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A Convenient Synthesis of 3,6-Substituted Carbazoles via Nickel Catalyzed Cross-Coupling

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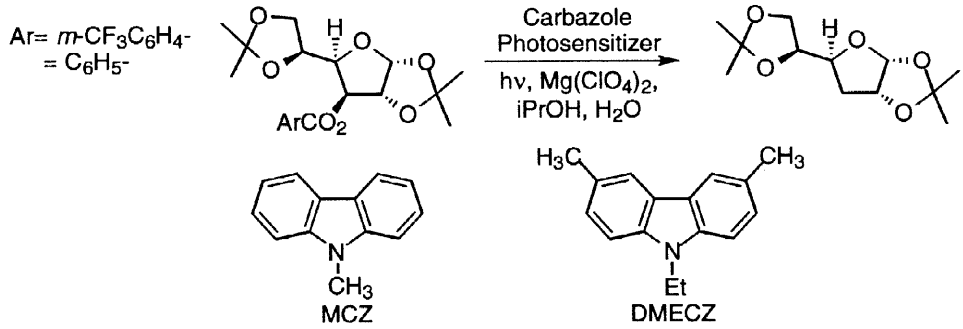
Abstract: Alkyl, vinyl and aryl substituted carbazoles at the 3- and 6-positions are prepared in high yield from the corresponding 3,6-dibromocarbazole via nickel catalyzed coupling with Grignard reagents (Corriu-Kumada coupling).

INTRODUCTION

Saito showed that benzoyl derivatives of secondary alcohols could be deoxygenated via a photoinduced electron-transfer (PET) mechanism using stoichiometric 9-methylcarbazole (MCZ) as the photosensitizer.[1] We recently reported that 3,6-dimethyl-9-ethylcarbazole (DMECZ) is a superior photosensitizer due the greater stability of its radical cation, an intermediate in the PET deoxygenation reaction.[2] Benzoates and *m*-(trifluoromethyl)benzoates of secondary and tertiary alcohols were easily deoxygenated using 10-20 mol % DMECZ as the photosensitizer.

Ambrose investigated the radical cation chemistry of carbazoles by cyclic voltammetry and demonstrated that the electrochemical oxidation of certain 3,6-disubstituted carbazoles showed improved reversibility indicating greater stability of the radical cation intermediate.[3,4] The substituents could enhance both the thermodynamic stability of the radical cation through inductive and resonance effects as well as the kinetic stability by blocking or slowing potential side reactions. With these observations as our guide, we are interested in the development of new carbazole-based photosensitizers and report here a simple and versatile synthesis of 3,6-disubstituted carbazole derivatives.



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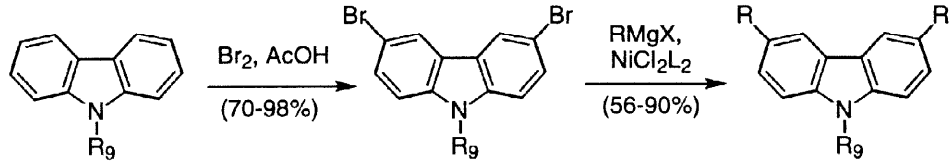
RESULTS

Carbazoles undergo electrophilic addition at the 3- and 6-positions. Bromination of 9-ethyl-, 9-isopropyl- and 9-phenylcarbazole (**1**) under previously described conditions gave the corresponding 9-substituted 3,6-dibromocarbazoles (**2**).[5] Bromination of 9-ethylcarbazole resulted in contamination with variable amounts of 1,3,6-tribromo-9-ethylcarbazole. While the products could be separated chromatographically, we found it more convenient to simply *N*-alkylate the more expensive 3,6-dibromocarbazole with diethylsulfate and sodium hydroxide in acetone (90 %).[6] Cross coupling with Grignard reagents proceeded in good yield independent of the 9-substituent. For example, with $NiCl_2$(dppp) as a catalyst, reaction with four equivalents of methylmagnesium bromide in ether at reflux gave the corresponding 3,6-dimethylcarbazole in 65-90 % yield. While as little as one mol percent of catalyst could effect the cross-coupling reaction, for large scale preparation of the desired product five mol percent catalyst was used. Table 1 shows that aliphatic, aromatic and heteroaromatic Grignard reagents undergo smooth cross-coupling to give the disubstituted carbazoles with $NiCl_2$(dppp) as the catalysts. This catalyst, however, was ineffective at promoting the cross-coupling with vinyl Grignard, consistent with previous reports by Kumada.[7,8] Kumada showed that changing the ligand on nickel could dramatically alter the reactivity of the catalyst to promote certain cross-coupling reactions. The cross coupling of 3,6-dibromocarbazole with vinylmagnesium bromide was easily accomplished when $NiCl_2$(dmpe) was employed.[8] This catalyst, however, did not satisfactorily promote cross-coupling with other Grignard reagents. In such cases, the reaction gave either dehalogenation and other undesired side-reactions or proceeded at a reduced rate.

