Electronic Supplementary Information for

Catalytic Asymmetric Inverse Electron Demand Diels-Alder Reaction of Fulvenes with Azoalkenes

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Table of Contents

1 General Remarks

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl$_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, and brs = broad single). ^{13}C NMR spectra were recorded on a Bruker 75 MHz or 100 MHz spectrometer in CDCl$_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially available reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Diastereomeric ratios were determined from crude ^{1}H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralpak AS-H column, a chiralpak IC-H column or a chiralcel IE-H column with hexane and *i*-PrOH as solvents, and Azoalkenes[1] and fulvene[2] were prepared according to the literature procedure. The absolute configuration of **3f** were determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of these results.

2 General Procedure for Catalytic Asymmetric IEDDA reaction of Fulvene with Azoalkenes Catalyzed by Cu(I)/^{t}Bu-Box

Under argon atmosphere, ^{t}Bu-Box (6.5 mg, 0.022 mmol) and CuOTf•1/2 PhH (5.0 mg, 0.020 mmol) were dissolved in 1.0 mL of DCM, and stirred at room temperature for about 0.5 h. After the reaction temperature was dropped to -20 °C, α-halogeno-hydrozone **2** (0.2 mmol), Na$_2$CO$_3$ (0.5 mmol) were added sequentially. Then, the fulvene **1** (0.3 mmol) in 1.0 mL of DCM was added. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography to give the cycloaddition product, which was then directly analyzed by HPLC to determine the enantiomeric excess.
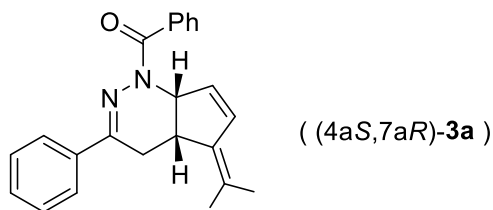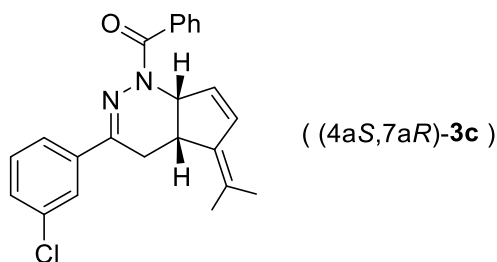
((4a*S*,7a*R*)-**3a**)

(4a*S*,7a*R*)-phenyl(3-phenyl-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)methanone (table 2, entry 1): Yield (73%); white solid; m.p. = 126 °C; $[\alpha]^{20}_D$ = -591.0 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.73 (m, 2H), 7.58 – 7.56 (m, 2H), 7.42 – 7.31 (m, 6H), 6.51 – 6.49 (m, 1H), 6.20 (d, *J* = 5.2 Hz, 1H), 5.54 (d, *J* = 7.2 Hz, 1H), 3.26 – 3.20 (m, 1H), 2.93 – 2.87 (m, 1H), 2.30 – 2.24 (m, 1H), 1.86 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 151.1, 140.6, 136.6, 135.5, 134.0, 131.7, 130.3, 129.9, 129.3, 128.4, 127.3, 125.6, 124.0, 58.7, 36.0, 26.0, 21.1, 20.8. HRMS (ESI+) Calcd. For C$_{23}$H$_{23}$N$_2$O ([M+H]$^+$): 343.1805, found: 343.1798. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 7.13 and 10.43 min.
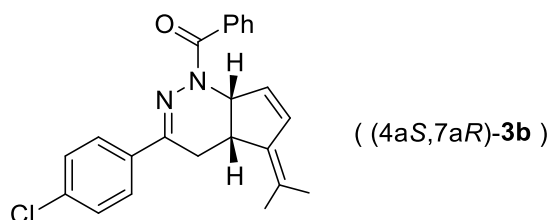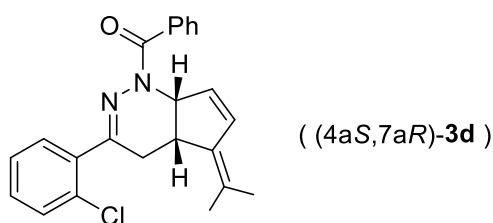

((4a*S*,7a*R*)-**3b**)

(4a*S*,7a*R*)-(3-(4-chlorophenyl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 2): Yield (80%); white solid; m.p. = 138 °C; $[\alpha]^{20}_D$ = -612.5 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.70 (m, 2H), 7.50 – 7.39 (m, 5H), 7.29 – 7.26 (m, 2H), 6.51 – 6.49 (m, 1H), 6.19 (d, *J* = 5.6 Hz, 1H), 5.52 (d, *J* = 7.6 Hz, 1H), 3.24 – 3.18 (m, 1H), 2.89 – 2.83 (m, 1H), 2.25 – 2.18 (m, 1H), 1.86 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 149.3, 140.5, 135.4, 135.2, 135.1, 134.0, 131.6, 130.4, 129.9, 128.6, 127.3, 126.8, 124.1, 58.5, 35.7, 25.8, 21.2, 20.8. HRMS (ESI+) Calcd. For C$_{23}$H$_{22}$ClN$_2$O ([M+H]$^+$): 377.1415, found: 377.1407. The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 6.31 and 9.27 min.

((4aS,7aR)-**3c**)

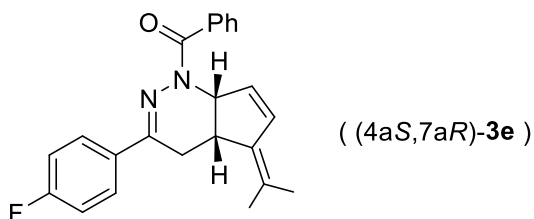**(4aS,7aR)-(3-(3-chlorophenyl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 3):** Yield (89%); white solid; m.p. = 122 °C; $[\alpha]^{20}_D$ = -148.9 (c 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.72 (m, 2H), 7.54-7.41 (m, 5H), 7.26 – 7.23 (m, 2H), 6.51 – 6.49 (m, 1H), 6.20 (d, J = 5.2 Hz, 1H), 5.52 (d, J = 8.0 Hz, 1H), 3.23- 3.17 (m, 1H), 2.89 – 2.83 (m, 1H), 2.23 – 2.16 (m, 1H), 1.87 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 148.7, 140.4, 138.5, 135.3, 134.5, 134.1, 131.6, 130.4, 129.9, 129.7, 129.1, 127.4, 125.8, 124.2, 123.6, 58.4, 35.5, 25.8, 21.2, 20.8. HRMS (ESI+) Calcd. For C$_{23}$H$_{22}$ClN$_2$O ([M+H]$^+$): 377.1415, found: 377.1400. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AS-H, i-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 6.34 and 8.90 min.

((4aS,7aR)-**3d**)

(4aS,7aR)-(3-(2-chlorophenyl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 4): Yield (93%); white solid; m.p. = 132 °C; $[\alpha]^{20}_D$ = -377.8 (c 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.72 (m, 2H), 7.42 – 7.35 (m, 4H), 7.29 – 7.22 (m, 3H), 6.54- 6.52 (m, 1H), 6.25 (d, J = 5.6 Hz, 1H), 5.49 (d, J = 7.6 Hz, 1H), 3.34 – 3.28 (m, 1H), 2.92 – 2.87 (m, 1H), 2.24 – 2.17 (m, 1H), 1.80 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.4, 154.5, 140.2, 137.4, 135.4, 133.8, 132.4, 131.8, 130.5, 130.02, 129.95, 129.9, 127.4, 127.0, 124.2, 59.9, 36.9, 30.4, 21.0, 20.9. HRMS (ESI+) Calcd. For C$_{23}$H$_{22}$ClN$_2$O ([M+H]$^+$): 377.1415, found: 377.1407. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak AS-H, i-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 7.28 and 10.22 min.
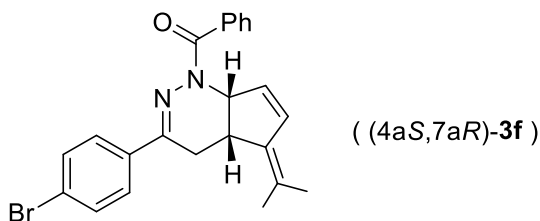
((4aS,7aR)-**3e**)

(4aS,7aR)-(3-(4-fluorophenyl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 5): Yield (93%); white solid; m.p. = 124 °C; $[\alpha]^{20}_{D}$ = -654.8 (c 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.72 (m, 2H), 7.58 – 7.41 (m, 5H), 7.03-6.98 (m, 2H), 6.52 – 6.50 (m, 1H), 6.20 (d, J = 5.2 Hz, 1H), 5.55 – 5.53 (m, 1H), 3.27 – 3.21 (m, 1H), 2.90 – 2.84 (m, 1H), 2.29 – 2.22 (m, 1H), 1.87 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.6, 164.7, 162.2, 149.9, 140.5, 135.5, 134.0, 132.79, 132.76, 131.7, 129.8, 127.5, 127.4, 127.3, 124.0, 115.5, 115.3, 58.5, 35.9, 26.0, 21.1, 20.8. HRMS (ESI+) Calcd. For C$_{23}$H$_{22}$FN$_2$O ([M+H]$^+$): 361.1711, found: 361.1708. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak AS-H, i-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 6.68 and 10.26 min.
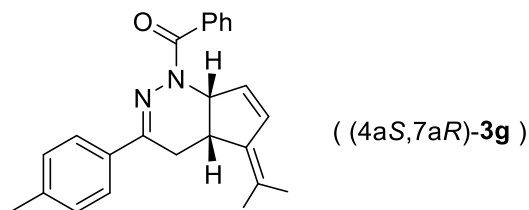

((4aS,7aR)-**3f**)

(4aS,7aR)-(3-(4-bromophenyl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 6): Yield (73%); white solid; m.p. = 151 °C; $[\alpha]^{20}_{D}$ = -539.2 (c 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 – 7.70 (m, 2H), 7.46 – 7.38 (m, 7H), 6.51 – 6.49 (m, 1H), 6.19 (d, J = 5.2 Hz, 1H), 5.51 (d, J = 7.6 Hz, 1H), 3.23 – 3.18 (m, 1H), 2.88 – 2.83 (m, 1H), 2.24 – 2.18 (m, 1H), 1.86 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 149.3, 140.5, 135.5, 135.4, 134.0, 131.62, 131.58, 130.4, 129.9, 127.4, 127.1, 124.1, 123.6, 58.5, 35.6, 25.7, 21.2, 20.8. HRMS (ESI+) Calcd. For C$_{23}$H$_{22}$BrN$_2$O ([M+H]$^+$): 421.0910, found: 421.0910. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak AS-H, i-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 6.65 and 9.20 min

((4a*S*,7a*R*)-**3g**)

(4a*S*,7a*R*)-phenyl(5-(propan-2-ylidene)-3-(p-tolyl)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)methanone (table 2, entry 7): Yield (80%); white solid; m.p. = 137 °C; $[\alpha]^{20}_D$ = -687.9 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.72 (m, 2H), 7.48 – 7.38 (m, 5H), 7.13 (m, 2H), 6.51 – 6.49 (m, 1H), 6.19 (d, *J* = 5.2 Hz, 1H), 5.54 (d, *J* = 7.6 Hz, 1H), 3.27 – 3.21 (m, 1H), 2.90 – 2.85 (m, 1H), 2.34 (s, 3H), 2.30 – 2.24 (m, 1H), 1.86 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.6, 151.5, 140.7, 139.5, 135.6, 134.0, 133.8, 131.8, 130.3, 130.0, 129.2, 127.3, 125.6, 123.9, 58.8, 36.2, 26.1, 21.2, 21.1, 20.8. HRMS (ESI+) Calcd. For C$_{24}$H$_{25}$N$_2$O ([M+H]$^+$): 357.1961, found: 357.1965. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 6.77 and 8.52 min.
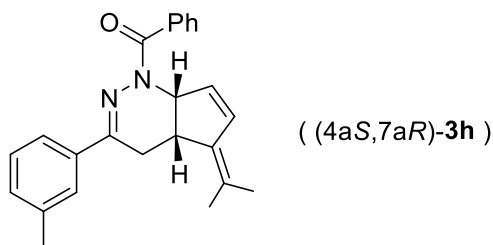

((4a*S*,7a*R*)-**3h**)

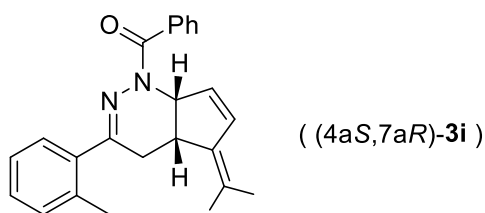**(4a*S*,7a*R*)-phenyl(5-(propan-2-ylidene)-3-(m-tolyl)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)methanone (table 2, entry 8):** Yield (73%); white solid; m.p. = 90 °C; $[\alpha]^{20}_D$ = -236.1 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.74 (m, 2H), 7.45 – 7.36 (m, 5H), 7.21 – 7.15 (m, 2H), 6.51 – 6.49 (m, 1H), 6.19 (d, *J* = 5.2 Hz, 1H), 5.54 (d, *J* = 7.6 Hz, 1H), 3.26 – 3.20 (m, 1H), 2.91 – 2.85 (m, 1H), 2.31 (s, 3H), 2.30 – 2.23 (m, 1H), 1.86 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.6, 151.3, 140.6, 138.0, 136.5, 135.5, 134.0, 131.7, 130.3, 130.05, 135.00, 128.3, 127.2, 126.3, 123.9, 122.8, 58.7, 36.1, 26.1, 21.4, 21.1, 20.8. HRMS (ESI+) Calcd. For C$_{24}$H$_{25}$N$_2$O ([M+H]$^+$): 357.1961, found: 357.1960. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 5.95 and 7.86 min.
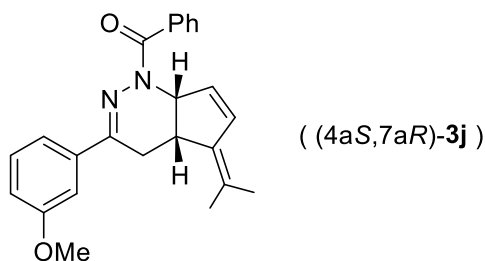
((4a*S*,7a*R*)-**3i**)

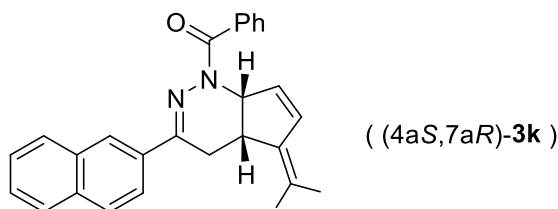**(4a*S*,7a*R*)-phenyl(5-(propan-2-ylidene)-3-(o-tolyl)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)methanone (table 2, entry 9):** Yield (75%); white solid; m.p. = 128 °C; $[\alpha]^{20}_D$ = -552.0 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 – 7.64 (m, 2H), 7.39 – 7.34 (m, 3H), 7.20 – 7.13 (m, 4H), 6.55 – 6.54 (m, 1H), 6.17 (d, *J* = 5.2Hz, 1H), 5.61 (d, *J* = 7.6 Hz, 1H), 3.39 – 3.34 (m, 1H), 2.72 – 2.66 (m, 1H), 2.37 – 2.31 (m, 1H), 2.18 (s, 3H), 1.81 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.4, 157.0, 140.5, 137.5, 135.9, 135.8, 133.8, 132.3, 130.9, 130.1, 129.4, 128.5, 128.0, 127.4, 125.7, 124.1, 59.0, 37.6, 30.5, 21.0, 20.8, 20.7. HRMS (ESI+) Calcd. For C$_{24}$H$_{25}$N$_2$O ([M+H]$^+$): 357.1961, found: 357.1951. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 6.98 and 17.65 min.

((4a*S*,7a*R*)-**3j**)

(4a*S*,7a*R*)-(3-(3-methoxyphenyl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 10): Yield (82%); white solid; m.p. = 138 °C; $[\alpha]^{20}_D$ = -660.0 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.73 (m, 2H), 7.44 – 7.39 (m, 3H), 7.23 – 7.21 (m, 1H), 7.15 – 7.13 (m, 2H), 6.89 – 6.88 (m, 1H), 6.51 – 6.49 (m, 1H), 6.20 (d, *J* = 5.2 Hz, 1H), 5.51 (d, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 3.23 – 3.17 (m, 1H), 2.92 – 2.86 (m, 1H), 2.24 - 2.18 (m, 1H), 1.86 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 159.6, 150.1, 140.5, 137.9, 135.7, 134.0, 131.6, 130.1, 129.8, 129.3, 127.2, 124.0, 118.0, 115.8, 109.9, 58.5, 55.0, 35.7, 25.8, 21.1, 20.8. HRMS (ESI+) Calcd. For C$_{24}$H$_{25}$N$_2$O$_2$ ([M+H]$^+$): 373.1911, found: 373.1905. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee

(Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.64 and 10.34 min.

((4a*S*,7a*R*)-**3k**)

(4a*S*,7a*R*)-(3-(naphthalen-2-yl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone (table 2, entry 11): Yield (59%); white solid; m.p. = 130 °C; $[α]^{20}_D$ = -618.6 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl3) δ 7.95 (s, 1H), 7.79 – 7.70 (m, 6H), 7.46 – 7.41 (m, 5H), 6.50 – 6.48 (m, 1H), 6.22 (d, J = 5.2 Hz, 1H), 5.53 (d, J = 7.2 Hz, 1H), 3.22 – 3.17 (m, 1H), 3.04 – 2.98 (m, 1H), 2.34 – 2.28 (m, 1H), 1.88 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 171.7, 150.3, 140.6, 134.1, 134.0, 131.6, 130.3, 130.0, 128.4, 128.1, 127.6, 127.3, 126.7, 126.3, 125.3, 124.0, 123.0, 58.7, 35.8, 25.7, 21.1, 20.8. HRMS (ESI+) Calcd. For C$_{27}$H$_{25}$N$_2$O ([M+H]$^+$): 393.1961, found: 393.1954. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak AS-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 6.69 and 9.73 min.
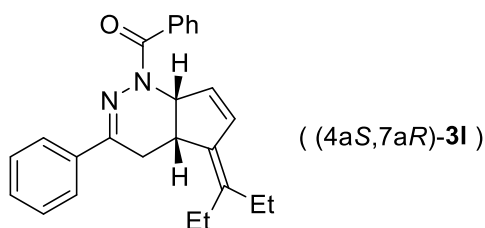

((4a*S*,7a*R*)-**3l**)

(4a*S*,7a*R*)-(5-(pentan-3-ylidene)-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone: Yield (95%); white solid; m.p. = 90 °C; $[α]^{20}_D$ = -561.8 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl3) δ 7.75 (m, 2H), 7.59 – 7.57 (m, 2H), 7.42 – 7.41 (m, 3H), 7.33 – 7.32 (m, 3H), 6.53 – 6.51 (m, 1H), 6.26 – 6.18 (m, 1H), 5.52 (d, *J* = 7.3 Hz, 1H), 3.24 – 3.18 (m, 1H), 2.92 – 2.87 (m, 1H), 2.27 – 2.20 (m, 5H), 1.12 (t, *J* = 7.5 Hz, 3H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 171.7, 150.5, 140.0, 136.6, 136.1, 135.5, 134.6, 131.5, 130.3, 130.0, 129.3, 128.4, 127.3, 125.6, 58.4, 35.3, 26.7, 25.4, 24.4, 13.9, 13.5. HRMS (ESI+) Calcd. For C$_{25}$H$_{27}$N$_2$O ([M+H]$^+$): 371.2118, found: 371.2116. The product was analyzed by HPLC to determine the enantiomeric excess:

97% ee (Chiralpak IE-H, *i*-propanol /hexane = 4/96, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.32 and 8.03 min.
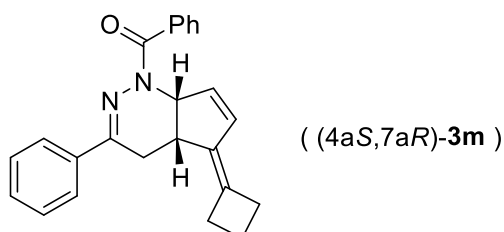

((4a*S*,7a*R*)-**3m**)

(4a*S*,7a*R*)-(5-cyclobutylidene-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone: Yield (87%); white solid; m.p. = 120 °C; $[\alpha]^{20}_D$ = -650.3 (*c* 0.23, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.71 (m, 2H), 7.59 – 7.57 (m, 2H), 7.39 – 7.31 (m, 6H), 6.22 – 6.21 (m, 1H), 6.12 (d, *J* = 5.6 Hz, 1H), 5.60 (d, *J* = 8 Hz, 1H), 3.30 – 3.29 (m, 1H), 2.76 – 2.74 (m, 1H), 2.72 – 2.70 (m, 4H), 2.57 – 2.50 (m, 1H), 2.10 – 2.06 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 171.4, 153.8, 137.3, 136.3, 135.4, 132.9, 132.6, 131.8, 130.3, 129.8, 129.4, 128.4, 127.2, 125.6, 59.3, 36.5, 30.1, 29.7, 25.7, 17.5. HRMS (ESI+) Calcd. For $C_{24}H_{23}N_2O$ ([M+H]⁺): 355.1805, found: 355.1797. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IC-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 16.71 and 17.38 min.

((4a*S*,7a*R*)-**3n**)

(4a*S*,7a*R*)-(5-cyclopentylidene-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone: Yield (73%); white solid; m.p. = 122 °C; $[\alpha]^{20}_D$ = -289.7 (*c* 0.23, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 2H), 7.58 – 7.56 (m, 2H), 7.41 – 7.39 (m, 3H), 7.32 – 7.30 (m, 3H), 6.36 – 6.34 (m, 1H), 6.16 (d, *J* = 5.2 Hz, 1H), 5.56 (d, *J* = 7.6 Hz, 1H), 3.19 – 3.13 (m, 1H), 2.92 – 2.86 (m, 1H), 2.39 – 2.32 (m, 5H), 1.74 – 1.70 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 171.6, 152.2, 136.8, 136.5, 135.4, 135.3, 133.03, 132.97, 130.3, 129.9, 129.9, 129.3, 128.4, 127.3, 125.6, 59.1, 37.3, 31.0, 30.8, 26.6, 26.4, 25.1. HRMS (ESI+) Calcd. For $C_{25}H_{25}N_2O$ ([M+H]⁺): 369.1961, found: 369.1959. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak IC-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 16.83 and 18.44
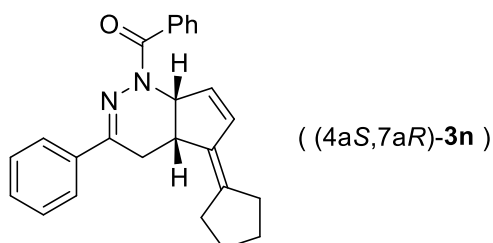
min.

((4a*S*,7a*R*)-**3o**)

(4a*S*,7a*R*)-(5-cyclohexylidene-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone: Yield (92%); white solid; m.p. = 110 °C; $[\alpha]^{20}_D$ = -596.4 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.74 (m, 2H), 7.57 – 7.56 (m, 2H), 7.41 – 7.39 (m, 3H), 7.32 – 7.30 (m, 3H), 6.54 – 6.52 (m, 1H), 6.20 (d, *J* = 5.2 Hz, 1H), 5.55 – 5.52 (m, 1H), 3.28 – 3.22 (m, 1H), 2.82 – 2.81 (m, 1H), 2.30 – 2.25 (m, 5H), 1.61 (d, *J* = 14.8 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.6, 151.0, 137.7, 136.4, 135.4, 134.1, 132.5, 131.1, 130.2, 129.9, 129.2, 128.3, 127.2, 125.5, 58.5, 35.3, 31.8, 31.3, 28.1, 27.9, 26.7, 26.5. HRMS (ESI+) Calcd. For C$_{26}$H$_{27}$N$_2$O ([M+H]$^+$): 383.2118, found: 383.2115. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak IC-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t$_r$ = 16.52 and 18.15 min.
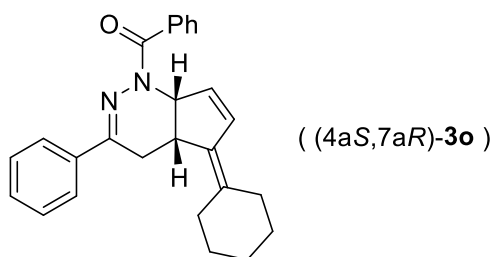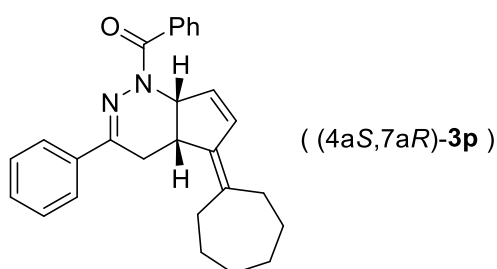

((4a*S*,7a*R*)-**3p**)

(4a*S*,7a*R*)-(5-cycloheptylidene-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone: Yield (89%); white solid; m.p. = 125 °C; $[\alpha]^{20}_D$ = -582.3 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.74 (m, 2H), 7.59 – 7.57 (m, 2H), 7.42 – 7.41 (m, 3H), 7.33 – 7.32 (m, 3H), 6.53 (dd, *J* = 6.0, 2.4 Hz, 1H), 6.23 – 6.22 (m, 1H), 5.51 (d, *J* = 7.6 Hz, 1H), 3.23 – 3.17 (m, 1H), 2.92 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.42 – 2.40 (m, 4H), 2.23 (dd, *J* = 16.0, 9.2 Hz, 1H), 1.72 – 1.64 (m, 3H), 1.57 – 1.55 (m, 5H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 150.6, 140.5, 136.6, 135.5, 134.1, 133.9, 131.5, 130.3, 129.9, 129.3, 128.4, 127.3, 125.6, 58.5, 35.5, 32.9, 32.1, 29.7, 28.9,

28.1, 27.9, 26.1. HRMS (ESI+) Calcd. For $C_{27}H_{29}N_2O$ ([M+H]$^+$): 397.2274, found: 397.2265. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 13.90 and 14.48 min.

