

Supporting Information

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A: General Information and Starting Materials	1
B: General Procedure for Cascade Reactions	2
C: Characterization Data.....	3
D: De- <i>tert</i> -butylation reaction	12
E: Mechanistic study.....	15
F: HPLC Analysis	16
G: NMR Analysis	39
H: Absolute Configuration and X-Ray Analysis Data.....	62
I: Reference	64

A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl_3 : δ 7.26, $(\text{CD}_3)_2\text{SO}$: δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl_3 : δ 77.16, $(\text{CD}_3)_2\text{SO}$: δ 39.6). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

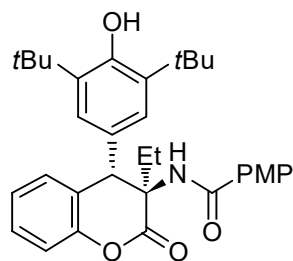
Starting Materials. All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted and catalysts **4a-h** were purchased from Sigma-Aldrich. The quinone methides and azlactones were prepared following the literature procedures.¹⁻²

B: General Procedure for Cascade Reactions

To a solution of CCl_4 (0.6 mL) were added quinone methides **1** (0.05 mmol), azlactones **2** (0.075 mmol) and catalyst **4e** (0.0025 mmol). The reaction mixture was stirred at room temperature for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired products.

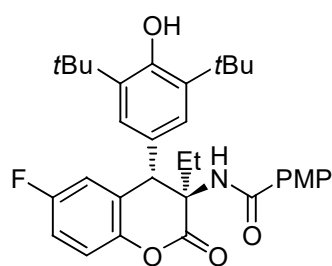
C: Characterization Data

N-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3aa)



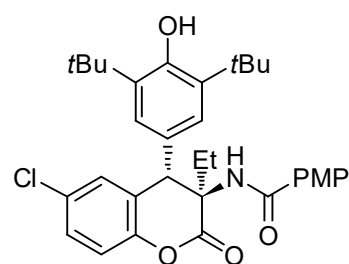
White solid, 91% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.65 (d, $J = 10.0$ Hz, 2H), 7.29-7.26 (m, 1H), 7.14-7.04 (m, 3H), 6.97 (s, 2H), 6.88 (d, $J = 10.0$ Hz, 2H), 5.74 (s, 1H), 5.54 (s, 1H), 5.21 (s, 1H), 3.84 (s, 3H), 2.07-2.03 (m, 1H), 1.65-1.61 (m, 1H), 1.31 (s, 18H), 0.97 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.6, 166.4, 162.5, 153.4, 150.9, 135.5, 129.0, 128.7, 128.4, 127.6, 126.3, 125.1, 124.7, 124.1, 116.6, 113.7, 61.9, 55.4, 46.9, 34.3, 30.2, 24.1, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{33}\text{H}_{40}\text{NO}_5$) requires m/z 530.2906, found m/z 530.2901. The enantiomeric ratio was determined to be 97:3 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 14.3 min (major), 21.4 min (minor).

N-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-6-fluoro-2-oxochroman-3-yl)-4-methoxybenzamide (3ba)



White solid, 82% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.66 (d, $J = 10.0$ Hz, 2H), 7.09-7.06 (m, 1H), 6.99-6.96 (m, 1H), 6.95 (s, 2H), 6.89 (d, $J = 10.0$ Hz, 2H), 6.87-6.85 (m, 1H), 5.73 (s, 1H), 5.58 (s, 1H), 5.24 (s, 1H), 3.85 (s, 3H), 2.02-1.96 (m, 1H), 1.68-1.61 (m, 1H), 1.32 (s, 18H), 0.97 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.6, 164.3 (d, $J = 1700.0$ Hz), 158.0, 153.6, 146.8 (d, $J = 10.0$ Hz), 135.7, 129.0, 127.5, 126.8 (d, $J = 30.0$ Hz), 126.2, 124.4, 117.8 (d, $J = 35.0$ Hz), 115.3, 115.1 (d, $J = 25.0$ Hz), 114.9, 113.7, 61.7, 55.4, 46.7, 34.3, 30.2, 24.3, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{33}\text{H}_{39}\text{FNO}_5$) requires m/z 548.2812, found m/z 548.2808. The enantiomeric ratio was determined to be 94:6 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 11.8 min (major), 15.6 min (minor).

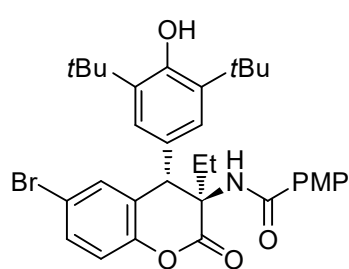
N-((3*R*,4*S*)-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ca)



White solid, 77% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.66 (d, $J = 10.0$ Hz, 2H), 7.25-7.23 (m, 1H), 7.14-7.13 (m, 1H), 7.05 (d, $J = 10.0$ Hz, 1H), 6.94 (s, 2H), 6.89 (d, $J = 10.0$ Hz, 2H), 5.74 (s, 1H), 5.53 (s, 1H), 5.25 (s, 1H), 3.84 (s, 3H), 2.04-1.96 (m, 1H), 1.67-1.61 (m, 1H), 1.32 (s, 18H), 0.97 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.6, 165.8, 162.6, 153.6, 149.4, 135.7, 129.3, 129.0, 128.6, 128.4, 127.5, 126.7, 126.1, 124.3, 117.9,

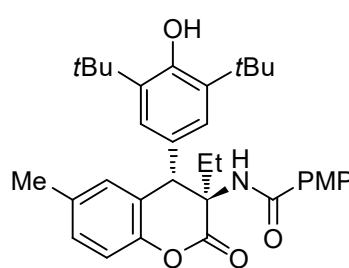
113.7, 61.7, 55.4, 46.8, 34.3, 30.2, 24.2, 8.0. HRMS (ESI): exact mass calculated for M^+ ($C_{33}H_{39}ClNO_5$) requires m/z 564.2517, found m/z 564.2513. The enantiomeric ratio was determined to be 98:2 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 11.4 min (major), 15.0 min (minor).

***N*-((3*R*,4*S*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3da)**



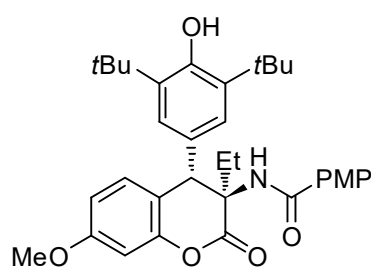
White solid, 74% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.66 (d, $J = 10.0$ Hz, 2H), 7.40-7.38 (m, 1H), 7.29 (s, 1H), 7.00 (d, $J = 5.0$ Hz, 1H), 6.94 (s, 2H), 6.88 (d, $J = 10.0$ Hz, 2H), 5.76 (s, 1H), 5.53 (s, 1H), 5.25 (s, 1H), 3.84 (s, 3H), 2.02-1.96 (m, 1H), 1.66-1.59 (m, 1H), 1.32 (s, 18H), 0.96 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.6, 165.8, 162.6, 153.6, 150.0, 135.7, 131.5, 131.3, 129.0, 127.5, 127.1, 126.1, 124.3, 118.3, 116.8, 113.7, 61.7, 55.4, 46.7, 34.3, 30.2, 24.2, 7.9. HRMS (ESI): exact mass calculated for M^+ ($C_{33}H_{39}BrNO_5$) requires m/z 608.2012, found m/z 608.2009. The enantiomeric ratio was determined to be 97:3 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 11.7 min (major), 15.6 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-6-methyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ea)**



White solid, 87% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.65 (d, $J = 10.0$ Hz, 2H), 7.07-7.05 (m, 1H), 7.00-6.99 (m, 1H), 6.97 (s, 2H), 6.95 (s, 1H), 6.88 (d, $J = 10.0$ Hz, 2H), 5.72 (s, 1H), 5.46 (s, 1H), 5.21 (s, 1H), 3.84 (s, 3H), 2.25 (s, 3H), 2.09-2.01 (m, 1H), 1.64-1.56 (m, 1H), 1.32 (s, 18H), 0.96 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.6, 166.5, 162.4, 153.4, 148.8, 135.4, 133.7, 129.1, 129.0, 128.8, 127.5, 126.4, 125.2, 124.2, 116.3, 113.7, 62.0, 55.4, 46.9, 34.3, 30.3, 24.0, 20.8, 8.0. HRMS (ESI): exact mass calculated for M^+ ($C_{34}H_{42}NO_5$) requires m/z 544.3063, found m/z 544.3059. The enantiomeric ratio was determined to be 97:3 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 17.4 min (major), 20.1 min (minor).

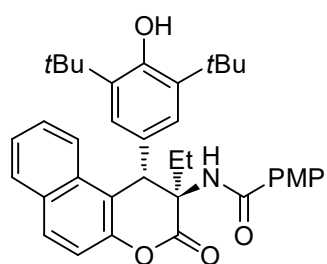
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-7-methoxy-2-oxochroman-3-yl)-4-methoxybenzamide (3fa)**



White solid, 85% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.65 (d, $J = 10.0$ Hz, 2H), 7.02 (d, $J = 10.0$ Hz, 1H), 6.95 (s, 2H), 6.88 (d, $J = 10.0$ Hz, 2H), 6.67 (s, 1H), 6.62-6.60 (m, 1H), 5.73 (s, 1H), 5.41 (s, 1H), 5.20 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.10-2.03 (m, 1H),

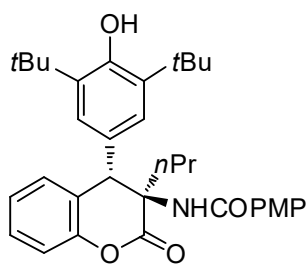
1.61-1.55 (m, 1H), 1.31 (s, 18H), 0.96 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.5, 166.4, 162.5, 159.7, 153.3, 151.6, 135.4, 129.3, 129.0, 127.5, 126.4, 125.5, 116.4, 113.7, 110.2, 102.0, 62.0, 55.5, 55.4, 46.3, 34.3, 30.2, 24.6, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{34}\text{H}_{42}\text{NO}_6$) requires m/z 560.3012, found m/z 560.3010. The enantiomeric ratio was determined to be 94:6 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 14.7 min (major), 26.3 min (minor).

***N*-((1*S*,2*R*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-ethyl-3-oxo-2,3-dihydro-1*H*-benzo[*f*]chromen-2-yl)-4-methoxybenzamide (3ga)**



White solid, 89% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.94-7.92 (m, 1H), 7.83-7.79 (m, 2H), 7.52-7.49 (m, 1H), 7.42-7.39 (m, 1H), 7.33-7.28 (m, 3H), 7.05 (s, 2H), 6.71-6.67 (m, 2H), 5.88 (s, 1H), 5.16 (s, 1H), 4.90 (s, 1H), 3.73 (s, 3H), 2.64-2.57 (m, 1H), 1.65-1.58 (m, 1H), 1.36 (s, 18H), 1.10 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.6, 166.3, 162.3, 153.5, 149.6, 136.2, 131.5, 130.9, 129.9, 128.9, 128.7, 127.3, 126.2, 125.8, 125.1, 124.9, 122.8, 117.0, 113.7, 113.6, 61.1, 55.3, 48.2, 34.3, 30.2, 22.8, 7.6. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{37}\text{H}_{42}\text{NO}_5$) requires m/z 580.3063, found m/z 580.3059. The enantiomeric ratio was determined to be 82:18 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 9.9 min (minor), 17.1 min (major).

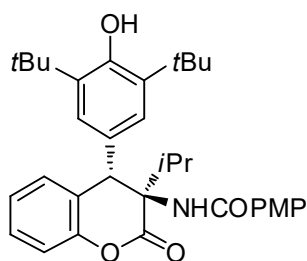
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-3-propylchroman-3-yl)-4-methoxybenzamide (3ab)**



White solid, 87% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.64 (d, $J = 10.0$ Hz, 2H), 7.30-7.26 (m, 1H), 7.14-7.10 (m, 2H), 7.08-7.05 (m, 1H), 6.97 (s, 2H), 6.88 (d, $J = 10.0$ Hz, 2H), 5.76 (s, 1H), 5.50 (s, 1H), 5.22 (s, 1H), 3.84 (s, 3H), 1.99-1.92 (m, 1H), 1.54-1.48 (m, 1H), 1.44-1.36 (m, 2H), 1.32 (s, 18H), 0.86 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.7, 166.5, 162.5, 153.4, 150.9, 135.5, 129.0, 128.6, 128.4, 127.5, 126.3, 125.1, 124.7, 124.2, 116.6, 113.7, 61.6, 55.4, 47.0, 34.3, 33.8, 30.2, 16.8, 14.1. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{34}\text{H}_{42}\text{NO}_5$) requires m/z 544.3063, found m/z 544.3061. The enantiomeric ratio was determined to be 92:8 by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 9:1, 0.8 mL/min]: 12.1 min (minor), 14.9 min (major).

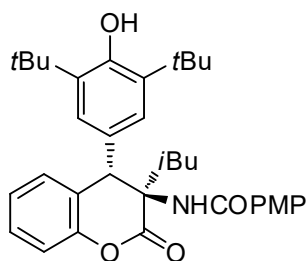
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-isopropyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ac)**

White solid, 72% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.62 (d, $J = 10.0$ Hz, 2H), 7.24-7.21 (m, 1H), 7.09-7.07 (m, 2H), 7.04-7.01 (m, 3H), 6.88 (d, $J = 10.0$ Hz,



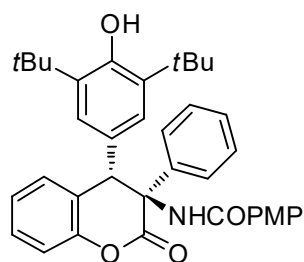
2H), 5.85 (s, 1H), 5.36 (s, 1H), 5.23 (s, 1H), 3.84 (s, 3H), 2.16-2.10 (m, 1H), 1.32 (s, 18H), 1.05 (d, $J = 10.0$ Hz, 3H), 1.01 (d, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.0, 165.7, 162.5, 153.4, 151.2, 135.7, 128.8, 128.2, 127.3, 127.2, 126.2, 125.9, 125.3, 124.1, 116.4, 113.8, 63.6, 55.4, 48.0, 34.3, 31.9, 30.2, 18.8, 18.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{34}\text{H}_{42}\text{NO}_5$) requires m/z 544.3063, found m/z 544.3058. The enantiomeric ratio was determined to be 96:4 by HPLC. [IC column, 254 nm, n -hexane:EtOH = 85:15, 0.8 mL/min]: 16.3 min (major), 19.1 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-isobutyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ad)**



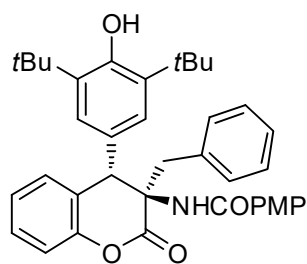
White solid, 87% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.64 (d, $J = 10.0$ Hz, 2H), 7.30-7.27 (m, 1H), 7.12-7.10 (m, 2H), 7.08-7.05 (m, 1H), 6.96 (s, 2H), 6.89 (d, $J = 10.0$ Hz, 2H), 5.74 (s, 1H), 5.64 (s, 1H), 5.21 (s, 1H), 3.84 (s, 3H), 1.98-1.94 (m, 2H), 1.87-1.79 (m, 1H), 1.31 (s, 18H), 1.00 (d, $J = 5.0$ Hz, 3H), 0.88 (d, $J = 5.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.4, 166.2, 162.4, 153.4, 150.8, 135.3, 128.9, 128.7, 128.4, 127.8, 126.5, 124.9, 124.8, 124.1, 116.5, 113.7, 61.8, 55.4, 47.0, 40.1, 34.3, 30.3, 24.3, 24.2, 24.1. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{34}\text{H}_{44}\text{NO}_5$) requires m/z 558.3219, found m/z 558.3215. The enantiomeric ratio was determined to be 91:9 by HPLC. [IC column, 254 nm, n -hexane:EtOH = 85:15, 0.8 mL/min]: 10.8 min (minor), 13.9 min (major).

***N*-((3*S*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-3-phenylchroman-3-yl)-4-methoxybenzamide (3ae)**



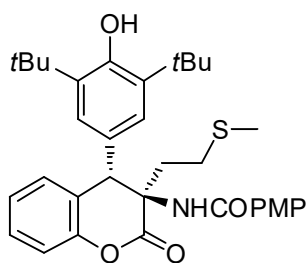
White solid, 88% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.74 (d, $J = 10.0$ Hz, 2H), 7.31-7.29 (m, 1H), 7.26-7.25 (m, 1H), 7.18-7.15 (m, 2H), 7.02-7.00 (m, 2H), 6.93 (d, $J = 10.0$ Hz, 2H), 6.78 (d, $J = 10.0$ Hz, 2H), 6.50-6.49 (m, 3H), 5.90 (s, 1H), 5.19 (s, 1H), 3.86 (s, 3H), 1.21 (s, 18H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 167.9, 167.4, 162.7, 153.5, 151.1, 135.1, 134.7, 129.1, 128.9, 128.7, 128.5, 128.4, 126.7, 126.4, 124.5, 124.3, 124.0, 116.8, 113.8, 66.4, 55.4, 48.4, 34.1, 30.1. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{37}\text{H}_{40}\text{NO}_5$) requires m/z 578.2906, found m/z 578.2902. The enantiomeric ratio was determined to be 97:3 by HPLC. [IC column, 254 nm, n -hexane:EtOH = 85:15, 0.8 mL/min]: 15.6 min (major), 25.5 min (minor).

***N*-((3*R*,4*S*)-3-benzyl-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxochroman-3-yl)-4-methoxybenzamide (3af)**



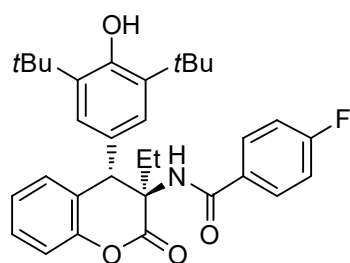
White solid, 83% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.47 (d, $J = 10.0$ Hz, 2H), 7.31-7.27 (m, 4H), 7.19-7.16 (m, 2H), 7.10 (s, 2H), 7.08-7.05 (m, 3H), 6.83 (d, $J = 10.0$ Hz, 2H), 5.81 (s, 1H), 5.40 (s, 1H), 5.26 (s, 1H), 3.82 (s, 3H), 3.47 (d, $J = 15.0$ Hz, 1H), 2.92 (d, $J = 15.0$ Hz, 1H), 1.37 (s, 18H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.7, 166.2, 162.4, 153.5, 150.9, 135.7, 134.1, 130.4, 128.9, 128.8, 128.7, 128.6, 127.7, 127.3, 126.4, 125.6, 124.7, 124.2, 116.6, 113.7, 61.8, 55.4, 48.1, 36.2, 34.4, 30.3. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{38}\text{H}_{42}\text{NO}_5$) requires m/z 592.3063, found m/z 592.3057. The enantiomeric ratio was determined to be 99:1 by HPLC. [IC column, 254 nm, n -hexane:EtOH = 85:15, 0.8 mL/min]: 13.7 min (major), 16.7 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(2-(methylthio)ethyl)-2-oxochroman-3-yl)-4-methoxybenzamide (3ag)**



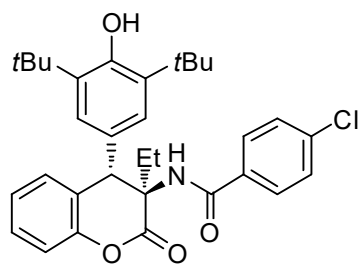
White solid, 86% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.68 (d, $J = 10.0$ Hz, 2H), 7.30-7.27 (m, 1H), 7.16-7.06 (m, 3H), 6.97 (s, 2H), 6.88 (d, $J = 10.0$ Hz, 2H), 6.70 (s, 1H), 5.58 (s, 1H), 5.23 (s, 1H), 3.84 (s, 3H), 2.67-2.56 (m, 2H), 2.27-2.21 (m, 1H), 2.01 (s, 3H), 1.98-1.92 (m, 1H), 1.31 (s, 18H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.5, 166.4, 162.5, 153.5, 150.7, 135.6, 129.1, 128.7, 128.5, 127.6, 126.0, 124.7, 124.4, 124.3, 116.6, 113.7, 62.0, 55.4, 47.0, 34.3, 30.2, 29.3, 28.0, 15.6. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{34}\text{H}_{42}\text{NO}_5\text{S}$) requires m/z 576.2784, found m/z 576.2780. The enantiomeric ratio was determined to be 91:9 by HPLC. [IC column, 254 nm, n -hexane:EtOH = 85:15, 0.8 mL/min]: 13.5 min (major), 15.6 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-fluorobenzamide (3ah)**



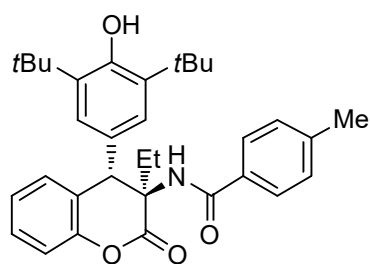
White solid, 72% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.71-7.68 (m, 2H), 7.30-7.27 (m, 1H), 7.14-7.10 (m, 2H), 7.08-7.05 (m, 3H), 6.97 (s, 2H), 5.81 (s, 1H), 5.54 (s, 1H), 5.23 (s, 1H), 2.10-2.02 (m, 1H), 1.68-1.64 (m, 1H), 1.32 (s, 18H), 0.97 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.2, 166.0, 164.9 (d, $J = 1000.0$ Hz), 153.5, 150.8, 135.6, 130.2 (d, $J = 10.0$ Hz), 129.5 (d, $J = 35.0$ Hz), 128.6 (d, $J = 100.0$ Hz), 127.5, 124.9, 124.6, 124.2, 116.6, 115.7, 115.5, 62.2, 46.8, 34.3, 30.2, 24.1, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{32}\text{H}_{37}\text{FNO}_4$) requires m/z 518.2707, found m/z 518.2701. The enantiomeric ratio was determined to be 96:4 by HPLC. [IC column, 254 nm, n -hexane:EtOH = 85:15, 0.8 mL/min]: 6.5 min (major), 9.1 min (minor).

4-Chloro-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3ai)



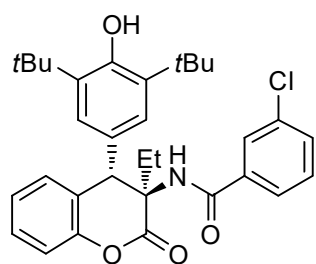
White solid, 85% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.62-7.60 (m, 2H), 7.37-7.35 (m, 2H), 7.30-7.26 (m, 1H), 7.14-7.10 (m, 2H), 7.08-7.05 (m, 1H), 6.96 (s, 2H), 5.84 (s, 1H), 5.52 (s, 1H), 5.23 (s, 1H), 2.10-2.03 (m, 1H), 1.69-1.63 (m, 1H), 1.32 (s, 18H), 0.97 (t, $J = 5.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.2, 166.1, 153.5, 150.8, 138.1, 135.6, 132.5, 128.8, 128.7, 128.6, 128.5, 127.5, 124.9, 124.6, 124.3, 116.6, 62.2, 46.8, 34.3, 30.2, 24.1, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{32}\text{H}_{37}\text{ClNO}_4$) requires m/z 534.2411, found m/z 534.2407. The enantiomeric ratio was determined to be 97:3 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 6.5 min (major), 9.1 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methylbenzamide (3aj)**



White solid, 87% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.57 (d, $J = 10.0$ Hz, 2H), 7.29-7.28 (m, 1H), 7.19 (d, $J = 10.0$ Hz, 2H), 7.14-7.10 (m, 2H), 7.07-7.04 (m, 1H), 6.97 (s, 2H), 5.79 (s, 1H), 5.53 (s, 1H), 5.21 (s, 1H), 2.38 (s, 3H), 2.10-2.02 (m, 1H), 1.67-1.63 (m, 1H), 1.32 (s, 18H), 0.97 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 167.1, 166.3, 153.4, 150.9, 142.3, 135.5, 131.2, 129.1, 128.7, 128.4, 127.6, 127.1, 125.1, 124.7, 124.1, 116.6, 62.0, 46.9, 34.3, 30.2, 24.1, 24.5, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{33}\text{H}_{40}\text{NO}_4$) requires m/z 514.2957, found m/z 514.2950. The enantiomeric ratio was determined to be 95:5 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 10.3 min (major), 12.9 min (minor).

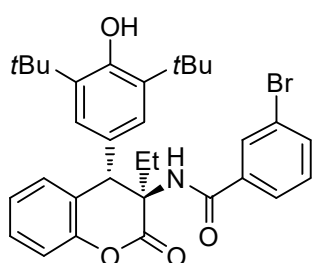
3-Chloro-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3ak)



White solid, 91% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.62 (s, 1H), 7.57-7.55 (m, 1H), 7.47-7.45 (m, 1H), 7.35-7.26 (m, 2H), 7.14-7.10 (m, 2H), 7.08-7.05 (m, 1H), 6.97 (s, 2H), 5.85 (s, 1H), 5.52 (s, 1H), 5.24 (s, 1H), 2.09-2.04 (m, 1H), 1.70-1.66 (m, 1H), 1.33 (s, 18H), 0.97 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.1, 165.9, 153.5, 150.8, 135.9, 135.6, 134.6, 131.9, 129.9, 128.7, 128.5, 127.5, 127.3, 125.4, 124.9, 124.5, 124.3, 116.6, 62.3, 46.7, 34.3, 30.2, 24.1, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{32}\text{H}_{37}\text{ClNO}_4$) requires m/z 534.2411, found m/z 534.2406. The enantiomeric ratio was determined to be 92:8

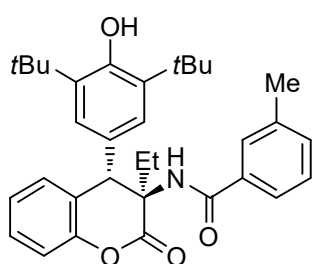
by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 9:1, 0.8 mL/min]: 9.0 min (major), 12.5 min (minor).

3-Bromo-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3al)



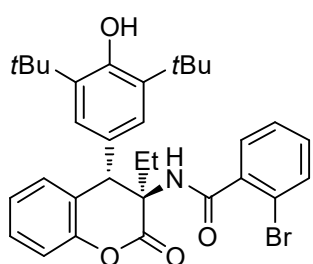
White solid, 87% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.77 (s, 1H), 7.63-7.61 (m, 2H), 7.30-7.26 (m, 2H), 7.14-7.10 (m, 2H), 7.08-7.05 (m, 1H), 6.97 (s, 2H), 5.82 (s, 1H), 5.52 (s, 1H), 5.24 (s, 1H), 2.09-2.04 (m, 1H), 1.69-1.64 (m, 1H), 1.33 (s, 18H), 0.97 (t, *J* = 10.0 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 166.0, 165.8, 153.5, 150.8, 136.2, 135.6, 134.8, 130.2, 130.1, 128.7, 128.5, 127.5, 125.9, 124.9, 124.5, 124.3, 122.6, 116.6, 62.3, 46.7, 34.3, 30.2, 24.1, 8.0. HRMS (ESI): exact mass calculated for M⁺ (C₃₂H₃₇BrNO₄) requires *m/z* 578.1906, found *m/z* 578.1901. The enantiomeric ratio was determined to be 93:7 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 9:1, 0.8 mL/min]: 9.5 min (major), 13.5 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-3-methylbenzamide (3am)**



White solid, 94% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.50 (s, 1H), 7.44-7.42 (m, 1H), 7.31-7.25 (m, 3H), 7.14-7.11 (m, 2H), 7.08-7.05 (m, 1H), 6.98 (s, 2H), 5.79 (s, 1H), 5.55 (s, 1H), 5.22 (s, 1H), 2.36 (s, 3H), 2.10-2.02 (m, 1H), 1.68-1.62 (m, 1H), 1.32 (s, 18H), 0.98 (t, *J* = 10.0 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 167.4, 166.2, 153.4, 150.9, 138.4, 135.5, 134.1, 132.6, 128.7, 128.4, 128.3, 127.8, 127.6, 125.1, 124.7, 124.2, 124.1, 116.6, 62.0, 46.8, 34.3, 30.2, 24.1, 21.3, 8.0. HRMS (ESI): exact mass calculated for M⁺ (C₃₃H₄₀NO₄) requires *m/z* 514.2957, found *m/z* 514.2952. The enantiomeric ratio was determined to be 92:8 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 9.3 min (major), 11.4 min (minor).

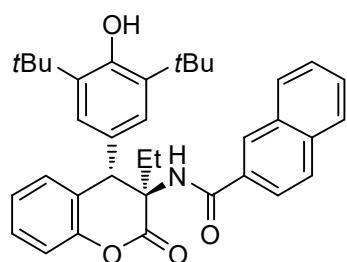
2-Bromo-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3an)



White solid, 92% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.55-7.52 (m, 2H), 7.33-7.28 (m, 2H), 7.25-7.23 (m, 1H), 7.14-7.13 (m, 1H), 7.08-7.04 (m, 2H), 7.00 (s, 2H), 6.06 (s, 1H), 5.24 (s, 1H), 5.22 (s, 1H), 2.24-2.17 (m, 1H), 1.74-1.66 (m, 1H), 1.37 (s, 18H), 1.02 (t, *J* = 10.0 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 166.3, 165.9, 153.5, 151.1, 136.2, 135.8, 133.7, 131.8, 130.7, 129.0, 128.6,

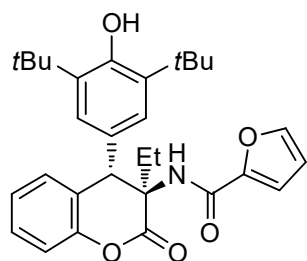
127.5, 126.9, 125.6, 125.0, 124.3, 119.3, 116.5, 62.7, 48.1, 34.3, 30.3, 23.9, 8.1. HRMS (ESI): exact mass calculated for M^+ ($C_{32}H_{37}BrNO_4$) requires m/z 578.1906, found m/z 578.1900. The enantiomeric ratio was determined to be 93:7 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 9.2 min (major), 13.6 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-2-naphthamide (3ao)**



White solid, 91% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.15 (s, 1H), 7.86-7.84 (m, 3H), 7.74-7.72 (m, 1H), 7.57-7.50 (m, 2H), 7.31-7.28 (m, 1H), 7.17-7.13 (m, 2H), 7.09-7.06 (m, 1H), 7.03 (s, 2H), 6.01 (s, 1H), 5.60 (s, 1H), 5.22 (s, 1H), 2.16-2.08 (m, 1H), 1.75-1.68 (m, 1H), 1.31 (s, 18H), 1.02 (t, J = 10.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 167.4, 166.3, 153.5, 150.9, 135.6, 134.9, 132.4, 131.4, 128.8, 128.7, 128.5, 128.4, 127.8, 127.7, 127.6, 127.5, 126.8, 125.1, 124.7, 124.2, 123.6, 116.6, 62.2, 47.0, 34.3, 30.2, 24.2, 8.1. HRMS (ESI): exact mass calculated for M^+ ($C_{36}H_{40}NO_4$) requires m/z 550.2957, found m/z 550.2951. The enantiomeric ratio was determined to be 94:6 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 9.6 min (major), 12.7 min (minor).

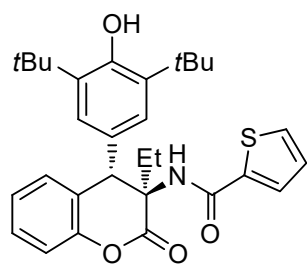
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)furan-2-carboxamide (3ap)**



White solid, 91% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.37 (s, 1H), 7.30-7.27 (m, 1H), 7.21-7.20 (m, 1H), 7.18-7.16 (m, 1H), 7.11 (d, J = 10.0 Hz, 1H), 7.08-7.05 (m, 1H), 6.96 (s, 2H), 6.51 (s, 1H), 6.04 (s, 1H), 5.52 (s, 1H), 5.21 (s, 1H), 2.04-1.97 (m, 1H), 1.62-1.55 (m, 1H), 1.31 (s, 18H), 0.96 (t, J = 10.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.1, 157.7, 153.4, 150.8, 147.5, 143.8, 135.4, 128.7, 128.4, 127.6, 124.7, 124.3, 124.2, 116.6, 115.2, 112.4, 61.8, 46.7, 34.3, 30.2, 24.0, 7.9. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{36}NO_5$) requires m/z 490.2593, found m/z 490.2589. The enantiomeric ratio was determined to be 91:9 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 11.1 min (major), 16.1 min (minor).

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)thiophene-2-carboxamide (3aq)**

White solid, 98% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.48-7.47 (m, 1H), 7.43-7.42 (m, 1H), 7.29-7.26 (m, 1H), 7.15-7.14 (m, 1H), 7.11-7.10 (m, 1H), 7.08-7.05 (m, 1H), 7.05-7.02 (m, 1H), 6.98 (s, 2H), 5.67 (s, 1H), 5.52 (s, 1H), 5.22 (s, 1H), 2.07-2.00 (m, 1H), 1.65-1.57 (m, 1H), 1.31 (s, 18H), 0.97 (t, J = 10.0 Hz, 3H).



10.0 min (major), 13.0 min (minor).

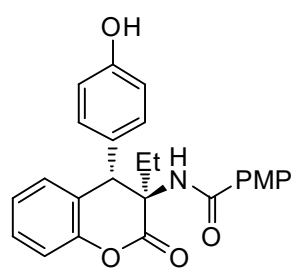
^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 166.1, 161.4, 153.5, 150.8, 138.1, 135.5, 130.5, 128.8, 128.7, 128.5, 127.6, 127.5, 124.8, 124.5, 124.2, 116.6, 62.2, 46.8, 34.3, 30.2, 24.1, 8.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{30}\text{H}_{30}\text{NO}_4\text{S}$) requires m/z 506.2365, found m/z 506.2360. The enantiomeric ratio was determined to be 94:6 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]:

D: De-*tert*-butylation reaction.



