# Straightforward Method for Synthesis of Highly Alkyl-Substituted Naphthacene and Pentacene Derivatives by Homologation

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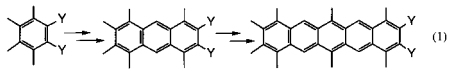
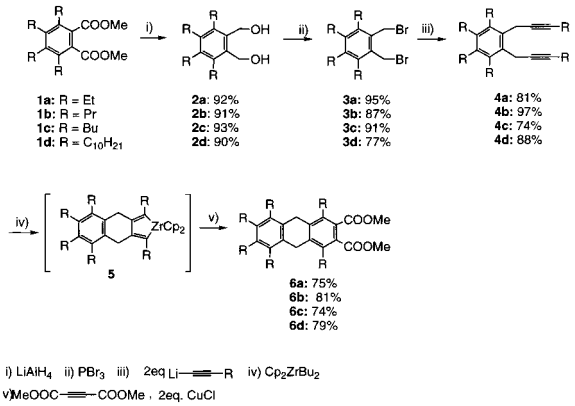
$\pi$-Conjugated compounds such as polyphenylenes, polyacetylenes, polythiophenes, and polyacenes have attracted much attention as organic conductive materials.[1] Among them, polyacenes have a very low band gap (0.1−0.5 eV)[2] compared with polyacetylenes (1.4 eV), and polythiophenes (1.71 eV).[1,2] Therefore, polyacenes have been widely recognized as a promising and useful organic conductive material.[2] In fact, recently, pentacene has been shown to be useful for organic solar batteries or semiconductors.[3] However, the established methods for synthesis of polyacenes have several critical problems. First, available acenes are very limited. Until now, heptacene has been the longest known member of acenes.[1a] Second, acenes such as pentacene have very poor solubility in organic solvents.[1a] It is well-known that these problems can be solved by introducing alkyl substituents into the $\pi$-conjugated aromatic compounds.[4] However, there is no systematic general method for the synthesis of highly alkyl-substituted acenes.[5] Diels−Alder-type reaction of furans or dienes has been known for the construction of the rings.[6] Dodecamethylnaphthacene could be prepared on the basis of the Diels−Alder reaction of furans with benzynes.[7] However, similar attempts to prepare alkyl-substituted pentacene derivatives have not been successful.[7] Here we would like to report a general and straightforward method for the synthesis of highly alkyl-substituted pentacenes and naphthacenes by homologation (eq 1).



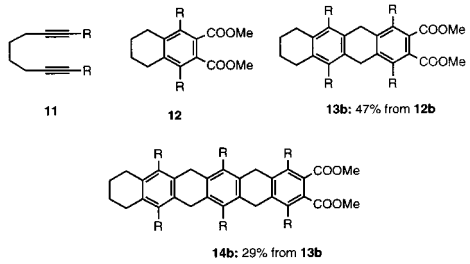
(1)

Recently, we reported the formation of highly alkyl-substituted phthalates **1** by the reaction of zirconacyclopentadienes with dimethyl acetylenedicarboxylate (DMAD) in the presence of $CuCl$[8] or $NiX_2(PPh_3)_2$ (X = Cl or Br).[9] First, we tried to prepare linear polycyclic compounds starting from the highly alkyl-substituted phthalates **1** by homologation. Homologation of linear polycyclic compounds is shown in Scheme 1. Reduction of **1** with $LiAlH_4$ gave **2**, and bromination of **2** afforded bis(bromomethyl)-benzene derivatives **3**. Coupling reaction of **3** with alkynyllithium produced diynes **4**. Intramolecular cyclization of diynes **4** with $Cp_2ZrBu_2$[10] in situ provided zirconacyclopentadienes **5**. Copper-mediated coupling reaction of **5** with DMAD gave dihydroanthracene derivatives **6**. Repetition of the same procedures (i)−(v) from **1** to **6** for the transformation of **6** to **8** provided the five-ring compound **8**. This homologation afforded odd-numbered ring compounds such as three-ring **6**, five-ring **8** (via **7**), and even seven-ring compounds **10** (from **8** via **9**) without any problem of purification.