((4a*S*,7a*R*)-**3q**)

(4a*S*,7a*R*)-phenyl(3-phenyl-5-(tetrahydro-4H-pyran-4-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)methanone: Yield (72%); white solid; m.p. = 118 °C; $[\alpha]^{30}_D$ = -293.6 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.74 (m, 2H), 7.58 – 7.56 (m, 2H), 7.49 – 7.39 (m, 3H), 7.35 – 7.32 (m, 3H), 6.51 (dd, *J* = 5.6, 2.0 Hz, 1H), 6.28 (d, *J* = 5.2 Hz, 1H), 5.57 (d, *J* = 7.6 Hz, 1H), 3.87 – 3.67 (m, 4H), 3.32 – 3.27 (m, 1H), 2.84 (dd, *J* = 16.0, 6.4 Hz, 1H), 2.45 – 2.43 (m, 4H), 2.31 (dd, *J* = 16.0, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.7, 150.9, 139.7, 136.4, 135.6, 135.4, 130.6, 130.4, 130.0, 129.4, 128.5, 127.4, 126.7, 125.6, 68.9, 68.7, 58.4, 35.4, 32.2, 31.8, 26.7. HRMS (ESI+) Calcd. For $C_{25}H_{25}N_2O_2$ ([M+H]$^+$): 385.1911, found: 385.1900. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE-H, *i*-propanol /hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.86 and 22.82 min.
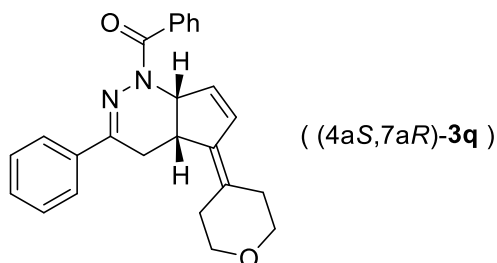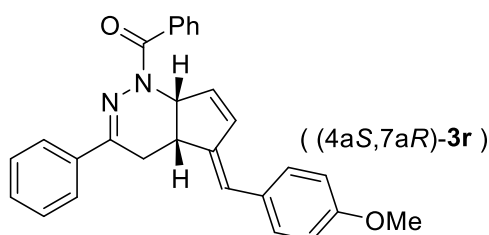

((4a*S*,7a*R*)-**3r**)

(4a*S*,7a*R*)-(E)-(5-(4-methoxybenzylidene)-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone(*Z/E* = 0.7 : 1): Yield (79%); white solid; m.p. = 158 °C; $[\alpha]^{30}_D$ = -796.4 (*c* 0.23, CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.60 (m, 5.1H), 7.43 – 7.24 (m, 15.3H), 6.96 – 6.86 (m, 4.1H), 6.48 – 6.26 (m, 4.4H), 5.82 (d, *J* = 7.6 Hz, 1H), 5.68 (d, *J* = 7.6 Hz, 0.7H), 3.98 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 2.1H), 3.46 (q, *J* = 6.8 Hz, 0.7H), 2.95 – 2.60 (m, 3.4H). 13C NMR (101 MHz, CDCl3) δ 171.5, 158.47, 158.45, 154.6, 153.4, 146.3, 146.1,

138.9, 138.1, 136.2, 136.1, 135.3, 134.3, 131.9, 130.55, 130.49, 130.1, 130.0, 129.6, 129.5, 129.4, 129.2, 128.5, 128.4, 127.4, 125.8, 121.9, 120.5, 114.2, 113.9, 60.3, 58.5, 55.3, 40.2, 37.2, 28.4, 25.0. HRMS (ESI+) Calcd. For $C_{28}H_{25}N_2O_2$ ([M+H]$^+$): 421.1911, found: 421.1901. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak AS-H, i-propanol /hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm); t_r = 11.55, 14.16, 17.50, 22.49 min.
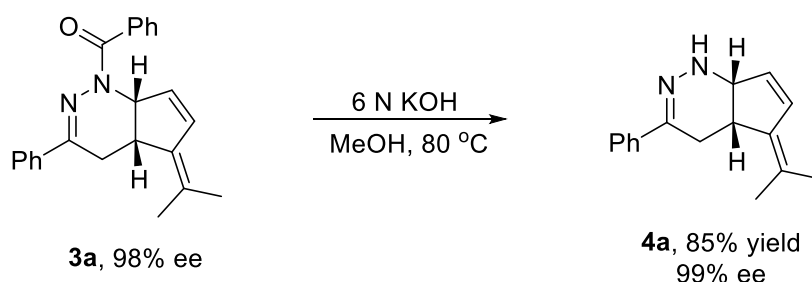
3 Synthetic Transformations

3a, 98% ee → 6 N KOH, MeOH, 80 °C → **4a**, 85% yield, 99% ee

To methanol (10 mL) was added **3a** (0.3 mmol) and KOH (6 mmol), and the reaction mixture was heated to 80 °C until the starting material was consumed (monitored by TLC). Then, the reaction mixture was neutralized by 1 N HCl and extracted by DCM, the combined organic solvent was dried with Na_2SO_4 and was concentrated in vacuum. The residue was purified by column chromatography to give the product, which was then directly analyzed by HPLC to determine the enantiomeric excess.

3a, 98% ee → Pd(OAc)$_2$ (0.5 mol%), CH$_2$N$_2$/Et$_2$O → **5a**, 99% yield, >20:1 d.r, 99% ee
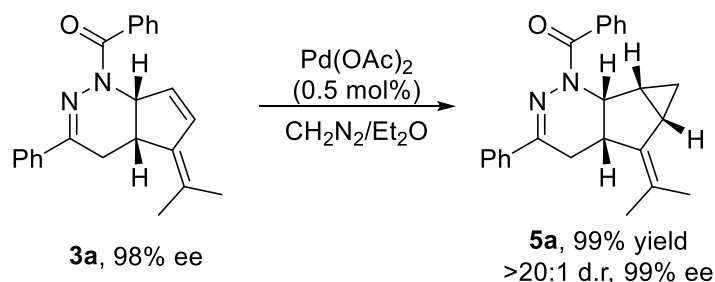
3a (0.3 mmol) was added to a dry solution of diazomethame (prepare from 100 mg N-methyl-N-nitrosourea, 1 mL ethyl ether) at 0 °C. Then catalytic amount of Pd(OAc)$_2$ was added in one portion and gas evolution was observed. After 1 h vigorous stirring at 0 °C, the organic solvent was concentrated in vacuum. The residue was purified by column chromatography to give the product,

which was then directly analyzed by HPLC to determine the enantiomeric excess.
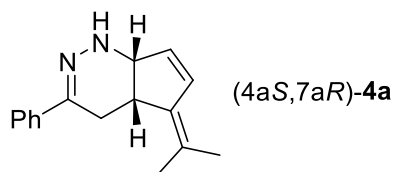
(4aS,7aR)-**4a**

(4aR,7aR)-3-phenyl-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazine:

Yield (85%); brown solid; m.p. = 21 °C; $[\alpha]^{30}_D$ = -198.0 (c 0.23, CH₂Cl₂); ^{1}H NMR (400 MHz, CDCl₃) δ 7.67 – 7.56 (m, 2H), 7.39 – 7.30 (m, 3H), 6.49 (dd, J = 5.6, 1.2 Hz, 1H), 5.73 (d, J = 4.8 Hz, 1H), 4.46 (d, J = 8.4 Hz, 1H), 3.32 – 3.27 (m, 1H), 2.80 (dd, J = 14.0, 6.4 Hz, 1H), 2.36 (dd, J = 14.0, 6.8 Hz, 1H), 1.84 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl₃) δ 155.1, 141.5, 137.8, 134.0, 133.4, 128.4, 128.3, 125.1, 123.3, 61.9, 40.3, 27.3, 21.00, 20.9. HRMS (ESI+) Calcd. For C₁₆H₁₉N₂ ([M+H]⁺): 239.1543, found: 239.1543. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak AD-H, i-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.95, 10.37 min.
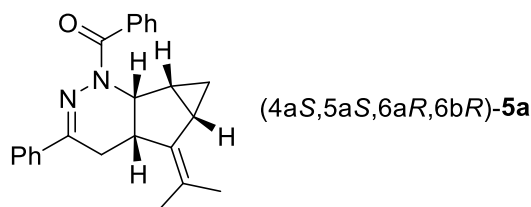

(4aS,5aS,6aR,6bR)-**5a**

phenyl((4aS,5aS,6aR,6bR)-3-phenyl-5-(propan-2-ylidene)-4a,5,5a,6,6a,6b-

hexahydrocyclopropa[4,5]cyclopenta[1,2-c]pyridazin-1(4H)-yl)methanone: Yield (99%); white

solid; m.p. = 42 °C; $[\alpha]^{30}_D$ = -88.0 (c 0.23, CH₂Cl₂); ^{1}H NMR (400 MHz, CDCl₃) δ 7.82 – 7.73 (m, 2H), 7.56 – 7.54 (m, 2H), 7.46 – 7.42 (m, 3H), 7.35 – 7.27 (m, 3H), 4.99 (dd, J = 9.2, 5.2 Hz, 1H), 3.16 – 2.94 (m, 2H), 2.57 – 2.43 (m, 1H), 2.13 – 2.05 (m, 1H), 2.03 – 1.93 (m, 1H), 1.86 (s, 3H), 1.77 (s, 3H), 0.73 – 0.68 (m, 1H), 0.59 – 0.56 (m, 1H). ^{13}C NMR (101 MHz, CDCl₃) δ 171.8, 145.3, 137.3, 136.9, 135.8, 130.04, 129.96, 129.0, 128.4, 127.3, 125.2, 123.6, 52.5, 30.6, 26.8, 23.7, 21.2, 20.7, 20.3, 11.1. HRMS (ESI+) Calcd. For C₂₄H₂₄N₂NaO ([M+Na]⁺): 379.1781, found: 379.1781. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak AD-H, i-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.03, 8.92 min.

4 References

1. M. C. Tong, X. Chen, J. Li, R. Huang, H. Tao, C. J. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4680.
2. S. Collins, Yaping Hong, Mark Kataoka, and Thelam Nguyen, *J. Org. Chem.* **1990**, 55, 3395-3398.

5 NMR and HPLC spectra

((4a*S*,7a*R*)-**3a**)
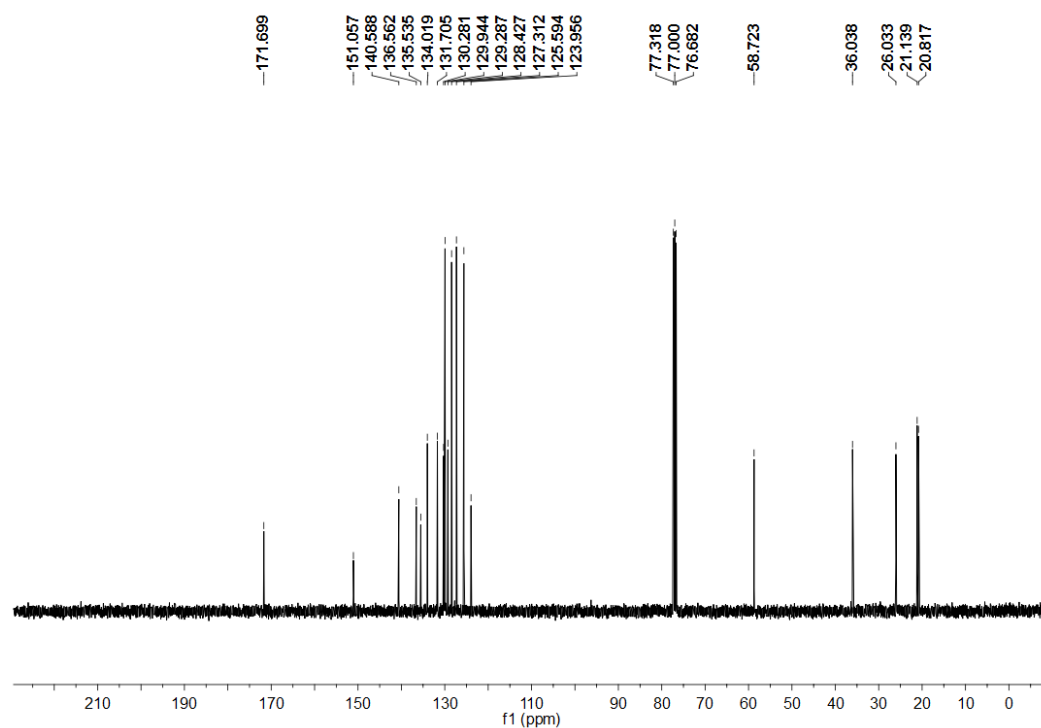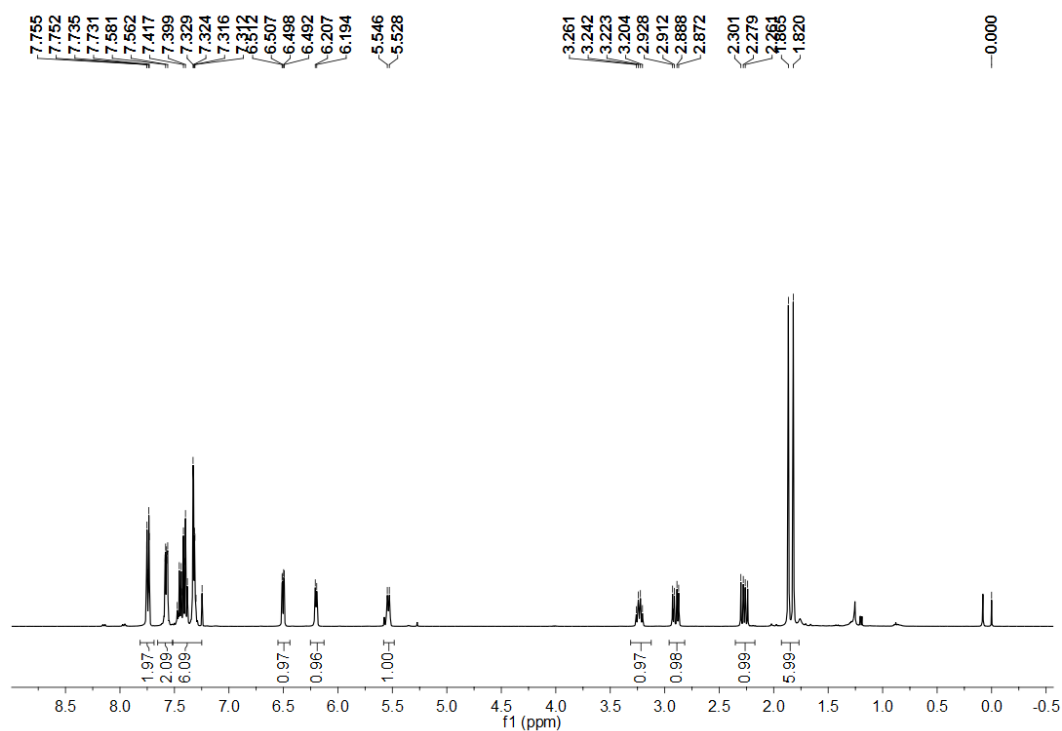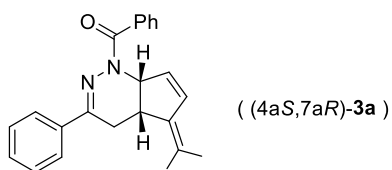
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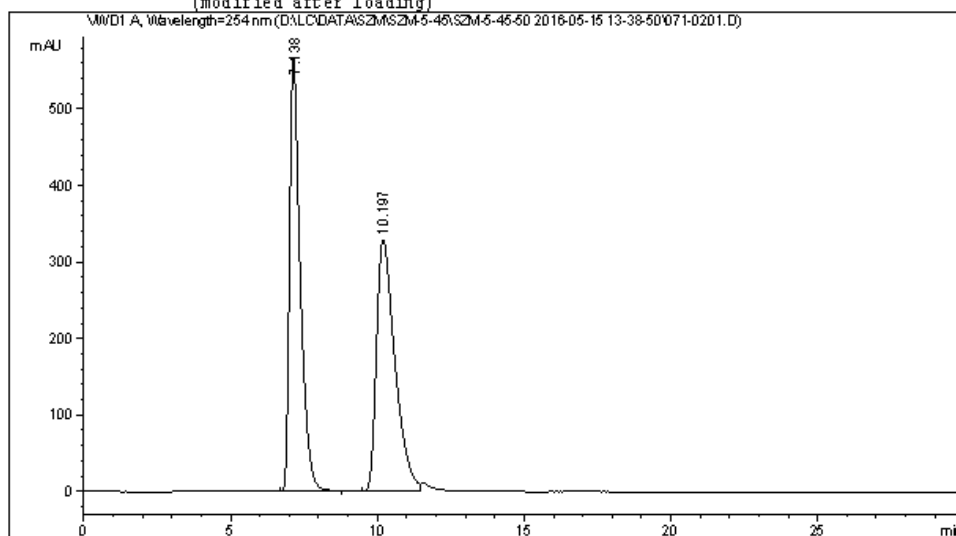

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Totals :                 2.87618e4   895.50674


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Instrument 1 5/15/2016 10:11:25 PM WZF   Page 1 of 1

S16

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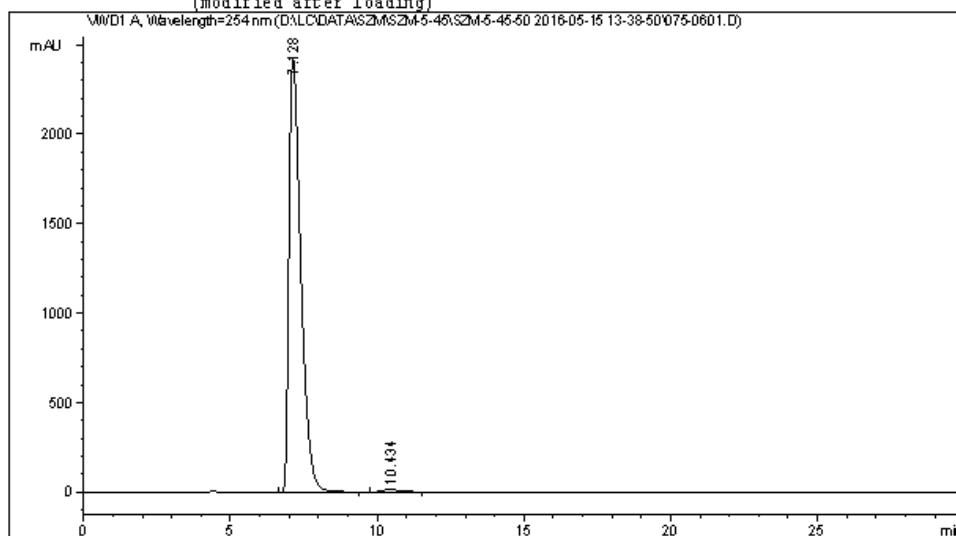

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Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Instrument 1 5/15/2016 10:14:40 PM WZF   Page 1 of 1
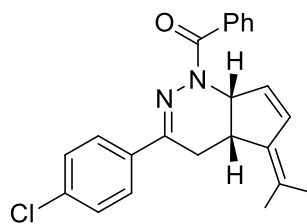
((4a*S*,7a*R*)-**3b**)
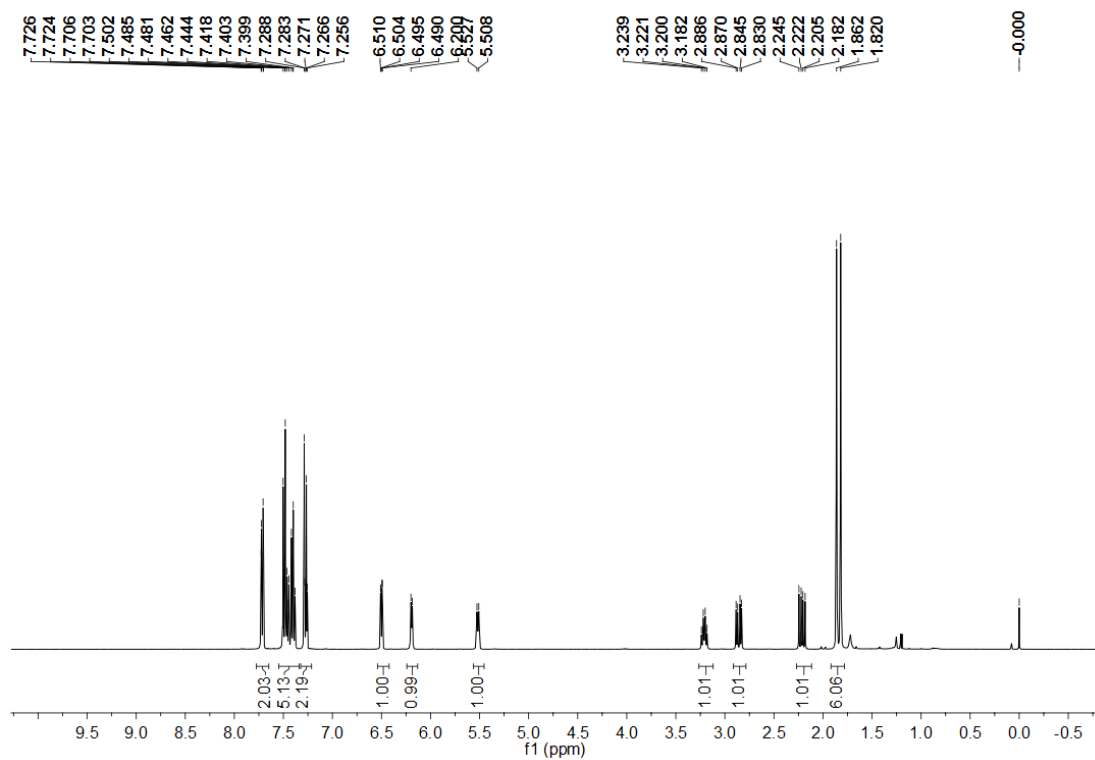
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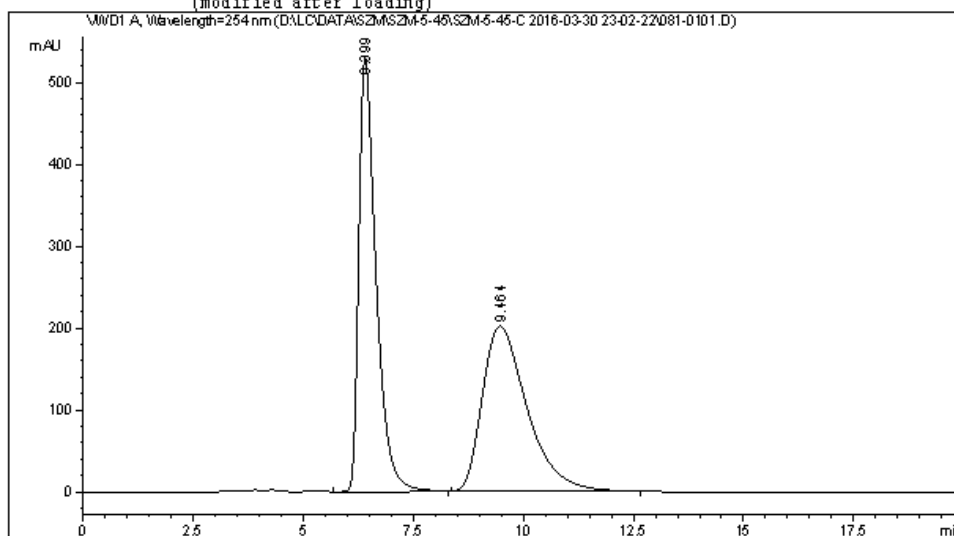


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Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
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Totals :                 2.88552e4   731.42328


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Instrument 1 5/14/2016 10:02:51 PM WZF   Page 1 of 1

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Last changed    : 5/14/2016 10:26:44 PM by WZF
                  (modified after loading)
```
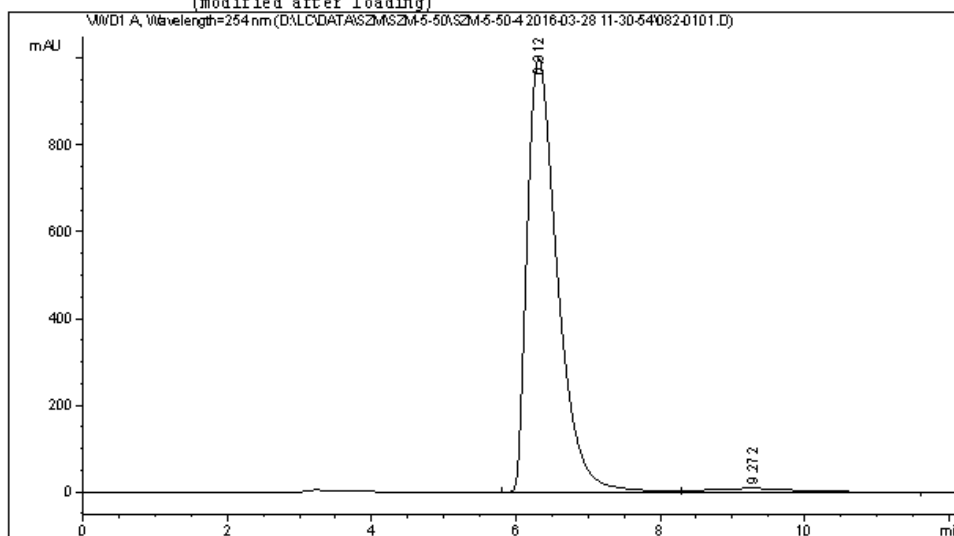

VWD1 A, Wavelength=254 nm (D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-4 2016-03-28 11-30-54\082-0101.D)

```
================================================================
                      Area Percent Report
================================================================

Sorted By             :        Signal
Multiplier            :        1.0000
Dilution              :        1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s     [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
  1   6.312 BV   0.4461 2.90942e4   998.96808   97.7392
  2   9.272 VB   0.9512  672.98792    8.50165    2.2608

Totals :                 2.97671e4  1007.46973


================================================================
```
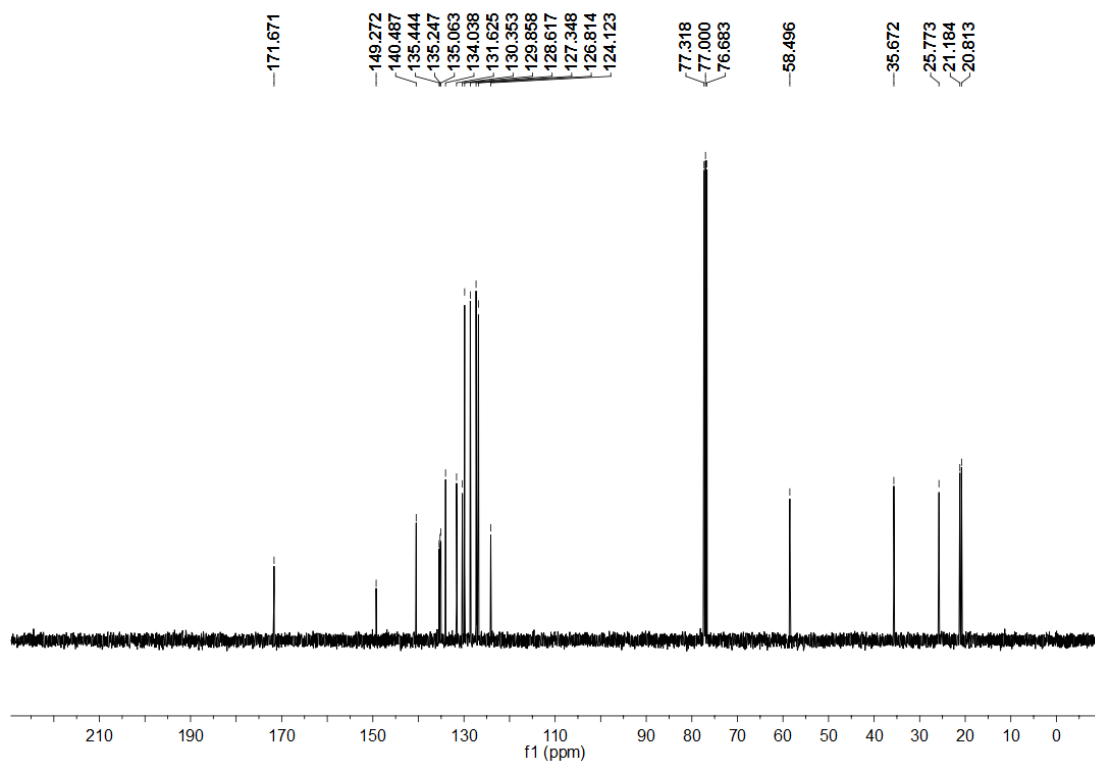
Instrument 1 5/14/2016 10:26:50 PM WZF   Page 1 of 1

((4a*S*,7a*R*)-**3c**)

7.741
7.738
7.721
7.717
7.538
7.435
7.429
7.416
7.257
7.238
7.213
6.508
6.499
6.494
6.202
6.189
5.529
5.509
3.233
3.215
3.194
3.176
2.887
2.871
2.847
2.831
2.230
2.207
2.166
1.871
1.826
0.000

2.01
5.12
2.23
0.98
0.97
1.00
0.98
0.99
1.01
5.94

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

171.698
148.669
140.447
138.481
135.314
134.529
134.062
131.586
130.445
129.895
129.659
129.117
127.372
125.763
124.233
123.615
77.318
77.000
76.682
58.446
35.490
25.769
21.227
20.814

210 190 170 150 130 110 90 70 50 40 30 20 10 0
f1 (ppm)

