Electronic Supplementary Information

Catalytic asymmetric aminolactonization of 1,2-disubstituted alkenoic acid esters: Efficient construction of aminolactones with all carbons quaternary stereo-centre

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Experimental Section

A) General
B) General procedure for the preparation of 4-arylbut-3-enoic acid
C) General procedure for the preparation of tert-butyl 4-arylbut-3-enoate
D) General procedure for the preparation of (E)-tert-butyl 5-arylpent-4-enoate
E) General Procedure for one-pot enantioselective Synthesis of N-nosyl-4-amino-5-arylbutyrolactones and N-nosyl-5-amino-6-arylvalerolactones (3a-i, 10, 7a-d and 13a-d)
F) Spectral Data of N-nosyl-4-amino-5-arylbutyrolactones and N-nosyl-5-amino-6-arylvalerolactones (3a-i, 10, 7a-d and 13a-d)
G) Spectral Data of alkenoic acid esters (1a-i, 8, 5a-d, 11a-d and 1a"
H) Synthesis and Spectral Data of compounds 14-16 and 2a"
I) References
J) NMR Spectra
K) 1D-nOe Spectra of compound 13a
L) HPLC Chromatograms
A) General:
All reactions were conducted using oven-dried glassware under an atmosphere of Argon (Ar). Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Flash chromatography was carried out using silica gel (230-400 mesh). TLC was performed on aluminium-backed plates coated with silica gel 60 with F254 indicator.
The $^1$H NMR spectra were recorded with a 200 and a 400 MHz and $^{13}$C NMR spectra were recorded with a 50 and a 100 MHz using CDCl$_3$, d$_6$-DMSO and CD$_3$OD. $^1$H NMR chemical shifts are expressed in parts per million ($\delta$) relative to CHCl$_3$ ($\delta = 7.26$), d$_6$-DMSO ($\delta = 2.48$) and CD$_3$OD ($\delta = 3.34$); $^{13}$C NMR chemical shifts are expressed in parts per million ($\delta$) relative to the CDCl$_3$ resonance ($\delta = 77.0$), d$_6$-DMSO ($\delta = 40.1$) and CD$_3$OD ($\delta = 49.2$). High resolution mass spectra (HRMS) were obtained under positive electron spray ionization (m/z values are given). HPLC analyses were done by Chiralpak IA column and IC column (4.6 mm $\times$ 250 mm and particle size 5µm and 3µm). Specific optical rotation values were measured on a Jasco-P1200 polarimeter. NOE experiment was done in 500 MHz NMR.

B) General procedure for the preparation of 4-arylbut-3-enoic acid:

(2-carboxyethyl)triphenylphosphonium bromide (1.2 eq) was suspended in dry THF. Aryl aldehyde (1 eq) was added. The mixture was cooled to – 78 $^0$C, then a solution of t-BuOK (2.5 eq) in dry THF was added continuously over 2 h. The reaction was stirred for 12-18 h during which it was allowed to warm to RT. The reaction was monitored by TLC analysis and after completion of the reaction THF was evaporated. 100 mL H$_2$O and 100 mL DCM was added. Aqueous layer was separated and acidified with 1(N) HCl up to pH=1. 100 ml Et$_2$O was added. The layers were separated and the aqueous layer was extracted with Et$_2$O (2 x100 mL). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was removed in vacuum (40 $^0$C). After flash chromatography on silica gel with hexane/EtOAc (3:1) 4-arylbut-3-enoic acids were obtained as a yellow solid (yield 50-65%).
C) General procedure for the preparation of tert-butyl 4-arylbut-3-enoate¹:

In a two-necked flask equipped with a magnetic stirring bar, anhydrous MgCl₂ (0.10 eq), BOC₂O (1.3 eq) and 4-arylbut-3-enoic acid (1.0 eq) were dissolved in 'BuOH (2.0eq). The mixture was stirred at 40 °C and for 2-3 days and monitored by TLC analysis. The crude reaction mixture was diluted with H₂O (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was separated, dried (MgSO₄) and filtered, and the solvent was removed by rotary evaporation. The crude mixture was then subjected for column chromatography on silica gel with light petroleum ether/Et₂O (9:1). The tert-butyl 4-arylbut-3-enoate esters 1a-g were obtained as light yellow oil (yield 85-95%).

D) General procedure for the preparation of (E)-tert-butyl 5-arylpent-4-enoate²:

To a heat-dried two-necked round-bottomed flask were added freshly distilled diisopropylamine (1.05 eq) and dry THF under argon. This solution was cooled to -78 °C, and n-BuLi (2.5 M in hexane, 1.05 eq) was then added via syringe. The mixture was stirred for 45 min, followed by addition of tert-butyl acetate (1 eq). The reaction mixture was stirred for 1 h. The resulting ester enolate-solution was was slowly added at -78 °C to the solution of bromide (1 eq) in THF via syringe. After stirring for 4 h at -78 °C the reaction mixture was quenched by addition of saturated NH₄Cl solution and allowed to warm up to room temperature. Then THF was evaporated and the aqueous layer was extracted with EtOAc. The combined extractes were dried over anhydrous MgSO₄, and concentrated under reduced
pressure. Flash chromatography on silica gel eluting with light petroleum ether/Et\_2O (9:1) furnished (E)-tert-butyl 5-arylpent-4-enoate esters 5a-b light yellow oil (yield 70-75%).

Aziridine reagents Ph\textsubscript{INSO}_2(4-NO\textsubscript{2}-C\textsubscript{6}H\textsubscript{4}) [Ph\textsubscript{INNs}] were prepared by literature procedure.\textsuperscript{3}

C2-symmetric bis-oxazoline ligands 4a-g were synthesized by following literature procedure.\textsuperscript{4}

**E) General Procedure for one-pot enantioselective Synthesis of N-nosyl-4-amino-5-arylbutyrolactones and N-nosyl-5-amino-6-arylvalerolactones**\textsuperscript{5} (3a-g, 10, 7a-b):

A 10 mL two-necked round bottom flask was charged with bis-oxazoline ligand 4g (0.010g, 0.0279 mmol, 0.12 equiv), Cu(OTf)\textsubscript{2} (0.009 g, 0.0248 mmol, 0.10 equiv) and 0.2 g of powdered molecular sieves (4Å). Anhydrous chloroform (1.2 mL) was injected and the resulting mixture was stirred for 30 min at rt. Then the reaction mixture was placed at 40° C and to this solution, substrate 1 (0.389 g, 1.23 mmol, 5.0 equiv) in 1.2 mL chloroform, Ph\textsubscript{INNs} (0.100 g, 0.247 mmol, 1.0 equiv) were added and the reaction mixture was allowed to stir at 40 °C under an argon atmosphere. As soon as all the nitrenoid reagent dissolved in the reaction medium, an additional amount of Cu(OTf)\textsubscript{2} (0.005 g, 0.0138 mmol) or ~ 0.2 g of silica gel (60-120 mesh) was added. On completion, the reaction was quenched by diluting with ethyl acetate (10 mL) and filtering through a short plug of silica gel. The silica gel was washed with additional 10 mL of ethyl acetate. The filtrate was concentrated by rotary evaporation under reduced pressure. The crude mass was subjected to purification by flash column chromatography using EtOAc/hexane as an eluent, which provided pure arylbutyrolactones and arylvalerolactones.

