

Supporting Information

Regioselective Synthesis of 6-Nitroindole Derivatives from Enaminones and Nitroaromatic Compounds *via* Transition Metal-Free C-C and C-N Bonds Formation

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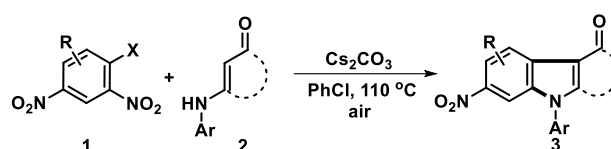
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General information

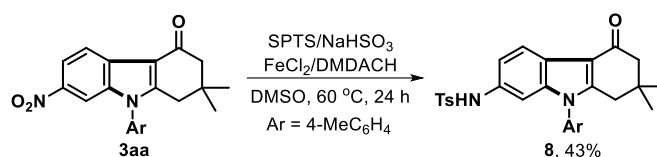
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under air using undistilled solvent, without any precautions to exclude air and moisture. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded in CDCl_3 on 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^1H NMR and ^{13}C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

General procedure for the regioselective synthesis of 6-nitroindole derivatives

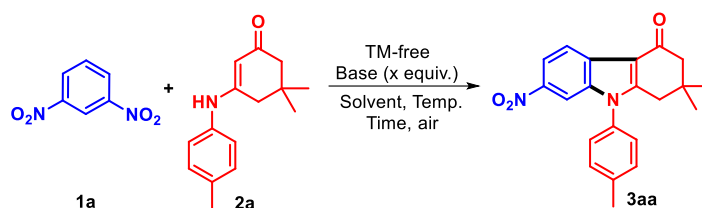


Nitroaromatic compound **1** (0.3 mmol), enaminone **2** (0.45 mmol), and cesium carbonate (1.0 mmol) in chlorobenzene (2 mL) were stirred at 110 °C for a certain time shown in Tables 2-3. Upon completion of the reaction (indicated by TLC), the organic solvent was removed under vacuum and the residue was directly subjected to flash silica gel column chromatographic purification by using petroleum/ethyl acetate as eluant to afford pure product **3**.

General procedure for the synthesis of **8**



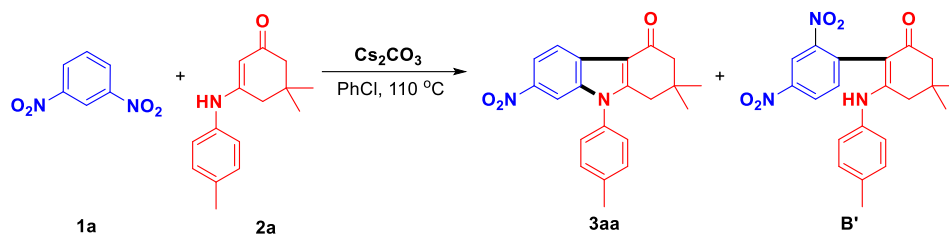
p-Toluenesulfonate (SPTS, 0.75 mmol), **3aa** (0.4 mmol), NaHSO_3 (1.5 mmol), FeCl_2 (10 mol %), and *trans*-*N,N'*-dimethyl-1,2-diaminocyclohexane (DMDACH, 20 mol %) in DMSO (2 mL) was stirred at 60 °C for 24 h. Upon completion of the reaction (indicated by TLC), the mixture was then poured into water (20 mL), extracted with dichloromethane (3×10 mL), and dried with anhydrous Na_2SO_4 . The organic solvent was removed under vacuum and the residue was directly subjected to flash silica gel column chromatographic purification by using petroleum/ethyl acetate as eluant to afford pure product **8**.

