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A Short-Step Synthesis of 1,6-Methano[10]annulene-3,4-dicarboximides and Their Benzene-, Naphthalene-, and Thiophene-Annulated Compounds

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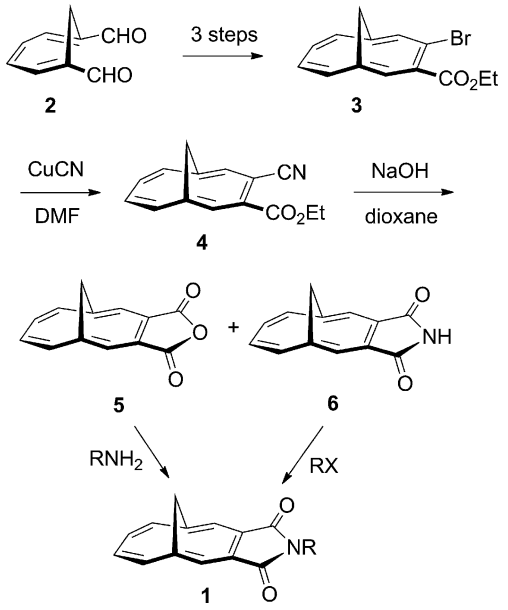
Triphenylphosphorane reagents **8** react with 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (**2**) under acidic as well as basic conditions to produce 1,6-methano[10]annulene-3,4-dicarboximides **1** in moderate -to- good yields. The reagents **8** react with 3,4-arene-annulated 1,3,5-cycloheptatriene-1,6-dicarbaldehydes **9**, **10**, and **11** to afford only the Wittig condensation products under acidic conditions but produce the arene-annulated annulenedicarboximides under basic conditions. The structures of some of the dicarboximides and the intermediate Wittig condensation products were determined by X-ray structural analysis. The emission properties of the dicarboximides were also studied.

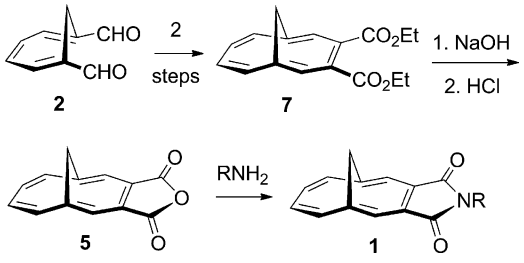
Introduction

Recently, we reported the synthesis and emission behavior of various *N*-substituted 1,6-methano[10]annulene-3,4-dicarboximides **1**,[1] and Zuo et al. independently reported their synthesis by a slightly different route.[2] The starting point for both syntheses is 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (**2**)[3] as shown in Schemes 1 and 2. The annulene derivative **3** can be obtained from **2** in three steps by the method reported by Neidlein,[4,5] and the subsequent cyanation and hydrolysis produce a mixture of dicarboxylic anhydride **5** and dicarboximide **6**. We synthesized various *N*-substituted dicarboximides **1** by either the condensation of **5** with an amine or the nucleophilic displacement of **6** with alkyl and aryl halides. In contrast, Zuo et al. obtained **5** from diester **2**[3c,6,7] and transformed **5** into **1**.

Both methods require five or six steps from **2** to **1**. In respect of the interesting emission behavior of **1**,[1] we envisioned a more efficient synthetic conversion from **2** to **1**. In this paper, we describe a short-step synthesis of **1** from **2** with the phosphorane reagents **8** that consists of a Wittig condensation and subsequent cyclization and also its application to the synthesis of benzene-, naphthalene-, and thiophene-annulated compounds.



Scheme 1. Outline of the previously reported synthetic method of **1** from **2**.



Scheme 2. A synthetic method of **1** reported by Zuo et al.

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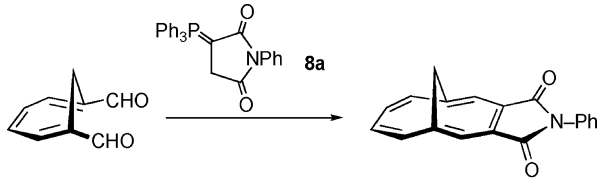
phene-annulated 1,6-methano[10]annulenedicarboximides. We also report the X-ray crystallographic analysis of some of the imides and intermediate Wittig condensation products as well as their emission properties.

Results and Discussion

First, the reaction of **2** with the triphenylphosphorane reagent **8a**,[8] obtained from triphenylphosphine and *N*-phenylmaleimide, was examined. The results under various conditions are presented in Table 1. Compound **1a**[1,2] was obtained under both acidic and basic conditions. In AcOH with a slight excess of **8a**, **1a** was obtained in a satisfactory yield (70%, Table 1, Entry 2). Under basic conditions, **1a** was obtained in moderate yields (Table 1, Entries 3–4). However, a larger amount of strong base tends to result in lower yields of the product (Table 1, Entries 5–6). The weak base pyridine was used as the solvent, but the yield was low (Table 1, Entry 7). As **8a** can be prepared in AcOH at reflux, **8a** prepared in situ was treated with **2** to provide **1a**; however, the yield was lower (48% yield) than that with preformed **8a** (Table 1, Entry 2). Under conditions similar to those of Table 1, Entry 2, phosphoranes **8b**–**8i** reacted with **2** to produce **1b**–**1h**[1] and **6** in fair-to-good yields (Figure 1). The reactivity of phosphoranes **8** with **2** is different depending on the substituent at the nitrogen atom; therefore, the reaction times also differ. Although some of the reactions produced moderate yields, we could successfully improve the synthesis of **1** from **2** by a one-step method with the phosphorane reagents **8**.

Table 1. Results of the reaction of **2** and **8a** under various conditions.



2 **1a**

Entry	Reaction conditions	Yield[a] of **1a** [%]
1	**2/8a** = 1.0:1.0, AcOH, reflux, 12 h	52 (33)[b]
2	**2/8a** = 1.0:1.5, AcOH, reflux, 16 h	70
3	**2/8a**/MeONa = 1.0:1.0:0.1, MeOH, reflux, 14 h	52 (22)[b]
4	**2/8a**/MeONa = 1.0:1.3:0.1, MeOH, reflux, 20 h	62
5	**2/8a**/MeONa = 1.0:1.3:0.5, MeOH, reflux, 10 h	26
6	**2/8a**/EtONa = 1.0:1.0:0.5, EtOH, reflux, 4 h	15
7	**2/8a** = 1.0:1.0, pyridine, reflux, 5 h	37

[a] Isolated yield after chromatographic purification. [b] The recovered yield of **1a** is in parentheses.

Secondly, we examined the reactions of the 3,4-arene-annulated 1,3,5-cycloheptatriene-1,6-dicarbaldehydes **9**,[9] **10**,[10] and **11**,[11] (Figure 2) with phosphoranes **8**. These dicarbaldehydes demonstrate different reactivity from that of **2**, that is, the reactions of these dicarbaldehydes under acidic conditions provided only the Wittig condensation products unaccompanied by the desired dicarboximides.

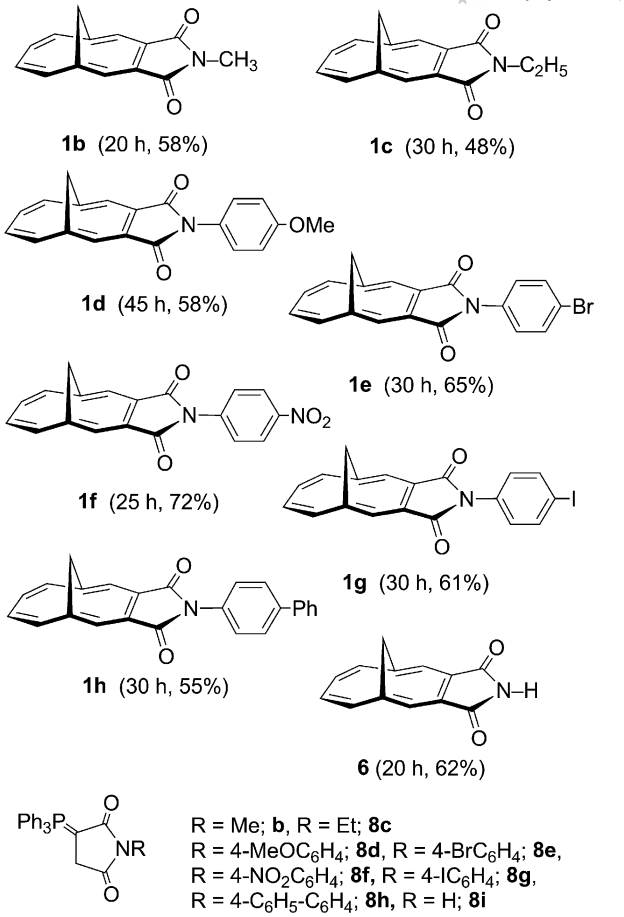


Figure 1. 1,6-Methano[10]annulene-3,4-dicarboximides **1b**–**1h** and **6** obtained by the reaction of **2** with the corresponding phosphoranes **8b**–**8i** (1.5 equiv.) in AcOH at reflux; the reaction times and yields are in parentheses.

