Synthesis of Pyrrolo[3,2-*b*]carbazole Derivatives via Palladium-Catalyzed C–H Activation

Rama Raju Jella, Rajagopal Nagarajan*

School of Chemistry, University of Hyderabad, Hyderabad 500046, India
Fax +91(40)23012460; E-mail: rnsc@uohyd.ernet.in

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Abstract: A simple method for the synthesis of different pyrrolo[3,2-*b*]carbazole derivatives by the reaction of 3-(acetylamino)carbazoles with various symmetrical diaryl-substituted alkynes via palladium-catalyzed C–H activation is reported.

Key words: 3-aminocarbazoles, palladium catalysis, pyrrolo[3,2-*b*]carbazoles, C–H activation, diarylacetylenes

The synthesis of different heteroaryl-condensed carbazoles has emerged as a major research area due to the promising biological properties of such compounds.[1,2] Their derivatives also show promising electronic and optical properties.[3] The pyrrolocarbazole skeleton, with a pyrrole ring fused to a carbazole, frequently occurs in marine alkaloids[4] such as the dictyodendrins A–E (Figure 1). These compounds have a broad spectrum of bioactivities including anticancer, antidiabetic, neurotrophic and protein kinase C (PKC) inhibitory properties.[5] Pyrrolo[3,2-*b*]carbazoles exhibit high antitumour activity with low toxicity against normal cell lines.[6a] In the literature, the synthesis of pyrrolo[3,2-*b*]carbazoles has been less explored than other pyrrolocarbazole analogues.[6b–e]

In recent years, direct C–H bond activation by using different transition-metal catalysts has attracted significant interest because these methods eliminate the multistep preparation of preactivated starting materials.[7,8] The palladium-catalyzed direct functionalization of C–H bonds via the C–H activation pathway represents an important and atom-economic strategy to prepare complex structures.[9] The transition-metal-catalyzed direct C–H bond activation of *N*-aryl amides coupled with alkynes has attracted much attention due to its sustainable and environmentally benign features.[7] In this paper, we wish to report the synthesis of different pyrrolo[3,2-*b*]carbazole derivatives in a regioselective manner via palladium-catalyzed C–H activation.

We started with the reaction of 3-(acetylamino)carbazole[10] **1a** and diphenylacetylene (**2a**) (Table 1) with 10 mol% of $Pd(OAc)_2$ using $Cu(OAc)_2$ as oxidant, and we obtained the product as a single regioisomer, but in trace yield (Table 1, entry 2). When $CuCl_2$ was used as oxidant, the yield was significantly improved, but a complex mixture of byproducts was observed (Table 1, entries 3 and 4). Meanwhile, when we used $Cu(OTf)_2$ as oxidant, the product **3a** was obtained without any byproducts, but in low yield. We continued optimization by using different additives (Ag_2CO_3, AgOAc, Ag_2O) and found that Ag_2O gave a moderate yield when used as additive (Table 1, entries 5–9). We also screened different palladium sources [$Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$]; $Pd(OAc)_2$ was found to be the best catalyst (Table 1, entries 6, 10 and 11). *N*,*N*-Dimethylacetamide (DMA) proved to be the best solvent, based on a better solubility of the starting materials. Finally, the best optimized conditions were as follows: 3-(acetylamino)carbazole (1.0 equiv), alkyne (1.5 equiv), $Pd(OAc)_2$ (10 mol%), $Cu(OTf)_2$ (1 equiv) and Ag_2O (1 equiv) in DMA at 120 °C under N_2 (Table 1, entry 6).

