Cycloaddition **Hot Paper**

Deutsche Ausgabe: DOI: 10.1002/ange.201503549
Internationale Ausgabe: DOI: 10.1002/anie.201503549

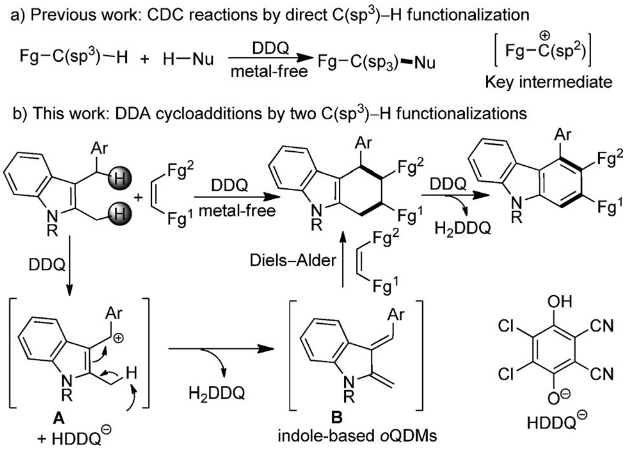
Metal-Free Dehydrogenative Diels–Alder Reactions of 2-Methyl-3-Alkylindoles with Dienophiles: Rapid Access to Tetrahydrocarbazoles, Carbazoles, and Heteroacenes**

*Liejin Zhou, Bing Xu, and Junliang Zhang**

Dedicated to Professor Xue-Long Hou on the occasion of his 60th birthday

Abstract: *An unprecedented strategy for in situ generation of indole-based ortho-quinodimethanes (oQDMs) from 2-methyl-3-alkylmethylindoles by either a metal-free DDQ- or BQ-mediated dehydrogenative process was developed. These oQDMs were trapped by electron-deficient dienophiles to provide a facile approach to synthetically valuable tetrahydrocarbazoles, carbazoles, and hetereoacenes. The salient features of this transformation include direct* $C(sp^3)$*–H bond functionalizations, readily available starting materials, metal-free conditions, high efficiency, operational simplicity, and ease of scale-up.*

Metal-free DDQ-mediated cross-dehydrogenative coupling (CDC) reactions have received much attention during the past years, and have become one of the efficient strategies for addressing the direct functionalization of $C(sp^3)$–H bonds (Scheme 1 a).[1–4] In 2006, Li and co-workers reported the first example of DDQ-mediated direct CDC reactions between benzyl ether and simple ketones and the cross-coupling products were obtained in moderate yields under neat conditions at 100 °C.[4a] A series of elegant DDQ-mediated CDC reactions between allylic/propargylic/benzylic $C(sp^3)$–H bonds and diverse coupling partners were then developed by the groups of Bao,[4b–c] Floreancig,[4d–g] Jiao,[4h] and Li[4i] Recently, several enantioselective versions of CDC reactions, through the combination of DDQ and either a chiral metal catalyst or organocatalyst, have been developed by the groups of Cozzi,[4j] Hayashi,[4k] Liu,[4l] and Wang.[4m] Despite this progress in $C(sp^3)$–H bond functionalizations for the formation of either C–C or C–X bonds, to the best of our knowledge, the metal-free dehydrogenative Diels–Alder (DDA) reaction with the formation of two C–C bonds in a single operation by a DDQ-mediated direct $C(sp^3)$–H bond functionalization has not been explored so far.[5] Herein, we report a novel DDQ-mediated direct DDA reaction between 2-methyl-3-arylmethylindoles and electron-deficient olefins to provide facile access to tetrahydrocarbazoles, carbazoles, and poly-heteroacenes (Scheme 1 b).



Scheme 1. Previous work and this work with a projected working hypothesis. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, Fg = functional group.

