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Diels–Alder Reaction of Tropones with Arynes: Synthesis of Functionalized Benzobicyclo[3.2.2]nonatrienones

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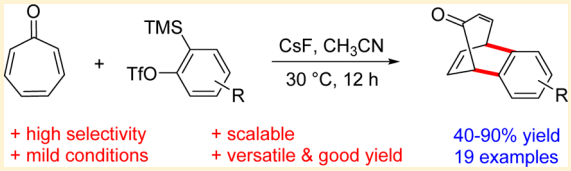
Supporting Information

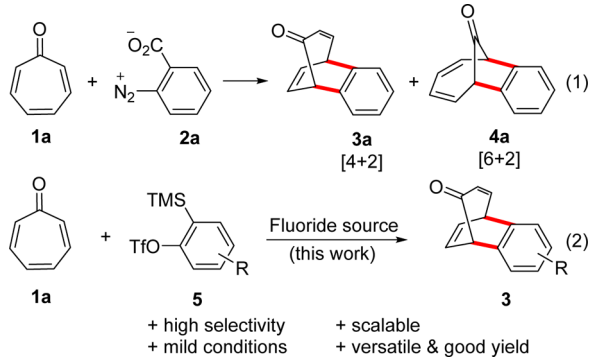
ABSTRACT: A new procedure for the mild, practical, and scalable Diels–Alder reaction of tropones with arynes is reported. Differently substituted tropones undergo selective [4 + 2] cycloaddition with arynes generated in situ by the fluoride-induced 1,2-elimination of 2-(trimethylsilyl)aryl triflates, allowing the formation of functionalized benzobicyclo[3.2.2]nonatrienone derivatives in moderate to good yields. In addition, the photophysical properties of the cycloadducts are presented.



Tropones are a valuable class of compounds that have attracted much attention of organic chemists from synthetic and theoretical perspectives.[1] The members of the troponoid family are known as important precursors for natural product synthesis[2] and are appropriate substrates for higher order cycloaddition reactions.[3] Depending on the reaction conditions and the coupling partner, tropones can react as a 4π, 6π, or 8π component in cycloaddition reactions. Some of the recent and noteworthy transformations involving tropones include the Cu-catalyzed [6 + 3] cycloaddition with azomethine ylides developed independently by Guo and co-workers and Wang and co-workers,[4] Al-catalyzed inverse-electron-demand Diels–Alder reaction with electron-rich olefins reported by Li and Yamamoto,[5] asymmetric Pd-catalyzed [6 + 3] cycloaddition with trimethylenemethane and its subsequent application to the synthesis of the welwitindolinone core uncovered by Trost and co-workers,[6] formal [8 + 3] cycloaddition with enals under N-heterocyclic carbene catalysis introduced by Nair and co-workers,[7] and the phosphine-catalyzed [6 + 3] cycloaddition with allylic compounds developed by Lu and co-workers.[8]

The synthetic utility of tropones as a 4π component in Diels–Alder reaction can result in the straightforward access to bicyclo[3.2.2] compounds. Tropones react with various electron-poor dienophiles[9] and electron-rich ones.[10] The use of highly electrophilic arynes[11] (generated from *o*-benzenediazonium carboxylate **2a**) as coupling partner for tropone Diels–Alder reaction was developed by Kende and co-workers in 1967.[12] However, the reaction was limited to only one example in low yield. In an attempt to study the Kende protocol, Tamano and co-workers observed the [6 + 2] adduct **4a** in addition to the Diels–Alder adduct **3a** (Scheme 1, eq 1).[13] In view of the potential biological properties of benzobicyclo-[3.2.2]nonatrienones,[14] a high yielding and broad scope synthesis of these compounds is highly desirable. We have been working on Diels–Alder reaction of arynes with interesting dienes such as pentafulvenes,[15a] 1,2-benzoquinones,[15b] and styrenes.[15c] Herein, we report a selective, scalable, and broad scope Diels–Alder reaction of tropones with arynes generated from 2-(trimethylsilyl)aryl triflates **5** leading to the practical synthesis of benzobicyclo[3.2.2]nonatrienone derivatives **3** (eq 2).

Scheme 1. Reaction of Tropone with Arynes



The present study was initiated with the optimization of reaction conditions for the selective [4 + 2] cycloaddition of tropones with arynes. In an initial experiment, treatment of tropone **1a** with aryne generated in situ from the triflate **5a**[16] using CsF in CH_3CN as solvent resulted in the formation of the Diels–Alder adduct **3a** in 62% yield (determined by ^{1}H NMR spectroscopy, Table 1, entry 1). It is noteworthy that the [6 + 2] adduct **4a** was observed in <3% yield (based on ^{1}H NMR) under the present reaction conditions. Compared to CsF, other common fluoride sources for aryne generation from **5a** such as

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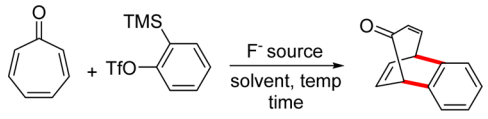
Table 1. Optimization of Reaction Conditions[a]



1a 5a 3a

entry	F⁻ source	solvent	temp (°C)	time (h)	yield of **3a** (%)[b]
1	CsF	CH_3CN	30	12	62
2[c]	KF	THF	30	12	39
3	TBAF	THF	30	12	<5
4	CsF	CH_3CN	0–rt	12	61
5[d]	**CsF**	**CH_3CN**	**30**	**12**	**77 (76)**
6[d]	CsF	CH_3CN	30	24	75
7[d]	CsF	CH_3CN	60	12	71
8[d,e]	CsF	CH_3CN	30	12	74

