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Synthesis of *o*-Carboxyarylacrylic Acids by Room Temperature Oxidative Cleavage of Hydroxynaphthalenes and Higher Aromatics with Oxone

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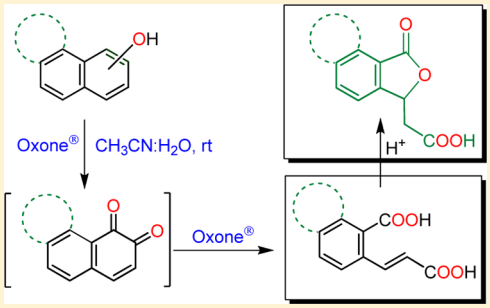
Supporting Information

ABSTRACT: A simple procedure for the synthesis of a variety of *o*-carboxyarylacrylic acids has been developed with Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$); the oxidation reaction involves the stirring of methoxy/hydroxy-substituted naphthalenes, phenanthrenes, anthracenes, etc. with Oxone in an acetonitrile−water mixture (1:1, v/v) at rt. Mechanistically, the reaction proceeds via initial oxidation of naphthalene to *o*-quinone, which undergoes cleavage to the corresponding *o*-carboxyarylacrylic acid. The higher aromatics are found to yield carboxymethyl lactones derived from the initially formed *o*-carboxyarylacrylic acids.



Oxidation of phenols has been extensively studied.[1−5] In particular, protocols for the oxidation of phenols to the corresponding ring-opened products, namely, muconic acids, are rather limited.[6] When naphthalenes undergo ring-opening oxidation, *ortho*-substituted cinnamaldehydes/cinnamic acids are obtained.[7] Cinnamic acids are well-known for their presence in various natural products[8] and are important in antioxidant, antifungal, anticarcinogenic, antiviral, and antibacterial activities.[9] While a number of synthetic procedures are known for cinnamic acids,[10] those reported for the synthesis of *o*-substituted cinnamic acids are scant.[11,12] One of the important *o*-substituted cinnamic acids is *o*-carboxycinnamic acid, which is widely used as a synthon for the preparation of *o*-carboxyhydrocinnamic acid,[13a] (*E*)-methyl-2-methoxycarbonyl-cinnamates,[13b] *o*-carboxycinnamamides,[11b] and methyl 2-carboxy-hydrocinnmates,[13d] etc. It should be noted that various indanones and indoles are frequently synthesized from *ortho*-substituted cinnamic acids.[11b,13c] The known synthetic methods for the latter are based on the oxidation of naphthols with different oxidation reagents, which include 85% aq. H_2O_2 in the presence of catalytic conc. H_2SO_4 in AcOH,[11a] CH_3COOOH/AcOH,[14] Na_2MoO_4/40% H_2O_2 in glacial AcOH,[11b] Se-based catalysts/H_2O_2,[12] etc. Ozonolysis of β-naphthol has also been reported to produce *o*-carboxycinnamic acid in 22% yield.[15]

In continuation of our ongoing research on IBX- and Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$)-mediated oxidation chemistry,[7b,16] we recently showed that naphthalene undergoes oxidation with Oxone, providing *o*-carboxycinnamic acid and naphthoquinone in 56 and 31% yields, respectively.[7b] This spurred us to comprehensively investigate oxidations of methoxy- and hydroxy-substituted naphthalenes with Oxone in view of environmentally benign, nontoxic, cheap, and easy handling attributes of the latter. It is noteworthy that Oxone is being increasingly employed in various oxidative transformations.[7b,16f,17,18] Herein, we report the rich oxidation chemistry of hydroxy-substituted aromatics with Oxone, which leads to *o*-carboxyarylacrylic acids and products derived thereof.

From the formation of *o*-carboxycinnamic acid by the oxidation of naphthalene with Oxone, we surmised that the C_1-C_2 bond of the former must undergo initial oxidation to the diketone followed by oxidative cleavage.[7b,16g] As the reaction necessitated reflux temperature and a long duration of 36 h for completion with 5 equiv of Oxone, we reasoned that e-rich naphthalenes should undergo oxidation faster to afford the corresponding carboxy-cinnamic acids. Indeed, the reaction of 2,7-dimethoxynaphthalene with 3 equiv of Oxone in an acetonitrile−water mixture led to the ring-opened product, i.e., 2-carboxy-4-methoxycinnamic acid, in 81% isolated yield within 12 h at rt. In contrast, the reactions of 1,7-dimethoxynaphthalene and substituted 1- and 2-methoxynaphthalenes containing various substituents such as Br, CN and COOH groups under similar conditions led to either poor yields or no reaction at all (cf. Supporting Information). Thus, we switched our attention to more reactive hydroxy-substituted naphthalenes and their homologous aromatics. Indeed, a variety of hydroxy-arenes were found to undergo oxidation, leading to products in respectable yields. In Table 1 are consolidated results of oxidations of a number of differently substituted α- and β-naphthols at rt. Depending on the reactivity, the duration of the reaction and equivalent amount of Oxone employed were modulated to maximize the yield in each case; the details of reaction time and Oxone equivalent employed are given in Table 1.