**F) Spectral Data of N-nosyl-4-amino-5-arylbutyrolactones and N-nosyl-5-amino-6-arylvalerolactones** (3a-i, 10, 7a-d and 13a-d):

4-nitro-N-((2S, 3R)-5-oxo-2-phenyltetrahydrofuran-3-yl)benzenesulfonamide(3a): White solid (0.072 g; 80%). M.p. 158-160 °C. FTIR (KBr, cm\textsuperscript{-1}): 3369, 2949, 2838, 1652, 1453, 1415, 1113, 1021. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz): δ 8.22 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.41-7.30 (m, 3H), 7.20-7.16 (m, 2H), 5.58 (d, J = 8.2 Hz, 1H), 5.27 (d, J = 4.8 Hz, 1H), 4.16-4.12 (m, 1H), 3.04-2.92 (dd, J = 7.4, 17.4 Hz, 1H), 2.56-2.44 (dd, J = 6, 17.8 Hz, 1H).
HPLC: Daicel Chiralpak IA (particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 15.06 min and minor 10.71 min). HRMS (ESI) calcd for C_{16}H_{14}N_{2}O_{6}NaS 385.0470, m/z [M+Na]^+ found 385.0484.

N-((2S, 3R)-2-(4-fluorophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3b): White solid (0.059 g; 63%). M.p. 134-136 °C. FTIR (KBr, cm⁻¹): 3400, 2950, 2840, 1651, 1453, 1412, 1113, 1021. ¹H NMR (d₆-DMSO, 200 MHz): δ 8.94 (d, J = 7.2 Hz, 1H), 8.29 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.49-7.40 (m, 2H), 7.29-7.23 (m, 2H), 5.29 (d, J = 4.4 Hz, 1H), 4.32-4.29 (m, 1H), 2.99-2.84 (dd, J = 6.8, 17.4 Hz, 2H). ¹³C NMR (d₆-DMSO, 100 MHz): δ 175.7 (C=O), 162.2 (d, J_C,F = 242.9 Hz), 150.0, 146.8, 134.5, 128.7 (d, J_C,F = 8.3 Hz), 128.2 (2C), 125.1 (2C), 116.1 (d, J_C,F = 21.4 Hz), 87.4, 56.9, 37.5. [α]_D 32 = −11.36 (c 0.1, Me₂CO) for 90% ee (HPLC: Daicel Chiralpak IA (particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 18.88 min and minor 12.92 min). HRMS (ESI) calcd for C_{16}H_{13}FNO_{6}NaS 403.0376, m/z [M+Na]^+ found 403.0389.

N-((2S, 3R)-2-(4-chlorophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3c): White solid (0.067 g; 68%). M.p. 146-148 °C. FTIR (KBr, cm⁻¹): 3391, 2952, 2839, 1648, 1453, 1411, 1101, 1015. ¹H NMR (d₆-DMSO, 200 MHz): δ 8.92 (d, J = 6.8 Hz, NH), 8.21 (d, J = 8.6 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.45-7.26 (m, 4H), 5.10 (d, J = 7.2 Hz, 1H), 4.26-4.14 (m, 1H), 2.81-2.69 (dd, J = 7.2, 17 Hz, 2H). ¹³C NMR (d₆-DMSO, 100 MHz): δ 173.5 (C=O), 149.9, 146.5, 137.2, 134.1 (2C), 129.4 (2C), 128.9, 128.4 (2C), 125.0 (2C), 83.4, 56.9, 37.2. [α]_D 32 = −8.79 (c 0.09, Me₂CO) for 86% ee (HPLC: Daicel Chiralpak IA (particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 17.68 min and minor 10.23 min). HRMS (ESI) calcd for C_{16}H_{12}ClN_{2}O_{6}S 395.0105, m/z [M-H]^− found 395.0109.

N-((2S, 3R)-2-(2-chlorophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3d): White solid (0.056 g; 57%). M.p. 122-124 °C. FTIR (KBr, cm⁻¹): 3437, 2952, 2841, 1647, 1452, 1410, 1151, 1112, 1017. ¹H NMR (d₆-DMSO, 200 MHz): δ 8.96 (d, J = 8.6 Hz, 1H), 8.25 (d, J = 8 Hz, 2H), 7.86 (d, J = 8 Hz, 2H), 7.55-7.38 (m, 4H), 5.50 (d, J = 6.6 Hz, 1H), 4.59-4.54 (m, 1H), 2.93-2.80 (dd, J = 7, 17.4 Hz, 2H). ¹³C NMR (d₆-DMSO, 100 MHz): δ 173.7 (C=O), 149.9, 146.4, 135.1, 133.9, 132.9, 131.1, 129.3, 128.1 (2C), 127.1, 124.9
(2C), 85.7, 56.3, 36.8. $[\alpha]_D^{32} = -9.92$ (c 0.1, Me$_2$CO) for 94% ee (HPLC: Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 9.90 min and minor 10.61 min). HRMS (ESI) calcd for C$_{16}$H$_{12}$ClN$_2$O$_6$S 395.0105, m/z [M-H]$^-$, found 395.0097.

