Supplementary Information

Selectivity-Switchable Oxidation of Tetraarylethylenes to Fused Polycyclic Compounds

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1. Table S1 CuCl-catalyzed dimmerization of enynes 1.

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<th>2b: 82%, Z/E = 0.7:1</th>
<th>2c: 87%, Z/E = 0.48:1</th>
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<tbody>
<tr>
<td>Et</td>
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<td>2d: 82%, Z/E = 0.65:1</td>
<td>2e: 84%, Z/E = 0.36:1</td>
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<td>2h: 70%, Z/E = 1:0.65</td>
<td>2i: 75%, Z/E = 1:0.24</td>
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<td>2j: 78%, Z/E = 0.91:1</td>
<td>2k: 80%, Z/E = 0.25:1</td>
<td>2l: 95%, Z/E = 1:0.79</td>
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<tr>
<td>2m: 65%, Z/E = 1:0.54</td>
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*The reaction was conducted with 1 (1 mmol), CuCl (10 mol%), DCE (4 mL), rt, 1-4 h, isolated yield.*
2. Experimental procedures and spectroscopic data

2.1 General information

All reactions were carried out under an inert atmosphere of dry N\textsubscript{2} in schlenk tube. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for \textsuperscript{1}H; 100 MHz for \textsuperscript{13}C; 376 MHz for \textsuperscript{19}F). \textsuperscript{1}H NMR and \textsuperscript{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using ESI mass spectrometer. Melting points (mp) were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

2.2 General procedures for the preparation of TAE 2

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, CuCl (10 mol\%, 10 mg), anhydrous DCE (4 mL), enynals 1 (1.0 equiv, 1.0 mmol) were added. The reaction was stirred at rt for 1-4 h and monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel (PE/EA = 5/1 as eluent) to afford the tetraarylethylene 2.

Tetraarylethylene 2a:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 92\%, 195.0 mg, Z/E = 1.0:1.5; mp. 139-140 °C; IR (KBr): 3056, 2920, 1677, 1580, 1546, 1489, 1399, 1361, 1233, 1123, 1061, 999, 951, 816, 749, 702, 671, 630, 512. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, Z-isomer) δ 7.13 (m, 10H), 6.29 (s, 2H), 2.49 (s, 6H), 2.34 (s, 6H). (E-isomer): δ 7.39 (m, 6H), 7.36-7.31 (m, 4H), 5.93 (s, 2H), 2.22 (s, 12H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, Z-isomer) δ 194.1, 157.8, 153.3, 139.7, 131.4, 129.5, 127.9, 127.6, 122.8, 112.5, 29.1, 14.4. (E-isomer): δ 194.1, 157.9, 152.5, 140.1, 130.1, 128.5, 128.1, 127.7, 122.6, 112.9, 29.0, 14.2.

HRMS (ESI) m/z = 425.1747 calcd. for C\textsubscript{28}H\textsubscript{22}O\textsubscript{4}[M+H]\textsuperscript{+}, found: 425.1743.
Tetraarylethylene 2b:
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 82%, 185.3 mg, Z/E = 0.7:1, mp. 165-166 °C; IR (KBr): 3113, 2946, 2872, 1676, 1580, 1542, 1512, 1354, 1234, 1118, 1092, 1061, 818, 767, 731, 670, 633, 517. $^1$H NMR (400 MHz, CDCl$_3$, Z-isomer) δ 6.94 (d, $J = 7.7$ Hz, 4H), 6.87 (d, $J = 7.9$ Hz, 4H), 6.20 (s, 2H), 2.38 (s, 6H), 2.25 (s, 6H), 2.19 (s, 6H). (E-isomer): δ 7.11-7.05 (m, 8H), 5.85 (s, 2H), 2.32 (s, 6H), 2.14 (s, 6H), 2.12 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, Z-isomer) δ 194.2, 157.6, 153.7, 137.3, 136.8, 131.2, 129.0, 128.5, 122.7, 112.2, 29.1, 21.2, 14.4. (E-isomer): δ 194.1, 157.8, 152.6, 137.5, 137.2, 130.0, 128.8, 128.6, 122.6, 112.7, 28.9, 21.3, 14.2. HRMS (ESI) m/z = 453.2065 calcd. for C$_{30}$H$_{29}$O$_4$ [M+H]$^+$, found: 453.2065.

Tetraarylethylene 2c:
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 87%, 196.6 mg, Z/E = 0.48:1, mp. 144-145 °C; IR (KBr): 3291, 2947, 2829, 2187, 1676, 1581, 1397, 1356, 1232, 1092, 1062, 948, 816, 759, 708, 632, 544. $^1$H NMR (400 MHz, CDCl$_3$, Z-isomer) δ 7.17 (d, $J = 2.9$ Hz, 2H), 7.00 (s, 2H), 6.94-6.89 (m, 2H), 6.84 (d, 2H), 6.20 (s, 2H), 2.39 (s, 6H), 2.24 (s, 6H), 2.08 (s, 6H). (E-isomer): δ 7.14 (d, $J = 7.4$ Hz, 2H), 7.08 (t, $J = 7.5$ Hz, 2H), 7.03 (s, 2H), 6.85 (d, $J = 9.2$ Hz, 2H), 5.81 (s, 2H), 2.25 (s, 6H), 2.12 (s, 6H), 2.10 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, Z-isomer) δ 194.1, 157.6, 153.4, 139.6, 137.3, 131.9, 129.5, 128.4, 128.3, 127.7, 122.8, 112.3, 29.1, 21.3, 14.4. (E-isomer): δ 194.0, 157.8, 152.6, 139.9, 137.6, 130.7, 128.5, 128.4, 128.0, 127.2, 122.6, 112.8, 28.9, 21.4, 14.1. HRMS (ESI) m/z = 475.1880 calcd. for C$_{30}$H$_{28}$NaO$_4$ [M+Na]$^+$, found: 475.1884.

Tetraarylethylene 2d:
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 82%, 196.8 mg, Z/E = 0.65:1, mp. 160-161 °C; IR (KBr): 3133, 2965, 1726, 1677, 1580, 1510, 1399, 1352, 1234, 1120, 1061, 950, 841, 669, 632, 528. $^1$H NMR (400 MHz, CDCl$_3$, Z-isomer) δ 7.04 (d, $J = 8.2$ Hz, 4H), 6.96 (d, $J = 8.1$ Hz, 4H), 6.29 (s, 2H), 2.58 (q, $J = 7.6$ Hz, 4H), 2.47 (s, 6H), 2.34 (s, 6H), 1.19 (t, $J = 7.6$ Hz, 6H). (E-isomer): δ 7.19 (m, 8H), 5.92 (s, 2H), 2.70 (q, $J = 7.6$ Hz, 4H), 2.20 (d, $J = 5.1$ Hz, 12H), 1.28 (t, $J = 7.6$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, Z-isomer) δ 194.2, 157.6, 153.7, 143.5, 137.0, 129.1, 128.5, 127.3, 122.7, 112.2, 29.1, 28.5, 15.2, 14.4. (E-isomer): δ 194.1, 157.7, 152.8, 144.1, 137.4, 131.3, 130.1, 127.6, 122.6, 112.7, 28.9, 28.8, 16.0, 14.1. HRMS (ESI) m/z = 481.2373 calcd. for C$_{32}$H$_{33}$O$_4$ [M+H]$^+$, found: 481.2367.
**Tetraarylethylene 2e:**
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 84%, 225.1 mg, Z/E = 0.36:1; mp. 246-247 °C; IR (KBr): 2960, 2866, 1676, 1639, 1580, 1395, 1361, 1267, 1233, 1111, 1019, 949, 813, 669, 639. 

