Electronic Supplementary Information

Diastereodivergent synthesis of bispirooxindoles via asymmetric Friedel–Crafts/aldol cascade reaction: co-catalyst effects on diastereoselective outcomes

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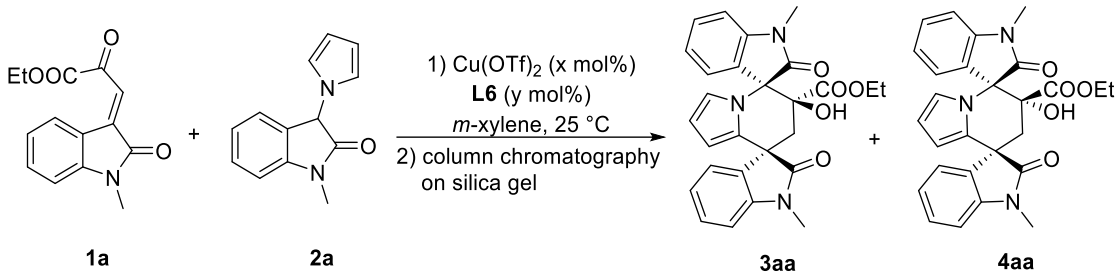
1. General methods

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 $CDCl_3$ 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). ^{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 procedures

2.1 Optimization of reaction conditions

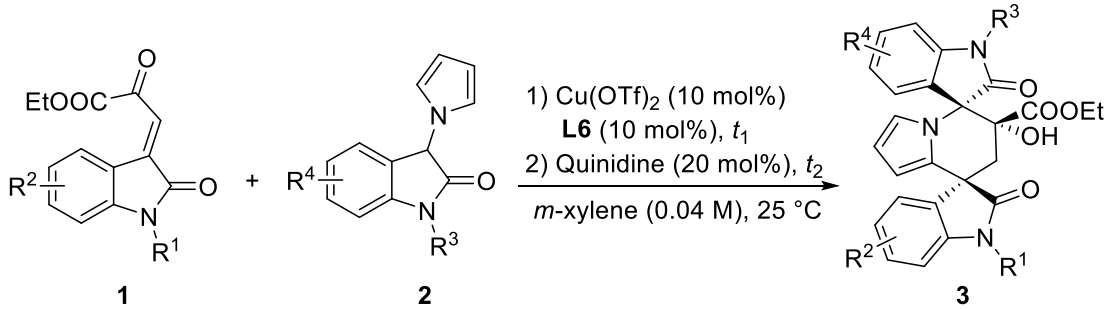
Table S1. Optimization of several other reaction parameters [a]



entry	concn (M)	**2a**/**1a**	**cat.** (x mol%)	**L** (y mol%)	time (h)	yield (%) [b]	**3aa/4aa** [c]	*ee* (%) [d]
1	0.1	2/1	10	10	1	92	90/10	87/96
2	0.2	2/1	10	10	0.5	88	80/20	83/90
3	0.07	2/1	10	10	1	93	80/20	87/98
4	0.05	2/1	10	10	1	90	75/25	89/99
5	0.04	2/1	10	10	1	95	82/18	90/99
6	0.03	2/1	10	10	1.5	96	80/20	89/99
7	0.04	1.8/1	10	10	4	91	81/19	87/96
8	0.04	1.5/1	10	10	18	93	75/25	67/88
9	0.04	2.2/1	10	10	1	94	85/15	91/99
10	0.04	2.5/1	10	10	0.5	93	80/20	91/99
11	0.04	2.2/1	10	12	2.5	90	80/20	90/99
12	0.04	2.2/1	10	15	7	91	70/30	91/99
13	0.04	2.2/1	12	10	1	92	75/25	90/99
14	0.04	2.2/1	15	10	0.5	92	74/26	91/99
15	0.04	2.2/1	5	5	5	93	80/20	90/99
16	0.04	2.2/1	2.5	2.5	8	90	73/27	90/99
17	0.04	2.2/1	1	1	24	< 40 [e]	–	–

[a] Unless otherwise noted, reactions were carried out with **1a** (0.05 mmol), **2a**, **cat**. and **L6** in *m*-xylene at 25 °C. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis. [d] Determined by chiral HPLC. [e] Determined by TLC analysis.

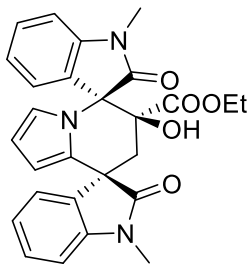
2.2 General procedure for the preparation of the adduct 3



Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** (0.01 mmol, 10 mol%) were combined into a vessel, and *m*-xylene (2.50 mL) was added *via* syringe. After the system was stirred at 25 °C for 0.5 h, the substrates **1** (0.1 mmol) and **2** (0.22 mmol, 2.2 equiv) were included. The reaction mixture was further stirred until the reaction was complete (detected by TLC). Then quinidine (0.02 mmol, 20 mol%) was introduced into the reaction mixture at 25°C. After the reaction was detected complete (by TLC analysis), 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 **3** as solids.

The racemic samples described in this part were synthesized according above procedure, which were catalyzed by $Cu(OTf)_2$ with mixed **L6** and *ent*-**L6** as ligands. Because equal amount of **L6** and *ent*-**L6** could not be accurately balanced, slight ee values (<15%) were observed in their racemic HPLC spectra.

