL). Layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL), the combined organic extract was dried over Na₂SO₄, volatiles were removed under reduced pressure and the resulted crude compound was purified by silica gel

column chromatography to afford the bromo-carbazole **20** as yellow solid (105.6 mg, 84%). *R*_f = 0.5 (20% EtOAc + Hexane); mp 162-164 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 7.7 Hz, 1H), 7.39 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.32 – 7.19 (m, 5H), 7.08 (d, *J* = 6.8 Hz, 2H), 5.66 (s, 2H), 4.06 (s, 3H), 2.54 (s, 3H), 2.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.3, 142.2, 140.6, 138.4, 134.8, 129.0, 127.3, 125.9, 125.6, 122.6, 121.2, 120.2, 116.4, 111.2, 109.0, 60.1, 49.2, 20.8, 16.0; IR (neat): *v*_{max} 751, 814, 1043, 1161, 1248, 1356, 1386, 1583, 2933 cm⁻¹; HRMS (ESIMS) calcd. For C₂₂H₂₁NOBr [M+H]⁺: calcd *m/z* 394.0807; found: 394.0807.

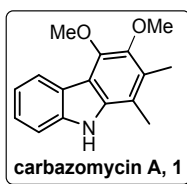
9-Benzyl-3,4-dimethoxy-1,2-dimethyl-9H-carbazole (21): To a freshly prepared solution of



NaOMe in MeOH were added bromo-carbazole (100.0 mg, 0.25 mmol) in DMF (3.0 mL), CuI and the reaction mixture was heated at 120 °C for 18 h. After completion of the reaction, it was filtered through a short plug of celite using EtOAc and the solution was washed with cold water, brine. The organic layer

was dried over Na₂SO₄, volatiles were removed under reduced pressure and the resulted crude compound was purified by silica gel column chromatography to afford the dimethoxy-carbazole **21** as off white solid (72.0 mg, 82%); mp 160-162 °C ; ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, *J* = 7.6 Hz, 1H), 7.37-7.19 (m, 6H), 7.11 (d, *J* = 7.1 Hz, 2H), 5.68 (s, 2H), 4.13 (s, 3H), 3.89 (s, 3H), 2.45 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.0, 144.4, 142.2, 138.9, 137.5, 129.9, 128.9, 127.2, 125.7, 125.3, 122.5, 122.2, 119.5, 115.7, 114.8, 108.7, 61.0, 60.4, 49.1, 15.0, 13.1; IR (neat): *v*_{max} 744, 1087, 1213, 1506, 1540, 1650, 2356, 3158 cm⁻¹; HRMS (ESIMS) calcd. For C₂₃H₂₄NO₂ [M+H]⁺: calcd *m/z* 346.1079; found: 346.1069.

3,4-dimethoxy-1,2-dimethyl-9H-carbazole (1, carbazomycin A): To a solution of benzyl

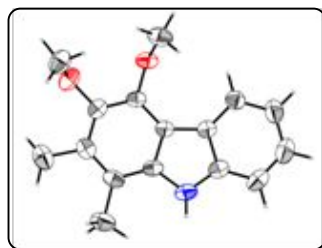


compound **21** (50.0 mg) in MeOH (5.0 mL) was added 10% Pd/C (50 mg) and hydrogen balloon pressure was applied while the reaction was stirred for 6 h. After completion of the reaction, as indicated by the TLC, filtered through a short plug of silica gel with the aid of EtOAc. Volatiles were removed under

reduced pressure and the resulted crude compound was purified by column chromatography

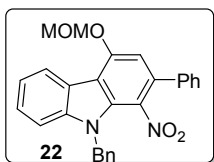
afforded the natural product carbazomycin A, **1** as pale brown solid (37.0 mg, 92%); mp 140-142 °C ; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 7.8 Hz, 1H), 7.81 (s, 1H), 7.44 – 7.33 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.10 (s, 3H), 3.89 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.0, 144.5, 139.4, 136.5, 128.8, 125.1, 122.9, 122.6, 119.5, 114.5, 113.5, 110.3, 61.1, 60.6, 13.7, 12.7; IR (neat): ν_{max} 1034, 1302, 1480, 2975, 3435 cm⁻¹; HRMS (ESIMS) calcd. For C₁₆H₁₈NO₂ [M+H]⁺: calcd *m/z* 256.0974; found: 256.0968.

