

Oxidative Ring Opening of 1,3-Diarylbenzo[c]heterocycles Using *m*-CPBA: Preparation of 1,2-Diaroylbenzenes

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An unprecedented oxidative cleavage of benzo[c]heterocycles using *m*-CPBA is reported. The reaction of 1,3-diaryl benzo[c]heterocycles with *m*-CPBA (*meta*-chloroperoxybenzoic acid) at room temperature for 5 min led to the formation of 1,2-diaroylbenzenes in good to excellent yields.

Introduction

Although benzo[c]thiophene (1) has been known for some time,^[1] its first report as a precursor of low band gap poly(benzo[c]thiophene) by Wudl and co-workers^[2] led to the synthesis and electrochemical polymerization of a more stable analog, namely, 1,3-dithienylbenzo[c]thiophene (2).^[3] During the last ten years, the synthesis and characterization of symmetrical as well as unsymmetrical 1,3-diarylbenzo-[c]thiophene 3 (Scheme 1) have been explored by our group.^[4] A detailed study of the photophysical properties of these benzannelated thienyl oligomers has also been carried out. The HOMO, LUMO, and band gap values of these heterocycles were correlated with their electronic structures.^[4d,5] A noteworthy application of 1,3-dithienylbenzo[c]thiophene includes its use as a fluorescent label to aid in understanding the structure and dynamics of nucleic acids.^[6] Thelakkat et al. outlined the syntheses of diarylamine-capped 1,3-dithienylbenzo[c]thiophene analogs for use as a promising light-harvesting and hole-transporting material in organic solar cells.^[7]



Scheme 1. Benzo[c]thiophenes 1–3.

Swager and co-workers reported the syntheses and characterizations of benzo[*c*]furan and benzo[*c*]thiophene-based push-pull systems for use as near-IR fluorophores.^[8] How-



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ever, the photochemical degradation of the 1,3-diarylbenzo[c]thiophene analogs is considered a drawback, limiting their optical applications.^[3b,9] Hence, there is plenty of opportunity to further explore the optical applications of these heterocycles, provided the stability issue is suitably addressed.^[10]

On the basis of theoretical calculations, the oxidation of oligothiophene analogs has been proposed to increase their stability.^[11] Furthermore, it has been established that the oxidation of one thiophene unit of a linear thienyl oligomer increases the electron deficiency, which in turn increases the electron delocalization, electron transport, and injection properties of the material.^[12] With this concept in mind, and also to increase the stability of the benzo[*c*]thiophene analogs, the oxidation of 1,3-diarylbenzo[*c*]thiophene was explored.

Results and Discussion

Accordingly, as a representative case, the reaction of 1,3diphenylbenzo[*c*]thiophene (**4a**) in DCM (dichloromethane) with a preformed mixture of KF/*m*-CPBA^[13] (*meta*-chloroperoxybenzoic acid) in CH₃CN/H₂O led to the disappearance of the fluorescent color of the heterocycle (Scheme 2).



Scheme 2. Oxidative cleavage of benzo[c]heterocycle 5a and 6a.

However, the usual workup followed by purification by column chromatography afforded only diketone 5a in 70% yield. This unexpected cleavage of the nonclassical thiophene framework prompted us to explore the reaction using *m*-CPBA.

To our surprise, the reaction of benzo[c]thiophene **4a** with 1.5 equiv. of *m*-CPBA in DCM at room temp. for 5 min afforded diketone **5a** in a better yield (84%). It should be noted that even with 1 equiv. of *m*-CPBA, the thio analog of diketone **5a** was not observed (confirmed by ¹³C NMR), and only **5a** was isolated. Under identical conditions, benzo[c]furan **6a** furnished diketone **5a** in 92% yield. Although the cleavage of **6a** is known to use singlet oxygen,^[14] recent reports on organic thin-film transistors (OTFT) and other optical applications of aroyl-capped oligothiophenes^[15] encouraged us to undertake a systematic study of this facile oxidative ring-opening reaction with other heterocycles.

To our delight, a large number of symmetrical as well as unsymmetrical benzo[c]heterocycles underwent a smooth oxidative cleavage with m-CPBA to furnish diketones in excellent yields (Table 1).

In the case of 1,3-dithienvlbenzo[c]thiophene (4b), the m-CPBA-mediated cleavage led to the isolation of unsymmetrical diketone 5b' formed through oxidation of a thiophene unit into a S,S-dioxide moiety (Table 1, Entry 1). However, the reaction with diarylbenzo[c]thiophenes 4c-4e afforded their respective diketones in excellent yields (Table 1, Entry 1). The oxidative ring-opening reaction of 1,3-diarylbenzo[c]furans 6a-6i proceeded with relatively better yields than their respective benzo[c]thiophenyl heterocycles (Table 1, Entry 2). Diarylbenzo[c]selenophenes 7a and 7b also underwent oxidative cleavage to furnish the corresponding diketones 5a and 5c in slightly reduced yields (Table 1, Entry 3). In the case of thiophene-tethered benzo[c]furans 8a-8c, oxidation of the thiophene unit was not observed (Table 1, Entry 4). Thus, the observed oxidation of the classical thiophene unit into the S,S-dioxide was found to be specific to the case of benzo[c]thiophene **4b.** As expected, the benzo [c] furans linked to the dihexylfluorene, pyrene, and diphenylmethane groups also led to their respective diketones in excellent yields (Table 1, Entries 5–7). The dibenzoheterocycle-tethered benzo[c]heterocycles also underwent smooth oxidative cleavage with m-CPBA to give the expected diketones (Table 1, Entries 8– 11). The N-hexylcarbazole-capped benzo[c]thiophenes 18a-18c furnished diketones 19a–19c in moderate yields (Table 1, Entry 9). The triphenylamine-linked diarylbenzo-[c] furans 23a-23d led to the diketones 24a-24d in 77-83% vields. The oxidative ring-opening reaction of the dibenzothiophene-linked benzo[c]furans 25 and 27 with m-CPBA also gave products formed by the oxidation of sulfur into sulfoxide as well as sulfone (Table 1, Entries 13 and 14).

The reaction of 2,5-diarylfurans **29a–29c** with *m*-CPBA in DCM at room temperature led to the isolation of *cis*diaroylethylenes **30a–30c** in 68–92% yields (Table 1, Entry 15). It should be noted that the cleavage of furan derivatives using *m*-CPBA was observed earlier.^[17] However, to the best of our knowledge, the cleavage of benzo[c]furan using *m*-CPBA was not known until now. Finally, the structures of representative diketones **11b** (Figure 1) and **24c** (Figure 2) were confirmed by single-crystal X-ray structure analyses.^[18]

Table 1. Oxidative cleavage of 1,3-diarylbenzo[c]heterocycles.



Table 1. (Continued).



[a] Isolated yields. [b] For Entries 13 and 14, 2 equiv. of *m*-CPBA was used.



Figure 1. X-ray crystal structure of compound 11b.



Figure 2. X-ray crystal structure of compound 24c.

To further understand the efficacy of this *m*-CPBA-mediated oxidative cleavage protocol, a comparative study was planned with the reported procedure for the cleavage of nonclassical furans using lead tetraacetate (LTA).^[3b] Accordingly, the oxidative cleavage of some representative 1,3diarylbenzo[*c*]furans was performed using LTA/*m*-CPBA, and the yields of the respective diaroylbenzenes isolated are presented in Table 2. In the case of the simple 1,3-diarylbenzo[*c*]furans **6d**, **6e**, and **6h**, the yields of the respective diaroylbenzenes were almost comparable between *m*-CPBA and LTA (Table 2, Entries 1–3). However, when treated with LTA, the carbazole- and triphenylamine-tethered benzo[*c*]furans furnished the corresponding diketones

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in low yields (Table 2, Entries 3–6). In the case of the dibenzothiophene-tethered benzo[c]furan 25 and 27, the oxidative cleavage with LTA was selective, affording the respective diaroylbenzenes 26a and 28a in better yields than with the *m*-CPBA protocol.

Table 2. Comparative study of oxidative cleavage of 1,3-diarylbenzo[*c*]furans using *m*-CPBA and LTA.

Entry	Benzo[c]furan	Diketone	Yield [%] ^[a]	Yield [%] ^[b]
1	6d	5d	93	76
2	6e	5e	86	85
3	6h	5h	88	84
4	20a	19a	82	25
5	20c	19c	80	21
6	23c	24c	81	23
7	23d	24d	83	24
8	25	26a	41	80
9	27	28a	44	83

[a] The yield obtained using *m*-CPBA. [b] The yield obtained using LTA.

A plausible mechanism for the oxidative cleavage of benzo[c]furan using m-CPBA has been outlined in Scheme 3. The benzo[c]furan unit undergoes an electrophilic hydroxylation at the 1-position through the aromatization of the benzene ring to form intermediate **31**, which upon ring opening may lead to the formation of the diaroylbenzenes.



Scheme 3. Mechanism for cleavage of nonclassical heterocycle.

