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Synthesis of Benzo[*c*] and Naphtho[*c*]heterocycle Diesters and Dinitriles via Homoelongation

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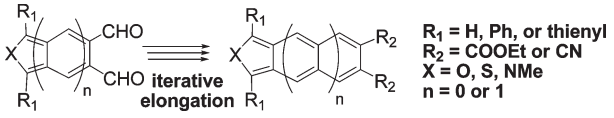

Syntheses of benzo[*c*] and naphtho[*c*]heterocycle diesters and dinitriles were achieved via our newly developed iterative elongation protocol. The photophysical and electrochemical properties of these conjugated systems are explored.

Introduction

Historically, benzo[2,3-*c*]heterocycles have been crucial players in the developments of many important areas in physical organic chemistry. While the early synthesis of 1,3-diphenylbenzo[*c*]furan (and the benzo[*c*]pyrrole and benzo[*c*]thiophene counterparts) was mainly intended as a stepping stone to understand aromaticity,[1] diphenylbenzo-[*c*]furan has since become a standard reactive diene to trap highly strained olefins.[2] Furthermore, benzo[*c*]furan and benzo[*c*]pyrrole deirvatives are often employed as synthetic building blocks of more extended conjugated systems.[3] These molecules have also been widely employed and implicated in material science. Wudl's pioneer study on benzo[*c*]thiophene-based polymers revealed a new class of low band gap materials.[4] More recently, pyroelectric property has been found in some tellurophene derivatives.[5] Computational study also identified naphtho[*c*]heterocycles as good candidates for light-harvesting dyes in solar cell.[6] Yet, despite such a rich heritage, the synthetic routes to these benzo[*c*]heterocycles are quite limited. Especially, benzo[2,3-*c*]heterocycle derivatives bearing electron-withdrawing substitutions on the six-membered ring are very rare in the literature.[7] To fill this gap, we wish to report a new method to construct benzo[*c*]heterocycle 5,6-diesters, 5,6-dinitriles, and their naphtho[*c*] analogues with an iterative strategy.

We recently developed an iterative synthesis of acene diesters and dinitriles.[8] Using aromatic *ortho*-dialdehydes as starting materials, this homoelongation protocol that combines a Wittig olefination and subsequent intramolecular Knoevenagel condensation produces acene diesters

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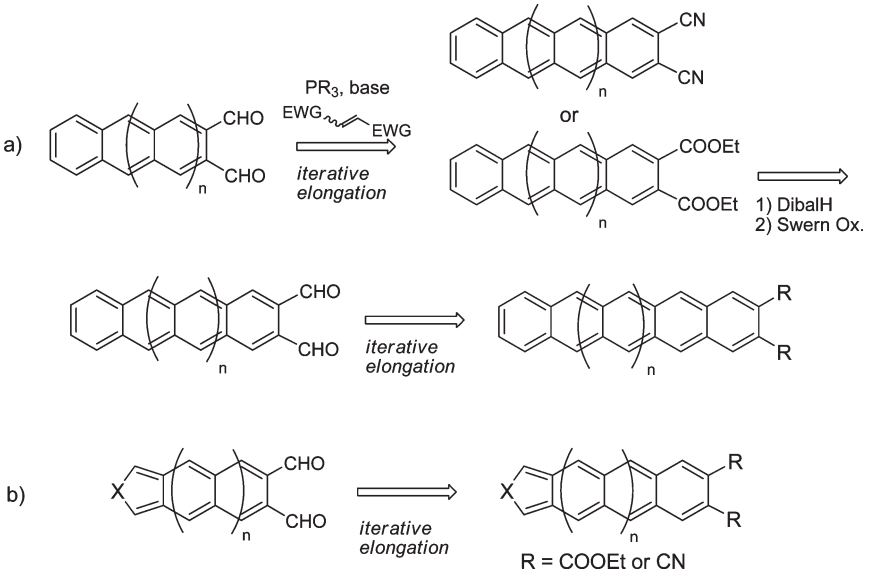
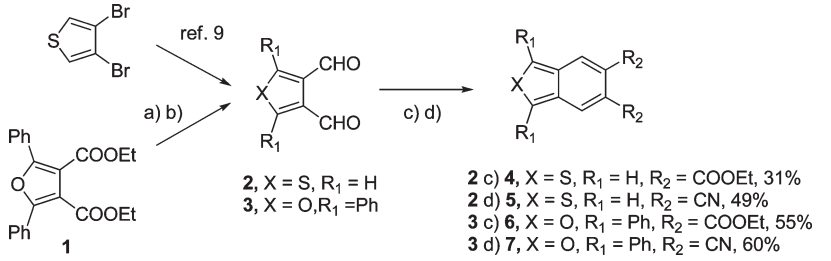
SCHEME 1. Iterative Elongation to Acene and Heteroacene



SCHEME 2. Synthesis of Benzo[*c*]thiophene and Benzo[*c*]furan Diesters and Dinitriles



Reagents and conditions: (a) $LiBH_4$, $B(OMe)_3$, THF, 45 °C, 93%; (b) $(COCl)_2$, DMSO, then Et_3N, 94%; (c) diethyl maleate, P(*n*-Oct)$_3$ for **4** and **5**, PEt_3 for **4** and **5**, DBU, dichloromethane; (d) fumaryl nitrile, P(*n*-Oct)$_3$ for **4** and **5**, PEt_3 for **4** and **5**, DBU, dichloromethane.

and dinitriles. The acene diesters thus produced can be converted into dialdehydes and undergo a further round of elongation (Scheme 1a). This new protocol opens the opportunity to synthesize acene[*c*]heterocycle diesters and dinitriles accordingly from appropriate dialdehydes (Scheme 1b).

Result and Discussion

Synthesis. As a start, thiophene-3,4-dicarbaldehyde **2** was synthesized from 3,4-dibromothiophene via a known double lithiation and formylation protocol.[9] 2,5-Diphenylfuran-3,4-dicarbaldehyde **3** was obtained from the known diethyl 2,5-diphenylfuran-3,4-dicarboxylate **1**[10] in two steps ($LiBH_4$ reduction, then Swern oxidation). The key elongation reaction was then carried out with the two compounds to give benzo[*c*]thiophenes **4** and **5** and diphenylbenzo[*c*]furans **6** and **7** as depicted in Scheme 2. Both triethylphosphine and trioctylphosphine can be employed in the elongation reaction. However, we noted that consistently triethylphosphine gave higher yield in this key step. This reagent was therefore used in all latter elongation reactions.

With this initial success, the most intuitive approach to diethyl 1,3-diphenylbenzo[*c*]thiophene-5,6- dicarboxylate **10**, 1,3-diphenylbenzo[*c*]thiophene-5,6-dicarbonitrile **11**, and their benzo[*c*]pyrrole analogues seems to be the homoelongation of the corresponding thiophene and pyrrole dialdehydes similar to the synthesis of **6** and **7** in Scheme 2. However, we found it is difficult to prepare the required dialdehyde in large scale. An alternative reaction sequence in Scheme 3 is therefore adopted to construct these aromatic heterocycles.