Table S1 Optimization of reaction conditions^a

Entry	Base (x equiv.)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^b
1	Cs ₂ CO ₃ (3.3)	DCE	110	12	9
2	Cs ₂ CO ₃ (3.3)	1,4-dioxane	110	12	38
3	Cs ₂ CO ₃ (3.3)	DMF	110	12	trace
4	Cs ₂ CO ₃ (3.3)	DMSO	110	12	trace
5	Cs ₂ CO ₃ (3.3)	MeCN	reflux	12	33
6	Cs ₂ CO ₃ (3.3)	EtOH	reflux	12	trace
7	Cs ₂ CO ₃ (3.3)	toluene	110	12	44
8	Cs ₂ CO ₃ (3.3)	<i>p</i> -xylene	110	12	38
9	Cs ₂ CO ₃ (3.3)	PhCl	110	12	50
10	Cs ₂ CO ₃ (2.3)	PhCl	110	12	49
11	Cs ₂ CO ₃ (1.3)	PhCl	110	12	40
12	--	PhCl	110	24	0
13	CsF (3.3)	PhCl	110	12	0
14	CsOAc (3.3)	PhCl	110	12	0
15	K ₂ CO ₃ (3.3)	PhCl	110	12	0
16	K ₃ PO ₄ (3.3)	PhCl	110	12	25
17	<i>t</i> -BuOK (3.3)	PhCl	110	12	trace
18	LiOMe (3.3)	PhCl	110	12	trace
19	KOH (3.3)	PhCl	110	12	trace
20	Et ₃ N (3.3)	PhCl	110	12	0
21	DABCO (3.3)	PhCl	110	12	0
22	Cs ₂ CO ₃ (3.3)	PhCl	110	12	83 (68) ^{c,d}
23	Cs ₂ CO ₃ (3.3)	PhCl	110	12	47 ^e
24	Cs ₂ CO ₃ (3.3)	PhCl	110	24	84 (64) ^{c,d}
25	Cs ₂ CO ₃ (3.3)	PhCl	90	12	51 ^c
26	Cs ₂ CO ₃ (3.3)	PhCl	110	5	59 ^c

^aReaction conditions: **1a** (0.45 mmol), **2a** (0.3 mmol), base (0-3.3 equiv) and solvent (2 mL) under air. ^bYields were determined by HPLC with an internal standard (biphenyl) on the basis of the ratio between the formed products and the initial amount of limiting reactant **2a**. ^c**1a** (0.3 mmol) and **2a** (0.45 mmol) were used. ^dIsolated yields. ^e**1a** (0.3 mmol) and **2a** (0.6 mmol) were used.

HRMS analysis of reaction intermediate

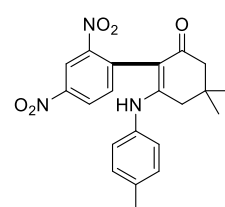


1,3-Dinitrobenzene (**1a**, 0.3 mmol), 5,5-dimethyl-3-(*p*-tolylamino)cyclohex-2-en-1-one (**2a**, 0.45 mmol), and cesium carbonate (1.0 mmol) in chlorobenzene (2 mL) were stirred at 110 °C under air for 1 h. The possible reaction intermediate **B'** was detected by HRMS analysis of the reaction mixture.

Elemental Composition Report

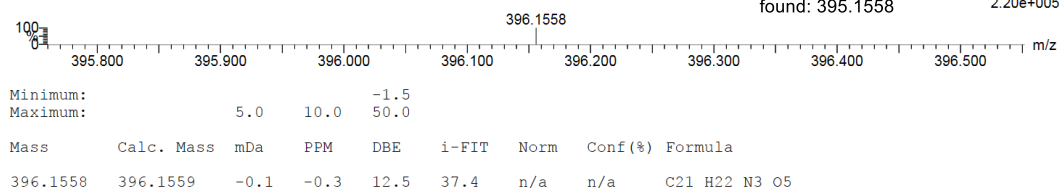
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 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
 3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
 Elements Used:
 C: 20-22 H: 20-22 N: 2-4 O: 3-6
 2080-1 249 (1.795)
 1: TOF MS ES+

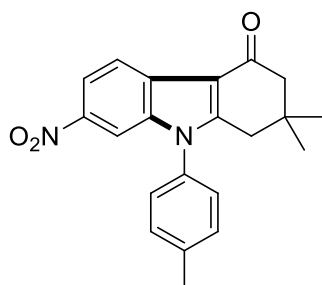


$\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$: 395.1554
 found: 395.1558

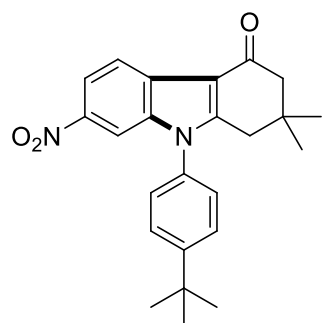
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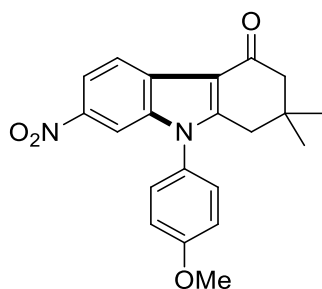
Analytical and spectral data for products:



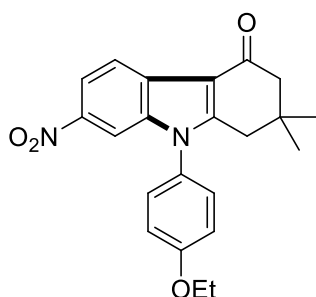
2,2-Dimethyl-7-nitro-9-*p*-tolyl-2,3-dihydro-1*H*-carbazol-4(9*H*)-one (3aa): Yield = 68%. Yellow solid. Mp = 141.5–142.9 °C. IR (KBr): ν = 2961, 2928, 2874, 1658, 1510, 1435, 1330, 1138, 1068, 875, 816, 728 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.34 (d, J = 8.7 Hz, 1H), 8.17 (dd, J = 8.7, 2.0 Hz, 1H), 8.04 (d, J = 1.9 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.72 (s, 2H), 2.52 (s, 5H), 1.15 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 155.6, 144.3, 140.2, 137.8, 132.4, 131.1, 129.5, 127.2, 121.6, 118.5, 112.6, 107.5, 52.4, 37.3, 35.7, 28.8, 21.5 ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 349.1547, found: 349.1550.



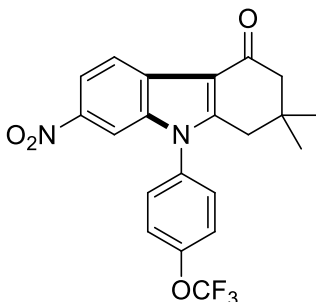
9-(4-*tert*-Butylphenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1*H*-carbazol-4(9*H*)-one (3ab): Yield = 60%. Yellow solid. Mp = 199.9–200.5 °C. IR (KBr): ν = 2959, 2902, 1660, 1509, 1438, 1335, 1177, 1067, 848, 737 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.35 (d, J = 8.7 Hz, 1H), 8.18 (dd, J = 8.7, 1.9 Hz, 1H), 8.08 (d, J = 1.9 Hz, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 2.73 (s, 2H), 2.52 (s, 2H), 1.45 (s, 9H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 155.6, 153.2, 144.3, 137.8, 132.3, 129.5, 127.5, 126.8, 121.6, 118.5, 112.7, 107.6, 52.4, 37.3, 35.7, 35.2, 31.5, 28.8 ppm. HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 391.2016, found: 391.2019.



9-(4-Methoxyphenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3ac): Yield = 64%. Brown solid. Mp = 198.0–200.8 °C. IR (KBr): ν = 2960, 2901, 1659, 1610, 1509, 1441, 1332, 1250, 1172, 1068, 1029, 875, 840, 754, 737 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.34 (d, J = 8.7 Hz, 1H), 8.17 (dd, J = 8.7, 1.8 Hz, 1H), 8.02 (d, J = 1.7 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 3.94 (s, 3H), 2.70 (s, 2H), 2.52 (s, 2H), 1.15 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 160.6, 155.8, 144.3, 138.1, 129.4, 128.7, 127.5, 121.6, 118.5, 115.7, 112.5, 107.5, 55.9, 52.4, 37.2, 35.7, 28.8 ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 365.1496, found: 365.1492.

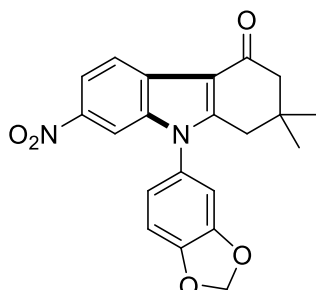


9-(4-Ethoxyphenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3ad): Yield = 64%. Yellow solid. Mp = 145.8–147.8 °C. IR (KBr): ν = 2972, 2936, 1656, 1511, 1334, 1251, 1172, 1048, 847, 734 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.34 (d, J = 8.7 Hz, 1H), 8.18 (dd, J = 8.7, 2.0 Hz, 1H), 8.02 (d, J = 1.9 Hz, 1H), 7.30–7.26 (m, 2H), 7.11 (d, J = 8.8 Hz, 2H), 4.16 (q, J = 7.0 Hz, 2H), 2.70 (s, 2H), 2.52 (s, 2H), 1.51 (t, J = 7.0 Hz, 3H), 1.15 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 160.0, 155.8, 144.3, 138.1, 129.4, 128.6, 127.3, 121.5, 118.5, 116.1, 112.5, 107.5, 64.3, 52.4, 37.2, 35.7, 28.8, 15.0 ppm. HRMS (m/z): calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 379.1652, found: 379.1641.



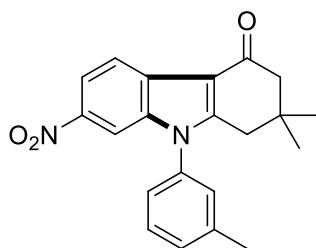
2,2-Dimethyl-7-nitro-9-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1H-carbazol-4(9H)-one (3ae): Yield = 70%. Yellow solid. Mp = 203.1–204.6 °C. IR (KBr): ν = 2967, 1655, 1514, 1443, 1335, 1254, 1166, 1069, 873, 834, 736, 685 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.36 (d, J =

8.7 Hz, 1H), 8.19 (dd, $J = 8.7, 1.4$ Hz, 1H), 8.03 (s, 1H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 2.72 (s, 2H), 2.53 (s, 2H), 1.17 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 193.6, 155.1, 150.0, 149.9, 144.5, 137.5, 133.5, 129.5, 129.1, 122.9, 121.8, 118.8, 113.1, 107.1, 52.3, 37.3, 35.8, 28.8$ ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 419.1213, found: 419.1223.



