

## SUPPORTING INFORMATION

### Synthesis of Indeno[de]Isochromene Derivatives from Arylvinyl Epoxides and Carbonyl Compounds via Tandem Nazarov and oxa-Pictet-Spengler Cyclizations

NagamSatish,<sup>a,b</sup> Siruvuri Krishnam Raju,<sup>a,b</sup> Jagadeesh Babu Nanubolu<sup>c</sup> and Gangarajula Sudhakar\*<sup>a,b</sup>

<sup>a</sup>Department of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology (IICT), Hyderabad500007, Telangana (India), and

<sup>b</sup>Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, UP (India) and

<sup>c</sup>Department of Analytical & Structural Chemistry, CSIR-IICT, Hyderabad-500007, Telangana (India)

Email: [gsudhakar@iict.res.in](mailto:gsudhakar@iict.res.in)

#### Table of contents

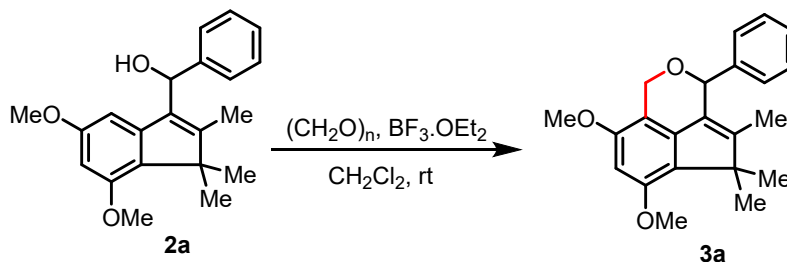
S. No	Content	Page
1	General information.....	2
2	Experimental Procedures.....	3-30
3	X-ray Crystallography Information.....	31-34
4	<sup>1</sup> H and <sup>13</sup> C NMR Spectra.....	35-78

## 1. General information

Reactions were run in oven-dried glassware under nitrogen or argon atmosphere. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F<sub>254</sub> precoated plates (20 × 20 cm) were visualized by exposure to ultraviolet light and staining with anisaldehyde, phosphomolybdic acid staining solutions followed by heating on hot plate. Flash chromatography (TELEDYNE ISCO combi flash Rf+) was carried out using silica gel (230-400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded (500 MHz, 400 MHz, 300 MHz, and CDCl<sub>3</sub>) as solvent at ambient temperature. <sup>1</sup>H and <sup>13</sup>C NMR Chemical shifts are reported in ppm (δ) values relative to the residual solvent peak. The residual solvent signals were used as reference and the chemical shift were converted to the TMS scale (CDCl<sub>3</sub>: δ<sub>H</sub> = 7.26 ppm, δ<sub>C</sub> = 77.00 ppm). <sup>1</sup>H NMR data is recorded as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, tt = triplet of triplet, ddd = doublet of doublet of doublet, brs = broad singlet, brd = broad doublet), integration, coupling constant (Hz) and assignment. Data for <sup>13</sup>C NMR are reported as chemical shift. Infrared spectrometric data were recorded on Bruker FT-IR spectrometer. Mass spectra were recorded for ESI and are given in mass units (m/z). High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer. Melting points were determined using Cintex melting point apparatus. Single crystal X-ray data for the compounds were collected on Bruker Smart Apex CCD diffractometer and Bruker D8 QUEST.

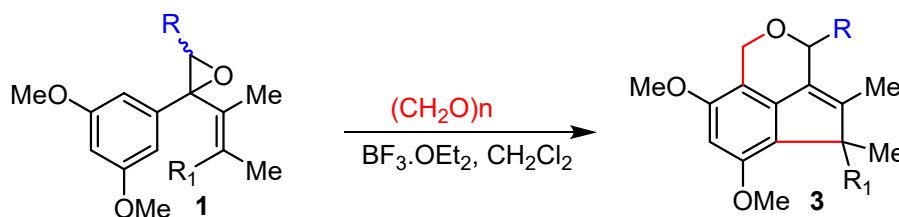
## 2. Experimental procedure

### Synthesis of 3a from 2a:



To a stirred solution of **2a** (100 mg, 0.3086 mmol, 1.0 equiv) and paraformaldehyde (32 mg, 1.0802 mmol, 3.5 equiv) in dry  $\text{CH}_2\text{Cl}_2$  (3 mL) was added  $\text{BF}_3 \cdot \text{OEt}_2$  (0.96 mL, 0.7716 mmol, 2.5 equiv) at room temperature under inert atmosphere. After completing the starting material (monitored the reaction using TLC), the reaction was quenched with  $\text{H}_2\text{O}$  or saturated  $\text{NaHCO}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with aq  $\text{NaCl}$ , dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The crude product was purified using silica gel column chromatography (EtOAc/ hexanes) to give the **3a** (97 mg, 93%) product colorless oil.

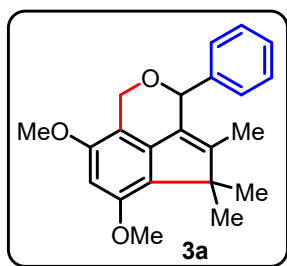
### General procedure for the synthesis of indeno[de]isochromene derivatives 3a-3i:



To a stirred solution of **1<sup>9a</sup>** (100 mg, 0.308 mmol, 1.0 equiv) and paraformaldehyde (13.8 mg, 0.463 mmol, 1.5 equiv) in dry  $\text{CH}_2\text{Cl}_2$  (3 mL) was added  $\text{BF}_3 \cdot \text{OEt}_2$  (7.4  $\mu\text{L}$ , 0.061 mmol, 0.2 equiv) at 0 °C and stirred at the same temperature under inert atmosphere. After completing of the starting material, the reaction was quenched with  $\text{H}_2\text{O}$  or saturated  $\text{NaHCO}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with aq  $\text{NaCl}$ , dried over  $\text{Na}_2\text{SO}_4$ , filtered, and

concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/ hexanes) to give the desired product **3**.

**6,8-Dimethoxy-4,5,5-trimethyl-3-phenyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3a):**

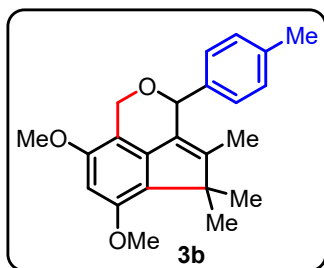


**Yield:** 92 mg, (89%); colorless oil;  $R_f = 0.5$  (15% EtOAc:hexanes);  $^1\text{H}$

**NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.37 – 7.28 (m, 5H), 6.21 (s, 1H), 5.70 (s, 1H), 4.68 (d,  $J = 14.6$  Hz, 1H), 4.50 (d,  $J = 14.6$  Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.54 (d,  $J = 1.0$  Hz, 3H), 1.36 (s, 3H), 1.33 (s, 3H);  $^{13}\text{C}$

**NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  154.9, 154.4, 147.6, 140.2, 138.9, 128.5, 128.4, 128.1, 128.1, 109.9, 91.9, 75.5, 59.3, 55.7, 55.5, 52.0, 22.1, 21.5, 9.6; **IR (Neat):**  $\nu_{\text{max}}$  2956, 2926, 2852, 1727, 1606, 1502, 1451, 1435, 1332, 1284, 1210, 1139, 1084, 1031, 1008, 699; **HRMS (ESI):** calcd for  $\text{C}_{22}\text{H}_{25}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  337.1798, found 337.1801.

**6,8-Dimethoxy-4,5,5-trimethyl-3-(p-tolyl)-3,5-dihydro-1H-cyclopenta[de]isochromene (3b):**

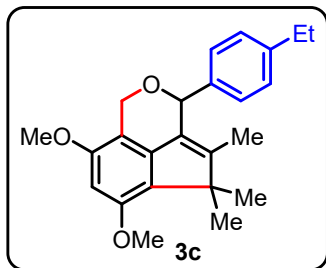


**Yield:** 92 mg, (89%); colorless solide (m. p. = 148 – 150 °C);  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H}$  **NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.22 (d,  $J = 8.0$  Hz, 2H), 7.13 (d,  $J = 8.0$  Hz, 2H), 6.20 (s, 1H), 5.67 (s, 1H), 4.66 (d,  $J = 14.6$  Hz, 1H), 4.47 (d,  $J = 14.6$  Hz, 1H), 3.87 (s, 3H),

3.79 (s, 3H), 2.34 (s, 3H), 1.55 (d,  $J = 0.9$  Hz, 3H), 1.35 (s, 3H), 1.32 (s, 3H);  $^{13}\text{C}$  **NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  154.9, 154.4, 147.4, 140.3, 137.8, 135.8, 129.1, 128.3, 128.3, 128.2, 110.0, 91.9, 75.3, 59.0, 55.7, 55.5, 51.9, 22.1, 21.5, 21.2, 9.6; **IR (Neat):**  $\nu_{\text{max}}$  2934, 2839, 1718, 1599, 1493, 1451, 1336, 1289, 1208, 1153, 1119, 1019, 748, 698; **HRMS (ESI):** calcd for  $\text{C}_{23}\text{H}_{27}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  351.1954, found 351.1941.

**6,8-Dimethoxy-4,5,5-trimethyl-3-(p-tolyl)-3,5-dihydro-1H-cyclopenta[de]isochromene (3c):**

**Yield:** 101 mg, (87%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (500 MHz,



$\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 8.1$  Hz, 2H), 7.16 (d,  $J = 8.1$  Hz, 2H), 6.20 (s, 1H), 5.68 (s, 1H), 4.66 (d,  $J = 14.6$  Hz, 1H), 4.47 (d,  $J = 14.6$  Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 2.63 (q,  $J = 7.6$  Hz, 2H), 1.56 (d,  $J = 0.9$  Hz, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.22 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$

**NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 172.5, 154.9, 154.4, 147.4, 144.1, 128.4, 128.3, 128.2, 127.9,

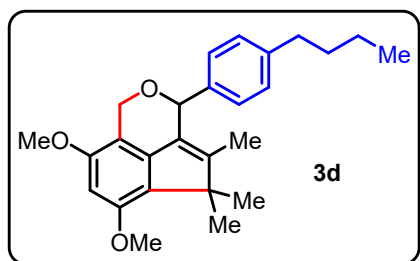
110.0, 91.9, 75.2, 59.0, 55.7, 55.5, 51.9, 28.6, 22.2, 21.5, 15.5, 9.7; **IR** (Neat):  $\nu_{\text{max}}$  2959, 2925,

2853, 1726, 1608, 1503, 1458, 1435, 1342, 1284, 1210, 1135, 1082, 1031, 1008, 822, 799;

**HRMS** (ESI): calcd for  $\text{C}_{24}\text{H}_{29}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  365.2111, found 365.2118.

**3-(4-Butylphenyl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3d):**

**Yield:** 119 mg, (89%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (500 MHz,



$\text{CDCl}_3$ )  $\delta$  7.24 (d,  $J = 8.0$  Hz, 2H), 7.14 (d,  $J = 8.0$  Hz, 2H), 6.20 (s, 1H), 5.67 (s, 1H), 4.66 (d,  $J = 14.5$  Hz, 1H), 4.48 (d,  $J = 14.5$  Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 2.62 – 2.55 (m, 2H), 2.14 (s, 1H), 1.65 – 1.56 (m, 3H), 1.55 (d,  $J = 0.8$  Hz,

3H), 1.35 (s, 3H), 1.32 (s, 3H), 0.91 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  **NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9,

154.4, 147.4, 142.8, 140.3, 136.0, 129.2, 128.8, 128.5, 128.3, 110.0, 91.9, 75.3, 59.1, 55.7, 55.5,

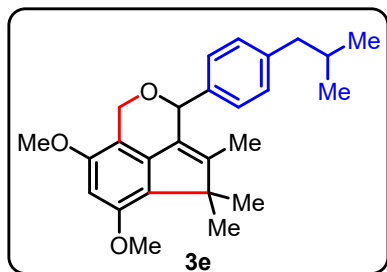
51.9, 50.7, 35.4, 33.6, 22.3, 22.2, 21.5, 13.9; **IR** (Neat):  $\nu_{\text{max}}$  2956, 2927, 2856, 1715, 1608,

1503, 1464, 1435, 1342, 1283, 1210, 1135, 1082, 1031, 1008, 799; **HRMS** (ESI): calcd for

$\text{C}_{26}\text{H}_{33}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  393.2424, found 393.2416.

