

## Supporting Information

### Silver-Catalyzed Stereoselective Domino Cycloisomerization-Vinylogous Aldol Reaction of *ortho*-Alkynylbenzaldehydes with 3-Alkylidene oxindoles: An Entry to Functionalized Isochromenes

Krishna Kumar, Bhuvnesh Singh and Ravi P. Singh\*

Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, 110 016, India

*E-mail:* ravips@chemistry.iitd.ac.in

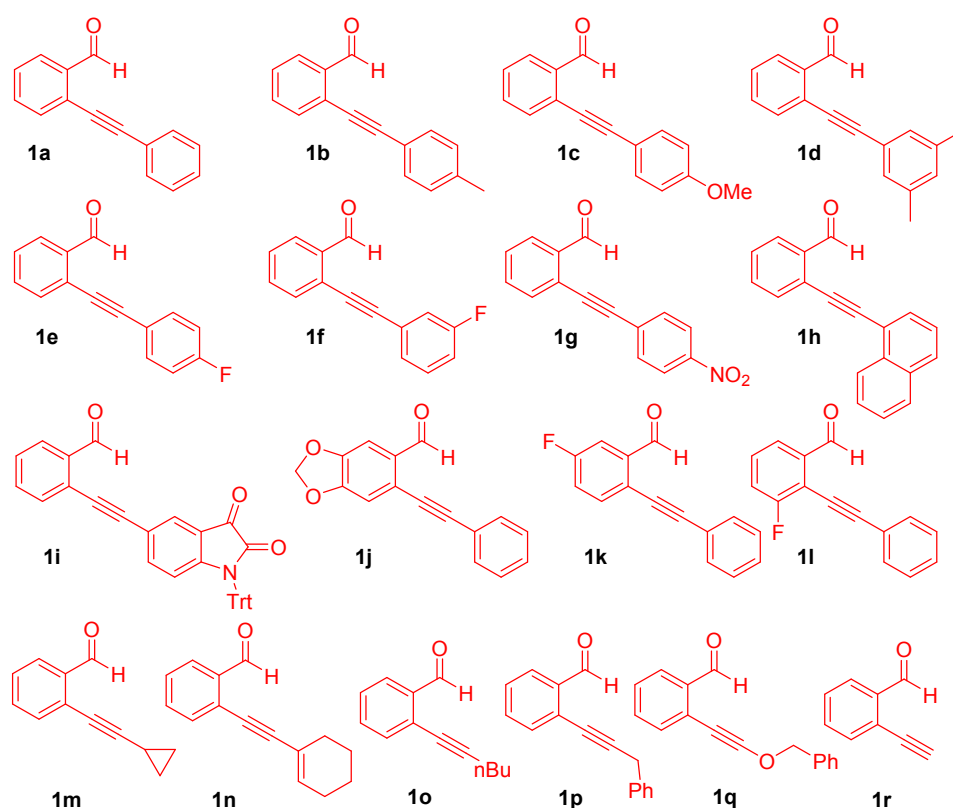
#### Table of Contents

Entry	Contents	Page no.
1.	General Information	S2
2.	Synthesis of starting materials	S2
3.	General procedure for the synthesis of substituted isochromenes product <b>3</b> and <b>4</b>	S3
4.	GC-MS characterization of the reaction intermediate <b>IV</b>	S18
5.	Crystallographic Description and ORTEP diagrams of <b>3q</b> and <b>4i</b>	S19-S22
6.	References	S23
7.	Copies of <sup>1</sup> H and <sup>13</sup> C NMR spectra	S24-S50

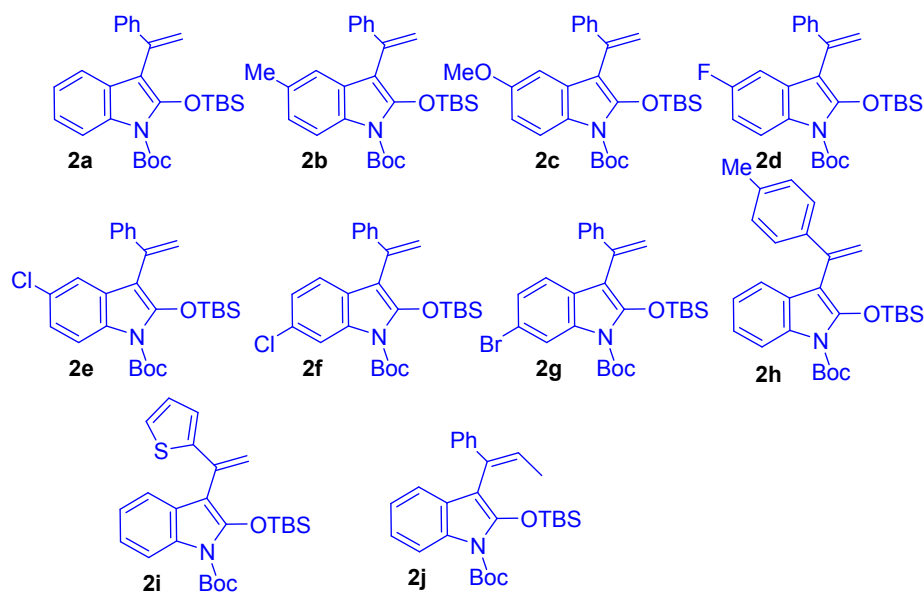
**1. General Information:** All solvents used to carry out reaction were dried using standard procedure and stored under nitrogen atmosphere. All the reactions were carried out under the Argon/Nitrogen atmosphere. Purification of the compounds was done by Column chromatographic on silica gel (100–200mesh). All products obtained were fully characterized by various spectroscopic techniques like  $^1\text{H}$  &  $^{13}\text{C}$  NMR, FT-IR, ESI-HRMS.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AV-300/400 instrument (300/400 and 75/100 MHz, respectively) in deuterated solvents. Internal reference assigned to residual protonated solvent signals or tetramethylsilane signal.  $^1\text{H}$  NMR data reported as follows: chemical shift ( $\delta$ , ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration.  $^{13}\text{C}$  NMR data reported as chemical shift ( $\delta$ , ppm). Perkin Elmer FT-IR spectrometer was used to record infrared spectra, and data reported in terms of frequency ( $\text{cm}^{-1}$ ) of absorption. ESI mass spectrometers were used to record high-resolution mass spectra. The GC-MS were recorded on Agilent 7890B instrument at 30 °C.

## 2. Synthesis of starting materials

Starting materials 2-Alkynyl Aryl<sup>1</sup> and 3-alkenyl-2-silyloxindoles<sup>2</sup> were prepared according to known literature procedures.

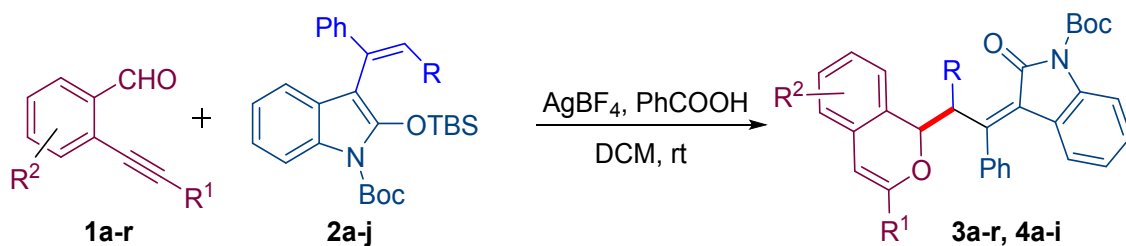


**S-Figure 1.** The structure of 2-Alkynyl Aryl 1



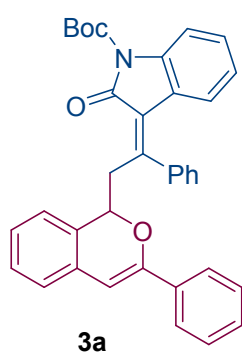
**S-Figure 2.** The structure of 3-alkenyl-2-silyloxyindoles **2**

### 3. General procedure for the synthesis of substituted isochromenes product



Silver tetrafluoroborate (20 mol%) was taken in pre-dried reaction vessel and nitrogen was purged using standard Schlenk techniques to maintain inert conditions. Completely dried DCM (1 mL) was added to the reaction vessel followed by addition of **1a-r** (0.2 mmol, 1 equiv.), **2a-j** (0.3 mmol, 1.5 equiv.) and benzoic acid (20 mol %). The content of reaction was stirred under inert atmosphere at room temperature. Progress of the reaction was monitored by thin layer chromatography (TLC) using EtOAc/Hexane (1:9) solvent system. After completion of the reaction (i.e. disappearance of **1a-r**), the reaction was quenched by adding water. The reaction mixture was extracted using DCM (5 ml  $\times$  3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluent: EtOAc/Hexane = 1/9-2/8, v/v).

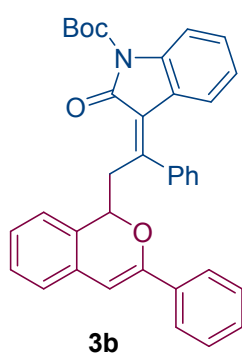
**tert-butyl (E)-2-oxo-3-(1-phenyl-2-(3-phenyl-1*H*-isochromen-1-yl)ethylidene)indoline-1-**



**3a**

**carboxylate (3a):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3a**. Yellow solid (87 mg, yield = 80%). *R<sub>f</sub>* = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.52–7.33 (m, 3H), 7.23 (s, 5H), 7.20–7.03 (m, 8H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.7 Hz, 1H), 6.30 (s, 1H), 6.10 (d, *J* = 7.6 Hz, 1H), 5.69 (dd, *J*<sub>1</sub> = 10.1, *J*<sub>2</sub> = 3.4 Hz, 1H), 4.28 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 10.2 Hz, 1H), 3.25 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 3.4 Hz, 1H), 1.53 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.6, 155.7, 151.2, 149.3, 141.1, 138.6, 134.8, 130., 130.7, 129.3, 128.7, 128.3, 128.1, 128.0, 127.5, 127.1, 126.6, 124.8, 124.7, 124.4, 123.9, 123.3, 123.1, 123.0, 114.4, 100.6, 84.0, 76.9, 40.3, 28.2; **FTIR (KBr)** cm<sup>-1</sup>, 3054, 2974, 2926, 2853, 1776, 1732, 1630, 1601, 1494, 1460, 1348, 1304, 1253, 1153, 1096, 1056, 975, 919, 842, 761, 700, 594. **HRMS ESI** (*m/z*) [*M*+Na]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>31</sub>NO<sub>4</sub>Na 564.2151; found 564.2167.