The reactions of **9** with an equivalent amount of **8a** and **8e** in AcOH at reflux presented the monocondensation products, **12a** and **12e**, as the sole products in 23 and 20% yield, respectively; the reactions of **9** with **8b** and **8c** produced a mixture of the monocondensation products, **12b** (53% yield) and **12c** (48% yield), accompanied by the double-condensation products, **13b** (27% yield) and **13c** (11% yield), respectively (Scheme 3). On the other hand, the reaction of **10** with **8b** in AcOH produced **14** in 46% yield (Scheme 4), and a mixture of the inseparable regioisomers **15** and **16** was obtained in 66% yield from the reaction of **11** with **8b** (Scheme 5). Thus, the reactions of these arene-annulated dicarbaldehydes **9**, **10**, and **11** with phosphoranes

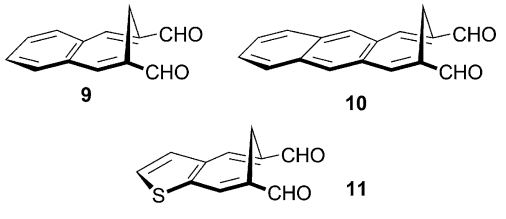
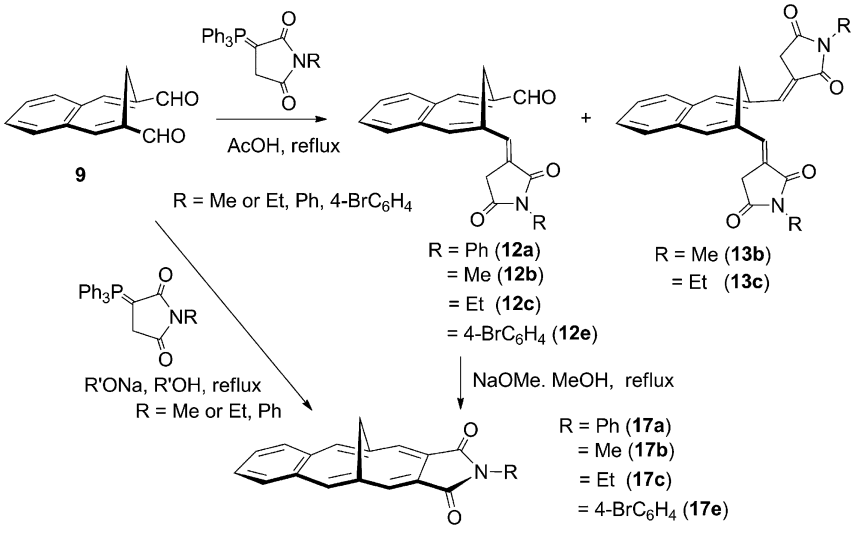
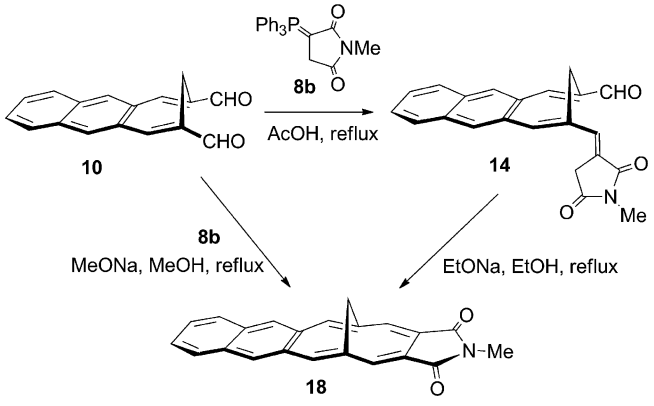


Figure 2. Structures of the 3,4-arene-annulated 1,3,5-cycloheptatriene-1,6-dicarbaldehydes **9**, **10**, and **11**.



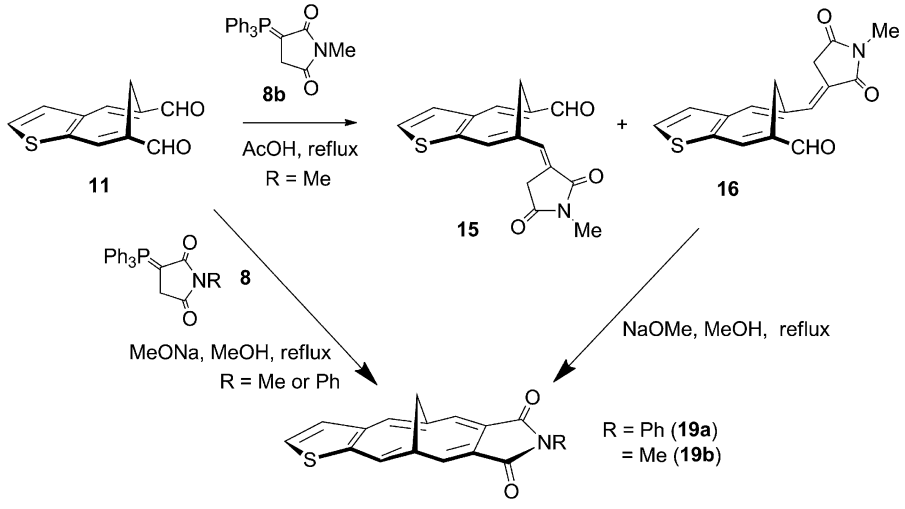
Scheme 3. Reaction of **9** with **8a**, **8b**, **8c**, and **8e**.



Scheme 4. Reaction of **10** with **8b**.

8 under acidic conditions do not produce the expected annulenedicarboximides but instead the condensation products **12** and **14**, in addition to a mixture of **15** and **16**, in contrast with the results for **2**. However, these monocondensation products were successfully converted to the desired annulenedicarboximides **17**, **18**, and **19**, respectively, by treatment with sodium alkoxide in an alcohol at reflux. Their yields are shown in Table 2 (Entries 1–6). In addition to the above results, it was found that these annulenedicarboximides could be synthesized directly by the reaction of the dicarbaldehydes with **8** under basic conditions with alkoxide. These results are also summarized in Table 2 (Entries 7–14). Although some yields of the annulenedicarboximides are still low and some reactions require relatively long reaction times, the results demonstrate that arene-annulated annulenedicarboximides can be synthesized in one step from suitable 1,2-dicarbaldehydes.

In the intermediate products **12** and **14** as well as in the mixture of **15** and **16**, the conjugated carbonyl group of the succinimide moiety is in a *syn* arrangement with the vinyl hydrogen atom Ha (Figure 3).[11] This was deduced from the somewhat low-field chemical shifts of the Ha protons in the NMR spectra[12] and was also confirmed by X-ray



Scheme 5. Reaction of **11** with **8a** and **8b**.

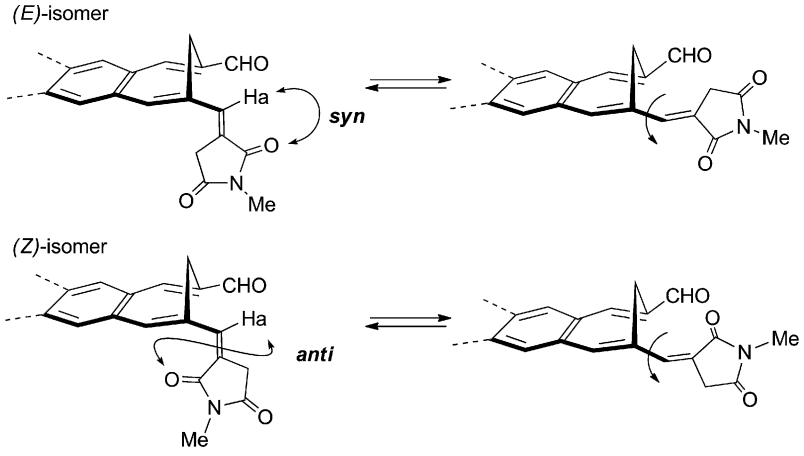


Figure 3. Structures of the (*E*) and (*Z*) stereoisomers of the intermediate products and their rotational isomers.

Table 2. Synthesis of **17**, **18**, and **19** from dicarbaldehydes **9**, **10**, and **11** with phosphoranes **8** and from the intermediates **12**, **14**, and **15**/**16** under basic conditions.

Entry	Substrate/reaction conditions	Product/ yield[a]
1	**12a/**MeONa (1.0 equiv.), MeOH, reflux, 24 h	**17a**/85%
2	**12b/**MeONa (1.0 equiv.), MeOH, reflux, 24 h	**17b**/70%
3	**12c/**MeONa (1.0 equiv.), MeOH, reflux, 24 h	**17c**/85%
4	**12e/**EtONa (1.0 equiv.), EtOH, reflux, 48 h	**17e**/33%
5	**14/**EtONa (1.0 equiv.), EtOH, reflux, 48 h	**18**/32%
6	**15** + **16/**MeONa (1.0 equiv.), Me, reflux, 3 h	**19b**/83%
7	**9** + **8a**[b]/MeONa (2.0 equiv.), MeOH, reflux, 70 h	**17a**/43%
8	**9** + **8b**[b]/MeONa (2.0 equiv.), MeOH, reflux, 70 h	**17b**/70%
9	**9** + **8c**[b]/MeONa (2.0 equiv.), MeOH, reflux, 70 h	**17c**/53%
10	**10** + **8b**[c]/MeONa (2.0 equiv.), MeOH, reflux, 70 h	**18**/33%
11	**10** + **8b**[b]/EtONa (2.0 equiv.), EtOH, reflux, 50 h	**18**/52%
12	**11** + **8a**[b]/MeONa (2.0 equiv.), MeOH, reflux, 55 h	**19a**/86%
13	**11** + **8b**[d]/MeONa (2.0 equiv.), MeOH, reflux, 40 h	**19b**/74%
14	**11** + **8b**[b]/EtONa (2.0 equiv.), EtOH, reflux, 40 h	**19b**/81%

[a] Isolated yield after chromatographic purification. [b] 1.5 equiv. of **8** relative to the dicarbaldehyde was used. [c] 1.0 equiv. of **8** relative to the dicarbaldehyde was used. [d] 1.2 equiv. of **8** relative to the dicarbaldehyde was used.

