ORGANIC LETTERS

2007
Vol. 9, No. 19
3725−3728

Carbon Networks Based on Benzocyclynes. 6. Synthesis of Graphyne Substructures via Directed Alkyne Metathesis§

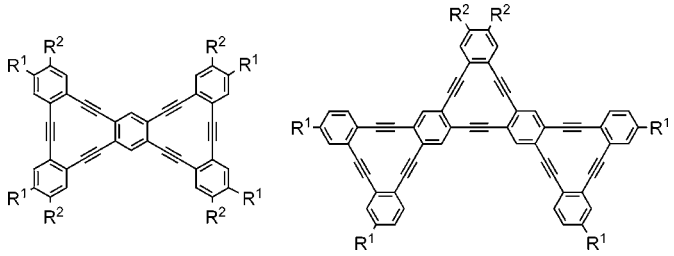
Charles A. Johnson II,† Yunyi Lu,‡ and Michael M. Haley*,†

Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403-1253, and Department of Chemistry, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

haley@uoregon.edu

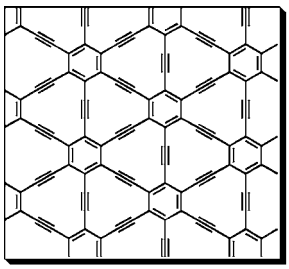
Received June 18, 2007

ABSTRACT

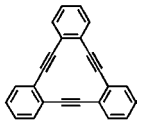


Intramolecular ring closing alkyne metathesis afforded the graphyne biscyclyne (3) in high macrocyclization yield and good overall yield. This methodology also furnished the tris[12]cyclyne 4, which contains the longest linear diphenylacetylene conjugation pathway for any graphyne substructure based on the tribenzo[12]cyclyne core.

Graphyne (**1**), a theoretical carbon allotrope composed of sp- and sp^2-hybridized carbon atoms, was first postulated 20 years ago[1] and continues to elicit interest from both a fundamental[2] and applied standpoint.[3] The highly unsaturated network, calculated as the most stable carbon allotrope containing alkyne units, is predicted to display a variety of desirable materials properties,[1,2b−d] such as high-temperature stability, a band gap (1.2 eV) lower than that of polyacetylene, and the ability to intercalate Li^+ and Na^+ ions without interlayer distortion. Despite these predicted advantageous properties, a suitable synthetic route for the preparation of **1** has not been elucidated.



1



2

Investigation of theoretical network properties via substructures based on similar structural motifs has proved highly successful for other carbon allotropes, such as graphdiyne[4] and polyphenylene.[5] However, the chemical

§ For Part 5, see ref 4b.

† University of Oregon.

‡ University of Illinois at Urbana−Champaign.

(1) Baughman, R. H.; Eckhardt, H.; Kertesz, M. *J. Chem. Phys.***1987**, *87*, 6687−6699.

(2) (a) Tahara, K.; Yoshimura, T.; Sonoda, M.; Tobe, Y.; Williams, R. V. *J. Org. Chem.* **2007**, *72*, 1437−1442. (b) Narita, N.; Nagai, S.; Suzuki, S.; Nakao, K. *Phys. Rev. B* **1998**, *58*, 11009−11014. (c) Narita, N.; Nagai, S.; Suzuki, S.; Nakao, K. *Phys. Rev. B* **2000**, *62*, 11146−11151. (d) Narita, N.; Nagai, S.; Suzuki, S. *Phys. Rev. B* **2001**, *64*, 245408−245414. (e) Zhou, Y.; Feng, S. *Solid State Commun.* **2002**, *122*, 307−310. (f) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101−1123.

