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Metal-Free, Brønsted Acid-Catalyzed Formal [3+2] Annulation of Quinone Monoacetals with 2-Naphthols

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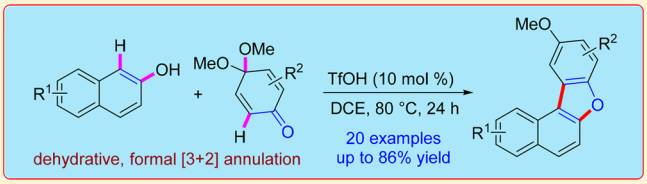
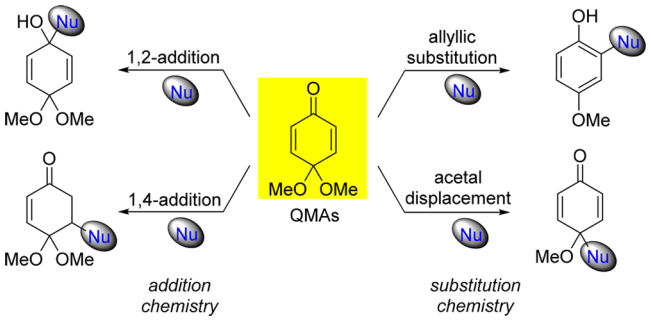
Supporting Information

ABSTRACT: An operationally simple and metal-free cross-coupling of quinone monoacetals (QMAs) with 2-naphthols catalyzed by triflic acid is reported. This formal [3+2] annulation allowed the synthesis of diverse naphtho[2,1-*b*]benzofuran derivatives in moderate to good yields. Preliminary mechanistic studies reveal the initial nucleophilic substitution of QMAs with 2-naphthols in preference to the mixed acetal formation and subsequent [3,3] sigmatropic rearrangement.



The quinone monoacetals (QMAs) are a unique and versatile class of compounds endowed with various reactivity profiles due to the presence of both the α,β-unsaturated keto functionality and the allyl acetal moiety in the same molecule.[1] Because of the multiple functionalities in QMAs, a variety of 1,2-addition reactions onto the carbonyl moiety[2] as well as diverse Michael reactions across the α,β-unsaturated carbonyl system are possible (Scheme 1).[3]

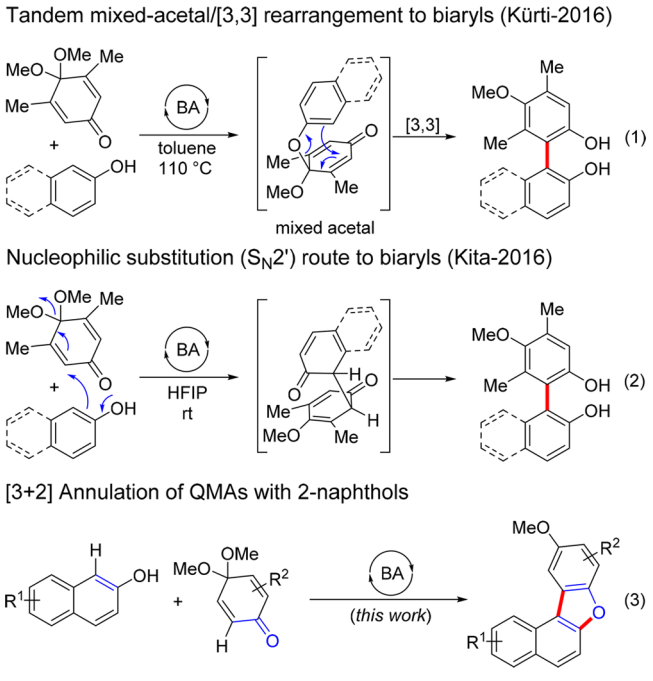
Scheme 1. Different Modes of Reactivity of QMAs



Moreover, with the employment of the electrophilic allyl acetal functionality, QMAs can undergo allylic substitution reactions[4] as well as the displacement of the acetal moiety via the 1,2-addition.[5] Usually, addition reactions involving QMAs are promoted by bases, whereas the substitution reactions proceed under acidic conditions. Compared to the well-known addition chemistry of QMAs, the nucleophilic substitution reaction engaging the allyl acetal moiety has received less attention.[6]

The interception of aryl nucleophiles with QMAs taking advantage of the allyl acetal reactivity can result in a convenient synthesis of oxygenated biaryls under metal-free conditions. In 2011, Kita and co-workers reported an elegant synthesis of functionalized biaryls by the reaction of QMAs with electron-rich arenes, and the reactions are catalyzed by sandwiched Brønsted acids.[7] Recently, Kürti and co-workers demonstrated the Brønsted acid-catalyzed direct arylation of phenols/naphthols using QMAs for the synthesis of non-C_2-symmetric biaryls (Scheme 2, eq 1).[8] Mechanistically, this reaction proceeds via the generation of mixed acetals from QMA and phenol/naphthol followed by the [3,3] sigmatropic rearrange-

Scheme 2. Brønsted Acid-Catalyzed Reactions of QMAs with Naphthols



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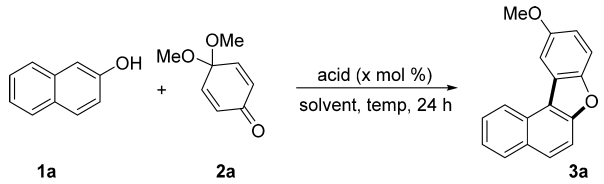
ment to afford the oxygenated biaryls. In the same year, the Kita group disclosed the closely related room-temperature biaryl synthesis by the reaction of QMAs with phenols (eq 2).[9] In this case, the reaction is initiated by the allylic acetal substitution followed by proton transfer to furnish the products. Inspired by these two reports, herein, we report the Brønsted acid-catalyzed formal [3+2] annulation of QMAs with 2-naphthols for the rapid synthesis of functionalized naphthobenzofuran derivatives (eq 3).

