

Supporting information

**Pd-Catalyzed asymmetric decarboxylative cycloaddition of vinylethylene car-
bonates with 3-cyanochromones**

Ijaz Khan, Can Zhao and Yong Jian Zhang*

School of Chemistry and Chemical Engineering, and Shanghai Key Laboratory of Electrical Insulation and Thermal Aging,
Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, 200240, China

E-mail: yjian@sjtu.edu.cn

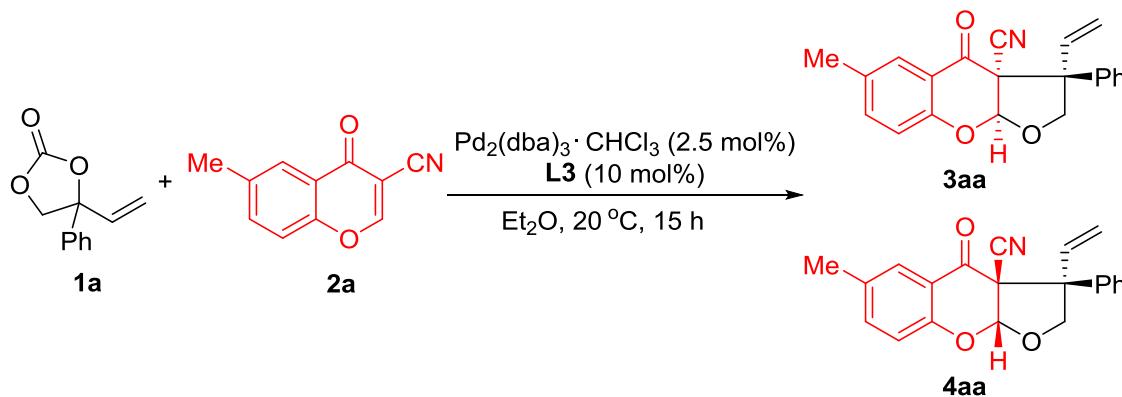
Table of Contents

General experimental details	S2
General procedure for the asymmetric cycloaddition of VEC,s 1 with 3-Cyanochromones 2	S2
Characterization of products 3aa/4aa-3mh/4mh	S3-S15
Procedure for transformation of 3aa to 5	S15
X-ray crystallography of 3ag , 4ag and 5	S14-S20
References	S20
NMR charts	S21-S44
HPLC charts	S45-S66

General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (Yantai Jian you Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shanghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University using ESI method. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with a Varian Mercury plus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ¹³C NMR spectra were routinely run with broadband decoupling. High performance liquid chromatography (HPLC) was performed with Thermo Fisher spectrometers using chiral column as noted for each compound. Diethyl ether was purified by distillation. Pd₂(dba)₃·CHCl₃ was purchased from Sino compound Co. and used as received. Substituted vinyl ethylene carbonates (VECs),¹ various 3-Cyanochromones² and Phosphoramidite ligands³ were synthesized according to the previously reported methods. All other chemicals were used as received from commercial resources.

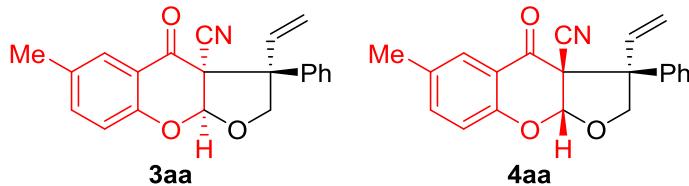
General procedure for asymmetric cycloaddition of VEC 1 with 3-Cyanochromones 2



To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd₂(dba)₃·CHCl₃ (5.2 mg, 0.005 mmol, 2.5 mol%), ligand **L3** (10.78 mg, 0.02 mmol, 10 mol %), VEC **1a** (38.0 mg, 0.2 mmol) and 3-Cyanochromones **2a** (37.0 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Anhydrous diethyl ether (2 mL) was added sequentially via syringe. The resulting mixture was stirred at 20 °C for 15 h. The solvent was removed in vacuo with the aid of a rotary evaporator. The crude product

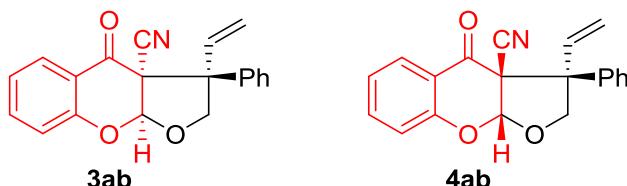
was purified by flash column chromatography on silica gel to afford the corresponding product **3aa** and **4aa**. The enantiomeric excesses of the products were determined by HPLC analysis using chiral stationary phases as indicated for each case.

(3*R*,3*aR*,9*aS*)-6-methyl-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4*H*-furo[2,3-*b*]chromene-3*a*(9*aH*)-carbonitrile (3aa**), (3*R*,3*aS*,9*aR*)-(4*aa*)**



Yield: 94% (62.2 mg); both diastereomer **3aa/4aa** with dr = 3.8:1; **3aa**; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 1.6 Hz, 1H), 7.33–7.29 (m, 2H), 7.16 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.11–7.02 (m, 3H), 6.70 (dd, *J* = 17.4, 10.9 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.14 (s, 1H), 5.47 (d, *J* = 10.9 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 4.91 (d, *J* = 9.6 Hz, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.4, 154.9, 138.6, 137.4, 135.6, 132.3, 128.8, 127.9, 127.6, 126.4, 119.1, 118.7, 118.0, 115.9, 105.0, 75.7, 60.6, 59.1, 20.3. **4aa**; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 1.5 Hz, 1H), 7.63–7.60 (m, 2H), 7.45–7.41 (m, 3H), 7.36–7.32 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.13 (s, 1H), 4.98 (d, *J* = 10.6 Hz, 1H), 4.82 (s, 2H), 4.66 (d, *J* = 17.1 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.3, 155.1, 139.2, 139.1, 137.9, 133.1, 128.6, 128.2, 127.9, 127.2, 119.7, 118.5, 115.8, 105.9, 78.7, 60.7, 59.9, 20.5; HRMS (ESI-MS): Calcd. for C₂₁H₁₇NO₃ (M+Na): 354.1106, Found: 354.1098; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, t_{major} = 9.0, 12.3 min, t_{minor} = 17.0, 14.8 min; 96, 96% ee.

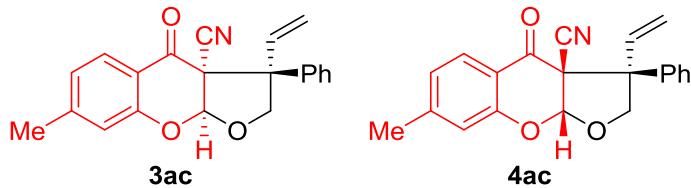
(3*R*,3*aR*,9*aS*)-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4*H*-furo[2,3-*b*]chromene-3*a*(9*aH*)-carbonitrile (3ab**), (3*R*,3*aS*,9*aR*)-(4*ab*)**



Yield: 96% (61 mg); both diastereomer **3ab/4ab** with dr = 2.1:1; **3ab**; ¹H NMR (400 MHz, CDCl₃) δ 7.63–7.59 (m, 2H), 7.45–7.41 (m, 1H), 7.37–7.30 (m, 2H), 7.09–7.05 (m, 2H), 6.92–6.88 (m, 1H), 6.71 (dd, *J* = 10.9, 17.4 Hz, 1H), 6.70 (dd, *J* = 0.6, 8.4 Hz, 1H), 6.18 (s, 1H), 5.49 (d, *J* = 10.9 Hz, 1H), 5.20 (d, *J* = 17.4 Hz, 1H), 4.95 (d, *J* = 9.5 Hz, 1H), 4.56 (d, *J* = 9.6 Hz, 1H); **4ab**; ¹H NMR (400 MHz,

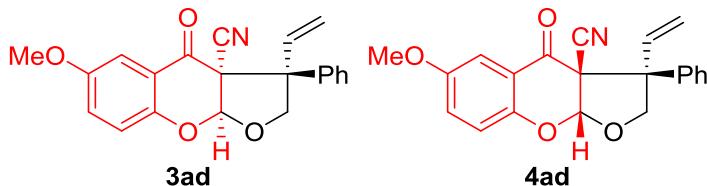
CDCl_3) δ 7.95 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.65–7.63 (m, 1H), 7.37–7.30 (m, 3H), 7.18–7.14 (m, 1H), 7.09–6.98 (m, 3H), 6.20 (dd, $J = 10.6, 17.2$ Hz, 1H), 6.17 (s, 1H), 5.98 (d, $J = 10.0$ Hz, 1H), 4.85 (d, $J = 9.0$ Hz, 1H), 4.82 (d, $J = 9.0$ Hz, 1H), 4.68 (d, $J = 17.1$ Hz, 1H); mixture of **3ab** and **4ab**, ^{13}C NMR (100 MHz, CDCl_3) δ 184.1, 183.3, 157.0, 156.7, 138.1, 138.0, 137.7, 137.4, 137.1, 135.3, 128.8, 128.6, 128.1, 127.9, 127.8, 127.7, 127.5, 126.8, 123.3, 122.5, 119.9, 119.8, 119.3, 118.7, 118.6, 118.0, 115.7, 115.6, 105.8, 104.9, 78.6, 75.7, 60.8, 60.7, 59.9, 59.08; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{15}\text{NO}_3$ ($\text{M}+\text{Na}$): 340.0950, Found: 340.0966; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 13.6, 19.2$ min, $t_{\text{minor}} = 20.8, 22.9$ min; 96, 94% ee.

(3*R*,3a*R*,9a*S*)-7-methyl-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9a*H*)-carbonitrile (3ac), (3*R*,3a*S*,9a*R*)-(4ac)



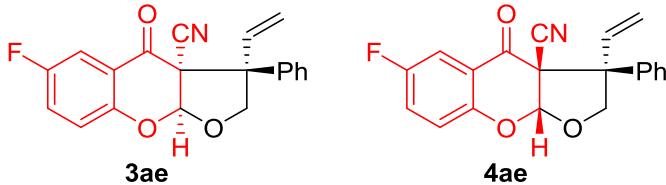
Yield: 90% (60 mg); both diastereomer **3ac**/**4ac** with $\text{dr} = 3.3:1$, **3ac**; ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.61 (m, 2H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.34–7.30 (m, 2H), 7.10–7.05 (m, 1H), 6.73–6.50 (m, 2H), 6.71 (dd, $J = 9.6, 17.2$ Hz, 1H), 6.14 (s, 1H), 5.47 (d, $J = 10.8$ Hz, 1H), 5.19 (d, $J = 17.6$ Hz, 1H), 4.92 (d, $J = 9.2$ Hz, 1H), 4.55 (d, $J = 10.0$ Hz, 1H), 2.24 (s, 3H); **4ac**; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0$ Hz, 1H), 7.64–7.62 (m, 1H), 7.45–7.40 (m, 3H), 7.11–7.02 (m, 1H), 7.01–6.87 (m, 2H), 6.20 (dd, $J = 17.2, 10.4$ Hz, 1H), 6.13 (s, 1H), 4.97 (d, $J = 10.4$ Hz, 1H), 4.84 (d, $J = 8.8$ Hz, 1H), 4.81 (d, $J = 8.8$ Hz, 1H), 4.67 (d, $J = 17.2$ Hz, 1H), 2.41 (s, 3H); mixture of **3ac** and **4ac**, ^{13}C NMR (100 MHz, CDCl_3) δ 183.5, 182.7, 157.0, 156.8, 150.2, 149.5, 139.0, 137.8, 137.3, 135.5, 128.7, 128.6, 128.1, 127.8, 127.6, 127.5, 126.8, 124.7, 124.0, 119.5, 119.1, 118.6, 118.0, 117.6, 117.5, 116.6, 115.8, 115.7, 105.8, 104.9, 78.6, 75.6, 60.5, 60.4, 59.8, 58.9, 22.1, 21.9; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}_3$ ($\text{M}+\text{Na}$): 354.1106, Found: 354.1093; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 15.7, 17.1$ min, $t_{\text{minor}} = 19.9, 35.6$ min; 96, 89% ee.

(3*R*,3a*R*,9a*S*)-6-methoxy-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9a*H*)-carbonitrile (3ad), (3*R*,3a*S*,9a*R*)-(4ad)



Yield: 90% (63 mg); both diastereomer **3ad**/**4ad** with **dr** = 3.8: 1, **3ad**; ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.30 (m, 2H), 7.11–7.02 (m, 3H), 7.00–7.94 (m, 2H), 6.66–6.63 (m, 1H), 6.71 (dd, J = 17.6, 11.2 Hz, 1H), 6.13 (s, 1H), 5.46 (d, J = 11.2 Hz, 1H), 5.19 (d, J = 17.2 Hz, 1H), 4.90 (d, J = 9.6 Hz, 1H), 4.53 (d, J = 9.6 Hz, 1H), 3.70 (s, 3H); **4ad**; ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.61 (m, 2H), 7.44–7.40 (m, 3H), 7.35–7.32 (m, 2H), 7.26–7.19 (m, 1H), 6.20 (dd, J = 17.2, 10.4 Hz, 1H), 6.11 (s, 1H), 4.97 (d, J = 10.4 Hz, 1H), 4.81 (s, 2H), 4.66 (d, J = 17.2 Hz, 1H), 3.81 (s, 3H); mixture of **3ad** and **4ad**, ^{13}C NMR (100 MHz, CDCl_3) δ 184.1, 183.2, 155.3, 154.7, 151.4, 151.3, 139.0, 137.9, 137.3, 135.5, 128.6, 128.5, 128.1, 127.8, 127.7, 127.5, 127.1, 126.7, 119.9, 119.6, 119.4, 119.0, 118.9, 115.7, 115.6, 107.7, 106.9, 105.9, 105.0, 78.6, 75.5, 60.5, 60.3, 60.2, 59.8, 59.0, 55.7, 55.6; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}_4$ ($\text{M}+\text{Na}$): 370.1055, Found: 370.1050; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, t_{major} = 23.1, 46.2 min, t_{minor} = 22.0, 27.7 min; 96, 91% ee.

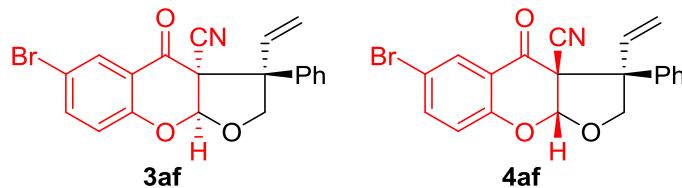
(3*R*,3*aR*,9*aS*)-6-fluoro-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4*H*-furo[2,3-*b*]chromene-3*a*(9*aH*)-carbonitrile (3ae), (3*R*,3*aS*,9*aR*)-(4ae)



Yield: 95% (64 mg); both diastereomer **3ae**/**4ae** with **dr** = 3.5:1, **3ae**; ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.28 (m, 2H), 7.26–7.23 (m, 1H), 7.11–7.00 (m, 3H), 6.69 (s, 1H), 6.67 (d, J = 4.4 Hz, 1H), 6.68 (dd, J = 17.2, 6.4 Hz, 1H), 6.16 (s, 1H), 5.50 (d, J = 10.8 Hz, 1H), 5.19 (d, J = 17.6 Hz, 1H), 4.95 (d, J = 9.6 Hz, 1H), 4.55 (d, J = 10.0 Hz, 1H); **4ae**; ^1H NMR (400 MHz, CDCl_3) δ 7.60–7.57 (m, 2H), 7.45–7.40 (m, 1H), 7.37–7.34 (m, 1H), 7.33–7.30 (m, 2H), 7.11–7.01 (m, 2H), 6.19 (dd, J = 17.2, 10.4 Hz, 1H), 6.15 (s, 1H), 5.00 (d, J = 10.8 Hz, 1H), 4.84 (d, J = 9.2 Hz, 1H), 4.70 (d, J = 9.2 Hz, 1H), 4.68 (d, J = 17.2 Hz, 1H); mixture of **3ae** and **4ae**, ^{13}C NMR (100 MHz, CDCl_3) δ 183.7, 183.6, 183.0, 182.9, 159.2, 158.7, 156.8, 156.2, 153.2, 153.1, 152.9, 152.8, 138.7, 137.5, 136.9, 135.1, 128.8, 128.6, 128.1, 128.0, 127.9, 127.6, 125.7, 125.5, 125.2, 124.9, 120.6, 120.5, 120.4, 120.3, 120.2, 119.9, 119.8, 119.5, 119.2, 119.1, 115.4, 115.3, 112.8, 112.6, 111.8, 111.6, 106.0, 105.1, 75.7, 60.6, 60.6, 60.4, 59.9, 59.1; HRMS (ESI-MS): Calcd. for $\text{C}_{20}\text{H}_{14}\text{FNO}_3$ ($\text{M}+\text{Na}$): 358.0855, Found: 358.0864; HPLC conditions: Chi-

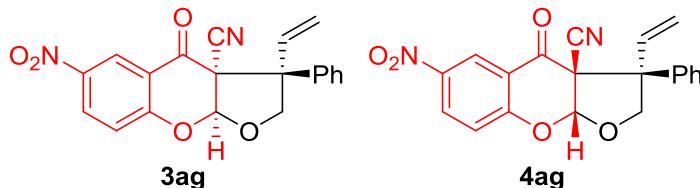
ralcel OD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, *t*_{major} = 18.9, 22.8 min, *t*_{minor} = 29.0, 35.7 min; 88, 92% ee.

(3*R*,3a*R*,9a*S*)-6-bromo-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4H-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3af), (3*R*,3a*S*,9a*R*)-(4af)



Yield: 92% (71 mg); both diastereomer **3af/4af** with **dr** = 1.7:1 **3af**; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 2.4 Hz, 1H), 7.43–7.38 (m, 2H), 7.30–7.26 (m, 1H), 7.10–7.03 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.8 Hz, 1H), 6.68 (dd, *J* = 17.6, 11.2 Hz, 1H), 6.15 (s, 1H), 5.49 (d, *J* = 11.6 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 4.54 (d, *J* = 10.0 Hz, 1H); **4af**; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 2.4 Hz, 1H), 7.70–7.67 (m, 2H), 7.59–7.56 (m, 2H), 7.45–7.44 (m, 1H), 7.36–7.32 (m, 1H), 7.11–7.02 (m, 1H), 6.15 (dd, *J* = 17.2, 11.6 Hz, 1H), 6.15 (s, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.85 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 9.2 Hz, 1H), 4.70 (d, *J* = 17.2 Hz, 1H); mixture of **3af** and **4af**, ¹³C NMR (100 MHz, CDCl₃) δ 183.2, 182.5, 155.9, 155.6, 140.6, 139.9, 138.7, 137.3, 136.8, 135.0, 129.9, 129.0, 128.8, 128.7, 128.1, 127.9, 127.9, 127.6, 121.0, 120.6, 120.1, 120.0, 119.8, 119.6, 116.0, 115.3, 115.2, 115.1, 105.9, 105.0, 78.7, 75.8, 60.6, 60.4, 59.9, 59.1; HRMS (ESI-MS): Calcd. for C₂₀H₁₄BrNO₃ (M+Na): 420.0055, Found: 420.0055; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, *t*_{major} = 20.3, 26.9 min, *t*_{minor} = 31.4, 42.0 min; 89, 90% ee.

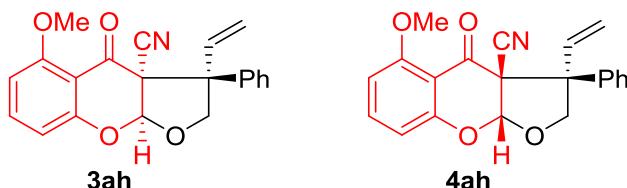
(3*R*,3a*R*,9a*S*)-6-nitro-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4H-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3ag), (3*R*,3a*S*,9a*R*)-(4ag)



Yield: 92% (67 mg); both diastereomer **3ag/4ag** with **dr** = 1:1 **3ag**; ¹H NMR (400 MHz, CDCl₃) δ 8.47 (d, *J* = 2.8 Hz, 1H), 8.14 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.30–7.26 (m, 2H), 7.07–6.96 (m, 3H), 6.78 (d, *J* = 9.2 Hz, 1H), 6.70 (dd, *J* = 17.6, 11.2 Hz, 1H), 6.27 (s, 1H), 5.54 (d, *J* = 10.8 Hz, 1H), 5.21 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 9.6 Hz, 1H), 4.58 (d, *J* = 9.6 Hz, 1H); **4ag**; ¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 2.8 Hz, 1H), 8.46 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.60–7.53 (m, 2H), 7.48–7.40 (m, 1H), 7.40–7.34 (m, 2H), 7.28–7.21 (m, 1H), 6.28 (s, 1H), 6.10 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.92 (d, *J* = 9.2 Hz, 1H), 4.84 (d, *J* = 9.2 Hz, 1H), 4.77 (d, *J* = 17.2 Hz, 1H); mixture of **3ag** and **4ag**, ¹³C

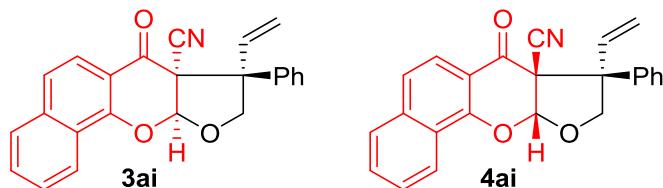
NMR (100 MHz, CDCl₃) δ 182.9, 182.3, 160.8, 160.4, 143.2, 142.4, 138.3, 136.8, 136.1, 134.5, 132.0, 131.2, 129.1, 128.8, 128.4, 128.1, 127.8, 127.7, 123.9, 123.1, 120.6, 120.3, 119.9, 119.3, 119.2, 117.6, 114.7, 114.6, 106.4, 105.5, 78.7, 76.2, 61.2, 60.4, 60.1, 59.3; HRMS (ESI-MS): Calcd. for C₂₀H₁₄N₂O₅ (M+Na): 385.0903, Found: 385.0789; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/1, t_{major} = 15.6, 17.8 min, t_{minor} = 20.8, 30.9 min; 78, 61% ee.

(3*R*,3a*R*,9a*S*)-5-methoxy-4-oxo-3-phenyl-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9aH)-carbonitrile (3ah), (3*R*,3a*S*,9a*R*)-(4ah)



Yield: 92% (64 mg); both diastereomer **3ah/4ah** with **dr** = 4.2:1, **3ah**; ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.24 (m, 3H), 7.15–7.05 (m, 3H), 6.68 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.41–6.35 (m, 2H), 6.13 (s, 1H), 5.42 (d, *J* = 10.8 Hz, 1H), 5.12 (d, *J* = 17.6 Hz, 1H), 4.83 (d, *J* = 9.6 Hz, 1H), 4.48 (d, *J* = 9.6 Hz, 1H), 3.74 (s, 3H); **4ah**; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.90 (dd, *J* = 16.4, 11.2 Hz, 1H), 7.65–7.62 (m, 2H), 7.53–7.46 (m, 1H), 7.44–7.38 (m, 1H), 7.34–7.31 (m, 1H), 6.68–6.65 (m, 1H), 6.22 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.06 (s, 1H), 5.29 (s, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.74 (s, 1H), 4.71 (d, *J* = 17.4 Hz, 1H), 3.94 (s, 3H); mixture of **3ah** and **4ah**, ¹³C NMR (100 MHz, CDCl₃) δ 181.9, 181.2, 160.8, 159.8, 158.5, 158.3, 139.1, 138.0, 137.8, 137.1, 135.7, 128.6, 128.5, 128.2, 127.9, 127.8, 127.6, 127.6, 119.1, 118.5, 116.1, 115.9, 111.2, 110.7, 110.6, 110.0, 106.1, 105.3, 105.2, 104.6, 78.0, 75.7, 62.6, 61.9, 60.1, 59.6, 56.4, 56.1; HRMS (ESI-MS): Calcd. for C₂₁H₁₇NO₄ (M+Na): 370.1055, Found: 370.1055; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, t_{major} = 13.6, 18.5 min, t_{minor} = 15.9, 20.8 min; 97, 95% ee.

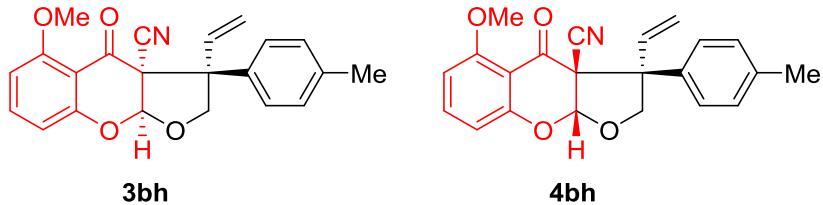
(8*R*,7a*R*,10a*S*)-7-oxo-8-phenyl-8-vinyl-8,9-dihydro-7H-benzo[2,3-b]chromene-7a(10aH)-carbonitrile (3ai), (8*R*,7a*S*,10a*R*)-(4ai)



Yield: 92% (68 mg); both diastereomer **3ai/4ai** with **dr** = 3.9:1, **3ai**; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.66–7.63 (m, 1H), 7.6–7.56 (m, 1H), 7.754–7.45 (m, 2H), 7.35–7.31 (m, 2H), 7.24 (dd, *J* = 12.4, 6.8 Hz, 1H), 6.90–6.86 (m, 2H), 6.76 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.77–6.73 (m, 1H), 6.35 (s, 1H), 5.50 (d, *J* = 11.2 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 4.61 (d, *J* =

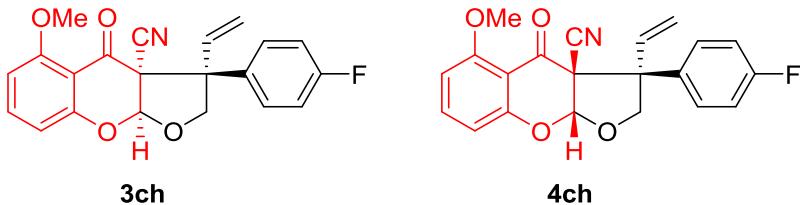
9.6 Hz, 1H); **4ai**; ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.0$ Hz, 1H), 7.85 (dd, $J = 14.8, 8.8$ Hz, 2H), 7.75–7.68 (m, 2H), 7.52–7.40 (m, 2H), 7.36–7.31 (m, 1H), 7.63 (d, $J = 1.3$ Hz, 2H), 6.77–6.73 (m, 1H), 6.71 (s, 1H), 6.16 (dd, $J = 17.2, 10.4$ Hz, 1H), 4.94 (d, $J = 9.2$ Hz, 1H), 4.88 (d, $J = 3.6$ Hz, 1H), 4.86 (d, $J = 4.8$ Hz, 1H), 4.70 (d, $J = 17.2$ Hz, 1H); mixture of **3ai** and **4ai**, ^{13}C NMR (100 MHz, CDCl_3) δ 183.5, 182.7, 155.9, 155.4, 139.0, 138.2, 137.7, 137.6, 137.1, 135.4, 130.8, 130.4, 128.9, 128.7, 128.6, 128.3, 128.1, 128.0, 127.8, 127.7, 127.3, 127.0, 126.6, 124.2, 123.9, 123.7, 123.5, 122.9, 122.1, 121.3, 120.6, 119.6, 119.4, 115.8, 114.6, 113.3, 106.6, 105.6, 78.8, 76.0, 60.7, 60.4, 59.9, 59.1; HRMS (ESI-MS): Calcd. for $\text{C}_{24}\text{H}_{17}\text{NO}_3$ ($\text{M}+\text{Na}$): 390.1206, Found: 390.1101; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/30, $t_{\text{major}} = 20.3, 34.8$ min, $t_{\text{minor}} = 36.7, 20.1$ min; 95, 90% ee.

(3*R*,3a*R*,9a*S*)-5-methoxy-4-oxo-3-(*p*-tolyl)-3-vinyl-2,3-dihydro-4*H*-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3bh), (3*R*,3a*S*,9a*R*)-(4bh)



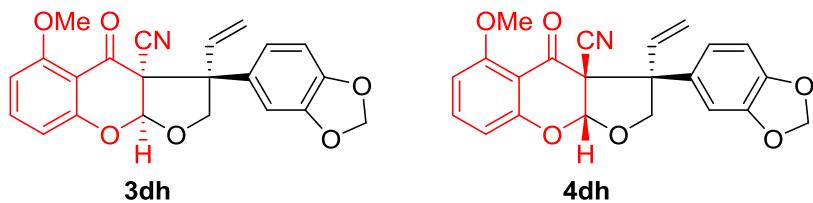
Yield: 93% (67.5 mg); both diastereomer **3bh**/**4bh** with $\text{dr} = 4.1:1$, **3bh**; ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.48 (m, 1H), 7.29–7.25 (m, 1H), 7.15–7.13 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 2H), 6.66 (dd, $J = 17.6, 10.8$ Hz, 1H), 6.41–6.38 (m, 2H), 6.13 (s, 1H), 5.40 (d, $J = 10.8$ Hz, 1H), 5.12 (d, $J = 17.2$ Hz, 1H), 4.77 (d, $J = 9.6$ Hz, 1H), 4.46 (d, $J = 9.2$ Hz, 1H), 3.72 (s, 3H), 2.18 (s, 3H); **4bh**; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.8$ Hz, 1H), 7.90 (dd, $J = 16.8, 8.4$ Hz, 1H) 7.48–7.41 (m, 1H), 7.35–7.30 (m, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.08 (d, $J = 17.6$ Hz, 1H), 6.68–6.65 (m, 1H), 6.22 (dd, $J = 17.2, 10.4$ Hz, 1H), 6.05 (s, 1H), 5.02 (d, $J = 10.8$ Hz, 1H), 4.72 (d, $J = 12.8$ Hz, 1H), 4.72 (d, $J = 13.2$ Hz, 1H), 4.69 (d, $J = 9.2$ Hz, 1H), 3.94 (s, 3H), 2.34 (s, 3H); mixture of **3bh** and **4bh**, ^{13}C NMR (100 MHz, CDCl_3) δ 182.0, 181.3, 160.8, 159.8, 158.5, 158.4, 138.2, 137.9, 137.7, 137.4, 136.9, 132.6, 129.2, 128.4, 128.3, 128.0, 127.9, 127.7, 118.7, 118.2, 116.2, 116.0, 111.3, 110.9, 110.6, 110.2, 106.1, 105.3, 105.2, 104.7, 77.9, 75.8, 62.6, 62.1, 59.6, 59.9, 56.4, 56.1, 20.9, 20.8; HRMS (ESI-MS): Calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}_4$ ($\text{M}+\text{Na}$): 384.1212, Found: 384.1212; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, $t_{\text{major}} = 12.6, 20.6$ min, $t_{\text{minor}} = 19.0, 14.6$ min; 96, 88% ee.

(3*R*,3a*R*,9a*S*)-3-(4-fluorophenyl)-5-methoxy-4-oxo-3-vinyl-2,3-dihydro-4*H*-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3ch), (3*R*,3a*S*,9a*R*)-(4ch)



Yield: 89% (65 mg); mixture of diastereomer **3ch**/**4ch** with **dr** = 2.8:1, **3ch**; ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.25 (m, 3H), 6.83–6.79 (m, 2H), 6.67 (dd, J = 17.2, 10.8 Hz, 1H), 6.44–6.37 (m, 2H), 6.13 (s, 1H), 5.45 (d, J = 11.2 Hz, 1H), 5.12 (d, J = 17.2 Hz, 1H), 4.79 (d, J = 9.2 Hz, 1H), 4.47 (d, J = 9.6 Hz, 1H), 3.77 (s, 3H); **4ch**; ^1H NMR (400 MHz, CDCl_3) δ 7.66–7.62 (m, 2H), 7.52 (dd, J = 16.8, 11.2 Hz, 1H), 7.12–7.08 (m, 2H), 6.84–6.78 (m, 1H), 6.69–6.66 (m, 1H), 6.20 (dd, J = 17.2, 10.8 Hz, 1H), 6.07 (s, 1H), 5.04 (d, J = 10.8 Hz, 1H), 4.73 (d, J = 9.2 Hz, 1H), 4.71 (d, J = 9.2 Hz, 1H), 4.69 (d, J = 17.2 Hz, 1H), 3.95 (s, 3H); mixture of **3ch** and **4ch**, ^{13}C NMR (100 MHz, CDCl_3) δ 181.9, 181.2, 163.1, 160.9, 160.6, 159.9, 158.5, 158.3, 138.0, 137.8, 137.5, 131.7, 131.6, 130.7, 130.3, 130.2, 119.4, 118.9, 116.0, 115.9, 115.5, 115.3, 114.6, 114.4, 110.6, 110.6, 106.2, 105.4, 105.2, 104.6, 78.2, 76.0, 62.5, 61.9, 59.7, 59.1, 56.4, 56.1; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{16}\text{FNO}_4(\text{M}+\text{Na})$: 388.0960, Found: 388.0961; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 13.3, 24.6 min, t_{minor} = 15.1, 17.4 min; 82, 87% ee.

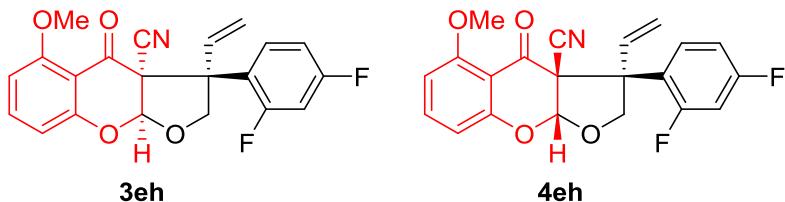
(3*R*,3*aR*,9*aS*)-3-(benzo[d][1,3]dioxol-5-yl)-5-methoxy-4-oxo-3-vinyl-2,3-dihydro-4*H*-furo[2,3-b]chromene-3*a*(9*aH*)-carbonitrile (3dh**), (3*R*,3*aS*,9*aR*)-(4**dh**)**



Yield: 90% (70.5 mg); both diastereomer **3dh**/**4dh** with **dr** = 6.1:1, **3dh**; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (dd, J = 16.8, 8.4 Hz, 1H), 6.82 (s, 1H), 6.71–6.54 (m, 2H), 6.61 (dd, J = 10.8, 6.4 Hz, 1H), 6.45 (dd, J = 8.4, 4.0 Hz, 2H), 6.13 (s, 1H), 5.83 (s, 2H), 5.42 (d, J = 10.8 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 4.70 (d, J = 9.2 Hz, 1H), 4.43 (d, J = 9.6 Hz, 1H) 3.77 (s, 3H); **4dh**; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, J = 16.8, 8.4 Hz, 1H), 7.27 (s, 1H), 7.17–7.08 (m, 2H), 6.83–6.81 (m, 1H), 6.70–6.57 (m, 1H), 6.18 (dd, J = 17.2, 10.8 Hz, 1H), 6.06 (s, 1H), 5.97 (s, 2H), 5.03 (d, J = 10.4 Hz, 1H), 4.77 (d, J = 17.2 Hz, 1H), 4.68 (d, J = 8.8 Hz, 1H), 4.64 (d, J = 8.8 Hz, 1H), 3.94 (s, 3H); mixture of **3dh** and **4dh**, ^{13}C NMR (100 MHz, CDCl_3) δ 181.9, 181.1, 160.8, 159.8, 158.4, 147.7, 147.0, 146.9, 146.8, 137.9, 137.8, 137.7, 137.1, 132.7, 129.3, 122.3, 121.8, 118.8, 118.4, 116.1, 115.9, 111.2, 110.8, 110.6, 110.1, 110.0, 109.3, 109.0, 108.0, 107.3, 106.1, 105.3, 105.2, 104.6, 101.2, 101.0, 78.0, 75.9, 62.4, 62.1, 61.0, 59.7, 56.3, 56.1; HRMS (ESI-MS): Calcd. for $\text{C}_{22}\text{H}_{17}\text{NO}_6(\text{M}+\text{Na})$: 414.0954, Found: 414.0961; HPLC conditions:

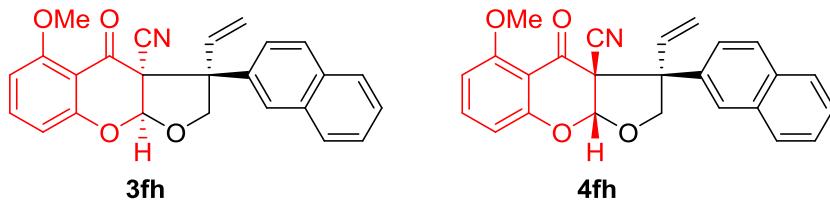
Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, *t*_{major} = 19.6, 34.1 min, *t*_{minor} = 23.5, 27.2 min; 76, 85% ee.

