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Preparation of 6,13-Bis(trimethylsilyl)pentacene and Formation of Second-Ring Diels−Alder Adduct of Pentacene

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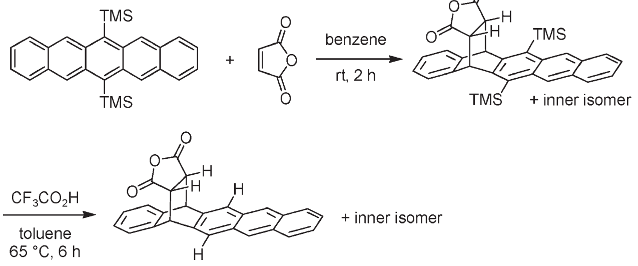
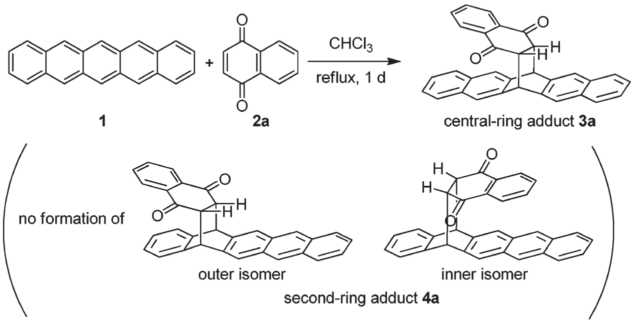
Received September 9, 2010



6,13-Bis(trimethylsilyl)pentacene was synthesized by a coupling reaction of bicyclic dilithiobutadiene with diiodonaphthalene followed by aromatization. Diels−Alder reaction of 6,13-bis(trimethylsilyl)pentacene with dienophiles afforded the corresponding second-ring adducts. Elimination of two silyl groups gave the second-ring Diels−Alder adducts of parent pentacene.

Nonsubstituted pentacene easily reacts with a series of dienophiles via Diels−Alder addition to give the corresponding central-ring adducts exclusively.[1,2] Theoretical study clearly showed that the inner rings of linear acenes are more reactive than outer rings.[3]Although some exceptions have been reported,[4] the regioselectivity is very high, and the formation of Diels−Alder adducts at the second-ring is not observed. For example, as shown in Scheme 1, naphthoquinone **2a** reacts with pentacene **1** to give central-ring adduct **3a** as a single product. The reaction with maleic anhydride (**2b**) also proceeds similarly to afford the corresponding central-ring adduct as a single product. The formation of second-ring adducts **4a**,**b** was not observed.

SCHEME 1



In this paper, we report the synthesis of the Diels−Alder adducts of parent pentacene at the second ring by using substituent effects of the trimethylsilyl group. It was reported that substitution at the 6,13-position on the pentacene skeleton significantly affects the regioselection to afford the corresponding second-ring adducts predominantly.[5] Then, we designed 6,13-bis(trimethylsilyl)pentacene (**11**) and reacted it with dienophiles to afford the expected second-ring Diels−Alder adducts. Desilylation of the adducts gave the desired second-ring adduct of nonsubstituted pentacene. In another experiment, Diels−Alder reaction of 5,14-dihydropentacene followed by dehydrogenation also gave the same second-ring adducts as mentioned below.

Bis-silylated pentacene **11** was successfully synthesized via the zirconium-mediated cyclization and the coupling reactions we developed so far[6,7] (Schemes 2 and 3). Cyclization of diyne **5** with Cp$_2$ZrBu$_2$ gave zirconacyclopentadiene **6**, which was converted into diiodobutadiene **7** by iodination in

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(1) Representative examples of the Diels−Alder reaction of parent pentacene: (a) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812. (b) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163. (c) Kitaguchi, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 800. (d) Mack, J.; Miller, G. P. *Fullerene Sci. Technol.* **1997**, *5*, 607. (e) Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Ohara, K.; Ono, N. *Chem.—Eur. J.* **2005**, *11*, 6212. (f) Yamada, H.; Okujimaa, T.; Ono, N. *Chem. Commun.* **2008**, 2957.

