SUPPORTING INFORMATION

for the
communication
entitled

$AlCl_3$-Catalyzed Annulations of Ynamides Involving a Torquoselective Process for the Simultaneous Control of Central and Axial Chirality

authored by

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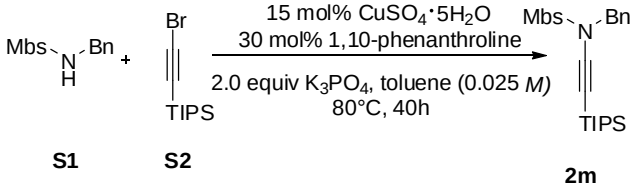
GENERAL EXPERIMENTAL INFORMATION

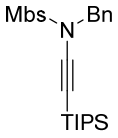
All reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker's Ascend^{TM} 400 NMR spectrometer using $CDCl_3$ as solvent with TMS or residual solvent as standard unless otherwise noted. ^{13}C NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as a standard. Infrared spectra were obtained on a Bruker ALPHA FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and $KMnO_4$ stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer. All spectral data obtained for new compounds are reported here.

General Procedure for Synthesis of TIPS-Terminated Ynamides.



S1 **S2** **2m**

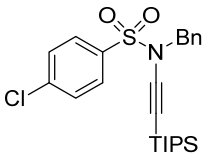
To a flame-dried screw-cap vial was added (in the following order) amide **S1** (554.7 mg, 2.00 mmol), $CuSO_4 \cdot 5H_2O$ (75.0 mg, 0.30 mmol), 1, 10-phenanthroline (108.1 mg, 0.60 mmol) and K_3PO_4 (849.1 mg, 4.00 mmol), toluene (8.0 mL, 0.25 *M* in amide), and the alkynyl bromide **S2** (627.0 mg, 2.40 mmol) under a nitrogen atmosphere. The vial was evacuated under vacuum and flushed with nitrogen three times, then sealed under nitrogen and heated to 80 ^{o}C. When the reaction was judged to be complete by TLC after 40 hours, the mixture was cooled to rt, filtered through a pad of silica gel, and purified by flash silica gel column chromatrography [gradient eluent: 50:1~20:1 petroleum ether/EtOAc + 3% NEt_3] to afford ynamide **2m** (906.3 mg, 1.98 mmol) in 99% yield.



2m

2m: R_f = 0.25 [20:1 petroleum ether/EtOAc]; white solid; mp = 45–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 21H), 3.87 (s, 3H), 4.50 (s, 2H), 6.91-6.95 (m, 2H), 7.27-7.30 (m, 5H), 7.77-7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 18.6, 55.6, 55.8, 70.3, 96.8, 114.2, 128.4, 128.6, 129.1, 129.3, 130.1,

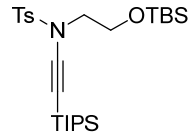
134.6, 163.8; IR (KBr) (cm^{-1}) 2943s, 2864s, 2166s, 1497s, 1595s, 1459m, 1370s, 1261s, 1162s, 1092m, 1027m; HRMS (ESI): m/z calcd for $C_{25}H_{35}NO_3SSiNa$ $[M+Na]^+$: 480.1999; found 480.1990.



2n

Ynamide **2n** (1.13 g, 2.45 mmol) was prepared from the corresponding amide (752.5 mg, 2.67 mmol) and alkynyl bromide (837.3 mg, 3.20 mmol) in 92% yield after stirred at 80 °C for 19.0 h.

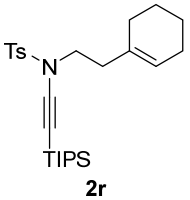
2n: R_f = 0.47 [20:1 petroleum ether/EtOAc]; white solid; mp = 49–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 21H), 4.53 (s, 2H), 7.26-7.31 (m, 5H), 7.41-7.45 (m, 2H), 7.73-7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 18.7, 55.9, 70.9, 96.1, 128.6, 128.7, 129.1, 129.3, 129.4, 134.2, 136.2, 140.3; IR (KBr) (cm^{-1}) 2943s, 2865s, 2163s, 1586w, 1477m, 1458m, 1373s, 1170s, 1094s; HRMS (ESI): m/z calcd for $C_{24}H_{32}ClNO_2SSiNa$ $[M+Na]^+$: 484.1504; found 484.1504.



2q

Ynamide **2q** (2.19 g, 4.29 mmol) was prepared from the corresponding amide (1.93 g, 5.87 mmol) and alkynyl bromide (1.84 g, 7.04 mmol) in 73% yield after stirred at 82 °C for 46.0 h.

2q: R_f = 0.38 [20:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.87 (s, 9H), 1.03 (s, 21H), 2.44 (s, 3H), 3.45 (t, 2H, J = 6.4 Hz), 3.82 (t, 2H, J = 6.4 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.80 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.2, 11.5, 18.5, 18.8, 21.8, 26.0, 53.4, 60.4, 69.2, 96.6, 127.9, 129.8, 135.0, 144.6; IR (film) (cm^{-1}) 2942s, 2864s, 2161s, 1598m, 1495m, 1463s, 1372s, 1307w, 1257m, 1172s; HRMS (ESI): m/z calcd for $C_{26}H_{47}NO_3SSi_2Na$ $[M+Na]^+$: 532.2707; found 532.2702.

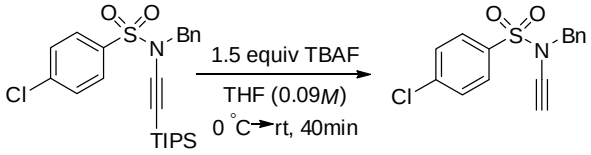


2r

Ynamide **2r** (910.3 mg, 1.98 mmol) was prepared from the corresponding amide (558.8 mg, 2.00 mmol) and alkynyl bromide (627.0 mg, 2.40 mmol) in 99% yield after stirred at 75 °C for 19.0 h.

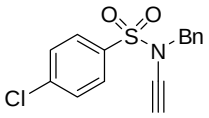
2r: R_f = 0.56 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 21H), 1.49-1.55 (m, 2H), 1.58-1.63 (m, 2H), 1.88-1.92 (m, 2H), 1.93-1.97 (m, 2H), 2.26 (t, 2H, *J* = 7.5 Hz), 2.44 (s, 3H), 3.38 (t, 2H, *J* = 7.6 Hz), 5.44 (s, 1H), 7.31 (d, 2H, *J* = 8.1 Hz), 7.79 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 18.8, 21.8, 22.4, 23.0, 25.4, 28.3, 36.2, 50.3, 69.7, 96.5, 124.4, 127.9, 129.7, 133.5, 135.0, 144.6; IR (film) (cm^{-1}) 2940s, 2864s, 2159s, 1598w, 1462m, 1372s, 1171s, 1093w ; HRMS (ESI): m/z calcd for $C_{26}H_{41}NO_2SSiNa$ $[M+Na]^+$: 482.2519; found 482.2513.

General Procedure for Synthesis of H-Terminated Ynamides.



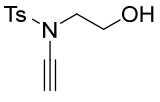
2n **6c**

To an oven-dried flask were added ynamide **2n** (850.3 mg, 1.84 mmol) and THF (20.5 mL, ynamide *concn* = 0.09 *M*). The solution was cooled to 0 °C, and TBAF (2.8 mL, 2.76 mmol, 1.0 *M* in THF) was added dropwise via syringe. After the addition was complete, the mixture was allowed to warm to rt. The reaction was judged to be complete by TLC analysis after 40 min, and saturated NH_4Cl solution (15 mL) was added to quench the reaction. The quenched mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* and purified by silica gel flash column chromatrography [gradient eluent: 40:1~10:1 petroleum ether/EtOAc + 3% NEt_3] to afford product **6c** (541.0 mg, 1.77 mmol) in 96% yield.



6c

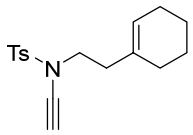
6c: R_f = 0.27 [20:1 petroleum ether/EtOAc]; white solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 1H), 4.53 (s, 2H), 7.27-7.31 (m, 5H), 7.44-7.47 (m, 2H), 7.73-7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 60.1, 76.1, 128.7, 128.77, 128.84, 129.2, 129.6, 134.1, 136.2, 140.5; IR (KBr) (cm^{-1}) 3280s, 2932w, 2138s, 1584m, 1475m, 1367s, 1183s, 1169s; HRMS (ESI): m/z calcd for $C_{15}H_{12}ClNO_2SNa$ $[M+Na]^+$: 328.0169; found 328.0165.



6i

Ynamide **6i** (109.5 mg, 0.46 mmol) was prepared from the corresponding ynamide **2q** (444.2 mg, 0.87 mmol) in 53% yield.

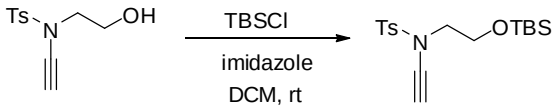
6i: R_f = 0.39 [1:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (brs, 1H), 2.46 (s, 3H), 2.78 (s, 1H), 3.50 (t, 2H, *J* = 5.3 Hz), 3.84 (t, 2H, *J* = 5.3 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), 7.81-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 53.7, 59.5, 60.0, 76.0, 127.9, 130.0, 134.3, 145.2; IR (film) (cm^{-1}) 3549s, 3277s, 2933m, 2131s, 1926w, 1596s, 1435m, 1348s, 1167s; HRMS (ESI): m/z calcd for $C_{11}H_{13}NO_3SNa$ $[M+Na]^+$: 262.0508; found 262.0516.



6j

Ynamide **6j** (1.56 g, 5.10 mmol) was prepared from the corresponding ynamide **2r** (2.85 g, 6.20 mmol) in 83% yield.

6j: R_f = 0.29 [20:1 petroleum ether/EtOAc]; pale brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49-1.55 (m, 2H), 1.56-1.62 (m, 2H), 1.88-1.92 (m, 2H), 1.94-1.97 (m, 2H), 2.24 (t, 2H, *J* = 7.7 Hz), 2.45 (s, 3H), 2.74 (s, 1H), 3.38 (t, 2H, *J* = 7.6 Hz), 5.43 (s, 1H), 7.35 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 22.3, 22.9, 25.3, 28.2, 36.2, 50.1, 59.3, 76.2, 124.4, 127.7, 129.9, 133.3, 134.9, 144.8; IR (film) (cm^{-1}) 3288w, 2928m, 2136w, 1597w, 1448w, 1368s, 1170s, 1093m; HRMS (ESI): m/z calcd for $C_{17}H_{21}NO_2SNa$ $[M+Na]^+$: 326.1185; found 326.1183.

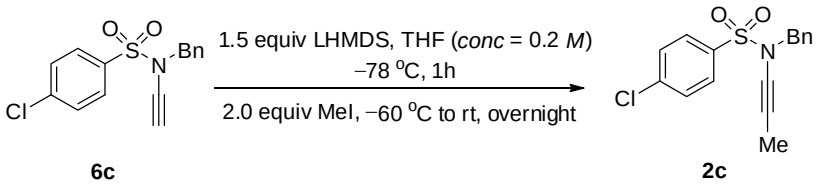


6i **6h**

To an oven-dried vial were added ynamide **6i** (52.0 mg, 0.22 mmol), imidazole (44.9 mg, 0.66 mmol), TBSCl (65.5 mg, 0.44 mmol), and DCM (4.0 mL, ynamide *concn* = 0.06 *M*). The mixture was stirred at rt for 18 h. And then the reaction mixture was poured into water and extracted with dichloromethane, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* and purified by silica gel flash column chromatrography [isocratic eluent: 20:1 petroleum ether/EtOAc] to afford product **6h** (37.9 mg, 0.11 mmol) in 49% yield.