(3*R*,3a*R*,9a*S*)-3-(2,4-difluorophenyl)-5-methoxy-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9a*H*)-carbonitrile (3eh), (3*R*,3a*S*,9a*R*)-(4eh)



Yield: 82 % (63.3 mg); both diastereomer **3eh**/**4eh** with **dr** = 2.4:1, **3eh**; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 16.8, 8.4 Hz, 1H), 7.46 (dd, *J* = 16.4, 8.4 Hz, 1H), 7.34 (s, 1H), 6.91–6.81 (m, 1H), 6.73–6.72 (m, 1H), 6.66–6.58 (m, 1H), 6.28 (s, 1H), 6.20 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 10.4 Hz, 1H), 4.70 (d, *J* = 17.2 Hz, 1H) 3.76 (s, 3H); **4eh**; ¹H NMR (400 MHz, CDCl₃) δ 8.72 (dd, *J* = 8.8, 6.0 Hz, 1H), δ 8.69 (dd, *J* = 9.2, 6.4 Hz, 1H), 7.22–7.17 (m, 1H), 7.11–7.05 (m, 1H), 6.86 (s, 1H), 6.61–6.54 (m, 1H), 6.12 (s, 1H), 5.09 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.64 (d, *J* = 9.6 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 4.57 (d, *J* = 9.6 Hz, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 4.03 (s, 3H); mixture of **3eh** and **4eh**, ¹³C NMR (100 MHz, CDCl₃) δ 181.9, 180.3, 163.8, 161.5, 161.2, 159.6, 158.9, 158.8, 158.3, 138.2, 137.1, 136.8, 136.8, 136.5, 132.4, 132.4, 132.3, 132.3, 130.1, 130.0, 130.0, 129.9, 120.0, 119.4, 119.3, 119.2, 119.2, 117.6, 115.8, 115.5, 111.7, 111.3, 111.2, 111.1, 111.0, 110.9, 110.9, 110.8, 110.7, 110.5, 110.54, 106.1, 106.0, 105.0, 104.9, 104.8, 104.7, 104.6, 104.5, 104.4, 104.3, 104.1, 79.6, 79.4, 75.9, 75.8, 61.4, 61.2, 59.2, 59.2, 58.0, 57.9, 56.4, 56.0, 29.6, 26.8; HRMS (ESI-MS): Calcd. for C₂₁H₁₅F₂NO₄ (M+Na): 406.0867, Found: 406.0860; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, *t*_{major} = 11.0, 16.2 min, *t*_{minor} = 8.7, 18.8 min; 87, 95% ee.

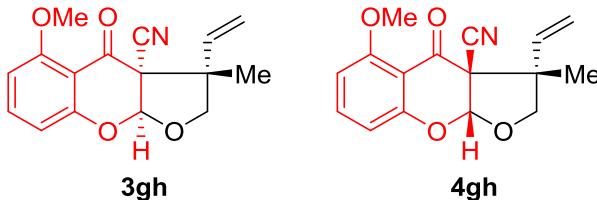
(3*R*,3a*R*,9a*S*)-5-methoxy-3-(naphthalen-2-yl)-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9a*H*)-carbonitrile (3fh), (3*R*,3a*S*,9a*R*)-(4fh)



Yield: 88% (70 mg); both diastereomer **3fh**/**4fh** with **dr** = 4.0:1, **3fh**; ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.65 (m, 2H), 7.64–7.57 (m, 2H), 7.52–7.45 (m, 1H), 7.11 (dd, *J* = 16.8, 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 11.2 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 6.20 (s, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 5.46 (d, *J* = 10.8 Hz,

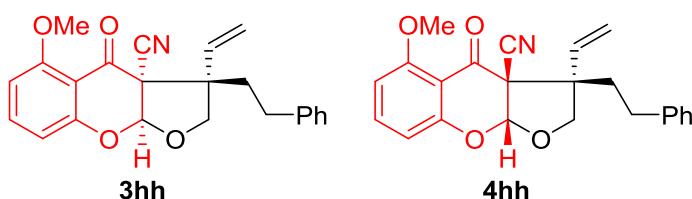
1H), 5.14 (d, J = 17.6 Hz, 1H), 4.90 (d, J = 9.6 Hz, 1H), 4.54 (d, J = 9.6 Hz, 1H), 3.36 (s, 3H); **4fh**; ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, J = 2.0 Hz, 1H), 8.98–7.81 (m, 3H), 7.54–7.49 (m, 2H), 7.44–7.38 (m, 2H), 6.69 (dd, J = 16.8, 8.4 Hz, 1H), 6.30 (dd, J = 17.2, 10.4 Hz, 1H), 6.11 (s, 1H), 5.28 (s, 1H), 5.06 (d, J = 10.8 Hz, 1H), 4.85 (d, J = 7.6 Hz, 1H), 4.73 (d, J = 17.2 Hz, 1H), 3.97 (s, 3H); mixture of **3fh** and **4fh**; ^{13}C NMR (100 MHz, CDCl_3) δ 181.9, 181.2, 160.9, 159.4, 158.5, 158.4, 138.2, 137.9, 137.7, 136.8, 136.3, 133.3, 132.4, 132.9, 132.4, 132.3, 128.5, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.5, 126.4, 126.4, 126.3, 126.1, 125.9, 119.6, 118.7, 116.2, 111.3, 111.2, 110.7, 109.9, 106.2, 105.4, 105.3, 104.8, 78.2, 75.9, 62.9, 60.3, 56.4, 55.7; HRMS (ESI-MS): Calcd. for $\text{C}_{25}\text{H}_{19}\text{NO}_4$ ($\text{M}+\text{Na}$): 420.1212, Found: 420.1225; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 7.5, 16.6 min, t_{minor} = 8.9, 11.0 min; 88, 80% ee.

(3S,3a*R*,9a*S*)-5-methoxy-3-methyl-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3gh), (3*S*,3a*S*,9a*R*)-(4gh)



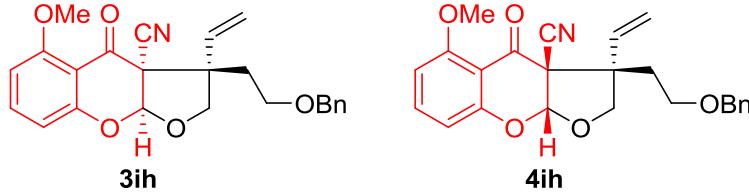
Yield: 86% (49.5 mg); mixture of diastereomer **3gh**/**4gh** with $\text{dr} = 1.9:1$, **3gh**; ^1H NMR (400 MHz, CDCl_3) δ 7.53–7.49 (m, 1H), 6.69–6.65 (m, 2H), 6.26 (dd, J = 17.2, 10.8 Hz, 1H), 6.01 (s, 1H), 5.39 (d, J = 10.8 Hz, 1H), 5.27 (d, J = 17.2 Hz, 1H), 4.30 (d, J = 8.8 Hz, 1H), 4.05 (d, J = 8.8 Hz, 1H), 3.94 (s, 3H), 1.33 (s, 3H); **4gh**; ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.49 (m, 1H), 6.69–6.62 (m, 2H), 6.00 (s, 1H), 5.90 (dd, J = 17.6, 10.8 Hz, 1H), 5.19 (d, J = 17.2 Hz, 1H), 5.07 (d, J = 10.8 Hz, 1H), 4.32 (d, J = 8.0 Hz, 1H), 4.05 (d, J = 8.8 Hz, 1H), 3.92 (s, 3H), 1.64 (s, 3H); mixture of **3gh** and **4gh**; ^{13}C NMR (100 MHz, CDCl_3) δ 181.4, 181.4, 160.8, 160.7, 158.9, 158.8, 138.4, 137.8, 137.7, 136.8, 117.8, 116.9, 115.8, 111.2, 110.9, 110.8, 110.7, 106.1, 106.0, 104.8, 104.6, 79.3, 78.7, 62.6, 61.9, 56.3, 51.4, 51.1, 29.6, 29.3, 21.3, 20.5; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_4$ ($\text{M}+\text{Na}$): 308.0899, Found: 308.0894; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, t_{major} = 20.9, 26.1 min, t_{minor} = 28.9, 22.7 min; 82, 91% ee.

(3*S*,3a*R*,9a*S*)-5-methoxy-4-oxo-3-phenethyl-3-vinyl-2,3-dihydro-4H-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3hh), (3*S*,3a*S*,9a*R*)-(4hh)



Yield: 90% (68 mg); both diastereomer **3hh**/**4hh** with $\text{dr} = 5.5:1$, **3hh**; ^1H NMR (400 MHz, CDCl_3) δ 7.49–7.45 (m, 1H), 7.25–7.20 (m, 2H), 7.17–7.13 (m, 1H), 7.07–7.05 (m, 2H), 6.67–6.63 (m, 2H), 6.21 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.98 (s, 1H), 5.57 (d, $J = 10.8$ Hz, 1H), 5.31 (d, $J = 15.2$ Hz, 1H), 4.35 (d, $J = 9.2$ Hz, 1H), 4.10 (d, $J = 9.2$ Hz, 1H), 3.90 (s, 3H), 2.72–2.64 (m, 1H), 2.42–2.32 (m, 1H), 1.99–1.87 (m, 2H); **4hh**; ^1H NMR (400 MHz, CDCl_3) δ 8.0–7.9 (m, 1H), 7.61–7.59 (m, 1H), 7.49–7.39 (m, 1H), 7.32–7.23 (m, 2H), 7.18–7.12 (m, 2H), 6.62–6.57 (m, 1H), 5.98 (s, 1H), 5.72 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.29 (d, $J = 17.6$ Hz, 1H), 5.23 (d, $J = 10.8$ Hz, 1H)), 4.43 (d, $J = 9.2$ Hz, 1H), 4.07 (d, $J = 8.0$ Hz, 1H), 3.92 (s, 3H), 3.35–3.23 (m, 1H), 2.79–2.74 (m, 1H), 2.53–2.46 (m, 1H), 2.35–2.28 (m, 1H); mixture of **3hh** and **4hh**, ^{13}C NMR (100 MHz, CDCl_3) δ 181.9, 181.7, 160.4, 158.8, 158.9, 140.7, 140.6, 137.9, 137.8, 136.9, 134.7, 128.5, 128.4, 128.3, 126.2, 126.1, 119.2, 117.9, 115.8, 115.6, 111.9, 111.2, 110.7, 110.6, 106.4, 105.7, 104.5, 104.3, 76.1, 74.5, 63.2, 62.0, 56.3, 56.1, 54.2, 53.4, 37.7, 35.1, 31.3, 29.6, 22.6, 22.5; HRMS (ESI-MS): Calcd. for $\text{C}_{23}\text{H}_{21}\text{NO}_4$ ($\text{M}+\text{Na}$): 398.1368, Found: 398.1367; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, $t_{\text{major}} = 11.0$, 17.7 min, $t_{\text{minor}} = 26.5$, 14.0 min; 92, 66% ee.

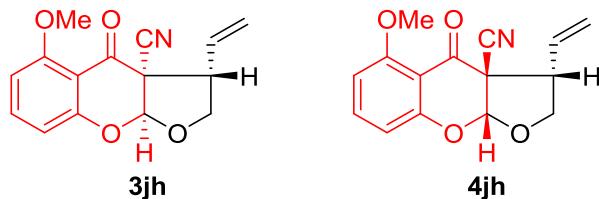
(3*S*,3a*R*,9a*S*)-3-(2-(benzyloxy)ethyl)-5-methoxy-4-oxo-3-vinyl-2,3-dihydro-4*H*-furo[2,3-b]chromene-3a(9a*H*)-carbonitrile (3ih), (3*S*,3a*S*,9a*R*)-(4ih)



Yield: 88% (71.6 mg); both diastereomer **3ih**/**4ih** with $\text{dr} = 3.4:1$, **3ai**; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 16.8, 8.4$ Hz, 1H), 7.33–7.20 (m, 5H), 6.67 (dd, $J = 16.0, 7.6$ Hz, 2H), 6.05 (dd, $J = 17.2, 10.4$ Hz, 1H), 5.96 (s, 1H), 5.46 (d, $J = 11.2$ Hz, 1H), 5.31 (d, $J = 17.6$ Hz, 1H), 4.31–4.34 (m, 1H), 4.36 (s, 2H), 4.11 (d, $J = 9.6$ Hz, 1H), 3.92 (s, 3H), 3.50–3.47 (m, 1H), 3.43–3.37 (m, 1H), 2.04–1.90 (m, 2H); **4ai**; ^1H NMR (400 MHz, CDCl_3) δ 8.01–7.91 (m, 1H), 6.61 (dd, $J = 8.8, 1.2$ Hz, 2H), 7.54–7.39 (m, 2H), 7.36–7.20 (m, 2H), 5.58 (dd, $J = 12.4, 8.4$ Hz, 1H), 5.90 (s, 1H), 5.56 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.19 (d, $J = 17.6$ Hz, 1H), 5.11 (d, $J = 10.6$ Hz, 1H), 4.45–4.31 (m, 1H), 4.31 (s, 2H), 4.24 (d, $J = 10.0$ Hz, 1H), 3.92 (s, 3H), 3.57–3.52 (m, 1H), 3.34–3.23 (m, 1H), 2.50–2.36 (m, 2H); mixture of **3ih** and **4ih**, ^{13}C NMR (100 MHz, CDCl_3) δ 182.1, 182.0, 160.8, 160.4, 159.2, 159.0, 138.1, 138.0, 137.8, 137.7, 136.3, 133.9, 128.4, 127.7, 127.6, 127.6, 127.5, 119.1, 118.0, 115.6, 115.7, 112.0, 111.3, 110.7, 110.6, 106.4, 105.6, 104.0, 103.6, 77.2, 76.9, 75.6, 73.1, 73.0, 66.4, 65.7, 63.1, 62.0, 56.3, 55.7, 53.3, 35.2, 33.1, 29.7; HRMS (ESI-MS): Calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_5$ ($\text{M}+\text{Na}$): 428.1473, Found: 428.1474; HPLC condi-

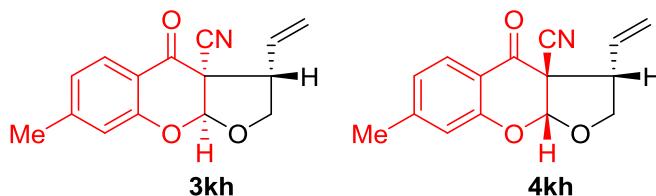
tions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, *t*_{major} = 33.6, 35.5 min, *t*_{minor} = 32.3, 30.6 min; 94, 87% ee.

(3*S*,3a*R*,9a*S*)-5-methoxy-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9aH)-carbonitrile (3jh), (3*S*,3a*S*,9a*R*)-(4jh)



Yield: 96% (52.2 mg); mixture of diastereomer **3jh/4jh** with **dr** = 7.5:1, **3jh**; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, *J* = 16.8, 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 5.98 (ddd, *J* = 19.2, 10.4, 8.4 Hz, 1H), 5.97 (s, 1H), 5.40 (d, *J* = 10.0 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 4.46 (dd, *J* = 17.2, 8.8 Hz, 1H), 4.09 (dd, *J* = 18.0, 9.2 Hz, 1H), 3.94 (s, 3H), 3.50 (q, *J* = 8.8 Hz, 1H); **4jh**; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (dd, *J* = 16.8, 8.4 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.98 (s, 1H), 5.59 (ddd, *J* = 26.8, 16.8, 9.6 Hz, 1H), 5.25 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.54 (dd, *J* = 9.2, 7.6 Hz, 1H), 4.15 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.93 (s, 3H), 3.68 (m, 1H); mixture of **3jh** and **4jh**; ¹³C NMR (100 MHz, CDCl₃) δ 181.1, 181.0, 161.5, 160.8, 158.7, 158.3, 138.0, 137.9, 132.0, 129.6, 122.4, 122.2, 116.9, 114.2, 110.8, 110.7, 110.4, 107.9, 106.1, 105.8, 104.0, 103.7, 73.4, 71.7, 59.8, 59.2, 56.4, 56.4, 51.6, 48.1; HRMS (ESI-MS): Calcd. for C₁₅H₁₃NO₄ (M+Na): 294.0742, Found: 294.0729; HPLC conditions: Chiralcel AD-H column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, *t*_{major} = 19.0, 21.3 min, *t*_{minor} = 16.8, 23.3 min; 95, 95% ee.

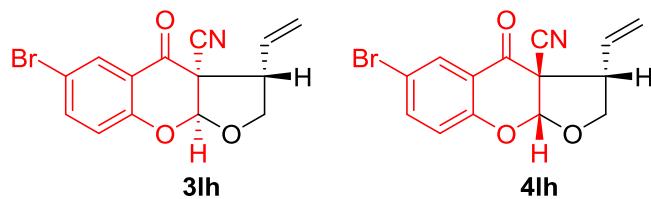
(3*S*,3a*R*,9a*S*)-7-methyl-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-b]chromene-3a(9aH)-carbonitrile (3kh), (3*S*,3a*S*,9a*R*)-(4kh)



Yield: 88% (45 mg); both diastereomer **3kh/4kh** with **dr** = 1.38:1, **3kh**; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 1H), 6.87–6.85 (m, 2H), 6.04 (s, 1H), 5.96 (ddd, *J* = 18.4, 10.0, 8.4 Hz, 1H), 5.40 (d, *J* = 10.0 Hz, 1H), 5.26 (d, *J* = 16.8 Hz, 1H), 4.49 (dd, *J* = 17.6, 8.8 Hz, 1H), 4.12 (dd, *J* = 17.6, 8.8 Hz, 1H), 3.48 (q, *J* = 8.8 Hz, 1H), 2.40 (s, 3H); **4kh**; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 1H), 6.98–6.94 (m, 2H), 6.02 (s, 1H), 5.52 (ddd, *J* = 26.4, 16.8, 9.6 Hz, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 4.60 (dd, *J* = 16.8, 8.8 Hz, 1H), 4.20 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.70–3.64 (m, 1H), 2.40 (s, 3H). mixture of **3kh** and **4kh**; ¹³C NMR (100 MHz, CDCl₃) δ 182.7, 182.5, 157.2, 156.7, 150.2, 150.1, 132.0, 129.4, 127.6, 127.2, 124.7, 124.6, 122.6, 122.1, 118.7, 118.5, 117.3, 116.6, 114.4,

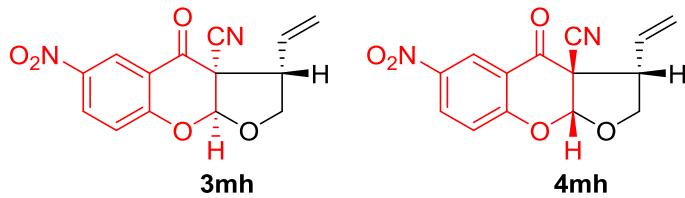
113.9, 104.6, 104.1, 73.4, 71.8, 58.9, 58.0, 51.0, 47.9, 22.0, 21.9; HRMS (ESI-MS): Calcd. for C₁₅H₁₃NO₃ (M+Na): 278.0895, Found: 278.0801; HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 0.400 ml/min, *i*-PrOH/hexanes = 1/5, t_{major} = 20.29, 27.98 min, t_{minor} = 24.5, 26.11 min; 82, 85% ee.

(3*S*,3a*R*,9a*S*)-6-bromo-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3lh), (3*S*,3a*S*,9a*R*)-(4kh)



Yield: 81% (51 mg); both diastereomer **3lh/4kh** with dr = 1:1.28, **3lh**; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 8.2, 2.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.05 (s, 1H), 5.95 (ddd, *J* = 18.4, 10.0, 8.4 Hz, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 4.62 (dd, *J* = 16.9, 7.6 Hz, 1H), 4.23 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.72–3.67 (m, 1H); **4lh**; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 2.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.07 (s, 1H), 5.49 (ddd, *J* = 26.8, 17.2, 10.0 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H) 5.27 (d, *J* = 17.2 Hz, 1H), 4.51 (dd, *J* = 17.6 8.8 Hz, 1H), 4.14 (dd, *J* = 18.0, 8.8 Hz, 1H), 3.46 (q, *J* = 8.8 Hz, 1H)); mixture of **3lh** and **4lh**, ¹³C NMR (101 MHz, Chloroform-*d*) δ 182.4, 182.0, 156.1, 155.6, 140.7, 140.6, 131.6, 130.1, 129.7, 128.9, 123.2, 122.8, 120.8, 120.6, 118.0, 116.2, 116.1, 116.0, 113.4, 104.8, 104.3, 73.6, 71.9, 58.9, 58.0, 51.1, 47.9; HRMS (ESI-MS): Calcd. for C₁₄H₁₀BrNO₃ (M+Na): 341.9844, Found: 341.9745; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 0.500 ml/min, *i*-PrOH/hexanes = 1/25, t_{major} = 47.6, 65.25 min, t_{minor} = 50.9, 41.6 min; 86, 80% ee.

(3*S*,3a*R*,9a*S*)-6-nitro-4-oxo-3-vinyl-2,3-dihydro-4H-furo[2,3-*b*]chromene-3a(9a*H*)-carbonitrile (3mh/4mh), (3*S*,3a*S*,9a*R*)-(4mh)



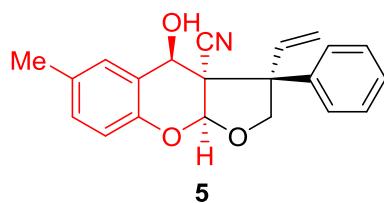
Yield: 85% (49 mg); both diastereomer **3mh/4mh** with dr = 1:1.16, **3mh**; ¹H NMR (400 MHz, CDCl₃) δ 8.78 (d, *J* = 2.8 Hz, 1H), 8.45 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.24 (d, *J* = 9.2 Hz, 1H) 6.17 (s, 1H), 5.46 (ddd, *J* = 18.4, 13.2, 9.6 Hz, 1H), 5.30 (d, *J* = 4.4 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.67 (dd, *J* = 9.2, 7.6 Hz, 1H), 4.28 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.79–3.73 (m, 1H); **4mh**; ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 2.8 Hz, 1H), 8.47 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H) 6.20 (s, 1H), 5.95 (ddd, *J* = 18.8, 10.4, 8.4Hz, 1H), 5.42 (d, *J* = 9.6 Hz, 1H), 5.25 (d, *J* = 3.2 Hz, 1H), 4.55 (dd, *J* = 17.6, 8.8 Hz, 1H),

4.19 (dd, $J = 18.0, 8.8$ Hz, 1H), 3.45 (q, $J = 8.4$ Hz, 1H); mixture of **3mh** and **4mh**, ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.9, 181.5, 161.0, 160.5, 143.3, 143.2, 132.2, 132.0, 131.0, 128.4, 124.3, 123.7, 123.5, 120.2, 120.1, 119.0, 116.2, 115.4, 112.8, 105.3, 104.8, 73.7, 72.0, 59.12, 58.1, 53.4, 51.1, 48.1; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$): 309.0590, Found: 309.0490; **HPLC conditions: Chiralcel OD-H column, 254 nm, flow rate: 0.4 ml/min, *i*-PrOH/hexanes = 1/1, $t_{\text{major}} = 28.71, 57.22$ min, $t_{\text{minor}} = 39.15, 36.82$ min; 80, 61% ee.**

Procedure for transformation of **3aa** to **5**

To a solution of product **3aa** (66.2 mg 0.2 mmol) in THF/MeOH (2:1, 3 ml) was added NaBH_4 (13.6 mg, 0.2 mmol, 1.8 eq) at 0 °C and reaction mixture was stirred for 0.5 h. The reaction mixture was quenched by water and extracted with ethyl acetate, dried over anhydrous Na_2SO_4 , filtered and concentrated. The residue was purified by flash chromatography (eluent: petroleum ether / ethyl acetate = 10/3) on silica to afford the product **5** (83%, 55.5 mg) as a white solid.

(*3R,3aS,4R,9aS*)-4-hydroxy-6-methyl-3-phenyl-3-vinyl-2,3-dihydro-4*H*-furo[2,3-*b*]chromene-3*a*(9*aH*)-carbonitrile (**5**)



Yield: 83% (55.5 mg); white solid; m.p. = 133–135 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.47–7.42 (m, 2H), 7.39–7.34 (m, 3H), 7.13–7.10 (m, 1H), 6.99–6.96 (m, 2H), 6.40 (dd, $J = 17.2, 10.4$ Hz, 1H), 6.01 (s, 1H), 5.29 (d, $J = 10.8$ Hz, 1H), 5.11 (d, $J = 8.0$ Hz, 1H), 4.94 (d, $J = 17.2$ Hz, 1H), 4.91 (s, 1H), 4.48 (d, $J = 8.0$ Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 141.6, 137.8, 133.2, 131.6, 129.0, 128.6, 127.7, 126.8, 125.0, 118.9, 118.3, 116.7, 105.7, 75.8, 69.2, 58.9, 55.5, 20.6; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{19}\text{NO}_3$ ($\text{M}+\text{Na}$): 356.1263, Found: 356.1260.

X-rays crystallography of **3ag** (CCDC1814953), **4ag** (CCDC 1814954) and **5** (CCDC1814955)

A single crystal of **3ag/4ag** and **5** was obtained from THF/Hexane solvent at room temperature. Diffraction data were collected on Bruker SMART Apex-III CMOS-Based X-ray diffractometer with Cu-K α . Radiation ($\lambda = 1.54178$). The empirical absorption correction was applied by using the SADABS program. The structure was solved using direct method, and refined by full matrix least-squares on F^2 (G.M Sheldrick, SHELXTL2014, program of crystal structure refinement, University of Göttingen, Germany).

Table S1 Crystal data and structure refinement for **3ag** (major diastereomer).

Identification code	3ag
Empirical formula	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_5$

Formula weight	362.33
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.6428 (3) alpha = 90 deg.
b/Å	14.2542(5) beta = 90 deg.
c/Å	17.8105(7) gamma = 90 deg.
Volume/Å ³	1686.44(12)
Z	4
Calculated density	1.427 Mg/m ³
Absorption coefficient	0.871 mm ⁻¹
F(000)	700
Crystal size/mm ³	0.05 × 0.04 × 0.03
Radiation	Cu-Kα (λ = 1.54178)
Theta range for data collection	3.972 to 66.760 deg.
Limiting indices	-7 <= h <= 7, -16 <= k <= 16, -21 <= l <= 20
Reflections collected/unique	19936/2973[R _{int} = 0.0257]
Data/restraints/parameters	2973/0/246
Goodness-of-fit on F ²	1.076
Final R indexes [I>2sigma(I)]	R ₁ = 0.0231, wR ₂ = 0.0617
R indexes [all data]	R ₁ = 0.0240, wR ₂ = 0.0625
Absolute structure parameter	-0.08(17)
Largest diff. peak/hole / e Å ⁻³	0.147/-0.107

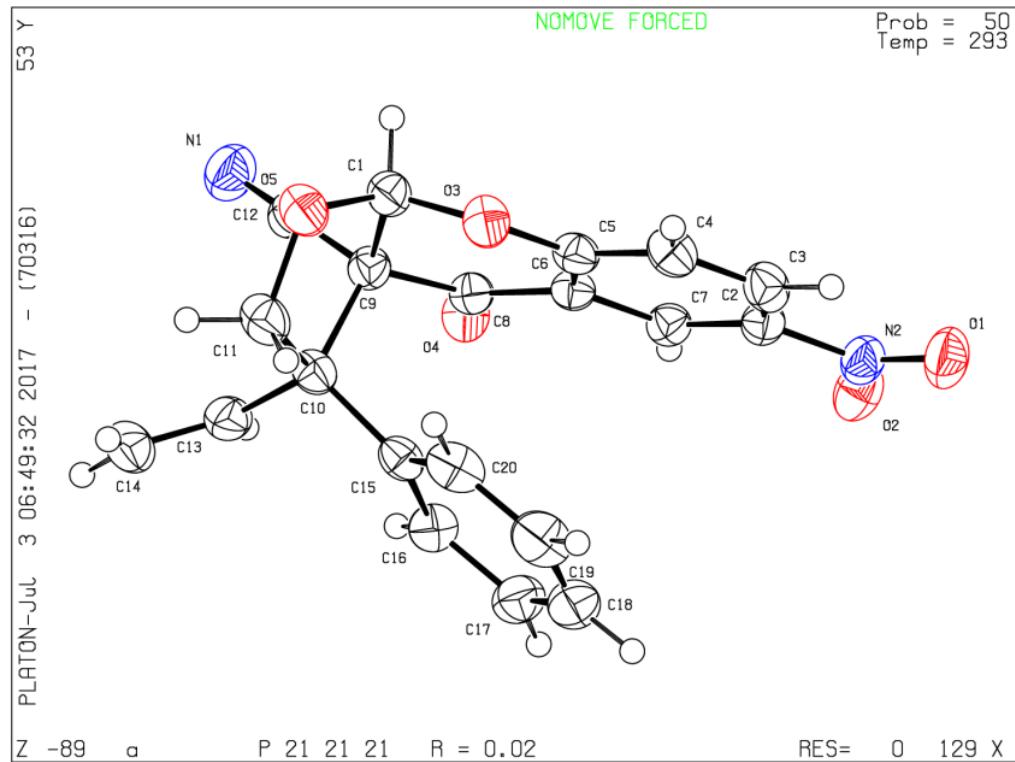


Figure S1: Molecular structure of 3ag (major diastereomer)

Table S2 Crystal data and structure refinement for 4ag (minor diastereomer).

Identification code	4ag
Empirical formula	C ₂₀ H ₁₄ N ₂ O ₅
Formula weight	362.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.4782 (3) alpha = 90 deg.
b/Å	14.6774(4) beta = 115.8240(10) deg.
c/Å	10.8540(3) gamma = 90 deg.
Volume/Å ³	1686.44(12)
Z	4
Calculated density	1.462 Mg/m ³
Absorption coefficient	0.893 mm ⁻¹

F(000)	688
Crystal size/mm ³	0.05 × 0.04 × 0.03
Radiation	Cu-Kα ($\lambda = 1.54178$)
Theta range for data collection/°	5.235 to 66.689
Limiting indices	-13 <= h <= 12, -17 <= k <= 17, -12 <= l <= 12
Reflections collected/unique	16118/2888 [R _{int} = 0.0230]
Data/restraints/parameters	2973/0/246
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R ₁ = 0.0310, wR ₂ = 0.0841
R indexes [all data]	R ₁ = 0.0344, wR ₂ = 0.0870
Largest diff. peak/hole / e Å ⁻³	0.262/-0.206

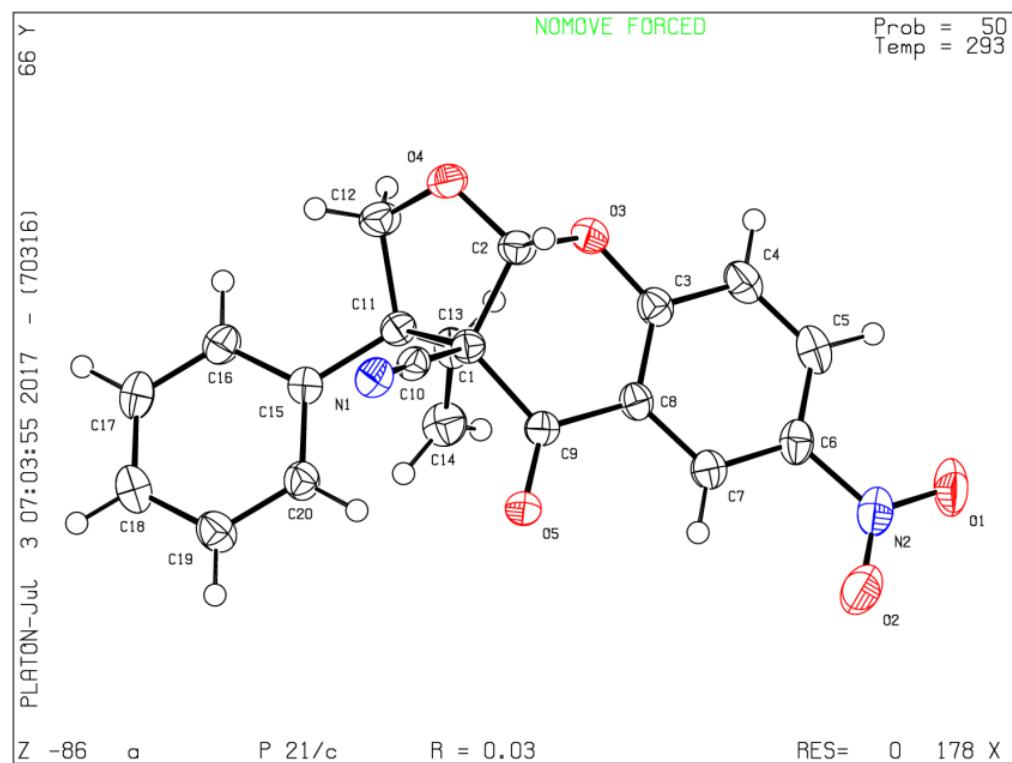


Figure S2: Molecular structure of 4ag (minor diastereomer)

Table S3 Crystal data and structure refinement for 5

Identification code	5
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Empirical formula	C ₂₁ H ₁₉ NO ₃
Formula weight	333.37
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.0542 (2) alpha = 90 deg.
b/Å	14.1154 (4) beta = 90 deg.
c/Å	17.6777(7) gamma = 90 deg.
Volume/Å ³	1760.22(9)
Z	4
Calculated density	1.258 Mg/m ³
Absorption coefficient	0.678 mm ⁻¹
F(000)	636
Crystal size/mm ³	0.05 × 0.04 × 0.03
Radiation	Cu-Kα (λ = 1.54178)
Theta range for data collection	5.906 to 66.588 deg.
Limiting indices	-8 <= h <= 7, -16 <= k <= 16, -21 <= l <= 19
Reflections collected/unique	14032 / 3094 [R _{int} = 0.1253]
Data/restraints/parameters	3094/0/230
Goodness-of-fit on F ²	1.051
Final R indexes [I>2sigma(I)]	R ₁ = 0.0457, wR ₂ = 0.1228
R indices [all data]	R ₁ = 0.0474, wR ₂ = 0.1258
Absolute structure parameter	-0.1(3)
Largest diff. peak/hole / e Å ⁻³	0.296 / -0.222