Conclusions

In summary, for the first time, a facile *m*-CPBA-mediated oxidative cleavage of a wide variety of 1,3-disubstituted benzo[*c*]furans was achieved at room temperature. The reaction was also found to be successful with nonclassical thiophene and selenophene analogs. Compared to the existing methods available for the cleavage of benzo[*c*]furans,^[3a,9,14] the present protocol using *m*-CPBA is simple, widely applicable, and also less time-consuming. In the case of the nitrogen-containing benzo[*c*]furans, the present method was found to be better than the method with LTA. The various types of heteroaroyl oligothiophenes reported herein may find application in the area of field-effect transistors as well as in organic solar cell (OSC) applications.^[15] There is plenty of chemistry to explore with readily available unsym-

metrical 1,2-diaroylbenzenes as intermediates for the syntheses of 9-arylanthracenes and annulated hetero-cycles.^[19]

Experimental Section

General Methods: The solvents were dried by standard procedures. All of the experiments were carried out under a nitrogen atmosphere unless otherwise stated. The progression of all of the reactions was monitored by TLC, using a hexanes/ethyl acetate mixture as the eluent. Column chromatography was carried out on silica gel (230–400 mesh, Merck) by increasing the solvent polarity. ¹H, ¹³C, and DEPT-135 spectroscopic data were recorded at room temperature in CDCl₃ using TMS as an internal standard with a Bruker 300 MHz spectrometer. The chemical shift values were quoted in parts per million (ppm), and the coupling constants (J) were quoted in Hertz (Hz). Elemental analysis data were recorded with a Elementar Vario Series Analyser (IISER, Pune) instrument. HRMS data were recorded with a MS001300-FINNIGAN MAT-95XL instrument. Commercially available m-CPBA (77%), purchased from Sigma-Aldrich, was used in the reactions. The required benzo[c]thiophenes 4a-4e, benzo[c]furans 6a-6i, and benzo[c]selenophenes 7a and 7b were prepared using reported procedures.[3a,3b,3e,4a,20]

Oxidative Cleavage of Benzo[c]thiophene 4a Using KF/m-CPBA Protocol:^[13] To a solution of KF (0.15 g, 2.62 mmol) in acetonitrile/ water (10 mL, 2 mL) was added 77% m-CPBA (0.58 g, 2.62 mmol), and the mixture was stirred at 0 °C for 30 min. To this, 1,3-diphenylbenzo[c]thiophene (4a, 0.30 g, 1.05 mmol) in DCM was added, and the mixture was stirred at room temperature for 5 min. The reaction mixture was then poured into a saturated sodium hydrogen carbonate solution, and the resulting mixture was extracted with DCM $(3 \times 15 \text{ mL})$. The combined organic extracts were washed with water $(2 \times 30 \text{ mL})$ and dried with Na₂SO₄. Removal of solvent followed by purification by column chromatography [silica gel, 5% EA (ethyl acetate)/hexane] afforded diketone 5a^[14d] (0.21 g, 70%) as a colorless solid; m.p. 138 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.63 (d, J = 7.2 Hz, 4 H, Ar), 7.54 (s, 4 H, Ar), 7.44 $(t, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{Ar}) 7.32-7.27 \text{ (m, 4 H, Ar) ppm.}^{13}\text{C NMR}$ $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 196.6, 140.0, 137.2, 133.0, 130.4, 129.8,$ 129.7, 128.3 ppm. Dept-135 (75 MHz, CDCl₃): δ = 133.0, 130.4, 129.8, 129.7, 128.3 ppm.

Oxidative Cleavage of Benzo[c]thiophene 4a Using *m*-**CPBA:** To a solution of benzo[c]thiophene **4a** (0.3 g, 1.05 mmol) in DCM (15 mL) was added *m*-**CPBA** (0.35 g, 1.57 mmol), and the reaction mixture was stirred at room temperature for 5 min. It was then poured into a saturated sodium hydrogen carbonate solution, and the resulting mixture was extracted with DCM (3×15 mL). The combined organic extracts were washed with water (2×30 mL) and dried with Na₂SO₄. Removal of solvent followed by purification by column chromatography (silica gel, 5% EA/hexane) afforded diketone **5a** (0.25 g, 84%).

Oxidative Cleavage of Benzo[*c*]**furan 6a Using** *m***-CPBA:** To a solution of benzo[*c*]**furan 6a** (0.5 g, 1.85 mmol) in DCM (15 mL) was added *m*-CPBA (0.62 g, 2.78 mmol), and the reaction mixture was stirred at room temperature for 5 min. It was then poured into a saturated sodium hydrogen carbonate solution, and the resulting mixture was extracted with DCM (3×30 mL). The combined organic extracts were washed with water (2×30 mL) and dried with Na₂SO₄. Removal of solvent followed by purification by column chromatography (silica gel, 5% EA/hexane) afforded diketone **5a** (0.46 g, 92%).



5c: The oxidative cleavage of benzo[c]thiophene 4c (0.55 g, 1.75 mmol) using m-CPBA (0.59 g, 2.63 mmol) followed by the usual workup and purification by column chromatography gave diketone 5c (0.48 g, 87%) as a colorless solid; m.p. 188–189 °C, ref.^[21] m.p. 189.7–191.6 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.62–7.59 (m, 8 H, Ar), 7.17 (d, J = 7.5 Hz, 4 H, Ar), 2.37 (s, 6 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.3, 143.8, 140.2, 134.7, 130.1, 130.0, 129.5, 129.0, 21.7 ppm. Dept-135 (75 MHz, CDCl₃): δ = 130.2, 130.0, 129.5, 129.0, 21.7 ppm.

5d: The oxidative cleavage of benzo[c]thiophene 4d (0.50 g, 1.58 mmol) using m-CPBA (0.53 g, 2.37 mmol) followed by the usual workup and purification by column chromatography gave diketone 5d (0.42 g, 83%) as a colorless solid; m.p. 122-123 °C, ref.^[21] m.p. 118.6–119.1 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.62–7.58 (m, 5 H, Ar), 7.51–7.50 (br. s, 3 H, Ar) 7.41 (t, J = 6.9 Hz, 1 H, Ar), 7.30–7.25 (m, 2 H, Ar), 6.76 (d, J = 8.1 Hz, 2 H, Ar), 3.74 (s, 3 H, OCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.7, 195.3, 163.6, 140.4, 139.8, 137.3, 133.0, 132.2, 130.4, 130.2, 130.0, 129.8, 129.6, 129.4, 129.1, 128.3, 113.6, 55.5 ppm. Dept-135 (75 MHz, $CDCl_3$): $\delta = 133.0, 132.20, 130.3, 130.0, 129.8, 129.6, 129.4, 128.3,$ 113.6, 55.5 ppm.

5e: The oxidative cleavage of benzo[c]thiophene **4e** (0.45 g, 1.29 mmol) using m-CPBA (0.43 g, 1.91 mmol) followed by the usual workup and purification by column chromatography gave diketone 5e (0.39 g, 86%) as a colorless solid; m.p. 139-140 °C, ref.^[21] m.p. 139.7–140.4 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.34 (d, J = 8.4 Hz, 1 H, Ar), 7.99–7.94 (m, 2 H, Ar), 7.84 (d, J = 8.7 Hz, 1 H, Ar), 7.73–7.28 (m, 9 H, Ar), 7.08 (d, J = 7.8 Hz, 2 H, Ar), 2.33 (s, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 197.5, 196.7, 143.9, 141.2, 140.5, 135.3, 134.9, 133.6, 132.9, 131.5, 130.9, 130.8, 130.5, 130.1, 129.6, 129.0, 128.1, 127.5, 126.4, 125.8, 125.8, 124.0, 21.6 ppm.

5b: The oxidative cleavage of benzo[c]furan **6b**^[3b] (0.53 g, 1.88 mmol) using m-CPBA (0.63 g, 2.82 mmol) followed by the usual workup and purification by column chromatography afforded diketone 5b (0.47 g, 89%) as a brown solid; m.p. 152-153 °C, ref.^[3b] m.p. 149–150 °C. IR (KBr): $\tilde{v} = 1638$, 1408, 1287 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.66–7.64 (m, 2 H, Ar), 7.58–7.56 (m, 4 H, Ar), 7.39–7.38 (m, 2 H, Ar), 6.99–6.96 (m, 2 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 188.3, 144.0, 139.4, 135.1, 135.0, 130.6, 129.2, 128.1 ppm. Dept-135 (75 MHz, CDCl₃): δ = 135.2, 135.0, 130.6, 129.2, 128.1 ppm.

Oxidative Cleavage of Benzo[c]furan 6c: Benzo[c]furan 6c (0.35 g, 1.17 mmol) was treated with m-CPBA (0.32 g, 1.85 mmol) followed by the usual workup and purification by column chromatography to give diketone 5c (0.35 g, 94%) as a colorless solid.

Oxidative Cleavage of Benzo[c]furan 6d: Benzo[c]furan 6d (0.4 g, 1.33 mmol) was treated with m-CPBA (0.36 g, 2.1 mmol) followed by the usual workup and purification by column chromatography to give diketone 5d (0.39 g, 93%) as a colorless solid.

Oxidative Cleavage of Benzo[c]furan 6e: Benzo[c]furan 6e (0.4 g, 1.19 mmol) was treated with m-CPBA (0.31 g, 1.79 mmol) followed by the usual workup and purification by column chromatography

5f: The oxidative cleavage of benzo[*c*]furan **6f** (0.50 g, 1.35 mmol) using *m*-CPBA (0.45 g, 2.03 mmol) followed by the usual workup and purification by column chromatography afforded diketone 5f (0.45 g, 90%) as a colorless solid; m.p. 128–130 °C, ref.^[22] m.p. 130– 131 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.05 (d, J = 8.4 Hz, 2 H, Ar), 7.73 (d, J = 8.4 Hz, 2 H, Ar) 7.61–7.52 (m, 6 H, Ar), 7.40 (d, J = 6.9 Hz, 2 H, Ar), 7.29–7.16 (m, 6 H, Ar) ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 197.9, 141.6, 135.3, 133.7, 133.2, 131.1,$ 131.0, 130.8, 130.2, 127.9, 127.8, 126.4, 125.5, 123.8 ppm. Dept-135 (75 MHz, CDCl₃): δ = 133.2, 131.1, 131.0, 130.2, 127.9, 127.8, 126.4, 125.5, 123.8 ppm.