```
================================================================
Acq. Operator    : WZF                        Seq. Line :    4
Acq. Instrument  : Instrument 1               Location : Vial 73
Injection Date   : 5/15/2016 3:14:36 PM          Inj :    1
                                             Inj Volume : 5 µl
Acq. Method      : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-50 2016-05-15 13-38-50\ASH-20-80-1ML-
                   254NM-30MIN.M
Last changed     : 5/15/2016 1:36:20 PM by WZF
Analysis Method  : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-50 2016-05-15 13-38-50\073-0401.D\DA.M (
                   ASH-20-80-1ML-254NM-30MIN.M)
Last changed     : 5/15/2016 10:12:55 PM by WZF
                   (modified after loading)
```
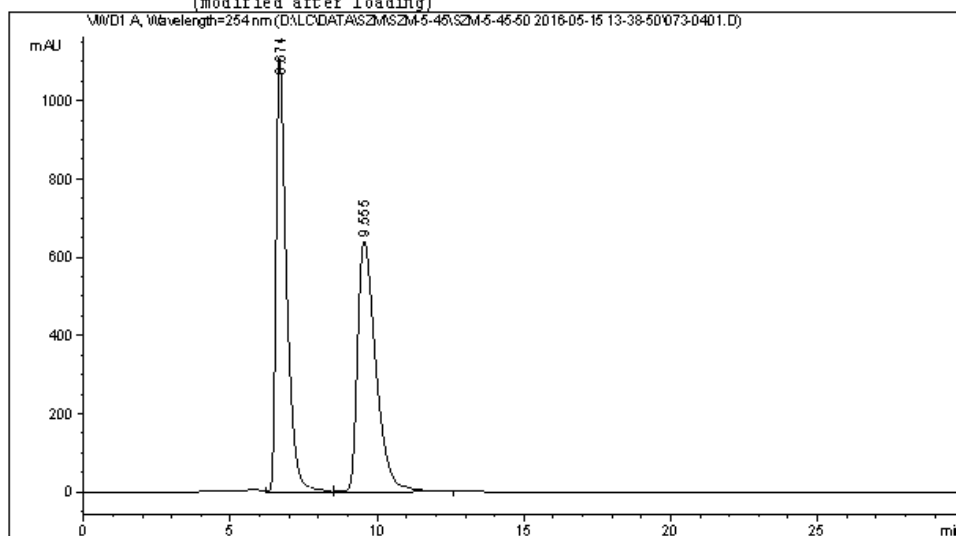


```
================================================================
                    Area Percent Report
================================================================

Sorted By            :        Signal
Multiplier           :        1.0000
Dilution             :        1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width      Area        Height       Area
  #   [min]        [min]   mAU   *s       [mAU  ]        %
----|-------|----|-------|----------|----------|--------|
  1   6.674 VV    0.3680  2.77251e4  1106.75330   49.8976
  2   9.555 VB    0.6630  2.78388e4   640.27997   50.1024

Totals :                  5.55638e4  1747.03326


================================================================
```

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-3 2016-03-28 11-05-02\081-0101.D
Sample Name: SZM-5-50-3

```
=================================================================
Acq. Operator   : LHC                          Seq. Line :   1
Acq. Instrument : Instrument 1                 Location : Vial 81
Injection Date  : 3/28/2016 11:06:37 AM              Inj :   1
                                              Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-3 2016-03-28 11-05-02\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-3 2016-03-28 11-05-02\081-0101.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:21:19 PM by WZF
                  (modified after loading)
```
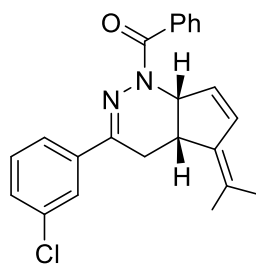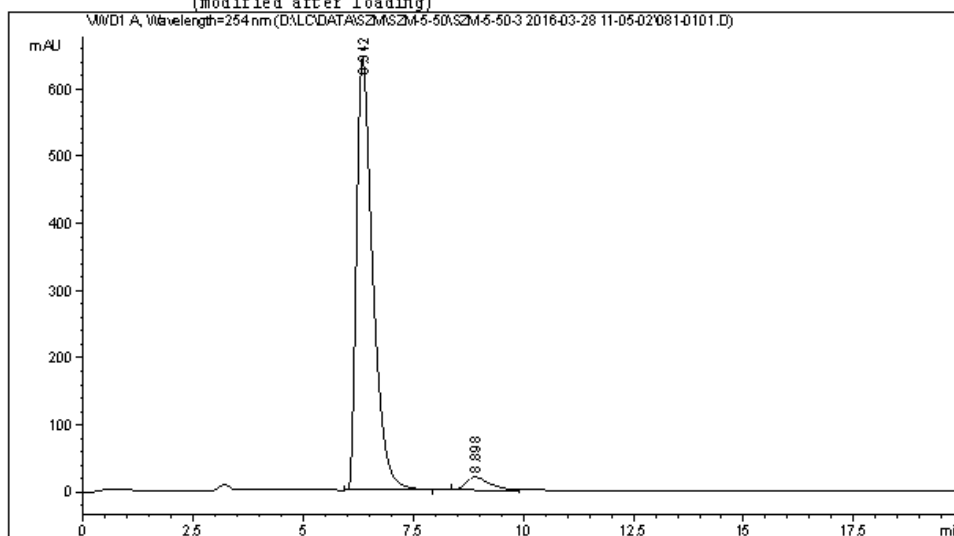


```
=================================================================
                      Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]       [min]   mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   6.342 BB   0.3871 1.65897e4   642.55939  95.7155
  2   8.898 VV   0.5656  742.60004   19.22858   4.2845

Totals :                 1.73323e4   661.78797
```

```
=================================================================
```

Instrument 1 5/14/2016 10:21:24 PM WZF   Page 1 of 1

((4a*S*,7a*R*)-**3d**)
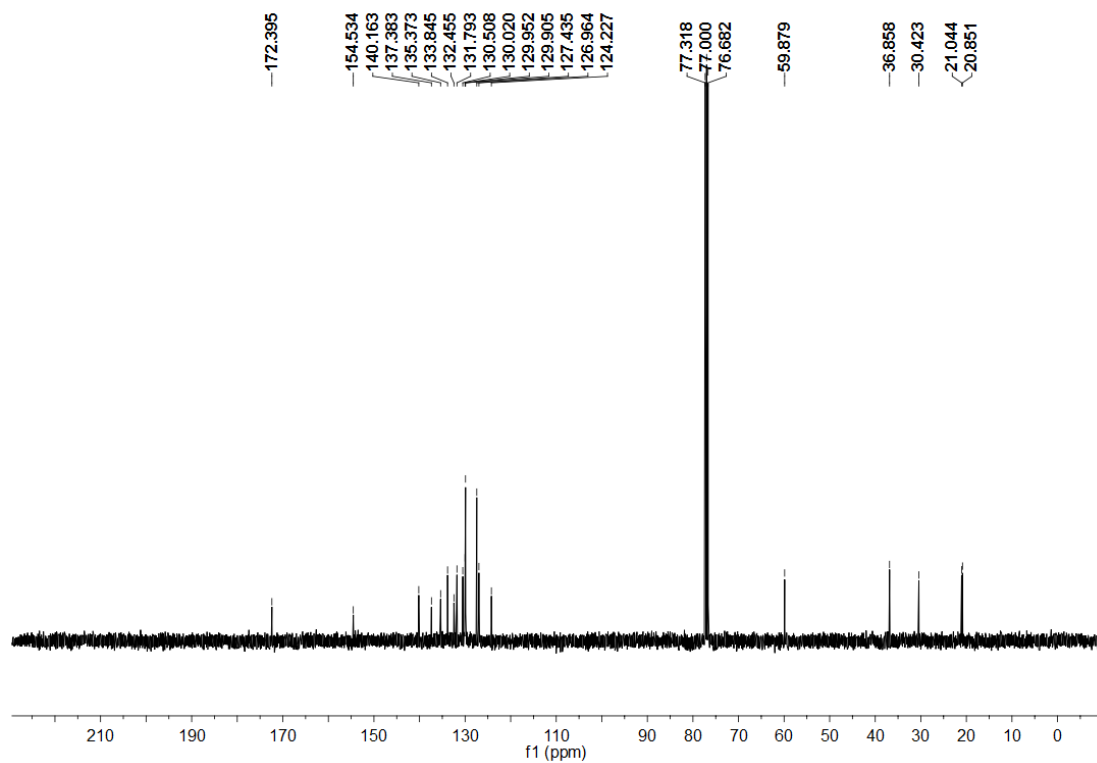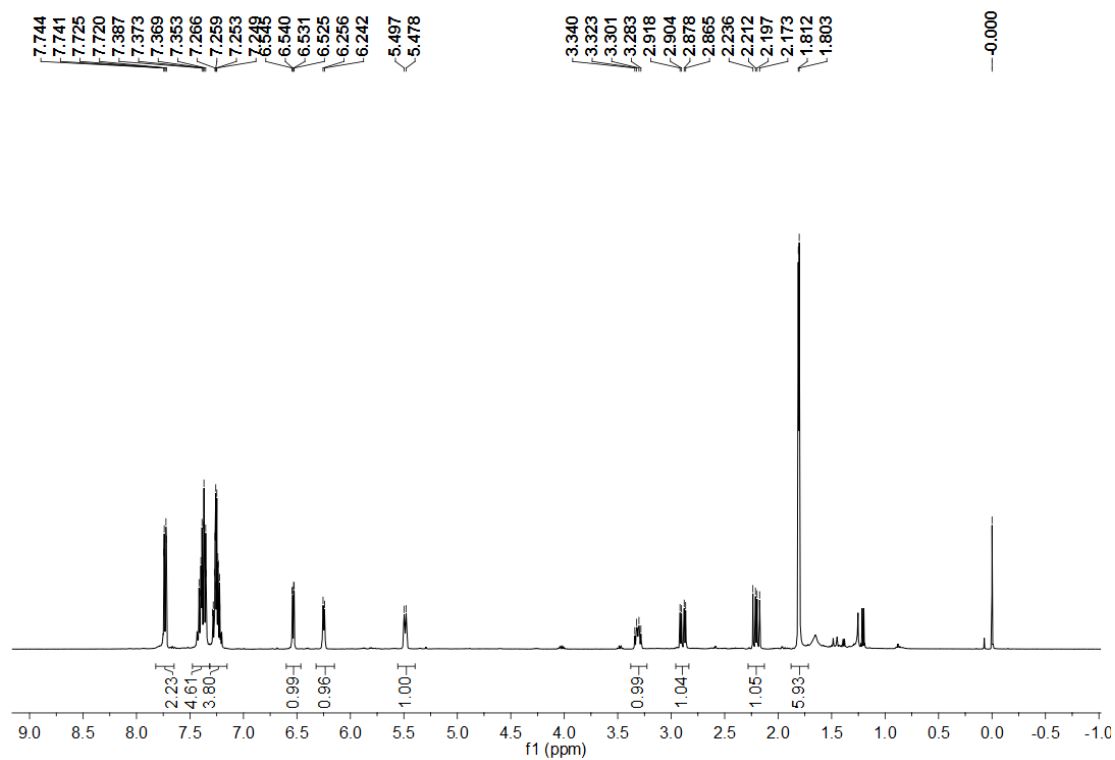
```
===================================================================
Acq. Operator     : WZF                      Seq. Line :   3
Acq. Instrument   : Instrument 1             Location : Vial 72
Injection Date    : 5/15/2016 2:43:05 PM         Inj :    1
                                          Inj Volume : 5 µl
Acq. Method       : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-50 2016-05-15 13-38-50\ASH-20-80-1ML-
                    254NM-30MIN.M
Last changed      : 5/15/2016 1:36:20 PM by WZF
Analysis Method   : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-50 2016-05-15 13-38-50\072-0301.D\DA.M (
                    ASH-20-80-1ML-254NM-30MIN.M)
Last changed      : 5/15/2016 10:12:19 PM by WZF
                    (modified after loading)
```
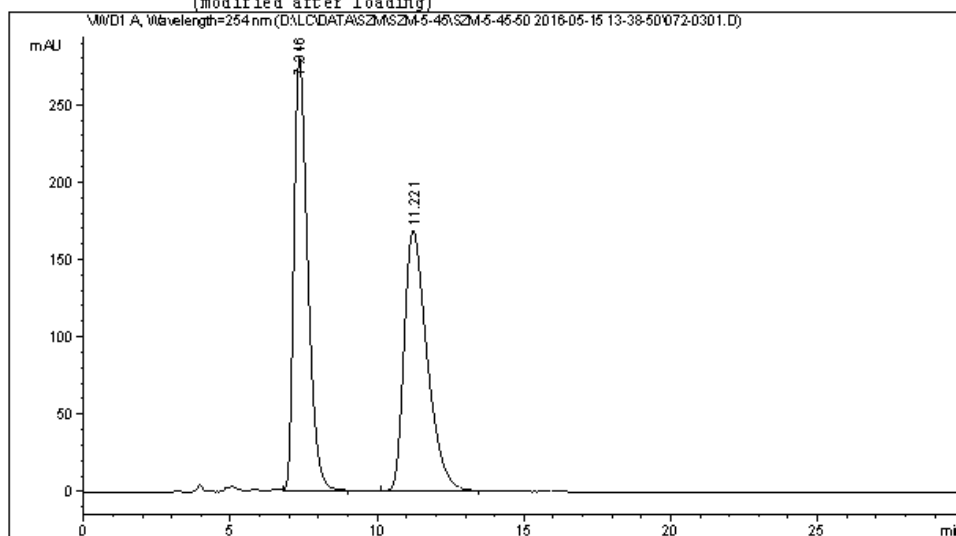


```
===================================================================
                        Area Percent Report
===================================================================

Sorted By            :       Signal
Multiplier           :       1.0000
Dilution             :       1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   7.346 VB    0.4998 9149.66797  279.53934  50.0163
  2  11.221 BB    0.8298 9143.70312  168.08777  49.9837

Totals :                  1.82934e4   447.62711


===================================================================
```

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-2 2016-03-28 17-24-20\083-0101.D
Sample Name: SZM-5-50-2

```
=================================================================
Acq. Operator   : LHC                      Seq. Line :    1
Acq. Instrument : Instrument 1             Location : Vial 83
Injection Date  : 3/28/2016 5:26:15 PM          Inj :    1
                                       Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-2 2016-03-28 17-24-20\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-2 2016-03-28 17-24-20\083-0101.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:18:07 PM by WZF
                  (modified after loading)
```
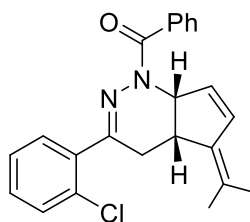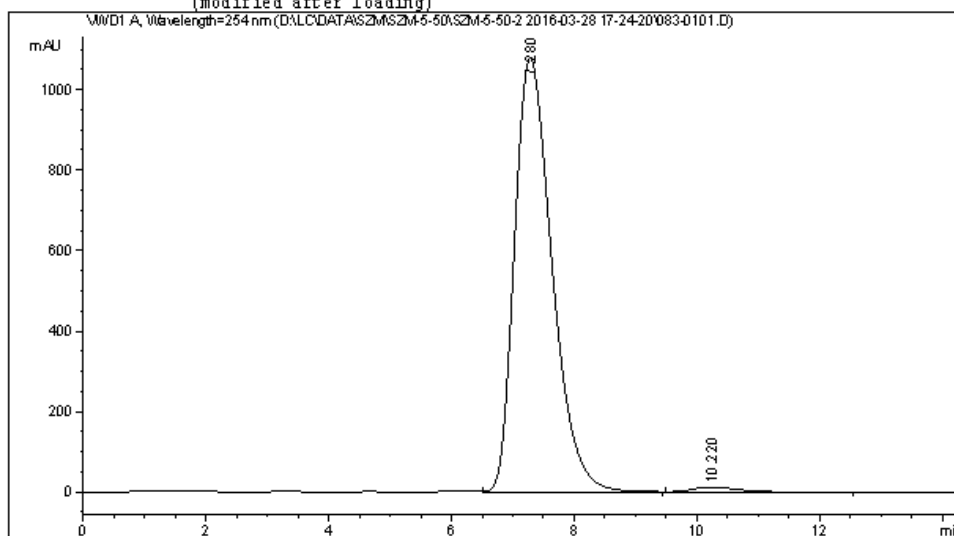


```
=================================================================
                     Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
  1   7.280 VB    0.6589 4.57762e4  1077.08020  98.5681
  2  10.220 BB    0.7376  664.98889   12.78951   1.4319

Totals :                 4.64412e4  1089.86971


=================================================================
```

Instrument 1 5/14/2016 10:18:12 PM WZF   Page 1 of 1
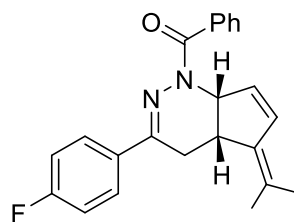
((4a*S*,7a*R*)-**3e**)
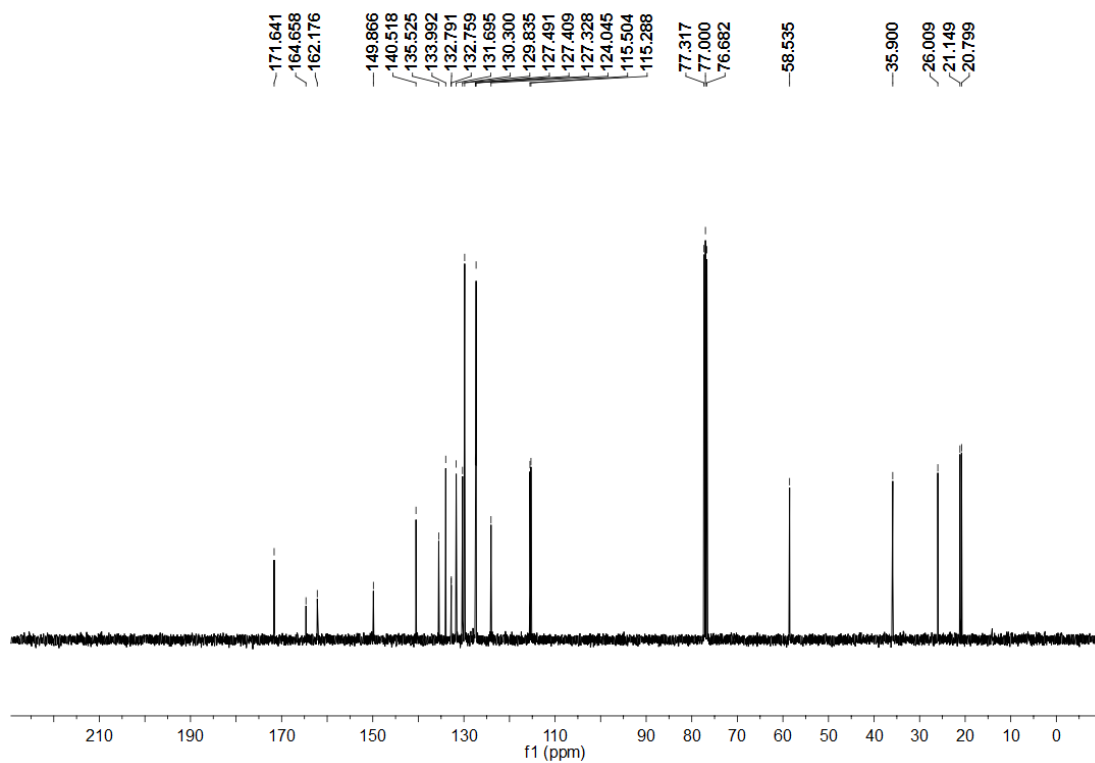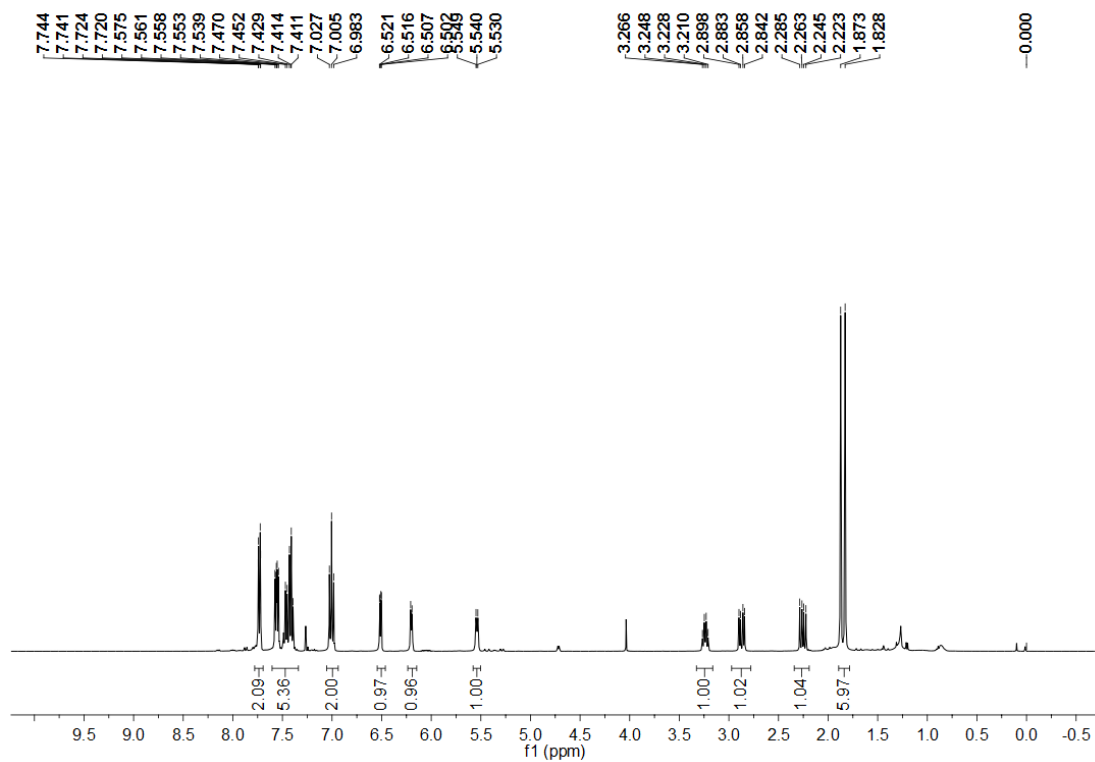
Data File D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\087-0701.D
Sample Name: SZM-5-45-J

```
========================================================================
Acq. Operator   : LHC                         Seq. Line :   7
Acq. Instrument : Instrument 1                 Location : Vial 87
Injection Date  : 3/31/2016 1:12:36 AM              Inj :   1
                                              Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\087-0701.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:14:13 PM by WZF
                  (modified after loading)
```
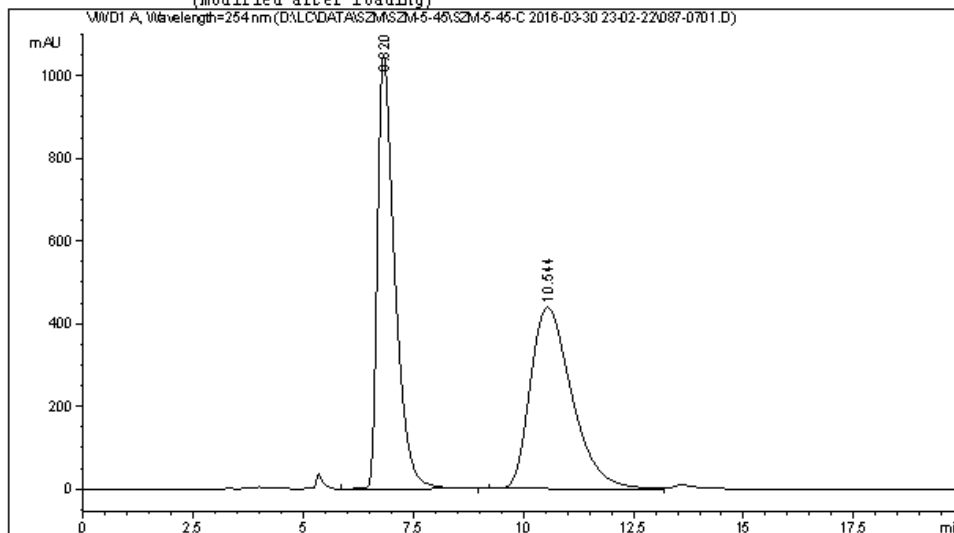


```
========================================================================
                      Area Percent Report
========================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
  1   6.820 BB    0.4071 2.87210e4  1048.05139  50.0225
  2  10.544 BB    1.0142 2.86952e4   439.14487  49.9775

Totals :                  5.74162e4  1487.19626


========================================================================
```

Instrument 1 5/14/2016 10:14:17 PM WZF   Page 1 of 1

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\083-0301.D
Sample Name: SZM-5-50-11

```
=================================================================
Acq. Operator   : LHC                        Seq. Line :   3
Acq. Instrument : Instrument 1               Location : Vial 83
Injection Date  : 3/31/2016 5:54:01 PM          Inj :   1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\083-0301.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:31:00 PM by WZF
                  (modified after loading)
```
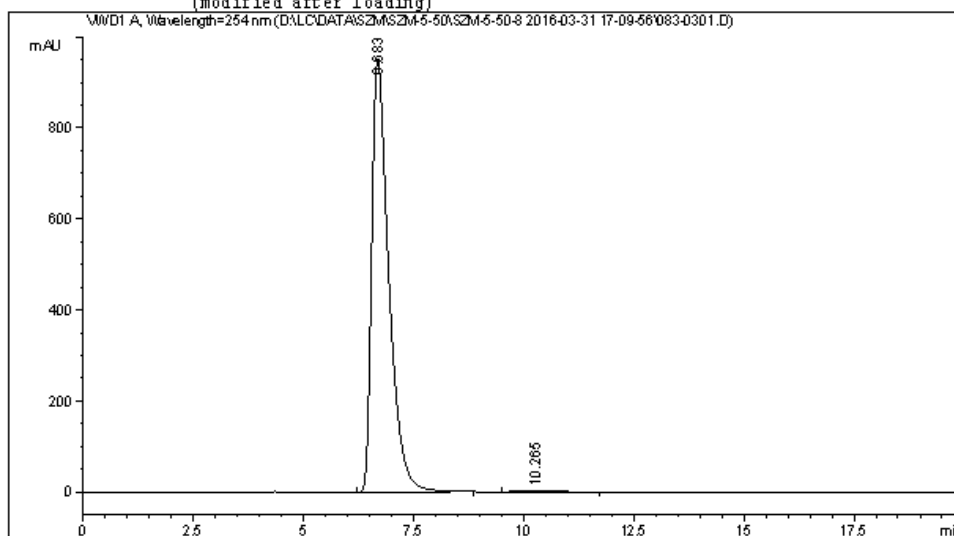