**3-(4-Isobutylphenyl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3e):**

**Yield:** 93 mg, (82%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (d,  $J = 8.1$  Hz, 2H), 7.10 (d,  $J = 8.1$  Hz, 2H), 6.21 (s, 1H), 5.66 (s, 1H), 4.67 (d,  $J = 14.5$

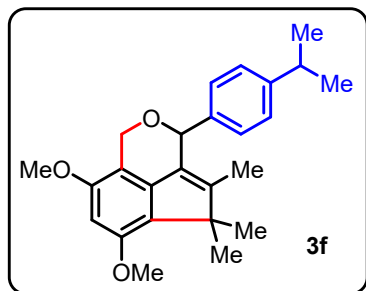


Hz, 1H), 4.50 (d,  $J = 14.5$  Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 2.46 (d,  $J = 7.2$  Hz, 2H), 1.89 – 1.79 (m, 1H), 1.53 (d,  $J = 1.0$  Hz, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 0.88 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 154.4, 147.5, 141.6, 140.4,

136.1, 129.2, 128.4, 128.2, 128.1, 110.0, 91.9, 75.4, 59.2, 55.7, 55.5, 51.9, 45.1, 30.2, 22.3, 22.1, 21.5, 9.6; **IR** (Neat):  $\nu_{\text{max}}$  2955, 2924, 2852, 1727, 1608, 1502, 1461, 1435, 1364, 1342, 1328, 1283, 1209, 1137, 1082, 1032, 1008, 795; **HRMS** (ESI): calcd for  $\text{C}_{26}\text{H}_{33}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  393.2424, found 393.2421.

**3-(4-Isopropylphenyl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3f):**

**Yield:** 92 mg, (81%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

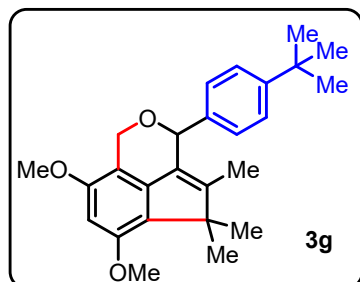


$\delta$  7.25 (d,  $J = 8.1$  Hz, 2H), 7.18 (d,  $J = 8.1$  Hz, 2H), 6.20 (s, 1H), 5.69 (s, 1H), 4.66 (d,  $J = 14.6$  Hz, 1H), 4.47 (d,  $J = 14.6$  Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 2.93 – 2.84 (m, 1H), 1.58 (d,  $J = 0.7$  Hz, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.23 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$

**NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 154.4, 148.7, 147.4, 140.3, 136.1, 128.3, 126.5, 110.5, 110.0, 91.9, 87.7, 75.2, 58.9, 55.7, 55.5, 51.9, 33.8, 24.0, 23.9, 22.2, 21.5, 9.7; **IR** (Neat):  $\nu_{\text{max}}$  2958, 2924, 2853, 1727, 1608, 1502, 1461, 1342, 1283, 1209, 1134, 1081, 1031, 821; **HRMS** (ESI): calcd for  $\text{C}_{25}\text{H}_{31}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  379.2267, found 379.2278.

**3-(4-(tert-Butyl)phenyl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3g):**

**Yield:** 88 mg, (85%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )

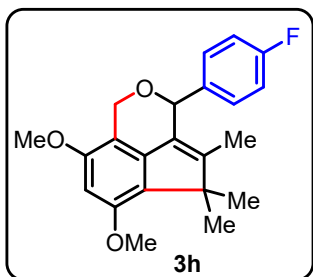


$\delta$  7.34 (d,  $J = 8.1$  Hz, 2H), 7.26 (d,  $J = 8.1$  Hz, 2H), 6.20 (s, 1H), 5.70 (s, 1H), 4.66 (d,  $J = 14.5$  Hz, 1H), 4.46 (d,  $J = 14.5$  Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 1.59 (d,  $J = 0.9$  Hz, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.30 (s, 9H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9,

154.4, 150.9, 147.4, 140.3, 135.6, 128.2, 128.0, 125.4, 110.0, 91.9, 75.0, 58.8, 55.7, 55.5, 51.9, 34.5, 31.3, 29.7, 22.2, 21.5, 9.7; **IR** (Neat):  $\nu_{\text{max}}$  2957, 2923, 2853, 1730, 1608, 1503, 1461, 1435, 1363, 1343, 1284, 1210, 1135, 1081, 1032; **HRMS** (ESI): calcd for  $\text{C}_{26}\text{H}_{33}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  393.2424, found 393.2415.

**3-(4-Fluorophenyl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene(3h):**

**Yield:** 115 mg, (87%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (400 MHz,

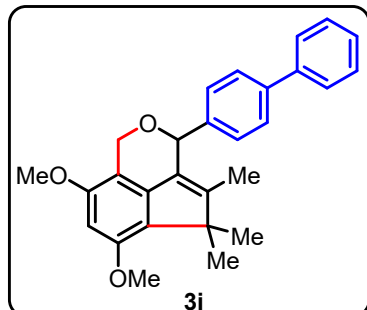


$\text{CDCl}_3$ )  $\delta$  7.32 (dd,  $J = 8.7, 5.5$  Hz, 2H), 7.02 (t,  $J = 8.7$  Hz, 2H), 6.21 (s, 1H), 5.66 (s, 1H), 4.67 (d,  $J = 14.6$  Hz, 1H), 4.48 (d,  $J = 14.6$  Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 1.53 (d,  $J = 1.0$  Hz, 3H), 1.35 (s, 3H), 1.32 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 161.6, 155.0,

154.5, 147.7, 140.0, 134.8, 130.1(d,  $J = 8.1$  Hz), 128.1(d,  $J = 4.6$  Hz), 115.4, 115.2, 109.8, 91.9, 74.9, 59.3, 55.7, 55.5, 52.0, 29.7, 22.1, 21.5, 9.6; **IR** (Neat):  $\nu_{\text{max}}$  2955, 2925, 2852, 1731, 1604, 1504, 1461, 1343, 1327, 1284, 1210, 1156, 1142, 1081, 1031, 1009, 828,798; **HRMS** (ESI): calcd for  $\text{C}_{22}\text{H}_{24}\text{FO}_3$  ( $\text{M}+\text{H}$ ) $^+$  355.1704, found 355.1696.

**3-([1,1'-Biphenyl]-4-yl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3i):**

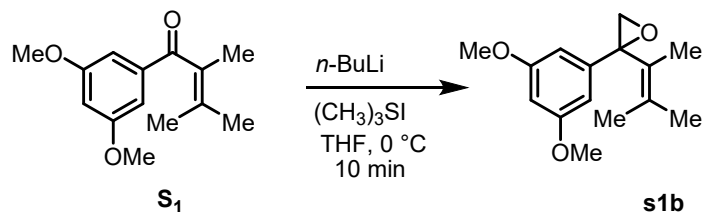
**Yield:** 110 mg, (86%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (400 MHz,



$\text{CDCl}_3$ )  $\delta$  7.60 – 7.53 (m, 4H), 7.46 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 6.22 (s, 1H), 5.75 (s, 1H), 4.70 (d,  $J = 14.6$  Hz, 1H), 4.53 (d,  $J = 14.6$  Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 1.60 (d,  $J = 0.9$  Hz, 3H), 1.38 (s, 3H), 1.34 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  155.0, 154.5, 147.7, 140.9, 140.8, 140.2, 137.9, 128.8, 128.7, 128.2, 128.1, 127.2, 127.1, 109.9, 91.9, 75.1, 59.2, 55.7, 55.5, 52.0, 22.2, 21.5, 9.7; **IR** (Neat):  $\nu_{\text{max}}$  2957, 2924, 2852, 1726, 1605, 1502, 1460, 1434, 1343, 1284, 1209, 1135, 1081, 1031, 1007, 763, 697; **HRMS** (ESI): calcd for  $\text{C}_{28}\text{H}_{29}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  413.2111, found 413.2099.

**General procedure for the Synthesis of 2-(3, 5-dimethoxyphenyl)-2-(3-methylbut-2-en-2-yl)oxirane (s1b)<sup>9f</sup>**

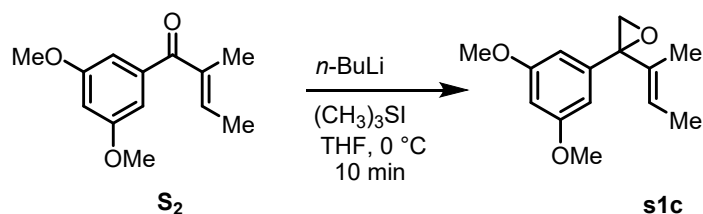


$\text{Me}_3\text{SI}$  (3.48 g, 17.094 mmol, 8.0 equiv) and  $n\text{-BuLi}$  (1.6 M in hexanes, 8.6 mL, 13.888 mmol, 6.5 equiv) were added sequentially to THF (149 mL) at 0 °C, and the resulting pale yellow solution was stirred for 2 min at 0 °C. A solution of  $\text{S}_1$  (500 mg, 2.136 mmol, 1.0 equiv) in THF (43 mL) at 0 °C was then added dropwise via cannulation over 10 min, and the resulting mixture was allowed to stir for an additional 10 min at 0 °C. Upon completion, the reaction contents were quenched by the addition of water (20 mL) and extracted with EtOAc (3  $\times$  10 mL). The



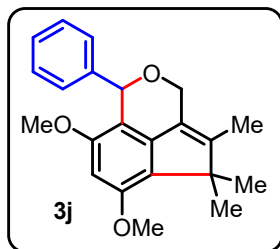
combined organic extracts were then washed with water (10 mL) and brine (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and concentrated. The resultant crude oil (**s1b**) was used in the next step without purification.

### Synthesis of (*E*)-2-(but-2-en-2-yl)-2-(3,5-dimethoxyphenyl)oxirane (**s1c**)<sup>9f</sup>



**s1c** was synthesized following the procedure used for **s1b**. Yield of **s1c** (101mg, 95%); colorless oil from **S<sub>2</sub>** (100mg, 0.4545 mmol);  $R_f = 0.7$  (10% EtOAc:hexanes);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.52 (d,  $J = 5.3$  Hz, 2H), 6.38 (d,  $J = 5.3$  Hz, 1H), 5.74 – 5.57 (m, 1H), 3.78 (s, 6H), 3.21 – 3.19 (m, 1H), 3.02 (d,  $J = 6.0$  Hz, 0.37H), 2.88 (d,  $J = 6.0$  Hz, 0.67H), 1.78 – 1.63 (m, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 160.7, 141.9, 141.4, 133.5, 133.3, 124.9, 124.8, 104.5, 103.6, 99.6, 99.5, 64.6, 59.7, 59.2, 56.3, 55.3, 20.1, 14.5, 13.3, 13.1; IR(Neat):  $\nu_{\text{max}}$  2929, 1598, 1461, 145, 1355, 1307, 1213, 1129, 1018, 935, 804; HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_3(\text{M}+\text{H})^+$  235.1328, found 235.1314.

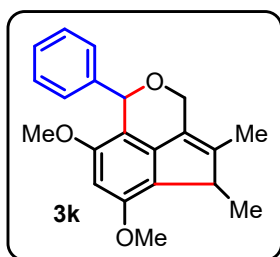
### 6,8-Dimethoxy-4,5,5-trimethyl-1-phenyl-3,5-dihydro-1H-cyclopenta[de]isochromene (**3j**):



**Yield:** 125 mg, (92%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.19 (m, 5H), 6.23 (s, 1H), 6.00 (s, 1H), 4.49 (d,  $J = 14.7$  Hz, 1H), 4.23 (d,  $J = 14.7$  Hz, 1H), 3.89 (s, 3H), 3.72 (s, 3H), 1.75 (d,  $J = 0.9$  Hz, 3H), 1.31 (s, 3H), 1.31 (s, 3H);  $^{13}\text{C}$

**NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  155.7, 154.8, 145.1, 140.3, 139.9, 128.8, 128.3, 128.1, 127.6, 126.7, 110.7, 91.7, 72.5, 58.8, 55.8, 55.4, 51.8, 22.0, 21.4, 9.5; **IR** (Neat):  $\nu_{max}$  2957, 2926, 2839, 1653, 1607, 1493, 1450, 1435, 1358, 1334, 1283, 1210, 1139, 1083, 1005, 860, 801, 699; **HRMS** (ESI): calcd for C<sub>22</sub>H<sub>25</sub>O<sub>3</sub> (M+H)<sup>+</sup> 337.1798, found 337.1799.

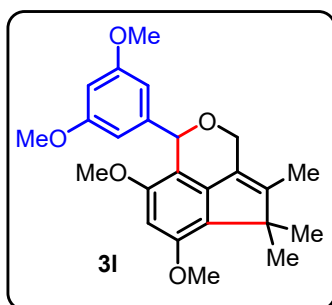
**6,8-Dimethoxy-4,5-dimethyl-1-phenyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3k):**



**Yield:** 122 mg, (88%); colorless oil; (*dr* 1:0.05, based on <sup>1</sup>H NMR);  $R_f$  = 0.5 (15% EtOAc/hexane); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.32 – 7.22 (m, 5H), 6.26 (s, 1H), 6.02 (s, 1H), 4.51 (d,  $J$  = 14.7 Hz, 1H), 4.23 (d,  $J$  = 14.7Hz, 1H), 3.91 (s, 3H), 3.73 (s, 3H), 3.40 (tt,  $J$  = 7.5, 3.7 Hz, 1H), 1.89 – 1.85 (m, 3H), 1.34 (d,  $J$  = 7.5 Hz, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  155.8, 155.0, 141.9, 140.6, 139.8, 128.8, 128.1, 127.6, 123.9, 110.9, 92.0, 72.4, 58.8, 55.8, 55.6, 46.9, 14.1, 11.9; **IR** (Neat):  $\nu_{max}$  2931, 2838, 1723, 1605, 1498, 1460, 1343, 1290, 1209, 1158, 1120, 1077, 747, 639; **HRMS** (ESI): calcd for C<sub>21</sub>H<sub>23</sub>O<sub>3</sub> (M+H)<sup>+</sup> 323.1641, found 323.1641.