10.1021/ol7014253 CCC: $37.00
Published on Web 08/18/2007

literature contains only three different graphyne substructures composed of fused tribenzo[12]cyclyne (**2**) subunits. The short conjugation pathways of the reported substructures, none of which are greater than two diphenylacetylene units in linear length ($n = 2$; e.g., **3**, Figure 1), are not sufficient

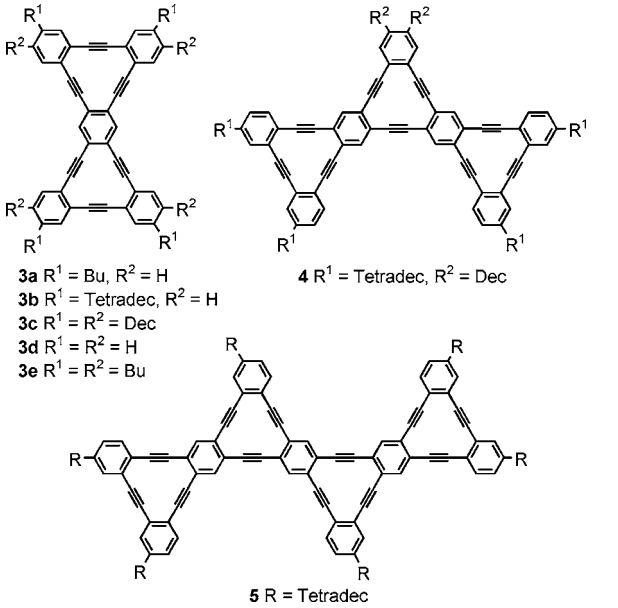


Figure 1. Target graphyne substructures **3**−**5**.

to extrapolate electronic properties of the bulk network. Work by our laboratory[4] and others[2a,3f,6] has shown that linear phenylacetylene conjugation length dominates electronic properties over the extent of conjugation for isomeric substructures. We therefore sought to extend the length of the linear conjugation pathway at least 2-fold beyond the current limit. Substructures **4** ($n = 3$) and **5** ($n = 4$) were proposed to accomplish this investigation (Figure 1).

In addition to isolating both **4** and **5**, we sought to develop a general method for construction of larger graphyne substructure topologies. The length of our previous intramolecular approach[3a] for **3d** as well as the dependence on probability of intermolecular routes[3c,d] make these techniques impractical for preparing **4** and **5**. The synthetic challenge associated with higher degrees of symmetry and construction of the monoyne linkage of subunit **2** appeared straightforwardly addressed with alkyne metathesis, which in recent years has seen an extensive increase in catalyst development[7−9] and use in macrocyclization.[3c,9,10] Alkyne metathesis displayed an unprecedented efficiency for *o*-benzocyclyne synthesis,[3c,9c] as shown by Vollhardt's preparation of **3d** in 6% yield via 6-fold intermolecular metathesis of 1,2-dipropynylbenzene and 1,2,4,5-tetrapropynylbenzene. The three-step route afforded an identical overall yield (4.4%) to our first isolation of **3d** by an 11-step convergent pathway.[3a] We hypothesized that an intramolecular route combining the efficiency of alkyne metathesis with preorganized propynyl groups would provide superior access to graphyne substructures. Production of graphyne biscyclyne **3** via this new route and comparison to previous syntheses[3a,c,d] was conducted to evaluate this assertion. Alkyl groups were incorporated into the substructure's peripheral arene rings to combat expected solubility problems.

Synthesis of tetrabutylbiscyclyne **3a** began with diyne **6a**, available in five steps (55% yield) from 4-butylaniline (see the Supporting Information). Desilylation of **6a** with base followed by 4-fold Pd-catalyzed cross-coupling with 1,2,4,5-tetraiodobenzene[11] gave penultimate octayne **7a** in 73% yield (Scheme 1). Treatment of **7a** with Schrock's W-alkylidyne catalyst[7] at 80 °C afforded cycle **3a**, with 50 mol % catalyst loading and 3.3 mM reaction concentration providing the highest yield (46%). Three components were recovered from each experimental trial, all readily identifiable by fluorescent emission color: biscyclyne **3a** (green), oligomer (turquoise), and starting material (**6a**, blue). Reaction monitoring by TLC showed that product distribution did not change after 3 h, suggesting that the catalyst had possibly become inactive. This result seems to confirm reports that 2-butyne polymerizes in the presence of Mo(VI) and W(VI) complexes and can deactivate the alkylidyne by a ring expansion polymerization mechanism.[9a,e]

