Green Chemistry

Accepted Manuscript

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DOI: 10.1039/C7GC03130K

Transition-metal-free and organic solvent-free conversion of N-substituted 2-aminobiaryls into corresponding carbazoles *via* intramolecular oxidative radical cyclization induced by peroxodisulfate

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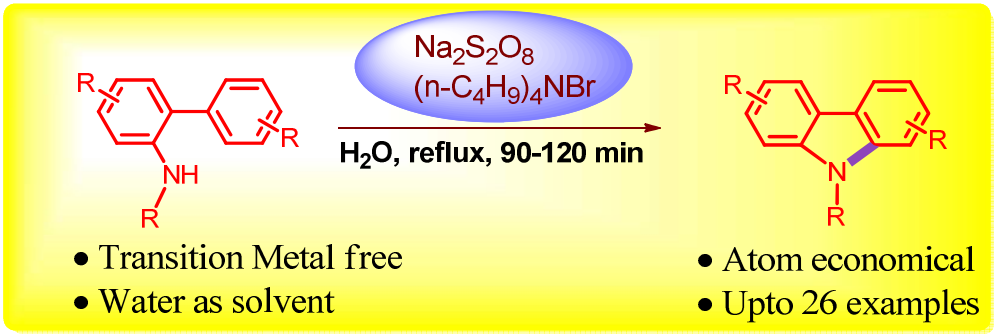

Abstract

An atom-economical and environmentally benign approach for the synthesis of N-substituted carbazoles from analogous 2-aminobiaryls using peroxodisulfate in water is reported. The reactions proceeded through an intramolecular oxidative radical cyclization of N-substituted 2-aminobiaryls with *in situ* reoxidation of the resulting radical species. While compared to known methods for the synthesis of N-substituted carbazoles from 2-amidobiaryls, this protocol is practical, efficient and do not require a transition metal catalyst and toxic organic solvents!

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Introduction

The carbazole and its derivatives are often found in a wide range of natural products[1] and pharmaceuticals[2] exhibit interesting biological activities like antibacterial,[3] antibiotic,[4] antihistaminic,[5] antiinflammatory,[6] antimalarial,[7] antioxidative,[8] antitumor,[9] antiviral[10] and psychotropics.[11] They are also used as precursors for the synthesis of functional materials in organic electronics.[12] A number of synthetic methods have been developed for the preparation of carbazoles and continues to be a topic of research interest. Among the various methods such as Borsche-Drechsel cyclization,[13] Pummerer cyclization,[14] Dielse-Alder reaction,[15] Buchwald-Hartwig amination,[16,17] Suzuki-Miyaura coupling,[18,19] dehydrogenative cyclization of diarylamines,[20] dehydrogenative C-H/N-H coupling of N-substituted 2-aminobiaryls,[21,22] double amination of 2,2′-dihalobiaryls,[23] nitrene insertion of 2-azido-biphenyls,[24] reductive amination of nitroaryls,[25] etc., thus far reported to synthesize carbazoles; the intramolecular C-H bond amination of 2-aminobiaryls is perhaps the most atom-economical route and being is used to attain a myriad of carbazole derivatives rapidly (Scheme 1). In this synthetic path (Scheme 1), generally, a variety of transition metal catalysts including Cu(II)[21(a),22(a)], Ir(I),[22(c)] Mn(IV),[21(a)] Pd(0),[21(b)] Pd(II),[21(c,e,f,g)] Rh(II)[22(d,e)] and their combinations have been utilized. Despite the high efficiency and wide tolerance of functionality, residual transition-metal contamination could adversely affect the biological properties of the final products.[1-3] Moreover, many transition metal catalysts are expensive, requires harsh reaction conditions and unstable at ambient conditions.[12] As a consequence, the development of a transition-metal-free and environmentally benign synthetic protocol for carbazoles synthesis is highly desirable.

Recently, with the objective of developing environmentally benign conditions for organic synthesis[26] and pollutants mineralization,[27] peroxodisulfate ($S_2O_8^{2-}$, known also as peroxydisulfate or persulfate) in aqueous solution has widely been utilized. For instances, deoximation,[28] oxidation,[29] cyclization,[30] polymerization,[30] and so on are readily performed using peroxodisulfate as a sole reagent. Since the peroxodisulfate is a white crystalline solid, cheaper, chemically stable at ambient conditions, water-soluble, convenient to transport, powerful one-electron oxidant with $E^o = 2.01$ V in aqueous solution and can be activated readily by heat/base/UV radiation.[26,27] Moreover, peroxodisulfate provides biodegradable sulfate (SO_4^{2-}) as the only byproduct. Nevertheless, peroxodisulfate has not yet been employed for the synthesis