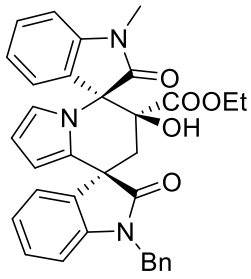
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3aa



3aa

White solid; mp 215–216 °C; 95% yield (44.8 mg), >20:1 *dr*, 95% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 44.771, t (minor) = 32.098]; $[\alpha]_D^{25}$ = 181.5 (c 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.44 – 7.39 (m, 2H), 7.35 – 7.31 (m, 1H), 7.25 – 7.19 (m, 2H), 7.04 – 6.96 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.26 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.06 (t, *J* = 3.2 Hz, 1H), 5.56 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.81 (qd, *J* = 7.2, 1.6 Hz, 2H), 3.38 (s, 3H), 3.31 – 3.26 (m, 4H), 2.50 (d, *J* = 15.6 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 171.4, 168.4, 142.9, 142.5, 132.9, 129.8, 128.8, 127.4, 125.2, 123.6, 123.3, 122.8, 122.1, 120.3, 110.4, 108.4, 108.0, 106.8, 77.9, 67.7, 61.2, 47.9, 34.2, 26.5, 26.3, 13.2; IR (KBr) ν_{max}: 3291, 3196, 2962, 2923, 2853, 1748, 1717, 1699, 1670, 1653, 1624, 1609, 1558, 1507, 1490, 1458, 1373, 1257, 1226, 1090, 1054, 1022, 801, 740, 709, 694 cm^{-1}; HRMS (ESI): m/z = 472.1878 (calcd for $C_{27}H_{25}N_3O_5$+H^+ = 472.1867).

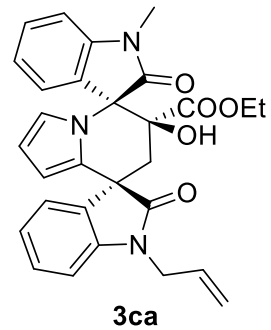
ethyl(3R,6'S,8'S)-1''-benzyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro [indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ba



3ba

White solid; mp 110–111 °C; 85% yield (46.5 mg), 95:5 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 14.904, t (minor) = 54.561]; $[\alpha]_D^{25}$ = 206.1 (c 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.41 – 7.39 (m, 1H), 7.36 – 7.18 (m, 9H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 16.8, 7.6 Hz, 2H), 6.30 – 6.29 (m, 1H), 6.09 (t, *J* = 3.2 Hz, 1H), 5.58 (d, *J* = 3.6 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.82 (d, *J* = 15.6 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 2H), 3.39 (s, 3H), 3.35 (d, *J* = 15.6 Hz, 1H), 2.57 (d, *J* = 15.2 Hz, 1H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 171.4, 168.4, 142.5, 141.9, 134.6, 132.9, 129.9, 128.7, 128.5, 127.4, 126.9, 125.3, 123.6, 123.3, 122.8, 122.1, 120.3, 110.5, 109.5, 108.0, 106.8, 77.9, 67.7, 61.3, 47.9, 43.7, 34.3, 26.3, 13.2; IR (KBr) ν_{max}: 2974, 2924, 1772, 1717, 1683, 1647, 1609, 1576, 1541, 1507, 1489, 1465, 1457, 1419, 1396, 1373, 1340, 1249, 1229, 1078, 929, 751, 696, 668 cm^{-1}; HRMS (ESI): m/z = 548.2174 (calcd for $C_{33}H_{29}N_3O_5$+H^+ = 548.2180).

ethyl(3R,6'S,8'S)-1''-allyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[i ndoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ca

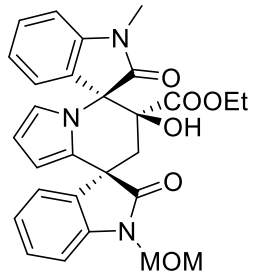


3ca

White solid; mp 207–208 °C; 95% yield (47.2 mg), >20:1 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 15.746, t (minor) = 26.650]; $[\alpha]_D^{25}$ = 103.6 (c 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.42 – 7.31 (m, 3H), 7.24 – 7.21 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.27 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.85 (ddt, *J* = 15.6, 10.4, 5.2 Hz, 1H), 5.58 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.28 – 5.24 (m, 2H), 4.46 – 4.40 (m, 1H), 4.34 – 4.28 (m, 1H), 3.81 (q, *J* = 7.2 Hz, 2H), 3.38 (s, 3H), 3.32 (d, *J* = 15.2 Hz, 1H), 2.52 (d, *J* = 15.6 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 171.4, 168.4, 142.5, 142.0, 132.9, 130.1, 129.9, 128.7,

127.4, 125.3, 123.5, 123.4, 122.8, 122.1, 120.3, 117.6, 110.4, 109.3, 108.0, 106.7, 77.9, 67.7, 61.2, 47.8, 42.2, 34.3, 26.3, 13.2; IR (KBr) ν_{max}: 2961, 2922, 2850, 1733, 1717, 1683, 1652, 1636, 1609, 1558, 1541, 1507, 1472, 1457, 1419, 1372, 1340, 1250, 1231, 1089, 1074, 1035, 929, 752, 696, 668 cm^{-1}; HRMS (ESI): m/z = 498.2039 (calcd for $C_{29}H_{27}N_3O_5+H^+$ = 498.2023).

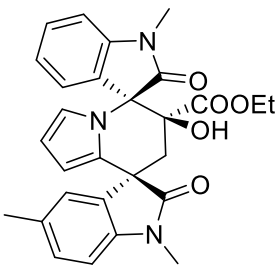
ethyl(3R,6'S,8'S)-6'-hydroxy-1''-(methoxymethyl)-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3da



3da

White solid; mp 106–107 °C; 88% yield (44.1 mg), >20:1 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 15.006, t (minor) = 30.067]; $[\alpha]_D^{25}$ = 106.3 (c 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.12 (t, *J* = 3.2 Hz, 1H), 5.66 (dd, *J* = 4.0, 2.0 Hz, 1H), 5.35 – 5.15 (m, 2H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.44 (s, 3H), 3.41 – 3.33 (m, 4H), 2.59 (d, *J* = 15.6 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 171.4, 168.3, 142.5, 141.0, 132.3, 129.9, 128.9, 127.3, 125.3, 124.0, 123.4, 122.9, 122.2, 120.4, 110.5, 109.9, 108.1, 106.9, 77.8, 71.3, 67.6, 61.3, 56.0, 48.2, 34.5, 26.3, 13.2; IR (KBr) ν_{max}: 2973, 2923, 2851, 1733, 1698, 1671, 1647, 1609, 1558, 1541, 1507, 1489, 1472, 1457, 1373, 1340, 1249, 1090, 1074, 752 cm^{-1}; HRMS (ESI): m/z = 502.1988 (calcd for $C_{28}H_{27}N_3O_6+H^+$ = 502.1973).

