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Reacting Cyclopropenones with Arynes: Access to Spirocyclic Xanthene–Cyclopropene Motifs

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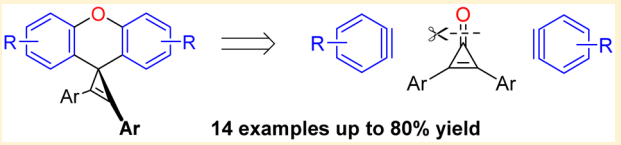
Supporting Information

ABSTRACT: A formal insertion of two aryne moieties into the carbon–oxygen double bond of cyclopropenone has been realized. Spirocyclic xanthene–cyclopropene scaffolds were obtained. Mechanistically, a sequence of a formal [2 + 2]-cycloaddition followed by electrocyclic ring opening and a terminating [4 + 2]-type cycloaddition is postulated. The use of an electron-rich aryne precursor led to ring cleavage of the cyclopropene to afford an unprecedented xanthylium salt.

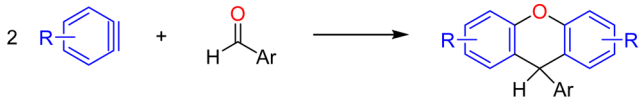


The use of arynes as synthetically useful intermediates has flourished in the recent past.[1] Formal [2 + 2]-cycloaddition reactions with carbon–carbon[2] and carbon–heteroatom[3,4] double bonds have found wide application. The enol form of several carbonyl and 1,3-dicarbonyl compounds reacts easily with arynes in a formal [2 + 2]-cycloaddition generating a benzocyclobutane derivative that affords, after immediate ring-opening, the 1-acylated-2-alkylated benzene derivative.[5] In contrast to easily enolizable carbonyl compounds, ketones such as acetone, benzophenone, or trifluoroacetophenone are only known to react with arynes in three-component reactions involving quinolines or phosphines.[6] In these latter reactions, the nitrogen- or phosphorus-containing nucleophile attacks the highly electrophilic double bond of the aryne. The emerging nucleophilic adduct is intercepted by the ketone.

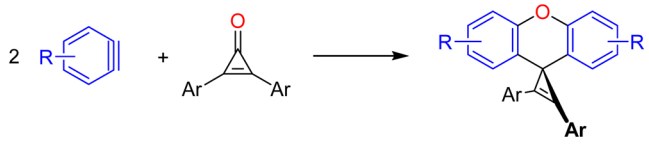
In contrast to ketones, aldehydes have been demonstrated to react with arynes by insertion into the carbon–oxygen double bond (Scheme 1A).[3c] It was assumed that, after the initial formation of the four-membered benzoxete, a subsequent electrocyclic ring-opening takes place leading to a highly reactive *o*-quinone methide, which directly reacts with a second aryne to generate the tricyclic xanthene derivative. Mechanistic experiments have revealed that the nucleophilicity of the aldehyde oxygen is crucial for a successful reaction. The higher the electron density at this oxygen, easily modulable by electron-donating substituents at the phenyl moiety, the better the yields.[3c]

Scheme 1. Reaction of Arynes with Aldehydes and Anticipated Reaction with Cyclopropenones

A) Reaction of Arynes with Benzaldehyde Derivatives:



B) Reaction of Arynes with Cyclopropenones (This Work):



Based upon these results, we were keen to test whether a ketone with a highly nucleophilic oxygen might also undergo a similar reaction.[7] Therefore, we turned our attention to cyclopropenones. Because of their aromatic character and the resulting zwitterionic structure,[8] they bear an extremely nucleophilic oxygen which has been used in various ring-opening and ring-enlargement processes.[8] In addition, the strained three-membered ring decreases the steric congestion around the carbon–oxygen double bond, thus facilitating the reaction. The anticipated transformation with two arynes in a similar way should give rise to spirocyclic xanthene–cyclopropene scaffolds (Scheme 1B).