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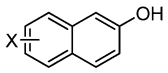
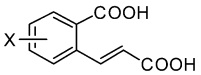
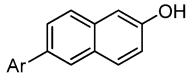
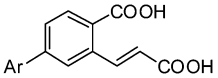
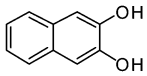
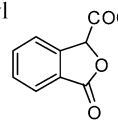
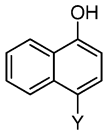
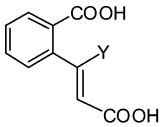
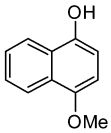
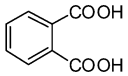
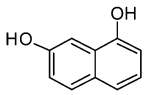
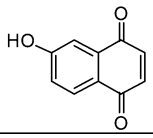
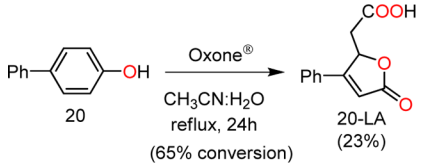
Table 1. Results of the Oxidation of Naphthols with Oxone in Acetonitrile−Water (1:1) at rt[a]

entry	substrate		product(s)		equiv./ time(h)	yield (%)[b]
1		1: X = H		1-CA	3/10	80
2		2: X = 6-Br		2-CA	3/12	82
3		3: X = 6-CN		2-CA	4/21	89
4		4: X = 1-OMe		1-CA	3/12	87
5		5: X = 6-*n*-Bu		5-CA	3/14	82
6		6: X = 7-OAc		6-CA	3/10	84
7		7: X = 6-CO_2H		7-CA	5/24	91
8		8: X = 6-$CONH_2$		8-CA	5/24	77
9		9: X = 6-CO_2Me		9-CA	4/18	83
10		10: Ar = *p*-tolyl		10-CA	4/21	95
11		11: Ar = *p*-anisyl		11-CA	4/18	84
12		12: Ar = *p*- hydroxyphenyl		12-CA	4/20	71
13		13		13-LA	3/14	50[c]
14		14: Y = H		14-CA	3/12	59[d]
15		15: Y= Br		15-CA	3/24	62
16		16: Y = Ph		16-CA	3/13	74
17		17: Y = CN		–	5/24	–[e]
18		18		18-A	4/16	76[f]
19		19		19-Q	3/10	15[g]

[a]All reactions were carried out with naphthol (1 equiv) and Oxone (3−5 equiv) in a CH_3CN-H_2O (1:1, v/v) mixture at rt. [b]Isolated yields, unless mentioned otherwise. [c]2,3-Dihydroxy-1,4-naphthoquinone (13-Q) was isolated in 15% yield. [d]1,4-Naphthoquinone (14-Q) was isolated in 31% yield. [e]No reaction. [f]1,4-Naphthoquinone (14-Q) was isolated in 12% yield. [g]Some unidentified polar product was observed.

As can be seen, *β*-naphthol underwent oxidation to completion in 10 h. Oxidation was found to occur nicely for a variety of naphthols bearing electron-donating as well as -withdrawing substituents. For naphthols containing electron-rich substituents such as OMe, *n*-Bu, and OAc, the corresponding acids were isolated in 87, 82, and 84% yields, respectively (Table 1, entries 4−6). All naphthols substituted with groups such as cyano, carboxy, amido, carboalkoxy, etc. were found to undergo oxidations rather slowly, leading to the corresponding *o*-carboxycinnamic acids in 89, 91, 77, and 83% yields, respectively (Table 1, entries 3 and 7−9). Good-to-excellent yields were obtained for *β*-naphthols substituted with tolyl, anisyl, and phenoxy groups at position 6 (Table 1, entries 10−12). Oxidation of 2,3-dihydroxynaphthalene led to caboxy-lactone in 50% yield over a period of 14 h; 2,3-dihydroxy-1,4-naphthoquindione was isolated in 15% yield (entry 13). *α*-Naphthols substituted with bromo and phenyl groups at position 4 led to respectable yields of *β*-substituted cinnamic acids (entries 15 and 16). The reaction was found to fail for 4-cyano-*α*-naphthol (entry 17).

Our efforts to carry out oxidations of anisoles and phenols likewise were frustrated by their poor reactivity even at high temperatures. Conceivably, these substrates are associated with higher activation barriers owing to a loss of aromaticity upon initial oxidation. For example, 4-phenylphenol was found to undergo oxidation at the reflux conditions of CH_3CN-H_2O over a period of 24 h, leading to the corresponding carboxymethyl lactone in 23% yield at 65% conversion (eq 1); the remainder was an intractable mixture.