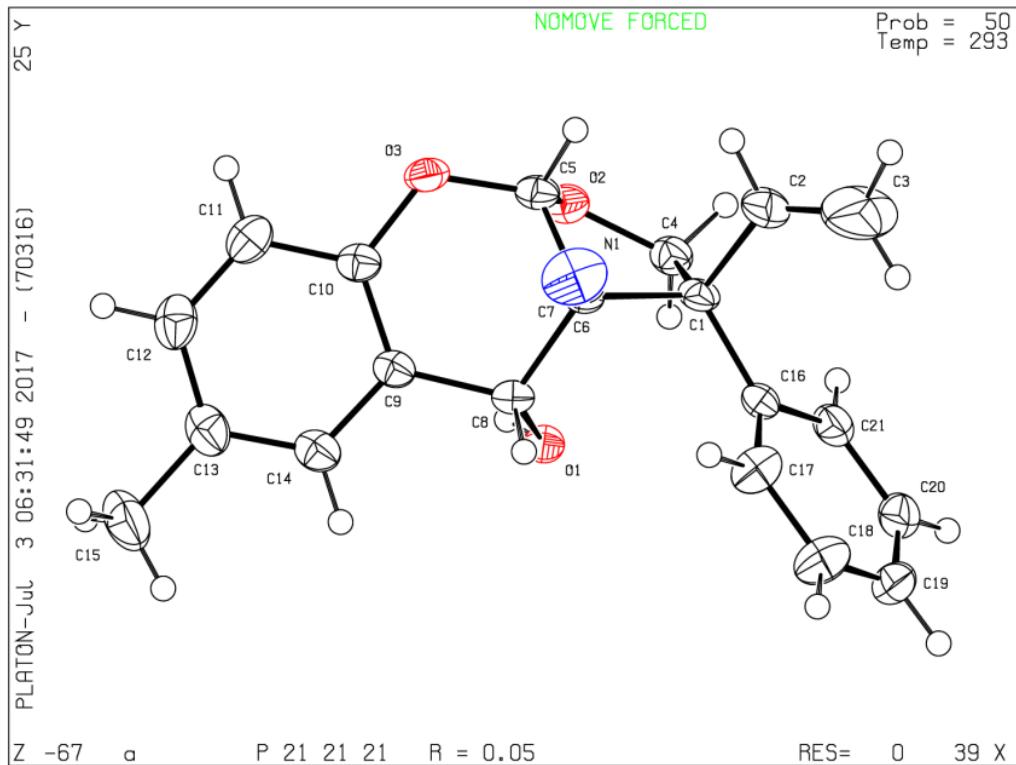
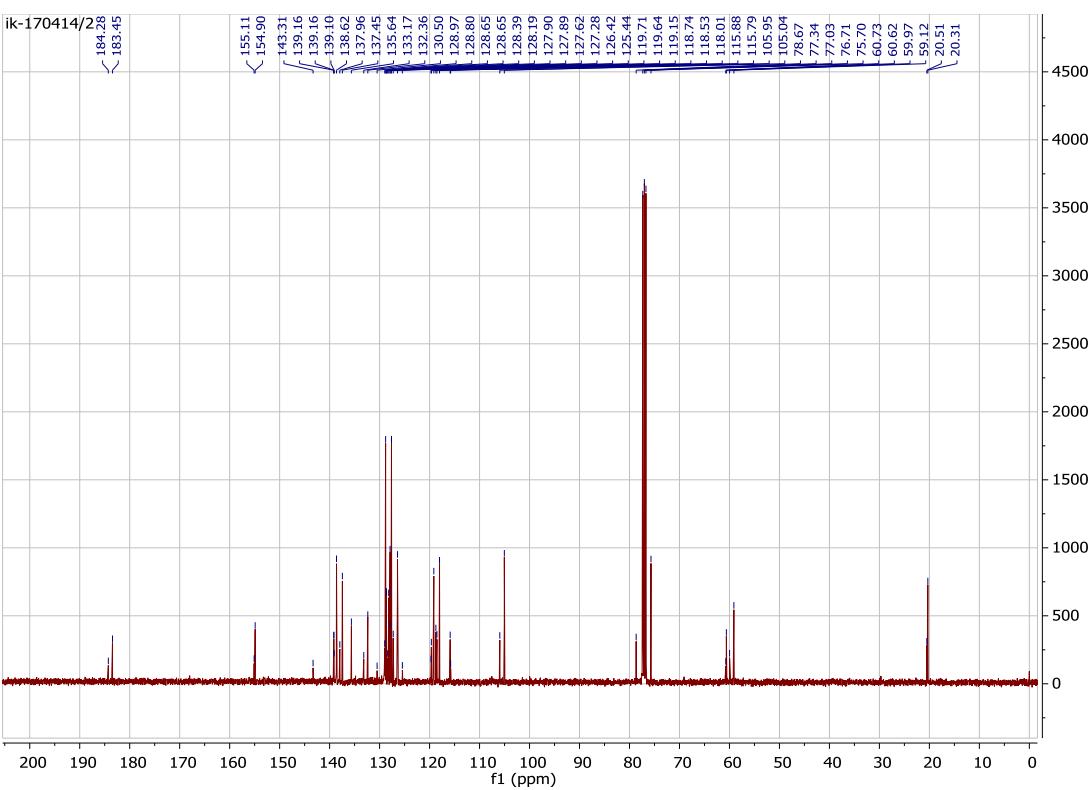
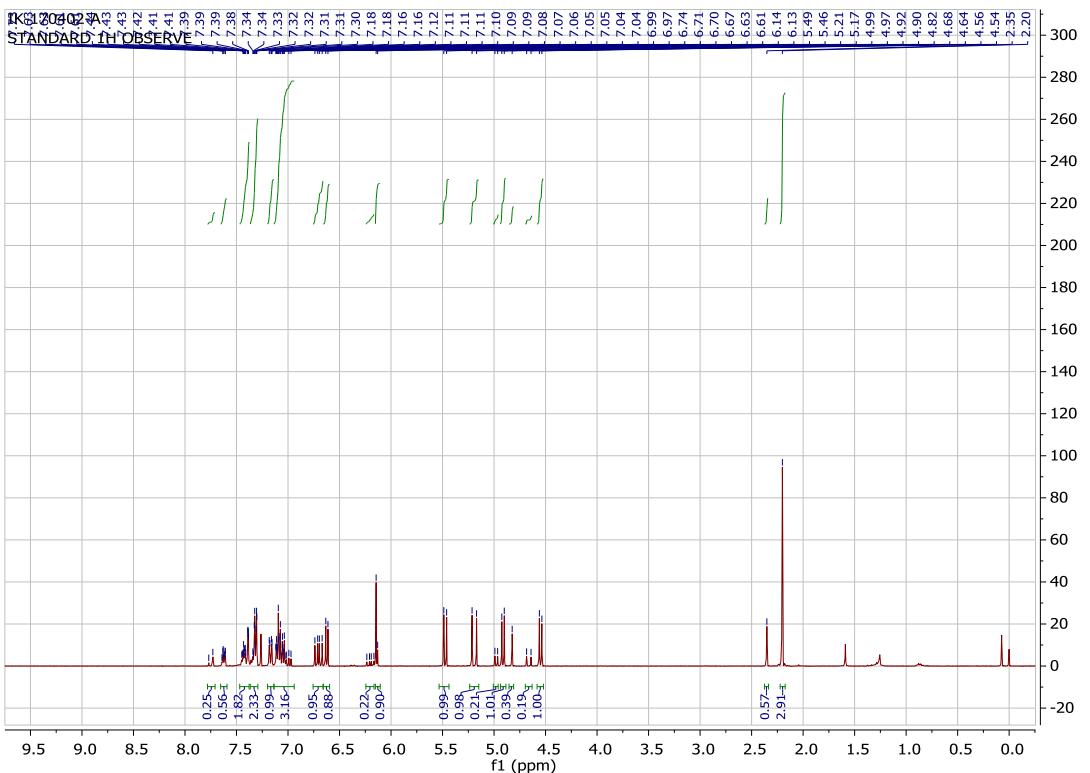
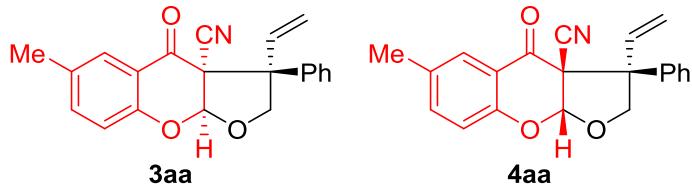
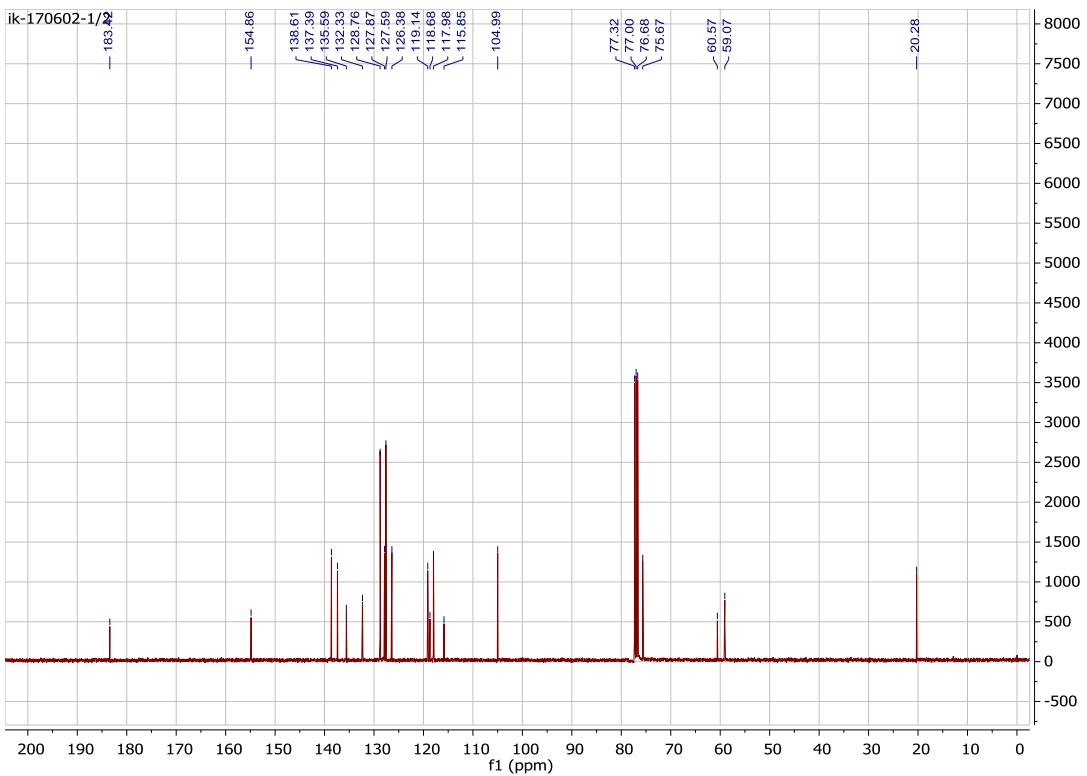
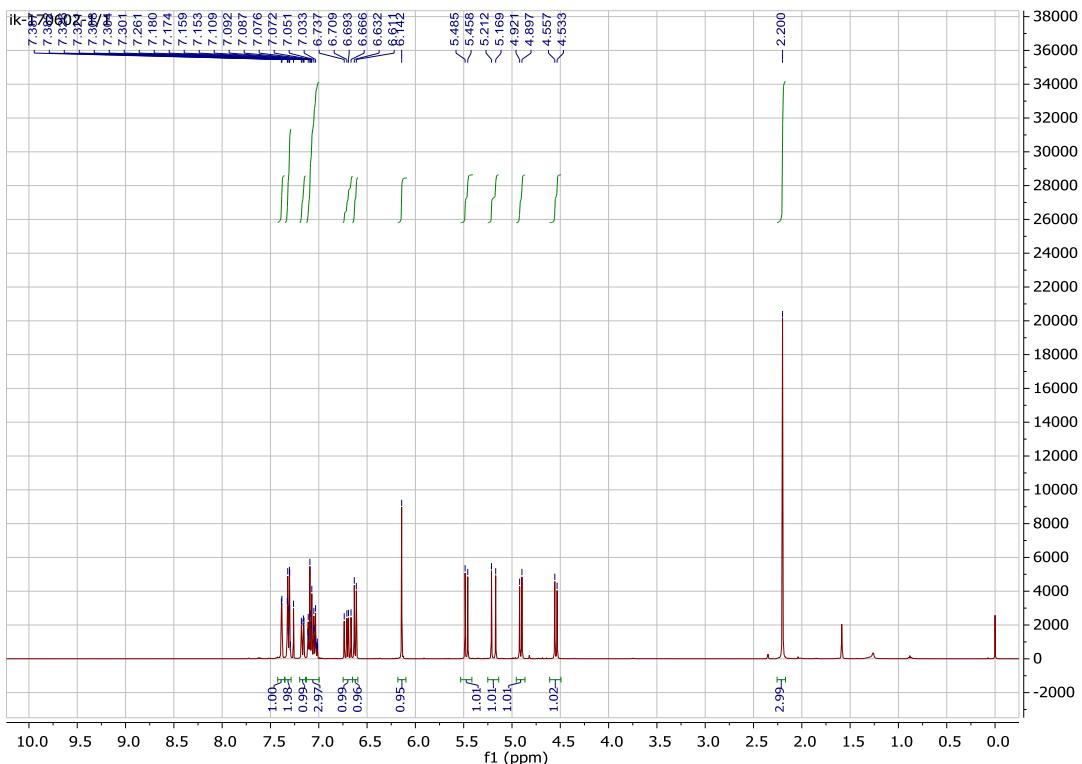
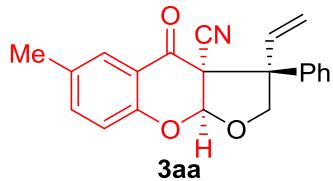


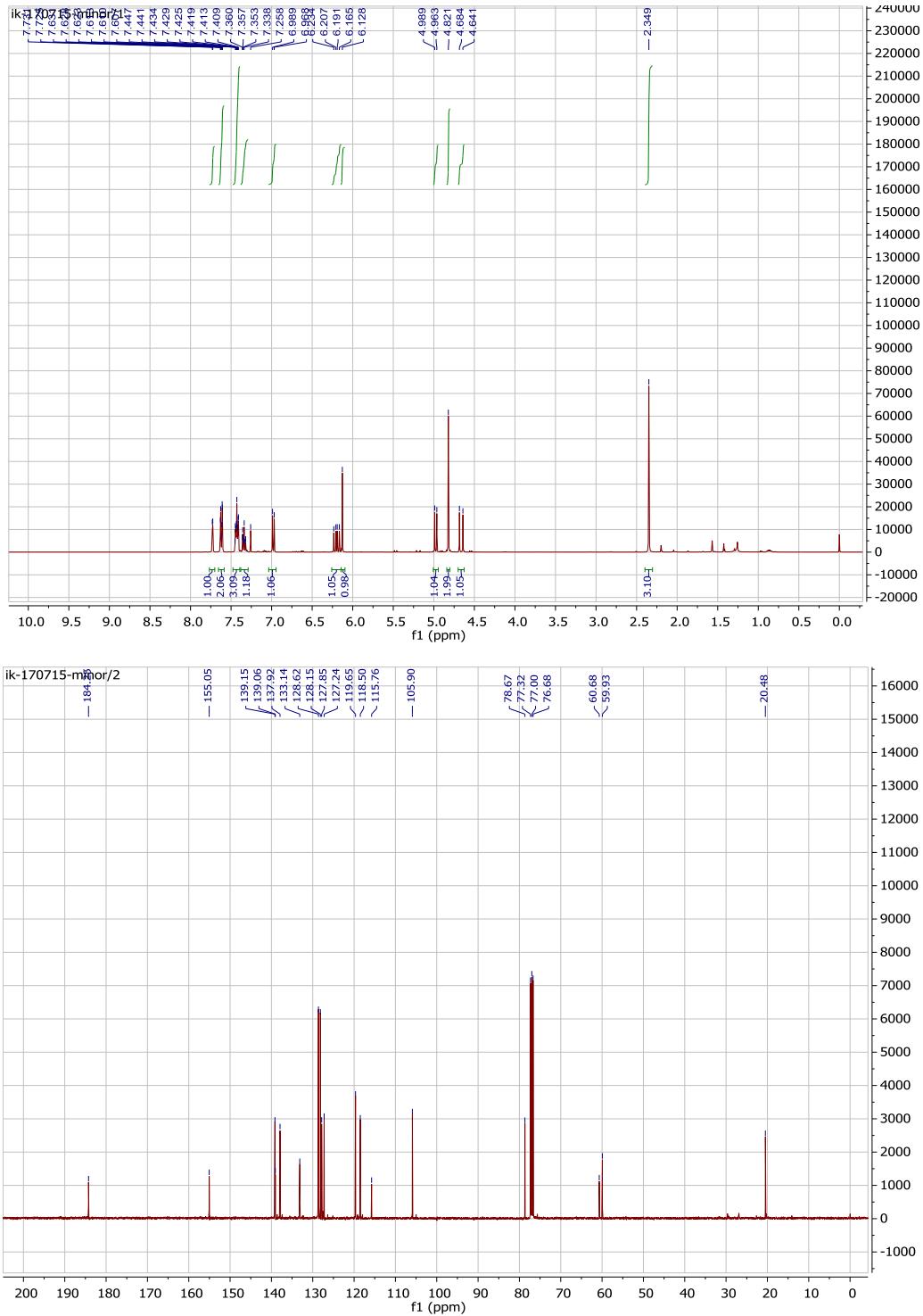
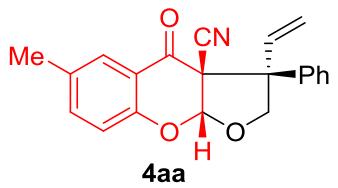
Figure S3: Molecular structure of 5

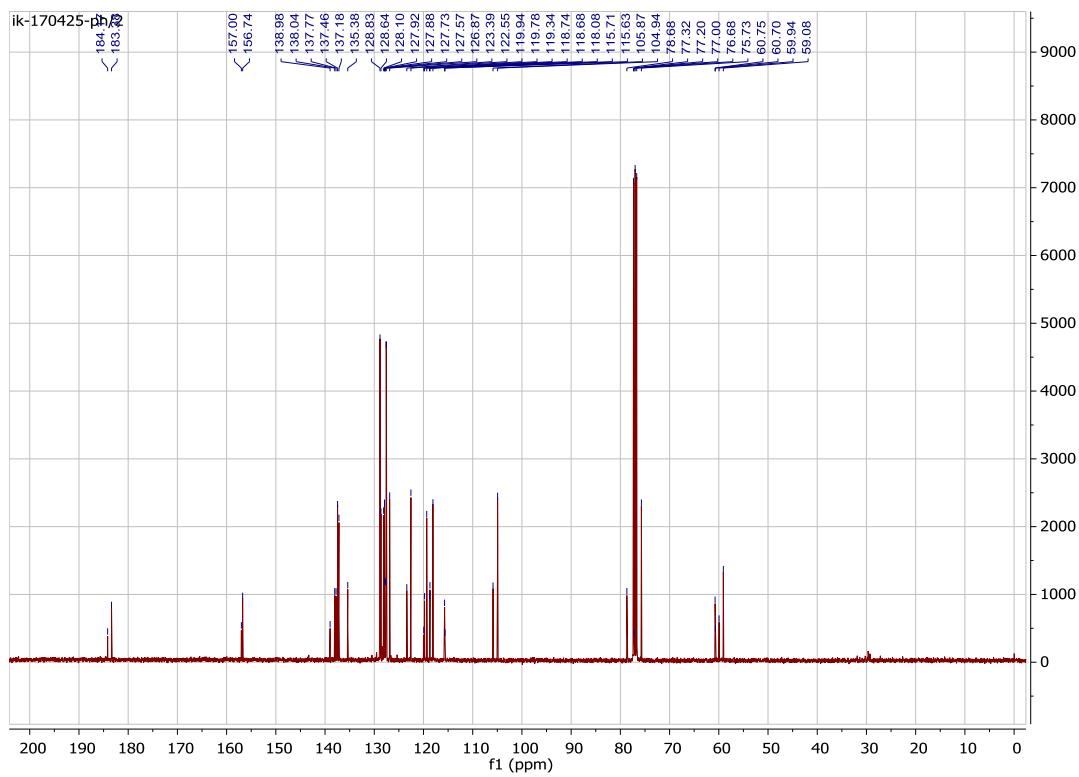
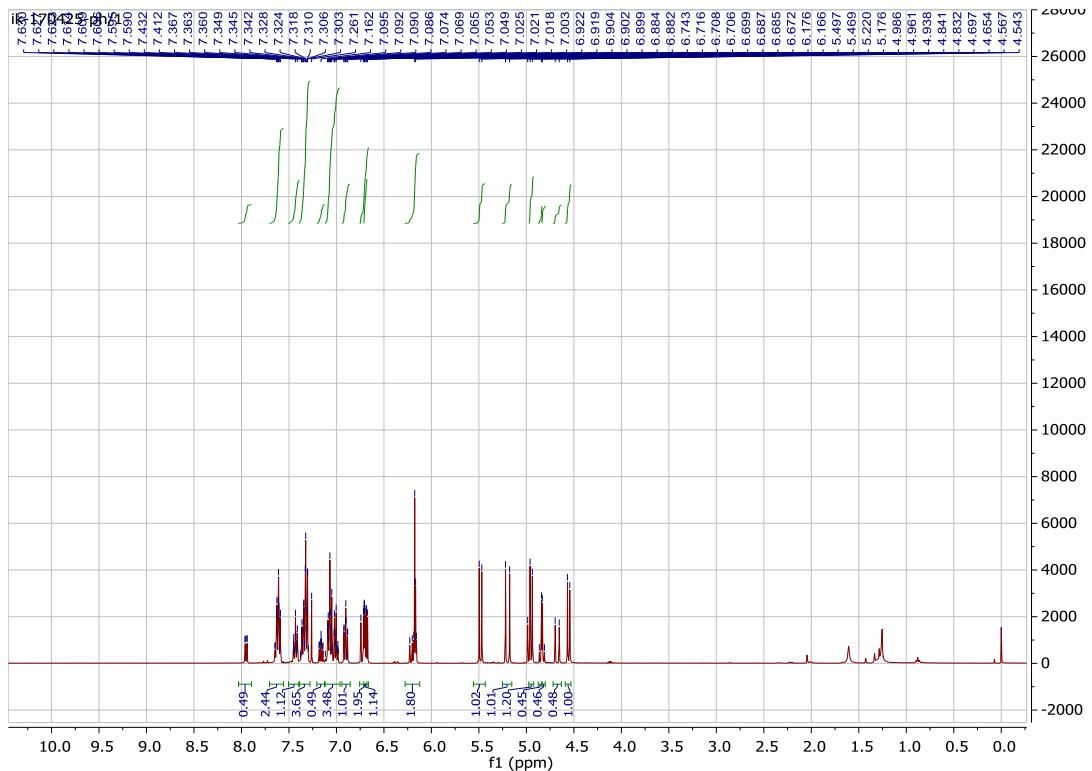
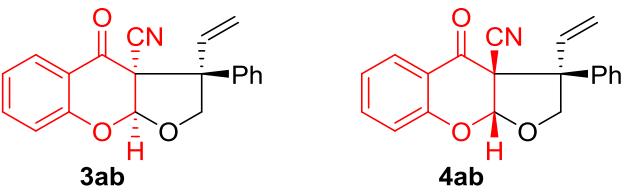
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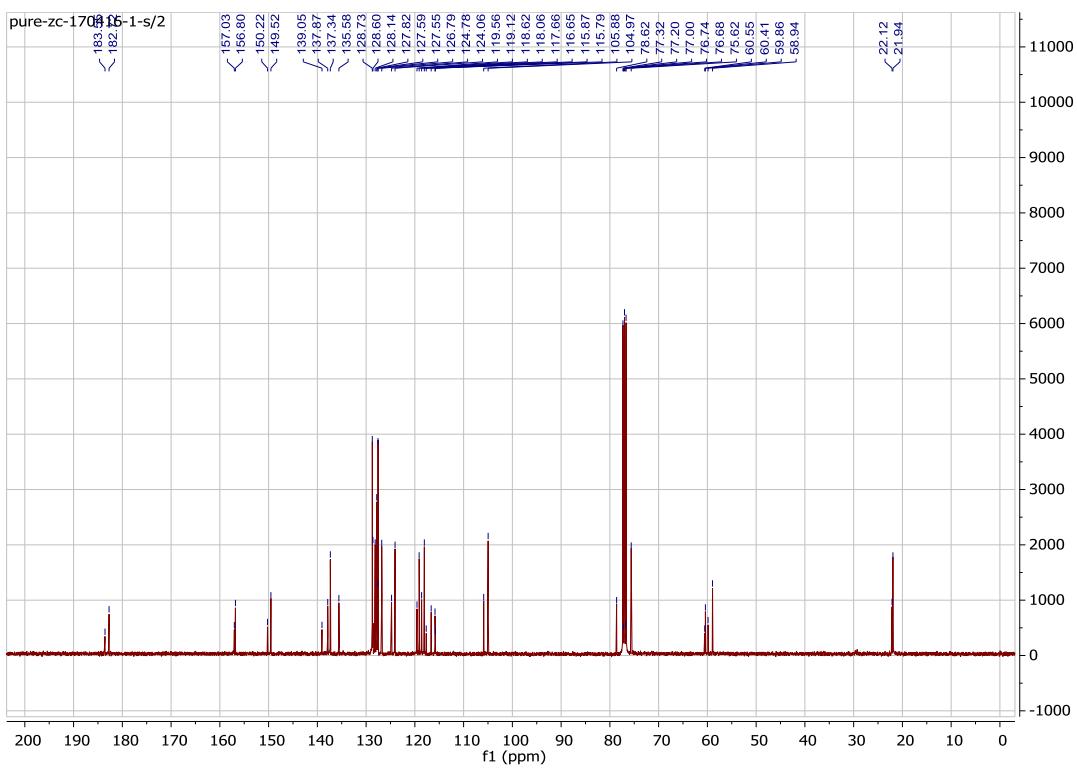
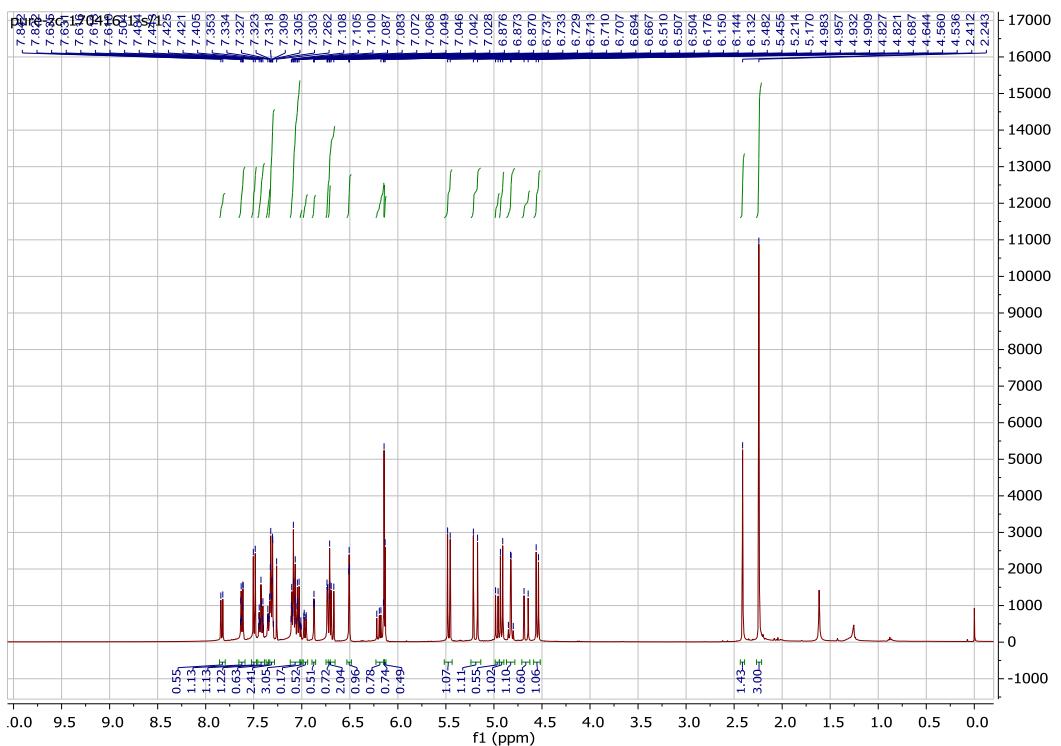
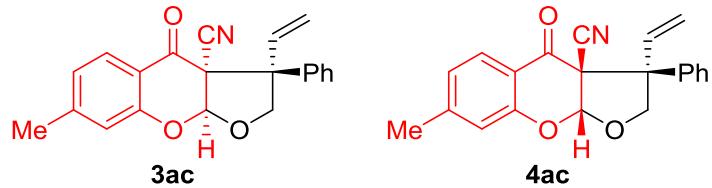
1. A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. J. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 6439.
2. H. Xiang, J. Chen, Z. Miao and C. Yang, *RSC Advances*, 2014, **4**, 16132.
3. M. Vuagnoux-d'Augustin and A. Alexakis, *Chem. Eur. J.*, 2007, **13**, 9647.

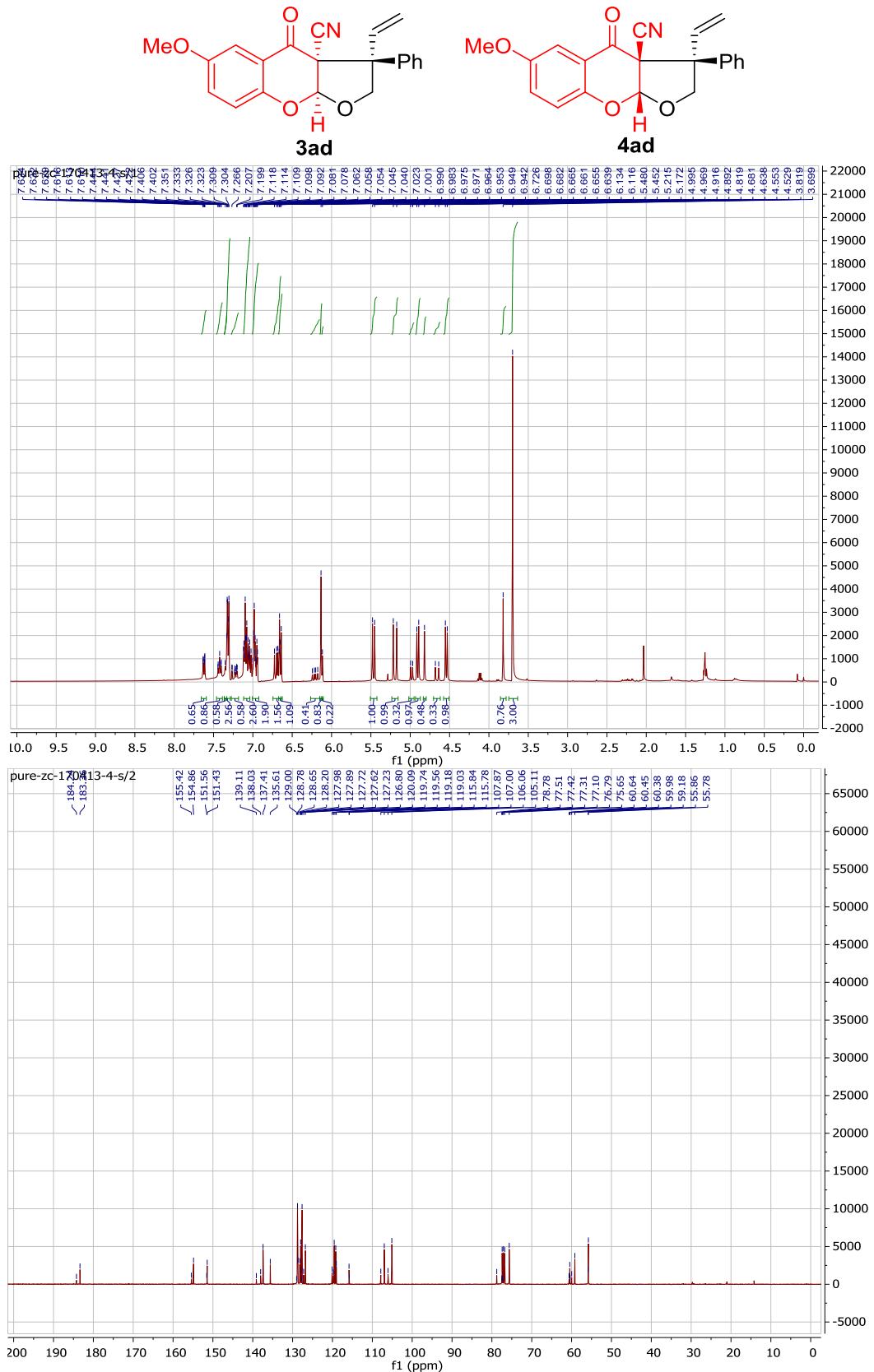


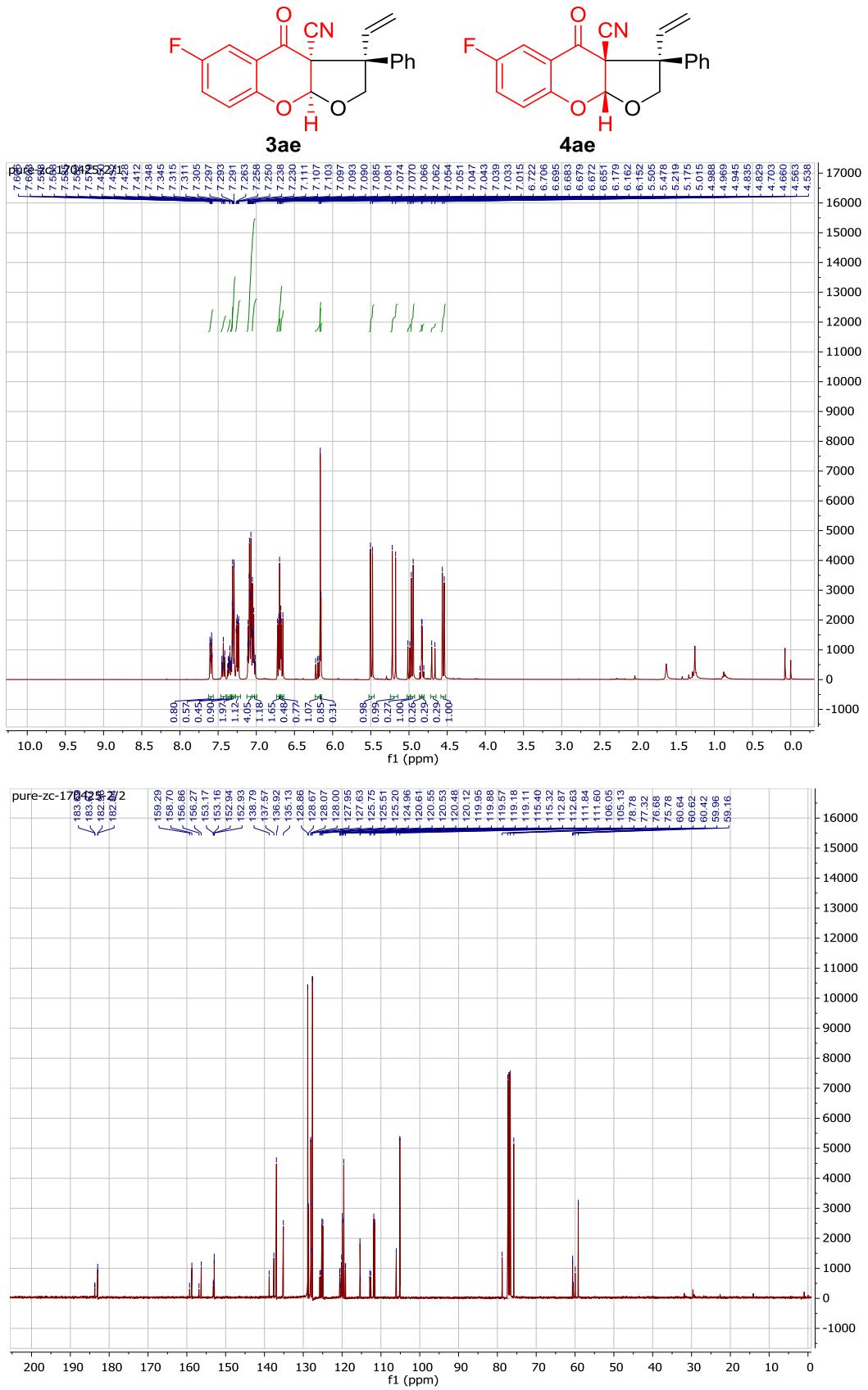


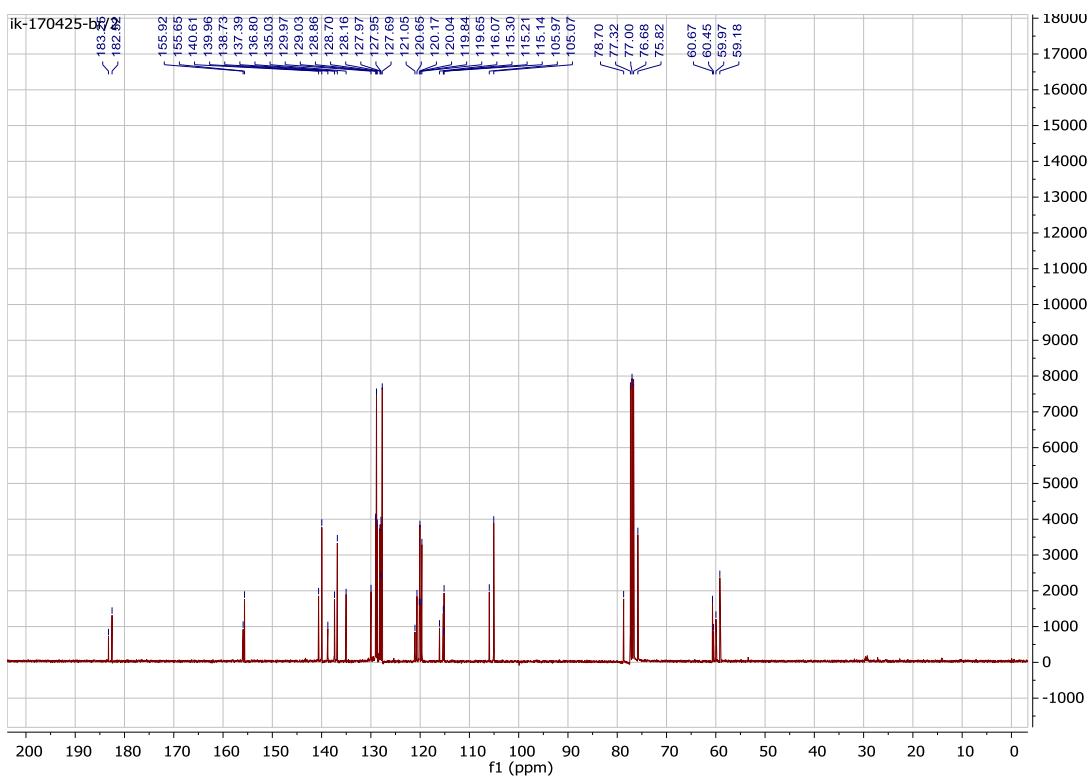
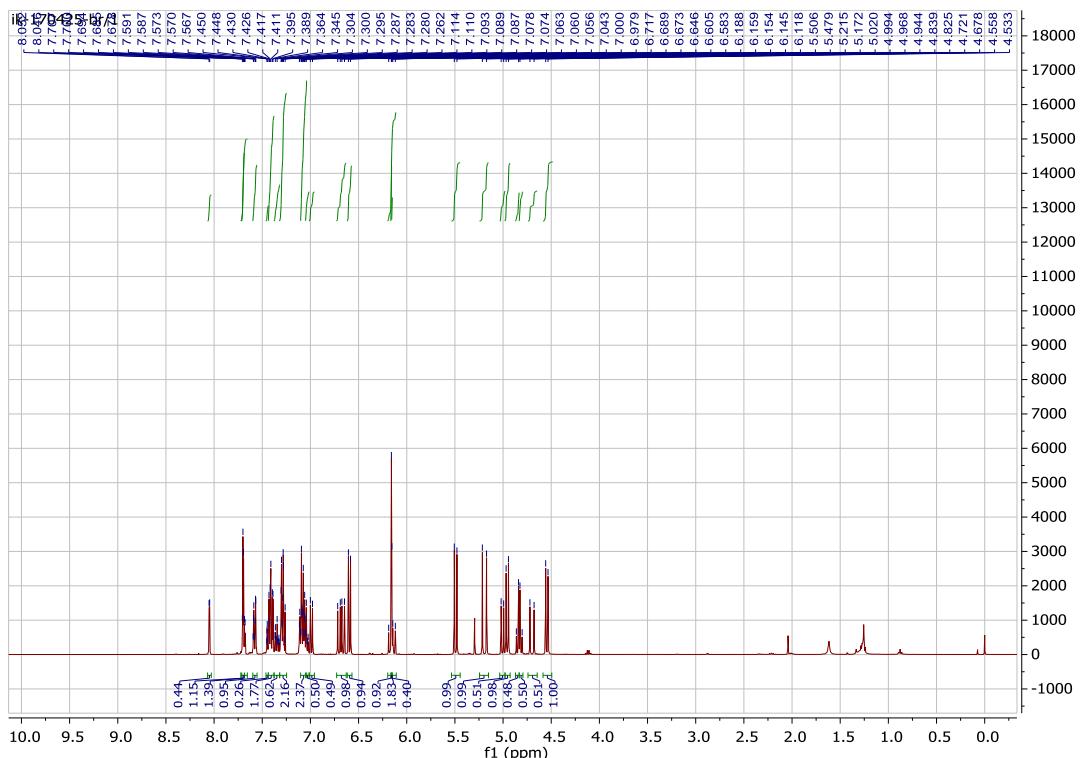
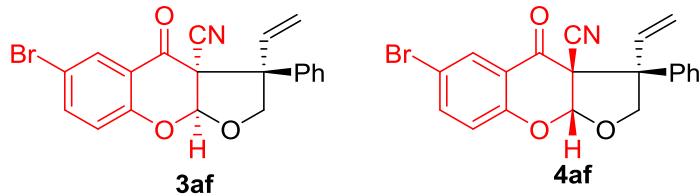