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ea

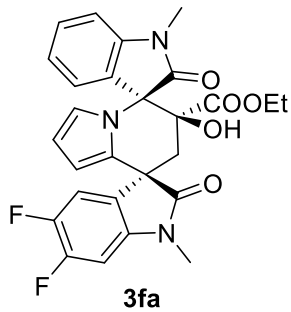


3ea

White solid; mp 133–134 °C; 90% yield (43.8 mg), >20:1 *dr*, 60% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 40.406, t (minor) = 30.586]; $[\alpha]_D^{25}$ = 300.5 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.33 (t, *J* = 7.6 Hz, 1H),

7.24 – 7.15 (m, 3H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.87 (dd, *J* = 10.8, 7.6 Hz, 2H), 6.26 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.06 (t, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 4.0, 2.0 Hz, 1H), 3.81 (qd, *J* = 7.2, 2.8 Hz, 2H), 3.38 (s, 3H), 3.27 (d, *J* = 15.6 Hz, 1H), 3.33 (s, 3H), 2.49 (d, *J* = 15.6 Hz, 1H), 2.42 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 171.4, 168.5, 142.5, 140.5, 133.3, 132.8, 129.8, 129.1, 127.5, 125.5, 124.0, 122.8, 122.1, 120.2, 110.3, 108.1, 108.0, 106.6, 77.9, 67.73, 61.2, 47.9, 34.3, 29.2, 26.4, 20.8, 13.2; IR (KBr) ν_{max}: 3219, 2962, 2923, 2854, 1733, 1718, 1697, 1653, 1636, 1608, 1558, 1541, 1506, 1490, 1472, 1457, 1419, 1371, 1340, 1246, 1070, 1030, 933, 805, 751, 697, 673 cm^{-1}; HRMS (ESI): m/z = 486.2035 (calcd for $C_{28}H_{27}N_3O_5+H^+$ = 486.2023).

ethyl(3R,6'S,8'S)-5'',6''-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3fa

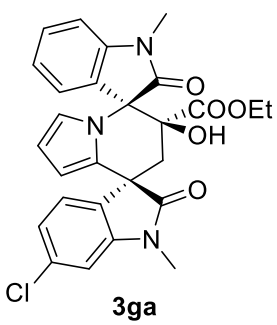


3fa

White solid; mp 125–126 °C; 84% yield (42.5 mg), 97:3 *dr*, 86% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 31.166, t (minor) = 15.200]; $[\alpha]_D^{25}$ = 199.0 (c 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.15 – 6.98 (m, 2H), 6.96 – 6.74 (m, 2H), 6.26 (s, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.58 (d, *J* = 3.6 Hz, 1H), 3.91 – 3.69 (m, 2H), 3.38 (s, 3H), 3.23 (s, 3H), 3.18 (d, *J* = 15.6 Hz, 1H), 2.51 (d, *J* = 15.2 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –134.8 (d, *J* = 19.6 Hz), –143.3 (d, *J* = 20.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 171.3, 168.2, 142.6, 139.2, 130.0, 128.098, 127.2, 124.3, 122.7, 122.2, 120.6, 113.2 (d, *J* = 19.6 Hz), 110.5, 108.2, 106.9, 98.8 (d, *J* = 23.0 Hz), 77.8, 67.5, 61.4, 47.9, 34.4, 26.7, 26.3, 13.2; IR (KBr) ν_{max}: 3214, 2964, 2922, 1733, 1697, 1653, 1647, 1608, 1541, 1506, 1490, 1457, 1419, 1370, 1340, 1247, 1091, 1070, 1029, 933, 752, 695, 673 cm^{-1}; HRMS (ESI): m/z = 508.1668 (calcd for $C_{27}H_{23}F_2N_3O_5+H^+$ = 508.1679).

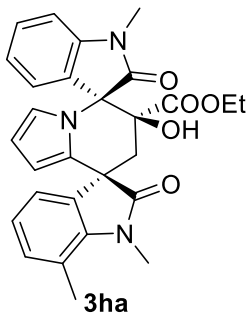
ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ga

White solid; mp 141–142 °C; 97% yield (48.9 mg), >20:1 *dr*, 96% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 41.777, t (minor) = 13.235]; $[\alpha]_D^{25}$ = 187.9 (c 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.37 – 7.28 (m, 2H), 7.20 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.05 – 6.99 (m, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.26 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.06 (t, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.80 (qd, *J* = 7.2, 3.2 Hz, 2H), 3.38 (s, 3H), 3.25 (s, 3H), 3.24 (d, *J* = 15.2 Hz, 1H), 2.49 (d, *J* = 15.6 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 171.3, 168.3, 144.1, 142.5, 134.6, 131.2, 129.9, 127.3, 124.6, 124.3, 123.4, 122.8, 122.1, 120.5, 110.5, 109.1, 108.1, 106.9, 77.8, 67.6, 61.3, 47.6, 34.3, 26.6, 26.3, 13.2; IR (KBr) ν_{max}: 3219, 2962, 2924, 2852, 1732, 1696, 1684, 1607, 1491, 1472, 1458, 1371, 1341, 1245, 1221, 1089, 1069, 1051, 1027, 934, 798, 751, 696, 673 cm^{-1}; HRMS (ESI): m/z = 506.1490 (calcd for $C_{27}H_{24}ClN_3O_5+H^+$ = 506.1477).



