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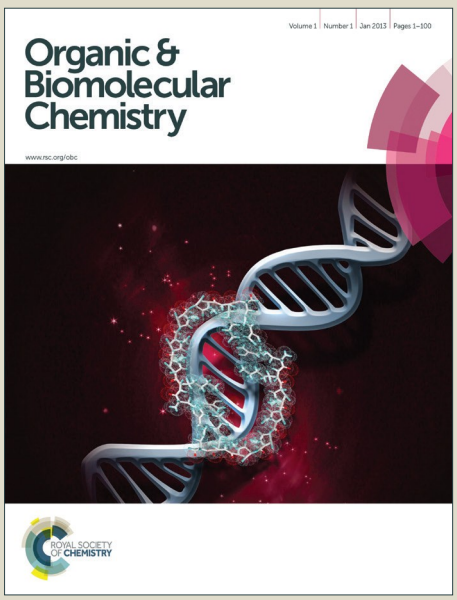

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Organic & Biomolecular Chemistry

ARTICLE

One-Pot Synthesis of Carbazoles via Tandem C-C Cross-Coupling and Reductive Amination

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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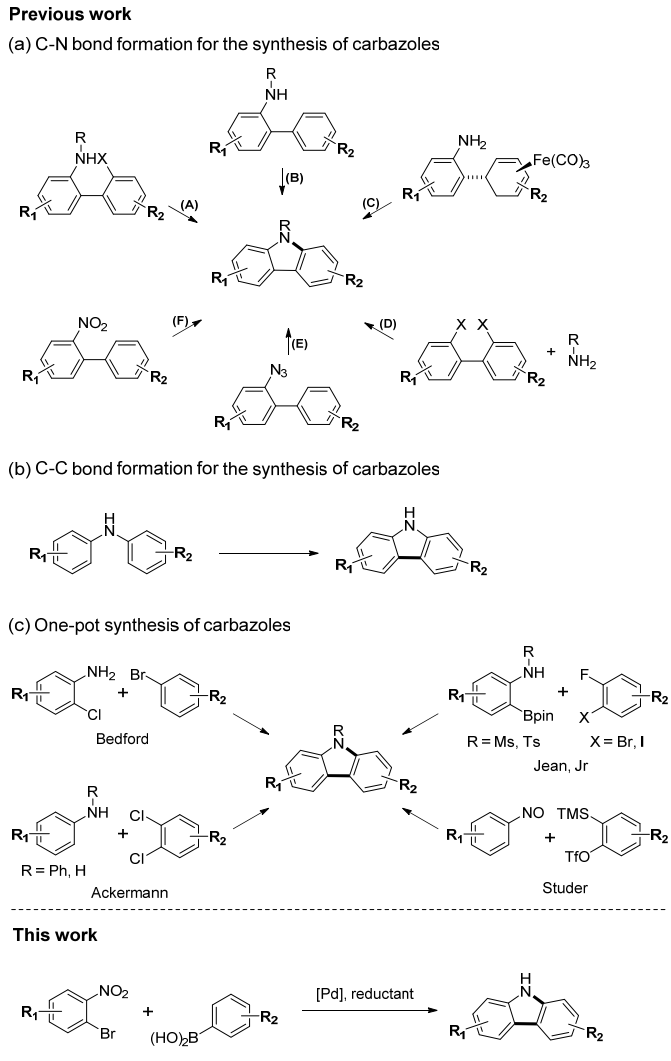
We have developed a highly efficient synthetic route to carbazoles that employs sequential C-C/C-N bond formation via Suzuki cross-coupling and Cadogan cyclization using commercially available or easily preparable starting materials. The developed method is compatible with electron neutral, rich or deficient substrates. The synthetic utility of this method was demonstrated by the concise syntheses of four natural products (glycozoline, glycozolicine, glycozolidine and clausenalene).

Introduction

The Carbazole is an ubiquitous structural motif in a large number of biologically active natural products and pharmaceuticals.[1] In addition, carbazole derivatives have been widely used as functional organic materials.[2] Thus, development of efficient synthetic routes to structurally diverse carbazoles represents an important objective in organic synthesis. Many methods have been developed for the preparation of carbazole.[3] The most widely used approaches for synthesis of the carbazole framework are C-N or C-C bond forming cyclizations from substituted biaryls or *N,N*-biaryl amines. Representative C-N bond forming reactions for synthesis of carbazoles are summarized in Scheme 1 (a): (A) transition metal free[4] or palladium catalyzed Buchwald-Hartwig[5] amination from 2-amino-2'-halo-biphenyls; (B) dehydrogenative C-H/N-H coupling of 2-amino-biphenyls[6]; (C) iron-mediated oxidative amination of iron complex[7]; (D) transition metal mediated double amination of 2,2'-dihalobiphenyls or cyclic diphenyleneiodoniums[8]; (E) transition metal free[9] or rhodium catalyzed[10] nitrene insertion of 2-azido-biphenyls; (F) reductive amination of 2-nitro-biphenyls[11]. Similarly, dehydrogenative C-C bond formation of *N,N*-biaryl amines leads to carbazoles (Scheme (b)).[12] Although these methods proceed in good yields and are tolerant of most organic functional groups. They require the preparation of complex starting materials, such as substituted biaryls or *N,N*-biaryl amines for the synthesis of diverse carbazoles. Therefore, we investigated the development of a one-pot C-C and C-N bond coupling reaction that utilizes commercially available or easily preparable starting materials.



Scheme 1. Various synthetic approaches to carbazoles.