(2) Theoretical calculations on the reactivity of pentacenes: (a) Manoharan, M.; De Proft, F.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1767. (b) Cheng, M. F.; Li, W. K. *Chem. Phys. Lett.* **2003**, *368*, 630. (c) Reddy, A. R.; Bendikov, M. *Chem. Commun.* **2006**, 1179.

(3) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643.

(4) Rare examples of formation of second-ring adducts of pentacene, which formed as a mixture with the corresponding central-ring adducts. See: (a) Murata, Y.; Kato, N.; Fujiwara, K.; Komatsu, K. *J. Org. Chem.* **1999**, *64*, 3483. (b) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.

(5) Diels−Alder reaction of pentacenes substituted at 6,13-positions: (a) Briggs, J. B.; Miller, G. P. *C. R. Chim.* **2006**, *9*, 916 and references cited therein. (b) Zhao, D. H.; Swager, T. M. *Org. Lett.* **2005**, *7*, 4357. (c) Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253. (d) Miller, G. P.; Mack, J. *Org. Lett.* **2000**, *2*, 3979. (e) Zhou, X.; Kitamura, M.; Shen, B.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2004**, *33*, 410. (f) Takahashi, T.; Kashima, K.; Li, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2007**, *129*, 15752.

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(7) (a) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (b) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (c) Seri, T.; Qu, H.; Zhou, L.; Kanno, K.; Takahashi, T. *Chem. Asian J.* **2008**, *3*, 388. (d) Takahashi, T.; Kashima, K.; Li, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2007**, *129*, 15752. (e) Zhou, L.; Nakajima, K.; Kanno, K.; Takahashi, T. *Tetrahedron Lett.* **2009**, *50*, 2722.

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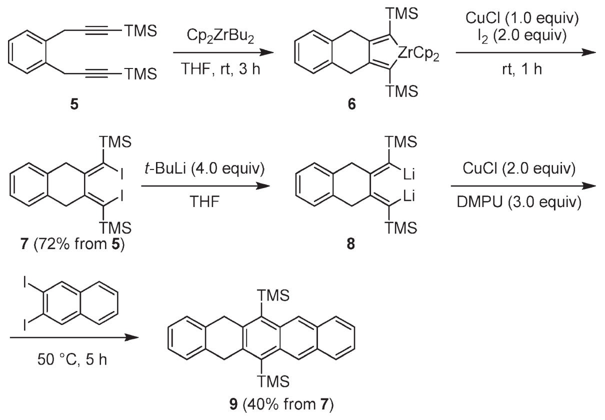
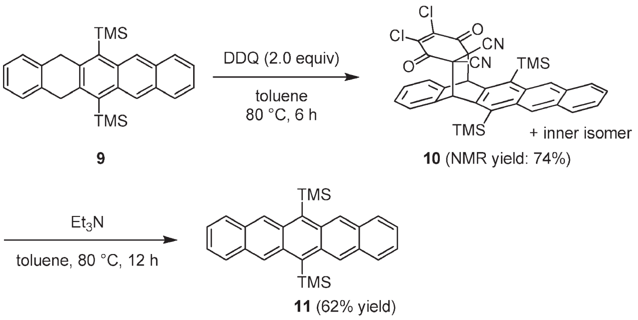
DOI: 10.1021/jo101774d

