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Supporting Information

Double Spirocyclization of Arylidene-Δ²-Pyrrolin-4-Ones with 3-Isothiocyanato Oxindoles

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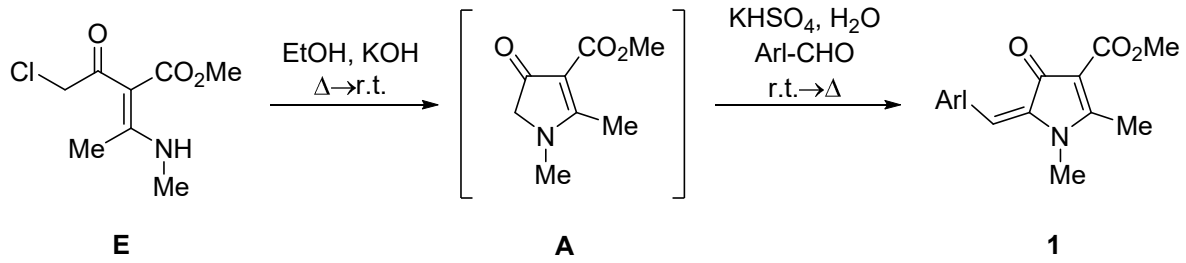
1. Materials and methods, syntheses, and characterization

Solvents for extractions and chromatography were of technical grade and were distilled prior to use. Extracts were dried over technical grade anhydrous Na_2SO_4. Melting points were determined on a Kofler micro hot stage and on SRS OptiMelt MPA100 – Automated Melting Point System (Stanford Research Systems, Sunnyvale, California, United States). The NMR spectra were obtained on a Bruker UltraShield 500 plus (Bruker, Billerica, Massachusetts, United States) at 500 MHz for ^{1}H and 126 MHz for ^{13}C nucleus, using DMSO-d_6 and $CDCl_3$ with TMS as the internal standard, as solvents. Mass spectra were recorded on an Agilent 6224 Accurate Mass TOF LC/MS (Agilent Technologies, Santa Clara, California, United States), IR spectra on a Perkin-Elmer Spectrum BX FTIR spectrophotometer (PerkinElmer, Waltham, Massachusetts, United States). Column chromatography (CC) was performed on silica gel (Silica gel 60, particle size: 0.035-0.070 mm (Sigma-Aldrich, St. Louis, Missouri, United States)). HPLC analyses were performed on an Agilent 1260 Infinity LC (Agilent Technologies, Santa Clara, California, United States) using CHIRALPAK IA-3 (0.46 cm ø × 25 cm), CHIRALPAK AD-H (0.46 cm ø × 25 cm), CHIRALCEL OD-H (0.46 cm ø × 25 cm) and CHIRALCEL AS-H (0.46 cm ø × 25 cm) as chiral column (CHIRAL TECHNOLOGIES, INC., West Chester, Pennsylvania, United States). All the commercially available chemicals used were purchased from Sigma-Aldrich (St. Louis, Missouri, United States).

Methyl 5-arylidene-2-methyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylates **1** [1] and 3-isothiocyanatooxindoles **2a** and **2b** [2-4] were prepared following the literature procedures.

Organocatalysts **Ia** [5], **II** [6] **IIIa** [5], **IV** [5], **Vb** [7], **VIa** [8], **VIb** [9], **VIIa** [10], **VIIb** [9], **IXa** [11], **IXb** [12], **IXc** [13], **Xb** [14], **XIa** [15], and **XIb** [11] were prepared following the literature procedures; organocatalysts **VIIIb** and **XII** were purchased from Sigma-Aldrich.

Synthesis of (*E*)-methyl 5-arylidene-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate – *General procedure 1* (*GP1*)



E **A** **1**

To a solution of enaminone **E** [1] (1 equivalent) in anhydrous EtOH at room temperature, KOH (1.05 equivalent, ω = 0.85) was added and the resulting reaction mixture was heated to 75°C. After the disappearance of the starting material (*ca*. 45 minutes) according to the TLC analysis (mobile phase: EtOAc/MeOH = 4:1) (*Figure S1*), the mixture was cooled to room temperature. $KHSO_4$ (0.5 equivalents) followed by the addition of H_2O (5 mL) were added and the mixture was stirred for 10 minutes at room temperature, followed by the addition of an aldehyde (1 equivalent). The mixture was heated to 75°C and stirred until the disappearance of the Δ^2-pyrrolin-4-one intermediate **A** (*ca*. 30 min) according to the TLC analysis (mobile phase: EtOAc/MeOH = 4:1) (*Figure S1*). Afterwards, the solution was cooled to room temperature followed by slow addition of ice-cold water (*ca*. 100 mL) until the formation of the precipitate. The precipitate was collected by filtration, washed with ice-cold water and dried under high vacuum at 60°C. Unless noted otherwise, the crude product was purified by recrystallization from MeOH/H_2O and dried under high vacuum at 60°C which afforded the product **1** (compounds **1c**, **1f**, **1g**, **1i**) as a brightly colored solid (*Figure S2*). Other 5-arylidene-2-methyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylates were prepared following the literature procedures [1].

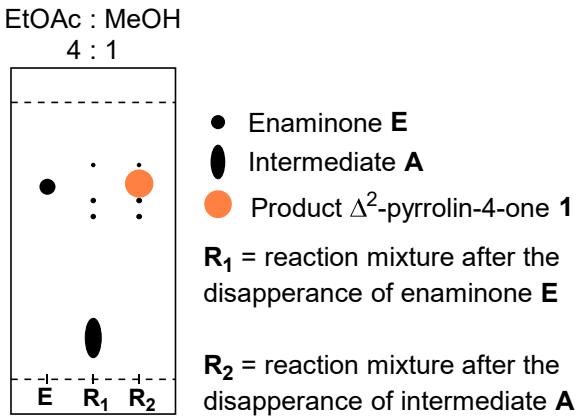


Figure S1. General TLC chromatogram for the reaction **E**→**A**→**1**.

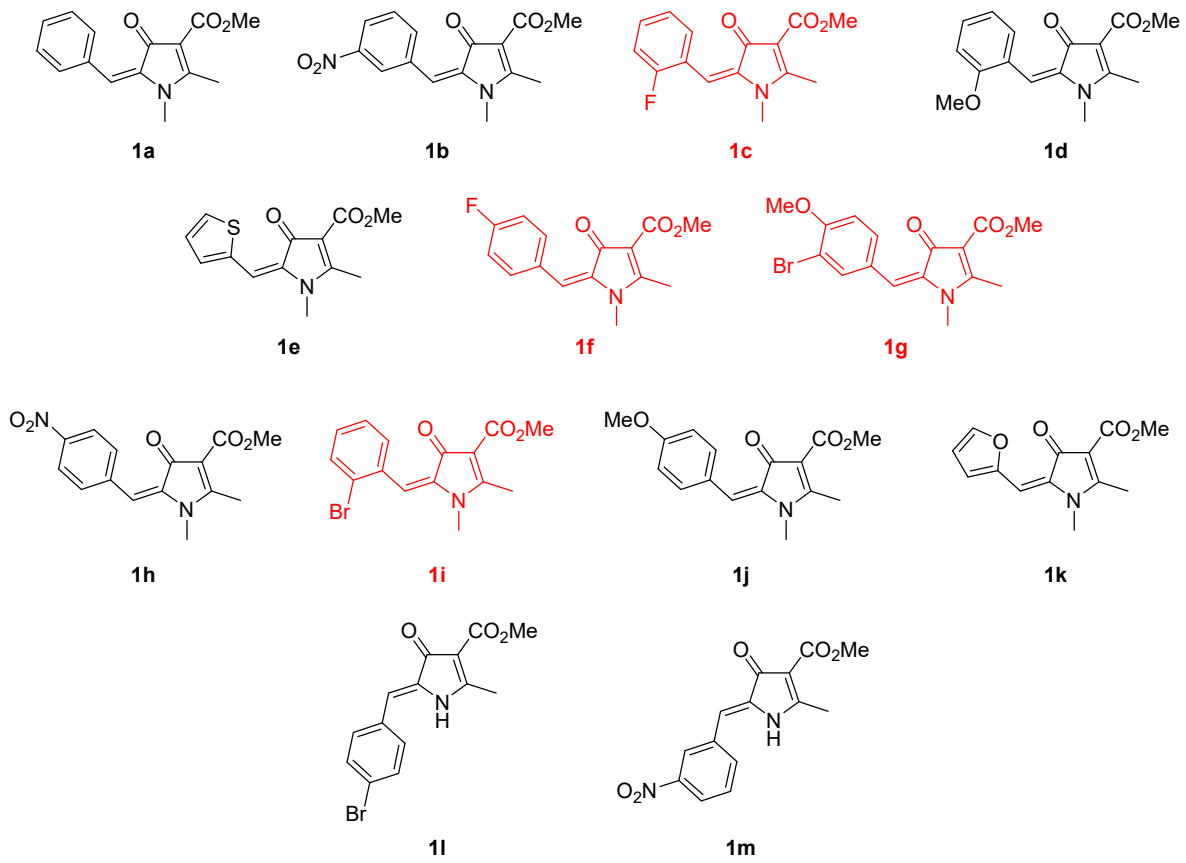
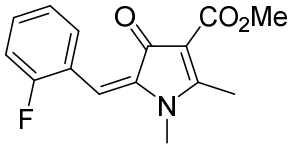


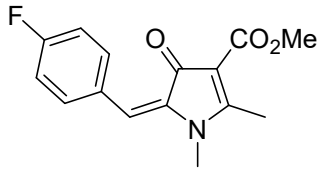
Figure S2. Applied 5-arylidene-2-methyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylates **1**; colorcode red – novel reported prrolones.

Methyl (*E*)-5-(2-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1c)



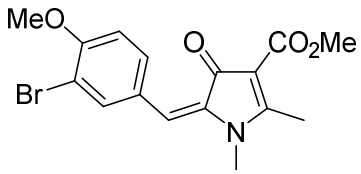
Following *GP1*. Prepared from methyl (*Z*)-2-(2-chloroacetyl)-3-(methylamino)but-2-enoate (**E**), (5 mmol, 1.028 g), 2-fluorobenzaldehyde (5 mmol, 621 mg), EtOH (15 mL), KOH (5.25 mmol, ω = 85%, 347 mg), and $KHSO_4$ (2.5 mmol, 340 mg). Yield: 702 mg (2.55 mmol, 51%) of bright yellow solid; mp = 218–220°C. EI-HRMS: *m*/*z* = 276.1030 (MH^+); $C_{15}H_{15}FNO_3$ requires: *m*/*z* = 276.1030 (MH^+); ν_{max} 3077, 1684, 1656, 1595, 1566, 1527, 1480, 1433, 1412, 1296, 1225, 1196, 1154, 1125, 1063, 1031, 973, 889, 860, 844, 798, 764, 619 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.65 (*s*, 3H, Me); 3.36 (*s*, 3H, Me); 3.60 (*s*, 3H, Me); 6.80 (*s*, 1H); 7.15 – 7.27 (*m*, 2H); 7.43 (*q*, *J* = 7.1 Hz, 1H); 8.13 (*t*, *J* = 7.9 Hz, 1H). ^{13}C-NMR (126 MHz, DMSO-d_6): δ 13.69, 29.56, 50.12, 101.89, 112.16 (*d*, *J* = 4.4 Hz), 115.03 (*d*, *J* = 21.9 Hz), 120.53 (*d*, *J* = 12.5 Hz), 123.63 (*d*, *J* = 3.3 Hz), 131.36 (*d*, *J* = 8.6 Hz), 131.52 (*d*, *J* = 1.3 Hz), 136.92, 160.15 (*d*, *J* = 249.3 Hz), 163.57, 173.45, 178.91.

Methyl (*E*)-5-(4-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1f)



Following *GP1*. Prepared from methyl (*Z*)-2-(2-chloroacetyl)-3-(methylamino)but-2-enoate (**E**), (9.87 mmol, 2.03 g), 4-fluorobenzaldehyde (9.87 mmol, 1.06 mL), EtOH (25 mL), KOH (10.36 mmol, ω = 85%, 684 mg), and $KHSO_4$ (4.92 mmol, 670 mg). Yield: 1.167 g (4.24 mmol, 43%) of yellow solid; mp = 166–168°C. EI-HRMS: *m*/*z* = 276.1033 (MH^+); $C_{15}H_{15}FNO_3$ requires: *m*/*z* = 276.1030 (MH^+); ν_{max} 3064, 3036, 2950, 1696, 1681, 1657, 1604, 1528, 1504, 1436, 1415, 1237, 1208, 1190, 1168, 1123, 1065, 979, 881, 834, 791, 775, 644 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.64 (*s*, 3H, Me), 3.37 (*s*, 3H, Me); 3.62 (*s*, 3H, Me); 6.91 (*s*, 1H, CH); 7.21 – 7.27 (*m*, 2H, Arl); 8.32 – 8.38 (*m*, 2H, Arl). ^{13}C-NMR (126 MHz, DMSO-d_6): δ 13.72, 29.69, 50.09, 101.93, 114.92 (*d*, *J* = 21.8 Hz), 121.73, 129.33 (*d*, *J* = 3.3 Hz), 133.72 (*d*, *J* = 8.3 Hz), 135.97 (*d*, *J* = 2.0 Hz), 161.76, 163.74, 171.84, 179.06.

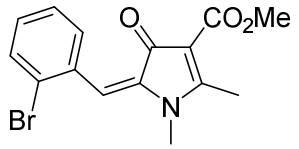
Methyl (*E*)-5-(3-bromo-4-methoxybenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1g)



Following *GP1*. Prepared from methyl (*Z*)-2-(2-chloroacetyl)-3-(methylamino)but-2-enoate (**E**), (5 mmol, 1.028 g), 3-bromo-4-methoxybenzaldehyde (5 mmol, 1.075 g), EtOH (15 mL), KOH (5.25 mmol, ω = 85%, 347 mg), and $KHSO_4$ (2.5 mmol, 340 mg). Yield: 752 mg (2.05 mmol, 41%) of dark-orange solid; mp = 177–181°C. EI-HRMS: *m*/*z* = 366.0331 (MH^+); $C_{16}H_{16}BrNO_4$ requires: *m*/*z* = 366.0335 (MH^+); ν_{max} 2944, 1660, 1602, 1578, 1523, 1490, 1438, 1415, 1298, 1267, 1205, 1179, 1057, 1009, 941, 904, 882, 808, 792, 780, 745, 683, 608 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.64 (*s*, 3H, Me); 3.37 (*s*, 3H, Me); 3.64 (*s*, 3H, Me); 3.92 (*s*, 3H, Me); 6.87 (*s*, 1H); 7.17 (*d*, *J* = 8.8 Hz, 1H); 8.23 (*dd*, *J* = 2.1; 8.8 Hz, 1H);

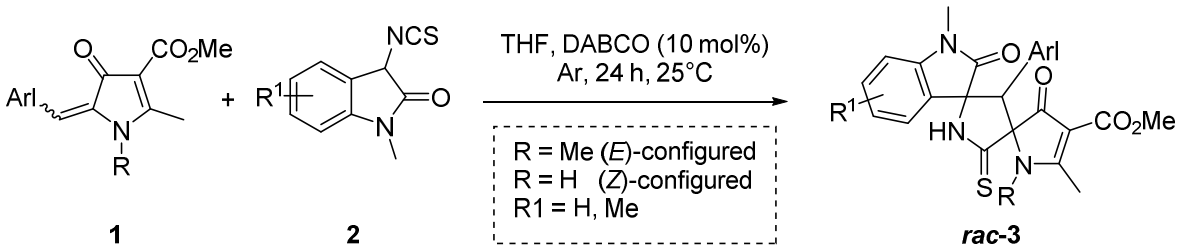
8.96 (*d*, *J* = 2.1 Hz, 1H). ^{13}C-NMR (126 MHz, DMSO-d_6): δ 13.72, 29.72, 50.12, 56.48, 101.90, 110.02, 111.99, 121.83, 126.93, 133.32, 135.33, 135.49, 156.63, 163.82, 171.10, 179.07.

Methyl (*E*)-5-(2-bromobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1i)



Following *GP1*. Prepared from methyl (*Z*)-2-(2-chloroacetyl)-3-(methylamino)but-2-enoate (**E**) (2.43 mmol, 500 mg), 2-bromobenzaldehyde (2.43 mmol, 450 mg), EtOH (12 mL), KOH (2.43 mmol, ω = 85%, 160 mg), and $KHSO_4$ (2.43 mmol, 331 mg); purification by rechrystallization from a mixture of DMF and H_2O. Yield: 366 mg (1.089 mmol, 45%) of yellow solid; mp = 189–192°C. EI-HRMS: *m*/*z* = 336.0237 (MH^+); $C_{15}H_{15}BrNO_3$ requires: *m*/*z* = 336.0230 (MH^+); ν_{max} 3056, 2952, 1674, 1619, 1557, 1524, 1505, 1464, 1431, 1413, 1396, 1368, 1289, 1251, 1208, 1188, 1170, 1116, 1070, 1016, 979, 903, 869, 854, 831, 797, 775, 760, 711 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.65 (*s*, 3H); 3.36 (*s*, 3H); 3.59 (*s*, 3H); 6.79 (*s*, 1H); 7.30 (*td*, *J* = 1.5; 7.5 Hz, 1H); 7.33–7.39 (*m*, 1H); 7.68 (*dd*, *J* = 1.2; 7.9 Hz, 1H); 7.86 (*dd*, *J* = 1.6; 7.7 Hz, 1H). ^{13}C-NMR (126 MHz, DMSO-d_6): δ 13.7, 29.6, 50.1, 102.0, 118.9, 123.6, 126.8, 130.6, 132.0, 132.8, 136.2, 163.5, 174.0, 179.0. (one signal missing)

Organocatalyzed bis-spiroheterocyclization – preparation of racemic mixtures – *General procedure 2* (*GP2*)



1 **2** ***rac*-3**

To a mixture of arylidene-Δ^2-pyrrolin-4-one **1** (0.1 mmol), 3-isothiocyanato oxindole **2** (0.13 mmol), and 1,4-diazabicyclo[2.2.2]octan (DABCO) (0.01 mmol, 1.12 mg) under Argon, anhydrous THF (1 mL) was added and the resulting reaction mixture was stirred at 25°C for 24 h. Volatile components were evaporated *in vacuo* and the residue was purified by column chromatography (Silica gel 60, mobile phase: EtOAc/petroleum ether = 2:1). Fractions containing the pure racemic product ***rac*-3** (*Figure S3*) were combined and volatile components evaporated *in vacuo* followed by HPLC analysis on chiral columns. Products ***rac*-3** (compunds ***rac*-3k–n**), that could not be separated on chiral columns, were fully characterized.

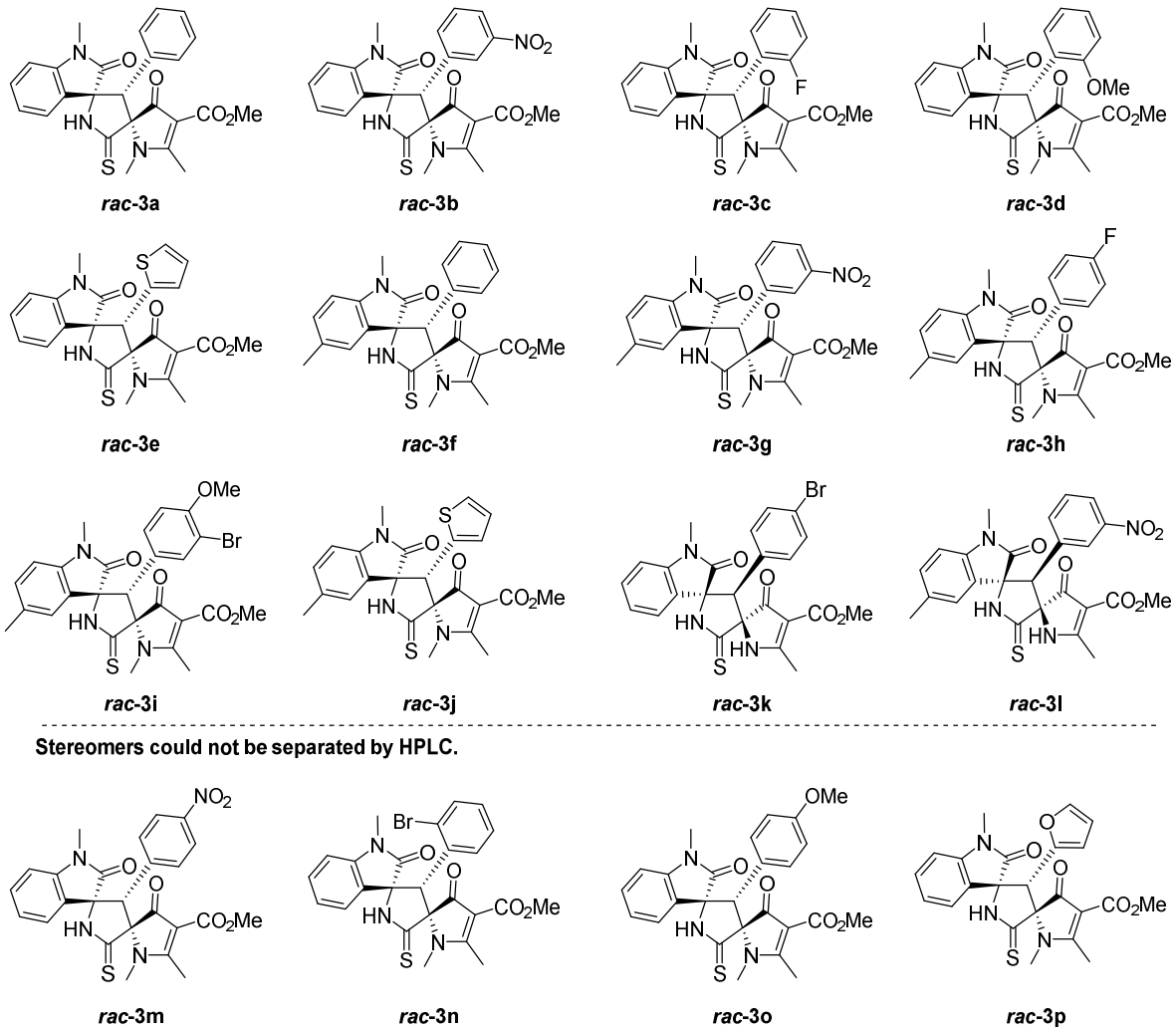
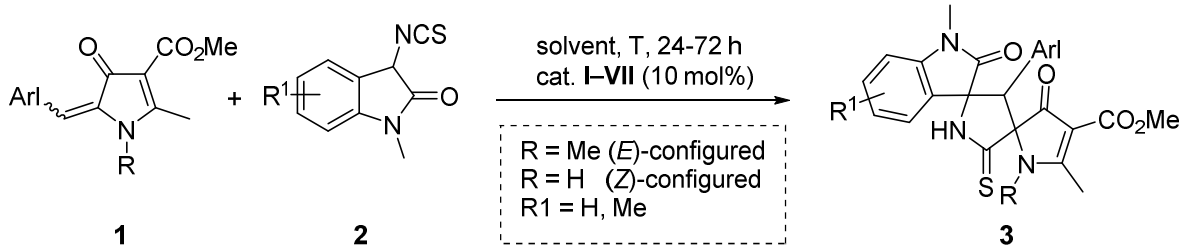


Figure S3. Synthesized racemic bis-spiroheterocycles ***rac*-3**.

Organocatalyzed stereoselective bis-spiroheterocyclization – *General procedure 3* (*GP3*)



1 **2** **3**

To a mixture arylidene-Δ²-pyrrolin-4-one **1** (0.1 mmol), 3-isothiocyanato oxindole **2** (0.13 mmol), and organocatalyst **I–XII** (10 mol%) under Argon, anhydrous solvent (1 mL) was added and and the resulting reaction mixture was stirred at 25°C for 24-72 h.

i) For catalyst and solvent screening (model reaction **1a**+**2a**→**3a**), volatile components were evaporated *in vacuo* and the residue was purified by flash column chromatography to remove the catalyst (Silica gel 60, mobile phase: EtOAc/petroleum ether = 2:1). Fractions containing the product **3a** were combined and volatile components evaporated *in vacuo* followed by determination of the enantiomeric excess and diastereomeric ratio by HPLC analysis.

ii) For the reaction scope synthesis (reactions **1**+**2**→**3**; compounds **3a–l**; *Figure S4*), volatile components were evaporated *in vacuo* and the residue was purified by column chromatography (Silica gel 60, mobile phase: EtOAc/petroleum ether = 2:1). Fractions containing the pure product **3** were combined and volatile components evaporated *in vacuo* followed by determination of the enantiomeric excess by HPLC analysis, determination of diastereomeric ratio by ^{1}H-NMR, and full characterization.

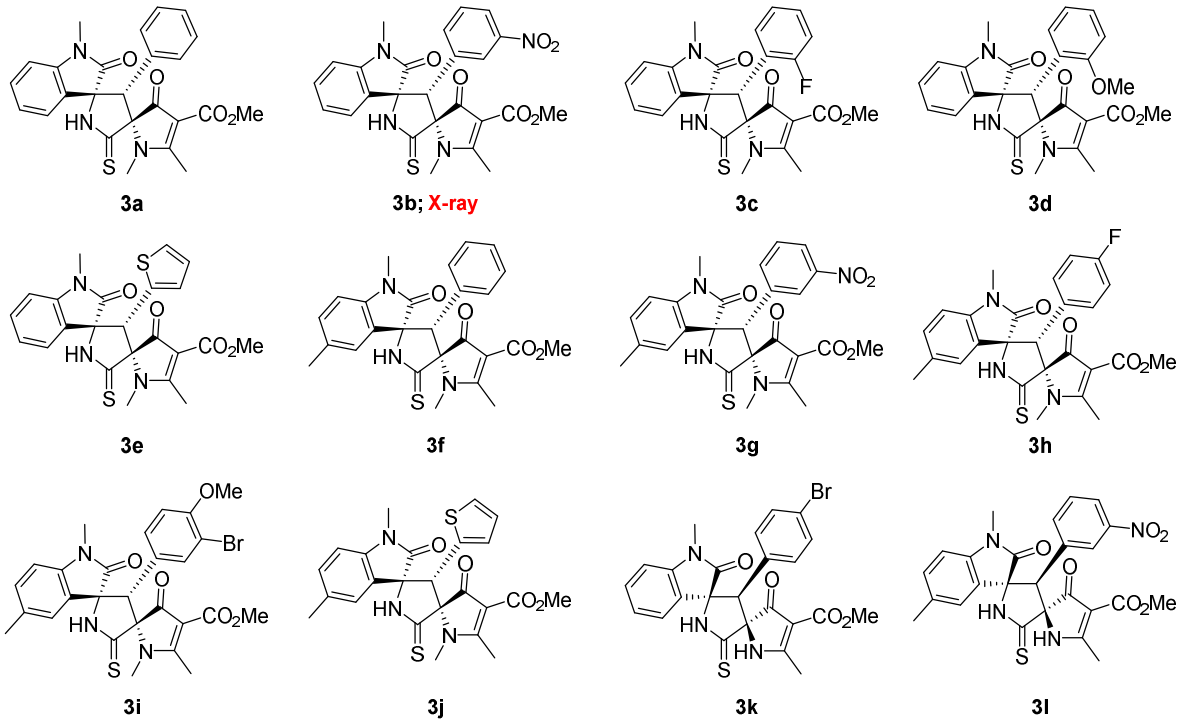
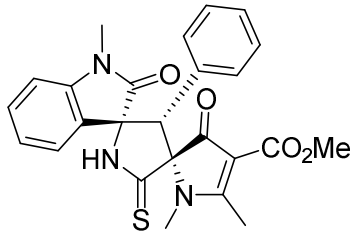


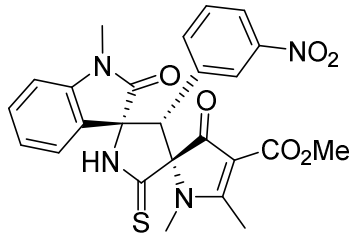
Figure S4. Synthesized nonracemic bis-spiroheterocycles **3**.

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-phenyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3a)



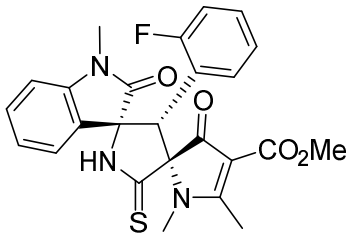
Following *GP2* and *GP3*. Prepared from methyl (*E*)-1,2-dimethyl-5-benzylidene-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1a**) (0.1 mmol, 25.7 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 24 h. Isolation of ***rac*-3a** and **3a**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3a**): 24 mg (0.0520 mmol, 52%) of white solid. **3a**: *dr* = 90:10. Yield: 31 mg (0.0671 mmol, 67%) white solid; mp = 278–279°C. $[\alpha]_D^{r.t.}$ = –4.4 (*c* = 0.64, $CHCl_3$). EI-HRMS: *m*/*z* = 462.1476 (MH^+); $C_{25}H_{24}N_3O_4S$ requires: *m*/*z* = 462.1482 (MH^+); ν_{max} 3190, 2946, 1720, 1682, 1526, 1494, 1471, 1437, 1418, 1374, 1350, 1201, 1158, 1112, 1090, 1064, 1022, 945, 752, 718, 701 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.53 (*s*, 3H); 3.08 (*s*, 3H); 3.56 (*s*, 3H); 3.75 (*m*, 3H); 4.88 (*s*, 1H); 6.75 (*d*, *J* = 7.9 Hz, 1H); 6.94 – 6.98 (*m*, 2H); 7.10 – 7.21 (*m*, 4H); 7.30 – 7.37 (*m*, 1H); 7.75 – 7.80 (*m*, 1H); 8.39 (br *s*, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.74, 26.82, 32.51, 51.16, 62.36, 73.30, 87.58, 101.67, 109.07, 124.44, 124.70, 126.87, 128.68, 128.77, 129.12, 130.20, 131.19, 142.98, 164.50, 174.09, 185.70, 192.87, 197.44. HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm. Major diastereomer: *t*R = 15.1 minutes (major); 30.8 minutes (minor) – 87% *ee*.

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3b)



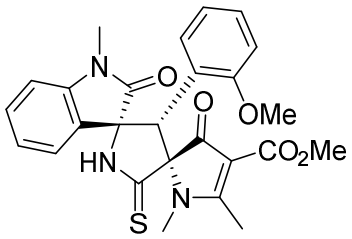
Following *GP2* and *GP3*. Prepared from methyl (*E*)-1,2-dimethyl-5-(3-nitrobenzylidene)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1b**) (0.1 mmol, 30.2 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 24 h. Isolation of ***rac*-3b** and **3b**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3b**): 35 mg (0.0691 mmol, 69%) of orange solid. **3b**: *dr* = 99:1. Yield: 26 mg (0.0513 mmol, 51%) orange solid; mp = 185–187°C. $[\alpha]_D^{r.t.}$ = –2.0 (*c* = 0.10, $CHCl_3$). EI-HRMS: *m*/*z* = 507.1324 (MH^+); $C_{25}H_{23}N_4O_6S$ requires: *m*/*z* = 507.1333 (MH^+); ν_{max} 3498, 3233, 3100, 2923, 2851, 1718, 1707, 1694, 1667, 1613, 1526, 1470, 1438, 1419, 1375, 1349, 1285, 1206, 1171, 1126, 1092, 1062, 1023, 982, 951, 921, 901, 853, 828, 804, 775, 760, 731 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.60 (*s*, 3H); 3.12 (*s*, 3H); 3.59 (*s*, 3H); 3.76 (*s*, 3H); 4.99 (*s*, 1H); 6.82 (*d*, *J* = 7.8 Hz, 1H); 7.13–7.16 (*m*, 1H); 7.20–7.25 (*m*, 1H); 7.33 (*t*, *J* = 8.0 Hz, 1H); 7.40 (*td*, *J* = 1.2; 7.7 Hz, 1H); 7.81 (*dd*, *J* = 1.2; 7.5 Hz, 1H); 7.96 (*t*, *J* = 2.1 Hz, 1H); 8.07 (*ddd*, *J* = 1.0; 2.3; 8.2 Hz, 1H); 8.36 (br *s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.95, 26.90, 32.51, 51.31, 60.63, 72.83, 86.98, 102.07, 109.40, 123.36, 123.65, 124.81, 124.84, 126.08, 129.89, 131.76, 132.68, 135.70, 142.90, 148.35, 164.24, 173.38, 186.40, 192.53, 196.44. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm. Major diastereomer: *t*R = 32.0 minutes (major); 49.4 minutes (minor) – 91% *ee*.

Methyl (3*R*,3'*S*,4'*R*)-3'-(2-fluorophenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3c)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-5-(2-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1c**) (0.1 mmol, 27.5 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 24 h. Isolation of ***rac*-3c** and **3c**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3c**): 40 mg (0.083 mmol, 83%) of white solid. **3c**: *dr* = 91:9. Yield: 24 mg (0.050 mmol, 50%) of white solid; mp = 235–237°C. $[\alpha]_D^{r.t.}$ = +11.0 (*c* = 0.10, $CHCl_3$). EI-HRMS: *m*/*z* = 480.1387 (MH^+); $C_{25}H_{23}FN_3O_4S$ requires: *m*/*z* = 480.1388 (MH^+); ν_{max} 3176, 2944, 1724, 1669, 1612, 1526, 1490, 1470, 1439, 1416, 1375, 1342, 1303, 1286, 1270, 1214, 1169, 1152, 1110, 1101, 1073, 1019, 1003, 986, 965, 943, 904, 892, 876, 841, 805, 780, 769, 754, 741, 717 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.56 (*s*, 3H); 3.09 (*s*, 3H); 3.59 (*s*, 3H); 3.77 (*s*, 3H); 5.42 (*s*, 1H); 6.75 (*dd*, *J* = 1.8; 7.7 Hz, 1H); 6.84 (*ddd*, *J* = 1.2; 8.3; 9.8 Hz, 1H); 7.01 (*td*, *J* = 1.3; 7.7 Hz, 1H); 7.15–7.24 (*m*, 2H); 7.36 (*td*, *J* = 1.2; 7.8 Hz, 1H); 7.41 (*td*, *J* = 1.7; 7.7 Hz, 1H); 7.84 (*m*, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.78, 26.85, 32.63, 51.23, 52.35, 52.38, 72.98, 86.92, 101.95, 108.95, 115.90, 116.08, 117.53, 117.63, 124.02, 124.05, 124.65, 125.22, 126.32, 129.66, 130.42, 130.49, 131.36, 142.89, 160.18, 162.18, 164.63, 174.12, 185.89, 192.37, 197.50. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 270 nm. Major diastereomer: *t*R = 13.6 minutes (major); 45.0 minutes (minor) – 85% *ee*.

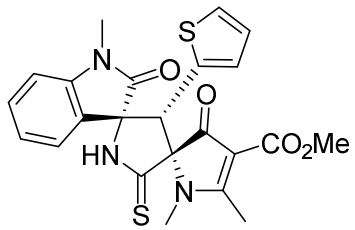
Methyl (3*R*,3'*S*,4'*R*)-3'-(2-methoxyphenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3d)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-5-(2-methoxybenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1d**) (0.1 mmol, 29 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 24 h. Isolation of ***rac*-3d** and **3d**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3d**): 13 mg (0.026 mmol, 26%) of brownish solid. **3d**: *dr* = 87:13. Yield: 13 mg (0.026 mmol, 26%) of white solid; mp = 225–227°C. $[\alpha]_D^{r.t.}$ = +42.0 (*c* = 0.10, $CHCl_3$). EI-HRMS: *m*/*z* = 492.1587 (MH^+); $C_{26}H_{26}N_3O_5S$ requires: *m*/*z* = 492.1588 (MH^+); ν_{max} 3192, 2951, 1722, 1683, 1651, 1612, 1529, 1489, 1469, 1439, 1419, 1374, 1347, 1296, 1248, 1211, 1171, 1148, 1122, 1103, 1067, 1020, 981, 943, 907, 868, 835, 815, 777, 756, 716, 706 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.49 (*s*, 3H); 3.16 (*s*, 3H); 3.34 (*s*, 3H); 3.41 (*s*, 3H); 3.77 (*s*, 3H); 5.47 (*s*, 1H); 6.63 (*dd*, *J* = 1.3; 8.3, Hz, 1H); 6.77 (*td*, *J* = 1.4; 7.6 Hz, 2H); 7.08–7.17 (*m*, 2H); 7.31 (*td*, *J* = 1.4; 7.7 Hz, 2H); 7.83 (*dd*, *J* = 1.2; 7.5 Hz, 1H); 8.11 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.48, 26.94, 32.19, 51.04, 52.67, 55.16, 72.68, 87.22, 101.01, 108.91, 110.54, 119.53, 120.15, 124.21, 125.41, 126.95, 128.22, 129.50, 130.92, 143.10, 157.99, 164.96, 174.93, 184.34, 192.79,

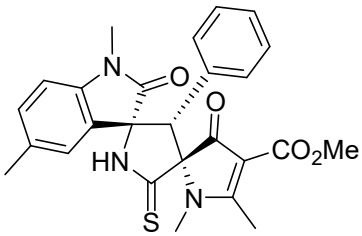
198.02. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm. Major diastereomer: *t*R = 14.2 minutes (major); 63.0 minutes (minor) – 80% *ee*.

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-2,3''-dioxo-3'-(thiophen-2-yl)-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3e)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-1,2-dimethyl-4-oxo-5-(thiophen-2-ylmethylene)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1e**) (0.1 mmol, 26.3 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 24 h. Isolation of ***rac*-3e** and **3e**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3e**): 21 mg (0.045 mmol, 45%) of white solid. **3e**: *dr* = 76:24. Yield: 20 mg (0.043 mmol, 43%) of yellowish solid; mp = 272–274°C. $[\alpha]_D^{r.t.}$ = +25.0 (*c* = 0.10, $CHCl_3$). EI-HRMS: *m*/*z* = 468.1041 (MH^+); $C_{23}H_{22}N_3O_4S_2$ requires: *m*/*z* = 468.1046 (MH^+); ν_{max} 3234, 3089, 3005, 2952, 2243, 1722, 1662, 1610, 1524, 1490, 1470, 1437, 1417, 1368, 1344, 1298, 1264, 1205, 1169, 1124, 1087, 1020, 998, 944, 903, 849, 783, 753, 730 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.63 (*s*, 3H); 3.08 (*s*, 3H); 3.60 (*s*, 3H); 3.77 (*s*, 3H); 5.17 (*s*, 1H); 6.47–6.59 (*m*, 1H); 6.72–6.86 (*m*, 2H); 7.14 (*dd*, *J* = 1.1; 5.2 Hz, 1H); 7.19 (*t*, *J* = 7.5 Hz, 1H); 7.38 (*t*, *J* = 7.8 Hz, 1H); 7.76 (*d*, *J* = 7.3 Hz, 1H); 8.07 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.94, 26.81, 32.48, 51.21, 57.60, 73.20, 86.72, 101.80, 109.06, 124.55, 124.82, 126.58, 126.61, 126.87, 128.19, 130.89, 131.44, 143.31, 164.44, 173.48, 186.21, 192.78, 197.04. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm. Major diastereomer: *t*R = 12.0 minutes (major); 52.1 minutes (minor) – 96% *ee*.

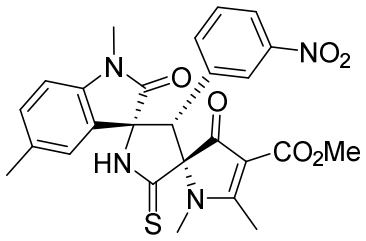
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-2,3''-dioxo-3'-phenyl-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3f)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-5-benzylidene-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1a**) (0.1 mmol, 26 mg), 3-isothiocyanato-1,5-dimethylindolin-2-one (**2b**) (0.13 mmol, 29 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 48 h. Isolation of ***rac*-3f** and **3f**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3f**): 11 mg (0.023 mmol, 23%) of white solid. **3f**: *dr* = 99:1. Yield: 15 mg (0.0315 mmol, 31%) of yellowish solid; mp = 273–280°C. $[\alpha]_D^{r.t.}$ = +3.2 (*c* = 0.09, CH_2Cl_2). EI-HRMS: *m*/*z* = 476.1632 (MH^+); $C_{26}H_{26}N_3O_4S$ requires: *m*/*z* = 476.1639 (MH^+); ν_{max} 3160, 2945, 2923, 1719, 1696, 1652, 1527, 1490, 1437, 1353, 1207, 1141, 1104, 1065, 1020, 980, 810, 738, 707, 698, 670 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.31 (*s*, 3H); 2.53 (*s*, 3H); 3.07 (*s*, 3H); 3.54 (*s*, 3H); 3.76 (*s*, 3H); 4.87 (*s*, 1H); 6.64 (*d*, *J* = 7.6 Hz, 1H); 6.96 (*d*, *J* = 7.5 Hz, 2H); 7.15 (*dt*, *J* = 7.3, 4H); 7.59 (*s*, 1H); 8.29 (*s*, 1H, NH). ^{13}C-NMR (126

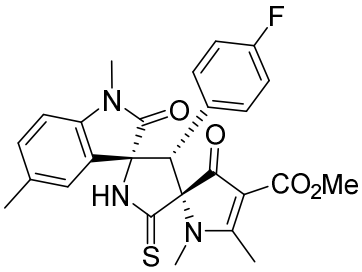
MHz, $CDCl_3$): δ 14.72, 21.09, 26.94, 32.46, 51.14, 62.30, 73.32, 87.60, 101.60, 108.92, 125.33, 126.84, 128.61, 128.74, 129.07, 130.28, 131.43, 134.46, 140.55, 164.49, 173.99, 185.64, 193.02, 197.36. HPLC: Chiralpak AD-H, *n*-Hexane/EtOH = 85:15, flow rate 1.0 mL/min, λ = 300 nm. Major diastereomer: *t*R = 20.3 minutes (major); 34.3 minutes (minor) – 98% *ee*.

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3g)



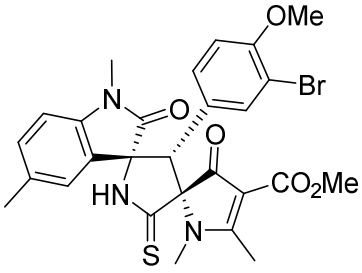
Following *GP2* and *GP3*. Prepared from methyl (*E*)-1,2-dimethyl-5-(3-nitrobenzylidene)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1b**) (0.1 mmol, 30.2 mg), 3-isothiocyanato-1,5-dimethylindolin-2-one (**2b**) (0.13 mmol, 29 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 48 h. Isolation of ***rac*-3g** and **3g**: purification by column chromatography (EtOAc/petroleum ether = 2:1). Yield (***rac*-3g**): 18 mg (0.0346 mmol, 34%) of white solid. **3g**: *dr* = 94:6. Yield: 21 mg (0.0403 mmol, 40%) of white solid; mp = 160–164°C. $[\alpha]_D^{r.t.}$ = +11.1 (*c* = 0.7, $CHCl_3$). EI-HRMS: *m*/*z* = 521.1482 (MH^+); $C_{26}H_{25}N_4O_6S$ requires: *m*/*z* = 521.1489 (MH^+); ν_{max} 2946, 2921, 1718, 1688, 1607, 1528, 1500, 1436, 1418, 1348, 1201, 1141, 1096, 1063, 1015, 901, 810, 771, 730, 692, 657 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.37 (*s*, 3H); 2.61 (*s*, 3H); 3.11 (*s*, 3H); 3.57 (*s*, 3H); 3.77 (*s*, 3H); 4.99 (*s*, 1H); 6.72 (*d*, *J* = 7.9 Hz, 1H); 7.14 – 7.21 (*m*, 2H); 7.34 (*t*, *J* = 8.0 Hz, 1H); 7.63 (*d*, *J* = 1.6 Hz, 1H); 7.97 (*t*, *J* = 2.1 Hz, 1H); 8.05 – 8.09 (*m*, 1H); 8.48 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.90, 21.16, 26.91, 32.44, 51.27, 60.52, 72.89, 87.03, 101.98, 109.18, 123.34, 123.57, 125.42, 126.08, 129.85, 131.98, 132.83, 134.87, 135.62, 140.45, 148.34, 164.26, 173.28, 186.33, 192.65, 196.35. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm. Major diastereomer: *t*R = 9.5 minutes (major); 18.6 minutes (minor) – 94% *ee*.