The conversion of *ortho*-dibenzoyl benzene to benzo[*c*]thiophene and benzo[*c*]pyrrole is one of the best-established entries to these structures.[11] We took full advantage of this prior knowledge in this study (Scheme 3). The required diketones **8** and **9** can be easily synthesized from **6** and **7** almost quantitatively through oxidation under ambient light. Treatment of the diketones **8** and **9** with phosphorus pentasulfide furnished benzo[*c*]thiophenes **10** and **11** very efficiently. Likewise, reductive amination of **8** and **9** produced benzo[*c*]pyrroles **12** and **13** in respectable yields.

After we accomplished the synthesis of benzo[*c*]heterocycle diesters and dinitriles, the obvious next step was to

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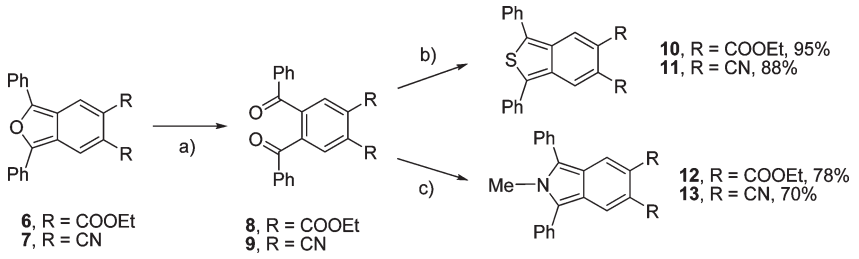
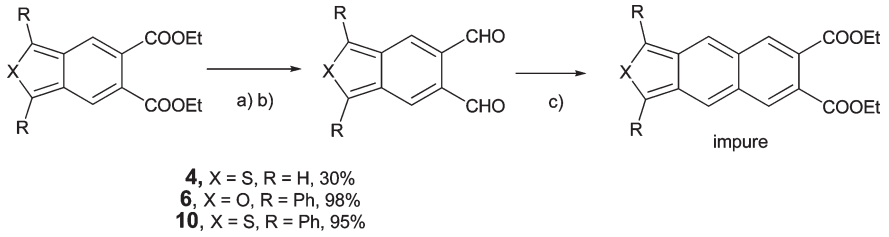
SCHEME 3. Synthesis of Benzo[*c*]thiophene and Benzo[*c*]pyrrole Diesters and Dinitriles



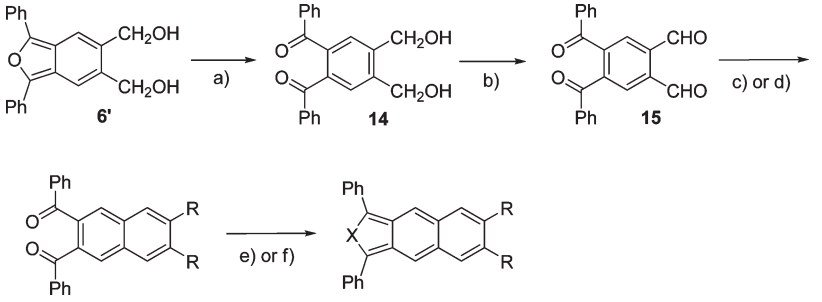
Reagents and conditions: (a) *hν*, air (O_2), dichloromethane, rt, 48 h, 99%; (b) P_2S_5, refluxing pyridine; (c) CH_3NH_2 in refluxing MeOH then $NaBH_4$/diglyme at rt.

SCHEME 4. Failed Synthesis of Naphtho[*c*]furan and Naphtho[*c*]thiophene Derivatives via Direct Elongation



Reagents and conditions: (a) Dibal-H; (b) $(COCl)_2$, DMSO, then Et_3N; (c) diethyl maleate, PEt_3, DBU, dichloromethane.

SCHEME 5. Synthesis of Naphtho[*c*]thiophene Diester and Dinitrile and the Naphtho[*c*]pyrrole Counterpart



Reagents and conditions: (a) *hν*, air (O_2), dichloromethane, rt, 48 h, 98%; (b) $(COCl)_2$, DMSO, then Et_3N, 42%; (c) diethyl maleate, PEt_3, DBU, dichloromethane; (d) fumaryl nitrile, PEt_3, DBU, dichloromethane; (e) P_2S_5, refluxing pyridine, 95%; (f) CH_3NH_2, in refluxing methanol then $NaBH_4$/diglyme at rt.

employ the same strategy to the synthesis of naphtho[*c*]heterocycles. Unfortunately, the direct elongation strategy failed to produce these compounds cleanly. As shown in Scheme 4, the conversion of diesters **4**, **6**, and **10** to dialdehydes can be achieved in moderate to very good (30% for **4** and nearly quantitative for **6** and **10** over two steps) yields. However, we were not able to carry out the key elongation step without substantial decomposition of the desired products (yields monitored using internal standard $< 10\%$ in all cases). Judged from the NMR spectrum of the crude reaction mixture, these unidentified side products seem to be of polymeric nature. After many futile efforts to optimize this step, we concluded that such decomposition is probably inevitable under the reaction condition. This predicament forced us to exploit alternative synthetic strategies.

From the synthesis of **10**−**13**, we learned that the *ortho*-diketones are very effective precursors of benzo[*c*]heterocycles. To employ this strategy in the synthesis of naphtho[*c*]-heterocycles, we need to devise an efficient access to **16** and **17**. We found this can also be easily accomplished using our homoelongation reaction. As shown in Scheme 5, the diol **6′** (intermediate in Scheme 4) can be oxidized to give diketone **14**, which was then converted to dialdehyde **15** with Swern oxidation. The homoelongation to diester **16** and dinitrile **17** was duly accomplished with standard elongation procedures. The cyclization reactions to naphtho[*c*]thiophenes **18** and **20** and naphtho[*c*]pyrroles **19** and **21** were carried out as in Scheme 3 using phosphorus pentasulfide and reductive amination, respectively.