(eq. 1)

In a logical progression, we sought to establish the oxidation chemistry of anthracenes, phenanthrenes and higher condensed aromatics such as helicenes. Oxidation of anthracene has been shown in our earlier investigation to lead to anthraquinone and bianthronyl.[7b] In phenantherenes, the C_9-C_{10} bond is highly susceptible to oxidation. The reaction of phenanthrene with Oxone in CH_3CN-H_2O (1:1 mixture) at reflux led to diphenic acid and 3,4,5,6-dibenzo-*α*-pyranone, derived from a cascade oxidation, Dakin reaction,[19] hydrolysis, and lactonization, in 59 and 23% isolated yields (cf. eq 2).

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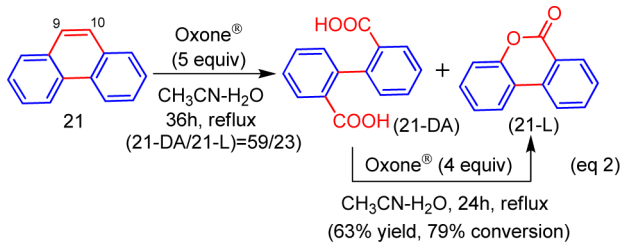
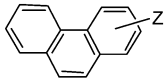
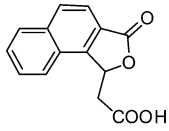
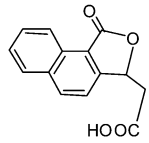
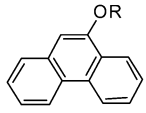
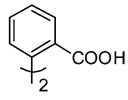
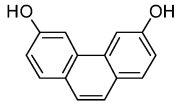
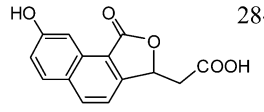
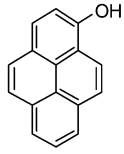
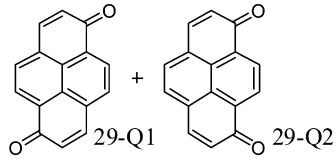
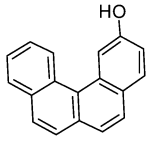
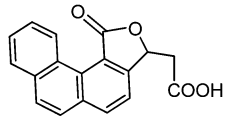
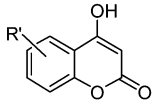
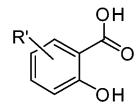
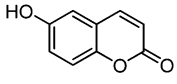
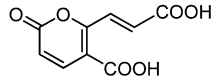


On the basis of these results, a higher reactivity was anticipated for hydroxy-susbstituted phenathrenes and higher condensed aromatics. All regioisomeric hydroxy-phenanthrenes were thus subjected to oxidation. As can be seen in Table 2, 2- and 3-hydroxyphenanthrenes led to carboxymethyl lactones in 85 and 82% isolated yields, respectively (Table 2, entries 2 and 3).[20] However, 1- and 4-hydroxynaphthalenes yielded regioisomeric carboxymethyl-substituted lactones in 58 and 40% isolated yields together with the corresponding 1,4-quinones in 27 and 14% yields, respectively (entries 4 and 1); in both cases, the reactions were comparatively slower with the conversions being incomplete even after 24 h. We found that the reactions of all methoxy-substituted phenanthrenes were sluggish with the exception of the 9-methoxy derivative. Oxidation of the latter led to diphenic acid in 85% yield in 18 h, while the hydroxy-analogue reacted much faster yielding the same product in 12 h (Table 2, entries 6 and 5). 3,6-Dihydroxynaphthalene, however, was found to be too reactive, leading to carboxymethyl-substituted lactone in 52% yield. 2-Hydroxytetrahelicene yielded the carboxymethyl lactone in 79% yield, while 1-hydroxypyrene afforded a regioisomeric mixture of diquinones in 89% yield; 1,6-diketopyrene was found to be

Table 2. Oxidation of Hydroxy-Substituted Phenanthrenes, Pyrene, Tetrahelicenes, and Coumarins with Oxone in Acetonitrile–Water (1:1) at rt[a]

entry	substrate		product		equiv./ time (h)	yield (%)[b]
1		22: Z = 1-OH		22-LA	5/22	40[c]
2		23: Z= 2-OH			4/24	85
3		24: Z = 3-OH		24-LA	4/24	82
4		25: Z = 4-OH			4/24	58[d]
5		26: R = H		21-DA	3/12	84
6		27: R = Me			3/18	85
7		28		28-LA	3/14	52
8		29		29-Q1 + 29-Q2	2/12	60+29
9		30		30-LA	4/22	79
10		31: R′ = H		31-A	3/12	84
11		32: R′ = 5,6-DiMe		32-A	2/12	82
12		33		33-XA	5/24	–[e]

[a]All reactions were carried out with a naphthol analogue (eq 1) and Oxone (3–5 equiv) in $CH_3CN–H_2O$ (1:1, v/v) mixture at rt. [b]Isolated yields unless mentioned otherwise. [c]Phenanthrene-1,4-diquinone (22-Q) was isolated in 27% yield with 95% conversion. [d]14% Phenanthrene-1,4-diquinone (22-Q) was isolated while conversion was 84%. [e]No reaction was found to occur.