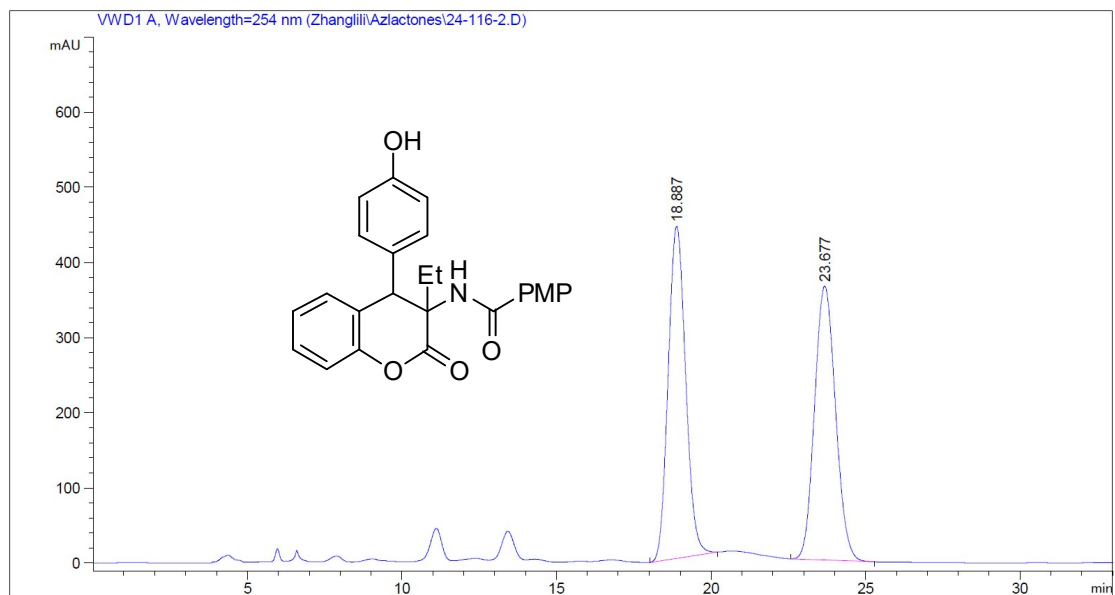
To a solution of **3aa** (17.1 mg, 0.032 mmol) in dry toluene (1.5 mL) was added AlCl_3 (21.5 mg, 5.0 eq) in one portion. The reaction solution was stirred at room temperature for 24 h and 1.5 mL H_2O was added to quench the reaction. The aqueous phase was extracted with CH_2Cl_2 (3×1.0 mL) and the organic layer was dried with anhydrous Na_2SO_4 and reduced in vacuum to give a residue, which was purified by column chromatography to afford the product **5** as a white solid (10.7 mg, 80% yield, 94:6 e.r., >20:1 d.r.).

N-((3*R*,4*S*)-3-ethyl-4-(4-hydroxyphenyl)-2-oxochroman-3-yl)-4-methoxybenzamide (**5**)

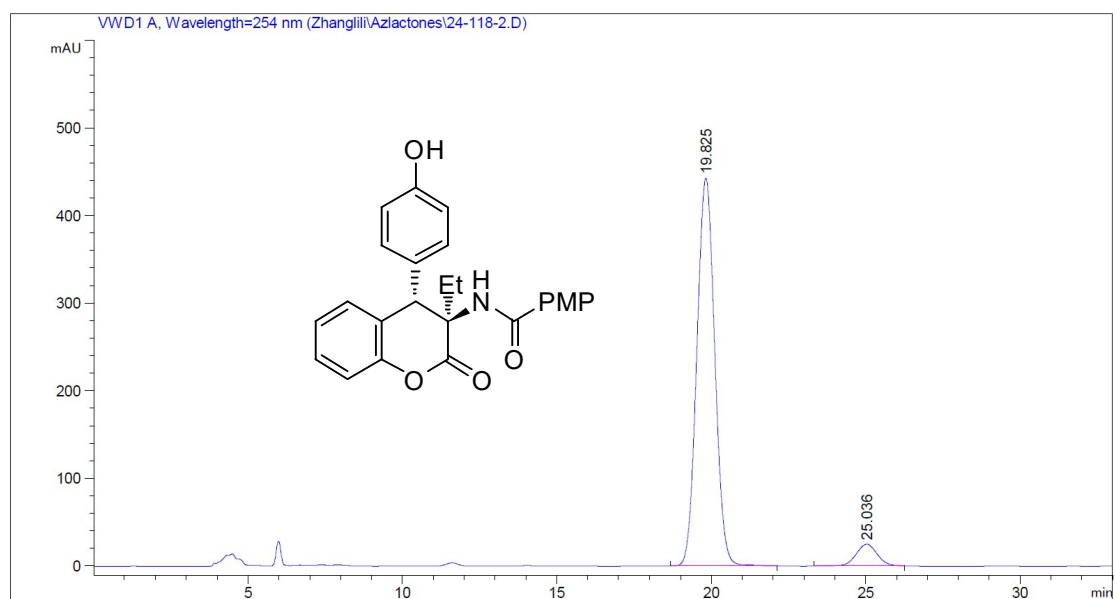


White solid, 80% yield. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 500 MHz): δ (ppm) 9.46 (s, 1H), 8.13 (s, 1H), 7.56 (d, $J = 10.0$ Hz, 2H), 7.25-7.22 (m, 1H), 7.10-7.04 (m, 3H), 6.92 (d, $J = 10.0$ Hz, 2H), 6.87 (d, $J = 10.0$ Hz, 2H), 6.70 (d, $J = 10.0$ Hz, 2H), 4.89 (s, 1H), 3.75 (s, 3H), 1.96-1.88 (m, 1H), 1.51-1.44 (m, 1H), 0.89 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 125 MHz): δ (ppm) 167.1, 166.4, 162.2, 157.3, 151.6, 130.7, 129.8, 129.7, 128.8, 127.2, 126.3, 125.9, 124.4, 115.9, 115.8, 113.9, 61.1, 55.8, 48.4, 24.5, 8.3. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{25}\text{H}_{24}\text{NO}_5$) requires m/z 418.1654, found m/z 418.1650. The enantiomeric ratio was determined to be 94:6 by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 85:15, 0.8 mL/min]: 19.8 min (major), 25.0 min (minor).

***N*-((3*R*,4*S*)-3-ethyl-4-(4-hydroxyphenyl)-2-oxochroman-3-yl)-4-methoxybenzamide
(5)**

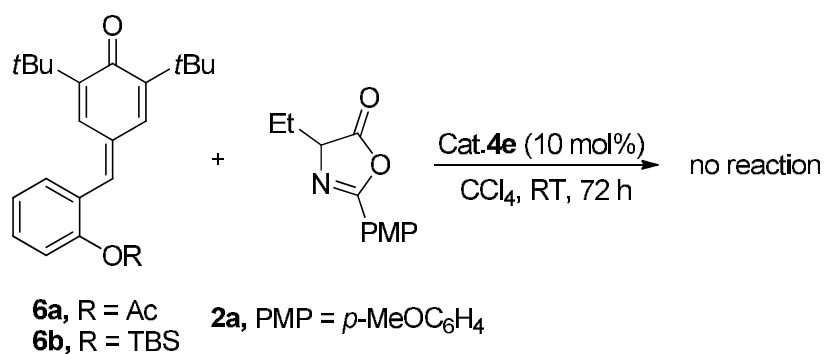


#	Time	Area	Height	Width	Symmetry	Area %
1	18.887	17332.9	441.8	0.6167	0.893	50.206
2	23.677	17190.6	364.4	0.7384	0.888	49.794



#	Time	Area	Height	Width	Symmetry	Area %
1	19.825	17822	442.4	0.636	0.967	93.849
2	25.036	1168.1	24.7	0.7291	1.026	6.151

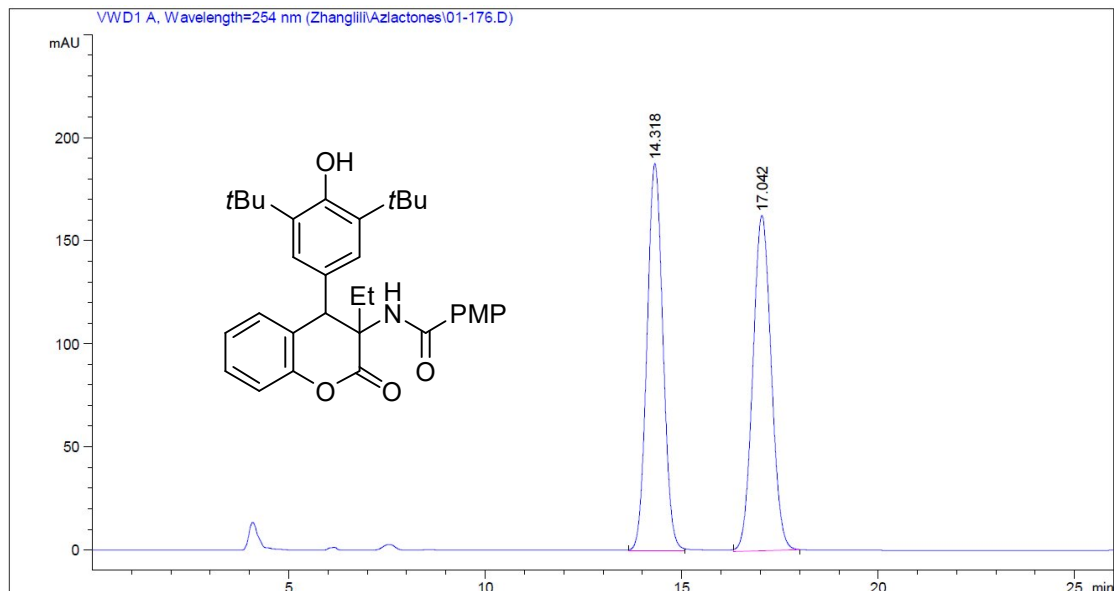
E: Mechanistic study



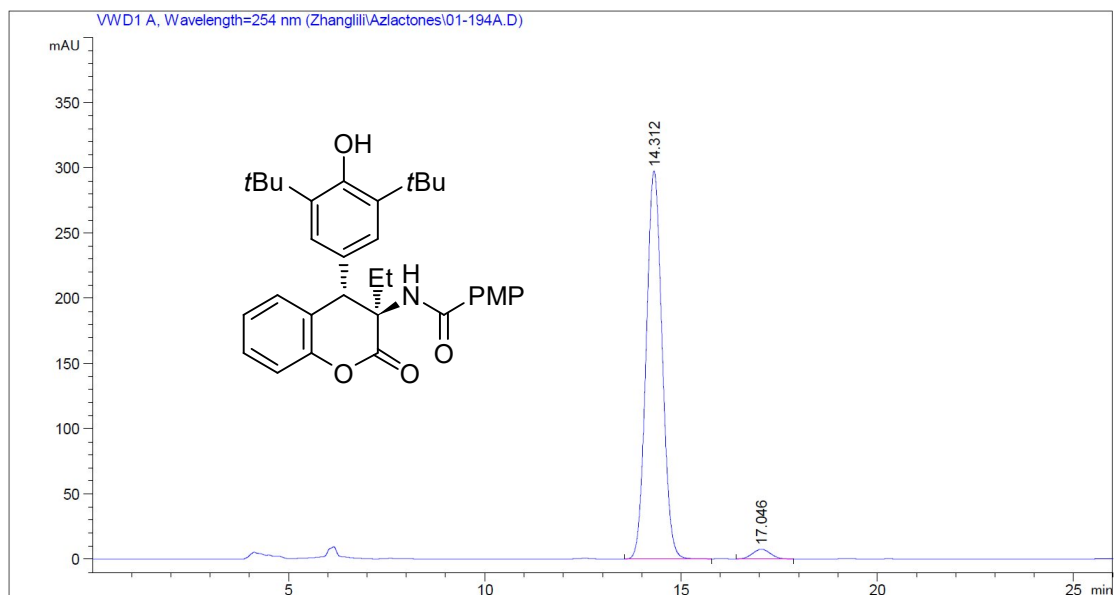
To a solution of CCl₄ (0.3 mL) were added Ac (or TBS)-protected quinone methides **6** (0.05 mmol), azlactone **2a** (0.075 mmol) and catalyst **4e** (0.005 mmol). The reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by TLC analysis, which indicated that almost no reaction occurred.

F: HPLC Analysis

N-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3aa)

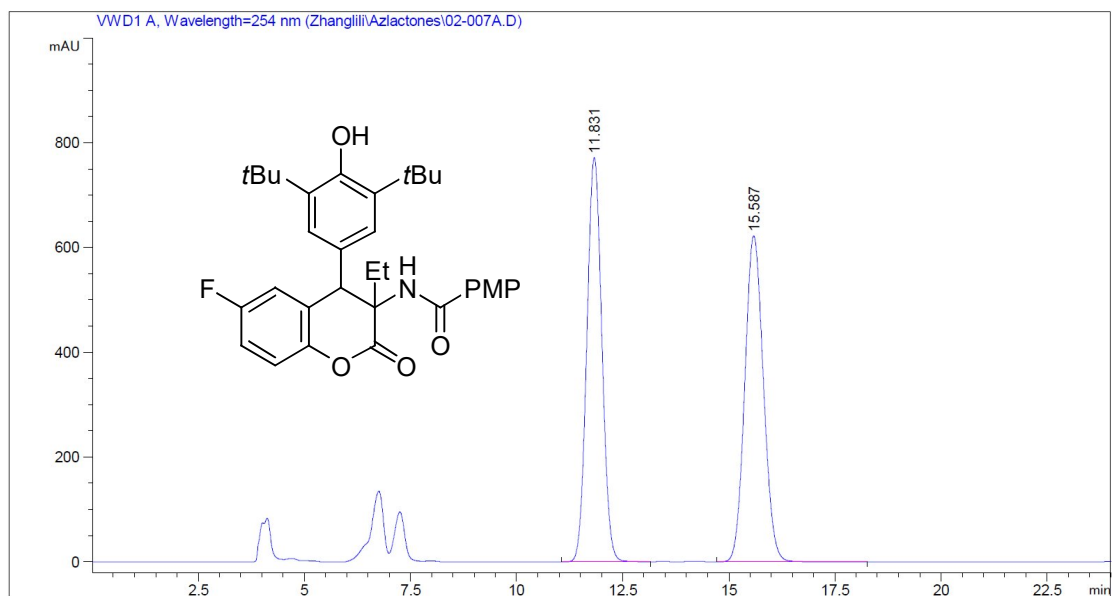


#	Time	Area	Height	Width	Symmetry	Area %
1	14.318	5292.5	187.7	0.4699	0.942	49.970
2	17.042	5298.9	162.7	0.5429	0.941	50.030

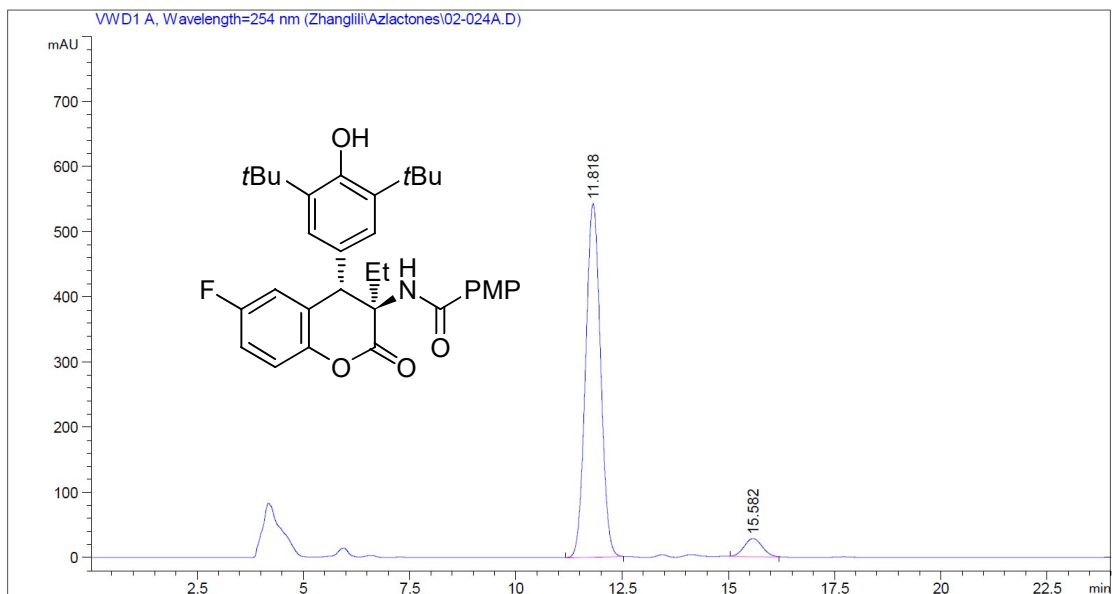


#	Time	Area	Height	Width	Symmetry	Area %
1	14.312	8412.2	297.5	0.4713	0.93	97.135
2	17.046	248.1	7.6	0.5447	0.939	2.865

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-6-fluoro-2-oxochroman-3-yl)-4-methoxybenzamide (3ba)**

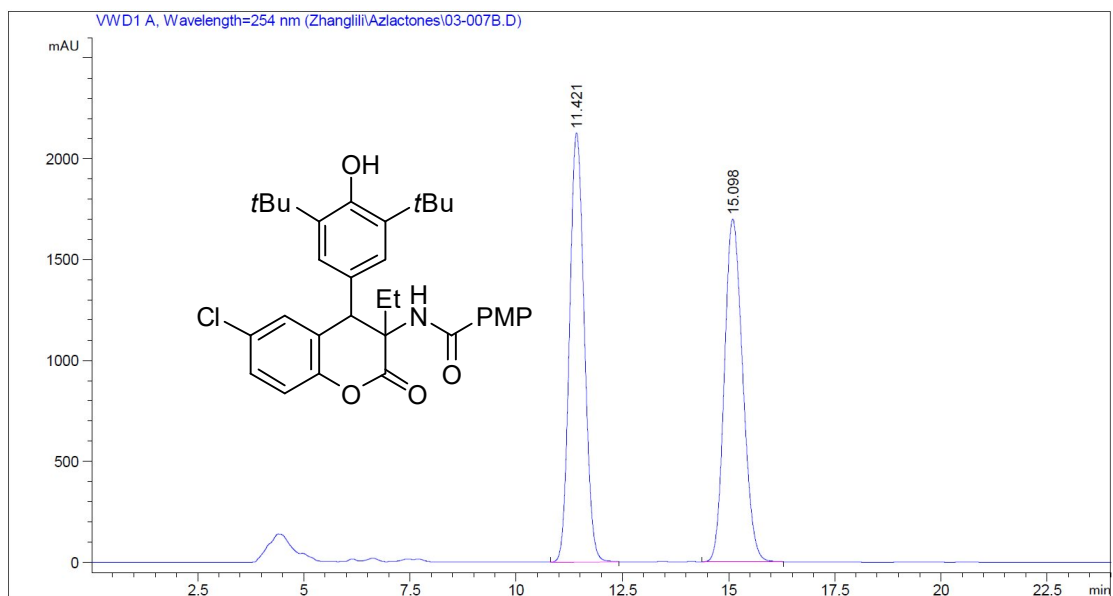


#	Time	Area	Height	Width	Symmetry	Area %
1	11.831	18979	771.7	0.3849	0.939	49.980
2	15.587	18993.9	622.7	0.4769	0.882	50.020

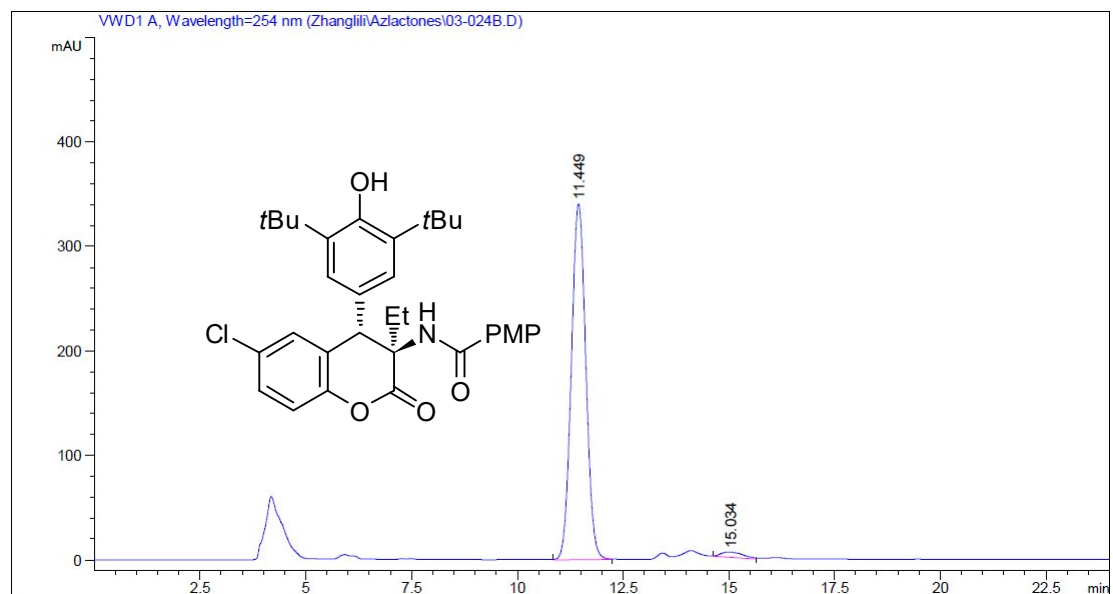


#	Time	Area	Height	Width	Symmetry	Area %
1	11.818	13307.5	543.1	0.4084	0.965	94.109
2	15.582	833	28	0.4953	0.941	5.891

***N*-((3*R*,4*S*)-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ca)**

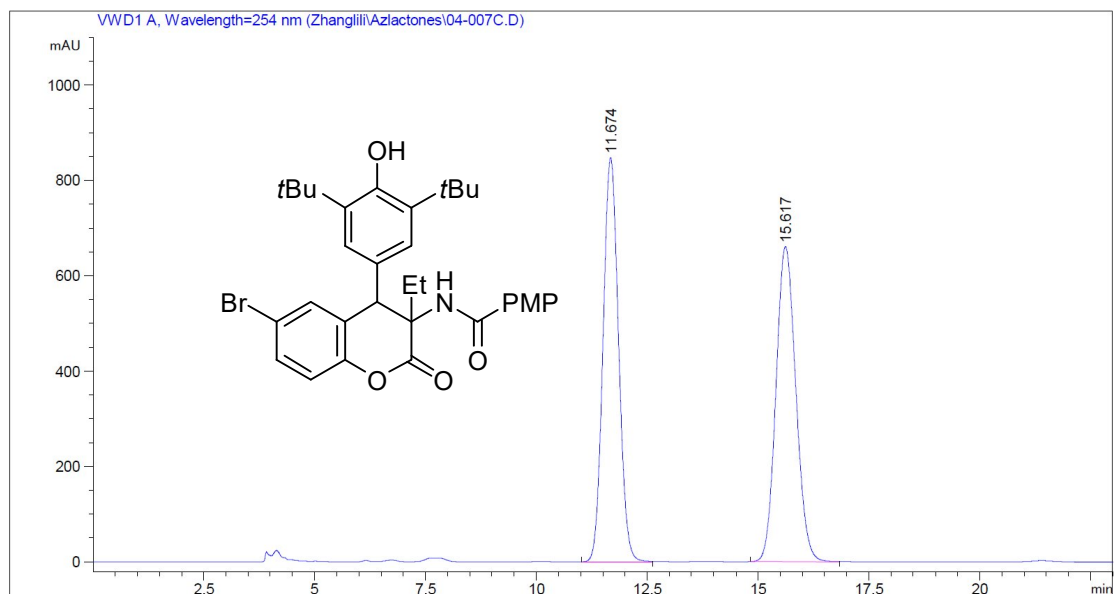


#	Time	Area	Height	Width	Symmetry	Area %
1	11.421	51177.9	2128.6	0.4007	0.874	50.028
2	15.098	51121	1699.9	0.5012	0.805	49.972

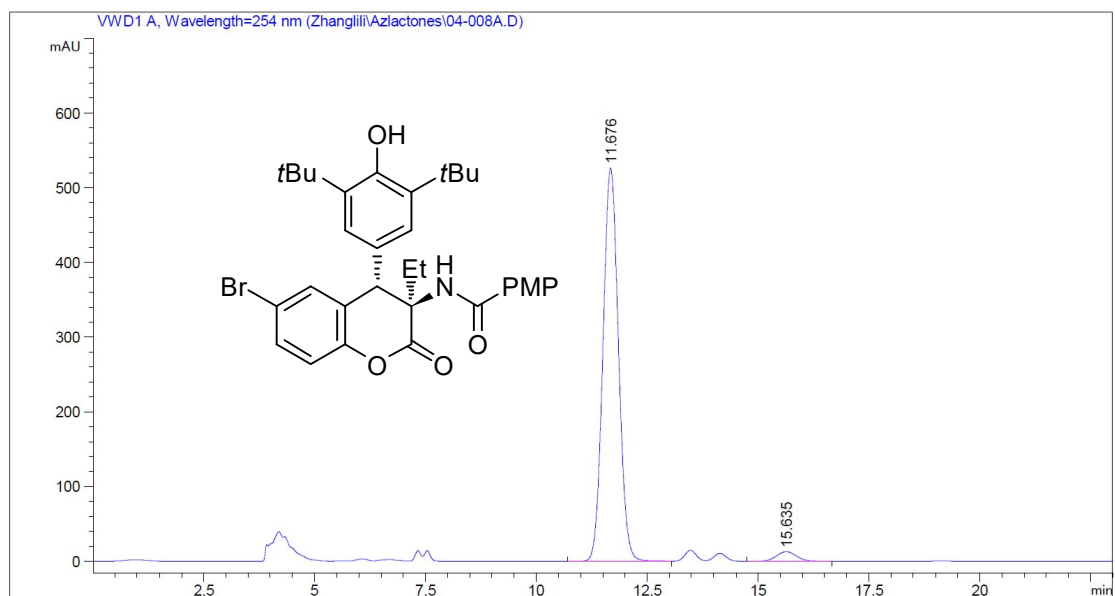


#	Time	Area	Height	Width	Symmetry	Area %
1	11.449	8089.6	340.6	0.3958	0.959	97.829
2	15.034	179.5	4.9	0.6077	0.467	2.171

***N*-((3*R*,4*S*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3da)**

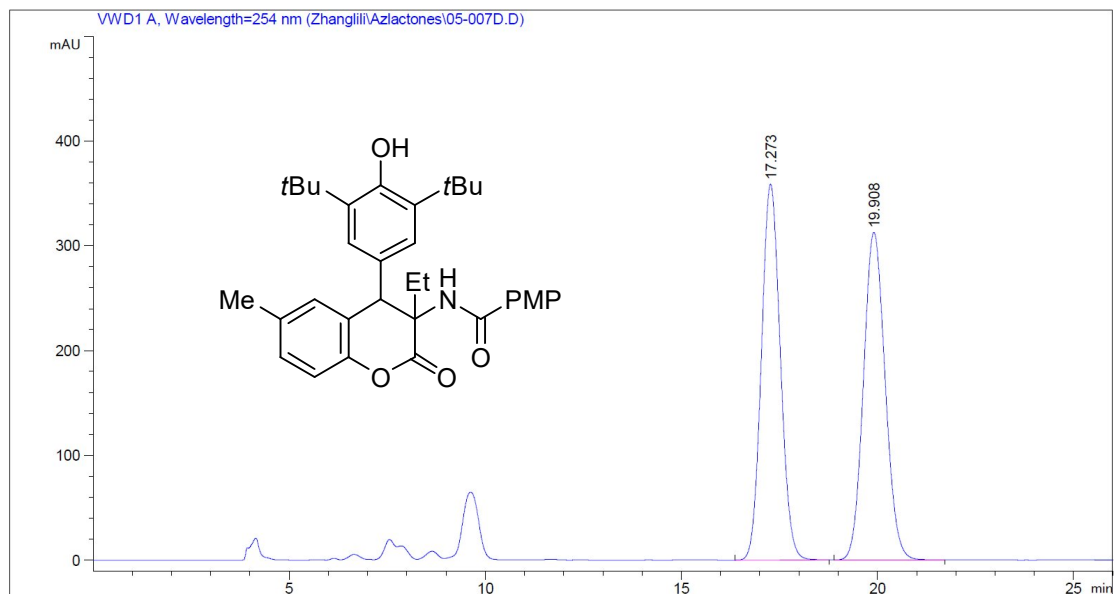


#	Time	Area	Height	Width	Symmetry	Area %
1	11.674	20595	847.9	0.4048	0.916	50.035
2	15.617	20566	660.9	0.5186	0.879	49.965

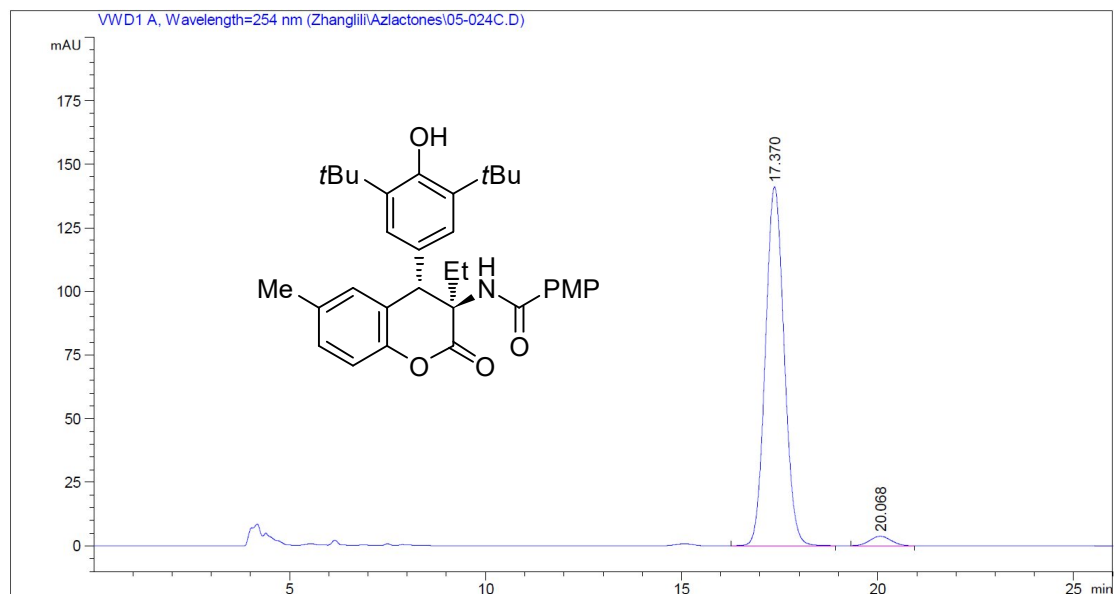


#	Time	Area	Height	Width	Symmetry	Area %
1	11.676	12760.4	526.1	0.3789	0.929	96.918
2	15.635	405.8	13	0.484	0.923	3.082

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-6-methyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ea)**

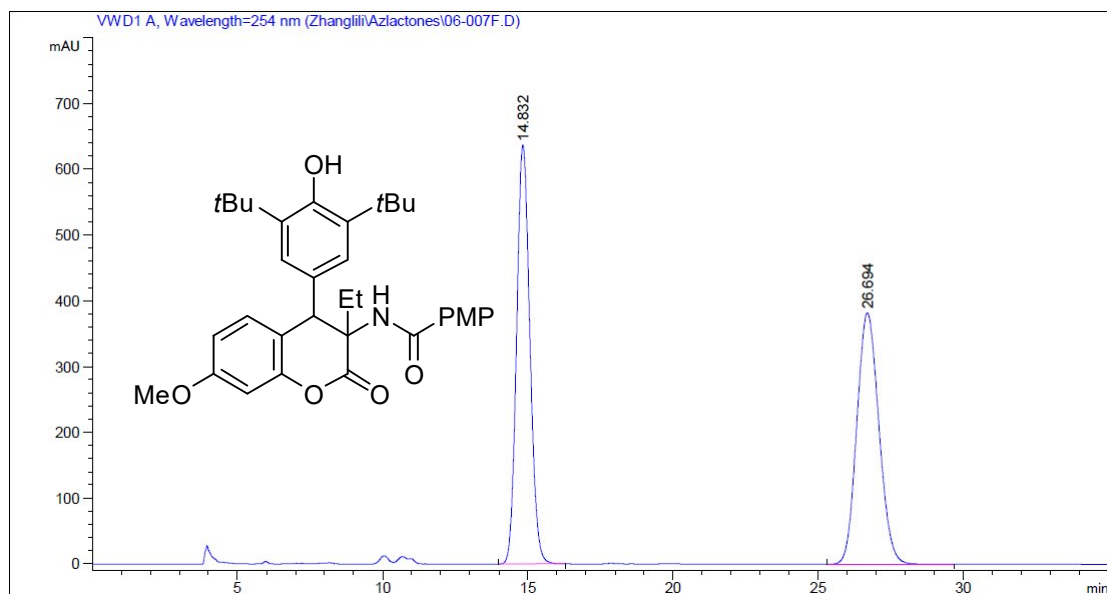


#	Time	Area	Height	Width	Symmetry	Area %
1	17.273	12004	358.9	0.5575	0.897	49.939
2	19.908	12033.3	312.8	0.6411	0.89	50.061

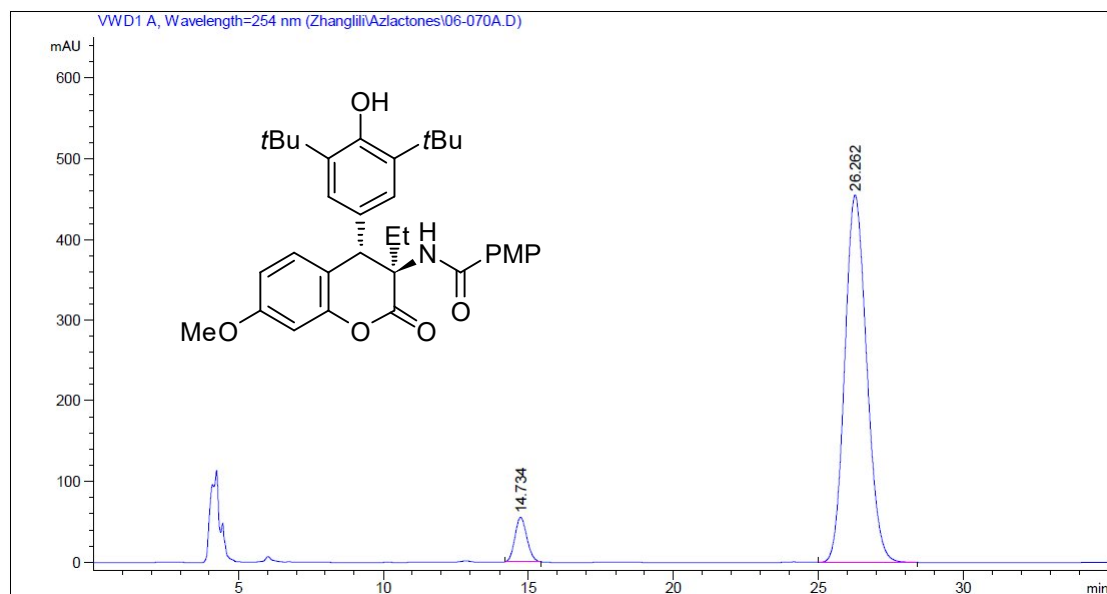


#	Time	Area	Height	Width	Symmetry	Area %
1	17.37	4680.5	141.1	0.553	0.915	97.127
2	20.068	138.4	3.7	0.6215	0.926	2.873

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-7-methoxy-2-oxochroman-3-yl)-4-methoxybenzamide (3fa)**