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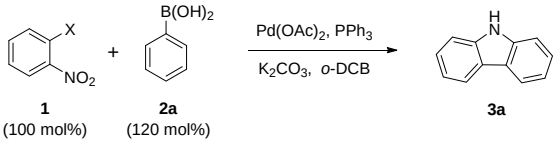
†Electronic Supplementary Information (ESI) available: Details of experimental procedures and spectroscopic data for all new com-pounds (^{1}H NMR, ^{13}C NMR, IR, MS), including images of NMR spectra. See DOI: 10.1039/x0xx00000x

Table 1. Optimization of the reaction conditions[a]



1 (100 mol%) **2a** (120 mol%) **3a**

Entry	**1**, X	Catalyst (mol%)	Reductant	T (^oC)	time (h)	Y (%)[b]
1	1a, I	Pd(OAc) (2)	PPh_3	150	16	24
2	1b, Br	Pd(OAc) (2)	PPh_3	150	16	56
3	1c, Cl	Pd(OAc) (2)	PPh_3	150	16	31
4	1b, Br	Pd(OAc) (2)	PEt_3	150	16	12
5	1b, Br	Pd(OAc) (2)	$P(OEt)_3$	150	16	21
6	1b, Br	$Pd_2(dba)_3$ (2)	PPh_3	150	16	41
7	1b, Br	$Pd(PPh_3)_4$ (2)	PPh_3	150	16	29
8	1b, Br	Pd(OAc) (1)	PPh_3	150	16	17
9	1b, Br	Pd(OAc) (4)	PPh_3	150	16	13
10	1b, Br	Pd(OAc) (2)	PPh_3	180	16	72
11	1b, Br	Pd(OAc) (2)	PPh_3	180	24	78
12[c]	1b, Br	Pd(OAc) (2)	PPh_3	Reflux	24	66
⇨ **13**[d]	**1b, Br**	**Pd(OAc) (2)**	**PPh_3**	**180**	**24**	**86**

[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), catalyst (quantity noted), reductant (250 mol%), K_2CO_3 (200 mol%), *o*-DCB (1.0 mL) under air in pressure tubes. [b]Isolated yield by flash column chromatography. [c]Using reflux condenser. [d]**2a** (130 mol%).

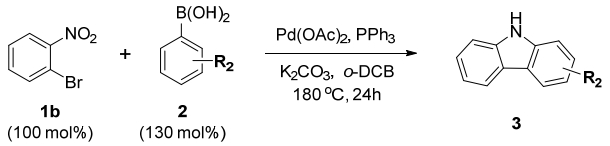
More recently, one-pot syntheses of carbazoles have been developed (Scheme 1 (c)).[13] Bedford[13a] and Ackermann[13b, 13d] reported a palladium catalyzed domino Buchwald-Hartwig amination and C-H activation of 2-chloroanilines with aryl bromides or anilines with dichloroarenes. Jean, Jr[13c] reported the Pd-catalyzed tandem Suzuki cross-coupling and S_NAr reaction of aniline-derived boronic esters with 2-fluoro-3-halobenzenes. Studer[13f] reported a transition metal-free cascade reaction of nitrosoarenes with *in situ* generated arynes.

We envision a one-pot reaction sequence of C-C cross-coupling and C-N bond forming cyclization to develop a step-economic method to prepare carbazoles. We considered the Suzuki reaction[14] and Cadogan cyclization[15] for the one-pot reaction. Both reactions are widely used methods for C-C cross-coupling or reductive amination and use similar phosphine reagents for ligand or reductant[15d]. Herein, we present a highly efficient synthetic method to carbazoles that consists of palladium-catalyzed tandem C-C/C-N bond formation via Suzuki reaction and reductive Cadogan cyclization (Scheme 1).

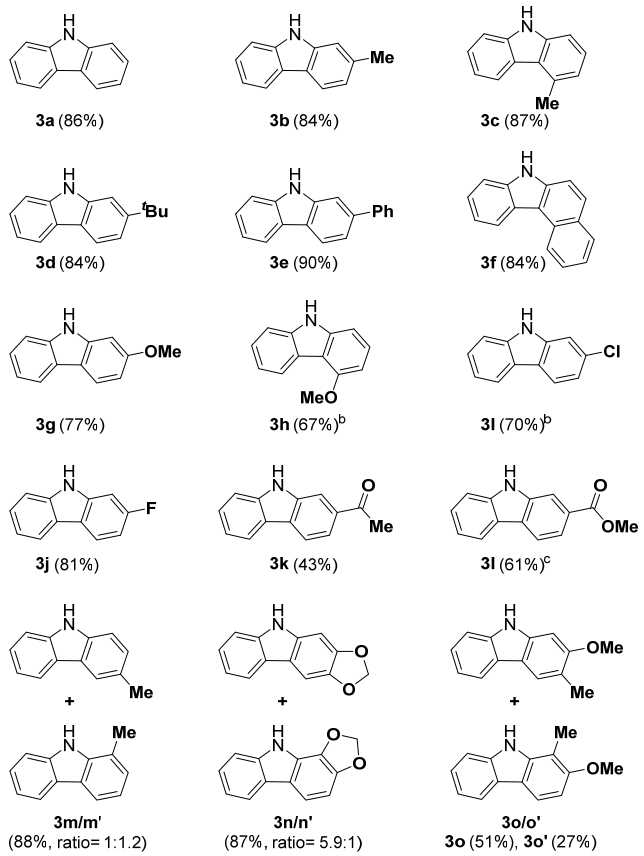
Results and discussion

Initially, we explored the domino reaction of 2-iodonitrobenzene **1a** with phenylboronic acid **2a** in the presence of $Pd(OAc)_2$ and triphenylphosphine in *o*-DCB at 150 ^oC, which delivered the carbazole **3a** and 2-nitrobiphenyl in 24% and 20% yield (Table 1, entry 1). Based on this result, other 2-halonitrobenzenes were assayed, and it was found that 2-bromonitrobenzene **1b** was the most efficient (Table 1, entry 2).

Table 2. Substrate scope of various aryl boronic acids[a]



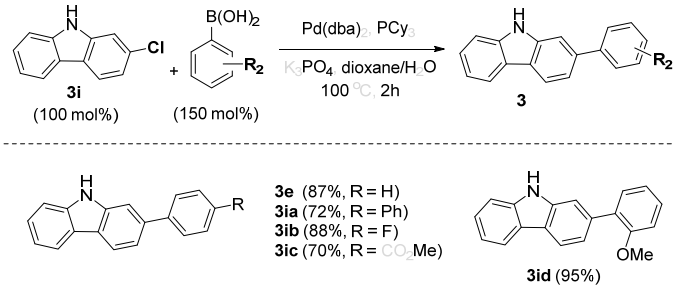
1b (100 mol%) **2** (130 mol%) **3**



[a]As given in Table 1, entry 13. [b]48h. [c]Pd(OAc) (5 mol%), 48h.; yields of isolated material. See ESI† for details.