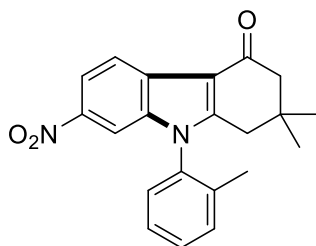
9-(Benzo[d][1,3]dioxol-5-yl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3af):

Yield = 58%. Yellow solid. Mp = 177.9–179.8 °C. IR (KBr): $\nu = 2971, 2893, 1657, 1517, 1332, 1239, 1040, 842, 739$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 8.34$ (d, $J = 8.7$ Hz, 1H), 8.18 (dd, $J = 8.7, 2.0$ Hz, 1H), 8.05 (d, $J = 1.9$ Hz, 1H), 7.02 (d, $J = 8.1$ Hz, 1H), 6.87–6.79 (m, 2H), 6.17 (s, 2H), 2.72 (s, 2H), 2.52 (s, 2H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 193.6, 155.7, 149.3, 149.0, 144.3, 138.0, 129.4, 128.5, 121.6, 121.3, 118.6, 112.6, 109.3, 108.3, 107.4, 102.6, 52.3, 37.2, 35.7, 28.8$ ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 379.1288, found: 379.1279.

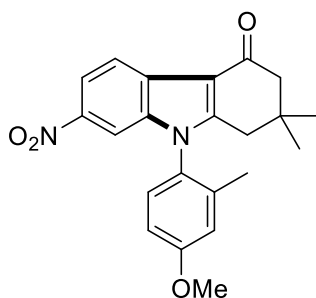


2,2-Dimethyl-7-nitro-9-m-tolyl-2,3-dihydro-1H-carbazol-4(9H)-one (3ag): Yield = 68%.

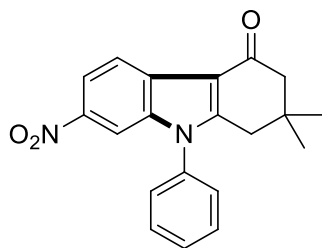
Yellow solid. Mp = 162.1–163.2 °C. IR (KBr): $\nu = 2957, 2882, 1665, 1513, 1437, 1335, 1138, 830, 736$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 8.35$ (d, $J = 8.7$ Hz, 1H), 8.18 (dd, $J = 8.7, 2.0$ Hz, 1H), 8.04 (d, $J = 1.9$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.17 (d, $J = 7.7$ Hz, 2H), 2.72 (s, 2H), 2.53 (s, 2H), 2.51 (s, 3H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 193.7, 155.5, 144.3, 140.9, 137.8, 135.0, 130.8, 130.3, 129.5, 127.9, 124.5, 121.6, 118.6, 112.7, 107.6, 52.4, 37.3, 35.7, 28.8, 21.7$ ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 349.1547, found: 349.1546.



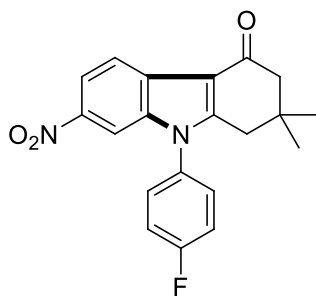
2,2-Dimethyl-7-nitro-9-o-tolyl-2,3-dihydro-1H-carbazol-4(9H)-one (3ah): Yield = 63%. Yellow solid. Mp = 138.6–139.9 °C. IR (KBr): ν = 2969, 2901, 1650, 1513, 1438, 1340, 1065, 880, 738, 655 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.37 (d, J = 8.7 Hz, 1H), 8.19 (dd, J = 8.7, 2.0 Hz, 1H), 7.80 (d, J = 1.9 Hz, 1H), 7.59–7.41 (m, 3H), 7.26 (d, J = 3.7 Hz, 1H), 2.70–2.54 (m, 2H), 2.53–2.42 (m, 2H), 1.97 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.6, 155.9, 144.4, 137.5, 136.5, 133.9, 132.1, 130.7, 129.4, 128.7, 128.1, 121.7, 118.6, 112.6, 107.3, 52.4, 36.9, 35.7, 29.2, 28.3, 17.5 ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 349.1547, found: 349.1549.



