Electronic Supplementary Information for

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

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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, $\alpha$-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.
(4aS,7aR)-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; [α]$_D^{20}$ = −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.

(4aS,7aR)-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; [α]$_D^{20}$ = −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)\textendash}(3\textendash(3\text{-}chlorophenyl)\textendash5\text{-}((propan\text{-}2\text{-}ylidene)\textendash4,4a,5,7a\text{-}tetrahydro\textendash1H\textendashcyclopenta[c]pyridazin\textendash1\text{-}yl)(phenyl)methanone (table 2, entry 3): Yield (89\%); white solid; m.p. = 122 °C; [α]_{D}^{20} = -148.9 (c 0.23, CH_{2}Cl_{2}); \textsuperscript{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). \textsuperscript{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\textsuperscript{+}) Calcd. For C_{23}H_{22}ClN_{2}O ([M\text{+}H\textsuperscript{+}]): 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\textsubscript{R} = 6.34 and 8.90 min.

(4aS,7aR)\textendash}(3\textendash(2\text{-}chlorophenyl)\textendash5\text{-}((propan\text{-}2\text{-}ylidene)\textendash4,4a,5,7a\text{-}tetrahydro\textendash1H\textendashcyclopenta[c]pyridazin\textendash1\text{-}yl)(phenyl)methanone (table 2, entry 4): Yield (93\%); white solid; m.p. = 132 °C; [α]_{D}^{20} = -377.8 (c 0.23, CH_{2}Cl_{2}); \textsuperscript{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). \textsuperscript{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\textsuperscript{+}) Calcd. For C_{23}H_{22}ClN_{2}O ([M\text{+}H\textsuperscript{+}]): 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\textsubscript{R} = 7.28 and 10.22 min.
(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; [α]D20 = -654.8 (c 0.23, CH2Cl2); 1H NMR (400 MHz, CDCl3) 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). 13C NMR (101 MHz, CDCl3) 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 C23H22FN2O ([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); tR = 6.68 and 10.26 min.

(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; [α]D20 = -539.2 (c 0.23, CH2Cl2); 1H NMR (400 MHz, CDCl3) 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). 13C NMR (101 MHz, CDCl3) δ 171.7, 149.3, 140.5, 135.5, 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 C23H22BrN2O ([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); tR = 6.65 and 9.20 min.
(4aS,7aR)-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; [α]$_D^{20}$ = -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.

(4aS,7aR)-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; [α]$_D^{20}$ = -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$_{23}$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.
(4aS,7aR)-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; [α]D = -552.0 (c 0.23, CH2Cl2); 1H NMR (400 MHz, CDCl3) 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 = 5.2 Hz, 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). 13C NMR (101 MHz, CDCl3) 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 C24H25N2O+ ([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); tR = 6.98 and 17.65 min.

(4aS,7aR)-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; [α]D = -660.0 (c 0.23, CH2Cl2); 1H NMR (400 MHz, CDCl3) 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). 13C NMR (101 MHz, CDCl3) 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 C24H25N2O2 ([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, \( \lambda = 254 \) nm); \( t_r = 7.64 \) and 10.34 min.

\((4aS,7aR,3k)\)

\((4aS,7aR)-(3-(naphthalen-2-yl)-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone \text{(table 2, entry 11)}: \) Yield (59\%); white solid; m.p. = 130 °C; \([\alpha]^{20}_{D} = -618.6 \text{ (c 0.23, CH}_2\text{Cl}_2)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.95 \) (s, 1H), 7.79 – 7.70 (m, 6H), 7.46 – 7.41 (m, 5H), 6.50 – 6.48 (m, 1H), 6.22 (d, \( J = 5.2 \text{ Hz, 1H} \)), 5.53 (d, \( J = 7.2 \text{ Hz, 1H} \)), 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, CDCl\(_3\)) \( \delta 171.7, 150.3, 140.6, 134.1, 134.0, 131.6, 130.3, 130.0, 128.4, 128.1, 127.6, 127.3, 126.7, 126.3, 125.3, 124.0, 123.0, 58.7, 35.8, 25.7, 21.1, 20.8. \) 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, \( \lambda = 254 \) nm); \( t_r = 6.69 \) and 9.73 min.