Tetrahydrocarbazole scaffolds are frequently found in natural products and as building blocks in organic synthesis.[6] Meanwhile, carbazoles and derivatives have received considerable attention because of their frequent occurrence in biologically active natural and unnatural products, and in organic functional materials (Figure 1).[7,8] To advance organic materials science, the design of novel scaffolds and improvements in synthetic methods for these compounds are critically important. Obviously, those methodologies which are based on direct C–H functionalization have advantages over the classic reactions as they do not require the prefunctionalization of starting materials. However, despite the progress made in the synthesis of extended π systems by direct $C(sp^2)$–H activation,[9] the development of novel methodologies through direct $C(sp^3)$–H functionalization still remain a considerable challenge. During our recent endeavors directed toward in situ generation of heterocycle-based *ortho*-quinodimethanes (*o*QDMs)[10] via a cascade process consisting of $C(sp^3)$–H functionalization,[11] we envis-

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[**] We are grateful to the 973 programs (2015CB856600), National Natural Science Foundation of China (21425205, 21372084), Shanghai Eastern Scholar Program for financial supports.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503549.

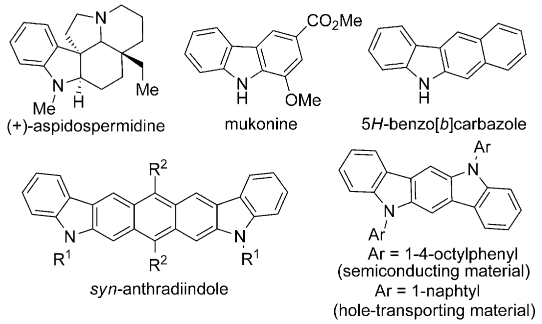
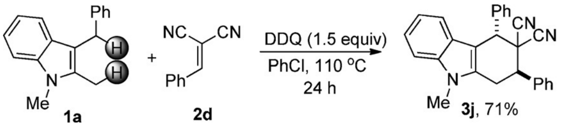


Figure 1. Carbazole and tetrahydrocarbazole scaffolds in natural products and materials science.

aged that the indole-based *o*QDM[12] **B** might be generated in situ from 2-methyl-3-arylmethylindoles by a DDQ-mediated dehydrogenative process for direct $C(sp^3)$–H functionalizations. In the presence of suitable dienophiles, a subsequent Diels–Alder cycloaddition might take place. If this hypothesis is successful, it will provide rapid access to various synthetically valuable tetrahydrocarbazoles, carbazoles, and poly-heteroacenes from readily available starting materials in an efficient manner.

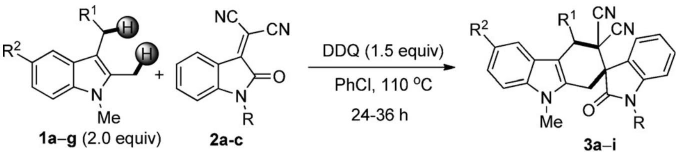
To test our hypothesis, 3-benzyl-1,2-dimethyl-1*H*-indole (**1a**) and the dienophile **2a** (for structure see Table 1) were chosen as the model substrates and subjected to various reaction conditions (for details see Table S1 in the Supporting Information). Because of the crucial role of the generation of indole-based *o*QDM intermediates, a series of oxidants were firstly evaluated. To our delight, DDQ was found to be the most efficient oxidant, thus furnishing the desired product **3a** in 96 % yield. Oxone gave **3a** but in lower yield (45 %), while other oxidants such as $PhI(OAc)_2$ and $AgNO_3$ were almost ineffective. It was found that PhCl was proven to be the most favorable solvent after screening different solvents. The solvent effect may be attributed to DDQ having different oxidation capabilities in different solvents.[3i]

With the optimized reaction conditions in hand, we then explored the reaction scope by variation of the indole components (Table 1). Different aryl groups (R^1) were compatible under the reaction conditions, thus delivering the desired products **3a**–**h** in 91–98 % yields with moderate diastereoselectivities (entries 1–8). Notably, the substrate **2c**, with an easily removable protecting group (4-methoxybenzyl), was compatible with the oxidative DDQ conditions and thus delivered the corresponding product **3i** in excellent yield (entry 9). We were also pleased to find that the less reactive 2-benzylidenemalononitrile (**2d**) could be employed as a dienophile, thus delivering the desired product **3j** in 71 % yield as a single diastereomer [Eq. (1)].