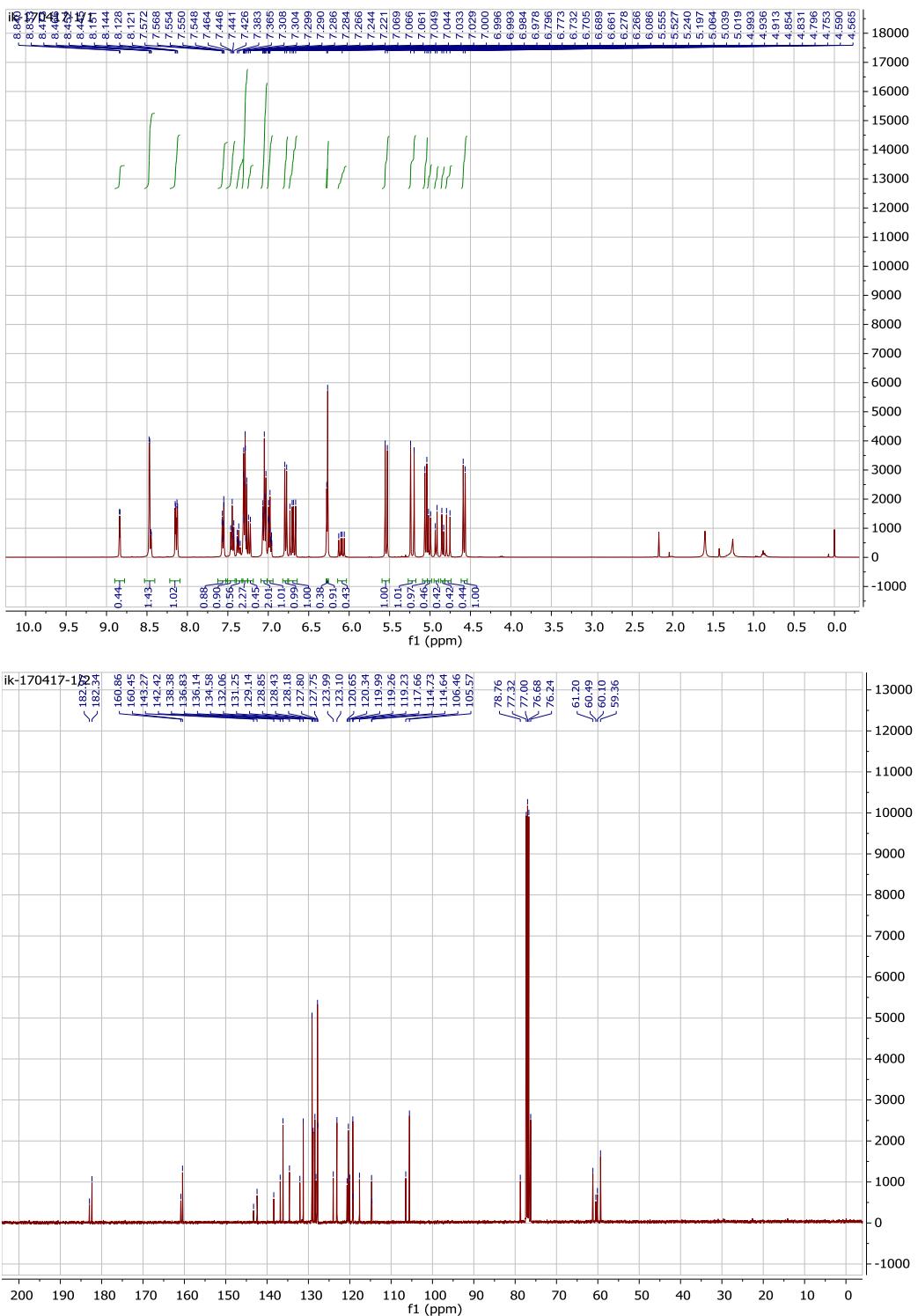
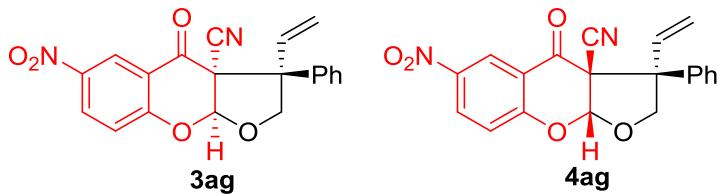


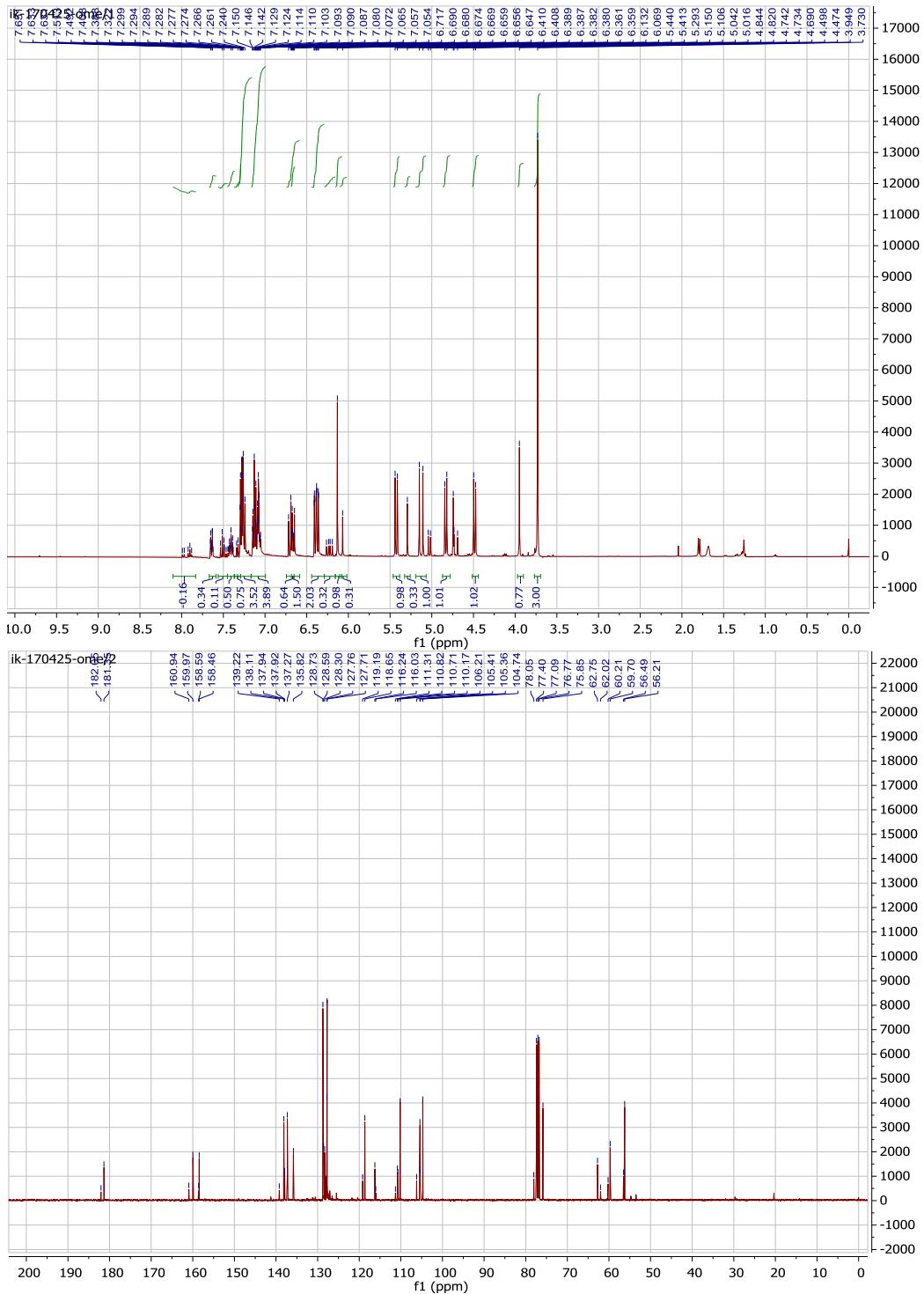
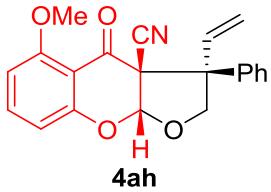
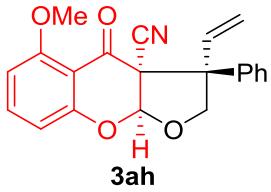


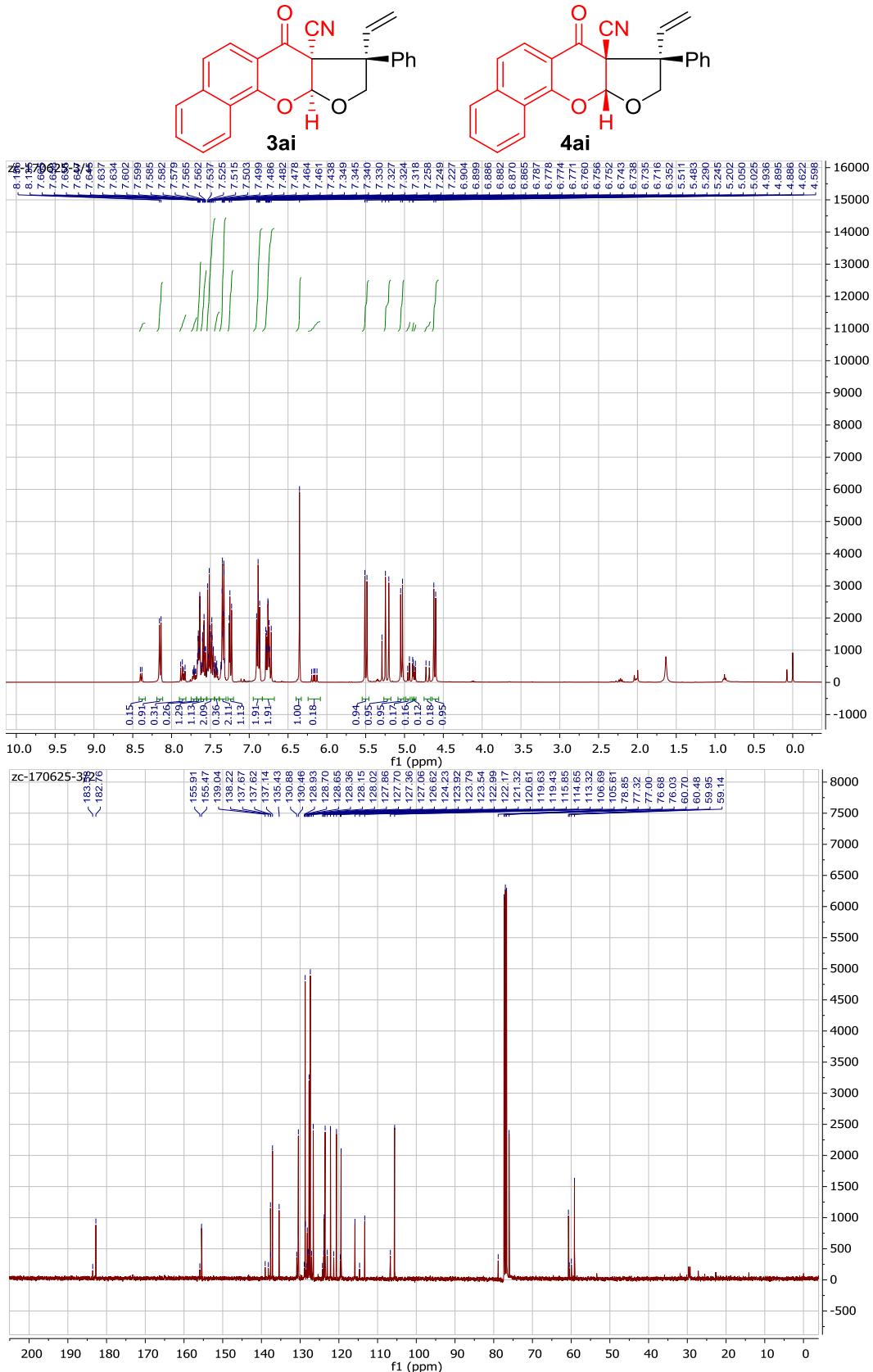


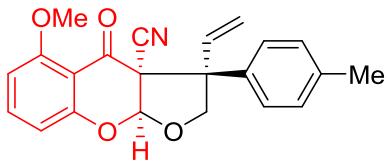




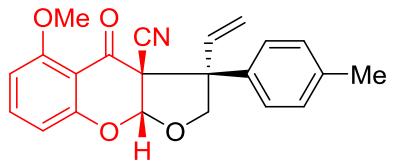




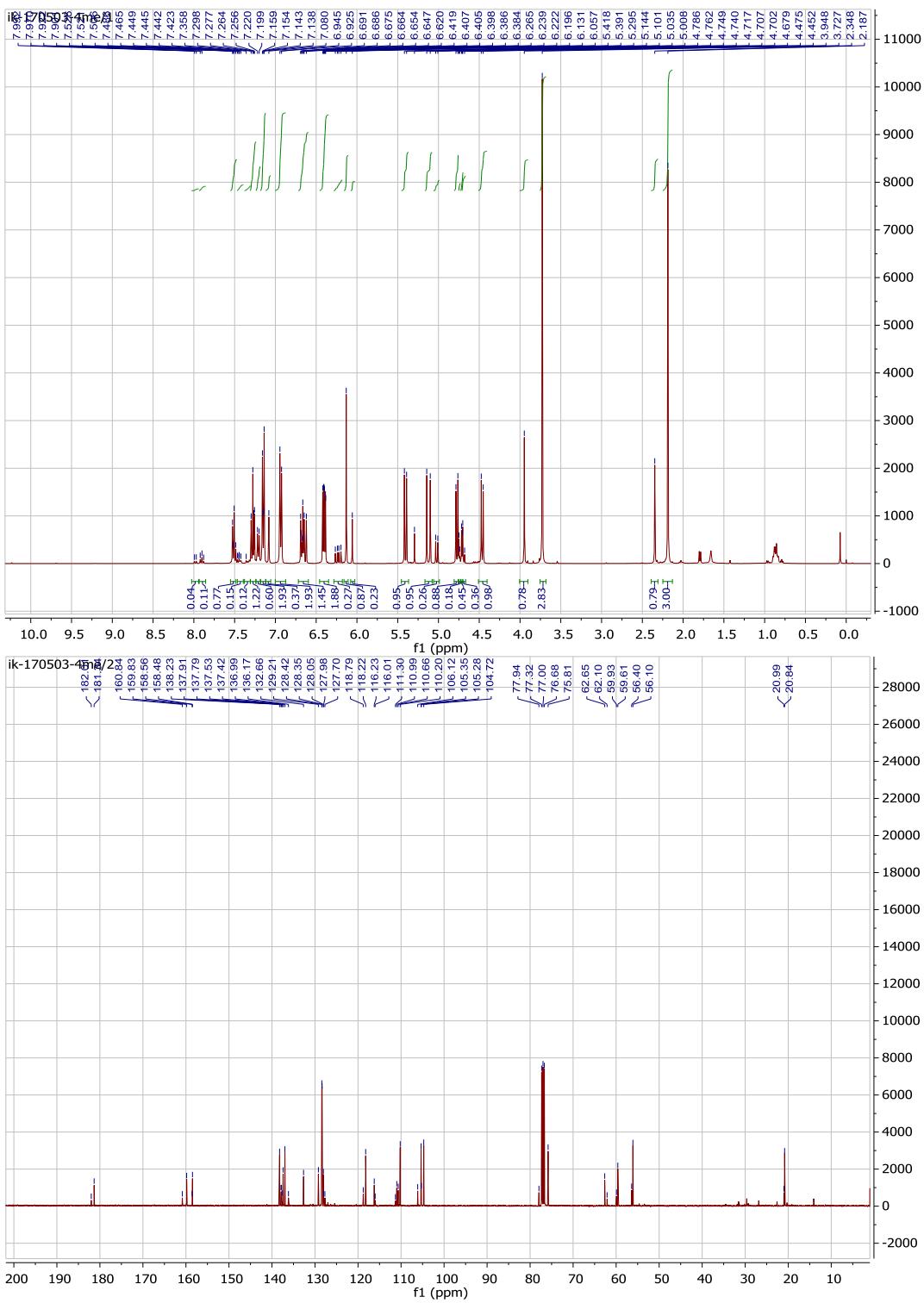


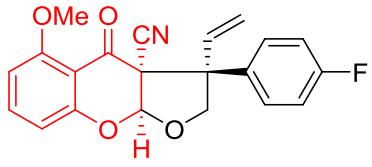


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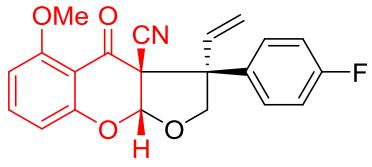


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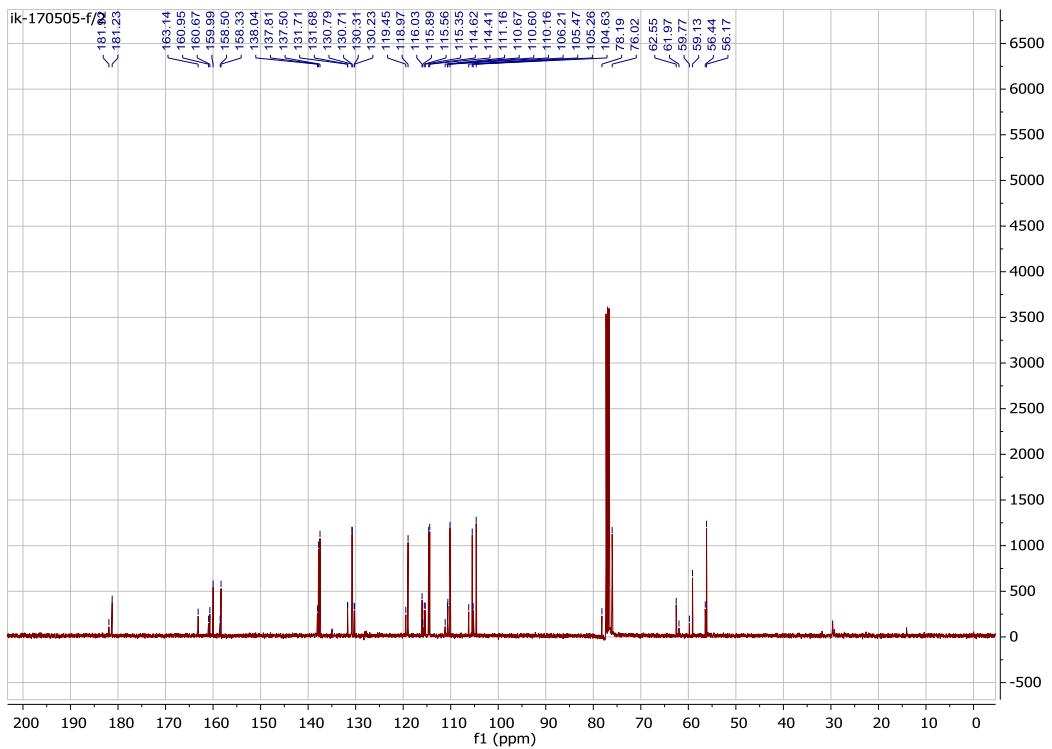
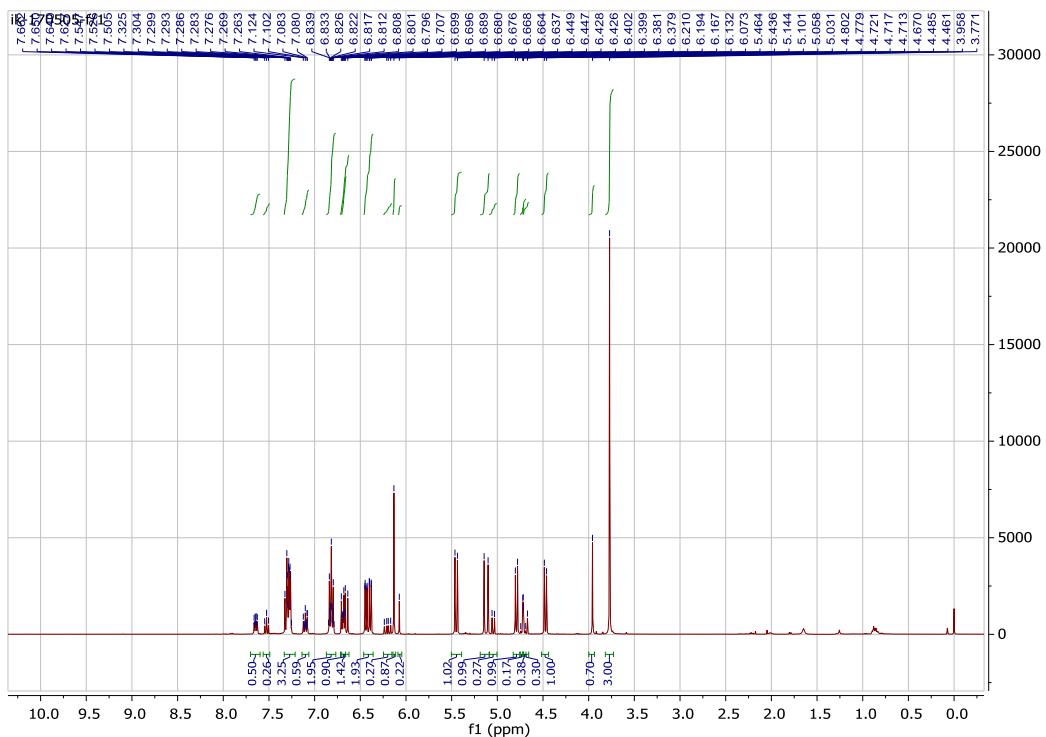


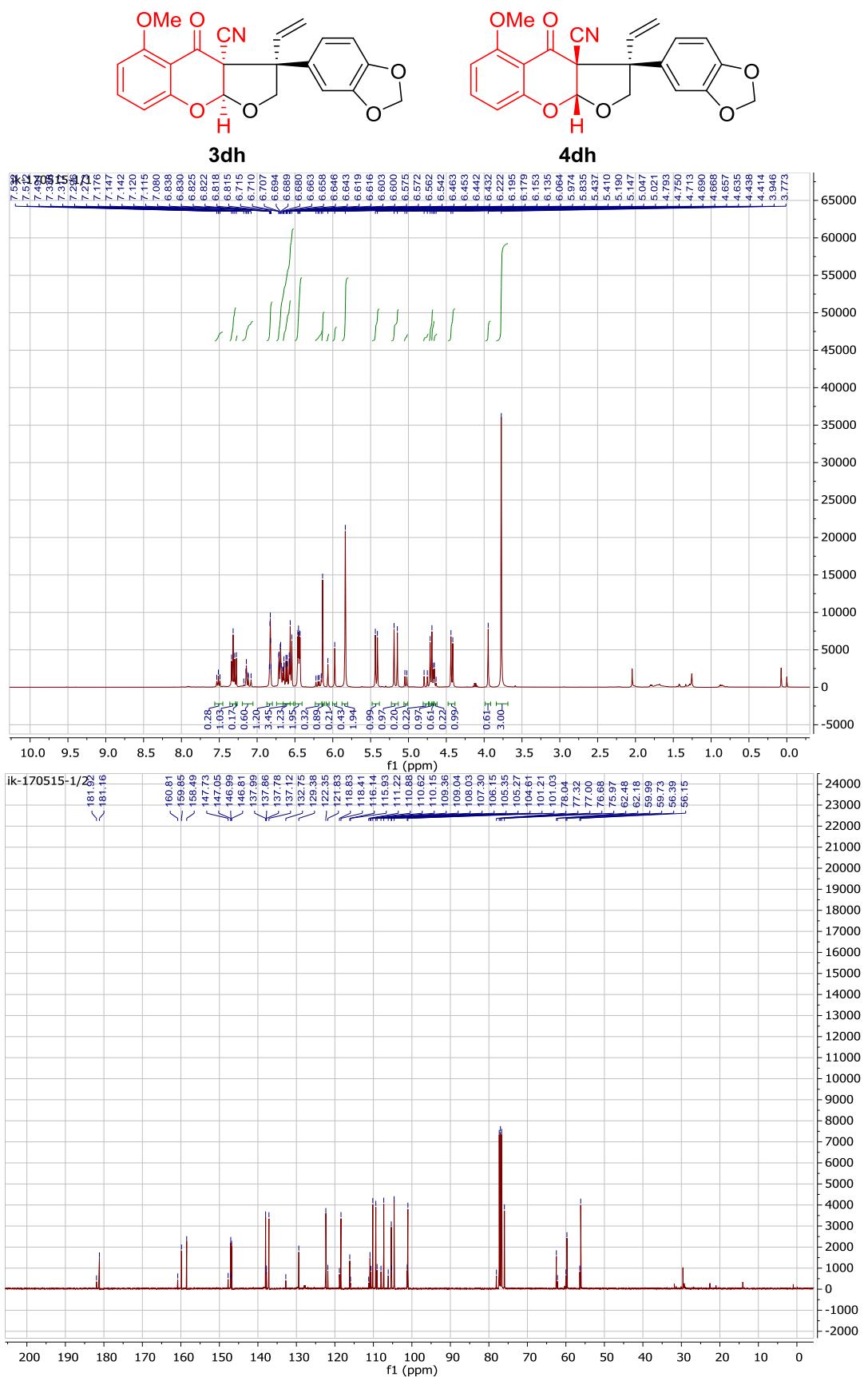


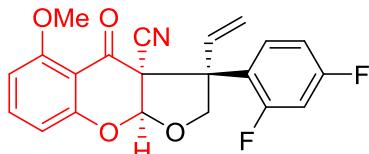
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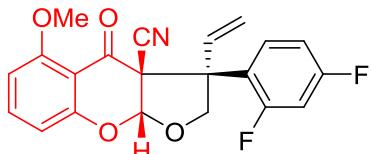
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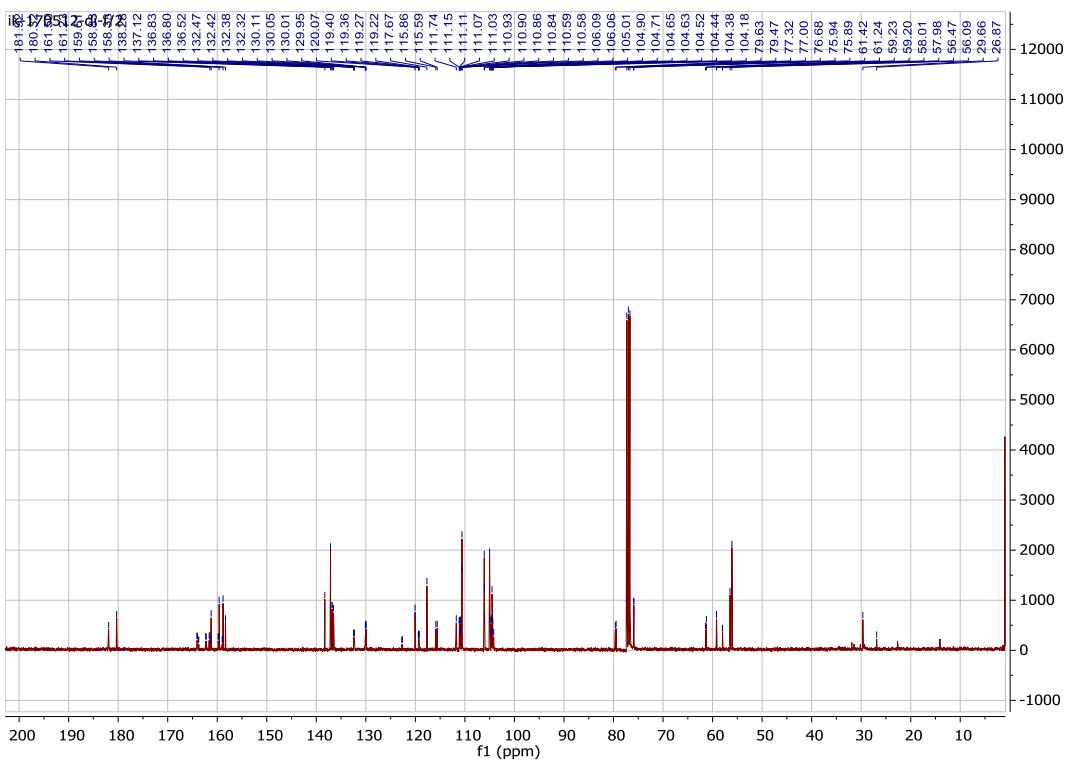
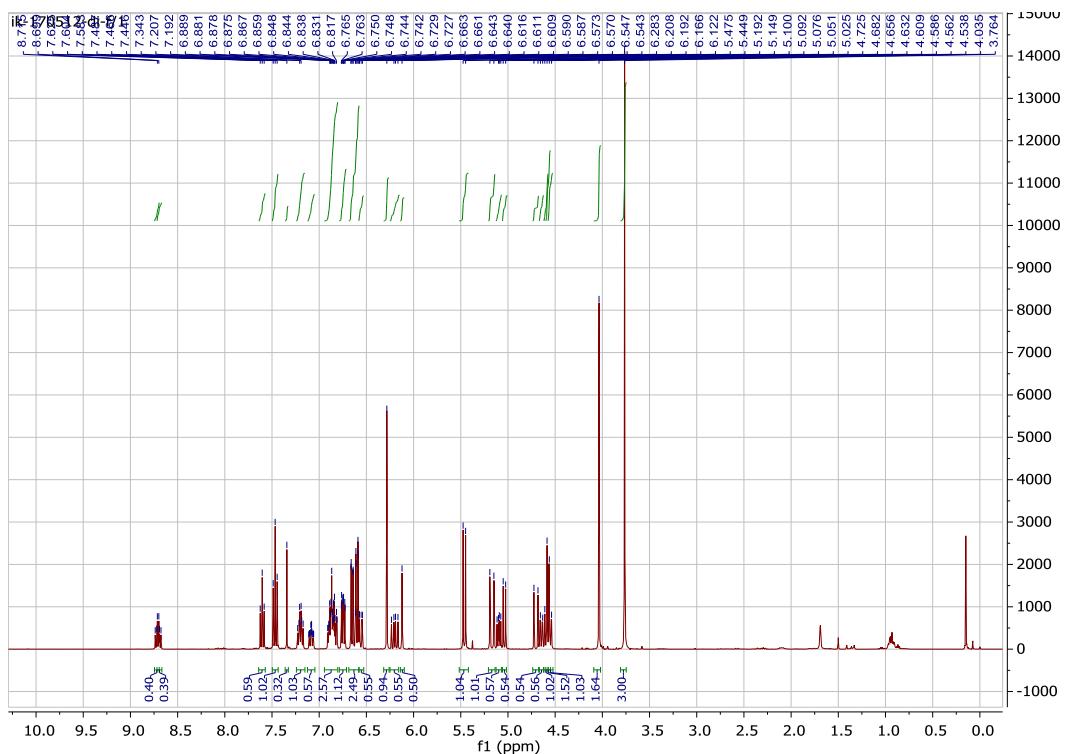


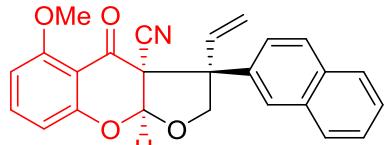


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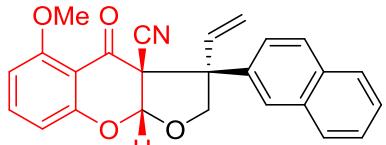


