Supporting Information

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A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H 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). 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). 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 and *β*-functionalized ketones were from commercial sources and used without purification unless otherwise noted. The quinone methides and bifunctional organocatalysts were prepared following the literature procedures.[1-2]

B: General Procedure for Cascade Reactions

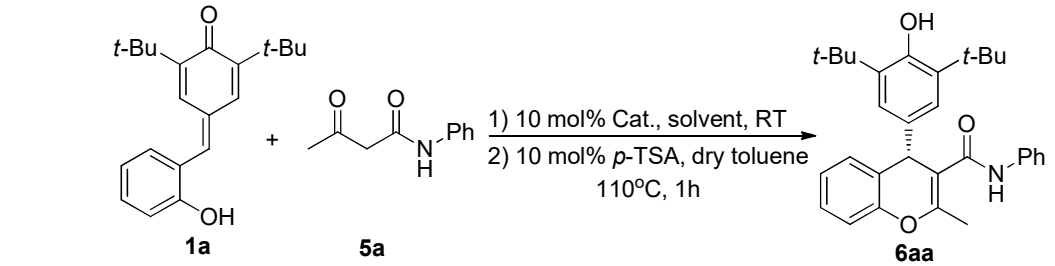
Malononitrile

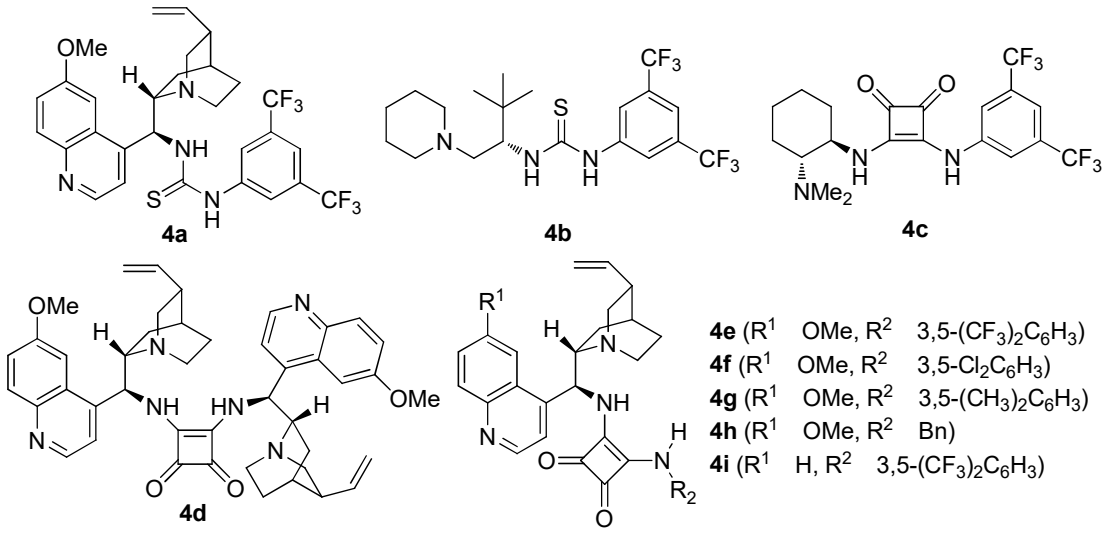
To a solution of $CHCl_3$ (1.0 mL) were added quinone methides **1** (0.05 mmol), malononitrile **2** (0.06 mmol) and catalyst **4e** (0.0025 mmol). The reaction mixture was stirred at room temperature for 24-48h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

β-Functionalized ketone

To a solution of CH_2Cl_2 (1.0 mL) were added quinone methides **1** (0.05 mmol), *β*-functionalized ketones **2** (0.06 mmol) and catalyst **4e** (0.0025 mmol). The reaction mixture was stirred at room temperature for 2-96h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the intermediate product, which was treated with 5 mol% of *p*-TSA in dry toluene (0.5 mL) at 110^{o}C and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **6**.

C: Screening of Catalysts and Condition Optimization





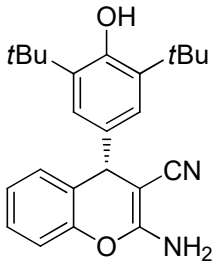
Entry[a]	Cat.	Solvent	*t* [h]	Yield[%][b]	e.r.[c]
1	**4a**	CH_2Cl_2	24	91	65:35
2	**4b**	CH_2Cl_2	24	77	50:50
3	**4c**	CH_2Cl_2	24	84	45:55
4	**4d**	CH_2Cl_2	24	77	46:54
5	**4e**	CH_2Cl_2	24	86	89:11
6	**4f**	CH_2Cl_2	24	74	83:17
7	**4g**	CH_2Cl_2	24	61	78:22
8	**4h**	CH_2Cl_2	24	65	66:34
9	**4i**	CH_2Cl_2	24	90	81:19
10	**4e**	$CHCl_3$	24	82	82:18
11	**4e**	toluene	24	67	80:20
12	**4e**	DCE	24	99	83:17
13	**4e**	$PhCF_3$	24	67	78:22
14	**4e**	anisole	24	61	75:25
15	**4e**	xylenes	24	51	82:18
16[d]	**4e**	CH_2Cl_2	24	85	92.5:7.5
17[d,e]	**4e**	CH_2Cl_2	48	81	91.5:8.5
18[d,f]	**4e**	CH_2Cl_2	48	80	94:6
19[d,f,g]	**4e**	**CH_2Cl_2**	**48**	**85**	**94:6**

[a] Reaction conditions: a mixture of **1a** (0.05 mmol), **5a** (0.06 mmol) and catalyst (10 mol%) in the solvent (0.3 mL) was stirred at room temperature for 24-48h. After column chromatography, the immediate product was treated with 10 mol% of *p*-TSA in dry toluene (0.5 mL) at 110 °C for 1h.

[b] Yield of isolated product.
[c] Determined by HPLC analysis.
[d] 1.0 mL CH_2Cl_2 was used.
[e] The reaction temperature is 0^oC.
[f] 5 mol% catalyst was used.
[g] 5 mol% *p*-TSA was used.

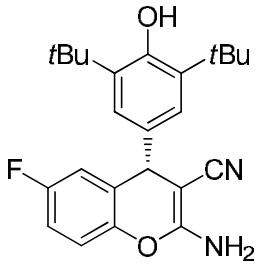
D: Characterization Data

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3a)



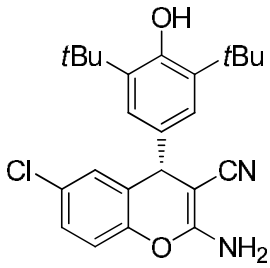
White solid, 97% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.21-7.17 (m, 1H), 7.05-6.99 (m, 3H), 6.93 (s, 2H), 5.10 (s, 1H), 4.66 (s, 1H), 4.55 (s, 2H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.2, 152.8, 148.8, 135.9, 135.3, 129.6, 127.9, 124.9, 124.2, 123.5, 120.1, 116.1, 61.5, 40.7, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{29}N_2O_2$) requires m/z 377.2224, found m/z 377.2227. The enantiomeric ratio was determined to be 97.5:2.5 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 18.4 min (minor), 21.1 min (major).

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-4*H*-chromene-3-carbonitrile (3b)



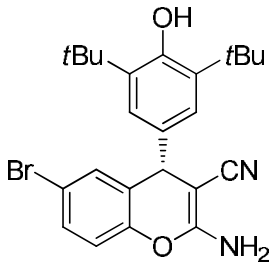
White solid, 94% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.99-6.96 (m, 1H), 6.91-6.86 (m, 3H), 6.73-6.71 (m, 1H), 5.13 (s, 1H), 4.61 (s, 1H), 4.56 (s, 2H), 1.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.2 (d, J = 965.0 Hz), 159.1, 153.0, 144.7 (d, J = 10.0 Hz), 136.1, 134.6, 125.3 (d, J = 30.0 Hz), 124.2, 119.8, 117.6 (d, J = 30.0 Hz), 115.6 (d, J = 95.0 Hz), 115.0 (d, J = 95.0 Hz), 60.9, 41.0, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{28}FN_2O_2$) requires m/z 395.2129, found m/z 395.2135. The enantiomeric ratio was determined to be 96:4 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.5 mL/min]: 30.2 min (minor), 32.5 min (major).

(*S*)-2-amino-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3c)



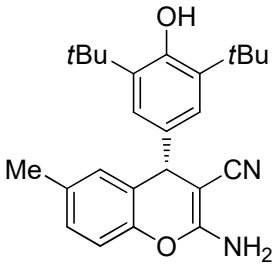
Yellow solid, 74% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.16-7.14 (m, 1H), 7.02-7.01 (m, 1H), 6.96-6.94 (m, 1H), 6.90 (s, 2H), 5.14 (s, 1H), 4.59 (s, 1H), 4.57 (s, 2H), 1.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.9, 153.0, 147.3, 136.1, 134.6, 129.8, 129.3, 128.1, 125.3, 124.1, 119.6, 117.6, 61.4, 40.8, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{28}ClN_2O_2$) requires m/z 411.1839, found m/z 411.1842. The enantiomeric ratio was determined to be 94:6 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 16.5 min (minor), 18.2 min (major).

(*S*)-2-amino-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3d)



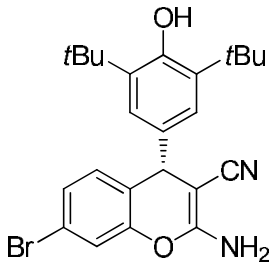
Yellow solid, 91% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.31-7.28 (m, 1H), 7.17-7.16 (m, 1H), 6.90-6.89 (m, 3H), 5.14 (s, 1H), 4.59 (s, 1H), 4.57 (s, 2H), 1.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.9, 153.1, 147.8, 136.1, 134.6, 132.2, 131.0, 125.7, 124.1, 119.6, 118.0, 117.3, 61.4, 40.7, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{28}BrN_2O_2$) requires m/z 455.1329, found m/z 455.1336. The enantiomeric ratio was determined to be 95:5 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 17.2 min (minor), 19.2 min (major).

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-methyl-4*H*-chromene-3-carbonitrile (3e)



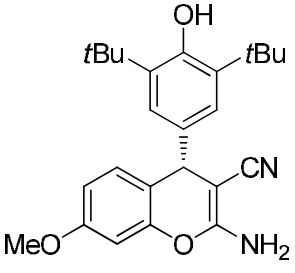
Yellow solid, 98% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.99-6.97 (m, 1H), 6.92-6.88 (m, 3H), 6.84 (s, 1H), 5.10 (s, 1H), 4.59 (s, 1H), 4.52 (s, 2H), 2.23 (s, 3H), 1.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.4, 152.7, 146.8, 135.9, 135.5, 134.4, 129.7, 128.6, 124.1, 123.0, 120.3, 115.9, 61.5, 40.8, 34.3, 30.2, 20.8. HRMS (ESI): exact mass calculated for M^+ ($C_{25}H_{31}N_2O_2$) requires m/z 391.2380, found m/z 391.2387. The enantiomeric ratio was determined to be 97:3 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 15.7 min (minor), 18.0 min (major).

(*S*)-2-amino-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3f)



Yellow solid, 96% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.17-7.16 (m, 2H), 6.90-6.89 (m, 3H), 5.29 (s, 1H), 5.12 (s, 1H), 4.59 (s, 2H), 1.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.8, 153.0, 149.1, 136.1, 134.6, 130.9, 128.1, 124.2, 122.7, 120.5, 119.6, 119.4, 61.5, 40.4, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{28}BrN_2O_2$) requires m/z 455.1334, found m/z 455.1338. The enantiomeric ratio was determined to be 94.5:5.5 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 18.8 min (minor), 20.6 min (major).

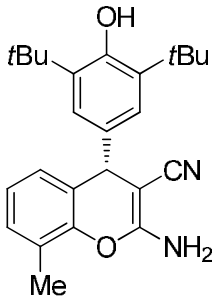
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7-methoxy-4*H*-chromene-3-carbonitrile (3g)



Yellow solid, 93% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.93-6.91 (m, 3H), 6.63-6.61 (m, 1H), 6.54-6.53 (m, 1H), 5.09 (s, 1H), 4.59 (s, 1H), 4.53 (s, 2H), 3.78 (s, 3H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.1, 159.0, 152.7, 149.3, 135.9, 135.4, 130.2, 124.2, 120.1, 115.5, 111.5, 101.1, 61.9, 55.5, 40.1, 34.3, 30.3. HRMS (ESI):

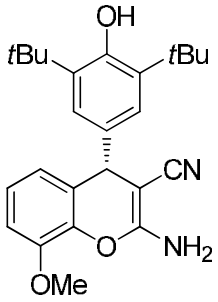
exact mass calculated for M^+ ($C_{25}H_{31}N_2O_3$) requires m/z 407.2329, found m/z 407.2334. The enantiomeric ratio was determined to be 98:2 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 22.3 min (minor), 25.0 min (major).

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-methyl-4*H*-chromene-3-carbonitrile (3h)



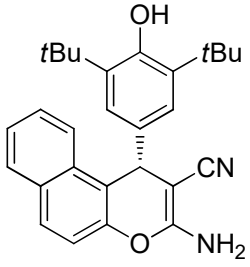
Yellow oil, 71% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.03-7.02 (m, 1H), 6.95-6.92 (m, 3H), 6.87-6.86 (m, 1H), 5.09 (s, 1H), 4.65 (s, 1H), 4.57 (s, 2H), 2.30 (s, 3H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.3, 152.7, 147.2, 135.8, 135.4, 129.3, 127.1, 125.3, 124.3, 124.2, 123.2, 120.2, 61.5, 40.8, 34.3, 30.2, 15.8. HRMS (ESI): exact mass calculated for M^+ ($C_{25}H_{31}N_2O_2$) requires m/z 391.2386, found m/z 391.2390. The enantiomeric ratio was determined to be 96:4 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 12.7 min (minor), 13.8 min (major).

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-methoxy-4*H*-chromene-3-carbonitrile (3i)



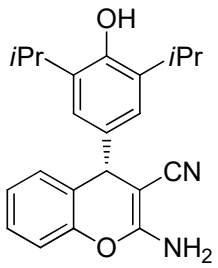
White solid, 97% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.99-6.94 (m, 3H), 6.78-6.77 (m, 1H), 6.64-6.62 (m, 1H), 5.10 (s, 1H), 4.67 (s, 2H), 4.65 (s, 1H), 3.89 (s, 3H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.3, 152.8, 147.3, 138.4, 135.9, 135.2, 124.6, 124.5, 124.2, 121.0, 120.1, 110.0, 61.2, 56.0, 40.8, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{25}H_{31}N_2O_3$) requires m/z 407.2335, found m/z 407.2339. The enantiomeric ratio was determined to be 97:3 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 19.9 min (minor), 25.4 min (major).

(*S*)-3-amino-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (3j)



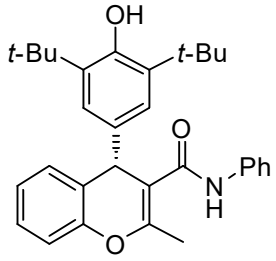
Yellow solid, 96% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.81-7.75 (m, 3H), 7.44-7.38 (m, 2H), 7.25-7.23 (m, 1H), 6.93 (s, 2H), 5.18 (s, 1H), 5.04 (s, 1H), 4.55 (s, 2H), 1.32 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.9, 152.5, 147.2, 135.9, 134.9, 131.3, 130.9, 129.2, 128.4, 127.0, 125.0, 123.9, 123.6, 120.3, 116.6, 116.0, 63.0, 38.2, 34.2, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{28}H_{31}N_2O_2$) requires m/z 427.2380, found m/z 427.2386. The enantiomeric ratio was determined to be 95:5 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 22.7 min (minor), 24.6 min (major).

(*S*)-2-amino-4-(4-hydroxy-3,5-diisopropylphenyl)-4*H*-chromene-3-carbonitrile (3k)



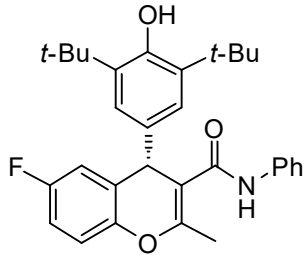
Yellow solid, 99% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.20-7.17 (m, 1H), 7.04-6.99 (m, 3H), 6.82 (s, 2H), 4.67 (s, 1H), 4.57 (s, 2H), 3.12-3.06 (m, 2H), 1.24 (d, *J* = 5.0 Hz, 6H), 1.20 (d, *J* = 5.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.1, 149.2, 148.6, 136.5, 133.8, 129.6, 127.9, 124.9, 123.4, 122.9, 120.0, 116.1, 61.3, 40.6, 27.3, 22.7. HRMS (ESI): exact mass calculated for M^+ ($C_{22}H_{25}N_2O_2$) requires m/z 349.1916, found m/z 349.1919. The enantiomeric ratio was determined to be 93:7 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 96:4, 0.8 mL/min]: 73.7 min (minor), 80.6 min (major).

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6aa)



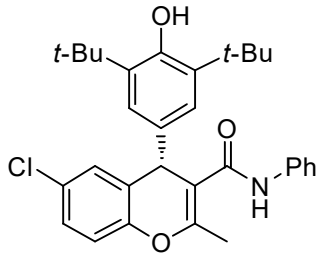
White solid, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24-7.17 (m, 4H), 7.15 (s, 2H), 7.14-7.06 (m, 3H), 7.05-6.99 (m, 3H), 5.22 (s, 1H), 4.75 (s, 1H), 2.41 (s, 3H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.5, 155.8, 153.3, 149.4, 138.1, 137.1, 136.0, 128.9, 128.9, 127.5, 124.5, 124.1, 124.1, 123.9, 119.3, 116.3, 109.1, 42.8, 34.4, 30.2, 18.7. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{36}NO_3$) requires m/z 470.2695, found m/z 470.2691. The enantiomeric ratio was determined to be 94:6 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 9.9 min (major), 15.7 min (minor).

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ba)



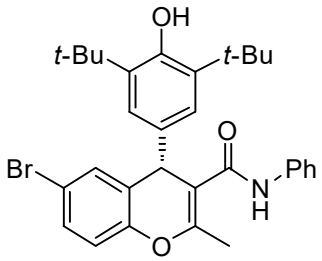
Yellow solid, 89% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24-7.22 (m, 2H), 7.18-7.17 (m, 2H), 7.12 (s, 2H), 7.05-7.02 (m, 2H), 6.99-6.97 (m, 1H), 6.87-6.83 (m, 1H), 6.76-6.74 (m, 1H), 5.25 (s, 1H), 4.71 (s, 1H), 2.39 (s, 3H), 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.3, 158.8 (d, *J* = 965.0 Hz), 155.6, 153.5, 145.5, 138.0, 137.3, 135.5, 128.9, 125.8 (d, *J* = 30.0 Hz), 124.1, 124.0, 119.3, 117.6 (d, *J* = 30.0 Hz), 114.8 (d, *J* = 95.0 Hz), 114.6 (d, *J* = 95.0 Hz), 108.4, 42.9, 34.4, 30.2, 18.6. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{35}FNO_3$) requires m/z 488.2601, found m/z 488.2595. The enantiomeric ratio was determined to be 95:5 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 10.0 min (major), 15.6 min (minor).

(*S*)-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ca)



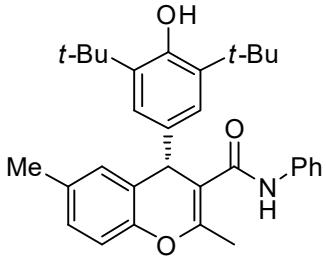
White solid, 73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24-7.22 (m, 2H), 7.18-7.17 (m, 2H), 7.11-7.10 (m, 3H), 7.05-7.03 (m, 3H), 6.97-6.95 (m, 1H), 5.25 (s, 1H), 4.68 (s, 1H), 2.38 (s, 3H), 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.1, 155.3, 153.6, 148.0, 137.9, 137.3, 135.4, 128.9, 128.6, 127.7, 126.0, 124.1, 124.0, 119.3, 117.8, 110.0, 109.1, 42.7, 34.4, 30.2, 18.5. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{35}ClNO_3$) requires m/z 504.2305, found m/z 504.2300. The enantiomeric ratio was determined to be 95:5 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 9.6 min (major), 14.9 min (minor).

(*S*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6da)



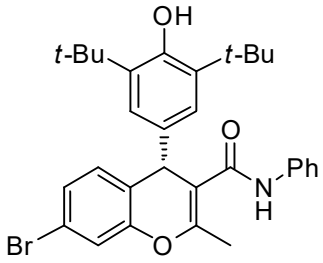
Yellow solid, 73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24-7.22 (m, 2H), 7.19-7.17 (m, 3H), 7.11 (s, 2H), 7.05-7.03 (m, 2H), 6.92-6.90 (m, 1H), 5.26 (s, 1H), 4.68 (s, 1H), 2.38 (s, 3H), 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.1, 155.2, 153.6, 148.6, 137.9, 137.3, 135.4, 131.5, 130.6, 128.9, 126.5, 124.1, 124.0, 119.4, 118.2, 116.2, 109.3, 42.6, 34.4, 30.2, 18.5. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{35}BrNO_3$) requires m/z 548.1800, found m/z 548.1795. The enantiomeric ratio was determined to be 95:5 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 10.2 min (major), 15.6 min (minor).

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,6-dimethyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ea)



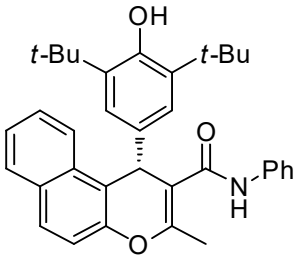
White solid, 99% yield. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 7.24-7.18 (m, 4H), 7.15 (s, 2H), 7.10 (s, 1H), 7.04-7.03 (m, 1H), 6.95-6.90 (m, 2H), 6.86 (s, 1H), 5.22 (s, 1H), 4.68 (s, 1H), 2.40 (s, 3H), 2.24 (s, 3H), 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.6, 156.1, 153.3, 147.4, 138.2, 137.1, 136.2, 133.5, 128.9, 128.9, 128.2, 124.1, 123.8, 119.3, 116.0, 109.1, 42.9, 34.4, 30.2, 20.8, 18.7. HRMS (ESI): exact mass calculated for M^+ ($C_{32}H_{38}NO_3$) requires m/z 484.2852, found m/z 484.2849. The enantiomeric ratio was determined to be 96:4 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 8.8 min (major), 17.2 min (minor).

(*S*)-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6fa)



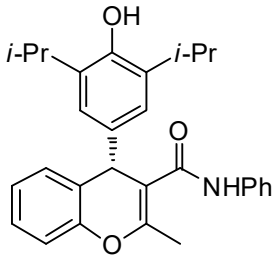
White solid, 86% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24-7.22 (m, 2H), 7.20-7.16 (m, 3H), 7.13-7.11 (m, 3H), 7.05-7.02 (m, 2H), 6.95-6.93 (m, 1H), 5.23 (s, 1H), 4.70 (s, 1H), 2.38 (s, 3H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.1, 155.0, 153.5, 150.0, 137.9, 137.3, 135.5, 130.2, 128.9, 128.2, 127.2, 124.0, 123.5, 120.3, 119.5, 119.4, 109.5, 42.4, 34.4, 30.2, 18.5. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{35}BrNO_3$) requires m/z 548.1800, found m/z 548.1795. The enantiomeric ratio was determined to be 93:7 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 13.1 min (minor), 17.1 min (major).

(*S*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-methyl-*N*-phenyl-1*H*-benzo[*f*] chromene-2-carboxamide (6ga)



White solid, 68% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.03-8.01 (m, 1H), 7.80-7.78 (m, 1H), 7.72-7.71 (m, 1H), 7.47-7.44 (m, 1H), 7.42-7.27 (m, 7H), 7.24 (s, 2H), 7.11-7.07 (m, 1H), 5.34 (s, 1H), 5.13 (s, 1H), 2.40 (s, 3H), 1.35 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.8, 154.0, 153.0, 147.9, 138.1, 136.6, 135.3, 131.2, 129.0, 128.6, 128.6, 126.5, 124.5, 124.3, 124.0, 123.0, 119.4, 117.4, 111.2, 39.6, 34.3, 30.2, 18.3. HRMS (ESI): exact mass calculated for M^+ ($C_{35}H_{38}NO_3$) requires m/z 520.2852, found m/z 520.2847. The enantiomeric ratio was determined to be 77:23 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 10.8 min (major), 32.3 min (minor).

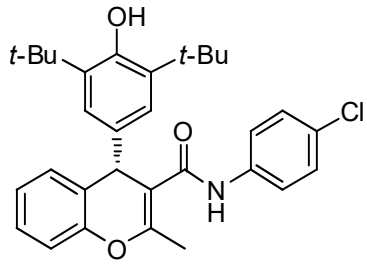
(*S*)-4-(4-hydroxy-3,5-diisopropylphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ha)



White solid, 69% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.25-7.19 (m, 4H), 7.16-7.11 (m, 2H), 7.06-6.96 (m, 6H), 4.83 (s, 1H), 4.79 (s, 1H), 3.15-3.09 (m, 2H), 2.42 (s, 3H), 1.25 (d, J = 5.0 Hz, 6H), 1.29 (d, J = 5.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.5, 155.6, 149.6, 149.3, 138.0, 137.3, 134.9, 128.9, 128.8, 127.5, 124.4, 124.1, 123.9, 122.6, 119.5, 116.3, 109.0, 42.6, 27.4, 22.7, 18.7. HRMS (ESI): exact mass calculated for M^+ ($C_{29}H_{32}NO_3$) requires m/z 442.2382, found m/z 442.2377. The enantiomeric ratio was determined to be 96:4 by HPLC. [IA column, 254 nm, n-hexane:EtOH = 95:5, 0.8 mL/min]: 20.3 min (major), 25.4 min (minor).

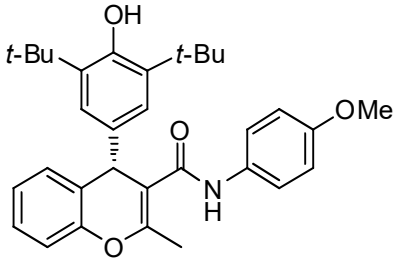
(*S*)-*N*-(4-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ab)

White solid, 97% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.20-7.18 (m, 2H), 7.15-6.95 (m, 9H), 5.22 (s, 1H), 4.73 (s, 1H), 2.40 (s, 3H), 1.40 (s, 18H). ^{13}C NMR



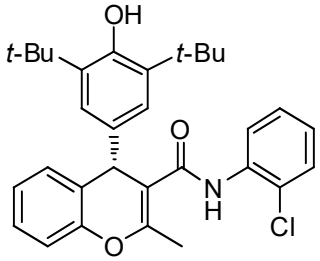
($CDCl_3$, 125 MHz): δ (ppm) 166.4, 156.3, 153.4, 149.3, 137.2, 136.7, 136.0, 128.9, 128.8, 128.7, 127.6, 124.3, 124.2, 124.1, 120.5, 116.3, 108.8, 42.7, 34.4, 30.2, 18.7. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{35}ClNO_3$) requires m/z 504.2305, found m/z 504.2300. The enantiomeric ratio was determined to be 96:4 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 9.9 min (major), 25.6 min (minor).

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-methoxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ac)



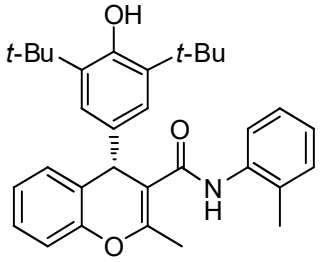
Yellow solid, 83% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.15-7.07 (m, 6H), 7.01-7.00 (m, 3H), 6.79-6.77 (m, 2H), 5.20 (s, 1H), 4.75 (s, 1H), 3.76 (s, 3H), 2.40 (s, 3H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.3, 156.1, 153.2, 149.5, 137.0, 136.1, 131.3, 128.9, 127.5, 124.5, 124.1, 124.0, 121.0, 116.3, 114.1, 109.2, 55.5, 42.7, 34.4, 30.2, 18.6. HRMS (ESI): exact mass calculated for M^+ ($C_{32}H_{38}NO_4$) requires m/z 500.2801, found m/z 500.2796. The enantiomeric ratio was determined to be 90:10 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 14.9 min (major), 40.3 min (minor).

(*S*)-*N*-(2-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ad)



White solid, 79% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.31-8.30 (m, 1H), 7.67 (s, 1H), 7.24-7.13 (m, 6H), 7.03-6.94 (m, 3H), 5.14 (s, 1H), 4.80 (s, 1H), 2.48 (s, 3H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.5, 157.8, 153.4, 149.3, 136.8, 135.2, 134.7, 128.9, 128.4, 127.4, 127.4, 124.3, 124.2, 123.9, 121.8, 116.3, 108.5, 42.5, 34.3, 30.1, 18.8. HRMS (ESI): exact mass calculated for M^+ ($C_{31}H_{35}ClNO_3$) requires m/z 504.2305, found m/z 504.2301. The enantiomeric ratio was determined to be 94:6 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 6.8 min (major), 10.9 min (minor).

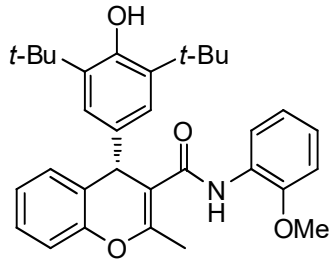
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-(*o*-tolyl)-4*H*-chromene-3-carboxamide (6ae)



White solid, 84% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.92-7.90 (m, 1H), 7.21-7.13 (m, 5H), 7.01-6.97 (m, 5H), 5.18 (s, 1H), 4.79 (s, 1H), 2.48 (s, 3H), 1.52 (s, 3H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.4, 157.2, 153.5, 149.3, 137.1, 136.2, 135.1, 130.2, 128.4,

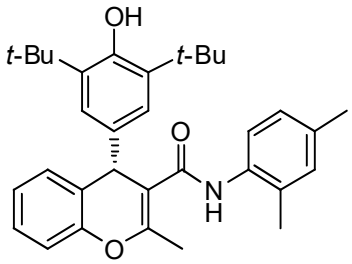
127.4, 126.6, 124.2, 123.8, 122.0, 116.4, 110.0, 108.4, 42.6, 34.4, 30.1, 18.7, 16.7. HRMS (ESI): exact mass calculated for M^+ ($C_{32}H_{38}NO_3$) requires m/z 484.2852, found m/z 484.2847. The enantiomeric ratio was determined to be 93:7 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 10.6 min (major), 21.1 min (minor).

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(2-methoxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6af)



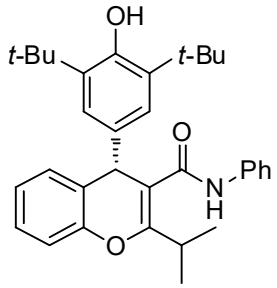
White solid, 80% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.29-8.27 (m, 1H), 7.68 (s, 1H), 7.17-7.13 (m, 4H), 7.02-6.91 (m, 4H), 6.76-6.75 (m, 1H), 5.13 (s, 1H), 4.83 (s, 1H), 3.57 (s, 3H), 2.41 (s, 3H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.5, 155.2, 152.9, 149.7, 148.1, 136.3, 135.1, 128.6, 127.8, 127.3, 125.1, 124.0, 123.9, 123.5, 120.9, 120.1, 116.2, 110.0, 109.7, 55.8, 42.5, 34.3, 30.2, 18.6. HRMS (ESI): exact mass calculated for M^+ ($C_{32}H_{38}NO_4$) requires m/z 500.2801, found m/z 500.2795. The enantiomeric ratio was determined to be 93:7 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 9.3 min (major), 17.3 min (minor).

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(2,4-dimethylphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ag)



White solid, 68% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.72-7.71 (m, 1H), 7.20-7.13 (m, 4H), 7.00-6.97 (m, 3H), 6.90 (s, 1H), 6.84 (s, 1H), 5.17 (s, 1H), 4.79 (s, 1H), 2.46 (s, 3H), 2.24 (s, 3H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.4, 156.8, 153.5, 149.4, 137.0, 135.2, 134.0, 133.5, 130.8, 128.4, 127.7, 127.4, 127.1, 125.0, 124.1, 123.8, 122.3, 116.3, 108.5, 42.6, 34.4, 30.1, 20.8, 18.7, 16.7. HRMS (ESI): exact mass calculated for M^+ ($C_{33}H_{40}NO_3$) requires m/z 498.3008, found m/z 498.3002. The enantiomeric ratio was determined to be 96:4 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 14.9 min (major), 31.1 min (minor).

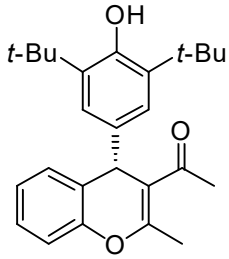
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-isopropyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ah)



Yellow solid, 74% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.23-7.14 (m, 7H), 7.11-7.10 (m, 1H), 7.06-6.99 (m, 4H), 5.22 (s, 1H), 4.69 (s, 1H), 3.60-3.55 (m, 1H), 1.41 (s, 18H) 1.33-1.30 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.4, 162.6, 153.3, 149.7, 138.2, 137.2, 136.2, 128.9, 128.6, 127.4, 124.9, 124.0, 123.9, 123.8, 119.2, 116.3, 108.0, 43.1,

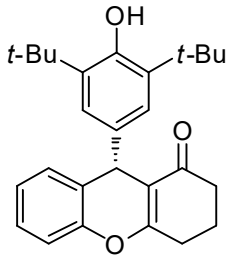
34.5, 30.3, 30.1, 20.3, 19.8. HRMS (ESI): exact mass calculated for M^+ ($C_{33}H_{40}NO_3$) requires m/z 498.3008, found m/z 498.3002. The enantiomeric ratio was determined to be 99:1 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 8.0 min (minor), 9.6 min (major).

(*S*)-1-(4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromen-3-yl) ethanone (6ai)



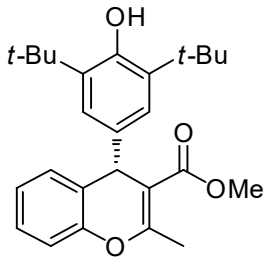
Yellow solid, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.17-7.12 (m, 2H), 7.03-7.00 (m, 4H), 5.05 (s, 1H), 4.90 (s, 1H), 2.45 (s, 3H), 2.18 (s, 3H), 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 199.2, 159.1, 152.5, 149.3, 136.3, 136.0, 128.8, 127.3, 125.8, 124.4, 123.9, 116.2, 114.6, 42.1, 34.3, 30.3, 30.0, 20.0. HRMS (ESI): exact mass calculated for M^+ ($C_{26}H_{33}O_3$) requires m/z 393.2430, found m/z 393.2425. The enantiomeric ratio was determined to be 95:5 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 5.1 min (major), 5.6 min (minor).

(*S*)-9-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (6aj)



Yellow solid, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.19-7.15 (m, 2H), 7.07-7.04 (m, 2H), 7.00 (s, 2H), 5.02 (s, 1H), 5.01 (s, 1H), 2.75-2.61 (m, 2H), 2.48-2.34 (m, 2H), 2.09-2.05 (m, 2H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 197.0, 166.5, 152.2, 149.8, 136.6, 135.4, 129.8, 127.2, 126.3, 124.9, 124.2, 116.3, 115.3, 37.1, 37.0, 34.3, 30.3, 27.9, 20.5. HRMS (ESI): exact mass calculated for M^+ ($C_{27}H_{33}O_3$) requires m/z 405.2430, found m/z 405.2424. The enantiomeric ratio was determined to be 93:7 by HPLC. [IA column, 254 nm, n-hexane:IPA = 95:5, 0.8 mL/min]: 10.5 min (major), 12.3 min (minor).

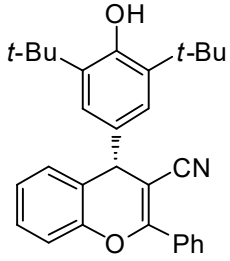
(*S*)-methyl 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxylate (6ak)



Yellow solid, 53% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.17-7.10 (m, 2H), 7.04-7.00 (m, 2H), 6.97 (s, 2H), 5.02 (s, 1H), 4.96 (s, 1H), 3.70 (s, 3H), 2.47 (s, 3H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 167.8, 160.3, 152.2, 150.0, 137.1, 135.4, 129.1, 127.2, 125.7, 124.5, 124.2, 116.0, 106.9, 51.2, 41.0, 34.2, 30.3, 19.5. HRMS (ESI): exact mass calculated for M^+ ($C_{26}H_{33}O_4$) requires m/z 409.2379, found m/z 409.2374. The enantiomeric ratio was determined to be 90:10 by HPLC. [IA column, 254 nm, n-hexane:IPA = 9:1, 0.8 mL/min]: 5.2 min (major), 5.9 min (minor).

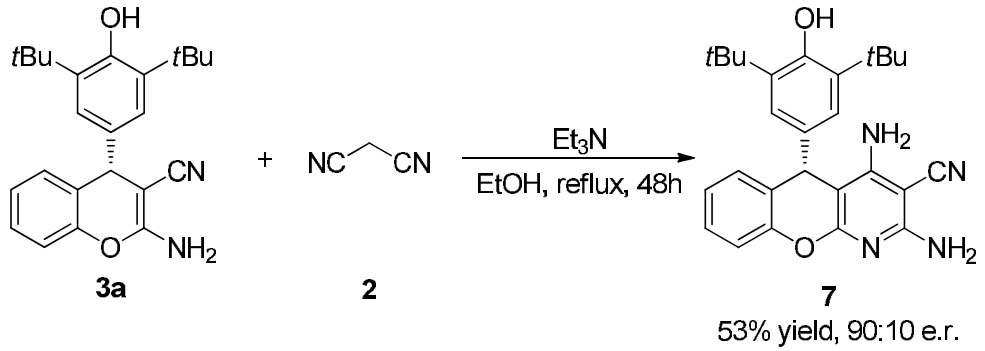
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenyl-4*H*-chromene-3-carbonitrile

(6al)



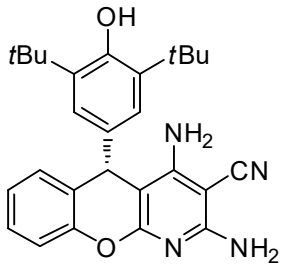
Yellow solid, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.89-7.88 (m, 2H), 7.50-7.49 (m, 3H), 7.26-7.24 (m, 1H), 7.17-7.16 (m, 1H), 7.11-7.10 (m, 2H), 7.04 (s, 2H), 5.16 (s, 1H), 4.81 (s, 1H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 160.0, 153.2, 149.5, 136.2, 134.4, 132.0, 131.0, 129.4, 128.5, 128.2, 128.1, 125.3, 124.5, 122.4, 119.2, 116.7, 89.1, 43.0, 34.3, 30.2. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{32}NO_2$) requires m/z 438.2433, found m/z 438.2434. The enantiomeric ratio was determined to be >99:1 by HPLC. [IA column, 254 nm, n-hexane:IPA = 95:5, 0.8 mL/min]: 7.8 min (major), 8.3 min (minor).

E: The Synthetic Transformations



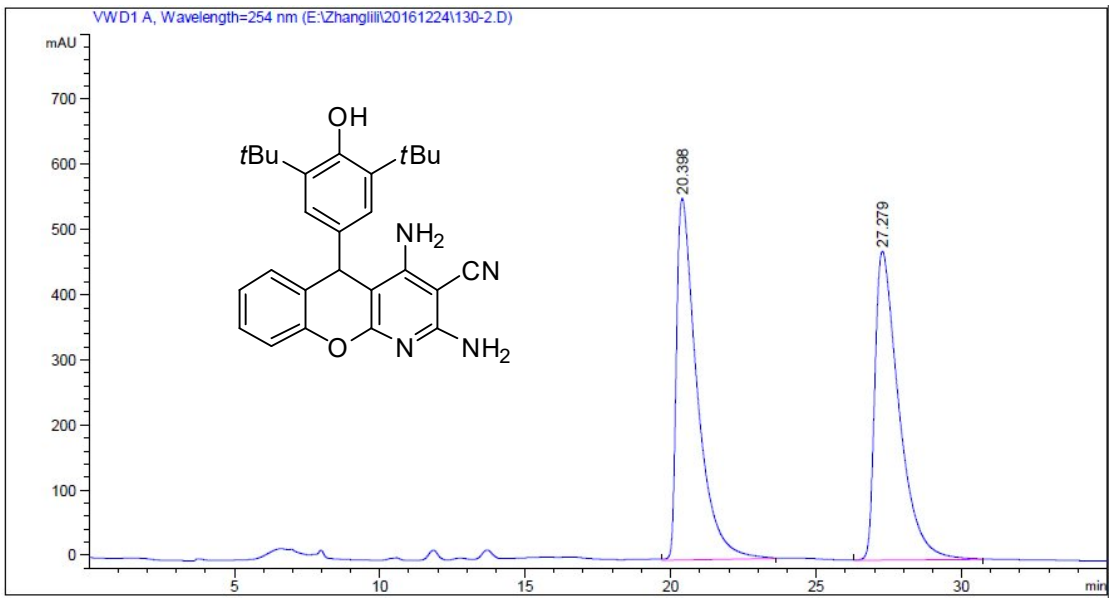
To a solution of **3a** (64.0 mg, 0.17 mmol) and malononitrile **2** (22.0 mg, 0.17 mmol) in 4.0 mL of ethanol was added Et_3N (0.05 mmol) dropwise at room temperature. The resulting mixture was refluxed for 48h and then allowed to cool to room temperature. The solvent was removed under vacuum and the residue was purified by silica gel chromatography to afford the desired product **7** as a yellow solid (39.4 mg, 53% yield, 90:10 e.r.).

(*S*)-2,4-diamino-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5*H*-chromeno[2,3-*b*] pyridine-3-carbonitrile (7)

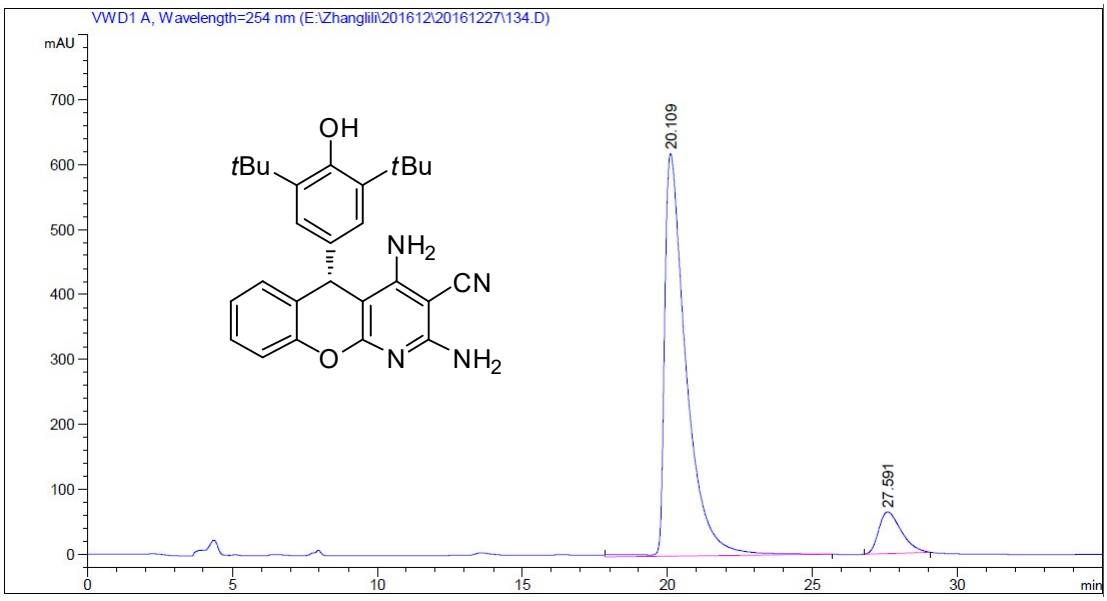


Yellow solid, 53% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.19-7.16 (m, 1H), 7.13-7.08 (m, 2H), 7.03-6.99 (m, 3H), 5.17 (s, 1H), 5.02 (s, 2H), 4.87 (s, 1H), 4.74 (s, 2H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.2, 158.7, 156.7, 153.3, 149.3, 137.0, 134.8, 129.2, 128.0, 124.3, 123.9, 123.8, 117.2, 116.1, 92.4, 73.0, 40.6, 34.4, 30.3. HRMS (ESI): exact mass calculated for M^+ ($C_{27}H_{31}N_4O_2$) requires m/z 443.2447, found m/z 443.2451. The enantiomeric ratio was determined to be 90:10 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 93:7, 0.8 mL/min]: 27.6 min (minor), 20.1 min (major).