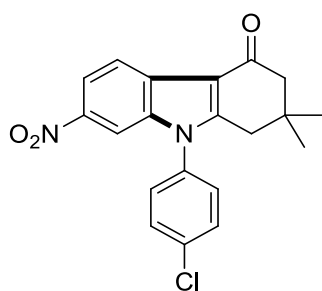
9-(4-Methoxy-2-methylphenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3ai): Yield = 55%. Yellow solid. Mp = 171.4–172.6 °C. IR (KBr): ν = 2965, 2901, 1648, 1504, 1337, 1245, 1055, 739 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.35 (d, J = 8.7 Hz, 1H), 8.18 (dd, J = 8.7, 1.9 Hz, 1H), 7.82 (d, J = 1.8 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 2.5 Hz, 1H), 6.94 (dd, J = 8.5, 2.7 Hz, 1H), 3.92 (s, 3H), 2.70–2.42 (m, 4H), 1.93 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.5, 161.0, 156.4, 144.3, 137.9, 129.6, 129.3, 126.3, 121.6, 118.5, 117.0, 113.2, 112.4, 107.3, 55.8, 52.4, 36.9, 35.7, 29.2, 28.3, 17.7 ppm. HRMS (m/z): calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 379.1652, found: 379.1651.



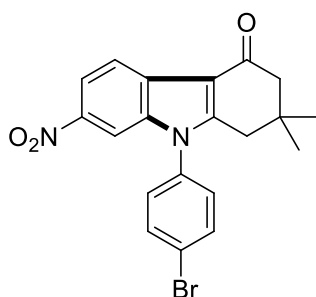
2,2-Dimethyl-7-nitro-9-phenyl-2,3-dihydro-1H-carbazol-4(9H)-one (3aj): Yield = 62%. Yellow solid. Mp = 172.1–173.6 °C. IR (KBr): ν = 3090, 2959, 2866, 1656, 1509, 1439, 1337, 1181, 1069, 881, 858, 826, 775, 740, 724, 693, 658 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.36 (d, J = 8.7 Hz, 1H), 8.19 (dd, J = 8.7, 2.0 Hz, 1H), 8.05 (d, J = 1.9 Hz, 1H), 7.70–7.61 (m, 3H), 7.39 (dd, J = 8.0, 1.3 Hz, 2H), 2.73 (s, 2H), 2.53 (s, 2H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 155.4, 144.4, 137.7, 135.1, 130.6, 130.0, 129.5, 127.5, 121.7, 118.6, 112.8, 107.5, 52.4, 37.3, 35.7, 28.8 ppm. HRMS (m/z): calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3$ [$\text{M}+\text{H}$] $^+$ 335.1390, found: 335.1397.



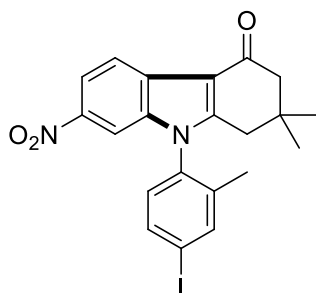
9-(4-Fluorophenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3ak): Yield = 55%. Yellow solid. Mp = 159.2–160.3 °C. IR (KBr): ν = 2961, 2927, 1655, 1508, 1337, 1227, 850, 729 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.35 (d, J = 8.7 Hz, 1H), 8.18 (dd, J = 8.7, 2.0 Hz, 1H), 8.00 (d, J = 1.9 Hz, 1H), 7.42–7.33 (m, 4H), 2.70 (s, 2H), 2.52 (s, 2H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.6, 163.1 (d, J = 249.8 Hz), 155.4, 144.4, 137.8, 131.0 (d, J = 3.3 Hz), 129.4 (d, J = 8.8 Hz), 121.7, 118.7, 117.9, 117.6, 112.9, 107.2, 52.3, 37.2, 35.7, 28.8 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ = -109.63 ppm. HRMS (m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{FN}_2\text{O}_3$ [$\text{M}+\text{H}$] $^+$ 353.1296, found: 353.1313.



9-(4-Chlorophenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3al): Yield = 63%. Yellow solid. Mp = 189.4–189.9 °C. IR (KBr): ν = 3093, 2947, 2869, 1657, 1608, 1513, 1493, 1403, 1333, 1179, 1089, 1014, 879, 850, 736 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.35 (d, J = 8.7 Hz, 1H), 8.18 (dd, J = 8.7, 1.9 Hz, 1H), 8.02 (d, J = 1.8 Hz, 1H), 7.65 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 2.72 (s, 2H), 2.52 (s, 2H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.6, 155.1, 144.4, 137.5, 136.1, 133.6, 130.9, 129.5, 128.8, 121.8, 118.7, 113.0, 107.1, 52.3, 37.3, 35.7, 28.8 ppm. HRMS (m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 369.1000, found: 369.0095.

