Supplementary Information

Box-Copper Catalyzed Asymmetric Inverse-Electron-Demand *oxa*-Hetero-Diels−Alder Reaction for Efficient Synthesis of Spiro Pyranyl-Oxindole Derivatives

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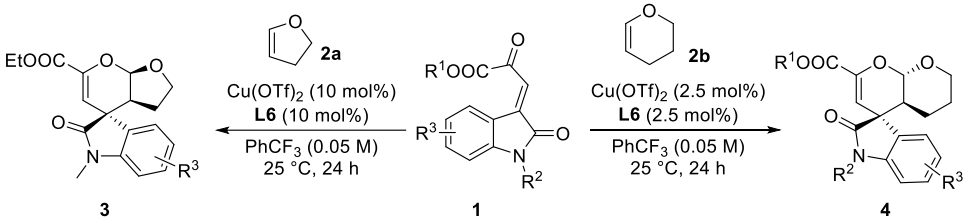
1. General methods

All reactions were carried out under an atmosphere of nitrogen in oven-dried glasswares with magnetic stirring, unless otherwise indicated. All solvents employed in the reactions were distilled from appropriate drying agent prior to use. All other reagents were used as obtained unless otherwise noted. Flash Chromatography was performed with si1ica gel (300–400 mesh) from Yantai Chemical Industry Research Institute, P. R. China. Analyical thin-layer chromatography was performed with 0.2 ± 0.03 mm coated commercial silica gel plates (GF-254, particle size 0.04–0.05 mm). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on Varian Inova (400 MHz and 100 MHz, respectively) spectometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR, δ 77.23 ppm for carbon NMR; DMSO-d_6, δ 2.50 ppm for proton NMR, δ 39.52 ppm for carbon NMR). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (J) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a Varian 1000 FT-IR spectrometer. Mass spectra were carried out using Agilent 6120 Quadrupole LC/MS system with ESI resource. High-resolution mass spectra (HRMS) for all the compounds were determined on Micromass GCT-TOF mass spertrometer with ESI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using CHIRALCEL AD-H and OD-H columns. X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractomrter. Optical rotations are performed on Rudolph Aupol IV and reported as follows: $[\alpha]_D^{25}$ (c in g per 100 mL, solvent).

2. Typical experimental procedure

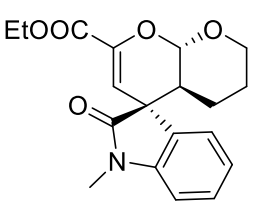


2.1 General procedure for the preparation of 3 and 4

Under N_2 atmosphere, $Cu(OTf)_2$ (0.0025–0.01 mmol, 2.5–10 mol%) and **L6** (0.0025–0.01 mmol, 2.5–10 mol%) were charged into a flame-dried vessel, and anhydrous $PhCF_3$ (2 mL) was added *via* syringe. The resulting mixture was stirred at room temperature for 0.5 h. Then the substrates **1** (0.1 mmol) and **2a** or **2b** (0.2 mmol, 2 equiv) was introduced into the vessel. The reaction mixture was stirred at 25 ℃ until the reaction was detected complete. The solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (3/1) as eluent to give **3** or **4** as solids. All the products described in this manuscript were obtained as a mixture all diastereomers.

The racemic samples described in this work were synthesized according above procedure, which were catalyzed by $Cu(OTf)_2$ with mixed **L6** and *ent*-**L6** as ligands at 0.025 mmol scale. Because equal amount of **L6** and *ent*-**L6** could not be accurately balanced, slight ee values (<10%) were observed in their racemic HPLC spectra.

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4a

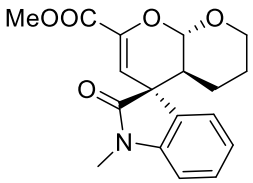


4a

White solid; mp 160–161 ℃; 94% yield (both diastereomers) >99:1 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 12.087, t (minor) = 15.133]; $[\alpha]_D^{25}$ = +148.9 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.6, 1.7 Hz, 1H), 7.16 – 7.02 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 5.60 (d, *J* = 8.9 Hz, 1H), 4.23 (qq, *J* = 7.5, 3.7 Hz, 2H), 4.13 – 4.00 (m, 1H), 3.63 (td, *J* = 12.0, 2.5 Hz,

1H), 3.20 (s, 3H), 1.94 (ddd, *J* = 12.7, 8.9, 4.2 Hz, 1H), 1.65 – 1.38 (m, 2H), 1.36 – 1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 161.2, 144.1, 143.3, 129.2, 128.6, 122.8, 122.7, 108.3, 107.7, 97.5, 66.3, 61.0, 50.5, 41.7, 26.0, 24.7, 21.7, 13.7; IR (KBr) ν_{max}: 2947, 2925, 2871, 1719, 1700, 1649, 1608, 1493, 1471, 1370, 1345, 1303, 1275, 1260, 1223, 1176, 1136, 1080, 1057, 1016, 991, 926, 841, 765, 751, 671, 650 cm^{-1}; HRMS (ESI): m/z = 366.1310 (calcd for $C_{19}H_{21}NO_5$+Na^+ = 366.1312).

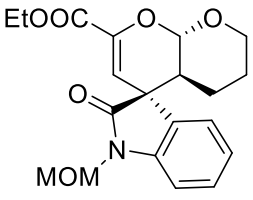
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4b



4b

White solid; mp 140–141 ℃; 76% yield (both diastereomers), 96:4 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 13.307, t (minor) = 18.928]; $[\alpha]_D^{25}$ = +191.7 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.5, 1.8 Hz, 1H), 7.16 – 7.06 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.70 (s, 1H), 5.63 (d, *J* = 8.9 Hz, 1H), 4.09 (dd, *J* = 11.8, 4.6 Hz, 1H), 3.80 (s, 3H), 3.65 (td, *J* = 12.0, 2.5 Hz, 1H), 3.22 (s, 3H), 1.96 (ddd, *J* = 12.8, 8.9, 4.2 Hz, 1H), 1.48 (d, *J* = 13.7 Hz, 2H), 1.37 – 1.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 161.8, 143.9, 143.3, 128.6, 122.8, 121.4, 119.3, 108.6, 107.7, 97.5, 66.3, 51.9, 50.5, 41.7, 26.0, 24.7, 21.7; IR (KBr) ν_{max}: 2932, 2867, 1729, 1709, 1639, 1611, 1494, 1371, 1349, 1304, 1282, 1222, 1198, 1169, 1130, 1087, 1024, 991, 956, 883, 763, 673, 653 cm^{-1}; HRMS (ESI): m/z = 352.1145 (calcd for $C_{18}H_{19}NO_5$+Na^+ = 352.1155).

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-(methoxymethyl)-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4b

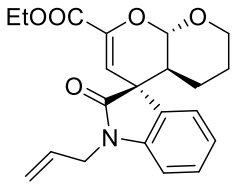


4d

White solid; mp 63–64 ℃; 93% yield (both diastereomers), >99:1 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 10.943, t (minor) = 12.549]; $[\alpha]_D^{25}$ = +185 (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.18 – 7.08 (m, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 5.69 (d, *J* = 1.6 Hz, 1H), 5.59 (dd, *J* = 9.0, 1.6 Hz, 1H), 5.21 – 4.99 (m, 2H), 4.25 (qq, *J* = 7.2, 2.6, 2.1 Hz, 2H), 4.14 – 3.99 (m, 1H),

3.65 (tt, *J* = 12.1, 2.1 Hz, 1H), 3.33 (s, 3H), 2.04 – 1.93 (m, 1H), 1.65 – 1.36 (m, 3H), 1.34 – 1.23 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 161.2, 144.2, 141.6, 128.7, 128.7, 123.4, 122.9, 109.3, 108.2, 97.5, 71.3, 66.4, 61.2, 56.0, 50.9, 41.6, 24.7, 21.9, 13.7; IR (KBr) ν_{max}: 2935, 2864, 1716, 1643, 1610, 1487, 1466, 1342, 1321, 1296, 1276, 1242, 1175, 1113, 1083, 1055, 1017, 991, 914, 754, 663, 618 cm^{-1}; HRMS (ESI): m/z = 396.1404 (calcd for $C_{20}H_{23}NO_6$+Na^+ = 396.1418).

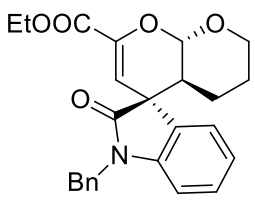
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-allyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4e



4e

White solid; mp 37–38 ℃; 88% yield (both diastereomers), 99:1 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 11.027, t (minor) = 13.066]; $[\alpha]_D^{25}$ = +149.7 (*c* 0.18, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.18 – 7.04 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.82 (ddt, *J* = 16.1, 10.4, 5.3 Hz, 1H), 5.69 (s, 1H), 5.62 (d, *J* = 8.9 Hz, 1H), 5.30 – 5.14 (m, 2H), 4.43 (ddd, *J* = 16.1, 5.1, 2.3 Hz, 1H), 4.25 (qq, *J* = 6.2, 3.6 Hz, 3H), 4.09 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.65 (td, *J* = 12.0, 2.6 Hz, 1H), 1.97 (ddd, *J* = 12.7, 8.9, 4.2 Hz, 1H), 1.60 (tdt, *J* = 12.4, 8.8, 4.5 Hz, 1H), 1.54 – 1.44 (m, 1H), 1.38 – 1.22 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 161.3, 144.2, 142.5, 130.5, 129.2, 128.5, 122.8, 122.8, 117.3, 108.7, 108.3, 97.5, 66.3, 61.1, 50.5, 42.2, 41.7, 24.7, 21.8, 13.7; IR (KBr) ν_{max}: 2936, 2864, 2361, 2341, 1710, 1644, 1610, 1487, 1465, 1353, 1321, 1302, 1275, 1225, 1175, 1083, 1018, 992, 917, 753, 668 cm^{-1}; HRMS (ESI): m/z = 392.1477 (calcd for $C_{21}H_{23}NO_5$+Na^+ = 392.1468).

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-benzyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4f

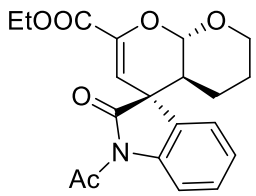


4f

White solid; mp 156–157 ℃; 86% yield (both diastereomers), 98:2 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.721, t (minor) = 19.254]; $[\alpha]_D^{25}$ = +152.5 (*c* 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.21 (td, *J* = 7.7, 1.4 Hz, 1H), 7.14 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.8 Hz,

1H), 5.73 (s, 1H), 5.67 (d, *J* = 8.9 Hz, 1H), 5.06 – 4.78 (m, 2H), 4.27 (qd, *J* = 7.2, 2.0 Hz, 2H), 4.11 (dd, *J* = 11.9, 4.5 Hz, 1H), 3.68 (td, *J* = 12.0, 2.5 Hz, 1H), 2.01 (ddd, *J* = 11.8, 8.9, 4.3 Hz, 1H), 1.66 – 1.55 (m, 1H), 1.55 – 1.46 (m, 1H), 1.38 (ddd, *J* = 15.9, 11.5, 6.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 161.3, 144.2, 142.5, 135.0, 129.36, 128.5, 128.4, 127.3, 126.8, 122.9, 108.8, 108.4, 97.6, 66.4, 61.1, 50.5, 43.8, 41.8, 24.8, 21.9, 13.7; IR (KBr) ν_{max}: 2928, 2868, 2851, 1709, 1648, 1611, 1467, 1351, 1320, 1276, 1228, 1220, 1177, 1077, 1038, 983, 754, 741, 697, 658 cm^{-1}; HRMS (ESI): m/z = 442.1635 (calcd for $C_{25}H_{25}NO_5$+Na^+ = 442.1625).

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-acetyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4g



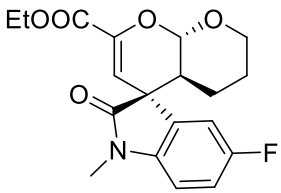
4g

White solid; mp 123–124 ℃; 63% yield (both diastereomers), 94:6 *dr*, 96% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 11.168, t (minor) = 16.163]; $[\alpha]_D^{25}$ = +127.3 (*c* 0.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.32 (m, 1H), 7.28 – 7.23 (m, 1H), 7.16 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.73 (s, 1H), 5.53 (d, *J* = 9.0 Hz, 1H), 4.27 (pd, *J* = 7.2, 4.1 Hz, 3H), 3.66 (td, *J* = 12.0, 2.7 Hz, 1H), 2.68 (s, 3H), 1.96 (ddd, *J* = 12.7, 8.9, 3.9 Hz, 1H), 1.51 (dd, *J* = 13.8, 9.0 Hz, 3H), 1.34 – 1.28 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 170.1, 161.0, 144.4, 139.7, 128.9, 128.3, 125.5, 122.5, 116.2, 107.5, 97.4, 66.4, 61.3, 51.0, 42.6, 26.3, 24.7, 21.8, 13.7; IR (KBr) ν_{max}: 2920, 2850, 2360, 2341, 1748, 1716, 1651, 1462, 1372, 1334, 1299, 1260, 1238, 1199, 1163, 1132, 1115, 1085, 1054, 1032, 1016, 994, 904, 862, 766, 757 cm^{-1}; HRMS (ESI): m/z = 394.1266 (calcd for $C_{20}H_{21}NO_6$+Na^+ = 394.1261).

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-fluoro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4h

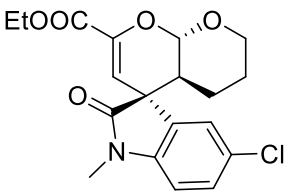
White solid; mp 132–133 ℃; 93% yield (both diastereomers), 99:1 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.926, t (minor) = 13.741]; $[\alpha]_D^{25}$ = +167.8 (*c* 0.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (td, *J* = 8.8, 2.5 Hz, 1H), 6.88 (dd, *J* = 7.7, 2.5 Hz, 1H),

6.78 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.65 (s, 1H), 5.60 (d, *J* = 8.9 Hz, 1H), 4.25 (dtd, *J* = 8.4, 7.0, 6.4, 3.7 Hz, 2H), 4.09 (dt, *J* = 12.1, 3.0 Hz, 1H), 3.64 (td, *J* = 12.2, 2.4 Hz, 1H), 3.20 (s, 3H), 1.90 (ddd, *J* = 12.8, 8.8, 4.2 Hz, 1H), 1.66 – 1.55 (m, 1H), 1.52 – 1.44 (m, 1H), 1.33 – 1.23 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –119.1; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 161.1, 159.1 (d, *J* = 240.0 Hz), 144.4, 139.2, 130.9 (d, *J* = 8.0 Hz), 114.8 (d, *J* = 23.0 Hz), 111.1 (d, *J* = 76.0 Hz), 108.3 (d, *J* = 8.0 Hz), 107.5, 97.4, 66.3, 61.2, 50.9, 41.6, 26.2, 24.6, 21.7, 13.7; IR (KBr) ν_{max}: 2859, 1712, 1645, 1618, 1489, 1450, 1277, 1261, 1227, 1093, 1080, 994, 880, 811, 670 cm^{-1}; HRMS (ESI): m/z = 384.1228 (calcd for $C_{19}H_{20}FNO_5$+Na^+ = 384.1218).



4h

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-chloro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4i



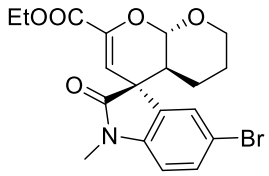
4i

White solid; mp 162–163 ℃; 93% yield (both diastereomers), 99:1 *dr*, 99% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.250, t (minor) = 14.271]; $[\alpha]_D^{25}$ = +187.1 (*c* 0.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 8.3, 1.6 Hz, 1H), 5.65 (d, *J* = 1.6 Hz, 1H), 5.63 – 5.57 (m, 1H), 4.34 – 4.17 (m, 2H), 4.10 (dd, *J* = 12.9, 4.1 Hz, 1H), 3.65 (t, *J* = 12.0 Hz, 1H), 3.21 (s, 3H), 2.01 – 1.84 (m, 1H), 1.49 (d, *J* = 13.8 Hz, 1H), 1.38 – 1.18 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 161.1, 144.5, 141.9, 131.0, 128.5, 128.2, 123.4, 108.7, 107.3, 97.4, 66.3, 61.2, 50.7, 41.6, 26.2, 24.6, 21.7, 13.7; IR (KBr) ν_{max}: 2968, 2942, 2860, 1715, 1651, 1608, 1488, 1381, 1365, 1322, 1304, 1287, 1273, 1220, 1081, 1057, 1024, 993, 849, 817, 774, 666 cm^{-1}; HRMS (ESI): m/z = 400.0930 (calcd for $C_{19}H_{20}ClNO_5$+Na^+ = 400.0922).

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-bromo-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4j

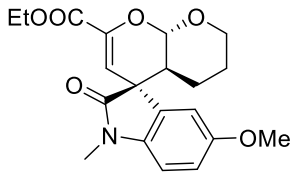
White solid; mp 181–182 ℃; 95% yield (both diastereomers), >99:1 *dr*, 99% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4

nm, t (major) = 10.738, t (minor) = 13.323]; $[\alpha]_D^{25}$ = +177.8 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 5.64 (s, 1H), 5.59 (d, *J* = 8.9 Hz, 1H), 4.26 (qd, *J* = 7.2, 4.3 Hz, 2H), 4.15 – 4.03 (m, 1H), 3.64 (td, *J* = 12.1, 2.5 Hz, 1H), 3.20 (s, 3H), 1.91 (ddd, *J* = 12.7, 8.9, 4.1 Hz, 1H), 1.60 (ddt, *J* = 12.6, 8.8, 4.4 Hz, 1H), 1.53 – 1.44 (m, 1H), 1.36 – 1.23 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 161.1, 144.5, 142.4, 131.4, 131.3, 126.1, 115.4, 109.2, 107.3, 97.4, 66.3, 61.2, 50.6, 41.6, 26.1, 24.6, 21.7, 13.7; IR (KBr) ν_{max}: 2969, 2940, 2855, 1713, 1651, 1606, 1493, 1485, 1322, 1304, 1286, 1273, 1261, 1219, 1082, 1057, 1024, 993, 847, 814, 773, 664 cm^{-1}; HRMS (ESI): m/z = 446.0413 (calcd for $C_{19}H_{20}BrNO_5$+Na^+ = 444.0417).



4j

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-methoxy-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4k

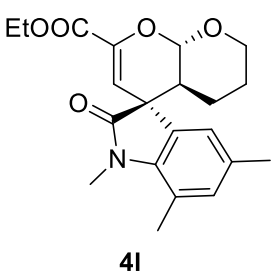


4k

White solid; mp 190–191 ℃; 94% yield (both diastereomers), >99:1 *dr*, 98% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 14.524, t (minor) = 16.544]; $[\alpha]_D^{25}$ = +154.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.76 (s, 1H), 6.74 – 6.71 (m, 1H), 5.68 (s, 1H), 5.60 (d, *J* = 8.9 Hz, 1H), 4.24 (qq, *J* = 7.4, 3.8 Hz, 2H), 4.12 – 4.03 (m, 1H), 3.78 (s, 3H), 3.64 (td, *J* = 12.0, 2.5 Hz, 1H), 3.18 (s, 3H), 1.91 (ddd, *J* = 12.7, 8.9, 4.2 Hz, 1H), 1.58 (tq, *J* = 12.4, 4.2 Hz, 1H), 1.51 – 1.42 (m, 1H), 1.34 – 1.24 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 161.3, 156.0, 144.1, 136.7, 130.6, 112.8, 110.0, 108.3, 108.1, 97.5, 66.3, 61.1, 55.3, 50.9, 41.8, 26.1, 24.7, 21.7, 13.7; IR (KBr) ν_{max}: 2966, 2926, 2871, 1708, 1644, 1598, 1493, 1464, 1440, 1357, 1318, 1289, 1276, 1259, 1230, 1204, 1174, 1139, 1116, 1083, 1057, 1020, 996, 839, 802, 774, 666 cm^{-1}; HRMS (ESI): m/z = 396.1426 (calcd for $C_{20}H_{23}NO_6$+Na^+ = 396.1418).

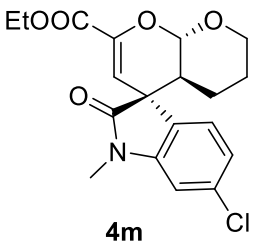
Ethyl-(3*S*,4a'*S*,8a'*S*)-1,5,7-trimethyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4l

White solid; mp 158–159 ℃; 83% yield (both diastereomers), 97:3 *dr*, 97% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 9.212, t (minor) = 10.499]; $[\alpha]_D^{25}$ = +180.7 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.75 (d, *J* = 1.7 Hz, 1H), 5.66 (s, 1H), 5.61 (d, *J* = 8.9 Hz, 1H), 4.24 (qd, *J* = 7.1, 4.8 Hz, 2H), 4.08 (ddd, *J* = 9.9, 4.5, 2.3 Hz, 1H), 3.64 (td, *J* = 12.0, 2.5 Hz, 1H), 3.46 (s, 3H), 2.52 (s, 3H), 2.26 (s, 3H), 1.88 (ddd, *J* = 12.7, 8.9, 4.1 Hz, 1H), 1.61 – 1.46 (m, 2H), 1.36 – 1.23 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 161.4, 143.9, 138.6, 132.6, 132.3, 129.9, 121.4, 119.0, 108.9, 97.6, 66.3, 61.0, 50.0, 42.0, 29.3, 24.7, 21.7, 20.3, 18.3, 13.7; IR (KBr) ν_{max}: 2921, 2857, 1721, 1700, 1633, 1602, 1474, 1343, 1306, 1262, 1177, 1135, 1110, 1084, 1067, 1042, 1019, 996, 958, 850, 778, 747, 677 cm^{-1}; HRMS (ESI): m/z = 394.1619 (calcd for $C_{21}H_{25}NO_5$+Na^+ = 394.1625).



4l

Ethyl-(3*S*,4a'*S*,8a'*S*)-6-chloro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4m

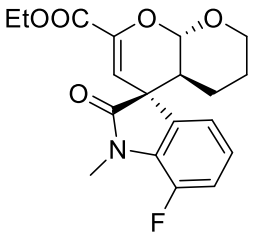


4m

White solid; mp 181–182 ℃; 92% yield (both diastereomers), >99:1 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 12.572, t (minor) = 21.554]; $[\alpha]_D^{25}$ = +102.8 (*c* 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.98 (m, 2H), 6.85 (d, *J* = 1.7 Hz, 1H), 5.63 (s, 1H), 5.59 (d, *J* = 8.9 Hz, 1H), 4.25 (qq, *J* = 7.2, 3.8 Hz, 2H), 4.08 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.63 (td, *J* = 12.0, 2.6 Hz, 1H), 3.20 (s, 3H), 1.91 (ddd, *J* = 12.7, 8.9, 4.1 Hz, 1H), 1.64 – 1.42 (m, 2H), 1.38 – 1.15 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 161.1, 144.5, 144.4, 134.4, 127.6, 123.7, 122.7, 108.5, 107.6, 97.4, 66.3, 61.2, 50.3, 41.6, 26.1, 24.6, 21.7, 13.7; IR (KBr) ν_{max}: 2931, 2855, 1724, 1711, 1637, 1607, 1366, 1278, 1252, 1174, 1132, 1087, 1068, 1056, 1021, 1005, 993, 925, 841, 776, 764, 665 cm^{-1}; HRMS (ESI): m/z = 400.0930 (calcd for $C_{19}H_{20}ClNO_5$+Na^+ = 400.0922).

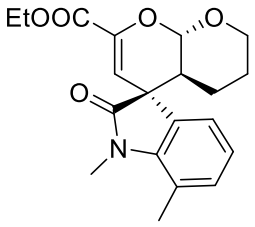
Ethyl-(3*S*,4a'*S*,8a'*S*)-7-fluoro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4n

White solid; mp 104–105 ℃; 90% yield (both diastereomers), 98:2 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 12.046, t (minor) = 17.247]; $[\alpha]_D^{25}$ = +162.0 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 6.99 (m, 2H), 6.91 (dd, *J* = 6.2, 2.1 Hz, 1H), 5.66 (s, 1H), 5.60 (d, *J* = 8.9 Hz, 1H), 4.26 (qq, *J* = 7.5, 3.6 Hz, 2H), 4.13 – 4.00 (m, 1H), 3.65 (td, *J* = 12.0, 2.6 Hz, 1H), 3.42 (s, 3H), 1.92 (ddd, *J* = 12.7, 8.8, 4.1 Hz, 1H), 1.59 (ddt, *J* = 12.5, 8.0, 4.4 Hz, 1H), 1.53 – 1.46 (m, 1H), 1.38 – 1.23 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –136.2; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 161.2, 148.2, 144.3, 132.1, 130.0, 123.4 (d, *J* = 6.0 Hz), 118.6, 116.5 (d, *J* = 18.0 Hz), 107.7, 97.3, 66.3, 61.2, 50.8, 41.8, 28.5, 24.6, 21.7, 13.7; IR (KBr) ν_{max}: 2923, 2857, 1712, 1656, 1627, 1483, 1371, 1322, 1301, 1277, 1236, 1138, 1110, 1083, 1061, 1053, 1026, 992, 983, 865, 789, 770, 756, 736, 678 cm^{-1}; HRMS (ESI): m/z = 384.1224 (calcd for $C_{19}H_{20}FNO_5$+Na$^+$ = 384.1218).



4n

Ethyl-(3*S*,4a'*S*,8a'*S*)-1,7-dimethyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4o

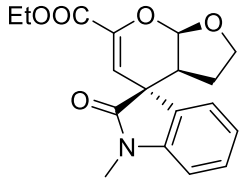


4o

White solid; mp 125–126 ℃; 95% yield (both diastereomers), 98:2 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 11.430, t (minor) = 13.997]; $[\alpha]_D^{25}$ = +161.0 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 7.01 (m, 1H), 6.99 – 6.92 (m, 2H), 5.67 (s, 1H), 5.62 (d, *J* = 8.9 Hz, 1H), 4.25 (qd, *J* = 7.1, 3.8 Hz, 2H), 4.15 – 4.01 (m, 1H), 3.65 (td, *J* = 12.0, 2.6 Hz, 1H), 3.49 (s, 3H), 2.58 (s, 3H), 1.91 (ddd, *J* = 12.7, 8.9, 4.1 Hz, 1H), 1.59 (dtd, *J* = 12.6, 8.3, 4.2 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.35 – 1.22 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 161.3, 144.0, 141.0, 132.2, 129.8, 122.7, 120.7, 119.3, 108.7, 97.6, 66.3, 61.0, 49.9, 42.0, 29.4, 24.7, 21.7, 18.5, 13.7; IR (KBr) ν_{max}: 2942, 2864, 1721, 1674, 1484, 1365, 1321, 1242, 1183, 983, 834, 754, 647 cm^{-1}; HRMS (ESI): m/z = 380.1477 (calcd for $C_{20}H_{23}NO_5$+Na$^+$ = 380.1468).

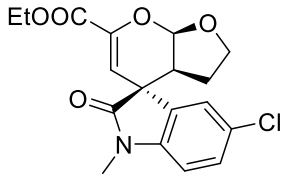
Ethyl-(3a*S*,4*S*,7a*R*)-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo[2,3-b] pyran-4,3'-indoline]-6-carboxylate 3a

White solid; mp 172–173 ℃; 93% yield (both diastereomers), 88:12 *dr*, 80% *ee* for the major, 60% *ee* for the minor [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.944, t (minor) = 23.288]; $[\alpha]_D^{25}$ = –148.0 (*c* 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.80 (d, *J* = 3.3 Hz, 2H), 4.32 – 4.19 (m, 3H), 4.01 – 3.84 (m, 1H), 3.24 (s, 3H), 2.53 – 2.36 (m, 1H), 2.30 – 2.20 (m, 1H), 2.10 – 2.01 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 161.3, 142.9, 141.8, 132.6, 128.6, 123.4, 122.7, 108.0, 105.3, 99.3, 68.2, 61.1, 47.6, 43.9, 26.1, 24.1, 13.7; IR (KBr) ν_{max}: 2921, 1703, 1650, 1608, 1489, 1469, 1369, 1346, 1301, 1254, 1195, 1136, 1083, 1069, 1045, 1022, 1000, 928, 885, 844, 765, 749, 683 cm^{-1}; HRMS (ESI): m/z = 352.1166 (calcd for $C_{18}H_{19}NO_5$+Na^+ = 352.1155).



3a

Ethyl-(3a*S*,4*S*,7a*R*)-5'-chloro-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3b

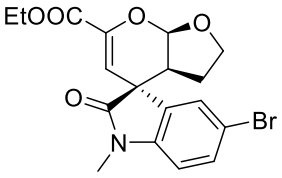


3b

White solid; mp 181–182 ℃; 85% yield (both diastereomers), 87:13 *dr*, 99% *ee* for the major, 99% *ee* for the minor [Daicel Chiralcel IA-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.201, t (minor) = 18.577]; $[\alpha]_D^{25}$ = –124.2 (*c* 0.24, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 8.3, 1.9 Hz, 1H), 7.22 – 7.10 (m, 1H), 6.79 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.15 – 5.54 (m, 2H), 4.32 – 4.19 (m, 3H), 3.94 (dt, *J* = 9.3, 7.5 Hz, 1H), 3.22 (s, 3H), 2.43 (tt, *J* = 12.1, 9.7 Hz, 1H), 2.34 – 2.18 (m, 1H), 2.13 – 1.96 (m, 1H), 1.32 – 1.27 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 161.2, 143.3, 140.4, 134.1, 128.5, 128.1, 124.0, 108.9, 104.5, 99.2, 68.2, 61.3, 47.7, 43.7, 26.3, 24.0, 13.7; IR (KBr) ν_{max}: 2920, 2893, 1728, 1712, 1648, 1607, 1491, 1475, 1362, 1344, 1249, 1183, 1146, 1096, 1070, 1047, 1020, 989, 960, 882, 864, 842, 820, 766, 739, 680 cm^{-1}; HRMS (ESI): m/z = 386.0779 (calcd for $C_{18}H_{18}ClNO_5$+Na^+ = 386.0766).

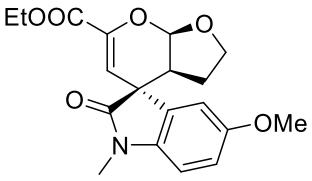
Ethyl-(3a*S*,4*S*,7a*R*)-5'-bromo-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3c

White solid; mp 201–202 ℃; 93% yield (both diastereomers), 88:12 *dr*, 99% *ee* for the major, 99% *ee* for the minor [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.690, t (minor) = 20.131]; $[\alpha]_D^{25}$ = –173.2 (*c* 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.28 (s, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.82 – 5.74 (m, 2H), 4.36 – 4.14 (m, , 3H), 3.94 (q, *J* = 8.6, 8.1 Hz, 1H), 3.22 (s, 3H), 2.55 – 2.34 (m, 1H), 2.32 – 2.17 (m, 1H), 2.12 – 1.96 (m, 1H), 1.36 – 1.26 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 161.2, 143.3, 140.8, 134.5, 131.4, 126.7, 115.3, 109.4, 104.5, 99.2, 68.2, 61.3, 47.7, 43.7, 26.3, 24.0, 13.7; IR (KBr) ν_{max}: 2955, 2889, 1728, 1714, 1647, 1605, 1489, 1420, 1363, 1342, 1249, 1181, 1093, 1070, 1047, 1019, 1005, 988, 882, 864, 842, 818, 765, 675 cm^{-1}; HRMS (ESI): m/z = 430.0265 (calcd for $C_{18}H_{18}BrNO_5$+Na^+ = 430.0261).



3c

Ethyl-(3a*S*,4*S*,7a*R*)-5'-methoxy-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3d

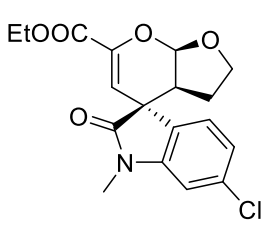


3d

White solid; mp 201–202 ℃; 84% yield (both diastereomers), 84:16 *dr*, 98% *ee* for the major, 77% *ee* for the minor [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 16.390, t (minor) = 22.553]; $[\alpha]_D^{25}$ = –155.2 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.64 (m, 3H), 6.22 – 5.52 (m, 2H), 4.38 – 4.14 (m, 3H), 4.00 – 3.88 (m, 1H), 3.76 (s, 3H), 3.21 (s, 3H), 2.55 – 2.35 (m, 1H), 2.30 – 2.15 (m, 1H), 2.13 – 1.94 (m, 1H), 1.34 – 1.24 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 161.3, 156.0, 142.9, 135.2, 133.8, 112.7, 110.9, 108.4, 105.4, 99.2, 68.3, 61.1, 55.4, 48.0, 43.9, 26.2, 24.1, 13.7; IR (KBr) ν_{max}: 2920, 2894, 1727, 1708, 1647, 1598, 1494, 1455, 1352, 1287, 1251, 1227, 1157, 1101, 1068, 1049, 1036, 886, 834, 813, 771, 684, cm^{-1}; HRMS (ESI): m/z = 382.1251 (calcd for $C_{19}H_{21}NO_6$+Na^+ = 382.1261).

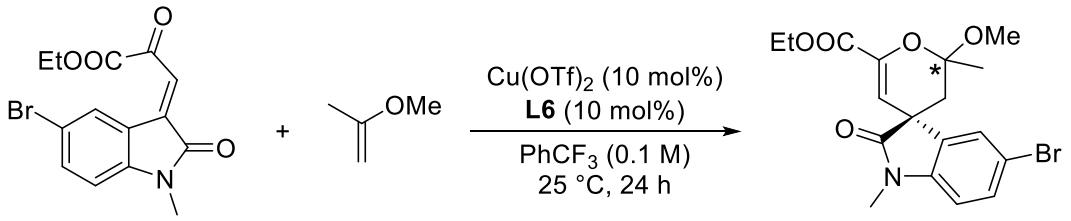
Ethyl-(3a*S*,4*S*,7a*R*)-6'-chloro-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3e

White solid; mp 67–68 ℃; 91% yield (both diastereomers), 85:15 *dr*, 83% *ee* for the major, 50% *ee* for the minor [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 18.481, t (minor) = 34.963]; $[\alpha]_D^{25}$ = –192.0 (*c* 0.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 – 6.99 (m, 2H), 6.87 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.13 – 5.46 (m, 2H), 4.39 – 4.12 (m, 3H), 4.04 – 3.83 (m, 1H), 3.22 (s, 3H), 2.53 – 2.33 (m, 1H), 2.32 – 2.17 (m, 1H), 2.11 – 1.96 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 161.2, 143.1, 143.0, 134.4, 130.9, 124.4, 122.5, 108.7, 104.7, 99.2, 68.2, 61.2, 47.3, 43.8, 26.3, 24.0, 13.7; IR (KBr) ν_{max}: 2919, 2851, 1716, 1650, 1605, 1493, 1366, 1298, 1248, 1106, 1071, 1049, 1023, 1002, 930, 893, 846, 718, 682 cm^{-1}; HRMS (ESI): m/z = 386.0777 (calcd for $C_{18}H_{18}ClNO_5+Na^+$ = 386.0766).



3e

2.2 Procedure for the preparation of 5



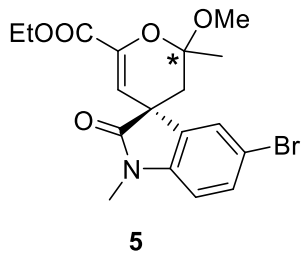
1j **2c** **5**

Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** (0.01 mmol, 10 mol%) were charged into a flame-dried vessel, and anhydrous $PhCF_3$ (1 mL) was added *via* syringe. The resulting mixture was stirred at room temperature for 0.5 h. Then the substrates **1j** (0.1 mmol) and **2c** (0.4 mmol, 4 equiv) was introduced into the vessel. The reaction mixture was stirred at 25 ℃ for 24 h. When the reaction was detected complete (by TLC analysis), the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (3/1) as eluent to give **5** as a white solid.

Ethyl-(3*R*)-5-bromo-2'-methoxy-1,2'-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 5

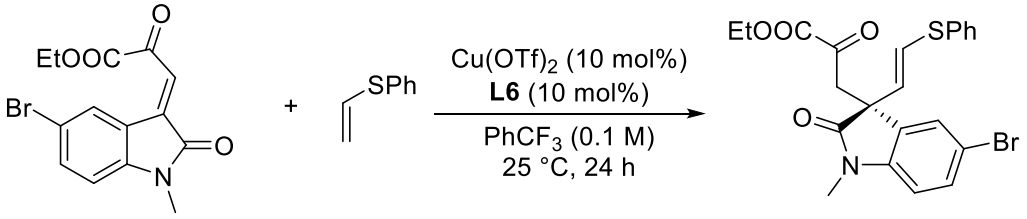
White solid; mp 56–57 ℃; 92% yield (both diastereomers), 99:1 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t

(major) = 6.932, t (minor) = 8.501]; $[\alpha]_D^{25}$ = +62.1 (*c* 0.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 5.77 (s, 1H), 4.38 – 4.04 (m, 2H), 3.39 (s, 3H), 3.20 (s, 3H), 2.50 (d, *J* = 14.1 Hz, 1H), 2.10 (d, *J* = 14.0 Hz, 1H), 1.63 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 161.7, 142.0, 141.5, 133.8, 130.8, 130.3, 115.1, 110.5, 109.0, 98.6, 60.9, 48.6, 47.2, 39.6, 26.4, 22.1, 13.7; IR (KBr) ν_{max}: 2936, 2836, 1719, 1650, 1605, 1466, 1362, 1335, 1294, 1260, 1229, 1200, 1179, 1156, 1126, 1095, 1076, 1050, 1021, 852, 832, 808, 649 cm^{-1}; HRMS (ESI): m/z = 432.0426 (calcd for $C_{18}H_{20}BrNO_5+H^+$ = 432.0417).



5

2.3 Procedure for the preparation of 6



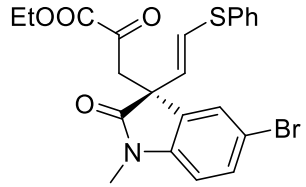
1j **2d** **6**

Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** (0.01 mmol, 10 mol%) were charged into a flame-dried vessel, and anhydrous $PhCF_3$ (1 mL) was added *via* syringe. The resulting mixture was stirred at room temperature for 0.5 h. Then the substrates **1j** (0.1 mmol) and **2d** (0.2 mmol, 2 equiv) was introduced into the vessel. The reaction mixture was stirred at 25 ℃ for 24 h. When the reaction was detected complete (by TLC analysis), the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (3/1) as eluent to give **6** as a white solid.

Ethyl-(*S*,*E*)-3-(5-bromo-1-methyl-2-oxo-3-(2-(phenylthio)vinyl)indolin-3-yl)-2-oxopropanoate 6

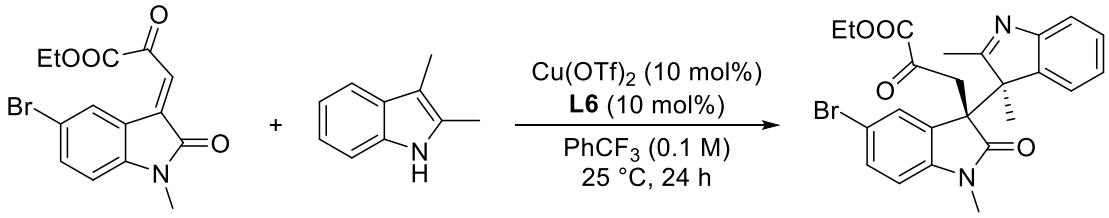
White solid; mp 86–87 ℃; 88% yield (both diastereomers),90:10 *E*/*Z*, 99% *ee* for the major, 99% *ee* for the minor [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 95/5, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 25.165, t (minor) = 42.134]; $[\alpha]_D^{25}$ =

–193.0 (*c* 0.12, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.14 (m, 7H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.25 (d, *J* = 15.2 Hz, 1H), 5.75 (d, *J* = 15.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.85 – 3.43 (m, 2H), 3.23 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 175.4, 159.1, 142.8, 133.1, 131.2, 130.7, 129.9, 128.8, 127.1, 127.0, 126.89, 126.1, 114.7, 109.7, 62.4, 51.3, 45.1, 26.3, 13.4; IR (KBr) ν_{max}: 2932, 1713, 1651, 1605, 1488, 1466, 1336, 1296, 1261, 1230, 1095, 1052, 941, 817, 742, 701, 649 cm^{-1}; HRMS (ESI): m/z = 496.0199 (calcd for $C_{22}H_{20}SBrNO_4+Na^+$ = 496.0189).



6

2.4 Procedure for the preparation of 7



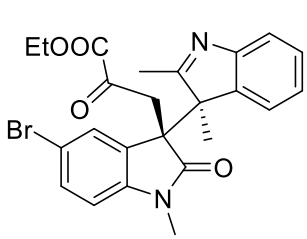
1j **2e** **7**

Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** (0.01 mmol, 10 mol%) were charged into a flame-dried vessel, and anhydrous $PhCF_3$ (1 mL) was added *via* syringe. The resulting mixture was stirred at room temperature for 0.5 h. Then the substrates **1j** (0.1 mmol) and **2e** (0.2 mmol, 2 equiv) was introduced into the vessel. The reaction mixture was stirred at 25 ℃ for 24 h. When the reaction was detected complete (by TLC analysis), the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (3/1) as eluent to give **7** as a yellow solid.

Ethyl-3-(5-bromo-3-(2,3-dimethyl-3H-indol-3-yl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 7

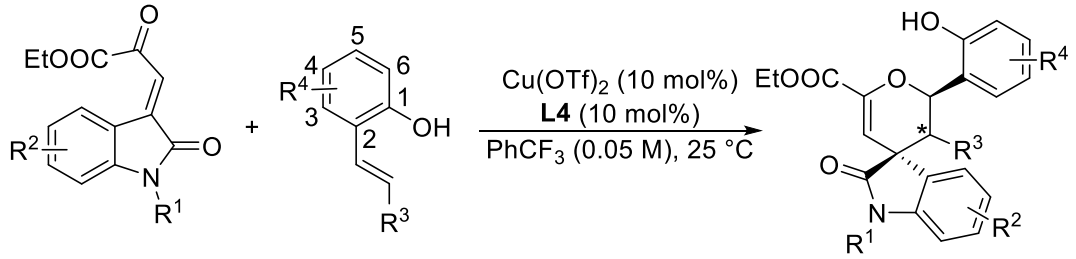
Yellow solid; mp 92–93 ℃; 33% yield, 83:17 *dr*, 0% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 23.056, t (minor) = 26.836]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.51 – 7.32 (m, 3H),

7.19 (d, *J* = 1.8 Hz, 1H), 7.05 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 4.25 (qd, *J* = 7.1, 1.7 Hz, 2H), 4.16 – 3.90 (m, 2H), 3.23 (s, 3H), 2.32 (s, 3H), 2.17 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 177.5, 159.3, 143.4, 134.7, 133.3, 131.4, 130.8, 129.8, 126.7, 117.8, 116.8, 114.4, 109.4, 107.7, 106.5, 62.3, 52.3, 46.9, 29.2, 26.3, 13.4, 11.1, 7.9; IR (KBr) ν_{max}: 2918, 2850, 1718, 1705, 1606, 1487, 1467, 1363, 1340, 1260, 1095, 1054, 1022, 806, 730, 689, 648, 632 cm^{-1}; HRMS (ESI): m/z = 505.0727 (calcd for $C_{24}H_{23}BrN_2O_4$+Na^+ = 505.0733).



7

2.5 General procedure for the preparation of 9



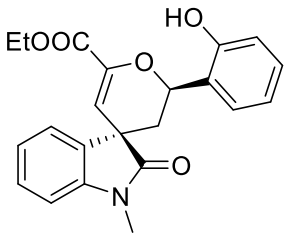
1 **8** **9**

Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol %) and **L4** (0.01 mmol, 10 mol %) were charged into a flame-dried vessel, and anhydrous $PhCF_3$ (2 mL) was added *via* syringe. The resulting mixture was stirred at room temperature for 0.5 h. Then the substrates **1** (0.1 mmol) and **8** (0.12 mmol, 1.2 equiv) was introduced into the vessel. The reaction mixture was stirred at 25 ℃ until the reaction was detected complete. The solvent was removed under reduced pressure, the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (3/1) as eluent to give **9** as solids.

The racemic samples described in this work were synthesized according above procedure, which were catalyzed by $Cu(OTf)_2$ with mixed **L4** and *ent*-**L4** as ligands in toluene. Because equal amount of **L4** and *ent*-**L4** could not be accurately balanced, slight ee values (<10%) were observed in their racemic HPLC spectra. And a little amount of unseperate byproduct was detected in some cases due to the use of toluene as reaction media. In addition, for the preparation of racemic **9a**, the reaction was

stirred at 90 ℃ for extra 3 h to give **9a** with relatively low diastereoselectivity.

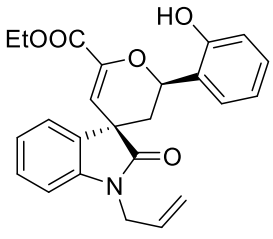
Ethyl(2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9a



9a

White solid; mp 83–84 ℃; 95% yield (both diastereomers), 98:2 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 16.723, t (minor) = 12.119]; $[\alpha]_D^{25}$ = –104.6 (*c* 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.21 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.95 – 6.80 (m, 4H), 5.88 (d, *J* = 1.7 Hz, 1H), 5.61 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.26 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.26 (s, 3H), 2.58 (dd, *J* = 13.7, 12.3 Hz, 1H), 2.09 (dt, *J* = 13.7, 2.0 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 161.6, 153.7, 146.0, 142.3, 132.5, 129.1, 128.5, 126.2, 124.0, 123.8, 122.7, 119.9, 116.4, 108.5, 108.1, 73.0, 61.2, 47.1, 36.1, 26.3, 13.7; IR (KBr) ν_{max}: 3411, 1713, 1687, 1644, 1609, 1491, 1469, 1457, 1371,1352, 1296, 1243, 1169, 1133, 1112, 1087, 1044, 1019, 983, 859, 822, 752, 688 cm^{-1}; HRMS (ESI): m/z = 380.1499 (calcd for $C_{22}H_{21}NO_5$+H^+ = 380.1492).

Ethyl (2'*R*,3*R*)-1-allyl-2'-(2-hydroxyphenyl)-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9b

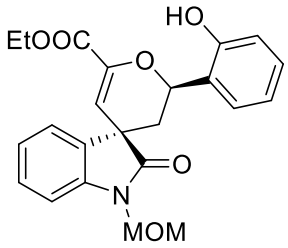


9b

White solid; mp 81–82 ℃; 88% yield (both diastereomers), 93:7 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 75/25, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 9.166, t (minor) = 6.158]; $[\alpha]_D^{25}$ = –98.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.23 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.96 – 6.78 (m, 4H), 5.92 – 5.87 (m, 1H), 5.82 (dq, *J* = 10.5, 5.4 Hz, 1H), 5.63 (dd, *J* = 12.4, 2.1 Hz, 1H), 5.33 – 5.13 (m, 2H), 4.51 – 4.15 (m, 4H), 2.71 – 2.46 (m, 1H), 2.11 (dt, *J* = 13.6, 2.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 161.7, 153.7, 146.0, 141.4, 132.5, 130.5, 129.1, 128.3, 126.3, 124.1, 123.8, 122.6, 120.0, 117.4, 116.3, 109.0, 108.4, 72.9, 61.3, 47.1, 42.2, 36.4, 13.7; IR (KBr) ν_{max}: 3456, 1732,

1701, 1609, 1486, 1458, 1357, 1298, 1268, 1240, 1209, 1181, 1098, 1086, 1028, 1013, 860, 819, 771, 758, 732, 691 cm^{-1}; HRMS (ESI): m/z = 406.1659 (calcd for $C_{24}H_{23}NO_5+H^+$ = 406.1649).

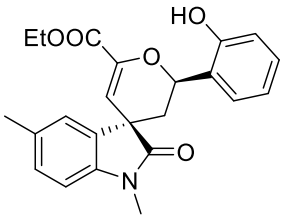
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1-(methoxymethyl)-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9c



9c

White solid; mp 67–68 ℃; 82% yield (both diastereomers), 96:4 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 15.888, t (minor) = 8.507]; $[\alpha]_D^{25}$ = –100.0 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 – 7.06 (m, 3H), 6.94 – 6.75 (m, 3H), 5.90 (d, *J* = 1.7 Hz, 1H), 5.62 (dd, *J* = 12.3, 2.1 Hz, 1H), 5.26 – 5.04 (m, 2H), 4.27 (qt, *J* = 6.4, 3.3 Hz, 2H), 3.33 (s, 3H), 2.57 (t, *J* = 13.0 Hz, 1H), 2.11 (dt, *J* = 13.7, 2.0 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 161.7, 153.5, 146.1, 140.4, 132.1, 129.1, 128.5, 126.3, 124.2, 123.9, 123.2, 120.0, 116.2, 109.6, 108.1, 72.6, 71.2, 61.3, 55.9, 47.4, 36.6, 13.7; IR (KBr) ν_{max}: 2936, 1719, 1646, 1610, 1485, 1457, 1366, 1345, 1292, 1246, 1198, 1172, 1128, 1090, 1076, 1045, 1019, 984, 913, 821, 752, 691 cm^{-1}; HRMS (ESI): m/z = 410.1605 (calcd for $C_{23}H_{23}NO_6+H^+$ = 410.1598).

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,5-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9e

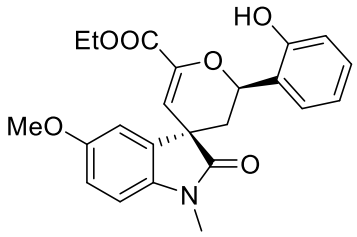


9e

White solid; mp 235–236 ℃; 92% yield (both diastereomers), 98:2 *dr*, 98% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.211, t (minor) = 8.387]; $[\alpha]_D^{25}$ = –140.0 (*c* 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 15.8, 8.1 Hz, 4H), 6.98 (d, *J* = 24.6 Hz, 1H), 6.90 – 6.84 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.88 (s, 1H), 5.60 (d, *J* = 12.1 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.24 (s, 3H), 2.61 (t, *J* = 13.1 Hz, 1H), 2.36 (s, 3H), 2.12 (d, *J* = 13.7 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 161.5, 154.1, 145.7, 139.9, 132.5, 132.3, 129.2, 128.7, 126.1,

124.86, 123.6, 119.9, 116.7, 108.9, 107.8, 73.5, 61.2, 47.0, 35.9, 26.3, 20.7, 13.7; IR (KBr) ν_{max}: 3218, 1728, 1680, 1649, 1605, 1498, 1459, 1367, 1291, 1264, 1239, 1156, 1106, 1089, 1074, 1036, 1022, 985, 969, 867, 822, 800, 779, 757, 666 cm^{-1}; HRMS (ESI): m/z = 394.1655 (calcd for $C_{23}H_{23}NO_5+H^+$ = 394.1649).

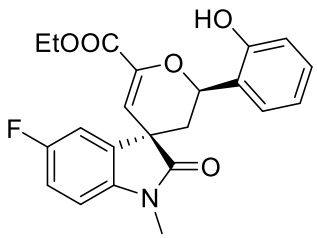
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-5-methoxy-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9f



9f

White solid; mp 198–199 ℃; 88% yield (both diastereomers), 98:2 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 75/25, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.385, t (minor) = 8.791]; $[\alpha]_D^{25}$ = –187.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 1H), 7.15 (dt, *J* = 15.6, 7.3 Hz, 1H), 6.99 (d, *J* = 28.8 Hz, 2H), 6.91 – 6.76 (m, 4H), 5.95 – 5.81 (m, 1H), 5.59 (d, *J* = 12.1 Hz, 1H), 4.32 – 4.18 (m, 2H), 3.79 (s, 3H), 3.22 (s, 3H), 2.55 (t, *J* = 13.1 Hz, 1H), 2.09 (d, *J* = 13.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 161.6, 155.9, 153.6, 146.1, 135.7, 133.8, 129.0, 126.2, 123.9, 119.9, 116.3, 112.6, 111.7, 108.4, 108.4, 72.8, 61.2, 55.5, 47.5, 36.1, 26.4, 13.6; IR (KBr) ν_{max}: 2979, 1725, 1678, 1637, 1603, 1497, 1458, 1371, 1299, 1289, 1275, 1253, 1241, 1232, 1137, 1107, 1073, 1038, 1023, 818, 766, 668 cm^{-1}; HRMS (ESI): m/z = 410.1606 (calcd for $C_{23}H_{23}NO_6+H^+$ = 410.1598).

Ethyl (2'*R*,3*R*)-5-fluoro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9g

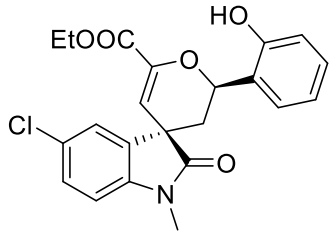


9g

White solid; mp 96–97 ℃; 93% yield (both diastereomers), 97:3 *dr*, 97% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 11.465, t (minor) = 14.901]; $[\alpha]_D^{25}$ = –65.4 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.70 (s, 1H), 7.53 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.22 (dtd, *J* = 22.1, 8.3, 7.7, 2.1 Hz, 2H), 7.13 (dd, *J* = 8.6, 4.3 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.86 – 5.74 (m, 1H), 5.63 (dd, *J* = 11.8, 2.2 Hz, 1H), 4.23 (q, *J* = 7.0

Hz, 2H), 3.19 (s, 3H), 2.24 – 1.92 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −119.4; ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.4, 161.6, 158.6 (d, *J* = 236.0 Hz), 153.8, 146.8, 139.2, 134.3 (d, *J* = 8.0 Hz), 128.9, 126.4, 125.8, 119.2, 115.2, 114.7 (d, *J* = 23.0 Hz), 112.4 (d, *J* = 25.0 Hz), 109.6 (d, *J* = 8.0 Hz), 108.1, 70.4, 61.0, 47.6, 36.7, 26.7, 14.0; IR (KBr) ν_{max}: 2961, 1725, 1689, 1493, 1458, 1259, 1087, 1020, 862, 799, 752, 699, 670, 630, 616 cm^{-1}; HRMS (ESI): m/z = 398.1410 (calcd for $C_{22}H_{20}FNO_5$+H^+ = 398.1398).

Ethyl (2'*R*,3*R*)-5-chloro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9h



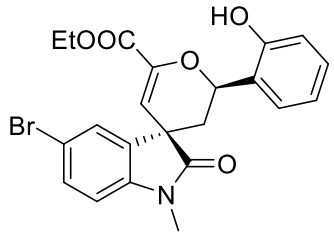
9h

White solid; mp 211–212 ℃; 94% yield, 99:1 *dr*, 98% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 13.110, t (minor) = 11.333]; $[\alpha]_D^{25}$ = –215.1 (*c* 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.23 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 6.92 – 6.80 (m, 3H), 6.68 (s, 1H), 5.85 (d, *J* = 1.8 Hz, 1H), 5.54 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.27 (p, *J* = 7.0 Hz, 2H), 3.24 (s, 3H), 2.57 (t, *J* = 13.1 Hz, 1H), 2.11 (dt, *J* = 13.8, 2.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 161.4, 153.6, 146.3, 140.9, 134.1, 129.2, 128.4, 128.0, 126.2, 124.5, 123.6, 120.1, 116.4, 109.0, 107.6, 73.0, 61.3, 47.2, 35.9, 26.4, 13.6; IR (KBr) ν_{max}: 3411, 1705, 1638, 1605, 1485, 1458, 1361, 1344, 1300, 1274, 1256, 1179, 1139, 1117, 1096, 1011, 822, 775, 763, 656, 628 cm^{-1}; HRMS (ESI): m/z = 414.1113 (calcd for $C_{22}H_{20}ClNO_5$+H^+ = 414.1103).

Ethyl (2'*R*,3*R*)-5-bromo-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9i

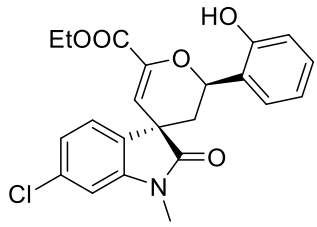
White solid; mp 217–218 ℃; 92% yield, 99:1 *dr*, 99% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 14.380, t (minor) = 10.363]; $[\alpha]_D^{25}$ = –148.0 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 2.0 Hz, 1H), 7.47 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.25 (s, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.82 (dh, *J* = 24.0, 7.8 Hz, 4H), 5.91 – 5.76 (m, 1H), 5.62 – 5.45 (m, 1H),

4.26 (p, *J* = 7.0 Hz, 2H), 3.24 (s, 3H), 2.56 (t, *J* = 13.1 Hz, 1H), 2.10 (dt, *J* = 13.7, 2.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 161.4, 153.6, 146.4, 141.3, 134.5, 131.3, 129.1, 127.2, 126.2, 123.7, 120.1, 116.3, 115.3, 109.5, 107.6, 72.8, 61.3, 47.2, 35.9, 26.4, 13.7; IR (KBr) ν_{max}: 3452, 1715, 1704, 1629, 1600, 1478, 1458, 1366, 1342, 1298, 1240, 1175, 1160, 1117, 1086, 1056, 1017, 999, 820, 758, 733, 698 cm^{-1}; HRMS (ESI): m/z = 458.0601 (calcd for $C_{22}H_{20}BrNO_5$+H$^+$ = 458.0598).



9i

Ethyl (2'*R*,3*R*)-6-chloro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9j



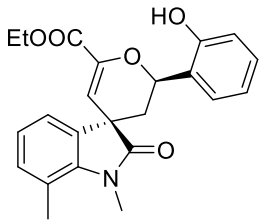
9j

White solid; mp 103–104 ℃; 82% yield (both diastereomers), 93:7 *dr*, 89% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 90/10, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 21.280, t (minor) = 15.597]; $[\alpha]_D^{25}$ = –128.3 (*c* 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.16 – 7.05 (m, 2H), 6.97 – 6.83 (m, 3H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.83 (d, *J* = 1.7 Hz, 1H), 5.64 – 5.46 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.23 (s, 3H), 2.65 – 2.42 (m, 1H), 2.17 – 1.97 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 161.6, 153.4, 146.4, 143.5, 134.4, 130.9, 129.0, 126.2, 124.9, 123.9, 122.4, 120.1, 116.1, 108.8, 107.6, 72.5, 61.3, 46.8, 36.2, 26.4, 13.6; IR (KBr) ν_{max}: 2961, 1717, 1699, 1685, 1652, 1647, 1605, 1491, 1457, 1367, 1295, 1247, 1170, 1088, 1073, 1042, 1016, 818, 754, 712, 668 cm^{-1}; HRMS (ESI): m/z = 414.1113 (calcd for $C_{22}H_{20}ClNO_5$+H$^+$ = 414.1103).