(*S*)-2,4-diamino-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5*H*-chromeno[2,3-*b*] pyridine-3-carbonitrile (7)

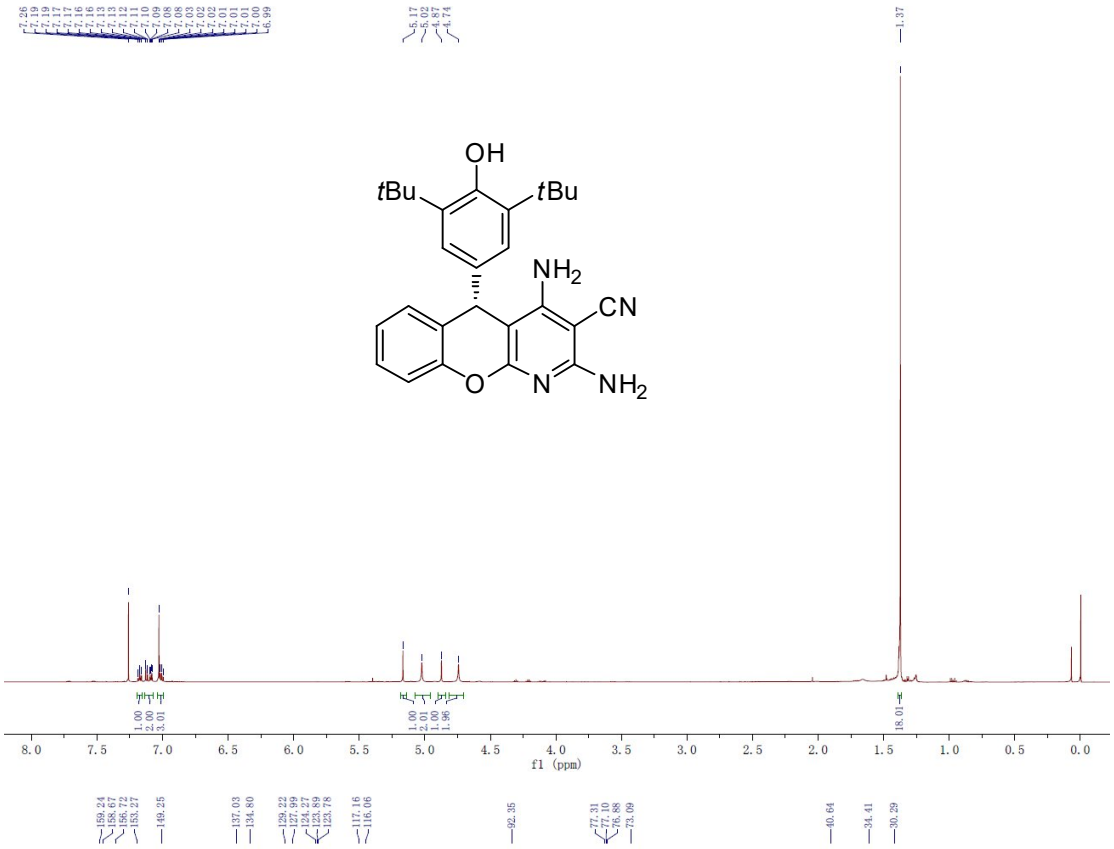


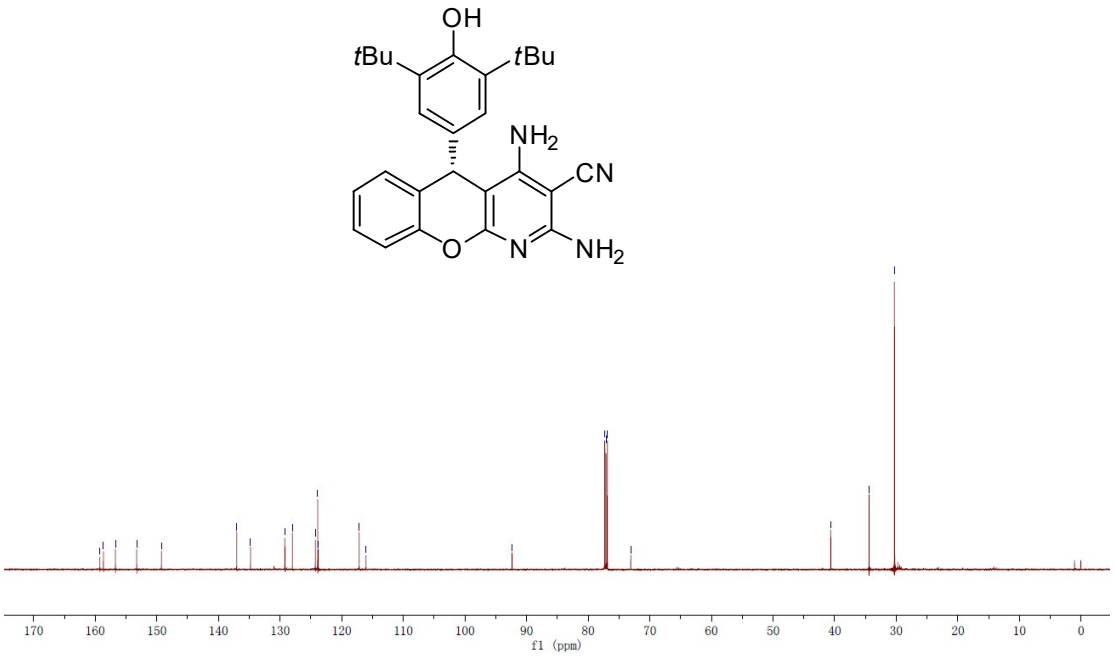
#	Time	Area	Height	Width	Symmetry	Area %
1	20.398	27396.6	555.2	0.8225	0.369	50.099
2	27.279	27288.1	474.3	0.9589	0.431	49.901

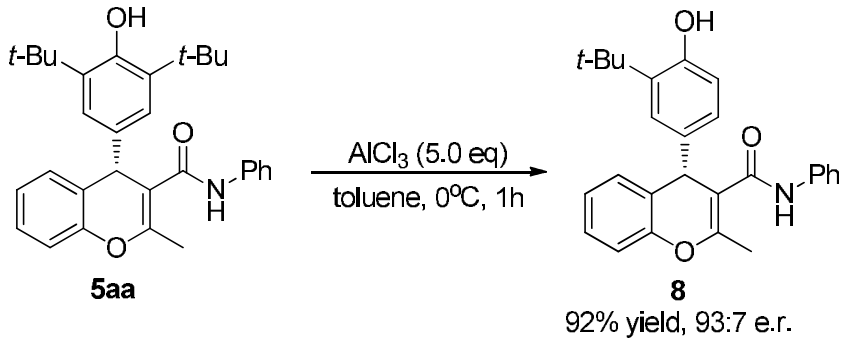


#	Time	Area	Height	Width	Symmetry	Area %
1	20.109	31886.7	619.6	0.8577	0.375	90.184
2	27.591	3470.7	64	0.9041	0.624	9.816

(*S*)-2,4-diamino-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5*H*-chromeno[2,3-*b*] pyridine-3-carbonitrile (7)

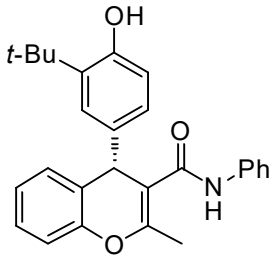






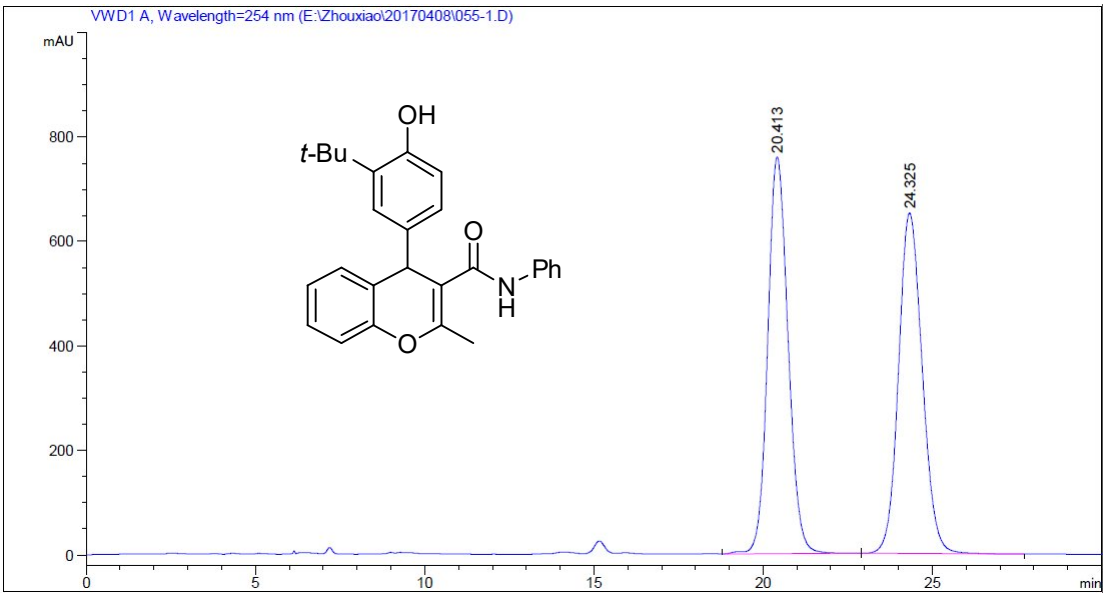
To a solution of compound **5aa** (17.6 mg, 0.038 mol) in dry toluene (1.5 mL) was added $AlCl_3$ (25.27 mg, 5.0 eq) at 0°C and the reaction mixture was stirred at 0°C for 1h. Then the solvent was concentrated under reduced pressure to give a residue, which was purified by flash column chromatography on silica gel to afford the product **8** as a white solid (14.5 mg, 92% yield, 93:7 e.r.).

(*S*)-4-(3-(*tert*-butyl)-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (8)

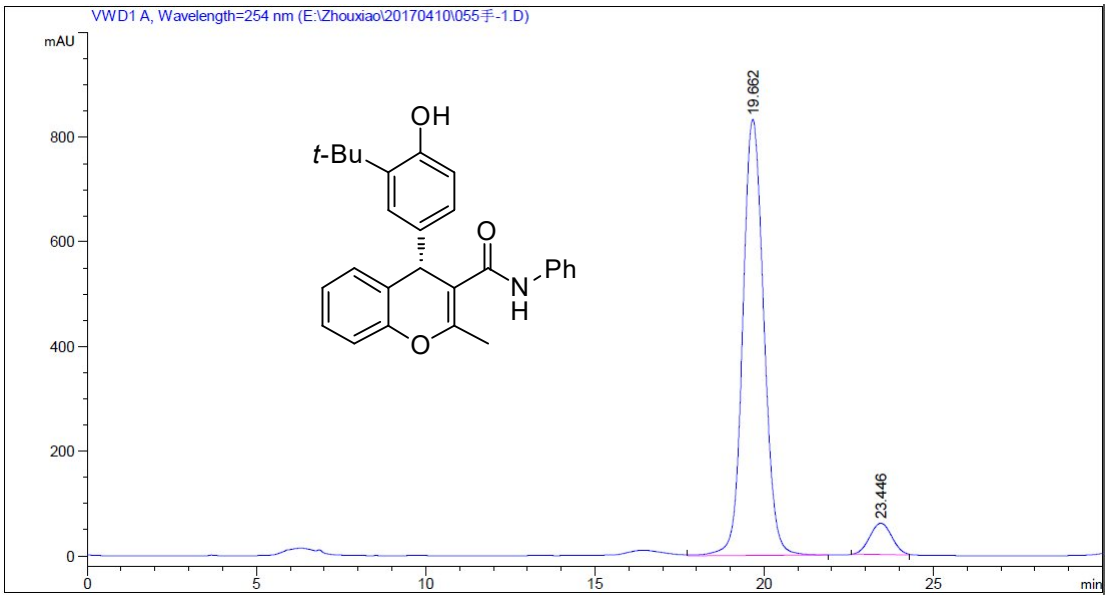


White solid, 92% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27-7.26 (m, 1H), 7.24-7.21 (m, 4H), 7.16-7.13 (m, 2H), 7.06-6.95 (m, 5H), 6.63-6.62 (m, 1H), 5.38 (s, 1H), 4.79 (s, 1H), 2.38 (s, 3H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.7, 155.2, 153.9, 149.3, 137.9, 137.1, 137.0, 128.9, 127.6, 126.2, 126.2, 124.2, 124.2, 124.1, 119.6, 117.8, 116.3, 110.0, 109.1, 42.3, 34.6, 29.5, 18.7. HRMS (ESI): exact mass calculated for M^+ ($C_{27}H_{28}NO_3$) requires m/z 414.2069, found m/z 414.2064. The enantiomeric ratio was determined to be 93:7 by HPLC. [IA column, 254 nm, n-hexane:IPA = 95:5, 0.8 mL/min]: 19.7 min (major), 23.4 min (minor).

(*S*)-4-(3-(*tert*-butyl)-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (8)

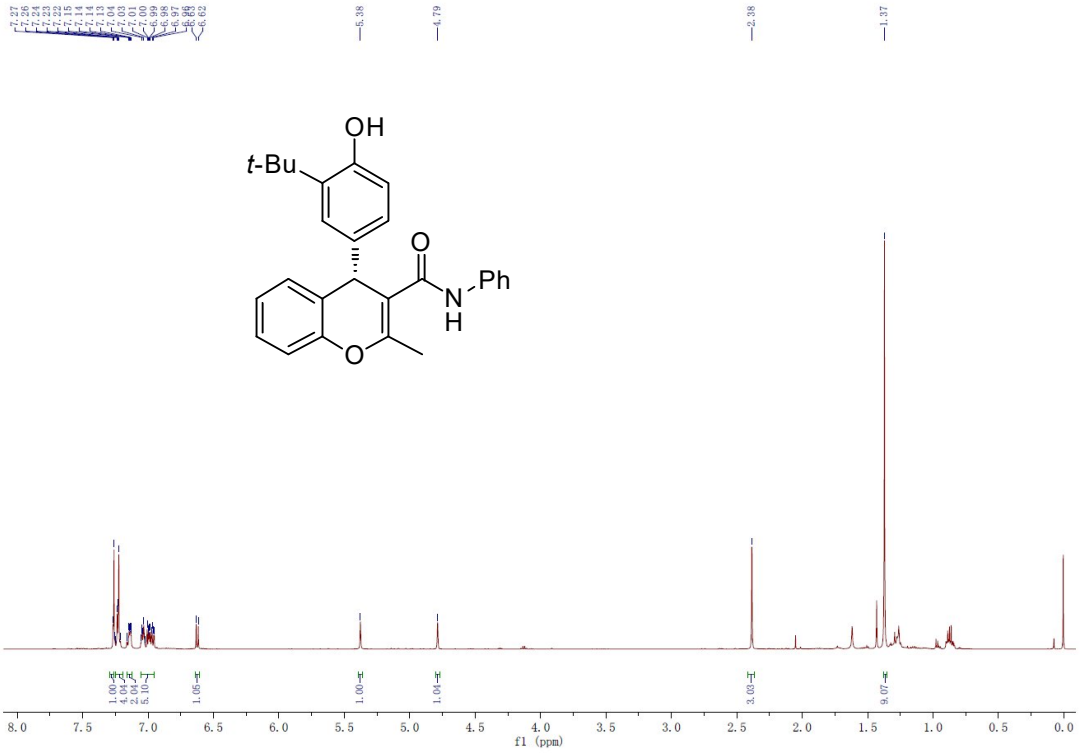


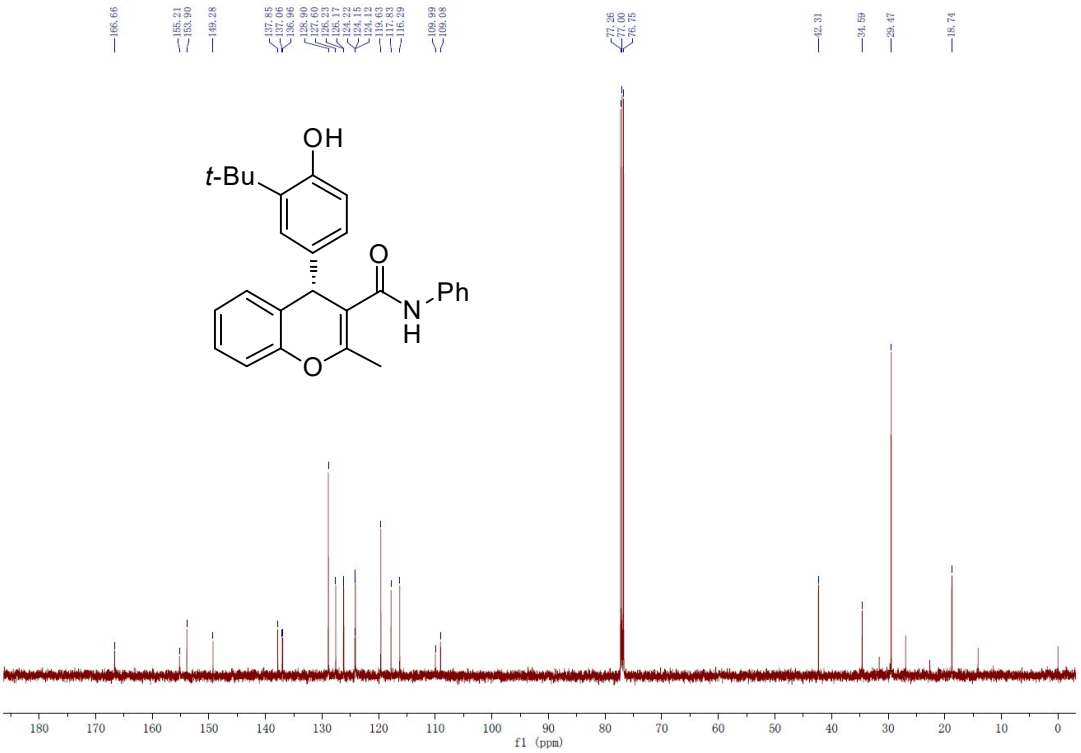
#	Time	Area	Height	Width	Symmetry	Area%
1	20.413	31761	759.6	0.6467	0.834	49.998
2	24.325	31763.2	652.3	0.7571	0.831	50.002



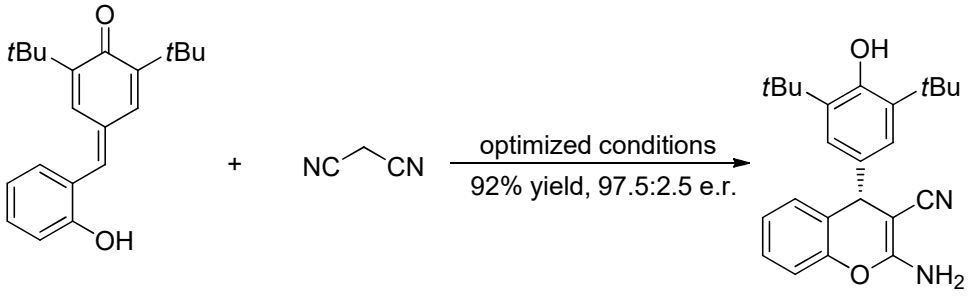
#	Time	Area	Height	Width	Symmetry	Area%
1	19.662	35930.5	833.3	0.7187	0.879	92.995
2	23.446	2706.7	59.8	0.7543	0.964	7.005

(*S*)-4-(3-(*tert*-butyl)-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (8)





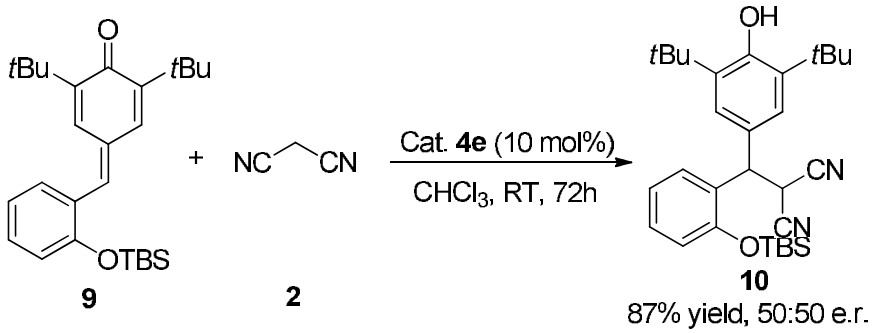
F: Gram Scale Reaction



1a 852.5 mg (2.75 mmol) + **2** 217.8 mg (3.30 mmol) → **3a** 920.0 mg

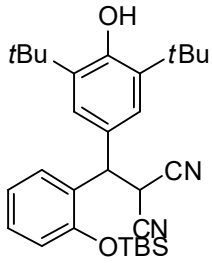
To a solution of $CHCl_3$ (50.0 mL) were added quinone methide **1a** (852.5 mg, 2.75 mmol), malononitrile **2** (217.8 mg, 3.3 mmol) and catalyst **4e** (88.0 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 48h. The solvent is evaporated to give the crude product, which is purified by silica gel chromatography to provide the desired product **3a** as a white solid (920.0 mg, 92% yield, 97.5:2.5 e.r.).

G: The Mechanistic Study



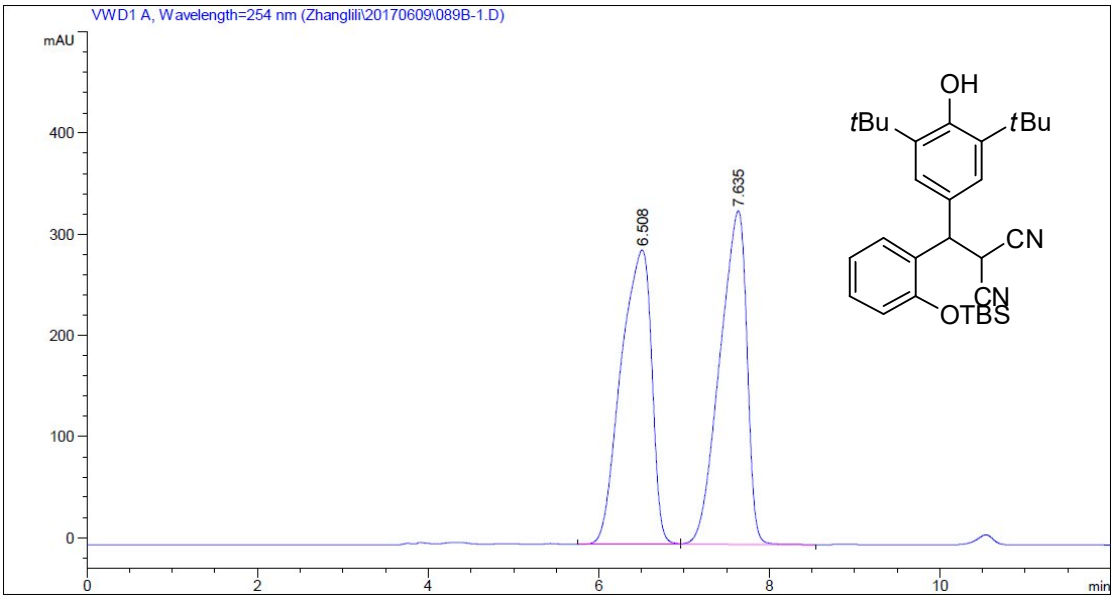
To a solution of $CHCl_3$ (0.3 mL) were added TBS-protected quinone methide **9** (21.2 mg, 0.05 mmol), malononitrile **2** (3.96 mg, 0.06 mmol) and catalyst **4e** (3.15 mg, 0.005 mmol). The reaction mixture was stirred at room temperature for 72h. The solvent is evaporated to give the crude product, which is directly purified by silica gel chromatography to provide the desired product **10** as a white solid (21.3 mg, 87% yield, 50:50 e.r.).

2-((2-((*tert*-Butyldimethylsilyl)oxy)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl) methyl)malononitrile (10)

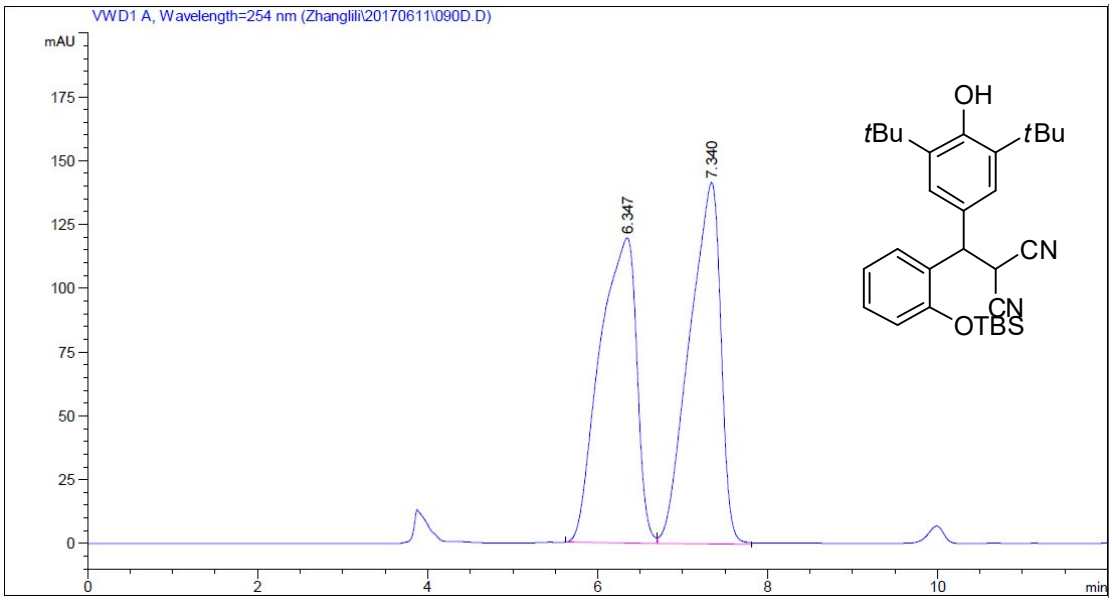


White solid, 87% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27-7.25 (m, 1H), 7.23-7.20 (m, 1H), 7.14 (s, 2H), 7.01-6.98 (m, 1H), 6.88 (d, J = 10.0 Hz, 1H), 5.24 (s, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.42 (d, J = 10.0 Hz, 1H), 1.41 (s, 18H), 0.99 (s, 9H), 0.31 (s, 3H), 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 153.7, 153.0, 136.2, 129.2, 128.4, 128.3, 127.1, 124.9, 121.5, 118.7, 112.6, 112.5, 44.9, 34.4, 30.1, 28.4, 25.9, 18.3, -3.9, -4.2. HRMS (ESI): exact mass calculated for M^+ ($C_{30}H_{43}N_2O_2Si$) requires m/z 491.3094, found m/z 491.3090. The enantiomeric ratio was determined to be 50:50 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 98:2, 0.8 mL/min]: 6.3 min, 7.3 min.

2-((2-((*tert*-Butyldimethylsilyl)oxy)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl) methyl)malononitrile (10)

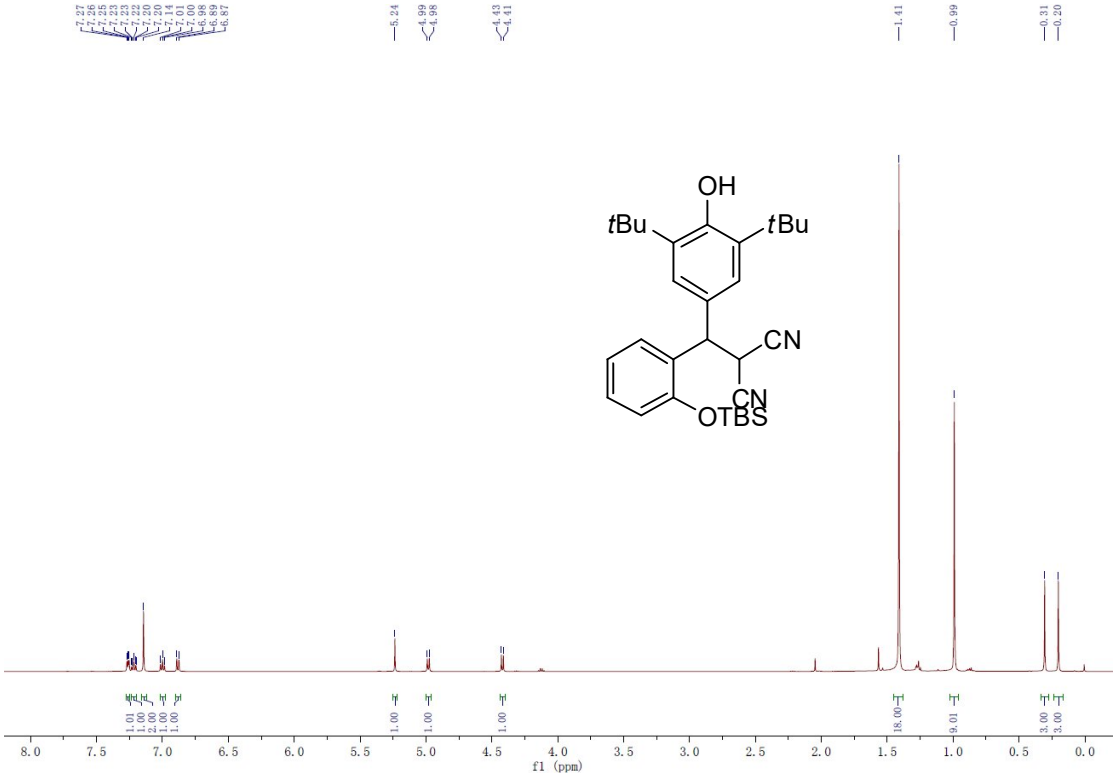


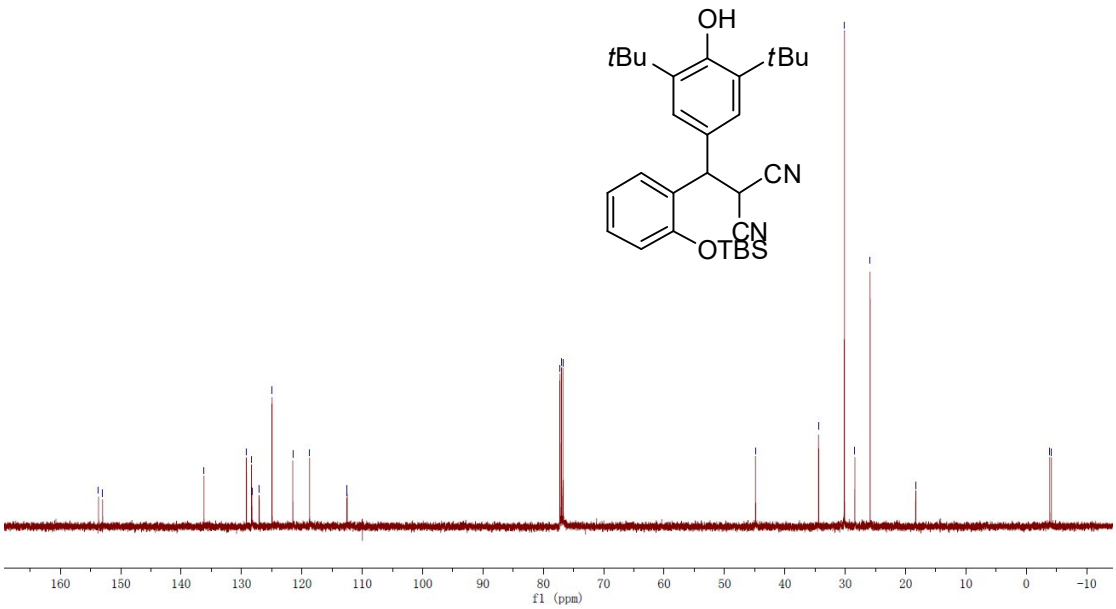
#	Time	Area	Height	Width	Symmetry	Area %
1	6.508	7281.9	291.1	0.4219	2.059	50.013
2	7.635	7278.1	329.9	0.3663	2.046	49.987



#	Time	Area	Height	Width	Symmetry	Area %
1	6.347	3607.6	119.4	0.5034	0	49.922
2	7.34	3618.9	141.5	0.4264	2.222	50.078

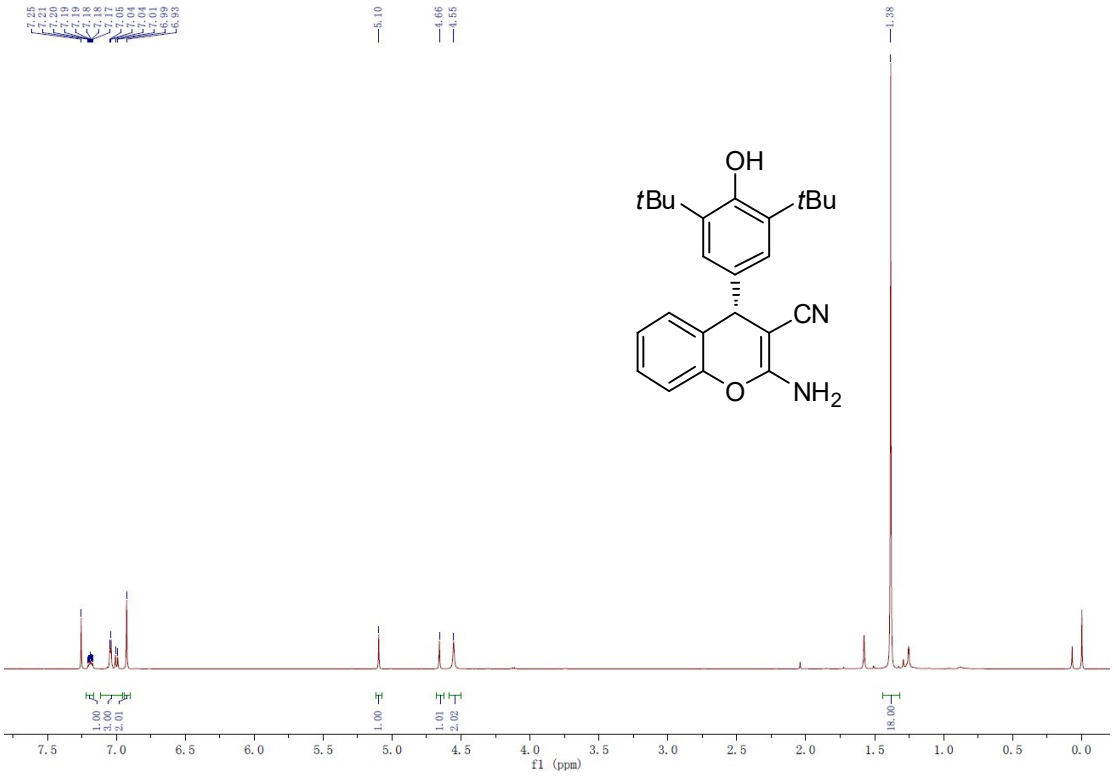
2-((2-((*tert*-Butyldimethylsilyl)oxy)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl) methyl)malononitrile (10)

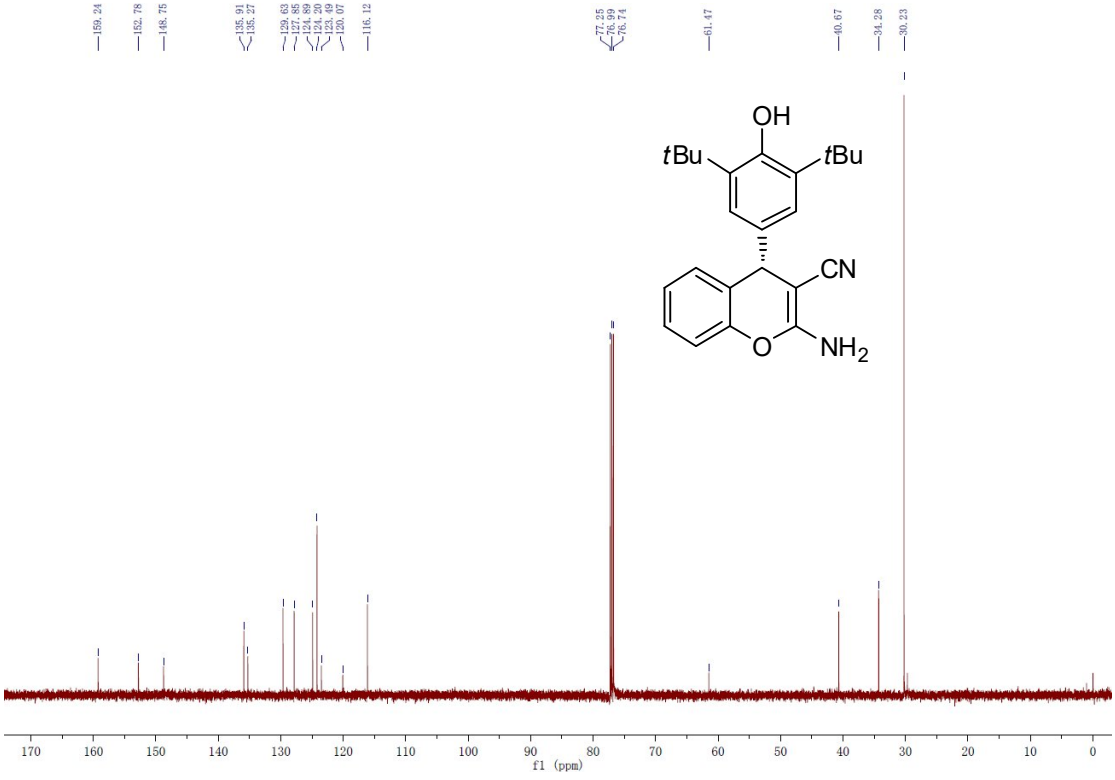




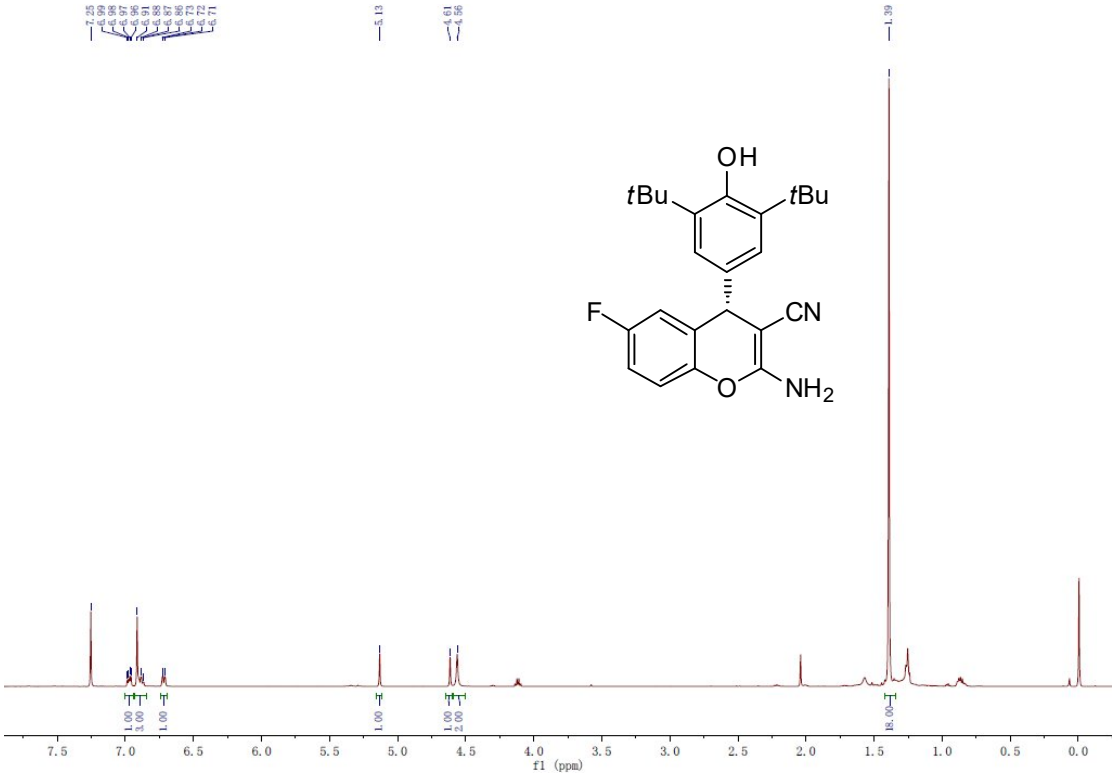
H: NMR Analysis

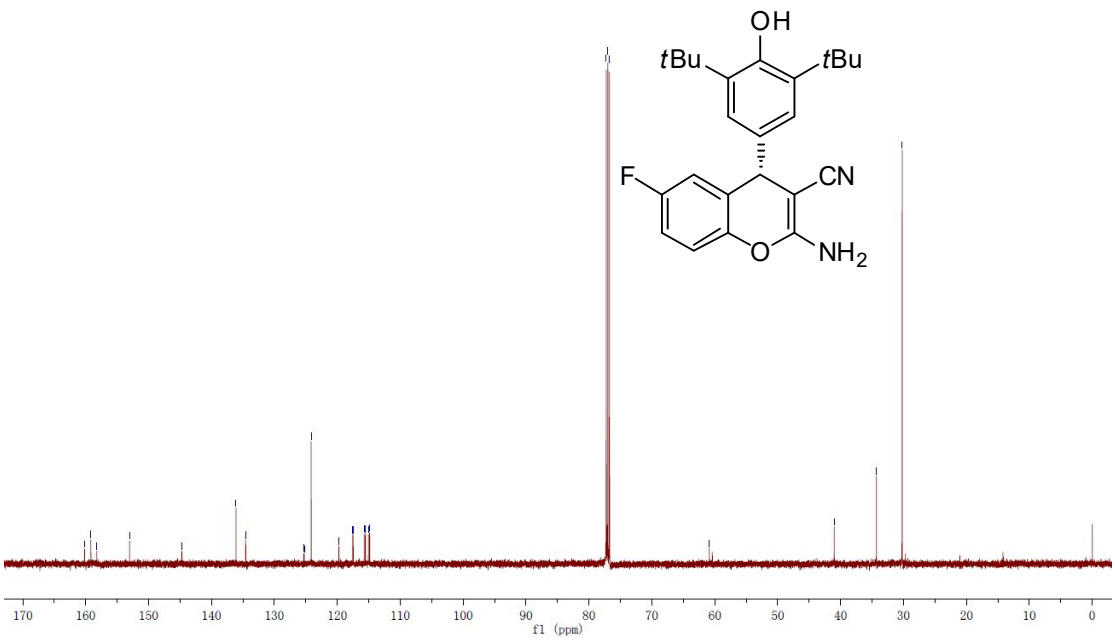
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3a)



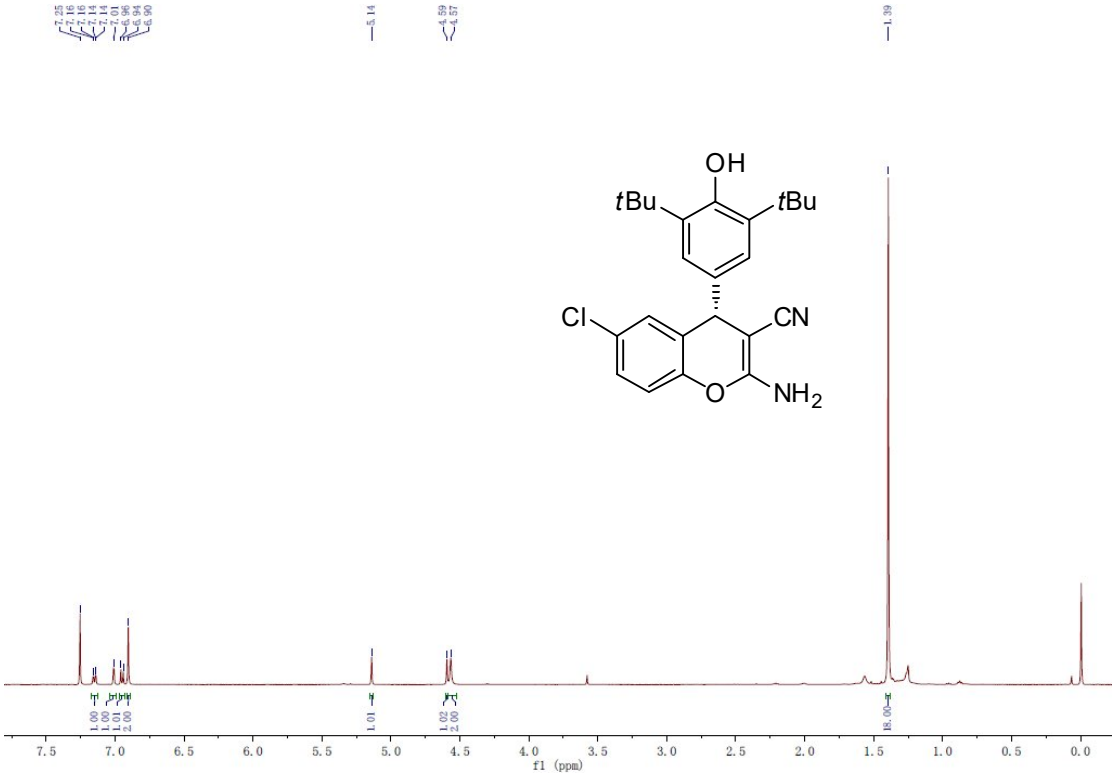


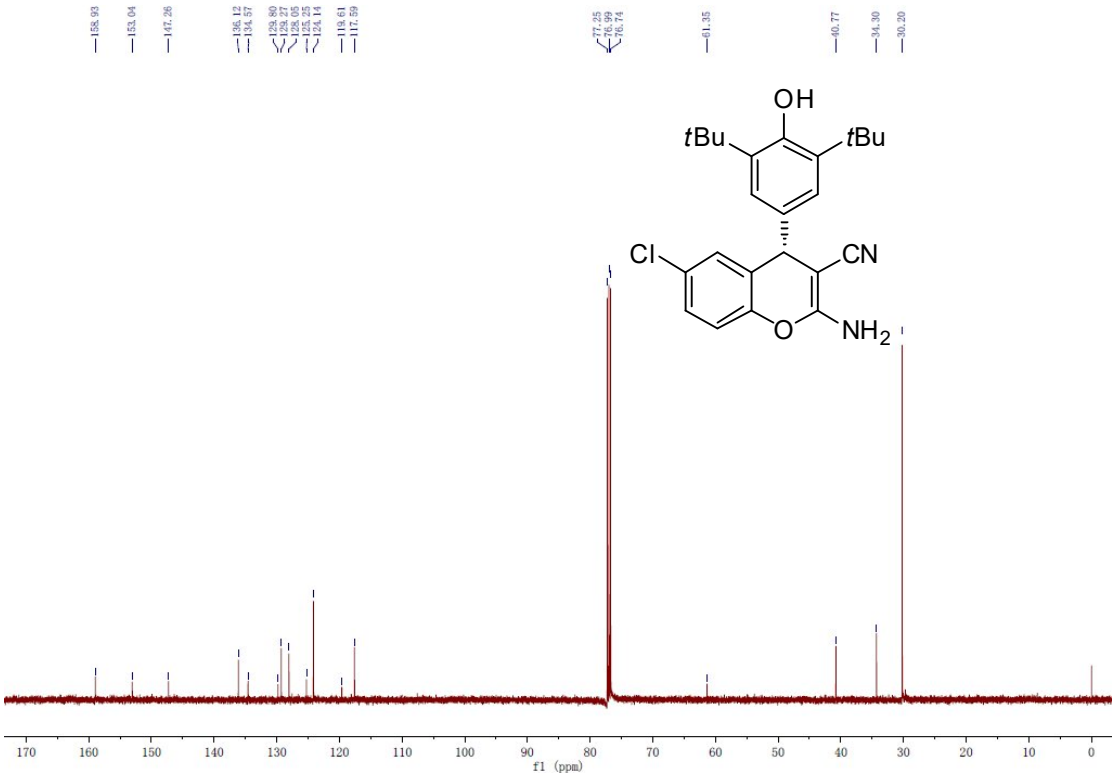
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-4*H*-chromene-3-carbonitrile (3b)



