Phenylated Benzotetraphenes (Dibenzanthracenes) by Nickel-Catalyzed Diphenylacetylene Cycloadditions to Linear [3]Phenylenes

Zhenhua Gu, K. Peter C. Vollhardt*

Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720-1460, USA
Fax +1(510)6435208; E-mail: kpcv@berkeley.edu

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Abstract: Ni(COD)(PMe$_3$)$_2$ catalyzes the cycloaddition of diphenylacetylene to the four-membered rings of linear [3]phenylene and its 2,3,7,8-tetrakis(trimethylsilyl) derivative. The reaction proceeds via initial formation of the 5,6-diphenylbenzo[3,4]cyclobuta[1,2-*b*]phenanthrene frame, followed by a competitive second, nonregioselective alkyne insertion to furnish the corresponding phenyl-substituted benzo[*k*]- and -[*m*]tetraphenes.

Key words: alkynes, arenes, cycloaddition, nickel, polycycles

Substituted polycyclic aromatic hydrocarbons are the subject of immense current interest because they feature as components of optoelectronic materials,[1] as building blocks for the bottom-up assembly of novel carbon allotropes,[2] as platforms for the construction of functional molecular assemblies,[3] in biological studies of the metabolism of environmental pollutants,[4] and as scaffolds in natural products synthesis.[5] The functionalization of the parent systems (if available) by classical electrophilic aromatic substitution is limited by the rules of regioselectivity, solubility problems, and side reactions, particularly in the case of larger systems. Consequently, substantial effort has been devoted to the development of synthetic methods that assemble targets with controlled topologies.[1–6] In this vein, we have recently reported on the nickel-catalyzed cycloaddition of diphenylacetylene (and, briefly, two other alkynes) to the four-membered rings of angular phenylenes **1**–**3** (Figure 1).[7,8] This transformation features a haptotropic Ni(PMe$_3$) unit that undergoes kinetically controlled, remarkably regioselective, sequential Ni insertions along the bay-regions to furnish primarily phenacene (oligophenanthrene) derivatives. Thus, and most pertinent for the results to be described, **1** converted with 1 equivalent of diphenylacetylene into only 11,12-diphenylbenzo[3,4]cyclobuta[1,2-*a*]phenanthrene **4** and phenacene **5**, in the absence of regioisomer **6** (Scheme 1). Notably, double insertion to give **5** competed with single addition to give **4**.[7]

As such, and in view of the plethora of phenylene frames that have become available during the past decades,[9] this methodology provides, in principle, a useful complement to existing strategies toward specifically substituted polycyclic benzenoids. However, a considerable number of the phenylenes contain linear substructures, as exemplified by the smallest representative, linear [3]phenylene **7a**. It was therefore of interest to establish its basic feasibility to serve as a substrate in these reactions and, if successful, compare their outcome with that observed for **1** under identical conditions.

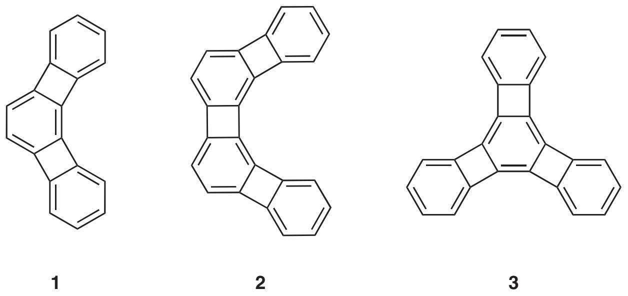
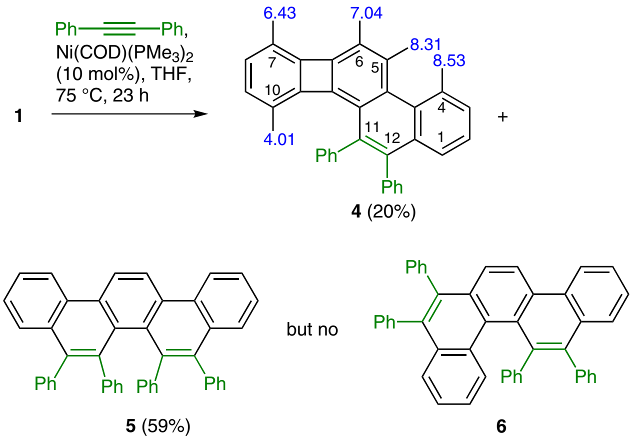