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,7-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9k

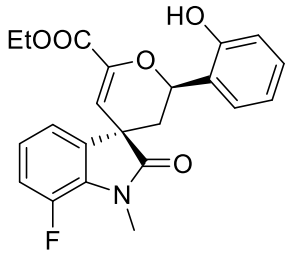
White solid; mp 84–85 ℃; 95% yield (both diastereomers), 96:4 *dr*, 96% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 20.484, t (minor) = 11.478]; $[\alpha]_D^{25}$ = –102.6 (*c* 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.15 – 7.05 (m, 2H), 7.03 – 6.92 (m, 2H), 6.89 – 6.77 (m, 2H), 5.86 (d, *J* = 1.7 Hz, 1H), 5.59 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.25 (qd, *J* =

7.1, 1.9 Hz, 2H), 3.53 (s, 3H), 2.60 (s, 3H), 2.58 – 2.48 (m, 1H), 2.06 (dt, *J* = 13.7, 1.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 161.7, 153.7, 145.8, 134.0, 133.2, 132.2, 129.0, 126.2, 123.9, 122.5, 122.1, 119.9, 119.7, 116.3, 108.8, 72.7, 61.2, 46.5, 36.5, 29.7, 18.6, 13.6; IR (KBr) ν_{max}: 3340, 1699, 1642, 1597, 1456, 1361, 1298, 1247, 1174, 1137, 1118, 1093, 1064, 1010, 757, 750, 701 cm^{-1}; HRMS (ESI): m/z = 394.1660 (calcd for $C_{23}H_{23}NO_5$+H^+ = 394.1649).



9k

Ethyl (2'*R*,3*R*)-7-fluoro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9l



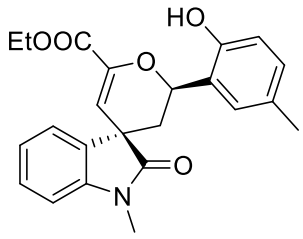
9l

White solid; mp 92–93 ℃; 92% yield (both diastereomers), 94:6 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 90/10, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 26.956, t (minor) = 9.556]; $[\alpha]_D^{25}$ = –108.6 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.01 (m, 6H), 6.87 (td, *J* = 7.5, 1.2 Hz, 1H), 6.81 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.86 (d, *J* = 1.8 Hz, 1H), 5.57 (dd, *J* = 12.4, 2.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.47 (d, *J* = 2.8 Hz, 3H), 2.55 (dd, *J* = 13.8, 12.3 Hz, 1H), 2.10 (dt, *J* = 13.8, 2.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −135.8; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 161.5, 153.6, 148.6, 146.2, 135.2 (d, *J* = 3.0 Hz), 129.1, 129.0 (d, *J* = 8.0 Hz), 127.2 (d, *J* = 11.0 Hz), 126.20, 123.7, 123.1 (d, *J* = 6.0 Hz), 120.1, 119.8 (d, *J* = 4.0 Hz), 116.4 (d, *J* = 19.0 Hz), 116.3, 107.8, 72.7, 61.3, 47.3, 47.2, 36.3, 28.8, 28.8, 13.6; IR (KBr) ν_{max}: 3363, 1716, 1695, 1644, 1628, 1598, 1477, 1457, 1367, 1296, 1240, 1173, 1131, 1119, 1086, 1056, 1019, 754, 733, 698 cm^{-1}; HRMS (ESI): m/z = 420.1226 (calcd for $C_{22}H_{20}FNO_5$+Na^+ = 420.1218).

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-5-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9m

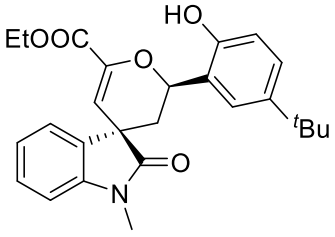
White solid; mp 231–232 ℃; 60% yield (both diastereomers), 99:1 *dr*, 85% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 19.636, t (minor) = 12.410]; $[\alpha]_D^{25}$ = –75.0 (*c* 0.14, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.93 (dd, *J* = 17.1, 8.0 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.62 (s, 1H), 5.87 (s, 1H), 5.56 (d, *J* = 12.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.25 (s, 3H), 2.56 (t, *J* = 13.0 Hz, 1H), 2.23 (s, 3H), 2.08 (d, *J* = 13.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 161.6, 151.4, 146.0, 142.3, 132.6, 129.5, 129.1, 128.4, 126.7, 124.0, 123.5, 122.7, 116.3, 108.4, 108.1, 73.08, 61.2, 47.1, 36.3, 26.3, 20.0, 13.6; IR (KBr) ν_{max}: 3239, 2925, 1734, 1693, 1610, 1489, 1374, 1353, 1273, 1241, 1188, 1176, 1122, 1108, 1088, 1019, 817, 766, 738, 689, 644 cm^{-1}; HRMS (ESI): m/z = 416.1472 (calcd for $C_{23}H_{23}NO_5$+Na^+ = 416.1468).



9m

Ethyl (2'*R*,3*R*)-2'-(5-(tert-butyl)-2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9n

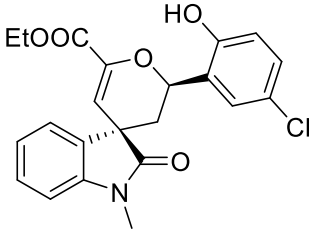


9n

White solid; mp 93–94 ℃; 92% yield (both diastereomers), 98:2 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 29.446, t (minor) = 7.340]; $[\alpha]_D^{25}$ = –126.3 (*c* 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.09 (m, 3H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 5.92 – 5.84 (m, 1H), 5.66 – 5.55 (m, 1H), 4.26 (qt, *J* = 7.4, 3.6 Hz, 2H), 3.27 (s, 3H), 2.61 (t, *J* = 13.0 Hz, 1H), 2.13 (d, *J* = 13.7 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 161.6, 151.5, 146.02, 142.7, 142.3, 132.6, 128.5, 126.0, 124.1, 123.1, 122.9, 122.7, 116.0, 108.3, 108.1, 73.3, 61.2, 47.1, 36.0, 33.7, 31.0, 26.3, 13.6; IR (KBr) ν_{max}: 2961, 1716, 1646, 1610, 1490, 1469, 1422, 1371, 1295, 1272, 1190, 1170, 1111, 1086, 988, 919, 820, 751, 689, 668 cm^{-1}; HRMS (ESI): m/z = 436.2115 (calcd for $C_{26}H_{29}NO_5$+H^+ = 436.2118).

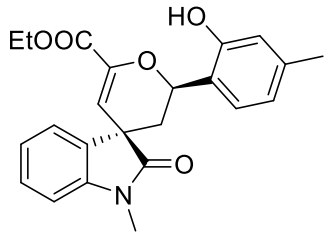
Ethyl (2'*R*,3*R*)-2'-(5-chloro-2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9o

White solid; mp 92–93 ℃; 75% yield (both diastereomers), 97:3 *dr*, 88% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 90/10, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 12.213, t (minor) = 9.915]; $[\alpha]_D^{25}$ = –102.9 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.20 (d, *J* = 2.7 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 5.87 (d, *J* = 1.6 Hz, 1H), 5.60 (dd, *J* = 12.4, 2.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.25 (s, 3H), 2.54 (t, *J* = 13.0 Hz, 1H), 2.01 (dt, *J* = 13.7, 2.1 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 162.1, 152.3, 145.9, 142.2, 132.3, 128.8, 128.5, 126.2, 125.2, 124.5, 124.0, 122.8, 117.4 108.5, 108.2, 71.2, 61.5, 47.1, 35.8, 26.3, 13.6; IR (KBr) ν_{max}: 2933, 1717, 1686, 1609, 1491, 1470, 1372, 1349, 1260, 1195, 1109, 1091, 1053, 1021, 815, 752 cm^{-1}; HRMS (ESI): m/z = 414.1091 (calcd for $C_{22}H_{20}ClNO_5$+H^+ = 414.1103).



9o

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-4-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9p

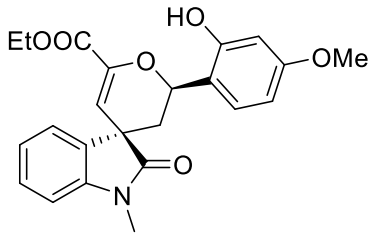


9p

White solid; mp 89–90 ℃; 92% yield (both diastereomers), 93:7 *dr*, 94% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 75/25, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 15.510, t (minor) = 22.949]; $[\alpha]_D^{25}$ = –101.9 (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.15 – 7.05 (m, 2H), 7.04 – 6.98 (m, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.59 (d, *J* = 1.6 Hz, 1H), 5.86 (d, *J* = 1.8 Hz, 1H), 5.61 (dd, *J* = 12.3, 1.9 Hz, 1H), 4.25 (qd, *J* = 7.1, 1.4 Hz, 2H), 3.25 (s, 3H), 2.61 (dd, *J* = 13.7, 12.4 Hz, 1H), 2.20 (s, 3H), 2.04 (dd, *J* = 13.7, 4.0 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 161.9, 153.7, 146.1, 142.3, 139.2, 132.6, 128.4, 125.9, 124.1, 122.7, 120.7, 120.6, 116.9, 108.3, 108.1, 72.4, 61.2, 47.2, 35.9, 26.3, 20.6, 13.6; IR (KBr) ν_{max}: 2977, 1716, 1686, 1646, 1610, 1490, 1470, 1419, 1371, 1296, 1243, 1132, 1107, 1087, 1018, 947,

806, 753, 741, 729, 687 cm^{-1}; HRMS (ESI): m/z = 394.1649 (calcd for $C_{23}H_{23}NO_5+H^+$ = 394.1649).

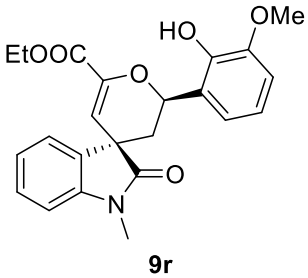
Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-4-methoxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9q



9q

White solid; mp 156–157 ℃; 91% yield (both diastereomers), 98:2 *dr*, 91% *ee* [Daicel Chiralcel IA-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 45.899, t (minor) = 29.764]; $[\alpha]_D^{25}$ = –126.5 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 2H), 7.11 (dd, *J* = 14.6, 7.0 Hz, 2H), 7.02 (d, *J* = 9.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.40 (s, 2H), 5.88 (d, *J* = 1.7 Hz, 1H), 5.58 – 5.51 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.27 (s, 3H), 2.65 (t, *J* = 13.1 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 161.7, 160.3, 155.4, 145.9, 142.3, 132.6, 128.5, 126.9, 124.0, 122.6, 116.0, 108.5, 108.1, 105.8, 102.1, 73.0, 61.3, 54.8, 47.1, 36.0, 26.3, 13.6; IR (KBr) ν_{max}: 3412, 1734, 1705, 1610, 1520, 1491, 1472, 1423, 1372, 1306, 1286,1256, 1234, 1205, 1171, 1110, 1100, 1088, 1036, 1019, 959, 837, 810, 770, 687 cm^{-1}; HRMS (ESI): m/z = 410.1590 (calcd for $C_{23}H_{23}NO_6+H^+$ = 410.1598).

Ethyl(2'*R*,3*R*)-2'-(2-hydroxy-3-methoxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9r

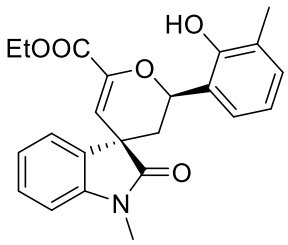


9r

White solid; mp 215–216 ℃; 92% yield, 99:1 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 18.934, t (minor) = 45.530]; $[\alpha]_D^{25}$ = –127.8 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 1H), 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.21 – 7.09 (m, 2H), 6.95 (s, 1H), 6.89 (dt, *J* = 8.0, 4.1 Hz, 2H), 6.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 5.84 (d, *J* = 1.8 Hz, 1H), 5.72 (dd, *J* = 12.1, 2.1 Hz, 1H), 4.25 (qd, *J* = 7.2, 2.8 Hz, 2H), 3.84 (s, 3H), 3.24 (s, 3H), 2.39 (dd, *J* = 13.7, 12.1 Hz, 1H), 2.06 (dt, *J* = 13.9, 2.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.26, 161.81, 146.8, 145.6, 142.3, 141.8, 132.8,

128.2, 125.0, 124.1, 122.6, 119.6, 118.4, 109.7, 107.9, 107.6, 70.1, 60.9, 55.6, 47.3, 36.6, 26.2, 13.7; IR (KBr) ν_{max}: 3376, 1725, 1699, 1609, 1485, 1470, 1374, 1351, 1278, 1250, 1220, 1176, 1139, 1121, 1114, 1093, 1075, 1045, 1020, 969, 779, 755, 740, 730, 687 cm^{-1}; HRMS (ESI): m/z = 410.1590 (calcd for $C_{23}H_{23}NO_6+H^+$ = 410.1598).

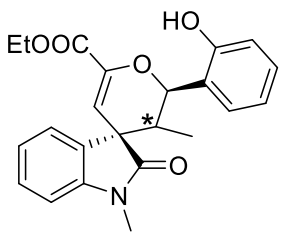
Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-3-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9s



9s

White solid; mp 168–169 ℃; 81% yield, 99:1 *dr*, 95% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 95/5, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 60.586, t (minor) = 55.470]; $[\alpha]_D^{25}$ = –126.9 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.16 – 7.05 (m, 2H), 7.01 – 6.95 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.83 – 6.72 (m, 2H), 5.90 (d, *J* = 1.7 Hz, 1H), 5.56 (dd, *J* = 12.4, 2.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 3H), 2.63 (dd, *J* = 13.7, 12.4 Hz, 1H), 2.25 (s, 3H), 2.10 (dt, *J* = 13.8, 2.0 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 161.4, 152.4, 145.8, 142.3, 132.5, 130.5, 128.5, 125.3, 123.9, 123.8, 123.0, 122.6, 119.6, 108.8, 108.1, 74.2, 61.2, 47.0, 36.0, 26.3, 15.5, 13.7; IR (KBr) ν_{max}: 3214, 1731, 1716, 1683, 1607, 1470, 1372, 1325, 1296, 1269, 1252, 1243, 1205, 1189, 1168, 1107, 1082, 1043, 1015, 963, 845, 787, 761, 687 cm^{-1}; HRMS (ESI): m/z = 416.1478 (calcd for $C_{23}H_{23}NO_5+Na^+$ = 416.1468).

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,3'-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9t

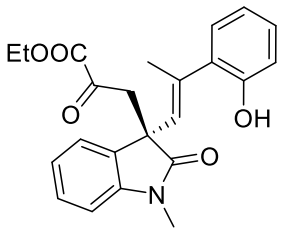


9t

White solid; mp 87–88 ℃; 78% yield (both diastereomers), 92:8 *dr*, 67% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 95/5, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 78.289, t (minor) = 90.193]; $[\alpha]_D^{25}$ = –35.0 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.19 (td, *J* = 7.6, 2.4 Hz, 2H), 6.99 – 6.90 (m, 2H), 6.86 (d, *J* = 8.2 Hz, 1H), 5.92 (s, 1H), 5.46 (d, *J* = 11.1 Hz, 1H), 4.36 – 4.18 (m, 2H), 3.30 (d, *J* = 10.4 Hz, 3H), 1.34 (s, 4H), 0.34 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2,

162.0, 154.1, 145.7, 143.0, 129.3, 129.1, 128.4, 128.2, 125.0, 122.9, 122.6, 119.9, 116.1, 108.9, 107.9, 61.1, 51.9, 38.3, 26.2, 13.6, 10.8; IR (KBr) ν_{max}: 2983, 1716, 1685, 1652, 1609, 1490, 1470, 1458, 1372, 1350, 1273, 1208, 1121, 1087, 1072, 752, 688 cm^{-1}; HRMS (ESI): m/z = 394.1648 (calcd for $C_{23}H_{23}NO_5+H^+$ = 394.1649).

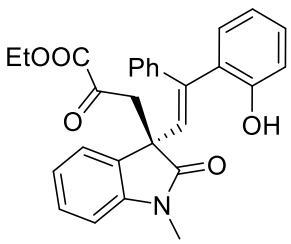
Ethyl-(*S*,*E*)-3-(3-(2-(2-hydroxyphenyl)prop-1-en-1-yl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 9v



9v

White solid; mp 78–79 ℃; 88% yield, 99:1 *E*/*Z*, 0% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 8.115, t (minor) = 12.871]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.04 (m, 2H), 7.03 – 6.94 (m, 2H), 6.90 (dd, *J* = 8.0, 4.9 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 5.79 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.82 (d, *J* = 18.3 Hz, 1H), 3.40 – 3.19 (m, 4H), 1.46 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 177.1, 159.5, 151.8, 143.2, 137.2, 130.9, 130.3, 128.7, 128.3, 128.2, 127.8, 123.8, 122.8, 119.5, 115.6, 108.1, 62.3, 49.9, 46.9, 26.2, 17.9, 13.4; IR (KBr) ν_{max}: 2926, 1718, 1686, 1609, 1490, 1470, 1447, 1373, 1261, 1090, 1053, 1022, 836, 751 cm^{-1}; HRMS (ESI): m/z = 394.1646 (calcd for $C_{23}H_{23}NO_5+H^+$ = 394.1649).

Ethyl-(*S*,*E*)-3-(3-(2-(2-hydroxyphenyl)-2-phenylvinyl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 9w

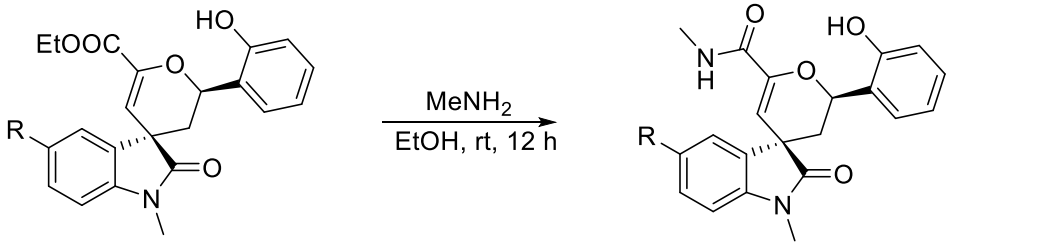


9w

White solid; mp 94–95 ℃; 65% yield, 90:10 *E*/*Z*, 60% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 9.175, t (minor) = 12.384]; $[\alpha]_D^{25}$ = +81.2 (*c* 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.17 (td, *J* = 7.8, 1.3 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.07 – 6.89 (m, 5H), 6.80 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.73 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.70 – 6.66 (m, 2H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.26 (s, 1H), 4.22 (qd, *J* = 7.2, 1.5 Hz, 2H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.25 (dd, *J* = 17.9, 1.4 Hz, 1H), 2.84 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 176.5, 159.4, 152.6, 142.7, 141.6, 137.9, 131.7, 129.8, 129.6, 128.6,

128.5, 128.4, 128.0, 127.0, 126.9, 123.8, 122.4, 119.4, 116.0, 107.9, 99.5, 62.3, 50.6, 46.2, 25.7, 13.4; IR (KBr) ν_{max}: 3186, 1744, 1718, 1685, 1610, 1493, 1470, 1446, 1391, 1350, 1253, 1234, 1055, 830, 751, 736, 700 cm^{-1}; HRMS (ESI): m/z = 456.1812 (calcd for $C_{28}H_{25}NO_5+H^+$ = 456.1805).

2.6 General procedure for the preparation of 12

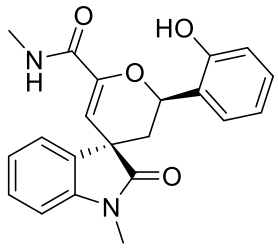


R = H: **9a**, 98:2 *dr*, 93% *ee*
R = Br: **9i**, 99:1 *dr*, 99% *ee*

R = H: **12a**, 92% yield, 99:1 *dr*, 93% *ee*
R = Br: **12b**, 90% yield, 96:4 *dr*, 99% *ee*

9a or **9i** (0.1 mmol) was added into a vessel, methylamine alcohol solution (2 mL) was added *via* syringe and the system was stirred at room temperature for 12 h. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/petroleum ether (1/1) as eluent to give **12a** or **12b** as a white solid.

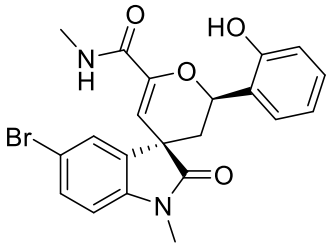
(2'*R*,3*R*)-2'-(2-Hydroxyphenyl)-N,1-dimethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxamide 12a



12a

White solid; mp 151–152 ℃; 92% yield, 99:1 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.272, t (minor) = 8.579]; $[\alpha]_D^{25}$ = –105.4 (*c* 0.21, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.34 – 7.11 (m, 3H), 7.07 – 6.88 (m, 2H), 6.86 – 6.63 (m, 4H), 5.68 (s, 1H), 5.59 (d, *J* = 12.1 Hz, 1H), 3.10 (s, 3H), 2.68 (d, *J* = 4.9 Hz, 3H), 2.38 (t, *J* = 13.0 Hz, 1H), 1.86 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 162.3, 153.4, 148.4, 142.0, 132.9, 128.9, 128.1, 126.3, 125.2, 124.0, 122.7, 119.5, 115.5, 108.0, 104.1, 70.7, 47.4, 36.6, 26.3, 25.6; IR (KBr) ν_{max}: 3276, 2961, 2925, 2301, 1698, 1645, 1608, 1540, 1490, 1457, 1372, 1351, 1291, 1262, 1127, 1039, 1020, 979, 750, 686, 624, 612 cm^{-1}; HRMS (ESI): m/z = 387.1303 (calcd for $C_{21}H_{20}N_2O_4+Na^+$ = 387.1315).

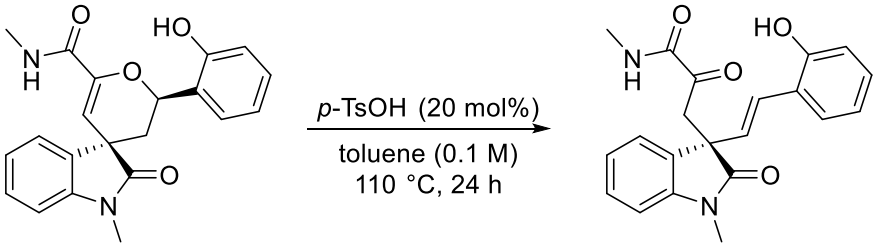
(2'*R*,3*R*)-5-Bromo-2'-(2-hydroxyphenyl)-N,1-dimethyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxamide 12b



12b

White solid; mp 283–284 ℃; 90% yield (both diastereomers), 96:4 *dr*, 99% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 16.811, t (minor) = 8.168]; $[\alpha]_D^{25}$ = –200.9 (*c* 0.11, EtOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 7.94 (q, *J* = 4.7 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.54 (ddd, *J* = 17.2, 8.0, 1.9 Hz, 2H), 7.16 (td, *J* = 7.7, 1.8 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.89 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.57 (dd, *J* = 8.8, 5.1 Hz, 1H), 5.50 (s, 1H), 3.15 (s, 3H), 2.69 (d, *J* = 4.7 Hz, 3H), 2.08 – 1.99 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.6, 161.4, 153.6, 149.7, 142.2, 135.5, 131.1, 128.7, 126.8, 126.6, 126.0, 119.2, 115.0, 114.2, 110.9, 102.8, 70.6, 47.2, 37.0, 26.6, 25.8; IR (KBr) ν_{max}: 3417, 2924, 1724, 1643, 1605, 1545, 1506, 1456, 1359, 1343, 1274, 1256, 1173, 1134, 1081, 1057, 1036, 1015, 976, 863, 812, 768, 614 cm^{-1}; HRMS (ESI): m/z = 465.0413 (calcd for $C_{21}H_{19}BrN_2O_4$+Na^+ = 465.0420).

2.7 Procedure for the preparation of 13

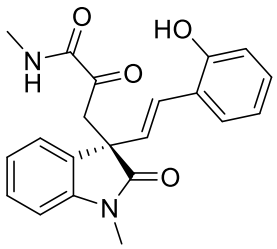


12a, 99:1 *dr*, 93% *ee* **13**, 63% yield, 92% *ee*

Under N_2 atmosphere, **12a** (0.1 mmol) was added into a vessel, anhydrous toluene (2 mL) was added *via* syringe and the system was stirred at 110 ℃ for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/petroleum ether (1/1) as eluent to give **13** as a white solid.

(*S*,*E*)-3-(3-(2-Hydroxystyryl)-1-methyl-2-oxoindolin-3-yl)-N-methyl-2-oxopropan

amide 13



13

White solid; mp 120–121 ℃; 63% yield, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 26.367, t (minor) = 33.210]; $[\alpha]_D^{25}$ = –108.7 (*c* 0.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.82 – 6.69 (m, 3H), 6.64 (d, *J* = 16.5 Hz, 2H), 6.35 (d, *J* = 16.1 Hz, 1H), 4.06 (d, *J* = 19.1 Hz, 1H), 3.66 (d, *J* = 19.0 Hz, 1H), 3.29 (s, 3H), 2.78 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 177.5, 159.8, 153.2, 143.6, 129.7, 128.6, 128.4, 128.1, 127.4, 125.9, 123.2, 122.9, 122.2, 119.9, 115.6, 108.0, 51.5, 42.7, 26.2, 25.4; IR (KBr) ν_{max}: 3416, 2914, 1726, 1653, 1612, 1536, 1511, 1453, 1327, 1323, 1277, 1286, 1144, 1131, 1036, 1014, 977, 812, 777, 618 cm^{-1}; HRMS (ESI): m/z = 387.1306 (calcd for $C_{21}H_{20}N_2O_4+Na^+$ = 387.1315).

3. X-ray data of chiral 3c, 4j, 9i and 12b

3.1 Crystal structure determination of compound 3c:

Crystal data and structure refinement for **3c**:

Empirical formula	$C_{18}H_{18}BrNO_5$
Formula weight	408.24
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *P* 21 21 21
Unit cell dimensions	*a* = 5.7193 (6) Å, *α* = 90 deg.
	b = 17.0464 (16) Å, *β* = 90 deg.
	c = 18.2530 (18) Å, *γ* = 90 deg.
Volume	1779.5(3) $Å^3$
Z, Calculated density	4, 1.524 Mg/cm^3

Absorption coefficient	2.338 mm^{-1}
F(000)	832
Crystal size	0.600 × 0.150 × 0.060 mm
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	2.531 to 27.462 deg.
Limiting indices	$-4 \le h \le 7$, $-22 \le k \le 20$, $-23 \le l \le 10$
Reflections collected / unique	6271/3932 [*R*(int) = 0.0797]
Completeness to theta = 25.24	99.5%
Data / restraints / parameters	3932/0/228
Goodness-of-fit on F^2	1.139
Final R indexes [I>=2σ (I)]	R_1 = 0.0898, wR_2 = 0.2169
Final R indexes [all data]	R_1 = 0.1554, wR_2 = 0.2537
Largest diff. peak/hole / e$Å^{-3}$	0.713 and –1.121
Absolute structure parameter	0.080(19)

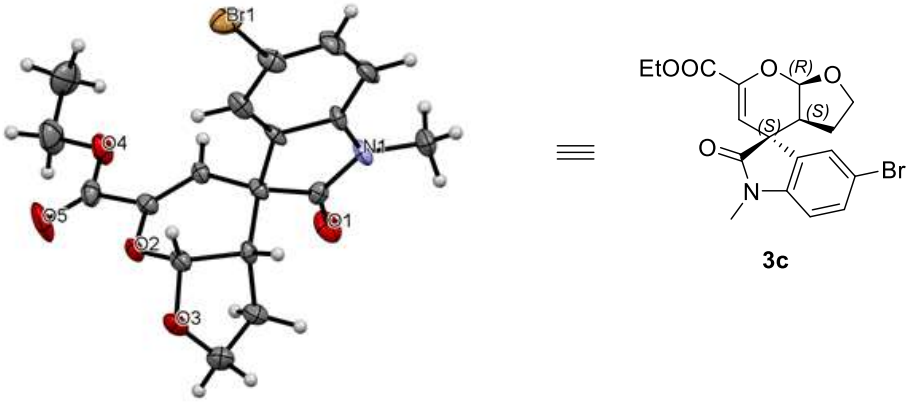


Figure S1. OPTEP drawing of **3c** (40% thermal ellipsoids)

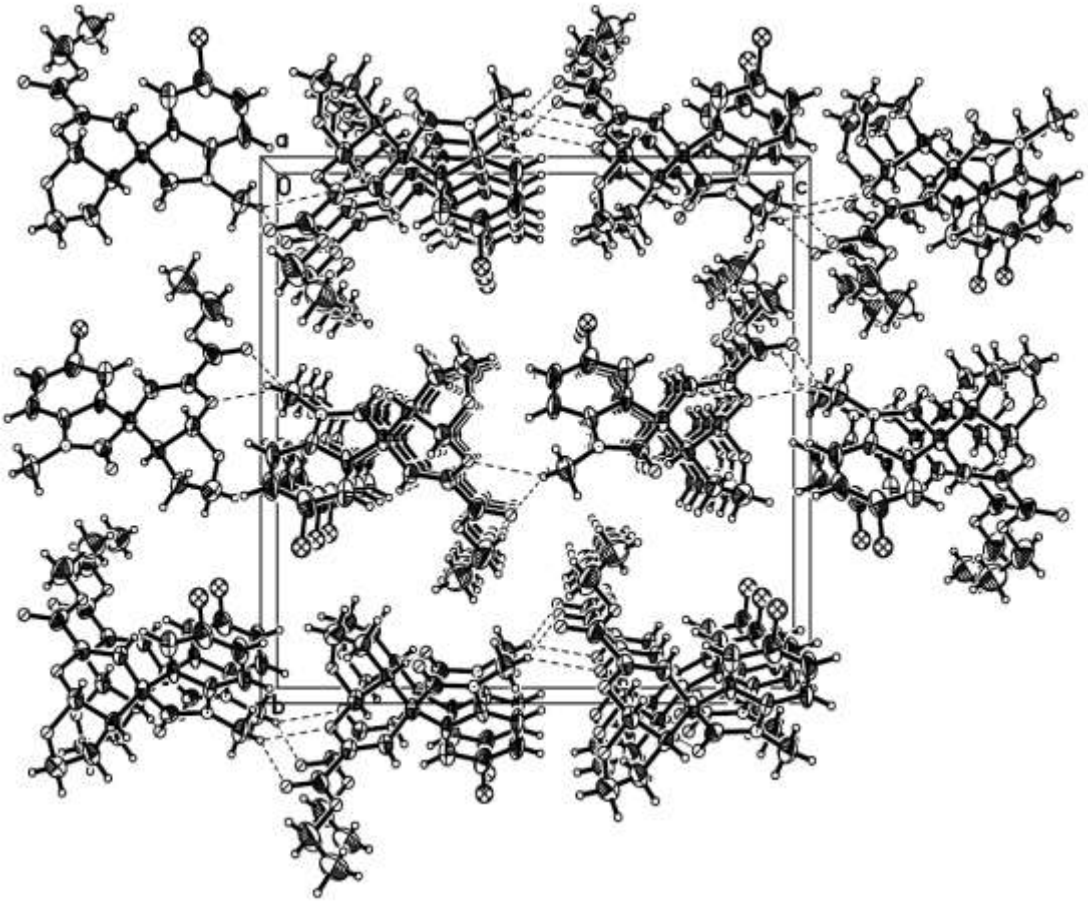


Figure S2. Packing of moleculars in a unit cell of **3c**

The crystal was prepared from the solution of **3c** in DCM and *n*-hexane. CCDC 1550834 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

3.2 Crystal structure determination of compound 4j:

Crystal data and structure refinement for **4j**:

Empirical formula	$C_{19}H_{20}BrNO_5$
Formula weight	422.26
Temperature	120 K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *P* 21 21 21

Unit cell dimensions	a = 6.12950(10) Å, α = 90 deg.
	b = 15.9652(4) Å, β = 90 deg.
	c = 18.5922(5) Å, γ = 90 deg.
Volume	1819.41(7) Å^3
Z, Calculated density	4, 1.542 Mg/cm^3
Absorption coefficient	2.289 mm^{-1}
F(000)	864
Crystal size	0.34 × 0.25 × 0.22 mm
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	2.54 to 27.44 deg.
Limiting indices	$-7 \le h \le 7$, $-29 \le k \le 20$, $-24 \le l \le 24$
Reflections collected / unique	28025/4160 [R(int) = 0.0696]
Completeness to theta = 25.242	99.7%
Data / restraints / parameters	4160/0/237
Goodness-of-fit on F^2	1.197
Final R indexes [I>=2σ (I)]	R_1 = 0.0297, wR_2 = 0.0606
Final R indexes [all data]	R_1 = 0.0391, wR_2 = 0.0652
Largest diff. peak/hole / eÅ^{-3}	0.304 and -0.329
Absolute structure parameter	0.032(6)

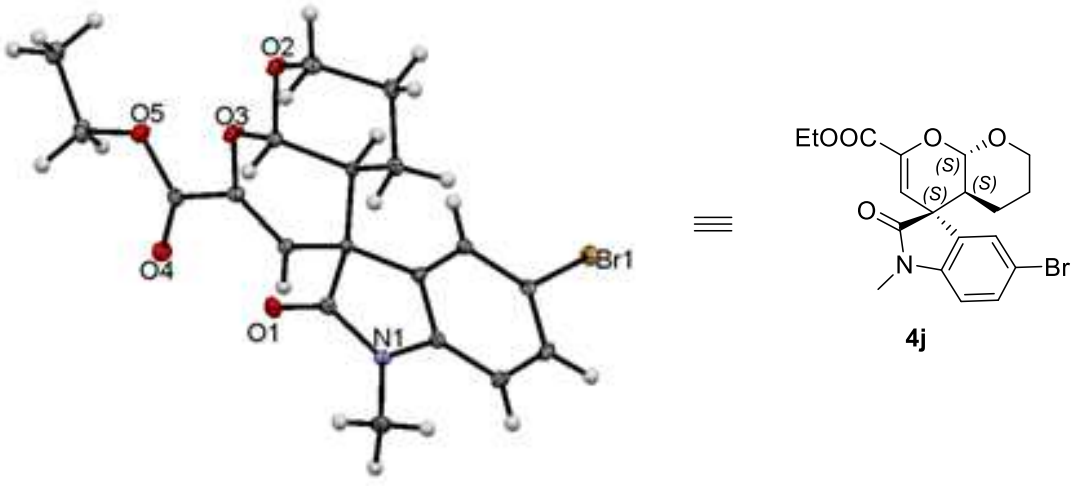


Figure S1. OPTEP drawing of **4j** (40% thermal ellipsoids)

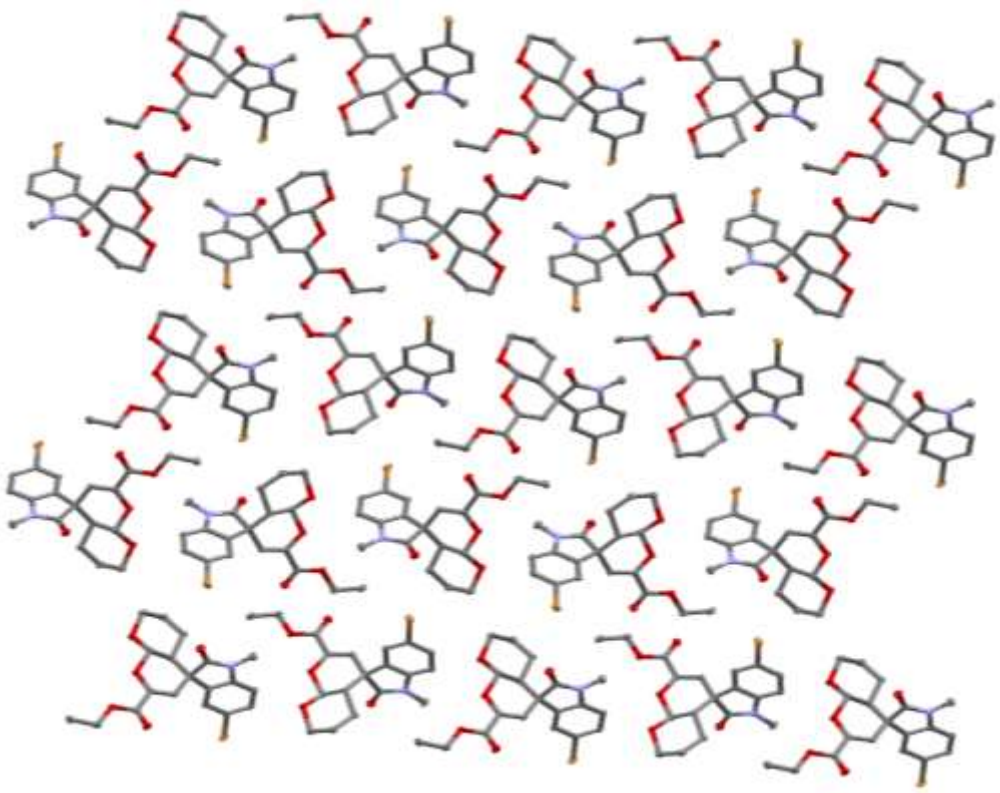


Figure S2. Packing of moleculars in a unit cell of **4j**

The crystal was prepared from the solution of **4j** in DCM and *n*-hexane. CCDC 2040769 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

3.3 Crystal structure determination of compound 9i:

Crystal data and structure refinement for **9i**:

Empirical formula	$C_{22}H_{20}BrNO_5$ $CHCl_3$ (M+$CHCl_3$)
Formula weight	577.66 (M+ $CHCl_3$)
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 21
Unit cell dimensions	a = 9.6151(4) Å, α = 90 deg.
	b = 14.8507(5) Å, β = 118.7867(12) deg.
	c = 9.7033(4) Å, γ = 90 deg.

Volume	1214.32(8) $Å^3$
Z, Calculated density	2, 1.580 Mg/cm^3
Absorption coefficient	2.058 mm^{-1}
F(000)	584
Crystal size	0.25 x 0.23 x 0.20 mm
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	2.395 to 27.513 deg.
Limiting indices	$-12 \le h \le 12$, $-19 \le k \le 19$, $-12 \le l \le 12$
Reflections collected / unique	19735/5578 [R(int) = 0.0334]
Completeness to theta = 27.51	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5486/1/301
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	$R_1 = 0.0297$, $wR_2 = 0.1018$
Final R indexes [all data]	$R_1 = 0.0420$, $wR_2 = 0.0606$
Largest diff. peak/hole / $eÅ^{-3}$	0.968 and - 0.901
Absolute structure parameter	0.021(4)

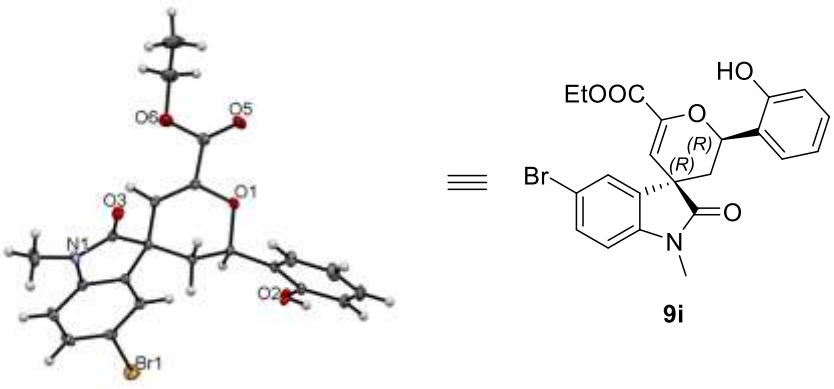


Figure S1. OPTEP drawing of **9i** (40% thermal ellipsoids)

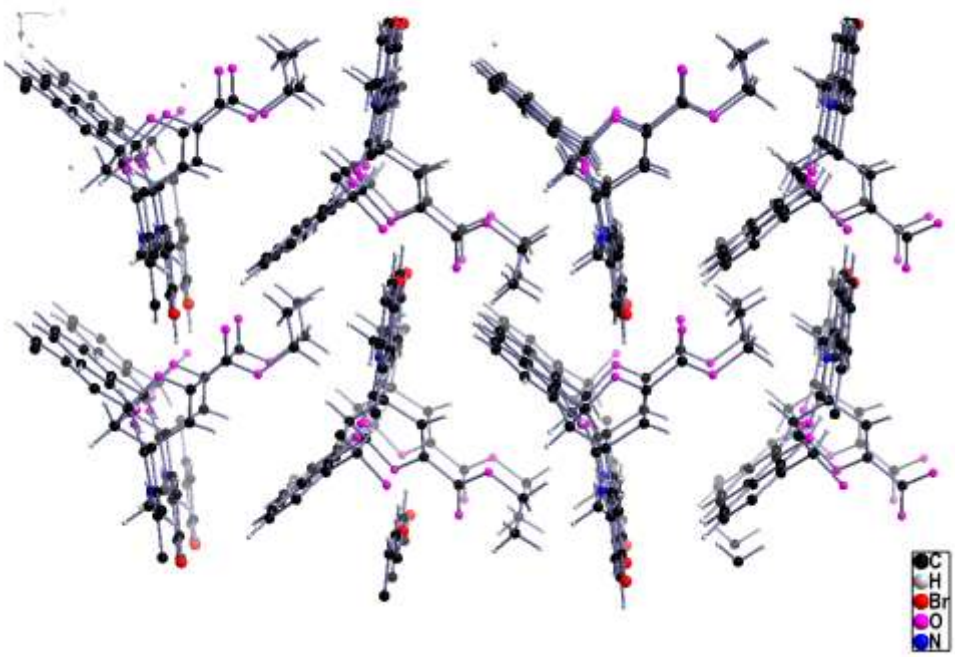


Figure S2. Packing of moleculars in a unit cell of **9i**

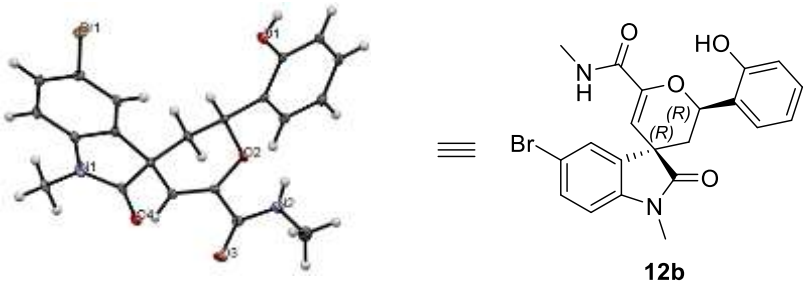
The crystal was prepared from the solution of **9i** in $CHCl_3$. CCDC 1543203 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

3.4 Crystal structure determination of compound 12b:

Crystal data and structure refinement for **12b**:

Empirical formula	$C_{21}H_{19}BrN_2O_4$
Formula weight	443.29
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2
Unit cell dimensions	a = 16.2892(11) Å, α = 90 deg.
	b = 8.2430(5) Å, β = 108.044(2) deg.
	c = 15.3465(11) Å, c = 90 deg.
Volume	108.044(2) $Å^3$
Z, Calculated density	4, 1.503 Mg/cm^3

Absorption coefficient	2.128 mm^{-1}
F(000)	904
Crystal size	0.25 x 0.15 x 0.05 mm
Radiation	MoK\α (λ = 0.71073)
Theta range for data collection	2.57 to 27.55 deg.
Limiting indices	-21≤ h ≤ 20, -10 ≤ k ≤ 10, -19≤ l ≤ 19
Reflections collected / unique	16441/4468 [R(int) = 0.0698]
Completeness to theta = 27.55	99.4%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4468/1/260
Goodness-of-fit on F^2	0.984
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0660
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.0693
Largest diff. peak/hole / $eÅ^{-3}$	0.301 and –0.553
Absolute structure parameter	0.005(7)



12b

Figure S3. OPTEP drawing of **12b** (40% thermal ellipsoids)

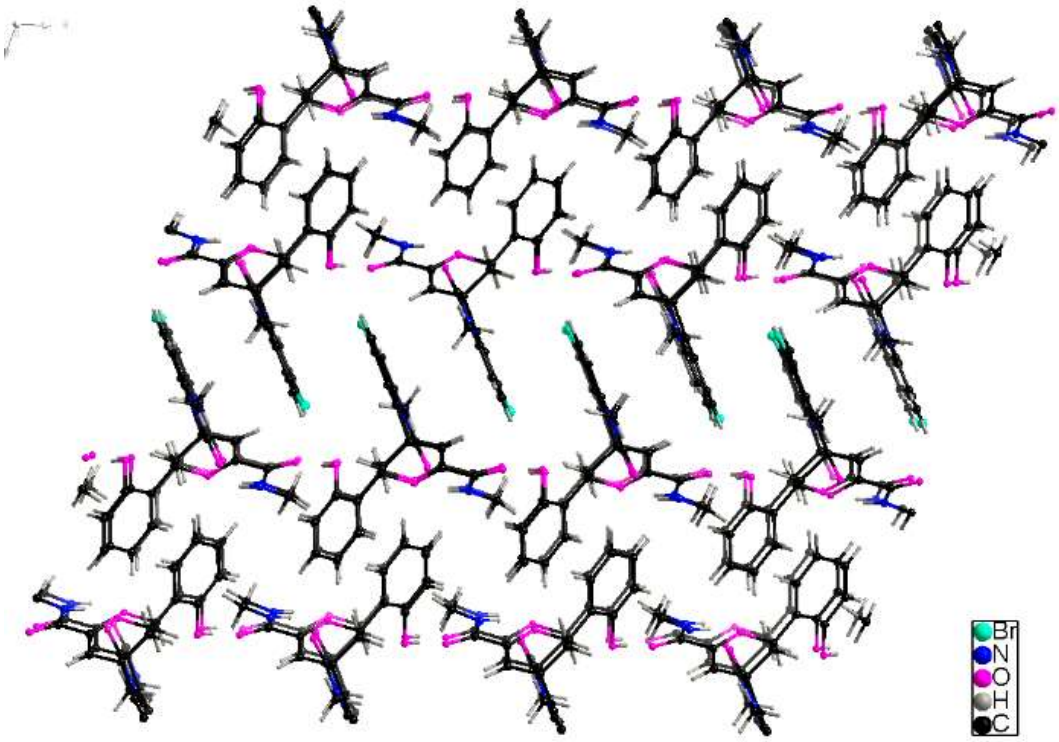
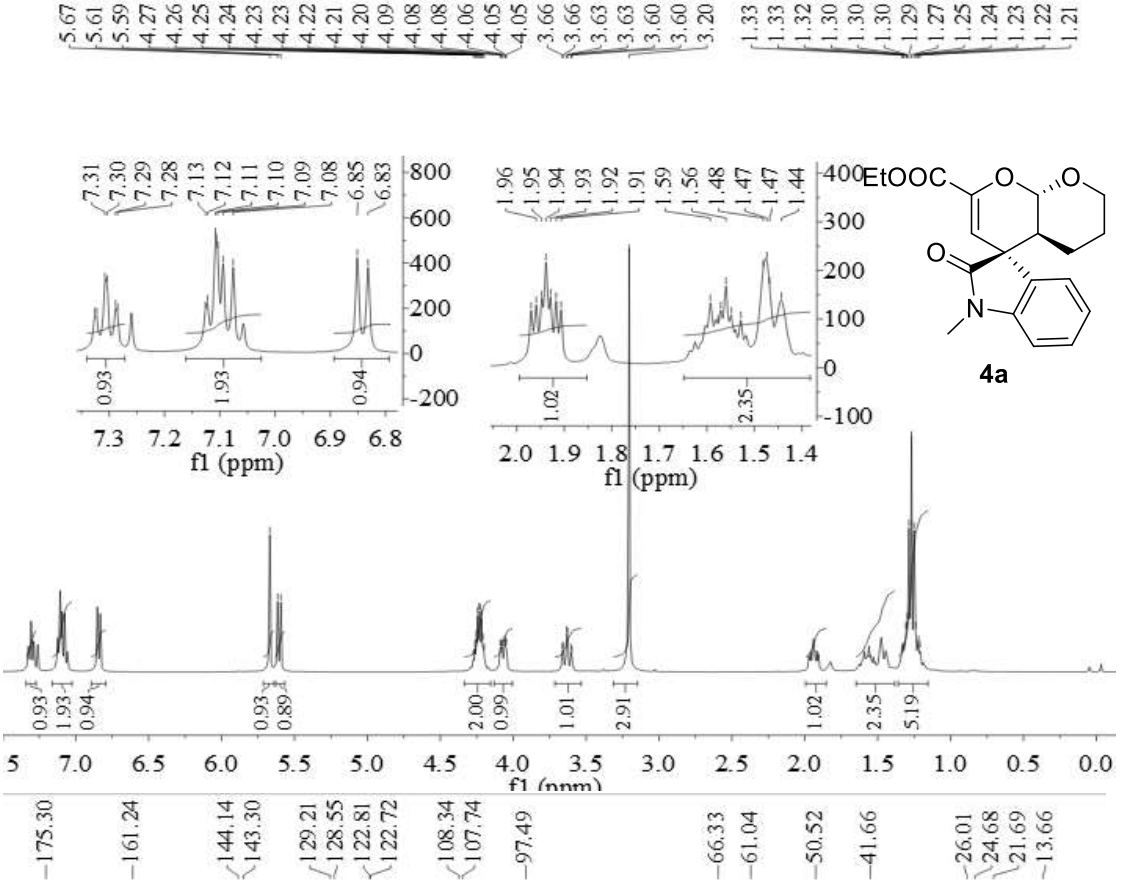


Figure S4. Packing of moleculars in a unit cell of **12b**

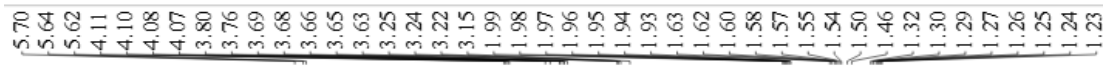
The crystal was prepared from the solution of **12b** in EtOH. CCDC 1549570 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

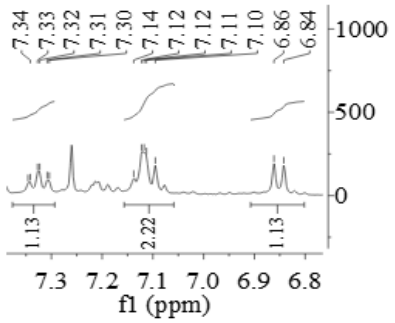
4. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

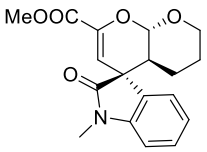
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4a



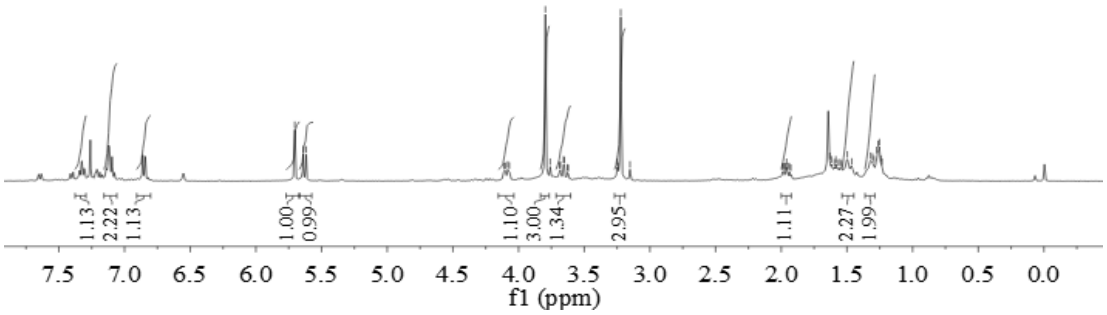
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4b

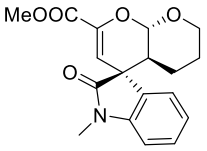




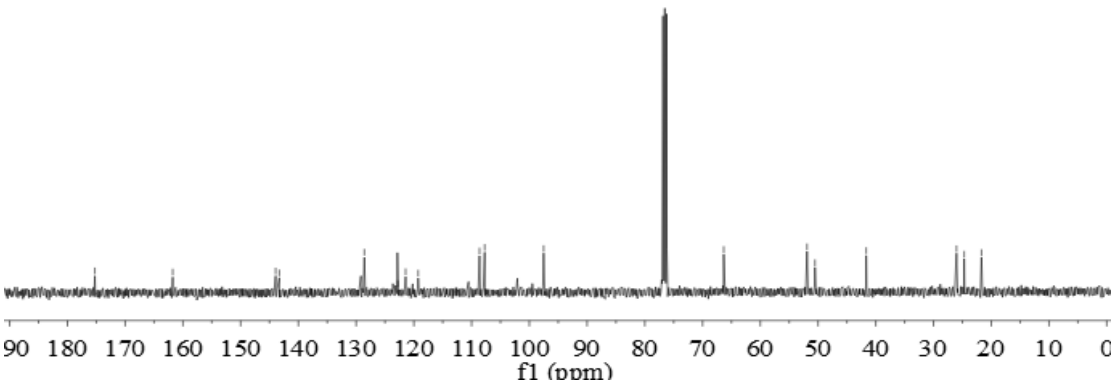


4b

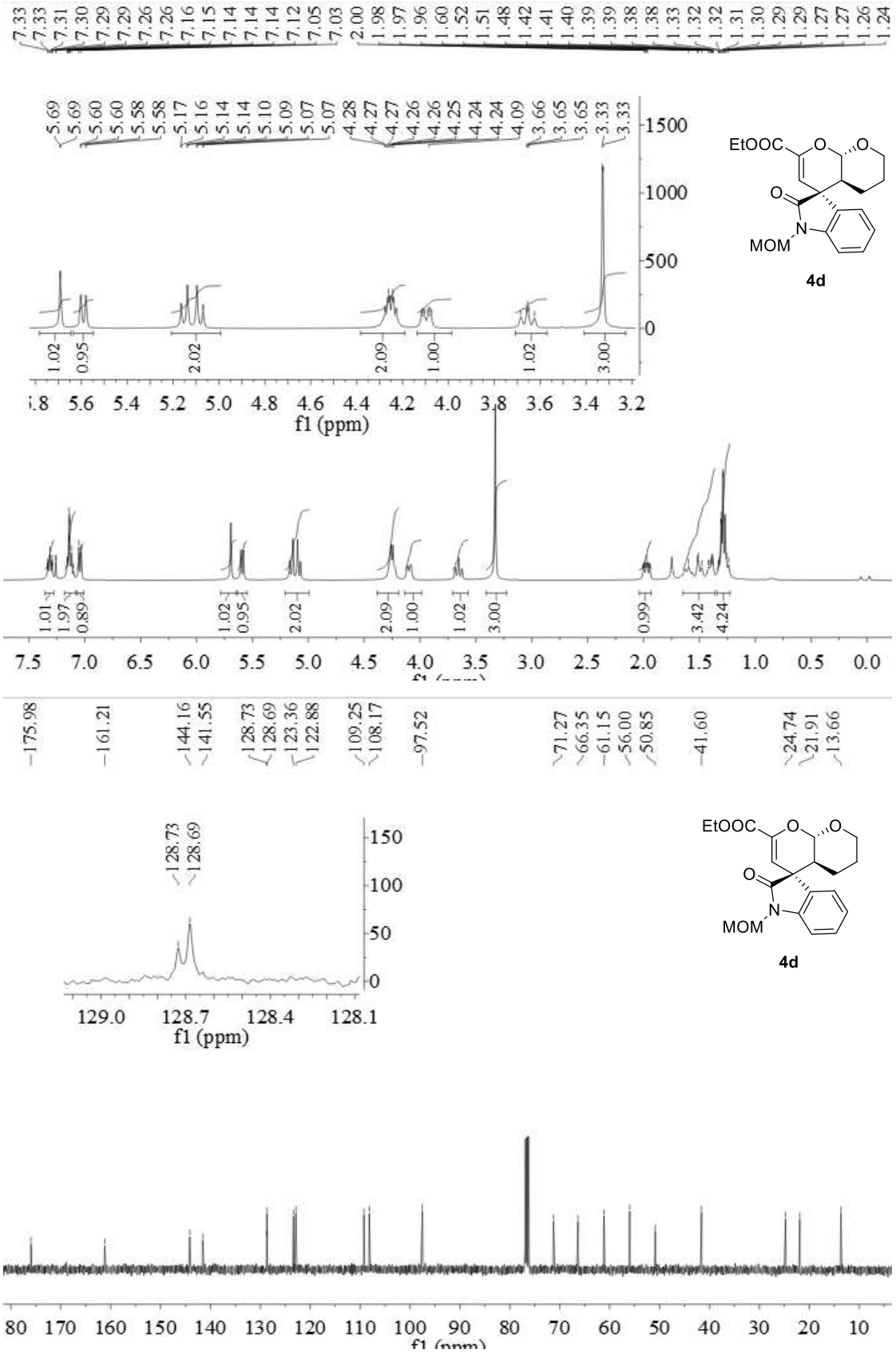




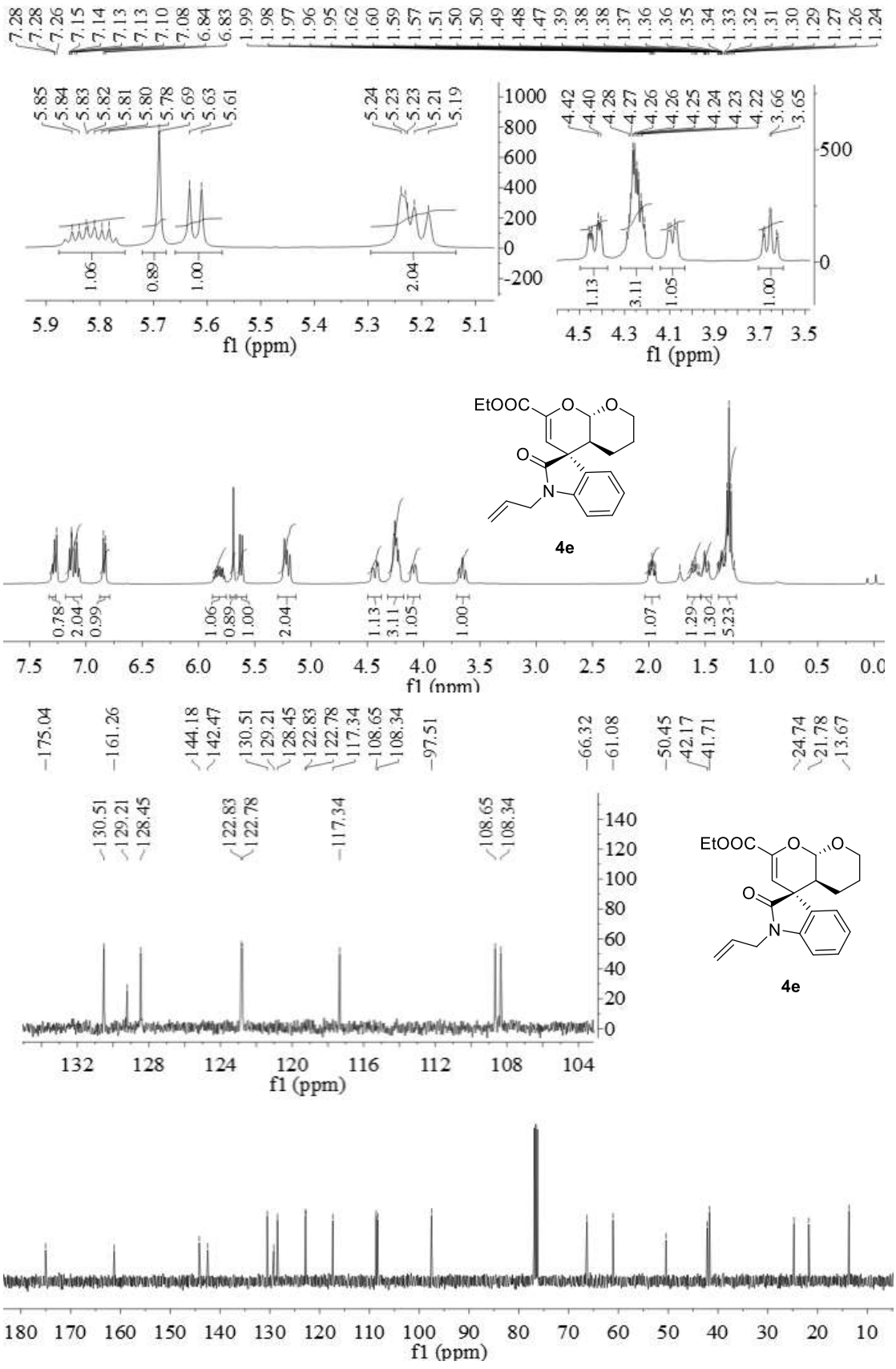
4b



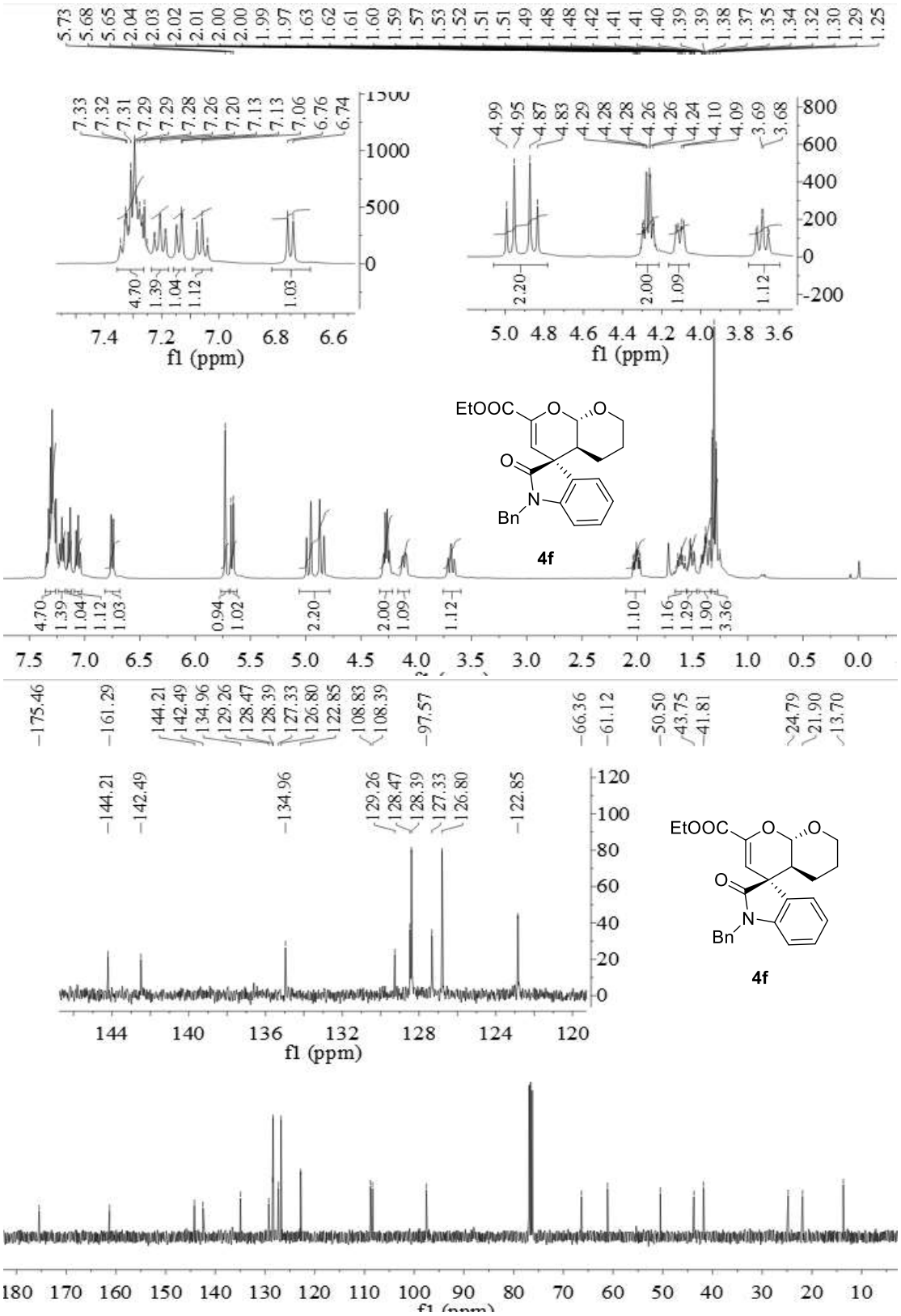
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-(methoxymethyl)-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4d