Thus chosen for further studies. When other reductants such as PEt_3 and $P(OEt)_3$[15e] were used, the yield of the reaction did not improve (Table 1, entries 4 and 5). Moreover, other catalysts such as $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ were not effective in this transformation (Table 1, entries 6 and 7). Reductant and catalyst screening indicated that $Pd(OAc)_2$ and PPh_3 were the best choices. To improve the yield, the catalyst loading, as well as reaction temperature and time were surveyed. Increasing and decreasing the catalyst loading were not efficient (Table 1, entries 8 and 9). However, the yield did increase with a higher temperature and longer reaction time (Table 1, entries 10 and 11). Coupling reaction was not efficient in atmospheric pressure (Table 1, entry 12). Using 130 mol% phenylboronic acid **2a**, gave the best result (Table 1, entry 13).

We next examined the substrate scope with respect to the substituted arylboronic acid (Table 2). Under the optimized conditions, *o*-bromonitrobenzene **1b** was coupled to a diverse range of arylboronic acids **2** to form carbazoles **3a**-**3o** in moderate to excellent yields.

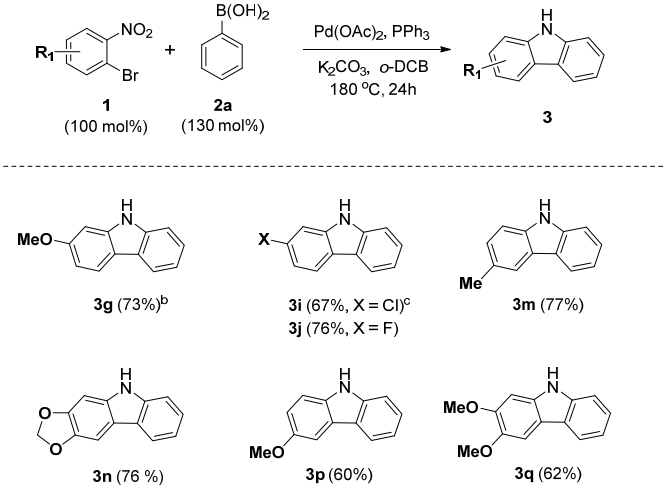


Scheme 2. Further functionalization of 3-chlorocarbazole (3i). [a]See ESI† for details.

Notably, electron neutral and electron rich arylboronic acids possessing alkyl, aryl, and alkoxy substituents were tolerated in the one-pot reaction (**3a–3h, 3m-o**), as *o*-, *m*- and *p*-substituted arylboronic acids and 3,4-disubstitued arylboronic acids afforded the corresponding products (**3a–3h, 3m-o**) in good to high yields. Aryl boronic acids possessing bulky groups at the *para* position such as *t*-butyl and phenyl were also converted to carbazoles in excellent yields. As expected, coupling of *m*-substituted arylboronic acids with *o*-bromonitrobenzene **1b** gave a mixture of corresponding 1- and 3-substituted carbazoles as regioisomers. In these experiments, 3-substituted carbazoles were obtained as major regioisomer except with 3-tolylboronic acid. In particular, 3,4-(methylenedioxy)phenylboronic acid gave a 5.9:1 mixture of **3n** and **3n',** demonstrating moderate regioselectivity, while 3-tolylboronic acid and 4-methoxy-3-methylphenylboronic acid gave mixtures with low regioselectivity (**3m**[16]**/m', 3o**[17]**/o'**).

In addition, we explored the scope of electron deficient arylboronic acids possessing fluorine, chlorine, ketone, and ester moieties and found they also gave the desired products (**3i–3l**). Slightly lower yields were observed for electron deficient arylboronic acids except for 4-fluorophenylboronic acid.

Table 3. Substrate scope of various *o*-bromonitrobenzenes [a]



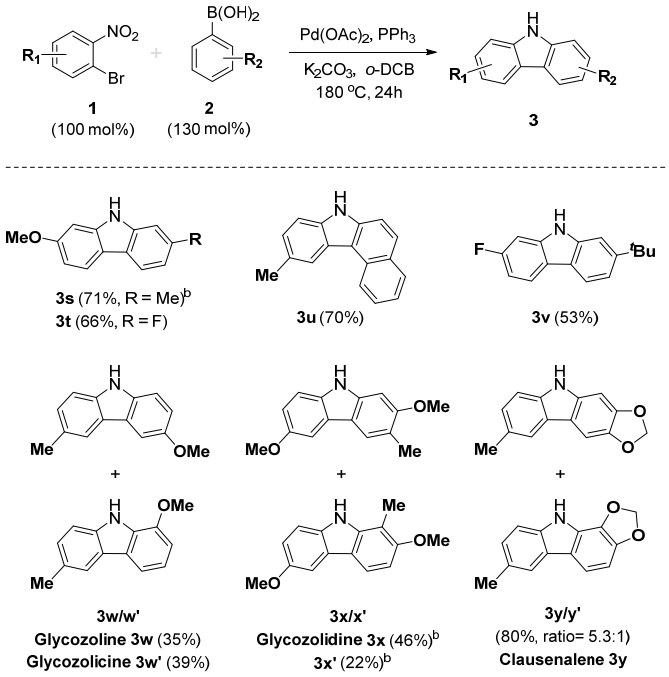
[a]As given in Table 1, entry 13. [b]48h. [c]Pd(OAc) (5 mol%), 48h.; yields of isolated material. See ESI† for details.

In particular, 4-fluoro and 4-chloroboronic acids were tolerated under these coupling conditions. Halogen containing carbazoles are useful for the introduction of additional functionalization. Thus, we examined the further functionalization of 3-chlorocarbazole **3i** (Scheme 2). Under modified Suzuki cross-coupling conditions[18] for unprotected *N*-heterocycles, 3-chlorocarbazole **3i** was coupled to a diverse range of arylboronic acids to form functionalized carbazoles (**3e, 3ia-3id)** in good to excellent yields.

To demonstrate the efficiency of this method, we conducted the gram scale synthesis of carbazole **3a**. Coupling reaction of 2-bromonitrobenzene **1b** (1 g, 5 mmol) with phenylboronic acid **2a** (750 mg, 6.5 mmol) afforded the carbazole **3a** in 75% yields.

