JOC The Journal of Organic Chemistry

Article

Oxidative Coupling of Carbazoles: A Substituent-Governed Regioselectivity Profile

Sudesh Mallick, Sudhakar Maddala, Kalidass Kollimalayan, and Parthasarathy Venkatakrishnan

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02322 • Publication Date (Web): 06 Dec 2018

Just Accepted

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Oxidative Coupling of Carbazoles: A Substituent-Governed Regioselectivity Profile

Sudesh Mallick, Sudhakar Maddala, Kalidass Kollimalayan and

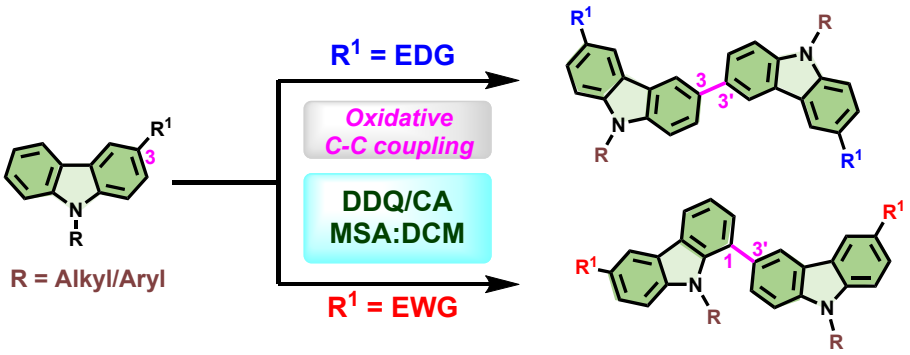
Parthasarathy Venkatakrishnan*

Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600 036,

Tamil Nadu, INDIA

pvenkat@iitm.ac.in

ABSTRACT

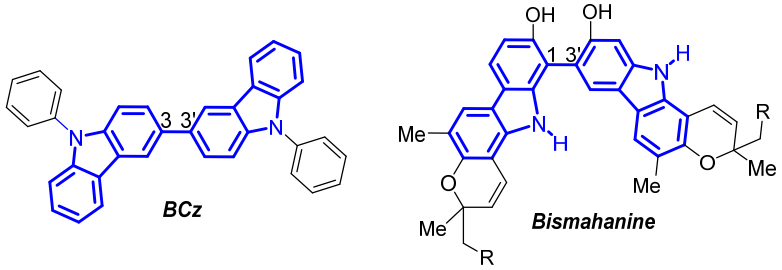


Oxidative C–C coupling of carbazoles possessing various substituents are demonstrated, in presence of organic (metal-free) recyclable oxidants, such as, DDQ or CA/H^+ for accessing bicarbazole regioisomers. Differently substituted carbazoles are examined to showcase regioselectivity discrimination (3,3'- versus 1,3'-bicarbazoles), and preferences based on sterics and electronics in oxidative coupling. Finally, a mechanism that involves carbazole radical cation has been traced (evidenced) and proposed based on the UV-vis-NIR absorption and EPR spectroscopy results. This study underlines the strategic chemical preparation of a series of bicarbazoles in an efficient manner.

Introduction

Carbazoles (Cz) — 2,2'-connected diphenylamines — are inextricable heteroaromatic skeletons in the fields of organic, medicinal and polymer chemistry.[1] Very importantly, bicarbazoles (BCz) are found to showcase potential application in organic electronics[2] and photonics,[3] sensing[4] and memory devices[5] because of their advantageous/exemplary characteristics, such as, low ionization potentials, excellent glassy nature (T_g) and blue luminescence, etc.[6] In particular, they have been identified as important bio-skeletons in several natural products.[7] For example, BCz is an excellent host material for high-efficiency phosphorescent OLEDs[2d,8] and bismahanine is a naturally occurring alkaloid showing excellent biological activity (Chart 1).[9]

Chart 1.



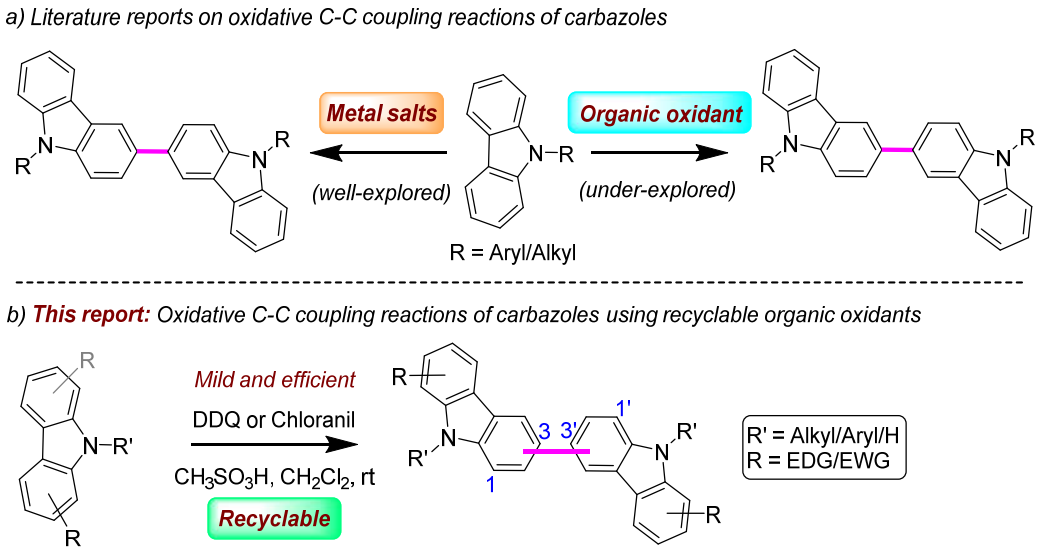
Syntheses of bicarbazoles have always been achieved by transition metal-based C–C coupling reactions[10] which are most often limited due to the following reasons: (i) catalysts and ligands used are expensive, (ii) high temperatures, strong bases and long reaction duration are inevitable, (iii) dehalogenation and homocoupling are commonly observed side reactions, and (iv) contamination of metal impurities with the isolated products in trace amounts. Especially, the presence of metal impurities in final products hampers their performance in electronic devices and introduces toxicity in biological studies. The other commonly exploited method to introduce C–C bond between electron rich arene carbazole is the oxidative coupling.[11] Generally, this approach leads to several side products (oligomers,

higher oligomers or polymers) through possible active sites. Hence this approach mostly relies on blocking of the active sites by substituents appropriately, and as a consequence, a thorough understanding of this reaction is deemed necessary. A careful literature survey revealed that the oxidative coupling of carbazoles (often with electron donating substituents) is mainly based on either metal salts[12a-d] or halogen-containing agents[12e-g] (Scheme 1a), while only a few reports exist on the utility of organic oxidants for the synthesis of bicarbazoles under harsh conditions, and that too only after blocking the active sites appropriately.[13] In continuation to our interest in the rapid synthesis of interesting hole-transporting materials,[14] we have recently reported a quinone-based recyclable organic oxidant (metal-free) for an economic, efficient and simple synthesis of tetrarylaminobiaryls/diarylaminobiaryls starting from diaryl/triarylamines.[15] Expanding this idea further, we envisioned that *N*-phenylcarbazoles (E_{ox} = 1.24 V vs SCE)[16] that are more planar and conjugated than triphenylamines (TPA, E_{ox} = 0.97 V vs SCE)[17] may also undergo oxidative C–C coupling under chloranil (CA, E_{red} = 0.02 V vs SCE)[18] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, E_{red} = 0.60 V vs SCE)[18] in presence of organic acids (organic oxidants) to yield bicarbazoles via a possible electron transfer. We also questioned the effect of substituents and sterics on the reactivity and regioselectivity in the oxidative coupling of carbazoles.

Thus, in this paper, we have reported the oxidative synthesis of 3,3'-bicarbazole as well as 1,3'-bicarbazole/1,1'-bicarbazole simply by changing the electronic nature (electron donating or electron withdrawing) of substituents on precursor carbazole using quinone-based organic recyclable oxidants (Scheme 1b). Moreover, we have thoroughly investigated the influence of sterics/electronics on the coupling and regioselectivity, compatibility of various functional groups, and the efficiency of the organic oxidants (DDQ/CA) in the oxidative coupling reaction of carbazoles. Such a chemical synthesis of bicarbazoles by tuning the nature of

substituents, and investigation of the regioselectivity/steric aspects of chemical oxidative coupling of carbazoles has been heretofore unreported. Further, based on UV-vis-NIR absorption and EPR spectroscopic studies and previous reports, it is shown that the mechanism of formation of bicarbazoles involves a radical cation pathway. Most importantly, the synthesized bicarbazoles can be structurally elaborated further, if need be, to arrive at a gamut of functional organic materials of interest and various carbazole-based natural products.

Scheme 1. Conditions explored for the oxidative coupling of carbazoles in the literature and in this report.

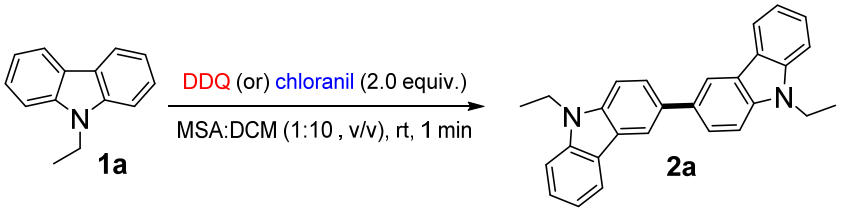


Results and Discussion

Initially, the reaction conditions for the oxidative coupling were optimized with the commercially available *N*-ethylcarbazole **1a** (E_{ox} = 1.12 V vs SCE).[19] The results are consolidated in Table 1 (see SI for complete optimization details). Among various organic oxidants screened, DDQ and chloranil (CA) provided the oxidative coupling product in near quantitative yields. The best optimized condition for the oxidative coupling is: *N*-ethylcarbazole (0.8 mmol), DDQ/CA (1.6 mmol), and methanesulphonic acid

(MSA):dichloromethane (DCM) (1:10, v/v), which afforded *N,N'*-diethyl-3,3'-bicarbazole **2a** in quantitative yields (>99%) at room temperature, in less than a minute (entry 1, Table 1). Any anomaly from the above optimized conditions caused discouraging results. In brief, absence of either oxidant or MSA did not afford the coupled product indicating the importance/role of oxidant and acid in the above reaction (entries 2-3, Table 1, *vide-infra*). Increasing or decreasing the amount of oxidant led to reduction in the product yield (entries 4-7, Table 1). Altering the oxidant (to PIFA or other quinone-based organic reagents, such as, quinone (Q), 1,4-naphthoquinone (NQ), etc.) in place of DDQ/CA was not worthwhile (entries 8-9, Table 1). Other Brønsted acids attempted, instead of MSA, did not give fruitful results (entry 10, Table 1). Also, changing the solvent gave depressed results (entry 11, Table 1). Longer reaction duration affected the yield of bicarbazole negatively. One may notice from Table 1 that the oxidative C–C coupling

Table 1. Optimization results with *N*-Ethylcarbazole **1a**.[a]



entry	Deviation from standard conditions	Time	Yield (%)
1	None	1 min	>99
2	Without chloranil (or) DDQ	6 h	0
3	Without MSA	6 h	0
4[b]	DDQ (1.0 equiv)	1 min	87
5[b]	Chloranil (1.0 equiv.)	1 min	79
6[c]	DDQ (10 equiv.)	1 min	88
7[c]	Chloranil (10 equiv.)	1 min	85
8	1.3 equiv. PIFA as oxidant in DCE	12 h	0
9	1,4-Quinone/1,4-Napthaquinone (2.0 equiv.)	12 h	36[b]/0
10	AcOH instead of MSA	12 h	0
11[b]	Toluene/Acetonitrile in place of DCM	10 min	60/83

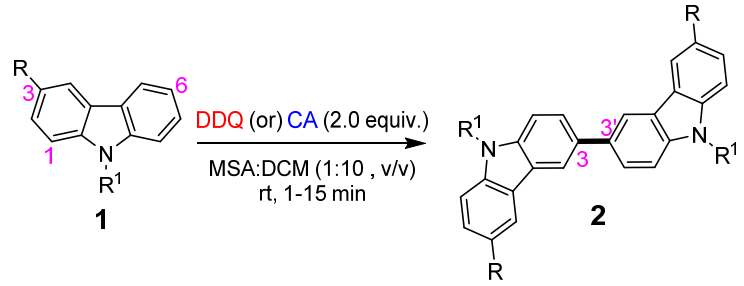
[a]All of the reactions were stirred at room temperature and vanishing of the starting material was monitored by TLC. [b]Starting material was isolated. [c]Polar spots were found in TLC.

reaction of *N*-ethylcarbazole **1a** to offer **2a** is efficient (near quantitative yields in less than a minute) in presence of the organic oxidant DDQ/CA and MSA, which is more attractive than the earlier methods involving harsh conditions (see SI for comparison).[13d] In principle, oxidative coupling of *N*-alkylcarbazole may occur at any of its active 1,3,6, and 8 positions. Under the above reaction condition, only 3,3'-coupled product was obtained regioselectively, and the oligomeric or polymeric side products through other active (1, 6 and 8) positions were not observed at all. The isolated bicarbazole products were free from contaminants, such as, excess quinones or hydroquinone after the reaction (see SI), facilitating easy purification. Besides, the hydroquinone produced after the reaction can be recycled/reused after aerobic oxidation or treatment with conc. HNO_3 to the corresponding DDQ or chloranil, as reported earlier.[15,20] The present methodology is indeed mild and efficient.

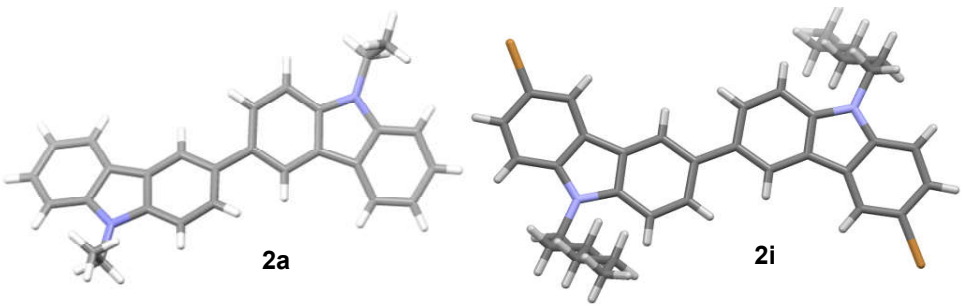
Having optimized the reaction conditions, the scalability of this reaction was examined. For this, one gram of **1a** was subjected to DDQ/H^+ conditions to provide **2a** in quantitative yields, within 1 min. After this successful attempt, we primarily tested the efficacy of the above reaction with several *N*-alkylcarbazole derivatives (E_{ox} ranging between ca. 1.09–1.35 V vs SCE, Scheme 2 and Table S1)[16] decorated by various electron donating (ED) and withdrawing (EW) substituents at 3-position; the other active positions 1, 6 and 8 were left open. As expected, all the *N*-alkylcarbazoles (such as, R = hexyl, **1b**; R = decyl, **1c**; R = benzyl, **1d**) under the above optimized conditions underwent oxidative coupling to give 3,3'-coupled products in good to excellent yields (79–99%, Scheme 2). In an analogous manner, compounds **1e-g** also conveniently afforded the corresponding 3,3'-bicarbazoles in very good yields (92–98%). It is to be noted that the oxidative coupling did not occur at 1-position of the carbazole ring containing ethyl/methoxy group. Similarly, biphenyl-substituted carbazole **1h** when subjected to oxidative coupling conditions led to 71% of the bicarbazole **2h** (10

min.), which otherwise was obtained in 82% (15 min.) and 98% yields (15 min.) under chloranil/H^+ (2.0 equiv. as well as 8.0 equiv., respectively) conditions. To our excitement, carbazoles containing electron withdrawing substituents, such as, –Br (**1i**), –COOMe (**1j**) and –COOH (**1k**) at 3-position were also conveniently converted to the corresponding symmetrical 3,3'-bicarbazoles (**2j-l**) in good to excellent (84–99%) yields demonstrating excellent functional group compatibility. To our surprise, compounds **1f**,**g**,**k** did not offer the corresponding bicarbazoles under CA conditions, and the unreacted starting material was recovered quantitatively. This may probably be reasoned to the mild oxidizing ability of CA. Fortunately, the compounds **2a** (CCDC 1865706) and **2i** (CCDC 1864769) were crystallized and their structures were unequivocally confirmed by X-ray structural analysis.

Scheme 2. Oxidative coupling results of *N*-alkylcarbazoles.

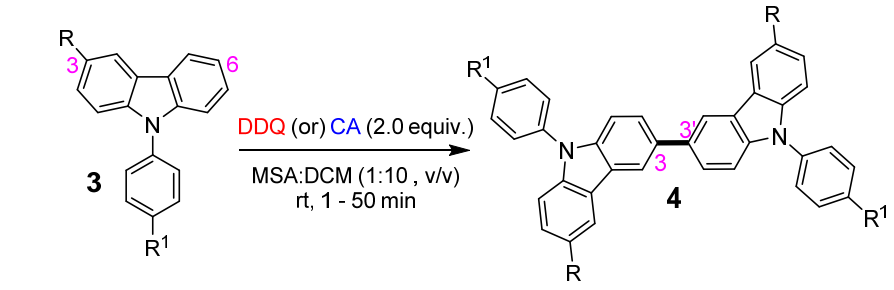


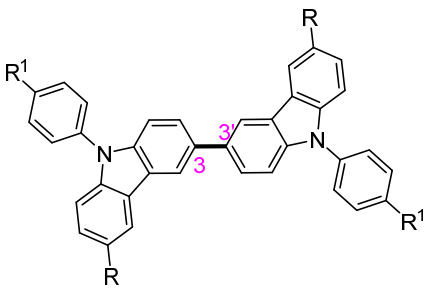
2a: R = H, R^1 = Et; 1 min, 99% (1 min, >99%)
2b: R = H, R^1 = Hex; 1 min, 79% (1 min, 91%)
2c: R = H, R^1 = Dec; 1 min, 79% (1 min, 82%)
2d: R = H, R^1 = Bz; 1 min, >99% (1 min, >99%)
2e: R = Et, R^1 = Et; 1 min, 98% (1 min, 98%)
2f: R = OMe, R^1 = Et; 1 min, 92%
2g: R = OMe, R^1 = Hex; 1 min, 94%
2h: R = Biph, R^1 = Hex; 10 min, 71% (15 min, 82%)
2i: R = Br, R^1 = Hex; 1 min, >99% (1 min, 97%)
2j: R = COOMe, R^1 = Et; 1 min, 92% (15 min, 65%)
2k: R = COOH, R^1 = Et; 15 min, 84%



The oxidative C–C coupling was then investigated with various *N*-phenylcarbazoles (Scheme 3, E_{ox} ranging between ca. 1.22–1.36 V vs SCE, Table S1).[16] Principally, *N*-phenylcarbazole possesses 3-open (*para* to *N*) positions and 4-open (*ortho* to *N*) positions active for oxidative coupling. When simple *N*-phenylcarbazole **3a** (E_{ox} = 1.24 V vs SCE)[16] was subjected to the optimized condition, only the symmetrical regioselective product, i.e., 3,3'-coupled product of carbazole, was formed immediately in near quantitative yields (**4a**, 97%, Scheme 3); the product 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) due to oxidative coupling at the *N*-phenyl site or other/oligomeric side products from carbazole ring were not obtained at all. Similarly, 3-substituted *N*-phenylcarbazole derivatives **3b-d** underwent smooth oxidative coupling to provide 3,3'-bicarbazoles (**4b-d**, 84–99%) in good to excellent yields. To our surprise, carbazoles with substituents (irrespective of their nature) on the *N*-phenyl ring (**3e-j**) proceeded very efficiently to yield the corresponding oxidative coupling products **4e-j**. The *ortho*-coupled products were not isolated.

Scheme 3. Oxidative coupling results of *N*-phenylcarbazoles.