Methyl (3*R*,3'*S*,4'*R*)-3'-(4-fluorophenyl)-1,1'',5,5''-tetramethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3h)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-5-(4-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1f**) (0.1 mmol, 28 mg), 3-isothiocyanato-1,5-dimethylindolin-2-one (**2b**) (0.13 mmol, 29 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 48 h. Isolation of ***rac*-3h** and **3h**: purification by column chromatography (EtOAc/petroleum ether = 1:2). Yield (***rac*-3h**): 20 mg (0.0405 mmol, 40%) of white solid. **3h**: *dr* = 94:6. Yield: 22.5 mg (0.0455 mmol, 45%) of white solid; mp = 150–156°C. $[\alpha]_D^{r.t.}$ = +61.5 (*c* = 0.13, $CHCl_3$). EI-HRMS: *m*/*z* = 494.1539 (MH^+); $C_{26}H_{25}FN_3O_4S$ requires: *m*/*z* = 494.1544 (MH^+); ν_{max} 2948, 1716, 1689, 1606, 1528, 1511, 1500, 1437, 1418, 1353, 1232, 1204, 1164, 1141, 1096, 1063, 1012, 891, 838, 805, 788, 769, 737, 689, 657 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.34 (*s*, 3H); 2.57 (*s*, 3H); 3.06 (*s*, 3H); 3.60 (*s*, 3H); 3.77 (*s*, 3H); 4.84 (*s*, 1H); 6.65 (*d*, *J* = 7.9 Hz, 1H); 6.80 – 6.87 (*m*, 2H); 6.95 – 7.01 (*m*, 2H); 7.12 – 7.17 (*m*, 1H); 7.57 – 7.61 (*m*, 1H); 8.16 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.82, 21.14, 26.86, 32.58, 51.19, 62.09, 73.48, 87.43, 101.95, 108.90, 115.71, 115.88, 125.29, 125.95, 125.98, 126.70, 131.23, 131.29, 131.58, 134.61, 140.49, 161.82, 163.80, 164.38, 173.83, 185.99, 192.96, 197.34. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm. Major diastereomer: *t*R = 5.6 minutes (major); 26.4 minutes (minor) – 95% *ee*.

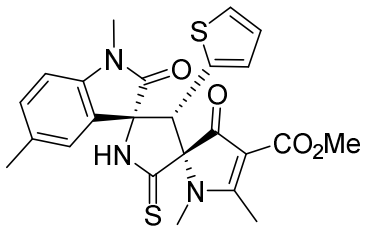
Methyl (3*R*,3'*S*,4'*R*)-3'-(4-bromo-3-methoxyphenyl)-1,1'',5,5''-tetramethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3i)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-5-(3-bromo-4-methoxybenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1g**) (0.1 mmol, 37 mg), 3-isothiocyanato-1,5-dimethylindolin-2-one (**2b**) (0.13 mmol, 29 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 72 h. Isolation of ***rac*-3i** and **3i**: purification by column chromatography (EtOAc/petroleum ether = 1:2). Yield (***rac*-3i**): 9 mg (0.0154 mmol, 15%) of white solid. **3i**: *dr* = 82:18. Yield: 11 mg (0.0188 mmol, 18%) of white solid; mp = 176–180°C. $[\alpha]_D^{r.t.}$ = +12.6 (*c* = 0.8, $CHCl_3$). EI-HRMS: *m*/*z* = 584.0850 (MH^+); $C_{27}H_{26}BrN_3O_5S$ requires: *m*/*z* = 584.0849 (MH^+); ν_{max} 2929, 1716, 1686, 1604, 1526, 1499, 1436, 1354, 1288, 1261, 1199, 1140, 1096, 1055, 1016, 812, 770, 680, 659 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.38 (*s*, 3H); 2.55 (*s*, 3H); 3.08 (*s*, 3H); 3.50 (*s*, 3H); 3.61 (*s*, 3H); 3.75 (*s*, 3H); 4.53 (*s*, 1H); 6.85 (*dd*, *J* = 2.4; 8.8 Hz, 1H); 6.96 (*t*, *J* = 8.5 Hz, 2H); 7.03 – 7.07 (*m*, 1H); 7.23 – 7.27 (*m*, 1H); 7.32 – 7.37 (*m*, 1H); 11.37 (*s*, 1H). ^{13}C-NMR (126 MHz, DMSO-d_6): δ 14.36, 20.70, 26.62, 31.91, 50.30, 56.11, 59.73, 73.09, 87.44, 100.32, 109.44, 110.34, 112.88, 123.62, 123.98, 127.12, 129.58, 131.12, 132.58, 133.22, 140.58, 155.27, 163.32, 173.24, 185.03, 191.47, 195.70. HPLC: Chiralpak AD-H, *n*-

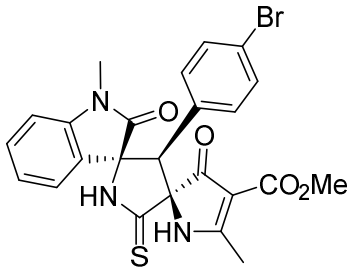
Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm. Major diastereomer: *t*R = 9.9 minutes (major); 19.2 minutes (minor) – 85% *ee*.

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-2,3''-dioxo-3'-(thiophen-2-yl)-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3j)



Following *GP2* and *GP3*. Prepared from methyl (*E*)-1,2-dimethyl-4-oxo-5-(thiophen-2-ylmethylene)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1e**) (0.1 mmol, 26.3 mg), 3-isothiocyanato-1,5-dimethylindolin-2-one (**2b**) (0.13 mmol, 29 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 74 h. Isolation of ***rac*-3j** and **3j**: purification by column chromatography (EtOAc/petroleum ether = 1:2). Yield (***rac*-3j**): 12 mg (0.0249 mmol, 25%) of white solid. **3j**: *dr* = 90:10. Yield: 18 mg (0.0373 mmol, 37%) of white solid; mp = 210–216°C. $[\alpha]_D^{r.t.}$ = +49.5 (*c* = 0.6, $CHCl_3$). EI-HRMS: *m*/*z* = 482.1195 (MH^+); $C_{24}H_{24}N_3O_4S_2$ requires: *m*/*z* = 482.1203 (MH^+); ν_{max} 2917, 1718, 1686, 1605, 1524, 1499, 1435, 1416, 1353, 1291, 1200, 1140, 1094, 1063, 1015, 910, 813, 756, 698, 665, 611 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.34 (*s*, 3H); 2.63 (*s*, 3H); 3.07 (*s*, 3H); 3.58 (*s*, 3H); 3.77 (*s*, 3H); 5.14 (*s*, 1H); 6.56 (*d*, *J* = 3.6 Hz, 1H); 6.69 (*d*, *J* = 8.0 Hz, 1H); 6.78 (*dd*, *J* = 3.6; 5.1 Hz, 1H); 7.11 – 7.19 (*m*, 2H); 7.56 – 7.61 (*m*, 1H); 8.32 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 14.89, 21.11, 26.83, 32.42, 51.17, 57.52, 73.30, 86.80, 101.71, 108.87, 125.42, 126.51, 126.59, 126.84, 128.08, 131.02, 131.62, 134.56, 140.87, 164.46, 173.40, 186.16, 192.93, 196.97. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm. Major diastereomer: *t*R = 7.5 minutes (major); 26.6 minutes (minor) – 98% *ee*.

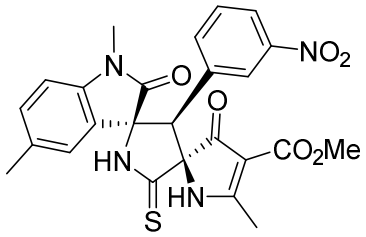
Methyl (3*S*,3'*R*,4'*S*)-3'-(4-bromophenyl)-1,5''-dimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3k)



Following *GP2* and *GP3*. Prepared from methyl (*Z*)-5-(4-bromobenzylidene)-2-methyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1l**) (0.1 mmol, 32 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 24 h. Isolation of ***rac*-3k** and **3k**: purification by column chromatography (EtOAc/petroleum ether = 1:2). Yield (***rac*-3k**): 38 mg (0.072 mmol, 72%) of yellow-orange solid. **3k**: *dr* = 81:19. Yield: 4 mg (0.0076 mmol, 7%) of pale-green solid; mp = 200–203°C. $[\alpha]_D^{r.t.}$ = +521.0 (*c* = 0.10, $CHCl_3$). EI-HRMS: *m*/*z* = 526.0427 (MH^+); $C_{24}H_{21}BrN_3O_4S$ requires: *m*/*z* = 526.0431 (MH^+); ν_{max} 3269, 2945, 1669, 1613, 1511, 1491, 1471, 1440, 1376, 1353, 1314, 1199, 1167, 1132, 1092, 1057, 1010, 956, 863, 828, 752 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.61 (*s*, 3H); 3.15 (*s*, 3H); 3.72 (*s*, 3H); 4.36 (*s*, 1H); 6.78 (*d*, *J* = 7.8 Hz, 1H); 6.90 – 6.96

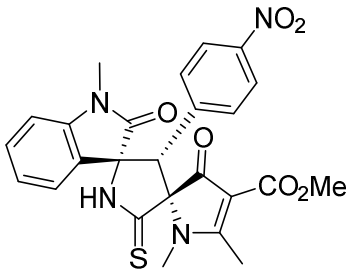
(*m*, 2H); 7.18 – 7.26 (*m*, 3H); 7.37 (*t*, *J* = 7.7 Hz, 1H); 7.65 (*d*, *J* = 7.4 Hz, 1H); 8.08 (*s*, 1H, NH); 8.34 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 18.09, 26.99, 51.20, 58.71, 72.91, 80.42, 102.78, 109.70, 123.53, 123.58, 124.56, 124.82, 128.19, 130.98, 131.74, 132.00, 143.41, 164.13, 174.97, 183.04, 191.38, 200.40. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm. Major diastereomer: *t*R = 27.2 minutes (minor); 40.4 minutes (major) – 18% *ee*.

Methyl (3*S*,3'*R*,4'*S*)-1,5,5''-trimethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3l)



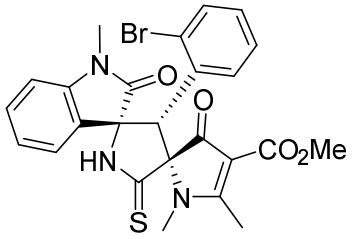
Following *GP2* and *GP3*. Prepared from methyl (*Z*)-2-methyl-5-(3-nitrobenzylidene)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1m**) (0.1 mmol, 29 mg), 3-isothiocyanato-1,5-dimethylindolin-2-one (**2b**) (0.13 mmol, 29 mg), catalyst **IXb** (0.01 mmol, 6.3 mg), anhydrous (trifluoromethyl)benzene, 25°C, 74 h. Isolation of ***rac*-3l** and **3l**: purification by column chromatography (EtOAc/petroleum ether = 1:2). Yield (***rac*-3l**): 15 mg (0.0296 mmol, 29%) of white solid. **3l**: *dr* = 84:16. Yield: 10 mg (0.0197 mmol, 19%) of white solid; mp = 190–196°C. $[\alpha]_D^{r.t.}$ = –32.0 (*c* = 0.9, $CHCl_3$). EI-HRMS: *m*/*z* = 507.1329 (MH^+); $C_{25}H_{23}N_4O_6S$ requires: *m*/*z* = 507.1333 (MH^+); ν_{max} 2940, 1692, 1621, 1607, 1529, 1498, 1439, 1349, 1316, 1291, 1196, 1166, 1097, 1055, 1008, 812, 753, 734, 689 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.37 (*s*, 3H); 3.02 (*s*, 3H); 3.55 (*s*, 3H); 4.37 (*s*, 1H); 6.89 (*d*, *J* = 8.0 Hz, 1H); 7.19 – 7.24 (*m*, 1H); 7.39 – 7.43 (*m*, 1H); 7.45 – 7.51 (*m*, 2H); 7.92 (*t*, *J* = 2.1 Hz, 1H); 8.05 – 8.09 (*m*, 1H); 9.67 (*s*, 1H, NH); 11.30 (*s*, 1H, NH) one Me group is overlapped with the signal for the DMSO. ^{13}C-NMR (126 MHz, DMSO-d_6): δ 16.64, 20.60, 26.45, 50.13, 58.18, 73.14, 80.71, 99.94, 109.43, 123.61, 123.68, 124.42, 124.60, 130.04, 131.23, 132.04, 133.22, 136.38, 141.00, 147.54, 163.20, 173.34, 184.56, 191.31, 198.76. HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm. Major diastereomer: *t*R = 19.2 minutes (minor); 27.6 minutes (major) – 57% *ee*.

Methyl *rel*-(3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-(4-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3m)



Following *GP2*. Prepared from methyl (*E*)-1,2-dimethyl-5-(4-nitrobenzylidene)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1h**) (0.1 mmol, 30 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), DABCO (0.01 mmol, 1.2 mg), THF, 25°C, 24 h. Isolation of ***rac*-3m**: purification by column chromatography (EtOAc/petroleum ether = 2:1). ***rac*-3m**: *dr* = 57:43. Yield: 44 mg (0.087 mmol, 87%) of orange solid; mp = 195–199°C. EI-HRMS: *m*/*z* = 507.1329 (MH^+); $C_{25}H_{23}N_4O_6S$ requires: *m*/*z* = 507.1333 (MH^+); ν_{max} 3505, 3168, 2946, 2169, 1717, 1677, 1609, 1519, 1492, 1470, 1437, 1417, 1372, 1345, 1199, 1108, 1062, 1020, 945, 887, 850, 777, 753, 734 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6) for the major diastereomer: δ 2.57 (*s*, 3H); 3.11 (*s*, 3H); 3.50 (*s*, 3H); 3.61 (*s*, 3H); 4.76 (*s*, 1H); 7.07 – 7.12 (*m*, 2H); 7.27 – 7.34 (*m*, 2H); 7.46 (*td*, *J* = 1.2; 7.8 Hz, 1H); 7.57 (*d*, *J* = 6.7 Hz, 1H); 8.04 – 8.12 (*m*, 2H); 11.46 (*s*, 1H, NH). ^{1}H-NMR (500 MHz, DMSO-d_6) for the minor diastereomer: δ 2.61 (*s*, 3H); 3.14 (*s*, 3H); 3.30 (*s*, 3H); 3.58 (*s*, 3H); 4.54 (*s*, 1H); 7.01 (*d*, *J* = 7.8 Hz, 1H); 7.22 (*t*, *J* = 7.5 Hz, 1H); 7.39 (*td*, *J* = 1.3; 7.7 Hz, 1H); 7.87 – 7.92 (*m*, 2H); 8.63 (*dd*, *J* = 1.2; 7.6 Hz, 1H); 11.49 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, DMSO-d_6) for both diastereomers: δ 14.42, 26.70, 26.91, 29.76, 31.87, 50.32, 50.35, 52.24, 59.79, 71.67, 72.76, 87.22, 88.41, 100.36, 100.46, 109.46, 109.89, 123.05, 123.08, 123.45, 124.02, 124.10, 124.68, 126.70, 128.58, 129.76, 130.87, 131.15, 131.19, 137.86, 138.62, 142.94, 143.64, 147.24, 163.29, 163.38, 172.97, 174.65, 184.01, 185.48, 189.16, 191.12, 193.57, 195.30.

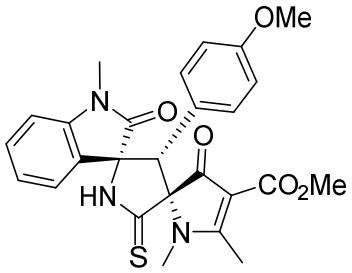
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(2-bromophenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3n)



Following *GP2*. Prepared from methyl (*E*)-5-(2-bromobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1i**) (0.1 mmol, 34 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), **DABCO** (0.01 mmol, 1.2 mg), THF, 25°C, 24 h. Isolation of ***rac*-3n**: purification by column chromatography (EtOAc/petroleum ether = 2:1). ***rac*-3n**: *dr* = 72:28. Yield: 25 mg (0.046 mmol, 46%) of pale-brown solid; mp = 196–200°C. EI-HRMS: *m*/*z* = 540.0588 (MH^+); $C_{25}H_{23}BrN_3O_4S$ requires: *m*/*z* = 540.0587 (MH^+); ν_{max} 3232, 2929, 1717, 1658, 1611, 1525, 1490, 1470, 1435, 1416, 1373, 1349, 1201, 1102, 1061, 1021, 980, 864, 830, 800, 749 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) for the major diastereomer: δ 2.45 (*s*, 3H); 2.96 (*s*, 3H); 3.59 (*s*, 3H); 3.68 (*s*, 3H); 5.74 (*s*, 1H); 6.65 (*d*, *J* = 7.8 Hz, 1H); 6.95 – 7.00 (*m*, 1H); 7.06 – 7.15 (*m*, 2H); 7.23 – 7.34 (*m*, 2H); 7.48 (*dd*, *J* = 1.6; 8.1 Hz, 1H); 7.83 (*d*, *J* = 7.4 Hz, 1H); 8.10 (*s*, 1H, NH). ^{1}H-NMR (500 MHz, $CDCl_3$) for the minor diastereomer: δ 2.37 (*s*, 3H); 3.05 (*s*, 3H); 3.54 (*s*, 3H); 3.68 (*s*, 3H); 5.49 (*s*, 1H); 7.59 – 7.64 (*m*, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) for the major diastereomer: δ 14.81, 26.81, 33.27, 51.21, 58.63, 74.10, 86.93, 102.51, 108.99, 124.27, 125.91, 125.93, 127.03, 127.66, 129.96, 130.14, 130.79, 131.23, 133.81, 142.86, 164.63, 174.06, 185.96, 192.02,

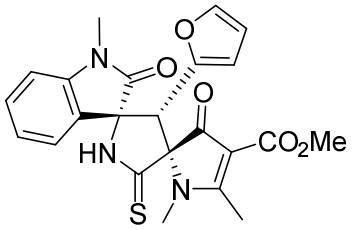
197.70. ^{13}C-NMR (126 MHz, $CDCl_3$) for the minor diastereomer: δ 14.96, 26.76, 33.35, 51.27, 61.59, 85.48, 88.95, 102.96, 108.50, 124.00, 125.61, 126.99, 127.77, 128.89, 129.80, 130.24, 130.67, 131.12, 133.68, 143.23, 164.18, 170.24, 173.09, 184.41, 189.98.

Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(4-methoxyphenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3o)



Following *GP2*. Prepared from methyl (*E*)-5-(4-methoxybenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1j**) (0.1 mmol, 29 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), **DABCO** (0.01 mmol, 1.2 mg), THF, 25°C, 24 h. Isolation of ***rac*-3o**: purification by column chromatography (EtOAc/petroleum ether = 2:1). ***rac*-3o**: *dr* = 87:13. Yield: 25 mg (0.051 mmol, 51%) of yellow solid; mp = 189–194°C. EI-HRMS: *m*/*z* = 492.1584 (MH^+); $C_{26}H_{26}N_3O_5S$ requires: *m*/*z* = 492.1588 (MH^+); ν_{max} 3197, 2947, 2837, 2244, 1711, 1665, 1611, 1513, 1491, 1470, 1439, 1415, 1373, 1350, 1306, 1288, 1254, 1201, 1181, 1169, 1090, 1064, 1027, 945, 911, 797, 773, 756, 724 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) for the major diastereomer: δ 2.55 (*s*, 3H); 3.07 (*s*, 3H); 3.60 (*s*, 3H); 3.70 (*s*, 3H); 3.76 (*s*, 3H); 4.82 (*s*, 1H); 6.61 – 6.66 (*m*, 2H); 6.73 (*d*, *J* = 7.8 Hz, 1H); 6.89 – 6.95 (*m*, 2H); 7.18 (*t*, *J* = 7.6 Hz, 1H); 7.34 (*td*, *J* = 1.2; 7.8 Hz, 1H); 7.73 – 7.80 (*m*, 1H); 8.17 (br *s*, 1H, NH). ^{1}H-NMR (500 MHz, $CDCl_3$) for the minor diastereomer: δ 2.61 (*s*, 3H); 3.12 (*s*, 3H); 3.33 (*s*, 3H); 3.64 (*s*, 3H); 3.75 (*s*, 3H); 4.42 (*s*, 1H); 6.51 – 6.55 (*m*, 2H); 7.01 – 7.05 (*m*, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) for the major diastereomer: δ 14.81, 26.82, 32.59, 51.15, 55.24, 62.42, 73.48, 87.60, 101.79, 108.98, 114.08, 121.80, 124.42, 124.69, 126.98, 130.68, 131.16, 143.02, 159.71, 164.50, 174.13, 185.74, 193.00, 197.77.

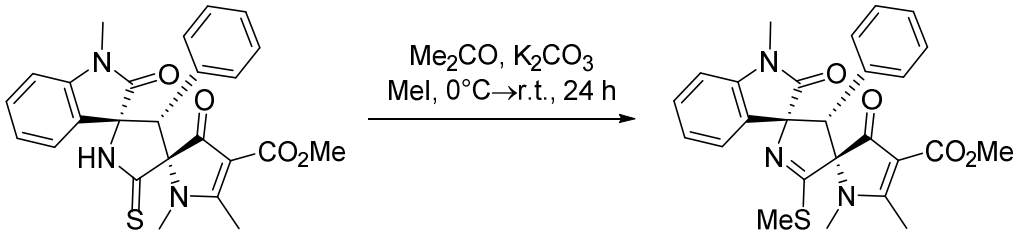
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(furan-2-yl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3p)



Following *GP2*. Prepared from methyl (*E*)-5-(furan-2-ylmethylene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1k**) (0.1 mmol, 25 mg), 3-isothiocyanato-1-methylindolin-2-one (**2a**) (0.13 mmol, 27 mg), **DABCO** (0.01 mmol, 1.2 mg), THF, 25°C, 24 h. Isolation of ***rac*-3p**: purification by column chromatography (EtOAc/petroleum ether = 2:1). ***rac*-3p**: *dr* = 66:34. Yield: 32 mg (0.071 mmol, 71%) of yellowish solid; mp = 271–273°C. EI-HRMS: *m*/*z* = 452.1281 (MH^+); $C_{23}H_{22}N_3O_5S$ requires: *m*/*z* = 452.1275 (MH^+); ν_{max} 3505, 3147, 2946, 17201677, 1662, 1610, 1519, 1493, 1470, 1437, 1417, 1372, 1350, 1345, 1201, 1157, 1110, 1089, 1063, 1018, 946, 932, 905, 886, 821, 774, 752 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6) for the major diastereomer: δ 2.61 (*s*, 3H); 3.17 (*s*, 3H); 3.35 (*s*, 3H); 3.63 (*s*, 3H); 4.68 (*s*, 1H); 6.08 (*d*, *J* = 3.4 Hz, 1H); 6.32 (*dd*, *J* = 1.8; 3.4 Hz, 1H); 7.14 (*d*, *J* = 7.8 Hz,

1H); 7.25 – 7.30 (*m*, 1H); 7.45 – 7.51 (m, 2H); 7.53 (*dd*, *J* = 1.2; 7.4 Hz, 1H); 11.37 (*s*, 1H, NH). ^{1}H-NMR (500 MHz, DMSO-d_6) for the minor diastereomer: δ 2.67 (*s*, 3H); 3.21 (*s*, 3H); 3.24 (*s*, 3H); 3.64 (*s*, 3H); 4.51 (*s*, 1H); 5.82 (*d*, *J* = 3.4 Hz, 1H); 6.12 (*dd*, *J* = 1.8; 3.4 Hz, 1H); 7.06 (*d*, *J* = 7.8 Hz, 1H); 7.13 (*td*, *J* = 1.0; 7.6 Hz, 1H); 7.38 (*td*, *J* = 1.3; 7.7 Hz, 1H); 8.41 (*dd*, *J* = 1.2; 7.5 Hz, 1H); 11.40 (*s*, 1H, NH). ^{13}C-NMR (126 MHz, DMSO-d_6) for both diastereomers: δ 14.30, 14.36, 26.66, 26.90, 29.58, 31.25, 46.37, 50.27, 50.31, 53.36, 70.42, 71.29, 86.10, 86.80, 99.42, 99.78, 108.65, 109.03, 109.11, 109.64, 110.50, 110.86, 122.81, 123.44, 123.80, 124.77, 127.32, 128.30, 130.53, 131.04, 142.88, 143.35, 143.52, 143.72, 144.61, 145.79, 163.47, 163.60, 172.90, 174.61, 183.78, 184.71, 188.93, 191.24, 193.45, 195.22.

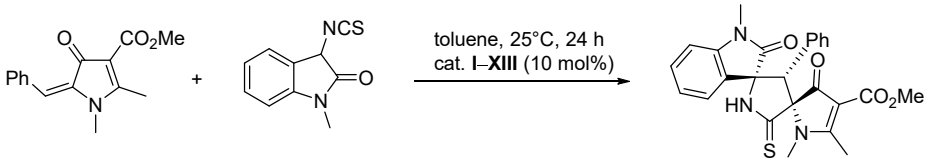
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-5'-(methylthio)-2,3''-dioxo-3'-phenyl-1'',3''-dihydro-3'*H*-dispiro[indoline-3,2'-pyrrole-4',2''-pyrrole]-4''-carboxylate (4)



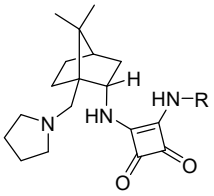
3a **4**

To a solution of thioamide **3a** (0.130 mmol, 60 mg) in anhydrous acetone (0.5 mL) under Argon at 0°C, K_2CO_3 (0.156 mmol, 21.6 mg) and MeI (0.156 mmol, 9.7 µL) were added. The resulting reaction mixture was stirred at room temperature for 24 h. Volatile components were evaporated *in vacuo* and the residue was purified by column chromatography (Silica gel 60, EtOAc/petroleum ether = 2:1). Fractionc containing the pure product **4** were combined and volatile components evaporated *in vacuo*. Yield: 53.7 mg (0.113 mmol, 87%) white solid; *dr* = 96:4; mp = 275–277°C. $[\alpha]_D^{r.t.}$ = +98.5 (*c* = 0.26, $CHCl_3$). EI-HRMS: *m*/*z* = 476.1636 (MH^+); $C_{26}H_{26}N_3O_4S$ requires: *m*/*z* = 476.1639 (MH^+); ν_{max} 2930, 1726, 1674, 1612, 1574, 1531, 1495, 1469, 1443, 1373, 1347, 1203, 1150, 1091, 1009, 859, 840, 794, 770, 749, 713, 679, 661, 642 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.45 (*s*, 3H); 2.59 (*s*, 3H); 3.20 (*s*, 3H); 3.50 (*s*, 3H); 3.82 (*s*, 3H); 4.81 (*s*, 1H); 6.81 (*d*, *J* = 7.7 Hz, 1H), 6.90 – 6.96 (*m*, 2H); 7.09 – 7.18 (*m*, 4H); 7.32 (*td*, *J* = 1.2; 7.7 Hz, 1H); 7.63 (*dd*, *J* = 1.1; 7.5 Hz, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 13.68, 14.65, 26.69, 32.01, 51.20, 62.85, 84.20, 89.93, 101.78, 108.61, 124.02, 124.48, 127.89, 128.51, 128.67, 129.98, 130.64, 131.86, 143.23, 164.57, 172.51, 174.74, 183.56, 191.99.

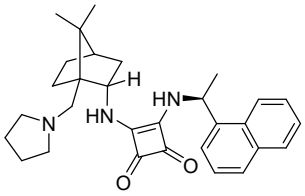
2. HPLC data



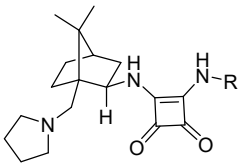
1a **2a** **3a**



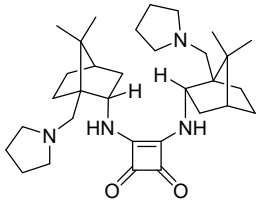
Ia; *dr* = 97:3, 19% *ee* (+)
70% yield



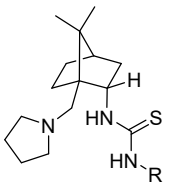
II; *dr* = 94:6, 5% *ee* (+)
65% yield



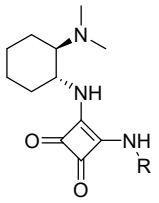
IIIa; *dr* = 83:17, 11% *ee* (–)
31% yield



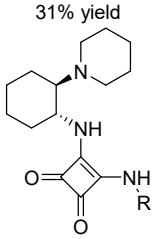
IV; *dr* = 94:6, 8% *ee* (+)
57% yield



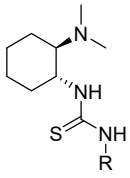
Vb; *dr* = 77:23, 39% *ee* (–)
59% yield



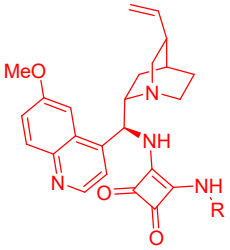
VIa; *dr* = 94:6, 42% *ee* (–)
39% yield
VIb; *dr* = 93:7, 79% *ee* (–)
59% yield



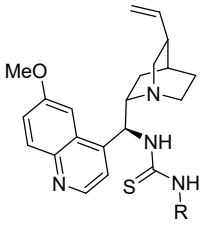
VIIa; *dr* = 95:5, 22% *ee* (–)
61% yield
VIIb; *dr* = 85:15, 9% *ee* (–)
65% yield



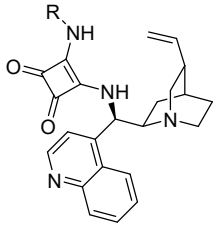
VIIIb; *dr* = 90:10, 79% *ee* (–)
49% yield



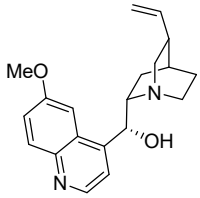
IXa; *dr* = 94:6, 60% *ee* (+)
63% yield
IXb; *dr* = 95:5, 79% *ee* (+)
60% yield
IXc; *dr* = 93:7, 66% *ee* (+)
52% yield



Xb; *dr* = 85:15, 77% *ee* (+)
64% yield



XIa; *dr* = 78:22, 32% *ee* (–)
40% yield
XIb; *dr* = 93:7, 78% *ee* (–)
51% yield

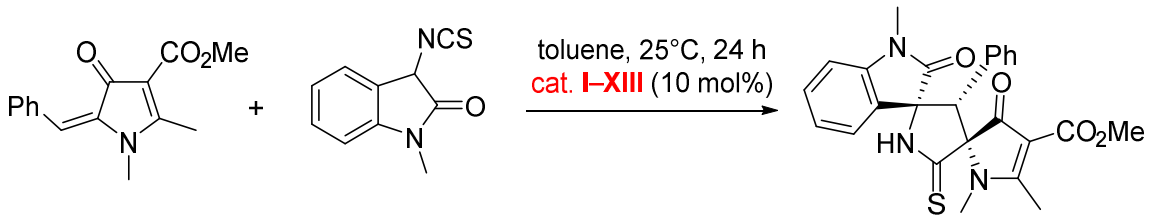


XII; *dr* = 96:4, 49% *ee* (+)
64% yield

a; R = 3,5-F_3C-(C_6H_3)-CH_2-
b; R = 3,5-F_3C-(C_6H_3)-
c; R = 4-O_2N-(C_6H_4)-

Figure S5. Applied organocatalysts **I**–**XII**.

Table S1. Evaluation of organocatalysts **I–XII** in bis-spiroheterocyclization of 5-arylidene-Δ²-pyrrolin-4-one **1a** with 3-isothiocyanatooxindole **2a**.[a]

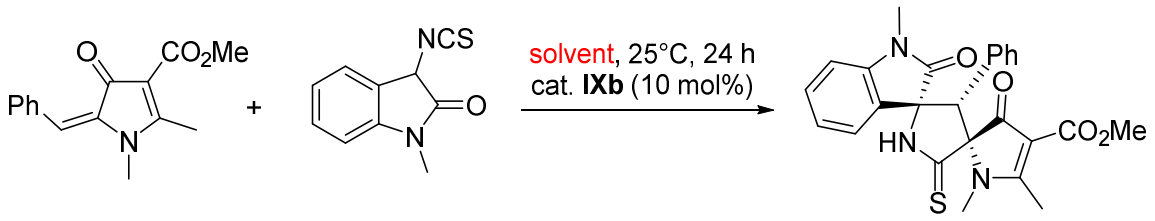


1a **2a** **3a**

	Catalyst	Yield (%)	*dr*[b]	*ee* (%)
1	**Ia**	70	97:3	19 (+)
2	**II**	65	96:4	5 (+)
3	**IIIa**	31	83:17	11 (−)
4	**IV**	57	96:4	8 (+)
5	**Vb**	59	77:23	39 (+)
6	**VIa**	39	94:6	42 (−)
7	**VIb**	59	93:7	79 (−)
8	**VIIa**	61	95:5	22 (−)
9	**VIIb**	65	85:15	9 (−)
10	**VIIIb**	49	90:10	79 (−)
11	**IXa**	63	94:6	60 (+)
12	**IXb**	60	95:5	79 (+)
13	**IXc**	52	93:7	66 (+)
14	**Xb**	64	85:15	77 (+)
15	**XIa**	40	78:22	32 (−)
16	**XIb**	51	93:7	78 (−)
17	**XII**	64	96:4	49 (+)

[a] 5-Arylidene-Δ²-pyrrolin-4-one **1a** (0.1 mmol), 3-isothiocyanato oxindole **2a** (0.13 mmol), catalyst **I–XII** (10 mol%), anhydrous toluene (1 mL), 25°C, 24 h; *ee* and *dr* determined by HPLC after flash column chromatography.

Table S2. Evaluation of organocatalyst **IXb** in bis-spiroheterocyclization of 5-arylidene-Δ²-pyrrolin-4-one **1a** with 3-isothiocyanatooxindole **2a**.[a]

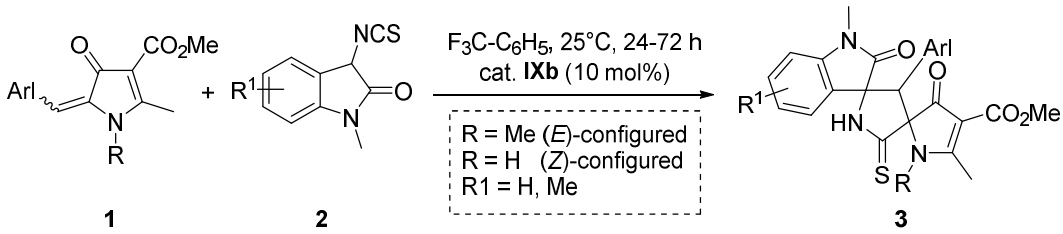


1a **2a** **3a**

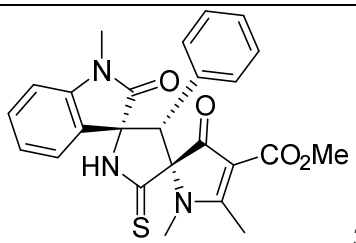
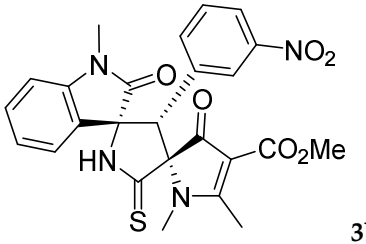
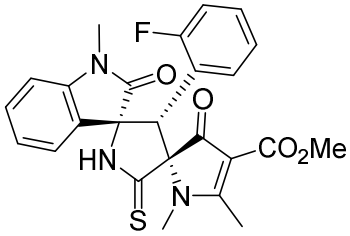
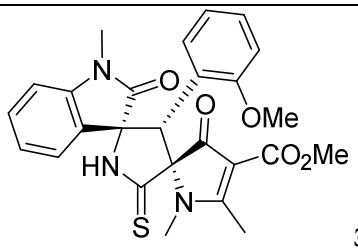
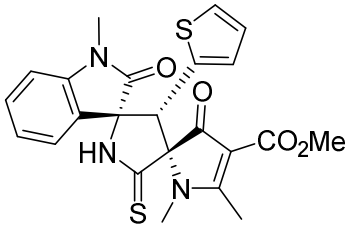
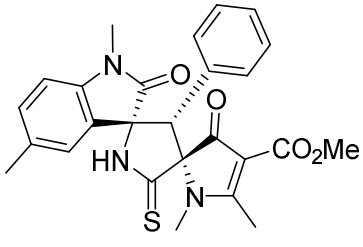
	Solvent	Yield (%)	*dr*[b]	*ee* (%)
1	toluene	60	95:5	79
2	1,4-dioxane	46	93:7	83
3	Et_2O	35	80:20	75
4	1,2-dimetoxyethane	49	95:5	78
5	THF	55	94:6	82
6	CH_2Cl_2	61	93:7	6
7	$PhCF_3$	67	93:7	87
8	acetone	44	94:6	87
9	*t*-butyl methyl ketone	41	95:5	87
10	MeCN	30	79:21	52
11	MeOH	34	86:14	36

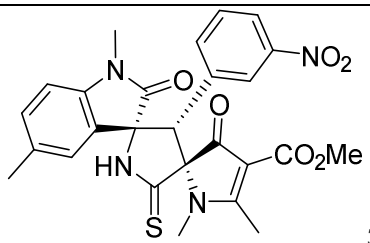
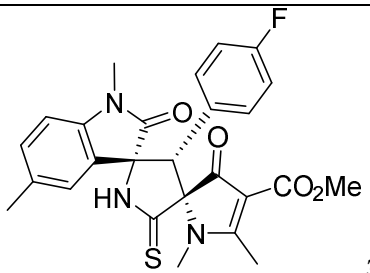
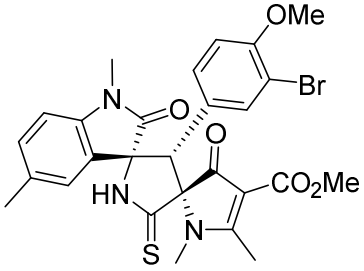
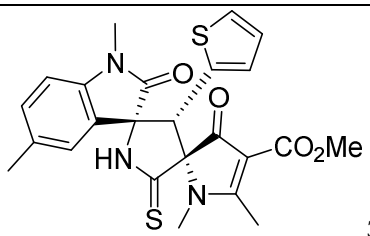
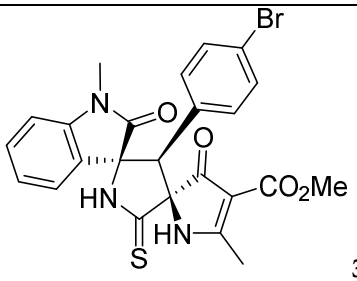
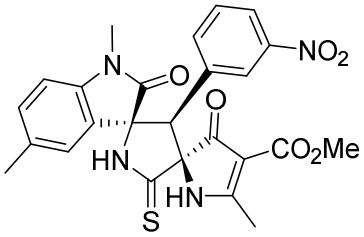
[a] 5-Arylidene-Δ²-pyrrolin-4-one **1a** (0.1 mmol), 3-isothiocyanato oxindole **2a** (0.13 mmol), catalyst **IXb** (10 mol%), solvent (1 mL), 25°C, 24 h; *ee* and *dr* determined by HPLC after flash column chromatography.

Table S3. Bis-spiroheterocyclization of various 5-arylidene-Δ²-pyrrolin-4-ones **1** with 3-isothiocyanatooxindoles **2** under optimized reaction conditions.[a]



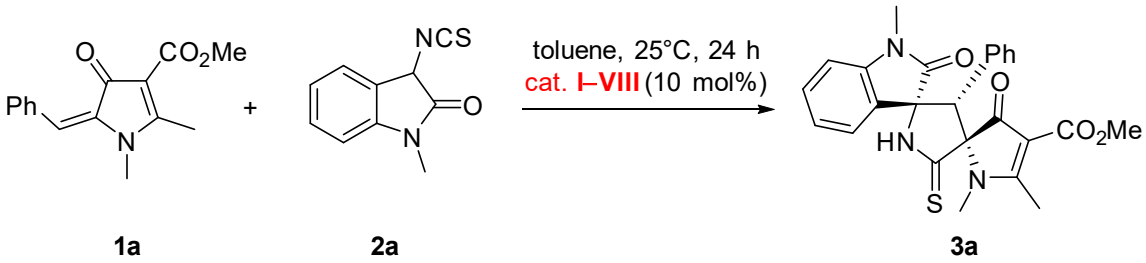
1 **2** **3**

	Product	Yield (%)	*dr*	*ee* (%)
1	 **3a**	67	93:7	Major: 87
2	 **3b**	51	99:1	Major: 91
3	 **3c**	50	91:9	Major: 85
4	 **3d**	26	87:13	Major: 80
5	 **3e**	43	76:24	Major: 96
6	 **3f**	31	99:1	Major: 98

7	 **3g**	40	94:6	Major: 94
8	 **3h**	45	94:6	Major: 95
9	 **3i**	18	82:18	Major: 85
10	 **3j**	37	90:10	Major: 98
11	 **3k**	7	81:19	Major: 21
12	 **3l**	19	84:16	Major: 57

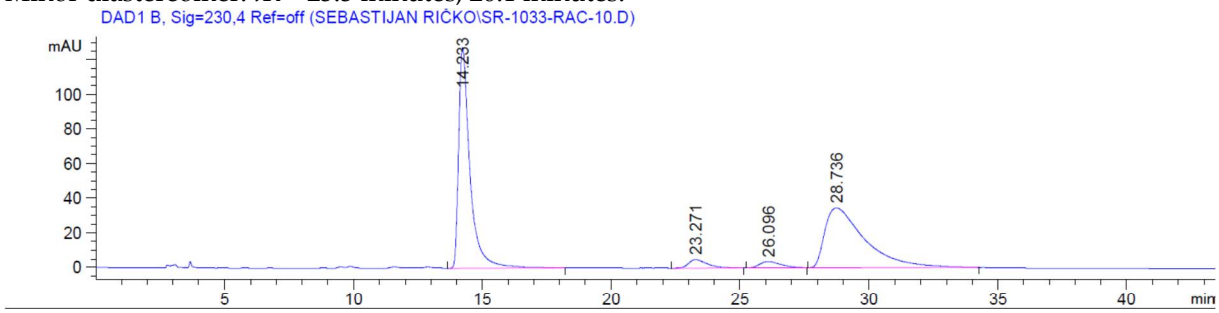
[a] 5-Arylidene-Δ²-pyrrolin-4-one **1** (0.1 mmol), 3-isothiocyanato oxindole **2** (0.13 mmol), catalyst **IXb** (10 mol%), anhydrous (trifluoromethyl)benzene (1 mL), 25°C, 24-72 h; *ee* determined by HPLC after the isolation of **3** by column chromatography; *dr* determined by ^{1}H-NMR ($CDCl_3$) after the isolation of **3** by column chromatography.

Screening of catalysts (Table S1)



1a **2a** **3a**

Conditions for separation of the racemic mixture:
HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.2 minutes; 28.7 minutes.
Minor diastereomer: *t*R = 23.3 minutes; 26.1 minutes.