With these optimized conditions, we examined the scope of the reaction by taking different N^9-substituted and 6-substituted 3-aminocarbazoles **1** (Table 2). A variety of internal alkynes **2** having electron-donating or electron-withdrawing groups were also employed in this reaction. The reaction went smoothly with the 6-methyl-substituted 3-aminocarbazole **1** (R^1 = Et, R^2 = Me), and gave the product **3f** in 70% yield, while the 6-bromo-substituted 3-

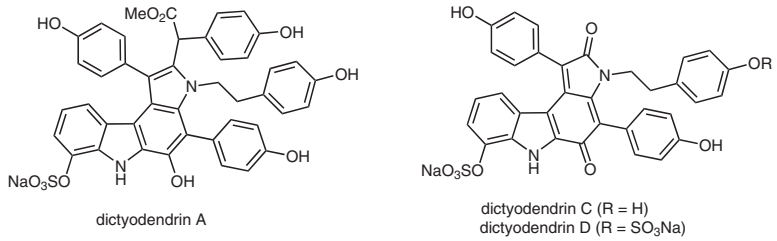

Figure 1 Naturally occurring pyrrolocarbazole alkaloids

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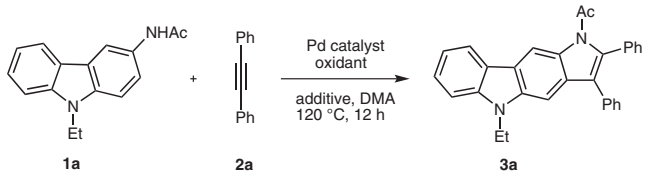
Table 1 Optimization of the Reaction Conditions for the Synthesis of Pyrrolo[3,2-*b*]carbazole **3a**[a]

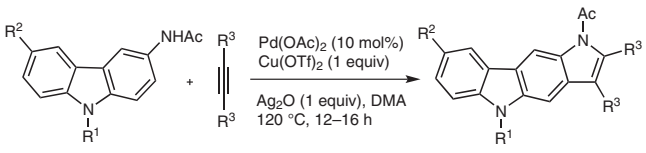


1a 2a 3a

Entry	Catalyst (10 mol%)	Oxidant (equiv)	Additive (equiv)	Yield[b] (%) of **3a**
1	$Pd(OAc)_2$	air	–	–
2	$Pd(OAc)_2$	$Cu(OAc)_2$ (2.0)	–	trace
3	$Pd(OAc)_2$	$CuCl_2$ (2.0)	–	30
4	$Pd(OAc)_2$	$CuCl_2$ (2.0)	Ag_2CO_3 (1.0)	24
5	$Pd(OAc)_2$	$Cu(OTf)_2$ (2.0)	–	35
6	$Pd(OAc)_2$	$Cu(OTf)_2$ (1.0)	Ag_2O (1.0)	64
7	$Pd(OAc)_2$	$Cu(OTf)_2$ (1.0)	Ag_2CO_3 (1.0)	20
8	$Pd(OAc)_2$	$Cu(OTf)_2$ (1.0)	AgOAc (1.0)	12
9	$Pd(OAc)_2$	$Cu(OTf)_2$ (0.5)	Ag_2O (1.0)	30
10	$PdCl_2$	$Cu(OTf)_2$ (1.0)	Ag_2O (1.0)	25
11	$Pd(PPh_3)_2Cl_2$	$Cu(OTf)_2$ (1.0)	Ag_2O (1.0)	10

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.6 mmol), Pd catalyst (10 mol%), DMA (3.0 mL), 120 °C, under N_2.
[b] Isolated yield.

Table 2 Synthesis of Various Pyrrolo[3,2-*b*]carbazole Derivatives **3**



1 2 3a–m

3	R^1	R^2	R^3	Time (h)	Yield (%)
3a	Et	H	Ph	12	64
3b	Me	H	Ph	12	62
3c	*n*-Bu	H	Ph	12	64
3d	Bn	H	Ph	12	58
3e	Et	Br	Ph	16	54
3f	Et	Me	Ph	12	70
3g	Et	H	4-MeC_6H_4	12	68
3h	Et	H	4-$MeOC_6H_4$	12	68
3i	Et	H	4-ClC_6H_4	14	52
3j	Et	H	3,5-$Me_2C_6H_3$	12	66
3k	Et	Me	4-$MeOC_6H_4$	12	72
3l	Et	Cl	4-$MeOC_6H_4$	14	58
3m	*n*-Hex	H	4-$MeOC_6H_4$	12	68

aminocarbazole **1** (R^1 = Et, R^2 = Br) gave the product **3e** in 54% yield. The diarylacetylenes bearing electron-donating groups gave better yields than the alkynes with electron-withdrawing groups. We also investigated the reaction with unsymmetrically disubstituted alkynes, but ended up with inseparable mixtures of products in low yields.