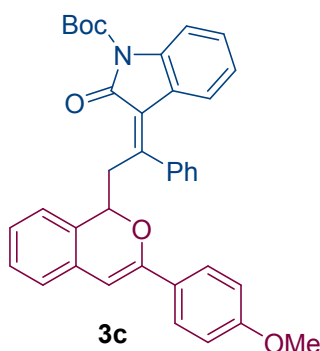
**tert-butyl (E)-2-oxo-3-(1-phenyl-2-(3-(*p*-tolyl)-1*H*-isochromen-1-yl)ethylidene)indoline-**



**3b**

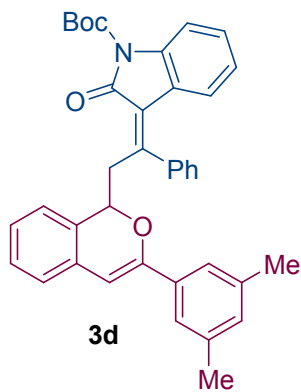
**1-carboxylate (3b):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3b**. Yellow solid (75 mg, yield = 68%). *R<sub>f</sub>* = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 6H), 7.21–7.01 (m, 5H), 6.97 (d, *J* = 6.9 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.28 (s, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.66 (d, *J* = 7.5 Hz, 1H), 4.34 (dd, *J*<sub>1</sub> = 12.4, *J*<sub>2</sub> = 10.8 Hz, 1H), 3.23 (d, *J* = 10.5 Hz, 1H), 2.22 (s, 3H), 1.53 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.4, 155.6, 151.3, 149.3, 141.1, 138.6, 138.1, 131.9, 131.0, 130.6, 129.3, 129.2, 128.7, 128.6, 128.0, 127.4, 127.2, 126.3, 124.7, 124.2, 123.8, 123.2, 123.1, 123.0, 114.3, 99.8, 83.8, 40.1, 28.1, 21.3; **FTIR (KBr)** cm<sup>-1</sup>, 3058, 3027, 2977, 2925, 1774, 1727, 1513, 1459, 1347, 1298, 1251, 1151, 1094, 1058, 785, 745, 701, 595. **HRMS ESI** (*m/z*) [*M*+Na]<sup>+</sup>, calcd for C<sub>37</sub>H<sub>33</sub>NO<sub>4</sub>Na 578.2307; found 578.2301.

**tert-butyl (E)-3-(2-(3-(4-methoxyphenyl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**

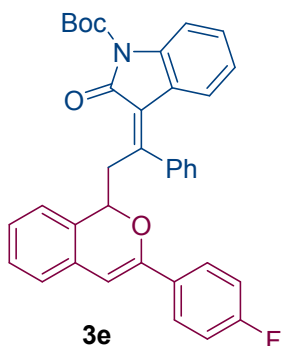


**oxoindoline-1-carboxylate (3c):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3c**. Yellow solid (101 mg, yield = 87%). *R*<sub>f</sub> = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 5H), 7.24–7.01 (m, 4H), 6.85–6.62 (m, 3H), 6.31 (s, 1H), 6.17 (d, *J* = 7.7 Hz, 1H), 5.73 (dd, *J*<sub>1</sub> = 10.1, *J*<sub>2</sub> = 3.4 Hz, 1H), 4.47 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 10.2 Hz, 1H), 3.77 (s, 3H), 3.24 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 3.5 Hz, 1H), 1.61 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.4, 159.8, 155.5, 151.1, 149.3, 141.1, 138.6, 131.2, 130.5, 129.5, 129.2, 128.7, 128.7, 128.1, 127.4, 127.2, 126.2, 126.2, 124.8, 124.2, 123.7, 123.3, 123.1, 123.0, 114.4, 113.4, 99.0, 83.9, 55.3, 40.1, 28.2; **FTIR** (KBr) cm<sup>-1</sup>, 3061, 2977, 2929, 2846, 1775, 1729, 1603, 1510, 1463, 1350, 1302, 1252, 1155, 1095, 1059, 1031, 1003, 976, 853, 784, 748, 702, 594; **HRMS ESI** (*m/z*) [*M*+Na]<sup>+</sup>, calcd for C<sub>37</sub>H<sub>33</sub>NO<sub>5</sub>Na 594.23; found 594.2274.

**tert-butyl (E)-3-(2-(3-(3,5-dimethylphenyl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**



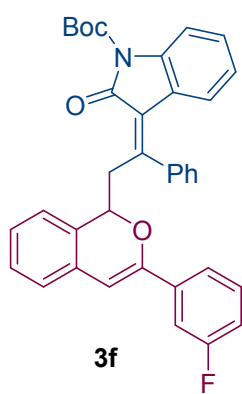
**oxoindoline-1-carboxylate (3d):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3d**. Yellow solid (66 mg, yield = 58%). *R*<sub>f</sub> = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.44–7.20 (m, 6H), 7.19–6.99 (m, 7H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.77 (s, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.32 (s, 1H), 6.10 (d, *J* = 7.5 Hz, 1H), 5.65 (dd, *J*<sub>1</sub> = 10.3, *J*<sub>2</sub> = 3.6 Hz, 1H), 4.46 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 10.4 Hz, 1H), 3.11 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 3.7 Hz, 1H), 2.06 (s, 6H), 1.50 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.5, 155.4, 151.6, 149.3, 141.1, 138.6, 137.4, 134.7, 131.20, 130.8, 130.2, 129.4, 129.2, 128.7, 128.6, 128.1, 127.3, 126.4, 124.9, 124.2, 124.0, 123.3, 123.2, 123.0, 122.8, 114.4, 100.4, 83.9, 76.5, 40.1, 28.2, 21.3; **FTIR** (KBr) cm<sup>-1</sup>, 3057, 2974, 2926, 2860, 1776, 1725, 1626, 1600, 1463, 1351, 1302, 1253, 1155, 1095, 1025, 1004, 977, 920, 846, 788, 747, 703, 596; **HRMS ESI** (*m/z*) [*M*+Na]<sup>+</sup>, calcd for C<sub>38</sub>H<sub>35</sub>NO<sub>4</sub>Na 592.2464; found 592.2463.



**tert-butyl (E)-3-(2-(3-(4-fluorophenyl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-oxoindoline-1-carboxylate (3e):** The *E/Z* ratio

(>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3e**. Yellow solid (73 mg, yield = 66%).  $R_f$  = 0.5 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J$  = 8.2 Hz, 1H), 7.557.31 (m, 6H), 7.20 (ddd,  $J_1$  = 17.6,  $J_2$  = 10.1,  $J_3$  = 6.6 Hz, 4H), 7.06 (d,  $J$  = 6.9 Hz, 1H), 6.87 (t,  $J$  = 8.7 Hz, 2H), 6.73 (t,  $J$  = 7.7 Hz, 1H), 6.33 (s, 1H), 6.18 (d,  $J$  = 7.8 Hz, 1H), 5.76 (dd,  $J_1$  = 10.1,  $J_2$  = 3.2 Hz, 1H), 4.39 (dd,  $J_1$  = 13.1,  $J_2$  = 10.3 Hz, 1H), 3.28 (dd,  $J_1$  = 13.2,  $J_2$  = 3.3 Hz, 1H), 1.63 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 155.5, 150.2, 149.2, 141.1, 138.6, 131.0, 130.6, 130.5, 129.3, 128.8, 128.2, 127.2, 126.7, 126.6, 126.5, 124.8, 124.4, 124.0, 123.3, 123.1, 122.9, 115.1, 114.8, 114.5, 100.3, 84.1, 77.0, 40.4, 28.2, 25.7; FTIR (KBr)  $\text{cm}^{-1}$ , 3064, 2979, 2925, 2853, 1775, 1732, 1600, 1507, 1463, 1349, 1303, 1252, 1154, 1096, 1060, 1003, 976, 840, 785, 749, 703, 594; HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{36}\text{H}_{30}\text{FNO}_4\text{Na}$  582.2057; found 582.2080.

**tert-butyl (E)-3-(2-(3-(3-fluorophenyl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**



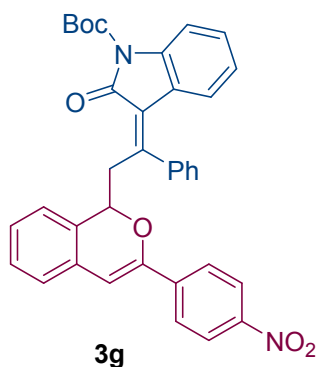
**oxoindoline-1-carboxylate (3f):** The *E/Z* ratio (>19:1) was determined

by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3f**.