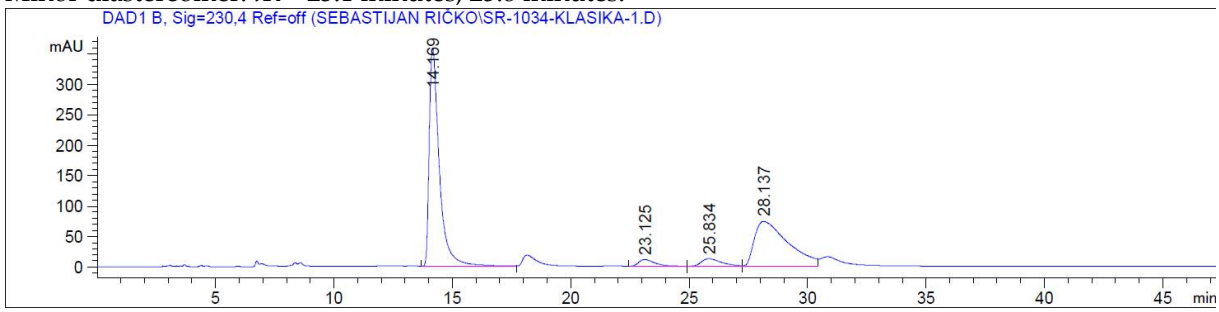
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.233	BB	0.4539	3907.07129	127.35112	48.2698
2	23.271	BB	0.7569	245.97148	4.92276	3.0388
3	26.096	BB	0.8342	204.53429	3.60367	2.5269
4	28.736	BB	1.5490	3736.66138	34.46172	46.1645
Totals :				8094.23843	170.33927	

Table S1, Entry 1

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
1 **3a**		70	93:7	19 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.2 minutes (major); 28.1 minutes (minor).
Minor diastereomer: *t*R = 23.1 minutes; 25.8 minutes.



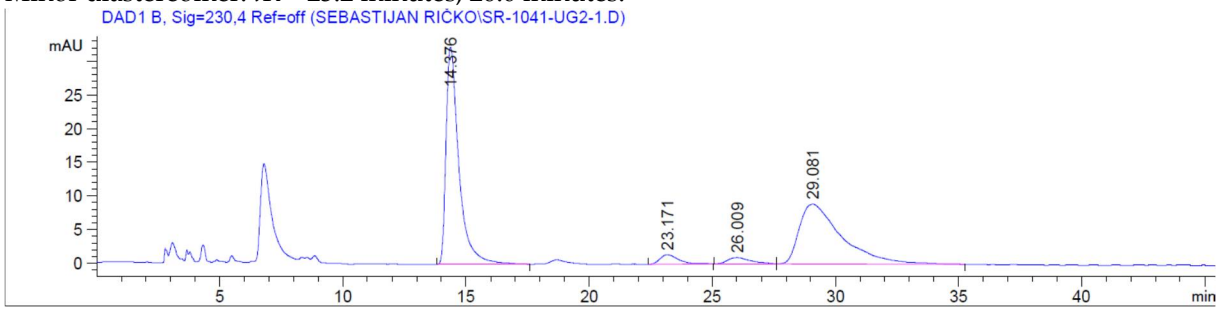
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.169	BV	0.4407	1.05862e4	358.34497	55.5132
2	23.125	BB	0.6989	512.89288	11.14523	2.6896
3	25.834	BV	0.8827	717.42676	12.29667	3.7621
4	28.137	VV	1.4176	7253.22607	73.48060	38.0352
Totals :				1.90698e4	455.26747	

Table S1, Entry 2

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
2	**3a**	65	94:6	5 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (major); 29.1 minutes (minor).
Minor diastereomer: *t*R = 23.2 minutes; 26.0 minutes.



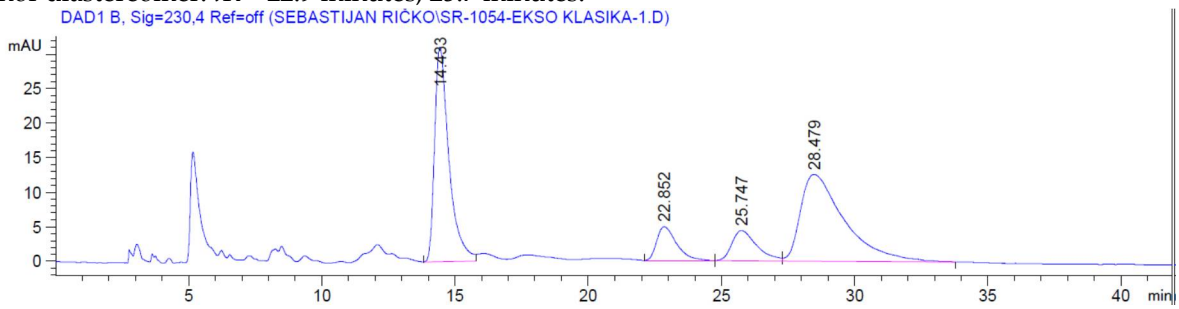
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.376	BB	0.5456	1176.18506	32.24003	49.4043
2	23.171	BB	0.7942	74.39867	1.42236	3.1250
3	26.009	BV	0.9569	60.73893	9.46273e-1	2.5513
4	29.081	VB	1.7077	1069.41052	8.88837	44.9194
Totals :				2380.73317	43.49703	

Table S1, Entry 3

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
3	**3a**	31	83:17	11 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.4 minutes (major); 28.5 minutes (minor).
Minor diastereomer: *t*R = 22.9 minutes; 25.7 minutes.



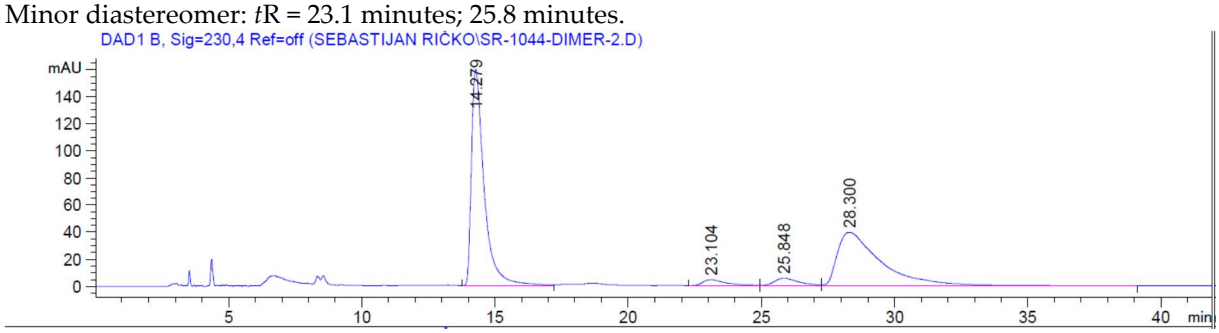
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.433	BV	0.5624	1167.79480	31.07993	36.9891
2	22.852	BV	0.8011	255.99689	4.90368	8.1085
3	25.747	VV	0.9904	288.93494	4.42155	9.1518
4	28.479	VB	1.6304	1444.40137	12.59083	45.7505

Table S1, Entry 4

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
4 **3a**		57	94:6	8 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (major); 28.3 minutes (minor).
Minor diastereomer: *t*R = 23.1 minutes; 25.8 minutes.



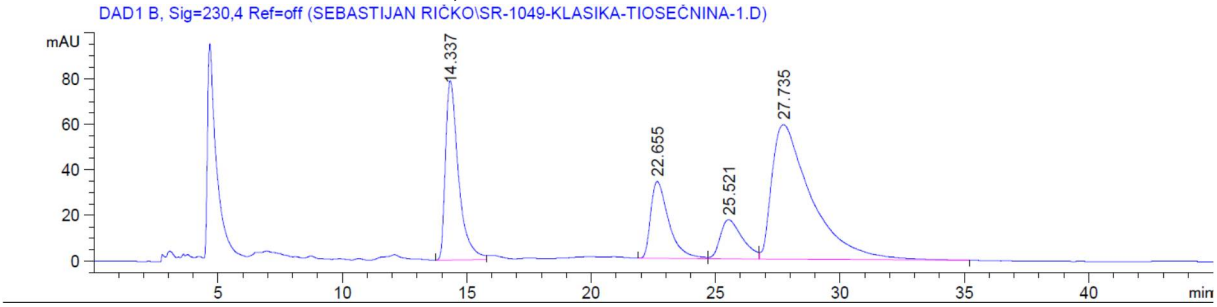
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.279	BV	0.4918	5299.91260	159.45564	50.7903
2	23.104	BV	0.8918	270.77036	4.41294	2.5949
3	25.848	VV	0.9483	351.57193	5.54078	3.3692
4	28.300	VB	1.6300	4512.62793	39.46461	43.2456
Totals :				1.04349e4	208.87397	

Table S1, Entry 5

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
5	**3a**	59	77:23	39 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (minor); 27.7 minutes (major).
Minor diastereomer: *t*R = 22.7 minutes; 25.5 minutes.



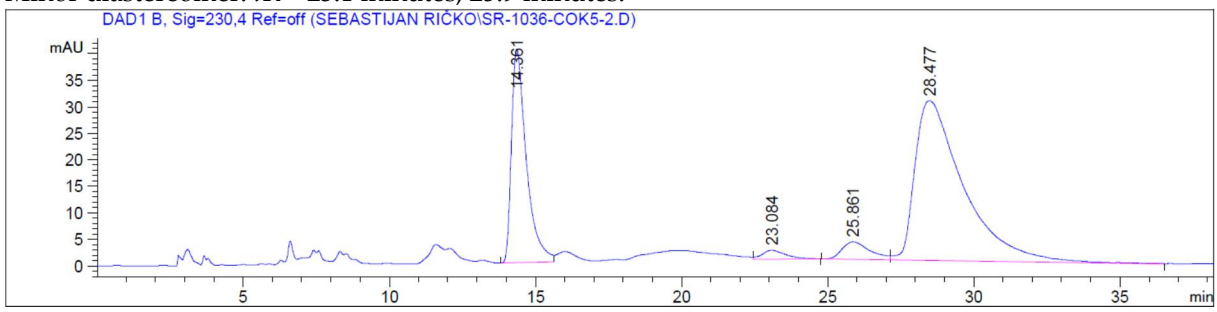
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.337	BV	0.5492	2868.12598	78.70261	23.5940
2	22.655	BV	0.7727	1701.71033	33.72332	13.9988
3	25.521	VV	0.9287	1065.10229	17.14762	8.7618
4	27.735	VB	1.6098	6521.21777	58.98644	53.6454

Table S1, Entry 6

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
6	**3a**	39	94:6	42 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.4 minutes (minor); 28.5 minutes (major).
Minor diastereomer: *t*R = 23.1 minutes; 25.9 minutes.



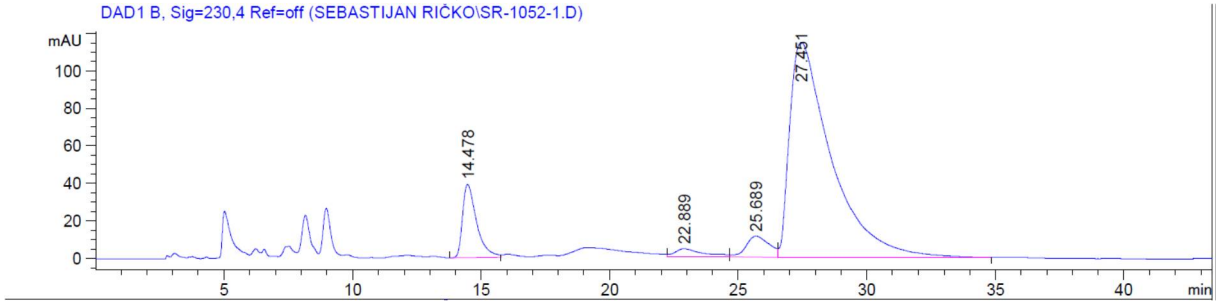
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.361	BV	0.5257	1430.52429	40.34666	27.3512
2	23.084	VB	0.8277	99.27532	1.69405	1.8981
3	25.861	BV	1.0237	219.96614	3.30835	4.2057
4	28.477	VB	1.6306	3480.43628	30.15343	66.5450
Totals :				5230.20203	75.50249	

Table S1, Entry 7

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
7	**3a**	59	93:7	79 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.5 minutes (minor); 27.5 minutes (major).
Minor diastereomer: *t*R = 22.9 minutes; 25.7 minutes.



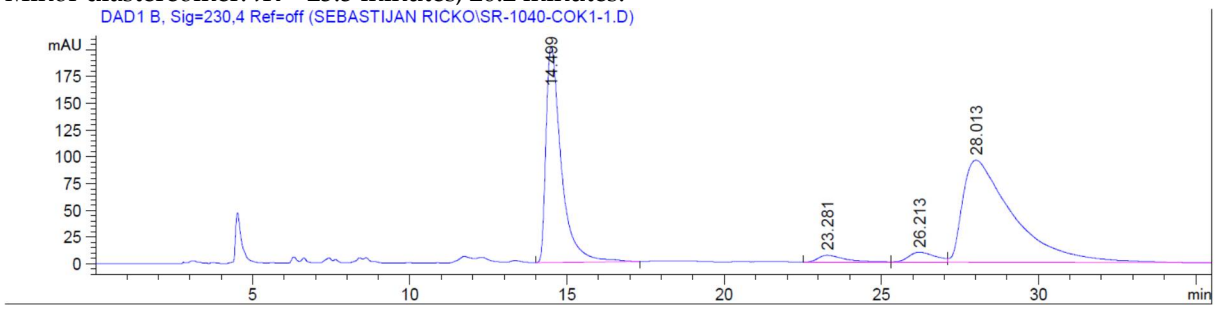
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.478	BV	0.5730	1487.44055	38.99953	9.6553
2	22.889	VV	1.1122	350.96564	4.44977	2.2782
3	25.689	VV	0.9194	699.48425	11.21954	4.5405
4	27.451	VB	1.6145	1.28675e4	114.54868	83.5259

Table S1, Entry 8

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
8	**3a**	61	95:5	22 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.5 minutes (minor); 28.1 minutes (major).
Minor diastereomer: *t*R = 23.3 minutes; 26.2 minutes.



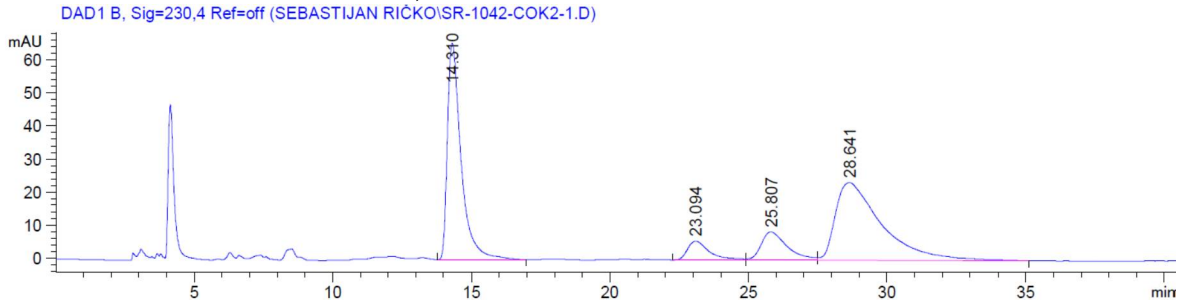
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.499	BB	0.5064	6823.84277	201.88010	37.1463
2	23.281	BV	0.8657	373.84018	6.39832	2.0350
3	26.213	VV	0.9093	548.69031	9.23374	2.9869
4	28.013	VBA	1.5502	1.06238e4	95.47191	57.8318

Table S1, Entry 9

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
9	**3a**	65	85:15	9 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (minor); 28.6 minutes (major).
Minor diastereomer: *t*R = 23.1 minutes; 25.8 minutes.



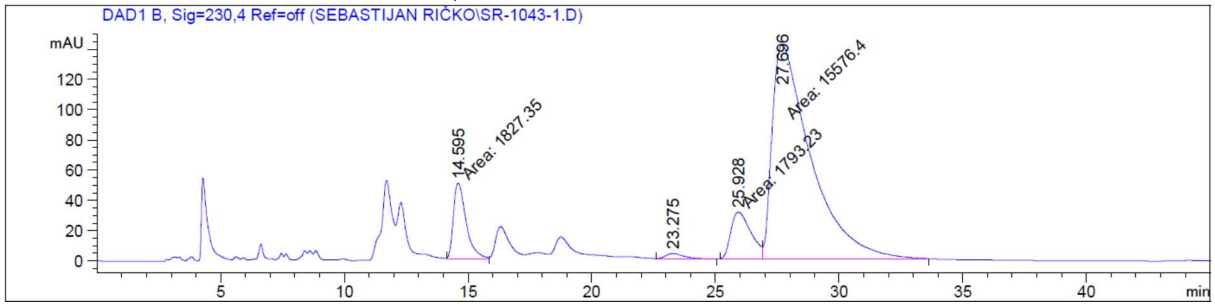
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.310	BB	0.5141	2256.04102	65.45843	38.5872
2	23.094	BV	0.8269	312.42731	5.66917	5.3437
3	25.807	VV	0.9833	556.37122	8.54837	9.5161
4	28.641	VB	1.5987	2721.76782	23.50952	46.5529
Totals :				5846.60736	103.18549	

Table S1, Entry 10

	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
10	**3a**		49	90:10	79 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.6 minutes (minor); 27.7 minutes (major).
Minor diastereomer: *t*R = 23.3 minutes; 25.9 minutes.



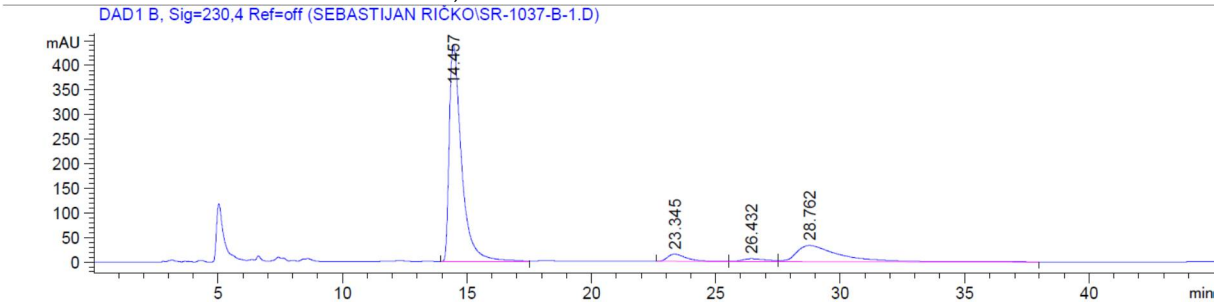
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.595	MM	0.6025	1827.35156	50.54627	9.4347
2	23.275	BB	0.7622	171.36247	3.45769	0.8848
3	25.928	MM	0.9574	1793.22827	31.21567	9.2586
4	27.696	MM	1.8273	1.55764e4	142.07478	80.4219
Totals :				1.93683e4	227.29441	

Table S1, Entry 11

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
11	**3a**	63	94:6	60 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.5 minutes (major); 28.8 minutes (minor).
Minor diastereomer: *t*R = 23.3 minutes; 26.4 minutes.



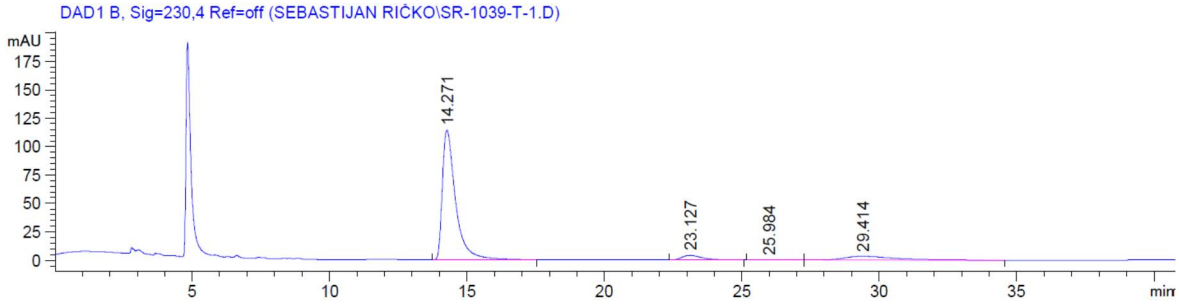
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.457	BV	0.5169	1.51633e4	441.22498	75.2285
2	23.345	BV	0.7913	780.51837	14.79960	3.8723
3	26.432	VV	1.0052	367.03360	5.50971	1.8209
4	28.762	VB	1.7029	3845.49976	32.63084	19.0783

Table S1, Entry 12

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
12	**3a**	60	95:5	79 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (major); 29.4 minutes (minor).
Minor diastereomer: *t*R = 23.1 minutes; 25.9 minutes.



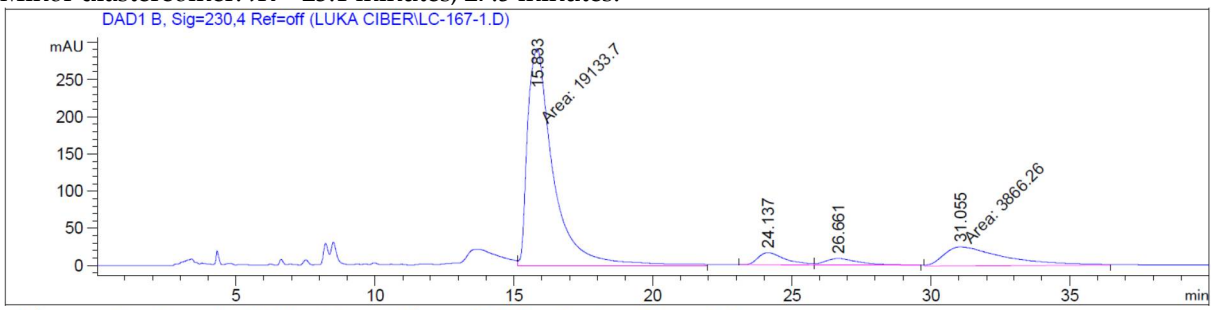
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.271	BB	0.5034	3830.71387	114.17145	85.1403
2	23.127	BB	0.7816	203.10097	3.96485	4.5141
3	25.984	BB	0.7594	20.47176	3.68916e-1	0.4550
4	29.414	BB	1.7631	445.01138	3.39084	9.8907
Totals :				4499.29798	121.89606	

Table S1, Entry 13

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
13 **3a**		52	93:7	66 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.5 minutes (major); 29.1 minutes (minor).
Minor diastereomer: *t*R = 23.1 minutes; 27.5 minutes.



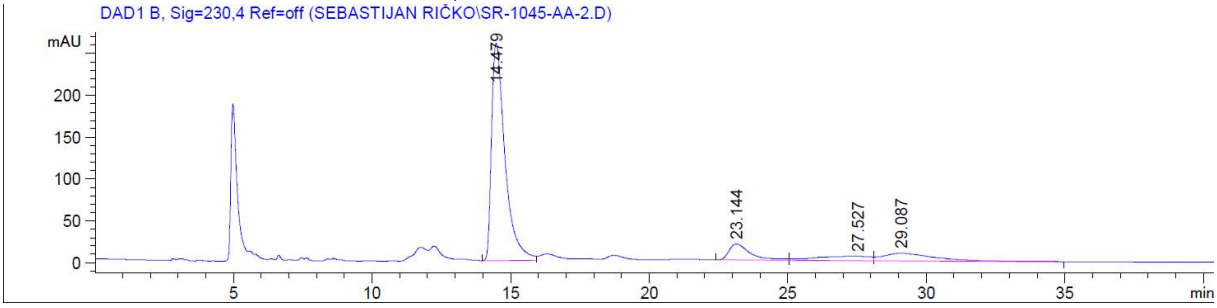
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.833	MM	1.0902	1.91337e4	292.50098	77.1659
2	24.137	BV	1.0164	1094.74219	16.15976	4.4151
3	26.661	VB	1.1734	700.82745	8.57576	2.8264
4	31.055	MM	2.5154	3866.25928	25.61730	15.5926
Totals :				2.47955e4	342.85380	

Table S1, Entry 14

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
14 **3a**		64	85:15	77 (3*R*,3'*S*,4'*R*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.5 minutes (major); 29.1 minutes (minor).
Minor diastereomer: *t*R = 23.1 minutes; 27.5 minutes.



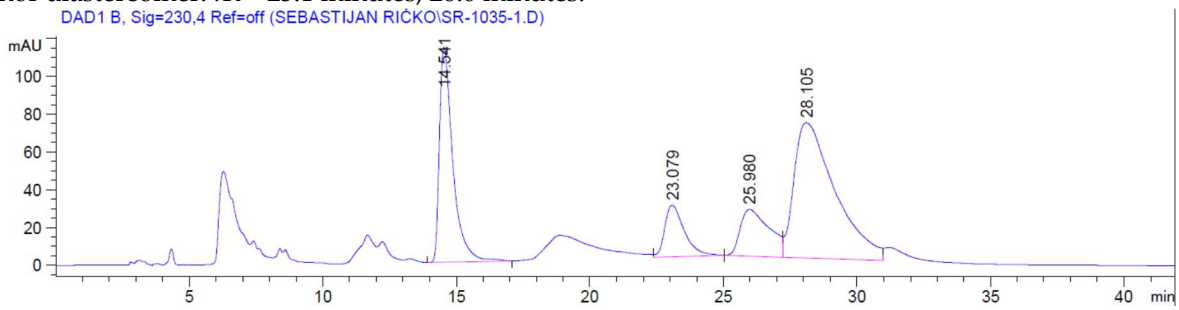
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.479	BV	0.5057	8770.49121	259.88300	74.9491
2	23.144	BV	0.8138	1049.15405	19.19147	8.9657
3	27.527	VV	1.7083	719.22180	5.19145	6.1462
4	29.087	VB	1.7161	1163.05652	9.19216	9.9390

Table S1, Entry 15

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
15 **3a**		40	78:22	32 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.5 minutes (minor); 28.1 minutes (major).
Minor diastereomer: *t*R = 23.1 minutes; 26.0 minutes.



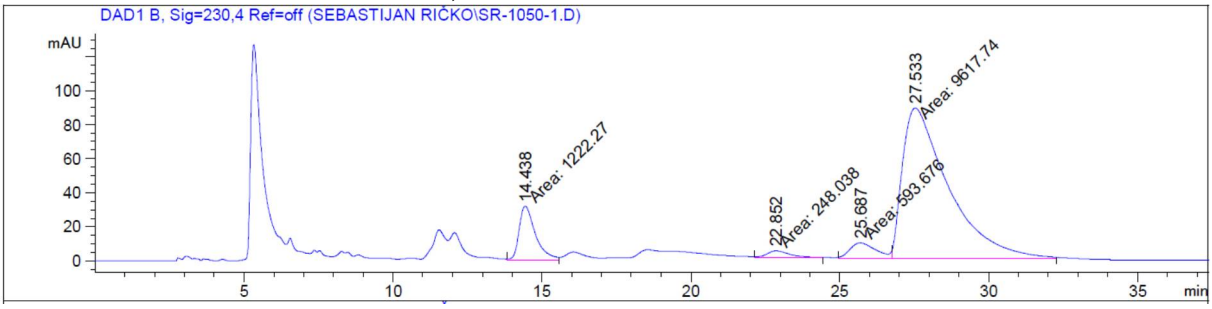
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.541	BB	0.5293	3998.02026	113.96587	26.6750
2	23.079	VB	0.7649	1399.16870	27.34564	9.3353
3	25.980	BV	1.1061	1887.74268	24.85325	12.5951
4	28.105	VV	1.5447	7702.96924	71.74204	51.3946

Table S1, Entry 16

Product	Catalyst	Yield (%)	*dr*	*ee* (%)
16	**3a**	51	93:7	78 (3*S*,3'*R*,4'*S*)

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.4 minutes (minor); 27.5 minutes (major).
Minor diastereomer: *t*R = 22.9 minutes; 25.7 minutes.



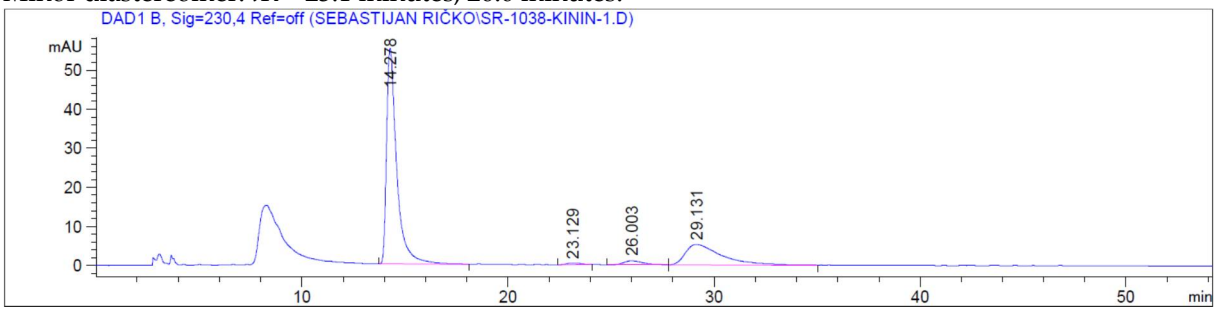
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.438	MM	0.6381	1222.26746	31.92694	10.4631
2	22.852	MM	0.9817	248.03845	4.21090	2.1233
3	25.687	MM	1.0452	593.67596	9.46630	5.0821
4	27.533	MM	1.8041	9617.74219	88.84933	82.3315
Totals :				1.16817e4	134.45347	

Table S1, Entry 17

	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
17	**3a**		64	96:4	49 (3*R*,3'*S*,4'*R*)

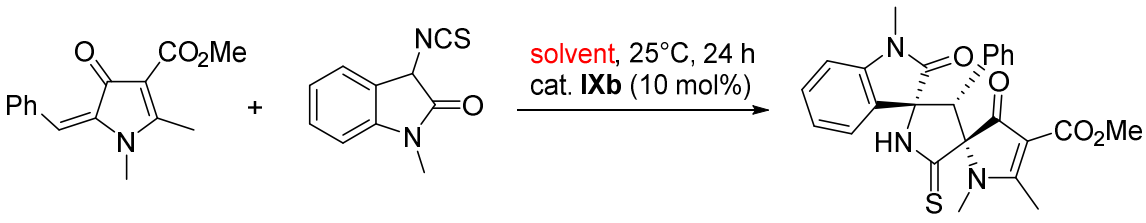
HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (major); 29.1 minutes (minor).
Minor diastereomer: *t*R = 23.1 minutes; 26.0 minutes.



Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.278	BB	0.5091	1898.25769	55.21992	72.1339
2	23.129	BB	0.5574	18.52749	3.99256e-1	0.7040
3	26.003	BV	0.8046	70.03498	1.04672	2.6613
4	29.131	VB	1.6744	644.75348	5.25884	24.5007
Totals :				2631.57364	61.92473	

Screening of solvents (Table S2)



1a **2a** **3a**

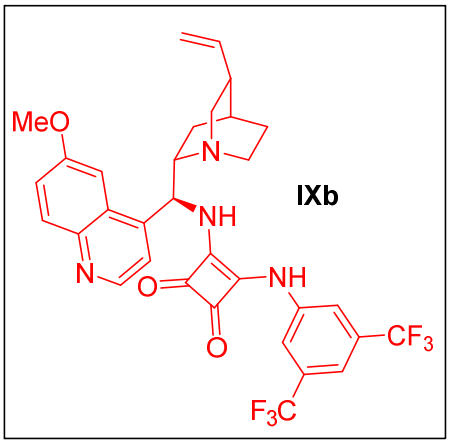
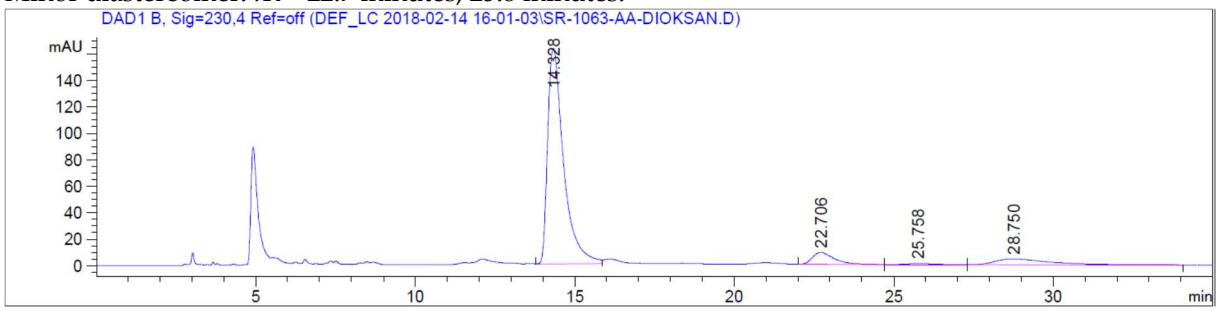


Table S2, Entry 2

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
2	**3a**	1,4-dioxane	**IXb**	46	93:7	83

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (minor); 28.8 minutes (major).
Minor diastereomer: *t*R = 22.7 minutes; 25.8 minutes.



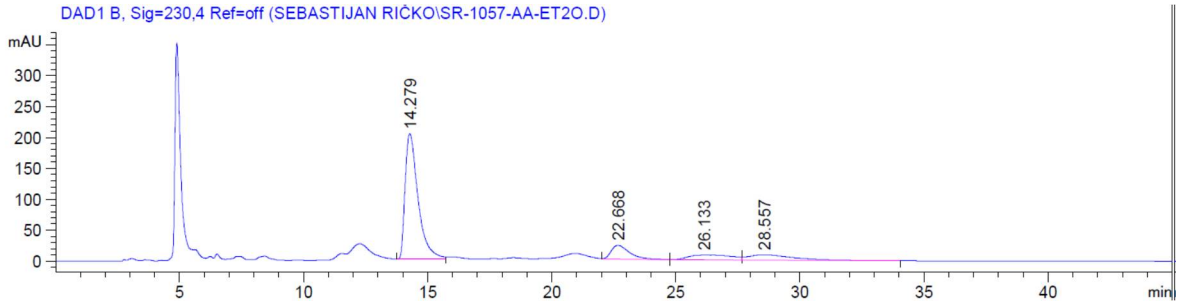
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.328	BV	0.5210	5655.65820	162.91135	85.0962
2	22.706	VB	0.7066	434.18036	9.06840	6.5328
3	25.758	BB	0.8194	43.15456	7.49924e-1	0.6493
4	28.750	BB	1.7094	513.20129	4.30943	7.7217

Table S2, Entry 3

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
3	**3a**	Et_2O	**IXb**	35	80:20	75

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.3 minutes (minor); 28.6 minutes (major).
Minor diastereomer: *t*R = 22.7 minutes; 26.1 minutes.



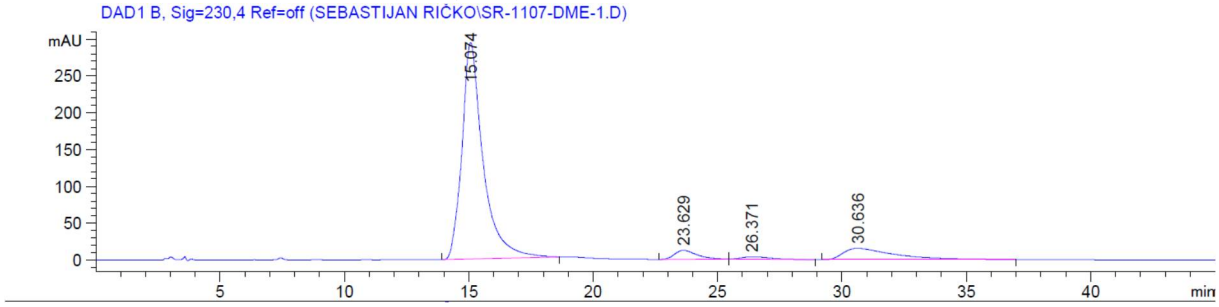
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.279	BV	0.5527	7388.92480	202.96564	70.2176
2	22.668	VB	0.7891	1167.26477	22.50603	11.0926
3	26.133	BV	1.6817	900.90814	7.39315	8.5614
4	28.557	VB	1.6546	1065.79932	8.64332	10.1284

Table S2, Entry 4

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
4	**3a**	1,2-dimethoxyethane	**IXb**	49	95:5	78

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 15.1 minutes (minor); 30.6 minutes (major).
Minor diastereomer: *t*R = 23.6 minutes; 26.4 minutes.



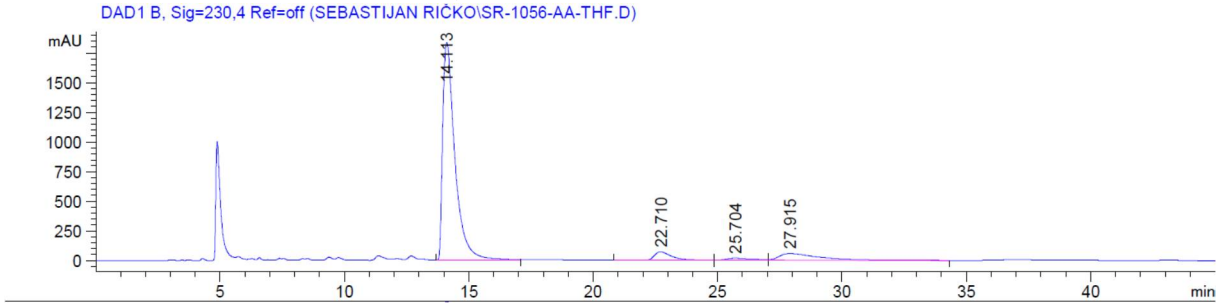
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.074	BB	0.8418	1.73278e4	293.89914	84.5014
2	23.629	BB	0.9158	748.16199	12.16074	3.6485
3	26.371	BB	0.9909	252.73581	3.27295	1.2325
4	30.636	BB	1.8908	2177.24268	15.27582	10.6176

Table S2, Entry 5

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
5	**3a**	THF	**IXb**	55	94:6	82

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.1 minutes (minor); 27.9 minutes (major).
Minor diastereomer: *t*R = 22.7 minutes; 25.7 minutes.



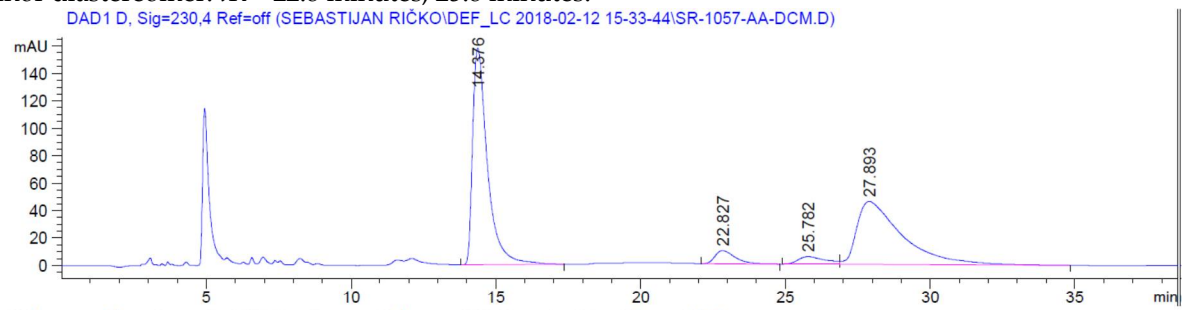
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.113	BV	0.5145	6.26878e4	1835.27515	84.9673
2	22.710	BV	0.7224	3460.78467	71.28317	4.6908
3	25.704	VV	1.0498	1274.48584	17.41442	1.7274
4	27.915	VB	1.6151	6355.69971	57.07891	8.6145

Table S2, Entry 6

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
6	**3a**	CH_2Cl_2	**IXb**	61	93:7	6

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.4 minutes (minor); 27.9 minutes (major).
Minor diastereomer: *t*R = 22.8 minutes; 25.8 minutes.



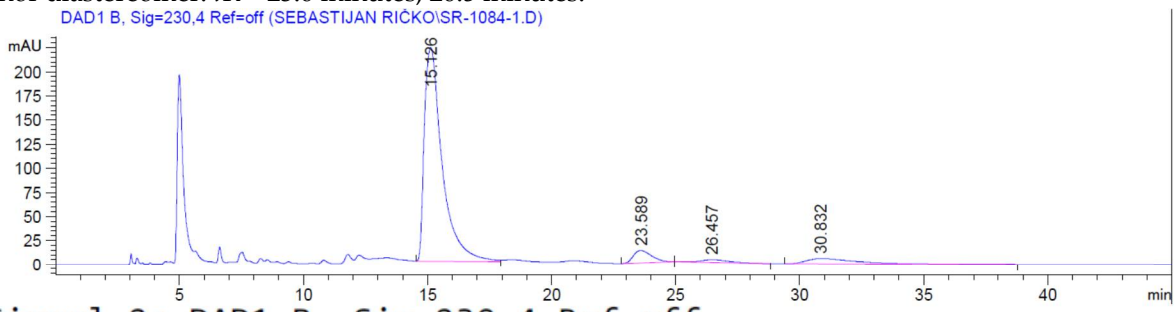
Signal 3: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.376	VB	0.5330	5619.05078	157.97694	49.0988
2	22.827	BB	0.7237	457.90225	9.61270	4.0011
3	25.782	BV	0.9296	356.51566	5.44703	3.1152
4	27.893	VB	1.5357	5010.89795	45.82704	43.7848
Totals :				1.14444e4	218.86371	

Table S2, Entry 7

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
7	**3a**	$PhCF_3$	**IXb**	67	93:7	87

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 15.1 minutes (minor); 30.8 minutes (major).
Minor diastereomer: *t*R = 23.6 minutes; 26.5 minutes.



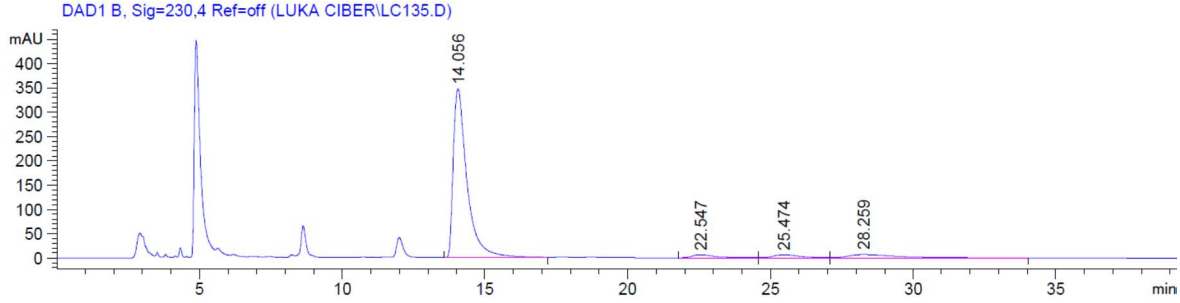
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.126	BV	0.7526	1.11129e4	221.76564	86.5891
2	23.589	BB	0.8073	671.15222	12.97811	5.2295
3	26.457	BB	1.1027	249.58058	3.03732	1.9447
4	30.832	BB	1.7867	800.42645	5.54958	6.2367

Table S2, Entry 8

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
8	**3a**	Acetone	**IXb**	44	94:6	87

HPLC: Chiralpak IA-3, n-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: tR = 14.1 minutes (minor); 28.3 minutes (major).
Minor diastereomer: tR = 22.5 minutes; 25.5 minutes.



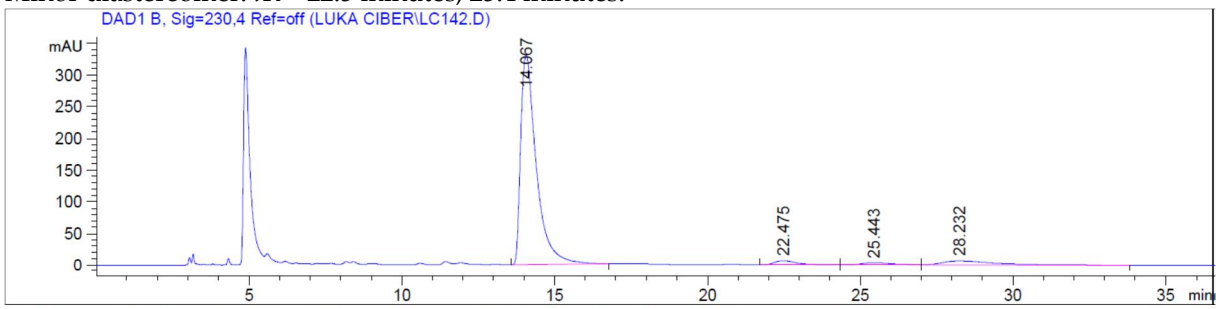
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.056	BB	0.4977	1.16131e4	347.67554	88.2211
2	22.547	BV	0.8131	347.19418	6.20201	2.6375
3	25.474	VV	0.9579	392.80927	6.07855	2.9841
4	28.259	VB	1.6146	810.52069	6.76129	6.1573

Table S2, Entry 9

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
9	**3a**	*t*-butyl methyl ketone	**IXb**	41	95:5	87

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.1 minutes (minor); 28.2 minutes (major).
Minor diastereomer: *t*R = 22.5 minutes; 25.4 minutes.