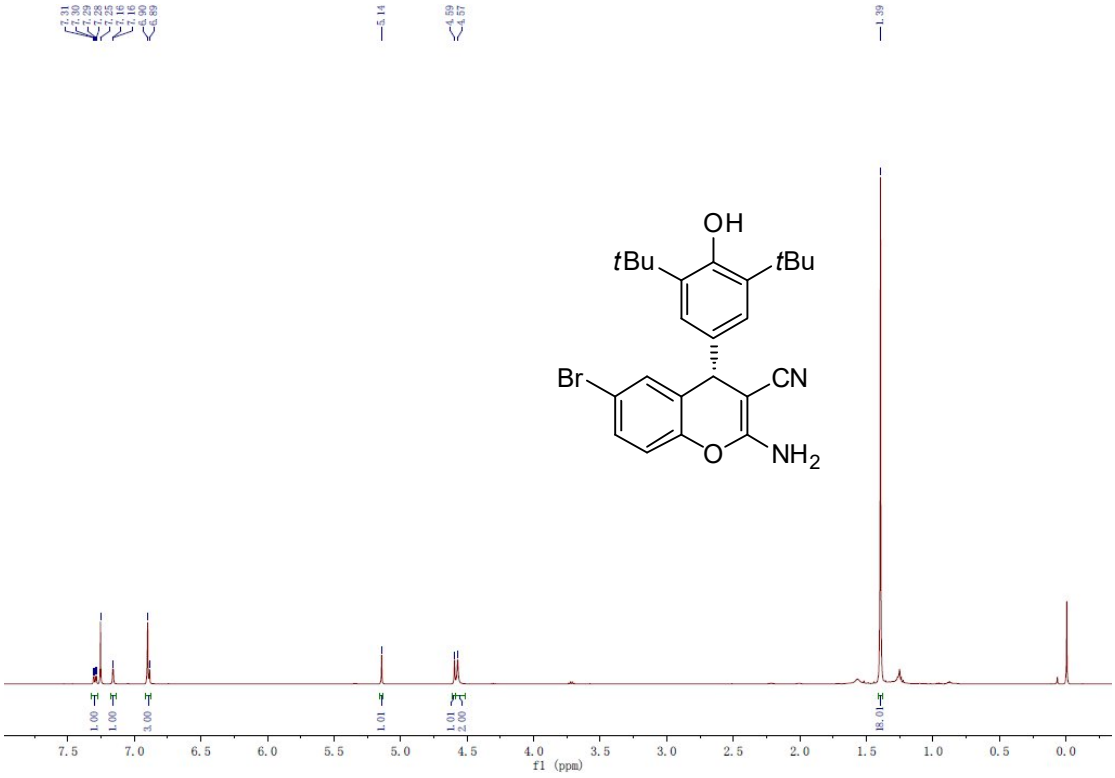


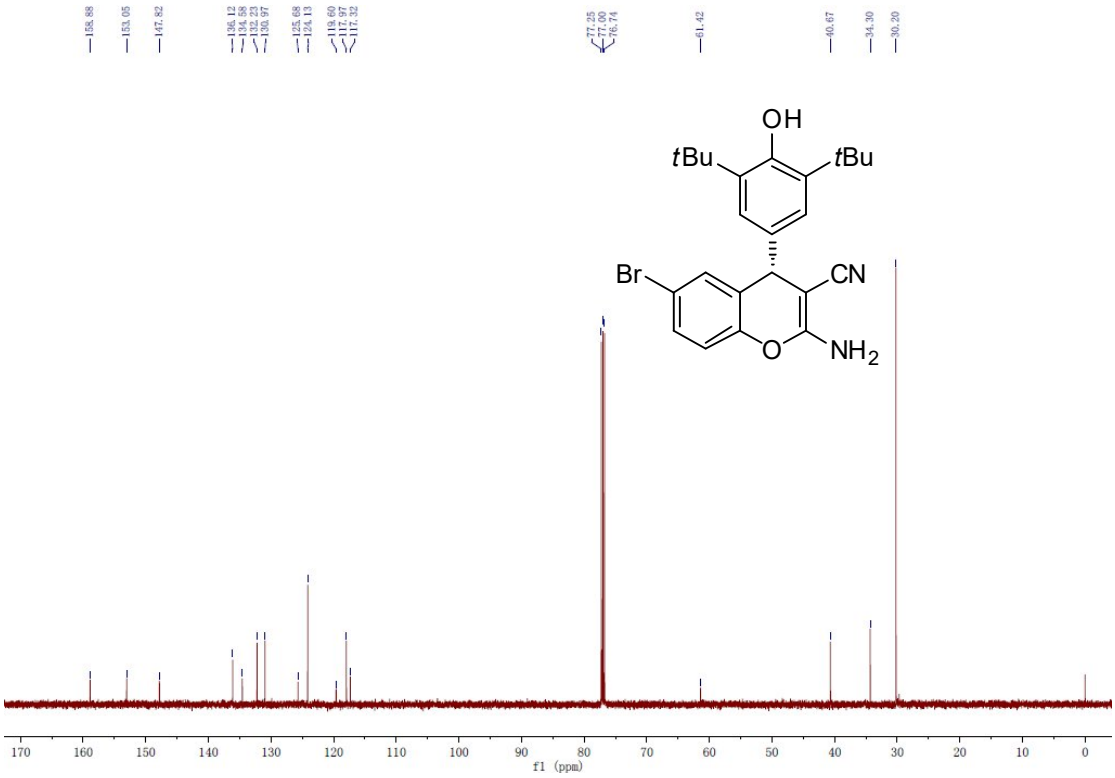
(*S*)-2-amino-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3c)





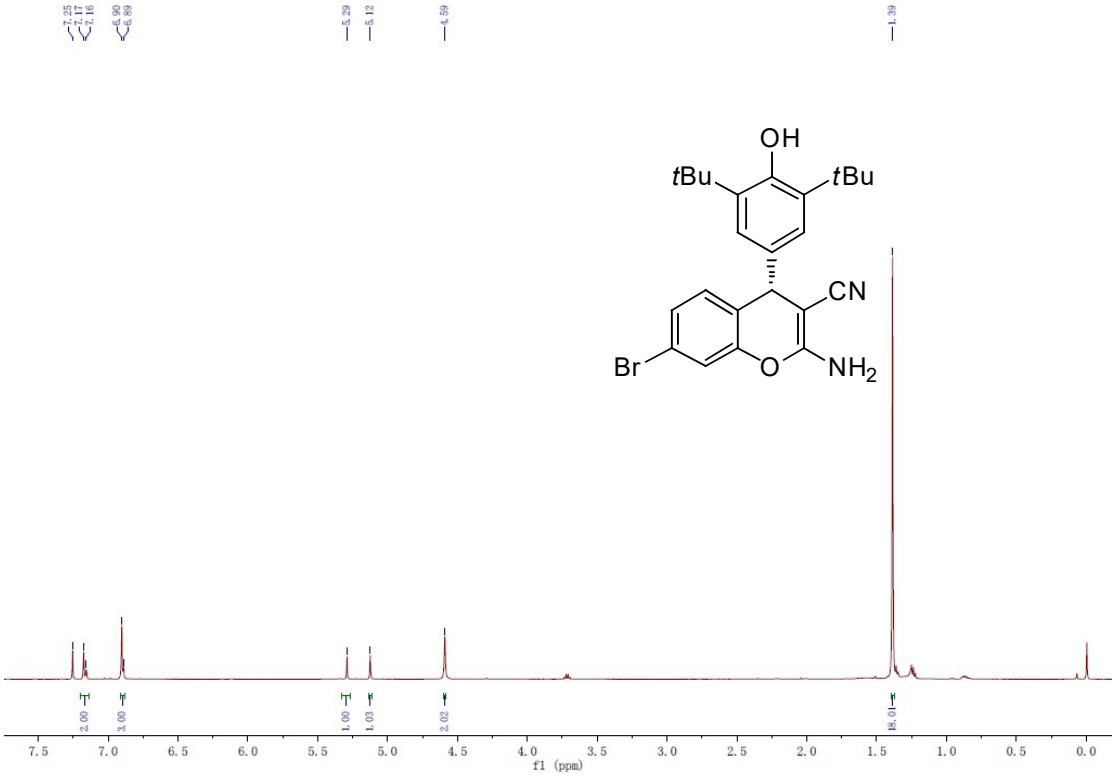
(*S*)-2-amino-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3d)

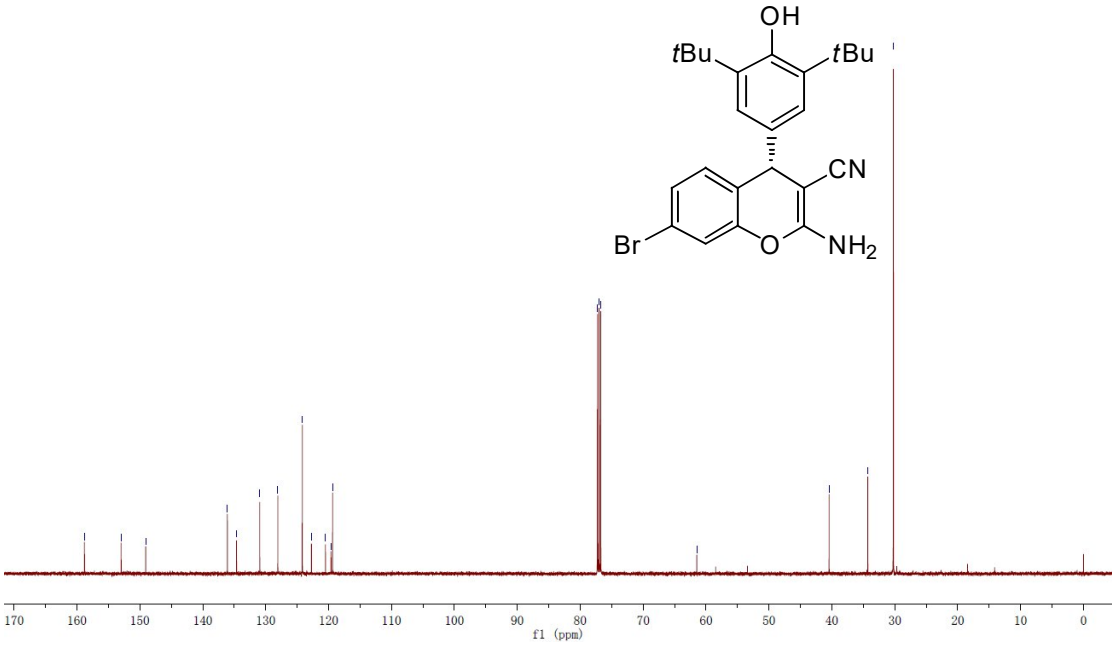




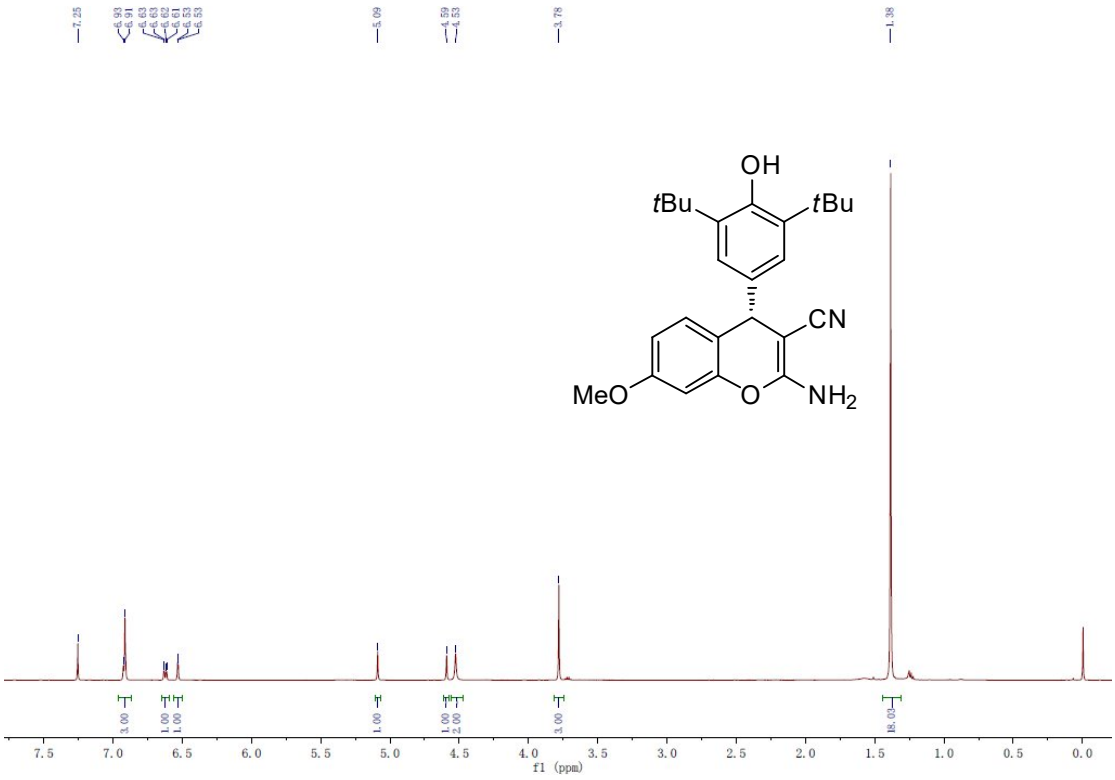
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-methyl-4*H*-chromene-3-carbonitrile (3e)

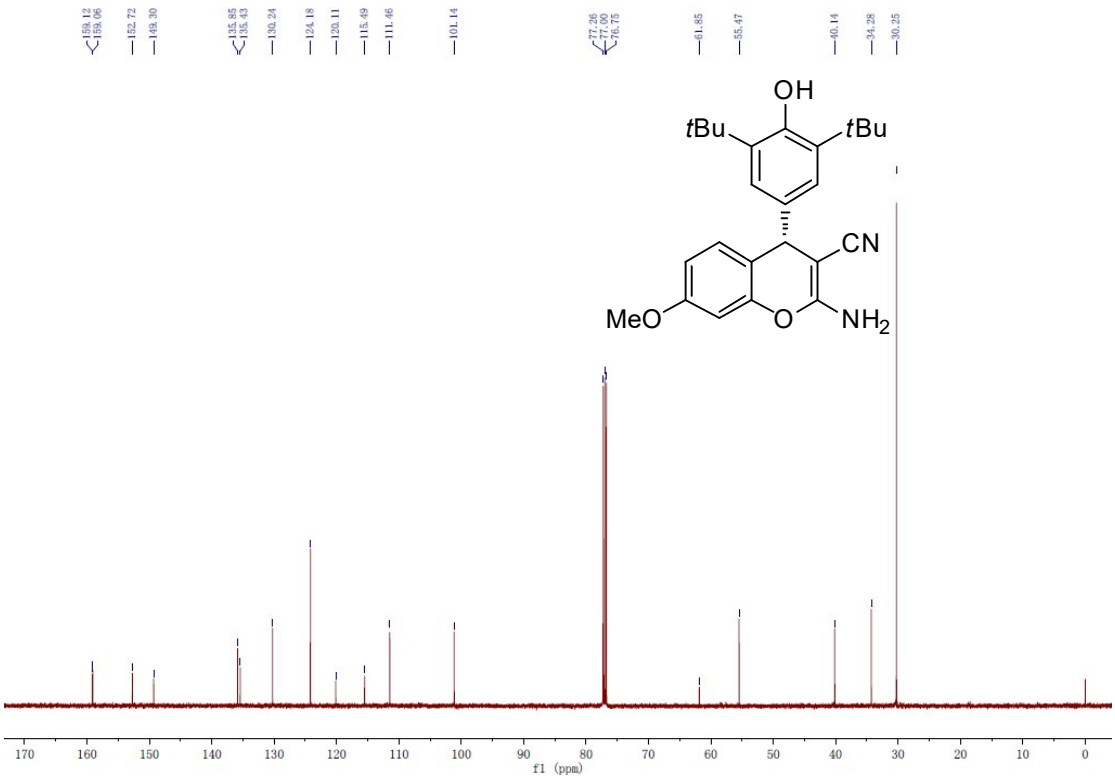
(*S*)-2-amino-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3f)



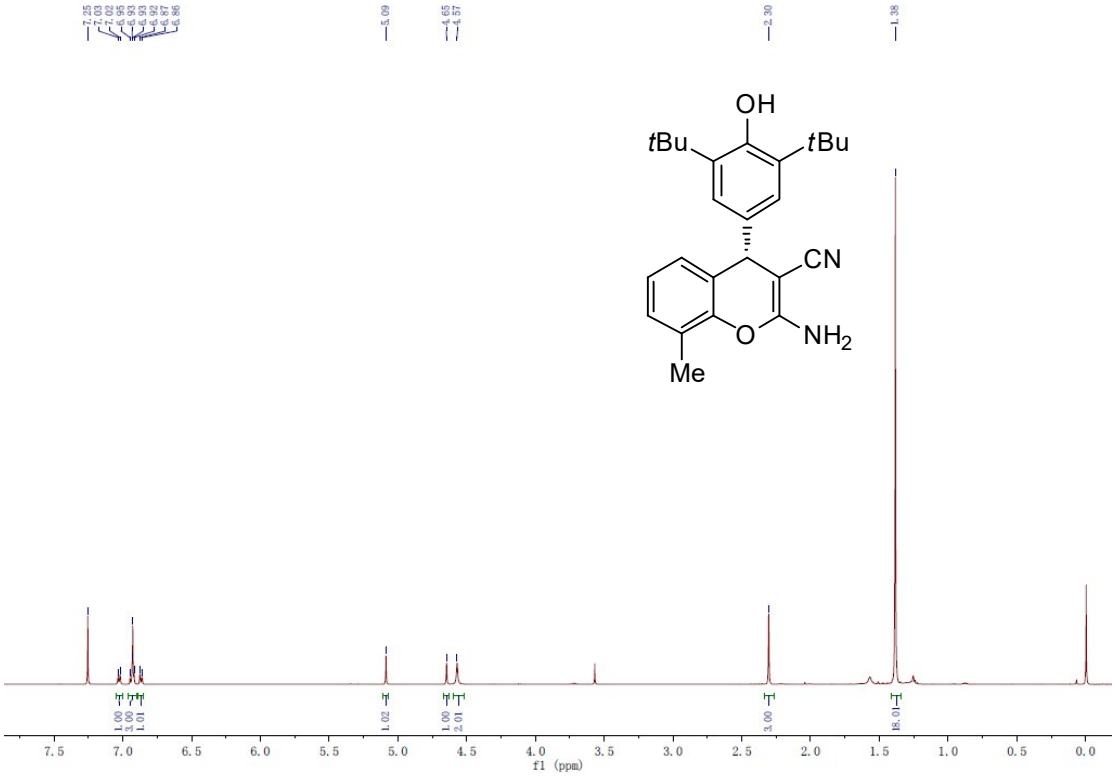


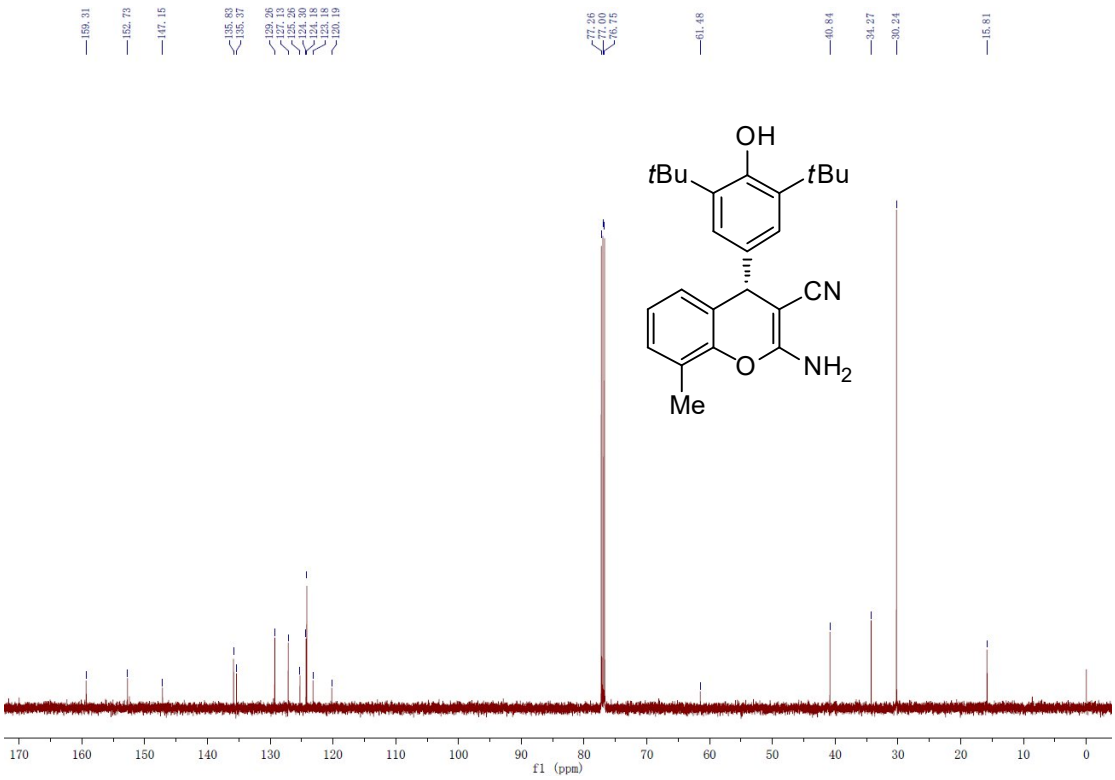
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7-methoxy-4*H*-chromene-3-carbonitrile (3g)



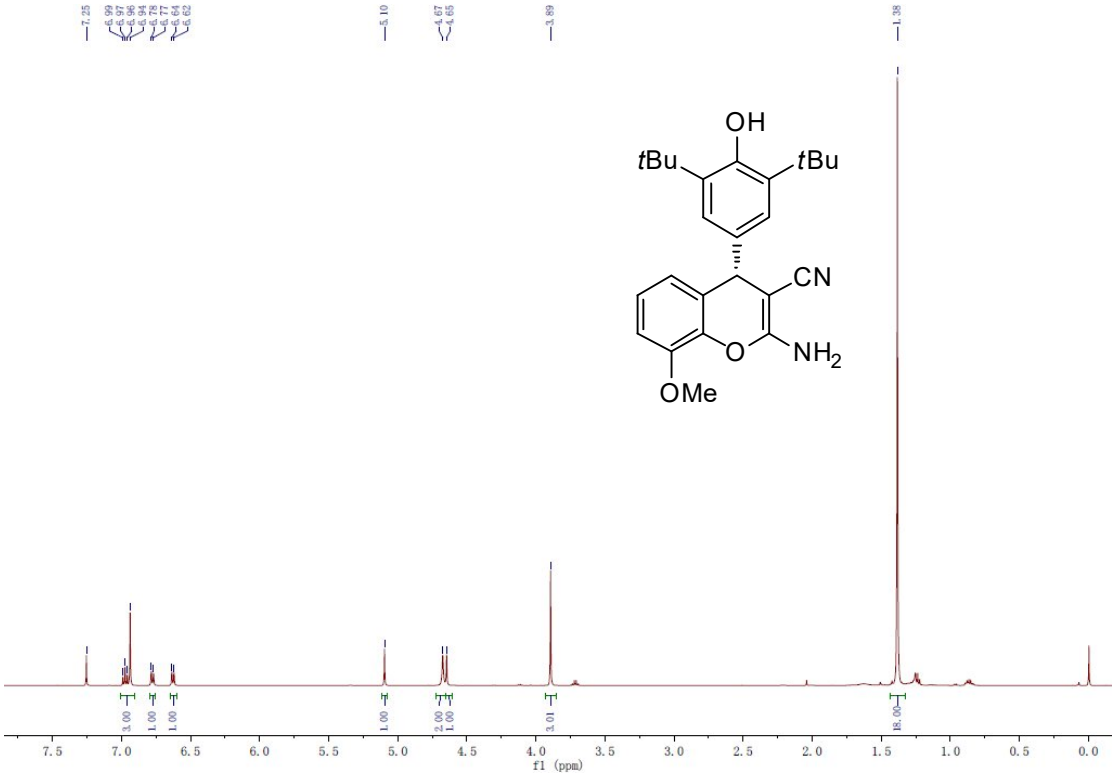


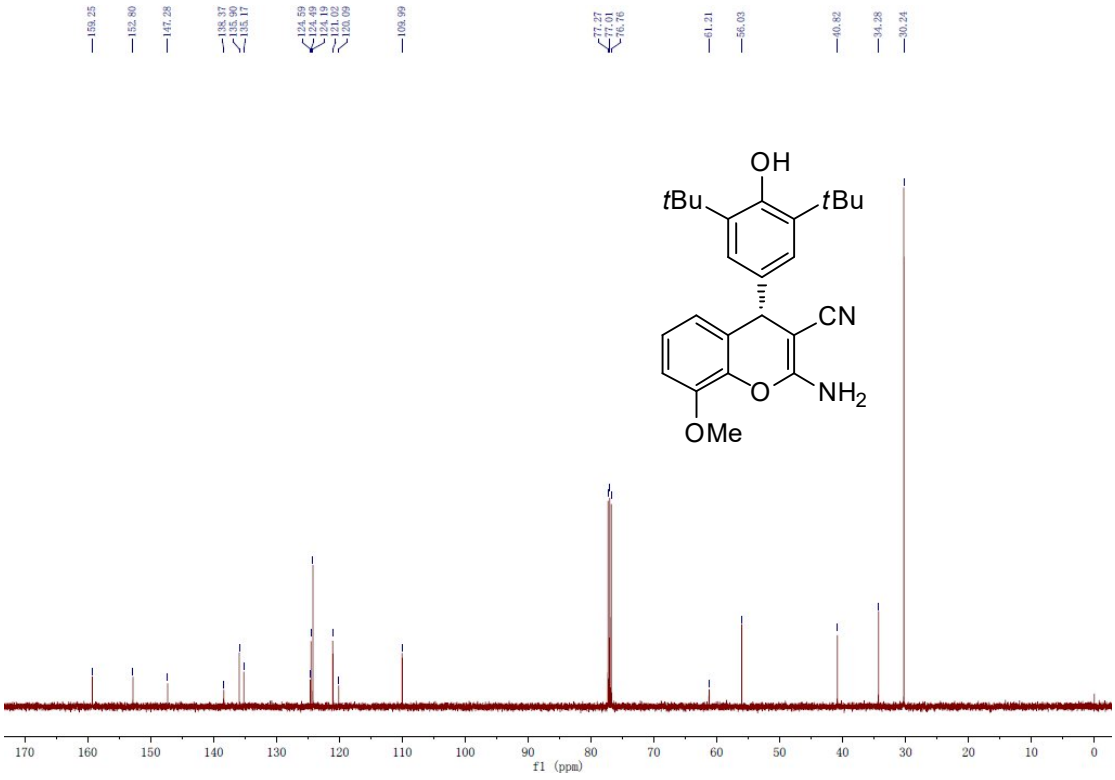
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-methyl-4*H*-chromene-3-carbonitrile (3h)



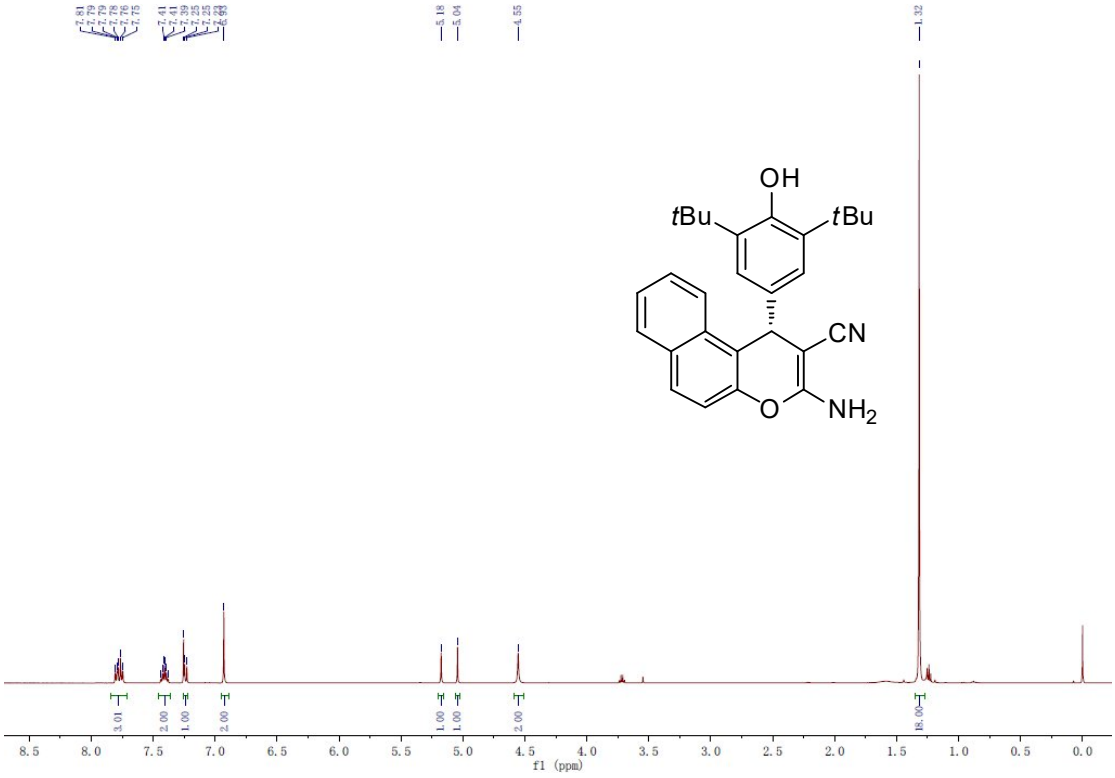


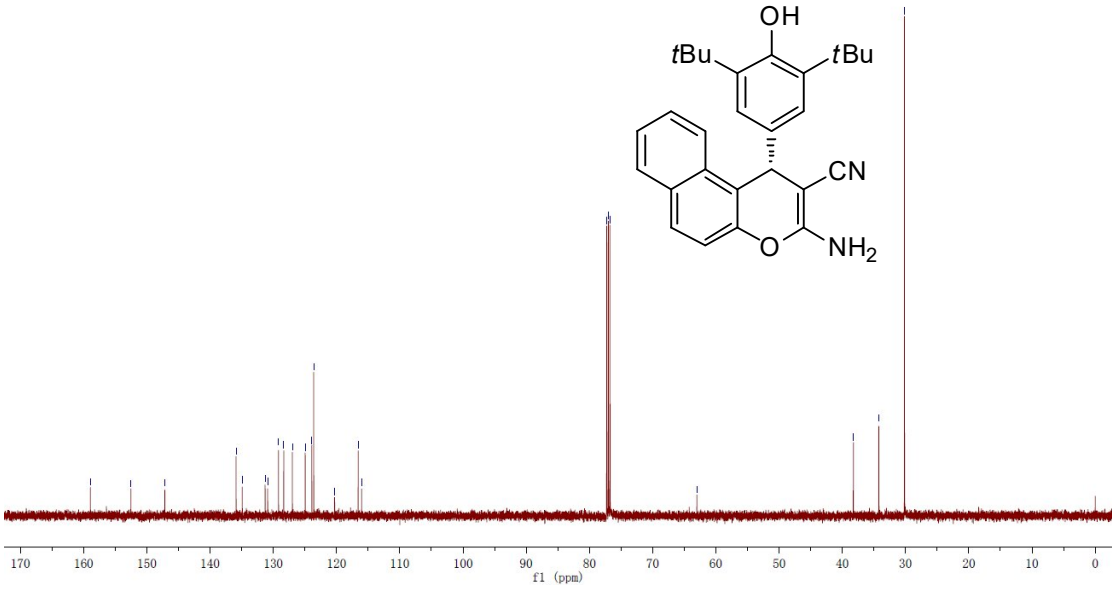
(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-methoxy-4*H*-chromene-3-carbonitrile (3i)



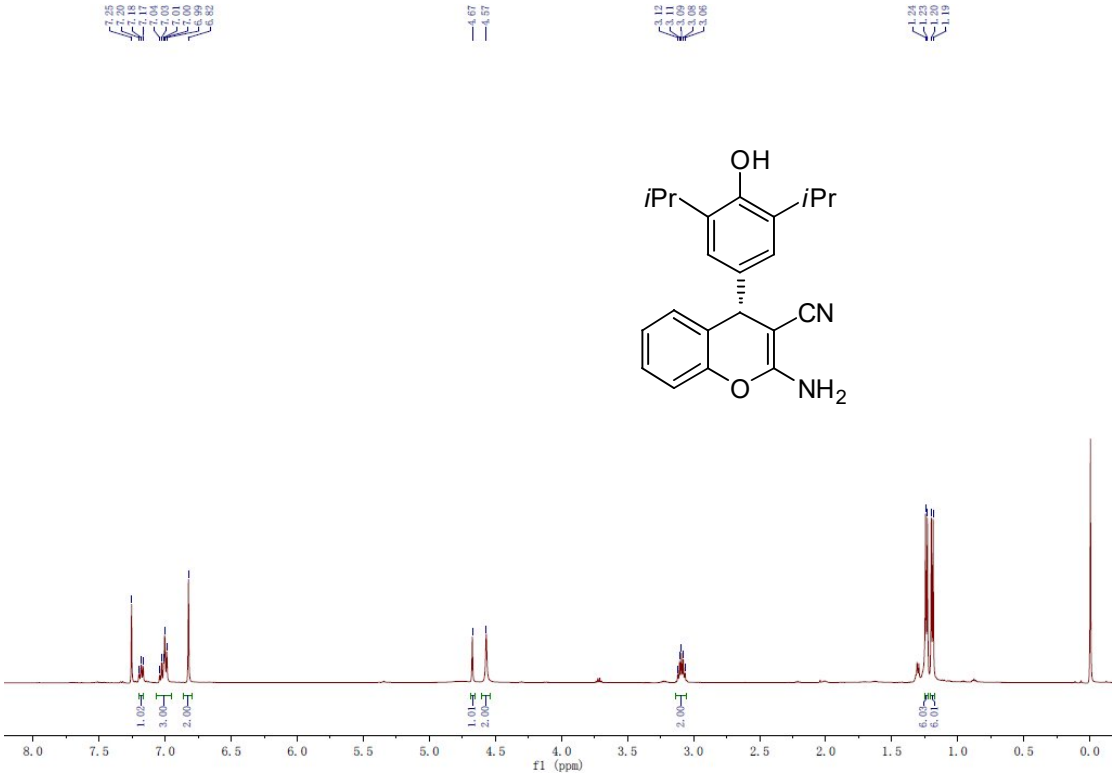


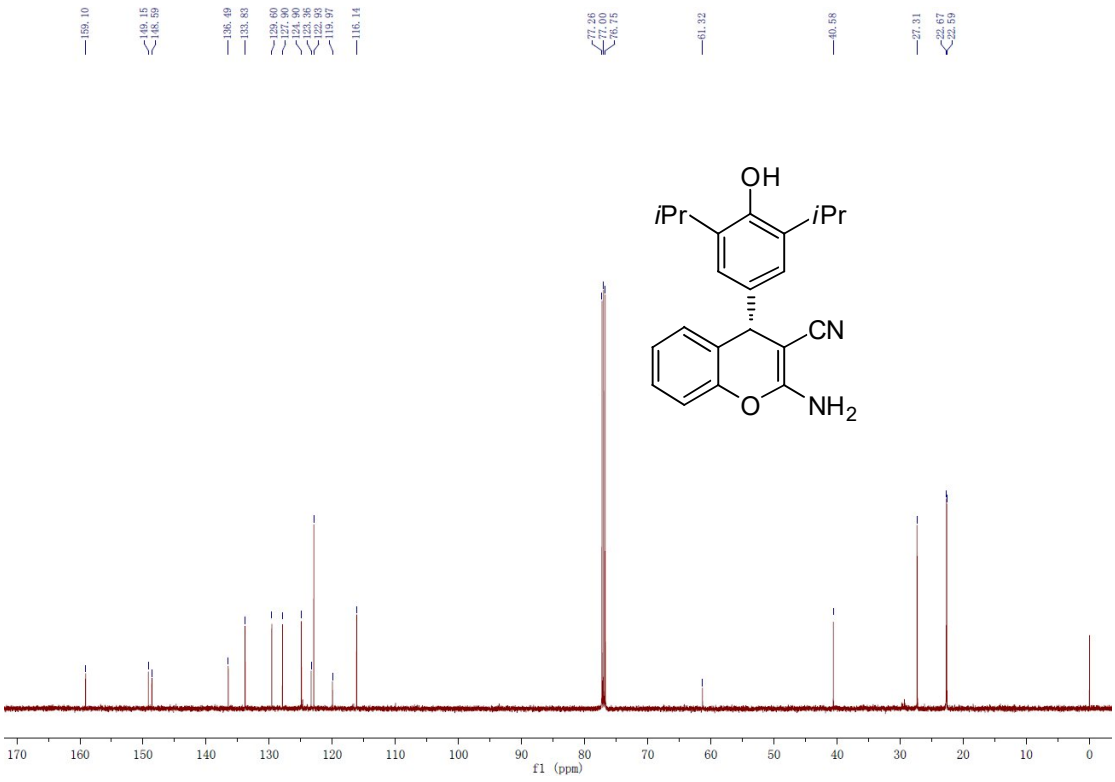
(*S*)-3-amino-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (3j)



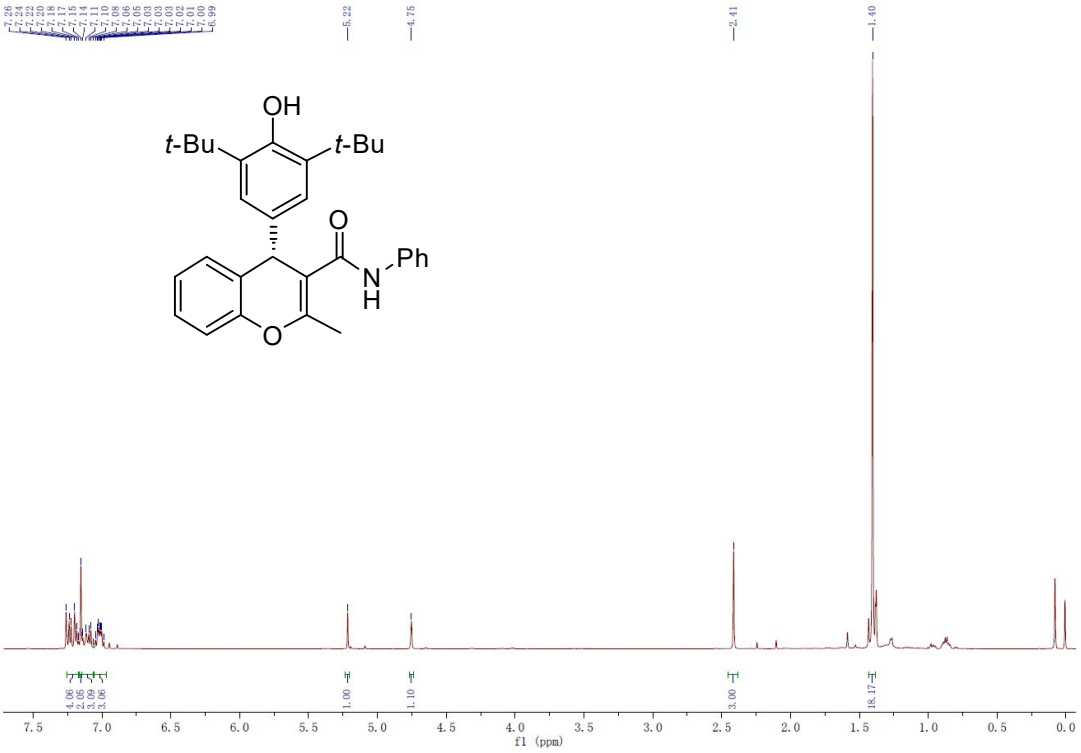


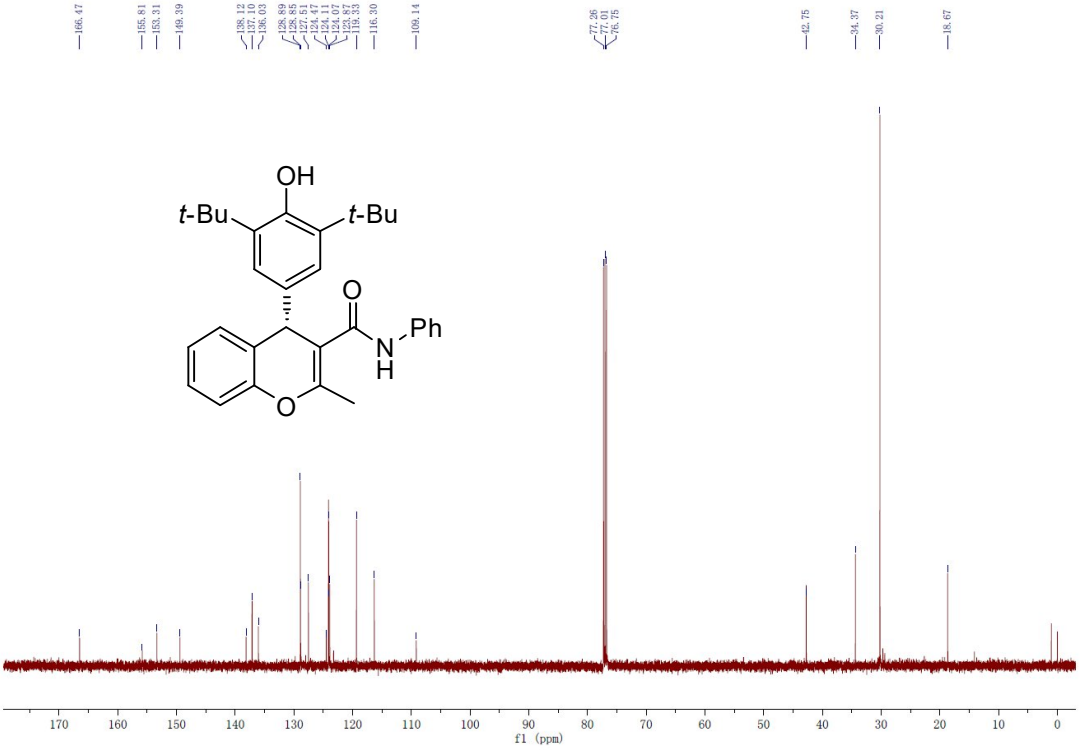
(*S*)-2-amino-4-(4-hydroxy-3,5-diisopropylphenyl)-4*H*-chromene-3-carbonitrile (3k)



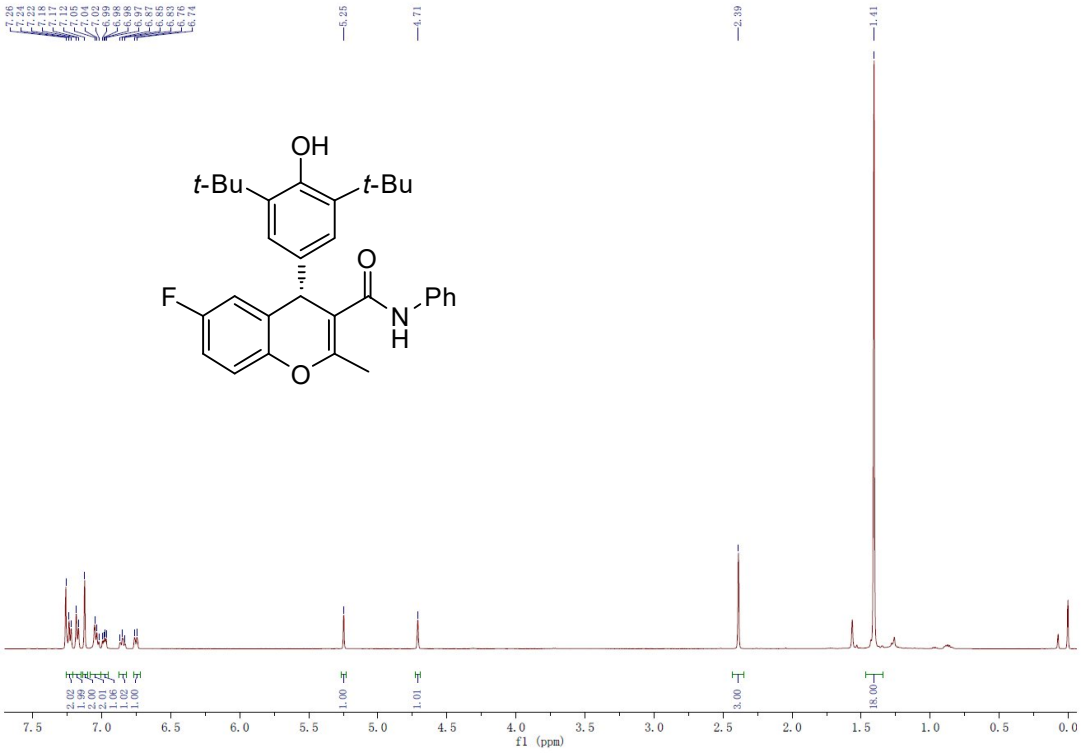


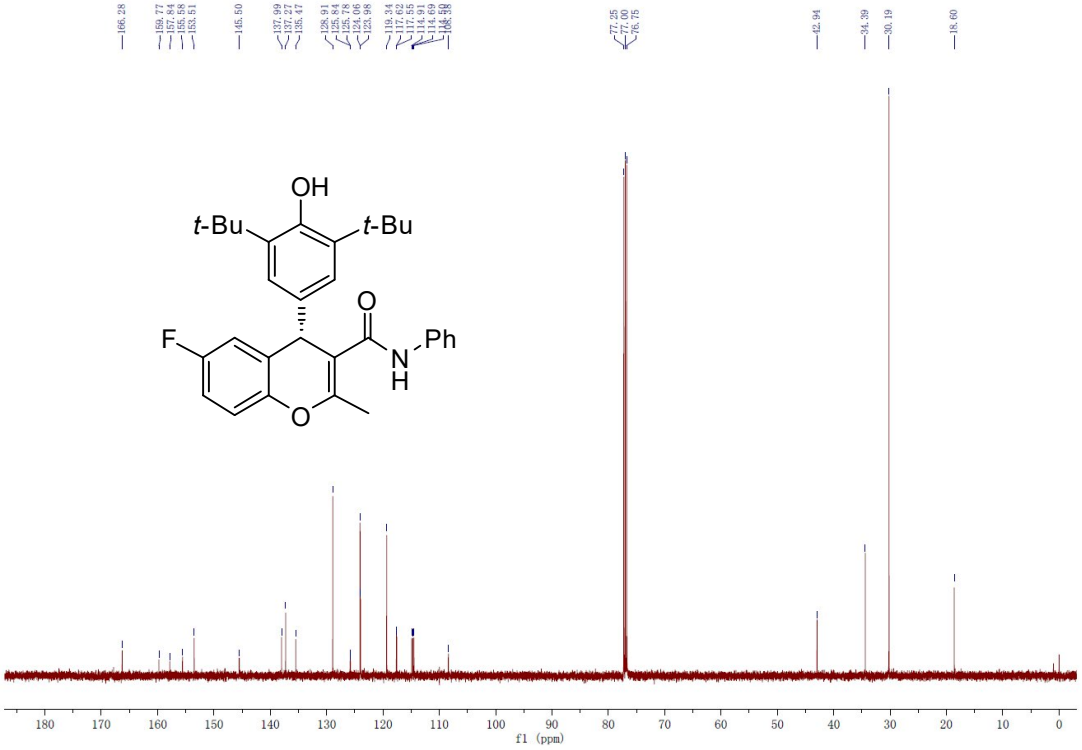
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6aa)