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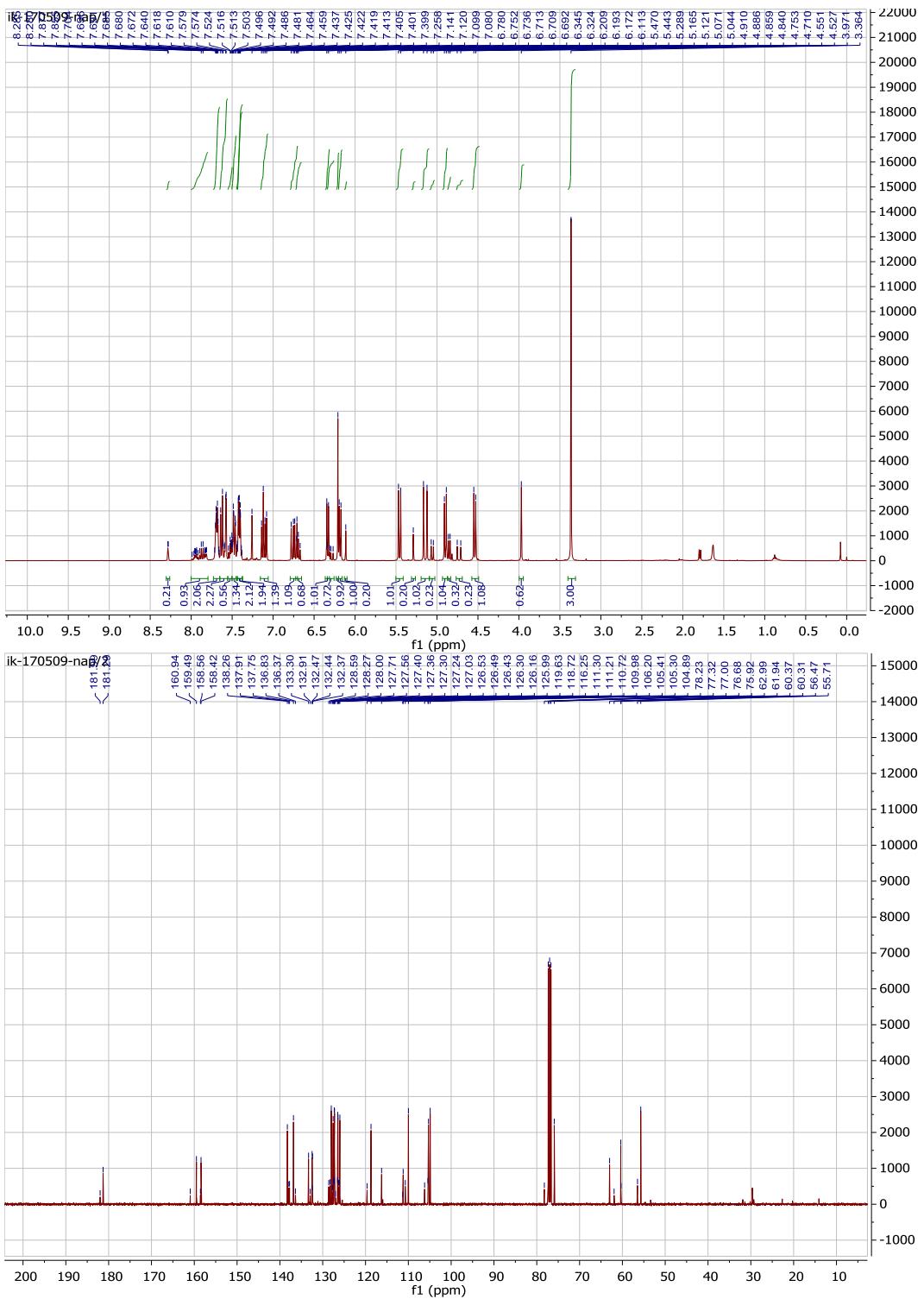


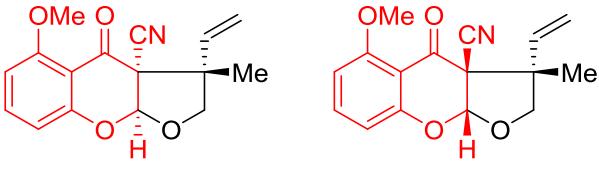


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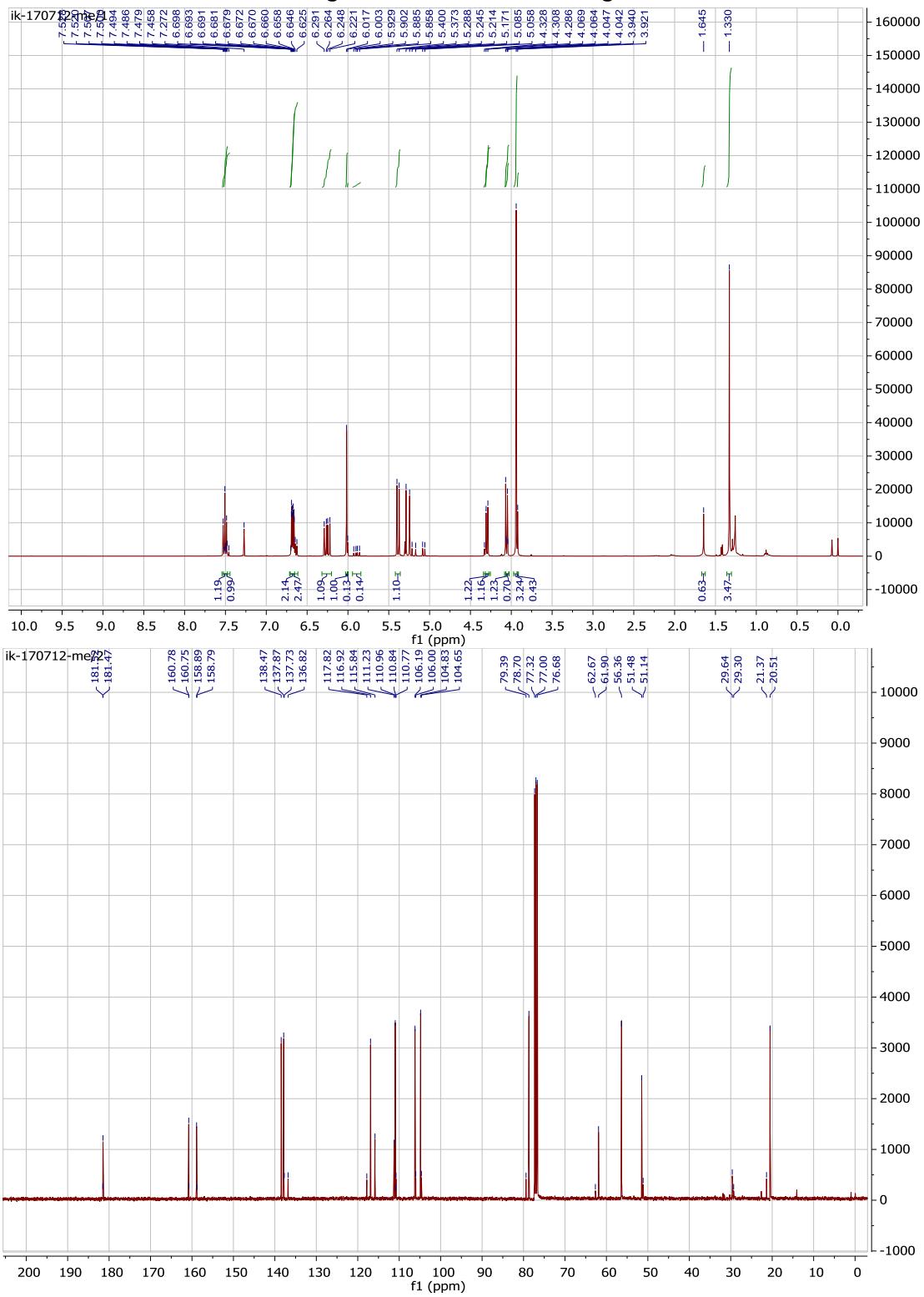
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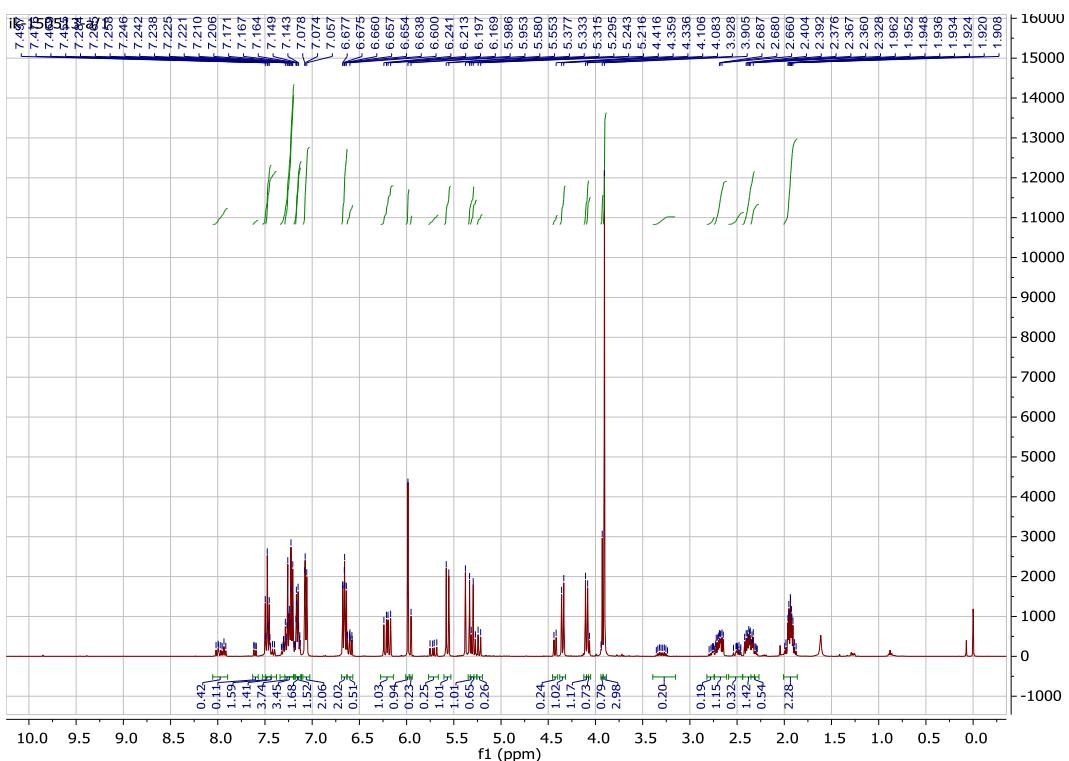
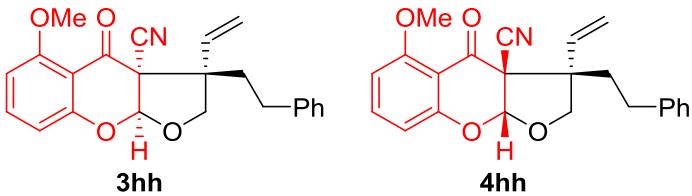


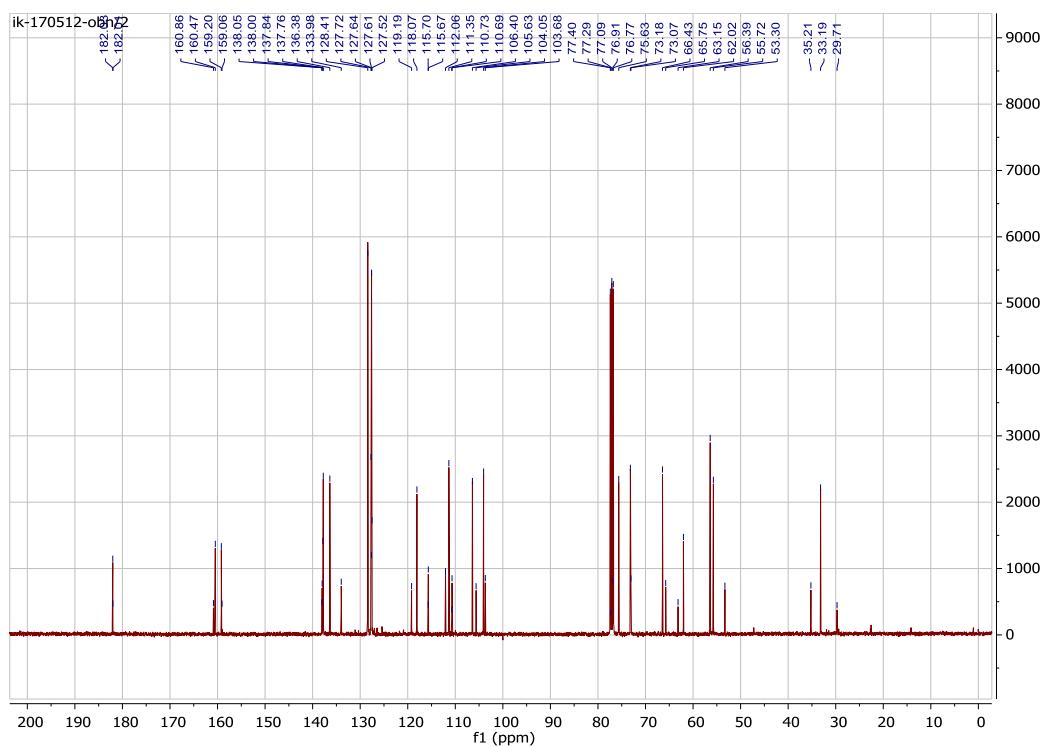
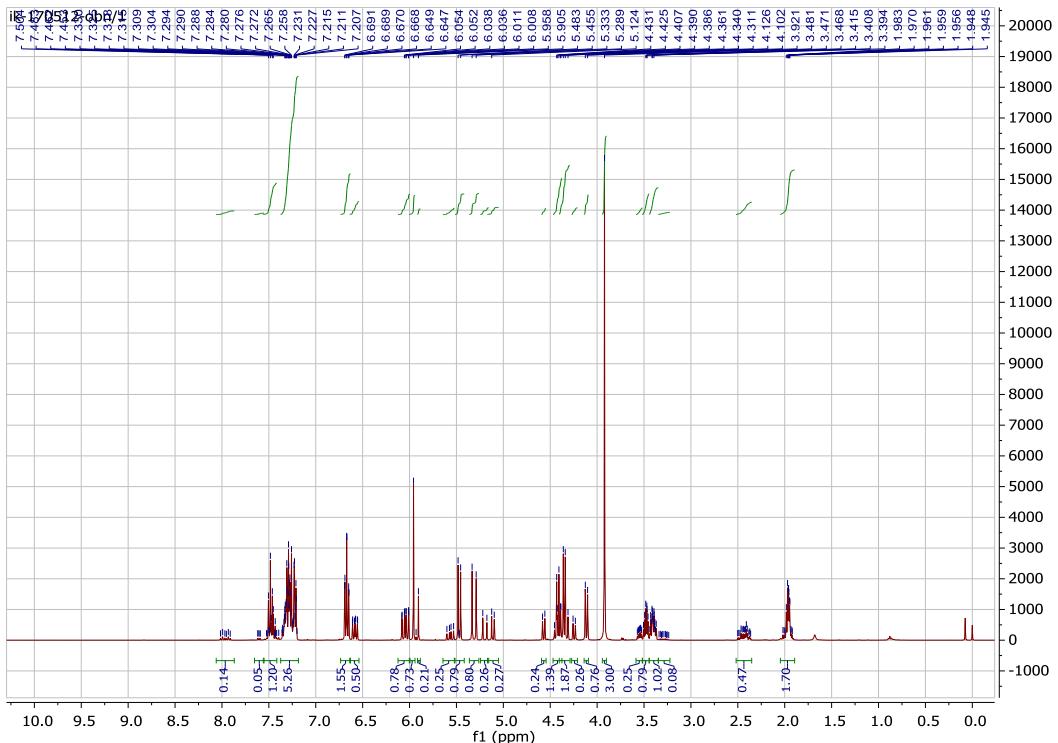
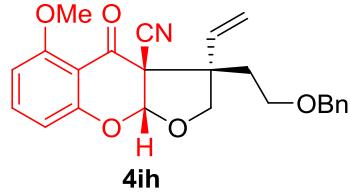
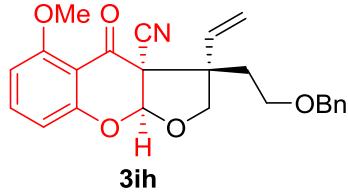


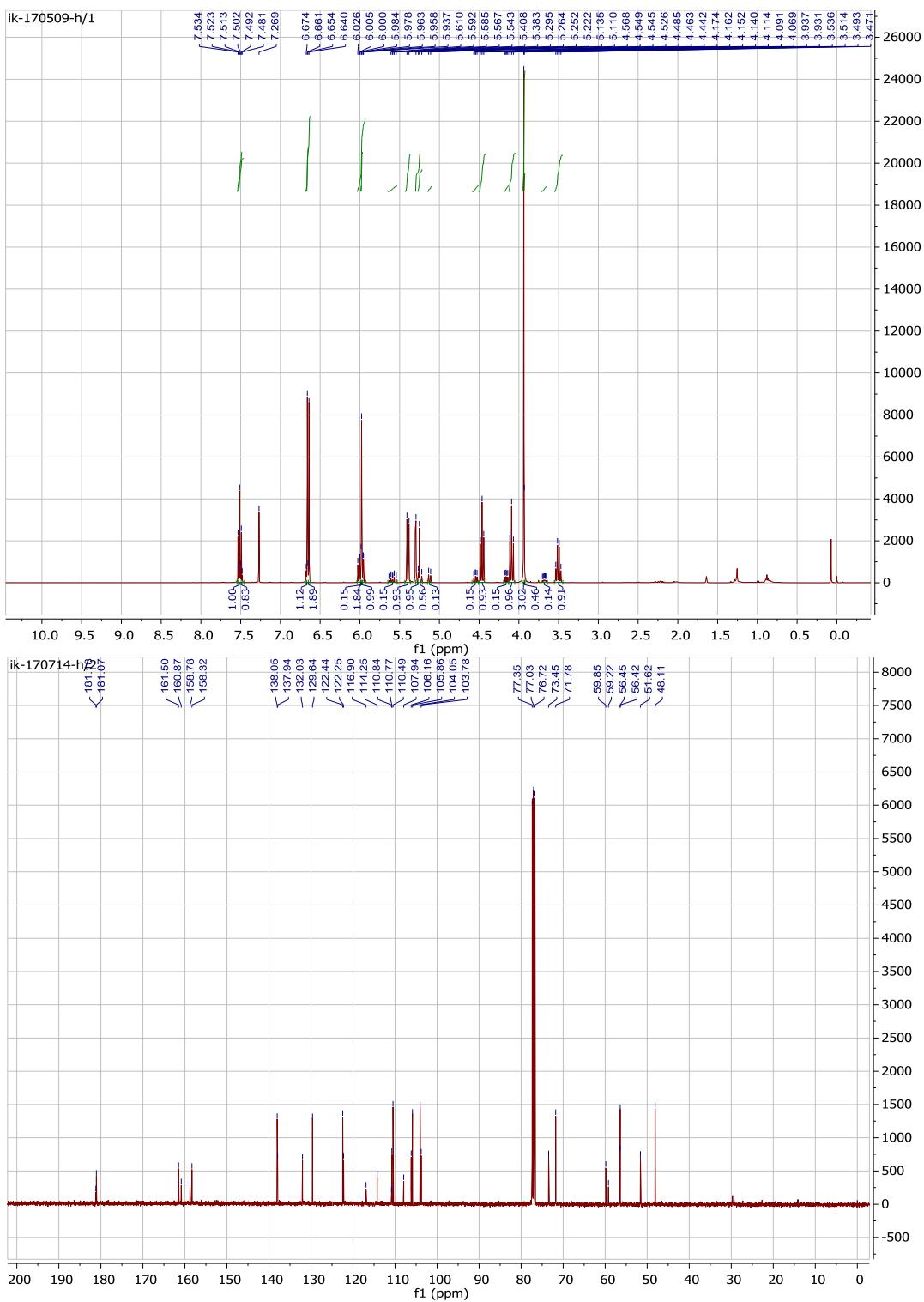
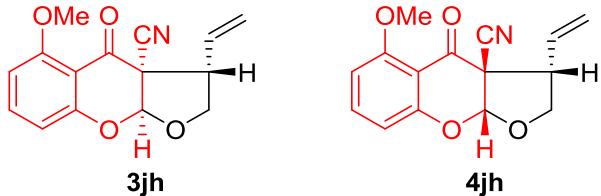
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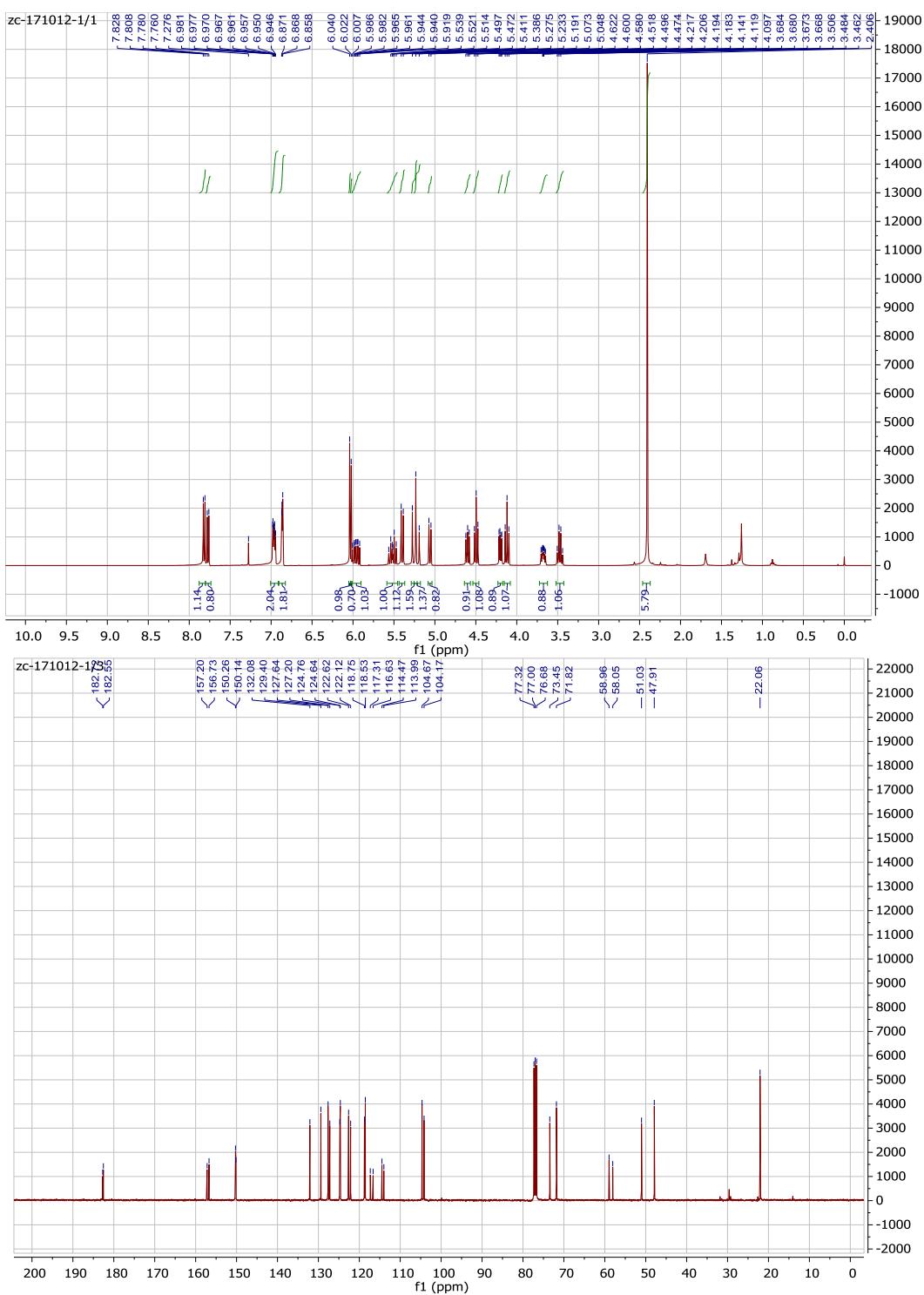
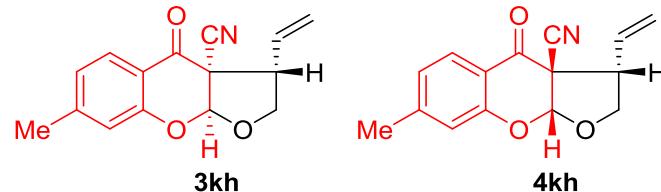
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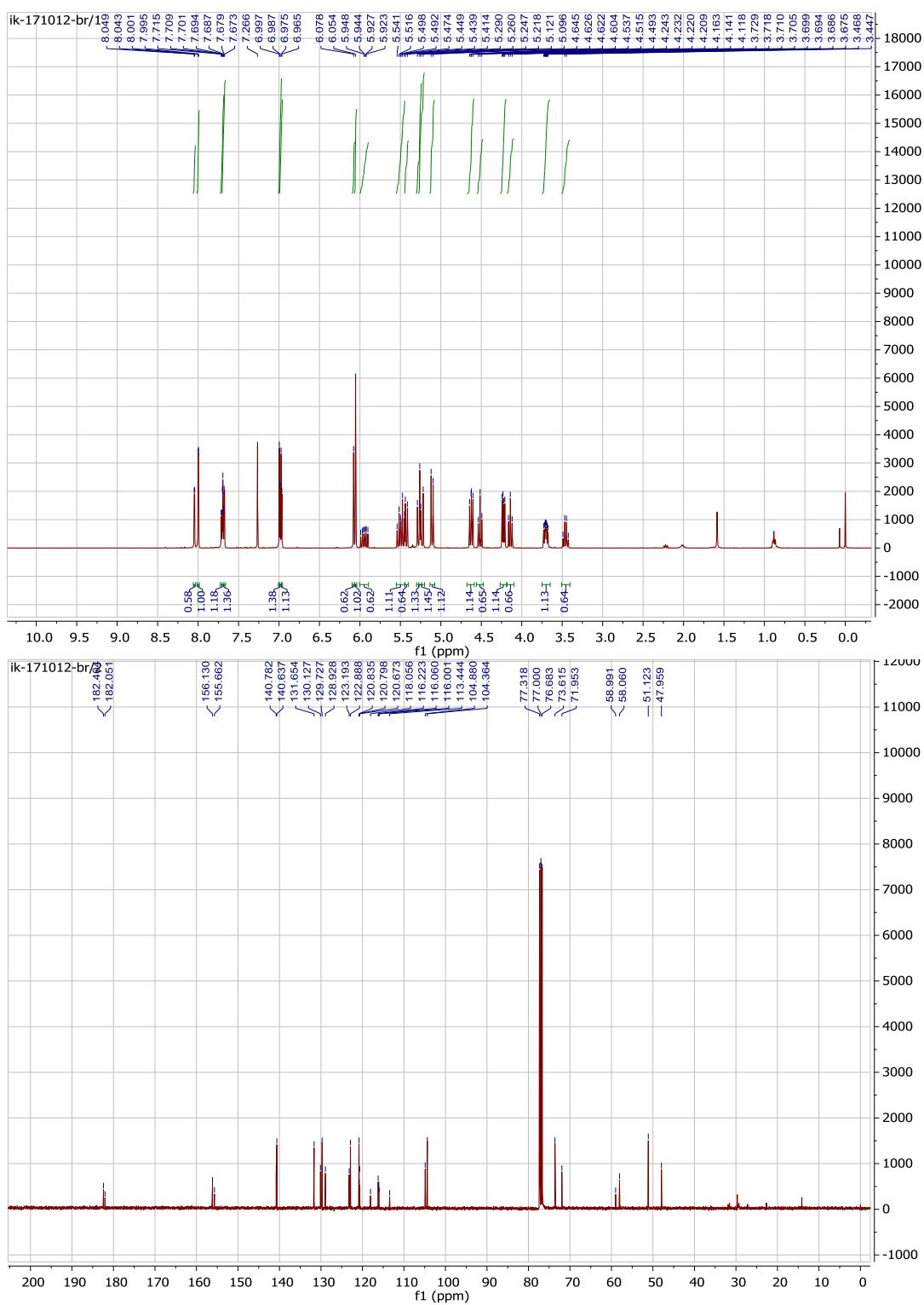
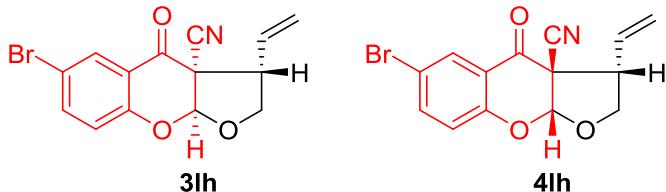


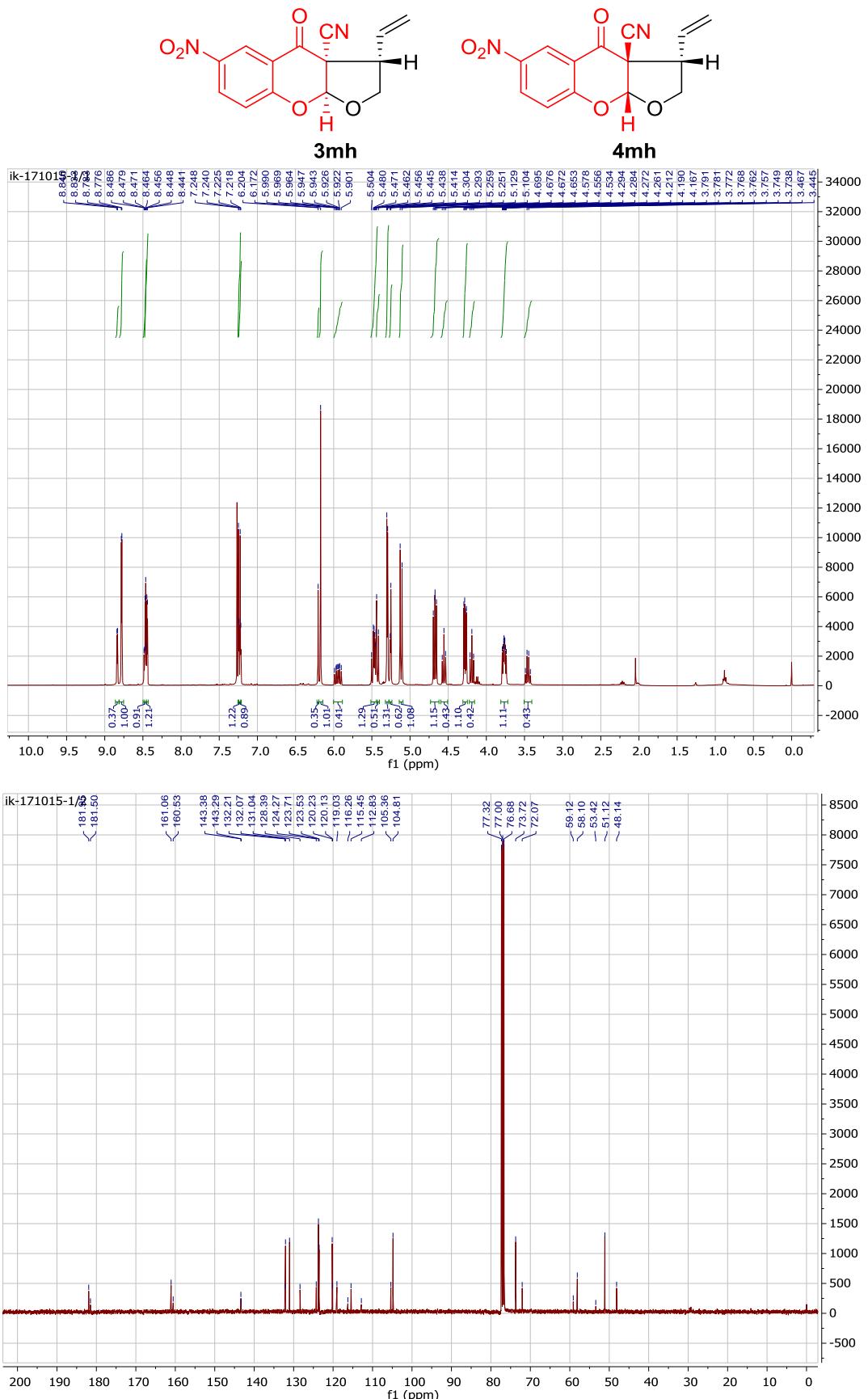


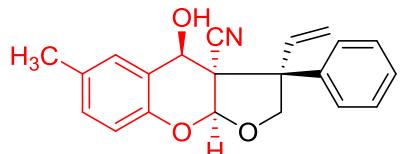




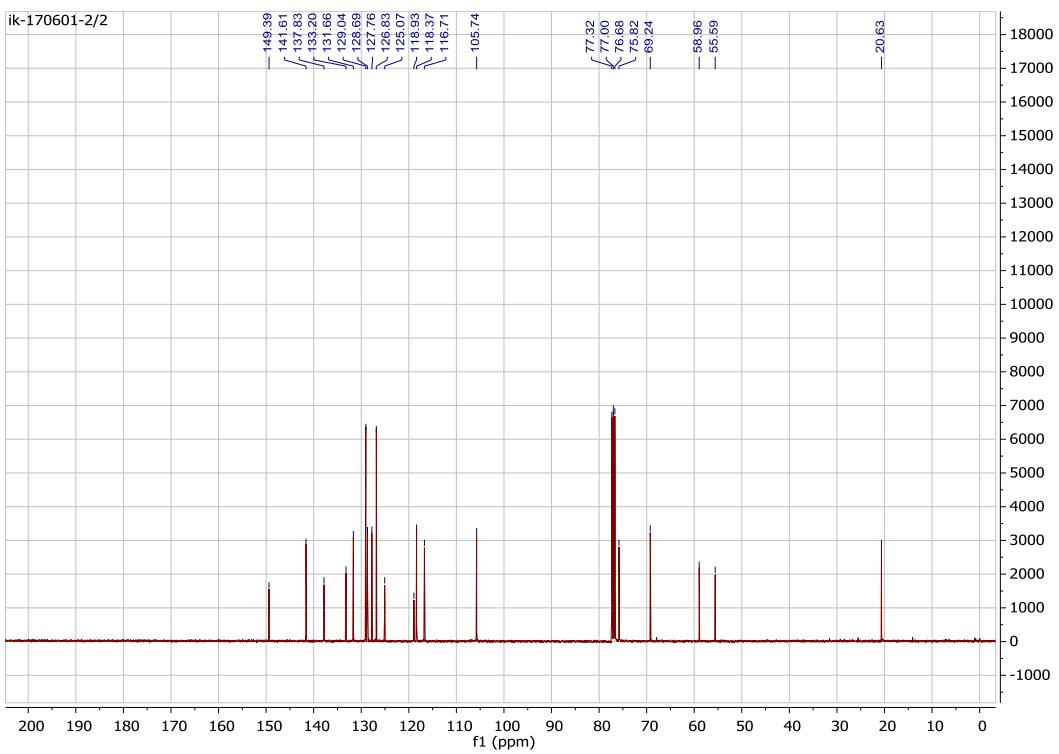
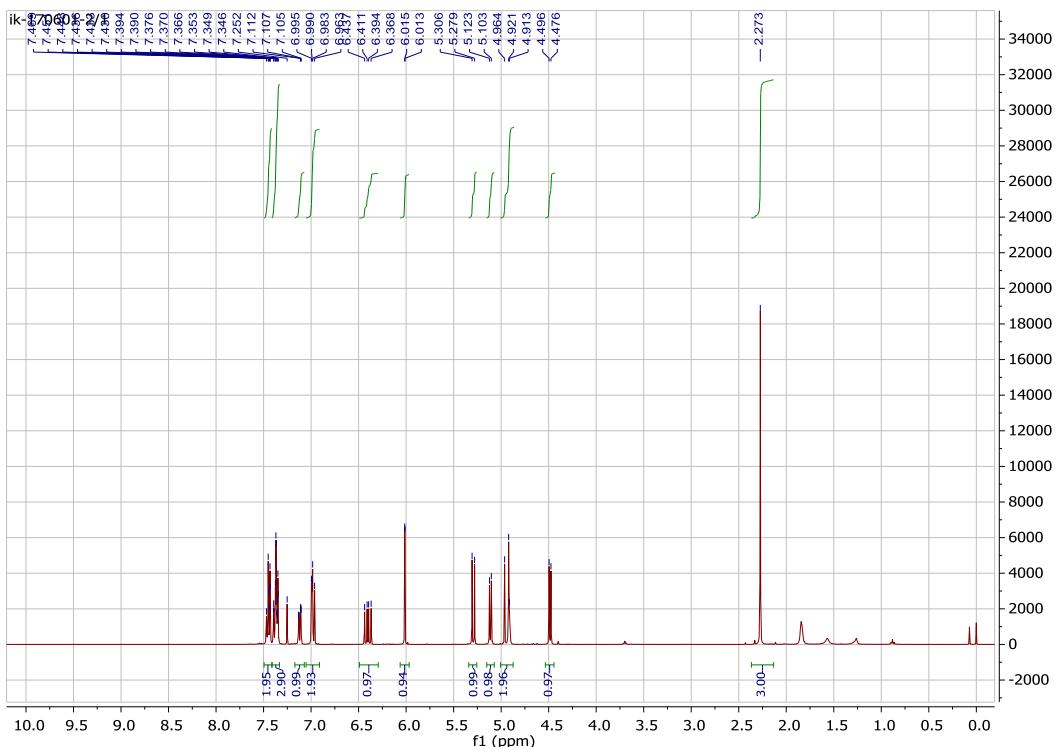