(1)

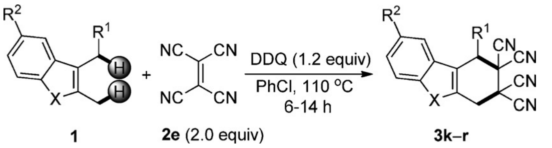
Table 1: The scope of the 2-methyl-3-arylmethylindoles **1** reacting with **2**.[a]



Entry	**1**, R^1/R^2	**2**, R	**3**, Yield [%][b]	d.r.[c]
1	**1a**, Ph/H	**2a**, Bn	**3a**, 96	3.6:1
2	**1b**, 2-$CH_3C_6H_4$/H	**2a**, Bn	**3b**, 98	3.7:1
3	**1c**, 4-$CH_3C_6H_4$/H	**2a**, Bn	**3c**, 91	3.3:1
4	**1d**, Ph/CH_3	**2a**, Bn	**3d**, 97	3.5:1
5	**1e**, 4-ClC_6H_4/H	**2a**, Bn	**3e**, 94	3.4:1
6	**1f**, 1-naphthyl/H	**2a**, Bn	**3f**, 95	3.1:1
7	**1g**, 3-$CF_3C_6H_4$/H	**2a**, Bn	**3g**, 96	3.4:1
8	**1a**, Ph/H	**2b**, Me	**3h**, 89	3.3:1
9	**1a**, Ph/H	**2c**, PMB	**3i**, 95	3.4:1

[a] Reactions were conducted at 0.2 mmol scale of **2**. [b] Yields of isolated products. [c] Determined by determined by crude NMR. PMB = *para*-methoxy benzyl.

Table 2: The scope of the 2-methyl-3-arylmethylindoles **1** reacting with **2e**.[a]

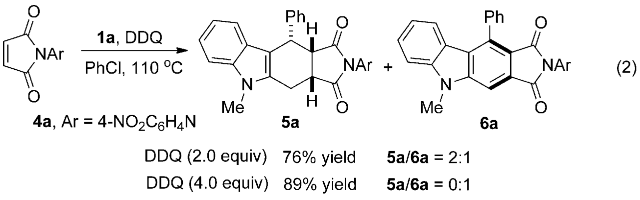


Entry	**1**, R^1/R^2/X	*t* [h]	**3**	Yield [%][b]
1[c]	**1a**, Ph/H/NCH_3	10	**3k**	86
2	**1i**, Ph/CO_2Me/NCH_3	10	**3l**	78
3	**1j**, Ph/NO_2/NCH_3	14	**3m**	82
4	**1k**, 4-$NO_2C_6H_4$/H/NCH_3	10	**3n**	85
5	**1l**, H/H/NCH_3	10	**3o**	62
6	**1m**, H/H/NBoc	6	**3p**	58
7[d]	**1n**, *n*-C_5H_9/H/NCH_3	6	**3q**	42
8	**1o**, Ph/H/O	24	**3r**	53

[a] Reactions were conducted at 0.2 mmol scale of **1**. [b] Yield of isolated product. [c] DCE instead of PhCl in 60 °C. [d] $PhCH_3$ instead of PhCl. DCE = 1,2-dichloroethane, Boc = *tert*-butoxycarbonyl.