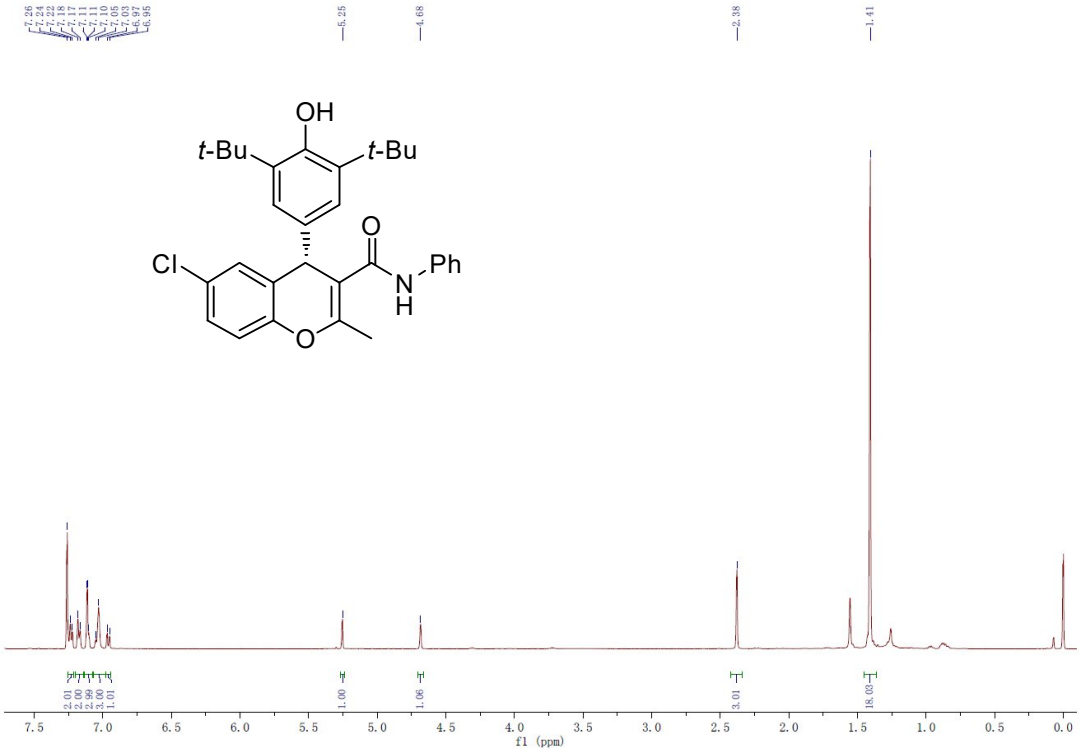


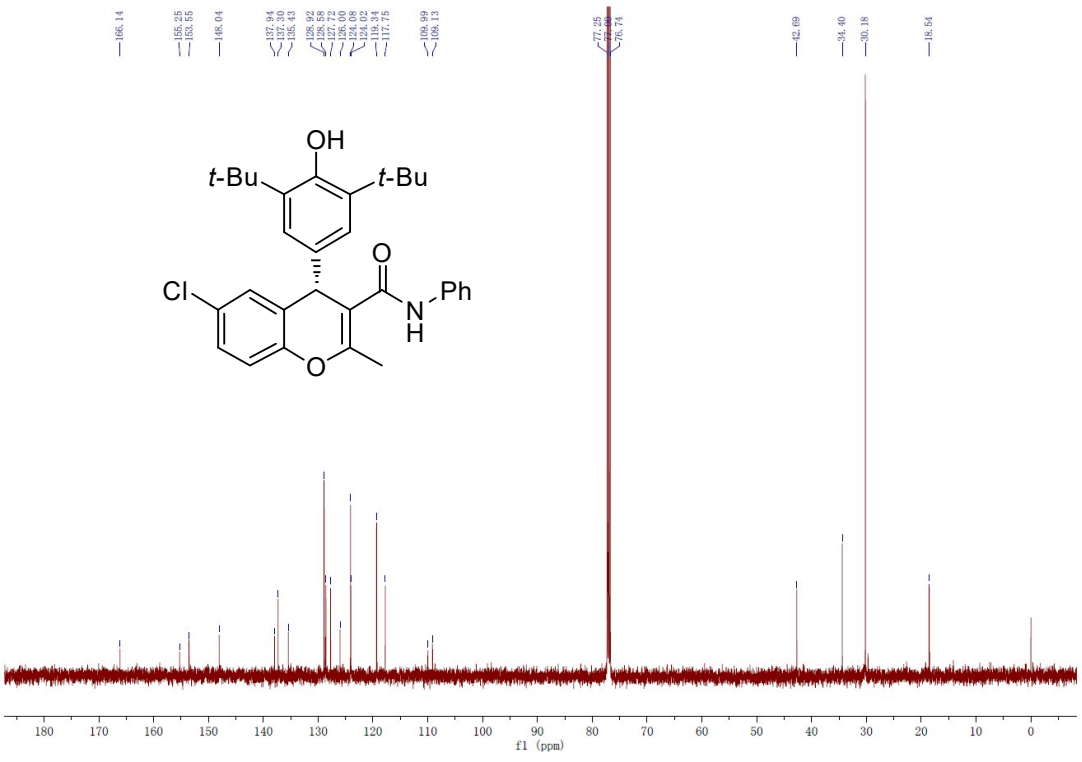
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ba)



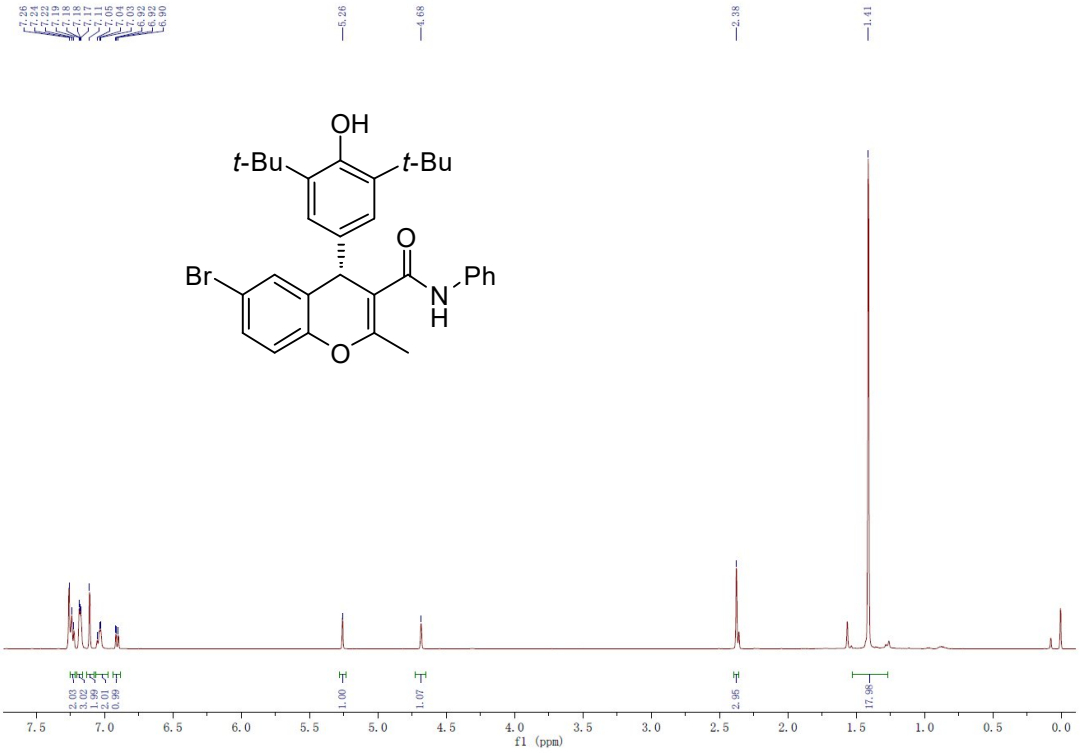


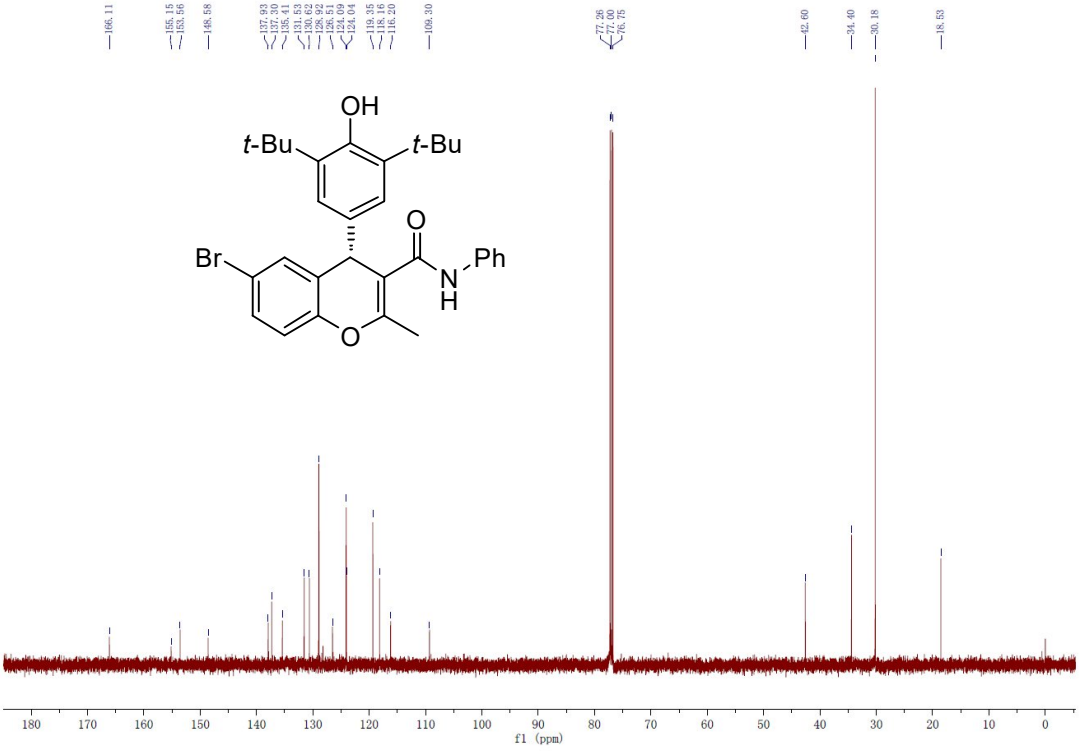
(*S*)-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ca)



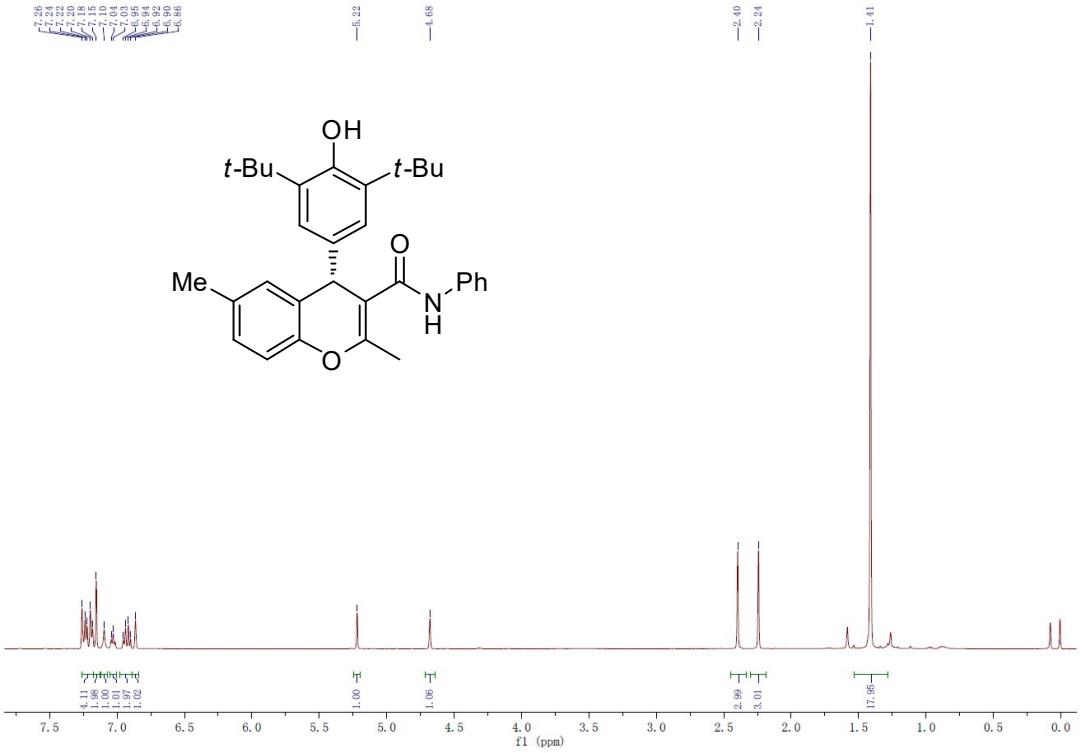


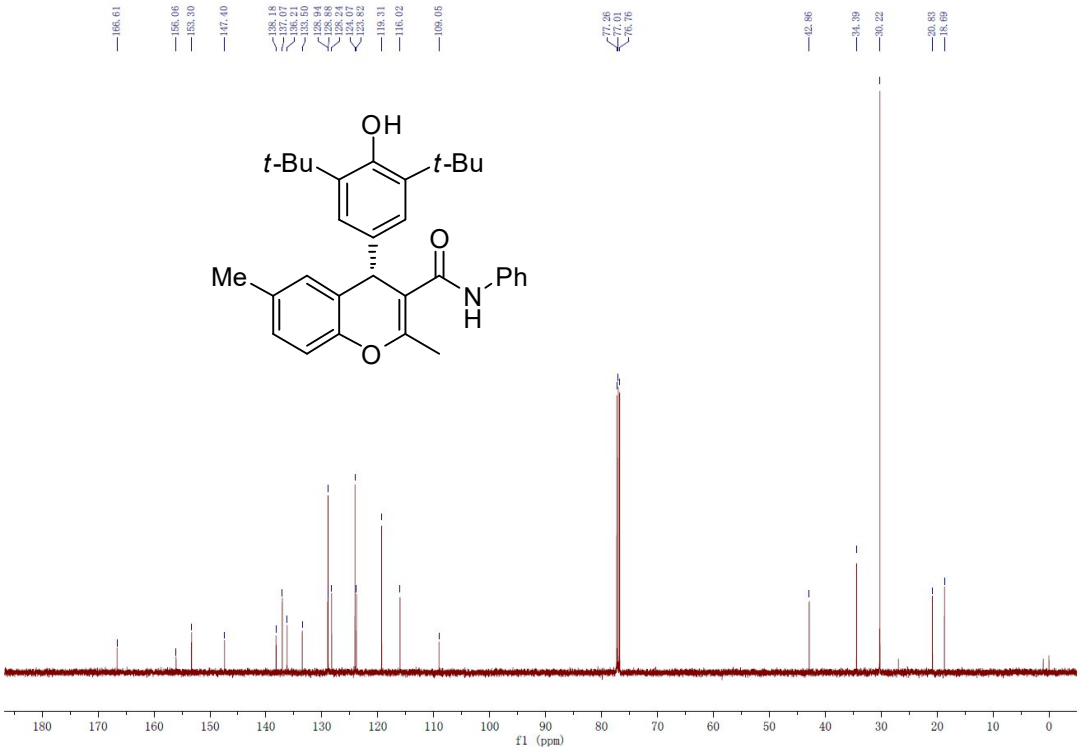
(*S*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6da)



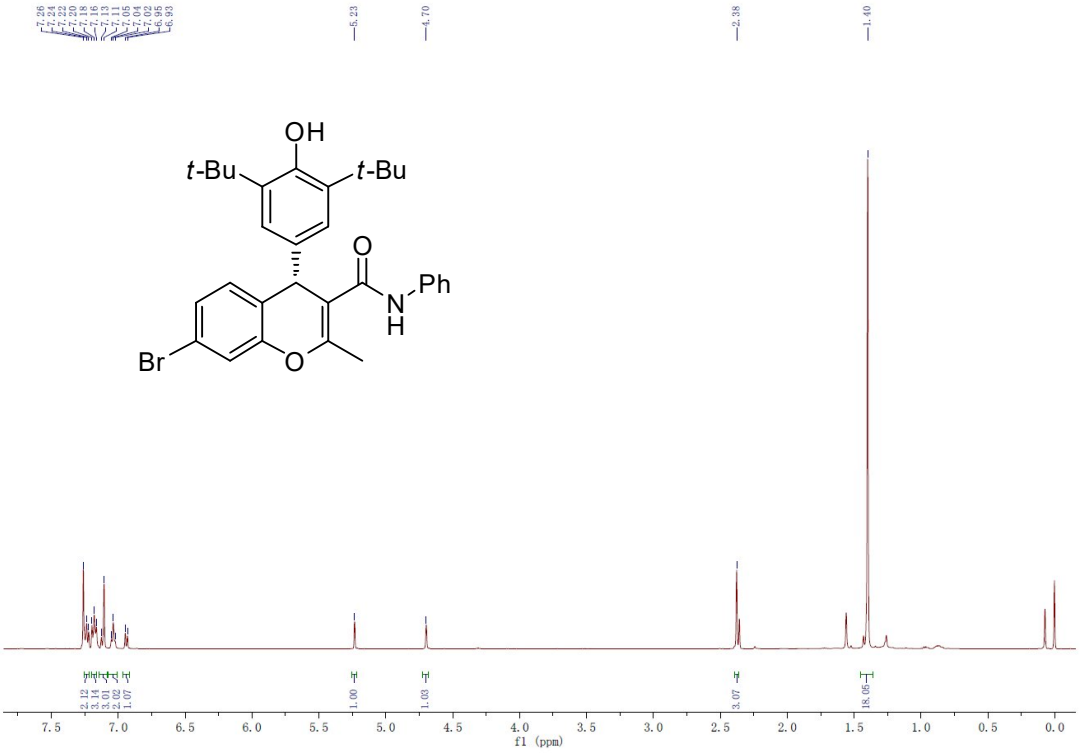


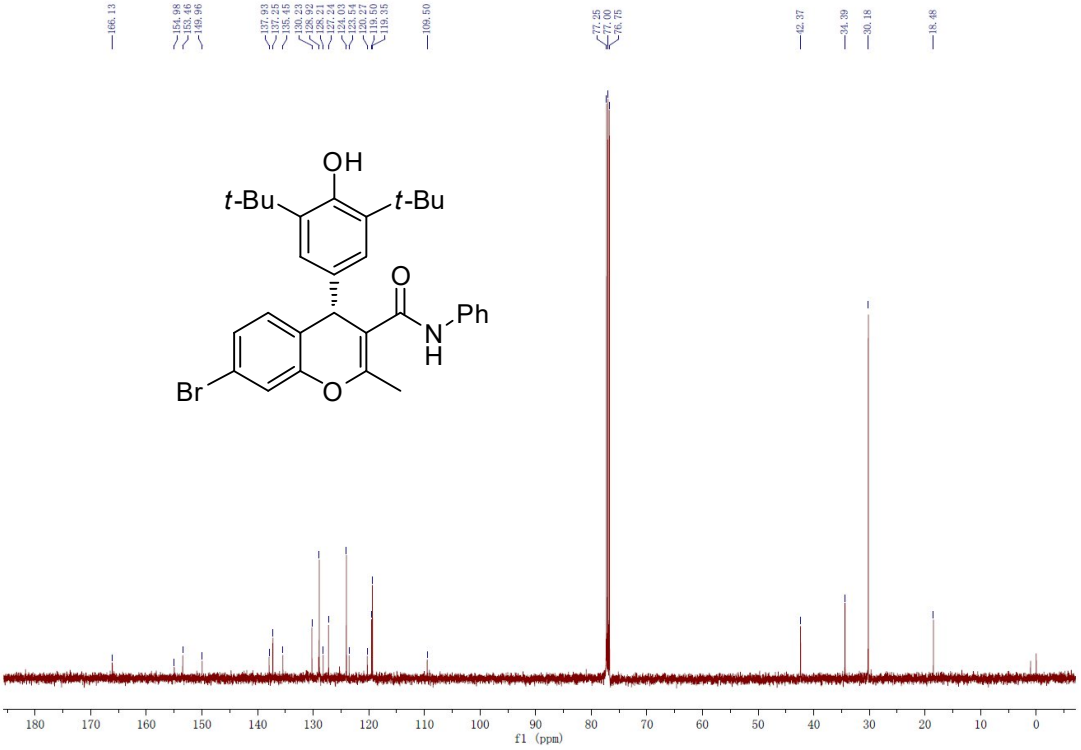
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,6-dimethyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ea)



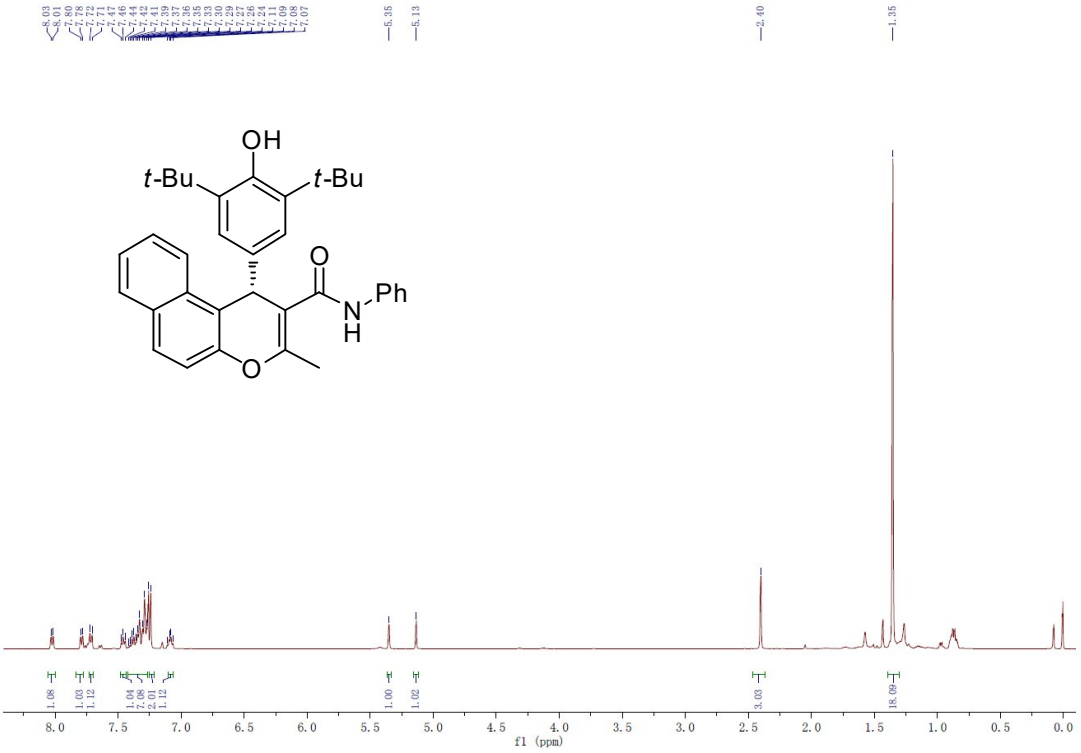


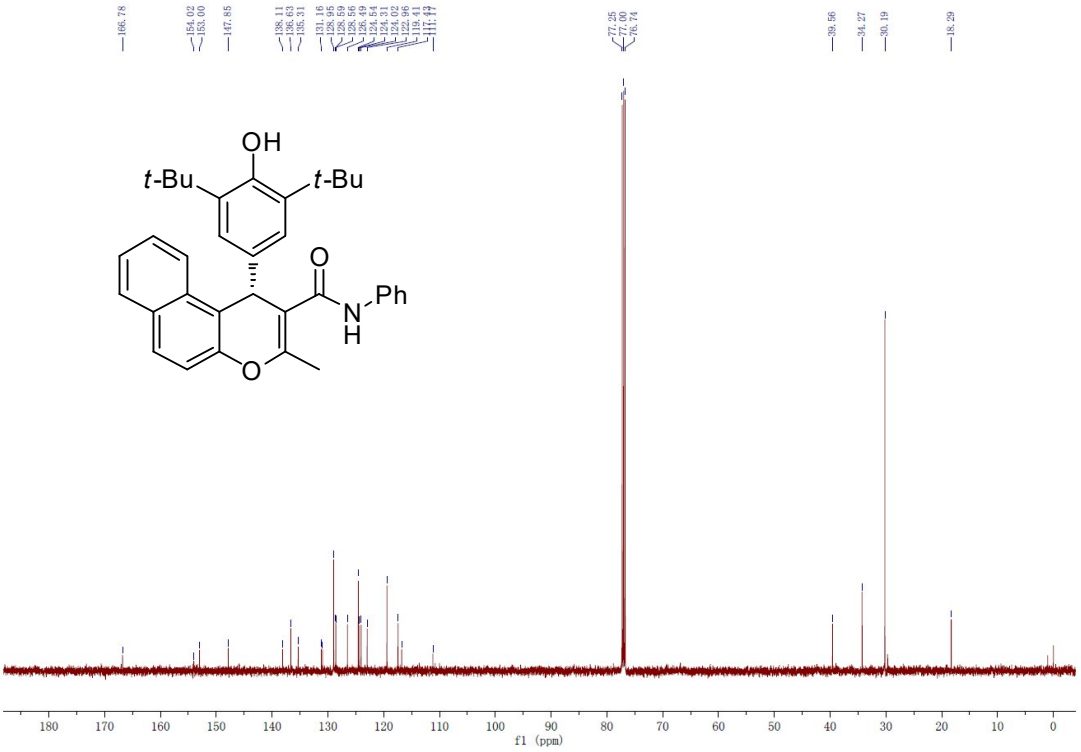
(*S*)-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6fa)



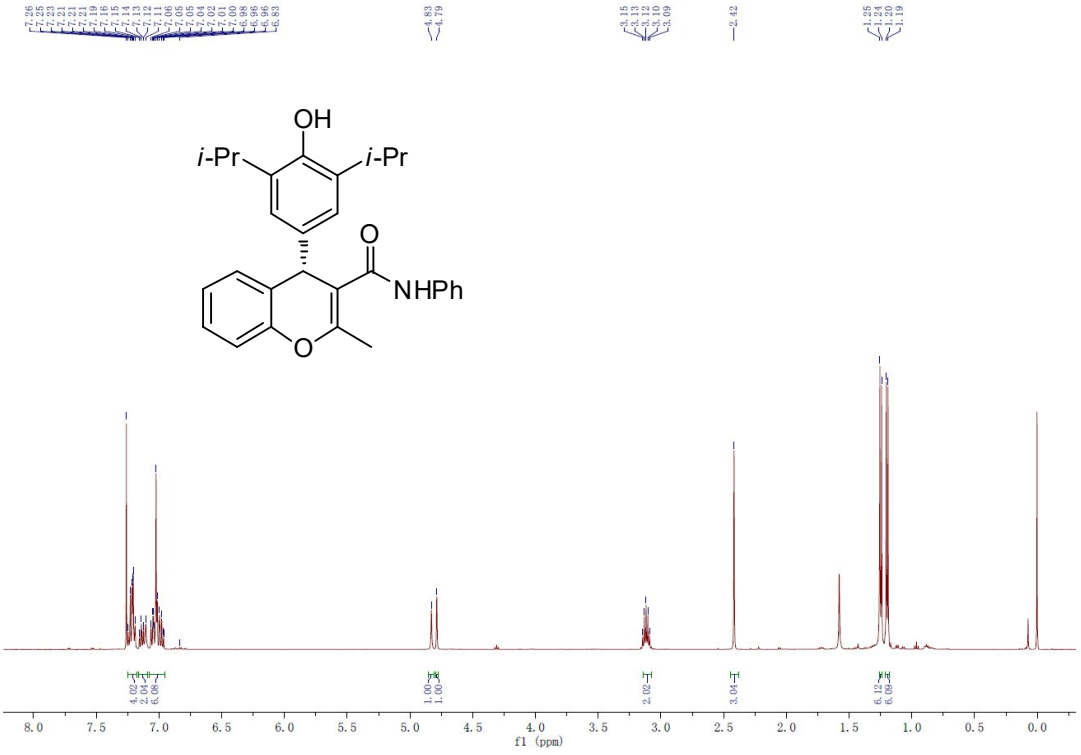


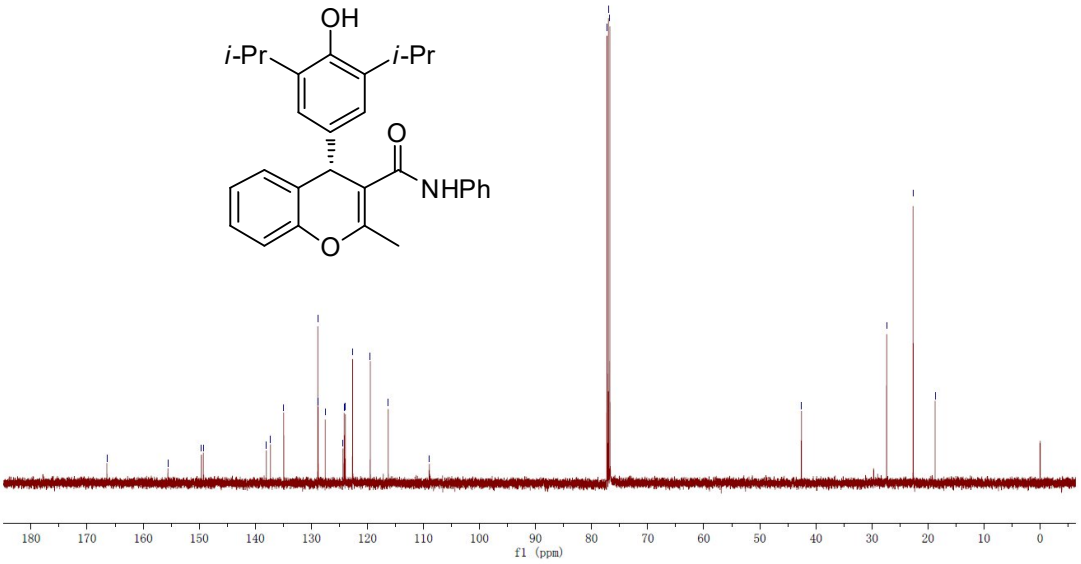
(*S*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-methyl-*N*-phenyl-1*H*-benzo[*f*] chromene-2-carboxamide (6ga)



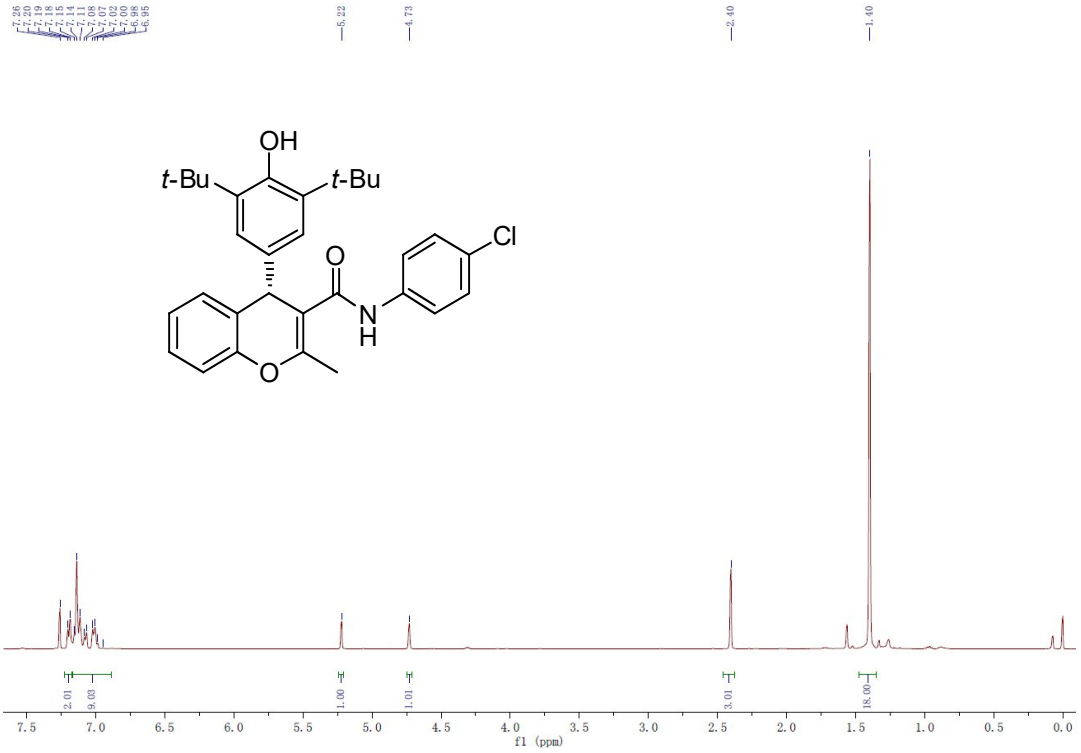


(*S*)-4-(4-hydroxy-3,5-diisopropylphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ha)

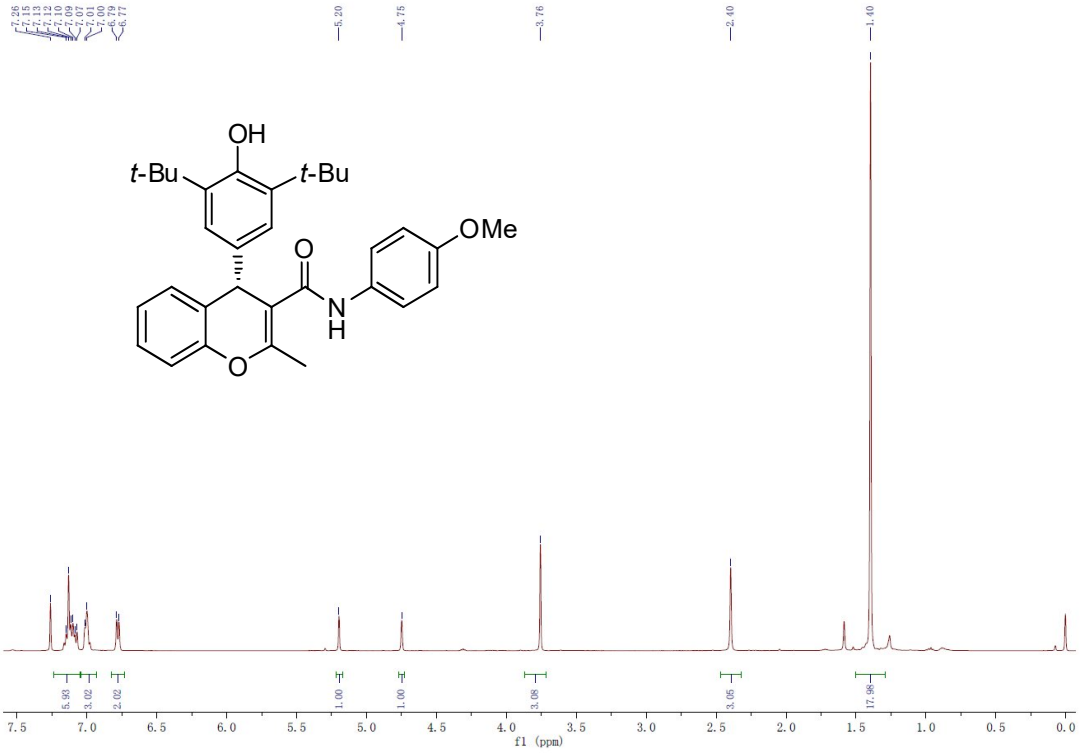


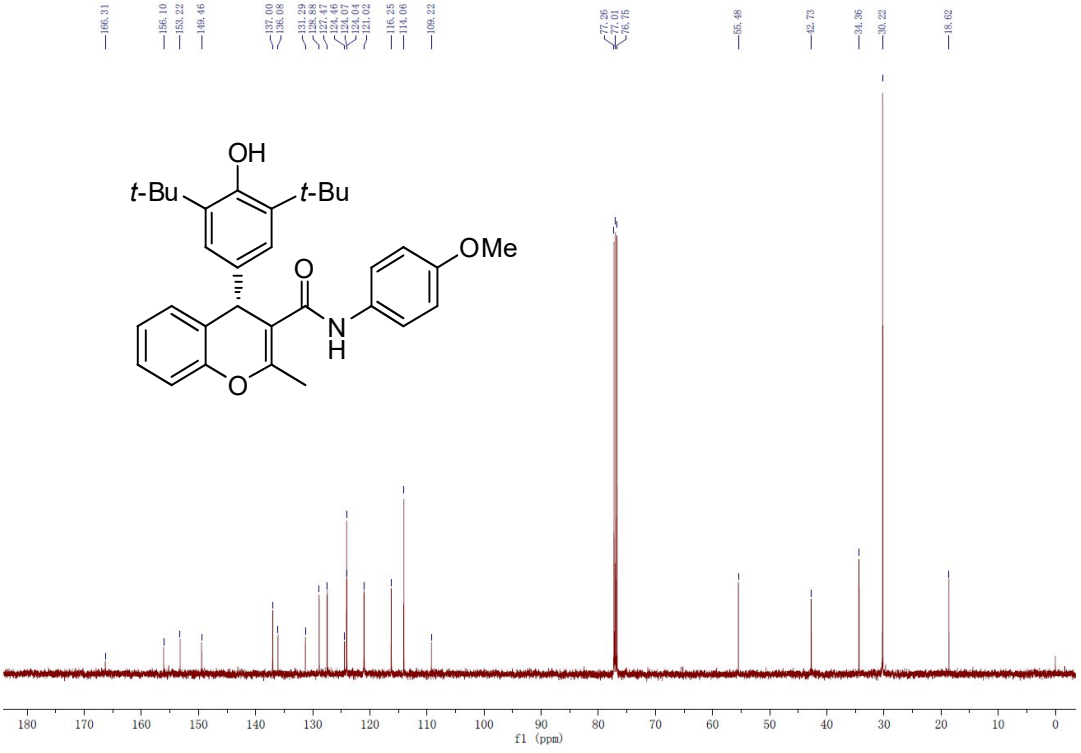


(*S*)-*N*-(4-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ab)

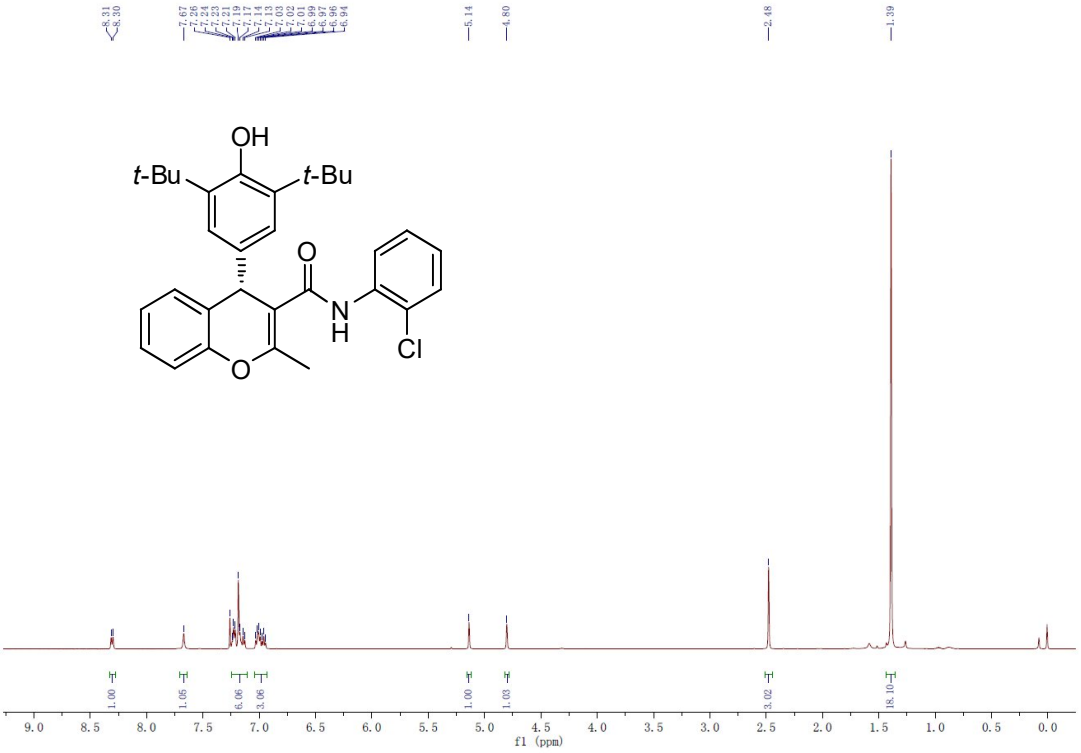


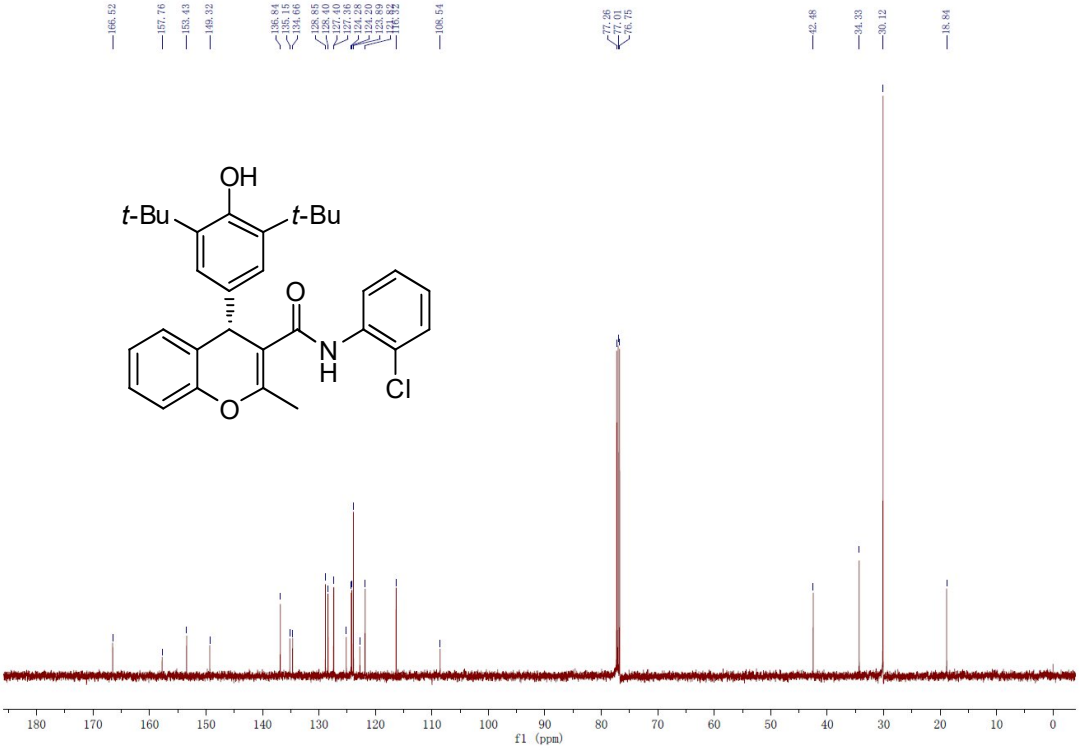
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-methoxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ac)



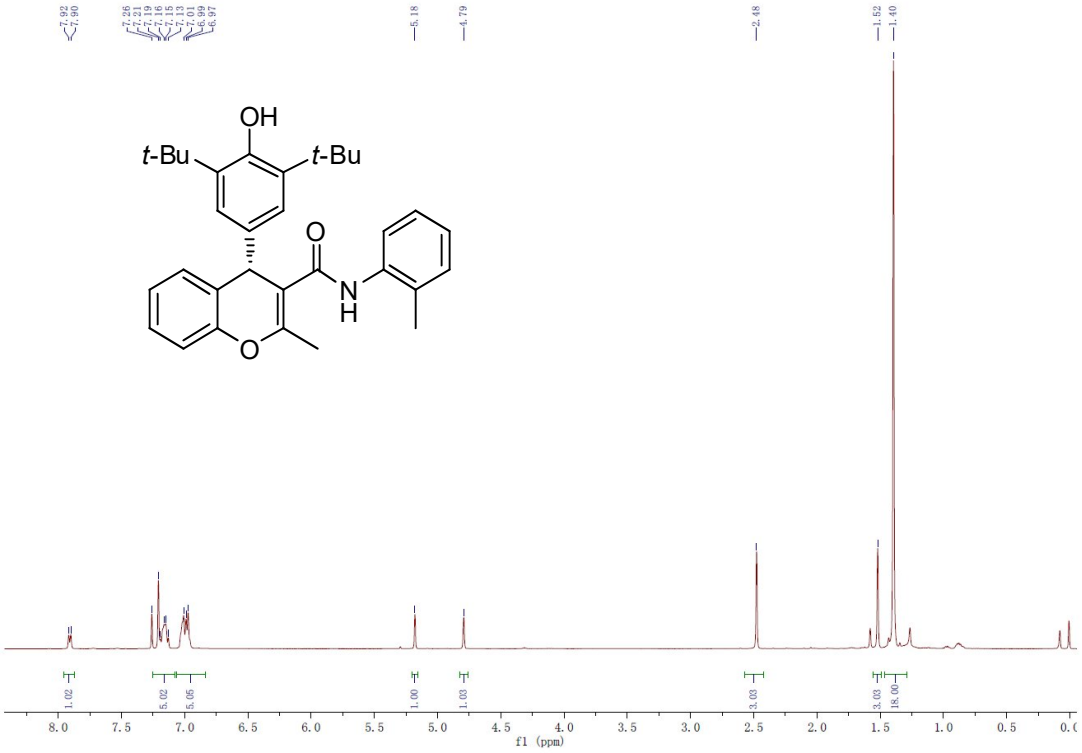


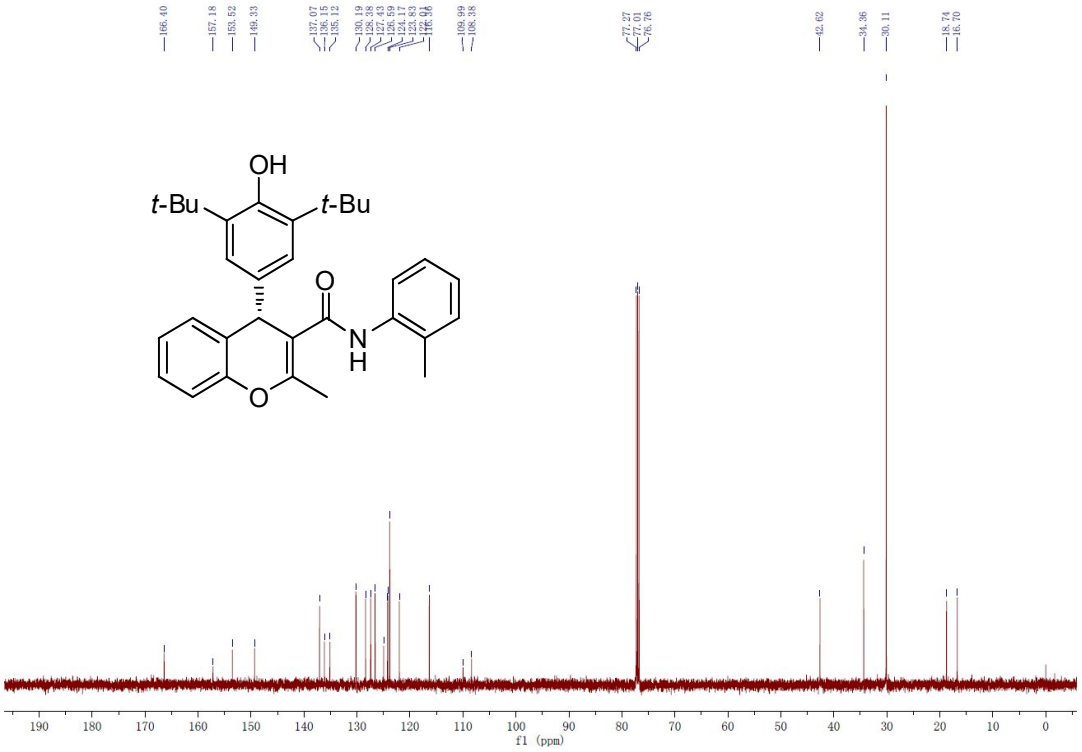
(*S*)-*N*-(2-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ad)