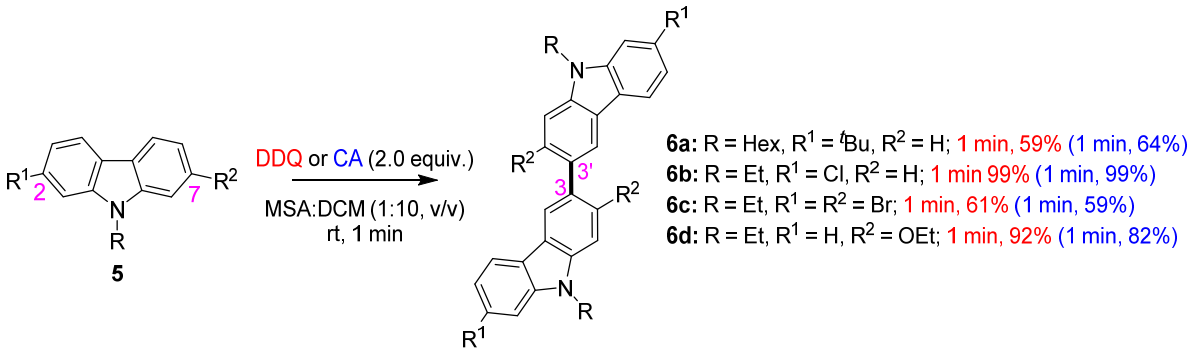
4a: R^1 = H, R = H; 1 min, 97% (1 min, 94%)
4b: R^1 = H, R = Ph; 1 min, >99% (1 min, >99%)
4c: R^1 = H, R = biPh; 30 min, 85% (50 min, 81%)
4d: R^1 = H, R = Br; 5 min, 84% (15 min, 84%)
4e: R^1 = Me, R = Br; 1 min, >99% (50 min, 81%)
4f: R^1 = Me, R = H; 1 min, >99% (1 min, >99%)
4g: R^1 = Ph, R = H; 1 min, >99% (1 min, >99%)
4h: R^1 = F, R = H; 1 min, >99% (1 min, >99%)
4i: R^1 = Br, R = H; 1 min, >99% (1 min, >99%)
4j: R^1 = $COCH_3$, R = H; 1 min, 82% (45 min, 73%)

The observed results are encouraging and are superior to those reported earlier.[12a,g,13d] From the above set of experiments, it is found that while the course of the reaction is unaltered, the yields as well as the duration of oxidative coupling were notably affected by the nature of substituents either at the carbazole nitrogen (as in **2a-d**, **2f-g**) or at the carbazole ring (as in **2g-i**, **2j-k** and **4a-d**), and not mainly by substituents at the *N*-phenyl ring (as in **4e-j**). This may be ascribed to the effective conjugation (electronic effect) present within the ring (**2e-k** and **4a-d**) and the less effective conjugation experienced by the tilted (tilt angle deduced from X-ray is ca. 43-57°) *N*-phenyl ring (**4e-j**, steric effect by *ortho* hydrogens).[21] In general, carbazoles containing ED group proceeded effectively when compared to carbazoles with EW groups. The results of oxidative coupling in the case of *N*-alkylcarbazoles are better when compared to *N*-phenylcarbazoles, which is probably due to the relatively high ionization potentials of the latter.[16,19] It is important to mention that in all the above cases coupling occurred only at 6-position (the open active position *para* to carbazole nitrogen) regioselectively to offer 3,3'-bicarbazole as observed in the earlier cases.[12a,g,13d] The preference to other possible 1,1'- and 1,3'-coupled products (via open positions *ortho* to carbazole nitrogen) was not identified at this stage. This could probably be due to severe steric effects at the reactive sites (i.e., 1-position) exerted by substituents at the carbazole nitrogen. Advantageously, no oligomeric or polymeric carbazole side products were observed under the tested reaction conditions, although there were active positions open and that the bicarbazoles could further be oxidized easily (E_{ox} = 0.8 V vs SCE).[16] In all the above cases, DDQ is found to be an efficient oxidant when compared to chloranil; especially, in cases **2h**, **2j**, **4c-e** and **4k**, reaction with chloranil took longer duration and resulted in slightly lower yields. This means that both chloranil and DDQ are suitable oxidants for carbazoles containing electron donating groups, and for carbazoles with electron withdrawing groups, DDQ turns out to be the best choice. Indeed, this method offers a high flexibility to

synthesize 3,3'-bicarbazoles with various substituents directly in one-step without having to introduce them at a later stage after coupling, which is actually very cumbersome and tedious.[8a]

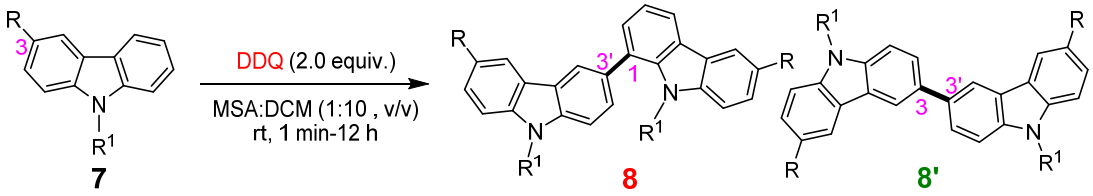
Further to understand the preferences for electronics and sterics in oxidative coupling, 2-substituted (two open active positions; position 3 is sterically encumbered and position 6 is steric-free) as well as 2,7-disubstituted carbazoles (**5a-5d**, both the positions 3 and 6 are sterically conjested) were subjected to the optimized C–C coupling conditions (Scheme 4). As expected, both 2-*tert*-butyl-*N*-ethylcarbazole (**5a**) and 2-chloro-*N*-ethylcarbazole (**5b**) underwent oxidative coupling smoothly at the steric-free position-6 to provide 3,3'-bicarbazoles **6a** and **6b**, respectively. It must be noted that oxidative coupling in these cases occurs at the less hindered site (i.e., 6-position) of the carbazole though there is another open site (3-position) situated adjacent to the 2-substituent. On the other hand, 2,7-dibromocarbazole **5c** successfully led to a sterically hindered 2,2',7,7'-tetrabromo-3,3'-bicarbazole product **6c** in moderate yields via the open active position. This means that if both the active open positions (3- and 6-) contain a neighboring substituent each (at 2 and 7), oxidative coupling happens through any of the free active position which once again may be decided by the electronic effect of the substituent. Added to our excitement, when 2-methoxy-*N*-ethylcarbazole **5d** was treated with DDQ or CA/H^+, it provided the sterically hindered bicarbazole **6d** in excellent yields overcoming the steric barrier. It is noteworthy that the C–C coupling occurred at the carbazole ring containing the electron-rich –OMe substituent, as opposed to other cases (**5a**,**b**), supporting the strong contribution of electronic (mesomeric) over steric effects.

Scheme 4. Oxidative coupling results of 2,7-disubstituted *N*-ethylcarbazoles.



Interestingly, carbazoles containing strong electron withdrawing groups **7a-g** (Scheme 5, E_{ox} > 1.3 V vs SCE, Table S1)[19b] behaved differently. To our surprise, the 3-cyano (–CN) substituted carbazole **7a** offered a mixture of 3,3'-symmetrical (**8'a**, 48%) as well as 1,3'-unsymmetrical bicarbazoles (**8a**, 52%) under DDQ/H^+ conditions, as evidenced by the ^{1}H NMR spectrum. The same reaction did not offer any oxidative coupling product under CA/H^+ conditions probably due to its weak oxidizing ability (E_{red} = 0.02 V vs SCE).[18] In contrast, 3-cyano-*N*-phenyl-carbazole **7b** afforded the oxidative 1,3'-unsymmetrical coupling product **8b** in 60% yield. Similarly, 3-nitrocarbazoles **7c-d** yielded 1,3'-bicarbazoles **8c-d** in 60-77% yield, besides the corresponding 3,3'-bicarbazoles in 23-40% yield in just 1–5 minutes. In line with this, carbazoles with other electron withdrawing functional groups, such as, formyl (–CHO, **7e-g**) and acetyl (–$COCH_3$, **7h**), at 3-position also provided 1,3'-bicarbazoles (**8e-h**) almost exclusively (68–86%) under the oxidative coupling conditions; the other 3,3'-bicarbazole was formed in 5–12% yield. These substrates required longer reaction time (12 h) than usual, and in some cases (**7b**, **7g** and **7h**) unreacted starting material was also isolated. Note that carbazoles substituted by strong electron withdrawing groups, –CH=$C(CN)_2$ (**7i**) furnished 1,3'-bicarbazole **8i** in relatively lower yields. The low yield in the case of **7i** → **8i** is probably due to the generation of polar polymeric product which may postulate a radical intermediacy (vide infra) under the reaction conditions; *N*-vinylcarbazole is known to undergo radical polymerization under oxidative (or electrochemical) conditions.[22] Stirring the

Scheme 5. Oxidative coupling results of carbazoles containing EWD groups.



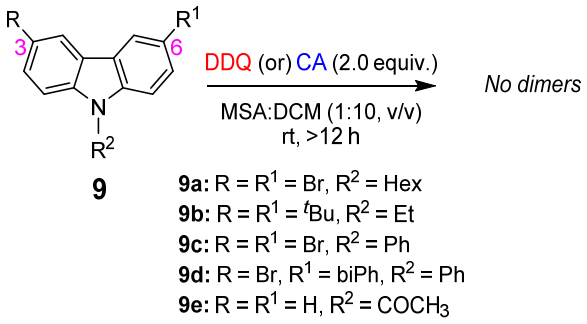
8a: R^1 = Hex, R = CN, 5 min, 52% (48%)
8b: R^1 = Ph, R = CN, 12 h, 60%
8c: R^1 = Et, R = NO_2, 5 min, 77% (23%)
8d: R^1 = Ph, R = NO_2, 1 min, 60% (40%)
8e: R^1 = Et, R = CHO, 12 h, 84% (<5%)
8f: R^1 = Hex, R = CHO, 12 h, 83% (12%)
8g: R^1 = Ph, R = CHO, 12 h, 86%
8h: R^1 = Hex, R = $COCH_3$, 5 min, 68%
8i: R^1 = Et, R = $CH=C(CN)_2$, 1 min, 50%

reaction in all the above cases for longer period (i.e., 12 h) did not improve/affect the yield of the 1,3'-bicarbazoles **8** very much, suggesting the stability of the products under the reaction conditions. Indeed, tuning the electronic nature of substituents at position-3 leads to 1,3'-bicarbazoles over 3,3'-bicarbazoles is remarkable.

In all the above cases of carbazole, the ring containing withdrawing group is not involved in oxidative coupling, probably due to the relatively electron deficient nature of the same compared to the other ring of the carbazole unit. Moreover, the facile exclusive formation of unsymmetrical 1,3'-bis(carbazoles) over 3,3'-bis(carbazoles) from a monosubstituted (EWG) carbazole through oxidative coupling is remarkable. To the best of our knowledge, this type of unsymmetrical oxidative coupling of carbazoles containing EW group to afford 1,3'-carbazoles is not yet reported in the literature and is reported here for the first time. Most importantly, DDQ is found to be very effective for carbazoles containing EW groups when compared to chloranil. This may be understood very readily based on the differences in their oxidation potentials and their ability to perform oxidation effectively (E_{red} 0.02 < 0.70 V vs SCE).

At this point, we questioned as to whether 1,1'-bicarbazole could be attained at all under the oxidative coupling conditions, after blocking the active 3- and 6-positions of carbazole (E_{ox} = 1.38 – 1.64 V vs SCE, Scheme 6, Table S1). With this in mind, substrate **9a/9b** (with two open 1- and 8- positions *ortho* to *N*-) was subjected to the oxidative coupling reaction (DDQ or CA/H^+, Scheme 6). Unfortunately, no oxidatively coupled product was obtained even after stirring the reaction for long duration (>12 h). This indicates that positions 3 and 6 are more active than the 1 and 8 positions of carbazole as supported by the calculations reported earlier.[16,17] To see if coupling can be enforced at the *para* position of the *N*-phenyl ring, both the active 3- and 6-positions of *N*-phenylcarbazole were substituted or blocked as in **9c-d**, and they were subjected to oxidative coupling condition for prolonged (36 h) hours. This led to no dimer formation (either at 1-/8-position or the *para* position of the *N*-phenyl ring) and the unreacted starting material was isolated quantitatively (Scheme 6), which in turn highlighted the steric effect offered by the *N*-alkyl/-phenyl ring at 1,8-positions and abstention of nitrogen lone pair from conjugation with the tilted *N*-phenyl ring. Similarly, *N*-acylcarbazole **9e** (with open 1,3,6 and 8 positions, E_{ox} = 1.64 V vs SCE) also did not afford any oxidative coupling product, which could be reasoned due to the effective engagement of nitrogen lone pair in resonance with the *N*-acyl unit rather than with the rings. This once again emphasized the role of nitrogen lone pair and its availability on the carbazole nitrogen in effecting oxidative coupling reactions successfully (for example, E_{ox} of TPA < E_{ox} of *N*-phenylcarbazole). The above results clue that the oxidative coupling is very mild and selective under the tested conditions.

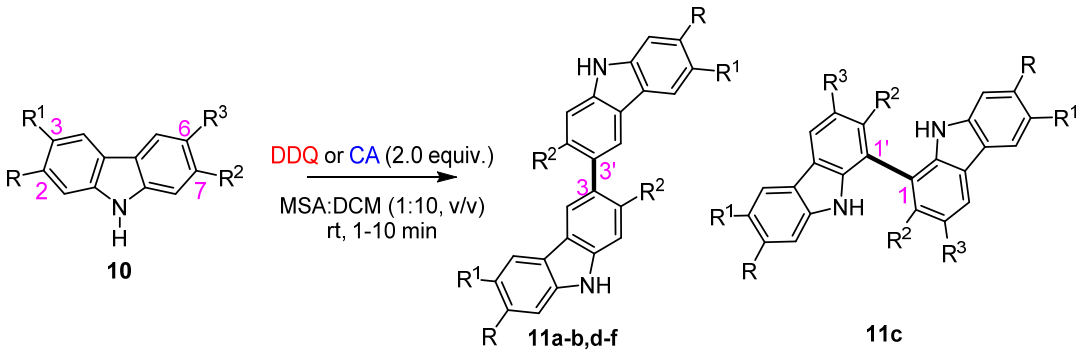
Scheme 6. Oxidative coupling results of 3,6-disubstituted carbazoles.



To validate if this method can be further extended to 9*H*-carbazole and to understand the steric influence/contribution of substituents at the 9-position of carbazole towards 1,1'- or 1,3'-dimers, a set of 9*H*-carbazoles containing substituents at 3, 3 and 6, 2, and 2 and 7 positions were examined under the oxidative coupling conditions (Scheme 7). The simple 9*H*-carbazole **10a** (E_{ox} = 1.16 V vs SCE)[19] when subjected to oxidative coupling yielded 3,3'-bicarbazole **11a** in 93% under DDQ/H^+, and in 83% under chloranil/H^+ conditions. Similarly, 3-ethylcarbazole **10b** also afforded the bicarbazole **11b** (83–94%) selectively without formation of other products, as observed in earlier cases. When both the active positions of carbazole are blocked and the *ortho* positions are free from sterics as in 3,6-dibromosubstituted 9*H*-carbazole **10c**, the oxidative coupling yielded 1,1'-bicarbazole **11c** in low yield (36%) emphasizing the role of sterics (due to substituents) at carbazole nitrogen restricting 1,1'-bicarbazole formation in **9a-c**. The 2-substituted or 2,7-disubstituted 9*H*-carbazoles **10d-f** also provided 3,3'-bicarbazoles (**11d-f**) in good to moderate yields. Noticeably, the sterically-free 6-position underwent oxidative coupling preferably over 1, 3 or 8 positions as seen with **10e-f**. It is important to state that the sterically hindered product **11f** is also accessible from **10f** in appreciable yields. That is, when two active positions (3- and 6-) are open with a substituent at its neighboring position, say at 2 (as in **10d**, **5c**), the oxidative coupling occurs at the sterically-free site, that is at 6 (as in **11d**, **6c**), which once

again proposes electronics play a crucial role overcoming sterics in oxidative coupling reactions.

Scheme 7. Oxidative coupling results of 9*H*-carbazoles.



11a: R = R^1 = R^2 = R^3 = H; 1 min, 93% (1 min, 83%)
11b: R = R^2 = R^3 = H; R^1 = Et; 1 min 94% (1 min, 83%)
11c: R = R^2 = H; R^1 = R^3 = Br; 5 min, 36%
11d: R = Me; R^1 = R^2 = R^3 = H; 1 min, 85% (1 min, 75%)
11e: R = Cl; R^1 = R^2 = R^3 = H; 1 min, 74% (1 min, 67%)
11f: R = R^2 = Br; R^1 = R^3 = H; 5 min 67% (10 min, 74%)

From all of the above experiments one may carefully notice that the reactivity trend mostly follows the E_{ox} of the precursor carbazoles. It is inferred that higher the oxidation potential (E_{ox} > 1.6 V vs SCE), greater is the difficulty to effect oxidation. Moreover, the nature and stability of the intermediates also play crucial roles in the course of oxidative coupling. In early days, various oxidation pathways of carbazole were proposed and studied by electrochemical means. These studies suggested the involvement of an electrochemically generated carbazole cation radical (Cz•+) before coupling to bicarbazoles (BCzs).[16,19] Well known is the fact that several electron-rich aromatic compounds, including carbazoles, form charge-transfer complexes with various electron-deficient compounds such as DDQ/CA.[23] To garner insights into the mechanism of oxidative C–C coupling of carbazoles mediated by DDQ or CA/H^+, the reaction course was monitored initially by UV-vis-NIR absorption spectroscopy. As expected, a 1:1 mixture of solutions of *N*-ethylcarbazole (**1a**, λ_{max} = 332, 347 nm) and DDQ (λ_{max} = 353, 387 nm) in DCM (in the absence of acid) turned blue

corresponding to the absorption at a λ_{max} value of 647 nm in the visible region (see Figure 1), which may be attributed to a charge-transfer (CT) complex formed between the electron donor carbazole and acceptor DDQ.[23] The addition of weak acids, such as AcOH, did not affect the CT complex (**1a**–DDQ) and the CT band (shape and position) very much. In contrast, step-wise addition of MSA to the blue-colored solution, immediately resulted in the evolution of two new bands at ca. 638 and 1117 nm. This near-IR band resembled the absorption spectrum recorded after the treatment of BCz **2a** with either DDQ/H^+ or one-electron oxidant TPA-salt (tris(4-bromophenyl)ammoniumyl hexachloroantimonate salt). Based on the experiments with bicarbazole **2a** and based on the previous literature evidences,[13d,16] one may attribute this new set of main bands to the radical cation of the 3,3'-bicarbazole (**2a**•+) and not to the inter-valence charge-transfer band of distonic cation radical after oxidative coupling. This supports the role of MSA in promoting electron-transfer (donor → acceptor) during oxidative coupling of carbazole. Treatment of Cz with MSA alone did not result in the formation of bicarbazole, which indicates the absence of arenium cation mechanism.[18c,d] To add to this, the treatment of **1a** with TPA-salt also resulted a minor absorption band corresponding to **1a**•+ notably at ca. 735 nm, which rapidly diminished in intensity and grew as a new band at 1170 nm with time (see SI). It appears that the oxidative coupling of carbazole via **1a**•+ proceeds very rapidly as soon as the CT complex was treated with acids, such as, MSA. At this point, it is important to recall that the bimolecular rate constant for the electrochemical oxidative coupling of carbazoles is calculated to be ca. 10^8–10^6 mol^{-1} s^{-1},[16] which is far higher (three to five orders of magnitude) than that of triphenylamines, supports our observation. Consequently, we could not capture the radical cation of *N*-ethylcarbazole (**1a**•+) generated under oxidative conditions by UV-vis absorption spectroscopic means. Hence, 3,6-di-*tert*-butyl-*N*-ethylcarbazole (**9b**), where the active positions are blocked and the generated radical cation would be trapped within the carbazole

rings without further possibiliy for oxidative coupling, was chosen for our study. As observed earlier, a 1:1 mixture of **9b** and DDQ formed a charge-transfer complex (**9b**–DDQ, λ_{max} abs = 678 nm) which upon addition of MSA finally resulted new absorption bands at around 725 as well as 815 nm,[13d,16] which was very different from that of the bicarbazole radical cation (**2a**•+) and also resembled the absorption spectrum obtained by the treatment of **9b**/**1a** with TPA-salt (λ_{max} = 728, 816 nm) pointing to the formation/involvement of the carbazole radical cation (**9b**•+/**1a**•+) intermediate during the oxidative coupling of carbazoles. This result is in line with the earlier studies and further highlights the stability of radical cations of 3,6-disubstituted carbazoles (for example, **9b**) as well as the 3,3'-bicarbazole (for example, **2a**) under the reaction conditions. Also, an EPR spectrum recorded for **9b** under the reaction condition revealed a stable strong broad signal with no hyperfine structure and a *g* value of 2.1646 resembling that of the one with TPA-salt (*g* = 2.1649). This explains the intermediacy of **1a**•+ in the oxidative coupling reactions.