Next, we turned our attention to the domino reaction of phenylboronic acid with a broad range of substituted *o*-bromonitrobenzenes (Table 3). Under the optimized conditions, the one-pot reaction of substituted *o*-bromonitrobenzenes **1** with phenylboronic acid **2a** were converted to the corresponding carbazoles in good yields, and similar results with respect to substrate scope of various aryl boronic acids were observed (Table 3, **3g, 3i, 3j, 3m and 3n**). These approaches constitute an alternative route that avoids the regioselectivity issue in the synthesis of 1- or 3-substituted carbazoles (**3m – 3q**).

Table 4. Substrate scope of substituted *o*-bromonitrobenzenes with aryl boronic acids[a]



[a]As given in Table 1, entry 13. [b]48h.; yields of isolated material. See ESI† for details.

The scope and limitations of the domino reaction with respect to various substituted *o*-bromonitrobenzenes and arylboronic acids were next investigated under the optimized conditions(Table 4). Coupling reactions of 1-bromo-4-methoxy-2-nitrobenzene with 3-tolylboronic acid and 4-fluorophenylboronic acid afforded the corresponding carbazoles **3s** and **3t** in 71% and 66% yields. Likewise, *o*-bromonitrobenzenes possessing methyl and fluoro substituents were coupled to arylboronic acids to form carbazoles **3u** and **3v** in 70% and 53% yield. This tandem reaction was applied to the syntheses of three bioactive carbazole alkaloids, glycozoline **3w**[19], glycozolicine **3w'**[20], glycozolidine **3x**[13a, 21] and clausenalene **3y**[22], in good yields and moderate regioselectivity.

Conclusions

In conclusion, we have developed highly efficient synthetic methods for carbazoles that are palladium-catalyzed sequential C-C/C-N bond formations via Suzuki cross-coupling and reductive Cadogan cyclization. Electron neutral, rich and deficient substrates were tolerated in this method. The synthetic utility of this method was demonstrated by the concise syntheses of four naturally occurring bioactive carbazole alkaloids, glycozoline **3w**, glycozolicine **3w'**, glycozolidine **3x** and clausenalene **3y** from commercially available simple starting materials. Future studies will focus on further applications of this one-pot strategy to the syntheses of complex natural products.

Experimental

General Information

All reactions were run under an atmosphere of air under anhydrous conditions unless otherwise indicated. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), dimethylformamide (DMF) and toluene (PhMe) were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Pressure tubes (13 x 100 mm, PYREXPLUS) were dried in oven for overnight and cooled under a stream of nitrogen prior to use. All commercial reagents were used directly without further purification. The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F_{254}). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using hexanes-EtOAc (v/v) or hexanes-acetone (v/v). Infrared spectra were recorded on a Varian 2000 FT-IR. High-resolution mass spectra (EI) were obtained on a Jeol JMS700 HRMS at the Korea Basic Science Center(KBSI), Daegu, Korea and Low-resolution mass spectra (EI) Varian 450-GC/Varian 220-MS and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion ($[M+H]^+$ or $[M+Na]^+$). Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded with a Bruker (300 MHz) spectrometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc.

General Procedure for Carbazole Synthesis. To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were added *o*-bromonitrobenzene **1** (0.5 mmol, 100 mol%), aryl boronic acid **2** (0.65 mmol, 130 mol%), Pd(OAc) (0.01 mmol, 2 mol%), PPh_3 (1.25 mmol, 250 mol %), K_2CO_3 (1 mmol, 200 mol%) and *o*-DCB (1 mL, 0.5 M concentration with respect to *o*-bromonitrobenzene **1**. The mixture was heated at 180 ^oC (oil bath temperature) for 24-48 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) under the conditions noted to furnish the corresponding product.

9H-carbazole (3a)[6e]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3a** as a white solid (72 mg, 86% yield); ^1H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 8.12 (d, J = 7.8 Hz, 3H), 7.56 (d, J = 8.1 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.21 – 7.16 (m, 3H); ^{13}C NMR (75 MHz, DMSO) δ 139.79, 125.54, 122.48, 120.18, 118.53, 110.98; FTIR (neat): υ 3379, 2946, 1450, 1033 cm^{-1}; LRMS *m/z* (EI) 166.8 (M^+-1), 139.0, 83.4, 62.8.

2-Methyl-9H-carbazole (3b)[23a]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3b** as a white solid (76 mg 84% yield); ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 7.9 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.24 – 7.18 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.09, 139.59, 136.15, 125.41, 123.58, 121.19, 121.12, 120.14, 120.13, 119.46, 110.86, 110.60, 22.21; FTIR (neat) υ 3394, 2920, 1652, 1530, 1365 cm^{-1}; LRMS *m/z* (EI) 179.8 (M^+-1), 151.8, 76.8, 62.8.

4-Methyl-9H-carbazole (3c)[10]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3c** as a white solid (79 mg 87% yield); ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, J = 7.9 Hz, 1H), 8.09 (br s, 1H), 7.50 – 7.39 (m, 2H), 7.37 – 7.31 (m, 1H), 7.32 – 7.26 (m, 2H), 7.02 (dd, J = 7.3, 0.8 Hz, 1H), 2.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.54, 139.51, 133.49, 125.77, 125.29, 123.93, 122.68, 121.90, 120.99, 119.44, 110.49, 108.26, 20.92; FTIR (neat) υ 3396, 3200, 2924, 1653, 1521, 1267, 1048 cm^{-1}; LRMS *m/z* (EI) 181.3 (M^+), 182.3, 180.4, 177.5, 155.3, 125.8, 93.7.

2-(Tert-butyl)-9H-carbazole (3d)[11d]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3d** as a white solid (94 mg 84% yield); ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 7.0 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.94 (s, 1H), 7.44 (d, J = 1.6 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.32 (dd, J = 8.3, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.72, 139.89, 139.82, 125.40, 123.49, 121.03, 120.21, 119.90, 119.41, 117.65, 110.57, 107.25, 35.25, 31.90; FTIR (neat) υ 3194, 2916, 1650, 1525, 1267 cm^{-1}; LRMS *m/z* (EI) 222.7 (M^+-1), 207.8, 180.0, 167.0, 89.9.