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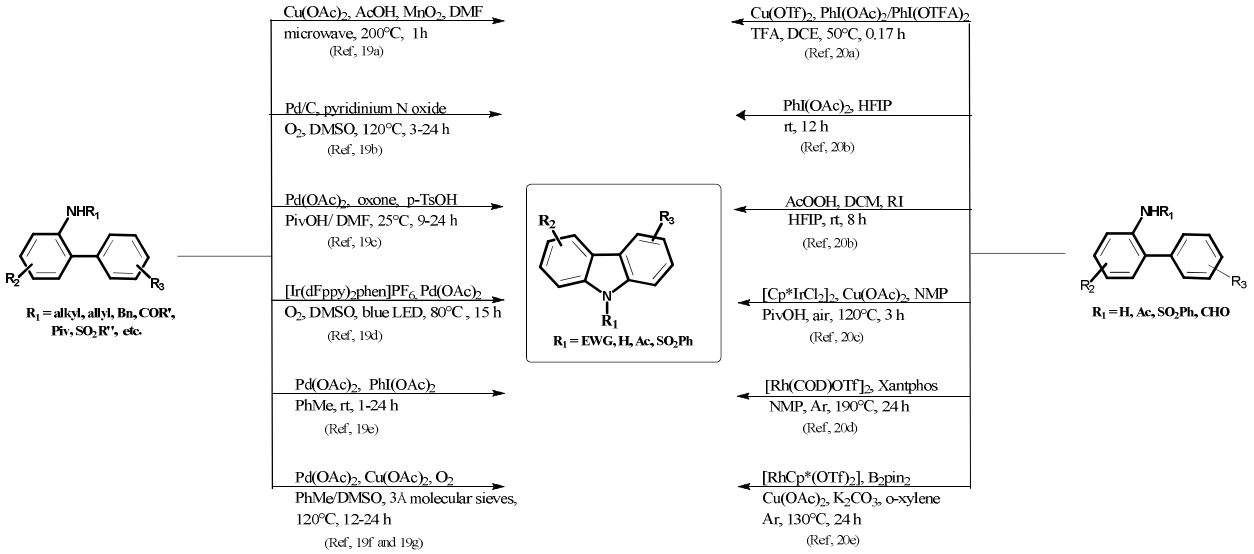
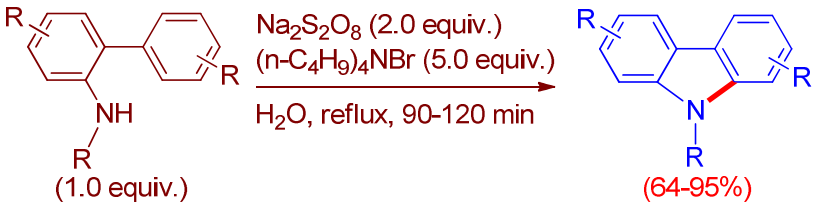
of carbazole and its derivatives. In view of this and in continuation of our interest in the development of green methodologies,[31] herein, we disclose our finding on the synthesis of N-substituted carbazoles from analogues 2-aminobiaryls using peroxodisulfate in water as an oxidizing agent, cf. Scheme 2. Moreover, a plausible mechanism for the reaction is reported, vide infra.



Scheme 1. Various methods of synthesis of carbazoles from 2-aminobiaryl and its derivatives yet reported in the literatures.



Scheme 2. $S_2O_8^{2-}$-induced synthesis of N-substituted carbazoles from analogous 2-aminobiaryls in water reported here.

Results and Discussion

We began our investigation using 2-acetamidobiphenyl (**A1**) as the model substrate. To our delight, **A1** (1 mmol) underwent intramolecular C-H bond amination rapidly upon the treatment with $Na_2S_2O_8$ (1 mmol) in water at reflux conditions, affording 9-acetylcarbazole (**C1**) in 29% yield (Entry 1, Table 1). The structure of **C1** was confirmed by IR and NMR analysis, cf. Supporting Information. The use of other green solvents such as glycols, ethyl alcohol and

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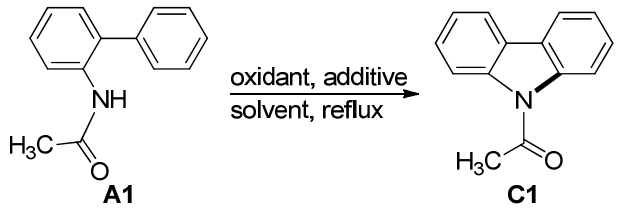
dimethyl sulfoxide was inadequate and gave lower product yields (Entries 2-4, Table 1). Next, the effect of counter-ion of peroxodisulfate was tested. When $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ was used as oxidant instead of $Na_2S_2O_8$, a lower yield of desired product was obtained (Entries 5-6, Table 1). In contrast, when tetrabutylammonium peroxodisulfate {TBAPS, $[(n\text{-}C_4H_9)_4N]_2S_2O_8$} *in situ* generated from the mixture of $Na_2S_2O_8$ and tetrabutylammonium bromide was used instead of $Na_2S_2O_8$, a significant amount of **C1** was obtained in short duration (Entry 7, Table 1). Thus, TBAPS was taken as oxidant for further all optimizations and reactions. Later, we explored the stoichiometry of TBAPS to **A1**. The best result was obtained with 1:2 ratios of **A1** and TBAPS, cf. Entry 11 in Table 1. Decreasing the amount of TBAPS from 1 equiv. to 0.5 equiv. led to a lower yield of **C1** (Entry 12, Table 1). However, increasing the amount of TBAPS to 2.0 equiv. and above neither increased the yield nor lowered the reaction time drastically (Entries 13-14, Table 1). Further optimizations revealed that the reaction atmosphere was crucial for the outcome of the reaction. The reaction proceeded efficiently under nitrogen gas atmosphere while the involvement of air brings down yield of the product, cf. Entries 15-16 in Table 1. Thus, the optimized reaction conditions for the transformation of N-substituted 2-aminobiaryls into corresponding carbazoles (Scheme 2) are substrate (1.0 mmol), TBAPS (2.0 mmol) and water (3 mL) under reflux conditions at nitrogen gas atmosphere.

