Supporting Information

Visible light-photocatalysed carbazole synthesis via formal (4+2) cycloaddition of indole-derived bromides and alkynes

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel.

$^1$H NMR spectra were recorded on 400 and 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity ((s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on 100 and 150 MHz with complete proton decoupling spectrophotometers. Chemical shifts are reported in ppm relative to the central line of the heptalet at 77.0 ppm for CDCl$_3$ or 39.6.0 ppm for DMSO-d$_6$. Mass spectra were measured on a MS spectrometer. The high-resolution mass spectroscopic (HRMS) data were obtained on a Shimadazu LCMS-IT-TOF spectrometer.

2. Preparation and Spectral Data of Substrates

2.1 Preparation of Substrates 1a – 1h

2.1.1 Substrates 1a-1h were prepared according to the following general procedures A:$^{1,2,3}$

![Chemical Reaction Diagram]

To a solution of 1-methylindole (A, 26 mmol) in anhydrous DCE (30 mL) taken in a round-bottom flask at 0 °C under nitrogen was added ethyl 3-chloro-3-oxopropanoate (20 mmol) in anhydrous DCE (30 mL) by a syring under nitrogen. Zirconiumtetrachloride (30 mmol) was added under a flow of nitrogen. The reaction temperature was then gradually increased to room temperature, and the
reaction was stirred overnight at room temperature. After the completion of the reaction as indicated by TLC, the resultant mixture was quenched with water (100 mL) and extracted with EtOAc. The combined organic phase was washed with water (100 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. Purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/CH₂Cl₂ (20:1:2) providing the acylation product B which was used to next step.

A flame dried round bottom flask equipped with a magnetic stir bar was charged with B (1.0 equiv) from above procedure and anhydrous THF (0.1 M), and then cooled to -78 °C. A solution of NaHMDS in THF (1.1 eq., 2.0 M) was then added dropwise and the mixture was allowed to be stirred for 30 min. TMSCl (1.1 eq.) was then added and the mixture continued to be stirred for 1 h. NBS (1.1 eq.) was then added and the reaction was allowed to be stirred at -78 °C. When the reaction finished as judged by TLC analysis, the mixture was poured into a separatory funnel containing Et₂O and H₂O. The layers were separated and the aqueous layer was extracted with Et₂O. The combined organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by chromatography on silica gel eluting with petroleum ether/CH₂Cl₂ (1:2) to afford the desired products 1a-1h.

2.1.2 Spectral Data of Substrates

**Ethyl 2-bromo-3-(1-methyl-1H-indol-3-yl)-3-oxopropanoate (1a)**

White solid, mp. 126 - 127 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.67 – 8.26 (m, 1H), 7.93 (s, 1H), 7.53 – 7.27 (m, 3H), 5.42 (s, 1H), 4.27 (q, J = 8.0 Hz, 2H), 3.88 (s, 3H), 1.27 (t, J = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 182.0, 165.7, 137.3, 136.8, 126.5, 123.9, 123.2, 122.4, 112.4, 109.8, 63.0, 47.8, 33.7, 13.8; IR (in KBr): 3526, 3437, 3099, 1768, 1754, 1626, 1522, 1455, 1360, 1238, 1145, 1082, 834, 793 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₄H₁₄NO₃Br: 324.0230; found: 324.0238; MS (EI): m/z = 323.04.
Ethyl 2-bromo-3-(1,5-dimethyl-1H-indol-3-yl)-3-oxopropanoate (1b)

White solid, mp. 161 - 162 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.18 (s, 1H), 7.88 (s, 1H), 7.25 (d, \(J = 8.4\) Hz, 1H), 7.17 (d, \(J = 8.3\) Hz, 1H), 5.42 (s, 1H), 4.40 – 4.17 (m, 2H), 3.85 (s, 3H), 2.49 (s, 3H), 1.27 (t, \(J = 6.0\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 181.8, 165.4, 136.7, 135.6, 132.7, 126.6, 125.2, 121.9, 111.9, 109.5, 63.0, 47.8, 33.8, 21.6, 14.0; IR (in KBr): 3526, 3437, 3103, 1755, 1664, 1636, 1526, 1484, 1268, 1237, 1140, 1087, 836, 803, 702 cm\(^{-1}\); HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{15}\)H\(_{16}\)NO\(_3\)Br: 338.0386; found: 338.0396; MS (EI): m/z = 337.03.

Ethyl 2-bromo-3-(5-methoxy-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1c)

White solid, mp. 122 - 123 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.95 – 7.72 (m, 2H), 7.21 (d, \(J = 8.9\) Hz, 1H), 6.94 (dd, \(J_1 = 8.9\) Hz, \(J_2 = 2.5\) Hz, 1H), 5.40 (s, 1H), 4.26 (q, \(J = 7.1\) Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 1.27 (t, \(J = 7.1\) Hz, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm) 182.0, 165.5, 156.6, 136.7, 132.1, 127.3, 114.0, 111.9, 110.7, 103.4, 62.9, 55.4, 47.5, 33.7, 13.7; IR (in KBr): 3526, 3437, 3103, 2967, 1755, 1664, 1636, 1526, 1484, 1268, 1237, 1140, 1087, 836, 803, 702 cm\(^{-1}\); HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{15}\)H\(_{16}\)NO\(_4\)Br: 354.0335; found: 354.0345; MS (EI): m/z = 353.07.

Ethyl 2-bromo-3-(5-fluoro-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1d)

White solid, mp. 127 - 128 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.96 (dd, \(J_1 = 9.5\) Hz, \(J_2 = 2.4\) Hz, 1H), 7.90 (s, 1H), 7.27 – 7.16 (m, 1H), 7.00 (td, \(J_1 = 8.9\) Hz, \(J_2 = 2.4\) Hz, 1H), 5.41 (s, 1H), 4.25 (dd, \(J_1 = 14.1\) Hz, \(J_2 = 7.0\) Hz, 2H), 3.83 (s, 3H), 1.26 (t, \(J = 7.1\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 181.7, 165.4, 160.9, 158.5, 137.7, 133.7, 127.2 (d, \(J = 11.2\) Hz), 112.2 (d, \(J = 26.4\) Hz), 110.8 (d, \(J = 9.8\) Hz), 107.8 (d, \(J = 25.1\) Hz), 63.2, 47.7, 34.2,
14.1; IR (in KBr): 3525, 3438, 3116, 1768, 1586, 1534, 1477, 1263, 1111, 1078, 837, 804 cm\(^{-1}\); HRMS (ESI): m/z \([M+H]^+\) calcd for C\(_{14}H_{13}NO_3FBr\): 342.0145; found: 342.0136; MS (EI): \(m/z = 341.00\).

**Ethyl 2-bromo-3-(5-bromo-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1e)**

![Structure of 1e]

White solid, mp. 155 - 156 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.52 (s, 1H), 7.91 (s, 1H), 7.42 (d, \(J = 8.6\) Hz, 1H), 7.21 (d, \(J = 8.6\) Hz, 1H), 5.38 (s, 1H), 4.28 (m, 2H), 3.86 (s, 3H), 1.28 (t, \(J = 7.1\) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 181.7, 165.2, 137.2, 135.7, 127.8, 126.6, 124.6, 116.6, 111.6, 111.2, 63.1, 47.6, 34.0, 14.0; IR (in KBr): 3525, 3437, 3101, 1754, 1662, 1636, 1526, 1457, 1361, 1276, 1235, 1122, 1088, 793, 702 cm\(^{-1}\); HRMS (ESI): m/z \([M+H]^+\) calcd for C\(_{14}H_{13}NO_3Br_2\): 401.9345; found: 401.9335; MS (EI): \(m/z = 400.93\).