crystallographic analysis of **12e** and **14**. ORTEP drawings of **12e** and **14** are presented in Figures 4 and 5. The cycloheptatriene part in **14** has an unusual almost-planar structure.[13] This stereochemical relationship of the vinylidene succinimide opportunely demonstrates the advantage of access to reaction sites for the subsequent intramolecular aldol condensation. On the basis of the numbers of ^{1}H and ^{13}C NMR signals, the double-condensation products **13b** and **13c** are found to possess a symmetrical structure around the long molecular axis. From this fact and the chemical shifts of the vinyl hydrogen atom Ha, it is clear that they also possess the same stereochemical relationship with respect to the vinyl group. The structures of the new annulenedicarboximides were confirmed by spectroscopic and/or combustion analyses. The crystal structures of **1a**, **17b**, and **18** were determined by X-ray crystallographic analysis. Their ORTEP drawings are shown in Figures 6–8 and reveal that their 1,6-methano[10]annulene skeletons do not exhibit significant structural deformation, but slight bond alternation between single and double C–C bonds is observed. The deviation of the C–C bond lengths of the parent 1,6-methano[10]annulene[14] from the average length (1.396 Å) is ±0.024 Å[15] and that for the annulene part in **1a** from the average length (1.395 Å) is ±0.023 Å; therefore, the annulation of the five-membered imide ring does not have any effect on the 1,6-methano[10]annulene skeleton. On the other hand, the deviation from the average length in **17b** (1.402 Å) is ±0.053 Å, and that from the average length in **18** (1.404 Å) is ±0.080 Å, which clearly demonstrates that the bond alternation of the annulene ring is attributable to the benzene and naphthalene annulations.

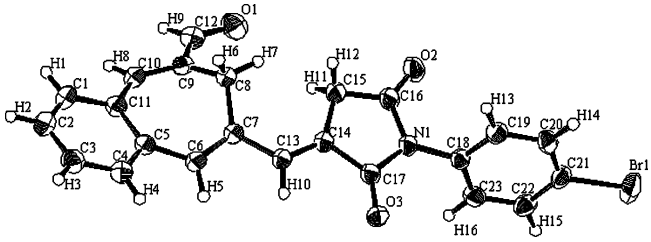


Figure 4. An ORTEP drawing of **12e** showing our numbering system.

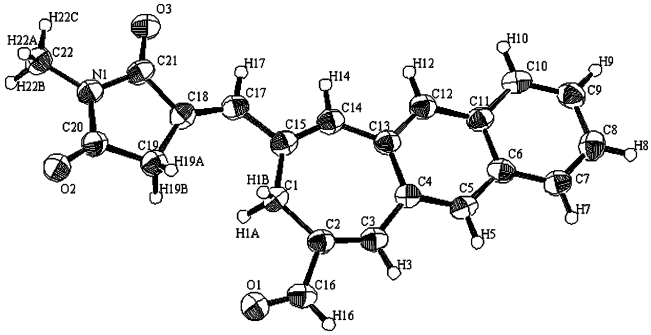


Figure 5. An ORTEP drawing of **14** showing our numbering system. One of two independent structures is shown.

As described above, we accomplished a short-step synthesis of various *N*-substituted 1,6-methano[10]annulene-3,4-dicarboximides **1** and their arene-annulated analogs

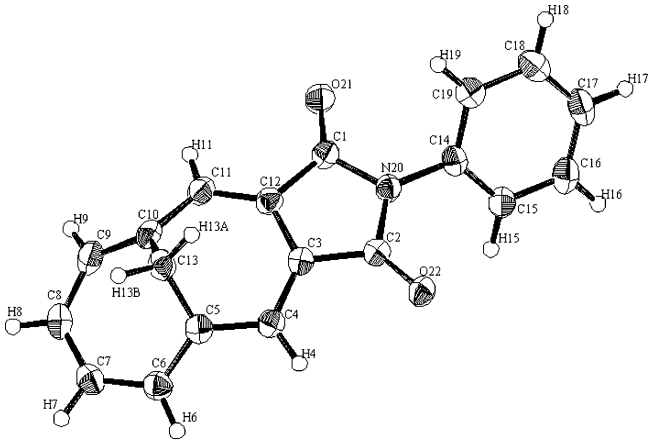


Figure 6. An ORTEP drawing of **1a** showing our numbering system.

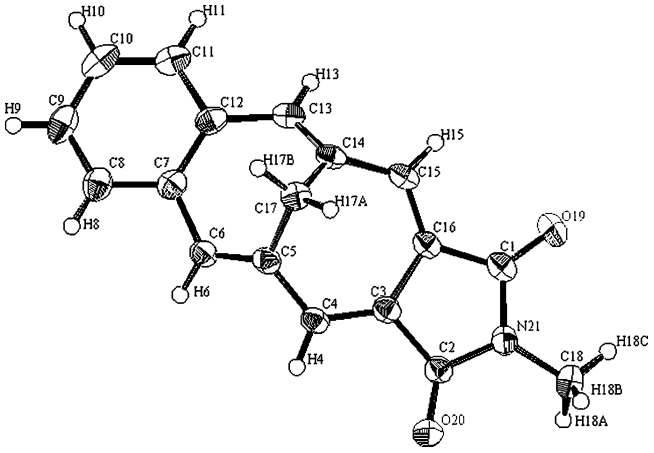


Figure 7. An ORTEP drawing of **17b** showing our numbering system.

from dicarbaldehydes **2** and **9**–**11**. Although **2** reacts with phosphorane reagents **8** under acidic conditions directly to produce **1**, **9**–**11** react with **8** under the same acidic conditions to produce only the Wittig condensation products.

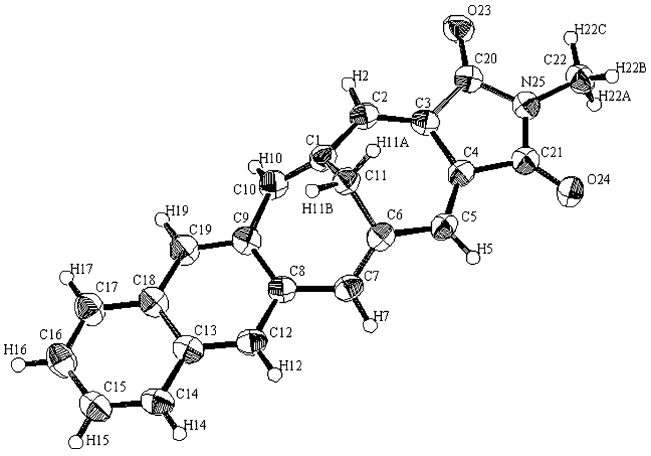
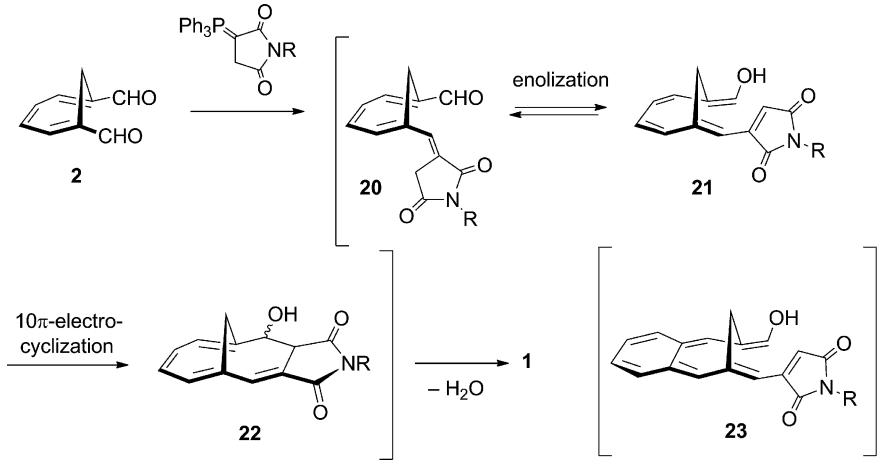


Figure 8. An ORTEP drawing of **18** showing our numbering system.

The different results depending on the dicarbaldehyde used can be rationalized by the following mechanistic speculation. As many 10π-electrocyclizations to form the carbon framework of 1,6-methano[10]annulene have been reported,[3c,16,17] a route from the condensation product **20** to **1** via **21** and **22** is very plausible (Scheme 6). That is, the enolization of **20**, the subsequent 10π-electrocyclization to generate the skeleton of 1,6-methano[10]annulene, and the final dehydration of **22** results in the formation of the aromatic ring to produce **1**. The use of acetic acid as the solvent can assist the enolization and also the dehydration. On the other hand, similar enol intermediates derived from **9**–**11**, such as **23** in Scheme 6, should be hard to form because of the disruption of aromaticity by the formation of a partial quinodimethane structure.

The photophysical data of the *N*-methyldicarboximides **1b**, **17b**, **18**, and **19b** are listed in Table 3. The UV/Vis absorption spectra show four main absorption bands above 240 nm, except for that of **18**, which has three main bands.[18] From their wavelengths and relatively small molar coefficients, the longest-wavelength bands in the absorption



Scheme 6. A possible reaction mechanism from **2** to **1** under acidic conditions and the corresponding intermediate **23** to **21** starting from **9**.

spectra (except for that of **18**) can be assigned to the n–π* transition of the imide carbonyl groups. The other absorption bands can be assigned to π–π* transitions, which exhibit relatively high molar coefficients and clear redshifts along with a degree of π-conjugation. In particular, the third-lowest energy bands in the spectra show an obvious redshift of 40–60 nm as a result of arene annulation. As the longest-wavelength absorption for **18** at 422 nm exhibits a greater molar coefficient than those of the n–π* transition bands of the other compounds, it can be assigned to a π–π* transition. The n–π* transition absorption band of **18** is probably concealed by the longest-wavelength band. All of the dicarboximides show emission upon excitation of the long-wavelength bands. The benzene-annulated compound **17b** displays a comparable emission quantum yield (10%) to that of **1b**. However, the quantum yields of **18** and **19b** were found to be less than 1%.