Since dithienyl benzo[*c*]thiophene-based polymers are known to be exceptional low band gap materials,[4] we next ventured to synthesize systems with the 1,3-diphenyl substituents in previous compounds replaced with 1,3-dithienyl ones. The synthesis of key intermediate diester **22** was somewhat serendipitous. When diethyl 2,3-bis(5-bromothiophene-2-carbonyl)succinate (made

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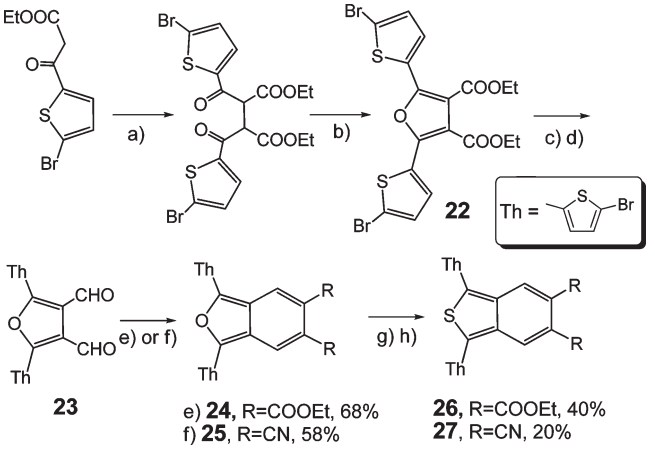
SCHEME 6. Synthesis of 1,3-Dithienylbenzo[*c*]thiophene Diester and Dinitrile and the Benzo[*c*]furan Counterparts



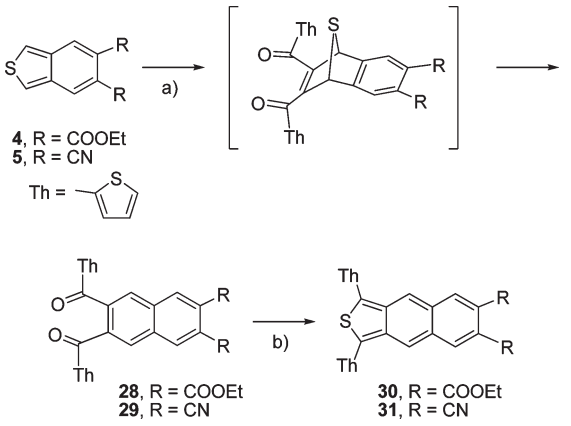
Reactions and conditions: (a) i. Na/ EtOH, rt, ii. I_2/THF.ether, rt; (b) P_2S_5, refluxing pyridine, 29% (over two steps); (c) Dibal-H, 97%; (d) $(COCl)_2$, DMSO, then Et_3N, 99%; (e) diethyl maleate, PEt_3, DBU, dichloromethane; (f) fumaryl nitrile, PEt_3, DBU, dichloromethane; (g) *hν*, air (O_2), dichloromethane, rt, 48 h; (h) P_2S_5, refluxing pyridine.

from oxidative dimerization of enolate of ethyl 3-(5-bromothiophen-2-yl)-3-oxopropionate)[9,12] was mixed with phosphorus pentasulfide, the diketone underwent cyclization to give furan **22** instead of the expected terthiophene. A likely explanation for this unanticipated result is that the intermediate monothioketone might undergo a facile cyclization (presumably with enol form of γ-ketone) faster than the formation of bis-thioketone. With the general procedure depicted in Scheme 2 (except the reductant was changed from $LiBH_4$ to DibalH), diester **22** was converted to dialdehyde **23**. The elongation reaction was also carried out accordingly to give 1,3-dithienylbenzo[*c*]furans **24** and **25** in decent yield. These two compounds were then converted into 1,3-dithienylbenzo[*c*]thiophenes **26** and **27**, respectively, using the two-step reaction sequence described in Scheme 6.

In principle, 1,3-dithienyl naphtho[*c*]thiophene derivatives can be synthesized from **24** and **25** in five steps using the strategy depicted in Scheme 4. However, Diels−Alder cycloaddition between **4** (or **5**) and 1,4-dithienylbut-2-yne-1,4-dione (synthesized via a known procedure[13]) provides a much more convergent retro-synthesis of the required naphthalene diketones **28** and **29**. As shown in Scheme 7, such cycloaddition yielded the bridge sulfide intermediates, which undergo spontaneous desulfurization to furnish the naphthalene derivatives. The subsequent cyclization was carried out according to the established procedure to give the target dithienyl naphtho[*c*]thiophenes **30** and **31** in moderate yields.

Photophysical and Electrochemical Study. The photophysical and electrochemical properties of these heteroacenes are listed in Table 1. Bathochromic shifts are observed in all of the derivatives compared with their parent systems. With two ester substituents, most of the systems exhibit 15−20 nm red shifts. The only notable deviation is compound **10**, which exhibits a red shift of 42 nm. The bathochromic shifts for the

SCHEME 7. Synthesis of 1,3-Dithienyl Naphtho[*c*]thiophene Diester and Dinitrile



Reactions and conditions: (a) ThCO−C≡C−COTh, Diels−Alder reaction; (b) P_2S_5, refluxing pyridine.

dicyano compounds are universally larger than their diester counterparts. Besides **13**, all such red shifts fall between 40 and 60 nm. The electron-withdrawing substitutions have similar effects on the emission spectra, but the bathochromic shifts in the fluorescence spectrum are generally larger than those found in the absorption spectrum. Like simple acenes, the emission quantum yields decrease with the decrease of optical band gap. The Stoke shifts in all diphenyl substituted are around 100 nm. On the other hand, the Stoke shifts of dithienyl derivatives **26**, **27**, **30**, and **31** are approximately 140 nm.

The HOMO levels of these compounds are probed by cyclic voltammetry. The results clearly demonstrate that the electron-withdrawing groups lower both HOMO and LUMO levels. Since the stabilization effect on the LUMO orbitals is apparently more pronounced, the observed red shifts can be accounted for. Similarly, the replacement of 1,3-diphenyl substitutions with 1,3-dithienyl elevates both HOMO and LUMO levels in benzo series compounds (comparing **6**, **7** and **24**, **25**, as well as in **10**, **11**, **26**, **27**). However, in the diarylnaphtho[*c*]thiophene series (**18**, **20**, **30**, **31**), such substitution effect only affects HOMO levels.

Conclusion

In summary, we have synthesized a series of benzo[*c*]heterocycle and naphtho[*c*]heterocycle diesters and dinitriles via a homoelongation strategy. Due to the presence of electron-withdrawing ester and nitrile groups, these compounds show moderate red shifts in UV and fluorescence spectra compared to the unsubstituted parent systems. The energy levels of frontier orbitals can also be modulated through substitution effect. Some of these compounds can be employed as synthons in the synthesis of higher acenes. Others have good potential as building blocks in various optical and electronic devices.[14,15] Both possibilities are currently being exploited in our group.

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TABLE 1. Photochemical and Electrochemical Data of the Benzo[*c*]heterocycle and Naphtho[*c*]heterocycle Diesters and Dinitriles