**Ethyl 2-bromo-3-(6-chloro-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1f)**

![Structure of 1f]

White solid, mp. 138 - 139 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.27 (d, \(J = 8.5\) Hz, 1H), 7.93 (s, 1H), 7.36 (s, 1H), 7.30 (d, \(J = 10.0\) Hz, 1H), 5.39 (s, 1H), 4.28 (m, 2H), 3.85 (s, 3H), 1.27 (t, \(J = 7.1\) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 181.8, 165.3, 137.5, 137.2, 129.6, 124.8, 123.5, 123.1, 112.3, 109.9, 63.2, 47.7, 33.9, 14.1; IR (in KBr): 3414, 3108, 2997, 1758, 1652, 1531, 1467, 1368, 1302, 1214, 1130, 1017, 920, 823, 707 cm\(^{-1}\); HRMS (ESI): m/z \([M+H]^+\) calcd for C\(_{14}H_{13}NO_3ClBr\): 357.9840; found: 357.9853; MS (EI): \(m/z = 357.00\).

**Ethyl 2-bromo-3-(1,4-dimethyl-1H-indol-3-yl)-3-oxopropanoate (1g)**

Light yellow solid, mp. 93 - 95 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.83 (s, 1H), 7.20 (d, \(J = 7.7\) Hz, 1H), 7.13 (d, \(J = 8.1\) Hz, 1H), 7.05 (d, \(J = 7.1\) Hz, 1H), 5.50 (s, 1H), 4.25 (dd, \(J_1 = 12.7\) Hz, \(J_2 = 6.6\) Hz, 2H), 3.81 (s, 3H), 2.81 (s, 3H), 1.25 (t, \(J = 7.7\) Hz, 3H).
7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 181.3, 165.6, 138.1, 137.5, 133.1, 124.9, 124.7, 123.9, 113.8, 107.3, 62.7, 48.9, 33.5, 22.5, 13.7; IR (in KBr): 3524, 3438, 3117, 1764, 1752, 1662, 1497, 1434, 1360, 1276, 1112, 832, 743 cm$^{-1}$; HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{16}$NO$_3$Br: 338.0386; found: 338.0394; MS (EI): m/z = 337.03.

Ethyl 2-bromo-3-(1,7-dimethyl-1H-indol-3-yl)-3-oxopropanoate (1h)

White solid, mp. 137 - 138 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.21 (d, $J$ = 7.9 Hz, 1H), 7.77 (s, 1H), 7.15 (t, $J$ = 7.6 Hz, 1H), 7.00 (d, $J$ = 7.2 Hz, 1H), 5.39 (s, 1H), 4.25 (q, $J$ = 7.1 Hz, 2H), 4.09 (s, 3H), 2.73 (s, 3H), 1.26 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 181.5, 165.4, 138.2, 135.8, 127.4, 126.4, 123.1, 121.7, 120.2, 111.7, 63.0, 47.8, 38.0, 19.4, 14.0; IR (in KBr): 3526, 3437, 3102, 1761, 1663, 1631, 1536, 1456, 1365, 1315, 1151, 1101, 832, 724 cm$^{-1}$; HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{16}$NO$_3$Br: 338.0386; found: 338.0395; MS (EI): m/z = 337.03.

2.2 Tert-butyl 3-(2-bromo-3-ethoxy-3-oxopropanoyl)-1H-indole-1-carboxylate (1i)
could be prepared with the following procedures B.$^4$

To a solution of indole (A, 26 mmol) in anhydrous DCE (30 mL) taken in a round-bottom flask at 0 °C under nitrogen was added ethyl 3-chloro-3-oxopropanoate (20 mmol) in anhydrous DCE (30 mL) by a syring under nitrogen.
Zirconiumtetrachloride (30 mmol) was added under a flow of nitrogen. The reaction was then gradually increased to room temperature, and stirred overnight at room temperature. After completion of the reaction as indicated by TLC, the resultant mixture was quenched with water (100 mL) and extracted with EtOAc. The combined organic layer was washed with water (100 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. Purified by flash column chromatography eluting with petroleum ether/EtOAc/dichloromethane provided the acylation product B which was used to next step.

To a solution of ethyl 3-(1H-indol-3-yl)-3-oxopropanoate (B, 1.0 eq.) and DMAP (0.33 eq.) in dry CH₂Cl₂ (0.4 M) was added di-tert-butyl dicarbonate (1.0 eq.). The resulting mixture was stirred at 0 °C for 1 h and then warmed to 25 °C for 12 h. Solvent was removed in vacuo and the residue was triturated with ether (2 x 25 ml) to afford the N-Boc-protected indole product C as a light yellow solid. C was used to the next step without further purification.

1i could be obtained with the same bromination method in procedures A from tert-butyl 3-(3-ethoxy-3-oxopropanoyl)-1H-indole-1-carboxylate (C).

1i, white solid, mp. 119 - 121 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.39 (s, 1 H), 8.36 – 8.25 (m, 1 H), 8.09 (d, J = 7.6 Hz, 1 H), 7.37 (dd, J₁ = 9.4 Hz, J₂ = 3.8 Hz, 2 H), 5.48 (s, 1 H), 4.29 (q, J = 7.1 Hz, 2 H), 1.71 (s, 9 H), 1.29 (t, J = 7.1 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 183.1, 164.8, 148.4, 135.1, 133.2, 127.2, 125.8, 124.5, 122.4, 116.3, 114.9, 85.9, 63.3, 47.4, 28.1, 14.1; IR (in KBr): 3526, 3437, 3137, 2984, 1764, 1732, 1643, 1548, 1377, 1261, 1238, 1162, 1122, 1026, 836, 687, 591 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₈H₂₀NO₅Br: 410.0598; found: 410.0608; MS (EI): m/z = 409.05.

2.3 Preparation of ethyl 2-bromo-3-(1H-indol-3-yl)-3-oxopropanoate (1j)
To a solution of tert-butyl 3-(2-bromo-3-ethoxy-3-oxopropanoyl)-1H-indole-1-carboxylate (Ii) in DCM (0.2 M), TFA (40 eq.) was added at 0 °C, after stirred for 2.5 h, TFA and DCM was removed under vacuo, the residue was purified by flash column chromatography (DCM/PE=2:1 ) to give the desired product as white solid.

**1j**, white solid, mp. 138 - 139 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.06 (s, 1H), 8.34 (d, J = 6.4 Hz, 1H), 8.12 (d, J = 3.0 Hz, 1H), 7.71 – 7.41 (m, 1H), 7.41 – 7.08 (m, 2H), 5.59 (s, 1H), 4.24 (dd, J₁ = 7.0 Hz, J₂ = 2.2 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 183.1, 165.9, 136.5, 134.2, 125.6, 124.2, 123.3, 122.0, 113.9, 112.2, 63.5, 47.6, 14.1; IR (in KBr): 3524, 3438, 3120, 1772, 1736, 1631, 1517, 1430, 1239, 1146, 833, 755 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₂NO₃Br: 310.0073; found: 310.0075; MS (EI): m/z = 309.15.

### 2.4 Preparation of 2-bromo-3-(1-methyl-1H-indol-3-yl)-3-oxo-N-phenyl propanamide (1k).⁶

![Chemical reaction diagram](image)

The xylene (0.5 M) solution of aniline (1.0 eq.) and the keto ester (A, 1.0 eq.) was heated at 165 °C overnight. After cooled to below 100 °C, toluene was then added. Upon cooling the crystals of keto amide was precipitated. After filtration, the keto amide was used to next step without further purification.