The substrate scope for in situ generation of heterocycle-based *o*QDMs was further investigated with the use of tetracyanoethylene (**2e**) as the dienophile (Table 2). It was interesting to find that electron-withdrawing groups on the aryl moiety (R^1) and the indole moiety did not affect the reaction. For example, the substrates **1i** and **1j**, bearing an electron-withdrawing ester and nitro moiety, respectively, underwent the DDA reaction, thus producing the corresponding tetrahydrocarbazoles **3l** and **3m** in good yields (entries 2 and 3). The compound **1k**, having an electron-deficient nitro substituent on the aryl group could also afford the desired product **3n** in 85 % yield. Importantly, R^1 could also be an H (**1l**) and aliphatic group (**1n**) and the corresponding products were obtained in moderate yields (entries 5 and 7). Furthermore, the compound **1m**, with a Boc protecting group, was applicable to this transformation (entry 6), thus further extending the substrate scope. It is interesting to find that benzofuran-fused *o*QDMs might be also generated in situ from the corresponding 3-benzyl-2-methylbenzofuran (**1o**), thus leading to the tetrahydrodibenzo[*b*,*d*]furan derivative **3r** in reasonable yield (entry 8).

To our surprise, other than the desired cycloadduct **5a**, a new aromatic product carbazole (**6a**) was isolated as a minor product when *N*-(4-*n*itrophenyl)-maleimide (**4a**) was used as the dienophile, in the presence of 2.0 equivalents of DDQ [Eq. (2)]. The carbazole **6a** was produced as the sole product by increasing the DDQ loading to 4.0 equivalents. This result suggested that **6a** should be generated from **5a** by DDQ-mediated oxidation. In contrast, when the Boc-protected **1m** was used, the tetrahydrocarbazole **5m** was isolated in 52% yield and could not undergo further oxidation to the carbazole, thus indicating that the electron-deficient indole moiety of **5m** may hinder this additional oxidation [Eq. (3)].



With the high synthetic value of carbazole in mind, a number of 2-methyl-3-arylmethylindoles (**1a**–**r**) bearing different substituents were examined (Table 3). To our delight, the desired carbazoles **6a**–**h** could be obtained in good yields in the presence of 4 equivalents of DDQ in chorobenzene at 110°C (entries 1–8). It is noteworthy that this novel process consists of four C(sp^3)–H bond functionalizations and two C(sp^2)–H bond functionalizations in a single operation. Furthermore, *N*-phenylmaleimide (**4b**), the NH-free maleimide **4c**, and even maleic anhydride are applicable to this process to afford the desired carbazoles **6i**–**k** in moderate to good yields (entries 9–11). The lower yield for **6k** may be attributed to the moisture-sensitive anhydride during the work-up and purification by column chromatography. Further studies showed that diethyl acetylenedicarboxylate could be used as a dienophile to produce the desired product carbazole **6l**, having ester groups, in moderate yield [Eq. (4)]. It is noteworthy that this carbazole ester skeleton was a key subunit in a number of natural products such as the clausines E, G, H, L, M, and R, as well as mukonine and mukonidine.[7]

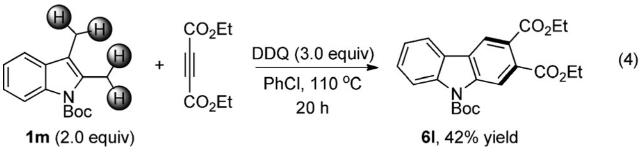
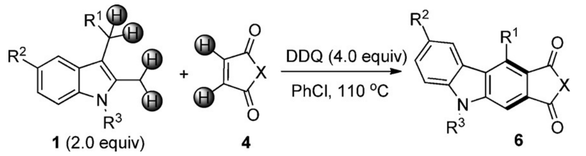


Table 3: Synthesis of carbazoles through a DDQ-mediated cascade process.[a]