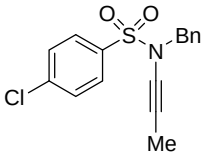
6h: R_f = 0.25 [20:1 petroleum ether/EtOAc]; white solid; mp = 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.86 (s, 9H), 2.45 (s, 3H), 2.72 (s, 1H), 3.44 (t, 2H, *J* = 6.1 Hz), 3.81 (t, 2H, *J* = 6.1 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.81 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.3, 18.4, 21.8, 26.0, 53.3, 58.9, 60.5, 76.4, 127.8, 129.9, 135.0, 144.8; IR (KBr) (cm^{-1}) 3270s, 2928m, 2857m, 2132m, 1597w, 1473w, 1364s, 1353s, 1255w, 1170s, 1108s; HRMS (ESI): m/z calcd for $C_{17}H_{27}NO_3SSiNa$ $[M+Na]^+$: 376.1373; found 376.1374.

General Procedure for Alkyl-Substituted Ynamides.



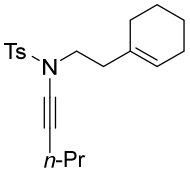
6c **2c**

To an oven-dried flask were charged with ynamide **6c** (244.6 mg, 0.80 mmol) and THF (4.0 mL, ynamide *concn* = 0.20 *M*). To this solution at -78 °C was added LHMDS (1.20 mL, 1.0 *M* in THF), and then the mixture was allowed to warm to -60 °C. After the reaction was stirred at -60 °C for 1 h, MeI (0.10 mL, 1.60 mmol) was added, the resulting mixture was warmed to rt slowly, stirred overnight (12 h) and monitored using TLC analysis, water (10 mL) was added to quench the reaction. The quench mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4, filtrered, concentrated *in vacuo* and purified by silica gel flash column chromatrography [gradient eluent: 30:1~10:1 petroleum ether/EtOAc] to afford the product **2c** (253.3 mg, 0.79 mmol) in 99% yield.



2c

2c: R_f = 0.30 [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H), 4.48 (s, 2H), 7.27-7.31 (m, 5H), 7.44-7.48 (m, 2H), 7.73-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.4, 55.9, 66.7, 72.1, 128.4, 128.6, 128.7, 129.1, 129.4, 134.7, 136.4, 140.1; IR (KBr) (cm^{-1}) 3088m, 2917w, 2265w, 1583m, 1476m, 1455m, 1375s, 1184s, 1172s, 1091s, 1084s; HRMS (ESI): m/z calcd for $C_{16}H_{14}ClNO_2SNa$ $[M+Na]^+$: 342.0326; found 342.0311.



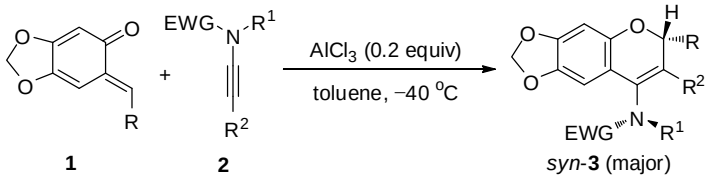
2f

Ynamide **2f** (636.0 mg, 1.84 mmol) was prepared from the corresponding ynamide **5j** (910.3 mg, 3.00 mmol) in 61% yield after stirred at rt for 20.0 h.

2f: R_f = 0.46 [20:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, 3H, *J* = 7.4 Hz), 1.46-1.55 (m, 4H), 1.57-1.62 (m, 2H), 1.88-1.92 (m, 2H), 1.93-1.98 (m, 2H), 2.20-2.26 (m, 4H), 2.44 (s, 3H), 3.33 (t, 2H, *J* = 7.6 Hz), 5.43 (s, 1H), 7.33 (d, 2H, *J* = 8.0 Hz), 7.78 (d, 2H, *J* = 8.3 Hz); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 13.5, 20.6, 21.7, 22.3, 22.5, 22.9, 25.3, 28.3, 36.3, 50.3, 70.3, 73.3, 124.0, 127.7, 129.7, 133.7, 135.0, 144.3; IR (film) (cm^{-1}) 2930s, 2251m, 1597m, 1494w, 1449m, 1365s, 1170s, 1093m, 1063w; HRMS (ESI): m/z calcd for $C_{20}H_{27}NO_2SNa$ $[M+Na]^+$: 368.1655; found 368.1655.

General Procedure for Synthesis of 4-Amino-2*H*-Chromenes.

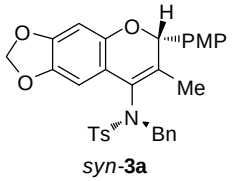


General Procedure A: To an oven-dried sealed tube were added ynamide **2a**[1] (59.9 mg, 0.20 mmol), **1a**[2] (61.5 mg, 0.24 mmol) and $AlCl_3$ (5.3 mg, 0.04 mmol), then added toluene (2.67 mL, ynamide *concn* = 0.075 *M*) at –40 °C. When the reaction was judged to be complete by TLC after stirred at –40 °C for 2.0 h, the mixture was filtered through a pad of silica gel, concentrated *in vacuo*, and purified using silica gel flash column chromatography [gradient eluent: 8:1~5:1 petroleum ether/EtOAc] to afford a separable 11:1 mixture of 4-amino-2*H*-chromenes *syn*-**3a** (97.8 mg, 0.18 mmol) and *anti*-**3a** (8.9 mg, 0.02 mmol) in 96% yield.

General Procedure B: The same as procedure A except that the reaction temperature was 0 °C instead of –40 °C.

General Procedure C: The same as procedure A, except that the reaction was carried out with 0.4 equiv of $AlCl_3$ at rt instead of 0.2 equiv of $AlCl_3$ at –40 °C.

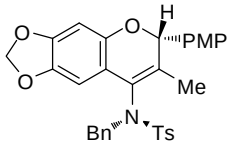
General Procedure D: The same as procedure A, except that the reaction temperature was 50 °C instead of –40 °C.



syn-**3a**

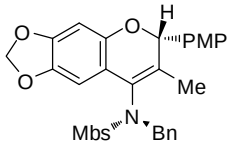
syn-**3a**: R_f = 0.41 [4:1 petroleum ether/EtOAc]; white solid; mp = 74–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 3H), 2.45 (s, 3H), 3.78 (s, 3H), 4.10 (d, 1H, *J* = 14.0 Hz), 4.89 (d, 1H, *J* = 14.0 Hz), 5.36 (s, 1H), 5.77 (d, 1H, *J* = 1.4 Hz), 5.81 (d, 1H, *J* = 1.4 Hz), 6.02 (s, 1H), 6.25 (s, 1H), 6.85-6.89 (m, 2H), 7.15-7.18 (m, 2H), 7.23-7.26 (m, 3H), 7.32 (d, 2H, *J* = 7.9 Hz), 7.43-7.47 (m, 2H), 7.84 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 21.7, 52.6, 55.3, 80.7, 99.5, 101.2, 103.3, 113.2, 114.0, 127.5, 127.7, 128.2, 128.4, 129.6, 129.7, 129.8, 130.0, 133.5, 135.5, 138.4, 141.9, 143.9, 147.6, 148.2, 160.0;

IR (KBr) (cm^{-1}) 2926w, 1651w, 1608m, 1510m, 1481m, 1444m, 1342m, 1251m, 1160s, 1093w; HRMS (ESI): m/z calcd for $C_{32}H_{30}NO_6S$ $[M+H]^+$: 556.1788; found 556.1771.



anti-**3a**

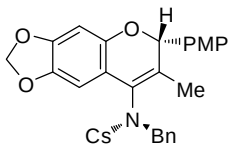
anti-**3a**: R_f = 0.31 [4:1 petroleum ether/EtOAc]; white solid; mp = 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H), 2.44 (s, 3H), 3.78 (s, 3H), 4.50 (d, 1H, *J* = 13.8 Hz), 4.76 (d, 1H, *J* = 13.8 Hz), 5.51 (s, 1H), 5.80-5.81 (m, 2H), 6.08 (s, 1H), 6.25 (s, 1H), 6.74-6.78 (m, 2H), 6.96-6.99 (m, 2H), 7.24-7.33 (m, 7H), 7.77 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9, 21.7, 53.9, 55.4, 81.6, 98.8, 101.1, 103.7, 113.9, 114.0, 127.4, 127.7, 128.4, 128.5, 129.0, 129.8, 130.2, 130.7, 133.3, 135.6, 137.8, 141.6, 143.8, 147.5, 148.5, 159.9; IR (KBr) (cm^{-1}) 2925w, 1610w, 1508m, 1482m, 1443w, 1331m, 1253m, 1162s, 1091w; HRMS (ESI): m/z calcd for $C_{32}H_{30}NO_6S$ $[M+H]^+$: 556.1788; found 556.1787.



3b

General procedure A was followed, a separable 9:1 mixture of 4-amino-2*H*-chromenes *syn*-**3b** (101.3 mg, 0.18 mmol) and *anti*-**3b** (11.2 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2b**[3] (63.1 mg, 0.20 mmol) in 98% yield after stirred at –40 ^{o}C for 2.0 h.

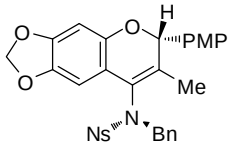
syn-**3b**: R_f = 0.23 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 4.11 (d, 1H, *J* = 14.0 Hz), 4.87 (d, 1H, *J* = 14.0 Hz), 5.37 (s, 1H), 5.78 (d, 1H, *J* = 1.4 Hz), 5.82 (d, 1H, *J* = 1.4 Hz), 6.12 (s, 1H), 6.25 (s, 1H), 6.85-6.89 (m, 2H), 6.96-7.00 (m, 2H), 7.15-7.17 (m, 2H), 7.23-7.26 (m, 3H), 7.43-7.46 (m, 2H), 7.86-7.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 52.6, 55.4, 55.9, 80.7, 99.5, 101.2, 103.4, 113.3, 114.0, 114.1, 114.5, 127.6, 128.2, 128.4, 129.79, 129.81, 130.0, 133.1, 133.4, 135.6, 141.9, 147.6, 148.2, 160.0, 163.2; IR (KBr) (cm^{-1}) 2906w, 2837w, 1609w, 1595w, 1482m, 1342m, 1263m, 1158s, 1093w; HRMS (ESI): m/z calcd for $C_{32}H_{30}NO_7S$ $[M+H]^+$: 572.1737; found 572.1735.



3c

General procedure A was followed, a separable 13:1 mixture of 4-amino-2*H*-chromenes *syn*-**3c** (102.7 mg, 0.18 mmol) and *anti*-**3c** (7.9 mg, 0.01 mmol) were from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2c** (64.0 mg, 0.20 mmol) in 96% yield after stirred at –40 ^{o}C for 3.7 h.

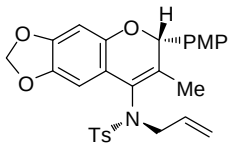
syn-**3c**: R_f = 0.56 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 3H), 3.78 (s, 3H), 4.14 (d, 1H, *J* = 14.0 Hz), 4.88 (d, 1H, *J* = 13.9 Hz), 5.37 (s, 1H), 5.80 (d, 1H, *J* = 1.4 Hz), 5.83 (d, 1H, *J* = 1.4 Hz), 6.05 (s, 1H), 6.26 (s, 1H), 6.86 (d, 2H, *J* = 8.7 Hz), 7.17-7.20 (m, 2H), 7.23-7.29 (m, 3H), 7.42 (d, 2H, *J* = 8.6 Hz), 7.47 (d, 2H, *J* = 8.6 Hz), 7.86 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 52.9, 55.4, 80.7, 99.6, 101.3, 103.1, 113.0, 114.1, 127.3, 128.4, 128.5, 129.1, 129.6, 129.7, 129.8, 130.0, 133.5, 135.2, 139.5, 139.8, 142.0, 147.9, 148.3, 160.1; IR (KBr) (cm^{-1}) 2926w, 2902w, 1652w, 1608m, 1511m, 1480m, 1351s, 1253m, 1159s; HRMS (ESI): m/z calcd for $C_{31}H_{27}ClNO_6S$ $[M+H]^+$: 576.1242; found 576.1241.



