

Nonplanar Tub-Shaped Benzocyclooctatetraenes via Halogen-Radical Ring Opening of Dihydrobiphenylenes

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ABSTRACT: A novel tandem Ru-catalyzed [2+2+2] cycloaddition of arylenyne to dihydrobiphenylenes followed by halogen-radical ring opening has been developed for the construction of tub-shaped halogenated benzocyclooctatetraenes (bCOT's). Cross-couplings and Diels–Alder reactions of the brominated bCOT's allow the formation of the corresponding eight-membered ring-fused PAH's. The halogen-radical ring opening probably occurs via a selective formation of a bis-allyl radical at the 1,3-cyclohexadiene moiety, halogenation at the bridgehead carbon, and finally electrocyclic ring opening.

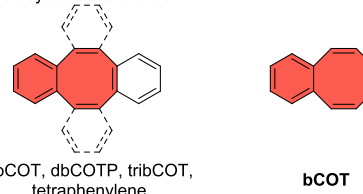


Cyclooctatetraenes (COT) are nonplanar tub-shaped hydrocarbon compounds having a D_{2d} conformation (more stable in its dynamic equilibrium than the planar D_{4h} and delocalized D_{8h} conformations) that have attracted a great deal of interest due to their electronic properties that result from having cyclic conjugated eight- π -electron systems.¹ They are also very useful sterically demanding ligands for metals.² These important features triggered an enormous effort throughout the years that aimed to develop an efficient synthesis of these archetypical medium-sized carbocycles³ with the aim of understanding their aromatic and antiaromatic properties according to Hückel's rules.⁴ More recently, nanographenes containing nonhexagonal rings are being considered as ideal models of defective graphene for building new semiconductor materials.⁵ In particular, distortion from planarity caused by the presence of eight-membered rings or the introduction of [8]circulene moieties that induce a deep curvature in the aromatic lattice and deeply influence the electronic and optical properties has attracted considerable attention.⁶ Consequently, the development of efficient synthetic methods for COT-embedded arenes is greatly significant and in high demand. In this context, synthetic approaches to dbCOT's,⁷ dbCOTP's,⁸ tribCOT's,⁹ and tetraphenylenes¹⁰ are relatively well studied while the simple benzocyclooctatetraenes (bCOT's) have received significantly less synthetic attention (Scheme 1).¹¹ The parent benzocyclooctatetraene unit had also been observed in pioneer Günther's¹² studies of Birch reduction of biphenylene in which the double protonation of the dianion occurred at the bridgehead position giving 4a,8b-dihydrobiphenylene.¹³ This reactive species very rapidly evolved to the more stable benzocyclooctatetraene via thermal electrocyclic ring opening (Scheme 1).

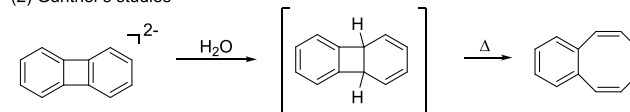
On the contrary, a mild and powerful method for assembling 1,3-cyclohexadiene units (dihydrobiphenylene isomers) had been recently developed in our group via Ru(II)-catalyzed

Scheme 1. COT-Embedded Polycyclic Arenes, Birch Reduction of Biphenylene, and Formation of Cyclooctatetraenes by Halogen-Radical Ring Opening of 1,8b-Dihydrobiphenylenes

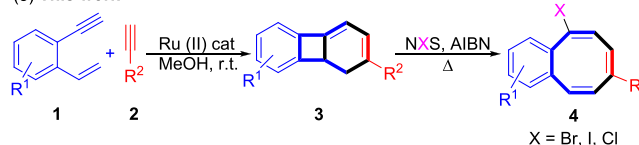
(1) (Poly)benzofused cyclooctatetraenes



(2) Günther's studies



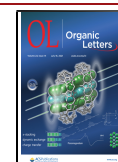
(3) This work



[2+2+2] cycloaddition of arylenyne and alkynes.¹⁴ This type of cyclohexadiene has been utilized in efficient synthetic manipulations such as oxidations and Diels–Alder reactions.¹⁵ Moreover, a tandem Ru-catalyzed [2+2+2] cyclization/iodine-mediated ring expansion of enediynes led to a straightforward