```
=================================================================
                      Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU  ]       %
----|-------|----|-------|----------|----------|--------|
  1   6.683 BB   0.3995 2.55972e4   952.40466  99.4755
  2  10.265 BB   0.6722  134.96884    2.38393   0.5245

Totals :                 2.57322e4   954.78859


=================================================================
```

Instrument 1 5/14/2016 10:31:05 PM WZF   Page 1 of 1

((4a*S*,7a*R*)-**3f**)

7.724
7.721
7.717
7.704
7.700
7.464
7.449
7.445
7.442
7.430
7.418
7.415
7.403
7.399
7.382
6.510
6.504
6.496
6.490
6.200
6.187
5.522
5.503
3.234
3.216
3.196
3.177
2.882
2.867
2.842
2.827
2.240
2.217
2.199
2.176
1.860
1.819
0.000

2.04
7.27
1.01
1.00
1.00
1.01
0.97
1.03
3.08
2.99

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

171.690
149.263
140.485
135.528
135.433
134.051
131.622
131.581
130.372
129.866
127.361
127.080
124.149
123.613
77.318
77.000
76.682
58.488
35.641
25.710
21.199
20.824

210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S30

Data File D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\085-0501.D
Sample Name: SZM-5-45-G

```
=================================================================
Acq. Operator   : LHC                        Seq. Line :    5
Acq. Instrument : Instrument 1               Location : Vial 85
Injection Date  : 3/31/2016 12:29:29 AM           Inj :    1
                                             Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\085-0501.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:12:54 PM by WZF
                  (modified after loading)
```
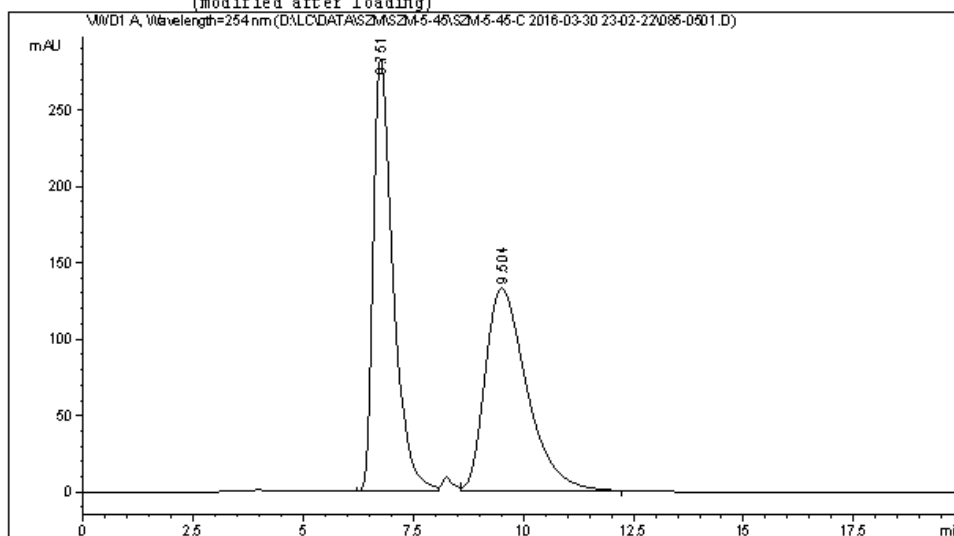


```
=================================================================
                      Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s     [mAU  ]      %
----|-------|----|-------|----------|----------|--------|
  1   6.751 BV    0.4718 8908.26563  283.23007  50.3720
  2   9.504 VB    1.0035 8776.67773  132.88991  49.6280

Totals :                  1.76849e4   416.11998


=================================================================
```

Instrument 1 5/14/2016 10:12:57 PM WZF   Page 1 of 1

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\081-0101.D
Sample Name: SZM-5-50-8

```
==================================================================
Acq. Operator   : LHC                        Seq. Line :   1
Acq. Instrument : Instrument 1               Location : Vial 81
Injection Date  : 3/31/2016 5:11:35 PM           Inj :   1
                                             Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\ SZM\ SZM-5-50\ SZM-5-50-8 2016-03-31 17-09-56\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\ SZM\ SZM-5-50\ SZM-5-50-8 2016-03-31 17-09-56\081-0101.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:29:56 PM by WZF
                  (modified after loading)
```
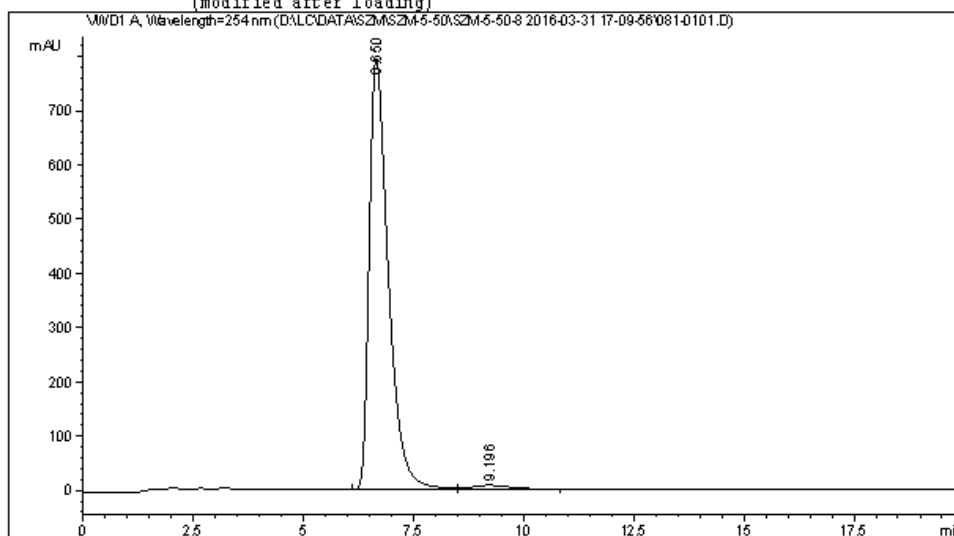


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :        Signal
Multiplier            :        1.0000
Dilution              :        1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   6.650 BB    0.4530 2.37782e4   793.55023  98.2326
  2   9.196 BB    0.7535  427.82095    7.14865   1.7674

Totals :                  2.42060e4   800.69888


==================================================================
```
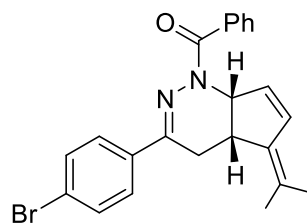
Instrument 1 5/14/2016 10:30:00 PM WZF   Page 1 of 1
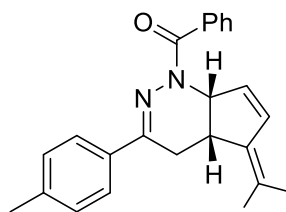
((4a*S*,7a*R*)-**3g**)
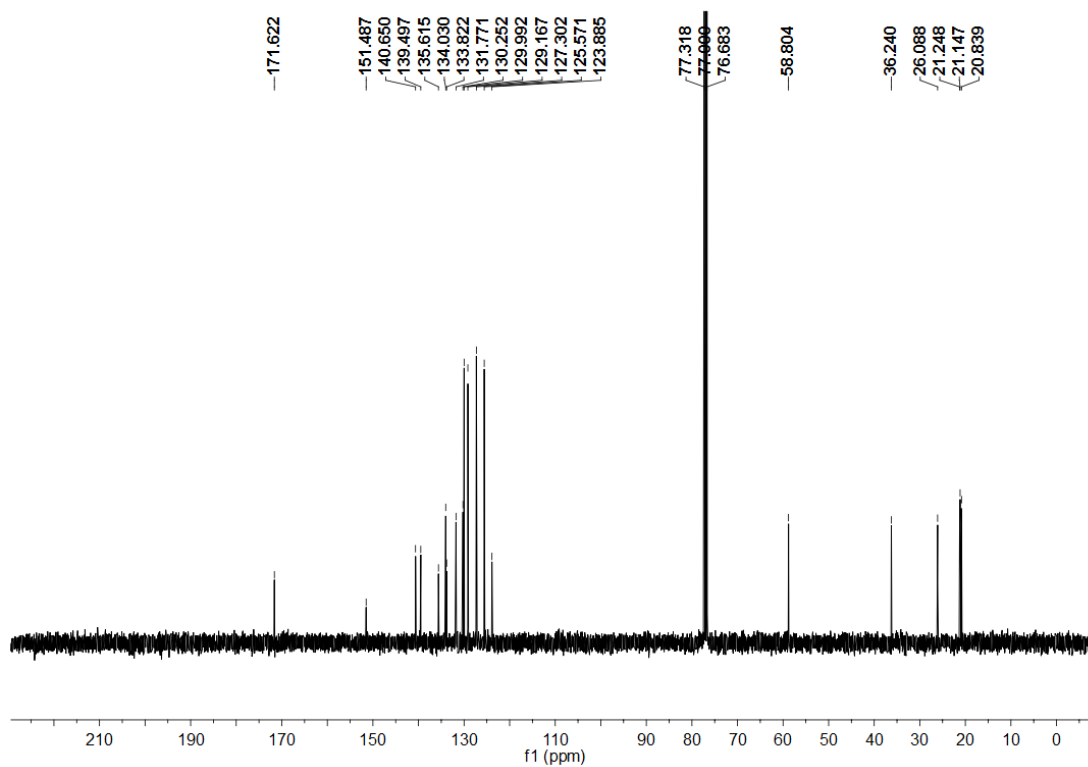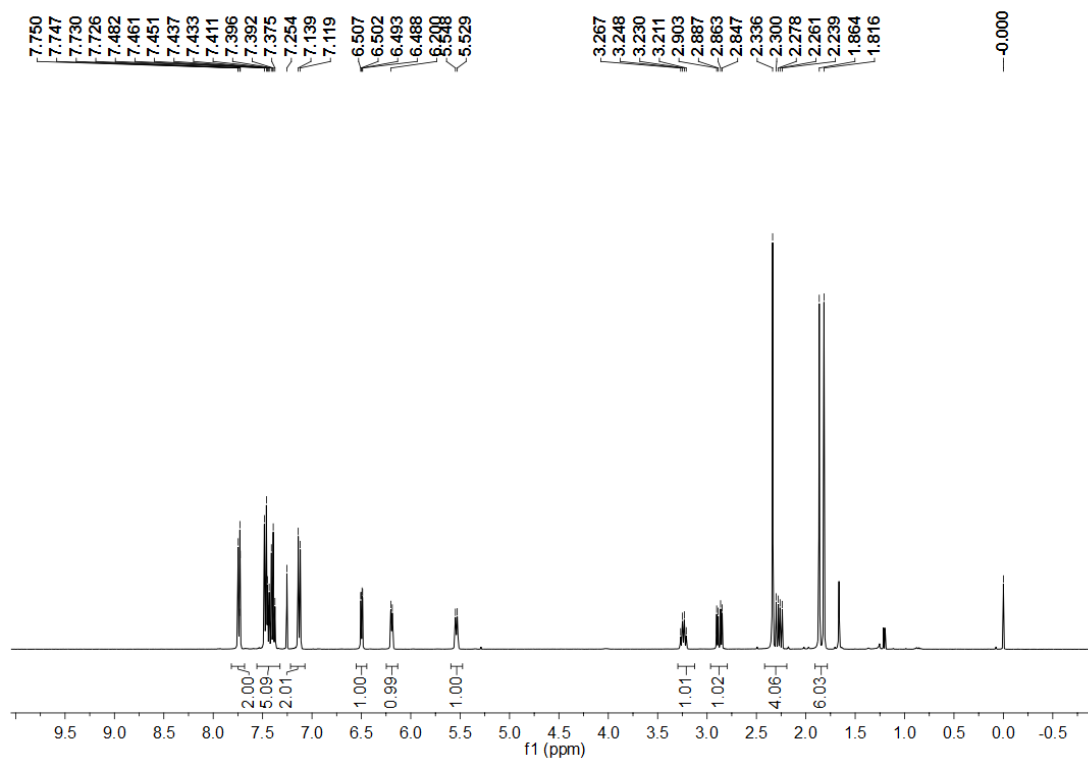
Data File D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\084-0401.D
Sample Name: SZM-5-45-F

```
=================================================================
Acq. Operator   : LHC                      Seq. Line :    4
Acq. Instrument : Instrument 1             Location : Vial 84
Injection Date  : 3/31/2016 12:07:58 AM          Inj :    1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\084-0401.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:12:20 PM by WZF
                  (modified after loading)
```



```
=================================================================
                        Area Percent Report
=================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]  mAU   *s     [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
  1   6.772 BV    0.4803 7861.48926  247.16179  49.9608
  2   8.522 VB    0.6610 7873.83447  181.31389  50.0392

Totals :                 1.57353e4   428.47568


=================================================================
```

Instrument 1 5/14/2016 10:12:24 PM WZF   Page 1 of 1

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-7 2016-03-30 10-44-58\081-0101.D
Sample Name: SZM-5-50-7

```
==================================================================
Acq. Operator   : LHC                        Seq. Line :   1
Acq. Instrument : Instrument 1               Location : Vial 81
Injection Date  : 3/30/2016 10:46:27 AM         Inj :   1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-7 2016-03-30 10-44-58\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-7 2016-03-30 10-44-58\081-0101.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 11/20/2017 7:13:32 PM by LHC
                  (modified after loading)
```



```
==================================================================
                       Area Percent Report
==================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU  ]       %
----|-------|----|-------|----------|----------|--------|
  1   6.678  BB   0.4702 1.19242e4   380.78717  99.9055
  2   8.348  MM   0.4232   11.27725 4.44163e-1   0.0945

Totals :                 1.19355e4   381.23133


==================================================================
```

Instrument 1 11/20/2017 7:13:42 PM LHC   Page 1 of 1

S35
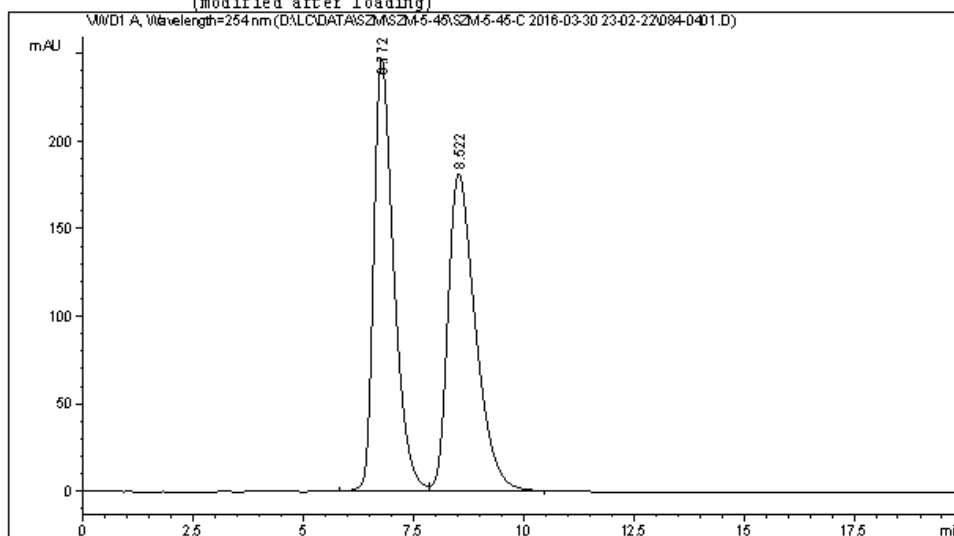
((4a*S*,7a*R*)-**3h**)

Data File D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\083-0301.D
Sample Name: SZM-5-45-E

```
==================================================================
Acq. Operator   : LHC                          Seq. Line :    3
Acq. Instrument : Instrument 1                  Location : Vial 83
Injection Date  : 3/30/2016 11:46:32 PM              Inj :    1
                                                Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\083-0301.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:11:52 PM by WZF
                  (modified after loading)
```
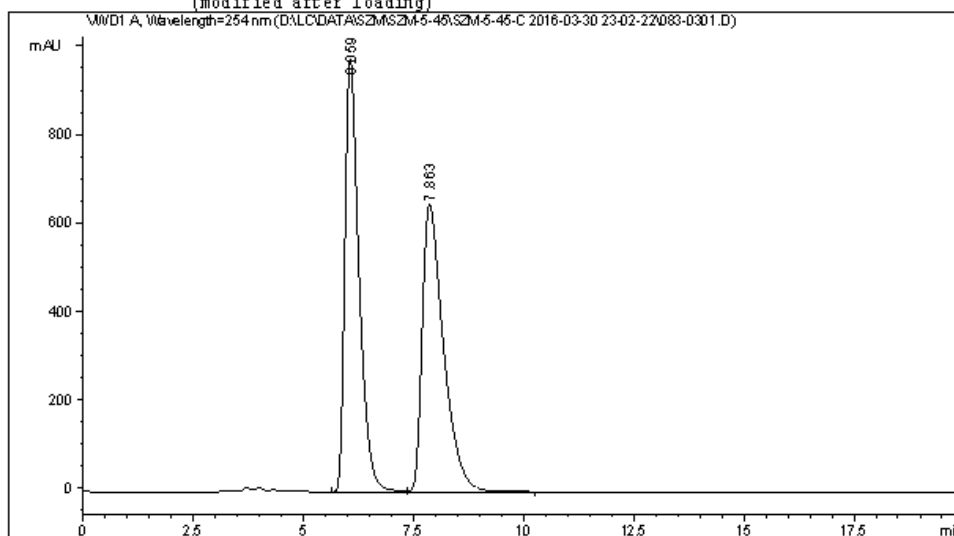


```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   6.059 BV    0.3345 2.18704e4   980.55292  50.0591
  2   7.863 VB    0.5022 2.18188e4   650.16644  49.9409

Totals :                  4.36892e4  1630.71936


==================================================================
```
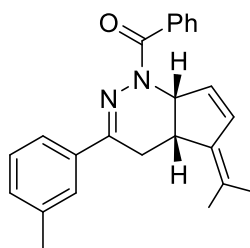
Instrument 1 5/14/2016 10:11:56 PM WZF   Page 1 of 1

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\082-0201.D
Sample Name: SZM-5-50-6

```
=================================================================
Acq. Operator   : LHC                        Seq. Line :    2
Acq. Instrument : Instrument 1               Location : Vial 82
Injection Date  : 3/30/2016 10:06:28 PM           Inj :    1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\082-0201.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:28:32 PM by WZF
                  (modified after loading)
```
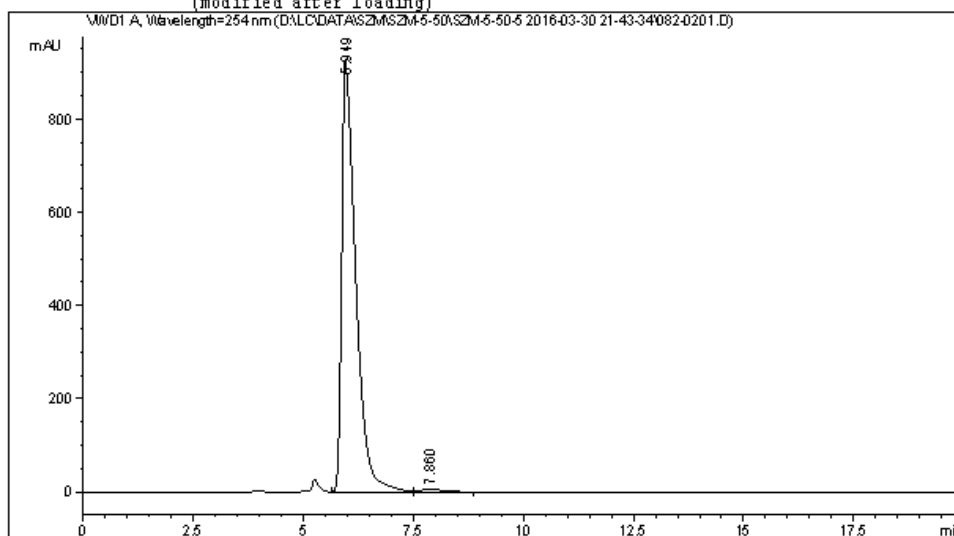


```
=================================================================
                     Area Percent Report
=================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU  ]       %
----|-------|----|-------|----------|----------|--------|
  1   5.949 VV    0.3302 2.04086e4   930.22241  98.9624
  2   7.860 VB    0.4731  213.97714    6.23669   1.0376

Totals :                 2.06225e4   936.45910


=================================================================
```
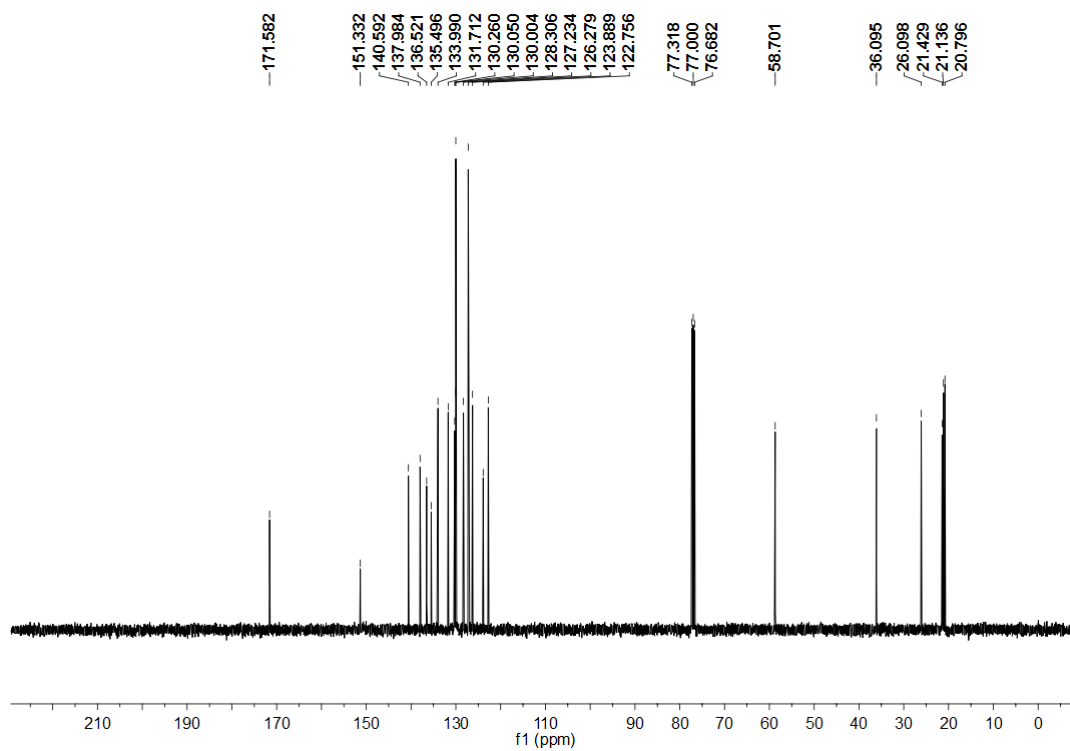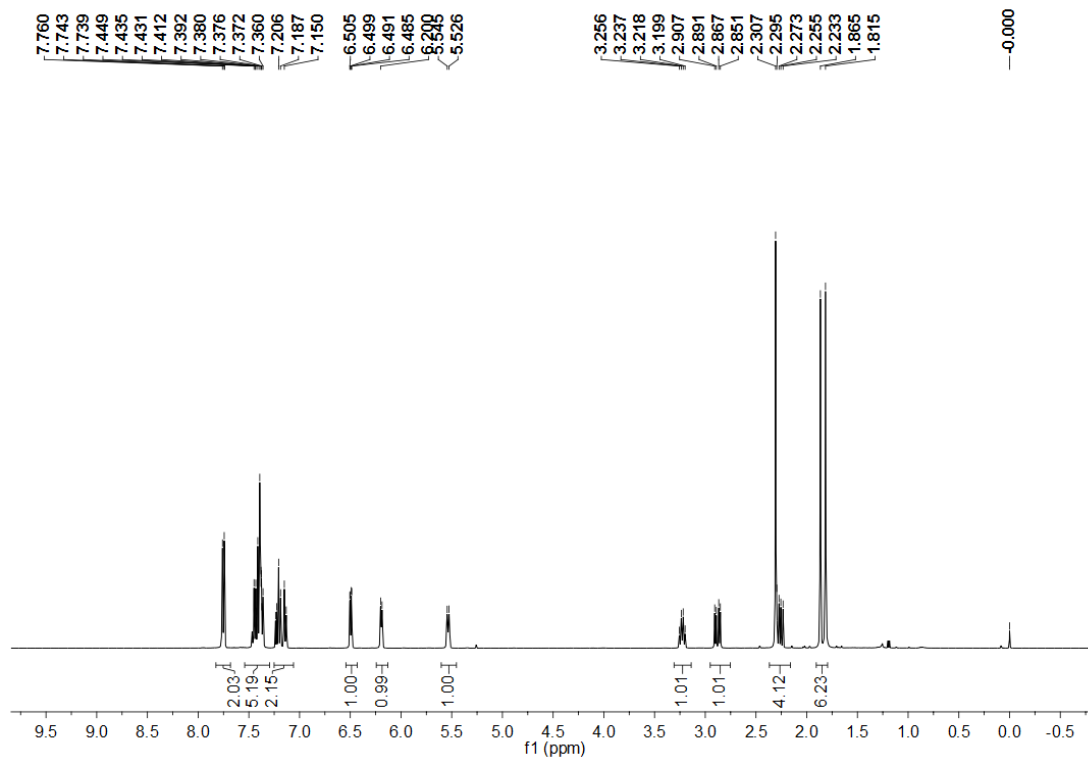
Instrument 1 5/14/2016 10:28:36 PM WZF   Page 1 of 1

S38

((4a*S*,7a*R*)-**3i**)

7.664
7.661
7.645
7.641
7.386
7.369
7.357
7.342
7.338
7.202
7.186
7.175
7.132

6.552
6.547
6.538
6.533
6.173
6.124
5.605

3.394
3.375
3.357
3.338

2.677
2.370
2.350
2.331
1.870
1.810
1.794

0.000

2.00
3.11
4.31
1.01
1.00
1.01
1.02
1.02
1.05
3.02
6.08

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

172.392

156.963
140.513
137.508
135.880
135.799
133.752
132.292
130.913
130.121
129.412
128.537
127.969
127.410
125.734
124.066

77.318
77.000
76.683

59.031

37.567

30.549

21.049
20.813
20.666

210 190 170 150 130 110 90 70 50 30 10 0
f1 (ppm)