3d

General procedure A was followed except the reaction was carried out at rt, a separable 17:1 mixture of 4-amino-2*H*-chromenes *syn*-**3d** (93.7 mg, 0.16 mmol) and *anti*-**3d** (5.5 mg, 0.01 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2d**[3] (66.1 mg, 0.20 mmol) in 85% yield after stirred at rt for 0.5 h.

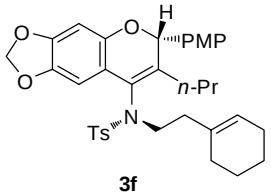
syn-**3d**: R_f = 0.44 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 59–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 3H), 3.80 (s, 3H), 4.18 (d, 1H, *J* = 14.0 Hz), 4.95 (d, 1H, *J* = 13.9 Hz), 5.39 (s, 1H), 5.77 (d, 1H, *J* = 1.4 Hz), 5.82 (d, 1H, *J* = 1.4 Hz), 5.89 (s, 1H), 6.28 (s, 1H), 6.88 (d, 2H, *J* = 8.7 Hz), 7.21-7.24 (m, 2H), 7.27-7.31 (m, 3H), 7.41 (d, 2H, *J* = 8.6 Hz), 8.06 (d, 2H, *J* = 8.9 Hz), 8.33 (d, 2H, *J* = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 53.4, 55.4, 80.7, 99.7, 101.4, 102.6, 112.5, 114.2, 124.6, 127.0, 128.62, 128.64, 128.9, 129.5, 129.7, 130.1, 133.7, 134.8, 142.0, 146.8, 148.1, 148.4, 150.2, 160.2; IR (KBr) (cm^{-1}) 2925w, 1608m, 1531m, 1510m, 1481m, 1442m, 1350s, 1250m, 1163s; HRMS (ESI): m/z calcd for $C_{31}H_{27}N_2O_8S$ $[M+H]^+$: 587.1483; found 587.1480



3e

General procedure A was followed, a separable 11:1 mixture of 4-amino-2*H*-chromenes *syn*-**3e** (91.8 mg, 0.18 mmol) and *anti*-**3e** (8.3 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2e**[4] (49.9 mg, 0.20 mmol) in 99% yield after stirred at –40 °C for 2.0 h.

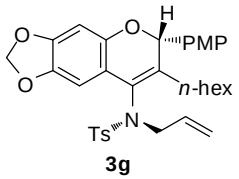
syn-**3e**: R_f = 0.39 [4:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 3H), 2.43 (s, 3H), 3.69-3.77 (m, 1H), 3.80 (s, 3H), 4.22-4.27 (m, 1H), 5.04-5.07 (m, 1H), 5.08-5.10 (m, 1H), 5.54 (s, 1H), 5.78 (d, 1H, *J* = 1.4 Hz), 5.81 (d, 1H, *J* = 1.4 Hz), 5.80-5.88 (m, 1H), 6.13 (s, 1H), 6.23 (s, 1H), 6.88-6.92 (m, 2H), 7.29 (d, 2H, *J* = 8.0 Hz), 7.48-7.52 (m, 2H), 7.79 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 21.7, 52.3, 55.4, 81.0, 99.4, 101.2, 103.5, 113.9, 114.1, 119.5, 127.7, 128.5, 129.87, 129.90, 129.93, 132.3, 132.9, 138.1, 141.9, 143.9, 147.7, 148.1, 160.1; IR (film) (cm^{-1}) 2911m, 1653w, 1609s, 1510s, 1481s, 1442s, 1390m, 1346s, 1271s, 1250s, 1161s; HRMS (ESI): m/z calcd for $C_{28}H_{28}NO_6S$ $[M+H]^+$: 506.1632; found 506.1630.



3f

General procedure A was followed, 4-amino-2*H*-chromene *syn*-**3f** (97.8 mg, 0.16 mmol) was prepared from *o*-quinone methide **1a** (56.5 mg, 0.22 mmol) and ynamide **2f** (63.5 mg, 0.18 mmol) in 88% yield after stirred at –40 °C for 2.0 h.

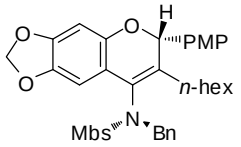
syn-**3f**: R_f = 0.45 [4:1 petroleum ether/EtOAc]; white solid; mp = 57–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, 3H, *J* = 7.2 Hz), 1.39-1.53 (m, 4H), 1.56-1.58 (m, 1H), 1.82 (s, 2H), 1.92 (s, 2H), 1.98-2.22 (m, 4H), 2.28-2.36 (m, 1H), 2.43 (s, 3H), 3.19-3.26 (m, 1H), 3.57-3.64 (m, 1H), 3.79 (s, 3H), 5.33 (s, 1H), 5.68 (s, 1H), 5.76 (t, 1H, *J* = 1.3 Hz), 5.79(t, 1H, *J* = 1.3 Hz), 6.13 (d, 1H, *J* = 1.0 Hz), 6.21 (d, 1H, *J* = 1.0 Hz), 6.88 (d, 2H, *J* = 8.6 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 7.53 (d, 2H, *J* = 8.6 Hz), 7.81 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 21.1, 21.7, 22.4, 22.9, 25.3, 28.6, 33.0, 37.3, 48.4, 55.3, 78.2, 99.4, 101.1, 103.9, 114.0, 114.4, 123.3, 127.7, 128.5, 129.8, 129.9, 130.2, 134.3, 135.7, 138.0, 141.9, 143.8, 147.7, 148.0, 160.0; IR (KBr) (cm^{-1}) 2928w, 1609w, 1584w, 1511m, 1481m, 1441m, 1344m, 1272m, 1251m, 1160s; HRMS (ESI): m/z calcd for $C_{35}H_{39}NO_6SNa$ $[M+Na]^+$: 624.2390; found 624.2379.



3g

General procedure A was followed, a separable 11:1 mixture of 4-amino-2*H*-chromenes *syn*-**3g** (95.9 mg, 0.17 mmol) and *anti*-**3g** (8.7 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2g**[5] (63.9 mg, 0.20 mmol) in 91% yield after stirred at –40 °C for 3.2 h.

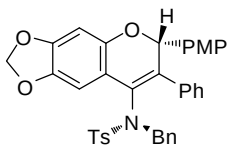
syn-**3g**: R_f = 0.51 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, 3H, *J* = 7.1 Hz), 1.11-1.27 (m, 7H), 1.33-1.46 (m, 1H), 1.81-1.88 (m, 1H), 2.29-2.36 (m, 1H), 2.42 (s, 3H), 3.69-3.76 (m, 1H), 3.77 (s, 3H), 4.21-4.27 (m, 1H), 5.02-5.08 (m, 2H), 5.67 (s, 1H), 5.74 (d, 1H, *J* = 1.4 Hz), 5.78 (d, 1H, *J* = 1.5 Hz), 5.76-5.85 (m, 1H), 6.18 (s, 1H), 6.21 (m, 1H), 6.86-6.90 (m, 2H), 7.29 (d, 2H, *J* = 8.1 Hz), 7.53 (d, 2H, *J* = 8.7 Hz), 7.80 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.6, 22.7, 28.0, 29.7, 30.7, 31.6, 52.4, 55.3, 78.1, 99.3, 101.1, 103.7, 114.0, 114.2, 119.4, 127.6, 128.2, 129.83, 129.85, 130.1, 133.0, 136.1, 138.0, 141.9, 143.8, 147.7, 148.0, 160.0; IR (film) (cm^{-1}) 2927s, 1644m, 1608s, 1510s, 1480s, 1442s, 1390m, 1347s, 1305m, 1268s, 1160s, 1089s; HRMS (ESI): m/z calcd for $C_{33}H_{38}NO_6S$ $[M+H]^+$: 576.2414; found 576.2407.



3h

General procedure A was followed, a separable 7:1 mixture of 4-amino-2*H*-chromenes *syn*-**3h** (97.6 mg, 0.15 mmol) and *anti*-**3h** (13.9 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2h**[6] (77.1 mg, 0.20 mmol) in 87% yield after stirred at –40 °C for 1.5 h.

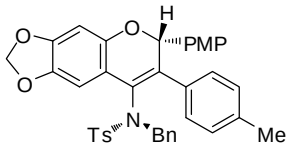
syn-**3h**: R_f = 0.36 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12-0.23 (m, 1H), 0.80-0.90 (m, 5H), 0.93-1.06 (m, 3H), 1.11-1.18 (m, 2H), 1.64-1.72 (m, 1H), 2.02-2.10 (m, 1H), 3.74 (s, 3H), 3.86 (s, 3H), 4.09 (d, 1H, *J* = 14.0 Hz), 4.88 (d, 1H, *J* = 14.0 Hz), 5.54 (s, 1H), 5.73 (d, 1H, *J* = 1.3 Hz), 5.78 (d, 1H, *J* = 1.4 Hz), 6.05 (s, 1H), 6.25 (s, 1H), 6.85 (d, 2H, *J* = 8.7 Hz), 6.99 (d, 2H, *J* = 8.9 Hz), 7.12-7.14 (m, 2H), 7.23-7.24 (m, 3H), 7.49 (d, 2H, *J* = 8.6 Hz), 7.90 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 27.3, 29.7, 30.8, 31.6, 52.3, 55.3, 55.8, 77.5, 99.6, 101.1, 103.6, 113.3, 113.8, 114.5, 127.0, 128.1, 128.4, 129.78, 129.79, 129.9, 130.0, 133.0, 135.7, 137.5, 141.9, 147.6, 148.2, 159.9, 163.2; IR (film) (cm^{-1}) 2928m, 1608m, 1596m, 1498m, 1481s, 1441m, 1347m, 1306m, 1262s, 1159s; HRMS (ESI): m/z calcd for $C_{37}H_{40}NO_7S$ $[M+H]^+$: 642.2520; found 642.2516.



3i

General procedure B was followed, a separable 7:1 mixture of 4-amino-2*H*-chromenes *syn*-**3i** (107.0 mg, 0.17 mmol) and *anti*-**3i** (15.3 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2i**[1] (72.3 mg, 0.20 mmol) in 99% yield after stirred at 0 ^{o}C for 0.5 h.

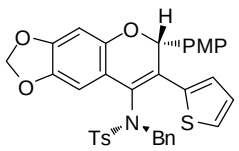
syn-**3i**: R_f = 0.42 [4:1 petroleum ether/EtOAc]; white solid; mp = 220–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.75 (s, 3H), 4.32 (d, 1H, *J* = 14.0 Hz), 4.40 (d, 1H, *J* = 13.9 Hz), 5.52 (s, 1H), 5.85 (s, 1H), 5.92 (s, 1H), 6.30-6.34 (m, 3H), 6.60 (d, 2H, *J* = 7.5 Hz), 6.85 (d, 2H, *J* = 8.3 Hz), 6.94-6.98 (m, 2H), 7.05-7.09 (m, 4H), 7.14-7.32 (m, 5H), 7.60 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 52.0, 55.3, 81.7, 100.1, 101.4, 104.9, 113.9, 114.0, 127.3, 128.0, 128.4, 128.5, 128.55, 128.59, 128.7, 128.8, 129.4, 130.5, 131.0, 134.7, 136.4, 136.7, 136.8, 142.6, 143.8, 148.4, 149.0, 160.2; IR (KBr) (cm^{-1}) 2924w, 1737w, 1649w, 1609m, 1511m, 1481s, 1442m, 1384w, 1315m, 1252m, 1148s; HRMS (ESI): m/z calcd for $C_{37}H_{32}NO_6S$ $[M+H]^+$: 618.1945; found 618.1942.