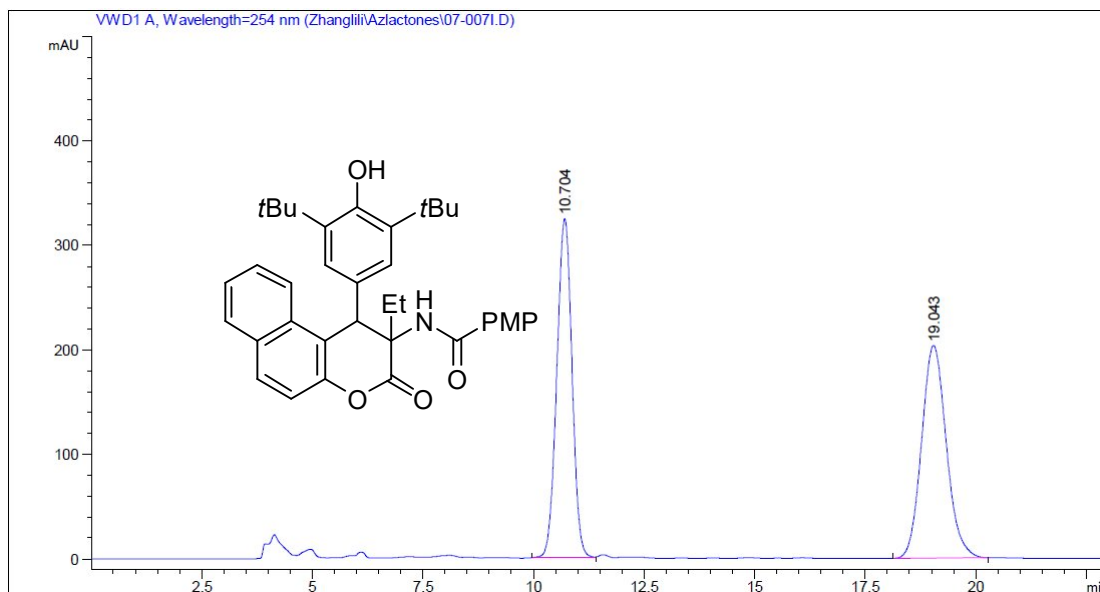


#	Time	Area	Height	Width	Symmetry	Area %
1	14.832	20188.6	637.4	0.4915	0.865	50.043
2	26.694	20153.6	382.2	0.8341	0.87	49.957

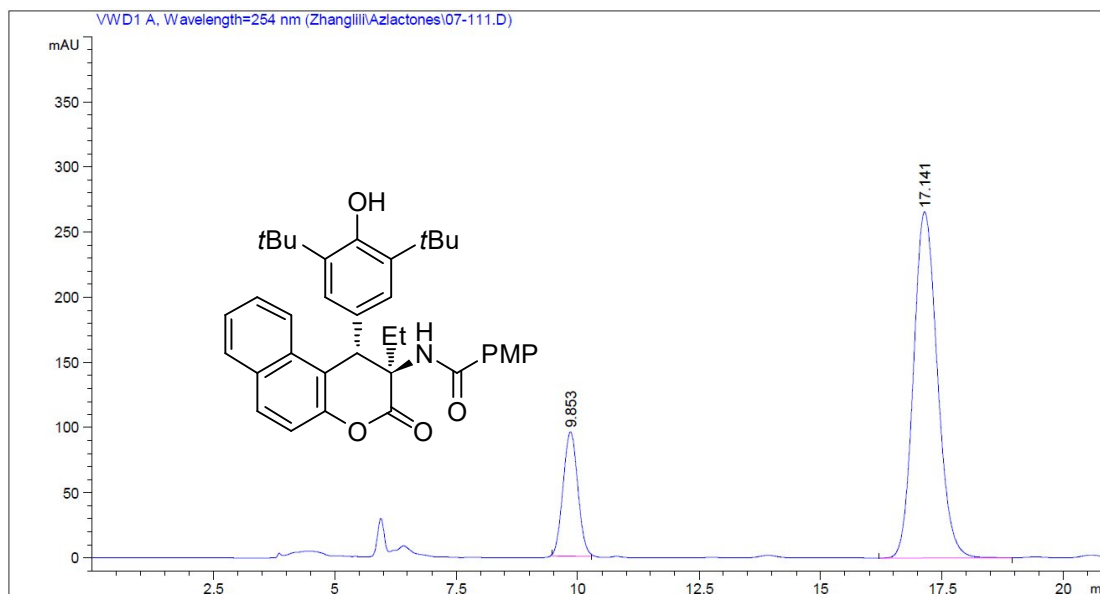


#	Time	Area	Height	Width	Symmetry	Area %
1	14.734	1583.8	55.2	0.4786	0.878	6.198
2	26.262	23967.9	455.9	0.8763	0.849	93.802

***N*-((1*S*,2*R*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-ethyl-3-oxo-2,3-dihydro-1*H*-benzo[*f*]chromen-2-yl)-4-methoxybenzamide (3ga)**

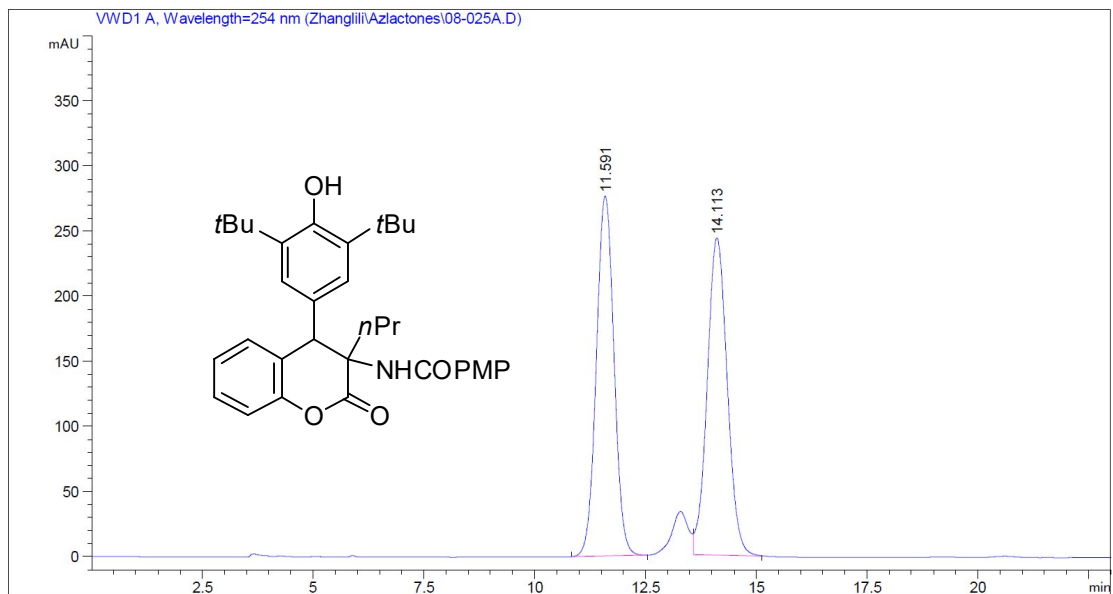


#	Time	Area	Height	Width	Symmetry	Area %
1	10.704	7763.2	324.6	0.3986	1.053	49.525
2	19.043	7912.2	203.6	0.6476	0.9	50.475

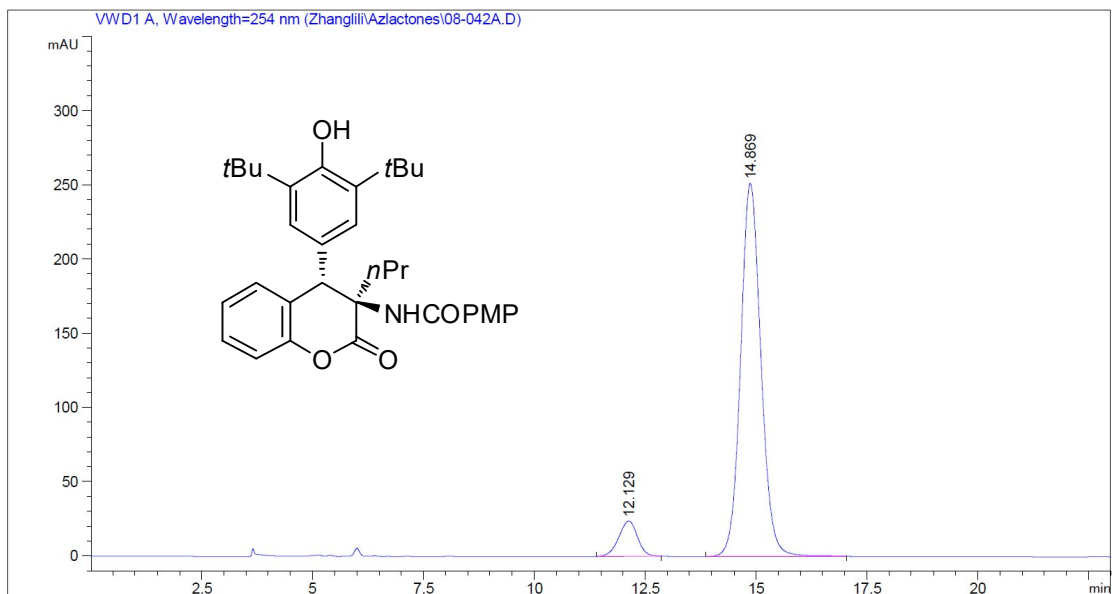


#	Time	Area	Height	Width	Symmetry	Area %
1	9.853	2008.9	95.2	0.3516	0.98	18.138
2	17.141	9066.6	265.5	0.5283	0.821	81.862

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-3-propylchroman-3-yl)-4-methoxybenzamide (3ab)**

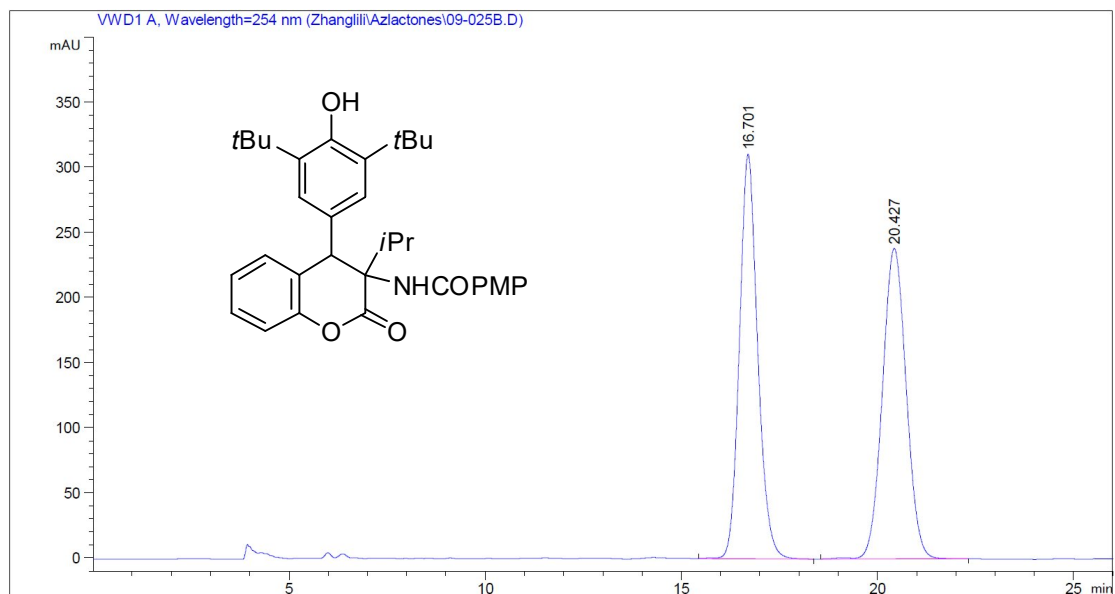


#	Time	Area	Height	Width	Symmetry	Area %
1	11.591	7647.6	276.5	0.4609	0.968	49.962
2	14.113	7659.2	243.6	0.524	0.913	50.038

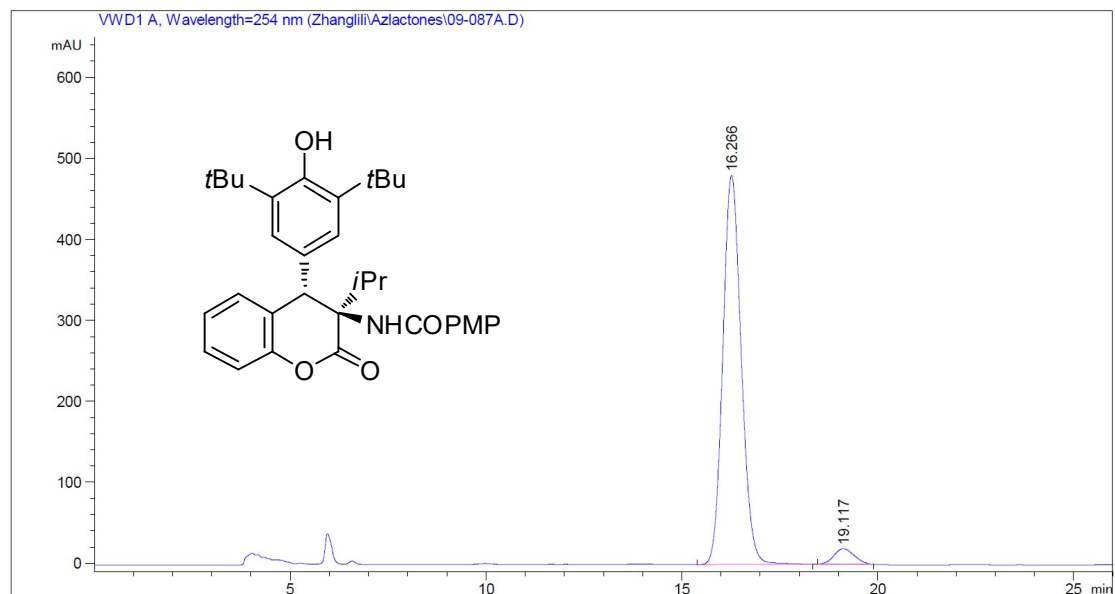


#	Time	Area	Height	Width	Symmetry	Area %
1	12.129	696.5	23.8	0.4887	1.11	8.007
2	14.869	8001.8	251.4	0.5305	0	91.993

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-isopropyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ac)**

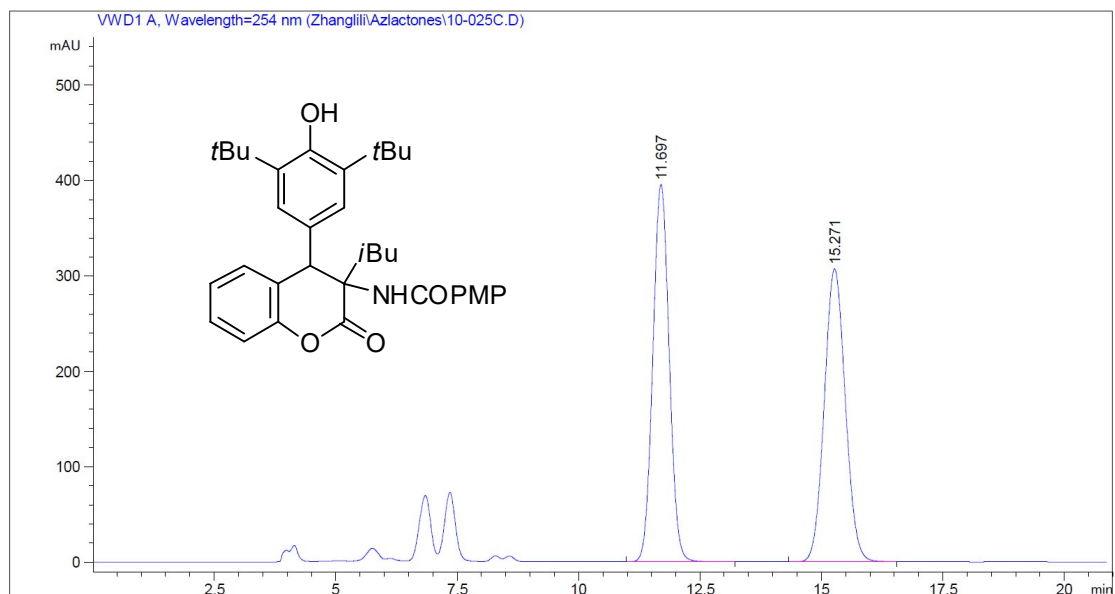


#	Time	Area	Height	Width	Symmetry	Area %
1	16.701	10043.2	310.6	0.5389	0.863	49.952
2	20.427	10062.4	238.5	0.7031	0.963	50.048

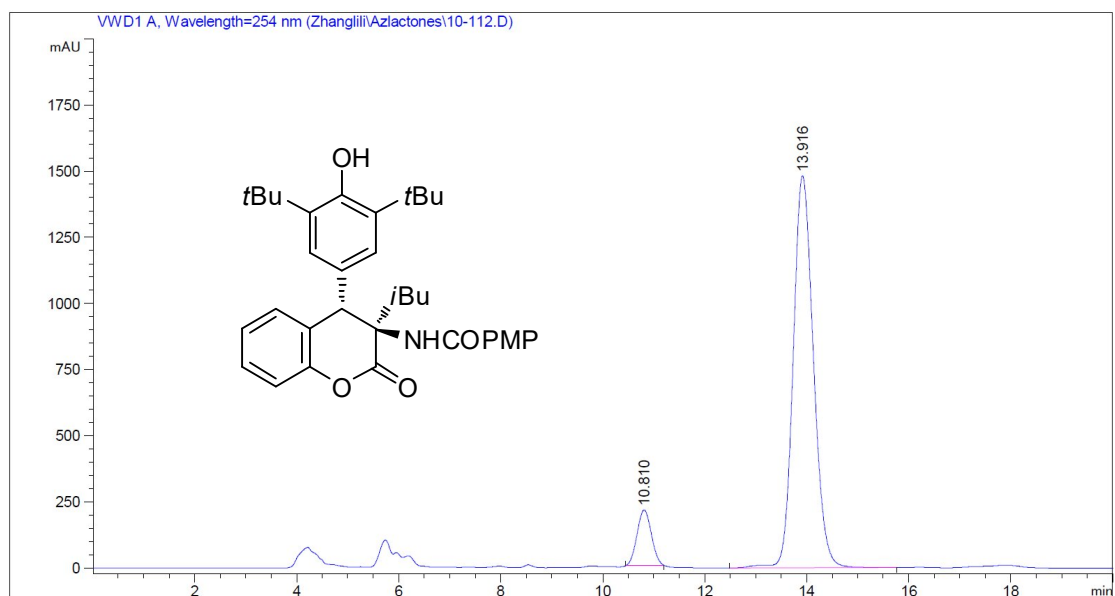


#	Time	Area	Height	Width	Symmetry	Area %
1	16.266	15701.8	480.7	0.5445	0.857	95.792
2	19.117	689.8	19.1	0.601	0.817	4.208

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-isobutyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ad)**

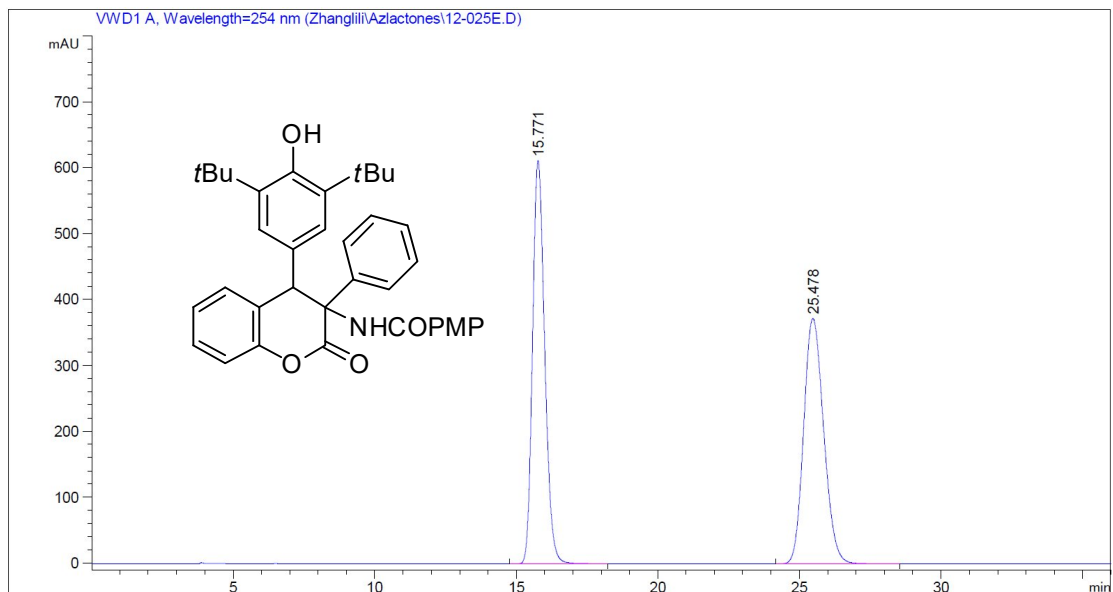


#	Time	Area	Height	Width	Symmetry	Area %
1	11.697	9261.3	395.4	0.3663	0.948	50.060
2	15.271	9239.2	307	0.4692	0.918	49.940

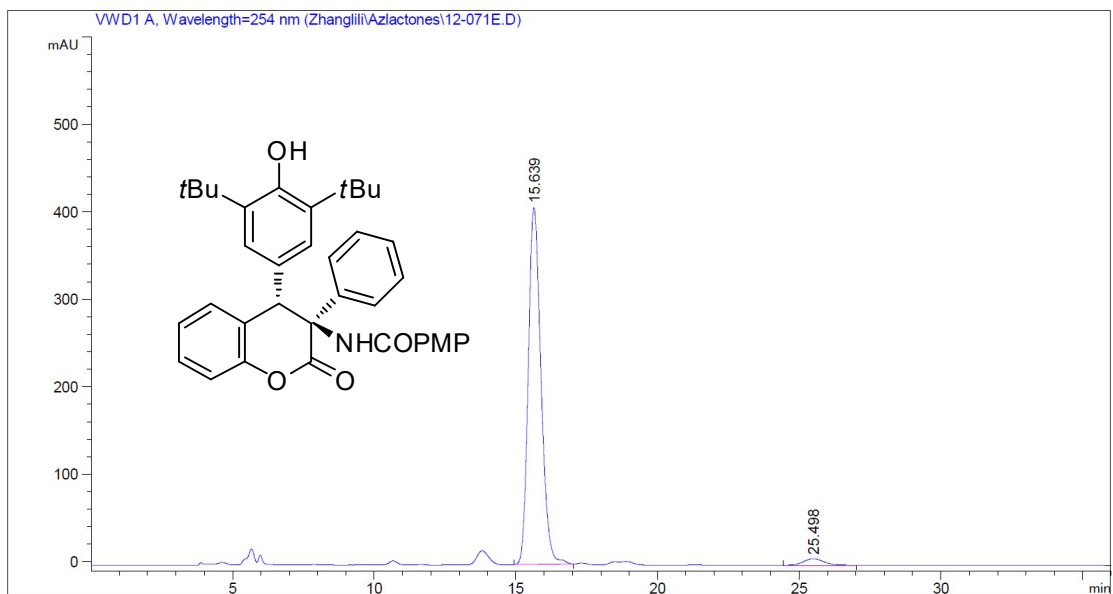


#	Time	Area	Height	Width	Symmetry	Area %
1	10.81	4127.1	210.8	0.3263	0.951	9.194
2	13.916	40759.7	1481.4	0.4239	0.841	90.806

***N*-((3*S*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-3-phenylchroman-3-yl)-4-methoxybenzamide (**3ae**)**

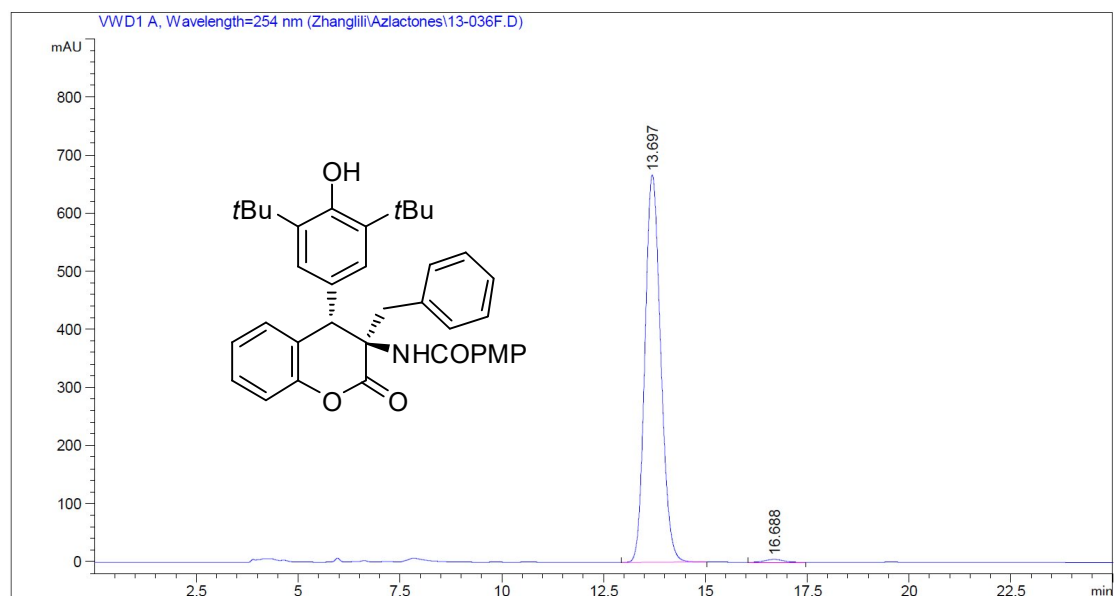
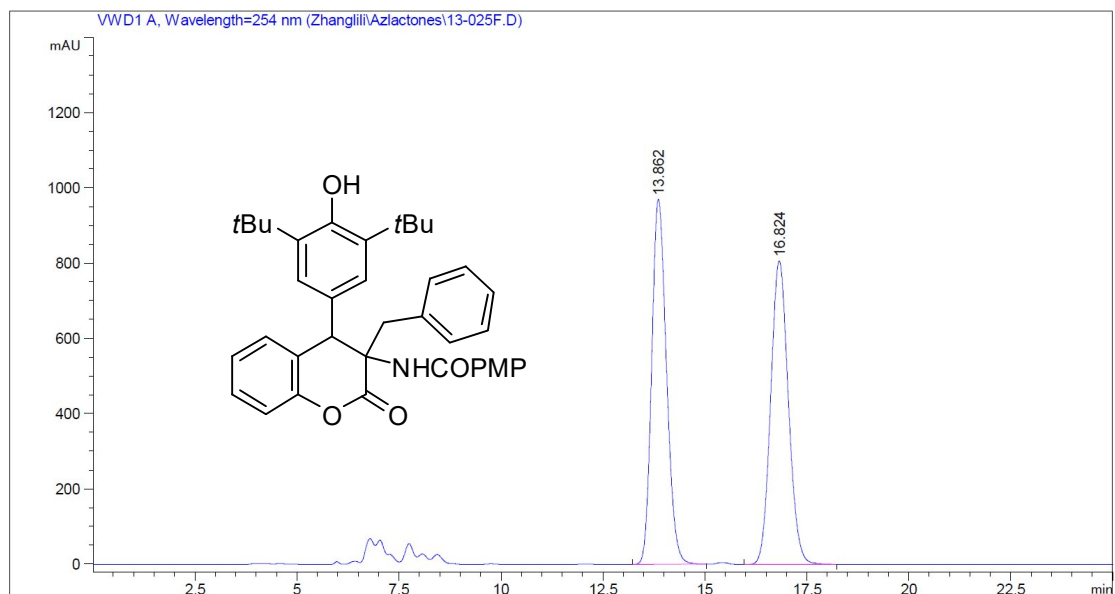


#	Time	Area	Height	Width	Symmetry	Area %
1	15.771	18285.6	611.8	0.4607	0.777	49.999
2	25.478	18286.6	372.2	0.7592	0.813	50.001

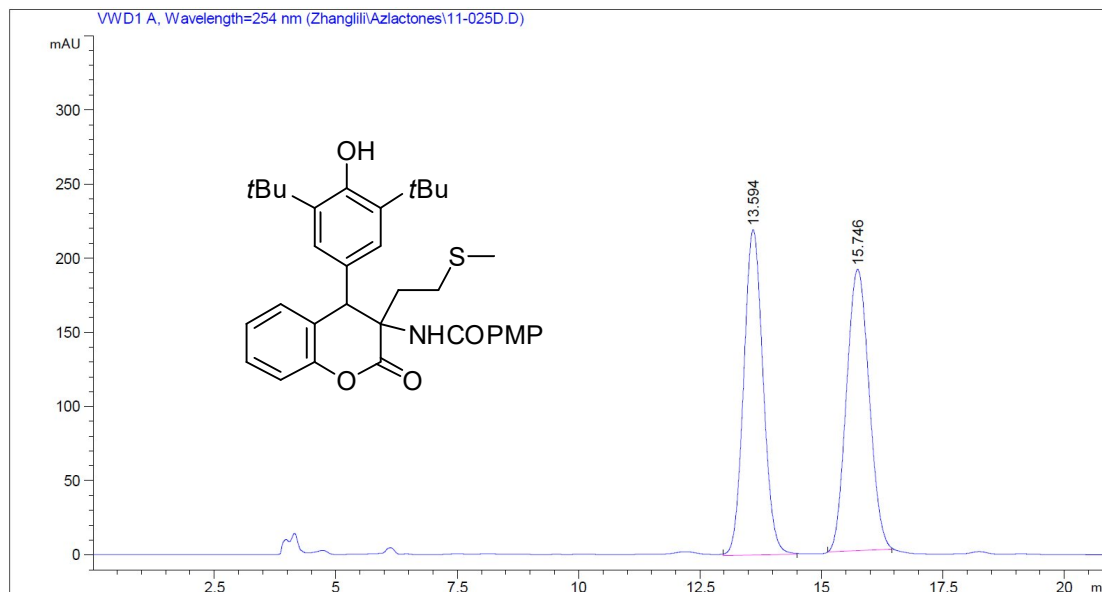


#	Time	Area	Height	Width	Symmetry	Area %
1	15.639	12677.8	407.9	0.5181	0.772	97.155
2	25.498	371.2	7.5	0.8284	0.879	2.845

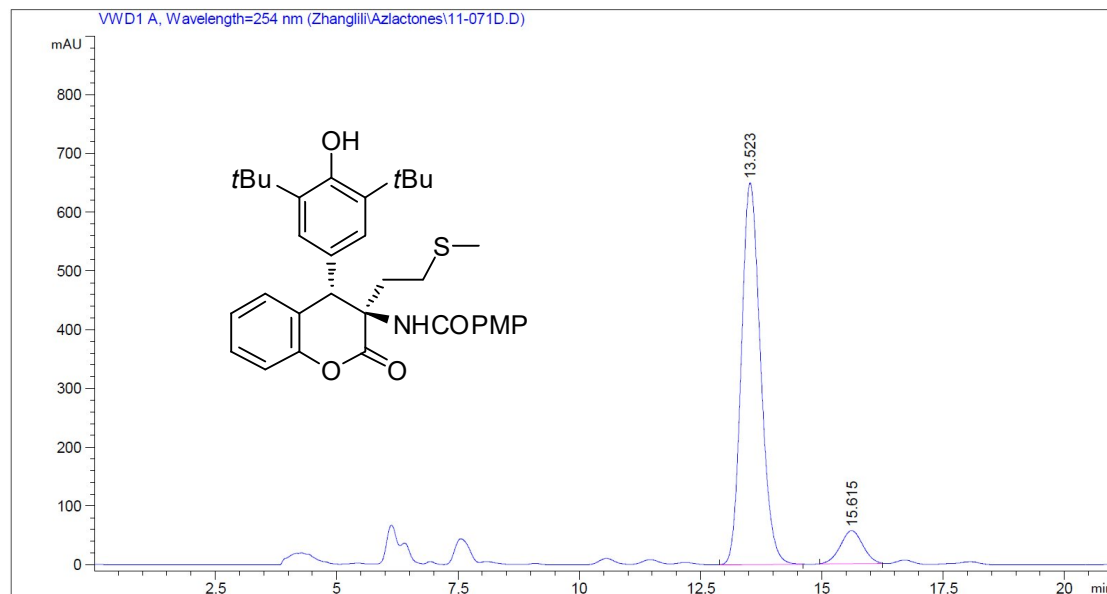
***N*-((3*R*,4*S*)-3-benzyl-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxochroman-3-yl)-4-methoxybenzamide (3af)**



***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(2-(methylthio)ethyl)-2-oxochroman-3-yl)-4-methoxybenzamide (3ag)**

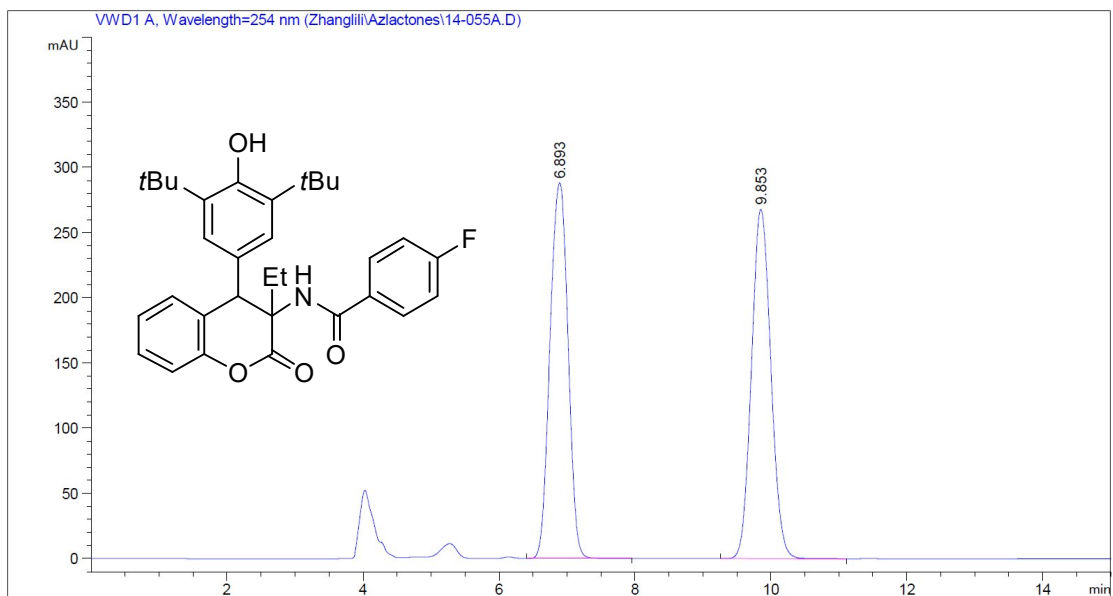


#	Time	Area	Height	Width	Symmetry	Area %
1	13.594	6082.4	219.6	0.4617	0.909	49.797
2	15.746	6132.1	189.6	0.5389	0.938	50.203