	UV λ_{max}/nm (band gap in eV)	PL λ_{max}/nm (quantum yield)	E_{ox} (HOMO)	LUMO
benzo[*c*]thiophene[14a]	343 (in MeOH)	–	–	–
4	342 (3.27)	417 (28%)		
5	356 (3.17)	422 (2%)	1.17 (−5.67)	−2.50
1,3-diphenylbenzo[*c*]furan	414	484 (99%)	0.64 (−5.14)	–
6	433 (2.55)	524 (80%)	0.88 (−5.38)	−2.83
7	458 (2.40)	546 (72%)	1.14 (−5.64)	−3.24
1,3-diphenylbenzo[*c*]thiophene[14b]	369	–	–	–
10	411 (2.69)	519 (79%)	1.12 (−5.62)	−2.93
11	431 (2.56)	536 (61%)	1.36 (−5.86)	−3.30
N-methyl-1,3-diphenylbenzo[*c*]indoline[14b]	377	453	0.54 (−5.04)	–
12	392 (2.83)	497 (70%)	0.72 (−5.22)	−2.39
13	406 (2.71)	507 (71%)	0.95 (−5.45)	−2.74
1,3-diphenylnaphtho[*c*]thiophene[11]	513	–	–	–
18	532 (2.12)	626 (19%)	0.76 (−5.26)	−3.14
20	562 (1.99)	659 (12%)	0.91 (−5.41)	−3.42
19	522 (2.15)	621 (17%)	0.36 (−4.86)	−2.71
21	562 (1.98)	663 (5%)	0.55 (−5.05)	−3.07
24	475 (2.28)	580 (34%)	0.79 (−5.29)	−3.01
25	509 (2.13)	610 (28%)	1.00 (−5.50)	−3.37
1,3-dithienylbenzo[*c*]thiophene[14e]	433	532	0.87 (−5.37)	–
26	458 (2.30)	591 (37%)	0.95 (−5.45)	−3.15
27	476 (2.20)	618 (30%)	1.13 (−5.63)	−3.43
1,3-dithienylnaphtho[*c*]thiophene[14f]	546	–	0.62	–
30	565 (1.88)	699 (13%)	0.52 (−5.02)	−3.14
31	600 (1.77)	742 (2%)	0.66 (−5.16)	−3.39

Experimental Section

Diethylbenzo[*c*]thiophene-5,6-dicarboxylate (4). Dialdehyde **2** (100 mg, 0.71 mmol) and diethyl maleate (184 mg, 1.07 mmol) were dissolved in CH_2Cl_2, and the solution was immersed in an ice bath. To this cooled solution were then slowly added a CH_2Cl_2 solution of tri-*n*-octylphosphine (397 mg, 1.07 mmol in 4 mL) and DBU (11 mg, 0.07 mmol). After being stirred for 1 h at room temperature, the reaction was directly concentrated in vacuo and the residue was purified with flash chromatography (CH_2Cl_2/hexane = 9/1) to give the pure diester product (62 mg, 31%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2 H), 7.85 (s, 2 H), 4.35 (q, J = 7.1 Hz, 4 H), 1.36 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.81, 136.53, 126.81, 124.81, 120.64, 61.34, 14.12; FAB$^+$-HRMS (M + H$^+$) calcd for $C_{14}H_{15}O_4S$ 279.0691, found 279.0698.

Benzo[*c*]thiophene-5,6-dicarbonitrile (5). The dialdehyde **2** (100 mg, 0.71 mmol) and fumaronitrile (84 mg, 1.08 mmol) were dissolved in CH_2Cl_2 (4 mL), and the solution was immersed in an ice bath. To this chilled solution were slowly added a CH_2Cl_2 solution of tri-*n*-octylphosphine (397 mg, 1.07 mmol in 4 mL) and DBU (11 mg, 0.07 mmol). The reaction was stirred at room temperature for 1 h before being concentrated. The residue was then purified with flash chromatography (CH_2Cl_2) to give the pure product (64 mg, 49%) as a lightly brown powder: IR (KBr) ν (cm^{-1}) 3129, 3118, 2219, 1391, 1156, 915, 906, 769; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2 H), 8.07 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.57, 131.63, 123.50, 116.47, 107.34; EI-HRMS (M$^+$) calcd for $C_{10}H_4N_2S$ 184.0095, found 184.0097.

Diethyl 1,3-diphenylisobenzofuran-5,6-dicarboxylate (6). To a solution of diethyl maleate (1.00 g, 5.79 mmol) in CH_2Cl_2 (11.6 mL) was added triethylphosphine solution (1.0 M in THF, 5.8 mL, 5.8 mmol), and the reaction was stirred at room temperature for 30 min. This solution of the Wittig reagent was slowly added to a CH_2Cl_2 solution of dialdehyde **3** (1.00 g, 3.62 mmol in 5.8 mL). (This reverse addition sequence was employed for the elongation of all furan derivatives to avoid the Diels−Alder reaction between the furan moiety and diethyl maleate or fumaronitrile.) The reaction was stirred for 2 h before DBU (55 mg, 0.362 mmol) was added. The reaction was stirred at room temperature for 16 h. The reaction was then concentrated, and the remaining crude product was purified on flash chromatography (CH_2Cl_2/hexane = 4/1) to give the diester **6** as a yellow solid (907 mg, 60%): IR (KBr) ν (cm^{-1}) 3057, 2982, 1721, 1283, 1243, 1114, 761, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2 H), 7.93 (d, J = 7.9 Hz, 4 H), 7.51 (dd, J = 7.9, 7.5 Hz, 4 H), 7.36 (t, J = 7.5 Hz, 2 H), 4.37 (q, J = 7.1 Hz, 4 H), 1.38 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.88, 146.86, 130.66, 129.37, 128.70, 128.37, 125.58, 124.33, 120.44, 61.80, 14.42; FAB$^+$-HRMS (M$^+$) calcd for $C_{26}H_{22}O_5$ 414.1467, found 414.1464.

1,3-Diphenylisobenzofuran-5,6-dicarbonitrile (7). To a CH_2Cl_2 solution of fumaronitrile (50 mg, 0.637 mmol in 2 mL) was added a solution of triethylphosphine (1.0 M in THF, 0.64 mL, 0.64 mmol), and the reaction was stirred for 30 min. The Wittig reagent thus generated was slowly added to a CH_2Cl_2 solution of dialdehyde **3** (110 mg, 0.398 mmol in 6.4 mL). The reaction was stirred for 2 h before DBU (6 mg, 0.039 mmol) was added. The elongation reaction was stirred for 16 h at room temperature. The solvent was removed in vacuo, and the residual crude product was purified by flash chromatography. The dicyano product **7** (70 mg, 55%) was isolated as a reddish powder: IR (KBr) ν (cm^{-1}) 3129, 3118, 2219, 1391, 1156, 914, 905, 769; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (s, 2 H), 8.16 (d, J = 7.9 Hz, 4 H), 7.59 (dd, J = 7.9, 7.4 Hz, 4 H), 7.50 (t, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.32, 132.16, 129.40, 129.27, 128.64, 125.75, 118.15, 116.57, 106.91; FAB$^+$-HRMS (M$^+$) calcd for $C_{22}H_{12}N_2O$ 320.0950, found 320.0945.

Diethyl 4,5-dibenzoylphthalate (8). A CH_2Cl_2 solution of diester **6** was (1.00 g, 2.41 mmol in 500 mL) was stirred under ambient light and atmosphere oxygen for 48 h. The solvent was then removed to give the pure diketone product **8** (1.015 g, 99%): IR (KBr) ν (cm^{-1}) 3062, 2983, 1728, 1668, 1297, 1254, 1129, 712; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2 H), 7.65 (d, J = 7.8 Hz, 4 H), 7.54 (t, J = 7.5 Hz, 2 H), 7.38 (dd, J = 7.8, 7.5 Hz, 4 H), 4.38 (q, J = 7.1 Hz, 4 H), 1.36 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.76, 166.13, 142.10, 136.30, 133.78, 133.61, 129.99, 129.79, 128.57, 62.25, 14.03; FAB$^+$-HRMS (M + H$^+$) calcd for $C_{26}H_{23}O_6$ 431.1495, found 431.1500.