We have recently reported the Lewis acid-catalyzed selective reactions of 2-naphthols with donor–acceptor cyclopropanes[10] or aziridines[11] for the synthesis of naphthalene-fused cyclopentanes and benzoindolines, respectively. With these results, we envisioned that the Lewis acid-catalyzed reaction of 2-naphthols with QMAs could result in a dehydrative [3+2] annulation leading to naphthobenzofuran derivatives.[4b−d,12] With this background, the present study was initiated by treating the 2-naphthol **1a** with QMA **2a** in the presence of various Lewis acids.[13,14]

Interestingly, using 20 mol % $Bi(OTf)_3$, the reaction afforded the naphthobenzofuran derivative **3a** in 68% yield (Table 1, entry 1).[15] The reactions performed using other metal triflates such as AgOTf and $Sn(OTf)_2$ under identical conditions resulted in a moderate yield of **3a**, whereas $Mg(OTf)_2$ produced only traces of **3a** (entries 2–4). Gratifyingly, the reaction furnished a 75% yield of **3a** when carried out in TfOH as the catalyst (entry 5). Impressed by the catalytic activity of TfOH, the reaction was attempted in other Brønsted acids such as AcOH, TFA, and TsOH. The results indicated that these acids are not active under the present conditions (entries 6–8). Screening various solvents revealed that DCE is the best solvent for this annulation (entries 9–12). The reaction was not working at 30 °C (entry 13), and the reaction performed at 100 °C produced **3a** in a yield of only 50% (entry 14). Finally, performing the reaction using 10 mol % TfOH improved the yield of **3a** to 83% (entry 15).[16]

With the optimized reaction conditions in hand, we then studied the substrate scope of this annulation reaction (Scheme 3). Substituents on the 7-position and 6-position of 2-naphthol are tolerated well, and in all cases, the naphthobenzofuran derivatives were formed in good yields (**3a**–**3g**). Substrates having alkyl and aryl substitution at the 4-position of 2-naphthol afforded the desired product only in low yields (**3h**, **3i**). The reaction performed using phenanthren-9-ol furnished the expected product **3j** in 66% yield. In addition, a series of substrates having an alkyl, aryl, and halogen substitution on the QMAs underwent a smooth annulation reaction leading to the formation of diverse naphthobenzofuran derivatives in moderate to good yields. The reaction of **1a** with 2-substituted QMAs resulted in a single product in moderate to good yields (**3k**–**3p**). However, the reaction of **1a** with 3-substituted QMAs furnished a regioisomeric mixture of products (**3q**, **3r**).

Table 1. Optimization of the Reaction Conditions[a]