The poor solubility of **3a** prompted us to investigate alternate solubilizing groups and substitution patterns. Both

(3) (a) Kehoe, J. M.; Kiley, J. H.; English, J. J.; Johnson, C. A.; Petersen, R. C.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969−972. (b) Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2103−2108. (c) Miljanic, O. S.; Vollhardt, K. P. C.; Whitener, G. D. *Synlett* **2003**, 29−34. (d) Iyoda, M.; Sirinintasak, S.; Nishiyama, Y.; Vorasingha, A.; Sultana, F.; Nakao, K.; Kuwatani, Y.; Matsuyama, H.; Yoshida, M.; Miyake, Y. *Synthesis* **2004**, 1527−1531. (e) Sonoda, M.; Sakai, Y.; Yoshimura, T.; Tobe, Y.; Kamada, K. *Chem. Lett.* **2004**, *33*, 972−973. (f) Yoshimura, T.; Inaba, A.; Sonoda, M.; Tahara, K.; Tobe, Y.; Williams, R. V. *Org. Lett.* **2006**, *8*, 2933−2936.

(4) (a) Spitler, E. L.; Johnson, C. A.; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344−5386. (b) Marsden, J. A.; Haley, M. M. *J. Org. Chem.* **2005**, *70*, 10213−10226.

(5) Miljanic, O. S.; Vollhardt, K. P. C. In *Carbon-Rich Compounds*: *From Molecules to Materials*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: New York, 2006; pp 140−197.

(6) (a) Tykwinski, R. R.; Schreiber, M.; Carlon, R. P.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1996**, *79*, 2249−2281. (b) Tykwinski, R. R.; Schreiber, M.; Gramlich, V.; Seiler, P.; Diederich, F. *Adv. Mater.* **1996**, *8*, 226−231. (c) Rodriguez, J. G.; Esquivias, J.; Lafuente, A.; Diaz, C. *J. Org. Chem.* **2003**, *86*, 8120−8128. (d) Meier, H.; Mühling, B.; Kolshorn, H. *Eur. J. Org. Chem.* **2004**, 1033−1042. (e) Zucchero, A. J.; Wilson, J. N.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11872−11881.

(7) (a) Schrock. R. R. *Acc. Chem. Res.* **1986**, *19*, 342−348. (b) Schrock. R. R. *Polyhedron* **1995**, *14*, 3177−3195.

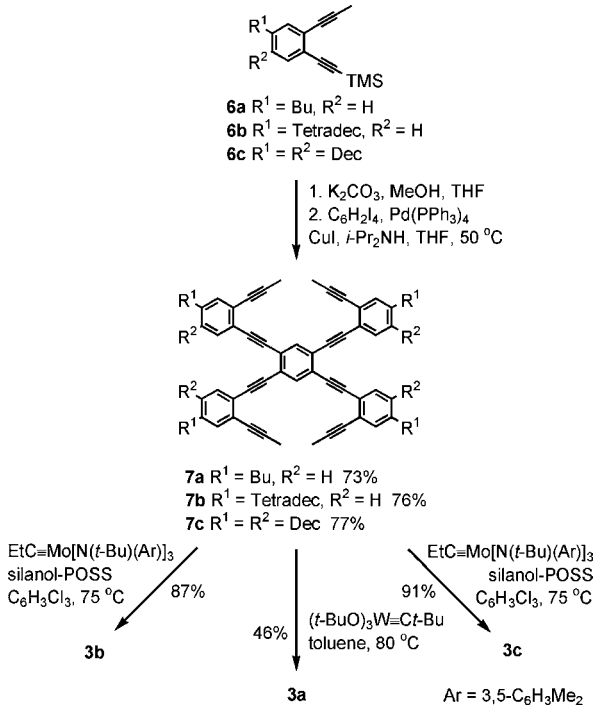
(8) (a) Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1998**, *120*, 7973−7974. (b) Brizius, G.; Bunz, U. H. F. *Org. Lett.* **2002**, *4*, 2829−2831. (c) Sashuk, V.; Ignatowska, J.; Grela, K. *J. Org. Chem.* **2004**, *69*, 7748−7751. (d) Maraval, V.; Lepetit, C.; Camanade, M.-N.; Majoral, J.-P.; Chauvin, R. *Tetrahedron Lett.* **2006**, *47*, 2155−2159.