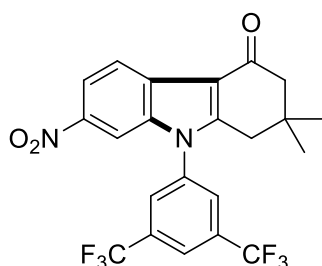


9-(4-Bromophenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3am): Yield = 64%. Yellow solid. Mp = 210.7–211.2 °C. IR (KBr): ν = 2960, 2948, 1656, 1513, 1438, 1332, 1067, 1010, 848, 736 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.34 (d, J = 8.7 Hz, 1H), 8.17 (dd, J = 8.7, 1.9 Hz, 1H), 8.02 (d, J = 1.8 Hz, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 2.72 (s, 2H), 2.52 (s, 2H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.6, 155.0, 144.5, 137.4, 134.1, 133.9, 129.5, 129.0, 124.1, 121.8, 118.8, 113.1, 107.2, 52.3, 37.3, 35.7, 28.8 ppm. HRMS (m/z): calcd for $\text{C}_{20}\text{H}_{18}^{81}\text{BrN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 415.0475, found: 415.0472.



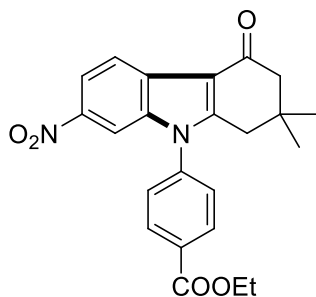
9-(4-Iodo-2-methylphenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3an): Yield = 71%. Yellow solid. Mp = 180.6–182.3 °C. IR (KBr): ν = 2959, 2931, 1648, 1512, 1336, 1177, 865, 734 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.36 (d, J = 8.7 Hz, 1H), 8.20 (dd, J = 8.7, 2.0 Hz, 1H), 7.88 (d, J = 1.2 Hz, 1H), 7.82–7.77 (m, 2H), 6.99 (d, J = 8.2 Hz, 1H), 2.69–2.42 (m,

4H), 1.93 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.4, 155.5, 144.5, 141.1, 138.9, 137.4, 137.2, 133.7, 130.3, 129.4, 121.9, 118.7, 112.8, 107.0, 96.7, 52.3, 36.9, 35.7, 29.2, 28.3, 17.2 ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{20}\text{IN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 475.0513, found: 475.0525.

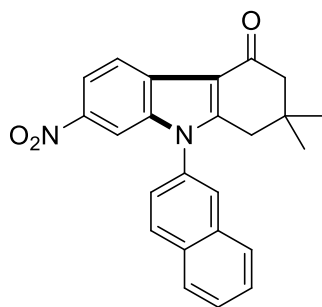


9-(3,5-Bis(trifluoromethyl)phenyl)-2,2-dimethyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one

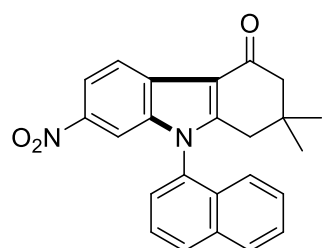
(3ao): Yield = 62%. Yellow solid. Mp = 180.1–181.3 °C. IR (KBr): ν = 3042, 2969, 2933, 1656, 1515, 1435, 1340, 1276, 1131, 1056, 889, 726, 709, 682 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.45 (d, J = 8.7 Hz, 1H), 8.28 (dd, J = 8.7, 1.8 Hz, 1H), 8.21 (s, 1H), 8.04 (d, J = 1.9 Hz, 1H), 7.96 (s, 2H), 2.76 (s, 2H), 2.60 (s, 2H), 1.24 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.5, 154.4, 144.9, 137.3, 137.0, 134.8, 134.4, 134.1, 129.6, 128.0, 124.0, 124.0, 124.0, 122.3, 121.2, 119.3, 113.8, 106.8, 52.2, 37.2, 35.9, 28.8 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ = -65.24 ppm. HRMS (m/z): calcd for $\text{C}_{22}\text{H}_{17}\text{F}_6\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 471.1138, found: 471.1156.