Yellow solid (80 mg, yield = 72%).  $R_f$  = 0.5 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J$  = 8.2 Hz, 1H), 7.42 - 7.32 (m, 5H), 7.30-6.95 (m, 7H), 6.95-6.85 (m, 1H), 6.72 (t,  $J$  = 7.7 Hz, 1H), 6.39 (s, 1H), 6.21 (d,  $J$  = 7.9 Hz, 1H), 5.79 (dd,  $J_1$  = 10.1,  $J_2$  = 3.2 Hz, 1H), 4.29 (dd,  $J_1$  = 13.1,  $J_2$  = 10.2 Hz, 1H), 3.35 (dd,  $J_1$  = 13.2,  $J_2$  = 3.2 Hz, 1H),

1.63 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 164.3, 161.1, 155.5, 149.8, 149.81, 149.2, 141.0, 138.6, 137.1, 137.0, 130.8, 130.3, 129.4, 129.3, 129.3, 128.8, 128.8, 128.2, 127.6, 127.1, 124.7, 124.5, 124.2, 123.3, 123.1, 122.9, 120.2, 120.2, 115.1, 114.8, 114.4, 111.8, 111.4, 101.5, 84.0, 40.4, 28.2; FTIR (KBr)  $\text{cm}^{-1}$ , 2927, 2853, 1775, 1730, 1609, 1488, 1463, 1350, 1306, 1253, 1157, 1096, 1055, 1001, 785, 749, 699; HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{36}\text{H}_{30}\text{FNO}_4\text{Na}$  582.2057; found 582.2043.

**tert-butyl (E)-3-(2-(3-(4-nitrophenyl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**



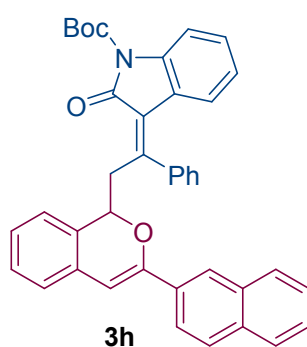
**oxoindoline-1-carboxylate (3g):** The *E/Z* ratio (>19:1) was

determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3g**. Yellow solid (84 mg, yield = 72%).  $R_f$

= 0.4 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92

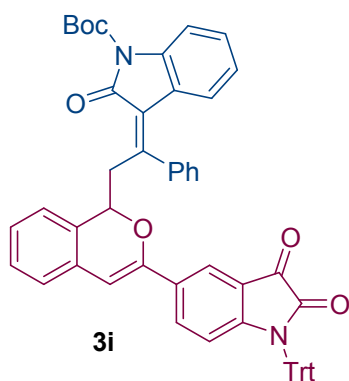
(d,  $J = 8.7$  Hz, 2H), 7.59 (d,  $J = 8.2$  Hz, 1H), 7.46 (d,  $J = 8.7$  Hz, 2H), 7.26 (s, 4H), 7.23–7.14 (m, 4H), 7.1–6.98 (m, 2H), 6.64 (t,  $J = 7.7$  Hz, 1H), 6.49 (s, 1H), 6.11 (d,  $J = 7.9$  Hz, 1H), 5.72 (d,  $J = 10.1$  Hz, 1H), 4.28 (t, 12.0 Hz, 1H), 3.18 (d,  $J = 13.2$  Hz, 1H), 1.53 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 155.0, 148.9, 148.6, 147.0, 140.9, 140.9, 138.4, 131.0, 129.6, 129.4, 129.0, 128.9, 128.4, 128.0, 127.5, 127.1, 125.0, 124.9, 124.8, 124.6, 123.4, 123.3, 123.1, 122.7, 114.4, 104.5, 84.2, 77.2, 40.4, 28.1, 1.1; FTIR (KBr)  $\text{cm}^{-1}$ , 3078, 2978, 2930, 2853, 1776, 1733, 1598, 1513, 1463, 1369, 1345, 1302, 1253, 1154, 1095, 1057, 976, 857, 839, 811, 787, 753, 703, 594; HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_6\text{Na}$  609.2002; found 609.2024.

**tert-butyl (E)-3-(2-(3-(naphthalen-2-yl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**



**oxoindoline-1-carboxylate (3h):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3h**. Yellow solid (83 mg, yield = 70%).  $R_f = 0.65$  (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 8.6$  Hz, 1H), 7.86–7.67 (m, 3H), 7.57–7.47 (m, 1H), 7.47–7.37 (m, 1H), 7.35–7.28 (m, 3H), 7.25–7.20 (m, 2H), 7.21–7.06 (m, 3H), 7.06 – 6.87 (m, 4H), 6.63 (t,  $J = 7.7$  Hz, 1H), 6.59–6.51 (m, 1H), 6.08 (s, 1H), 6.02 (dd,  $J = 7.7, 4.7$  Hz, 2H), 3.88 (d,  $J = 2.3$  Hz, 1H), 3.85 (s, 1H), 1.70 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 157.5, 152., 149.4, 141.6, 138.5, 134.0, 133.7, 130.7, 130.5, 130.4, 129.3, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 127.6, 127.0, 126.3, 126.2, 125.9, 125.8, 125.7, 125.1, 124.8, 123.9, 123.7, 123.3, 123.2, 123.0, 114.4, 105.5, 84.3, 78.3, 77.3, 41.4, 28.3, 1.1; FTIR (KBr)  $\text{cm}^{-1}$ , 3054, 2967, 2925, 2856, 1771, 1732, 1613, 1461, 1369, 1348, 1306, 1251, 1149, 1097, 1028, 979, 923, 843, 788, 773, 750, 699, 595; HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{40}\text{H}_{33}\text{N}_2\text{O}_4\text{Na}$  614.2307; found 614.2300.

**tert-butyl (E)-3-(2-(3-(2,3-dioxo-1-tritylindolin-5-yl)-1H-isochromen-1-yl)-1-**

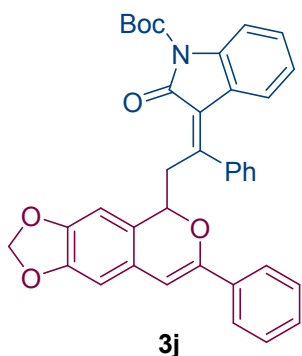


**phenylethylidene)-2-oxoindoline-1-carboxylate (3i):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3i**. Dark red solid (111 mg, yield = 65%).  $R_f = 0.5$  (EtOAc/Hexane = 1/3);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.2$  Hz, 1H), 7.56 (d,  $J = 1.6$  Hz, 2H), 7.45 (d,  $J = 6.9$  Hz, 7H), 7.42–7.37 (m, 2H), 7.37–7.27 (m, 9H), 7.22–7.07 (m, 5H), 7.00 (dd,  $J_1 = 12.6, J_2 = 8.9$  Hz, 2H), 6.90

(d,  $J = 6.3$  Hz, 2H), 6.72 (t,  $J = 7.7$  Hz, 1H), 6.26 (d,  $J = 7.9$  Hz, 1H), 6.21 (d,  $J = 8.7$  Hz, 1H), 6.18 (s, 1H), 5.84 (dd,  $J = 8.1, 4.4$  Hz, 1H), 3.82- 3.60 (m, 2H), 1.67 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  182.4, 165.8, 159.3, 156.0, 151.1, 149.0, 148.5, 141.0, 140.9, 140.6, 138.3, 130.2, 129.9, 129.5, 129.0, 128.6, 128.5, 127.8, 127.2, 127.0, 124.0, 123.2, 122.7, 122.6, 118.5, 100.8, 84.1, 75.2, 40.5, 29.5, 28.0; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3058, 2978, 2928, 2855, 1739, 1618, 1486, 1348, 1302, 1253, 1153, 1097, 1061, 1001, 905, 841, 787, 745, 703, 631, 596, 467. **HRMS ESI** ( $m/z$ ) [ $\text{M}+\text{Na}$ ] $^+$ , calcd for  $\text{C}_{57}\text{H}_{44}\text{N}_2\text{O}_6\text{Na}$  875.3097; found 875.3088.

*tert*-butyl

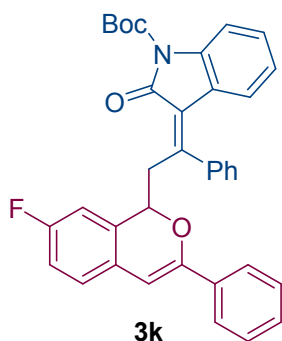
**(*E*)-2-oxo-3-(1-phenyl-2-(7-phenyl-5*H*-[1,3]dioxolo[4,5-*g*]isochromen-5-yl)ethylidene)indoline-1-carboxylate (3j):** The *E/Z* ratio (>19:1)



was determined by  $^1\text{H NMR}$  analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3j**. Brown solid (85 mg, yield = 74%).  $R_f = 0.4$  (EtOAc/Hexane = 1/9);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.67 (d,  $J = 8.2$  Hz, 1H), 7.39–7.30 (m, 3H), 7.30–7.19 (m, 5H), 7.15–7.02 (m, 4H), 6.71 (s, 1H), 6.64 (t,  $J = 6.0$  Hz, 1H), 6.49 (s, 1H), 6.20 (s, 1H), 6.12 (d,  $J = 7.6$  Hz, 1H), 5.84 (s, 2H), 5.61 (dd,  $J_1 = 10.0, J_2 = 3.2$  Hz, 1H), 4.17 (dd,  $J_1 = 13.1, J_2 = 10.1$  Hz, 1H), 3.23 (dd,  $J_1 = 13.1, J_2 = 3.3$  Hz, 1H), 1.54 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 155.7, 149.6, 149.3, 147.3, 146.3, 141.1, 138.6, 134.7, 129.3, 128.7, 128.7, 128.0, 128.0, 127.6, 127.1, 125.2, 124.6, 124.5, 124.3, 123.3, 123.1, 123.0, 114.4, 105.6, 104.7, 100.9, 100.7, 84.0, 77.3, 40.4, 28.2; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3061, 2977, 2927, 1775, 1732, 1599, 1482, 1370, 1350, 1302, 1250, 1155, 1096, 1043, 939, 846, 758, 696; **HRMS ESI** ( $m/z$ ) [ $\text{M}+\text{Na}$ ] $^+$ , calcd for  $\text{C}_{37}\text{H}_{31}\text{NO}_6\text{Na}$  608.2049; found 608.2031.