$N'-(2S, 3R)-2-(2$-bromophenyl)-5-oxotetrahydrofuran-3-yl)-4$-nitrobenzenesulfonamide (3e): White solid (0.061 g; 56%). M.p. 130-132 °C. FTIR (KBr, cm$^{-1}$): 3411, 2951, 2842, 1649, 1529, 1454, 1409, 1159, 1109, 1020. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.20 (d, $J = 8.8$ Hz, 2H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.39-7.16 (m, 4H), 5.50 (d, $J = 4.8$ Hz, 1H), 4.56 (d, $J = 5.6$ Hz, 1H), 4.09-4.08 (m, 1H), 2.89-2.83 (dd, $J = 7.6$, 17.6 Hz, 1H), 2.78-2.72 (dd, $J = 6$, 17.6 Hz, 1H). $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ 173.8 (C=O), 150.1, 146.6, 135.6, 133.6, 131.6, 131.0, 129.7, 128.8 (2C), 127.5, 125.2 (2C), 83.4, 55.9, 35.8. $[\alpha]_D^{32} = -6.65$ (c 0.09, Me$_2$CO) for 80% ee (HPLC: Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 9.72 min and minor 10.74 min). HRMS (ESI) calcd for C$_{16}$H$_{12}$BrN$_2$O$_6$S 438.9599, m/z [M-H]$^-$, found 438.9608.

$N'-(2S, 3R)-2-(3$-bromophenyl)-5-oxotetrahydrofuran-3-yl)-4$-nitrobenzenesulfonamide (3f): White solid (0.068 g; 62%). M.p. 168-170 °C. FTIR (KBr, cm$^{-1}$): 3400, 2950, 2842, 1653, 1454, 1412, 1114, 1020. $^1$H NMR (d$_6$-DMSO, 200 MHz): $\delta$ 8.98 (s, NH), 8.28 (d, $J = 7.2$ Hz, 2H), 7.88 (d, $J = 7.4$ Hz, 2H), 7.54-7.37 (m, 3H), 7.31-7.24 (m, 1H), 5.50 (d, $J = 6.2$ Hz, 1H), 4.40 (m, 1H), 2.91-2.79 (dd, $J = 8$, 17.6 Hz, 2H). $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ 173.7 (C=O), 149.9, 146.4, 135.4, 133.4, 131.4, 129.6, 128.7, 128.3 (2C), 125.0 (2C), 123.4, 83.3, 55.7, 35.6. $[\alpha]_D^{32} = -4.94$ (c 0.1, Me$_2$CO) for 82% ee (HPLC: Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 9.78 min and minor 10.47 min). HRMS (ESI) calcd for C$_{16}$H$_{13}$BrN$_2$O$_6$NaS 462.9575, m/z [M+Na]$^+$, found 462.9575.

$N'-(2S, 3R)-2-(4$methoxyphenyl)-5-oxotetrahydrofuran-3-yl)-4$-nitrobenzenesulfonamide (3g): White solid (0.084 g; 87%). M.p. 164-166 °C. FTIR (KBr, cm$^{-1}$): 3427, 2948, 2845, 1646, 1530, 1451, 1410, 1277, 1113, 1049, 1018. $^1$H NMR (d$_6$-DMSO, 200 MHz): $\delta$ 8.86 (s, NH), 8.21 (d, $J = 8.8$ Hz, 2H), 7.79 (d, $J = 8.6$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.77 (d, $J = 6.8$ Hz, 2H), 5.04 (d, $J = 7.8$ Hz, 1H), 4.25-4.21 (m, 1H), 3.73 (s, 3H), 2.88-2.75 (dd, $J = 8.2$, 17.6 Hz, 2H). $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ 173.8 (C=O), 160.3, 149.9, 146.7,
129.3 (2C), 128.4 (4C), 125.0 (2C), 114.4, 84.4, 56.9, 55.7, 36.5. [α]D
32 = −7.15 (c 0.09, Me2CO) for 77% ee (HPLC: Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 0.8 ml/min, 254 nm, major 27.06 min and minor 17.56 min). HRMS (ESI) calcd for
C17H16N2O3NaS 415.0576, m/z [M+Na]+, found 415.0585.

4-nitro-N-((2S,3R)-5-oxo-2-(p-tolyl)tetrahydrofuran-3-yl)benzenesulfonamide (3h):
White solid (0.077 g; 83%). M.p. 126-128 °C. FTIR (KBr, cm−1): 3390, 2953, 2843, 1652, 1534, 1454, 1412, 1353, 1169, 1053. 1H NMR (d6-DMSO, 200 MHz): δ 8.66 (d, J = 8.6 Hz, NH), 8.26 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.00-6.87 (m, 4H), 5.47 (d, J = 8.8 Hz, 1H), 4.03-3.97 (m, 1H), 2.81-2.69 (dd, J = 7.0, 17.0 Hz, 2H), 2.19 (s, 3H). 13C NMR (d6-DMSO, 100 MHz): δ 171.8 (C=O), 149.8, 145.6, 139.0, 135.6, 129.4, 127.9, 127.9, 127.7, 124.3, 124.0, 84.4, 56.2, 36.2, 21.3. [α]D
32 = −7.33 (c 0.1, Me2CO) for 88% ee (HPLC: Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 13.04 min and minor 9.77 min). HRMS (ESI) calcd for
C17H16N2O3NaS 399.0627, m/z [M+Na]+, found 399.0638.

N-((2S,3R)-2-(benzo[d][1,3]dioxol-5-yl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzene
sulfonamide (3i): Light yellow solid (0.082 g; 82%). M.p. 194-196 °C. FTIR (KBr, cm−1):
3416, 2952, 2843, 1646, 1527, 1453, 1452, 1406, 1286, 1109, 1054, 1017. 1H NMR (d6-DMSO, 200 MHz): δ 8.84 (bs, NH), 8.23 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.0 Hz, 3H), 5.93 (s, 2H), 4.96 (d, J = 8.2 Hz, 1H), 4.22 (m, 1H), 2.84-2.71 (dd, J = 7.8, 16.8 Hz, 2H). 13C NMR (d6-DMSO, 100 MHz): δ 173.6 (C=O), 149.9, 148.3, 147.8, 146.8, 130.3, 128.5, 124.9, 122.3, 108.6, 107.8, 101.9, 84.4, 56.8, 36.5. [α]D
32 = −9.81 (c 0.1, Me2CO) for 85% ee (HPLC: Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 17.69 min and minor 10.12 min). LCMS (ESI) m/z : 405.0 [M-H]+, 424.4 [M+NH4]+.