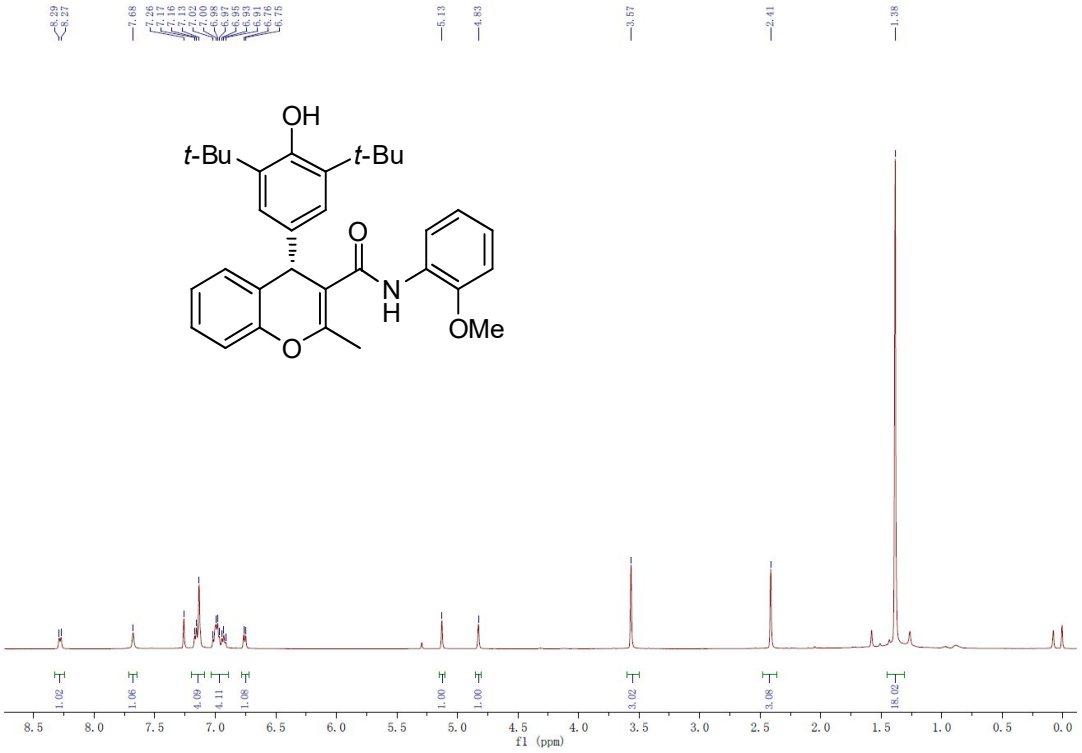


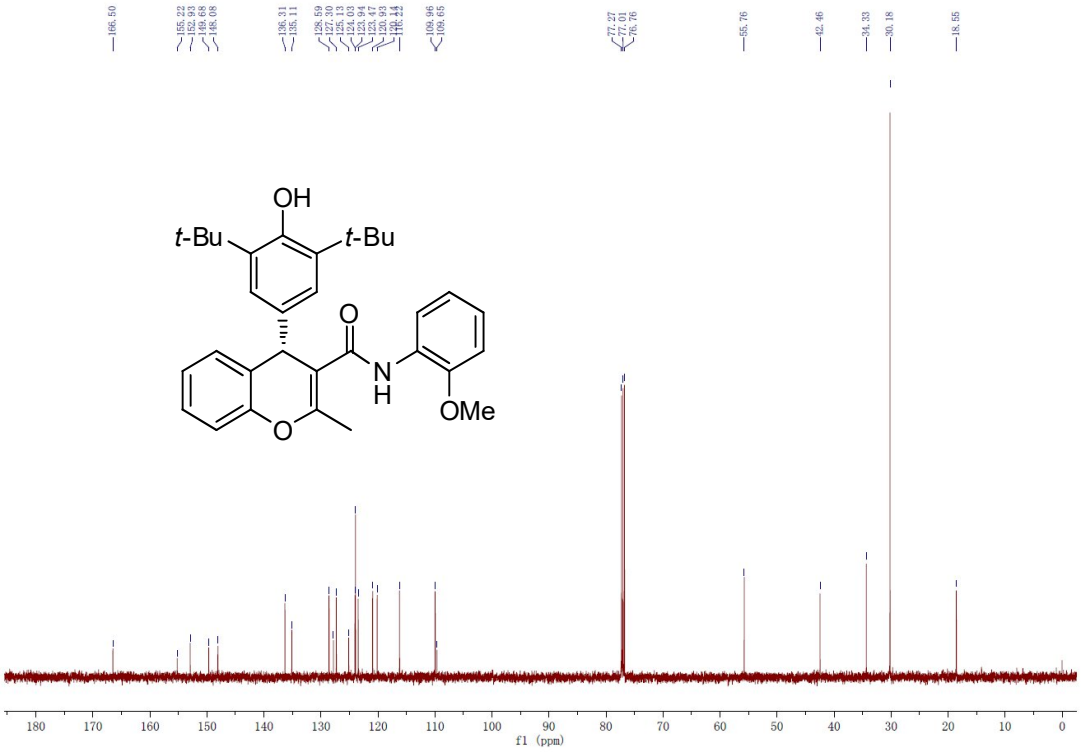
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-(*o*-tolyl)-4*H*-chromene-3-carboxamide (6ae)



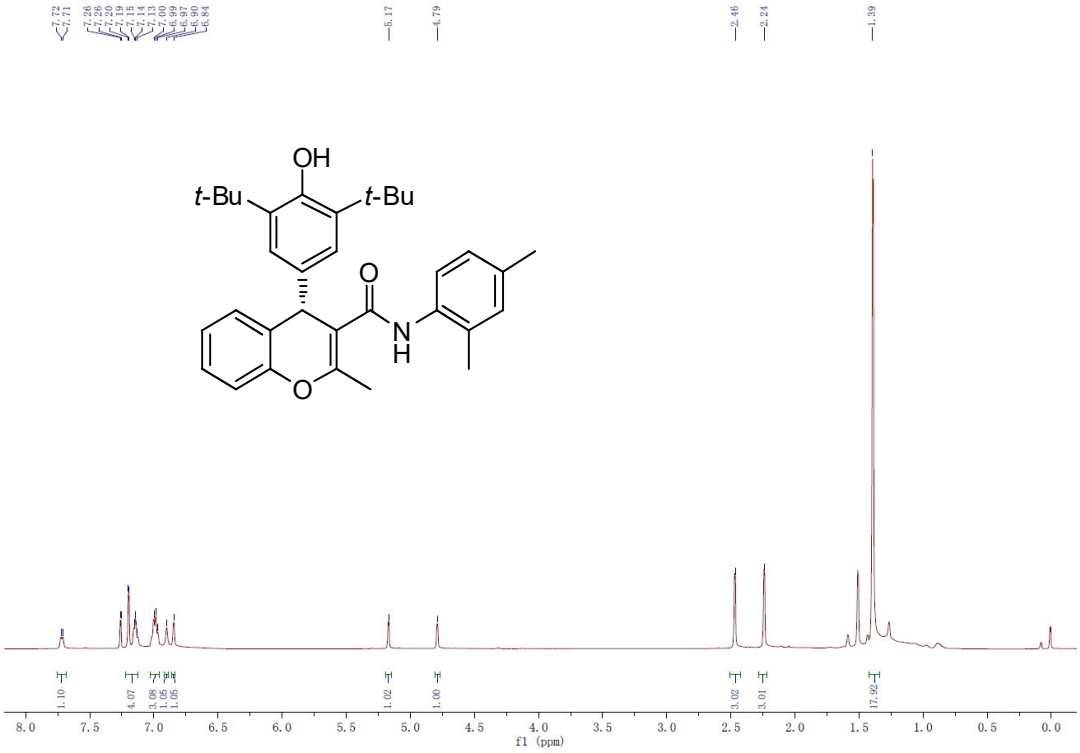


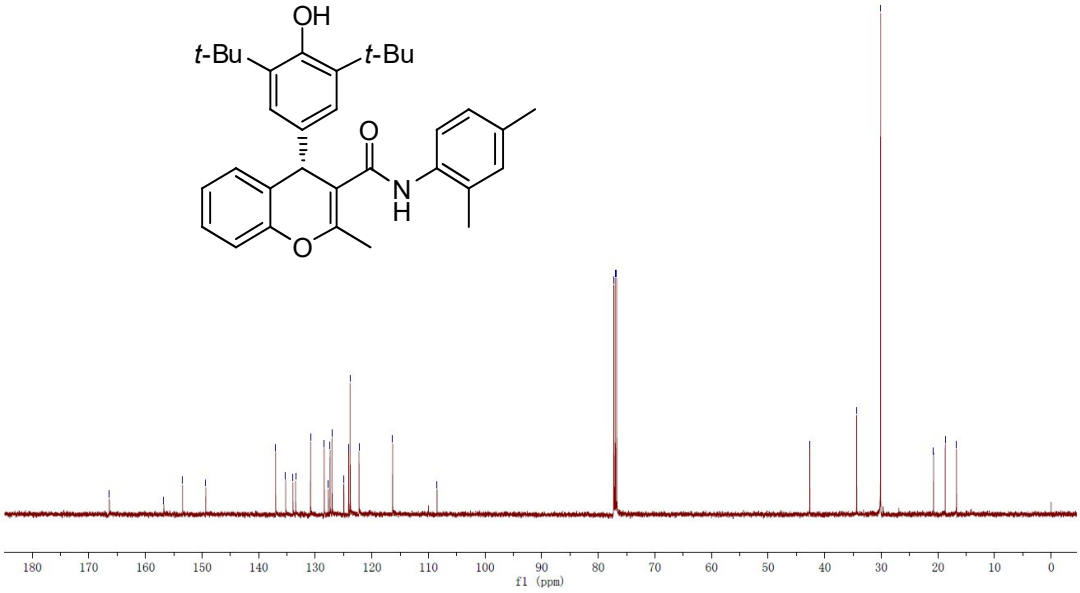
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(2-methoxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6af)



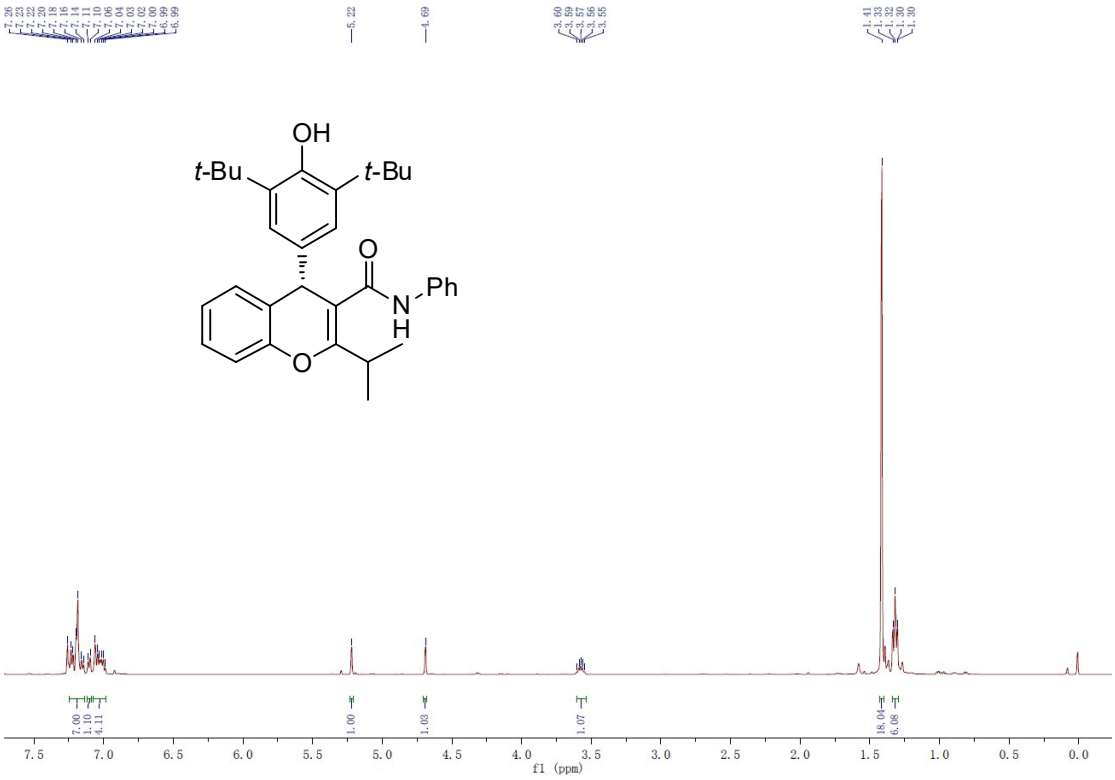


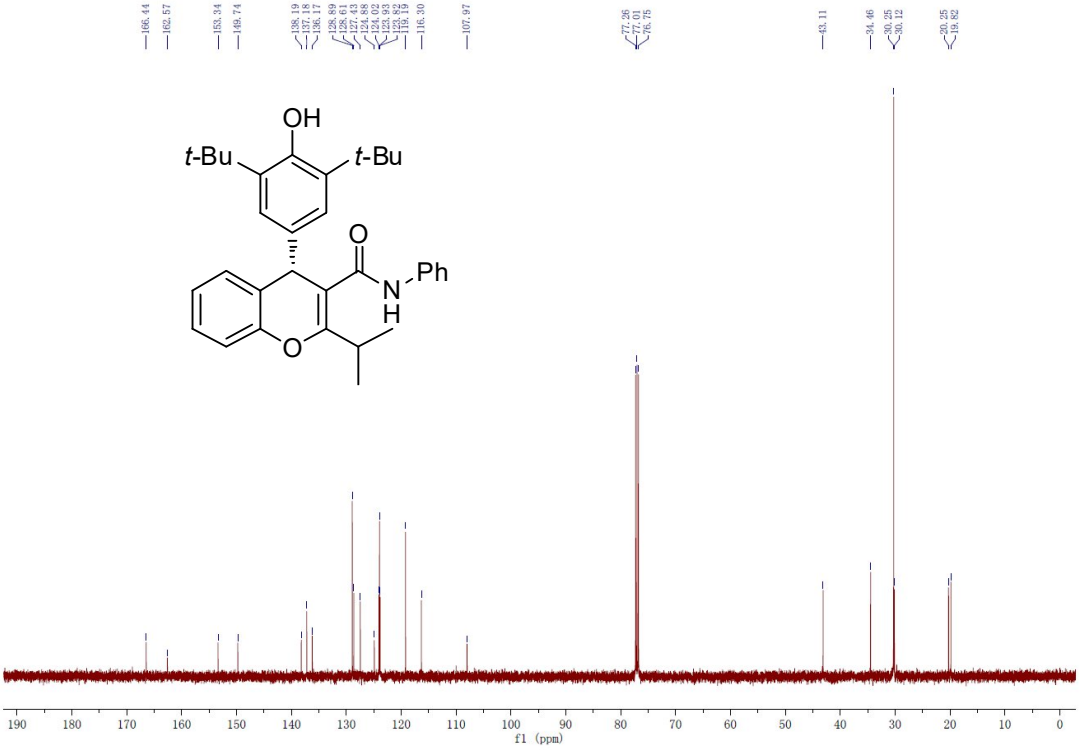
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(2,4-dimethylphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ag)



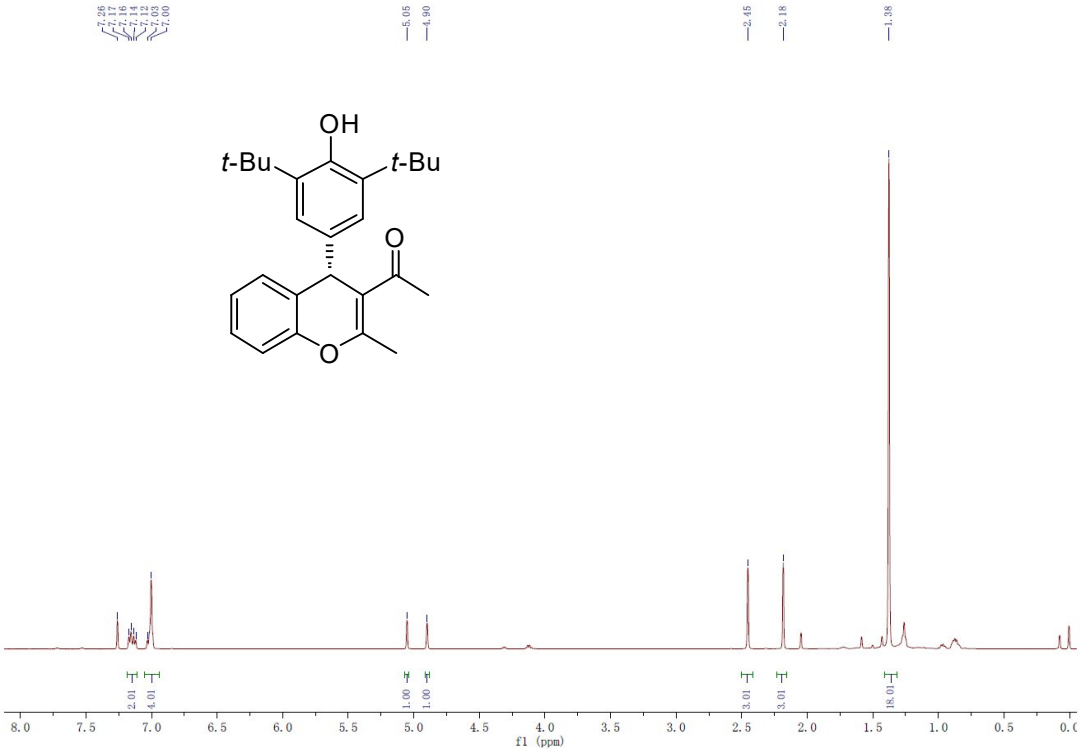


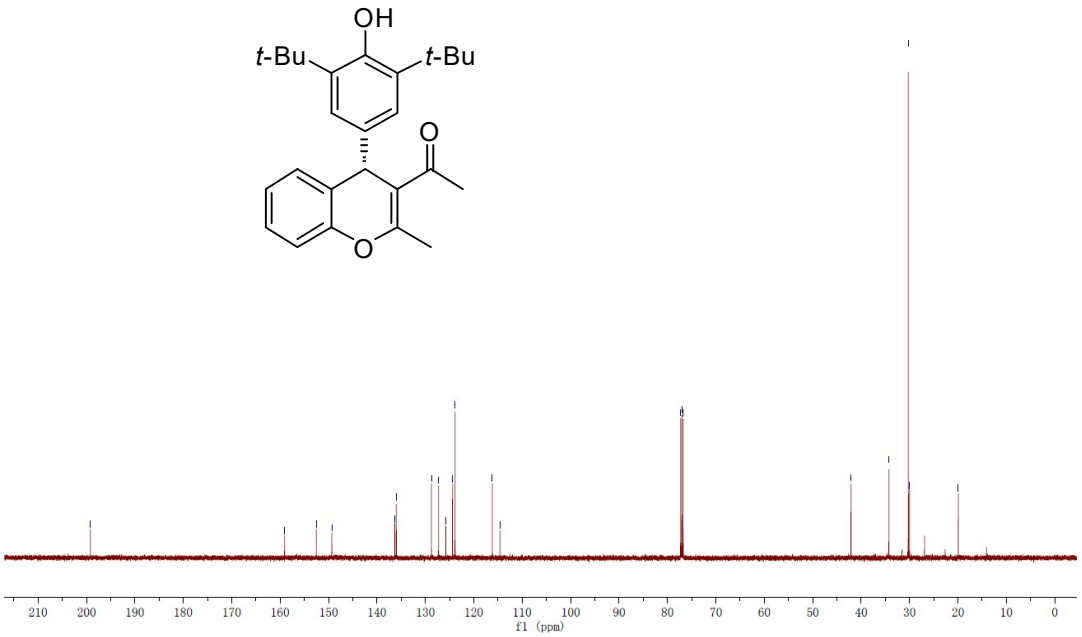
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-isopropyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ah)



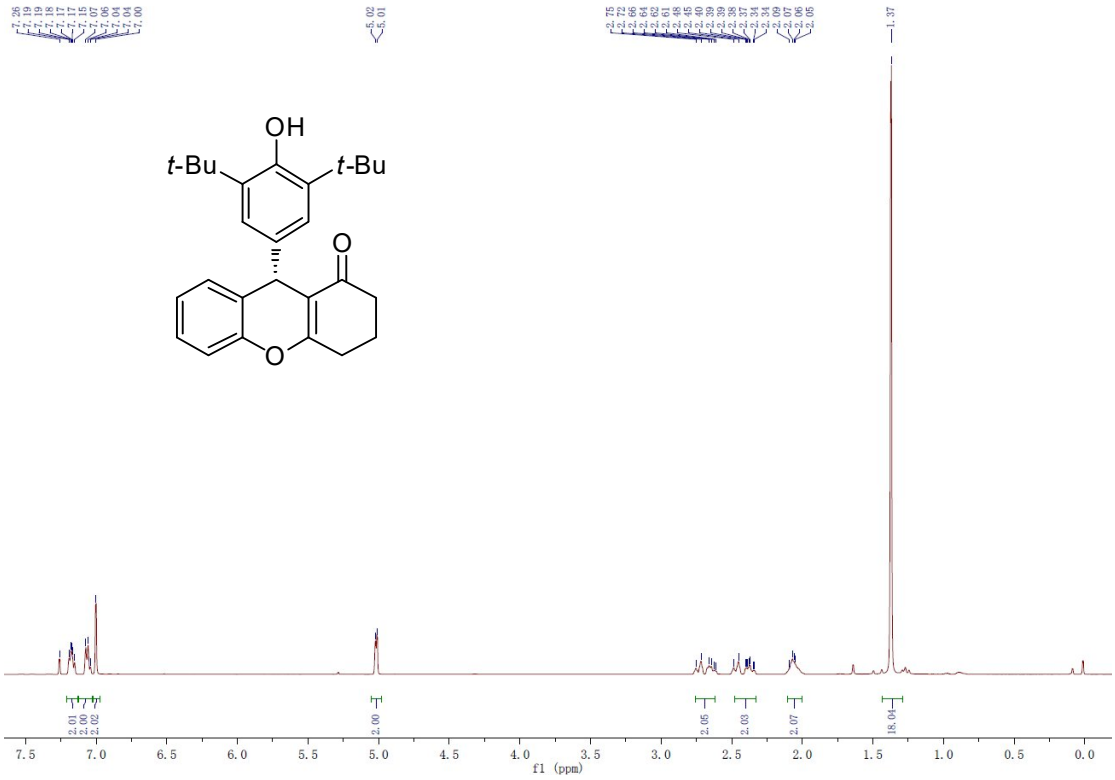


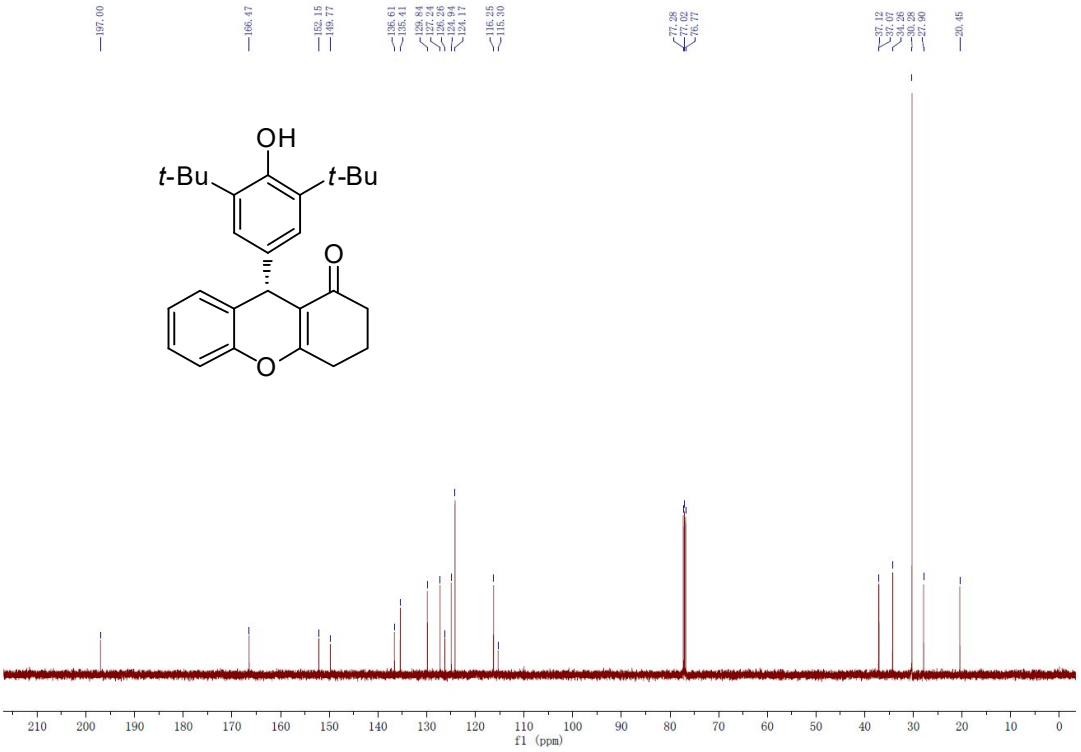
(*S*)-1-(4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromen-3-yl)ethanone (6ai)



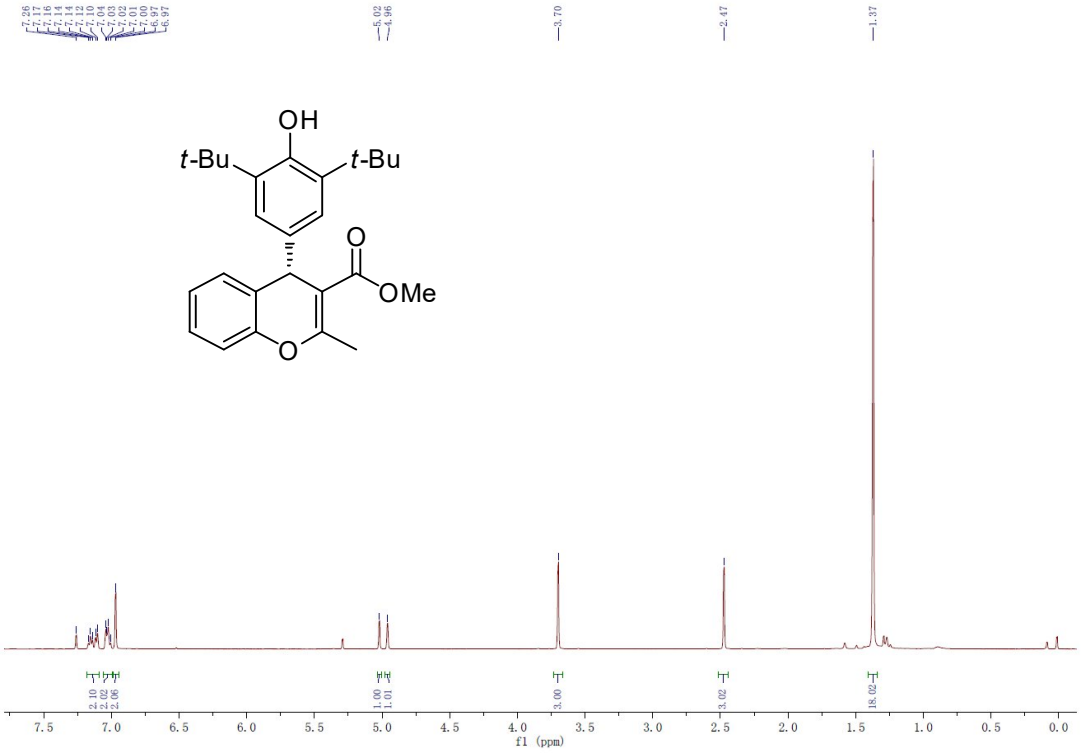


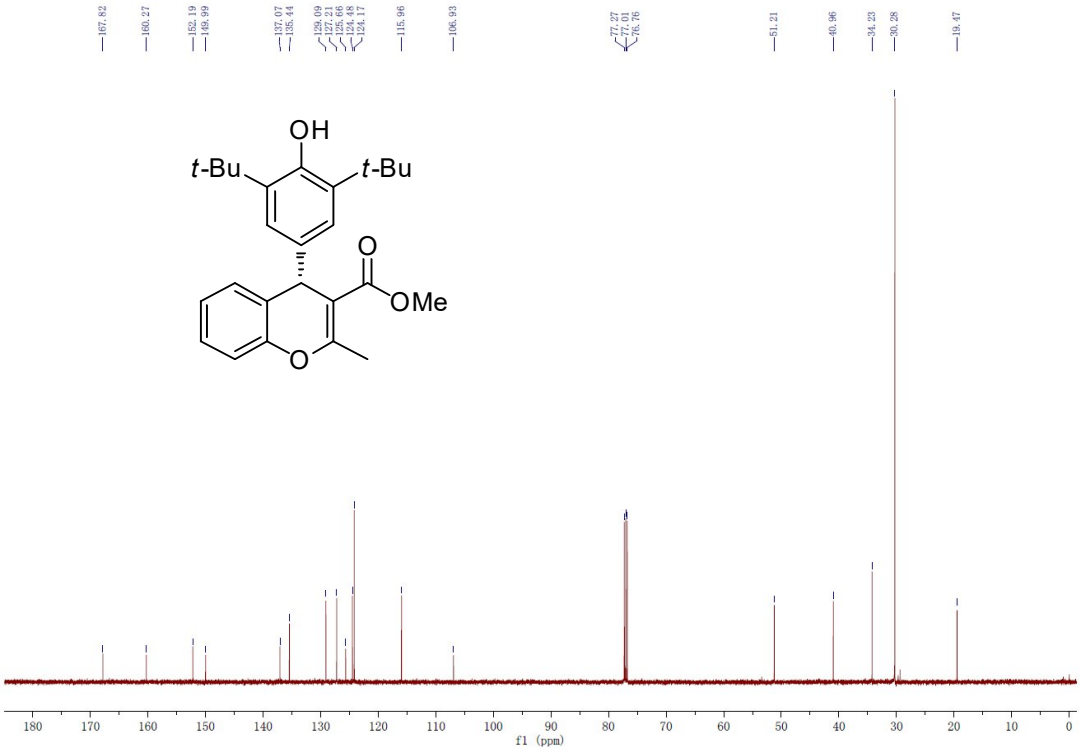
(*S*)-9-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (6aj)



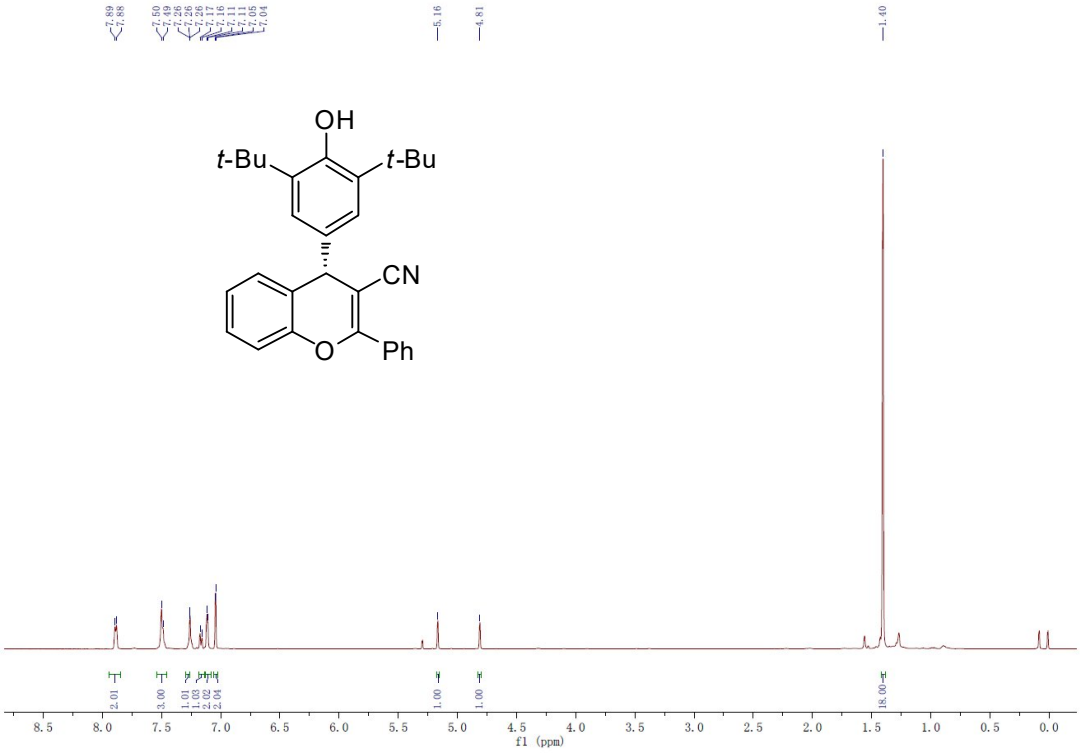


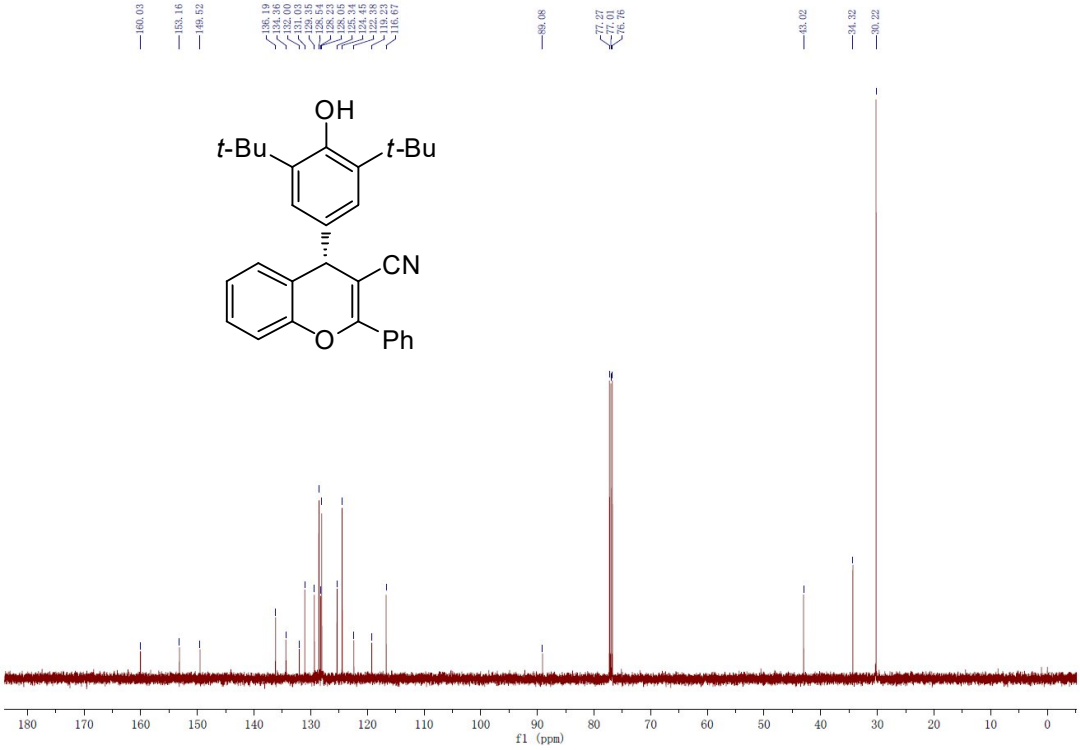
(*S*)-methyl 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxylate (6ak)





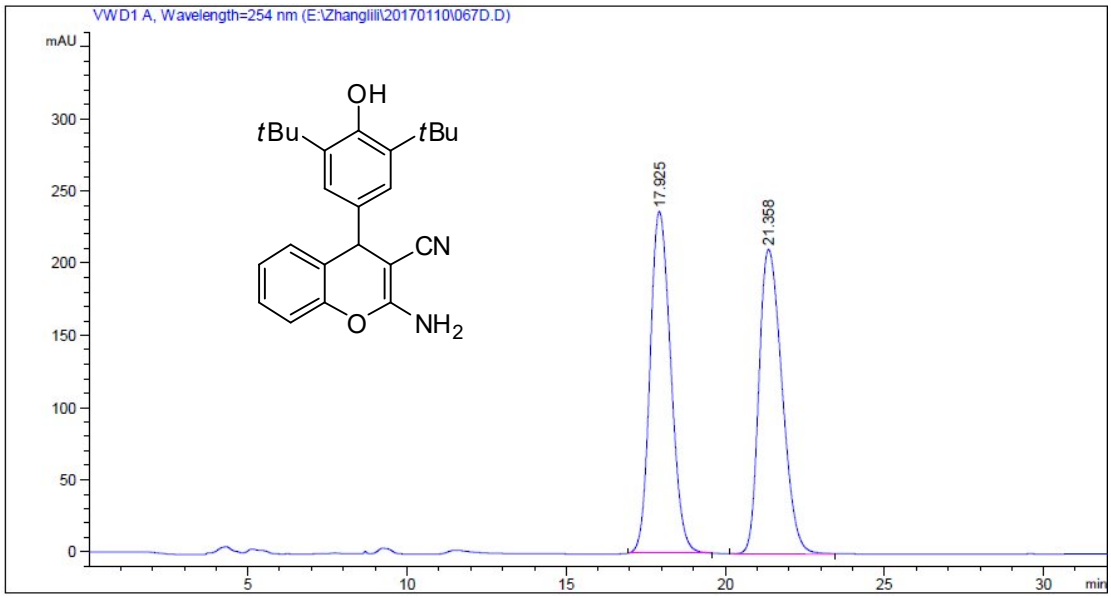
(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenyl-4*H*-chromene-3-carbonitrile (6al)



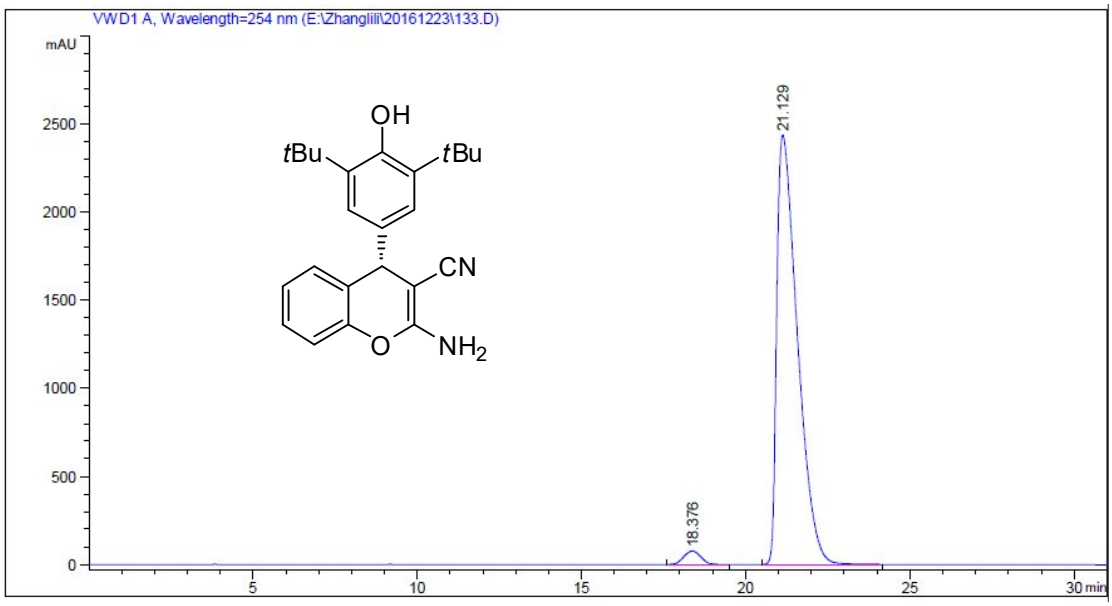


I: HPLC Analysis

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3a)

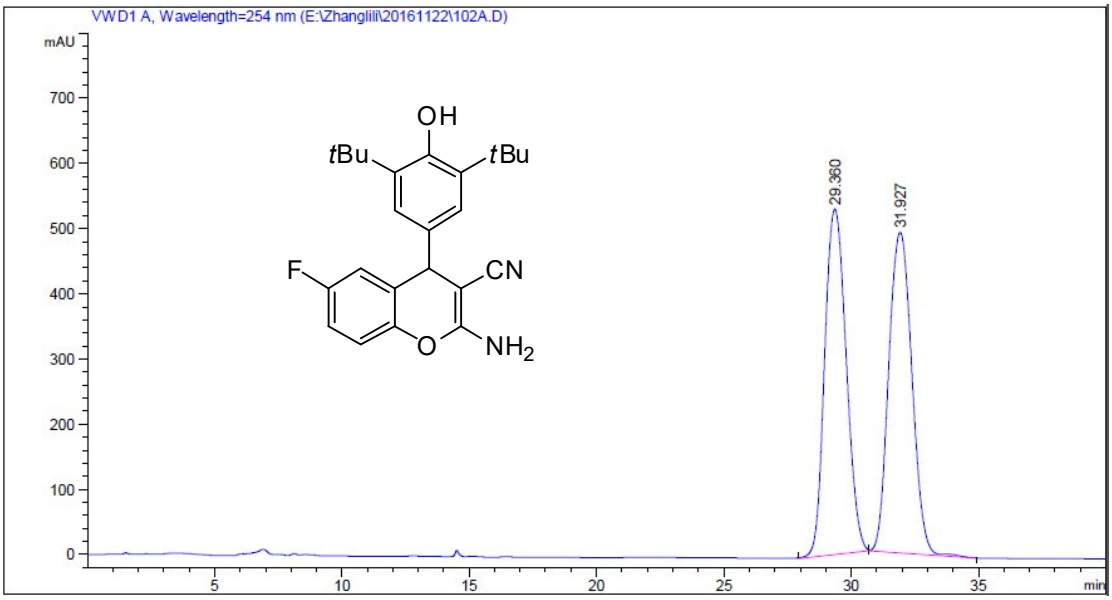


#	Time	Area	Height	Width	Symmetry	Area %
1	17.925	10694.6	236.6	0.7534	0.784	50.171
2	21.358	10621.6	210.8	0.8396	0.686	49.829

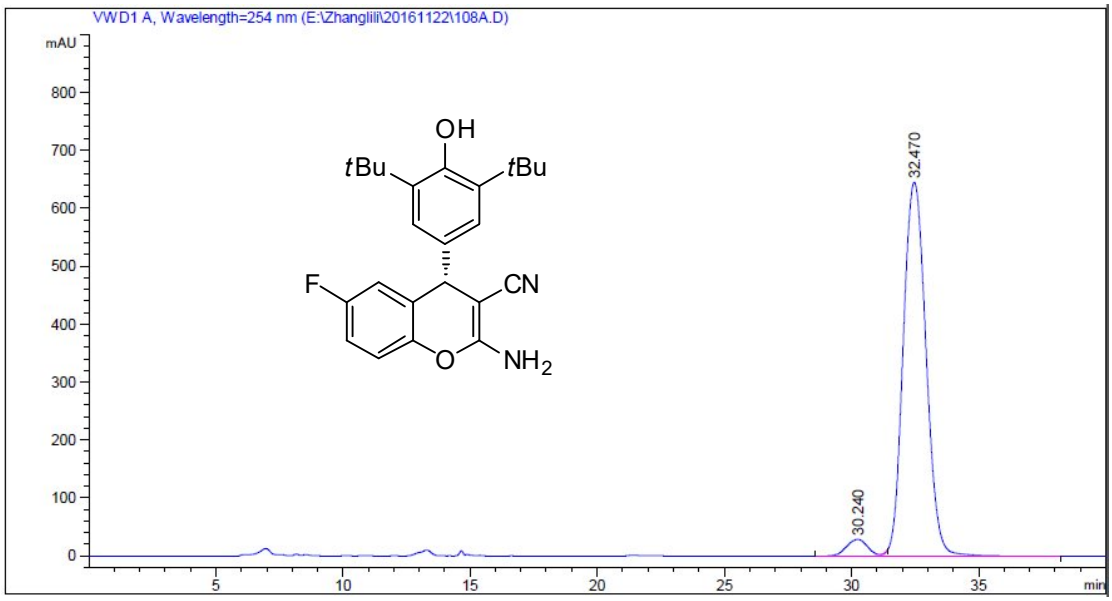


#	Time	Area	Height	Width	Symmetry	Area %
1	18.376	2762.5	76	0.6056	0.982	2.533
2	21.129	106293.7	2435.6	0.7235	0	97.467

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-4*H*-chromene-3-carbonitrile (3b)