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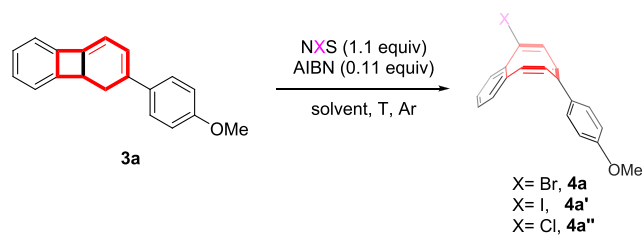
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assembly of benzo-fused bridged ketones.¹⁶ However, to the best of our knowledge, the radical opening of benzo-fused cyclohexadienes has not been investigated even though such combined processes have synthetic potential for accessing interesting functionalized scaffolds. Herein, we report an efficient tandem process based on a Ru-catalyzed [2+2+2] cycloaddition of arylenyne **1** with alkynes **2** to 1,8b-dihydrobiphenylenes **3**¹⁴ followed by halogen-radical ring opening to benzocyclooctatetraenes **4** (Scheme 1). The halogenated (mainly, bromo derivatives) bCOT's have proved to be privileged functionalized structural units for accessing PAH's that combine aromatic and antiaromatic properties.¹⁷

Inspired by Günther's observations, we began our investigation by examining the well-known Wohl–Ziegler bromination¹⁸ of dihydrobiphenylene **3a**. Thus, as a proof of concept, the use of NBS and AIBN as radical initiators in CCl₄ at rt promoted the formation of the desired bromobenzocyclooctatetraene **4a**, although in low yield (Table 1, entry 1).

Table 1. Optimization of Halogen-Radical Ring Opening of 1,8b-Dihydrobiphenylene **3a to Halobenzocyclooctatetraenes **4a** (X = Br), **4a'** (X = I), and **4a''** (X = Cl)^a**



entry	solvent	T (°C)	yield of 4a ^b
1	CCl ₄	rt	30
2	CCl ₄	reflux	85
3	DCM	reflux	32
4	CHCl ₃	reflux	38
5	heptane	reflux	44
6	CH ₃ CN	reflux	40
7	1,4-dioxane	reflux	61
8	DCE	reflux	66
9	benzene	reflux	65
10	CCl ₄ (darkness)	reflux	53
11	CCl ₄ (no AIBN)	reflux	30
12	CCl ₄ (no NBS)	reflux	SM (50)
13 ^c	CCl ₄	reflux	77, 4a'
14 ^d	CCl ₄	reflux	36, 4a''

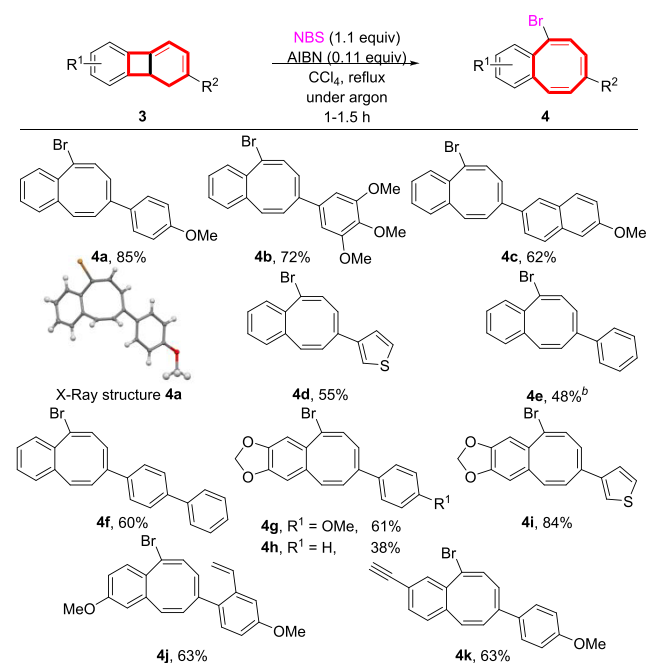
^aReaction conditions: **3a** (0.2–0.3 mmol) in solvent (0.036 M), NBS (1.1 equiv), AIBN (0.11 equiv), 1–1.5 h. ^bIsolated yield. ^cNIS. ^dNCS.