4-nitro-N-((2S, 3R)-6-oxo-2-phenyltetrahydro-2H-pyran-3-yl)benzenesulfonamide (7a):
White solid (0.078 g; 84%). M.p. 138-140 °C. FTIR (KBr, cm−1): 3227, 2926, 2831, 1654, 1526, 1457, 1383, 1349, 1158, 1092, 1041. 1H NMR (CDCl3, 200 MHz): δ 8.09 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.23-7.04 (m, 5H), 5.03 (d, J = 7.8 Hz, 2H), 3.74-3.54 (m, 1H), 2.78-2.68 (m, 2H), 2.38-2.29 (m, 1H), 2.03-1.93 (m, 1H). 1H NMR (d6-DMSO, 200 MHz): δ 8.48 (s, NH), 8.11 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.23-7.04 (m, 5H), 5.04 (d, J = 9.2 Hz, 1H), 3.78-3.66 (m, 1H), 2.62 (t, J = 5.4, 8.8 Hz, 2H), 1.92-1.76 (m, 2H).
$^{13}$C NMR (d$_6$-DMSO, 100 MHz): δ 170.4 (C=O), 149.8, 147.2, 137.8, 128.7 (2C), 128.3 (2C), 128.1 (2C), 126.8, 125.1(2C), 82.9, 52.8, 30.2, 28.5. [α]$_D^{32}$ = −18.20 (c 0.6, Me$_2$CO) for 89% ee (HPLC: Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 60/40, 1.0 ml/min, 254 nm, major 9.43 min and minor 10.52 min). HRMS (ESI) calcd for C$_{17}$H$_{16}$N$_2$O$_6$NaS 399.0627, m/z [M+Na]$^+$, found 399.0628.

$N$-((2S, 3R)-2-(4-fluorophenyl)-6-oxotetrahydro-2H-pyran-3-yl)-4-nitrobenzenesulfonamide (7b): White solid (0.077 g; 79%). M.p. 102-104 °C. FTIR (KBr, cm$^{-1}$): 3413, 2967, 2844, 1646, 1534, 1455, 1412, 1168, 1113, 1016. $^1$H NMR (d$_6$-DMSO, 200 MHz): δ 8.54 (d, $J$ = 8.6 Hz, NH), 8.18 (d, $J$ = 7.4 Hz, 2H), 7.66 (d, $J$ = 7.6 Hz, 2H), 7.38 (t, $J$ = 7.6, 5.6 Hz, 2H), 6.92 (t, $J$ = 8.6, 8 Hz, 2H), 5.06 (d, $J$ = 9.6 Hz, 1H), 3.85-3.68 (m, 1H), 2.63 (t, $J$ = 6, 5.6 Hz, 2H), 1.97-1.89 (m, 2H). $^{13}$C NMR (d$_6$-DMSO, 50 MHz): δ 170.8 (C=O), 162.4 (d, $^1$J$_{CF}$ = 241.5 Hz), 149.4, 146.9, 135.3, 129.5 (d, $^3$J$_{CF}$ = 8 Hz), 127.9 (2C), 124.7 (2C), 115.4 (d, $^2$J$_{CF}$ = 20.5 Hz), 84.2, 52.7, 28.5, 26.6. [α]$_D^{32}$ = −34.82 (c 0.5, Me$_2$CO) for 92% ee (HPLC: Daicel Chiralpak IC(particle size 5µm), hexane/EtOAc = 60/40, 1.0 ml/min, 254 nm, major 13.66 min and minor 11.95 min). HRMS (ESI) calcd for C$_{17}$H$_{15}$FN$_2$O$_6$NaS 417.0533, m/z [M+Na]$^+$, found 417.0546.

$N$-((2S, 3R)-2-(4-chlorophenyl)-6-oxotetrahydro-2H-pyran-3-yl)-4-nitrobenzenesulfonamide (7c): White solid (0.078 g; 77%). M.p. 131-133 °C. FTIR (KBr, cm$^{-1}$): 3388, 2950, 2838, 1654, 1534, 1451, 1412, 1169, 1112, 1020. $^1$H NMR (d$_6$-DMSO, 200 MHz): δ 8.62 (d, $J$ = 8.8 Hz, NH), 8.21 (d, $J$ = 8.8 Hz, 2H), 7.67 (d, $J$ = 8.8 Hz, 2H), 7.25-7.13 (m, 4H), 5.09 (d, $J$ = 9.8 Hz, 1H), 3.87-3.65 (m, 1H), 2.71 (t, $J$ = 7.2, 6.6 Hz, 2H), 2.03-1.93 (m, 2H). $^{13}$C NMR (d$_6$-DMSO, 100 MHz): δ 170.4 (C=O), 149.5, 147.1, 136.9, 134.1, 129.8, 128.5, 128.1, 124.8, 81.7, 55.4, 28.7, 27.7. [α]$_D^{32}$ = −22.73 (c 0.5, Me$_2$CO) for 84% ee (HPLC: Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 14.05 min and minor 19.95 min). HRMS (ESI) calcd for C$_{17}$H$_{15}$ClN$_2$O$_6$NS 410.0339, m/z [M]$^+$, found 410.0317.

$N$-((2S, 3R)-2-(2-bromophenyl)-6-oxotetrahydro-2H-pyran-3-yl)-4-nitrobenzenesulfonamide (7d): White solid (0.082 g; 73%). M.p. 162-164 °C. FTIR (KBr, cm$^{-1}$): 3408, 2950, 2842, 1647, 1531, 1452, 1413, 1162, 1019. $^1$H NMR (d$_6$-DMSO, 400 MHz): δ 8.61 (d, $J$ = 8.8 Hz, NH), 8.22 (d, $J$ = 8.8 Hz, 2H), 7.79 (d, $J$ = 8.8 Hz, 2H), 7.46-7.37 (m, 2H), 7.29-7.26 (m, 1H), 7.17-7.13 (m, 1H), 5.43 (d, $J$ = 9.2 Hz, 1H), 4.00-3.92 (m, 1H), 2.66 (t, $J$ = 6.8, 7.2
HPLC: Daicel Chiralpak IA (particle size 3 µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 11.29 min and minor 12.00 min. LCMS (ESI) m/z: 454.9 [M+H]+, 472.4 [M+NH4]+.

4-nitro-N-((R)-1-((S)-3-oxo-1, 3-dihydroisobenzofuran-1-yl)propyl)benzenesulfonamide (10): Light Yellow solid (0.070 g; 75%). M.p. 228-230 °C. FTIR (KBr, cm⁻¹): 3385, 2951, 2835, 1654, 1455, 1420, 1113, 1023. ¹H NMR (CDCl₃, 400 MHz): δ 8.32 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.69-7.65 (m, 1H), 7.59-7.46 (m, 2H), 5.40 (d, J = 4.8 Hz, 1H), 4.64-4.61 (m, 1H), 3.89-3.84 (m, 1H), 1.69-1.46 (m, 2H), 0.94 (t, J = 7.2, 7.6 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 170.7 (C=O), 163.7, 149.9, 146.9, 136.2, 134.5, 130.4, 129.7, 128.8, 128.4(2C), 124.3 (2C), 83.8, 52.6, 29.6, 25.7. [α]D³² = −22.65 (c 0.2, Me₂CO) for 79% ee (HPLC: Daicel Chiralpak IA (particle size 5 µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 15.02 min and minor 11.17 min). HRMS (ESI) calced for C₁₇H₁₆N₂O₆NaS 399.0627, m/z [M+Na]+, found 399.0624.

