Organic LETTERS
Letter
Cite This: Org. Lett. 2018, 20, 457−460
pubs.acs.org/OrgLett

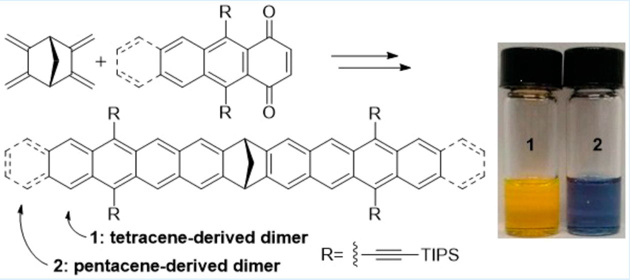
Modular Synthesis of Rigid Polyacene Dimers for Singlet Fission

Thomas J. Carey, Ethan G. Miller, Alexander T. Gilligan, Tarek Sammakia,* and Niels H. Damrauer*

Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado 80309, United States

Ⓢ *Supporting Information*

ABSTRACT: An improved, modular synthesis of rigid, geometrically well-defined, alkyne-substituted tetracene (**1**) and pentacene (**2**) dimers is reported. The synthesis is rooted in sequential Diels−Alder reactions of a norbornyl tetraene with triisopropylsilylacetylene-substituted (TIPS-acetylene) quinone dienophiles. The incorporation of solubilizing and stabilizing TIPS-acetylene groups early in the synthesis affords a mild and reliable route, providing access, for the first time, to norbornyl-bridged pentacene dimers. A preliminary exploration of the excited state behavior of these molecules is also described.



Singlet fission (SF) is a photophysical process wherein a singlet excited state is converted first to a singlet-coupled pair of triplet states (^{1}TT) and then to separate triplets.[1,2] Initially invoked in crystalline polyacene systems (anthracene[3] and tetracene[4,5]) to understand processes competing with fluorescence, recent interest has focused on the application of SF to solar energy strategies as SF permits high-energy photons to proportionate into multiple excitations, thereby utilizing excess energy that would be otherwise wasted as heat.[2,6,7] Of particular interest has been the study of molecular dimers, as these are the simplest systems capable of SF and offer a platform based on homogeneous samples for understanding mechanistic details for the development of efficient SF systems.[8−19] With few exceptions,[13,17−19] the dimer subunits are connected by rotatable single bonds (chromophore-to-chromophore or chromophore-to-bridge) such that conformational freedom in the ground and excited states becomes a significant part of the mechanistic landscape. Rigid dimers have the advantage of offering a greater degree of certainty as to the nature of the electronic states, their relative energetics, and their couplings, all of which are impacted by the relative orientation of the chromophore subunits. Inspired by bis-naphthalene energy transfer systems explored by Paddon-Row,[20] we have been studying a platform consisting of acene arms joined by a central bicyclo[2.2.1]heptane (i.e., norbornyl) moiety (e.g., Figure 1).[13,17,19,21−23] In this platform, variation in the structural and electronic properties of polyacene dimers is possible, and we have been interested in establishing design rules to understand and control rates and yields for important photophysical events within SF. Key issues involve the role of orbital symmetry in pathways affecting electronic coupling between states[21−23] as well as the role of state energetics during photoreactions. In this paper, we report the synthesis of norbornyl-linked acene dimers, including a pentacene-derived dimer that impacts energetics. Our approach is amenable to the preparation of other, related molecules that can also address the impact of symmetry and allows us to prepare other geometries by altering the substrates employed in the synthesis.

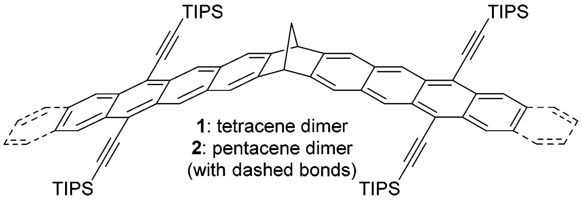


Figure 1. Dimeric targets **1** and **2**.