X-Ray data for **1**:



Single crystal X-ray data was collected on Bruker smart Apex CCD diffractometer, equipped with a Mo–K_α radiation ($\lambda = 0.7103 \text{ \AA}$) source at 298 K. Data reduction was carried out with *saint* software. Structure solution and refinements were performed with the help of *SHELX-2014/7* program available in the WinGX package;³ C₁₆H₁₇NO₂, M = 255.31, monoclinic, *C* 2/*c*, *a* = 16.69(8) Å, *b* = 16.79(8) Å, *c* = 19.37(10) Å, $\alpha = 90^\circ$, $\beta = 100.03(2)^\circ$, $\gamma = 90^\circ$, *V* = 5349.3(5) Å³, *Z* = 16, $\rho_{\text{calcd}} = 1.268 \text{ g/cm}^3$, *R*1 = 0.0654 and *wR*2 = 0.1689. (CCDC 1849826).

9-Benzyl-4-(methoxymethoxy)-1-nitro-2-phenyl-9H-carbazole (22): To a stirring solution of

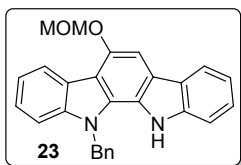


carbazole **16a** (150 mg, 0.38mmol) in dichloromethane (5 mL) at 0 °C were added DIPEA (0.1 mL, 0.57 mmol) and MOMCl (40 μL, 0.5 mmol), the solution was warmed to room temperature and stirred for 6 h. After completion of the reaction as indicated by TLC, diluted with

dichloromethane (10 mL) and H₂O (5 mL), layers were separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layer was dried over Na₂SO₄ and volatiles were removed under reduced pressure to give crude compound, which was purified by silica gel column chromatography (10% EtOAc + Hexane) to afford the MOM compound as bright yellow solid (152 mg, 91%). *R*_f = 0.5 (20% EtOAc + Hexane); mp 153-155 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.44 (d, *J* = 7.8 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.37 (dddd, *J* = 14.9, 11.9, 6.9, 2.0 Hz, 7H), 7.24 – 7.16 (m, 3H), 7.05 – 6.98 (m, 2H), 6.88 (s, 1H), 5.52 (s, 2H), 5.46 (s, 2H), 3.60 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 153.7, 141.8, 137.9, 136.6, 134.7, 132.1,

130.7, 128.7, 128.5, 128.3, 128.2, 127.6, 126.6, 126.1, 123.4, 121.3, 121.1, 114.9, 109.5, 107.0, 94.6, 56.7, 47.7; IR (neat): ν_{\max} 749, 943, 1081, 1158, 1340, 1457, 1522, 1586, 2923 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: calcd m/z 439.1658; found: 439.1647.

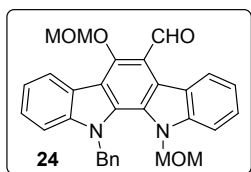
12-Benzyl-5-(methoxymethoxy)-11,12-dihydroindolo[2,3-a]carbazole (23): In a 10 mL



monowave glass vial, compound **22** (120 mg) was taken in 1,2-dichlorobenzene (0.5 mL) and added triethylphosphite (0.5 mL), closed with silicone cap and heated up to 180 °C for 3 h (2 x 90 min) in monowave 50 (Anton paar) reactor. The reaction mixture was purified by column

chromatography (15% EtOAc + Hexane) to afford indolo-carbazole **23** as dark brown solid (83 mg, 75%). R_f = 0.3 (20% EtOAc + Hexane); mp 144-146 °C; ^1H NMR (500 MHz, DMSO- d_6) δ 11.36 (s, 1H), 8.37 (d, J = 7.7 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 4.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.28 – 7.15 (m, 7H), 6.11 (s, 2H), 5.60 (s, 2H), 3.56 (s, 3H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 147.5, 140.6, 139.7, 138.9, 129.1, 128.0, 127.7, 127.1, 125.2, 124.7, 123.7, 123.3, 122.6, 122.1, 120.8, 120.1, 119.2, 112.1, 111.9, 110.2, 95.9, 95.0, 56.4, 47.8.; IR (neat): ν_{\max} 753, 1019, 1156, 1454, 2948, 3422, 3885 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 407.1760; found: 407.1751.