With the above information that suggests the presence of Cz•+ during oxidative coupling and also in analogy with the previous reports, a step-wise mechanism has been proposed for the formation of BCz from Cz under DDQ or CA/H^+ conditions (Scheme 8). As may be seen, the formation of the charge-transfer complex (Cz-DDQ) between carbazole and DDQ is the first step. Next, the addition of strong acid promotes rapid electron transfer from electron-rich carbazole to the electron-deficient protonated DDQ (more electrophilic). The Cz•+ thus formed dimerizes immediately to form a dication ($BCzH_2^{2+}$) which further loses two protons immediately to produce bicarbazole BCz in the last step. Now,

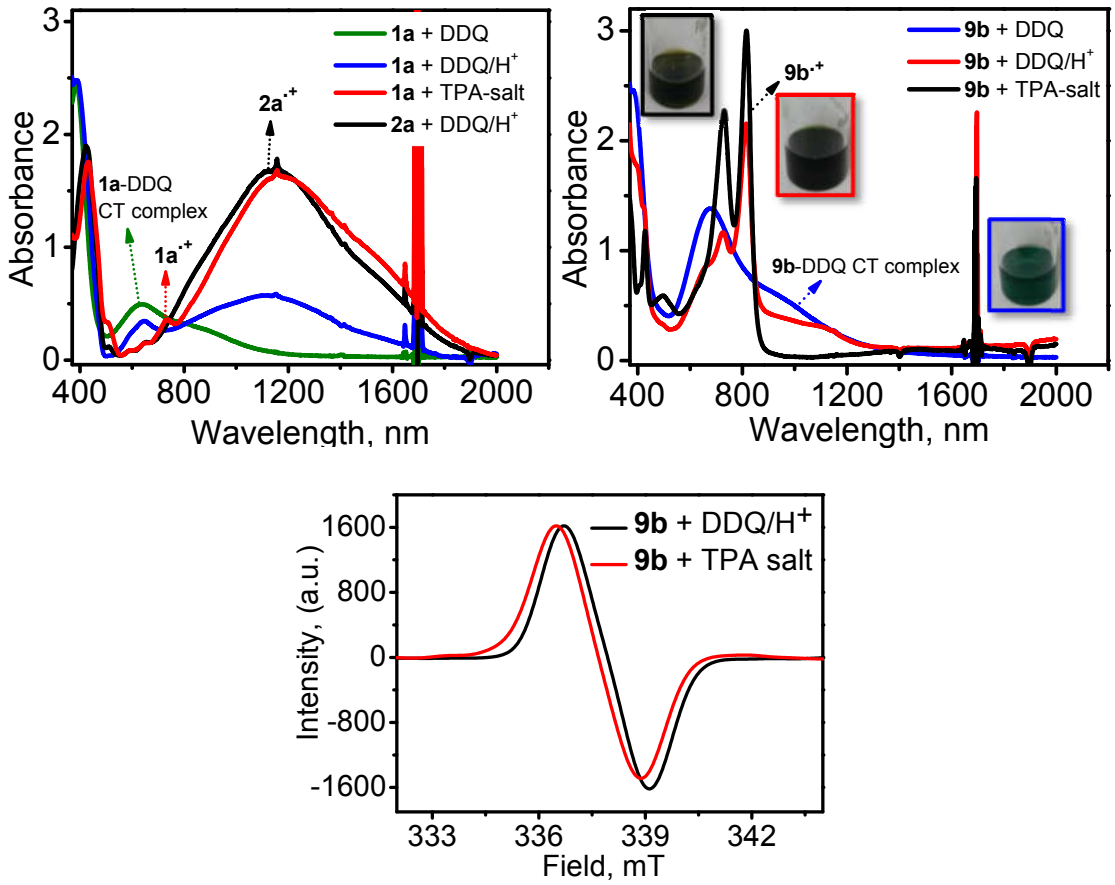
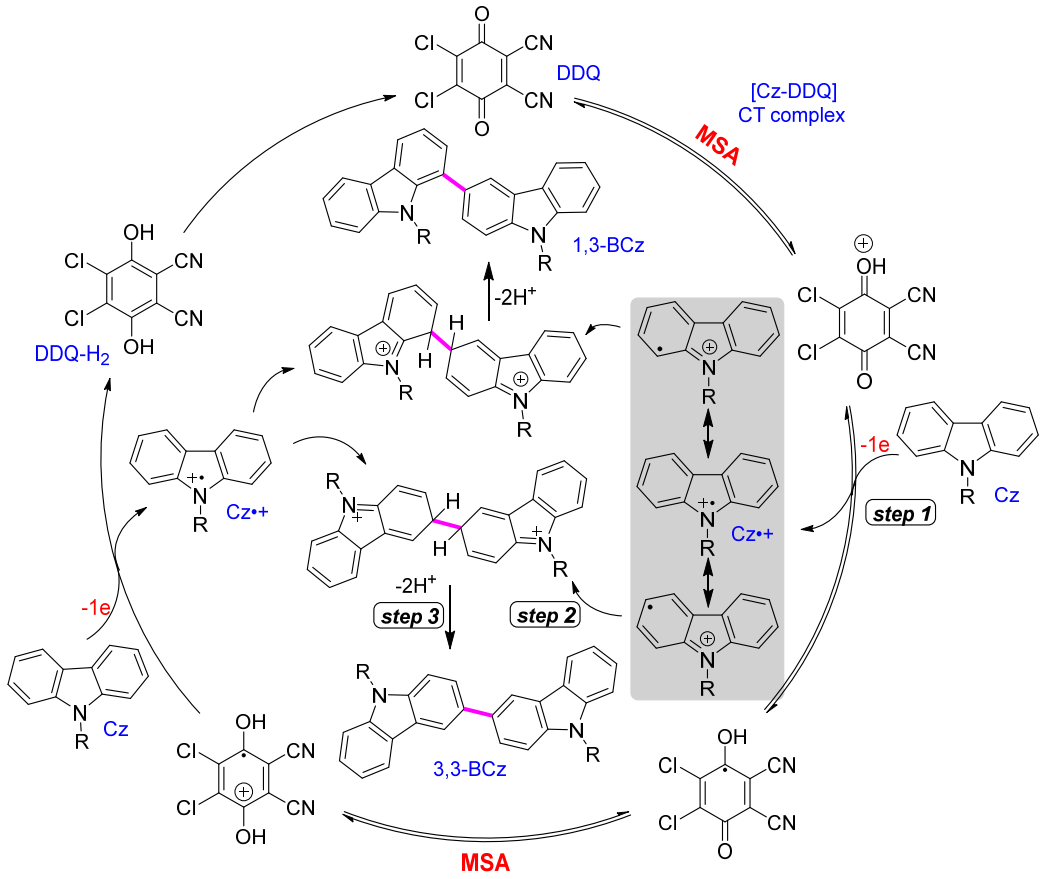


Figure 1. (Left) UV-vis-NIR absorption spectroscopy studies of **1a**→**2a** for tracing carbazole radical cation (**1a**•+) intermediate. (Right) UV-vis-NIR absorption spectrum of **9b**•+ species under the optimized conditions. (Bottom) EPR spectrum of **9b** upon treatment with DDQ/H^+ as well as TPA-salt showing the presence of radical cation (**9b**•+) mediacy in the oxidative coupling reactions. Photographs reveal the color of the intermediates generated during the reaction.

simple comparison of the redox potentials of the monomer Cz (E_{ox} = 1.16 V vs SCE) and bicarbazole BCz (E_{ox} = 0.80, 1.1 V vs SCE)[24] dictates that the latter is a better electron donor than the former, and hence BCz must further undergo oxidation by donating an electron either to Cz or to DDQ under the reaction conditions and generate BCz•+, which ultimately is neutralized under the regular work-up conditions (using aqueous bases, TEA, etc).[25] Thus, excess amounts of oxidant in the reaction medium may lead to higher oligomers or polymers rapidly (as seen in Table 1). A similar mechanism involving Cz•+ was proposed when metal-based oxidants were used for the oxidative coupling reactions.[12a,g] The other possible

coupling pathways postulated in the literature are: (i) aromatic electrophilic substitution-type reaction of Cz•+ with neutral Cz leading to

Scheme 8. Mechanistic proposal for the oxidative coupling of carbazoles.



distonic cation radical and subsequent loss of an electron and two protons leading to aromatization, (ii) initial hydride ion abstraction from Cz by DDQ followed by an aromatic electrophilic substitution-type reaction of Cz+ with neutral Cz and loss of proton and aromatization, and (iii) protonation (weak) of carbazole to provide the quaternary ammonium salt, and then loss of a hydrogen atom to give the carbazolyl cation radical that initiates coupling. Among the possible reaction mechanisms, the one involving radical cation dimerization proposed herein and the electrophilic substitution-type reaction by the radical cation are meaningful insofar as the high reactivity of carbazoles is concerned. But, on candid comparison of the bimolecular rate constant values of oxidative coupling for a set of

carbazoles, it makes more sense to believe that the oxidative coupling of carbazoles proceeds via a radical cation dimerization followed by deprotonation pathway.

Conclusions

In summary, we have developed an efficient methodology (metal-free, mild, simple, economic) for the oxidative coupling of carbazoles using recyclable organic oxidants (DDQ or CA/MSA). It is found that the oxidative coupling of electron-rich carbazoles proceeded very readily when compared to their electron-deficient analogs. Interestingly, the introduction of strong electron withdrawing groups, such as,–NO_2, –CN, –$COCH_3$ and –CHO at 3-position of carbazole led to 1,3'-carbazole dimers in a regioselective manner. Such a substituent-based selectivity/reactivity profile in the regioisomeric discrimination of the oxidative dimerization of carbazoles is heretofore unreported. The proposed conditions offer excellent functional group tolerance, and even sterically hindered carbazoles underwent oxidative coupling smoothly to provide dimers in very good yields. By means of UV-vis-NIR absorption and EPR spectroscopy, it is shown that the mechanism of oxidative dimerization of carbazoles involves the intermediacy of carbazole cation radical (Cz•+). Presently, our research efforts are towards the development of novel transformations using this reagent system, and development of interesting carbazole dimers of biological importance.

EXPERIMENTAL SECTION

General Aspects. All reagents were used as purchased. Solvents, such as, dichloromethane (DCM), dimethyl sulphoxide (DMSO), acetonitrile (ACN) and 1,2-dichloroethane (DCE) were dried and distilled over CaH_2, toluene was distilled over sodium. All reactions were carried out in oven-dried glassware under N_2 gas atmosphere and were monitored by TLC analysis using Merck silica gel (60 F_{254}) pre-coated plates (0.25 mm). The compounds were visualized under a UV lamp (366 or 254 nm) in UV chamber or using phosphomolybdic acid (PMA) or 2,4-dinitrophenyl hydrazine (2,4-DNP) solutions as stains to indicate the compound as a spot to the nacked-eye. The crude product was purified by silica gel (100-200 mesh or 60-120 mesh) column chromatography. Melting points reported are corrected. The infrared spectra of compounds were recorded on a JASCO FT/IR-4100 spectrometer using dry KBr pellet and IR signals are quoted in wavenumbers (cm^{-1}). ^1H (400 or 500 MHz) and ^{13}C (100 or 125 MHz) NMR spectra were recorded at ambient temperature using a Bruker Avance FT-NMR (400 or 500 MHz) spectrometer in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) with TMS as the internal reference. All chemical shift values are reported in parts per million (ppm, δ). While ^1H NMR spectra are referenced to the residual proton solvent peak ($CDCl_3$, δ = 7.26 ppm; DMSO-d_6, δ = 2.50 ppm) or calibrated to tetramethylsilane (δ = 0.00), ^{13}C NMR spectra are referenced to $CDCl_3$, δ = 77.16 ppm or DMSO-d_6, δ = 39.51 ppm, respectively. The ^1H NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, multiplet; dd, doublet of doublet; td, triplet of doublet; dt, doublet of triplet; tt, triplet of triplet; bs, broad singlet, and their coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Q-Tof Micro micromass spectrometer. UV-vis absorption spectra for simple starting materials were recorded on a AGILENT 8453 diode-array spectrophotometer

and UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-3100 UV-vis-NIR absorption spectrophotometer using commercially purchased spectroscopic grade solvents.

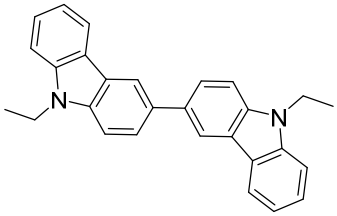
The starting materials, such as 3-bromo-9-(*p*-tolyl)-9*H*-carbazole (**3e**), carbazole (**10a**), 3-ethyl-9*H*-carbazole (**10b**), 2-chloro-9*H*-carbazole (**10e**) and 2,7-dibromo-9*H*-carbazole (**10f**) were commercially purchased and were used as received. Other carbazoles, such as, *N*-ethyl carbazole (**1a**),[26] 9-hexyl-9*H*-carbazole (**1b**),[27] 9-decyl-9*H*-carbazole (**1c**),[28] 9-benzyl-9*H*-carbazole (**1d**),[29] 9-ethyl-3-methoxy-9*H*-carbazole (**1g**),[30] 3-bromo-9-hexyl-9*H*-carbazole (**1j**),[31] methyl 9-ethyl-9*H*-carbazole-3-carboxylate (**1k**),[32] 9-ethyl-9*H*-carbazole-3-carboxylic acid (**1l**),[33] 9-phenyl carbazole (**3a**),[34] 3,9-diphenyl-9*H*-carbazole (**3b**),[35] 3-bromo-9-phenyl-9*H*-carbazole (**3d**),[36] 9-(*p*-tolyl)-9*H*-carbazole (**3f**),[37] 9-(1,1'-biphenyl-4-yl)-9*H*-carbazole (**3g**),[38] 9-(4-fluorophenyl)-9*H*-carbazole (**3h**),[39] 9-(4-bromophenyl)-9*H*-carbazole (**3j**),[40] 9-(*p*-acetylphenyl)-9*H*-Carbazole (**3k**),[41] *N*-ethyl-2,7-dibromocarbazole (**5c**),[42] 2-ethoxy-9-ethyl-9*H*-carbazo le (**5d**),[43] 9-hexyl-9*H*-carbazole-3-carbonitrile (**7a**),[44] 9-phenyl-9*H*-carbazole-3-carbonitrile (**7b**),[45] 9-ethyl-3-nitro-9*H*-carbazole (**7c**),[46] 3-nitro-9-phenyl-9*H*-carbazole (**7d**),[46] 9-ethyl-3-formyl-9*H*-carbazole (**7e**),[47] 9-hexyl-3-formyl-9*H*-carbazole (**7f**),[48] 9-phenyl-9*H*-carbazole-3-carbaldehyde (**7g**),[45] 3-acetyl-9-hexyl-9*H*-carbazole (**7h**),[49] 9-ethyl-3-(dicyanovinyl)-9*H*-carbazole (**7i**),[50] 3,6-dibromo-9-hexyl-9*H*-carbazole (**9a**),[51] 3,6-di-*tert*-butyl-9-ethyl-9*H*-carbazole (**9b**),[52] 3,6-dibromo-9-phenyl-9*H*-carbazole (**9c**),[53] 3-(biphenyl-2-yl)-6-bromo-9-phenyl-9*H*-carbazole (**9d**),[54] 9-acetyl-9*H*-carbazole (**9e**),[55] 3,6-dibromo-9*H*-carbazole (**10c**),[56] 2-(*tert*-butyl)-9H-carbazole (**10d**)[57] were synthesized according to the literature reported procedures, characterized by ^{1}H and ^{13}C NMR spectroscopy and the data were verified with the cited literature reports.[26-57]

Synthesis of 3,3'- and 1,3'-bicarbazoles via the oxidative C–C coupling method. A general procedure for the synthesis of 3,3'- and 1,3'-bicarbazoles from the corresponding carbazole precursors is described below.

General procedure for the oxidative coupling of carbazoles. A solution of the carbazole derivative (0.8 mmol, 1.0 equiv.) in dry DCM (10.0 mL) was cooled to 0 °C, and methanesulphonic acid (MSA) was added slowly at this temperature. After stirring the contents for few minutes at 0 °C, DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 370 mg, 1.6 mmol, 2.0 equiv.) or chloranil (401 mg, 1.6 mmol, 2.0 equiv.) was added. Immediately, the color of the reaction mixture turned blue-green to blue depending on the substrate. The progress of the reaction was monitored by TLC (thin layer chromatography) regularly. As soon as the starting material disappeared completely, as noticed by TLC, the saturated $NaHCO_3$ solution was carefully added under ice-cold conditions. The whole of the reaction contents was transferred into a separating funnel and the organic portion was extracted into chloroform (3 × 10 mL). The combined organic layer was washed once again with saturated sodium bicarbonate solution (in case of DDQ as the oxidant) or 2N NaOH (in case of chloranil as the oxidant). Now, the aqueous portion appeared orange to red in color and the organic portion remained colorless. The organic layer was then washed with brine (saturated sodium chloride) solution, dried over anhydrous Na_2SO_4, filtered and dried under vacuum. The crude residue was purified by silica-gel column chromatography using hexane-ethyl acetate mixtures as the eluent. The pure products isolated were colorless, pale yellow to dark brown solids or liquids.

A typical procedure for the synthesis of *N*,*N*'-diethyl-3,3'-bicarbazole, starting from *N*-ethyl carbazole is given below.

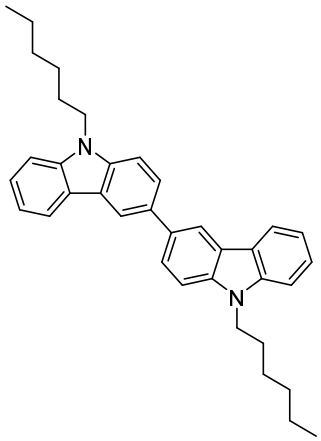
Typical procedure for the synthesis of *N*,*N*-diethylbicarbazole (2a) from *N*-ethyl carbazole (1a).[24] To a solution of *N*-ethyl carbazole (159 mg, 0.81 mmol, 1.0 equiv.) in dry dichloromethane (10.0 mL) at 0 °C methanesulphonic acid (1.0 mL) was introduced. After stirring the contents for a period of 2 3 minutes at this temperature, DDQ (370 mg, 1.63 mmol, 2.0 equiv.) was added. Immediately, the reaction mixture turned into deep-blue colour. The reaction mixture stirred further and allowed to reach room temperature slowly. The advancement of the reaction was noted carefully by TLC. As soon as the reaction was complete (1 min, as noticed on TLC), saturated $NaHCO_3$ solution was added carefully into the flask under ice-cold conditions. The organic portions were extracted into chloroform (3 × 10 mL) as the colorless layer. The combined organic layer was repeatedly washed with saturated $NaHCO_3$ solution to remove 2,3-dichloro-5,6-dicyanobenzoquinone completely, followed by washing with brine, dried over anhydrous Na_2SO_4, filtered, concentrated and dried. The crude product obtained was subjected to silica-gel column chromatography using hexane-ethyl acetate mixtures (5% ethyl acetate in hexane) as the eluent. The pure product (off-white solid) was obtained in quantitative yield (157 mg, 0.81 mmol, >99%).



Time: 1 min (DDQ/chloranil). Yield: 157 mg, >99% (Chloranil); 157 mg, >99% (DDQ). Off-white solid. R_f = 0.4 (19:1, hexane/EtOAc). Mp: 191-192 ˚C (lit.[24] 189 ˚C). IR (KBr, cm^{-1}): 3049, 2973, 2927, 1599, 1470, 1379. ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 1.28 Hz, 2H), 8.19 (d, J = 7.72 Hz, 2H), 7.83 (dd, J = 8.44 and 1.68 Hz, 2H), 7.49 (d, J = 8.48 Hz, 2H), 7.48 (dt, J = 8.0 and 1.20 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.25 (dt, J = 8.0 and 1.20 Hz, 2H), 4.41 (q, J = 7.2 Hz, 4H), 1.47 (t, J = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz,

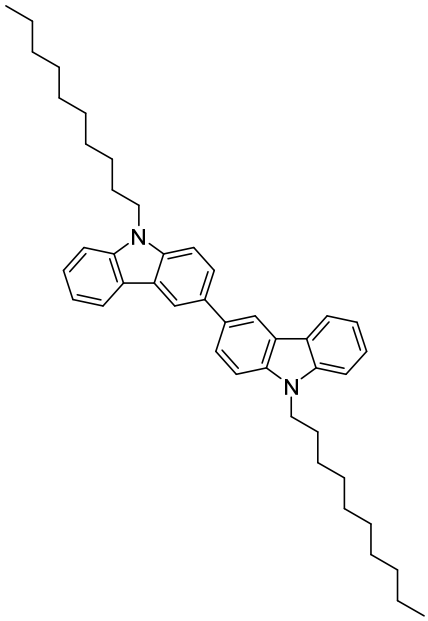
$CDCl_3$): δ 140.5, 139.1, 133.5, 125.8, 125.7, 123.6, 123.3, 120.6, 119.1, 118.9, 108.8, 108.7, 37.7, 14.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{28}H_{25}N_2$, 389.2018; found, 389.2025.

9,9'-Dihexyl-9*H*,9'*H*-3,3'-bicarbazole (2b)[58]



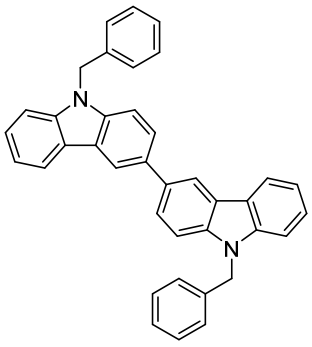
Time: 1 min (DDQ/chloranil). Yield: 161 mg, 79% (DDQ); 186 mg, 91% (chloranil). Pale yellow gummy liquid. R_f = 0.3 (19:1, hexane/EtOAc). IR (neat, cm^{-1}): 3051, 2952, 2926, 1465, 1378, 1238. ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 1.32 Hz, 2H), 8.19 (d, *J* = 7.68 Hz, 2H), 7.83 (dd, *J* = 8.44 and 1.68 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.48 (dt, *J* = 8.40 and 1.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.25 (dt, *J* = 8.0 and 1.0 Hz, 2H), 4.35 (t, *J* = 7.24 Hz, 4H), 1.91 (q, *J* = 7.24 Hz, 4H), 1.47-1.23 (m, 12H), 0.88 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.1, 139.7, 133.5, 125.8, 125.7, 123.6, 123.2, 120.6, 119.1, 118.9, 109.0, 108.9, 43.4, 31.8, 29.2, 27.2, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{36}H_{41}N_2$, 501.3270; found, 501.3291.

9,9'-Didecyl-9*H*,9'*H*-3,3'-bicarbazole (2c)



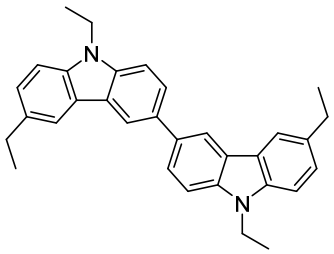
Time: 1 min (DDQ/chloranil). Yield: 197 mg, 79% (DDQ); 205 mg, 82% (chloranil). Pale brown gummy liquid. R_f = 0.2 in hexane. IR (KBr, cm^{-1}): 3054, 3018, 2922, 1623, 1593, 1492, 1452, 1362, 1324, 1278, 1258, 1229, 1176, 1164, 1068, 1011. ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, J = 1.44 Hz, 2H), 8.18 (d, J = 7.64 Hz, 2H), 7.83 (dd, J = 8.48 and 1.8 Hz, 2H), 7.49 (d, J = 8.52 Hz, 2H), 7.48 (dt, J = 8.16 and 1.08 Hz, 2H), 7.43 (d, J = 8.04 Hz, 2H), 7.24 (dt, J = 8.0 and 1.2 Hz, 2H), 4.34 (t, J = 7.2 Hz, 4H), 1.92 (qt, J = 7.2 Hz, 4H), 1.47-1.22 (m, 28H), 0.87 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.1, 139.7, 133.6, 125.8, 125.7, 123.6, 123.2, 120.6, 119.1, 118.9, 109.0, 108.9, 43.4, 32.0, 29.69, 29.67, 29.6, 29.4, 29.2, 27.5, 22.8, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{44}H_{56}N_2$, 612.4443; found, 612.4427.