3j

General procedure B was followed, a separable 7:1 mixture of 4-amino-2*H*-chromenes *syn*-**3j** (109.5 mg, 0.17 mmol) and *anti*-**3j** (15.6 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2j**[7] (75.1 mg, 0.20 mmol) in 99% yield after stirred at 0 ^{o}C for 0.5 h.

syn-**3j**: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp =172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.40 (s, 3H), 3.77 (s, 3H), 4.34 (d, 1H, *J* = 14.0 Hz), 4.43 (d, 1H, *J* = 14.0 Hz), 5.51 (s, 1H), 5.86 (s, 1H), 5.92 (s, 1H), 6.21 (d, 2H, *J* = 7.8 Hz), 6.32 (s, 1H), 6.66 (d, 2H, *J* = 7.4 Hz), 6.76 (d, 2H, *J* = 7.8 Hz), 6.85 (d, 2H, *J* = 8.2 Hz), 7.03-7.13 (m, 5H), 7.19-7.23 (m, 2H), 7.28-7.31 (m, 1H), 7.59 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.7, 52.2, 55.3, 81.8, 100.1, 101.4, 104.9, 114.0, 128.39, 128.45, 128.5, 128.56, 128.61, 128.62, 128.7, 128.8, 129.3, 130.5, 131.0, 133.9, 134.8, 136.3, 137.06, 137.12, 142.6, 143.7, 148.3, 148.9, 160.1; IR (KBr) (cm^{-1}) 2923m, 2840w, 1738w, 1649w, 1607s, 1511s, 1482s, 1442m, 1389w, 1317s, 1259s, 1153s; HRMS (ESI): m/z calcd for $C_{38}H_{34}NO_6S$ $[M+H]^+$: 632.2101; found 632.2098.

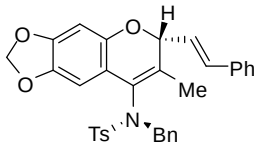


3k

General procedure B was followed, a separable 7:1 mixture of 4-amino-2*H*-chromenes *syn*-**3k** (76.8 mg, 0.12 mmol) and *anti*-**3k** (11.0 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2k**[8] (73.5 mg, 0.20 mmol) in 70% yield after stirred at 0 °C for 2.0 h.

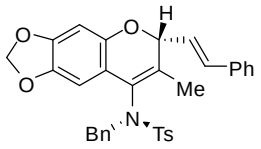
syn-**3k**: R_f = 0.31 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 204–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.77 (s, 3H), 4.44 (d, 1H, *J* = 13.8 Hz), 4.82 (d, 1H, *J* = 13.8 Hz), 5.77 (s, 1H), 5.81 (d, 1H), 5.89 (s, 1H), 6.18 (s, 1H), 6.31 (s, 1H), 6.47 (d, 1H, *J* = 3.7 Hz), 6.69 (t, 1H, *J* = 4.3 Hz), 6.88 (d, 2H, *J* = 8.6 Hz), 7.04-7.05 (m, 3H), 7.15-7.23 (m, 5H), 7.54 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 53.2, 55.3, 80.4, 99.7, 101.4, 104.6, 114.0, 114.3, 126.25, 126.28, 127.3, 128.0, 128.2, 128.39, 128.43, 128.8, 129.3, 129.7, 130.4, 130.7, 134.6, 137.8, 138.0, 142.2, 143.9, 148.4, 148.7, 160.0; IR (KBr) (cm^{-1}) 2925w, 1608w, 1510m, 1480s, 1444w, 1352w, 1265m, 1161s, 1090w; HRMS (ESI): m/z calcd for $C_{35}H_{29}NO_6S_2Na$ $[M+Na]^+$: 646.1329; found 646.1298.

General procedure C was followed, a separable 8:1 mixture of 4-amino-2*H*-chromenes *syn*-**3l** (71.0 mg, 0.13 mmol) and *anti*-**3l** (8.9 mg, 0.02 mmol) were prepared from *o*-quinone methide **1b**[2] (60.5 mg, 0.24 mmol) and ynamide **2a** (59.9 mg, 0.20 mmol) in 72% yield after stirred at rt for 15.7 h.



syn-**3l**

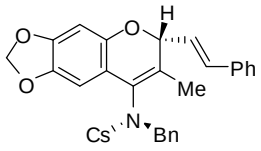
syn-**3l**: R_f = 0.54 [4:1 petroleum ether/EtOAc]; white solid; mp = 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 3H), 2.43 (s, 3H), 4.06 (d, 1H, *J* = 14.0 Hz), 4.89 (d, 1H, *J* = 14.0 Hz), 4.97 (d, 1H, *J* = 6.2 Hz), 5.81 (s, 1H), 5.84 (s, 1H), 5.96 (s, 1H), 6.23 (dd, 1H, *J* = 6.2, 16.0 Hz), 6.39 (s, 1H), 6.82 (d, 1H, *J* = 16.0 Hz), 7.17-7.19 (m, 2H), 7.22-7.24 (m, 2H), 7.28-7.32 (m, 6H), 7.40 (d, 2H, *J* = 7.5 Hz), 7.82 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 21.7, 52.5, 79.8, 99.4, 101.2, 103.5, 113.1, 124.2, 127.0, 127.7, 128.1, 128.3, 128.35, 128.37, 128.7, 129.6, 129.9, 133.1, 134.3, 135.7, 136.4, 138.2, 141.9, 143.9, 147.6, 148.5; IR (KBr) (cm^{-1}) 3029w, 2901w, 1704w, 1598w, 1497w, 1482s, 1441m, 1267w, 1185m, 1157s, 1092m; HRMS (ESI): m/z calcd for $C_{33}H_{30}NO_5S$ $[M+H]^+$: 552.1839; found 552.1836.



anti-**3l**

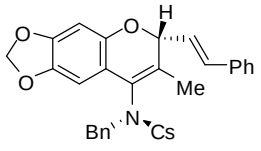
anti-**3l**: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp = 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 3H), 2.44 (s, 3H), 4.48 (d, 1H, *J* = 13.6 Hz), 4.71 (d, 1H, *J* = 13.6 Hz), 5.02 (d, 1H, *J* = 7.7 Hz), 5.82 (d, 2H, *J* = 4.7 Hz), 6.02 (dd, 1H, *J* = 7.7, 15.8 Hz), 6.06 (s, 1H), 6.36 (s, 1H), 6.51 (d, 1H, *J* = 15.8 Hz), 7.15-7.23 (m, 3H), 7.28-7.34 (m, 9H), 7.74 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 21.7, 53.9, 80.7, 98.8, 101.2, 103.8, 114.3, 124.5, 126.87, 126.89, 127.7, 128.4, 128.5, 128.7, 129.8, 130.3, 132.5, 132.9, 135.4, 136.2, 137.9, 141.7, 143.7, 147.6, 148.2; IR (KBr) (cm^{-1}) 2919w, 1737w, 1648w, 1597w, 1503m, 1480s, 1439m, 1341s, 1162s, 1146s; HRMS (ESI): m/z calcd for $C_{33}H_{30}NO_5S$ $[M+H]^+$: 552.1839; found 552.1840.

General procedure C was followed, a separable 8:1 mixture of 4-amino-2*H*-chromenes *syn*-**3m** (65.9 mg, 0.12 mmol) and *anti*-**3m** (8.2 mg, 0.01 mmol) were prepared from *o*-quinone methide **1b** (60.5 mg, 0.24 mmol) and ynamide **2c** (64.0 mg, 0.20 mmol) in 65% yield after stirred at rt for 16.0 h.



syn-**3m**

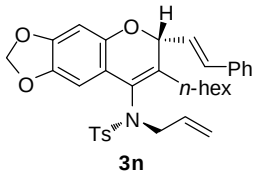
syn-**3m**: R_f = 0.44 [4:1 petroleum ether/EtOAc]; white solid; mp = 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 3H), 4.09 (d, 1H, *J* = 14.0 Hz), 4.89 (d, 1H, *J* = 14.0 Hz), 4.98 (d, 1H, *J* = 6.2 Hz), 5.83 (d, 1H, *J* = 1.4 Hz), 5.86 (d, 1H, *J* = 1.4 Hz), 5.97 (s, 1H), 6.23 (dd, 1H, *J* = 6.2, 16.0 Hz), 6.40 (s, 1H), 6.79 (d, 1H, *J* = 16.0 Hz), 7.18-7.21 (m, 2H), 7.23-7.33 (m, 6H), 7.39 (d, 2H, *J* = 7.2 Hz), 7.44 (d, 2H, *J* = 8.6 Hz), 7.84 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 52.8, 79.8, 99.6, 101.4, 103.2, 112.8, 124.2, 126.9, 127.0, 128.37, 128.41, 128.5, 128.8, 129.1, 129.6, 130.0, 133.2, 134.3, 135.4, 136.3, 139.5, 139.7, 142.1, 147.9, 148.6; IR (KBr) (cm^{-1}) 2923w, 1626w, 1586w, 1480m, 1442m, 1394w, 1352m, 1267m, 1162s; HRMS (ESI): m/z calcd for $C_{32}H_{26}ClNO_5SNa$ $[M+Na]^+$: 594.1112; found 594.1112.



anti-**3m**

anti-**3m**: R_f = 0.38 [4:1 petroleum ether/EtOAc]; white solid; mp = 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 3H), 4.47 (d, 1H, *J* = 13.6 Hz), 4.79 (d, 1H, *J* = 13.6 Hz), 5.03 (d, 1H, *J* = 7.6 Hz), 5.82 (d, 1H, *J* = 1.4 Hz), 5.84 (d, 1H, *J* = 1.4 Hz), 5.94 (s, 1H), 6.03 (dd, 1H, *J* = 7.6, 15.8 Hz), 6.36 (s,

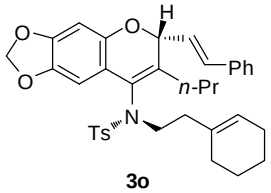
1H), 6.52 (d, 1H, J = 15.8 Hz), 7.17-7.24 (m, 3H), 7.27-7.35 (m, 7H), 7.43 (d, 2H, J = 8.6 Hz), 7.76 (d, 2H, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 54.3, 80.6, 98.9, 101.4, 103.3, 113.8, 124.2, 126.4, 126.9, 128.5, 128.59, 128.64, 128.77, 128.81, 129.0, 129.4, 130.3, 133.1, 135.2, 136.1, 139.3, 139.4, 141.8, 147.7, 148.2; IR (KBr) (cm^{-1}) 3027w, 2922w, 1649w, 1587w, 1481s, 1440m, 1394w, 1349m, 1284w, 1268w, 1164s, 1144m; HRMS (ESI): m/z calcd for $C_{32}H_{26}ClNO_5SNa$ $[M+Na]^+$: 594.1112; found 594.1099.



3n

General procedure C was followed, a separable 9:1 mixture of 4-amino-2*H*-chromenes *syn*-**3n** (84.9 mg, 0.15 mmol) and *anti*-**3n** (9.4 mg, 0.02 mmol) were prepared from *o*-quinone methide **1b** (70.0 mg, 0.27 mmol) and ynamide **2g** (72.8 mg, 0.23 mmol) in 72% yield after stirred at rt for 26.0 h.

syn-**3n**: R_f = 0.44 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 6.9 Hz), 1.20-1.30 (m, 7H), 1.45-1.55 (m, 1H), 1.89-1.96 (m, 1H), 2.32-2.37 (m, 1H), 2.41 (s, 3H), 3.67 (dd, 1H, J = 7.8, 14.8 Hz), 4.23 (dd, 1H, J = 6.1, 14.8 Hz), 5.03 (d, 1H, J = 17.4 Hz), 5.06 (d, 1H, J = 10.3 Hz), 5.26 (d, 1H, J = 6.2 Hz), 5.81 (d, 2H, J = 10.8 Hz), 6.06 (s, 1H), 6.29 (dd, 1H, J = 6.2, 16.0 Hz), 6.37 (s, 1H), 6.92 (d, 1H, J = 16.0 Hz), 7.15-7.35 (m, 6H), 7.42 (d, 2H, J = 7.5 Hz), 7.78 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.7, 22.8, 28.2, 29.8, 30.4, 31.7, 52.4, 77.0, 99.3, 101.2, 103.9, 114.1, 119.4, 124.6, 127.1, 127.7, 127.9, 128.3, 128.8, 129.9, 133.2, 134.7, 135.9, 136.5, 138.0, 142.0, 143.8, 147.7, 148.4; IR (film) (cm^{-1}) 2955m, 2926m, 1643w, 1624w, 1598w, 1502m, 1481s, 1441m, 1391w, 1349m, 1267m, 1161s; HRMS (ESI): m/z calcd for $C_{34}H_{37}NO_5SNa$ $[M+Na]^+$: 594.2285; found 594.2285.