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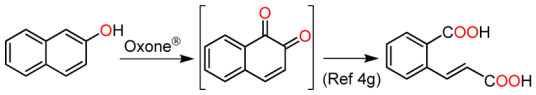
formed in 60%, while 1,8-diketopyrene was isolated in 29% yield. 4-Hydroxycoumarins yielded the corresponding salicylic acids in excellent isolated yields in 12 h (Table 2, entries 10–11). Notably, the deactivated 6-hydroxycoumarin was found to be unreactive at rt (Table 2, entry 12).

Insofar as the mechanism of the oxidation of naphthols is concerned, the initial reaction of α- and β-naphthols with Oxone leads to quinones, eq 3 (cf. Supporting Information,



(eq 3)

Scheme S5); the formation of the latter from β-naphthol is evidenced from the red coloration of the reaction mixture and signals attributable to its formation in the ^{1}H NMR monitoring of the reaction. However, for α-naphthol, 1,4-naphthoquinone is readily isolated. We believe that the quinone may result from initial formation of the epoxide, which opens up under the acidic conditions involving Oxone; indeed, this pathway best explains the formation of 2-carboxycinnamic acid from 1-methoxy-2-naphthol as well as the lack of formation of 2,2′-binaphthol. The *o*-quinone subsequently must undergo oxidative cleavage to the diacid by the attack of Oxone. Indeed, the formation of the diacid by the reaction of *o*-quinone with Oxone has been shown by Ishihara and co-workers earlier to proceed via the anhydride intermediate produced by Baeyer-Villger oxidation (cf. Scheme S5).[4g] Isomerization of the initially formed *Z*-*o*-cinnamic acid to the observed *E*-*o*-carboxycinnamic acid may occur in a facile manner under the employed acidic reaction conditions and is indeed well-known (cf. Supporting Information).[12b]

In contrast to hydroxynaththalenes that lead to *o*-carboxycinnamic acids on oxidation with Oxone, phenantherenes and helicenes yield the carboxymethyl lactones. Formation of the latter can be readily understood from the initial formation of *o*-carboxyarylacrylic acids, which undergo intramolecular Michael addition (cf. Supporting Information). The question as to why the *o*-carboxyarylacrylic acids derived from napththalenes, i.e., cinnamic acids, do not yield carboxymethyllactones can be reasoned based on resonance and steric effects. We believe that additional benzoannulation in *o*-carboxyarylacrylic acids derived from hydroxyphenanthrenes and helicenes may render the β-carbon of the acrylic acids considerably electrophilic for cyclization. Further, the steric effects may reduce the conformational flexibility of the *o*-carboxy group, whereby the cyclization is accelerated.

In conclusion, we have shown from a comprehensive investigation that oxidations of hydroxyaromatics with Oxone occur in a facile manner at rt leading to a variety of *o*-carboxyarylacrylic acids and carboxymethyl-substituted lactones; the latter are indeed derived from the initially formed *o*-carboxyarylacrylic acids by Michael addition. In addition to the access to a variety of *o*-carboxyarylacrylic acids, the rich oxidation chemistry of hydroxy-susbtituted aromatics with Oxone is demonstrated to lead to highly functionalized molecular entities.

EXPERIMENTAL SECTION

Solvents were distilled prior to use, and double distilled water was used for the reaction. All the reactions were carried out in an open atmosphere without any precaution. The products were isolated by column chromatography with a silica gel of 100–200 μm particle size. NMR spectra were recorded with 400 and 500 MHz spectrometers. IR spectra were recorded on an FT-IR spectrophotometer. Mass spectral analyses were carried out with an ESI-QTOF instrument. Melting point was measured with a Guna melting point apparatus and are uncorrected.

General Procedure for Oxidation of Hydroxy-Substituted Naphthalenes, Phenanthrenes, and Pyrenes. The procedure for a representative case, namely, α-naphthol, is as follows. To a solution of α-naphthol (0.20 g, 1.39 mmol) in 10 mL of an acetonitrile–water (1:1, v/v) mixture was incrementally added Oxone (2.56 g, 4.17 mmol). After completion of the reaction, as judged from TLC analysis, the reaction mixture was extracted with ethyl acetate multiple times. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was subjected to a short-pad silica gel column chromatography to get hold of *o*-carboxycinnamic acid (157 mg, 0.82 mmol, 59%) and 1,4-naphthoquinone (68 mg, 0.43 mmol, 31%).

All oxidations were carried out with the substrates employed in 0.4–1.4 mmol scale. All products were characterized by their spectroscopic data (cf. Supporting Information).

Characterization Data of Oxidation Products. *(E)-o-Carboxycinnamic Acid (1-CA).*[7b] Yield 106 mg (80%); colorless solid. R_f (10% MeOH/EtOAc): 0.2; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.41 (d, J = 15.7 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 15.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 121.8, 128.2, 130.2, 130.8, 131.6, 132.6, 135.3, 143.0, 167.9, 168.7.