9,9'-Dibenzyl-9*H*,9'*H*-3,3'-bicarbazole (2d)



Time: 1 min (DDQ/chloranil). Yield: 207 mg, > 99% (DDQ); 207 mg, > 99% (chloranil). Amorphous white solid. R_f = 0.3 (19:1, hexane/EtOAc). Mp: 238-240 °C. IR (KBr, cm^{-1}): 3051, 3028, 3008, 2923, 1627, 1602, 1485, 1456, 1376, 1330, 1258, 1212, 1154, 1064, 1027. ^1H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, J = 1.7 Hz, 2H), 8.19 (dd, J = 7.65 and 0.5 Hz, 2H), 7.76 (dd, J = 8.4 and 1.4 Hz, 2H), 7.43 (t, J = 8.3 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.29-7.21 (m, 8H), 7.17 (d, J = 8.0 Hz, 4H), 5.52 (s, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.3, 140.0, 137.4, 133.9, 128.9, 127.6, 126.6, 126.1, 125.9, 123.8, 123.4, 120.6, 119.4, 119.1, 109.3, 109.2, 46.9. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{38}H_{28}N_2$, 512.2252; found, 512.2256.

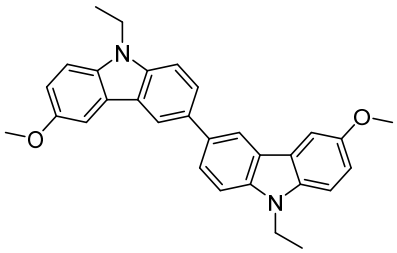
6,6',9,9'-Tetraethyl-9*H*,9'*H*-3,3'-bicarbazole (2e)



Time: 1 min (DDQ/chloranil). Yield: 44 mg, 98% (DDQ); 44 mg, 98% (chloranil). Dull white solid. R_f = 0.35 (19:1, hexane/EtOAc). Mp: 216-217 °C. IR (KBr, cm^{-1}): 3009, 2961,

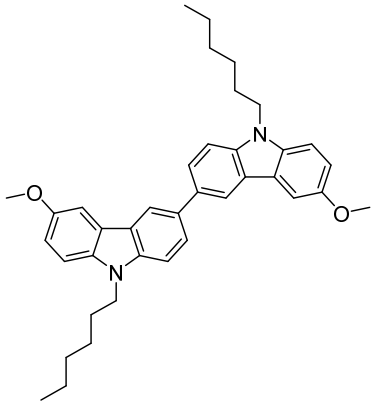
2926, 2853, 1735, 1483, 1451, 1380, 1346, 1309, 1231, 1216, 1151. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 2H), 8.03 (s. 2H), 7.82 (dd, J = 8.4 and 1.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.38-7.31 (m, 4H), 4.40 (q, J = 7.2 Hz, 4H), 2.87 (q, J = 7.6 Hz, 4H), 1.47 (t, J = 7.2 Hz, 6H), 1.37 (t, J = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.4, 139.1, 135.0, 133.4, 126.1, 125.5, 123.6, 123.5, 119.4, 119.1, 108.7, 108.5, 37.8, 29.9, 16.7, 14.0. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{32}H_{32}N_2$, 444.2565; found, 444.2554.

9,9'-Diethyl-6,6'-dimethoxy-9*H*,9'*H*-3,3'-bicarbazole (2f)[59]



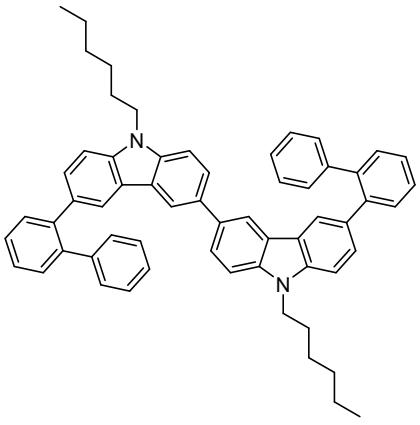
Time: 1 min (DDQ). Yield: 28 mg, 61% (DDQ). Dull white solid. R_f = 0.39 (9:1, hexane/EtOAc). Mp: 101-102 °C. IR (KBr, cm^{-1}): 2967, 2920, 2852, 1740, 1725, 1632, 1595, 1569, 1485, 1448, 1329, 1277, 1214, 1199, 1173, 1151, 1089, 1032. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 1.68 Hz, 2H), 7.47 (d, J = 8.44 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.14 (dd, J = 8.56 and 1.84 Hz, 2H), 4.39 (q, J = 7.2 Hz, 4H), 3.96 (s, 6H), 1.46 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8, 139.7, 135.7, 133.2, 125.7, 123.6, 123.5, 119.1, 115.1, 109.4, 108.9, 103.7, 56.4, 37.9, 14.1. The above reaction was not successful with chloranil and the starting material was recovered quantitatively.

9,9'-Dihexyl-6,6'-dimethoxy-9*H*,9'*H*-3,3'-bicarbazole (2g)



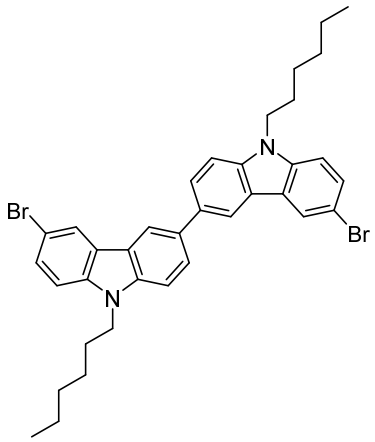
Time: 1 min (DDQ). Yield: 43 mg, 94% (DDQ). Pale yellow gummy liquid. R_f = 0.5 (19:1, hexane/EtOAc). IR (KBr, cm^{-1}): 2953, 2923, 1736, 1631, 1579, 1486, 1459, 1325, 1289, 1253, 1215, 1166, 1096, 1032. ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 2H), 7.80 (d, J = 8.08 Hz, 2H), 7.69 (s, 2H), 7.46 (d, J = 8.44 Hz, 2H), 7.33 (d, J = 8.72 Hz, 2H), 7.13 (dd, J = 8.6 Hz and 1.36 Hz, 2H), 4.31 (t, J = 7.2 Hz, 4H), 3.97 (s, 6H), 1.89 (qt, J = 7.2 Hz, 4H), 1.45-1.24 (m, 12H), 0.88 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.6, 140.2, 136.1, 133.0, 125.6, 123.5, 123.3, 118.9, 115.0, 109.6, 109.1, 103.5, 56.3, 43.5, 31.8, 29.2, 27.2, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{38}H_{44}N_2O_2$, 560.3403; found, 560.3372. The above reaction was unsuccessful with chloranil and the starting material was recovered quantitatively.

6,6'-Bis([1,1'-biphenyl]-2-yl)-9,9'-dihexyl-9*H*,9'*H*-3,3'-bicarbazole (2h)



Time: 10 min (DDQ)/15 min (chloranil). Yield: 58 mg, 71% (DDQ)/67 mg, 82% (chloranil). White solid. R_f = 0.4 (19:1, hexane/EtOAc). Mp: 79-80 °C. IR (KBr, cm^{-1}): 3054, 3017, 2954, 2928, 1627, 1599, 1489, 1473, 1464, 1451, 1433, 1379, 1348, 1333, 1303, 1266, 1242, 1216, 1194, 1153, 1124. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H), 8.06 (s, 2H), 7.78 (d, J = 8.28 Hz, 2H), 7.59 (d, J = 6.56 Hz, 2H), 7.49-7.41 (m, 8H), 7.23-7.12 (m, 14H), 4.28 (t, J = 7.2 Hz, 4H), 1.89 (qt, J = 7.2 Hz, 4H), 1.37-1.24 (m, 12H), 0.87 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.1, 141.6, 140.9, 139.9, 133.6, 132.6, 131.3, 130.8, 130.2, 128.3, 128.0, 127.6, 127.1, 126.4, 125.6, 123.7, 123.1, 121.7, 119.0, 109.1, 108.2, 43.5, 31.7, 29.2, 27.2, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{60}H_{56}N_2$, 804.4443; found, 804.4417.

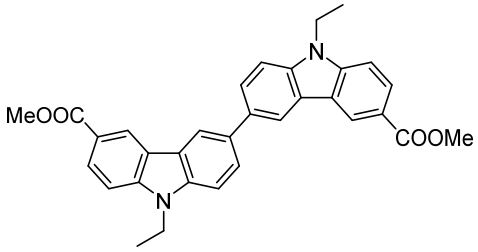
6,6'-Dibromo-9,9'-dihexyl-9*H*,9'*H*-3,3'-bicarbazole (2i)



Time: 1 min (DDQ/chloranil). Yield: 66 mg, >99% (DDQ); 65 mg, 97% (chloranil). Pale brown solid. R_f = 0.2 in hexane. Mp: 126-128 °C. IR (KBr, cm^{-1}): 2953, 2925, 1471, 1375. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 1.2 Hz, 2H), 8.28 (d, J = 1.6 Hz, 2H), 7.82 (dd, J = 8.48 and 1.6 Hz, 2H), 7.55 (dd, J = 8.64 and 1.6 Hz, 2H), 7.47 (d, J = 8.48 Hz, 2H), 7.28 (d, J = 8.64 Hz, 2H), 4.28 (t, J = 7.2 Hz, 4H), 1.88 (qt, J = 7.2 Hz, 4H), 1.45-1.24 (m, 12H), 0.89 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.9, 139.6, 133.5, 128.4, 126.2,

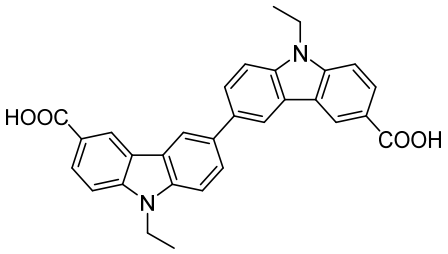
124.8, 123.3, 122.5, 119.1, 111.7, 110.3, 109.3, 43.4, 31.7, 29.1, 27.1, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{36}H_{38}N_2NaBr_2$, 679.1299; found, 679.1310.

Dimethyl 9,9'-diethyl-9*H*,9'*H*-[3,3'-bicarbazole]-6,6'-dicarboxylate (2j)



Time: 1 min (DDQ/chloranil). Yield: 47 mg, 92% (DDQ); 33 mg, 65% (chloranil). White amorphous solid. R_f = 0.4 (8:2, hexane/EtOAc). Mp: 174-176 °C. IR (KBr, cm^{-1}): 3054, 2922, 1593, 1492, 1452, 1362, 1324, 1228, 1179, 1068, 1011. ^1H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 1.2 Hz, 2H), 8.48 (d, *J* = 1.6 Hz, 2H), 8.20 (dd, *J* = 8.64 and 1.6 Hz, 2H), 7.88 (dd, *J* = 8.44 and 1.6 Hz, 2H), 7.54 (d, *J* = 8.44 Hz, 2H), 7.43 (d, *J* = 8.64 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 4H), 4.0 (s, 6H), 1.51 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.1, 143.2, 139.9, 134.2, 127.6, 126.2, 123.9, 123.2, 123.1, 121.0, 119.4, 109.3, 108.2, 52.1, 38.1, 14.0. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{32}H_{28}N_2O_4$, 504.2049; found, 504.2057.

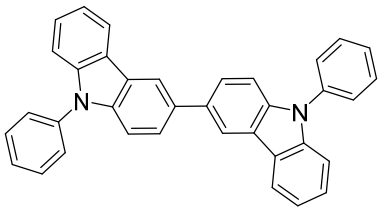
9,9'-Diethyl-9*H*,9'*H*-[3,3'-bicarbazole]-6,6'-dicarboxylic acid (2k)



Time: 15 min (DDQ). Yield: 41 mg, 84% (DDQ). Light brown solid. R_f = 0.4 (EtOAc). Mp: 212-214 °C. IR (KBr, cm^{-1}): 3404, 3248, 2956, 2924, 1676, 1637, 1599, 1479, 1408, 1294,

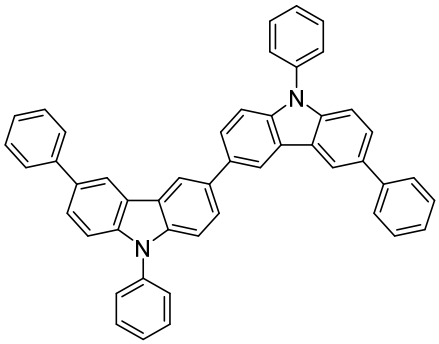
1273, 1251, 1231, 1129. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.64 (bs, 2H), 9.00 (s, 2H), 8.85 (s, 2H), 8.12 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 4.58 (q, J = 7.2 Hz, 4H), 1.41 (t, J = 7.2 Hz, 6H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 168.0, 142.5, 139.3, 132.7, 127.1, 125.5, 123.0, 122.9, 122.2, 121.1, 118.8, 109.9, 108.9, 37.4, 13.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{30}H_{25}N_2O_4$, 477.1814; found, 477.1824. The above reaction was not successful with chloranil and the unreacted starting material was recovered completely.

9,9'-Diphenyl-9*H*,9'*H*-3,3'-bicarbazole (4a):[24]



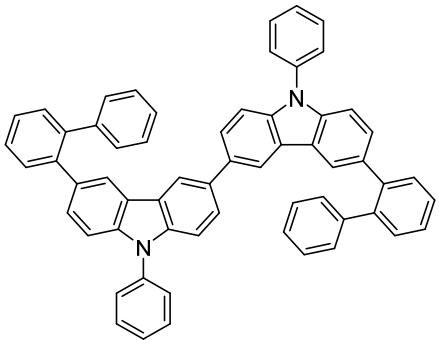
Time: 1 min (DDQ/chloranil). Yield: 191 mg, 97% (DDQ); 186 mg, 94% (chloranil). Dull white solid. R_f = 0.35 (19:1, hexane/EtOAc). Mp: 199-200 °C (lit.[24] 200 °C). IR (KBr, cm^{-1}): 3050, 2929, 2851, 1596, 1499, 1453, 1359. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 1.6 Hz, 2H), 8.25 (d, J = 7.6 Hz, 2H), 7.79 (dd, J = 8.8 and 1.68 Hz, 2H), 7.67-7.61 (m, 8H), 7.52 (d, J = 8.4 Hz, 2H), 7.52-7.41 (m, 6H), 7.33 (dt, J = 8.0 and 2.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.5, 140.2, 137.9, 134.5, 130.0, 127.5, 127.2, 126.2, 126.0, 124.1, 123.7, 120.6, 120.1, 119.0, 110.1, 110.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{36}H_{25}N_2$, 485.2018; found, 485.2032.

6,6',9,9'-Tetraphenyl-9*H*,9'*H*-3,3'-bicarbazole (4b)[60]



Time: 1 min (DDQ/chloranil). Yield: 64 mg, >99% (DDQ); 64 mg, >99% (chloranil). Dull white crystalline solid. R_f = 0.4 (19:1, hexane/EtOAc). Mp: 117-119 °C. IR (KBr, cm^{-1}): 3048, 1638, 1594, 1499, 1472, 1452, 1410, 1363, 1272, 1233. ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 1.2 Hz, 2H), 8.47 (d, J = 1.2 Hz, 2H), 7.82 (dd, J = 8.4 and 1.6 Hz, 2H), 7.79-7.75 (m, 4H), 7.69 (dd, J = 8.4 and 1.6 Hz, 2H), 7.67-7.62 (m, 8H), 7.56-7.47 (m, 10H), 7.36 (t, J = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.1, 141.0, 140.6, 137.9, 134.5, 133.7, 130.1, 128.9, 127.7, 127.5, 127.2, 126.7, 126.1, 125.7, 124.3, 124.26, 119.09, 119.05, 110.4, 110.3. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{48}H_{32}N_2Na$, 659.2463; found, 659.2438.

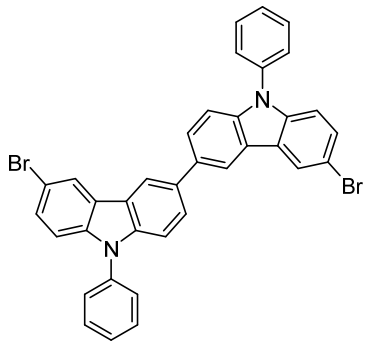
6,6'-Bis([1,1'-biphenyl]-2-yl)-9,9'-diphenyl-9*H*,9'*H*-3,3'-bicarbazole (4c)



Time: 30 min (DDQ)/50 min (chloranil). Yield: 34 mg, 85% (DDQ); 32 mg, 81% (chloranil). Pale brown solid. R_f = 0.6 (8:2, hexane/EtOAc). Mp: 310-312 °C. IR (KBr, cm^{-1}): 3020,

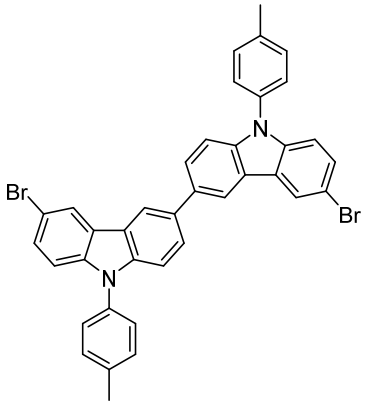
2362, 1597, 1497, 1463, 1365, 1278. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 8.8 Hz, 2H), 8.75-8.70 (m, 3H), 8.56 (dd, J = 8.8 and 2.0 Hz, 1H), 8.49 (d, J = 9.2 Hz, 1H), 8.45 (d, J = 8.0 Hz, 3H), 8.37 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.81-7.59 (m, 14H), 7.58-7.51 (m, 2H), 7.48-7.39 (m, 4H), 7.26-7.16 (m, 4H), 6.70 (d, J = 6.8 Hz, 1H), 6.38 (t, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.3, 131.4, 130.9, 130.3, 130.2, 129.4, 128.9, 128.6, 128.1, 127.3, 127.2, 127.0, 126.6, 126.4, 126.1, 125.0, 124.7, 123.9, 123.7, 123.4, 123.2, 121.9, 121.5, 120.6, 110.5, 110.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{60}H_{41}N_2$, 789.3270; found, 789.3256.

6,6'-Dibromo-9,9'-diphenyl-9*H*,9'*H*-3,3'-bicarbazole (4d)[61]



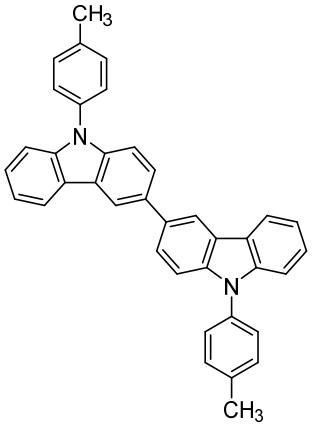
Time: 5 min (DDQ)/15 min (chloranil). Yield: 54 mg, 84% (DDQ); 54 mg, 84% (chloranil). Dull white amorphous solid. R_f = 0.5 (19:1, hexane/EtOAc). Mp: 222-224 °C. IR (KBr, cm^{-1}): 2955, 2921, 1733, 1637, 1628, 1597, 1500, 1467, 1429, 1356, 1321, 1273, 1226, 1181, 1056, 1013. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 1.2 Hz, 2H), 8.35 (d, J = 1.6 Hz, 2H), 7.77 (dd, J = 8.40 and 1.6 Hz, 2H), 7.64 (t, J = 8.0 Hz, 4H), 7.57 (dd, J = 8.4 and 1.2 Hz, 4H), 7.54-7.47 (m, 6H), 7.30 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.6, 140.2, 137.4, 134.6, 130.2, 128.9, 128.0, 127.1, 126.6, 125.4, 123.3, 123.1, 119.1, 113.0, 111.6, 110.5. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd. for $C_{36}H_{22}N_2KBr_2$, 678.9787; found, 678.9753.

6,6'-Dibromo-9,9'-di(*p*-tolyl)-9*H*,9'*H*-3,3'-bicarbazole (4e)[62]



Time: 1 min (DDQ)/50 min (chloranil). Yield: 33 mg, >99% (DDQ); 27 mg, 81% (chloranil). Pale yellow solid. R_f = 0.3 (19:1, hexane/EtOAc). Mp: 194-196 °C. IR (KBr, cm^{-1}): 3126, 1638, 1513, 1462, 1429, 1411, 1355, 1341, 1276, 1229, 1168. ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 1.6 Hz, 2H), 8.34 (d, J = 1.6 Hz, 2H), 7.76 (dd, J = 8.4 and 1.6 Hz, 2H), 7.49 (dd, J = 8.4 and 1.6 Hz, 2H), 7.48-7.37 (m, 10H), 7.27 (d, J = 8.4 Hz, 2H), 2.51 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.7, 140.3, 138.0, 134.7, 134.5, 130.8, 128.8, 127.0, 126.6, 125.3, 123.3, 123.0, 119.1, 112.8, 111.6, 110.5, 21.4.

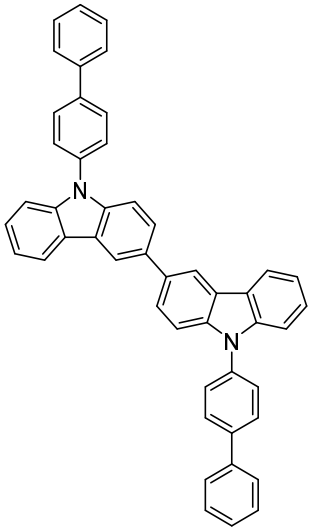
9,9'-Bis(*p*-tolyl)-9*H*,9'*H*-3,3'-bicarbazole (4f)[62]



Time: 1 min (DDQ/chloranil). Yield: 51 mg, >99% (DDQ); 51 mg, >99% (chloranil). Off-white solid. R_f = 0.65 (19:1, hexane/EtOAc). Mp: 74-76 °C. IR (KBr, cm^{-1}): 3034, 2924, 2857, 1605, 1514, 1456, 1361, 1326. ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 2H), 8.24 (d, J =

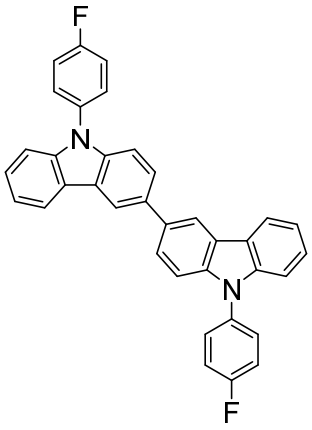
7.6 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.56-7.40 (m, 14H), 7.36-7.28 (m, 2H), 2.52 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.6, 140.3, 137.5, 135.2, 134.4, 130.6, 127.1, 126.1, 125.9, 124.0, 123.6, 120.5, 119.9, 119.0, 110.2, 110.0, 21.4.