*tert*-butyl

**(*E*)-3-(2-(7-fluoro-3-phenyl-1*H*-isochromen-1-yl)-1-phenylethylidene)-2-**



**oxoindoline-1-carboxylate (3k):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H NMR}$  analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3k**. Yellow solid (86 mg, yield = 77%).  $R_f = 0.4$  (EtOAc/Hexane = 1/9);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 8.2$  Hz, 1H), 7.43–7.32 (m, 3H), 7.26 (bs, 5H), 7.18–7.04 (m, 4H), 7.00–6.88 (m, 2H), 6.82 (td,  $J_1 = 8.4, J_2 = 2.5$  Hz, 1H), 6.64 (t,  $J = 7.7$

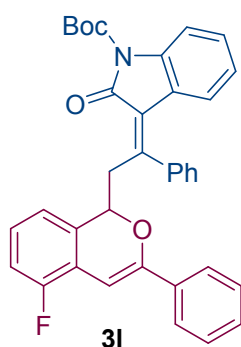
Hz, 1H), 6.28 (s, 1H), 6.13 (d,  $J = 7.9$  Hz, 1H), 5.65 (dd,  $J_1 = 10.1, J_2 = 3.1$  Hz, 1H), 4.22 (dd,  $J_1 = 13.1, J_2 = 10.2$  Hz, 1H), 3.26 (dd,  $J_1 = 13.2, J_2 = 3.2$  Hz, 1H), 1.54 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 160.1, 155.2, 150.5, 149.2, 140.9, 138.6, 134.5, 132.6, 132.5, 129.4,



129.3, 129.3, 128.8, 128.3, 128.0, 127.6, 127.1, 127.0, 125.4, 125.3, 124.8, 124.6, 123.3, 123.1, 122.9, 115.0, 114.7, 144.5, 111.9, 111.6, 99.8, 84.0, 40.1, 28.2, 1.1; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3057, 2976, 2930, 1784, 1723, 1603, 1494, 1465, 1348, 1301, 1250, 1155, 1096, 1053, 977, 837, 744, 691, 592; **HRMS ESI** ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{36}\text{H}_{30}\text{FNO}_4\text{Na}$  582.2057; found 582.2058.

*tert*-butyl

**(*E*)-3-(2-(5-fluoro-3-phenyl-1*H*-isochromen-1-yl)-1-phenylethylidene)-2-**



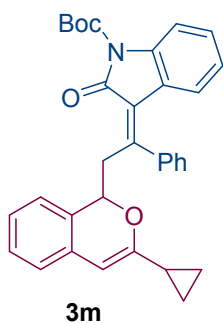
**3l**

**oxoindoline-1-carboxylate (3l):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3l**. Yellow solid (75 mg, yield = 67%).  $R_f$  = 0.45 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.76 (d,  $J$  = 8.2 Hz, 1H), 7.49 (dd,  $J_1$  = 7.7,  $J_2$  = 1.7 Hz, 2H), 7.33 (bs, 4H), 7.30–7.19 (m, 4H), 7.19–7.09 (m, 2H), 7.05 (t,  $J$  = 7.3 Hz, 1H), 7.01–6.89 (m,

1H), 6.73 (t,  $J$  = 7.7 Hz, 1H), 6.60 (s, 1H), 6.20 (d,  $J$  = 7.7 Hz, 1H), 5.79 (dd,  $J_1$  = 10.1,  $J_2$  = 3.4 Hz, 1H), 4.33 (dd,  $J_1$  = 13.2,  $J_2$  = 10.2 Hz, 1H), 3.37 (dd,  $J_1$  = 13.2,  $J_2$  = 3.5 Hz, 1H), 1.62 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 158.6, 155.1, 151.8, 149.3, 141.0, 138.6, 134.5, 132.6, 132.6, 129.4, 128.8, 128.6, 128.1, 127.3, 127.2, 124.9, 124.9, 123.3, 123.1, 122.9, 120.1, 119.2, 119.0, 114.7, 114.5, 114.4, 93.1, 93.0, 84.0, 76.5, 40.1, 36.7, 28.2, 1.1; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3089, 3058, 2954, 2933, 2859, 1726, 1609, 1567, 1463, 1347, 1296, 1249, 1151, 1093, 1058, 841, 751, 700, 609; **HRMS ESI** ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{36}\text{H}_{30}\text{FNO}_4\text{Na}$  582.2057; found 582.2051.

*tert*-butyl

**(*E*)-3-(2-(3-cyclopropyl-1*H*-isochromen-1-yl)-1-phenylethylidene)-2-**



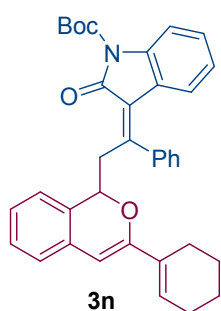
**3m**

**oxoindoline-1-carboxylate (3m)** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3m**. Yellow solid (81 mg, yield = 80%).  $R_f$  = 0.6 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.78 (d,  $J$  = 8.2 Hz, 1H), 7.46 (s, 5H), 7.11 (ddd,  $J_1$  = 24.5,  $J_2$  = 15.2,  $J_3$  = 7.9 Hz, 5H), 6.86 (d,  $J$  = 7.3 Hz, 1H), 6.73 (t,  $J$  = 7.7 Hz, 1H), 6.18 (d,  $J$  = 7.9 Hz, 1H), 5.59 (s, 1H), 5.51 (dd,  $J$

= 9.9, 3.4 Hz, 1H), 4.23 (dd,  $J_1$  = 13.1,  $J_2$  = 10.1 Hz, 1H), 3.35 (dd,  $J_1$  = 13.2,  $J_2$  = 3.4 Hz, 1H), 1.68 (s, 9H), 1.25–1.12 (m, 1H), 0.70–0.60 (m, 1H), 0.60–0.45 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 156.4, 156.3, 149.5, 141.4, 138.65, 131.3, 129.8, 129.3, 128.8, 128.7, 128.0,

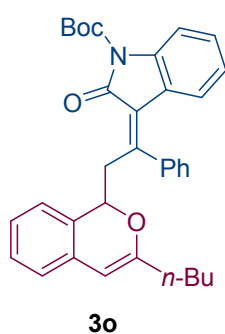
127.5, 125.6, 124.5, 124.3, 123., 123.20, 123.1, 122.4, 114.5, 98.4, 84.2, 76.8, 40.1, 28.3, 13.6, 5.7, 4.8; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3074, 2978, 2925, 2868, 1779, 1733, 1643, 1601, 1463, 1349, 1302, 1253, 1154, 1096, 784, 749, 704, 598; **HRMS ESI** ( $m/z$ )  $[M+Na]^+$ , calcd for  $\text{C}_{33}\text{H}_{31}\text{NO}_4\text{Na}$  528.2151; found 528.2157.

**tert-butyl (E)-3-(2-(3-(cyclohex-1-en-1-yl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**



**oxoindoline-1-carboxylate (3n):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3n**. Yellow solid (70 mg, yield = 64%).  $R_f$  = 0.6 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J$  = 8.2 Hz, 1H), 7.49-7.33 (m, 3H), 7.33-7.21 (m, 2H), 7.07 (dt,  $J_1$  = 11.2,  $J_2$  = 5.8 Hz, 2H), 7.00 (t,  $J$  = 6.1 Hz, 2H), 6.92 (d,  $J$  = 7.4 Hz, 1H), 6.63 (t,  $J$  = 7.7 Hz, 1H), 6.05 (d,  $J$  = 7.8 Hz, 1H), 5.94 (s, 1H), 5.84 (s, 1H), 5.47 (dd,  $J$  = 10.4, 3.5 Hz, 1H), 4.53 (dd,  $J_1$  = 13.0,  $J_2$  = 10.6 Hz, 1H), 2.84 (dd,  $J_1$  = 13.1,  $J_2$  = 3.5 Hz, 1H), 2.11 (m, 2H), 1.84 (m, 2H), 1.59 (s, 9H), 1.55-1.48 (m, 2H), 1.44-1.36 (m, 2H), 0.89-0.72 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 154.9, 151.6, 149.5, 141.0, 138.4, 131.4, 131.2, 130.8, 128.7, 128.6, 127.9, 127.3, 126.1, 126.0, 124.8, 124.1, 124.06, 123.3, 123.1, 123.1, 114.3, 99.6, 84.0, 75.7, 39.7, 28.3, 25.5, 24.0, 22.6, 22.0; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3054, 2926, 2860, 1770, 1727, 1599, 1458, 1346, 1301, 1250, 1150, 1094, 1033, 975, 917, 844, 784, 746, 700, 594; **HRMS ESI** ( $m/z$ )  $[M+Na]^+$ , calcd for  $\text{C}_{36}\text{H}_{35}\text{NO}_4\text{Na}$  568.2464; found 568.2465.