Gilman reported that 3-bromo-9-ethylcarbazole and 3,6-dibromo-9-ethylcarbazole could undergo lithium-halogen exchange to give the 3-lithio and 3,6-dilithio- species, respectively. Condensation with carbon dioxide gave the corresponding mono and diacid in high yield.[9] We have demonstrated that 3,6-dilithio-9-ethylcarbazole can be alkylated with iodomethane or diethylsulfate to give the corresponding 3,6-dialkyl-9-ethylcarbazoles **3a** and **3e** in satisfactory yield. For the alkylation with iodomethane, GC-MS analysis of the crude reaction mixture



1 **2** **3**

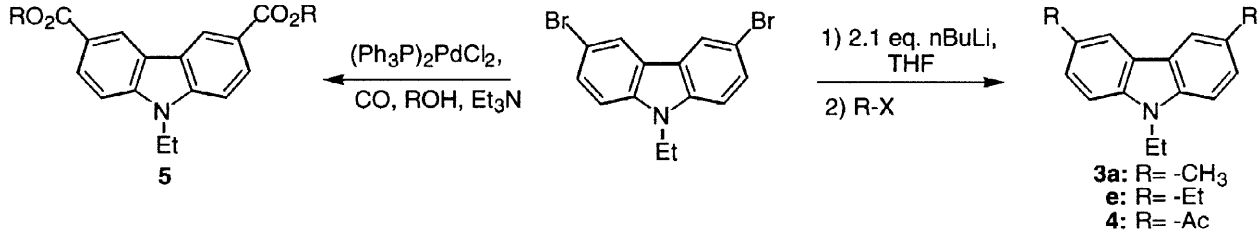
Table 1

entry	R_9	yield of **2**	R-MgX	Catalyst[a]	Conditions	yield of **3**
a	ethyl	70%	methyl-	$NiCl_2$(dppp)	ether, reflux	90%
b			vinyl-	$NiCl_2$(dmpe)	THF, RT	82%
c			phenyl-	$NiCl_2$(dppp)	THF, reflux	75%
d			2-thienyl-	$NiCl_2$(dppp)	ether, reflux	83%
e			ethyl-	$NiCl_2$(dppp)	ether, reflux	88%
f	isopropyl	85%	methyl-	$NiCl_2$(dppp)	ether, reflux	83%
g			vinyl-	$NiCl_2$(dmpe)	THF, RT	85%
h			phenyl-	$NiCl_2$(dppp)	THF, reflux	78%
i			4-fluorophenyl-	$NiCl_2$(dppp)	THF, reflux	70%
j	phenyl	98%	methyl-	$NiCl_2$(dppp)	ether, reflux	81%
k			vinyl-	$NiCl_2$(dmpe)	THF, RT	82%
l			phenyl-	$NiCl_2$(dppp)	THF, reflux	56%

[a] dppp= 1,3-bis(diphenylphosphino)propane, dmpe= 1,2-bis(dimethylphosphino)ethane

indicated other products were produced; the mass spectra of these minor products were consistent with 3-methyl-9-ethylcarbazole and 1,3,6-trimethyl-9-ethylcarbazole.