9,9'-Bis([1,1'-biphenyl]-4-yl)-9*H*,9'*H*-3,3'-bicarbazole (4g)[63]



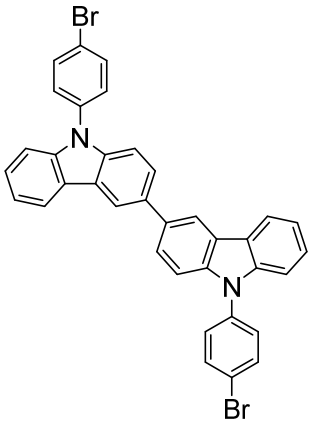
Time: 1 min (DDQ/chloranil). Yield: 31 mg, >99% (DDQ); 31 mg, >99% (chloranil). White amorphous solid. R_f = 0.4 (19:1, hexane/EtOAc). Mp: 219-221 °C. IR (KBr, cm^{-1}): 1658, 1638, 1618, 1563, 1556, 1522, 1485, 1448, 1415. ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 2H), 8.26 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 8.4 Hz, 4H), 7.81 (d, J = 9.2 Hz, 2H), 7.76-7.68 (m, 8H), 7.59 (d, J = 8.4 Hz, 2H), 7.56-7.49 (m, 6H), 7.49-7.39 (m, 4H), 7.34 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.5, 140.5, 140.2, 137.1, 134.6, 129.1, 128.7, 127.8, 127.4, 127.3, 126.3, 126.0, 124.2, 123.8, 120.6, 120.2, 119.1, 110.3, 110.1.

9,9'-Bis(4-fluorophenyl)-9*H*,9'*H*-3,3'-bicarbazole (4h)



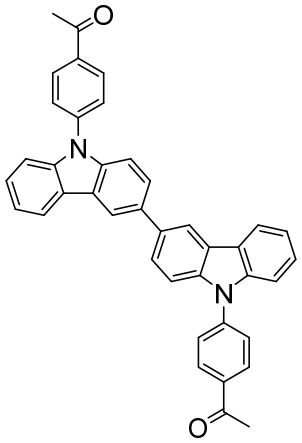
Time: 1 min (DDQ/chloranil). Yield: 52 mg, >99% (DDQ); 52 mg, >99% (chloranil). Dull white solid. R_f = 0.7 (19:1, hexane/EtOAc). Mp: 86-88 °C. IR (KBr, cm^{-1}): 3055, 2925, 2857, 1603, 1509, 1457, 1364, 1324, 1173. ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 1.2 Hz, 2H), 8.24 (d, J = 7.6 Hz, 2H), 7.77 (dd, J = 8.4 and 2.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 4H), 7.39-7.30 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.7 (d, J = 246.88 Hz), 141.6, 140.3, 133.8 (d, J = 3.39 Hz), 129.1 (d, J = 8.78 Hz),129.0, 126.3, 126.0, 124.1, 123.6, 120.6, 120.2, 119.1, 117.0 (d, J = 22.24 Hz), 109.9, 109.8. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{36}H_{22}F_2N_2$, 520.1751; found, 520.1735.

9,9'-Bis(4-bromophenyl)-9*H*,9'*H*-3,3'-bicarbazole (4i)[64]



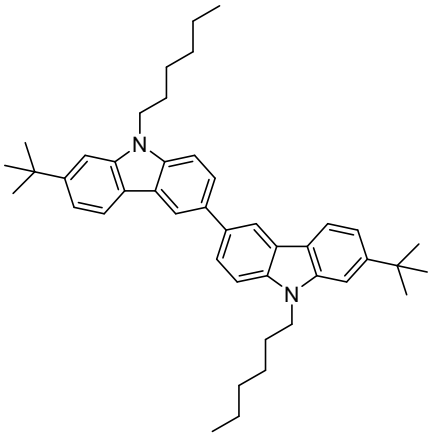
Time: 1 min (DDQ/chloranil). Yield: 64 mg, >99% (DDQ); 64 mg, >99% (chloranil). Pale yellow solid. R_f = 0.3 in hexane. Mp: 92-94 °C. IR (KBr, cm^{-1}): 3019, 2954, 2929, 1684, 1625, 1595, 1480, 1337. ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 1.2 Hz, 2H), 8.23 (d, J = 7.6 Hz, 2H), 7.77 (dt, J = 7.2 and 2.0 Hz, 2H), 7.76 (d, J = 8.8 Hz, 4H), 7.51 (d, J = 8.8 Hz, 4H), 7.47 (d, J = 8.8 Hz, 2H), 7.45-7.39 (m, 4H), 7.33 (dt, J = 7.2 and 1.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.3, 140.0, 137.0, 134.7, 133.3, 128.8, 126.4, 126.1, 124.3, 123.9, 121.1, 120.7, 120.5, 119.1, 110.0, 109.9.

9,9'-Bis(4-acetylphenyl)-9*H*,9'*H*-3,3'-bicarbazole (4j)



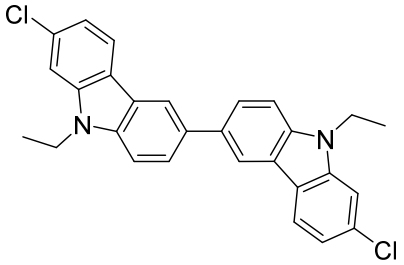
Time: 1 min (DDQ)/45 min (chloranil). Yield: 47 mg, 82% (DDQ); 42 mg, 73% (chloranil). Grey solid. R_f = 0.2 (19:1, hexane/EtOAc). Mp: >320 °C. IR (KBr, cm^{-1}): 3018, 2958, 2926, 1681, 1599, 1512, 1468, 1449, 1413, 1363, 1326, 1268, 1227, 1171, 1111, 1014. ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 1.6 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 8.23 (d, J = 8.4 Hz, 4H), 7.79 (dd, J = 8.8 and 1.6 Hz, 2H), 7.76 (d, J = 8.4 Hz, 4H), 7.58 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.46 (dt, J = 7.2 and 1.2 Hz, 2H), 7.36 (dt, J = 7.2 and 1.2 Hz, 2H), 2.72 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.2, 142.4, 140.9, 139.6, 135.7, 134.9, 130.3, 126.6, 126.2, 124.7, 124.2, 120.9, 120.7, 119.2, 110.2, 110.1, 26.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{40}H_{29}N_2O_2$, 569.2229; found, 569.2239.

7,7'-Di(*tert*-butyl)-9,9'-dihexyl-9*H*,9'*H*-3,3'-bicarbazole (6a)



Time: 1 min (DDQ/chloranil). Yield: 24 mg, 59% (DDQ); 26 mg, 64% (chloranil). Light yellow gummy liquid. R_f = 0.55 (19:1, hexane/EtOAc). IR (neat, cm^{-1}): 2957, 2927, 2852, 1600, 1465, 1256, 821, 802, 640. ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 2H), 8.09 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.40 (s, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.34 (t, J = 7.2 Hz, 4H), 1.92 (qt, J = 7.2 Hz, 4H), 1.47 (s, 18H), 1.39-1.26 (m, 12H), 0.88 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.4, 141.2, 139.9, 133.4, 125.1, 123.5, 120.8, 120.0, 118.8, 116.9, 108.8, 105.3, 43.1, 35.4, 32.0, 31.7, 29.2, 27.2, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{44}H_{56}N_2$, 612.4443; found, 612.4471.

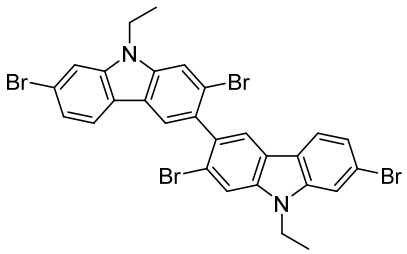
7,7'-Dichloro-9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole (6b)



Time: 1 min (DDQ/chloranil). Yield: 46 mg, 99% (DDQ); 46 mg, 99% (chloranil). Dull white solid. R_f = 0.46 (8:2, hexane/EtOAc). Mp: 201-203 °C. IR (KBr, cm^{-1}): 3066, 3016, 2980, 2936, 2895, 1626, 1593, 1492, 1474, 1455, 1439, 1381, 1344, 1326, 1231, 1216, 1157,

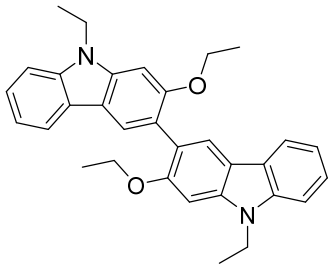
1126, 1073, 1000. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 1.2 Hz, 2H), 7.22 (dd, J = 8.0 and 1.6 Hz, 2H), 4.36 (q, J = 6.8 Hz, 4H), 1.48 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.1, 139.5, 133.9, 131.7, 126.0, 123.2, 121.9, 121.4, 119.5, 119.1, 109.1, 108.9, 38.0, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{28}H_{22}Cl_2N_2$, 456.1160; found, 456.1199.

2,2',7,7'-Tetrabromo-9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole (6c)



Time: 1 min (DDQ/chloranil). Yield: 22 mg, 61% (DDQ); 21 mg, 59% (chloranil). Dull white solid. R_f = 0.49 (19:1, hexane/EtOAc). Mp: 218-220 °C. IR (KBr, cm^{-1}): 3077, 3008, 2962, 2920, 2852, 1684, 1616, 1509, 1404, 1204, 1136, 1053, 1044. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.74 (s, 2H), 7.58 (s, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.34 (q, J = 7.2 Hz, 4H), 1.50 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.4, 140.4, 134.0, 123.0, 122.8, 122.3, 121.9, 121.8, 121.6, 120.1, 112.4, 112.1, 38.2, 14.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{28}H_{21}Br_4N_2$, 700.8438; found, 700.8436.

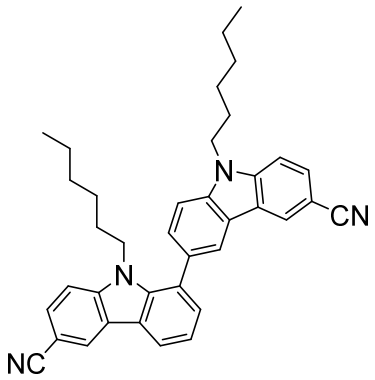
7,7'-Diethoxy-9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole (6d)



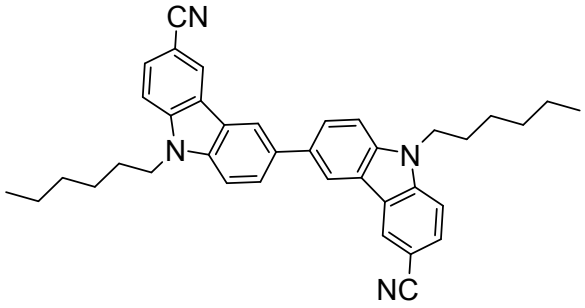
Time: 1 min (DDQ/chloranil). Yield: 44 mg, 92% (DDQ); 39 mg, 82%. Dull white solid. R_f = 0.36 (9:1, hexane/EtOAc). Mp: 159-161 °C. IR (KBr, cm^{-1}): 3015, 2979, 2925, 1636, 1631, 1603, 1458, 1349, 1313, 1285, 1228, 1216, 1192, 1120. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.40-7.35 (m, 4H), 7.22-7.15 (m, 2H), 6.93 (s, 2H), 4.38 (q, J = 6.8 Hz, 4H), 4.14 (q, J = 6.8 Hz, 4H), 1.48 (t, J = 7.2 Hz, 6H), 1.31 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.9, 140.7, 140.1, 124.1, 123.7, 123.5, 122.2, 119.7, 118.9, 116.4, 108.3, 92.5, 64.7, 37.7, 15.1, 14.0. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{32}H_{32}N_2O_2$, 476.2464; found, 476.2459.

Carbazoles containing electron withdrawing groups **7a-7i** did not undergo oxidative coupling under chloranil/H^+ conditions, and in all the cases, starting material was recovered quantitatively.

9,9'-Dihexyl-9*H*,9'*H*-[1,3'-bicarbazole]-6,6'-dicarbonitrile (8a) and 9,9'-dihexyl-9*H*,9'*H*-[3,3'-bicarbazole]-6,6'-dicarbonitrile (8'a)



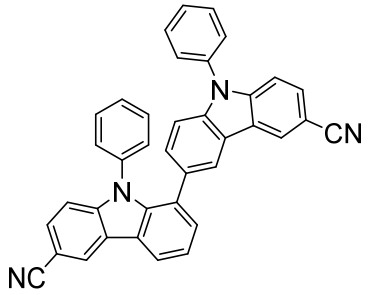
8a: Time: 5 min (DDQ). Yield: 52 mg, 52% (DDQ). Dark brown solid. R_f = 0.2 (7:3, hexane/EtOAc). Mp: 121-123 °C. IR (KBr, cm^{-1}): 3016, 2955, 2934, 2859, 2220, 1599, 1479, 1367, 1189. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (d, J = 0.8 Hz, 1H), 8.44 (d, J = 1.2 Hz, 1H), 8.32 (d, J = 1.2 Hz, 1H), 7.82 (dd, J = 8.4 and 1.6 Hz, 1H), 7.74 (dd, J = 8.8 and 1.6 Hz, 1H), 7.73 (dd, J = 8.8 and 1.6 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 4.37 (t, J = 7.2 Hz, 2H), 4.35 (t, J = 7.2 Hz, 2H), 2.1-1.8 (m, 4H), 1.38-1.26 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.63, 142.58, 142.1, 141.6, 140.4, 130.2, 130.0, 129.7, 129.5, 129.4, 128.7, 127.8, 125.6, 122.9, 122.5, 122.2, 120.9, 120.5, 120.4, 117.4, 109.9, 109.7, 109.6, 108.9, 102.7, 102.2, 43.8, 43.7, 39.4, 31.6, 29.0, 27.0, 22.6, 14.1. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{38}H_{38}N_4$, 550.3096; found, 550.3076.



8'a: Yield: 48 mg, 48% (DDQ). Brown solid. R_f = 0.7 (7:3, hexane/EtOAc). Mp: 161-163 °C. IR (KBr, cm^{-1}): 2957, 2925, 2854, 2218, 1594, 1480, 1261, 1219. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 1.2 Hz, 2H), 8.38 (d, J = 1.2 Hz, 2H), 7.89 (dd, J = 8.4 and 2.0 Hz,

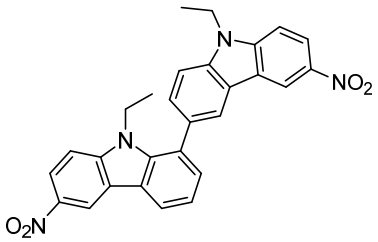
2H), 7.72 (dd, *J* = 8.4 and 1.6 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 4.37 (t, *J* = 7.2 Hz, 4H), 1.93 (qt, *J* = 7.2 Hz, 4H), 1.37-1.29 (m, 12H), 0.88 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 142.7, 140.3, 134.3, 129.2, 127.0, 125.5, 123.3, 122.7, 120.7, 119.4, 114.2, 109.9, 109.6, 43.7, 31.6, 29.1, 27.1, 22.6, 14.1. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{38}H_{38}N_4$, 550.3096; found, 550.3100.

9,9'-Diphenyl-9*H*,9'*H*-[1,3'-bicarbazole]-6,6'-dicarbonitrile (8b)

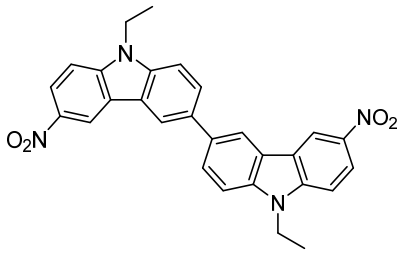


Time: 12 h (DDQ). Yield: 631 mg, 60% (DDQ). Brown amorphous solid. R_f = 0.1 (9:1, hexane/EtOAc). Mp: 190-192 °C. IR (KBr, cm^{-1}): 3066, 3019, 2924, 2852, 2221, 1597, 1476, 1449, 1366. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.52 (s, 1H), 8.38 (s, 1H), 7.77 (dd, *J* = 8.4 and 1.6 Hz, 1H), 7.72-7.65 (m, 6H), 7.63-7.53 (m, 9H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 143.3, 143.2, 142.8, 141.4, 141.1, 136.2, 136.0, 130.9, 130.53, 130.51, 130.1, 129.9, 129.6, 129.1, 128.9, 128.7, 128.6, 127.5, 127.1, 125.7, 123.3, 122.8, 122.1, 121.3, 120.3, 120.2, 117.8, 117.5, 111.1, 110.8, 110.1, 110.0, 103.9, 103.4. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd. for $C_{38}H_{22}N_4K$, 573.1482; found, 573.1493.

9,9'-Diethyl-6,6'-dinitro-9*H*,9'*H*-1,3'-bicarbazole (8c) and 9,9'-diethyl-6,6'-dinitro-9*H*,9'*H*-1,3'-bicarbazole (8'c)



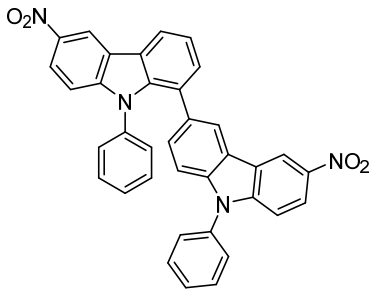
8c: Time: 5 min (DDQ). Yield: 38 mg and 77% (DDQ). Pale yellow solid. R_f = 0.3 (8:2, hexane/EtOAc). Mp: 195-197 °C. IR (KBr, cm^{-1}): 2920, 2858, 1641, 1636, 1634, 1589, 1503, 1465, 1321, 1226, 1120, 1087. ^1H NMR (500 MHz, $CDCl_3$): δ 9.58 (d, J = 2.0 Hz, 1H), 9.08 (d, J = 2.5 Hz, 1H), 8.46 (dd, J = 9.0 and 2.5 Hz, 1H), 8.45 (dd, J = 9.0 and 2.0 Hz, 1H), 8.40 (d, J = 1.5 Hz, 1H), 7.85 (dd, J = 8.5 and 1.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.51-7.45 (m, 3H), 4.50 (q, J = 7.2 Hz, 2H), 4.48 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.6, 143.5, 142.3, 141.6, 141.5, 141.1, 140.6, 130.6, 130.4, 129.7, 128.4, 123.5, 122.60, 122.55, 122.50, 122.3, 120.8, 120.6, 118.4, 117.8, 109.8, 109.0, 108.6, 108.4, 38.7, 38.6, 14.1. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{28}H_{22}N_4O_4$, 478.1641; found, 478.1653.



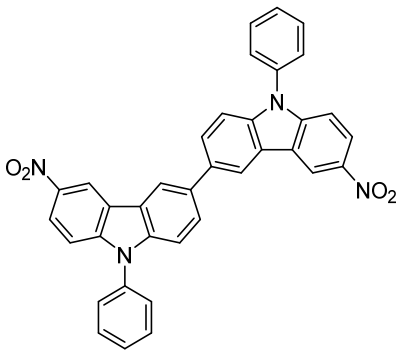
8'c: Time: 5 min (DDQ). Yield: 11 mg, 23% (DDQ). Yellow solid. R_f = 0.34 (8:2, hexane/EtOAc). Mp: 197-199 °C. IR (KBr, cm^{-1}): 2923, 2852, 1681, 1600, 1508, 1466, 1333, 1289, 1195, 1170. ^1H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, J = 1.6 Hz, 2H), 8.48 (d, J = 1.2 Hz, 2H), 8.43 (dd, J = 7.2 Hz and 2.0 Hz, 2H), 7.94 (dd, J = 6.8 Hz and 1.6 Hz, 2H), 7.61 (d, J = 6.8 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 4.49 (q, J = 6.8 Hz, 4H), 1.55 (t, J = 6.8 Hz, 6H).

Due to the poor solubility, ^{13}C NMR spectrum could not be obtained. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{28}H_{23}N_4O_4$, 479.1719; found, 479.1699.

6,6'-Dinitro-9,9'-diphenyl-9*H*,9'*H*-1,3'-bicarbazole (8d) and 6,6'-dinitro-9,9'-diphenyl-9*H*,9'*H*-3,3'-bicarbazole (8'd)

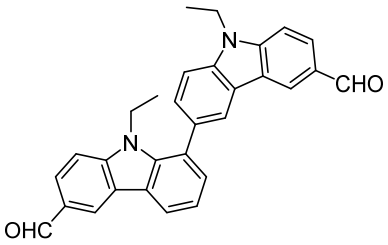


8d: Time: 1 min (DDQ). Yield: 14 mg, 60% (DDQ). Yellow solid. R_f = 0.4 (19:1, hexane/EtOAc). Mp: 193-195 °C. IR (KBr, cm^{-1}): 2926, 1658, 1616, 1595, 1593, 1574, 1501, 1452, 1343, 1330, 1314, 1219, 1104, 1032. ^1H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 9.14 (s, 1H), 8.46 (s, 1H), 8.37 (d, *J* = 9.2 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.74-7.67 (m, 5H), 7.64-7.56 (m, 8H), 7.45 (d, *J* = 9.2 Hz, 2H), 7.39 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 144.5, 143.4, 142.2, 141.9, 141.8, 136.2, 136.0, 131.2, 130.8, 130.63, 130.60, 130.5, 129.9, 129.34, 129.31, 129.1, 129.0, 127.5, 127.2, 123.6, 123.0, 122.7, 122.5, 122.3, 120.8, 120.7, 117.7, 111.1, 110.3, 110.1, 109.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{36}H_{23}N_4O_4$, 575.1719; found, 575.1716.