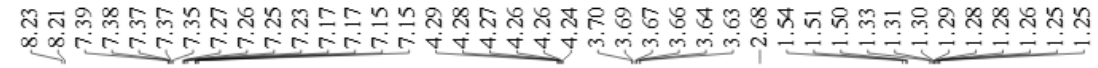
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-allyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4e

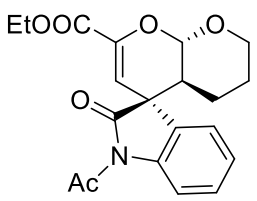


Ethyl-(3*S*,4a'*S*,8a'*S*)-1-benzyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4f

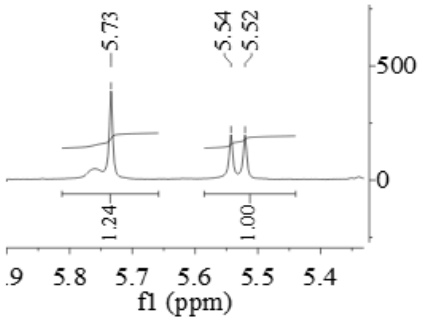


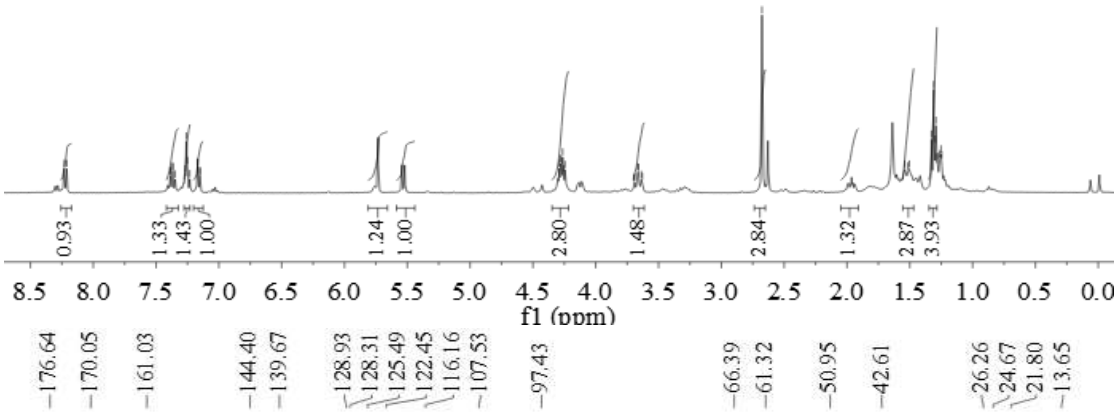
Ethyl-(3*S*,4a'*S*,8a'*S*)-1-acetyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4g

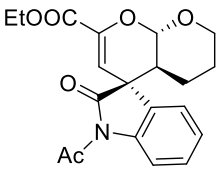




4g

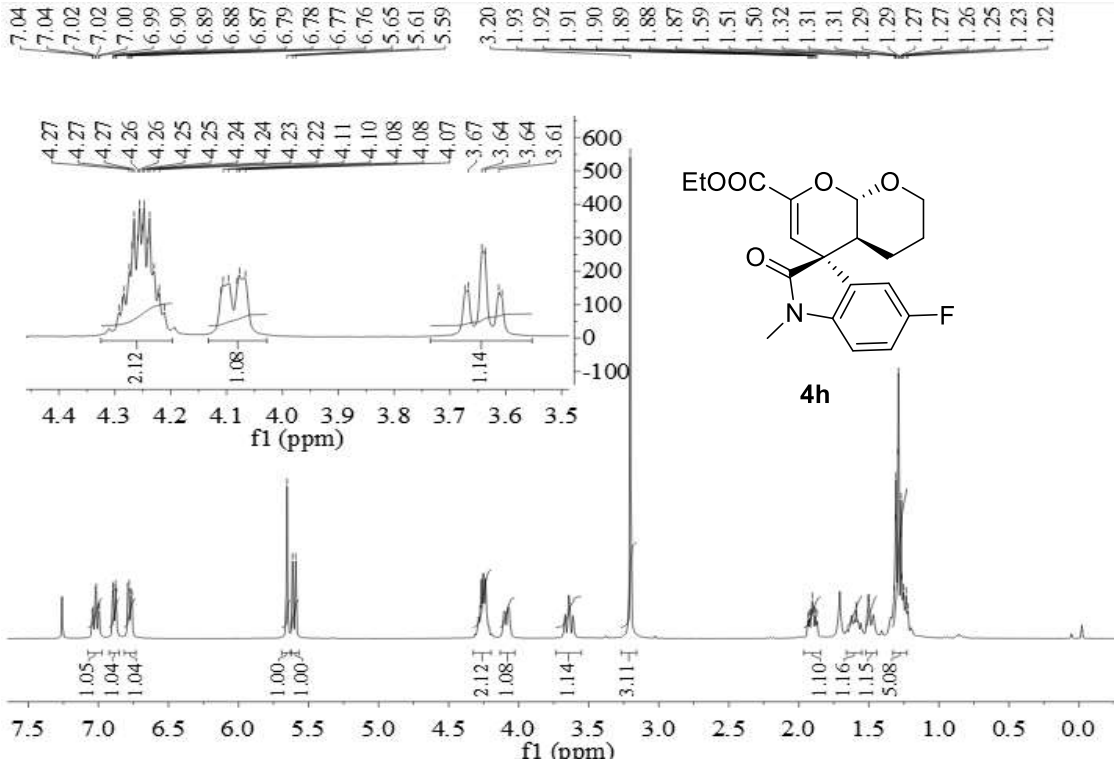


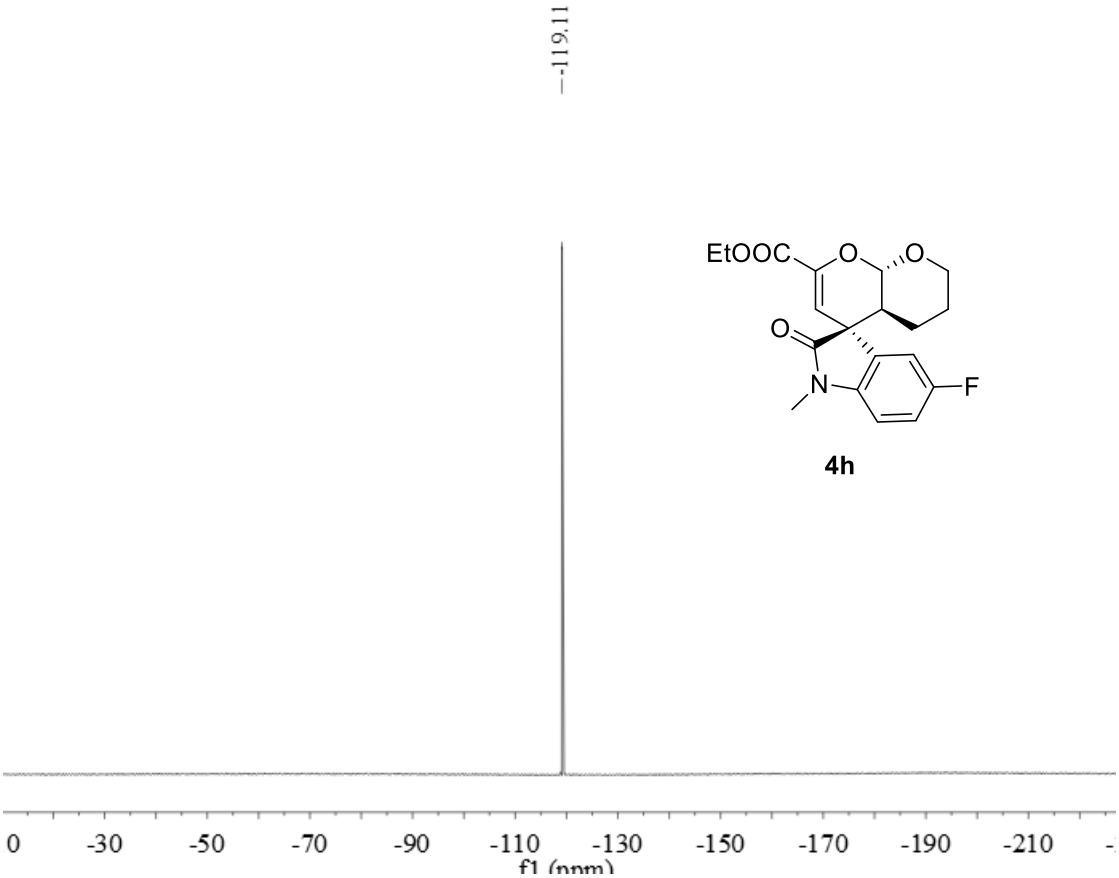


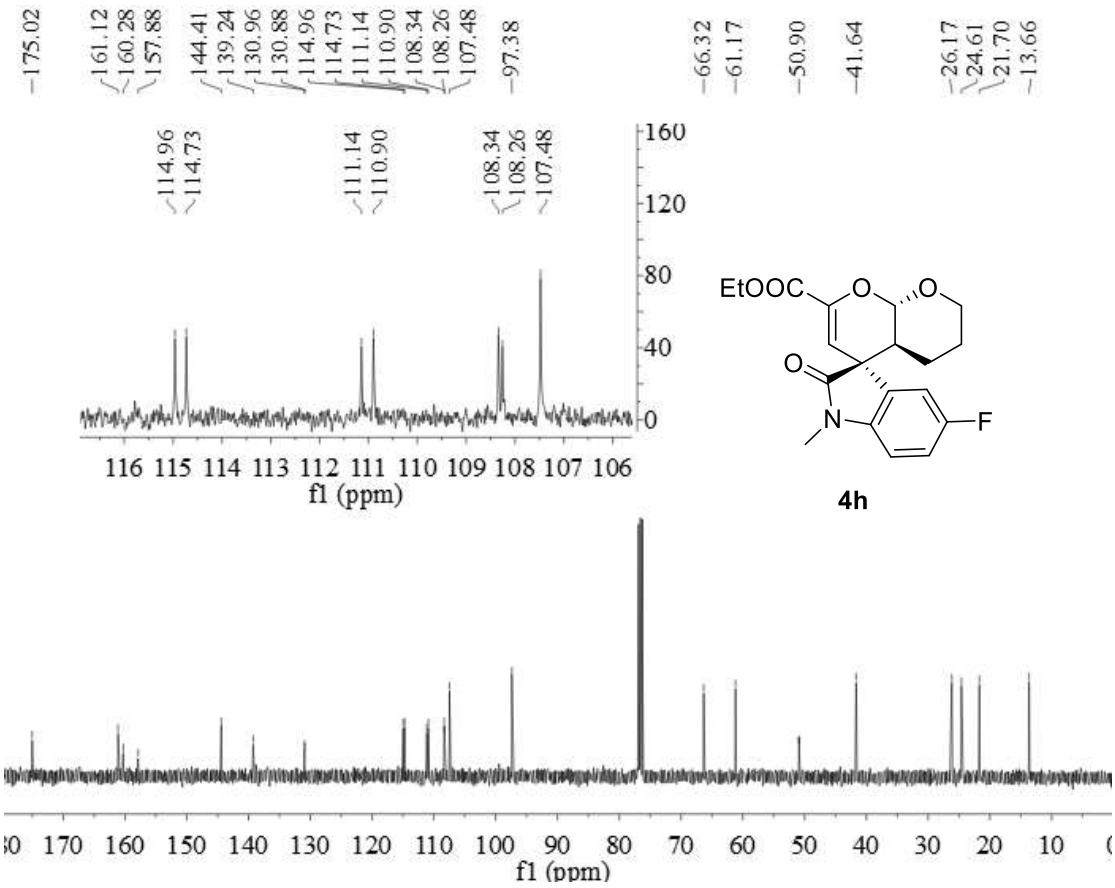


4g

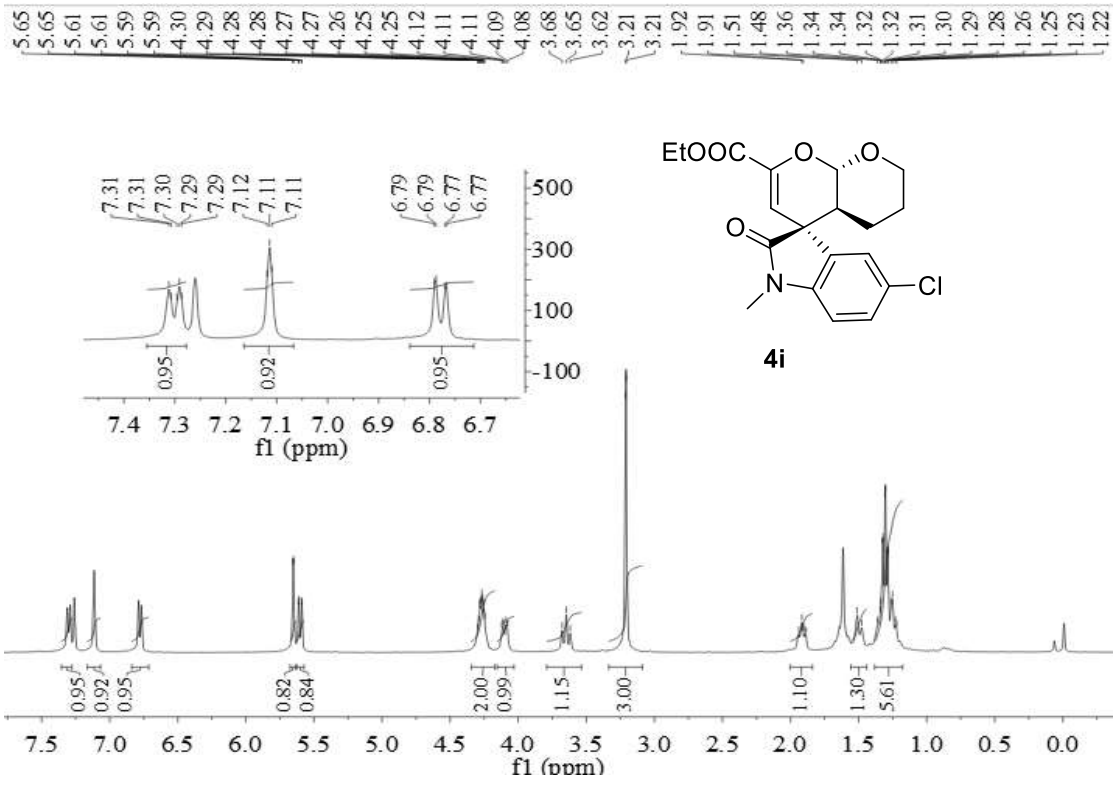
Ethyl-(3*S*,4a'*S*,8a'*S*)-5-fluoro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4h

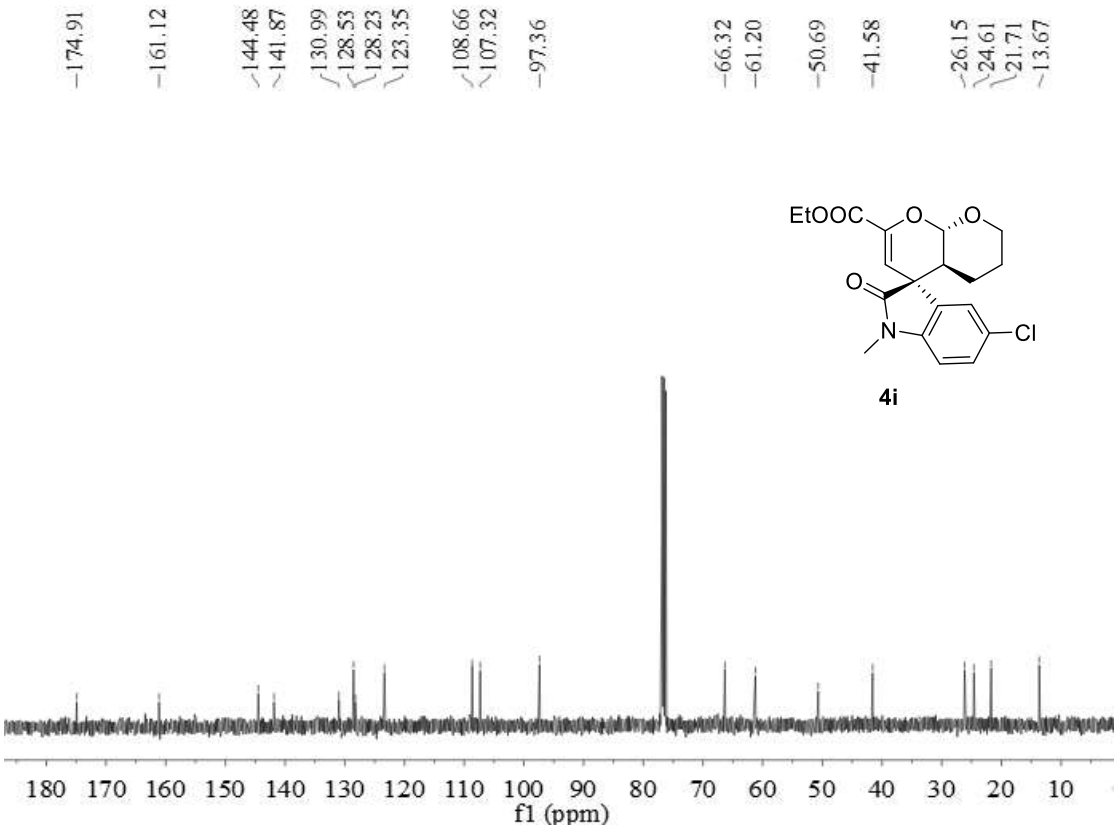




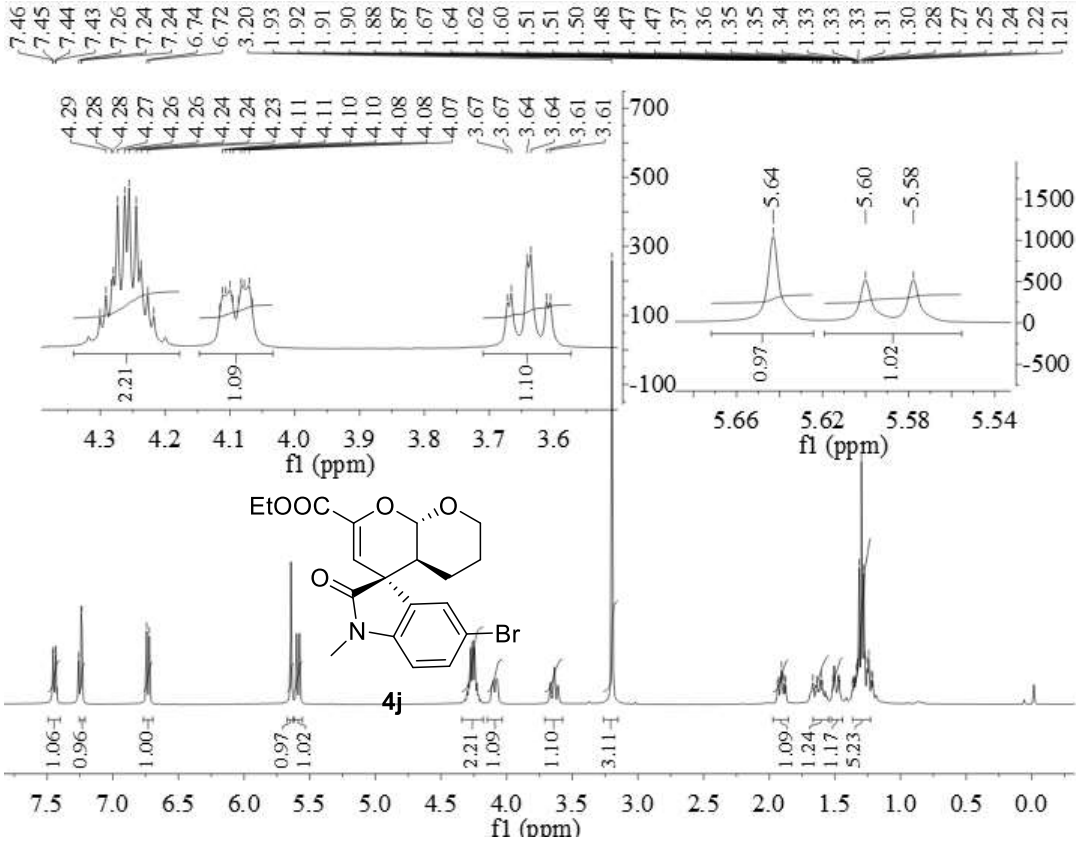


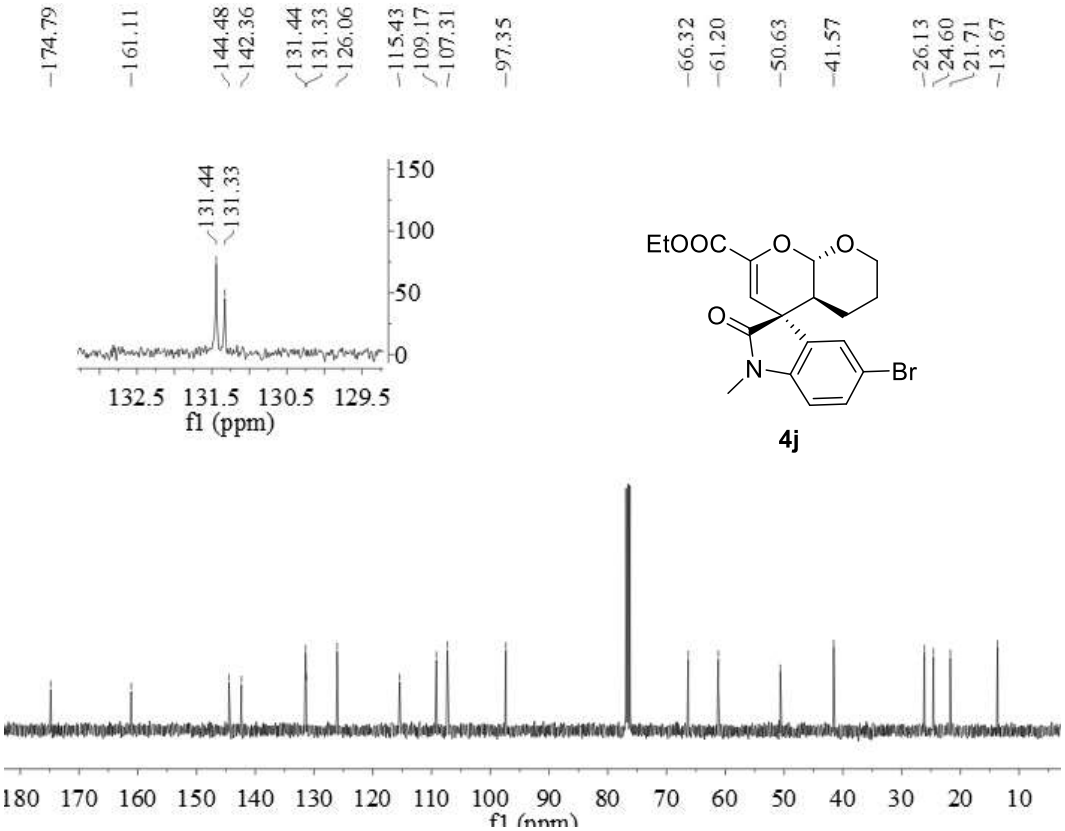
Ethyl-(3*S*,4a'*S*,8a'*S*)-5-chloro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4i



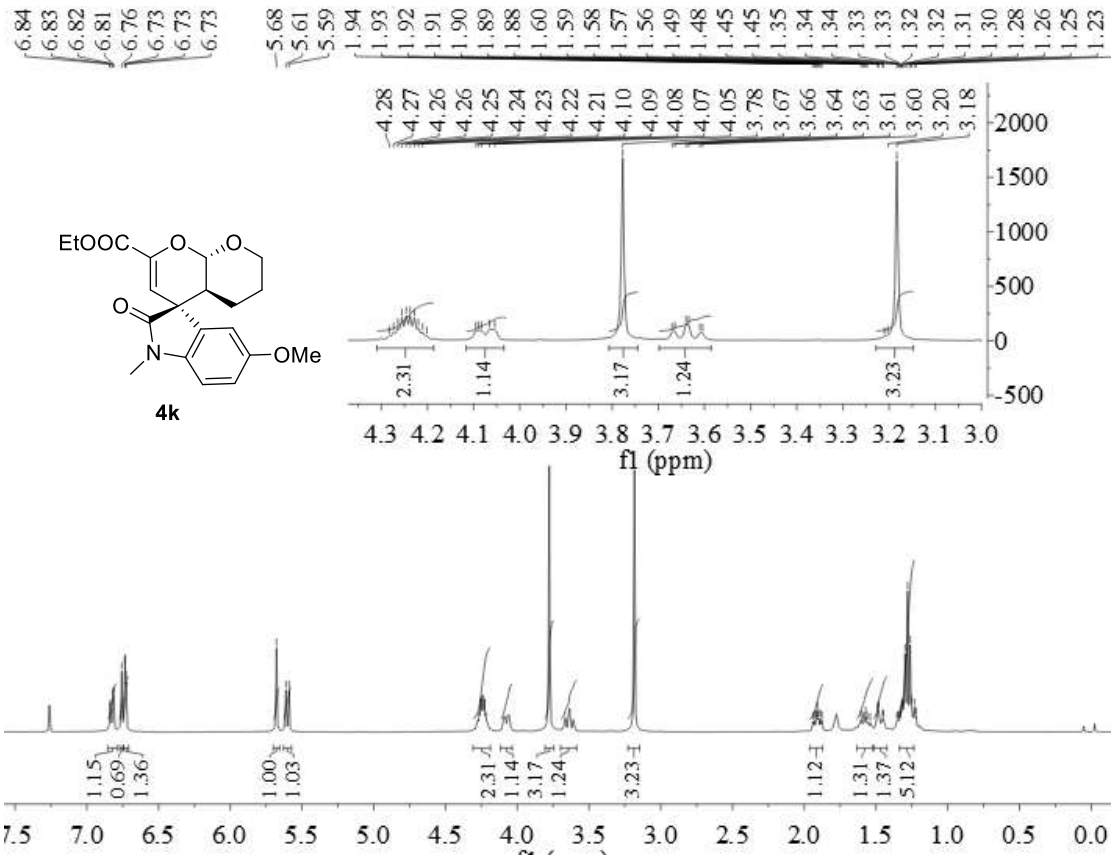


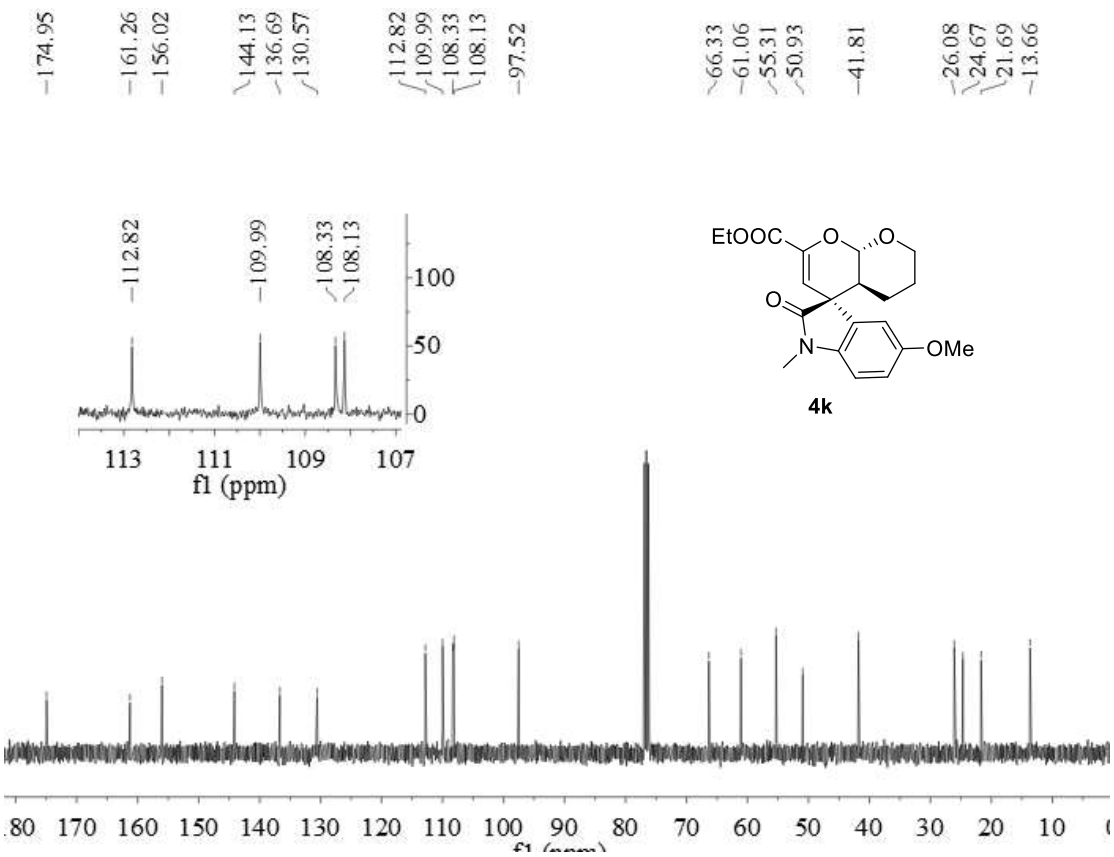
Ethyl-(3*S*,4a'*S*,8a'*S*)-5-bromo-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4j



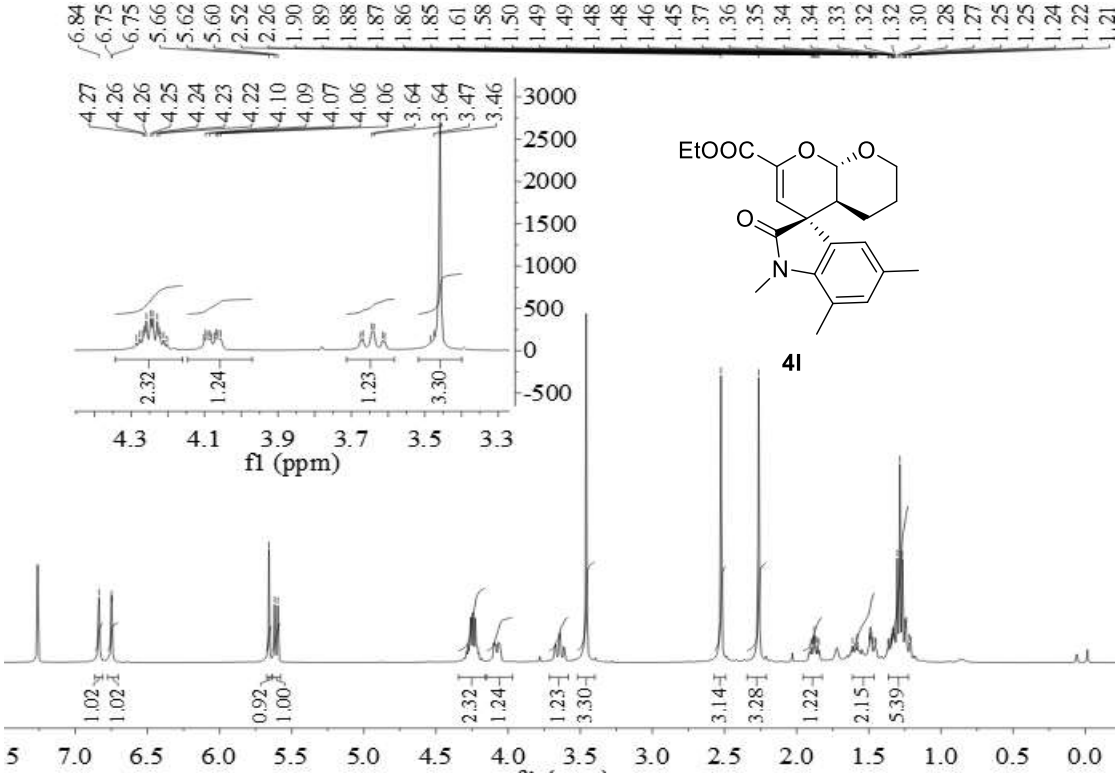


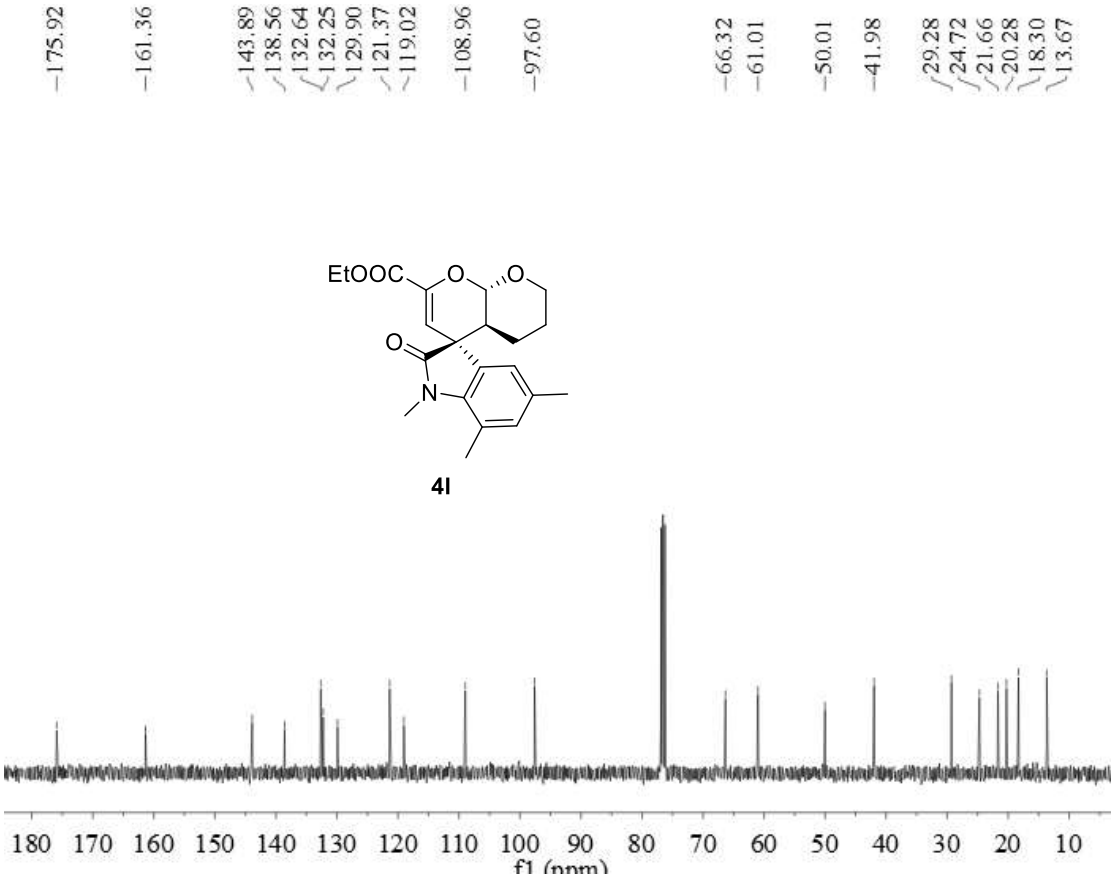
Ethyl-(3*S*,4a'*S*,8a'*S*)-5-methoxy-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4k



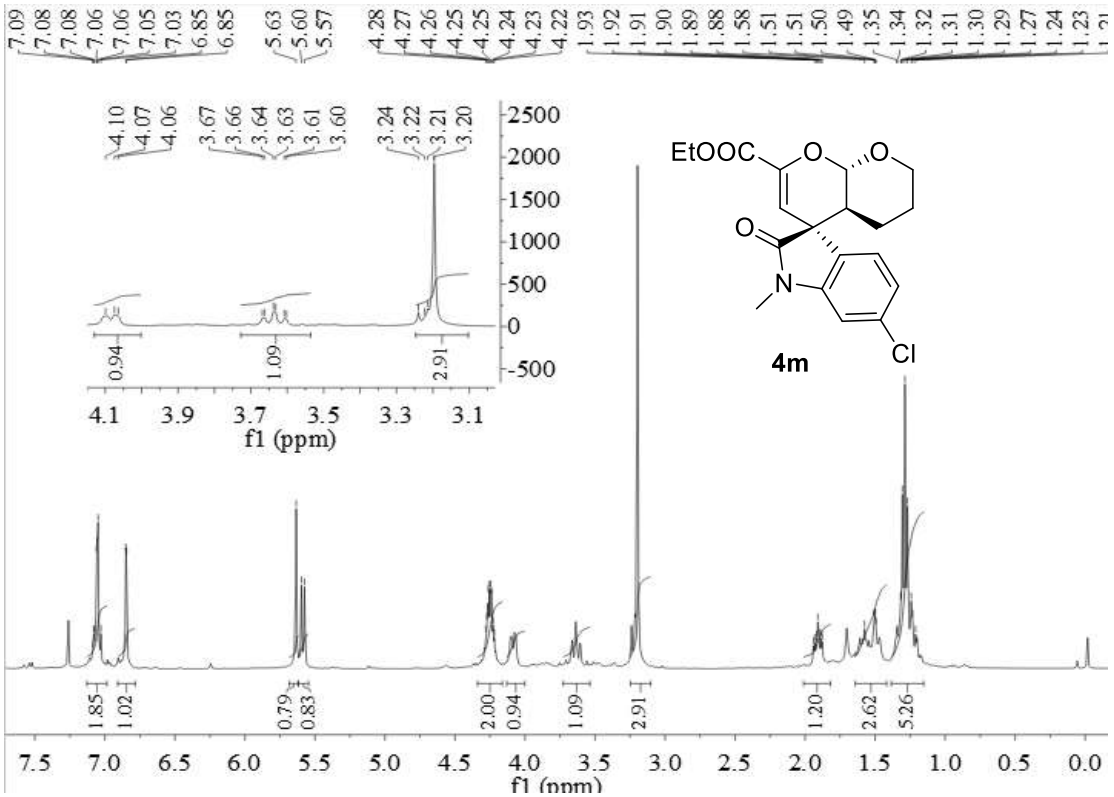


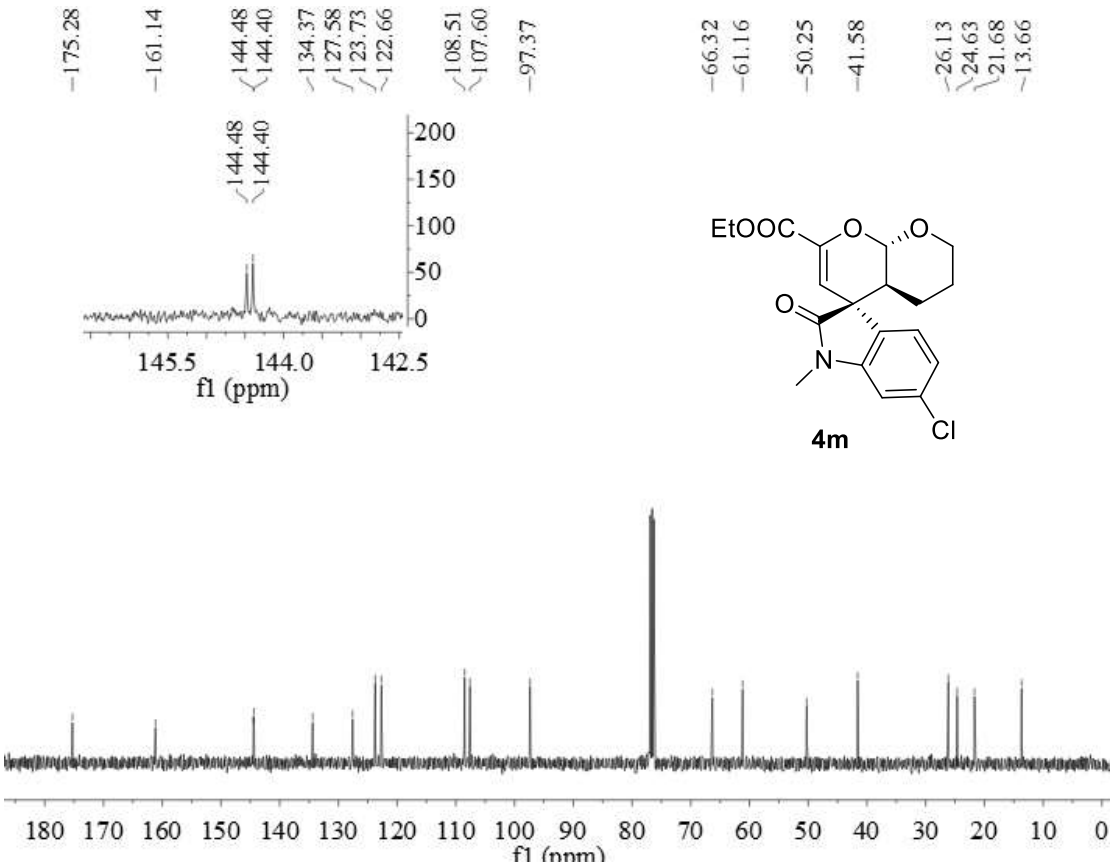
Ethyl-(3*S*,4a'*S*,8a'*S*)-1,5,7-trimethyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4l



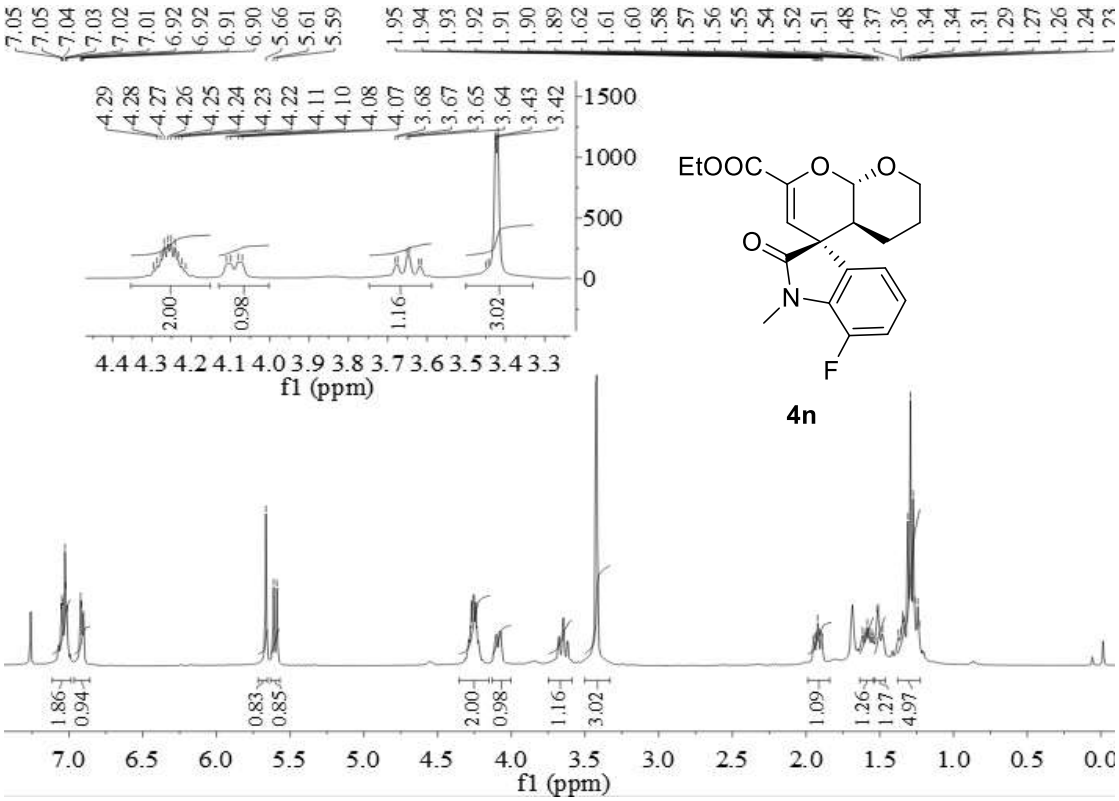


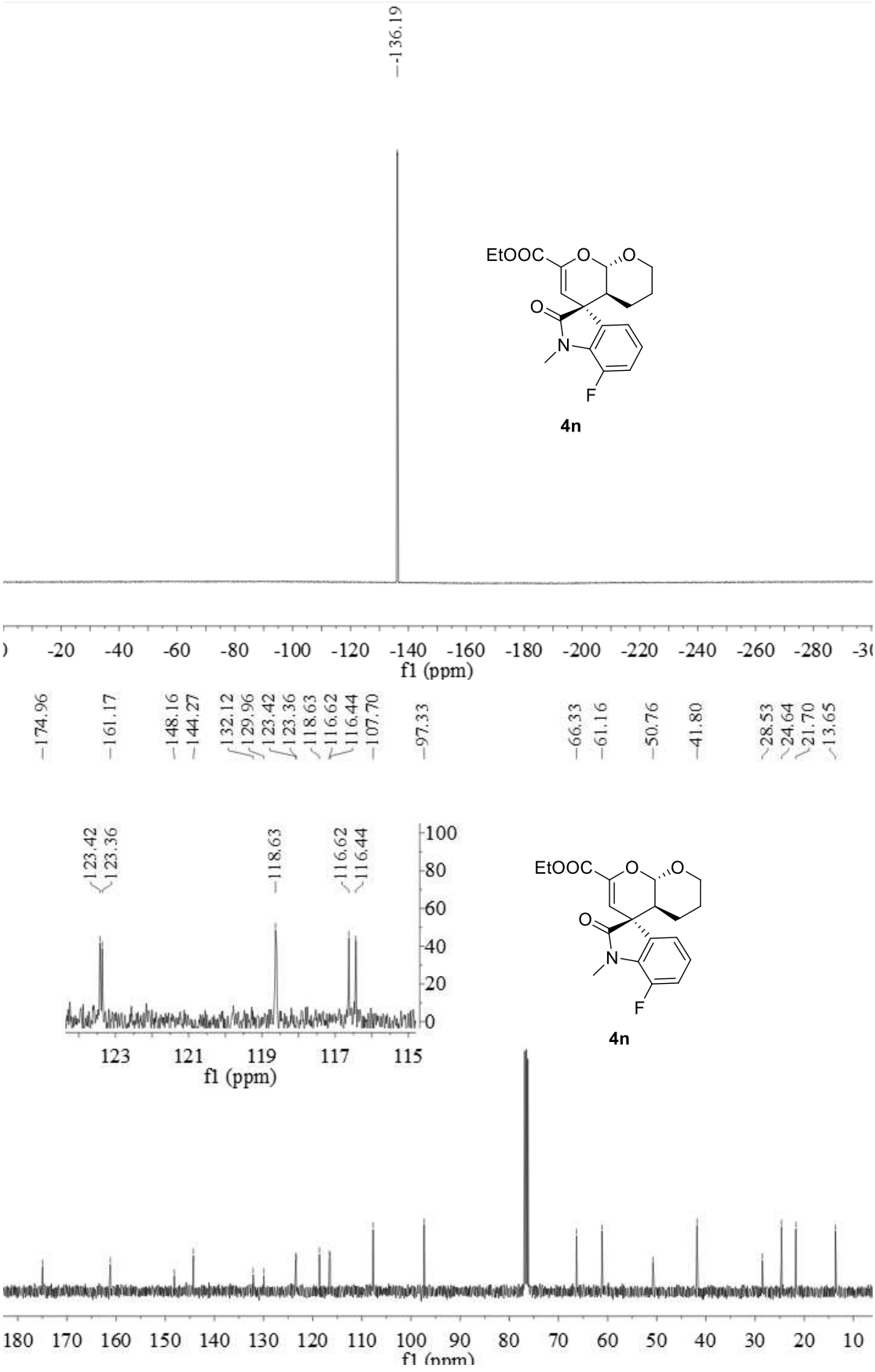
Ethyl-(3*S*,4a'*S*,8a'*S*)-6-chloro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4m



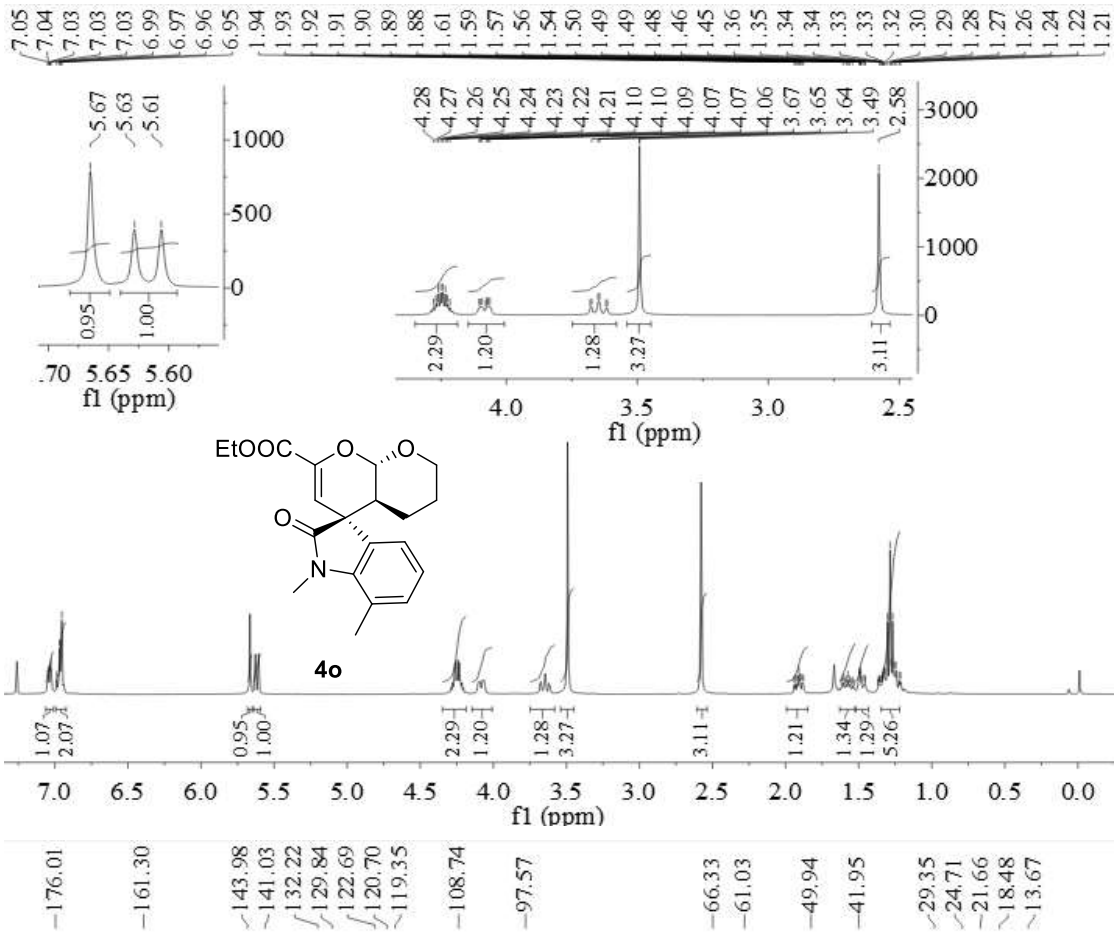


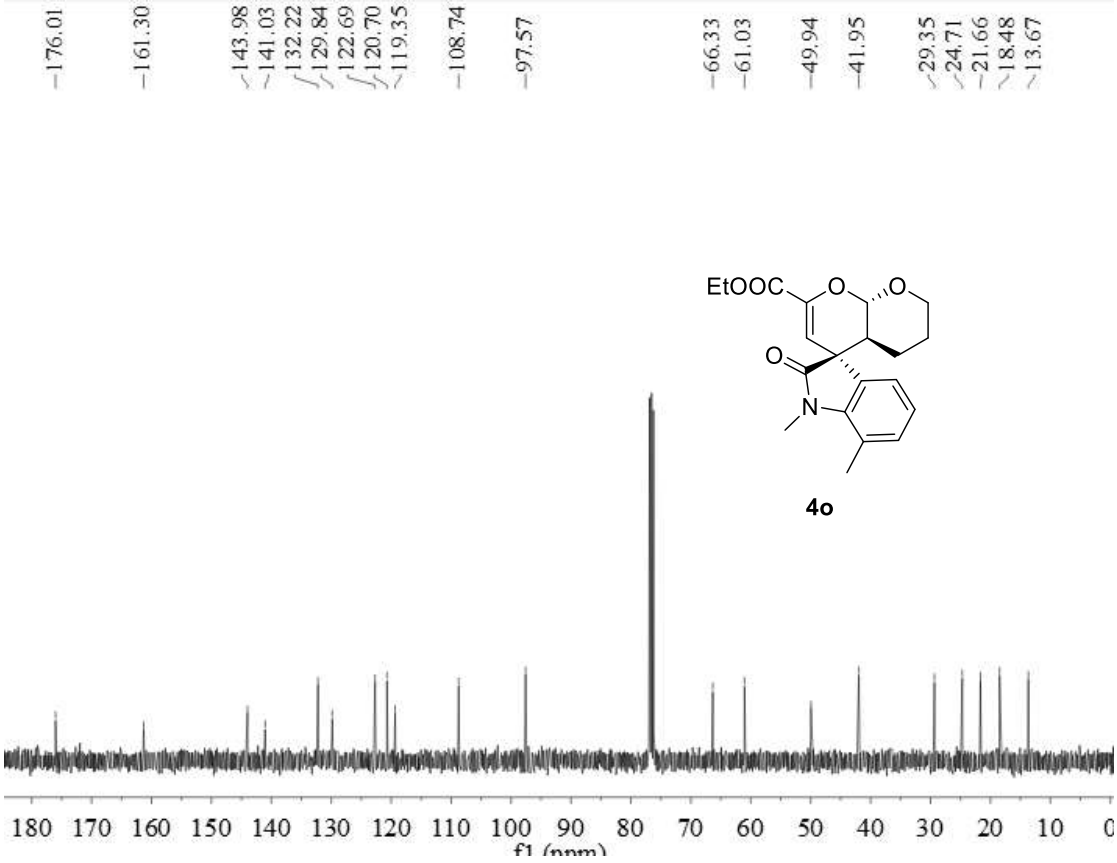
Ethyl-(3*S*,4a'*S*,8a'*S*)-7-fluoro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4n