5g: The required benzo[c]furan 6g was prepared using the procedure similar to that of 6f. Benzo[c]furan 6g (0.3 g, 0.67 mmol) was treated with m-CPBA (0.22 g, 1.00 mmol, 1.5 equiv.) in DCM to give diketone 5g (0.27 g, 87%) as a thick, orange liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.63–7.60 (m, 2 H, Ar), 7.52–7.50 (m, 2 H, Ar), 7.18 (d, J = 3.6 Hz, 2 H, Ar), 6.66 (d, J = 3.3 Hz, 2 H, Ar), 2.72 (t, J = 7.5 Hz, 4 H, CH₂) 1.60–1.53 (m, 4 H, CH₂), 1.32–1.16 (m, 12 H, CH₂), 0.81 (t, J = 6.0 Hz, 6 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 188.1, 157.3, 141.6, 139.4, 135.8, 130.4, 129.1, 125.6, 31.5, 31.3, 30.7, 28.7, 22.5, 14.1 ppm. Dept-135 $(75 \text{ MHz}, \text{CDCl}_3)$: $\delta = 135.8, 130.4, 129.1, 125.6, 31.5, 31.3, 30.7,$ 28.7, 22.5, 14.1 ppm. C₂₈H₃₄O₂S₂ (466.70): calcd. C 72.06, H 7.34, S 13.74; found C 71.81, H 7.39, S 13.68.

5h: Benzo[c]furan **6h**^[16b] (0.50 g, 1.81 mmol) was treated with m-CPBA (0.61 g, 2.72 mmol, 1.5 equiv.) in DCM to give diketone 5h (0.44 g, 88%) as a brown solid; m.p. 134-135 °C, ref.^[21] m.p. 132.5-133.3 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.49 (d, J = 7.5 Hz, 3 H, Ar), 7.56–7.53 (m, 4 H, Ar), 7.45–7.39 (m, 2 H, Ar), 7.31–7.26 (m, 2 H, Ar), 6.99–6.96 (m, 1 H, Ar) ppm. ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 196.6, 188.3, 144.1, 139.8, 139.6, 137.2, 135.0, 134.9,$ 133.1, 130.5, 130.5, 129.8, 129.7, 129.1, 128.3, 128.0 ppm. Dept-135 (75 MHz, CDCl₃): δ = 135.0, 134.9, 133.1, 130.6, 130.5, 129.9, 129.8, 129.1, 128.4, 128.0 ppm.

5i: The ring-opening reaction of 3-(3,4-dimethylphenyl)isobenzofuran-1(3H)-one with freshly prepared p-anisylmagnesium bromide followed by acidic workup gave benzo[c]furan 6i as a fluorescent, yellow solid. Benzo[c]furan 6i (0.50 g, 1.52 mmol) was treated with m-CPBA (0.51 g, 2.29 mmol, 1.5 equiv.) in DCM to give diketone 5i (0.47 g, 94%) as a colorless solid; m.p. 132 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3): \delta = 7.61 \text{ (d}, J = 8.4 \text{ Hz}, 2 \text{ H}, \text{Ar}), 7.50 \text{ (s}, 4 \text{ H},$ Ar), 7.41 (s, 1 H, Ar), 7.35 (d, J = 7.8 Hz, 1 H, Ar), 7.03 (d, J = 7.5 Hz, 1 H, Ar), 6.76 (d, J = 8.7 Hz, 2 H, Ar), 3.74 (s, 3 H, OCH₃), 2.19 (s, 3 H, CH₃), 2.13 (s, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 196.6, 195.3, 163.5, 142.6, 140.3, 140.2, 136.7, 135.1,$ 132.2, 130.9, 130.3, 130.0, 130.0, 129.5, 129.3, 127.8, 113.6, 55.5, 20.0, 19.6 ppm. Dept-135 (75 MHz, CDCl₃): δ = 132.2, 130.9, 130.1, 130.0, 129.5, 129.3, 127.8, 113.6, 55.5, 20.1, 19.7 ppm.

Oxidative Cleavage of Benzo[c]selenophene 7a: Benzo[c]selenophene 7a (0.30 g, 0.90 mmol) was treated with m-CPBA (0.30 g, 1.35 mmol) in DCM to give diketone 5a (0.19 g, 75%) as a colorless solid.

Oxidative Cleavage of Benzo[c]selenophene 7b: Benzo[c]selenophene **7b** (0.32 g, 1.34 mmol) was treated with *m*-CPBA (0.30 g, 1.34 mmol)1.33 mmol) in DCM to give diketone 5c (0.22 g, 78%) as a colorless solid.

9a: Benzo[c]furan 8a (0.50 g, 1.34 mmol) was treated with m-CPBA (0.45 g, 2.02 mmol, 1.5 equiv.) in DCM to give diketone **9a** (0.46 g,

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88%) as a brown solid; m.p. 140–142 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.67–7.64 (m, 1 H, Ar), 7.56–7.50 (m, 5 H, Ar), 7.30–7.18 (m, 3 H, Ar), 7.1 (d, *J* = 8.1 Hz, 2 H, Ar), 7.03 (d, *J* = 3.9 Hz, 1 H, Ar), 6.98–6.94 (m, 1 H, Ar), 2.31 (s, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.2, 187.9, 146.7, 144.0, 142.1, 139.8, 139.4, 136.2, 135.9, 134.7, 130.4, 130.3, 130.0, 129.6, 129.0, 128.9, 128.2, 126.6, 125.8, 124.1, 21.7 ppm. Dept-135 (75 MHz, CDCl₃): δ = 135.9, 130.4, 130.3, 130.0, 129.6, 129.0, 128.9, 128.2, 126.6, 125.8, 124.1, 21.7 ppm. Dept-135 (75 MHz, CDCl₃): δ = 135.9, 130.4, 130.3, 130.0, 129.6, 129.0, 128.2, 126.6, 125.8, 124.1, 21.7 ppm. HRMS (EI): calcd. for C₂₃H₁₆O₂S₂ 388.0592; found 388.0587.

9b: Benzo[*c*]furan **8b** (0.50 g, 1.34 mmol) was treated with *m*-CPBA (0.45 g, 2.02 mmol) in DCM to give diketone **9b** (0.35 g, 85%) as a thick, brown liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.27-8.26$ (m, 1 H, Ar), 7.84 (d, J = 8.1 Hz, 1 H, Ar), 7.76–7.65 (m, 2 H, Ar), 7.57–7.48 (m, 3 H, Ar), 7.44 (d, J = 6.6 Hz, 1 H, Ar), 7.33–7.27 (m, 3 H, Ar), 7.20–7.15 (m, 2 H, Ar), 7.04 (d, J = 3.3 Hz, 1 H, Ar), 6.94–6.91 (m, 2 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 197.6$, 188.2, 146.8, 142.5, 140.3, 136.1, 135.8, 135.2, 133.6, 133.1, 131.5, 130.8, 130.7, 130.5, 128.6, 128.2, 127.7, 126.7, 126.5, 124.8, 125.6, 124.2, 124.0 ppm. Dept-135 (75 MHz, CDCl₃): $\delta = 135.8$, 133.1, 131.5, 130.8, 130.7, 130.5, 128.6, 128.2, 128.2, 127.7, 126.7, 126.7, 126.5, 125.8, 125.6, 124.2, 124.0 ppm. C₂₆H₁₆O₂S₂ (424.53): calcd. C 73.56, H 3.80, S 15.11; found C 73.83, H 3.71, S 15.02.

9c: The required benzo[*c*]furan **8c** was prepared by adopting a procedure similar to that for **8b**. Benzo[*c*]furan **8c** (0.3 g, 0.82 mmol) was treated with *m*-CPBA (0.27 g, 1.24 mmol) to afford diketone **9c** (0.27 g, 86%) as a brown solid; m.p. 146–147 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.68–7.66 (m, 2 H, Ar), 7.60–7.55 (m, 3 H, Ar), 7.40 (d, *J* = 3.9 Hz, 1 H, Ar), 7.28–7.22 (m, 3 H, Ar), 7.05–6.99 (m, 3 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 188.3, 187.8, 147.0, 144.1, 142.0, 139.3, 139.1, 136.2, 136.1, 135.2, 135.0, 130.7, 130.6, 129.2, 129.1, 128.3, 128.0, 126.7, 125.9, 124.2 ppm. Dept-135 (75 MHz, CDCl₃): δ = 136.1, 135.2, 135.0, 130.7, 130.6, 129.3, 128.0, 126.8, 125.9, 124.2 ppm. C₂₀H₁₂O₂S₃ (380.49): calcd. C 63.13, H 3.18, S 25.28; found C 63.26, H 3.13, S 25.35.