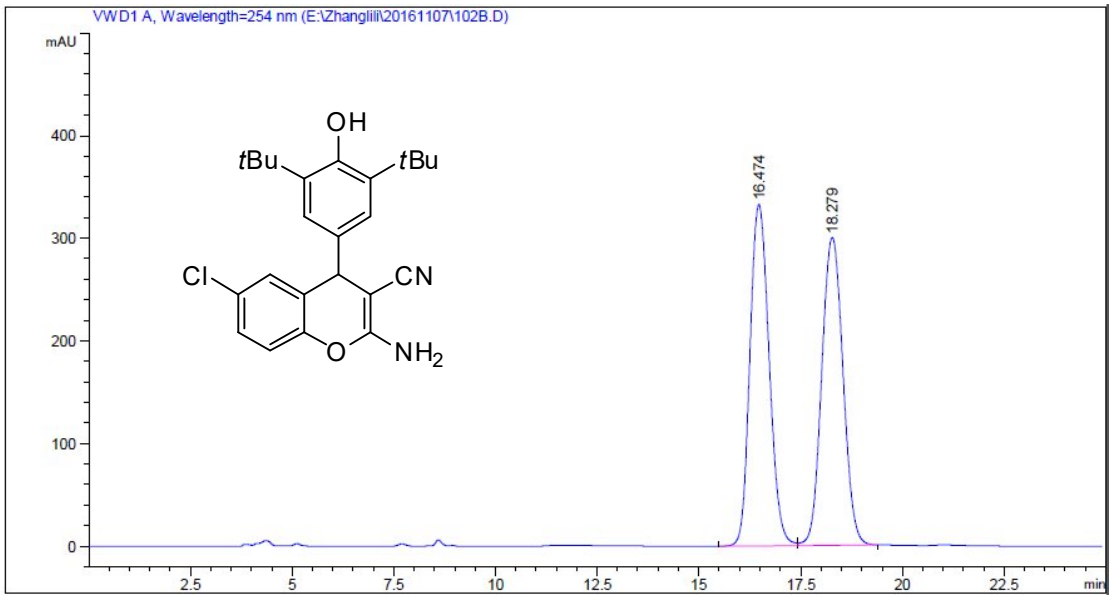


#	Time	Area	Height	Width	Symmetry	Area %
1	29.36	31031.7	530.1	0.9756	0.867	50.012
2	31.927	31016.3	491.7	1.0185	0	49.988

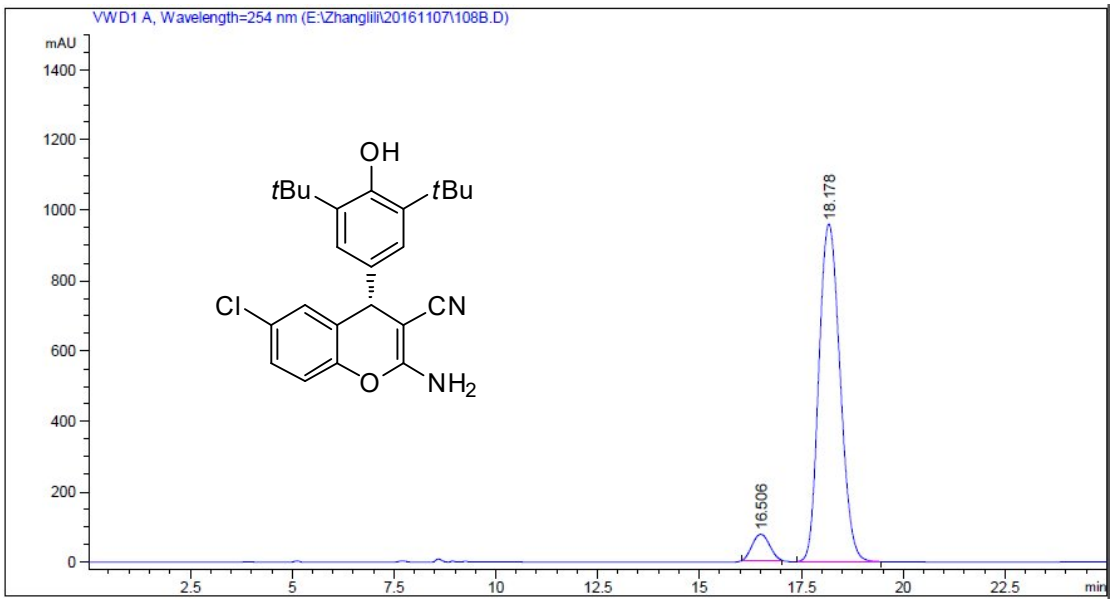


#	Time	Area	Height	Width	Symmetry	Area %
1	30.24	1673.4	29	0.9224	1.093	3.996
2	32.47	40201.4	645	0.9962	1.092	96.004

(*S*)-2-amino-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3c)

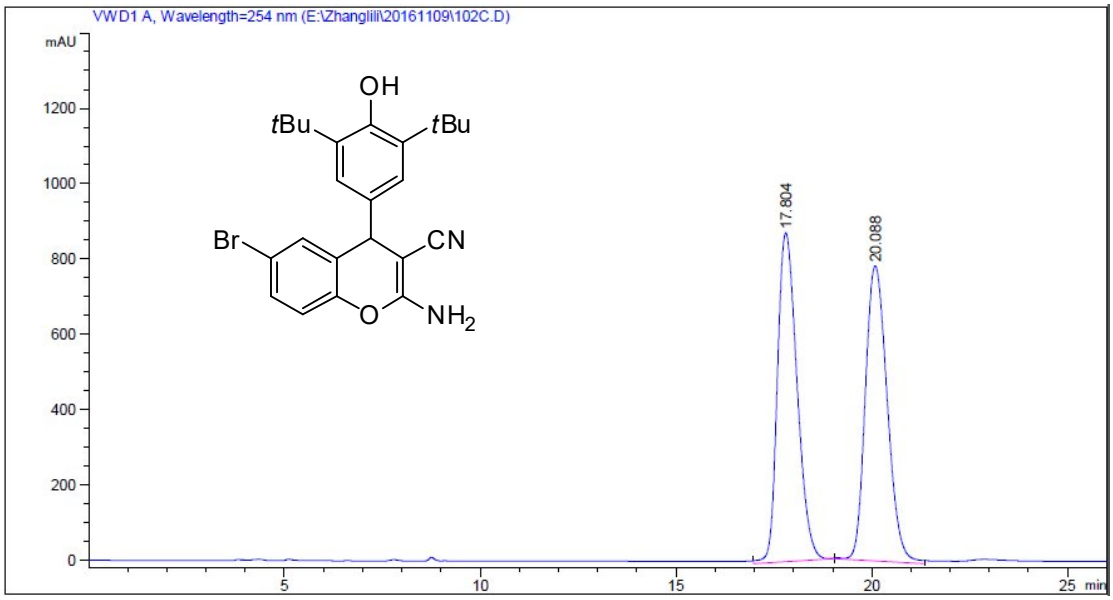


#	Time	Area	Height	Width	Symmetry	Area %
1	16.474	10894.8	332.6	0.5192	0.828	49.976
2	18.279	10905.3	299.9	0.5792	0.941	50.024

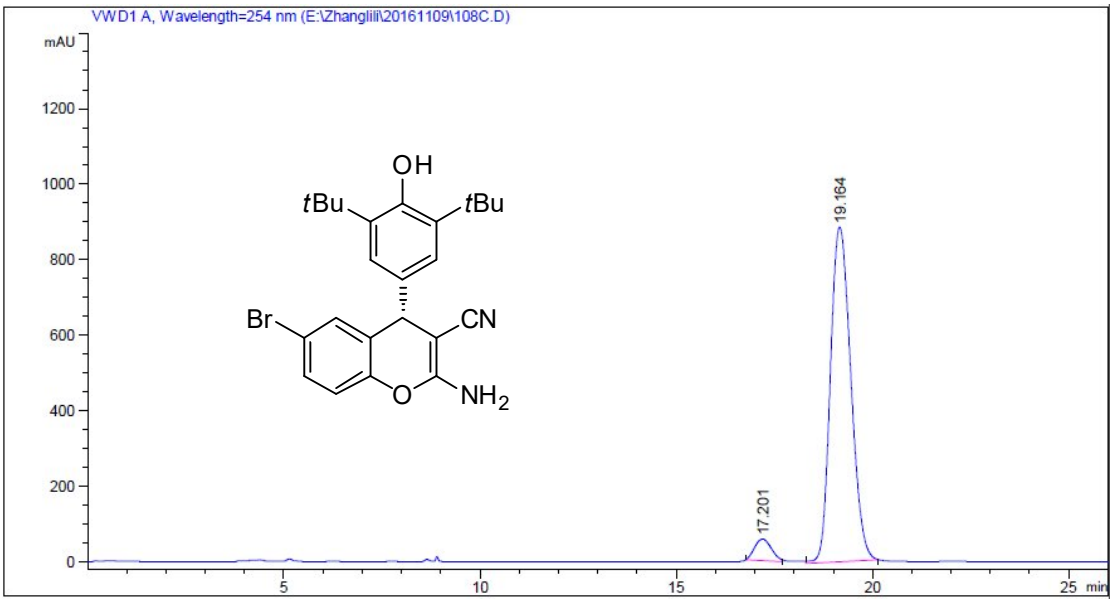


#	Time	Area	Height	Width	Symmetry	Area %
1	16.506	2210	74.7	0.4931	0.939	5.987
2	18.178	34700.5	960.4	0.5972	0	94.013

(*S*)-2-amino-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3d)

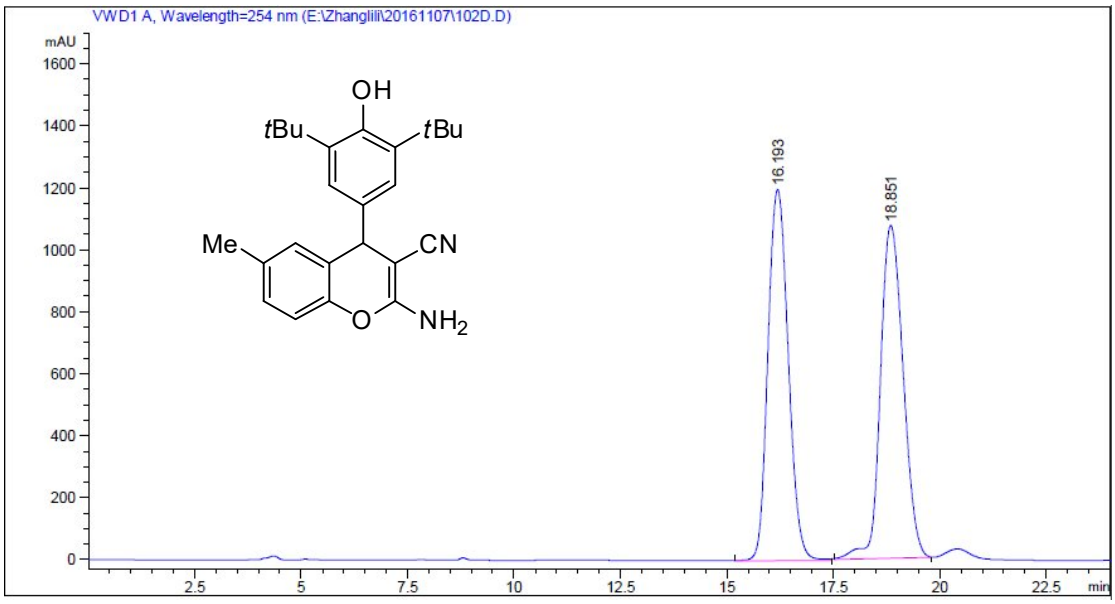


#	Time	Area	Height	Width	Symmetry	Area %
1	17.804	30357.2	873.5	0.5792	0.72	49.898
2	20.088	30481.6	783.8	0.6482	0.784	50.102

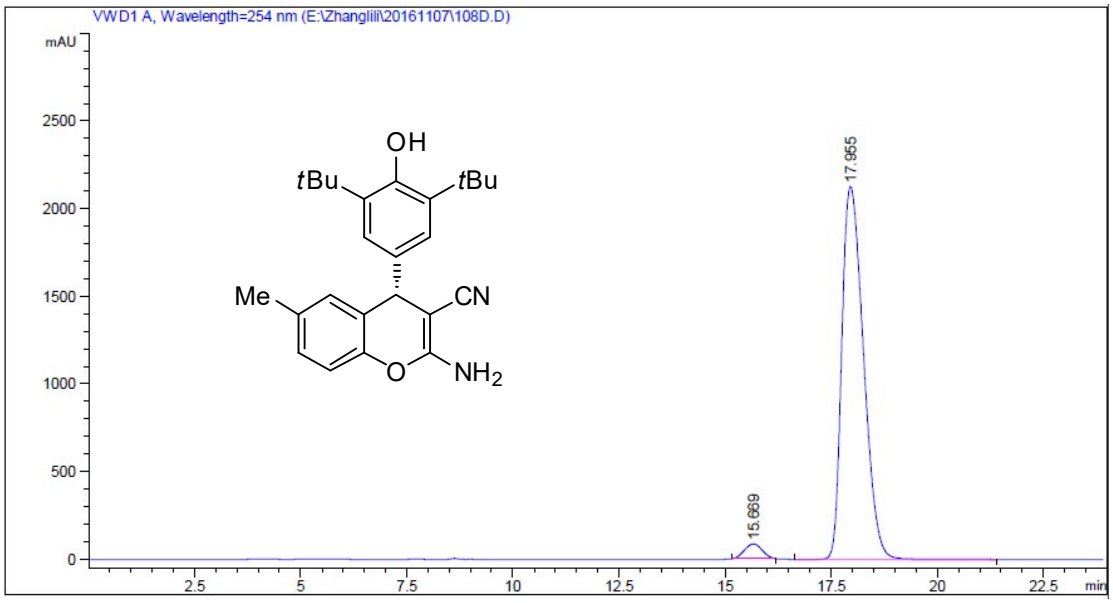


#	Time	Area	Height	Width	Symmetry	Area %
1	17.201	1721.2	57.5	0.4993	0.828	5.105
2	19.164	31995.7	886.4	0.6016	0.803	94.895

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-methyl-4*H*-chromene-3-carbonitrile (3e)

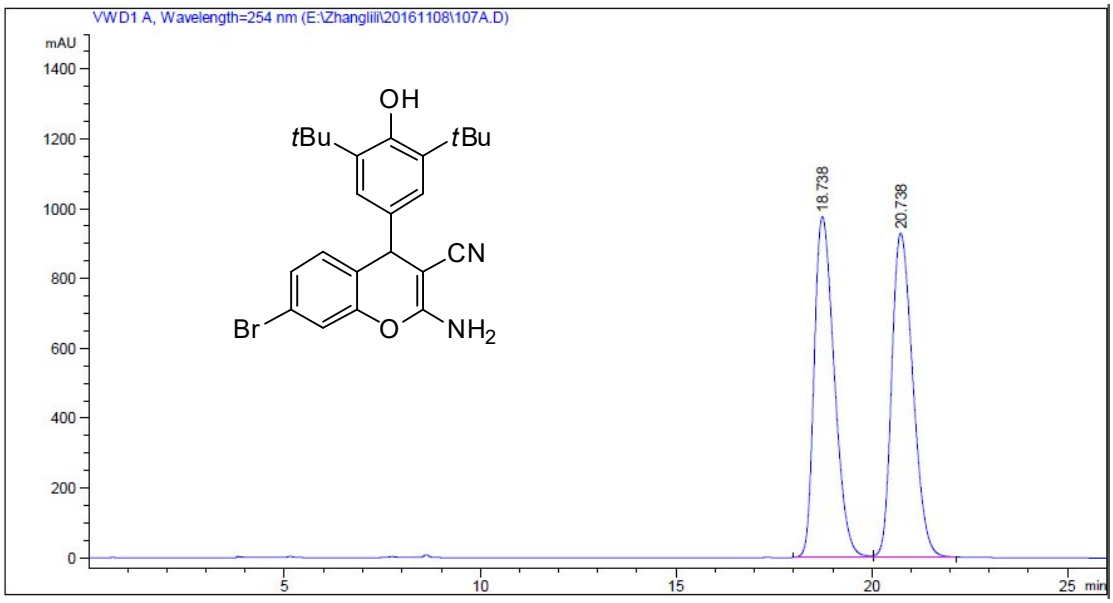


#	Time	Area	Height	Width	Symmetry	Area %
1	16.193	39715.7	1198.5	0.5523	0.868	49.827
2	18.851	39992.1	1073.3	0.621	0.824	50.173

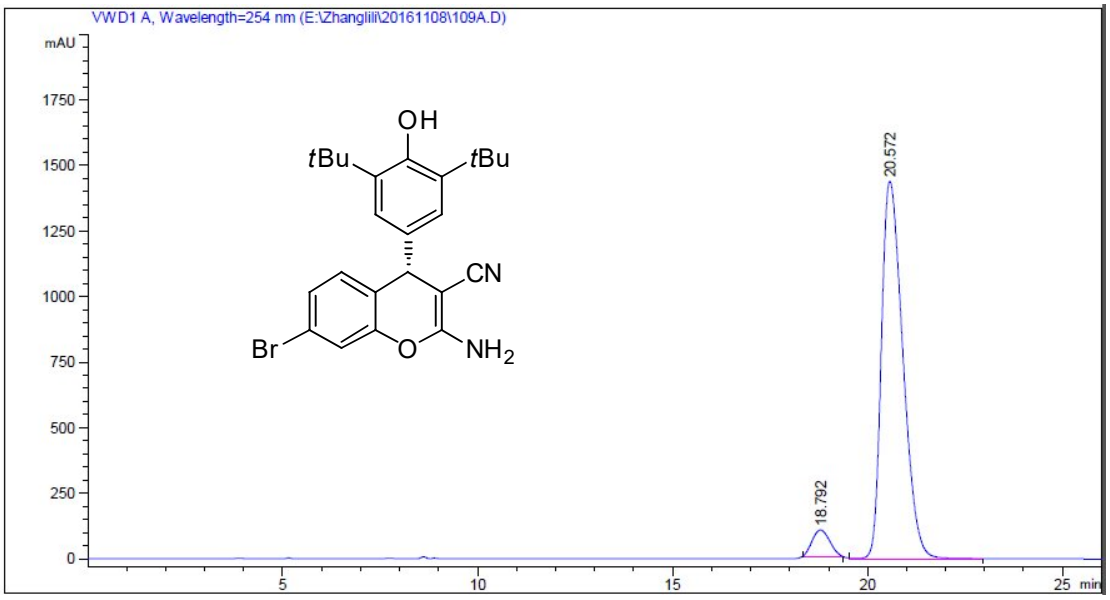


#	Time	Area	Height	Width	Symmetry	Area %
1	15.669	2466.1	84.1	0.4885	1.011	3.145
2	17.955	75937	2126.5	0.5952	0.636	96.855

(*S*)-2-amino-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (3f)

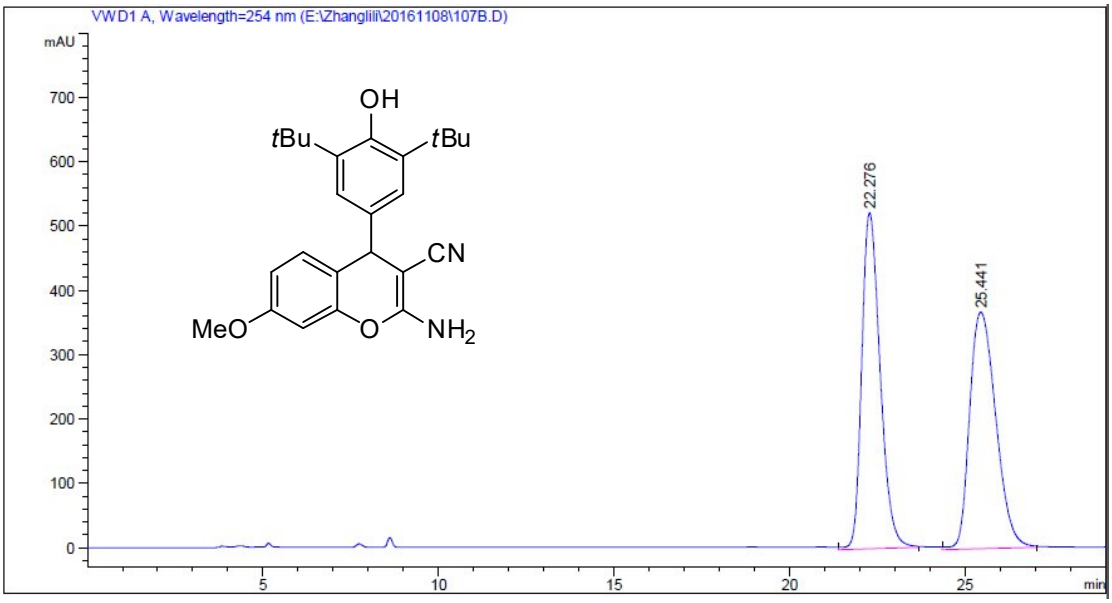


#	Time	Area	Height	Width	Symmetry	Area %
1	18.738	34753.9	977.4	0.5926	0.665	49.943
2	20.738	34833.7	929.3	0.6247	0.708	50.057

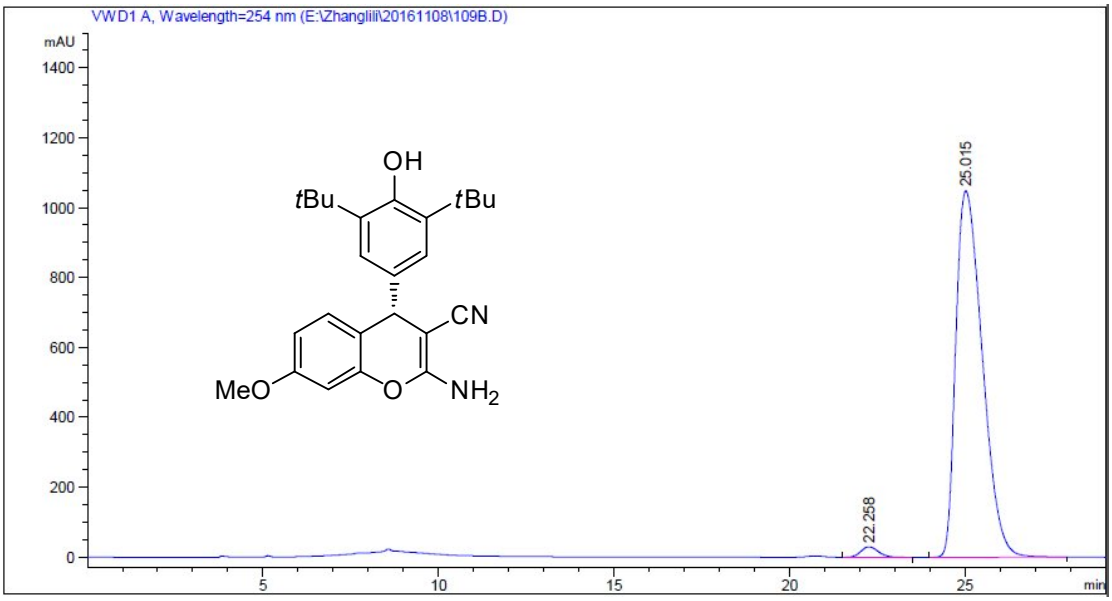


#	Time	Area	Height	Width	Symmetry	Area %
1	18.792	3148.1	101	0.5193	0.878	5.418
2	20.572	54952.1	1439.2	0.6128	0	94.582

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7-methoxy-4*H*-chromene-3-carbonitrile (3g)

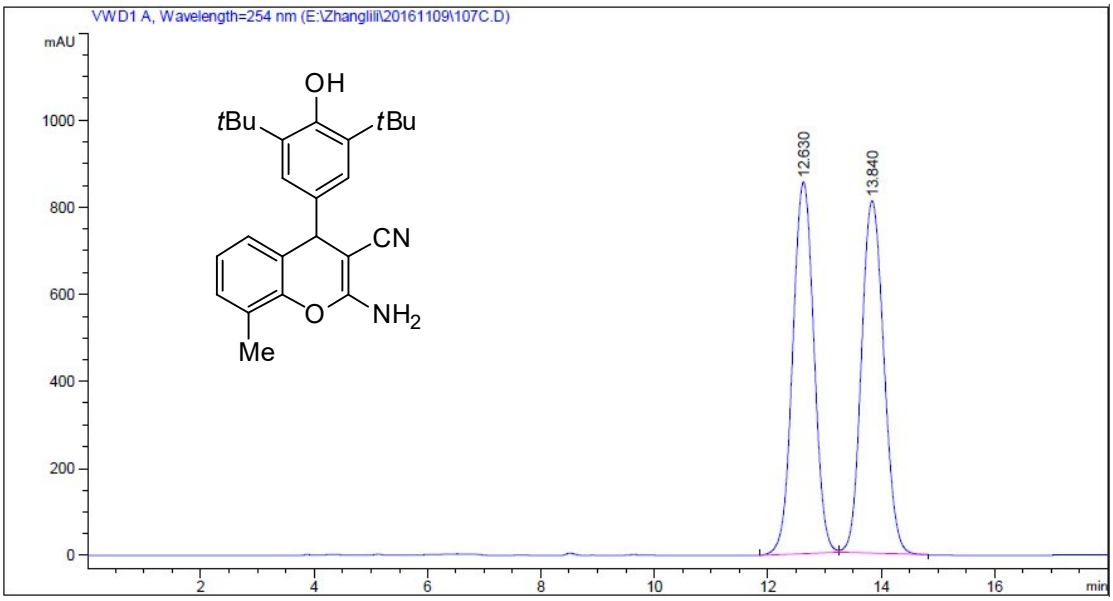


#	Time	Area	Height	Width	Symmetry	Area %
1	22.276	19004.4	522.3	0.6064	0.715	49.870
2	25.441	19103.7	367.7	0.8658	0.713	50.130

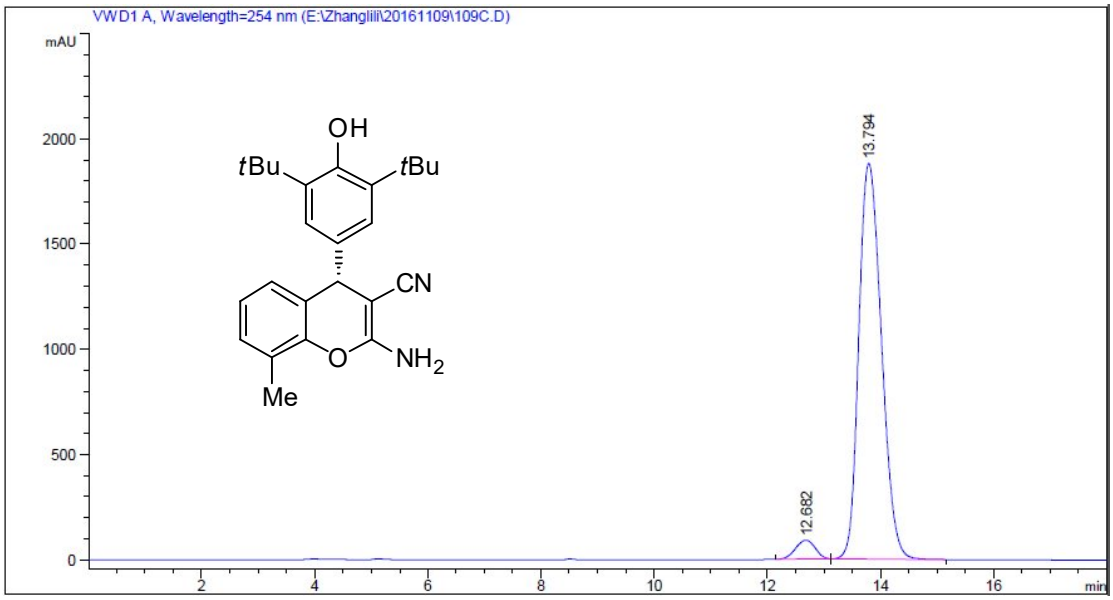


#	Time	Area	Height	Width	Symmetry	Area %
1	22.258	1067.9	30.5	0.5832	0.837	1.905
2	25.015	54996.2	1049.9	0.873	0.584	98.095

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-methyl-4*H*-chromene-3-carbonitrile (3h)

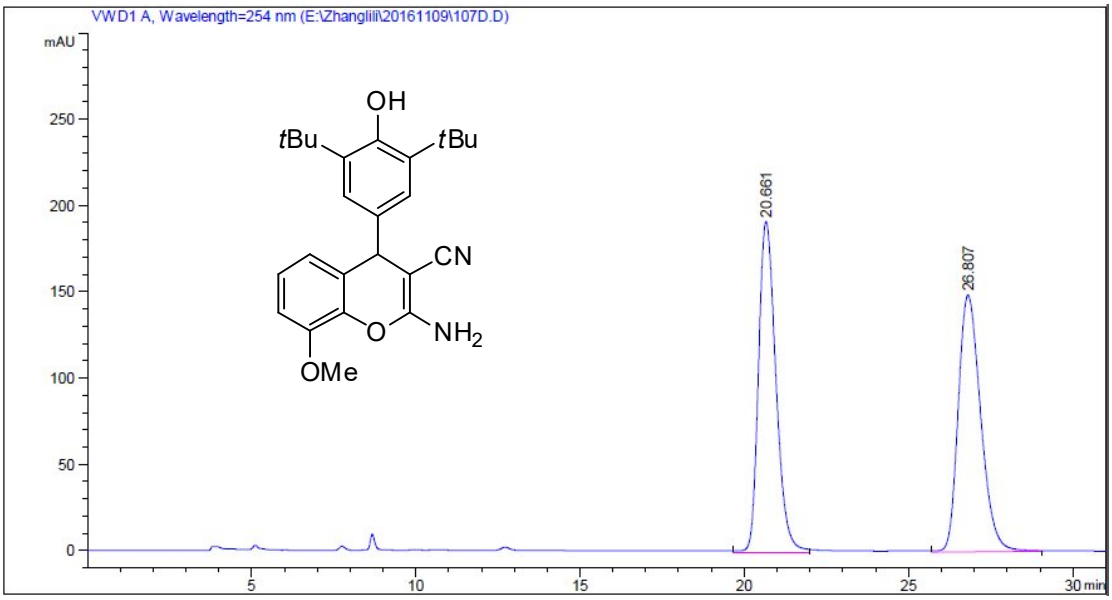


#	Time	Area	Height	Width	Symmetry	Area %
1	12.63	22172.8	853.5	0.4294	0	50.088
2	13.84	22095	809.2	0.4481	0	49.912

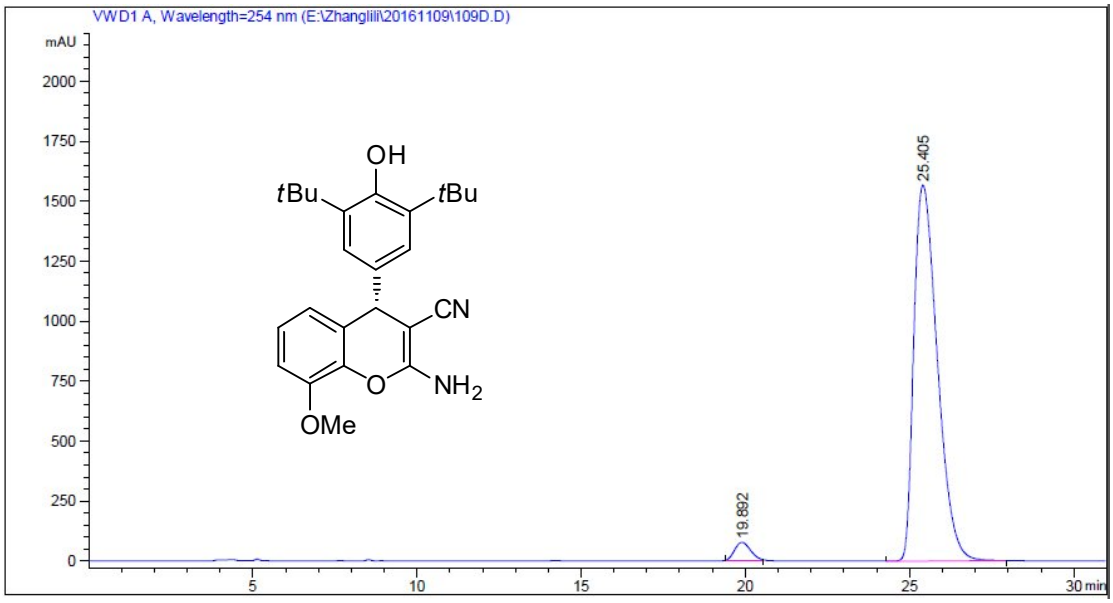


#	Time	Area	Height	Width	Symmetry	Area %
1	12.682	2186.1	89.7	0.4063	1.095	4.023
2	13.794	52156.7	1880.3	0.441	0	95.977

(*S*)-2-amino-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-methoxy-4*H*-chromene-3-carbonitrile (3i)

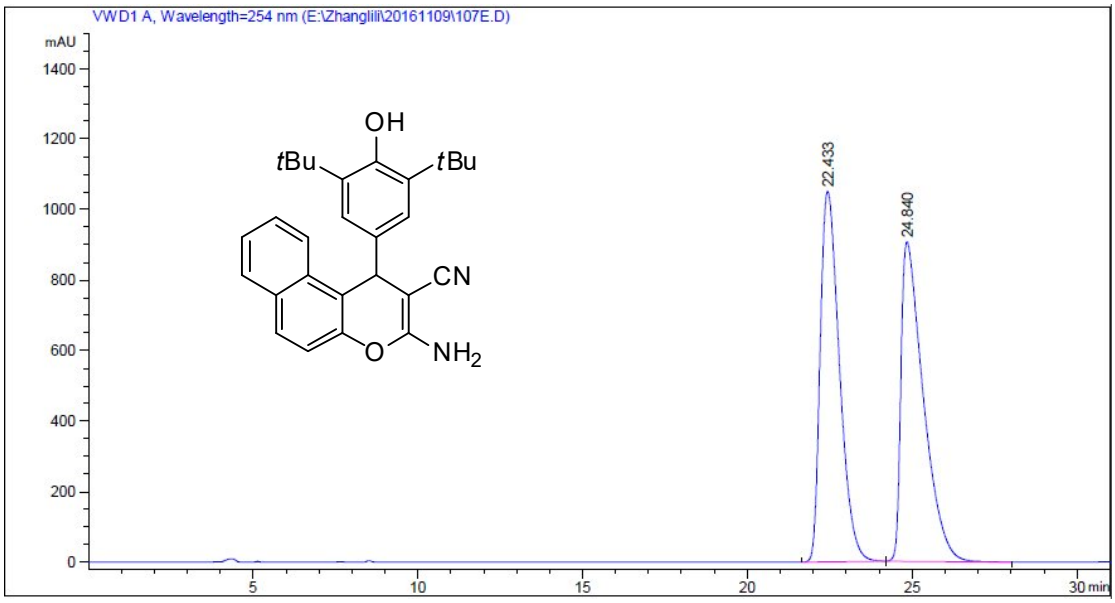


#	Time	Area	Height	Width	Symmetry	Area %
1	20.661	7087.6	192.1	0.6148	0.739	49.945
2	26.807	7103.1	148.9	0.7952	0.737	50.055

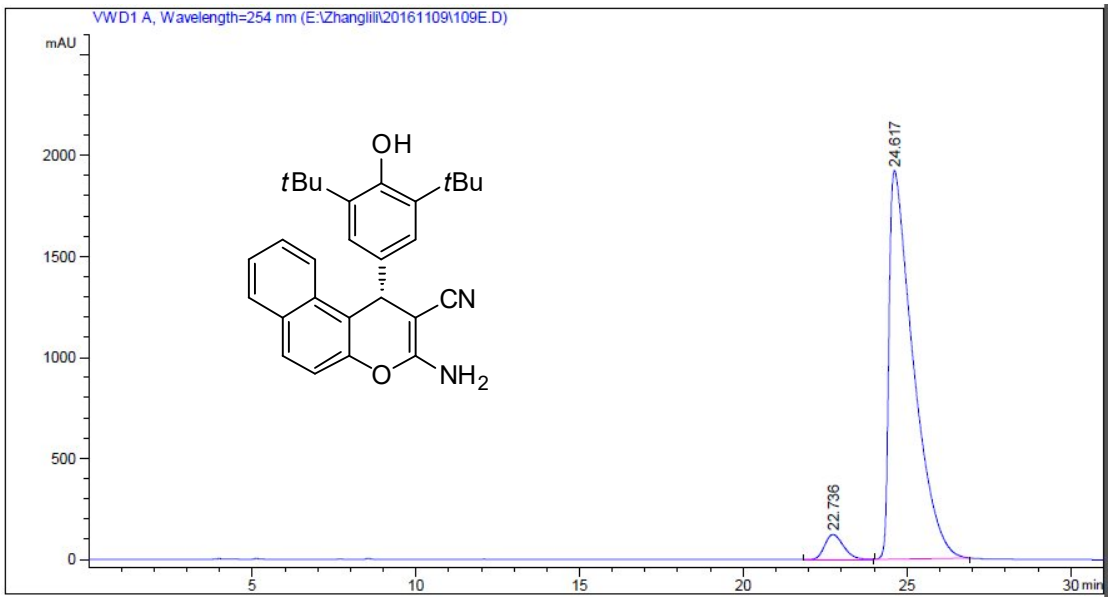


#	Time	Area	Height	Width	Symmetry	Area %
1	19.892	2426.6	73.8	0.5479	0.83	3.023
2	25.405	77838.9	1566.2	0.8201	0	96.977

(*S*)-3-amino-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (3j)

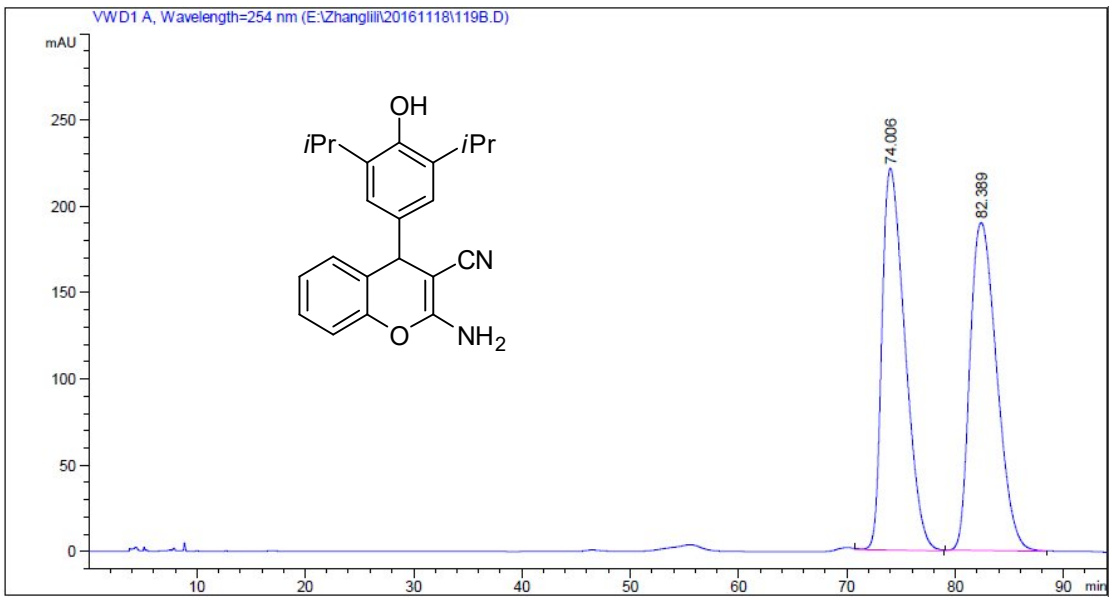


#	Time	Area	Height	Width	Symmetry	Area %
1	22.433	42590.8	1050.8	0.6734	0	49.967
2	24.84	42647.2	906.2	0.7064	0	50.033

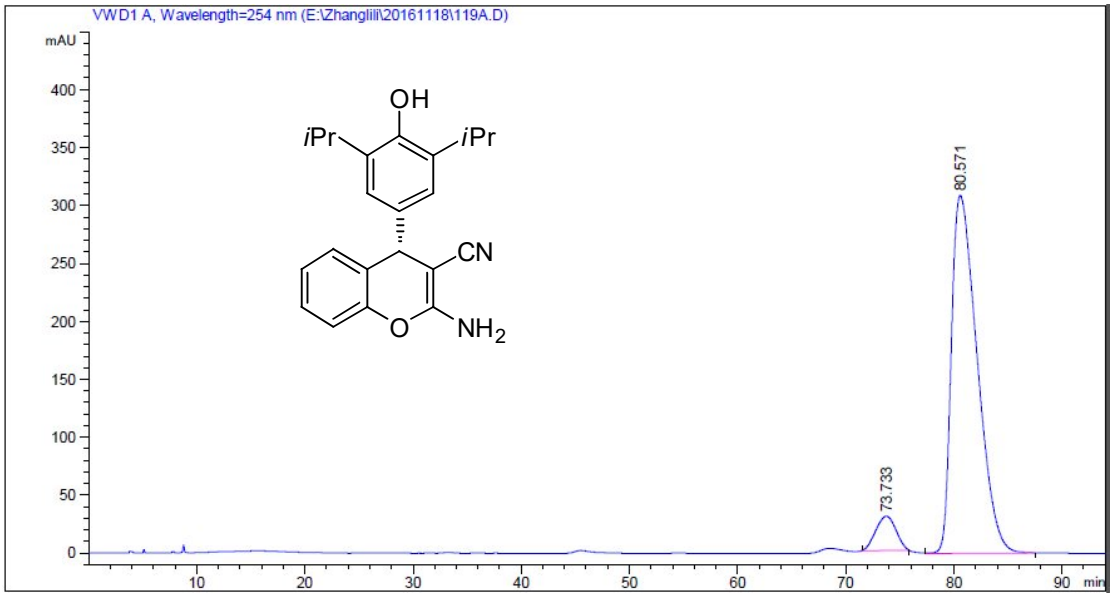


#	Time	Area	Height	Width	Symmetry	Area %
1	22.736	4973.4	123.3	0.6723	0.761	4.812
2	24.617	98388	1922.7	0.7076	0	95.188

(*S*)-2-amino-4-(4-hydroxy-3,5-diisopropylphenyl)-4*H*-chromene-3-carbonitrile (3k)

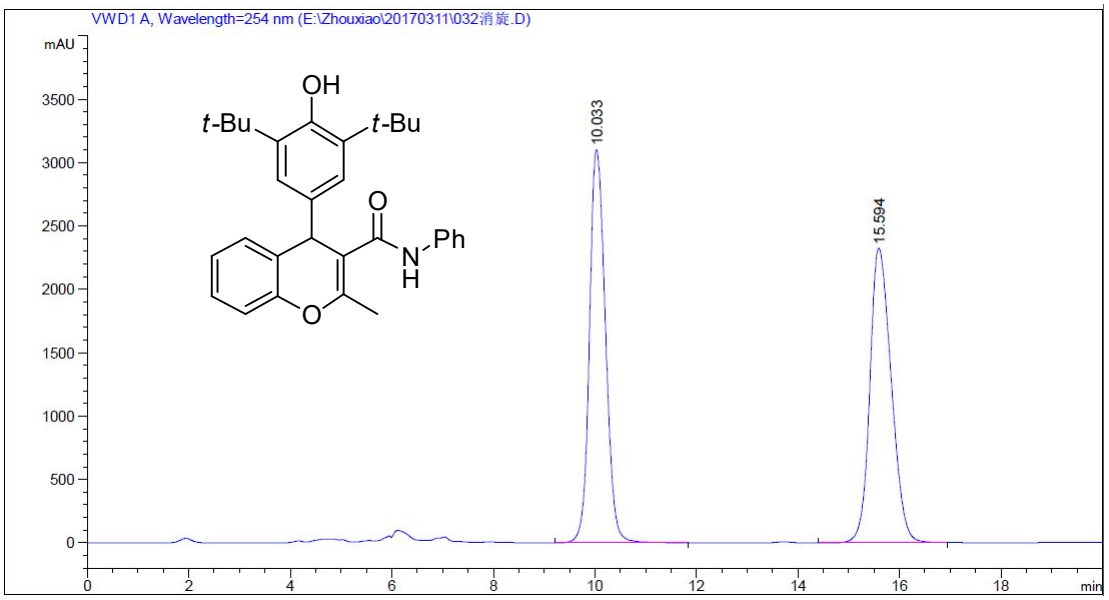


#	Time	Area	Height	Width	Symmetry	Area %
1	74.006	32531.8	221.2	2.2659	0	49.911
2	82.389	32647.3	190.1	2.6941	0	50.089

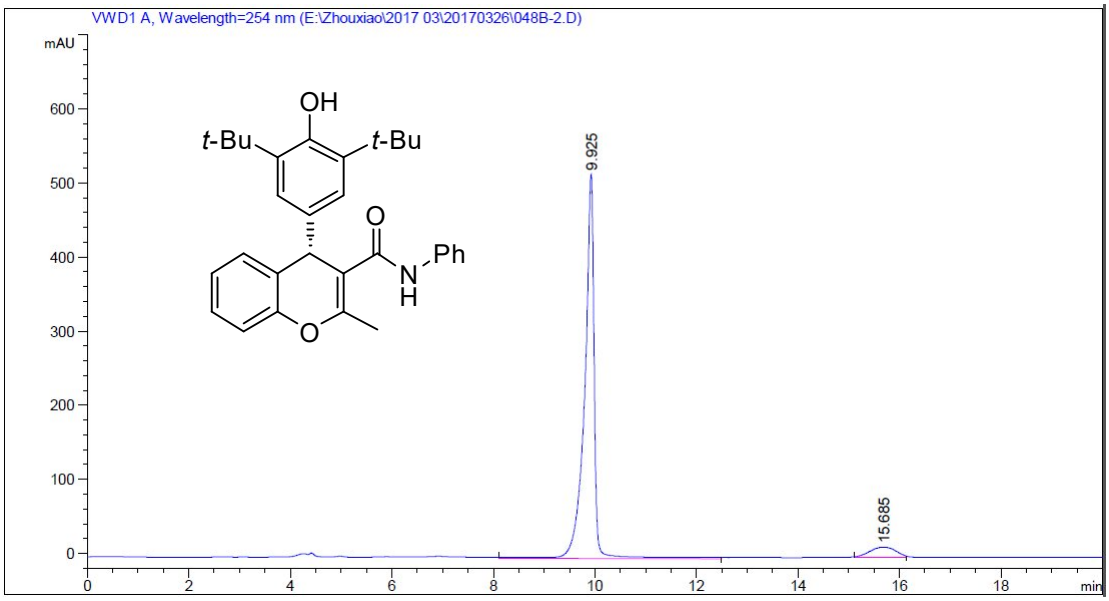


#	Time	Area	Height	Width	Symmetry	Area %
1	73.733	3843.1	29.6	2.1668	1.051	7.011
2	80.571	50974.2	308.9	2.7505	0.502	92.989