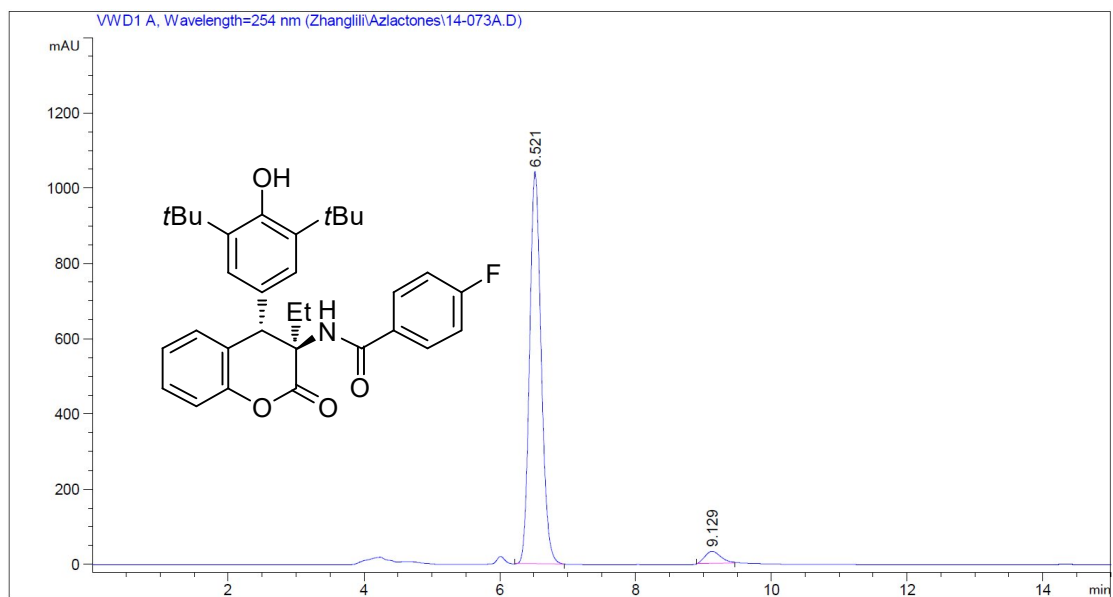


#	Time	Area	Height	Width	Symmetry	Area %
1	13.523	17878.1	649.9	0.4585	0.807	90.835
2	15.615	1803.9	56.2	0.5346	0.989	9.165

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-fluorobenzamide (3ah)**

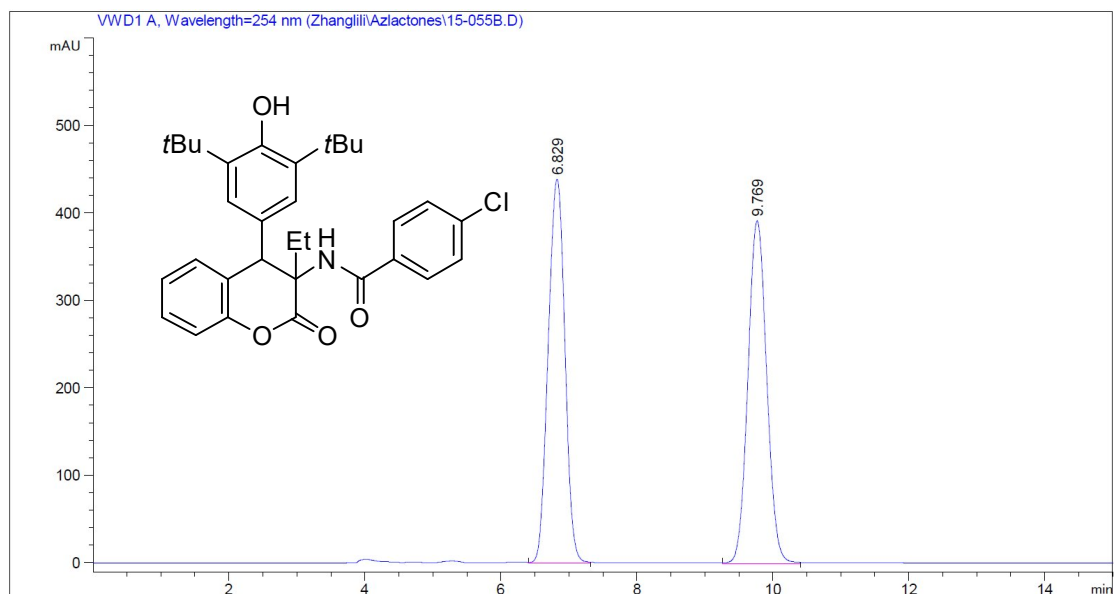


#	Time	Area	Height	Width	Symmetry	Area %
1	6.893	5304.2	288.1	0.2988	1.076	50.004
2	9.853	5303.4	267.9	0.3099	0.903	49.996

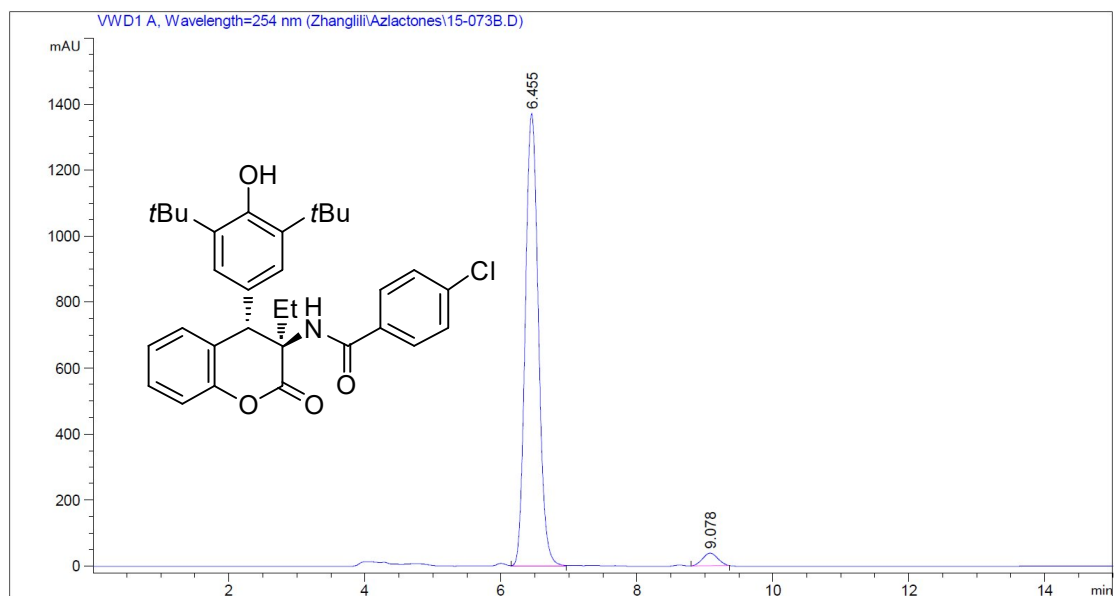


#	Time	Area	Height	Width	Symmetry	Area %
1	6.521	12358.7	1043.1	0.1975	0.851	96.013
2	9.129	513.2	32	0.2675	0.793	3.987

4-Chloro-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3ai)

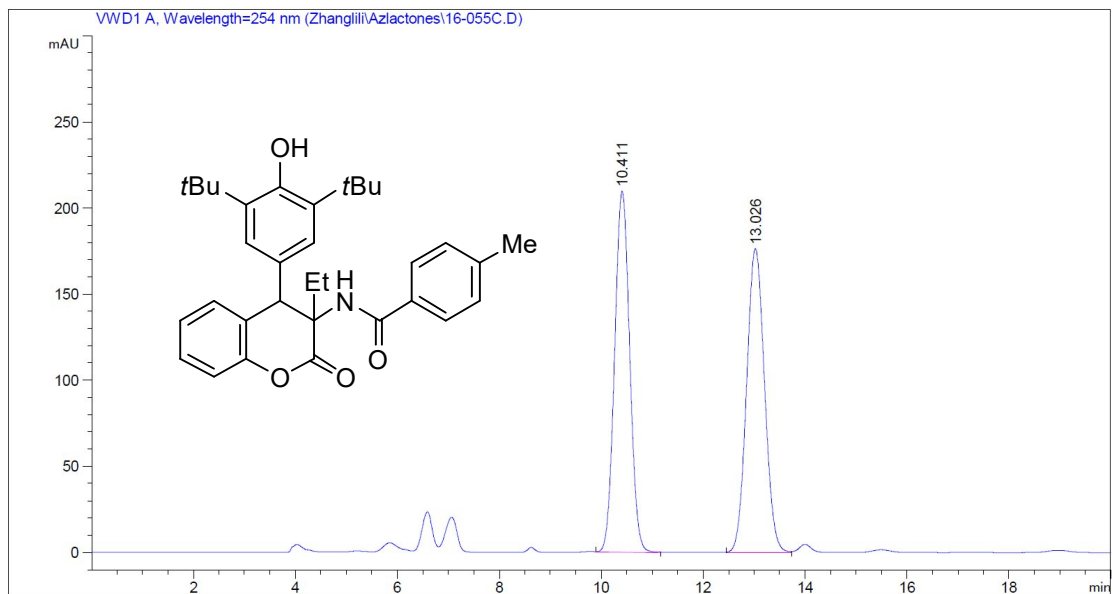


#	Time	Area	Height	Width	Symmetry	Area %
1	6.829	7477.7	438.5	0.2842	1.099	49.903
2	9.769	7506.8	391.4	0.3196	0.93	50.097

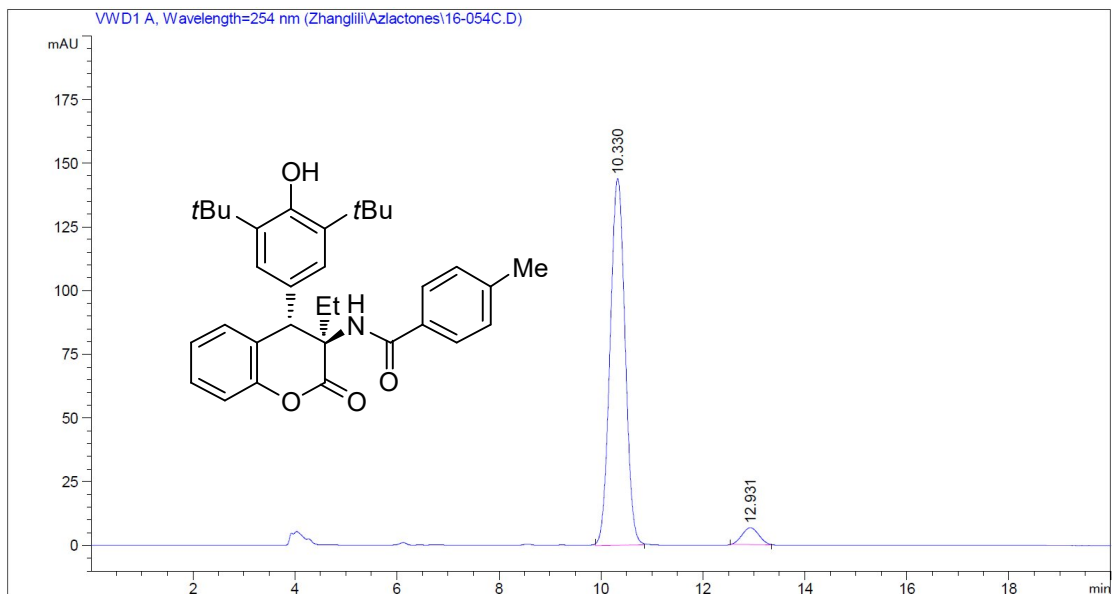


#	Time	Area	Height	Width	Symmetry	Area %
1	6.455	18270.1	1371.6	0.222	0.914	96.884
2	9.078	587.5	38	0.258	0.956	3.116

***N*-(3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methylbenzamide (3aj)**

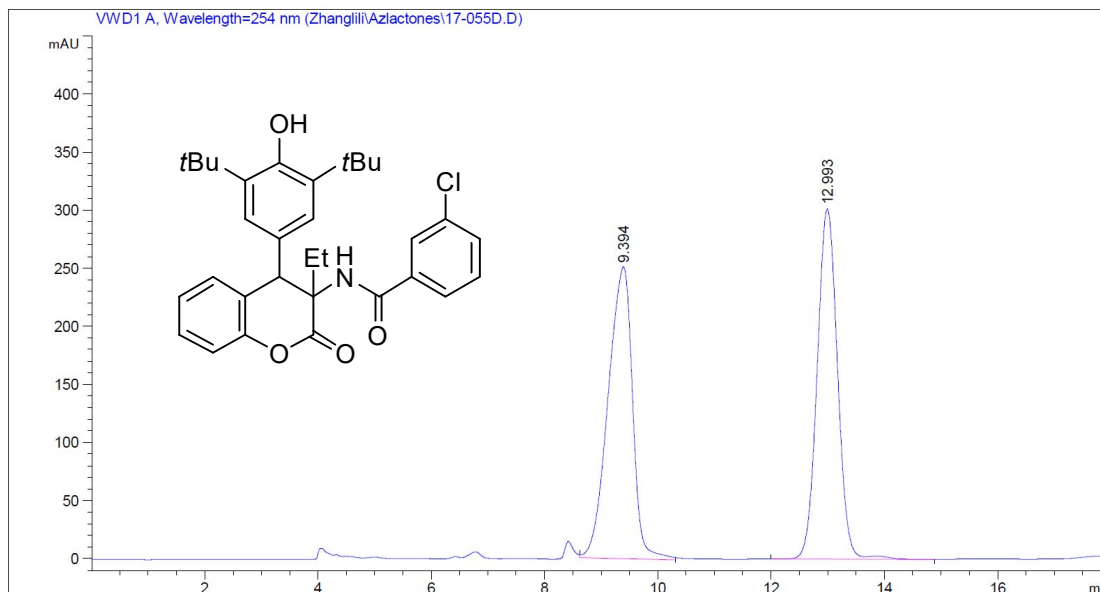


#	Time	Area	Height	Width	Symmetry	Area %
1	10.411	4310.1	209.6	0.3426	0.959	49.825
2	13.026	4340.4	176.7	0.4093	0.928	50.175

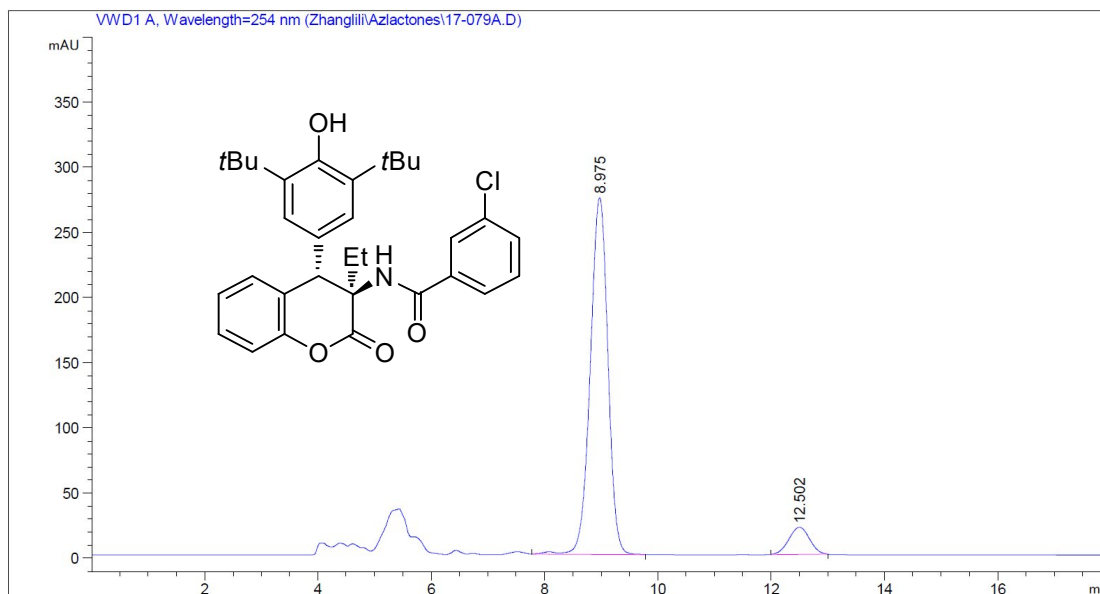


#	Time	Area	Height	Width	Symmetry	Area %
1	10.33	2941	144	0.3404	0.988	95.017
2	12.931	154.2	6.7	0.384	0.953	4.983

3-Chloro-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3ak)

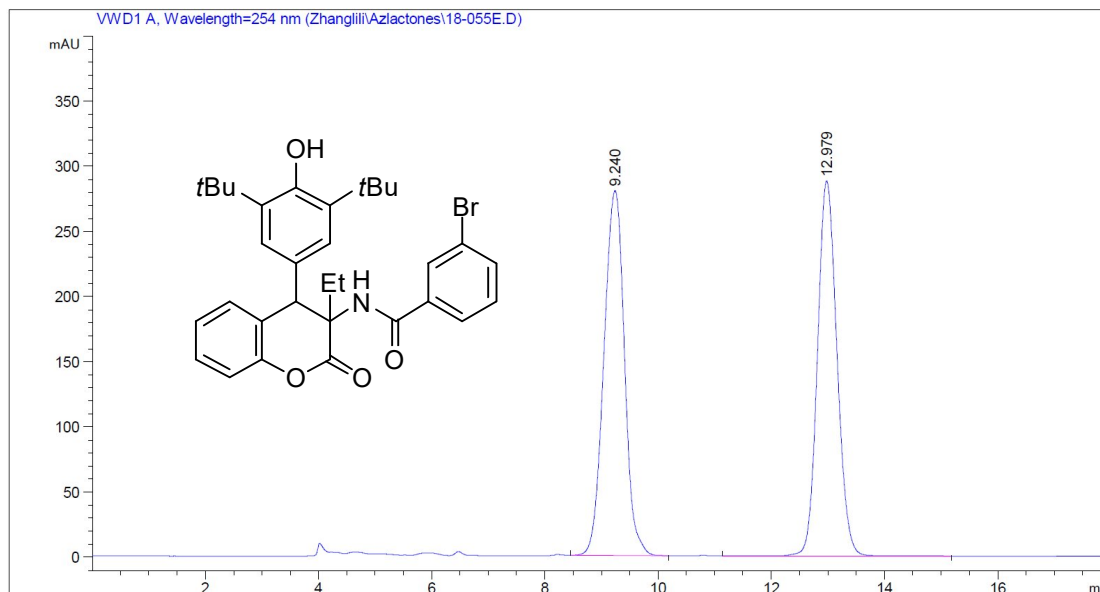


#	Time	Area	Height	Width	Symmetry	Area %
1	9.394	7526.2	251.1	0.4996	1.573	49.989
2	12.993	7529.6	301.4	0.3862	0.961	50.011

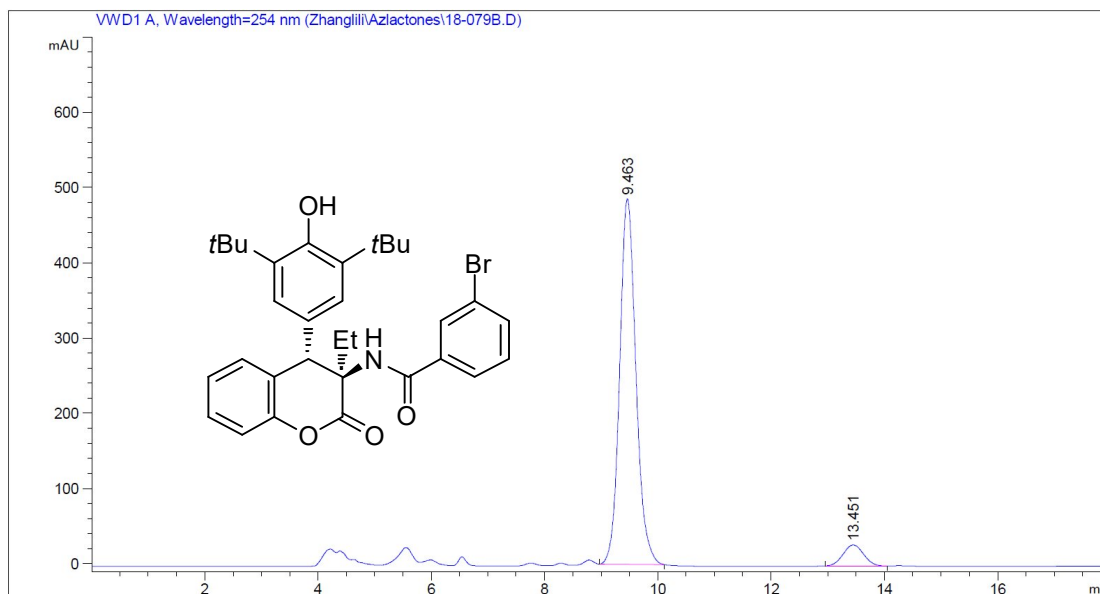


#	Time	Area	Height	Width	Symmetry	Area %
1	8.975	5923.3	273.7	0.3606	1.109	91.876
2	12.502	523.8	20.7	0.421	1.018	8.124

3-Bromo-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3a)

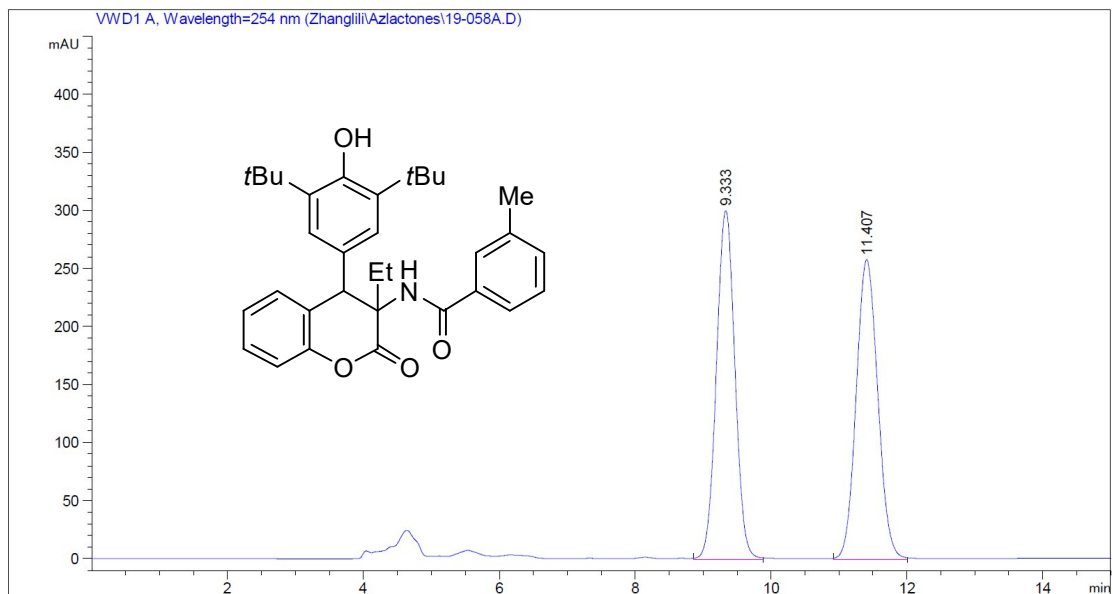


#	Time	Area	Height	Width	Symmetry	Area %
1	9.24	7051.1	279.9	0.4199	1.13	50.644
2	12.979	6871.8	287.9	0.3978	0.865	49.356

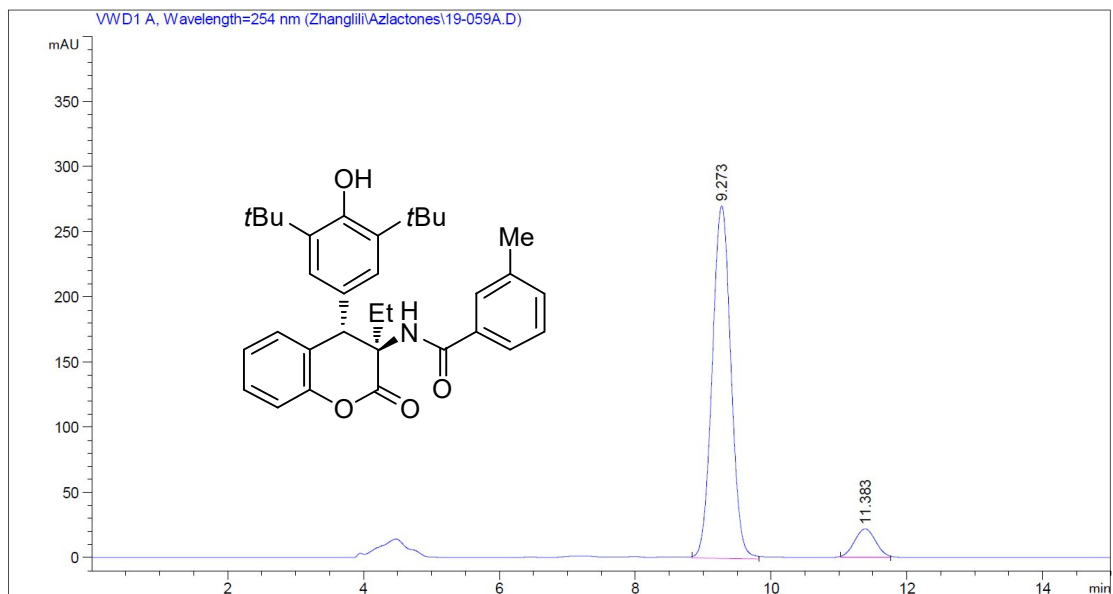


#	Time	Area	Height	Width	Symmetry	Area %
1	9.463	9693.2	485.8	0.3325	0.863	93.199
2	13.451	707.3	28.1	0.4201	0.958	6.801

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-3-methylbenzamide (3am)**

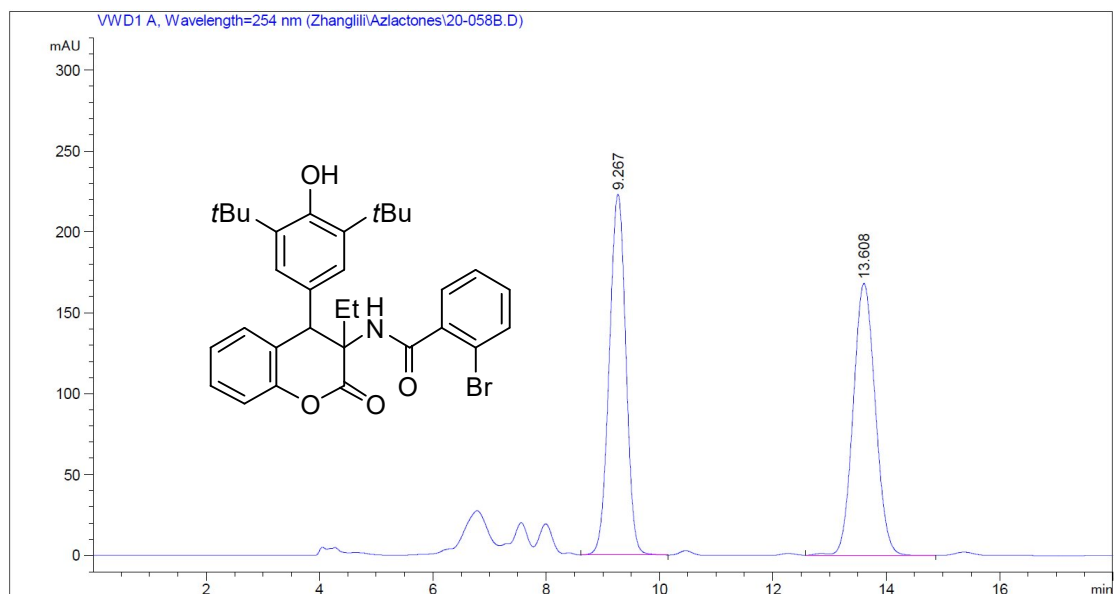


#	Time	Area	Height	Width	Symmetry	Area %
1	9.333	5670.2	300.2	0.3148	0.981	49.949
2	11.407	5681.8	258.1	0.3669	0.909	50.051

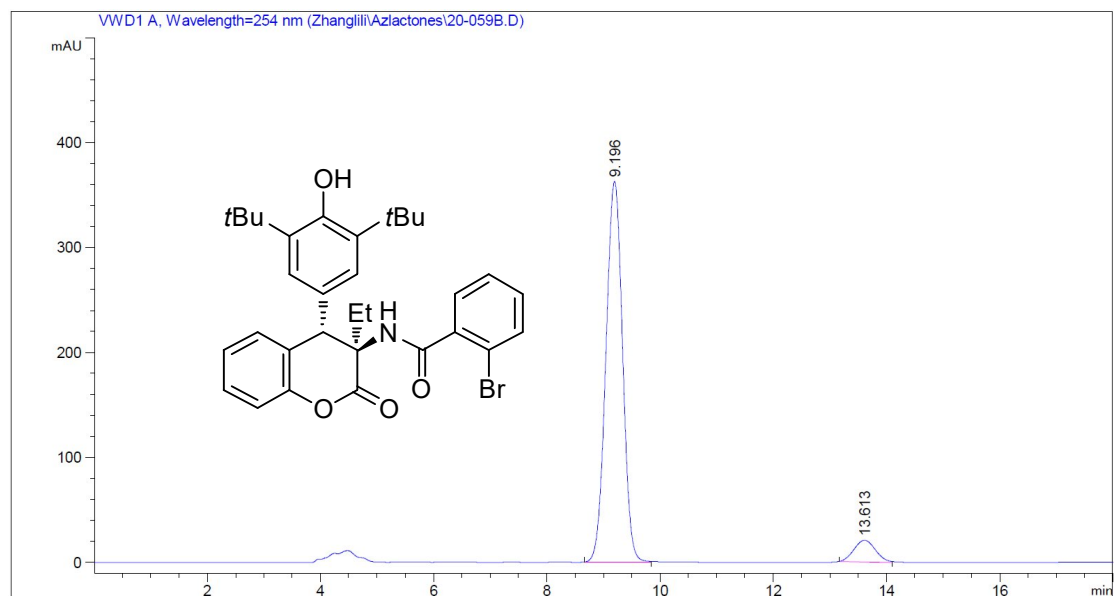


#	Time	Area	Height	Width	Symmetry	Area %
1	9.273	5163.9	270.5	0.3182	0.979	91.917
2	11.383	454.1	21.5	0.352	0.978	8.083

2-Bromo-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3an)

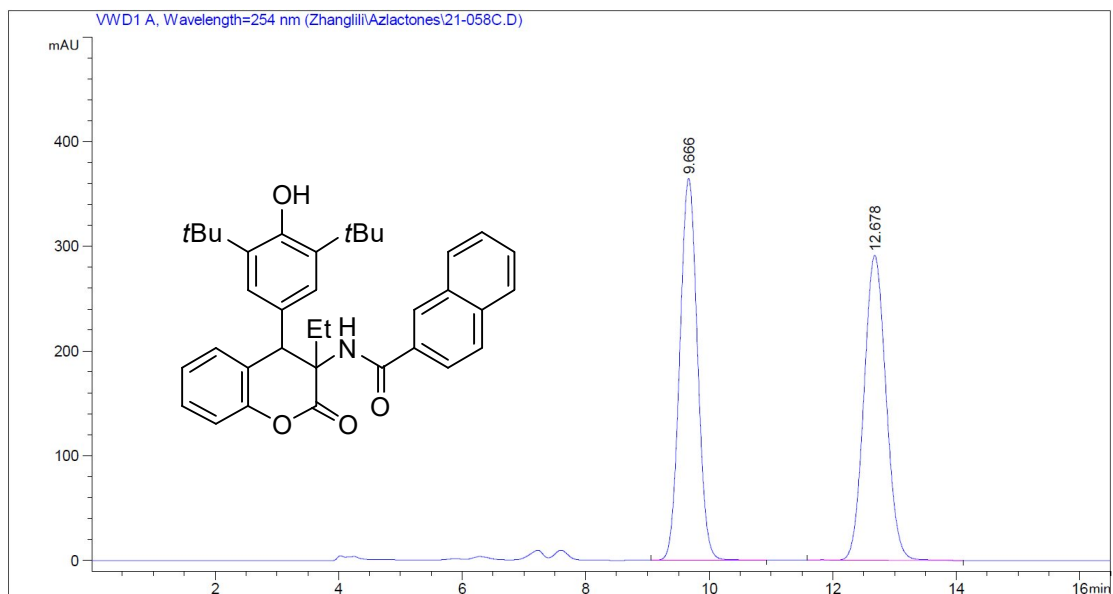


#	Time	Area	Height	Width	Symmetry	Area %
1	9.267	4537.9	223	0.3204	1.059	49.956
2	13.608	4545.9	168	0.4237	0.916	50.044

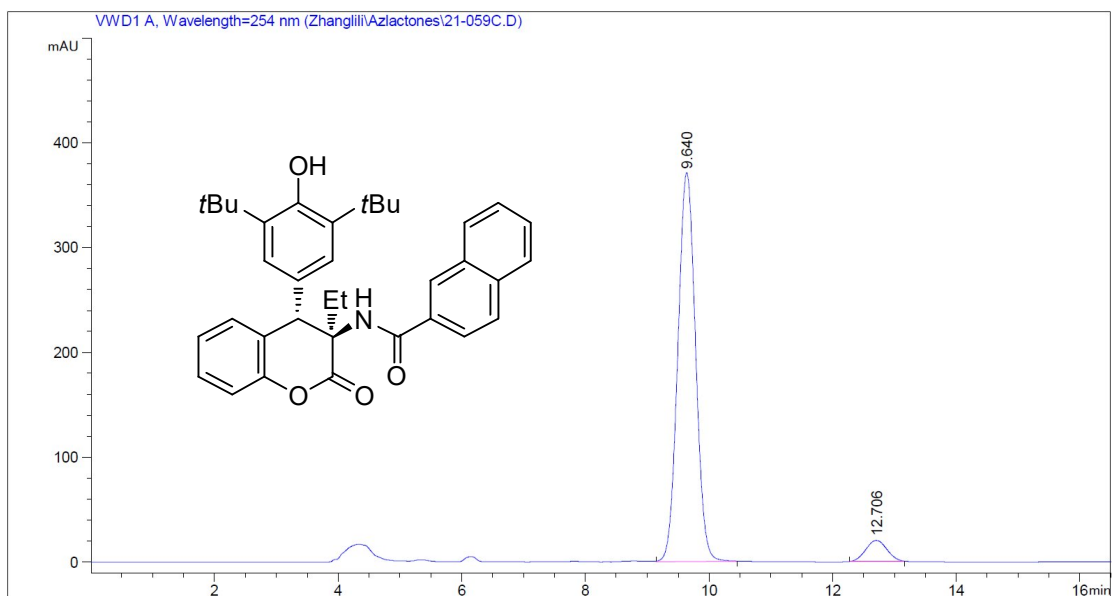


#	Time	Area	Height	Width	Symmetry	Area %
1	9.196	7441.1	363.2	0.3415	1.034	93.018
2	13.613	558.5	20.9	0.4454	0.939	6.982

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-2-naphthamide (3ao)**

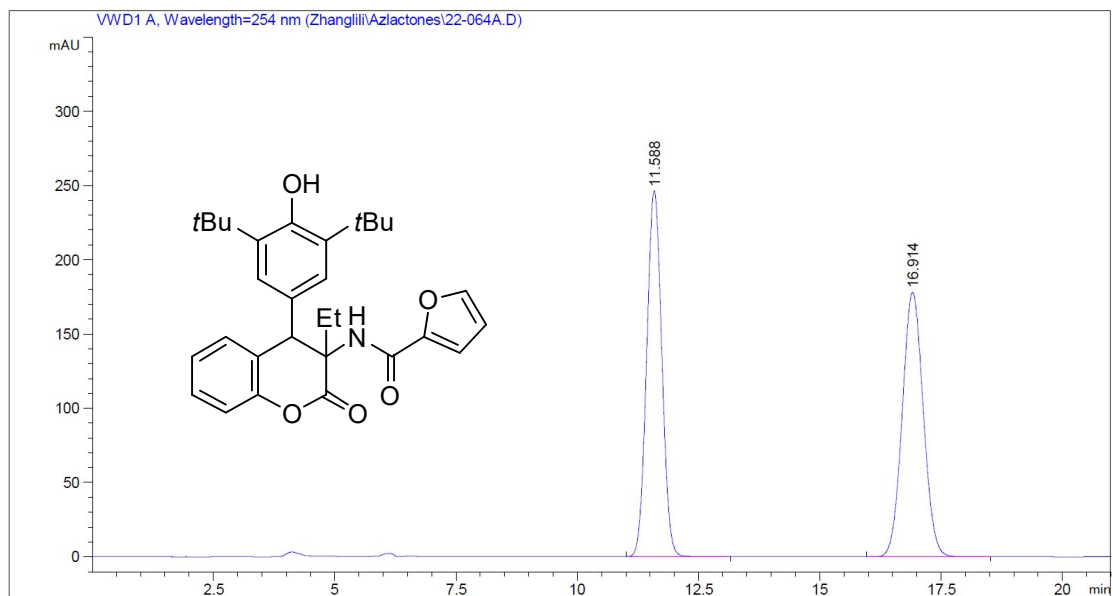


#	Time	Area	Height	Width	Symmetry	Area %
1	9.666	7227.2	364.8	0.3102	0.959	50.076
2	12.678	7205.3	291.1	0.3857	0.91	49.924