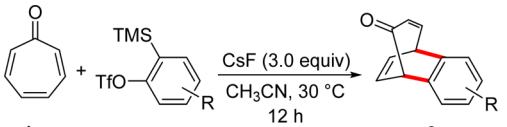
[a]Standard conditions: **1a** (0.25 mmol), **5a** (0.30 mmol), fluoride source (0.6 mmol), solvent (1.0 mL), 30 °C, and 12 h. [b]The yields were determined by ^{1}H NMR analysis of crude products using CH_2Br_2 as the internal standard. Isolated yield on 0.50 mmol scale in parentheses. [c]0.6 mmol of 18-crown-6 was used as an additive. [d]Reaction performed using 1.5 equiv of **5a** and 3.0 equiv of CsF. [e]10 mL of CH_3CN was used.

KF/18-crown-6 and tetrabutylammonium fluoride (TBAF) afforded **3a** in low yields (entries 2, 3). The reaction carried out at 0 °C to rt furnished comparable results (entry 4). Interestingly, when the reaction was performed using 1.5 equiv of aryne precursor **5a** and 3.0 equiv of CsF, the desired product **3a** was formed in 77% yield (76% isolated yield, entry 5). Further experiments to improve the yield of **3a** by increasing the reaction time, performing the reaction at 60 °C, and carrying out the reaction under dilute conditions were not successful (entries 6–8). Moreover, when the reaction was carried out in a 10 mmol scale under the optimized conditions (entry 5), the product **3a** was obtained in 76% yield indicating that the present reaction is easily scalable.

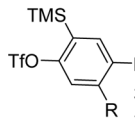
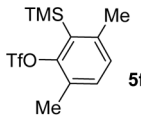
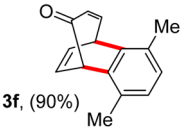
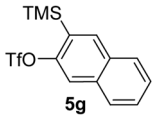
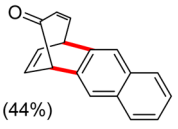
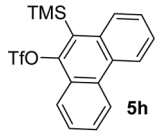
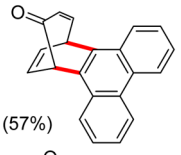
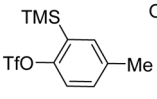
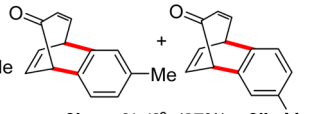
After establishing the optimized condition for the selective Diels–Alder reaction of tropones with arynes, we then examined the generality of this reaction (Table 2). The parent benzyne derived from **5a** worked well, and the symmetrical aryne precursors **5b** and **5c** that are electronically dissimilar resulted in the formation of the benzobicyclo[3.2.2]-nonatrienones **3b** and **3c** in moderate to good yields (entries 2, 3).[17] Moreover, the indane- and tetrahydronaphthalene-derived arynes generated from **5d** and **5e** furnished the desired product **3d** and **3e** in moderate yields (entries 4, 5). In addition, the 3,6-dimethyl benzyne derived from **5f** underwent smooth Diels–Alder reaction with tropone (entry 6), and the symmetrical naphthalene and phenanthrene-derived arynes generated from **5g** and **5h** afforded the target bicyclic product **3g** and **3h** in moderate yields (entries 7, 8). Furthermore, the Diels–Alder reaction of the unsymmetrical aryne generated from **5i** with tropone resulted in the formation of an inseparable mixture of regioisomers **3i**/**3i′** in a 1:1 ratio and 87% yield (entry 9).

We then focused our attention on the feasibility of this reaction with various tropone derivatives (Table 3). The 2-methoxy tropone reacted with aryne generated from **5a** to afford the product **3j** in 83% yield and with a high regioselectivity of 20:1. The high regioselectivity in this case is attributed to the relative electron-richness of the diene system near to the -OMe group. The structure of the

Table 2. Substrate Scope: Variation of the Aryne Moiety[a]



1a 5 3

entry	aryne precursor	product(s), yield (%)
1–4	 **5b-5e**	**3b**, R = Me, (72%) **3c**, R = $O(CH_2)O$, (50%) **3d**, R = $(CH_2)_3$, (63%) **3e**, R = $(CH_2)_4$, (46%)[b]
5	 **5f**	 **3f**, (90%)
6	 **5g**	 **3g**, (44%)
7	 **5h**	 **3h**, (57%)
8	 **5i**	 **3i** [1:1][c], (87%) **3i'**

[a]General conditions: **1a** (0.50 mmol), **2** (0.75 mmol), CsF (1.5 mmol), CH_3CN (2.0 mL), 30 °C, and 12 h. Yields of the isolated products are given. [b]Reaction was run on 0.25 mmol scale. [c]Regioisomer ratio determined by ^{1}H NMR of the crude reaction mixture.

regioisomer **3j** was confirmed by single crystal X-ray analysis.[18] The 2-benzyloxy tropone also showed the similar reactivity profile and furnished the product **3k** in 84% yield and 20:1 ratio. Interestingly, the reaction of aryne with 2-tosyloxy tropone resulted in the formation of the opposite regioisomer **3l′** in 40% yield and 1:20 ratio. The regioselectivity in this case may be due to the stereoelectronic effect. Moreover, 2-halogenated tropones are well tolerated under the present reaction conditions, leading to the formation of separable regioisomers in good yields (**3m**–**3o**, **3m′**–**3o′**). Additionally, 2-phenyl tropone also afforded the desired products as inseparable mixture of regioisomers **3p**/**3p′** in 81% yield and 1:2.1 ratio. Furthermore, 2-aryl tropones having electron-donating and -withdrawing groups at the 4-position of the aryl ring underwent smooth Diels–Alder reaction with arynes, and the desired products are formed as an inseparable mixture of regioisomers in good yields.