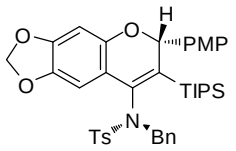


3o

General procedure A was followed, 4-amino-2*H*-chromene *syn*-**3o** (111.6 mg, 0.19 mmol) was prepared from *o*-quinone methide **1b** (60.5 mg, 0.24 mmol) and ynamide **2f** (69.1 mg, 0.20 mmol) in 93% yield after stirred at –40 °C for 4.5 h.

syn-**3o**: R_f = 0.50 [4:1 petroleum ether/EtOAc]; white solid; mp = 67–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, 3H, J = 7.3 Hz), 1.47-1.65 (m, 5H), 1.82 (s, 2H), 1.92 (s, 2H), 1.99-2.25 (m, 4H), 2.32-2.40 (m,

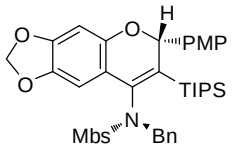
1H), 2.42 (s, 3H), 3.14-3.21 (m, 1H), 3.56-3.63 (m, 1H), 5.28 (d, 1H, *J* = 6.2 Hz), 5.34-5.36 (m, 1H), 5.80 (s, 1H), 5.82 (s, 1H), 6.01 (s, 1H), 6.29 (dd, 1H, *J* = 6.2, 16.0 Hz), 6.37 (s, 1H), 6.94 (d, 1H, *J* = 16.0 Hz), 7.18-7.25 (m, 1H), 7.28-7.33 (m, 4H), 7.42-7.44 (m, 2H), 7.78 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 21.3, 21.7, 22.4, 23.0, 25.3, 28.6, 32.7, 37.5, 48.4, 77.0, 99.3, 101.2, 104.1, 114.2, 123.3, 124.6, 127.1, 127.7, 128.1, 128.3, 128.7, 129.9, 134.3, 134.9, 135.5, 136.5, 137.9, 141.9, 143.8, 147.7, 148.4; IR (KBr) (cm^{-1}) 2926w, 1625w, 1598w, 1502m, 1480s, 1440m, 1347m, 1265m, 1159s, 1097m; HRMS (ESI): m/z calcd for $C_{36}H_{39}NO_5SNa$ $[M+Na]^+$: 620.2441; found 620.2454.



3p

General procedure D was followed, a separable 12:1 mixture of 4-amino-2*H*-chromenes *syn*-**3p** (126.6 mg, 0.18 mmol) and *anti*-**3p** (10.5 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2l** (88.3 mg, 0.20 mmol) in 98% yield after stirred at 50 ^{o}C for 30.0 h.

syn-**3p**: R_f = 0.42 [4:1 petroleum ether/EtOAc]; white solid; mp = 175–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, 9H, *J* = 7.4 Hz), 1.08 (d, 9H, *J* = 7.4 Hz), 1.22-1.30 (m, 3H), 2.46 (s, 3H), 3.78 (s, 3H), 4.47 (d, 1H, *J* = 13.9 Hz), 4.84 (d, 1H, *J* = 13.9 Hz), 5.01 (s, 1H), 5.67-5.68 (m, 2H), 5.80 (s, 1H), 6.19 (s, 1H), 6.81-6.84 (m, 2H), 7.07-7.10 (m, 2H), 7.15-7.22 (m, 3H), 7.34 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.6 Hz), 7.87 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 19.86, 19.92, 21.7, 53.7, 55.3, 78.3, 99.5, 101.1, 104.6, 113.2, 115.1, 128.3, 128.4, 129.9, 130.1, 131.2, 131.4, 134.6, 135.4, 137.8, 140.8, 141.0, 144.2, 148.3, 150.5, 159.6; IR (KBr) (cm^{-1}) 2948w, 2867w, 1609w, 1510m, 1480m, 1352m, 1252m, 1161s, 1124w; HRMS (ESI): m/z calcd for $C_{40}H_{47}NO_6SSiNa$ $[M+Na]^+$: 720.2786; found 720.2783.

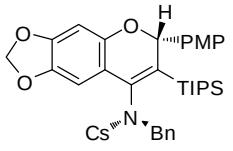


3q

General procedure D was followed, a separable 8:1 mixture of 4-amino-2*H*-chromenes *syn*-**3q** (106.1 mg, 0.15 mmol) and *anti*-**3q** (13.3 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2m** (91.5 mg, 0.20 mmol) in 84% yield after stirred at 50 ^{o}C for 30.0 h.

syn-**3q**: R_f = 0.37 [4:1 petroleum ether/EtOAc]; white solid; mp = 166–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, 9H, *J* = 7.4 Hz), 1.08 (d, 9H, *J* = 7.4 Hz), 1.20-1.26 (m, 3H), 3.78 (s, 3H), 3.89 (s, 3H), 4.47 (d, 1H, *J* = 13.9 Hz), 4.82 (d, 1H, *J* = 13.8 Hz), 5.13 (s, 1H), 5.68 (s, 2H), 5.81 (s, 1H), 6.20 (s,

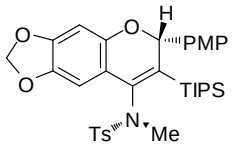
1H), 6.81-6.85 (m, 2H), 6.99-7.02 (m, 2H), 7.08-7.11 (m, 2H), 7.15-7.21 (m, 3H), 7.63-7.67 (m, 2H), 7.89-7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.3, 19.8, 19.9, 53.7, 55.3, 55.9, 78.3, 99.5, 101.1, 104.7, 113.2, 114.6, 115.1, 128.31, 128.34, 129.9, 130.4, 131.2, 131.4, 132.6, 134.7, 135.3, 140.92, 140.95, 148.3, 150.5, 159.6, 163.5; IR (KBr) (cm^{-1}) 2945m, 2867m, 1741w, 1596m, 1550w, 1510m, 1498m, 1481s, 1351m, 1263s, 1160s; HRMS (ESI): m/z calcd for $C_{40}H_{47}NO_7SSiNa$ $[M+Na]^+$: 736.2735; found 736.2721.



3r

General procedure D was followed, a separable 5:1 mixture of 4-amino-2*H*-chromenes *syn*-**3r** (79.8 mg, 0.11 mmol) and *anti*-**3r** (16.0 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2n** (92.4 mg, 0.20 mmol) in 67% yield after stirred at 50 ^{o}C for 45.0 h.

syn-**3r**: R_f = 0.54 [4:1 petroleum ether/EtOAc]; white solid; mp = 188–189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (d, 9H, *J* = 7.4 Hz), 1.09 (d, 9H, *J* = 7.4 Hz), 1.19-1.30 (m, 3H), 3.78 (s, 3H), 4.55 (d, 1H, *J* = 13.9 Hz), 4.77 (d, 1H, *J* = 13.9 Hz), 5.09 (s, 1H), 5.70 (s, 2H), 5.83 (s, 1H), 6.21 (s, 1H), 6.80-6.84 (m, 2H), 7.09-7.12 (m, 2H), 7.16-7.22 (m, 3H), 7.48-7.52 (m, 2H), 7.61-7.64 (m, 2H), 7.86-7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 19.8, 19.9, 54.2, 55.3, 78.3, 99.6, 101.2, 104.3, 113.2, 114.9, 128.4, 128.5, 129.66, 129.74, 129.8, 131.2, 131.3, 134.3, 135.4, 139.4, 139.8, 140.7, 141.1, 148.6, 150.4, 159.6; IR (KBr) (cm^{-1}) 2949m, 2868w, 1609w, 1546w, 1510m, 1483m, 1356m, 1262m, 1250m, 1166s; HRMS (ESI): m/z calcd for $C_{39}H_{44}ClNO_6SSiNa$ $[M+Na]^+$: 740.2239; found 740.2229.

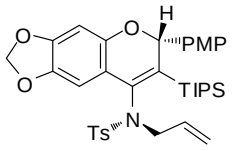


3s

General procedure D was followed, a separable 14:1 mixture of 4-amino-2*H*-chromenes *syn*-**3s** (110.1 mg, 0.18 mmol) and *anti*-**3s** (7.9 mg, 0.01 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2o** (73.1 mg, 0.20 mmol) in 95% yield after stirred at 50 ^{o}C for 30.0 h.

syn-**3s**: R_f = 0.51 [4:1 petroleum ether/EtOAc]; white solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, 9H, *J* = 7.4 Hz), 1.17 (d, 9H, *J* = 7.5 Hz), 1.50-1.55 (m, 3H), 2.45 (s, 3H), 3.06 (s, 3H), 3.79 (s, 3H), 5.00 (s, 1H), 5.67 (s, 2H), 5.85 (s, 1H), 6.18 (s, 1H), 6.85 (d, 2H, *J* = 8.7 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.69 (d, 2H, *J* = 8.7 Hz), 7.82 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 19.5, 19.6, 21.7, 38.5, 55.3, 78.1, 99.4, 101.1, 103.8, 113.3, 114.3, 128.1, 130.0, 130.1, 131.0, 131.3, 136.4, 141.2,

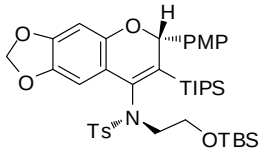
143.4, 144.2, 148.6, 150.3, 159.6; IR (KBr) (cm^{-1}) 2948w, 2867w, 1609w, 1556w, 1510m, 1480s, 1385w, 1353m, 1257m, 1164s; HRMS (ESI): m/z calcd for $C_{34}H_{43}NO_6SSiNa$ $[M+Na]^+$: 644.2473; found 644.2452.



3t

General procedure D was followed, a separable 14:1 mixture of 4-amino-2*H*-chromenes *syn*-**3t** (117.2 mg, 0.18 mmol) and *anti*-**3t** (8.4 mg, 0.01 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2p** (78.3 mg, 0.20 mmol) in 97% yield after stirred at 50 ^oC for 30.0 h.

syn-**3t**: R_f = 0.45 [4:1 petroleum ether/EtOAc]; white solid; mp = 185–186 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, 9H, *J* = 7.5 Hz), 1.19 (d, 9H, *J* = 7.5 Hz), 1.50-1.58 (m, 3H), 2.44 (s, 3H), 3.77 (s, 3H), 3.81 (dd, 1H, *J* = 7.5, 13.6 Hz), 4.40 (dd, 1H, *J* = 6.2, 13.6 Hz), 4.86-4.97 (m, 2H), 4.90 (s, 1H), 5.63 (d, 1H, *J* = 1.4 Hz), 5.64 (d, 1H, *J* = 1.4 Hz), 5.71-5.81 (m, 1H), 5.84 (s, 1H), 6.15 (s, 1H), 6.82-6.85 (m, 2H), 7.35 (d, 2H, *J* = 8.0 Hz), 7.65-7.69 (m, 2H), 7.83-7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 19.5, 19.9, 21.7, 52.8, 55.2, 78.3, 99.4, 101.0, 103.8, 113.2, 115.8, 119.8, 128.3, 130.0, 130.1, 131.3, 131.6, 134.1, 136.5, 141.01, 141.03, 144.3, 148.4, 149.9, 159.6; IR (KBr) (cm^{-1}) 2948m, 2867m, 1610w, 1584w, 1562w, 1509m, 1482s, 1352m, 1262m, 1250m, 1162s; HRMS (ESI): m/z calcd for $C_{36}H_{45}NO_6SSiNa$ $[M+Na]^+$: 670.2629; found 670.2622.