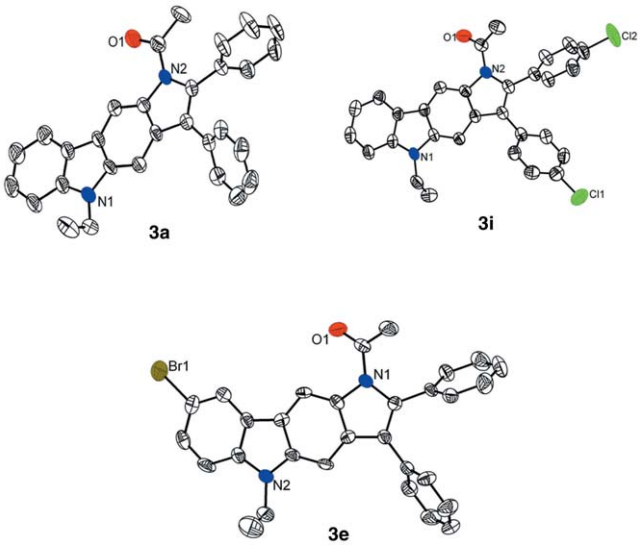
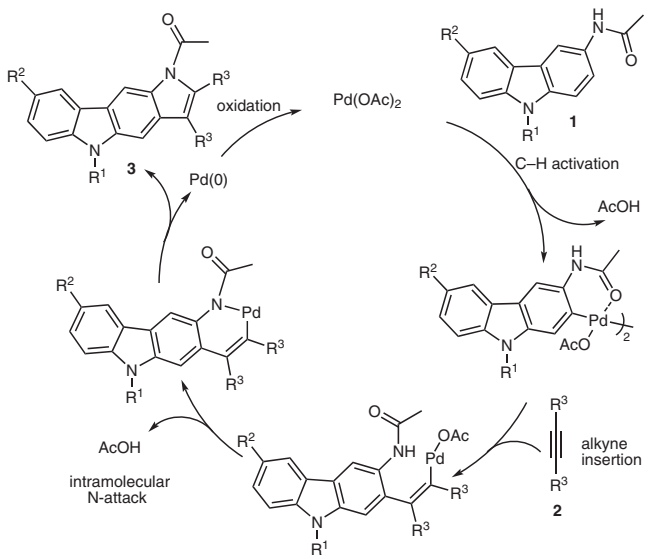


Figure 2 X-ray crystal structures of **3a**, **3e** and **3i**

The structures of products **3a**, **3e** and **3i** were further confirmed by single crystal X-ray analysis,[11] as shown in Figure 2.

Based on the literature,[9f] the mechanism for the palladium-catalyzed C–H activation reaction involves a six-membered palladacycle generated by the acetylamino group, that gives a vinylic palladium(II) intermediate by the insertion of alkyne **2** (Scheme 1). Intramolecular amide attack and subsequent deprotonation gives a palladium amide intermediate, which on reductive elimination affords the corresponding pyrrolocarbazole product **3**. $Cu(OTf)_2$ and Ag_2O are utilized for the reoxidation of the palladium(0) complex to the palladium(II) species in the reaction.

In summary, we have developed a simple method with easily prepared starting materials for the synthesis of different pyrrolo[3,2-*b*]carbazoles in moderate to good yields via palladium-catalyzed C–H activation. The reaction occurs regioselectively giving exclusively one regioisomer. The reaction works well with various symmetrical diaryl-substituted alkynes bearing electron-donating or electron-withdrawing substituents.