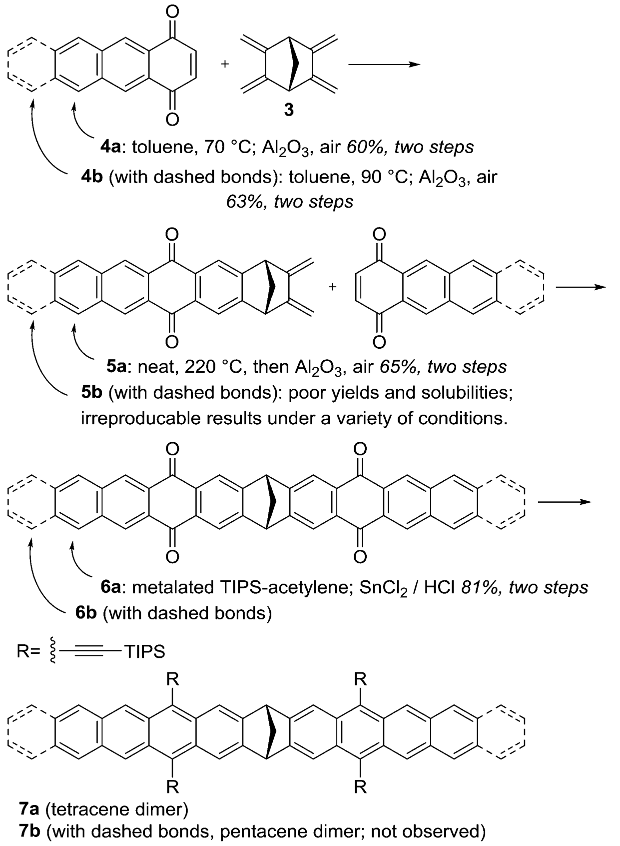
Our route builds on prior work we recently reported that describes the preparation of norbornyl-linked tetracene dimers.[17] In that work, we prepared a central moiety consisting of a norbornyl core functionalized with two exocyclic diene units (**3**, Scheme 1).[24−26] The dienes were then employed to install the two acene arms via sequential Diels−Alder reactions with 1,4-anthracenedione (**4a**) to provide bis(quinone) **6a**. Functionalization of this product then provided the desired target molecule, **7a**, for photophysical studies.[19] This synthesis provided the desired material in useful yields; however, application of this route to the synthesis of the corresponding pentacene homologue (**7b**) failed. We encountered difficulties in handling several of the intermediates, which were poorly soluble in common solvents used for chromatography, and which underwent partial decomposition to a greater extent than the analogous intermediates in the synthesis of the corresponding tetracene dimers (**7a** as well as an unsubstituted version). Despite extensive efforts, we were unable to overcome these obstacles and sought an alternative approach that addresses the issues of solubility and stability early in the synthesis.

It is well-known that the incorporation of TIPS-acetylene into acene structures provides enhanced solubility and stability toward oxidation and other decomposition pathways. In the

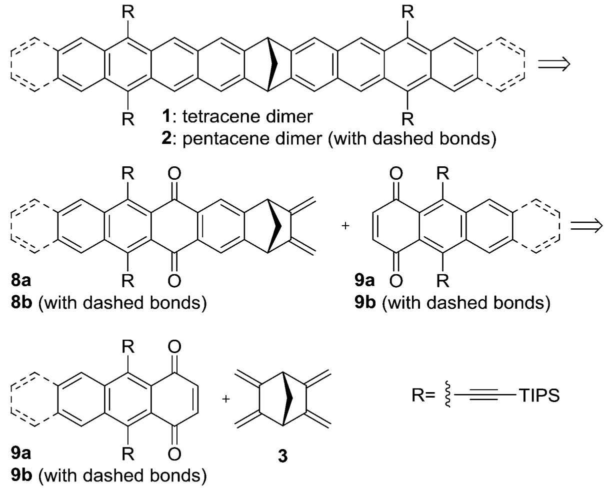
Received: December 6, 2017
Published: January 5, 2018