Table 1. Selected results of screening the optimal conditions for the synthesis of N-substituted carbazoles from the analogous 2-aminobiaryls[a]



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Entry	Solvent[b]	Oxidant (mmol)	Atmosphere	Time (min)	Yield (%)[c]
1	water	$Na_2S_2O_8$ (1)	N_2	120	29
2	glycol	$Na_2S_2O_8$ (1)	N_2	120	trace
3	ethyl alcohol	$Na_2S_2O_8$ (1)	N_2	120	<10
4	dimethyl sulfoxide	$Na_2S_2O_8$ (1)	N_2	120	trace
5	water	$K_2S_2O_8$ (1)	N_2	120	24
6	water	$(NH_4)_2S_2O_8$ (1)	N_2	120	13
7	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (1)	N_2	120	58
8	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (1.1)	N_2	120	58
9	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (1.3)	N_2	120	66
10	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (1.5)	N_2	120	76
11	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (2)	N_2	90	93
12	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (0.5)	N_2	180	17
13	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (2.5)	N_2	90	93
14	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (3)	N_2	90	95
15	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (2)	open air	90	47
16	water	$[(n\text{-}C_4H_9)_4N]_2S_2O_8$ (2)	air	90	38

[a] General conditions: Unless stated otherwise all reactions were performed in a Schlenk tube with 1.0 mmol of **A1**, oxidant and solvent (3 mL).
[b] All solvents and water were double-distilled and de-aerated prior to use.
[c] Isolated yields.

Having optimized the reaction conditions, the scope and limitations of the methodology (Scheme 2) was investigated and the results obtained are listed in Table 2. Initially, substrates **A2-A7** with different substitution patterns on the aryl part of the 2-amidobiaryls were screened. Functional groups including CH_3, OCH_3, F and Cl were well compatible with the oxidation system, and the desired products **C2-C7** were obtained in 64-91% yields. Afterwards, substrates **A8-A11** bearing various electron-donating and electron-withdrawing functional groups on the acetanilide ring were employed. Unsurprisingly, the reaction proceeded smoothly and afforded the desired products in moderate to good yields (Table 3) under the optimized reaction conditions (Table 1). Subsequently, the substrates **A12-A13** bearing both electron-donating and electron-withdrawing groups on the aromatic rings were employed. Indeed, regardless of the functional groups; expected products **C12-C13** were obtained in 72-83% yields. Notably, steric hindered substrates **A5-A7** and **A11** showed good reactivity, which is not a common feature with transition metal-catalyzed methodologies reported for synthesis of carbazole derivatives, cf. Scheme 1.[19,20]

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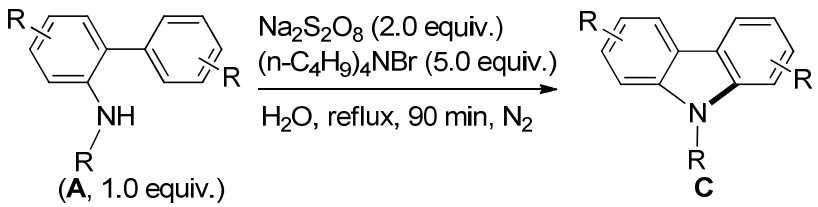
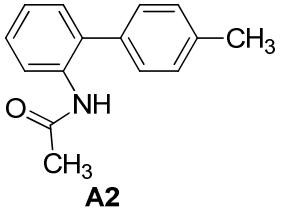
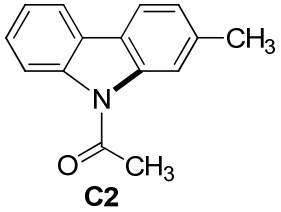
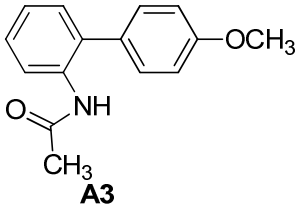
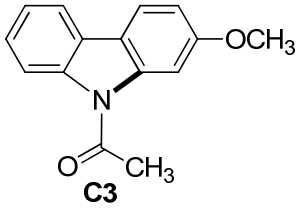
Next, the effects of N-substituents on the efficiencies of the reaction were also explored (Table 2). N-sulfonyl-containing (arylsulfonyl (**A14-A18**) and methylsulfonyl (**A19-A22**) substrates reacted to produce the required carbazoles (**C14-C22**, Entries 13-21, Table 2) in good yield. However, *tert*-butyl [1,1'-biphenyl]-2-ylcarbamate (**A23**), ethyl [1,1'-biphenyl]-2-ylcarbamate (**A24**), N-methyl-[1,1'-biphenyl]-2-amine (**A25**), N-benzyl-[1,1'-biphenyl]-2-amine (**A26**) and 2-aminobiphenyl (**A27**) did not undergo the intramolecular C-H amination effectively and afforded expected carbazole derivatives in very poor yield (< 30%), cf. Table 2. Thus, the peroxodisulfate may be used as oxidizing agent for the synthesis of carbazoles functionalized by electron with drawing groups at N-atom. Nevertheless, this transformation is compatible to various functional groups including chloro, fluoro, methoxy, aceyl and sulfonyl groups that generally advantageous for further modifications.