Gratifyingly, when the reaction temperature is increased at reflux, the yield of **4a** increases to 89% (Table 1, entry 2). Other solvents were then tested. The use of chlorinated solvents like CHCl₃ or CH₂Cl₂ or nonpolar heptane or polar CH₃CN afforded **4a** but in lower yields (Table 1, entries 3–6). By contrast, polar ethereal or aprotic solvents such as 1,4-dioxane or DCE and a nonpolar solvent like benzene gave **4a** in fairly good yields (Table 1, entries 7–9). Experimental reaction conditions using CCl₄ as a solvent were then examined. Thus, performing the reaction in the absence of light led to a lower yield of **4a** (Table 1, entry 10) as did not using AIBN as a radical initiator (Table 1, entry 11). In addition, the presence of NBS is mandatory for the

consumption of starting product **3a**, while the rest gave rise to a complex mixture (Table 1, entry 12).¹⁹ The use of other halogen sources (NIS and NCS) is also feasible, affording the corresponding iodinated (**4a'**) and chlorinated (**4a''**) benzocyclooctatetraenes albeit in lower yields (Table 1, entries 13 and 14).

With the optimized conditions in hand, we next investigated the scope of the reaction (Scheme 2). For dihydrobipheny-

Scheme 2. Radical Ring Opening of Dihydrobiphenylenes **3 to bCOT's **4**^a**



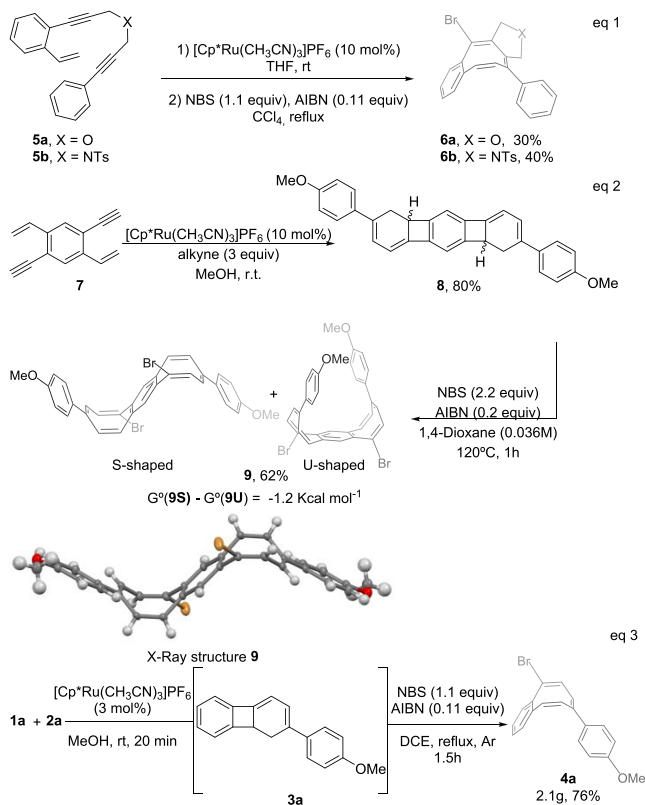
^aReaction conditions: **3** (0.2–0.3 mmol) in CCl₄ (0.036 M), NBS (1.1 equiv), AIBN (0.11 equiv), 1–1.5 h. Isolated yield. The ORTEP drawing of **4a** shows ellipsoids at the 50% contour probability level.