DOI: 10.1021/acs.orglett.7b03817

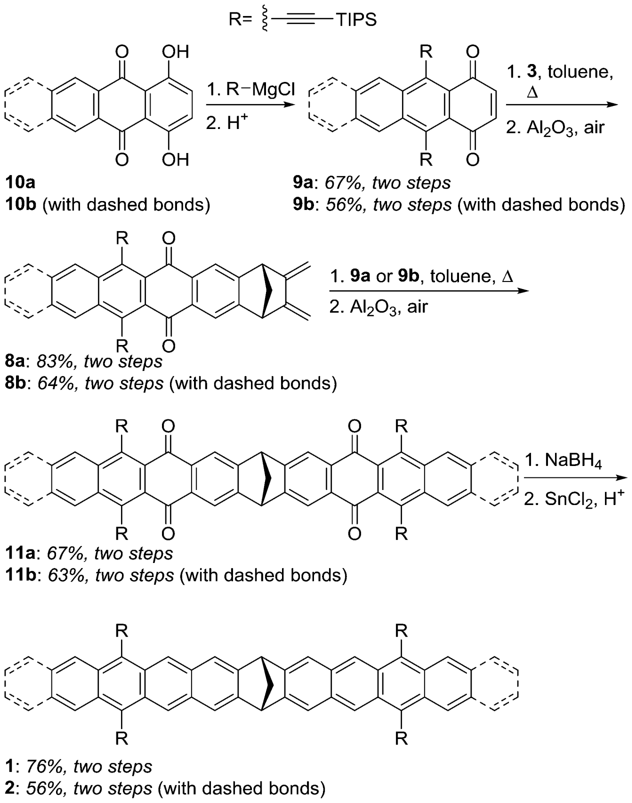
Scheme 1. Prior Synthesis of Tetracene Dimer 7a and Efforts toward the Synthesis of Analogous Pentacene Dimer 7b



Scheme 2. Retrosynthesis of Dimeric Targets 1 and 2



Scheme 3. Synthesis of Dimeric Targets 1 and 2



case of pentacene, the optimal placement of this substituent is at the central ring as in **2**.[27,28] In our prior work, incorporation of the TIPS-acetylene substituents occurred very late in the synthesis and also did not afford the optimal placement on the pentacene as it was not on the central ring (compare compounds **2**, Figure 1, and **7b**, Scheme 1). We hypothesized that this suboptimal placement offered insufficient protection from oxidative decomposition, and we sought an alternate approach that incorporates the TIPS-acetylene moieties in the optimal position early in the synthesis. This also offers enhanced solubility for the synthetic intermediates, a problem that was encountered in our previous route. Our studies, first on a model system and then on the desired compound, are described below.

We wished to maintain elements of our prior synthesis in our revised approach, including the use of tetraene **3** as a central structure from which to construct the acene arms. Our retrosynthesis, with tetraene **3** as a structure goal, is shown in Scheme 2. Our previous studies[17] and other precedence in the literature[24−26] suggested that the Diels−Alder reactivity of **3** would preclude a one-pot, double Diels−Alder reaction, and we therefore planned a synthesis with sequential Diels−Alder reactions to construct the two acene arms.[29] The latter Diels−Alder reaction in the synthesis would then be between diene **8a** or **8b** and quinone **9a** or **9b**, while the initial Diels−Alder would be between tetraene **3** and the same quinone (**9a** or **9b**). Synthesis of quinone **9b** was envisioned to proceed by the addition of metalated TIPS-acetylene to quinone **10b** (Scheme 3),[30] which is a known homologue of quinizarin (**10a**; Scheme 3), providing our desired functionalized quinone with enhanced solubility.[31] We first studied this approach on a model using the more readily available quinizarin, rather than quinone **10b**, and prepared compound **1**, a constitutional isomer of our previously synthesized tetracene dimer **7a**, as described below.

Our synthesis began with the addition of metalated TIPS-acetylene (prepared via deprotonation with *i*-PrMgCl) to quinizarin to provide the corresponding diol. This compound was not isolated but treated with acid (HCl) in situ to promote the loss of two molecules of water and provide quinone **9a** in 67% yield over two steps (Scheme 3). Quinone **9a** was then utilized in a Diels−Alder reaction with tetraene **3** (toluene, 80 °C) to provide the mono-Diels−Alder adduct. This material was not isolated but subjected to aromatization (Al_2O_3, air) to provide diene **8a** in 83% yield over two steps. Diene **8a** was then subjected to a second Diels–Alder reaction with quinone **9a** (toluene, 90 °C) to provide the Diels–Alder adduct, which was directly subjected to aromatization (Al_2O_3, air) to provide bis(quinone) **11a** in 67% yield over two steps. Bis(quinone) **11a** was then reduced with $NaBH_4$ to provide the corresponding tetraol as a mixture of isomers and subsequently treated with $SnCl_2$/HCl to provide tetracene dimer **1** in 76% yield over two steps. A direct comparison of this route to the one that we have previously reported[17] reveals that the yield for each corresponding step is comparable or slightly higher. More importantly, the conditions for the second Diels–Alder reaction are significantly milder (90 °C in toluene vs 210 °C as a neat film). The intermediates are well behaved, bench stable (we have not observed degradation for the duration of this work, a period of several months with storage at room temperature), and display enhanced solubility relative to the corresponding compounds in our original route.