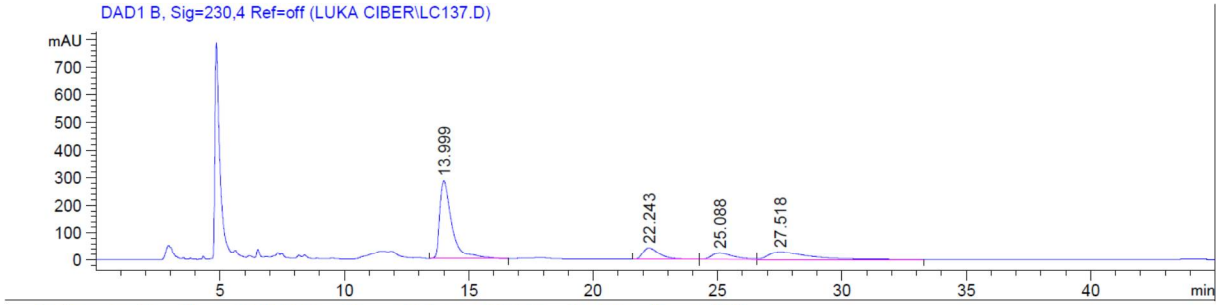
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.067	BB	0.5299	1.18156e4	331.41995	89.7038
2	22.475	BB	0.7337	333.94366	6.91179	2.5353
3	25.443	BV	0.9777	244.44264	3.67658	1.8558
4	28.232	VB	1.4510	777.81152	6.59983	5.9051

Table S2, Entry 10

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
10	**3a**	MeCN	**IXb**	30	79:21	52

HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.0 minutes (minor); 27.5 minutes (major).
Minor diastereomer: *t*R = 22.2 minutes; 25.1 minutes.



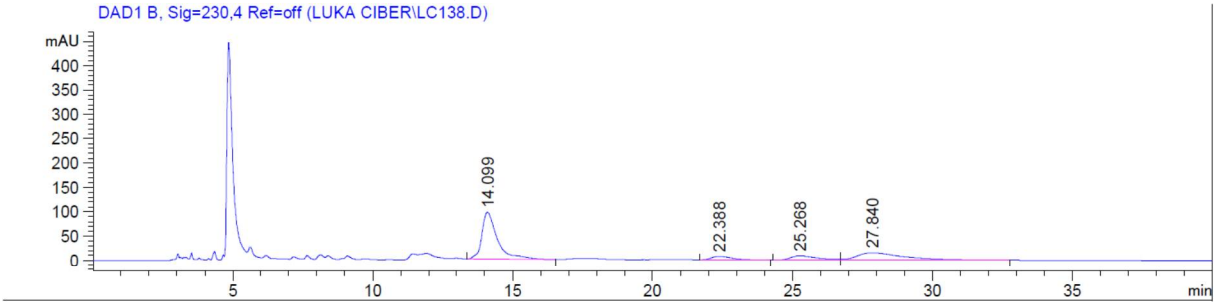
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.999	BB	0.5081	9750.85840	284.33344	59.9968
2	22.243	BV	0.7085	1991.64954	42.98843	12.2546
3	25.088	VV	0.8727	1417.75977	24.01851	8.7234
4	27.518	VB	1.5321	3092.02075	28.76409	19.0251

Table S2, Entry 11

	Product	Solvent	Catalyst	Yield (%)	*dr*	*ee* (%)
11	**3a**	MeOH	**IXb**	34	86:14	36

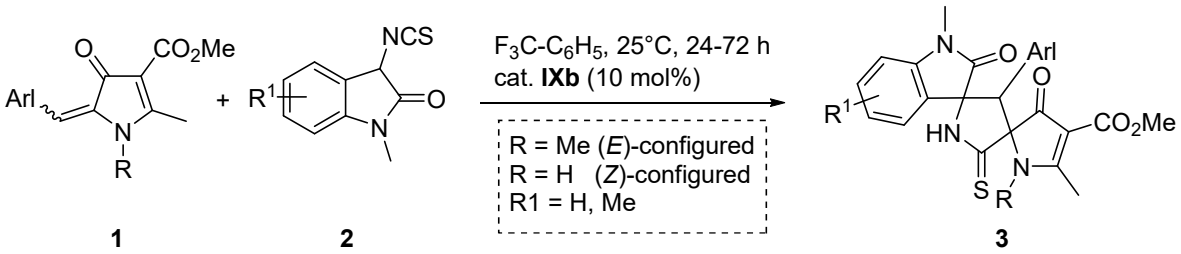
HPLC: Chiralpak IA-3, *n*-Hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 14.1 minutes (minor); 27.8 minutes (major).
Minor diastereomer: *t*R = 22.4 minutes; 25.3 minutes.



Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.099	BB	0.5715	3766.30469	96.89168	58.2976
2	22.388	BB	0.7019	360.88467	7.51940	5.5860
3	25.268	BV	0.9278	572.97620	8.75196	8.8689
4	27.840	VB	1.5556	1760.31201	15.28451	27.2474

Variation of arylidene-Δ²-pyrrolin-4-ones 2 and 3-isothiocyanatooxindoles 3 under optimized reaction conditions (Table S3)



1 **2** **3**

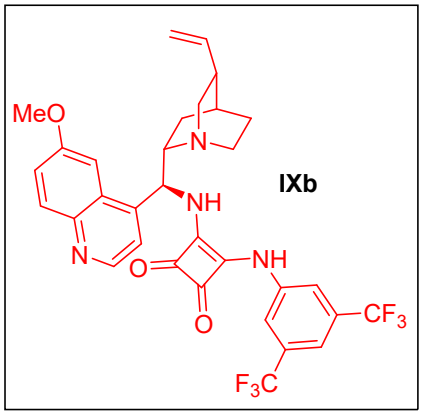
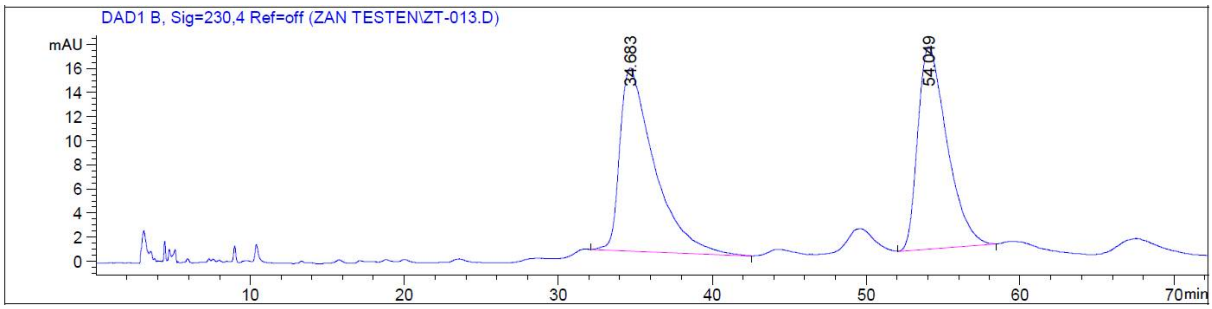


Table S3, Entry 2

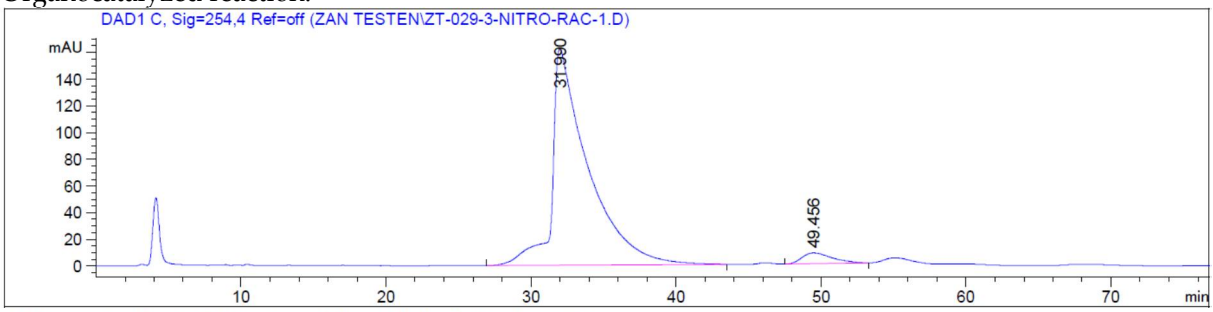
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
2	**3b**	**IXb**	51	99:1	Major: 91

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm.
Major diastereomer: *t*R = 32.0 minutes (major); 49.4 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 3: DAD1 C, Sig=254,4 Ref=off

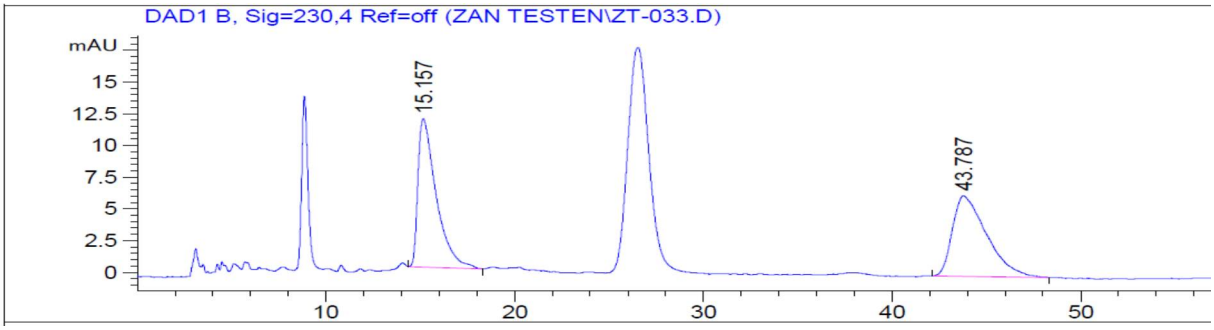
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.990	BB	2.2207	2.79764e4	162.16838	95.9713
2	49.456	BB	1.7149	1174.40283	8.08386	4.0287
Totals :				2.91508e4	170.25224	

Table S3, Entry 3

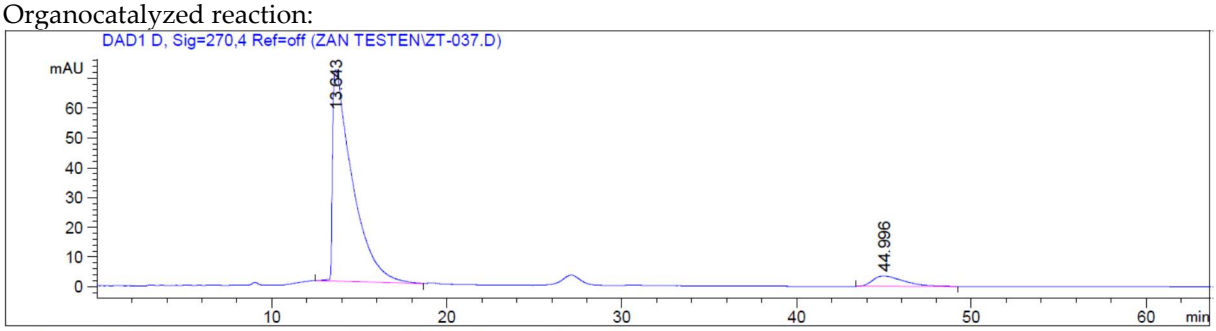
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
3	**3c**	**IXb**	50	91:9	Major: 85

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 270 nm.
Major diastereomer: *t*R = 13.6 minutes (major); 45.0 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 4: DAD1 D, Sig=270,4 Ref=off

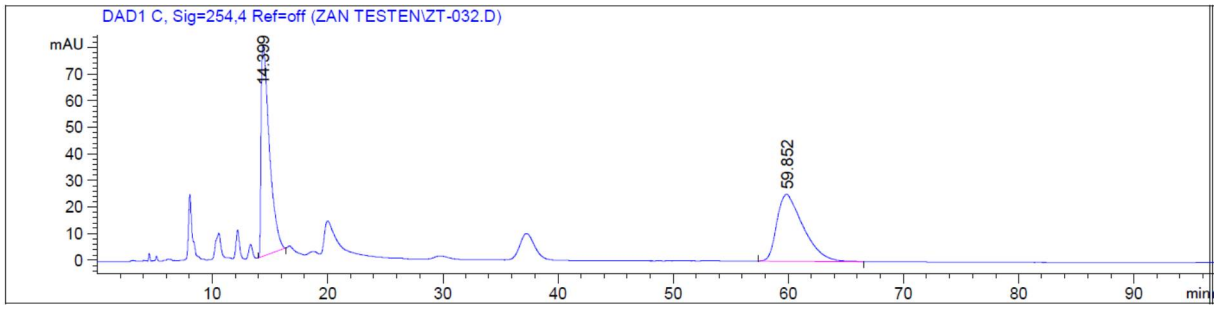
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.643	BB	1.0588	5545.19531	71.03220	92.8251
2	44.996	BB	1.4558	428.61234	3.48276	7.1749
Totals :				5973.80765	74.51497	

Table S3, Entry 4

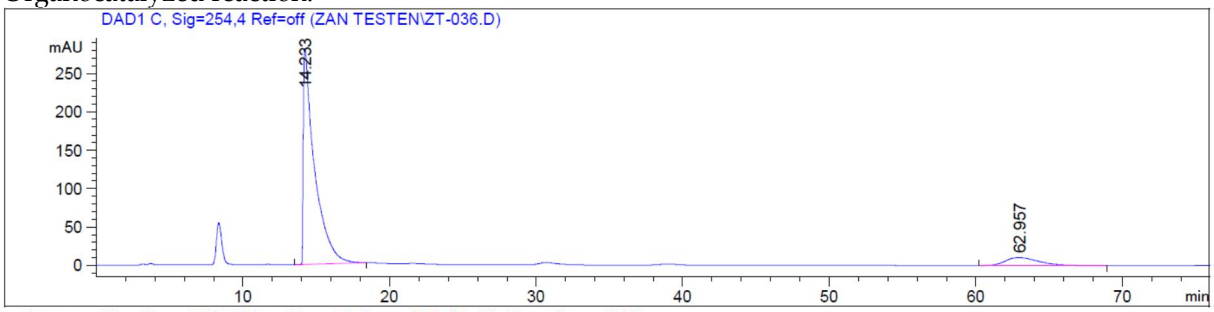
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
4	**3f**	**IXb**	26	87:13	Major: 80

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm.
Major diastereomer: *t*R = 14.2 minutes (major); 63.0 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 3: DAD1 C, Sig=254,4 Ref=off

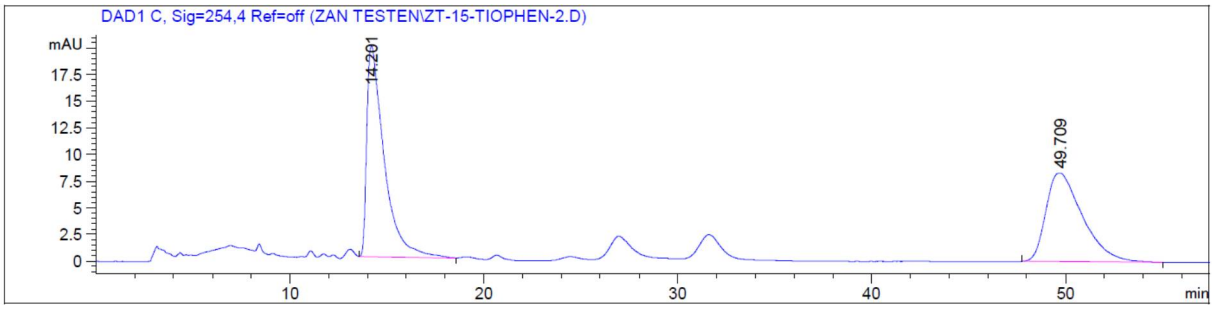
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.233	BB	0.7304	1.49496e4	281.12567	90.1274
2	62.957	BB	1.8853	1637.59363	10.42137	9.8726
Totals :				1.65872e4	291.54704	

Table S3, Entry 5

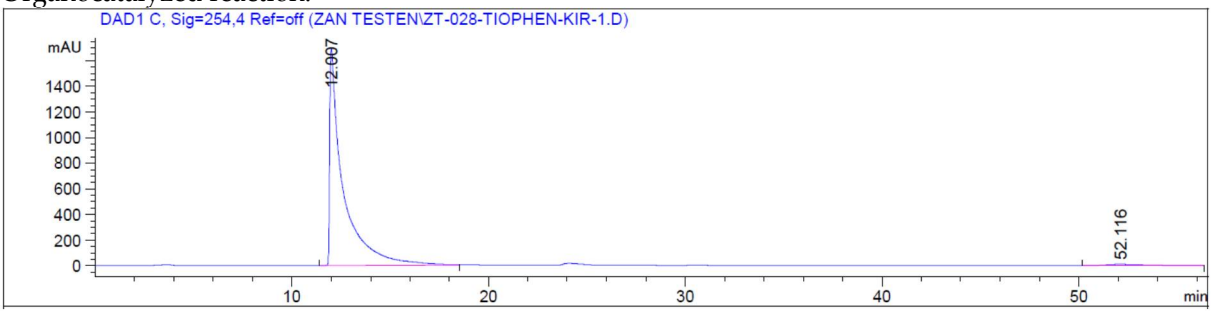
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
5	**3h**	**IXb**	43	76:24	Major: 96

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm.
Major diastereomer: *t*R = 12.0 minutes (major); 52.1 minutes (minor).

Racemate:



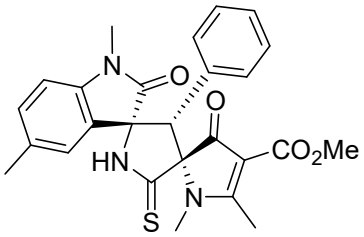
Organocatalyzed reaction:



Signal 3: DAD1 C, Sig=254,4 Ref=off

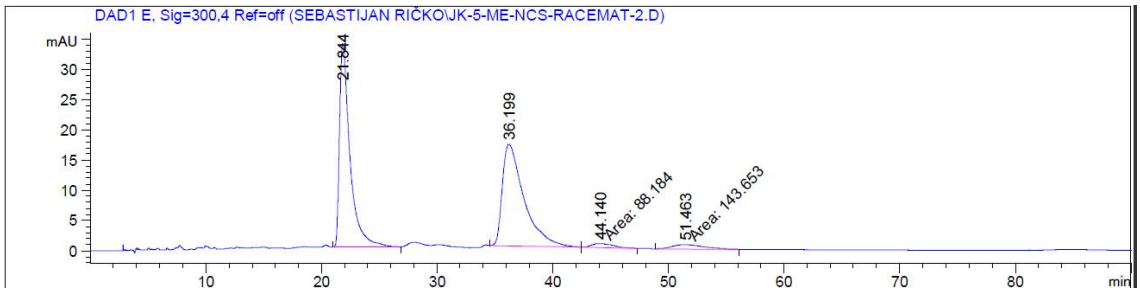
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.007	BV	0.6140	8.07435e4	1694.37085	98.1431
2	52.116	BBA	1.9299	1527.71753	10.97567	1.8569
Totals :				8.22713e4	1705.34651	

Table S3, Entry 6

	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
6	 **3i**	**IXb**	31	99:1	Major: 98

HPLC: Chiralpak AD-H, *n*-Hexane/EtOH = 85:15, flow rate 1.0 mL/min, λ = 300 nm.
Major diastereomer: *t*R = 20.3 minutes (major); 34.3 minutes (minor).

Racemate:



Organocatalyzed reaction:

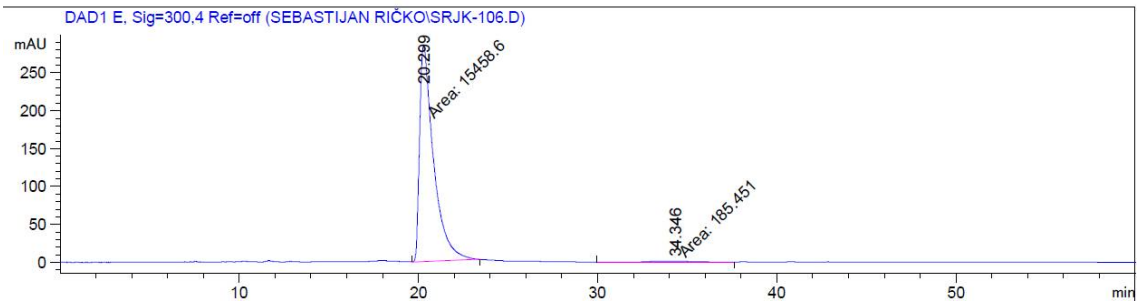
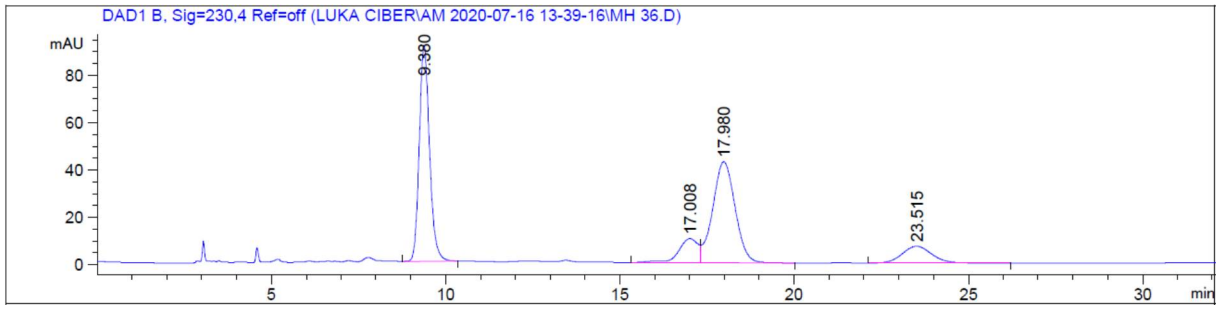


Table S3, Entry 7

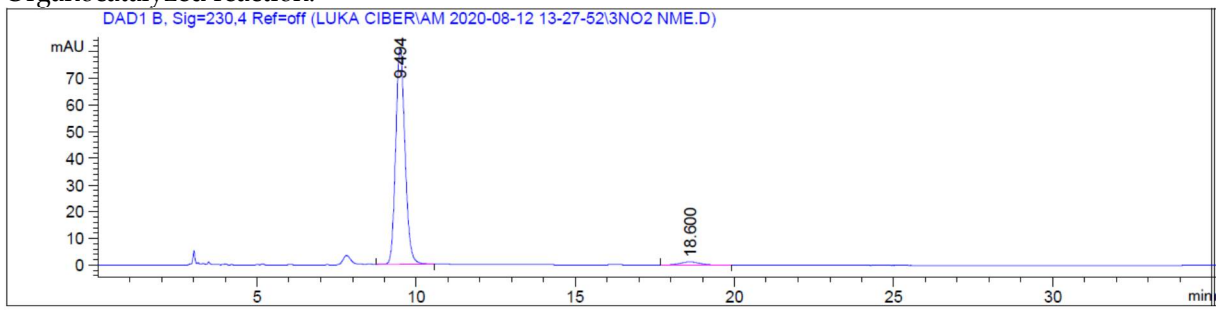
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
7	**3g**	**IXb**	40	94:6	Major: 94

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 9.5 minutes (major); 18.6 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 2: DAD1 B, Sig=230,4 Ref=off

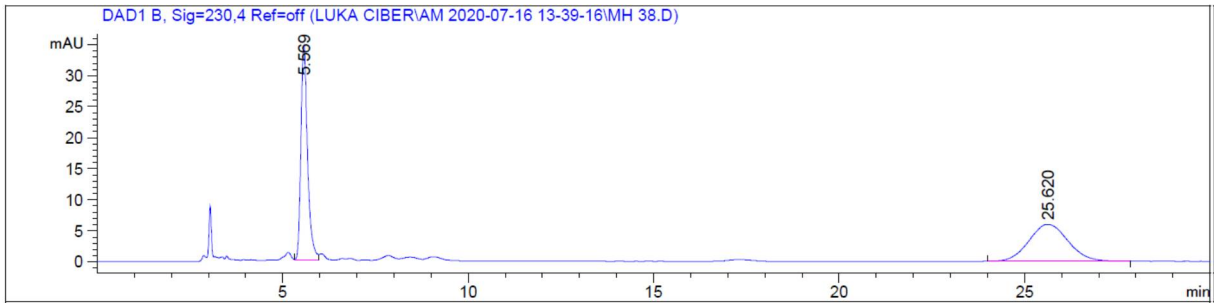
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.494	BB	0.3127	1641.46301	80.90995	96.9547
2	18.600	BB	0.5682	51.55716	1.16074	3.0453
Totals :				1693.02017	82.07069	

Table S3, Entry 8

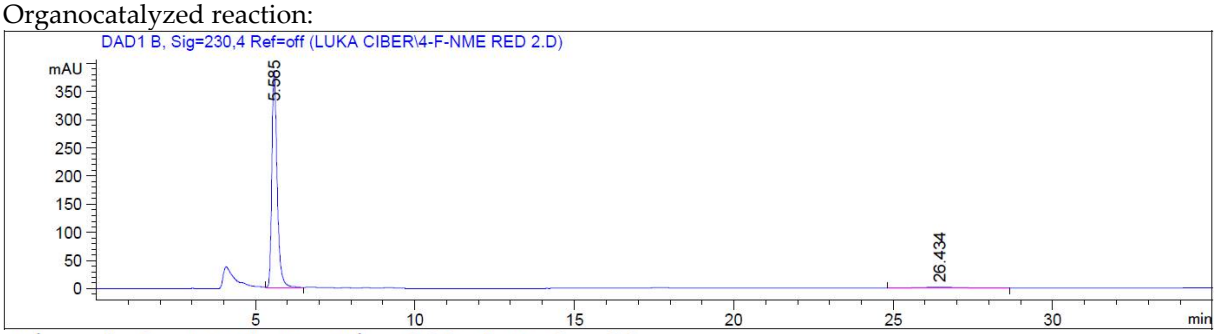
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
8	**3h**	**IXb**	45	94:6	Major: 95

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 5.6 minutes (major); 26.4 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 2: DAD1 B, Sig=230,4 Ref=off

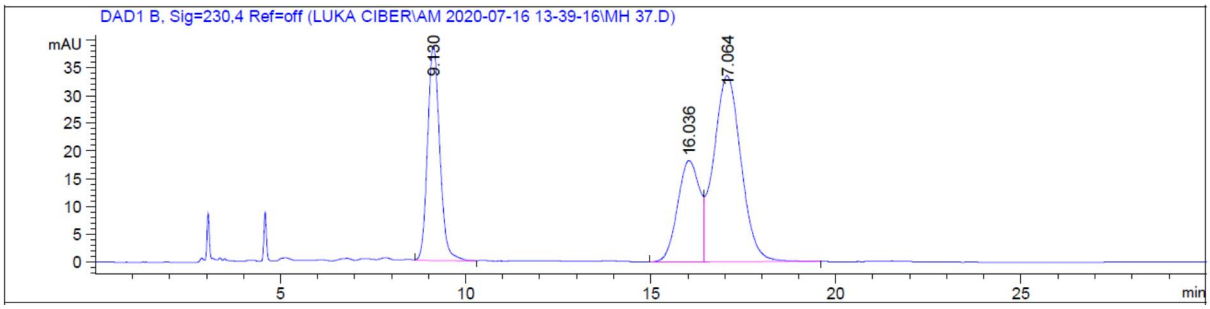
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.585	VV	0.1781	4570.10156	386.01978	97.3062
2	26.434	BB	0.9261	126.51520	1.66578	2.6938
Totals :				4696.61676	387.68556	

Table S3, Entry 9

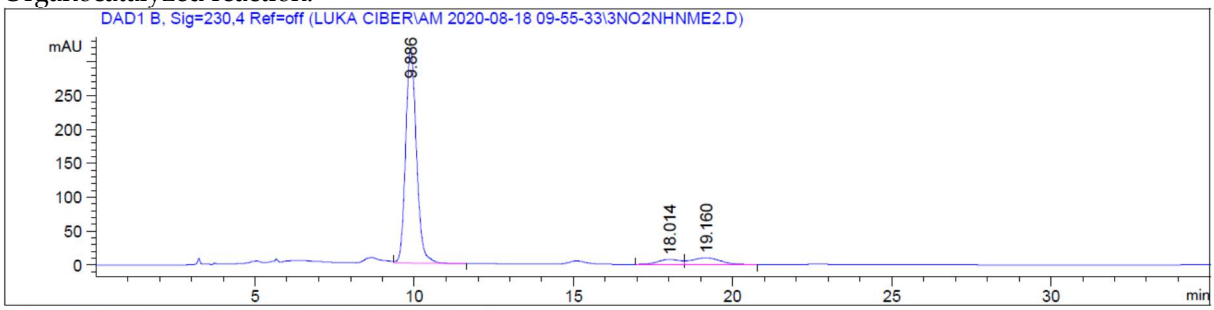
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
9	**3i**	**IXb**	18	82:18	Major: 85

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 9.9 minutes (major); 19.2 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 2: DAD1 B, Sig=230,4 Ref=off

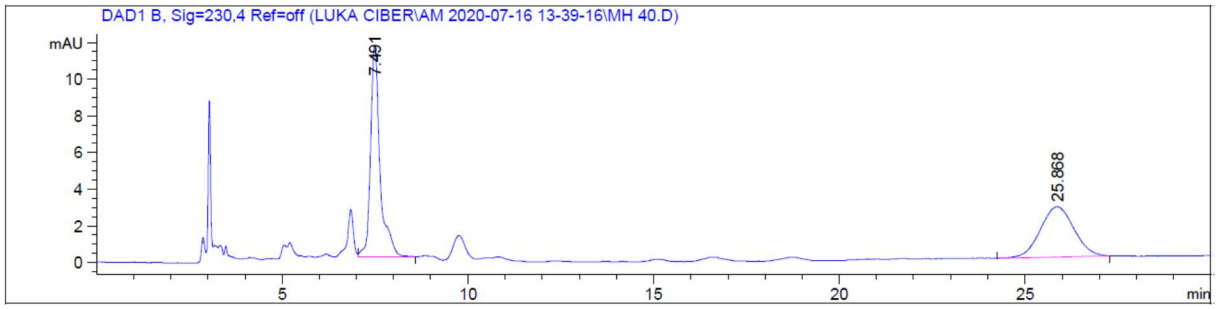
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.886	VB	0.3622	7438.60840	316.52081	88.7570
2	18.014	BV	0.6925	350.07782	7.33936	4.1771
3	19.160	VB	0.9042	592.18719	9.51404	7.0659
Totals :				8380.87341	333.37422	

Table S3, Entry 10

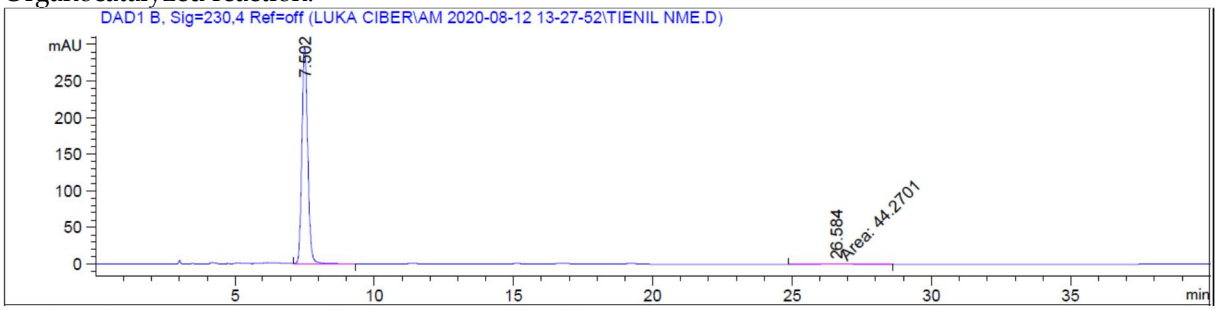
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
10	**3j**	**IXb**	37	90:10	Major: 99

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 230 nm.
Major diastereomer: *t*R = 9.5 minutes (major); 18.6 minutes (minor).

Racemate:



Organocatalyzed reaction:



Signal 2: DAD1 B, Sig=230,4 Ref=off

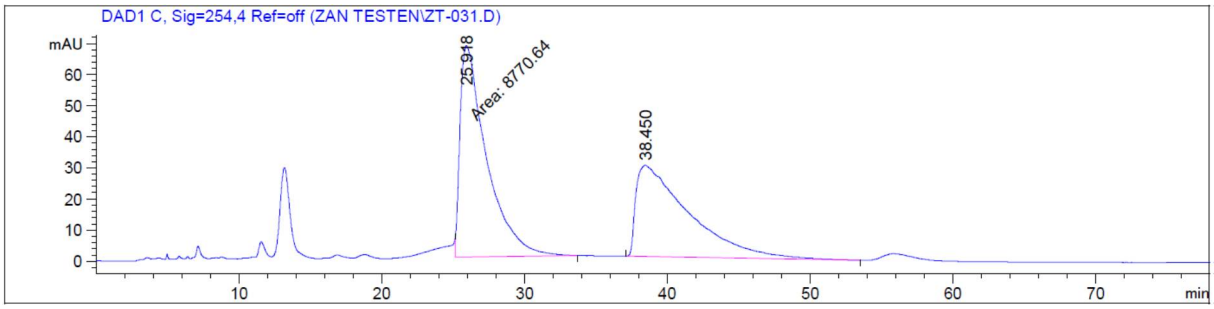
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.502	VB	0.2266	4326.34619	295.77759	98.9871
2	26.584	MM	1.1496	44.27015	6.41846e-1	1.0129
Totals :				4370.61634	296.41943	

Table S3, Entry 11

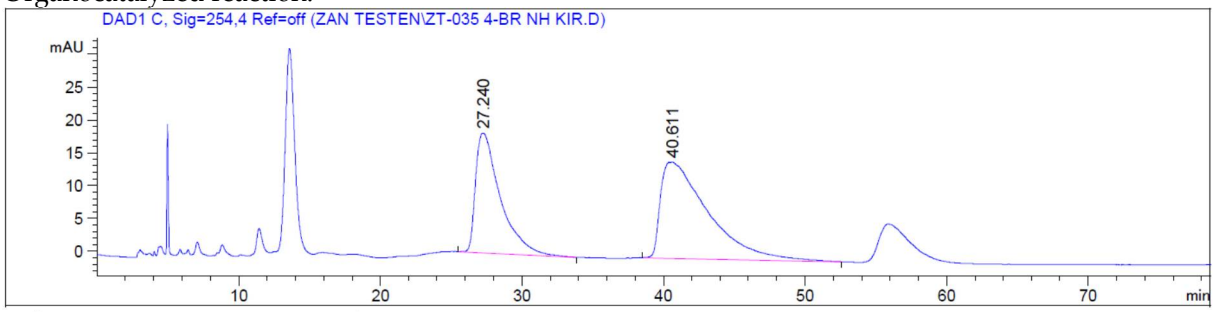
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
11	**3j**	**IXb**	7	81:19	Major: 21

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm.
Major diastereomer: *t*R = 27.2 minutes (minor); 40.6 minutes (major).

Racemate:



Organocatalyzed reaction:



Signal 3: DAD1 C, Sig=254,4 Ref=off

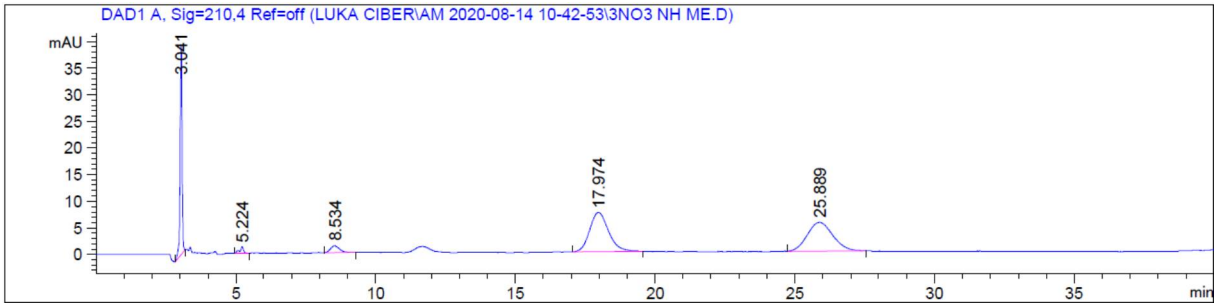
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.240	BB	1.6595	2210.91650	18.19717	39.3822
2	40.611	BB	2.7343	3403.08521	14.59470	60.6178
Totals :				5614.00171	32.79187	

Table S3, Entry 12

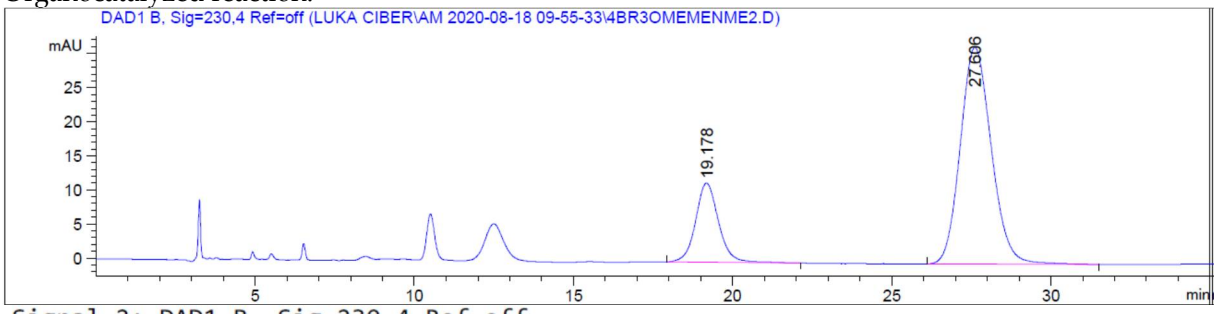
	Product	Catalyst	Yield (%)	*dr*	*ee* (%)
12	**3l**	**IXb**	19	84:16	Major: 57

HPLC: Chiralpak AD-H, *n*-Hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 210 nm.
Major diastereomer: *t*R = 19.2 minutes (minor); 27.6 minutes (major).