Table 2. Substrate scope for the transformation of N-substituted 2-aminobiaryls into analogous carbazoles.[a]



Entry	Substrate	Product	Yield [b, c] (%)
1	 **A2**	 **C2**	86
2	 **A3**	 **C3**	81

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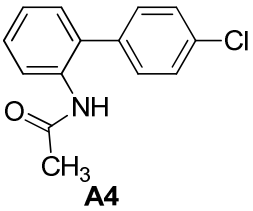
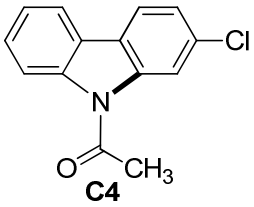
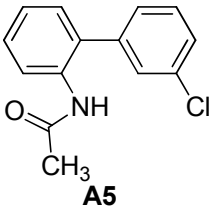
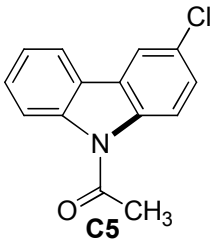
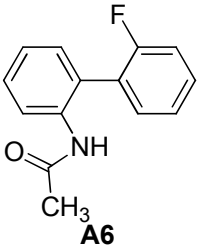
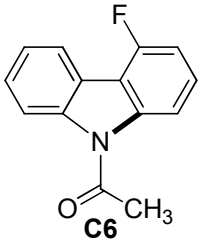
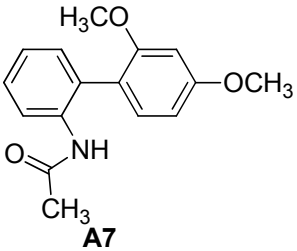
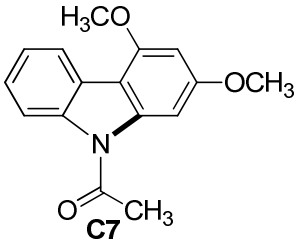
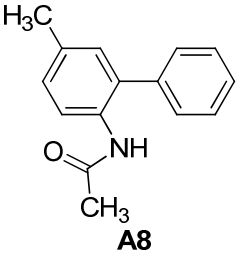
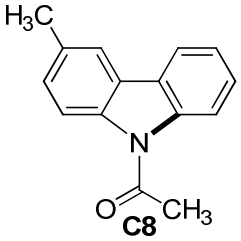
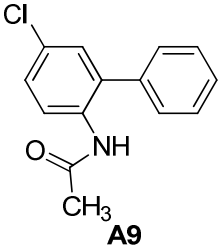
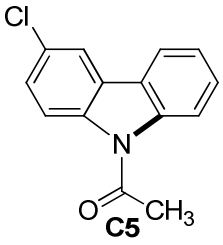
3	 **A4**	 **C4**	89
4	 **A5**	 **C5**	91
5	 **A6**	 **C6**	86
6	 **A7**	 **C7**	64
7	 **A8**	 **C8**	88
8	 **A9**	 **C5**	87

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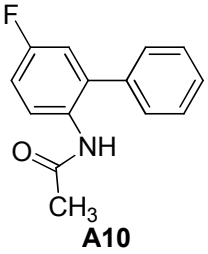
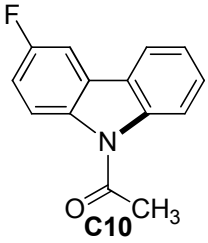
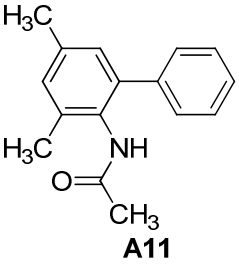
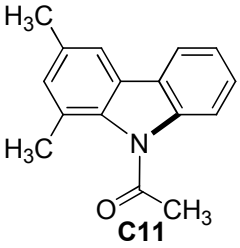
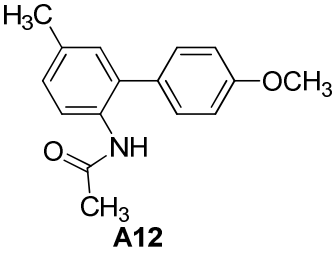
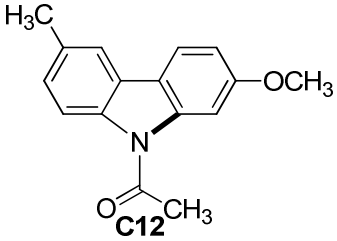
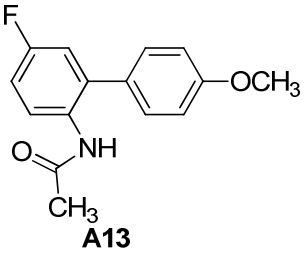
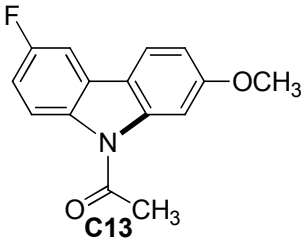
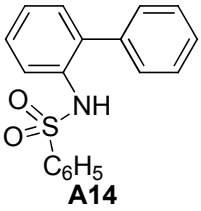
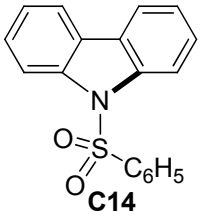
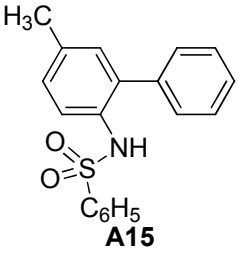
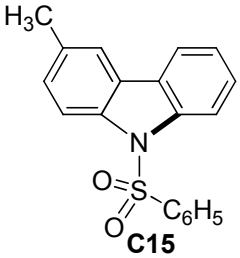
9	 **A10**	 **C10**	89
10	 **A11**	 **C11**	85
11	 **A12**	 **C12**	72
12	 **A13**	 **C13**	83
13	 **A14**	 **C14**	86
14	 **A15**	 **C15**	91