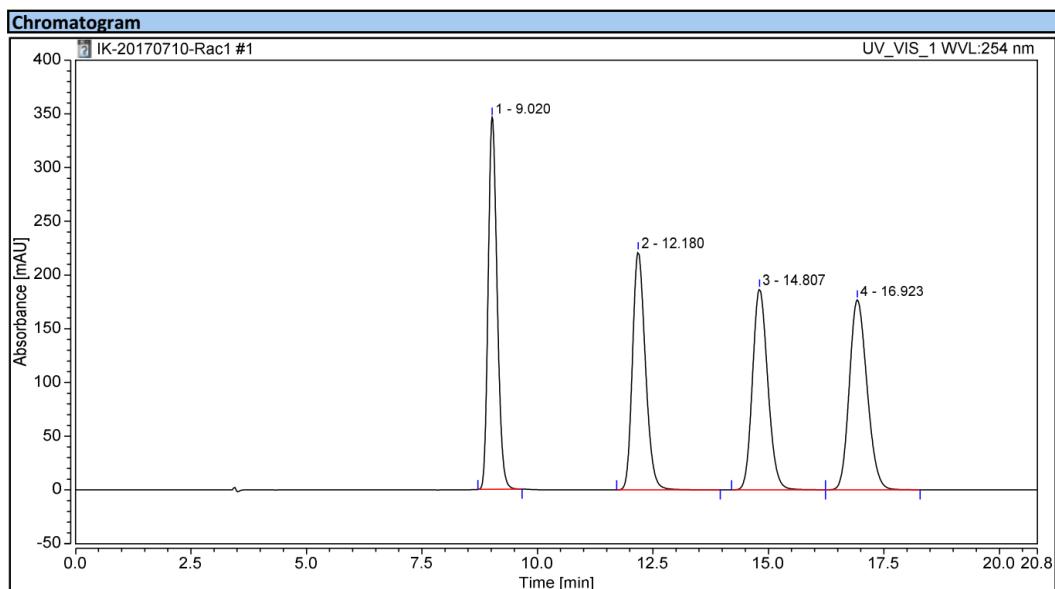
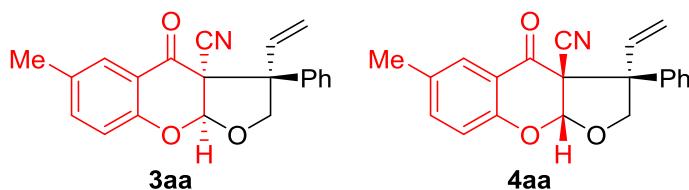




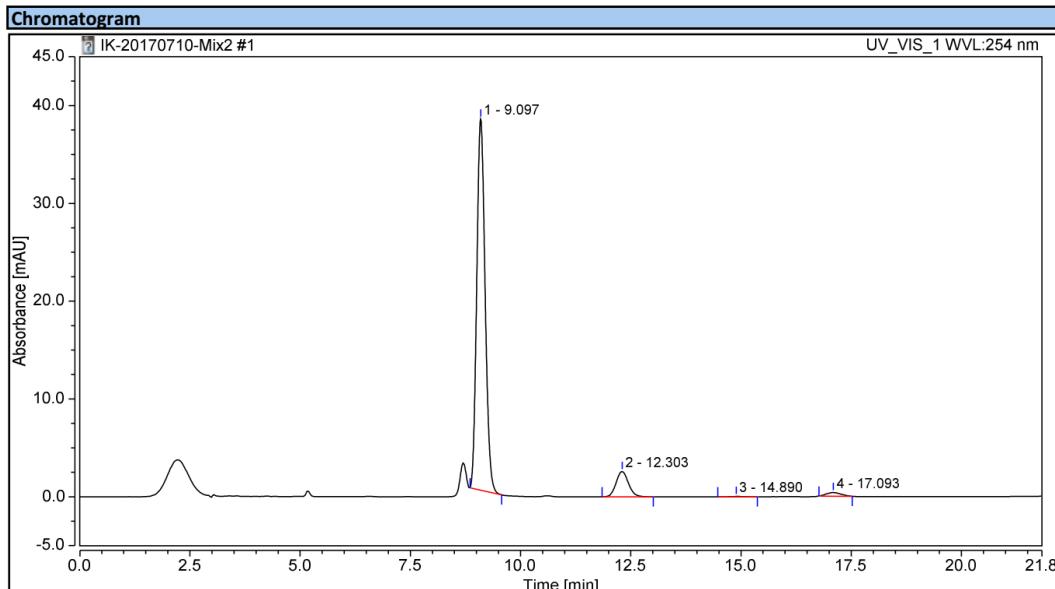


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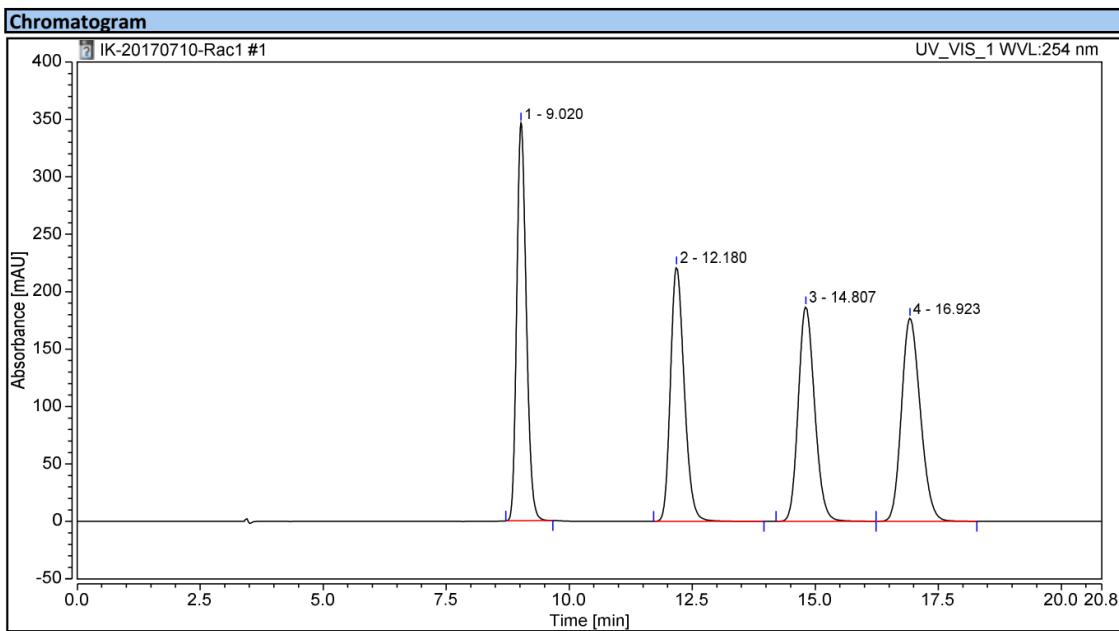
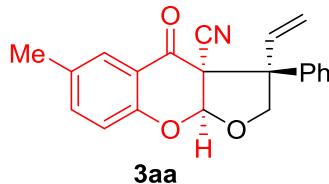




Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.020	77.888	346.282	25.93	37.18	n.a.
2		12.180	71.882	221.510	23.93	23.78	n.a.
3		14.807	72.036	186.872	23.98	20.06	n.a.
4		16.923	78.603	176.712	26.17	18.97	n.a.
Total:		300.409	931.376	100.00	100.00		

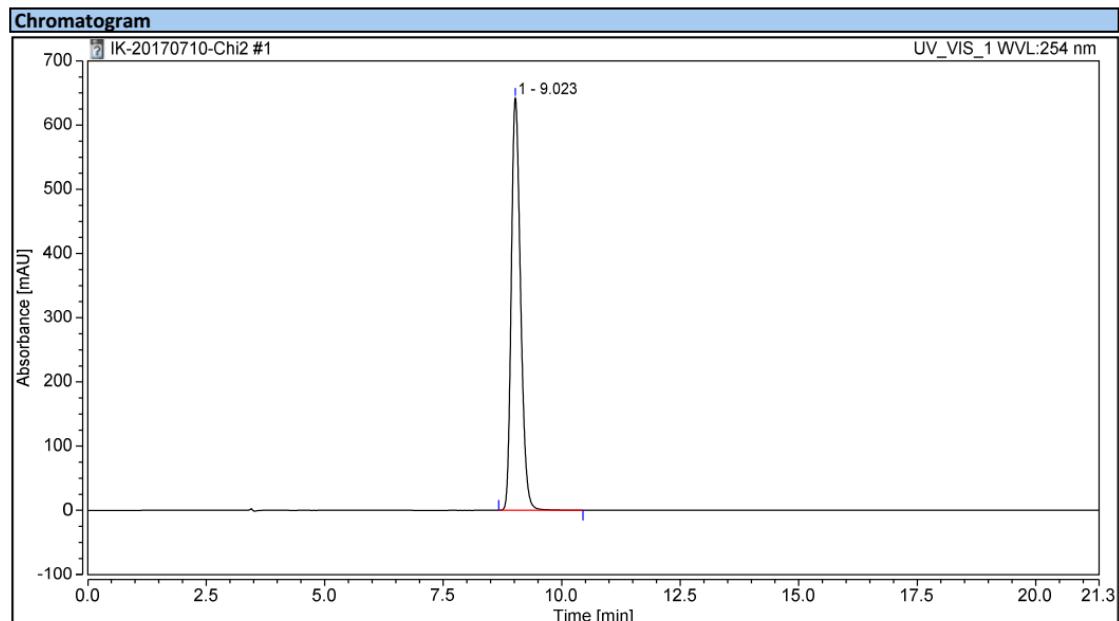


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.097	8.324	37.963	89.22	92.63	n.a.
2		12.303	0.845	2.602	9.06	6.35	n.a.
3		14.890	0.017	0.044	0.19	0.11	n.a.
4		17.093	0.143	0.373	1.53	0.91	n.a.
Total:		9.329	40.982	100.00	100.00		



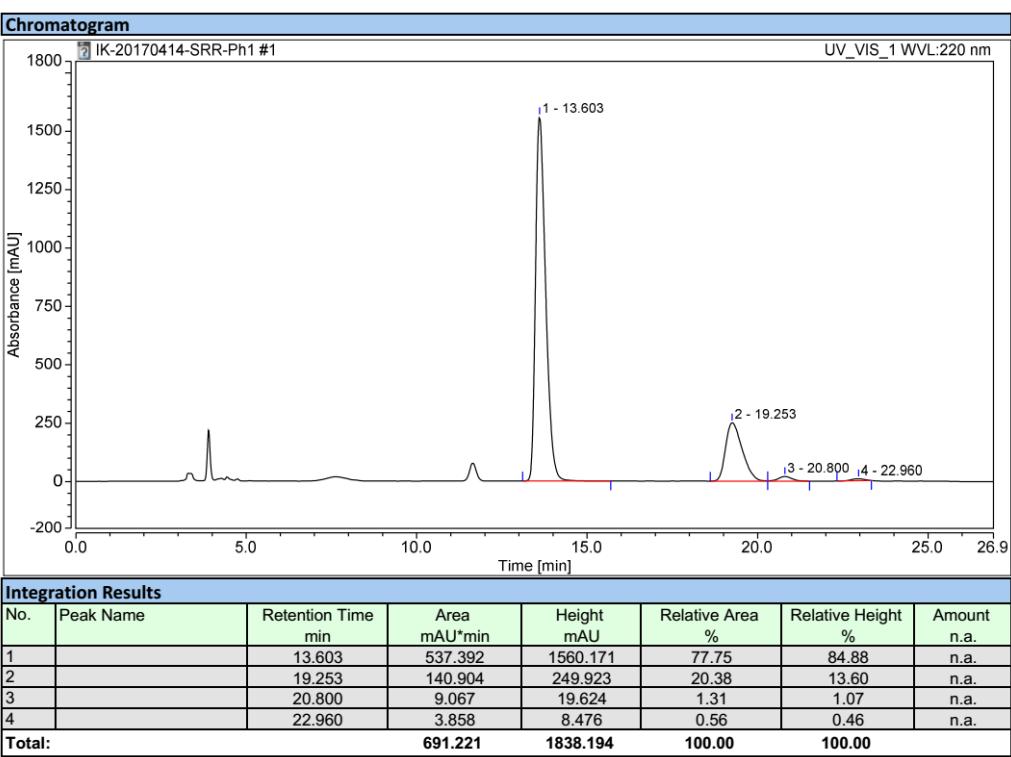
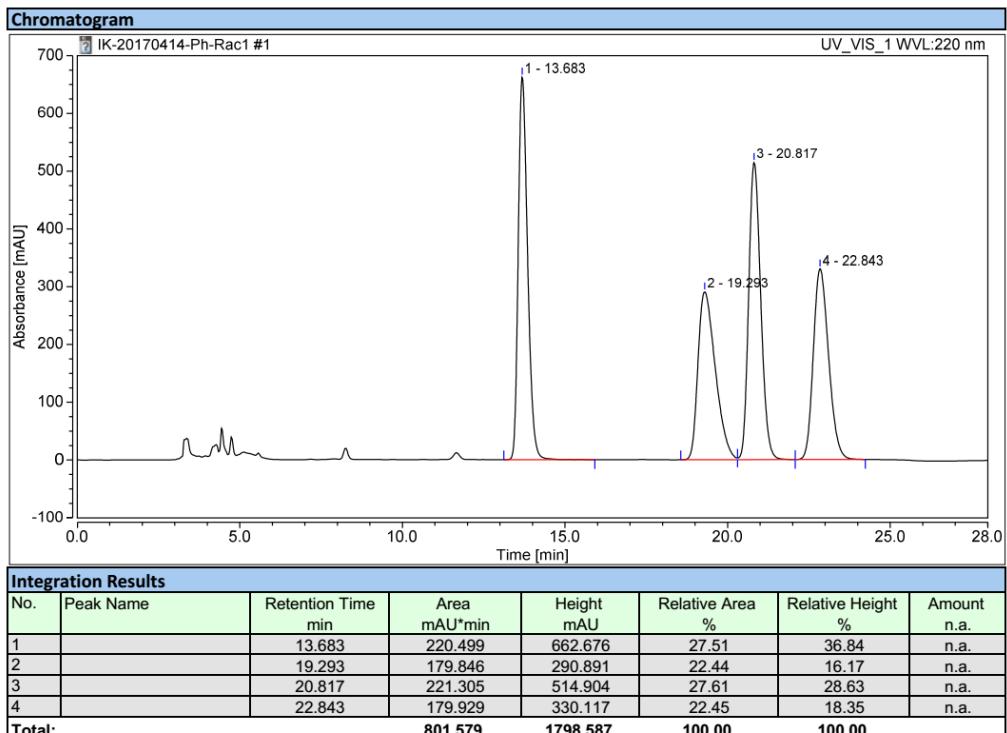
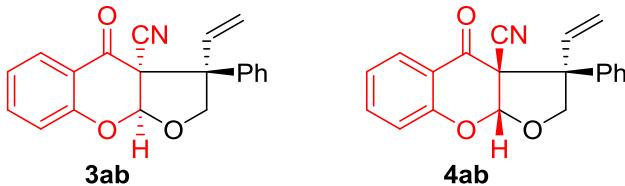
Integration Results

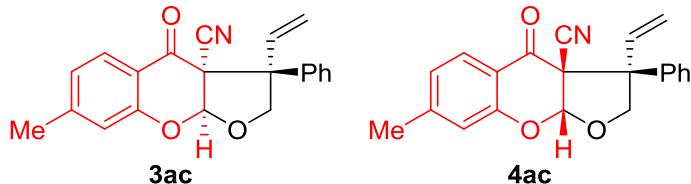
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.020	77.888	346.282	25.93	37.18	n.a.
2		12.180	71.882	221.510	23.93	23.78	n.a.
3		14.807	72.036	186.872	23.98	20.06	n.a.
4		16.923	78.603	176.712	26.17	18.97	n.a.
Total:			300.409	931.376	100.00	100.00	



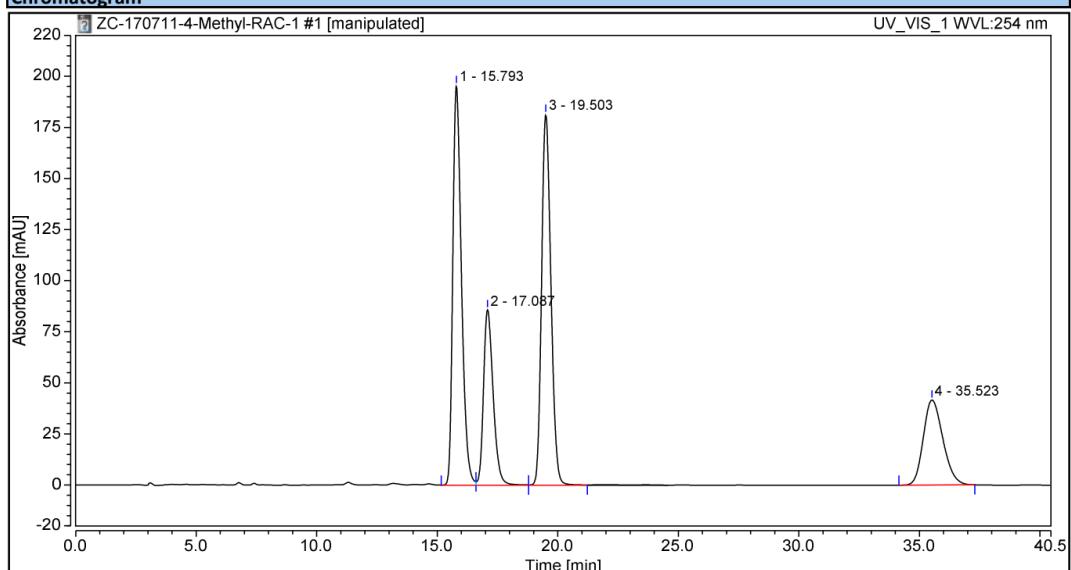
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.023	146.102	641.928	100.00	100.00	n.a.
Total:			146.102	641.928	100.00	100.00	





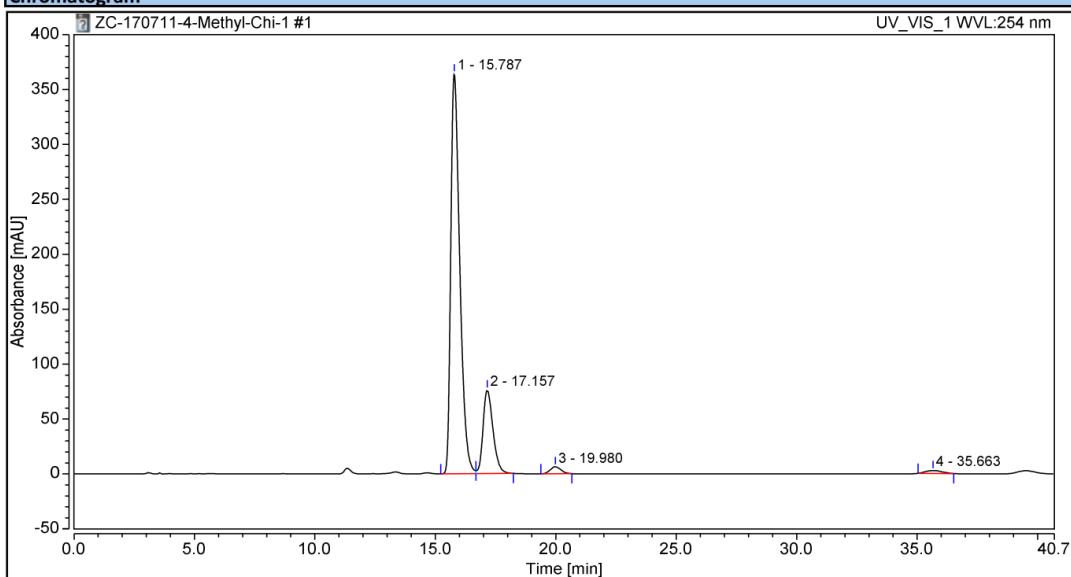
Chromatogram



Integration Results

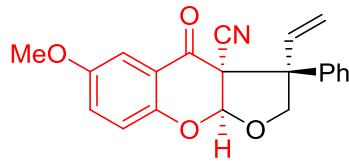
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.793	81.124	195.546	33.57	38.76	n.a.
2		17.087	39.853	85.819	16.49	17.01	n.a.
3		19.503	81.489	181.453	33.72	35.97	n.a.
4		35.523	39.180	41.636	16.21	8.25	n.a.
Total:		241.647	504.454		100.00	100.00	

Chromatogram

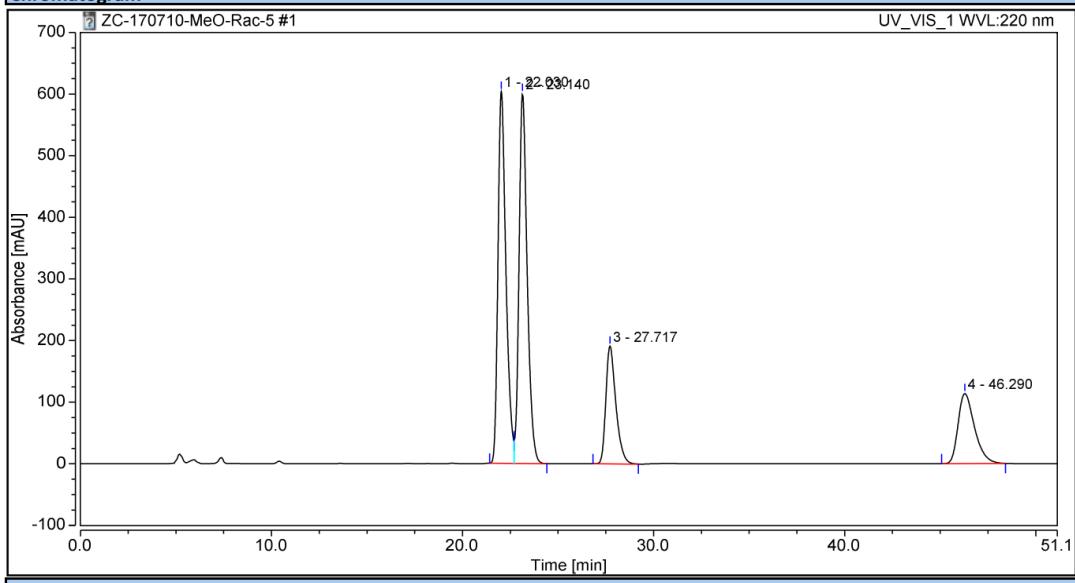


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.787	157.690	364.136	79.02	81.06	n.a.
2		17.157	36.556	76.167	18.32	16.95	n.a.
3		19.980	3.314	6.377	1.66	1.42	n.a.
4		35.663	2.002	2.565	1.00	0.57	n.a.
Total:		199.562	449.246		100.00	100.00	



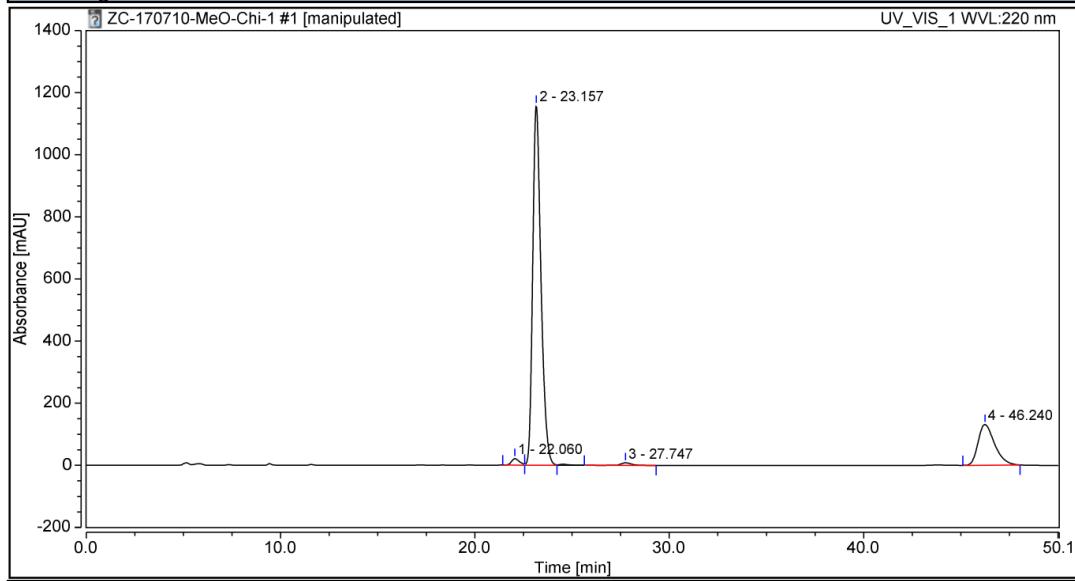
Chromatogram



Integration Results

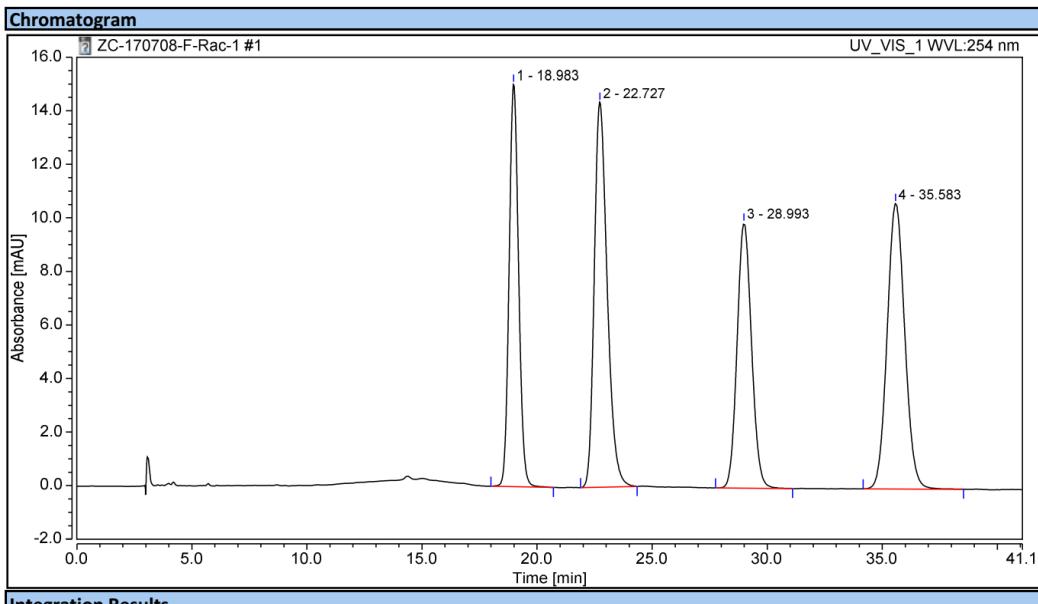
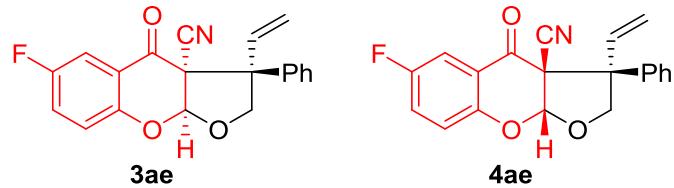
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.030	291.795	603.641	35.64	40.01	n.a.
2		23.140	297.505	600.455	36.34	39.80	n.a.
3		27.717	115.949	190.995	14.16	12.66	n.a.
4		46.290	113.531	113.760	13.87	7.54	n.a.
Total:		818.781	1508.851	100.00	100.00		

Chromatogram



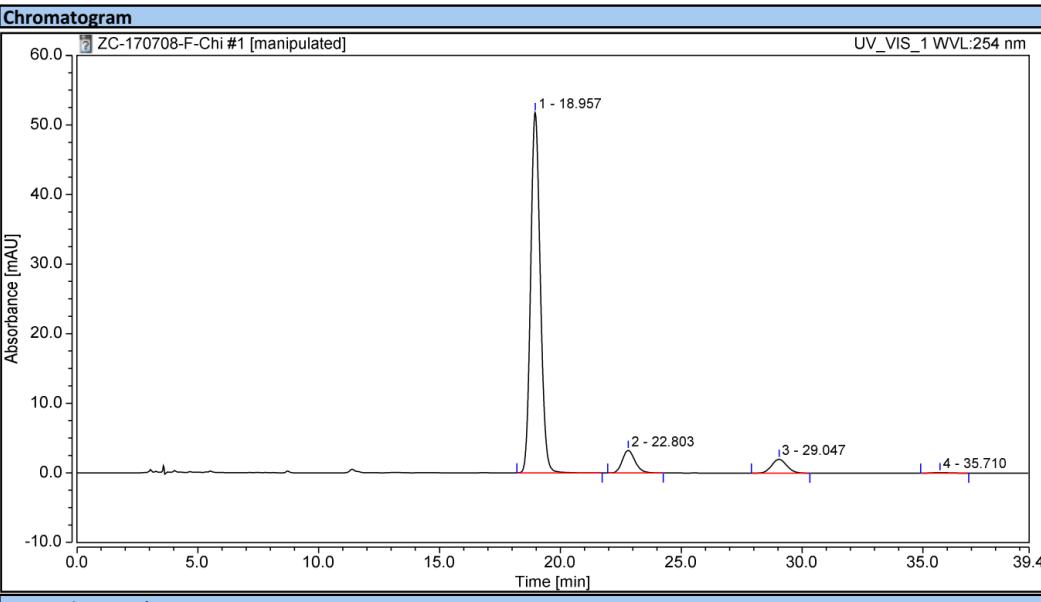
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.060	9.998	21.389	1.39	1.62	n.a.
2		23.157	571.925	1159.208	79.74	87.77	n.a.
3		27.747	6.035	8.682	0.84	0.66	n.a.
4		46.240	129.242	131.498	18.02	9.96	n.a.
Total:		717.201	1320.777	100.00	100.00		



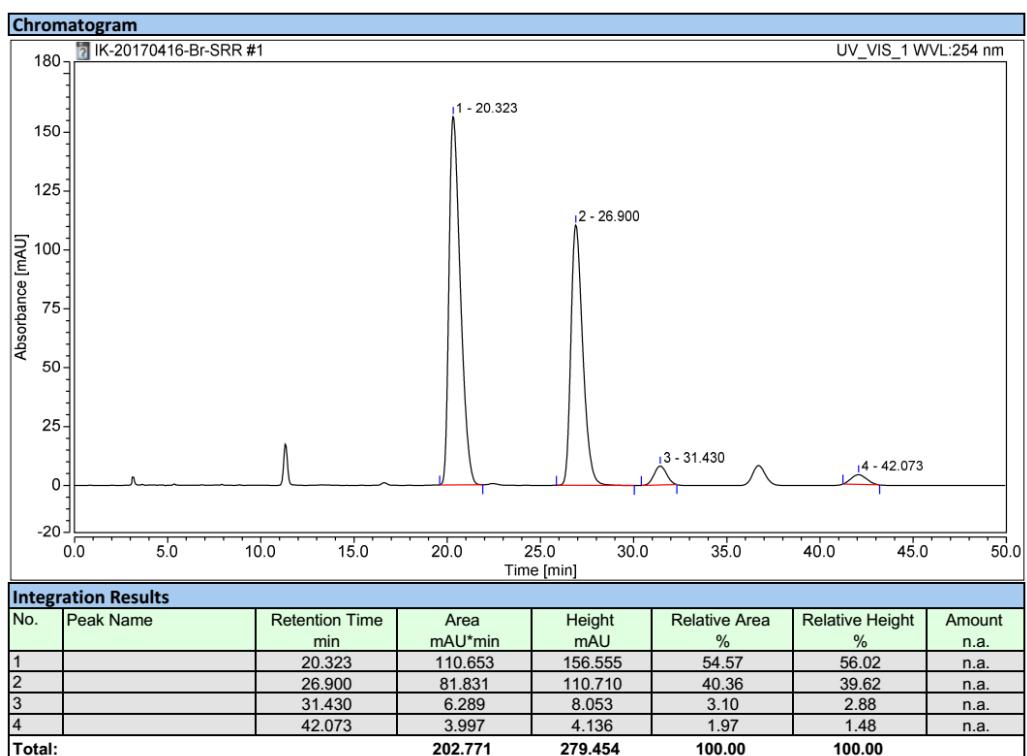
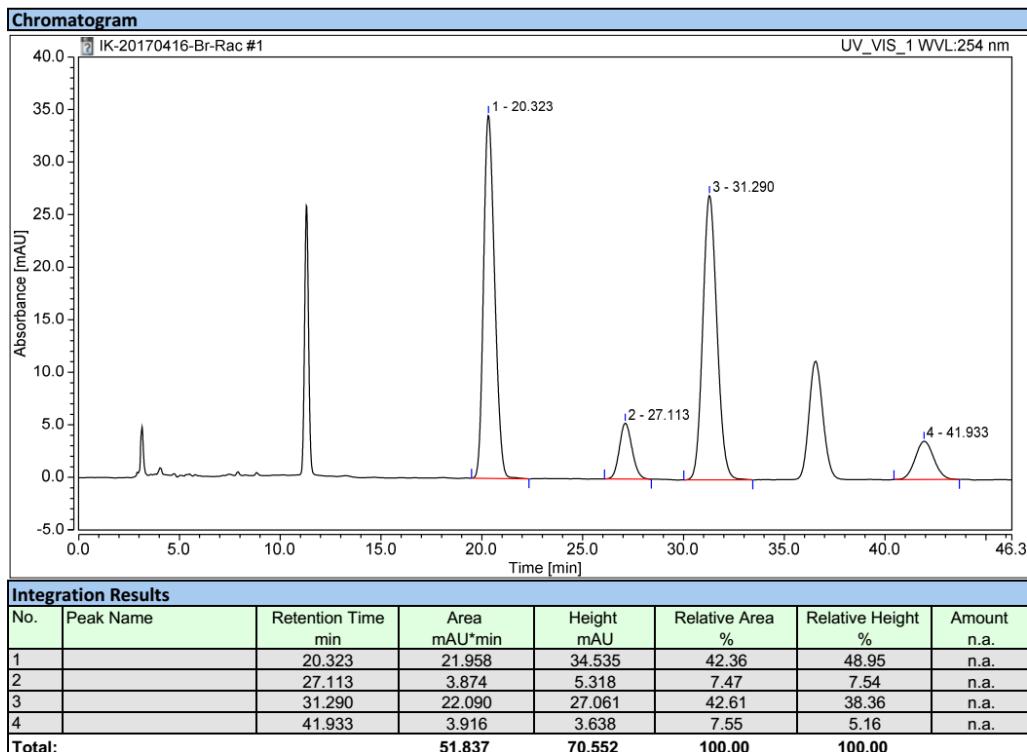
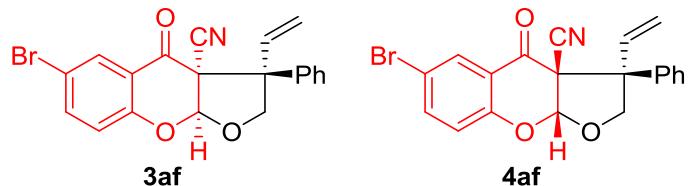
Integration Results