Racemate:



Organocatalyzed reaction:

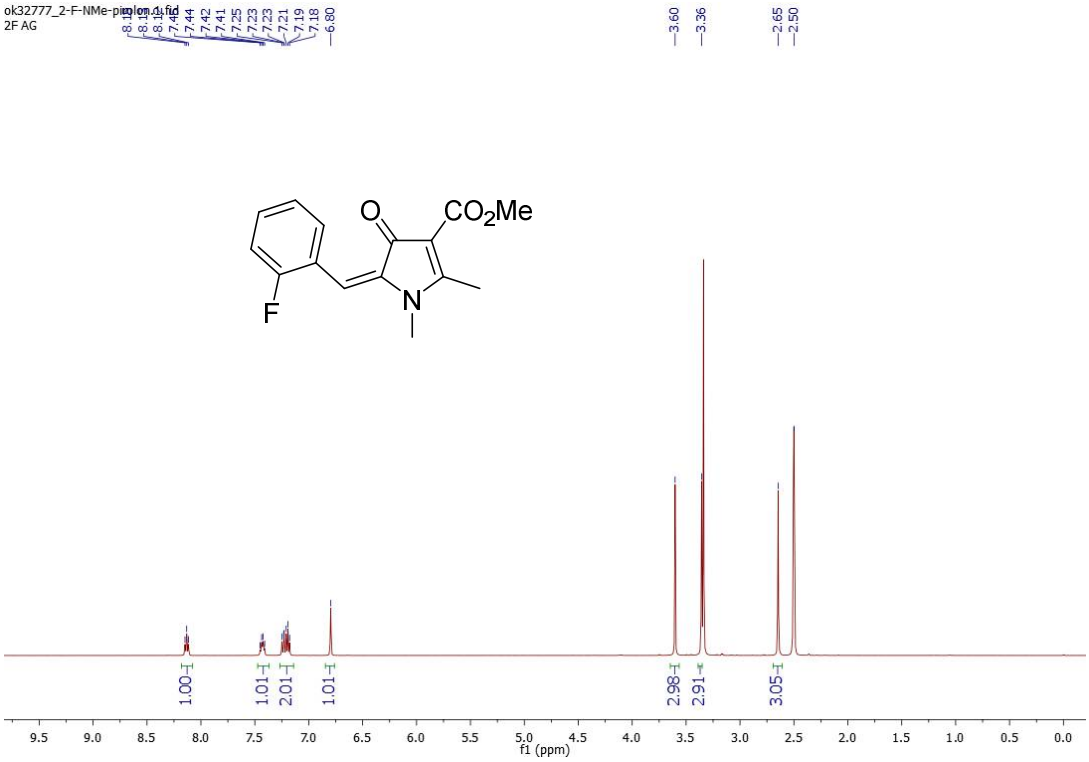


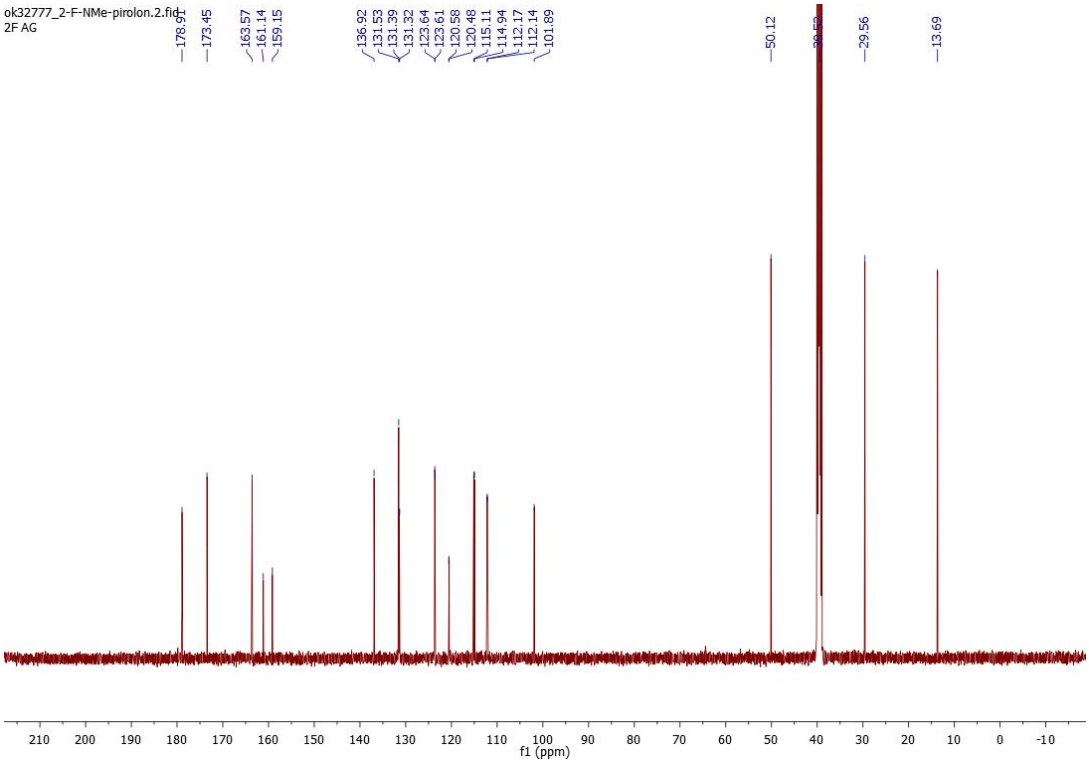
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.178	BB	0.7499	583.26465	11.61492	21.3073
2	27.606	BB	1.0444	2154.12915	31.79610	78.6927
Totals :				2737.39380	43.41101	

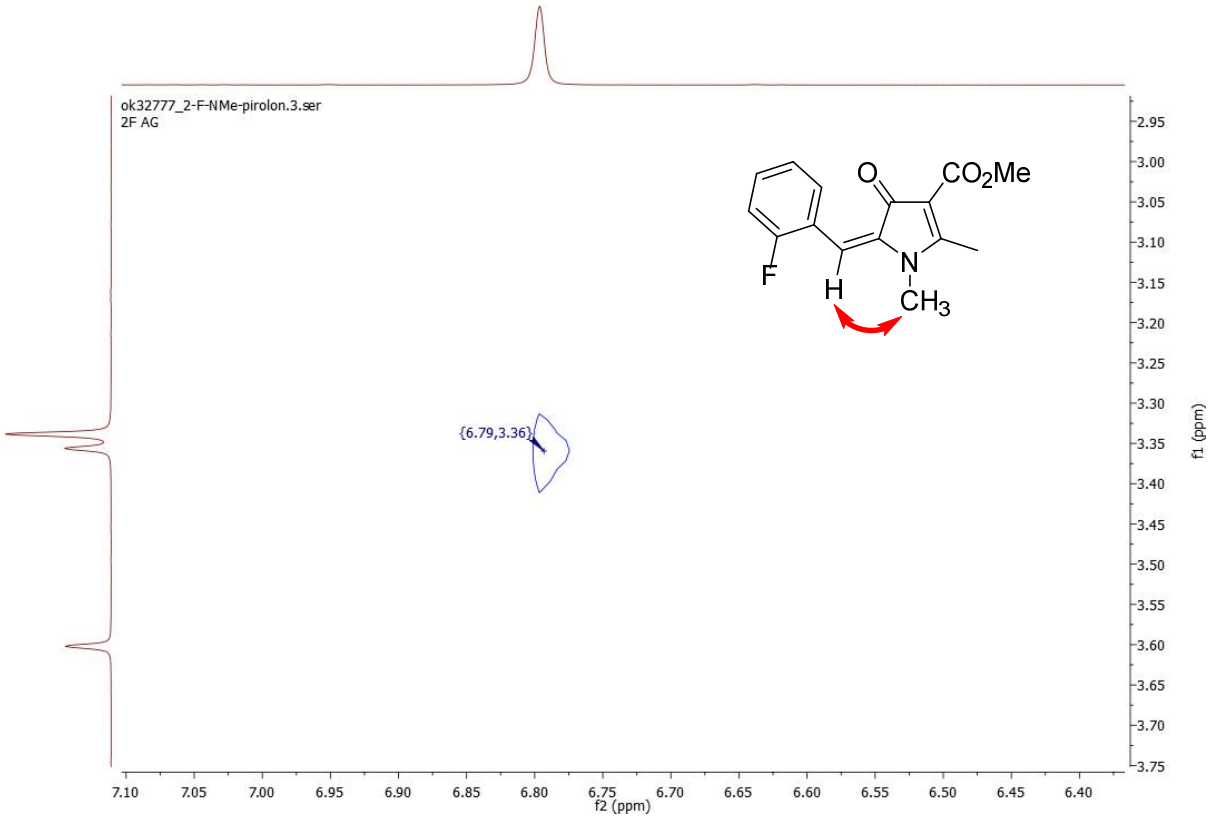
3. Copies of ^{1}H- and ^{13}C-NMR spectra

Methyl (*E*)-5-(2-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1c)

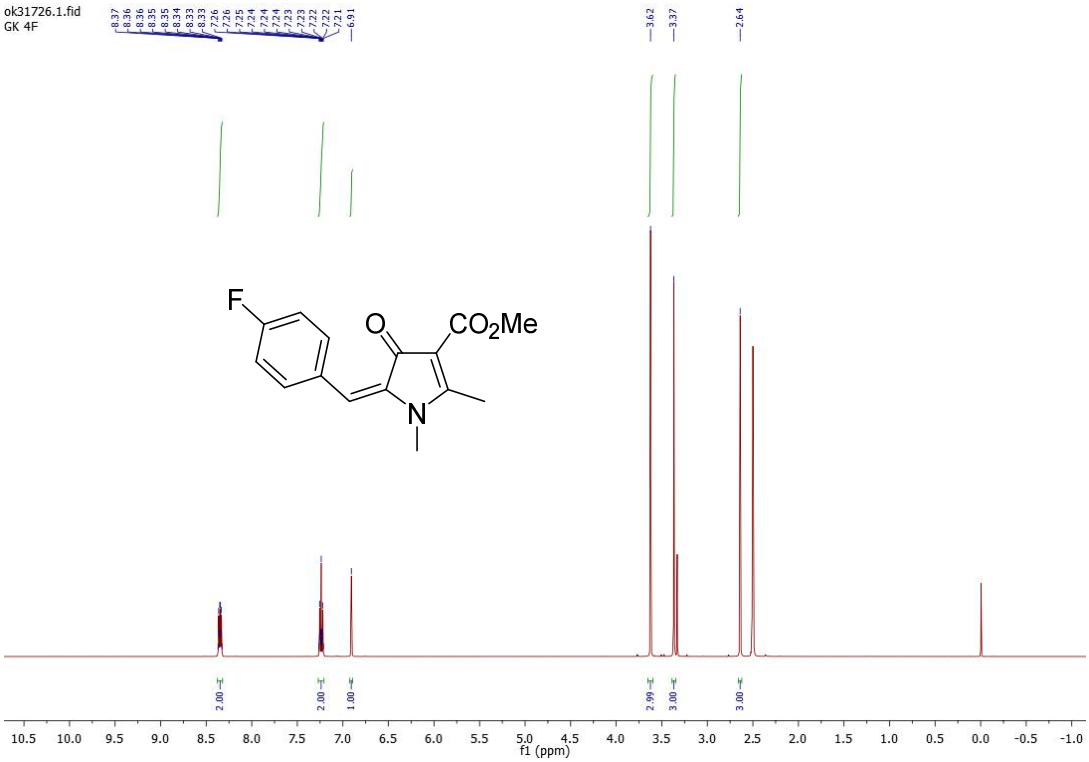


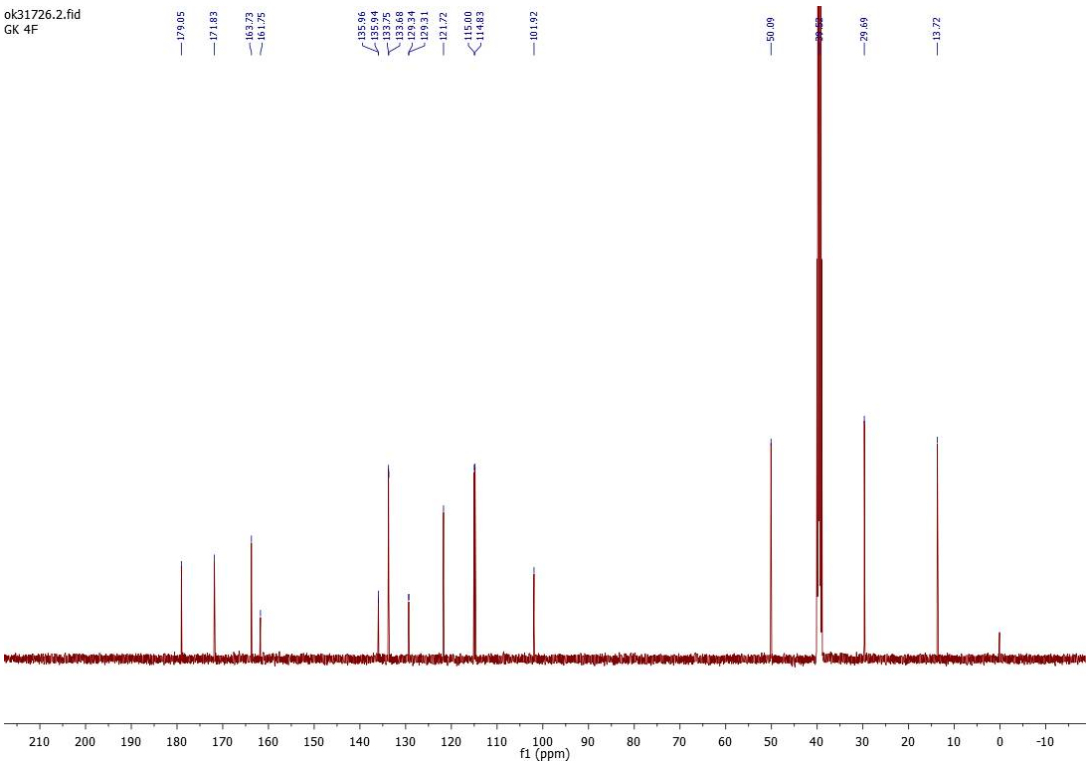


NOESY

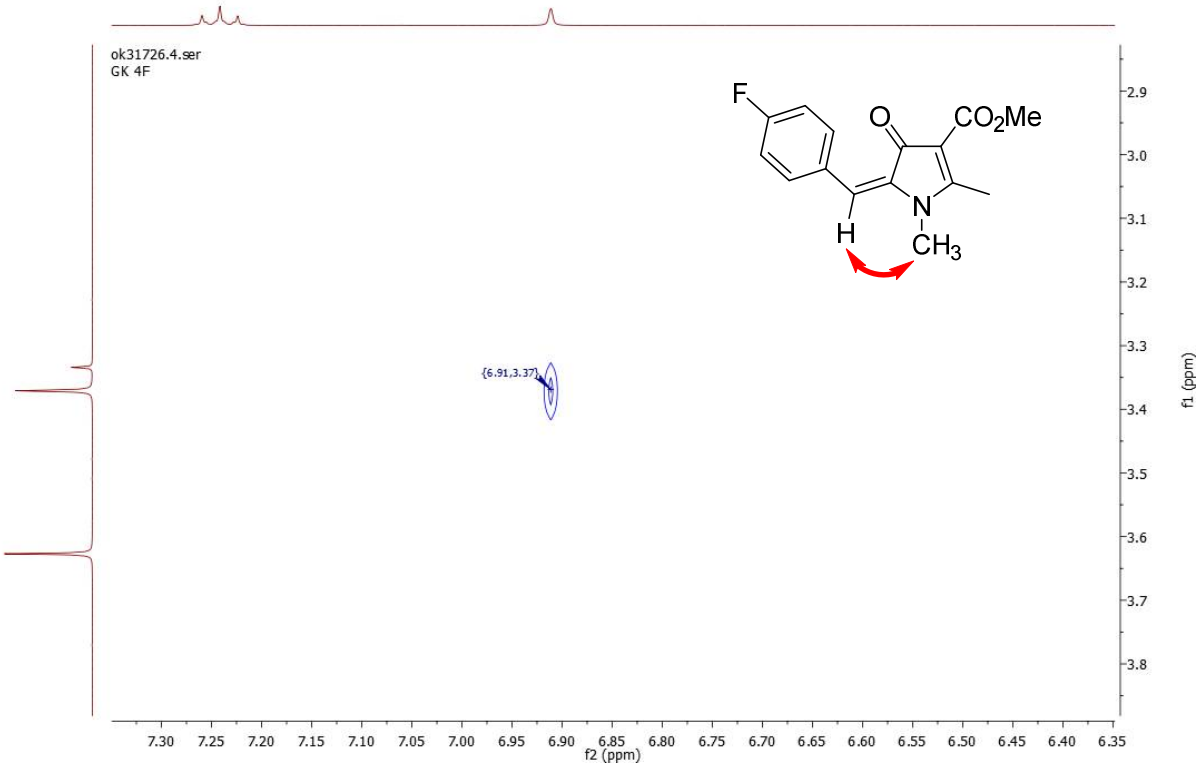

ok32777_2-F-NMe-pirolon.3.ser
2F AG
{6.79,3.36}
O
CO2Me
F
H
N
CH3
f2 (ppm)
f1 (ppm)

Methyl (*E*)-5-(4-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1f)

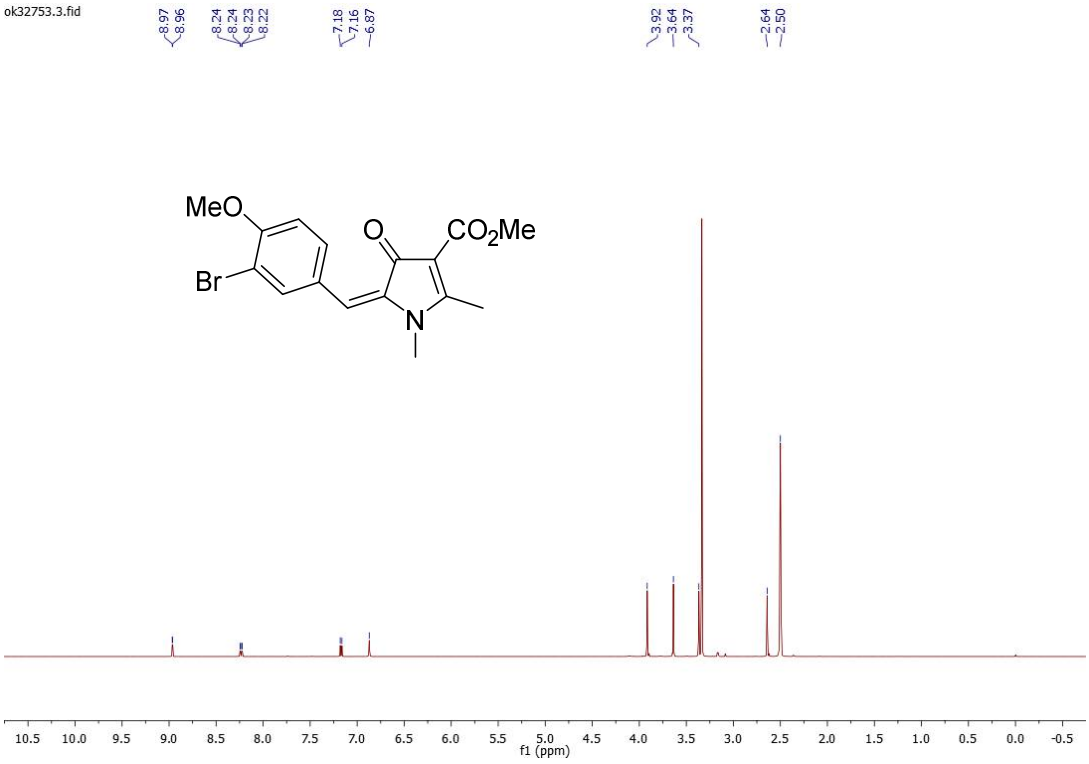


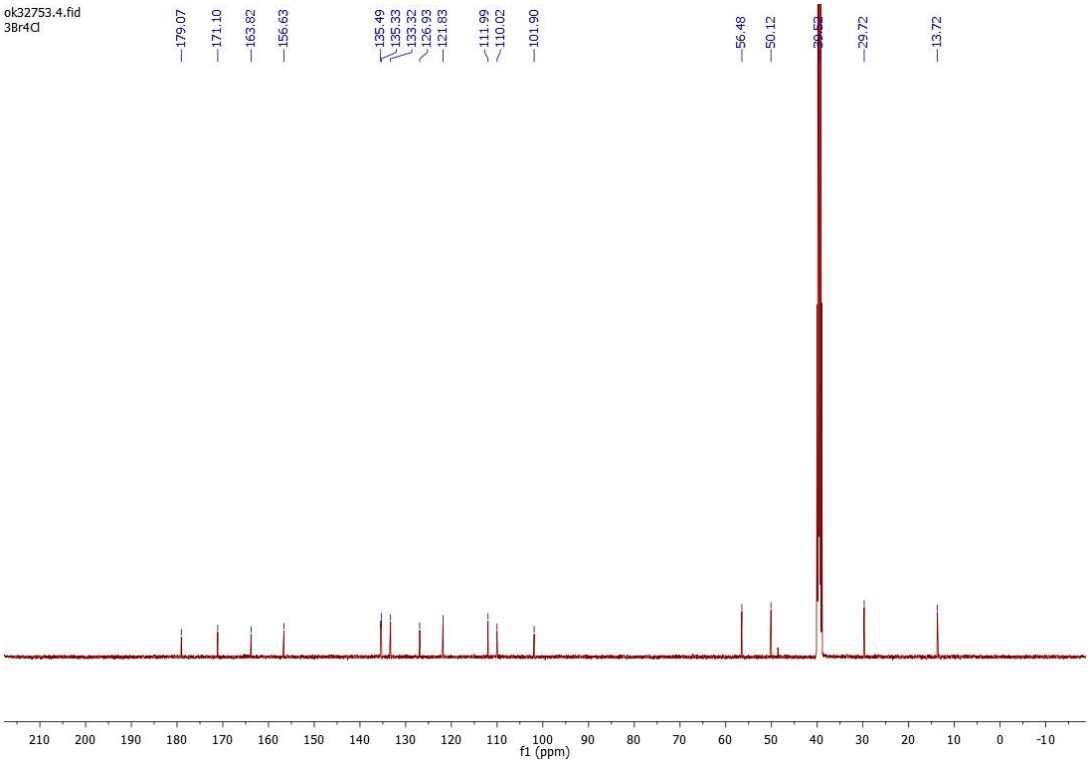


NOESY

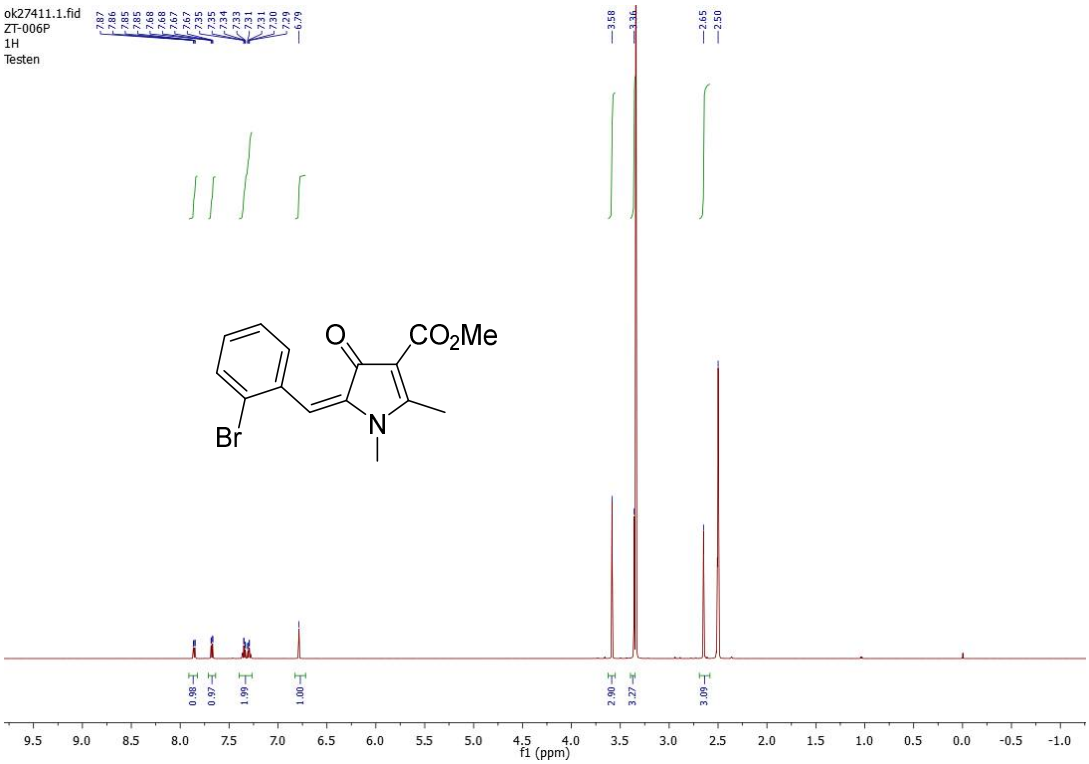


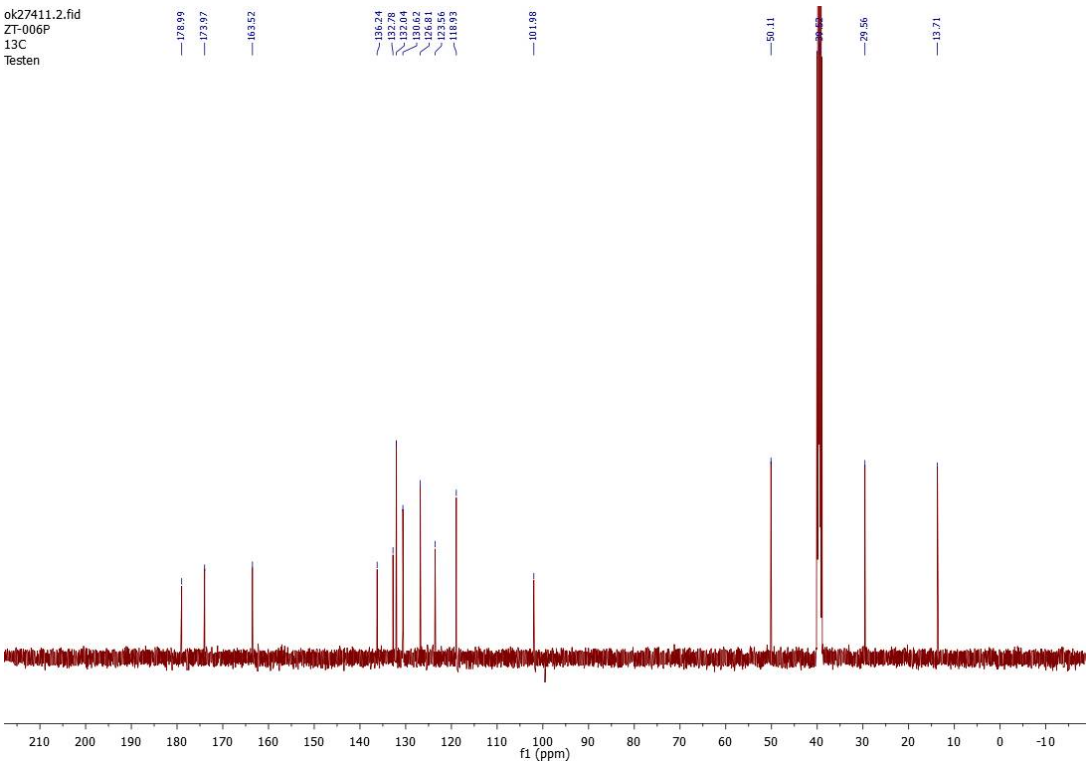
Methyl (*E*)-5-(3-bromo-4-methoxybenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1g)



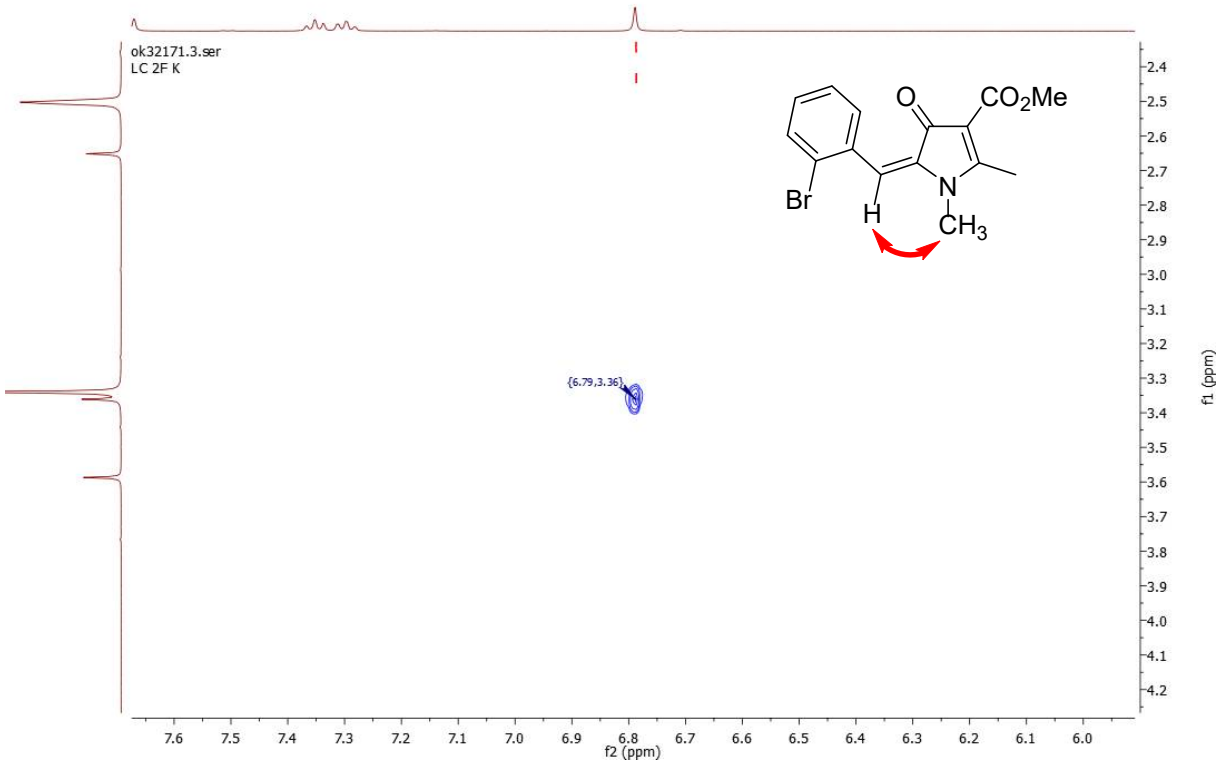


Methyl (*E*)-5-(2-bromobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1i)

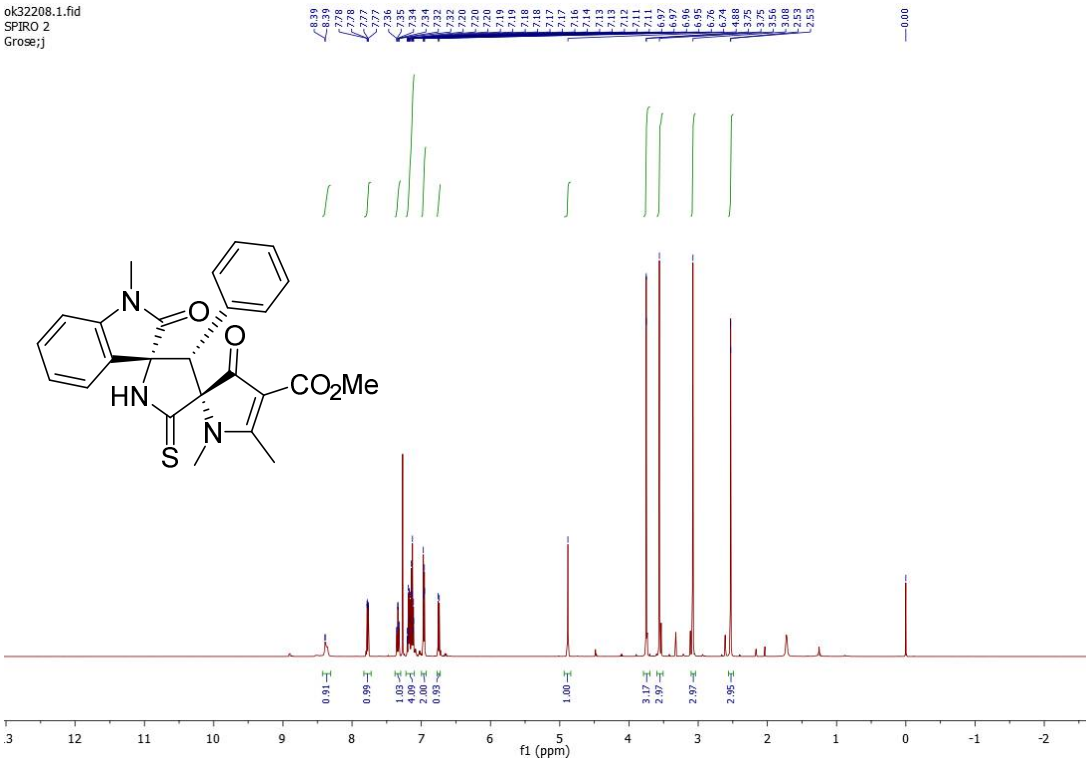


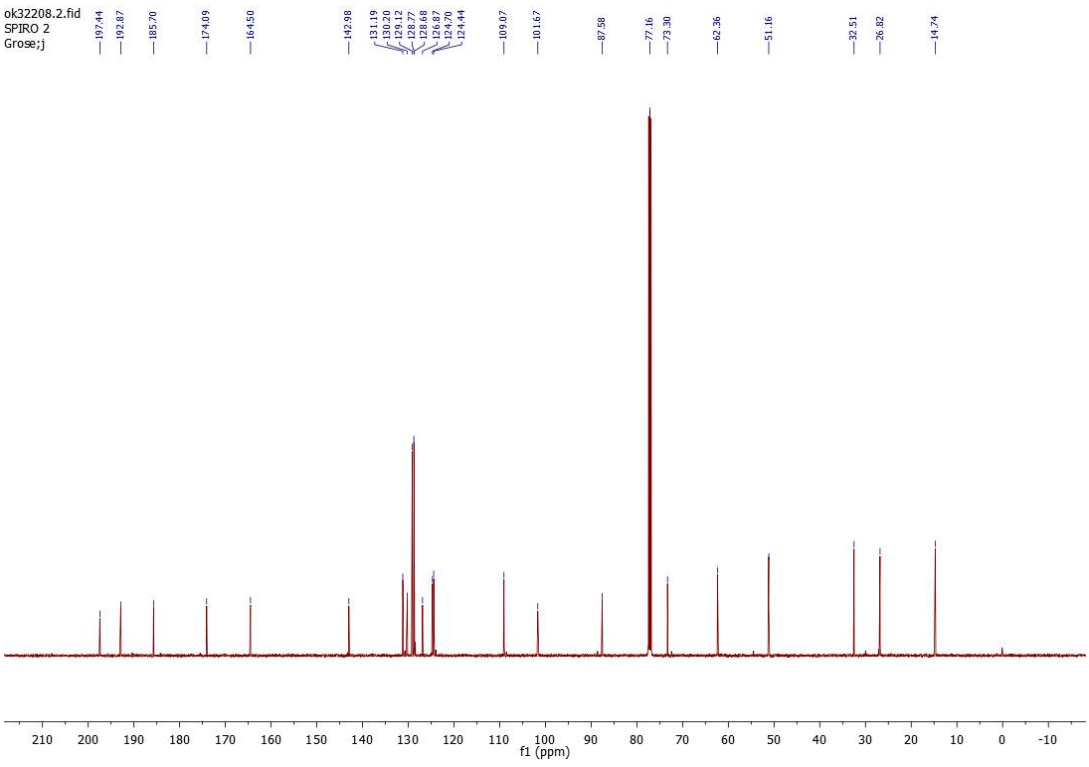


NOESY

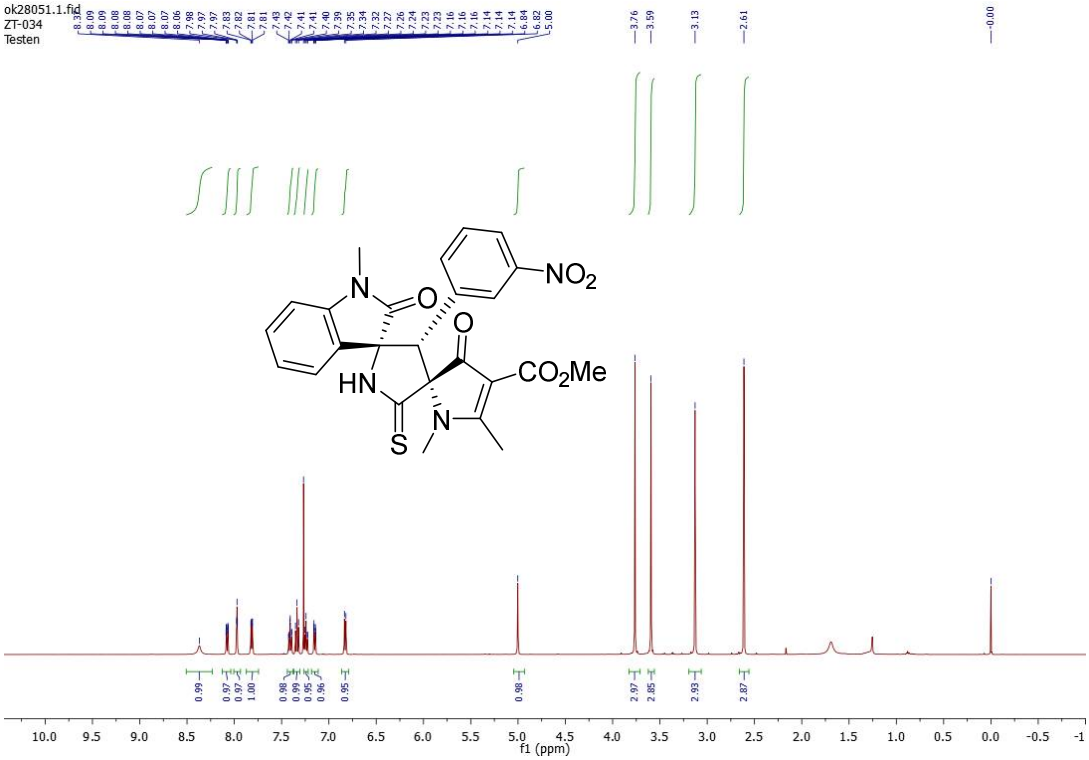


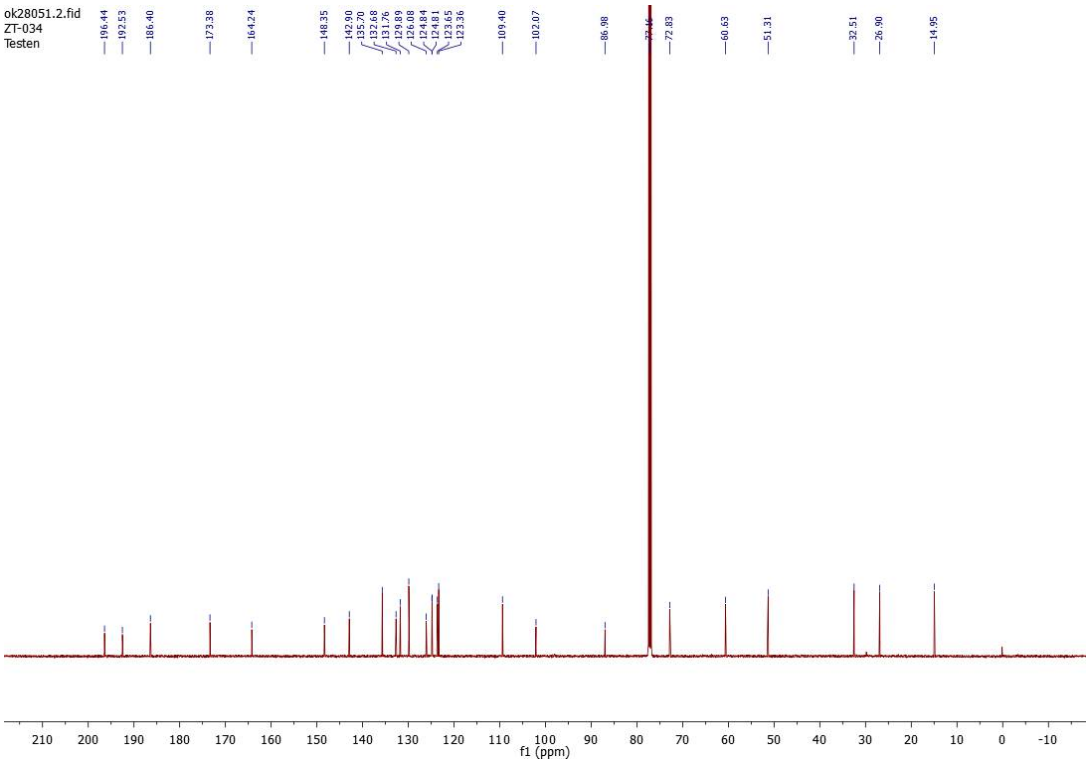
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-phenyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3a)



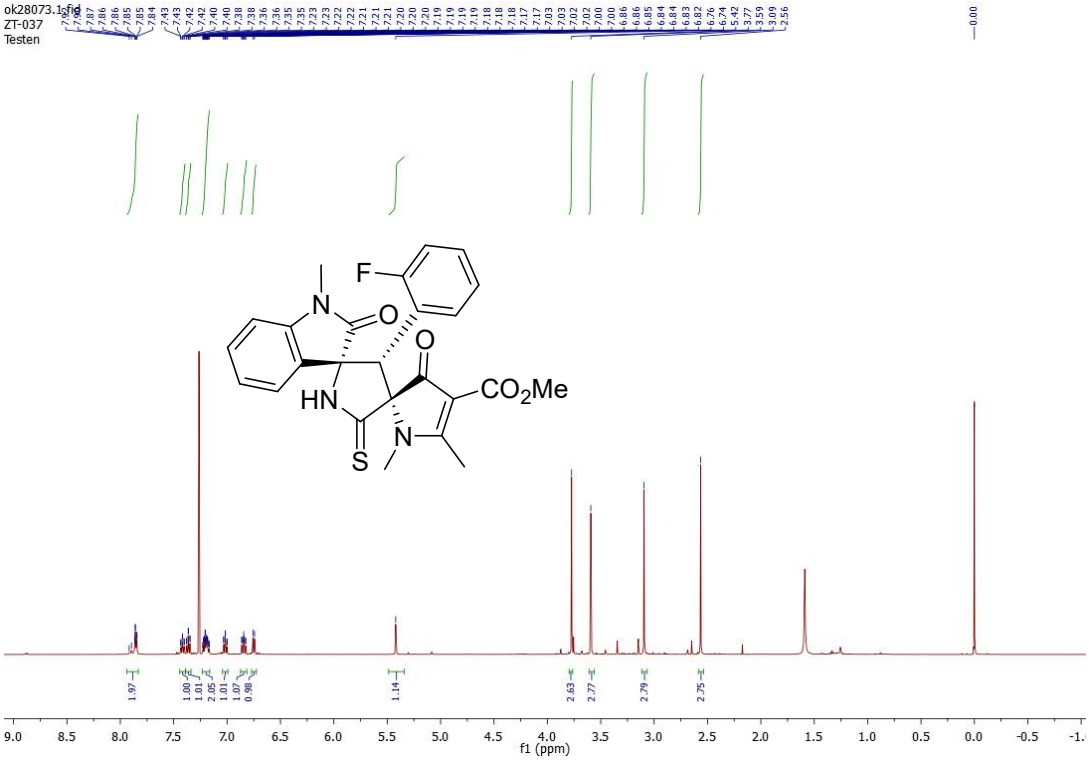


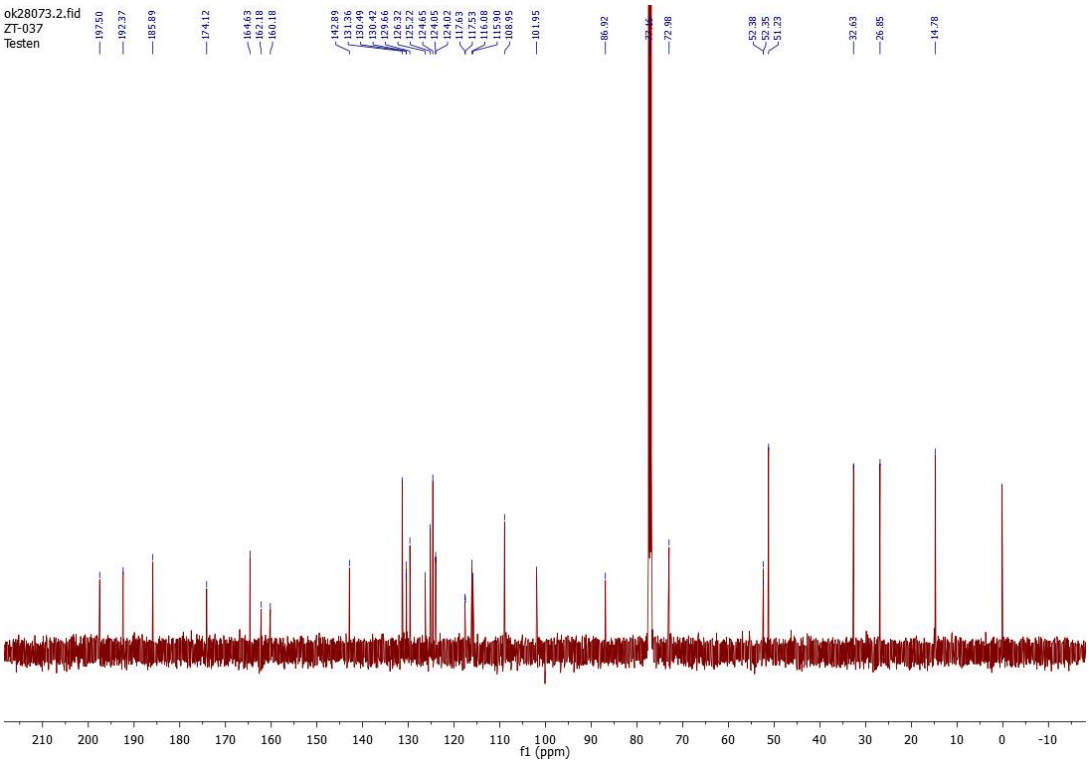
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3b)



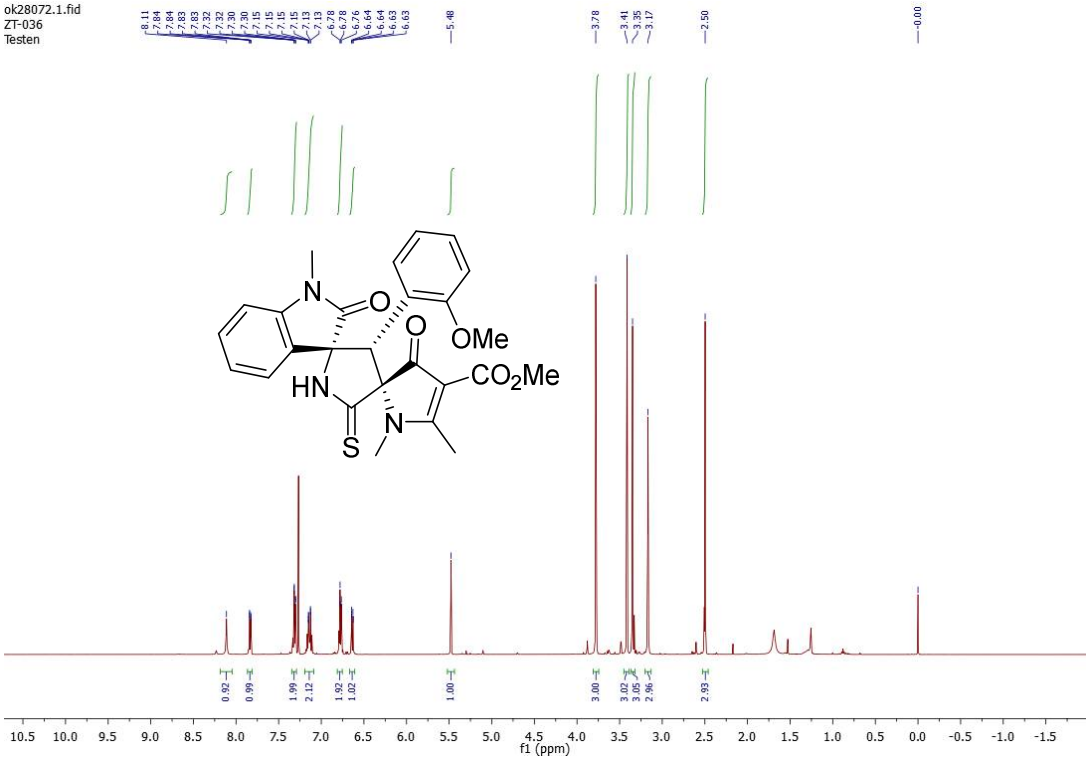


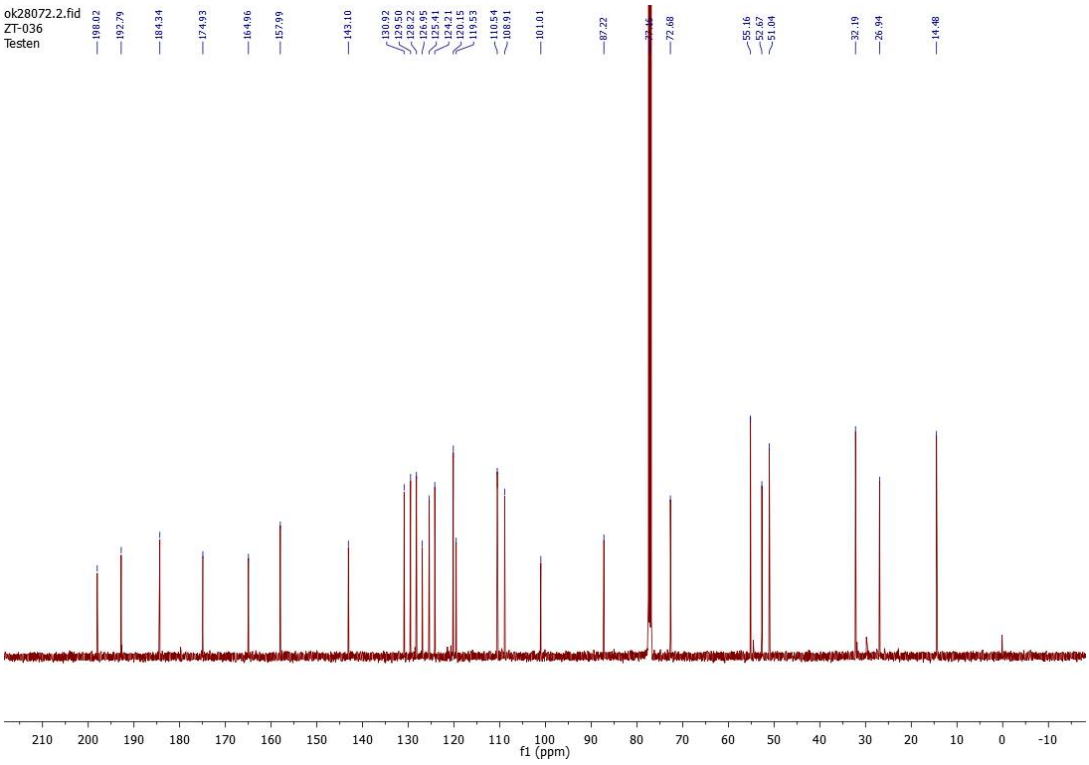
Methyl (3*R*,3'*S*,4'*R*)-3'-(2-fluorophenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3c)