The reaction of tropolone **1s** with aryne resulted in the formation of the cycloadduct **3s** in 55% yield as a single regioisomer (Scheme 2). The regioselectivity may be due to the involvement of the diene near to the electron-donating -OH group in the cycloaddition reaction. Moreover, the O-arylation product was not observed under this reaction conditions. This also indicates that the Diels–Alder reaction proceeds faster

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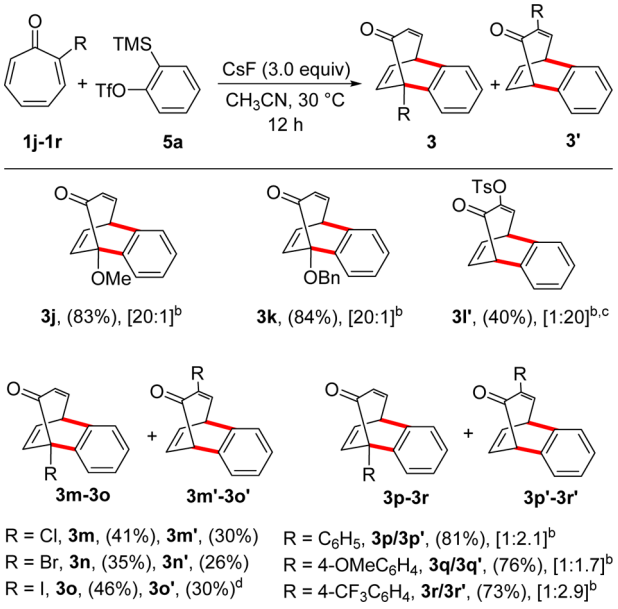
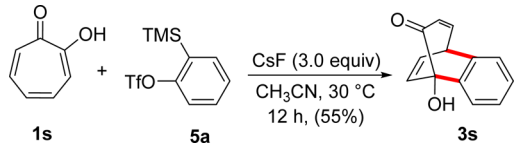
Table 3. Substrate Scope: Variation of Tropones[a]



[a]General conditions: **1** (0.5 mmol), **5a** (0.75 mmol), CsF (1.5 mmol), CH_3CN (2.0 mL), 30 °C, and 12 h. Yields of the isolated products are given. [b]Regioisomer ratio determined by ^1H NMR analysis of the crude reaction mixture. [c]Reaction was carried out using 2.0 equiv of **5a**. [d]Reaction was run on 0.25 mmol scale.

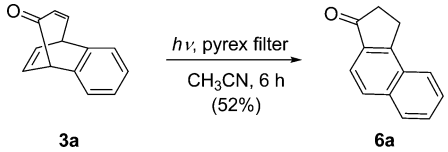
Scheme 2. Reaction of Tropolone with Aryne



than the aryne O−H insertion in the reaction of tropolone with arynes.[19]

The application of the tropone-aryne [4 + 2] cycloaddition reaction has been examined by the photochemical rearrangement of the cycloadduct **3a** to form the functionalized naphthalene derivative **6a**.[12] Thus, irradiation of the CH_3CN solution of **3a** using a medium pressure mercury lamp (450 W) for 6 h resulted in the formation of **6a** in 52% yield (Scheme 3). It may be mentioned that the reaction proceeds via the photochemical 1,3-acyl migration followed by isomerization.

Scheme 3. Photochemical 1,3-Acyl Migration



Finally, we carried out preliminary studies on the photophysical properties of some of the cycloadducts. Absorption and emission spectra of compounds **3a**, **3c**, and **3l′** are presented in Figure 1. Notably, **3a** possesses an isolated C−C double bond and enone and benzene chromophores in a nonconjugated arrangement. The absorption spectrum of **3a** (22 μM, CH_3CN at 30 °C) showed peaks at 275, 225, and 195 nm, and the peak at 275 nm corresponds to n−π^* transition of

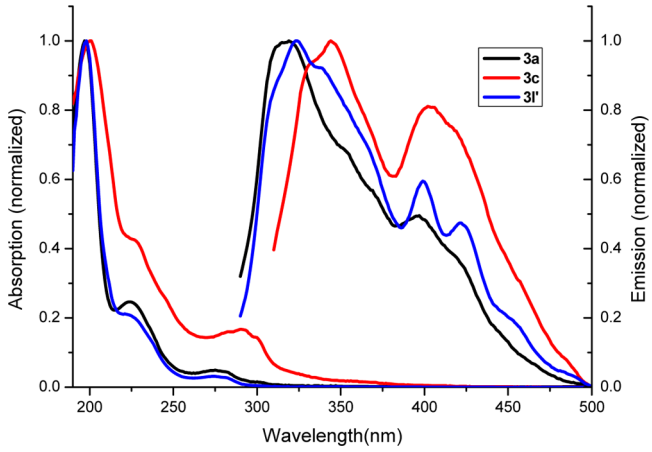


Figure 1. Normalized absorption and fluorescence spectra of **3a**, **3c**, and **3l′** in CH_3CN.

the enone moiety. All three derivatives **3a**, **3c**, and **3l′** showed weak fluorescence while exciting at 270 and 290 nm. Emission spectrum of **3a** (λ_{ex} = 270 nm, CH_3CN at 30 °C) showed a weak emission centered at 323 and 400 nm.