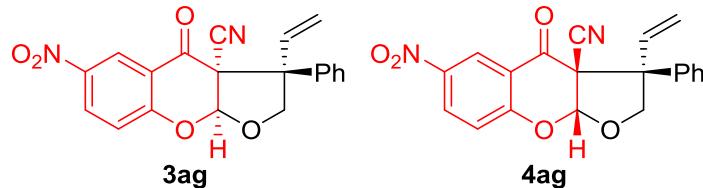
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.983	7.181	15.038	21.62	30.08	n.a.
2		22.727	9.362	14.382	28.19	28.77	n.a.
3		28.993	7.189	9.906	21.65	19.81	n.a.
4		35.583	9.474	10.670	28.53	21.34	n.a.
Total:		33.206	49.997	100.00	100.00		



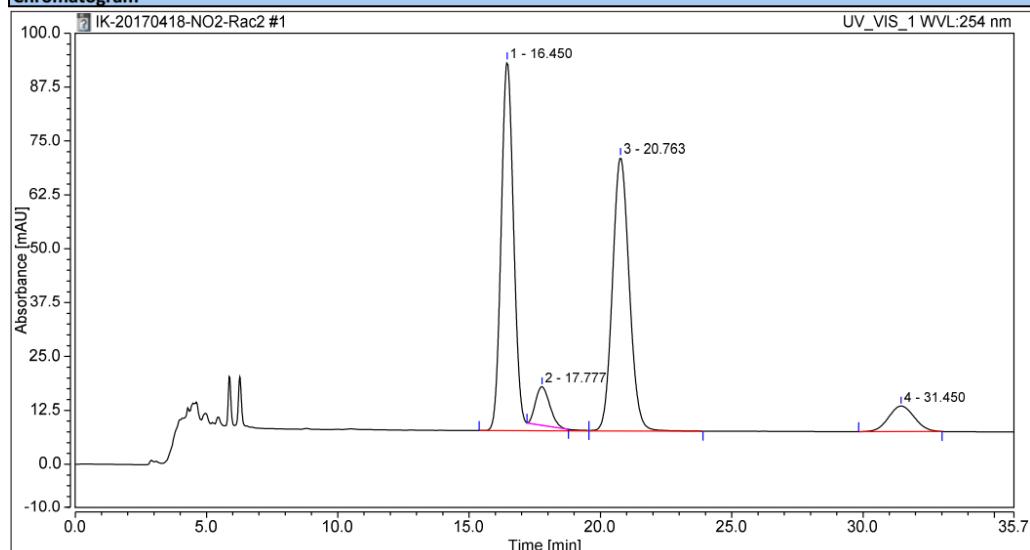
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.957	24.055	51.803	87.16	90.67	n.a.
2		22.803	2.000	3.247	7.25	5.68	n.a.
3		29.047	1.461	1.991	5.29	3.49	n.a.
4		35.710	0.083	0.091	0.30	0.16	n.a.
Total:		27.600	57.131	100.00	100.00		





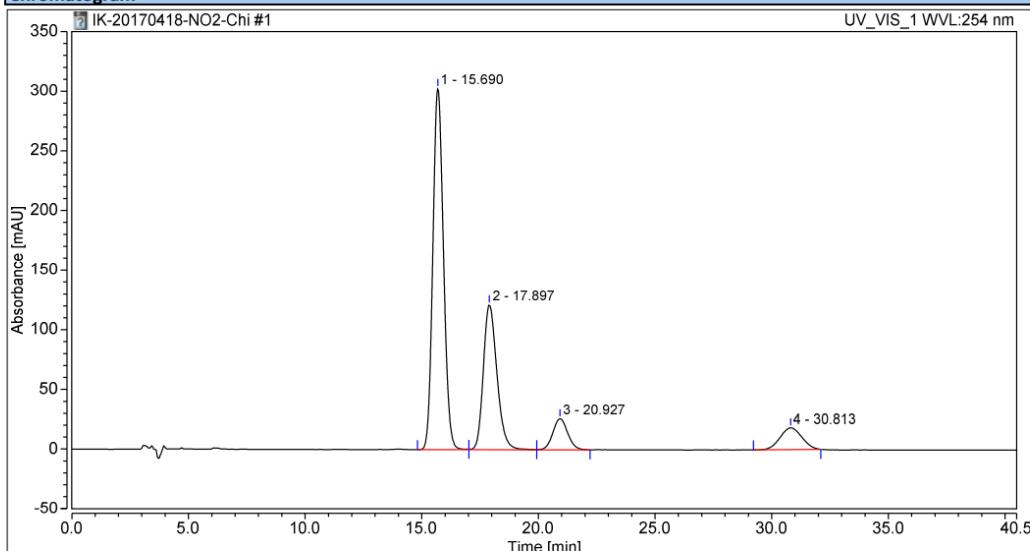
Chromatogram



Integration Results

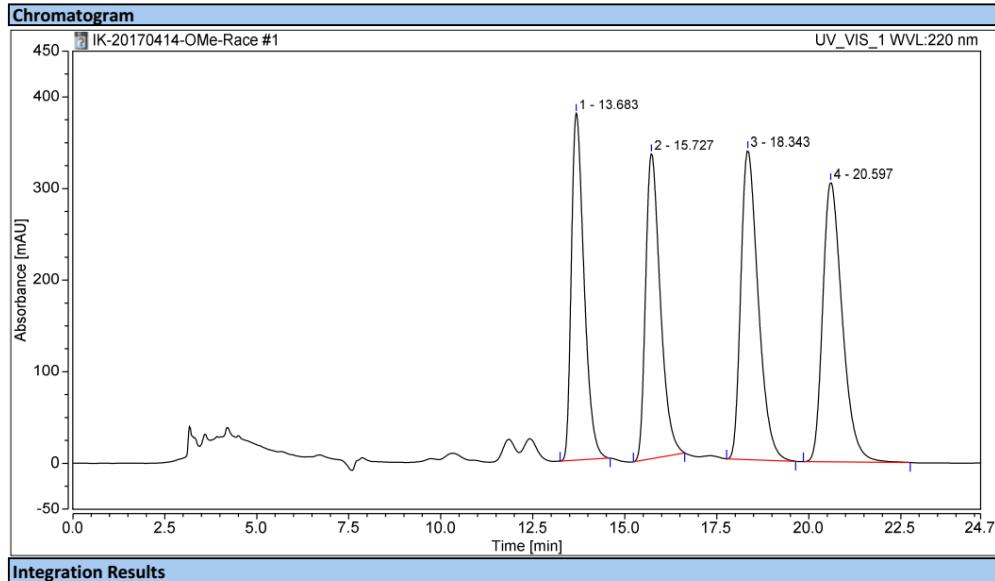
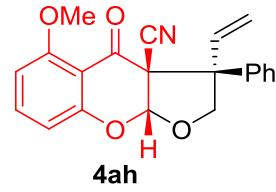
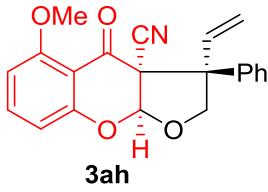
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.450	48.790	85.577	45.13	52.21	n.a.
2		17.777	5.596	8.966	5.18	5.47	n.a.
3		20.763	46.987	63.446	43.46	38.71	n.a.
4		31.450	6.749	5.924	6.24	3.61	n.a.
Total:		108.122	163.912	100.00	100.00		

Chromatogram

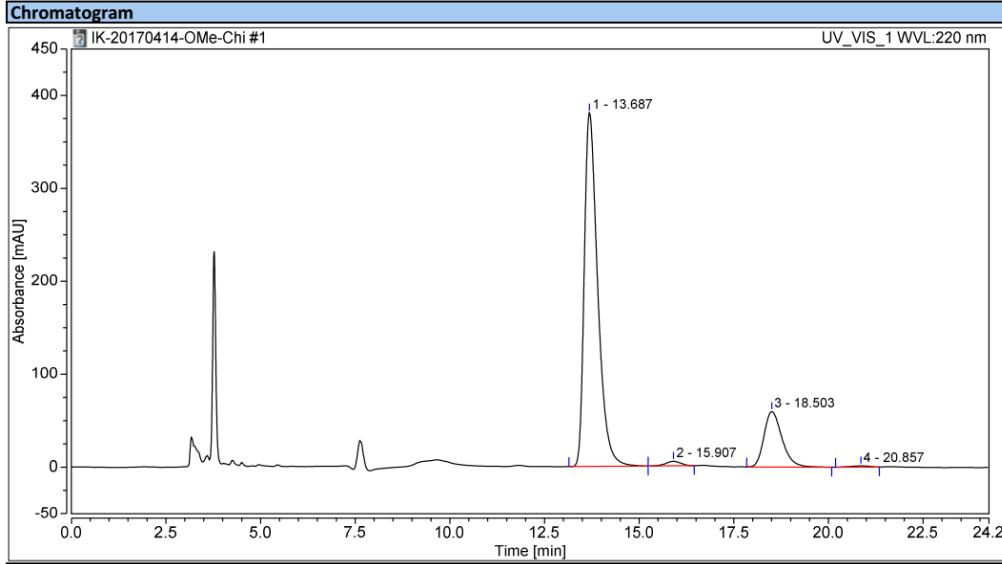


Integration Results

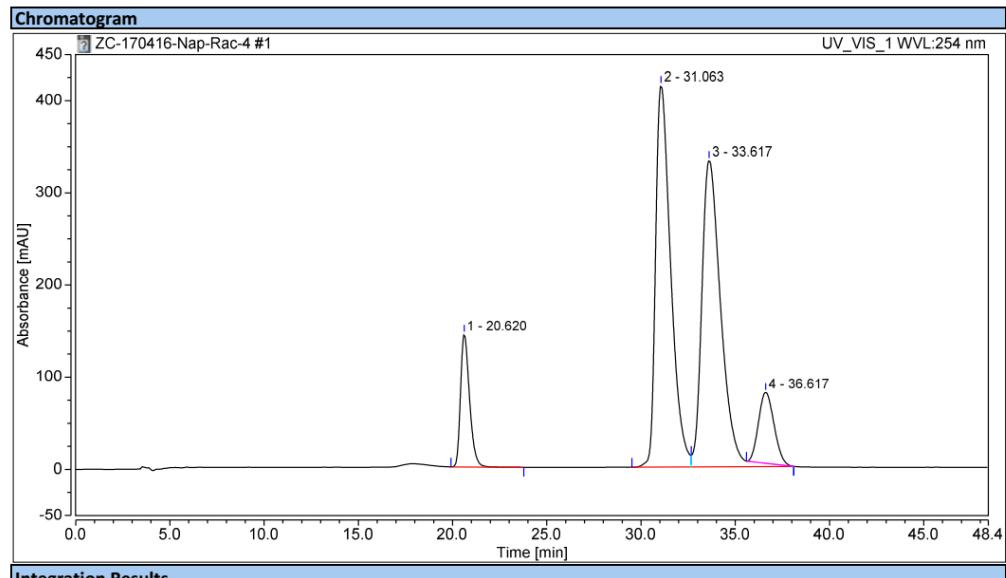
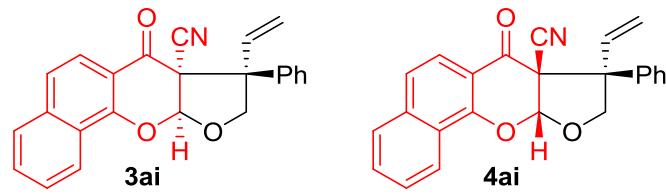
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.690	159.634	302.950	56.88	64.63	n.a.
2		17.897	82.050	121.535	29.23	25.93	n.a.
3		20.927	19.188	26.048	6.84	5.56	n.a.
4		30.813	19.786	18.232	7.05	3.89	n.a.
Total:		280.659	468.766	100.00	100.00		



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.683	151.666	378.844	22.34	27.96	n.a.
2		15.727	154.077	333.126	22.69	24.59	n.a.
3		18.343	185.063	337.727	27.26	24.93	n.a.
4		20.597	188.101	305.216	27.71	22.53	n.a.
Total:		678.907	1354.914	100.00	100.00	100.00	

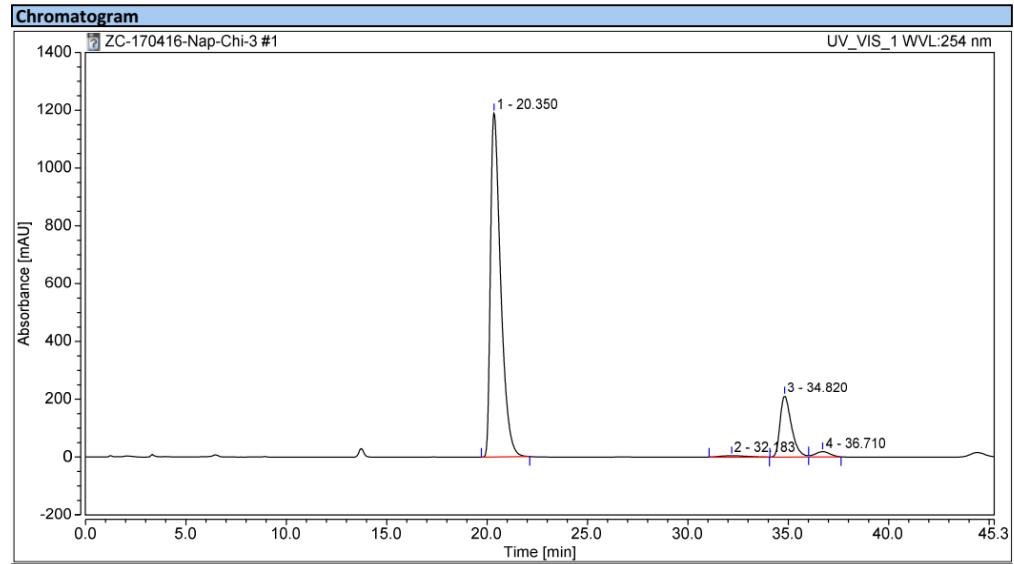


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.687	156.072	380.579	81.26	85.22	n.a.
2		15.907	2.313	4.909	1.20	1.10	n.a.
3		18.503	32.912	59.714	17.14	13.37	n.a.
4		20.857	0.762	1.368	0.40	0.31	n.a.
Total:		192.058	446.570	100.00	100.00	100.00	



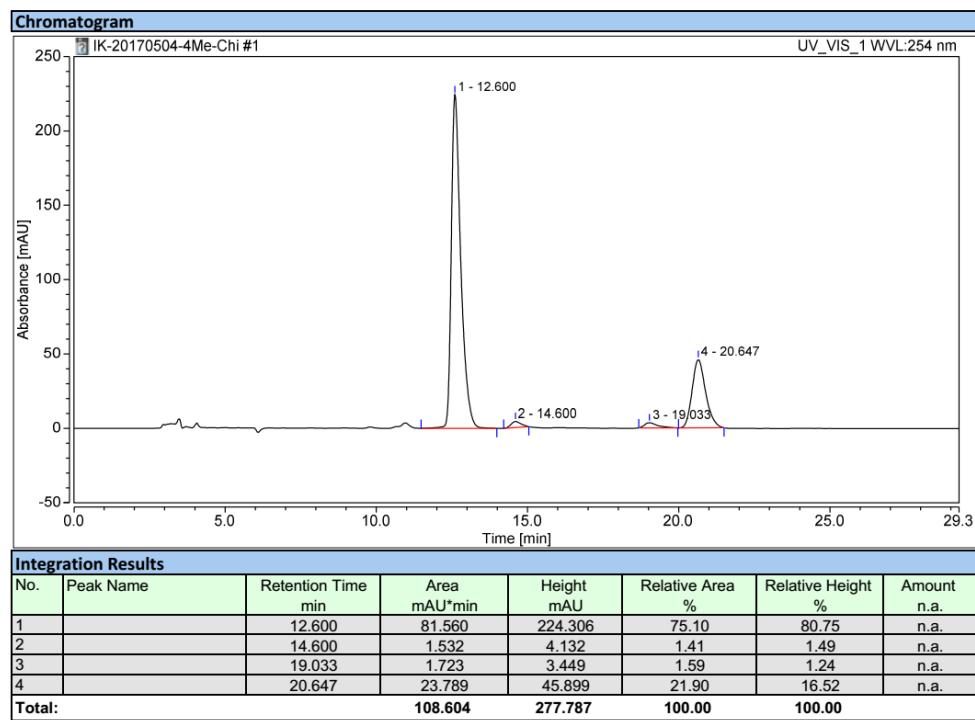
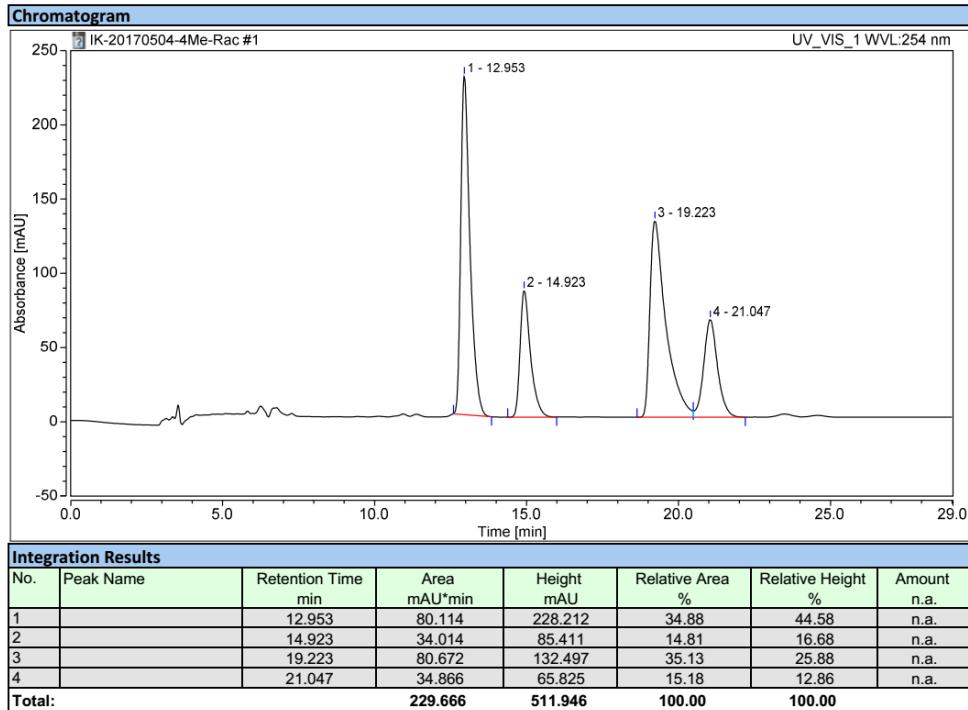
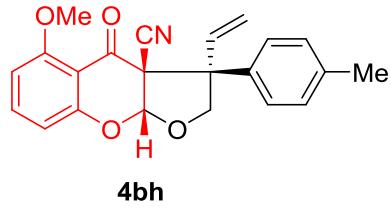
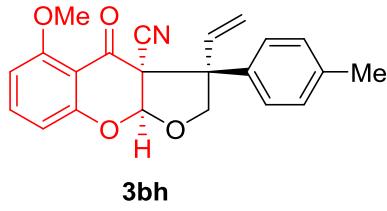
Integration Results

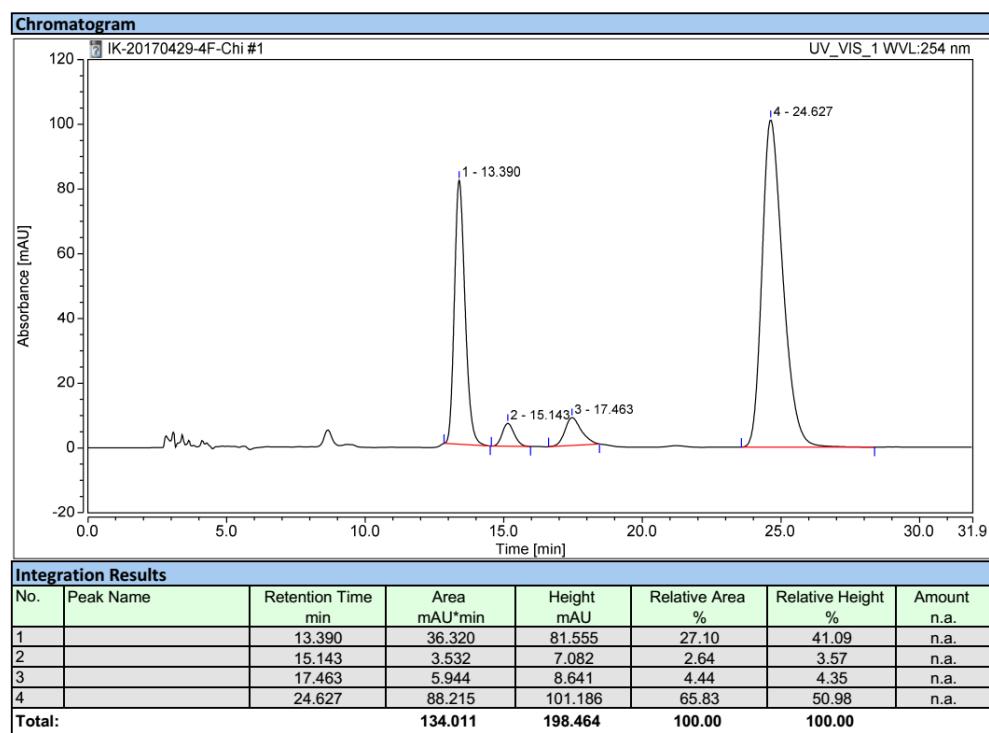
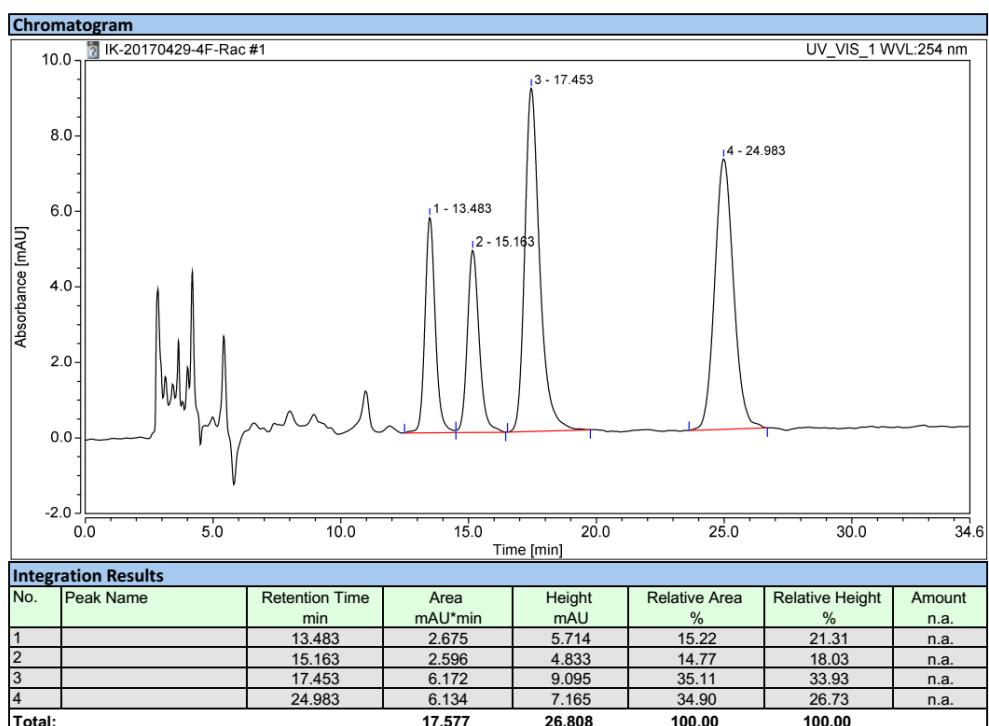
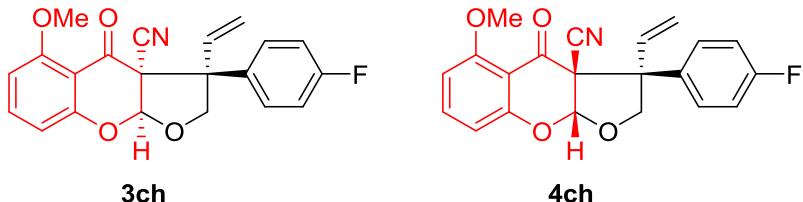
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.620	79.849	144.067	8.60	14.88	n.a.
2		31.063	384.858	414.287	41.45	42.80	n.a.
3		33.617	390.151	332.611	42.02	34.36	n.a.
4		36.617	73.560	77.085	7.92	7.96	n.a.
Total:			928.419	968.050	100.00	100.00	

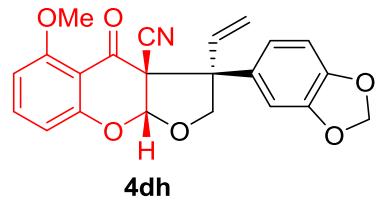
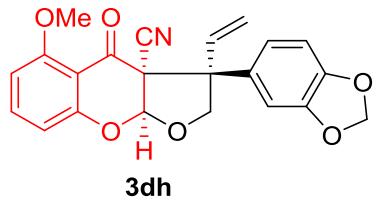


Integration Results

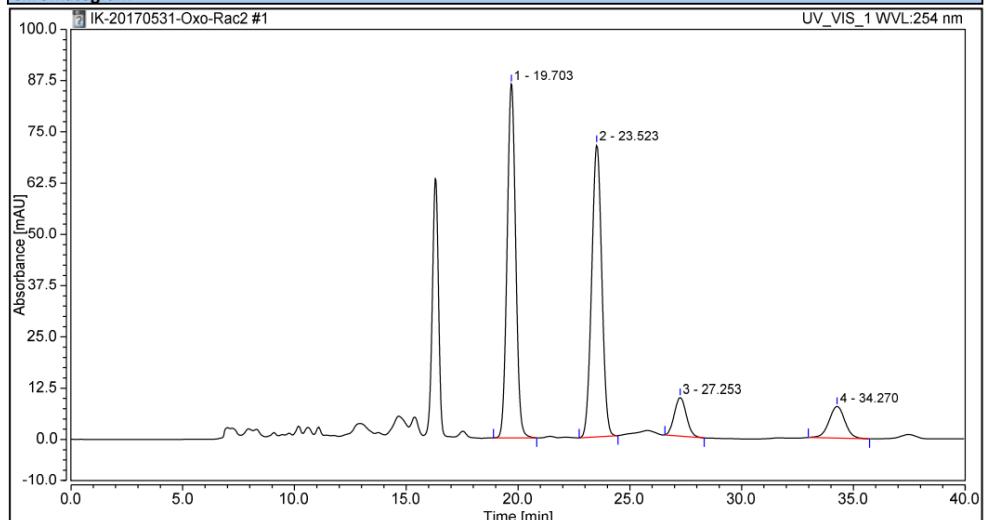
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.350	701.916	1191.145	81.35	83.59	n.a.
2		32.183	6.956	4.688	0.81	0.33	n.a.
3		34.820	138.674	211.124	16.07	14.82	n.a.
4		36.710	15.315	18.014	1.77	1.26	n.a.
Total:			862.861	1424.971	100.00	100.00	







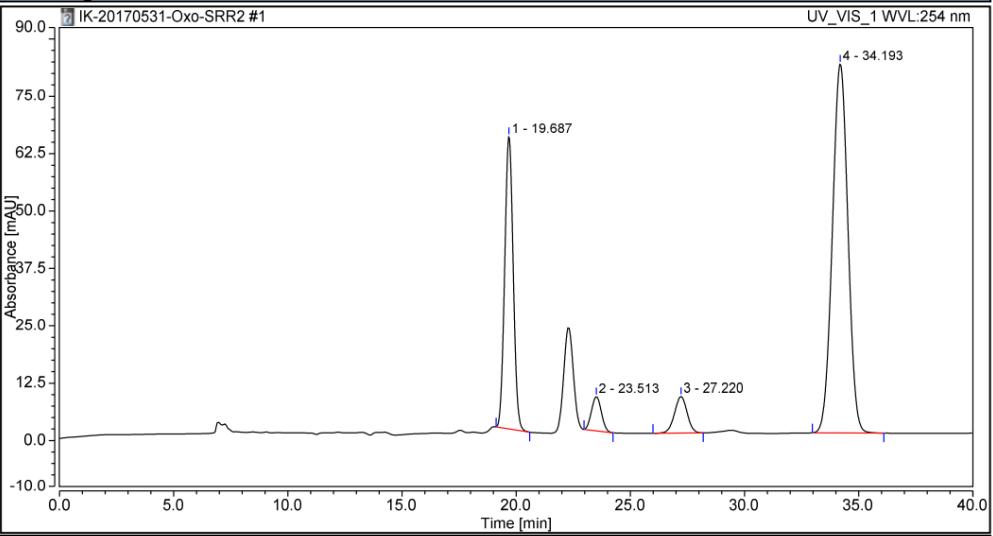
Chromatogram



Integration Results

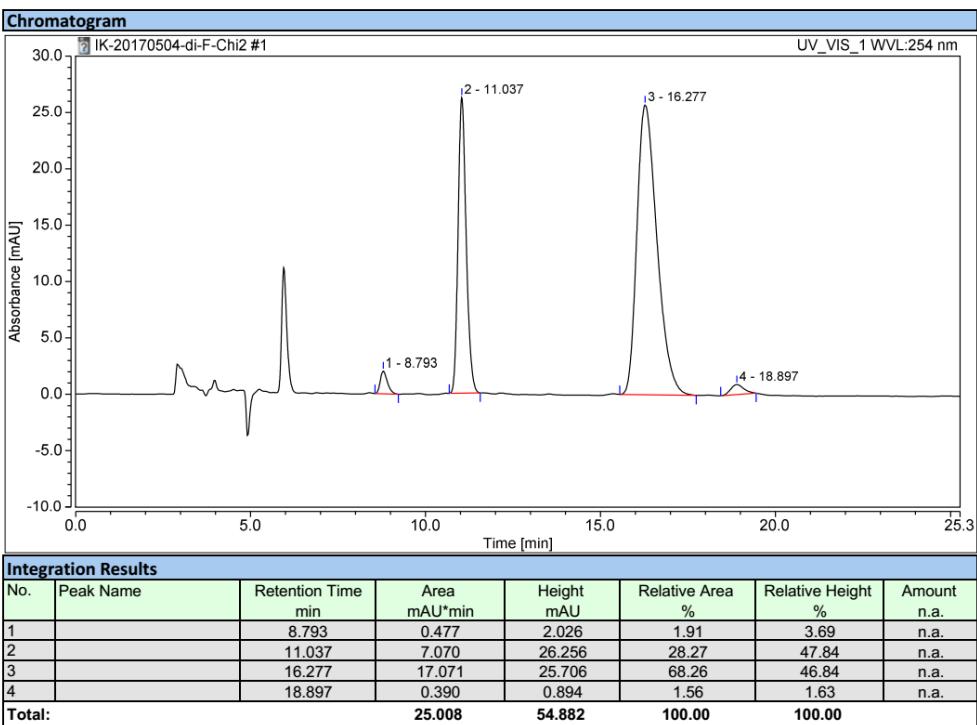
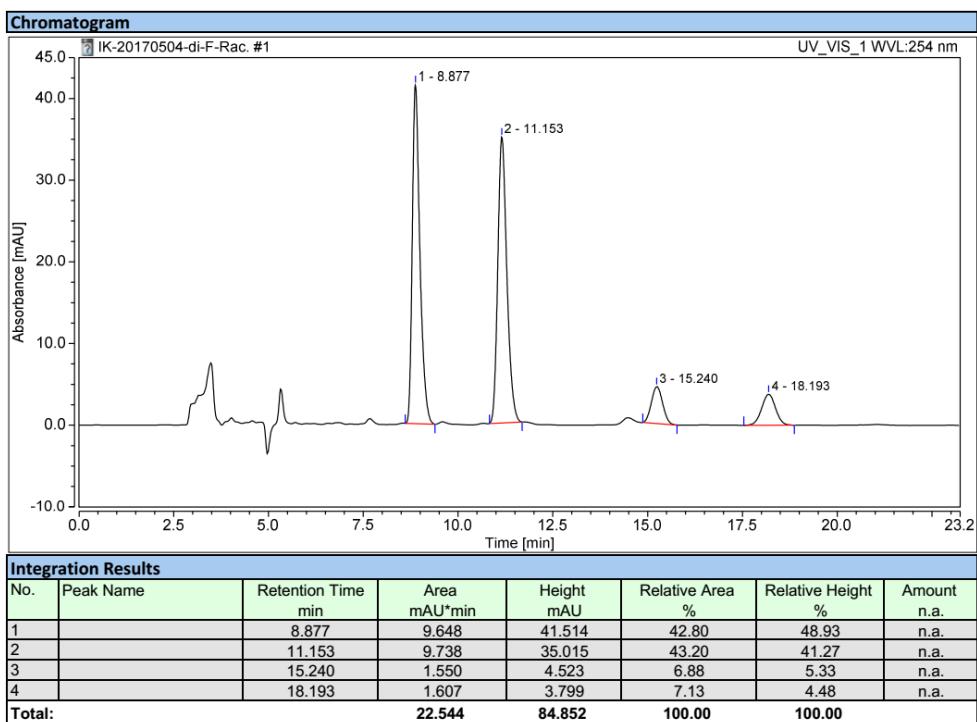
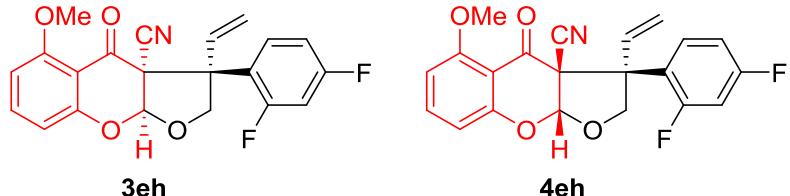
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.703	38.184	86.340	43.47	49.40	n.a.
2		23.523	37.445	71.297	42.63	40.80	n.a.
3		27.253	5.856	9.401	6.67	5.38	n.a.
4		34.270	6.353	7.729	7.23	4.42	n.a.
Total:		87.838	174.766	100.00	100.00	100.00	