To test our notion, unsubstituted aryne precursor **1a** and commercially available diphenylcyclopropenone (**2a**) were chosen. The use of CsF as fluoride source and acetonitrile as solvent at 30 °C turned out to be the best conditions, affording the desired product **3aa** in 64% yield (Table 1). Methyl and halogen substituents at the phenyl group of the cyclopropenone were tolerated (**3ab–af**), even though in several cases both the temperature and the reaction time had to be increased. The yields decreased from the fluorine-containing **3ac** to the iodine-substituted **3af**. We interpret this decrease as a result of the lower solubility with heavier halogens. Nitro substituents, even in the *meta*-position to the three-membered ring, completely shut down the reaction. This is probably a consequence of a less nucleophilic carbonyl oxygen of the cyclopropenone. Consistent with this observation is the observation that cyclopropenones **2g–j** bearing electron-rich residues gave the best results of up to 80% yield for the methoxy substituent

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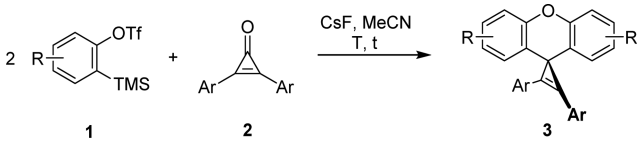
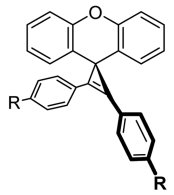
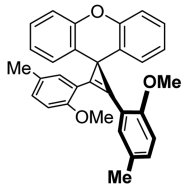
Table 1. Scope of the 2-fold Aryne Insertion into the Carbon−Oxygen Bond of Cyclopropenones To Afford Xanthene−Cyclopropene Motifs[a]

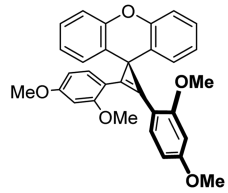




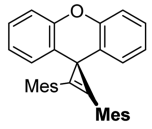
3aa	R = H, 64%	(30 °C, 24 h)
3ab	R = Me, 62%	(30 °C, 24 h)
3ac	R = F, 61%	(30 °C, 24 h)
3ad	R = Cl, 54%	(45 °C, 24 h)
3ae	R = Br, 46%	(45 °C, 72 h)
3af	R = I, 25%	(60 °C, 24 h)
3ag	R = OMe, 80%	(30 °C, 24 h)



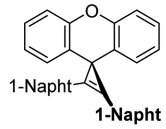
3ah, 78% (30 °C, 24 h)



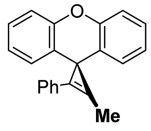
3ai, 65% (30 °C, 24 h)



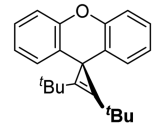
3aj, 79% (30 °C, 24 h)



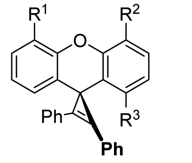
3ak, 17% (60 °C, 24 h)



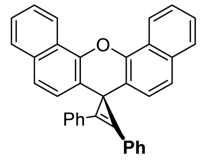
3al, 0%



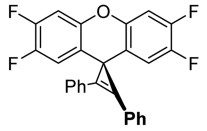
3am, 0%



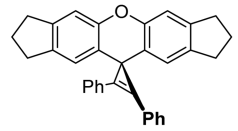
41% (30 °C, 24 h)
3ba R^1, R^2 = Me, R^3 = H
3b'a R^1, R^3 = Me, R^2 = H
3ba : **3b'a** = 2.5 : 1[b]



3ca, 56% (30 °C, 24 h)



3da, 37% (45 °C, 24 h)



3ea, 0%

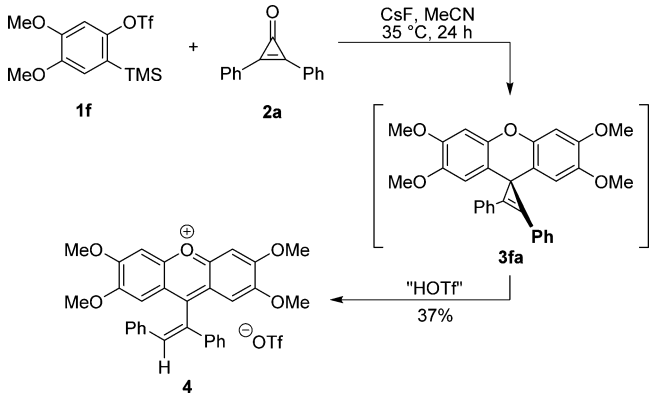
[a]Reaction conditions: **1** (0.25 mmol), **2** (0.10 mmol), CsF (0.90 mmol), MeCN (4.0 mL), yield of isolated product based on **2**. [b]Ratio determined via ^{1}H NMR.