Table 3. Photophysical data of the *N*-methyldicarboximides **1b**, **17b**, **18**, and **19b**.

	UV/Vis absorption λ_{max} [nm] ($\log\varepsilon$)	λ_{em} [nm] (Φ)[a]
1b	246 (4.39), 286 (4.69), 325 (3.81), 420 (3.11)	470 (0.097)[b]
17b	276 sh (4.39), 305 (4.65), 367 (3.72), 436 sh (3.21)	527 (0.10)
18	278 (4.48), 318 (4.75), 422 (3.81)	568 (0.0058)
19b	285 (4.37), 315 (4.75), 359 (3.89), 437 (3.21)	532 (0.0028)

[a] Photoexcitation at the longest-wavelength absorption maximum. [b] Taken from ref.[1]

Conclusions

We have demonstrated a short-step synthesis of the annulenedicarboximides **1**, **17**, **18**, and **19** by the reactions of 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (**2**) and its arene-annulated dicarbaldehydes **9**, **10**, and **11** with phosphorane **8**. Although **1** can be obtained in one step under either acidic or basic conditions, **17**, **18**, and **19** were obtained in one step only under basic conditions. The synthesis of **1** by our method presents a clear improvement compared with previously reported procedures. The dicarbaldehydes **9**, **10**, and **11** react with phosphorane **8** to produce mono- and double-condensation products, the former of which can be transformed to the annulenedicarboximides **17**, **18**, and **19**. The crystal structures of some annulenedicarboximides and the intermediate condensation products were determined by X-ray analysis. The structures of the latter can conveniently rationalize the basic intramolecular cyclization.

Experimental Section

General Remarks: Melting points were measured with a Yanaco MP-3 instrument. IR spectra were recorded with JEOL Diamond-20 and JASCO FT/IR-4100 spectrometers. UV/Vis spectra were recorded with a Shimadzu UV-2550 spectrometer. Emission spectra were recorded with a Shimadzu RT-5300PC spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with JEOL lambda 400 and ECA500 spectrometers. Tetramethylsilane (δ = 0 ppm) was used as the internal standard for ^{1}H NMR spectra, and $CDCl_3$ (δ = 77.0 ppm) was used as the internal standard for ^{13}C NMR spectra. Mass spectra were recorded with a JMS-700 mass spectrometer. Column chromatography was performed with Silica gel 60N from Kanto Chem. Phthalaldehyde, thiophene-2,3-dicarbaldehyde, triphenylphosphine, *N*-phenylmaleimide, *N*-methylmaleimide, and *N*-ethylmaleimide were purchased from Tokyo Chemical Industry, Inc. A pentanedial aqueous solution was purchased from Aldrich Chem. Co. 2,3-Naphthaldehyde was prepared from phthalaldehyde and 2,5-dimethoxytetrahydrofuran by the method of Lepage et al.[19] The dicarbaldehyde **2** was prepared in five steps from 1,3,5-cycloheptatriene according to the method of Vogel et al.[20] The dicarbaldehydes **9** and **10** were prepared from phthalaldehyde and 2,3-naphthaldehyde with pentanedial by the method of Lepage et al.[9] The phosphorane reagents **8a** and **8i** was prepared from the corresponding maleimides with triphenylphosphine by the method of Hedaya et al.[8a]

Preparation of Phosphorane Reagents 8: A mixture of *N*-substituted maleimide (10.0 mmol) and triphenylphosphine (10.5 mmol) in AcOH (20 mL) under a nitrogen atmosphere was heated to reflux with an oil bath for 3 h, and then the solvent was removed under vacuum. The slightly brown residual oil was crystallized by the addition of diethyl ether or diethyl ether/acetone. The crystalline product was collected by suction filtration and washed well with dry diethyl ether.

***N*-Phenyltriphenylphosphoranylidenesuccinimide (8a):** Colorless solid (90% yield), m.p. 165–167 °C (ref.[8a] 176.5–178.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (m, 9 H), 7.53 (m, 6 H), 7.46 (m, 2 H), 7.39 (m, 2 H), 7.23 (tt, J = 7.4, 1.4 Hz, 1 H), 3.16 (d, J = 1.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.0 (d, $^3J_{C,P}$ = 16.7 Hz), 169.9 (d, $^2J_{C,P}$ = 15.5 Hz), 134.1, 133.4 (d, $^2J_{C,P}$ = 10.7 Hz), 132.7 (d, $^4J_{C,P}$ = 2.4 Hz), 129.2 (d, $^3J_{C,P}$ = 11.9 Hz), 128.5, 126.7, 126.7, 125.5 (d, $^1J_{C,P}$ = 91.8 Hz), 37.0 (d, $^2J_{C,P}$ = 9.5 Hz), 36.0 (d, $^1J_{C,P}$ = 137.1 Hz) ppm.

***N*-Methyltriphenylphosphoranylidenesuccinimide (8b):** Colorless solid (78% yield), m.p. 158–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (m, 9 H), 7.52 (m, 6 H), 3.01 (s, 3 H), 2.99 (d, J = 1.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3 (d, $^3J_{C,P}$ = 16.4 Hz), 171.2 (d, $^2J_{C,P}$ = 15.2 Hz), 133.3 (d, $^2J_{C,P}$ = 10.7 Hz), 132.6 (d, $^4J_{C,P}$ = 2.4 Hz), 129.1 (d, $^3J_{C,P}$ = 12.2 Hz), 125.6 (d, $^1J_{C,P}$ = 93.2 Hz), 36.9 (d, $^2J_{C,P}$ = 10.4 Hz), 35.3 (d, $^1J_{C,P}$ = 139.9 Hz), 24.3 ppm. MS (FAB): *m*/*z* (%) = 374 (100) [M + H]$^+$, 279 (18), 262 (10), 183 (11). HRMS: calcd. for $C_{23}H_{21}NO_2P$ [M + H]$^+$ 374.1304; found 374.1313.

***N*-Ethyltriphenylphosphoranylidenesuccinimide (8c):** Colorless solid (85% yield), m.p. 171–173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (m, 9 H), 7.52 (m, 6 H), 3.58 (q, J = 7.0 Hz, 2 H), 2.98 (d, J = 1.4 Hz, 2 H) 1.20 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.0 (d, $^3J_{C,P}$ = 16.1 Hz), 170.9 (d, $^2J_{C,P}$ = 15.5 Hz), 133.3 (d, $^2J_{C,P}$ = 10.4 Hz), 132.6 (d, $^4J_{C,P}$ = 2.5 Hz), 129.1 (d, $^3J_{C,P}$ = 12.0 Hz), 125.7 (d, $^1J_{C,P}$ = 92.0 Hz), 36.6 (d, $^2J_{C,P}$ = 10.5 Hz), 35.1 (d, $^1J_{C,P}$ = 137.9 Hz), 32.8, 13.8 ppm. MS (FAB): *m*/*z* (%) = 388 (100) [M + H]$^+$, 280 (12), 279 (59), 262 (10), 137 (21), 107 (10), 89 (11), 77 (12). HRMS: calcd. for $C_{24}H_{23}NO_2P$ [M + H]$^+$ 388.1461; found 388.1469.

***N*-(4-Methoxyphenyl)triphenylphosphoranylidenesuccinimide (8d):**[8b,21] Colorless solid (82% yield), m.p. 171–172 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (m, 9 H), 7.53 (m, 6 H), 7.36 (dt, J = 9.0, 2.7 Hz, 2 H), 6.93 (dt, J = 9.0, 2.7 Hz, 2 H), 3.78 (s, 3 H), 3.14 (d, J = 1.2 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.2 (d, $^3J_{C,P}$ = 15.8 Hz), 170.1 (d, $^2J_{C,P}$ = 15.6 Hz), 158.2, 133.4 (d, $^2J_{C,P}$ = 10.8 Hz), 132.7 (d, $^4J_{C,P}$ = 2.6 Hz), 129.2 (d, $^3J_{C,P}$ = 12.2 Hz), 127.9, 127.0, 125.5 (d, $^1J_{C,P}$ = 93.2 Hz), 114.0, 55.5, 37.0 (d, $^2J_{C,P}$ = 10.1 Hz), 35.9 (d, $^1J_{C,P}$ = 137.1 Hz) ppm. MS (FAB): *m*/*z* (%) =

466 (100) [M + H]$^+$, 279 (39), 262 (13), 183 (11), 155 (11), 138 (13), 137 (29), 107 (14), 91 (10), 90 (10), 89 (14), 77 (15). HRMS: calcd. for $C_{29}H_{25}NO_3P$ [M + H]$^+$ 466.1567; found 466.1568.

***N*-(4-Bromophenyl)triphenylphosphoranylidenesuccinimide (8e):** Colorless solid (83% yield), m.p. 163–165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (m, 9 H), 7.54 (m, 6 H), 7.55 (dt, J = 8.9, 2.4 Hz, 2 H), 7.44 (dt, J = 8.9, 2.4 Hz, 2 H), 3.14 (d, J = 1.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.7 (d, $^3J_{C,P}$ = 16.4 Hz), 169.3 (d, $^2J_{C,P}$ = 16.4 Hz), 133.3 (d, $^2J_{C,P}$ = 10.2 Hz), 133.2, 132.8 (d, $^4J_{C,P}$ = 3.2 Hz), 131.5, 129.2 (d, $^3J_{C,P}$ = 12.9 Hz), 128.0, 125.2 (d, $^1J_{C,P}$ = 92.0 Hz), 120.0, 36.9 (d, $^2J_{C,P}$ = 10.4 Hz), 36.3 (d, $^1J_{C,P}$ = 136.1 Hz) ppm. MS (FAB): *m*/*z* (%) = 514 (67) [M + H]$^+$, 513 (22), 287 (29), 280 (20), 279 (100), 262 (23), 201 (14), 185 (14), 183 (21), 155 (17), 138 (21), 137 (45), 120 (10), 107 (20), 91 (14), 90 (14), 89 (21), 77 (21). HRMS: calcd. for $C_{28}H_{22}{}^{79}BrNO_2P$ [M + H]$^+$ 514.0566; found 514.0567.