SCHEME 2



SCHEME 3

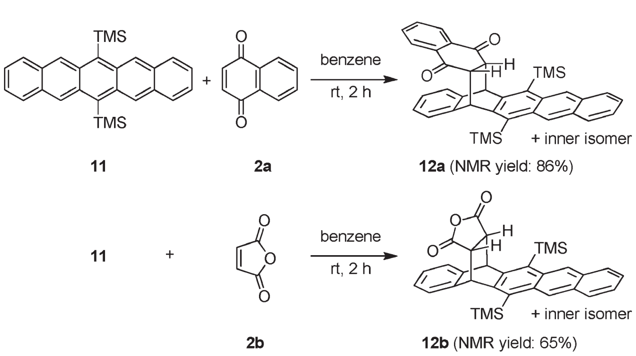


the presence of CuCl.[8] Diiodobutadiene was treated with 4 equiv of *t*-BuLi to afford dilithiobutadiene **8**, which coupled with 2,3-diiodonaphthalene to give 6,13-bis(trimethylsilyl)-5,14-dihydropentacene (**9**) in 40% yield.[7e]

Dihydropentacene **9** was aromatized via the disilylpentacene−DDQ adduct **10** as shown in Scheme 3. The reaction of **9** with 2.0 equiv of DDQ gave the corresponding DDQ adduct **10** as a mixture of the inner and outer isomers in high yield. We recently reported that the DDQ moiety was effectively removed from DDQ adducts of substituted pentacenes by treatment with 50 equiv of γ-terpinene.[7d] However, the reaction of DDQ adduct **10** with 50 equiv of γ-terpinene caused not only removal of DDQ but also protodesilylation to give only nonsubstituted pentacene as blue precipitate. Probably the protodesilylation proceeded to give nonsubstituted pentacene. After several trials, we found that Et_3N effectively deactivated the eliminated DDQ even in the absence of γ-terpinene. Then, elimination of DDQ from **10** was performed by the reaction with Et_3N in toluene at 80 °C for 12 h. Thus, bis(trimethylsilyl)pentacene **11** was obtained in 62% isolated yield (Scheme 3).

Disilylpentacene **11** was definitely assigned by NMR and UV−vis absorption spectra as described below. The ^1H NMR spectrum of pentacene **11** showed the peak of methyl protons at 0.82 ppm and those of aromatic protons at 8.96, 7.88−7.91, and 7.32−7.34 ppm as singlet, multiplet, and multiplet, respectively. The ^{13}C NMR spectrum of **11** showed the peak of TMS carbons at 4.4 ppm, and three peaks of CH carbons at 125.2, 127.4, and 128.3 ppm and two peaks of quartenary carbons at 129.9 and 135.0 ppm and the peaks of TMS-attached carbon at 139.8 ppm. The UV−vis spectrum of **11** showed absorption maxima at 607, 561, 522 nm.

SCHEME 4



As expected, Diels−Alder reaction of disilylpentacene **11** smoothly proceeded at the second-ring with high regioselectivity (Scheme 4). Treatment of pentacene **11** with 2.5 equiv of naphthoquinone in benzene at room temperature for 2 h gave the corresponding second-ring adduct **12a** in 86% yield as a mixture of the inner and outer isomers. The reaction with maleic anhydride (**2b**) also proceeded at the second-ring to afford adduct **12b** in 65% NMR yield. The structure of **12b** was verified by X-ray analysis as shown in Figure. 1.