With the amide product B in hand, substrates 2-bromo-3-(1-methyl-1H-indol-3-yl)-3-oxo-N-phenylpropanamide (1k) could be obtained with the same bromination procedure in the procedures A.

**1k**, white solid, mp. 187 - 189 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.18 (s, 1H), 8.40 – 8.26 (m, 1H), 7.95 (s, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.47 – 7.25 (m, 5H), 7.12 (d, J = 7.4 Hz, 1H), 5.41 (s, 1H), 3.87 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ (ppm) 182.9, 162.3, 138.4, 138.2, 137.1, 128.6, 125.9, 123.9, 123.3, 122.6, 121.2, 119.3, 111.9, 110.8, 50.8, 33.6; IR (in KBr): 3422, 3109, 1686, 1593, 1550, 1530,
1463, 1448, 1373, 1128, 1085, 750, 690 cm\(^{-1}\); HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{18}\)H\(_{15}\)N\(_2\)O\(_2\)Br: 371.0390; found: 371.0405; MS (EI): m/z = 370.10.

2.5 Preparation of 2-bromo-1-(1-methyl-1H-indol-3-yl)butane-1,3-dione (II)

![](image)

1-(1-methyl-1H-indol-3-yl)butane-1,3-dione (A) could be prepared according to the literature reported\(^7\). Then substrate 2-bromo-1-(1-methyl-1H-indol-3-yl)-butane-1,3-dione (II) could be obtained with the same bromination procedure in the procedures A. The substrate II was the mixture of ketone and enol form (about 3:1).

II, white solid, mp. 156 - 157 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.38 (d, \(J = 5.2\) Hz, 1H), 7.88 (d, \(J = 23.7\) Hz, 1H), 7.37 (s, 3H), 5.42 (s, 1H), 5.37 (s, 1H), 3.87 (s, 3H), 2.44 (s, 2H), 2.37 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 199.2, 198.7, 182.3, 137.4, 137.2, 137.1, 126.4, 126.4, 124.1, 123.4, 122.5, 113.1, 112.8, 109.9, 67.5, 56.6, 34.0, 26.5, 26.5; IR (in KBr): 3525, 3437, 3099, 1769, 1732, 1626, 1527, 1349, 1262, 1148, 1034, 832, 760 cm\(^{-1}\); HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{13}\)H\(_{12}\)NO\(_2\)Br: 294.0124; found: 294.0126.

2.6 Preparation of 2-bromo-1-(1-methyl-1H-indol-3-yl)-2-phenylethanone (1m)

Substrates 2-bromo-1-(1-methyl-1H-indol-3-yl)-2-phenylethanone (1m) could also be prepared through the same procedure in procedures A from 1-methylindole and phenylacetyl chloride.

1m, light yellow solid; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.42 (d, \(J = 5.8\) Hz, 1H), 7.67 (s, 1H), 7.58 (d, \(J = 7.3\) Hz, 2H), 7.43 – 7.14 (m, 6H), 6.13 (s, 1H), 3.73 (s,
3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 185.8, 137.4, 137.1, 135.8, 128.8, 128.8, 126.7, 123.8, 123.1, 122.6, 112.9, 109.8, 52.5, 33.7, 33.6; MS (EI): m/z = 292.94.

2.7 Preparation of (Z)-methyl 2-bromo-3-(1-methyl-1H-indol-3-yl)acrylate (1n)

(Z)-methyl 2-bromo-3-(1-methyl-1H-indol-3-yl)acrylate (1n) could be prepared according to the literature. $^8$ $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 8.60 (s, 1H), 8.38 (s, 1H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.42 – 7.28 (m, 2H), 7.28 – 7.21 (m, 1H), 3.89 (s, 3H), 3.84 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 164.3, 136.3, 132.6, 132.2, 128.6, 123.1, 121.1, 118.4, 109.9, 109.8, 106.2, 53.2, 33.6; MS (EI): m/z = 327.00.
3. Details for Condition Optimization

Table S1. Photocatalyst effects for the visible light photocatalyzed formal (4+2) cycloaddition reaction.\(^a\)

\[
\begin{align*}
\text{Entry} & \quad \text{Photocatalyst} & \quad \text{Time (h)} & \quad \text{Yield (%)}^b \\
1 & \text{Ru(bpy)}_3\text{Cl}_2\cdot6\text{H}_2\text{O} & 20 & 39 \\
2 & \text{Ru(bpy)}_3(\text{PF}_6)_2 & 20 & 12 \\
3 & \text{Ru(bpz)}_3(\text{PF}_6)_2 & 20 & \text{trace} \\
4 & \text{fac-Ir(ppy)}_3 & 20 & 76 \\
5 & \text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6 & 20 & 25 \\
6 & \text{Ir[(dF(CF}_3\text{ppy})]_2(dtbbppy)PF}_6 & 20 & 42 \\
7 & \text{Ir(ppy)}_2(\text{bpy})\text{PF}_6 & 20 & \text{trace} \\
8 & \text{Eosin Y} & 20 & \text{NR} \\
\end{align*}
\]

\(^a\) The reactions were carried out with 1a (0.1 mmol), 2a (0.1 mmol), photocatalyst (2 mol%) and Na\(_2\text{HPO}_4\) (0.12 mmol) in dry DMF (1.0 mL) under Ar, and irradiated under 3 W blue LEDs at room temperature. \(^b\) Isolated yields.
Table S2. Solvent effects for the visible light photocatalyzed formal (4+2) cycloaddition reaction.\textsuperscript{a}

<table>
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<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)\textsuperscript{b}</th>
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</table>

\textsuperscript{a} The reactions were carried out with 1a (0.1 mmol), 2a (0.1 mmol), fac-Ir(ppy)\textsubscript{3} (2 mol\%) and Na\textsubscript{2}HPO\textsubscript{4} (0.12 mmol) in dry solvent (1.0 mL) under Ar, and irradiated under 3 W blue LEDs at room temperature. \textsuperscript{b} Isolated yields.
Table S3. Base effects for visible light photocatalyzed formal (4+2) cycloaddition reaction.\textsuperscript{a}

\[
\begin{array}{cccc}
\hline
\text{Entry} & \text{Base} & \text{Time (h)} & \text{Yield (%)}^b \\
\hline
1 & \text{Na}_2\text{HPO}_4 & 20 & 83 \\
2 & \text{NaHCO}_3 & 20 & 82 \\
3 & \text{Na}_2\text{CO}_3 & 20 & 95 \\
4 & \text{K}_2\text{CO}_3 & 20 & 89 \\
5^c & -- & 20 & 7 \\
\hline
\end{array}
\]

\textsuperscript{a} The reactions were carried out with \textbf{1a} (0.1 mmol), \textbf{2a} (0.1 mmol), \textit{fac-Ir(ppy)}\textsubscript{3} (2 mol\%) and base (0.12 mmol) in dry DCM (1.0 mL) under Ar, and irradiated under 3 W blue LEDs at room temperature. \textsuperscript{b} Isolated yield. \textsuperscript{c} Without base.
4. General Procedure and Spectral Data of Products

4.1 General procedure for the synthesis of product 3

To a 10 mL schlenk tube equipped with a magnetic stirrer bar was added 1 (0.3 mmol, 1.0 eq.), 2 (0.3 mmol, 1.0 eq.), Na$_2$CO$_3$ (0.36 mmol, 1.2 eq.), fac-Ir(ppy)$_3$ (2 mol%, 0.006 mmol) and 3 mL dry CH$_2$Cl$_2$. The resulting mixture was degassed through ‘freeze-pump-thaw’ procedure three times, and then the solution was stirred at room temperature under the irradiation of 3W blue LEDs for 20 hours. Upon the completion of the cycloaddition reaction as monitored by TLC, the solvent was evaporated under reduced pressure, the residue was purified by flash chromatography on silica gel to give the desired product 3.