\((4aS,7aR)-(5-(pentan-3-ylidene)-3-phenyl-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazin-1-yl)(phenyl)methanone: \) Yield (95\%); white solid; m.p. = 90 °C; \([\alpha]^{20}_{D} = -618.6 \text{ (c 0.23, CH}_2\text{Cl}_2)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.75 \) (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, \( J = 7.3 \text{ Hz, 1H} \)), 3.24 – 3.18 (m, 1H), 2.92 – 2.87 (m, 1H), 2.27 – 2.20 (m, 5H), 1.12 (t, \( J = 7.5 \text{ Hz, 3H} \)), 1.03 (t, \( J = 7.5 \text{ Hz, 3H} \)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 171.7, 150.5, 140.0, 136.6, 136.1, 135.5, 134.6, 131.5, 130.3, 130.0, 129.3, 128.4, 127.3, 125.6, 58.4, 35.3, 26.7, 25.4, 24.4, 13.9, 13.5. \) 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.

(4aS,7aR)- (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; [α]_D^{20} = -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 C₂₄H₂₃N₂O ([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.

(4aS,7aR)- (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; [α]_D^{20} = -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, 129.3, 128.4, 127.3, 125.6, 59.1, 37.3, 31.0, 30.8, 26.6, 26.4, 25.1. HRMS (ESI+) Calcd. For C₂₅H₂₅N₂O ([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.

(4aS,7aR)-(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; [α]^{20}_{D} = -596.4 (c 0.23, CH₂Cl₂);

^1^H NMR (400 MHz, CDCl₃) 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). ^1^C NMR (101 MHz, CDCl₃) 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); tᵣ = 16.52 and 18.15 min.

(4aS,7aR)-(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; [α]^{20}_{D} = -582.3 (c 0.23, CH₂Cl₂);

^1^H NMR (400 MHz, CDCl₃) δ 7.76 – 7.74 (m, 2H), 7.57 – 7.56 (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). ^1^C NMR (101 MHz, CDCl₃) 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_{26}N_{2}O ([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, \( \lambda = 254 \text{ nm} \)); \( t_r = 13.90 \) and 14.48 min.

(4aS,7aR) - 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; \([\alpha]_{D}^{20} = -293.6 \) (c 0.23, CH_{2}Cl_{2}); \(^1H\) NMR (400 MHz, CDCl_{3}) \( \delta \): 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, \( J = 5.6, 2.0 \text{ Hz}, 1\text{H} \)), 6.28 (d, \( J = 5.2 \text{ Hz}, 1\text{H} \)), 5.57 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 3.87 – 3.67 (m, 4H), 3.32 – 3.27 (m, 1H), 2.84 (dd, \( J = 16.0, 6.4 \text{ Hz}, 1\text{H} \)), 2.45 – 2.43 (m, 4H), 2.31 (dd, \( J = 16.0, 8.8 \text{ Hz}, 1\text{H} \)). \(^{13}C\) NMR (101 MHz, CDCl_{3}) \( \delta \): 171.7, 150.9, 139.7, 136.4, 135.6, 135.4, 130.6, 130.4, 130.0, 129.4, 128.5, 127.4, 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_{2}O_{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, \( \lambda = 254 \text{ nm} \)); \( t_r = 18.86 \) and 22.82 min.

(4aS,7aR)-(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; \([\alpha]_{D}^{20} = -796.4 \) (c 0.23, CH_{2}Cl_{2}); \(^1H\) NMR (400 MHz, CDCl_{3}) \( \delta \): 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, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 5.68 (d, \( J = 7.6 \text{ Hz}, 0.7\text{H} \)), 3.98 (q, \( J = 6.4 \text{ Hz}, 1\text{H} \)), 3.85 (s, 3\text{H} \)), 3.81 (s, 2.1H), 3.46 (q, \( J = 6.8 \text{ Hz}, 0.7\text{H} \)), 2.95 – 2.60 (m, 3.4H). \(^{13}C\) NMR (101 MHz, CDCl_{3}) \( \delta \): 171.5, 158.47, 158.45, 154.6, 153.4, 146.3, 146.1,
138.9, 138.1, 136.2, 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_{2}O_{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

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 (0.3 mmol) was added to a dry solution of diazomethane (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)-3-phenyl-5-(propan-2-ylidene)-4,4a,5,7a-tetrahydro-1H-cyclopenta[c]pyridazine:
Yield (85%); brown solid; m.p. = 21 °C; [α]_D^30 = -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). \(^1^3\)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.