Scheme 1 Proposed mechanism for palladium-catalyzed C–H activation

Unless otherwise stated, all commercial reagents were used without further purification. All solvents were dried and distilled according to standard procedures. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a Bruker AV-400 instrument. The chemical shifts are reported in ppm downfield to TMS (δ = 0) for ^{1}H NMR data and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR data. The coupling constants *J* are given in Hz. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer by using KBr pellets. Mass spectra were recorded on either a VG7070H mass spectrometer using EI techniques or a Shimadzu LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonius MACH 3 diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates (Merck 60 F254) were used. Column chromatography was performed on silica gel (100–200 mesh) in glass columns for compound purification. Melting points were measured in open capillary tubes and are uncorrected.

Palladium-Catalyzed Synthesis of Pyrrolo[3,2-*b*]carbazoles 3; General Procedure

To a Schlenk tube, a 3-(acetylamino)carbazole **1** (0.4 mmol), a diarylacetylene **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol%), Ag_2O (1.0 equiv), $Cu(OTf)_2$ (1.0 equiv) and DMA (3.0 mL) were added successively under N_2. The mixture was stirred at r.t. for a few min. Then, the tube was placed in a preheated (120 °C) oil bath, and stirred. After completion of the reaction (TLC monitoring), the solution was cooled to r.t., diluted with EtOAc (30 mL), washed with H_2O (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 8.5:1.5) to afford the product **3**.

1-(5-Ethyl-2,3-diphenyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3a)

Brown solid; yield: 0.110 g (64%); mp 162–164 °C.

IR (KBr): 2964, 1689, 1601, 1473, 1439, 1394, 1300, 1261, 1099, 800, 744 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.29 (s, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 7.51–7.47 (m, 1 H), 7.41–7.32 (m, 12 H), 7.28–7.24 (m, 1 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 2.06 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 141.1, 138.1, 135.9, 133.6, 133.3, 131.8, 130.8, 130.2, 129.0, 128.5, 128.3, 126.9, 125.7, 123.9, 123.6, 122.5, 120.6, 118.5, 108.1, 108.0, 97.1, 37.5, 28.1, 13.5.

MS (ESI, +): *m*/*z* = 429 [M + H]$^+$.

Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.22; H, 5.58; N, 6.65.

1-(5-Methyl-2,3-diphenyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3b)

Colorless solid; yield: 0.102 g (62%); mp 130–132 °C.

IR (KBr): 3379, 3055, 2928, 1682, 1599, 1422, 1365, 1298, 1091, 802, 744 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.30 (s, 1 H), 8.27 (d, *J* = 7.6 Hz, 1 H), 7.53–7.19 (m, 14 H), 3.84 (s, 3 H), 2.08 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 142.2, 139.3, 135.8, 133.5, 133.3, 131.8, 130.8, 130.2, 129.1, 128.5, 128.3, 126.9, 125.7, 123.9, 123.4, 122.3, 120.5, 118.5, 108.1, 107.9, 97.2, 29.2, 28.1.

MS (ESI, +): *m*/*z* = 415 [M + H]$^+$.

Anal. Calcd for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 84.12; H, 5.32; N, 6.81.

1-(5-Butyl-2,3-diphenyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3c)

Brown solid; yield: 0.117 g (64%); mp 194–196 °C.

IR (KBr): 3387, 3055, 2953, 2860, 1691, 1602, 1466, 1394, 1296, 1126, 879 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.29 (s, 1 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 7.51–7.47 (m, 1 H), 7.40–7.33 (m, 12 H), 7.28–7.24 (m, 1 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 2.06 (s, 3 H), 1.85 (t, *J* = 7.4 Hz, 2 H), 1.41–1.35 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 141.6, 138.7, 135.9, 133.6, 133.3, 131.7, 130.8, 130.2, 129.0, 128.5, 128.3, 126.9, 125.6, 123.8, 123.5, 122.4, 120.5, 118.4, 108.4, 107.9, 97.3, 42.8, 30.9, 28.0, 20.5, 13.9.

MS (ESI, +): *m*/*z* = 456 [M]$^+$.

Anal. Calcd for $C_{32}H_{28}N_2O$: C, 84.18; H, 6.18; N, 6.14. Found: C, 83.75; H, 6.51; N, 6.23.