(**3ag**). Naphthyl-substituted cyclopropenone **2k** yielded only 17% of the desired product at 60 °C. The higher temperature was necessary because of its poor solubility in acetonitrile. The even less soluble bis(5-anthracenyl)cyclopropenone showed no reactivity. Two aryl moieties seem to be crucial for a successful reaction since cyclopropenones with one or two aliphatic moieties, such as methylphenylcyclopropenone or bis(*tert*-butyl)cyclopropenone, showed no conversion to **3al** and **3am**, irrespective of varying reaction times and temperatures, despite full consumption of the starting materials.

Varying the aryne gave xanthenes **3ba**/**3b′a** and **3ca** in acceptable yields. Whereas the 3-methyl-substituted aryne precursor **1b** resulted in a regioisomeric mixture with a slight preference for the sterically less congested isomer **3ba**, the respective aryne precursor based on naphthalene afforded **3ca** as a single isomer. To conduct the transformation with the fluorine-containing aryne precursor, an increased reaction temperature proved to be essential. Since different aryne precursors commonly require different reaction temperatures, we abstained from investigating whether different arynes might be used for mixed xanthene−cyclopropene scaffolds.

Starting with a silylindanyl triflate, the electron-rich xanthene derivative **3ea** is formed but decomposes during workup. This result can be explained by a closer look at the behavior of aryne precursors whose π system is even more electron-rich than in the case of indane. When the transformation was conducted with the bis(methoxy)-substituted precursor, the anticipated xanthene congener was formed. However, because of its high electron density, traces of acid lead to a cleavage of the highly strained cyclopropene moiety, resulting in xanthylium triflate **4**.[9] This cationic compound proved to be stable and could be purified by column chromatography. NOESY investigations confirmed the *trans*-arrangement of the Ph residues in **4**. The same ring opening occurs in the case of **3ea**, but the carbocation is not sufficiently stable and decomposes further. In general, slightly electron-rich xanthene cores as in the case of **3ba**/**3b′a** and **3ca** could be purified via column chromatography on neutral or basic alumina, whereas all other products are stable on silica gel.

Scheme 2. Transformation to Xanthylium Triflate 4



To prove the structure of the products unambiguously, we obtained single crystals of **3aa**. The X-ray crystallographic analysis[10,11] confirmed the generated xanthene−cyclopropene motif. The two π systems are mutually twisted by almost exactly 90°. The molecular structure (one of two independent molecules) is depicted in Figure 1. Although single crystals of the xanthylium triflate **4** were obtained, the structure, although qualitatively confirming the nature of **4**, could not be refined satisfactorily because of severe disorder.

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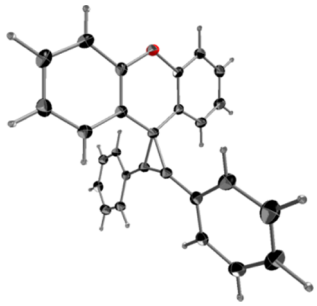
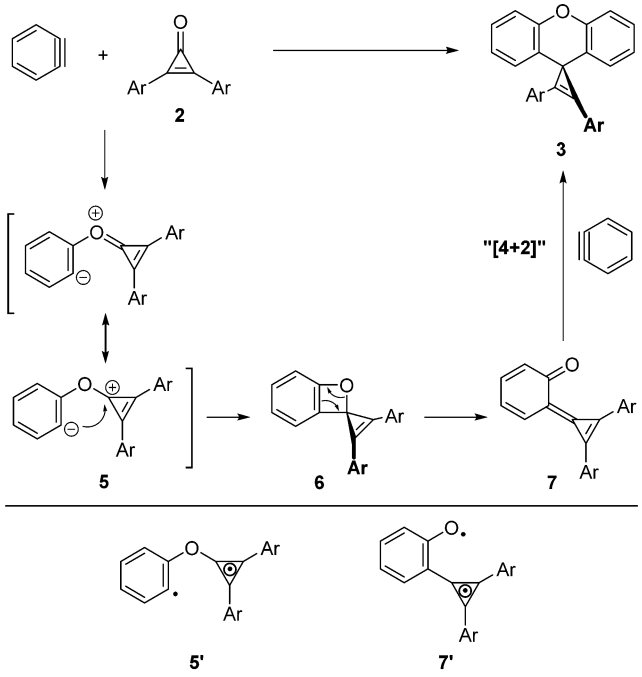