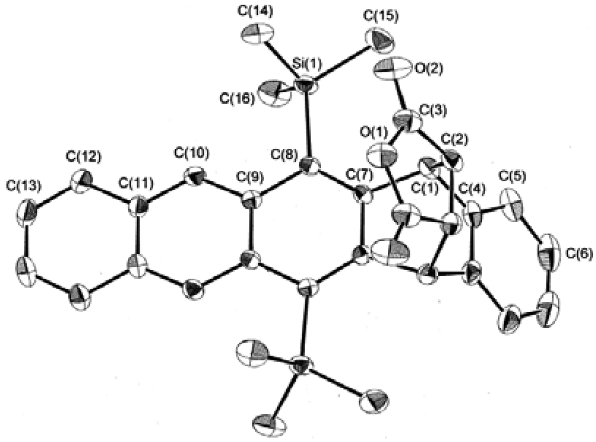
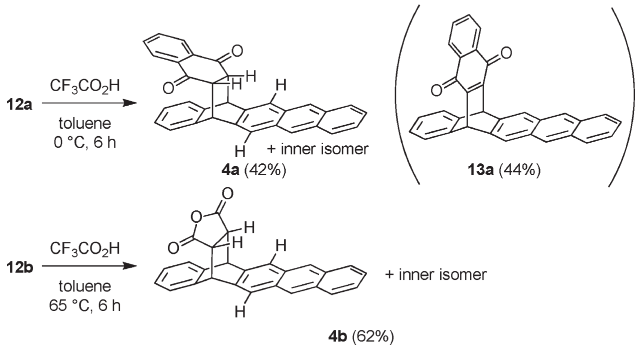


FIGURE 1. Structure of second-ring adduct **12b** (inner isomer).

SCHEME 5



As shown in Scheme 5, two silyl groups of the Diels−Alder adducts **12** were removed by treatment with CF_3CO_2H effectively. When naphthoquinone adduct **12a** was treated with CF_3CO_2H in toluene at 0 °C, the desired second-ring adduct of nonsubstituted pentacene **4a** was obtained in 42%

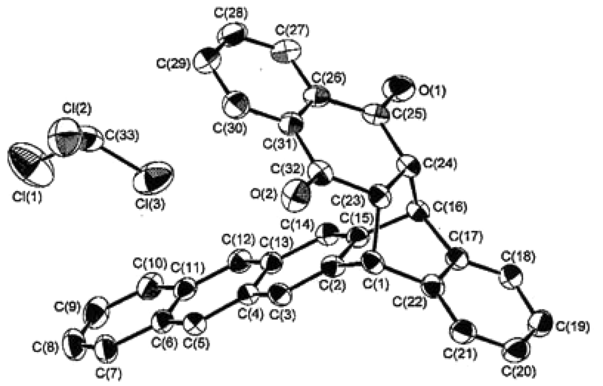


FIGURE 2. Structure of second-ring adduct of pentacene **4a** (inner isomer).

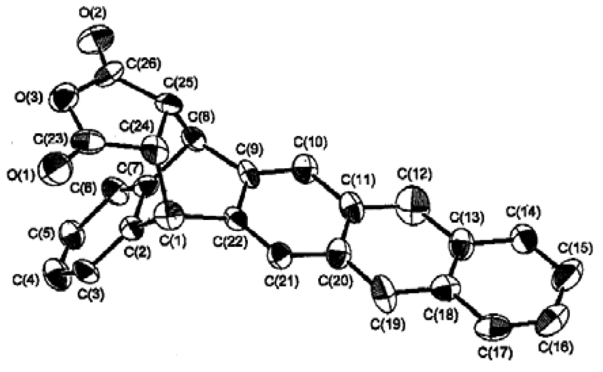


FIGURE 3. Structure of second-ring adduct of pentacene **4b** (outer isomer).

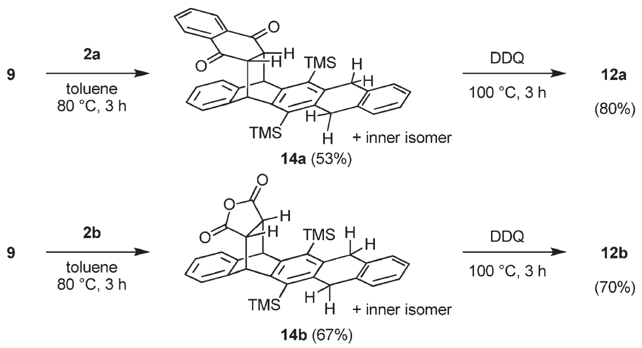
isolated yield. If the reaction was carried out at 65 °C, dehydrogenation of the naphthoquinone moiety was also occurred to give **13a** in 44% yield. In the case of maleic anhydride adduct **12b**, even at 65 °C no dehydrogenation occurred to give the desired second-ring adduct of pentacene **4b** in 82% NMR yield and 62% isolated yield.