S39

Data File D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\082-0201.D
Sample Name: SZM-5-45-D

```
=================================================================
Acq. Operator   : LHC                      Seq. Line :    2
Acq. Instrument : Instrument 1             Location : Vial 82
Injection Date  : 3/30/2016 11:25:01 PM        Inj :    1
                                        Inj Volume : 5 μl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\082-0201.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:11:04 PM by WZF
                  (modified after loading)
```



```
=================================================================
                     Area Percent Report
=================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
  1    7.007 VB   0.4036 2.13671e4   788.37201  50.5964
  2   17.568 BBA  1.7334 2.08633e4   179.46416  49.4036

Totals :                 4.22304e4   967.83617


=================================================================
```
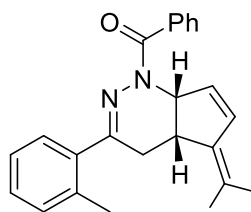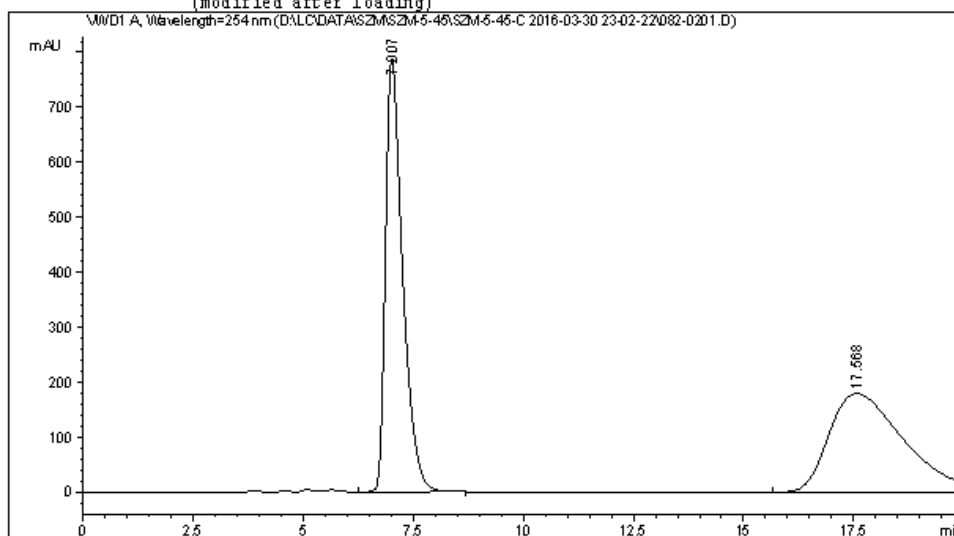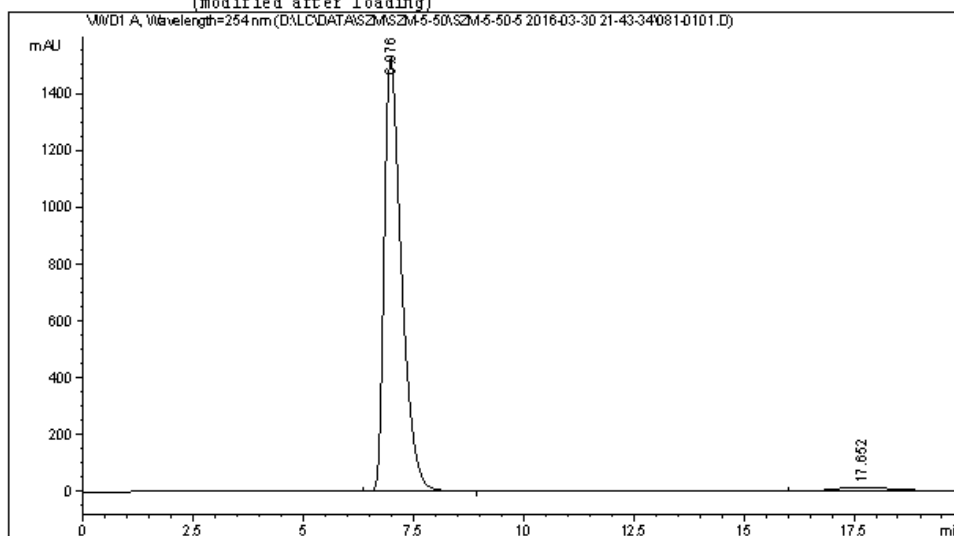
Instrument 1 5/14/2016 10:11:08 PM WZF   Page 1 of 1

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\081-0101.D
Sample Name: SZM-5-50-5

```
=================================================================
Acq. Operator    : LHC                      Seq. Line :    1
Acq. Instrument  : Instrument 1             Location : Vial 81
Injection Date   : 3/30/2016 9:45:12 PM         Inj :    1
                                         Inj Volume : 5 µl
Acq. Method      : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\ASH-20-80-1ML-
                   254NM-20MIN.M
Last changed     : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\081-0101.D\DA.M (
                   ASH-20-80-1ML-254NM-20MIN.M)
Last changed     : 5/14/2016 10:27:43 PM by WZF
                   (modified after loading)
```


VWD1 A, Wavelength=254 nm (D\LC\DATA\SZM\SZM-5-50\SZM-5-50-5 2016-03-30 21-43-34\081-0101.D)

```
=================================================================
                        Area Percent Report
=================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width      Area        Height      Area
  #   [min]        [min]   mAU   *s      [mAU  ]        %
----|-------|----|-------|----------|----------|--------|
  1   6.976  BB   0.4104  4.15658e4  1521.63916  96.4436
  2  17.652  BBA  1.2822  1532.74951   14.20427   3.5564

Totals :                   4.30985e4  1535.84343


=================================================================
```

Instrument 1 5/14/2016 10:27:48 PM WZF   Page 1 of 1

S41

((4a*S*,7a*R*)-**3j**)

7.755
7.751
7.735
7.731
7.435
7.418
7.406
7.387
7.228
7.207
7.152
7.135
7.132
6.887
6.885
6.881
6.506
6.500
6.492
6.486
6.523
6.513
5.505

3.675

3.187
2.917
2.902
2.877
2.861
2.219
2.202
2.179
1.857
1.815

0.000

2.13
3.32
1.23
2.11
1.04
1.00
1.00
1.04
3.09
1.05
1.04
1.05
6.15

f1 (ppm)

171.654
159.556
150.093
140.538
137.915
135.667
134.022
131.576
130.107
129.844
129.310
127.209
123.982
118.050
115.816
109.925
77.318
77.000
76.682
58.548
55.022
35.703
25.817
21.129
20.780

f1 (ppm)

Data File D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\086-0601.D
Sample Name: SZM-5-45-H

```
=================================================================
Acq. Operator   : LHC                         Seq. Line :   6
Acq. Instrument : Instrument 1                Location : Vial 86
Injection Date  : 3/31/2016 12:51:02 AM            Inj :   1
                                             Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-C 2016-03-30 23-02-22\086-0601.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:13:37 PM by WZF
                  (modified after loading)
```
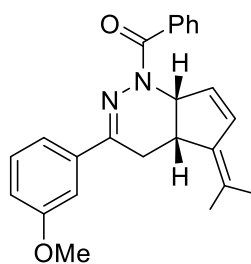


```
=================================================================
                      Area Percent Report
=================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   7.733 BB   0.4658 8571.19141  267.33536  51.0992
  2  10.384 VB   0.6404 8202.44629  185.23439  48.9008

Totals :                  1.67736e4   452.56975


=================================================================
```
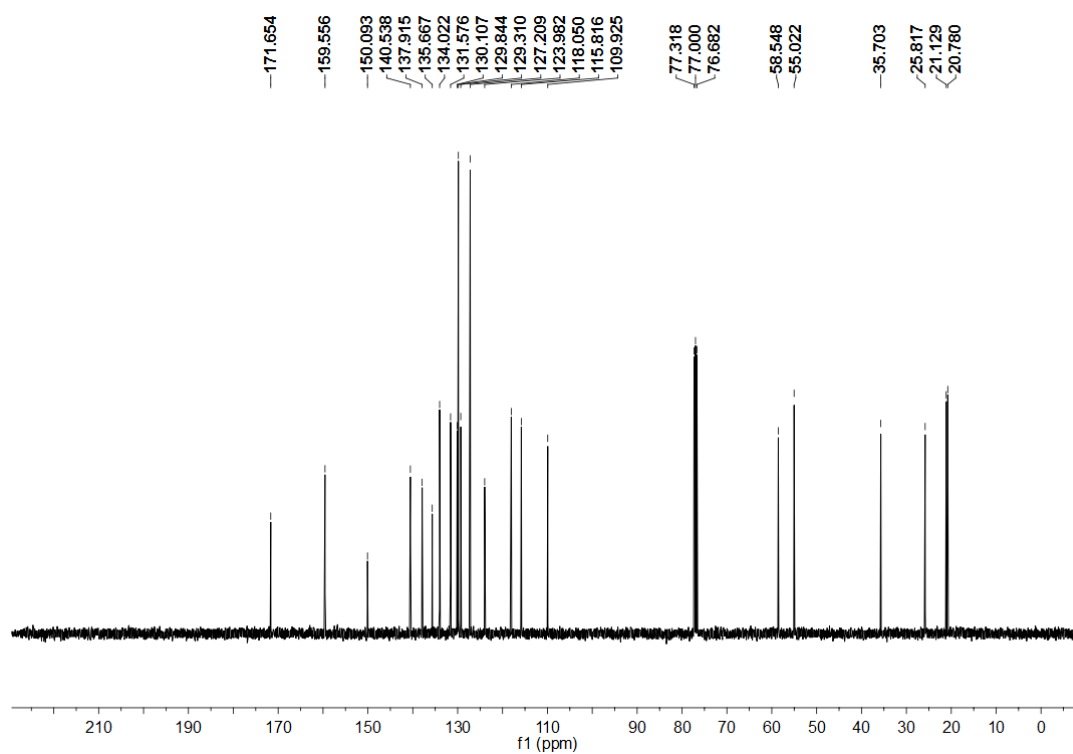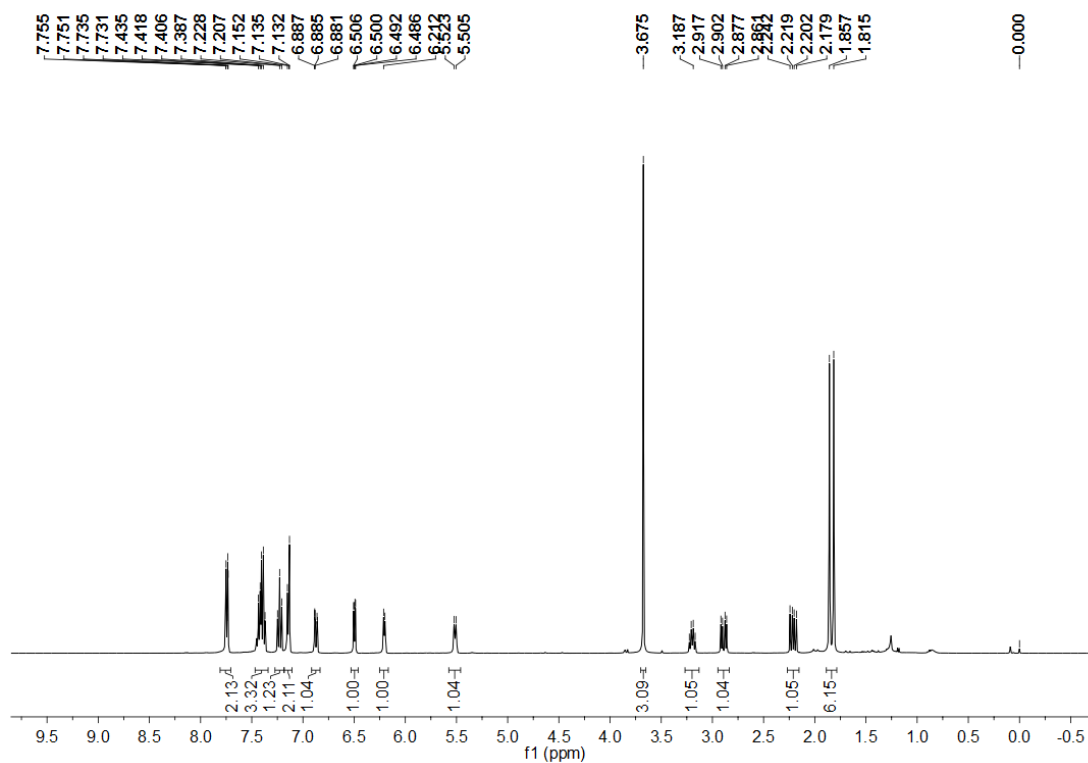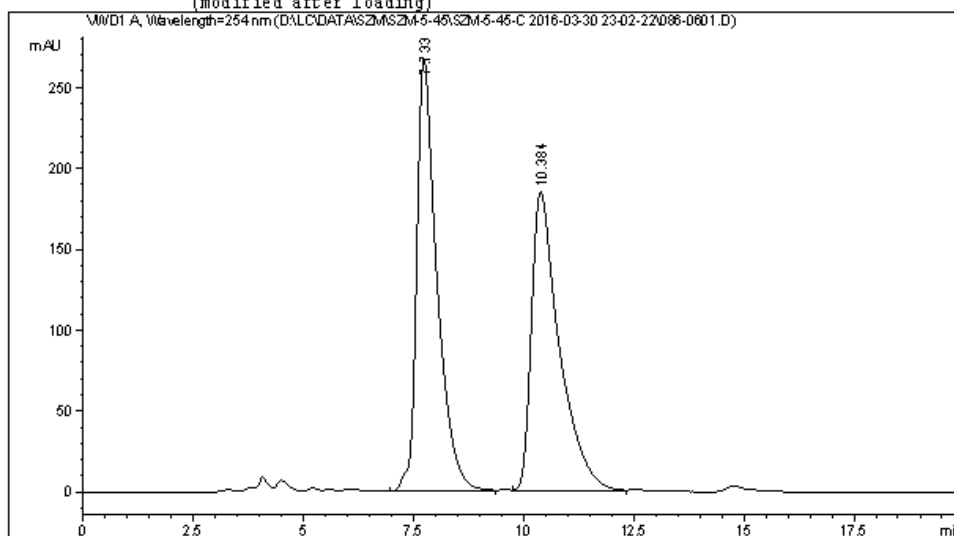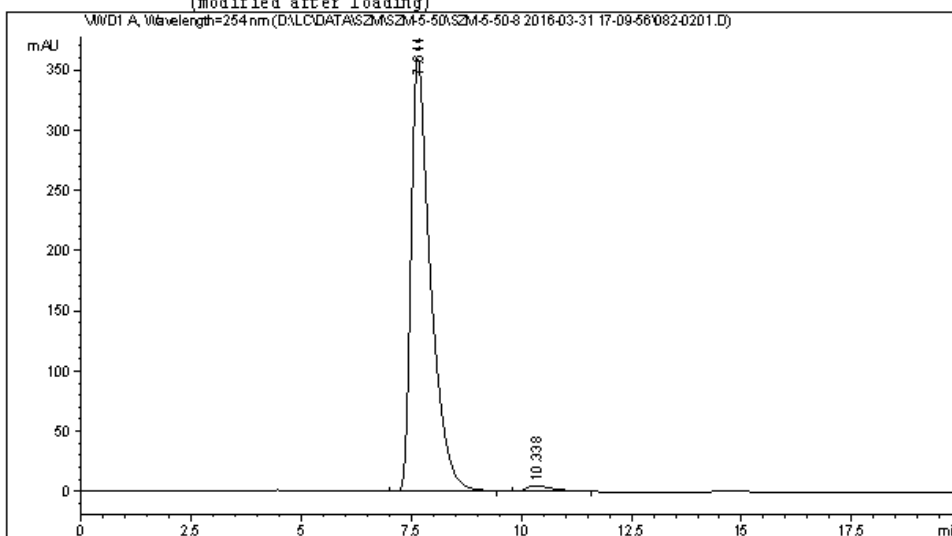
Instrument 1 5/14/2016 10:13:41 PM WZF   Page 1 of 1

S43

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\082-0201.D
Sample Name: SZM-5-50-9

```
====================================================================
Acq. Operator   : LHC                       Seq. Line :    2
Acq. Instrument : Instrument 1              Location : Vial 82
Injection Date  : 3/31/2016 5:32:49 PM            Inj :    1
                                            Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-8 2016-03-31 17-09-56\082-0201.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:30:24 PM by WZF
                  (modified after loading)
```



```
====================================================================
                       Area Percent Report
====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s    [mAU  ]      %
----|-------|----|-------|----------|----------|--------|
  1   7.644 BB   0.4523  1.11106e4   359.47760  98.2102
  2  10.338 BB   0.5670   202.48689    4.89565   1.7898

Totals :                  1.13131e4   364.37325


====================================================================
```

Instrument 1 5/14/2016 10:30:31 PM WZF   Page 1 of 1

S44

((4aS,7aR)-**3k**)

7.951
7.792
7.773
7.770
7.721
7.717
7.697
7.461
7.451
7.444
7.438
7.434
7.428
7.424
7.409
7.405
6.491
6.482
6.477
6.224
6.211
5.540
5.522

3.224
3.206
3.186
3.168
3.037
3.021
2.997
2.981

2.339
2.316
1.878
1.855
1.808

0.000

1.12
6.24
5.18

0.97
0.96

1.00

0.97
1.01

1.06

2.95
3.04

171.666

150.307
140.616
134.098
134.036
131.623
130.307
129.982
128.386
128.146
127.571
127.321
126.705
126.333
125.315
124.001
123.985
123.318
77.000
76.683

58.658

35.798

25.715
21.235
20.824

```
===================================================================
Acq. Operator   : WZF                      Seq. Line :    5
Acq. Instrument : Instrument 1             Location : Vial 74
Injection Date  : 5/15/2016 3:46:16 PM          Inj :    1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-50 2016-05-15 13-38-50\ASH-20-80-1ML-
                  254NM-30MIN.M
Last changed    : 5/15/2016 1:36:20 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-45\SZM-5-45-50 2016-05-15 13-38-50\074-0501.D\DA.M (
                  ASH-20-80-1ML-254NM-30MIN.M)
Last changed    : 5/15/2016 10:13:56 PM by WZF
                  (modified after loading)
```
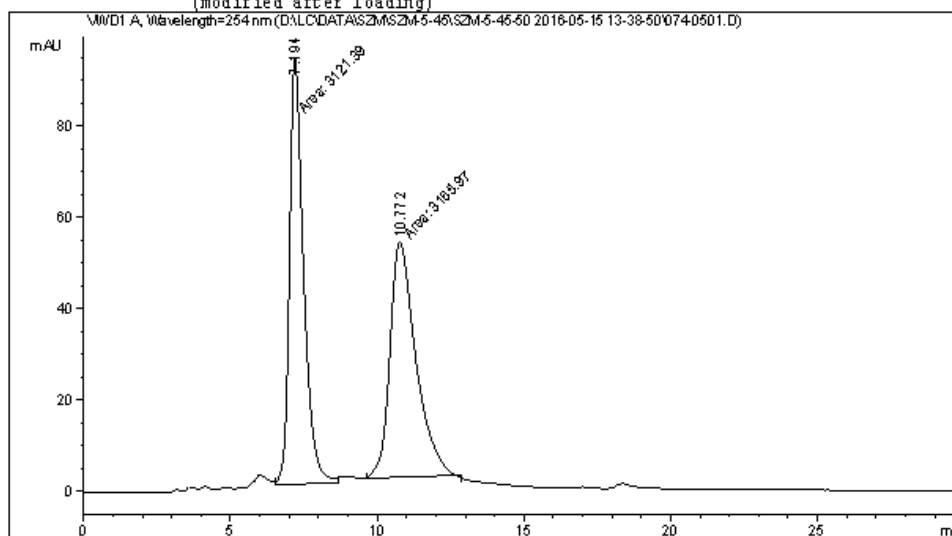


```
===================================================================
                        Area Percent Report
===================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   mAU   *s     [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   7.194 MM    0.5579 3121.38794   93.25528  49.6454
  2  10.772 MM    1.0224 3165.97461   51.60939  50.3546

Totals :                  6287.36255  144.86467


===================================================================
```

Data File D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-10 2016-04-05 16-13-27\081-0101.D
Sample Name: SZM-5-50-10

```
========================================================================
Acq. Operator   : LHC                        Seq. Line :   1
Acq. Instrument : Instrument 1               Location : Vial 81
Injection Date  : 4/ 5/2016 4:15:15 PM          Inj :   1
                                             Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-10 2016-04-05 16-13-27\ASH-20-80-1ML-
                  254NM-20MIN.M
Last changed    : 3/28/2016 11:02:44 AM by LHC
Analysis Method : D:\LC\DATA\SZM\SZM-5-50\SZM-5-50-10 2016-04-05 16-13-27\081-0101.D\DA.M (
                  ASH-20-80-1ML-254NM-20MIN.M)
Last changed    : 5/14/2016 10:31:43 PM by WZF
                  (modified after loading)
```



```
========================================================================
                       Area Percent Report
========================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   6.691 BB    0.4311 3.42152e4  1191.64990  99.0898
  2   9.727 VB    0.6935  314.28152    6.04935   0.9102

Totals :                 3.45295e4  1197.69926


========================================================================
```
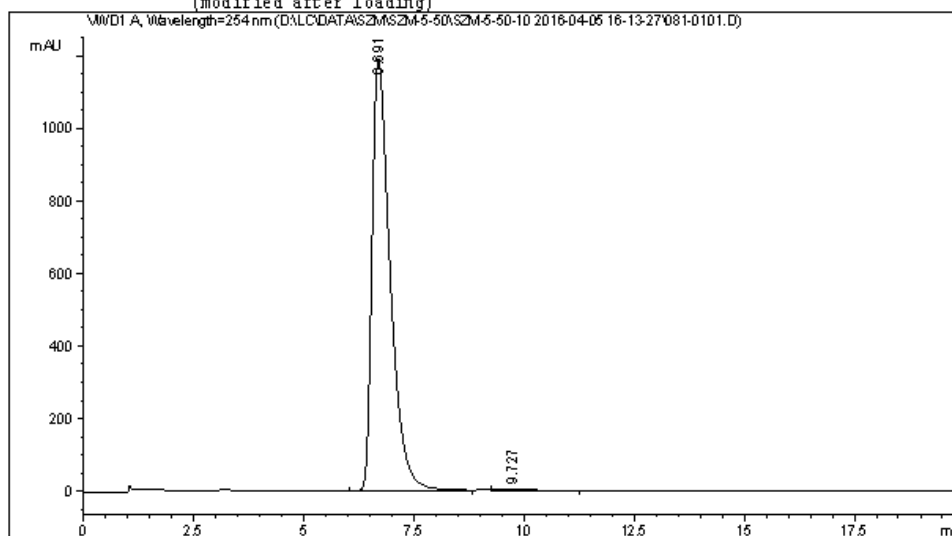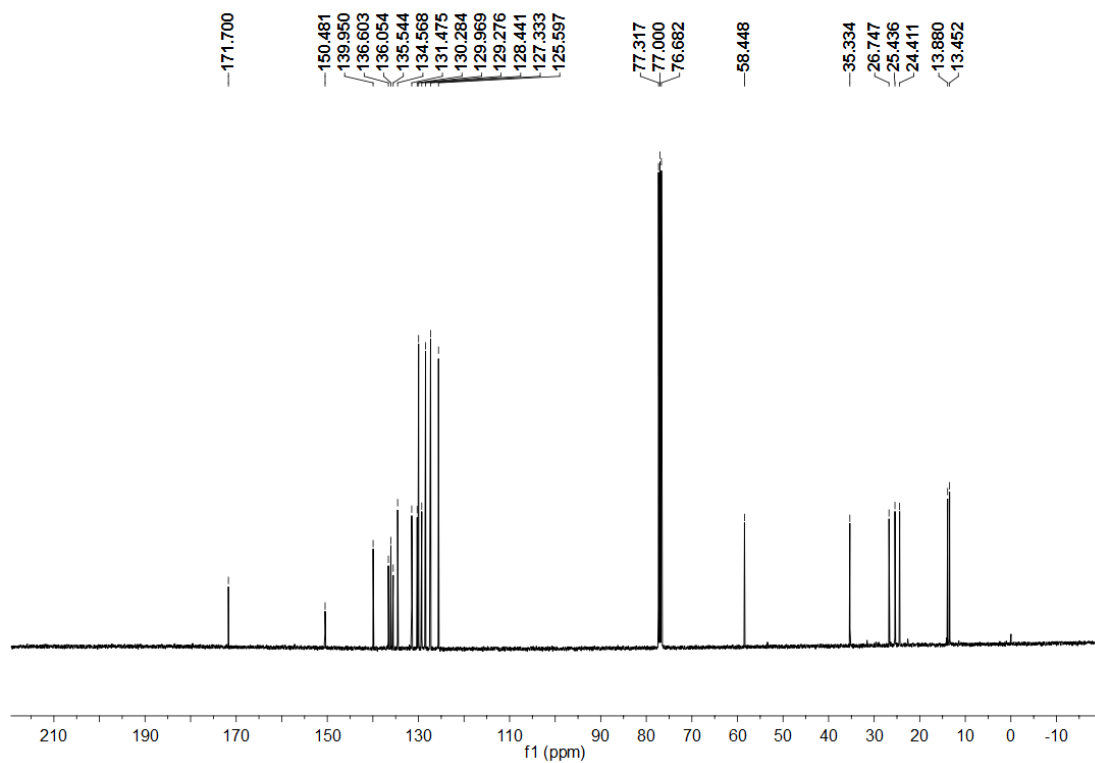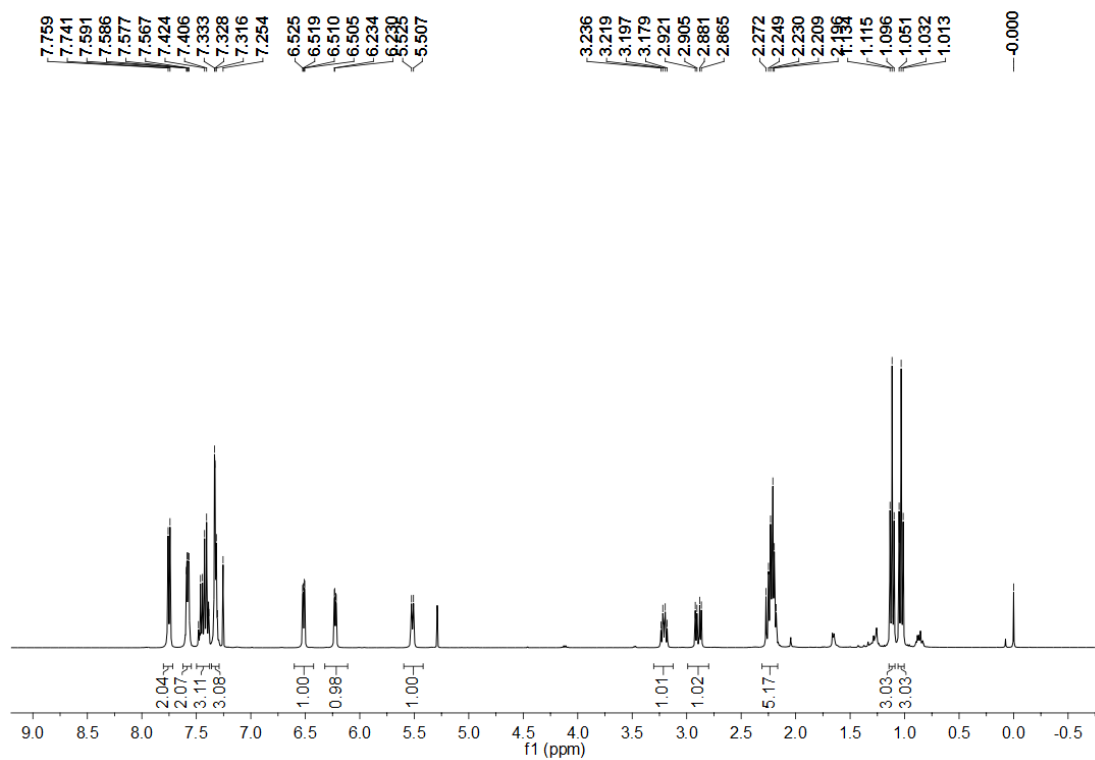
Instrument 1 5/14/2016 10:31:54 PM WZF   Page 1 of 1