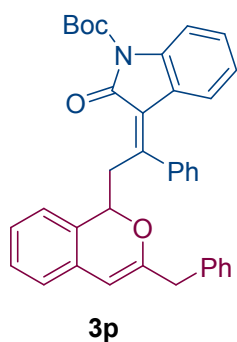
**tert-butyl (E)-3-(2-(3-butyl-1H-isochromen-1-yl)-1-phenylethylidene)-2-oxoindoline-1-**



**carboxylate (3o):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3o**. Yellow solid (42 mg, yield = 40%).  $R_f$  = 0.6 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J$  = 8.2 Hz, 1H), 7.41 (s, 4H), 7.20 (dd,  $J_1$  = 15.4,  $J_2$  = 8.5 Hz, 2H), 7.15 - 6.97 (m, 4H), 6.78 (d,  $J$  = 7.2 Hz, 1H), 6.65 (t,  $J$  = 7.7 Hz, 1H), 6.14 (d,  $J$  = 7.9 Hz, 1H), 5.56 (dd,  $J_1$  = 10.0,  $J_2$  = 2.5 Hz, 1H), 5.41 (s, 1H), 3.83 (dd,  $J_1$  = 12.6,  $J_2$  = 10.4 Hz, 1H), 3.43 (dd,  $J_1$  = 12.9,  $J_2$  = 2.4 Hz, 1H), 1.60 (s, 9H), 1.32-1.04 (m, 5H), 0.87-0.65 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 157.2, 155.9, 149.4, 142.0, 138.6, 130.8, 130.0, 129.2, 128.7, 128.7, 127.9, 125.9, 124.6, 123.4, 123.1, 122.6,

114.5, 99.5, 84.2, 77.4, 40.9, 32.9, 28.5, 28.3, 22.4, 13.9; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3059, 2926, 2861, 1721, 1641, 1609, 1563, 1463, 1349, 1300, 1251, 1156, 1092, 1019, 849, 788, 744, 697, 591; **HRMS ESI** ( $m/z$ )  $[M+Na]^+$ , calcd for  $\text{C}_{34}\text{H}_{35}\text{NO}_4\text{Na}$  544.2464; found 544.2467.

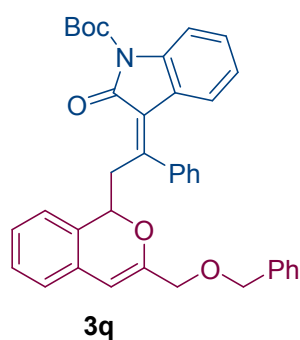
**tert-butyl (E)-3-(2-(3-benzyl-1H-isochromen-1-yl)-1-phenylethylidene)-2-oxoindoline-1-**



**carboxylate (3p):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3p**. Yellow solid (84 mg, yield = 76%).  $R_f$  = 0.6 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J$  = 8.2 Hz, 1H), 7.51–7.30 (m, 4H), 7.18–7.00 (m, 10H), 6.74 (dd,  $J_1$  = 5.6,  $J_2$  = 2.9 Hz, 1H), 6.65 (t,  $J$  = 7.7 Hz, 1H), 6.14 (d,  $J$  = 7.8 Hz, 1H), 5.54 (dd,  $J_1$  = 10.3,  $J_2$  = 2.3 Hz, 1H), 5.29

(s, 1H), 3.92 (dd,  $J_1$  = 13.0,  $J_2$  = 10.5 Hz, 1H), 3.34 (dd,  $J_1$  = 13.1,  $J_2$  = 2.5 Hz, 1H), 2.82 (q,  $J$  = 15.8 Hz, 2H), 1.61 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) 165.9, 156.8, 154.8, 149.4, 141.9, 138.6, 137.3, 130.5, 130.0, 129.4, 128.8, 128.7, 128.2, 127.9, 127.2, 126.4, 126.2, 124.4, 124.1, 123.4, 123.0, 122.9, 114.5, 101.2, 84.3, 77.4, 40.8, 39.5, 28.3; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3063, 2971, 2926, 2856, 1779, 1729, 1651, 1600, 1491, 1461, 1351, 1303, 1252, 1154, 1097, 1029, 1002, 846, 785, 752, 704, 593; **HRMS ESI** ( $m/z$ )  $[M+Na]^+$ , calcd for  $\text{C}_{37}\text{H}_{33}\text{NO}_4\text{Na}$  578.2307; found 578.2320.

**tert-butyl (E)-3-(2-(3-((benzyloxy)methyl)-1H-isochromen-1-yl)-1-phenylethylidene)-2-**

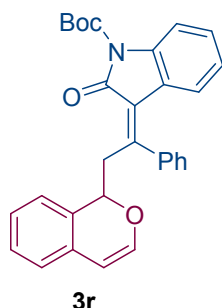


**oxoindoline-1-carboxylate (3q):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3q**. Yellow solid (55 mg, yield = 47%).  $R_f$  = 0.5 (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J$  = 8.2 Hz, 1H), 7.41 (s, 4H), 7.37–7.10 (m, 10H), 7.03–6.85 (m, 1H), 6.72 (t,  $J$  = 7.7 Hz, 1H), 6.21 (d,  $J$  = 7.9 Hz, 1H), 5.84 (s, 1H),

5.69 (dd,  $J_1$  = 10.2,  $J_2$  = 2.1 Hz, 1H), 4.43 (s, 2H), 3.91 (dd,  $J_1$  = 12.8,  $J_2$  = 10.5 Hz, 1H), 3.53 (d,  $J$  = 13.4 Hz, 2H), 3.35 (d,  $J$  = 13.7 Hz, 1H), 1.68 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 156.7, 151.3, 149.1, 141.9, 138.6, 138.1, 130.5, 129.8, 129.4, 129.2, 128.8, 128., 128.09, 127.9, 127.7, 127.7, 127.1, 126.8, 124.7, 124.2, 123.4, 123.1, 123.0, 114.5, 101.5, 84.3, 77.7, 72.4, 68.6, 40.9, 28.3; **FTIR** (KBr)  $\text{cm}^{-1}$ , 3064, 3027, 2979, 2931, 2861, 1729, 1655, 1603,

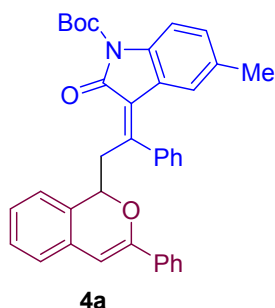
1459, 1347, 1297, 1250, 1149, 1093, 1009, 743, 694, 592. **HRMS ESI** (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>38</sub>H<sub>35</sub>NO<sub>5</sub>Na 608.2413; found 608.2411.

*tert*-butyl



**(E)-3-(2-(1*H*-isochromen-1-yl)-1-phenylethylidene)-2-oxoindoline-1-carboxylate (3r)**: The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **3r**. Yellow solid (65 mg, yield = 70%). *R<sub>f</sub>* = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.49 (bs, 4H), 7.38-7.31 (m, 1H), 7.24-7.16 (m, 3H), 6.94 (dd, *J* = 5.9, 2.7 Hz, 1H), 6.77 (t, *J* = 7.7 Hz, 1H), 6.24 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 5.7 Hz, 1H), 5.73 (dd, *J* = 10.4, 3.0 Hz, 1H), 5.68 (d, *J* = 5.7 Hz, 1H), 3.80 (dd, *J*<sub>1</sub> = 12.8, *J*<sub>2</sub> = 10.5 Hz, 1H), 3.60 (dd, *J*<sub>1</sub> = 12.8, *J*<sub>2</sub> = 3.0 Hz, 1H), 1.72 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 166.1, 156.8, 149.3, 143.0, 141.8, 138.6, 131.1, 129.5, 129.4, 129.0, 129.0, 128.7, 128.5, 128.0, 127.7, 126.8, 126.8, 124.9, 124.0, 123.4, 123.2, 123.1, 123.0, 114.5, 104.5, 84.3, 40.8, 28.3; **FTIR** (KBr) cm<sup>-1</sup>, 3057, 3023, 2982, 2931, 2858, 1726, 1625, 1599, 1462, 1351, 1302, 11, 1225, 1201, 1152, 1095, 1067, 1044, 1000, 979, 844, 769, 746, 704, 596; **HRMS ESI** (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>30</sub>H<sub>27</sub>NO<sub>4</sub>Na 488.1838; found 488.1838.

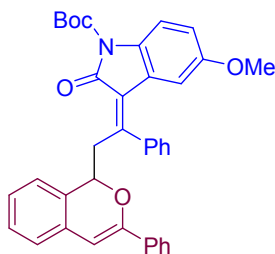
*tert*-butyl



**(E)-5-methyl-2-oxo-3-(1-phenyl-2-(3-phenyl-1*H*-isochromen-1-yl)ethylidene)indoline-1-carboxylate (4a)**: The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4a**. Yellow solid (86 mg, yield = 75%). *R<sub>f</sub>* = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.3 Hz, 1H), 7.50-7.43 (m, 2H), 7.40-7.29 (m, 5H), 7.27-7.11 (m, 7H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.39 (s, 1H), 5.92 (s, 1H), 5.78 (dd, *J*<sub>1</sub> = 10.1, *J*<sub>2</sub> = 3.4 Hz, 1H), 4.36 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 10.2 Hz, 1H), 3.33 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 3.4 Hz, 1H), 1.98 (s, 3H), 1.61 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.8, 155.2, 151.2, 149.3, 141.2, 136.4, 134.8, 132.5, 130.8, 130.7, 129.2, 128.6, 128.3, 128.1, 128.0, 127.5, 127.1, 126.6, 124.9, 124.8, 124.4, 123.9, 123.8, 123.0, 114.2, 100.5, 83.8, 76.9, 40.2, 29.7, 28.2, 21.1; **FTIR** (KBr) cm<sup>-1</sup>, 3060, 2988, 2924, 2854, 1729, 1609, 1482, 1452, 1371, 1338,

1302, 1283, 1253, 1161, 1115, 1053, 981, 943, 911, 846, 815, 761, 737, 687, 531; **HRMS ESI** (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>37</sub>H<sub>33</sub>NO<sub>4</sub>Na 578.2307; found 578.2322.