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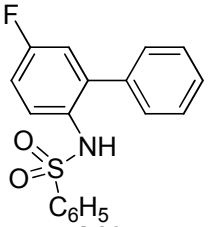
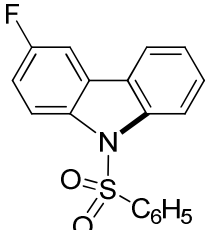
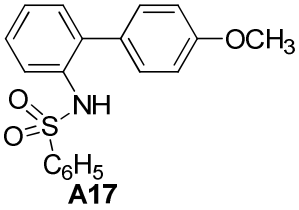
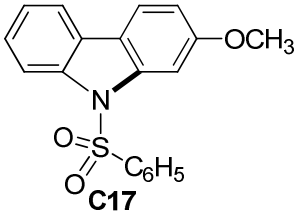
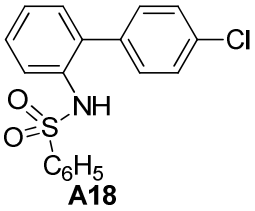
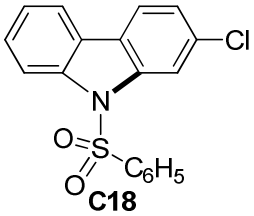
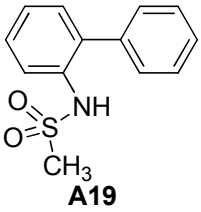
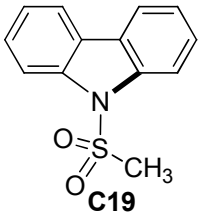
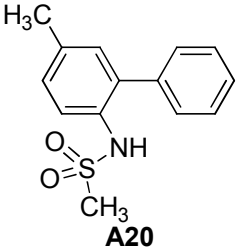
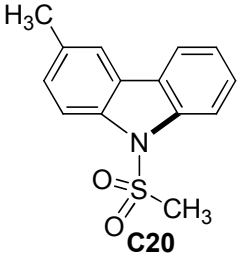
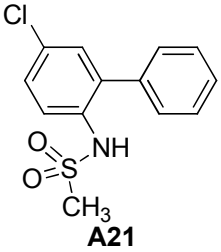
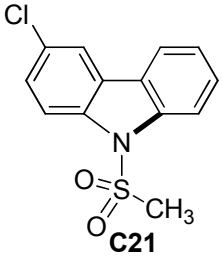
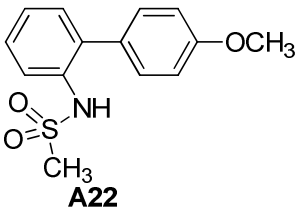
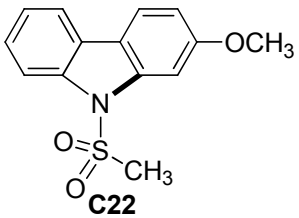
15	 **A16**	 **C16**	87
16	 **A17**	 **C17**	79
17	 **A18**	 **C18**	92
18	 **A19**	 **C19**	89
19	 **A20**	 **C20**	94
20	 **A21**	 **C21**	85
21	 **A22**	 **C22**	81

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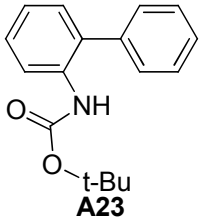
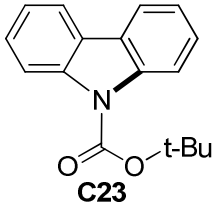
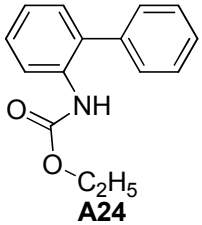
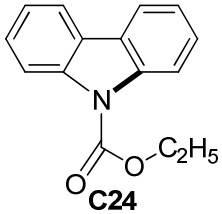
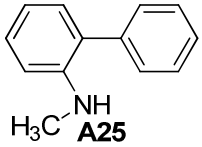
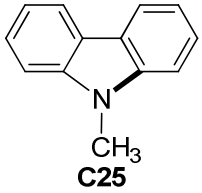
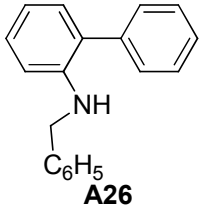
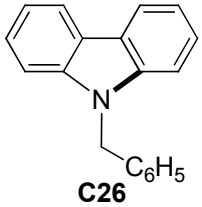
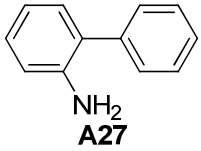
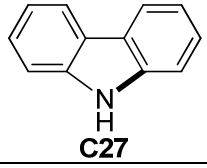
22	 **A23**	 **C23**	17
23	 **A24**	 **C24**	28
24	 **A25**	 **C25**	ND[d]
25	 **A26**	 **C26**	ND[d]
26	 **A27**	 **C27**	ND[d]