We were disappointed to find that 3,6-dilithio-9-ethylcarbazole was unreactive toward oxaziridine.[10] Attempted reaction with (camphorylsulfonyl)oxaziridine in THF did not provide any hydroxylated product. 3,6-Dimethoxycarbazole was previously synthesized from a 3,6-dibromo precursor via a copper (I) promoted substitution.[11] Reactions of the dilithio species with *N*-methoxy-*N*-methylacetamide provided 3,6-diacetyl-9-ethylcarbazole (**4**) in 64 % yield.[12] This procedure represents an alternative to the Friedel-Crafts acylation of the 9-substituted carbazole.[13] Various esters of 9-ethylcarbazole-3,6-dicarboxylate (**5**) have been synthesized in five steps from 9-ethylcarbazole as potential antiviral agents related to tilorone.[14] We found that palladium catalyzed carbonylation of 3,6-dibromo-9-ethylcarbazole in *n*-butanol gave the corresponding dibutyl ester of **5** is 82 % yield,[15,16] providing easy access to this class of compounds.



DISCUSSION

Carbazole and methylated analogs were first isolated from coal tar and the carbazole ring system is a common structural subunit of a number of alkaloids and medicinally useful agents.[17,18] Since the first observation of the photoconductive properties of poly-*N*-vinylcarbazole, polymers containing pendent carbazole groups have received considerable interest.[19] Some of these polymers also show nonlinear optical (NLO) properties.[20]

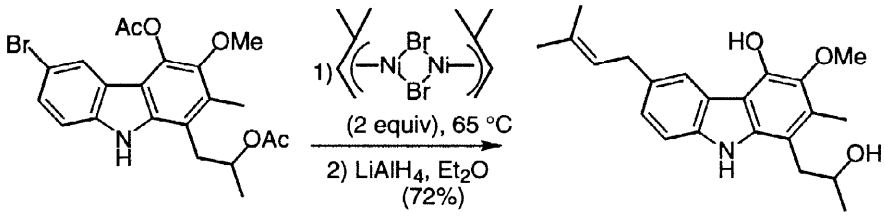
A number of methods for the synthesis of substituted carbazoles have been developed and 3,6-dimethyl-9-ethylcarbazole has been synthesized a number of times. Carbazoles undergo facile electrophilic addition at the 3- and 6-positions and conditions have been established for obtaining the mono- and disubstituted products.[17,18] Buu-Hoï and Hoán synthesized 3,6-dimethyl-9-ethylcarbazole by formylation of 9-ethylcarbazole followed by Wolff-Kishner reduction, then a second formylation Wolff-Kishner reduction sequence.[6] Kuroki and Tsunashima synthesized over thirty methylated carbazoles by various methods and suggested the Täuber synthesis starting from the corresponding 2,2'-diaminobiphenyl for 3,6-disubstituted carbazoles.[21] Our general approach to 3,6-disubstituted carbazoles was by functionalization of the corresponding 3,6-dibromide via an organometallic cross-coupling reaction.

An early observation that transition metals could catalyze the cross coupling of organometallic reagents to aryl and vinyl halides was reported by Tamura and Kochi.[22] Since that time, a number of labs have further developed this cross-coupling reaction which has also been extended to vinyl and aryl triflates. Corriu and Kumada simultaneously reported that Ni(II) could effectively couple Grignard reagents with aryl and vinyl halides.[23,23] We have applied this method to the synthesis of 3,6-disubstituted carbazoles which we have found useful as photosensitizers for the PET deoxygenation of benzoyl derivatives.[2] We have synthesized a number of 3,6-disubstituted carbazoles using alkyl, vinyl and aromatic Grignard reagents; many of these products have not been previously reported.

Palladium catalyzed coupling of 3,6-diiodo-9-ethylcarbazole with phenylacetylene and styrene has been reported.[25] Presumably, similar coupling reactions with organotin reagents would also be successful. For simple substituents, it would appear that the Corriu-Kumada coupling described here is most convenient and

economical. Mono-bromination of 9-alkyl carbazoles have also been reported,[26] thus these methods should provide access to 3-substituted carbazoles as well as unsymmetrical 3,6-disubstituted carbazole derivatives.