*tert*-butyl

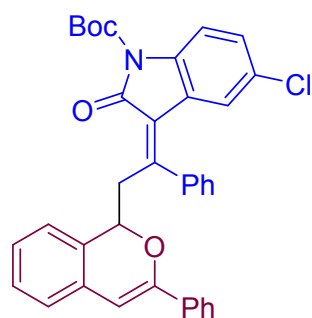


**4b**

**(E)-5-methoxy-2-oxo-3-(1-phenyl-2-(3-phenyl-1H-isochromen-1-yl)ethylidene)indoline-1-carboxylate (4b):** The *E/Z* ratio (>19:1) was

determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4b**. Yellow solid (86 mg, yield = 72%). R<sub>f</sub> = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 8.9 Hz, 1H), 7.51–7.43 (m, 2H), 7.42–7.28 (m, 4H), 7.24–7.12 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.71 (dd, *J*<sub>1</sub> = 8.9, *J*<sub>2</sub> = 2.6 Hz, 1H), 6.39 (s, 1H), 5.80 (dd, *J*<sub>1</sub> = 10.1, *J*<sub>2</sub> = 3.2 Hz, 1H), 5.71 (d, *J* = 2.5 Hz, 1H), 4.36 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 10.3 Hz, 1H), 3.37 (s, 3H), 3.31 (d, *J* = 3.3 Hz, 1H), 1.61 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.8, 155.8, 155.5, 151.1, 149.3, 141.0, 134.80, 132.4, 130.8, 130.6, 129.4, 129.2, 128.7, 128.3, 128.1, 128.0, 127.6, 127.1, 126.7, 124.7, 124.4, 124.0, 123.8, 115.4, 115.1, 108.0, 100.6, 83.8, 76.9, 55.0, 40.3, 28.2; **FTIR** (KBr) cm<sup>-1</sup>, 3060, 2988, 2930, 2828, 1726, 1608, 1484, 1452, 1338, 1300, 1282, 1253, 1158, 1100, 1052, 1007, 943, 813, 762, 697, 608, 531; **HRMS ESI** (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>37</sub>H<sub>33</sub>NO<sub>5</sub>Na 594.23; found 594.2273.

*tert*-butyl

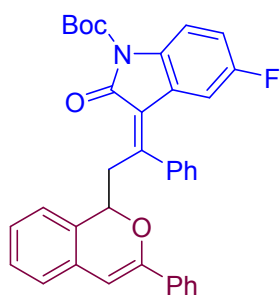


**4c**

**(E)-5-chloro-2-oxo-3-(1-phenyl-2-(3-phenyl-1H-isochromen-1-yl)ethylidene)indoline-1-carboxylate (4c):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR

analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4c**. Yellow solid (79 mg, yield = 66%). R<sub>f</sub> = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.7 Hz, 1H), 7.51–7.34 (m, 5H), 7.34–7.12 (m, 9H), 7.12–7.04 (m, 1H), 6.41 (s, 1H), 6.05 (s, 1H), 5.77 (dd, *J*<sub>1</sub> = 10.1, *J*<sub>2</sub> = 2.7 Hz, 1H), 4.59–4.31 (m, 1H), 3.26 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 3.0 Hz, 1H), 1.60 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 164.9, 157.6, 151.0, 149.1, 140.4, 137.0, 134.7, 130.8, 130.5, 129.6, 129.4, 129.1, 128.8, 128.4, 128.4, 128.2, 128.1, 127.2, 126.9, 126.7, 124.7, 124.4, 124.3, 124.1, 124.0, 123.2, 115.6, 100.6, 84.3, 40.3, 28.2; **FTIR** (KBr) cm<sup>-1</sup>, 3102, 3070, 2988, 2927, 2849, 1733, 1610, 1492, 1454, 1372, 1333, 1294, 1275, 1156, 1102, 1055, 983, 934, 812, 764, 693, 606; **HRMS ESI** (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>30</sub>NO<sub>4</sub>ClNa 598.1761; found 598.1774.

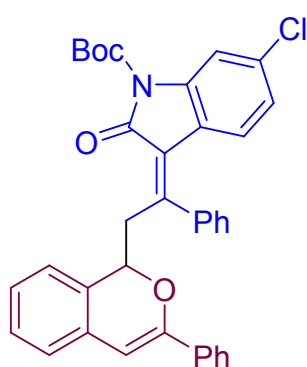
*tert*-butyl



**4d**

**(E)-5-fluoro-2-oxo-3-(1-phenyl-2-(3-phenyl-1*H*-isochromen-1-yl)ethylidene)indoline-1-carboxylate (4d):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4d**. Yellow solid (88 mg, yield = 75%). *R<sub>f</sub>* = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J*<sub>1</sub> = 9.0, *J*<sub>2</sub> = 4.9 Hz, 1H), 7.46 (dd, *J*<sub>1</sub> = 4.5, *J*<sub>2</sub> = 2.6 Hz, 2H), 7.37 (dd, *J*<sub>1</sub> = 27.8, *J*<sub>2</sub> = 11.5 Hz, 5H), 7.2–7.12 (m, 6H), 7.10 (dd, *J*<sub>1</sub> = 20.4,

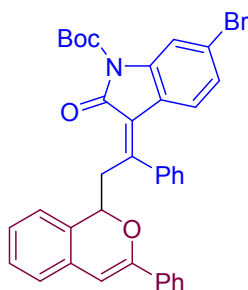
*J*<sub>2</sub> = 5.7 Hz, 1H), 6.95–6.78 (m, 1H), 6.40 (s, 1H), 5.96–5.69 (m, 2H), 4.41 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 10.3 Hz, 1H), 3.29 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 3.4 Hz, 1H), 1.60 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165., 160.5, 157.5, 157.3, 151.1, 149.2, 140.5, 134.7, 134.6, 130.8, 130.5, 129.6, 129.1, 128.4, 128.2, 128.0, 126.9, 126.7, 124.7, 124.3, 124.0, 115.6, 115.5, 115.3, 115.0, 110.4, 110.0, 100.6, 84.1, 76.8, 40.4, 29.8, 28.2; FTIR (KBr) cm<sup>-1</sup>, 3050, 2991, 2925, 2853, 1730, 1600, 1452, 1476, 1370, 1347, 1303, 1275, 1150, 1096, 1054, 948, 912, 870, 817, 763, 698, 614, 593, 533; HRMS ESI (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>30</sub>FNO<sub>4</sub>Na 582.2057; found 582.2076.



**4e**

*tert*-butyl **(E)-6-chloro-2-oxo-3-(1-phenyl-2-(3-phenyl-1*H*-isochromen-1-yl)ethylidene)indoline-1-carboxylate (4e):** The *E/Z* ratio (>19:1) was determined by <sup>1</sup>H NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4e**. Yellow solid (75 mg, yield = 65%). *R<sub>f</sub>* = 0.6 (EtOAc/Hexane = 1/9); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 1.8 Hz, 1H), 7.53–7.43 (m, 3H), 7.43–7.29 (m, 5H), 7.25–7.11 (m, 6H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.71 (dd,

*J*<sub>1</sub> = 8.4, *J*<sub>2</sub> = 1.8 Hz, 1H), 6.41 (s, 1H), 6.06 (d, *J* = 8.5 Hz, 1H), 5.75 (dd, *J*<sub>1</sub> = 10.2, *J*<sub>2</sub> = 3.3 Hz, 1H), 4.42 (dd, *J*<sub>1</sub> = 13.1, *J*<sub>2</sub> = 10.3 Hz, 1H), 3.25 (dd, *J*<sub>1</sub> = 13.2, *J*<sub>2</sub> = 3.4 Hz, 1H), 1.61 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.0, 156.2, 151.1, 149.0, 140.8, 139.3, 134.7, 134.3, 130.8, 130.5, 129., 128.94, 128.3, 128.2, 128.0, 127.3, 127.0, 126.6, 124.7, 124.3, 124.0, 123.8, 123.4, 121.4, 115.0, 100.6, 84.4, 40.3, 28.1; FTIR (KBr) cm<sup>-1</sup>, 3062, 2978, 2935, 2870, 1779, 1734, 1599, 1457, 1425, 1369, 1347, 1305, 1281, 1248, 1152, 1109, 1078, 1061, 1023, 975, 921, 845, 814, 763, 693, 610, 548; HRMS ESI (m/z) [M+Na]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>30</sub>NO<sub>4</sub>ClNa 598.1761; found 598.1759.

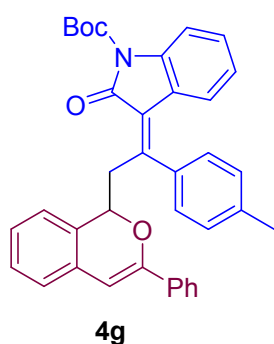


**4f**

*tert*-butyl **(E)-6-bromo-2-oxo-3-(1-phenyl-2-(3-phenyl-1*H*-isochromen-1-yl)ethylidene)indoline-1-carboxylate (4f):** The *E/Z* ratio

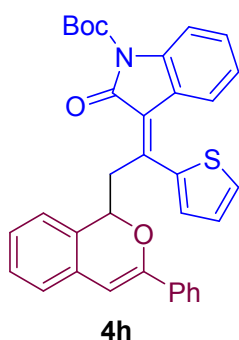
(>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4f**. Yellow solid (82 mg, yield = 66%).  $R_f = 0.6$  (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 1.7$  Hz, 1H), 7.46 (dd,  $J_1 = 7.6$ ,  $J_2 = 1.8$  Hz, 3H), 7.42–7.29 (m, 5H), 7.25–7.11 (m, 6H), 7.07 (d,  $J = 7.2$  Hz, 1H), 6.87 (dd,  $J_1 = 8.4$ ,  $J_2 = 1.8$  Hz, 1H), 6.41 (s, 1H), 6.00 (d,  $J = 8.4$  Hz, 1H), 5.74 (dd,  $J_1 = 10.2$ ,  $J_2 = 3.3$  Hz, 1H), 4.42 (dd,  $J_1 = 13.1$ ,  $J_2 = 10.3$  Hz, 1H), 3.24 (dd,  $J_1 = 13.2$ ,  $J_2 = 3.4$  Hz, 1H), 1.61 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 156.5, 151.1, 149.0, 140.8, 139.4, 134.7, 130.8, 130.5, 129.3, 128.9, 128.4, 128.2, 128.0, 127.3, 127.0, 126.7, 126.41, 124.7, 124.3, 124.1, 124.1, 122.4, 121.9, 117.8, 100.6, 84.5, 40.3, 28.2; FTIR (KBr)  $\text{cm}^{-1}$ , 3121, 3052, 2980, 2929, 2853, 1779, 1730, 1594, 1491, 1472, 1454, 1369, 1347, 1309, 1281, 1155, 1107, 1057, 1024, 973, 847, 808, 762, 690, 604, 538; HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{36}\text{H}_{30}\text{NO}_4\text{BrNa}$  642.13; found 642.1280.