^bThe reaction time was 4 h.

lenes **3** arising from electron-rich arylalkynes **2** and arylenyne **1a** (R¹ = H), either the trialkoxyphenyl **3b**, the 6-methoxynaphthyl **3c**, or the heteroaryl 3-thiophene **3d** behaves similarly giving fairly good yields of the corresponding bCOT's **4b–d**. Not unexpectedly, the parent phenyl dihydrobiphenylene **3e** affords the benzocyclooctatetraene **4e** in a moderate yield (48%), probably due to the lower electron richness of the influential aryl ring involved in the electrocyclic opening.²⁰ Curiously, with an extended conjugated π -system, such as in dihydrobiphenylene **3f**, the ring opening was favorably affected giving rise to the biphenyl benzocyclooctatetraene **4f** in a fairly good yield. On the contrary, dihydrobiphenylenes **3** arising from the electron-rich dialkoxy arylenyne **1b** (R¹/R² = OCH₂O) and electron-rich alkynes **2** gave rise to the corresponding benzocyclooctatetraenes **4g–i** in moderate to good yields, showing the versatility of combining one or two electron-rich partners. Interestingly, the vinyl substituent on dihydrobiphenylene **3j**, derived from Ru-catalyzed dimerization of 1-ethynyl-4-methoxy-2-vinylbenzene **1c**,¹⁴ or the ethynyl substituent on **3k** [from Ru-catalyzed cycloaddition of **1d** (R¹ = alkynyl) and **2a**] remained intact under the radical conditions giving the corresponding styrenic bCOT **4j** and acetylenic bCOT **4k** in fairly good yields that might be capable of future manipulations.²¹

Interestingly, the heteroannulated benzocyclooctatetraenes **6a** and **6b** could be assembled in moderate yields via a one-pot, two-step process from arylenyne **5a** and **5b** bearing an O and a NTs group as linkers (Scheme 3, eq 1).¹⁶ Double tandem

Scheme 3. Heteroannulated bCOT's **6a** and **6b**, Linear BenzodiCOT **9**, and Scale-Up Synthesis of bCOT **4a**^a



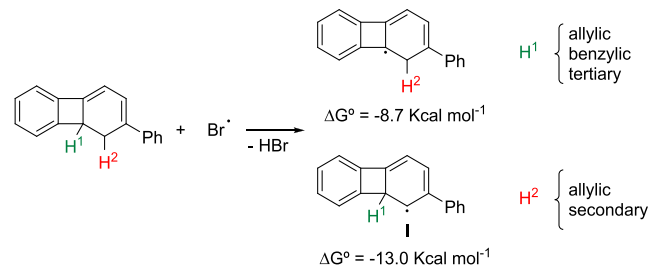
^aThe ORTEP drawing of **9** shows ellipsoids at the 50% contour probability level.

processes were also accessible. Thus, a simple and straightforward entry to the linear benzodiCOT **9** (benzo[1,2:4,5]di[8]-annulene),²² an appealing nonbenzenoid PAH structure with intriguing electronic and aromatic properties,²³ was achieved from 1,4-diethynyl-2,5-divinylbenzene **7**. The double Ru-catalyzed [2+2+2] cycloaddition of **7** with alkyne **2a** led to the linear tetrahydro[3]phenylene **8** in an excellent 80% yield. The halogen-radical double ring opening of **8** with NBS in DCE occurred uneventfully to give the benzodiCOT **9** in a satisfactory 62% yield as a mixture of U- and S-shaped conformers in solution, the S-shaped form being 1.2 kcal mol⁻¹ more stable than the U-shaped form as shown by DFT calculations (Scheme 3, eq 2).²⁴ ¹H NMR spectra of **9** reveal the presence of the two conformers at rt in a 1:2.5 ratio, U- and S-shaped, which could be thermally equilibrated to 1:1.5 ratio at 100 °C. Single crystals of **9** suitable for X-ray diffraction analysis were grown from a solution in a hot CHCl₃/hexane mixture by slow evaporation of the solvents. **9** shows an S-shaped geometry with the bromine atoms on opposite faces with respect to the central benzene plane. In addition, the two eight-membered rings are considerably bent up and down from the plane of the central benzene unit with a large dihedral angle of ~138°. Similar to COT, the two eight-membered rings adopt a tub-shaped conformation, with large bond length

alternation. The bonds of the central six-membered rings are within the typical range of 1.39–1.40 Å, revealing an aromatic benzenoid character. Scaling up was also feasible as shown by performing a tandem process from initial enyne **1a** and arylalkyne **2a** without the isolation of dihydrobiphenylene **3a**. Thus, reaction of **1a** (8.1 mmol) and **2a** (9.7 mmol) in MeOH under catalytic conditions (as little as 3% Ru) followed by a rapid replacement of the solvent with the apolar DCE to perform the radical reaction allowed us to obtain bCOT **4a** (2.1 g) in a 76% overall yield (Scheme 3, eq 3).