(3R,5R,6S)-tert-butyl 3-methyl-5-(4-nitrophensulfonamido)-2-oxo-6-(p-tolyl)tetrahydro-2H-pyran-3-carboxylate (13a): White solid (0.103 g; 85%). M.p. 160-162 °C. FTIR (KBr, cm⁻¹): 3434, 2952, 2842, 1647, 1532, 1452, 1406, 1163, 1113, 1052, 1017. ¹H NMR (CDCl₃, 200 MHz): δ 7.99 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.08 (s, 5H), 4.91-4.86 (m, 1H & NH), 3.91-3.88 (m, 1H), 2.71 (d, J = 12.8 Hz, 1H), 1.97 (t, J = 13.0, 13.8 Hz, 1H), 1.58 (s, 9H), 1.54 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 170.6 (C=O), 169.1 (C=O), 149.9, 145.2, 136.2, 129.6, 128.9, 127.9, 127.4, 124.3, 84.9, 84.2, 52.3, 51.7, 40.5, 28.0, 23.1. [α]D³² = −61.32 (c 0.5, Me₂CO) for 90% ee (HPLC: Daicel Chiralpak IA (particle size 3 µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 7.74 min and minor 8.53 min). HRMS (ESI) calced for C₂₃H₂₆N₂O₆NaS 513.1308, m/z [M+Na]+, found 513.1320.

(3R,5R,6S)-tert-butyl 3-methyl-5-(4-nitrophensulfonamido)-2-oxo-6-(p-tolyl)tetrahydro-2H-pyran-3-carboxylate (13b): White solid (0.109 g; 87%). M.p. 160-162 °C. FTIR (KBr, cm⁻¹): 3399, 2952, 2836, 1653, 1453, 1413, 1114, 1032. ¹H NMR (CDCl₃, 200 MHz): δ 8.04 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 6.99-6.88 (m, 4H), 4.85 (d, J = 10.4 Hz, 1H), 4.69 (d, J = 7.2 Hz, 1H), 3.87 (m, 1H), 2.81-2.72 (dd, J = 4.8, 14.4 Hz, 1H), 2.28 (s, 3H), 1.974 (t, J = 13, 14.4, 1H), 1.59 (s, 9H), 1.56 (s, 3H). ¹³C NMR (d₆-DMSO, 100 MHz): δ
171.2 (C=O), 161.1 (C=O), 149.8, 146.9, 138.8, 134.6, 129.3, 127.9, 127.8, 125.1, 124.9, 83.8, 83.4, 51.0, 51.6, 28.1, 22.9, 21.1. \([\alpha]_D^{32} = -34.54\) (c 0.3, Me\(_2\)CO) for 96% ee (HPLC: Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 8.59 min and minor 10.23 min). HRMS (ESI) calcd for C\(_{24}\)H\(_{28}\)N\(_2\)O\(_8\)NaS 527.1464, m/z \([M+Na]^+\), found 527.1472.

\((3R,5R,6S)\)-tert-butyl 6-(4-fluorophenyl)-3-methyl-5-(4-nitrophenylsulfonamido)-2-oxo tetrahydro-2H-pyran-3-carboxylate (13c): White solid (0.102 g; 81%). M.p. 146-148 °C. FTIR (KBr, cm\(^{-1}\)): 3435, 2953, 2844, 1641, 1532, 1455, 1349, 1162, 1119, 1053, 1016. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \(\delta 8.09\) (d, \(J = 8.6\) Hz, 2H), 7.53 (d, \(J = 8.8\) Hz, 2H), 7.12-7.05 (m, 2H), 6.78 (t, \(J = 8.4, 8.6\) Hz, 2H), 5.11 (d, \(J = 10.4\) 1H), 4.91 (d, \(J = 10.4\) 1H), 3.89-3.85 (m, 1H), 2.65-2.56 (dd, \(J = 3.4, 13.6\) 1H), 1.96 (t, \(J = 12.8, 13.0\) Hz, 1H), 1.58 (s, 9H), 1.51 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 170.4\) (C=O), 168.9 (C=O), 163.4 (d, \(^1\)JC,F = 266.4 Hz), 150.0, 145.6, 132.3, 129.3 (d, \(^3\)JC,F = 8.4 Hz), 128.0 (2C), 124.3 (2C), 115.9 (d, \(^2\)JC,F = 21.7 Hz), 84.3, 52.5, 51.8, 40.4, 28.1, 23.0. \([\alpha]_D^{32} = -66.32\) (c 0.1, Me\(_2\)CO) for 98% ee (HPLC: Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 7.56 min and minor 8.28 min). LCMS (ESI) m/z : 526.0 [M+NH\(_4\)]\(^+\).

\((3R,5R,6S)\)-tert-butyl 6-(2-bromophenyl)-3-methyl-5-(4-nitrophenylsulfonamido)-2-oxo tetrahydro-2H-pyran-3-carboxylate (13d): White solid (0.111 g; 79%). M.p. 126-128 °C. FTIR (KBr, cm\(^{-1}\)): 3426, 2950, 2841, 1651, 1531, 1454, 1350, 1163, 1111, 1018. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \(\delta 7.98\) (d, \(J = 8.0\) Hz, 2H), 7.53 (d, \(J = 8.0\) Hz, 2H), 7.29-7.26 (m, 1H), 7.21 (d, \(J = 8.0\) Hz, 1H), 7.11 (t, \(J = 6.8, 7.6\) Hz, 1H), 7.00 (t, \(J = 7.2, 7.6\) Hz, 1H), 5.52 (d, \(J = 8.0\) Hz, 1H), 5.09 (d, \(J = 4.4\) Hz, 1H), 3.98 (bs, 1H), 2.70 (d, \(J = 11.2\) Hz, 1H, 1H), 2.09 (m, 1H), 1.59 (s, 9H), 1.57 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 170.1\) (C=O), 168.3 (C=O), 149.8, 145.1, 136.2, 132.5, 130.6, 128.8, 128.3, 127.5, 124.1, 123.1, 84.1, 81.7, 53.4, 51.6, 41.1, 27.9, 22.9. \([\alpha]_D^{32} = -94.19\) (c 0.7, Me\(_2\)CO) for 94% ee (HPLC: Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 7.56 min and minor 9.17 min). HRMS (ESI) calcd for C\(_{23}\)H\(_{25}\)BrN\(_2\)O\(_8\)NaS 591.0413, m/z [M+Na]^+\), found 591.0421.