4.2 Spectral Data of Products

**Ethyl 4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3aa)**

84% yield, white solid, mp. 180 - 181 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 11.81 (s, 1H), 8.48 (d, $J = 8.0$ Hz, 1H), 7.73 (s, 1H), 7.49 – 7.38 (m, 5H), 7.37 – 7.26 (m, 2H), 4.42 (dd, $J_1 = 14.2$ Hz, $J_2 = 7.1$ Hz, 2H), 3.36 (s, 3H), 1.41 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 170.9, 158.8, 142.8, 141.2, 139.6, 130.21, 129.2, 128.1, 127.3, 125.2, 123.1, 122.4, 120.6, 118.0, 111.5, 108.6, 102.7, 60.9, 32.6, 14.3; IR (in KBr): 2980, 1652, 1627, 1602, 1467, 1372, 1330, 1258, 1195, 1062, 1017, 906, 796, 753, 702 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{22}$H$_{19}$NO$_3$: 345.1365; found: 345.1345.

**Ethyl 4-hydroxy-9-methyl-1-(p-tolyl)-9H-carbazole-3-carboxylate (3ab)**
85% yield, white solid, mp. 154 - 156 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.79 (s, 1H), 8.46 (d, J = 7.9 Hz, 1H), 7.70 (s, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.32 (dt, J₁ = 12.7 Hz, J₂ = 6.3 Hz, 4H), 7.27 – 7.22 (m, 2H), 4.40 (q, J = 7.0 Hz, 2H), 3.37 (s, 3H), 2.44 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 158.4, 142.6, 141.0, 136.8, 136.4, 129.9, 129.1, 128.5, 124.9, 122.8, 122.2, 120.3, 117.8, 111.3, 108.4, 102.5, 60.8, 32.6, 21.3, 14.4; IR (in KBr): 3117, 2993, 1770, 1747, 1605, 1515, 1488, 1465, 1374, 1329, 1248, 1189, 1143, 1059, 795, 734 cm⁻¹; HRMS (ESI): m/z [M⁺] calcd for C₂₃H₂₁NO₄: 359.1521; found: 359.1515.

**Ethyl 4-hydroxy-1-(4-methoxyphenyl)-9-methyl-9H-carbazole-3-carboxylate (3ac)**

55% yield; white solid, mp. 136 - 137 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.80 (s, 1H), 8.47 (d, J = 7.8 Hz, 1H), 7.70 (s, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 4.42 (q, J = 7.0 Hz, 2H), 3.90 (s, 3H), 3.39 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 158.6, 158.3, 142.7, 140.9, 131.5, 131.0, 129.1, 124.9, 122.8, 122.2, 120.3, 117.4, 113.2, 111.2, 108.4, 102.4, 60.8, 55.3, 32.5, 14.4; IR (in KBr): 3118, 3099, 1765, 1665, 1628, 1605, 1517, 1378, 1245, 1180, 1144, 1030, 832, 797, 730 cm⁻¹; HRMS (ESI): m/z [M⁺] calcd for C₂₃H₂₁NO₄: 375.1471; found: 375.1466.

**Ethyl 1-(4-bromophenyl)-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ad)**

90% yield, white solid, mp. 183 – 185 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.75 (s, 1H), 8.40 (d, J = 7.6 Hz, 1H), 7.61 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.24 (dd, J₁ = 21.8 Hz, J₂ = 12.8 Hz, 4H), 4.37 (q, J = 7.0 Hz, 2H), 3.37 (s, 3H), 2.44 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 158.4, 158.3, 142.7, 140.9, 131.5, 131.0, 129.1, 124.9, 122.8, 122.2, 120.3, 117.4, 113.2, 111.2, 108.4, 102.4, 60.8, 55.3, 32.5, 14.4; IR (in KBr): 3118, 3099, 1765, 1665, 1628, 1605, 1517, 1378, 1245, 1180, 1144, 1030, 832, 797, 730 cm⁻¹; HRMS (ESI): m/z [M⁺] calcd for C₂₃H₂₁NO₄: 375.1471; found: 375.1466.
2H), 3.31 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 170.6, 158.8, 142.4, 141.1, 138.5, 131.7, 131.1, 129.1, 125.3, 123.1, 122.3, 121.5, 120.7, 116.5, 111.7, 108.6, 102.8, 61.1, 33.1, 14.6; IR (in KBr): 3046, 2977, 1764, 1748, 1658, 1603, 1371, 1298, 1192, 1142, 1098, 797, 696, 554 cm\(^{-1}\); HRMS (ESI): m/z [M]\(^+\) calcd for C\(_{22}\)H\(_{18}\)BrNO\(_3\): 423.0470; found: 423.0465.

**Ethyl 1-(4-chlorophenyl)-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ae)**

90% yield, white solid, mp. 188 - 190 °C; 1H NMR (600 MHz, CDCl3) δ (ppm) 11.82 (s, 1H), 8.47 (d, J = 7.8 Hz, 1H), 7.68 (s, 1H), 7.46 (dd, J\(_1\) = 20.5 Hz, J\(_2\) = 7.7 Hz, 3H), 7.40 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 7.0 Hz, 2H), 4.42 (q, J = 7.2 Hz, 2H), 3.38 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 170.5, 158.6, 142.4, 141.0, 137.9, 133.2, 131.3, 129.1, 128.1, 125.1, 122.9, 122.2, 120.5, 116.4, 111.5, 108.5, 102.7, 61.0, 32.9, 14.5; IR (in KBr): 3046, 2977, 1656, 1604, 1465, 1372, 1331, 1252, 1192, 1062, 1015, 798, 729 cm\(^{-1}\); HRMS (ESI): m/z [M]\(^+\) calcd for C\(_{22}\)H\(_{18}\)ClNO\(_3\): 379.0975; found: 379.0974.

**Ethyl 4-hydroxy-9-methyl-1-(4-(trifluoromethyl)phenyl)-9H-carbazole-3-carboxylate (3af)**

83% yield, white solid, mp. 176 - 177 °C; 1H NMR (600 MHz, CDCl3) δ (ppm) 11.86 (s, 1H), 8.48 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.71 (s, 1H), 7.60 (d, J = 7.9 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.41 – 7.29 (m, 2H), 4.43 (q, J = 7.1 Hz, 2H), 3.38 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) 170.5, 158.8, 143.3, 142.2, 141.0, 130.3, 129.3 (q, J\(_1\) = 31.9 Hz), 129.2, 125.2, 124.9 (q, J = 3.4 Hz), 124.1 (q, J = 269.6 Hz), 122.9, 122.1, 120.6, 116.2, 111.6, 108.5, 102.8, 61.1, 33.1, 14.5; IR (in KBr): 3059, 2957, 1661, 1608, 1470, 1375, 1327, 1252, 1162, 1106, 1069, 794, 747, 733 cm\(^{-1}\); HRMS (ESI): m/z [M+H]\(^+\) calcd for C\(_{23}\)H\(_{18}\)NO\(_3\)F\(_3\): 414.1312; found: 414.1315.
Ethyl 1-(3-fluorophenyl)-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ag)