**1H NMR** (400 MHz, CDCl$_3$, Z-isomer) δ 7.11 (d, J = 8.4 Hz, 4H), 7.01 (d, J = 8.4 Hz, 4H), 6.32 (s, 2H), 2.48 (s, 6H), 2.35 (s, 6H), 2.20 (s, 18H). (E-isomer): δ 7.37 (d, J = 8.3 Hz, 4H), 7.21 (d, J = 8.3 Hz, 4H), 5.92 (s, 2H), 2.19 (s, 6H), 1.37 (s, 18H), 1.25 (s, 6H). 

**13C NMR** (100 MHz, CDCl$_3$, Z-isomer) δ 194.2, 157.6, 153.5, 150.4, 136.7, 131.0, 129.1, 124.6, 122.8, 112.3, 34.5, 31.2, 29.2, 14.4. (E-isomer): δ 194.1, 157.6, 152.8, 151.0, 137.1, 129.8, 128.4, 124.9, 122.6, 112.6, 34.7, 31.5, 28.9, 14.1. 

**HRMS (ESI)** m/z = 559.2819 calcd. for C$_{36}$H$_{40}$O$_4$Na$^+$ [M+H]$^+$, found: 559.2825.

**Tetraarylethylene 2f:**
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 88%, 213.0 mg, Z/E = 0.78:1; mp. 155-156 °C; IR (KBr): 3002, 2933, 2837, 1675, 1639, 1609, 1511, 1463, 1398, 1358, 1246, 1175, 1060, 1032, 951, 837, 735, 668, 631. 

**1H NMR** (400 MHz, CDCl$_3$, Z-isomer) δ 7.09 (d, J = 8.3 Hz, 4H), 6.71 (d, J = 8.3 Hz, 4H), 6.30 (s, 2H), 3.79 (s, 6H), 2.48 (s, 6H), 2.36 (s, 6H). (E-isomer): δ 7.21 (d, J = 8.2 Hz, 4H), 6.89 (d, J = 8.2 Hz, 4H), 6.01 (s, 2H), 3.87 (s, 6H), 2.26 (d, J = 11.4 Hz, 12H). 

**13C NMR** (100 MHz, CDCl$_3$, Z-isomer) δ 194.2, 158.8, 157.6, 153.8, 128.16, 122.7, 122.6, 113.4, 112.1, 55.1, 29.1, 14.4. (E-isomer): δ 194.1, 159.3, 157.8, 153.1, 131.4, 127.9, 122.6, 113.5, 112.7, 55.4, 55.1, 29.0, 14.2. 

**HRMS (ESI)** m/z = 4485.1959 calcd. for C$_{30}$H$_{29}$O$_6$Na$^+$ [M+H]$^+$, found: 485.1961.

**Tetraarylethylene 2g:**
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 82%, 188.6 mg, Z/E = 1:0; mp. 160-161 °C; IR (KBr): 3180, 3023, 2162, 1678, 1581, 1488, 1399, 1354, 1234, 1090, 1062, 951, 835, 790, 673, 514. 

**1H NMR** (400 MHz, CDCl$_3$, Z-isomer) δ 7.10-7.02 (m, 4H), 6.86 (t, J = 8.3 Hz, 4H), 6.29 (s, 2H), 2.48 (s, 6H), 2.35 (s, 6H). (E-isomer): δ 7.28 (t, J = 6.5 Hz, 4H), 7.11 (d, J = 7.6 Hz, 4H), 5.96 (s, 2H), 2.24 (s, 12H). 

**13C NMR** (100 MHz, CDCl$_3$, Z-isomer) δ 194.0, 162.0 (d, J = 249.6 Hz), 158.0, 152.9, 135.5 (d, J = 3.4 Hz), 134.3 (d, J = 8.1 Hz), 128.3, 115.2 (d, J = 21.6 Hz), 112.7, 77.4, 77.1, 76.7, 29.1, 14.4. (E-isomer): δ 193.8, 162.5 (d, J = 247.3 Hz), 158.2, 152.3, 1315.8 (d, J = 3.4 Hz), 131.8 (d, J = 8.1 Hz), 127.5, 122.8 (d, J = 11.5 Hz), 113.1, 112.7, 29.0, 14.2. 

**19F NMR** (376 MHz, CDCl$_3$, Z-isomer) δ -113.3. (E-isomer): δ -113.3. **HRMS (ESI)** m/z = 483.1378 calcd. for C$_{28}$H$_{22}$F$_2$NaO$_2$Na$^+$ [M+H]$^+$, found: 483.1378.
Tetraarylethylene 2h:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 70%, 161 mg, Z/E = 1:0.65, mp. 160-161 °C; IR (KBr): 3158, 2936, 1675, 1637, 1584, 1482, 1423, 1263, 1231, 1149, 951, 834, 768, 632. \(^1\)H NMR (400 MHz, CDCl\(_3\)), Z-isomer \(\delta\) 7.05 (d, \(J = 7.0\) Hz, 2H), 7.02 (d, \(J = 7.4\) Hz, 2H), 6.84 (d, \(J = 7.1\) Hz, 2H), 6.78 (d, \(J = 9.7\) Hz, 2H), 6.24 (s, 2H), 2.41 (s, 6H), 2.28 (s, 6H). (E-isomer): \(\delta\) 7.27 (dd, \(J = 14.3, 7.2\) Hz, 2H), 7.07 (d, \(J = 7.7\) Hz, 2H), 6.97 (d, \(J = 9.5\) Hz, 2H), 6.82 (d, \(J = 5.4\) Hz, 2H), 5.91 (s, 2H), 2.15 (s, 12H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)), Z-isomer \(\delta\) 193.9, 162.4 (d, \(J = 249.7\) Hz), 158.2, 152.3, 141.5 (d, \(J = 7.6\) Hz), 129.5 (d, \(J = 8.4\) Hz), 127.1 (d, \(J = 2.8\) Hz), 125.9, 122.9, 118.0 (d, \(J = 22.0\) Hz), 114.9 (d, \(J = 21.1\) Hz). 113.0, 29.1, 14.4. (E-isomer): \(\delta\) 193.7, 162.7 (d, \(J = 246.2\) Hz), 158.4, 151.6, 141.8 (d, \(J = 7.8\) Hz), 129.7 (d, \(J = 8.2\) Hz), 128.7 (d, \(J = 2.0\) Hz), 127.3, 122.8, 117.1 (d, \(J = 21.7\) Hz), 114.8 (d, \(J = 21.0\) Hz), 113.4, 29.0, 14.2. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)), Z-isomer \(\delta\) -113.2. (E-isomer): \(\delta\) -113.5. HRMS (ESI) m/z = 461.1559 calcd. for C\(_{28}\)H\(_{23}\)F\(_4\)O\(_4\)\(^+\) [M+H]\(^+\), found: 461.1561.