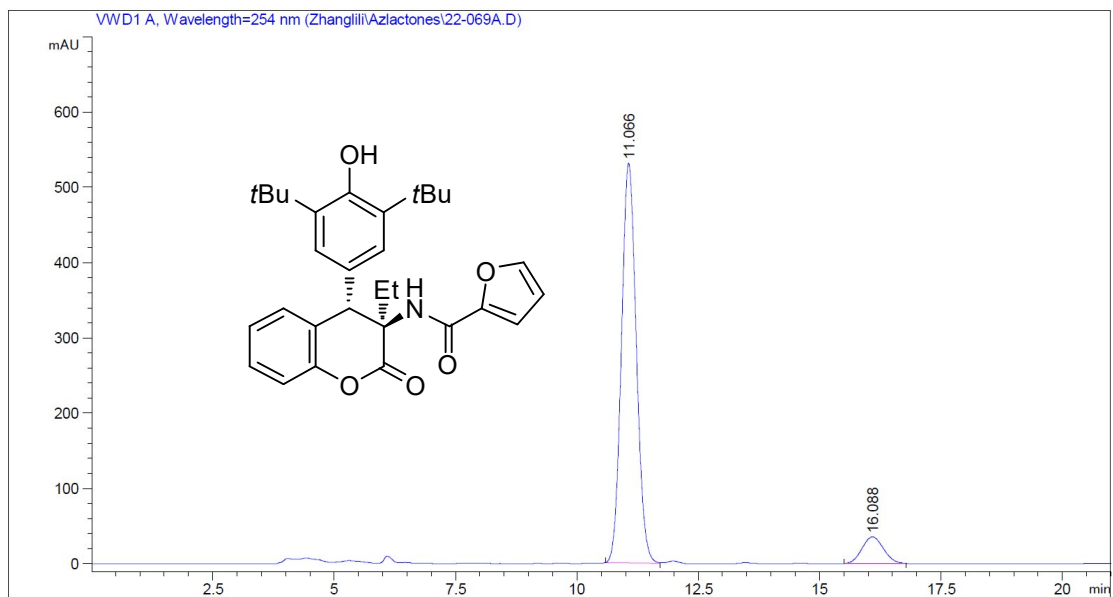


#	Time	Area	Height	Width	Symmetry	Area %
1	9.64	7375.1	371.2	0.3311	0.967	93.915
2	12.706	477.8	20.1	0.3953	0.964	6.085

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)furan-2-carboxamide (3ap)**

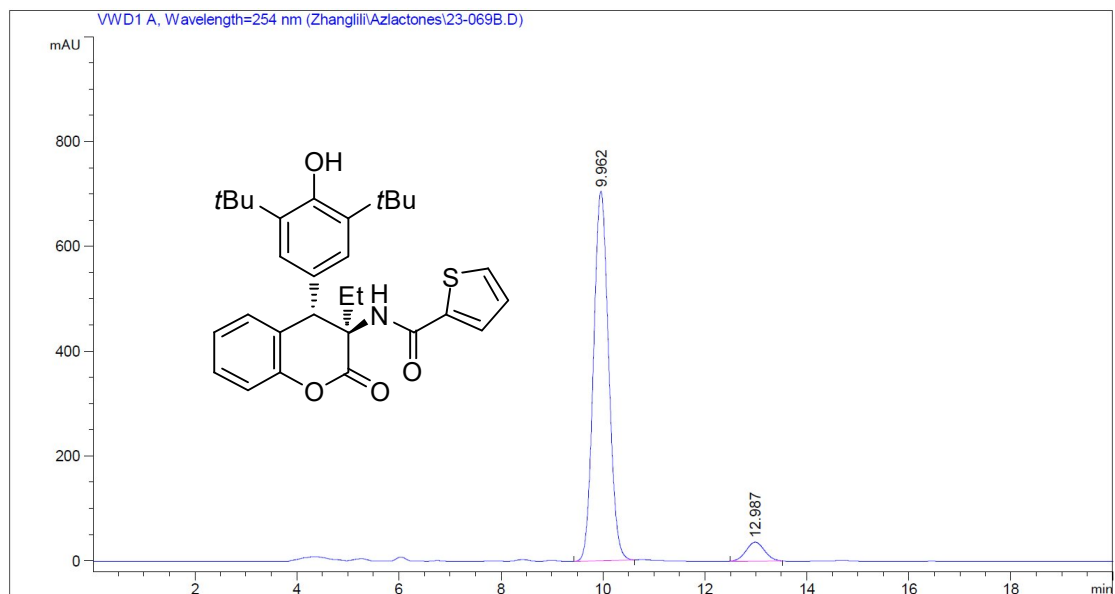
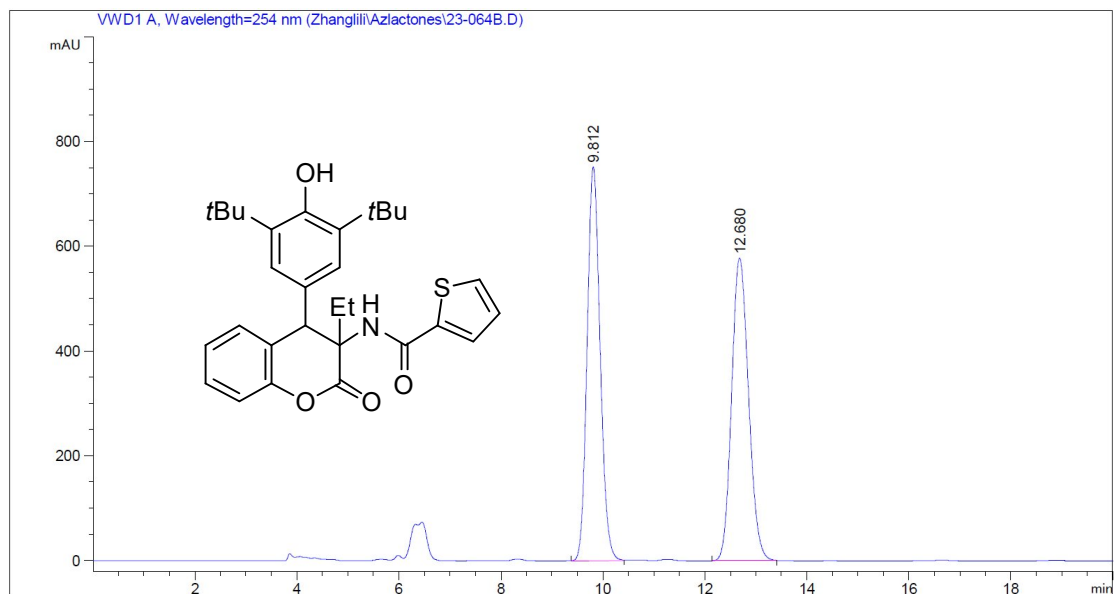


#	Time	Area	Height	Width	Symmetry	Area %
1	11.588	5351.5	246.4	0.3394	0.96	49.939
2	16.914	5364.7	178.1	0.4704	0.932	50.061



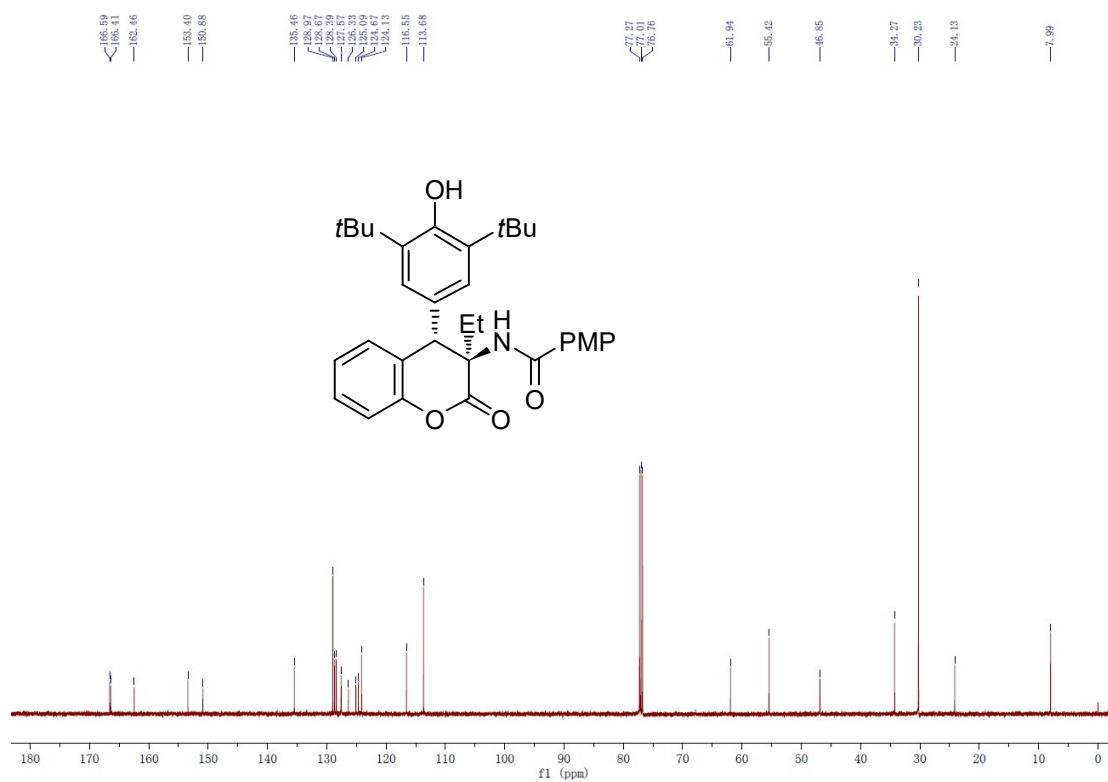
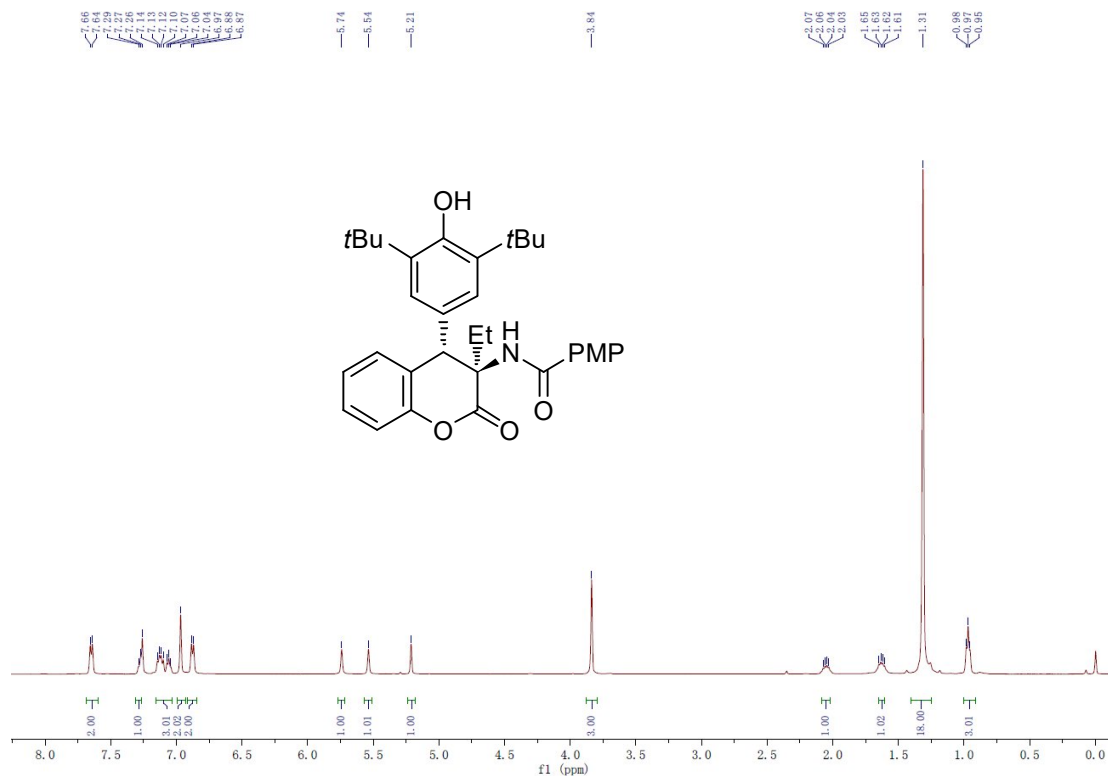
#	Time	Area	Height	Width	Symmetry	Area %
1	11.066	11303.3	530.7	0.355	0.91	91.114
2	16.088	1102.4	35.6	0.5166	0.92	8.886

***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)thiophene-2-carboxamide (3aq)**

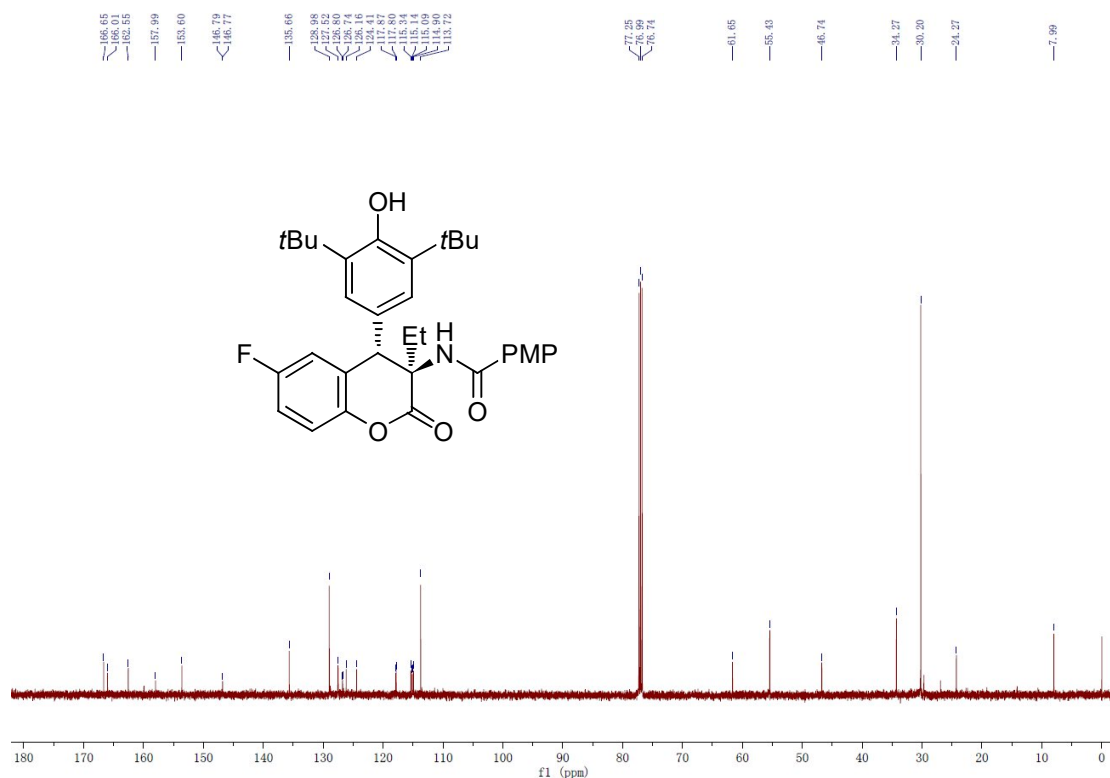
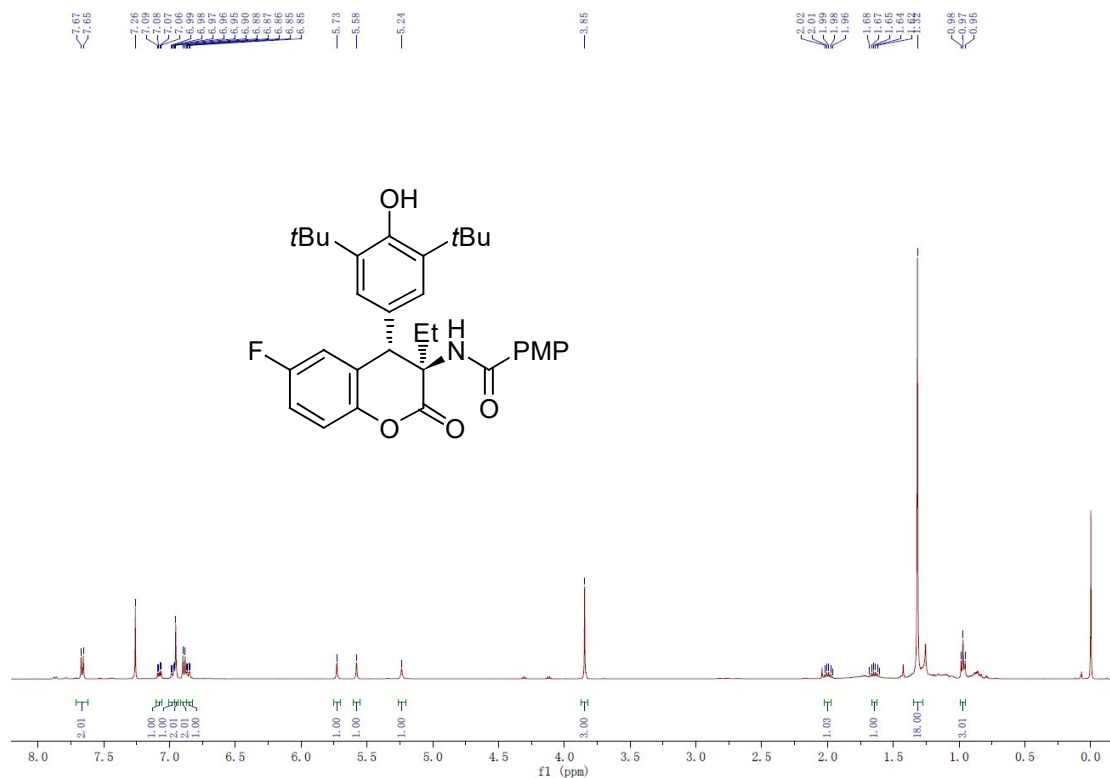


G: NMR Analysis

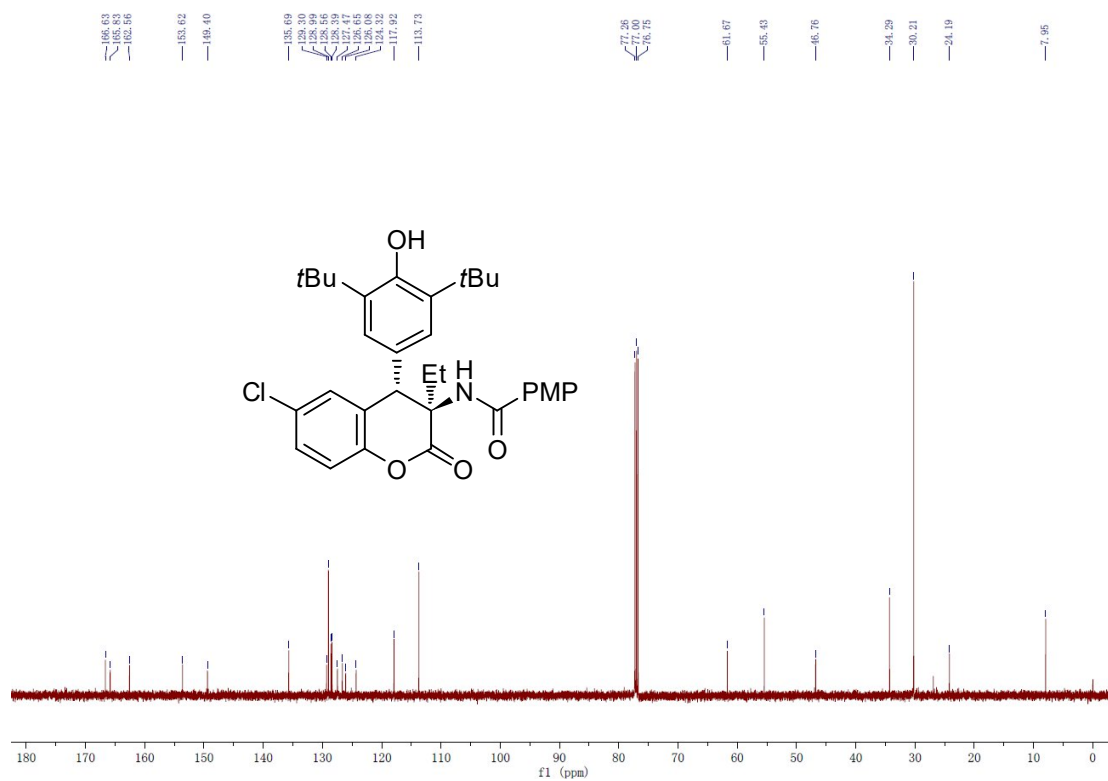
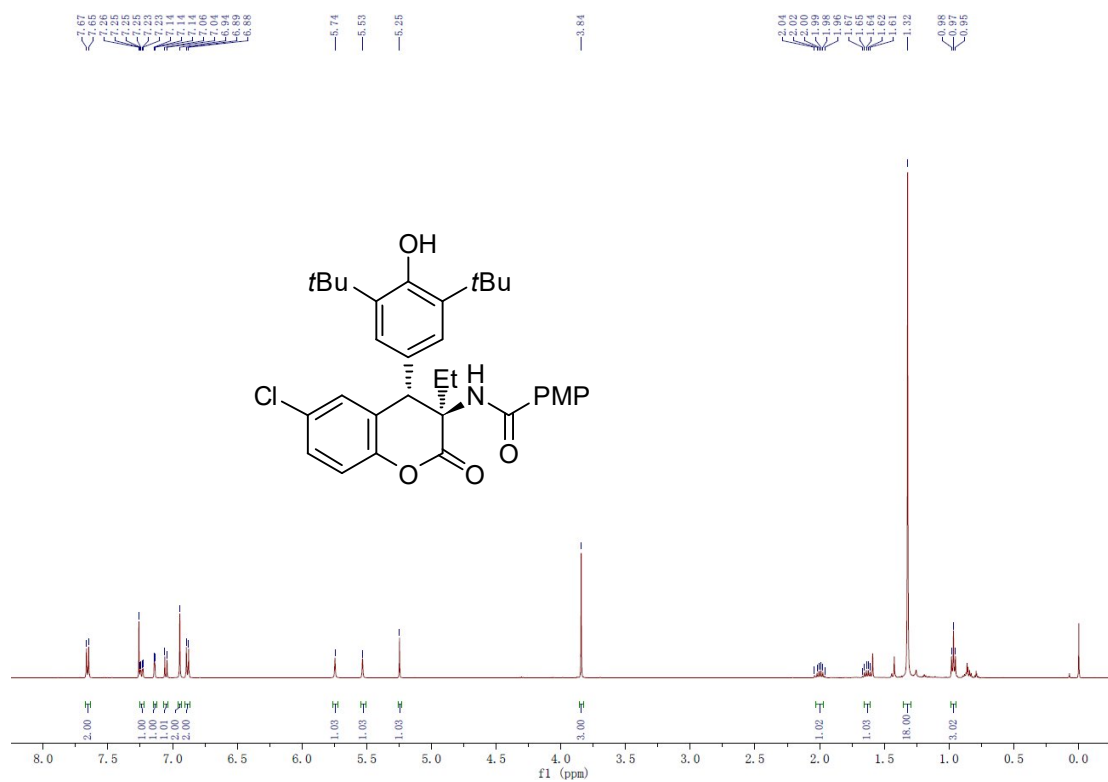
N-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3aa)



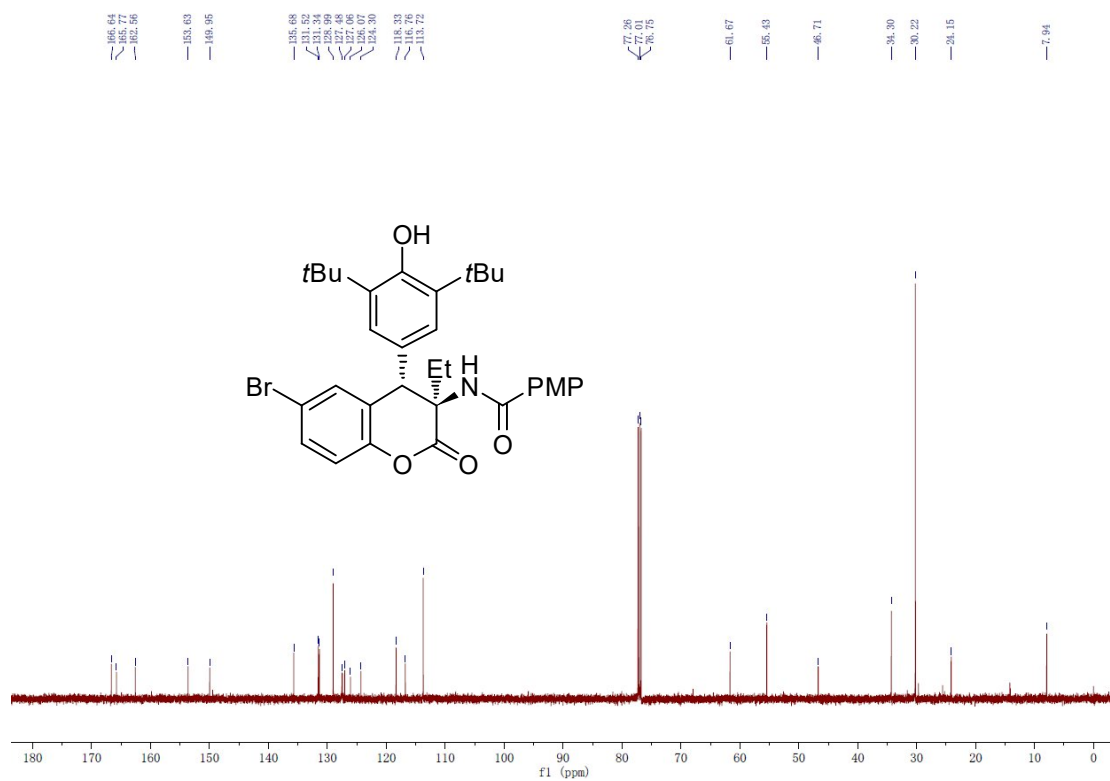
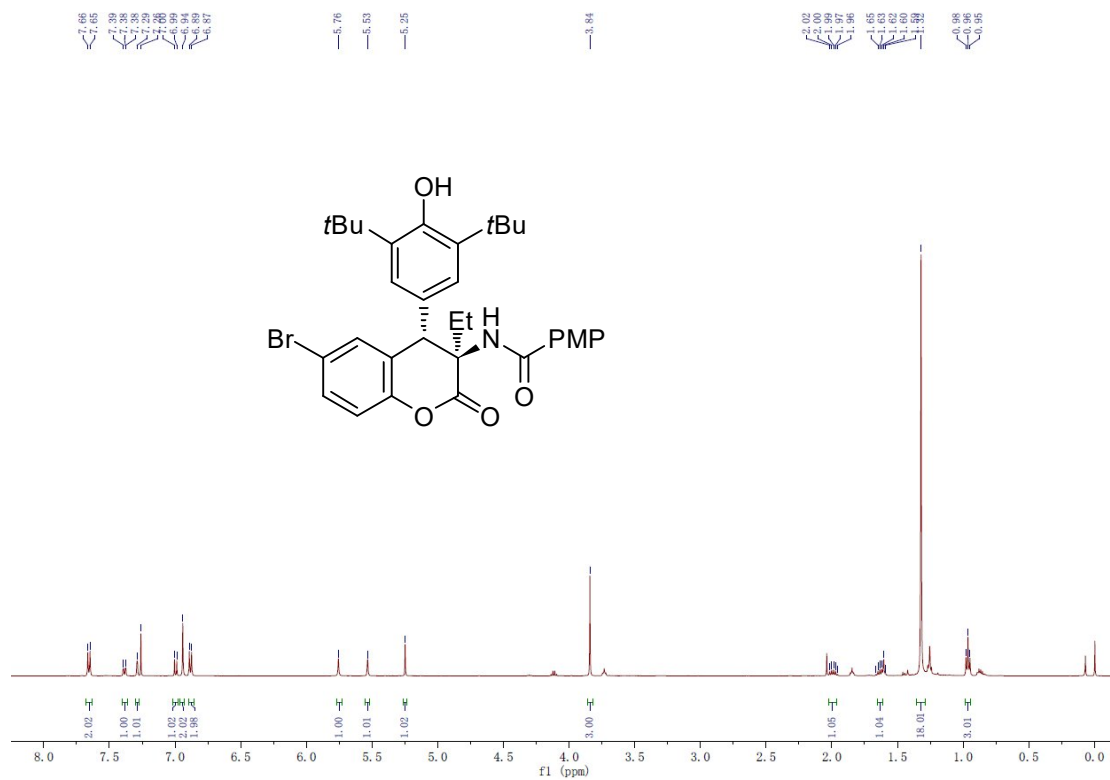
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-6-fluoro-2-oxochroman-3-yl)-4-methoxybenzamide (3ba)**



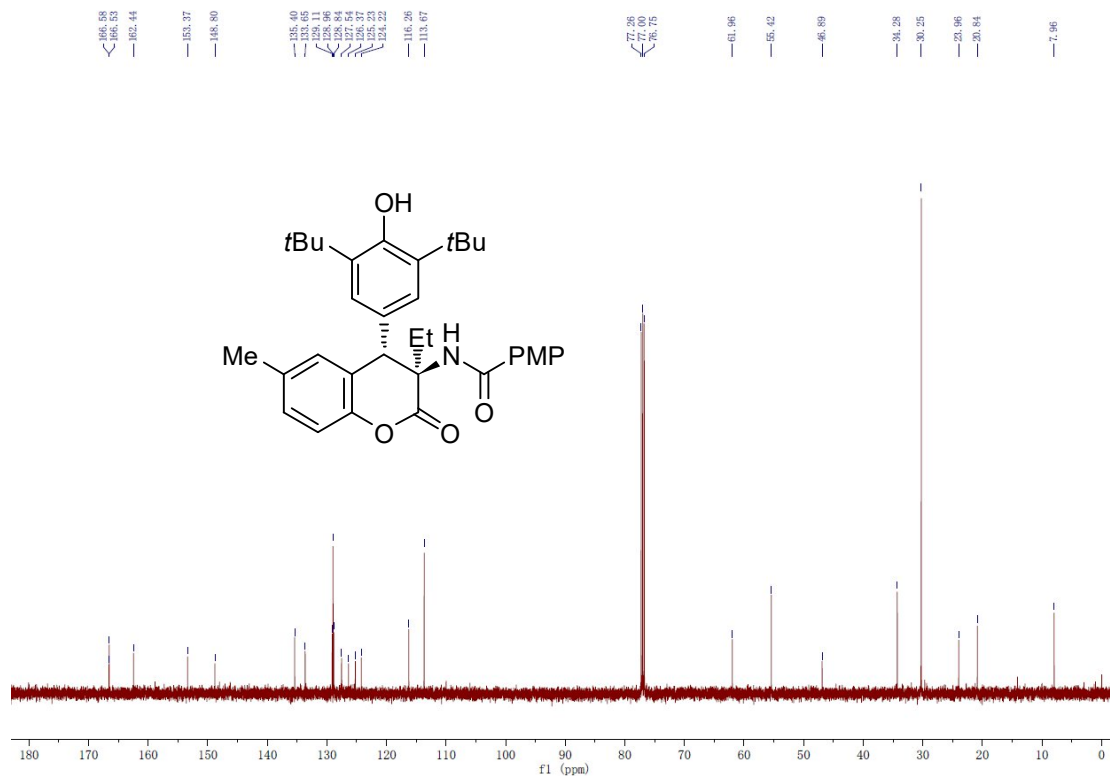
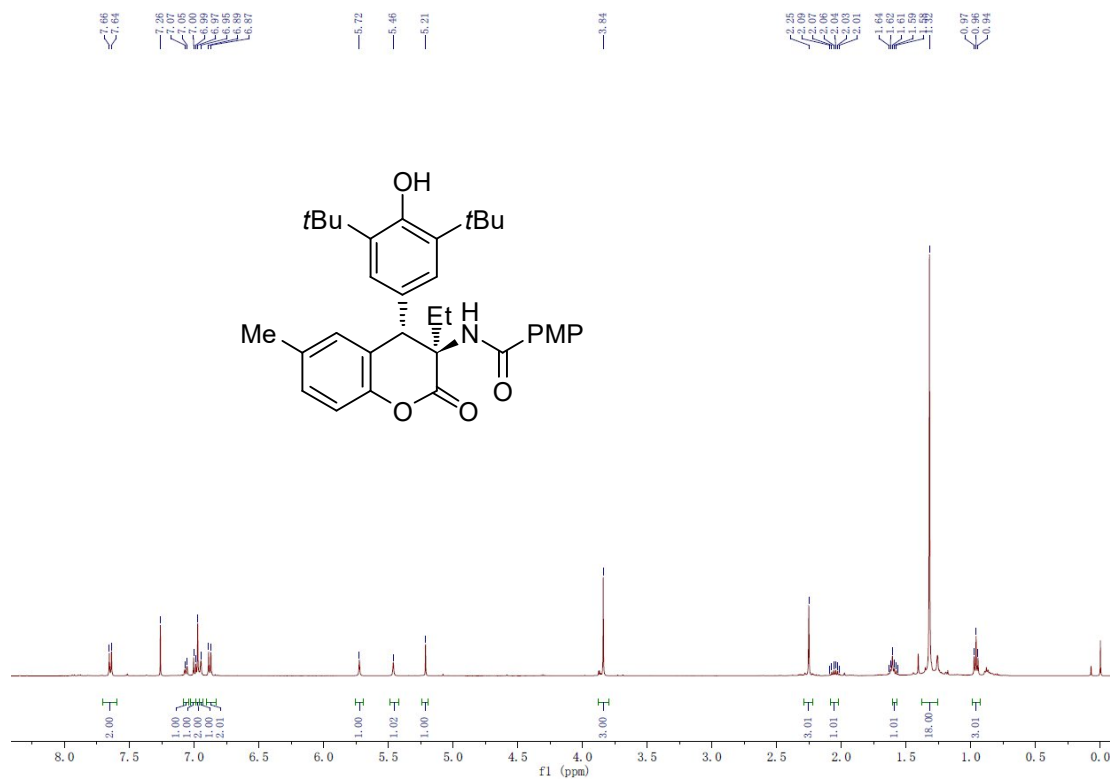
***N*-((3*R*,4*S*)-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ca)**