Encouraged by this result, we then prepared quinizarin homologue **10b** as described by Patney via the Friedel–Crafts reaction of 2,3-naphthoic anhydride and hydroquinone ($AlCl_3 \cdot NaCl$, 210 °C).[31] Addition of metalated TIPS-acetylene (prepared via deprotonation with *i*-PrMgCl) to **10b** followed by acidic workup and treatment with TFA provided quinone **9b** in 56% yield (Scheme 3). Quinone **9b** was then subjected to a Diels–Alder reaction with tetraene **3** (toluene, 90 °C) to provide the mono-Diels–Alder adduct. This material was not isolated but subjected to aromatization (Al_2O_3, air) to provide diene **8b** in 64% yield over two steps. Diene **8b** was subjected to a second Diels–Alder reaction with quinone **9b** (toluene, 100 °C) to provide the Diels–Alder adduct, which was directly subjected to aromatization (Al_2O_3, air) to provide bis(quinone) **11b** in 63% yield over two steps. The bis(quinone) (**11b**) was then reduced with $NaBH_4$ to provide the corresponding tetraol as a mixture of isomers and then treated with $SnCl_2$/HCl to provide bis(pentacene) compound **2** in 56% yield. We note that both **1** and **2** are stable for extended periods of time under nitrogen.

The UV–vis absorption spectra for compounds **1** and **2** exhibit interesting features characteristic of these types of rigid dimers. In Figure 2 are shown normalized data collected in chloroform at 298 K. The key element of these spectra that highlights dimer character is the two-peaked feature in the UV (290 and 326 nm for **1** and 308 and 333 nm for **2**). This heralds Davydov splitting of what is normally a single $S_3 \leftarrow S_0$ transition in monomer models, and it occurs because the $S_3 \leftarrow S_0$ is polarized along the long axis of the chromophore: the bluer peak in the dimer arises due to an out-of-phase combination of the two individual chromophore transition dipole moments, whereas the redder peak arises due to the in-phase combination.[13,19] Because of the obtuse angle between chromophores imposed by the norbornyl bridge, the bluer transition in the Davydov split pair is weaker than its redder counterpart. Also observed for these two molecules is a single vibronic progression in the visible, with a significant red shift for the pentacenic **2** (the lowest energy and peak transition in this progression is at 530 nm for **1** and 637 nm for **2**). That no Davydov splitting is observed for either molecule in this lower energy spectral region is the expected result given that the $S_1 \leftarrow S_0$ transition in monomer models is short-axis polarized. In these rigid dimers, the out-of-phase combination of transition dipole moments represents a dark transition and only the in-phase combination is observed.

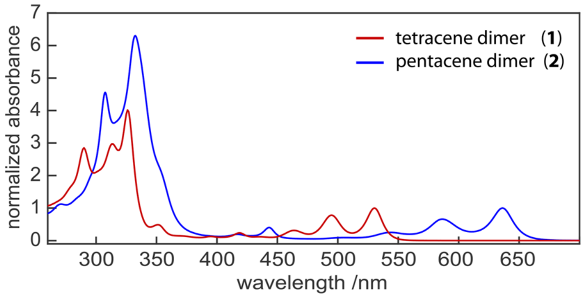


Figure 2. Normalized UV–vis spectra for **1** (red) and **2** (blue) collected at 298 K in chloroform.

A preliminary exploration of excited-state behavior was made using ultrafast transient absorption spectroscopy applied to compounds **1** and **2** at room temperature in toluene. The difference between the excited and ground state absorption spectra was recorded at two time-points: 1 and 10 ps after photoexcitation (top and bottom of Figure 3). For the tetracene-derived dimer (**1**), there is little notable evolution of features during the first 10 ps, suggesting that ^{1}TT formation, i.e., the initial stage of SF, is either not occurring (as has been seen for the constitutional isomer **7a**[19]) or is a minor component in the excited-state evolution (as has been seen for the parent tetracene dimer with no TIPS-acetylene substituents[13]). A more detailed exploration over a longer time range is needed to fully characterize this system, as the hallmarks of fission can be subtle in cases where the photophysical reaction is slightly endergonic, as is expected here.[13,19]