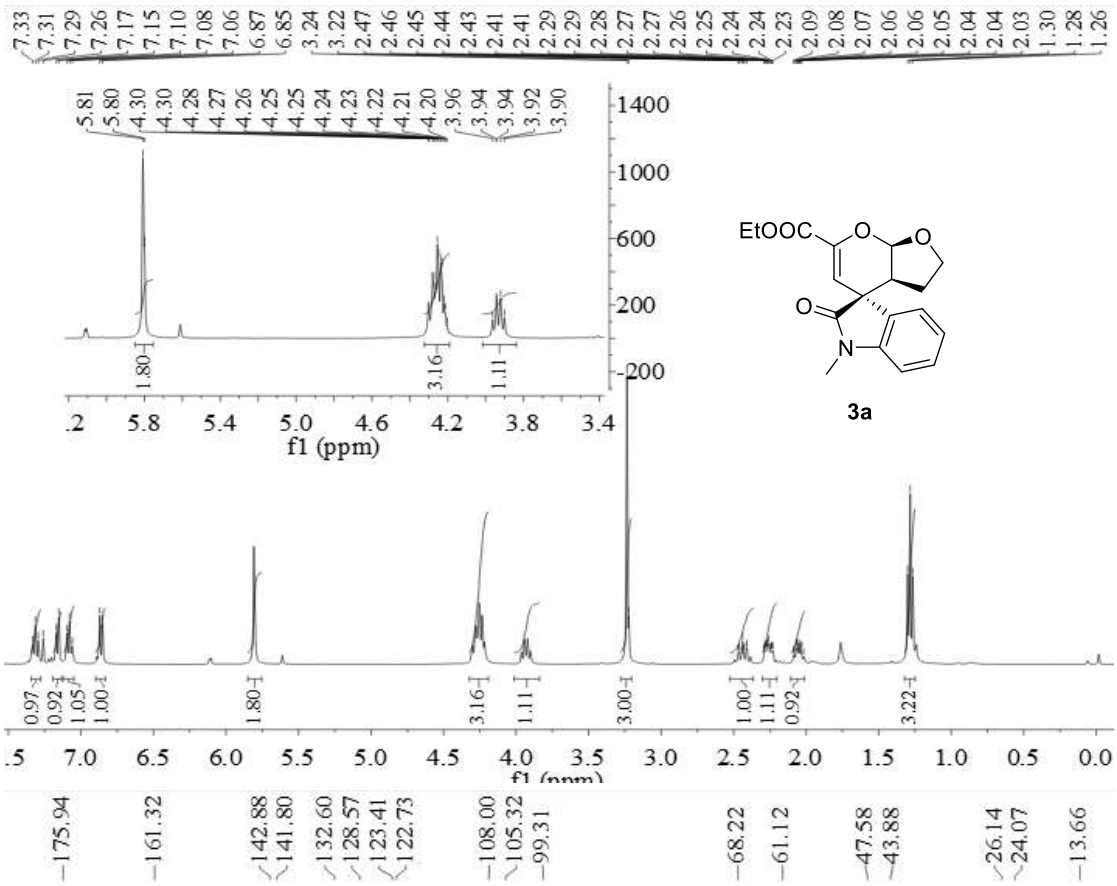

-136.19
EtOOC
O
O
O
N
F
4n
f1 (ppm)
-174.96
-161.17
-148.16
-144.27
-132.12
-129.96
-123.42
-123.36
-118.63
-116.62
-116.44
-107.70
-97.33
-66.33
-61.16
-50.76
-41.80
-28.53
-24.64
-21.70
-13.65
123.42
123.36
118.63
116.62
116.44
f1 (ppm)
EtOOC
O
O
O
N
F
4n
f1 (ppm)

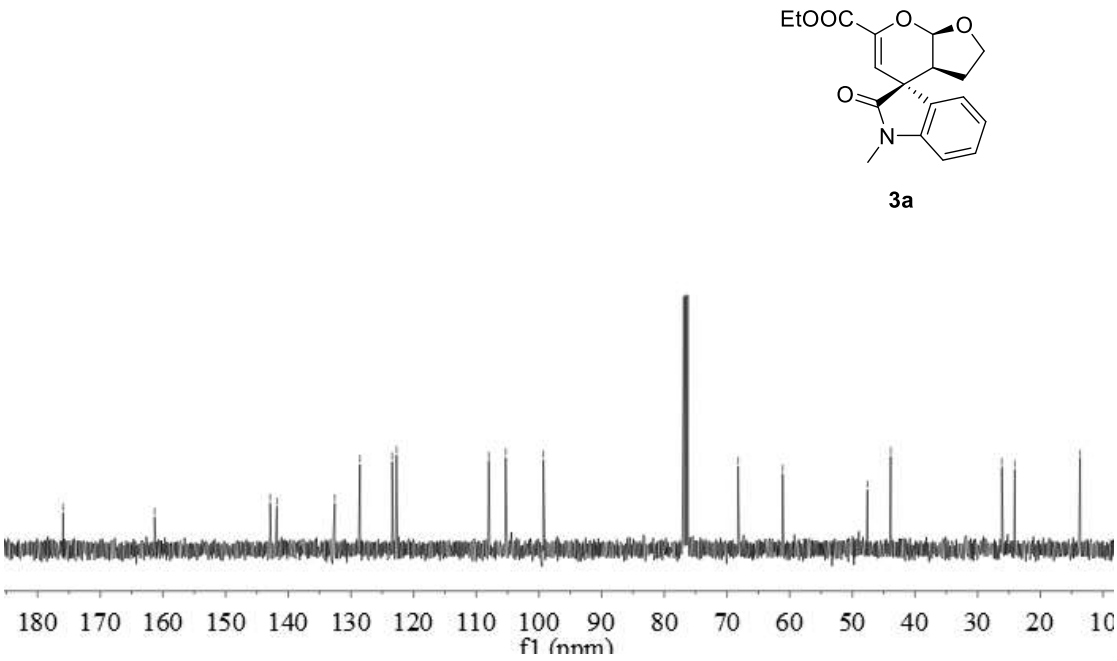
Ethyl-(3*S*,4a'*S*,8a'*S*)-1,7-dimethyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4o



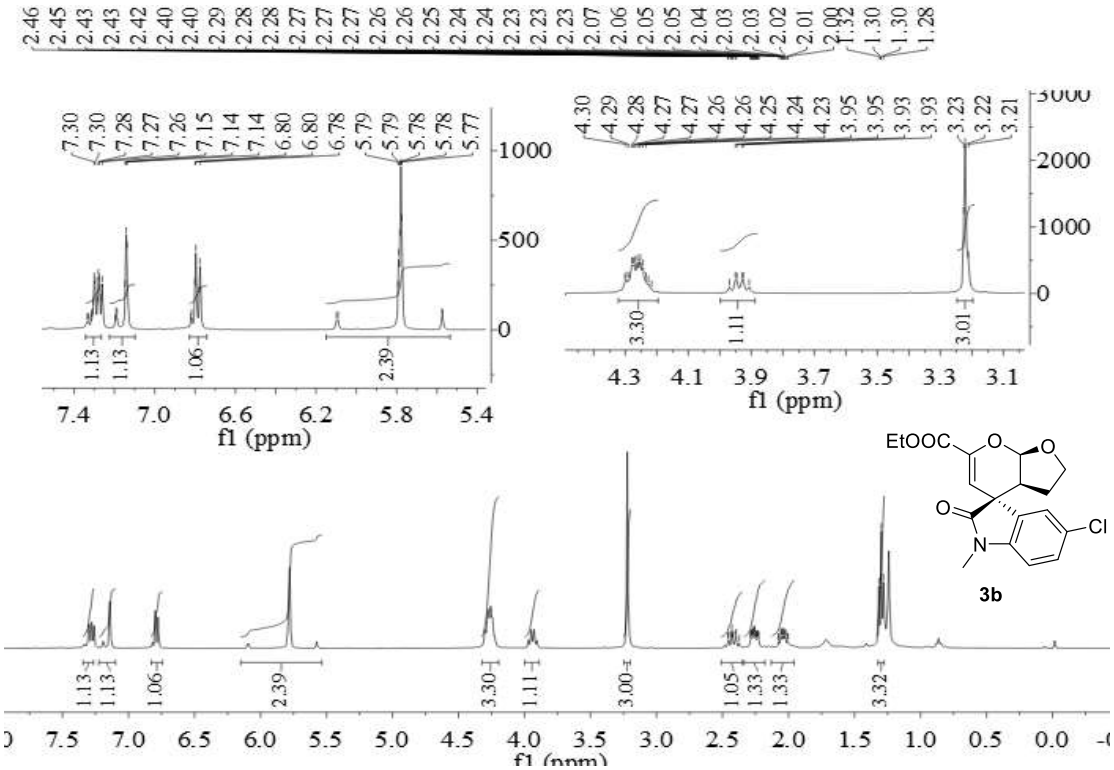


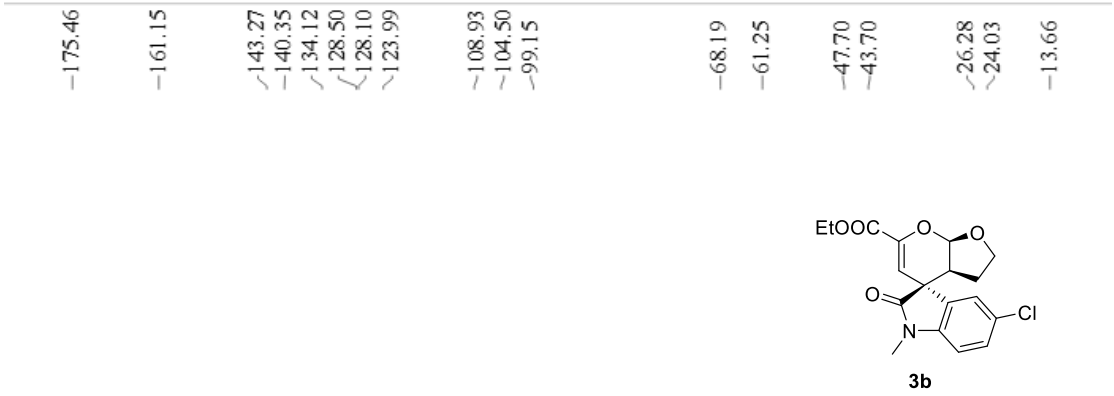
Ethyl-(3a*S*,4*S*,7a*R*)-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo[2,3-b] pyran-4,3'-indoline]-6-carboxylate 3a

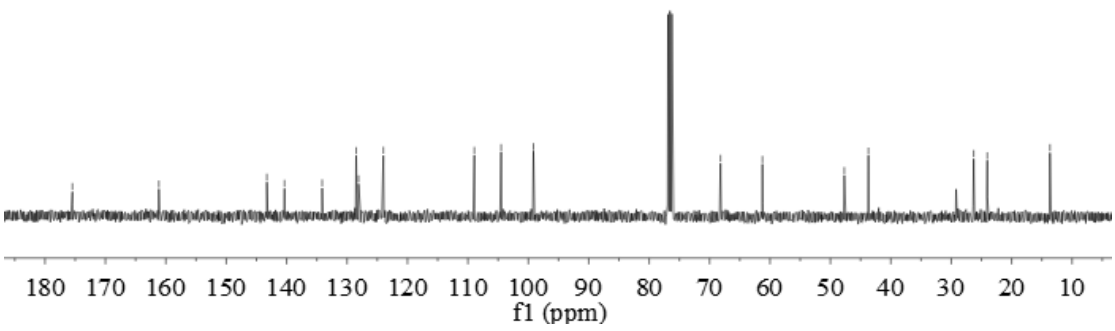




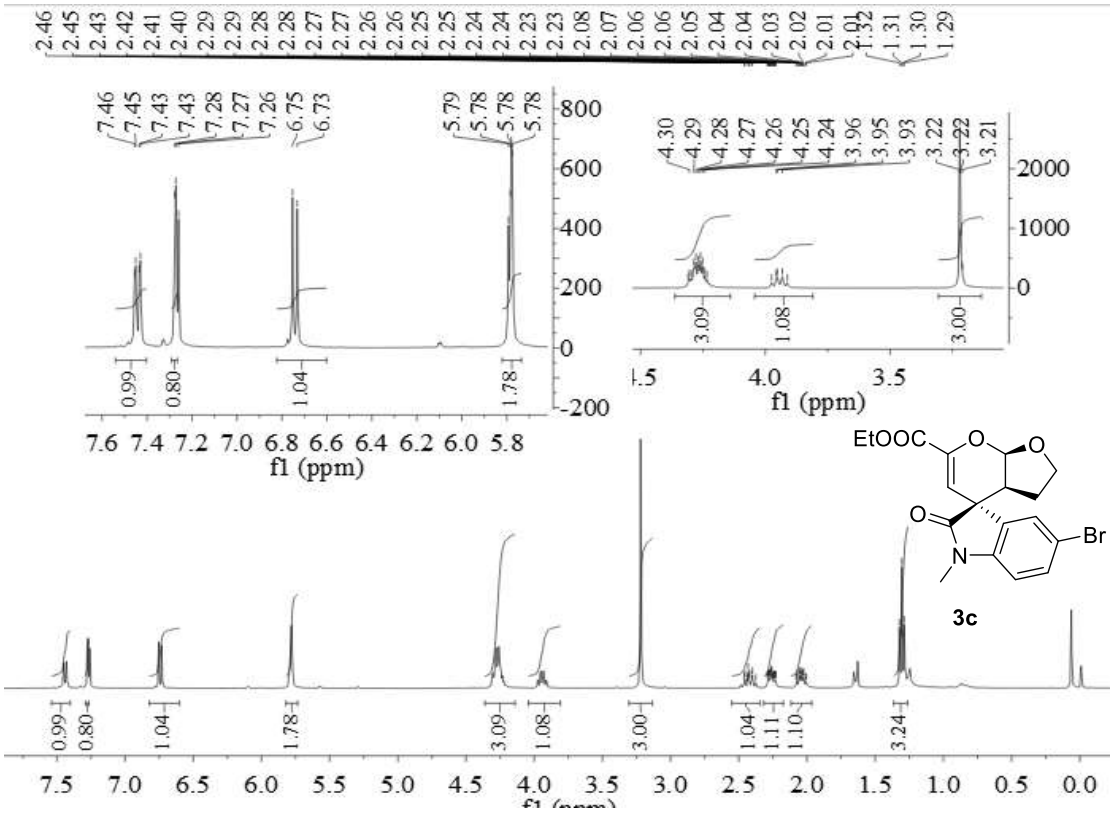
Ethyl-(3a*S*,4*S*,7a*R*)-5'-chloro-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3b



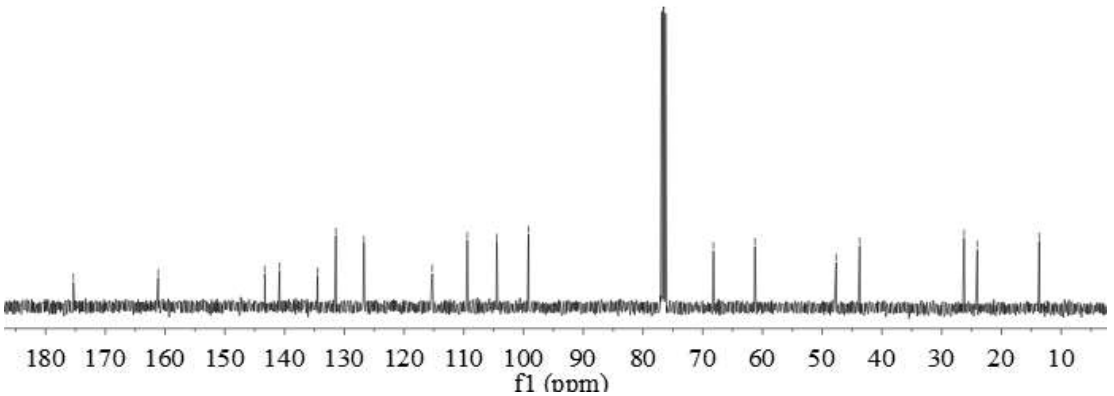




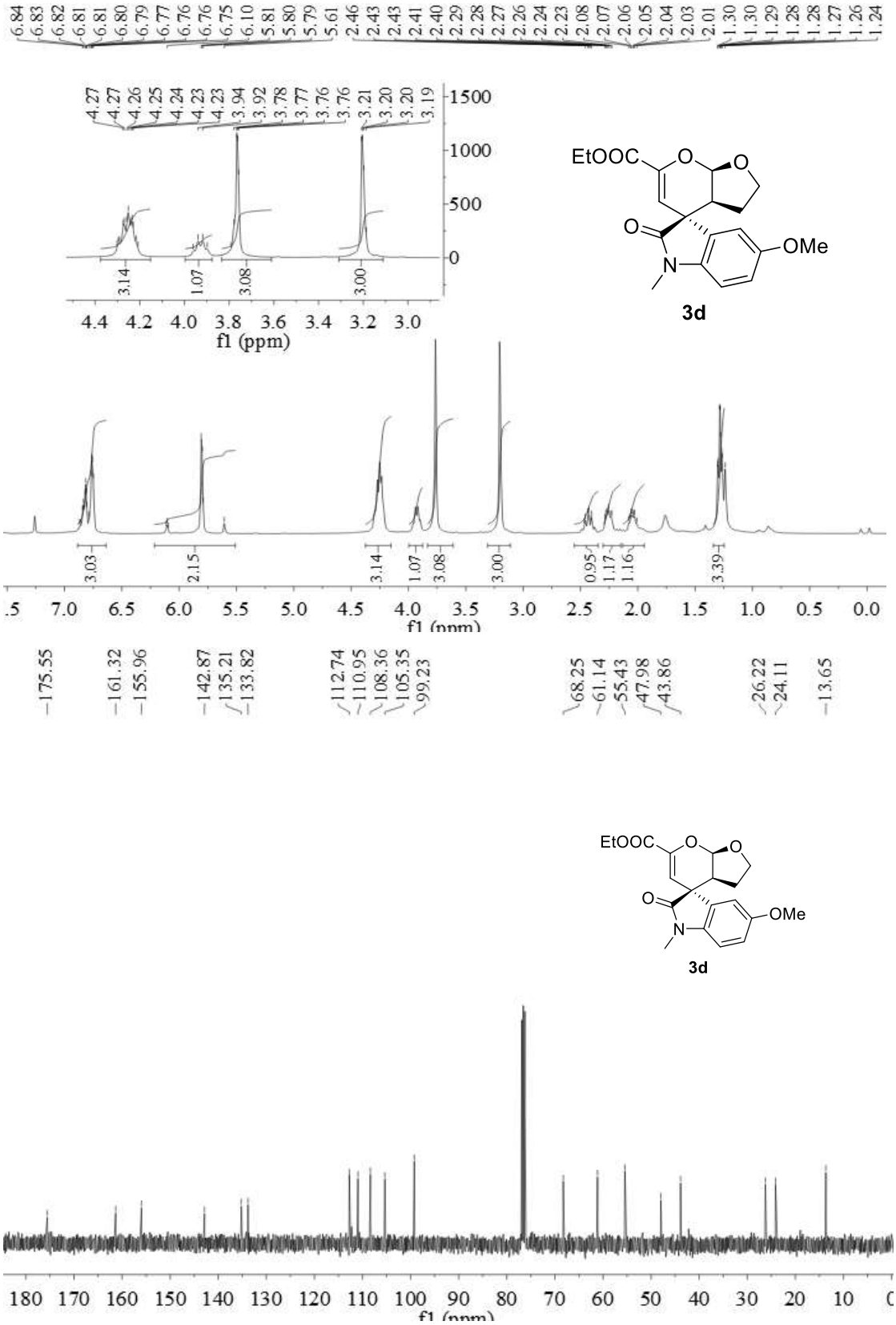
Ethyl-(3a*S*,4*S*,7a*R*)-5'-bromo-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3c



3c

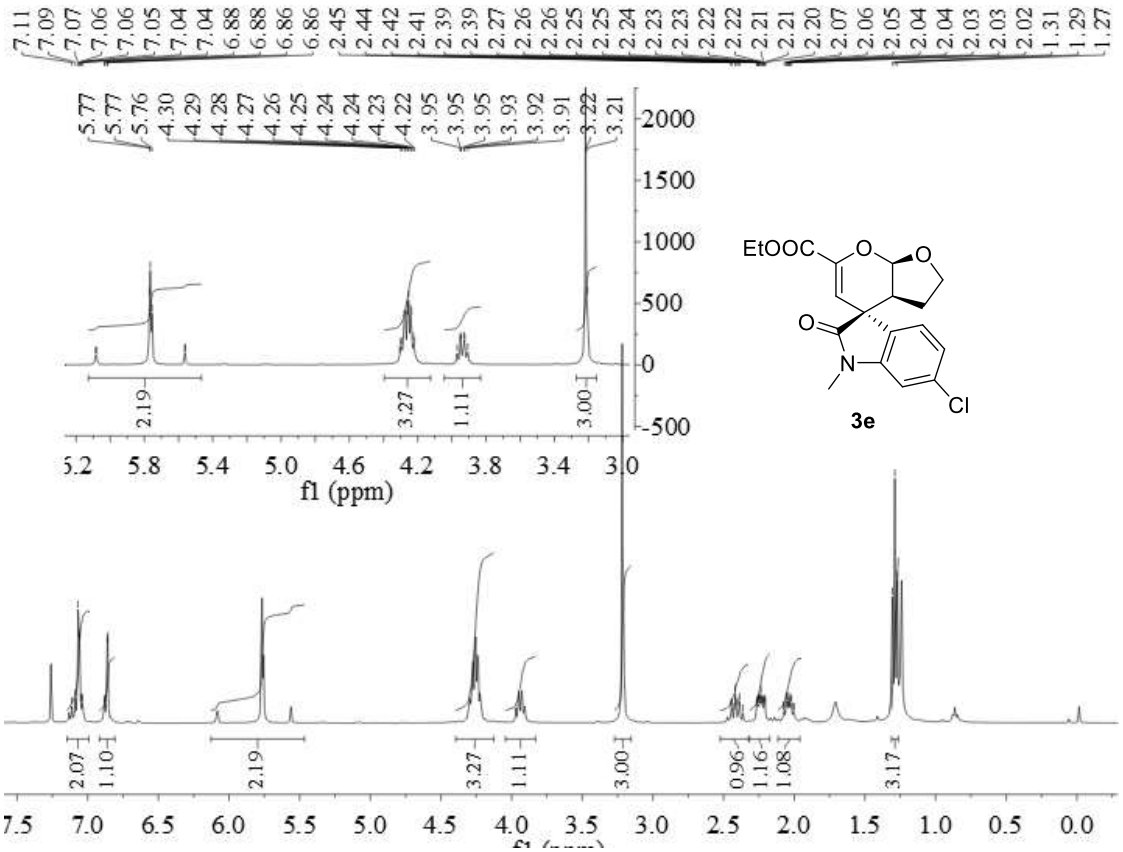


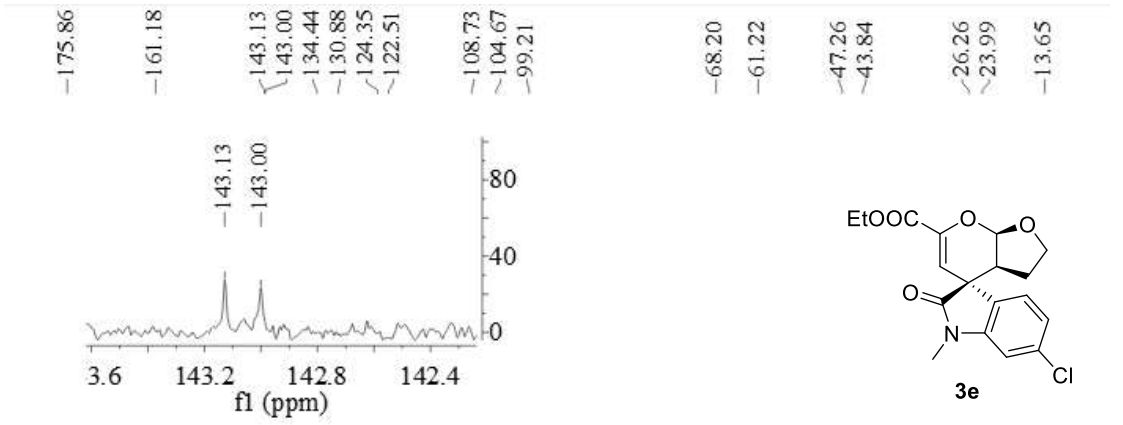
Ethyl-(3a*S*,4*S*,7a*R*)-5'-methoxy-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3d

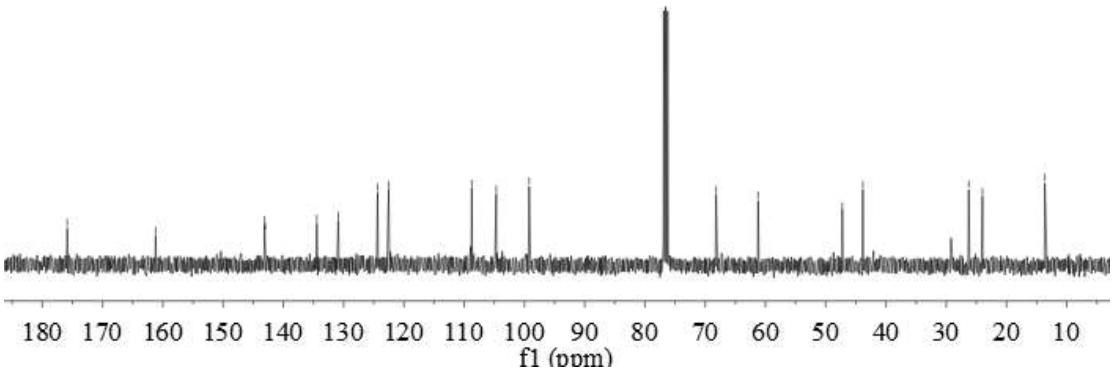


Ethyl-(3a*S*,4*S*,7a*R*)-6'-chloro-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo

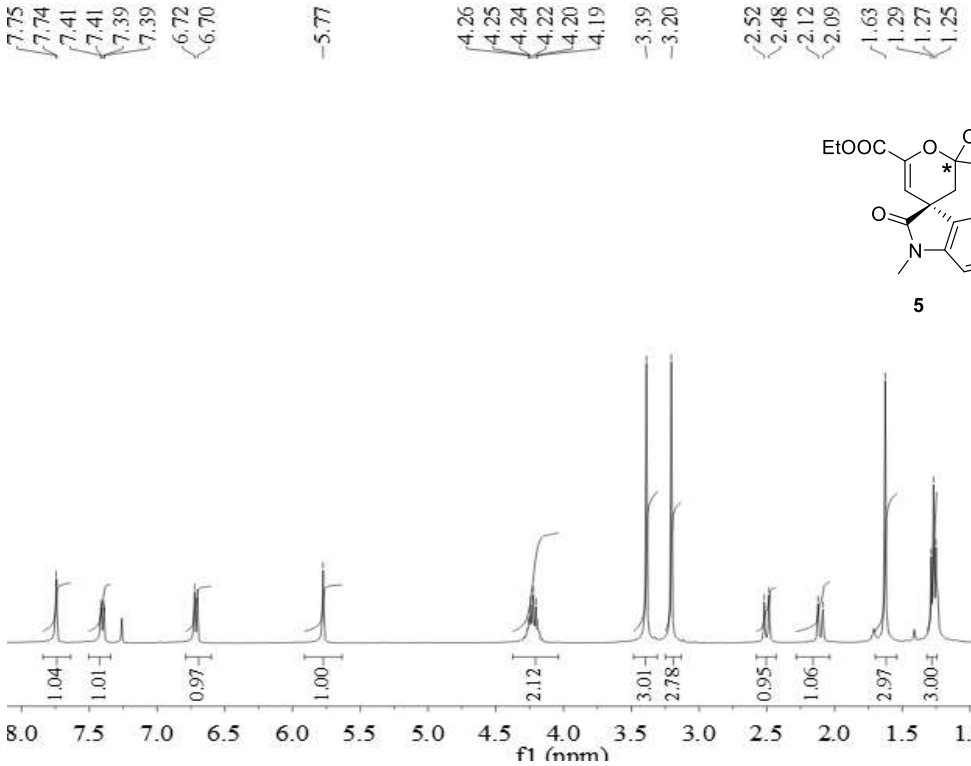
[2,3-b]pyran-4,3'-indoline]-6-carboxylate 3e

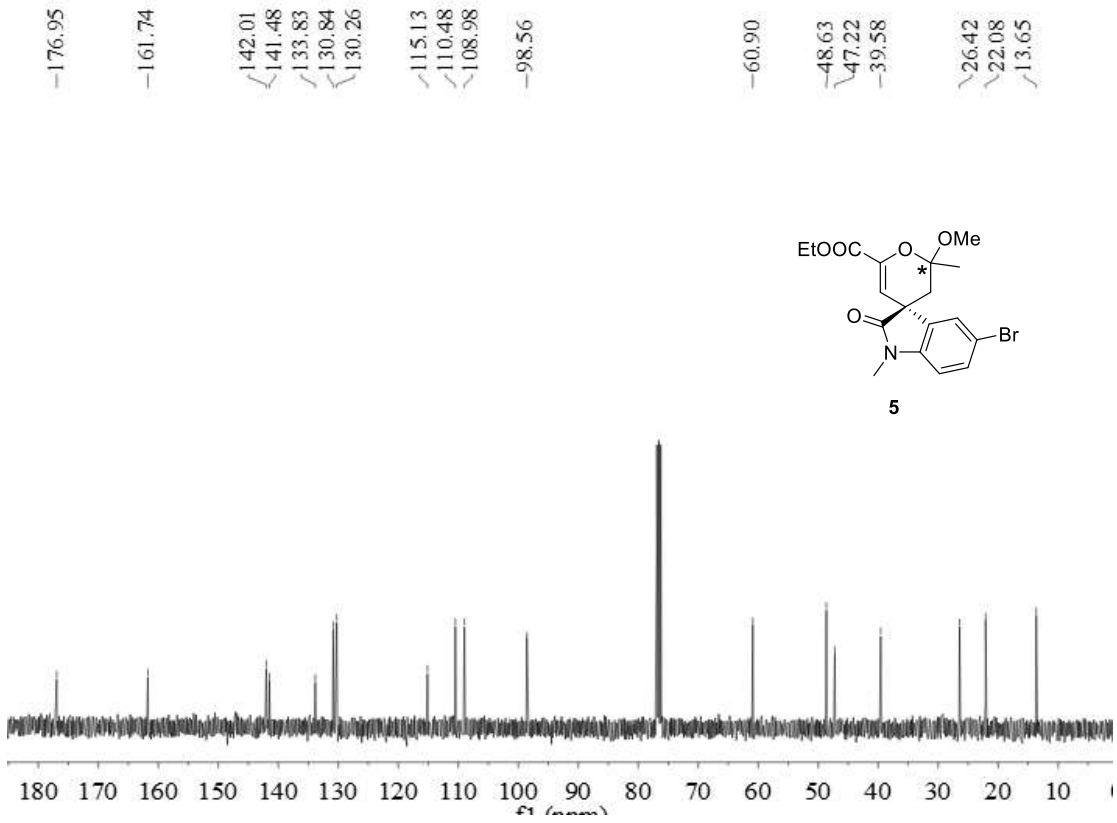




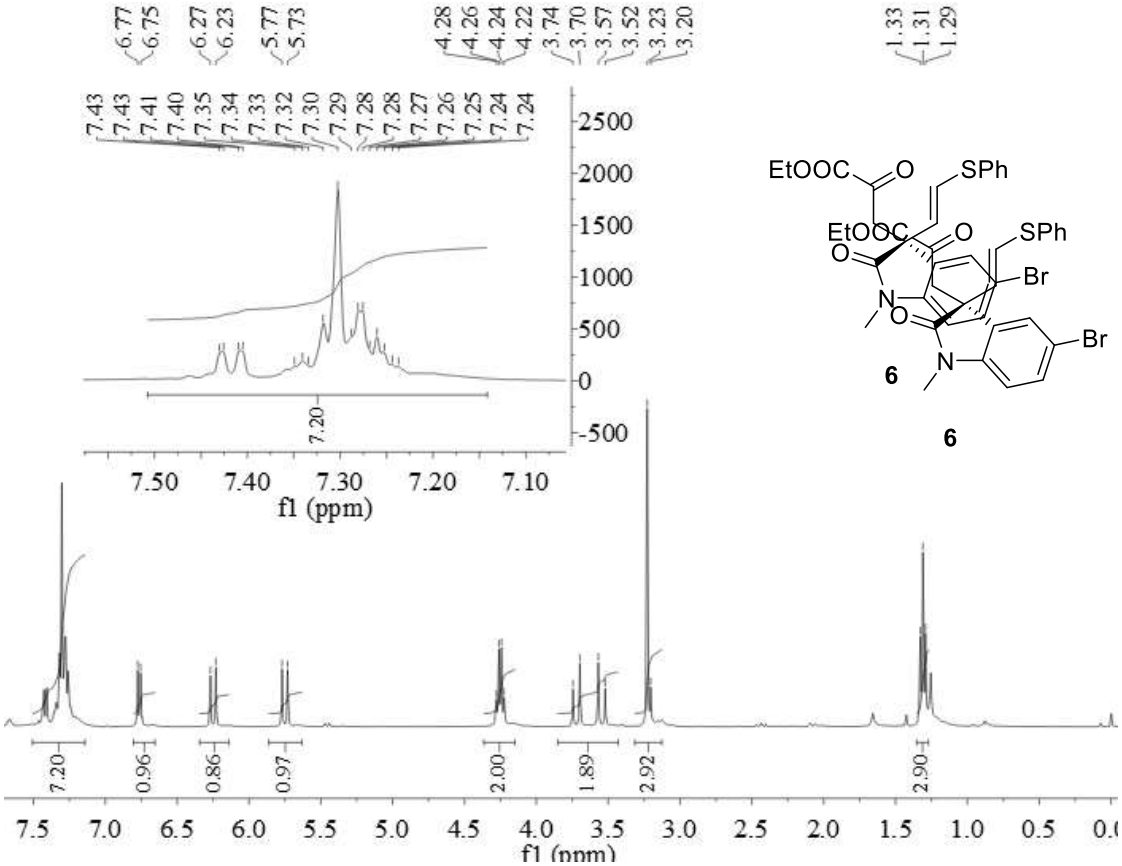


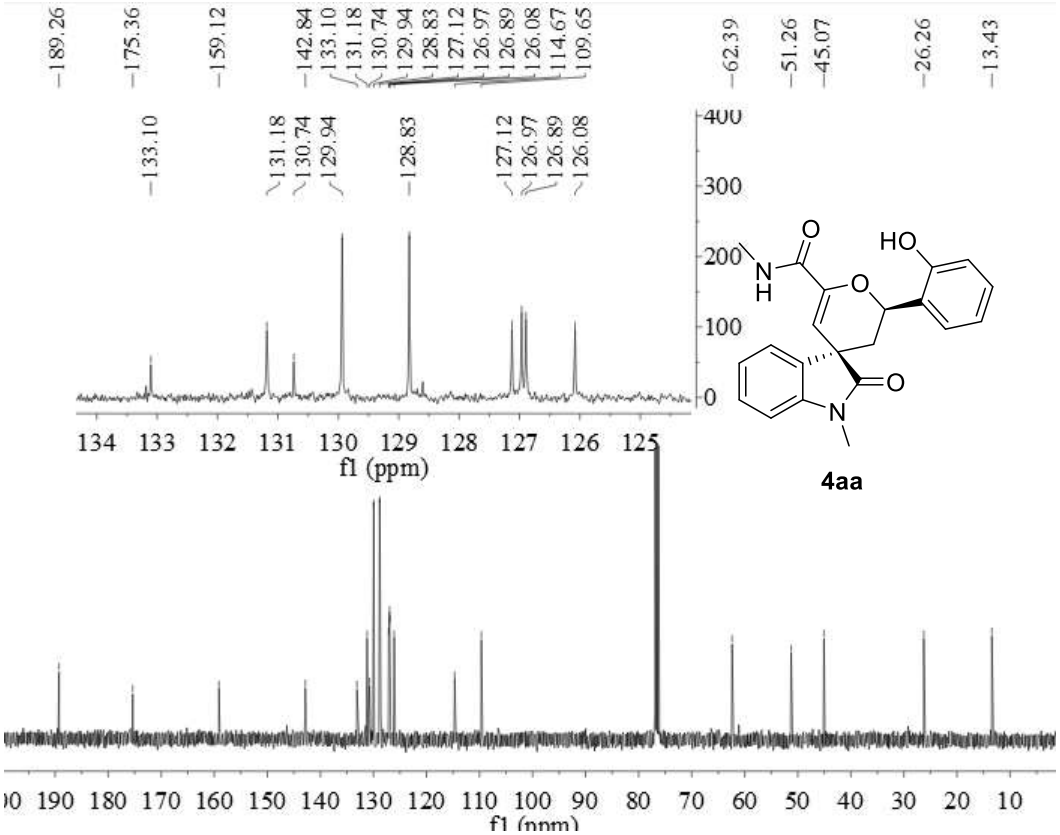
Ethyl-(3*R*)-5-bromo-2'-methoxy-1,2'-dimethyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxylate 5



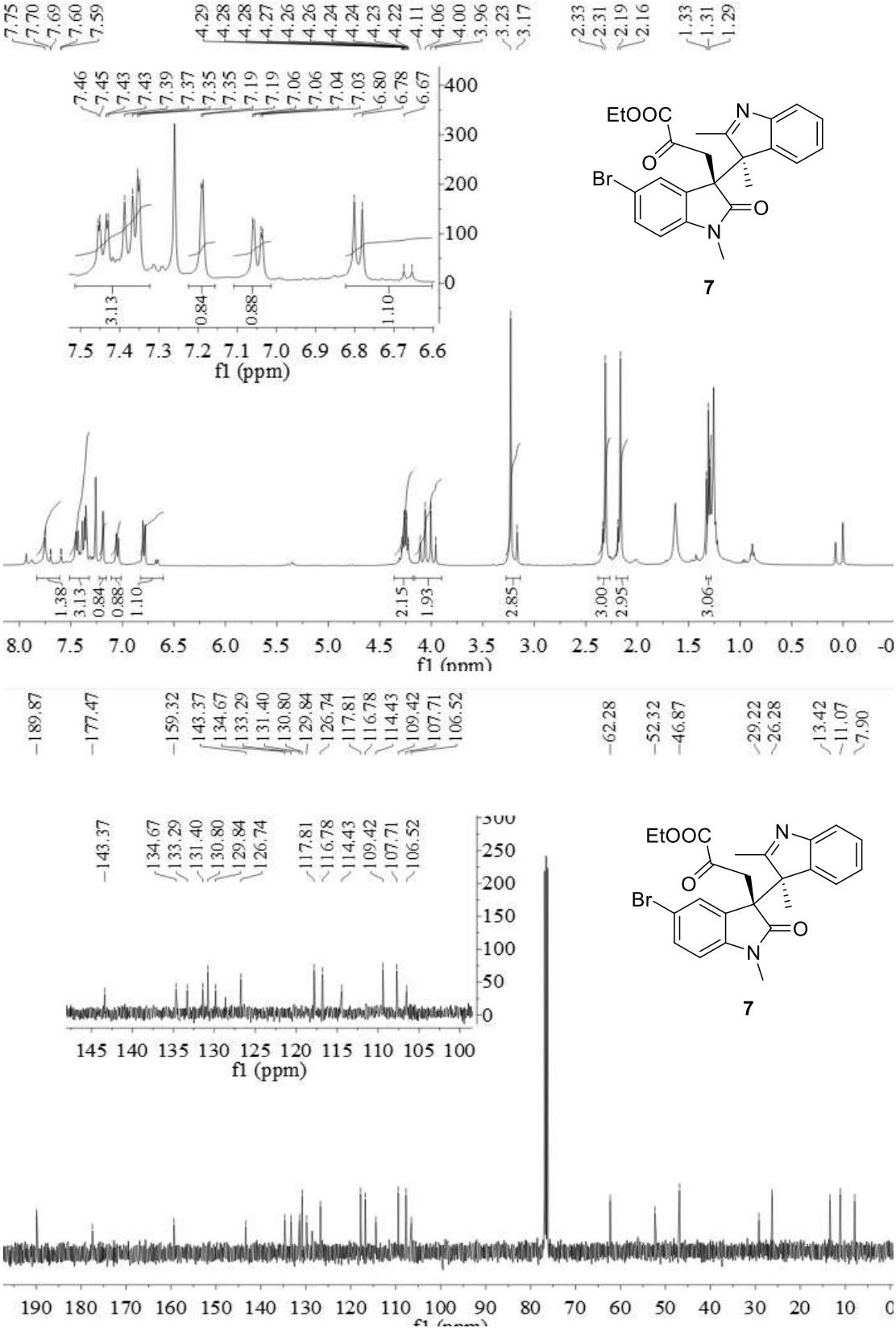


Ethyl-(*S*,*E*)-3-(5-bromo-1-methyl-2-oxo-3-(2-(phenylthio)vinyl)indolin-3-yl)-2-oxopropanoate 6

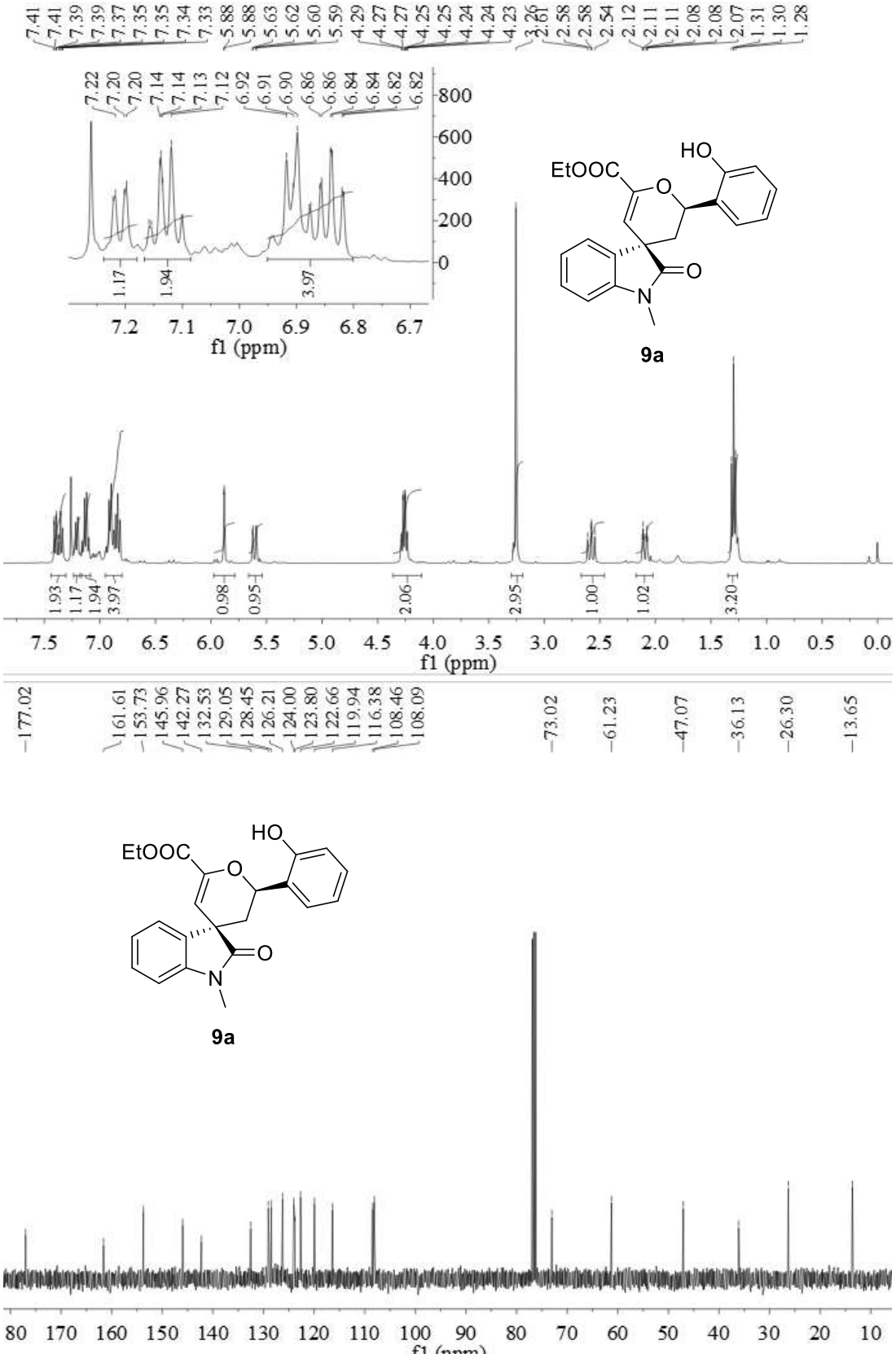




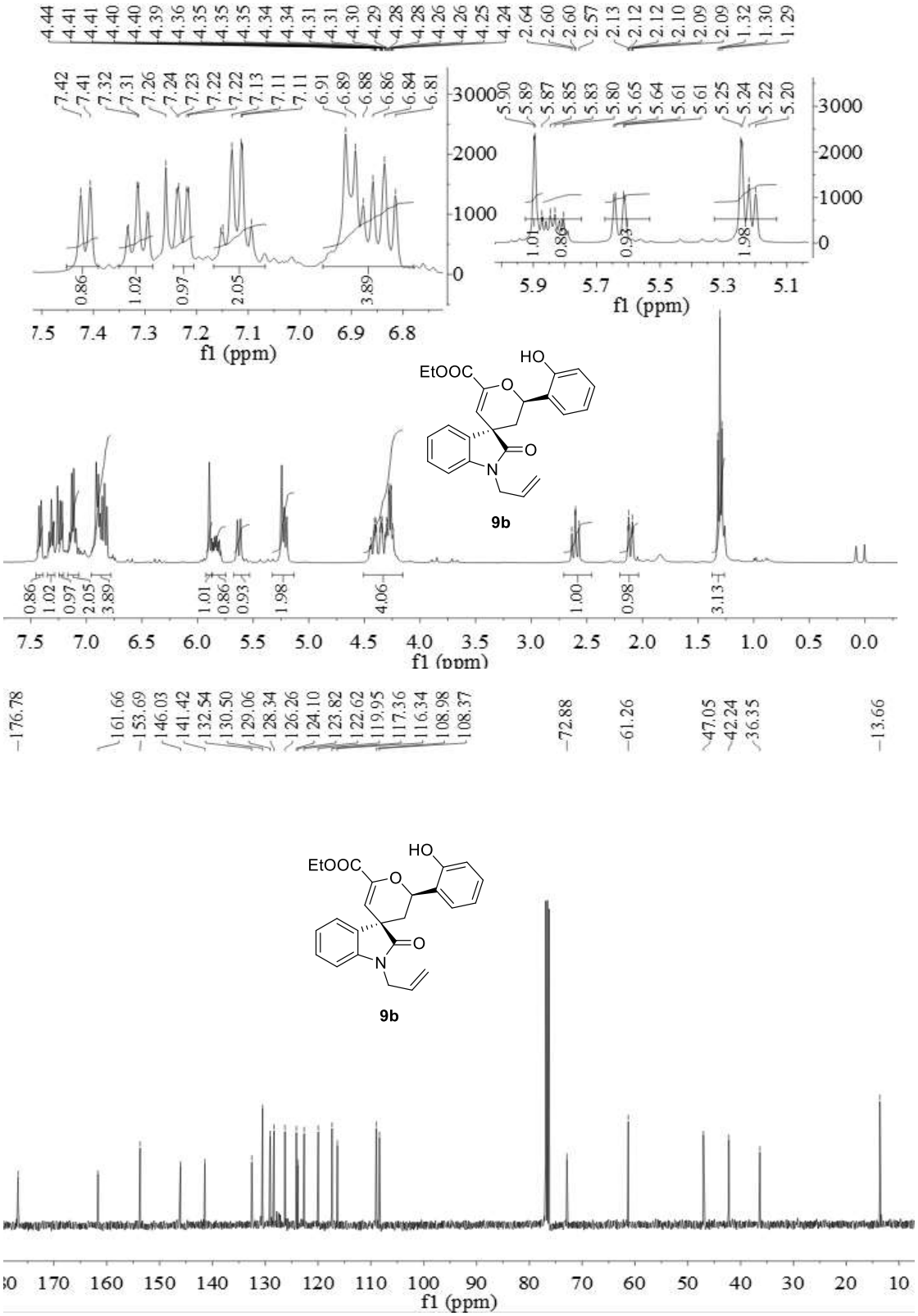
Ethyl-3-(5-bromo-3-(2,3-dimethyl-3H-indol-3-yl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 7



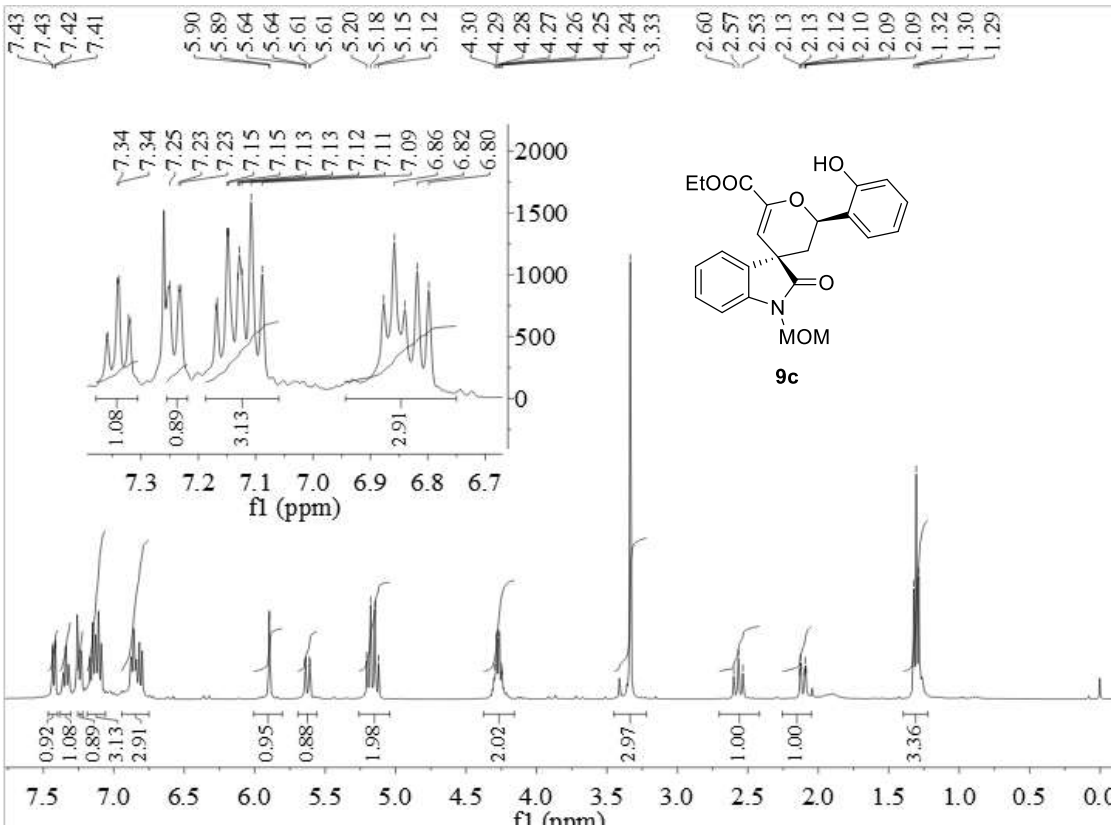
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate 9a

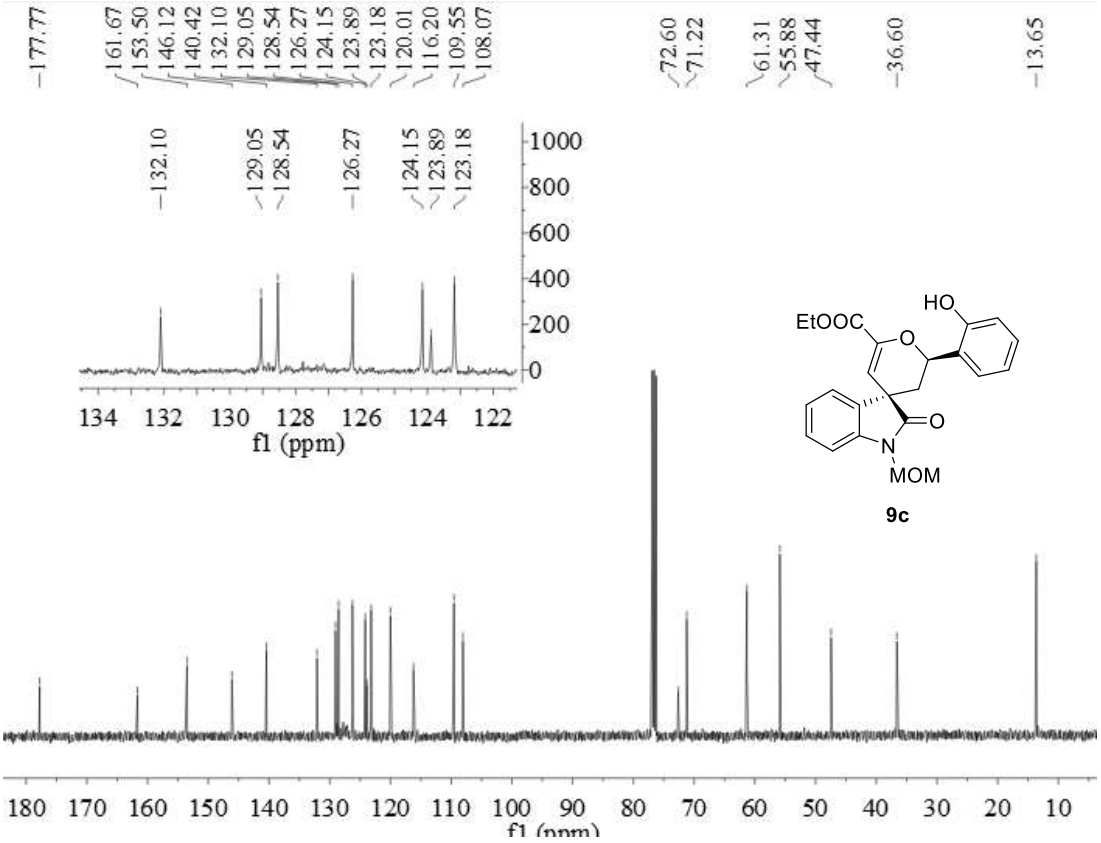


Ethyl (2'*R*,3*R*)-1-allyl-2'-(2-hydroxyphenyl)-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate 9b

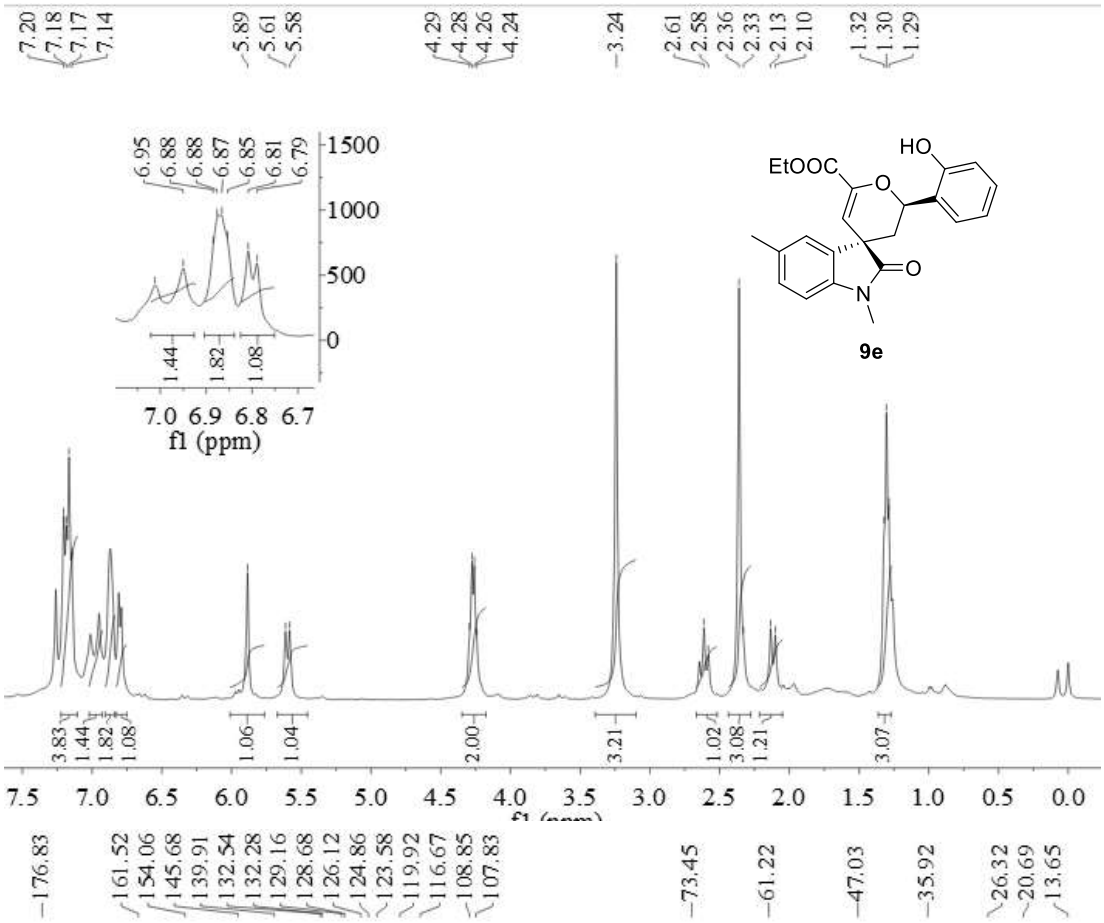


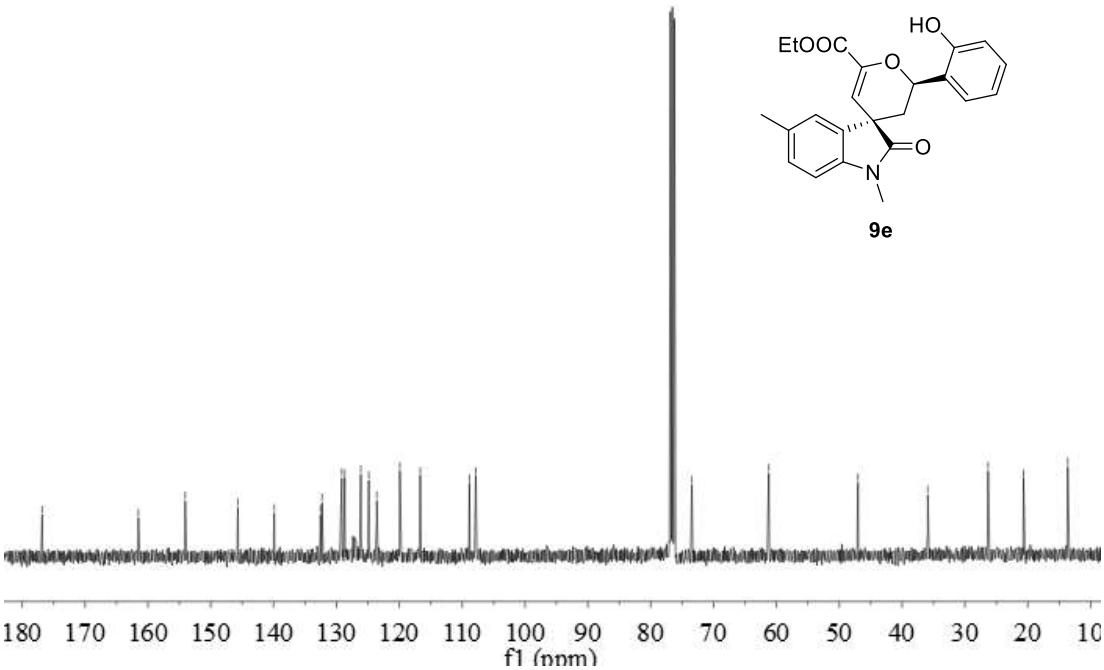
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1-(methoxymethyl)-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9c