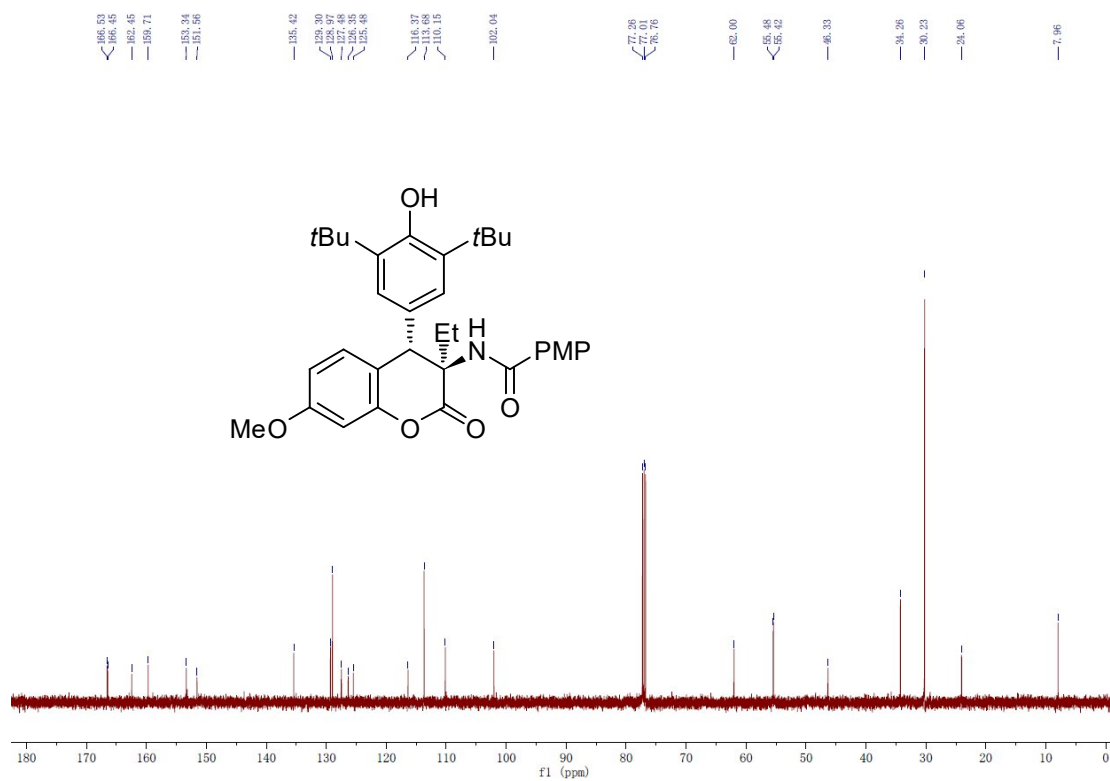
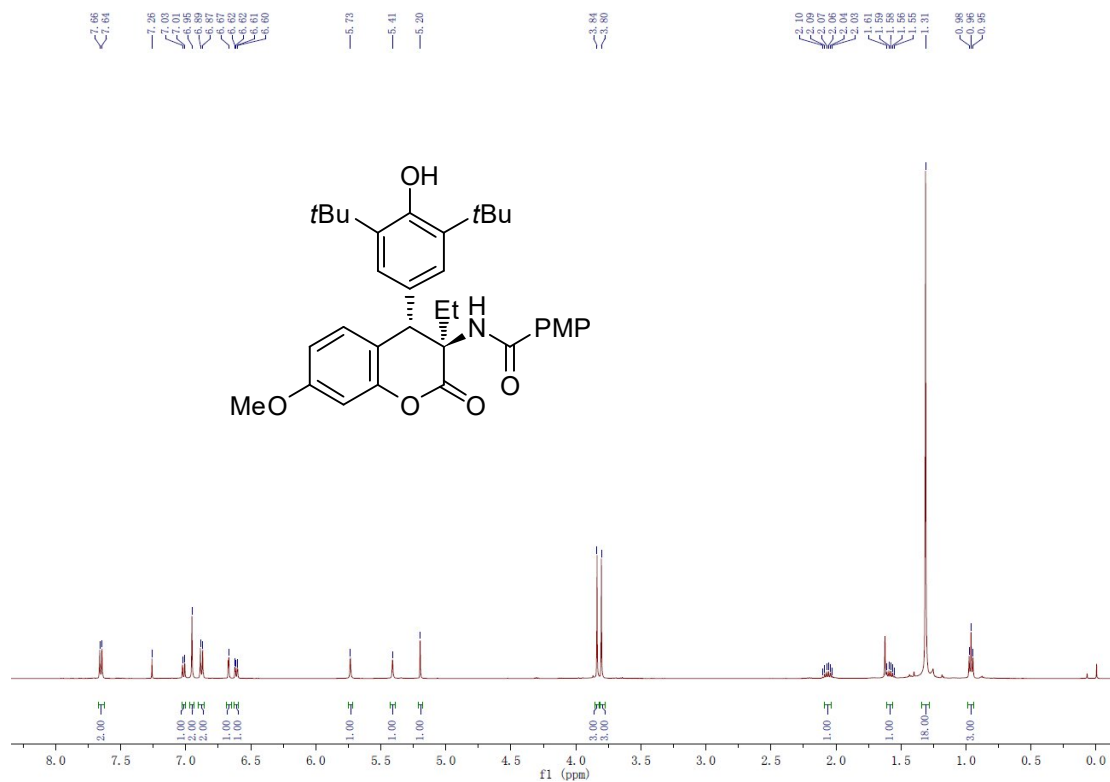
***N*-((3*R*,4*S*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methoxybenzamide (3da)**



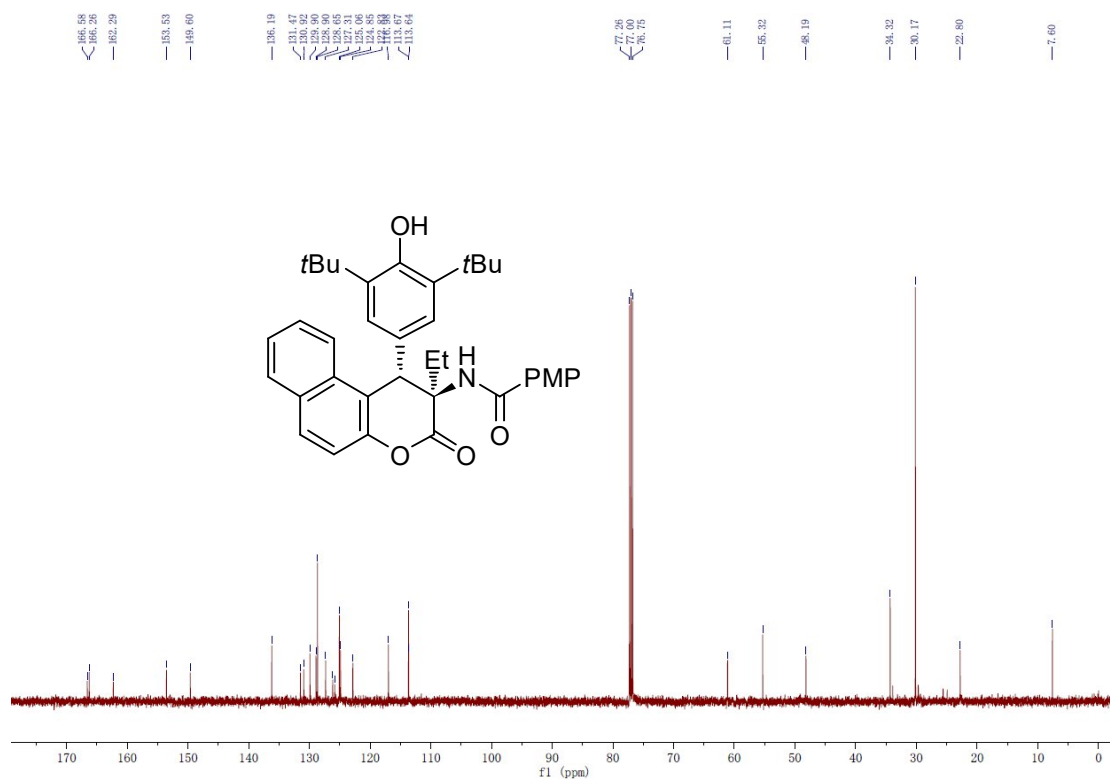
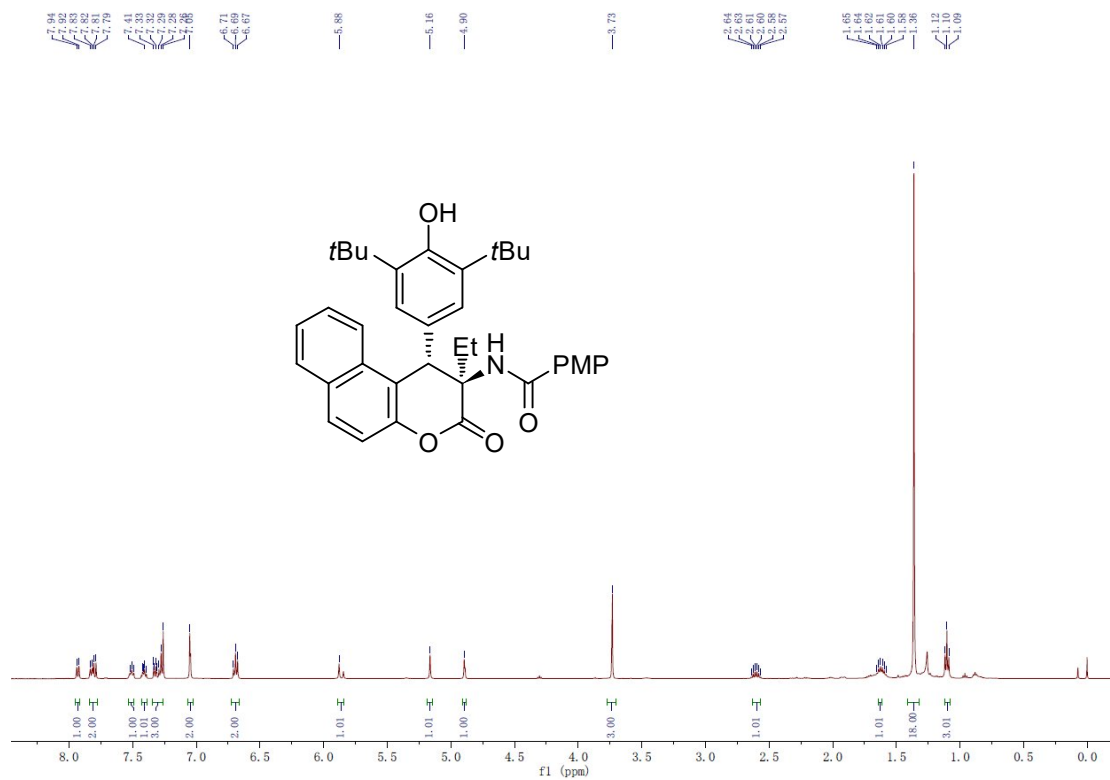
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-6-methyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ea)**



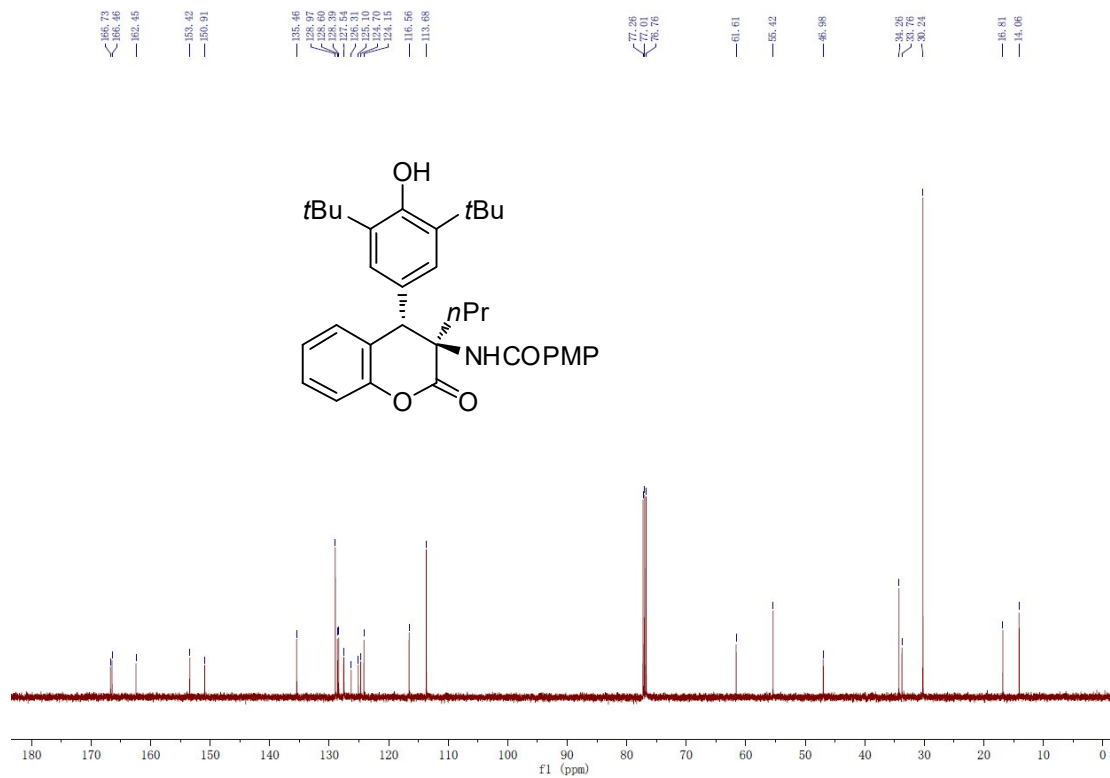
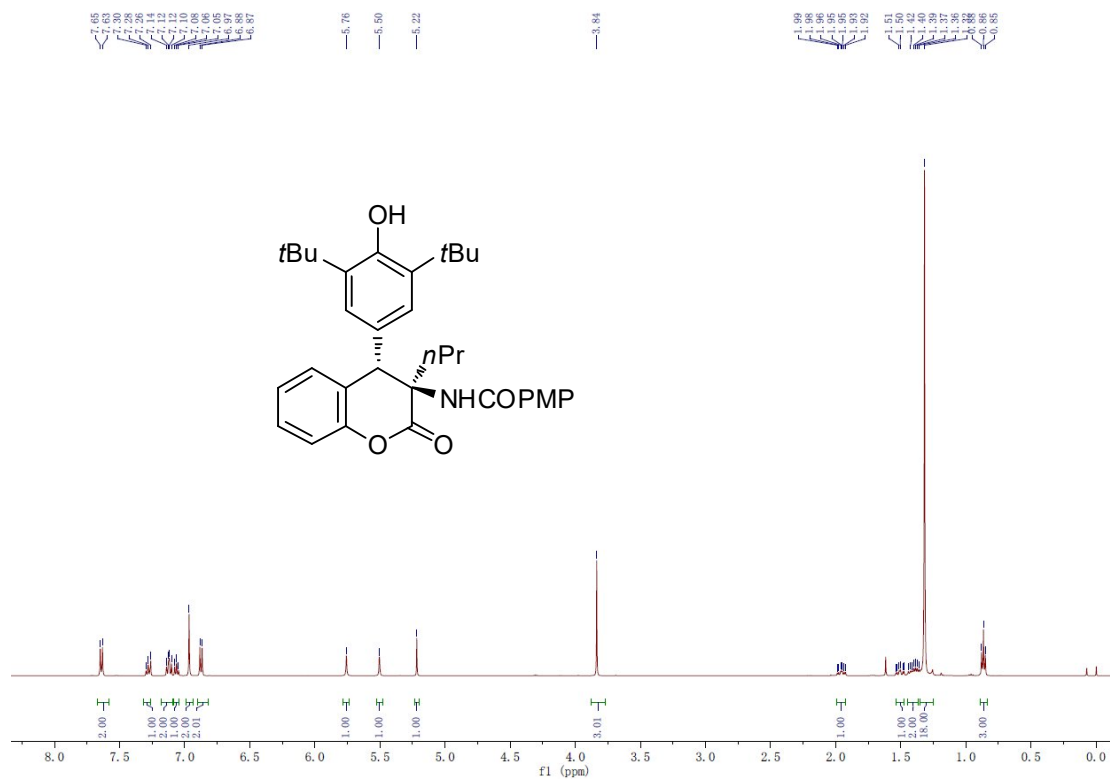
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-7-methoxy-2-oxochroman-3-yl)-4-methoxybenzamide (3fa)**



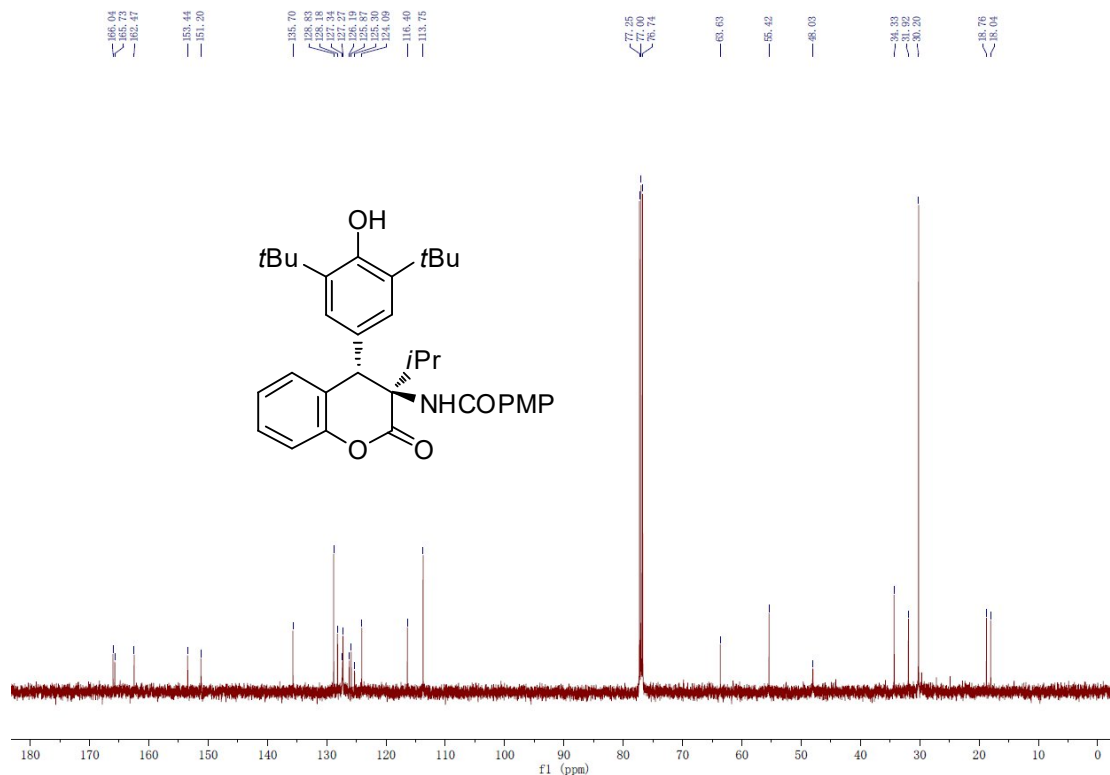
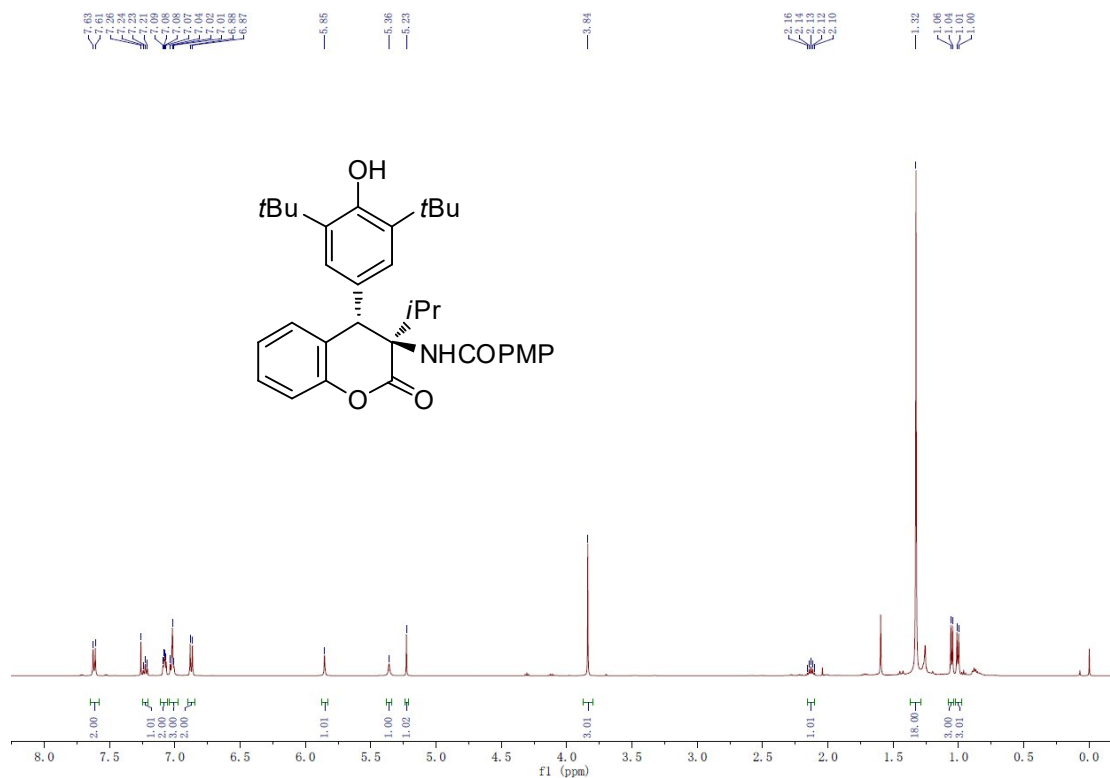
***N*-((1*S*,2*R*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-ethyl-3-oxo-2,3-dihydro-1*H*-benzo[*f*]chromen-2-yl)-4-methoxybenzamide (3ga)**



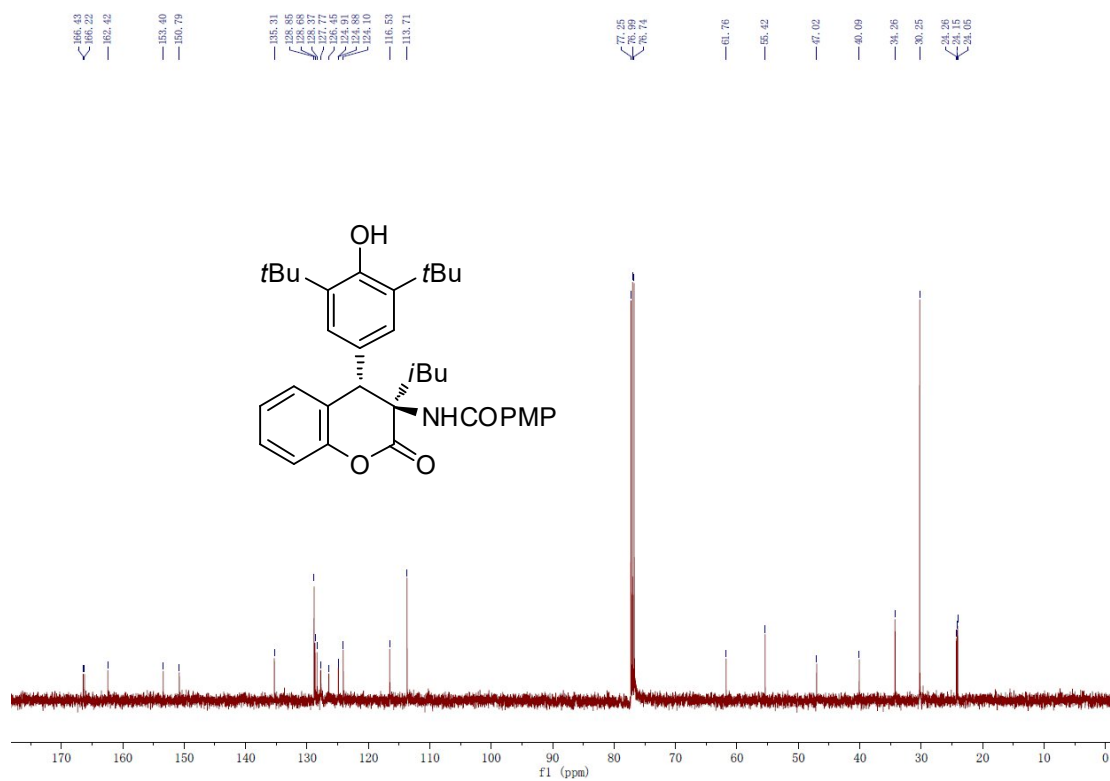
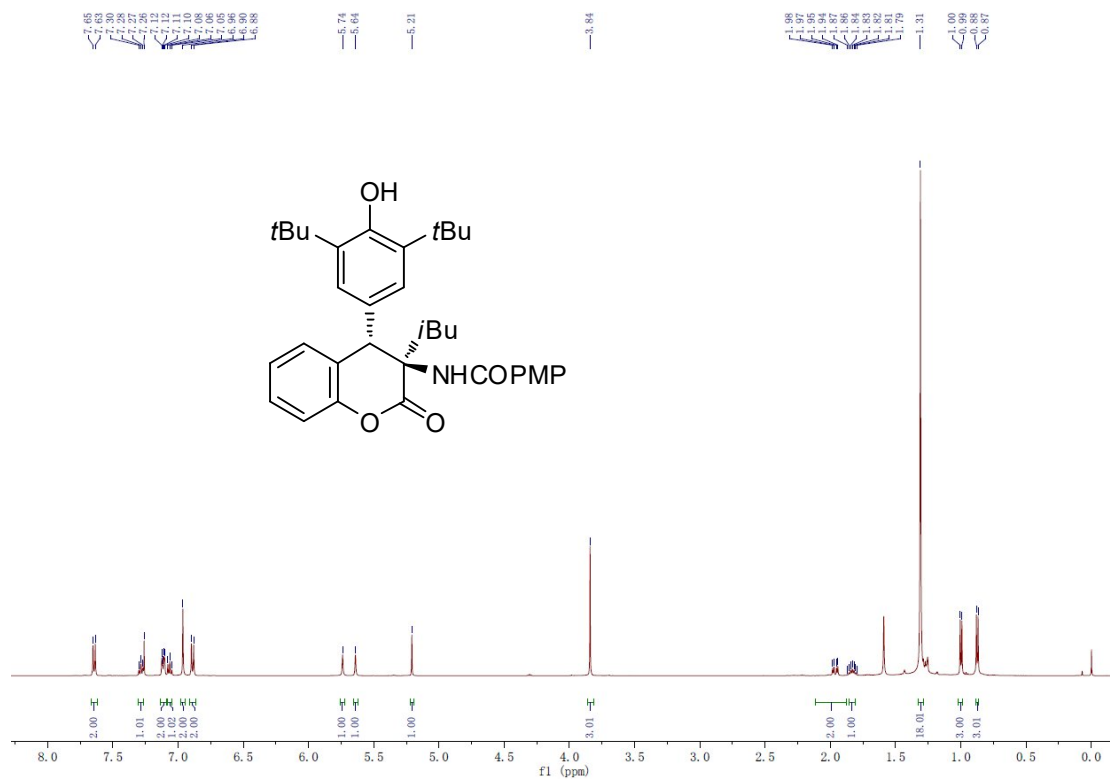
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-3-propylchroman-3-yl)-4-methoxybenzamide (3ab)**



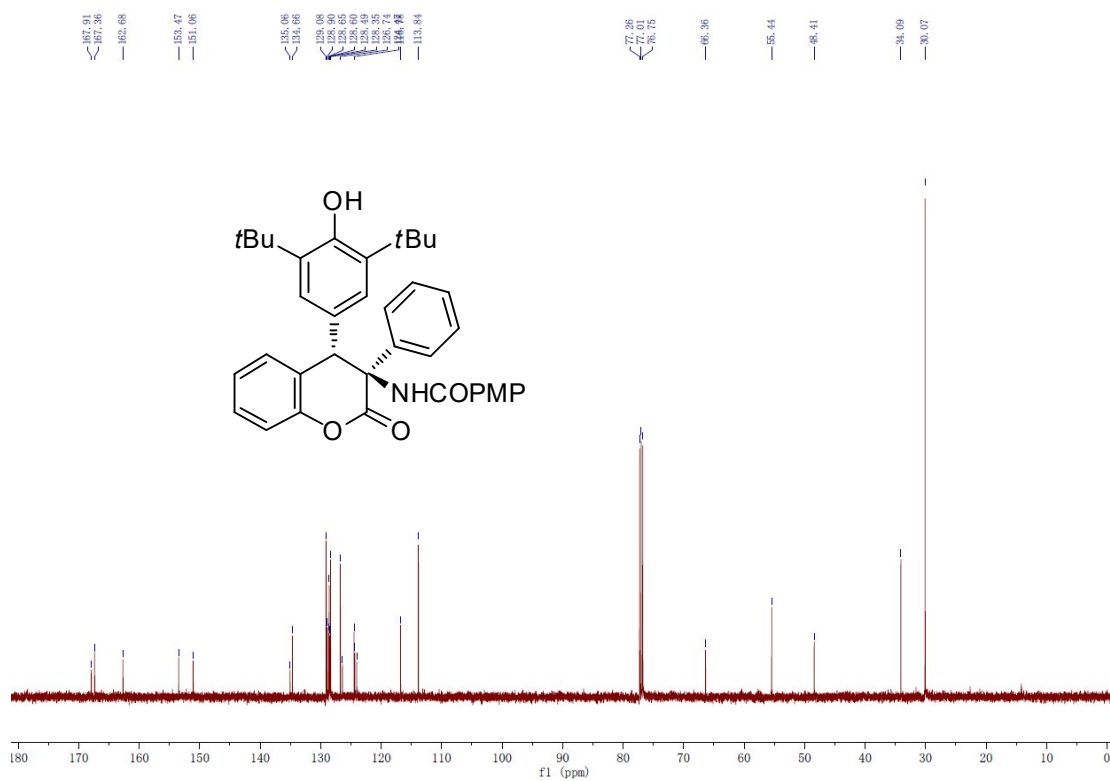
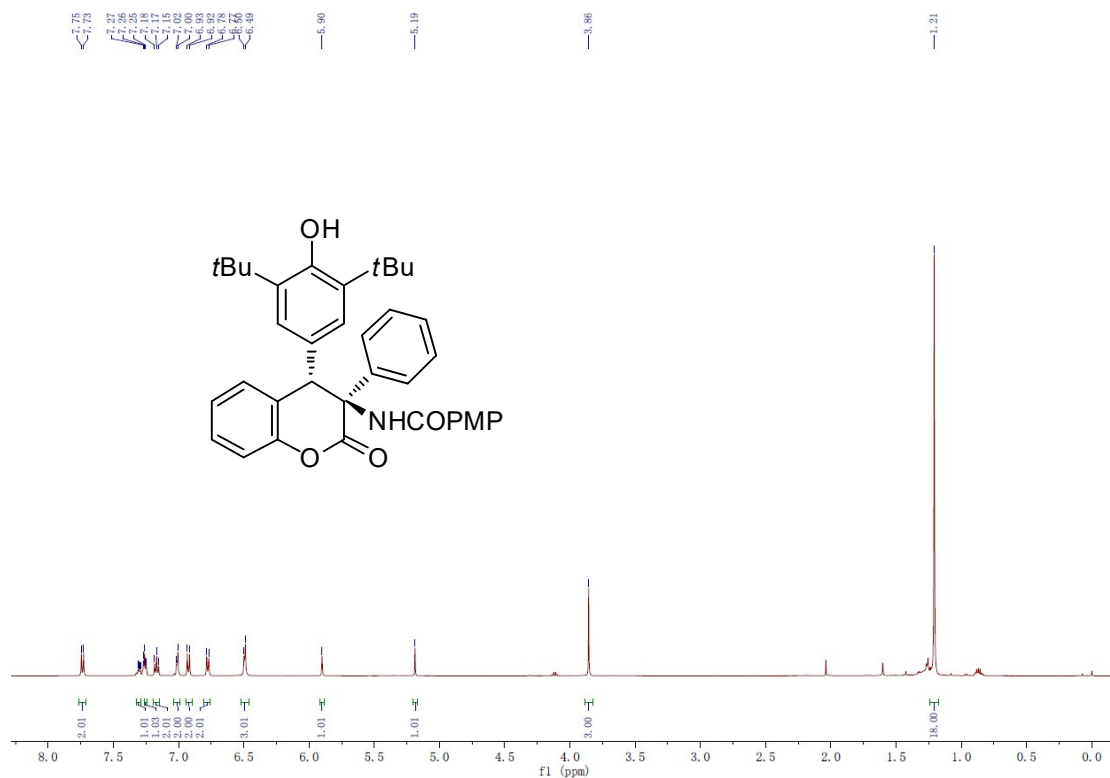
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-isopropyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ac)**