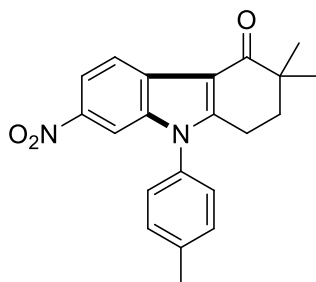
Ethyl 4-(2,2-dimethyl-7-nitro-4-oxo-3,4-dihydro-1H-carbazol-9(2H)-yl)benzoate (3ap): Yield = 31%. Yellow solid. Mp = 209.0–209.5 °C. IR (KBr): ν = 2923, 2363, 1718, 1662, 1509, 1439, 1275, 1129, 866, 738 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.40–8.32 (m, 3H), 8.19 (dd, J = 8.7, 2.0 Hz, 1H), 8.07 (d, J = 1.9 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H), 4.48 (q, J = 7.1 Hz, 2H), 2.75 (s, 2H), 2.54 (s, 2H), 1.46 (t, J = 7.1 Hz, 3H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.6, 165.4, 154.8, 144.5, 138.9, 137.2, 131.9, 131.9, 129.6, 127.3, 121.8, 118.8, 113.2, 107.2, 61.9, 52.3, 37.4, 35.8, 28.7, 14.5, 14.4 ppm. HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 407.1601, found: 407.1606.



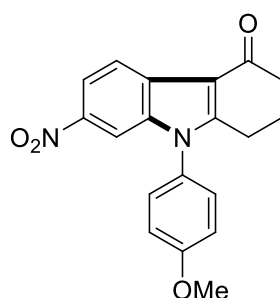
2,2-Dimethyl-9-(naphthalen-2-yl)-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3aq): Yield = 56%. Yellow solid. Mp = 208.2–210.2 °C. IR (KBr): ν = 3059, 2957, 2868, 1664, 1507, 1428, 1326, 1140, 1066, 861, 831, 738 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.38 (d, J = 8.7 Hz, 1H), 8.19 (dd, J = 8.7, 2.0 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 1.9 Hz, 1H), 8.05–8.00 (m, 1H), 7.99–7.94 (m, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.71–7.63 (m, 2H), 7.44 (dd, J = 8.6, 2.0 Hz, 1H), 2.77 (s, 2H), 2.54 (s, 2H), 1.15 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 155.7, 144.4, 137.9, 133.6, 133.4, 132.4, 130.9, 129.5, 128.4, 128.3, 128.0, 127.9, 126.5, 124.5, 121.7, 118.6, 112.8, 107.5, 52.4, 37.4, 35.7, 28.7 ppm. HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 385.1547, found: 385.1556.



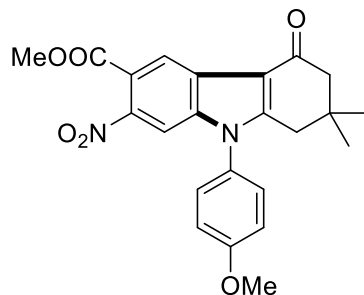
2,2-Dimethyl-9-(naphthalen-1-yl)-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3ar): Yield = 61%. Yellow solid. Mp = 208.8–209.4 °C. IR (KBr): ν = 2959, 2926, 1655, 1513, 1441, 1332, 1100, 775, 734 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.42 (d, J = 8.7 Hz, 1H), 8.21 (dd, J = 8.7, 2.0 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 1.9 Hz, 1H), 7.73–7.67 (m, 1H), 7.66–7.59 (m, 1H), 7.55 (dd, J = 7.2, 0.8 Hz, 1H), 7.50–7.44 (m, 1H), 7.05 (d, J = 8.4 Hz, 1H), 2.67–2.40 (m, 4H), 1.12 (s, 3H), 1.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.7, 156.8, 144.4, 138.6, 134.8, 131.3, 131.1, 130.5, 129.4, 129.1, 128.5, 127.7, 126.7, 125.9, 121.8, 121.7, 118.6, 112.7, 107.6, 52.4, 36.8, 35.7, 29.0, 28.2 ppm. HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 385.1547, found: 385.1559.



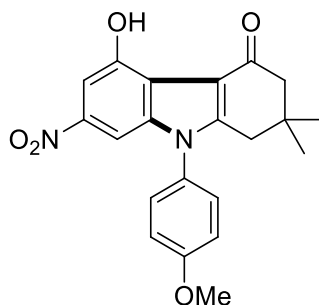
3,3-Dimethyl-7-nitro-9-*p*-tolyl-2,3-dihydro-1*H*-carbazol-4(9*H*)-one (3au): Yield = 28%. Yellow solid. Mp = 141.5–142.9 °C. IR (KBr): ν = 2964, 2921, 1658, 1515, 1333, 1308, 1070, 819, 744 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.38 (d, J = 8.7 Hz, 1H), 8.18 (dd, J = 8.7, 2.0 Hz, 1H), 8.05 (d, J = 1.9 Hz, 1H), 7.43 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 2.87 (t, J = 6.2 Hz, 2H), 2.51 (s, 3H), 2.08 (t, J = 6.2 Hz, 2H), 1.29 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 199.4, 155.1, 144.4, 140.1, 137.8, 132.5, 131.1, 130.4, 127.1, 121.8, 118.4, 112.0, 107.4, 42.1, 37.2, 24.5, 21.5, 20.7 ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 349.1547, found: 349.1550.