**1-(3,5-Dimethoxyphenyl)-6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene (3l):**

**Yield:** 142 mg, (89%); colorless oil;  $R_f$  = 0.5 (15% EtOAc/hexane); **<sup>1</sup>H NMR (400 MHz,**

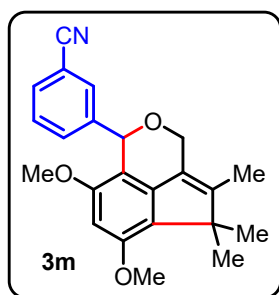


**CDCl<sub>3</sub>)**  $\delta$  6.43 (dd,  $J$  = 2.3, 0.5 Hz, 2H), 6.37 (t,  $J$  = 2.3 Hz, 1H), 6.22 (s, 1H), 5.93 (s, 1H), 4.49 (d,  $J$  = 14.7Hz, 1H), 4.27 (d,  $J$  = 14.7 Hz, 1H), 3.89 (s, 3H), 3.75 (s, 6H), 3.74 (s, 3H), 1.74 (d,  $J$  = 1.0 Hz, 3H), 1.30 (s, 3H), 1.29 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  160.5, 155.7, 154.8, 145.0, 142.5, 140.1, 128.3, 126.7, 110.5, 107.0, 99.4, 91.9, 72.3, 58.9, 55.8,

55.4, 55.3, 51.8, 21.9, 21.4, 9.5; **IR** (Neat):  $\nu_{max}$  2956, 2924, 2840, 1604, 1498, 1460, 1429, 1355, 1283, 1205, 1154, 1067, 1023, 836; **HRMS** (ESI): calcd for  $C_{24}H_{29}O_3$  (M+H)<sup>+</sup> 397.2009, found 397.2012.

**3-(6,8-Dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromen-1-yl)benzotrile (3m):**

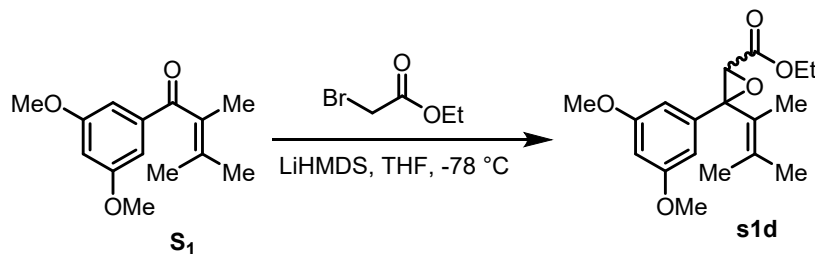
**Yield:** 131 mg, (90%); colorless oil;  $R_f = 0.5$  (15% EtOAc/hexane); **<sup>1</sup>H NMR (500 MHz,**



**CDCl<sub>3</sub>)**  $\delta$  7.63 – 7.54 (m, 2H), 7.49 – 7.47 (m, 1H), 7.43 (t,  $J = 7.8$  Hz, 1H), 6.24 (s, 1H), 5.95 (s, 1H), 4.53 (d,  $J = 14.7$  Hz, 1H), 4.18 (d,  $J = 14.7$  Hz, 1H), 3.91 (s, 3H), 3.73 (s, 3H), 1.76 (d,  $J = 0.8$  Hz, 3H), 1.31 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  155.6, 155.2, 145.9,

141.8, 140.1, 133.3, 132.3, 131.3, 128.9, 128.4, 125.9, 119.1, 112.1, 109.1, 91.7, 71.7, 59.3, 55.6, 55.4, 51.9, 21.8, 21.4, 9.6; **IR** (Neat):  $\nu_{max}$  2958, 2925, 2851, 2228, 1605, 1497, 1460, 1435, 1357, 1283, 1210, 1137, 1084, 1026, 803; **HRMS** (ESI): calcd for  $C_{23}H_{24}O_3N$ (M+H)<sup>+</sup> 362.1750, found 362.1738.

**General procedure for the synthesis of divinyl epoxyester from arylvinyl ketone:<sup>9f</sup>**

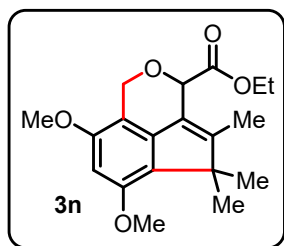


A solution of ethyl bromoacetate (0.63 mL, 5.470 mmol, 4.0 equiv) in dry THF (7 mL) was cooled to -78 °C under N<sub>2</sub> atmosphere before drop-wise addition of LiHMDS (5.47 mL, 5.470

mmol, 1M solution in THF, 4.0 equiv). After 30 min, **S**<sub>1</sub> (320 mg, 1.367 mmol, 1.0 equiv) in dry THF (4 mL) was added drop-wise over 5 min and stirred for 15-20 min at -78 °C. The temperature was raised to rt and stirred for 15 min. After completion of the starting material, the reaction was quenched with H<sub>2</sub>O and extracted with EtOAc. The organic layer was washed with aq NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified using basic Al<sub>2</sub>O<sub>3</sub> flash column chromatography (EtOAc/hexane) to give **s1d** as (420 mg, 96%) a colorless oil; *R*<sub>f</sub> = 0.6 (15% EtOAc/hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.59 (d, *J* = 2.3 Hz, 2H), 6.48 (d, *J* = 2.3 Hz, 0.47H), 6.41 (t, *J* = 2.3 Hz, 0.27H), 6.37 (t, *J* = 2.3 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 1H), 3.78 (s, 1.5H), 3.77 (s, 6H), 2.00 (s, 3H), 1.75 (s, 0.67H), 1.73 (s, 0.72H), 1.72 (s, 3H), 1.68 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 0.79H), 1.02 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.4, 166.7, 161.0, 160.3, 137.8, 130.5, 126.8, 105.2, 104.5, 99.9, 67.2, 64.0, 61.1, 61.0, 55.3, 22.1, 22.0, 20.2, 20.0, 14.9, 14.1, 13.9; IR (Neat): *v*<sub>max</sub> 2993, 2924, 2857, 2839, 1753, 1727, 1594, 1456, 1426, 1375, 1345, 1333, 1299, 1253, 1201, 1152, 1063, 1028, 848, 694; HRMS (ESI): calcd for C<sub>18</sub>H<sub>25</sub>O<sub>5</sub>(M+H)<sup>+</sup> 321.1696, found 321.1690.

**Ethyl6,8-dimethoxy-4,5,5-trimethyl-3,5-dihydro-1H-cyclopenta[de]isochromene-3-carboxylate (3n):**

**Yield:** 96 mg, (92%); colorless oil; *R*<sub>f</sub> = 0.5 (15% EtOAc/hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



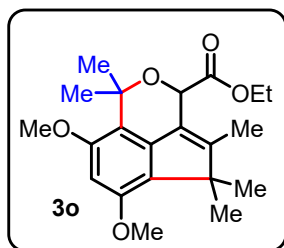
δ 6.20 (s, 1H), 5.31 (s, 1H), 5.14 (d, *J* = 14.6 Hz, 1H), 4.84 (d, *J* = 14.6 Hz, 1H), 4.19 (qd, *J* = 7.1, 1.1 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 1.91 (d, *J* = 0.8 Hz, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.7, 154.9, 154.4, 149.5, 137.9,

127.8, 123.6, 108.6, 92.0, 71.6, 61.0, 60.2, 55.7, 55.5, 52.1, 21.7, 21.4, 14.2, 10.0; IR (Neat):

$\nu_{max}$  2959, 2927, 2866, 1744, 1649, 1608, 1503, 1452, 1435, 1365, 1347, 1281, 1191, 1091, 1034, 1008, 897, 801; **HRMS** (ESI): calcd for  $C_{19}H_{25}O_5$  (M+H)<sup>+</sup> 333.1696, found 333.1694.

**Ethyl 6,8-dimethoxy-1,1,4,5,5-pentamethyl-3,5-dihydro-1H-cyclopenta[de]isochromene-3-carboxylate (3o):**

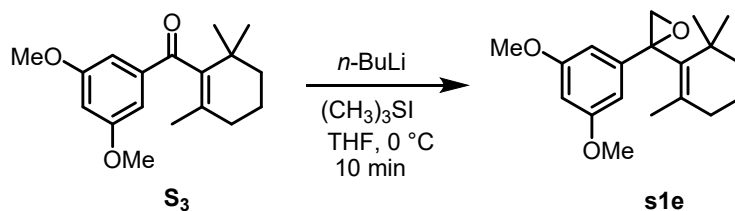
**Yield:** 96 mg, (85%); colorless oil;  $R_f$  = 0.5 (15% EtOAc/hexane); **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



$\delta$  6.21 (s, 1H), 5.25 (d,  $J$  = 1.6 Hz, 1H), 4.39 – 4.20 (m, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 1.77 (d,  $J$  = 1.5 Hz, 3H), 1.68 (s, 3H), 1.57 (s, 3H), 1.33 (t,  $J$  = 7.1 Hz, 3H), 1.29 (s, 3H), 1.28 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  170.8, 155.1, 154.1, 146.8, 138.9, 128.1, 124.5, 117.0,

75.4, 70.1, 61.3, 55.7, 55.3, 51.9, 27.8, 26.3, 21.5, 21.4, 14.1, 9.4; **IR** (Neat):  $\nu_{max}$  2962, 2926, 2854, 1754, 1734, 1602, 1491, 1461, 1355, 1307, 1270, 1213, 1177, 1129, 1089, 1018, 935, 804; **HRMS** (ESI): calcd for  $C_{18}H_{23}O_4$  (M-C<sub>3</sub>H<sub>5</sub>O)<sup>+</sup> 303.1590, found 303.1590.

**General procedure for the Synthesis of 2-(3,5-dimethoxyphenyl)-2-(2,6,6-trimethylcyclohex-1-en-1-yl)oxirane (s1e)**

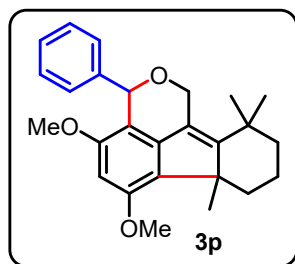


**s1e** was synthesized following the procedure used for **s1b**. Yield of **s1e** (1.04 g, 99%); white solid (m. p. = 90 – 92 °C) from **S3** (1 g, 3.4722 mmol);  $R_f$  = 0.7 (10% EtOAc:hexanes); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  6.47 (d,  $J$  = 2.3 Hz, 2H), 6.35 (t,  $J$  = 2.3 Hz, 1H), 3.77 (s, 6H), 3.00 (d,  $J$  = 6.6

Hz, 1H), 2.86 (d,  $J = 6.6$  Hz, 1H), 2.17 – 1.99 (m, 2H), 1.78 (m, 1H), 1.69 (s, 3H), 1.43 (s, 3H), 1.15 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 144.4, 135.8, 134.7, 133.0, 125.5, 103.6, 98.8, 60.2, 59.7, 55.3, 40.5, 34.8, 31.9, 30.3, 29.2, 29.0, 21.2, 18.9; IR (Neat):  $\nu_{\text{max}}$  2930, 1595, 1458, 1425, 1343, 1200, 1151, 1059, 839, 700; HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{27}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  303.1954, found 303.1946.