In summary, we have developed a new protocol for a scalable and mild method for the Diels−Alder reaction of tropones with arynes. The reaction allows the synthesis of various bridged benzobicyclo[3.2.2]nonatrienone derivatives in moderate to good yields. Given the importance of functionalized benzobicyclo[3.2.2]nonatrienones, the method presented herein is a practical method to synthesize these molecules.

EXPERIMENTAL SECTION

All reactions were carried out at room temperature (30 °C) under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps unless otherwise specified. Dry CH_3CN was purchased from commercial sources and was stored under argon over 4 Å molecular sieves. The tropone **1a** and tropolone **1s** were purchased from commercial sources and were used without further purification. The 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **5a** and the other symmetrical and unsymmetrical aryne precursors (**5b**−**5i**) were synthesized following literature procedure.[16] CsF was dried by heating at 110 °C for 12 h and left to cool under argon. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ as 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 ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). HRMS measurements were carried out using the ESI method and an ion-trap mass analyzer.

General Procedure for the Diels−Alder Reaction of Tropones with Arynes. To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added dry CsF (0.228 g, 1.50 mmol). Then the screw-capped tube was evacuated and backfilled with argon. To this was added CH_3CN (2.0 mL) under argon atmosphere. The resultant solution was kept stirring at 30 °C. To this stirring solution were added corresponding tropone derivative **1** (0.50 mmol) and aryne precursor **2** (0.75 mmol). Then the reaction mixture was kept stirring at 30 °C. When TLC showed the completion of the reaction (typically after 12 h), the mixture was diluted with CH_2Cl_2 (5.0 mL), filtered through a short pad of silica gel, and eluted with CH_2Cl_2 (15 mL). The solvent was evaporated, and the crude residue was purified by column chromatography on silica gel to afford the corresponding benzobicyclo[3.2.2]nonatrienones derivatives **3** in moderate to good yields.

5,9-Dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3a).[12] Yellow solid (0.069 g, 76%). R_f (pet. ether/EtOAc = 90/10): 0.36. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38−7.36 (m, 1H), 7.29−7.22 (m, 2H), 7.19−7.15 (m, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.61 (t, J = 7.3 Hz,

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1H), 5.25 (d, J = 10.9 Hz, 1H), 4.62 (d, J = 6.8 Hz, 1H), 4.30 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 152.8, 142.7, 138.8, 136.3, 129.4, 127.6, 126.8, 126.3, 125.1, 63.0, 45.4. HRMS calculated $[M + H]^+$ for $C_{13}H_{11}O$: 183.0804, found 183.0806. FTIR (cm^{-1}): 3618, 1740, 1664, 1626, 1546, 1515, 1461, 1338, 1230, 1155, 912.

2,3-Dimethyl-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3b). Pale brown solid (0.076 g, 72%). R_f (pet. ether/EtOAc = 90/10): 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.24 (dd, J_1 = 8.5 Hz, J_2 = 10.9 Hz, 1H), 7.18 (s, 1H), 7.03 (s, 1H), 6.93 (t, J = 7.2 Hz, 1H), 6.60 (t, J = 7.3 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 4.58 (d, J = 6.7 Hz, 1H), 4.24 (t, J = 7.2 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 153.2, 140.4, 139.0, 134.8, 134.3, 133.6, 129.5, 128.9, 126.5, 125.0, 62.5, 44.9, 19.5, 19.4. HRMS calculated $[M + H]^+$ for $C_{15}H_{15}O$: 211.1117, found 211.1120. FTIR (cm^{-1}): 3743, 3565, 1741, 1674, 1515, 1462, 1425, 1395, 1228, 772.

5,9-Dihydro-6*H*-5,9-ethenocyclohepta[4,5]benzo[1,2-*d*]-[1,3]dioxol-6-one (3c). Pale brown solid (0.057 g, 50%). R_f (pet. ether/EtOAc = 90/10): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.22 (m, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.86 (s, 1H), 6.73 (s, 1H), 6.60 (t, J = 7.1 Hz, 1H), 5.94 (d, J = 5.5 Hz, 2H), 5.22 (d, J = 11.0 Hz, 1H), 4.50 (d, J = 6.7 Hz, 1H), 4.16 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 152.9, 146.3, 145.9, 139.1, 137.0, 129.8, 129.6, 125.0, 108.7, 106.6, 101.5, 62.7, 45.2. HRMS calculated $[M + H]^+$ for $C_{14}H_{11}O_3$: 227.0703, found 227.0703. FTIR (cm^{-1}): 3648, 1741, 1706, 1692, 1676, 1647, 1626, 1546, 1531, 1514, 1478, 1151, 939.