1-(5-Benzyl-2,3-diphenyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3d)

Colorless solid; yield: 0.114 g (58%); mp 210–212 °C.

IR (KBr): 3414, 2922, 1684, 1601, 1437, 1369, 1178, 1024, 958, 877 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 (s, 1 H), 8.28 (d, *J* = 7.2 Hz, 1 H), 7.43–7.38 (m, 6 H), 7.32–7.13 (m, 13 H), 5.51 (s, 2 H), 2.05 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 141.7, 138.9, 137.2, 135.9, 133.3, 133.2, 132.0, 130.8, 130.1, 129.1, 128.7, 128.5, 128.3, 127.3, 126.9, 126.4, 125.9, 123.79, 123.73, 122.5, 120.6, 119.0, 108.7, 108.0, 97.7, 46.6, 28.0.

MS (ESI, –): *m*/*z* = 490 [M]$^-$.

Anal. Calcd for $C_{35}H_{26}N_2O$: C, 85.69; H, 5.34; N, 5.71. Found: C, 85.51; H, 5.41; N, 5.65.

1-(8-Bromo-5-ethyl-2,3-diphenyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3e)

Yellow solid; yield: 0.109 g (54%); mp 202–204 °C.

IR (KBr): 3057, 2974, 1685, 1458, 1392, 1302, 1186, 1109, 964, 860 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 1 H), 8.36 (d, *J* = 1.6 Hz, 1 H), 7.57–7.55 (m, 1 H), 7.39–7.37 (m, 8 H), 7.34–7.25 (m, 4 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 2.06 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 139.7, 138.3, 136.4, 133.4, 133.1, 131.9, 130.7, 130.2, 129.7, 128.6, 128.5, 128.4, 128.2, 127.0, 125.4, 123.7, 123.3, 121.3, 111.2, 109.5, 108.2, 97.3, 37.7, 28.0, 13.4.

MS (ESI, –): *m*/*z* = 506 $[M]^-$.

Anal. Calcd for $C_{30}H_{23}BrN_2O$: C, 71.01; H, 4.57; N, 5.52. Found: C, 71.12; H, 4.52; N, 5.61.

1-(5-Ethyl-8-methyl-2,3-diphenyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3f)
Brown solid; yield: 0.124 g (70%); mp 104–106 °C.

IR (KBr): 3443, 3055, 2922, 2854, 1682, 1483, 1367, 752, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.25 (s, 1 H), 8.07 (s, 1 H), 7.38–7.28 (m, 13 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 2.58 (s, 3 H), 2.06 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 139.4, 138.4, 135.8, 133.6, 133.3, 131.6, 130.8, 130.2, 128.9, 128.5, 128.3, 127.8, 126.9, 123.9, 123.7, 122.4, 120.7, 107.9, 107.8, 97.0, 37.5, 28.1, 21.4, 13.5.

MS (ESI, –): *m*/*z* = 441 [M – H].

Anal. Calcd for $C_{31}H_{26}N_2O$: C, 84.13; H, 5.92; N, 6.33. Found: C, 84.31; H, 5.85; N, 6.29.

1-(5-Ethyl-2,3-di-*p*-tolyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3g)
Brown solid; yield: 0.124 g (68%); mp 220–222 °C.

IR (KBr): 3412, 3028, 2974, 1687, 1602, 1469, 1394, 1302, 1184, 1018, 962, 881 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (s, 1 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.39 (d, *J* = 5.2 Hz, 2 H), 7.28–7.23 (m, 5 H), 7.19 (d, *J* = 8.0 Hz, 4 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 2.40 (s, 6 H), 2.06 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 141.1, 138.4, 138.1, 136.4, 135.9, 131.7, 130.6, 130.4, 130.0, 129.2, 129.1, 125.5, 123.6, 123.5, 122.3, 120.6, 118.4, 108.1, 108.0, 97.1, 37.5, 28.0, 21.4, 21.3, 13.5.

MS (ESI, +): *m*/*z* = 457 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{28}N_2O$: C, 84.18; H, 6.18; N, 6.14. Found: C, 84.07; H, 6.09; N, 6.19.