3ga

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',7''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ha

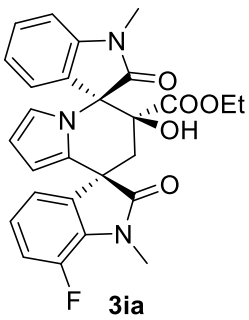


3ha

White solid; mp 135–136 °C; 88% yield (42.6 mg), >20:1 *dr*, 90% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 26.760, t (minor) = 13.759]; $[\alpha]_D^{25}$ = 147.9 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.36 – 7.29 (m, 1H), 7.25 – 7.17 (m, 2H), 7.16 – 7.07 (m, 2H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.25 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.06 (t, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.79 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.52 (s, 3H), 3.38 (s, 3H), 3.24 (d, *J* = 15.2 Hz, 1H), 2.65 (s, 3H), 2.47 (d, *J* = 15.6 Hz, 1H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 171.4, 168.4, 142.5, 140.5, 133.5, 132.5, 129.8, 127.5, 125.7, 123.4, 122.9, 122.1, 121.4, 120.2, 120.0, 110.3, 108.0, 106.7, 77.9, 67.7, 61.2, 47.3, 34.5, 29.9, 26.3, 18.5, 13.2; IR (KBr) ν_{max}: 2973, 2927, 2891, 1748, 1716, 1684, 1670, 1647, 1576, 1541, 1507, 1489, 1457, 1418, 1374, 1087, 1047, 684, 668,

644, 630, 614 cm^{-1}; HRMS (ESI): m/z = 486.2036 (calcd for $C_{28}H_{27}N_3O_5+H^+$ = 486.2023).

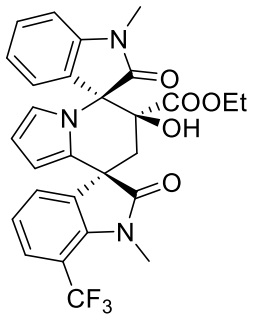
ethyl(3R,6'S,8'S)-7''-fluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ia



3ia

White solid; mp 108–109 °C; 91% yield (44.5 mg), >20:1 *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) = 33.869, t (minor) = 31.395]; $[\alpha]_D^{25}$ = 184.1 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 – 7.09 (m, 4H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.26 (dd, *J* = 16.0, 8.0 Hz, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.60 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.80 (qq, *J* = 7.2, 3.2 Hz, 2H), 3.46 (d, *J* = 2.4 Hz, 3H), 3.38 (s, 3H), 3.25 (d, *J* = 15.6 Hz, 1H), 2.52 (d, *J* = 15.6 Hz, 1H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –135.7; ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 171.3, 168.3, 147.2 (d, *J* = 243.6 Hz), 142.5, 135.6, 129.9, 129.5 (d, *J* = 8.7 Hz), 127.4, 124.7, 124.2 (d, *J* = 6.2 Hz), 122.8, 122.1, 120.4, 119.2, 116.9, 116.7, 110.4, 108.1, 106.9, 77.8, 67.6, 61.3, 48.1, 34.4, 29.1, 26.3, 13.2; IR (KBr) ν_{max}: 2973, 2922, 1772, 1733, 1698, 1684, 1652, 1647, 1616, 1558, 1521, 1507, 1497, 1473, 1464, 1418, 1339, 883, 746, 693, 626 cm^{-1}; HRMS (ESI): m/z = 490.1779 (calcd for $C_{27}H_{24}FN_3O_5+H^+$ = 490.1773).

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7''-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ja

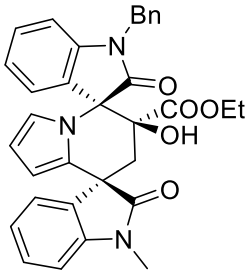


3ja

White solid; mp 215–216 °C; 94% yield (50.6 mg), 91:9 *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) = 26.934, t (minor) = 16.233]; $[\alpha]_D^{25}$ = 142.8 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.28 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.27 (t, *J* = 2.4 Hz, 1H), 6.08 (t, *J* = 3.2 Hz, 1H), 5.56 (dd, *J* = 4.0, 1.6 Hz, 1H), 3.80 (qd, *J* = 7.2, 4.4 Hz, 2H), 3.46

(q, *J* = 2.4 Hz, 6H), 3.39 (s, 3H), 3.24 (d, *J* = 15.6 Hz, 1H), 2.52 (d, *J* = 15.6 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –52.6, –53.1; ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 171.3, 168.2, 142.6, 140.8, 135.5, 130.0, 127.3, 127.1, 126.8, 126.8, 124.5, 122.9, 122.8, 122.1, 120.6, 110.5, 108.2, 106.9, 77.8, 67.5, 61.3, 46.5, 34.6, 29.2, 26.3, 13.2; IR (KBr) ν_{max}: 2920, 2849, 1747, 1717, 1699, 1652, 1647, 1608, 1558, 1507, 1489, 1457, 1363, 1340, 1244, 1143, 1112, 1090, 1072, 1025, 753, 701 cm^{-1}; HRMS (ESI): m/z = 540.1751 (calcd for $C_{28}H_{24}F_3N_3O_5$+H^+ = 540.1741).

ethyl(3R,6'S,8'S)-1-benzyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro [indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ab