Knölker has synthesized a number of naturally occurring, bioactive carbazoles via coupling of (η^4-cyclohexadienylium)iron tricarbonyl with substituted anilines followed by oxidative cyclization to give the carbazole skeleton.[27] In recent syntheses of the carbazole containing natural products neocarazostatin B, lavanduquinocin and carquinostatin A, a C6 allyl group was introduced via a nickel mediated coupling of a highly functionalized 6-bromo-carbazole.[27-30] Two equivalents of the dimeric π-allyl nickel bromide reagent was required for this coupling reaction.



(±)-Neocarazostatin B

CONCLUSION

A short, simple synthesis of 3,6-substituted carbazoles is described via a nickel (II) catalyzed cross-coupling of the corresponding 3,6-dibromocarbazole with Grignard reagents. The 3,6-dibromocarbazoles are readily available by electrophilic bromination of the corresponding 9-substituted carbazole. The method described here along with previously reported work such as the palladium catalyzed coupling[25] and lithiation chemistry[11] provides access to a wide variety of 3,6-disubstituted carbazole derivatives. We are currently investigating the utility of some of these carbazoles as potential excited state electron donors for use in organic synthesis.

EXPERIMENTAL

Commercially available 3,6-dibromocarbazole, 9-ethylcarbazole, 9-isopropylcarbazole and 9-phenylcarbazole were recrystallized from ethanol prior to use. All other commercially obtained chemicals were used as received. $NiCl_2$(dppp) was obtained from Strem Chemical and $NiCl_2$(dmpe) was prepared as previously reported.[31] 2-Thienyl magnesium bromide was prepared from 2-bromothiophene. All reactions were performed under an argon atmosphere. Ether and THF were freshly distilled from a sodium/benzophenone ketyl. Melting points were recorded on a MelTemp 3.0 apparatus and are uncorrected. Proton and carbon-13 NMR data were recorded at 300 and 75 MHz, respectively in $CDCl_3$. Chemical shifts are reported in ppm downfield from TMS (δ=0); coupling constants are given in Hertz. GC-MS were recorded on a Hewlett-Packard 5890 series II GC with a 5971 series mass selective detector (electron impact ionization). Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Carbazoles **3b,d,g,k** decomposed over time; thus, we were unable to obtain satisfactory elemental analyses on these compounds.

3,6-Dibromo-9-ethylcarbazole. A typical procedure is given for the bromination of 9-ethylcarbazole. To a stirred solution of 9-ethylcarbazole (2.0 g, 10.2 mmol) in acetic acid (100 mL) was added bromine (1.1 mL, 20.4 mmol) in acetic acid (1.1 mL), dropwise at room temperature over 20 min. After the addition was complete, the reaction mixture was poured into ice-cold water. The precipitate was collected by suction filtration and the products purified by flash column chromatography on silica eluting with 10% ether in hexanes. The first product to elute was 1,3,6,-tribromo-9-ethylcarbazole (0.105 g, 3%), mp 150-151 °C (lit.[32] mp 145-8 °C). ^{1}H

NMR: δ 8.06 (d, *J*= 1.8, 1H), 8.01 (d, *J*= 1.8, 1H), 7.72 (d, *J*= 1.8, 1H), 7.57 (dd, *J*= 8.7, 1.8, 1H), 7.28 (d, *J*= 8.7, 1H), 4.70 (q, *J*= 7.1, 2H), 1.42 (t, *J*= 7.1, 3H). The lower Rf product was 3,6-dibromo-9-ethylcarbazole (**2a**, 2.52 g, 70 %) which was obtained as white needles after recrystallization from ethanol, mp 140-141°C (lit.[4] mp 137-138 °C). ^{1}H NMR: δ 8.12 (d, *J*= 1.9, 2H), 7.55 (dd, *J*= 8.7, 1.9, 2H), 7.26 (d, *J*= 5.4, 2H), 4.29 (q, *J*= 7.2, 2H), 1.39 (t, *J*= 7.2, 3H). ^{13}C NMR: δ 138.8, 129.0, 123.5, 123.3, 111.9, 110.1, 37.8, 13.7. MS (EI): *m/z* 351 (M+, 50%), 353 (M+2, 100%), 355 (M+4, 50%).