Figure 1. Molecular structure (50% ellipsoid probability) of **3aa** in the solid state (one of two independent molecules). The oxygen atom is shown in red.[10,11]

Scheme 3 (top) depicts a plausible reaction mechanism assuming a nonradical pathway.[12] As the initial step we expect

Scheme 3. (Top) Proposed Reaction Mechanism Assuming a Nonradical Pathway; (Bottom) Potential Biradicalic Intermediates 5′ and 7′



an attack by the strongly nucleophilic oxygen of the cyclopropenone at the strained in-plane π system of the aryne, forming zwitterionic intermediate **5**. This species can undergo a ring closure to the spirocyclic benzoxete derivative **6**. Electrocyclic ring-opening affords reactive *o*-quinone methide **7**, which reacts in a formal [4 + 2]-cycloaddition with a second aryne to generate the desired xanthene−cyclopropene motif **3**. Recent theoretical studies on analogous Diels−Alder reactions (e.g. tropone and benzyne) have shown that also a biradicalic pathway might be possible. Therefore, putative biradicalic intermediates are depicted in Scheme 3 (bottom).[12] All of our investigations to generalize this reaction to other nonenolizable ketones such as benzophenone, fluorenone, and dibenzosuberone showed no conversion; starting materials were recovered. These results demonstrate again the necessity of the extremely nucleophilic oxygen as it is found in cyclopropenone.

In conclusion, we have developed the first direct formal [2 + 2]-cycloaddition of an aryne with a carbon−oxygen double bond of a ketone, followed by further reaction of the emerging *o*-quinone methide with a second aryne to give spirocyclic xanthene−cyclopropene motifs. With respect to the cyclopropenone, electron-withdrawing and -donating substituents at the aryl moiety were tolerated, furnishing the spirocyclic compounds in yields up to 80%. Variation of the aryne moiety is limited to slightly electron-rich, neutral, or electron-deficient aryne precursors. Electron-rich xanthene−cyclopropene cores evade the strained spirocyclic structure by formation of xanthylium salts. These investigations nicely complement previously studied reactions of arynes with other compounds of aromatic character such as tropone, furan, or anthracene.

EXPERIMENTAL SECTION

General Experimental Methods. All solvents were distilled before use unless otherwise stated. Acetonitrile was purchased extra dry over molecular sieves. Air- and moisture-sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a 200, 300, 400, or 600 MHz instrument using residual signals from $CHCl_3$, δ = 7.26 ppm and δ = 77.16 ppm, CH_2Cl_2, δ = 5.32 ppm and δ = 53.84 ppm, and CH_3OH, δ = 3.31 ppm and δ = 49.00 ppm, as internal references for ^{1}H and ^{13}C chemical shifts, respectively. Additionally, tetramethylsilane (δ = 0.0 ppm) was added to the NMR samples. Structure elucidation was performed by a combination of NOESY, H,H−COSY, HSQC, and HMBC experiments. ESI-HRMS mass spectrometry was carried out on an FTICR instrument. IR spectra were measured on an ATR spectrometer. UV spectra were measured with a common photometer.

General Procedure for the Synthesis of Xanthene−Cyclopropene Motifs. CsF (9.0 equiv) was placed in a round-bottom flask, which was heated for 2 h at 100 °C. After the CsF was cooled to ambient temperature, cyclopropenone (1.0 equiv), MeCN (25 μmol/mL), and aryne precursor (2.5 equiv) were added, and the mixture was stirred at the given temperature and time. Solvent was evaporated, and the crude product was purified by column chromatography on silica gel (as otherwise stated) to afford the desired product.