11-Benzyl-6-(methoxymethoxy)-12-(methoxymethyl)-11,12-dihydroindolo[2,3-a]carbazole-

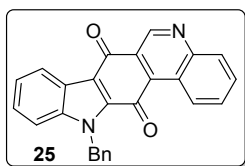


5-carbaldehyde (24): To a stirring solution of DMF (0.5 mL) and POCl_3 (32 μL , 0.34 mmol) at 0 °C was added indolo-carbazole **23** (70 mg, 0.17 mmol) in DMF (1 mL). The reaction mixture was warmed to room

temperature and stirred for 3 h. After completion, the reaction mixture was diluted with cold water (5 mL) and EtOAc (10 mL), layers were separated and aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic extract was washed with sat. NaHCO_3 solution (5 mL) and dried over Na_2SO_4 , volatiles were removed under reduced pressure to give crude compound, which was purified by silica gel flash column chromatography to afford the aldehyde compound. This compound was directly subjected to *N*-MOM protection. To a stirring solution of indolo-carbazole aldehyde (75 mg, 0.17 mmol) in DMF (1 mL) at 0 °C were added NaH (15 mg, 0.35 mmol) and MOMCl (21 μL , 0.26 mmol), the solution was warmed to room temperature and was stirred for 3 h. After completion of the reaction as indicated by TLC, it was diluted with EtOAc (10 mL) and cold H_2O (5 mL), layers were separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layer was dried over

Na₂SO₄ and volatiles were removed under reduced pressure gave crude compound, which was purified by silica gel column chromatography (10% EtOAc + Hexane) afforded the di-MOM compound as pale brown solid (70 mg, 85%); *R_f* = 0.5 (20% EtOAc + Hexane); mp 130-132°C; ¹H NMR (400 MHz, CDCl₃) δ 10.91 (s, 1H), 9.17 (d, *J* = 8.2 Hz, 1H), 8.45 – 8.32 (m, 1H), 7.56 – 7.47 (m, 2H), 7.45 – 7.31 (m, 8H), 7.24 – 7.17 (m, 1H), 5.86 (s, 2H), 5.46 (s, 2H), 5.22 (s, 2H), 3.70 (s, 3H), 2.89 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.6, 154.5, 145.3, 143.3, 136.9, 134.5, 129.0, 127.6, 127.1, 126.3, 126.2, 126.0, 125.7, 125.0, 123.5, 122.6, 122.2, 122.0, 121.6, 119.0, 116.5, 111.8, 110.8, 101.6, 79.2, 58.6, 55.3, 50.8; IR (neat): *ν*_{max} 752, 962, 1078, 1172, 1256, 1336, 1449, 1600, 1716, 2938 cm⁻¹; HRMS (ESIMS) calcd. For C₃₀H₂₇N₂O₄ [M+H]⁺: calcd *m/z* 479.1971; found: 479.1966.

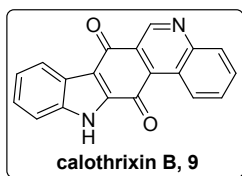
12-Benzyl-7H-indolo[3,2-*j*]phenanthridine-7,13(12H)-dione (25): To a solution of di-MOM



compound **24** (50 mg, 0.1 mmol) in 1 mL of acetonitrile and H₂O (10:1) was added CAN (cerium ammonium nitrate, 165 mg, 0.3 mmol) and the reaction mixture was stirred at room temperature for 14 h. After completion of the reaction diluted with EtOAc (10 mL) and H₂O (5 mL), layers were

separated; the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic extract was washed with 1*N* NaOH (5 mL), the resulted organic layer was dried over Na₂SO₄ and volatiles were removed under reduced pressure to give crude compound, which was purified by silica gel column chromatography (15% EtOAc + Hexane) to afford carboquinone as orange solid (28 mg, 69%); mp 262-264 °C; *R_f* = 0.4 (20% EtOAc + Hexane); ¹H NMR (500 MHz, CDCl₃) δ 9.79 (s, 1H), 9.54 (d, *J* = 8.7 Hz, 1H), 8.45 (d, *J* = 7.3 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.77 – 7.68 (m, 1H), 7.50 – 7.38 (m, 3H), 7.36 – 7.18 (m, 5H), 6.00 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 182.1, 181.1, 152.2, 147.9, 140.2, 136.3, 135.2, 133.3, 131.4, 130.4, 130.2, 128.9, 128.1, 127.9, 127.7, 126.6, 125.2, 124.5, 124.0, 123.3, 123.2, 117.8, 111.6, 48.6; IR (neat): *ν*_{max} 764, 1302, 1461, 1708, 2855, 2923 cm⁻¹; HRMS (ESIMS) calcd. For C₂₆H₁₇N₂O₂ [M+H]⁺: calcd *m/z* 389.1290; found: 389.1284.