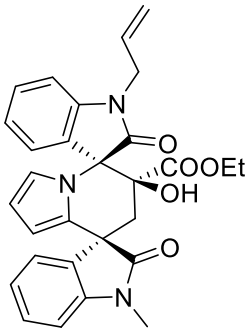


3ab

White solid; mp 109–110 °C; 89% yield (50.6 mg), 93:7 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 23.361, t (minor) = 17.937]; $[\alpha]_D^{25}$ = 168.1 (c 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.41 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.22 (m, 3H), 7.14 – 6.95 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.37 – 6.23 (m, 1H), 6.11 (t, *J* = 3.6 Hz, 1H), 5.61 (d, *J* = 3.6 Hz, 1H), 5.36 (d, *J* = 15.2 Hz, 1H), 4.89 (d, *J* = 15.2 Hz, 1H), 3.87 – 3.66 (m, 2H), 3.36 (d, *J* = 15.6 Hz, 1H), 3.32 (s, 3H), 2.59 (d, *J* = 15.6 Hz, 1H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 171.6, 168.4, 142.9, 141.8, 135.3, 132.9, 129.7, 128.8, 128.4, 127.6, 127.6, 127.4, 125.4, 123.6, 123.3, 122.9, 122.1, 120.1, 110.5, 109.1, 108.4, 106.7, 77.8, 67.5, 61.2, 47.9, 44.3, 34.5, 26.5, 13.1; IR (KBr) ν_{max}: 3178, 2964, 2922, 1733, 1697, 1683, 1671, 1653, 1610, 1541, 1488, 1465, 1458, 1374, 1354, 1251, 1222, 1152, 1092, 1050, 1031, 932, 752, 743, 703, 692, 683 cm^{-1}; HRMS (ESI): m/z = 570.1989 (calcd for $C_{33}H_{29}N_3O_5$+Na^+ = 570.1999).

ethyl(3R,6'S,8'S)-1-allyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[i ndoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ac

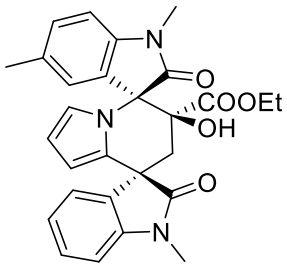
White solid; mp 206–207 °C; 88% yield (43.7 mg), >20:1 *dr*, 89% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 19.869, t (minor) = 12.425]; $[\alpha]_D^{25}$ = 208.1 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.53 – 7.42 (m, 2H), 7.38 – 7.23 (m, 3H), 7.10 – 6.99 (m,



3ac

2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.32 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.11 (t, *J* = 3.4 Hz, 1H), 6.09 – 5.95 (m, 1H), 5.62 (dd, *J* = 4.0, 2.0 Hz, 1H), 5.46 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.37 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.76 – 4.59 (m, 1H), 4.54 – 4.37 (m, 1H), 3.86 (qd, *J* = 7.2, 2.8 Hz, 2H), 2.36 (d, *J* = 15.6 Hz, 1H), 3.32 (s, 3H), 2.57 (d, *J* = 15.2 Hz, 1H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 171.0, 168.4, 142.9, 141.8, 132.9, 131.0, 129.7, 128.8, 127.5, 125.3, 123.6, 123.3, 122.9, 122.0, 120.2, 118.1, 110.4, 109.0, 108.4, 106.8, 77.9, 67.5, 61.2, 47.9, 42.7, 34.3, 26.5, 13.1; IR (KBr) ν_{max}: 3176, 2962, 2918, 2851, 1732, 1670, 1654, 1610, 1488, 1420, 1374, 1353, 1253, 1222, 1211, 1185, 1151, 1092, 1048, 1031, 993, 933, 797, 763, 752, 711, 691, 683, 636, 624 cm^{-1}; HRMS (ESI): m/z = 498.2032 (calcd for $C_{29}H_{27}N_3O_5$+H^+ = 498.2023).

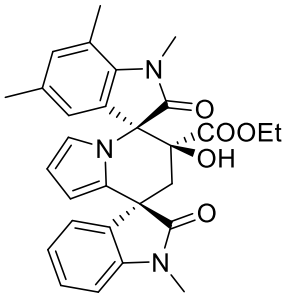
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ad



3ad

White solid; mp 223–224 °C; 92% yield (44.8 mg), >20:1 *dr*, 91% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 24.439, t (minor) = 20.738]; $[\alpha]_D^{25}$ = 209.6 (c 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.50 – 7.33 (m, 2H), 7.24 (td, *J* = 7.6, 1.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.05 – 6.92 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.26 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.82 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.36 (s, 3H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.26 (s, 3H), 2.49 (d, *J* = 15.6 Hz, 1H), 2.31 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 171.4, 168.5, 142.9, 140.2, 133.0, 131.5, 130.1, 128.8, 127.4, 125.2, 123.6, 123.6, 123.2, 120.3, 110.3, 108.4, 107.8, 106.6, 77.9, 67.8, 61.2, 47.9, 34.2, 26.5, 26.3, 20.9, 13.2; IR (KBr) ν_{max}: 3177, 2987, 2971, 2906, 1733, 1698, 1653, 1609, 1558, 1541, 1506, 1472, 1457, 1418, 1374, 1346, 1249, 1226, 1092, 1080, 1051, 1037, 811, 766, 718, 696, 681, 625 cm^{-1}; HRMS (ESI): m/z = 486.2026 (calcd for $C_{28}H_{27}N_3O_5$+H^+ = 486.2023).

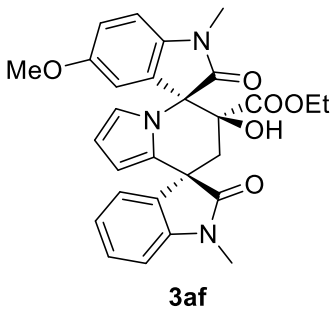
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ae