2,3-Diphenylspiro[cyclopropane-1,9′-xanthen]-2-ene (***3aa***): 30 °C, 24 h; column chromatography, eluent: *n*-pentane/EtOAc = 200:1; white solid, 22.9 mg (64%); mp 159−160 °C dec; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (ddd, J = 7.7, 7.0, 1.3 Hz, 2H), 6.90 (dd, J = 7.8, 1.6 Hz, 2H), 7.07 (dd, J = 8.1, 1.3 Hz, 2H), 7.09−7.14 (m, 2H), 7.29−7.36 (m, 2 H), 7.35−7.43 (m, 4H), 7.68 (dd, J = 8.3, 1.3 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.5, 107.4, 116.0, 122.9, 124.8, 126.2, 126.3, 126.9, 129.0, 129.1, 130.2, 154.3; IR (neat) $\tilde{\nu}$ 3027, 1829, 1476, 1444, 1246, 1096 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 323 (4.32), 308 (4.51), 299 (4.45), 255 (4.60), 198 (4.85); HRMS (ESI) calcd for $C_{27}H_{19}O$ $[M + H]^+$ 359.1430, found 359.1431.

2,3-Di-p-tolylspiro[cyclopropane-1,9′-xanthen]-2-ene (***3ab***): 30 °C, 24 h; column chromatography, eluent *n*-pentane/EtOAc = 400:1; white solid, 24.0 mg (62%); mp 155−156 °C dec; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.37 (s, 6H), 6.83 (ddd, J = 7.7, 7.0, 1.3 Hz, 2H), 6.86−6.89 (m, 2H), 7.04−7.07 (m, 2 H), 7.10 (ddd, J = 8.2, 7.0, 1.7 Hz, 2H), 7.19−7.22 (m, 4H), 7.55−7.58 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 27.2, 106.2, 115.9, 122.9, 123.4, 124.9, 126.6, 126.8, 129.7, 130.0, 139.2, 154.3; IR (neat) $\tilde{\nu}$ 2990, 2917, 1832, 1510, 1476, 1251 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 331 (4.35), 314 (4.52), 303 (4.44), 239 (4.47), 227 (4.53), 200 (4.81); HRMS (ESI) calcd for $C_{29}H_{22}O$ $[M + H]^+$ 387.1743, found 387.1743.

2,3-Bis(4-fluorophenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (***3ac***): 30 °C, 24 h; column chromatography, eluent *n*-pentane; white solid, 24.1 mg (61%); mp 152−153 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.86 (dd, J = 4.6, 1.3 Hz, 4H), 6.99−7.19 (m, 8H), 7.53−

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7.73 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.5, 105.8 (d, ^5J = 1.7 Hz), 116.1, 116.4 (d, ^2J = 22.0 Hz), 122.3 (d, ^4J = 2.7 Hz), 123.0, 124.6, 125.8, 127.2, 131.9 (d, ^3J = 8.7 Hz), 154.3, 163.1 (d, ^1J = 250.9 Hz); ^{19}F NMR (375 MHz, $CDCl_3$) δ −110.4; IR (neat) $\tilde{\nu}$ 3044, 1822, 1597, 1503, 1447, 1216 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 321 (4.26), 306 (4.46), 297 (4.41), 224 (4.56), 198 (4.83); HRMS (ESI) calcd for $C_{27}H_{17}F_2O$ $[M + H]^+$ 395.1242, found 395.1242.

*2,3-Bis(4-chlorophenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3ad**):* 45 °C, 24 h; column chromatography, eluent *n*-pentane/EtOAc = 1000:1; yellow solid, 23.1 mg (54%); mp 163−164 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80−6.91 (m, 4H), 7.07 (ddd, J = 8.1, 1.2, 0.6 Hz, 2H), 7.11−7.18 (ddd, J = 8.1, 6.1, 2.6 Hz, 2H), 7.34−7.41 (m, 4H), 7.54−7.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 106.9, 116.2, 123.0, 124.5, 124.6, 125.6, 127.3, 129.4, 131.3, 135.3, 154.3; IR (neat) $\tilde{\nu}$ 3068, 1831, 1479, 1446, 1253, 1087 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 334 (4.32), 317 (4.46), 307 (4.40), 237 (4.37), 227 (4.45), 200 (4.75); HRMS (ESI) calcd for $C_{27}H_{17}Cl_2O$ $[M + H]^+$ 427.0651, found 427.0652.