***N*-(4-Nitrophenyl)triphenylphosphoranylidenesuccinimide (8f):** Colorless solid (68% yield), m.p. 144–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (d, J = 9.2 Hz, 2 H), 9.15 (d, J = 9.2 Hz, 2 H), 7.65 (m, 9 H), 7.57 (m, 6 H), 3.18 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.4 (d, ^3J = 16.5 Hz), 168.4 (d, ^2J = 16.2 Hz), 145.2, 140.2, 133.4 (d, ^3J = 10.5 Hz), 133.0 (d, $^4J_{C,P}$ = 2.5 Hz), 129.3 (d, ^3J = 12.3 Hz), 126.2, 124.8 (d, ^1J = 92.7 Hz), 123.8, 37.3 (d, ^1J = 136.2 Hz), 36.8 (d, ^3J = 13.1 Hz) ppm. MS (FAB): *m*/*z* (%) = 481 (100) [M + H]$^+$, 480 (24), 287 (32), 279 (57), 262 (31), 183 (29), 155 (16), 138 (18), 137 (39), 107 (21), 91 (19), 90 (16), 89 (24), 77 (25), 69 (23). HRMS: calcd. for $C_{28}H_{22}N_2O_4P$ [M + H]$^+$ 481.1312; found 481.1315.

***N*-(4-Iodophenyl)triphenylphosphoranylidenesuccinimide (8g):** Colorless solid (75% yield), m.p. 145–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (dt, J = 8.7, 2.3 Hz, 2 H), 7.64 (m, 9 H), 7.53 (m, 6 H), 7.26 (dt, J = 8.7, 2.3 Hz, 2 H), 3.14 (d, J = 2.3 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.76 (d, $^3J_{C,P}$ = 16.1 Hz), 169.2 (d, $^2J_{C,P}$ = 15.8 Hz), 137.5, 133.9, 133.4 (d, $^2J_{C,P}$ = 10.4 Hz), 132.8 (d, $^4J_{C,P}$ = 2.6 Hz), 129.2 (d, $^3J_{C,P}$ = 12.2 Hz), 128.3, 125.2 (d, $^1J_{C,P}$ = 93.2 Hz), 91.4, 36.9 (d, $^2J_{C,P}$ = 10.4 Hz), 36.3 (d, $^1J_{C,P}$ = 138.3 Hz) ppm. MS (FAB): *m*/*z* (%) = 562 (100) [M + H]$^+$, 561 (46), 536 (38), 287 (39), 279 (94), 262 (32), 154 (53), 137 (33), 136 (49). HRMS: calcd. for $C_{28}H_{22}NO_2PI$ [M + H]$^+$ 562.0427; found 562.0435.

***N*-(Biphenyl-4-yl)triphenylphosphoranylidenesuccinimide (8h):** Colorless solid (71% yield), m.p. 160–162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (m, 11 H), 7.54 (m, 10 H), 7.41 (t, J = 7.6 Hz, 2 H), 7.32 (tt, J = 7.6, 1.9 Hz, 1 H), 3.18 (d, J = 1.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.0 (d, $^3J_{C,P}$ = 16.1 Hz), 169.8 (d, $^2J_{C,P}$ = 15.6 Hz), 141.1, 139.5, 133.4 (d, $^2J_{C,P}$ = 10.1 Hz), 132.7 (d, $^4J_{C,P}$ = 2.4 Hz), 129.23, 129.18 (d, $^3J_{C,P}$ = 12.8 Hz), 128.6, 127.3, 127.2, 127.0, 126.8, 125.4 (d, $^1J_{C,P}$ = 92.0 Hz), 37.1 (d, $^2J_{C,P}$ = 12.7 Hz), 36.2 (d, $^1J_{C,P}$ = 137.0 Hz) ppm. MS (FAB): *m*/*z* (%) = 512 (100) [M + H]$^+$, 511 (56), 510 (27), 288 (18), 287 (63), 279 (37), 262 (28), 185 (15), 183 (25), 154 (15). HRMS: calcd. for $C_{34}H_{27}NO_2P$ [M + H]$^+$ 512.1774; found 512.1775.

Triphenylphosphoranylidenesuccinimide (8i): Colorless solid (64% yield), m.p. 194–196 °C (ref.[8a] 220 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (m, 9 H), 7.53 (m, 6 H), 7.21 (br, 1 H), 3.03 (d, J = 1.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.7 (d, $^3J_{C,P}$ = 16.7 Hz), 170.7 (d, $^2J_{C,P}$ = 14.3 Hz), 133.4 (d, $^2J_{C,P}$ = 10.7 Hz), 132.8 (d, $^4J_{C,P}$ = 2.4 Hz), 129.2 (d, $^3J_{C,P}$ = 13.1 Hz), 125.4 (d, $^1J_{C,P}$ = 91.8 Hz), 38.3 (d, $^2J_{C,P}$ = 9.5 Hz), 36.7 (d, $^1J_{C,P}$ = 135.9 Hz) ppm.

***N*-Phenyl-1,6-methano[10]annulene-3,4-dicarboximide (1a):** A mixture of **2** (29.6 mg, 0.200 mmol) and phosphorane **8a** (131 mg, 0.300 mmol) in AcOH (2 mL) under a nitrogen atmosphere was heated to reflux with an oil bath for 16 h, and then the solvent was removed under vacuum. The residue was carefully poured into a cold $NaHCO_3$ aqueous solution and extracted with $CHCl_3$ (10 mL × 3). The combined organic layers were washed with brine and dried with Mg_2SO_4. The solvent was evaporated, and the brown residue was purified by silica gel chromatography (hexane/EtOAc 85:15) to give **1a** (40.2 mg, 70%) as yellow prisms, m.p. 159–160 °C (ref.[2] 170–171 °C; ref.[1a] 158–159 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 2 H), 7.64 (m, 2 H), 7.49 (m, 4 H), 7.40 (m, 1 H), 7.36 (m, 2 H), 0.21 (dt, J = 9.9, 1.2 Hz, 1 H), –0.14 (dt, J = 9.9, 1.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 132.1, 130.9, 130.1, 129.2, 129.0, 128.1, 128.0, 126.5, 119.6, 35.5 ppm.

Synthesis of *N*-Substituted and Unsubstituted 1,6-Methano[10]annulene-3,4-dicarboximides (1b–1h and 6): The reactions of **2** with phosphorane **8** under the conditions of Table 1 and Figure 1 gave **1b**–**1h** and **6**. The products were purified by silica gel chromatography (hexane/EtOAc).

***N*-Methyl-1,6-methano[10]annulene-3,4-dicarboximide (1b):** Yellow prisms (26.0 mg, 58%),[22] m.p. 169–170 °C (ref.[1a] 168–170 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 2 H), 7.57 (m, 2 H), 7.33 (m, 2 H), 3.21 (s, 3 H), 0.18 (dt, J = 9.9, 1.2 Hz, 1 H), –0.21 (dt, J = 9.9, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 130.4, 129.9, 129.2, 128.7, 119.4, 35.8, 24.5 ppm.

***N*-Ethyl-1,6-methano[10]annulene-3,4-dicarboximide (1c):** Yellow microcrystals (23.2 mg, 48%),[22] m.p. 164–166 °C (ref.[1a] 163–165 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 2 H), 7.58 (m, 2 H), 7.32 (m, 2 H), 3.77 (q, J = 7.2 Hz, 2 H), 1.28 (t, J = 7.2 Hz, 3 H), 0.19 (dt, J = 9.8, 1.2 Hz, 1 H), –0.22 (dt, J = 9.8, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 130.4, 129.9, 129.2, 128.8, 119.4, 35.7, 33.4, 14.0 ppm.

***N*-(4-Methoxyphenyl)-1,6-methano[10]annulene-3,4-dicarboximide (1d):** Yellow microcrystals (37.3 mg, 58%),[22] m.p. 216–218 °C (ref.[1a] 217–218 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 2 H), 7.62 (m, 2 H), 7.36 (m, 4 H), 7.02 (dt, J = 9.0, 2.8 Hz, 2 H), 3.85 (s, 3 H), 0.22 (dt, J = 9.9, 1.2 Hz, 1 H), –0.16 (dt, J = 9.9, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 159.3, 130.9, 130.1, 129.3, 128.3, 128.0, 124.8, 119.7, 114.5, 55.7, 35.6 ppm.

***N*-(4-Bromophenyl)-1,6-methano[10]annulene-3,4-dicarboximide (1e):** Yellow microcrystals (48.7 mg, 65%)[22] m.p. 210–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 2 H), 7.64 (m, 2 H), 7.62 (dt, J = 8.8, 2.4 Hz, 2 H), 7.39 (dt, J = 8.8, 2.4 Hz, 2 H), 7.36 (m, 2 H), 0.20 (dt, J = 9.8, 1.2 Hz, 1 H), –0.14 (dt, J = 9.8, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 132.3, 131.3, 131.2, 130.3, 129.5, 128.04, 127.99, 121.8, 119.9, 35.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1750 (s), 1374 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 367 (62) [M]$^+$, 365 (63) [M]$^+$, 323 (15), 321 (16), 286 (10), 227 (10), 168 (43), 143 (13), 141 (12), 140 (100), 169 (71). $C_{19}H_{12}BrNO_2{\cdot}0.2H_2O$ (369.8): calcd. C 61.71, H 3.38, N 3.79; found C 61.55, H 3.54, N 3.78.