(9) (a) Zhang, W.; Kraft, S.; Moore, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 329−335. (b) Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 11863−11870. (c) Zhang, W.; Brombosz, S. M.; Mendoza, J. L.; Moore, J. S. *J. Org. Chem.* **2005**, *70*, 10198−10201. (d) Cho, H. M.; Weissman, H.; Wilson, S. R.; Moore, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 14742−14743. (e) Zhang, W.; Moore, J. S. *Adv. Synth. Catal.* **2007**, *349*, 93−120.

(10) Inter alia: (a) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043. (b) Fürstner, A.; Mathes, C.; Lehmann, C. W. *Chem. Eur. J.* **2001**, *7*, 5299−5317. (c) Fürstner, A.; Castanet, A.-S.; Radkowski, K.; Lehmann, C. W. *J. Org. Chem.* **2003**, *68*, 1521−1528. (d) Ghalit, N.; Poot, A. J.; Fürstner, A.; Rijkers, D. T. S.; Liskamp, R. M. J. *Org. Lett.* **2005**, *7*, 2961−2964. (e) Vintonyak, V. V.; Maier, M. E. *Org. Lett.* **2007**, *9*, 655−658.

(11) Mattern, D. L.; Chen, X. *J. Org. Chem.* **1991**, *56*, 5903−5907.

Scheme 1



lengthening of the alkyl groups from butyl to tetradecyl (**3b**) as well as incorporation of eight alkyl substituents into the peripheral arene rings (**3c**) were attempted. The Mo-amido catalytic system optimized by Moore[9] was also considered to overcome the incomplete reaction of starting material.

Reaction of **7b**, prepared analogously to **7a** starting from 4-tetradecylaniline, with the Mo-alkylidyne and 4-nitrophenol, using the literature method for intermolecular metathesis,[9] provided no greater than 10% product formation with the remainder of **7b** unreacted. Increased catalyst loading (30 mol %) and temperature (75 °C) afforded an improved yield (~30%) but still incomplete conversion of **7b** to either macrocycle or oligomer. Replacement of the phenol with silanol−POSS, a ligand found to preferentially limit polymerization of 2-butyne via steric bulk,[9d] provided complete consumption of **7b** as well as excellent yield for **3b** (87%) under highly concentrated conditions (32 mM) and short reaction time (30 min). Disappointingly, cycle **3b** proved equally poorly soluble and complete removal of the POSS cocatalyst was also problematic.

Production of octasubstituted **3c** began with arene **6c**, available in two steps from 1,2-didecyl-4,5-diiodobenzene[12] (see the Supporting Information). Higher dilution (1.7 mM) and increased reaction time (14 h) were used to produce **3c** in high yield, the result of enhanced macrocycle solubility and propensity for further metathesis scrambling under the concentrated conditions favoring **3b**. The good solubility of **3c** in organic solvents permitted removal of the POSS cocatalyst and successful acquisition of a ^{13}C NMR spectrum, the latter a notable deficiency of both tetrasubstituted **3a** and **3b**.

The efficiency of our new intramolecular metathesis route, as evidenced by a minimum 3-fold increase in overall and cyclization yield when compared with previous reported analogues **3d**,**e** (Table 1), prompted us to next target **4** and