Tetraarylethylene 2i:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 75%, 172.5 mg, Z/E = 1:0.24, mp. 177-178 °C; IR (KBr): 3139, 2993, 1677, 1580, 1487, 1447, 1403, 1356, 1231, 1099, 953, 824, 759, 673, 632, 535. \(^1\)H NMR (400 MHz, CDCl\(_3\)), Z-isomer \(\delta\) 7.14 (t, \(J = 7.2\) Hz, 4H), 6.95 (d, \(J = 7.5\) Hz, 2H), 6.91 (d, \(J = 10.8\) Hz, 2H), 6.29 (s, 2H), 2.52 (s, 6H), 2.34 (s, 6H). (E-isomer): \(\delta\) 7.43 (dd, \(J = 13.8, 6.9\) Hz, 2H), 7.34 (t, \(J = 7.2\) Hz, 2H), 7.23-7.19 (m, 4H), 5.91 (s, 2H), 2.20 (s, 12H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)), only for Z-isomer \(\delta\) 194.0, 160.3 (d, \(J = 248.8\) Hz), 158.1, 151.1, 132.1, 130.0, 129.9, 126.9, 124.8, 123.7, 122.9, 115.6, 115.4, 112.2, 29.1, 14.4. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)), only for Z-isomer \(\delta\) -112.9. HRMS (ESI) m/z = 461.1559 calcd. for C\(_{28}\)H\(_{23}\)F\(_4\)O\(_4\)\(^+\) [M+H]\(^+\), found: 461.1559.

Tetraarylethylene 2j:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 78%, 191.9 mg, Z/E = 0.91:1, mp. 181-182 °C; IR (KBr): 3051, 2923, 1677, 1582, 1487, 1398, 1233, 1090, 1061, 1014, 951, 833, 790, 735, 669, 631, 516. \(^1\)H NMR (400 MHz, CDCl\(_3\)), Z-isomer \(\delta\) 7.17 (d, \(J = 8.2\) Hz, 4H), 7.08 (d, \(J = 8.2\) Hz, 4H), 6.31 (s, 2H), 2.50 (s, 6H), 2.36 (s, 6H). (E-isomer): \(\delta\) 7.37 (d, \(J = 8.1\) Hz, 4H), 7.26 (d, \(J = 8.1\) Hz, 4H), 6.00 (s, 2H), 2.26 (s, 12H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.9, 158.1, 152.6, 137.9, 133.7, 132.6, 128.4, 127.5, 122.8, 112.9, 29.1, 14.4. (E-isomer): \(\delta\) 193.7, 158.4, 151.9, 137.9, 133.8, 131.5, 128.4, 122.9, 113.3, 29.0, 14.2. HRMS (ESI) m/z = 515.0787 calcd. For C\(_{28}\)H\(_{23}\)Cl\(_2\)NaO\(_4\)\(^+\) [M+Na]\(^+\), found: 515.0789.
Tetraarylethylene 2k:
Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 80%, 268.8 mg, Z/E = 0.25:1, mp. 175-176 °C; \textbf{IR} (KBr): 3102, 3075, 1639, 1484, 1444, 1384, 1129, 1006, 892, 691, 618, 477. \textbf{1H NMR} (400 MHz, CDCl$_3$, Z-isomer) $\delta$ 7.69 (d, $J = 7.7$ Hz, 4H), 7.45-7.38 (m, 16H), 7.20-7.14 (m, 10H), 6.44 (s, 2H). (E-isomer): $\delta$ 7.63 (d, $J = 7.7$ Hz, 4H), 7.40-7.32 (m, 8H), 7.24 (d, $J = 7.5$ Hz, 4H), 7.06 (d, $J = 6.2$ Hz, 4H), 7.03-7.01 (m, 6H), 6.95 (d, $J = 7.6$ Hz, 4H), 5.98 (s, 2H). $\textbf{13C NMR}$ (100 MHz, CDCl$_3$, only for E-isomer) $\delta$ 191.6, 154.9, 153.4, 140.4, 137.8, 133.0, 131.7, 130.3, 129.2, 129.0, 128.7, 128.4, 128.1, 127.9, 127.1, 122.1, 117.1. $\textbf{HRMS}$ (ESI) m/z = 695.2199 calcd. for C$_{48}$H$_{32}$NO$_4$ [M+H]$^+$, found: 695.2199.

Difuranethylene 2l:
Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 95%, 167.2 mg, Z/E = 1:0.79; \textbf{IR} (KBr): 3086, 3008, 1710, 1676, 1580, 1397, 1358, 1232. $\textbf{1H NMR}$ (400 MHz, CDCl$_3$, Z-isomer) $\delta$ 6.58 (s, 2H), 2.36 (s, 12H), 1.68 (m, 2H), 0.62 (m, 4H), 0.27 (m, 4H). (E-isomer): $\delta$ 6.20 (s, 2H), 2.54 (s, 6H), 2.26 (s, 6H), 1.93 (m, 2H), 0.83 (m, 4H), 0.51 (m, 4H). $\textbf{13C NMR}$ (100 MHz, CDCl$_3$, Z-isomer) $\delta$ 194.1, 157.6, 150.4, 132.3, 122.2, 110.6, 29.1, 14.7, 13.2, 7.4. (E-isomer): $\delta$ 194.1, 157.1, 150.3, 132.5, 122.2, 109.0, 29.01, 14.5, 14.2, 7.0. $\textbf{HRMS}$ (ESI) m/z = 353.1747 calcd. for C$_{22}$H$_{25}$O$_4$ [M+H]$^+$, found: 353.1748.

Difuranethylene 2m:
Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 65%, 143 mg, Z/E = 1:0.54; \textbf{IR} (KBr): 2928, 2857, 1677, 1584, 1463, 1398, 1354, 1232, 1117, 951, 672. $\textbf{1H NMR}$ (400 MHz, CDCl$_3$, only for E-isomer) $\delta$ 6.18 (s, 2H), 2.41 (s, 6H), 2.35 (t, $J = 7.9$ Hz, 4H), 2.28 (s, 6H), 1.37-1.19 (m, 16H), 0.81 (t, $J = 6.3$ Hz, 6H). $\textbf{13C NMR}$ (100 MHz, CDCl$_3$, only for E-isomer) $\delta$ 194.1, 156.8, 152.3, 129.0, 122.5, 108.3, 32.2, 31.6, 29.3, 29.0, 28.9, 22.6, 14.3, 14.0. $\textbf{HRMS}$ (ESI) m/z = 441.2999 calcd. for C$_{28}$H$_{41}$O$_4$ [M+H]$^+$, found: 441.2998.