3ae

White solid; mp 221–222 °C; 94% yield (46.9 mg), >20:1 *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) = 21.796, t (minor) = 24.560]; $[\alpha]_D^{25}$ = 238.8 (c 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.47 – 7.35 (m, 2H), 7.23 (td, *J* = 7.6, 1.2 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.78 (m, 2H), 6.26 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.56 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.63 (s, 3H), 3.32 (d, *J* = 15.6 Hz, 1H), 3.26 (s, 3H), 2.54 (s, 3H), 2.43 (d, *J* = 15.6 Hz, 1H), 2.25 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 172.3, 168.5, 142.9, 137.7, 133.9, 133.0, 131.3, 128.8, 128.2, 125.3, 123.5, 123.2, 121.5, 120.4, 119.3, 110.2, 108.4, 106.5, 78.0, 67.5, 61.1, 47.9, 33.9, 29.7, 26.5, 20.5, 18.6, 13.2; IR (KBr) ν_{max}: 3178, 2971, 2917, 1732, 1698, 1671, 1647, 1608, 1558, 1541, 1506, 1497, 1457, 1418, 1374, 1339, 1248, 1224, 1092, 1050, 811, 765 cm^{-1}; HRMS (ESI): m/z = 500.2190 (calcd for $C_{29}H_{29}N_3O_5$+H^+ = 500.2180).

ethyl(3R,6'S,8'S)-6'-hydroxy-5-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3af

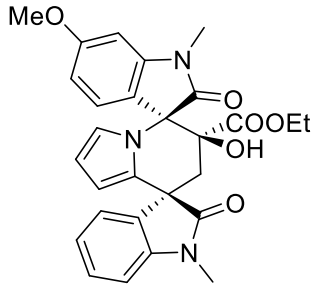


3af

White solid; mp 173–174 °C; 91% yield (45.6 mg), >20:1 *dr*, 75% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 40.833, t (minor) = 30.704]; $[\alpha]_D^{25}$ = 404.0 (c 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.46 – 7.35 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.73 (m, 3H), 6.27 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.06 (t, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 4.0, 1.6 Hz, 1H), 3.84 (qd, *J* = 7.2, 2.0 Hz, 2H), 3.77 (s, 3H), 3.36 (s, 3H), 3.28 (d, *J* = 15.6 Hz, 1H), 3.26 (s, 3H), 2.49 (d, *J* = 15.6 Hz, 1H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 171.1, 168.4, 155.2, 142.9, 135.9, 132.9, 128.8, 128.6, 125.1, 123.6, 123.2, 120.4, 113.0, 111.5, 110.4, 108.4, 108.2, 106.9, 77.8, 67.9,

61.2, 55.3, 47.9, 34.1, 29.2, 26.4, 13.2; IR (KBr) ν_{max}: 3219, 3197, 2965, 2921, 1733, 1698, 1653, 1636, 1609, 1558, 1507, 1490, 1464, 1457, 1419, 1373, 1290, 1247, 1232, 1091, 1053, 1030, 802, 751, 692 cm^{-1}; HRMS (ESI): m/z = 502.1965 (calcd for $C_{28}H_{27}N_3O_6+H^+$ = 502.1973).

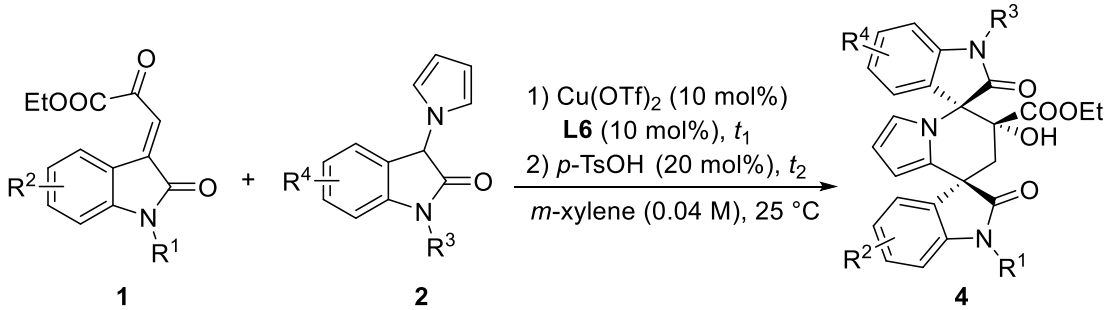
ethyl(3R,6'S,8'S)-6'-hydroxy-6-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ag



3ag

White solid; mp 191–192 °C; 90% yield (45.1 mg), >20:1 *dr*, 79% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 23.041, t (minor) = 15.995]; $[\alpha]_D^{25}$ = 170.0 (c 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.46 – 7.31 (m, 2H), 7.26 – 7.16 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 6.25 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.05 (t, *J* = 3.2 Hz, 1H), 5.54 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.85 (qd, *J* = 7.2, 2.8 Hz, 2H), 3.81 (s, 3H), 3.36 (s, 3H), 3.26 (d, *J* = 15.6 Hz, 1H), 3.26 (s, 3H), 2.50 (d, *J* = 15.6 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 171.9, 168.5, 161.1, 144.0, 142.9, 133.0, 128.8, 125.2, 123.8, 123.5, 123.265, 120.1, 119.5, 110.3, 108.4, 106.6, 105.6, 95.9, 77.9, 67.3, 61.2, 55.1, 47.9, 34.2, 26.5, 26.3, 13.3; IR (KBr) ν_{max}: 3355, 2986, 2408, 1717, 1459, 1258, 1053, 927, 891, 765, 654, 622 cm^{-1}; HRMS (ESI): m/z = 502.1987 (calcd for $C_{28}H_{27}N_3O_6+H^+$ = 502.1973).

2.3 General procedure for the preparation of the adduct 4

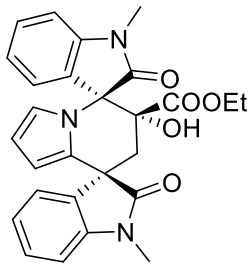


Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** (0.01 mmol, 10 mol%) were combined into a vessel, and *m*-xylene (2.50 mL) was added *via* syringe. After the catalyst system was stirred at 25 °C for 0.5 h, the substrates **1** (0.1 mmol)

and **2** (0.22 mmol, 2.2 equiv) were included and the reaction mixture was further stirred until the reaction was complete (detected by TLC). Then *p*-TsOH (0.02 mmol, 20 mol%) was introduced to promote the subsequent intramolecular aldol reaction at 25 °C. Once the reaction was detected complete (by TLC analysis), 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 **4** as solids.