4,5-Dibenzoylphthalonitrile (9). A CH_2Cl_2 solution dicyano **7** was (100 mg, 0.312 mmol in 500 mL) was stirred under ambient light and atmosphere oxygen for 48 h. The solvent was then

removed to give the pure diketone product **8** (0.103 g, 98%): IR (KBr) ν (cm^{-1}) 3100, 3035, 2233, 1679, 1660, 1292, 1257, 689; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2 H), 7.59−7.64 (m, 6 H), 7.42−7.45 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.03, 144.44, 135.40, 134.74, 134.02, 130.08, 129.18, 117.60, 114.42; EI-HRMS ($M + H^+$) calcd for $C_{22}H_{13}N_2O_2$ 337.0977, found 337.0991.

Diethyl 1,3-diphenylbenzo[*c*]thiophene-5,6-dicarboxylate (10). Diester **8** (78 mg, 0.181 mmol) and phosphorus pentasulfide (P_2S_5, 81 mg, 0.181 mmol) were dissolved in pyridine (1.5 mL), and the solution was refluxed for 15 min. The mixture was then purified by flash chromatography (under N_2, CH_2Cl_2/hexane = 4/1, under nitrogen) to give the benzo[*c*]thiophene product **10** (74 mg, 95%): IR (KBr) ν (cm^{-1}) 3058, 2993, 1714, 1559, 1540, 1275, 1236, 1052; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 2 H), 7.65 (d, J = 7.8 Hz, 4 H), 7.52 (dd, J = 7.8, 7.4 Hz, 4 H), 7.43 (t, J = 7.4 Hz, 2 H), 4.33 (q, J = 7.1 Hz, 4 H), 1.34 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.18, 138.30, 133.87, 133.25, 129.53, 129.49, 128.55, 127.74, 124.55, 61.66, 14.37; FAB^+-HRMS (M^+) calcd for $C_{26}H_{22}O_4S$ 430.1239, found 430.1231.

1,3-Diphenylbenzo[*c*]thiophene-5,6-dicarbonitrile (11). Diketone **9** (50 mg, 0.149 mmol) and phosphorus pentasulfide (P_2S_5, 66 mg, 0.148 mmol) were dissolved in pyridine (2 mL), and the solution was refluxed for 15 min. After being cooled back to room temperature, the reaction mixture was purified by flash chromatography (CH_2Cl_2/hexane = 4/1, under nitrogen) to give the pure **11** (44 mg, 88%) as an orange solid: IR (KBr) ν (cm^{-1}) 3055, 2231, 1558, 1540, 1470, 1424, 761, 699; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2 H), 7.48−7.60 (m, 10 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 139.97, 131.46, 131.10, 131.00, 129.38, 129.00, 125.54, 116.28, 106.30; FAB^+-HRMS (M^+) calcd for $C_{22}H_{12}N_2S$ 336.0721, found 336.0725.

Diethyl 2-methyl-1,3-diphenyl-2*H*-isoindole-5,6-dicarboxylate (12). To a methanol solution of diester **8** (100 mg, 0.232 mmol in 2 mL) was added methylamine (40% in methanol, 0.05 mL, 0.511 mmol). The reaction was refluxed for 30 min before being cooled back to room temperature. $NaBH_4$ (0.4 M in diglyme, 0.29 mL, 0.116 mmol) was then added, and the mixture was stirred for another 30 min. The reaction was quenched with ice water (1 mL), and the mixture was purified by flash chromatography (under N_2, CH_2Cl_2/hexane = 4/1). Benzo[*c*]pyrrole **12** was isolated as an orange solid (77 mg, 78%): IR (KBr) ν (cm^{-1}) 3052, 2986, 2958, 1719, 1288, 1237, 1221, 1110; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2 H), 7.53 (m, 8 H), 7.40−7.44 (m, 2 H), 4.30 (q, J = 7.1 Hz, 4 H), 3.86 (s, 3 H), 1.32 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.10, 131.19, 130.43, 129.12, 128.05, 127.69, 125.38, 123.56, 121.59, 61.28, 35.22, 14.43; FAB^+-HRMS (M^+) calcd for $C_{27}H_{25}NO_4$ 427.1784, found 427.1777.

2-Methyl-1,3-diphenyl-2*H*-isoindole-5,6-dicarbonitrile (13). To a methanol solution of diketone **9** (100 mg, 0.297 mmol in 3 mL) was added methylamine (40% in methanol, 0.07 mL, 0.654 mmol). After being refluxed for 30 min, the reaction was cooled back to room temperature. To this solution was added $NaBH_4$ (0.4 M in diglyme, 0.37 mL, 0.149 mmol), and the reductive cyclization reaction was stirred for 30 min before being quenched by ice water (1 mL). The solvents were removed in vacuo, and the residue was purified by flash chromatography (CH_2Cl_2/hexane = 3/1, under nitrogen) to give the benzo[*c*]-pyrrole **13** as a red solid (69 mg, 70%): IR (KBr) ν (cm^{-1}) 3051, 2923, 2216, 1350, 1255, 897, 760, 703; ^1H NMR (400 MHz, DMSO-d_6) δ 8.25 (s, 2 H), 7.70 (d, J = 7.6 Hz, 4 H), 7.63 (dd, J = 7.6, 7.3 Hz, 4 H), 3.92 (s, 3 H), 7.54 (t, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 130.16, 129.19, 129.14, 128.81, 128.61, 119.53, 117.69, 102.86, 35.71; FAB^+-HRMS (M^+) calcd for $C_{23}H_{15}N_3$ 333.1266, found 333.1271.

4,5-Bis(hydroxymethyl)-1,2-phenylenebis(phenylmethanone) (14). A CH_2Cl_2 (800 mg, 2.42 mmol in 800 mL) solution of diol **6′** was stirred under ambient light and atmosphere oxygen for 48 h. The solvent was removed to give the diketone (819 mg, 98%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 4 H), 7.58 (s, 2 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.32 (dd, J = 7.8, 7.5 Hz, 4 H), 4.79 (s, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.96, 141.99, 138.97, 136.97, 133.22, 129.76, 129.41, 128.43, 62.10; FAB^+-HRMS ($M + H^+$) calcd for $C_{22}H_{19}O_4$ 347.1283, found 347.1284.