2.3 General procedures for the preparation of tricyclic product 3

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, m-CPBA (4.0 equiv), CH$_2$Cl$_2$ (4 mL), TAE 2 (1.0 equiv, 0.2 mmol) were added. The reaction was stirred at rt for 4h and monitored by TLC. After that, the mixture was extracted with saturated aqueous NaHCO$_3$ solution and water, dried over anhydrous MgSO$_4$ and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 3/1 as eluent) to afford the tricyclic product 3.
**Tricyclic product 3a:**
Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 61%. 55.6 mg, mp. 218-219 °C; IR (KBr): 3059, 2954, 1715, 1676, 1602, 1490, 1423, 1385, 1353, 1248, 1155, 1076, 1012, 938, 884, 767, 734, 698, 652, 621. **1H NMR** (400 MHz, CDCl₃) δ 7.29 (t, J = 7.4 Hz, 1H), 7.24-7.19 (m, 5H), 7.13 (d, J = 6.2 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 5.91 (s, 1H), 4.57 (s, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 2.11 (s, 3H), 1.97 (s, 3H). **13C NMR** (100 MHz, CDCl₃) δ 202.2, 201.7, 198.6, 194.0, 174.3, 161.4, 141.2, 131.3, 130.6, 129.6, 129.3, 129.1, 129.0, 128.5, 128.4, 112.0, 98.9, 96.0, 89.5, 61.5, 29.40, 27.7, 24.0, 14.8. **HRMS** (ESI) m/z = 457.1646 calcd. for C₂₉H₂₅O₆⁺ [M+H]⁺, found: 457.1646.

**Tricyclic product 3b:**
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 58%, 56.1 mg, IR (KBr): 3015, 2924, 1714, 1606, 1505, 1421, 1384, 1352, 1186, 1110, 1013, 938, 884, 805, 734, 619. **1H NMR** (400 MHz, CDCl₃) δ 7.10 (d, J = 10.0 Hz, 6H), 7.04 (d, J = 7.8 Hz, 2H), 5.98 (s, 1H), 4.62 (s, 1H), 2.37 (s, 3H), 2.33 (s, 6H), 2.28 (s, 3H), 2.19 (s, 3H), 2.04 (s, 3H). **13C NMR** (100 MHz, CDCl₃) δ 202.3, 201.9, 198.7, 194.1, 174.4, 160.8, 141.0, 140.5, 139.1, 129.7, 129.5, 129.3, 128.5, 126.6, 112.0, 98.9, 95.91, 89.6, 61.5, 29.4, 27.7, 24.1, 21.5, 21.4, 14.9. **HRMS** (ESI) m/z = 485.1959 calcd. for C₃₀H₂₃O₇⁺ [M+H]⁺, found: 485.1955.

**Tricyclic product 3c:**
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 53%, 51.3 mg; IR (KBr): 3043, 2924, 1715, 1604, 1422, 1384, 1354, 1269, 1237, 1213, 1179, 1150, 1108, 1104, 940, 773, 736, 700, 650, 620. **1H NMR** (400 MHz, CDCl₃) δ 7.19-7.11 (m, 4H), 7.07 (s, 1H), 6.97-6.91 (m, 3H), 5.96 (s, 1H), 4.62 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.19 (s, 3H), 2.04 (s, 3H). **13C NMR** (100 MHz, CDCl₃) δ 202.3, 201.8, 198.7, 194.0, 174.3, 161.4, 141.2, 138.5, 138.1, 131.3, 130.1, 129.9, 129.4, 129.2, 128.7, 128.3, 126.6, 125.4, 112.0, 98.9, 96.0, 89.5, 61.5, 29.4, 27.7, 24.1, 21.4, 21.2, 14.8. **HRMS** (ESI) m/z = 485.1959 calcd. for C₃₀H₂₃O₇⁺ [M+H]⁺, found: 485.1958.

**Tricyclic product 3d:**
Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 50%, 51.2 mg, mp. 164-165 °C; IR (KBr): 3018, 2964, 2930, 2870, 1676, 1580, 1511, 1399, 1357, 1233, 1115, 1019, 950, 840, 816, 738, 668, 632. **1H NMR** (400 MHz, CDCl₃) δ 7.14-7.10 (m, 6H), 7.07 (d, J = 8.3 Hz, 2H), 5.98 (s, 1H), 4.62 (s, 1H), 2.63 (m, 4H), 2.37 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H), 1.22 (m, 6H). **13C NMR** (100 MHz, CDCl₃) δ 202.3, 201.8, 198.8, 194.1, 174.5, 160.8, 147.2, 145.3, 140.5, 129.5, 128.6, 128.5, 128.40, 128.1, 126.9, 112.0, 98.9, 95.93, 89.7, 61.6, 29.5, 28.7, 27.7, 24.1, 15.2, 14.9, 14.8. **HRMS** (ESI) m/z = 535.2091 calcd. for C₃₂H₂₃NaO₆⁺ [M+Na]⁺, found: 535.2089.
Tricyclic product 3e:
Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 40%, 45.5 mg, mp. 85-86 °C; IR (KBr): 3176, 2962, 2361, 2336, 1715, 1681, 1598, 1352, 1110, 834, 757, 674, 561. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.27 (m, 4H), 7.16 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.01 (s, 1H), 4.63 (s, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 2.05 (s, 3H), 1.30 (d, $J = 2.2$ Hz, 18H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.3, 201.8, 198.9, 194.3, 174.6, 160.6, 154.2, 152.1, 140.5, 129.2, 128.3, 128.2, 126.7, 125.9, 125.5, 112.0, 99.0, 95.9, 89.7, 61.6, 34.9, 34.7, 31.2, 31.1, 29.4, 27.7, 24.0, 14.9. HRMS (ESI) m/z = 569.2898 calcd. for C$_{36}$H$_{46}$O$_8$ [M+H]$^+$, found: 569.2891.

Tricyclic product 3f:
Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 51%, 52.7 mg; IR (KBr): 3006, 2935, 2841, 1712, 1603, 1509, 1421, 1384, 1294, 1180, 1005, 939, 885, 736, 622, 582. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19 (d, $J = 8.7$ Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 5.96 (s, 1H), 4.60 (s, 1H), 3.80 (d, $J = 2.1$ Hz, 6H), 2.38 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.3, 201.9, 198.7, 194.1, 174.5, 161.3, 160.1, 159.8, 139.2, 131.0, 130.3, 123.6, 122.0, 114.4, 114.1, 112.0, 98.9, 95.9, 89.7, 61.5, 55.3, 55.2, 29.4, 27.7, 24.1, 14.9. HRMS (ESI) m/z = 517.1857 calcd. for C$_{36}$H$_{46}$O$_8$ [M+H]$^+$, found: 517.1857.