2,3,5,9-Tetrahydro-5,9-ethenocyclohepta[*f*]inden-6(1*H*)-one (3d). Yellow solid (0.070 g, 63%). R_f (pet. ether/EtOAc = 90/10): 0.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.27 (m, 2H), 7.13 (s, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.63 (t, J = 7.3 Hz, 1H), 5.29 (d, J = 10.9 Hz, 1H), 4.62 (d, J = 6.8 Hz, 1H), 4.28 (t, J = 7.5 Hz, 1H), 2.95−2.86 (m, 4H), 2.12 (p, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 153.2, 142.9, 142.4, 141.1, 139.1, 134.3, 129.6, 125.0, 123.7, 121.3, 63.0, 45.4, 32.6, 32.5, 25.7. HRMS calculated $[M + H]^+$ for $C_{16}H_{15}O$: 223.1117, found 223.1119. FTIR (cm^{-1}): 3678, 1770, 1741, 1705, 1692, 1674, 1659, 1626, 1546, 1531, 1515, 1483, 1372, 1230, 888.

1,2,3,4,6,10-Hexahydro-7*H*-6,10-ethenocyclohepta[*b*]-naphthalen-7-one (3e). Yellow solid (0.028 g, 46% on 0.25 mmol scale). R_f (pet. ether/EtOAc = 90/10): 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.26 (m, 1H), 7.11 (s, 1H), 6.96−6.92 (m, 2H), 6.60 (t, J = 7.4 Hz, 1H), 5.29 (dd, J_1 = 11.0 Hz, J_2 = 1.7 Hz, 1H), 4.58 (d, J = 6.6 Hz, 1H), 4.24 (t, J = 7.4 Hz, 1H), 2.75 (bs, 4H, CH_2), 1.82−1.79 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 153.1, 139.9, 139.0, 135.5, 135.0, 133.2, 129.5, 128.4, 125.8, 125.2, 62.6, 45.0, 29.3, 29.2, 23.3. HRMS calculated $[M + H]^+$ for $C_{17}H_{17}O$: 237.1274, found 237.1276. FTIR (cm^{-1}): 3678, 1770, 1740, 1661, 1626, 1547, 1426, 1315, 1150, 771.

1,4-Dimethyl-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3f). White solid (0.095 g, 90%). R_f (pet. ether/EtOAc = 90/10): 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 9.1 Hz, 1H), 6.94−6.89 (m, 3H), 6.59 (t, J = 7.4 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H), 4.93 (d, J = 6.9 Hz, 1H), 4.57 (t, J = 7.6 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 152.2, 141.2, 138.8, 134.3, 133.8, 130.4, 129.7, 128.4, 127.9, 125.6, 59.2, 41.3, 19.4, 19.0. HRMS calculated $[M + H]^+$ for $C_{15}H_{15}O$: 211.117, found 211.1119. FTIR (cm^{-1}): 3743, 1834, 1741, 1665, 1547, 1514, 1497, 1460, 1375, 1229, 1034, 771.

6,10-Dihydro-7*H*-6,10-ethenocyclohepta[*b*]naphthalen-7-one (3g). Yellow solid (0.051 g, 44%). R_f (pet. ether/EtOAc = 90/10): 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.80−7.76 (m, 2H), 7.64 (s, 1H), 7.48−7.45 (m, 2H), 7.30 (dd, J_1 = 8.6 Hz, J_2 = 10.9 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.64 (t, J = 7.4 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H), 4.76 (d, J = 6.8 Hz, 1H), 4.44 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 152.6, 139.4, 138.6, 133.7, 132.4, 132.1, 129.4, 127.9, 127.5, 126.5, 126.3, 125.8, 123.4, 62.7, 45.2. HRMS calculated $[M + H]^+$ for $C_{17}H_{13}O$: 233.0961, found 233.0962. FTIR (cm^{-1}): 3565, 1740, 1673, 1513, 1462, 1395, 1230, 811.

9,13-Dihydro-10*H*-9,13-ethenocyclohepta[*l*]phenanthren-10-one (3h). Pale brown solid (0.081 g, 57%). R_f (pet. ether/EtOAc = 90/10): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78−8.74 (m, 2H), 8.34 (d, J = 8.2 Hz, 1H), 8.22−8.19 (m, 1H), 7.71−7.64 (m, 4H), 7.46−7.41 (m, 1H), 7.09 (t, J = 7.1 Hz, 1H), 6.80 (t, J = 7.1 Hz, 1H), 5.68 (d, J = 6.8 Hz, 1H), 5.31−5.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 152.9, 139.6, 139.2, 131.0, 130.3, 130.0, 129.8, 129.5, 128.7, 127.4, 127.2, 126.7, 126.5, 125.9, 123.7, 123.6, 123.4, 122.6, 58.2, 40.0. HRMS calculated $[M + Na]^+$ for $C_{21}H_{14}ONa$: 305.0937, found 305.0935. FTIR (cm^{-1}): 3619, 1740, 1673, 1512, 1453, 1425, 1373, 1338, 1278, 1230, 839.

2-Methyl-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3i) and 2-methyl-5,9-dihydro-6*H*-5,9-ethenobenzo[7]-annulen-6-one (3i′). Inseparable mixture of regioisomers, yellow solid (0.085 g, 87%, the regioisomer ratio determined by ^{1}H NMR analysis of crude reaction mixture is 1:1). R_f (pet. ether/EtOAc = 90/10): 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.22 (m, 2H), 7.20 (s, 1H), 7.12 (d, J = 7.4 Hz, 1H), 6.94−6.89 (m, 1H), 6.61−6.56 (m, 1H), 5.25−5.22 (m, 1H), 4.60−4.57 (m, 1H), 4.27−4.22 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 153.1, 142.8, 139.1, 136.0, 129.6, 128.4, 127.3, 126.0, 125.1, 124.8, 63.0, 45.4, 21.1. HRMS calculated $[M + H]^+$ for $C_{14}H_{13}O$: 197.0961, found 197.0963. FTIR (cm^{-1}): 3618, 1740, 1665, 1626, 1515, 1497, 1462, 1425, 1374, 1289, 1014, 771.