**4,6-Dimethoxy-6b,10,10-trimethyl-3-phenyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3p):**

**Yield:** 126 mg, (98%); white solide (m. p. = 112 – 114 °C); (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.22 (m, 5H), 6.26 (s, 1H), 6.00 (s,



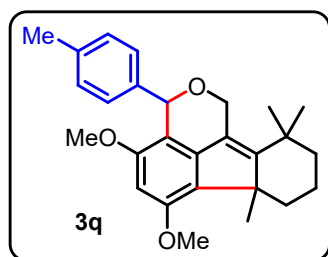
1H), 4.92 (d,  $J = 15$  Hz, 0.36H), 4.76 (d,  $J = 15$  Hz, 0.66H), 4.43 (d,  $J = 15$  Hz, 0.366H), 4.35 (d,  $J = 15$  Hz, 0.66H), 3.87 (s, 3H), 3.73 (s, 3H), 2.47 (d,  $J = 12.8$  Hz, 1H), 1.90 (q,  $J = 13.7$  Hz, 1H), 1.64 – 1.53 (m, 2H), 1.46 (s, 3H), 1.26 (s, 3H), 1.18 (s, 1H), 1.15 (s, 3H), 1.08 (m, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 155.3, 154.2, 153.9, 153.6, 140.3, 139.8, 130.2, 128.8, 128.7, 128.1, 127.6, 125.4, 125.2, 111.9, 111.2, 92.3, 92.0, 72.4, 71.9, 61.2, 60.6, 55.9, 55.8, 55.4, 53.1, 52.8, 43.3, 43.0, 37.1, 36.9, 35.9, 35.4, 32.9, 32.3, 26.2, 25.9, 21.8, 21.2, 19.4; IR (Neat):  $\nu_{\text{max}}$  2993, 2929, 2846, 1606, 1495, 1454, 1208, 1047, 755; HRMS (ESI): calcd for  $\text{C}_{26}\text{H}_{31}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  391.2267, found 391.2270.

**4,6-Dimethoxy-6b,10,10-trimethyl-3-(p-tolyl)-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3q):**

**Yield:** 130 mg, (97%); colorless oil; (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 – 7.10 (m, 4H), 6.25 (s, 1H), 5.97 (s, 1H), 4.91 (d,  $J = 15$

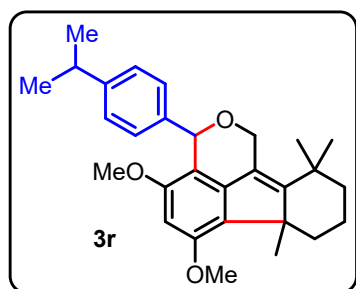
Hz, 0.33H), 4.75 (d,  $J = 15$  Hz, 0.66H), 4.37 (t,  $J = 15$  Hz, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 2.47 (d,  $J = 13.2$  Hz, 1H), 2.33 (s, 3H), 1.89 (m, 1H), 1.55 (m, 2H), 1.45 (s, 3H), 1.25 (s, 3H), 1.17 (s,



1H), 1.14 (s, 3H), 1.07 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 155.3, 154.1, 153.8, 153.5, 139.9, 139.8, 137.2, 136.9, 130.2, 130.2, 128.8, 128.8, 128.7, 125.5, 125.3, 112.1, 111.4, 92.2, 92.0, 71.9, 71.6, 60.8, 60.4, 55.9, 55.8, 55.4, 53.1, 52.8, 43.3, 43.0, 37.1,

36.8, 35.9, 35.3, 32.9, 32.3, 26.2, 25.9, 21.8, 21.2, 19.4; IR (Neat):  $\nu_{\text{max}}$  2926, 2842, 1604, 1499, 1459, 1356, 1329, 1208, 1124, 1089, 1044, 1015, 806, 757; HRMS (ESI): calcd for  $\text{C}_{27}\text{H}_{33}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  405.2424, found 405.2423.

### 3-(4-Isopropylphenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3r):



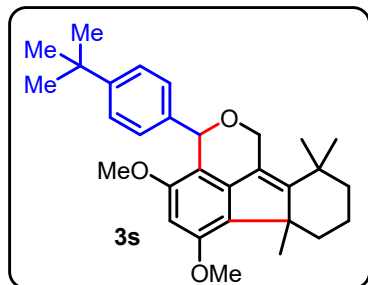
**Yield:** 137 mg, (96%); colorless oil; (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 – 7.12 (m, 4H), 6.25 (s, 1H), 5.97 (s, 1H), 4.91 (d,  $J = 15.0$  Hz, 0.34H), 4.75 (d,  $J = 15.0$  Hz, 0.66H), 4.41 (t,  $J = 15.0$  Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 2.89 (m, 1H), 2.47 (d,  $J = 13.0$  Hz, 1H),

1.90 (m, 1H), 1.55 (m, 2H), 1.45 (s, 3H), 1.26 (s, 3H), 1.24 (d,  $J = 6.9$  Hz, 6H), 1.18 (s, 1H), 1.15 (s, 3H), 1.13 – 1.04 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 155.3, 154.1, 153.7, 153.5, 148.1, 148.0, 139.9, 139.8, 137.5, 137.2, 130.2, 130.2, 128.7, 128.6, 126.2, 125.6, 125.3, 112.2, 111.5, 92.2, 92.0, 71.9, 71.7, 60.9, 60.5, 55.9, 55.8, 55.4, 53.1, 52.8, 43.3, 43.1, 37.1, 36.8, 35.9, 35.4, 33.8, 32.9, 32.4, 26.2, 25.9, 24.0, 24.0, 21.8, 21.2, 19.4; IR (Neat):  $\nu_{\text{max}}$  2928, 2842, 1605, 1498, 1460, 1356, 1329, 1280, 1207, 1089, 1047, 1014, 909, 812, 732; HRMS (ESI): calcd for  $\text{C}_{29}\text{H}_{37}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  433.2737, found 433.2712.

**3-(4-(tert-Butyl)phenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3s):**

**Yield:** 144mg, (97%); colorless oil; (*dr* 3:2, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);

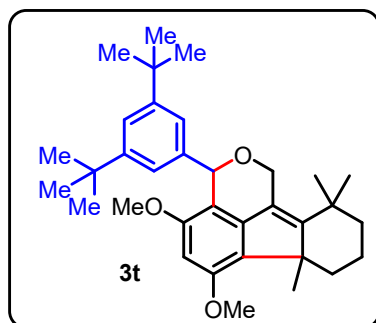
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.32 (m, 2H), 7.22 – 7.15 (m, 2H), 6.25 (s, 1H), 5.95 (s, 1H), 4.92 (d,  $J = 15.0$  Hz, 0.41H), 4.76 (d,  $J = 15.0$  Hz, 0.58H), 4.41 (d,  $J = 13$  Hz, 0.51H), 4.37



(d,  $J = 13$  Hz, 0.47H), 3.87 (s, 3H), 3.74 (s, 3H), 2.46 (d,  $J = 12.9$  Hz, 1H), 1.90 (m, 1H), 1.56 (m, 2H), 1.45 (s, 3H), 1.31 (s, 9H), 1.26 (s, 3H), 1.18 (s, 1H), 1.15 (s, 3H), 1.09 -1.07 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 155.3, 154.1, 153.7, 153.4,

150.2, 150.2, 139.8, 139.8, 137.1, 136.8, 130.2, 130.1, 128.3, 128.3, 125.5, 125.3, 125.0, 112.1, 111.5, 92.2, 92.0, 71.8, 71.5, 60.8, 60.5, 55.9, 55.8, 55.4, 53.0, 52.8, 43.3, 43.0, 37.1, 36.8, 35.9, 35.3, 34.5, 32.9, 32.3, 31.4, 26.2, 25.9, 21.8, 21.2, 19.3; IR (Neat):  $\nu_{\text{max}}$  2931, 2868, 1605, 1498, 1461, 1358, 1329, 1207, 1124, 1089, 1044, 1015, 909, 810, 754, 732; HRMS (ESI): calcd for  $\text{C}_{30}\text{H}_{39}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  447.2893, found 447.2880.

**3-(3,5-di-tert-Butylphenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3t):**



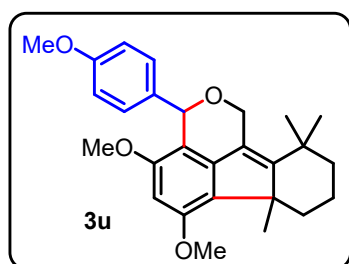
**Yield:** 158 mg, (95%); colorless oil; (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (m, 1H), 7.09 (dd,  $J = 18.1, 1.7$  Hz, 2H), 6.25 (s, 1H), 6.00 (s, 1H), 4.94 (d,  $J = 15.0$  Hz, 0.34H), 4.77 (d,  $J = 15.0$  Hz, 0.67H), 4.45 (d,  $J = 9.8$  Hz, 0.51H), 4.42 (d,  $J = 9.8$  Hz, 0.46H),

3.87 (s, 3H), 3.73 (s, 3H), 2.48 (d,  $J = 12.9$  Hz, 1H), 1.96 – 1.84 (m, 1H), 1.65 – 1.53 (m, 2H), 1.47 (s, 3H), 1.37 (s, 1H), 1.27 (s, 21H), 1.17 (s, 3H), 1.03 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,



**CDCl<sub>3</sub>**)  $\delta$  155.2, 155.1, 154.0, 153.5, 153.3, 150.1, 150.1, 139.8, 139.7, 138.9, 138.5, 130.2, 130.1, 125.6, 125.3, 122.9, 122.8, 121.3, 121.3, 112.6, 112.0, 92.4, 92.1, 72.5, 72.2, 61.0, 60.6, 55.9, 55.7, 55.4, 55.4, 53.0, 52.7, 43.5, 42.9, 37.0, 36.9, 36.3, 35.1, 34.8, 32.9, 32.3, 31.5, 26.2, 25.8, 22.0, 20.9, 19.4; **IR** (Neat):  $\nu_{max}$  2955, 2869, 1600, 1496, 1462, 1359, 1328, 1244, 1206, 1089, 1013, 874, 75; **HRMS** (ESI): calcd for C<sub>34</sub>H<sub>47</sub>O<sub>3</sub> (M+H)<sup>+</sup> 503.3525, found 503.3519.

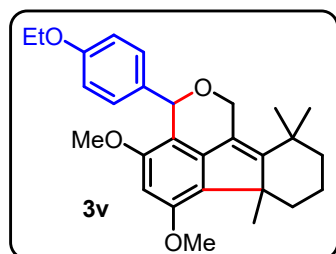
**4,6-Dimethoxy-3-(4-methoxyphenyl)-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3u):**



**Yield:** 132mg, (95%); colorless oil; (*dr* 2:1, based on <sup>1</sup>H NMR); *R<sub>f</sub>* = 0.5 (10% EtOAc/hexane); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.18 (d, *J* = 8.6 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.84 (m, 2H), 6.25 (s, 1H), 5.96 (s, 1H), 4.90 (d, *J* = 15.0 Hz, 0.31H), 4.74 (d, *J* = 15.0 Hz, 0.64H), 4.40 (d, *J* = 15.0 Hz, 0.32H), 4.35 (d, *J* = 15.0 Hz, 0.65H), 3.87 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 2.47 (d, *J* = 13.0 Hz, 1H), 1.90 (m, 1H), 1.63 – 1.52 (m, 2H), 1.45 (s, 3H), 1.26 (s, 3H), 1.18 (s, 1H), 1.15 (s, 3H), 1.08 (m, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  159.0, 155.3, 155.2, 154.1, 153.8, 153.5, 139.9, 139.8, 132.4, 132.0, 130.2, 130.1, 130.0, 129.9, 125.5, 125.2, 113.4, 112.2, 111.5, 92.3, 92.0, 71.8, 71.4, 60.7, 60.2, 55.9, 55.8, 55.4, 55.2, 53.0, 52.8, 43.3, 43.0, 37.1, 36.8, 35.9, 35.3, 32.9, 32.3, 26.2, 25.9, 21.8, 21.2, 19.3; **IR** (Neat):  $\nu_{max}$  2928, 2840, 1607, 1504, 1460, 1330, 1244, 1208, 1173, 1089, 1037, 909, 816, 756, 734; **HRMS** (ESI): calcd for C<sub>27</sub>H<sub>33</sub>O<sub>4</sub>(M+H)<sup>+</sup> 421.2373, found 421.2365.

**3-(4-Ethoxyphenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3v):**

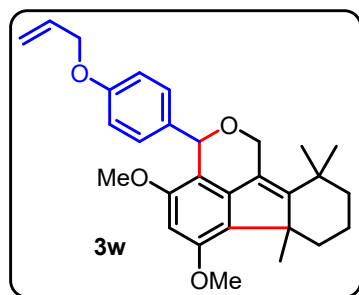
**Yield:**138 mg, (96%); colorless oil; (*dr* 1.7:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (d,  $J = 8.5$  Hz, 2H), 6.83 (d,  $J = 8.5$  Hz, 2H), 6.25 (s, 1H), 5.95 (s, 1H), 4.89 (d,  $J = 15.0$  Hz, 0.36H), 4.73 (d,  $J = 15.0$  Hz, 0.64H), 4.41 (d,  $J = 15.0$  Hz,



0.35H), 4.35 (d,  $J = 15.0$ Hz, 0.65H), 4.01 (q,  $J = 7.0$  Hz, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 2.47 (d,  $J = 13.0$  Hz, 1H), 1.90 (m, 1H), 1.57 (m, 2H), 1.45 (s, 3H), 1.40 (t,  $J = 7.0$  Hz, 3H), 1.26 (s, 3H), 1.18 (s, 1H), 1.15 (s, 3H), 1.14 – 1.05 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 155.2, 154.0, 153.7, 139.8, 132.2, 131.8, 130.1, 130.0, 129.9, 125.4, 125.2, 113.9, 92.2, 92.0, 71.8, 71.4, 63.3, 60.7, 60.2, 55.9, 55.8, 55.3, 53.0, 52.8, 43.3, 43.0, 37.1, 36.8, 35.9, 35.3, 32.9, 32.3, 29.7, 26.1, 25.9, 21.8, 21.2, 19.3, 14.9; IR (Neat):  $\nu_{\text{max}}$ 2922, 2849, 1607, 1504, 1462, 1330, 1242, 1210, 1172, 1046, 910, 810, 755,733; HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{35}\text{O}_4(\text{M}+\text{H})^+$  435.2529, found 435.2524.