In an effort to gain further insights into the reaction mechanism, DFT calculations were performed to analyze all possible radical pathways.²⁴ We began the mechanistic studies by elucidating the selectivity of the initial radical formation because two different radicals can be formed depending on the abstractions of the tertiary hydrogen H¹ of the cyclobutene moiety or one of the two secondary hydrogens H² on the 1,3-cyclohexadiene core. Even though tertiary C–H bonds are weaker than secondary ones, the presence of the cyclobutene moiety dramatically changes the reactivity of the 1,3-cyclohexadiene core, making the formation of the secondary bis-allylic radical **I** 4.3 kcal mol⁻¹ more favorable than that of the allylic benzylic tertiary radical (Scheme 4). Atomic spin

Scheme 4. Bond Dissociation Energies (BDE's) of H¹ and H²



densities were then computed for the more stable allylic/secondary radical **I**, showing that, as expected, it is mainly divided among the three carbons of the central six-membered ring.²⁴

We then evaluate the three possible evolution pathways for the most stable radical **I** (Figure 1): (a) six- π -electron electrocyclic ring opening followed by trapping of the resulting radical with Br₂ to afford the observed cyclooctatetraene **4e** ($\Delta G^\ddagger = 39.2$ kcal mol⁻¹, red pathway), (b) radical opening of the cyclobutane ring followed trapping with Br₂ to afford terphenyl **II** ($\Delta G^\ddagger = 19.4$ kcal mol⁻¹, blue pathway), and (c) the most favorable one ($\Delta G^\ddagger = 5.7$ kcal mol⁻¹, black pathway) that involves direct bromination of the resonance structure of **I** with the radical into the tertiary, allylic, and benzylic position to give rise to the brominated dihydrobiphenylene **III**. Once **III** had been established as the most favorable product of radical bromination of **3e**, the observed product **4e** would be formed through a six- π -electrocyclic ring opening.²⁴

The utility of the brominated bCOT's **4** was tested in the preparation of valuable COT-embedded PAH's (Scheme 5). Suzuki cross-coupling between **4a** and phenylboronic acid affords the expected phenyl-substituted bCOT **10** in 70% yield (Scheme 5, eq 1). Sonogashira couplings were also satisfactorily carried out under typical reaction conditions. Alkynyl-substituted COT's **11a** and **11b** were obtained in good to excellent yields using trimethylsilylacetylene **2l** and

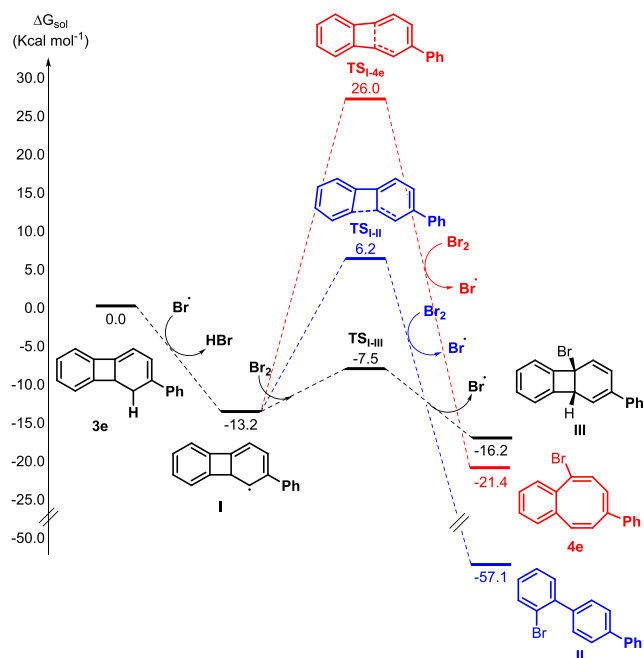
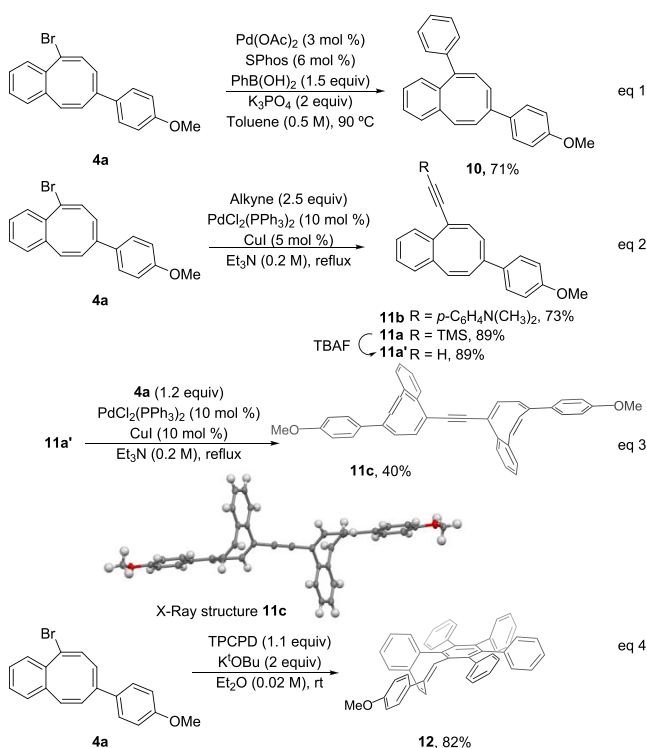