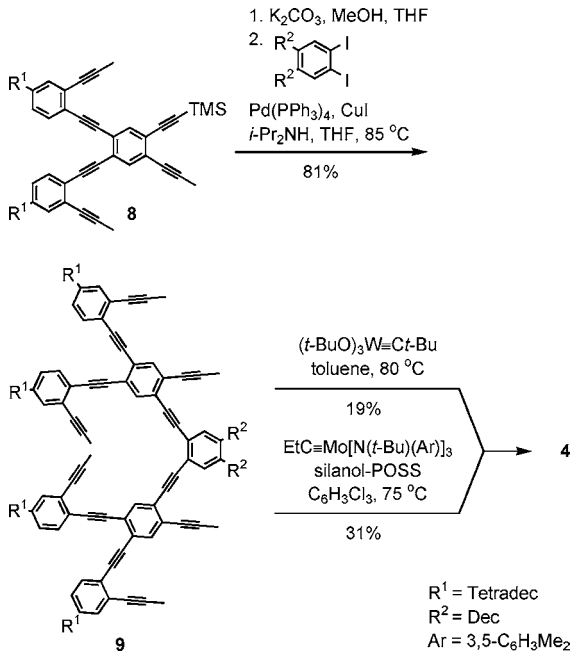
Table 1. Comparison of Route Efficiency for Biscyclyne **3**

cycle	steps	cyclization yield (%)	overall yield (%)	ref
3d	11	<15	4	6
3d	3	6	4	7b
3e	8	1	<1	8
3a	8	46	19	this work
3b[a]	8	87	21	this work
3c	7	91	17	this work

[a] Isolated as 9:1 mixture with silanol−POSS.

5. Construction of larger substructures required an additional key intermediate (**8**), available in five steps (48%) from **6b** (see the Supporting Information). Polyyne **9** was obtained by 2-fold cross-coupling of desilylated **8** with 1,2-didecyl-4,5-diiodobenzene (Scheme 2). Alkyne metathesis of **9**

Scheme 2



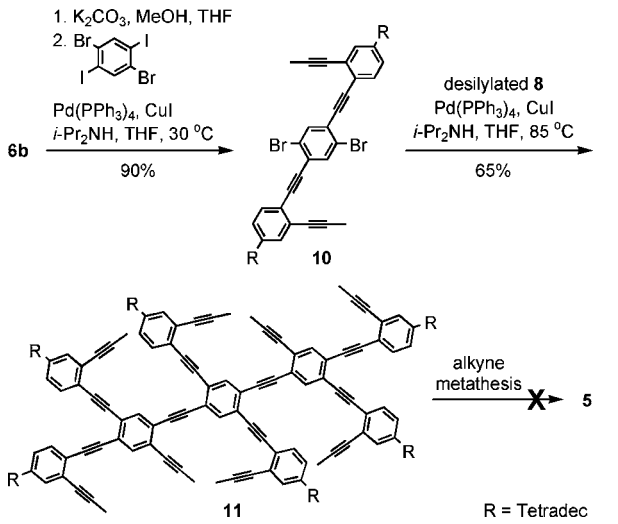
afforded triscyclyne **4** in 19−31%, with the Mo-amido catalyst and POSS ligand providing the higher yield. As with **3c**, cycle **4** proved highly soluble in chlorinated organic solvents, a factor attributed to the 1,2-didecylarene substitution.

To target substructure **5**, sequential cross-coupling of desilylated intermediates **6b** and **8** to 1,4-dibromo-2,5-

(12) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294−1301.

diiodobenzene[13] was required and furnished precursor **11** in 59% yield (Scheme 3). Attempts to produce **5** via 4-fold

Scheme 3



metathesis of **11** with Schrock's catalyst or the Mo-alkylidyne with the 4-nitrophenol ligand afforded oligomeric material or return of starting material, respectively. Use of the Mo-amido catalyst with the POSS ligand resulted in complete consumption of starting material and production of a single discrete component, which spectroscopy identified as an intermediate with three of the four [12]cyclyne subunits cyclized. The poor solubility of this intermediate as well as a kinetic energy barrier elucidated from modeling studies are likely factors which prevented further conversion to tetrakis[12]cyclyne target **5**.

Macrocyclization of **3a**−**c** and **4** results in an upfield shift of the aromatic proton resonances ($\Delta\delta \approx 0.2-0.6$ ppm), reflecting the paratropic nature of the [12]cyclyne subunit.[14] The largest $\Delta\delta$ values (−0.47, −0.58) are associated with the internal arene rings and agree with calculations[2a] indicating decreased aromaticity from fusion with multiple paratropic-[12]cyclyne cores.