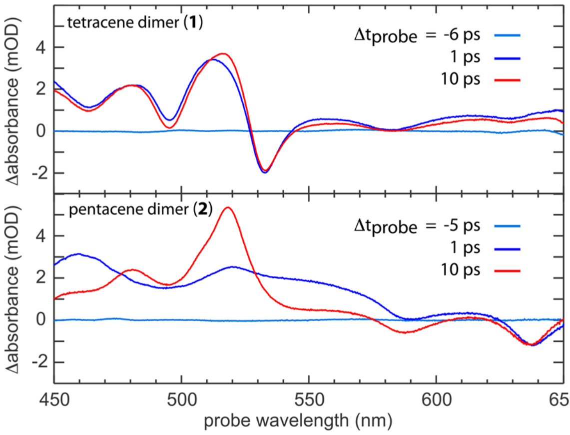


Figure 3. Transient absorption spectra collected for **1** (top) and **2** (bottom) at 298 K in toluene following ∼50 fs pulsed excitation at 530 nm (**1**) and 550 nm (**2**). See the Supporting Information for experimental details.

In stark contrast, in the pentacene-derived dimer (**2**), there is a marked evolution of features. In particular, the broad excited-state absorption (ESA) between 450 and 580 nm observed at 1 ps gives way to a spectrum at 10 ps that is dominated by a sharp ESA transition at 518 nm and a higher energy vibronic shoulder at 480 nm (Figure 3, bottom). This overall spectrum is a hallmark of triplet electronic character that has been previously observed to form rapidly in SF dimer systems that take advantage of TIPS-acetylenepentacene-like chromophores.[10,11] The time scale at which this feature also arises in **2**, significantly less than 10 ps, rules out triplet formation by intersystem crossing (as this process generally occurs on much longer time scales) and is strong evidence that ^{1}TT forms rapidly and efficiently in this system where the photophysical reaction is now more exergonic. A detailed study to establish rate constants and further probe the photophysical behavior of these molecules is underway.

The successful preparation of the norbornyl-bridged bis(pentacene) dimer **2**, culminating in the observation of rapid ^{1}TT formation following photoexcitation, illustrates the importance of considering not only the properties of the target molecule but also those of the intermediates in the synthesis. By altering our approach to incorporate stabilizing substituents early in the synthesis, we have solved issues of solubility and stability of the intermediates, and have a streamlined and flexible route. We expect this approach to be useful for the preparation of other sensitive, norbornyl-bridged bis(acene) dimers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03817.

> Experimental procedures and spectroscopic data (^{1}H and ^{13}C NMR) for all new compounds and a description of the transient absorption spectrometer (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: tarek.sammakia@colorado.edu.
*E-mail: niels.damrauer@colorado.edu.

ORCID

Tarek Sammakia: 0000-0003-3703-5672
Niels H. Damrauer: 0000-0001-8337-9375

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge support from the National Science Foundation through Grant No. CHE-1665375. We acknowledge the University of Colorado Boulder Central Analytical Laboratory Mass Spectrometry Core Facility (partially funded by NIH S10 RR026641) for mass spectrometry analysis. This manuscript is based upon work conducted while T.S. was supported by, and serving at, the National Science Foundation.

■ REFERENCES

(1) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford University Press: New York, 1999.

(2) Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891−6936.

(3) Singh, S.; Jones, W. J.; Siebrand, W.; Stoicheff, B. P.; Schneider, W. G. *J. Chem. Phys.* **1965**, *42*, 330−342.

(4) Swenberg, C. E.; Stacy, W. T. *Chem. Phys. Lett.* **1968**, *2*, 327−328.

(5) Merrifield, R.; Avakian, P.; Groff, R. P. *Chem. Phys. Lett.* **1969**, *3*, 386−388.

(6) Hanna, M. C.; Nozik, A. J. *J. Appl. Phys.* **2006**, *100*, 074510.

(7) Dexter, D. L. *J. Lumin.* **1979**, *18−19*, 779−784.

(8) Müller, A. M.; Avlasevich, Y. S.; Schoeller, W. W.; Müllen, K.; Bardeen, C. J. *J. Am. Chem. Soc.* **2007**, *129*, 14240−14250.