**Yield:**138 mg, (93%); colorless oil; (*dr*1.8:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 – 7.11 (m, 2H), 6.90 – 6.83 (m, 2H), 6.24 (s, 1H), 6.05 (m, 1H), 5.95 (s, 1H), 5.40 (dd,  $J = 17.3, 1.6$  Hz, 1H), 5.27 (dd,  $J = 10.5, 1.4$  Hz, 1H), 4.89 (d,  $J = 15.0$  Hz, 0.35H), 4.74 (d,  $J = 15.0$  Hz, 0.65H), 4.52 (d,  $J = 5.3$  Hz, 2H), 4.41 (d,  $J = 15.0$  Hz, 0.35H), 4.35 (d,  $J = 15.0$  Hz, 0.65H), 3.87 (s, 3H), 3.73 (s, 3H), 2.47 (d,  $J = 12.9$  Hz, 1H), 1.90 (m, 1H), 1.56 (m, 2H), 1.45 (s, 3H), 1.26 (s, 3H), 1.19 (m, 1H), 1.15 (s, 3H), 1.08 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 155.3, 155.2, 154.1, 153.8, 153.5, 139.9, 139.8, 133.4, 132.6, 132.2, 130.2, 130.1, 130.0, 129.9, 125.4, 125.2, 113.9, 92.2, 92.0, 71.8, 71.4, 63.3, 60.7, 60.2, 55.9, 55.8, 55.3, 53.0, 52.8, 43.3, 43.0, 37.1, 36.8, 35.9, 35.3, 32.9, 32.3, 29.7, 26.1, 25.9, 21.8, 21.2, 19.3, 14.9; IR (Neat):  $\nu_{\text{max}}$ 2922, 2849, 1607, 1504, 1462, 1330, 1242, 1210, 1172, 1046, 910, 810, 755,733; HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{35}\text{O}_4(\text{M}+\text{H})^+$  435.2529, found 435.2524.

**3-(4-(Allyloxy)phenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3w):**

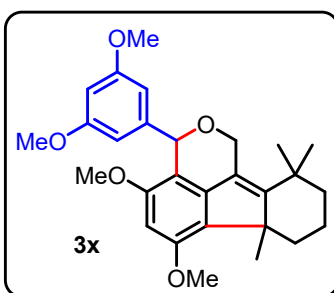


**Yield:**138 mg, (93%); colorless oil; (*dr*1.8:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 – 7.11 (m, 2H), 6.90 – 6.83 (m, 2H), 6.24 (s, 1H), 6.05 (m, 1H), 5.95 (s, 1H), 5.40 (dd,  $J = 17.3, 1.6$  Hz, 1H), 5.27 (dd,  $J = 10.5, 1.4$  Hz, 1H), 4.89 (d,  $J = 15.0$  Hz, 0.35H), 4.74 (d,  $J = 15.0$

Hz, 0.65H), 4.52 (d,  $J = 5.3$  Hz, 2H), 4.41 (d,  $J = 15.0$  Hz, 0.35H), 4.35 (d,  $J = 15.0$  Hz, 0.65H), 3.87 (s, 3H), 3.73 (s, 3H), 2.47 (d,  $J = 12.9$  Hz, 1H), 1.90 (m, 1H), 1.56 (m, 2H), 1.45 (s, 3H), 1.26 (s, 3H), 1.19 (m, 1H), 1.15 (s, 3H), 1.08 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 155.3, 155.2, 154.1, 153.8, 153.5, 139.9, 139.8, 133.4, 132.6, 132.2, 130.2, 130.1, 130.0, 129.9,

125.4, 125.2, 117.6, 114.2, 114.2, 112.1, 111.4, 92.2, 92.0, 71.8, 71.4, 68.8, 60.8, 60.2, 55.9, 55.8, 55.4, 53.0, 52.8, 43.3, 43.0, 37.1, 36.8, 35.9, 35.3, 32.9, 32.3, 26.2, 25.9, 21.8, 21.2, 19.3; **IR** (Neat):  $\nu_{max}$  2926, 2843, 1605, 1502, 1459, 1329, 1237, 1172, 1089, 1014, 915, 805, 732; **HRMS** (ESI): calcd for  $C_{29}H_{35}O_4(M+H)^+$  447.2529, found 447.2505.

**3-(3,5-Dimethoxyphenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3x):**

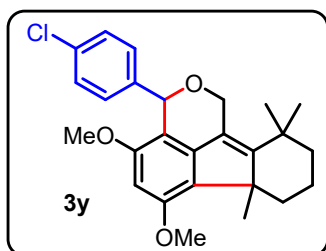


**Yield:** 146 mg, (98%); colorless oil; (*dr* 1.9:1, based on  $^1H$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  6.47 – 6.38 (m, 3H), 6.24 (s, 1H), 5.92 (s, 1H), 4.94(d,  $J = 15$  Hz, 0.37H), 4.77 (d,  $J = 15.0$  Hz, 0.72H), 4.41 (t,  $J = 15.0$  Hz, 1H), 3.86 (s, 3H), 3.76 (s, 6H), 3.73 (s, 3H), 2.45 (d,  $J = 12.8$  Hz, 1H), 1.94 - 1.86 (m, 1H), 1.64 – 1.53 (m, 2H), 1.49 – 1.46 (m, 1H), 1.45 (s, 3H), 1.26 (s, 3H), 1.18 (s, 3H), 1.12 – 1.02 (m, 1H);  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**  $\delta$  155.7, 150.6, 150.5, 149.4, 149.1, 148.9, 137.9, 137.7, 135.0, 134.9, 125.4, 120.5, 120.3, 106.7, 106.1, 102.3, 102.1, 94.7, 94.5, 87.5, 87.3, 67.2, 67.0, 56.3, 56.0, 51.1, 51.0, 50.6, 50.5, 48.3, 48.0, 38.5, 38.27, 32.3, 32.1, 31.1, 30.5, 28.2, 27.5, 21.4, 21.1, 17.0, 16.4, 14.6; **IR** (Neat):  $\nu_{max}$  2926, 2843, 1598, 1459, 1326, 1286, 1201, 1059, 910, 836, 734, 612; **HRMS** (ESI): calcd for  $C_{28}H_{35}O_5(M+H)^+$  451.2479, found 451.2465.

**3-(4-Chlorophenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3y):**

**Yield:** 126 mg, (90%); colorless oil; (*dr* 2.5:1, based on  $^1H$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.30 – 7.26 (m, 2H), 7.19 (dd,  $J = 18.1, 8.4$  Hz,

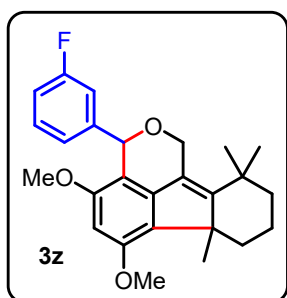
2H), 6.25 (s, 1H), 5.94 (s, 1H), 4.91 (d,  $J = 15.0$  Hz, 0.3H), 4.76 (d,  $J = 15.0$  Hz, 0.7H), 4.42 (d,  $J = 15.0$  Hz, 0.3H), 4.32 (d,  $J = 15.0$  Hz, 0.7H), 3.87 (s, 3H), 3.74 (s, 3H), 2.47 (d,  $J = 13.0$  Hz,



1H), 1.90 (q,  $J = 13.7$  Hz, 1H), 1.59 – 1.54 (m, 2H), 1.48 (d,  $J = 13.2$  Hz, 1H), 1.45 (s, 3H), 1.26 (s, 3H), 1.15 (s, 3H), 1.12 – 0.99 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 155.2, 154.3, 154.2, 154.0, 139.8, 139.7, 138.9, 138.4, 133.4, 130.2, 130.0, 128.2, 125.1,

124.8, 111.4, 110.6, 92.2, 91.9, 71.8, 71.2, 61.3, 60.6, 55.8, 55.7, 55.3, 53.1, 52.9, 43.3, 43.0, 37.1, 36.8, 35.8, 35.3, 32.9, 32.3, 26.1, 25.9, 21.7, 21.1, 19.3; IR (Neat):  $\nu_{\text{max}}$  2930, 2841, 1601, 1492, 1460, 1355, 1330, 1207, 1125, 1088, 1013, 908, 806, 730; HRMS (ESI): calcd for  $\text{C}_{26}\text{H}_{30}\text{ClO}_3$  ( $\text{M}+\text{H}$ ) $^+$  425.1883, found 425.1874.

### 3-(3-Fluorophenyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3z):



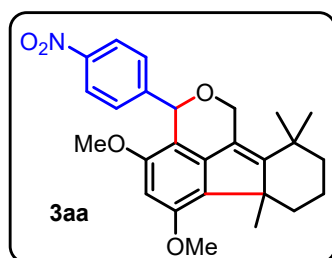
**Yield:**124 mg, (91%); colorless oil; (*dr* 2.7:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.27 (m, 1H), 7.08 (t,  $J = 8.7$  Hz, 1H), 7.00 – 6.89 (m, 2H), 6.26 (s, 1H), 5.96 (s, 1H), 4.93 (d,  $J = 15.1$  Hz, 0.28H), 4.78 (d,  $J = 14.9$  Hz, 0.72H), 4.44 (d,  $J = 15.1$  Hz, 0.28H), 4.35 (d,  $J = 14.9$  Hz, 0.72H), 3.88 (s, 3H),

3.75 (s, 3H), 2.47 (d,  $J = 13.0$  Hz, 1H), 1.90 (q,  $J = 13.7$  Hz, 1H), 1.58 (m, 2H), 1.48 (d,  $J = 14.7$  Hz, 1H), 1.45 (s, 3H), 1.26 (s, 3H), 1.16 (s, 3H), 1.14 – 1.05 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.1, 161.6, 155.3, 155.3, 154.3(d,  $J = 10.0$  Hz), 142.8, 142.7, 139.7, 130.2, 129.5(d,  $J = 8.0$  Hz), 125.0, 124.8, 124.4, 124.3, 115.8, 115.5, 114.5, 114.3, 110.5, 92.2, 92.0, 71.8, 71.2, 61.4, 60.8, 55.8, 55.7, 55.4, 53.1, 52.9, 43.2, 43.0, 37.1, 36.8, 35.8, 35.3, 32.9, 32.3, 26.1, 25.9, 21.7, 21.2, 19.3; IR (Neat):  $\nu_{\text{max}}$  2927, 2845, 1598, 1491, 1443, 1356, 1330, 1241, 1209, 1126,

1088, 1016, 805, 765, 732; **HRMS** (ESI): calcd for  $C_{26}H_{30}O_3F(M+H)^+$  409.2173, found 409.2173.

**4,6-Dimethoxy-6b,10,10-trimethyl-3-(4-nitrophenyl)-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3aa):**

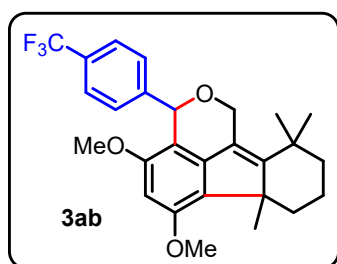
**Yield:** 130mg, (90%); colorless oil; (*dr* 2:1, based on  $^1H$  NMR);  $R_f$  = 0.5 (10% EtOAc/hexane);



$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.19 – 8.16 (m, 2H), 7.45 (d,  $J$  = 8.5 Hz, 2H), 6.27 (s, 1H), 6.00 (s, 1H), 4.94 (d,  $J$  = 15.0 Hz, 0.3H), 4.82 (d,  $J$  = 14.9 Hz, 0.7H), 4.49 (d,  $J$  = 15.0 Hz, 0.3H), 4.30 (d,  $J$  = 14.9 Hz, 0.7H), 3.89 (s, 3H), 3.75 (s, 3H), 2.48 (d,  $J$  = 13.0 Hz, 1H),

1.90 (q,  $J$  = 13.6 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.49 (d,  $J$  = 13.2 Hz, 1H), 1.45 (s, 3H), 1.26 (s, 3H), 1.15 (s, 3H), 1.11 – 1.01 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  155.2, 154.9, 154.6, 154.5, 147.5, 147.4, 139.6, 130.2, 129.6, 129.4, 124.3, 123.3, 109.6, 92.1, 91.9, 72.0, 71.1, 62.3, 61.2, 55.6, 55.4, 53.2, 53.0, 43.2, 43.0, 37.1, 36.9, 35.8, 35.4, 32.8, 32.3, 29.7, 26.0, 25.8, 21.6, 21.1, 19.2; **IR** (Neat):  $\nu_{max}$  2922, 2852, 1602, 1519, 1460, 1345, 1278, 1209, 1090, 1016, 840, 754; **HRMS** (ESI): calcd for  $C_{26}H_{30}O_5N(M+H)^+$  436.2118, found 436.2120.