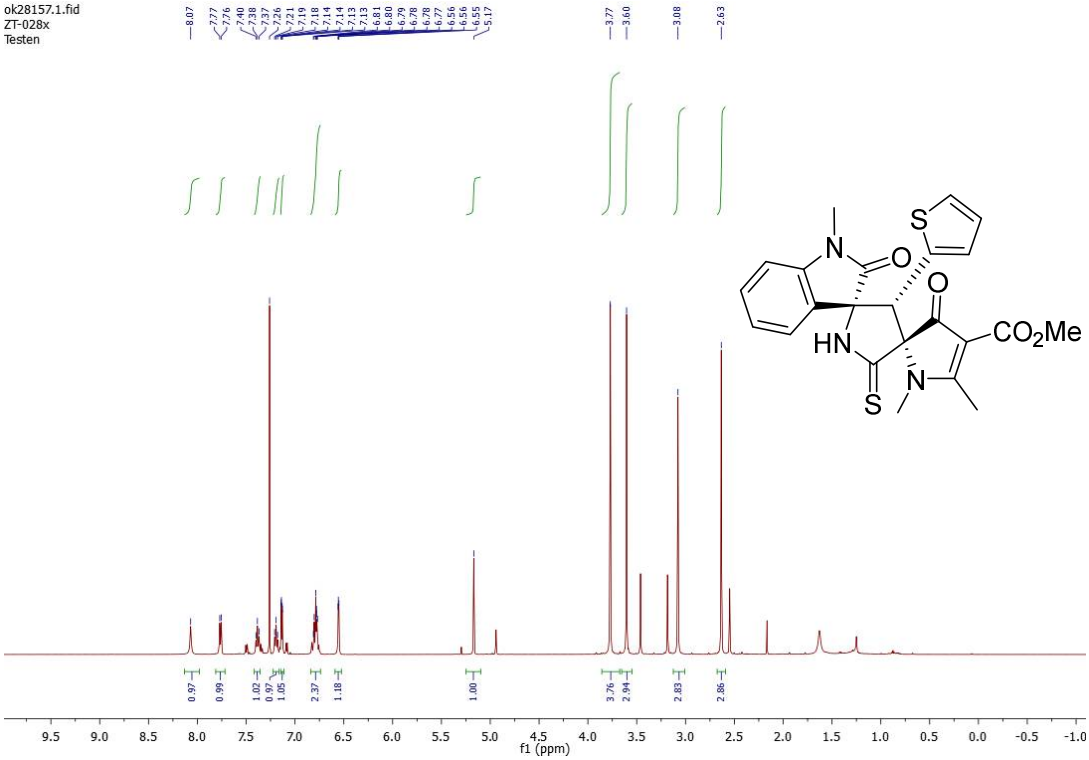


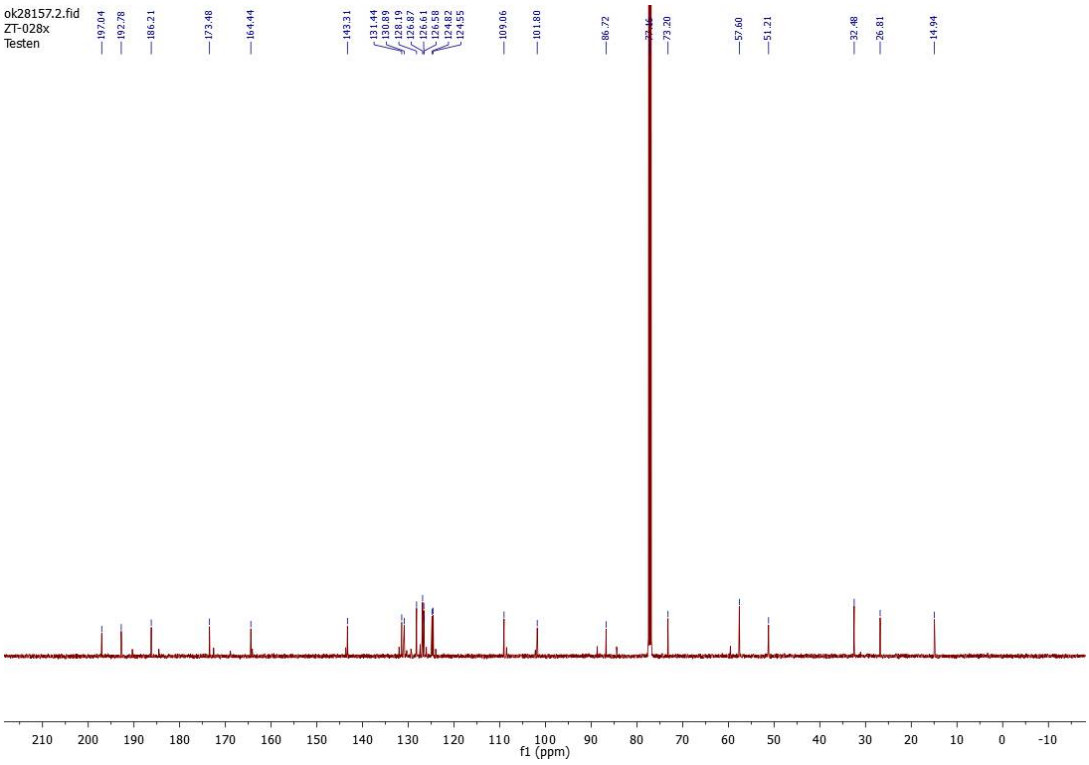
Methyl (3*R*,3'*S*,4'*R*)-3'-(2-methoxyphenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3d)



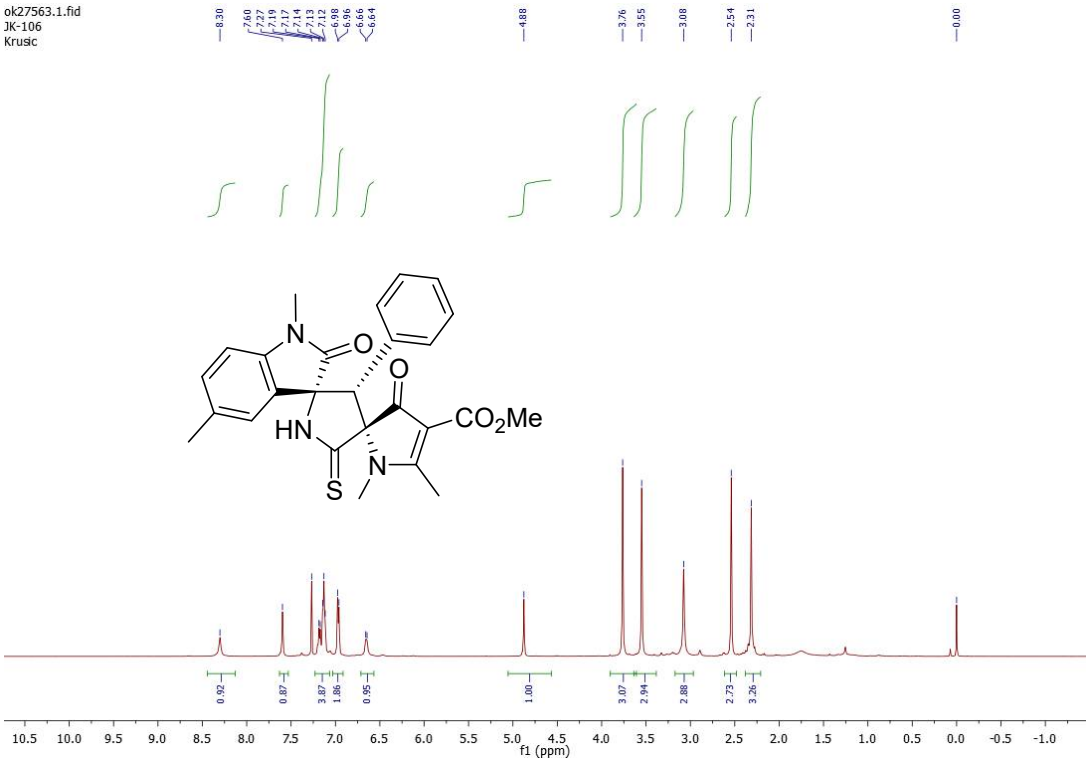


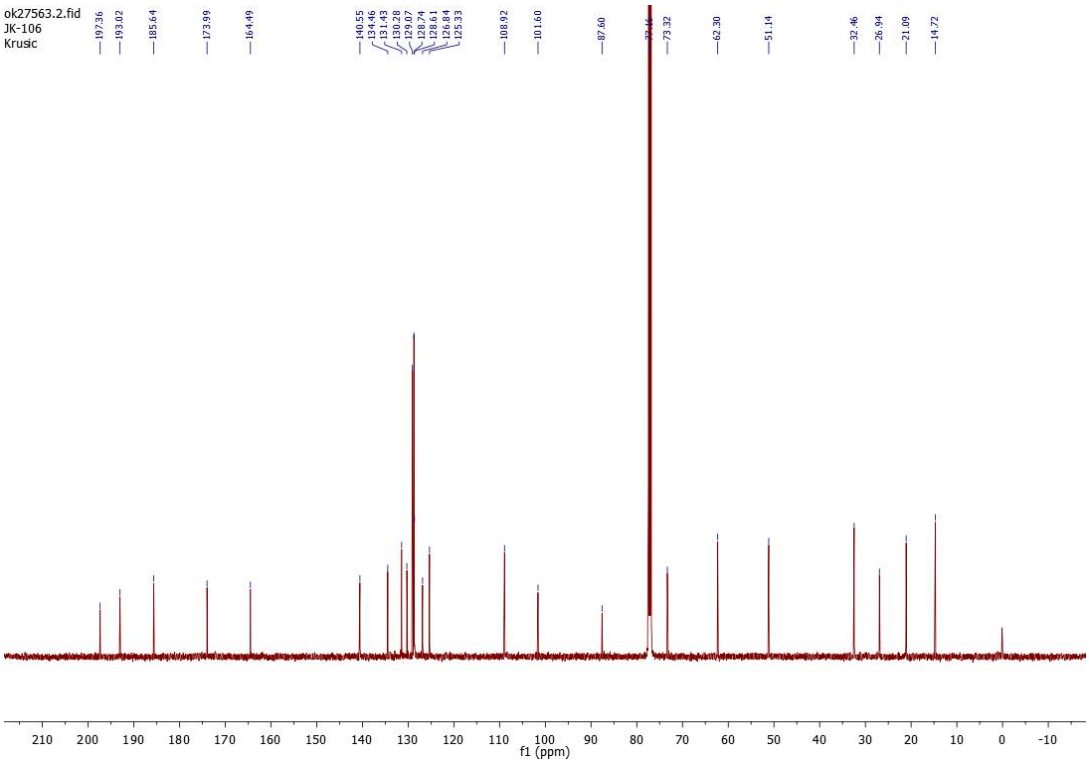
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-2,3''-dioxo-3'-(thiophen-2-yl)-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3e)



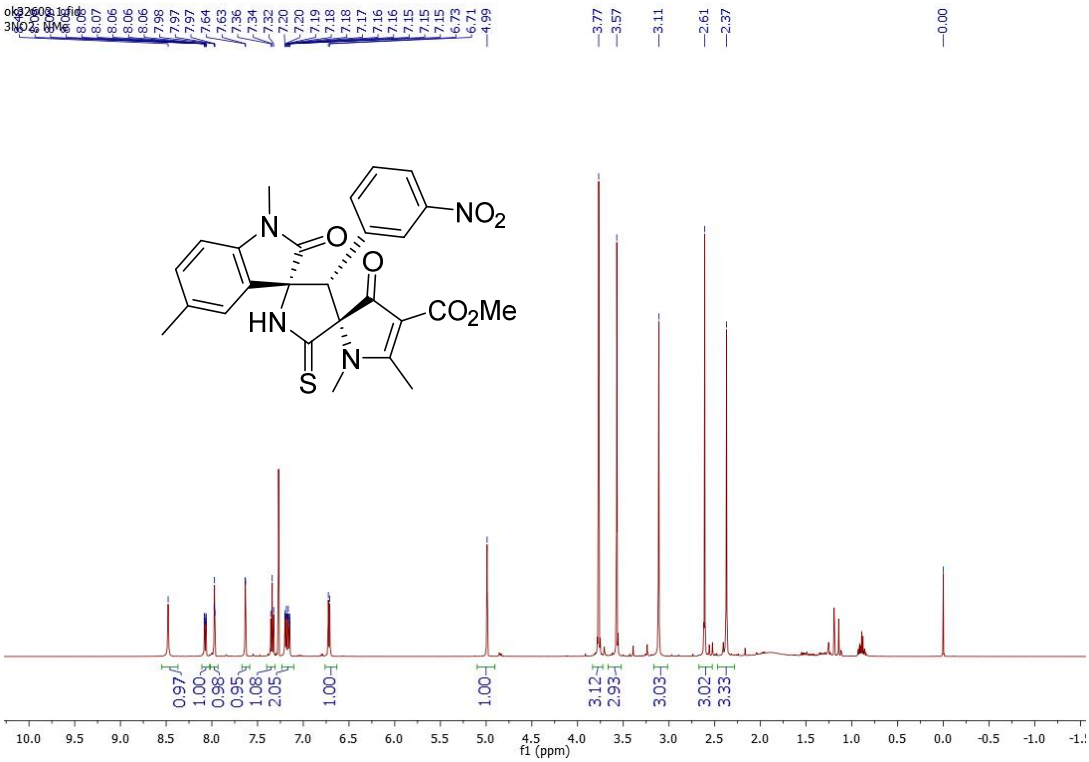


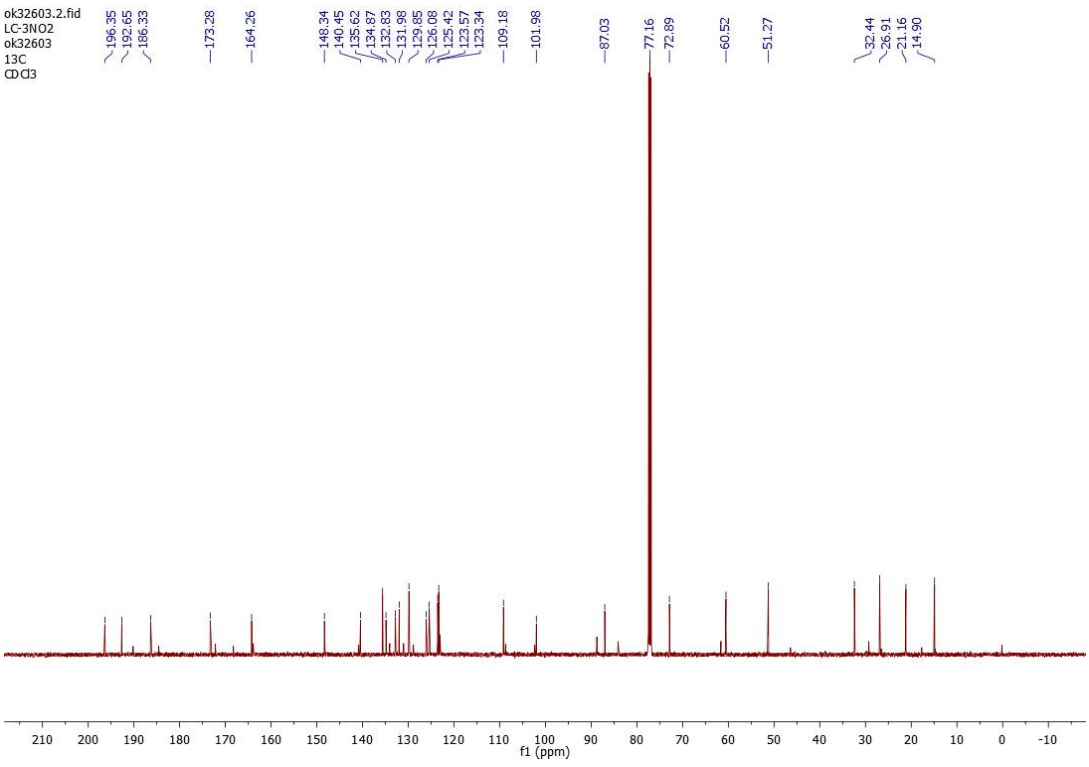
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-2,3''-dioxo-3'-phenyl-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3f)



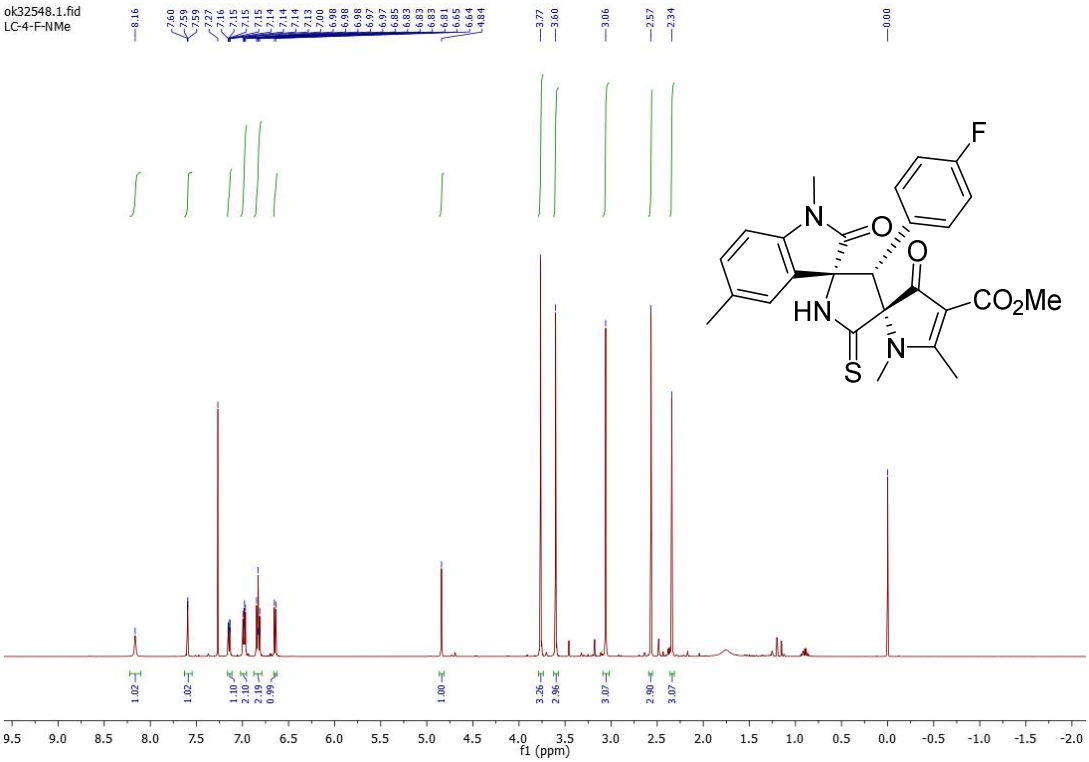


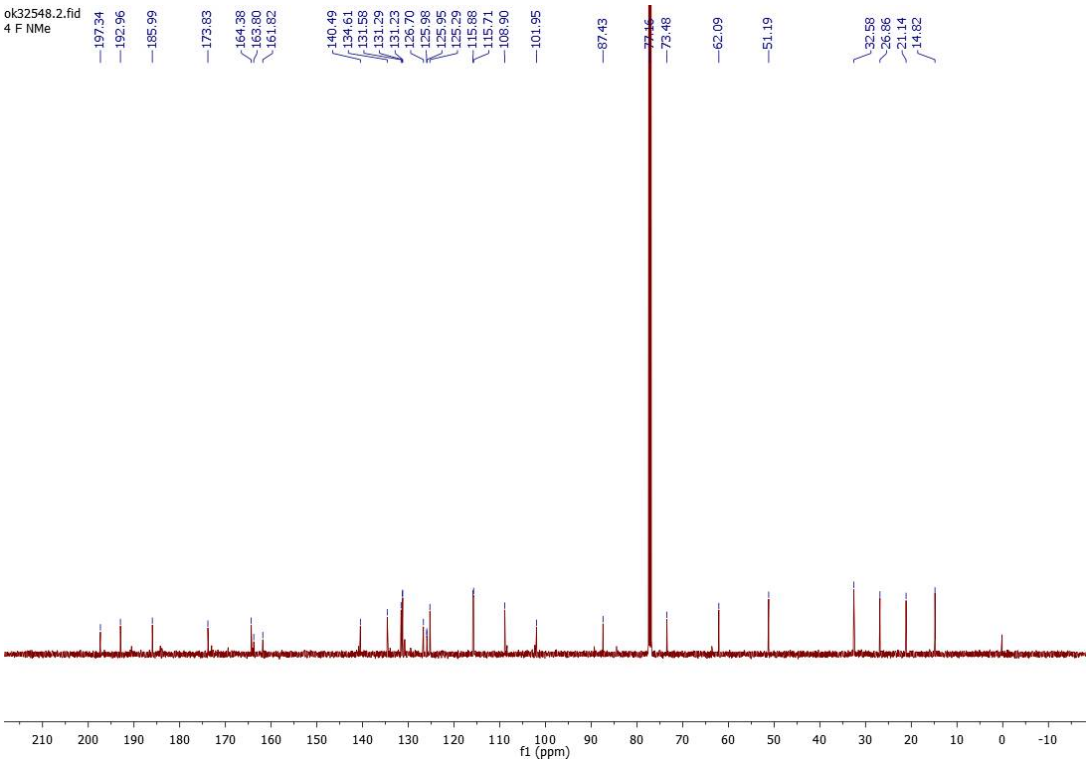
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3g)



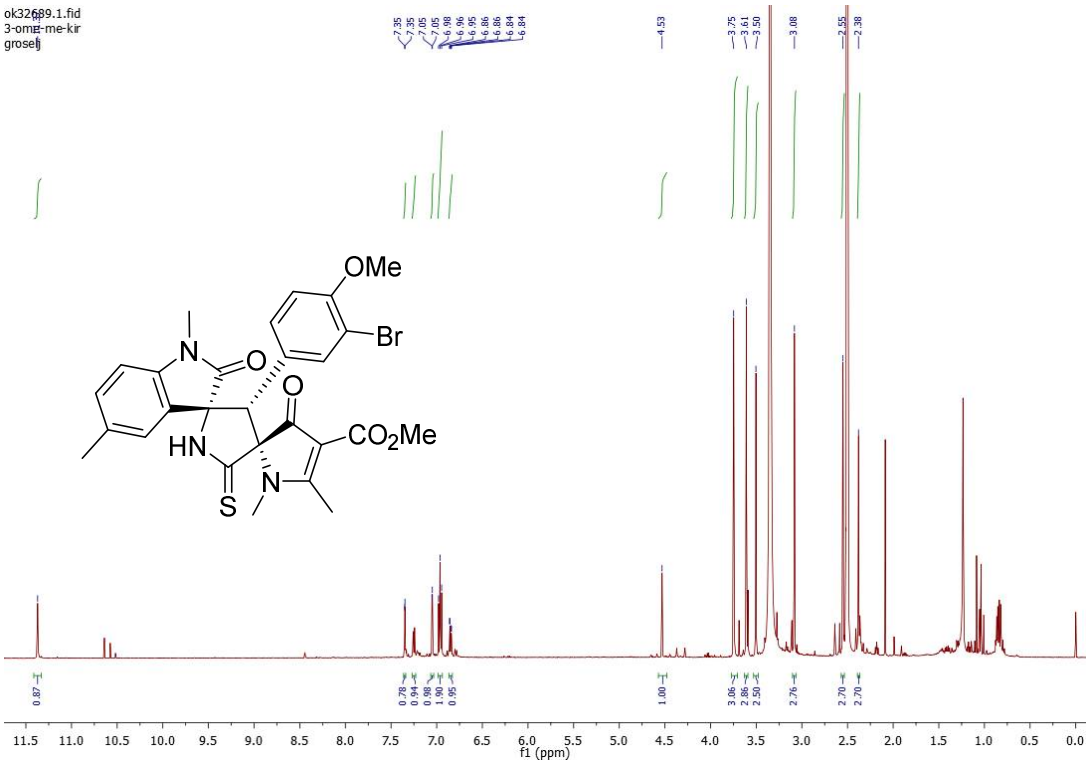


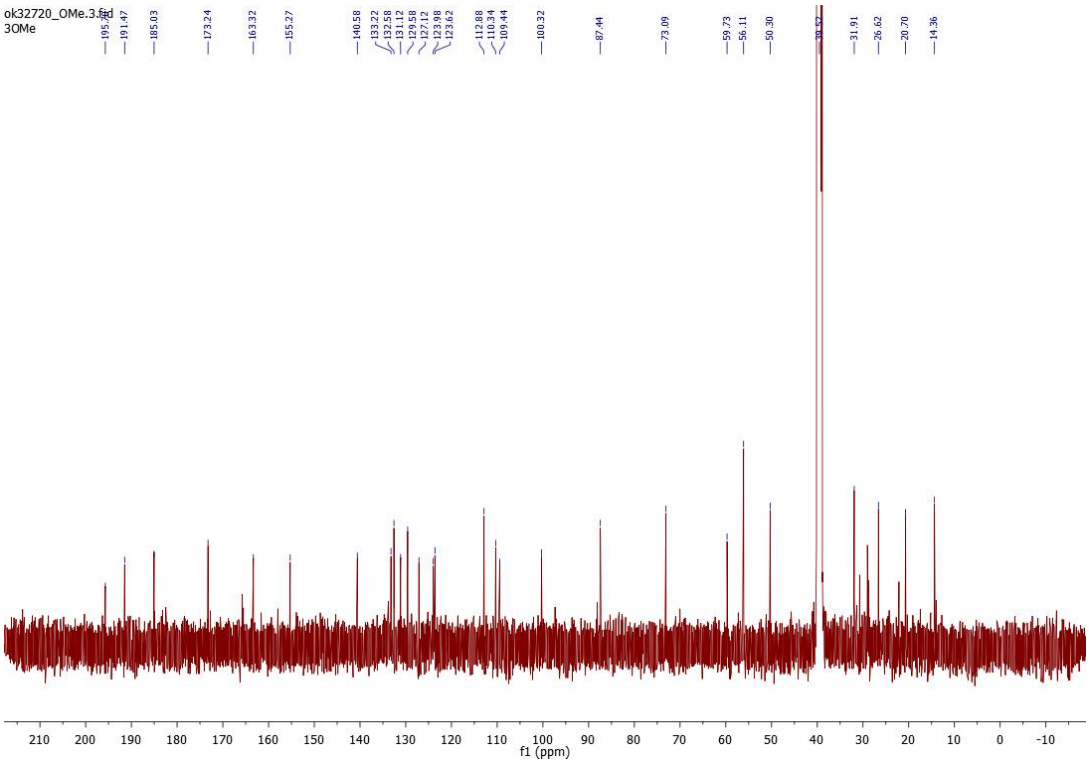
Methyl (3*R*,3'*S*,4'*R*)-3'-(4-fluorophenyl)-1,1'',5,5''-tetramethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3h)



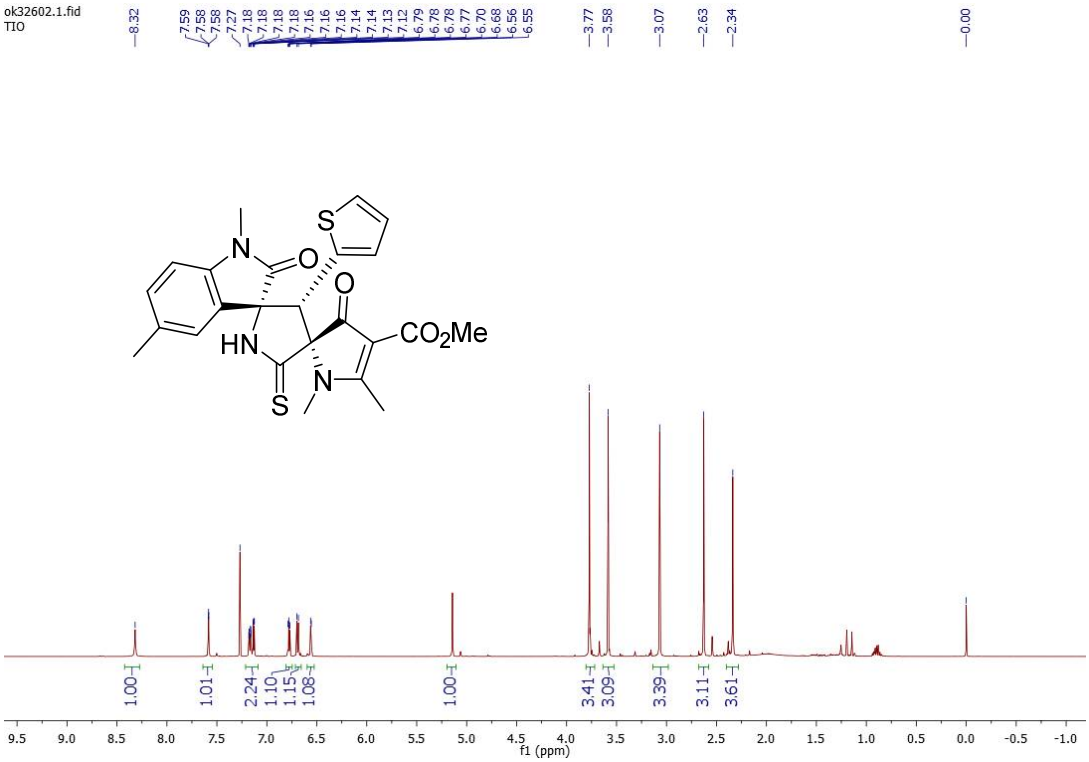


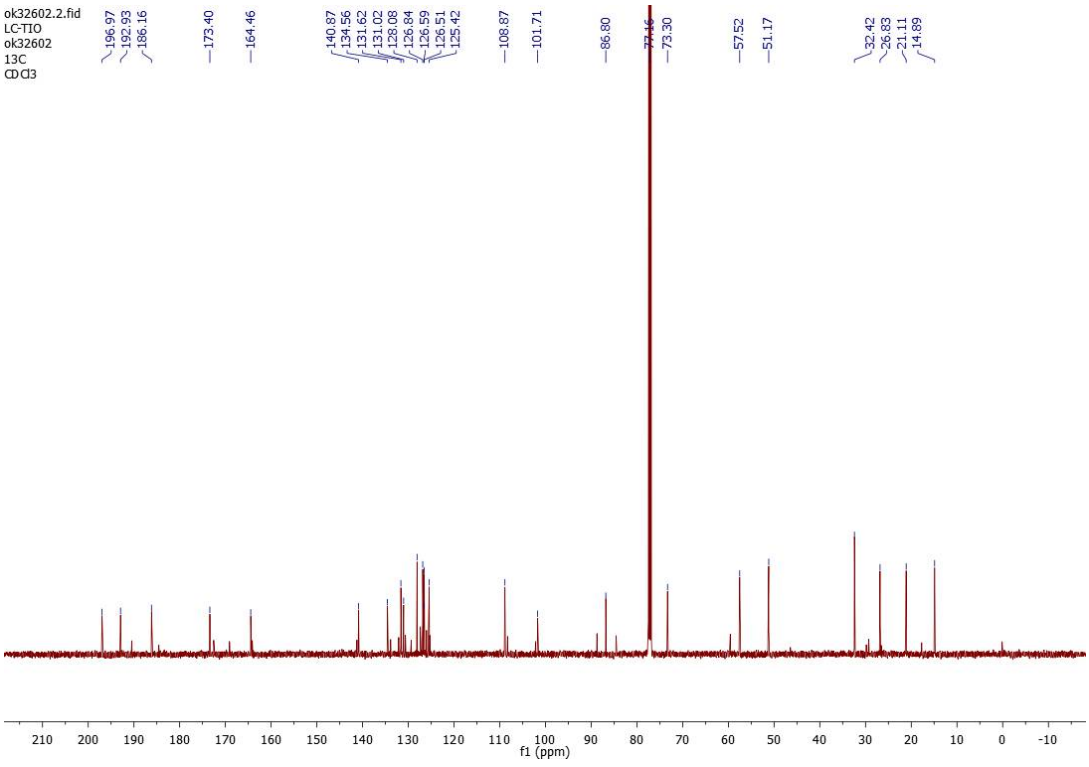
Methyl (3*R*,3'*S*,4'*R*)-3'-(4-bromo-3-methoxyphenyl)-1,1'',5,5''-tetramethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3i)



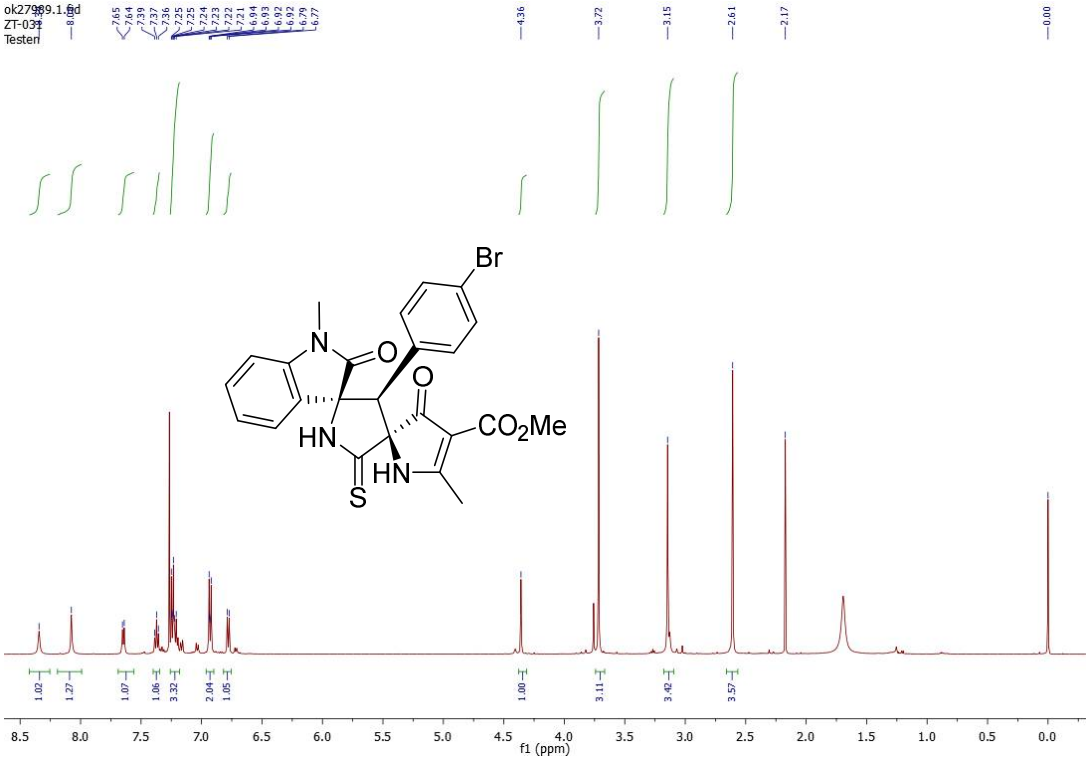


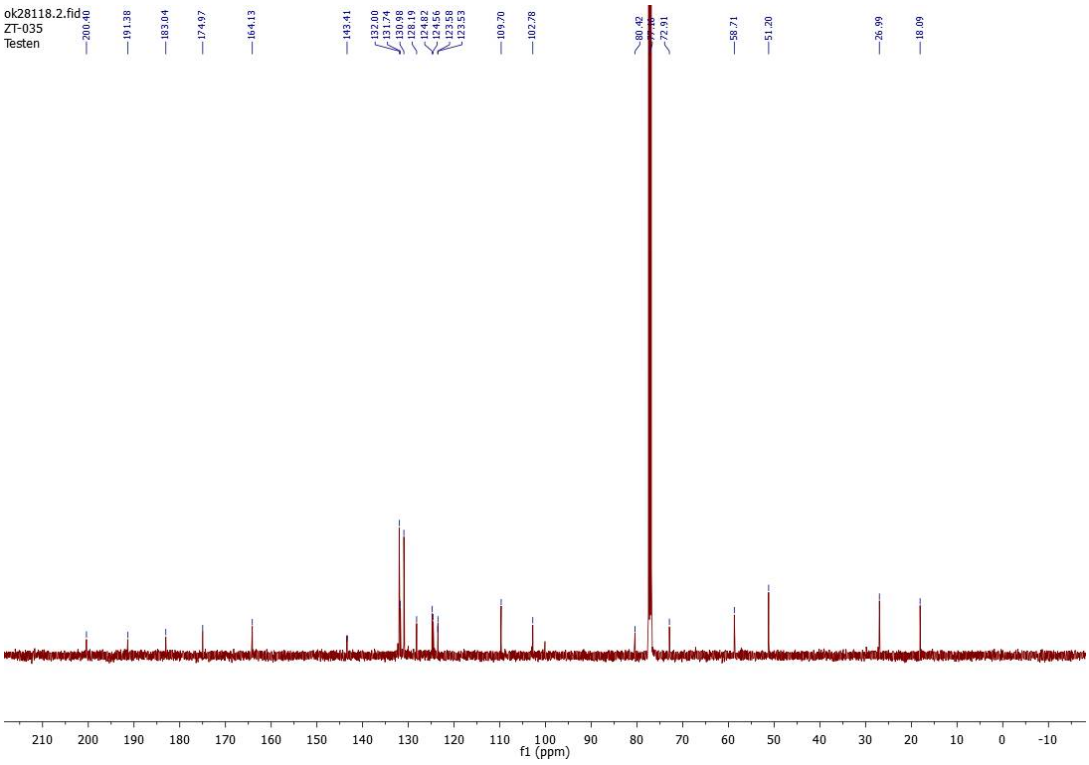
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-2,3''-dioxo-3'-(thiophen-2-yl)-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3j)



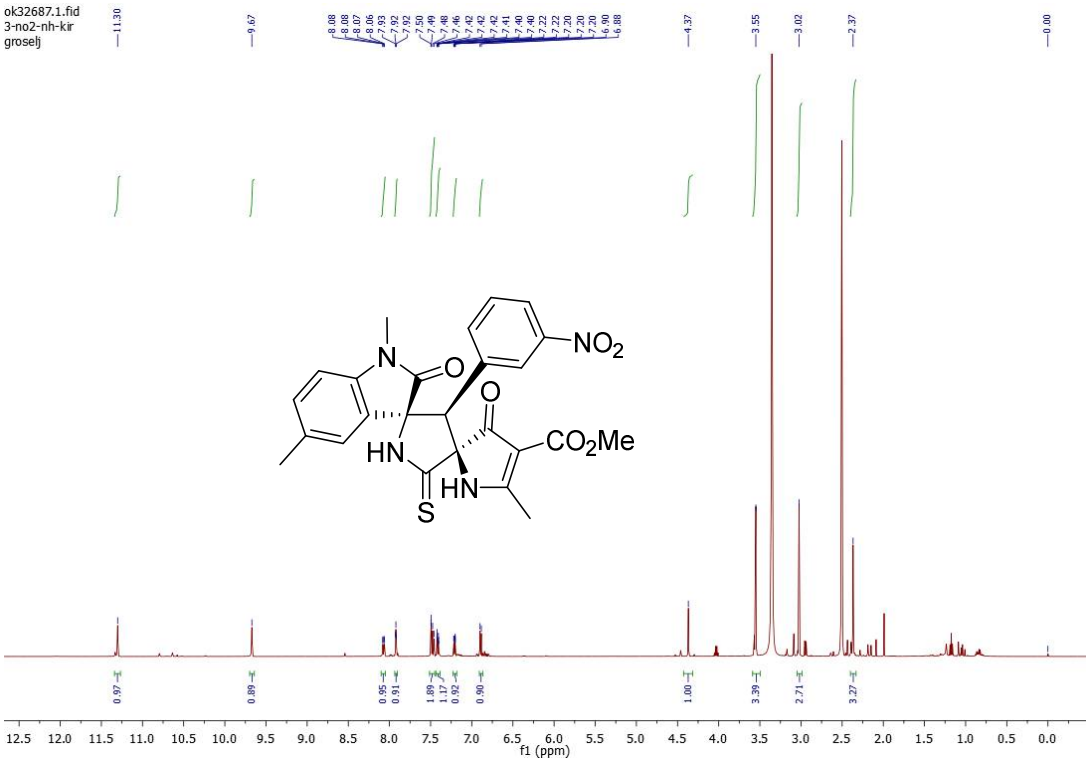


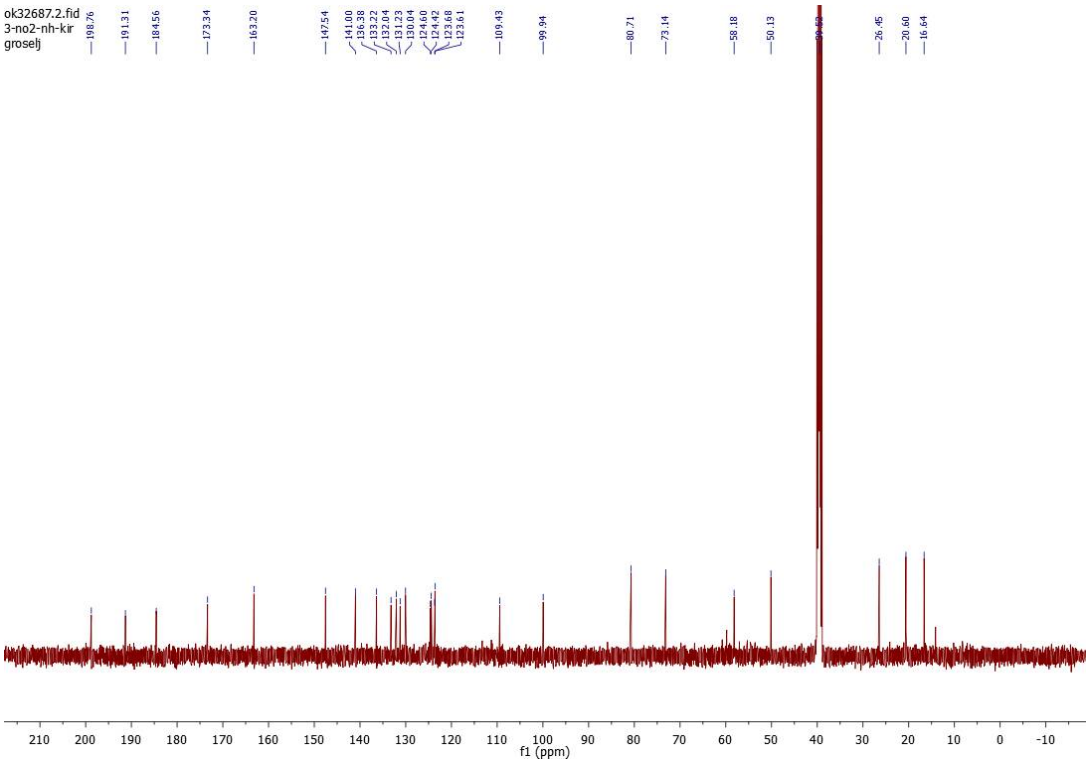
Methyl (3*S*,3'*R*,4'*S*)-3'-(4-bromophenyl)-1,5''-dimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3k)