*2,3-Bis(4-bromophenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3ae**):* 45 °C, 72 h; column chromatography, eluent *n*-pentane; yellow solid, 23.7 mg (46%); mp 170−171 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.78−6.92 (m, 4H), 7.07 (ddd, J = 8.1, 1.4, 0.7 Hz, 2H), 7.15 (ddd, J = 8.1, 5.7, 2.6 Hz, 2H), 7.45−7.58 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 107.2, 116.2, 123.0, 123.7, 124.6, 124.9, 125.5, 127.3, 131.5, 132.4, 154.2; IR (neat) $\tilde{\nu}$ 3065, 1829, 1480, 1446, 1252, 1096 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 337 (4.34), 320 (4.48), 309 (4.42), 238 (4.33), 222 (4.47), 200 (4.75); HRMS (ESI) calcd for $C_{27}H_{17}Br_2O$ $[M + H]^+$ 514.9641, found 514.9640.

*2,3-Bis(4-iodophenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3af**):* 60 °C, 24 h; column chromatography, eluent, *n*-pentane; yellow solid, 15.3 mg (25%); mp 169−170 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.77−6.92 (m, 4H), 7.06 (ddd, J = 8.2, 1.2, 0.6 Hz, 2H), 7.15 (ddd, J = 8.2, 5.9, 2.5 Hz, 2 H), 7.32−7.41 (m, 4H), 7.69−7.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 95.6, 107.6, 116.2, 123.0, 124.6, 125.4, 125.5, 127.3, 131.6, 138.3, 154.2; IR (neat) $\tilde{\nu}$ 2918, 1827, 1480, 1445, 1303, 1053 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 344 (4.36), 327 (4.49), 317 (4.38), 252 (4.17), 220 (4.42), 195 (4.74); HRMS (ESI) calcd for $C_{27}H_{17}I_2O$ $[M + H]^+$ 610.9363, found 610.9363.

*2,3-Bis(4-methoxyphenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3ag**):* 30 °C, 24 h; column chromatography, eluent *n*-pentane/EtOAc = 40:1; white solid, 15.3 mg (25%); mp 153−154 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.81 (s, 6H), 6.77−6.97 (m, 8H), 7.00−7.16 (m, 4H), 7.53−7.63 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.5, 95.6, 107.6, 116.2, 123.0, 124.6, 125.4, 125.5, 127.3, 131.6, 138.3, 154.2; IR (neat) $\tilde{\nu}$ 2956, 2823, 1824, 1601, 1445, 1209 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 343 (4.49), 324 (4.56), 308 (4.46), 246 (4.41), 200 (4.83); HRMS (ESI) calcd for $C_{29}H_{23}O_3$ $[M + H]^+$ 419.1642, found 419.1641.

*2,3-Bis(2-methoxy-5-methylphenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3ah**):* 30 °C, 24 h; column chromatography, eluent *n*-pentane/EtOAc = 40:1; white solid, 34.8 mg (78%); mp 175−176 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.26 (s, 6H), 3.70 (s, 6H), 6.77 (d, J = 8.4 Hz, 2H), 6.81−6.90 (m, 4H), 6.99−7.13 (m, 6H), 7.56 (d, J = 2.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.5, 27.3, 55.3, 103.4, 111.0, 115.3, 116.1, 122.4, 125.3, 126.1, 128.9, 129.7, 130.6, 132.7, 154.3, 157.1; IR (neat) $\tilde{\nu}$ 2924, 2836, 1576, 1446, 1241, 973 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 363 (4.19), 347 (4.24), 299 (4.16), 239 (4.04), 205 (4.82); HRMS (ESI) calcd for $C_{31}H_{27}O_3$ $[M + H]^+$ 447.1955, found 447.1955.