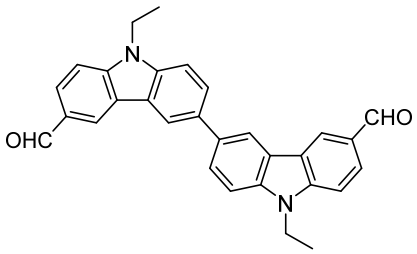
8'd: Time: 1 min (DDQ). Yield: 10 mg, 40% (DDQ). Dark yellow solid. R_f = 0.48 (9:1, hexane/EtOAc). Mp: 188-190 °C. IR (KBr, cm^{-1}): 2923, 2857, 1673, 1614, 1610, 1508, 1333, 1179, 1137, 1048. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (d, J = 2.0 Hz, 2H), 8.53 (d, J = 1.2 Hz, 2H), 8.36 (dd, J = 9.2 and 2.0 Hz, 2H), 7.87 (dd, J = 8.8 and 1.6 Hz, 2H), 7.75-7.66 (m, 4H), 7.64-7.56 (m, 4H), 7.53 (d, J = 8.4 Hz, 2H), 7.52 (t, J = 8.0 Hz, 2H), 7.43 (d, J = 9.2 Hz, 2H). Due to the poor solubility, ^{13}C NMR spectrum could not be obtained. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{36}H_{23}N_4O_4$, 575.1719; found, 575.1743.

9,9'-Diethyl-9*H*,9'*H*-[1,3'-bicarbazole]-6,6'-dicarbaldehyde (8e) and 9,9'-diethyl-9*H*,9'*H*-[3,3'-bicarbazole]-6,6'-dicarbaldehyde (8'e)[65]



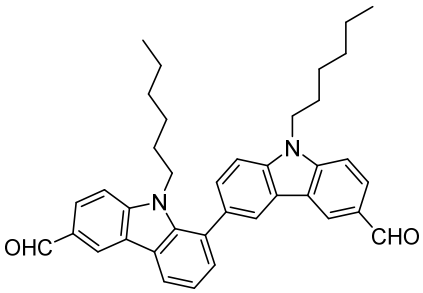
8e: Time: 12 h (DDQ). Yield: 83 mg, 84% (DDQ). Pale yellow solid. R_f = 0.3 (8:2, hexane/EtOAc). Mp: 192-194 °C. IR (KBr, cm^{-1}): 3017, 2980, 2935, 2819, 1682, 1595, 1478, 1366, 1236. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (s, 1H), 10.12 (s, 1H), 9.11 (d, J = 1.2 Hz, 1H), 8.67 (d, J = 1.2 Hz, 1H), 8.41 (d, J = 1.2 Hz, 1H), 8.14 (dd, J = 8.8 and 1.6 Hz, 1H), 8.08 (dd, J = 8.8 and 1.6 Hz, 1H), 7.83 (dd, J = 8.4 and 1.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.59-7.51 (m, 4H), 4.48 (q, J = 7.2 Hz, 2H), 4.47 (q, J = 7.2 Hz, 2H), 1.54 (t, J = 7.2 Hz, 3H), 1.53 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.2, 191.8, 144.2, 144.0, 141.8, 141.7, 140.1, 130.1, 129.8, 129.7, 129.6, 129.1, 127.9, 127.6, 126.1, 124.6, 123.7, 123.0, 122.4, 120.9, 118.5, 109.6, 109.4, 109.3, 108.8, 38.5, 38.4,

14.10, 14.06. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd. for $C_{30}H_{24}N_2O_2K$, 483.1475; found, 483.1456.

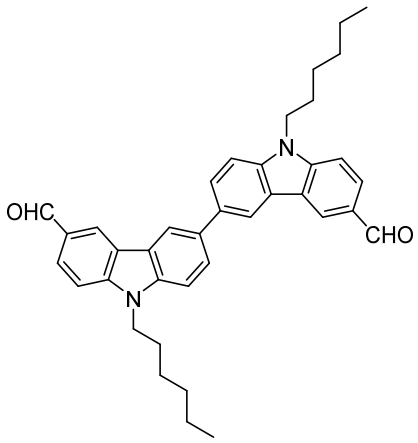


8'e: Time: 12 h (DDQ). Yield: 5 mg, <5% (DDQ). Pale yellow solid. R_f = 0.35 (8:2, hexane/EtOAc). Mp:100-102 °C. IR (KBr, cm^{-1}): 3019, 2973, 2959, 2926, 2856, 2741, 1732, 1686, 1625, 1588, 1478, 1444, 1380, 1332, 1285, 1272, 1214, 1174, 1149, 1127, 1090, 1048, 1018, 1007. ^1H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 2H), 8.53 (d, J = 1.2 Hz, 2H), 8.45 (d, J = 1.2 Hz, 2H), 8.03 (dd, J = 8.4 and 1.2 Hz, 2H), 7.77 (dd, J = 8.8 and 1.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 4.37 (q, J = 7.2 Hz, 4H), 1.45 (t, J = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.7, 143.5, 140.0, 135.1, 129.8, 129.1, 127.6, 125.6, 124.5, 122.0, 111.3, 109.1, 38.2, 13.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{30}H_{24}N_2O_2Na$, 467.1735; found, 467.1762.

9,9'-Dihexyl-9*H*,9'*H*-[1,3'-bicarbazole]-6,6'-dicarbaldehyde (8f) and 9,9'-dihexyl-9*H*,9'*H*-[3,3'-bicarbazole]-6,6'-dicarbaldehyde (8'f)[66]



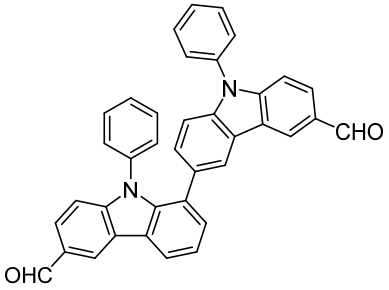
8f: Time: 12 h (DDQ). Yield: 47 mg, 83% (DDQ). Pale brown solid. R_f = 0.2 (4:1, hexane/EtOAc). Mp: 105-107 °C. IR (KBr, cm^{-1}): 3019, 2954, 2929, 2857, 2735, 1684, 1625, 1595, 1480, 1454, 1363, 1337, 1275, 1215, 1191, 1174, 1149. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 10.11 (s, 1H), 9.11 (d, J = 1.2 Hz, 1H), 8.66 (d, J = 1.2 Hz, 1H), 8.40 (d, J = 1.2 Hz, 1H), 8.13 (dd, J = 8.8 and 1.2 Hz, 1H), 8.07 (dd, J = 8.8 and 1.6 Hz, 1H), 7.81 (dd, J = 8.4 and 1.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.56-7.45 (m, 4H), 4.40 (t, J = 7.2 Hz, 2H), 4.38 (t, J = 7.2 Hz, 2H), 1.97-1.89 (m, 4H), 1.39-1.28 (m, 12H), 0.89 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.1, 191.7, 144.6, 144.4, 142.2, 141.7, 140.6, 130.0, 129.7, 129.62, 129.59, 129.1, 129.0, 127.8, 127.5, 126.0, 124.5, 123.5, 123.0, 122.3, 120.8, 118.4, 109.8, 109.6, 109.5, 109.0, 44.0, 43.8, 39.4, 31.6, 29.12, 29.08, 27.1, 22.7, 14.12, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{38}H_{41}N_2O_2$, 557.3168; found, 557.3140.



8'f: Time: 12 h (DDQ). Yield: 7 mg, 12% (DDQ). Pale brown solid. R_f = 0.49 (9:1, hexane/EtOAc). Mp: 192-194 °C. IR (KBr, cm^{-1}): 2926, 2856, 1684, 1595, 1470, 1372, 1140. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 2H), 8.70 (s, 2H), 8.48 (s, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 4.39 (q, J = 7.2 Hz, 4H), 1.94 (qt, J = 7.2 Hz, 4H), 1.46-1.30 (m, 12H), 0.88 (t, J = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.9, 144.7, 140.5, 134.4, 128.7, 127.3, 126.6, 124.4, 123.8,

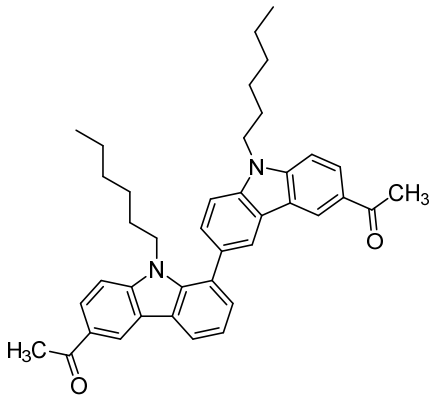
123.4, 119.4, 109.9, 109.3, 43.8, 31.7, 29.1, 27.1, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{38}H_{41}N_2O_2$, 557.3168; found, 557.3153.

9,9'-Diphenyl-9*H*,9'*H*-[1,3'-bicarbazole]-6,6'-dicarbaldehyde (8g)



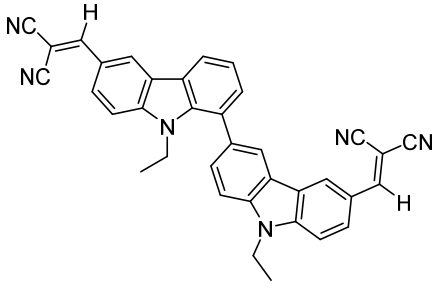
8g: Time: 12 h (DDQ). Yield: 86 mg, 86% (DDQ). White amorphous solid. R_f = 0.2 (8:2, hexane/EtOAc). Mp: 184-186 °C. IR (KBr, cm^{-1}): 3019, 2954, 2929, 2857, 2735, 1684, 1625, 1595, 1480, 1454, 1363, 1337, 1275, 1215, 1191, 1174, 1149. ^1H NMR (400 MHz, $CDCl_3$): δ 10.16 (s, 1H), 10.15 (s, 1H), 9.17 (d, J = 0.8 Hz, 1H), 8.73 (d, J = 1.2 Hz, 1H), 8.47 (d, J = 1.2 Hz, 1H), 8.07 (dd, J = 8.8 and 1.2 Hz, 1H), 8.02 (dd, J = 8.4 and 1.2 Hz, 1H), 7.77 (dd, J = 8.4 and 1.6 Hz, 1H), 7.73-7.66 (m, 5H), 7.63-7.57 (m, 7H), 7.56 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.1, 191.7, 145.04, 145.01, 142.9, 141.5, 141.3, 136.5, 136.3, 130.9, 130.5, 130.4, 130.0, 129.95, 129.5, 129.3, 129.0, 128.8, 128.6, 127.9, 127.5, 127.2, 126.4, 124.4, 123.8, 123.4, 122.2, 121.2, 118.7, 110.9, 110.72, 110.70, 110.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{38}H_{25}N_2O_2$ 541.1916; found, 541.1887.

6,6'-Diacetyl -9,9'-dihexyl-9*H*,9'*H*-1,3'-bicarbazole (8h)



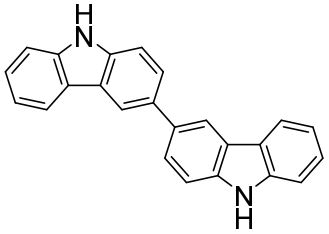
Time: 5 min (DDQ). Yield: 68 mg, 68% (DDQ). Pale brown solid. R_f = 0.2 (9:1, hexane/EtOAc). Mp: 75-77 °C. IR (KBr, cm^{-1}): 2929, 2862, 1666, 1595, 1470, 1360, 1356, 1270, 1153. ^1H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 8.80 (s, 1H), 8.41 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.52-7.43 (m, 4H), 4.39 (t, *J* = 7.2 Hz, 2H), 4.37 (t, *J* = 7.2 Hz, 2H), 2.76 (s, 3H), 2.74 (s, 3H), 1.94 (qt, *J* = 7.2 Hz, 2H), 1.93 (qt, *J* = 7.2 Hz, 2H), 1.47-1.34 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 198.3, 197.7, 143.8, 143.7, 142.2, 141.8, 140.6, 129.7, 129.4, 129.3, 128.8, 128.7, 127.5, 127.0, 126.7, 126.6, 126.3, 123.7, 123.6, 122.33, 122.27, 120.2, 109.6, 109.0, 108.9, 108.8, 43.9, 43.7, 39.6, 31.67, 31.65, 29.2, 29.1, 27.1, 26.8, 26.7, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{40}H_{44}N_2O_2$, 584.3403; found, 584.3381.

6,6'-Dicyanovinylidene-9,9'-diethyl-9*H*,9'*H*-1,3'-bicarbazole (8i)



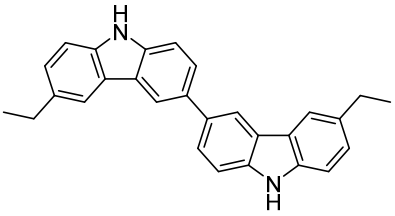
Time: 1 min (DDQ). Yield: 65 mg, 50% (DDQ). Bright orange solid. R_f = 0.5 (7:3, hexane/EtOAc). Mp: 192-193 °C. IR (KBr, cm^{-1}): 2972, 2927, 2857, 2339, 2213, 1626, 1584, 1481, 1382, 1344, 1299. ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.40 (s, 1H), 8.37-8.34 (m, 1H), 8.16-8.12 (m, 1H), 7.87 (dd, J = 7.2 and 1.6 Hz, 1H), 7.85 (dd, J = 7.2 and 1.6 Hz, 1H), 7.68 (dd, J = 8.4 and 1.6 Hz, 1H), 7.56-7.49 (m, 3H), 7.48-7.38 (m, 2H), 6.86 (s, 1H), 5.23 (s, 1H), 4.45 (q, J = 7.2 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 1.51 (t, J = 7.2 Hz, 3H), 1.49 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.9, 151.0, 147.4, 141.0, 140.4, 139.7, 139.6, 133.8, 133.7, 128.2, 126.7, 126.3, 126.2, 123.8, 123.6, 123.53, 123.45, 123.2, 121.4, 120.92, 120.87, 120.83, 119.3, 119.2, 116.9, 112.7, 109.4, 109.2, 109.1, 108.9, 38.0, 37.9, 14.0, 13.98. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{36}H_{24}N_6$, 540.2062; found, 540.2070.

9*H*,9'*H*-3,3'-Bicarbazole (11a)[67]



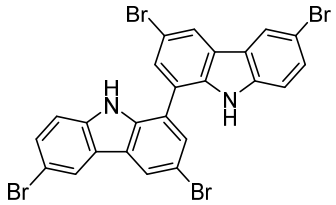
Time: 1 min (DDQ/chloranil). Yield: 126 mg, 93% (DDQ); 112 mg, 83% (chloranil). Dull white solid. R_f = 0.3 (4:1, hexane/EtOAc). Mp: >310 °C (lit. 375 °C, decomposition). IR (KBr, cm^{-1}): 3591, 3421, 3394, 1638, 1603, 1488, 1467, 1455, 1419, 1400, 1321, 1239. ^1H NMR (400 MHz, DMSO-d_6): δ 10.86-10.68 (bs, 2H), 8.29 (d, J = 5.6 Hz, 2H), 8.07 (t, J = 6.4 Hz, 2H), 7.69 (t, J = 6.8 Hz, 2H), 7.53-7.47 (m, 2H), 7.46-7.39 (m, 2H), 7.36-7.28 (m, 2H), 7.16-7.08 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 140.0, 138.5, 132.4, 125.1, 124.7, 122.9, 122.5, 119.6, 118.1, 117.7, 110.7, 110.6.

6,6'-Diethyl-9*H*,9'*H*-3,3'-bicarbazole (11b)



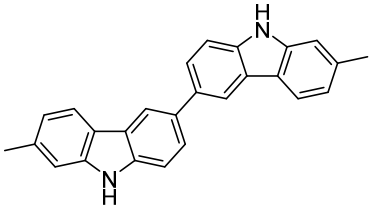
Time: 1 min (DDQ/chloranil). Yield: 37 mg, 94% (DDQ); 33 mg, 83% (chloranil). Grey solid. R_f = 0.45 (9:1, hexane/EtOAc). Mp: 240-241 °C. IR (KBr, cm^{-1}): 3473, 3394, 3265, 2956, 2926, 2855, 1636, 1496, 1463, 1337, 1321, 1245, 1058, 1021. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 1.0 Hz, 2H), 7.99 (s, 2H), 7.99 (bs, 2H), 7.76 (dd, J = 8.5 and 1.5 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.29 (dd, J = 8.5 and 1.0 Hz, 2H), 2.85 (q, J = 7.5 Hz, 4H), 1.36 (t, J = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.1, 138.6, 135.7, 134.0, 126.4, 125.7, 124.2, 123.9, 119.3, 119.0, 110.9, 110.6, 29.2, 16.6. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{28}H_{24}N_2$, 388.1939; found, 388.1929.

3,3',6,6'-Tetrabromo-9*H*,9'*H*-1,1'-bicarbazole (11c)



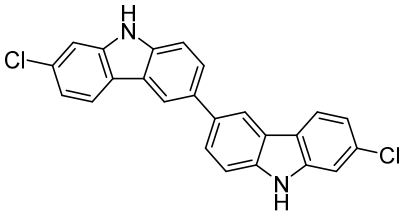
Time: 5 min (DDQ). Yield: 36 mg, 36% (DDQ). Pale green solid. R_f = 0.6 (8:2, hexane/EtOAc). Mp: >300 °C. IR (KBr, cm^{-1}): 3429, 2925, 2857, 1595, 1471, 1166, 1036. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (bs, 2H), 8.09 (s, 2H), 8.04 (s, 2H), 7.69 (s, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.1, 137.4, 130.9, 130.2, 124.7, 124.5, 123.9, 122.5, 113.4, 112.8, 112.5, 104.8. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd. for $C_{24}H_{12}N_2Br_4K$, 682.7371; found, 682.7390.

7,7'-Dimethyl-9*H*,9'*H*-3,3'-bicarbazole (11d)



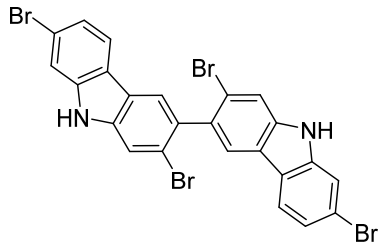
Time: 1 min (DDQ/chloranil). Yield: 62 mg, 85% (DDQ); 55 mg, 75% (chloranil). Grey solid. R_f = 0.31 (8:2, hexane/EtOAc). Mp: >300 °C. IR (KBr, cm^{-1}): 3420, 3040, 2936, 2863, 1678, 1617, 1428, 1200, 1138, 1049. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s. 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.99 (bs, 2H), 7.73 (dd, J = 8.0 and 1.5 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.26 (s, 2H), 7.08 (d, J = 8.0 Hz, 2H), 2.55 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.6, 138.7, 136.3, 125.4, 124.2, 121.2, 120.2, 119.9, 119.5, 118.8, 111.0, 110.8, 22.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{26}H_{21}N_2$, 361.1705; found, 361.1689.

7,7'-Dichloro-9*H*,9'*H*-3,3'-bicarbazole (11e)



Time: 1 min (DDQ/ chloranil). Yield: 30 mg, 74% (DDQ); 27 mg, 67% (chloranil). Dull white solid. R_f = 0.49 (8:2, hexane/EtOAc). Mp: 236-238 °C. IR (KBr, cm^{-1}): 3411, 2956, 2925, 2853, 1731, 1647, 1459, 1046, 1026. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.42 (bs, 2H), 8.51 (d, J = 1.5 Hz, 2H), 8.24 (d, J = 8.5 Hz, 2H), 7.82 (dd, J = 8.5 and 2.0 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 2.0 Hz, 2H), 7.20 (dd, J = 8.5 and 2.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 140.8, 139.1, 132.7, 130.0, 125.4, 122.5, 121.7, 121.6, 118.7, 118.3, 111.5, 110.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{24}H_{14}N_2Cl_2Na$ 423.0432; found, 423.0425.

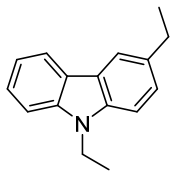
2,2',7,7'-Tetrabromo-9*H*,9'*H*-3,3'-bicarbazole (11f)



Time: 5 min (DDQ)/10 min (chloranil). Yield: 44 mg, 67% (DDQ); 49 mg, 74% (chloranil). Dull white solid. R_f = 0.28 (9:1, hexane/EtOAc). Mp: 244-245 °C. IR (KBr, cm^{-1}): 3395, 2922, 2835, 1707, 1632, 1596, 1508, 1462, 1428, 1075. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (bs, 2H), 7.98 (s, 2H), 7.86 (d, J = 6.8 Hz, 2H), 7.79 (s, 2H), 7.62 (d, J = 1.2 Hz, 2H), 7.36 (dd, J = 6.8 and 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.9, 139.8, 134.7, 123.6, 122.9, 122.32, 122.30, 122.1, 121.8, 120.1, 114.5, 114.1. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{24}H_{12}Br_4N_2$, 643.7734; found, 643.7730.