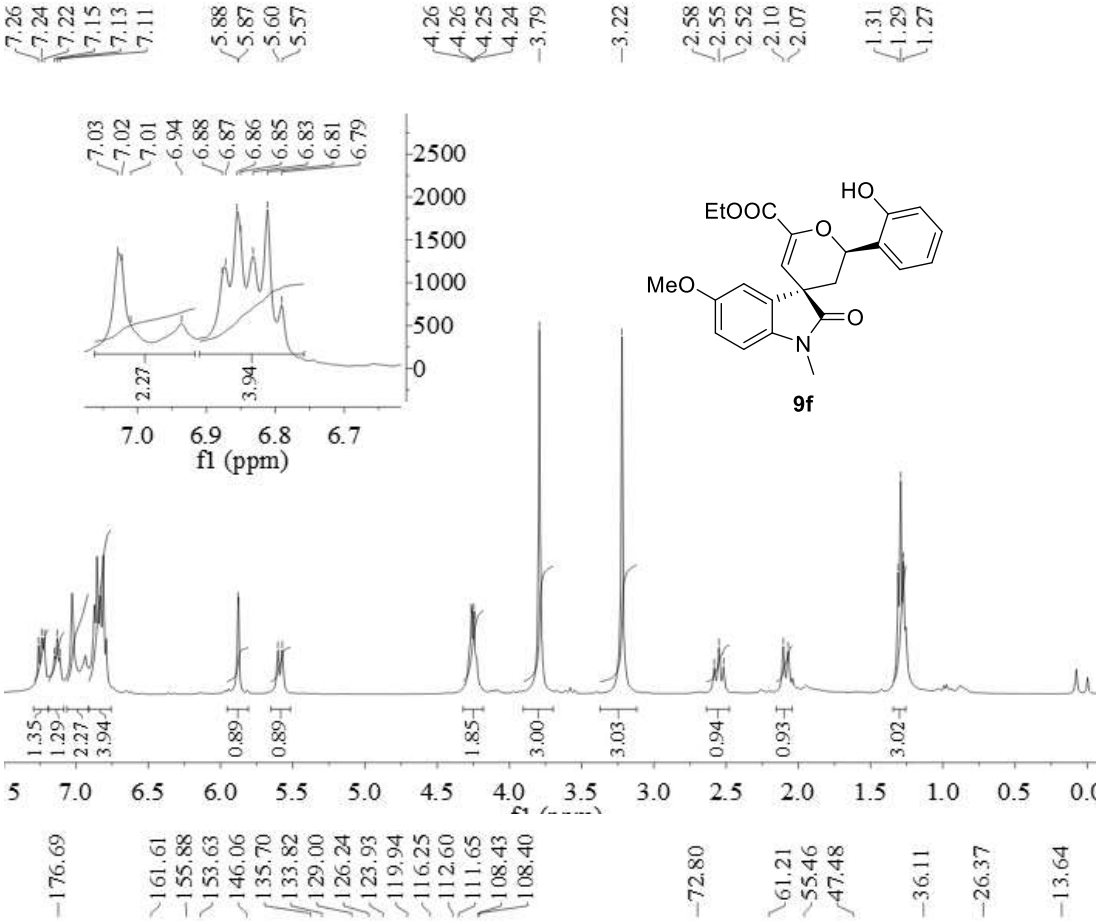


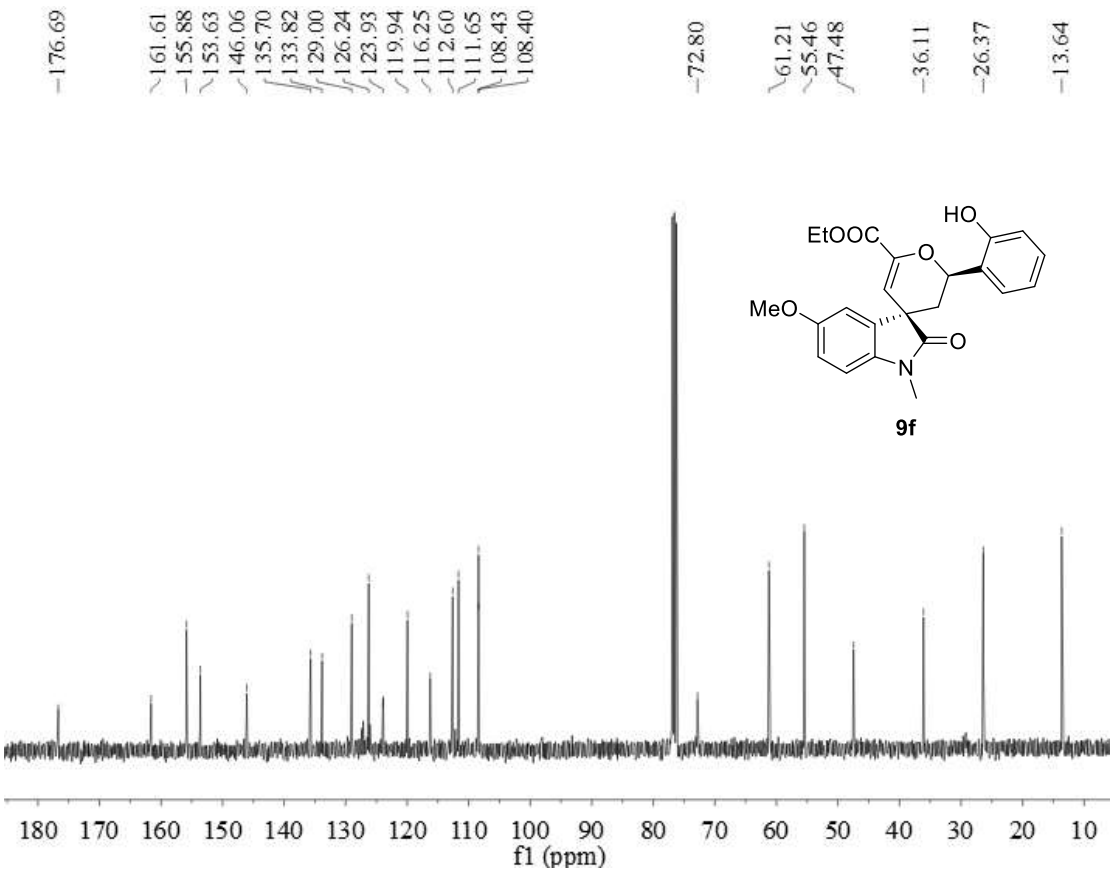
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,5-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9e



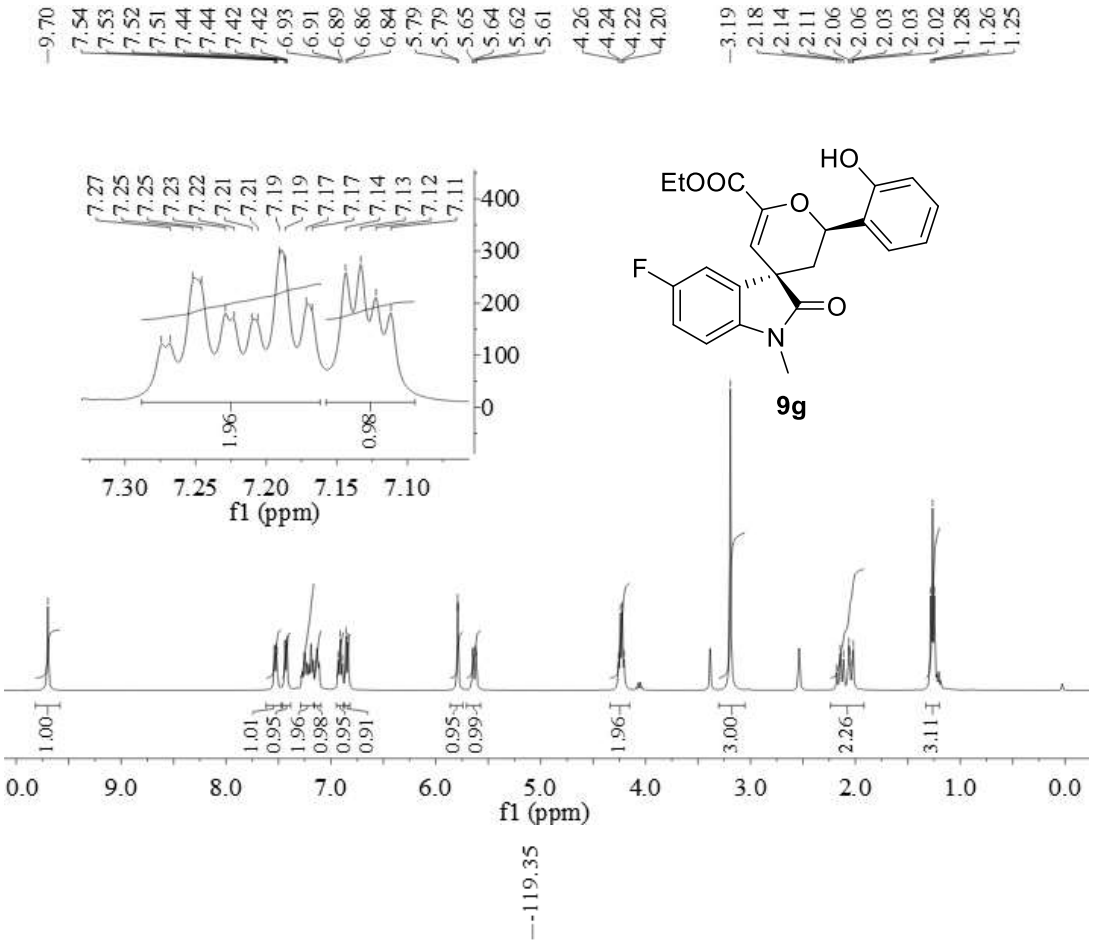


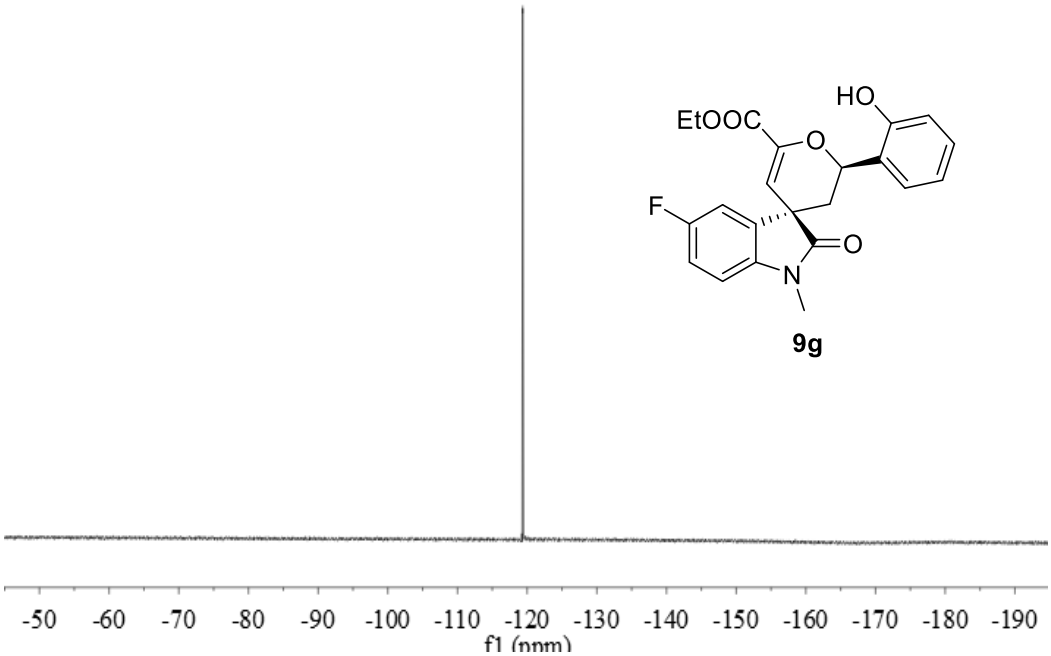
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-5-methoxy-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9f

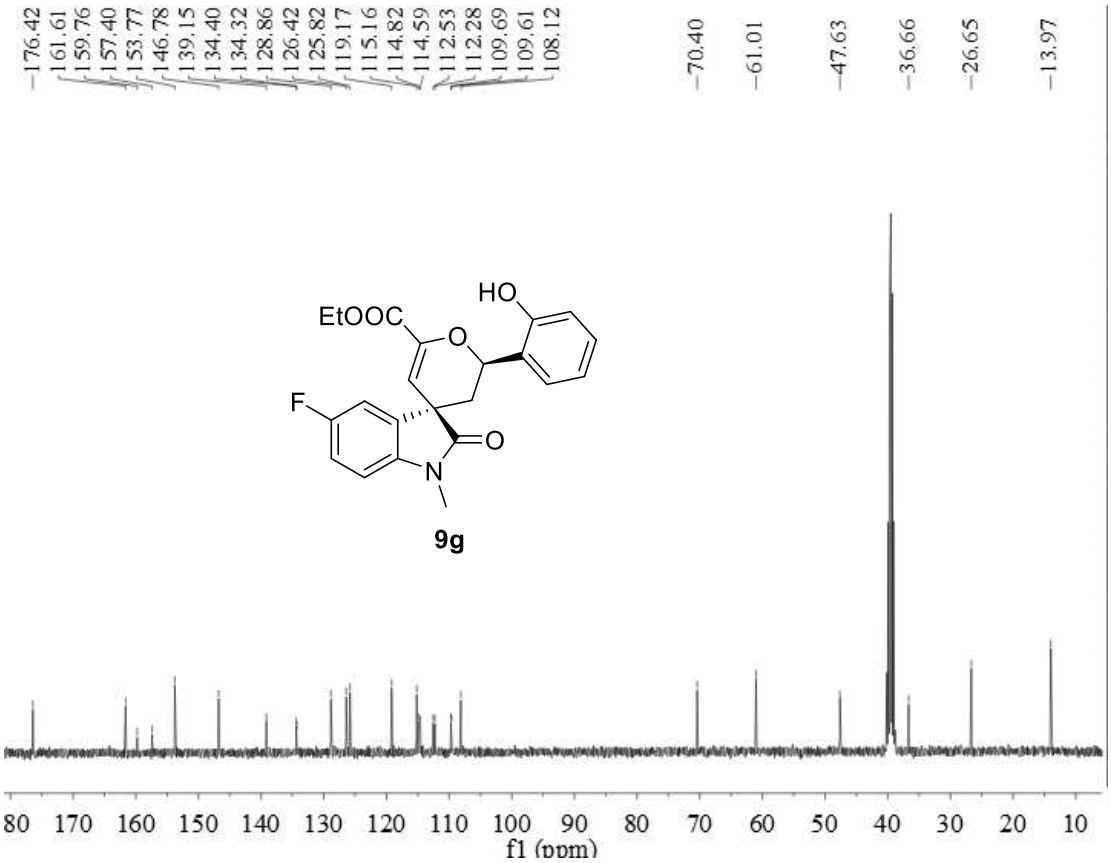




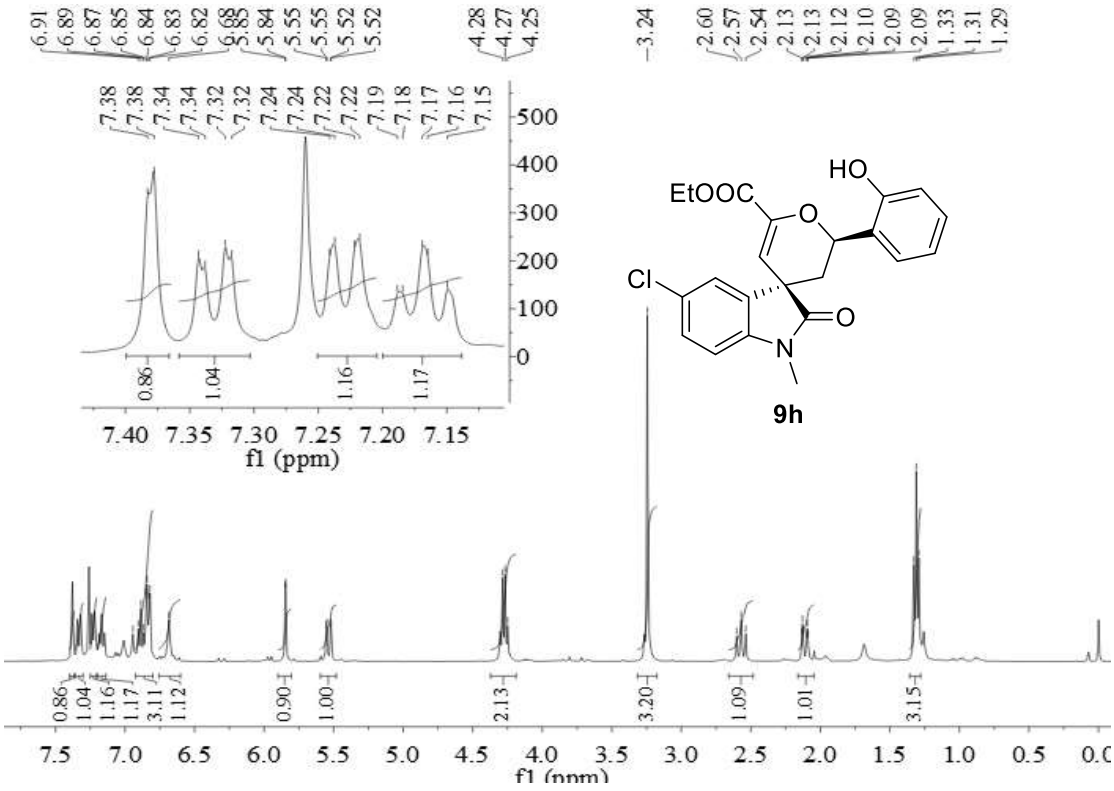
Ethyl (2'*R*,3*R*)-5-fluoro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9g

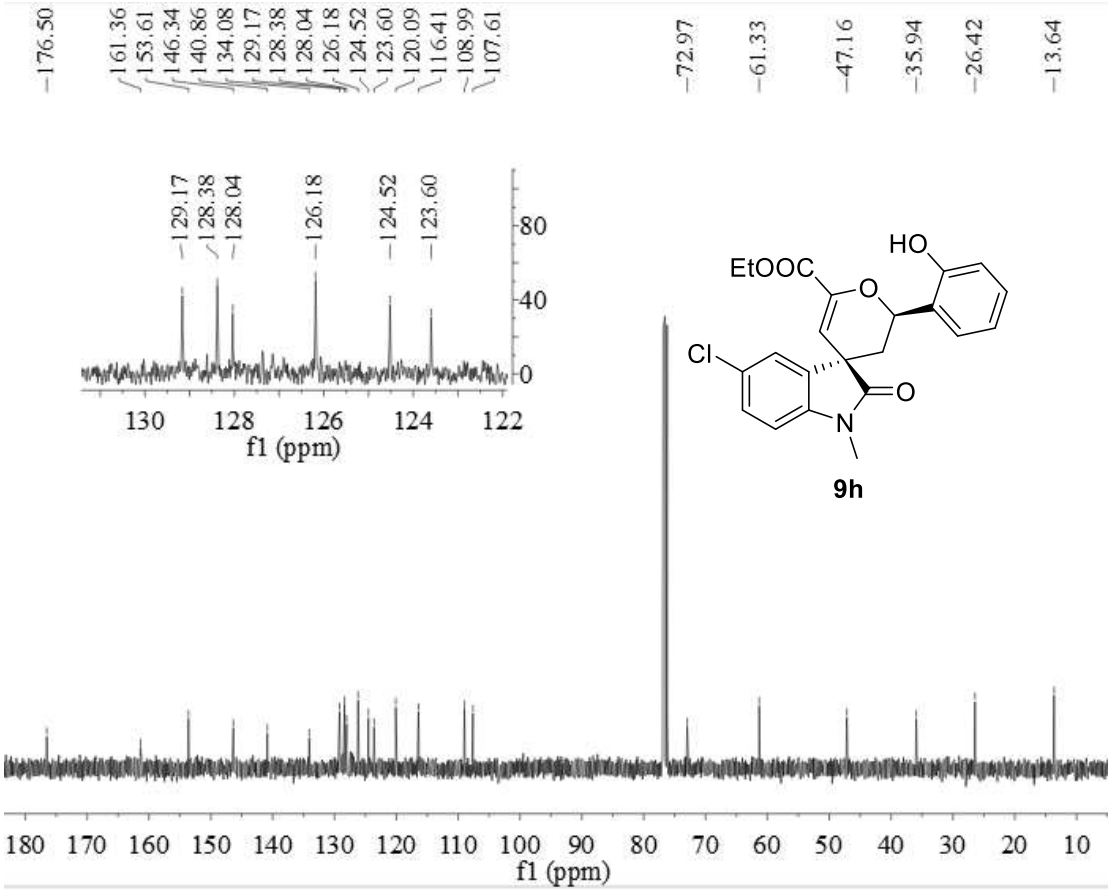




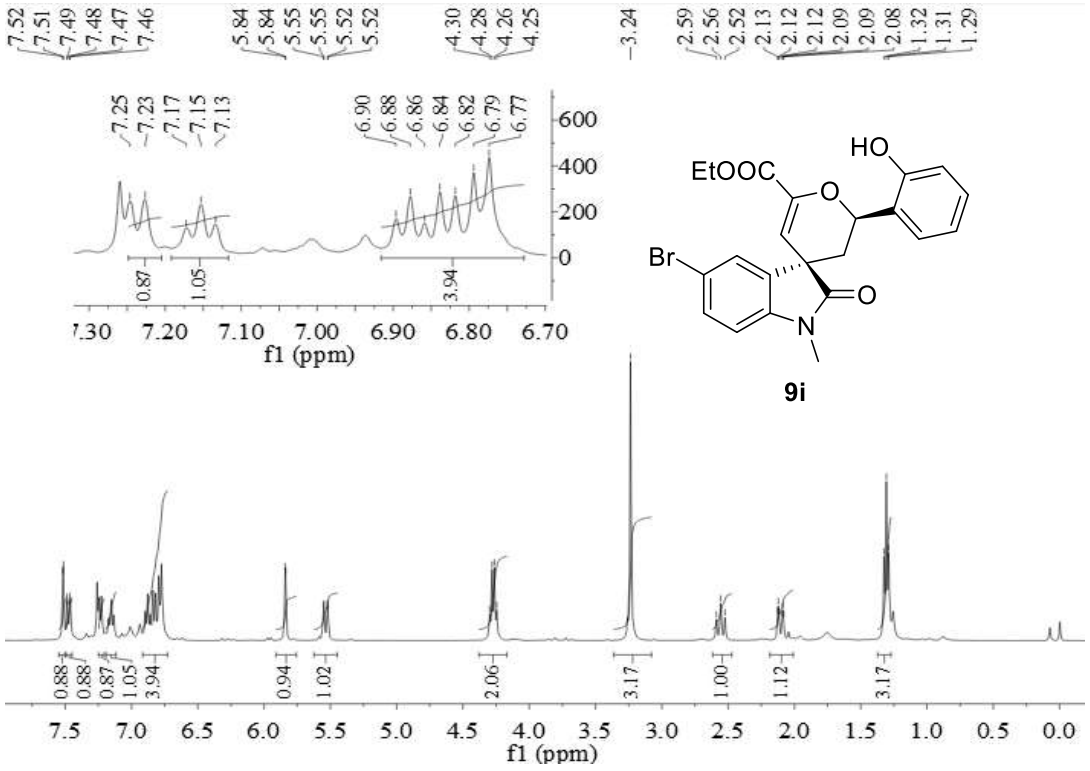


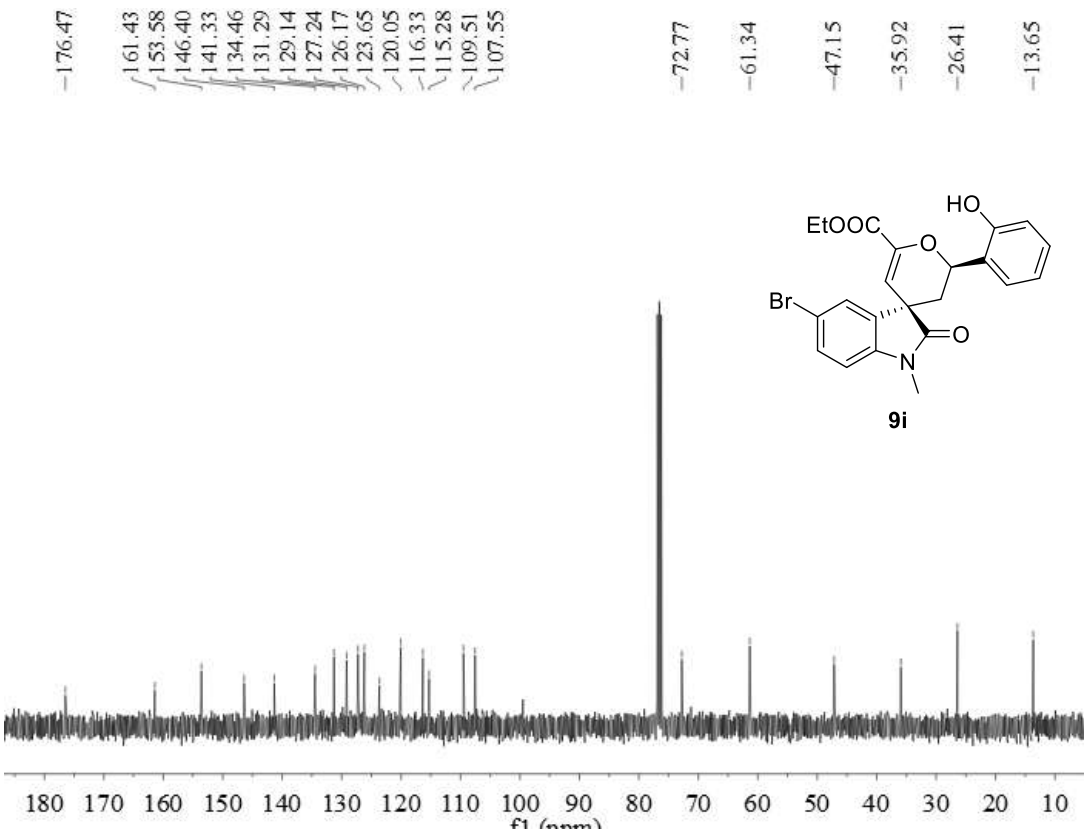
Ethyl (2'*R*,3*R*)-5-chloro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9h



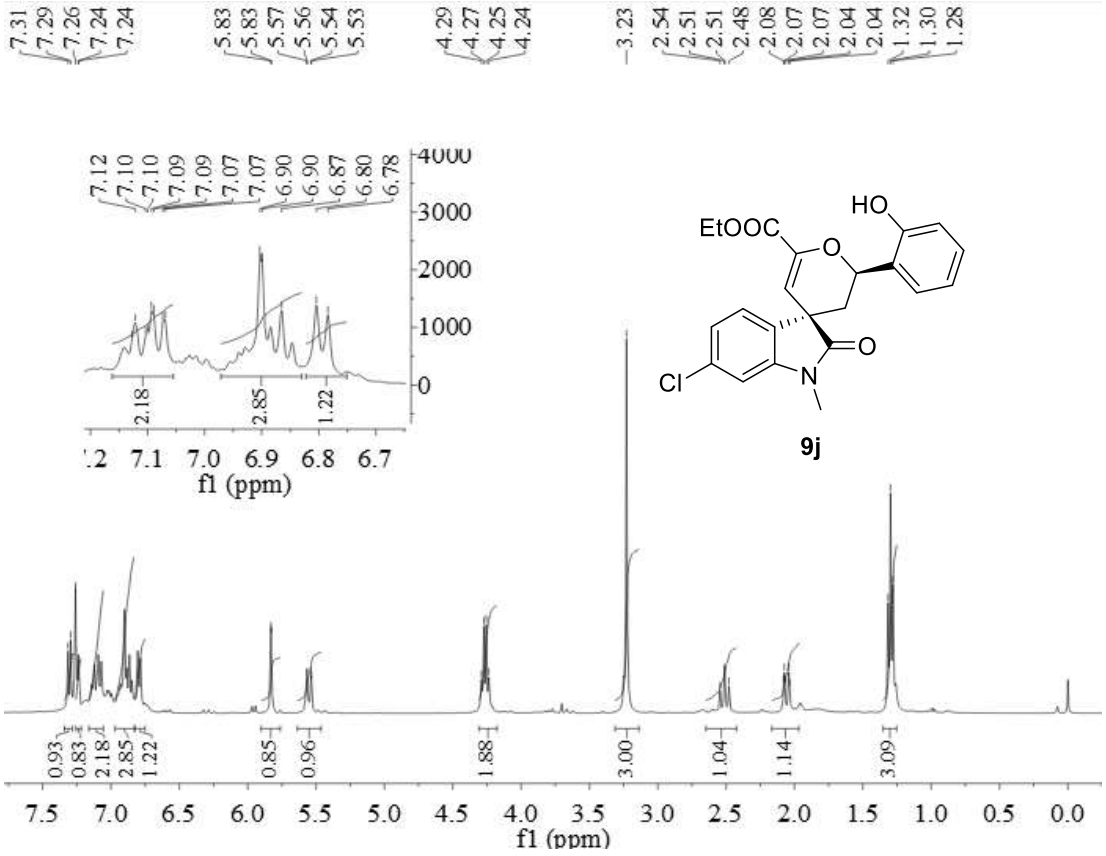


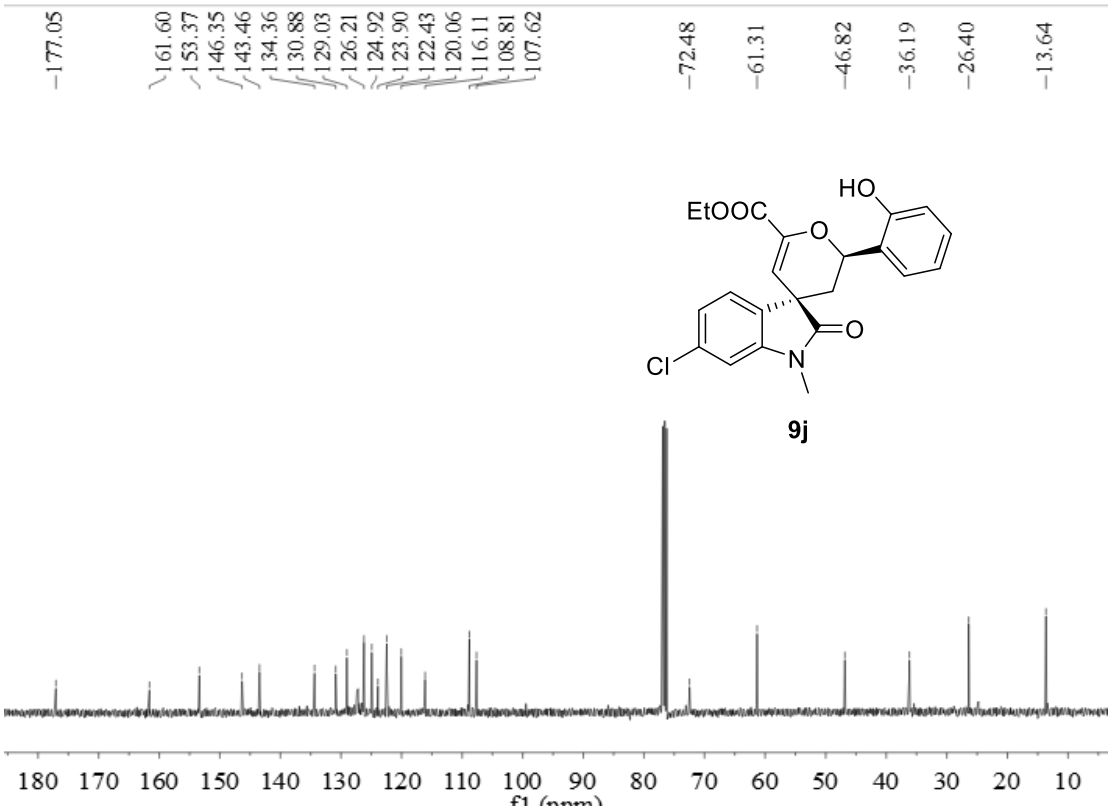
Ethyl (2'*R*,3*R*)-5-bromo-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9i



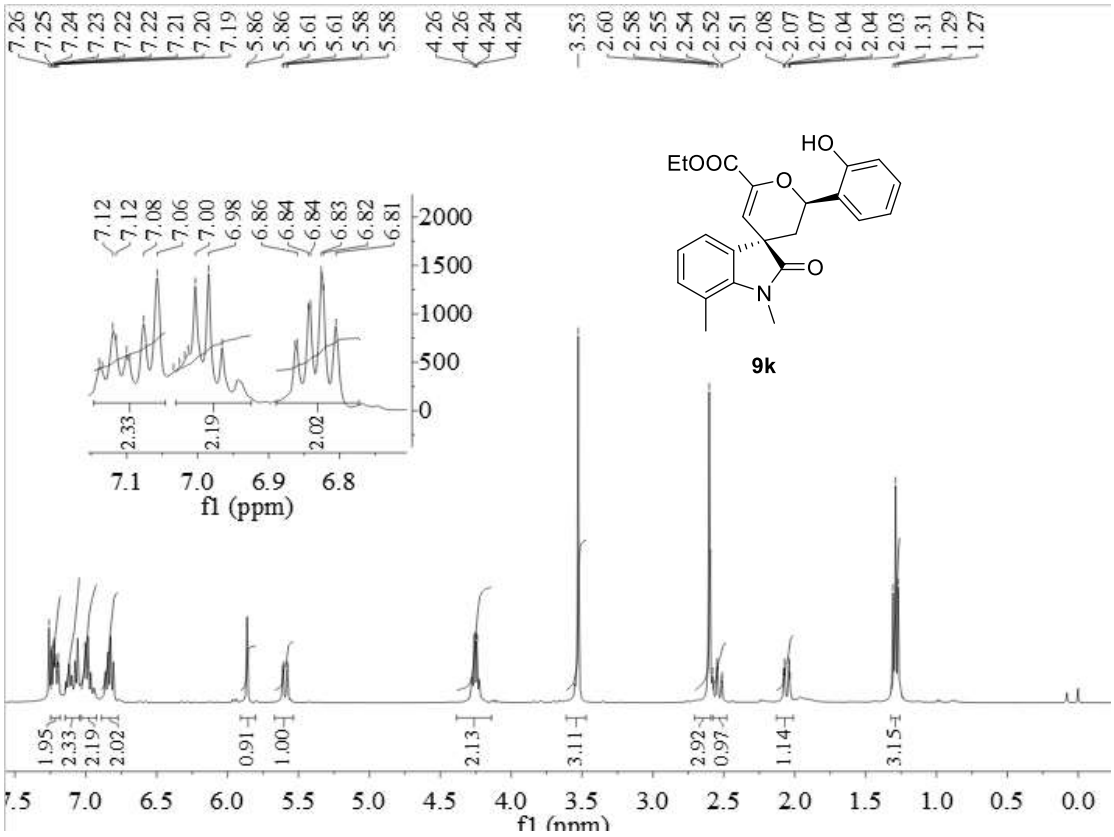


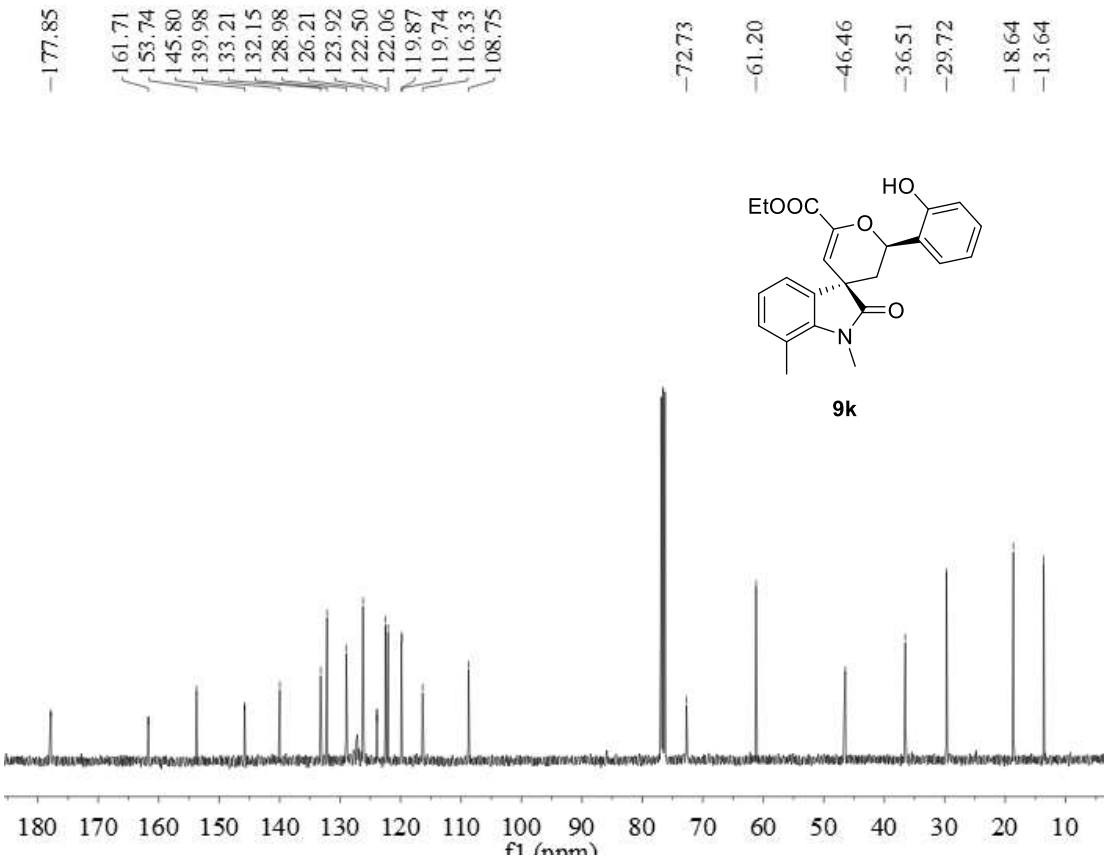
Ethyl (2'*R*,3*R*)-6-chloro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9j



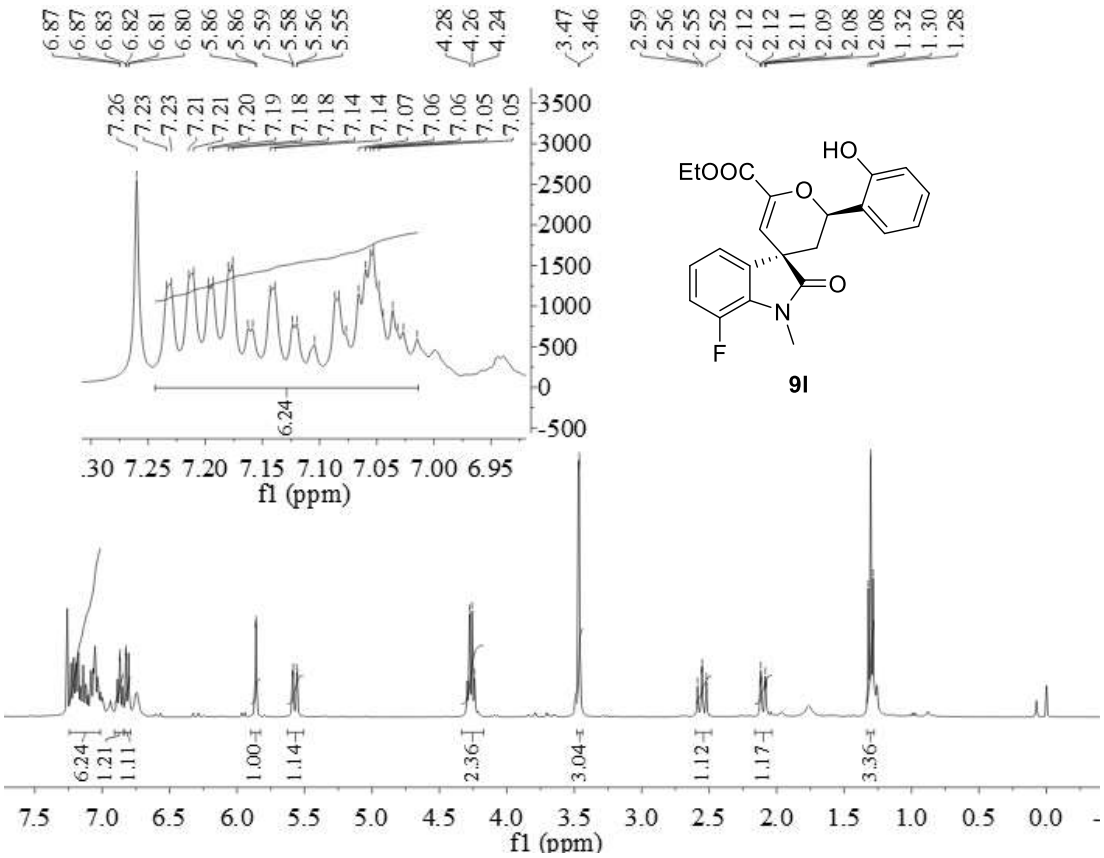


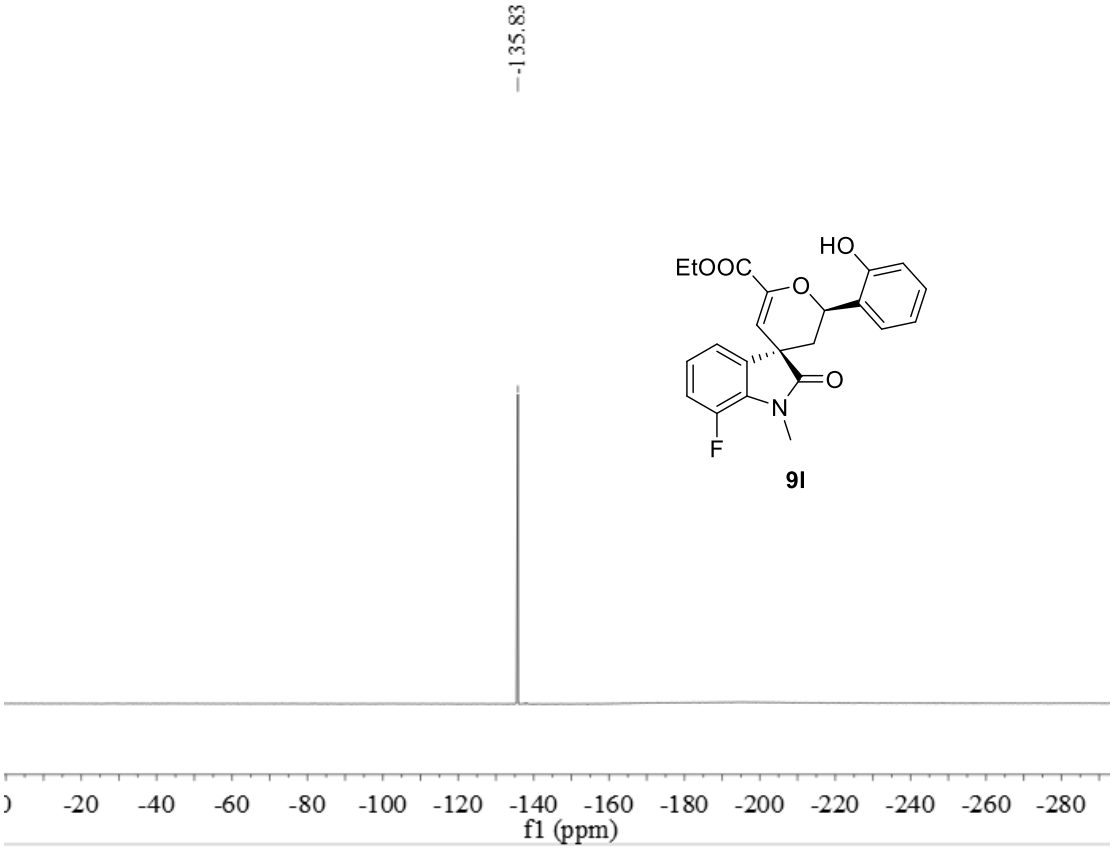
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,7-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9k

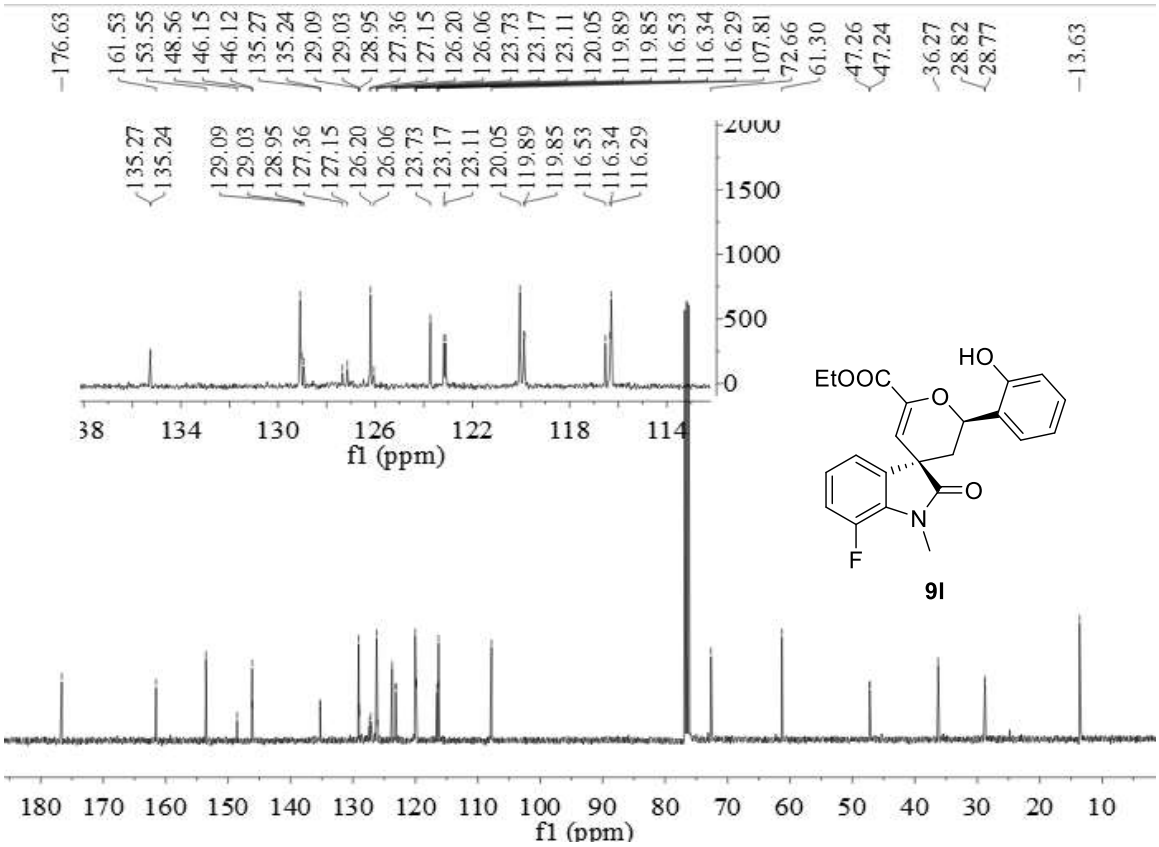




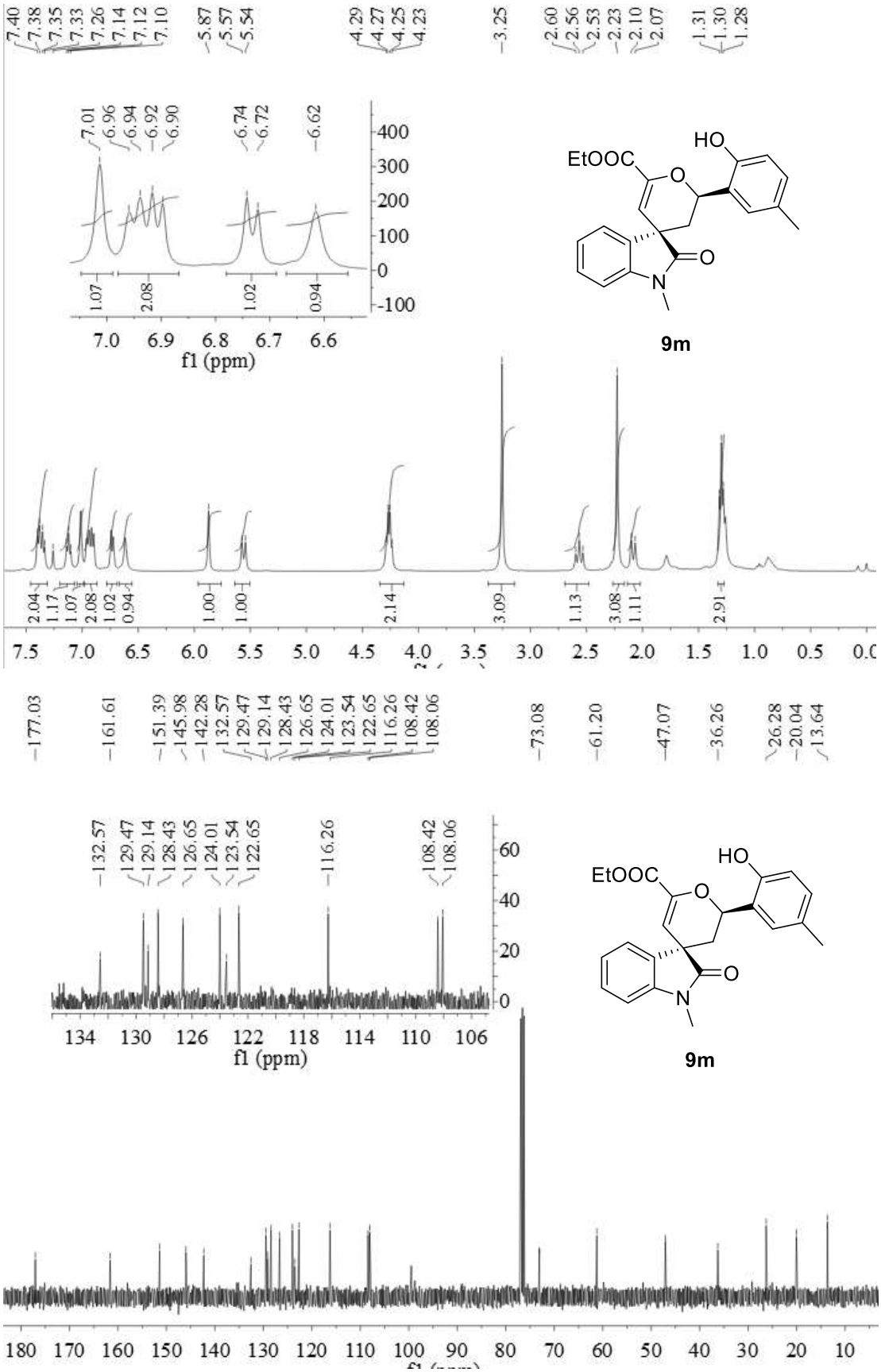
Ethyl (2'*R*,3*R*)-7-fluoro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9l



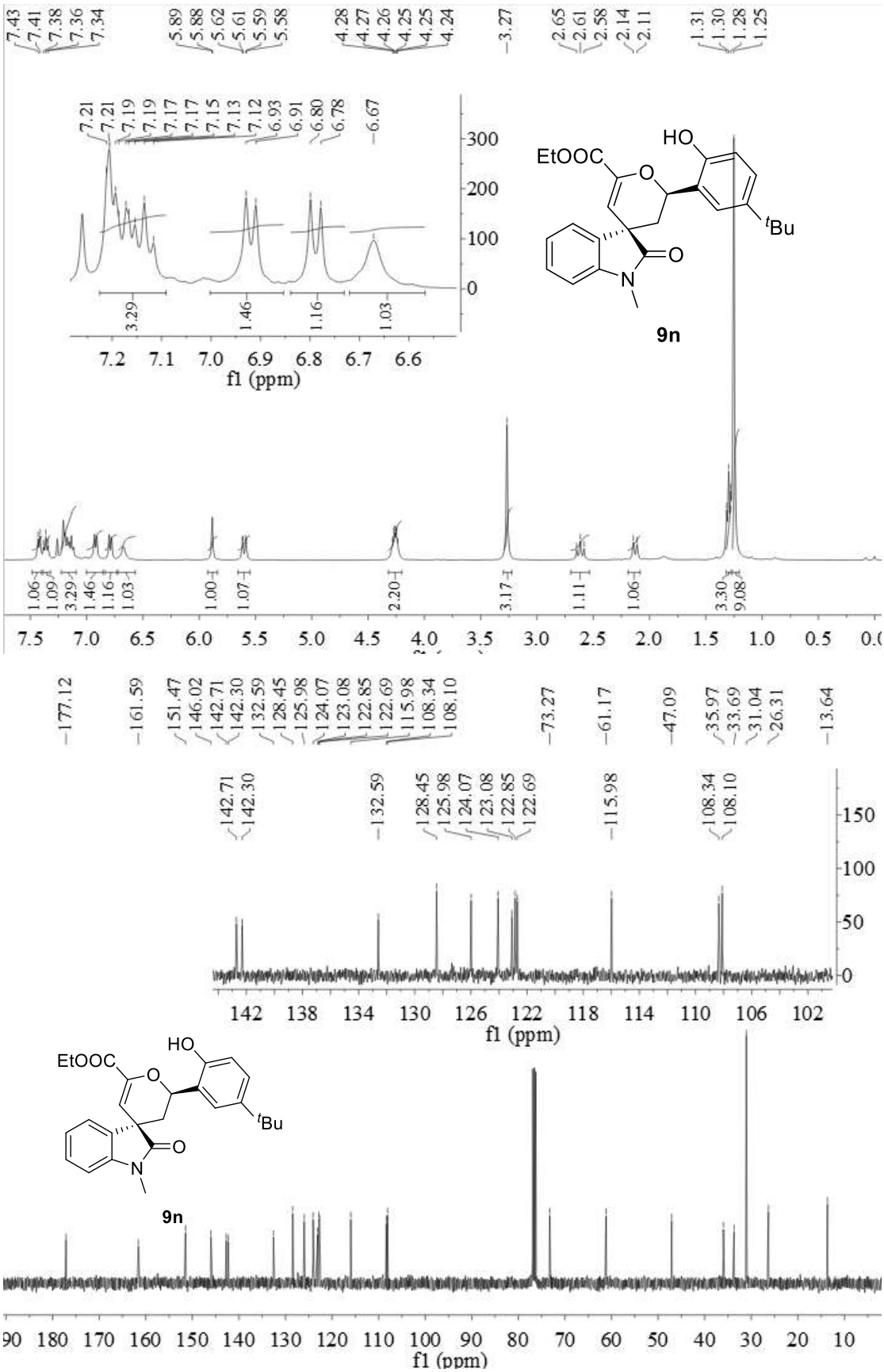

-135.83
HO
EtOOC
O
O
N
F
9l
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)


176.63
161.53
153.55
148.56
146.15
146.12
135.27
135.24
129.09
129.03
128.95
127.36
127.15
126.20
126.06
123.73
123.17
123.11
120.05
119.89
119.85
116.53
116.34
116.29
107.81
72.66
61.30
47.26
47.24
36.27
28.82
28.77
13.63
2000
1500
1000
500
0
38
134
130
126
122
118
114
f1 (ppm)
HO
EtOOC
O
O
N
F
9l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

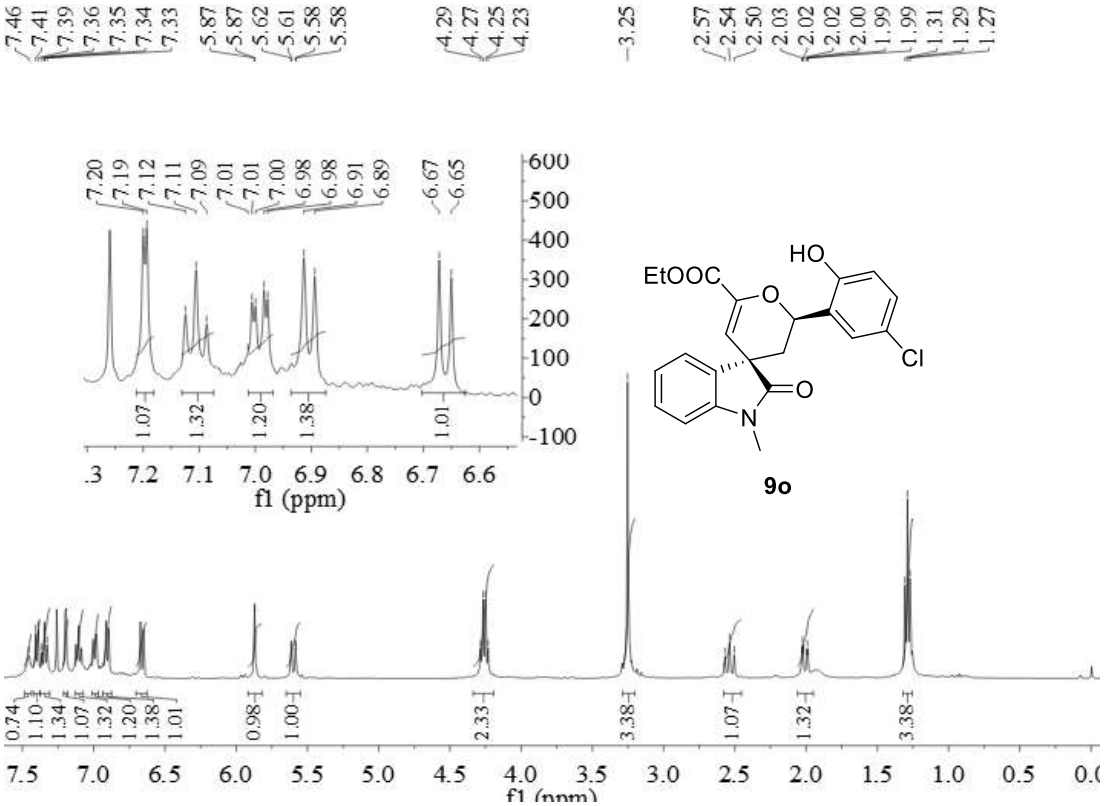
Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-5-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9m