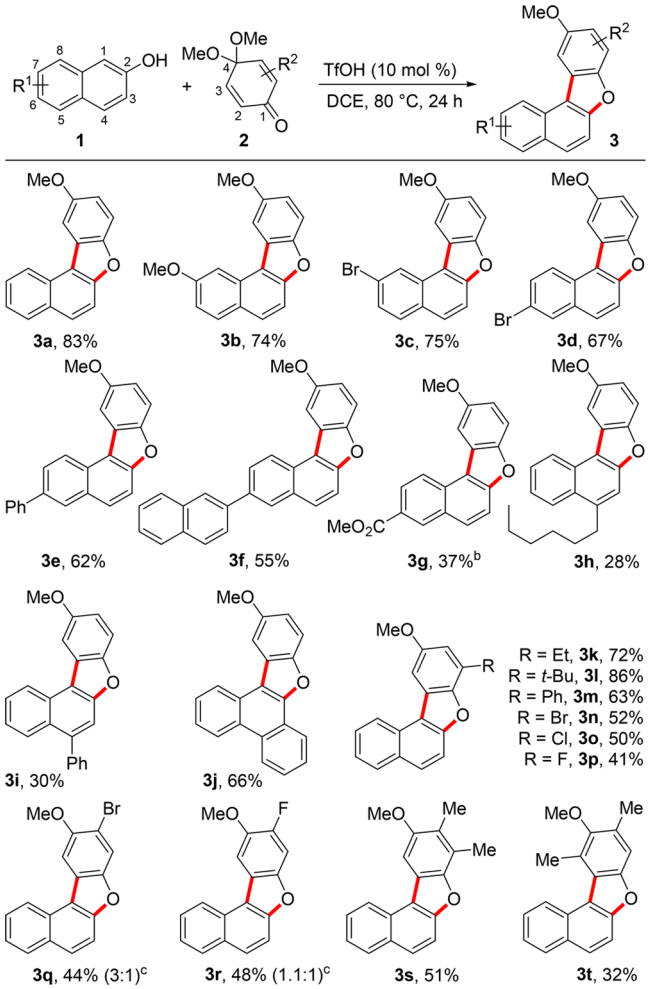


1a 2a 3a

entry	acid (mol %)	solvent	temp (°C)	yield of **3a** (%)[b]
1	$Bi(OTf)_3$ (20)	DCE	80	68
2	AgOTf (20)	DCE	80	56
3	$Sn(OTf)_2$ (10)	DCE	80	53
4	$Mg(OTf)_2$ (10)	DCM	80	<5
5	TfOH (20)	DCE	80	75
6	AcOH (20)	DCE	80	<5
7	TFA (20)	DCE	80	<5
8	$TsOH·H_2O$ (20)	DCE	80	<5
9	TfOH (20)	HFIP	80	31
10	TfOH (20)	toluene	80	24
11	TfOH (20)	DCM	80	44
12	TfOH (20)	$CHCl_3$	80	72
13	TfOH (20)	DCE	30	<5
14	TfOH (20)	DCE	100	50
15	TfOH (10)	DCE	80	84 (83)

[a]All reactions were carried out in 0.25 mmol of **1a** and 0.3 mmol of **2a** in 1.0 mL of a solvent unless otherwise specified. [b]The yields were determined by the ^1H NMR analysis of crude products using CH_2Br_2 as the internal standard. The yield of the isolated product in a 0.5 mmol scale is given in parentheses.

Scheme 3. Substrate Scope of This Annulation Reaction[a]



[a]General conditions: **1** (0.50 mmol), **2** (0.60 mmol), TfOH (10.0 mol %), and DCE (2 mL) at 80 °C for 24 h. Isolated yields of **3** after column chromatography are given. [b]The product contains methyl 6-methoxy-2-naphthoate as an inseparable impurity. [c]The regioisomer ratio was determined by ^1H NMR, and the major regioisomer was given.

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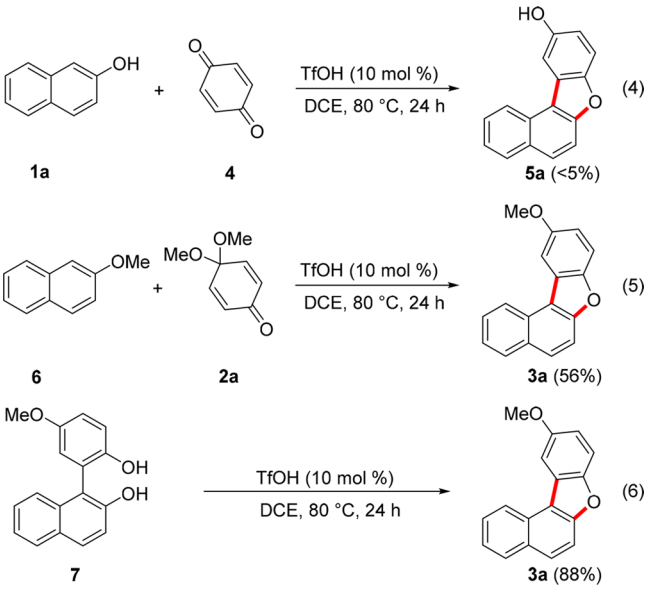
Engaging disubstituted QMAs in this annulation resulted in the formation of the target products in moderate yields (**3s**, **3t**). Disappointingly, the reaction of 2-naphthols with iminoquinonemonoacetals did not afford the desired annulated product under the present reaction conditions.[17] Furthermore, the performed reactions using phenols instead of naphthols did not afford the desired products under the present reaction conditions.

To shed light on the mechanism of this transformation, we have performed a few mechanistic experiments (Scheme 4).

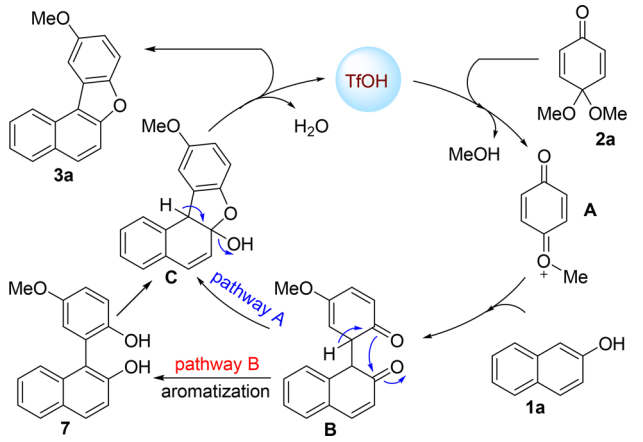
Scheme 4. Mechanistic Experiments



Treatment of 2-naphthol **1a** with *p*-benzoquinone **4** under the present reaction conditions did not afford the expected product **5a** (eq 4).[18] This indicates the involvement of the highly activated oxocarbenium intermediate in the present annulation with QMAs (possible via the Brønsted acid activation of QMAs), which could not be generated in the reaction with **4**. Moreover, the reaction of 2-methoxy naphthalene with **2a** under the present reaction conditions afforded **3a** in a 56% yield (eq 5). This experiment rules out the feasibility of the tandem mixed acetal formation followed by the [3,3] sigmatropic rearrangement mechanism proposed by Kürti and co-workers.[8] This also shows that the allylic acetal substitution followed by the proton transfer suggested by Kita and co-workers[9] is the key step in the present annulation. Furthermore, when the phenol biaryl **7** was subjected to the present conditions, **3a** was smoothly formed in 88% yield demonstrating the intermediacy of the biaryl **7** in the present annulation reaction (eq 6).[19]