The structures of **4a** (inner isomer) and **4b** (outer isomer) were verified by X-ray analysis, and the results are shown in Figures 2 and 3, respectively.

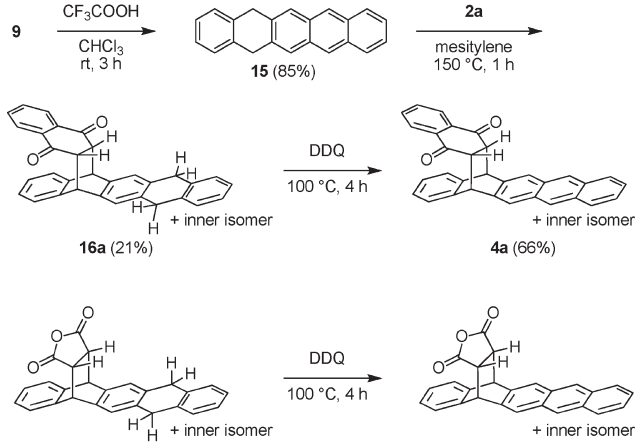
The structures of **4a** and **4b** were also characterized by NMR and UV−vis absorption spectra as described below. ^{1}H NMR spectrum of second-ring adduct **4a** showed the peak of bridge head protons at 5.17 ppm and aliphatic protons at 3.48 ppm. Aromatic ring protons of 1,4-naphthoquinone moiety appeared at 7.24−7.26 ppm and 7.36−7.38 ppm. A singlet signal at 7.72 ppm assigned to two protons of the central aromatic ring. Two protons of the second aromatic ring appeared at 8.16 ppm. Signals of eight protons of two side rings appeared at 7.40−7.42, 7.50−7.51, 7.82−7.83, and 7.88−7.90 ppm as multiplet. ^{13}C NMR showed two bridge head carbons at 49.9 ppm

Instead of disilylpentacene **11**, bis(trimethylsilyl)-5,14-dihyropentacene **9** was also used for the formation of second-ring adduct of pentacene as shown in Scheme 6. Diels−Alder reaction of **9** with naphthoquinone **2a** gave the corresponding second-ring adduct **14a** in 53% yield. Aromatization of **14a** with DDQ gave **12a** in 80% yield. The reaction with maleic anhydride **2b** also gave the corresponding second-ring

SCHEME 6



SCHEME 7



adduct **14b** in 67% yield. After aromatization, pentacene−maleic anhydride adduct **12b** was obtained in 70% yield.

Similarly, desilylated dihydropentacene was also applicable for the alternative synthesis of the second-ring adducts of nonsubstituted pentacene as shown in Scheme 7. Bis(trimethylsilyl)dihyropentacene **9** was treated with CF_3CO_2H to remove two silyl groups, and dihydropentacene **15** was obtained in 85% isolated yield.[9] Next, dihydropentacene **15** was treated with naphthoquinone under heating. However, the desired second-ring adduct **16a** was obtained in 21% yield along with byproduct. This is probably due to the higher reaction temperature than that of disilylated dihydropentacene **9**, and such forced conditions would cause the undesired side reaction.

In a similar way, the maleic anhydride adduct **16b** was formed from dihydropentacene **15** and maleic anhydride (**2b**) in 71% NMR yield and 60% isolated yield. The second-ring adduct **4b** was obtained by aromatization in 62% isolated yield.

As mentioned above, the central ring of pentacene is more reactive than others. Usually, Diels−Alder reaction occurred at the central ring. If a bulky and good leaving group substituent, such as trimethylsilyl, was introduced to the central ring of pentacene, the steric hindrance effect on the reaction position led to the Diels−Alder reaction occurring at the second ring. In the case of dihydropentacene, first dienophiles react with anthrancene moiety. Actually, the central ring of anthrancene **15** is the second ring of pentacene.