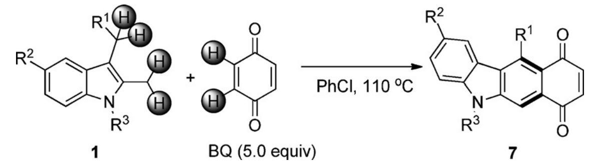
Entry	**1**, R^1/R^2/R^3	**4**, X	**6**, Yield [%][b]
1	**1a**, Ph/H/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6a**, 89
2	**1c**, 4-$CH_3C_6H_4$/H/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6b**, 81
3	**1d**, Ph/CH_3/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6c**, 74
4	**1e**, 4-ClC_6H_4/H/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6d**, 85
5	**1f**, 1-naphthyl/H/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6e**, 74
6	**1p**, 4-$CH_3OC_6H_4$/H/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6f**, 82
7	**1q**, Ph/F/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6g**, 71
8	**1r**, 4-FC_6H_4/H/CH_3	**4a**, 4-$NO_2C_6H_4N$	**6h**, 77
9	**1a**, Ph/H/CH_3	**4b**, PhN	**6i**, 78
10	**1a**, Ph/H/CH_3	**4c**, NH	**6j**, 78
11	**1a**, Ph/H/CH_3	**4d**, O	**6k**, 47

[a] Reactions were conducted at 0.2 mmol scale of **4**. [b] Yield of isolated product.

Inspired by the above results, we then turned our attention to benzoquinone (BQ) as the dienophile. After several attempts, we are pleased to find that benzoquinone could not only be functionalized as a substrate, but also acted as an oxidant, which led to carbazole derivatives in a cascade reaction (Table 4). In general, moderate to excellent yields are obtained. Notably, it was found that both electron-rich and electron-deficient aryl groups (R^1) were compatible under the reaction conditions, thus delivering the corresponding 5H-benzo[b]carbazole-7,10-diones **7b**–**o** were in 64–94% yields (entries 2–15). As expected, the substrate **1x**, having a free NH, delivered the product in a lower yield (entry 14), while compound **1y**, having a benzyl protecting group, furnished the desired product **7q** in satisfactory yield (entry 15). Furthermore, the reaction of **1a** with BQ could be easily scaled up to a gram scale (4 mmol of **1a**), thus furnishing 1.10 grams of the synthetically valuable **7a** without loss of efficiency.

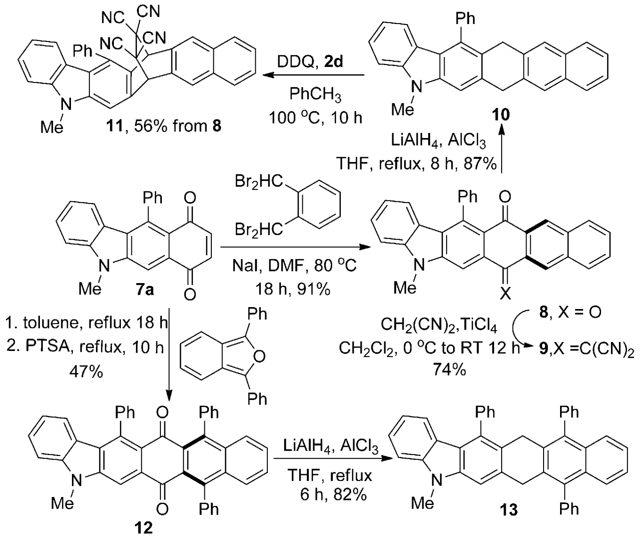
With the knowledge that fused linear (hetero)acenes[13] have long been known as promising materials for applications in high-performance and low-cost organic thin-film transistors, we paid attention to the synthesis of the extended π-system heteroarenes from **7a** (Scheme 2). The treatment of **7a** with 1,2-bis(dibromomethyl)benzene in the presence of NaI in DMF at 80°C delivered the compound **8** with multifused aromatic rings in 91% yield. Gratifyingly, the bis(carbonyl) groups of **8** could undergo highly selective Knoevenagel condensation with malononitrile in the presence of $TiCl_4$ and pyridine to furnish the compound **9** in 74% yield. Alternatively, the reduction of **8** with $LiAlH_4$ and $AlCl_3$ could deliver the heteroacene **10**,[14] which is a very stable precursor compared to the corresponding unstable and air-sensitive heteroacene.[15] It should be noted that **10** could undergo the dehydrogenation reaction in the presence of DDQ to give the corresponding unstable (hetero)acene, which was trapped in situ by **2d**, thus furnishing the desired cycloadduct **11** in 56% overall yield over three steps from **8**.