From 3,6-dibromocarbazole: In an oven dried, 250 mL, round-bottomed flask equipped with a magnetic stir bar and a rubber septum was placed 3,6-dibromocarbazole (1.0 g, 3.1 mmol) and sodium hydroxide pellets (0.12g, 3.1 mmol) in 100 mL of dry acetone under an argon atmosphere. Diethyl sulfate (0.42 mL, 3.0 mmol) was added dropwise over 15 min. to the stirred reaction mixture at room temperature. After the addition, the reaction was stirred for four hours after which time all solids were removed by filtration and the solvent removed under reduced pressure to give a yellow solid. The residue was dissolved in ethyl acetate (50 mL) and successively washed with sodium bicarbonate, brine and water. The organic layer was dried over sodium sulfate, filtered and the solvent removed under reduced pressure to give a pale yellow solid. Recrystallization from ethanol gave **2a** (0.77g, 70% yield). The filtrate was evaporated and the resulting solid recrystallized to give additional product (0.22 g, 20% yield).

3,6-Dibromo-9-isopropylcarbazole. White prisms from ethanol, mp 130-131 °C (lit.[33] mp 128 °C). ^{1}H NMR: δ 8.11 (d, *J*= 1.9, 2H), 7.51 (dd, *J*= 8.8, 1.9, 2H), 7.36 (d, *J*= 8.8, 2H), 4.89 (septet, *J*= 7.0, 1H), 1.65 (d, *J*= 7.0, 6H). ^{13}C NMR: δ 138.3, 128.7, 123.9, 123.2, 111.8, 111.6, 47.1, 20.8. MS (EI): *m/z* 365 (M+, 50%), 367 (M+2, 100%), 369 (M+4, 48%).

3,6-Dibromo-9-phenylcarbazole. White needles from ethanol, mp 162-163 °C (lit.[4] mp 159-160 °C). ^{1}H NMR: δ 8.18 (d, *J*= 1.9, 2H), 7.63-7.58 (m, 2H), 7.51-7.46 (m, 5H), 7.23 (d, *J*= 8.7, 2H). ^{13}C NMR: δ 139.8, 136.7, 130.1, 129.3, 128.1, 126.9, 123.9, 123.2, 113.0, 111.5. MS (EI): *m/z* 399 (M+, 52%), 401 (M+2, 100 %), 403 (M+4, 50%).

Anal. Calcd for $C_{18}H_{11}Br_2N$: C, 53.90; H, 2.76; N, 3.49 Found: C, 53.78; H, 2.79; N, 3.41.

3,6-Dimethyl-9-ethylcarbazole (3a). A typical procedure for the Ni(II) catalyzed cross coupling is given for the preparation of **3a** from 3,6-dibromo-9-ethylcarbazole. In an oven dried, 1-L, three neck, round-bottomed flask equipped with a magnetic stir bar, a reflux condenser and a rubber septum was placed **2a** (2.0 g, 6.0 mmol) and [1,3-bis(diphenylphosphino)propane] nickel (II) chloride (0.16 g, 5.0 mmol) in 80 mL of dry ether under an argon atmosphere. To the stirred solution at room temperature was added, methylmagnesium bromide (18.0 mmol) dropwise over 20 min. via an addition funnel. During the addition, the color of the solution turned from orange to yellow to brown. After the addition, the reaction mixture was heated at reflux for two hours after which time the reaction was judged complete by TLC analysis. The reaction mixture was cooled to room temperature, then carefully quenched with saturated aqueous ammonium chloride at which point, a brown precipitate forms. All of the contents of the reaction were transferred to a separatory funnel and successively washed with sodium bicarbonate, brine and deionized water. The combined aqueous layers were extracted with ethyl acetate. The combined organic extracts were dried over sodium sulfate, filtered and the solvent removed under reduced pressure to give a yellow solid. Recrystallization from ethanol gave **3a** (0.99 g, 78% yield) as white needles, mp 66-7 °C (lit.[4] mp 62-63 °C). The filtrate was evaporated and the resulting solid recrystallized from ethanol to give additional product (0.16 g, 13% yield). ^{1}H NMR: δ 7.91 (s, 2H), 7.31 (s, 4H), 4.34 (q, *J*= 7.2, 2H), 2.58 (s, 6H), 1.14 (t, *J*= 7.2, 3H). ^{13}C NMR: δ 138.4, 127.6, 126.7, 122.8, 120.3, 108.0, 37.5, 21.3, 12.7.