Tricyclic product 3g:
Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 43%, 31.5 mg; IR (KBr): 3022, 2928, 2854, 1716, 1677, 1602, 1507, 1419, 1385, 1352, 1232, 1199, 1107, 1013, 938, 885, 838, 737, 701, 620. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.15-7.11 (m, 2H), 7.10-7.06 (m, 2H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 8.3$ Hz, 2H), 5.85 (s, 1H), 4.56 (s, 1H), 2.28 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H), 1.97 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.2, 201.5, 198.4, 193.9, 174.2, 163.8 (d, $J = 254.3$ Hz), 163.1 (d, $J = 251.7$ Hz), 160.1, 140.1, 131.6 (d, $J = 8.4$ Hz), 130.6 (d, $J = 8.6$ Hz), 127.2 (d, $J = 3.5$ Hz), 125.0 (d, $J = 3.5$ Hz), 116.6, 116.4, 116.0, 115.8, 112.0, 98.8, 96.0, 89.4, 61.3, 29.4, 27.7, 24.0, 14.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -107.72, -110.53. HRMS (ESI) m/z = 493.1457 calcd. for C$_{28}$H$_{32}$F$_2$O$_6$ [M+H]$^+$, found: 493.1453.

Tricyclic product 3h:
Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 38%, 37.4 mg, mp. 91-92 °C; IR (KBr): 3010, 2948, 1713, 1629, 1384, 1351, 1110, 1012, 928, 883, 830, 726, 703, 647. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (dd, $J = 15.0, 7.6$ Hz, 2H), 7.12 (t, $J = 8.2$ Hz, 1H), 7.05 (t, $J = 8.3$ Hz, 1H), 6.97 (d, $J = 8.3$ Hz, 2H), 6.90 (d, $J = 12.8$ Hz, 2H), 5.91 (s, 1H), 4.65 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H), 2.05 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.1, 201.5, 198.0, 194.0, 174.2, 162.7 (d, $J = 249.4$ Hz), 162.5 (d, $J = ...
247.8 Hz), 160.4, 140.7, 133.0, 132.9, 133.0 (d, J = 8.1 Hz), 130.9 (d, J = 8.3 Hz), 103.7 (d, J = 8.1 Hz), 130.3 (d, J = 8.3 Hz), 125.4, 124.1, 117.8 (d, J = 21.1 Hz), 116.5 (d, J = 22.5 Hz), 115.4 (d, J = 23.2 Hz), 112.0, 98.7, 96.1, 89.3, 61.3, 29.4, 27.7, 24.0, 14.8. 19F NMR (376 MHz, CDCl3) δ -110.26, -111.67. HRMS (ESI) m/z = 515.1277 calcd. for C28H22F2O6Na+ [M+Na]+, found: 515.1281

**Tricyclic product 3i:**
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 32%, 31.5 mg; IR (KBr): 3014, 2928, 2851, 1727, 1677, 1488, 1451, 1355, 1234, 1108, 1013, 941, 759, 672, 551. 1H NMR (400 MHz, CDCl3) δ 7.37 (d, J = 5.8 Hz, 1H), 7.32 (d, J = 5.5 Hz, 1H), 7.15 (m, 2H), 7.11 (m, 2H), 7.02 (d, J = 9.9 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H), 6.06 (s, 1H), 4.68 (s, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 202.0, 197.4, 194.2, 173.7, 159.7 (d, J = 252.0 Hz), 159.6, 159.1 (d, J = 254.5 Hz), 139.4, 132.4 (d, J = 8.6 Hz), 131.3 (d, J = 8.2 Hz), 131.0 (d, J = 2.2 Hz), 129.9 (d, J = 2.9 Hz), 124.6 (d, J = 3.2 Hz), 124.2 (d, J = 3.4 Hz), 116.3 (d, J = 22.0 Hz), 116.0 (d, J = 21.6 Hz), 124.6, 124.6, 124.2, 124.2, 116.4, 116.2, 115.9, 112.2, 99.0, 96.0, 89.9, 89.8, 61.8, 29.4, 27.6, 24.0, 14.7. 19F NMR (376 MHz, CDCl3) δ -110.28, -111.54. HRMS (ESI) m/z = 493.1457 calcd. for C28H23F2Cl2O6+ [M+H]+, found: 493.1458.

**Tricyclic product 3j:**
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 50%, 52.4 mg; IR (KBr): 3062, 2955, 1677, 1488, 1422, 1385, 1351, 1267, 1227, 1199, 1153, 1092, 1014, 938, 884, 845, 738, 703, 651, 580. 1H NMR (400 MHz, CDCl3) δ 7.30 (d, J = 8.3 Hz, 4H), 7.15 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 5.92 (s, 1H), 4.64 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 202.1, 201.4, 198.1, 193.8, 174.1, 160.2, 140.3, 137.1, 135.6, 131.0, 129.7, 129.6, 129.5, 129.0, 127.4, 112.0, 98.7, 96.0, 89.4, 61.4, 29.4, 27.7, 24.0, 14.8. HRMS (ESI) m/z = 525.0866 calcd. for C28H23Cl2O6+ [M+H]+, found: 425.0826.

**2.4 General procedures for the preparation of indene derivatives 4**

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, dimmer product 2 (1.0 equiv, 0.2 mmol), FeCl3 (4.0 equiv) was placed, then CH3NO2 (4 mL) and CH2Cl2 (4 mL) was added in order. The reaction was stirred at 60 °C for 4h and monitored by TLC. After that, the mixture was extracted with saturated aqueous NaHCO3 solution and water, dried over anhydrous MgSO4 and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 5/1 as eluent) to afford the indene derivative 4.
Indenone derivative 4a:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 91%, 69.2 mg, mp. 238-239 °C; IR (KBr): 3010, 2924, 2851, 2361, 2334, 1706, 1637, 1485, 1442, 1356, 1274, 1224, 1183, 1110, 1023, 892, 735, 696, 537. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48-7.42 (m, 3H), 7.39-7.35 (m, 2H), 7.25 (m, 5H), 7.20 (s, 1H), 2.61 (s, 3H), 2.51 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.9, 202.5, 195.2, 154.9, 144.6, 142.7, 141.0, 132.7, 132.1, 129.9, 129.8, 129.1, 128.3, 128.2, 127.2, 119.7, 31.8, 30.5, 16.3. HRMS (ESI) m/z = 403.1305 calcd. for C$_{28}$H$_{30}$NaO$_3$ $^+$/[M+Na]$^+$, found: 403.1311.

Indenone derivative 4b:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 90%, 73.5 mg, mp. 196-197 °C; IR (KBr): 3020, 2949, 2828, 2362, 2334, 1760, 1707, 1590, 1482, 1442, 1279, 1220, 1179, 1110, 955, 830, 763, 676, 536. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31-7.22 (m, 5H), 7.15 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 2.59 (s, 3H), 2.51 (s, 3H), 2.41 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.1, 202.5, 195.4, 154.3, 144.4, 142.9, 140.8, 140.0, 138.1, 132.5, 132.3, 129.8, 129.6, 128.9, 128.3, 127.5, 127.1, 119.6, 31.8, 30.5, 21.6, 21.4, 16.3. HRMS (ESI) m/z = 409.1798 calcd. for C$_{28}$H$_{32}$O$_3$ $^+$/[M+H]$^+$, found: 409.1794.