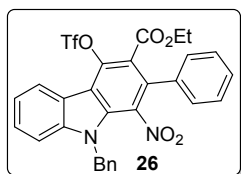
7H-Indolo[3,2-*j*]phenanthridine-7,13(12H)-dione, Calothrixin B (9): To a solution of AlCl₃



(65 mg, 0.5 mmol) in anisole (0.5 mL) at 0 °C was added a solution of compound **25** (20 mg, 0.05 mmol) in anisole (0.5 mL), the reaction mixture was heated at 80 °C for 8 h. After completion of the reaction (by TLC), it was cooled to room temperature, filtered through celite with the aid of

EtOAc, the volatiles were removed under reduced pressure and the crude compound was purified by column chromatography (20% EtOAc + Hexane) to afford calothrixin B, **9** as orange solid (10.7 mg, 72%). $R_f = 0.3$ (20% EtOAc + Hexane); mp 298-300 °C; $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 13.16 (s, 1H), 9.63 (s, 1H), 9.59 (d, $J = 8.6$ Hz, 1H), 8.20-8.17 (m, 2H), 8.00 – 7.93 (m, 1H), 7.93 – 7.86 (m, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.51 – 7.45 (m, 1H), 7.40 (t, $J = 7.1$ Hz, 1H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 180.9, 180.4, 151.2, 147.5, 138.4, 138.1, 132.7, 131.6, 130.3, 129.8, 127.2, 127.2, 124.9, 124.3, 123.7, 122.6, 122.3, 115.5, 114.0; IR (neat): ν_{max} 987, 1076, 1437, 1648, 2949, 3458 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{19}\text{H}_{11}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd m/z 299.0821; found: 299.0819.

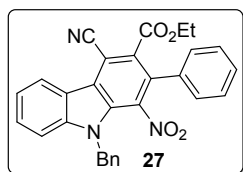
Ethyl 9-benzyl-1-nitro-2-phenyl-4-(((trifluoromethyl)sulfonyl)oxy)-9H-carbazole-3-carboxylate (26): To a stirring solution of carbazole **16g** (150.0 mg, 0.32 mmol) in



dichloromethane (5.0 mL) at 0 °C were added pyridine (40.0 μL , 0.48 mmol) and Tf_2O (70.0 μL , 0.42 mmol), the reaction was warmed to room temperature and was allowed to stir for 3 h. After completion of the reaction (monitored by TLC) it was diluted with dichloromethane (5.0 mL),

quenched by the addition of sat.aq. NaHCO_3 (1.0 mL), H_2O (5.0 mL), layers were separated and the aqueous layer was extracted with dichloromethane (2 x 5 mL). The combined organic extract was dried over Na_2SO_4 and the volatiles were removed under reduced pressure to give the crude compound, which was purified by silica gel column chromatography (25% EtOAc + Hexane) to yield the triflate compound **26** as pale yellow solid (177.0 mg, 92%). $R_f = 0.5$ (40% EtOAc + Hexane); mp: 145-147 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.46 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.59 (m, 1H), 7.49 – 7.43 (m, 2H), 7.40 – 7.33 (m, 3H), 7.30 (dt, $J = 3.8, 2.1$ Hz, 2H), 7.27 – 7.22 (m, 3H), 6.98 (dd, $J = 6.8, 2.8$ Hz, 2H), 5.44 (s, 2H), 3.95 (q, $J = 7.2$ Hz, 2H), 0.86 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.9, 142.7, 139.9, 135.4, 133.7, 132.6, 131.8, 129.2, 129.0, 129.9, 128.9, 128.2, 128.0, 127.6, 125.7, 123.4, 122.4, 120.2, 119.7, 119.2, 110.4, 62.0, 47.6, 13.3; IR (neat): ν_{max} 751, 841, 1233, 1377, 1488, 1595, 2201 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}_7\text{F}_3\text{S}$ $[\text{M}+\text{H}]^+$: calcd m/z 599.1100; found: 599.1108.