1-(5-Ethyl-2,3-bis(4-methoxyphenyl)-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3h)
Brown solid; yield: 0.133 g (68%); mp 232–234 °C.

IR (KBr): 3449, 2976, 2841, 1682, 1602, 1396, 1365, 1244, 1126, 1024, 962, 875 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (s, 1 H), 8.25 (d, *J* = 7.6 Hz, 1 H), 7.50–7.46 (m, 1 H), 7.40–7.36 (m, 2 H), 7.30–7.25 (m, 5 H), 6.93–6.90 (m, 4 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 3.85 (s, 6 H), 2.07 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 159.6, 158.4, 141.0, 138.1, 135.6, 132.0, 131.6, 131.2, 129.3, 125.9, 125.5, 123.6, 123.2, 122.3, 120.6, 118.4, 114.0, 113.8, 108.1, 97.0, 55.2, 55.0, 37.5, 28.0, 13.5.

MS (ESI, +): *m*/*z* = 489 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{28}N_2O_3$: C, 78.67; H, 5.78; N, 5.73. Found: C, 78.56; H, 5.71; N, 5.66.

1-(2,3-Bis(4-chlorophenyl)-5-ethyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3i)
Brown solid; yield: 0.104 g (52%); mp 202–204 °C.

IR (KBr): 3437, 3055, 1682, 1604, 1477, 1392, 1128, 1086, 1012, 875, 821 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (s, 1 H), 8.24 (d, *J* = 7.6 Hz, 1 H), 7.52–7.48 (m, 1 H), 7.44–7.36 (m, 5 H), 7.31–7.28 (m, 3 H), 7.24–7.22 (m, 3 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 2.10 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 141.2, 138.1, 134.8, 134.6, 133.1, 131.9, 131.4, 129.0, 128.8, 128.6, 125.9, 123.4, 123.2, 122.8, 120.7, 118.6, 108.2, 108.0, 96.8, 37.5, 28.2, 13.5.

MS (ESI, +): *m*/*z* = 498 $[M + 2 H]^+$.

Anal. Calcd for $C_{30}H_{22}Cl_2N_2O$: C, 72.44; H, 4.46; N, 5.63. Found: C, 72.59; H, 4.42; N, 5.71.

1-(2,3-Bis(3,5-dimethylphenyl)-5-ethyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3j)
Brown solid; yield: 0.128 mg (66%); mp 106–108 °C.

IR (KBr): 3449, 2918, 1693, 1601, 1466, 1442, 1304, 1157, 1033, 848, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.27 (s, 1 H), 8.25 (d, *J* = 7.6 Hz, 1 H), 7.50–7.46 (m, 1 H), 7.40–7.39 (m, 2 H), 7.27–7.23 (m, 1 H), 7.01–6.96 (m, 6 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 2.31–2.30 (m, 12 H), 2.07 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7, 141.1, 138.1, 137.8, 137.5, 136.2, 133.4, 133.1, 131.7, 130.0, 129.3, 128.5, 128.0, 125.5, 123.7, 122.3, 120.6, 118.4, 108.1, 107.9, 97.2, 37.5, 28.0, 21.4, 21.2, 13.5.

MS (ESI, +): *m*/*z* = 485 $[M + H]^+$.

Anal. Calcd for $C_{34}H_{32}N_2O$: C, 84.26; H, 6.66; N, 5.78. Found: C, 84.15; H, 6.62; N, 5.71.

1-(5-Ethyl-2,3-bis(4-methoxyphenyl)-8-methyl-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3k)
Brown solid; yield: 0.144 g (72%); mp 212–214 °C.

IR (KBr): 3412, 2932, 1685, 1610, 1493, 1392, 1367, 1298, 1246, 1174, 1032, 962, 877 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (s, 1 H), 8.05 (s, 1 H), 7.33–7.24 (m, 7 H), 6.93–6.89 (m, 4 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 3.84 (s, 6 H), 2.57 (s, 3 H), 2.06 (s, 3 H), 1.37 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 159.6, 158.4, 139.3, 138.3, 135.5, 133.0, 132.0, 131.5, 131.2, 129.2, 127.7, 126.8, 125.9, 125.6, 123.8, 123.2, 122.1, 120.6, 114.0, 113.8, 108.0, 107.8, 96.9, 55.26, 55.20, 37.5, 28.0, 21.4, 13.5.