S10
G) Spectral Data of alkenoic acid esters (1a-i, 8, 5a-d, 11a-d and 1a’):

\( (E)-\text{tert-buty1 4-phenylbut-3-enolate (1a):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.34-7.16 \) (m, 5H), 6.37 (d, \( J = 15.6 \) Hz, 1H), 6.25-6.10 (m, 1H), 3.05 (d, \( J = 6.8 \) Hz, 2H), 1.37 (s, 9H).

\( (E)-\text{tert-buty1 4-(4-chlorophenyl)but-3-enolate (1c):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.41-7.23 \) (m, 4H), 6.42 (d, \( J = 16.4 \) Hz, 1H), 6.33-6.18 (m, 1H), 3.15 (d, \( J = 6.6 \) Hz, 2H), 1.46 (s, 9H).

\( (E)-\text{tert-buty1 4-(4-fluorophenyl)but-3-enolate (1b):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.38-7.25 \) (m, 2H), 7.12-7.09 (m, 2H), 6.42 (d, \( J = 15.8 \) Hz, 1H), 6.26-6.12 (m, 1H), 3.14 (d, \( J = 7 \) Hz, 2H), 1.47 (s, 9H).

\( (E)-\text{tert-buty1 4-(2-chlorophenyl)but-3-enolate (1d):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.39-7.15 \) (m, 4H), 6.85 (d, \( J = 16 \) Hz, 1H), 6.40-6.21 (m, 1H), 3.21 (d, \( J = 7 \) Hz, 2H), 1.48 (s, 9H).

\( (E)-\text{tert-buty1 4-(2-bromophenyl)but-3-enolate (1e):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta 7.40-7.23 \) (m, 3H), 7.15-6.97 (m, 1H), 6.83 (d, \( J = 15.6 \) Hz, 1H), 6.34-6.24 (m, 1H), 3.24-3.22 (dd, \( J = 1.6, 7.2 \) Hz, 2H), 1.49 (s, 9H).

\( (E)-\text{tert-buty1 4-(3-bromophenyl)but-3-enolate (1f):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.39-7.12 \) (m, 4H), 6.44-6.21 (m, 2H), 3.15 (d, \( J = 5.6 \) Hz, 2H), 1.47 (s, 9H).

\( (E)-\text{tert-buty1 4-(4-methoxyphenyl)but-3-enolate (1g):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.30 \) (d, \( J = 8.6 \) Hz, 2H), 6.84 (d, \( J = 8.6 \) Hz, 2H), 6.41 (d, \( J = 15.8 \) Hz, 1H), 3.80 (s, 3H), 3.12 (d, \( J = 6.8 \) Hz, 2H), 1.46 (s, 9H).

\( (E)-\text{tert-buty1 4-(p-tolyl)but-3-enolate (1h):} \) Light yellow oil. \(^1\)H NMR (CDCl\(_3\), 200 MHz): \( \delta 7.30-7.10 \) (m, 4H), 6.45 (d, \( J = 15.8 \) Hz, 1H), 6.32-6.17 (m, 1H), 3.16 (d, \( J = 6.8 \) Hz, 2H), 2.34 (s, 3H), 1.48 (s, 9H).
(E)-tert-butyl 4-(benzo[d][1,3]dioxol-5-yI)but-3-enoate (1i): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 6.93 (s, 1H), 6.88-6.72 (m, 2H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.18-6.07 (m, 1H), 5.92 (s, 2H), 3.13 (d, $J = 7.0$ Hz, 2H), 1.47 (s, 9H).

tert-butyl 2-(but-1-en-1-yl)benzoate (8): $E:Z = 82 : 18$. Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.84 (d, $J = 7.4$ Hz, 0.22H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.52-7.19 (m, 3.66H), 7.05 (d, $J = 15.6$ Hz, 1H), 6.77 (d, $J = 11.6$ Hz, 0.22H), 6.21-6.07 (m, 1H), 5.75-5.39 (m, 0.22H), 2.30-2.09 (m, 2.44H), 1.59 (s, 9H), 1.14 (t, $J = 7.4$, 7.4 Hz, 3H), 1.03 (t, $J = 7.4$, 7.4 Hz, 0.66H).

(E)-tert-butyl 5-phenylpent-4-enoate (5a): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.35-7.16 (m, 5H), 6.42 (d, $J = 15.8$ Hz, 1H), 6.27-6.16 (m, 1H), 2.51-2.34 (m, 4H), 1.45 (s, 9H).

(E)-tert-butyl 5-(4-fluorophenyl)pent-4-enoate (5b): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.33-7.24 (m, 2H), 7.08-6.92 (m, 2H), 6.38 (d, $J = 15.6$ Hz, 1H), 6.17-6.03 (m, 1H), 2.50-2.33 (m, 4H), 1.44 (s, 9H).

(E)-tert-butyl 5-(4-chlorophenyl)pent-4-enoate (5c): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.39-7.25 (m, 4H), 6.38 (d, $J = 15.8$ Hz, 1H), 6.25-6.14 (m, 1H), 2.55-2.35 (m, 4H), 1.45 (s, 9H).

(E)-tert-butyl 5-(2-bromophenyl)pent-4-enoate (5d): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.55-7.46 (m, 2H), 7.28-7.21 (m, 1H), 7.11-7.03 (m, 1H), 6.76 (d, $J = 15.6$ Hz, 1H), 6.24-6.09 (m, 1H), 2.56-2.43 (m, 4H), 1.47 (s, 9H).

di-tert-butyl 2-cinnamyl-2-methylmalonate (11a): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.32-7.23 (m, 5H), 6.45 (d, $J = 15.8$ Hz, 1H), 6.19-6.05 (m, 1H), 2.69 (d, $J = 7.4$ Hz, 2H), 1.46 (s, 9H), 1.37 (s, 3H).