***N*-(4-Nitrophenyl)-1,6-methano[10]annulene-3,4-dicarboximide (1f):** Bright yellow microcrystals (47.9 mg, 72%)[22] m.p. 271–272 °C (ref.[1a] 268–270 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 2 H), 8.37 (dt, J = 9.2, 2.5 Hz, 2 H), 7.82 (dt, J = 9.2, 2.5 Hz, 2 H), 7.67 (m, 2 H), 7.39 (m, 2 H), 0.19 (dt, J = 9.9, 1.3 Hz, 1 H), –0.10 (dt, J = 9.9, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 146.4, 138.1, 131.6, 130.5, 129.7, 127.6, 126.5, 124.5, 120.1, 35.5 ppm.

***N*-(4-Iodophenyl)-1,6-methano[10]annulene-3,4-dicarboximide (1g):** Yellow plates (50.4 mg, 61%)[22] m.p. 225–227 °C. ^{1}H NMR

(500 MHz, $CDCl_3$): δ = 8.36 (s, 2 H), 7.83 (dt, J = 6.9, 2.3 Hz, 2 H), 7.64 (m, 2 H), 7.36 (m, 2 H), 7.26 (dt, J = 6.9, 2.3 Hz, 2 H), 0.19 (dt, J = 9.8, 1.2 Hz, 1 H), –0.14 (dt, J = 9.8, 1.1 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.8, 138.3, 132.0, 131.2, 130.3, 129.5, 128.2, 128.0, 119.9, 93.3, 35.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1766 (s), 1711 (s), 1698 (vs), 1153 (s), 1137 (s), 815 (s), 772 (s), 754 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 413 (100) $[M]^+$, 369 (11), 242 (15), 168 (25), 140 (56). HRMS: calcd. for $C_{19}H_{12}INO_2$ $[M]^+$ 412.9913; found. 412.9911.

***N*-(Biphenyl-4-yl)-1,6-methano[10]annulene-3,4-dicarboximide (1h):** Light yellow prisms (39.7 mg, 55%),[22] m.p. 232–237 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 2 H), 7.72 (dt, J = 8.4, 1.7 Hz, 2 H), 7.64 (m, 2 H), 7.62 (dm, 2 H), 7.56 (dt, J = 8.4, 1.7 Hz, 2 H), 7.46 (tm, J = 7.2 Hz, 2 H), 7.37 (m, 3 H), 0.24 (d, J = 9.9 Hz, 1 H), –0.14 (d, J = 9.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 141.1, 140.6, 131.4, 131.1, 130.3, 129.4, 129.0, 128.3, 128.0, 127.7, 127.4, 126.9, 119.8, 35.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1763 (s), 1704 (vs), 1518 (s), 1488 (s), 1154 (s), 765 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 363 (68) $[M]^+$, 319 (10), 286 (7), 207 (10), 168 (43), 152 (23), 140 (100), 139 (68), 86 (11), 84 (28), 69 (14). $C_{25}H_{17}NO_2 \cdot 0.2H_2O$ (367.0): calcd. C 81.81, H 4.78, N 3.82; found C 81.80, H 4.86, N 3.74.

1,6-Methano[10]annulene-3,4-dicarboximide (6): Yellow microcrystals (25.9 mg, 62%),[22] m.p. 249–251 °C (ref.[1a] 248–250 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 2 H), 7.96 (br, 1 H), 7.61 (m, 2 H), 7.34 (m, 2 H), 0.10 (dt, J = 9.9, 1.3 Hz, 1 H), –0.20 (dt, J = 9.9, 1.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 130.8, 130.3, 129.4, 129.1, 119.5, 35.4 ppm.

6*H*-Cyclohepta[*b*]thiophene-5,7-dicarbaldehyde (11): A 50% aqueous solution of pentanedial (6.00 g, 30.0 mmol) was added dropwise to a solution of thiophene-2,3-dicarbaldehyde (2.80 g, 20.0 mmol) and piperidine (4.40 mL) in AcOH (25 mL) at 100 °C under a nitrogen atmosphere. This mixture was heated at 120 °C for 2 h and then cooled to room temperature. The resultant dark brown mixture was diluted with water (300 mL) and extracted with $CHCl_3$ (100 mL × 3). The combined organics layers were washed with a saturated $NaHCO_3$ aqueous solution and brine and dried with Mg_2SO_4. The solvent was evaporated, and the residue was crystallized from hexane/$CHCl_3$ to give **11** (3.77 g, 92%) as yellow needles, m.p. 194–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 9.56 (s, 1 H), 7.64 (d, J = 5.2 Hz, 1 H), 7.50 (s, 1 H), 7.45 (s, 1 H), 7.30 (d, J = 5.2 Hz, 1 H), 3.29 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 190.5, 140.7, 140.5, 139.3, 138.7, 134.4, 133.5, 130.4, 130.1, 18.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1667 (vs), 1615 (s), 1600 (vs), 1422 (s), 1410 (s), 1230 (s), 1215 (vs), 1169 (vs), 1127 (s), 948 (s), 888 (s), 758 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 204 (100) $[M]^+$, 175 (72), 147 (76), 145 (13), 121 (10). HRMS calcd. for $C_{11}H_8O_2S$ $[M]^+$ 204.0245; found 204.0248. $C_{11}H_8O_2S$ (204.2) calcd. C 64.69, H 3.95, S 15.70; found C 64.99, H 3.98, S 16.78.

Reaction of 3,4-Benzocyclohepta-1,3,5-triene-1,6-dicarbaldehyde (9) with Phosphoranes 8 in AcOH: A mixture of **9** (100 mg, 0.505 mmol) and (220 mg, 0.505 mmol) in AcOH (4 mL) under a nitrogen atmosphere was heated to reflux with an oil bath for 18 h, and then the solvent was removed under vacuum. The residue was carefully poured into a mixture of cold $NaHCO_3$ aqueous solution and $CHCl_3$ and extracted with $CHCl_3$ (15 mL × 3). The combined organic layers were washed with brine and dried with Mg_2SO_4. The solvent was evaporated, and the residue was purified by silica gel chromatography ($CHCl_3$/EtOAc 70:30) to give **12a** (41.3 mg, 23%) as yellow microcrystals, m.p. 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.62 (s, 1 H), 7.56 (d, J = 7.2 Hz, 1 H), 7.51–7.36 (m, 10 H), 7.10 (s, 1 H), 4.16 (d, J = 2.0 Hz, 2 H), 3.19 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 173.4, 170.6, 147.9, 140.5, 139.7, 137.1, 136.4, 136.1, 134.5, 132.2, 132.0, 131.8, 129.8, 129.3, 128.7, 128.4, 126.6, 123.8, 34.2, 22.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1765 (m), 1703 (vs), 1666 (s), 1631 (m), 1386 (s), 1375 (s), 1178 (s), 755 (s), 741 (m), 701 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 355 (100) $[M]^+$, 337 (49), 293 (21), 235 (18), 207 (41), 178 (69), 165 (30), 149 (26), 139 (16), 91 (24), 69 (26), 57 (39). HRMS: calcd. for $C_{23}H_{17}N_2O_3$ $[M]^+$ 355.1208; found 355.1212.

Similarly, the products **12b**–**12c**, **12e**, **13b**, **13c**, **14**, and a mixture of **15** and **16** (Schemes 3–5) were obtained.

6-Formyl-1-(*N*-methylsuccinimidylidenemethyl)-3,4-benzocyclohepta-1,3,5-triene (12b): Yellow prisms (78.3 mg, 53%),[23] m.p. 188–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 7.55 (d, J = 7.3 Hz, 1 H), 7.42–7.49 (m, 4 H), 7.29 (td, J = 2.0, 0.8 Hz, 1 H), 7.05 (d, J = 0.8 Hz, 1 H), 3.69 (d, J = 2.0 Hz, 2 H), 3.14 (s, 2 H), 3.11 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 174.3, 171.6, 147.7, 139.9, 139.6, 137.0, 136.0, 135.2, 134.4, 131.8, 131.7, 129.6, 128.1, 124.2, 25.0, 33.8, 22.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1759 (s), 1694 (vs), 1665 (vs), 1628 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 293 (100) $[M]^+$, 275 (17), 264 (19), 208 (25), 207 (18), 206 (15), 190 (14), 189 (11), 181 (16), 180 (31), 179 (93), 178 (74), 177 (16), 176 (17), 169 (25), 165 (28), 152 (20), 151 (12), 141 (13), 139 (12), 137 (11), 115 (13), 89 (15). $C_{18}H_{15}NO_3 \cdot 0.2H_2O$ (296.9): calcd. C 72.81, H 5.23, N 4.72; found C 72.81, H 5.31, N 4.69.

1,6-Bis(*N*-methylsuccinimidylidenemethyl)-3,4-benzocyclohepta-1,3,5-triene (13b): Yellow solid (53.2 mg, 27%),[23] m.p. 270–273 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.37 (m, 4 H), 7.29 (t, J = 2.2 Hz, 2 H), 7.00 (s, 2 H), 3.52 (d, J = 2.2 Hz, 4 H), 3.11 (s, 6 H), 2.90 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 170.9, 136.3, 136.0, 134.29, 134.28, 131.4, 128.0, 124.0, 34.1, 32.9, 25.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1758 (s), 1698 (vs), 1433 (s), 1277 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 388 (100) $[M]^+$, 329 (19), 303 (15), 302 (13), 301 (11), 277 (12), 276 (23), 275 (13), 272 (10), 264 (30), 250 (11), 245 (13), 218 (18), 217 (24), 215 (38), 203 (22), 202 (32), 192 (18), 191 (25), 190 (13), 189 (17), 179 (43), 178 (40), 166 (11), 165 (26), 152 (17), 137 (17), 108 (14), 101 (12). $C_{23}H_{20}N_2O_4 \cdot 0.7H_2O$ (401.0): calcd. C 68.88, H 5.38, N 6.99; found C 68.99, H 5.37, N 7.00.