**4,6-Dimethoxy-6b,10,10-trimethyl-3-(4-(trifluoromethyl)phenyl)-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3ab):**



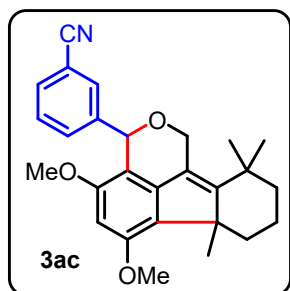
**Yield:** 140 mg, (92%); colorless oil; (*dr* 3:1, based on  $^1H$  NMR);  $R_f$  = 0.5 (10% EtOAc/hexane);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.57 (d,  $J$  = 8.1 Hz, 2H), 7.39 (d,  $J$  = 8.1 Hz, 2H), 6.27 (s, 1H), 6.00 (s, 1H), 4.93 (d,  $J$  = 15.1 Hz, 0.25H), 4.79 (d,  $J$  = 14.9 Hz, 0.75H), 4.43 (d,  $J$

= 15.1 Hz, 0.25H), 4.31 (d,  $J$  = 14.9 Hz, 0.75H), 3.88 (s, 3H), 3.75 (s, 3H), 2.47 (d,  $J$  = 12.9 Hz,

1H), 1.90 (q,  $J = 13.6$  Hz, 1H), 1.58 (m, 2H), 1.46 (s, 3H), 1.26 (s, 3H), 1.19 (m, 1H), 1.15 (s, 3H), 1.13 – 1.04 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 154.5, 154.4, 154.2, 144.5, 144.0, 139.8, 139.7, 130.2, 129.8, 129.5, 129.0, 128.9, 125.1, 125.0, 124.9, 124.6, 111.0, 110.2, 92.1, 91.9, 71.9, 71.3, 61.7, 60.9, 55.7, 55.7, 55.4, 53.1, 52.9, 43.2, 43.0, 37.1, 36.9, 35.8, 35.3, 32.9, 32.3, 26.1, 25.9, 21.7, 21.1, 19.3; IR (Neat):  $\nu_{\text{max}}$  2929, 2844, 1613, 1498, 1461, 1324, 1209, 1163, 1122, 1066, 1016, 758, 733; HRMS (ESI): calcd for  $\text{C}_{27}\text{H}_{30}\text{O}_3\text{F}_3(\text{M}+\text{H})^+$  459.2141, found 459.2127.

**3-(4,6-Dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromen-3-yl)benzonitrile (3ac):**

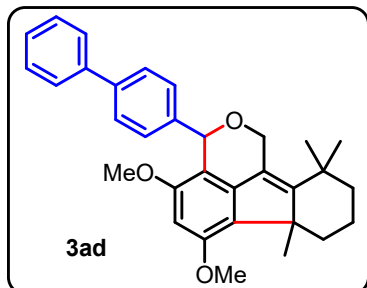
**Yield:** 128mg, (93%); colorless oil; (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 6.27 (s, 1H), 5.95 (s, 1H), 4.93 (d,  $J = 15.0$  Hz, 0.35H), 4.80 (d,  $J = 14.9$  Hz, 0.65H), 4.44 (d,  $J = 15.0$  Hz, 0.35H), 4.26 (d,  $J = 14.9$  Hz, 0.65H), 3.89 (s, 3H), 3.75 (s, 3H), 2.47 (d,  $J = 13.0$  Hz, 1H), 1.90 (q,  $J = 13.6$  Hz, 1H), 1.57 (d,  $J = 11.2$  Hz, 2H), 1.45 (s, 3H), 1.26 (s, 3H), 1.21 (s, 1H), 1.16 (s, 3H), 1.14 - 1.08 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 154.7, 154.6, 154.4, 142.3, 141.7, 139.8, 139.6, 133.3, 133.2, 132.4, 132.3, 131.3, 130.3, 129.0, 128.9, 124.7, 124.4, 119.2, 112.1, 110.4, 109.4, 92.1, 91.9, 71.8, 71.0, 62.0, 60.9, 55.7, 55.6, 55.4, 53.2, 53.0, 43.2, 43.1, 37.1, 36.9, 35.7, 35.4, 32.8, 32.3, 26.1, 25.9, 21.6, 21.2, 19.2; IR (Neat):  $\nu_{\text{max}}$  2928, 2843, 2230, 1602, 1496, 1461, 1356, 1330, 1209, 1088, 1050, 910, 804, 732, 690; HRMS (ESI): calcd for  $\text{C}_{27}\text{H}_{30}\text{O}_3\text{N}(\text{M}+\text{H})^+$  416.2220, found 416.2201.

**3-([1,1'-Biphenyl]-4-yl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3ad):**

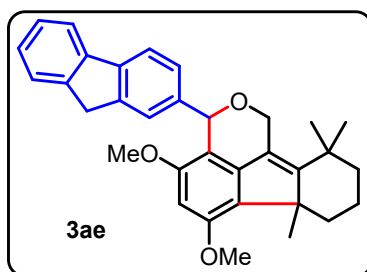
**Yield:** 147mg, (95%); colorless oil; (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.52 (m, 4H), 7.41 (t,  $J = 7.7$  Hz, 2H), 7.37 – 7.29 (m, 3H), 6.38 (s, 0.8H), 6.28 (s, 1H), 6.04 (s, 1H), 4.95 (d,  $J = 15.1$  Hz, 0.35H), 4.80 (d,  $J = 14.9$  Hz, 0.65H), 4.48 (d,  $J = 15.1$  Hz, 0.35H), 4.42 (d,  $J = 14.9$  Hz,

0.65H), 4.24 (s, 0.26H), 3.88 (s, 3H), 3.77 (s, 3H), 3.71 (s, 1H), 2.48 (d,  $J = 13.0$  Hz, 1H), 2.20 - 2.08 (m, 0.63), 1.90 (m, 1H), 1.74 – 1.66 (m, 0.61), 1.65 – 1.53 (m, 2H), 1.47 (s, 3H), 1.40 (s, 1H), 1.27 (s, 3H), 1.22 - 1.18 (m, 1H), 1.16 (s, 3H), 1.15 – 1.09 (m, 1H), 0.89 (s, 0.85);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7, 155.4, 155.3, 154.2, 154.0, 153.7, 141.0, 141.0, 140.4, 139.8, 139.3, 138.9, 138.6, 134.6, 132.1, 130.3, 130.2, 129.2, 129.1, 128.7, 127.2, 127.1, 126.9, 125.4, 125.1, 111.8, 111.1, 107.1, 98.3, 92.3, 92.0, 72.0, 71.6, 61.2, 60.6, 58.6, 55.9, 55.8, 55.4, 55.3, 53.1, 52.9, 43.3, 43.0, 39.3, 37.1, 36.9, 35.9, 35.7, 35.3, 33.2, 32.9, 32.3, 28.3, 27.8, 26.2, 25.9, 23.0, 21.8, 21.2, 19.3, 19.2; IR (Neat):  $\nu_{\text{max}}$  2929, 2842, 1722, 1600, 1493, 1459, 1329, 1206, 1067, 1013, 755, 696; HRMS (ESI): calcd for  $\text{C}_{32}\text{H}_{35}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  467.2586, found 467.2579.

**3-(9H-Fluoren-2-yl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3ae):**

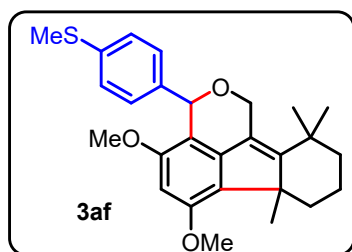


**Yield:** 143 mg, (90%); white solid (m.p = 170-172  $^{\circ}\text{C}$ ); (*dr* 1:0.16, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (m, 2H), 7.51 (d,  $J = 7.3$  Hz, 1H), 7.44 (s, 1H), 7.34 (m, 1H), 7.30 – 7.20 (m, 2H), 6.28 (s,

1H), 6.07 (s, 1H), 4.93 (d,  $J = 15.0$  Hz, 0.1H), 4.78 (d,  $J = 14.9$  Hz, 0.9H), 4.51 (d,  $J = 15.0$  Hz,

0.1H), 4.41 (d,  $J = 14.9$  Hz, 0.91H), 3.89 (s, 3H), 3.86 (s, 2H), 3.73 (s, 3H), 2.49 (d,  $J = 13.0$  Hz, 1H), 1.91 (m, 1H), 1.58 (m, 2H), 1.47 (s, 3H), 1.26 (s, 3H), 1.19 (m, 1H), 1.15 (s, 3H), 1.13 – 1.08 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 154.2, 153.9, 143.6, 143.2, 141.5, 141.3, 139.9, 138.6, 130.2, 127.5, 126.7, 126.6, 125.6, 125.2, 125.0, 119.9, 119.3, 111.4, 92.1, 72.1, 60.5, 55.8, 55.4, 52.9, 43.3, 36.9, 36.9, 36.0, 32.3, 25.9, 21.2, 19.3; IR (Neat):  $\nu_{\text{max}}$  2929, 2842, 1604, 1498, 1459, 1356, 1329, 1208, 1125, 1089, 1013, 908, 757, 733; HRMS (ESI): calcd for  $\text{C}_{33}\text{H}_{35}\text{O}_3$  (M+H) $^+$  479.2580, found 479.2593.

**4,6-Dimethoxy-6b,10,10-trimethyl-3-(4-(methylthio)phenyl)-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3af):**



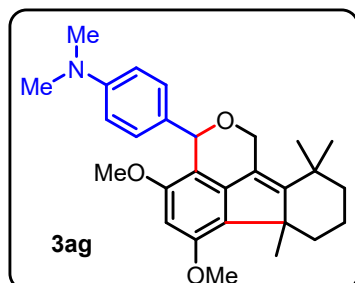
**Yield:** 128 mg, (89%); colorless oil; (*dr* 2:1, based on  $^1\text{H}$  NMR);  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 – 7.11 (m, 4H), 6.25 (s, 1H), 5.95 (s, 1H), 4.91 (d,  $J = 15.1$  Hz, 0.35H), 4.75 (d,  $J = 14.9$  Hz, 0.65H), 4.41 (d,  $J = 15.1$  Hz,

0.35H), 4.34 (d,  $J = 14.9$  Hz, 0.65H), 3.87 (s, 3H), 3.73 (s, 3H), 2.51 – 2.43 (m, 1H), 2.46 (s, 3H), 1.90 (q,  $J = 13.7$  Hz, 1H), 1.55 (m, 2H), 1.45 (s, 3H), 1.26 (s, 3H), 1.18 (m, 1H), 1.15 (s, 3H), 1.13 – 1.03 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 155.2, 154.2, 154.0, 153.7, 139.9, 139.8, 137.6, 137.2, 136.8, 130.2, 130.2, 130.0, 129.3, 129.2, 126.2, 126.1, 125.3, 125.2, 125.0, 111.7, 111.0, 92.2, 92.0, 71.8, 71.4, 61.0, 60.4, 55.9, 55.8, 55.4, 53.1, 52.8, 43.3, 43.0, 37.1, 36.8, 35.9, 35.3, 32.9, 32.3, 26.1, 25.9, 21.8, 21.2, 19.3, 15.8, 15.7; IR (Neat):  $\nu_{\text{max}}$  2925, 2841, 1696, 1598, 1494, 1459, 1329, 1280, 1209, 1125, 1089, 1014, 806, 757; HRMS (ESI): calcd for  $\text{C}_{27}\text{H}_{33}\text{O}_3\text{S}$  (M+H) $^+$  437.2144, found 437.2162.