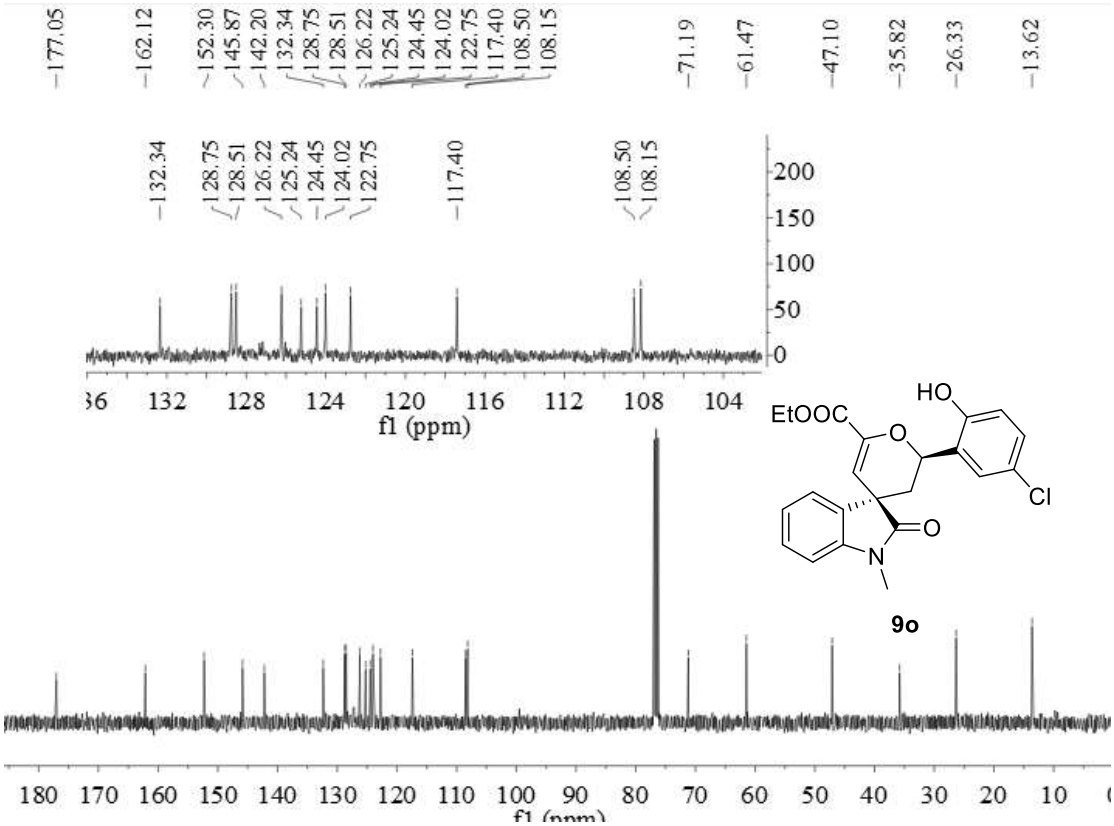


Ethyl (2'*R*,3*R*)-2'-(5-(tert-butyl)-2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9n

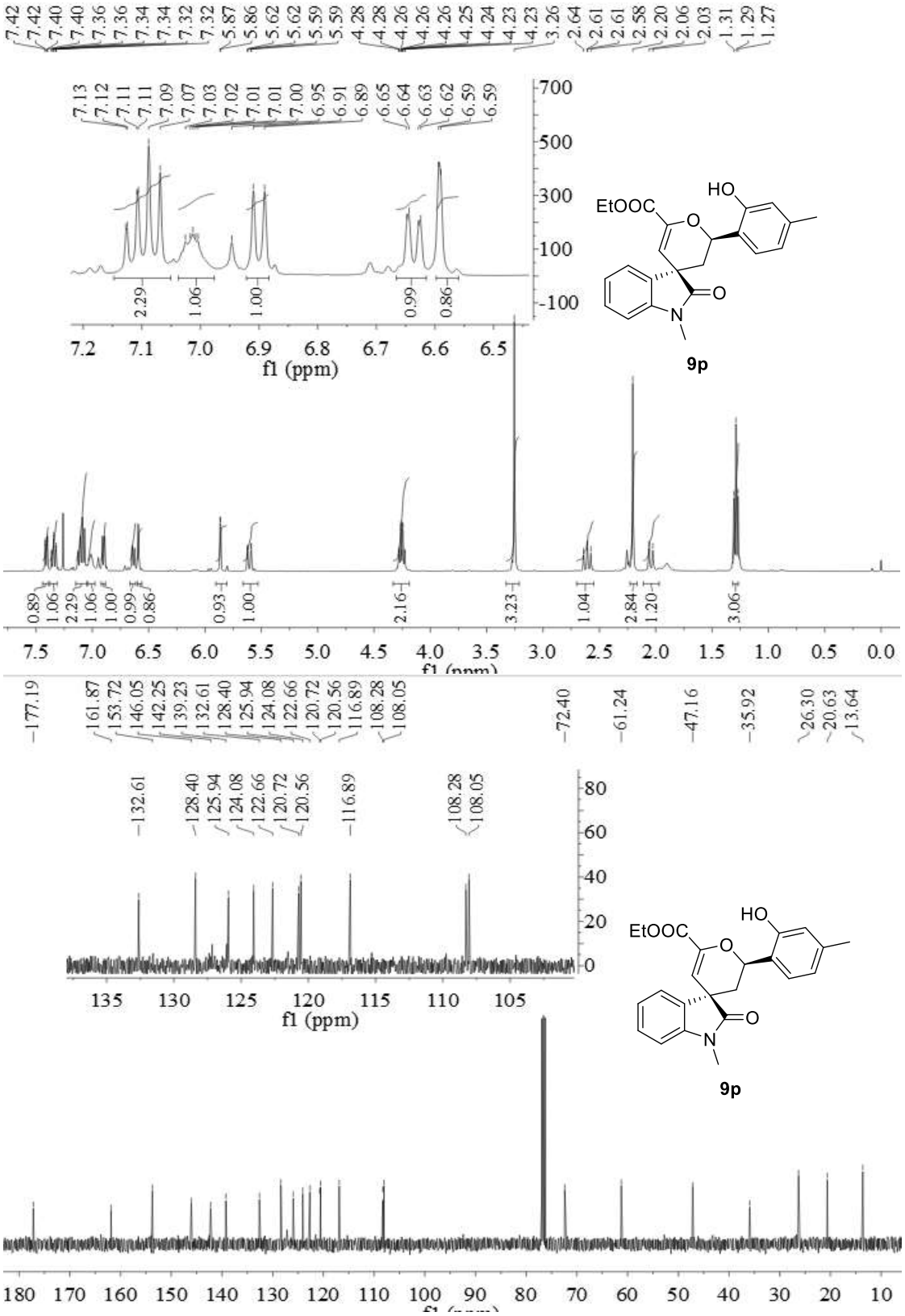


Ethyl (2'*R*,3*R*)-2'-(5-chloro-2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9o

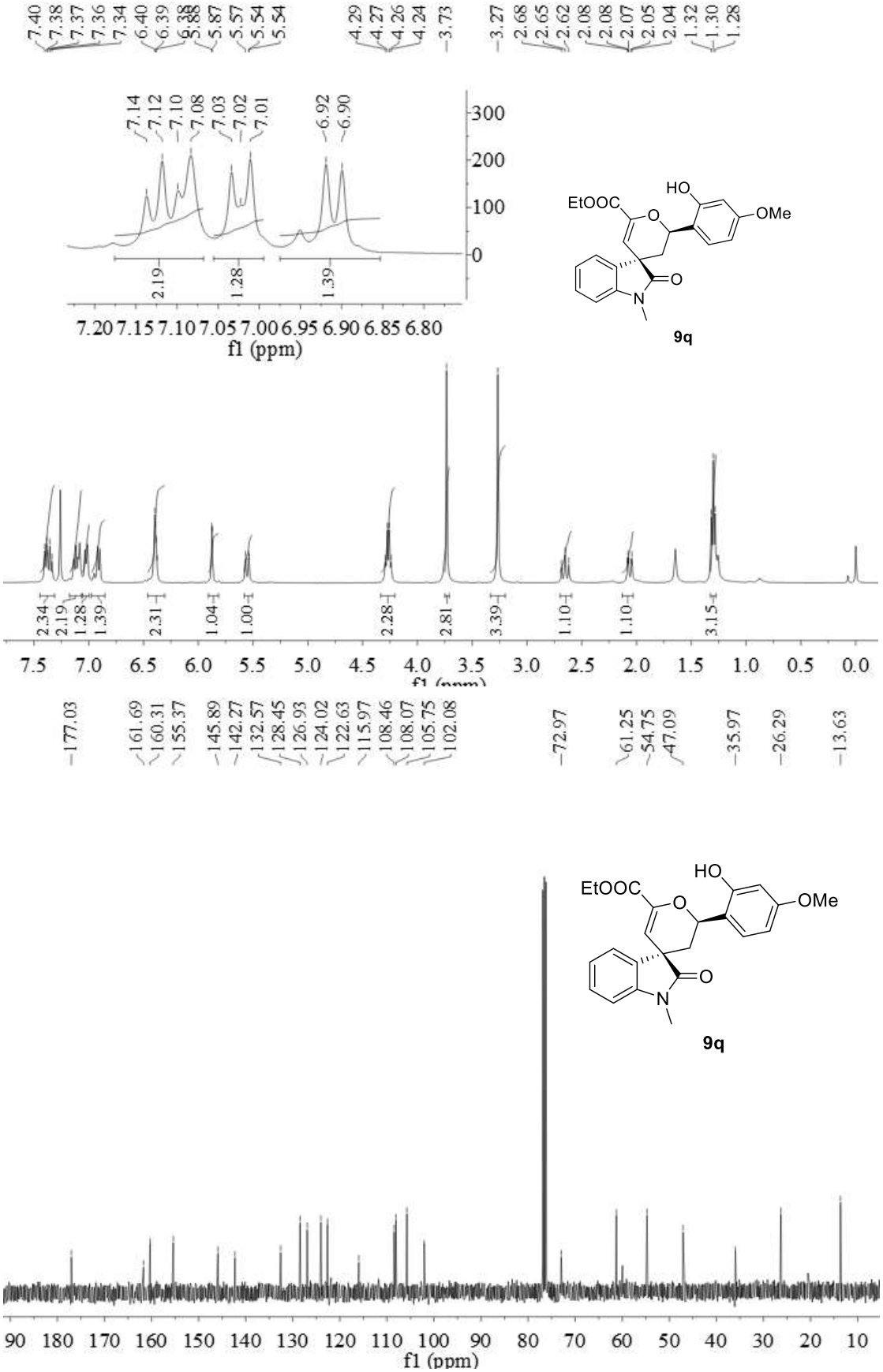




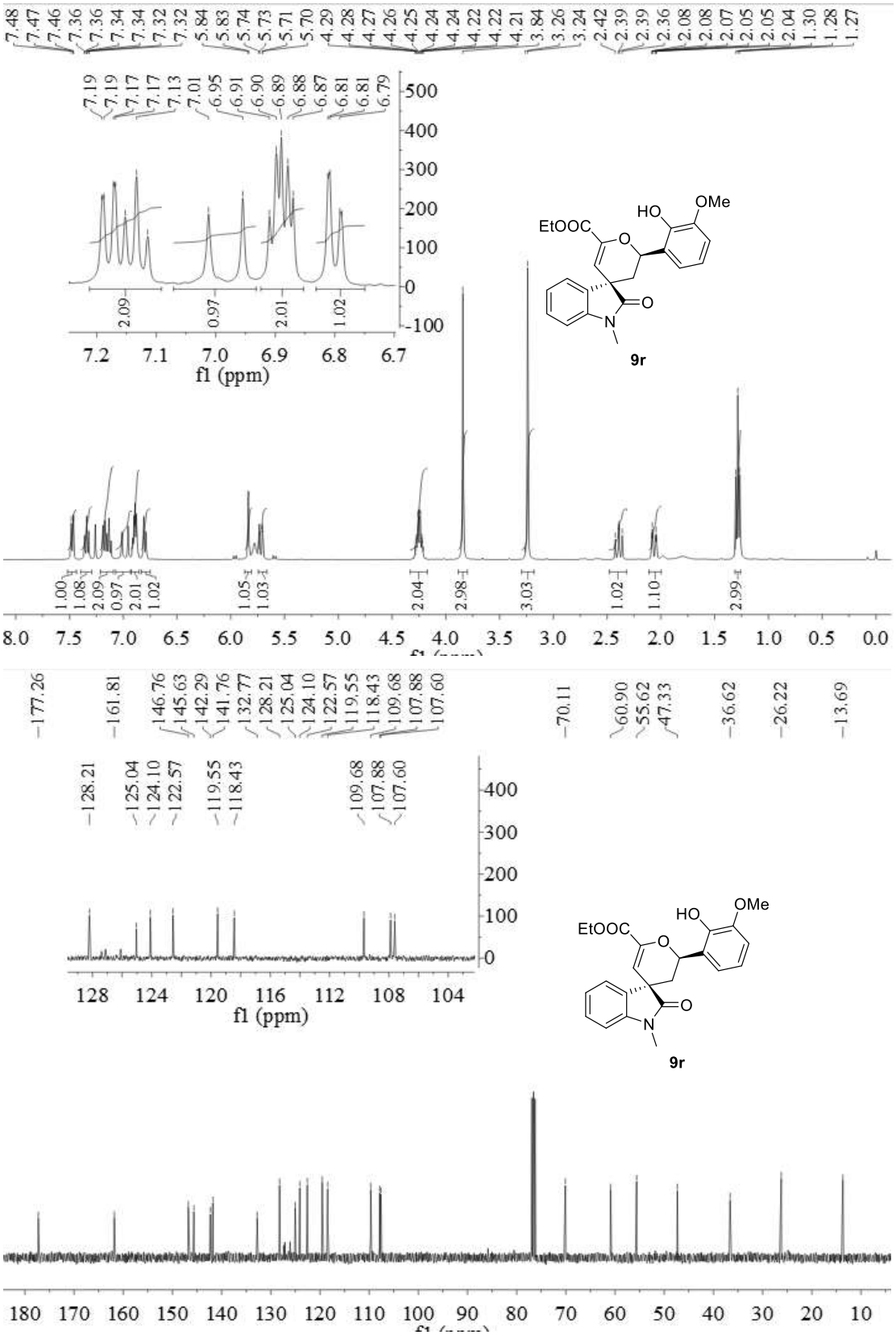
Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-4-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9p



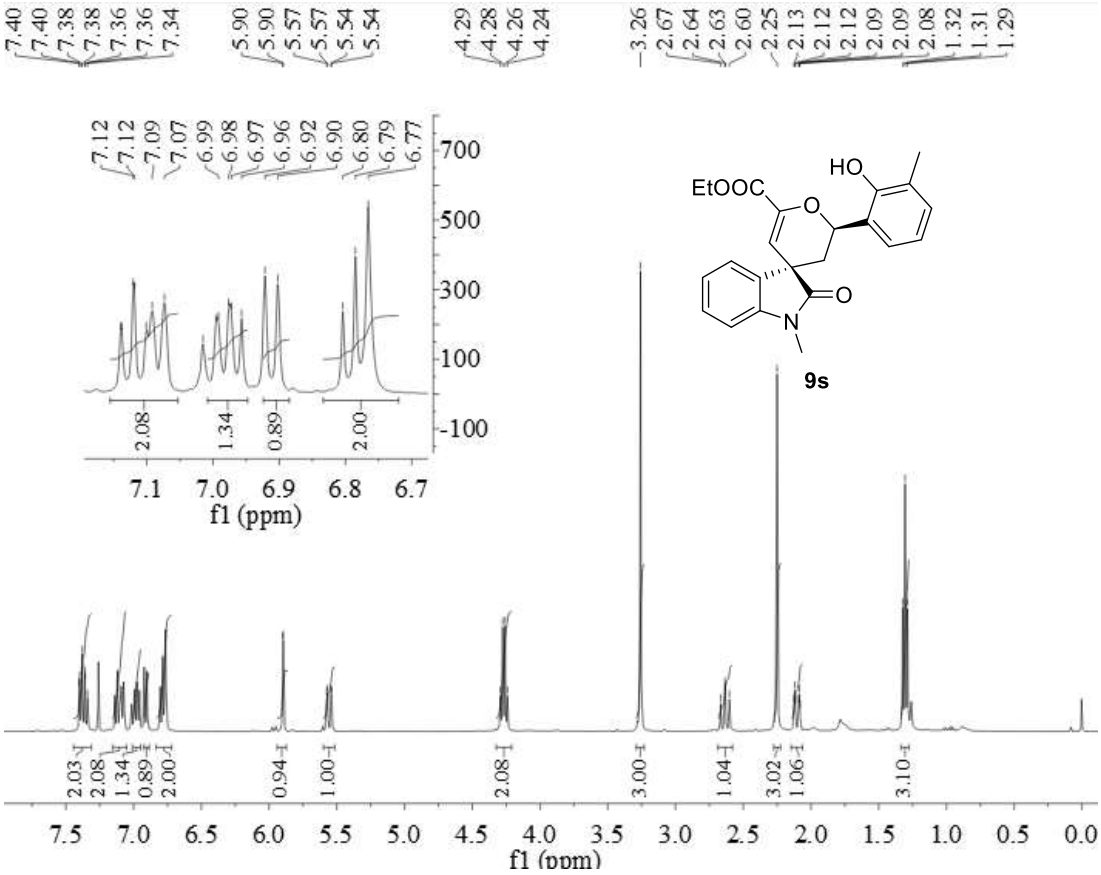
Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-4-methoxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9q

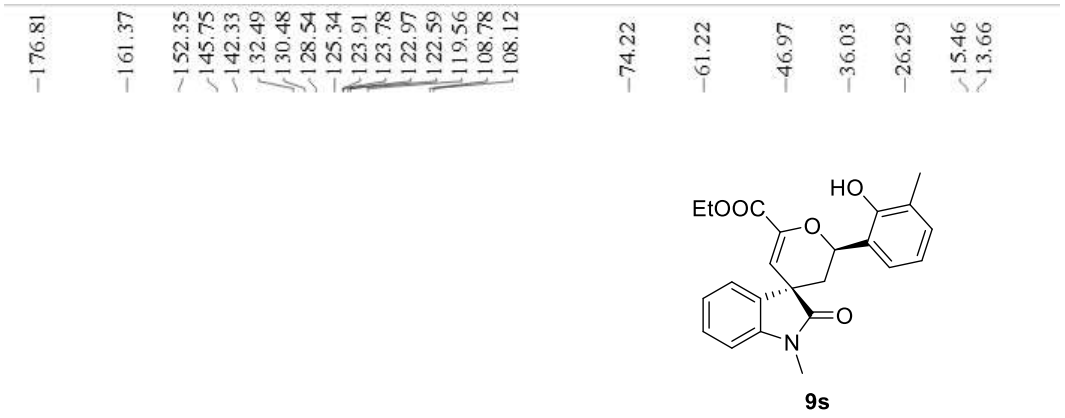


Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-3-methoxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9r

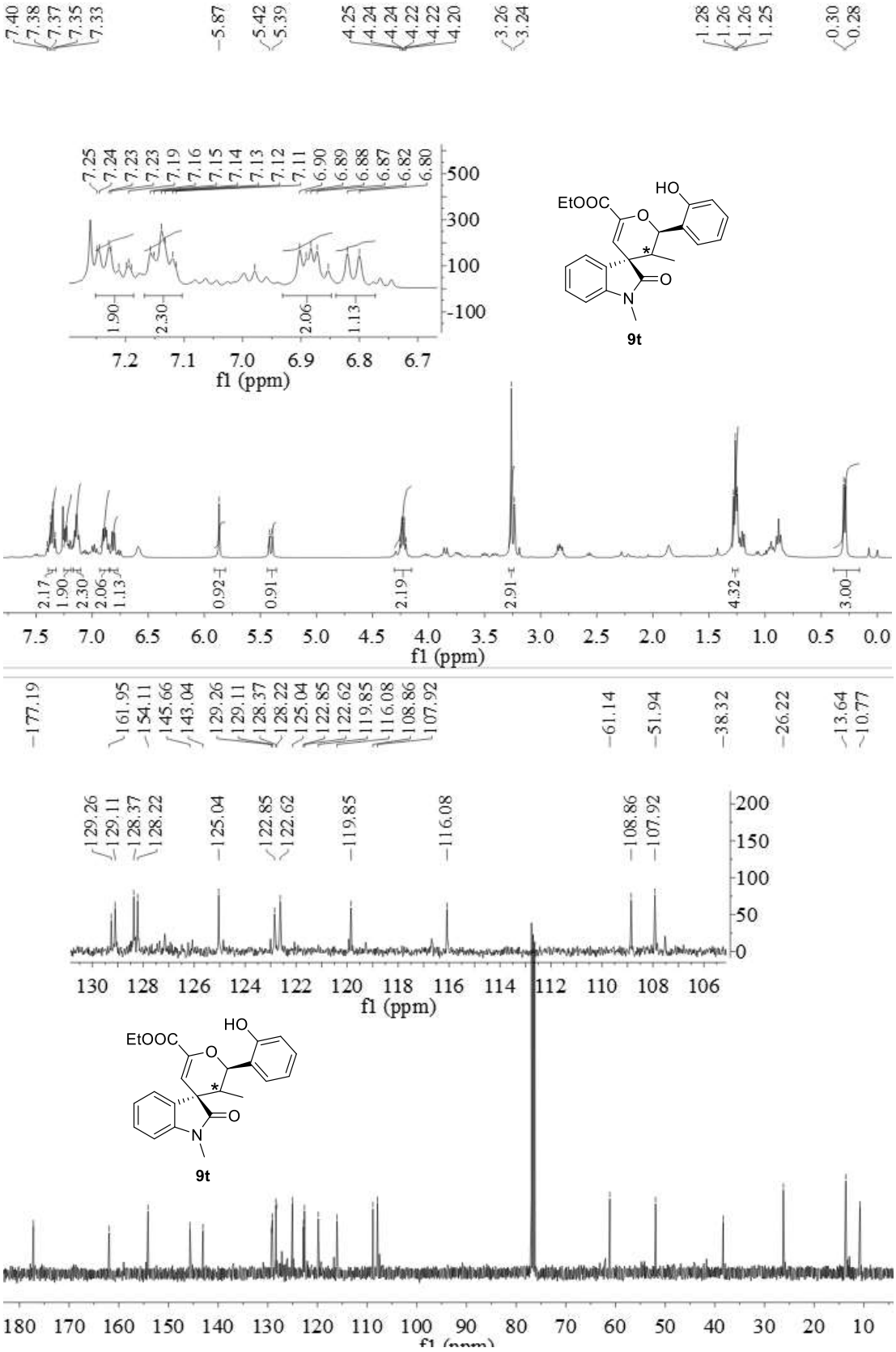


Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-3-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9s

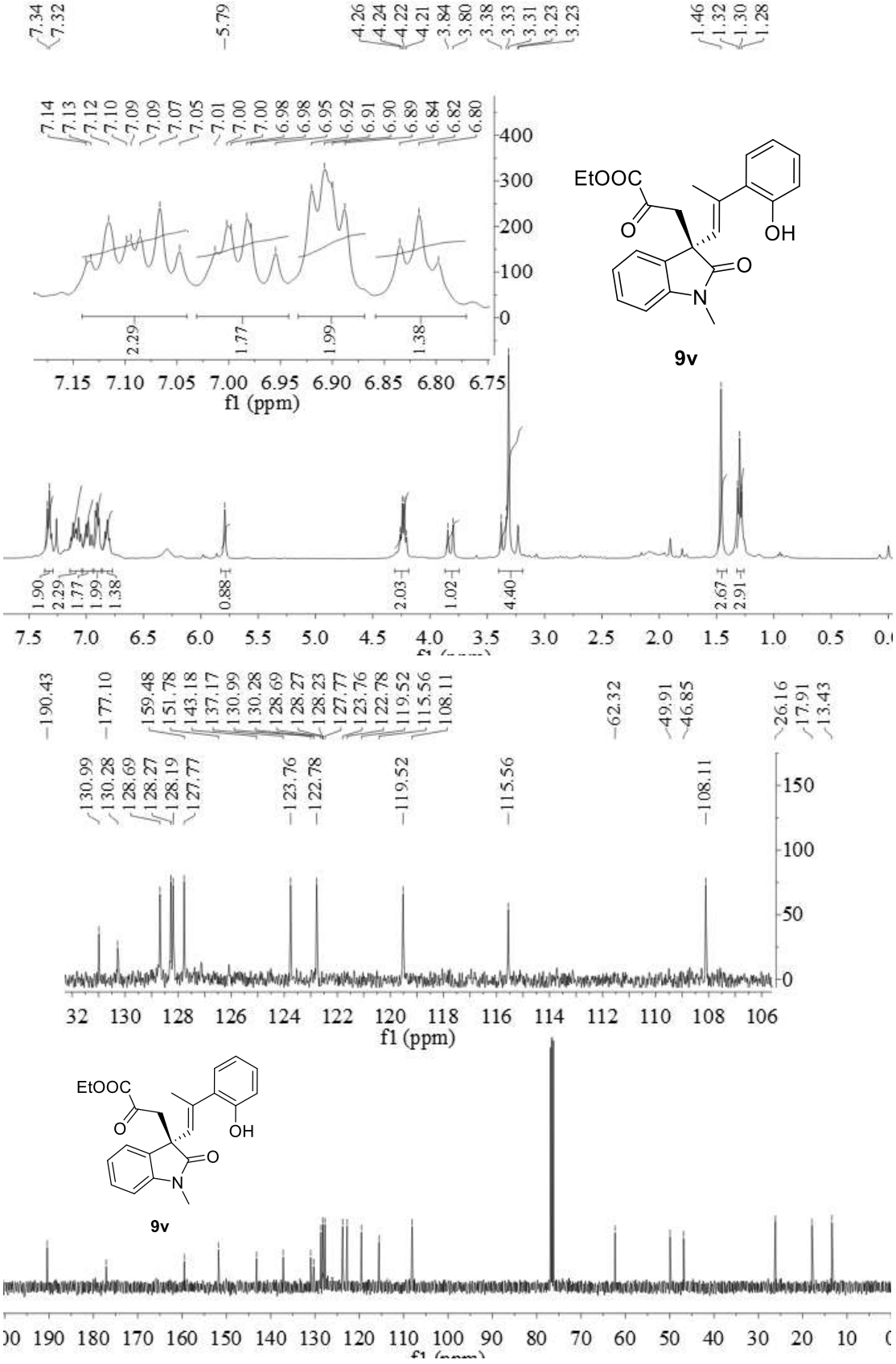




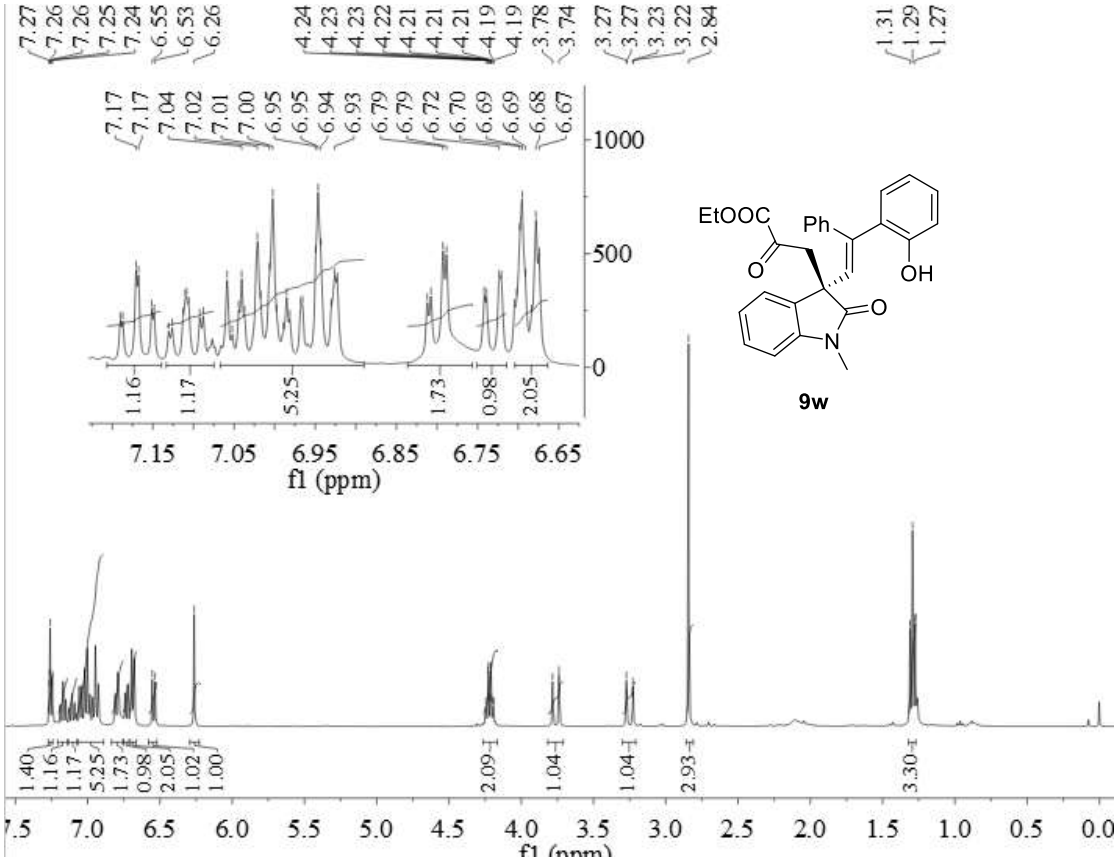
Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,3'-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9t

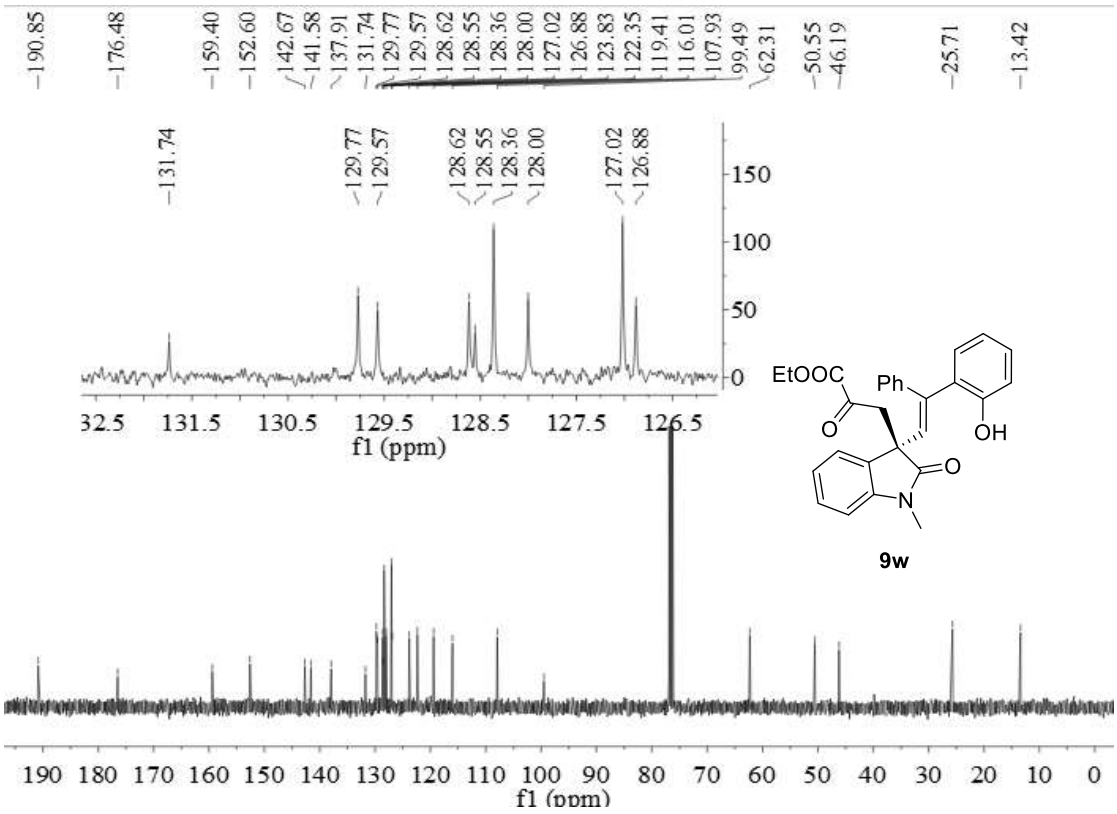


Ethyl-(*S*,*E*)-3-(3-(2-(2-hydroxyphenyl)-2-phenylvinyl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 9v

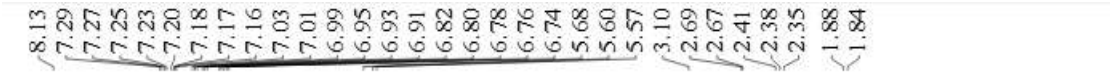


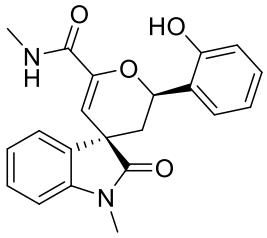
Ethyl-(*S*,*E*)-3-(3-(2-(2-hydroxyphenyl)-2-phenylvinyl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 9w



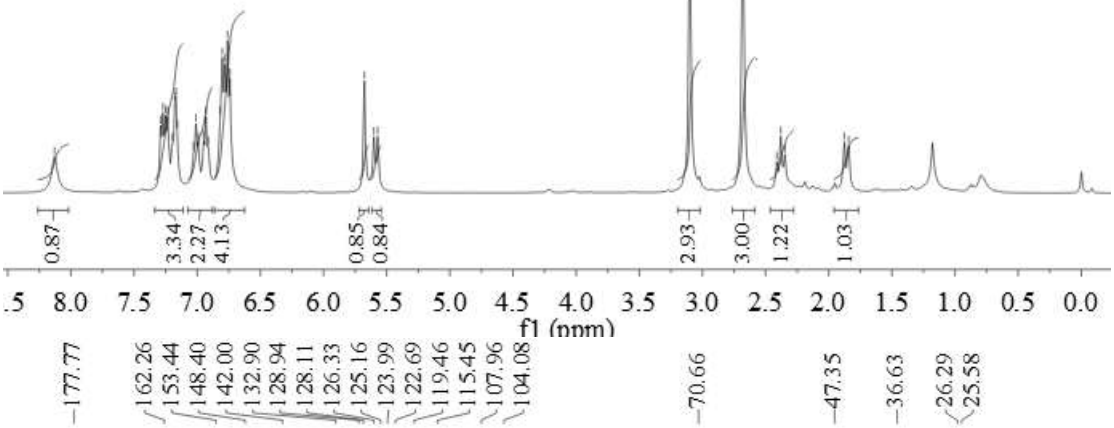


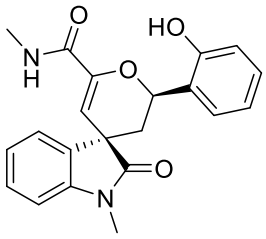
(2'*R*,3*R*)-2'-(2-Hydroxyphenyl)-N,1-dimethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxamide 12a



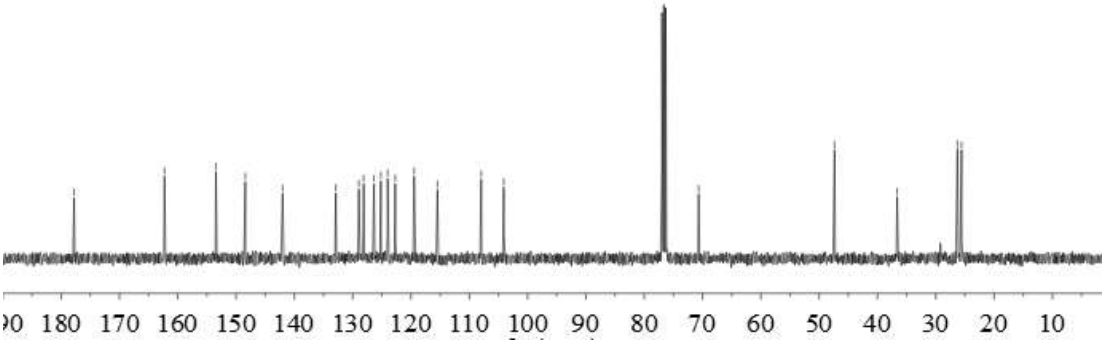


12a

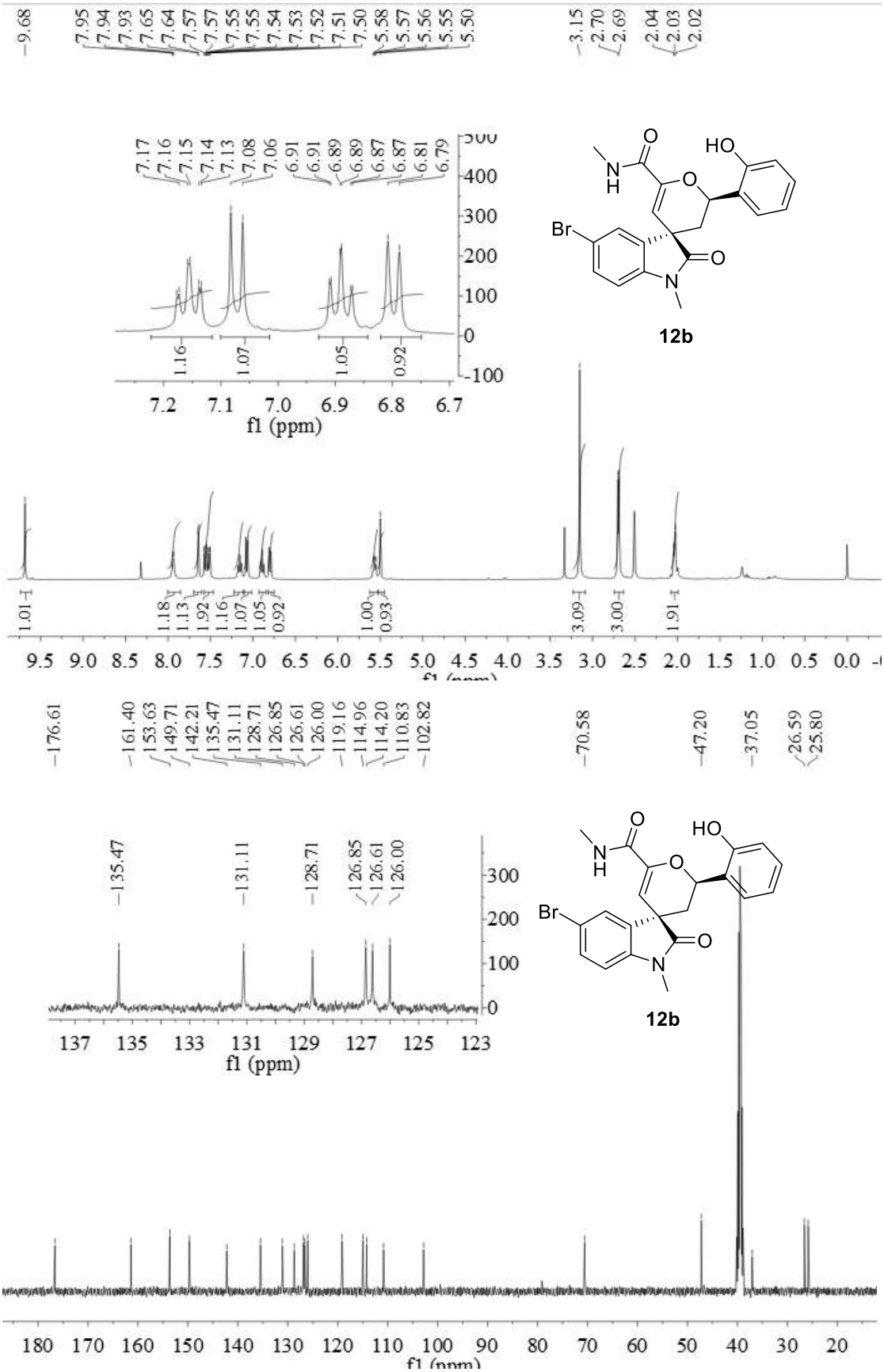




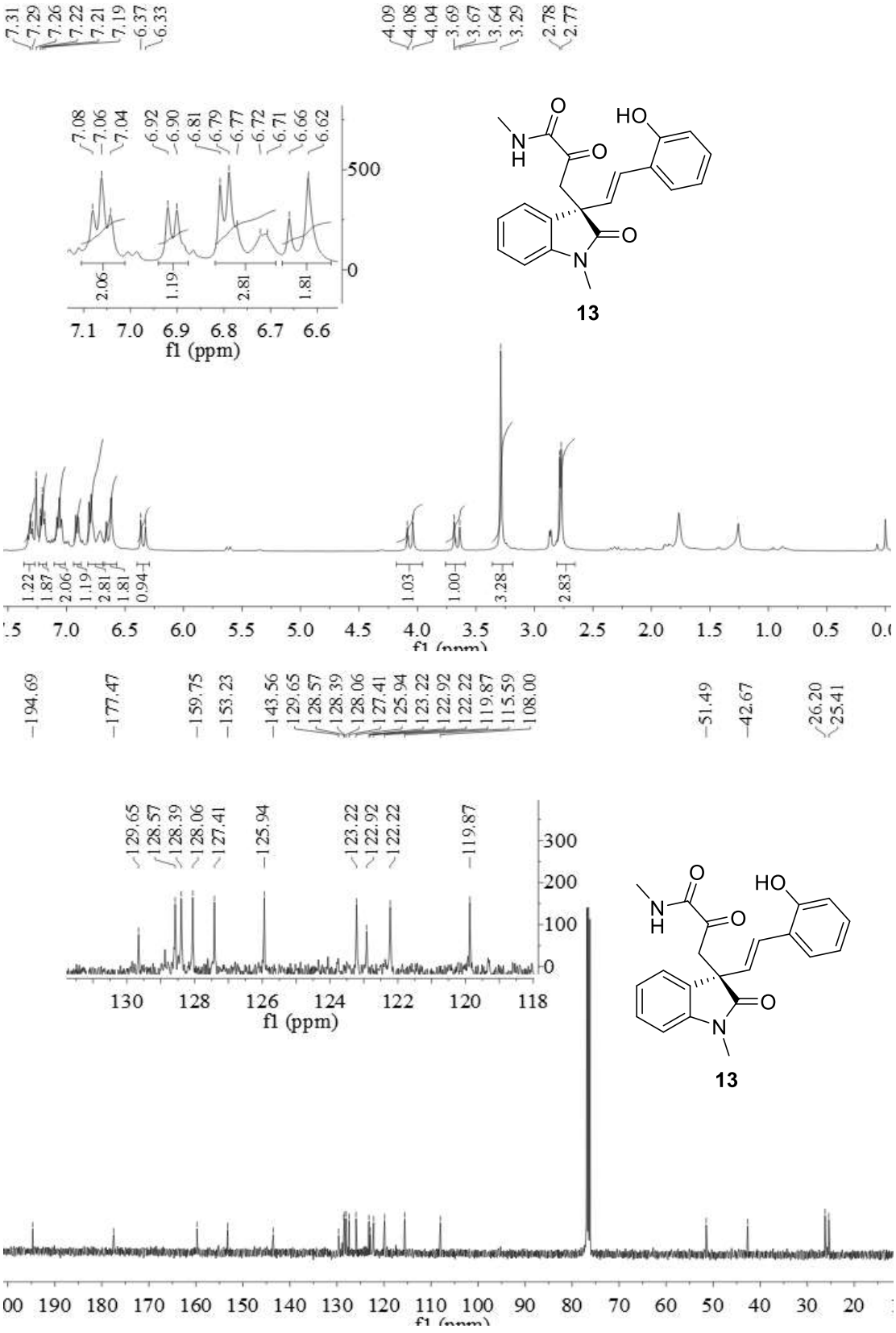
12a



(2'*R*,3*R*)-5-Bromo-2'-(2-hydroxyphenyl)-N,1-dimethyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxamide 12b

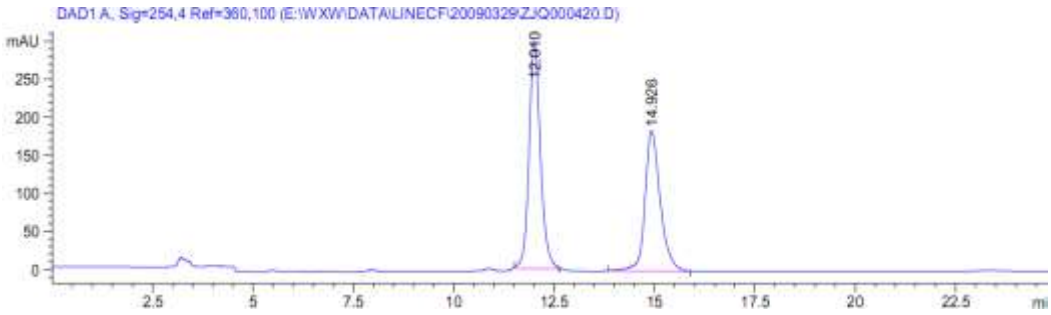


(*S*,*E*)-3-(3-(2-Hydroxystyryl)-1-methyl-2-oxoindolin-3-yl)-N-methyl-2-oxopropan amide 13

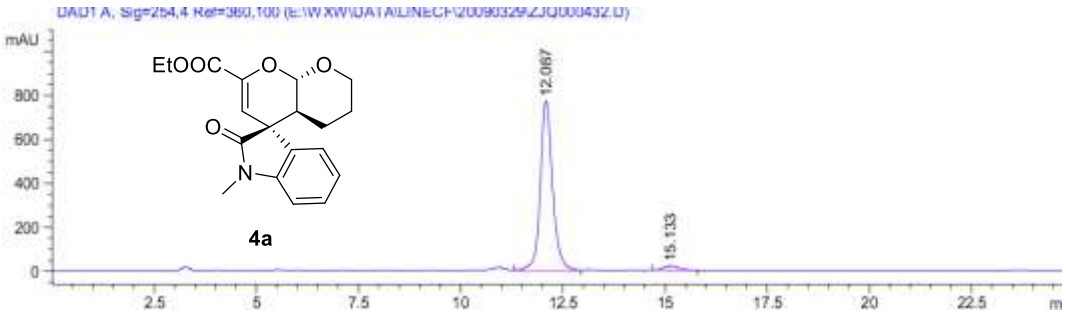


5. HPLC spectra

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro[indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4a

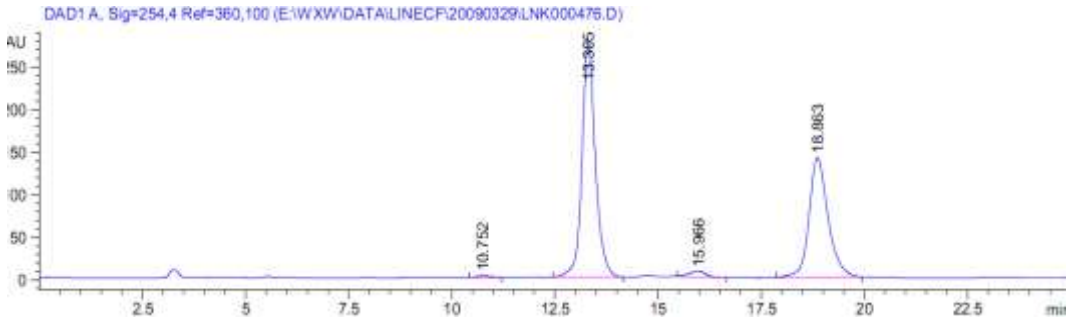


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.010	MM R	0.3275	5837.26318	297.04694	54.2712
2	14.926	BB	0.3989	4918.47314	184.56526	45.7288

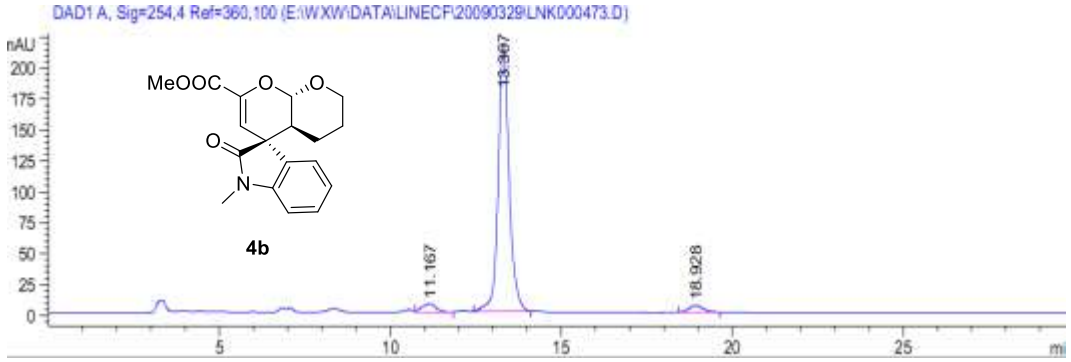


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.087	VB	0.3099	1.60170e4	772.60522	96.9208
2	15.133	BB	0.3817	508.86807	20.07600	3.0792

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro[indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4b

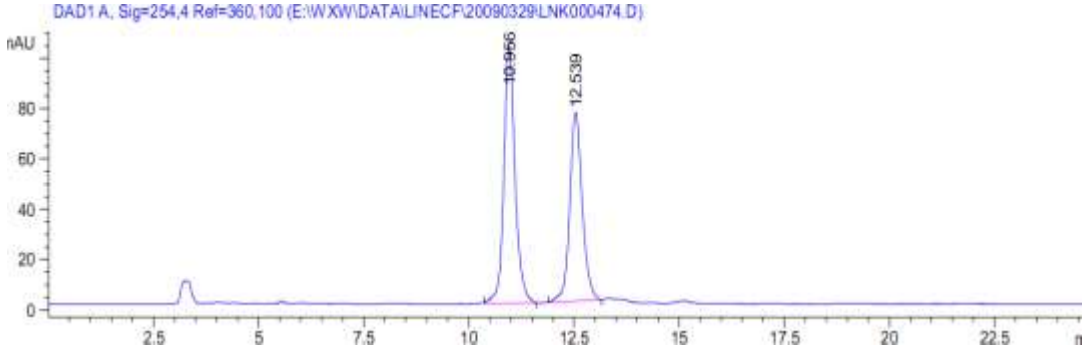


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.752	BB	0.3003	54.88220	2.68702	0.5001
2	13.305	BB	0.3375	6194.37500	274.22784	56.4408
3	15.966	BB	0.4140	192.70087	6.93989	1.7558
4	18.863	BB	0.4821	4533.04590	140.61958	41.3034

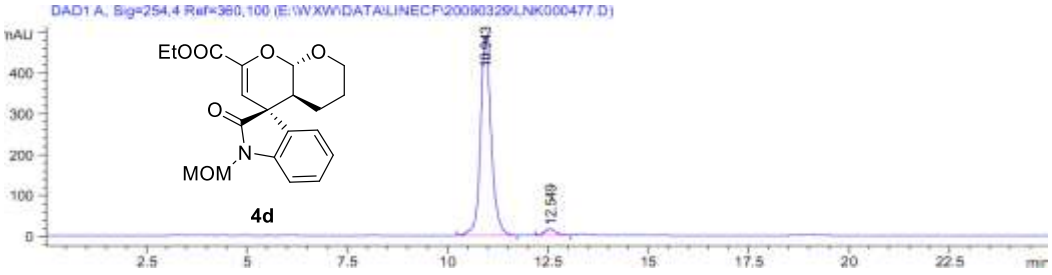


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.167	VB	0.3886	182.03857	6.50266	3.5533
2	13.307	BB	0.3345	4781.81055	214.19316	93.3390
3	18.928	BB	0.4539	159.20613	5.30844	3.1076

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-(methoxymethyl)-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro [indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4d

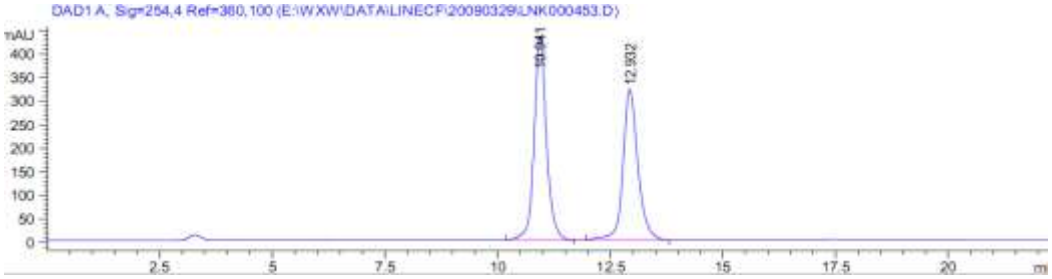


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.956	BB	0.2773	1896.75244	102.80277	54.9727
2	12.539	BB	0.3135	1553.59802	75.05650	45.0273

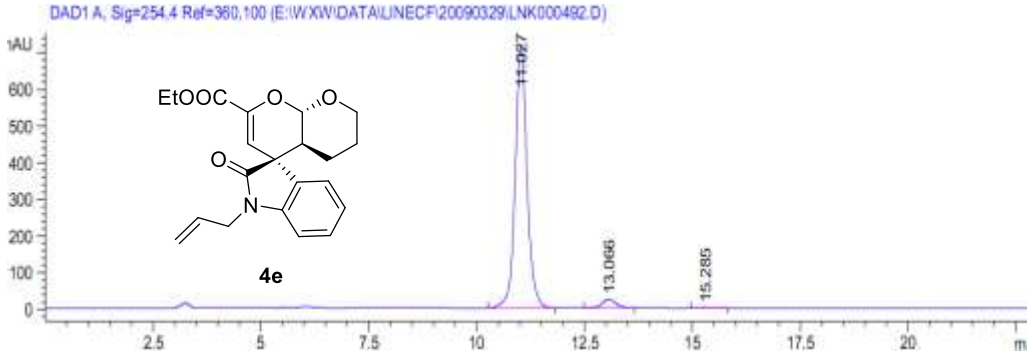


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.943	BB	0.2779	9004.24316	486.66345	96.7267
2	12.549	BB	0.3066	304.70853	15.15050	3.2733

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-allyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro[indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4e

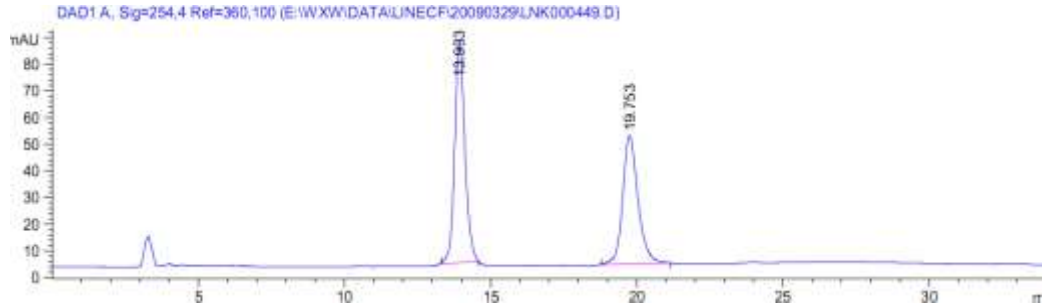


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.941	BB	0.2855	8194.08789	431.67407	52.8284
2	12.932	BB	0.3435	7316.67139	319.10590	47.1716

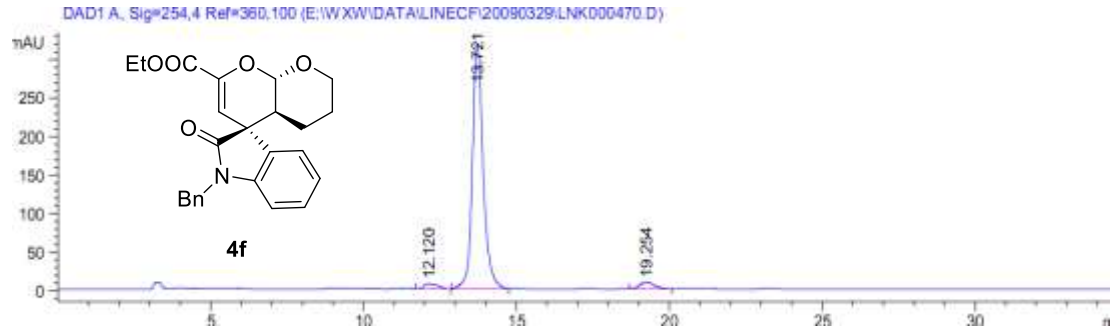


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.027	BB	0.2854	1.35841e4	715.71893	95.9715
2	13.066	BB	0.3380	534.81958	23.81756	3.7785
3	15.285	BB	0.3568	35.39359	1.49165	0.2501

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-benzyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro[indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4f

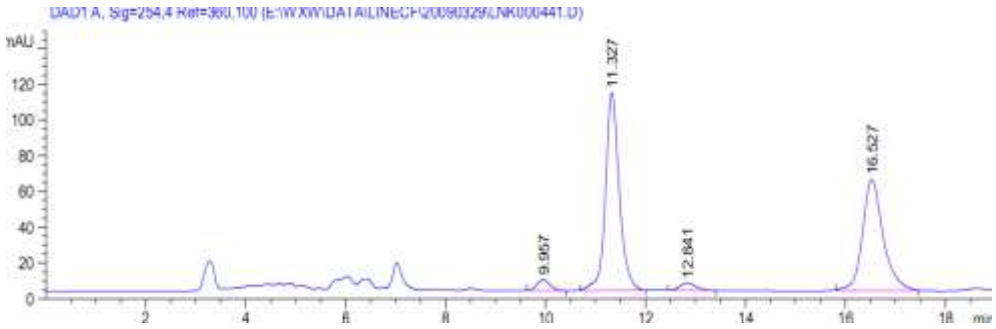


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.933	MM R	0.4044	2018.16931	83.17106	53.4362
2	19.753	MM R	0.6075	1758.61572	48.24860	46.5638