From the lithiation of 3,6-dibromo-9-ethylcarbazole: A solution of 3,6-dibromo-9-ethylcarbazole (100 mg, 0.28 mmol) in THF (2.8 mL) was cooled to -78°C and *n*-Butyllithium (0.2 mL, 0.56 mmol) was added

slowly. The solution was stirred for 30 min at -78°C, then iodomethane (0.04 mL, 0.56 mmol) was added dropwise. The reaction mixture was allowed to warm to 0 °C and stirred for 20 min. The reaction was quenched with saturated ammonium chloride solution and the layers separated. The aqueous phase was extracted with ether and the combined organic extracts washed with brine, dried over magnesium sulfate, filtered and evaporated to give an oil. Purification by flash column chromatography on silica eluting with 10% ether in hexanes gave **3a** (47 mg, 75%) as a white powder.

3,6-Divinyl-9-ethylcarbazole (3b). a colorless oil.[34] ^{1}H NMR: δ 8.11 (d, *J*= 1.5, 2H), 7.56 (dd, *J*= 8.5, 1.5, 2H), 7.33 (d, *J*= 8.5, 2H), 6.90 (dd, *J*= 17.5, 10.9, 1H), 5.78 (d, *J*= 17.5, 1H), 5.20 (*J*= 10.9, 1H), 4.32 (q, *J*= 7.2, 2H), 1.42 (t, *J*= 7.2, 3H). ^{13}C NMR: δ 141.0, 138.3, 129.9, 125.0, 124.0, 119.3, 111.9, 109.4, 38.6, 14.7. MS (EI): *m/z* 247 (M+, 100%).

3,6-Diphenyl-9-ethylcarbazole (3b). White needles from ether/hexanes , mp 184.5-185.5 °C. ^{1}H NMR: δ 8.37 (d, *J*= 1.4, 2H), 7.77-7.72 (m, 6H), 7.50-7.46 (m, 6H), 7.34 (t, *J*= 7.3, 2H), 4.42 (q, *J*= 7.2, 2H), 1.49 (t, *J*= 7.2, 3H). ^{13}C NMR: δ 142.1, 139.9, 132.5, 128.8, 127.3, 126.5, 125.4, 123.6, 119.0, 108.9, 37.9, 13.9. MS (EI): *m/z* 347 (M+, 100%).

Anal. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03 Found: C, 89.84; H, 6.14; N, 4.02.

3,6-Di-(2-thienyl)-9-ethylcarbazole (3d). Yellow powder from chloroform/hexanes, mp 216-218 °C (dec.). ^{1}H NMR: δ 8.35 (d, *J*= 1.7, 2H), 7.75 (dd, *J*= 8.4, 1.7, 2H), 7.41-7.35 (m, 4H), 7.28-7.24 (m, 2H), 7.12 (dd, *J*= 5.1, 3.6, 2H), 4.38 (q, *J*= 7.2, 2H), 1.46 (t, *J*= 7.2, 3H). ^{13}C NMR: δ 145.6, 139.9, 128.0, 126.0, 124.6, 123.7, 123.3, 122.1, 118.1, 108.9, 37.8, 13.9. MS (EI): *m/z* 359 (M+, 100%).

3,6,9-Triethylcarbazole (3e). Colorless prisms from ethanol, mp 84-86 °C (lit.[4] mp 81-5 °C). ^{1}H NMR: δ 7.90 (s, 2H), 7.28 (s, 4H), 4.29 (q, *J*= 7.3, 2H), 2.82 (q, *J*= 7.6, 2H), 1.38 (t, *J*= 7.2, 3H), 1.33 (t, *J*= 7.6, 3H). ^{13}C NMR: δ 138.6, 134.4, 125.6, 122.9, 119.0, 108.1, 37.5, 28.9, 16.7, 13.8. MS (EI): *m/z* 236 (100%), 251 (M+, 56%).