2-Phenyl-9H-carbazole (3e)[6d]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3e** as a white solid (110 mg 90% yield); ^1H NMR (300

MHz, Acetone-d_6) δ 10.50 (s, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.57 – 7.32 (m, 6H), 7.21 (td, J = 8.2, 4.3 Hz, 1H); ^{13}C NMR (75 MHz, DMSO): δ 141.26, 140.43, 140.35, 137.88, 128.99, 127.12, 127.06, 125.70, 122.23, 121.88, 120.68, 120.32, 118.76, 117.89, 111.06, 108.93; FTIR (neat) υ 3377, 3268, 1692, 1528, 1367, 1227 cm^{-1}; LRMS *m/z* (EI): 242.8 (M^+-1), 120.3, 76.7, 50.9.

7H-Benzo[c]carbazole (3f)[23b]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3f** as a white solid (91 mg 84% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 8.3 Hz, 1H), 8.58 (d, J = 7.8 Hz, 1H), 8.44 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.36 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.52, 137.16, 130.03, 129.32, 127.55, 127.01, 124.46, 124.09, 123.38, 123.13, 122.16, 120.36, 115.54, 112.71, 111.25; FTIR (neat) υ 3396, 2920, 1876, 1465, 1267, 1120 cm^{-1}; LRMS *m/z* (EI): 217.7 (M^++1), 216.8, 188.8, 108.2, 95.3.

2-Methoxy-9H-carbazole (3g)[16c]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3g** as a white solid (76 mg, 77% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.96 (d, J = 3.4 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.24 – 7.18 (m, 1H), 6.92 (d, J = 2.1 Hz, 1H), 6.86 (dd, J = 8.5, 2.2 Hz, 1H), 3.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.21, 140.93, 139.63, 124.69, 123.67, 121.19, 119.70, 119.63, 117.39, 110.44, 108.29, 94.83, 55.77; FTIR (neat) υ 3395, 1336, 1200, 1030 cm^{-1}; LRMS *m/z* (EI): 197.7 (M^++1), 196.7, 181.8, 153.8, 127.8.

4-Methoxy-9H-carbazole (3h)[13f]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3h** as a white solid (66 mg, 67% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, J = 7.8 Hz, 1H), 8.02 (s, 1H), 7.43 – 7.38 (m, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.32, 140.92, 138.72, 126.77, 125.01, 123.12, 122.67, 119.70, 112.60, 110.07, 103.62, 100.42, 55.51; FTIR (neat) υ 3386, 2938, 1405, 1248, 1184, 1045 cm^{-1}; LRMS *m/z* (EI): 197.8 (M^++1), 196.7, 181.9, 153.9, 128.0.

2-Chloro-9H-carbazole (3i)[6e]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3i** as a white solid (71 mg, 70% yield); ^{1}H NMR (300 MHz, DMSO) δ 11.43 (s, 1H), 8.12 (d, J = 8.2 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.20 – 7.14 (m, 2H); ^{13}C NMR (75 MHz, DMSO) δ 140.30, 140.08, 129.88, 125.98, 121.81, 121.57, 121.31, 120.35, 119.09, 118.68, 111.23, 110.61; FTIR (neat) υ 3393, 3128, 1636, 1406, 1321, 1178, 754 cm^{-1}; LRMS *m/z* (EI): 200.7 (M^+-1), 165.7, 138.8, 100.3.

2-Fluoro-9H-carbazole (3j)[11d]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3j** as a white solid (75 mg, 81% yield)**;** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.03 – 7.97 (m, 2H), 7.44 – 7.39 (m, 2H), 7.26 – 7.21 (m, 1H), 7.11 (dd, J = 9.6, 2.2 Hz, 1H), 7.02 – 6.93 (m, 1H); ^{13}C NMR (75 MHz, DMSO) δ 161.18 (d, J = 238.6 Hz), 140.41, 140.28, 125.25, 122.07, 121.46 (d, J = 10.6 Hz), 119.97, 119.20, 119.00, 111.02, 106.49 (d, J = 24.1 Hz), 97.34 (d, J = 26.1 Hz); FTIR (neat) υ 3411, 2919, 1362, 1263 cm^{-1}; LRMS *m/z* (EI): 186.2 (M^++1), 185.2, 184.3, 157.3, 92.8.

1-(9H-Carbazole-2-yl)ethan-1-one (3k)[11d]. Purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3k** as a white solid (41 mg, 43% yield); ^{1}H NMR (300 MHz, DMSO) δ 11.56 (s, 1H), 8.22 (t, J = 8.3 Hz, 2H), 8.08 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 197.86, 141.29, 139.15, 134.10, 127.03, 126.13, 121.59, 121.15, 120.06, 119.12, 118.66, 111.39, 111.35, 26.98; FTIR (neat) υ 3332, 1738, 1366, 1216, 889, 779 cm^{-1}; LRMS *m/z* (EI) : 210.2 (M^++1), 209.3, 194.3, 166.3, 139.3.

Methyl-9H-carbazole-2-carboxylate (3l)[6e]. Purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3l** as a white solid (69 mg, 61% yield); ^{1}H NMR (300 MHz, DMSO) δ 11.58 (s, 1H), 8.21 (t, J = 8.8 Hz, 2H), 8.12 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 166.95, 141.10, 139.05, 127.06, 126.30, 126.20, 121.60, 121.10, 120.14, 119.25, 119.16, 112.35, 111.42, 52.05; FTIR (neat) υ 3337, 2937, 1738, 1365, 1216, 888 cm^{-1}; LRMS *m/z* (EI): 226.2 (M^++1), 225.2, 194.2, 166.2, 139.2, 97.2, 83.2, 69.7.

3-Methyl-9H-carbazole (3m) and 1-Methyl-9H-carbazole (3m'). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3m**/**3m'** as a white solid (80 mg, 88% yield, **3m:3m'**=1:1.2 (determined by ^{1}H NMR and GC-Mass spectrometer)). GC (Varian 450-GC, SPB^{TM}-680 (30 m x 0.25 mm x 0.25 µm), T_0 : 60 ^{o}C (hold 4 min), T_1 : Ramp, 250 ^{o}C at 10 ^{o}C/min, Carrier: He (1.0 mL/min), Total time 60 min), $t_{3m'}$ = 21.95 min, t_{3m} = 22.32 min, Ratio (**3m:3m'** = 1:1.2).