**4-(4,6-Dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromen-3-yl)-N,N-dimethylaniline (3ag):**

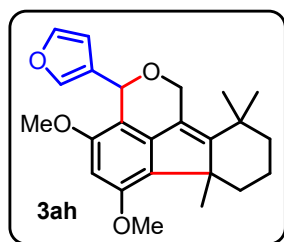
**Yield:**138mg, (96%); colorless oil;(dr 2.3:1, based on  $^1\text{H}$  NMR);  $R_f$ = 0.5 (10% EtOAc/hexane);



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 – 7.06 (m, 2H), 6.70 – 6.66 (m, 2H), 6.24 (s, 1H), 5.95 (s, 1H), 4.89 (d,  $J$  = 15.0 Hz, 0.3H), 4.72 (d,  $J$  = 15.0 Hz, 0.7H), 4.38 (d,  $J$  = 15.0 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 2.93 (s, 6H), 2.47 (d,  $J$  = 12.9 Hz, 1H), 1.90 (m, 1H),

1.57 (s, 2H), 1.45 (s, 3H), 1.25 (s, 3H), 1.18 (m, 1H), 1.16 (s, 3H), 1.13 – 1.02 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 155.2, 153.9, 153.4, 153.2, 150.1, 150.0, 140.0, 139.9, 130.1, 129.7, 129.6, 127.8, 127.6, 125.7, 125.5, 112.0, 111.9, 92.2, 92.1, 71.7, 71.6, 60.2, 60.0, 55.9, 55.8, 55.4, 53.0, 52.7, 43.3, 43.0, 40.5, 37.1, 36.8, 36.0, 35.3, 32.9, 32.3, 26.2, 25.9, 21.9, 21.2, 19.4; IR (Neat):  $\nu_{\text{max}}$ 2927, 2838, 1612, 1519, 1461, 1350, 1336, 1202, 1124, 1091, 1013, 908, 803, 756, 730; HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{36}\text{O}_3\text{N}(\text{M}+\text{H})^+$  434.2689, found 434.2689.

**3-(Furan-3-yl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3ah):**



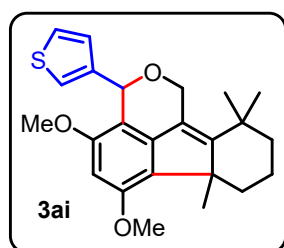
**Yield:**110 mg, (87%); colorless oil; (dr 2:1, based on  $^1\text{H}$  NMR);  $R_f$ = 0.5 (10% EtOAc/hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.45 (m, 1H), 6.31 – 6.26 (m, 1H), 6.22 (s, 1H), 6.00 – 5.88 (m, 2H), 5.00 (d,  $J$  = 15.0 Hz, 0.3H), 4.85 (d,  $J$  = 14.7 Hz, 0.7H), 4.45 (d,  $J$  = 14.7 Hz, 1H),

3.86 (s, 3H), 3.75 (s, 3H), 2.46 (d,  $J$  = 13.0 Hz, 1H), 1.97 – 1.83 (m, 1H), 1.57 (m, 2H), 1.53 – 1.47 (m, 1H), 1.43 (s, 3H), 1.27 (s, 3H), 1.20 (s, 3H), 1.14 – 1.07 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 154.3, 154.1, 153.9, 153.2, 153.1, 142.8, 139.8, 139.7, 130.0, 124.9, 124.7, 110.2, 110.2, 109.9, 109.4, 92.2, 92.1, 65.6, 61.3, 61.2, 56.0, 55.9, 55.3, 53.1, 52.8, 43.3, 43.0,

37.1, 36.8, 35.8, 35.3, 32.9, 32.3, 26.2, 25.8, 21.7, 21.2, 19.3; **IR** (Neat):  $\nu_{max}$  2926, 2849, 1627, 1608, 1499, 1461, 1357, 1330, 1212, 1128, 1087, 1011, 808, 738; **HRMS** (ESI): calcd for  $C_{24}H_{29}O_4(M+H)^+$  381.2060, found 381.2084.

**4,6-Dimethoxy-6b,10,10-trimethyl-3-(thiophen-3-yl)-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3ai):**

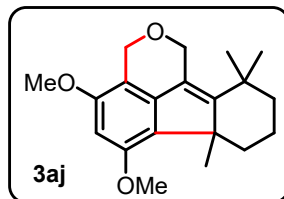
**Yield:** 106 mg, (81%); colorless oil; (*dr* 2:1, based on  $^1H$  NMR);  $R_f$  = 0.5 (10% EtOAc/hexane);



**$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.31 – 7.28 (m, 1H), 6.93 (m, 1H), 6.72 (m, 1H), 6.25 (s, 1H), 6.16 (s, 1H), 5.00 (d,  $J$  = 15.1 Hz, 0.3H), 4.83 (d,  $J$  = 14.9 Hz, 0.7H), 4.56 (d,  $J$  = 14.9 Hz, 0.7H), 4.52 (d,  $J$  = 15.1 Hz, 0.3H), 3.87 (s, 3H), 3.78 (s, 3H), 2.46 (d,  $J$  = 13.0 Hz, 1H), 1.89 (q,  $J$  =

13.7 Hz, 1H), 1.57 (m, 2H), 1.48 (d,  $J$  = 14.5 Hz, 1H), 1.44 (s, 3H), 1.26 (s, 3H), 1.18 (s, 3H), 1.09 – 1.08 (m, 1H);  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**  $\delta$  155.3, 155.7, 154.4, 154.7, 153.7, 144.3, 144.1, 139.6, 139.6, 130.7, 127.3, 127.9, 126.1, 125.1, 124.5, 124.6, 111.5, 92.6, 67.7, 67.4, 60.7, 60.7, 55.3, 55.3, 55.9, 53.5, 52.5, 43.3, 42.8, 37.4, 36.0, 35.9, 35.6, 33.0, 32.4, 26.0, 25.1, 21.8, 21.6, 19.3; **IR** (Neat):  $\nu_{max}$  2924, 2852, 1708, 1605, 1498, 1461, 1357, 1209, 1168, 1088, 1042, 1014, 701; **HRMS** (ESI): calcd for  $C_{24}H_{29}O_3S(M+H)^+$  397.1831, found 397.1852.

**4,6-Dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3aj):**



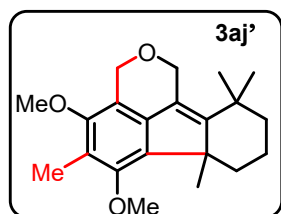
**Yield:** 92mg, (89%); colorless oil;  $R_f$  = 0.5 (10% EtOAc/hexane);  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  6.20 (s, 1H), 4.94 (d,  $J$  = 14.5 Hz, 1H), 4.76 (d,  $J$  = 14.5 Hz, 2H), 4.57 (d,  $J$  = 14.5 Hz, 1H), 3.83 (s, 3H), 3.81 (s,

3H), 2.44 (d,  $J$  = 11.3 Hz, 1H), 1.89 (q,  $J$  = 13.8 Hz, 1H), 1.62 – 1.50 (m, 3H), 1.43 (s, 3H),

1.25(s, 3H), 1.26 (s, 3H), 1.15 – 1.05 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.5, 153.8, 153.6, 139.6, 130.2, 125.2, 110.5, 92.2, 66.8, 62.6, 55.8, 55.5, 52.9, 43.2, 36.9, 35.6, 32.6, 29.7, 25.9, 21.4, 19.3; IR (Neat):  $\nu_{\text{max}}$  2925, 2838, 1607, 1501, 1459, 1358, 1328, 1280, 1209, 1127, 1078, 994, 929, 800, 730; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_3(\text{M}+\text{H})^+$  315.1954, found 315.1950.

**4,6-Dimethoxy-5,6b,10,10-tetramethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3aj')**:

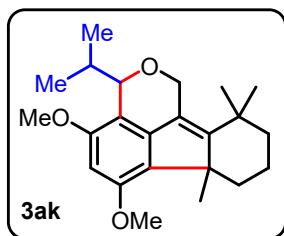
To a stirred solution of **s1e** (100 mg, 0.3300 mmol, 1.0 equiv) and paraformaldehyde (198 mg,



6.6006 mmol, 20 equiv) in dry  $\text{CH}_2\text{Cl}_2$  (3.3 mL) was added  $\text{BF}_3 \cdot \text{OEt}_2$  (8.2  $\mu\text{L}$ , 0.0660 mmol, 0.2 equiv) at 0  $^\circ\text{C}$  and stirred at the same temperature. After completing of the starting material, the reaction was

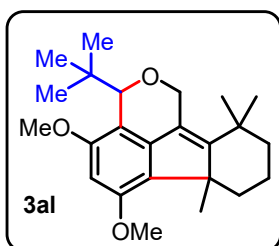
quenched with  $\text{H}_2\text{O}$  or saturated  $\text{NaHCO}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with aq  $\text{NaCl}$ , dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/ hexanes) to give **3aj** as (94 mg, 87%); colorless oil;  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.93 (d,  $J = 14.5$  Hz, 1H), 4.80 (d,  $J = 14.5$  Hz, 2H), 4.66 (d,  $J = 14.5$  Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.42 (d,  $J = 14.3$  Hz, 1H), 2.22 (s, 3H), 2.01 - 1.89 (m, 1H), 1.68 – 1.51 (m, 3H), 1.46 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 1.24 - 1.21 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 153.4, 151.9, 138.4, 137.1, 125.2, 120.3, 118.0, 66.9, 63.0, 61.3, 60.6, 53.3, 43.0, 36.8, 36.5, 32.7, 26.0, 22.6, 19.4, 9.5; IR (Neat):  $\nu_{\text{max}}$  2928, 2862, 1601, 1465, 1411, 1352, 1211, 1099, 997, 936; HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{29}\text{O}_3(\text{M}+\text{H})^+$  329.2111, found 329.2096.

**3-Isopropyl-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3ak):**



**Yield:** 92 mg, (78%); colorless oil; (*dr* 2:1, based on  $^1\text{H NMR}$ );  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.19 (s, 1H), 4.95 – 4.74 (m, 2H), 4.55 – 4.46 (m, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.49 – 2.36 (m, 1H), 2.18 – 2.06 (m, 1H), 1.96 – 1.81 (m, 1H), 1.62 – 1.48 (m, 2H), 1.40 (s, 3H), 1.25 (s, 6H), 1.21 – 1.13 (m, 1H), 1.08 (d,  $J = 6.6$  Hz, 3H), 1.02 – 0.99 (m, 1H), 0.94 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 153.7, 153.5, 153.5, 152.8, 139.8, 139.2, 130.6, 130.2, 125.9, 125.1, 113.9, 113.6, 92.2, 91.9, 75.4, 62.4, 60.8, 55.7, 55.5, 55.3, 52.7, 52.5, 43.4, 43.2, 37.0, 36.8, 35.6, 35.4, 32.7, 32.3, 31.6, 30.9, 21.7, 21.3, 19.7, 19.5, 19.4, 19.3, 19.2, 18.1; **IR** (Neat):  $\nu_{\text{max}}$  2927, 2842, 1601, 1496, 1460, 1356, 1327, 1209, 1086, 1008, 903, 802, 757, 732; **HRMS** (ESI): calcd for  $\text{C}_{23}\text{H}_{33}\text{O}_3(\text{M}+\text{H})^+$  357.2424, found 357.2438.

**3-(tert-Butyl)-4,6-dimethoxy-6b,10,10-trimethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3al):**

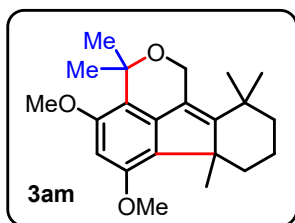


**Yield:** 88mg, (72%); colorless oil; (*dr* 1:0.1, based on  $^1\text{H NMR}$ );  $R_f = 0.5$  (10% EtOAc/hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.22 (s, 1H), 5.12 (d,  $J = 15.6$  Hz, 1H), 4.84 (d,  $J = 15.6$  Hz, 1H), 4.63 (s, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 2.45 (d,  $J = 14.5$  Hz, 1H), 1.97 – 1.83 (m, 1H), 1.60 – 1.58 (m, 1H), 1.56 – 1.52 (m, 2H), 1.41 (s, 3H), 1.25 (s, 3H), 1.21 (s, 3H), 1.09 – 1.02 (m, 1H), 0.97 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 153.9, 153.6, 139.8, 129.9, 124.8, 112.0, 92.1, 63.2, 55.4, 55.2, 52.4, 43.6, 38.8, 36.7, 35.8, 32.3, 29.7, 28.4, 25.6, 21.0, 19.4; **IR** (Neat):

$\nu_{max}$  2923, 2856, 1613, 1498, 1463, 1359, 1329, 1213, 1070, 1005, 804, 765; **HRMS** (ESI): calcd for  $C_{24}H_{35}O_3(M+H)^+$  371.2580, found 371.2581.