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6aa)

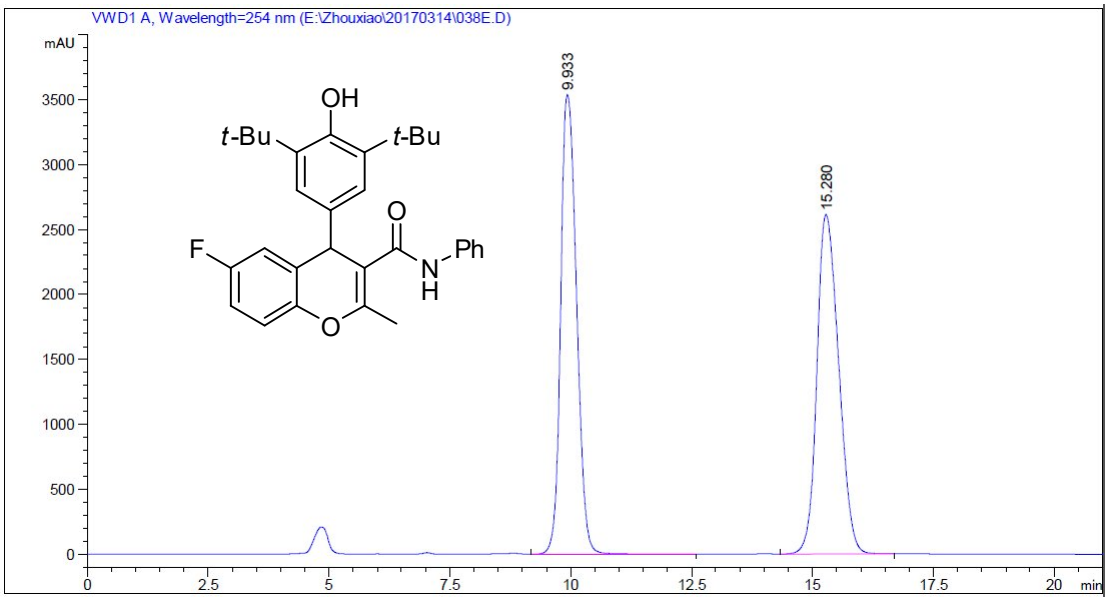


#	Time	Area	Height	Width	Symmetry	Area%
1	10.033	67820	3098.6	0.3434	0.756	50.017
2	15.594	67774.6	2320.5	0.4868	0.702	49.983

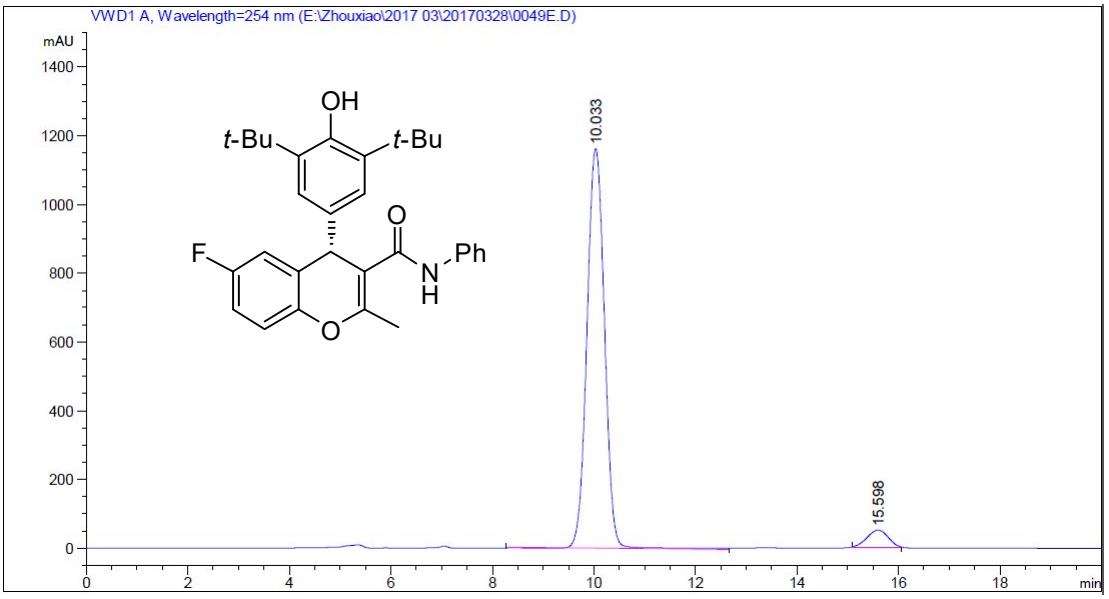


#	Time	Area	Height	Width	Symmetry	Area%
1	9.925	6931	518.8	0.2226	1.825	93.826
2	15.685	456	13.2	0.5743	1.07	6.174

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ba)

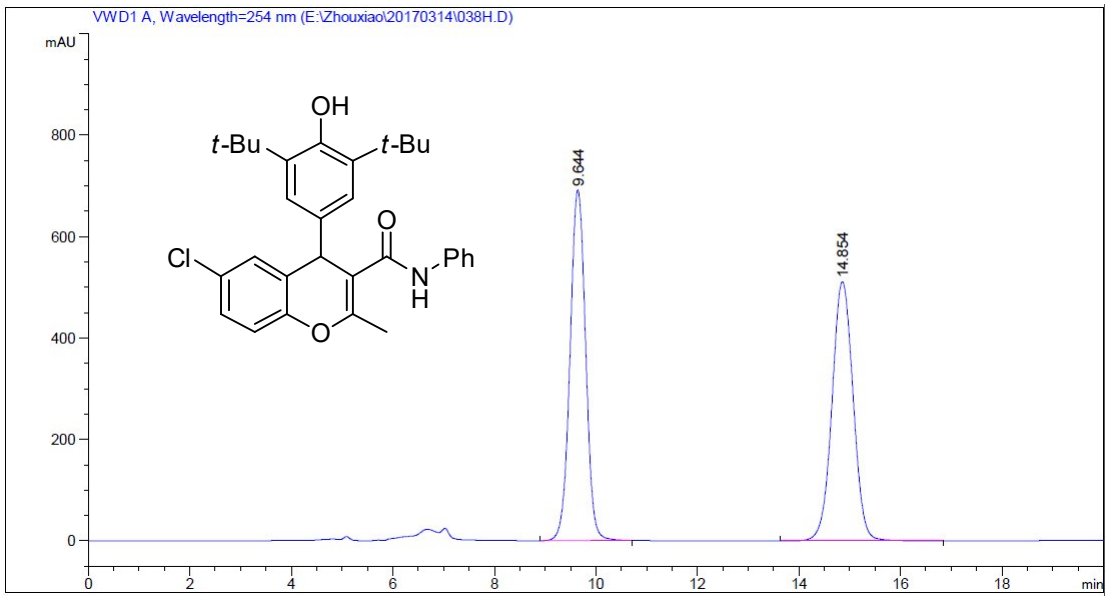


#	Time	Area	Height	Width	Symmetry	Area%
1	9.933	80665.8	3537.2	0.3571	0.71	49.604
2	15.28	81954.3	2613.6	0.4918	0.691	50.396

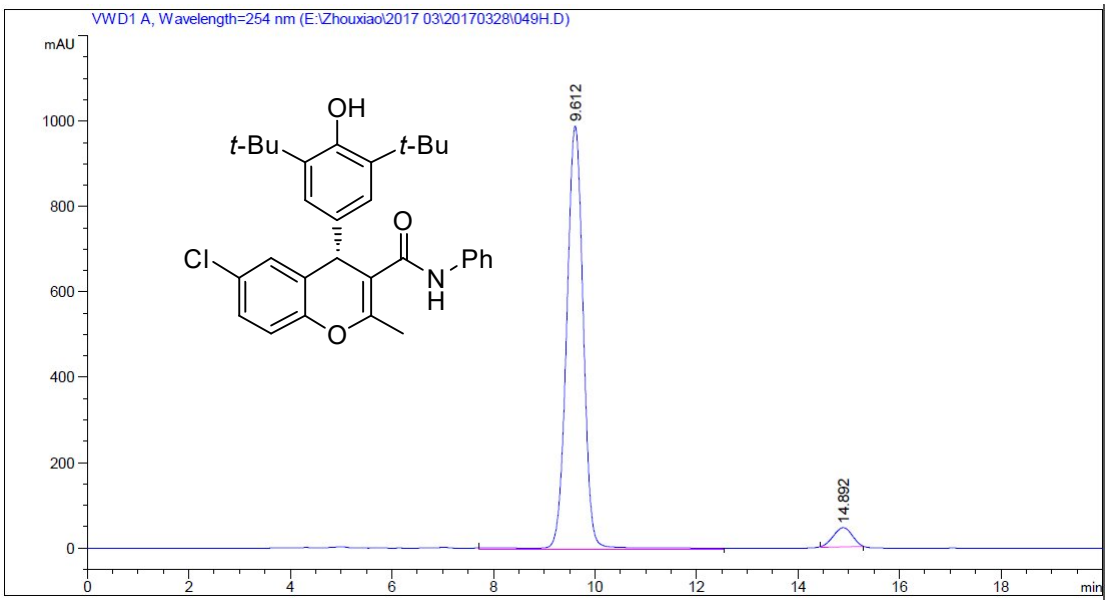


#	Time	Area	Height	Width	Symmetry	Area%
1	10.033	27887.1	1162.2	0.3999	0.932	94.824
2	15.598	1522.1	0.4947	1.099	1.099	5.176

(*S*)-6-chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ca)

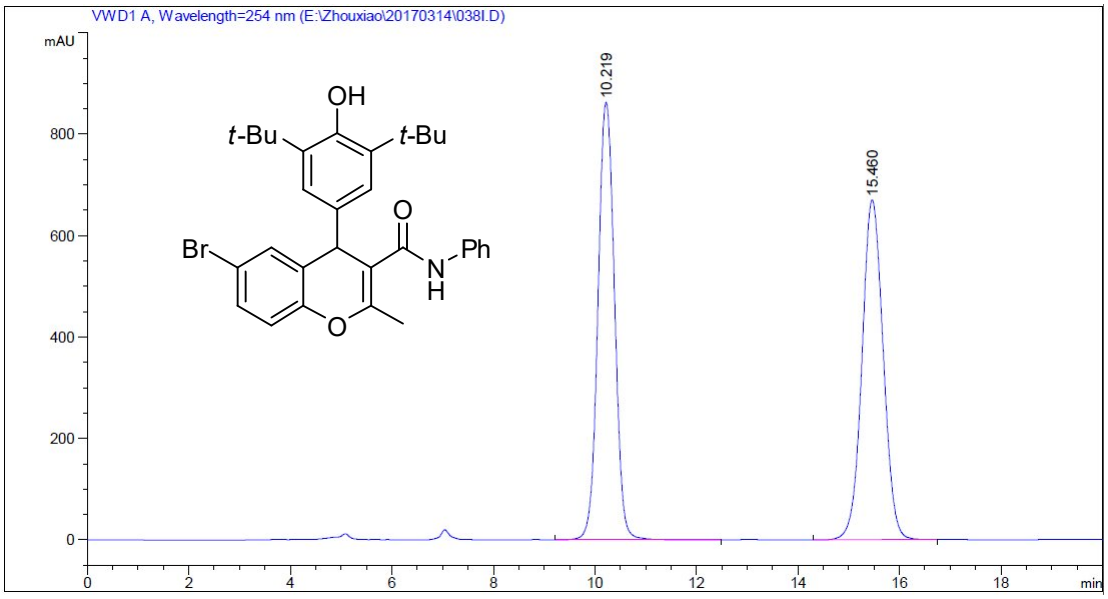


#	Time	Area	Height	Width	Symmetry	Area%
1	9.644	14723.9	690.8	0.3347	0.974	49.882
2	14.854	14793.4	511	0.4537	0.936	50.118

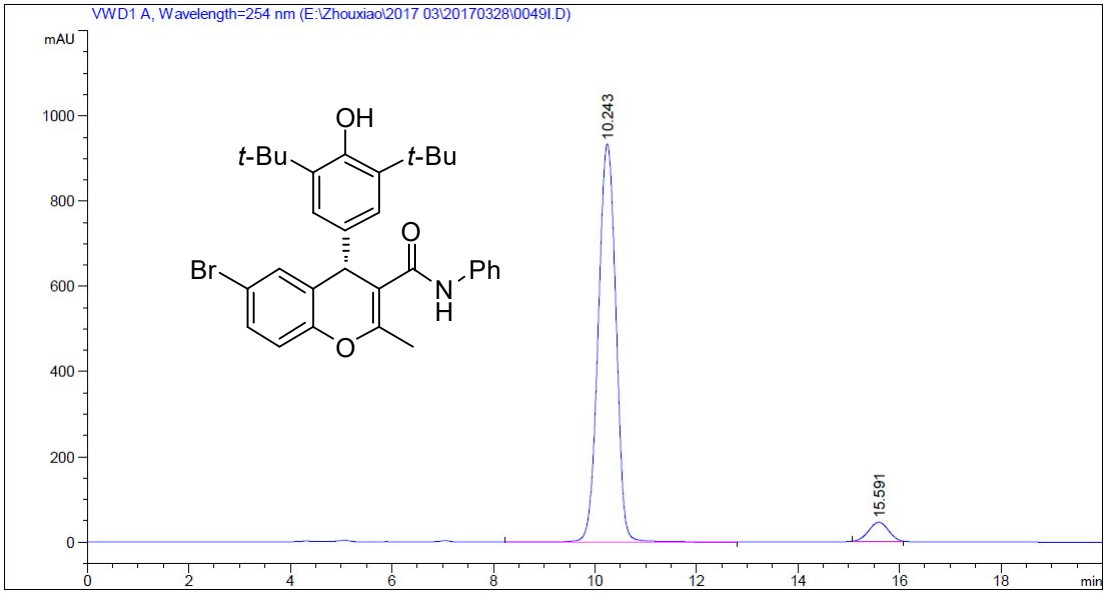


#	Time	Area	Height	Width	Symmetry	Area%
1	9.612	22737.3	991.6	0.3822	1.001	95.115
2	14.892	1167.8	45	0.4329	1.101	4.885

(*S*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6da)

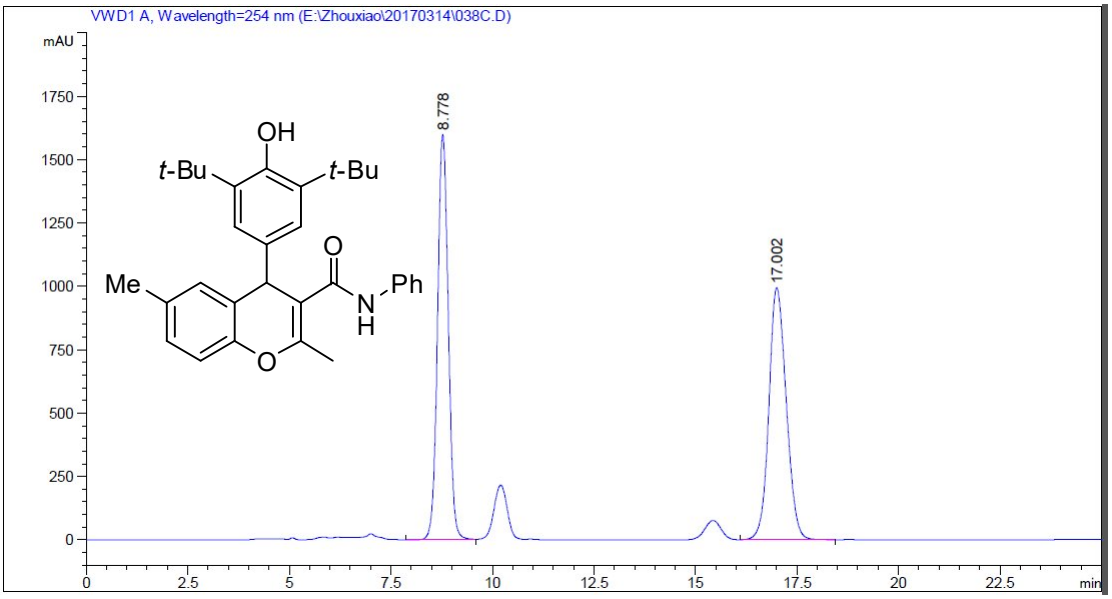


#	Time	Area	Height	Width	Symmetry	Area%
1	10.219	19537.3	863.1	0.3571	0.923	50.071
2	15.46	19481.5	670	0.4532	0.905	49.929

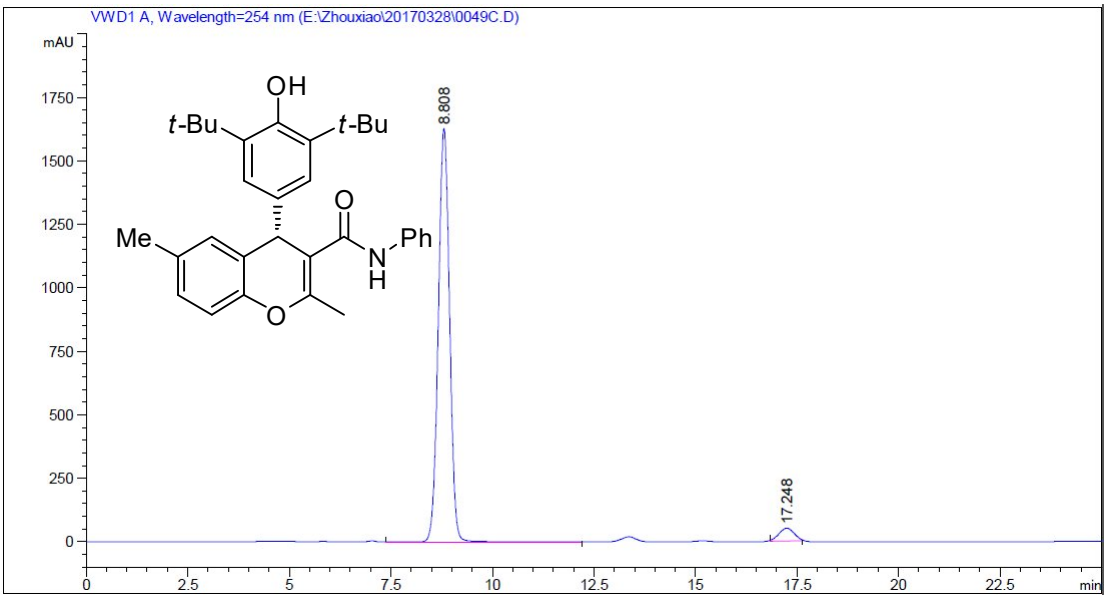


#	Time	Area	Height	Width	Symmetry	Area%
1	10.243	22787.9	935.2	0.4061	1.002	94.864
2	15.591	1233.6	45	0.4572	1.027	5.136

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,6-dimethyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ea)

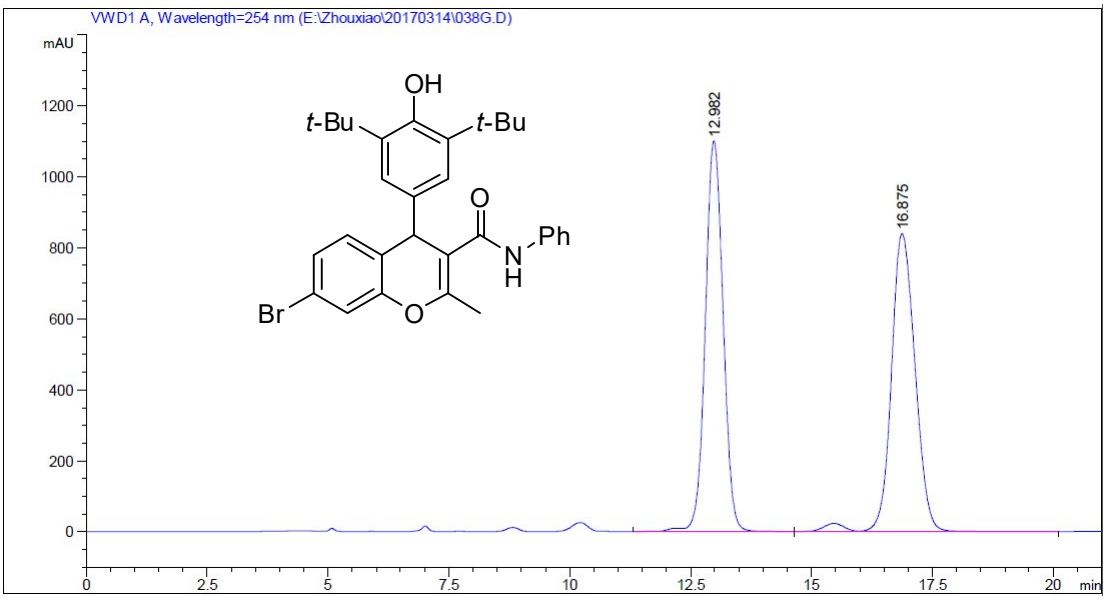


#	Time	Area	Height	Width	Symmetry	Area%
1	8.778	29386.5	1599.2	0.2864	0.891	49.878
2	17.002	29530.7	993.8	0.4597	0.796	50.122

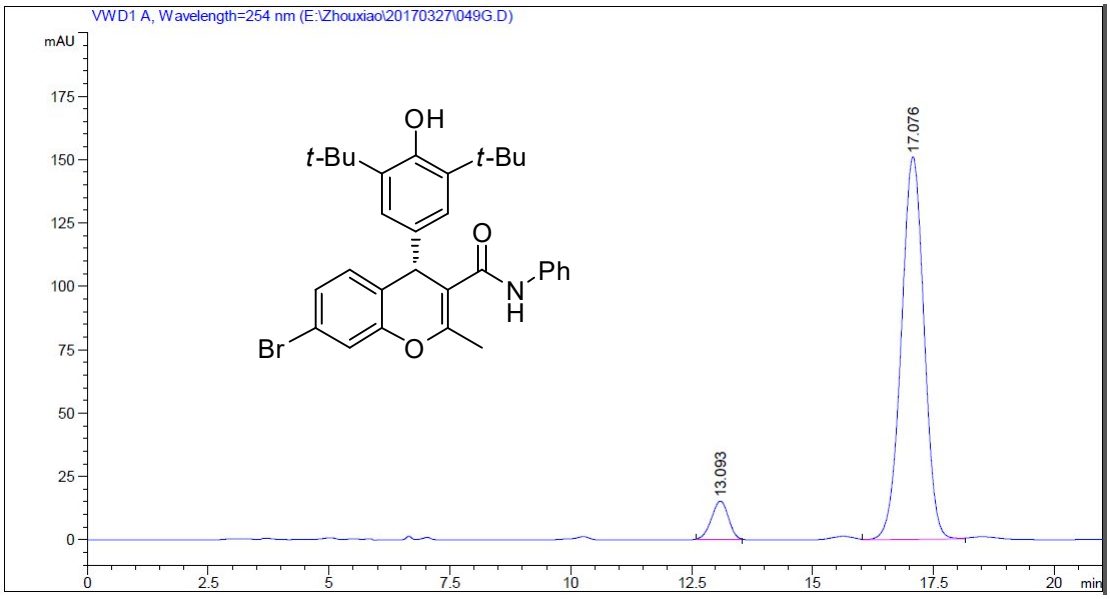


#	Time	Area	Height	Width	Symmetry	Area%
1	8.808	31829.9	1627.7	0.3259	0.952	95.980
2	17.248	1333	50.4	0.441	1.046	4.020

(*S*)-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6fa)

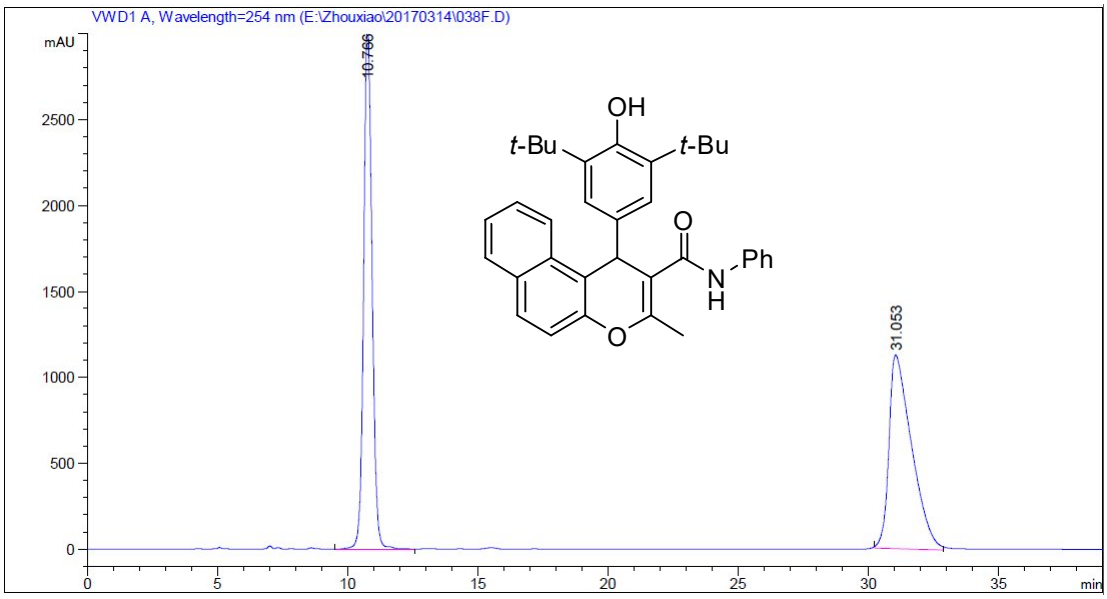


#	Time	Area	Height	Width	Symmetry	Area%
1	12.982	28287.2	1100.2	0.3999	0.932	49.367
2	16.875	29012.2	839.4	0.5287	0.889	50.633

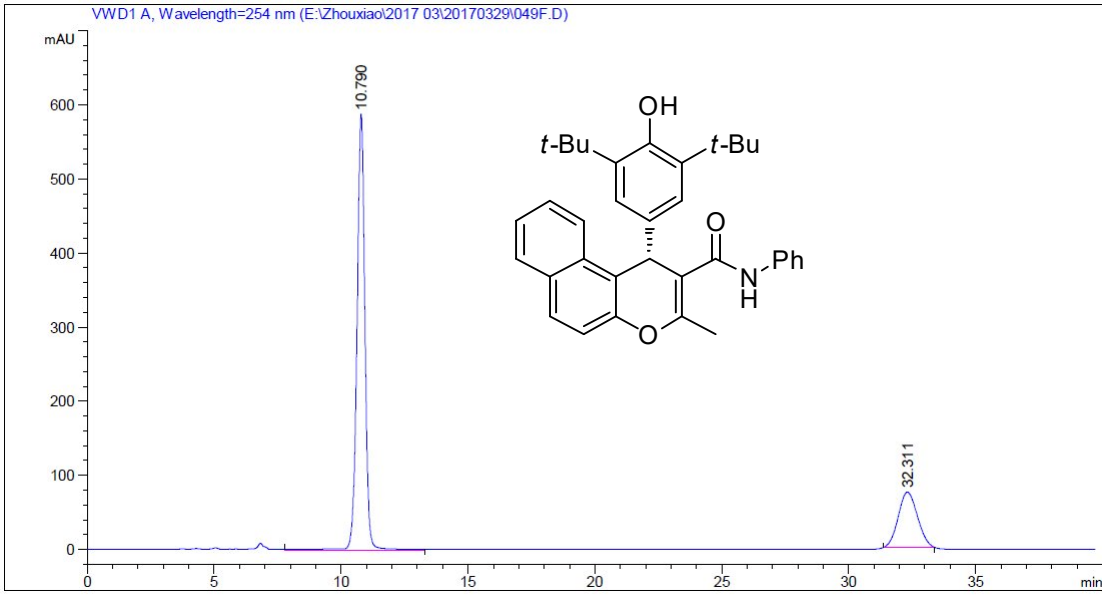


#	Time	Area	Height	Width	Symmetry	Area%
1	13.093	364.9	15.1	0.4038	1.074	6.899
2	17.076	4923.8	150.8	0.5442	1.015	93.101

(*S*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-methyl-*N*-phenyl-1*H*-benzo[*f*] chromene-2-carboxamide (6ga)

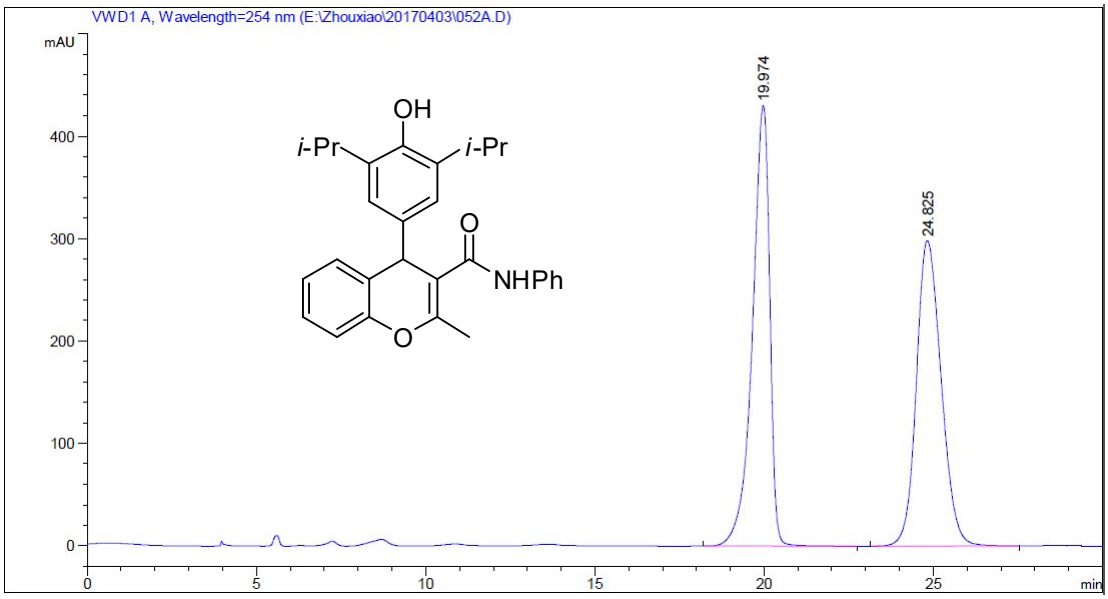


#	Time	Area	Height	Width	Symmetry	Area%
1	10.766	68116.8	3068	0.3378	0.816	50.020
2	31.053	68061.1	1127.3	1.0063	0.414	49.980

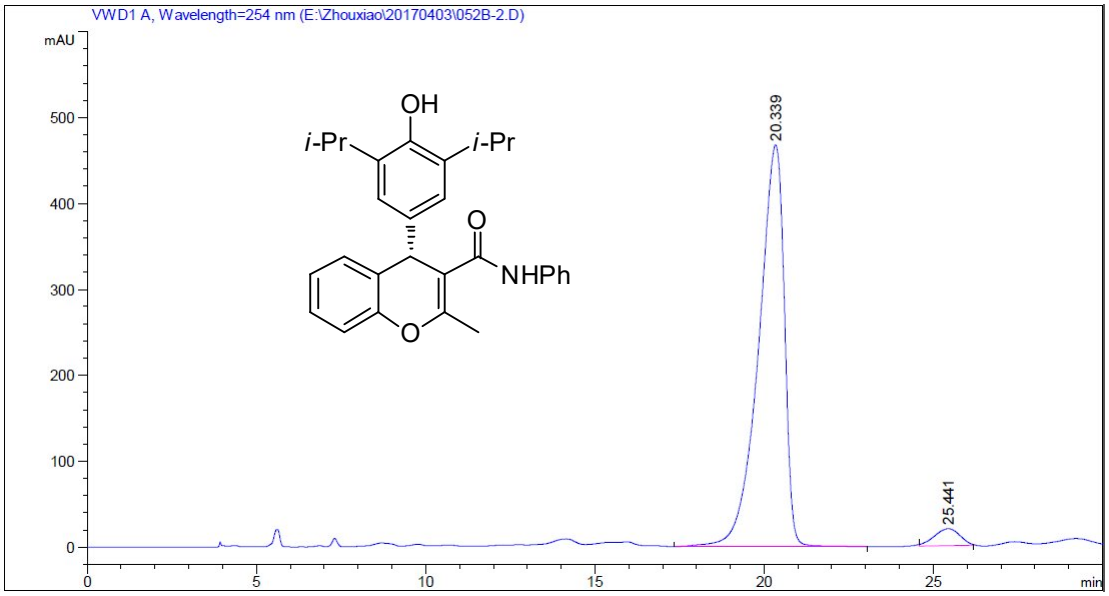


#	Time	Area	Height	Width	Symmetry	Area%
1	10.79	12980.7	588.8	0.3674	1.056	76.855
2	32.311	3909.2	74.5	0.8747	0.887	23.145

(*S*)-4-(4-hydroxy-3,5-diisopropylphenyl)-2-methyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ha)

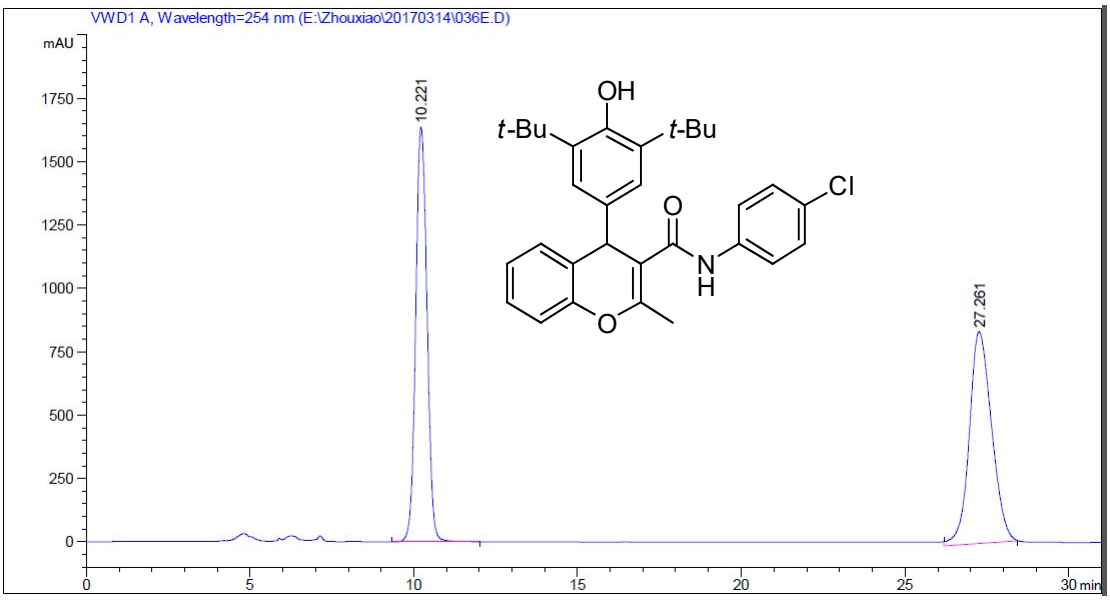


#	Time	Area	Height	Width	Symmetry	Area%
1	19.974	15243.2	430.2	0.5414	1.619	50.097
2	24.825	15184.3	298.3	0.794	0.765	49.903

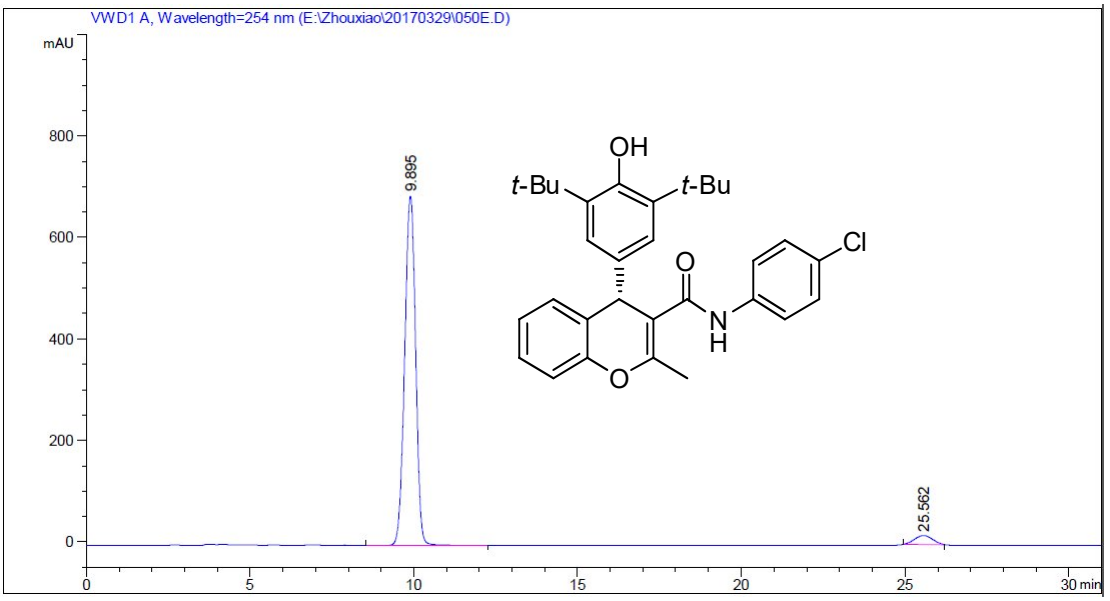


#	Time	Area	Height	Width	Symmetry	Area%
1	20.339	24709.6	467.5	0.8016	1.907	96.029
2	25.441	1021.7	19.6	0.8702	1.191	3.971

(*S*)-*N*-(4-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ab)

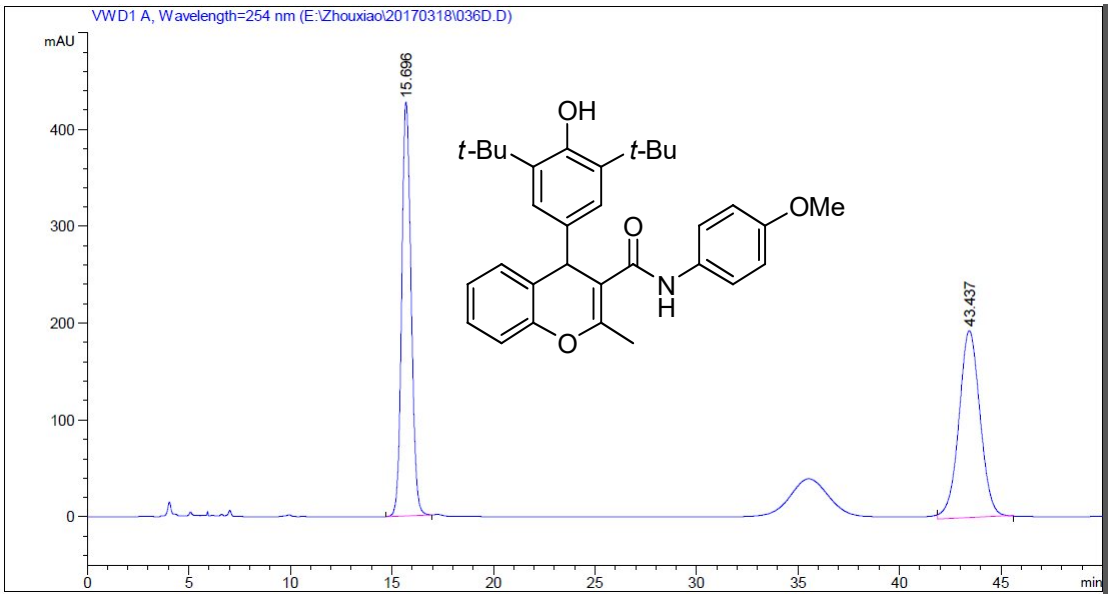


#	Time	Area	Height	Width	Symmetry	Area%
1	10.221	39344.3	1633.8	0.382	0.856	49.871
2	27.261	39547.8	834.8	0.7895	0.776	50.129

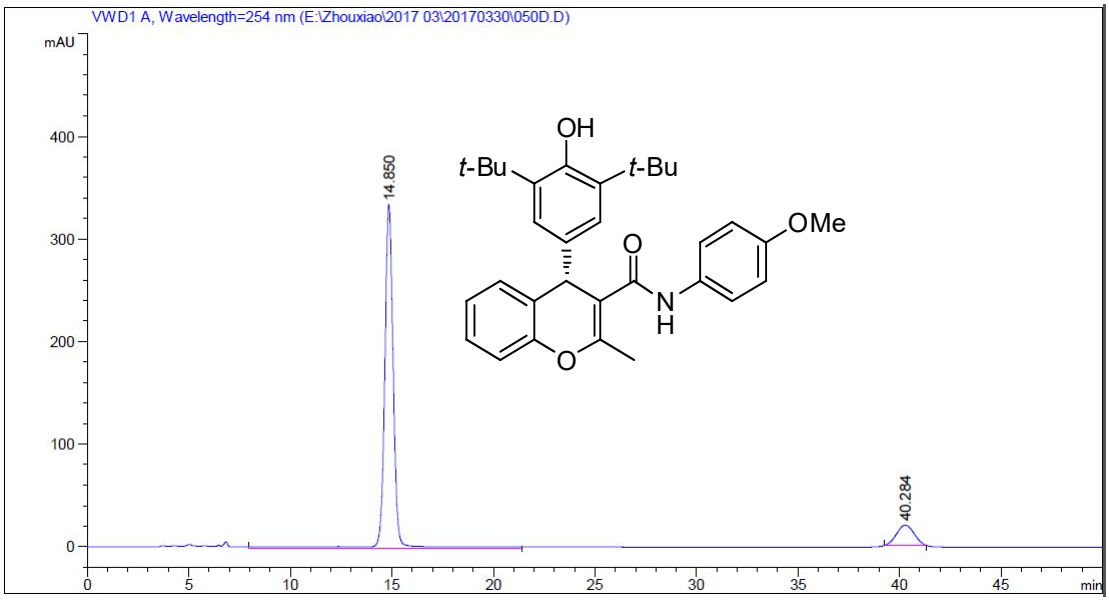


#	Time	Area	Height	Width	Symmetry	Area%
1	9.895	16210	690	0.3916	1.044	95.908
2	25.562	691.6	18	0.6414	0.97	4.092

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-methoxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ac)

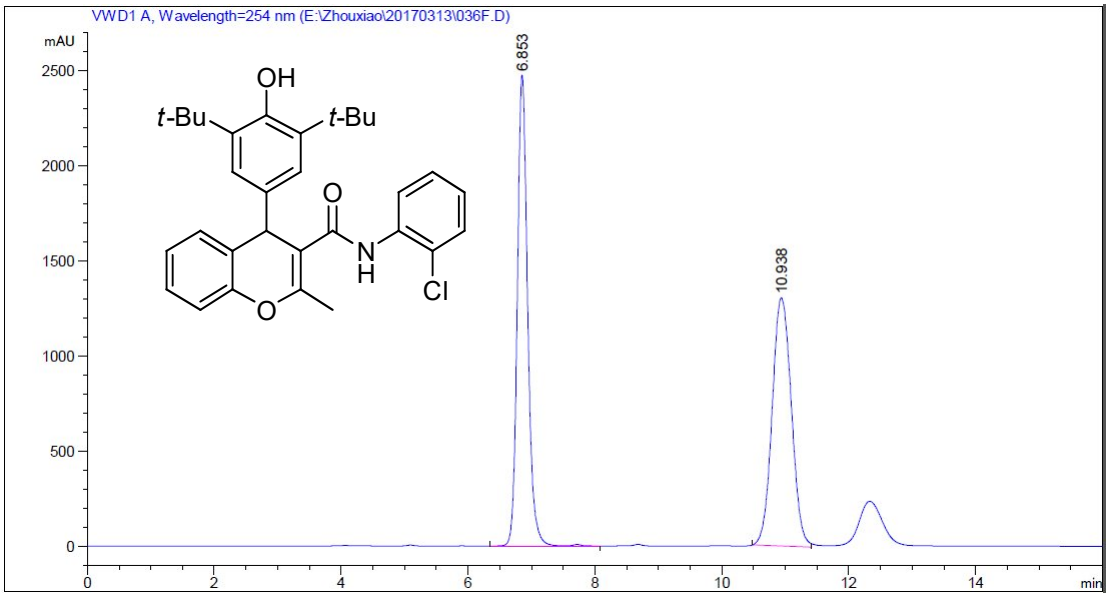


#	Time	Area	Height	Width	Symmetry	Area%
1	15.696	13728	427.3	0.5018	0.813	49.577
2	43.437	13962.5	193.1	1.205	0.95	50.423

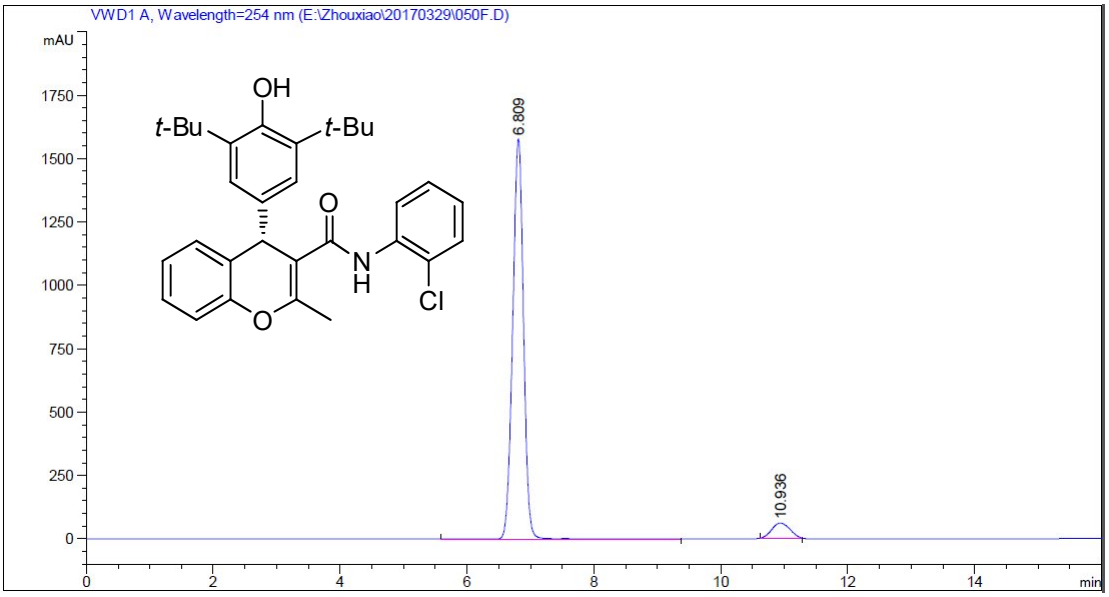


#	Time	Area	Height	Width	Symmetry	Area%
1	14.85	10492.8	335	0.5221	0.923	89.864
2	40.284	1183.5	19.8	0.9965	0.968	10.136

(*S*)-*N*-(2-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ad)