(E)-di-tert-butyl 2-(3-(2-bromophenyl)allyl)-2-methylmalonate (11d): Light yellow oil. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.50 (t, $J = 7.8$, 11 Hz, 2H), 7.24-7.21 (m, 1H), 7.11-7.04 (m, 1H), 6.79 (d, $J = 15.6$ Hz, 1H), 6.16-6.00 (m, 1H), 2.74 (d, $J = 7.6$ Hz, 2H), 1.46 (s, 9H), 1.38 (s, 3H).
**H) Synthesis and Spectral Data of compounds 14-16 and 2a':**

**{(4R, 5S)}-4-amino-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (14):** To a well stirred solution of 3g (0.16 g, 0.408 mmol) taken in 3 mL CH3CN:DMSO (49:1) at rt, 1.1 equiv 4-methoxythiophenol (0.055 mL, 0.449 mmol) and 1.1 equiv of K2CO3 (0.62 g, 0.449 mmol) were added and the reaction mixture was allowed to stir for 4 h. Upon completion of the reaction the reaction mixture was filtered using MeOH as an eluent. Solvent was evaporated under reduced pressure and the crude yellow oil was immediately used in the next step.

**tert-butyl ((2S, 3R)-2-(4-methoxyphenyl)-5-oxotetrahydrofuran-3-yl)carbamate (15):**

The crude yellow oil was taken in 10 mL dry THF. 3.3 equiv of BOC2O (0.309 mL, 1.346 mmol) was added and the reaction mixture was allowed to stir for overnight. Solvent was evaporated under reduced pressure and 20 mL of EtOAc was added. The organic layer washed with H2O (2 x 15 mL) and the dried over Na2SO4. Concentration and column chromatography (20% EtOAc in hexane) gave titled compound 15 as white solid (0.102 g, yield 82% in overall two steps). M.p. 112-114 °C. 1H NMR (CDCl3, 200 MHz): δ 7.35-7.27 (m, 2H), 6.95-6.90 (m, 2H), 5.41 (bs, NH), 4.91 (d, J = 5.6 Hz, 1H), 4.27 (m, 1H), 3.83 (s, 3H), 3.03-2.86 (dd, J = 7.8, 25.6 Hz, 1H), 2.55-2.44 (dd, J = 4.8, 17.8 Hz, 1H), 1.45 (s, 9H). 13C NMR (CDCl3, 100 MHz): δ 173.5 (C=O), 159.9, 128.9 (2C), 126.8 (2C), 114.4, 86.1, 78.5, 56.6, 55.5, 34.4, 28.4.
(S)-3-((tert-butoxycarbonyl)amino)-4-(4-methoxyphenyl)butanoic acid (16): Compound 15 (0.1 g, 0.16 mmol) was taken in 4 mL MeOH. After addition of 10% Pd-C (0.1 equiv), the reaction mixture was purged with H₂ and the reaction mixture was stirred under the H₂ atmosphere for 1.5 h. On completion, the mixture was passed through a celite pad, washed with MeOH (3 x 20 mL), on solvent evaporation pure compound 16 was obtained as a colourless solid (0.097 g, yield 96%). M.p. 102-104 °C. ¹H NMR (CD₃OD, 200 MHz): δ 7.12 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8 Hz, 2H), 4.11-4.04 (m, 1H), 3.76 (s, 3H), 2.71(m, 2H), 2.48 (m, 2H), 1.37 (s, 9H). ¹³C NMR (CD₃OD, 50 MHz): δ 173.9 (C=O), 158.6, 156.6, 130.4, 130.2, 113.6, 78.8, 54.4, 41.6, 39.7, 27.8. [α]D²⁶ = -17.4 (c 1.1, EtOH), [Lit⁷. [α]D²⁰ = −18.7 (c 1, EtOH).

methyl 2-((2R,3R)-1-((4-nitrophenyl)sulfnyl)-3-phenylazirdin-2-yl)acetate (2a)': White solid (0.054 g, 61% yield). M.p. 138-140 °C. ¹H NMR (CDCl₃, 200 MHz): δ 8.26 (d, J = 8.6 Hz, 2H), 8.07 (d, J = 8.8 Hz, 2H), 7.22-7.02 (m, 5H), 4.09 (d, J = 3.8 Hz, 1H), 3.71 (s, 3H), 3.22-3.03 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.9 (C=O), 151.0, 147.1, 141.3, 135.5, 128.6, 128.4, 127.6, 126.3, 54.7, 52.2, 50.9, 38.3. [α]D³² = −12.11 (c 0.18, Me₂CO) for 72% ee (HPLC: Daicel Chiralpak IA (particle size 3µm), hexane/iPrOH = 85/15, 1.0 ml/min, 254 nm, major 13.56 min and minor 9.58 min).

I) References:
J) NMR Spectra:

$^1$H NMR of compound 3a (200 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3a (50 MHz, CDCl$_3$)
$^1$H NMR of compound 3c (200 MHz, $d_6$-DMSO)

$^{13}$C NMR of compound 3c (100 MHz, $d_6$-DMSO)
$^1$H NMR of compound 3b (200 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3b (100 MHz, d$_6$-DMSO)
$^1$H NMR of compound 3d (200 MHz, d$_6$-DMSO)

$^{13}$C NMR of compound 3d (100 MHz, d$_6$-DMSO)
$^1$H NMR of compound 3e (400 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3e (100 MHz, d$_6$-DMSO)
$^1$H NMR of compound 3f (200 MHz, $d_6$-DMSO)

$^{13}$C NMR of compound 3f (100 MHz, $d_6$-DMSO)
$^1$H NMR of compound 3g (200 MHz, d$_6$-DMSO)

$^{13}$C NMR of compound 3g (100 MHz, d$_6$-DMSO)
$^1$H NMR of compound 3h (200 MHz, $d_6$-DMSO)

$^{13}$C NMR of compound 3h (100 MHz, $d_6$-DMSO)
$^1$H NMR of compound 3i (200 MHz, d$_6$-DMSO)

$^{13}$C NMR of compound 3i (100 MHz, d$_6$-DMSO)
$^1$H NMR of compound 10 (400 MHz, CDCl$_3$)

$^{13}$C NMR of compound 10 (100 MHz, CDCl$_3$)
$^1$H NMR of compound 7a (200 MHz, CDCl$_3$)

$^1$H NMR of compound 7a (200 MHz, d$_6$-DMSO)
$^1$C NMR of compound 7a (100 MHz, d$_6$-DMSO)

$^1$H NMR of compound 7b (200 MHz, d$_6$-DMSO)
\[ {\text{\(^{13}\text{C}\) NMR of compound 7b (50 MHz, d\text{\(_6\)}-\text{DMSO})}} \]

\[ {\text{\(^{1}\text{H}\) NMR of compound 7c (200 MHz, d\text{\(_6\)}-\text{DMSO})}} \]
$^{13}$C NMR of compound 7c (100 MHz, d$_6$-DMSO)