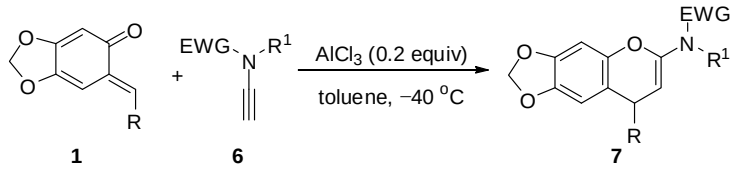
3u

General procedure D was followed, a separable 11:1 mixture of 4-amino-2*H*-chromenes *syn*-**3u** (135.1 mg, 0.18 mmol) and *anti*-**3u** (12.3 mg, 0.02 mmol) were prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **2q** (102.0 mg, 0.20 mmol) in 96% yield after stirred at 50 ^oC for 35.5 h.

syn-**3u**: R_f = 0.49 [4:1 petroleum ether/EtOAc]; white solid; mp = 74–75 °C; ^1H NMR (400 MHz, $CDCl_3$) δ –0.07 (s, 3H), –0.06 (s, 3H), 0.79 (s, 9H), 1.10 (d, 9H, *J* = 7.4 Hz), 1.20 (d, 9H, *J* = 7.5 Hz), 1.48-1.53 (m, 3H), 2.46 (s, 3H), 3.18-3.25 (m, 1H), 3.38-3.44 (m, 1H), 3.73-3.82 (m, 1H), 3.79 (s, 3H), 3.95-4.02 (m, 1H), 4.92 (s, 1H), 5.64 (d, 1H, *J* = 1.4 Hz), 5.68 (d, 1H, *J* = 1.4 Hz), 5.84 (s, 1H), 6.17 (s, 1H), 6.82-6.85 (m, 2H), 7.35 (d, 2H, *J* = 8.0 Hz), 7.65 (d, 2H, *J* = 8.7 Hz), 7.83 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.4, –5.3, 12.8, 18.5, 19.6, 19.9, 21.7, 26.0, 50.8, 55.3, 60.7, 78.3, 99.5, 101.1, 103.6,

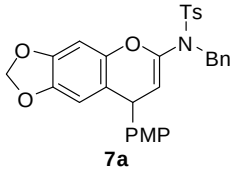
113.2, 115.0, 128.4, 129.9, 130.1, 131.3, 133.7, 136.3, 141.1, 141.2, 144.4, 148.6, 150.1, 159.6; IR (KBr) (cm^{-1}) 2950m, 2867m, 1610w, 1510m, 1480s, 1388w, 1355m, 1261s, 1163s, 1099s; HRMS (ESI): m/z calcd for $C_{41}H_{59}NO_7SSi_2Na$ $[M+Na]^+$: 788.3443; found 788.3413.

General Procedure for Synthesis of 2-Amino-4*H*-Chromenes.



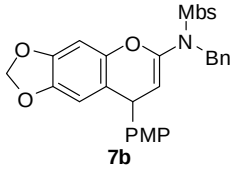
General procedure A: To an oven-dried sealed tube were added ynamide **6a**[9] (57.1 mg, 0.20 mmol), **1a** (61.5 mg, 0.24 mmol) and $AlCl_3$ (5.3 mg, 0.04 mmol), then added toluene (2.67 mL, ynamide *concn* = 0.075 *M*) at –40 °C. When the reaction was judged to be complete by TLC after stirred at –40 °C for 3.0 h, the reaction mixture was warmed to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified using silica gel flash column chromatography [gradient eluent: 10:1~7:1 petroleum ether/EtOAc] to afford 2-amino-4*H*-chromene **7a** (97.1 mg, 0.18 mmol) in 90% yield.

General procedure B: The same as procedure A, except that the reaction was carried out uing 0.4 equiv $AlCl_3$ at 0 °C instead of 0.2 equiv $AlCl_3$ at –40 °C.



7a

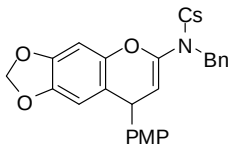
7a: R_f = 0.32 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.76 (s, 3H), 4.45 (d, 1H, *J* = 13.6 Hz), 4.47 (d, 1H, *J* = 4.2 Hz), 4.63 (d, 1H, *J* = 13.5 Hz), 4.86 (d, 1H, *J* = 4.0 Hz), 5.81 (d, 1H, *J* = 1.2 Hz), 5.86 (d, 1H, *J* = 1.2 Hz), 6.20 (s, 1H), 6.24 (s, 1H), 6.69-6.77 (m, 4H), 7.27-7.31 (m, 7H), 7.77 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 41.5, 51.7, 55.4, 97.8, 101.4, 105.4, 107.9, 114.0, 115.1, 128.0, 128.1, 128.6, 129.1, 129.3, 129.6, 135.3, 136.3, 137.9, 141.1, 144.0, 144.1, 144.8, 146.8, 158.5; IR (KBr) (cm^{-1}) 2900w, 2830w, 1916w, 1695m, 1606m, 1508s, 1479s, 1439m, 1359s, 1303m, 1247s, 1163s, 1149s, 1090s; HRMS (ESI): m/z calcd for $C_{31}H_{28}NO_6S$ $[M+H]^+$: 542.1632; found 542.1637.



7b

General procedure A was followed, 2-amino-4*H*-chromene **7b** (106.1 mg, 0.19 mmol) was prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **6b**[9] (60.3 mg, 0.20 mmol) in 95% yield after stirred at –40 °C for 2.0 h.

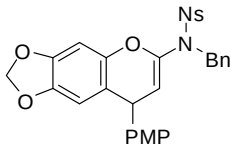
7b: R_f = 0.21 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 69–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.90 (s, 3H), 4.44 (d, 1H, *J* = 13.5 Hz), 4.47 (d, 1H, *J* = 4.1 Hz), 4.62 (d, 1H, *J* = 13.5 Hz), 4.86 (d, 1H, *J* = 4.1 Hz), 5.81 (d, 1H, *J* = 1.3 Hz), 5.86 (d, 1H, *J* = 1.3 Hz), 6.22 (s, 1H), 6.24 (s, 1H), 6.69-6.76 (m, 4H), 6.95-6.99 (m, 2H), 7.27-7.29 (m. 5H), 7.80-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 51.6, 55.4, 55.8, 97.8, 101.4, 105.4, 107.9, 114.0, 114.2, 115.1, 128.0, 128.6, 129.1, 129.3, 130.3, 130.8, 135.3, 137.9, 141.2, 144.1, 144.8, 146.8, 158.4, 163.3; IR (KBr) (cm^{-1}) 2903w, 2840w, 1696w, 1597m, 1479m, 1349s, 1259s, 1175m, 1160s, 1093m; HRMS (ESI): m/z calcd for $C_{31}H_{28}NO_7S$ $[M+H]^+$: 558.1581; found 558.1584.



7c

General procedure B was followed, 2-amino-4*H*-chromene **7c** (102.9 mg, 0.18 mmol) was prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **6c** (61.2 mg, 0.20 mmol) in 92% yield after stirred at 0 °C for 0.5 h.

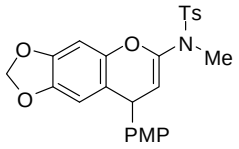
7c: R_f = 0.48 [4:1 petroleum ether/EtOAc]; white solid; mp = 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.46 (d, 1H, *J* = 13.6 Hz), 4.47 (d, 1H, *J* = 3.9 Hz), 4.64 (d, 1H, *J* = 13.5 Hz), 4.87 (d, 1H, *J* = 4.1 Hz), 5.82 (d, 1H, *J* = 1.2 Hz), 5.86 (d, 1H, *J* = 1.2 Hz), 6.21 (s, 1H), 6.24 (s, 1H), 6.70-6.76 (m, 4H), 7.28 (s, 5H), 7.45-7.49 (m, 2H), 7.80 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 51.9, 55.4, 97.7, 101.5, 105.8, 108.0, 114.1, 115.1, 128.2, 128.7, 129.1, 129.33, 129.34, 129.6, 135.0, 137.8, 137.9, 139.7, 140.8, 144.3, 144.8, 146.9, 158.6; IR (KBr) (cm^{-1}) 2906w, 2833w, 1697w, 1607w, 1583w, 1506m, 1480s, 1358s, 1246s, 1168s, 1150s; HRMS (ESI): m/z calcd for $C_{30}H_{25}ClNO_6S$ $[M+H]^+$: 562.1086; found 562.1085.



7d

General procedure B was followed, 2-amino-4*H*-chromene **7d** (89.3 mg, 0.16 mmol) was prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **6d** (63.3 mg, 0.20 mmol) in 78% yield after stirred at 0 °C for 46min.

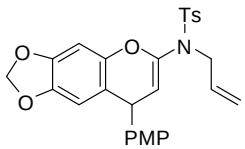
7d: R_f = 0.38 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 4.49 (d, 1H, *J* = 3.2 Hz), 4.51 (d, 1H, *J* = 13.3 Hz), 4.69 (d, 1H, *J* = 13.5 Hz), 4.90 (d, 1H, *J* = 4.1 Hz), 5.83 (d, 1H, *J* = 1.3 Hz), 5.88 (d, 1H, *J* = 1.4 Hz), 6.17 (s, 1H), 6.25 (s,1H), 6.72-6.78 (m, 4H), 7.27-7.30 (m, 5H), 8.00-8.04 (m, 2H), 8.30-8.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 52.2, 55.4, 97.6, 101.6, 106.2, 108.0, 114.1, 114.9, 124.3, 128.4, 128.8, 129.0, 129.3, 129.4, 134.5, 137.5, 140.4, 144.5, 144.7, 145.2, 147.1, 150.4, 158.6; IR (KBr) (cm^{-1}) 2924m, 2854w, 1698w, 1607w, 1479m, 1363m, 1350m, 1243m, 1170s, 1150s; HRMS (ESI): m/z calcd for $C_{30}H_{25}N_2O_8S$ $[M+H]^+$: 573.1326; found 573.1325.



7e

General procedure A was followed, 2-amino-4*H*-chromene **7e** (93.8 mg, 0.20 mmol) was prepared from *o*-quinone methide **1a** (76.9 mg, 0.30 mmol) and ynamide **6e**[10] (52.3 mg, 0.25 mmol) in 81% yield after stirred at –40 ^{o}C for 1.5 h.

7e: R_f = 0.34 [4:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.07 (s, 3H), 3.79 (s, 3H), 4.61 (d, 1H, *J* = 4.1 Hz), 5.04 (d, 1H, *J* = 4.2 Hz), 5.84 (d, 1H, *J* = 1.3 Hz), 5.88 (d, 1H, *J* = 1.3 Hz), 6.25 (s, 1H), 6.32 (s, 1H), 6.84-6.88 (m, 2H), 7.12-7.16 (m, 2H), 7.27 (d, 2H, *J* =9.0 Hz), 7.72 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, DMSO) δ 21.0, 36.2, 40.0, 55.1, 97.6, 101.2, 101.4, 107.5, 113.9, 115.2, 127.6, 128.8, 129.7, 134.6, 137.9, 143.7, 143.8, 144.0, 144.4, 146.5, 158.1; IR (film) (cm^{-1}) 2906w, 1767w, 1695m, 1671m, 1608m, 1509s, 1480s, 1353m, 1304m, 1247s, 1175s, 1152s; HRMS (ESI): m/z calcd for $C_{25}H_{24}NO_6S$ $[M+H]^+$: 466.1319; found 466.1321.

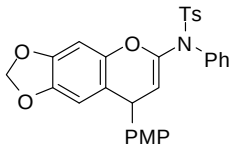


7f

General procedure A was followed, 2-amino-4*H*-chromene **7f** (86.6 mg, 0.18 mmol) was prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **6f**[10] (47.1 mg, 0.20 mmol) in 88% yield after stirred at –40 ^{o}C for 2.0 h.