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; [α]_D^30 = -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). \(^1^3\)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


5 NMR and HPLC spectra
Area Percent Report

Signal at Wavelength 254 nm

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Sample Name: S4H-5-45-50

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Seq. Line: 3

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Area Percent Report

Area: 100.0000

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Total: 5.356356 1747.00256

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Page 1 of 1
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Sample Name: SIM-5-50-9

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Inj: 1

Injection Volume: 5 µl

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Last Changed: 3/19/2015 11:36:02 AM by WEP

Area Percent Report
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Sorted By: Signal
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Dilution: 1.0000

Use Multiplier & Dilution Factor with ID70m

Signal L: VARI A, Wavelength=254 nm

Peak Ret Time Type Width Area Height Area
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1 6.382 NR 0.3371 1.6397 844 55835 99.738
2 8.890 W 0.5556 742.6004 19.22958 4.2045

Totals: 1.7323 661.70797

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Instrument 1 3/14/2015 10:21:34 PM WEP

Page 1 of 1
Area Percent Report

Signal at 254 nm

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Area Percent Report

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISSTDs

Signal 1: Wavelength-254 nm

Peak RetTime  Type  Width  Area  Height  Area
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1  6.829  0.0001  2.572  1048.631  285  2228
2  10.544 0.0142  2.895  5197.1487 49.0776

Totals : 5197.1487 49.0776

Instrument 1 3/14/2016 10:14:17 PM WEP

Page 1 of 1

Sample Name: S2H-5-50-L1

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Area Percent Report

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Instrument 1 3/14/2016 10:31:05 PM WFP
(4aS,7aR)-3h

**Graphical Representation**

- Molecular structure
- NMR spectrum with peaks labeled

**NMR Data**

- Peak frequencies and chemical shifts are indicated.

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S36
Area Percent Report

Sorted By: Signal
Multiplier: 1.000
Dilution: 1.000
Use Multiplier & Dilution Factor with IS70m

Signal in VAnil A, Wavelength-254 nm

Peak Ret Time Type Width Area Height Area
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1 5.999 W 0.3302 2.048569 936.22241 98.9824
2 7.860 W 0.4711 213.57714 6.23665 1.0776

Totals: 2.562061 936.45916

Instrument 1 3/14/2016 10:29:36 PM WEP

Page 1 of 1
Area Percent Report

Signal at Wavelength=254 nm

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2 10.384 RN 0.5404 4202 44529 1812 23439 49.5088

Totals : 1.67736e+4 432.55973

Instrument 1 5/14/2016 10:13:41 PM WFP
Sample Name: SIM-5-10-9

**Area Percent Report**

**Sorted By**: Signal
**Multiplier**: 1.0000
**Dilution**: 1.0000

*Use Multiplier & Dilution Factor with IS706*

**Signal**: UV-Vis A, Wavelength=254 nm

**Peak RetTime Type** | **Width** | **Area** | **Height** | **Area**
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**Totals**: 11313.64 364.37325

**Data File**: D:\LCO\DAT\294.929\SIM-5-10-9\SIM-5-10-9 2015-03-31 17-38-59,062-9201.D

**Sample Name**: SIM-5-10-9

**Injection Date**: 3/31/2015 3:38:29 PM
**Inj Volume**: 5 µl

**Last Changed**: 3/31/2015 12:05:44 PM by LHC

**Analysis Method**: D:\LCO\DAT\294.929\SIM-5-10-9\SIM-5-10-9 2015-03-31 17-38-59,062-9201.D, R.B. (A11-09-00-046-0011.R.0)

**Last Changed**: 3/31/2015 10:30:24 PM by WEP

(modified after loading)
Area Percent Report

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**Area Percent Report**

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Dilution: 1.0000

Use Multiplier & Dilution Factor with ISEs

Signal is VDA 1, Wavelength=254 nm

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Instrument 1 11/20/2017 7:08:36 PM SGS
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Sample File: SEM-3-46-C

Area Percent Report

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Instrument: 1 5/10/2016 9:49:33 PM WEF
(4aS,7aR)-3n
Area Percent Report

Signal 1: Wavelength=354 nm

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S55
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Sample Name: 50701911-5600-23-03-2

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Acq. Instrument : INSTRUMENT 1
Location : Vial 62
Injection Date : 4/28/2015 1:25:01 PM
[Inj. Volume : 5 µL]
Last Changed : 4/28/2015 1:50:20 PM by WZ
Last Changed : 5/14/2016 9:00:44 PM by WZ

(Modified after loading)

Area Percent Report

Sealed By : Signal
Multiplier : 1.0000
Division : 1.0000
Use Multiplier & Division Factor with SDS