78% yield, white solid, mp. 181 - 182 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ (ppm) 11.84 (s, 1H), 8.48 (d, $J = 7.6$ Hz, 1H), 7.72 (s, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.43 (dd, $J_1 = 14.4$ Hz, $J_2 = 7.3$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.24 (s, 1H), 7.19 (d, $J = 9.8$ Hz, 1H), 7.14 (t, $J = 8.4$ Hz, 1H), 4.43 (q, $J = 7.1$ Hz, 2H), 3.40 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 170.5, 162.1 (d, $J = 246.5$ Hz), 158.7, 142.3, 141.6 (d, $J = 7.7$ Hz), 141.0, 129.3 (d, $J = 8.4$ Hz), 129.0, 125.9 (d, $J = 2.7$ Hz), 125.2, 122.9, 122.2, 120.5, 117.0 (d, $J = 21.0$ Hz), 116.5 (d, $J = 1.9$ Hz), 114.1 (d, $J = 20.9$ Hz), 111.5, 108.5, 102.7, 61.0, 32.8, 14.5; IR (in KBr): 3076, 2983, 1656, 1609, 1584, 1469, 1373, 1329, 1268, 1210, 1063, 789, 730 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{22}$H$_{18}$FNO$_3$: 363.1271; found: 363.1263.

Ethyl 1-butyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ah)

67% yield, white solid, mp. 112 - 113 °C; $^1$HNMR (600 MHz, CDCl$_3$) δ (ppm) 11.64 (s, 1H), 8.44 (d, $J = 7.7$ Hz, 1H), 7.61 (s, 1H), 7.47 (t, $J = 7.7$ Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 4.44 (q, $J = 7.1$ Hz, 2H), 4.06 (s, 3H), 3.09 – 3.00 (m, 2H), 1.74 – 1.66 (m, 2H), 1.47 (dt, $J_1 = 19.3$ Hz, $J_2 = 7.3$ Hz, 5H), 0.99 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 170.6, 157.8, 143.4, 140.8, 128.11, 124.8, 122.9, 122.5, 120.2, 116.9, 111.6, 108.2, 102.6, 60.8, 34.7, 32.6, 32.1, 22.6, 14.6, 14.2; IR (in KBr): 3525, 3438, 3118, 2961, 2927, 1771, 1735, 1629, 1604, 1506, 1337, 1265, 1169, 1047, 932, 795, 748 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{20}$H$_{23}$NO$_3$: 325.1678; found: 325.1672.

Ethyl 4-hydroxy-1-(3-hydroxypropyl)-9-methyl-9H-carbazole-3-carboxylate (3ai)

81% yield, light yellow solid, mp. 113 - 114 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 11.58 (s, 1H), 8.38 (d, $J = 7.6$ Hz, 1H), 7.54 (s, 1H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.33 – 7.11 (m, 2H), 4.39 (dd, $J_1 = 14.2$ Hz, $J_2 = 7.1$ Hz, 2H), 3.97 (s, 3H), 3.73 (t, $J = 6.1$ Hz,
2H), 3.25 – 2.83 (m, 2H), 2.06 – 1.73 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 170.6, 158.0, 143.4, 140.9, 128.2, 125.0, 122.9, 122.5, 120.4, 116.0, 111.8, 108.4, 102.7, 62.1, 61.0, 35.1, 32.2, 29.0, 14.7; IR (in KBr): 3419, 2990, 2980, 2903, 1708, 1663, 1629, 1602, 1467, 1400, 1363, 1329, 1244, 1216, 1076, 1017, 807, 777, 734 cm⁻¹; HRMS (ESI): m/z [M]^+ calcd for C19H21NO4: 327.1471; found: 327.1464.

Ethyl 1-benzyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3aj)

60% yield, white solid, mp. 176 - 177 °C; 1H NMR (600 MHz, CDCl3) δ (ppm) 11.75 (s, 1H), 8.46 (d, J = 7.8 Hz, 1H), 7.68 (s, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.33 – 7.23 (m, 4H), 7.18 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 4.47 (s, 2H), 4.42 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 170.6, 158.4, 143.8, 141.0, 140.5, 130.3, 128.5, 127.7, 126.0, 124.9, 122.8, 122.3, 120.3, 113.0, 111.7, 108.2, 102.7, 60.8, 38.5, 31.6, 14.4; IR (in KBr): 3421, 3394, 3062, 2908, 2844, 1655, 1626, 1508, 1463, 1373, 1323, 1254, 1226, 1125, 797, 733, 696 cm⁻¹; HRMS (ESI) m/z [M]^+ calcd for C23H21NO3: 359.1521; found: 359.1513

Ethyl 1-cyclopropyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ak)

86% yield, white solid, mp. 148 - 150 °C; 1H NMR (600 MHz, CDCl3) δ (ppm) 11.72 (s, 1H), 8.43 (d, J = 7.7 Hz, 1H), 7.66 (s, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 4.31 (s, 3H), 2.41 – 2.25 (m, 1H), 1.45 (t, J = 7.1 Hz, 3H), 1.12 – 1.01 (m, 2H), 0.94 – 0.85 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm) 170.6, 158.4, 144.9, 140.8, 127.3, 124.9, 122.9, 122.5, 120.4, 117.0, 111.2, 108.4, 102.3, 60.9, 32.4, 14.7, 13.9, 8.3; IR (in KBr): 3421, 3394, 3062, 2908, 2844, 1655, 1626, 1508, 1463, 1373, 1323, 1254, 1226, 1125, 797, 733, 696 cm⁻¹; HRMS (ESI) m/z [M]^+ calcd for C19H19NO3: 327.1446.
309.1365; found: 309.1355.

**Ethyl 1-cyclohexyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3al)**

73% yield, white solid, mp. 157 - 158 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 11.60 (s, 1H), 8.40 (d, $J = 7.7$ Hz, 1H), 7.69 (s, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.33 – 7.17 (m, 2H), 4.41 (dd, $J_1 = 13.6$ Hz, $J_2 = 6.7$ Hz, 2H), 4.01 (s, 3H), 3.28 (t, $J = 10.3$ Hz, 1H), 2.01 (d, $J = 11.5$ Hz, 2H), 1.92 (d, $J = 12.0$ Hz, 2H), 1.82 (d, $J = 12.0$ Hz, 1H), 1.59 – 1.29 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 170.7, 157.6, 143.2, 141.1, 124.8, 123.9, 122.9, 122.8, 122.5, 120.2, 111.8, 108.3, 102.8, 60.8, 38.5, 35.1, 32.8, 27.2, 26.4, 14.6; IR (in KBr): 3421, 3392, 2845, 2815, 1654, 1606, 1508, 1463, 1375, 1313, 1259, 1226, 1196, 1127, 719, 680, 643 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{22}$H$_{25}$NO$_3$: 351.1834; found: 351.1837.

**Diethyl 4-hydroxy-9-methyl-9H-carbazole-1,3-dicarboxylate (3am)**

64% yield, white solid; mp. 146 - 148 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ (ppm) 12.09 (s, 1H), 8.43 (s, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.36 (t, $J = 7.4$ Hz, 1H), 4.47 (qd, $J_1 = 7.1$ Hz, $J_2 = 3.3$ Hz, 4H), 3.93 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 170.2, 166.4, 161.2, 143.3, 141.4, 131.4, 125.6, 122.9, 122.0, 121.1, 112.4, 109.1, 108.1, 102.9, 61.4, 61.25, 34.0, 14.6, 14.6; IR (in KBr): 3424, 3392, 2845, 2815, 1654, 1606, 1508, 1463, 1375, 1313, 1259, 1226, 1196, 1127, 719, 680, 643 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{19}$H$_{19}$NO$_5$: 341.1263; found: 341.1258.