3-Methyl-9H-carbazole (3m)[6e]. ^{1}H NMR (300 MHz, DMSO) δ 11.10 (s, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.89 (s, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H): ^{13}C NMR (75 MHz, DMSO) δ 139.98, 137.96, 127.08, 126.82, 125.29, 122.54, 122.22, 120.02, 119.90, 118.23, 110.85, 110.63, 21.10; FTIR (neat) υ 3442, 1701, 1371, 1207 cm^{-1}; LRMS *m/z* (EI): 182.2 (M^++1), 181.2, 180.3, 152.3, 90.2, 77.2, 63.2, 51.1.

1-Methyl-9H-carbazole (3m')[13f]. ^{1}H NMR (300 MHz, DMSO) δ 11.16 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.20 – 7.10 (m, 2H), 7.10 – 7.02 (m, 1H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 139.79, 139.04, 125.94, 125.29, 122.79, 121.95, 120.17, 120.05, 118.62, 118.46, 117.60, 111.03, 17.00; FTIR (neat) υ 3442, 1701, 1371, 1207 cm^{-1}; LRMS *m/z* (EI): 181.2 (M^+), 180.2, 152.3, 135.2, 77.2, 63.2, 51.1.

5H-[1,3]dioxolo[4,5-b]carbazole (3n) and 5H-[1,3]dioxolo[4,5-a]carbazole (3n'). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3n**/**3n'** as a white solid (90 mg, 87% yield, **3n:3n'**=5.9:1 (determined by ^{1}H NMR and GC-Mass spectrometer)). GC: (Varian 450-GC, SPB^{TM}-680 (30 m x 0.25 mm x 0.25 µm), T_0 : 60 ^{o}C (hold 4 min), T_1 : Ramp, 250 ^{o}C at 10 ^{o}C/min, Carrier: He (1.0 mL/min), Total time 60 min), $t_{3n'}$ = 25.38 min, t_{3n} = 26.90 min, Ratio (**3n:3n'** = 5.9:1).

5H-[1,3]dioxolo[4,5-b]carbazole (3n)[23c]. ^{1}H NMR (300 MHz, DMSO) δ 11.08 (s, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.62 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.09 – 7.02 (m,

2H), 6.03 (s, 2H); ^{13}C NMR (75 MHz, DMSO) δ 146.72, 141.52, 139.56, 135.14, 123.76, 122.83, 119.26, 118.20, 115.40, 110.79, 100.69, 99.36, 92.16; FTIR (neat) υ 3397, 1710, 1266, 1043, 936, 748 cm^{-1}; LRMS *m/z* (EI): 212.0 (M^++1), 211.2.

5H-[1,3]dioxolo[4,5-a]carbazole (3n'). ^{1}H NMR (300 MHz, DMSO) δ 11.35 (s, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 15.0 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.16 – 7.06 (m, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.13 (s, 2H); FTIR (neat) υ 3397, 1710, 1266, 1043, 936, 748 cm^{-1}; LRMS *m/z* (EI): 211.9 (M^++1), 211.1, 154.2.

3-Methoxy-2-methyl-9Hcarbazole (3o)[12k]. Purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3o** as a yellow solid (54mg, 51% yield); ^{1}H NMR (300 MHz, Acetone-d_6) δ 10.10 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.81 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 – 7.08 (m, 1H), 7.02 (s, 1H), 3.90 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 158.18, 140.73, 140.68, 124.60, 124.12, 121.94, 119.79, 119.42, 118.89, 116.68, 111.28, 93.30, 55.67, 16.92; FTIR (neat) υ 3313, 3069, 1783, 1689, 1404, 1270, 1169 cm^{-1}; LRMS *m/z* (EI): 212.2(M^++1), 211.3, 196.6, 195.7, 167.5.

1-Methoxy-2-methyl-9Hcarbazole (3o')[23e]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3o'** as a yellow solid (29mg, 27% yield); ^{1}H NMR (300 MHz, Acetone-d_6) δ 10.16 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.19 – 7.10 (m, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 156.86, 141.66, 141.42, 125.16, 124.60, 120.13, 119.56, 118.53, 118.01, 111.33, 107.65, 104.63, 56.46, 10.15; FTIR (neat) υ 3313, 3069, 1783, 1689, 1404, 1270, 1169 cm^{-1}; LRMS *m/z* (EI): 212.3 (M^++1), 211.4, 196.6, 195.7, 167.7.

3-Methoxy-9H-carbazole (3p)[6e]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3p** as a brown solid (59 mg, 60% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.85 (s, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.44 – 7.30 (m, 2H), 7.28 – 7.12 (m, 2H), 7.05 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.88, 140.32, 134.42, 125.89, 123.76, 123.34, 120.34, 119.10, 115.16, 111.46, 110.88, 103.13, 56.14; FTIR (neat) υ 3405, 1788, 1685, 1400, 1260, 1031 cm^{-1}; LRMS *m/z* (EI): 198.3 (M^++1), 197.4, 182.7, 181.7, 154.3, 101.5.

2,3-Dimethoxy-9H-carbazole (3q)[23d]. Purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3q** as a white solid (70 mg, 62% yield); ^{1}H NMR (300 MHz, DMSO) δ 10.98 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.66 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $DMSO_3$) δ 149.18, 143.71, 139.56, 134.63, 123.67, 123.00, 119.26, 118.12, 114.30, 110.72, 103.33, 94.62, 56.21, 55.63; FTIR (neat) υ 3337, 2917, 1402, 1186, 1090 cm^{-1}; LRMS *m/z* (EI): 228.2 (M^++1), 227.5, 212.7, 211.7, 184.5.