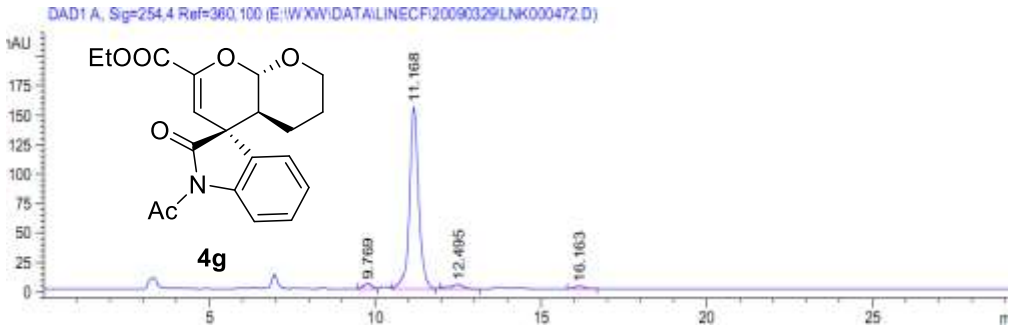


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.120	VB	0.3932	204.05815	7.14549	2.4711
2	13.721	BB	0.3678	7759.70703	316.79370	93.9695
3	19.254	BB	0.4936	293.92038	8.89187	3.5594

Ethyl-(3*S*,4a'*S*,8a'*S*)-1-acetyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro[indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4g

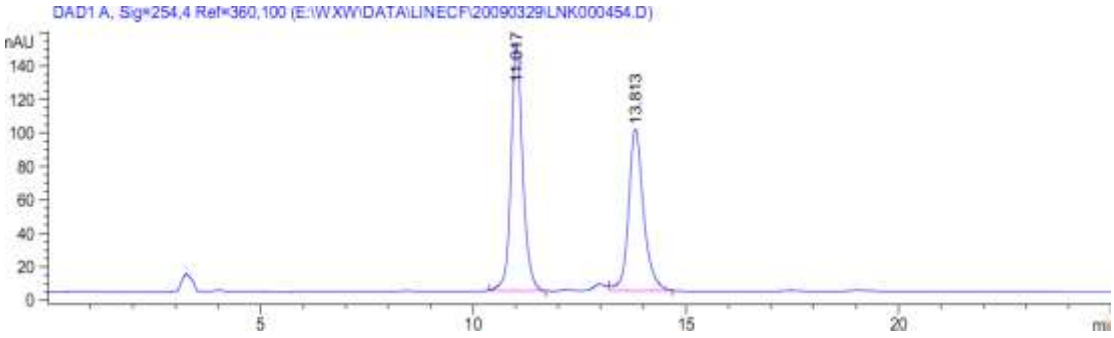


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.957	BB	0.2798	110.86740	6.10669	2.6876
2	11.327	BB	0.2879	2125.10913	110.74290	51.5158
3	12.841	BB	0.3472	91.56317	4.02854	2.2196
4	16.527	BB	0.4330	1797.61816	62.23427	43.5770

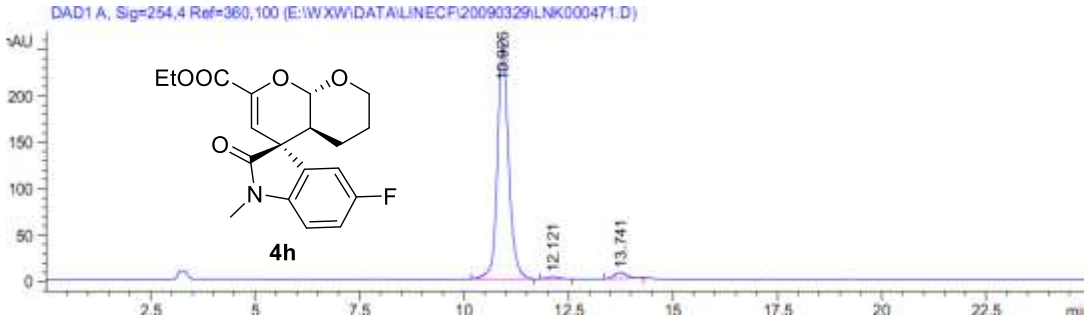


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.769	BV	0.2524	76.65792	4.64903	2.4027
2	11.168	VB	0.2855	2949.37134	153.98323	92.4414
3	12.495	BB	0.4240	111.89490	3.72971	3.5071
4	16.163	BB	0.3499	52.60800	2.14678	1.6489

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-fluoro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro[indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4h

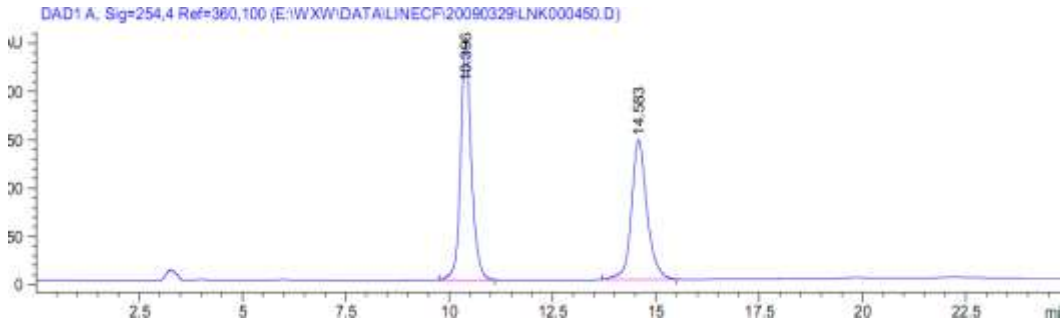


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.017	BB	0.2878	2834.57202	147.73360	54.4191
2	13.813	VB	0.3669	2374.20654	96.53751	45.5809

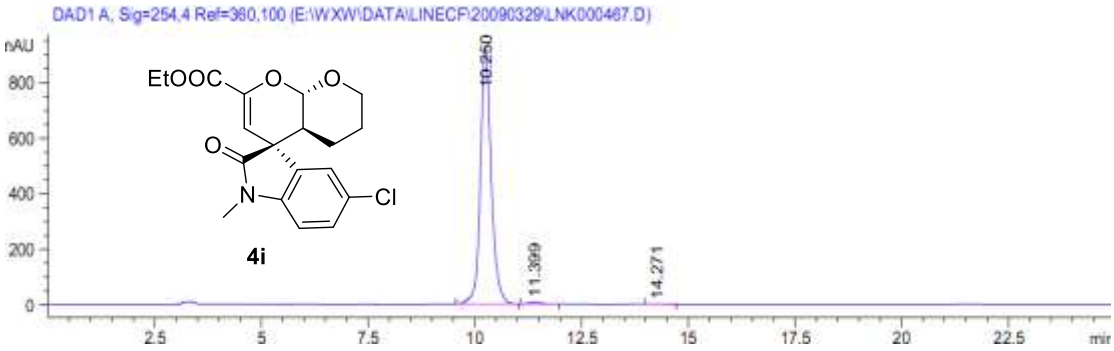


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.926	BB	0.2760	4708.45117	254.34621	96.3520
2	12.121	BB	0.2843	48.59465	2.55041	0.9944
3	13.741	BB	0.3219	129.67451	6.30725	2.6536

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-chloro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro [indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4i

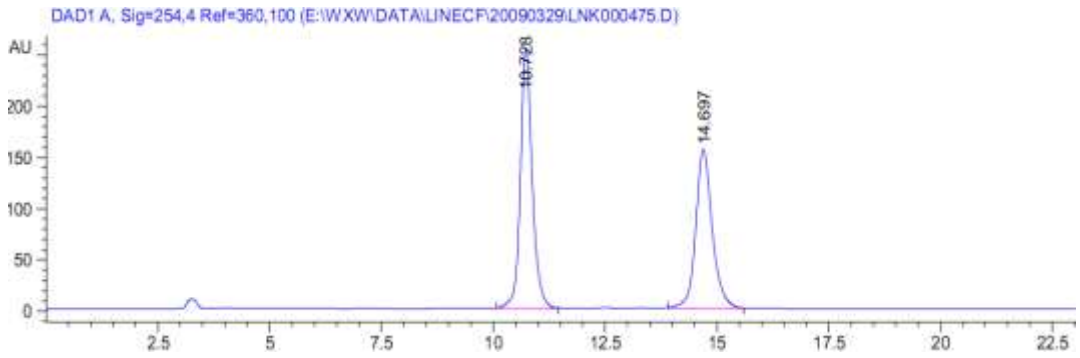


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.396	BB	0.2724	4454.45752	244.68129	53.9118
2	14.583	BB	0.3949	3808.03027	144.73979	46.0882

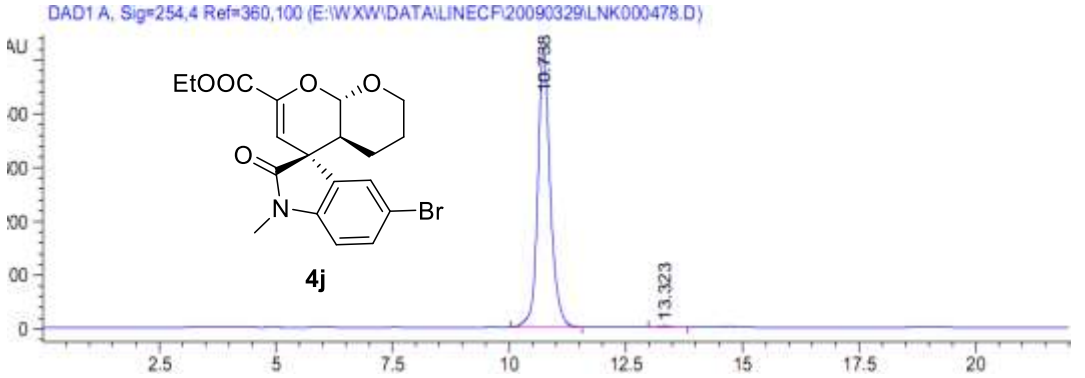


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.250	BB	0.2641	1.63457e4	925.41730	98.8751
2	11.399	BB	0.2957	157.20070	7.98390	0.9509
3	14.271	BB	0.3126	28.75981	1.37202	0.1740

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-bromo-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4j

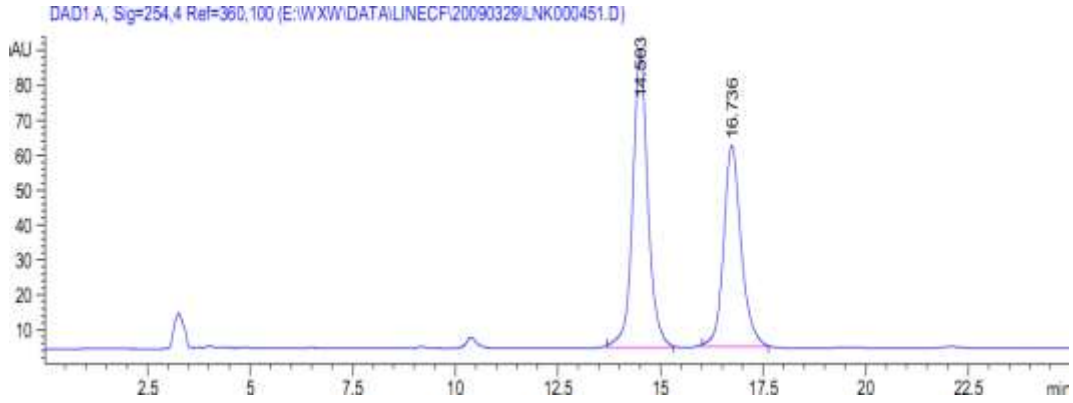


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.728	BB	0.2767	4665.54639	253.49553	53.9320
2	14.697	BB	0.3861	3985.25464	154.91707	46.0680

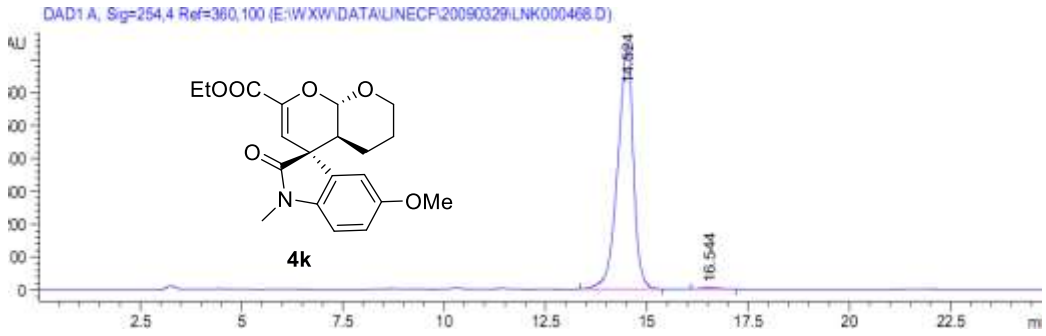


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.738	BB	0.2779	9683.71094	518.58679	99.5324
2	13.323	BB	0.3220	45.49331	2.15739	0.4676

Ethyl-(3*S*,4a'*S*,8a'*S*)-5-methoxy-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4k

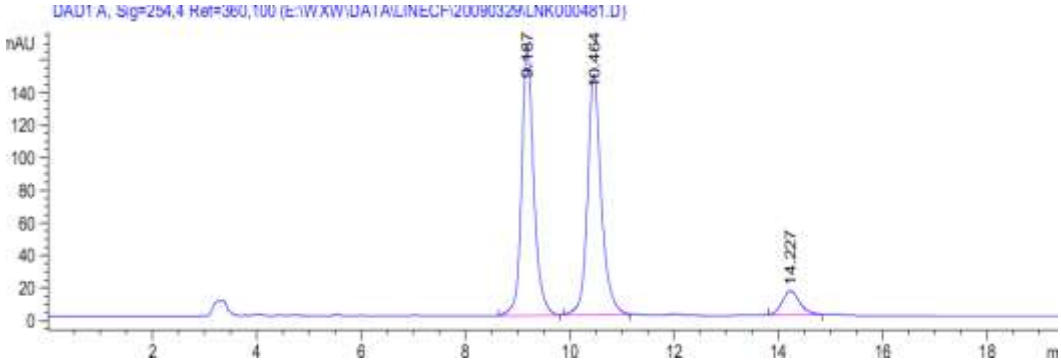


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.503	BB	0.3872	2190.33447	84.83643	56.0969
2	16.736	BB	0.4467	1714.21924	57.68462	43.9031

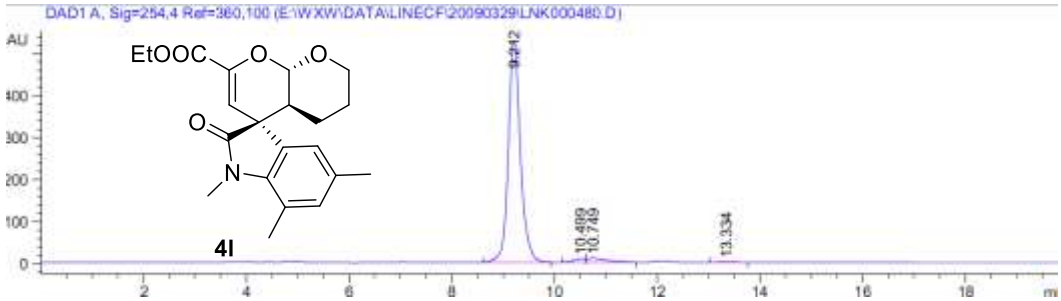


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.524	BB	0.4046	1.98912e4	742.25098	99.3367
2	16.544	BB	0.4180	132.81369	4.81237	0.6633

Ethyl-(3*S*,4a'*S*,8a'*S*)-1,5,7-trimethyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4l

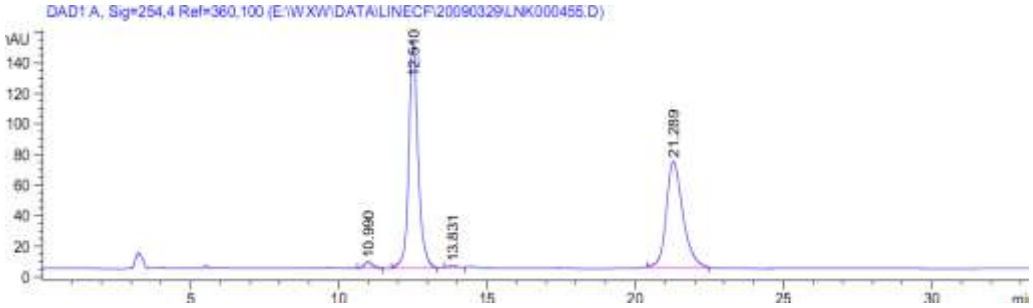


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.187	BB	0.2416	2667.77417	165.88712	46.6740
2	10.464	BB	0.2744	2708.00146	147.33783	47.3778
3	14.227	BB	0.3554	339.98495	14.61717	5.9482

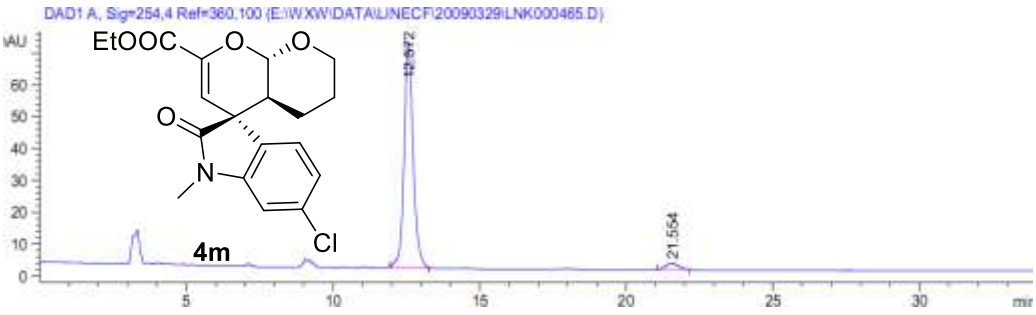


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.212	BB	0.2445	8591.64063	526.04712	95.3137
2	10.499	BV	0.2226	125.16537	8.56043	1.3886
3	10.749	VB	0.3821	267.00815	9.32289	2.9621
4	13.334	BB	0.3083	30.25476	1.42164	0.3356

Ethyl-(3*S*,4a'*S*,8a'*S*)-6-chloro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'*H*-spiro [indoline-3,4'-pyrano[2,3-*b*]pyran]-2'-carboxylate 4m

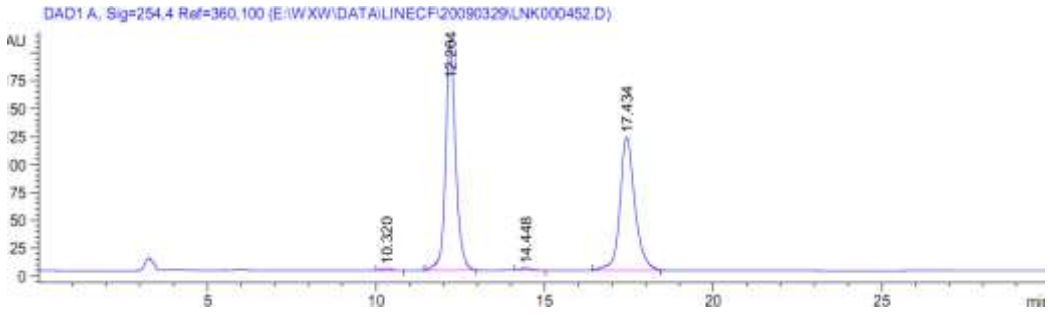


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.990	BB	0.3055	84.59505	4.15579	1.3936
2	12.510	BB	0.3261	3242.03125	148.86288	53.4069
3	13.831	BB	0.2731	20.87761	1.16491	0.3439
4	21.289	BB	0.5905	2722.93115	69.59356	44.8556

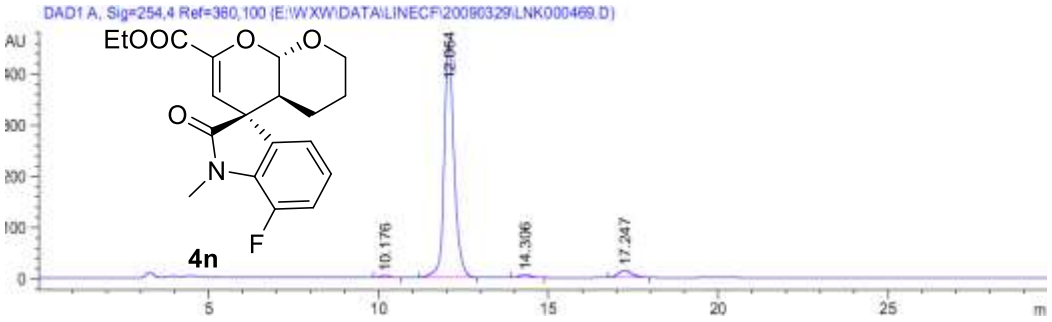


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.572	BB	0.3212	1513.23401	70.84232	96.5902
2	21.554	MM R	0.5124	53.42019	1.73742	3.4098

Ethyl-(3*S*,4a'*S*,8a'*S*)-7-fluoro-1-methyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4n

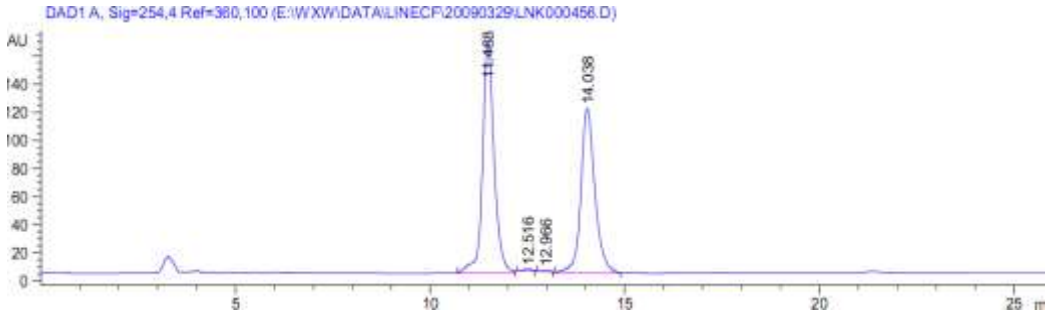


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.320	BB	0.2928	35.94599	1.89945	0.4491
2	12.204	BB	0.3105	4245.49121	204.24701	53.0391
3	14.448	BB	0.3516	43.33517	1.90386	0.5414
4	17.434	BB	0.4631	3679.67749	119.55741	45.9704

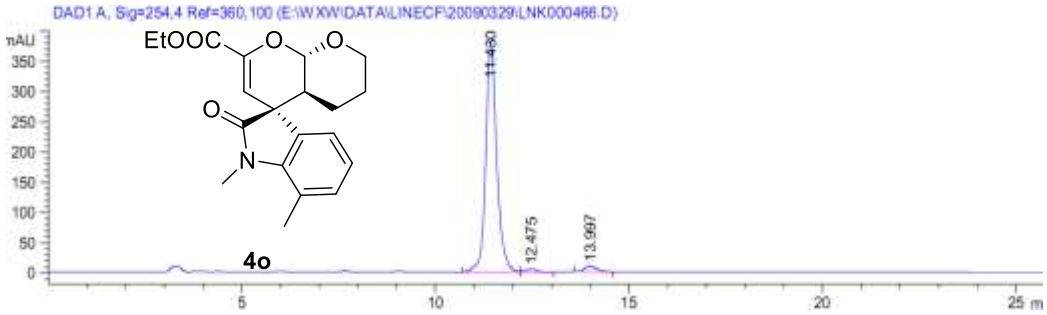


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.176	BB	0.2932	68.15168	3.56302	0.6871
2	12.064	BB	0.3055	9337.32910	458.69473	94.1320
3	14.306	BB	0.3501	123.70676	5.42459	1.2471
4	17.247	BB	0.4278	390.21054	13.80235	3.9338

Ethyl-(3*S*,4a'*S*,8a'*S*)-1,7-dimethyl-2-oxo-4a',6',7',8a'-tetrahydro-5'H-spiro [indoline-3,4'-pyrano[2,3-b]pyran]-2'-carboxylate 4o

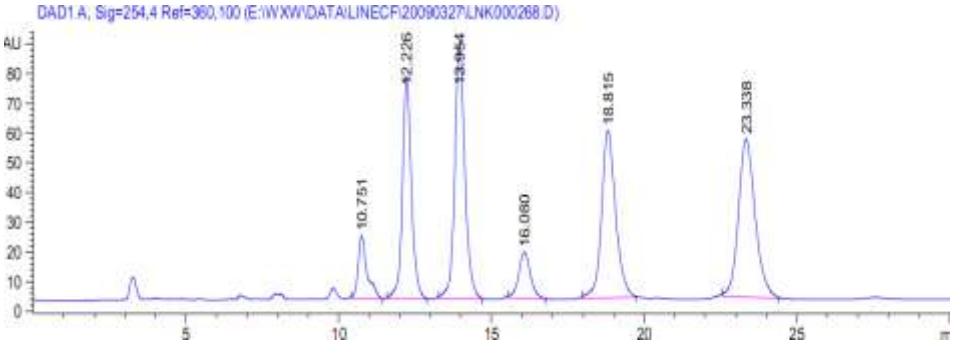


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.488	BB	0.3060	3380.42969	164.30180	53.2745
2	12.516	MM R	0.2236	19.70224	1.46831	0.3105
3	12.966	MM R	0.2464	13.96570	9.44507e-1	0.2201
4	14.038	VB	0.3739	2931.21045	117.14506	46.1949

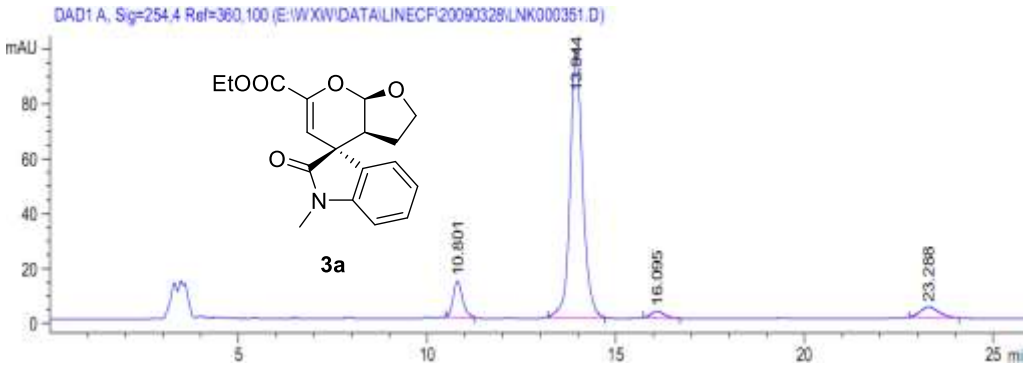


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.430	BB	0.2960	7501.94043	380.56445	95.8281
2	12.475	BB	0.3164	101.46614	5.13864	1.2961
3	13.997	BB	0.3476	225.13338	9.81604	2.8758

Ethyl-(3a*S*,4*S*,7a*R*)-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo[2,3-b] pyran-4,3'-indoline]-6-carboxylate 3a

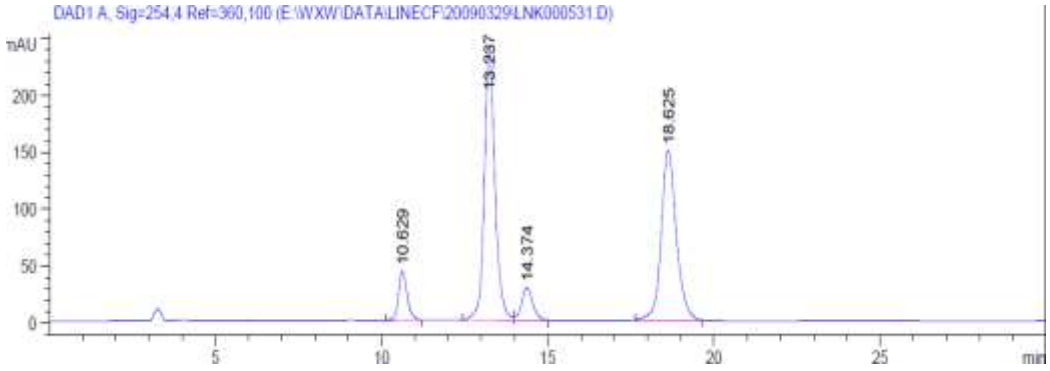


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.751	BB	0.2965	430.66455	21.07034	5.2725
2	12.226	BB	0.3056	1524.06018	74.84279	18.6587
3	13.954	BB	0.3442	1964.79907	85.47923	24.0545
4	16.080	BB	0.4011	418.91193	15.61116	5.1286
5	18.815	BB	0.4819	1803.22607	56.26804	22.0764
6	23.338	BB	0.5805	2026.43823	53.19208	24.8092

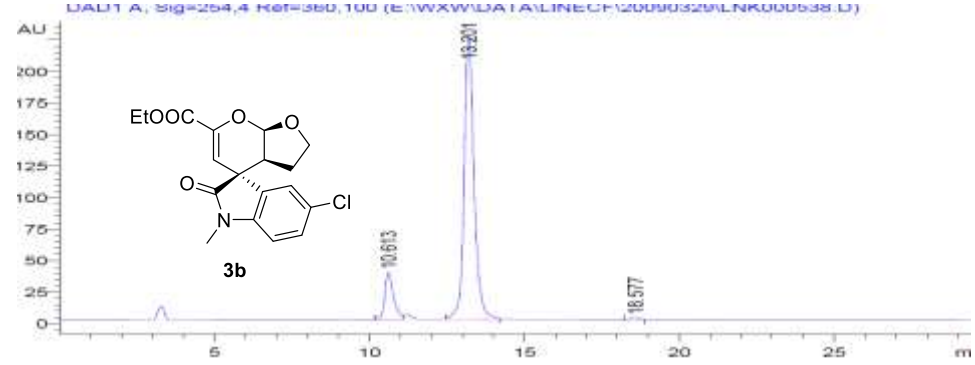


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.801	BB	0.2670	238.85457	13.46161	8.8673
2	13.944	BB	0.3471	2261.82666	98.07587	83.9691
3	16.095	BB	0.3690	58.42741	2.44328	2.1691
4	23.288	BB	0.5208	134.53406	3.78362	4.9945

Ethyl-(3a*S*,4*S*,7a*R*)-5'-chloro-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-b]pyran-4,3'-indoline]-6-carboxylate 3b

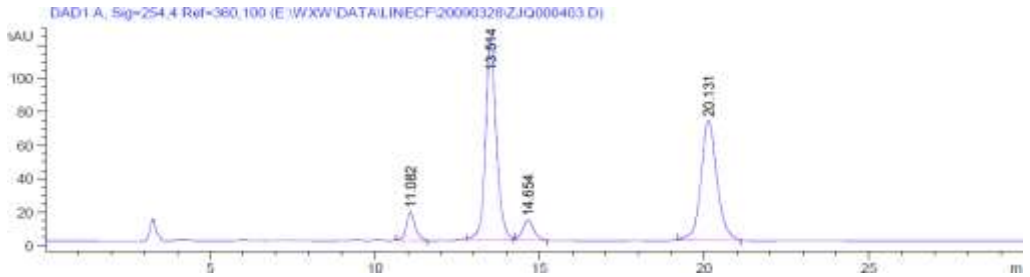


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.629	BB	0.2701	786.42365	43.66556	6.7838
2	13.237	BB	0.3363	5356.98096	240.07552	46.2104
3	14.374	BB	0.3599	696.31366	29.23241	6.0065
4	18.625	BB	0.4779	4752.87549	149.90973	40.9992

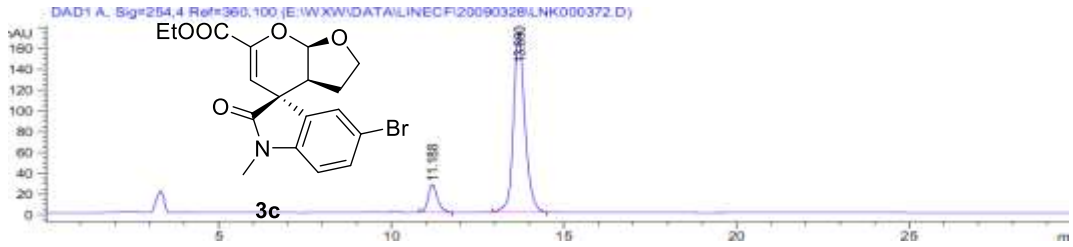


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.613	BV	0.2859	734.50970	37.60733	12.7552
2	13.201	BB	0.3337	4996.41260	224.43411	86.7657
3	18.577	MM R	0.3798	27.58817	1.21064	0.4791

Ethyl-(3a*S*,4*S*,7a*R*)-5'-bromo-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-*b*]pyran-4,3'-indoline]-6-carboxylate 3c

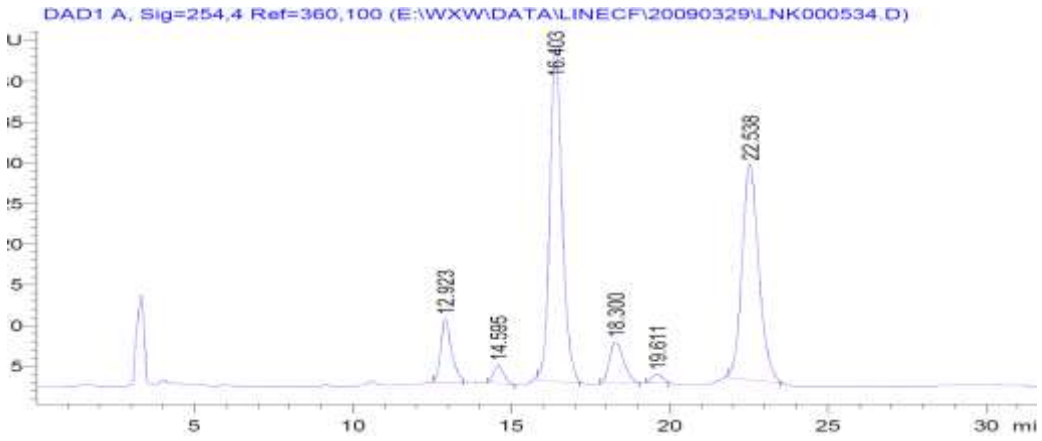


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.082	BB	0.2895	332.47650	17.19897	5.7236
2	13.514	BB	0.3422	2758.70532	120.91506	47.4910
3	14.654	BB	0.3635	293.25732	12.06721	5.0484
4	20.131	BB	0.5127	2424.46533	71.65974	41.7370

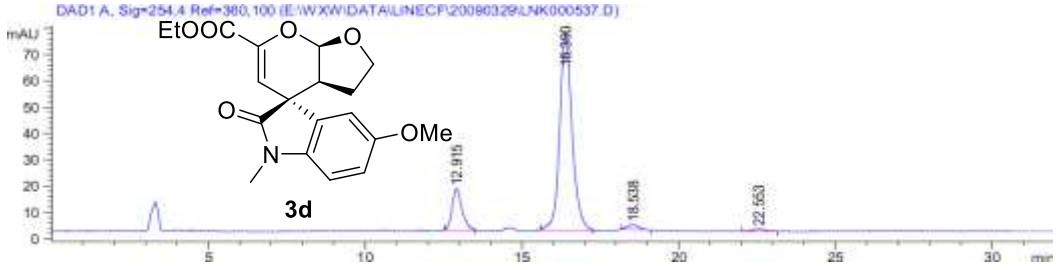


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.188	BB	0.2856	507.82199	26.73195	11.3762
2	13.690	BB	0.3484	3956.09229	170.67818	88.6238

Ethyl-(3a*S*,4*S*,7a*R*)-5'-methoxy-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro[furo [2,3-*b*]pyran-4,3'-indoline]-6-carboxylate 3d

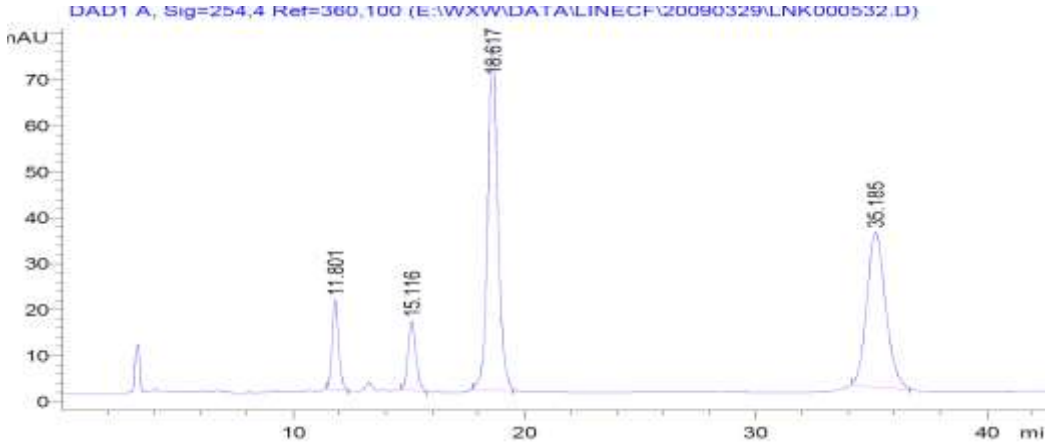


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.923	BB	0.3447	181.47644	7.76368	7.2576
2	14.595	BB	0.3318	50.73218	2.27792	2.0289
3	16.403	BB	0.4124	1108.98450	40.88911	44.3504
4	18.300	BB	0.4644	160.84711	5.12163	6.4326
5	19.611	MM R	0.4150	27.06433	1.08689	1.0824
6	22.538	BB	0.5628	971.40411	26.42713	38.8483

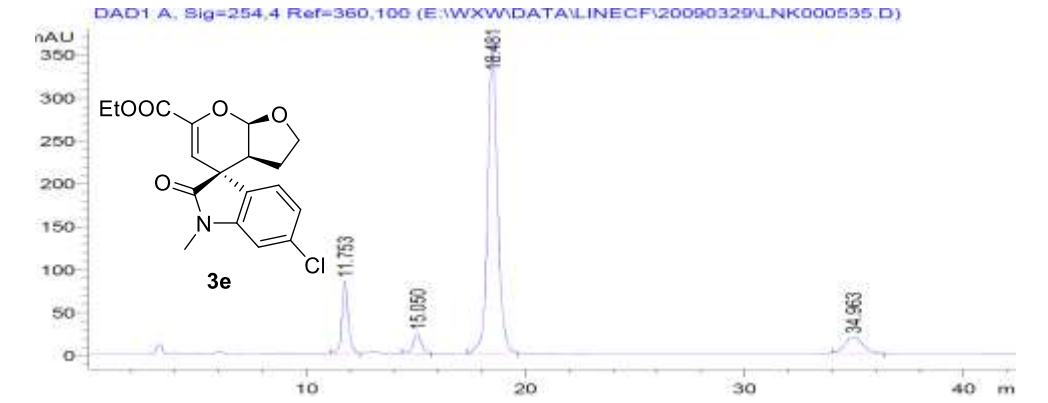


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.915	BB	0.3339	349.98914	15.83376	14.1639
2	16.390	BB	0.4144	2052.26880	74.25538	83.0541
3	18.538	BB	0.3739	44.98888	1.69358	1.8207
4	22.553	MM R	0.5438	23.75512	7.28012e-1	0.9614

Ethyl-(3a*S*,4*S*,7a*R*)-6'-chloro-1'-methyl-2'-oxo-2,3,3a,7a-tetrahydrospiro [furo[2,3-*b*]pyran-4,3'-indoline]-6-carboxylate 3e

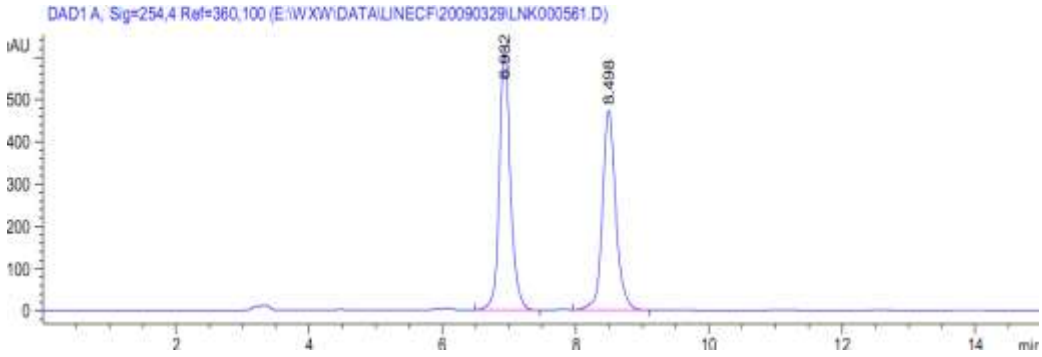


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.801	BB	0.2912	377.18604	19.54281	7.6232
2	15.116	BB	0.3599	353.62659	14.95205	7.1471
3	18.617	BB	0.4654	2307.94507	74.92004	46.6454
4	35.185	BB	0.8552	1909.09387	33.68399	38.5843

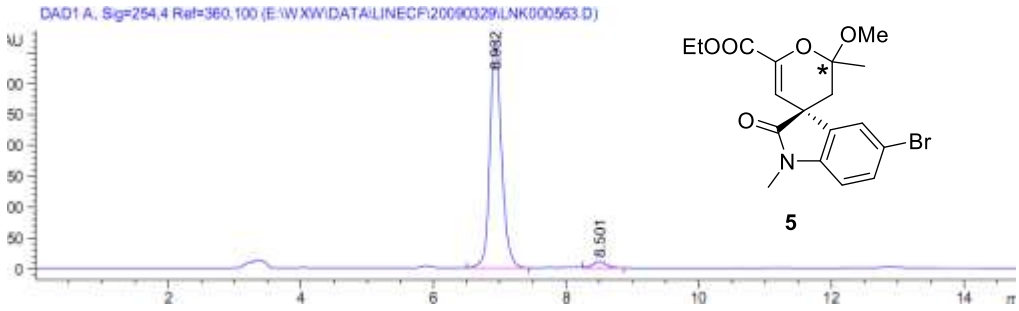


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.753	BB	0.2999	1678.19324	83.70175	11.5652
2	15.050	BB	0.3811	573.53693	22.67105	3.9525
3	18.481	BB	0.4705	1.12107e4	358.81314	77.2577
4	34.963	BB	0.8397	1048.34155	18.76808	7.2246

Ethyl-(3*R*)-5-bromo-2'-methoxy-1,2'-dimethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate 5



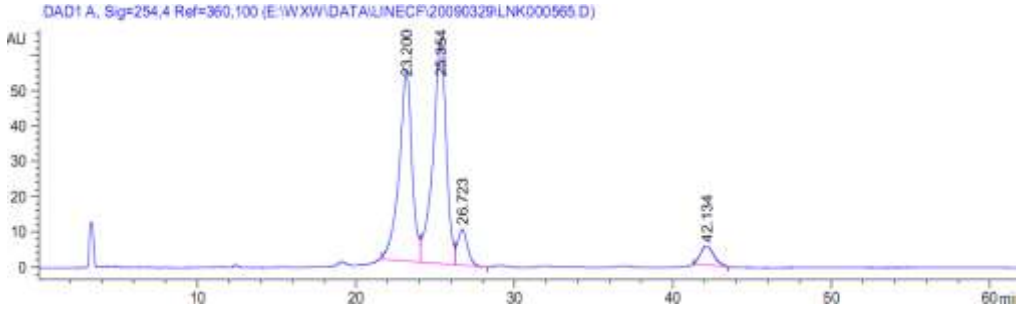
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.932	BB	0.1738	7150.37744	623.34607	52.2221
2	8.498	VB	0.2071	6541.85889	473.73734	47.7779



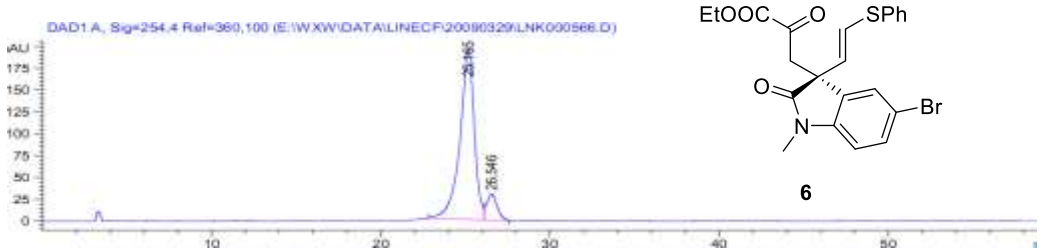
5

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.932	BB	0.1833	4431.47803	365.97577	96.7341
2	8.501	BB	0.2184	149.61469	10.36438	3.2659

Ethyl-(*S*,*E*)-3-(5-bromo-1-methyl-2-oxo-3-(2-(phenylthio)vinyl)indolin-3-yl)-2-oxopropanoate 6



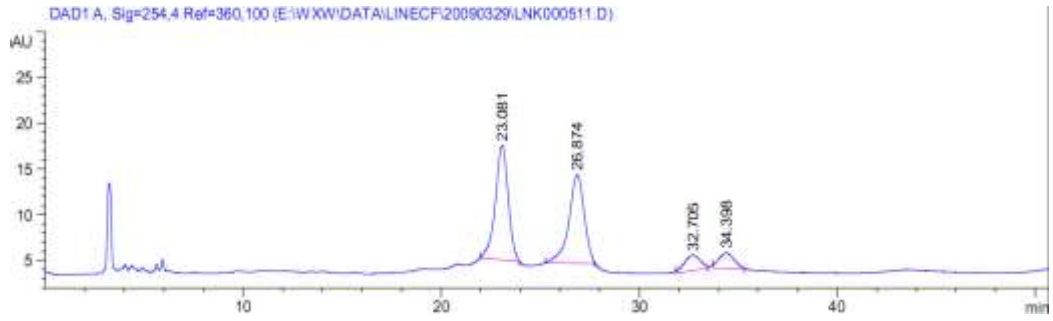
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.200	BV	0.8133	3050.51318	54.14260	40.7615
2	25.354	VV	0.8521	3674.71167	63.22395	49.1022
3	26.723	VB	0.6306	439.76517	10.20808	5.8762
4	42.134	BB	0.7594	318.81830	5.36433	4.2601



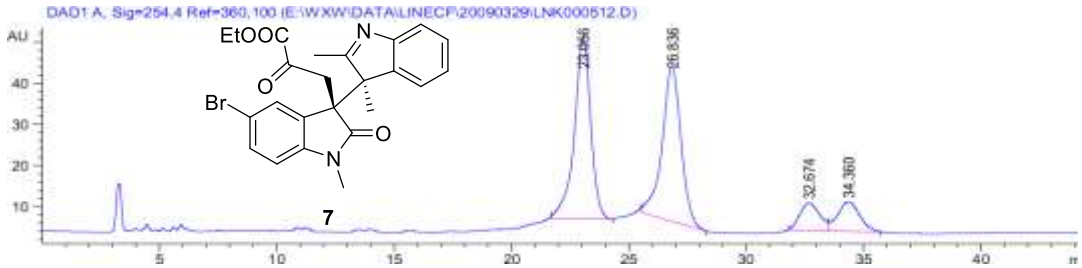
6

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.165	BV	0.8635	1.15330e4	194.57463	90.1348
2	26.546	VB	0.6352	1262.28638	29.61836	9.8652

Ethyl-3-(5-bromo-3-(2,3-dimethyl-3H-indol-3-yl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 7



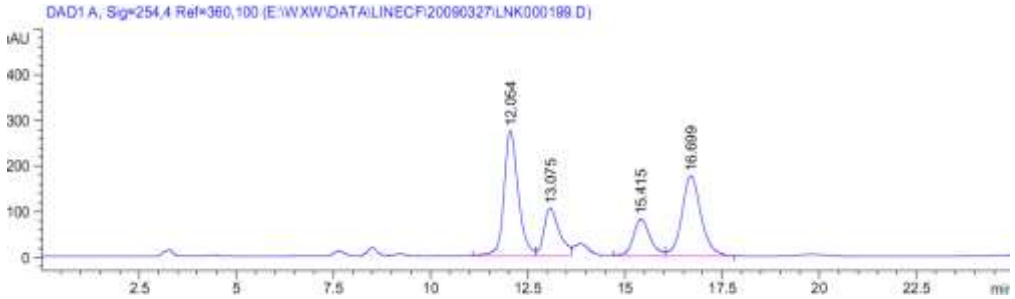
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.081	MM R	0.7502	563.14813	12.51120	44.5178
2	26.874	MM R	0.8934	519.87250	9.69842	41.0968
3	32.705	MM R	0.9197	91.24595	1.65346	7.2131
4	34.398	MM R	0.9039	90.72884	1.67285	7.1723



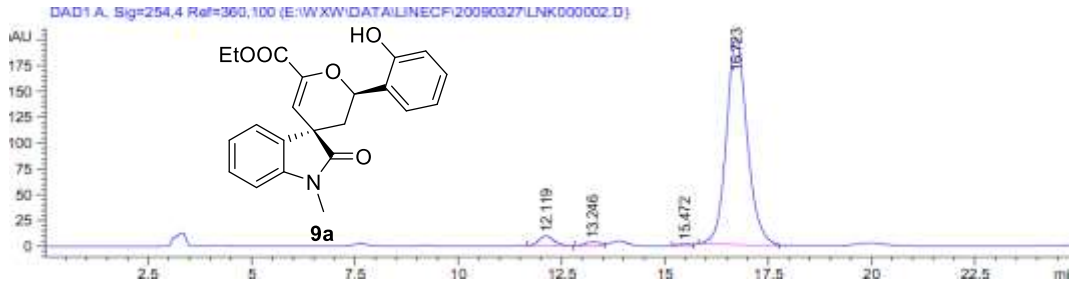
7

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.056	BB	0.7264	2153.54126	44.20094	41.9140
2	26.836	BB	0.8353	2108.66357	37.77490	41.0406
3	32.674	BV	0.8834	405.60217	6.74695	7.8942
4	34.360	VB	0.9459	470.19055	7.21833	9.1512

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxylate 9a

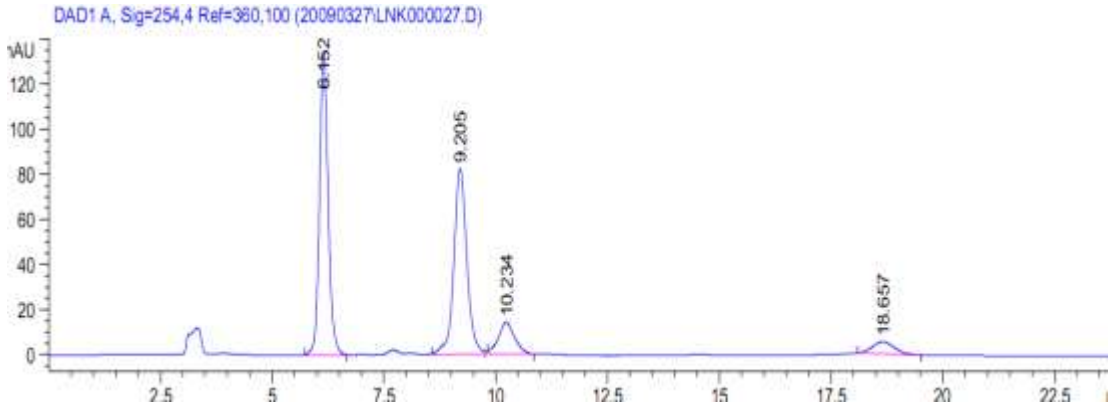


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.054	BV	0.3857	6994.57031	274.13824	38.1120
2	13.075	VV	0.4098	2881.30151	104.46043	15.6996
3	15.415	BV	0.4527	2444.81348	81.33291	13.3213
4	16.699	VB	0.5202	6031.97900	175.84213	32.8670

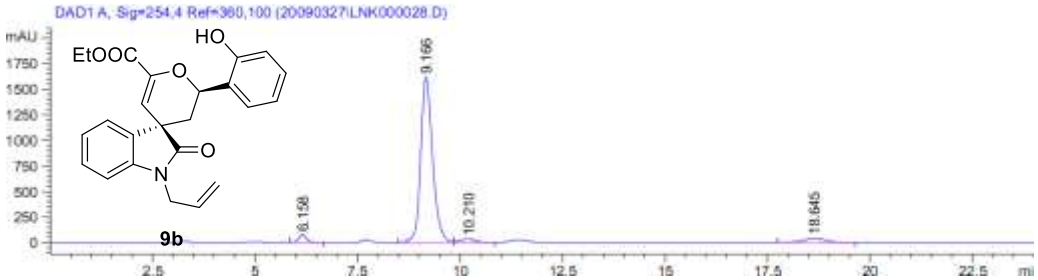


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.119	BB	0.3869	244.38368	9.54034	3.2892
2	13.246	BV	0.3998	101.55199	3.75148	1.3668
3	15.472	MM R	0.4193	48.71481	1.93636	0.6557
4	16.723	MM R	0.5856	7035.20166	200.23108	94.6883

Ethyl (2'*R*,3*R*)-1-allyl-2'-(2-hydroxyphenyl)-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxylate 9b

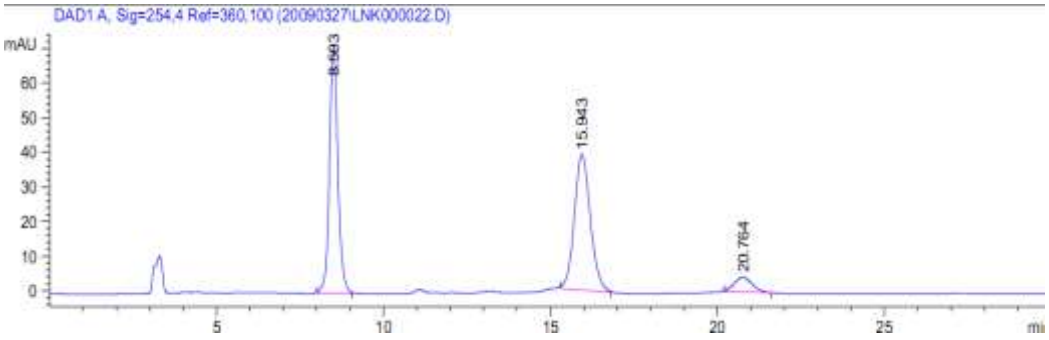


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.152	BB	0.2084	1818.82751	133.99493	45.2267
2	9.205	BB	0.3032	1660.04761	82.34208	41.2785
3	10.234	BB	0.3689	358.97867	14.10462	8.9263
4	18.657	BB	0.5200	183.72543	5.33153	4.5685

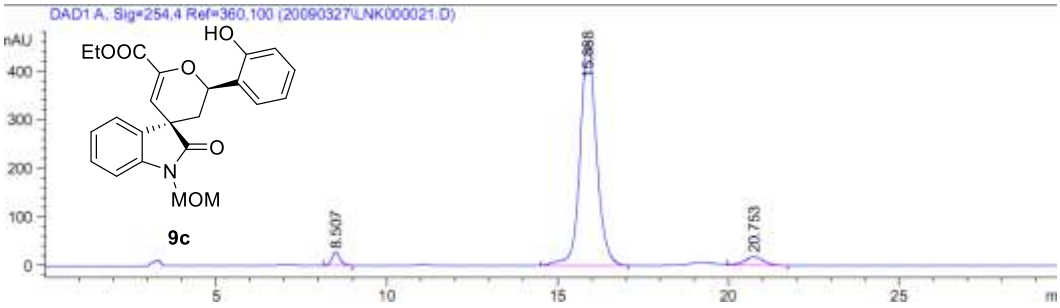


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.158	VB	0.2049	1047.68359	77.89876	2.8840
2	9.166	BV	0.3079	3.27062e4	1617.28748	90.0313
3	10.210	VB	0.3891	954.05750	36.00725	2.6263
4	18.645	BB	0.5760	1619.64514	42.36364	4.4584

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1-(methoxymethyl)-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9c

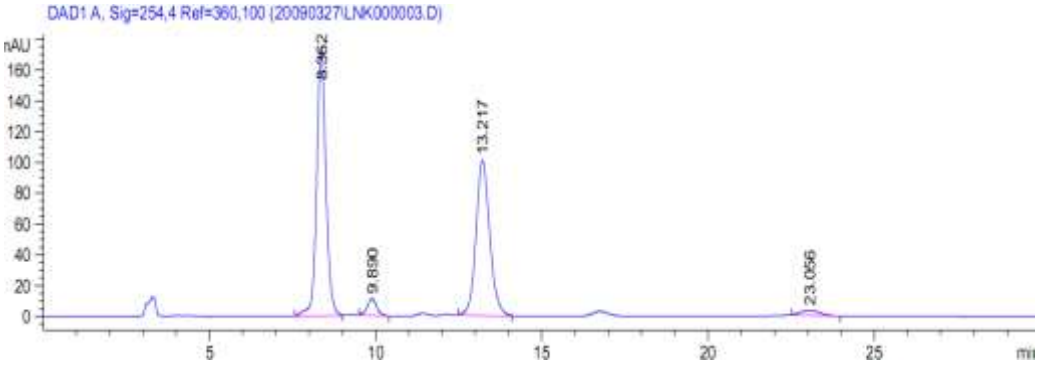


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.503	BB	0.2675	1259.61096	71.50252	46.2512
2	15.943	BB	0.5107	1309.37170	39.30514	48.0784
3	20.764	BB	0.5434	154.42879	4.19619	5.6704

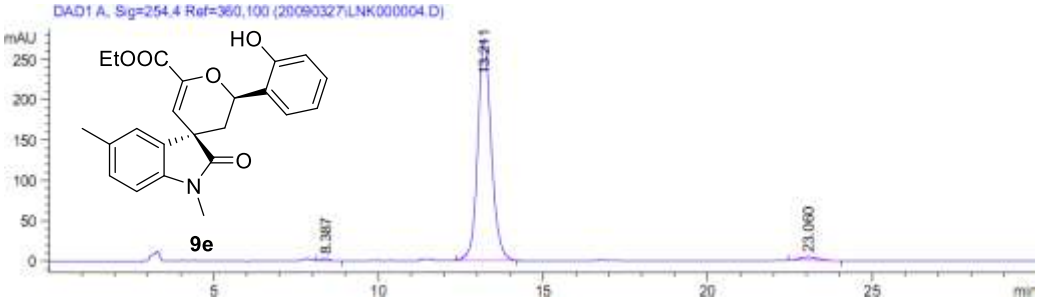


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.507	BB	0.2652	465.59503	26.73774	2.8060
2	15.888	BB	0.5065	1.53972e4	459.97644	92.7937
3	20.753	VB	0.6232	730.14520	17.62795	4.4003

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,5-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9e