The mechanistic rationale for this Brønsted acid-catalyzed annulation can be advanced along the following lines (Scheme 5). The reaction is likely initiated by the activation of the QMA **2a** by TfOH, leading to the generation of the highly electrophilic oxocarbenium intermediate **A**. This is followed by the nucleophilic addition of 2-naphthol to **A**, forming the diketone intermediate **B**. Intramolecular cyclization generates the intermediate **C**, followed by the elimination of a water molecule, and delivers the naphthobenzofuran **3a** (pathway A). Alternatively, the intermediate **B** can undergo aromatization via

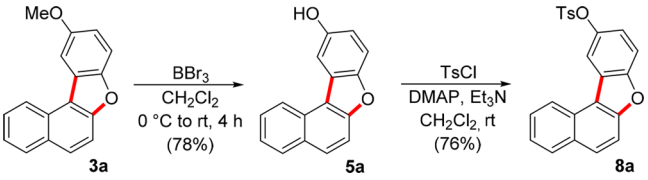
Scheme 5. Tentative Mechanism of the Reaction



proton transfer to form the phenol biaryl **7**, which can be converted into **3a** via the intermediate **C** (pathway B).

The demethylation of naphthobenzofuran **3a** can easily be achieved under the BBr_3 conditions. The desired phenol **5a** was isolated in a 78% yield (Scheme 6). The phenol **5a** on

Scheme 6. Product Functionalization



treatment with TsCl resulted in the formation of the tosylate derivative **8a** in 76% yield. The tosylate **8a** could undergo various cross-coupling reactions for carbon−carbon and carbon−nitrogen bond-forming reactions.[20]

In conclusion, we have developed a metal-free synthesis of naphthobenzofuran derivatives by the Brønsted acid-catalyzed dehydrative, formal [3+2] annulation of 2-naphthols with QMAs. The reaction products are formed in moderate to good yields with a reasonable substrate scope. Mechanistically, the reaction proceeds via the substitution at the allyl acetal moiety (Kita), and our preliminary study rules out the tandem mixed acetal formation followed by the [3,3] sigmatropic rearrangement suggested by Kürti.

EXPERIMENTAL SECTION

General Information. Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry 1,2-dichloroethane was purchased from commercial sources and stored under argon over sodium wire. Quinone monoacetals were synthesized from the corresponding phenols following the literature procedure.[8] 2-Naphthol, 6-bromonaphthol, 7-bromonaphthol, and 7-methoxynaphthol were purchased from commercial sources and were used without further purification. Other naphthols (**1e**,[21] **1f**,[21] **1h**,[22] and **1i**[22]) were prepared following the literature procedure. Trifluoromethanesulfonic acid was purchased from commercial sources and was used without further purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ as a solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$ δ H = 7.26 ppm, δ C = 77.16 ppm). HRMS measurements were carried out using the ESI method and ion-trap mass analyzer.

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Infrared (IR) spectra were recorded on an FT-IR spectrometer as thin films using NaCl plates.

General Procedure for the Synthesis of Quinone Monoacetals. To a solution of the corresponding phenol (10.0 mmol) in MeOH (40 mL) was added phenyliodonium diacetate (PIDA) (3.86 g, 12.0 mmol, 1.2 equiv for 4-methoxy phenols/7.09g, 22.0 mmol, 2.2 equiv for 4-unsubstituted phenols), and the mixture was stirred at room temperature and monitored by TLC analysis (typically 2 h). The reaction was quenched with saturated $NaHCO_3$ (50 mL) and then extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine and dried with anhydrous Na_2SO_4, and the solvent was removed in vacuo to give the crude product, which was purified by flash column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to give the desired product as a light yellow oil.

General Procedure for the Synthesis of Naphthobenzofuran Derivatives. To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the corresponding naphthol **1** (0.5 mmol) followed by the addition of DCE (2.0 mL) under an argon atmosphere. Quinone monoacetal **2** (0.6 mmol) was added followed by the addition of trifluoromethanesulfonic acid (4.4 μL, 0.05 mmol). The screw-capped tube was evacuated and backfilled with argon. Then the reaction mixture was placed in a preheated oil bath at 80 °C for 24 h under argon conditions. Then the reaction was stopped, and the reaction mixture was cooled. The solvent was evaporated, and the crude residue was preadsorbed on silica gel and purified by flash column chromatography (petroleum ether/EtOAc = 95:5) on silica gel to afford the corresponding naphthobenzofuran derivatives **3**.