(E)-5-Bromo-2-carboxycinnamic Acid (2-CA).[12b] Yield 199 mg (82%); colorless solid. R_f (20% MeOH/EtOAc): 0.4; mp 175–178 °C; IR (KBr) cm^{-1} 2900–2500 (br), 1681, 1632, 1583; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.50 (d, J = 16.0 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 8.02 (s, 1H), 8.23 (d, J = 16.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 123.4, 126.4, 130.4, 130.8, 132.8, 132.9, 137.7, 141.5, 167.8, 167.9.

(E)-2-Carboxy-5-cyanocinnamic Acid (3-CA). Yield 171 mg (89%); colorless solid. R_f (20% MeOH/EtOAc): 0.3; mp 187–190 °C; IR (KBr) cm^{-1} 3100–2600 (br), 2234, 1724, 1698, 1639; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.61 (d, J = 16.0 Hz, 1H), 7.93–7.99 (m, 2H), 8.16 (d, J = 16.0 Hz, 1H), 8.36 (d, J = 1.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 115.0, 118.2, 124.1, 131.3, 132.1, 133.2, 135.6, 135.9, 140.6, 167.57, 167.65; ESI-MS$^-$ m/z calcd for $C_{11}H_6NO_4$ 216.0296 [M − H]$^-$, found 216.0298.

(E)-5-n-Butyl-2-carboxycinnamic Acid (5-CA). Yield 100 mg (82%); colorless solid. R_f (EtOAc): 0.3; mp 138–142 °C; IR (KBr) cm^{-1} 3000–2600 (br), 2961, 2932, 2859, 1685; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, J = 7.5 Hz, 3H), 1.35–1.41 (m, 2H), 1.63–1.67 (m, 2H), 2.71 (t, J = 7.7 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.87 (d, J = 15.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.8, 22.3, 33.1, 35.6, 119.7, 126.2, 128.0, 130.1, 132.1, 136.5, 146.8, 149.1, 172.9, 173.0; ESI-MS$^-$ m/z calcd for $C_{14}H_{16}O_4$ 247.0970 [M − H]$^-$, found 247.0977.

(E)-4-Acetoxy-2-carboxycinnamic Acid (6-CA). Yield 159 mg (84%); colorless solid. R_f (EtOAc): 0.2; mp 130–135 °C; IR (KBr) cm^{-1} 3000–2700 (br), 1752, 1698; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.29 (s, 3H), 6.40 (d, J = 16.0 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.62 (s, 1H), 7.88 (d, J = 8.8 Hz, 1H), 8.27 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 21.3, 122.0, 124.1, 126.1, 129.7, 132.7, 132.9, 142.1, 151.5, 167.8, 167.9, 169.5; EI-MS$^-$ m/z calcd for $C_{12}H_9O_6$ 249.0399 [M − H]$^-$, found 249.0398.

(E)-2,5-Dicarboxycinamic Acid (7-CA). Yield 114 mg (91%); colorless solid. R_f (30% MeOH/EtOAc): 0.3; mp 240–242 °C; IR (KBr) cm^{-1} 3000–2600 (br), 1695; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.42 (d, J = 16.0 Hz, 1H), 7.95–8.0 (m, 2H), 8.21–8.30 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 122.7, 128.7, 130.5, 131.1, 134.3, 135.1, 135.5, 142.3, 166.7, 167.6, 168.1; ESI-MS$^-$ m/z calcd for $C_{11}H_7O_6$ 235.0242 [M − H]$^-$, found 235.0249.

(E)-5-Amido-2-carboxycinnamic Acid (8-CA). Yield 108 mg (77%); colorless solid. R_f (50% MeOH/EtOAc): 0.3; mp 128–130 °C; IR (KBr) cm^{-1} 3200–3000 (br), 1693, 1671, 1638; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.57 (d, J = 15.8 Hz, 1H), 7.61 (s, 1H), 7.91–7.96

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(m, 2H), 8.24−8.31 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 122.6, 126.8, 129.2, 130.8, 133.9, 135.2, 137.5, 142.4, 167.0, 167.8, 168.3; EI-MS$^-$ m/z calcd for $C_{11}H_8NO_5$ 234.0402 [M − H]$^-$, found 234.0409.

(E)-5-Carbomethoxy-2-carboxycinamic Acid (9-CA). Yield 151 mg (83%); colorless solid. R_f (20% MeOH/EtOAc): 0.4; mp 198−200 °C; IR (KBr) cm^{-1} 2900−2600 (br), 1734, 1687, 1626; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.89 (s, 3H), 6.45 (d, J = 16.0 Hz, 1H), 7.99−8.02 (m, 2H), 8.22−8.26 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 53.1, 123.0, 128.7, 130.4, 131.3, 133.1, 135.5, 135.7, 142.1, 165.8, 167.6, 168.0; ESI-MS$^-$ m/z calcd for $C_{12}H_9O_6$ 249.0399 [M − H]$^-$, found 249.0398.