The racemic samples described in this part were synthesized according above procedure, which were catalyzed by $Cu(OTf)_2$ with mixed **L6** and *ent*-**L6** as ligands. Because equal amount of **L6** and *ent*-**L6** could not be accurately balanced, slight ee values (<15%) were observed in their racemic HPLC spectra.

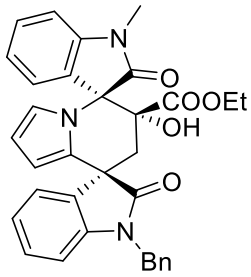
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4aa



4aa

White solid; mp 131–132 °C; 91% yield (43.3 mg), >20:1 *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) = 12.056, t (minor) = 20.443]; $[\alpha]_D^{25}$ = –161.9 (c 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.97 – 5.88 (m, 1H), 5.63 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.16 (s, 1H), 4.11 – 3.94 (m, 3H), 3.31 (s, 3H), 3.21 (s, 3H), 2.00 (d, *J* = 14.0 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 171.7, 170.9, 144.1, 142.4, 136.0, 130.7, 127.8, 127.4, 127.3, 126.7, 124.3, 122.5, 122.2, 116.8, 109.0, 107.6, 107.2, 105.9, 76.3, 66.7, 62.8, 47.9, 34.8, 26.3, 26.3, 13.4; IR (KBr) ν_{max}: 2973, 2922, 1733, 1700, 1670, 1636, 1608, 1558, 1521, 1507, 1473, 1457, 1419, 1372, 1339, 1258, 1105, 1094, 754, 745, 700 cm^{-1}; HRMS (ESI): m/z = 472.1879 (calcd for $C_{27}H_{25}N_3O_5+H^+$ = 472.1867).

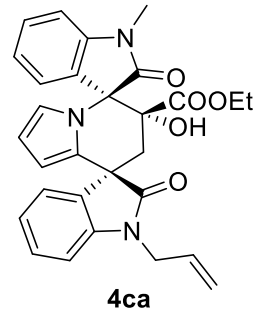
ethyl(3R,6'R,8'S)-1''-benzyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ba



4ba

White solid; mp 125–126 °C; 85% yield (46.4 mg), 90:10 *dr*, 89% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 11.110, t (minor) = 19.014]; $[\alpha]_D^{25}$ = –66.2 (c 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.70 (m, 2H), 7.54 – 7.45 (m, 2H), 7.43 – 7.29 (m, 4H), 7.27 – 7.16 (m, 2H), 7.09 – 6.77 (m, 3H), 6.43 – 5.91 (m, 2H), 5.59 – 5.74 (m, 1H), 5.26 – 5.06 (m, 1H), 4.99 – 4.80 (m, 1H), 4.24 (s, 1H), 4.19 – 3.75 (m, 3H), 3.50 – 3.29 (s, 3H), 2.12 (d, *J* = 14.4 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 171.7, 170.9, 144.1, 141.4, 136.1, 135.9, 130.7, 128.5, 128.2, 127.9, 127.3, 127.1, 126.9, 126.7, 124.3, 122.6, 122.2, 116.8, 109.1, 108.2, 107.6, 105.9, 76.3, 66.6, 62.9, 47.9, 43.7, 34.8, 25.9, 13.4; IR (KBr) ν_{max}: 2962, 2927, 2851, 1733, 1717, 1685, 1608, 1489, 1466, 1457, 1363, 1341, 1259, 1174, 1129, 1084, 1055, 1024, 799, 747, 700, 669 cm^{-1}; HRMS (ESI): m/z = 548.2178 (calcd for $C_{33}H_{29}N_3O_5$+H^+ = 548.2180).

ethyl(3R,6'R,8'S)-1''-allyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ca

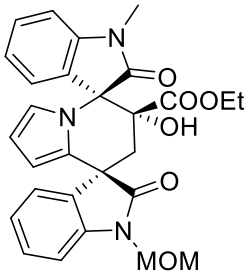


4ca

White solid; mp 122–123 °C; 82% yield (40.7 mg), >20:1 *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) = 10.918, t (minor) = 20.258]; $[\alpha]_D^{25}$ = –68.9 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.45 (td, *J* = 8.0, 1.2 Hz, 1H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6, 0.8 Hz, 1H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 (t, *J* = 5.2 Hz, 2H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.98 – 5.84 (m, 2H), 5.64 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.39 – 5.18 (m, 2H), 4.56 – 4.32 (m, 2H), 4.16 (s, 1H), 4.11 – 3.95 (m, 3H), 3.21 (s, 3H), 2.02 (d, *J* = 13.6 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 171.7, 170.9, 144.1, 141.5, 136.1, 131.2, 130.7, 127.8, 127.3, 127.2, 126.7, 124.3, 122.5, 122.1, 117.1, 116.8, 109.0, 108.0, 107.6, 105.9, 76.3, 66.6, 62.8, 47.8, 42.2, 34.8, 25.9, 13.4; IR (KBr) ν_{max}: 2963, 2923, 2851, 1733, 1717, 1706, 1684, 1647, 1608, 1558, 1541, 1507, 1489, 1472, 1457, 1363, 1340, 1259, 1085, 1025, 753,

702, 693, 669 cm^{-1}; HRMS (ESI): m/z = 498.2037 (calcd for $C_{29}H_{27}N_3O_5+H^+$ = 498.2023).