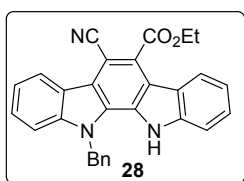
Ethyl 9-benzyl-4-cyano-1-nitro-2-phenyl-9H-carbazole-3-carboxylate (27): To a stirring



solution of triflate **26** (150.0 mg, 0.25 mmol) in DMF (3.0 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (29.0 mg, 0.025) and $\text{Zn}(\text{CN})_2$ (88.0 mg, 0.75 mmol), the reaction mixture was heated at 120 °C for 18 h. After completion of the

reaction, solids were filtered, the filtrate was diluted with cold H₂O and was extracted with EtOAc (3 x 5 mL), the combined organic extract was dried over Na₂SO₄ and volatiles were removed under reduced pressure to give the crude compound, which was purified by silica gel column chromatography (30% EtOAc + Hexane) to afford the cyano compound **27** as orange solid (102.0 mg, 86%). R_f = 0.3 (40% EtOAc + Hexane); mp: 188-190 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.83 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.61 (m, 1H), 7.51 – 7.45 (m, 2H), 7.42 – 7.34 (m, 3H), 7.31 – 7.28 (m, 2H), 7.24 (dt, *J* = 6.8, 2.8 Hz, 3H), 6.98 – 6.93 (m, 2H), 5.45 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.00 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 165.2, 143.4, 137.6, 135.3, 133.2, 131.3, 130.0, 129.9, 129.5, 129.2, 128.9, 128.30 128.1, 127.3, 125.7, 122.5, 122.4, 120.0, 115.7, 110.4, 104.8, 62.5, 47.5, 13.5; IR (neat): ν_{max} 751, 1222, 1267, 1538, 1728, 2231 cm⁻¹; HRMS (ESIMS) calcd. For C₂₉H₂₂N₃O₄ [M+H]⁺: calcd *m/z* 476.1610; found: 476.1591.

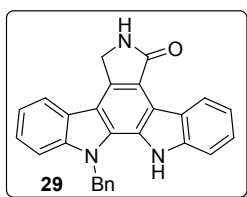
Ethyl 11-benzyl-6-cyano-11,12-dihydroindolo[2,3-a]carbazole-5-carboxylate (28): In a 10 mL



monowave glass vial, compound **27** (100.0 mg) was taken in 1,2-dichlorobenzene (0.5 mL) and added triethylphosphite (0.5 mL), closed with silicone cap and heated up to 180 °C for 180 min (2x90 min) in monowave 50 (Anton paar) reactor. After completion of the reaction it was

directly purified by column chromatography (25-35% EtOAc + Hexane) to afford indolo-carbazole **28** as light brown solid (70.0 mg, 75%) and **27** (20 mg, 19%). R_f = 0.5 (50% EtOAc + Hexane); mp: 282-282 °C; ¹H NMR (400 MHz, DMSO) δ 12.27 (s, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.57 (dt, *J* = 14.8, 7.4 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26-7.12 (m, 5H), 6.23 (s, 2H), 4.68 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, DMSO) δ 167.2, 141.2, 141.1, 138.1, 129.2, 127.9, 127.6, 127.5, 127.3, 127.0, 124.5, 122.0, 121.7, 121.4, 121.1, 121.0, 120.6, 119.12, 118.5, 118.4, 112.9, 111.6, 93.8, 62.8, 48.0, 14.4; IR (neat): ν_{max} 758, 1024, 1226, 1458, 1542, 1731, 2857, 2925 cm⁻¹; HRMS (ESIMS) calcd. For C₂₉H₂₂N₃O₂ [M+H]⁺: calcd *m/z* 444.1712; found: 444.1703.