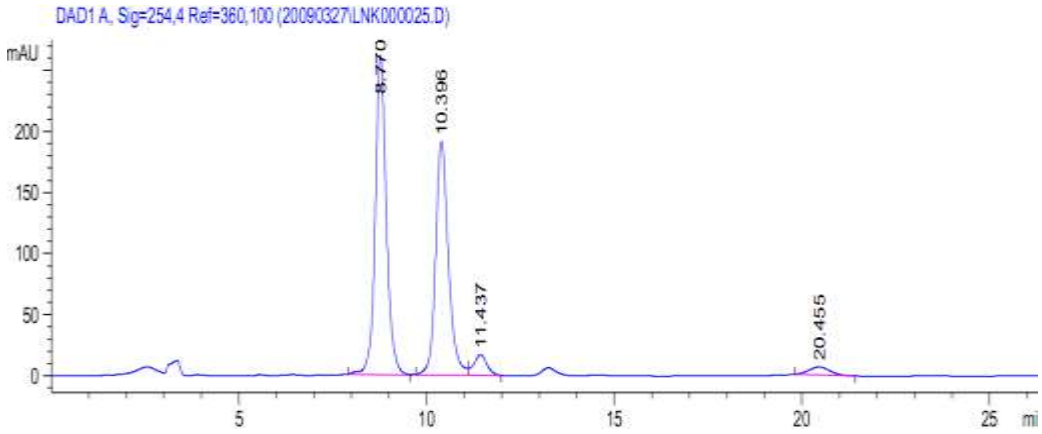


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.362	BB	0.2929	3358.79639	174.20824	50.9555
2	9.890	BB	0.3029	215.57236	10.80069	3.2704
3	13.217	BB	0.4363	2889.20435	100.83002	43.8314
4	23.056	BB	0.5587	128.05304	3.27137	1.9427

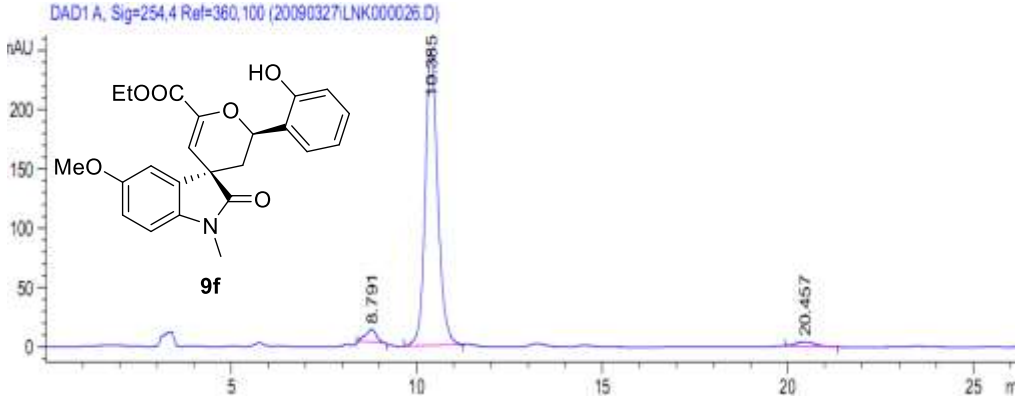


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.387	VB	0.2769	52.49780	2.84999	0.6510
2	13.211	BB	0.4336	7829.94824	273.82190	97.0989
3	23.060	BB	0.5903	181.44005	4.48233	2.2500

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-5-methoxy-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9f

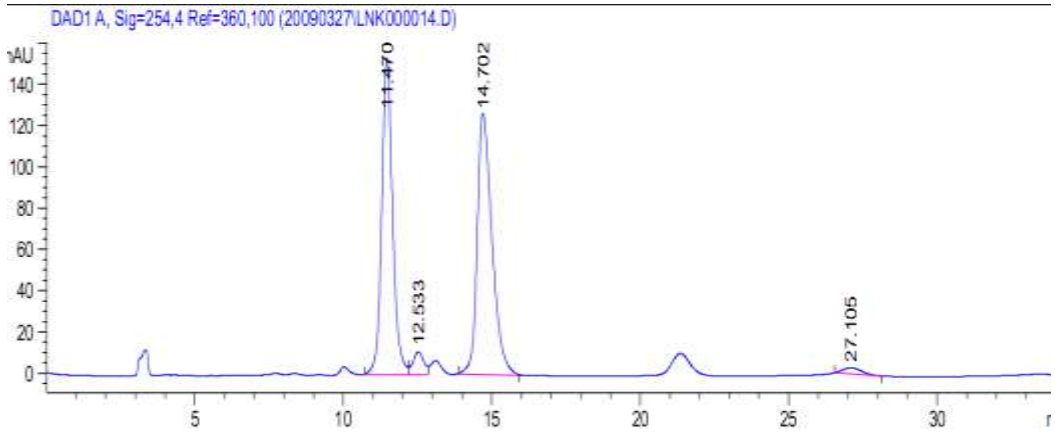


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.770	BB	0.3093	5360.87598	261.36469	50.7842
2	10.396	BB	0.3559	4522.99561	191.22839	42.8469
3	11.437	BB	0.3643	416.89713	16.98600	3.9493
4	20.455	BB	0.5753	255.41197	6.63238	2.4195

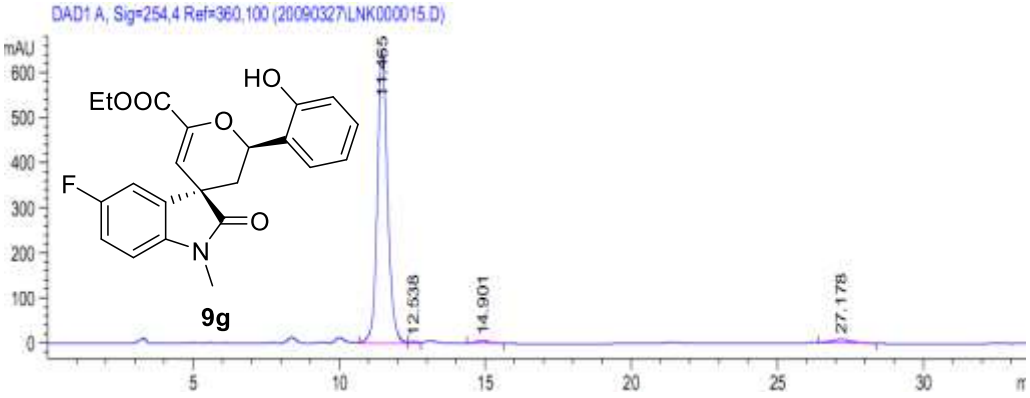


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.791	MM R	0.3361	219.91698	10.90433	3.5428
2	10.385	BB	0.3580	5855.68018	249.33177	94.3331
3	20.457	BB	0.5449	131.85168	3.58689	2.1241

Ethyl (2'*R*,3*R*)-5-fluoro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9g

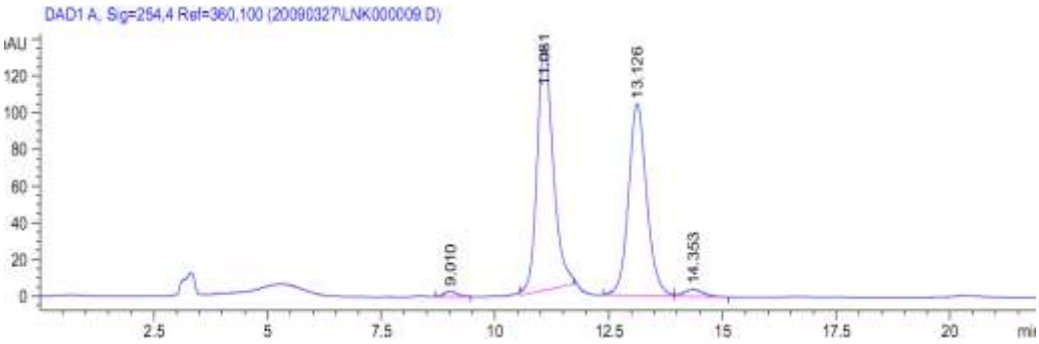


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.470	BB	0.3849	3903.25659	153.37061	44.8511
2	12.533	BV	0.3757	280.07782	11.04964	3.2183
3	14.702	BB	0.5262	4384.60303	126.56998	50.3821
4	27.105	BB	0.6131	134.76987	3.05261	1.5486

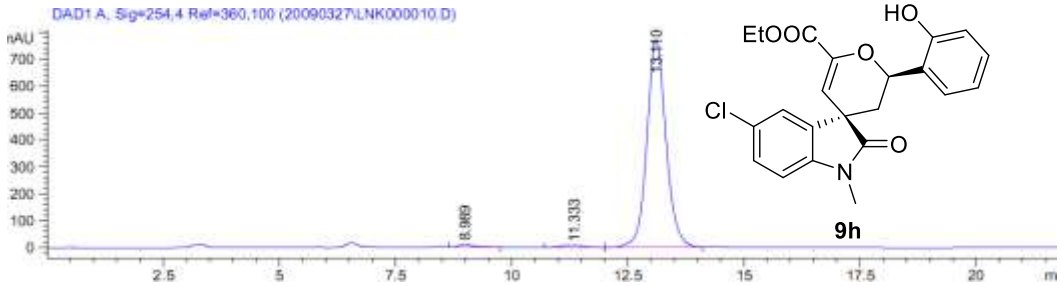


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.465	BB	0.3703	1.58331e4	649.73273	96.1774
2	12.538	BV	0.3308	82.17564	3.67639	0.4992
3	14.901	BB	0.4673	185.98126	6.03924	1.1297
4	27.178	BB	0.7279	361.12943	7.21533	2.1937

Ethyl (2'*R*,3*R*)-5-chloro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9h

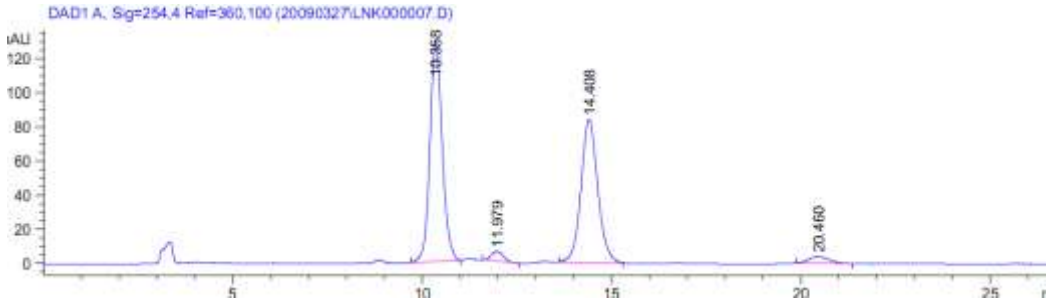


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.010	BB	0.2873	53.55437	2.82286	0.8422
2	11.081	MM R	0.4094	3274.27563	133.29955	51.4922
3	13.126	BB	0.4253	2916.85889	104.62659	45.8714
4	14.353	BB	0.4425	114.08827	3.84095	1.7942

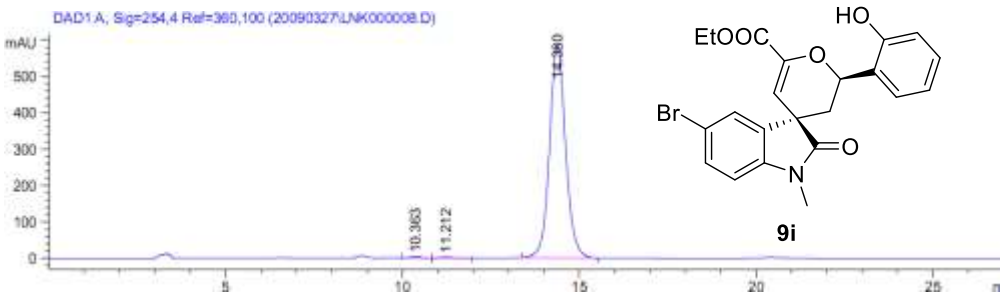


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.989	BB	0.3401	261.27390	11.04163	1.1678
2	11.333	BV	0.4902	241.12262	6.69437	1.0778
3	13.110	VB	0.4335	2.18698e4	769.71008	97.7544

Ethyl (2'*R*,3*R*)-5-bromo-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9i

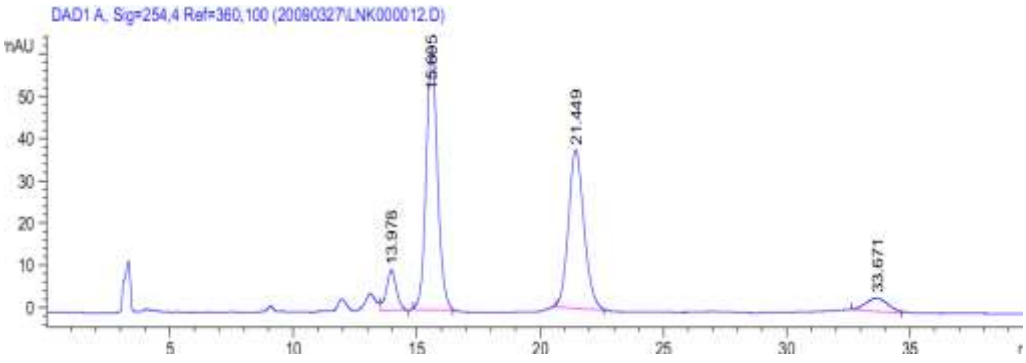


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.358	BB	0.3448	2913.79297	129.36554	50.3975
2	11.979	BB	0.3405	128.84715	5.81618	2.2286
3	14.408	BB	0.4671	2589.68457	84.14172	44.7917
4	20.460	BB	0.5684	149.29741	3.86732	2.5823

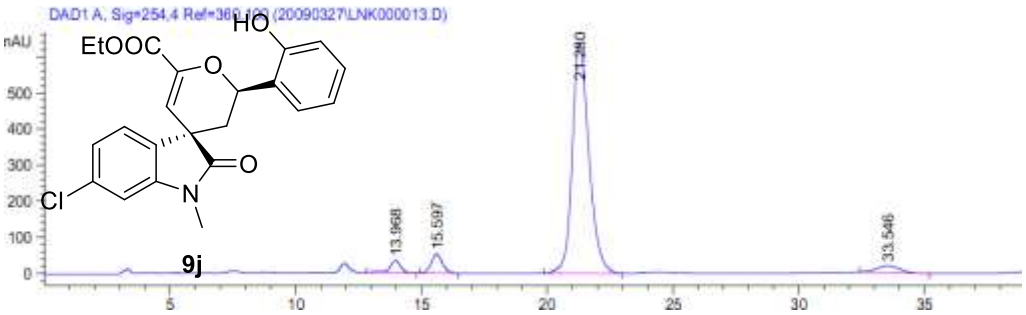


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.363	BV	0.3177	88.98271	4.36727	0.4784
2	11.212	VB	0.3374	67.30452	3.00380	0.3619
3	14.380	BB	0.4793	1.84420e4	585.83435	99.1597

Ethyl (2'*R*,3*R*)-6-chloro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9j

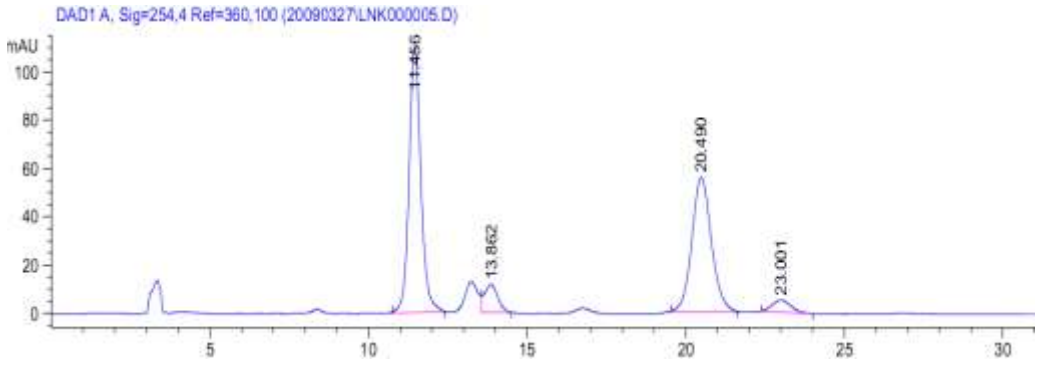


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.978	VB	0.4281	266.72836	9.42606	6.5299
2	15.605	BB	0.4860	1976.27563	61.98442	48.3819
3	21.449	BB	0.6731	1642.40869	37.49339	40.2084
4	33.671	MM R	1.0616	199.32948	3.12933	4.8799

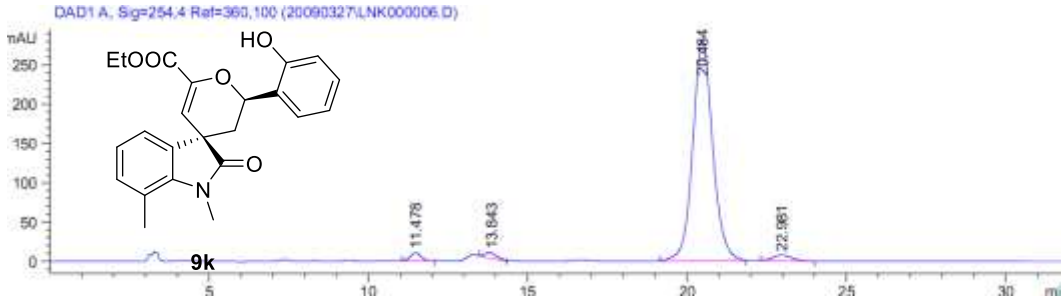


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.968	BB	0.4610	1070.91882	34.22635	3.2048
2	15.597	BB	0.4860	1662.04651	52.40936	4.9738
3	21.280	BB	0.7027	2.94381e4	637.58710	88.0959
4	33.546	BB	0.9795	1244.88574	19.37881	3.7254

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,7-dimethyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9k

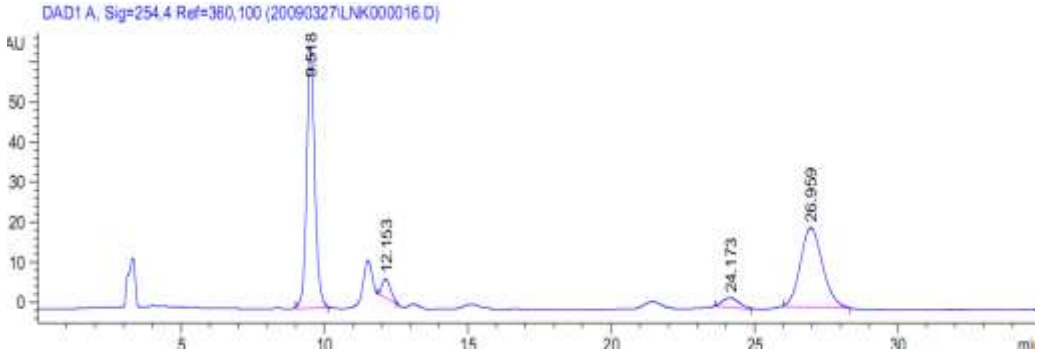


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.456	BB	0.3925	2839.08179	109.48750	49.0800
2	13.862	VB	0.4425	343.74103	11.50884	5.9424
3	20.490	BB	0.6581	2400.12427	55.76483	41.4917
4	23.001	BB	0.6050	201.64821	4.93243	3.4860

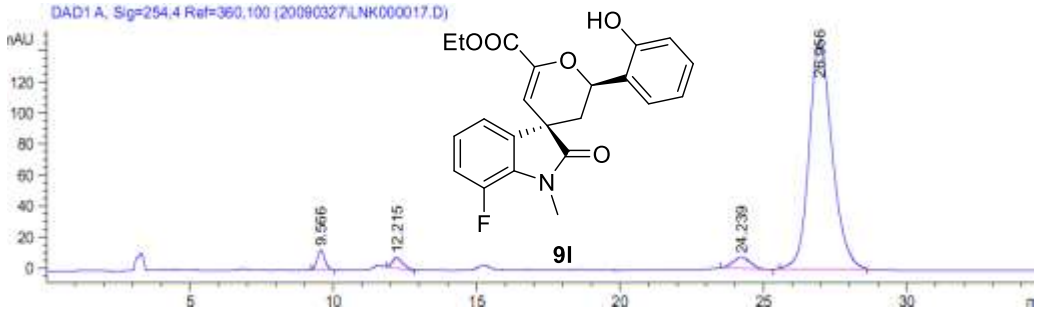


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.478	BB	0.3561	234.82748	10.21978	1.8093
2	13.843	MM R	0.4706	194.80270	6.89891	1.5009
3	20.484	BB	0.6645	1.22637e4	281.37967	94.4878
4	22.981	BB	0.6032	285.80978	6.92953	2.2021

Ethyl (2'*R*,3*R*)-7-fluoro-2'-(2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9l

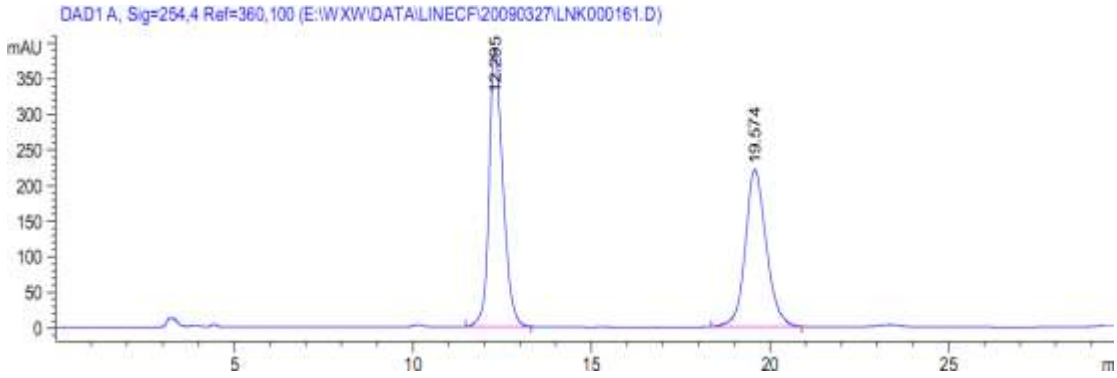


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.518	BB	0.2965	1282.92688	65.49512	50.3692
2	12.153	MM R	0.3382	97.38918	4.79935	3.8236
3	24.173	MM R	0.6773	96.86373	2.38354	3.8030
4	26.959	BB	0.7999	1069.86816	19.87949	42.0042

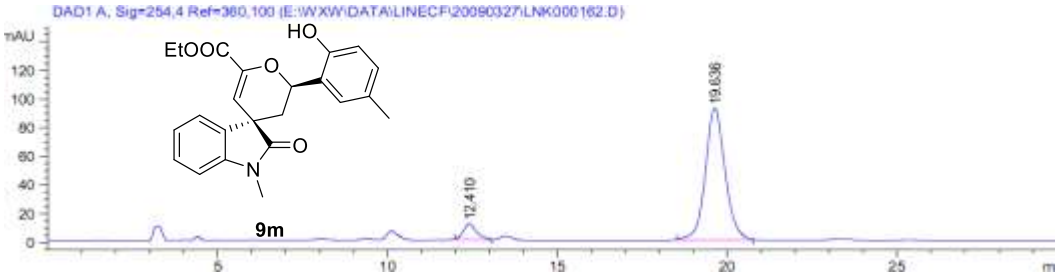


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.566	BB	0.2837	234.28789	12.67134	2.6138
2	12.215	MM R	0.4595	192.02715	6.96575	2.1423
3	24.239	BB	0.6411	302.46597	7.21517	3.3744
4	26.956	BB	0.8500	8234.75586	146.89319	91.8695

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-5-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9m

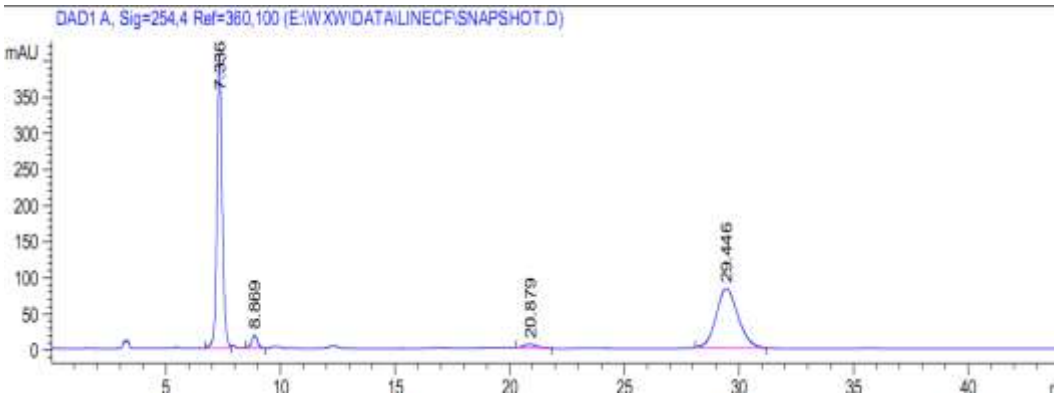


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.295	BB	0.4082	1.04853e4	389.35651	53.6746
2	19.574	BB	0.6221	9049.68359	220.81812	46.3254

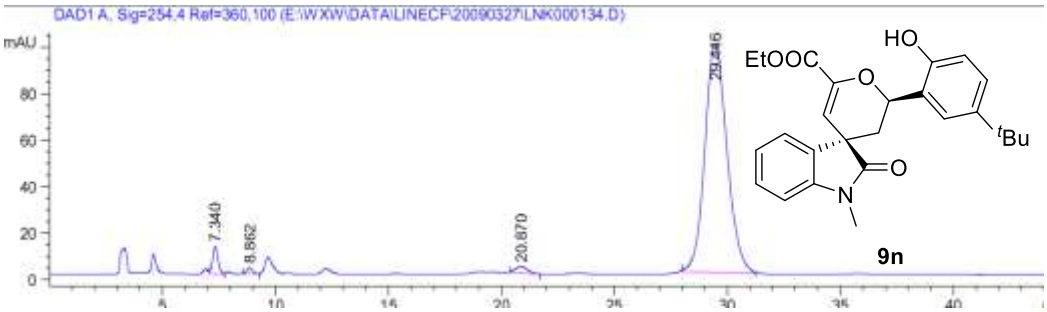


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.410	BB	0.4009	298.65817	11.13603	7.4253
2	19.636	BB	0.6134	3723.53076	92.15330	92.5747

Ethyl (2'*R*,3*R*)-2'-(5-(tert-butyl)-2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxylate 9n

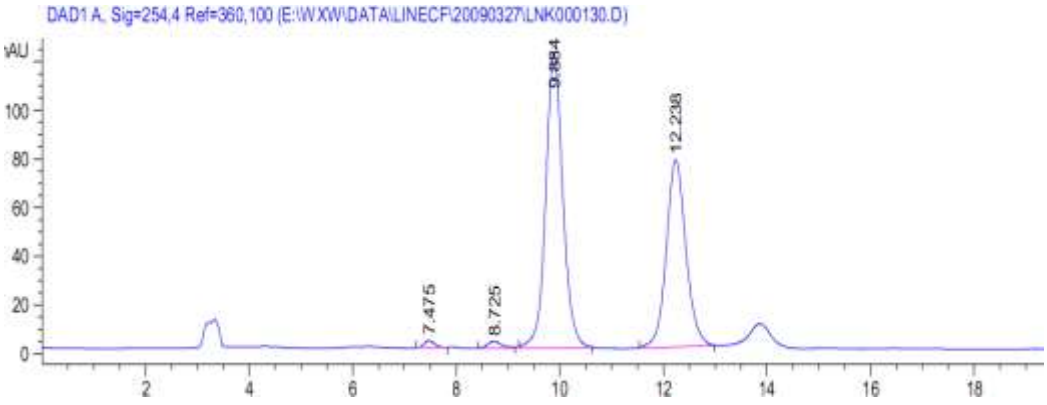


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.336	BV	0.2417	6457.59863	405.61664	52.0472
2	8.869	BB	0.2673	311.94751	17.55669	2.5142
3	20.879	BB	0.5812	198.05103	5.16645	1.5963
4	29.446	BB	1.0152	5439.60303	81.86147	43.8423

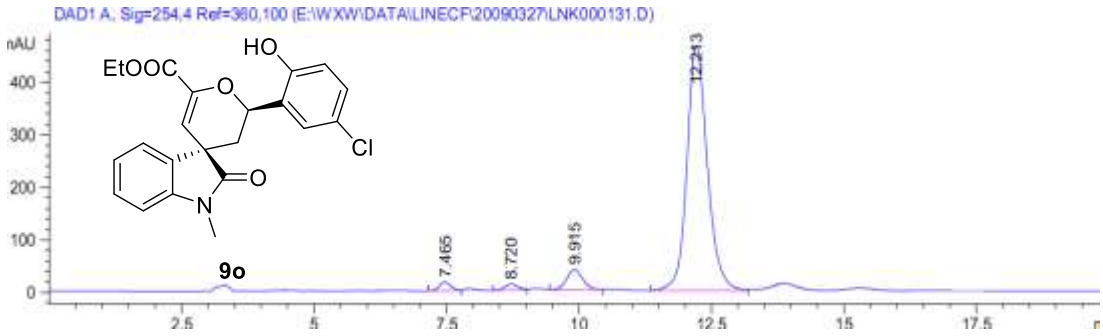


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.340	VB	0.2556	198.64308	11.84856	2.8362
2	8.862	BB	0.2588	43.20865	2.58841	0.6169
3	20.870	BB	0.5196	95.81676	2.68979	1.3680
4	29.446	BB	1.0377	6666.28516	98.23561	95.1789

Ethyl (2'*R*,3*R*)-2'-(5-chloro-2-hydroxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9o

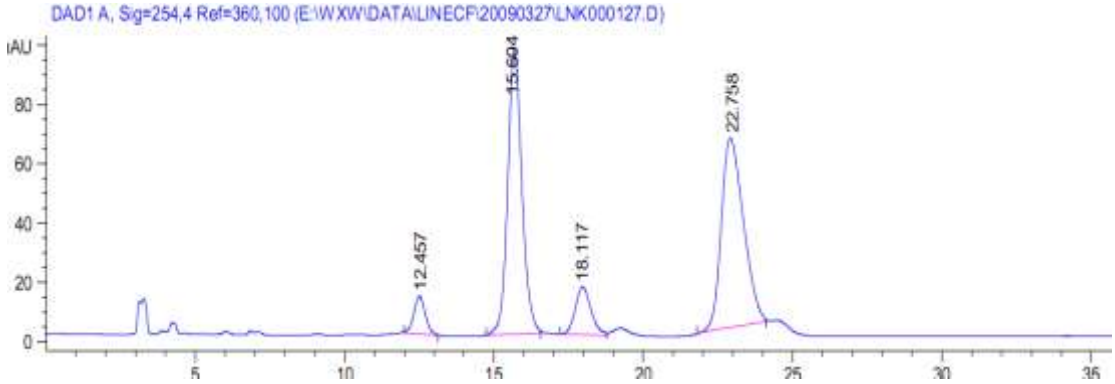


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.475	BB	0.2081	39.82860	2.90324	0.8135
2	8.725	BB	0.2742	52.83976	2.90475	1.0792
3	9.884	BB	0.3496	2779.27563	121.16463	56.7645
4	12.238	BB	0.4015	2024.20886	76.79546	41.3428

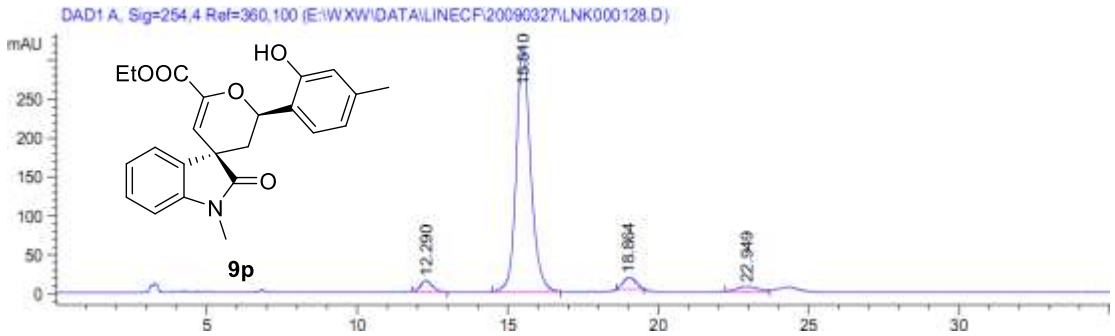


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.465	BV	0.2254	246.26666	16.57381	1.7920
2	8.720	BV	0.2681	206.30502	11.68094	1.5012
3	9.915	VB	0.3212	794.76880	38.13157	5.7833
4	12.213	BB	0.4068	1.24952e4	466.11136	90.9235

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-4-methylphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9p

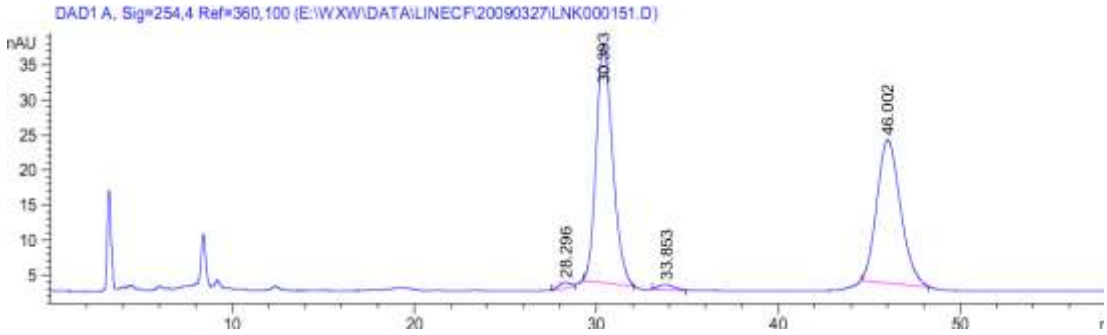


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.457	BB	0.3969	332.80569	12.73566	4.5242
2	15.604	BB	0.4980	3145.75928	96.07786	42.7639
3	18.117	BB	0.5511	581.86841	16.04621	7.9100
4	22.758	BB	0.7897	3295.68457	64.11639	44.8020

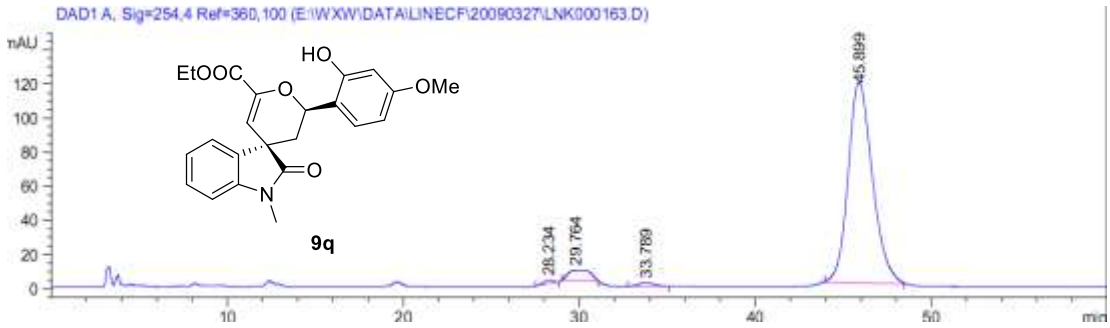


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.290	BB	0.4109	393.19601	14.56518	3.3650
2	15.510	BB	0.5046	1.05314e4	316.15125	90.1290
3	18.864	MM R	0.4791	429.66769	14.94637	3.6771
4	22.949	BV	0.7609	330.55057	6.57035	2.8289

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-4-methoxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9q

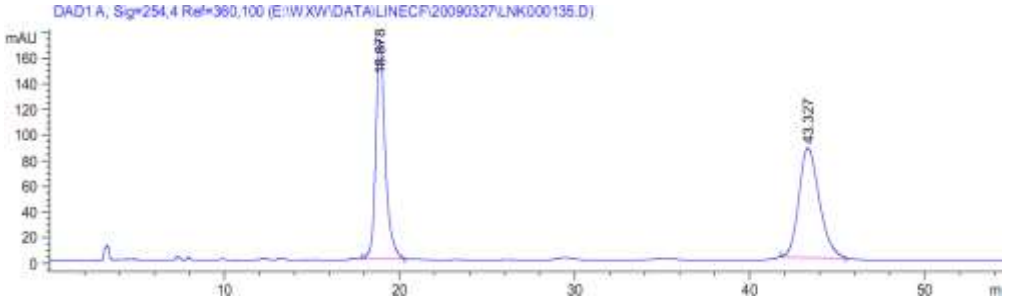


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.296	MM R	0.7999	39.79426	8.29152e-1	0.9794
2	30.393	BB	0.9513	2134.70874	33.96127	52.5373
3	33.853	MM R	1.0208	46.74310	7.63208e-1	1.1504
4	46.002	BB	1.2882	1841.97571	20.42399	45.3329

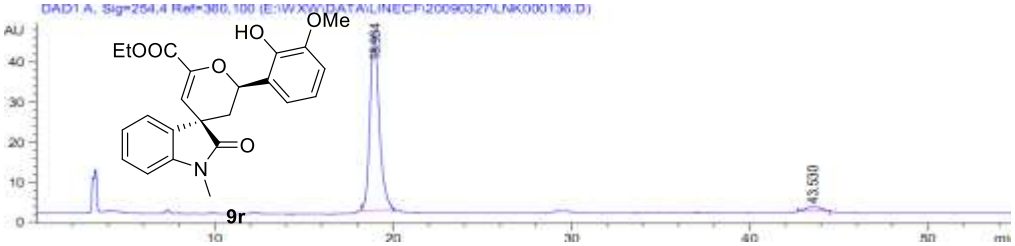


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.234	MM R	0.6104	73.82506	2.01578	0.6126
2	29.764	MM R	1.4604	524.72772	5.98821	4.3542
3	33.789	MM R	1.0402	139.70941	2.23847	1.1593
4	45.899	BB	1.4069	1.13128e4	117.75182	93.8739

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-3-methoxyphenyl)-1-methyl-2-oxo-2',3'-dihydro spiro[indoline-3,4'-pyran]-6'-carboxylate 9r

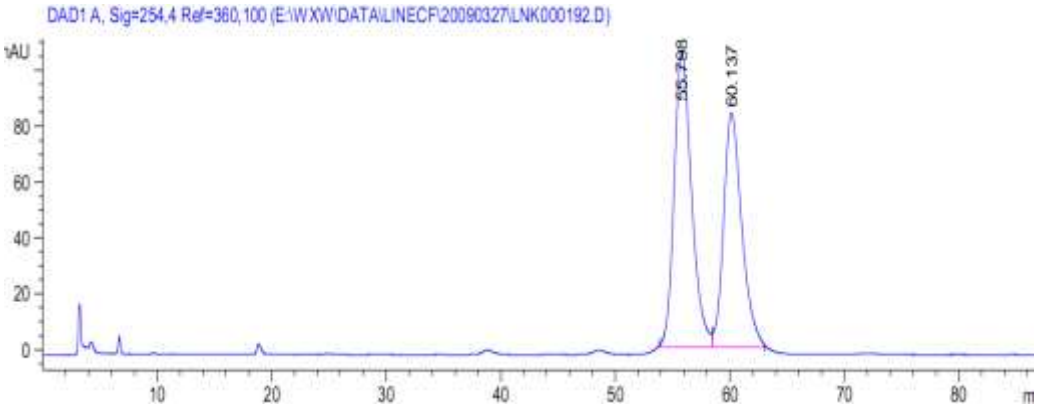


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.878	BB	0.5605	6400.74854	171.08636	47.8155
2	43.327	BB	1.2481	6985.60156	85.77898	52.1845

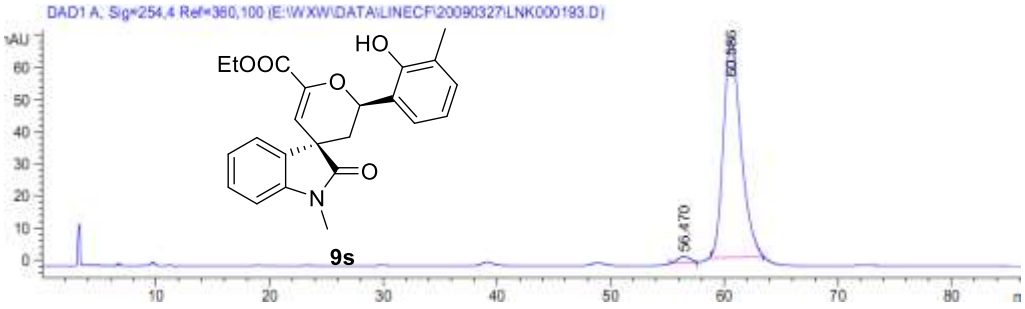


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.934	BB	0.5405	1602.65662	44.46686	95.9846
2	43.530	MM R	1.0169	67.04601	1.09884	4.0154

Ethyl (2'*R*,3*R*)-2'-(2-hydroxy-3-methylphenyl)-1-methyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxylate 9s

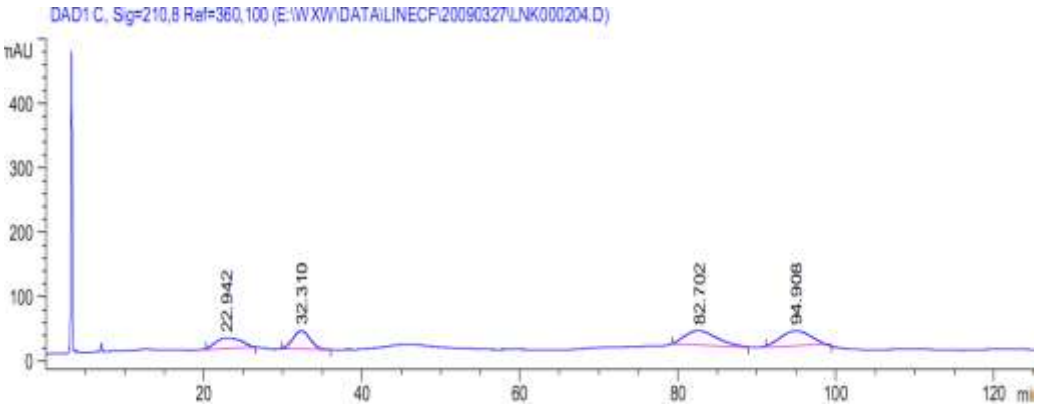


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.798	BB	1.5966	1.11205e4	105.08260	54.7737
2	60.137	BB	1.6472	9182.09668	83.61021	45.2263

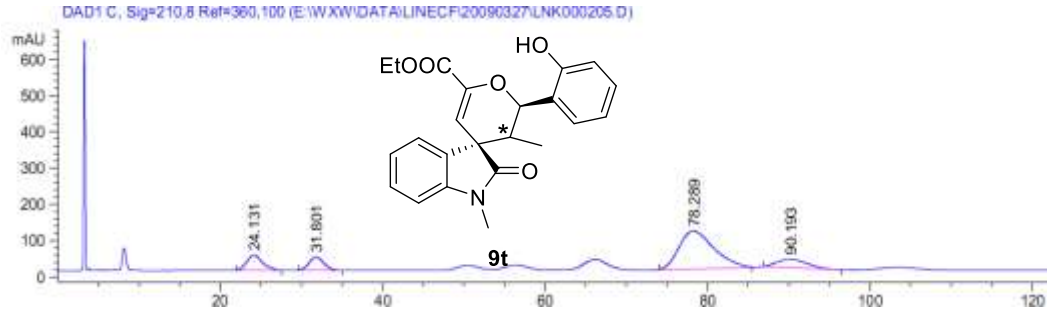


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	56.470	MM R	1.3332	164.96535	2.06224	2.2216
2	60.586	BB	1.5703	7260.64551	67.42653	97.7784

Ethyl (2'*R*,3*R*)-2'-(2-hydroxyphenyl)-1,3'-dimethyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxylate 9t

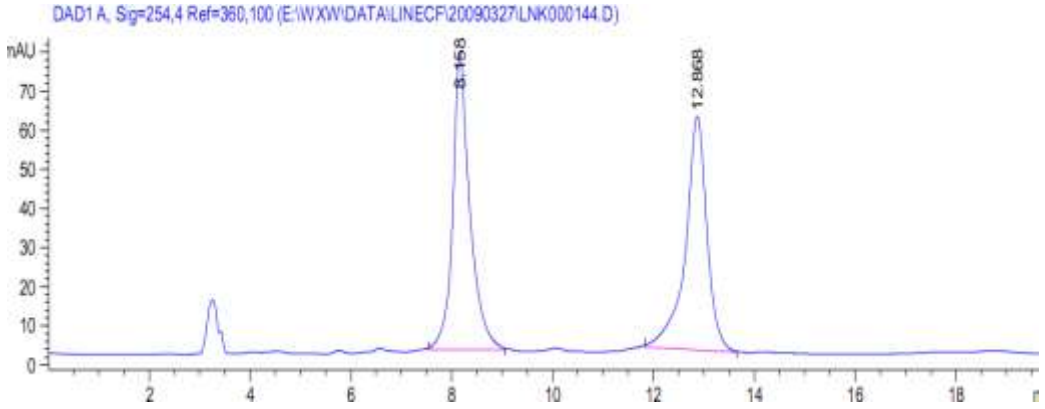


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.942	MM R	3.7737	3722.04639	16.43859	18.4693
2	32.310	BB	1.8104	4200.38867	28.32001	20.8429
3	82.702	BB	3.2406	6195.11475	22.38603	30.7409
4	94.908	MM R	3.0921	6035.09912	22.89668	29.9469

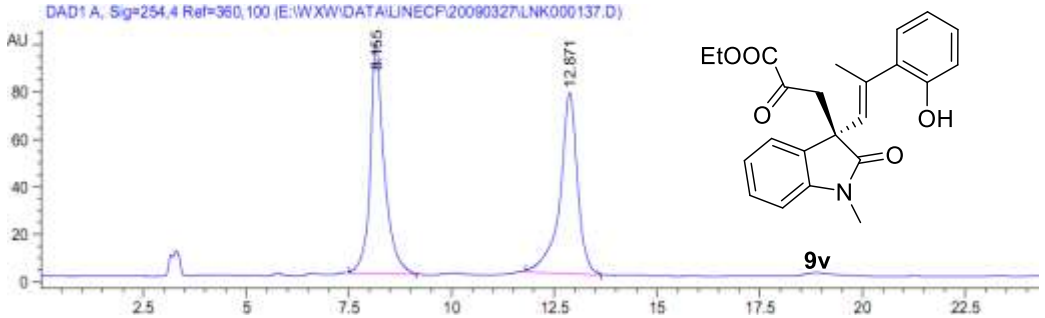


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.131	BB	1.8916	5644.10645	41.84425	11.7802
2	31.801	BB	1.6667	4558.94434	36.41339	9.5153
3	78.289	MM R	5.0233	3.16312e4	104.94801	66.0196
4	90.193	BB	3.0510	6077.58154	23.42393	12.6849

Ethyl-(*S*,*E*)-3-(3-(2-(2-hydroxyphenyl)prop-1-en-1-yl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 9v

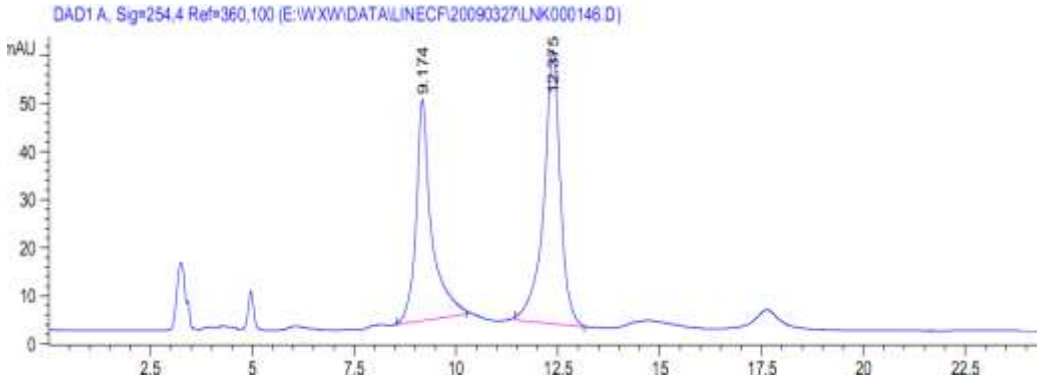


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.158	BB	0.3313	1790.37341	75.86448	50.2115
2	12.868	BB	0.4307	1775.29358	59.73475	49.7885

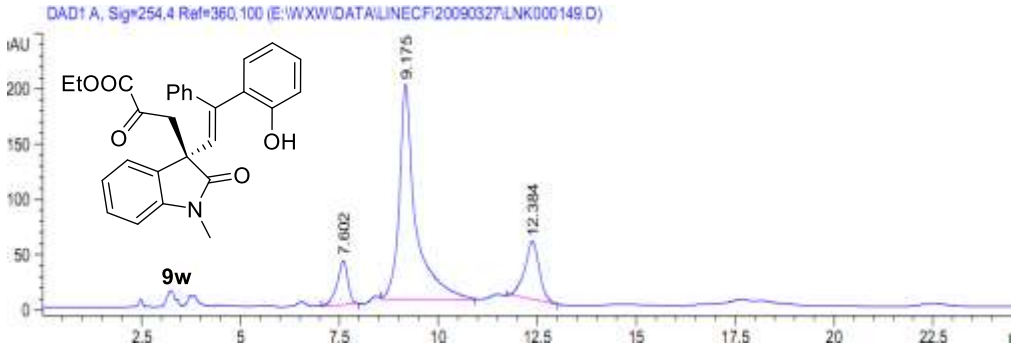


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.155	BB	0.3297	2291.95093	97.70203	50.4314
2	12.871	BB	0.4282	2252.74219	76.35545	49.5686

Ethyl-(*S*,*E*)-3-(3-(2-(2-hydroxyphenyl)-2-phenylvinyl)-1-methyl-2-oxoindolin-3-yl)-2-oxopropanoate 9w

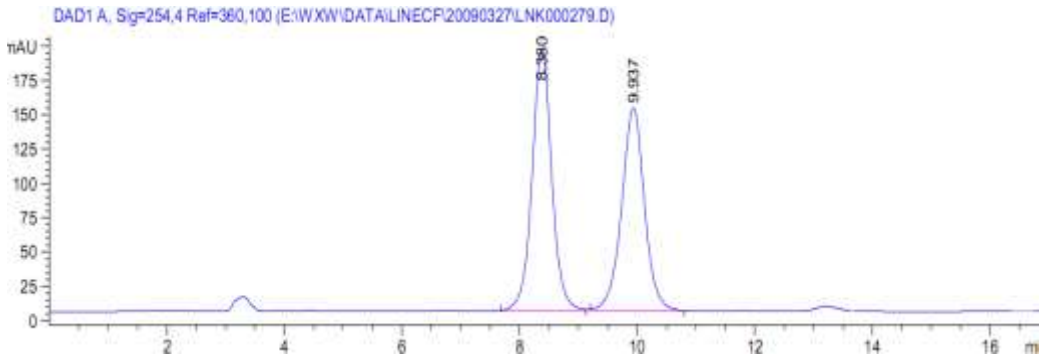


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.174	BB	0.3702	1223.53979	46.01573	43.0388
2	12.375	BB	0.4142	1619.33545	56.87083	56.9612

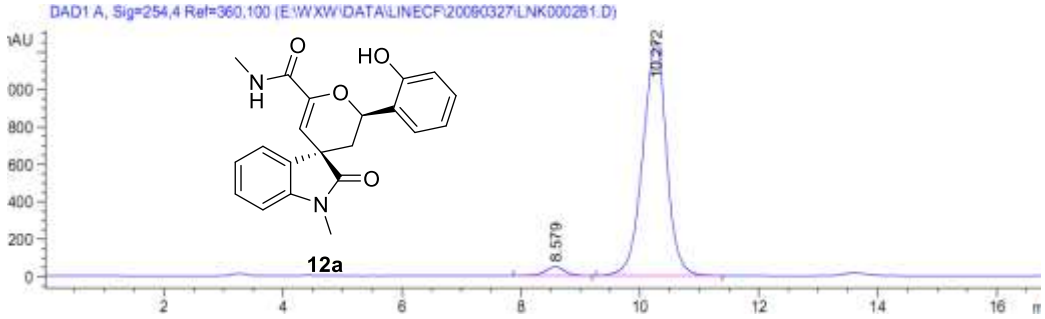


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.602	MM R	0.3192	767.70575	40.08863	9.9137
2	9.175	MM R	0.4821	5630.79736	194.67307	72.7125
3	12.384	MM R	0.4291	1345.41528	52.26243	17.3738

(2'*R*,3*R*)-2'-(2-Hydroxyphenyl)-N,1-dimethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-6'-carboxamide 12a

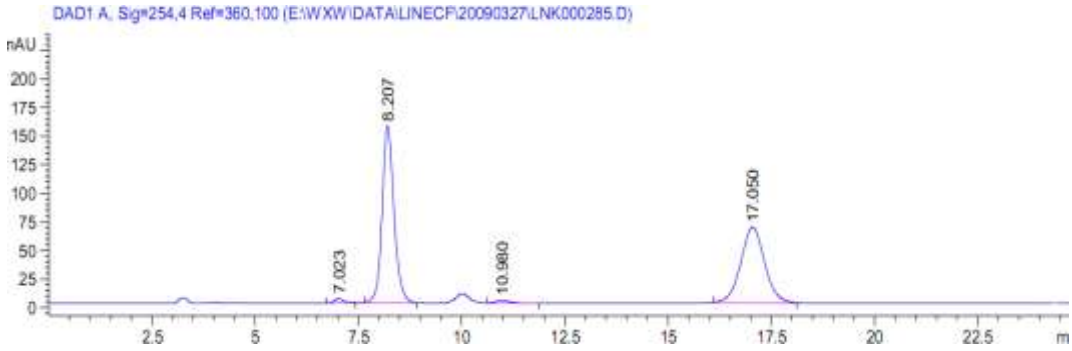


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.380	BB	0.3563	4448.54346	190.59363	52.4965
2	9.937	BB	0.4117	4025.44092	147.83041	47.5035

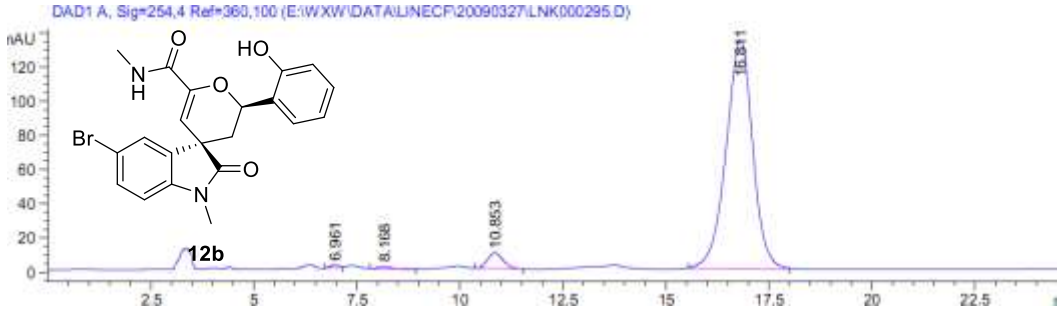


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.579	BB	0.3603	1143.31653	48.27978	3.1905
2	10.272	BB	0.4251	3.46917e4	1252.48169	96.8095

(2'*R*,3*R*)-5-Bromo-2'-(2-hydroxyphenyl)-N,1-dimethyl-2-oxo-2',3'-dihydrospiro [indoline-3,4'-pyran]-6'-carboxamide 12b

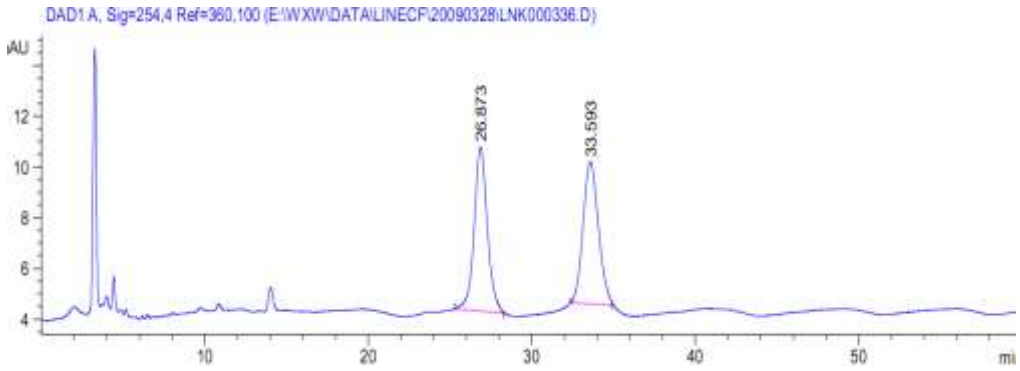


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.023	BB	0.2343	58.46277	3.78347	0.9908
2	8.207	BB	0.3029	3097.85278	155.17172	52.5001
3	10.980	BB	0.3592	59.34491	2.53461	1.0057
4	17.050	BB	0.6185	2685.00586	66.29771	45.5034

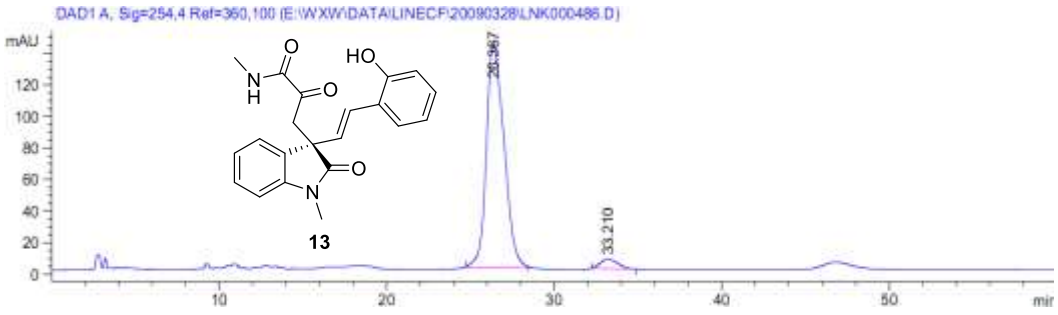


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.961	MM R	0.2419	23.40681	1.61266	0.3714
2	8.168	VB	0.3385	31.66816	1.41829	0.5025
3	10.853	BB	0.4146	242.51257	9.10797	3.8480
4	16.811	BB	0.6873	6004.71582	133.35417	95.2781

(*S*,*E*)-3-(3-(2-Hydroxystyryl)-1-methyl-2-oxoindolin-3-yl)-N-methyl-2-oxopropan amide 13



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.873	MM R	0.9370	364.00021	6.47490	49.9536
2	33.593	MM R	1.0849	364.67700	5.60233	50.0464



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.367	BB	1.0372	1.02837e4	142.29344	95.8769
2	33.210	BB	0.9135	442.23703	5.96092	4.1231