MS (ESI, +): *m*/*z* = 503 $[M + H]^+$.

Anal. Calcd for $C_{33}H_{30}N_2O_3$: C, 78.86; H, 6.02; N, 5.57. Found: C, 78.69; H, 6.12; N, 5.65.

1-(8-Chloro-5-ethyl-2,3-bis(4-methoxyphenyl)-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3l)
Brown solid; yield: 0.121 g (58%); mp 196–198 °C.

IR (KBr): 3414, 2932, 1685, 1610, 1458, 1392, 1298 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (s, 1 H), 8.18 (s, 1 H), 7.42–7.23 (m, 7 H), 6.92–6.90 (m, 4 H), 4.31 (q, *J* = 7.2 Hz, 2 H), 3.84 (s, 6 H), 2.06 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 159.7, 158.5, 139.3, 138.5, 136.1, 131.9, 131.2, 130.0, 128.1, 125.7, 125.4, 124.8, 123.9, 121.2, 120.2, 114.0, 113.9, 109.0, 108.2, 97.2, 55.27, 55.20, 37.7, 28.0, 13.5.

MS (ESI, +): *m*/*z* = 524 $[M + 2 H]^+$.

Anal. Calcd for $C_{32}H_{27}ClN_2O_3$: C, 73.49; H, 5.20; N, 5.36. Found: C, 73.32; H, 5.31; N, 5.15.

1-(5-Hexyl-2,3-bis(4-methoxyphenyl)-1,5-dihydropyrrolo[3,2-*b*]carbazol-1-yl)ethanone (3m)
Brown solid; yield: 0.148 g (68%); mp 204–206 °C.

IR (KBr): 3441, 2928, 1691, 1604, 1583, 1439, 1363, 1244, 1174, 1026, 962, 829 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (s, 1 H), 8.25 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.41–7.38 (m, 2 H), 7.32–7.26 (m, 5

H), 6.94–6.92 (m, 4 H), 4.29 (t, J = 7.0 Hz, 2 H), 3.86 (s, 6 H), 2.08 (s, 3 H), 1.90–1.83 (m, 2 H), 1.38–1.30 (m, 6 H), 1.28 (t, J = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 159.6, 158.4, 141.5, 138.6, 135.6, 132.0, 131.6, 131.2, 129.3, 125.9, 125.5, 123.5, 123.2, 122.1, 120.5, 118.4, 114.0, 113.8, 108.3, 108.0, 97.2, 55.27, 55.20, 43.0, 31.5, 28.6, 28.0, 26.9, 22.5, 14.0.

MS (ESI, +): m/z = 543 $[M - H]^-$.

Anal. Calcd for $C_{36}H_{36}N_2O_3$: C, 79.38; H, 6.66; N, 5.14. Found: C, 79.18; H, 6.61; N, 5.21.

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(11) The crystal data for compounds **3a**, **3e** and **3i** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 892569 (**3a**), 892570 (**3e**) and 892571 (**3i**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk] or via www.ccdc.cam.ac.uk/data_request/cif. Compound **3a**: $C_{30}H_{24}N_2O$; unit cell parameters: a = 10.2471(14) Å, b = 11.6921(11) Å, c = 19.105(3) Å, β = 99.605(11)°, space group *P21/c*. Compound **3e**: $C_{30}H_{23}BrN_2O$; unit cell parameters: a = 6.6599(13) Å, b = 19.948(4) Å, c = 17.974(3) Å, β = 98.107(18)°, space group *P21/n*. Compound **3i**: $C_{30}H_{22}Cl_2N_2O$; unit cell parameters: a = 8.3466(18) Å, b = 33.171(5) Å, c = 10.746(3) Å, β = 126.096(16)°, space group *P21/c*.