6-Formyl-1-(*N*-ethylsuccinimidylidenemethyl)-3,4-benzocyclohepta-1,3,5-triene (12c): Yellow prisms (74.5 mg, 48%),[22] m.p. 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 7.54 (d, J = 7.2 Hz, 1 H), 7.46 (m, 4 H), 7.29 (td, J = 2.2, 0.8 Hz, 1 H), 7.04 (s, 1 H), 3.94 (d, J = 2.2 Hz, 1 H), 3.68 (q, J = 7.2 Hz, 2 H), 3.14 (s, 2 H), 1.22 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 174.2, 171.4, 147.9, 139.9, 139.7, 137.2, 136.2, 135.2, 134.5, 132.0, 131.8, 129.7, 128.2, 124.4, 34.0, 28.3, 22.3, 13.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1756 (vs), 1688 (vs), 1672 (vs), 1626 (vs), 1439 (s), 1409 (s), 1398 (vs), 1381 (s), 1339 (vs), 1214 (vs), 1156 (vs), 1136 (vs), 1041 (s), 744 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 307 (100) $[M]^+$, 278 (13), 236 (13), 208 (43), 191 (11), 179 (100), 169 (45), 151 (31), 141 (20), 115 (16), 94 (16), 89 (37), 76 (27). $C_{19}H_{17}NO_3 \cdot 0.1H_2O$ (309.1): calcd. C 73.82, H 5.61, N 4.35; found C 73.75, H 5.61, N, 4.45.

1,6-Bis(*N*-ethylsuccinimidylidenemethyl)-3,4-benzocyclohepta-1,3,5-triene (13c): Yellow solid (22.8 mg, 11%),[22] m.p. 248–252 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (m, 4 H), 7.28 (t, J = 2.1 Hz, 2 H), 6.99 (s, 2 H), 3.68 (q, J = 7.2 Hz, 4 H), 3.51 (d, J = 2.1 Hz, 4 H), 2.90 (s, 2 H), 1.23 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 170.6, 136.2, 136.0, 134.1, 134.2, 131.4, 127.9, 124.1, 34.1, 33.9, 32.9, 13.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1763 (s), 1700 (vs), 1630 (s), 1399 (s), 1342 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 416 (100) $[M]^+$, 371 (13), 343 (19), 317 (16), 290 (42),

278 (36), 264 (13), 244 (66), 215 (58), 202 (55), 192 (77), 179 (99), 165 (51), 151 (41), 139 (17), 123 (46), 108 (96), 95 (63), 84 (71), 71 (56). $C_{25}H_{24}N_2O_4 \cdot 0.2H_2O$ (420.1): calcd. C 71.48, H 5.85, N 6.67; found C 71.24, H 5.86, N 6.65.

6-Formyl-1-[*N*-(4-bromophenyl)succinimidylidenemethyl]-3,4-benzocyclohepta-1,3,5-triene (12e): Yellow prisms (44.4 mg, 20%),[22] m.p. 244–246 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.61 (s, 1 H), 7.61 (m, 2 H), 7.56 (d, J = 7.5 Hz, 1 H), 7.48 (m, 4 H), 7.41 (dt, J = 1.9, 0.9 Hz, 1 H), 7.10 (s, 1 H), 4.16 (d, J = 2.0 Hz, 2 H), 3.17 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.0, 173.0, 170.2, 147.9, 140.8, 139.6, 137.0, 136.8, 136.0, 134.5, 132.4, 132.0, 131.9, 131.2, 129.8, 128.4, 128.1, 123.4, 122.4, 34.1, 22.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1703 (s), 1672 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 435 (100) $[M]^+$, 433 (99) $[M]^+$, 236 (16), 235 (22), 234 (13), 208 (34), 207 (31), 206 (19), 181 (12), 180 (22), 179 (78), 178 (75), 177 (14), 176 (11), 170 (12), 169 (33), 165 (21), 152 (13), 141 (10). HRMS: calcd. for $C_{23}H_{16}{}^{79}BrNO_3$ $[M]^+$ 433.0314; found 433.0310.

1-Formyl-6-(*N*-methylsuccinimidylidenemethyl)naphtho[2,3:3,4]cyclohepta-1,3,5-triene (14): Yellow prisms (77.6 mg, 46%),[23] m.p. 261–265 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.62 (s, 1 H), 8.03 (s, 1 H), 7.90 (m, 3 H), 7.58 (m, 3 H), 7.36 (td, J = 1.8, 0.8 Hz, 1 H), 7.00 (s, 1 H), 3.93 (d, J = 1.8 Hz, 2 H), 3.28 (s, 2 H), 3.12 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 174.2, 171.5, 148.9, 141.2, 140.6, 137.4, 135.9, 133.6, 133.4, 132.5, 132.4, 132.0, 131.7, 128.3, 128.24, 128.16, 127.7, 123.8, 34.0, 24.9, 22.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1760 (s), 1686 (vs), 1670 (vs), 1645 (s), 1632 (s), 1436 (s), 1275 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 343 (100) $[M]^+$, 229 (64), 228 (86), 226 (33), 215 (26), 202 (28). HRMS: calcd. for $C_{22}H_{17}NO_3$ $[M]^+$ 334.1208; found 334.1206. $C_{22}H_{17}NO_3$ (343.4): calcd. C 76.95, H 4.99, N 4.08; found C 76.61, H 5.21, N 4.07.

Mixture of 5-Formyl-7-(*N*-methylsuccinimidylidenemethyl)-6*H*-cyclohepta[*b*]thiophene (15) and 7-Formyl-5-(*N*-methylsuccinimidylidenemethyl)-6*H*-cyclohepta[*b*]thiophene (16): Yellow solid (98.9 mg, 66%),[23] m.p. 173–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.58 (s, 1 H), 9.56 (s, 1 H), 7.60 (d, J = 5.2 Hz, 1 H), 7.53 (s, 1 H), 7.49 (s, 1 H), 7.48 (s, 1 H), 7.27 (m, 3 H), 7.19 (d, J = 5.2 Hz, 1 H), 7.16 (s, 1 H), 7.10 (s, 1 H), 4.02 (m, 4 H), 3.22 (m, 4 H), 3.11 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 191.4, 174.33, 174.28, 171.5, 171.4, 143.6, 141.7, 141.3, 139.5, 138.3, 137.8, 134.9, 134.3, 134.1, 133.2, 132.2, 131.9, 130.5, 130.21, 130.19, 130.1, 129.5, 127.9, 125.0, 124.8, 34.0, 33.9, 25.0, 24.9, 23.4, 23.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1760 (s), 1693 (vs), 1664 (s) 1432 (s), 1382 (s), 1280 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 299 (100) $[M]^+$, 270 (24), 214 (19), 213 (17), 185 (78), 171 (13), 139 (11). HRMS: calcd. for $C_{16}H_{13}NO_2S$ $[M]^+$ 299.0616; found 299.0616.

***N*-Phenyl-2,7-methanobenzo[10]annulene-4,5-dicarboximide (17) from 12:** A mixture of **12a** (35.5 mg, 0.100 mmol) and NaOMe (5.4 mg, 0.10 mmol) in MeOH (4 mL) under a nitrogen atmosphere was gently heated to reflux with an oil bath for 24 h. The resultant reaction mixture was carefully poured into a 0.1 M HCl aqueous solution and extracted with $CHCl_3$ (10 mL × 3). The combined organic layers were washed with a saturated $NaHCO_3$ aqueous solution and brine and dried with Mg_2SO_4. The solvent was evaporated, and the residue was purified by silica gel chromatography ($CHCl_3$) to give **17a** (28.7 mg, 85%) as yellow microcrystals, m.p. 219–222 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (t, J = 1.2 Hz, 2 H), 8.04 (m, 2 H), 7.63 (m, 2 H), 7.53–7.49 (m, 4 H), 7.46 (dt, J = 7.1, 1.6 Hz, 2 H), 7.41 (tt, J = 7.1, 1.6 Hz, 1 H), 1.47 (dt, J = 10.7, 1.1 Hz, 1 H), 0.37 (td, J = 10.7, 1.3 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.2, 136.7, 134.9, 132.2, 131.9, 129.2, 128.6, 128.5, 128.3, 127.3, 127.0, 126.7, 32.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1760 (m), 1698 (vs), 1379 (s), 1152 (s), 741 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 337 (100) $[M]^+$, 293 (34), 292 (16), 278 (7), 217 (17), 190 (62), 189 (60). $C_{23}H_{15}NO_2 \cdot 0.1H_2O$ (339.2): calcd. C 81.45, H 4.52, N 4.13; found C 71.49, H 4.51, N 4.15.

Similarly, the products **17b**, **17c**, **17e**, **18**, **19a**, and **19b** (Schemes 3–5 and Table 2) were obtained.

***N*-Methyl-2,7-methanobenzo[10]annulene-4,5-dicarboximide (17b):** Yellow prisms (19.3 mg, 70% based on **12b**),[24] m.p. 226–228 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (t, J = 1.1 Hz, 2 H), 8.01 (m, 2 H), 7.60 (m, 2 H), 7.43 (t, J = 1.1 Hz, 2 H), 3.20 (s, 3 H), 1.43 (dt, J = 8.4, 1.0 Hz, 1 H), 0.35 (dt, J = 8.4, 1.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 135.5, 134.8, 131.6, 128.4, 128.1, 127.5, 126.8, 32.3, 24.5 ppm. IR [attenuated total reflectance (ATR)]: $\tilde{\nu}_{max}$ = 1749 (m), 1687 (vs) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 275 (100) $[M]^+$, 274 (21), 190 (75), 189 (51), 95 (18). HRMS: calcd. for $C_{18}H_{13}NO_2$ $[M]^+$ 275.0946, found 275.0939.