**Ethyl 4-hydroxy-9-methyl-1-(thiophen-2-yl)-9H-carbazole-3-carboxylate (3an)**
46% yield, light yellow solid, mp. 212 - 213 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 11.81 (s, 1H), 8.41 (d, $J = 7.9$ Hz, 1H), 7.81 (s, 1H), 7.61 – 7.34 (m, 2H), 7.27 (dd, $J_1 = 22.8$ Hz, $J_2 = 16.8$ Hz, 2H), 7.19 – 6.74 (m, 2H), 4.39 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.0$ Hz, 2H), 3.44 (s, 3H), 1.40 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 170.6, 159.3, 143.3, 141.0, 140.0, 130.9, 128.5, 126.8, 125.9, 125.3, 123.1, 122.2, 120.7, 111.5, 109.2, 108.6, 102.7, 61.1, 31.9, 14.6; IR (in KBr): 3525, 3438, 3119, 2988, 1772, 1733, 1627, 1603, 1507, 1427, 1404, 1327, 1264, 1246, 1141, 1055, 834, 795, 738 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{20}$H$_{17}$NO$_3$S: 351.0929; found: 351.0923

**Ethyl 4-hydroxy-2,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ao)**

64% yield; white solid, mp : 149 - 151 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 12.39 (s, 1H), 8.40 (d, $J = 7.6$ Hz, 1H), 7.35 (dd, $J_1 = 19.1$ Hz, $J_2 = 11.2$ Hz, 4H), 7.20 (dd, $J_1 = 32.4$ Hz, $J_2 = 7.8$ Hz, 4H), 4.41 (dd, $J_1 = 14.1$ Hz, $J_2 = 7.0$ Hz, 2H), 3.00 (s, 3H), 2.32 (s, 3H), 1.39 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 172.4, 159.5, 142.3, 141.0, 139.0, 136.5, 131.3, 128.2, 127.4, 124.6, 122.7, 122.3, 120.2, 118.6, 109.5, 108.3, 103.5, 61.2, 31.9, 20.9, 14.4; IR (in KBr): 3525, 3438, 3119, 2986, 1772, 1734, 1597, 1507, 142, 1398, 1298, 1247, 1077, 901, 832, 811, 752 cm$^{-1}$; HRMS (ESI): m/z [M]$^+$ calcd for C$_{23}$H$_{21}$NO$_3$: 359.1521; found: 359.1513.

**Diethyl 4-hydroxy-9-methyl-1-phenyl-9H-carbazole-2,3-dicarboxylate (3ap)**

36 h, 46% yield, yellow solid, mp. 149 - 150 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 12.23 (s, 1H), 8.44 (d, $J = 7.7$ Hz, 1H), 7.63 – 7.30 (m, 6H), 7.30 – 7.15 (m, 2H), 4.37 (dd, $J_1 = 14.1$ Hz, $J_2 = 7.0$ Hz, 2H), 3.91 (dd, $J_1 = 14.1$ Hz, $J_2 = 7.1$ Hz, 2H), 3.14 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 169.8, 168.3, 159.0, 141.7, 141.3, 135.7,
133.5, 131.7, 128.1, 127.7, 125.6, 123.4, 121.9, 120.8, 116.2, 111.6, 108.6, 99.3, 61.7, 61.0, 32.1, 14.2, 13.92; IR (in KBr): 3429, 3055, 2982, 2903, 1725, 1656, 1600, 1371, 1309, 1232, 1191, 1064, 950, 803, 735, 689 cm⁻¹; HRMS (ESI): m/z [M]⁺ calcd for C₂₅H₂₃NO₅: 417.1576; found: 417.1577.

**Ethyl 4-hydroxy-9-methyl-1,2-diphenyl-9H-carbazole-3-carboxylate (3aq)**

27% yield, white solid, mp. 181 - 183 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 12.37 (s, 1H), 8.50 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.36 – 7.21 (m, 2H), 7.19 – 6.77 (m, 10H), 3.89 (q, J = 7.1 Hz, 2H), 3.09 (s, 3H), 0.64 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 171.7, 158.8, 141.8, 141.6, 141.2, 141.1, 137.5, 132.0, 129.7, 127.1, 126.6, 126.3, 125.3, 125.0, 123.0, 122.1, 120.4, 118.5, 110.5, 108.4, 103.1, 60.4, 32.0, 13.1.; IR (in KBr): 2981, 1656, 1501, 1478, 1396, 1656, 1334, 1308, 1242, 1199, 1001, 860, 818, 722, 692 cm⁻¹; HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₈H₂₃NO₃: 444.1570; found: 444.1583.

**Ethyl 4-hydroxy-6,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ba)**

84% yield, white solid, mp. 173 - 175 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.85 (s, 1H), 8.28 (s, 1H), 7.70 (s, 1H), 7.62 – 7.34 (m, 5H), 7.28 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 8.3 Hz, 1H), 4.41 (q, J = 7.2 Hz, 2H), 3.33 (s, 3H), 2.56 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.7, 158.5, 142.7, 139.5, 135.8, 130.1, 129.8, 128.9, 127.9, 127.1, 126.3, 122.9, 122.4, 117.9, 111.2, 108.2, 102.4, 60.9, 32.7, 21.6, 14.5; IR (in KBr): 3307, 2977, 2924, 1652, 1629, 1474, 1370, 1301, 1258, 1168, 1058, 795, 726, 700 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₂₃H₂₁NO₃: 360.1594; found: 360.1597.

**Ethyl 4-hydroxy-6-methoxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3ca)**

74% yield, white solid, mp. 177 - 178 °C; ¹H NMR (600
$\text{MHz, CDCl}_3 \delta \text{ (ppm)} \ 11.87 \ (s, 1\text{H}), \ 7.99 \ (s, 1\text{H}), \ 7.69 \ (s, 1\text{H}), \ 7.49 - 7.41 \ (m, 4\text{H}), \ 7.32 - 7.18 \ (m, 2\text{H}), \ 7.10 \ (d, J = 8.8 \text{ Hz}, 1\text{H}), \ 4.41 \ (q, J = 7.0 \text{ Hz}, 2\text{H}), \ 3.97 \ (s, 3\text{H}), \ 3.33 \ (s, 3\text{H}), \ 1.41 \ (t, J = 7.1 \text{ Hz, 3H}); ^{13}\text{C NMR (100 MHz, CDCl}_3 \delta \text{ (ppm)} \ 170.7, \ 158.6, \ 154.4, \ 142.9, \ 139.4, \ 135.9, \ 130.0, \ 128.8, \ 127.9, \ 127.1, \ 122.7, \ 117.9, \ 114.5, \ 111.3, \ 109.2, \ 105.4, \ 102.1, \ 60.9, \ 56.01, \ 32.8, \ 14.5; \ IR \text{ (in KBr): 3421, 2983, 1658, 1625, 1474, 1432, 1373, 1263, 1227, 1057, 862, 793, 728 cm}^{-1}; \ HRMS \text{ (ESI): m/z [M+H]}^+ \text{ calcd for C}_{23}\text{H}_{21}\text{NO}_4: 376.1543; \text{ found: 376.1541.}\

\text{Ethyl 6-fluoro-4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3da)}$