Indenone derivative 4c:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 92%, 75.1 mg, mp. 125-126 °C; IR (KBr): 3018, 2925, 2848, 2361, 2334, 1706, 1603, 1446, 1354, 1274, 1211, 1178, 1110, 964, 754, 689. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (t, J = 7.5 Hz, 1H), 7.26 (s, 1H), 7.20-7.05 (m, 6H), 6.96 (d, J = 7.5 Hz, 1H), 2.60 (s, 3H), 2.51 (s, 3H), 2.35 (s, 3H), 2.28 (d, J = 6.2 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.1, 202.5, 195.4, 154.3, 144.4, 142.9, 140.8, 140.0, 138.1, 132.5, 132.3, 129.8, 129.6, 129.2, 128.9, 128.3, 127.5, 127.1, 119.6, 31.8, 30.5, 21.6, 21.4, 16.3. HRMS (ESI) m/z = 409.1793 calcd. for C$_{28}$H$_{32}$O$_3$ $^+$/[M+H]$^+$, found: 409.1798.

Indenone derivative 4d:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 85%, 74.2 mg, mp. 196-197 °C; IR (KBr): 3021, 2964, 2931, 2854, 1707, 1643, 1499, 1415, 1356, 1274, 1224, 1182, 1109, 1017, 910, 839, 748, 673. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.25 (s, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 2.67 - 2.59 (m, 5H), 2.54 (s, 3H), 2.30 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H), 1.23 (t, J = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.1, 202.6, 195.5, 154.4, 146.2, 144.5, 144.3, 143.0, 140.8, 132.5, 132.3, 129.8, 129.4, 128.6, 128.4, 127.7, 127.5, 127.4, 119.7, 31.8, 30.6, 28.8, 28.7, 16.3, 15.3, 15.2. HRMS (ESI) m/z = 459.1936 calcd. for C$_{28}$H$_{32}$NaO$_3$ $^+$/[M+Na]$^+$, found: 459.1935.
Indenone derivative 4e:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 81%, 79.7 mg, mp. 184-185 °C; IR (KBr): 3013, 2958, 2827, 2362, 2334, 1705, 1651, 1358, 1272, 1176, 1110, 1012, 840, 672, 562. \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (d, \(J = 8.3\) Hz, 2H), 7.34 (d, \(J = 8.3\) Hz, 2H), 7.28 (d, \(J = 8.4\) Hz, 2H), 7.25-7.19 (m, 3H), 2.59 (s, 3H), 2.52 (s, 3H), 2.28 (s, 3H), 1.37 (s, 9H), 1.29 (s, 9H). \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 205.1, 202.7, 195.6, 154.2, 153.2, 151.1, 144.5, 143.0, 140.7, 132.3, 132.1, 129.5, 129.2, 128.2, 127.5, 127.1, 126.0, 125.1, 119.8, 35.0, 34.7, 31.8, 31.3, 30.6, 16.3. HRMS (ESI) \(m/z = 493.2737\) calcd. for C\(_{34}\)H\(_{39}\)O\(_3\)\([\text{M+H}]^+\), found: 493.2732.

Indenone derivative 4f:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 50%, 44 mg, mp. 210-211 °C; IR (KBr): 3222, 2927, 2840, 2361, 2334, 1702, 1602, 1503, 1461, 1355, 1293, 1251, 1177, 1109, 1026, 837, 741, 671, 541. \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (d, \(J = 8.7\) Hz, 2H), 7.23 (m, 3H), 6.98 (d, \(J = 8.7\) Hz, 2H), 6.82 (d, \(J = 8.8\) Hz, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 2.61 (s, 3H), 2.53 (s, 3H), 2.29 (s, 3H). \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 205.2, 202.6, 195.6, 160.7, 159.2, 153.3, 144.4, 143.0, 140.7, 132.3, 131.5 131.2, 130.1, 127.6, 124.4, 122.6, 119.5, 114.5, 113.8, 55.3, 55.2, 31.8, 30.5, 16.3. HRMS (ESI) \(m/z = 463.1516\) calcd. for C\(_{28}\)H\(_{22}\)NO\(_4\)\([\text{M+Na}]^+\), found: 463.1520.

Indenone derivative 4g:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 81%, 67.4 mg, mp. 157-158 °C; IR (KBr): 3015, 2928, 2854, 2361, 2336, 1581, 1481, 1437, 1355, 1272, 1244, 12123, 1186, 1108, 1075, 956, 876, 785, 764, 739, 683, 521. \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (m, 1H), 7.16 (m, 4H), 7.07 (m, 1H), 7.02-6.94 (m, 3H), 2.60 (s, 3H), 2.52 (s, 3H), 2.29 (s, 3H). \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 204.5, 202.3, 194.3, 163.1 (d, \(J = 234.8\) Hz), 162.5 (d, \(J = 251.4\) Hz), 154.2, 152.9, 145.0, 142.1, 141.3, 133.3, 131.5, 131.2 (d, \(J = 8.3\) Hz), 129.8 (d, \(J = 8.4\) Hz), 126.7, 125.6 (d, \(J = 3.0\) Hz), 124.0 (d, \(J = 3.2\) Hz), 119.8, 117.1 (d, \(J = 21.1\) Hz), 116.7 (d, \(J = 22.7\) Hz), 115.5 (d, \(J = 21.3\) Hz), 115.2 (d, \(J = 22.6\) Hz), 31.7, 30.5, 16.3 \[^{19}\text{F NMR}\] (376 MHz, CDCl\(_3\)) \(\delta\) -110.51, -112.46. HRMS (ESI) \(m/z = 417.1297\) calcd. for C\(_{28}\)H\(_{26}\)F\(_2\)O\(_3\)\([\text{M+Na}]^+\), found: 417.1295.

Indenone derivative 4h:
Red solid, purified by chromatography (PE/EA = 5/1), yield = 88%, 78.8 mg, mp. 199-200 °C; IR (KBr): 3019, 2996, 2831, 1708, 1590, 1531, 1485, 1352, 1275, 1178, 1111, 1091, 959, 836, 770, 674, 514. \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 8.4\) Hz, 2H), 7.30 (d, \(J = 8.4\) Hz, 2H), 7.25 (d, \(J = 8.9\) Hz, 2H), 7.20-7.13 (m, 3H), 2.59 (s, 3H), 2.52 (s, 3H), 2.29 (s, 3H). \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 204.6, 202.3, 194.5, 153.9 144.9, 142.2, 141.3, 136.1, 134.6, 133.1,
131.8, 131.1, 130.2, 129.7, 129.7, 128.7, 128.1, 126.9, 119.6, 31.7, 30., 16.32. **HRMS** (ESI) \( m/z = 471.0525 \) calcd. for \( \text{C}_{26}\text{H}_{18}\text{Cl}_{2}\text{NaO}_{3}^+ [\text{M+Na}]^+ \), found: 471.0529.