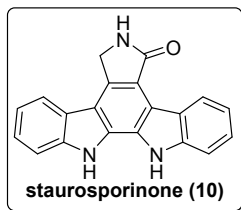
12-Benzyl-6,7,12,13-tetrahydro-5H-indolo[2,3-a]pyrrolo[3,4-c]carbazol-5-one (29): To a



suspension of Raney Ni (100 mg) in MeOH (1 mL) was added cyano-ester compound **28** (40.0 mg) in 3 mL MeOH-DMF (1:3) and kept under the balloon pressure of H₂ gas for 48 h. After completion of the reaction (by TLC), it was filtered through celite with the aid of EtOAc and the volatiles

were removed under reduced pressure and the crude compound was purified by column chromatography (30-40% EtOAc + Hexane) to afford **29** as light brown solid (26.0 mg, 72%); mp: > 300 °C; R_f = 0.3 (50% EtOAc + Hexane); ^1H NMR (500 MHz, DMSO- d_6) δ 11.81 (s, 1H), 9.33 (d, J = 7.9 Hz, 1H), 8.55 (s, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.3 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.24-7.14 (m, 6H), 6.24 (s, 2H), 5.00 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 172.7, 140.7, 140.5, 138.7, 133.5, 129.3, 129.0, 127.7, 127.1, 125.7, 125.2, 123.0, 122.7, 121.8, 120.9, 119.8, 119.5, 117.7, 114.9, 112.0, 111.0, 47.9, 45.8; IR (neat): ν_{max} 765, 1332, 1450, 1658, 2505, 2954, 3221, 3327 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{27}\text{H}_{20}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: calcd m/z 402.1606; found 402.1603.

6,7,12,13-Tetrahydro-5H-indolo[2,3-a]pyrrolo[3,4-c]carbazol-5-one, staurosporinone (10):



To a solution of AlCl_3 (66 mg, 0.5 mmol) in anisole (0.5 mL) at 0 °C was added a solution of compound **29** (20.0 mg, 0.05 mmol) in anisole (0.5 mL), further the reaction mixture was heated at 110 °C for 1 h. After completion of the reaction (by TLC), it was cooled to room temperature, filtered through celite with the aid of EtOAc, the volatiles were removed under reduced pressure and the crude compound was purified by column chromatography (40-50% EtOAc + Hexane) to afford staurosporinone **10** as brownish-red solid (14.8 mg, 95%). R_f = 0.2 (50% EtOAc + Hexane); mp > 300 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 11.60 (s, 1H), 11.42 (s, 1H), 9.23 (d, J = 7.9 Hz, 1H), 8.48 (s, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.48-7.43 (m, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 4.97 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 172.4, 139.2, 139.0, 132.9, 127.9, 125.4, 125.2, 125.0 (2C), 122.8, 122.6, 121.1, 119.9, 118.9 (2C), 115.6, 114.1, 111.9, 111.3, 45.3; IR (neat): ν_{max} 760, 1245, 1381, 1456, 1647, 1731, 2856, 2922 cm^{-1} ; HRMS (ESIMS) calcd. For $\text{C}_{20}\text{H}_{14}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: calcd m/z 312.1137; found 312.1135.

Table 2: ^1H and ^{13}C data comparison table for calothrixin B (9)

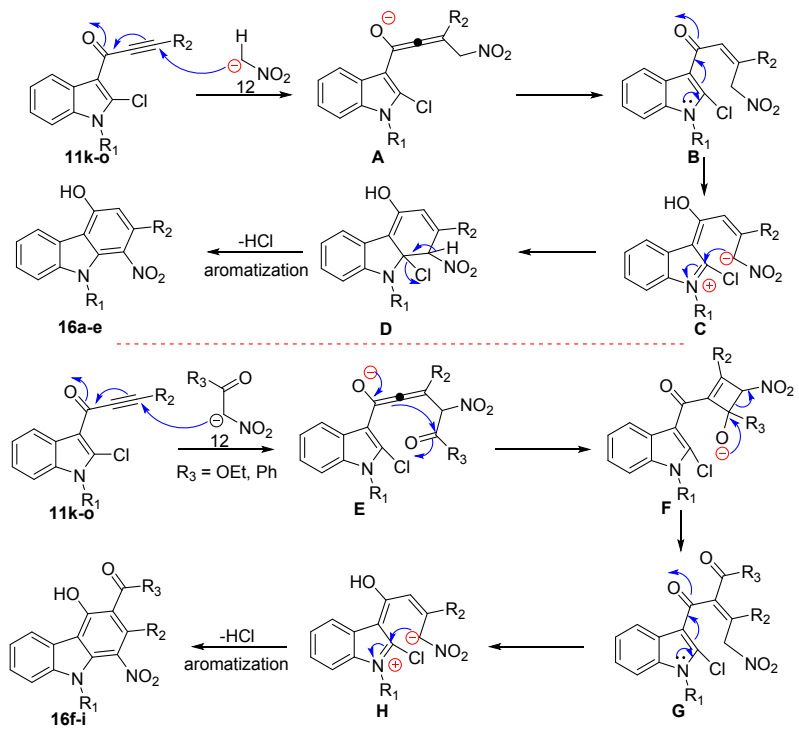
^1H NMR data of calothrixin B (C.-H. Cheon et.al.) ⁵ 500 MHz, (DMSO- d_6)	^1H NMR data of our synthetic calothrixin B (400 MHz) (DMSO- d_6)	^{13}C NMR data of calothrixin B (C.-H. Cheon et.al.) ⁵ 125 MHz, (DMSO- d_6)	^{13}C NMR data of our synthetic calothrixin B (101 MHz) (DMSO- d_6)
13.18 (s, 1H)	13.16 (s, 1H),	180.9, 180.4	180.9, 180.4
9.63 (s, 1H)	9.63 (s, 1H)	151.2, 147.5	151.2, 147.5
9.59 (d, J = 8.5 Hz, 1H)	9.59 (d, J = 8.6 Hz, 1H)	138.4, 138.1	138.4, 138.1