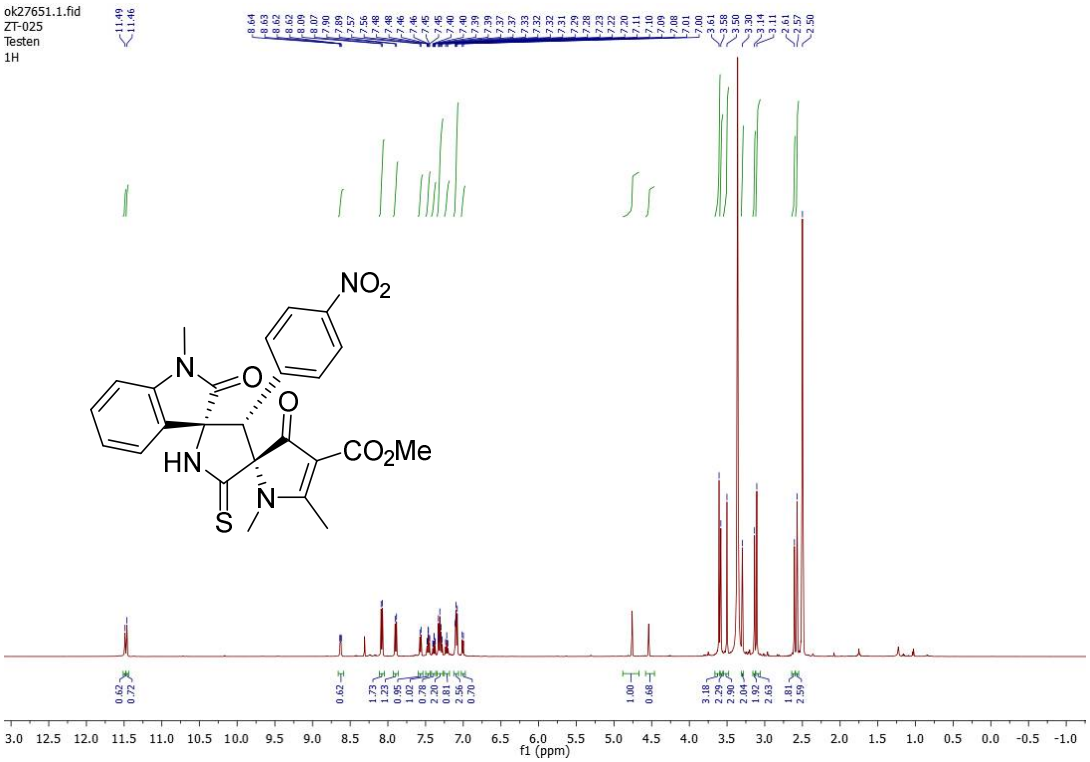


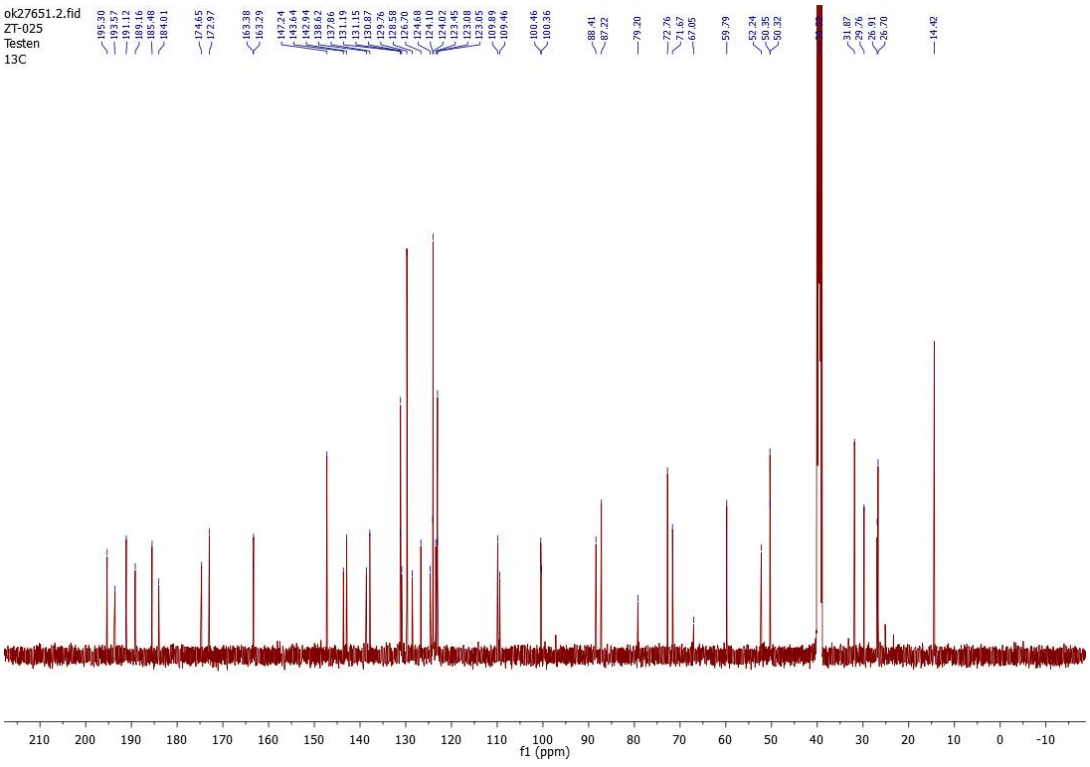
Methyl (3*S*,3'*R*,4'*S*)-1,5,5''-trimethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3l)



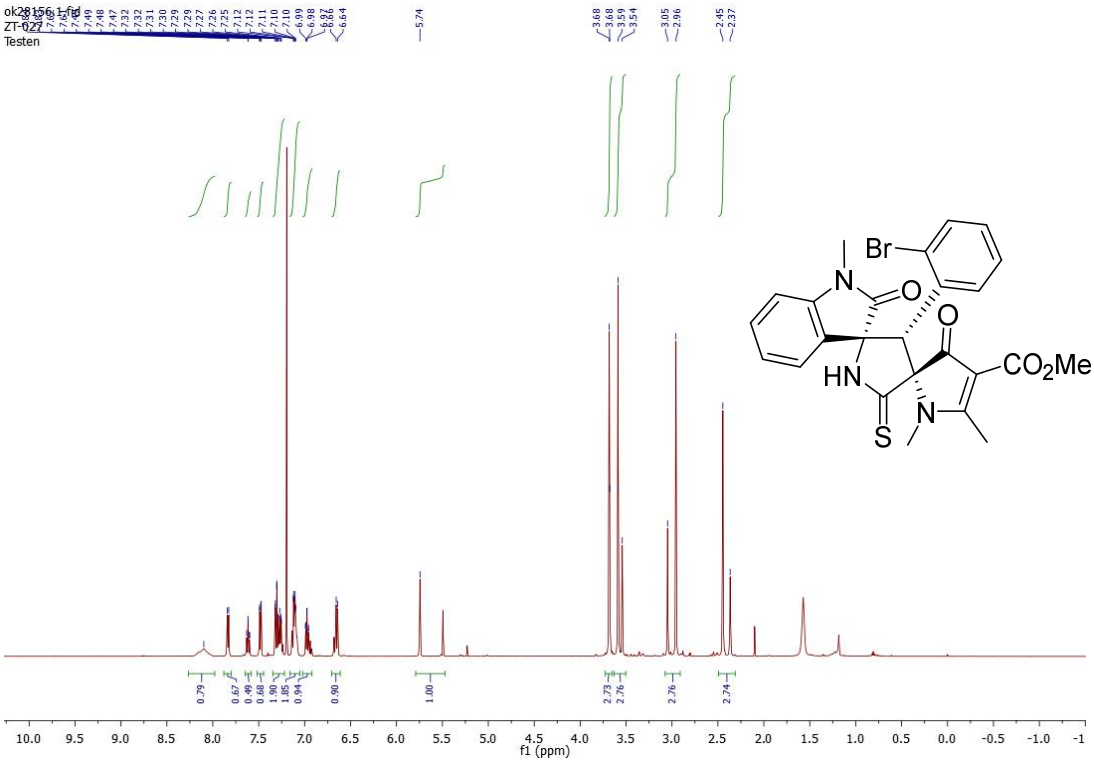


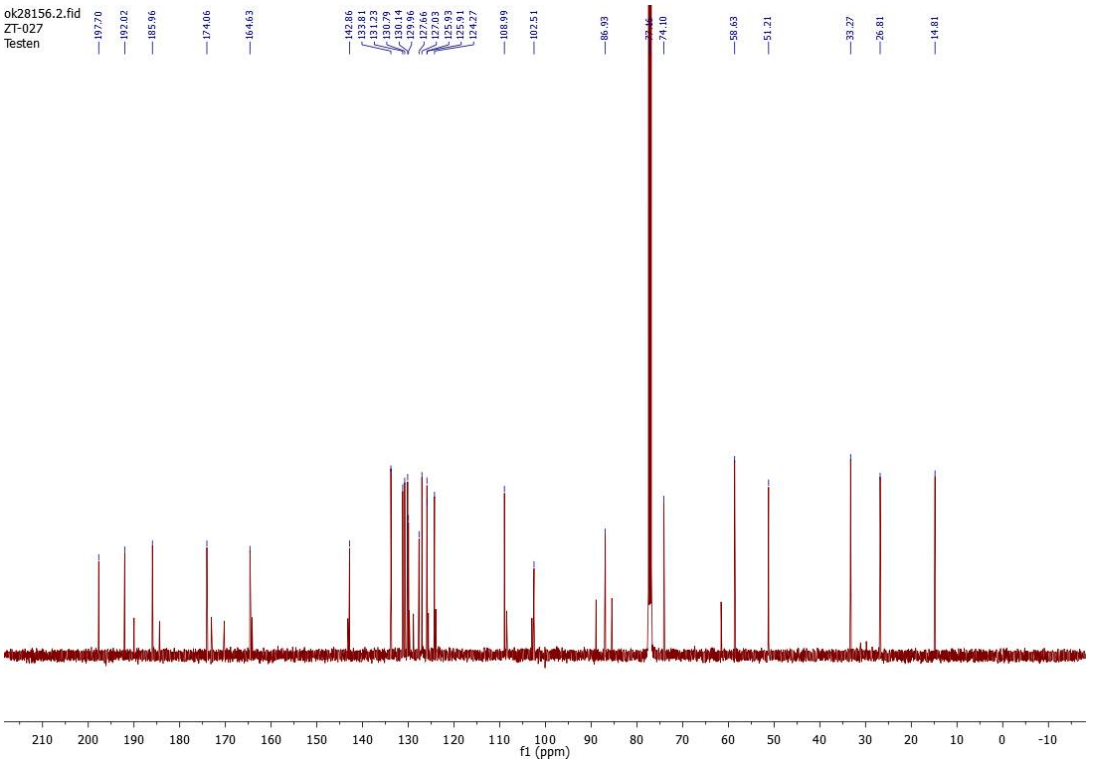
Methyl *rel*-(3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-(4-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3m)



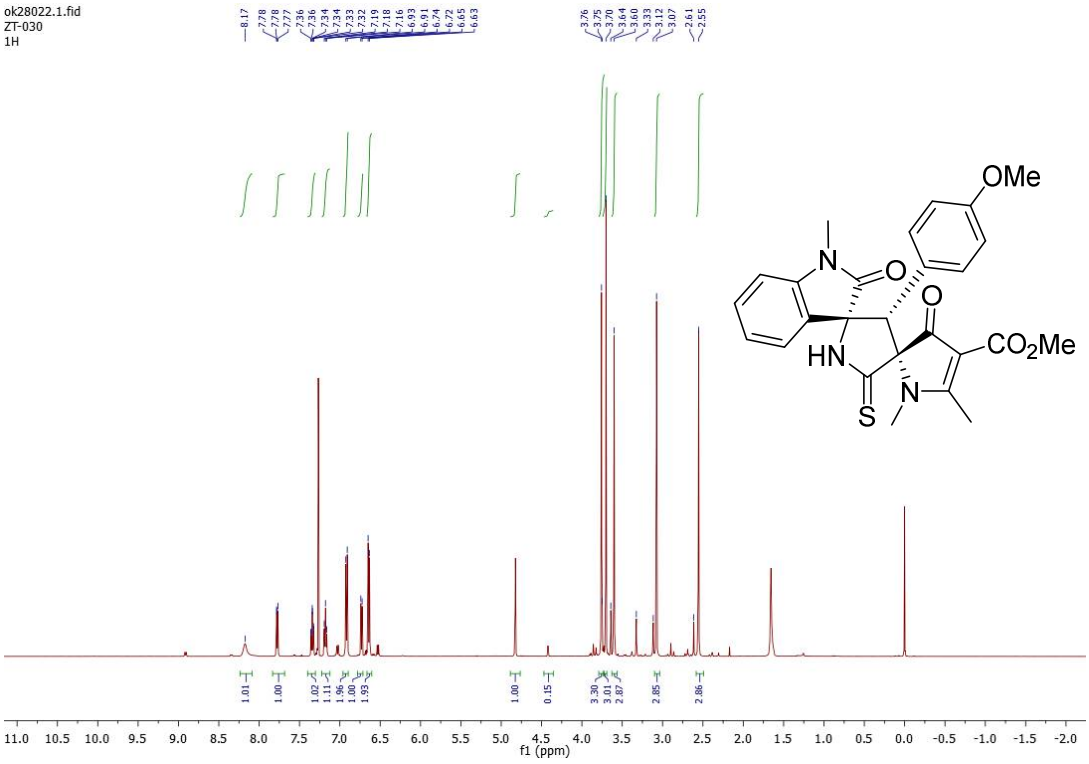


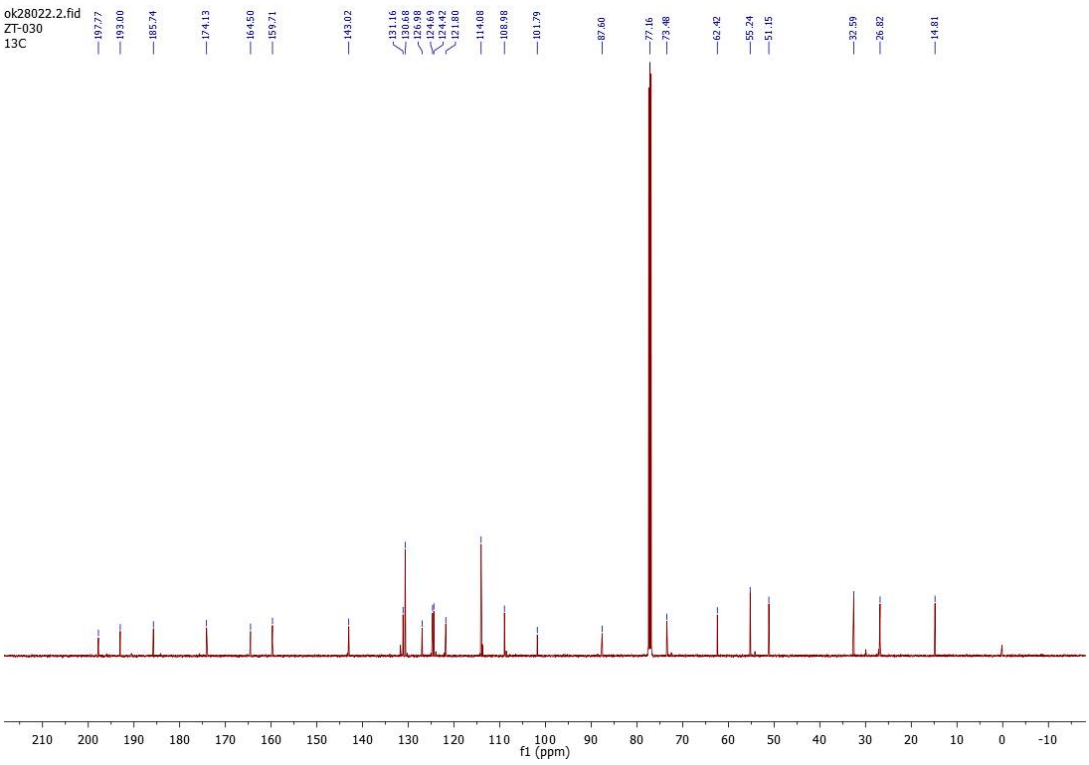
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(2-bromophenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3n)



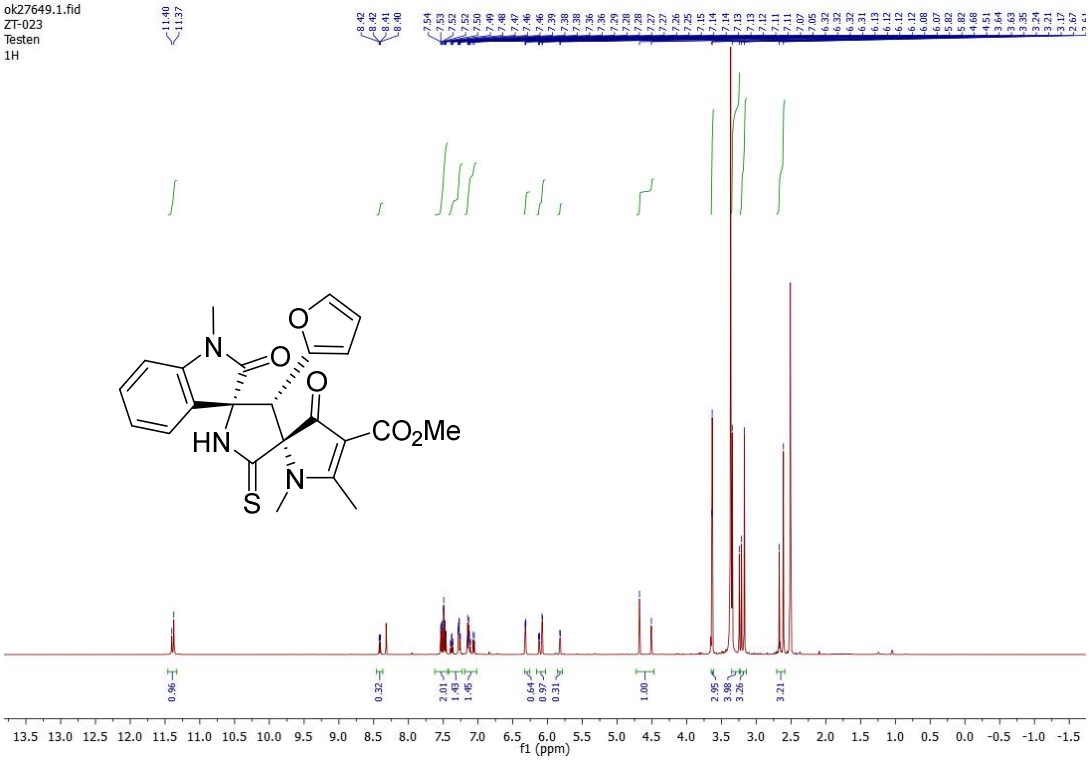


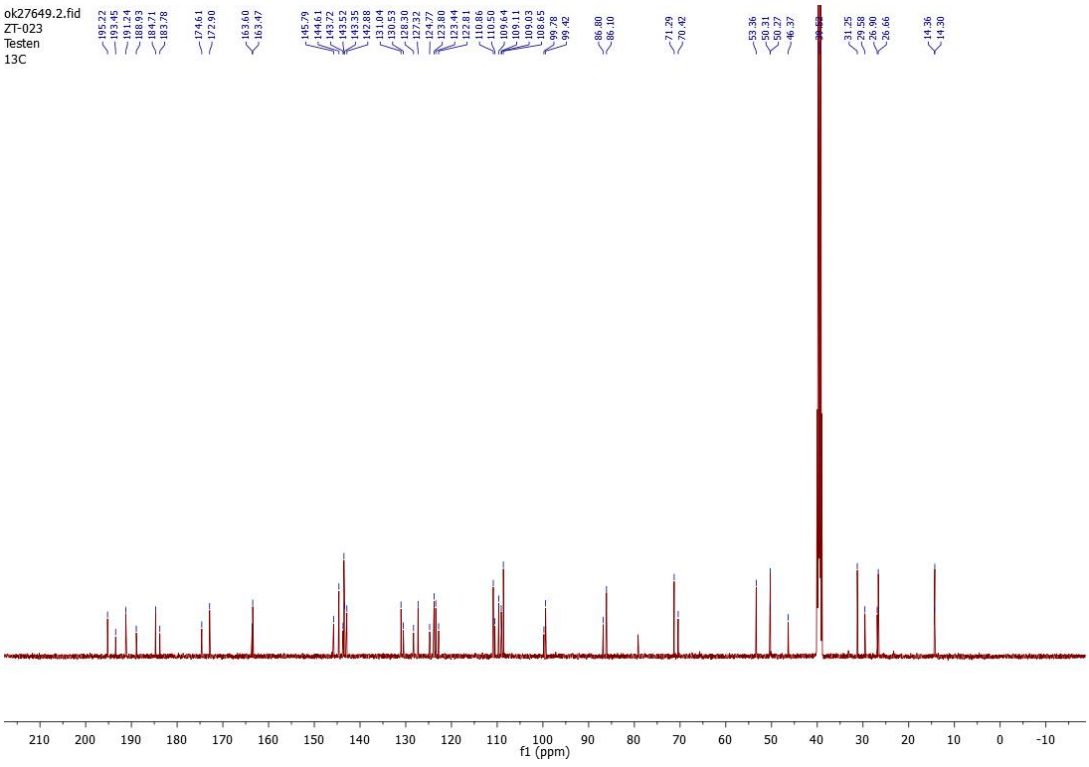
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(4-methoxyphenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3o)



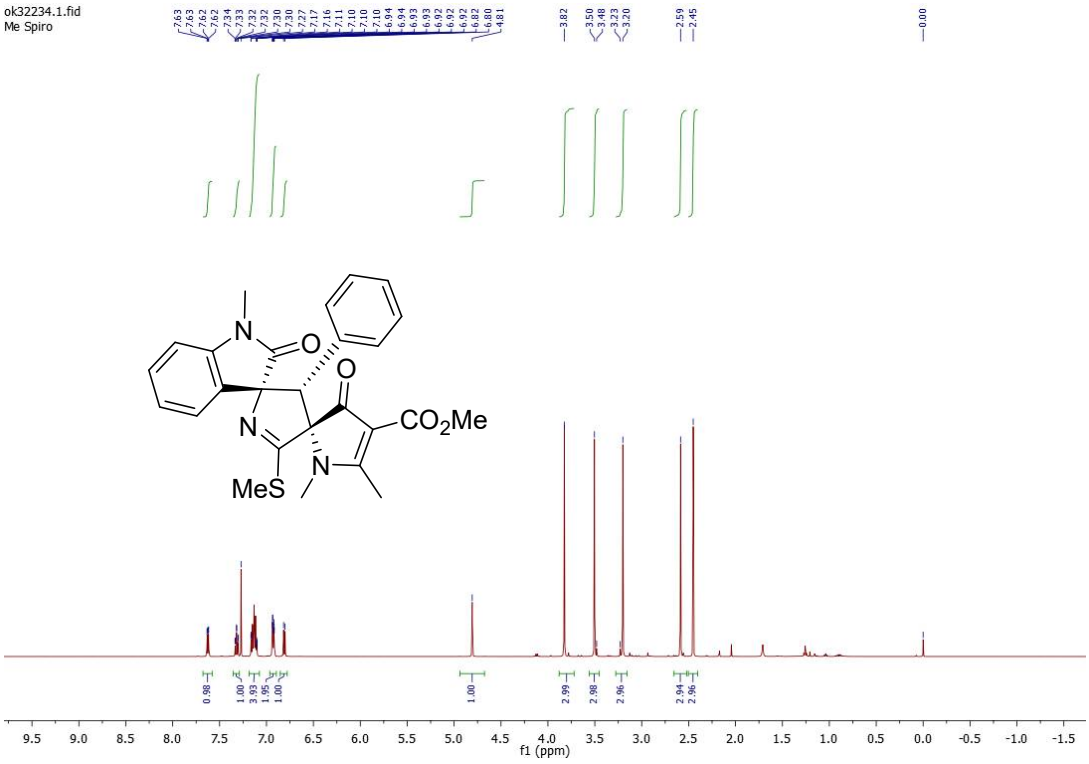


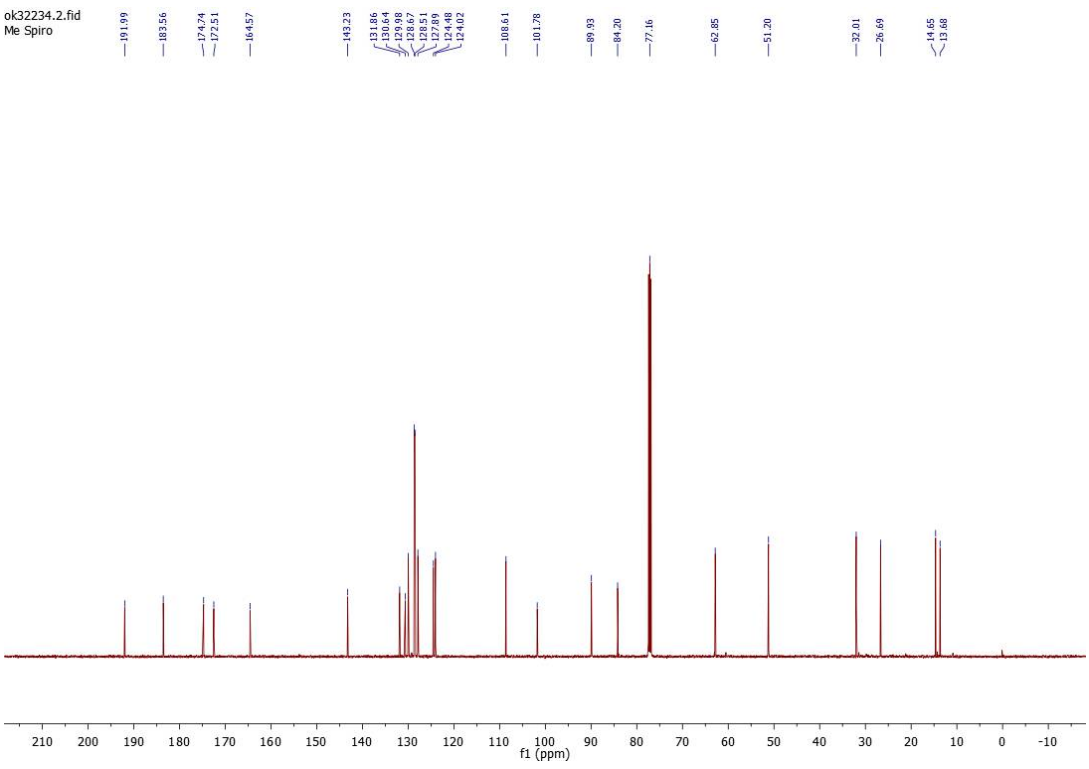
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(furan-2-yl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3p)





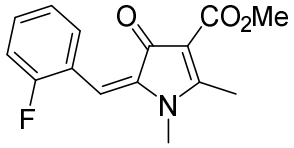
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-5'-(methylthio)-2,3''-dioxo-3'-phenyl-1'',3''-dihydro-3'*H*-dispiro[indoline-3,2'-pyrrole-4',2''-pyrrole]-4''-carboxylate (4)





4. Copies of HRMS reports of products

Methyl (*E*)-5-(2-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1c)



Qualitative Compound Report

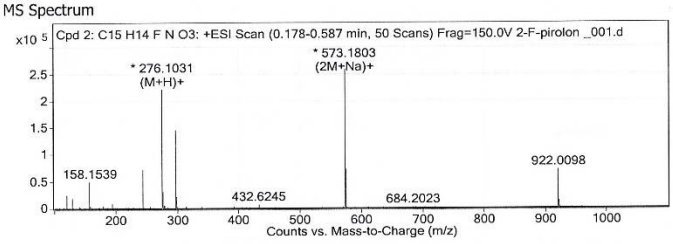
Data File	2-F-pirolon _001.d	**Sample Name**	2-F-pirolon
Sample Type	Sample	**Position**	Vial 11
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	9/8/2020 9:15:13 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C15 H14 F N O3	573.1801	0.243	Find by Molecular Feature	275.0956

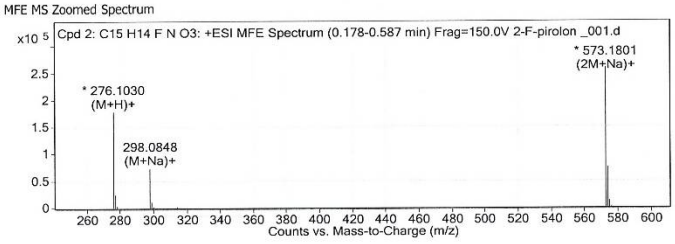
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
276.103	276.103	0.1	C15 H15 F N O3	(M+H)+	✓
276.103	276.1017	-1.3	C13 H13 F N4 O2	(M+H)+	

MS Spectrum

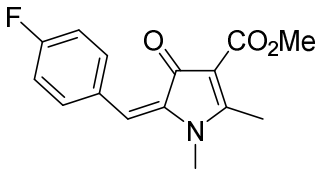


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (*E*)-5-(4-fluorobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1f)



4-F pivalon

Qualitative Compound Report

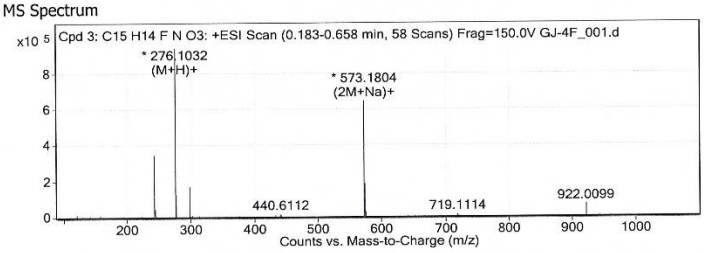
Data File	GJ-4F_001.d	**Sample Name**	GJ-4F
Sample Type	Sample	**Position**	Vial 25
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	12/11/2019 3:18:13 PM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C15 H14 F N O3	276.1033	0.246	Find by Molecular Feature	275.0956

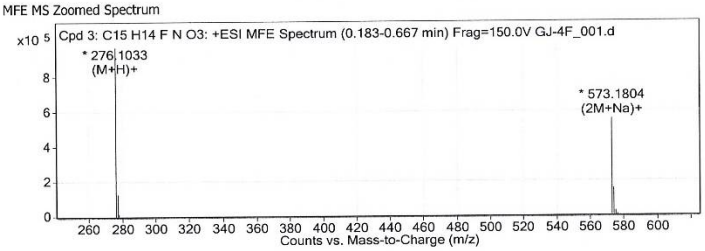
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
276.1033	276.103	-0.2	C15 H15 F N O3	(M+H)+	✓

MS Spectrum

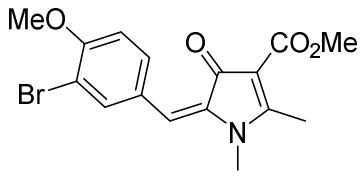


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (*E*)-5-(3-bromo-4-methoxybenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1g)



Qualitative Compound Report

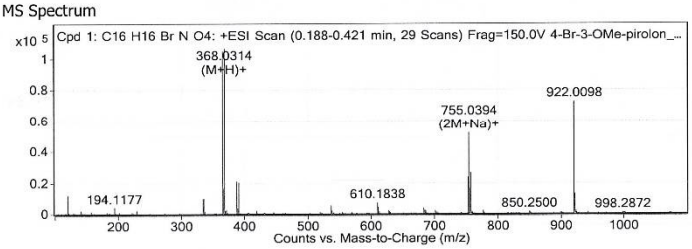
Data File	4-Br-3-OMe-pirolon_001.d	**Sample Name**	4-Br-3-OMe-pirolon
Sample Type	Sample	**Position**	Vial 54
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	9/2/2020 1:40:56 PM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C16 H16 Br N O4	366.0331	0.244	Find by Molecular Feature	365.0256

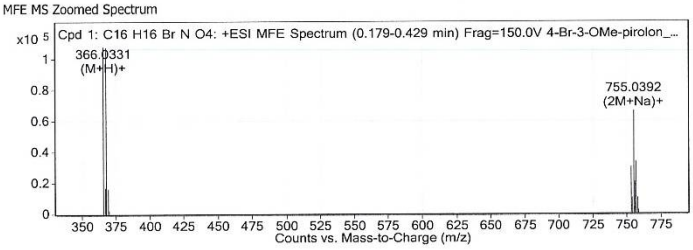
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
366.0331	366.0333	0.2	C11 H16 Br F N4 O4	(M+H)+	
366.0331	366.0335	0.4	C16 H17 Br N O4	(M+H)+	✓
366.0331	366.0322	-0.9	C14 H15 Br N4 O3	(M+H)+	
366.0331	366.032	-1.1	C10 H20 Br F O8	(M+H)+	
366.0331	366.032	-1.1	C9 H14 Br F N7 O3	(M+H)+	
366.0331	366.0347	1.6	C13 H18 Br F N O5	(M+H)+	
366.0331	366.0347	1.6	C12 H12 Br F N8	(M+H)+	
366.0331	366.0349	1.8	C17 H13 Br N5	(M+H)+	

MS Spectrum

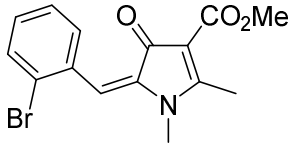


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (*E*)-5-(2-bromobenzylidene)-1,2-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1i)



Qualitative Compound Report

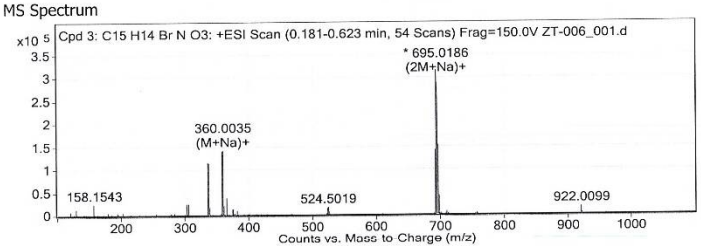
Data File	ZT-006_001.d	**Sample Name**	ZT-006
Sample Type	Sample	**Position**	Vial 51
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/4/2020 9:39:27 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C15 H14 Br N O3	693.0206	0.243	Find by Molecular Feature	335.0161

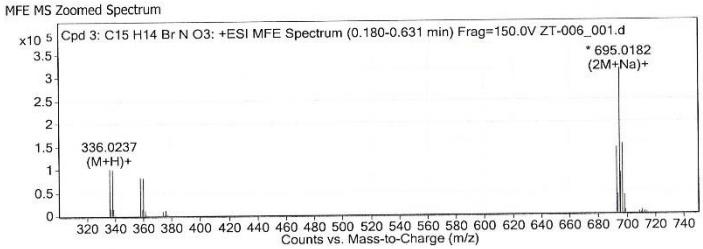
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
336.0237	336.023	-0.7	C15 H15 Br N O3	(M+H)+	✓
373.9796	373.9815	1.9	C18 H12 Br K N2	(M+K)+	

MS Spectrum

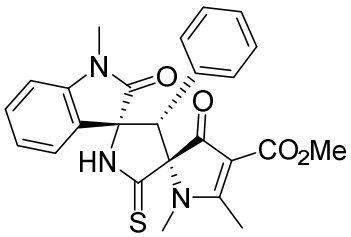


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-phenyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3a)



Qualitative Compound Report

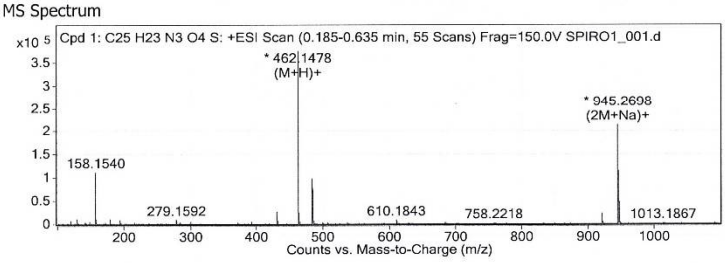
Data File	SPIRO1_001.d	**Sample Name**	SPIRO1
Sample Type	Sample	**Position**	Vial 2
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	6/30/2020 10:17:28 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C25 H23 N3 O4 S	462.1476	0.243	Find by Molecular Feature	461.1402

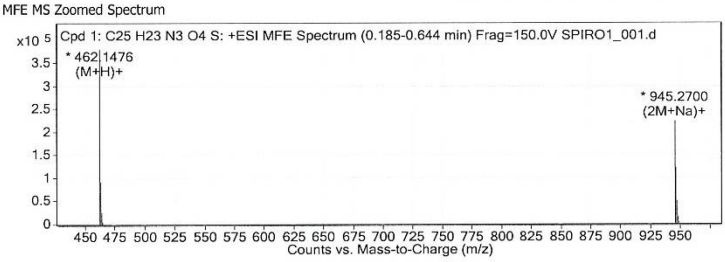
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
462.1476	462.1475	0	C31 H18 N4 O	(M+H)+	
462.1476	462.148	0.5	C18 H26 N2 O12	(M+H)+	
462.1476	462.148	0.5	C17 H20 N9 O7	(M+H)+	
462.1476	462.1482	0.7	C25 H24 N3 O4 S	(M+H)+	✓
462.1476	462.1469	-0.7	C23 H22 N6 O3 S	(M+H)+	
462.1476	462.1467	-0.9	C16 H24 N5 O11	(M+H)+	
462.1476	462.1467	-0.9	C15 H18 N12 O6	(M+H)+	
462.1476	462.1494	1.8	C19 H22 N6 O8	(M+H)+	
462.1476	462.1494	1.8	C18 H16 N13 O3	(M+H)+	
462.1476	462.1455	-2	C22 H26 N2 O7 S	(M+H)+	

MS Spectrum

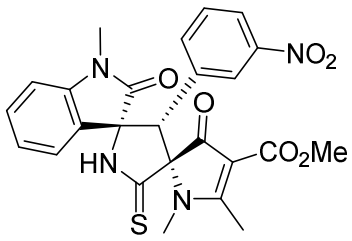


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3b)



Qualitative Compound Report

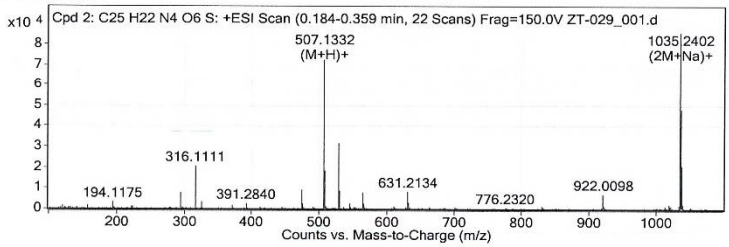
Data File	ZT-029_001.d	**Sample Name**	ZT-029
Sample Type	Sample	**Position**	Vial 43
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/8/2018 3:09:26 PM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C25 H22 N4 O6 S	1035.2385	0.232	Find by Molecular Feature	506.1252

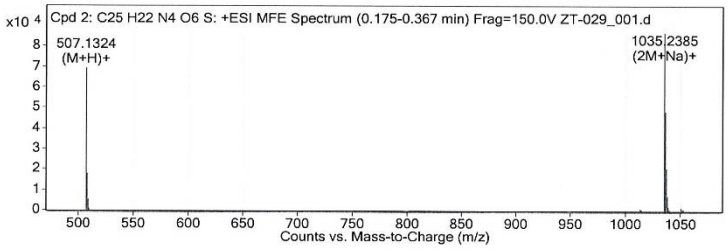
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
507.1324	507.1326	0.2	C16 H21 N13 O3 S2	(M+H)+	
507.1324	507.1326	0.2	C17 H27 N6 O8 S2	(M+H)+	
507.1324	507.1319	-0.5	C23 H21 N7 O5 S	(M+H)+	
507.1324	507.1319	-0.5	C24 H27 O10 S	(M+H)+	
507.1324	507.1319	-0.5	C22 H15 N14 S	(M+H)+	
507.1324	507.1333	0.9	C25 H23 N4 O6 S	(M+H)+	✓
507.1324	507.1333	0.9	C24 H17 N11 O S	(M+H)+	
507.1324	507.134	1.6	C18 H23 N10 O4 S2	(M+H)+	
507.1324	507.1306	-1.8	C22 H25 N3 O9 S	(M+H)+	
507.1324	507.1306	-1.8	C21 H19 N10 O4 S	(M+H)+	

MS Spectrum

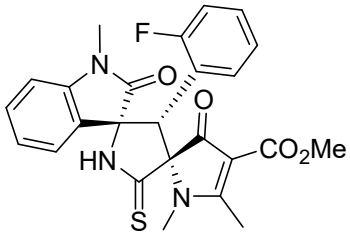


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-3'-(2-fluorophenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3c)



Qualitative Compound Report

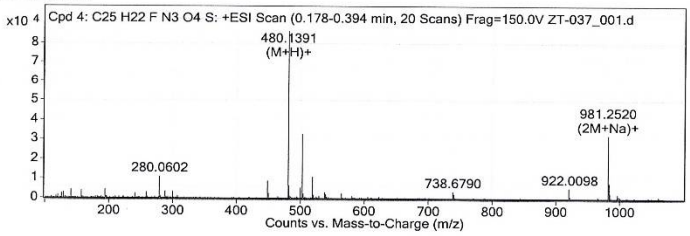
Data File	ZT-037_001.d	**Sample Name**	ZT-037
Sample Type	Sample	**Position**	Vial 15
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	9/19/2018 11:09:47 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C25 H22 F N3 O4 S	480.1387	0.236	Find by Molecular Feature	479.1317

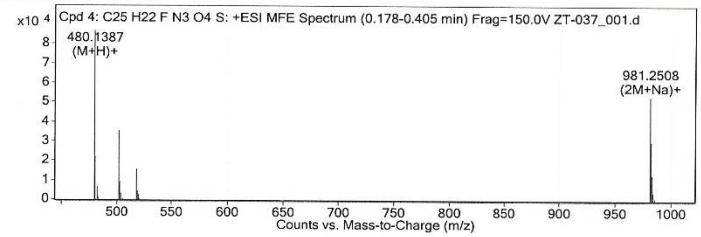
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
480.1387	480.1388	0.1	C25 H23 F N3 O4 S	(M+H)+	✓
480.1387	480.139	0.3	C30 H24 O4 S	(M+H)+	
480.1387	480.1395	0.8	C15 H20 N12 O5 S	(M+H)+	
480.1387	480.1395	0.8	C16 H26 N5 O10 S	(M+H)+	
480.1387	480.1395	0.8	C18 H23 F N9 O2 S2	(M+H)+	
480.1387	480.1376	-1	C28 H22 N3 O3 S	(M+H)+	
480.1387	480.1397	1	C23 H24 N6 O2 S2	(M+H)+	
480.1387	480.1374	-1.2	C23 H21 F N6 O3 S	(M+H)+	
480.1387	480.1401	1.4	C27 H25 F O5 S	(M+H)+	
480.1387	480.1401	1.4	C26 H19 F N7 S	(M+H)+	