### Idenone derivative 4i

Red oil, purified by chromatography (PE/EA = 5/1), yield = 63%, 71.3 mg; IR (KBr): 3054, 2921, 2855, 1709, 1669, 1588, 1446, 1402, 1353, 1320, 1240, 1173, 1123, 1004, 900, 691, 544. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.71 (d, \( J = 7.8 \) Hz, 2H), 7.57 (d, \( J = 7.7 \) Hz, 2H), 7.42 (m, 6H), 7.37 (m, 2H), 7.30 (t, \( J = 7.5 \) Hz, 2H), 7.25 (d, \( J = 4.2 \) Hz, 2H), 7.22 (m, 5H), 7.03 (m, 2H), 6.92 (m, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 197.7, 195.7, 194.2, 154.4, 145.0, 144.5, 138.6, 137.6, 136.5, 136.4, 135.4, 133.5, 133.3, 132.1, 130.2, 130.1, 130.0, 129.8, 129.6, 129.2, 129.1, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 120.8. **HRMS** (ESI) \( m/z = 567.1955 \) calcd. for \( \text{C}_{41}\text{H}_{27}\text{O}_{3}^+ [\text{M+H}]^+ \), found: 567.1953.

#### 2.5 General procedures for the preparation of furyl ketone 5

Refer to the general procedures for the preparation of tricyclic product 3.

Furyl ketone 5:

Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 50%, 35.2 mg; IR (KBr): 3118, 3010, 2926, 1679, 1577, 1530, 1400, 1235, 1153, 1095, 1065, 1043, 1021, 952, 854, 743, 682, 632, 561. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.44 (s, 1H), 2.70 (s, 3H), 2.58-2.51 (m, 1H), 2.47 (s, 3H), 1.26-1.22 (m, 2H), 1.08-1.01 (m, 2H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 193.4, 188.9, 162.1, 150.6, 123.2, 116.6, 29.0, 17.2, 14.8, 11.5. **HRMS** (ESI) \( m/z = 215.0679 \) calcd. for \( \text{C}_{11}\text{H}_{12}\text{NaO}_{3}^+ [\text{M+Na}]^+ \), found: 215.0681.

#### 2.6 General procedures for the preparation of 1,3-diene 6

Refer to the general procedures for the preparation of tricyclic product 4.
1,3-Diene 6:

Red oil, purified by chromatography (PE/EA = 5/1), yield = 38%; 32.0 mg; IR (KBr): 3008, 2957, 2924, 2854, 1676, 1581, 1491, 1397, 1358, 1298, 1229, 1131, 950, 808, 741, 670, 635, 566. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.40 (t, \(J = 7.3\) Hz, 2H), 6.29 (s, 2H), 3.61 (t, \(J = 6.6\) Hz, 4H), 2.65 (s, 6H), 2.58 (q, \(J = 6.8\) Hz, 4H), 2.35 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.9, 158.5, 150.2, 127.3, 125.0, 123.1, 107.7, 43.7, 32.2, 29.1, 14.6. HRMS (ESI) \(m/z\) = 445.0944 calcd. for C\(_{22}\)H\(_{24}\)C\(_{12}\)NaO\(_4\)\(^+\) [M+Na]\(^+\), found: 445.0952.

2.7 General procedures for the preparation of intermediate \(E-7a\)

A sealed tube was charged with \(m\)-CPBA (1.0 equiv), CH\(_2\)Cl\(_2\) (4 mL), dimmer product \(E-2a\) (1.0 equiv, 0.2 mmol). The resulting mixture was placed at rt in a sealed vessel under air for 1h without stir, and monitored by TLC. After that, the mixture was extracted with saturated aqueous NaHCO\(_3\) solution and water, dried over anhydrous MgSO\(_4\) and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 3:1 as eluent) to afford the intermediate \(E-7a\).

Intermediate \(E-7a\):
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 58%, 51 mg; IR (KBr): 3067, 2957, 2920, 2851, 1715, 1674, 1577, 1352, 1234, 1177, 1122, 948, 729, 702, 629. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53-7.44 (m, 5H), 7.37-7.33 (m, 3H), 7.16 (dd, \(J = 6.5, 2.9\) Hz, 2H), 6.28 (s, 1H), 6.24 (s, 1H), 2.52 (s, 3H), 2.26 (s, 3H), 2.24 (d, \(J = 0.7\) Hz, 6H), 1.91 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 202.3, 196.7, 194.3, 193.4, 160.3, 150.4, 147.1, 139.5, 138.6, 137.9, 133.8, 131.5, 130.9, 129.8, 129.1, 128.4, 128.1, 123.35, 117.5, 30.6, 28.9, 26.5, 14.3. HRMS (ESI) \(m/z\) = 441.1697. calcd. for C\(_{30}\)H\(_{29}\)O\(_8\)\(^+\) [M+H]\(^+\), found: 441.1695.
2.8 General procedures for the preparation of intermediate oxabicycle 9

![Chemical structure of intermediates 2 and 9](image)

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, dimmer product 2 (1.0 equiv, 0.2 mmol), FeCl₃ (4.0 equiv) was placed, then CH₃NO₂ (4 mL) and CH₂Cl₂ (4 mL) was added in order. The reaction was stirred at 0 °C for 1 h and monitored by TLC. After that, the mixture was extracted with saturated aqueous sodium NaHCO₃ solution and water, dried over anhydrous MgSO₄ and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 5/1 as eluent) to afford the intermediate 9.

**Oxabicycle 9a:**
Red oil, purified by chromatography (PE/EA = 5/1), yield = 40%, 35.2 mg; IR (KBr): 3022, 2962, 2890, 1772, 1715, 1650, 1558, 1513, 1421, 1393, 1368, 1368, 1368, 1236, 1129, 1016, 929, 883, 796, 632. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.30 (m, 3H), 7.27 (m, 5H), 7.19 (d, J = 7.3 Hz, 2H), 5.53 (s, 1H), 4.19 (s, 1H), 2.44 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 198.5, 197.6, 193.5, 172.7, 163.0, 162.0, 139.2, 131.4, 129.8, 129.5, 129.3, 128.9, 128.8, 128.3, 128.2, 113.4, 109.4, 91.5, 83.0, 49.4, 29.7, 29.1, 20.9, 15.1. HRMS (ESI) m/z = 441.1697 calcd. for C₂₈H₂₅O₅⁺ [M+H]⁺, found: 441.1704.

**Oxabicycle 9b:**
Red oil, purified by chromatography (PE/EA = 5/1), yield = 23%, 31.6 mg; IR (KBr): 3013, 2908, 1795, 1771, 1736, 1699, 1649, 1559, 1540, 1421, 1395, 1263, 1132, 1053, 956, 876, 785, 664. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 7.2 Hz, 2H), 7.57 (m, 5H), 7.50 (m, 5H), 7.36 (m, 3H), 7.28 (m, 5H), 7.26-7.21 (m, 6H), 6.99 (d, J = 4.3 Hz, 4H), 6.43 (s, 1H), 4.62 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 199.8, 193.2, 192.7, 191.6, 161.9, 160.0, 142.8, 141.2, 140.7, 138.0, 136.2, 136.1, 133.4, 133.3, 133.1, 132.4, 130.4, 130.1, 129.9, 129.8, 129.3, 129.2, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.25, 127.9, 127.6, 109.9, 91.9, 62.4. HRMS (ESI) m/z = 689.2323 calcd. for C₄₈H₃₅O₅⁺ [M+H]⁺, found: 689.2319.
3. Copies of NMR Spectra