**4,6-Dimethoxy-3,3,6b,10,10-pentamethyl-3,6b,7,8,9,10-hexahydro-1H-indeno[1,2,3-de]isochromene (3am):**

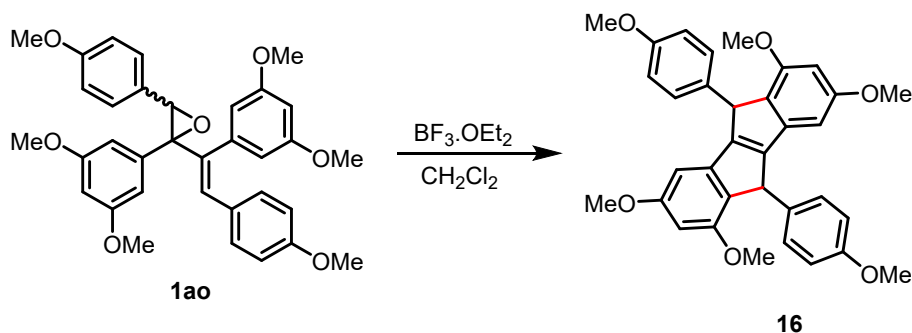
**Yield:** 84 mg, (74%); colorless oil;  $R_f$  = 0.5 (10% EtOAc/hexane);  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**



$\delta$  6.22 (s, 1H), 4.86 (q,  $J$  = 15.1 Hz, 2H), 3.83 (s, 6H), 2.45 (d,  $J$  = 11.3 Hz, 1H), 1.89 (q,  $J$  = 13.5 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 3H), 1.53 (s, 3H), 1.42 (s, 3H), 1.26 (s, 3H), 1.25 (s, 3H), 1.08 (td,  $J$  = 13.2, 3.7 Hz,

1H);  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**  $\delta$  154.9, 153.3, 152.5, 139.3, 130.5, 125.8, 118.3, 92.7, 72.9, 60.5, 55.7, 55.3, 52.4, 43.3, 36.8, 35.5, 32.5, 27.4, 26.0, 25.0, 21.5, 19.3; **IR** (Neat):  $\nu_{max}$  2928, 2844, 1600, 1458, 1353, 1320, 1277, 1206, 1090, 1017, 816, 751; **HRMS** (ESI): calcd for  $C_{22}H_{31}O_3(M+H)^+$  343.2267, found 343.2265.

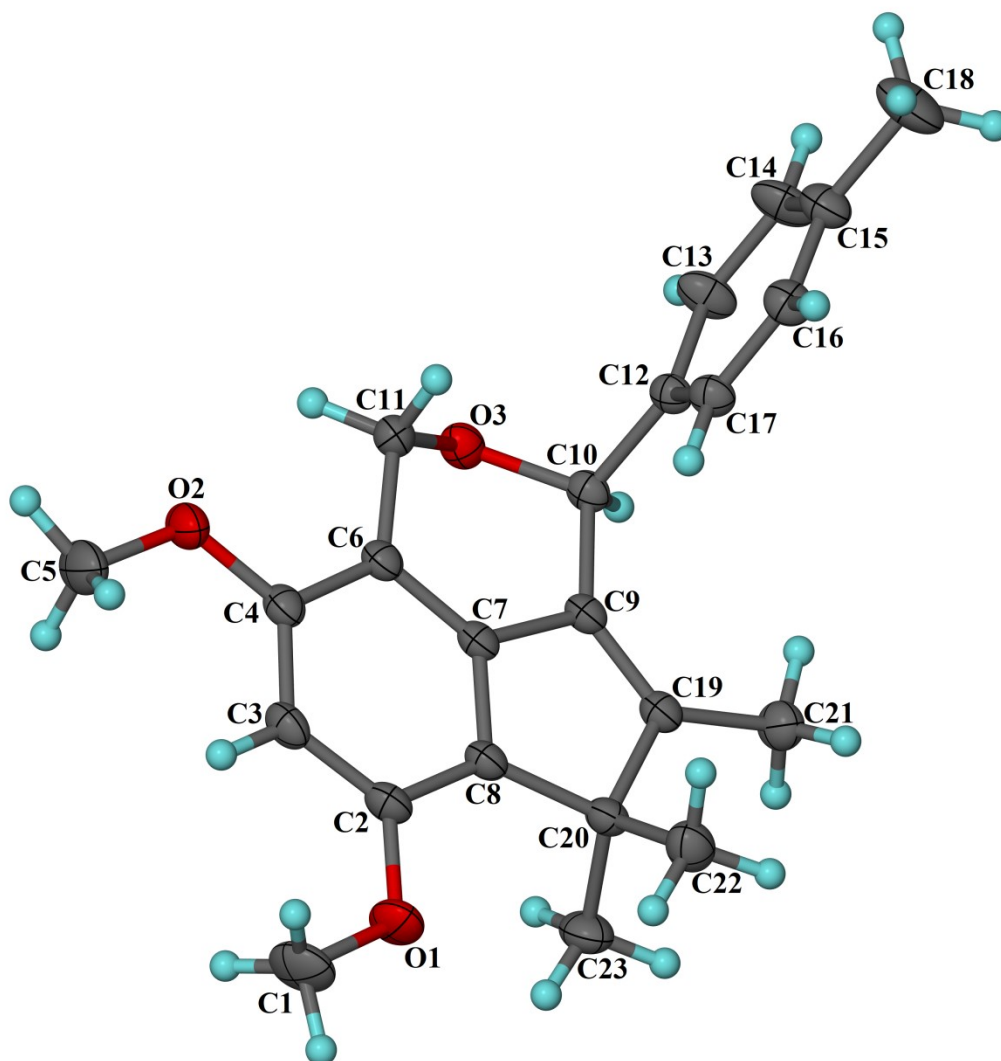
**2,4,7,9-Tetramethoxy-5,10-bis(4-methoxyphenyl)-5,10-dihydroindeno[2,1-a]indene (16):**



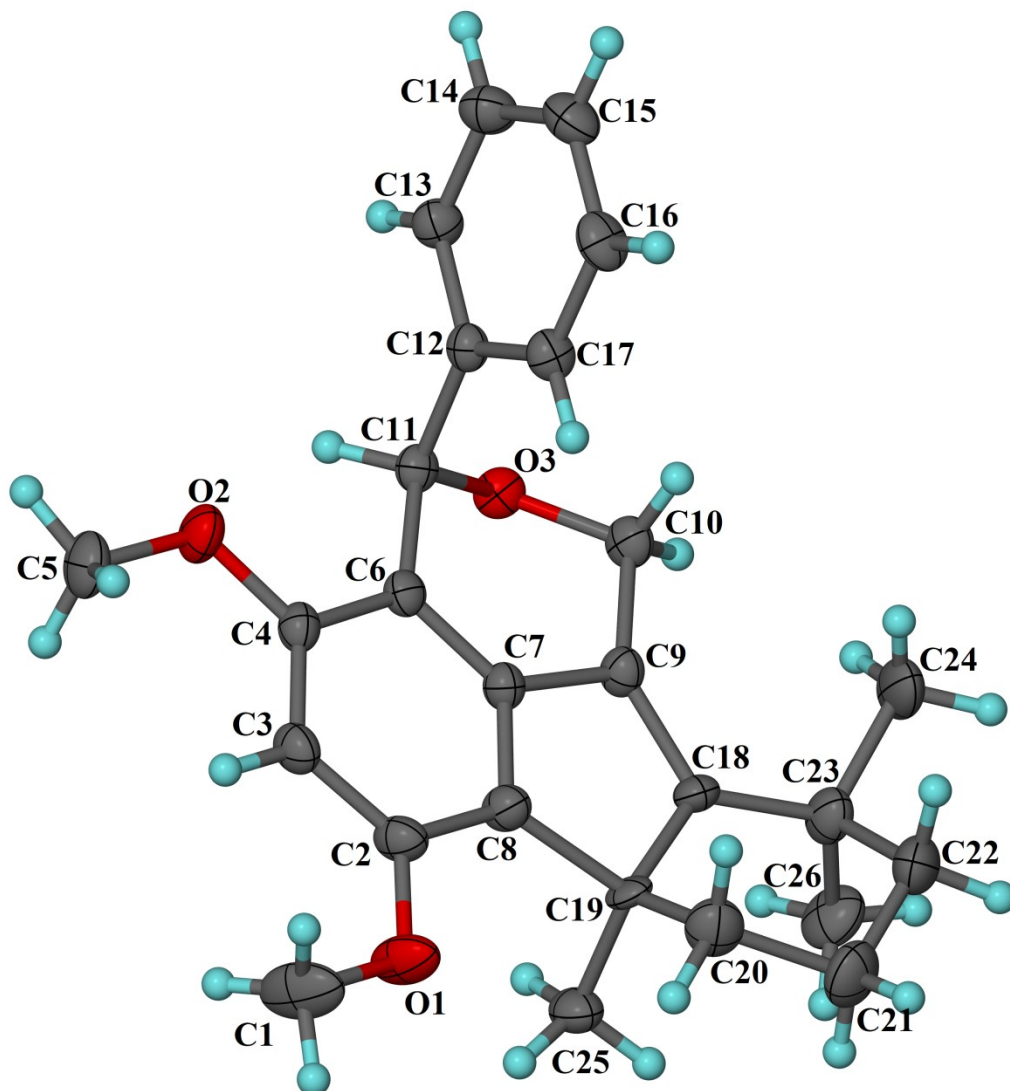
To a stirred solution of **1ao** (100 mg, 0.1805 mmol, 1.0 equiv) in dry  $CH_2Cl_2$  (1.8 mL) was added  $BF_3 \cdot OEt_2$  (3.6  $\mu$ L, 0.0361 mmol, 0.01M, 0.2 equiv) at 0  $^\circ C$  and stirred at the same

temperature. After completing of the starting material, the reaction was quenched with H<sub>2</sub>O or saturated NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with aq NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/ hexanes) to give **16** as (92 mg, 95%) a colorless oil; R<sub>f</sub> = 0.4 (20% EtOAc/hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.14 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 6.29 (d, J = 2.1 Hz, 1H), 6.22 (d, J = 2.1 Hz, 1H), 4.83 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.9, 157.0, 155.1, 153.9, 140.8, 130.4, 129.5, 128.3, 127.9, 124.9, 123.3, 112.7, 97.0, 95.1, 54.5, 54.4, 54.1, 46.9, 28.7; IR (Neat): ν<sub>max</sub> 2958, 2922, 2852, 1612, 1510, 1478, 1362, 1250, 1210, 1050, 842, 799, 772, 577, 560; HRMS (ESI): calcd for C<sub>34</sub>H<sub>33</sub>O<sub>6</sub>(M+H)<sup>+</sup> 537.2271, found 537.2269.

### 3. X-ray Crystallography Information



**Figure caption:** ORTEP diagram of **3b** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.



**Figure caption:** ORTEP diagram of **3p** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

**Crystal data for 3b:**  $C_{23}H_{26}O_3$ ,  $M = 350.44$ , Monoclinic, Space group  $P2_1/c$  (No. 14),  $a = 12.435(8)\text{\AA}$ ,  $b = 10.019(7)\text{\AA}$ ,  $c = 15.766(10)\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 100.344(9)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1932(2)\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.205\text{g/cm}^3$ ,  $F_{000} = 752$ , Bruker D8 QUEST PHOTON-100, Mo-K $\alpha$



radiation,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 293(2)\text{K}$ ,  $2\theta_{\text{max}} = 55^\circ$ ,  $\mu = 0.078 \text{ mm}^{-1}$ , 24142 reflections collected, 4432 unique ( $R_{\text{int}} = 0.0669$ ), 241 parameters,  $RI = 0.0609$ ,  $wR2 = 0.1485$ ,  $R$  indices based on 3041 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), Final  $Goof = 1.040$ , largest difference hole and peak =  $-0.173$  and  $0.232 \text{ e.\AA}^{-3}$ . **CCDC 2076802** contains the supplementary crystallographic data for this paper which can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>

**Crystal data for 3p:**  $\text{C}_{26}\text{H}_{30}\text{O}_3$ ,  $M = 390.50$ , Monoclinic, Space group  $P2_1/n$  (No.14),  $a = 15.149(5)\text{\AA}$ ,  $b = 7.696(3)\text{\AA}$ ,  $c = 19.735(6)\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 104.073(8)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2231.7(13)\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.162 \text{ g/cm}^3$ ,  $F_{000} = 840$ , Bruker D8 QUEST PHOTON-100, Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 293(2)\text{K}$ ,  $2\theta_{\text{max}} = 50^\circ$ ,  $\mu = 0.074 \text{ mm}^{-1}$ , 24226 reflections collected, 3919 unique ( $R_{\text{int}} = 0.0520$ ), 353 parameters,  $RI = 0.0533$ ,  $wR2 = 0.1311$ ,  $R$  indices based on 3139 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), Final  $Goof = 1.073$ , largest difference hole and peak =  $-0.167$  and  $0.235 \text{ e.\AA}^{-3}$ . **CCDC 2076801** contains the supplementary crystallographic data for this paper which can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>

**Data collection and Structure solution details:** Single crystal X-ray data were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and Photon 100 detector. An I $\mu$ s microfocus Mo source ( $\lambda=0.71073\text{\AA}$ ) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Integration and scaling of intensity data were accomplished using SAINT program.<sup>1</sup> The structures were solved by Direct Methods using SHELXS97<sup>2</sup> and refinement was

carried out by full-matrix least-squares technique using SHELXL-2014/7.<sup>2-3</sup> Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}$  for methyl atoms.

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL Version 2014/7, <http://shelx.uni-ac.gwdg.de/SHELX/index.php>
3. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

#### 4. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