(E)-2-Carboxy-5-(4-tolyl)cinnamic Acid (10-CA). Yield 181 mg (95%); colorless solid. R_f (EtOAc): 0.4; mp 239−242 °C; IR (KBr) cm^{-1} 3000−2600 (br), 1705, 1683, 1631, 1602; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.36 (s, 3H), 6.60 (d, J = 16.1 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 8.01 (s, 1H), 8.38 (d, J = 16.1 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.2, 122.3, 125.9, 127.4, 127.8, 129.9, 130.1, 131.6, 136.1, 136.3, 138.4, 143.2, 143.9, 168.0, 168.4; ESI-MS$^-$ m/z calcd for $C_{17}H_{13}O_4$ 281.0813 [M − H]$^-$, found 281.0813.

(E)-2-Carboxy-5-(4-anisyl)cinnamic Acid (11-CA). Yield 150 mg (84%); colorless solid. R_f (10% MeOH/EtOAc): 0.4; mp 138−140 °C; IR (KBr) cm^{-1} 3500−2500 (br), 1706, 1601; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.81 (s, 3H), 6.59 (d, J = 16.0 Hz, 1H), 7.05 (d, J = 9.1 Hz, 2H), 7.75−7.80 (m, 3H), 7.95 (d, J = 8.2 Hz, 2H), 7.99 (s, 1H), 8.38 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 55.7, 114.9, 122.3, 125.7, 127.5, 128.9, 129.1, 131.2, 131.8, 136.4, 143.3, 143.7, 160.2, 168.0, 168.4; EI-MS$^-$ m/z calcd for $C_{17}H_{13}O_5$ 297.0763 [M − H]$^-$, found 297.0765.

(E)-2-Carboxy-5-(4-phenoxy)cinnamic Acid (12-CA). Yield 127 mg (71%); colorless solid. mp 180−182 °C; R_f (10% MeOH/EtOAc): 0.5; IR (KBr) cm^{-1} 3100−2600, 1686, 1599; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.57 (d, J = 16.0 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 7.66−7.73 (m, 3H), 7.93 (d, J = 8.7 Hz, 2H), 8.39 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 116.3, 122.1, 125.4, 127.3, 128.7, 128.9, 129.6, 131.8, 136.4, 143.4, 144.2, 158.5, 168.0, 168.4; ES-MS$^-$ m/z calcd for $C_{16}H_{11}O_5$ 283.0606 [M − H]$^-$, found 283.0600.

3-Oxo-1,3-dihydroisobenzofuran-1-carboxylic Acid (13-LA). Yield 119 mg (50%); colorless solid. R_f (50% EtOAc/pet. ether): 0.5; mp 137−140 °C; IR (KBr) cm^{-1} 3200−2600 (br), 2924, 1768; ^{1}H NMR (400 MHz, CD_3OD) δ 6.06 (s, 1H), 7.63−7.66 (m, 1H), 7.76−7.81 (m, 2H), 7.89 (d, J = 7.56 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 78.1, 123.1, 124.9, 125.4, 130.2, 134.9, 145.5, 168.9, 170.7; EI-MS$^+$ m/z calcd for $C_9H_7O_4$ 179.0344 [M + H]$^+$, found 179.0344.

2,3-Dihydroxy-1,4-naphthoquinone (13-Q). Yield 35 mg (15%); red solid. R_f (EtOAc): 0.4; mp 146−148 °C; IR (KBr) cm^{-1} 3339, 1674, 1632, 1590. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74−7.76 (m, 2H), 7.90−7.91 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 125.8, 130.5, 134.1, 141.1, 181.3; ES-MS$^-$ m/z calcd for $C_{10}H_5O_4$ 189.0187 [M − H]$^-$, found 189.0194.

1,4-Naphthoquinone (14-Q).[7b] Yield 68 mg (31%); yellow solid. R_f (5% EtOAc/pet. ether): 0.5; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98 (s, 2H), 7.75−7.78 (m, 2H), 8.0−8.01 (m, 2H).

β-Bromo-2-carboxycinnamic Acid (15-CA). Yield 69 mg (62%); colorless solid. R_f (20% MeOH/EtOAc): 0.3; mp 137−140 °C; IR (KBr) cm^{-1} 3100−2600 (br), 1812, 1693, 1641; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.18 (s, 1H), 7.83 (t, J = 7.5 Hz, 1H), 7.97 (t, J = 7.78 Hz, 1H), 8.01 (d, J = 7.76 Hz, 1H), 8.90 (d, J = 8.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 103.5, 125.8, 126.5, 127.9, 133.4, 135.9, 136.1, 157.2, 165.8, 166.8.