*10-Methoxynaphtho[2,1-b]benzofuran (**3a**):*[23] white solid, 0.103 g in 0.5 mmol scale, 83% yield; R_f 0.45 (petroleum ether/EtOAc = 95:5); mp 69−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.77 (s, 1H), 7.70 (d, J = 8.7 Hz, 2H), 7.55 (dd, J_1 = 8.1 Hz, J_2 = 15.5 Hz, 2H), 7.09 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 155.1, 150.7, 130.3, 129.2, 129.1, 128.5, 127.1, 125.4, 124.3, 123.2, 117.41, 113.6, 112.8, 112.1, 105.4, 56.1; HRMS [M + H]$^+$ calcd for $C_{17}H_{13}O_2$ 249.0910, found 249.0911; FTIR (cm^{-1}) 3019, 1625, 1524, 1476, 1328.

*2,10-Dimethoxynaphtho[2,1-b]benzofuran (**3b**):* light yellow solid, 0.102 g in 0.5 mmol scale, 74% yield; R_f 0.30 (petroleum ether/EtOAc = 95:5); mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.72 (s, 1H), 7.68 (s, 1H), 7.54 (dd, J_1= 4.7 Hz, J_2 = 8.7 Hz, 2H), 7.17 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 7.0 Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 156.0, 155.9, 150.7, 130.8, 130.4, 128.5, 125.6, 125.5, 116.7, 115.8, 112.5, 112.0, 110.3, 106.0, 103.1, 56.2, 55.5; HRMS [M + H]$^+$ calcd for $C_{18}H_{15}O_3$ 279.1016, found 279.1018; FTIR (cm^{-1}) 3019, 1630, 1593, 1523, 1439, 1369.

*2-Bromo-10-methoxynaphtho[2,1-b]benzofuran (**3c**):* white solid, 0.122 g in 0.5 mmol scale, 75% yield; R_f 0.45 (petroleum ether/EtOAc = 95:5); mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.73 (t, J = 7.7 Hz, 2H), 7.61−7.58 (m, 2H), 7.52 (t, J = 9.9 Hz, 2H), 7.05 (dd, J_1 = 2.4 Hz, J_2 = 8.9 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.4, 150.7, 130.7, 130.0, 128.7, 128.3, 127.6, 125.6, 124.8, 121.5, 116.6, 113.7, 113.2, 112.2, 105.5, 56.3; HRMS [M + H]$^+$ calcd for $C_{17}H_{12}O_2Br$ 327.0015, found 327.0023; FTIR (cm^{-1}) 3019, 1630, 1523, 1370, 1289, 1215.

*3-Bromo-10-methoxynaphtho[2,1-b]benzofuran (**3d**):* white solid, 0.110 g in 0.5 mmol scale, 67% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.7 Hz, 1H), 8.04 (s, 1H), 7.67−7.60 (m, 3H), 7.57 (s, 1H), 7.51 (d, J = 8.9 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.0, 150.8, 131.5, 131.2, 130.2, 127.4, 124.9, 124.7, 117.9, 117.6, 114.1, 113.9, 112.3, 105.3, 56.2; HRMS [M + H]$^+$ calcd for $C_{17}H_{12}O_2Br$ 327.0015, found 327.0022; FTIR (cm^{-1}) 3019, 1619, 1592, 1513, 1434, 1244.

*10-Methoxy-3-phenylnaphtho[2,1-b]benzofuran (**3e**):* white solid, 0.101 g in 0.5 mmol scale, 62% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 137−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8.4 Hz, 1H), 8.18 (s, 1H), 7.93 (dd, J = 18.0, 8.7 Hz, 2H), 7.80−7.77 (m, 3H), 7.71 (d, J = 8.9 Hz, 1H), 7.59−7.52 (m, 3H), 7.43 (t, J = 7.1 Hz, 1H), 7.10 (dd, J = 8.8, 1.8 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.3, 150.9, 141.1, 137.1, 130.7, 129.0, 128.9, 128.2, 127.5, 127.2, 126.7, 125.4, 123.8, 117.5, 113.8, 113.3, 112.3, 105.5, 56.2; HRMS [M + H]$^+$ calcd for $C_{23}H_{17}O_2$ 325.1233, found 325.1227; FTIR (cm^{-1}) 3019, 1619, 1590, 1496, 1217.

*10-Methoxy-3-(naphthalen-2-yl)naphtho[2,1-b]benzofuran (**3f**):* white solid, 0.103 g in 0.5 mmol scale, 55% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 184−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.6 Hz, 1H), 8.31 (s, 1H), 8.20 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.99−7.90 (m, 5H), 7.85 (d, J = 1.8 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.57−7.50 (m, 2H), 7.11 (dd, J = 8.9, 2.0 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 155.4, 151.0, 138.4, 137.0, 133.9, 132.8, 130.9, 129.0, 128.7, 128.4, 128.3, 127.8, 127.6, 126.9, 126.5, 126.1, 125.8, 125.5, 123.9, 117.6, 113.8, 113.4, 112.3, 105.7, 56.3; HRMS [M + H]$^+$ calcd for $C_{27}H_{19}O_2$ 375.1380, found 375.1379; FTIR (cm^{-1}) 3054, 1476, 1422, 1265.