2-Methoxy-7-methyl-9H-carbazole (3s)[20d]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3s** as a white solid (75 mg, 71% yield); ^{1}H NMR (300 MHz, DMSO) δ 10.98 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.21 (s, 1H), 6.96 – 6.88 (m, 2H), 6.73 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz DMSO) δ 158.14, 141.07, 140.22, 133.50, 120.54, 120.44, 120.03, 119.02, 116.32, 110.73, 107.42, 94.53, 55.25, 21.65.; FTIR (neat) υ 3394, 1726, 1366, 1219, 1091 cm^{-1}; LRMS *m/z* (EI): 212.5 (M^++1), 211.6, 196.6, 195.7, 168.5.

2-Fluoro-7-methoxy-9H-carbazole (3t). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3t** as a white solid (71 mg, 66% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.87 (d, J = 8.5 Hz, 1H),, 7.85 (d, *J* = 8.3 Hz, 1H), 7.06 (dd, *J* = 9.5, 2.3 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.90 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.87, 141.31, 120.78, 120.38, 120.25, 116.91, 108.55, 107.82, 107.50, 97.63, 97.27, 95.02, 55.78; FTIR (neat) υ 3192, 2843, 1539, 1406, 1155 cm^{-1}; LRMS *m/z* (EI): 216.5 (M^++1), 215.5, 200.6, 199.7, 172.5, 171.5; HRMS *m/z* (EI): calcd. For $C_{13}H_{10}FNO$ (M^+) 215.0747, found 215.0746.

10-Methyl-7H-benzo[c]carbazole (3u)[23f]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3u** as a white solid (81 mg , 70% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 8.3 Hz, 1H), 8.37 (s, 1H), 8.31 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.29 (d, J = 8.4 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.41, 136.78, 130.09, 129.60, 129.27, 127.27, 126.90, 125.87, 124.27, 123.39, 122.98, 122.06, 115.22, 112.79, 110.88, 21.96; FTIR (neat) υ 3470, 2897, 1696, 1542, 1267, 1152 cm^{-1}; LRMS *m/z* (EI): 232.7 (M^++1), 231.2, 230.2, 228.8, 197.2, 118.8.

2-(Tert-butyl)-7-fluoro-9H-carbazole (3v). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3v** as a yellow solid (64 mg, 53% yield); ^{1}H NMR (300 MHz, DMSO) δ 11.24 (s, 1H), 8.04 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.43 (s, 1H), 7.23 (dd, *J* = 10.3, 2.1 Hz, 2H), 6.99 – 6.91 (m, 1H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, DMSO) δ 160.94 (d, *J* = 237.8 Hz), 148.29, 140.61, 140.44, 121.08 (d, *J* = 10.5 Hz), 119.71, 119.50, 119.20, 117.01, 107.26, 106.27 (d, *J* = 24.1 Hz), 97.30 (d, *J* = 26.0 Hz), 34.76, 31.60; FTIR (neat) υ 3475, 3187, 1741, 1598, 1266 cm^{-1}; LRMS *m/z* (EI): 242.1 (M^++1), 241.1, 227.4, 226.5, 198.2; HRMS *m/z* (EI): calcd. For $C_{16}H_{16}FN$ (M^+) 241.1268, found 241.1267.

Glycozoline (3w)[19d]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3w** as a yellow solid (37 mg, 35% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.77 (s, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.06 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.94 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.87, 138.69, 134.89, 128.45, 127.32, 123.76, 123.64, 120.25, 115.01, 111.41, 110.56, 103.23, 56.19, 21.54.; FTIR (neat) υ 3410, 2894, 1706, 1492, 1266, 1131 cm^{-1}; LRMS *m/z* (EI): 212.1 (M^++1), 211.2, 197.2, 196.3, 168.2, 167.2.

Glycozolicine (3w')[20d]. Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3w'** as a yellow solid (41 mg, 39% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.87 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.00 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.79, 137.57, 130.24, 128.76, 127.19, 124.32, 123.96, 120.54, 119.61, 112.94, 110.71, 105.87, 55.59, 21.56; FTIR (neat) υ 3410, 2894, 1706, 1492, 1266, 1131 cm^{-1};

LRMS *m/z* (EI): 212.2 (M^++1), 211.3, 197.2, 196.3, 169.1, 168.2, 142.1.

Glycozolidine (3x)[20d]. Purified by flash column chromatography (SiO_2) using 7% acetone in hexanes as eluant to give **3x** as a white solid (56mg, 46% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.56 (s, 1H), 7.46 (d, *J* = 2.2 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.63 (s, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.50, 153.90, 140.10, 134.23, 123.96, 121.47, 118.98, 116.17, 113.10, 111.10, 102.53, 92.53, 56.14, 55.52, 16.87; FTIR (neat) υ 3389, 3066, 1787, 1637, 1509, 1365, 1270 cm^{-1}; LRMS *m/z* (EI): 242.3 (M^++1), 241.3, 227.2, 226.3, 198.2, 183.2, 154.1.

2,6-Dimethoxy-1-methyl-9H-carbazole (3x'). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3x'** as a white solid (27mg, 22% yield). ^{1}H NMR (300 MHz, DMSO) δ 10.76 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, DMSO). δ 155.44, 153.04, 141.29, 135.08, 123.59, 117.97, 116.79, 113.20, 111.23, 106.54, 103.49, 102.67, 56.08, 55.56, 10.24; FTIR (neat) υ 3389, 3066, 1787, 1637, 1509, 1365, 1270 cm^{-1}; LRMS *m/z* (EI): 242.3 (M^++1), 241.3, 227.2, 226.3, 198.2, 197.2, 183.2, 154.1.

Clausenalene (3y) and 7-Methyl-10H-[1,3]dioxolo[4,5-a]carbazole (3y'). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3y**/**3y'** as a white solid (61 mg, 80% yield, **3y:3y'**=5.3:1 (determined by ^{1}H NMR and GC-Mass spectrometer)). GC: (Varian 450-GC, SPB^{TM}-680 (30 m x 0.25 mm x 0.25 µm), T_0 : 60 ^{o}C (hold 4 min), T_1 : Ramp, 250 ^{o}C at 10 ^{o}C/min, Carrier: He (1.0 mL/min), Total time 60 min), $t_{3y'}$ = 26.98 min, t_{3y} = 28.69 min, Ratio (**3y:3y'** = 5.3:1).