**tert-butyl (E)-2-oxo-3-(2-(3-phenyl-1H-isochromen-1-yl)-1-(p-tolyl)ethylidene)indoline-1-carboxylate (4g):**



The  $E/Z$  ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4g**. Yellow solid (82 mg, yield = 73%).  $R_f = 0.6$  (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.2$  Hz, 1H), 7.42 (d,  $J = 6.0$  Hz, 2H), 7.37–7.00 (m, 12H), 6.75 (t,  $J = 7.7$  Hz, 1H), 6.38 (s, 1H), 5.79 (dd,  $J_1 = 10.0$ ,  $J_2 = 3.1$  Hz, 1H), 4.23 (dd,  $J_1 = 13.0$ ,  $J_2 = 10.3$  Hz,

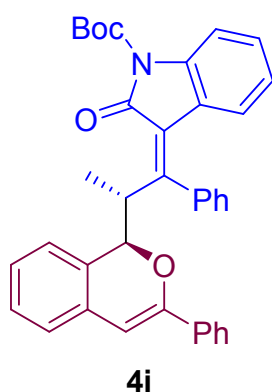
1H), 3.39 (dd,  $J_1 = 13.1$ ,  $J_2 = 3.2$  Hz, 1H), 2.35 (s, 3H), 1.63 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 156.4, 151.2, 149.3, 138.8, 138.5, 138.1, 134.7, 130.7, 129.9, 128.5, 128.2, 128.1, 127.9, 127.7, 127.1, 126.6, 124.8, 124.5, 124.3, 123.9, 123.2, 123.0, 114.4, 100.5, 84.0, 40.5, 28.2, 21.5; FTIR (KBr)  $\text{cm}^{-1}$ , 3068, 2965, 2925, 2853, 1741, 1722, 1601, 1462, 1350, 1303, 1259, 1153, 1092, 1057, 1030, 911, 810, 765, 748, 691, 584; HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{37}\text{H}_{33}\text{NO}_4\text{Na}$  578.2307; found 578.2311.



**tert-butyl (E)-2-oxo-3-(2-(3-phenyl-1H-isochromen-1-yl)-1-(thiophen-2-yl)ethylidene)indoline-1-carboxylate (4h):** The  $E/Z$  ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4h**. Yellow solid (85 mg, yield = 78%).  $R_f = 0.6$  (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 8.2$  Hz, 1H), 7.51–7.37 (m, 2H), 7.29 (d,  $J = 5.0$  Hz, 1H), 7.18 (s, 2H), 7.1-

7.09 (m, 5H), 7.09–7.04 (m, 1H), 7.01 (d,  $J = 7.3$  Hz, 1H), 6.93–6.86 (m, 1H), 6.82–6.68 (m, 2H), 6.36 (s, 1H), 5.77 (dd,  $J_1 = 9.7$ ,  $J_2 = 4.0$  Hz, 1H), 4.12 (dd,  $J_1 = 13.1$ ,  $J_2 = 9.8$  Hz, 1H), 3.41 (dd,  $J_1 = 13.1$ ,  $J_2 = 4.1$  Hz, 1H), 1.56 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 149.2, 147.9, 142.5, 138.7, 134.6, 130.9, 130.6, 129.1, 128.4, 128.2, 128.0, 127.9, 127.8, 126.7, 125.9, 124.8, 124.5, 124.0, 123.4, 122.0, 122.7, 114.6, 100.5, 84.1, 41.4, 28.2; FTIR (KBr)  $\text{cm}^{-1}$ , 2960, 2924, 2856, 1776, 1733, 1630, 1592, 1491, 1459, 1370, 1341, 1295, 1251, 1152, 1097, 1054, 968, 843, 789, 763, 709, 691. HRMS ESI ( $m/z$ )  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{34}\text{H}_{29}\text{NO}_4\text{SNa}$  570.1715; found 570.1728.

**tert-butyl (*E*)-2-oxo-3-(1-phenyl-2-(3-phenyl-1*H*-isochromen-1-yl)propylidene)indoline-1-carboxylate (**4i**):**



**1-carboxylate (**4i**):** The *E/Z* ratio (>19:1) was determined by  $^1\text{H}$  NMR analysis of the crude product. The crude mixture was purified by general procedure to give an inseparable mixture of diastereomers **4i**.

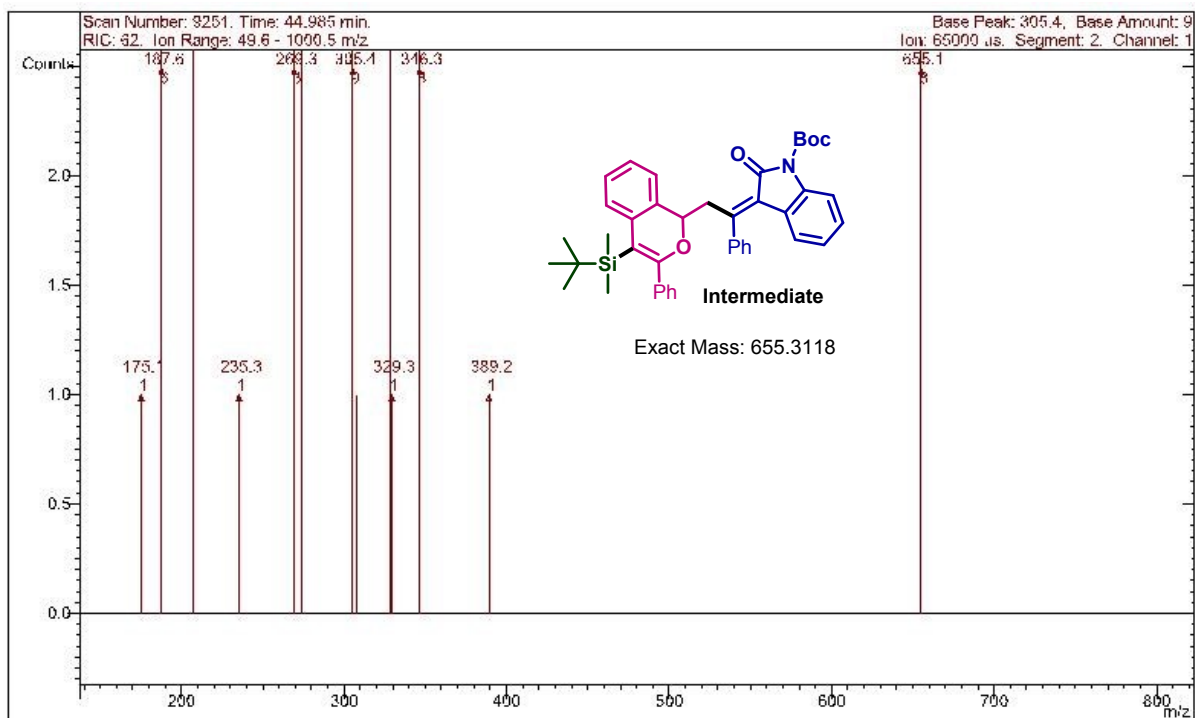
Off white solid (80 mg, yield = 72%).  $R_f = 0.6$  (EtOAc/Hexane = 1/9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 7.5$  Hz, 1H), 7.67 (dd,  $J_1 = 10.3$ ,  $J_2 = 5.7$  Hz, 1H), 7.64–7.49 (m, 4H), 7.27 (t,  $J = 7.3$  Hz, 2H), 7.21–7.01 (m, 5H), 7.01–6.86 (m, 3H), 6.68 (d,  $J = 7.7$  Hz, 1H), 6.65 (s, 1H), 5.81–5.66 (m, 1H), 5.61 (d,  $J = 7.8$  Hz, 1H), 5.26 (d,  $J = 10.4$

Hz, 1H), 1.58 (s, 3H), 1.54 (s, 6H), 0.88 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 164.98, 159.75, 150.98, 149.05, 138.30, 137.13, 134.40, 131.36, 129.73, 129.35, 128.90, 128.78, 128.51, 128.42, 128.24, 127.84, 127.06, 126.22, 125.74, 124.70, 124.60, 123.21, 123.12, 114.04, 101.43, 83.40, 79.40, 34.73, 28.22, 14.74. FTIR (KBr)  $\text{cm}^{-1}$ , 3064, 2956, 2925, 2854, 1779, 1735, 1631, 1600, 1460, 1372, 1347, 1293, 13, 1153, 1094, 1056, 1028, 797, 762, 691. HRMS ESI ( $m/z$ )  $[\text{M}+\text{H}]^+$ , calculated for  $\text{C}_{37}\text{H}_{34}\text{NO}_4$  556.2488; found 556.2516.