***N*-Ethyl-2,7-methanobenzo[10]annulene-4,5-dicarboximide (17c):** Yellow microcrystals (24.7 mg, 85% based on **12c**),[24] m.p. 175–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (t, J = 1.2 Hz, 2 H), 8.01 (m, 2 H), 7.60 (m, 2 H), 7.43 (br s, 2 H), 3.76 (q, J = 7.2 Hz, 2 H), 1.44 (dt, J = 10.6, 1.1 Hz, 1 H), 1.28 (t, J = 7.2 Hz, 3 H), 0.35 (dt, J = 10.6, 1.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 135.5, 135.0, 131.8, 128.6, 128.2, 127.9, 126.9, 33.6, 32.4, 13.7 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 1754 (s), 1693 (vs), 1402 (s), 740 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 289 (100) $[M]^+$, 274 (75), 261 (26), 247 (12), 218 (16), 190 (91), 187 (11), 123 (14), 109 (14), 94 (80), 83 (24). $C_{19}H_{15}NO_2 \cdot 0.1H_2O$ (291.1): calcd. C 78.39, H 5.26, N 4.81; found C 78.77, H 5.31, N 4.77.

***N*-(4-Bromophenyl)-2,7-methanobenzo[10]annulene-4,5-dicarboximide (17e):** Yellow microcrystals (13.5 mg, 33% based on **12e**),[24] m.p. 216–219 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42 (s, 2 H), 8.04 (m, 2 H), 7.63 (m, 4 H), 7.51 (s, 2 H), 7.38 (dt, J = 8.6, 1.7 Hz, 2 H), 1.44 (d, J = 10.7 Hz, 1 H), 0.36 (d, J = 10.7 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.8, 136.9, 134.8, 132.2, 131.8, 131.1, 128.6, 128.4, 128.0, 127.0, 127.0, 122.0, 32.1 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 1763 (m), 1708 (s), 1379 (s), 799 (m), 735 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 417 (100) $[M]^+$, 415 (98) $[M]^+$, 373 (18), 372 (10), 371 (18), 218 (11), 217 (19), 191 (13), 190 (76), 189 (66), 168 (21). HRMS: calcd. for $C_{23}H_{14}{}^{79}BrNO_2$ $[M]^+$ 415.0208; found 415.0206.

***N*-Methyl-2,7-methanonaphtho[2,3][10]annulene-4,5-dicarboximide (18):** Yellow microplates (10.2 mg, 32% based on **14**),[24] m.p. 240–243 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 2 H), 8.22 (t, J = 1.2 Hz, 2 H), 8.03 (m, 2 H), 7.61 (m, 2 H), 7.38 (s, 2 H), 3.20 (s, 3 H), 1.80 (dt, J = 10.9, 1.2 Hz, 1 H), 1.14 (dt, J = 10.9, 1.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 135.8, 133.5, 132.3, 131.5, 130.7, 128.0, 127.8, 127.0, 126.8, 32.4, 24.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 1751 (m), 1690 (vs) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 325 (100) $[M]^+$, 324 (31), 239 (56), 237 (17). $C_{22}H_{15}NO_2$ (325.4): calcd. C 81.21, H 4.65, N 4.30; found C 81.30, H 4.94, N 4.40.

***N*-Phenyl-2,7-methanothieno[2,3][10]annulene-4,5-dicarboximide (19a):** Yellow microcrystals (29.5 mg, 86% based on **11**),[24] m.p. 140–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.53 (m, 1 H), 8.44 (m, 1 H), 7.95 (s, 1 H), 7.86 (s, 1 H), 7.76 (d, J = 5.5 Hz, 1 H), 7.60 (d, J = 5.5 Hz, 1 H), 7.56–7.46 (m, 4 H), 7.40 (tt, J = 7.1, 1.6 Hz, 1 H), 0.74 (dm, J = 10.6 Hz, 1 H), –0.10 (dt, J = 10.6, 1.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7 (2 C), 141.8, 139.9, 135.2, 134.4, 132.2, 129.2, 128.7, 128.2, 128.1, 128.0, 127.9, 126.6, 126.2, 124.2, 121.6, 120.3, 33.2 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 1754 (s), 1701 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 343 (100) $[M]^+$, 342 (15), 299 (34), 298 (16), 223 (12), 196 (49), 195 (40). HRMS: calcd. for $C_{21}H_{13}NO_2S$ $[M]^+$ 343.0667; found 343.0666.

***N*-Methyl-2,7-methanothieno[2,3][10]annulene-4,5-dicarboximide (19b):** Golden yellow microcrystals (28.5 mg, 83% based on a mix-

ture of **15** and **16**),[24] m.p. 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (m, 1 H), 8.31 (m, 1 H), 7.88 (s, 1 H), 7.80 (s, 1 H), 7.74 (d, J = 5.5 Hz, 1 H), 7.58 (d, J = 5.5 Hz, 1 H), 3.21 (s, 3 H), 0.73 (dt, J = 10.6, 1.2 Hz, 1 H), –0.11 (dt, J = 10.6, 1.2 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.94, 168.92, 140.7, 139.4, 133.7, 132.9, 129.2, 128.1, 128.0, 127.8, 126.2, 124.2, 120.7, 119.4, 32.8, 24.1 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 1757 (s), 1698 (vs) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 343 (100) $[M]^+$, 342 (15), 299 (34), 298 (16), 223 (12), 196 (49), 195 (40). HRMS calcd. for $C_{16}H_{11}NO_2S$ $[M]^+$ 281.0510; found; 281.0504. $C_{16}H_{11}NO_2S$ (281.3): calcd. C 68.31, H 3.94, N 4.98, S 11.40; found C 68.62, H 3.98, N 4.98, S 12.00.

X-ray Crystallographic Analysis: The diffraction measurements were conducted with a Rigaku R-AXIS RAPID diffractometer. The crystal data for **1a** are as follows: monoclinic, space group $P2_1/c$ (no. 14), a = 9.2687(2) Å, b = 14.8940(3) Å, c = 10.1047(2) Å, β = 94.1965(9)°, V = 1391.19(5) Å^3, Z = 4, μ = 7.192 cm^{-1}, R = 0.0454, $wR2$ = 0.1090, $R1$ = 0.0401 [$I > 2.0\sigma(I)$], and S = 1.082. The crystal data for **12e** are as follows: monoclinic, space group $P2_1$ (no. 4), a = 6.8512(2) Å, b = 20.2644(4) Å, c = 13.6466(3) Å, β = 92.8941(7)°, V = 1892.22(6) Å^3, Z = 4, μ = 31.659 cm^{-1}, R = 0.0387, $wR2$ = 0.0966, $R1$ = 0.0364 [$I > 2.0\sigma(I)$], and S = 1.0569. The crystal data for **14** are as follows: triclinic, space group $P\bar{1}$ (no. 1), a = 6.0211(1) Å, b = 12.4895(3) Å, c = 21.5614(5) Å, α = 89.983(2)°, β = 89.999(2)°, γ = 81.989(2)°, V = 1605.60(6) Å^3, Z = 4, μ = 7.672 cm^{-1}, R = 0.0743, $wR2$ = 0.1752, $R1$ = 0.0676 [$I > 2.0\sigma(I)$], and S = 1.007. The crystal data for **17b** are as follows: monoclinic, space group $P2_1/c$ (no. 14), a = 8.9068(3) Å, b = 12.5694(4) Å, c = 12.3307(4) Å, β = 107.233(2)°, V = 1318.50(8) Å^3, Z = 4, μ = 7.316 cm^{-1}, R = 0.0699, $wR2$ = 0.1564, $R1$ = 0.0622 [$I > 2.0\sigma(I)$], and S = 1.143. The crystal data for **18** are as follows: orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.5236(2) Å, b = 8.7190(3) Å, c = 27.3097(9) Å, V = 1553.37(8) Å^3, Z = 4, μ = 7.140 cm^{-1}, R = 0.0588, $wR2$ = 0.1298, $R1$ = 0.0543 [$I > 2.0\sigma(I)$], and S = 1.122. CCDC-988796 (for **1a**), -988798 (for **12e**), -988797 (for **14**), -988795 (for **17b**), and -988794 (for **18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of new compounds and UV/Vis absorption and emission spectra of **1b**, **17b**, **18**, and **19b**.

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[10] Dicarbaldehyde **11** was obtained by condensation of thiophene-2,3-dicarbaldehyde and pentanedial; see the Experimental Section for details.

[11] Although the structures of **12**, **14**, **15**, and **16** in Schemes 3–5 are drawn as the rotational isomer shown at the left side of Figure 3 for convenience, the crystal structures of **12e** and **14** were revealed to be the other isomer shown at the right side in Figure 3. The two rotational isomers should be in equilibrium in solution.

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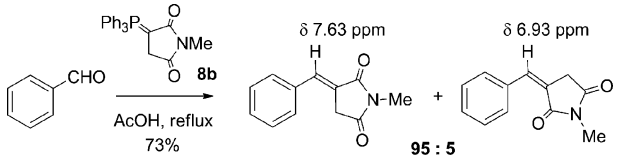

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[21] No spectroscopic data of **8d** are reported in ref.[8b]

[22] The actual quantity of the product and its yield in a reaction with 0.2 mmol of the dicarbaldehyde.

[23] The actual quantity of the product and its yield in a reaction with 0.505 mmol of the dicarbaldehyde.

[24] The actual quantity of the product and its yield in a reaction with 0.1 mmol of the dicarbaldehyde.

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