S47

((4a*S*,7a*R*)-**3l**)

```
=================================================================
Acq. Operator   : LHC                      Seq. Line :   1
Acq. Instrument : Instrument 1             Location : Vial 54
Injection Date  : 12/13/2016 9:21:51 AM         Inj :   1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\WL-3-WUTONG-RAC 2016-12-13 09-20-26\IE-96-4-
                  245NM-30MIN.M
Last changed    : 12/13/2016 9:20:36 AM by LHC
                  (modified after loading)
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\WL-3-WUTONG-RAC 2016-12-13 09-20-26\054-0101.D\
                  DA.M (IE-96-4-245NM-30MIN.M)
Last changed    : 11/20/2017 7:08:40 PM by SXS
                  (modified after loading)
```



```
=================================================================
                        Area Percent Report
=================================================================

Sorted By          :      Signal
Multiplier         :      1.0000
Dilution           :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
 #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   7.324 VV   0.2006 9676.86914  726.25989  48.8577
  2   8.032 VV   0.2327 1.01294e4   650.27850  51.1423
```
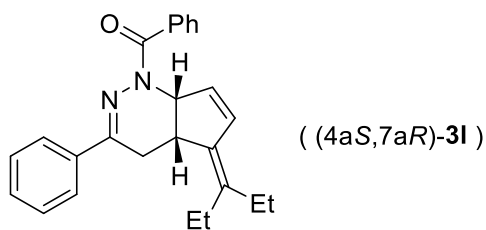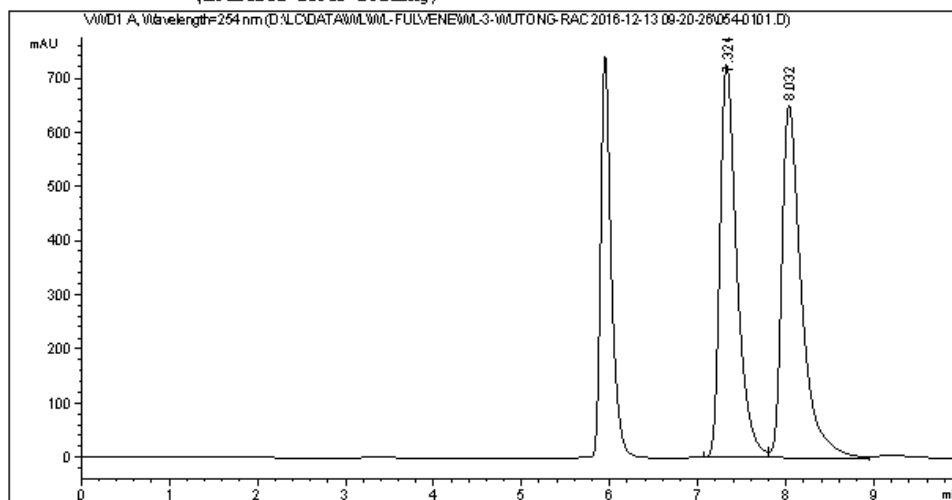
Data File D:\LC\DATA\WL\WL-FULVENE\WL-3-WUTONG-OPT 2016-12-13 20-52-49\055-0101.D
Sample Name: WL-3-WUTONG-OPT

```
================================================================
Acq. Operator   : LHC                          Seq. Line :   1
Acq. Instrument : Instrument 1                  Location : Vial 55
Injection Date  : 12/13/2016 8:54:21 PM              Inj :   1
                                              Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\WL-3-WUTONG-OPT 2016-12-13 20-52-49\IB-96-4-
                  245NM-30MIN.M
Last changed    : 12/13/2016 8:51:29 PM by LHC
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\WL-3-WUTONG-OPT 2016-12-13 20-52-49\055-0101.D\
                  DA.M (IB-96-4-245NM-30MIN.M)
Last changed    : 11/20/2017 7:07:17 PM by SXS
                  (modified after loading)
```



```
================================================================
                        Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area        Height     Area
 #   [min]        [min]   mAU   *s     [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
 1   7.867 VV    0.2565  988.90131    60.42138   1.7406
 2   8.606 VV    0.3252 5.58252e4   2672.65942  98.2594

Totals :                5.68141e4   2733.08080
```
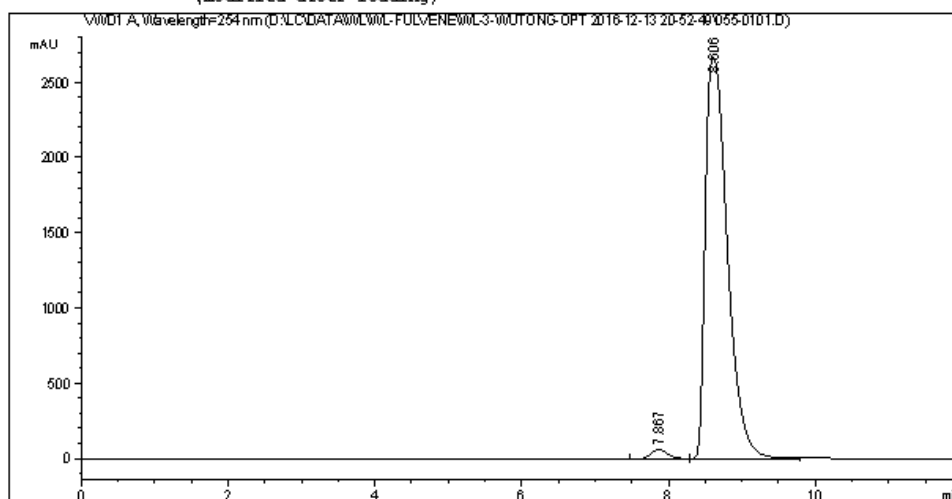
((4a*S*,7a*R*)-**3m**)

7.722
7.703
7.586
7.578
7.567
7.392
7.373
7.328
7.323
7.315
7.311
6.219
6.209
6.205
6.129
6.115
5.613
5.593

3.304
3.285
2.758
2.742
2.719
2.703
2.573
2.556
2.087
2.077
2.071
2.057

0.000

2.08
2.11
6.37

1.02
0.98

1.00

1.01

1.11
4.04
1.05

2.09

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

171.371

153.783
137.294
136.346
135.357
132.919
132.619
131.760
130.261
129.822
129.373
128.357
127.228
125.608

77.318
77.000
76.682

59.338

36.469
30.110
29.700
25.717
17.450

210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S51

Data File D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-C-D-E 2016-05-03 21-22-36\071-0101.D
Sample Name: szm-5-59-c

===
Acq. Operator   : WZF   Seq. Line :   1
Acq. Instrument : Instrument 1   Location : Vial 71
Injection Date : 5/3/2016 9:23:58 PM   Inj :   1
                                              Inj Volume : 5 µl
Acq. Method   : D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-C-D-E 2016-05-03 21-22-36\ICH-20-80-1ML-
                  254NM-25MIN.M
Last changed   : 4/28/2016 3:58:30 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-C-D-E 2016-05-03 21-22-36\071-0101.D\DA.M
                  (ICH-20-80-1ML-254NM-25MIN.M)
Last changed   : 5/14/2016 9:56:18 PM by WZF
                  (modified after loading)
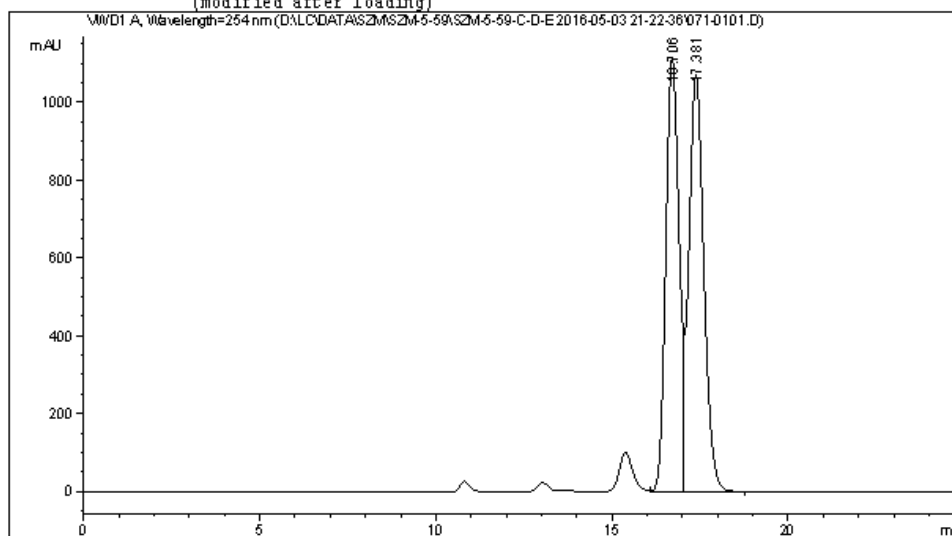
VWD1 A, Wavelength=254 nm (D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-C-D-E 2016-05-03 21-22-36\071-0101.D)

===
                         Area Percent Report
===

Sorted By   :   Signal
Multiplier   :   1.0000
Dilution   :   1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width   Area   Height   Area
  #   [min]   [min]   mAU   *s   [mAU   ]   %
----|-------|----|-------|----------|----------|--------|
  1 16.706 VV   0.4051 2.91916e4 1112.79346 48.0660
  2 17.381 VB   0.4477 3.15408e4 1068.72375 51.9340

Totals :   6.07325e4 2181.51721

===
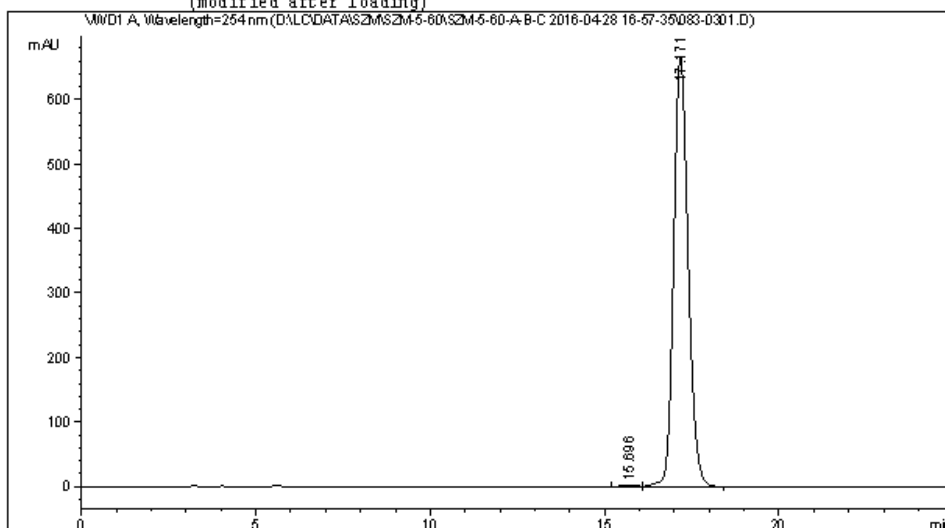
Instrument 1 5/14/2016 9:56:23 PM WZF   Page 1 of 1

S52

Data File D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\083-0301.D
Sample Name: SZM-5-60-C

```
================================================================
Acq. Operator   : WZF                     Seq. Line :   3
Acq. Instrument : Instrument 1            Location : Vial 83
Injection Date  : 4/28/2016 5:51:42 PM        Inj :   1
                                        Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\ICH-20-80-1ML-
                  254NM-25MIN.M
Last changed    : 4/28/2016 3:58:30 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\083-0301.D\DA.M
                  (ICH-20-80-1ML-254NM-25MIN.M)
Last changed    : 5/14/2016 9:49:28 PM by WZF
                  (modified after loading)
```
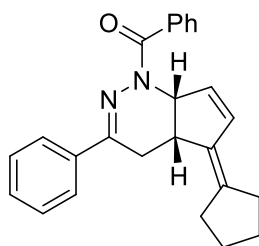


```
================================================================
                    Area Percent Report
================================================================

Sorted By           :       Signal
Multiplier          :       1.0000
Dilution            :       1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  15.696 BV    0.3486   71.94296    2.86219   0.3734
  2  17.171 VB    0.4459 1.91947e4   665.17780  99.6266

Totals :                 1.92666e4   668.03999


================================================================
```
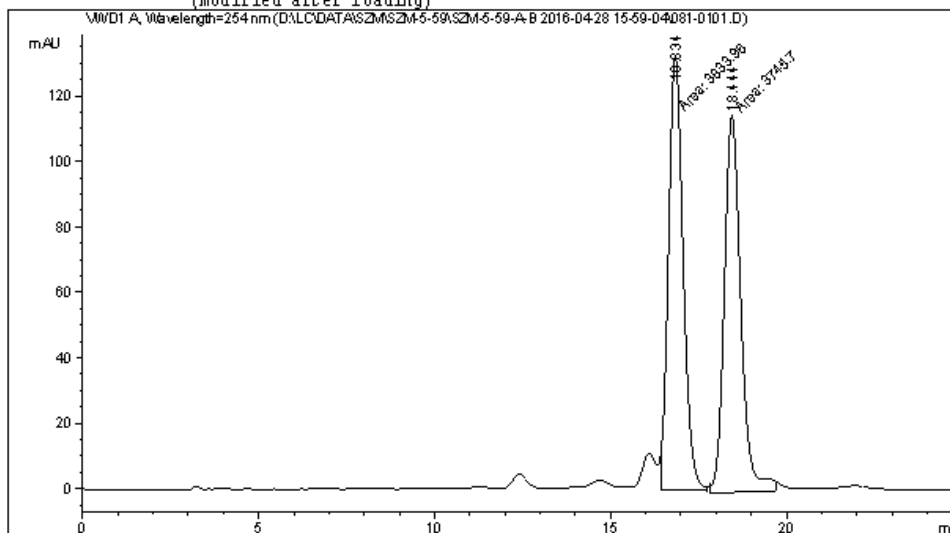
Instrument 1 5/14/2016 9:49:33 PM WZF   Page 1 of 1

((4a*S*,7a*R*)-**3n**)

7.745
7.725
7.580
7.572
7.561
7.407
7.392
7.388
7.323
7.318
7.310
7.305
6.355
6.346
6.341
6.170
6.157
5.574
5.555
3.187
3.169
3.150
3.132
2.919
2.904
2.880
2.864
2.385
2.374
2.365
2.357
1.719
1.703
0.000

2.00
2.08
3.37
3.16
1.03
0.96
1.00
1.02
1.07
5.22
4.17

f1 (ppm)

171.649
152.173
136.826
136.474
135.447
135.280
133.049
132.972
130.280
129.900
129.302
128.385
127.272
125.596
77.338
77.021
76.703
59.093
37.297
30.965
30.751
26.620
26.410
25.130

f1 (ppm)

```
=================================================================
Acq. Operator   : WZF                          Seq. Line :    1
Acq. Instrument : Instrument 1                 Location : Vial 81
Injection Date  : 4/28/2016 4:00:29 PM              Inj :    1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-A-B 2016-04-28 15-59-04\ICH-20-80-1ML-
                  254NM-25MIN.M
Last changed    : 4/28/2016 3:58:30 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-A-B 2016-04-28 15-59-04\081-0101.D\DA.M (
                  ICH-20-80-1ML-254NM-25MIN.M)
Last changed    : 5/14/2016 9:53:29 PM by WZF
                  (modified after loading)
```



```
=================================================================
                     Area Percent Report
=================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  16.834 MM   0.4818 3833.96387  132.62325  50.5822
  2  18.444 MM   0.5433 3745.70020  114.90802  49.4178

Totals :                 7579.66406  247.53127


=================================================================
```

S55

Data File D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\081-0101.D
Sample Name: SZM-5-60-A

```
=====================================================================
Acq. Operator   : WZF                       Seq. Line :    1
Acq. Instrument : Instrument 1              Location : Vial 81
Injection Date  : 4/28/2016 4:58:47 PM         Inj :    1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\ICH-20-80-1ML-
                  254NM-25MIN.M
Last changed    : 4/28/2016 3:58:30 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\081-0101.D\DA.M
                  (ICH-20-80-1ML-254NM-25MIN.M)
Last changed    : 5/14/2016 9:45:09 PM by WZF
                  (modified after loading)
```
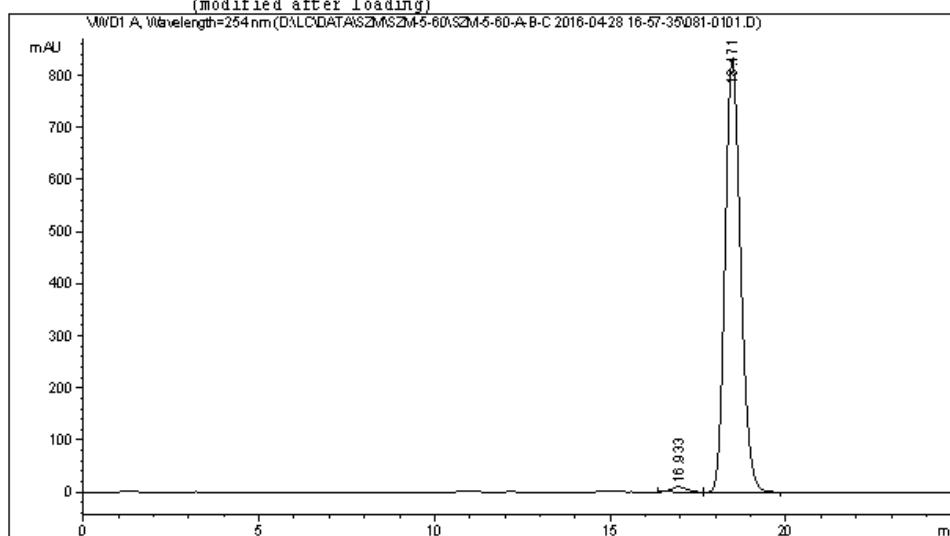


```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
  1  16.933 BV   0.4450  286.03668    9.56381   1.1036
  2  18.471 VB   0.4790 2.56322e4   828.27850  98.8964

Totals :                2.59183e4   837.84231
```
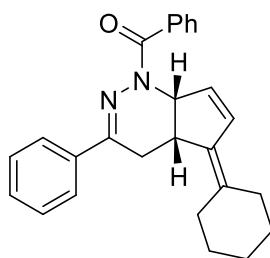
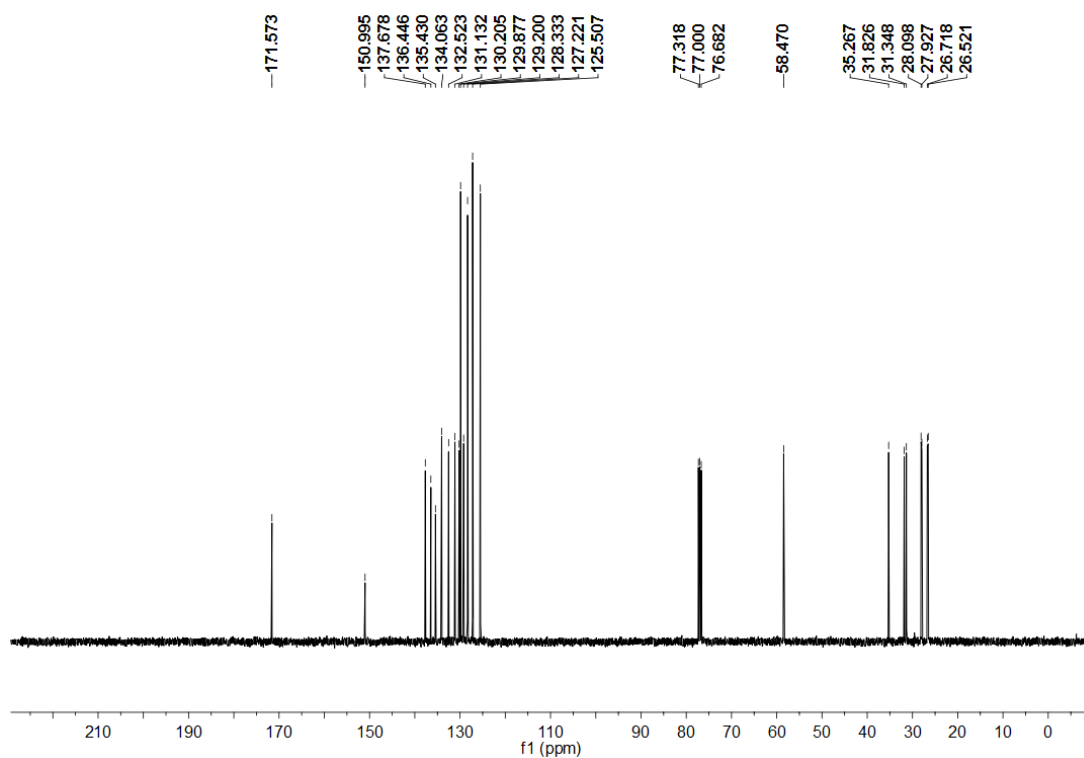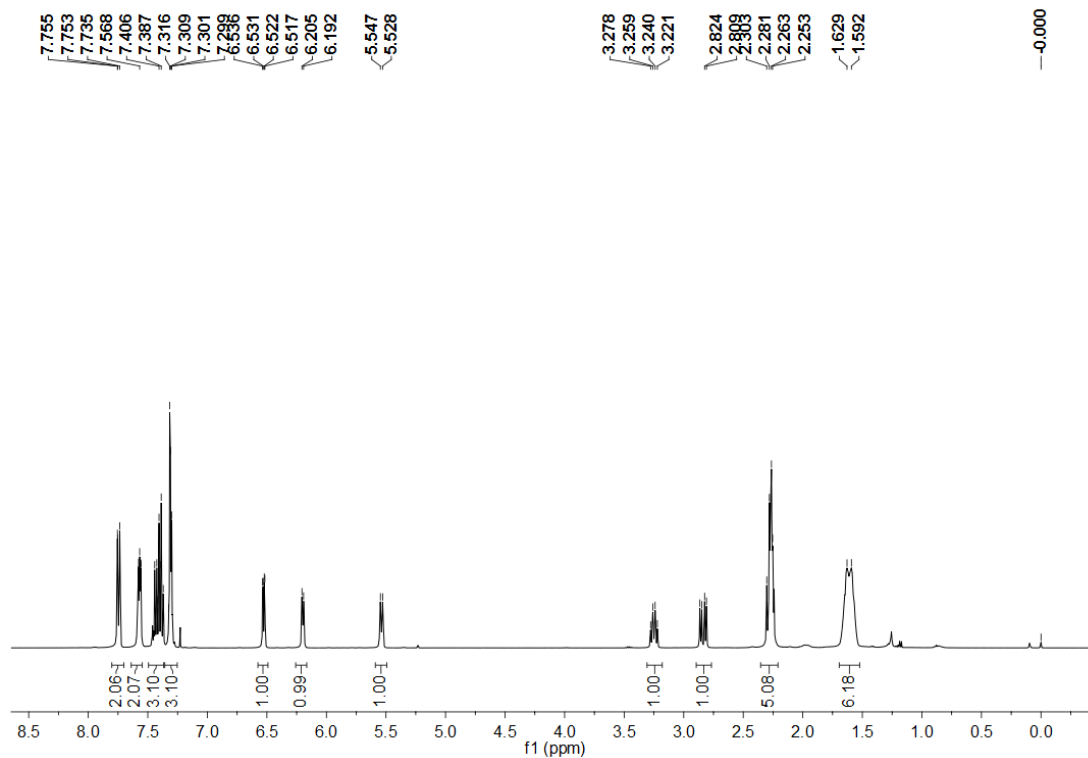===

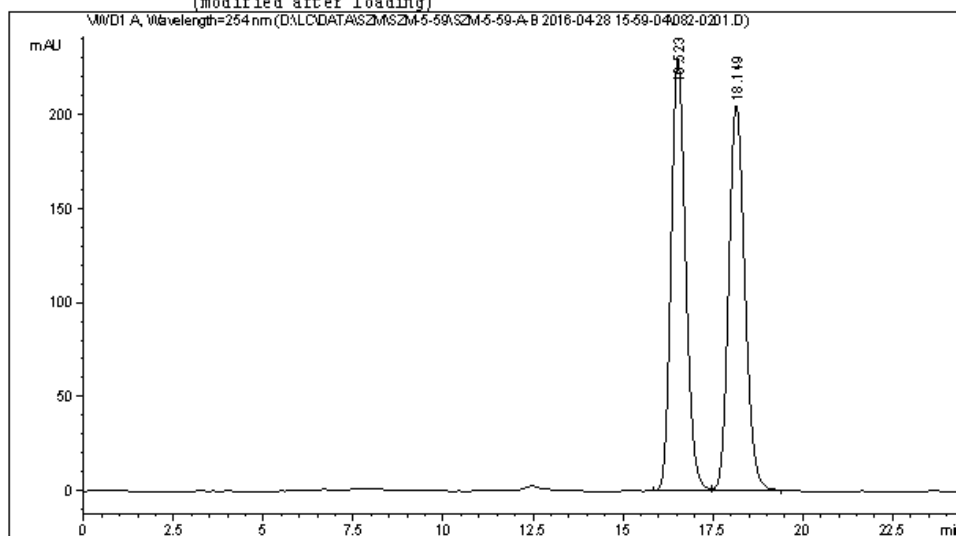Instrument 1 5/14/2016 9:45:15 PM WZF   Page 1 of 1

((4a*S*,7a*R*)-**3o**)

S57

Data File D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-A-B 2016-04-28 15-59-04\082-0201.D
Sample Name: SZM-5-59-B

```
=================================================================
Acq. Operator   : WZF                        Seq. Line :    2
Acq. Instrument : Instrument 1               Location : Vial 82
Injection Date  : 4/28/2016 4:26:47 PM              Inj :    1
                                             Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-A-B 2016-04-28 15-59-04\ICH-20-80-1ML-
                  254NM-25MIN.M
Last changed    : 4/28/2016 3:58:30 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-59\SZM-5-59-A-B 2016-04-28 15-59-04\082-0201.D\DA.M (
                  ICH-20-80-1ML-254NM-25MIN.M)
Last changed    : 5/14/2016 9:54:57 PM by WZF
                  (modified after loading)
```



```
=================================================================
                      Area Percent Report
=================================================================

Sorted By           :      Signal
Multiplier          :      1.0000
Dilution            :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU   *s     [mAU  ]        %
----|-------|----|-------|----------|----------|--------|
  1  16.523 BV   0.4347 6473.54395  229.95941  50.2671
  2  18.149 VB   0.4829 6404.75293  204.73796  49.7329

Totals :                 1.28783e4   434.69737


=================================================================
```