Z- 2a
Tetraarylethylene 2a
Tetraarylethylene 2b
Tetraarylethylene 2c
Tetraarylethylene 2d

\[
\text{Et} \quad \text{Et} \\
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\end{flalign}

\[
\begin{array}{c}
\text{Et} \\
\text{Et}
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{Et} \\
\text{Et}
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{Et} \\
\text{Et}
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{Et} \\
\text{Et}
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
Tetraarylethylene 2e
Tetraarylethylene 2f

MeO

OMe

O

O

4.12 ppm
3.99 ppm
3.85 ppm
2.94 ppm
6.53 ppm
5.88 ppm
4.79 ppm

MeO

OMe

O

O
Tetraarylethylene 2h

\[ \text{Chemical structure image} \]

\[ \text{NMR spectrum image} \]
Tetraarylethylene 2i
Tetraarylethylene 2j
Tetraarylethylene 2k

\[ \text{Diagram of molecular structure} \]

\[ \text{NMR spectrum} \]

\[ \text{Diagram of molecular structure} \]
Difuranethylene 2l

\[ \text{Structure of Difuranethylene 2l} \]

\[ \text{NMR Spectrum of Difuranethylene 2l} \]
Tricyclic product 3b
Tricyclic product 3c
Tricyclic product 3d
Tricyclic product 3e

![Chemical Structure Image]

![NMR Spectrum Image]
Tricyclic product 3f

\[
\text{MeO} \quad \text{MeO} - \text{Ph}
\]

\[
\text{MeO} \quad \text{MeO} - \text{Ph}
\]

\[
\text{MeO} \quad \text{MeO} - \text{Ph}
\]
Tricyclic product 3g
Tricyclic product 3h
Tricyclic product 3i
Tricyclic product 3j

\[ \begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Cl} & \quad \text{Cl}
\end{align*} \]
Indenone derivative 4a
Indenone derivative 4d
Indenone derivative 4e

\[
\begin{align*}
\text{Chemical Structure 1} & \quad \text{Chemical Structure 2}
\end{align*}
\]
Indenone derivative 4h
Indenone derivative 4i
Furyl ketone 5
1,3-Diene 6

\[
\text{Cl} - \text{\(\begin{array}{c}
\text{O} \\
\text{O}
\end{array}\)} - \text{\(\begin{array}{c}
\text{O} \\
\text{O}
\end{array}\)} - \text{Cl}
\]

\[
\text{Cl} - \text{\(\begin{array}{c}
\text{O} \\
\text{O}
\end{array}\)} - \text{\(\begin{array}{c}
\text{O} \\
\text{O}
\end{array}\)} - \text{Cl}
\]
Intermediate $E$-7a
Oxabicycle 9a
4. NOE spectrum of 6
5. X-ray diffraction analysis

5.1 Crystal data and structure refinement for E-2a

X-ray structure for E-2a

CCDC number 1508958
Bond precision: C-C = 0.0022 Å  Wavelength=0.71073
Cell: a=5.6126(11)  b=8.3452(17)  c=12.3393
alpha=88.55(3)  beta=78.74(3)  gamma=87.54(3)
Temperature: 296 K

Calculated  Reported
Volume 566.2(2)  566.2(2)
Space group P -1  P -1
Hall group -P 1  -P 1
Moiety formula C_{28} H_{24} O_{4}  C_{28} H_{24} O_{4}
Sum formula C_{28} H_{24} O_{4}  C_{28} H_{24} O_{4}
Mr 424.47  424.50
Dx,g cm^{-3} 1.245  1.245
Z 1  1
Mu (mm^{-1}) 0.082  0.082
F000  224.0  224.1
F000' 224.11
h,k,l,max 7,10,15  7,10,15
Nref 2597  2537
Tmin,Tmax
Tmin'
Correction method= Not given
Data completeness= 0.977  Theta(max)= 27.480
R(reflections)= 0.0450(2009)  wR2(reflections)= 0.1323(2537)
S = 1.065  Npar= 146
5.2 Crystal data and structure refinement for 3a

X-ray structure for 3a

3a

CCDC number 1508959
Identification code 3a
Empirical formula C_{28}H_{24}O_{6}
Formula weight 456.47
Temperature 293(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions

\[ a = 10.4453(16) \text{ Å}, \quad \alpha = 86.506(4)°. \]
\[ b = 10.5990(16) \text{ Å}, \quad \beta = 84.424(3)°. \]
\[ c = 10.8669(18) \text{ Å}, \quad \gamma = 71.570(3)°. \]
Volume 1135.4(3) Å³
Z 2
Density (calculated) 1.335 Mg/m³
Absorption coefficient 0.094 mm⁻¹
F(000) 480
Crystal size 0.180 x 0.140 x 0.120 mm³
Theta range for data collection 1.884 to 25.999°.
Index ranges -12 ≤ h ≤ 12, -13 ≤ k ≤ 9, -11 ≤ l ≤ 13
Reflections collected 6867
Independent reflections 4445 [R(int) = 0.0237]
Completeness to theta = 25.242° 99.8%
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7456 and 0.6473
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4445 / 0 / 311
Goodness-of-fit on F² 1.019
Final R indices [I>2σ(I)] R1 = 0.0567, wR2 = 0.1442
R indices (all data) R1 = 0.0825, wR2 = 0.1630
Extinction coefficient n/a
Largest diff. peak and hole 0.226 and -0.165 e.Å⁻³

S63
5.3 Crystal data and structure refinement for 4a

X-ray structure for 4a

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>CCDC number</td>
<td>1508960</td>
</tr>
<tr>
<td>Identification code</td>
<td>4a</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{26}$H$</em>{20}$O$_3$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>380.42</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.2062(14) Å  alpha = 90°.</td>
</tr>
<tr>
<td></td>
<td>b = 19.416(3) Å   beta = 109.487(3)°.</td>
</tr>
<tr>
<td></td>
<td>c = 10.5696(14) Å gamma = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1974.5(5) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.280 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.083 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>800</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.210 x 0.170 x 0.130 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.098 to 25.500°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11&lt;=h&lt;=12, -23&lt;=k&lt;=23, -12&lt;=l&lt;=12</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>11277</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3682 [R (int) = 0.0351]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>100.0%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7456 and 0.6635</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3682 / 0 / 265</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.056</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0551, wR2 = 0.1314</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0708, wR2 = 0.1410</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.235 and -0.233 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
6. Frontier molecular orbitals of ethylene and $E$-isomer of 2a.

<table>
<thead>
<tr>
<th></th>
<th>FMO</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital Shape</td>
<td>•</td>
<td><img src="image1" alt="HOMO" /></td>
<td><img src="image2" alt="LUMO" /></td>
</tr>
<tr>
<td>Energy</td>
<td>-10.12 eV</td>
<td>4.92 eV</td>
<td></td>
</tr>
</tbody>
</table>

The molecular orbitals were computed at the HF/6-31G(d) level based on the B3LYP/6-311++G(d,p) optimized geometries. The initial coordinate of $E$-isomer of 2a was from the crystal structure. The HOMO-LUMO energy gap of $E$-isomer of 2a was calculated to be smaller than that of ethylene by 6.01 eV.