84% yield, white solid, mp. 185 - 187 °C; $^1\text{H NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \ 11.72 \ (s, 1\text{H}), 8.01 \ (d, J = 8.8 \text{ Hz}, 1\text{H}), \ 7.65 \ (s, 1\text{H}), 7.29 \ (d, J = 81.5 \text{ Hz}, 5\text{H}), \ 7.07 \ (dd, J_1 = 12.1 \text{ Hz}, J_2 = 5.0 \text{ Hz}, 2\text{H}), 4.36 \ (dd, J_1 = 14.0 \text{ Hz}, J_2 = 7.0 \text{ Hz}, 2\text{H}), \ 3.25 \ (s, 3\text{H}), 1.38 \ (t, J = 7.0 \text{ Hz, 3H}); ^{13}\text{C NMR (100 MHz, CDCl}_3 \delta \text{ (ppm)} \ 170.6, \ 158.6, \ 157.8 \ (d, J = 235.5 \text{ Hz}), \ 143.3, \ 139.2, \ 137.5, \ 130.1, \ 129.6, \ 128.0, \ 127.4, \ 122.7 \ (d, J = 10.0 \text{ Hz}), \ 118.1, \ 112.8 \ (d, J = 25.5 \text{ Hz}), \ 111.2 \ (d, J = 3.3 \text{ Hz}), \ 109.0 \ (d, J = 9.1 \text{ Hz}), \ 108.7 \ (d, J = 24.7 \text{ Hz}), \ 102.5, \ 61.1, \ 33.0, \ 14.6; \ IR \text{ (in KBr): 2988, 2940, 1771, 1663, 1632, 1470, 1373, 1330, 1311, 1247, 1154, 1051, 875, 764, 707 cm}^{-1}; \ HRMS \text{ (ESI): m/z [M+H]}^+ \text{ calcd for C}_{22}\text{H}_{18}\text{NO}_3\text{F: 364.1343; found: 364.1346.}\

\text{Ethyl 6-bromo-4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3ea)}$

82% yield, white solid, mp : 175 - 177 °C; $^1\text{H NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \ 11.69 \ (s, 1\text{H}), 8.43 \ (s, 1\text{H}), \ 7.65 \ (s, 1\text{H}), \ 7.30 \ (d, J = 81.4 \text{ Hz}, 6\text{H}), \ 7.03 \ (d, J = 8.5 \text{ Hz}, 1\text{H}), \ 4.36 \ (dd, J_1 = 13.7 \text{ Hz}, J_2 = 6.8 \text{ Hz}, 2\text{H}), \ 3.23 \ (s, 3\text{H}), \ 1.38 \ (t, J = 6.9 \text{ Hz, 3H}); ^{13}\text{C NMR (100 MHz, CDCl}_3 \delta \text{ (ppm)} \ 170.6, \ 158.5, \ 142.7, \ 139.7, \ 139.1, \ 130.2, \ 129.7, \ 128.1, \ 127.7, \ 127.4, \ 125.3, \ 123.8, \ 118.0, \ 113.3, \ 110.6, \ 109.9, \ 102.9, \ 61.1, \ 33.0, \ 14.6; \ IR \text{ (in KBr): 3118, 3098, 2928, 1771, 1663, 1628, 1595, 1507, 1427, 1427, 1328, 1291, 1254, 1192, 1121, 1050, 875,

**Ethyl 7-chloro-4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3fa)**

87% yield, white solid, mp. 175 - 177 °C; ¹H NMR (CDCl₃, 600 MHz), δ (ppm) 11.80 (s, 1H), 8.35 (d, J = 8.3 Hz, 1H), 7.73 (s, 1H), 7.46 (dd, J₁ = 12.6 Hz, J₂ = 6.7 Hz, 5H), 7.34 – 7.26 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 3.32 (s, 3H), 1.41 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.5, 158.2, 142.7, 141.6, 139.1, 130.8, 130.0, 129.3, 127.9, 127.3, 123.6, 120.7, 117.9, 110.9, 108.6, 103.0, 61.0, 32.8, 14.5; IR (in KBr): 2983, 1663, 1602, 1466, 1421, 1375, 1248, 1190, 1147, 1057, 911, 769, 711 cm⁻¹; HRMS (EI): m/z [M+H]⁺ calcd for C₂₂H₁₈NO₃Cl: 380.1048; found: 380.1058.

**Ethyl 4-hydroxy-5,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ga)**

88% yield, white solid, mp. 135 - 137 °C; ¹H NMR (CDCl₃, 600 MHz, CDCl₃) δ (ppm) 12.30 (s, 1H), 7.73 (d, J = 0.6 Hz, 1H), 7.53 – 7.34 (m, 5H), 7.28 (m, 1H), 7.20 (s, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.26 (s, 3H), 3.11 (s, 3H), 1.38 (t, J = 6.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 171.6, 158.5, 143.4, 142.2, 140.3, 134.2, 130.2, 129.7, 128.19, 127.3, 125.6, 123.7, 121.8, 117.7, 112.2, 106.5, 102.4, 61.0, 33.3, 24.6, 14.4; IR (in KBr): 3523, 3438, 3120, 2985, 1773, 1735, 1645, 1597, 1495, 1442, 1404, 1323, 1250, 1184, 1081, 1037, 893, 800, 780 cm⁻¹; HRMS (ESI): m/z [M-H]⁻ calcd for C₂₃H₂₁NO₃: 358.1446; found: 358.1449.

**Ethyl 4-hydroxy-8,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ha)**

84% yield, white solid, mp. 200 - 201 °C; ¹H NMR (CDCl₃) δ (ppm) 11.81 (s, 1H), 8.35 (d, J = 7.4 Hz, 1H), 7.74
(s, 1H), 7.53 – 7.44 (m, 3H), 7.40 (t, $J = 6.7$ Hz, 1H), 7.33 – 7.06 (m, 3H), 4.42 (dd, $J_1$ = 14.1 Hz, $J_2$ = 7.1 Hz, 2H), 3.56 (s, 3H), 2.75 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 170.7, 158.4, 144.5, 140.8, 139.9, 129.5, 129.3, 128.5, 128.1, 126.9, 123.5, 121.0, 120.8, 120.5, 118.0, 112.0, 103.0, 60.9, 36.8, 20.5, 14.5; IR (in KBr): 3523, 3440, 3120, 2983, 1773, 1735, 1627, 1595, 1469, 1398, 1328, 1251, 1145, 1032, 880, 800, 713 cm$^{-1}$; HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{23}$H$_{21}$NO$_3$: 360.1594; found: 360.1596.

**9-tert-butyl 3-ethyl 4-hydroxy-1-phenyl-9H-carbazole-3,9-dicarboxylate (3ia)**

![Chemical Structure](image)

82% yield, white solid, mp. 183 - 184 $^\circ$C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 11.71 (s, 1H), 8.44 (d, $J = 7.7$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.88 (s, 1H), 7.57 (d, $J = 7.6$ Hz, 2H), 4.46 (q, $J_1 = 15.2$ Hz, $J_2 = 7.5$ Hz, 4H), 4.33 (t, $J = 7.4$ Hz, 1H), 4.14 (t, $J = 7.1$ Hz, 3H), 1.23 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 170.4, 157.7, 149.8, 141.2, 141.0, 139.3, 130.2, 128.9, 127.1, 126.7, 126.5, 124.5, 123.4, 123.1, 122.0, 115.7, 113.6, 107.3, 84.5, 61.5, 27.7, 14.6; IR (in KBr): 3411, 3043, 2983, 1731, 1672, 1626, 1444, 1369, 1326, 1220, 1187, 1111, 785, 749, 700 cm$^{-1}$; HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{26}$H$_{25}$NO$_5$: 430.1668; found: 430.1660.