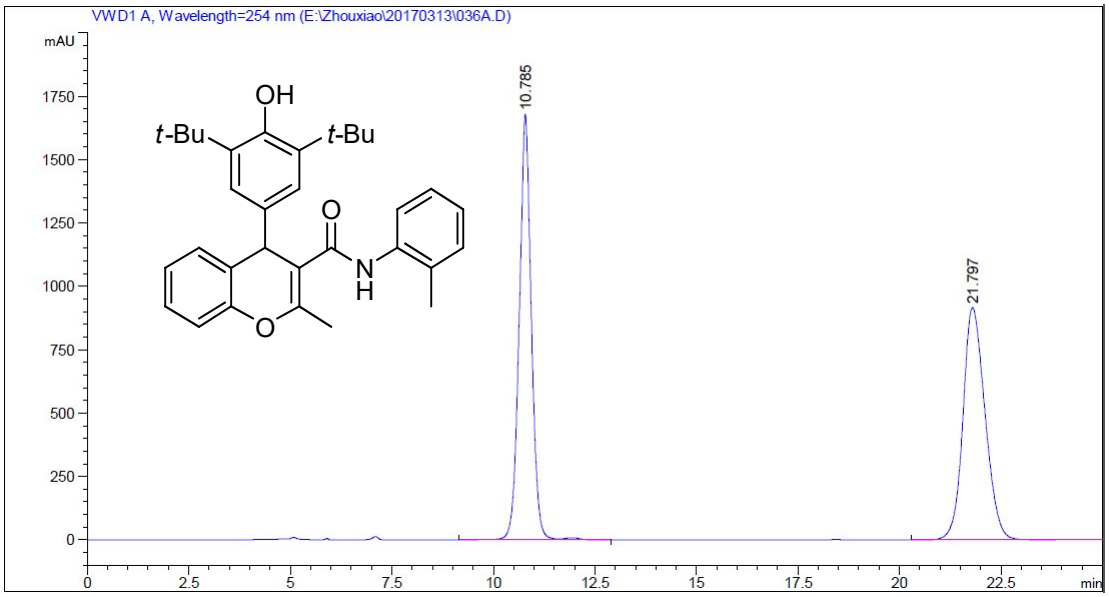


#	Time	Area	Height	Width	Symmetry	Area%
1	6.853	27943.7	2476.8	0.1722	0.81	50.504
2	10.938	27385.5	1304.7	0.3498	0.893	49.496

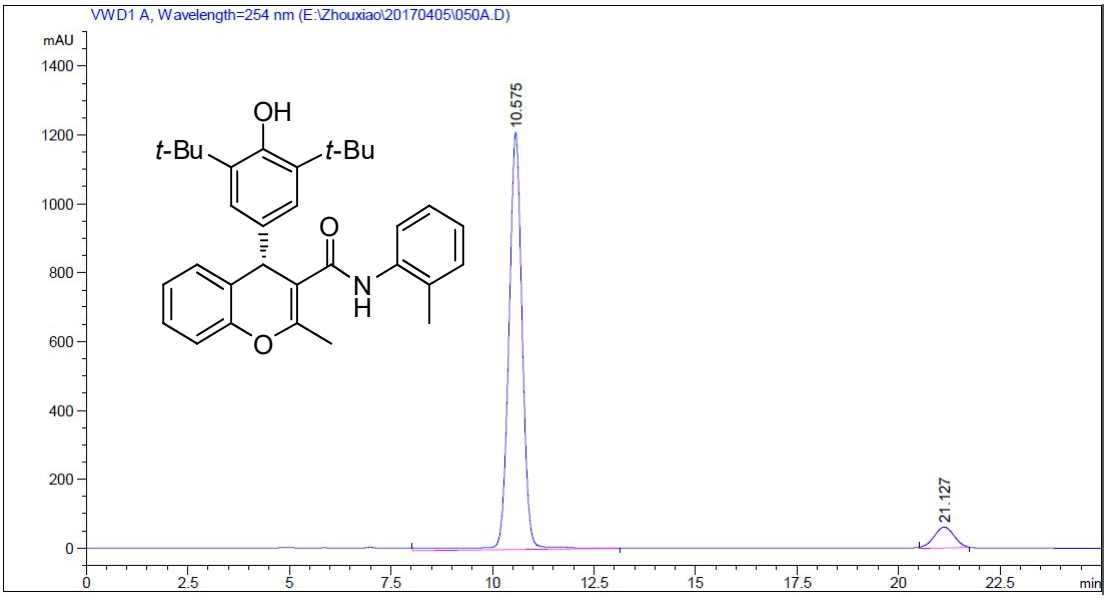


#	Time	Area	Height	Width	Symmetry	Area%
1	6.809	18963.2	1579.2	0.2001	1.049	93.909
2	10.936	1230	61	0.3363	0.88	6.091

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-*N*-(*o*-tolyl)-4*H*-chromene-3-carboxamide (6ae)

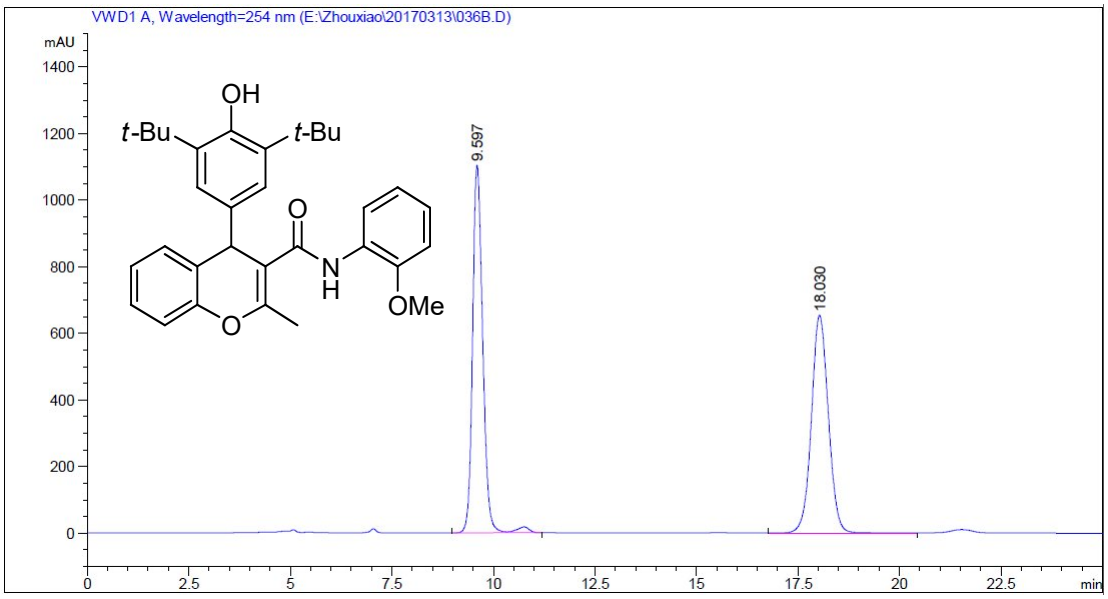


#	Time	Area	Height	Width	Symmetry	Area%
1	10.785	34777.4	1678.1	0.2923	0.978	50.017
2	21.797	34754	916.5	0.5844	0.739	49.983

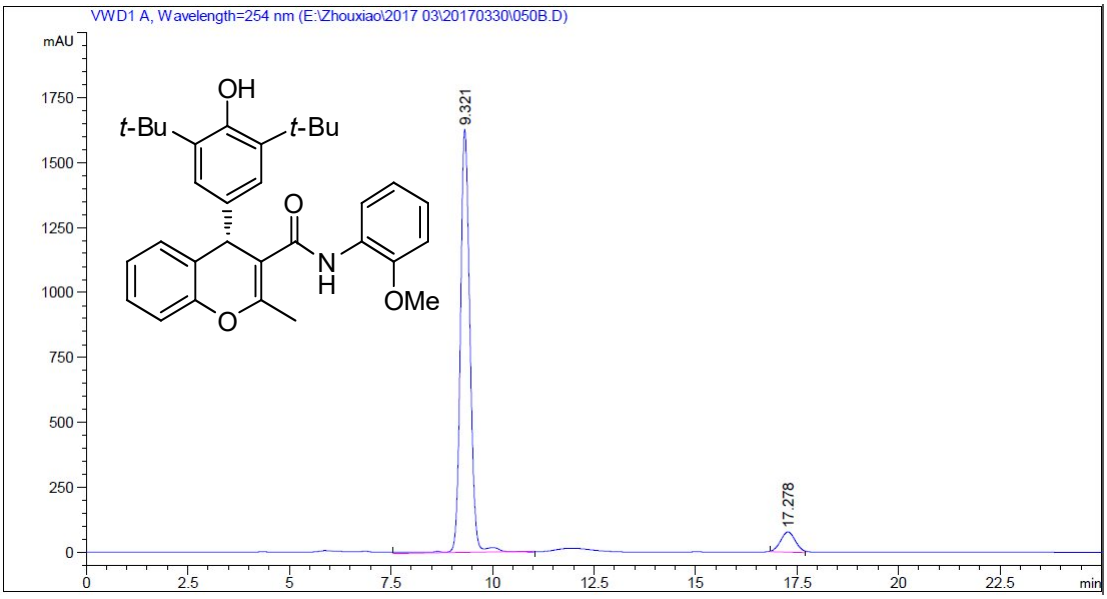


#	Time	Area	Height	Width	Symmetry	Area%
1	10.575	28311.3	1210.9	0.3897	1.026	92.975
2	21.127	2139.1	61.1	0.5835	1.024	7.025

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(2-methoxyphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6af)

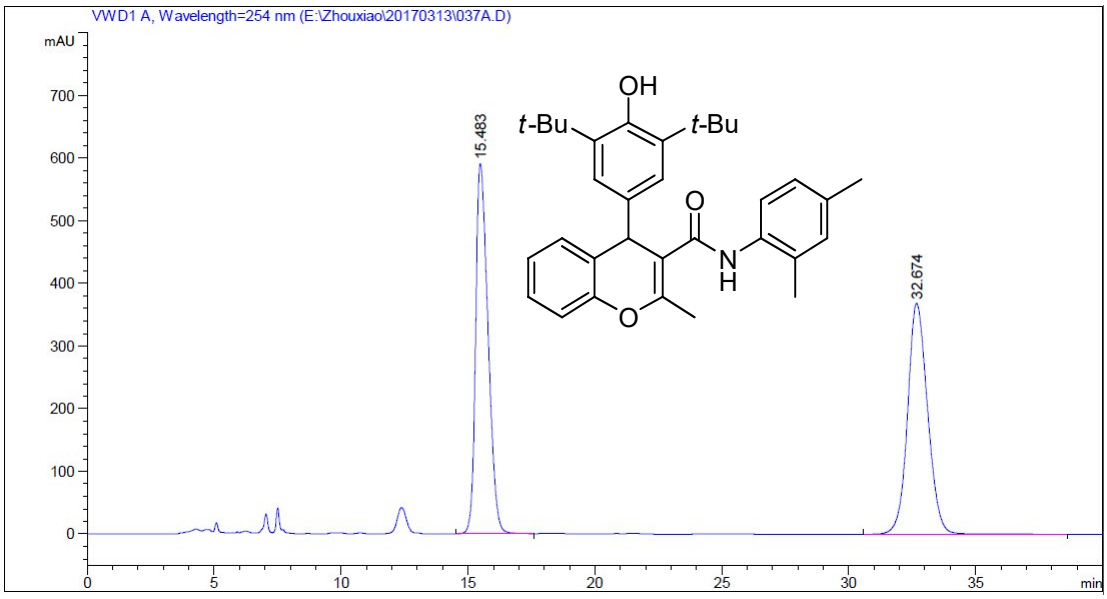


#	Time	Area	Height	Width	Symmetry	Area%
1	9.597	19373.2	1104.9	0.2648	0.756	50.525
2	18.03	18970.8	653.9	0.4465	0.893	49.475

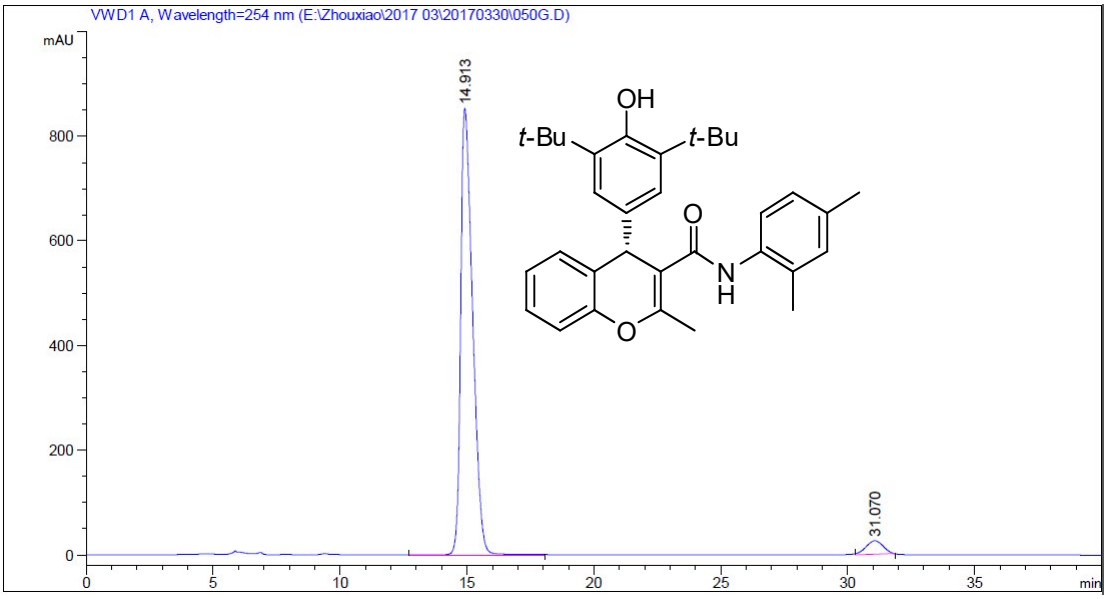


#	Time	Area	Height	Width	Symmetry	Area%
1	9.321	26618.9	1629.1	0.2723	0.824	93.158
2	17.278	1955	77	0.423	0.945	6.842

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-(2,4-dimethylphenyl)-2-methyl-4*H*-chromene-3-carboxamide (6ag)

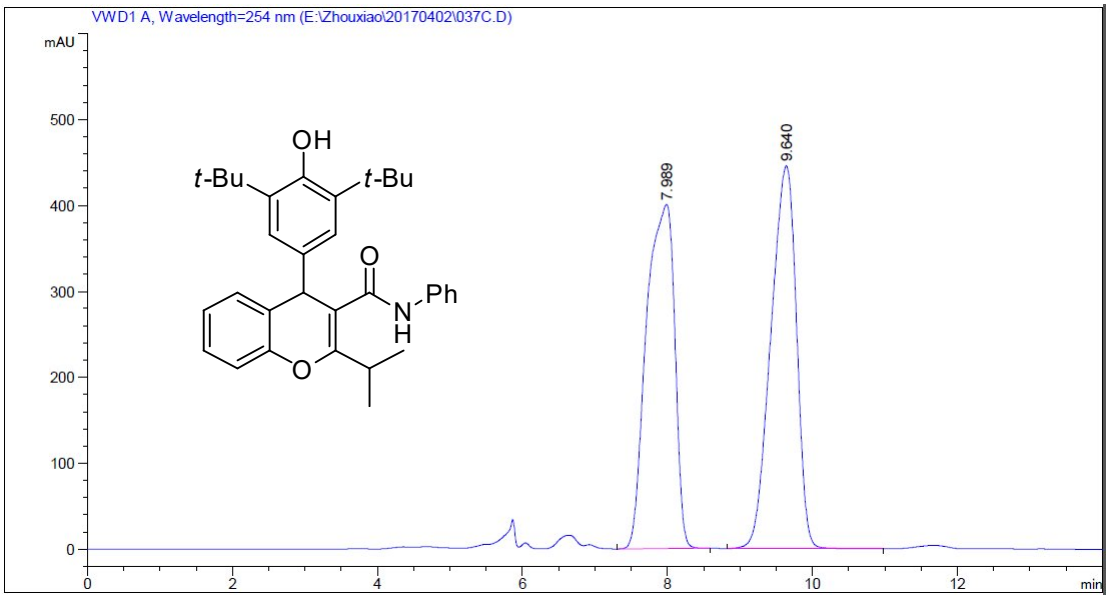


#	Time	Area	Height	Width	Symmetry	Area%
1	15.483	20095.7	591.1	0.5296	0.571	49.912
2	32.674	20166.2	368.2	0.8369	0.801	50.088

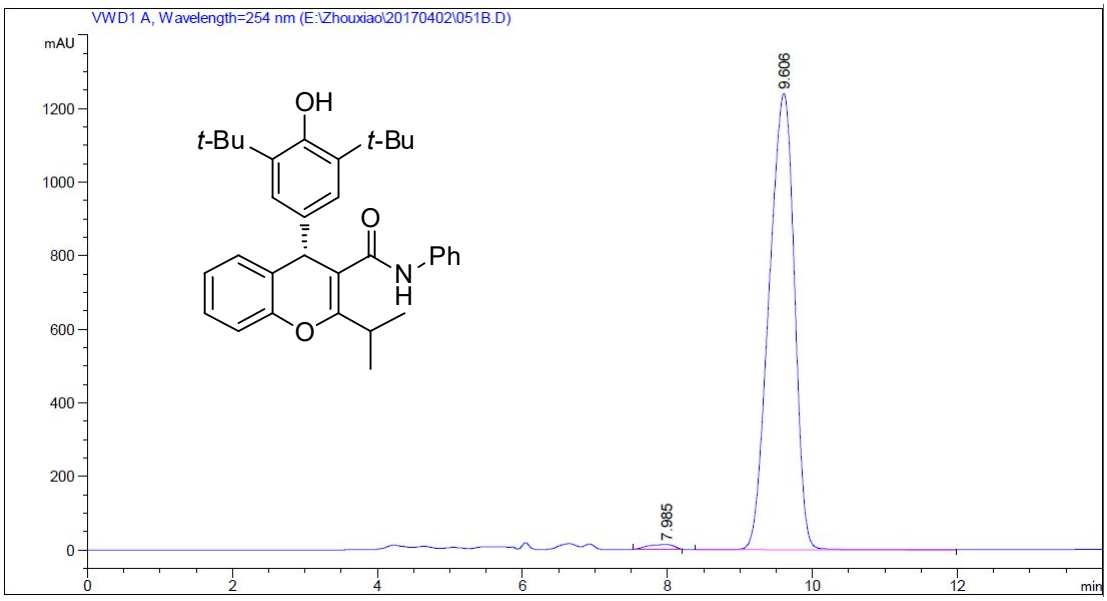


#	Time	Area	Height	Width	Symmetry	Area%
1	14.913	28014.2	854.8	0.5462	0.513	95.909
2	31.07	1194.9	25.6	0.7776	1.08	4.091

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-isopropyl-*N*-phenyl-4*H*-chromene-3-carboxamide (6ah)

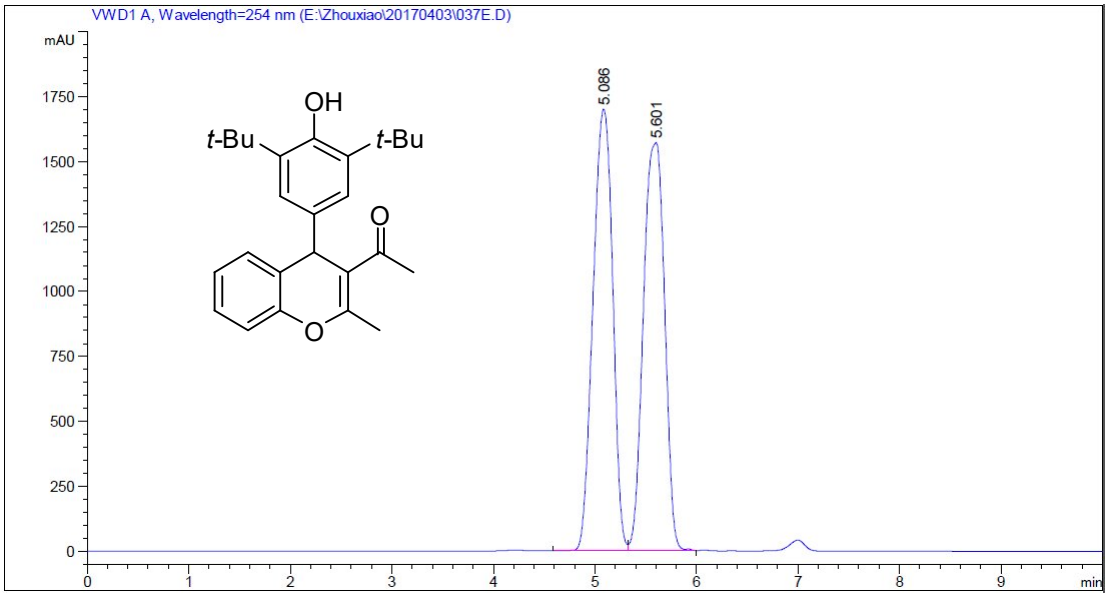


#	Time	Area	Height	Width	Symmetry	Area%
1	7.989	10806.9	400.6	0.3687	2.242	49.713
2	9.64	10931.8	445.6	0.4012	1.449	50.287

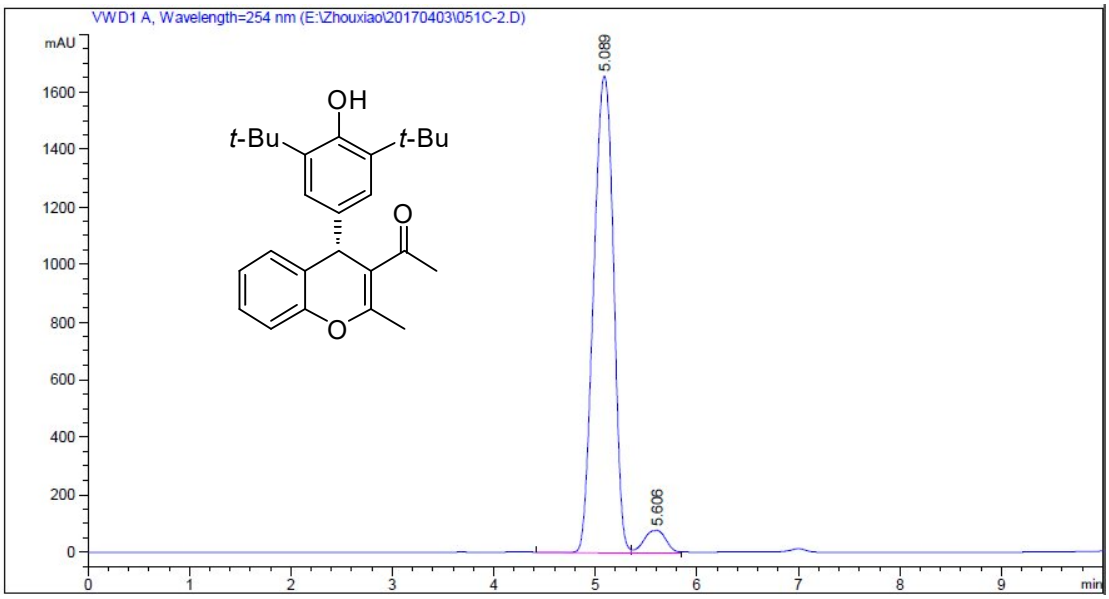


#	Time	Area	Height	Width	Symmetry	Area%
1	7.985	350.3	13.5	0.4325	2.368	1.149
2	9.606	30139.1	1239.8	0.4052	1.325	98.851

(*S*)-1-(4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromen-3-yl) ethanone (6ai)

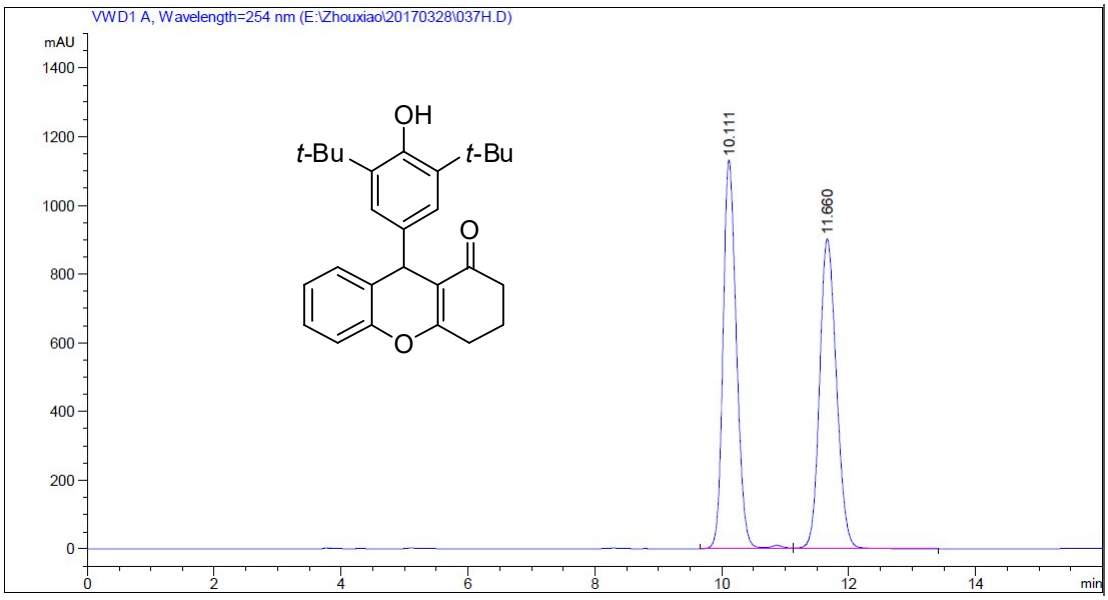


#	Time	Area	Height	Width	Symmetry	Area%
1	5.086	22855	1700.3	0.2188	1.128	50.055
2	5.601	22804.7	1570.4	0.2373	1.318	49.945

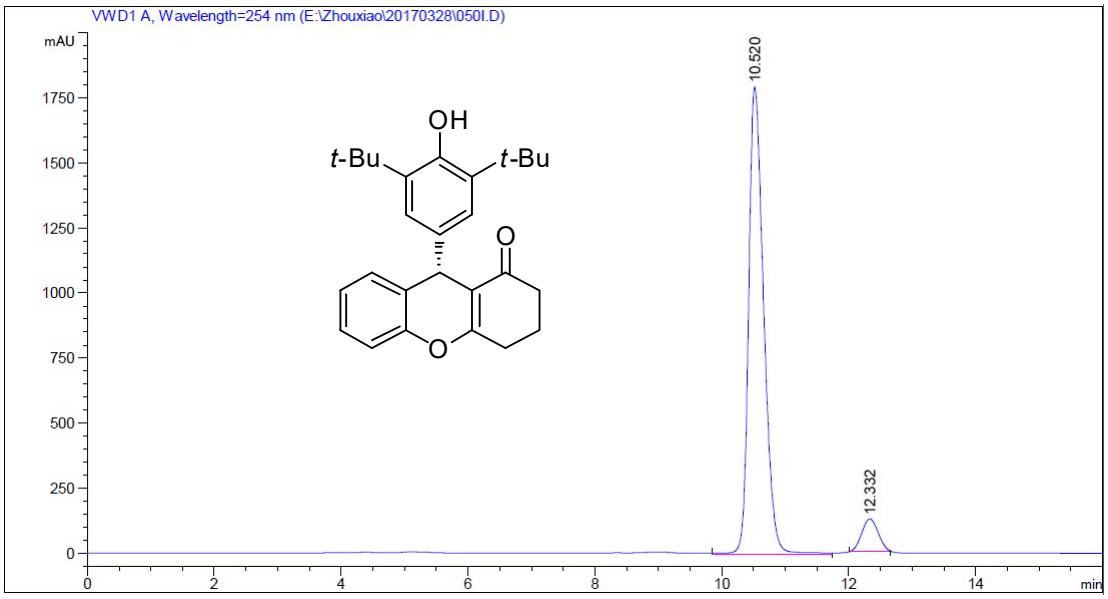


#	Time	Area	Height	Width	Symmetry	Area%
1	5.089	22444.3	1656.4	0.2258	1.122	94.947
2	5.606	1194.4	78.6	0.2532	1.35	5.053

(*S*)-9-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (6aj)

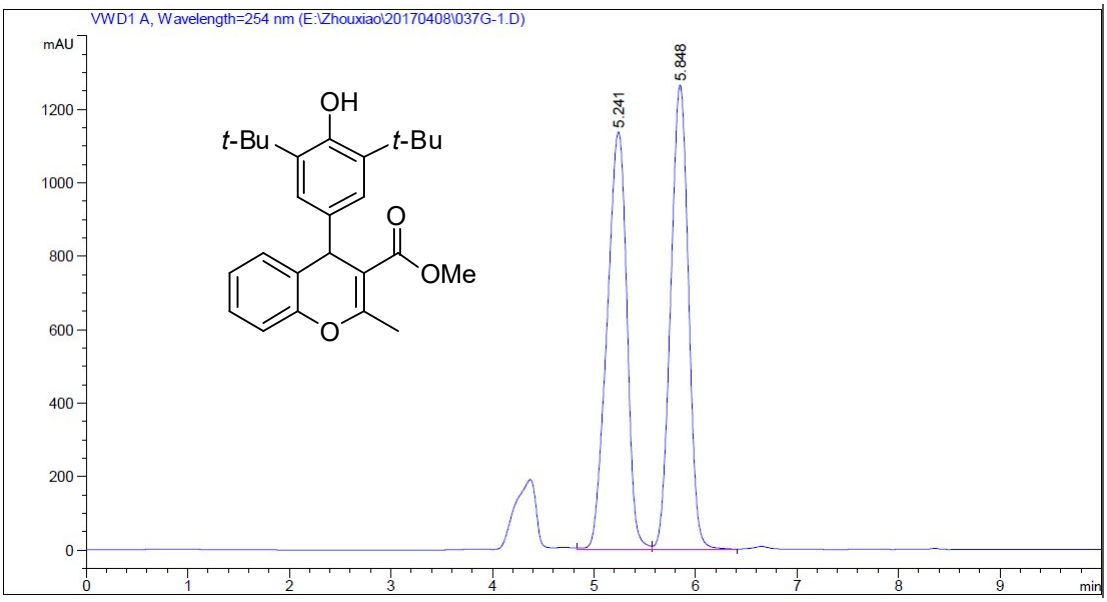


#	Time	Area	Height	Width	Symmetry	Area%
1	10.111	16644.6	1131.2	0.2248	0.751	50.042
2	11.66	16616.9	901.5	0.2871	0.795	49.958

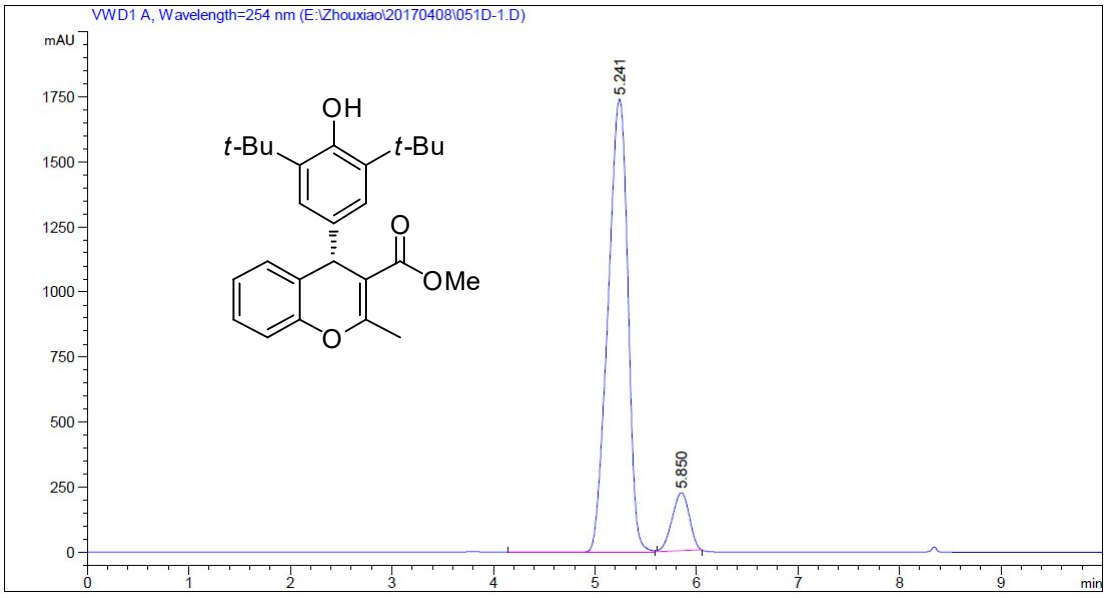


#	Time	Area	Height	Width	Symmetry	Area%
1	10.52	29630.5	1796.8	0.2748	0.654	92.911
2	12.332	2260.9	125.4	0.3005	0.928	7.089

(*S*)-methyl 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-methyl-4*H*-chromene-3-carboxylate (6ak)

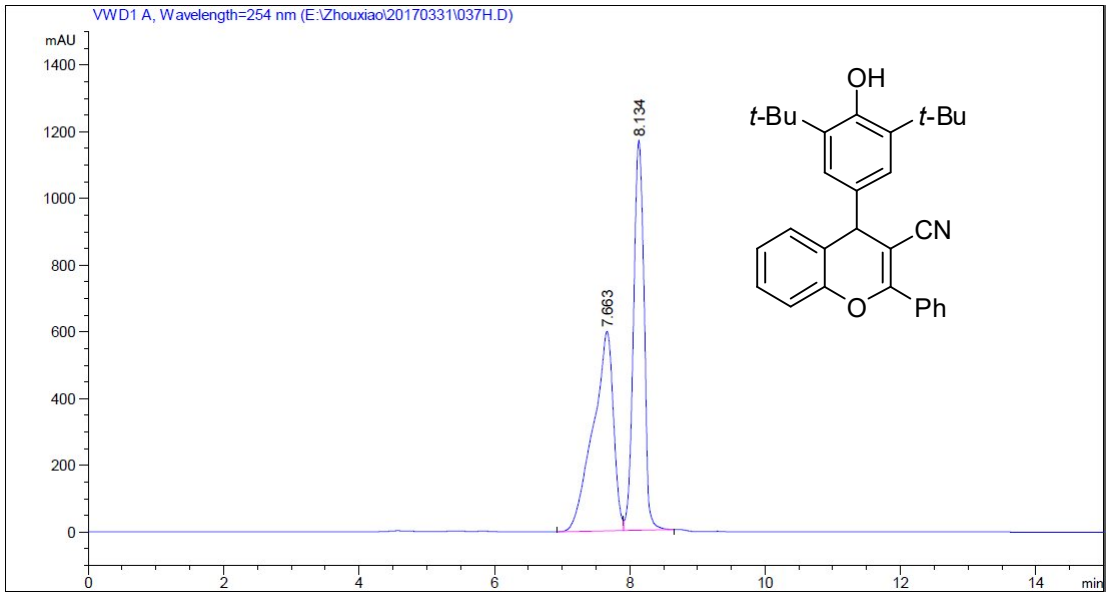


#	Time	Area	Height	Width	Symmetry	Area%
1	5.241	15436.4	1136.1	0.2095	1.3	50.126
2	5.848	15359	1263.4	0.1908	1.055	49.874

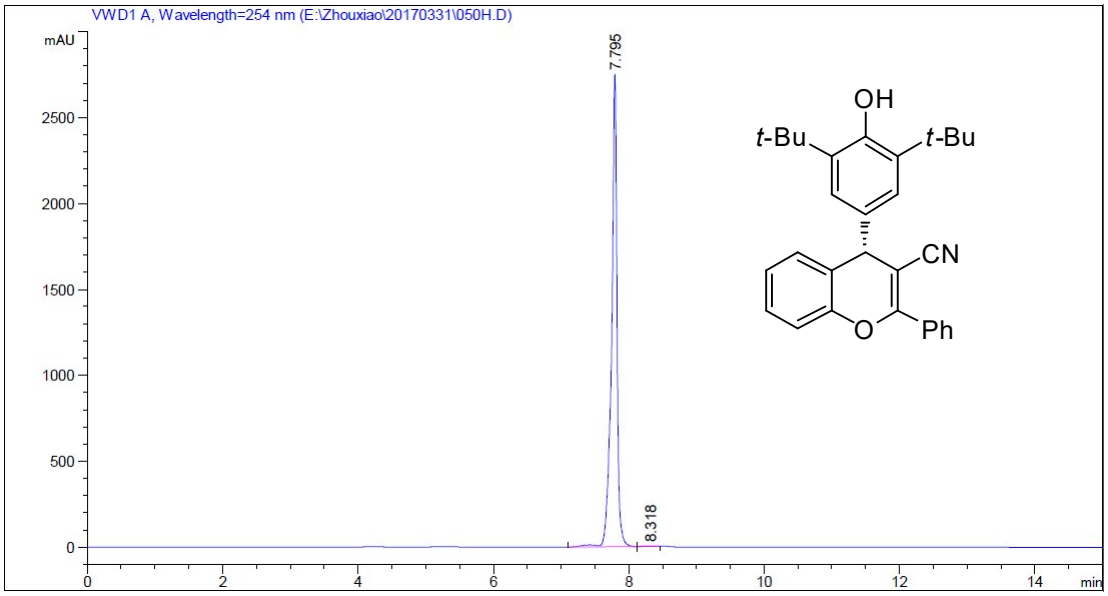


#	Time	Area	Height	Width	Symmetry	Area%
1	5.241	23699.3	1741.6	0.2268	1.298	90.027
2	5.85	2625.4	223	0.1962	1.132	9.973

(*S*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenyl-4*H*-chromene-3-carbonitrile (6al)

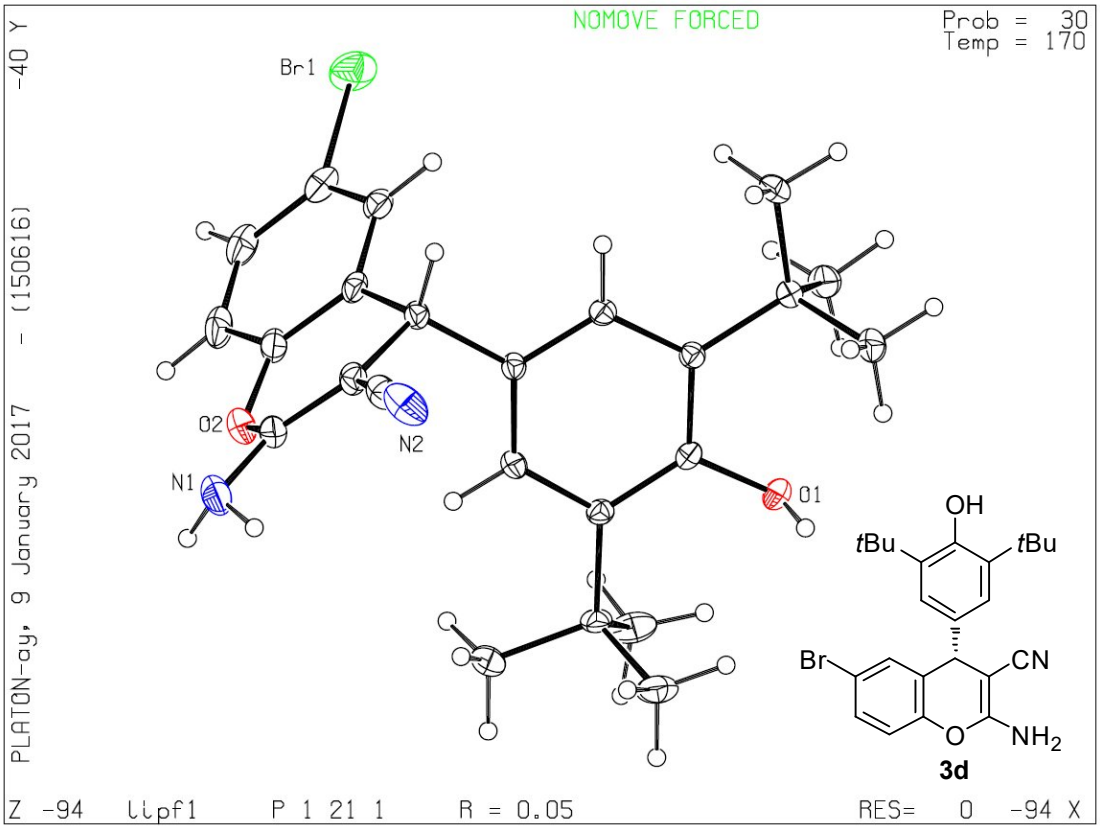


#	Time	Area	Height	Width	Symmetry	Area%
1	7.663	12535.8	597.9	0.2896	2.116	49.665
2	8.134	12704.9	1168.4	0.1799	0.973	50.335



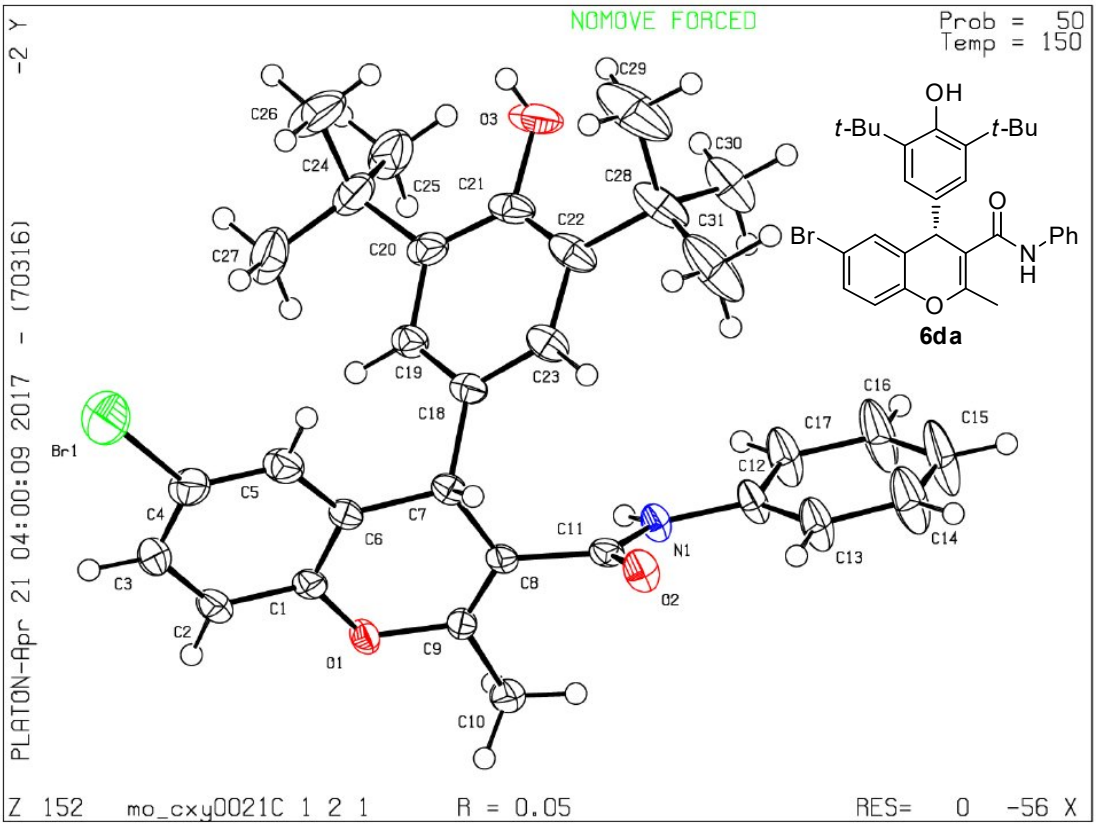
#	Time	Area	Height	Width	Symmetry	Area%
1	7.795	15224.8	2748	0.0789	1.579	99.664
2	8.318	51.4	3.6	0.2143	0.744	0.336

J: Absolute Configuration and X-Ray Analysis Data



Crystal data and structure refinement for 3d.

Identification code	**3d**
Empirical formula	$C_{24}H_{27}BrN_2O_2$
Formula weight	455.38
Temperature/K	170.03
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.4410(8)
b/Å	9.3621(7)
c/Å	11.5467(9)
α/°	90
β/°	93.816(2)
γ/°	90
Volume/Å^3	1126.18(15)
Z	2
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	2.651
F(000)	472.0
Crystal size/mm^3	0.4 × 0.35 × 0.28
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.674 to 136.794
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$
Reflections collected	27406
Independent reflections	4111 [R_{int} = 0.0903, R_{sigma} = 0.0416]
Data/restraints/parameters	4111/2/270
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1401
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.1402
Largest diff. peak/hole / e Å^{-3}	0.40/-0.91
Flack parameter	-0.01(3)


NOMOVE FORCED
Prob = 50
Temp = 150
-2 Y
PLATON-Apr 21 04:00:09 2017 - (70316)
Z 152 mo_cxy0021C 1 2 1
R = 0.05
RES= 0 -56 X
OH
t-Bu
t-Bu
Br
O
N
H
Ph
6da
Br1
O1
O2
O3
N1
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31

Crystal data and structure refinement for 6da.

Identification code	**6da**
Empirical formula	C31H34BrNO3
Formula weight	548.50
Temperature/K	150.0
Crystal system	monoclinic
Space group	C2
a/Å	23.095(3)
b/Å	9.4325(9)
c/Å	14.3653(14)
α/°	90
β/°	114.589(3)
γ/°	90
Volume/Å3	2845.6(5)
Z	4
ρcalcg/cm3	1.280
μ/mm-1	1.475
F(000)	1144.0
Crystal size/mm3	0.4 × 0.24 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.734 to 55.124
Index ranges	-30 ≤ h ≤ 30, -12 ≤ k ≤ 12, -17 ≤ l ≤ 18
Reflections collected	35274
Independent reflections	6549 [Rint = 0.0580, Rsigma = 0.0455]
Data/restraints/parameters	6549/2/333
Goodness-of-fit on F2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0478, wR2 = 0.0875
Final R indexes [all data]	R1 = 0.0742, wR2 = 0.0964
Largest diff. peak/hole / e Å-3	0.74/-0.79
Flack parameter	-0.012(3)

K: References

1. K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen, D. Enders, *Angew. Chem. Int. Ed*. **2016**, *55*, 12104-12108.
2. J. P. Malerich, K. Hagihara, V. H. Rawal, *J. Am. Chem. Soc.* **2008**, *130*, 14416-14417.