11a: The ring-opening reaction of 9,9-dihexyl-9H-fluoren-2-yl lactone^[5c] with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[c]furan 10a as a thick, orange liquid. The oxidative ring-opening reaction of benzo[c] furan 10a (0.5 g, 0.93 mmol) with m-CPBA (0.31 g, 1.39 mmol) gave diketone 11a (0.43 g, 83%) as a pale yellow solid; m.p. 90 °C. IR (KBr): \tilde{v} = 2923, 1654, 1599, 1456, 1292 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.64–7.53 (m, 10 H, Ar), 7.26 (br. s, 3 H, Ar), 7.06 (d, J = 7.5 Hz, 2 H, Ar), 2.27 (s, 3 H, CH₃), 1.87-1.82 (m, 4 H, CH₂), 1.04–0.95 (m, 12 H, CH₂), 0.70–0.44 (m, 10 H, CH₂CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.5, 196.3, 152.1, 150.8, 146.0, 143.8, 140.4, 140.2, 139.8, 135.8, 134.8, 130.3, 130.1, 129.7, 129.4, 129.0, 128.4, 127.0, 124.0, 123.1, 120.7, 119.2, 55.2, 40.1, 31.5, 29.6, 23.7, 22.6, 21.6, 14.0 ppm. Dept-135 (75 MHz, CDCl₃): δ = 130.3, 130.1, 130.0, 129.7, 129.4, 129.0, 128.4, 127.0, 124.0, 123.1, 120.7, 119.2, 40.1, 31.5, 29.6, 23.7, 22.6, 21.6, 14.0 ppm. $C_{40}H_{44}O_2$ (556.79): calcd. C 86.29, H 7.97; found C 86.61, H 7.83.

11b: The ring-opening reaction of 9,9-dihexyl-9*H*-fluoren-2-yl lactone^[5c] with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10b**. The oxidative ring-opening reaction of benzo[*c*]furan **10b** with *m*-CPBA (1.5 equiv.) gave diketone **11b** (0.46 g, 81%) as a pale yellow solid; m.p. 130 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.65–7.54 (m, 10 H, Ar), 7.28 (br. s, 3 H, Ar), 6.76 (d, *J* = 8.4 Hz, 2 H, Ar), 3.75 (s, 3 H, OCH₃), 1.88–1.83 (m, 4 H, CH₂), 1.05–0.95 (m, 12 H, CH₂), 0.71–0.48 (m, 10 H, CH₂CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.7, 195.4, 163.6, 152.1, 150.8, 146.0, 140.0, 139.8, 135.8, 132.3, 130.3, 130.1, 129.8, 129.7, 129.2, 128.4, 127.0, 124.0, 123.1, 120.7, 119.2, 113.6, 55.4, 55.2, 40.1, 31.5, 29.7, 23.7, 22.6, 14.0 ppm. C₄₀H₄₄O₃ (572.79): calcd. C 83.88, H 7.74; found C 84.19, H 7.91. For the single-crystal X-ray structure analysis of **11b**, all of the calculations were performed with the SHELXL-97 program.^[23] Crystal data of **11b**: C₄₀H₄₄O₃, M = 572.75 gmol⁻¹, monoclinic crystal system, space group P 21/n, Z = 4, a = 16.7593(10) Å, b = 11.4989(6) Å, c= 17.1460(5) Å, $a = \gamma = 90^{\circ}$, $\beta = 90.449(2)^{\circ}$, V = 3304.2(3) Å³, and $D_{calcd.}$ = 1.151 Mgm⁻³. In total, 5850 independent reflections were collected, of which 3875 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by fullmatrix least-squares procedures to a final R value of 4.96%.

CCDC-867083 (for **11b**) contains 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.

11c: The ring-opening reaction of 9,9-dihexyl-9*H*-fluoren-2-yl lactone^[5c] with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[c]furan 10c as a fluorescent, thick, yellow liquid. Benzo[c]furan 10c (0.53 g, 0.92 mmol) was treated with m-CPBA (0.31 g, 1.39 mmol, 1.5 equiv.) in DCM to give diketone 11c (0.44 g, 80%) as a thick, yellow liquid. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 8.37 - 8.34 \text{ (m, 1 H, Ar)}, 7.82 \text{ (d, } J = 8.1 \text{ Hz},$ 1 H, Ar), 7.74–7.48 (m, 10 H, Ar), 7.40–7.37 (m, 2 H, Ar), 7.30– 7.23 (m, 4 H, Ar), 1.84–1.78 (m, 4 H, CH₂), 1.02–0.91 (m, 12 H, CH₂), 0.67–0.46 (m, 10 H, CH₂CH₃) ppm. ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 197.6, 196.8, 152.1, 150.9, 146.0, 141.5, 140.9, 139.7,$ 135.6, 135.3, 133.6, 132.7, 131.0, 131.0, 130.8, 130.4, 130.0, 129.3, 129.1, 128.4, 128.1, 127.7, 127.0, 126.5, 125.9, 123.9, 123.8, 123.1, 120.7, 119.2, 55.2, 40.0, 31.5, 29.6, 23.7, 22.6, 14.0 ppm. Dept-135 $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 132.7, 131.0, 130.8, 130.5, 130.0, 129.9,$ 128.4, 128.1, 127.8, 127.0, 126.5, 125.9, 123.9, 123.8, 123.1, 120.7, 119.2, 40.0, 31.5, 29.6, 23.7, 22.6, 14.0 ppm. C₄₃H₄₄O₂ (592.82): calcd. C 87.12, H 7.48; found C 87.51, H 7.76.

11d: The ring-opening reaction of 9,9-dihexyl-9H-fluoren-2-yl lactone^[5c] with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[c]furan 10d as a fluorescent, thick, orange liquid. Benzo[c]furan 10d (0.45 g, 0.81 mmol) was treated with m-CPBA (0.21 g, 1.21 mmol, 1.5 equiv.) in DCM to give diketone 11d (0.36 g, 78%) as a thick, yellow liquid. ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 7.66-7.51 \text{ (m, 9 H, Ar)}, 7.38 \text{ (dd, } {}^1J =$ $1.2 \text{ Hz}, {}^{2}J = 3.9 \text{ Hz}, 1 \text{ H}, \text{ Ar}), 7.28-7.26 \text{ (br. s, 3 H, Ar)}, 6.98-6.95$ (m, 1 H, Ar), 1.88–1.83 (m, 4 H, CH₂), 1.05–0.95 (m, 12 H, CH₂), 0.71-0.47 (m, 10 H, CH₂CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 196.5, 188.4, 152.1, 150.8, 146.1, 144.3, 139.86, 139.81, 139.72,$ 135.8, 135.1, 134.7, 130.54, 130.49, 130.04, 129.9, 129.0, 128.5, 127.9, 127.0, 123.9, 123.1, 120.8, 119.2, 55.3, 40.1, 31.5, 29.6, 23.7, 22.6, 14.0 ppm. Dept-135 (75 MHz, CDCl₃): δ = 135.1, 134.7, 130.54, 130.49, 130.04, 129.9, 129.0, 128.5, 127.9, 127.0, 123.9, 123.1, 120.8, 119.2, 40.1, 31.5, 29.6, 23.7, 22.6, 14.0 ppm. C₃₇H₄₀O₂S (548.78): calcd. C 80.98, H 7.35, S 5.84; found C 81.26, H 7.48, S 5.71.

13: Benzo[*c*]furan **12** (0.4 g, 0.98 mmol) was treated with *m*-CPBA (0.33 g, 1.47 mmol) in DCM to give diketone **13** (0.39 g, 94%) as a pale yellow solid; m.p. 65 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.43 (d, *J* = 9.3 Hz, 1 H, Ar), 8.02–7.79 (m, 8 H, Ar), 7.56–7.37 (m, 6 H, Ar), 6.86 (d, *J* = 8.1 Hz, 2 H, Ar), 2.10 (s, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 1.97, 196.7, 143.8, 141.2, 140.8, 134.7, 133.7, 131.6, 131.2, 130.8, 130.34, 130.29, 129.8, 129.5, 129.0, 128.9, 128.5, 126.9, 126.2, 126.1, 126.0, 124.6, 124.4, 123.9,

123.4, 21.4 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 130.2, 129.8, 128.9, 128.5, 128.0, 127.9, 127.6, 125.9, 125.2, 125.1, 125.0, 123.7, 122.4, 20.5 ppm. C₃₁H₂₀O₂ (424.50): calcd. C 87.71, H 4.75; found C 87.94, H 4.61.

15: Benzo[*c*]furan **14** (0.4 g, 1.07 mmol) was treated with *m*-CPBA (0.36 g, 1.60 mmol) in DCM to give diketone **15** (0.38 g, 91%) as a thick, yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.54–7.47 (m, 8 H, Ar), 7.20–7.03 (m, 9 H, Ar), 3.88 (s, 2 H, CH₂), 2.25 (s, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.2, 146.6, 143.7, 140.1, 139.9, 135.2, 134.5, 130.1, 130.0, 129.9, 129.43, 129.40, 128.9, 128.83, 128.79, 128.5, 126.3, 41.8, 21.6 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 130.1, 130.0, 129.9, 129.43, 128.79, 128.5, 126.3, 41.8, 21.6 ppm. C₂₈H₂₂O₂ (390.48): calcd. C 86.13, H 5.68; found C 86.47, H 5.49.

17a: Benzo[*c*]furan **16a** (0.4 g, 0.89 mmol) was treated with *m*-CPBA (0.30 g, 1.33 mmol) in DCM to give diketone **17a** (0.33 g, 80%) as a thick, red liquid. ¹H NMR (300 MHz, CDCl₃): δ = 8.25 (s, 1 H, Ar) 7.84–7.76 (m, 2 H, Ar), 7.70–7.67 (m, 1 H, Ar), 7.61–7.53 (m, 3 H, Ar), 7.49–7.36 (m, 3 H, Ar), 7.30–7.23 (m, 2 H, Ar), 6.66 (d, *J* = 3.6 Hz, 1 H), 2.65 (t, *J* = 7.5 Hz, 2 H, CH₂), 1.51–1.44 (m, 2 H, CH₂), 1.26–1.09 (m, 6 H, CH₂), 0.78 (t, *J* = 6.4 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.1, 187.9, 158.9, 157.5, 156.8, 141.5, 140.0, 139.8, 135.7, 132.6, 130.5, 130.3, 129.5, 129.1, 127.9, 125.6, 124.4, 123.7, 123.3, 123.2, 121.1, 111.9, 111.5, 31.4, 31.2, 30.7, 28.7, 22.5, 14.1 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.7, 130.5, 130.3, 129.6, 129.1, 127.9, 125.6, 123.3, 123.2, 121.1, 111.9, 111.5, 31.4, 31.2, 30.7, 28.7, 22.5, 14.1 ppm. C₃₀H₂₆O₃S (466.59): calcd. C 77.22, H 5.62, S 6.87; found C 77.41, H 5.48, S 6.96.