Figure 1



Scheme 1 Outcome of the nickel-catalyzed addition of diphenylacetylene to **1**; pertinent chemical shifts in **4** are shown in blue (see discussion)[7]

Thus, linear [3]phenylene **7a** (1 equiv), diphenylacetylene (0.83 equiv), and Ni(COD)(PMe$_3$)$_2$ (0.1 equiv) in tetrahydrofuran were heated to 75 °C for two days, during which time the solution turned red and a colorless solid consisting of 5,6,12,13-tetraphenylbenzo[*k*]tetraphene (5,6,12,13-tetraphenyldibenz[*a*,*h*]anthracene) (**9a**) precipitated. A combination of filtration and column chromatography allowed the isolation of 5,6-diphenylbenzo[3,4]cyclobuta[1,2-*b*]phenanthrene (**8a**), **9a**, and 5,6,8,9-tetraphenylbenzo[*m*]tetraphene (5,6,8,9-tetraphenyldibenz[*a*,*j*]anthracene) (**10a**) (Scheme 2) in good combined yield (81%). After benzo[3,4]cyclobuta[1,2-

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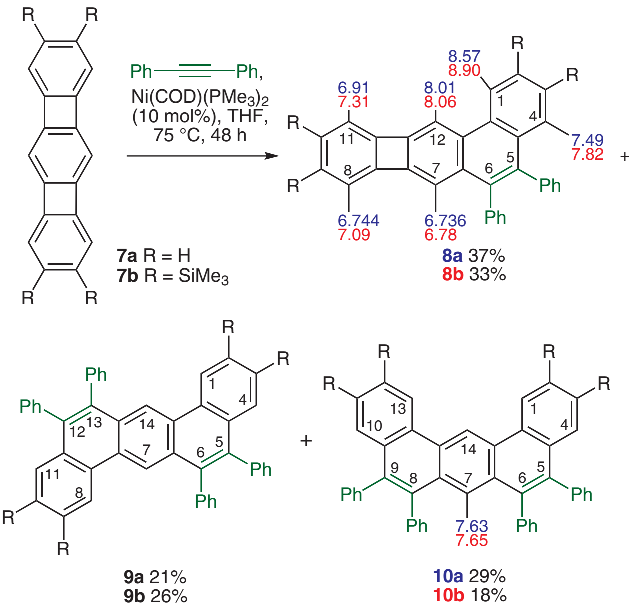
b]phenanthrene-7,12-dicarbonitrile,[10] lacking ^{13}C NMR data, fused biphenylene **8a** is only the second (and fully characterized) member of this type of carbon frame. Similarly, but now obviating the complication of insolubility, the tetrakis(trimethylsilyl)phenylene **7b**[9a] converted into the analogous pentacycles **8b**, **9b**, and **10b**. In this case, an NMR experiment demonstrated that the reaction goes cleanly to completion (2.2 equiv of alkyne, **9b**/**10b** ~1:1).



Scheme 2 Outcome of the nickel-catalyzed addition of diphenylacetylene to **7**; pertinent chemical shifts of **8** and **10** are shown in blue for **a** and red for **b** (see discussion)