4,5-Dibenzoylphthalaldehyde (15). To a cooled CH_2Cl_2 solution of oxalyl chloride (1.38 mL, 15.97 mmol in 6.90 mL at −78 °C) was slowly added a CH_2Cl_2 solution of DMSO (2.27 mL, 31.93 mmol in 4.54 mL). The mixed solution was stirred for 15 min before a CH_2Cl_2/DMSO mixed solution of diol **14** (790 mg, 2.28 mmol in 7 mL of DMSO and 14 mL of CH_2Cl_2) was slowly added. The reaction was left to stir for 16 h before triethylamine (6.77 mL, 47.90 mmol) was added. The reaction was warmed back to room temperature in 20 min, and the solvents were removed in vacuo. The residual solid was extracted with CH_2Cl_2, and the combined organic phase was dried over $MgSO_4$ and concentrated to give the crude product (787 mg). Since the dialdehyde is not stable enough for chromatography and other spectroscopic characterization, the purity was calibrated using NMR spectrum (328 mg, 42%, *p*-dimethoxylbenzene as internal standard): ^1H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 2 H), 8.16 (s, 2 H), 7.68 (d, J = 7.9 Hz, 4 H), 7.57 (t, J = 7.5 Hz, 2 H), 7.41 (dd, J = 7.9, 7.5 Hz, 4 H).

Diethyl 6,7-dibenzoylnaphthalene-2,3-dicarboxylate (16). Dialdehyde **15** (200 mg, 0.584 mmol, estimated by internal calibration) and diethyl maleate (141 mg, 0.818 mmol) were dissolved in CH_2Cl_2 (2.5 mL). To this solution were first slowly added triethylphosphine (1.0 M in THF, 0.85 mL, 0.85 mmol) and DBU (9 mg, 0.059 mmol). After being stirred at room temperature for 2 h, the reaction mixture was concentrated and the residual crude product was purified by flash chromatography (CH_2Cl_2/hexane = 19/1) to give pure diester **16** (152 mg, 54%): IR (KBr) ν (cm^{-1}) 3063, 2983, 1726, 1664, 1289, 1182, 1128, 712; ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2 H), 8.14 (s, 2 H), 7.79 (d, J = 7.8 Hz, 4 H), 7.56 (t, J = 7.5 Hz, 2 H), 7.42 (dd, J = 7.8, 7.5 Hz, 4 H), 4.41 (q, J = 7.2 Hz, 4 H), 1.40 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.81, 167.12, 139.57, 137.01, 133.52, 133.20, 131.67, 131.02, 130.60, 130.19, 128.70, 62.20, 14.31; FAB^+-HRMS ($M + H^+$) calcd for $C_{30}H_{25}O_6$ 481.1651, found 481.1648.

6,7-Dibenzoylnaphthalene-2,3-dicarbonitrile (17). Dialdehyde **15** (40 mg, 0.117 mmol, estimated by calibration) and fumaronitrile (12 mg, 0.154 mmol) were dissolved in CH_2Cl_2 (1 mL). The solution was cooled to 0 °C, and to this chilled mixture were slowly added triethylphosphine (1.0 M in THF, 0.16 mL, 0.16 mmol) and DBU (2 mg, 0.013 mmol). After being stirred at room temperature for 2 h, the solvent was removed and the residue was purified by flash chromatography (CH_2Cl_2/hexane = 9/1) to give the dicyano product **17** as a yellow solid (44 mg, 97%): IR (KBr) ν (cm^{-1}) 3066, 3026, 2233, 1660, 1285, 1264, 733, 702; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 2 H), 8.18 (s, 2 H), 7.76 (d, J = 7.6 Hz, 4 H), 7.60 (dd, J = 7.7, 7.6 Hz, 2 H), 7.44 (t, J = 7.7 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.94, 141.97, 136.44, 136.39, 134.12, 133.16, 130.46, 130.26, 128.97, 115.35, 113.03; FAB^+-HRMS ($M + H^+$) calcd for $C_{26}H_{15}N_2O_2$ 387.1134, found 387.1136.

Diethyl 1,3-diphenylnaphtho[2,3-*c*]thiophene-6,7-dicarboxylate (18). Diketone **16** (35 mg, 0.073 mmol) and phosphorus pentasulfide (P_2S_5, 32 mg, 0.072 mmol) were dissolved in pyridine (0.9 mL), and the solution was refluxed for 25 min. The reaction was cooled back to room temperature, and the naphtho[*c*]thiophene **18** (29 mg, 83%) was isolated in pure form after flash chromatography (CH_2Cl_2/hexane = 9/1, under nitrogen): IR (KBr) ν (cm^{-1}) 3057, 2980, 1718, 1455, 1269, 1236, 1114, 1055; ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 2 H), 8.12 (s, 2 H), 7.77 (d, J = 7.6 Hz, 4 H), 7.55 (dd, J = 7.6, 7.5 Hz,

4 H), 7.43 (t, J = 7.5 Hz, 2 H), 4.37 (q, J = 7.1 Hz, 4 H), 1.38 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.78, 135.61, 134.67, 134.24, 132.88, 129.91, 129.61, 129.57, 128.16, 127.63, 121.29, 61.66, 14.44; FAB$^+$-HRMS (M^+) calcd for $C_{30}H_{24}O_4S$ 480.1395, found 480.1388.

Diethyl 2-methyl-1,3-diphenyl-2*H*-benzo[*f*]isoindole-6,7-dicarboxylate (19). To a methanol solution of diketone **16** (50 mg, 0.104 mmol in 1 mL) was added a methanol solution of methylamine (40% in methanol, 0.02 mL, 0.196 mmol), and the mixed solution was refluxed for 30 min. After the mixture was cooled back to room temperature, $NaBH_4$ (0.4 M in diglyme, 0.74 mL, 0.294 mmol) was then slowly added. The reaction was stirred another 30 min before being quenched with ice water (0.5 mL). After the solvents were removed in vacuo, the residue was purified by flash chromatography (CH_2Cl_2, under nitrogen) to give the pure product as a deep red solid (19 mg, 40%): IR (KBr) ν (cm^{-1}) 3059, 2981, 2936, 1724, 1663, 1286, 1125, 1050; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 2 H), 8.12 (s, 2 H), 7.63 (d, J = 7.9 Hz, 4 H), 7.57 (dd, J = 7.9, 7.4 Hz, 4 H), 7.43 (t, J = 7.4 Hz, 2 H), 4.35 (q, J = 7.1 Hz, 4 H), 4.07 (s, 3 H), 1.37 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.31, 132.99, 131.95, 130.42, 129.20, 128.78, 127.63, 125.63, 124.36, 124.34, 119.51, 61.39, 35.99, 14.47; FAB$^+$-HRMS (M^+) calcd for $C_{31}H_{27}NO_4$ 477.1940, found 477.1949.

1,3-Diphenylnaphtho[2,3-*c*]thiophene-6,7-dicarbonitrile (20). Diketone **17** (30 mg, 0.078 mmol) and phosphorus pentasulfide (P_2S_5, 34 mg, 0.078 mmol) were dissolved in pyridine (0.9 mL). The solution was refluxed for 25 min. After being cooled back to room temperature, the mixture was purified by flash chromatography (CH_2Cl_2/hexane = 5/1 under nitrogen) to give the product as a red solid (21 mg, 70%): IR (KBr) ν (cm^{-1}) 3061, 2224, 1497, 1452, 1170, 921, 747, 687; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2 H), 8.21 (s, 2 H), 7.75 (d, J = 7.7 Hz, 4 H), 7.59 (dd, J = 7.7, 7.4 Hz, 4 H), 7.49 (t, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.74, 136.69, 135.48, 133.45, 129.80, 129.73, 128.82, 128.33, 122.66, 116.47, 107.14; EI-HRMS (M^+) calcd for $C_{26}H_{14}N_2S$ 386.0878, found 386.0884.