17b: The ring-opening reaction of dibenzofuranyl lactone^[5a] with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **16b** as a thick, yellow liquid. Benzo[*c*]furan **16b** (0.4 g, 0.97 mmol) was treated with *m*-CPBA (0.33 g, 1.46 mmol) in DCM to give diketone **17b** (0.35 g, 83%) as a thick, yellow liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.07-8.02$ (m, 2 H, Ar), 7.61–7.37 (m, 8 H, Ar), 7.30–7.06 (m, 6 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 197.4$, 196.3, 158.8, 156.8, 141.2, 140.6, 135.2, 133.5, 132.9, 131.6, 130.9, 130.8, 130.5, 130.3, 129.15, 129.12, 128.1, 127.9, 127.4, 126.4, 125.5, 124.5 124.0, 123.6, 123.3, 122.7, 121.0, 111.8, 111.4 ppm. DEPT-135 (75 MHz, CDCl₃): $\delta = 132.9$, 131.6, 130.9, 130.6, 130.3, 129.15, 129.12, 128.1, 127.9, 127.4, 0.4, 125.5, 124.0, 123.3, 122.7, 121.0, 111.8, 111.4 ppm. HRMS (EI): calcd. for C₃₀H₁₈O₃ 426.1256; found 426.1252.

19a: The known benzo[c]thiophene $18a^{[5a]}$ (0.5 g, 1.06 mmol) was treated with m-CPBA (0.36 g, 1.58 mmol) to give diketone 19a (0.347 g, 67%) as a thick, yellow liquid. ¹H NMR (300 MHz, $CDCl_3$): $\delta = 8.38$ (s, 1 H, Ar), 7.94 (d, J = 7.8 Hz, 1 H, Ar), 7.79 (d, J = 8.7 Hz, 1 H, Ar), 7.63–7.52 (m, 6 H, Ar), 7.37 (d, J =7.5 Hz, 1 H, Ar), 7.31 (d, J = 8.1 Hz, 1 H, Ar), 7.23 (d, J = 8.7 Hz, 1 H, Ar), 7.15 (t, J = 7.4 Hz, 1 H, Ar), 7.03 (d, J = 8.1 Hz, 2 H, Ar), 4.18 (t, J = 7.2 Hz, 2 H, NCH₂), 2.24 (s, 3 H, ArCH₃), 1.78-1.71 (m, 2 H, CH₂), 1.22–1.20 (m, 6 H, CH₂), 0.77 (t, J = 6.8 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.5, 196.2, 143.7, 143.2, 141.0, 140.9, 140.2, 134.8, 130.0, 129.9, 129.8, 129.5, 129.4, 128.9, 128.5, 128.0, 126.3, 123.7, 123.1, 122.4, 120.7, 119.8, 109.1, 108.2, 43.2, 31.46, 28.8, 26.8, 22.4, 21.6, 13.9 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 130.0, 129.9, 129.8, 129.5, 129.4, 128.9, 128.0, 126.3, 123.7, 120.6, 119.8, 109.1, 108.2, 43.2, 31.4, 28.8, 26.8, 22.4, 21.6, 13.9 ppm. C₃₃H₃₁NO₂ (473.61): calcd. C 83.69, H 6.60, N 2.96; found C 83.54, H 6.56, N 3.03.



19b: The known benzo[c]thiophene $18b^{[5a]}$ (0.5 g, 1.02 mmol) was treated with *m*-CPBA (0.34 g, 1.53 mmol) to give diketone 19b (0.33 g, 65%) as a pale yellow solid; m.p. 173–174 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 8.37$ (s, 1 H, Ar), 7.92 (d, J = 7.8 Hz, 1 H,Ar), 7.78 (d, J = 8.4 Hz, 1 H, Ar), 7.60–7.58 (m, 3 H, Ar), 7.51– 7.49 (m, 3 H, Ar), 7.36–7.27 (m, 2 H, Ar), 7.21 (d, J = 8.7 Hz, 1 H, Ar), 7.15–7.13 (m, 1 H, Ar), 6.69 (d, J = 8.7 Hz, 2 H, Ar), 4.15 $(t, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ NCH}_2), 3.66 (s, 3 \text{ H}, \text{ OCH}_3), 1.75-1.71 (m, 2)$ H, CH₂), 1.26–1.17 (m, 6 H, CH₂), 0.75 (t, J = 6.6 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.3, 195.5, 163.5, 143.3, 141.1, 140.9, 140.5, 132.2, 130.4, 129.9, 129.8, 129.6, 129.3, 128.6, 128.1, 126.4, 123.8, 123.2, 122.5, 120.7, 119.9, 113.5, 109.2, 108.3, 55.4, 43.3, 31.5, 28.9, 26.9, 22.5, 14.0 ppm. DEPT-135 $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 132.2, 129.9, 129.8, 129.6, 129.3, 128.1,$ 126.4, 123.8, 120.9, 119.9, 113.5, 109.2, 108.3, 55.4, 43.3, 31.5, 28.8, 26.9, 22.5, 14.0 ppm. C₃₃H₃₁NO₃ (489.61): calcd. C 80.95, H 6.38, N 2.86; found C 80.72, H 6.46, N 2.98.

19c: The known benzo[*c*]thiophene **18c**^[5a] (0.5 g, 1.09 mmol) was treated with *m*-CPBA (0.37 g, 1.63 mmol) to give diketone **19c** (0.32 g, 64%) as a thick, yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 8.47 (s, 1 H, Ar), 8.02 (d, *J* = 7.8 Hz, 1 H, Ar), 7.87 (dd, *J* = 1.5 Hz, *J* = 8.7 Hz, 1 H, Ar), 7.72–7.69 (m, 3 H, Ar), 7.67–7.59 (m, 3 H, Ar), 7.49–7.39 (m, 3 H, Ar), 7.37–7.23 (m, 4 H, Ar), 4.25 (t, *J* = 7.2 Hz, 2 H, NCH₂), 1.85–1.81 (m, 2 H, CH₂), 1.42–1.26 (m, 6 H, CH₂), 0.85 (t, *J* = 6.9 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.9, 196.2, 143.3, 141.1, 140.1, 137.4, 132.9, 130.3, 129.9, 129.86, 129.7, 129.6, 128.6, 128.3, 128.1, 126.4, 123.8, 123.2, 122.5, 120.7, 119.9, 109.3, 108.3, 43.3, 31.5, 28.9, 26.9, 22.5, 14.0 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 132.8, 130.3, 129.9, 129.8, 129.7, 129.6, 128.1, 126.4, 123.8, 120.7, 119.9, 109.3, 108.4, 43.3, 31.6, 28.9, 26.9, 22.5, 14.0 ppm. HRMS (EI): calcd. for C₃₂H₂₉NO₂ 459.2198; found 459.2206.

Oxidative Ring-Opening Reaction of Benzo[c]**-**furan **20a**: Benzo[c]-furan **20a** (0.5 g, 1.09 mmol) was treated with *m*-CPBA (0.37 g, 1.64 mmol) to give diketone **19a** (0.42 g, 82%) as a thick, yellow liquid.

Oxidative Ring-Opening Reaction of Benzo[*c*]**furan 20b:** The reaction of *N*-hexylcarbazole lactone^[5a] with *p*-anisylmagnesium bromide followed by acidic workup, as mentioned above, gave benzo[*c*]-furan **20b.** The oxidative ring-opening reaction of benzo[*c*]furan **20b** (0.5 g, 1.06 mmol) with *m*-CPBA (0.36 g, 1.58 mmol) afforded diketone **19b** (0.42 g, 82%) as a thick, yellow liquid.

Oxidative Ring-Opening Reaction of Benzo[c]furan 20c: The reaction of *N*-hexylcarbazole lactone^[5a] with phenylmagnesium bromide followed by acidic workup, as mentioned above, gave benzo-[c]furan **20c**. The oxidative ring-opening reaction of benzo[c]furan **20c** (0.5 g, 1.13 mmol) with *m*-CPBA (0.38 g, 1.69 mmol) gave diketone **19c** (0.41 g, 80%) as a thick, yellow liquid.