[a] Unless stated otherwise all reactions were performed in a Schlenk tube with 2.0 mmol of 2-amidobiaryls, 4.0 mmol of $Na_2S_2O_8$ and 10.0 mmol of TBAB in water at reflux temperature in the nitrogen gas atmosphere for 90-120 min.
[b] Isolated yield.
[c] All products were characterized by IR and NMR spectroscopy (Supporting Information) in comparison with known compounds from literature data.
[d] ND: not detected (common organic solvent-insoluble brown color materials were detected)

Preliminary experiments were carried out to probe the reaction mechanism. When 1 equiv. of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl or ascorbic acid was added in the reaction of **A1** under the standard conditions, no desired product **C1** observed. It indicated that the reaction follows a radical pathway as in line with the previously reported transformations initiated by $S_2O_8^{2-}$ ion.[26-30] On these bases, a plausible radical mechanism (Scheme 3) is outlined for the reaction (Scheme 2). Initially, the thermal decomposition of $S_2O_8^{2-}$ afforded sulfate

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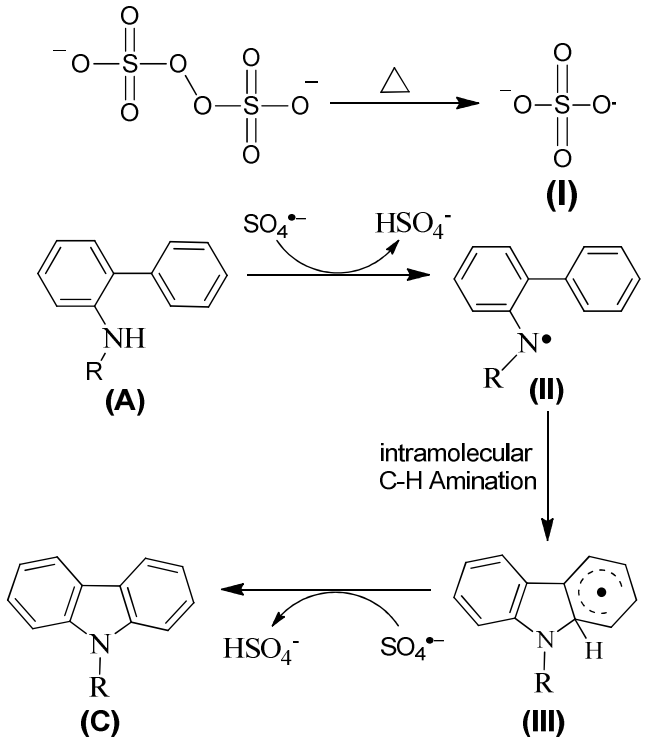
radical anions (**I**, $SO_4^{-\bullet}$); which abstract the hydrogen atoms from the substrates (**A**) to afford a nitrogen-centered amidyl radical (**II**). Then, Radical **II** undergoes intramolecular C-H amination to form a new radical intermediate (**III**), which was then oxidized by **I** followed by deprotonation by SO_4^{2-} afforded the desired carbazoles (**C**), cf. Scheme 3.



Scheme 3. A plausible mechanism for the formation of N-substituted carbazoles from 2-amidobiaryls in the presence of peroxodisulfate.

As mentioned at the outset, peroxodisulfate initiated transformations have several advantages over other reported protocols in view of both economic and environmental standpoints. Moreover, the reaction employs inexpensive starting materials and water as a solvent. Thus, we believe that the method reported here will find a bright future in industry for the synthesis of carbazoles and other related heterocyclic compounds. It is worth nothing that the price of 1.0 g of 9-acetylcarbazole with a purity of 95-98% is 100-150 USD from recognized suppliers that indicates the importance of development of a cost-effective protocol for it.

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Conclusion

In summary, we have developed an atom-economical and environmentally benign method for synthesis of carbazoles from 2-amidobiaryls. This transformation proceeded in water employing the inexpensive $S_2O_8^{2-}$ as an oxidant. Moreover, desired products in pure form are obtained in moderate to good yields by the easy workup consisting of simple filtration. Further utilization of the method to develop other heterocyclic compounds is currently under investigation and will be disclosed in due course.

Acknowledgments

The authors are pleased to acknowledge the financial support from the Council of Scientific and Industrial Research (CSIR), New Delhi, vide project no.: 02(0246)/15/EMR-II. Priya and D. C., respectively, thank the Department of Science and Technology (DST) and University Grant Commission (UGC), New Delhi, for their junior research fellowships (JRF).

Electronic supplementary information

Electronic supplementary information (general aspects, procedure and experimental characterization data) associated with this article can be found in the online version at www.

References

1 (a) Q. Yan, E. Gin, M. W. Kalwa, M. G. Banwell and P. D. Carr, *J. Org. Chem.,* 2017, **82**, 4148-4159; (b) N. Yedukondalu, G. Gupta, J. R. Nadkarni, V. K. Gupta, S. H. Syed and A. Ali, *RSC Adv.,* 2016, **6**, 83069-83077; (c) T. Janosik, N. Wahlström and J. Bergman, *Tetrahedron*, 2008, **64**, 9159-9180.