MS Spectrum

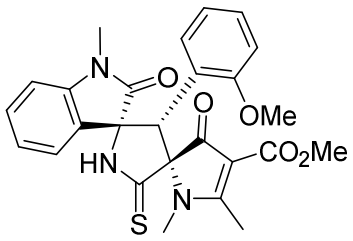


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-3'-(2-methoxyphenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3d)



Qualitative Compound Report

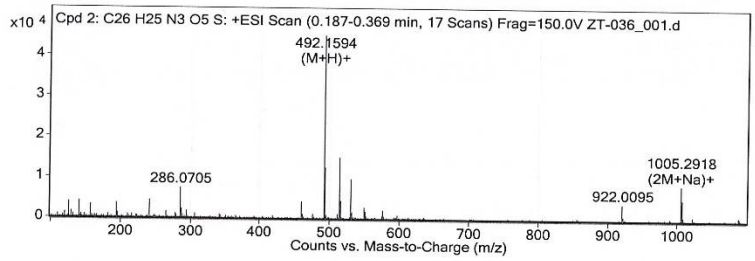
Data File	ZT-036_001.d	**Sample Name**	ZT-036
Sample Type	Sample	**Position**	Vial 13
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	9/19/2018 10:28:23 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C26 H25 N3 O5 S	492.1587	0.232	Find by Molecular Feature	491.1512

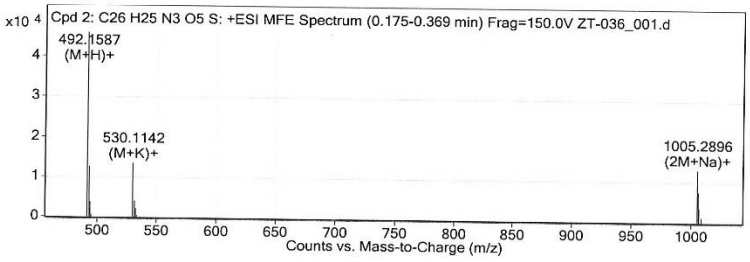
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
492.1587	492.1588	0	C26 H26 N3 O5 S	(M+H)+	✓
492.1587	492.1588	0	C25 H20 N10 S	(M+H)+	
492.1587	492.1581	-0.6	C17 H24 N12 O2 S2	(M+H)+	
492.1587	492.1581	-0.6	C18 H30 N5 O7 S2	(M+H)+	
492.1587	492.1595	0.7	C19 H26 N9 O3 S2	(M+H)+	
492.1587	492.1595	0.7	C20 H32 N2 O8 S2	(M+H)+	
492.1587	492.1576	-1.1	C32 H28 O S2	(M+H)+	
492.1587	492.1574	-1.3	C24 H24 N6 O4 S	(M+H)+	
492.1587	492.1601	1.4	C27 H22 N7 O S	(M+H)+	
492.1587	492.1601	1.4	C28 H28 O6 S	(M+H)+	

MS Spectrum

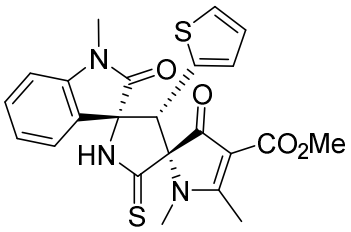


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-2,3''-dioxo-3'-(thiophen-2-yl)-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3e)



Qualitative Compound Report

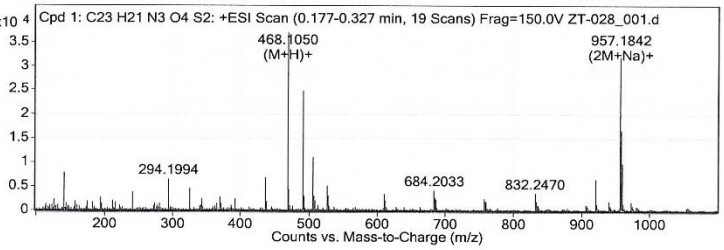
Data File	ZT-028_001.d	**Sample Name**	ZT-028
Sample Type	Sample	**Position**	Vial 42
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/8/2018 11:38:32 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C23 H21 N3 O4 S2	957.1812	0.227	Find by Molecular Feature	467.0973

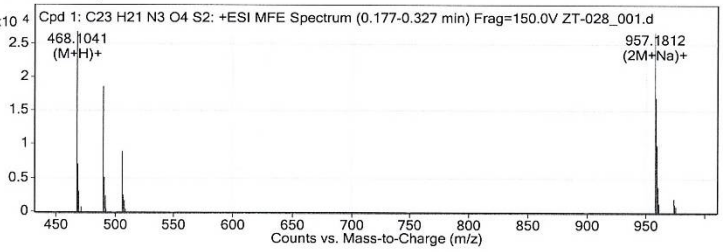
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
468.1041	468.1039	-0.2	C29 H16 N4 O S	(M+H)+	
468.1041	468.1044	0.3	C15 H18 N9 O7 S	(M+H)+	
468.1041	468.1044	0.3	C16 H24 N2 O12 S	(M+H)+	
468.1041	468.1046	0.5	C23 H22 N3 O4 S2	(M+H)+	✓
468.1041	468.1033	-0.8	C21 H20 N6 O3 S2	(M+H)+	
468.1041	468.1026	-1.5	C28 H20 O5 S	(M+H)+	
468.1041	468.1058	1.7	C16 H14 N13 O3 S	(M+H)+	
468.1041	468.1058	1.7	C17 H20 N6 O8 S	(M+H)+	
468.1041	468.106	1.8	C24 H18 N7 S2	(M+H)+	
468.1041	468.106	1.9	C25 H24 O5 S2	(M+H)+	

MS Spectrum

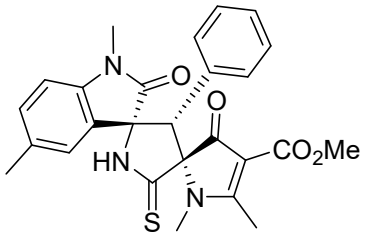


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-2,3''-dioxo-3'-phenyl-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3f)



Qualitative Compound Report

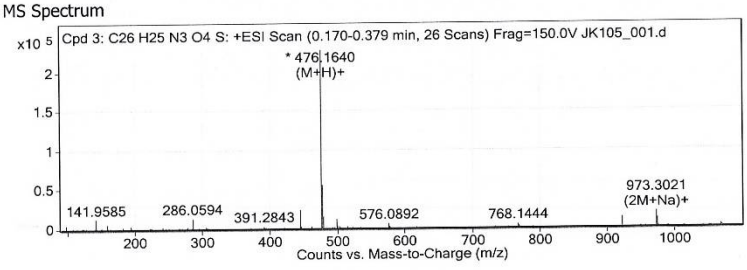
Data File	JK105_001.d	**Sample Name**	JK105
Sample Type	Sample	**Position**	Vial 3
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	5/24/2018 10:17:58 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C26 H25 N3 O4 S	476.1632	0.229	Find by Molecular Feature	475.157

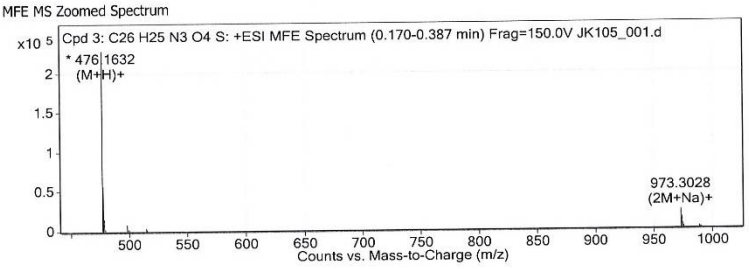
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
476.1632	476.1637	0.4	C19 H28 N2 O12	(M+H)+	
476.1632	476.1637	0.4	C18 H22 N9 O7	(M+H)+	
476.1632	476.1637	0.4	C17 H16 N16 O2	(M+H)+	
476.1632	476.1639	0.6	C26 H26 N3 O4 S	(M+H)+	✓
476.1632	476.1625	-0.7	C24 H24 N6 O3 S	(M+H)+	
476.1632	476.1623	-0.9	C17 H26 N5 O11	(M+H)+	
476.1632	476.1623	-0.9	C16 H20 N12 O6	(M+H)+	
476.1632	476.165	1.8	C20 H24 N6 O8	(M+H)+	
476.1632	476.1652	2	C27 H22 N7 S	(M+H)+	
476.1632	476.1652	2	C28 H28 O5 S	(M+H)+	

MS Spectrum

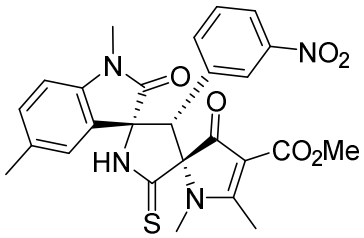


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3g)



Qualitative Compound Report

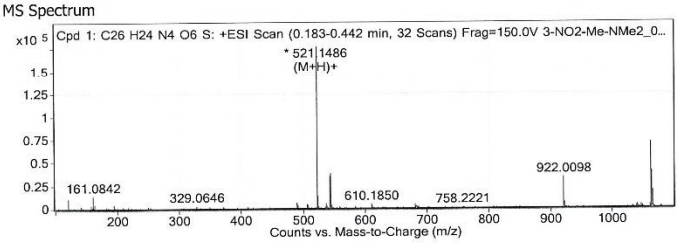
Data File	3-NO2-Me-NMe2_001.d	**Sample Name**	3-NO2-Me-NMe2
Sample Type	Sample	**Position**	Vial 41
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/13/2020 10:17:06 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C26 H24 N4 O6 S	521.1482	0.245	Find by Molecular Feature	520.1408

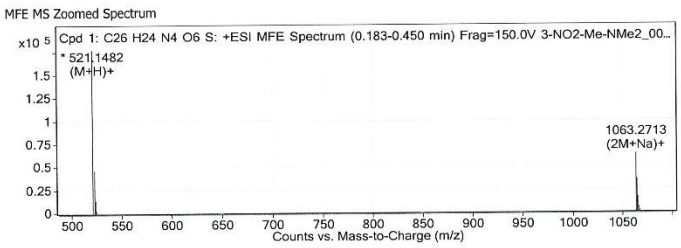
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
521.1482	521.1476	-0.6	C25 H29 O10 S	(M+H)+	
521.1482	521.1476	-0.6	C24 H23 N7 O5 S	(M+H)+	
521.1482	521.1476	-0.6	C23 H17 N14 S	(M+H)+	
521.1482	521.1489	0.7	C25 H19 N11 O S	(M+H)+	
521.1482	521.1489	0.8	C26 H25 N4 O6 S	(M+H)+	✓
521.1482	521.1463	-1.9	C23 H27 N3 O9 S	(M+H)+	
521.1482	521.1462	-1.9	C22 H21 N10 O4 S	(M+H)+	
521.1482	521.1503	2.1	C28 H27 N O7 S	(M+H)+	
521.1482	521.1503	2.1	C27 H21 N8 O2 S	(M+H)+	
521.1482	521.1508	2.6	C14 H29 N6 O13 S	(M+H)+	

MS Spectrum

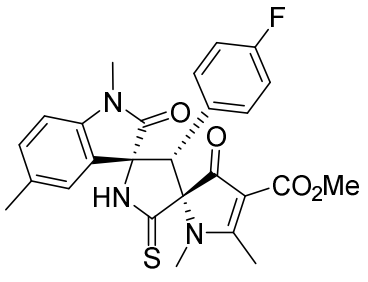


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-3'-(4-fluorophenyl)-1,1'',5,5''-tetramethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3h)



Qualitative Compound Report

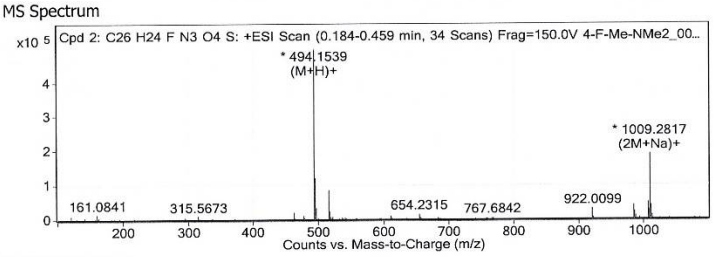
Data File	4-F-Me-NMe2_001.d	**Sample Name**	4-F-Me-NMe2
Sample Type	Sample	**Position**	Vial 42
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/13/2020 10:19:56 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C26 H24 F N3 O4 S	494.1539	0.246	Find by Molecular Feature	493.1469

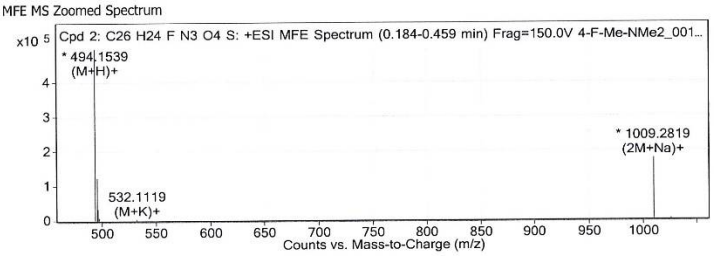
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
494.1539	494.1544	0.5	C26 H25 F N3 O4 S	(M+H)+	✓
494.1539	494.1531	-0.8	C24 H23 F N6 O3 S	(M+H)+	
532.1119	532.113	1.1	C29 H22 F K N4 O S	(M+K)+	
494.1539	494.1558	1.8	C28 H27 F O5 S	(M+H)+	
494.1539	494.1558	1.8	C27 H21 F N7 S	(M+H)+	
494.1539	494.1518	-2.2	C23 H27 F N2 O7 S	(M+H)+	
494.1539	494.1563	2.3	C13 H23 F N12 O6 S	(M+H)+	
494.1539	494.1563	2.3	C14 H29 F N5 O11 S	(M+H)+	
532.1119	532.1143	2.5	C31 H24 F K N O2 S	(M+K)+	

MS Spectrum

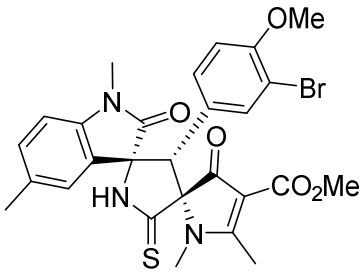


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-3'-(4-bromo-3-methoxyphenyl)-1,1'',5,5''-tetramethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3i)



Qualitative Compound Report

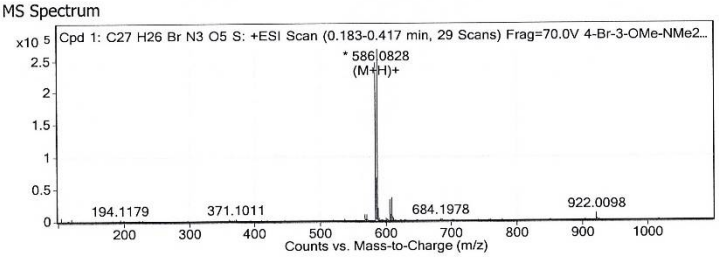
Data File	4-Br-3-OMe-NMe2_001.d	**Sample Name**	4-Br-3-OMe-NMe2
Sample Type	Sample	**Position**	Vial 62
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/19/2020 11:04:32 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C27 H26 Br N3 O5 S	584.085	0.245	Find by Molecular Feature	583.0775

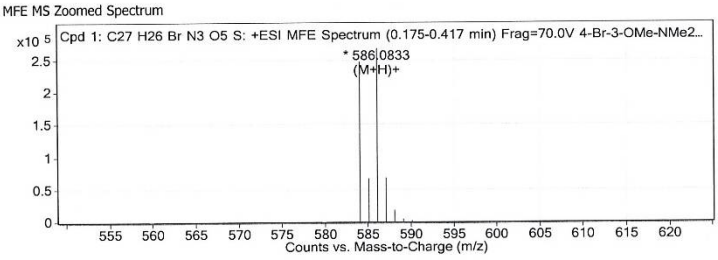
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
584.085	584.0849	-0.1	C27 H27 Br N3 O5 S	(M+H)+	✓
584.085	584.0849	-0.1	C26 H21 Br N10 S	(M+H)+	
584.085	584.0863	1.3	C28 H23 Br N7 O S	(M+H)+	
584.085	584.0863	1.3	C29 H29 Br O6 S	(M+H)+	
584.085	584.0836	-1.4	C25 H25 Br N6 O4 S	(M+H)+	
584.085	584.0868	1.8	C14 H25 Br N12 O7 S	(M+H)+	
584.085	584.0868	1.8	C15 H31 Br N5 O12 S	(M+H)+	
584.085	584.0823	-2.7	C24 H29 Br N2 O8 S	(M+H)+	
584.085	584.0822	-2.7	C23 H23 Br N9 O3 S	(M+H)+	
584.085	584.0881	3.1	C15 H21 Br N16 O3 S	(M+H)+	

MS Spectrum

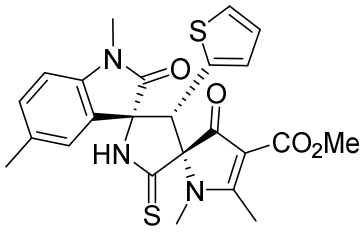


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*R*,3'*S*,4'*R*)-1,1'',5,5''-tetramethyl-2,3''-dioxo-3'-(thiophen-2-yl)-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3j)



Qualitative Compound Report

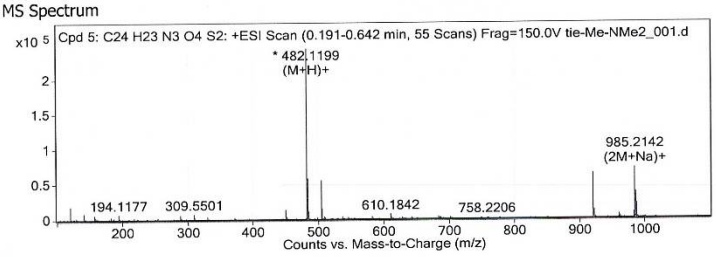
Data File	tie-Me-NMe2_001.d	**Sample Name**	tie-Me-NMe2
Sample Type	Sample	**Position**	Vial 43
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/13/2020 10:23:38 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 5: C24 H23 N3 O4 S2	482.1195	0.248	Find by Molecular Feature	481.1127

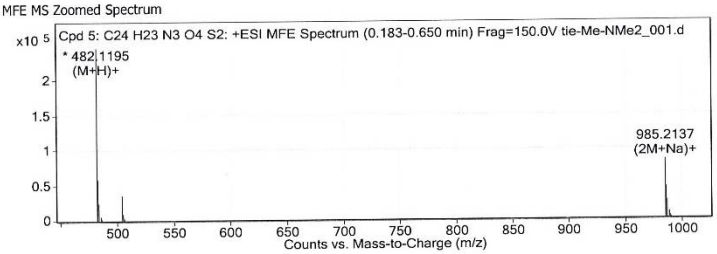
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
482.1195	482.1189	-0.5	C22 H22 N6 O3 S2	(M+H)+	
482.1195	482.1201	0.6	C17 H26 N2 O12 S	(M+H)+	
482.1195	482.1201	0.6	C16 H20 N9 O7 S	(M+H)+	
482.1195	482.1188	-0.7	C15 H24 N5 O11 S	(M+H)+	
482.1195	482.1187	-0.7	C14 H18 N12 O6 S	(M+H)+	
482.1195	482.1203	0.8	C24 H24 N3 O4 S2	(M+H)+	✓
482.1195	482.1214	2	C17 H16 N13 O3 S	(M+H)+	
482.1195	482.1214	2	C18 H22 N6 O8 S	(M+H)+	
482.1195	482.1216	2.2	C25 H20 N7 S2	(M+H)+	
482.1195	482.1216	2.2	C26 H26 O5 S2	(M+H)+	

MS Spectrum

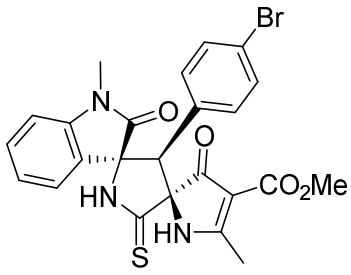


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*S*,3'*R*,4'*S*)-3'-(4-bromophenyl)-1,5''-dimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3k)



Qualitative Compound Report

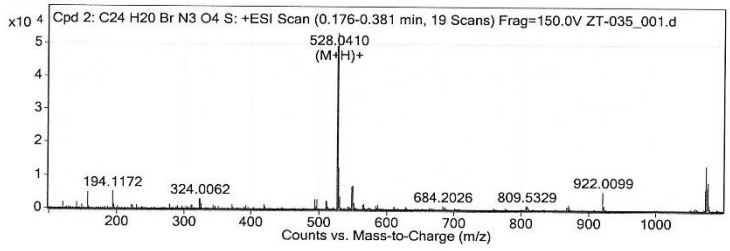
Data File	ZT-035_001.d	**Sample Name**	ZT-035
Sample Type	Sample	**Position**	Vial 11
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	9/19/2018 10:11:13 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C24 H20 Br N3 O4 S	526.0427	0.234	Find by Molecular Feature	525.0353

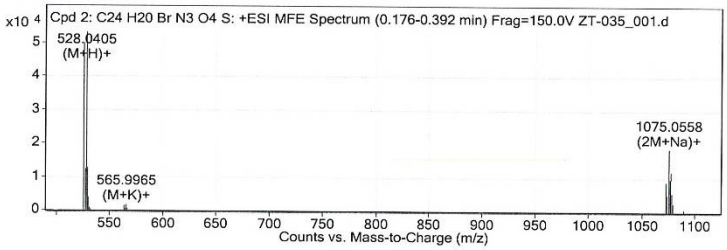
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
526.0427	526.0424	-0.3	C15 H19 Br N12 O S2	(M+H)+	
526.0427	526.0424	-0.3	C16 H25 Br N5 O6 S2	(M+H)+	
526.0427	526.0431	0.4	C24 H21 Br N3 O4 S	(M+H)+	✓
526.0427	526.0419	-0.8	C30 H23 Br S2	(M+H)+	
526.0427	526.0417	-1	C22 H19 Br N6 O3 S	(M+H)+	
526.0427	526.0438	1	C17 H21 Br N9 O2 S2	(M+H)+	
526.0427	526.0438	1	C18 H27 Br N2 O7 S2	(M+H)+	
526.0427	526.0444	1.7	C25 H17 Br N7 S	(M+H)+	
526.0427	526.0444	1.7	C26 H23 Br O5 S	(M+H)+	
526.0427	526.0404	-2.3	C21 H23 Br N2 O7 S	(M+H)+	

MS Spectrum

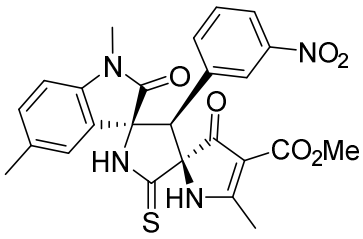


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl (3*S*,3'*R*,4'*S*)-1,5,5''-trimethyl-3'-(3-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (3l)



Qualitative Compound Report

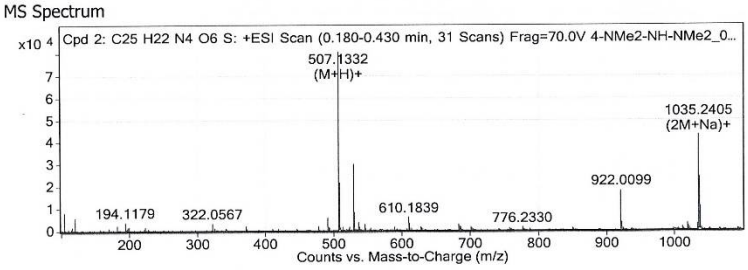
Data File	4-NMe2-NH-NMe2_001.d	**Sample Name**	4-NMe2-NH-NMe2
Sample Type	Sample	**Position**	Vial 63
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/19/2020 11:10:32 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C25 H22 N4 O6 S	507.1329	0.244	Find by Molecular Feature	506.125

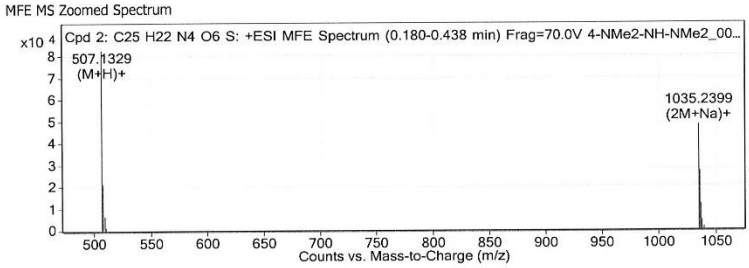
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
507.1329	507.1333	0.4	C25 H23 N4 O6 S	(M+H)+	✓
507.1329	507.1333	0.4	C24 H17 N11 O S	(M+H)+	
507.1329	507.1319	-0.9	C24 H27 O10 S	(M+H)+	
507.1329	507.1319	-0.9	C23 H21 N7 O5 S	(M+H)+	
507.1329	507.1319	-0.9	C22 H15 N14 S	(M+H)+	
507.1329	507.1346	1.8	C27 H25 N O7 S	(M+H)+	
507.1329	507.1346	1.8	C26 H19 N8 O2 S	(M+H)+	
507.1329	507.1306	-2.3	C22 H25 N3 O9 S	(M+H)+	

MS Spectrum

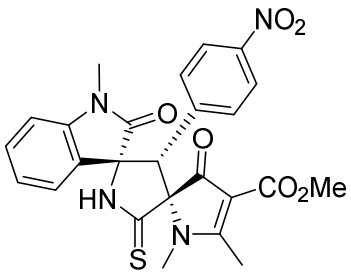


MFE MS Zoomed Spectrum



--- End Of Report ---

Methyl *rel*-(3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-3'-(4-nitrophenyl)-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3m)



Qualitative Compound Report

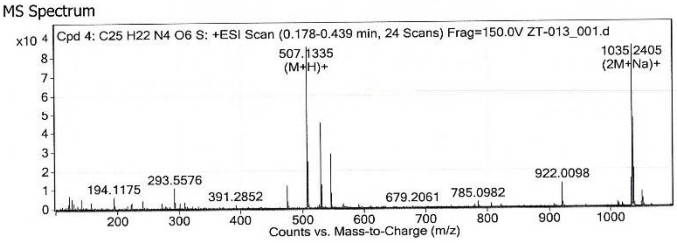
Data File	ZT-013_001.d	**Sample Name**	ZT-013
Sample Type	Sample	**Position**	Vial 7
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	5/8/2018 2:18:36 PM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C25 H22 N4 O6 S	1035.239	0.234	Find by Molecular Feature	506.1258

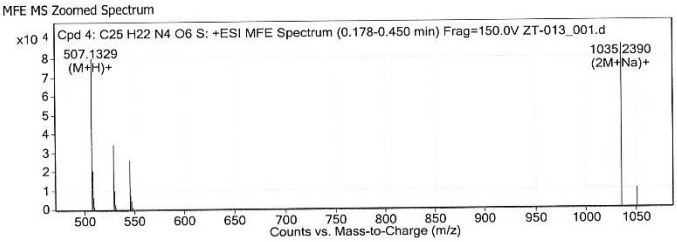
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
507.1329	507.1333	0.4	C25 H23 N4 O6 S	(M+H)+	✓
507.1329	507.1333	0.4	C24 H17 N11 O S	(M+H)+	
507.1329	507.1319	-1	C24 H27 O10 S	(M+H)+	
507.1329	507.1319	-1	C23 H21 N7 O5 S	(M+H)+	
507.1329	507.1319	-1	C22 H15 N14 S	(M+H)+	
507.1329	507.1346	1.7	C27 H25 N O7 S	(M+H)+	
507.1329	507.1346	1.7	C26 H19 N8 O2 S	(M+H)+	
1051.2117	1051.2098	-1.9	C42 H36 K N20 O8 S2	(2M+K)+	
507.1329	507.1306	-2.3	C22 H25 N3 O9 S	(M+H)+	

MS Spectrum



MFE MS Zoomed Spectrum



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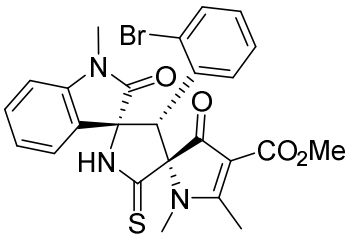
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(2-bromophenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3n)



Qualitative Compound Report

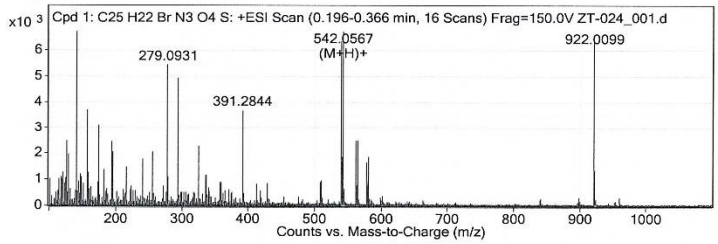
Data File	ZT-024_001.d	**Sample Name**	ZT-024
Sample Type	Sample	**Position**	Vial 24
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	7/17/2018 10:51:54 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C25 H22 Br N3 O4 S	540.0588	0.233	Find by Molecular Feature	539.0513

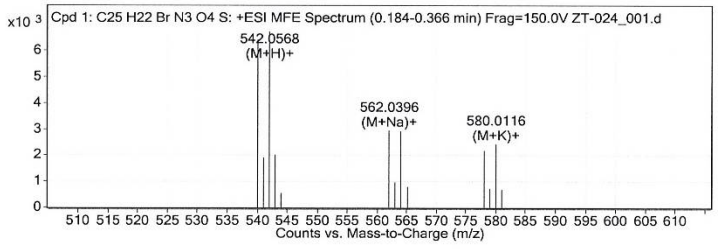
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
540.0588	540.0587	-0.1	C25 H23 Br N3 O4 S	(M+H)+	✓
540.0588	540.0601	1.3	C26 H19 Br N7 S	(M+H)+	
540.0588	540.0601	1.3	C27 H25 Br O5 S	(M+H)+	
540.0588	540.0574	-1.4	C23 H21 Br N6 O3 S	(M+H)+	
562.0396	562.038	-1.6	C21 H18 Br N9 Na O2 S	(M+Na)+	
540.0588	540.0606	1.8	C13 H27 Br N5 O11 S	(M+H)+	
540.0588	540.056	-2.8	C22 H25 Br N2 O7 S	(M+H)+	
562.0396	562.0366	-3	C20 H22 Br N5 Na O6 S	(M+Na)+	

MS Spectrum



MFE MS Zoomed Spectrum



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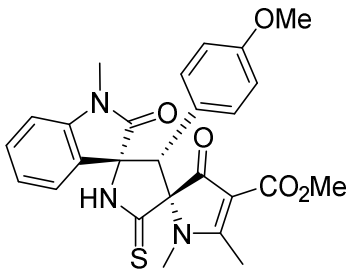
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(4-methoxyphenyl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3o)



Qualitative Compound Report

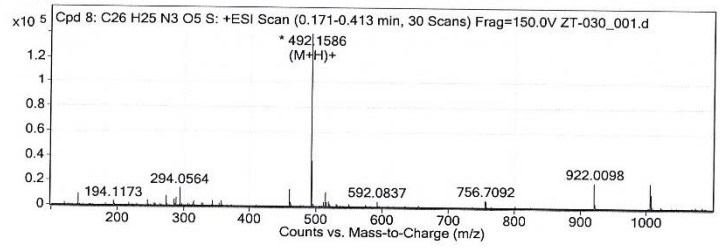
Data File	ZT-030_001.d	**Sample Name**	ZT-030
Sample Type	Sample	**Position**	Vial 63
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	9/7/2018 11:05:31 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 8: C26 H25 N3 O5 S	492.1584	0.235	Find by Molecular Feature	491.1511

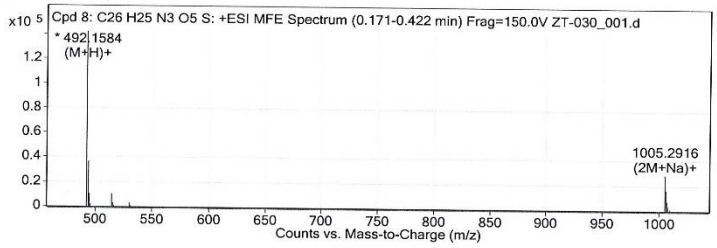
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
492.1584	492.1588	0.3	C26 H26 N3 O5 S	(M+H)+	✓
492.1584	492.1588	0.3	C25 H20 N10 S	(M+H)+	
492.1584	492.1581	-0.3	C17 H24 N12 O2 S2	(M+H)+	
492.1584	492.1576	-0.8	C32 H28 O S2	(M+H)+	
492.1584	492.1574	-1	C24 H24 N6 O4 S	(M+H)+	
492.1584	492.1595	1	C19 H26 N9 O3 S2	(M+H)+	
492.1584	492.1595	1	C20 H32 N2 O8 S2	(M+H)+	
492.1584	492.1601	1.7	C27 H22 N7 O S	(M+H)+	
492.1584	492.1601	1.7	C28 H28 O6 S	(M+H)+	
492.1584	492.1561	-2.3	C23 H28 N2 O8 S	(M+H)+	

MS Spectrum



MFE MS Zoomed Spectrum



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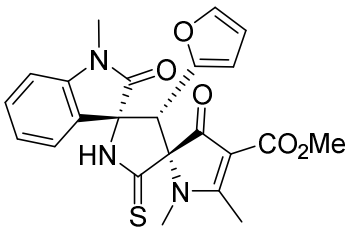
Methyl *rel*-(3*R*,3'*S*,4'*R*)-3'-(furan-2-yl)-1,1'',5''-trimethyl-2,3''-dioxo-5'-thioxo-1'',3''-dihydrodispiro[indoline-3,2'-pyrrolidine-4',2''-pyrrole]-4''-carboxylate (*rac*-3p)



Qualitative Compound Report

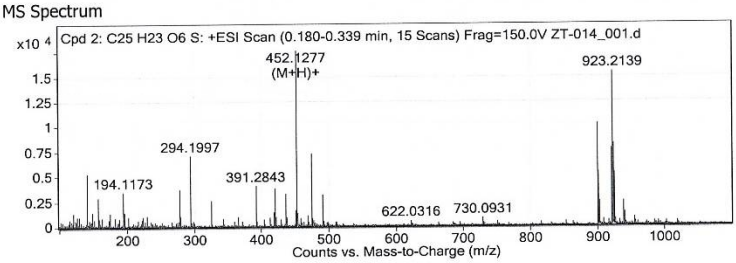
Data File	ZT-014_001.d	**Sample Name**	ZT-014
Sample Type	Sample	**Position**	Vial 32
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	7/18/2018 10:47:23 AM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C25 H23 O6 S	452.1281	0.232	Find by Molecular Feature	451.121

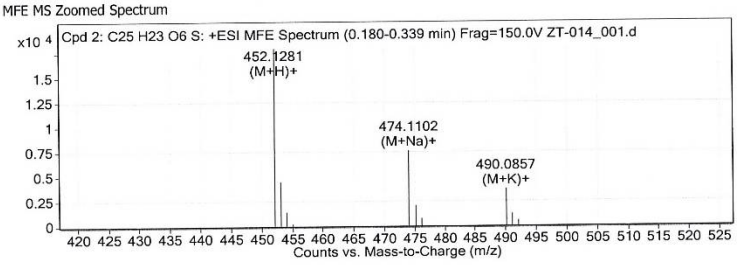
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
452.1281	452.1275	-0.6	C23 H22 N3 O5 S	(M+H)+	
452.1281	452.1275	-0.6	C22 H16 N10 S	(M+H)+	
452.1281	452.1288	0.7	C25 H24 O6 S	(M+H)+	✓
452.1281	452.1288	0.7	C24 H18 N7 O S	(M+H)+	
490.0857	490.0874	1.7	C28 H21 K N O3 S	(M+K)+	
452.1281	452.1261	-1.9	C21 H20 N6 O4 S	(M+H)+	
452.1281	452.1301	2.1	C26 H20 N4 O2 S	(M+H)+	
490.0857	490.0879	2.2	C13 H17 K N13 O4 S	(M+K)+	
474.1102	474.1126	2.4	C12 H21 N9 Na O8 S	(M+Na)+	
474.1102	474.1126	2.4	C13 H27 N2 Na O13 S	(M+Na)+	

MS Spectrum



MFE MS Zoomed Spectrum



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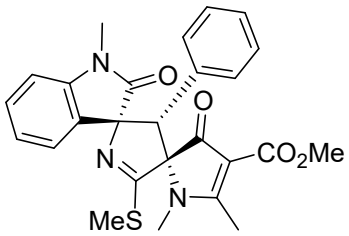
Methyl (3*R*,3'*S*,4'*R*)-1,1'',5''-trimethyl-5'-(methylthio)-2,3''-dioxo-3'-phenyl-1'',3''-dihydro-3'*H*-dispiro[indoline-3,2'-pyrrole-4',2''-pyrrole]-4''-carboxylate (4)



Qualitative Compound Report

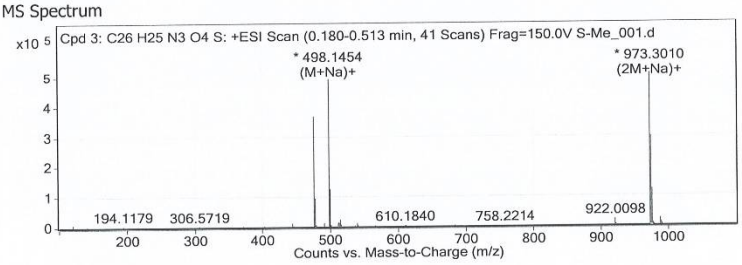
Data File	S-Me_001.d	**Sample Name**	S-Me
Sample Type	Sample	**Position**	Vial 58
Instrument Name	US10310002	**User Name**	TOF-PC\admin
Acq Method	Bypass.m	**Acquired Time**	8/4/2020 1:33:05 PM
IRM Calibration Status	Success	**DA Method**	Damijana.m
Comment			

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C26 H25 N3 O4 S	973.3009	0.244	Find by Molecular Feature	475.1571

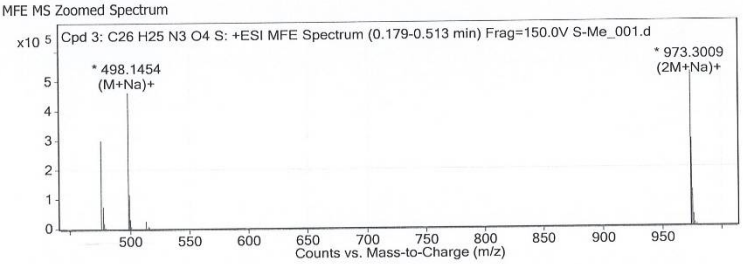
Compound Identification Results

Ion Mass	Calc Ion Mass	Difference	IonFormula	IonSpecies	Best
476.1636	476.1637	0.1	C18 H22 N9 O7	(M+H)+	
476.1636	476.1637	0.1	C19 H28 N2 O12	(M+H)+	
476.1636	476.1637	0.1	C17 H16 N16 O2	(M+H)+	
476.1636	476.1639	0.3	C26 H26 N3 O4 S	(M+H)+	✓
476.1636	476.1625	-1.1	C24 H24 N6 O3 S	(M+H)+	
476.1636	476.1623	-1.2	C17 H26 N5 O11	(M+H)+	
476.1636	476.165	1.4	C19 H18 N13 O3	(M+H)+	
476.1636	476.165	1.5	C20 H24 N6 O8	(M+H)+	
476.1636	476.1652	1.6	C28 H28 O5 S	(M+H)+	
476.1636	476.1652	1.6	C27 H22 N7 S	(M+H)+	

MS Spectrum



MFE MS Zoomed Spectrum



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5. X-Ray crystallography

Table S4. Crystal data and structure refinement for **3b**.

Empirical formula	$C_{24}H_{22}N_4O_6S$
Formula weight	494.52
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å^3]	17.6024(6)
b [Å^3]	18.0462(8)
c [Å^3]	18.1012(5)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	5750.0(4)
Z	4
ρ_{calc} [g/cm^3]	1.446
μ [mm^{-1}]	0.439
F(000)	2576.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
Reflections collected	19672
Independent reflections	13912
R_{int}	0.0252
Data/restraints/parameters	13912/0/729
GOF	1.030
R_1, wR_2 [I>=2σ (I)]	0.0490, 0.1048
R_1, wR_2 (all data)	0.0728, 0.1180
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.41
$(\Delta\rho)_{min}$ [e Å^{-3}]	-0.56
Flack parameter	-0.05(2)

General Information

Single-crystal X-ray diffraction data was collected on Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using monochromated Mo-Kα radiation (λ = 0.71073 Å) at 150 K. The data was processed using CrysAlis PRO [16]. Using Olex2.1.2. [17], the structures were solved by direct methods implemented in SHELXS [18] or SHELXT [19] and refined by a full-matrix least-squares procedure based on F^2 with SHELXT-2014/7 [20]. All nonhydrogen atoms were refined anisotropicallly. Hydrogen atoms were placed in geometrically calculated positions and were refined using a riding model. The drawings and the analysis of bond lengths, angles and intermolecular interactions were carried out using Mercury [21] and Platon [22].

Structural and other crystallographic details on data collection and refinement for compound **3b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC Deposition Number **2032993**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

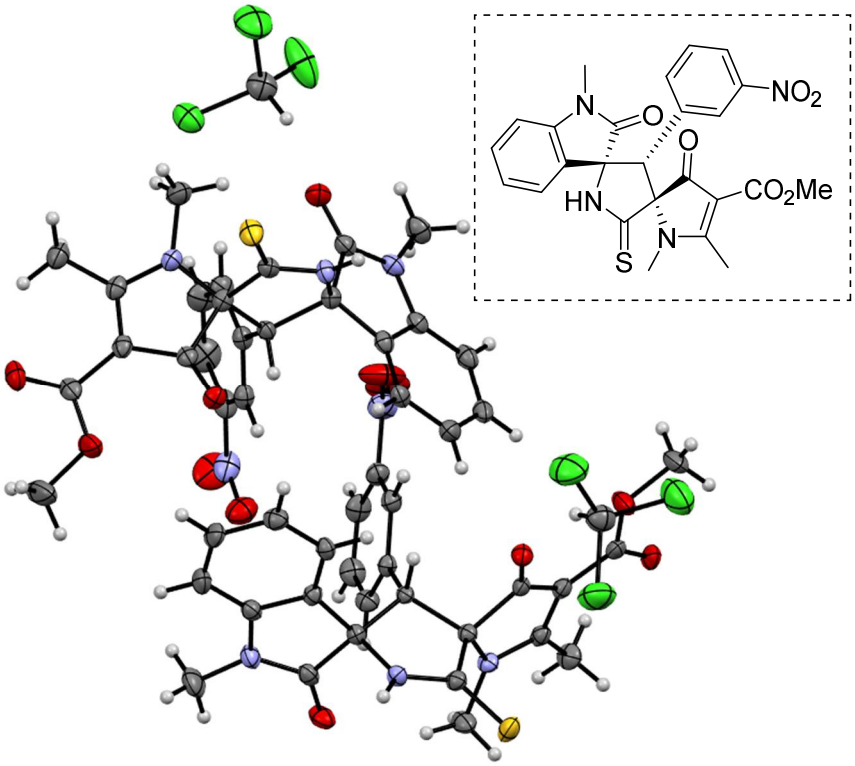

Figure S6. Molecular structure of product **3b**. Thermal ellipsoids are shown at 50% probability. The asymmetric unit contains two molecules of product **3b** and two molecules of chloroform.

6. References

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