Instrument 1 5/14/2016 9:55:01 PM WZF   Page 1 of 1

```
==================================================================
Acq. Operator   : WZF                       Seq. Line :   2
Acq. Instrument : Instrument 1              Location : Vial 82
Injection Date  : 4/28/2016 5:25:31 PM           Inj :   1
                                            Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\ICH-20-80-1ML-
                  254NM-25MIN.M
Last changed    : 4/28/2016 3:58:30 PM by WZF
Analysis Method : D:\LC\DATA\SZM\SZM-5-60\SZM-5-60-A-B-C 2016-04-28 16-57-35\082-0201.D\DA.M
                  (ICH-20-80-1ML-254NM-25MIN.M)
Last changed    : 5/14/2016 9:48:44 PM by WZF
                  (modified after loading)
```
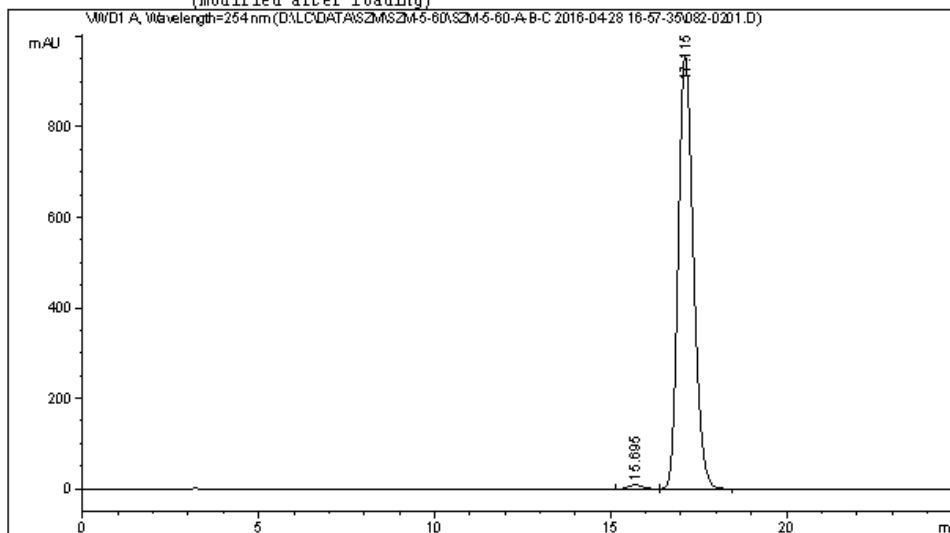


```
==================================================================
                    Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]  mAU   *s     [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
  1  15.695  BV   0.4133  256.11285    9.55233   0.8846
  2  17.115  VB   0.4636 2.86958e4   956.46973  99.1154

Totals :               2.89520e4    966.02205


==================================================================
```

((4a*S*,7a*R*)-**3p**)

7.761
7.758
7.741
7.737
7.586
7.578
7.567
7.424
7.405
7.334
7.329
7.317
7.256
6.537
6.531
6.522
6.517
6.225
5.524
5.521
5.505
3.227
3.210
3.188
3.170
2.952
2.937
2.912
2.896
2.416
2.401
2.266
2.251
1.713
1.696
1.640
1.568
1.553
0.000

2.04
2.07
3.18
3.14
1.00
0.99
1.03
1.01
1.05
4.31
1.24
3.25
5.01

171.725

150.567
140.468
136.588
135.496
134.113
133.929
131.520
130.276
129.949
129.261
128.423
127.312
125.579

77.317
77.000
76.682

58.540

35.530
32.872
32.091
29.676
28.921
28.118
27.891
26.057

```
================================================================
Acq. Operator   : LHC                      Seq. Line :    1
Acq. Instrument : Instrument 1              Location : Vial 41
Injection Date  : 11/16/2016 8:07:31 PM          Inj :    1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\WL-FULVENE-2 2016-11-16 20-06-10\IE-80-20-30MIN-
                  245NM.M
Last changed    : 11/16/2016 8:05:10 PM by LHC
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\WL-FULVENE-2 2016-11-16 20-06-10\041-0101.D\DA.M
                  (IE-80-20-30MIN-245NM.M)
Last changed    : 11/20/2017 7:10:12 PM by SXS
                  (modified after loading)
```
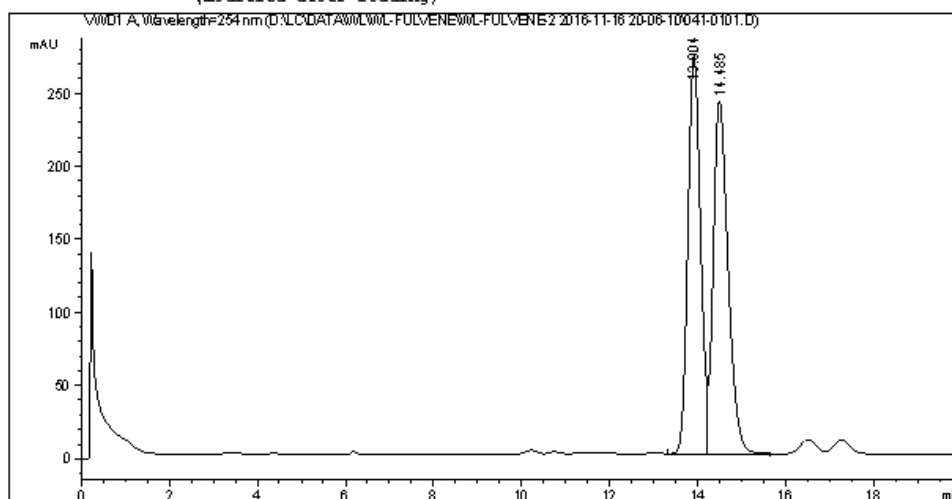


```
================================================================
                    Area Percent Report
================================================================


Sorted By           :      Signal
Multiplier          :      1.0000
Dilution            :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  13.904 VV   0.3109 5407.17432  271.58078  48.9699
  2  14.485 VB   0.3556 5634.65967  241.16479  51.0301

Totals :                 1.10418e4   512.74557
```

Data File D:\LC\DATA\WL\WL-FULVENE\WL-OPT 2016-11-17 15-03-41\045-0101.D
Sample Name: wl-heptane

```
================================================================
Acq. Operator   : HR                      Seq. Line :   1
Acq. Instrument : Instrument 1             Location : Vial 45
Injection Date  : 11/17/2016 3:04:59 PM          Inj :   1
                                           Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\WL-OPT 2016-11-17 15-03-41\IE-80-20-30MIN-245NM.
                  M
Last changed    : 11/16/2016 8:05:10 PM by LHC
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\WL-OPT 2016-11-17 15-03-41\045-0101.D\DA.M (IE-
                  80-20-30MIN-245NM.M)
Last changed    : 11/20/2017 7:11:36 PM by SXS
                  (modified after loading)
```
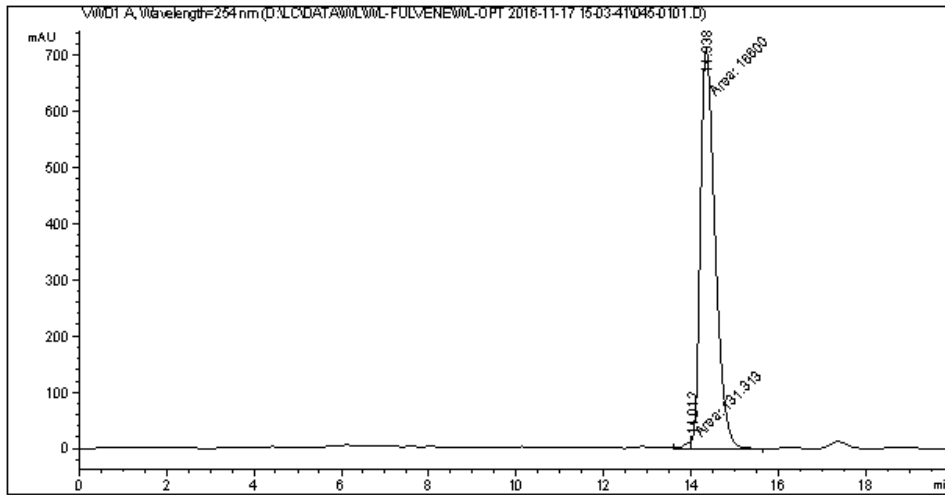


```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area        Height      Area
  #   [min]       [min]   mAU   *s     [mAU   ]        %
----|-------|----|-------|----------|----------|--------|
  1  14.012 MF    0.1486  131.31300   14.72354   0.7848
  2  14.338 FM    0.3903 1.66000e4   708.83008  99.2152

Totals :                 1.67313e4   723.55361
```
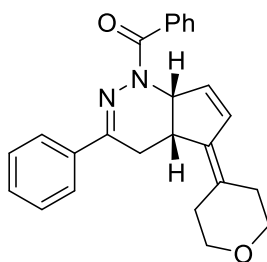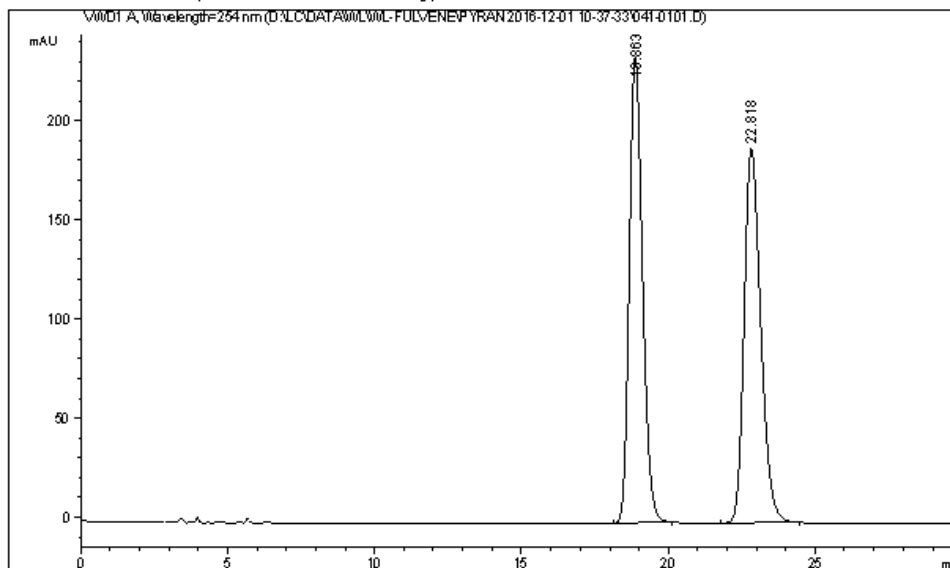
((4a*S*,7a*R*)-**3q**)
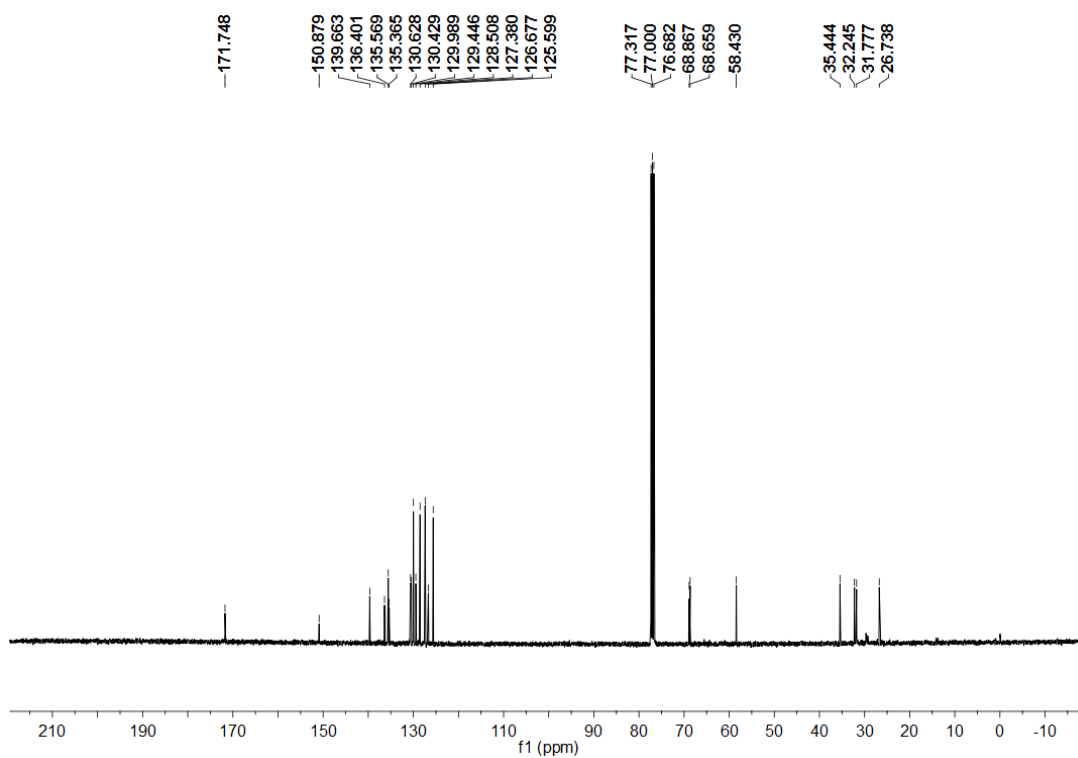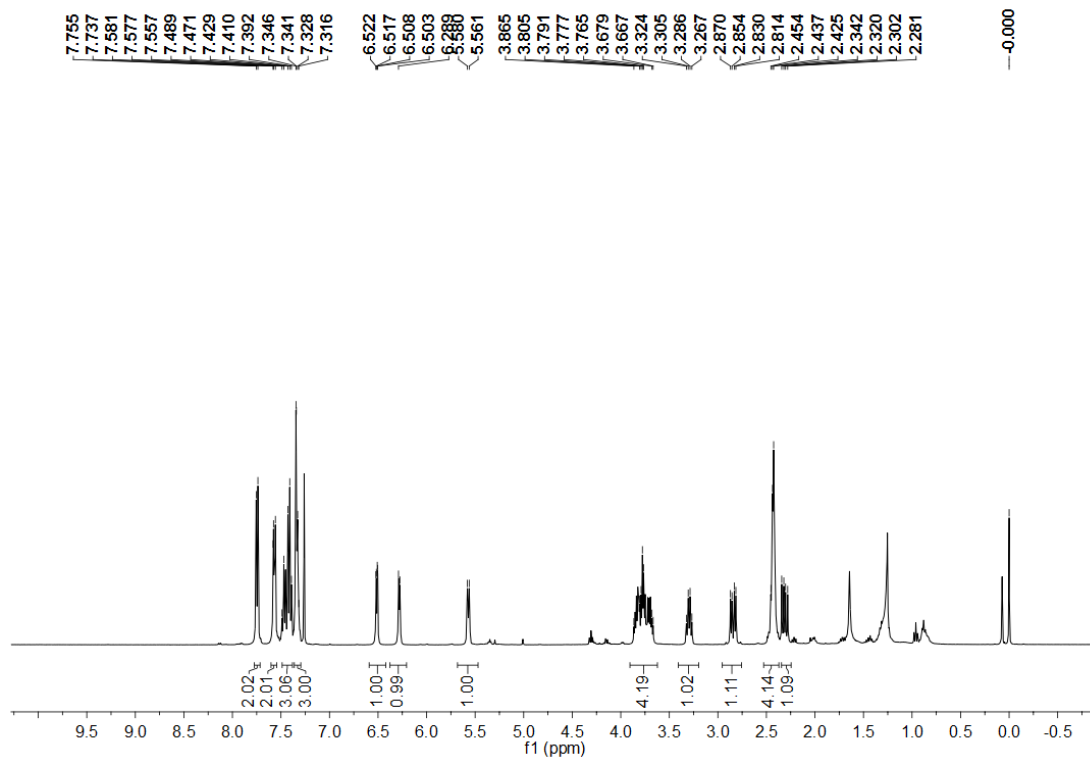
Data File D:\LC\DATA\WL\WL-FULVENE\PYRAN 2016-12-01 10-37-33\041-0101.D
Sample Name: pyran-rac

```
=================================================================
Acq. Operator   : LHC                        Seq. Line :   1
Acq. Instrument : Instrument 1                Location : Vial 41
Injection Date  : 12/1/2016 10:38:41 AM            Inj :   1
                                            Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\PYRAN 2016-12-01 10-37-33\IE-70-30-30MIN-254NM.M
Last changed    : 11/17/2016 3:01:35 PM by HR
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\PYRAN 2016-12-01 10-37-33\041-0101.D\DA.M (IE-
                  70-30-30MIN-254NM.M)
Last changed    : 11/20/2017 6:57:56 PM by SXS
                  (modified after loading)
```



```
=================================================================
                     Area Percent Report
=================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]  mAU   *s    [mAU  ]        %
----|-------|----|-------|----------|----------|--------|
  1  18.863 BB    0.4838 7371.16406  235.03664  49.8493
  2  22.818 BB    0.5980 7415.71777  188.81071  50.1507
```
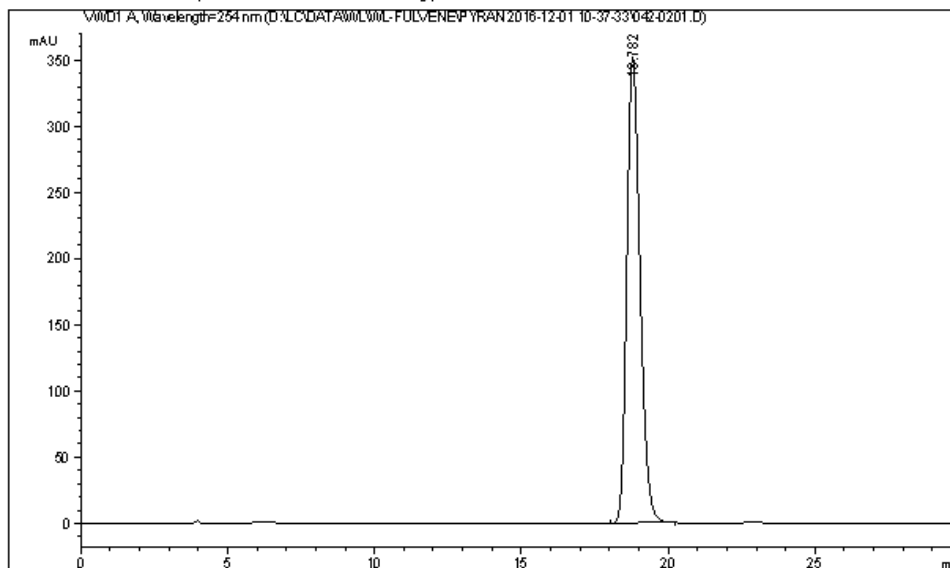
Instrument 1 11/20/2017 6:57:59 PM SXS   Page 1 of 2

Data File D:\LC\DATA\WL\WL-FULVENE\PYRAN 2016-12-01 10-37-33\042-0201.D
Sample Name: pyran-opt

```
==================================================================
Acq. Operator   : LHC                      Seq. Line :   2
Acq. Instrument : Instrument 1             Location : Vial 42
Injection Date  : 12/1/2016 11:10:06 AM         Inj :   1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\PYRAN 2016-12-01 10-37-33\IE-70-30-30MIN-254NM.M
Last changed    : 11/17/2016 3:01:35 PM by HR
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\PYRAN 2016-12-01 10-37-33\042-0201.D\DA.M (IE-
                  70-30-30MIN-254NM.M)
Last changed    : 11/20/2017 6:58:26 PM by SXS
                  (modified after loading)
```
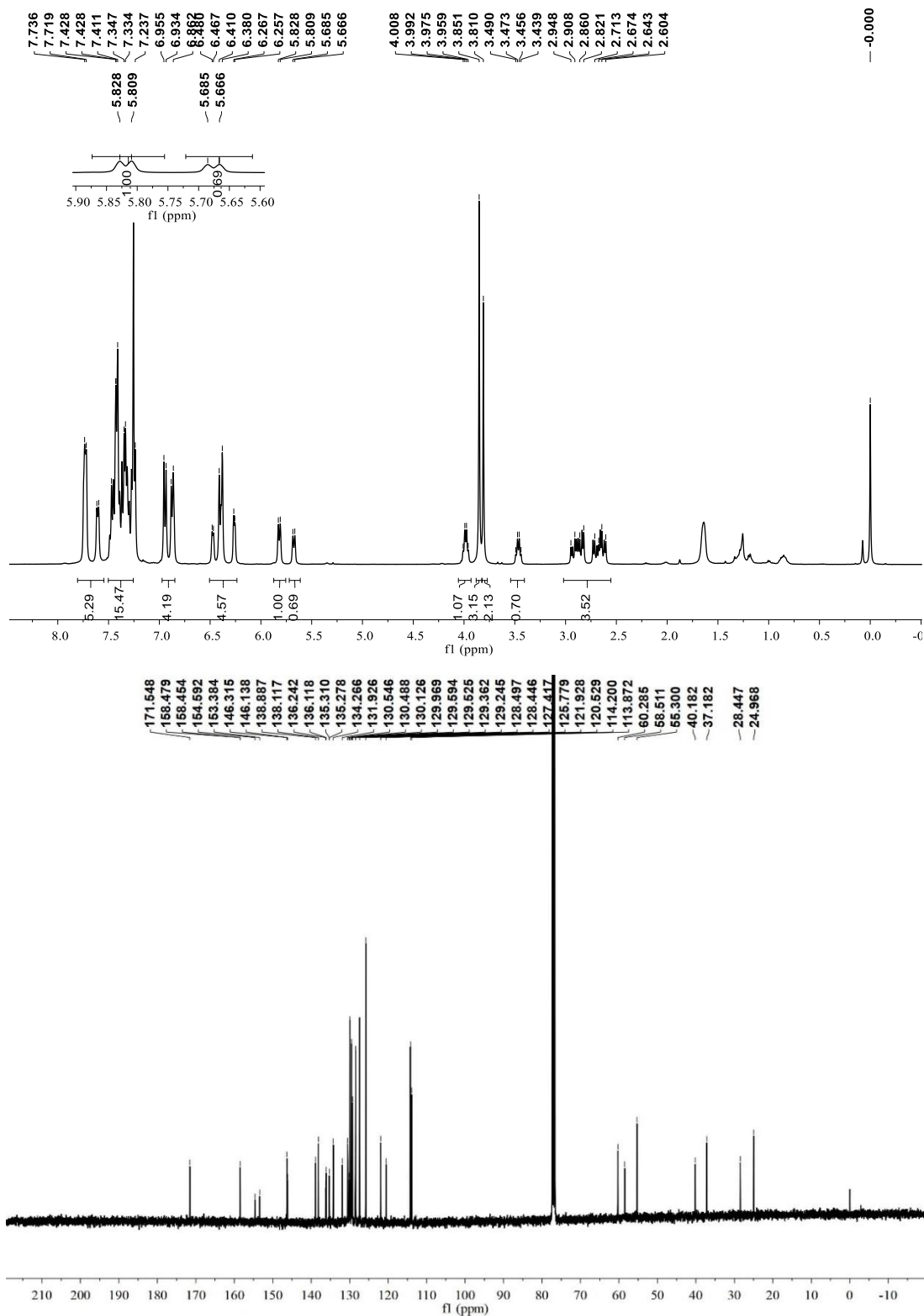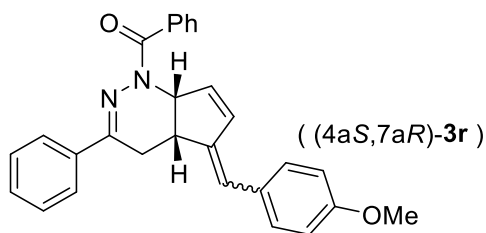


```
==================================================================
                     Area Percent Report
==================================================================

Sorted By             :        Signal
Multiplier            :        1.0000
Dilution              :        1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   mAU   *s     [mAU  ]      %
----|-------|----|-------|----------|----------|--------|
  1  18.782 BB    0.4854  1.10444e4   352.02325 100.0000
```

Instrument 1 11/20/2017 6:58:28 PM SXS   Page 1 of 2

((4a*S*,7a*R*)-**3r**)

Data File D:\LC\DATA\WL\WL-FULVENE\WL-P-OME-RAC 2016-12-10 16-35-47\051-0101.D
Sample Name: WL-p-OMe-RAC

```
================================================================
Acq. Operator   : LHC                      Seq. Line :    1
Acq. Instrument : Instrument 1              Location : Vial 51
Injection Date  : 12/10/2016 4:36:58 PM          Inj :    1
                                          Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\WL-P-OME-RAC 2016-12-10 16-35-47\AS-75-25-40MIN-
                  245NM.M
Last changed    : 12/10/2016 4:35:56 PM by LHC
                  (modified after loading)
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\WL-P-OME-RAC 2016-12-10 16-35-47\051-0101.D\DA.M
                  (AS-75-25-40MIN-245NM.M)
Last changed    : 11/20/2017 7:13:52 PM by SXS
                  (modified after loading)
```



```
================================================================
                      Area Percent Report
================================================================
```

```
Sorted By           :      Signal
Multiplier          :      1.0000
Dilution            :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```
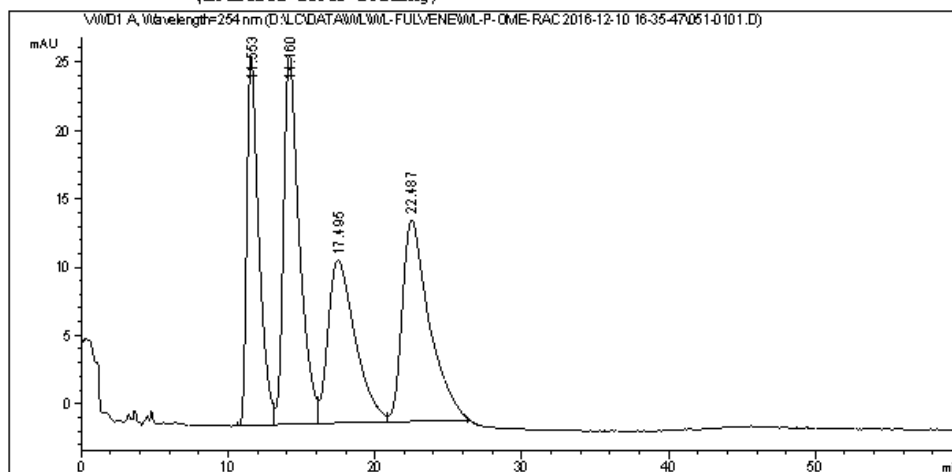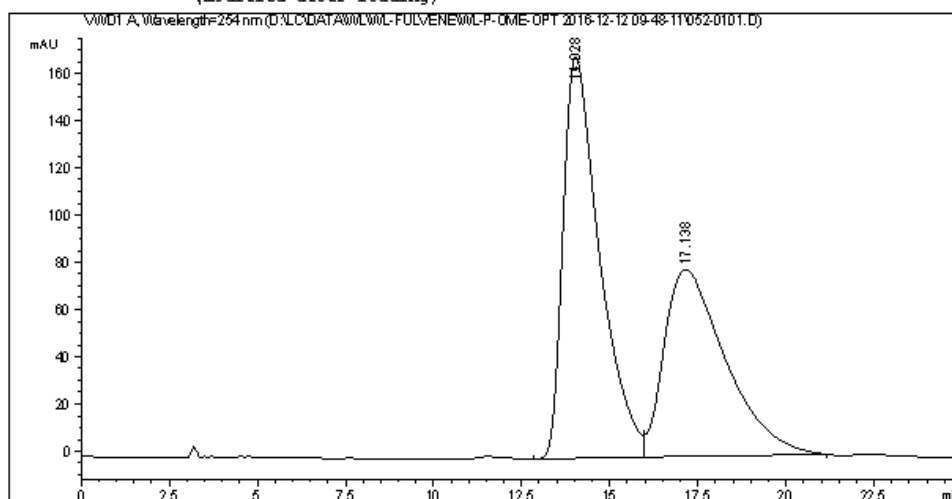
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.553	BB	0.8068	1538.50391	26.96998	22.0773
2	14.160	BV	1.0342	2018.63831	26.99029	28.9672
3	17.495	VV	1.5073	1528.81152	11.91370	21.9382
4	22.487	VB	1.5151	1882.75879	14.75334	27.0173