**Scheme 1.** Preparation of Odd-Numbered Ring Compounds




As for even-numbered ring compounds, tetrahydronaphthalene derivatives **12** prepared from diynes **11** were used as the starting compounds. The same procedures shown in Scheme 1 and Scheme 2 were applied to preparation of four-ring compounds **13b** and six-ring compounds **14b**.




Preparation of alkyl-substituted naphthacenes and pentacenes was performed in a similar way using substituted naphthalene dimethoxycarbonyl compounds **15b** and substituted anthracene dimethoxycarbonyl compounds **19b**, respectively, which were prepared by oxidation of **12** and **6**, with DDQ or chloranil (Scheme 3). The compounds **15** and **19** were treated with the

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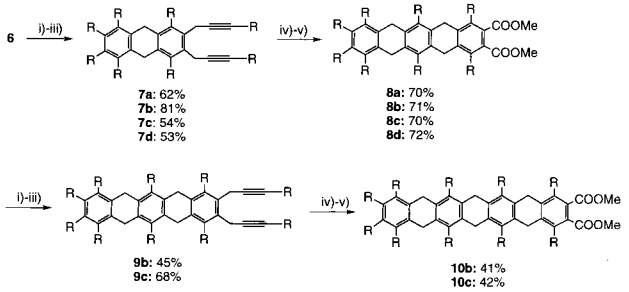
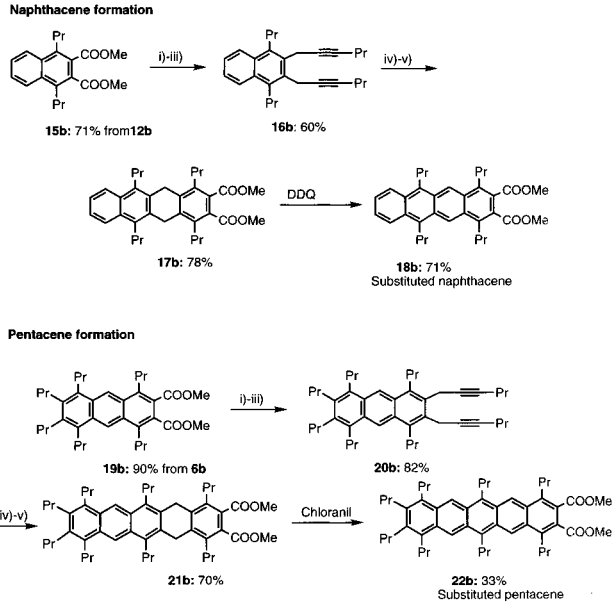
**Scheme 2.** Further Homologation of **6** to **10**




**Scheme 3.** Preparation of a Naphthacene Derivative and a Pentacene Derivative by Homologation




same reagents (i), (ii), (iii), (iv), and (v) as for the conversion of **1** to **6** to give the corresponding intermediates **17** and **21**, respectively. Alternatively, **21a** could be prepared from **8a** with chloranil (R = Et, isolated yield 40%). The oxidation of **17** and **21** with DDQ afforded naphthacene **18b**[11] and pentacene **22b**[12] in 71 and 33% yield, respectively. The structure of **18b**, and **21a** were determined by X-ray analysis as shown in Figures 1 and 2. The naphthacene derivative **18b** was a red compound, and its $^{13}$C NMR spectrum showed nine sp$^2$ carbons of the naphthacene ring in the range of 122−138 ppm. The pentacene derivative **22b** was deep-blue and soluble in organic solvents such as THF, $CHCl_3$, benzene, hexane, ether, AcOEt, and acetone. The $^1$H NMR spectrum of **22b** showed characteristic two singlets at 9.06 and 9.17 ppm assigned to protons attached to C5, C7, C12, C14 of the pentacene ring. In its $^{13}$C NMR spectrum, eleven sp$^2$ carbons are observed in the range of 120−138 pm.