3,6-Dimethyl-9-isopropylcarbazole (3f). Colorless prisms from ethanol, mp 65.5-67 °C. ^{1}H NMR: δ 7.85 (s, 2H), 7.34 (d, *J*= 8.5, 2H), 7.20 (d, *J*= 8.5, 2H), 4.85 (septet, *J*= 7.0, 1H), 2.50 (s, 6H), 1.62 (d, *J*= 7.0, 6H). ^{13}C NMR: δ 137.9, 127.4, 126.5, 123.2, 120.2, 109.6, 46.6, 21.2, 20.8. MS (EI): *m/z* 222 (100%), 237 (M+, 49%).

3,6-Divinyl-9-isopropylcarbazole (3g). white powder chloroform/isopropanol, mp 139-140 °C (dec.) ^{1}H NMR: δ 8.10 (d, *J*= 1.4, 2H), 7.53 (dd, *J*= 8.6, 1.4, 2H), 7.42 (d, *J*= 8.6, 2H), 6.89 (dd, *J*= 17.5, 10.9, 2H), 5.76 (dd, *J*= 17.5, 2H), 5.19 (d, *J*= 10.9, 2H), 4.92 (septet, *J*= 7.0, 1H), 1.68 (d, *J*= 7.0, 6H). ^{13}C NMR: δ 139.6, 137.3, 128.7, 123.8, 123.5, 118.3, 111.1, 110.1, 46.9, 20.8. MS (EI): *m/z* 246 (100%), 261 (M+, 91%).

3,6-Diphenyl-9-isopropylcarbazole (3h). White needles from ethanol, mp 153-154 °C. ^{1}H NMR: δ 8.37 (d, *J*= 1.6, 2H), 7.74-7.68 (m, 6H), 7.58 (d, *J*= 8.50, 2H), 7.50-7.44 (m, 4H), 7.36-7.30 (m, 2H), 5.02 (septet, *J*= 7.0, 1H), 1.74 (d, *J*= 7.0, 6H). ^{13}C NMR: δ 142.0, 139.4, 132.2, 128.8, 127.2, 126.4, 125.1, 124.0, 118.9, 110.3, 47.0, 20.9. MS (EI): *m/z* 361 (M+, 100%).

Anal. Calcd for $C_{27}H_{23}N$: C, 89.71; H, 6.41; N, 3.87 Found: C, 89.59; H, 6.46; N, 3.86.

3,6-Bis-(4-fluorophenyl)-9-isopropylcarbazole (3i). White prisms from ethanol, mp 161-162 °C. ^{1}H NMR: δ 8.29 (d, *J*= 1.5, 2H), 7.69-7.55 (m, 8H), 7.19-7.11 (m, 4H), 5.01 (septet, *J*= 7.1, 1H), 1.74 (d, *J*=

7.1, 6H). ^{13}C NMR: δ 162.0 (d, J_{C-F}= 45), 139.3, 138.0, 131.3, 128.7 (d, J_{C-F}= 7.7), 125.0, 123.9, 118.7, 115.5 (d, J_{C-F}= 21), 110.4, 47.0, 20.9. MS (EI): *m/z* 382 (100%), 397 (M+, 95%).

Anal. Calcd for $C_{26}H_{21}F_2N$: C, 81.59; H, 5.33; N, 3.52 Found: C, 81.61; H, 5.40; N, 3.51.

3,6-Dimethyl-9-phenylcarbazole (3j). White needles from isopropanol, mp 116-117 °C. ^{1}H NMR: δ 7.89 (s, 2H), 7.60-7.52 (m, 4H), 7.45-7.39 (m, 1H), 7.30 (d, *J*= 8.3, 2H), 7.20 (d, *J*= 8.3, 2H), 2.54 (s, 6H). ^{13}C NMR: δ 139.3, 138.1, 129.7, 129.0, 127.0, 126.8, 123.3, 120.1, 109.4, 21.4. MS (EI): *m/z* 271 (M+, 100%).

Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16 Found: C, 88.26; H, 6.43; N, 5.19.