5-Methoxy-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3j).[20] Inseparable mixture of regioisomers, pale brown solid (0.088 g, 83%, the regioisomer ratio 20:1 determined using ^{1}H NMR of the crude reaction mixture). **3j** was subsequently recrystallized from pet. ether/CH_2Cl_2. R_f (pet. ether/EtOAc = 90/10): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.2 Hz, 1H), 7.29−7.20 (m, 4H), 6.99 (dd, J_1 = 6.7 Hz, J_2 = 8.6 Hz, 1H), 6.60 (d, J = 8.7 Hz, 1H), 5.33 (d, J = 11.1 Hz, 1H), 4.34 (t, J = 7.4 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.0, 152.1, 140.8, 137.1, 136.8, 132.0, 127.6, 126.4, 125.3, 125.2, 124.5, 90.9, 52.88, 45.2. HRMS calculated $[M + Na]^+$ for $C_{14}H_{12}O_2Na$: 235.0730, found 235.0729. FTIR (cm^{-1}): 3565, 1834, 1741, 1681, 1547, 1515, 1463, 1425, 1396, 1369, 1340, 1288, 1229, 928.

5-(Benzyloxy)-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3k). Inseparable mixture of regioisomers, yellow viscous liquid (0.121 g, 84%, regioisomer ratio determined by ^{1}H NMR analysis of crude reaction mixture is 20:1). R_f (pet. ether/EtOAc = 90/10): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) (**3h**): δ 7.77−7.76 (m, 1H), 7.60 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.33−7.25 (m, 4H), 7.00 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 8.6 Hz, 1H), 5.43 (d, J = 11 Hz, 1H), 5.04 (d, J = 12.7 Hz, 1H), 4.89 (d, J = 12.7 Hz, 1H), 4.38 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (**3h**): δ 188.2, 152.2, 140.5, 139.0, 137.7, 136.9, 132.1, 128.5, 127.4, 127.0, 126.4, 125.1, 125.0, 124.6, 91.2, 67.2, 45.1. HRMS calculated $[M + Na]^+$ for $C_{20}H_{16}O_2Na$: 311.1043, found 311.1040. FTIR (cm^{-1}): 3567, 1741, 1681, 1515, 1459, 1372, 1340, 1117, 1026, 917.

6-Oxo-6,9-dihydro-5*H*-5,9-ethenobenzo[7]annulen-7-yl 4-Methylbenzenesulfonate (3l′). Inseparable mixture of regioisomers, yellow solid (0.070 g, 40%, the regioisomer ratio determined by ^{1}H NMR analysis of crude reaction mixture is 1:20). R_f (pet. ether/EtOAc = 90/10): 0.14. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 9.5 Hz, 1H), 7.28−7.13 (m, 6H), 6.94 (t, J = 7.3 Hz, 1H), 6.53 (t, J = 7.3 Hz, 1H), 4.61 (d, J = 6.8 Hz, 1H), 4.42−4.38 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.8, 145.2, 144.1, 142.0, 138.5, 137.7, 135.3, 132.2, 129.5, 129.3, 128.7, 127.6, 127.2, 126.5, 125.3, 61.8, 42.9, 21.8. HRMS calculated $[M + Na]^+$ for $C_{20}H_{16}O_4NaS$: 375.0662, found 375.0661. FTIR (cm^{-1}): 3643, 1834, 1692, 1514, 1462, 1374, 1229, 1061, 1031, 970.

5-Chloro-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3m). Yellow solid (0.044 g, 41%). R_f (pet. ether/EtOAc = 90/10): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.3 Hz, 1H), 7.37−7.27 (m, 4H), 6.96 (t, J = 7.4 Hz, 1H), 6.54 (d, J = 8.4 Hz, 1H), 5.48 (d, J = 10.9 Hz, 1H), 4.37 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 153.3, 140.2, 136.7, 136.4, 136.32, 128.1, 126.8, 126.5, 124.9, 123.9, 81.0, 45.1. HRMS calculated $[M + Na]^+$ for $C_{13}H_9OClNa$: 239.0234, found 239.0237. FTIR (cm^{-1}): 3678, 1687, 1514, 1464, 1367, 1229, 1138, 955, 898.

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7-Chloro-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3m′). Yellow solid (0.033 g, 30%). R_f (pet. ether/EtOAc = 90/10): 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 9.3 Hz, 1H), 7.38−7.36 (m, 1H), 7.24−7.20 (m, 1H), 7.18−7.14 (m, 2H), 6.95 (t, J = 7.0 Hz, 1H), 6.62 (t, J = 7.1 Hz, 1H), 4.86 (d, J = 6.9 Hz, 1H), 4.36 (t, J = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.8, 149.3, 142.0, 139.0, 135.5, 129.6, 127.8, 127.7, 127.2, 126.6, 125.3, 61.9, 45.2. HRMS calculated $[M + Na]^+$ for $C_{13}H_9OClNa$: 239.0234, found 239.0236. FTIR (cm^{-1}): 3744, 1832, 1743, 1686, 1649, 1540, 1514, 1459, 1423, 1396, 1331, 957.