In conclusion, this homologation procedure provides a general and straightforward method for synthesis of soluble acenes, and will expand the chemistry of these important compounds.

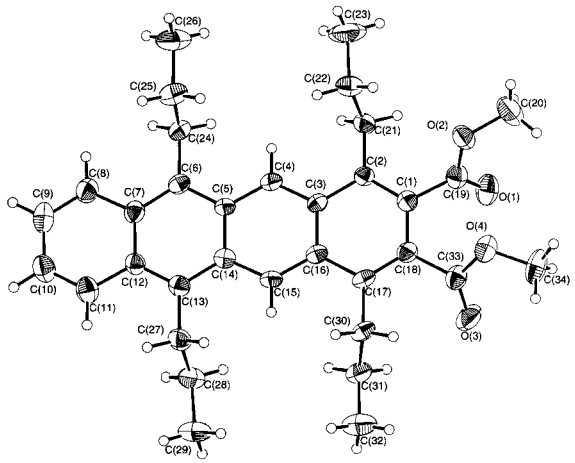



**Figure 1.** Perspective view of **18b**.

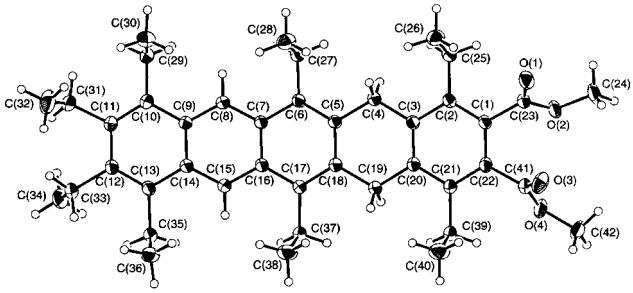



**Figure 2.** Perspective view of **21a**.

**Supporting Information Available:** Experimental details and spectroscopic characterization of new compounds and crystallographic data, positional and thermal parameters, and lists of bond lengths and angles for **18b** and **21a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **18b**: $^1$H NMR ($CDCl_3$, $Me_4Si$) $\delta$ 1.19 (t, $J$ = 7.3 Hz, 6H), 1.23 (t, $J$ = 7.3 Hz, 6H), 1.92−1.86 (m, 8H), 3.26 (t, $J$ = 8.1 Hz, 4H), 3.72 (t, $J$ = 8.1 Hz, 4H), 3.94 (s, 6H), 7.46 (dd, $J$ = 3.2, 7.0 Hz, 2H), 8.31 (dd, $J$ = 3.2, 7.0 Hz, 2H), 9.19 (s, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$) $\delta$ 14.81, 14.89, 24.67, 24.89, 30.73, 32.72, 52.25, 122.65, 125.12, 125.39, 126.67, 128.44, 128.77, 129.63, 134.16, 137.87, 169.58.

(12) **22b**: $^1$H NMR ($CDCl_3$, $Me_4Si$) $\delta$ 1.15 (t, $J$ = 7.2 Hz, 6H), 1.20 (t, $J$ = 7.3 Hz, 6H), 1.27 (t, $J$ = 7.5 Hz, 6H), 1.29 (t, $J$ = 7.4 Hz, 6H), 1.62−1.68 (m, 4H), 1.85−2.07 (m, 12H), 2.78 (t, $J$ = 7.5 Hz, 4H), 3.22−3.26 (m, 8H), 3.90 (bs, 4H), 3.94 (s, 6H), 9.06 (s, 2H), 9.17 (s, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$) $\delta$ 14.85, 15.05, 15.13, 24.36, 24.60, 24.87, 25.11, 31.33, 31.76, 32.67, 32.85, 52.26, 120.08, 122.74, 126.23, 127.57, 127.76, 128.35, 129.91, 133.37, 133.76, 136.77, 138.13, 169.65.