3,6-Divinyl-9-phenylcarbazole (3k). White powder from chloroform/hexanes, mp 135-136 (dec.). ^{1}H NMR: δ 8.08 (s, 2H), 7.50-7.39 (m, 7H), 7.24 (d, *J*= 8.6, 2H), 6.80 (dd, *J*= 17.6, 10.9, 2H), 5.72 (d, *J*= 17.6, 2H), 5.14 (d, *J*= 10.9, 2H). ^{13}C NMR: δ 141.0, 137.3, 130.1, 129.9, 127.5, 126.9, 124.4, 123.5, 118.3, 111.5, 109.9. MS (EI): *m/z* 295 (M+, 100%)

3,6,9-Triphenylcarbazole (3l). White needles from ethanol, mp 142-143 °C. ^{1}H NMR: δ 8.40 (s, 2H), 7.72 (d, *J*= 7.2, 2H), 7.68-7.58 (m, 8H), 7.55-7.45 (m, 7H), 7.37-7.31 (m, 2H). ^{13}C NMR: δ 141.9, 140,8, 137.6, 133.6, 130.0, 128.8, 127.6, 127.3, 127.0, 126.6, 125.7, 124.0, 118.9, 110.2. MS (EI): *m/z* 395 (M+, 100%).

3,6-Diacetyl-9-ethylcarbazole (4). White powder from ethyl acetate/hexanes, mp 179-180 °C (lit.[4] mp 182-183 °C). ^{1}H NMR: δ 8.79 (d, *J*= 1.6, 2H), 8.18 (dd, *J*= 8.7, 1.6, 2H), 7.45 (d, *J*= 8.7, 2H), 4.42 (q, *J*= 7.3, 2H), 2.75 (s, 6H), 1.48 (t, *J*= 7.3, 3H). ^{13}C NMR: δ 197.5, 143.4, 129.7, 127.0, 123.0, 122.1, 108.7, 38.2, 26.7, 13.8. MS (EI): *m/z* 264 (100%), 279 (M+, 43%).

Dibutyl 9-ethylcarbazole-3,6-dicarboxylate (5). 3,6-Dibromo-9-ethylcarbazole (353 mg, 1.0 mmol) and dichloro-bis-(triphenylphosphine)palladium(II) (35 mg, 0.05 mmol) were dissolved in a mixture of n-butanol (9.0 ml, 100 mmol) and triethylamine (5.6 ml, 4.0 mmol) which had been presaturated with carbon monoxide. Carbon monoxide was bubbled through the reaction mixture for 1 h at room temperature. The reaction mixture was then stirred at 110 °C under an atmosphere of carbon monoxide for 7.5 h, after which the reaction was judged complete by tlc analysis. The mixture was cooled to room temperature, quenched with saturated ammonium chloride and the layers separated. The aqueous phase was extracted with ethyl acetate and the combined organic extracts washed with brine, dried over anhydrous magnesium sulfate, filtered and evaporated. Flash column chromatography on silica eluting with 20% ether in hexanes gave **5** (324 mg, 82 %) as a white powder, mp 64-65 °C (lit.[15] mp 59-59.5 °C). ^{1}H NMR: δ 8.84 (d, *J*= 1.5, 2H), 8.21 (dd, *J*= 8.7, 1.5, 2H), 7.39 (d, *J*= 8.7, 2H), 4.38 (m, 6H), 1.87-1.78 (m, 4H), 1.58-1.51 (m, 4H), 1.44 (t, *J*= 7.1, 3H), 1.03 (t, *J*= 7.3, 6H). ^{13}C NMR: δ 167.1, 143.1, 127.8, 122.9, 122.7, 122.1, 108.3, 64.7, 38.0, 30.9, 19.3, 13.8, 13.7. (EI): *m/z* 395 (M+, 100%). Also isolated was butyl 3-bromo-9-ethylcarbazole-6-carboxylate (56 mg, 15 %) as a clear oil. 8.76 (d, *J*= 1.5, 1H), 8.27 (d, *J*= 1.8, 1H), 8.19 (dd, *J*= 8.7, 1.5, 1H), 7.58 (dd, *J*= 8.6, 1.8, 1H), 7.40 (d, *J*= 8.7, 1H), 7.30 (d, *J*= 8.6, 1H), 4.41-4.32 (m, 4H), 1.85-1.76 (m, 2H), 1.57-1.52 (m, 2H), 1.44 (t, *J*= 7.2, 3H), 1.02 (t, *J*= 7.4, 3H). MS (EI): *m/z* 373 (M+, 100%), 375 (M+2, 98%).

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