5-Bromo-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3n). Yellow solid (0.045 g, 35%). R_f (pet. ether/EtOAc = 90/10): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.3 Hz, 1H), 7.34−7.21 (m, 4H), 6.89 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 8.2 Hz, 1H), 5.49 (d, J = 10.9 Hz, 1H), 4.34 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.9, 153.3, 140.1, 137.4, 137.0, 136.3, 129.1, 128.2, 126.9, 124.9, 123.4, 45.2. HRMS calculated $[M + H]^+$ for $C_{13}H_9OBrNa$: 282.9729, found 282.9734. FTIR (cm^{-1}): 3648, 1835, 1740, 1681, 547, 1515, 1478, 1228, 1139, 925.

7-Bromo-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3n′). Yellow solid (0.034 g, 26%). R_f (pet. ether/EtOAc = 90/10): 0.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 9.3 Hz, 1H), 7.37−7.35 (m, 1H), 7.23−7.21 (m, 1H), 7.18−7.15 (m, 2H), 6.95 (t, J = 7.1 Hz, 1H), 6.61 (t, J = 7.2 Hz, 1H), 4.91 (d, J = 6.8 Hz, 1H), 4.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 153.6, 141.8, 138.9, 135.5, 129.7, 127.8, 127.2, 126.7, 125.3, 120.3, 61.6, 46.6. HRMS calculated $[M + Na]^+$ for $C_{13}H_9OBrNa$: 282.9729, found 282.9729. FTIR (cm^{-1}): 1681, 1476, 1319, 1231, 1196, 1143, 900.

5-Iodo-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3o). Yellow solid (0.035 g, 46%). R_f (pet. ether/EtOAc = 90/10): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92−7.89 (m, 1H), 7.34−7.29 (m, 1H), 7.26−7.18 (m, 2H), 7.14−7.12 (m, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.74−6.70 (m, 1H), 5.50 (d, J = 10.8 Hz, 1H), 4.32 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3, 153.4, 140.2, 139.4, 137.6, 136.9, 133.7, 128.2, 127.1, 124.9, 121.6, 65.8, 45.5. HRMS calculated $[M + Na]^+$ for $C_{13}H_9OINa$: 330.9590, found 330.9589. FTIR (cm^{-1}): 1670, 1625, 1468, 1451, 1366, 1222, 919, 820.

7-Iodo-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3o′). Yellow viscous liquid (0.023 g, 30%). R_f (pet. ether/EtOAc = 90/10): 0.52; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 9.1 Hz, 1H), 7.39−7.37 (m, 1H), 7.26−7.17 (m, 3H), 6.98 (t, J = 6.8 Hz, 1H), 6.63 (t, J = 7.1 Hz, 1H), 4.96 (d, J = 6.7 Hz, 1H), 4.24 (t, J = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 161.3, 141.9, 139.0, 135.6, 129.8, 127.8, 127.2, 126.7, 125.7, 125.3, 60.4, 48.5. HRMS calculated $[M + Na]^+$ for $C_{13}H_9OINa$: 330.9590, found 330.9589. FTIR (cm^{-1}): 1754, 1678, 1625, 1574, 1461, 1437, 1366, 1245, 1142, 1010, 922, 745.

5-Phenyl-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3p) and 7-Phenyl-5,9-dihydro-6*H*-5,9-ethenobenzo[7]-annulen-6-one (3p′). Inseparable mixture of regioisomers, yellow viscous liquid (0.105 g, 81%, the regioisomer ratio 1:2.1 was determined using ^{1}H NMR of the crude reaction mixture). R_f (pet. ether/EtOAc = 90/10): 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) major isomer (**3p′**) δ 7.61−7.59 (m, 1H), 7.53−7.49 (t, J = 7.4 Hz, 1H), 7.46−7.41 (m, 2H), 7.33−7.20 (m, 5H), 7.17−7.13 (m, 1H), 7.04−7.0 (m, 1H), 6.75−6.68 (m, 1H), 4.84 (d, J = 6.7 Hz, 1H), 4.45 (t, J = 7.6 Hz, 1H). Representative peaks of minor isomer (**3p**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.20 (m), 7.04−7.0 (m), 6.82 (d, J = 8.1 Hz), 6.75−6.68 (m), 5.42 (d, J = 10.9 Hz), 4.35 (t, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer (**3p′**): δ 190.0, 149.7, 142.5, 139.0, 138.6, 137.9, 129.8, 129.0, 127.8, 127.5, 127.4, 126.9, 125.4, 125.0, 124.7, 63.6, 45.5. Representative peaks of minor isomer (**3p**): δ 189.1, 150.9, 143.1, 140.1, 139.3, 136.5, 135.0, 133.9, 130.2, 128.7, 128.1, 127.5, 126.7, 126.2, 125.9, 67.8, 45.3. HRMS calculated $[M + H]^+$ for $C_{19}H_{15}O$: 259.1117, found 259.1116. FTIR (cm^{-1}): 3618, 1673, 1465, 1229, 1154, 1035, 911, 869.