The structural assignments of **8**–**10** rest on their characteristic spectral data. Thus, **8** exhibits the typical pattern of relatively shielded hydrogens adjacent to the cyclobutadienoid four-membered ring,[9] in conjunction with the diagnostic bay region phenanthrene signals (Scheme 2). In proceeding from **8a** to **8b**, the hydrogens *ortho* to trimethylsilyl experience the expected downfield displacement of ~0.3–0.4 ppm. One notes that an absorption corresponding to the extraordinarily high field signal for H10 in **4**, the result of the shielding effect of the adjacent phenyl group,[7] is now absent in **8** due to its altered topology. Phenylene **8a** is an isomer of **4**, and it is of interest to compare their spectral properties. Consideration of their respective dominant resonance forms in which the cyclobutadienoid character of the four-membered ring is minimized,[9] as drawn in Schemes 1 and 2, shows that the aromaticity of the central ring of the phenanthrene portion in **4** is disrupted, in contrast to that of the corresponding ring in **8a** where it is enhanced, relative to phenanthrene. To put it differently, the benzocyclobuta[*a*] fusion in **4** is less readily accommodated than the corresponding [*b*] fusion in **8a**. This simple analysis has been quantified by DFT calculations for the parent frames.[11] A tentative indication of decreased antiaromaticity in the latter is found in the relative deshielding of H11 ($\delta = 6.91$, $CDCl_3$) compared to H7 in **4** ($\delta = 6.43$, $CDCl_3$), the choice of these hydrogens predicated on their unencumbrance by differences in their local environment. Further corroboration of this notion was sought by X-ray analysis, an initiative also stimulated by the dearth of such data for similar phenylenes.[12] Unfortunately, **8a** produced only amorphous powders. However, X-ray quality crystals of **8b** could be grown from a saturated toluene–propan-2-ol solution followed by slow vapor diffusion of methanol (Figure 2).[13] While the presence of the silyl groups compromises a strict comparison of the bond distances in **8b** with those of **4**,[7] their perturbing substituent effect tapers off rapidly beyond the ring of attachment,[14] justifying a cautious structural evaluation of the relative aromaticity of the central phenanthrene ring. Gratifyingly, and in consonance with computational predictions (vide supra),[11] the averaged sum of its C–C bond lengths decreases along the series **4** (1.437 Å),[7] 9,10-diphenylphenanthrene (1.428 Å),[15] and **8b** (1.423 Å), a tentative sign of increasing delocalization.[11] Similarly, the average deviation of these distances from that of benzene (1.388 Å), also decreases (0.334, 0.276, and 0.247 Å, respectively). Finally, the best indicator of relative electronic activation is the HOMO–LUMO gap, as measured by the longest wavelength absorptions in the respective UV spectra. Indeed, λ_{max} (log ε) (**8a**) = 405 nm (3.93), whereas λ_{max} (log ε) (**4**) = 420 nm (3.66).[7] While the effect is attenuated relative to **4**, **8a** still incorporates a considerably electronically activated phenanthrene nucleus [cf. phenanthrene: highest $\lambda_{max} = 345$ nm, or the 'hexagonal squeeze'[16] tetraphene (benz[*a*]anthracene) λ = 384 nm].[17] One notes in this connection that areno-fused phenylenes are garnering increasing attention as air-stable organic electronic materials.[18]

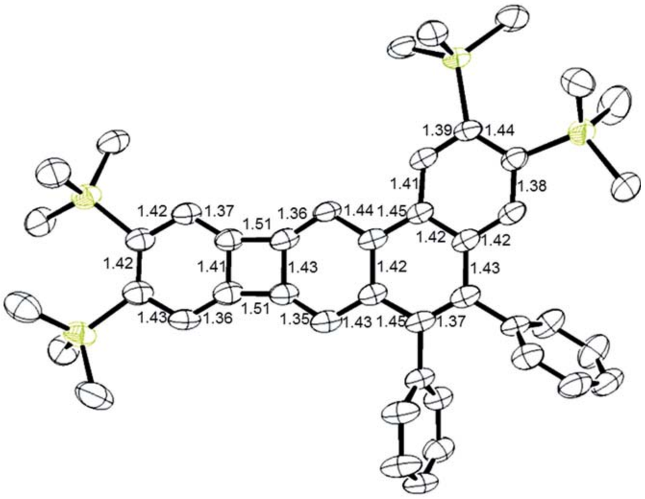


Figure 2 ORTEP diagram of **8b**; thermal ellipsoids are set at 50% probability, selected bond lengths (Å) are averaged over two molecules in the unit cell and rounded off in the last decimal (individual values ±0.006–9)