Analysis of the absorption spectra of macrocycles **2**,[15] **3a**−**c**, and **4** shows increased molar absorptivity and bathochromic shifts in both λ_{cutoff} and λ_{max} upon successive fusion of [12]cyclyne subunits (Figure 2). Substructures **3** and **4** retain the characteristic vibronic spectral pattern of **2**, indicative of a highly rigid and planar macrocycle.[16] HOMO−LUMO bandgaps calculated for **3a**−**c** (~2.73 eV) and **4** (2.43 eV) from the lowest energy absorption λ_{max} coincide with computed values reported by Tobe et al.[2a] Cyclynes **3** and **4** exhibit large Stokes shifts (89−104 nm) as well as batho-

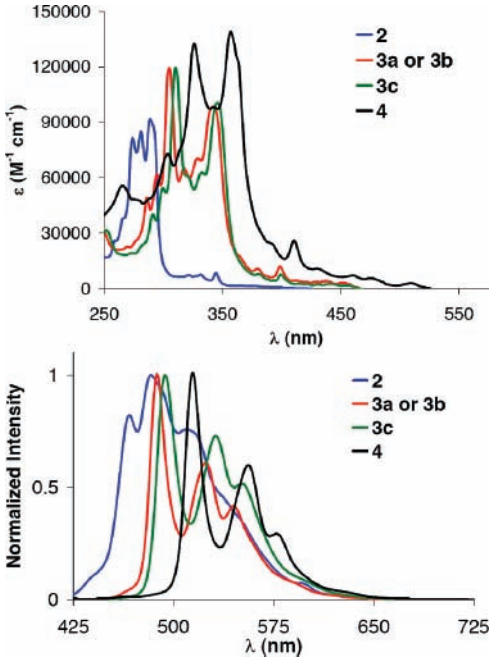


Figure 2. Absorption and emission spectra of **2**, **3a**−**c**, and **4**.

chromic λ_{em} and increased fluorescent quantum yield (**3a**−**c**: $\Phi_F = 0.19-0.21$; **4**: $\Phi_F = 0.27$) upon extension of the linear conjugation pathway. Cycle **3c** exhibits slightly lower energy absorption and emission values than **3a**,**b** due to incorporation of the four additional electron-donating alkyl substituents.

In conclusion, biscyclyne **3** was obtained in high overall yield via an intramolecular metathesis cyclization route. Substructure **4**, which contains the longest linear diphenylacetylene conjugation pathway and highest quantum yield for graphyne substructures based on the [12]cyclyne subunit, was also prepared. The assertion of linear phenylacetylene conjugation pathway dominance was confirmed by comparison of electronic properties of **4** ($n = 3$; absorption $\lambda_{cutoff} = 525$ nm, $\Phi_F = 0.27$, $\lambda_{em} = 515$ nm) with an isomeric trefoil topology ($n = 2$; $\lambda_{cutoff} \approx 500$ nm, $\Phi_F = 0.03$, $\lambda_{em} \approx 500$ nm) prepared by the Tobe group.[3f] Attempts to further elongate this chromophore linearly (i.e., **5**) were unsuccessful. Future work will include investigation of precipitation-driven metathesis, sequential macrocyclization of [12]cyclyne subunits to further limit intermolecular oligomerization, and incorporation of additional alkyl groups.

Acknowledgment. We thank the National Science Foundation (CHE-0414175 and -0718242) for support of this research. C.A.J. acknowledges the University of Oregon for a Doctoral Research Fellowship. We thank Prof. J. S. Moore for his technical advice.

Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL7014253

(13) Hart, H.; Harada, K.; Du, C. J. F. *J. Org. Chem* **1985**, *50*, 3104−3110.
(14) Juselius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2433−2437.
(15) Staab, H. A.; Graf, F. *Tetrahedron Lett.* **1966**, 751−757.
(16) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, UK, 1970. (b) Anstead, G.; Katzenellenbogen, J. A. *J. Phys. Chem.* **1988**, *92*, 6249−6258.