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[9] Luo, J.; Hart, H. *J. Org. Chem.* **1987**, *52*, 4833.

The second-ring adduct of pentacene was synthesized successfully via these two methods.

In summary, the present methods could produce the second-ring Diels−Alder adducts of nonsubstituted pentacene. The regiochemistry is in contrast to a direct reaction of pentacene with dienophiles affording the central-ring adducts. Such a regiocontrolled reaction was achieved by introduction of trimethylsilyl groups on the pentacene skeleton.

Experimental Section

General Procedure for Synthesis of the Second-Ring Diels−Alder Adduct of Pentacene. 6,13-Bis(trimethylsilyl)pentacene (96 mg, 0.23 mmol) and degassed benzene (2 mL) were added into a 20 mL dried Schlenk-tube under N_2. The above blue solution was degassed again by the freeze−pump method. Dienophile (92 mg, 0.58 mmol) was added. The blue color disappeared gradually. After 2 h, the blue color disappeared completely, the solvent was removed in vacuo, and the residue was purified by a silica gel chromatography (hexane/AcOEt = 5:1) to afford the title compound.

Bis(trimethylsilyl)pentacene−maleic anhydride adduct (12b): 65% NMR yield, 55% isolated yield; mixture of two isomers (ratio = 78:22). Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.74 (s, 18H), 3.50 (s, 2H), 5.54 (s, 2H), 7.29−7.31 (m, 2H), 7.46−7.51 (m, 4H), 7.93−7.96 (m, 2H), 8.69 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 4.2, 44.05, 47.6, 124.4, 125.6, 127.4, 127.9, 128.2, 130.2, 134.0, 136.2, 140.4, 140.9, 170.4; HRMS (ESI) calcd for $C_{32}H_{32}O_3Si_2Na$ ($M + Na^+$) 543.1788, found 543.1773. Minor isomer: only observed peaks are shown; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.78 (s, 18H), 3.59 (s, 2H), 5.54 (s, 2H), 7.38−7.40 (m, 2H), 8.72 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 4.2, 45.04, 47.0, 125.3, 127.6, 129.0, 130.4, 134.9, 137.4, 143.8, 170.7.

The bis(trimethylsilyl)pentacene−dienophile adduct (77 mg, 0.13 mmol) was treated with trifluoroacetic acid (38 μL, 0.52 mmol) under N_2 in toluene (2 mL) at 0 °C for 6 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with $CHCl_3$. The combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4. The solvent was evaporated, and the resulting solid was washed with $CHCl_3$ and methanol. Drying of the solid in vacuo gave the desired compound as yellow solid.

Pentacene−maleic anhydride adduct (4b): 62% isolated yield; mixture of two isomers (ratio = 69:31). Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.64 (s, 2H), 4.95 (s, 2H), 7.20−7.27 (m, 2H), 7.36−7.39 (m, 2H), 7.43−7.47 (m, 2H), 7.91 (s, 2H), 7.94−7.98 (m, 2H), 8.36 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 45.62, 47.9, 123.0, 125.6, 125.85, 126.4, 128.2, 128.4, 130.9, 132.3, 137.0, 137.8, 170.6; UV−vis ($CHCl_3$) λ_{max}/nm 378, 357, 342, 326; HRMS (ESI) calcd for $C_{26}H_{16}O_3Na$ ($M+Na^+$) 399.0997, found 399.1008. Minor isomer: only observed peaks are shown; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.62 (s, 2H), 4.93 (s, 2H), 7.90 (s, 2H), 8.35 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 45.56, 48.4, 124.3, 124.8, 125.82, 126.6, 127.8, 128.3, 130.9, 134.5, 140.4, 170.5.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.