2-Methyl-1,3-diphenyl-2*H*-benzo[*f*]isoindole-6,7-dicarbonitrile (21). To a solution of diketone **17** in THF/MeOH (40 mg, 0.104 mmol in 1 mL/2 mL) was added methylamine (40% in methanol, 0.03 mL, 0.294 mmol), and the reaction was refluxed for 30 min. After the mixture was cooled back to room temperature, $NaBH_4$ (0.4 M in diglyme, 0.13 mL, 0.052 mmol) was slowly added. After being stirred for another 30 min, the reaction was then quenched with ice water (0.5 mL). The solvents were removed in vacuo, and the crude product was purified by flash chromatography (CH_2Cl_2/hexane = 9/1, under nitrogen) to give the product as a purple solid (11 mg, 29%): IR (KBr) ν (cm^{-1}) 3059, 2919, 2224, 1668, 1654, 1512, 1454, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2 H), 8.12 (s, 2 H), 7.58−7.64 (m, 8 H), 7.47−7.53 (m, 2 H), 4.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.53, 131.16, 130.51, 129.43, 128.35, 127.21, 125.57, 124.24, 120.93, 117.21, 104.79, 36.16; FAB$^+$-HRMS (M^+) calcd for $C_{27}H_{17}N_3$ 383.1422, found 383.1422.

2,5-Bis(5-bromothiophen-2-yl)furan-3,4-dicarbaldehyde (23). To a cooled toluene solution of diester **22** (−45 °C, 230 mg, 0.431 mmol in 1 mL) was slowly added diisobutylaluminum hydride (1.0 M in toluene, 3.44 mL, 3.44 mmol). After being stirred for 4 h at the same temperature, the reaction was quenched with methanol (0.18 mL) and saturated sodium potassium tartrate (30 mL). The reaction was warmed back to room temperature and extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to give the intermediate diol (194 mg, 97%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (d, J = 4.0 Hz, 2 H), 7.28 (d, J = 4.0 Hz, 2 H), 5.13 (t, J = 5.2 Hz, 2 H), 4.51 (d, J = 5.2 Hz, 4 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.69, 132.90, 131.37, 125.52, 123.56, 111.85, 52.74; FAB$^+$-HRMS (M^+) calcd for $C_{14}H_{10}{}^{79}Br_2O_3S_2$ 447.8438, found 447.8445.

To a cooled CH_2Cl_2 solution of oxalyl chloride (−78 °C, 0.21 mL, 2.44 mmol in 1.05 mL) was slowly added a CH_2Cl_2 solution of DMSO (0.35 mL, 4.93 mmol in 0.7 mL), and the mixed solution was stirred at low temperature for 15 min. To this chilled solution was then slowly added a CH_2Cl_2/DMSO mixed solution of diol (185 mg, 0.411 mmol in 3.0 mL of CH_2Cl_2 and 1.5 mL of DMSO). Triethylamine (1.05 mL, 7.43 mmol) was slowly added after the reaction proceeded for 5 h. The reaction was then warmed back to room temperature in 20 min. The solvents were removed in vacuo, and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to give the dialdehyde **23** (183 mg, 99%): IR (KBr) ν (cm^{-1}) 3090, 2842, 1657, 1546, 1488, 1423, 1370, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 2 H), 7.69 (d, J = 4.1 Hz, 2 H), 7.16 (d, J = 4.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.63, 152.82, 131.37, 130.73, 130.67, 119.73, 118.90; FAB$^+$-HRMS (M^+) calcd for $C_{14}H_6{}^{79}Br_2O_3S_2$ 443.8125, found 443.8129.

Diethyl 1,3-bis(5-bromothiophen-2-yl)isobenzofuran-5,6-dicarboxylate (24). To a CH_2Cl_2 solution of diethyl maleate (56 mg, 0.325 mmol in 1.0 mL) was slowly added triethylphosphine (1.0 M in THF, 0.32 mL, 0.32 mmol), and the reaction mixture was stirred for 30 min at room temperature. The Wittig reagent thus generated was then slowly added to a CH_2Cl_2 solution of dialdehyde **23** (90 mg, 0.202 mmol in 0.96 mL). After being stirred for 2 h, DBU (3 mg, 0.020 mmol) was added and the reaction was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (CH_2Cl_2/hexane = 4/1 under nitrogen) to give **24** as an orange solid (80 mg, 68%): IR (KBr) ν (cm^{-1}) 3098, 2979, 1718, 1559, 1541, 1509, 1274, 1247; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2 H), 7.21 (d, J = 4.0 Hz, 2 H), 7.06 (d, J = 4.0 Hz, 2 H), 4.34 (q, J = 7.1 Hz, 4 H), 1.36 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.39, 141.48, 133.51, 131.28, 129.50, 124.26, 123.30, 119.82, 113.55, 61.96, 14.40; FAB$^+$-HRMS (M^+) calcd for $C_{22}H_{16}{}^{79}Br_2O_5S_2$ 581.8806, found 581.8792.

1,3-Bis(5-bromothiophen-2-yl)isobenzofuran-5,6-dicarbonitrile (25). To a CH_2Cl_2 solution of fumaronitrile (25 mg, 0.32 mmol in 0.96 mL) was slowly added triethylphosphine (1.0 M in THF, 0.32 mL, 0.32 mmol), and the mixed solution was stirred at room temperature for 30 min. The Wittig reagent thus generated was then slowly added to a CH_2Cl_2 solution of dialdehyde **23** (90 mg, 0.202 mmol in 0.32 mL). After the reaction was stirred for 2 h, DBU (3 mg, 0.020 mmol) was added and the reaction was stirred at room temperature for another 16 h. The solvent was then removed in vacuo, and the crude product was purified by flash chromatography (CH_2Cl_2 /hexane = 4/1, under nitrogen) to give the dicyano product **25** (57 mg, 58%): IR (KBr) ν (cm^{-1}) 3099, 2227, 1555, 1545, 1513, 1431, 899, 783; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.67 (s, 2 H), 7.72 (d, J = 3.2 Hz, 2 H), 7.39 (d, J = 3.2 Hz, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6, 45 °C) δ 141.63, 131.85, 131.09, 130.59, 126.56, 117.26, 115.63, 113.69, 107.41; FAB$^+$-HRMS (M^+) calcd for $C_{18}H_6{}^{79}Br_2N_2OS_2$ 487.8288, found 487.8289.