19d: The reaction of *N*-hexylcarbazole lactone^[5a] with 1-naphthylmagnesium bromide followed by acidic workup, as mentioned above, gave benzo[*c*]furan **20d**. Benzo[*c*]furan **20d** (0.45 g, 0.91 mmol) was treated with *m*-CPBA (0.31 g, 1.37 mmol) to give diketone **19d** (0.38 g, 81%) as a pale yellow solid; m.p. 136–138 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.25$ (s, 1 H, Ar), 8.1 (d, J =8.7 Hz, 1 H, Ar), 7.98 (d, J = 7.5 Hz, 1 H, Ar), 7.86 (d, J = 7.8 Hz, 1 H, Ar), 7.77 (d, J = 7.5 Hz, 1 H, Ar), 7.69–7.56 (m, 6 H, Ar), 7.50–7.45 (m, 1 H, Ar), 7.40–7.31 (m, 2 H, Ar), 7.27–7.22 (m, 2 H, Ar), 7.15–7.08 (m, 2 H, Ar), 4.21 (t, J = 7.0 Hz, 2 H, NCH₂), 1.84– 1.78 (m, 2 H, CH₂), 1.42–1.26 (m, 6 H, CH₂), 0.89–0.85 (m, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 197.7$, 196.5, 143.2, 141.8, 141.0, 140.7, 135.4, 133.6, 133.5, 132.7, 131.4, 130.8, 130.6, 130.5, 130.2, 129.9, 129.2, 129.0, 127.9, 127.5, 127.1, 126.3, 136.1, 125.5, 124.0, 123.3, 123.1, 122.5, 120.7, 119.9, 109.1, 108.2, 43.3, 31.5, 29.0, 26.9, 22.5, 14.0 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 132.7, 131.4, 130.6, 130.56, 129.9, 129.2, 127.9, 127.5, 127.1, 126.4, 126.1, 125.5, 124.0, 123.3, 120.7, 119.9, 109.1, 108.2, 43.3, 31.5, 29.0, 26.9, 22.5, 14.0 ppm. HRMS (EI): calcd. for C₃₆H₃₁NO₂ 509.2355; found 509.2353.

19e: Benzo[c]furan 20e (0.50 g, 1.11 mmol) was treated with m-CPBA (0.37 g, 1.67 mmol) to give diketone **19e** (0.40 g, 78%) as a thick, yellow liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.37$ (s, 1 H, Ar), 7.88 (d, J = 7.8 Hz, 1 H, Ar), 7.78 (d, J = 8.7 Hz, 1 H, Ar), 7.64–7.55 (m, 2 H, Ar), 7.51–7.47 (m, 2 H, Ar), 7.41–7.39 (m, 2 H, Ar), 7.33–7.24 (m, 2 H, Ar), 7.18 (d, J = 8.7 Hz, 1 H, Ar), 7.10 (t, J = 7.2 Hz, 1 H, Ar), 6.87 (t, J = 4.3 Hz, 1 H, Ar), 4.10 (t, J = 6.9 Hz, 2 H, NCH₂), 1.72–7.65 (m, 2 H, CH₂), 1.16–1.10 (m, 6 H, CH₂), 0.72 (t, J = 6.9 Hz, 3 H, CH₃) ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 195.9, 188.4, 144.05, 143.1, 140.9, 140.5,$ 139.6, 134.8, 134.4, 130.3, 129.8, 129.6, 128.9, 128.3, 127.9, 127.8, 126.2, 123.6, 122.9, 120.5, 119.8, 109.1, 108.2, 43.1, 31.4, 28.7, 26.7, 22.4, 13.9 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 134.8, 134.4, 130.3, 129.8, 129.6, 128.9, 127.9, 127.8, 126.2, 123.6, 120.5, 119.8, 109.1, 108.2, 43.1, 31.4, 28.7, 26.7, 22.4, 13.9 ppm. C₃₀H₂₇NO₂S (465.61): calcd. C 77.39, H 5.84, N 3.01, S 6.89; found C 77.15, H 5.97, N 3.19, S 6.74.

22a: The oxidative ring-opening reaction of benzo[*c*]furan **21a** (0.5 g, 1.06 mmol) with *m*-CPBA (0.36 g, 1.59 mmol) gave diketone **22a** (0.43 g, 83%) as a thick, yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 8.38 (s, 1 H), 7.96 (d, *J* = 7.8 Hz, 1 H, Ar), 7.79 (d, *J* = 8.7 Hz, 1 H, Ar), 7.63–7.56 (m, 6 H, Ar), 7.43–7.31 (m, 3 H, Ar), 7.27–7.15 (m, 4 H, Ar), 4.09 (d, *J* = 7.2 Hz, 2 H, NCH₂), 2.01–1.91 (m, 1 H, CH), 1.33–1.18 (m, 8 H, CH₂), 0.85–0.76 (m, 6 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.9, 196.2, 143.8, 141.6, 141.1, 140.0, 137.4, 132.8, 130.3, 129.9, 129.8, 129.7, 129.6, 128.6, 128.2, 128.1, 126.4, 123.7, 123.1, 122.5, 120.7, 119.9, 109.5, 108.6, 47.6, 39.4, 29.7, 28.8, 24.4, 23.0, 14.0, 10.9 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 132.8, 130.3, 129.9, 129.8, 129.7, 129.6, 128.2, 128.1, 126.4, 123.7, 120.7, 119.9, 109.5, 108.6, 47.6, 39.4, 29.7, 28.8, 24.4, 23.0, 14.0, 10.9 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 132.8, 130.3, 129.9, 129.8, 129.7, 129.6, 128.2, 128.1, 126.4, 123.7, 120.7, 119.9, 109.5, 108.6, 47.6, 39.4, 29.7, 28.8, 24.4, 23.0, 14.0, 10.9 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 132.8, 130.3, 129.9, 129.8, 129.7, 129.6, 128.2, 128.1, 126.4, 123.7, 120.7, 119.9, 109.5, 108.6, 47.6, 39.4, 29.7, 28.8, 24.4, 23.0, 14.0, 10.9 ppm. C₃₄H₃₃NO₂ (487.64): calcd. C 83.74, H 6.82, N 2.87; found C 83.98, H 6.75, N 2.94.

22b: Benzo[c]thiophene 21b (0.4 g, 0.51 mmol) was treated with m-CPBA (0.17 g, 0.77 mmol) followed by workup to give diketone 22b (0.31 g, 78%) as a thick, yellow liquid. ¹H NMR (300 MHz, $CDCl_3$): $\delta = 8.44$ (s, 1 H, Ar), 8.30 (s, 1 H, Ar), 8.25 (s, 1 H, Ar), 8.10 (d, J = 7.5 Hz, 1 H, Ar), 7.83 (d, J = 8.7 Hz, 1 H, Ar), 7.76 (d, J = 8.4 Hz, 1 H, Ar), 7.70 (d, J = 8.4 Hz, 1 H, Ar), 7.66–7.64 (m, 1 H, Ar), 7.57–7.54 (m, 5 H, Ar) 7.41–7.31 (m, 4 H, Ar), 7.25 (d, J = 8.1 Hz, 1 H, Ar), 7.20–7.14 (m, 1 H, Ar), 7.04 (d, J =8.1 Hz, 2 H, Ar), 4.10 (d, J = 6.9 Hz, 4 H, NCH₂), 2.23 (s, 3 H, CH3), 2.07-1.95 (m, 2 H, CH), 1.33-1.17 (m, 16 H, CH2), 0.89-0.77 (m, 12 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): *δ* = 196.5, 196.2, 144.1, 143.7, 141.3, 141.0, 140.5, 140.3, 140.1, 134.8, 134.5, 132.7, 130.1, 130.0, 129.8, 129.6, 129.4, 128.9, 128.6, 128.0, 126.1, 125.6, 125.3, 123.8, 123.7, 123.3, 122.9, 122.6, 122.6, 120.3, 119.1, 118.81, 118.7, 109.7, 109.2, 109.1, 108.7, 47.7, 47.5, 39.4, 31.0, 30.96, 28.81, 28.78, 24.39, 24.34, 23.04, 23.0, 21.6, 14.0, 10.9, 10.87 ppm. DEPT-135 (75 MHz, CDCl₃): $\delta = 130.15$, 130.06, 129.9, 129.7, 129.5, 129.0, 128.1, 126.2, 125.7, 125.7, 125.4, 123.9, 120.4, 119.2, 118.9, 118.8, 109.7, 109.3, 109.1, 108.8, 47.7, 47.5, 39.48, 39.45, 31.05, 31.0, 28.9, 28.8, 24.44, 24.4, 23.1, 23.07, 21.68, 14.11, 11.0, 10.9 ppm. HRMS (EI): calcd. for $C_{55}H_{58}N_2O_2$ 778.4498; found 778.4498.

24a: Benzo[*c*]furan **23a** (0.50 g, 1.13 mmol) was treated with *m*-CPBA (0.38 g, 1.69 mmol) in DCM to give diketone **24a** (0.4 g,

77%) as a pale yellow solid; m.p. 140–141 °C. IR (KBr): $\tilde{v} = 1646$, 1582, 1489, 1278 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.65$ –7.40 (m, 8 H, Ar), 7.26–7.19 (m, 5 H, Ar), 7.07–7.00 (m, 6 H, Ar), 6.82 (d, J = 8.7 Hz, 2 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 194.9$, 188.5, 152.2, 146.4, 144.3, 140.3, 139.6, 135.1, 134.7, 131.6, 130.4, 130.0, 129.65, 129.6, 129.4, 129.0, 128.0, 126.0, 124.7, 119.4 ppm. DEPT-135 (75 MHz, CDCl₃): $\delta = 135.1$, 134.7, 131.6, 130.4, 130.0, 129.6, 129.5, 129.0, 128.0, 126.0, 124.7, 119.4 ppm. HRMS (EI): calcd. for C₃₀H₂₁NO₂S 459.1293; found 459.1283.