Turning to the benzotetraphenes **9** and **10**, their spectral data are in agreement with those of the parent systems[19] and related tetraaryl derivatives.[20] The two topologies are readily distinguished by the NMR spectra, which reveal an additional carbon and proton signal for the less symmetrical **10**. Noticeable in **10** is the substantial shielding of H7 relative to that of this hydrogen in the parent compound (δ = 8.36, $CDCl_3$),[19b] caused by the cumulative effect of the two adjacent phenyl substituents. Tetraarylbenzotetraphenes of this type have been scrutinized for electronic applications,[21] which have also spurred increasing synthetic efforts to improve access to the general framework.[1o,5a,22]

In summary, we have complemented earlier work on the nickel-catalyzed cycloaddition of alkynes to angular phenylenes with that to the linear variant, as exemplified by the prototype linear [3]phenylene **7**. Unlike the former, which shows extensive regioselectivity, strained ring opening occurs from both the same and opposite sides of the fused array to assemble substituted benzotetraphenes. While this apparent flaw may be detrimental in the design of routes to specific systems, it can be advantageous when structural diversity is the goal. It will be interesting to apply this method to the larger phenylenes,[9a] as one can envisage the generation of a plethora of hitherto unobserved polycyclic benzenoid hydrocarbon systems.

Et_2O and THF were dried over Na with benzophenone as indicator. Toluene and *m*-xylene were distilled from CaH_2. UV/Vis spectra were recorded on a Hewlett-Packard HP 8453 UV/Vis ChemStation. NMR spectra were recorded on Bruker AVQ-400, AVB-400, DXR-500, and AV-500 instruments. THF-d_8 was purchased from Cambridge Isotope Labs and degassed before use. Reactions monitored by NMR were conducted in THF-d_8.

Cycloaddition of Diphenylacetylene to 7a: 5,6-Diphenylbenzo[3,4]cyclobuta[1,2-*b*]phenanthrene (8a), 5,6,12,13-Tetraphenylbenzo[*k*]tetraphene (9a), and 5,6,8,9-Tetraphenylbenzo[*m*]tetraphene (10a)

Under N_2, an Ace-glass tube was charged with phenylene **7a** (22.6 mg, 0.10 mmol), diphenylacetylene (14.8 mg, 0.083 mmol), $Ni(COD)(PMe_3)_2$ (2.6 mg, 0.0082 mmol), and THF (5 mL). The tube was sealed with a screw cap and the contents stirred at 75 °C for 48 h, during which the mixture turned red and colorless 5,6,12,13-tetraphenylbenzo[*k*]tetraphene (**9a**) (5.1 mg, 21%) precipitated. After its removal by filtration, the remainder was subjected to flash chromatography (silica gel, hexanes–CH_2Cl_2, gradient 10:1 to 5:1) to afford 5,6-diphenylbenzo[3,4]cyclobuta[1,2-*b*]phenanthrene (**8a**) (12.3 mg, 37%) and 5,6,8,9-tetraphenylbenzo[*m*]tetraphene (**10a**) (7.0 mg, 29%).

8a

Pale yellow solid; mp 264–265 °C (CH_2Cl_2).

IR (KBr): 3055, 1483, 1442, 1422, 764, 741, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 8.0 Hz, 1 H), 8.01 (s, 1 H), 7.58 (ddd, *J* = 1.5 Hz, 7.5, 8.5 Hz, 1 H), 7.49 (d, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.26–7.15 (m, 6 H), 7.15–7.09 (m, 4 H), 6.94–6.84 (m, 2 H), 6.91 (d, *J* = 7.5 Hz, 1 H), 6.744 (d, *J* = 8.0 Hz, 1 H), 6.736 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.9, 150.8, 148.6, 148.4, 139.9, 139.5, 138.1, 137.3, 132.6, 131.8, 130.96, 130.95, 130.93, 130.4, 129.2, 129.1, 127.8, 127.6, 127.5, 126.40, 126.39, 126.2, 126.1, 122.5, 118.9, 118.8, 115.6, 110.7.