7f: R_f = 0.34 [4:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.78 (s, 3H), 4.01 (d, 2H, *J* = 6.5 Hz), 4.60 (d, 1H, *J* = 4.2 Hz), 5.04 (d, 1H, *J* = 4.2 Hz), 5.13-5.22 (m, 2H), 5.74-5.84 (m, 1H), 5.81 (d, 1H, *J* = 1.4 Hz), 5.86 (d, 1H, *J* = 1.4 Hz), 6.24 (s, 1H), 6.31 (s, 1H), 6.82-6.85 (m, 2H), 7.10-7.14 (m, 2H), 7.26 (d, 2H, *J* = 8.2 Hz), 7.73 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100

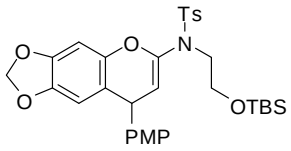
MHz, $CDCl_3$) δ 21.7, 41.7, 51.1, 55.4, 97.9, 101.4, 104.7, 107.9, 114.1, 115.2, 119.4, 128.1, 129.2, 129.6, 132.5, 136.4, 138.1, 141.7, 143.9, 144.2, 145.1, 146.8, 158.7; IR (film) (cm^{-1}) 2922m, 2836w, 1698m, 1662w, 1608m, 1509s, 1480s, 1439m, 1350s, 1165s, 1150s; HRMS (ESI): m/z calcd for $C_{27}H_{26}NO_6S$ $[M+H]^+$: 492.1475; found 492.1481.



7g

General procedure A was followed, 2-amino-4*H*-chromene **7g** (94.7 mg, 0.18 mmol) was prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **6g**[11] (54.3 mg, 0.20 mmol) in 90% yield after stirred at –40 °C for 4.0 h.

7g: R_f = 0.42 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 154–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.77 (s, 3H), 4.60 (d, 1H, *J* = 4.0 Hz), 5.15 (d, 1H, *J* = 4.0 Hz), 5.84 (d, 1H, *J* = 1.5 Hz), 5.87 (d, 1H, *J* = 1.4 Hz), 6.31 (s, 1H), 6.34 (s, 1H), 6.83 (d, 2H, *J* = 8.3 Hz), 7.13 (d, 2H, *J* = 8.3 Hz), 7.23 (d, 2H, *J* = 8.0 Hz), 7.30-7.36 (m, 5H), 7.61 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 41.8, 55.4, 98.1, 101.5, 104.0, 108.0, 114.2, 115.2, 127.9, 128.2, 128.4, 129.26, 129.27, 129.4, 136.7, 138.1, 139.6, 143.96, 143.99, 144.3, 145.1, 146.9, 158.7; IR (KBr) (cm^{-1}) 2899w, 2836w, 1702w, 1608w, 1505s, 1481s, 1440w, 1359s, 1304m, 1248s, 1166s, 1150s; HRMS (ESI): m/z calcd for $C_{30}H_{26}NO_6S$ $[M+H]^+$: 528.1475; found 528.1480.

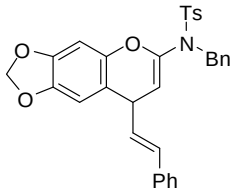


7h

General procedure A was followed, 2-amino-4*H*-chromene **7h** (94.3 mg, 0.15 mmol) was prepared from *o*-quinone methide **1a** (61.5 mg, 0.24 mmol) and ynamide **6h** (70.7 mg, 0.20 mmol) in 77% yield after stirred at –40 °C for 2.0 h.

7h: R_f = 0.46 [4:1 petroleum ether/EtOAc]; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.004 (s, 3H), 0.00 (s, 3H), 0.83 (s, 9H), 2.42 (s, 3H), 3.51 (t, 2H, *J* = 6.7 Hz), 3.76 (t, 2H, *J* = 6.7 Hz), 3.79 (s, 3H), 4.60 (d, 1H, *J* = 4.2 Hz), 5.04 (d, 1H, *J* = 4.2 Hz), 5.84 (d, 1H, *J* = 1.4 Hz), 5.88 (d, 1H, *J* = 1.4 Hz), 6.26 (s, 1H), 6.32 (s, 1H), 6.83-6.86 (m, 2H), 7.12 (d, 2H, *J* = 8.6 Hz), 7.25 (d, 2H, *J* = 8.6 Hz), 7.72 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.3, 18.4, 21.7, 26.0, 41.7, 50.0, 55.4, 61.3, 98.0, 101.4, 104.2, 107.9, 114.2, 115.1, 128.0, 129.1, 129.5, 136.5, 138.1, 142.2, 143.8, 144.2, 145.3, 146.9, 158.7;

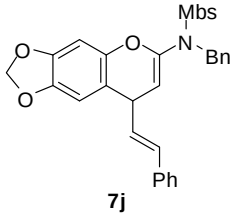
IR (film) (cm^{-1}) 2929s, 2856s, 1737s, 1697s, 1608s, 1510s, 1480s, 1440s, 1355s, 1303s, 1252s, 1151s, 1100s; HRMS (ESI): m/z calcd for $C_{32}H_{39}NO_7SSiNa$ $[M+Na]^+$: 632.2109; found 632.2105.



7i

General procedure B was followed, 2-amino-*H*-chromene **7i** (65.0 mg, 0.12 mmol) was prepared from *o*-quinone methide **1b** (60.5 mg, 0.24 mmol) and ynamide **6a** (57.1 mg, 0.20 mmol) in 60% yield after stirred at 0 ^oC for 1.0 h.

7i: R_f = 0.42 [4:1 petroleum ether/EtOAc]; white solid; mp = 107–108 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 4.08 (dd, 1H, *J* = 4.3, 8.0 Hz), 4.50 (d, 1H, *J* = 13.7 Hz), 4.57 (d, 1H, *J* = 13.7 Hz), 4.86 (d, 1H, *J* = 4.3 Hz), 5.86-5.92 (m, 3H), 6.20 (s, 1H), 6.26 (d, 1H, *J* = 15.7 Hz), 6.48 (s, 1H), 7.19-7.31 (m, 12H), 7.78 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 39.7, 51.6, 98.1, 101.5, 103.6, 107.7, 113.9, 126.5, 127.6, 128.0, 128.2, 128.57, 128.62, 129.2, 129.6, 132.4, 135.5, 136.4, 136.9, 141.6, 144.0, 144.2, 145.3, 147.0; IR (KBr) (cm^{-1}) 2922w, 1722w, 1697m, 1625w, 1598m, 1480s, 1454m, 1353s, 1263m, 1245m, 1152s; HRMS (ESI): m/z calcd for $C_{32}H_{28}NO_5S$ $[M+H]^+$: 538.1683; found 538.1685.

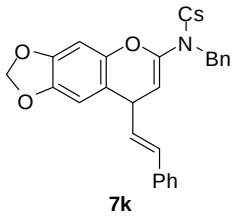


7j

General procedure B was followed, 2-amino-4*H*-chromene **7j** (67.5 mg, 0.12 mmol) was prepared from *o*-quinone methide **1b** (60.5 mg, 0.24 mmol) and ynamide **6b** (60.3 mg, 0.20 mmol) in 61% yield after stirred at 0 ^oC for 1.0 h.

7j: R_f = 0.26 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 66–67 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.08 (dd, 1H, *J* = 4.3, 8.0 Hz), 4.50 (d, 1H, *J* = 13.7 Hz), 4.56 (d, 1H, *J* = 13.7 Hz), 4.86 (d, 1H, *J* = 4.4 Hz), 5.87-5.93 (m, 3H), 6.22 (s, 1H), 6.26 (d, 1H, *J* = 15.8 Hz), 6.48 (s, 1H), 6.95 (d, 2H, *J* = 8.8 Hz), 7.19-7.32 (m, 10H), 7.83 (d, 2H, *J* = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 51.6, 55.8, 98.1, 101.5, 103.5, 107.7, 113.8, 114.2, 126.5, 127.6, 128.0, 128.55, 128.61, 129.1, 129.6, 130.3, 130.9, 132.4, 135.5, 136.9, 141.8, 144.2, 145.3, 147.0, 163.3; IR (KBr) (cm^{-1}) 2927w, 1697w, 1626w, 1595m,

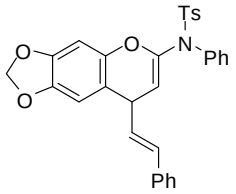
1577w, 1498s, 1481s, 1439w, 1353s, 1261m, 1183m, 1163s, 1150s; HRMS (ESI): m/z calcd for $C_{32}H_{28}NO_6S$ $[M+H]^+$: 554.1632; found 554.1638.



7k

General procedure B was followed, 2-amino-4*H*-chromene **7k** (56.8 mg, 0.10 mmol) was prepared from *o*-quinone methide **1b** (60.5 mg, 0.24 mmol) and ynamide **6c** (61.2 mg, 0.20 mmol) in 51% yield after stirred at 0 ^oC for 3.0 h.

7k: R_f = 0.50 [4:1 petroleum ether/EtOAc]; white solid; mp = 161–162 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 4.09 (dd, 1H, *J* = 4.3, 8.0 Hz), 4.51 (d, 1H, *J* = 13.7 Hz), 4.57 (d, 1H, *J* = 13.7 Hz), 4.88 (d, 1H, *J* = 4.3 Hz), 5.87-5.93 (m, 3H), 6.20 (s, 1H), 6.27 (d, 1H, *J* = 15.7 Hz), 6.49 (s, 1H), 7.19-7.24 (m, 1H), 7.25-7.31 (m, 9H), 7.44-7.48 (m, 2H), 7.80-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 51.8, 98.0, 101.6, 104.0, 107.8, 113.8, 126.6, 127.7, 128.2, 128.7, 129.2, 129.3, 129.5, 129.8, 132.2, 135.1, 136.9, 138.0, 139.7, 141.4, 144.3, 145.1, 147.2; IR (KBr) (cm^{-1}) 2901w, 1701m, 1629w, 1584w, 1504m, 1482s, 1359s, 1246m, 1190m, 1169s, 1151s; HRMS (ESI): m/z calcd for $C_{31}H_{24}ClNO_5SNa$ $[M+Na]^+$: 580.0956; found 580.0955.



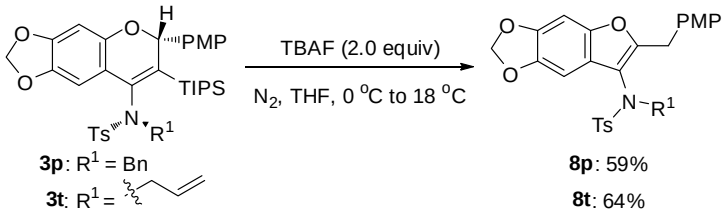
7l

General procedure B was followed, 2-amino-4*H*-chromene **7l** (29.2 mg, 0.06 mmol) was prepared from *o*-quinone methide **1b** (35.7 mg, 0.14 mmol) and ynamide **6g** (32.0 mg, 0.11 mmol) in 51% yield after stirred at 0 ^oC for 10.5 h.

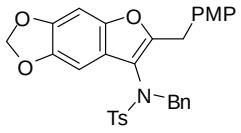
7l: R_f = 0.33 [4:1 petroleum ether/EtOAc]; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 4.25 (dd, 1H, *J* = 4.1, 8.3 Hz), 5.15 (d, 1H, *J* = 4.1 Hz), 5.89 (d, 1H, *J* = 1.4 Hz), 5.91 (d, 1H, *J* = 1.4 Hz), 6.14 (dd, 1H, *J* = 8.3, 15.7 Hz), 6.31 (s, 1H), 6.43 (d, 1H, *J* = 15.7 Hz), 6.55 (s, 1H), 7.20-7.23 (m, 2H), 7.28-7.36 (m, 10H), 7.64 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 40.2, 98.4, 101.6, 102.3, 107.8, 113.7, 126.6, 127.7, 128.0, 128.3, 128.5, 128.7, 129.3, 129.4, 130.1, 132.3, 136.7, 136.9, 139.6, 144.0, 144.3, 144.5, 145.4, 147.2; IR (film) (cm^{-1}) 2922w, 1767w, 1692w, 1596w, 1481s, 1446m,

1360m, 1300w, 1244m, 1166s, 1149s; HRMS (ESI): m/z calcd for $C_{31}H_{25}NO_5SNa$ $[M+Na]^+$: 546.1346; found 546.1351.

Procedure for Synthesis of 2-Alkyl Benzofurans.