$^1$H NMR of compound 7d (400 MHz, d$_6$-DMSO)
$^1$H NMR of compound 13a (200 MHz, CDCl$_3$)

$^{13}$C NMR of compound 7d (100 MHz, d$_6$-DMSO)
$^{13}$C NMR of compound 13a (100 MHz, CDCl$_3$)

$^1$H NMR of compound 13c (200 MHz, CDCl$_3$)
$^{13}$C NMR of compound 13c (100 MHz, CDCl$_3$)

$^1$H NMR of compound 13b (200 MHz, CDCl$_3$)
$^{13}$C NMR of compound 13b (100 MHz, d$_6$-DMSO)

$^1$H NMR of compound 13d (400 MHz, CDCl$_3$)
$^{13}$C NMR of compound 13d (100 MHz, CDCl$_3$)

$^1$H NMR of compound 1a (200 MHz, CDCl$_3$)
$^1$H NMR of compound 1c (200 MHz, CDCl$_3$)

$^1$H NMR of compound 1b (200 MHz, CDCl$_3$)
$^1$H NMR of compound 1d (200 MHz, CDCl$_3$)

$^1$H NMR of compound 1e (400 MHz, CDCl$_3$)
$^1$H NMR of compound 1f (200 MHz, CDCl$_3$)

$^1$H NMR of compound 1g (200 MHz, CDCl$_3$)
$^1$H NMR of compound 1h (200 MHz, CDCl$_3$)

$^1$H NMR of compound 1i (200 MHz, CDCl$_3$)

S37
$^1$H NMR of compound 8 (200 MHz, CDCl$_3$)

$^1$H NMR of compound 5a (200 MHz, CDCl$_3$)
$^1$H NMR of compound 5b (200 MHz, CDCl$_3$)

$^1$H NMR of compound 5c (200 MHz, CDCl$_3$)
$^1$H NMR of compound 5d (200 MHz, CDCl$_3$)

$^1$H NMR of compound 11a (200 MHz, CDCl$_3$)
\(^1\)H NMR of compound 11b (200 MHz, CDCl\(_3\))

\(^1\)H NMR of compound 11c (200 MHz, CDCl\(_3\))
$^{1}$H NMR of compound 11d (200 MHz, CDCl$_3$)

$^{1}$H NMR of compound 1a' (200 MHz, CDCl$_3$)
$^1$H NMR of compound 15 (200 MHz, CDCl$_3$)

$^{13}$C NMR of compound 15 (100 MHz, CDCl$_3$)
$^1$H NMR of compound 16 (200 MHz, CD$_3$OD)

$^{13}$C NMR of compound 16 (100 MHz, CD$_3$OD)
H NMR of compound 2a' (200 MHz, CDCl₃)

13C NMR of compound 2a' (50 MHz, CDCl₃)

K) 1D-nOe Spectra of compound 13a:
$^1$H NMR of compound 13a (500 MHz, CDCl$_3$)
1D-nOe spectrum of compound 13a (SR at 3.887 ppm, 500 MHz, CDCl₃)
1D-nOe spectrum of compound 13a (SR at 1.515ppm, 500 MHz, CDCl₃)
L) HPLC Chromatograms:

HPLC Chromatogram of compound 3a
HPLC Chromatogram of compound (±)3a
HPLC Chromatogram of compound 3c
HPLC Chromatogram of compound (±)3c

HPLC Chromatogram of compound 3b
HPLC Chromatogram of compound (±)3b
HPLC Chromatogram of compound 3d
HPLC Chromatogram of compound (±)3d

HPLC Chromatogram of compound 3e
HPLC Chromatogram of compound (±)3e
HPLC Chromatogram of compound 3f
HPLC Chromatogram of compound (±)3f
HPLC Chromatogram of compound 3g
HPLC Chromatogram of compound (±)3g
HPLC Chromatogram of compound 3h
HPLC Chromatogram of compound (±)3h

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### Area Percent Report

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

Signal 1: DAD1 A, Sig=254, Ref=360,100

<p>| Peak RetTime Type Width Area Height Area |
|------------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>#</th>
<th>[min]</th>
<th>[min]</th>
<th>[mAU*s]</th>
<th>[mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.332</td>
<td>BV</td>
<td>0.1083</td>
<td>4347.11523</td>
<td>574.42169</td>
</tr>
<tr>
<td>2</td>
<td>12.554</td>
<td>VV</td>
<td>0.2438</td>
<td>2937.47778</td>
<td>160.49480</td>
</tr>
</tbody>
</table>

Totals: 7284.59382 748.91649

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*** End of Report ***

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S62
HPLC Chromatogram of compound 3i
HPLC Chromatogram of compound (±)3i
HPLC Chromatogram of compound 10
**HPLC Chromatogram of compound (±)10**

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**Area Percent Report**

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Retention Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplier</td>
<td>1.0000</td>
</tr>
<tr>
<td>Dilution</td>
<td>1.0000</td>
</tr>
<tr>
<td>Use Multiplier &amp; Dilution Factor with ISTDs</td>
<td></td>
</tr>
</tbody>
</table>

**Signal 1: MWD1 A, Sig=254,20 Ref=off**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Sig Type</th>
<th>Area [mAU*sec]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.735</td>
<td>VV</td>
<td>8307.19359</td>
<td>484.42422</td>
<td>56.5664</td>
</tr>
<tr>
<td>2</td>
<td>13.952</td>
<td>VV</td>
<td>6378.54688</td>
<td>285.07380</td>
<td>43.4336</td>
</tr>
</tbody>
</table>

**Totals:**

1.46857e4 769.49722

Results obtained with enhanced integrator!

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***End of Report***
HPLC Chromatogram of compound 7a
HPLC Chromatogram of compound (±)7a
HPLC Chromatogram of compound 7b
HPLC Chromatogram of compound (±)7b
HPLC Chromatogram of compound 7c
HPLC Chromatogram of compound (±)7c
HPLC Chromatogram of compound 7d
HPLC Chromatogram of compound (±)7d
HPLC Chromatogram of compound 13a
HPLC Chromatogram of compound (±)13a
HPLC Chromatogram of compound 13c
HPLC Chromatogram of compound (±)13c
HPLC Chromatogram of compound 13b
HPLC Chromatogram of compound (±)13b
HPLC Chromatogram of compound 13d
HPLC Chromatogram of compound (±)13d
HPLC Chromatogram of compound 2a'
HPLC Chromatogram of compound (±) 2a’