Experimental procedure and characterization details for the newly synthesized carbazole derivatives

Preparation of 3,9-diethyl-9*H*-carbazole (1e)

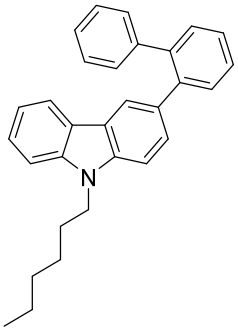


Into a flame dried two-neck round bottom flask, equipped with a magnetic stir bar and fitted with condenser, 3-ethylcarbazole (75 mg, 0.41 mmol) and 3 mL of dimethyl sulfoxide (DMSO) were added. To this, NaOH (65 mg, 1.63 mmol) was introduced at ice-cold temperature and stirred for 10 minutes. Finally, ethyl iodide (0.19 g, 1.2 mmol) was added and the temperature was raised to 110 °C. The contents were stirred at this temperature for 12

h. The progress of the reaction was monitored by TLC. After disappearance of the starting material (as observed by TLC), the reaction mixture was cooled to room temperature. The organic portions were extracted into ethyl acetate (3 × 10 mL). The combined organic layer was washed with 10% hypo solution, brine solution, dried over anhydrous sodium sulfate, filtered and concentrated at the rotary evaporator. The crude product thus obtained was purified by utilizing silica-gel column chromatography technique using hexane as the eluent to afford a grey color solid as the title product.

Time: 9 h. Yield: 82 mg, 90%. Grey solid. R_f = 0.75 (19:1, hexane/EtOAc). Mp: 44-46 °C. IR (KBr, cm^{-1}): 3049, 3017, 2964, 2929, 2871, 1604, 1573, 1489, 1471, 1450, 1381, 1344, 1331, 1231, 1150, 1124, 1088, 1057. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.6 Hz, 1H), 7.92 (s, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.35-7.29 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.83 (q, J = 7.6 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.3, 138.6, 134.9, 126.0, 125.5, 123.2, 123.0, 120.4, 119.3, 118.6, 108.5, 108.3, 37.6, 29.1, 16.7, 13.9. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{16}H_{17}N$, 223.1361; found, 223.1361.

Preparation of 3-([1,1'-biphenyl]-2-yl)-9-hexyl-9*H*-carbazole (1i)

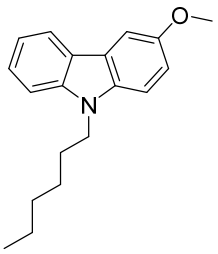


To the two neck round bottom flask equipped with a magnetic stir-bar and fitted with reflux condenser, 3-bromo-9-hexyl-9*H*-carbazole (400 mg, 1.21 mmol), 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (407 mg, 1.45 mmol), sodium carbonate (205 mg,

1.94 mmol) and 25 mL DME (dimethoxyethane) and 5 mL water were added. The contents were degassed with nitrogen gas for 15 minutes. Finally, $Pd(PPh_3)_4$, (56 mg, 0.05 mmol) was added and whole of the contents were stirred at 85 °C for 36 hours. The progress of the reaction was monitored by thin layer chromatography (TLC). After disappearance of the starting material (as checked by TLC), the reaction mixture was cooled down to room temperature. The solvent was evaporated at reduced pressure and the organic components were extracted into ethyl acetate (3 × 15 mL). The combined organic layer was washed with brine solution, dried over anhydrous sodium sulphate, filtered and concentrated at the rotary evaporator. The crude product thus obtained was purified by silica gel column chromatography using ethyl acetate-hexane mixtures as the eluent to get a pure white solid as the title product.

Time: 36 h. Yield: 407 mg, 84%. White solid. R_f = 0.7 (19:1, hexane:EtOAc). Mp: 61-63 °C. IR (KBr, cm^{-1}): 3055, 3017, 2954, 2928, 1627, 1599, 1489, 1473, 1464, 1433, 1379, 1348, 1333, 1303, 1266, 1242, 1216, 1153, 1124, 1073, 1008. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 7.61-7.54 (m, 1H), 7.48-7.41 (m, 4H), 7.40-7.35 (m, 1H), 7.22-7.10 (m, 8H), 4.23 (t, J = 7.2 Hz, 2H), 1.83 (qt, J = 7.2 Hz, 2H), 1.44-1.20 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.1, 141.5, 140.9, 140.8, 139.5, 132.4, 131.3, 130.8, 130.1, 128.2, 128.0, 127.6, 127.1, 126.4, 125.7, 123.1, 122.8, 121.6, 120.4, 118.9, 108.9, 108.1, 43.3, 31.7, 29.1, 27.1, 22.7, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{30}H_{30}N$, 404.2378; found, 404.2371.

Preparation of 9-hexyl-3-methoxy-9*H*-carbazole (1h)

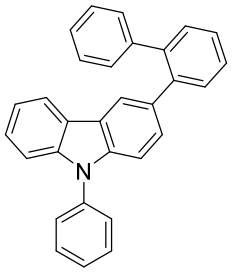


Into a two necked round bottom flask equipped with magnetic stir bar, 9-hexyl-3-bromo-9*H*-carbazole (1000 mg, 3.0 mmol) was taken and dissolved in DMF (6 mL). CuI (1200 mg, 6.36 mmol) was added into this. At last, NaOMe in MeOH (25 wt%, 2.5 mL, 10.0 mmol) was added into the reaction mixture which was then stirred to reflux at 159 °C for 16 h. The progress of the reaction was monitored by thin layer chromatography (TLC). As soon the starting material was completed (as noticed by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and quenched with saturated ammonium chloride. The organic portion was extracted into ethyl acetate (3 × 30 mL). The combined organic layer was washed with saturated ammonium chloride followed by brine solution. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by silica-gel column chromatography utilizing hexane and ethyl acetate mixture (19:1, v/v) as the eluent to afford the title compound as a colorless crystalline solid (weight, 850 mg, yield, >99%).

Time: 16 h. Yield: 850 mg, >99%. Colorless crystalline solid. R_f = 0.40 (19:1, hexane/EtOAc). Mp: 51-52 °C. IR (KBr, cm^{-1}): 3051, 3012, 2954, 2924, 1923, 1890, 1773, 1627, 1594, 1485, 1452, 1379, 1326, 1234, 1216, 1191, 1151, 1128, 1065, 1019. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 2.4 Hz, 1H), 7.44 (dt, J = 8.0 and 1.2 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.18 (dt, J = 8.0 and 1.2 Hz, 1H), 7.10 (dd, J = 8.8 and 2.4 Hz, 1H), 4.26 (t, J = 7.2 Hz, 2H), 3.93 (s, 3H), 1.84 (qt, J = 7.2 Hz, 2H), 1.41-1.22 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ

153.6, 141.1, 135.6, 125.7, 123.2, 122.7, 120.4, 118.3, 114.9, 109.5, 108.9, 103.5, 56.3, 43.3, 31.7, 29.1, 27.1, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{19}H_{23}NO$, 281.1780; found, 281.1792.

Preparation of 3-([1,1'-biphenyl]-2-yl)-9-phenyl-9*H*-carbazole (3c)

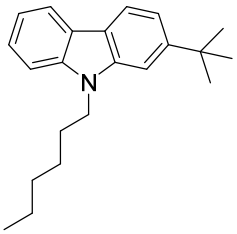


Into a two-neck round bottom flask containing 3-bromo-9-phenyl-9*H*-carbazole (1500 mg, 4.66 mmol), 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1560 mg, 5.59 mmol), and potassium carbonate (1030 mg, 7.46 mmol), DME (140 mL) and water (14 mL) were added. Before adding $Pd(PPh_3)_4$ (260 mg, 0.23 mmol) into the reaction vessel, the contents were degassed with nitrogen gas for ca. 20 minutes. The reaction was then continued to stir at 80 °C for 24 hours while monitoring the progress by TLC. After completion of the reaction, as noted by TLC, the solvent was evaporated under reduced pressure. The organic contents from the residue were extracted into ethyl acetate (3 × 40 mL). The combined organic layer was washed with brine solution, dried over anhydrous sodium sulphate, filtered, and concentrated at the rotary evaporator. The crude thus obtained was purified by silica-gel column chromatography using hexane and ethyl acetate mixtures as the eluent.

Time: 24 h. Yield: 1104 mg, 60%. White crystalline solid. R_f = 0.4 (19:1, hexane/EtOAc). Mp: 130-132 °C. IR (KBr, cm^{-1}): 3058, 3016, 2924, 1625, 1597, 1501, 1490, 1469, 1456, 1433, 1362, 1329, 1233, 1218, 1180, 1074, 1026, 1018, 1007. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 1.6 Hz, 1H), 7.59-7.51 (m, 5H), 7.49-7.36 (m, 6H), 7.26 (dt, J = 7.2 and 2.0 Hz, 1H), 7.22-7.11 (m, 6H), 7.08 (dd, J = 8.4 and 2.0 Hz, 1H). $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$): δ 142.0, 141.24, 141.17, 140.8, 139.7, 137.8, 133.6, 131.3, 130.8, 130.1, 130.0, 128.5, 128.0, 127.7, 127.5, 127.2, 127.1, 126.5, 126.0, 123.6, 123.3, 121.5, 120.3, 120.1, 110.0, 109.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{30}H_{22}N$, 396.1752; found, 396.1765.

Preparation of 2-(*tert*-butyl)-9-hexyl-9*H*-carbazole (5a)

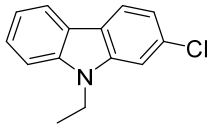


Into a oven dried two neck round bottom flask equipped with magnetic stir-bar, 2-(*tert*-butyl)-9*H*-carbazole (50 mg, 0.22 mmol) was added and dissolved in toluene (1 mL). To this, 1 mL NaOH solution (50% w/v) was added and stirred for few minutes. Further, 1-bromohexane (40 mg, 0.26 mmol) and tetrabutylammonium bromide (2 mg, 0.005 mmol) was added and the contents were stirred at reflux temperature for a period of 12 hours. The reaction progress was monitored by thin layer chromatography (TLC). As soon as the starting material was disappeared (as confirmed by TLC), the reaction mixture was cooled to room temperature and the organic components were extracted into ethyl acetate (3 × 7 mL). The combined organic layer was now washed with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated at the rotary evaporator. The crude product was then purified by silica-gel column chromatography using hexane as the eluent to afford the title compound.

Time: 12 h. Yield: 60 mg, 88%. colorless liquid. R_f = 0.75 (19:1, hexane/EtOAc). IR (neat, cm^{-1}): 3056, 2958, 2927, 2864, 1913, 1872, 1602, 1493, 1255, 850, 814. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 4.30 (t, J =

7.2 Hz, 2H), 1.87 (qt, *J* = 7.2 Hz, 2H), 1.45 (s, 9H), 1.39-1.25 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.4, 140.8, 140.7, 125.1, 122.9, 120.6, 120.2, 119.9, 118.7, 116.9, 108.7, 105.2, 43.0, 35.4, 32.0, 31.7, 29.1, 27.2, 22.7, 14.2. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd. for $C_{22}H_{29}N$, 307.2300; found, 307.2324.

Preparation of 2-chloro-9-ethyl-9*H*-carbazole (5b)



Into a flame dried two neck round bottom flask equipped with a magnetic stir-bar and fitted with condenser, 2-chlorocarbazole (64 mg, 0.32 mmol) was added and dissolved in dimethylsulfoxide (DMSO, 2 mL). To this, NaOH (33 mg, 0.83 mmol) was added at ice-cold temperatures and stirred for 10 minutes at the same temperature. After this time, ethyl iodide (129 mg, 0.83 mmol) was added, the temperature was raised to 110 °C and stirred for 12 hours while monitoring the progress of the reaction by TLC. After complete disappearance of the starting material (as checked by TLC), the reaction mixture was cooled to room temperature and the organic contents were extracted into ethyl acetate (3 × 10 mL). The organic extract was combined and washed with 10% hypo solution followed by brine solution, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was then purified by the silica gel column chromatography technique using hexane as the eluent to obtain the title product.

Time: 12 h. Yield: 71 mg, 97%. White solid. R_f = 0.7 (hexane). Mp: 86-87 °C. IR (KBr, cm^{-1}): 3062, 2977, 2932, 1593, 1492, 1474, 1454, 1441, 1325, 1231, 1156, 1131, 1125, 1072. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (td, *J* = 7.6 and 0.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.48 (dt, *J* = 7.6 and 1.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.24 (dt, *J* = 7.2 and 1.2 Hz, 1H), 7.18 (dd, *J* = 8.0 and 1.6 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* =

7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 140.6, 140.4, 131.5, 126.0, 122.6, 121.7, 121.3, 120.5, 119.45, 119.38, 108.8, 108.7, 37.8, 13.8. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd. for $C_{14}H_{12}ClNK$, 268.0295; found, 268.0268.

AUTHOR INFORMATION

Corresponding Author

Email: pvenkat@iitm.ac.in

ORCID

P. Venkatakrishnan: 0000-0002-0895-2861

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P.V.K is grateful to DST-SERB SB/S1/OC-47/2014, CSIR 02(0185)/13/EMRII, New Delhi, India for generous funding. Sudhakar, M. thanks CSIR for a SRF, and Sudesh, M. and Kalidass, K. thank IITM for their HTRA fellowship. Department of Chemistry, IIT Madras is acknowledged for the facilities. Mr. Ramkumar, Department of Chemistry, IIT Madras is acknowledged for the help with X-ray structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Elaborate synthetic as well as complete characterization (^{1}H and ^{13}C NMR, IR and mass spectral) details, ^{1}H and ^{13}C NMR scans of bicarbazole derivatives and other novel carbazole precursors, UV-vis absorption spectra of **1a, 2a** and **9b and** and UV-vis-NIR absorption spectral studies of the progress of the oxidative coupling reaction, Compiled electrochemical data, and Single crystal X-ray diffraction data of **2a** (CCDC 1864770)/**2i**(CCDC 1864769) along with their ORTEP drawings.

REFERENCES

1. (a) Campbell, N.; Barclay, B. M. Recent Advances in the Chemistry of Carbazole. *Chem. Rev*., **1947**, *40*, 359 380. (b) Yaqub, G.; Hussain, E. A.; Rehman, M. A.; Mateen, B. Advances in Synthesis of Carbazole and Its Derivatives. *Asian J. Chem.* **2009**, *21*, 2485 2520. (c) Chakraborty, D. P. Chemistry and Biology of Carbazole Alkaloids. In *The Alkaloids: Chemistry and Pharmacology;* Cordell, G. F., Ed.; Volume 44; Academic Press, Inc. 1993, pp 257 364. (d) Bashir, M.; Bano, A.; Ijaz, A. S.; Chaudhary, B. A. Recent Developments and Biological Activities of *N*-Substituted Carbazole Derivatives: A Review. *Molecules*, **2015**, *20*, 13496–13517. (e) Tsutsumi, L. S.; Gündisch, D.; Sun, D. Carbazole Scaffold in Medicinal Chemistry and Natural Products: A Review from 2010-2015. *Curr. Top. Med. Chem.* **2016**, *16*, 1290 1313. (f) Biswas, M.; Das, S. K. Recent progress in carbazole based polymers. *Polymer*, **1982**, *23*, 1713 1726. (g) Higginbotham, H.; Karon, K.; Ledwon, P.; Data, P. Carbazoles in Optoelectronic Applications. In *Display and Imaging;* Data, P., Luszczynska, B., Ulansk, J. Eds.; Volume 2; Old City Publishing Inc., 2017, pp 207-216. (h) Li, J.; Grimsdale, A. C. Carbazole-based polymers for organic photovoltaic devices. *Chem. Soc. Rev*. **2010**, *39*, 2399 2410. (i) Vetrichelvan, M.; Nagarajan, R.; Valiyaveettil, S.

Carbazole-Containing Conjugated Copolymers as Colorimetric/Fluorimetric Sensor for Iodide Anion. *Macromolecules* **2006**, *39*, 8303 8310.

2. (a) Nabavi, S. M. J.; Hosseinzadeh, B.; Tajbakhsh, M.; Alinezhad, H. The novel biscarbazole organic dyes for dye-sensitized solar cells. *J. Mater. Sci.: Mater. Electron*. **2018**, *29*, 3270 3280. (b) Kim, H. M.; Choi, J. M.; Lee, J. Y. Blue thermally activated delayed fluorescent emitters having a bicarbazole donor moiety. *RSC Adv*. **2016**, *6*, 64133–64139. (c) Romero, D. B.; Nüesch, F.; Benazzi, T.; Adés, D.; Siove, A.; Zuppiroli, L. Electroluminiscence from carbazole dimers . *Adv. Mater.* **1997**, *9*, 1158–1161. (d) Shih, C.-J.; Lee, C.-C.; Yeh, T.-H.; Biring, S.; Kesavan, K. K.; AlAmin, N. R.; Chen, M.-H.; Tang, W.-H.; Liu, S.-C.; Wong, K.-T. Versatile Exciplex-Forming Co-Host for Improving Efficiency and Lifetime of Fluorescent and Phosphorescent Organic Light-Emitting Diodes. *ACS Appl. Mater. Interfaces*, **2018**, *10*, 24090–24098. (e) Kim, J.; Lee, S.; Lee, J.; Lim, E.; Jung, B. J. 3,3'-Bicarbazole-Based Host Molecules for Solution-Processed Phosphorescent OLEDs. *Molecules* **2018**, *23*, 847–855.

3. Kato, S.-I.; Noguchi, H.; Kobayashi, A.; Yoshihara, T.; Tobita, S.; Nakamura, Y. Bicarbazoles: Systematic Structure-Property Investigations on a Series of Conjugated Carbazole Dimers. *J. Org. Chem*. **2012**, *77*, 9120 9133.

4. Matsuda, Y.; Ueno, K.; Yamaguchi, H.; Egami, Y.; Niimi, T. Organic Electroluminescent Sensor for Pressure Measurement. *Sensors* **2012**, *12*, 13899–13906.

5. Theiste, D. A.; Kloeppner, L. J.; Franz, S. F.; Giri, P.; Lin, R. Electrochemical Energy Storage Devices. U.S. patent US 20150346573, 2015.

6. Kim, M.; Jeon, S. K.; Hwang, S.-H.; Lee, S.-S.; Yu, E.; Lee, J. Y. Correlation of Molecular Structure with Photophysical Properties and Device Performances of

Thermally Activated Delayed Fluorescent Emitters. *J. Phys. Chem. C* **2016**, *120*, 2485–2493.

7. (a) Uvarani, C.; Jaivel, N.; Sankaran, M.; Chandraprakash, K.; Ata, A.; Mohan, P. S. Axially Chiral biscarbazoles and biological evaluation of the constituents from MurrayaKoenigii. *Fitoterapia* **2014**, *94*, 10–20. (b) Tesler, S.; Bringmann, G. Biarylic Biscarbazole Alkaloids: Occurrence, Steoreochemistry, Synthesis, and Bioactivity. *The Chemical Record* **2002**, *2*, 114–127.

8. (a) Sasabe, H.; Toyota, N.; Nakanishi, H.; Ishizaka, T.; Pu, Y.-J.; Kido, J. 3,3'-Bicarbazole-Based Host Materials for High-Efficiency Blue Phosphorescent OLEDs with Extremely Low Driving Voltage. *Adv. Mater*. **2012**, *24*, 3212–3217. (b) Grigalevicius, S.; Tavgeniene, D.; Krucaite, G.; Griniene, R.; Li, W.-C.; Luo, D.; Chang, C.-H. 9,9'-bis(2,2-diphenylvinyl)[3,3']bicarbazole as low cost efficient hole transporting materialfor application in red PhOLEDs. *Dyes and Pigm*. **2018**, *152*, 100–104.

9. Ito, C.; Thoyama, Y.; Omura, M. Kajiura, I.; Furukawa, H. Alkaloidal Constituents of MurrayaKoenigii. Isolation and Structural Elucidation of Novel Binary Carbazolequinones and Carbazole Alkaloids. *Chem. Pharm. Bull.* **1993**, *41*, 2096 2100.

10. Kim, M.; Lee, J. Y. Engineering of Interconnect Position of Bicarbazole for High External Quantum Efficiency in Green and Blue Phosphorescent Organic Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2014**, *6*, 14874 14880.

11. (a) Grzybowski, M.; Skonieczny, K.; Butenschçn, H.; Gryko, D. T. Comparision of oxidative aromatic coupling and the Scholl reaction. *Angew. Chem. Int. Ed.* **2013**, *52*, 9900–9930. (b) Sarhan, A. A. O.; Bolm, C. Iron(III) chloride in oxidative coupling reactions. *Chem. Soc. Rev*. **2009**, *38*, 2730–2744.

12. For oxidative C–C coupling using metal-based and halogen-containing agents, see: (a) Iles, D. H.; Ledwith, A. Acid-catalysed electron-transfer reactions of lead tetra-acetate:stable cation-radicals from carbazole derivatives. *Chem. Commun. (London)*, **1968**, 498–499. (b) Pankratov, A. N.; Stepanov, A. N. Oxidation and Homolytic Coupling Regioselectivity of Carbazole in Acidic Media. *Croat. Chem. Acta* **1997**, *70*, 585–598 and references cited therein. (c) Liu, L.; Carroll. P. J.; Kozlowski, M. C. Vanadium-Catalyzed Regioselective Oxidative Coupling of 2-Hydroxycarbazoles. *Org. Lett*. **2015**, *17,* 508 511. (d) Brütting, C.; Fritsche, R. F.; Kutz, S. K.; Börger, C.; Schmidt, A. W.; Kataeva, O.; Knölker, H. J. Synthesis of 1, 1'-and 2,2'-Bicarbazole Alkaloids by Iron(III) Catalyzed Oxidative Coupling of 2- and 1-Hydroxycarbazoles. *Chem. Eur. J.* **2018**, *24,* 458 470. (e) Bortoluzzi, M.; Marchetti, F.; Pampaloni, G.; Pinzino, C.; Zacchini, S. Oxidative Dimerization of Triarylamines Promoted by WCl_6, Including the Solid State Isolation and the Crystallographic Characterization of a Triphenylamonium Salt. *Inorg. Chem.* **2016**, *55*, 887–893 and references cited therein. (f) Siove, A.; David, R.; Ades, D.; Roux, C.; Leclerc, M. Homo- and Co-oxidative Polymerizations of Substituted Carbazole and Thiophene. *J. Chim. Phys.* **1995**, *92*, 787-790. (g) Tokuda, T.; Murashiro, K.; Kubo, M.; Masu, M.; Imanari, M.; Seki, H.; Aoki, N.; Ochiai, Y.; Kanoh, H.; Hoshino, K. Preparation and Characterization of Conducting Mixed-Valence 9,9'-Dimethyl-3,3'-bicarbazyl Rectangular Nanowires. *Langmuir* **2012**, *28*, 16430 16435.