Signal 1: VM1 A, Wavelength=354 nm

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1 15.595 EV 0.440 2.240 95.9223 0.8986
2 17.113 VII 0.467 2.81590646 95.9223 0.8986

Total: 2.81590646 95.9223 0.8986

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INSTRUMENT 1 5/14/2016 9:40:48 PM WZ

Page 1 of 1
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- **Sample Name**: VL-Naphtene

**Analysis Information**

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- **Location**: Vial 41
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- **Injection**: 1
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- **Analysis Method**: D:\LC\DATA\VL\VL-SULFENE\VL-SULFENE-2 2016-11-16 20-06-10\041-01G.L.D\DATA.M
  - **Latest Change**: 11/25/2017 7:32:12 PM by SGS

**Area Percent Report**

**Sorted By**: Signal
**Multiplier**: 1.0000
**Dilution**: 1.0000

Use Multiplier & Dilution Factor with IS/DE

**Signal**: 254 nm, Wavelength: 254 nm

<table>
<thead>
<tr>
<th>Peak SetTime Type</th>
<th>UVabs</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[mm]</td>
<td>[AU]</td>
<td>[AU]</td>
<td>[AU]</td>
</tr>
<tr>
<td></td>
<td>-------</td>
<td>------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>13.904 W</td>
<td>0.3109</td>
<td>5407.17432</td>
<td>271.50076</td>
</tr>
<tr>
<td>2</td>
<td>14.485 W</td>
<td>0.3556</td>
<td>5634.65967</td>
<td>241.16479</td>
</tr>
</tbody>
</table>

**Totals**: 1.1101864, $512.74557$

**Instruments**: 1
- **Date**: 11/20/2017 7:10:15 PM
- **User**: SGS

---

**S61**
### Area Percent Report

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplier</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**Use Multiplier & Dilution Factor with ISIDS**

#### Signal 1: 254 A, Wavelength-254 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td># [Min]</td>
<td>[Min] [DAU]</td>
<td>[DAU]</td>
<td>[DAU]</td>
</tr>
<tr>
<td>1 18.863 HB 0.4938 7301.16406</td>
<td>235.05664</td>
<td>49.849</td>
<td></td>
</tr>
<tr>
<td>2 22.818 HB 0.6280 7415.71777</td>
<td>188.81871</td>
<td>49.1867</td>
<td></td>
</tr>
</tbody>
</table>

Instrument 1 11/20/2017 6:57:39 PM SGS
Signal in VWD A, Wavelength=554 nm

<table>
<thead>
<tr>
<th>Peak Set/Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>[min]</td>
<td></td>
<td>[cm]</td>
<td>[AU]</td>
</tr>
<tr>
<td>1</td>
<td>14.160</td>
<td>0.343</td>
<td>1452.150</td>
<td>26.993</td>
<td>21.196</td>
</tr>
<tr>
<td>3</td>
<td>22.483</td>
<td>1.064</td>
<td>1858.785</td>
<td>27.607</td>
<td>22.607</td>
</tr>
</tbody>
</table>

Instrument: 11/20/2017 7:13:56 PM SGS
Data File: D:\LC\DATA\XL\UL-PULVENEXUL-F-ONE-077 2016-12-12 09-48-11\052-0101.0
Sample Name: UL-P-OHE-077

------------------------------------------------------------------------
Acq. Operator : JNC  Seq. Line : 1
Acq. Instrument : Instrument 1  Location : Vial 52
Injection Date : 12/12/2016 9:49:21 AM  Enl : 1
Inj Volume : 5 µl
Acq. Method : D:\LC\DATA\XL\UL-PULVENEXUL-F-ONE-077 2016-12-12 09-48-11\AS-75-25-42MIN-2455NM
Last changed : 11/16/2016 8:44:18 PM by JNC
Analysis Method : D:\LC\DATA\XL\UL-PULVENEXUL-F-ONE-077 2016-12-12 09-48-11\052-0101.0\DATA.M
[AS-75-25-42MIN-2455NM]
Last changed : 11/20/2017 7:12:58 PM by RCS

---

Area Percent Report

---

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

Signal at Wavelength=254 nm

Peak RetTime Type Width Area Height Area
#  [min]  [min]  [nAU]  %  [nAU]  %
---|--------|--------|--------|--------|
1  14.028  W  1.057  1.23997e+4  170.11163  55.5214
2  17.138  W  1.6282  9668.42773  79.3824  44.6286