24b: The ring-opening reaction of triphenylamino lactone^[5a] with freshly prepared 5-hexyl-2-thienylmagnesium bromide followed by acidic workup gave benzo[c]furan 23b as a thick, orange liquid. Benzo[c]furan 23b (0.40 g, 0.76 mmol) was treated with m-CPBA (0.26 g, 1.14 mmol) to give diketone 24b (0.32 g, 79%) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): δ = 7.56–7.53 (m, 1 H, Ar),7.52-7.43 (m, 5 H, Ar), 7.26-7.19 (m, 5 H, Ar), 7.07-7.05 (m, 6 H, Ar), 6.82 (d, J = 8.7 Hz, 2 H, Ar), 6.68 (d, J = 3.4 Hz, 1 H, Ar), 2.74 (t, J = 7.5 Hz, 2 H, CH₂), 1.64–1.54 (m, 2 H, CH₂), 1.30–1.20 (m, 6 H, CH₂), 0.80 (t, J = 6.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 195.0, 188.1, 157.1, 152.1, 146.4, 141.7, 140.2, 139.6, 135.7, 131.5, 130.2, 129.9, 129.8, 129.5, 129.3, 128.9, 126.0, 125.6, 124.6, 119.5, 31.4, 31.3, 30.7, 28.7, 22.5, 14.0 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.7, 131.4, 130.2, 129.9, 129.5, 129.3, 128.9, 125.9, 125.5, 124.6, 119.5, 31.4, 31.3, 30.7, 28.7, 22.5, 14.0 ppm. C₃₆H₃₃NO₂S (543.72): calcd. C 79.52, H 6.12, N 2.58, S 5.90; found C 79.36, H 6.17, N 2.63, S 5.84.

24c: The ring-opening reaction of triphenylamino lactone^[5a] with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[c]furan 23c as a thick, yellow liquid. Benzo-[c]furan 23c (0.52 g, 1.19 mmol) was treated with m-CPBA (0.40 g, 1.78 mmol) to give diketone 24c (0.44 g, 81%) as a pale yellow solid; m.p. 174–175 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.66 (d, J = 7.2 Hz, 2 H, Ar), 7.55–7.45 (m, 7 H, Ar), 7.35–7.30 (m, 2 H, Ar), 7.26–7.19 (m, 5 H, Ar), 7.07–7.04 (m, 5 H, Ar), 6.82 (d, J = 8.7 Hz, 2 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.8, 194.9, 152.2, 146.4, 140.7, 139.8, 137.3, 133.0, 131.6, 130.3, 129.9, 129.87, 129.63, 129.53, 129.38, 128.3, 126.1, 124.8, 119.4 ppm. DEPT-135 (75 MHz, CDCl₃): $\delta = 133.0$, 131.6, 130.3, 129.94, 129.87, 129.63, 129.53, 129.38, 128.3, 126.1, 124.8, 119.4 ppm. $C_{32}H_{23}NO_2$ (453.54): calcd. C 84.74, H 5.11, N 3.09; found C 84.36, H 4.90, N 3.24. For the single-crystal X-ray structure analysis of 24c, all of the calculations were performed with the SHELXL-97 program.^[23] Crystal data of 24c: $C_{32}H_{23}NO_2$, M =453.51 gmol⁻¹, triclinic crystal system, space group $P\overline{1}$, Z = 4, a =10.7599(3) Å, b = 13.0389(3) Å, c = 17.9453(5) Å, $a = 90.447(2)^{\circ}$, $\beta = 98.415(2)^\circ$, $\gamma = 108.904(2)^\circ$, $V = 2352.13(11) \text{ Å}^3$ and $D_{\text{calcd.}} =$ 1.281 Mg m⁻³. In total, 8280 independent reflections were collected, of which 6006 were considered as observed $[I > 2\sigma(I)]$. The structure was solved by direct methods and refined by full-matrix leastsquares procedures to a final R value of 3.64%.

CCDC-867364 (for **24c**) contains 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.

24d: The ring-opening reaction of triphenylamino lactone^[5a] with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **23d** as an orange solid. The oxidative ring-opening reaction of benzo[*c*]furan **23d** (0.50 g, 1.07 mmol) with *m*-CPBA (0.36 g, 1.61 mmol) gave diketone **24d** (0.43 g, 83%) as a pale yellow solid; m.p. 144–145 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.64 (d, *J* = 8.7 Hz, 2 H, Ar), 7.52–7.44 (m, 6 H, Ar), 7.24–7.19 (m, 4 H, Ar), 7.05–7.02 (m, 6 H, Ar), 6.82–6.77 (m, 4 H,



Ar), 3.76 (s, 3 H, OCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 195.5, 195.0, 163.5, 152.1, 146.4, 140.4, 140.2, 132.3, 131.6, 130.3, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 129.0, 124.7, 119.4, 113.6, 55.5 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 132.3, 131.6, 129.9, 129.8, 129.6, 129.3, 129.2, 126.0, 124.7, 119.4, 113.6, 55.5 ppm. HRMS (EI): calcd. for C₃₃H₂₅NO₃ 483.1834; found 483.1828.

Oxidative Cleavage of Benzo[c]furan 25: Benzo[c]furan 25 (0.60 g, 1.57 mmol) was treated with m-CPBA (0.70 g, 3.14 g) in DCM followed by workup and purification by column chromatography (silica gel, 5% EA/hexane for 26a, 15% EA/hexane for 26b, 25% EA/ hexane for 26c) to give diketones 26a-26c. Data for 26a: Pale yellow solid (256 mg, 41%); m.p. 110-112 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.43 (s, 1 H, Ar), 8.04–8.01 (m, 1 H, Ar), 7.79–7.71 (m, 5 H, Ar), 7.63-7.58 (m, 2 H, Ar), 7.54-7.52 (m, 1 H, Ar), 7.47-7.45 (m, 1 H, Ar), 7.42–7.37 (m, 2 H, Ar), 7.00–6.98 (m, 1 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.2, 188.2, 144.7, 144.0, 139.9, 139.8, 139.6, 135.4, 135.1, 135.0, 134.8, 133.7, 130.6, 130.4, 129.7, 129.2, 128.0, 127.8, 127.7, 127.4, 125.8, 124.8, 122.6, 122.0 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.0, 134.9, 130.6, 130.4, 129.7, 129.2, 128.0, 127.7, 127.4, 124.8, 123.3, 122.8, 122.6, 122.0 ppm. HRMS (EI): calcd. for C₂₄H₁₄O₂S₂ 398.0435; found 398.0440. Data for 26b: Pale brown solid (196 mg, 29%); m.p. 173-175 °C. IR (KBr): \tilde{v} = 1659, 1618, 1408, 1296, 1162 cm⁻¹. ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 8.11$ (s, 1 H, Ar), 8.0–7.94 (m, 1 H, Ar), 7.76-7.69 (m, 4 H, Ar), 7.64-7.55 (m, 4 H, Ar), 7.50-7.48 (m, 2 H, Ar), 7.07–7.01 (m, 1 H, Ar), 6.93–6.90 (m, 1 H, Ar) ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 195.1, 187.7, 143.6, 141.9, 139.5, 138.9,$ 137.8, 135.5, 135.2, 134.2, 132.2, 131.7, 131.2, 131.1, 130.9, 129.9, 129.6, 129.5, 128.9, 128.2, 128.1, 126.0, 122.3, 122.1 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.5, 135.2, 134.2, 131.7, 131.2, 131.1, 131.0, 129.7, 129.6, 129.5, 128.2, 126.0, 122.3, 122.1 ppm. HRMS (EI): calcd. for C₂₄H₁₄O₄S₂ 430.0334; found 430.0335. Data for **26c**: Pale brown solid (123 mg, 19%); m.p. 162 °C. IR (KBr): \tilde{v} = 1640, 1408, 1288, 1024 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.12 (s, 1 H, Ar), 7.94–7.89 (m, 2 H, Ar), 7.77–7.70 (m, 3 H, Ar), 7.66–7.55 (m, 5 H, Ar), 7.52–7.47 (m, 2 H, Ar), 7.06–7.03 (m, 1 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 195.5, 187.8, 149.0, 145.2, 143.7, 140.8, 139.6, 139.1, 137.5, 136.1, 135.3, 135.2, 132.8, 131.1, 131.0, 130.8, 130.1, 129.6, 129.4, 128.2, 127.6, 127.4, 122.6, 122.5 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.3, 135.2, 132.8, 131.1, 131.0, 130.8, 130.1, 129.7, 129.5, 128.2, 127.6, 127.4, 122.6, 122.5 ppm. HRMS (EI): calcd. for C24H14O3S2 414.0384; found 414.0380.

Oxidative Ring Opening of Benzolclfuran 27: The ring-opening reaction of dibenzothiophenyl lactone^[5a] with freshly prepared 1naphthylmagnesium bromide followed by acidic workup gave benzo[c]furan 27 as a thick, yellow liquid. Benzo[c]furan 27 (0.66 g, 1.55 mmol) was treated with m-CPBA (0.694 g, 3.09 mmol) in DCM followed by purification by column chromatography (silica gel, 5% EA/hexane for 28a, 15% EA/hexane for 28b, 25% EA/ hexane for 28c) to give diketones 28a-28c. Data for 28a: Pale yellow solid (296 mg, 44%); m.p. 88 °C. IR (KBr): $\tilde{v} = 1655$, 1419, 1246, 1066 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.12 (s, 1 H, Ar), 7.99 (d, J = 8.1 Hz, 1 H, Ar), 7.91–7.88 (m, 1 H, Ar), 7.78 (d, J = 8.1 Hz, 1 H, Ar), 7.73–7.68 (m, 2 H, Ar), 7.64–7.52 (d, 5 H, Ar), 7.48–7.43 (m, 2 H, Ar), 7.40–7.31 (m, 2 H, Ar), 7.28–7.23 (m, 1 H, Ar), 7.16–7.10 (m, 2 H, Ar) ppm. ¹³C NMR (CDCl₃, 75 MHz): *δ* = 197.3, 196.6, 144.7, 140.9, 140.5, 139.4, 135.4, 135.1, 134.9, 134.1, 133.3, 132.9, 131.6, 130.8, 130.6, 130.4, 129.1, 127.9, 127.3, 127.2, 127.1, 126.2, 125.1, 124.7, 123.9, 122.7, 122.5, 122.4, 121.8 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 133.0, 131.7, 130.9, 130.7, 130.5, 129.2, 128.0, 127.4, 127.3, 127.2, 126.3, 125.2, 124.8, 123.9, 122.8, 122.6, 122.5, 121.9 ppm. HRMS (EI): calcd. for