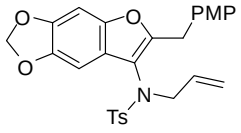


To an oven-dried sealed tube were added 2*H*-chromene **3p** (48.9 mg, 0.07 mmol) and THF (2.8 mL, *concn* = 0.025 *M*). The solution was cooled to 0 °C, and TBAF (0.14 mL, 0.14 mmol, 1.0 *M* in THF) was added under N_2 atmosphere. After the addition was complete, the mixture was stirred at 0 °C for 40 min, and then warmed to 18°C. The reaction was judged to be complete by TLC analysis after stirred for 24.0 h, then filtered through a pad of silica gel, concentrated *in vacuo*, and purified by silica gel flash column chromatography [gradient eluent: 8:1~4:1 petroleum ether/EtOAc] to afford **8p** (22.5 mg, 0.04 mmol) in 59% yield.



8p

8p: R_f = 0.31 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 41–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.55 (d, 1H, *J* = 16.0 Hz), 3.67 (d, 1H, *J* = 16.1 Hz), 3.75 (s, 3H), 4.32 (d, 1H, *J* = 13.5 Hz), 5.10 (d, 1H, *J* = 13.6 Hz), 5.85 (s, 1H), 5.89 (d, 2H, *J* = 5.7 Hz), 6.69 (s, 4H), 6.76 (s, 1H), 7.17-7.35 (m, 7H), 7.68 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.2, 53.8, 55.4, 94.3, 97.5, 101.4, 113.8, 115.9, 118.0, 127.9, 128.2, 128.7, 128.8, 129.4, 129.96, 130.04, 136.1, 136.8, 144.2, 144.4, 145.7, 148.6, 157.3, 158.3; IR (KBr) (cm^{-1}) 2919w, 2834w, 1611w, 1598w, 1513s, 1467s, 1386w, 1342s, 1300s, 1249s, 1163s, 1134s; HRMS (ESI): m/z calcd for $C_{31}H_{27}NO_6SNa$ $[M+Na]^+$: 564.1452; found 564.1445.

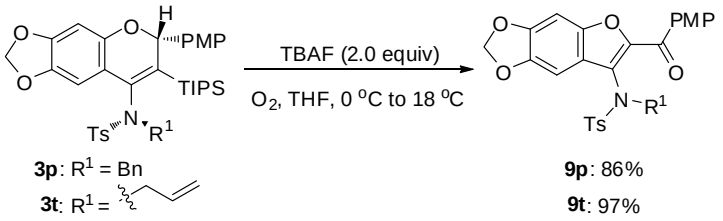


8t

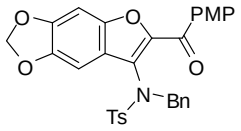
Benzofuran **8t** (16.0 mg, 0.03 mmol) was prepared from 2*H*-chromene **3t** (33.0 mg, 0.05 mmol) in 64% yield after stirred at 18°C for 39.0 h.

8t: R_f = 0.32 [4:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.78 (s, 3H), 3.91 (s, 2H), 3.96 (s, 1H), 4.29-4.36 (m, 1H), 4.96-4.98 (m, 1H), 5.00 (s, 1H), 5.69-5.79 (m, 1H), 5.89 (s, 2H), 5.94 (s, 1H), 6.81-6.85 (m, 3H), 7.15 (d, 2H, J = 8.6 Hz), 7.24 (d, 2H, J = 8.2 Hz), 7.64 (d, 2H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.5, 53.4, 55.4, 94.2, 97.7, 101.4, 114.0, 116.7, 118.7, 119.6, 127.9, 129.0, 129.9, 130.1, 133.0, 136.7, 144.1, 144.5, 145.8, 148.6, 156.8, 158.5; IR (film) (cm^{-1}) 2924w, 2870w, 1725w, 1612w, 1513s, 1462s, 1383w, 1351m, 1301m, 1248m, 1165s, 1133m, 1092m; HRMS (ESI): m/z calcd for $C_{27}H_{25}NO_6SNa$ $[M+Ma]^+$: 514.1295; found 514.1285.

Procedure for Synthesis of 2- Carbonyl Benzofurans.

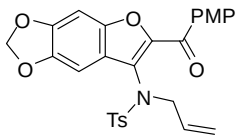


To an oven-dried sealed tube were added 2*H*-chromene **3p** (48.9 mg, 0.07 mmol) and THF (2.8 mL, *concn* = 0.025 *M*). The solution was cooled to 0 °C, and TBAF (0.14 mL, 0.14 mmol, 1.0 *M* in THF) was added under O_2 atmosphere. After the addition was complete, the mixture was stirred at 0 °C for 40 min and then warmed to 18°C. The reaction was judged to be complete by TLC analysis after stirred for 15.0 h, then filtered through a pad of silica gel, concentrated *in vacuo*, and purified by silica gel flash column chromatography [gradient eluent: 7:1~4:1 petroleum ether/EtOAc] to afford 2-carbonyl benzofuran **9p** (33.3 mg, 0.06 mmol) in 86% yield.



9p

9p: R_f = 0.22 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 203–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.90 (s, 3H), 4.81 (s, 1H), 5.30 (s, 1H), 6.00 (s, 2H), 6.82 (s, 1H), 6.91-6.95 (m, 3H), 7.07 (d, 2H, J = 8.0 Hz), 7.15-7.20 (m, 3H), 7.30-7.32 (m, 2H), 7.60 (d, 2H, J = 8.3 Hz), 7.74-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 55.3, 55.7, 93.2, 100.0, 102.1, 113.6, 121.9, 127.8, 127.9, 128.0, 128.5, 129.1, 129.6, 129.8, 132.2, 135.6, 136.9, 143.6, 146.3, 147.8, 149.3, 150.1, 163.5, 180.8; IR (KBr) (cm^{-1}) 2922w, 1640m, 1600s, 1460s, 1357s, 1313m, 1301m, 1250s, 1167s, 1141m; HRMS (ESI): m/z calcd for $C_{31}H_{25}NO_7SNa$ $[M+Na]^+$: 578.1244; found 578.1244.

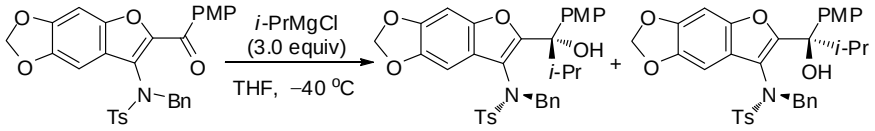


9t

2-carbonyl benzofuran **9t** (34.4 mg, 0.07 mmol) was prepared from 2*H*-chromene **3t** (45.4 mg, 0.07 mmol) in 97% yield after stirred at 18°C for 27.0 h.

9t: R_f = 0.21 [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.90 (s, 3H), 4.32 (s, 1H), 4.63 (s, 1H), 5.00 (dd, 1H, *J* = 1.4, 10.0 Hz), 5.09 (dd, 1H, *J* = 1.5, 17.1 Hz), 5.83-5.93 (m, 1H), 6.06 (s, 2H), 6.92-6.96 (m, 3H), 7.06 (d, 2H, *J* = 8.0 Hz), 7.21 (s, 1H), 7.56 (d, 2H, *J* = 8.2 Hz), 7.81 (d, 2H, *J* = 9.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 54.4, 55.7, 93.5, 100.1, 102.2, 113.6, 119.1, 122.1, 127.75, 127.84, 129.6, 129.9, 132.2, 133.7, 135.6, 143.6, 146.5, 147.9, 149.4, 150.2, 163.5, 180.8; IR (KBr) (cm^{-1}) 2920w, 1643m, 1599s, 1574m, 1510w, 1462s, 1425w, 1345s, 1264m, 1250s, 1168s, 1139m; HRMS (ESI): m/z calcd for $C_{27}H_{23}NO_7SNa$ $[M+Ma]^+$: 528.1087; found 528.1075.

Procedure for Synthesis of 2-Hydroxy Benzofurans.



9p *syn*-**10p** *anti*-**10p**

To an oven-dried sealed tube were added 2-carbonyl benzofuran **9p** (20.4 mg, 0.037 mmol) and THF (1.5 mL, *concn* = 0.025 *M*). The solution was cooled to –40 °C and *i*-PrMgCl (0.06 mL, 0.11 mmol, 2.0 *M* in diethyl ether). The reaction was judged to be complete by TLC analysis after stirred for 1.0 h, then filtered through a pad of silica gel, concentrated *in vacuo*, and purified by silica gel flash column chromatography [gradient eluent: 4:1~2:1 petroleum ether/Et_2O] to afford a 3:1 mixture of 2-hydroxy benzofurans *syn/anti*-**10p** (19.6 mg, 0.033 mmol) in 89% yield.

syn-**10p**: R_f = 0.29 [2:1 petroleum ether/diethyl ether]; *anti*-**10p**: R_f = 0.38 [2:1 petroleum ether/diethyl ether]; white solid; mp = 182–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47 (d, 3H, *J* = 6.8 Hz), 0.66 (d, 3H, *J* = 6.8 Hz), 0.70 (d, 9H, *J* = 6.7 Hz), 0.96 (d, 9H, *J* = 6.8 Hz), 2.33 (s, 3H), 2.41 (s, 9H), 2.45-2.53 (m, 1H), 2.73-2.84 (m, 3H), 3.77 (s, 9H), 3.80 (s, 3H), 4.00 (s, 1H), 4.06 (s, 3H), 4.55 (d, 3H, *J* = 14.3 Hz), 4.75-4.79 (m, 4H), 4.90 (d, 1H, *J* = 13.9 Hz), 5.47 (s, 3H), 5.69 (s, 1H), 5.81 (d, 3H, *J* = 1.4 Hz), 5.83 (d, 3H, *J* = 1.4 Hz), 5.84 (d, 1H, *J* = 1.4 Hz), 5.87 (d, 1H, *J* = 1.3 Hz), 6.73-6.77 (m, 6H), 6.81-6.84 (m, 10H), 6.85-6.88 (m, 2H), 6.95-6.99 (m, 6H), 7.03-7.07 (m, 5H), 7.22 (s, 3H), 7.24-7.25 (m, 8H), 7.39 (d, 8H, *J* = 8.8 Hz), 7.48-7.52 (m, 2H), 7.61 (d, 6H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ

15.7, 16.1, 17.6, 17.8, 21.7, 22.9, 29.9, 32.1, 37.7, 38.4, 54.9, 55.0, 55.3, 55.4, 79.2, 80.0, 93.6, 93.7, 97.8, 97.9, 101.3, 101.4, 113.1, 113.3, 116.6, 116.8, 119.1, 119.7, 126.6, 127.0, 127.7, 128.1, 128.20, 128.23, 128.7, 129.1, 129.7, 129.85, 129.89, 135.2, 135.5, 136.0, 136.1, 136.4, 136.9, 144.3, 144.37, 144.44, 144.5, 145.8, 145.9, 147.3, 158.3, 158.4, 158.5, 159.0; IR (KBr) (cm^{-1}) 3478m, 2962m, 2927m, 1608w, 1510m, 1464s, 1339m, 1292m, 1249m, 1172m, 1161s, 1145m; HRMS (ESI): m/z calcd for $C_{34}H_{33}NO_7SNa$ $[M+Ma]^+$: 622.1870; found 622.1851.

Discussions about the Barrier for the Epimerization Process of 3.

The actual "epimerization" process goes through a sequence of 6π-electrocyclic ring-opening and ring-closure of the chromene product **3**, although kinetic preference in the ring-closure could also be in play concomitantly. The barriers for these ring-openings and ring-closures are very low-much lower than that of 1,3,5-hextrienes. It can take place at temperature as low as 0 ^oC to RT with barrier Delta-E being as low as 10~12 $Kcal/mol^{-1}$.[12] In addition, for 1,3,5-hextrienes, donor heteroatoms substitutions at C3- position such as N, O, S can further lower the barrier.[13] Thus, by analogy, here for the 1-oxatriene intermediate with a donor atom (R-N-EWG at C4), the barrier should be even lower.

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