Table 4: Synthesis of 5H-benzo[*b*]carbazole-7,10-diones.[a]



Entry	$R^1/R^2/R^3$	*t* [h]	**7**, Yield [%][b]
1	**1a**, Ph/H/CH_3	12	**7a**, 91
2	**1b**, 2-$CH_3C_6H_4$/H/CH_3	10	**7b**, 92
3	**1c**, 4-$CH_3C_6H_4$/H/CH_3	10	**7c**, 84
4	**1d**, Ph/CH_3/CH_3	12	**7d**, 88
5	**1e**, 4-ClC_6H_4/H/CH_3	12	**7e**, 86
6	**1f**, 1-naphthyl/H/CH_3	12	**7f**, 89
7	**1g**, 3-$CF_3C_6H_4$/H/CH_3	12	**7g**, 71
8	**1p**, 4-$CH_3OC_6H_4$/H/CH_3	10	**7h**, 83
9	**1q**, Ph/F/CH_3	24	**7i**, 79
10	**1r**, 4-FC_6H_4/H/CH_3	12	**7j**, 94
11	**1s**, 4-BrC_6H_4/H/CH_3	12	**7k**, 83
12	**1t**, 3,4,5-$(CH_3O)_3C_6H_4$/H/CH_3	8	**7l**, 85
13[c]	**1u**, 4-NCC_6H_4/H/CH_3	48	**7m**, 80
14[c]	**1v**, 4-$CF_3C_6H_4$/H/CH_3	48	**7n**, 64
15[c]	**1w**, 4-$CO_2MeC_6H_4$/H/CH_3	48	**7o**, 77
16	**1x**, Ph/H/H	12	**7p**, 48
17[c]	**1y**, Ph/H/Bn	48	**7q**, 82

[a] Reactions were conducted at 0.2 mmol scale of **1** in the presence of 1.0 mmol of BQ. [b] Yield of isolated product. [c] Reacted for 48 h.



Scheme 2. Synthetic transformations of **7a**. DMF = *N*,*N*-dimethylformamide, PTSA = *para*-toluenesulfonic acid, THF = tetrahydrofuran.

Furthermore, the Diels–Alder cycloaddition of **7a** and 1,3-diphenylisobenzofuran, and subsequent aromatization under the catalysis of PTSA delivered another multifused ring system (**12**). Accordingly, the air-stable heteroacene **13** could be obtained in 82 % yield by the $LiAlH_4$-$AlCl_3$ reduction.

In summary, we have developed a novel strategy for the in situ generation of indole-based *ortho*-quinodimethanes (*o*QDMs) by using either a DDQ- or BQ-mediated dehydrogenative reaction of 2-methyl-3-arylmethylindoles under metal-free conditions. These in situ generated indole-based *o*QDMs could be trapped by electron-deficient dienophiles, thus delivering a facile approach to synthetically valuable N heterocycles such as tetrahydrocarbazoles, carbazoles, and 5H-benzo[b]carbazole-7,10-diones, which showed can be used in the synthesis of novel fused heteroacenes with potential applications in material science. The salient features of this transformation include a challenging direct C(sp^3)−H bond functionalization, readily available starting materials, metal-free conditions, high efficiency, operational simplicity, and ease of scale-up. Further studies will include extending the substrate scope to other aromatic system[16] for synthesis of (hetero)acenes, and investigating their physical and chemical properties. The results will be reported in due course.

Keywords: C−H activation · cycloaddition · heterocycles · oxidation · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9092–9096
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Received: April 18, 2015