*2,3-Bis(2,4-dimethoxyphenyl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3ai**):* 30 °C, 24 h; column chromatography, eluent *n*-pentane/EtOAc = 20:1; white solid, 31.0 mg (65%); mp 151−152 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.80 (s, 6H), 6.40−6.51 (m, 4H), 6.79−6.88 (m, 4H), 6.99−7.09 (m, 4H), 7.63 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 55.3, 55.4, 98.7, 100.9, 105.1, 109.7, 115.3, 122.4, 125.3, 125.9, 129.2, 132.8, 154.4, 160.1, 161.4; IR (neat) $\tilde{\nu}$ 2935, 2836, 1603, 1446, 1252, 1207 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 364 (4.34), 347 (4.39), 305 (4.13), 242 (4.43), 204 (4.78); HRMS (ESI) calcd for $C_{31}H_{27}O_5$ $[M + H]^+$ 479.1853, found 479.1851.

*2,3-Dimesitylspiro[cyclopropane-1,9′-xanthen]-2-ene (**3aj**):* 30 °C, 24 h; column chromatography, eluent, *n*-pentane/EtOAc = 200:1; white solid, 35.1 mg, (79%); mp 90−91 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 12H), 2.28 (s, 6H), 6.83−6.92 (m, 8H), 6.99 (dd, J = 8.1, 1.1 Hz, 2H), 7.09 (ddd, J = 8.1, 7.0, 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.1, 21.8, 32.0, 108.9, 115.8, 122.7, 124.7, 126.0, 126.8, 128.8, 129.4, 138.2, 139.3, 154.0; IR (neat) $\tilde{\nu}$ 2916, 1804, 1609, 1476, 1446, 1205 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 388 (3.96), 289 (4.35), 245 (4.45), 189 (4.86); HRMS (ESI) calcd for $C_{33}H_{31}O$ $[M + H]^+$ 443.2369, found 443.2366.

*2,3-Di(naphthalene-1-yl)spiro[cyclopropane-1,9′-xanthen]-2-ene (**3ak**):* 60 °C, 24 h; column chromatography, eluent *n*-pentane/CH_2Cl_2 = 100:1; white solid, 7.9 mg (17%); mp 158−159 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.86 (ddd, J = 7.9, 5.9, 2.4 Hz, 2H), 7.03−7.18 (m, 6H), 7.36 (ddd, J = 8.2, 6.8, 1.3 Hz, 2H), 7.42−7.56 (m, 4 H), 7.80 (dd, J = 7.1, 1.2 Hz, 2H), 7.80 (dd, J = 7.1, 1.2 Hz, 4H), 8.28 (ddd, J = 8.3, 0.7, 0.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.6, 107.3, 116.0, 122.9, 124.3, 125.0, 125.4, 126.0, 126.1, 126.5, 126.6, 127.0, 128.3, 129.1, 129.6, 132.1, 133.7, 154.0; IR (neat) $\tilde{\nu}$ 2921, 2851, 1570, 1476, 1447, 1206 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 364 (4.08), 351 (4.08), 310 (4.07), 279 (3.83), 210 (4.91); HRMS (ESI) calcd for $C_{35}H_{22}O$ $[M]^+$ 458.1665, found 458.1662.

*4′,5′-Dimethyl-2,3-diphenylspiro[cyclopropane-1,9′-xanthen]-2-ene (**3ba**) and 1′,5′-dimethyl-2,3-diphenylspiro[cyclopropane-1,9′-xanthen]-2-ene (**3b′a**):* 30 °C, 24 h, basic alumina oxide column, eluent *n*-pentane/EtOAc = 200:1; white solid, 15.8 mg (41%), 2.5:1 mixture (ratio determined by ^{1}H NMR); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.07 (s, 3H, Me-**3b′a**), 2.41 (s, 3H, Me-**3b′a**), 2.44 (s, 6H, 2 × Me-**3ba**), 6.65−6.76 (m, 8H), 6.94−7.03 (m, 4H), 7.32−7.36 (m, 4H), 7.37−7.45 (m, 8H), 7.62−7.77 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5, 15.7, 21.8, 27.6, 28.3, 107.5, 111.6, 114.6, 121.8, 122.0, 122.2, 122.3, 123.9, 124.3, 125.0, 125.6, 126.1, 126.2, 126.7, 127.7, 128.1, 128.1, 128.7, 128.8, 128.8, 128.8, 129.7, 130.0, 136.0, 152.2, 152.4, 155.9; HRMS (ESI) calcd for $C_{29}H_{23}O$ $[M + H]^+$ 387.1743, found 387.1743.