5-(4-Methoxyphenyl)-5,9-dihydro-6*H*-5,9-ethenobenzo[7]-annulen-6-one (3q) and 7-(4-Methoxyphenyl)-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3q′). Inseparable mixture of regioisomers, yellow viscous liquid (0.110 g, 76%, regioisomer ratio determined by ^{1}H NMR analysis of crude reaction mixture is 1:1.7). R_f (pet. ether/EtOAc = 90/10): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) of major isomer (**3q′**): δ 7.46−7.44 (m, 1H), 7.30−7.01 (m, 8H), 6.82 (d, J = 8.7 Hz, 2H), 4.83 (d, J = 6.8 Hz, 1H), 4.43 (t, J = 7.7 Hz, 1H), 3.78 (s, 3H). Representative peaks of minor isomer (**3q**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.6 Hz), 7.30−7.01 (m), 6.78 (d, J = 8.1 Hz), 6.73−6.70 (m), 5.39 (d, J = 10.9 Hz), 4.34 (t, J = 7.4 Hz), 3.89 (s). ^{13}C NMR (100 MHz, $CDCl_3$) of major isomer (**3q′**): δ 190.3, 159.1, 151.0, 148.7, 139.1, 138.6, 131.2, 130.2, 129.8, 128.6, 127.4, 126.8, 126.2, 125.0, 113.2, 63.6, 55.3, 45.5. Representative peaks of minor isomer (**3q**): δ 189.4, 158.6, 143.0, 142.6, 140.5, 136.5, 134.4, 134.1, 131.1, 130.3, 126.6, 125.9, 125.4, 124.7, 113.5, 67.3, 55.3, 45.3. HRMS calculated $[M + Na]^+$ for $C_{20}H_{16}O_2Na$: 311.1043, found 311.1040. FTIR (cm^{-1}): 3648, 1669, 1609, 1558, 1540, 1510, 1456, 1339, 1149, 1036, 770.

5-(4-(Trifluoromethyl)phenyl)-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3r) and 7-(4-(Trifluoromethyl)-phenyl)-5,9-dihydro-6*H*-5,9-etheno benzo[7]annulen-6-one (3r′). Yellow viscous liquid (0.119 g, 73%). (0.025 g, pure **3r′**, 0.094 g mixture of isomers, regioisomer ratio determined by ^{1}H NMR analysis of crude reaction mixture is 1:2.9). Data of major isomer **3r′**: R_f (pet. ether/EtOAc = 90/10): 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 2H), 7.46−7.44 (m, 1H), 7.37−7.35 (m, 1H), 7.31−7.26 (m, 1H), 7.24−7.22 (m, 4H), 7.03 (t, J = 7.1 Hz, 1H), 6.73 (t, J = 7.2 Hz, 1H), 4.83 (d, J = 6.8 Hz, 1H), 4.48 (t, J = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 150.9, 142.3, 141.5, 138.6, 136.3, 134.2, 129.9, 129.8, 129.5, 127.7, 127.1, 126.5, 125.2, 124.8 (q, J = 3.7 Hz), 63.65, 45.6. HRMS calculated $[M + Na]^+$ for $C_{20}H_{13}OF_3Na$: 349.0811, found 349.0810. FTIR (cm^{-1}): 3618, 1741, 1675, 1515, 1463, 1396, 1326, 1230, 1068, 753. Representative peaks of minor isomer (**3r**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.73 (m), 7.32−7.18 (m), 6.75−6.74 (m), 5.42 (d, J = 10.8 Hz), 4.40 (t, J = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.6, 151.3, 143.2, 143.0, 142.2, 139.2, 136.2, 134.2, 133.3, 130.7, 128.5, 127.7, 126.5, 128.5, 127.1, 124.8, (q, J = 3.6 Hz), 67.6, 45.4.

5-Hydroxy-5,9-dihydro-6*H*-5,9-ethenobenzo[7]annulen-6-one (3s).[20] White solid (0.055 g, 55%). R_f (pet. ether/EtOAc = 90/10): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.65 (m, 1H), 7.42−7.36 (m, 1H), 7.25−7.16 (m, 3H), 6.85−6.80 (m, 1H), 6.39 (d, J = 8.2 Hz, 1H), 5.51 (d, J = 10.7 Hz, 1H), 5.16 (bs, 1H), 4.41 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 155.0, 140.0, 139.7, 134.9, 127.3, 126.5, 124.9, 124.2, 122.3, 85.2, 45.8. HRMS calculated $[M + Na]^+$ for $C_{13}H_{10}O_2Na$: 221.0573, found 221.0573. FTIR (cm^{-1}): 3768, 1667, 1628, 1462, 1372, 1328, 1231, 918, 829, 744.

1,2-Dihydro-3*H*-cyclopenta[*a*]naphthalen-3-one (6a).[21] White solid (0.024 g, 52% yield). R_f (pet. ether/EtOAc = 80/20): 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.81−7.73 (m, 2H), 7.70−7.61 (m, 2H), 3.43 (t, J = 5.2 Hz, 2H), 2.84 (t, J = 5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 156.5, 136.7, 134.8, 130.7, 129.3, 129.0, 128.6, 127.2, 124.5, 119.6, 36.3, 24.5. HRMS calculated $[M + H]^+$ for $C_{13}H_{11}O$: 183.0804, found 183.0804. FTIR (cm^{-1}): 3672, 1699, 1625, 1587, 1460, 1381, 1302, 1242, 867, 744.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all products as well as the crystallographic CIF file for compound **3j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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