Diethyl 1,3-bis(5-bromothiophen-2-yl)benzo[*c*]thiophene-5,6-dicarboxylate (26). A CH_2Cl_2 solution of diester **24** (55 mg, 0.094 mmol in 275 mL) was stirred under ambient light and atmosphere oxygen for 48 h. The solvent was then removed in vacuo to give the crude diketone **24′** in nearly quantitative yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2 H), 7.17 (d, J = 4.0 Hz, 2 H), 7.08 (d, J = 4.0 Hz, 2 H), 4.40 (q, J = 7.2 Hz, 4 H), 1.37 (t, J = 7.2 Hz, 6 H). Compound **24′** thus obtained (50 mg, 0.083 mmol) and phosphorus pentasulfide (P_2S_5, 37 mg, 0.083 mmol) were dissolved in pyridine (0.8 mL). The solution was refluxed for 20 min before being cooled back to room temperature.

The whole solution was purified by flash chromatography (CH_2Cl_2/hexane = 4/1, under nitrogen) to give the product **26** as a reddish solid (20 mg, 40%): IR (KBr) ν (cm^{-1}) 3093, 2925, 1724, 1299, 1264, 1115, 1058, 777; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 2 H), 7.12 (d, J = 3.9 Hz, 2 H), 7.09 (d, J = 3.9 Hz, 2 H), 4.36 (q, J = 7.1 Hz, 4 H), 1.37 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.71, 135.53, 134.18, 131.32, 129.53, 128.72, 127.31, 124.25, 114.07, 61.93, 14.40; FAB$^+$-HRMS (M^+) calcd for $C_{22}H_{16}Br_2O_4S_3$ 597.8577, found 597.8571.

1,3-Bis(5-bromothiophen-2-yl)benzo[*c*]thiophene-5,6-dicarbonitrile (27). A CH_2Cl_2 solution of diester **25** (45 mg, 0.092 mmol in 225 mL) was stirred under ambient light and atmosphere oxygen for 48 h. The solvent was then removed in vacuo to give the crude diketone **25′** in nearly quantitative yield: ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2 H), 7.15 (d, J = 4.1 Hz, 2 H), 7.13 (d, J = 4.1 Hz, 2 H). Compound **25′** thus obtained (40 mg, 0.079 mmol) and phosphorus pentasulfide (P_2S_5, 35 mg, 0.079 mmol) were dissolved in pyridine (1.5 mL). The solution was refluxed for 20 min before being cooled back to room temperature. The whole solution was purified by flash chromatography (CH_2Cl_2/hexane = 3/1, under nitrogen) to give the product **27** as a reddish solid (8 mg, 20%): IR (KBr) ν (cm^{-1}) 3085, 2227, 1728, 1461, 1277, 1126, 1072, 1028; ^1H NMR (400 MHz, DMSO-d_6) δ 8.63 (s, 2 H), 7.57 (d, J = 3.9 Hz, 2 H), 7.45 (d, J = 3.9 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C) δ 133.75, 132.77, 132.27, 131.58, 131.48, 129.86, 116.67, 114.66, 108.04; FAB$^+$-HRMS (M^+) calcd for $C_{18}H_6{}^{79}Br_2N_2S_3$ 503.8060, found 503.8057.

6,7-Bis(thiophene-2-carbonyl)naphthalene-2,3-dicarboxylic acid diethyl ester (28). Compound **4** (100 mg, 0.359 mmol) and 1,4-dithienylbut-2-yne-1,4-dione (88 mg, 0.357 mmol) were dissolved in toluene (3 mL), and the solution was refluxed under nitrogen for 16 h. The solvent was evaporated, and the remaining solid was purified with flash chromatography (CH_2Cl_2/hexane = 19/1) to give pure **28** (113 mg, 64%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 2 H), 8.27 (s, 2 H), 7.71 (dd, J = 4.9, 1.0 Hz, 2 H), 7.57 (dd, J = 3.8, 1.0 Hz, 2 H), 7.11 (dd, J = 4.9, 3.8 Hz, 2 H), 4.42 (q, J = 7.1 Hz, 4 H), 1.40 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.16, 166.88, 143.53, 138.70, 135.30, 133.03, 131.52, 130.36, 128.17, 62.01, 14.09.

Diethyl 1,3-di(thiophen-2-yl)naphtho[2,3-*c*]thiophene-6,7-dicarboxylate (30). Compound **28** (90 mg, 0.183 mmol) and phosphorus pentasulfide (P_2S_5, 81 mg, 0.182 mmol) were dissolved in pyridine (2.0 mL), and the solution was refluxed under nitrogen for 20 min. After being cooled back to room temperature, the reaction mixture was purified with flash chromatography (CH_2Cl_2/hexane = 19/1, under nitrogen) to give pure **30** as a green-blue solid (51 mg, 57%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2 H), 8.14 (s, 2 H), 7.42−7.48 (m, 4 H), 7.18−7.22 (m, 2 H), 4.39 (q, J = 7.1 Hz, 4 H), 1.39 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.70, 135.56, 135.41, 132.77, 130.24, 128.45, 128.08, 126.88, 126.36, 126.16, 121.79, 61.75, 14.44; FAB$^+$-HRMS (M+) calcd for $C_{26}H_{20}O_4S_3$ 492.0524, found 492.0530.

6,7-Bis(thiophene-2-carbonyl)naphthalene-2,3-dicarbonitrile (29). Compound **5** (60 mg, 0.326 mmol) and 1,4-dithienylbut-2-yne-1,4-dione (80 mg, 0.325 mmol) were dissolved in toluene (4.0 mL), and the solution was refluxed under nitrogen for 16 h. The solvent was evaporated and the remaining solid was purified with flash chromatography (CH_2Cl_2/hexane = 9/1) to give pure **29** (78 mg, 60%) as a yellow solid: ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 2 H), 8.31 (s, 2 H), 7.77 (dd, J = 4.8, 1.0 Hz, 2 H), 7.56 (dd, J = 3.9, 1.0 Hz, 2 H), 7.14 (dd, J = 4.8, 3.9 Hz, 2 H).

1,3-Di(thiophen-2-yl)naphtho[2,3-*c*]thiophene-6,7-dicarbonitrile (31). Compound **29** (75 mg, 0.188 mmol) and phosphorus pentasulfide (P_2S_5, 84 mg, 0.189 mmol) were dissolved in pyridine (2.5 mL), and the solution was refluxed under nitrogen for 20 min. After being cooled back to room temperature, the reaction mixture was purified with flash chromatography (CH_2Cl_2/hexane = 8/1, under nitrogen) to give pure **31** as a green solid (30 mg, 40%): IR spectrum for **31** is unobtainable due to low stability; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 2 H), 8.24 (s, 2 H), 7.51 (dd, J = 5.2, 1.1 Hz, 2 H), 7.46 (dd, J = 3.7, 1.0 Hz, 2 H), 7.23 (dd, J = 5.2, 3.7 Hz, 2 H); ^{13}C spectrum for **31** is unobtainable due to low solubility; FAB$^+$-HRMS (M+) calcd for $C_{22}H_{10}N_2S_3$ 398.0006, found 398.0009.

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Supporting Information Available: Detailed synthetic procedures for some intermediates, ^1H and ^{13}C spectrum of most reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.