Figure 1. Free energy profiles for the radical bromination of **3e**. Energies are relative to **3e** and are mass balanced.

Scheme 5. Synthetic Applications of Brominated bCOT's^a



^aThe ORTEP drawing of **11c** shows ellipsoids at the 50% contour probability level.

alkynylaniline **2m**, respectively (Scheme 5, eq 2). To our delight, an efficient Sonogashira coupling between **4a** and alkynylCOT **11a'** (from desilylation of **11a**) renders uneventfully the interesting bis-COT derivative **11c**, as confirmed by X-ray analysis (Scheme 5, eq 3).²⁵ Finally, treatment of **4a** with KO^tBu¹⁰ generates a strained cyclic alkyne that could be subsequently trapped as a dienophile with

tetraphenylcyclopentadienone in a Diels–Alder reaction affording the π -extended dibenzoCOT **12** in very good yield (Scheme 5, eq 4). Note the higher reactivity of the triple bond in planarized systems containing one benzo-fused eight-membered ring (rt, 25 °C) as compared to the typical dibenzo-fused derivative (Ph₂O reflux, >250 °C).²⁶

In conclusion, we have developed a general synthetic method for constructing a new class of polycyclic arenes embedded with a brominated (halogenated) COT ring via a tandem Ru-catalyzed [2+2+2] cycloaddition of arylenyne to dihydrobiphenylenes followed by halogen-radical ring opening. The process involves the initial formation of a bis-allylic radical at the 1,3-cyclohexadiene core of the dihydrobiphenylene. Then, halogenation at the bridgehead position of the benzocyclobutene ring followed by a subsequent electrocyclic ring opening renders the observed cyclooctatetraene. This protocol provides a new synthetic approach to polycyclic arenes fused with an eight-membered ring (bCOT), which is expected to be applicable for the synthesis of diverse curved nanocarbons.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c01881>.

General experimental procedures, X-ray crystallographic data, NMR spectra, and DFT calculations (PDF)

Computational details, free energy profile for the isomerization of benzodiCOT **9** from the U- to S-shaped conformers, complete free energy profile for the radical bromination of dihydrobiphenylene **3e** and six- π -electron electrocyclic ring opening of brominated dihydrobiphenylene **III**, natural bond orbital analysis, references, and Cartesian coordinates, energy values, and imaginary frequencies for all of the stationary points involved throughout the DFT study (PDF)

Accession Codes

CCDC 2085992–2085994 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(24) See the [Supporting Information](#) for computational details.

(25) CCDC-2085994, 2085993, and 2085992 contain the supplementary crystallographic data for compounds **4a**, **9**, and **11c**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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