MS (EI, 70 eV): *m/z* (%) = 404 ($[M]^+$, 18), 91 (100).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{32}H_{20}$: 404.1565; found: 404.1571.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 289 (4.71), 303 (sh, 4.59), 314 (sh, 4.43), 326 (4.49), 364 (3.70), 384 (3.86), 405 nm (3.93).

9a

Colorless solid; mp >360 °C (dec; from THF, washed with CH_2Cl_2).

IR (KBr): 3053, 1489, 1440, 1433, 1069, 759, 704 cm^{-1}.

^1H NMR (500 MHz, CD_2Cl_2): δ = 8.94 (s, 2 H), 8.38 (d, *J* = 7.5 Hz, 2 H), 7.58–7.52 (m, 2 H), 7.50–7.42 (m, 4 H), 7.42–7.38 (m, 4 H), 7.38–7.33 (m, 6 H), 7.33–7.27 (m, 4 H), 7.27–7.20 (m, 6 H).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.98 (s, 2 H), 8.39 (d, *J* = 7.2 Hz, 2 H), 7.57–7.50 (m, 4 H), 7.60 (d, *J* = 7.6 Hz, 2 H), 7.40–7.29 (m, 10 H), 7.29–7.19 (m, 10 H).

HRMS-FAB: *m/z* $[M]^+$ calcd for $C_{46}H_{30}$: 582.2348; found: 582.2346.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 288 (sh, 4.55), 299 (4.79), 311 (4.85), 333 (sh, 4.18), 347 (4.12), 363 (4.04), 403 nm (3.29).

10a

Colorless solid; mp >360 °C (dec; CH_2Cl_2).

IR (KBr): 3060, 1514, 1482, 1439, 1070, 1029, 1000, 767, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 10.23 (s, 1 H), 9.18 (d, *J* = 8.0 Hz, 2 H), 7.78 (t, *J* = 8.0 Hz, 2 H), 7.63 (s, 1 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.55 (t, *J* = 7.0 Hz, 2 H), 7.26–7.15 (m, 10 H), 7.03–6.94 (m, 10 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.5, 138.9, 137.5, 136.8, 132.4, 131.04, 130.98, 130.6, 130.2, 128.3, 128.1, 127.63, 127.60, 127.3, 126.9, 126.6, 126.5, 126.0, 122.7, 115.8.

HRMS-FAB: *m/z* $[M]^+$ calcd for $C_{46}H_{30}$: 582.2348; found: 582.2346.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 267 (4.46), 302 (4.71), 314 (4.87), 336 (sh, 4.17), 349 (4.08), 366 nm (sh, 3.66).

Cycloaddition of Diphenylacetylene to 7b: 5,6-Diphenyl-2,3,9,10-tetrakis(trimethylsilyl)benzo[3,4]cyclobuta[1,2-*b*]phenanthrene (8b), 5,6,12,13-Tetraphenyl-2,3,9,10-tetrakis(trimethylsilyl)benzo[*k*]tetraphene (9b), and 5,6,8,9-Tetraphenyl-2,3,11,12-tetrakis(trimethylsilyl)benzo[*m*]tetraphene (10b)

Under N_2, an Ace-glass tube was charged with phenylene **7b** (30.8 mg, 0.06 mmol), diphenylacetylene (8.90 mg, 0.05 mmol), $Ni(COD)(PMe_3)_2$ (0.08 M in THF, 63 μL, 0.005 mmol), and THF (5 mL). The tube was sealed with a screw cap and the contents stirred at 75 °C for 48 h. The solvent was removed by rotary evaporation and the residue purified by flash chromatography (silica gel, hexanes–CH_2Cl_2, 5:1) to give 5,6-diphenyl-2,3,9,10-tetrakis(trimethylsilyl)benzo[3,4]cyclobuta[1,2-*b*]phenanthrene (**8b**) (11.3 mg, 33%), 5,6,12,13-tetraphenyl-2,3,9,10-tetrakis(trimethylsilyl)benzo[*k*]tetraphene (**9b**) (5.7 mg, 26%), and 5,6,8,9-tetraphenyl-2,3,11,12-tetrakis(trimethylsilyl)benzo[*m*]tetraphene (**10b**) (4.0 mg, 18%).