```
==================================================================
Acq. Operator   : LHC                        Seq. Line :   1
Acq. Instrument : Instrument 1                Location : Vial 52
Injection Date  : 12/12/2016 9:49:21 AM            Inj :   1
                                             Inj Volume : 5 µl
Acq. Method     : D:\LC\DATA\WL\WL-FULVENE\WL-P-OME-OPT 2016-12-12 09-48-11\AS-75-25-40MIN-
                  245NM.M
Last changed    : 11/16/2016 3:54:18 PM by LHC
Analysis Method : D:\LC\DATA\WL\WL-FULVENE\WL-P-OME-OPT 2016-12-12 09-48-11\052-0101.D\DA.M
                  (AS-75-25-40MIN-245NM.M)
Last changed    : 11/20/2017 7:12:55 PM by SXS
                  (modified after loading)
```
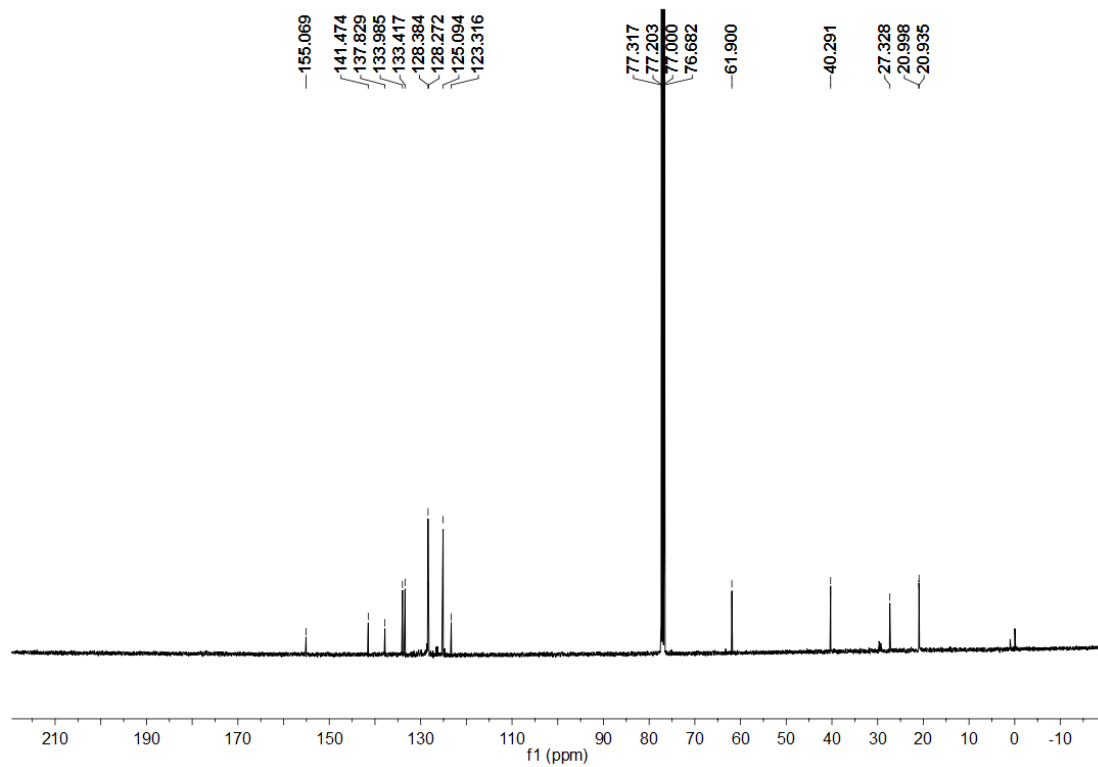


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]  mAU    *s    [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
  1  14.028 VV    1.0577 1.22597e4   170.11163  55.9214
  2  17.138 VB    1.6252 9663.42773   79.31624  44.0786

Totals :                  2.19232e4   249.42787
```

(4aS,7aR)-**4a**

7.614
7.610
7.593
7.380
7.376
7.359
7.340
7.330
7.327
7.309
7.261
6.496
6.493
6.482
6.479
5.739
5.726
4.475
4.454
3.322
3.304
3.286
3.268
2.794
2.778
2.389
2.337
1.837
1.777
0.000

2.12
3.37
1.00
0.93
0.91
0.99
1.09
1.06
2.99
3.08

10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

155.069
141.474
137.829
133.985
133.417
128.384
128.272
125.094
123.316
77.317
77.203
77.000
76.682
61.900
40.291
27.328
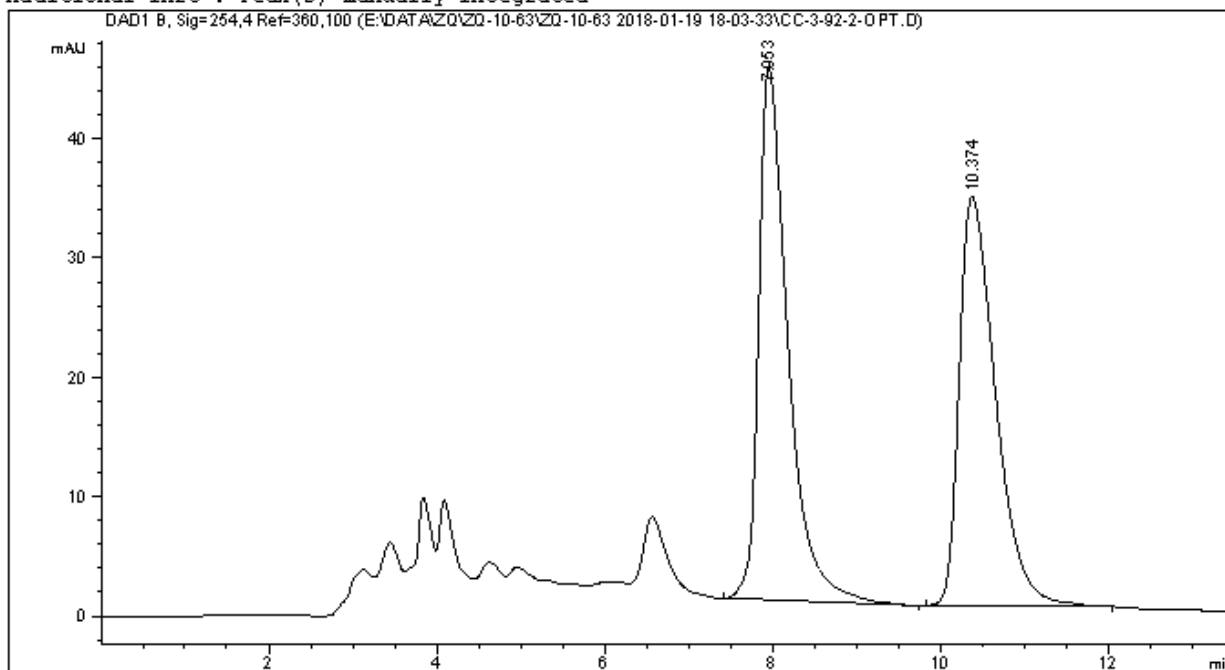20.998
20.935

210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Data File E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-19 18-03-33\CC-3-92-2-OPT.D
Sample Name: ZQ-10-63-rac

```
========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   1
Acq. Instrument : 1260                           Location :   71
Injection Date  : 1/19/2018 6:05:01 PM                Inj :   1
                                                Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-19 18-03-33\AD-80-20-254NM-15MIN.M
Last changed    : 1/19/2018 6:18:15 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-19 18-03-33\AD-80-20-254NM-15MIN.M (
                  Sequence Method)
Last changed    : 1/30/2018 5:36:34 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



```
========================================================================
                        Area Percent Report
========================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   7.953 BB   0.3615 1083.79163   44.59405  51.2522
  2  10.374 BB   0.4594 1030.83118   34.31964  48.7478

Totals :                 2114.62280   78.91369
```
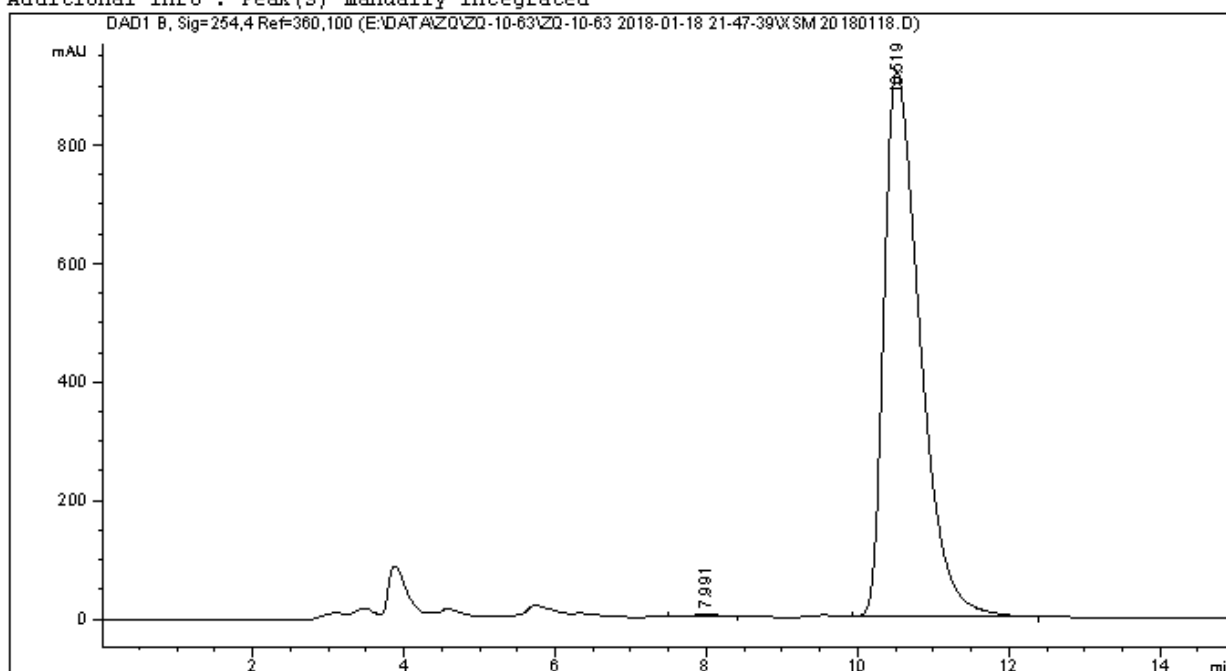
Data File E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\XSM 20180118.D
Sample Name: ZQ-10-63-opt

```
========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   1
Acq. Instrument : 1260                           Location :  79
Injection Date  : 1/18/2018 9:49:12 PM               Inj :   1
                                              Inj Volume : 10.000 µl
Acq. Method     : E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\AD-80-20-254NM-15MIN.M
Last changed    : 1/18/2018 10:02:47 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\AD-80-20-254NM-15MIN.M (
                  Sequence Method)
Last changed    : 1/30/2018 5:41:09 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
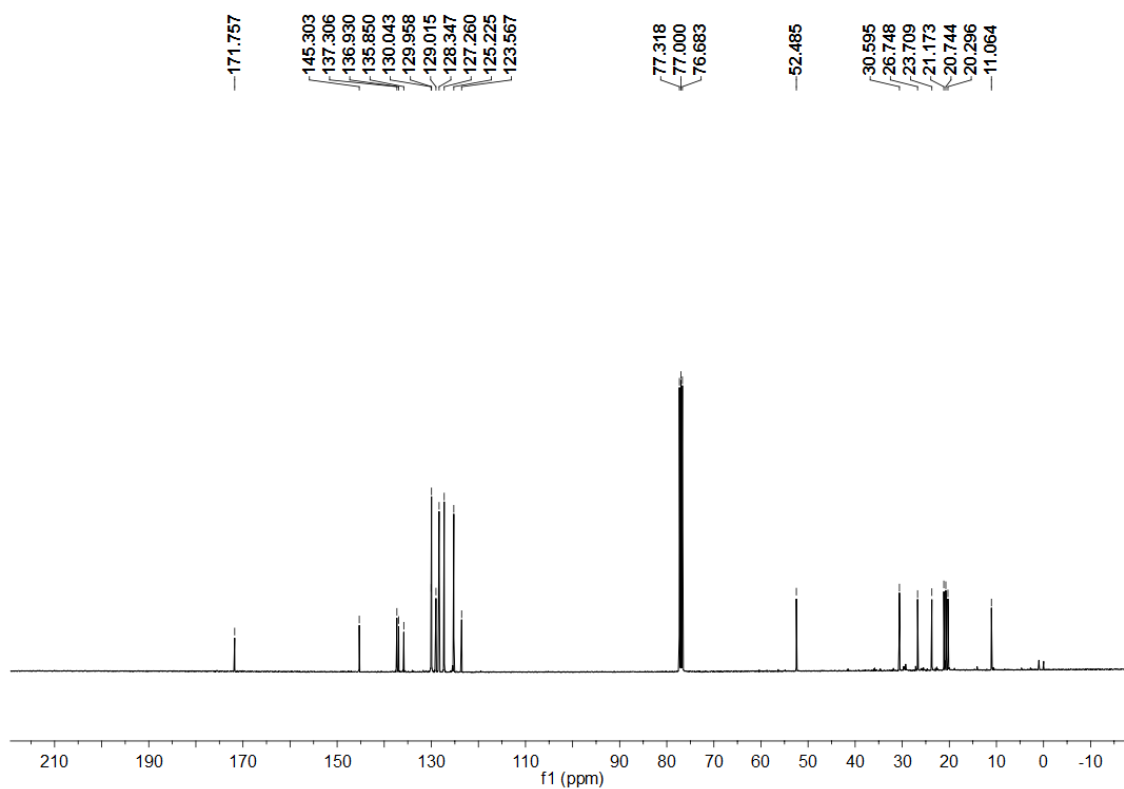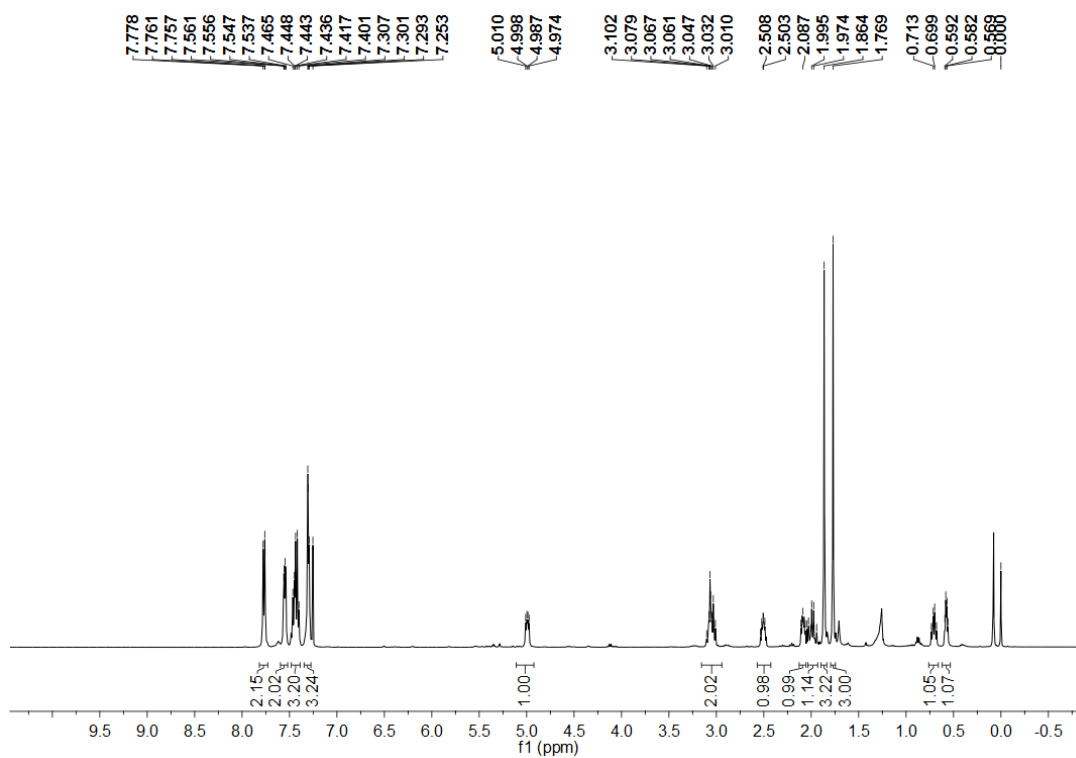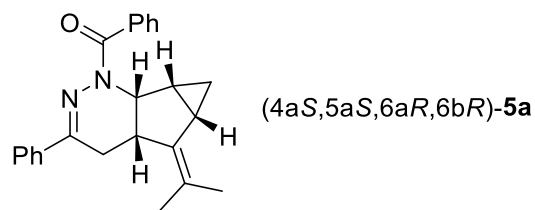


```
========================================================================
                         Area Percent Report
========================================================================

Sorted By            :       Signal
Multiplier           :       1.0000
Dilution             :       1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.991 BB   0.3144  111.74111     4.45842   0.3669
   2  10.519 BB   0.4973 3.03478e4    921.28625  99.6331

Totals :                 3.04595e4    925.74467
```
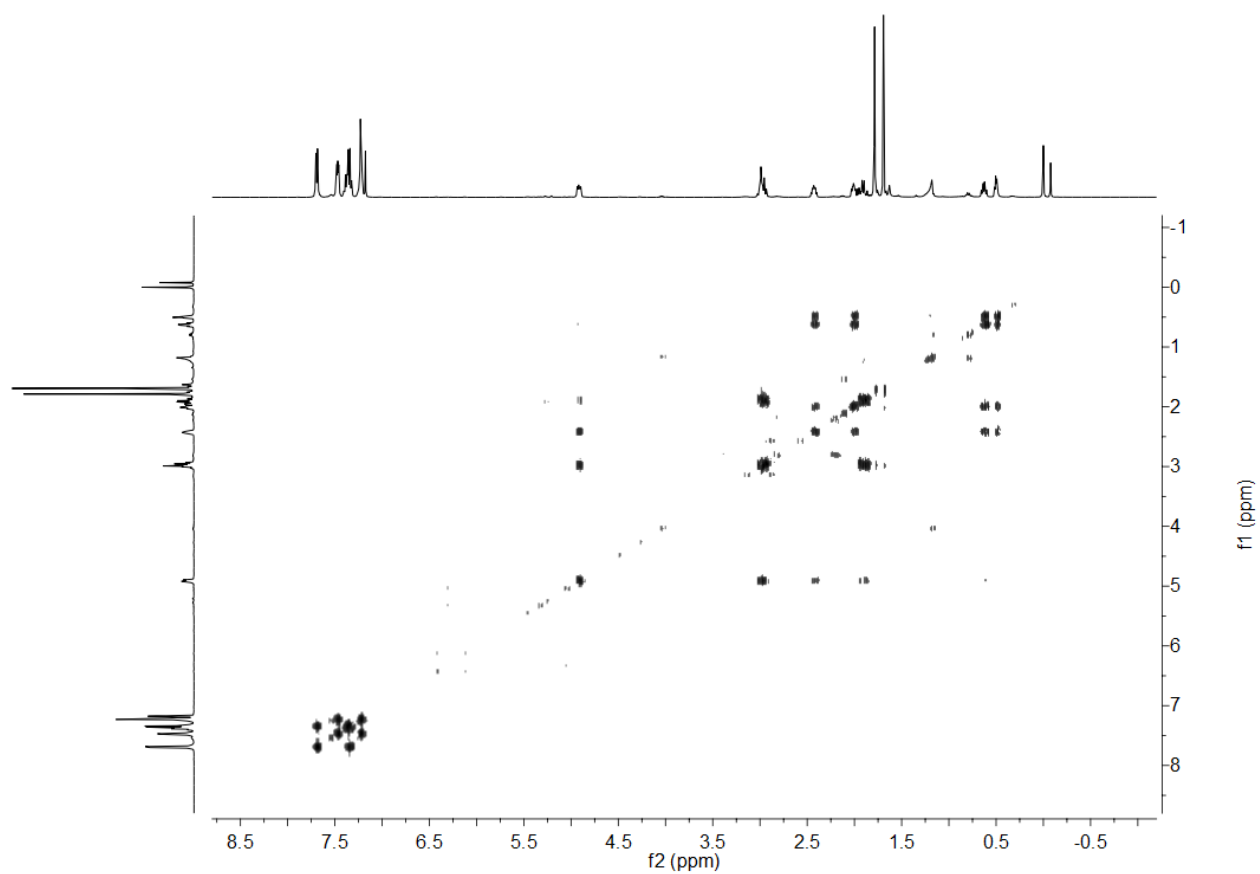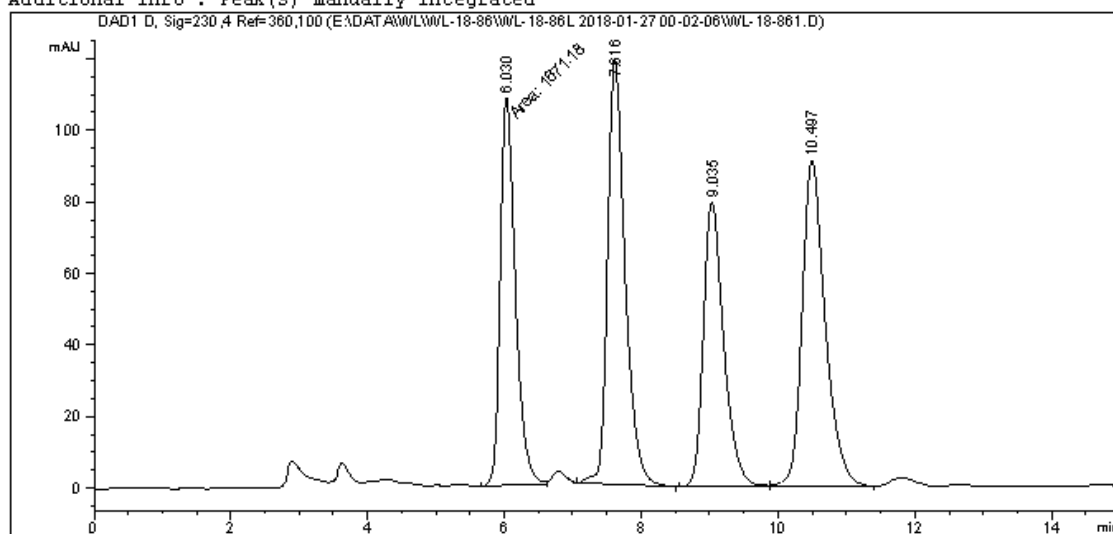
(4aS,5aS,6aR,6bR)-**5a**

```
========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Acq. Instrument : 1260                           Location :  98
Injection Date  : 1/27/2018 12:30:02 AM               Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WL\WL-18-86\WL-18-86L 2018-01-27 00-02-06\AdH-90-10-254NM-25min.M
Last changed    : 1/27/2018 12:45:10 AM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\WL\WL-18-86\WL-18-86L 2018-01-27 00-02-06\AdH-90-10-254NM-25min.M (
                  Sequence Method)
Last changed    : 1/30/2018 4:36:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```


DAD1 D, Sig=230,4 Ref=360,100 (E:\DATA\WL\WL-18-86\WL-18-86L 2018-01-27 00-02-06\WL-18-86l.D)

```
========================================================================
                        Area Percent Report
========================================================================

Sorted By          :       Signal
Multiplier         :       1.0000
Dilution           :       1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1   6.030 MF    0.2571 1671.18250   108.33324  22.2053
  2   7.616 BB    0.2681 2109.69629   118.28862  28.0320
  3   9.035 BB    0.3079 1625.44397    79.37770  21.5976
  4  10.497 BB    0.3515 2119.71777    90.76039  28.1651

Totals :                  7526.04053   396.75995
```

Data File E:\DATA\WL\WL-18-86\WL-18-86L 2018-01-27 00-02-06\WL-18-863.D
Sample Name: HUANBINGWAN-OPT-2

```
========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :    4
Acq. Instrument : 1260                           Location :  100
Injection Date  : 1/27/2018 1:03:18 AM               Inj :    1
                                              Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\WL\WL-18-86\WL-18-86L 2018-01-27 00-02-06\AdH-90-10-254NM-25min.M
Last changed    : 1/27/2018 12:45:10 AM by SYSTEM
Analysis Method : E:\DATA\WL\WL-18-86\WL-18-86L 2018-01-27 00-02-06\AdH-90-10-254NM-25min.M (
                  Sequence Method)
Last changed    : 1/30/2018 4:39:07 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



```
========================================================================
                         Area Percent Report
========================================================================

Sorted By           :      Signal
Multiplier          :      1.0000
Dilution            :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   6.031 MF   0.2593  6865.56592  441.22797  99.6823
  2   8.920 MM   0.3964    21.87943  9.19872e-1   0.3177

Totals :                 6887.44534  442.14784


========================================================================
                          *** End of Report ***
```
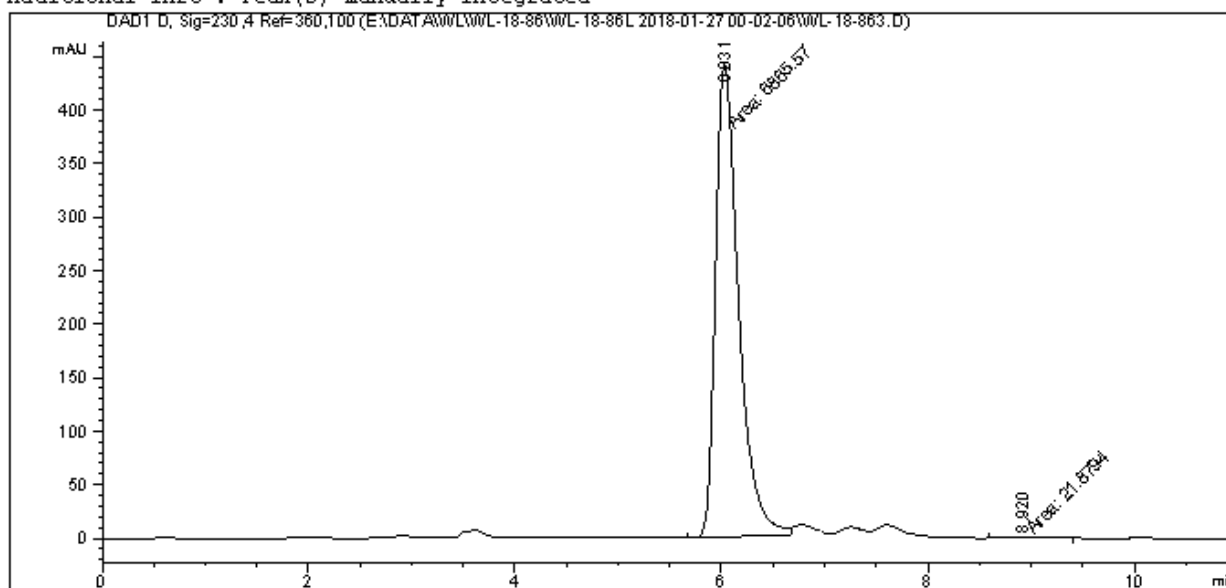
1260 1/30/2018 4:39:11 PM SYSTEM   Page 1 of 1