C₃₀H₁₈O₂S 442.1028; found 442.1024. Data for **28b**: Thick, light brown liquid (224 mg, 31%). ¹H NMR (300 MHz, CDCl₃): δ = 8.08 (d, J = 8.4 Hz, 1 H, Ar), 7.89 (d, J = 8.1 Hz, 1 H, Ar), 7.83(s, 1 H, Ar), 7.73 (d, J = 7.5 Hz, 2 H, Ar), 7.68–7.55 (m, 6 H, Ar), 7.52–7.44 (m, 4 H, Ar), 7.34 (t, J = 7.5 Hz, 2 H, Ar), 7.25 (d, J = 7.3 Hz, 1 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 196.9, 195.6, 142.3, 140.8, 140.1, 139.9, 137.8, 134.8, 134.0, 133.5, 133.3, 132.2, 131.3, 131.2, 131.0, 130.9, 130.8, 130.6, 129.0, 128.3, 128.1, 126.7, 125.0, 124.0, 122.2, 122.1, 122.0, 121.5 ppm. DEPT-135 $(75 \text{ MHz}, \text{ CDCl}_3): \delta = 134.1, 133.3, 132.2, 131.3, 131.2, 131.0,$ 130.9, 130.8, 129.0, 128.3, 128.1, 126.7, 125.0, 124.0, 122.2, 122.1, 122.0, 121.5 ppm. HRMS (EI): calcd. for C₃₀H₁₈O₄S 474.0926; found 474.0883. Data for 28c: Thick, light brown liquid (126 mg, 18%). ¹H NMR (300 MHz, CDCl₃): δ = 8.12 (d, J = 8.1 Hz, 1 H, Ar), 7.89–7.85 (m, 3 H, Ar), 7.79 (d, J = 8.1 Hz, 1 H, Ar), 7.71– 7.68 (m, 1 H, Ar), 7.66–7.57 (m, 5 H, Ar), 7.55–7.51 (m, 2 H, Ar), 7.50-7.41 (m, 2 H, Ar), 7.34-7.30 (m, 3 H, Ar) ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 196.9, 195.9, 148.7, 145.1, 141.1, 140.2,$ 140.1, 137.4, 136.0, 134.8, 133.4, 133.1, 132.7, 132.0, 131.2, 130.8, 130.7, 130.6, 130.2, 130.0, 129.0, 128.1, 128.0, 127.4, 127.2, 126.5, 125.2, 124.0, 122.3, 121.8 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 133.2, 132.7, 132.1, 131.2, 130.9, 130.6, 130.3, 130.1, 129.1, 128.1, 128.0, 127.5, 127.3, 126.6, 125.3, 124.0, 122.4, 121.9 ppm.

30a:^[24] 2,5-Diphenylfuran (**29a**, 0.50 g, 2.27 mmol) was treated with *m*-CPBA (0.76 g, 3.41 mmol) to give *cis*-1,4-diphenylbut-2ene-1,4-dione^[11] (**30a**, 0.49 g, 92%) as a pale yellow solid; m.p. 125 °C, ref.^[24] m.p. 133.5–134.5 °C. IR (KBr): $\tilde{v} = 1649$, 1588, 1444, 1294, 1185 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.85$ (d, J = 7.8 Hz, 4 H, Ar), 7.50–7.46 (m, 2 H, Ar), 7.39–7.34 (m, 4 H, Ar), 7.07 (s, 2 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 192.5$, 136.1, 135.6, 133.6, 128.8, 128.6 ppm. DEPT-135 (75 MHz, CDCl₃): $\delta = 135.6$, 133.6, 128.8, 128.6 ppm.

30b: The oxidative ring cleavage of known 2,5-bis(thiophen-2-yl) furan^[25] (**29b**, 0.48 g, 2.07 mmol) using *m*-CPBA (0.535 g, 3.10 mmol) gave *cis*-1,4-bis(thiophen-2-yl)but-2-ene-1,4-dione (**30b**, 0.35 g, 68%) as a brown solid; m.p. 178–180 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.87–7.85 (m, 4 H, Ar), 7.71 (d, *J* = 4.8 Hz, 2 H, Ar), 7.15 (t, *J* = 4.0 Hz, 2 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 181.4, 144.7, 135.8, 134.2, 133.6, 128.7 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.8, 134.2, 133.6, 128.7 ppm.

30c: 2-(4-Chlorophenyl)-5-phenylfuran (**29c**, 0.60 g, 2.36 mmol) was treated with *m*-CPBA (0.61 g, 3.53 mmol) to give *cis*-1-(4-chlorophenyl)-4-diphenylbut-2-ene-1,4-dione (**30c**, 0.57 g, 89%) as a pale yellow solid; m.p. 84–85 °C, ref.^[26] m.p. 83 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.86 (d, *J* = 7.8 Hz, 2 H, Ar), 7.80 (d, *J* = 8.4 Hz, 2 H, Ar), 7.50 (t, *J* = 7.2 Hz, 1 H, Ar), 7.41–7.33 (m, 4 H, Ar), 7.13 (d, *J* = 12 Hz, 1 H, Ar), 7.01 (d, *J* = 11.7 Hz, 1 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 191.9, 191.8, 140.0, 136.0, 135.9, 135.2, 134.4, 133.7, 130.0, 129.1, 128.8, 128.6 ppm. DEPT-135 (75 MHz, CDCl₃): δ = 135.9, 135.2, 133.7, 130.0, 129.1, 128.8, 128.7 ppm.

Oxidation of Benzo[c]furan 6d Using LTA: To a stirred suspension of benzo[c]furan **6d** (2.41 g, 8.03 mmol) in dry THF (40 mL) was added lead tetraacetate (3.56 g, 8.03 mmol), and the reaction mixture was stirred for 30 min at 50 °C. The reaction mixture was then poured into water (200 mL), and the resulting mixture was extracted with ethyl acetate (2×30 mL). The combined organic extracts were washed with a brine solution and dried with Na₂SO₄. Removal of solvent in vacuo followed by crystallization from methanol gave **5d** (1.94 g, 76%) as a colorless solid.

Oxidation of Benzo[*c*]**furan 6e Using LTA:** Following a similar procedure to that of **6d**, the oxidation of benzo[*c*]**furan 6e** (0.75 g,

2.24 mmol) using LTA (0.99 g, 2.23 mmol) gave diketone 5e (0.65 g, 85%) as a colorless solid.

Oxidation of Benzo[c]furan 6h Using LTA: Following a similar procedure to that of **6d**, the oxidation of benzo[c]furan **6h** (1.0 g, 3.62 mmol) using LTA (1.60 g, 3.62 mmol) gave diketone **5h** (0.88 g, 84%) as a brown solid.

Oxidation of Benzo[c]furan 20a Using LTA: Following a similar procedure to that of **6d**, the oxidation of benzo[*c*]furan **20a** (0.66 g, 1.44 mmol) using LTA (0.64 g, 1.44 mmol) gave diketone **19a** (0.26 g, 25%) as a brown solid.

Oxidation of Benzo[c]furan 20c Using LTA: Following a similar procedure to that of 6d, the oxidation of benzo[c]furan 20c (0.72 g, 1.62 mmol) using LTA (0.72 g, 1.62 mmol) gave diketone 19a (0.16 g, 21 %) as a thick, yellow liquid.

Oxidation of Benzo[c]furan 23c Using LTA: Following a similar procedure to that of **6d**, the oxidation of benzo[*c*]furan **23c** (0.59 g, 1.35 mmol) using LTA (0.61 g, 1.35 mmol) gave diketone **24c** (0.14 g, 23%) as a pale yellow solid.

Oxidation of Benzo[*c*]**furan 23d Using LTA:** Following a similar procedure to that of **6d**, the oxidation of benzo[c]furan **23d** (0.56 g, 1.20 mmol) using LTA (0.53 g, 1.20 mmol) gave diketone **24d** (0.14 g, 24%) as a pale yellow solid.

Oxidation of Benzo[c]furan 25 Using LTA: Following a similar procedure to that of **6d**, the oxidation of benzo[c]furan**25** (1.0 g, 2.61 mmol) using LTA (1.16 g, 2.61 mmol) gave diketone **26a** (0.83 g, 80%) as a pale yellow solid.

Oxidation of Benzo[c]furan 27 Using LTA: Following a similar procedure to that of **6d**, the oxidation of benzo[c]furan **27** (2.13 g, 5.0 mmol) using LTA (2.21 g, 5.0 mmol) gave diketone **28a** (1.83 g, 83%) as a colorless solid.

Supporting Information (see footnote on the first page of this article): Experimental procedures for benzo[*c*]heterocycles 6f, 7a, 7b, 8a, 8b, 12, 14, 16a, 20a, 20e, 21a, 21b, 23a, 25, and 29a–29c. Copies of the ¹H NMR, ¹³C NMR, and DEPT 135 spectra for benzo-[*c*]heterocycles 8a, 8b, 12, 14, 16a, and 21a. Copies of ¹H NMR, ¹³C NMR, DEPT 135, and HRMS spectra for all of the 1,2-diaroylbenzenes produced.

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