8.20 – 8.17 (m, 2H)	8.20 – 8.17 (m, 2H)	132.7, 131.6	132.7, 131.6
7.96 (t, $J = 7.5$ Hz, 1H)	8.00 – 7.93 (m, 1H)	130.3, 129.9	130.3, 129.8
7.91 – 7.88 (m, 1H)	7.93 – 7.86 (m, 1H)	127.2 (2C), 124.9	127.2 (2C), 124.9,
7.63 (d, $J = 8.2$ Hz, 1H)	7.63 (d, $J = 8.2$ Hz, 1H)	124.3, 123.4	124.3, 123.7,
7.48 (t, $J = 7.5$ Hz, 1H)	7.51 – 7.45 (m, 1H)	122.6, 122.3	122.6, 122.3,
7.42 – 7.39 (m, 1H)	7.40 (t, $J = 7.1$ Hz, 1H)	115.6, 114.0	115.5, 114.0

Table 3: ^1H and ^{13}C data comparison table for staurosporinone (10)

^1H NMR data of staurosporinone (Mohankrishnan et.al.) ⁶ 300 MHz, (DMSO-d ₆)	^1H NMR data of our synthetic staurosporinone (400 MHz) (DMSO-d ₆)	^{13}C NMR data of staurosporinone (Mohankrishnan et.al.) ⁶ 75.4 MHz, (DMSO-d ₆)	^{13}C NMR data of our synthetic staurosporinone (101 MHz) (DMSO-d ₆)
11.52 (s, 1H)	11.60 (s, 1H)	172.40, 139.19	172.4, 139.2,
11.35 (s, 1H)	11.42 (s, 1H)	139.06, 132.88	139.0, 132.9
9.24 (d, $J = 7.5$ Hz, 1H)	9.23 (d, $J = 7.9$ Hz, 1H),	127.83, 125.33	127.9, 125.4
8.51 (s, 1H)	8.48 (s, 1H)	125.16, 124.99 (2C)	125.2, 125.0 (2C)
8.06 (d, $J = 7.8$ Hz, 1H)	8.05 (d, $J = 7.7$ Hz, 1H)	122.76, 122.52	122.8, 122.6
7.80 (d, $J = 8.7$ Hz, 1H)	7.79 (d, $J = 8.1$ Hz, 1H)	121.08, 119.88	121.1, 119.9
7.74 (d, $J = 7.8$ Hz, 1H)	7.72 (d, $J = 8.1$ Hz, 1H)	118.92, 118.81, 115.57	118.9 (2C), 115.6
7.52-7.41 (m, 2H)	7.48-7.43 (m, 2H)	114.09, 111.86	114.1, 111.9
7.32 (t, $J = 7.4$ Hz, 1H)	7.31 (t, $J = 7.4$ Hz, 1H),	111.30, 45.25	111.3, 45.3
7.23 (t, $J = 7.5$ Hz, 1H)	7.23 (t, $J = 7.3$ Hz, 1H)		
4.96 (s, 2H)	4.97 (s, 2H)		

A possible mechanism for the formation of carbazoles **16a-I**



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