*2,3-Diphenylspiro[cyclopropane-1,7′-dibenzo[c,h]xanthen]-2-ene (**3ca**):* 30 °C, 24 h, basic alumina oxide column, eluent *n*-pentane/EtOAc = 200:1; white solid, 25.6 mg (56%); mp 147−148 °C dec; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.05 (ddd, J = 8.5, 6.8, 1.6 Hz, 2H), 7.21 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.35−7.56 (m, 8H), 7.68−7.79 (m, 4H), 7.88−7.98 (m, 4H), 8.38−8.46 (m, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 29.9, 116.7, 117.8, 120.1, 123.8, 125.1, 126.1, 129.0, 129.5, 129.6, 129.8, 129.8, 130.6, 131.7, 132.2, 154.6; IR (neat) $\tilde{\nu}$ 3056, 1512, 1450, 1375, 1342, 1155 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 329 (4.21), 314 (4.27), 256 (4.50), 217 (4.71); HRMS (EI) calcd for $C_{35}H_{22}O$ $[M - H]^+$ 457.1587, found 457.1592.

*2′,3′,6′,7′-Tetrafluoro-2,3-diphenylspiro[cyclopropane-1,9′-xanthen]-2-ene (**3da**):* 45 °C, 24 h; column chromatography, eluent *n*-pentane/EtOAc = 1000:1; white solid, 16.1 mg (37%); mp 159−160 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.64 (dd, J = 10.9, 8.5 Hz, 2H), 6.89 (dd, J = 10.7, 6.7 Hz, 2H), 7.35−7.54 (m, 6H), 7.56−7.73 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.5, 105.4 (d, ^2J = 21.1 Hz), 106.5, 112.5 (d, ^2J = 19.8 Hz), 121.5 (dd, $^{3,4}J$ = 7.7, 3.8 Hz), 124.8, 129.1, 129.6, 129.9, 146.6 (dd, $^{1,2}J$ = 243.4, 12.9 Hz), 148.7 (dd, $^{1,2}J$ = 247.6, 14.5 Hz), 149.1 (dd, $^{3,4}J$ = 9.4, 2.4 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ −139.1 (d, J = 22.0 Hz), −144.4 (d, J = 22.0 Hz); IR (neat) $\tilde{\nu}$ 3052, 1821, 1623, 1496, 1447, 1154 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 321 (4.30), 306 (4.49), 296 (4.41), 224 (4.47), 198 (4.83); HRMS (ESI) calcd for $C_{27}H_{14}F_4O$ $[M]^+$ 430.0975, found 430.0976.

*(E)-9-(1,2-Diphenylvinyl)-2,3,6,7-tetramethoxyxanthylium triflate (**4**):* 35 °C, 24 h; column chromatography, eluent CH_2Cl_2/MeOH = 10:1; crystallization from *n*-hexane/CH_2Cl_2; dark red crystals 23.0 mg (37%); mp 127−128 °C dec; ^{1}H NMR (300 MHz, CD_3OD) δ 3.73 (s, 6H), 4.20 (s, 6H), 7.03−7.14 (m, 5 H), 7.28 (s, 2H), 7.34−7.47 (m, 6H), 7.78 (s, 2H), 7.96 (s, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 57.1, 58.7, 101.1, 106.2, 119.4, 128.0, 129.9, 130.0, 130.0, 130.1, 130.5, 134.4, 136.8, 137.3, 141.8, 152.4, 157.0, 163.0, 163.9; ^{19}F NMR (188 MHz, CD_3OD) δ −76.5; IR (neat) $\tilde{\nu}$ 2941, 2835, 1627, 1493, 1261,

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1143 cm^{-1}; UV/vis (MeCN) λ_{max} (lg ε) 470 (4.65), 269 (4.65), 201 (4.62); HRMS (ESI) calcd for $C_{31}H_{27}O_5$ $[M - OTf]^+$ 479.1861, found 479.1853.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra of all new compounds. X-ray crystallographic data of compound **3aa**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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