*Methyl 10-Methoxynaphtho[2,1-b]benzofuran-3-carboxylate (**3g**):* white solid, 0.057 g in 0.5 mmol scale, 37% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.78−7.75 (m, 2H), 7.58 (d, J = 8.9 Hz, 1H), 7.14−7.07 (m, 1H), 4.02 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 156.5, 151.0, 132.2, 131.6, 131.0, 129.9, 129.6, 126.8, 126.0, 125.0, 123.5, 119.8, 117.7, 114.3, 113.9, 112.5, 105.6, 56.3, 52.4; HRMS [M + H]$^+$ calcd for $C_{19}H_{15}O_4$ 307.0965, found 309.0959; FTIR (cm^{-1}) 3019, 1602, 1586, 1449, 1366, 1327.

*4-Hexyl-10-methoxynaphtho[2,1-b]benzofuran (**3h**):* white solid, 0.047 g in 0.5 mmol scale, 28% yield; R_f 0.45 (petroleum ether/EtOAc = 95:5); mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.72 (t, J = 7.4 Hz, 1H), 7.60−7.55 (m, 3H), 7.06 (d, J = 8.9 Hz, 1H), 4.00 (s, 3H), 3.19 (t, J = 7.7 Hz, 2H), 1.87−1.79 (m, 2H), 1.48 (m, 2H), 1.36 (d, J = 2.8 Hz, 4H), 0.92 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.3, 150.1, 140.5, 129.8, 129.1, 126.9, 125.7, 125.4, 124.2, 124.1, 115.9, 113.1, 112.7, 112.1, 105.6, 56.3, 34.0, 31.9, 30.9, 29.6, 22.8, 14.3; HRMS [M + H]$^+$ calcd for $C_{23}H_{25}O_2$ 333.1849, found 333.1845; FTIR (cm^{-1}) 3019, 1620, 1525, 1215.

*10-Methoxy-5-phenylnaphtho[2,1-b]benzofuran (**3i**):* white solid, 0.048 g in 0.5 mmol scale, 30% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.87 (s, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.70 (s, 1H), 7.61−7.47 (m, 7H), 7.11 (d, J = 8.9 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 154.8, 151.0, 141.2, 140.7, 130.4, 129.6, 129.0, 128.5, 127.8, 127.7, 127.2, 125.5, 124.5, 123.6, 117.0, 113.9, 113.7, 112.3, 105.7, 56.3; HRMS [M + H]$^+$ calcd for $C_{23}H_{17}O_2$ 325.1233, found 325.1226; FTIR (cm^{-1}) 3019, 1619, 1474, 1337.

*12-Methoxyphenanthro[9,10-b]benzofuran (**3j**):* white solid, 0.098 g in 0.5 mmol scale, 66% yield; R_f 0.33 (petroleum ether/EtOAc = 95:5); mp 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (t, J = 8.9 Hz, 2H), 8.45 (d, J = 7.9 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 7.71−7.67 (m, 4H), 7.63−7.58 (m, 2H), 7.05 (d, J = 6.9 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 152.0, 150.7, 130.5, 128.57, 128.1, 127.4, 127.1, 127.1, 126.1, 125.0, 123.9, 123.8, 123.4, 122.3, 121.7, 114.4, 113.2, 112.2, 105.3, 56.2; HRMS [M + H]$^+$ calcd for $C_{21}H_{15}O_2$ 299.1067, found 299.1068; FTIR (cm^{-1}) 3019, 1614, 1517, 1217.

*8-Ethyl-10-methoxynaphtho[2,1-b]benzofuranan (**3k**):* white solid, 0.099 g in 0.5 mmol scale, 72% yield; R_f 0.48 (petroleum ether/EtOAc = 95:5); mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.82−7.64 (m, 3H), 7.54 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 1.7 Hz, 1H), 4.00 (s, 3H), 3.06 (q, J = 7.5 Hz, 2H), 1.44 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 154.9, 149.5, 130.5, 129.3, 129.2, 128.4, 127.1, 124.9, 124.3, 123.4, 117.9, 113.6, 113.1, 102.7, 56.3, 23.3, 14.3; HRMS [M + H]$^+$ calcd for $C_{19}H_{17}O_2$ 277.1223, found 277.1227; FTIR (cm^{-1}) 3019, 1605, 1527, 1452, 1341.

*8-(tert-Butyl)-10-methoxynaphtho[2,1-b]benzofuran (**3l**):* white solid, 0.131 g in 0.5 mmol scale, 86% yield; R_f 0.52 (petroleum ether/EtOAc = 95:5); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$)

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δ 8.62 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 10.7 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.77−7.73 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 1.5 Hz, 1H), 4.06 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.5, 149.3, 136.4, 130.5, 129.4, 129.2, 128.3, 127.1, 125.7, 124.26, 123.3, 117.4, 113.1, 112.1, 102.2, 56.2, 34.8, 30.0; HRMS $[M + H]^+$ calcd for $C_{21}H_{21}O_2$ 305.1536, found 305.1538; FTIR (cm^{-1}) 3018, 1602, 1526, 1449, 1366.