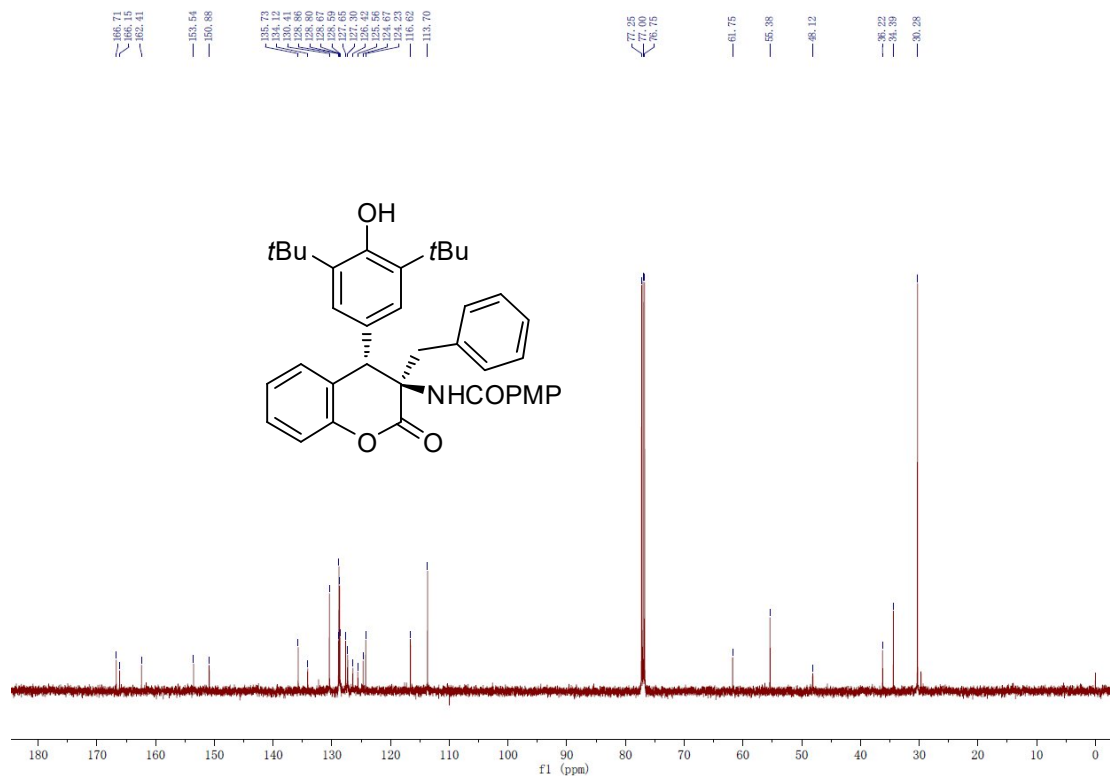
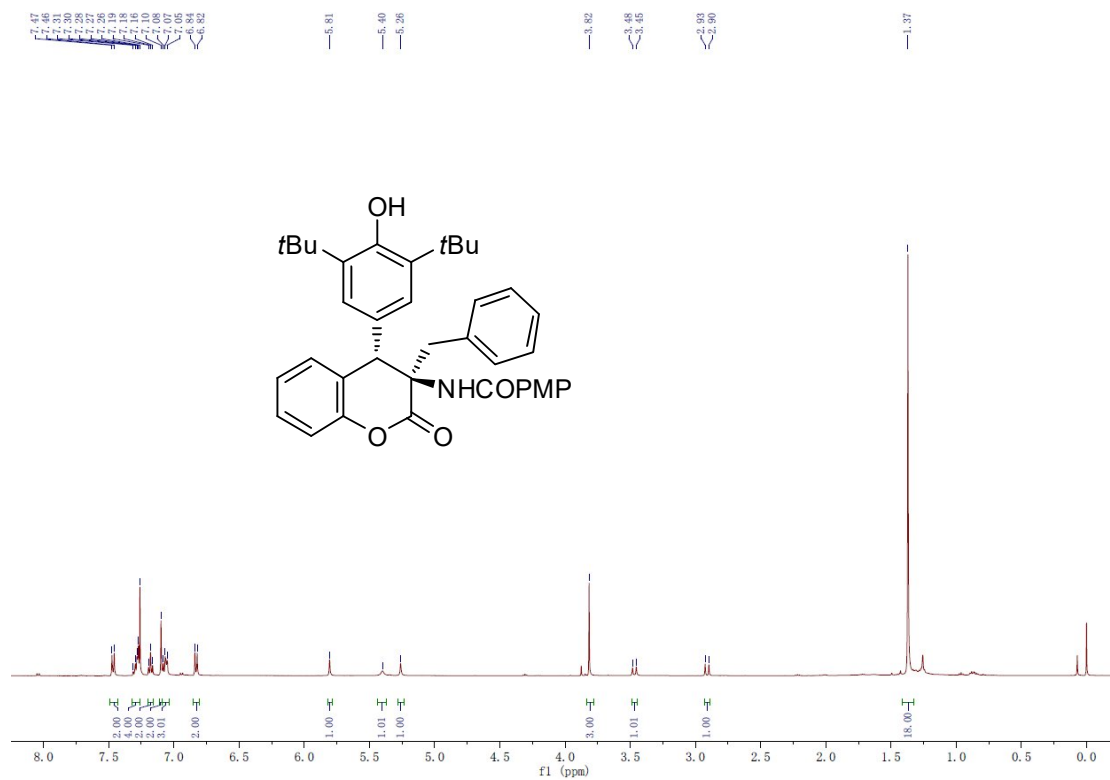
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-isobutyl-2-oxochroman-3-yl)-4-methoxybenzamide (3ad)**



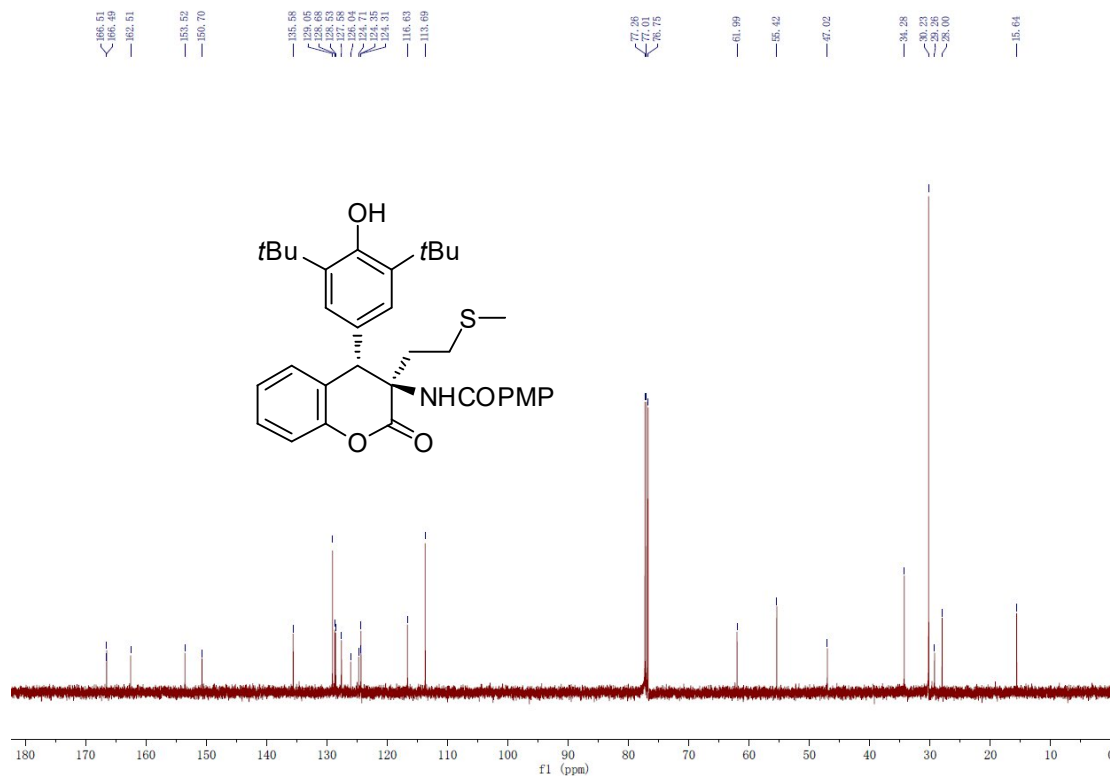
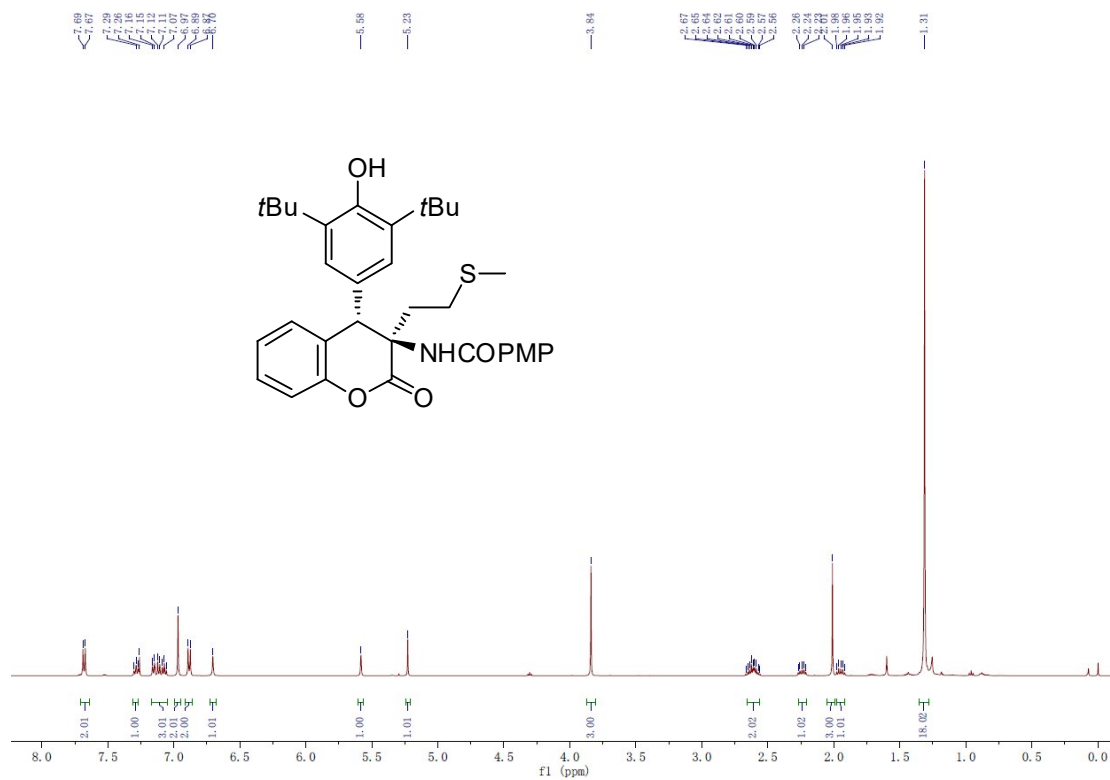
***N*-((3*S*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-3-phenylchroman-3-yl)-4-methoxybenzamide (3ae)**



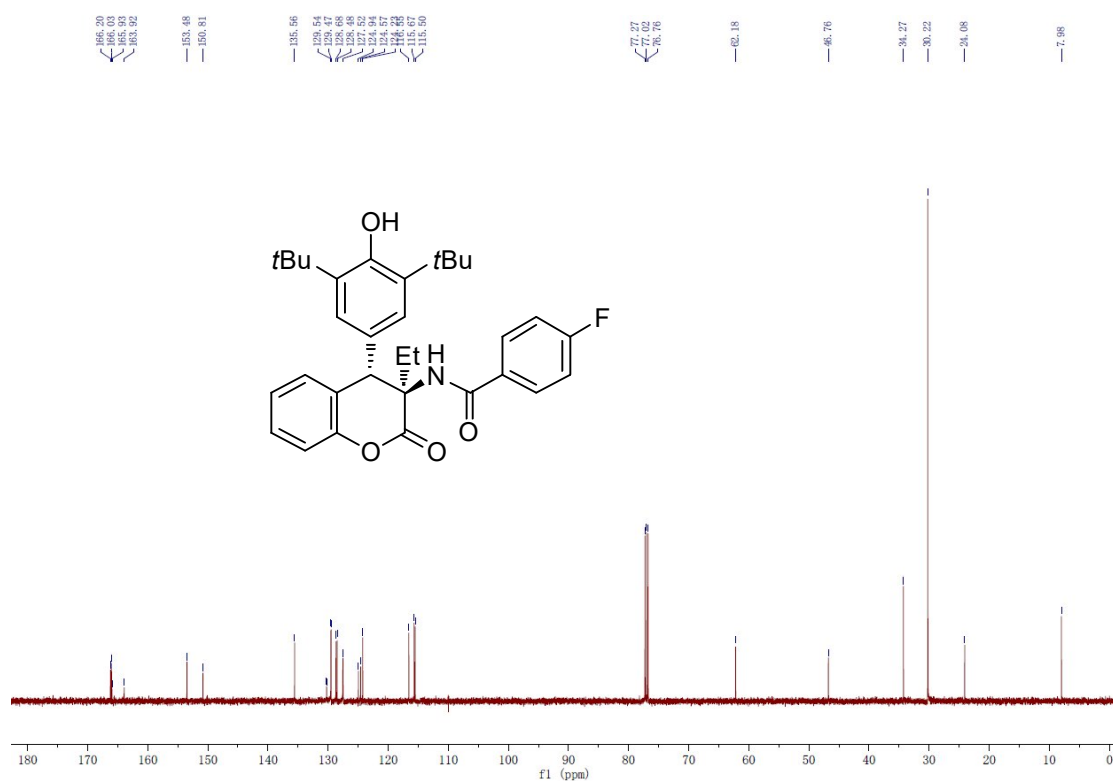
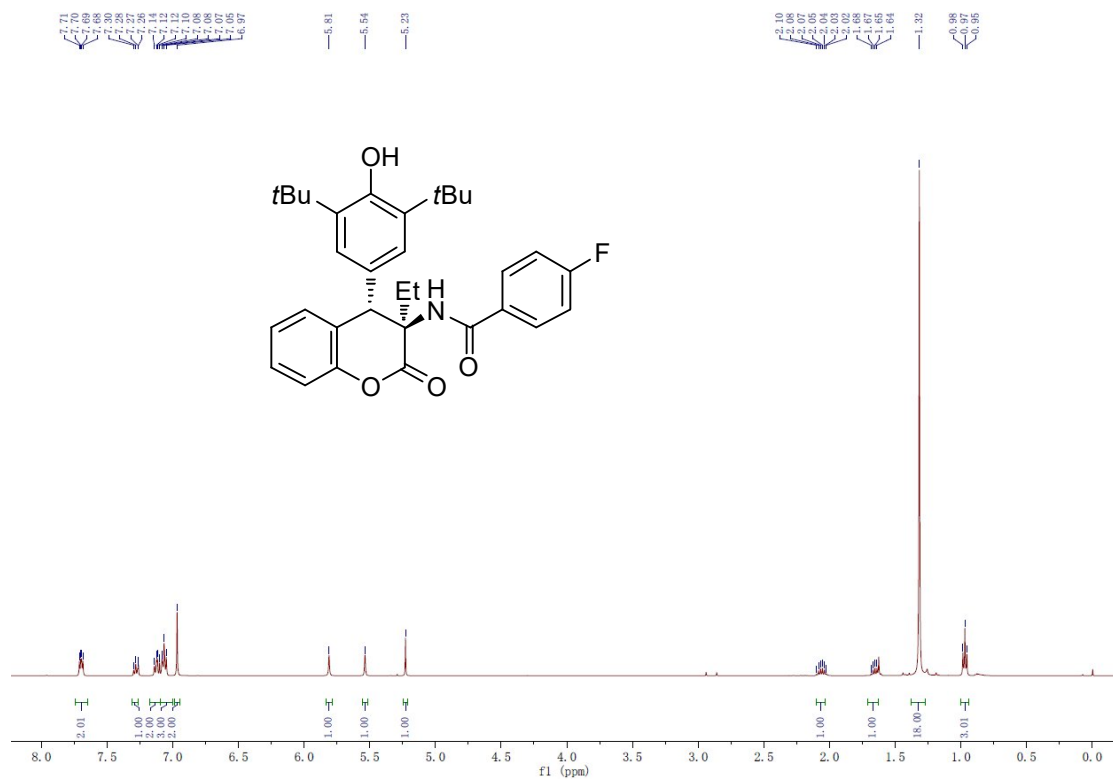
***N*-((3*R*,4*S*)-3-benzyl-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxochroman-3-yl)-4-methoxybenzamide (3af)**



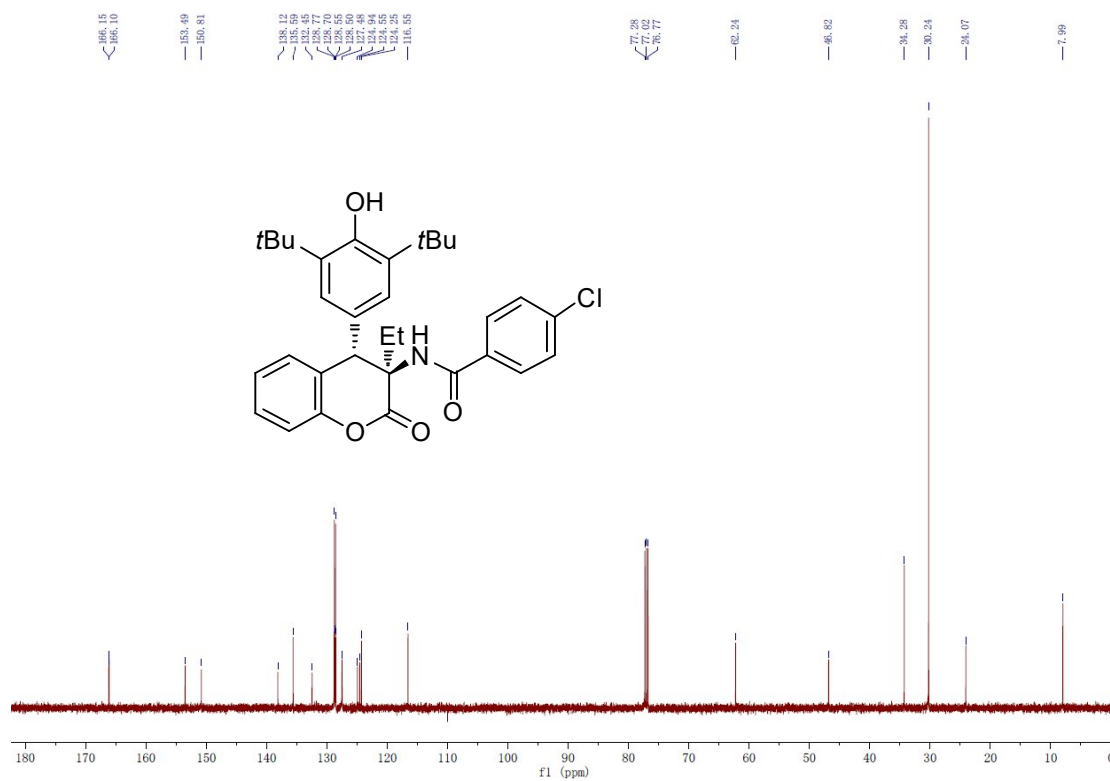
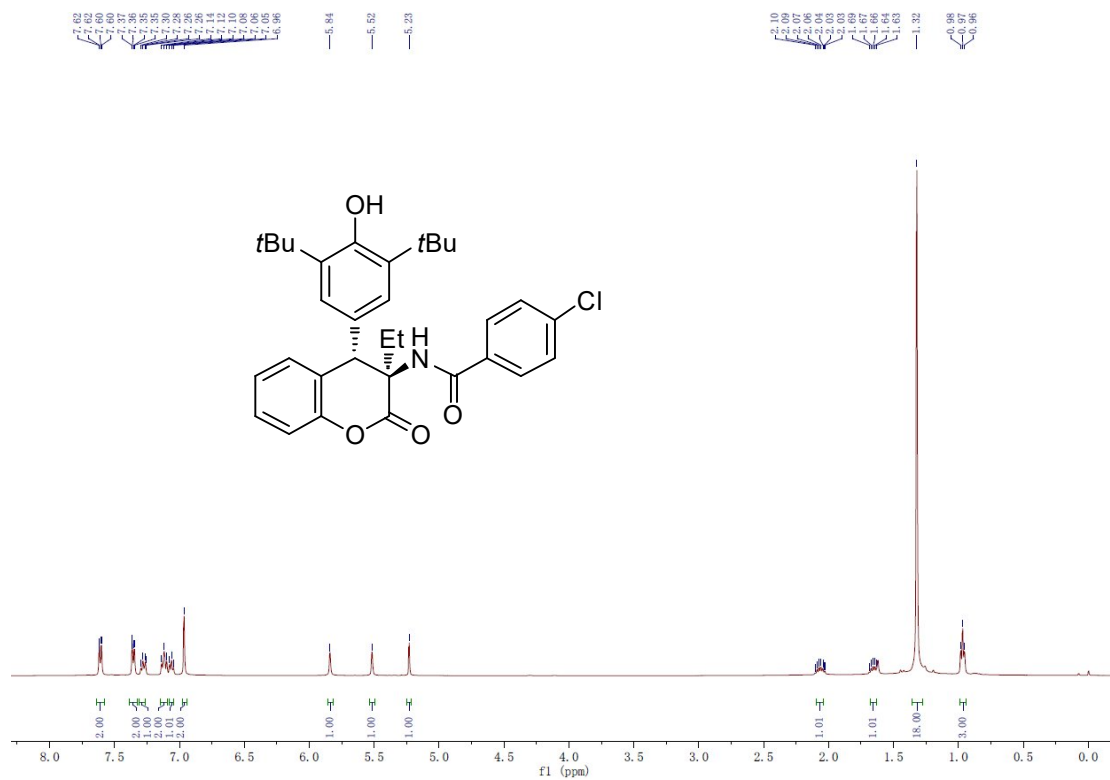
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(2-(methylthio)ethyl)-2-oxochroman-3-yl)-4-methoxybenzamide (3ag)**



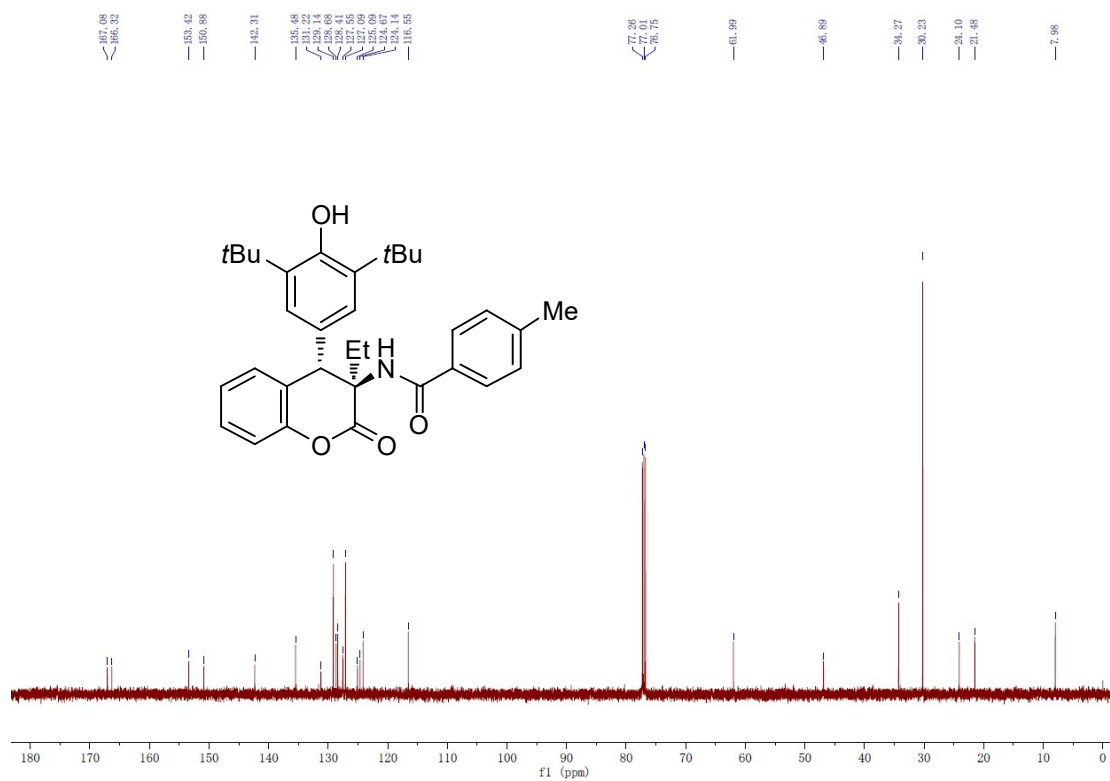
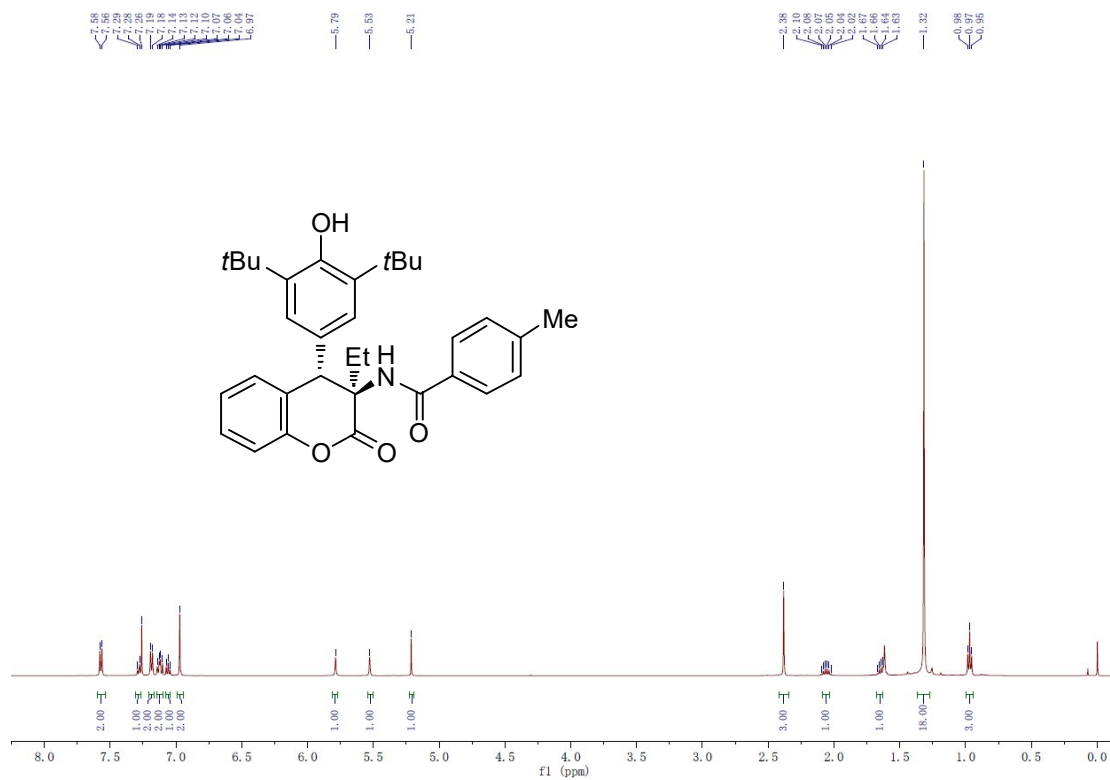
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-fluorobenzamide (3ah)**



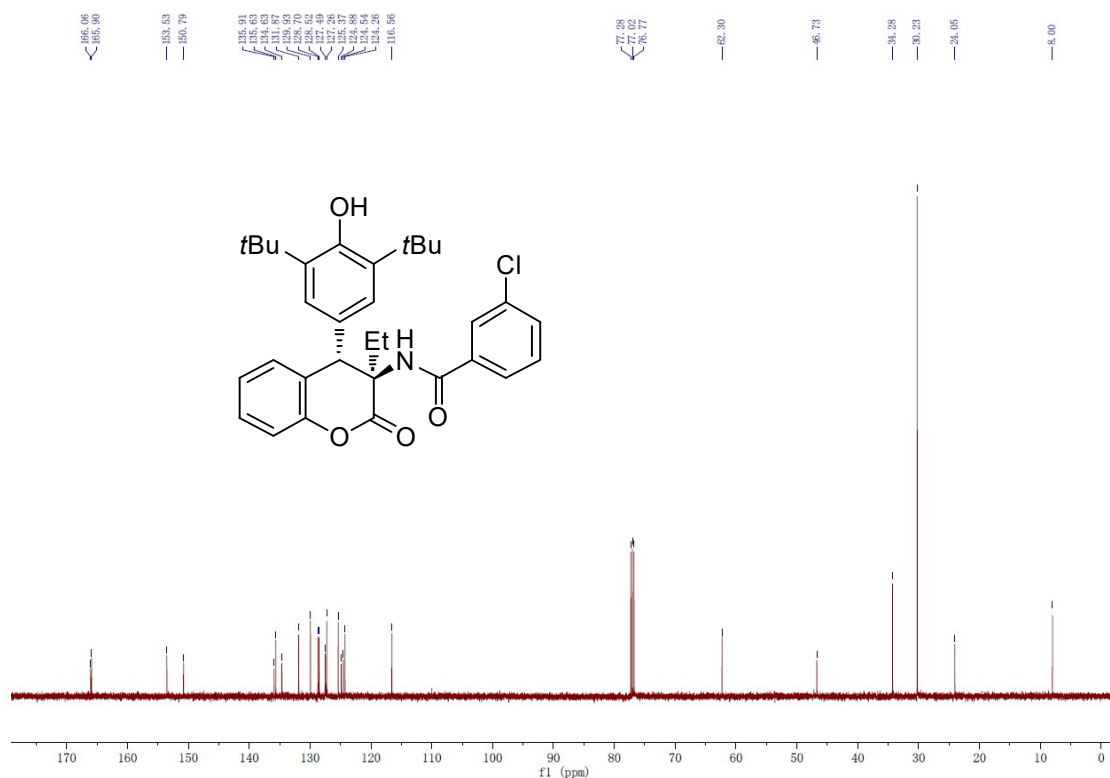
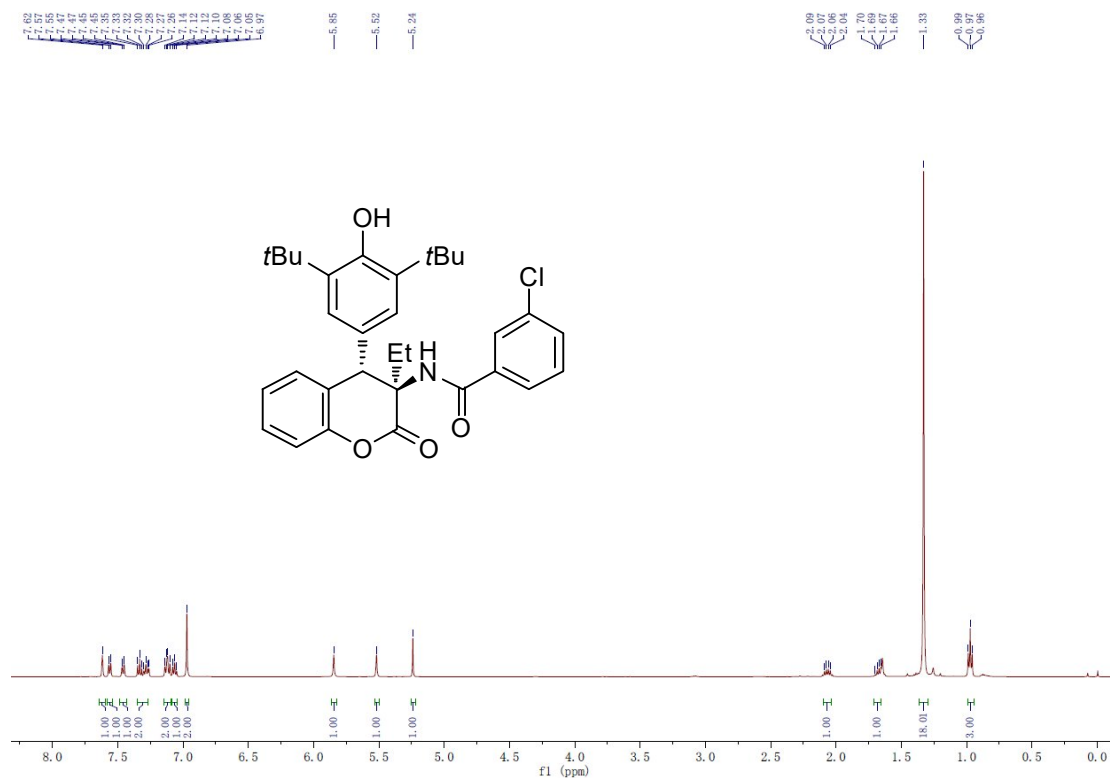
4-Chloro-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3ai)