8b

Pale yellow solid; mp 278–280 °C (CH_2Cl_2–hexanes).

IR (KBr): 3056, 2951, 1602, 1494, 1442, 1411, 1249, 1142, 1066, 1027, 854, 836, 755, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.06 (s, 1 H), 7.82 (s, 1 H), 7.31 (s, 1 H), 7.29–7.16 (m, 6 H), 7.124 (t, *J* = 9.0 Hz, 2 H), 7.120 (t, *J* = 9.0 Hz, 2 H), 7.09 (s, 1 H), 6.78 (s, 1 H), 0.52 (s, 9 H), 0.39 (s, 9 H), 0.33 (s, 9 H), 0.21 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 149.9, 149.7, 149.5, 148.9, 148.7, 142.51, 142.47, 139.9, 139.2, 138.5, 137.3, 135.4, 133.1, 131.0, 130.9, 130.7, 130.4, 129.6, 128.9, 127.6, 127.4, 126.42, 126.37, 124.40, 124.37, 116.0, 110.7, 2.17, 2.11, 2.02, 1.61.

HRMS-FAB: *m/z* $[M]^+$ calcd for $C_{44}H_{52}Si_4$: 692.3146; found: 692.3130.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.66), 304 (4.94), 317 (sh, 4.85), 334 (4.67), 371 (4.27), 392 (4.06), 413 nm (4.12).

Anal. Calcd for $C_{44}H_{52}Si_4$: C, 76.23; H, 7.56. Found: C, 76.13; H, 7.49.

9b
Colorless solid; mp >360 °C (dec; CH_2Cl_2–hexanes).

IR (KBr): 3051, 2950, 1490, 1462, 1441, 1251, 1152, 1120, 1062, 854, 834, 755, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.97 (s, 2 H), 8.75 (s, 2 H), 7.87 (s, 2 H), 7.42–7.36 (m, 4 H), 7.36–7.30 (m, 6 H), 7.29 (d, J = 6.8 Hz, 4 H), 7.26–7.21 (m, 6 H), 0.33 (s, 18 H), 0.20 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 143.1, 139.5, 139.2, 137.8, 137.1, 135.1, 131.2, 131.0, 130.9, 130.8, 129.6, 128.5, 128.4, 127.8, 127.6, 126.8, 126.5, 121.5, 1.78, 1.59.

HRMS-FAB: m/z $[M]^+$ calcd for $C_{58}H_{62}Si_4$: 870.3929; found: 870.3921.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.95), 299 (sh, 4.82), 308 (5.11), 321 (5.26), 341 (4.59), 355 (4.45), 372 (4.32), 410 nm (3.65).

10b
Colorless solid; mp 350–351 °C (dec; CH_2Cl_2–hexanes).

IR (KBr): 3054, 2952, 1491, 1441, 1261, 1250, 1115, 1030, 855, 834, 701, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.28 (s, 1 H), 9.47 (s, 2 H), 7.92 (s, 2 H), 7.65 (s, 1 H), 7.26–7.22 (m, 4 H), 7.21–7.15 (m, 6 H), 7.04–6.94 (m, 10 H), 0.63 (s, 18 H), 0.25 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 143.2, 139.2, 138.9, 137.9, 136.8, 135.5, 131.3, 131.1, 131.0, 130.7, 129.5, 128.7, 128.2, 127.6, 127.5, 127.3, 126.5, 126.1, 115.2, 2.18, 1.70.

HRMS-FAB: m/z $[M]^+$ calcd for $C_{58}H_{62}Si_4$: 870.3929; found: 870.3961.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 249 (4.73), 280 (4.52), 300 (sh, 4.50), 311 (4.74), 324 (4.92), 342 (sh, 4.30), 359 (4.20), 370 nm (sh, 3.93).

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Supporting Information (^1H and ^{13}C NMR spectra of new compounds) for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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