13. For oxidative C–C coupling using organic oxidants, see: (a) Moody, C.J.; Shah, P. Diels-Alder Reactivity of Pyrano[3,4-b]indol-3-ones. Part 4. Synthesis of the Carbazole Alkaloids Carbazomycin A and B and Hyellazole. *J Chem Soc, Perkin Trans 1* **1989**, 2463–2471. (b) Bringmann, G.; Ledermann, A.; François, G. Dimeric Murrayafoline, A, a Potential Bis-Carbazole Alkaloid: 'Biomimetic' Synthesis, Atropisomer

Separation, and Antimalarial Activity. *Heterocycles* **1995**, *40*, 293–300. (c) Knölker, H.-J.; Goesmann, H.; Hofmann, C. Transition Metal Complexes in Organic Synthesis, Part 31. A Novel Molybdenum-Mediated Synthesis of Carbazole Derivatives: Application to the Total Synthesis of Mukonal and 1,1'-Bis(2-hydroxy-3-methylcarbazole). *Synlett* **1996**, 737–740. (d) Beresford, P.; Iles, D. H.; Kricka, L. J.; Ledwith, A. Cation radicals: Oxidative Coupling of Carbazoles, 10,11-Dihydro-5*H*-dibenz[*b*, *f*]azepines and Related Derivatives by 2,3-Dichloro-5,6-*p*-benzoquinone and Tris-(*p*-bromophenyl)ammoniumyl salts. *J. Chem. Soc., Perkin Trans. 1* **1974**, 276–280. (e) Lin, G.; Zhang, A. Synthesis of Optically Pure Clausenamine-A and its Demethoxylated Analogs. *Tetrahedron.***2000**, *56,* 7163–7171.

14. (a) Moorthy, J. N.; Venkatakrishnan, P.; Natarajan, P.; Lin, Z.; Chow, T. J. Nondoped Pure-Blue OLEDs Based on Amorphous Phenylenevinylene-Functionalized Twisted Bimesitylenes. *J. Org. Chem.* **2010**, *75*, 2599–2609. (b) Moorthy, J. N.; Venkatakrishnan, P.; Huang, D.-F.; Chow, T. J. Blue Light-Emitting and Hole-Transporting Amorphous Molecular Materials based on Diarylaminobiphenyl-Functionalized Bimesitylenes. *Chem. Commun.* **2008**, 2146–2148.
15. Maddala, S.; Mallick, S.; Venkatakrishnan, P. Metal-Free Oxidative C–C Coupling of Arylamines Using a Quinone-Based Organic Oxidant. *J. Org. Chem*. **2017**, *82*, 8958–8972.
16. Ambrose, J. F.; Carpenter, L. L.; Nelson, R, F. Electrochemical and Spectroscopic Properties of Cation Radicals III. Reaction Pathways of Carbazolium Radical Ions. *J. Electrochem. Soc*. **1975**, *122*, 876–894.
17. Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. Anodic Oxidation Pathways of Aromatic Amines. Electrochemical and Electron Paramagnetic Resonance Studies. *J. Am. Chem. Soc.* **1966**, *88*, 3498–3503.

18. (a) Rathore, R.; Kochi, J. K. Acid Catalysis vs. Electron-Transfer Catalysis via Organic Cations or Cation-Radicals as the Reactive Intermediate. Are these Distinctive Mechanisms? *Acta Chem. Scand.* **1998**, *52*, 114–130. (b) Zhai, L.; Shukla, R.; Rathore, R. Oxidative C–C Bond Formation (Scholl Reaction) with DDQ as an Efficient and Easily Recyclable Oxidant. *Org. Lett.* **2009**, *11*, 3474–3477. (c) Zhai, L.; Shukla, R.; Wadumethrige, S. H.; Rathore, R. Probing the Arenium-Ion (Proton Transfer) versus the Cation-Radical (Electron Transfer) Mechanism of Scholl reaction Using DDQ as Oxidant. *J. Org. Chem.* **2010**, *75*, 4748–4760. (d) Yuan, J.; Jin, L.; Chen, R.; Tang, X..; Xie, X.; Tang, Y.; Huang, W. Eaton's Reagent Assisted Aromatic C–C Coupling of Carbazoles for Optoelectronic Applications. *New J. Chem.* **2018**, *42*, 14704–14708.

19. (a) Ambrose, J. F.; Nelson, R. F. Anodic Oxidation Pathways of Carbazoles I. Carbazole and *N*-Substituted Derivatives. *J. Electrochem. Soc.* **1968**, *115*, 1159. (b) Karon, K.; Lapkowsk, M. Carbazole Electrochemistry: A Short Review. *J. Solid State Electrochem.* **2015**, *19*, 2601–2610.

20. (a) Miyamura, H.; Shiramizu, M.; Matsubara, R.; Kobayashi, S. Aerobic Oxidation of Hydroquinone Derivatives Catalyzed by Polymer Incarcerated Platinum Catalyst. *Angew. Chem. Int. Ed.* **2008**, *47*, 8093–8095. (b) Newman, M. S.; Khanna, V. K. Oxidation of 2,3-Dichloro-5,6-dicyanohydroquinone to 2,3-Dichloro-5,6-dicyanobenzoquinone. *Org. Prep. Proc. Int.* **1985**, *17*, 422–423. (c) Brinker, U. H.; Tyner III, M.; Jones, W. M. 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ): A New Inexpensive Recovery by Anodic Oxidation of 2,3-Dichloro-5,6-dicyano-*p*-hydroquinone. *Synthesis*, **1975**, *10*, 671. (d) Scott, J. W.; Parrish, D. R.; Bizzarro, F. T. A Rapid and Mild Process for the Oxidation of 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) from 2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ). *Org. Prep. Proced. Int.* **1977**, *9*, 91–94.

21. (a) Tang, G.-M.; Chi, R.-H.; Wan, W.-Z.; Wang, Y.-T.; Cui, Y.-Z.; Ng, S. W. Synthesis, Crystal Structures, and Nonlinear Optic and Thermal Properties of Two Diiodocarbazole Derivatives. *J. Chem. Res.* **2017**, *41*, 79–81. (b) Zhao, H.; Wang, Y.; Harrington, S.; Ma, L.; Hu, S.; Wu, X.; Tang, H.; Xue, M.; Wang, Y. Remarkable Substitution Influence on the Mechanochromism of Cyanostilbene Derivatives. *RSC Adv*. **2016**, *6*, 66477–66483.

22. Ledwith, A. Mechanisms for Initiating Polymerization by Stable Organic Cations. In *Addition and Condensation Polymerization Processes;* Platzer, N. A. J., Ed.; Advances in Chemistry, Volume 91; American Chemical Society: Washington, DC, 1969; pp 317 334.

23. (a) Ong, E. L.; Sambhi, M. S. Spectrophotometric and thermodynamic study of donor-acceptor complexes of carbazole. *J. Phys. Chem.* **1972**, *76*, 2102–2104. (b) Walker, W.; Hiebert, J. D. 2,3-Dichloro-5,6-Dicyanobenzoquinone and Its Reactions. *Chem. Rev.* **1967**, *67*, 153–195.

24. Kim, Y. E.; Kwon, Y. S.; Lee, K. S.; Park, J. W.; Seo, H. J.; Kim, T. W. Synthesis and Electrochemical Properties of *N*-Substituted Bicarbazyl Derivatives. *Mol. Cryst. Liq. Cryst*. **2004**, *424*, 153 158.

25. (a) Kirchgessner, M.; Sreenath, K.; Gopidas, K. R. Understanding Reactivity Patterns of the DialkylanilineRadical Cation. *J. Org. Chem.* **2006**, *71*, 9849–9852. (b) Sreenath, K.; Suneesh, C. V.; Kumar, V. K. R.; Gopidas, K. R. Cu(II)- Mediated Generation of Triarylamine Radical Cations and Their Dimerization. An Easy Route to Tetraarylbenzidines. *J. Org. Chem.* **2008**, *73*, 3245–3251.

26. Bai, G.; Li, J.; Li, D.; Dong, C.; Han, X.; Lin, P. Synthesis and spectrum charesteristic of four new organic fluorescent dyes of pyrazoline compounds. *Dyes and Pigm*. **2007**, *75,* 93 98.

27. Hwang, S.-H.; Wang, P.; Moorefield, C. N.; Godínez, L. A.; Manríquez, J.; Bustos, E.; Newkome, G. R. Design, Self-assembly, and Photophysical Properties of Pentameric Metallomacrocycles: [M_5(*N*-hexyl[1,2-bis(2,2':6',2"-terpyridin-4-yl)]carbazole)$_5$] [M = Fe(II), Ru(II), and Zn(II)]. *Chem. Commun.* **2005**, 4672 4674.

28. Fink, A. D.; Gross, D. E.; Han, A.; Moore, J. S. Engineering Solid-State Morphologies in Carbazole-Ethynylene Macrocycles. *J. Am. Chem. Soc.* **2011**, *133,* 14063–14070.

29. Hensel, T.; Trpcevski, D.; Lind, C.; Grosjean, R.; Hammershøj, P.; Nielsen, C. B.; Brock-Nannestad, T.; Nielsen, B. E.; Schau-Magnussen, M.; Minaev, B.; Baryshnikov, G. V.; Pittelkow, M. Diazadioxa[8]circulenes: Planar Antiaromatic Cyclooctatetraenes. *Chem. Eur. J.* **2013**, *19*, 17097–17102.

30. Cheung, C. W.; Buchwald. S. L. Mild and General Palladium-Catalyzed Synthesis of Methyl Aryl Ethers Enabled by the Use of a Palladacycle Precatalyst. *Org. Lett.* **2013**, *15*, 3998 4001.

31. Wang, L.; Yin, L.; Wang, L.; Xie, B.; Ji, C.; Li, Y. Tuning Photovoltaic Performance of DOBT-based Dyes via Molecular Design with Ethynyl-linker and Terminal Electron-Donating Segment. *Dyes Pigm.* **2017**, *140*, 203 211.

32. Chen, P.-Z.; Weng, Y.-X.; Niu, L.-Y.; Chen, Y.-Z.; Wu, L.-Z.; Tung, C.-H.; Yang, Q.-Z. Light-Harvesting Systems Based on Organic Nanocrystals to Mimic Chlorosomes. *Angew. Chem. Int. Ed*. **2016**, *55*, 2759 2763.

33. Buu-Hoi, Ng. Ph.; Royer, R. Potential Nitrogen-Heterocycle Carcinogens. III. New Derivatives of *N*-Ethylcarbazole. *J. Org. Chem.* **1950**, *15*, 123 130.

34. Kwon, J. K.; Cho, J. H.; Ryu, Y.-S.; Oh, S. H.; Yum, E. K. *N*-Arylation of Carbazole by Microwave-Assisted Ligand-free Catalytic CuI Reaction. *Tetrahedron*, **2011**, *67,* 4820 4825.

35. Zende, V. M.; Schulzkeb, C.; Kapdi, A. R. Pincer CNC bis-*N*-heterocyclic carbenes: robust ligands for palladium-catalysed Suzuki-Miyaura arylation of bromoanthracene and related substrates. *Org. Chem. Front.* **2015**, *2,* 1397–1401.

36. Steinhoff, G. W.; Henry, M. C. Reaction of Benzyne with Nitrobenzene. A New Route to the Carbazole Ring System. *J. Org. Chem.* **1964**, *29*, 2808 2809.

37. Zhou, Y.; Verkade, J. G. Highly Efficient Ligands for the Palladium-Assisted Double *N*-Arylation of Primary Amines for One-Step Construction Carbazoles. *Adv. Synth. Catal.* **2010**, *352*, 616–620.

38. Maligres, P. E.; Krska, S. W.; Dormer, P. G. A Soluble Copper(I) Source and Stable Salts of Volatile Ligands for Copper-Catalyzed C–X Couplings. *J. Org. Chem.* **2012**, *77*, 7646 7651. (b) Tao, S.; Liu, N.; Dai, B. One-pot Two-step Synthesis of *N*-Arylcarbazole-based Skeleton. *RSC Adv.* **2016**, *6*, 43250 43260.

39. Wang, L.; Ji, E.; Liu, N.; Dai, B. Site-Selective *N*-Arylation of Carbazoles with Halogenated Fluorobenzenes. *Synthesis* **2016**, *48*, 737 750. (b) Chen, F.; Liu, N.; Ji, E.; Dai, B. Copper/ *β*-Diketone-Catalysed*N*-Arylation of Carbazoles. *RSC Adv.* **2015**, *5*, 51512–51523.

40. Lv, H.-J.; Ma, R.-F.; Zhang, X.-T.; Li, M.-H.; Wang, Y.-T.; Wang, S.; Xing, G.-W. Surfactant-Modulated Discriminative Sensing of HNO and H_2S with a Cu^{2+}-Complex-based Fluorescent Probe. *Tetrahedron*, **2016**, *72*, 5495–5501.

41. Watanabe, M.; Nishiyama, M.; Yamamoto, T.; Koie, Y. Palladium/Pt(*t*-Bu)$_3$-Catalyzed Synthesis of *N*-Aryl Azole and Application to the Synthesis of 4,4',4"-Tris(*N*-azolyl)triphenylamines. *Tetrahedron Lett.* **2000**, *41*, 481–483.

42. Kawabata, K.; Goto, H. Electrosynthesis of 2,7-Linked Polycarbazole Derivatives to Realize Low-Bandgap Electroactive Polymers. *Synth. Met.* **2010**, *160*, 2290 2298.

43. Lanke, S. K.; Sekar, N. Aggregation Induced Emissive Carbazole-Based Push Pull NLOphores: Synthesis, Photophysical Properties and DFT Studies. *Dyes Pigm.* **2016**, *124*, 82 92.

44. Tang, H.; Li, Y.; Wei, C.; Chen, B.; Yang, W.; Wu, H.; Cao, Y. Novel Yellow Phosphorescent Iridium Complexes Containing a Carbazole-Oxadiazole Unit Used in Polymeric Light-Emitting Diodes. *Dyes Pigm*. **2011**, *91*, 413 421.

45. Mochizuki, H.; Hasui, T.; Kawamoto, M.; Ikeda, T.; Adachi, C.; Taniguchi, Y.; Shirota, Y. A Novel Class of Photo- and Electroactive Polymers Containing Oxadiazole and Amine Moieties in a Side Chain. *Macromolecules*, **2003**, *36*, 3457 3464.

46. Huo, Z.; Li, Z.; Wang, T.; Zeng, H. Carbazole *N*-Substituent Effect Upon DTMA: Stabilizing and Photochromic Modulating. *Tetrahedron*, **2013**, *69*, 8964 8973.

47. (a) Shi, H.-P.; Dai, J.-X.; Shi, L.-W.; Xu, L.; Zhou, Z.-B.; Zhang, Y.; Zhou, W.; Dong, C. Synthesis, Photophysical and Electrochemical Properties of a Carbazole Dimer-Based Derivative with Benzothiazole Units. *Spectrochimica Acta Part A*, **2012**, *93*, 19–25. (b) Yang, Z.; Zhao, N.; Sun, Y.; Miao, F.; Liu, Y.; Liu, X.; Zhang, Y.; Ai, W.; Song, G.; Shen, X.; Yu, X.; Sun, J.; Wong, W.-Y. Highly Selective Red- and Green-Emitting Two Photon Fluorescent Probes for Cysteine Detection and their Bio-imaging in Living Cells. *Chem. Commun.* **2012**, *48*, 3442–3444.

48. Grigoras, M.; Antonoaia, N.-C. Synthesis and Characterization of Some Carbazole-Based Imine Polymers. *Euro. Polym. J.* **2005**, *41*, 1079–1089.

49. Sakthivel, P.; Kranthiraja, K.; Saravanan, C.; Gunasekar, K.; Kim, H. I.; Shin, W. S.; Jeong, J.-E.; Woo, H. Y.; Jin, S.-H. Carbazole Linked Phenylquinoline-Based Fullerene Derivatives as Acceptors for Bulk Heterojunction Polymer Solar Cells: Effect of Interfacial Contacts on Device Performance. *J. Mater. Chem. A*, **2014**, *2*, 6916–6921.

50. Nesterov, V. N.; Montoya, N. G.; Antipin, M. Yu.; Sanghadasa, M.; Clark, R. D.; Timofeeva, T. V. Three Polar Derivatives of *N*-Ethylcarbazole: Materials for Optical Applications. *Acta Crystallogr. C*, **2002**, *C 58*, 72 75.

51. He, C.; He, Q.; Chen, Q.; Shi, L.; Cao, H.; Cheng, J.; Deng, C.; Lin, T. Highly Fluorescent Intramolecular Dimers of Two Pyrenyl Substituted Fluorenes Bridged by 1,6-Hexanyl: Synthesis, Spectroscopic, and Self-Organized Properties. *Tetrahedron Lett.* **2010**, *51*, 1317–1321.

52. Ameen, S.; Lee, S. B.; Yoon, S. C.; Lee, J.; Lee, C. Diphenylaminocarbazoles by 1,8-Functionalization of Carbazole: Materials and Application to Phosphorescent Organic Light-Emitting Diodes. *Dyes Pigm.* **2016**, *124*, 35 44.

53. Ponce, M. B.; Cabrerizo, F. M.; Bonesi, S. M.; Erra-Balsells, R. Synthesis and Electronic Spectroscopy of Bromocarbazoles. Direct bromination of *N*- and *C*-Substituted Carbazoles by *N*-Bromosuccinimide or a *N*-Bromosuccinimide/Silica Gel System. *Helv. Chim. Acta.* **2006**, *89*, 1123 1139.

54. Feng-Wen, Y.; Cheng-Hao, C. Compound for Organic Electroluminescence Device. *U.S. Pat. Appl. Publ*. **2015**, US 20150214492 A1.

55. Kuwahara, A.; Nakano, K.; Nozaki, K. Double *N*-Arylation of Primary Amines: Carbazoles Synthesis from 2,2'-Biphenyldiols. *J. Org. Chem*. **2005**, *70*, 413–419.

56. Han, J.; Yin, H.; Liu, C.; Wang, J.; Jianb, X. Donor-Acceptor Copolymers Containing Phthalazinone-Thiophene Structure Synthesized by Low-Cost Copper-Catalyzed Ullmann Polymerization. *RSC Adv*. **2016**, *6*, 6772–6781.

57. Goo, D.-Y.; Woo, S. K. One-pot synthesis of carbazoles via tandem C C cross-coupling and reductive amination. *Org. Biomol. Chem.* **2016**, *14*, 122-130.

58. Grigalevicius, S.; Lideikis, E.; Grazulevicius, J. V.; Gaidelis, V.; Jankauskas, V. 3,3'-Bicarbazole-Based Dihydrazones for Electrographic Photoreceptors. *Environmental and Chemical Physics*, **2001**, *23,* 77 82.

59. Lee, J. M.; Lee, C. J.; Shaheed, A. Low Temperature Curable Hole Transport Material for Organic Light Emitting Device. *Rupub. Korean Kongkae Taeho Kongbo*, KR2017078345, **2017**.

60. Kim, J. K.; Kim, Y.-K.; Min, S.-H.; Yu, E. S.; Kim, B.-K.; Lee, B.-K.; Jang, K.; Jung, S.-H. Preparation of Carbazole Derivatives for Organic Optoelectronic Device. *PCT Int. Appl.* **2017**, WO 2017034085 A1 Mar 02, 2017.

61. Zhang, Q.; Zhuang, H.; He, J.; Xia, S.; Li, H.; Li, N.; Xu, Q.; Lu, J. Improved Ternary Memory Performance of Donor-Acceptor Structured Molecules Through Cyano Substitution. *J. Mater. Chem. C*, **2015**, *3*, 6778 6785.

62. Takeshi, I.; Kazunari, K.; Takeshi, T. Light-emitting device. *Jpn. Kokai Tokkyo Koho*, **2008**, JP 2008294161 A.

63. Ji, H. S.; Moon, S. Y.; Park, J. C.; Park, Y. U.; Kang, M. S.; Lee, B. S.; Kim, S. H. Organic Electronic Element Containing Light Efficiency Improving Layer and Electronic Device Containing the Same. *Repub. Korean Kongkae Taeho Kongbo*, KR 2015012835 A, **2015**.

64. Wu, C.-W.; Lin, H.-C. Synthesis and Characterization of Kinked and Hyperbranched Carbazole/Fluorene-Based Copolymers. *Macromolecules*, **2006**, *39*, 7232 7240.

65. Irgashev, R. A.; Kazin, N. A.; Makarova, N. I.; Dorogan, I. V.; Malov, V. V.; Tameev, A. R.; Rusinov, G. L.; Metelitsa, A. V.; Minkin, V. I.; Charushin, V. N. Synthesis and Properties of New π-Conjugated Imidazole/Carbazole Structures. *Dyes Pigm.* **2017**, *141,* 512 520.

66. Wang, H.; Chen, G,; Xu, X.; Chen, H.; Ji, S. The Synthesis and Optical Properties of Benzothiazole-Based Derivatives with Various π-Electron Donors as Novel Bipolar Fluorescent Compounds. *Dyes Pigm.* **2010**, *86,* 238 248.

67. (a) Budén, M. E.; Vaillard, V. A.; Martin, S. E.; Rossi, R. A. Synthesis of Carbazoles by Intramolecular Arylation of Diarylamide Anions. *J. Org. Chem.* **2009**, *74*, 4490–4498. (b) Gao, Y.; Hlil, A.; Wang, J.; Chen, K.; Hay, A. S. Synthesis of Homo- and Copoly(arylene bicarbazole)s via Nucleophilic Substitution Polycondensation Reactions of NH Groups with Activated Dihalides. *Macromolecules*, **2007**, *40*, 4744 4746.