(9) Johnson, J. C.; Akdag, A.; Zamadar, M.; Chen, X.; Schwerin, A. F.; Paci, I.; Smith, M. B.; Havlas, Z.; Miller, J. R.; Ratner, M. A.; Nozik, A. J.; Michl, J. *J. Phys. Chem. B* **2013**, *117*, 4680−4695.

(10) Zirzlmeier, J.; Lehnherr, D.; Coto, P. B.; Chernick, E. T.; Casillas, R.; Basel, B. S.; Thoss, M.; Tykwinski, R. R.; Guldi, D. M. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5325−5330.

(11) Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Trinh, M. T.; Choi, B.; Xia, J. L.; Taffet, E. J.; Low, J. Z.; Miller, J. R.; Roy, X.; Zhu, X. Y.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M. *J. Am. Chem. Soc.* **2015**, *137*, 8965−8972.

(12) Lukman, S.; Chen, K.; Hodgkiss, J. M.; Turban, D. H. P.; Hine, N. D. M.; Dong, S. Q.; Wu, J. S.; Greenham, N. C.; Musser, A. J. *Nat. Commun.* **2016**, *7*, 13622.

(13) Cook, J.; Carey, T. J.; Damrauer, N. H. *J. Phys. Chem. A* **2016**, *120*, 4473−4481.

(14) Korovina, N. V.; Das, S.; Nett, Z.; Feng, X.; Joy, J.; Haiges, R.; Krylov, A. I.; Bradforth, S. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2016**, *138*, 617−627.

(15) Margulies, E. A.; Miller, C. E.; Wu, Y.; Ma, L.; Schatz, G. C.; Young, R. M.; Wasielewski, M. R. *Nat. Chem.* **2016**, *8*, 1120−1125.

(16) Sakuma, T.; Sakai, H.; Araki, Y.; Mori, T.; Wada, T.; Tkachenko, N. V.; Hasobe, T. *J. Phys. Chem. A* **2016**, *120*, 1867−1875.

(17) Carey, T. J.; Snyder, J. L.; Miller, E. G.; Sammakia, T.; Damrauer, N. H. *J. Org. Chem.* **2017**, *82*, 4866−4874.

(18) Kumarasamy, E.; Sanders, S. N.; Tayebjee, M. J. Y.; Asadpoordarvish, A.; Hele, T. J. H.; Feummeler, E. G.; Pun, A. B.; Yablon, L. M.; Low, J. Z.; Paley, D. W.; Dean, J. C.; Choi, B.; Scholes, G. D.; Steigerwald, M.; Ananth, N.; McCamey, D. R.; Sfeir, M. Y.; Campos, L. M. *J. Am. Chem. Soc.* **2017**, *139*, 12488−12494.

(19) Cook, J. D.; Carey, T. J.; Arias, D. H.; Johnson, J. C.; Damrauer, N. H. *J. Phys. Chem. A* **2017**, *121*, 9229−9242.

(20) Scholes, G. D.; Ghiggino, K. P.; Oliver, A. M.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1993**, *115*, 4345−4349.

(21) Vallett, P. J.; Snyder, J. L.; Damrauer, N. H. *J. Phys. Chem. A* **2013**, *117*, 10824−10838.

(22) Alguire, E. C.; Subotnik, J. E.; Damrauer, N. H. *J. Phys. Chem. A* **2015**, *119*, 299−311.

(23) Damrauer, N. H.; Snyder, J. L. *J. Phys. Chem. Lett.* **2015**, *6*, 4456−4462.

(24) Florey, A.; Vogel, P. *Helv. Chim. Acta* **1975**, *58*, 1488−1492.

(25) Pilet, O.; Vogel, P. *Helv. Chim. Acta* **1981**, *64*, 2563−2570.

(26) Ashton, P. R.; Brown, G. R.; Isaacs, N. S.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Slawin, A. M. Z.; Smith, D. R.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 6330−6353.

(27) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15−18.

(28) Fudickar, W.; Linker, T. *J. Am. Chem. Soc.* **2012**, *134*, 15071−15082.

(29) We note that this approach is advantageous for the synthesis of asymmetric structures, which can be produced by using different dienophiles in the two Diels−Alder reactions.

(30) Laatsch, H. *Liebigs Ann. Chem.* **1986**, *1986*, 839−858.

(31) Patney, H. K. *J. Org. Chem.* **1988**, *53*, 6106−6109.