β-Phenyl-2-carboxycinnamic Acid (16-CA). Yield 87 mg (72%); colorless solid. R_f (20% MeOH/EtOAc): 0.4; mp 146−148 °C; IR (KBr) cm^{-1} 3000−2700 (br), 1683, 1613; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.36 (s, 1H), 7.13 (d, J = 7.36 Hz, 1H), 7.21−7.24 (m, 2H), 7.30−7.33 (m, 3H), 7.47 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.57 (dt, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 117.3, 125.8, 127.7, 128.1, 128.8, 129.4, 130.5, 132.1, 133.6, 140.3, 141.0, 155.9, 166.9, 167.6; ESI-MS$^-$ m/z calcd for $C_{16}H_{11}O_4$ 267.0657 [M − H]$^-$, found 267.0652.

o-Phthalic Acid (18-A).[21] Yield 148 mg (78%); colorless solid. R_f (25% MeOH/EtOAc): 0.2; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.56−7.60 (m, 2H), 7.64−7.68 (m, 2H).

6-Hydroxy-1,4-naphthoquinone (19-Q).[22] Yield 24 mg (15%); red solid. R_f (5% EtOAc/pet. ether): 0.4; ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD) δ 6.84 (s, 2H), 7.08 (dd, J_1 = 8.4 Hz, J_2 = 2.5 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H).

5-Oxo-3-phenyl-2,5-dihydro-2-furanacetic Acid (20-LA). Yield 65 mg (23%); colorless solid. R_f (25% EtOAc/pet. ether): 0.4; mp 122−124 °C; IR (KBr) cm^{-1} 3100−2900 (br), 1729, 1619, 1573; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55−2.59 (m, 1H), 2.97−3.02 (m, 1H), 5.91−5.93 (m, 1H), 6.34 (d, J = 1.6 Hz, 1H), 7.47−7.51 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.5, 77.9, 114.9, 127.1, 129.3, 129.5, 131.7, 166.3, 171.9, 173.9; EI-MS$^-$ m/z calcd for $C_{12}H_9O_4$ 217.0500 [M − H]$^-$, found 217.0507.

2,2′-Diphenic Acid (21-DA).[23] Yield 79 mg (59%); colorless solid. R_f (20% MeOH/EtOAc): 0.4; mp 251−254 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.15 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H).

Dibenzo[b,d]pyrone (21-L).[24] Yield 25 mg (23%); colorless solid. R_f (5% EtOAc/pet. ether): 0.32; IR (KBr) cm^{-1} 1729, 1606; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.36 (m, 2H), 7.47 (dt, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.57 (dt, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.79−7.82 (m, 1H), 8.05 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.39 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.8, 118.0, 121.2, 121.7, 122.7, 124.5, 128.8, 130.4, 130.6, 134.7, 134.8, 151.3, 161.2; EI-MS$^+$ m/z calcd for $C_{13}H_8O_2$ 196.0524 [M]$^+$, found 196.0517.

2-(3-Oxo-1,3-dihydronaphtho[2,1-c]furan-1-yl)acetic Acid (22-LA). Yield 105 mg (85%); colorless solid. R_f (10% MeOH/EtOAc): 0.3; mp 138−140 °C; IR (KBr) cm^{-1} 3000−2700 (br), 2921, 1752, 1735; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.76−2.82 (m, 1H), 3.44−3.48 (m, 1H), 6.32−6.34 (m, 1H), 7.74−7.80 (m, 3H), 8.12−8.19 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 39.4, 77.8, 120.4, 123.8, 125.1, 126.7, 128.5, 129.7, 129.8, 131.1, 136.3, 149.2, 170.6, 171.1; EI-MS$^-$ m/z calcd for $C_{14}H_9O_4$ 241.0500 [M − H]$^-$, found 241.0508.

1,4-Phenanthroquinone (22-Q).[4d] Yield 29 mg (27%); yellow solid. R_f (5% EtOAc/pet. ether): 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94−7.00 (m, 2H), 7.65 (dt, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 7.75 (dt, J_1 = 7.3 Hz, J_2 = 1.3 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 8.16−8.20 (m, 2H), 9.55 (d, J = 8.7 Hz, 1H).

2-(1-Oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic Acid (24-LA). Yield 153 mg (82%); colorless solid. R_f (10% MeOH/EtOAc): 0.3; mp 142−145 °C; IR (KBr) cm^{-1} 3000−2600 (br), 2921, 1733, 1706; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.74−2.81 (m, 1H), 3.24−3.29 (m, 1H), 5.96−5.98 (m, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.79−7.81 (m, 2H), 8.13 (d, J = 8.2 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.80 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 38.8, 77.5, 119.7, 120.1, 122.8, 127.8, 128.8, 129.4, 129.6, 133.5, 136.0, 152.0, 170.5, 171.5; EI-MS$^-$ m/z calcd for $C_{14}H_9O_4$ 241.0500 [M − H]$^-$, found 241.0506.