Clausenalene (3y)[22c]. Purified by recrystallization from dichloromethane and hexanes to give **3y** as a white solid. ^{1}H NMR (300 MHz, Acetone-d_6) δ 10.09 (s, 1H), 7.76 (s, 1H), 7.50 (s, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.09 (dd, J = 8.2, 1.2 Hz, 1H), 6.98 (s, 1H), 6.00 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 147.94, 142.82, 139.11, 136.64, 128.26, 126.07, 124.45, 119.77, 116.76, 111.26, 101.66, 99.82, 92.85, 21.48; FTIR (neat) : υ 3400, 3009, 1728, 1366, 1219, 1093, 533 cm^{-1}; LRMS *m/z* (EI): 225.9 (M^++1), 225.2.

7-Methyl-10H-[1,3]dioxolo[4,5-a]carbazole (3y'). ^{1}H NMR (300 MHz, Acetone-d_6) δ 10.17 (s, 1H), 7.81 (s, J = 0.6 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.17 (dd, J = 8.2, 1.2 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.07 (s, 2H), 2.46 (s, 3H); FTIR (neat) υ 3400, 3009, 1728, 1366, 1219, 1093, 533 cm^{-1}; LRMS *m/z* (EI): 225.9 (M^++1), 225.2.

General Procedure for Suzuki coupling of 3-chlorocarbazole (3i). To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar were 2-chloro-*9H*-carbazole **3i** (0.1 mmol, 100 mol%), aryl boronic acid **2** (0.15 mmol, 150 mol%), $Pd_2(dba)_3$ (0.01 mmol, 10 mol%), PCy_3 (0.25 mmol, 25 mol %), K_3PO_4 (1.27 M in water, 0.34 mmol) and dioxane (2 mL, 0.05 M concentration with respect to 2-chloro-*9H*-carbazole **3i**). The slurry was sealed and purged with Argon gas for 5 minutes. The mixture was heated at 100 ^{o}C (oil bath temperature) for 2 hr, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture, treated with saturated sodium bicarbonate solution, and extracted with dichloromethane (3x). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated *in vacuo* and purified by flash column chromatography (SiO_2) and recrystallization from dichloromethane and hexanes under the conditions noted to furnish the corresponding product.

2-([1,1'-Biphenyl]-4-yl)-9H-carbazole (3ia). Purified by recrystallization from dichloromethane and hexanes to give **3ia** as a white solid (23 mg, 72% yield); ^{1}H NMR (300 MHz, DMSO) δ 11.35 (s, 1H), 8.20 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.85 (s, 1H), 7.82 – 7.71 (m, 5H), 7.55 – 7.46 (m, 4H), 7.44 – 7.36 (m, 2H), 7.18 (t, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO) δ 140.41, 140.33, 140.20, 139.70, 138.77, 137.20, 129.03, 127.50, 127.21, 126.56, 125.70, 122.19, 121.94, 120.70, 120.30, 118.74, 117.72, 111.03, 108.74; FTIR (neat) υ 3403, 3101, 1753, 1691, 1530, 1368, 1206, 763 cm^{-1}; HRMS *m/z* (EI): calcd. For $C_{24}H_{17}N$ (M^+) 319.1361, found 319.1360.

2-(4-Fluorophenyl)-9H-carbazole (3ib). Purified by flash column chromatography (SiO_2) using 5% acetone in hexanes as eluant to give **3ib** as a yellow solid (23 mg, 88% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 1H), 8.10 (s, 1H) 8.09 (d, J = 7.4 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.58 (s, 1H), 7.46 – 7.40 (m, 3H), 7.30 – 7.22 (m, 1H), 7.19 – 7.11 (m, 2H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 163.17 (d, J = 243.9 Hz), 141.61, 141.56, 139.27 (d, J = 3.2 Hz), 138.56, 129.87 (d, J = 8.0 Hz), 126.59, 123.71, 123.33, 121.34, 121.00, 119.91, 119.11, 116.33 (d, J = 21.5 Hz), 111.80, 109.96; FTIR (neat) υ 3400, 1650, 1367, 1223, 724 cm^{-1}; LRMS *m/z* (EI): 262.2 (M^++1), 262.2; HRMS *m/z* (EI): calcd. For $C_{18}H_{12}FN$ (M^+) 261.0954, found 261.0953.

Methyl 4-(9H-carbazol-2-yl)benzoate (3ic). Purified by recrystallization from dichloromethane and hexanes to give **3ic** as a white solid (21 mg, 70% yield); ^{1}H NMR (300 MHz, DMSO) δ 11.39 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 1.3 Hz, 1H), 7.54 (dd, J = 8.2, 1.5 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.41 (td, J = 8.1, 0.9 Hz, 1H), 7.18 (td, J = 7.7, 0.5 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 166.18, 145.77, 140.47, 140.28, 136.26, 129.86, 128.01, 127.21, 125.98, 122.59, 122.03, 120.83, 120.47, 118.85, 117.91, 111.11, 109.26, 52.16; FTIR (neat) υ 3388, 2139, 1719, 1363, 1218, 1095, 702 cm^{-1}; HRMS *m/z* (EI): calcd. For $C_{20}H_{15}NO_2$ (M^+) 301.1103, found 301.1103.

2-(2-Methoxyphenyl)-9H-carbazole (3id). Purified by recrystallization from dichloromethane and hexanes to give **3id** as a white solid (26 mg, 95% yield); ^{1}H NMR (300 MHz, Acetone-d_6) δ 10.34 (s, 1H), 8.12 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 0.6 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.22 – 7.16 (m, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.05 (td, J = 7.4, 0.9 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 156.58, 140.45, 140.02, 136.01, 131.16, 131.07, 129.05, 125.98, 122.63, 121.60, 121.27, 120.82, 120.53, 119.99, 119.10, 112.23, 112.02, 111.32, 55.90; FTIR (neat) υ 3409, 3012, 1733, 1599, 1247, 1032, 866, 748 cm^{-1}; LRMS *m/z* (EI): 273.2 (M^+), 273.9, 258.3; HRMS *m/z* (EI): calcd. $C_{19}H_{15}NO$ (M^+) 273.1155, found 273.1154.

Acknowledgements

This work was supported by the 2013 Research Fund of University of Ulsan.

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