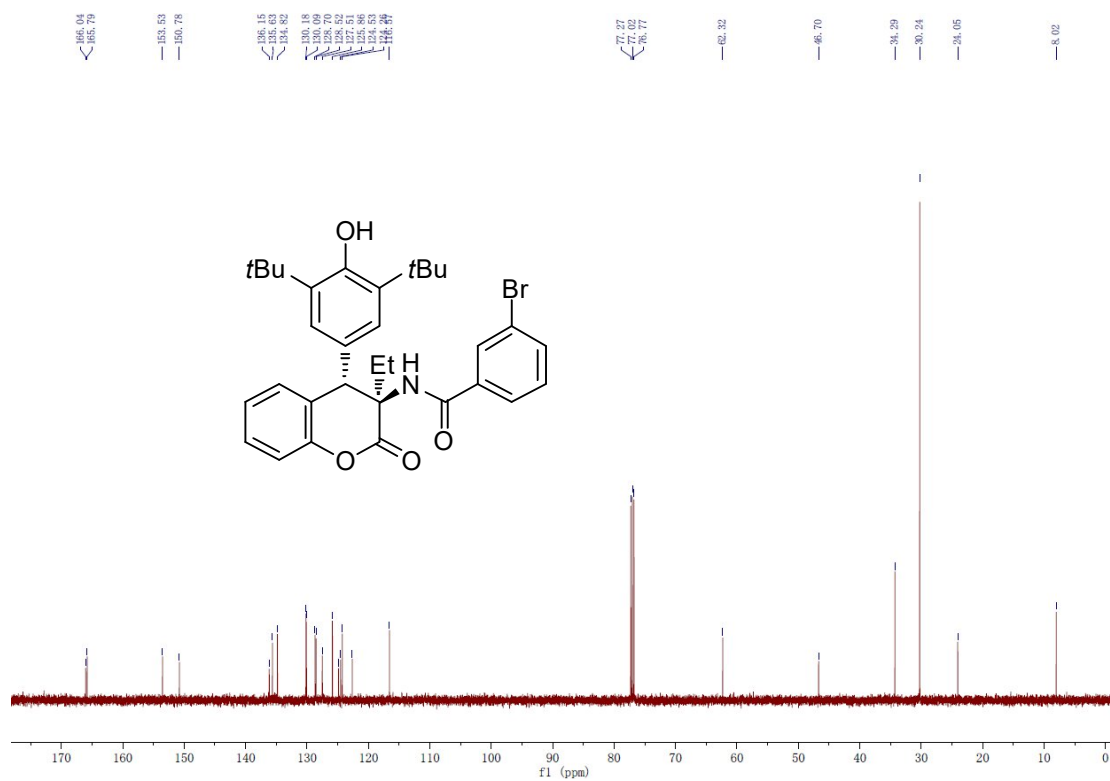
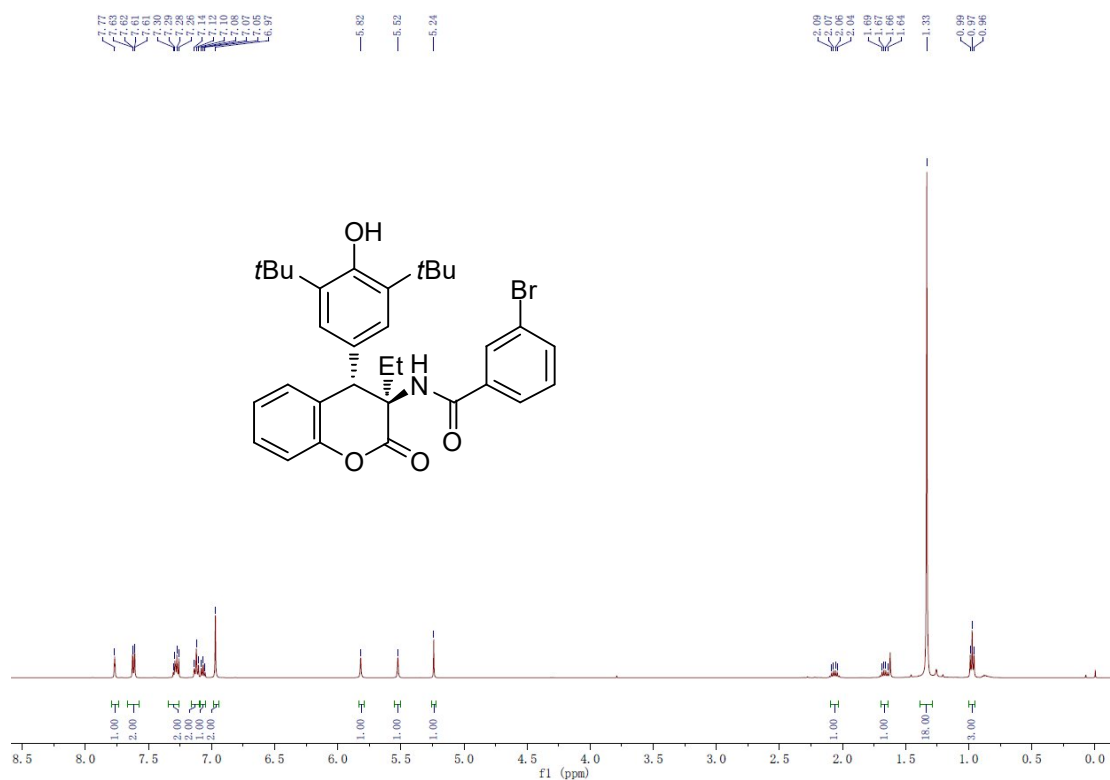
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-4-methylbenzamide (3aj)**



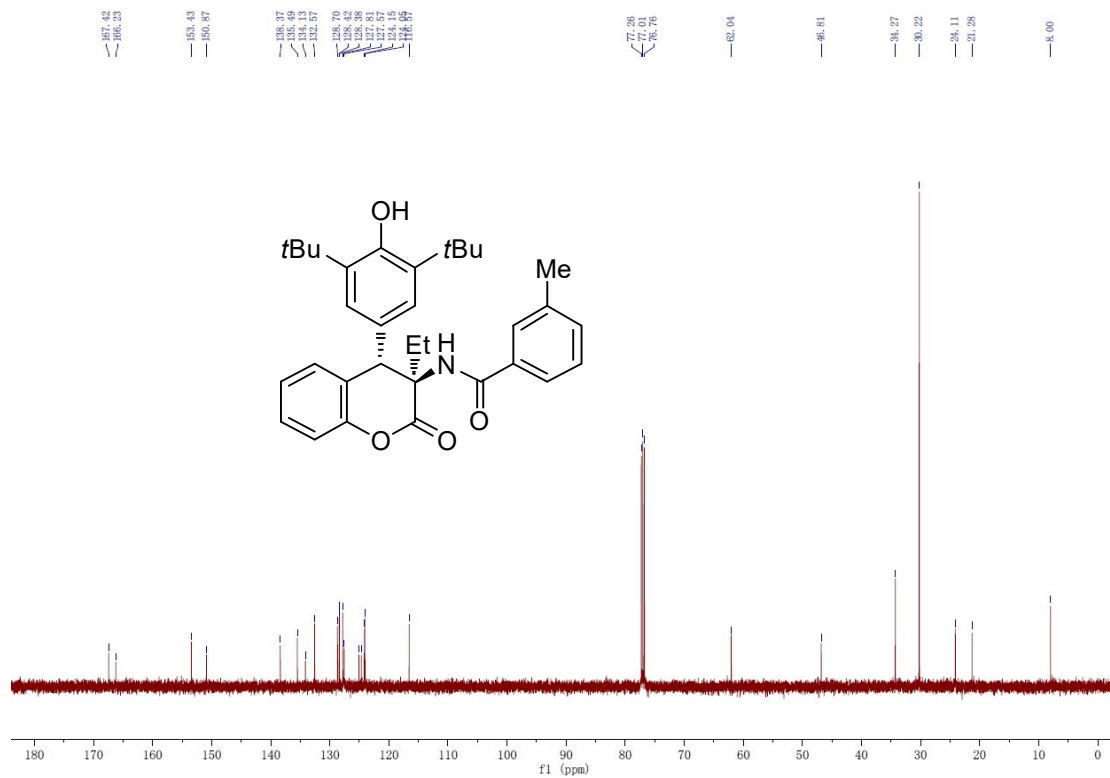
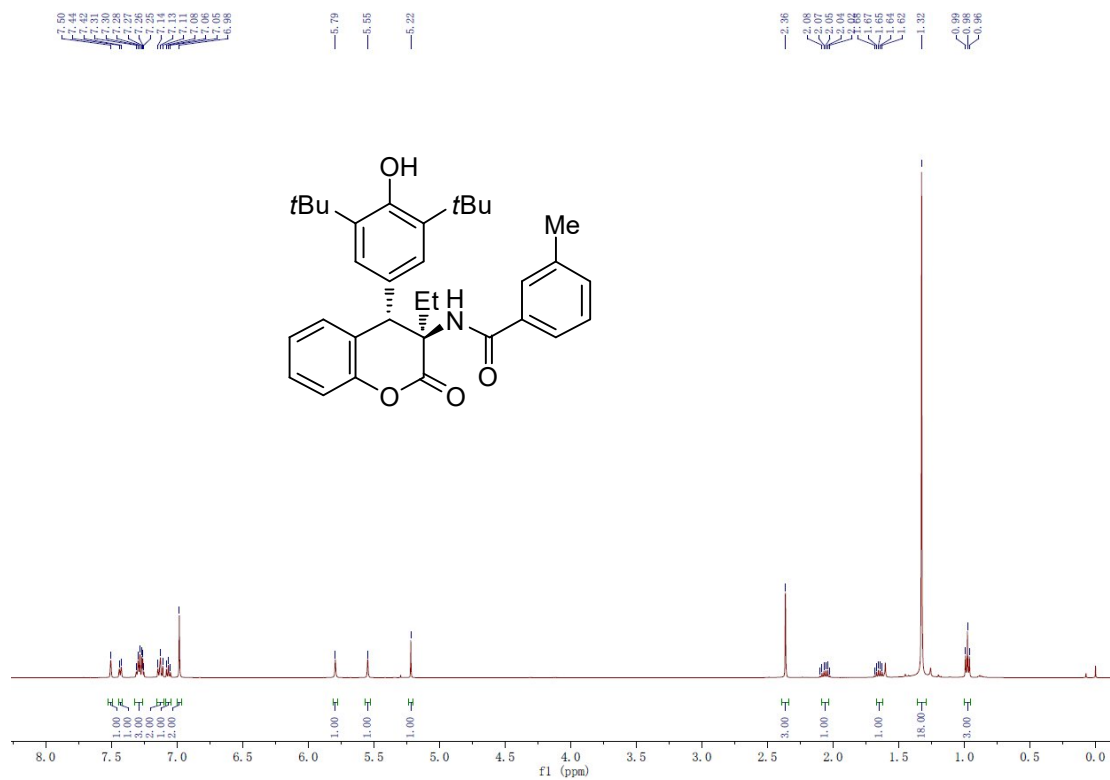
3-Chloro-N-((3R,4S)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3ak)



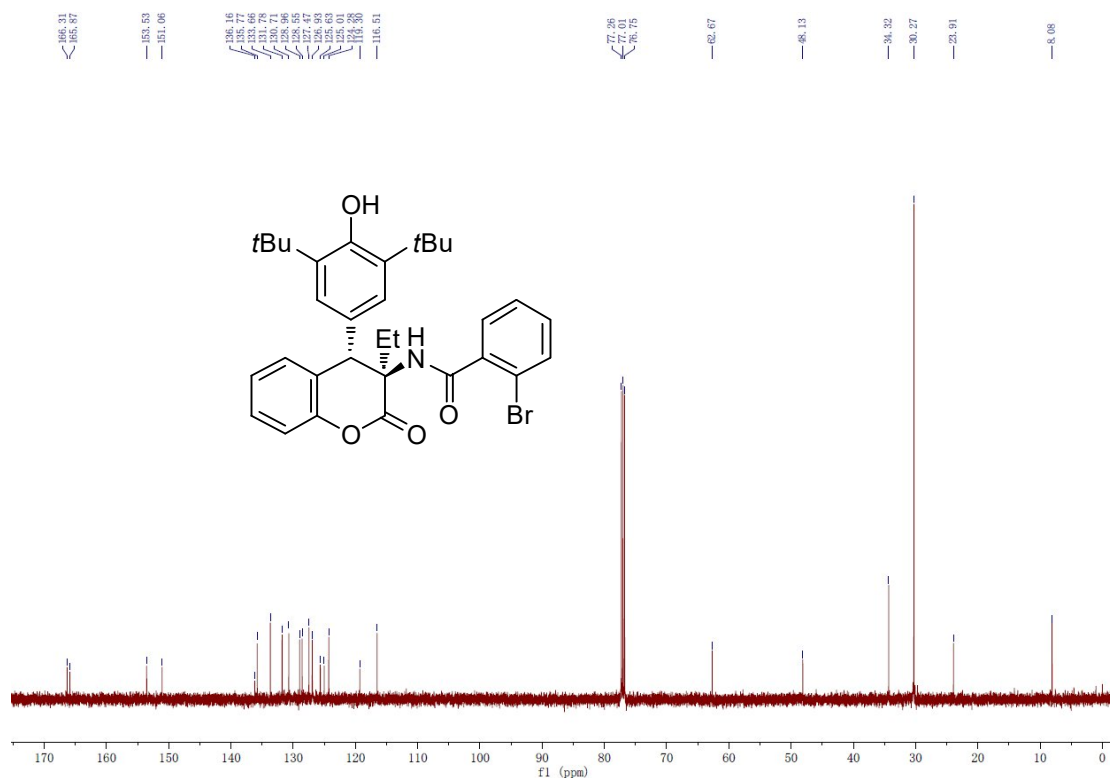
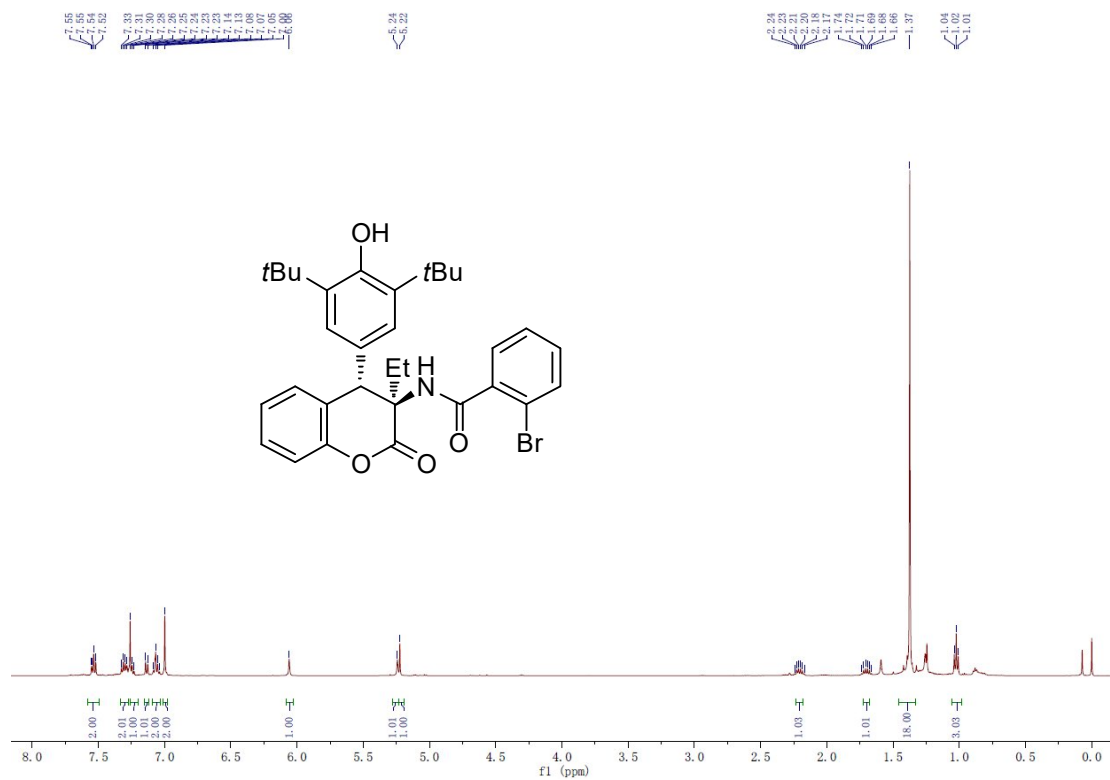
3-Bromo-*N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3al)



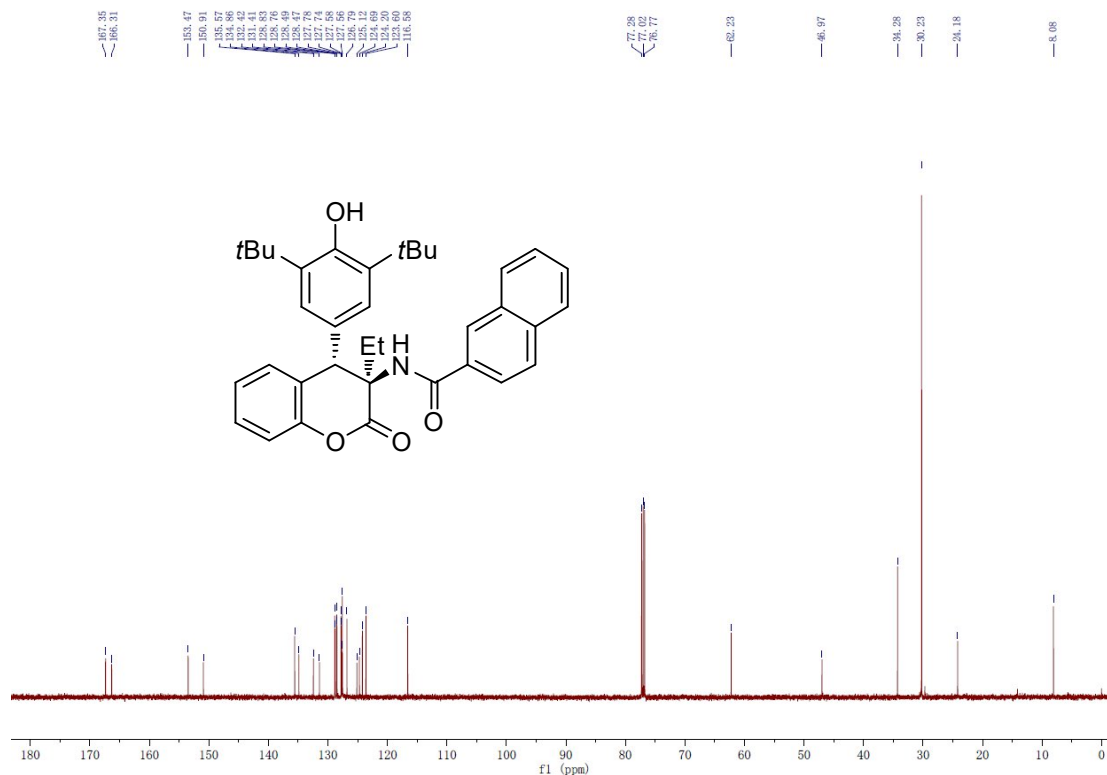
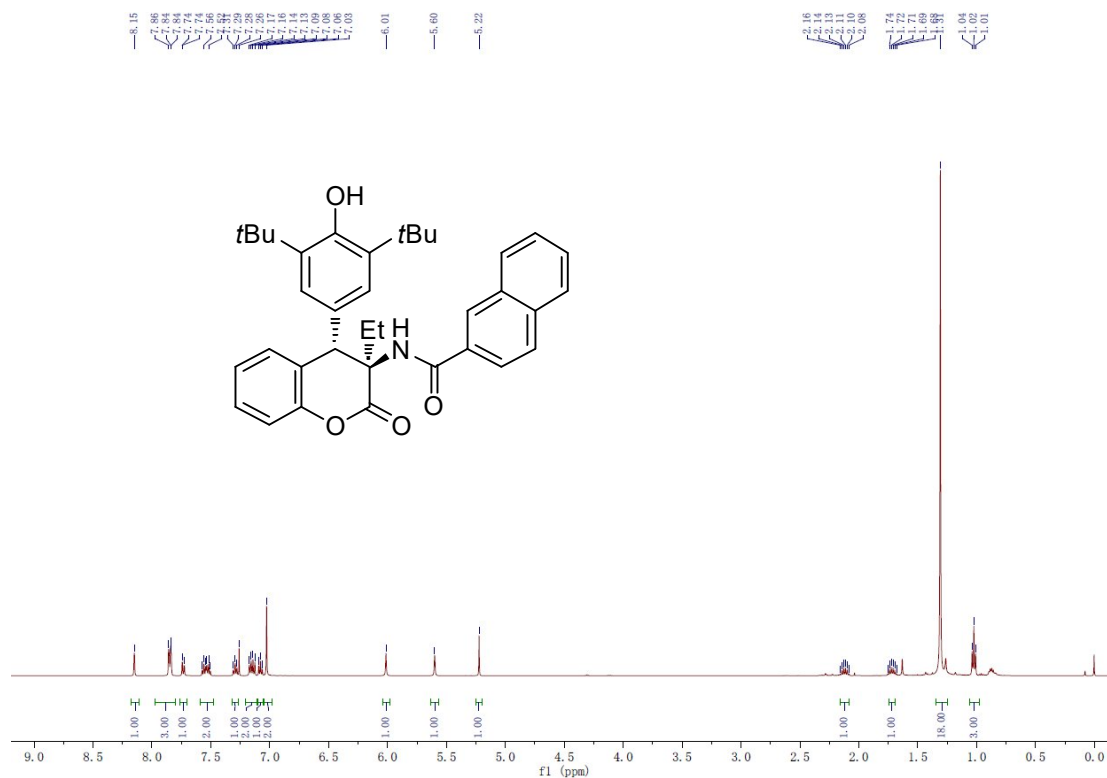
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-3-methylbenzamide (3am)**



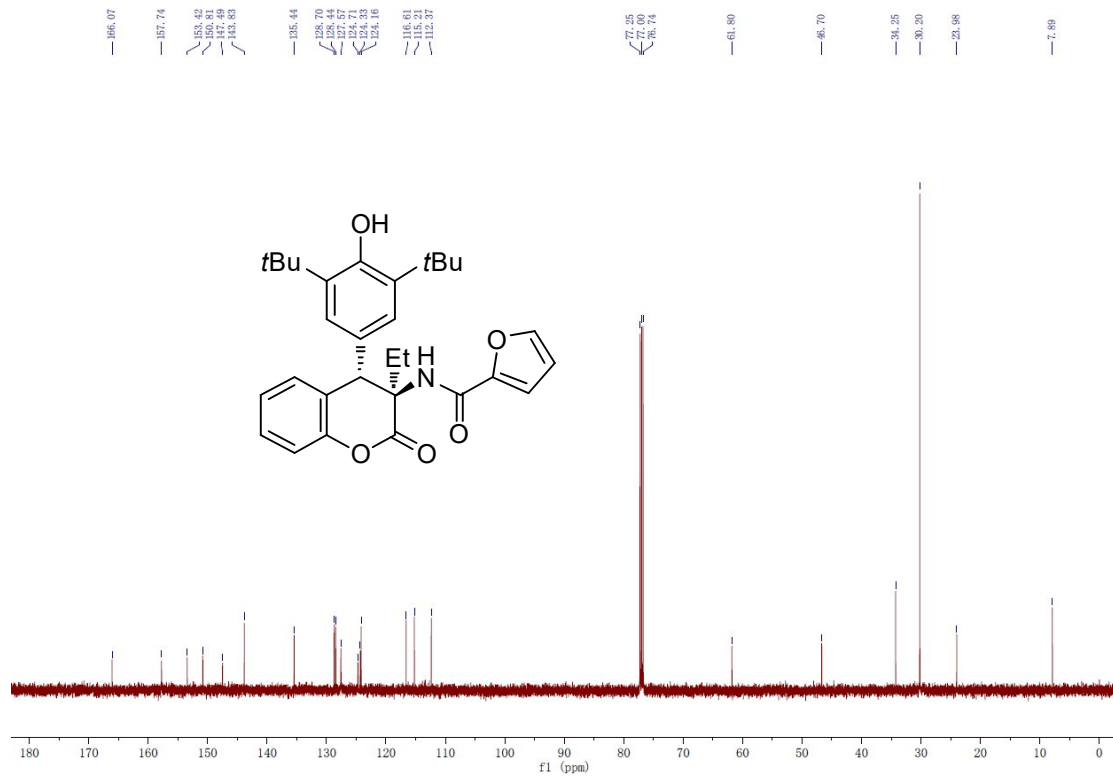
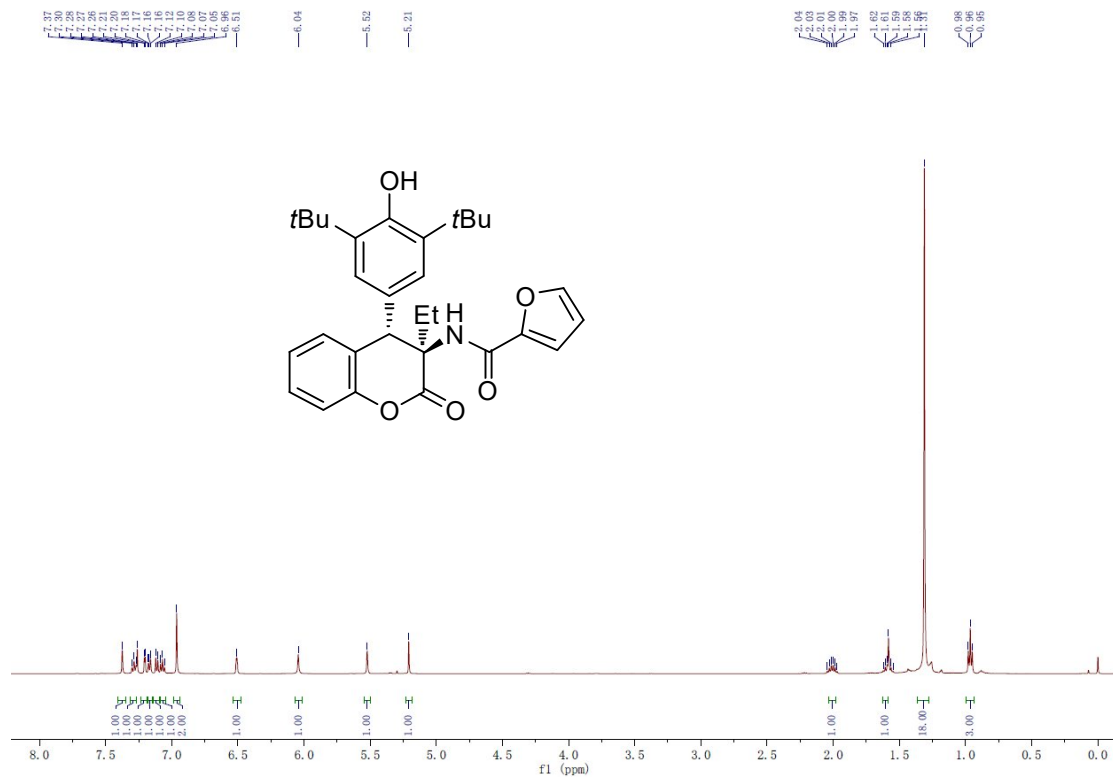
2-Bromo-N-((3R,4S)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)benzamide (3an)



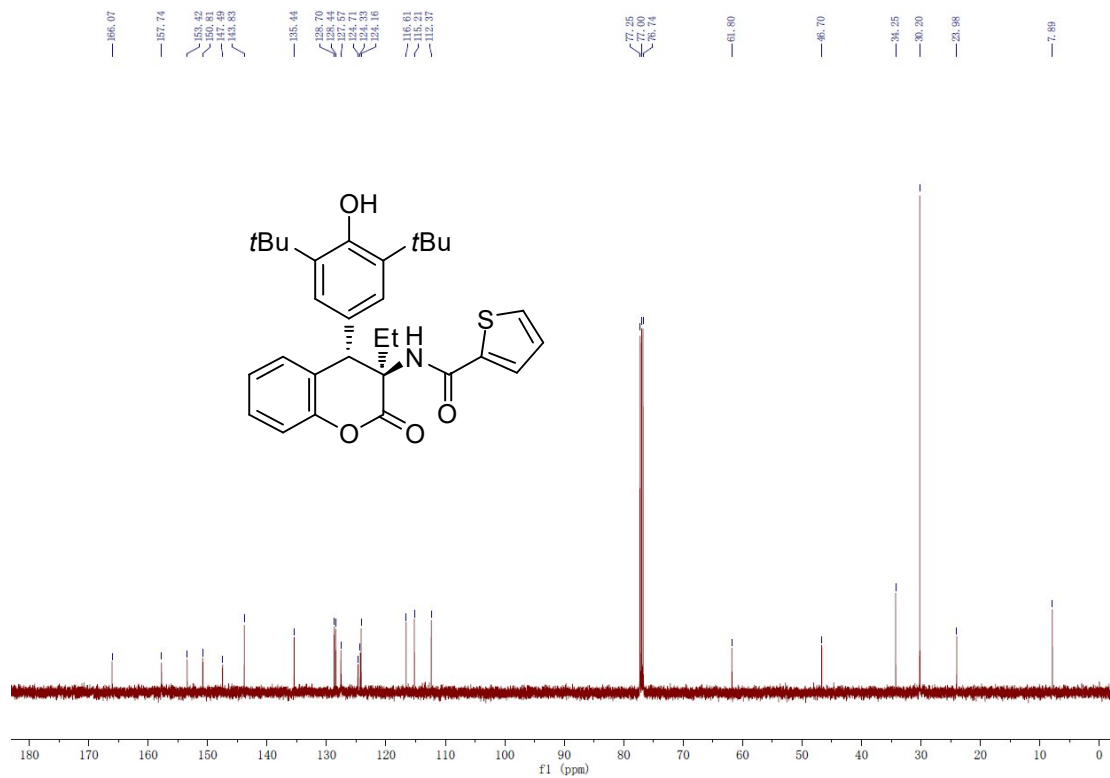
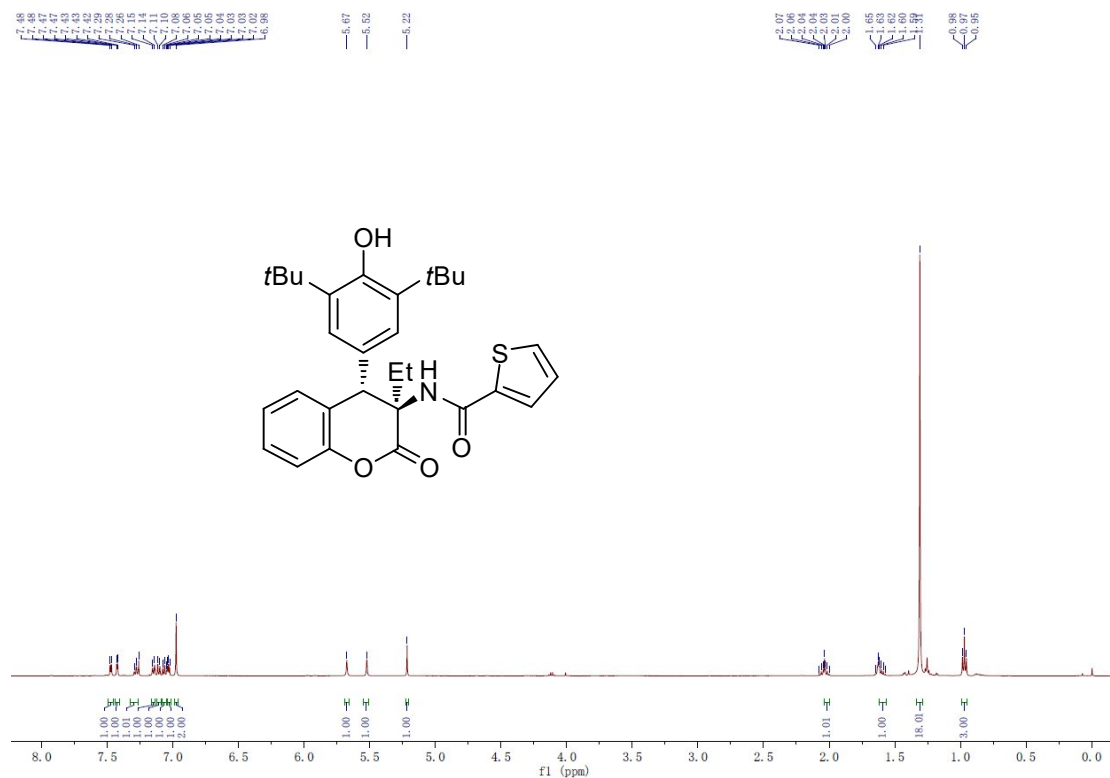
***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)-2-naphthamide (3ao)**



N-((3R,4S)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)furan-2-carboxamide (3ap)



***N*-((3*R*,4*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-ethyl-2-oxochroman-3-yl)thiophene-2-carboxamide (3aq)**



H: Absolute Configuration and X-Ray Analysis Data

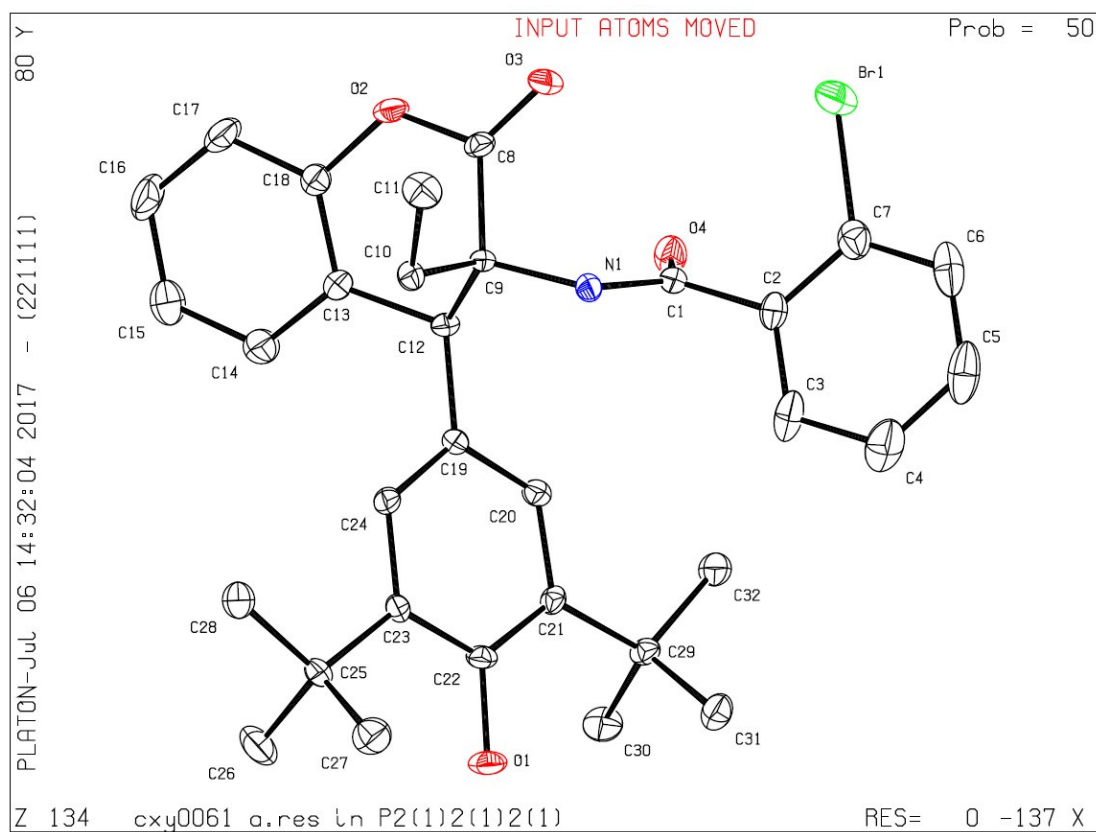


Table Crystal data and structure refinement for 3an.

Identification code	3an
Empirical formula	C ₃₂ H ₃₆ BrNO ₄
Formula weight	578.53
Temperature/K	150.0
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.3304(5)
b/Å	11.1679(5)
c/Å	24.5971(12)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2837.7(2)
Z	4
ρ _{calc} /g/cm ³	1.354
μ/mm ⁻¹	1.486
F(000)	1208.0
Crystal size/mm ³	0.42 × 0.38 × 0.31
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.926 to 52.864
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -30 ≤ l ≤ 30
Reflections collected	57777
Independent reflections	5823 [R _{int} = 0.0487, R _{sigma} = 0.0234]
Data/restraints/parameters	5823/8/351
Goodness-of-fit on F ²	1.038
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0337, wR ₂ = 0.0815
Final R indexes [all data]	R ₁ = 0.0396, wR ₂ = 0.0848
Largest diff. peak/hole / e Å ⁻³	0.78/-0.73
Flack parameter	0.127(2)

I: Reference

1. K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen, D. Enders, *Angew. Chem. Int. Ed.* **2016**, *55*, 12104-12108.
2. T. Wang, Z. Yu, D. L. Hoon, C. Y. Phee, Y. Lan, Y. Lu, *J. Am. Chem. Soc.* **2016**, *138*, 265-271.