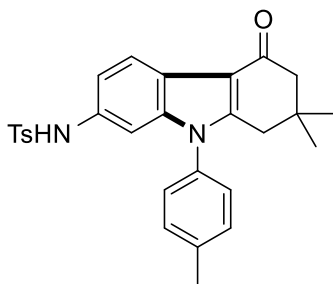
9-(4-Methoxyphenyl)-7-nitro-2,3-dihydro-1*H*-carbazol-4(9*H*)-one (3av): Yield = 41%. Yellow solid. Mp = 126.9–127.7 °C. IR (KBr): ν = 2960, 2923, 1511, 1423, 1334, 1244, 1023, 742, 683 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.36 (d, J = 8.7 Hz, 1H), 8.17 (dd, J = 8.7, 2.1 Hz, 1H), 8.02 (d, J = 2.1 Hz, 1H), 7.33–7.28 (m, 2H), 7.15–7.09 (m, 2H), 3.93 (s, 3H), 2.85 (t, J = 6.2 Hz, 2H), 2.65 (dd, J = 7.3, 5.5 Hz, 2H), 2.30–2.19 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 194.1, 160.3, 156.6, 144.1, 137.5, 129.4, 128.4, 127.3, 121.5, 118.3, 115.4, 113.4, 107.2, 55.7, 38.0, 23.2, 23.2 ppm. HRMS (m/z): calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 337.1183, found: 337.1178.



Methyl 9-(4-methoxyphenyl)-2,2-dimethyl-7-nitro-4-oxo-2,3,4,9-tetrahydro-1H-carbazole-6-carboxylate (3bc): Yield = 48%. Yellow solid. Mp = 110.6–112.5 °C. IR (KBr): ν = 2971, 2901, 1732, 1660, 1514, 1336, 1255, 1056, 847 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.57 (s, 1H), 7.73 (s, 1H), 7.30–7.26 (m, 2H), 7.15–7.11 (m, 2H), 3.94 (s, 3H), 3.94 (s, 3H), 2.70 (s, 2H), 2.52 (s, 2H), 1.15 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.4, 167.1, 160.8, 156.1, 144.3, 138.3, 128.6, 127.1, 127.1, 123.4, 123.0, 115.8, 113.0, 108.0, 56.0, 53.3, 52.3, 37.2, 35.7, 28.8 ppm. HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ 423.1551, found: 423.1557.



9-(4-Methoxyphenyl)-2,2-dimethyl-5,7-dinitro-2,3-dihydro-1H-carbazol-4(9H)-one (3dc): Yield = 30%. Yellow solid. Mp = 179.8–181.9 °C. IR (KBr): ν = 3082, 2961, 2851, 1612, 1517, 1441, 1408, 1336, 1280, 1256, 1173, 1020, 841, 774, 742, 643 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 11.11 (s, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.15–7.10 (m, 2H), 3.94 (s, 3H), 2.67 (s, 2H), 2.55 (s, 2H), 1.16 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 196.1, 160.8, 155.0, 151.8, 146.7, 139.4, 128.5, 127.3, 118.9, 115.7, 113.0, 103.5, 99.3, 56.0, 50.7, 36.9, 36.1, 28.7 ppm. HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 381.1445, found: 381.1451.



***N*-(2,2-Dimethyl-4-oxo-9-*p*-tolyl-2,3,4,9-tetrahydro-1*H*-carbazol-7-yl)-4-methylbenzenesulfonamide (8):** Yield = 43%. Yellow solid. Mp = 234.5–235.6 °C. IR (KBr): ν = 3258, 2961, 2937, 1645, 1493, 1407, 1335, 1158, 904, 659 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.05 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.21–7.13 (m, 4H), 7.04 (d, J = 1.8 Hz, 1H), 6.75 (dd, J = 8.3, 1.9 Hz, 1H), 6.64 (s, 1H), 2.63 (s, 2H), 2.49 (s, 3H), 2.46 (s, 2H), 2.37 (s, 3H), 1.11 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 193.8, 151.8, 143.7, 139.2, 138.8, 136.0, 133.0, 132.0, 130.6, 129.5, 127.4, 126.9, 122.6, 121.8, 118.8, 112.1, 106.1, 52.2, 37.0, 35.5, 28.6, 21.6, 21.2 ppm. HRMS (m/z): calcd for $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 473.1893, found: 473.1889.

The ^1H and ^{13}C NMR spectra of products