**Ethyl 4-hydroxy-1-phenyl-9H-carbazole-3-carboxylate (3ja)**

82% yield, white solid, mp. 183 - 184 $^\circ$C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 11.85 (s, 1H), 8.44 (s, 1H), 8.38 (d, $J = 7.7$ Hz, 1H), 7.84 (s, 1H), 7.59 (d, $J = 7.3$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.43 – 7.20 (m, 4H), 4.42 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 170.9, 159.0, 142.0, 138.3, 137.9, 129.2, 128.2, 127.4, 126.8, 125.4, 123.1, 120.8, 117.2, 111.5, 110.4, 103.9, 61.1, 14.6; IR (in KBr): 3420, 3397, 1646, 1506, 1450, 1375, 1344, 1249, 1180, 1130, 797, 765, 645 cm$^{-1}$; HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{21}$H$_{17}$NO$_3$: 332.1281; found: 332.1277.
4-hydroxy-9-methyl-N,1-diphenyl-9H-carbazole-3-carboxamide (3ka)

61% yield, white solid, mp. 230 - 231 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 13.19 (s, 1 H), 8.53 (d, J = 7.8 Hz, 1 H), 7.84 (s, 1 H), 7.58 (d, J = 7.9 Hz, 2 H), 7.51 (d, J = 3.6 Hz, 3 H), 7.49 – 7.45 (m, 2 H), 7.38 (t, J = 7.8 Hz, 2 H), 7.33 (dd, J₁ = 14.4 Hz, J₂ = 6.4 Hz, 3 H), 7.17 (t, J = 7.4 Hz, 1 H), 3.37 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 169.0, 159.1, 141.8, 141.1, 139.4, 136.9, 130.2, 128.9, 128.1, 127.5, 125.2, 125.0, 124.7, 123.2, 122.3, 121.0, 120.4, 117.6, 112.3, 108.5, 104.1, 32.7; IR (in KBr): 3404, 3060, 3024, 1645, 1587, 1509, 1465, 1346, 1257, 842, 738, 709 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₂₆H₂₀N₂O₂: 393.1598; found: 393.1604.

1-(4-hydroxy-9-methyl-1-phenyl-9H-carbazol-3-yl)ethanone (3la)

89% yield, light yellow solid, mp. 191 - 192 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 13.56 (s, 1H), 8.41 (d, J = 7.7 Hz, 1H), 7.42 (dd, J₁ = 20.4 Hz, J₂ = 11.4 Hz, 7H), 7.27 (dd, J₁ = 13.6 Hz, J₂ = 7.7 Hz, 2H), 3.30 (s, 3H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 202.9, 159.9, 143.0, 141.1, 139.3, 130.3, 130.1, 128.1, 127.4, 125.2, 123.0, 122.5, 120.7, 117.8, 111.4, 111.2, 108.7, 32.7, 26.7; IR (in KBr): 3524, 3438, 3118, 1765, 1733, 1593, 1517, 1324, 1255, 1186, 1103, 986, 838, 740 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₂₁H₁₇NO₂: 316.1332; found: 316.1328.
5. Synthetic Transformation

5.1 Reduction reaction of the product

A THF solution containing 0.1727 g (0.5 mmol) of ethyl 4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate was added slowly to stirred suspension of 0.038 g (1.0 mmol) of lithium aluminum hydride in THF (2 mL) at 0 °C, and the resultant mixture was then stirred at room temperature for one hour. After completion, the reaction was quenched sequentially with water (0.04 mL), 15% sodium hydroxide (0.08 mL), water (0.04 mL), then added anhydrous magnesium sulfate. After filtering out insoluble matter, the filtrate was concentrated to dryness under reduced pressure. Recrystallized from CH₂Cl₂/petro ether at -20 °C can obtain the desired product.

4, 66% yield, white solid, mp. 116 - 117 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.44 (d, J = 7.7 Hz, 1H), 8.12 (s, 1H), 7.48 – 7.38 (m, 5H), 7.37 – 7.15 (m, 3H), 6.93 (s, 1H), 5.07 (d, J = 5.3 Hz, 2H), 3.35 (s, 3H), 2.18 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 152.1, 141.8, 140.1, 139.7, 130.2, 127.9, 126.9, 125.1, 123.1, 122.0, 119.5, 117.5, 113.6, 112.8, 108.2, 65.1, 32.7; IR (in KBr): 3535, 1671, 1604, 1458, 1403, 1272, 1170, 1119, 999, 876, 731 cm⁻¹; HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₀H₁₇NO₂: 326.1160; found: 326.1152

5.2 Cross-coupling reaction of the product

1) Tf₂O, Et₃N, DCM 81% yield
2) 4-tolylboronic acid Pd(PPh₃)₄ (2.5 mol%), K₃PO₄, dioxane, 90 °C, 22 h 77% yield
To a solution of 3aa (0.3 mmol, 103.6 mg) and Et$_3$N (0.9 mmol, 0.12 mL) in CH$_2$Cl$_2$ (1 mL), Tf$_2$O (0.72 mmol, 203.2 mg) was added slowly to the stirred suspension at 0 °C, and the resultant mixture was then stirred at room temperature overnight. After completion, the reaction was quenched with saturated sodium bicarbonate, extracted with CH$_2$Cl$_2$, combined the organic phase and washed with brine, dried over anhydrous Na$_2$SO$_4$, the solvent was evaporated under reduced pressure, the residue was purified by flash chromatography on silica gel to give the desired product as white solid in a 81% yield. And the product was used to the cross-coupling reaction$^9$.

A mixture of 4-tolylboronic acid (0.11 mmol), ethyl 9-methyl-1-phenyl-4-(((trifluoromethyl)sulfonyl)oxy)-9H-carbazole-3-carboxylate (0.1 mmol), Pd(PPh$_3$)$_4$ (0.0025 mmol), and K$_3$PO$_4$ (0.15 mmol) in dioxane (1 mL) was heated to 90 °C for 22 h. The mixture was diluted with toluene (2 mL) and treated with aqueous 3 M NaOH (0.05 mL) and 30% H$_2$O$_2$ (0.05 mL) for 1 h at room temperature to oxidize the residual borane. The product was extracted with ethyl acetate, washed with brine, and dried over MgSO$_4$. Isolation by column chromatography over silica gel gave the desired compound in a 77% yield (average yield of two parallel reactions).

$^5$, 77% yield, white solid, mp. 154 - 156 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ (ppm) 7.98 (s, 1H), 7.77 – 7.42 (m, 6H), 7.35 (ddd, $J_1 = 26.7$ Hz, $J_2 = 13.5$ Hz, $J_3 = 7.4$ Hz, 5H), 6.94 (t, $J = 7.4$ Hz, 1H), 6.70 (d, $J = 7.9$ Hz, 1H), 4.10 (q, $J = 6.9$ Hz, 2H), 3.40 (s, 3H), 2.52 (s, 3H), 1.05 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 167.8, 142.6, 139.9, 139.7, 138.6, 137.3, 136.7, 130.4, 130.0, 129.0, 128.3, 128.1, 127.6, 125.9, 124.3, 123.1, 122.7, 120.8, 119.6, 108.7, 60.4, 32.9, 21.5, 13.9; IR (in KBr): 2985, 1703, 1555, 1447, 1398, 1339, 1240, 1185, 1013, 860, 821, 738 cm$^{-1}$; HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{29}$H$_{25}$NO$_2$: 420.1958; found: 420.1957.
References:

6. Copies of NMR Spectrums of Substrates

[Image of NMR spectra for substrates 1a]
7. Copies of NMR Spectrums of Products

![NMR Spectra](image)

**3aa**

**S-43**
8. Copies of NMR Spectrums of Synthetic Transformation Products