Totals :  2.13213e4  249.42787

Instrument 1 11/20/2017 7:12:38 PM RCS

Page 1 of 2
### Data File E:\DATA\ZQ-10-63\ZQ-10-63 2018-01-19 18-03-33\CC-3-92-2-0PT.D

Sample Name: ZQ-10-63 rac

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acq. Operator</td>
<td>SYSTEM</td>
</tr>
<tr>
<td>Acq. Instrument</td>
<td>1260</td>
</tr>
<tr>
<td>Injection Date</td>
<td>1/19/2018 5:05:01 PM</td>
</tr>
<tr>
<td>Inj. Volume</td>
<td>5.000 µl</td>
</tr>
<tr>
<td>Acq. Method</td>
<td>E:\DATA\ZQ-10-63\ZQ-10-63 2018-01-19 18-03-33\AD-80-20-254MM-15MIN.M</td>
</tr>
<tr>
<td>Last changed</td>
<td>1/19/2018 5:10:15 PM by SYSTEM</td>
</tr>
<tr>
<td>Analysis Method</td>
<td>E:\DATA\ZQ-10-63\ZQ-10-63 2018-01-19 18-03-33\AD-80-20-254MM-15MIN.M</td>
</tr>
<tr>
<td>Last changed</td>
<td>1/30/2018 5:36:34 PM by SYSTEM</td>
</tr>
<tr>
<td>Additional Info</td>
<td>Peak(s) manually integrated</td>
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</tbody>
</table>

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### Area Percent Report

<table>
<thead>
<tr>
<th>Signal</th>
<th>Multiplier</th>
<th>Dilution</th>
<th>Do not use Multiplier x Dilution Factor with ISIDs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0000</td>
<td>1.0000</td>
<td></td>
</tr>
</tbody>
</table>

**Signal 1: DAD1 B, Sig=254-4 Ref=360,103**

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[µA/s]</td>
<td>[µA]</td>
<td>%</td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>7.953</td>
<td>0.3515</td>
<td>1088.79136</td>
<td>44.59405</td>
<td>51.2522</td>
</tr>
<tr>
<td>2</td>
<td>10.374</td>
<td>0.4894</td>
<td>1030.83118</td>
<td>34.31964</td>
<td>48.7478</td>
</tr>
</tbody>
</table>

**Totals:**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2114.62290</td>
<td>78.91359</td>
<td></td>
</tr>
</tbody>
</table>

---

1260 1/30/2018 5:36:38 PM SYSTEM

Page 1 of 2

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S70
Data File E:\DATA\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\XM 2018G118.D
Sample Name: ZQ-10-63-opt

===================================================================================================
Acq. Operator : SYSTEM  Seq. Line : 1
Acq. Instrument : 1260  Location : 79
Injection Date : 1/10/2018 9:49:12 PM  Tag : 1
Inj Volume : 10.000 μl
Acq. Method : E:\DATA\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\AD-80-20-254MM-15MIN.M
Last changed : 1/10/2018 10:02:50 PM by SYSTEM
(modified after loading)
Analysis Method : E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\AD-80-20-254MM-15MIN.M
(modified after loading)
Analysis Method : E:\DATA\ZQ\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\AD-80-20-254MM-15MIN.M
Last changed : 1/30/2018 5:31:09 PM by SYSTEM
(modified after loading)
Addional Info : Peak(s) manually integrated

Diagnostic File, Sig=254,q Ref=300,100 (E:\DATA\ZQ-10-63\ZQ-10-63 2018-01-18 21-47-39\XM 2018G118.D)

===================================================================================================

Area Percent Report

===================================================================================================

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

Signal 1: DAD1 B, Sig=254,q Ref=300,100

Peak RetTime Type Width  Area  Height  Area
#  [min]  [min]  [μAU/sec]  [μAU]   %
---|--------|--------|----------|--------|
1  7.991  BB  0.3144  111.74111  4.45942  0.3669
2 10.519  BB  0.4973  3.05478e4  921.28525 99.6331

Totals :  3.05478e4  925.74457

1260 1/30/2018 5:41:13 PM SYSTEM
Area Percent Report

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

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

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.030</td>
<td>MF</td>
<td>0.2533</td>
<td>6665.56592</td>
<td>441.22797</td>
<td>95.6983</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.920</td>
<td>MH</td>
<td>0.3964</td>
<td>21.87543</td>
<td>9.19972e-1</td>
<td>0.3177</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 6007.44534 442.14704

*** End of Report ***