2 A. Głuszyńska, *Eur. J. Med. Chem.*, 2015*,* **94**, 405-426.

3 (a) P. Y. Wang, H. S. Fang, W. B. Shao, J. Zhou, Z. Chen, B. A. Song and S. Yang, *Bioorganic Med. Chem. Lett.*, 2017, **27**, 4294-4297; (b) M. Bashir, A. Bano, A. S. Ijaz and B. A. Chaudhary, *Molecules*, 2015, **20**, 13496-13517.

4 (a) N. Salih, J. Salimon and E. Yousif, *Arab. J. Chem.*, 2016, **9**, 781-786; (b) T. Nagappan, P. Ramasamy, M. E. A. Wahid , T. C. Segaran and C. S. Vairappan, *Molecules*, 2011, **16**, 9651-9664.

5 B. V. C. Stephens and L. A. R. Hall, *J. Pharm. Sci.*, 1950, **39**, 271-273.

6 Y. Nalli, V. Khajuria, S. Gupta, P. Arora, S. R. U. Hassan, Z. Ahmed and A. Ali, *Org. Biomol. Chem.,* 2016, **14**, 3322-3332.

7 T. Wang, P. Mäser, and D. Picard, *J. Med. Chem*., 2016, **13**, 6344-6352.

View Article Online
DOI: 10.1039/C7GC03130K

8 P. N. Reddy, P. Padmaja, B. R. Reddy and S. S. Jadav, 2017, **26**, 2243-2259.

9 (a) B. Li, Z. Z. Yue, J. M. Feng, Q. He, Z. H. Miao and C. H. Yang, *Eur. J. Med. Chem.*, 2013, **66**, 531-539; (b) K. Murali, H. A. Sparkes, B. V. Pandiyan and K. J. R. Prasad, *Eur. J. Med. Chem*., 2017, **128**, 319-331; (c) P. Padmaja, G. K. Rao, A. Indrasena, B. V. S. Reddy, N. Patel, A. B. Shaik, N. Reddy, P. K. Dubeya and M. P. Bhadra., *Org. Biomol. Chem*., 2015, **13**, 1404-1414.

10 A. W. Schmidt, K. R. Reddy and H. J. Knölker, *Chem. Rev.*, 2012, **112**, 3193-3328.

11 A. A. Pieper, S. L. McKnight and Joseph M. Ready, *Chem. Soc. Rev.,* 2014, **43**, 6716-6726.

12 (a) D. Gudeika, D. Volyniuk, V. Mimaite, R. Lytvyn, R. Butkute, O. Bezvikonnyi, G. Buika and J. V. Grazulevicius, *Dyes and Pigments*, 2017, **142**, 394-405; (b) S. Xu, C. Fang, Y. Wu, W. Wu, Q. Guo, J. Zeng, X. Wang, Y. Liu and S. Cao, *Dyes and Pigments*, 2017, **142**, 8-16.

13 (a) Fultz, M. W, *Name Reactions in Heterocyclic Chemistry II*, 2011, **13**, 91-101; (b) E. Drechsel, *J. Prakt. Chem.* 1858, **38**, 69; (c) W. Borsche, M. Feise, *Ber.* 1904, **20,** 378.

14 (a) M. T. Levick, I. Grace, S. Y. Dai, N. Kasch, C. Muryn, C. Lambert, M. L. Turner and D. J. Procter, *Org. Lett*., 2014, **16**, 2292-2295; (b) J. Bonjoch, J. Catena and N. Valls, *J. Org. Chem.,* 1996, **61**, 7106-7115.

15 (a) E. Sankar, J. Karunakaran, L. Dhivyapirabha, Arasambattu and K. Mohanakrishnan, *Chemistry Select*, 2017, **2**, 7899-7903; (b) M. Abualnaja, P. G. Waddell, W. Clegg and M. J. Hall, *Tetrahedron,* 2016, **72,** 5798-5806; (c) F. Sha, Y. Tao, C. Y. Tang, F. Zhang and X. Y. Wu*, J. Org. Chem.*, 2015, **80**, 8122-8133.

16 (a) J. P. Wolfe, S. Waga, J. F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.,* 1998, **31**, 805-818; (b) J. F. Hartwig, *Angew. Chem. Int. Ed*., 1998, **37**, 2046-2067; (c) J. P. Wolfe and S. L. Buchwald, *J. Org. Chem*., 2000, **65**, 1144-1157; (d) T. Kitawaki, Y. Hayashi, A. Ueno and N. Chida *Tetrahedron,* 2006, **62**, 6792-6801.

17 (a) S. Riedmller and B. J. Nachtsheim, *Beilstein J. Org. Chem*., 2013, **9**, 1202-1209; (b) D. Zhu, Q. Liu, B. Luo, M. Chen, R. Pi, P. Huang and S. Wen, *Adv. Synth. Catal*., 2013, **355**, 2172-2178; (c) T. Q. Hung, N. N. Thang, D. H. Hoang, T. T. Dang, A. Villinger and P. Langer, *Org. Biomol. Chem.,* 2014, **12**, 2596-2605.