2-(8-Hydroxy-1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic Acid (28-LA). Yield 62 mg (52%); colorless solid. mp 218−220 °C; R_f (15% MeOH/EtOAc) 0.32; IR (KBr) cm^{-1} 3500−2600 (br), 2923, 1738, 1702; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.68−2.74 (m, 1H), 3.18−3.22 (m, 1H), 5.87−5.89 (m, 1H), 7.21 (m, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 2.3 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 39.1, 77.2, 104.9, 116.4, 117.9, 120.0, 128.1, 130.9, 131.2, 135.8, 152.3, 158.8, 170.8, 171.5; EI-MS$^-$ m/z calcd for $C_{14}H_9O_5$ 257.0450 [M − H]$^-$, found 257.0455.

1,6-Diketopyrene (29-Q1). Yield 64 mg (60%); yellow solid. R_f (25% EtOAc/pet. ether): 0.5; mp 250−253 °C; IR (KBr) cm^{-1} 3000, 2921, 2851, 1636; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, J = 9.8 Hz, 2H), 7.68 (d, J = 9.8 Hz, 2H), 7.84 (d, J = 7.7 Hz, 2H), 8.49 (d, J = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.22, 129.9, 130.2, 130.6, 130.7, 133.7, 141.1, 185.4; EI-MS$^-$ m/z calcd for $C_{16}H_8O_2$ 232.0524 [M]$^-$, found 232.0523.

1,8-Diketopyrene (29-Q2). Yield 30 mg (29%); red solid. R_f (25% EtOAc/pet. ether): 0.45; mp 250−255 °C; IR (KBr) cm^{-1} 3000, 2921,

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2852, 1633; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, J = 10.1 Hz, 2H), 7.67−7.69 (m, 4H), 8.65 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.5, 129.4, 129.5, 131.1, 131.2, 132.2, 141.5, 185.2; EI-MS$^-$ m/z calcd for $C_{16}H_8O_2$ 232.0524 [M]$^-$, found 232.0524.

2-(1-Oxo-1,3-dihydrophenanthro[2,1-c]furan-3-yl)acetic Acid (30-LA). Yield 94 mg (79%); colorless solid. mp 140−142 °C; R_f (5% MeOH/EtOAc): 0.32; IR (KBr) cm^{-1} 3000−2700 (br), 2963, 2926, 1736, 1723; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01−3.11 (m, 2H), 5.98−5.99 (m, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.70−7.88 (m, 3H), 7.87−7.93 (m, 2H), 8.21 (d, J = 8.2 Hz, 1H), 10.12 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.6, 75.0, 118.8, 121.7, 126.53, 126.55, 128.0, 128.3, 129.0, 129.2, 130.2, 130.3, 133.7, 134.0, 136.7, 151.3, 170.1, 174.0; EI-MS$^-$ m/z calcd for $C_{18}H_{11}O_4$ 291.0657 [M − H]$^-$, found 291.0650.

2-Hydroxybenzoic Acid (31-A).[25] Yield 143 mg (84%); colorless solid. R_f (25% EtOAc/pet. ether): 0.5; IR (KBr) cm^{-1} 3238, 2900−2500 (br), 2855, 1656; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91−7.01 (m, 2H), 7.50−7.53 (m, 1H), 7.91−7.94 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.3, 117.8, 119.6, 130.9, 137.0, 162.1, 174.8.

5,6-Dimethyl-2-hydroxybenzoic Acid (32-A). Yield 141 mg (82%); colorless solid. R_f (25% EtOAc/pet. ether): 0.3; mp 188−190 °C; IR (KBr) cm^{-1} 3000−2600 (br), 2921, 2854, 1644, 1622; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 1H), 2.32 (s, 1H), 6.74 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 20.8, 108.4, 121.0, 124.9, 127.5, 146.5, 160.3, 174.9; ESI-MS$^-$ m/z calcd for $C_9H_9O_3$ 165.0551 [M − H]$^-$, found 165.0550.

(E)-2-Carboxy-4-methoxycinnamic Acid (S1-CA).[12b] Yield 81 mg (39%); colorless solid. R_f (20% MeOH/EtOAc): 0.4; mp 164−168 °C; IR (KBr) cm^{-1} 3000−2600 (br), 2849, 1682, 1596; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.83 (s, 3H), 6.34 (d, J = 16.0 Hz, 1H), 7.13−7.16 (m, 1H), 7.33 (d, J = 2.52 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 8.23 (d, J = 16.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 56.0, 115.2, 118.3, 119.6, 127.2, 129.7, 133.7, 142.3, 160.5, 168.1, 168.5.

6-Methoxy-1,4-naphthoquinone (S1-Q).[26] Yield 46 mg (25%); red solid. R_f (25% EtOAc/pet. ether): 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 6.91−6.93 (m, 2H), 7.22 (dd, J_1 = 2.5 Hz, J_2 = 8.6 Hz, 1H), 7.51 (d, J = 2.5 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00292.

^{1}H and ^{13}C NMR spectral reproductions for the products of oxidations, schemes of mechanism for some products, and ^{1}H NMR spectral reproductions for monitoring of the oxidations of 6-bromonaphthol (PDF)

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Notes

The authors declare no competing financial interest.

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