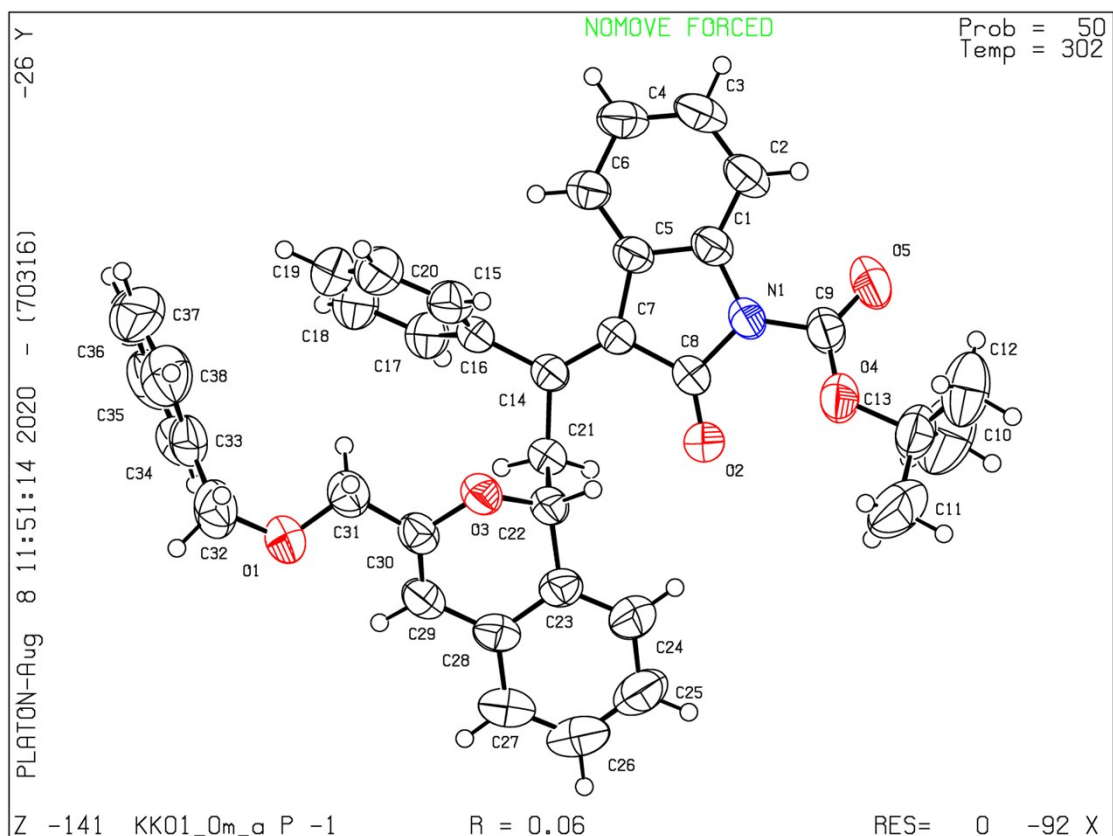


#### 4. GC-MS characterization of intermediate IV:

Silver tetrafluoroborate (20 mol%) was taken in the pre-dried reaction vessel and nitrogen was purged three times using standard Schlenk techniques to maintain inert conditions. Subsequently, dried DCM (1 mL) was added to the reaction vessel followed by addition of **1a** (0.2 mmol, 1 eq), **2a** (0.3 mmol, 1.5 eq) and benzoic acid (20 mol %). The resulting reaction mixture was stirred at room temperature under inert atmosphere. After one hour stirring, the aliquot was taken from the reaction mixture and diluted in acetonitrile solvent. Then after the mixture was filtered and injected in GC-MS for mass analysis. A mass peak of 655.13, similar to the silyl isochromene intermediate **IV** (655.31) was detected. This observation strongly supports the proposed mechanism.



**5. Crystallographic Data:**  
**(I) Crystal structure of compound 3q:**



**Figure S3.** Structure determination of **3q** by X-ray analysis

**X-Ray data collection, solution, and refinement for Compound 3q**

Bond precision: C-C = 0.0041 Å Wavelength=0.71073

Cell: a=10.5434(7) b=12.2090(8) c=12.9764(9)

alpha=89.428(2) beta=77.020(2) gamma=75.639(2)

Temperature: 302 K

	Calculated	Reported
Volume	1574.99(18)	1574.99(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1

Moiety formula	$C_{38}H_{35}NO_5$	$C_{38}H_{35}NO_5$
Sum formula	$C_{38}H_{35}NO_5$	$C_{38}H_{35}NO_5$
Mr	585.67	585.67
Dx,g cm-3	1.235	1.235
Z	2	2
Mu (mm-1)	0.081	0.081
F000	620.0	620.0
F000'	620.29	
h,k,lmax	14,16,17	14,16,17
Nref	7910	7910
Tmin,Tmax	0.983,0.987	0.983,0.987
Tmin'	0.980	

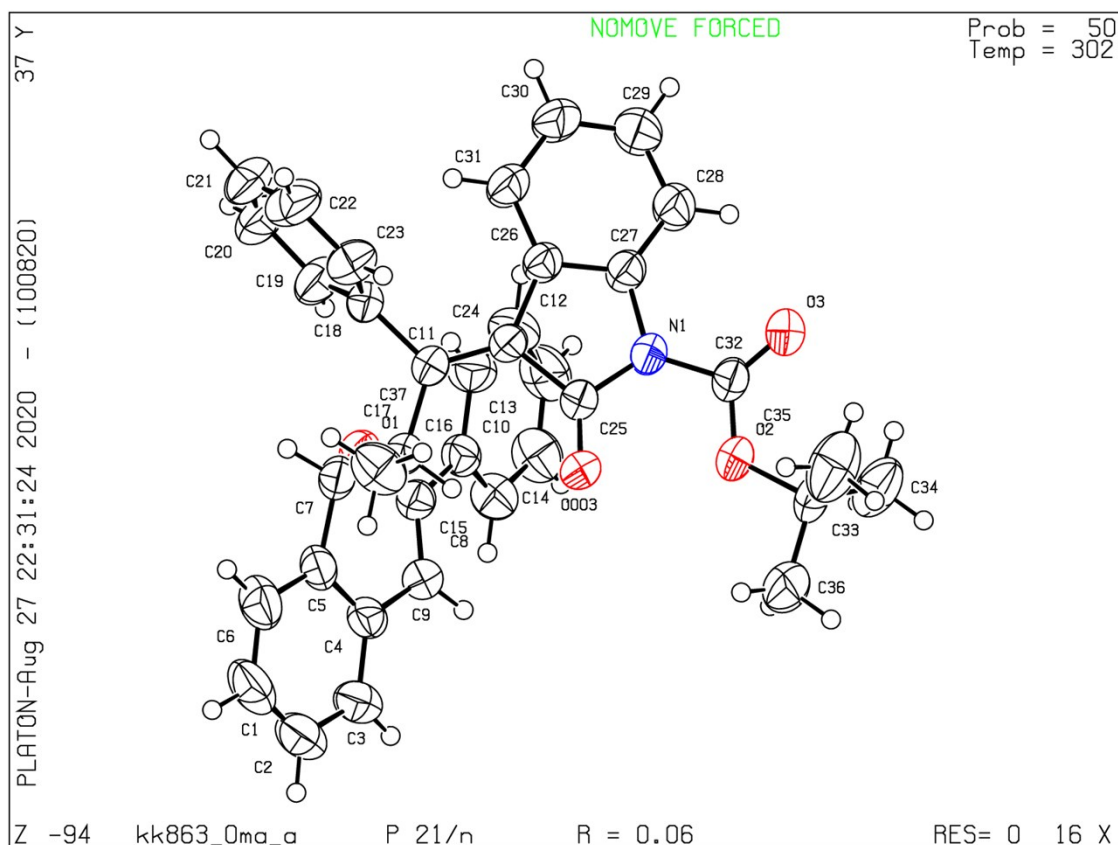
Correction method= # Reported T Limits: Tmin = 0.983 Tmax = 0.987  
AbsCorr = NONE

Data completeness= 1.000                      Theta(max)= 28.387

R(reflections)= 0.0626( 4522)                      wR2(reflections)= 0.2020( 7882)

S = 0.924                      Npar= 400

## (II) Crystal structure of compound 4i:



**Figure S4.** Structure determination of **4i** by X-ray analysis

**X-Ray data collection, solution, and refinement for Compound 4i**

Bond precision: C-C = 0.0034 Å Wavelength=0.71073

Cell: a=15.1432(6) b=12.4911(5) c=16.2178(6)

alpha=90 beta=104.238(1) gamma=90

Temperature: 302 K

	Calculated	Reported
Volume	2973.5(2)	2973.4(2)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn

Moiety formula	C <sub>37</sub> H <sub>33</sub> NO <sub>4</sub>	C <sub>37</sub> H <sub>33</sub> NO <sub>4</sub>
Sum formula	C <sub>37</sub> H <sub>33</sub> NO <sub>4</sub>	C <sub>37</sub> H <sub>33</sub> NO <sub>4</sub>
Mr	555.64	555.64
Dx,g cm-3	1.241	1.241
Z	4	4
Mu (mm-1)	0.080	0.080
F000	1176.0	1176.0
F000'	1176.53	
h,k,lmax	20,16,21	20,16,21
Nref	7443	7443
Tmin,Tmax	0.983,0.987	0.983,0.987
Tmin'	0.980	

Correction method= # Reported T Limits: Tmin=0.983 Tmax=0.987

AbsCorr = NONE

Data completeness= 1.000

Theta(max)= 28.357

R(reflections)= 0.0570( 3499)

wR2(reflections)= 0.1820( 7294)

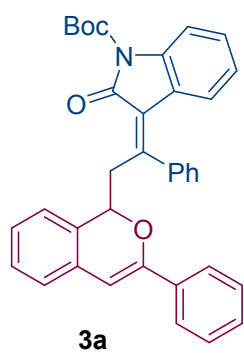
S = 0.939

Npar= 383

## 6. References

- (1) Tomás-Mendivil, E.; Starck, J.; Ortuno, J.-C.; Michelet, V. *Org. Lett.* **2015**, *17*, 6126.

(2) Rassa, G.; Zambrano, V.; Tanca, R.; Sartori, A.; Battistini, L.; Zanardi, F.; Curti, C.; Casiraghi, G. *Eur. J. Org. Chem.* **2012**, 3, 466.



### 7. $^1\text{H}$ and $^{13}\text{C}$ spectra of compound