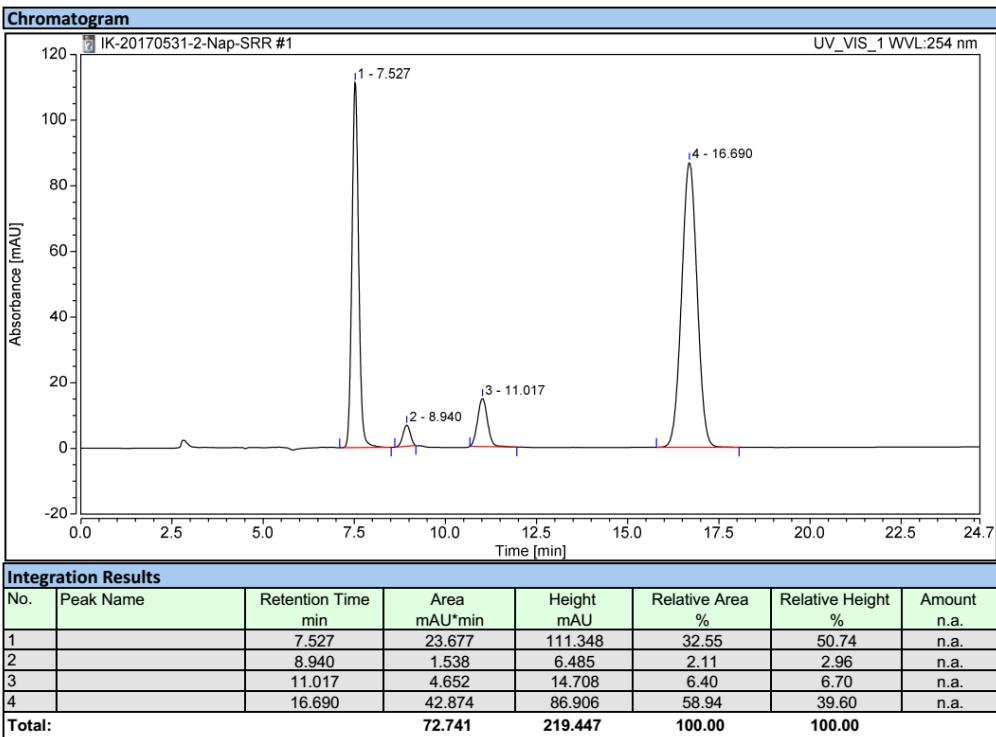
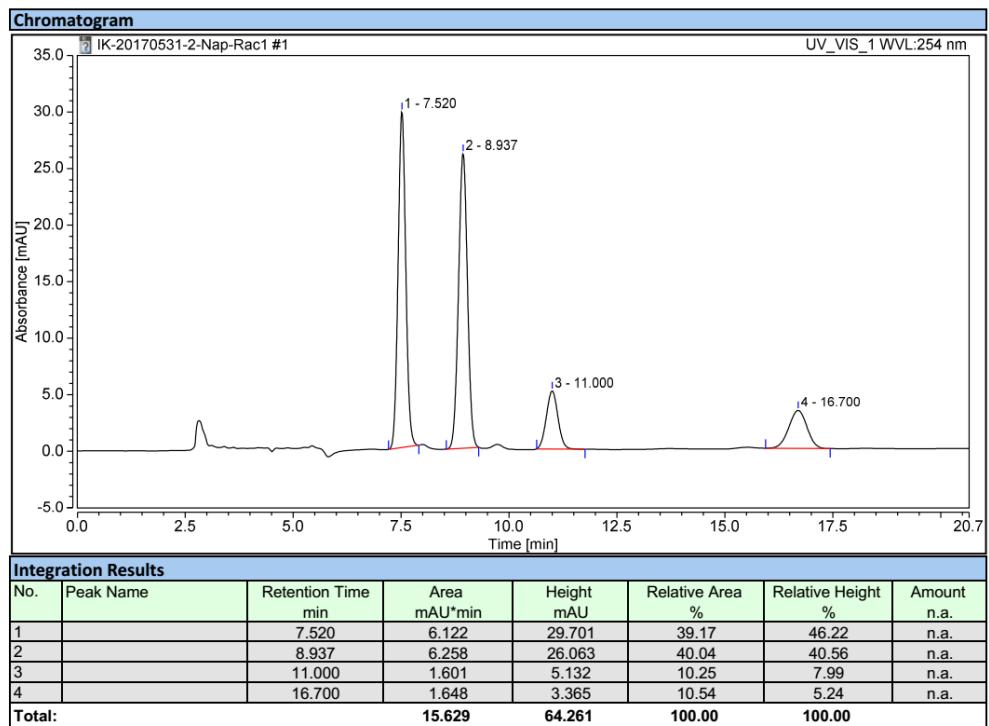
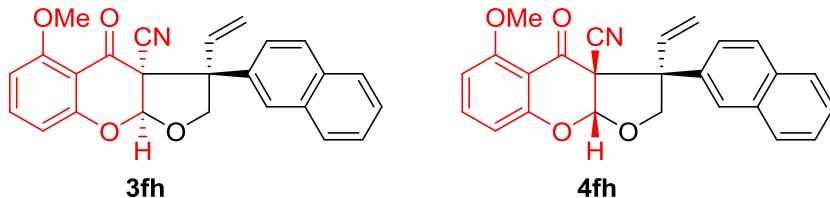
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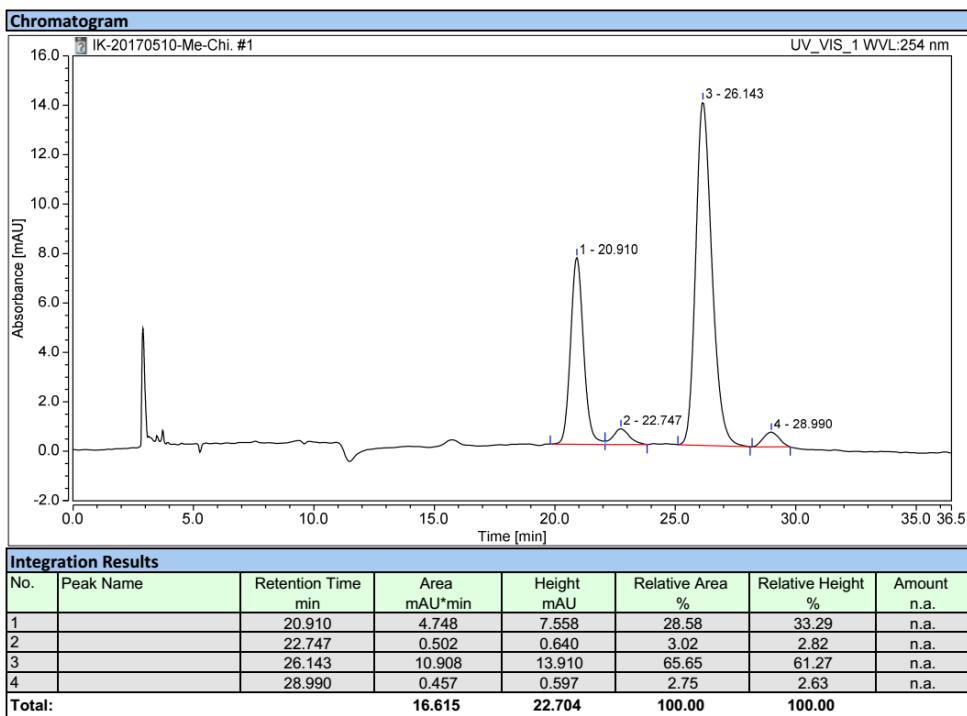
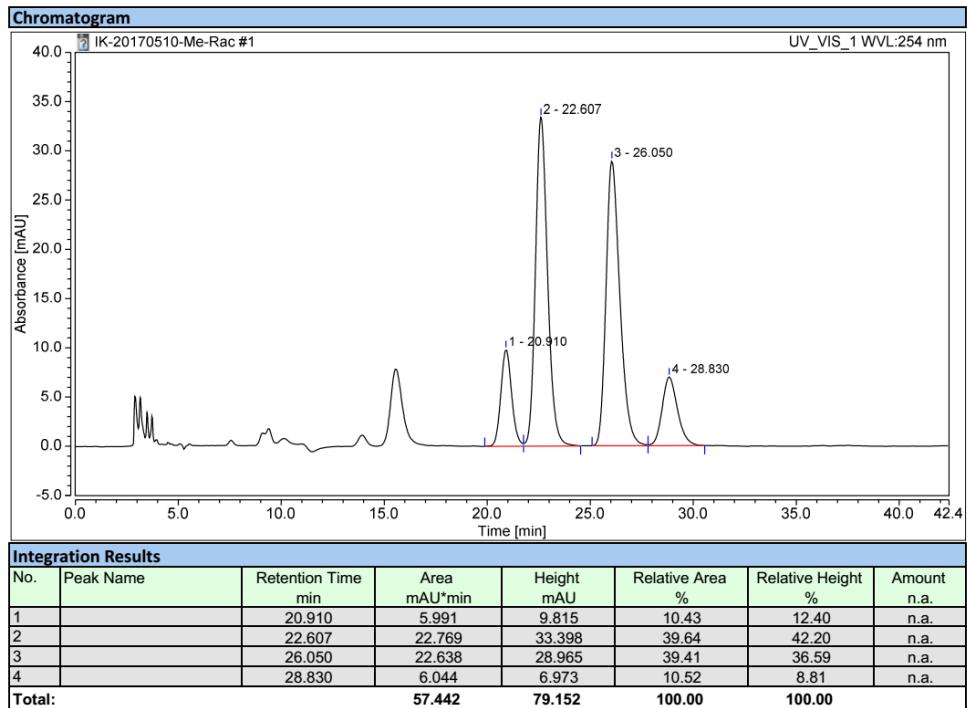
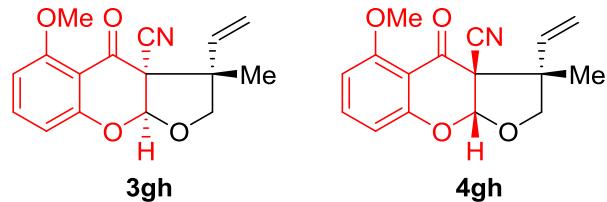


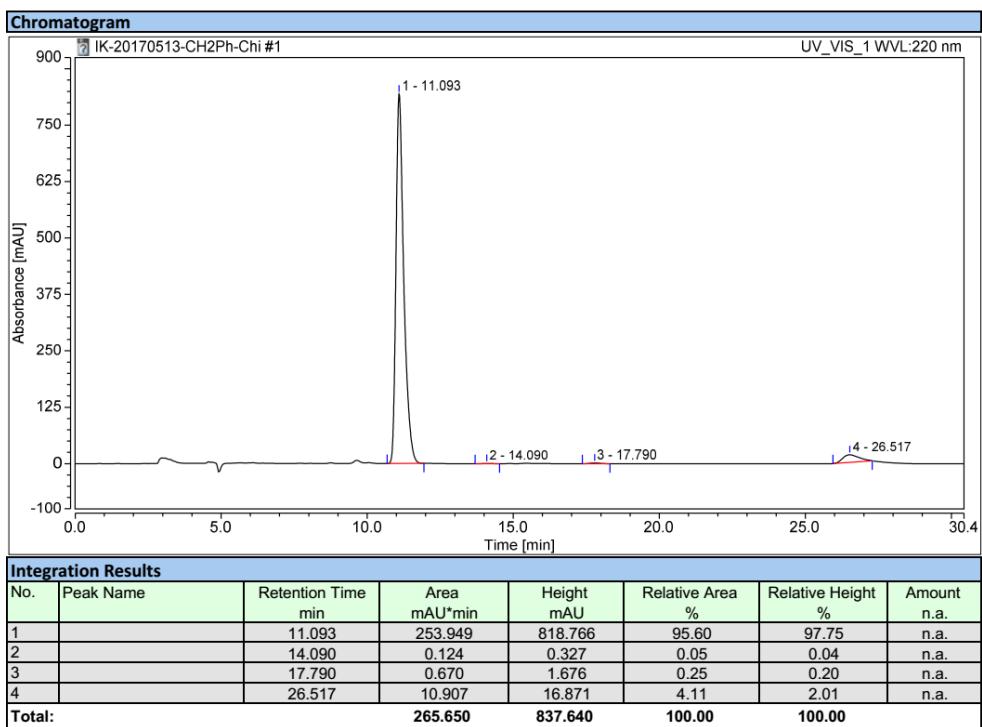
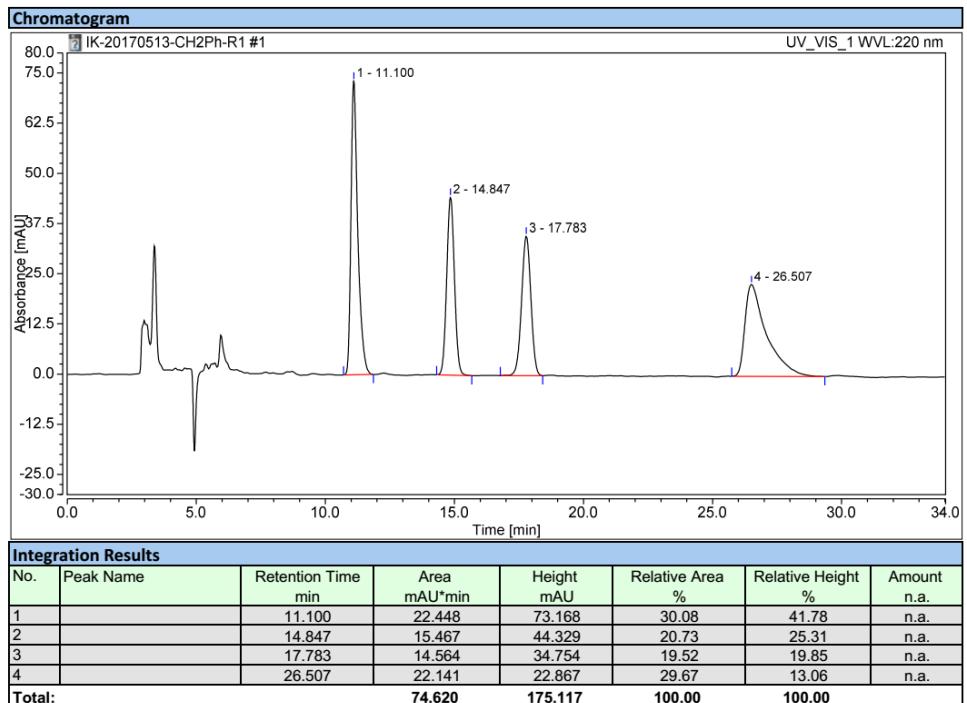
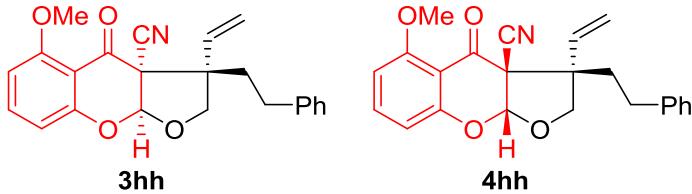
Integration Results

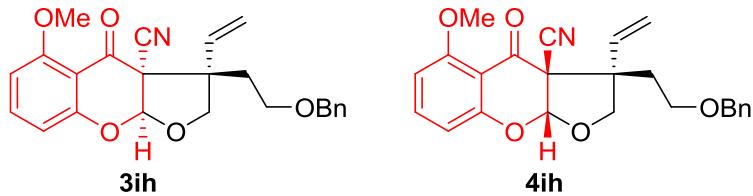
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.687	27.522	63.712	27.55	39.94	n.a.
2		23.513	3.744	7.464	3.75	4.68	n.a.
3		27.220	5.135	7.967	5.14	4.99	n.a.
4		34.193	63.494	80.374	63.56	50.39	n.a.
Total:		99.894	159.516	100.00	100.00	100.00	



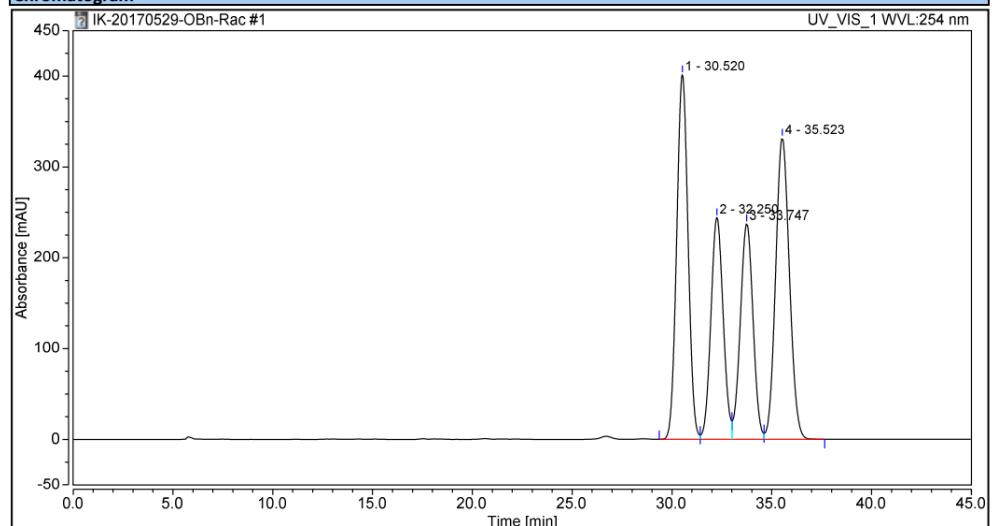








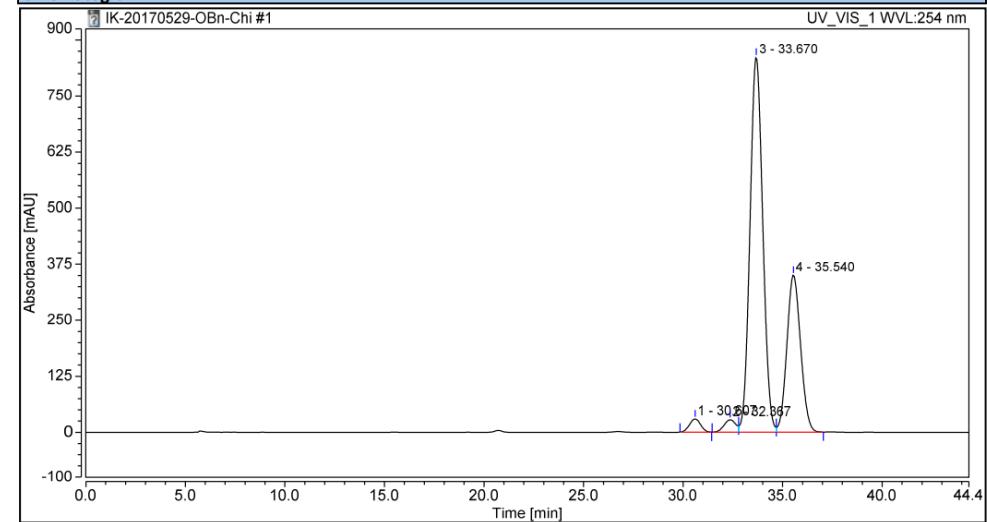
Chromatogram



Integration Results

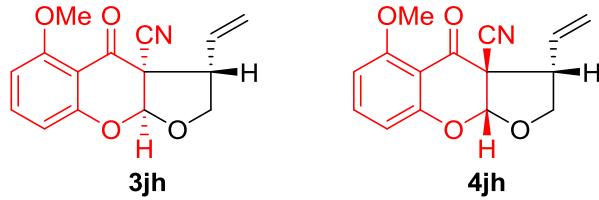
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		30.520	265.512	401.632	30.11	33.04	n.a.
2		32.250	174.815	244.381	19.82	20.11	n.a.
3		33.747	175.275	237.524	19.88	19.54	n.a.
4		35.523	266.265	331.879	30.19	27.31	n.a.
Total:		881.866	1215.415		100.00	100.00	

Chromatogram

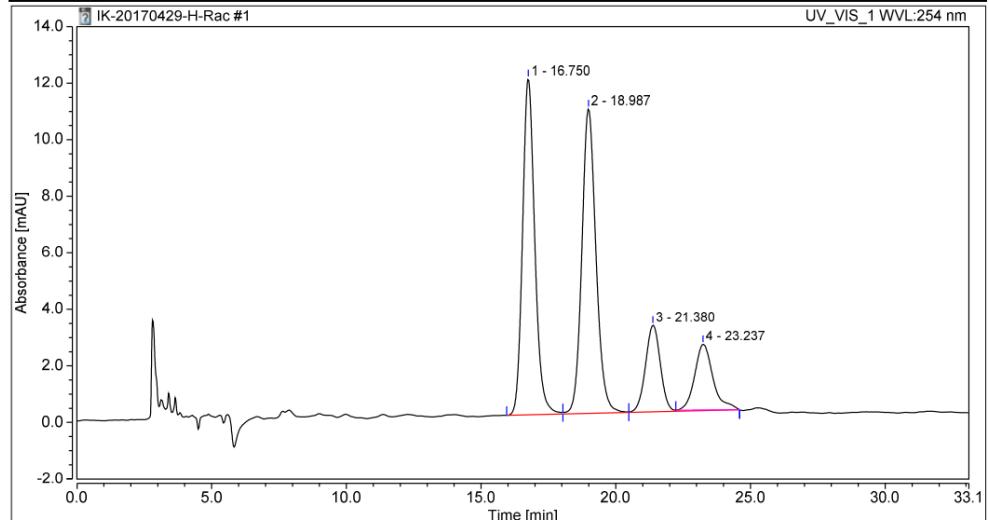


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		30.607	18.979	29.523	2.02	2.37	n.a.
2		32.367	18.553	27.647	1.97	2.22	n.a.
3		33.670	623.453	836.425	66.23	67.26	n.a.
4		35.540	280.320	349.963	29.78	28.14	n.a.
Total:		941.305	1243.558		100.00	100.00	



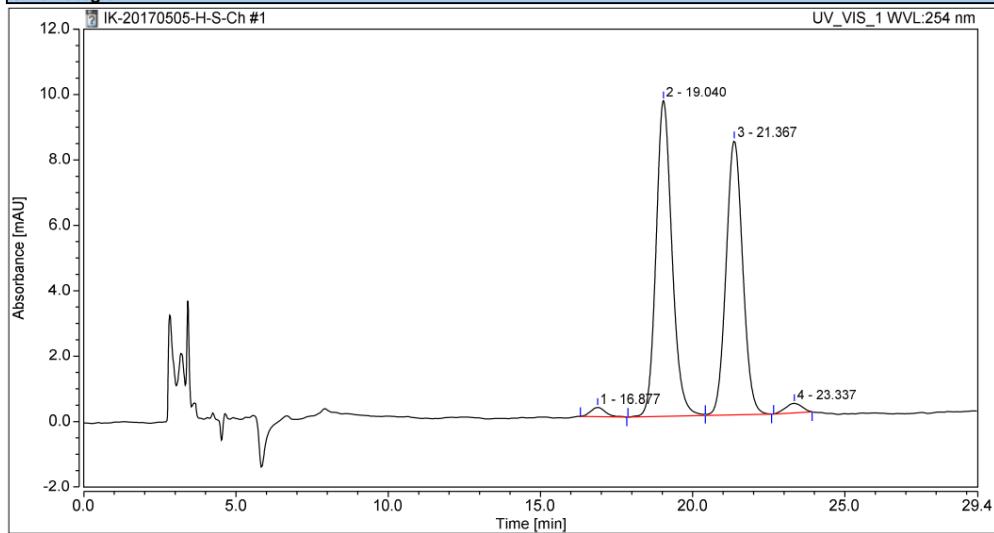
Chromatogram



Integration Results

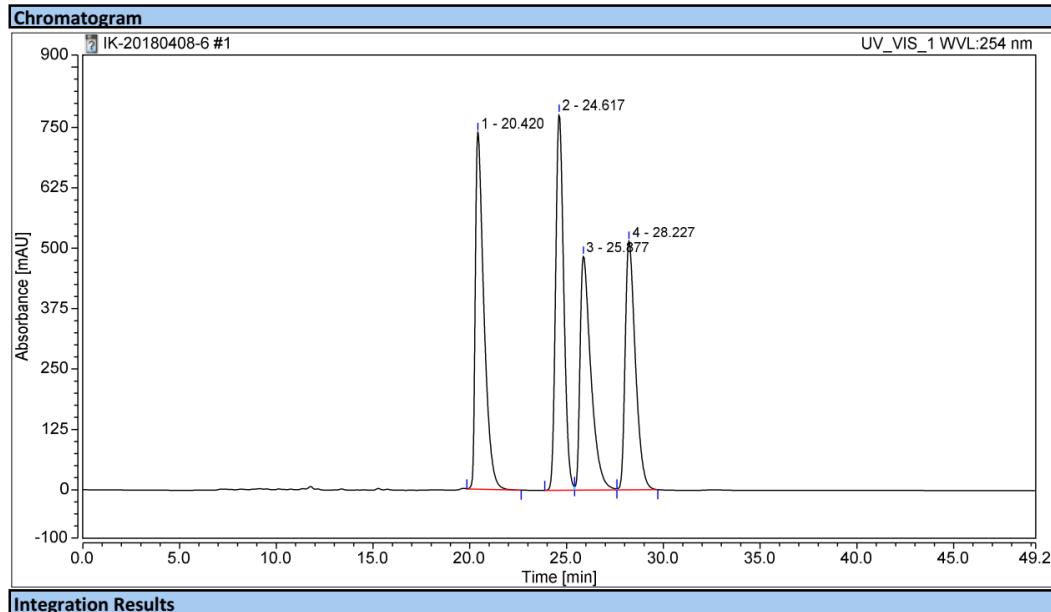
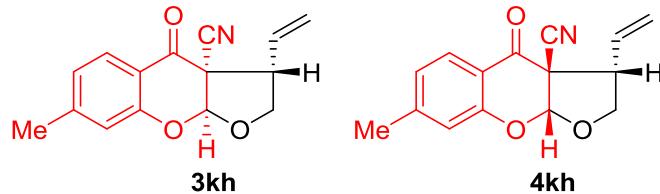
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.750	6.280	11.889	37.64	42.38	n.a.
2		18.987	6.569	10.777	39.37	38.41	n.a.
3		21.380	2.002	3.067	12.00	10.93	n.a.
4		23.237	1.832	2.323	10.98	8.28	n.a.
Total:		16.683	28.056	100.00	100.00	100.00	

Chromatogram



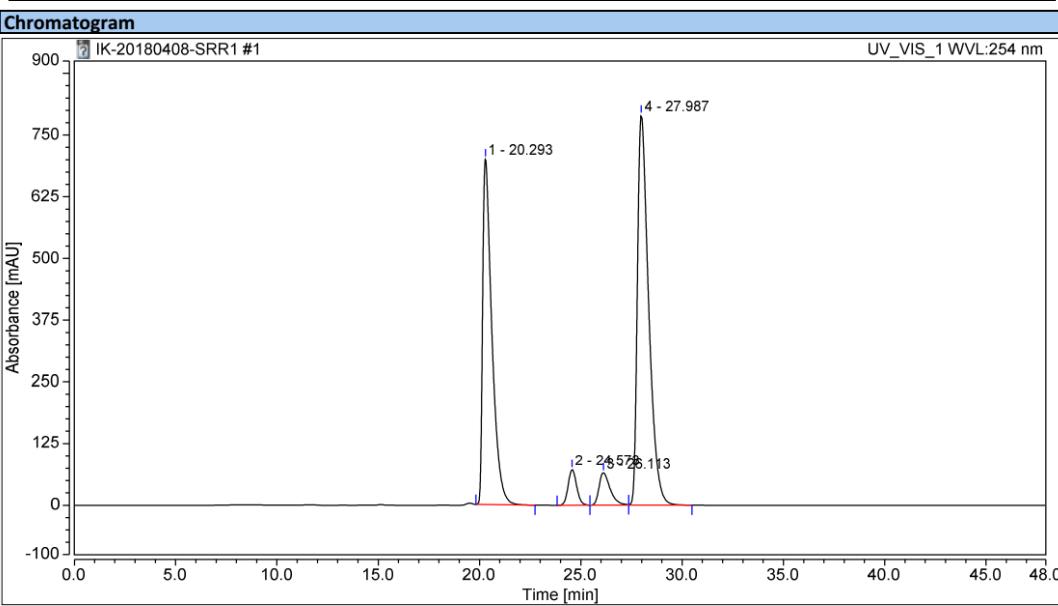
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.877	0.159	0.282	1.38	1.52	n.a.
2		19.040	5.881	9.657	50.96	51.87	n.a.
3		21.367	5.316	8.384	46.06	45.04	n.a.
4		23.337	0.185	0.293	1.60	1.57	n.a.
Total:		11.541	18.615	100.00	100.00	100.00	



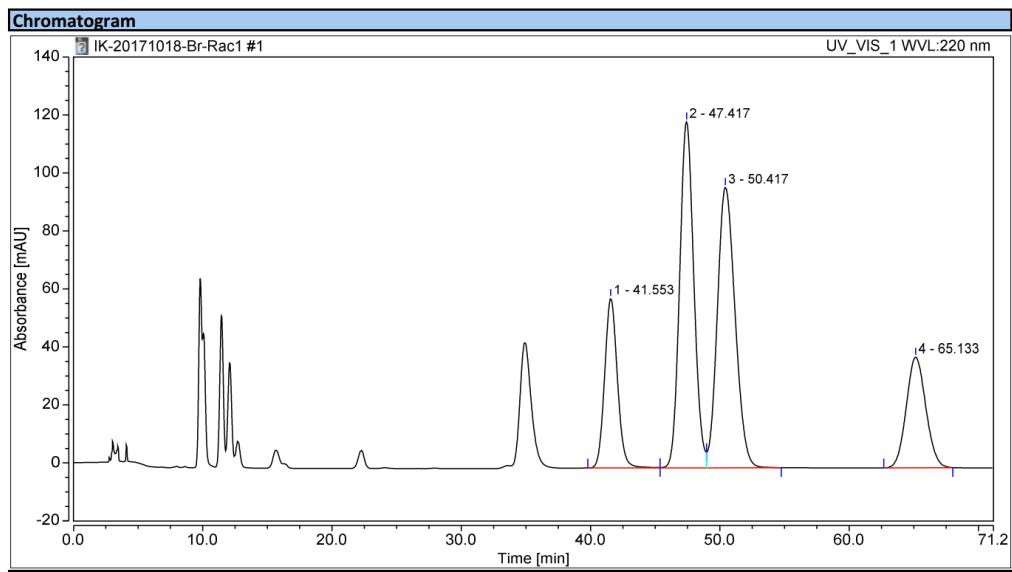
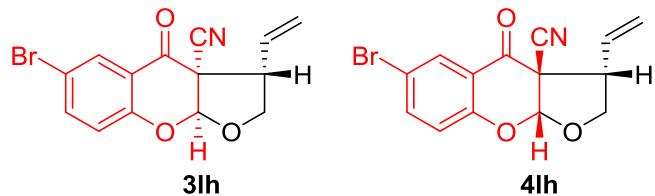
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.420	382.299	738.278	27.51	29.35	n.a.
2		24.617	379.434	778.460	27.30	30.94	n.a.
3		25.877	314.336	484.517	22.62	19.26	n.a.
4		28.227	313.798	514.516	22.58	20.45	n.a.
Total:		1389.867	2515.771	100.00	100.00		

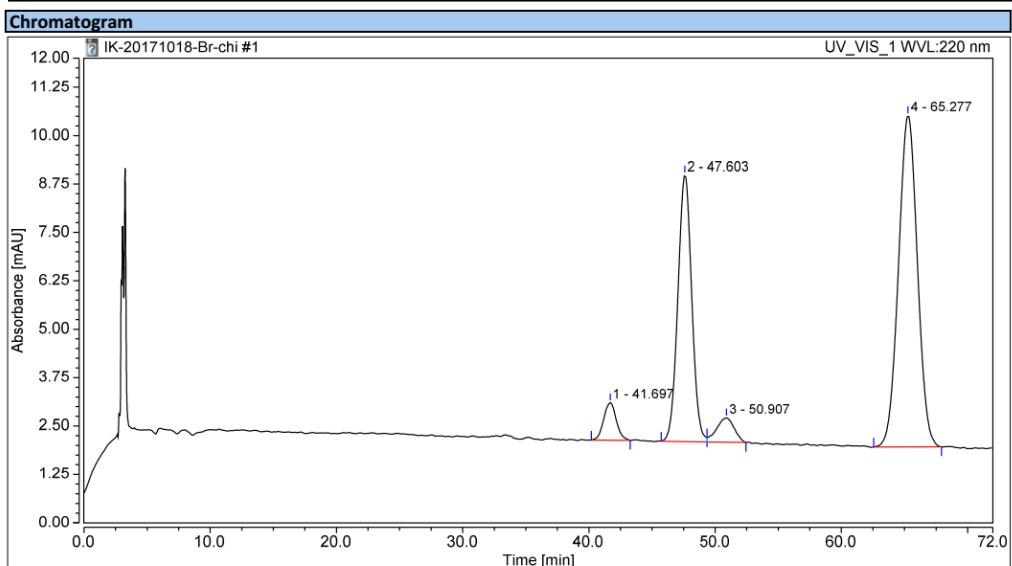


Integration Results

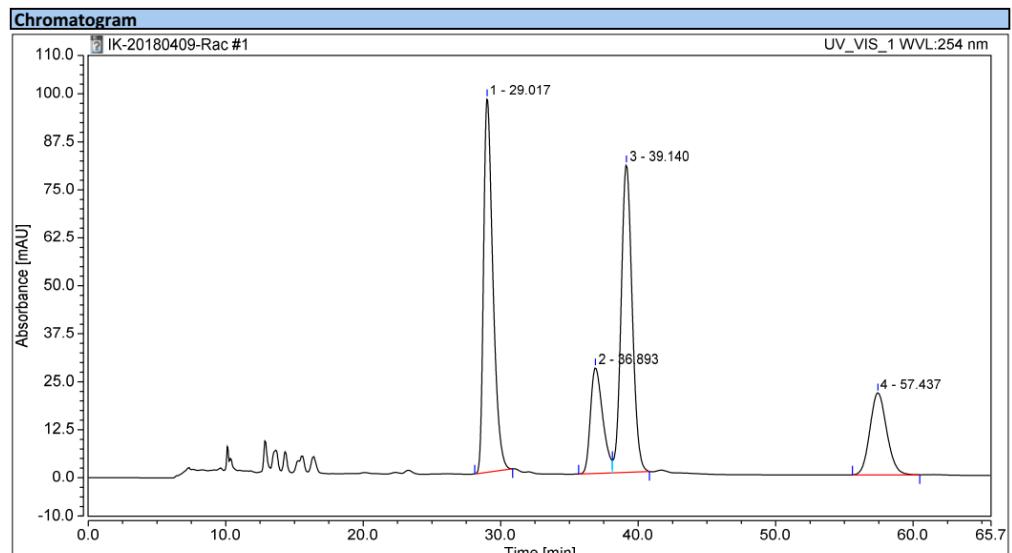
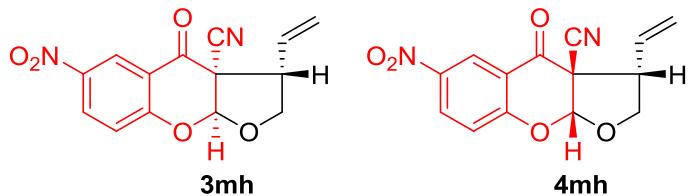
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.293	370.053	700.246	38.75	42.98	n.a.
2		24.573	35.503	72.568	3.72	4.45	n.a.
3		26.113	41.959	66.014	4.39	4.05	n.a.
4		27.987	507.567	790.453	53.14	48.52	n.a.
Total:		955.082	1629.281	100.00	100.00		



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		41.553	67.067	58.532	15.26	18.71	n.a.
2		47.417	151.671	119.364	34.50	38.16	n.a.
3		50.417	153.980	96.719	35.03	30.92	n.a.
4		65.133	66.854	38.214	15.21	12.22	n.a.
Total:			439.571	312.828	100.00	100.00	

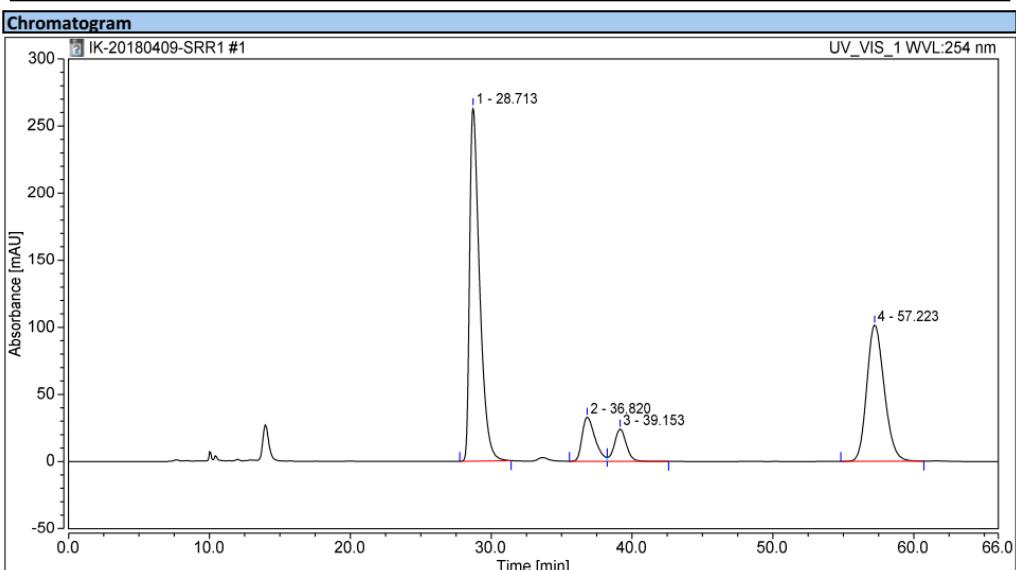


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		41.697	1.125	0.971	4.37	5.70	n.a.
2		47.603	8.737	6.886	33.97	40.40	n.a.
3		50.907	1.009	0.629	3.92	3.69	n.a.
4		65.277	14.846	8.558	57.73	50.21	n.a.
Total:			25.717	17.046	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.017	76.924	97.374	36.49	43.01	n.a.
2		36.893	28.414	27.540	13.48	12.16	n.a.
3		39.140	75.055	80.151	35.60	35.40	n.a.
4		57.437	30.434	21.358	14.44	9.43	n.a.
Total:		210.827	226.422		100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.713	215.966	263.455	51.39	62.43	n.a.
2		36.820	34.944	32.905	8.32	7.80	n.a.
3		39.153	23.473	24.052	5.59	5.70	n.a.
4		57.223	145.852	101.572	34.71	24.07	n.a.
Total:		420.234	421.984		100.00	100.00	