View Article Online
DOI: 10.1039/C7GC03130K

18 (a) I. C. F. R. Ferreira, M. J. R. P. Queiroza and G. Kirsch, *Tetrahedron Lett.,* 2003, **44**, 4327-4329; (b) M. Pudlo, D. Csanyi, F. Moreau, G. Hajos, Z. Riedlb and J. Sapia, *Tetrahedron*, 2007, 10320-10329.

19 (a) D. Y. Goo and S. K. Woo, *Org. Biomol. Chem*., 2016, **14**, 122; (b) R. Schroot, U. S. Schubert and M. Jager, *Macromolecules*, 2017, **50**, 1319-1330; (c) E. F. Damita, N. Nordina, A. Ariffina and K. Sulaiman, *Russ J Gen Chem*, 2017, **87**, 1800-1812.

20 (a) R. Hesse, K. K. Gruner, O. Kataeva, A. W. Schmidt and H. J. Knölker, *Chem. - Eur. J*., 2013, **19**, 14098-14111; (b) T. Gensch, M. Rönnefahrt, R. Czerwonka, A. Jäger, O. Kataeva, I. Bauer and H. J. Knölker, *Chem. - Eur. J*., 2012, **18**, 770-776.

21 (a) K. Takamatsu, K. Hirano, T. Satoh and M. Miura, *Org Lett.,* 2014, **16**, 2892-2895; (b) Y. Monguchi, H. Okami, T. Ichikawa, K. Nozaki, T. Maejima, Y. Oumi, Y. Sawama and H. Sajiki, *Adv. Synth. Catal.,* 2016, **358**, 3145-3151; (c) S. W. Youn, J. H. Bihn and B.S. Kim, *Org Lett.*, 2011, **13**, 3738-3741; (d) S. Choi, T. Chatterjee, W. J. Choi, Y. You and E. J. Cho, *ACS Catal.,* 2015, **5**, 4796-4802; (e) J. A. Jordan-Hore, C. C. C. Johansson, M. Gulias, E. M. Beck and M. J. Gaunt, *J. Am. Chem*. Soc., 2008, **130**, 16184-16186; (f) W. C. P. Tsang, N. Zheng and S. L. Buchwald, *J. Am. Chem. Soc*., 2005, **127**, 14560-14561; (g) W. C. P. Tsang, R. H. Munday, G. Brasche, N. Zheng and S. L. Buchwald, *J. Org. Chem.,* 2008, **73**, 7603-7610.

22 (a) S. H. Cho, J. Yoon and S. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 5996-6005; (b) A. P. Antonchick, R. Samanta and J. Lategahn, *Angew. Chem. Int. Ed*., 2011, **50**, 8605-8608; (c) C. Suzuki, K. Hirano, T. Satoh and M. Miura, *Org. Lett.,* 2015, **17**, 1597-1600; (d) W. Fan, S. Jiang and B. Feng, *Tetrahedron*, 2015, **71**, 4035-4038; (e) Q. Jiang, D. Duan-Mu, W. Zhong, H. Chen and H. Yan, *Chem. Eur. J.,* 2013, **19**, 1903-1907.

23 K. Nozaki, K. Takahashi, K. Nakano, T. Hiyama, H. Z. Tang, M. Fujiki, S. Yamaguchi and K. Tamao, *Angew. Chem. Int. Ed.*, 2003, **42**, 2051-2053.

24 (a) M. Pudlo, D. Csanyi, F. Moreau, G. Hajos, Z. Riedlb and J. Sapia, *Tetrahedron*, 2007, **63**, 10320-10329; (b) B. J. Stokes, B. Jovanovic, H. Dong, K. J. Richert, R. D. Riell and T. G. Driver, *J. Org. Chem.,* 2009, **74**, 3225-3228.

25 (a) D. Y. Goo and S. K. Woo, *Org. Biomol. Chem.,* 2016, **14**, 122. (b) I. C. F. R. Ferreira, M. J. R. P. Queiroza and G. Kirsch, *Tetrahedron Lett*., 2003, **44**, 4327-4329.

26 (a) B. Rajender and S. Palaniappan, *New J. Chem.*, 2015, **39**, 5382-5388. (b) R. Badri, M. Adlu and M. K. Mohammadi, *Arab. J. Chem.*, 2015, **8**, 62-65.

View Article Online
DOI: 10.1039/C7GC03130K

27 (a) W. S. Chen and C. P. Huang, *Chem. Eng. J.*, 2015, **266**, 279-288; (b) X. Xu, G. Pliego, J. A. Zazo, J. A. Casas and J. J. Rodriguez, *J. Hazard. Mater.*, 2016, **318**, 355-362.

28 M. Hirano, K. Kojima, S. Yakabe and T. Morimoto, *J. Chem. Research,* 2001, **7**, 277-279.

29 A. M. Kadavilpparampu, H. A. J. A. Lawati and F. E. O. Suliman, *Spectrochim Acta A Mol Biomol Spectrosc*., 2017, **183**, 247-259.

30 R. Anbarasan, J. Jayaseharan, M. Sudha, P. V. Nirmala and A. Gopalan, *Macromol. Chem. Phys*., 2000, **201**, 1869-1876.

31 Chaudhary, R.; Natarajan, P. *ChemistrySelect*, 2017, **2**, 6458; (b) Natarajan, P.; Manjeet, Kumar, N.; Thakur, S.; Mer, K. *Tetrahedron Lett*. 2017*,* **58***,* 658.