*10-Methoxy-8-phenylnaphtho[2,1-b]benzofuran (**3m**):* white solid, 0.102 g in 0.5 mmol scale, 63% yield; R_f 0.42 (petroleum ether/EtOAc = 95:5); mp 157−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.3 Hz, 1H), 8.16−7.89 (m, 4H), 7.89−7.71 (m, 3H), 7.68−7.54 (m, 3H), 7.51 (d, J = 7.3 Hz, 1H), 7.27 (d, J = 2.2 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 155.2, 148.2, 136.5, 130.5, 129.4, 129.2, 129.1, 128.8, 128.8, 128.1, 127.3, 126.5, 126.2, 124.5, 123.3, 117.5, 113.4, 113.1, 104.8, 56.4; HRMS $[M + H]^+$ calcd for $C_{23}H_{17}O_2$ 325.1223, found 325.1220; FTIR (cm^{-1}) 3021, 1610, 1521, 1471, 1432, 1334.

*8-Bromo-10-methoxynaphtho[2,1-b]benzofuran (**3n**):* white solid, 0.085 g in 0.5 mmol scale, 52% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 182−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.82−7.69 (m, 3H), 7.57 (t, J = 7.3 Hz, 1H), 7.27 (s, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.1, 130.6, 130.8, 129.5, 129.1, 127.5, 126.4, 124.8, 123.2, 116.3, 113.0, 105.3, 104.5, 56.5; HRMS $[M + H]^+$ calcd for $C_{17}H_{12}BrO_2$ 327.0015, found 327.0023; FTIR (cm^{-1}) 3019, 1626, 1524, 1370, 1332.

*10-Methoxy-3-(naphthalen-2-yl)naphtho[2,1-b]benzofuran (**3o**):* white solid, 0.072 g in 0.5 mmol scale, 50% yield; R_f 0.38 (petroleum ether/EtOAc = 95:5); mp 144−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.72−7.65 (m, 2H), 7.60 (s, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.05 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 155.2, 146.7, 130.5, 129.4, 129.0, 127.4, 126.6, 124.7, 123.1, 117.43, 117.2, 113.6, 112.9, 104.5, 56.4; HRMS $[M + H]^+$ calcd for $C_{17}H_{12}O_2Cl$ 283.0520, found 283.0524; FTIR (cm^{-1}) 3019, 1620, 1477, 1218.

*8-Fluoro-10-methoxynaphtho[2,1-b]benzofuran (**3p**):* white solid, 0.103 g in 0.5 mmol scale, 41% yield; R_f 0.40 (petroleum ether/EtOAc = 95:5); mp 107−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.80−7.68 (m, 2H), 7.60−7.55 (m, 2H), 6.89 (d, J = 12.0 Hz, 1H), 3.98 (d, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.5, 148.2 (d, J = 248.78 Hz), 130.7, 129.5, 129.5 (d, J = 7.81 Hz), 128.7, 124.8, 123.3, 113.8, 113.0, 112.3, 105.7, 101.3 (dd, J_1 = 9.7 Hz, J_2 = 13.8 Hz), 56.5; HRMS $[M + H]^+$ calcd for $C_{17}H_{12}O_2F$ 267.0816, found 267.0813; FTIR (cm^{-1}) 3021, 2974, 1618, 1521, 1472, 1215.

*9-Bromo-10-methoxynaphtho[2,1-b]benzofuran and 11-Bromo-10-methoxynaphtho[2,1-b]benzofuran (**3q** and **3q′**):* white solid, 0.072 g in 0.5 mmol scale, 44% yield; regioisomer ratio = 3:1; R_f 0.38 (petroleum ether/EtOAc = 95:5). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.84 (s, 1H), 7.74−7.65 (m, 3H), 7.59−7.55 (m, 2H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 152.5, 150.4, 130.5, 129.5, 129.0, 127.3, 124.6, 123.1, 117.1, 116.5, 112.8, 110.1, 104.1, 57.2. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.80 (s, 1H), 7.74−7.65 (m, 3H), 7.59−7.55 (m, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.1, 150.8, 129.3, 128.8, 128.6, 127.2, 124.4, 123.3, 117.1, 113.8, 112.9, 112.2, 110.1, 105.6, 56.3. HRMS: $[M + H]^+$ calcd for $C_{17}H_{12}BrO_2$, 327.0015; found, 327.0026. FTIR (cm^{-1}): 3019, 1628, 1586, 1526, 1477, 1218.

*9-Fluoro-10-methoxynaphtho[2,1-b]benzofuran and 11-Fluoro-10-methoxynaphtho[2,1-b]benzofuran (**3r** and **3r′**):* white solid, 0.064 g in 0.5 mmol scale, 48% yield; regioisomer ratio = 1.1:1; R_f 0.42 (petroleum ether/EtOAc = 95:5). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.2 Hz, 1H), 7.87 (dd, J_1 = 8.5, J_2 = 17.4 Hz, 2H), 7.76−7.70 (m, 3H), 7.58 (t, J = 7.4 Hz, 1H), 7.49−7.45 (m, 1H), 4.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (d, J = 254.2 Hz), 145.2 (d, J = 12.0 Hz), 130.6, 129.5, 129.1, 128.8, 127.3, 126.5, 124.6, 123.7, 123.1, 120.4, 112.8, 105.9, 100.8, 57.4. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 1H), 7.87 (dd, J_1 = 8.5, J_2 = 17.4 Hz, 2H), 7.80−7.78 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.19−7.17 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 (d, J = 246.6 Hz), 149.7 (d, J = 11.9 Hz), 134.7, 130.6, 130.0, 129.1, 128.8, 128.1, 127.9, 126.9, 123.7, 120.4, 117.3, 105.9, 100.6, 55.4. HRMS: $[M + H]^+$ calcd for $C_{17}H_{12}O_2F$, 267.0816; found, 267.0812. FTIR (cm^{-1}): 3019, 1630, 1602, 1585, 1523, 1470.

*10-Methoxy-8,9-dimethylnaphtho[2,1-b]benzofuran (**3s**):* white solid, 0.071 g in 0.5 mmol scale, 51% yield; R_f 0.53 (petroleum ether/EtOAc = 95:5); mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.76−7.69 (m, 2H), 7.61 (s, 1H), 7.53 (t, J = 7.5 Hz, 1H), 4.03 (s, 3H), 2.58 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.2, 150.2, 130.5, 129.3, 129.2, 127.6, 126.9, 124.7, 124.2, 123.4, 121.5, 118.3, 113.0, 100.3, 56.5, 12.6, 12.3; HRMS $[M + H]^+$ calcd for $C_{19}H_{17}O_2$ 277.1223, found 277.1221; FTIR (cm^{-1}) 3019, 1630, 1523, 1438, 1346, 1261.

*10-Methoxy-9,11-dimethylnaphtho[2,1-b]benzofuran (**3t**):* white solid, 0.044 g in 0.5 mmol scale, 32% yield; R_f 0.40 (petroleum ether/EtOAc = 95:5); mp 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.34 (s, 1H), 3.83 (s, 3H), 3.11 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 153.5, 152.7, 131.1, 130.2, 129.6, 128.8, 126.3, 126.1, 124.5, 124.0, 123.9, 119.6, 112.9, 111.2, 60.7, 18.1, 17.2; HRMS $[M + H]^+$ calcd for $C_{19}H_{17}O_2$ 277.1223, found 277.1220; FTIR (cm^{-1}) 3019, 1603, 1585, 1523, 1486, 1429, 1328.

Procedure for the BBr_3-Mediated Demethylation Reaction. To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added **3a** (0.100 g, 0.4 mmol) in anhydrous DCM (5 mL) cooled in an ice bath under an argon atmosphere. Then BBr_3 (1 M solution in DCM; 1 mL, 1 mmol) was added to the stirring mixture. This solution was stirred for 5 h after slowly warming to room temperature. The reaction mixture was quenched with a saturated $NaHCO_3$ solution, and the afforded suspension was extracted with CH_2Cl_2 (3 × 10 mL). Then the organic layer was washed with brine, dried over Na_2SO_4, and concentrated, and the crude reaction mixture was purified by flash column chromatography to afford naphtho[2,1-*b*]benzofuran-10-ol (**5a**) as a white solid (0.073 g, 78% yield): R_f 0.40 (petroleum ether/EtOAc = 70:30); mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.1 Hz, 1H), 8.01 (d, J = 6.8 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.82 (s, 1H), 7.77−7.63 (m, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 7.0 Hz, 1H), 5.01 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.8, 150.9, 130.5, 129.4, 129.2, 128.9, 127.3, 125.8, 124.5, 123.3, 117.4, 114.2, 113.0, 112.4, 107.8; HRMS $[M + H]^+$ calcd for $C_{16}H_{11}O_2$ 235.0754, found 235.0750; FTIR (cm^{-1}) 3019, 1626, 1524, 1470, 1373.

Procedure for the Tosylation of 5a. To a flame-dried screw-capped test tube equipped with a magnetic stir bar were added naphtho[2,1-*b*]benzofuran-10-ol (**5a**) (0.070 g, 0.3 mmol) and CH_2Cl_2. The resulting solution was stirred and cooled to 0 °C before adding 4-dimethylaminopyridine (0.007 g, 0.06 mmol), *p*-toluenesulfonyl chloride (0.062 g, 0.36 mmol), and triethylamine (42 μL, 0.3 mmol). The resulting solution was stirred at room temperature for 5 h under argon conditions. Then the reaction stopped, and the crude reaction mixture was purified by column chromatography on silica gel to afford naphtho[2,1-*b*]benzofuran-10-yl 4-methylbenzenesulfonate (**8a**) as a white solid (0.088 g, 76% yield): R_f 0.44 (petroleum ether/EtOAc = 95:5); mp 161−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.96−7.95 (m, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.73 (t, J = 8.6 Hz, 2H), 7.61−7.56 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.09 (dd, J = 8.8, 1.9 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 154.0, 145.6, 145.5, 132.4, 130.5, 129.9, 129.6, 129.4, 128.9, 128.8, 127.6, 125.6, 124.9, 123.2, 120.2, 117.0, 116.0, 112.7, 112.4, 21.8; HRMS $[M + H]^+$ calcd for $C_{23}H_{17}O_4S$ 389.0842, found 389.0835; FTIR (cm^{-1}) 3019, 1598, 1526, 1464, 1374, 1218.

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■ ASSOCIATED CONTENT

Supporting Information

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Details on mechanistic experiments and copies of ^{1}H and ^{13}C NMR spectra of all products (PDF)

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Notes

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