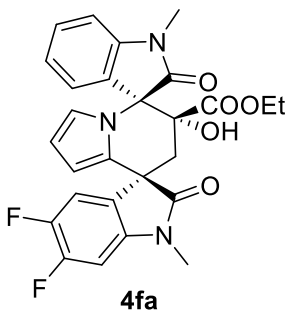
ethyl(3R,6'R,8'S)-6'-hydroxy-1''-(methoxymethyl)-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4da



4da

White solid; mp 102–103 °C; 89% yield (44.6 mg), >20:1 *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) = 9.081, t (minor) = 19.499]; $[\alpha]_D^{25}$ = –116.3 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.45 (td, *J* = 8.0, 1.2 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.01 (t, *J* = 3.6 Hz, 1H), 5.94 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.66 (dd, *J* = 4.0, 1.6 Hz, 1H), 5.34 – 5.15 (m, 2H), 4.187 (s, 1H), 4.15 – 3.95 (m, 3H), 3.40 (s, 3H), 3.22 (s, 3H), 2.06 (d, *J* = 14.0 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 171.6, 171.0, 144.0, 140.5, 135.5, 130.7, 127.7, 127.5, 127.3, 126.8, 124.3, 122.8, 122.6, 116.9, 109.1, 108.6, 107.7, 106.0, 71.3, 66.6, 62.9, 56.0, 48.2, 34.9, 29.2, 25.9, 13.4; IR (KBr) ν_{max}: 2962, 2926, 2850, 1733, 1684, 1647, 1608, 1558, 1521, 1489, 1457, 1340, 1259, 1090, 1023, 754, 704, 692, 669 cm^{-1}; HRMS (ESI): m/z = 502.1988 (calcd for $C_{28}H_{27}N_3O_6+H^+$ = 502.1973).

ethyl(3R,6'R,8'S)-5'',6''-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4fa

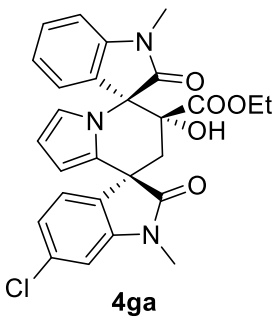


4fa

White solid; mp 226–227 °C; 85% yield (43.1 mg), >20:1 *dr*, 88% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 10.886, t (minor) = 15.959]; $[\alpha]_D^{25}$ = –230.0 (c 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 10.0, 6.4 Hz, 1H), 6.02 (t, *J* = 3.2 Hz, 1H), 5.93 (dd, *J* = 2.8, 1.2 Hz, 1H), 5.63 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.26 (s, 1H), 4.15 – 3.93 (m, 3H), 3.27 (s, 3H), 3.20 (s, 3H), 0.95 (d, *J* = 13.6 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$)

δ –138.0 (d, *J* = 20.7 Hz), –146.1 (d, *J* = 20.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 171.4, 170.8, 147.1, 144.7 (d, *J* = 12.7 Hz), 144.0, 138.6, 131.2 130.8, 127.2, 127.0, 124.0, 122.7, 117.1, 116.7 (d, *J* = 21.4 Hz), 109.2, 107.7, 105.9, 97.1 (d, *J* = 22.7 Hz), 66.7 63.0, 47.9, 34.4, 29.2, 26.5, 26.0, 13.3; IR (KBr) ν_{max}: 3064, 2966, 2927, 2851, 1734, 1717, 1685, 1608, 1506, 1491, 1470, 1456, 1421, 1368, 1341, 1248, 1139, 1128, 1113, 1092, 1054, 1022, 755, 711, 693, 668, 616 cm^{-1}; HRMS (ESI): m/z = 508.1694 (calcd for $C_{27}H_{23}F_2N_3O_5+H^+$ = 508.1679).

ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ga

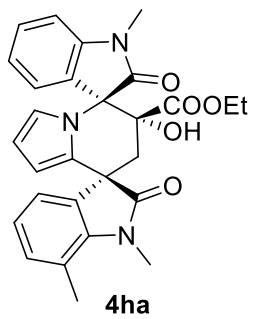


4ga

White solid; mp 246–247 °C; 91% yield (45.9 mg), >20:1 *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) = 11.515, t (minor) = 16.546]; $[\alpha]_D^{25}$ = –265.0 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.45 (td, *J* = 8.0, 1.2 Hz, 1H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.01 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.93 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.62 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.18 (s, 1H), 4.10 – 3.94 (m, 3H), 3.29 (s, 3H), 3.204 (s, 3H), 1.96 (d, *J* = 13.6 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 171.6, 170.9, 144.0, 143.6, 134.3, 133.1, 130.8, 127.8, 127.3, 127.2, 124.2, 122.6, 121.9, 116.9, 109.1, 107.8, 107.7, 106.0, 76.2, 66.7, 62.9, 47.6, 34.7, 26.4, 25.9, 13.4; IR (KBr) ν_{max}: 2962, 2922, 2851, 1733, 1705, 1684, 1670, 1652, 1636, 1558, 1521, 1490, 1457, 1419, 1366, 1258, 1081, 1023, 962, 822, 799, 753, 746, 703, 693, 679, 639 cm^{-1}; HRMS (ESI): m/z = 506.1487 (calcd for $C_{27}H_{24}ClN_3O_5+H^+$ = 506.1477).

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',7''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ha

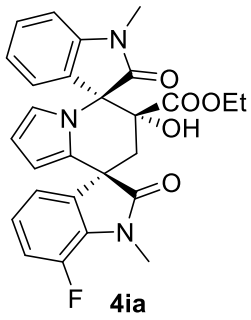
White solid; mp 175–176 °C; 62% yield (30.1 mg), >20:1 *dr*, 97% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 71.191, t (minor) = 69.357]; $[\alpha]_D^{25}$ = –135.7 (c 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 2H), 7.44 (td, *J* = 8.0, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6,



4ha

1.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.92 – 6.83 (m, 2H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.92 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.64 (dd, *J* = 4.0, 1.6 Hz, 1H), 4.11 (s, 1H), 4.08 – 3.92 (m, 3H), 3.59 (s, 3H), 3.20 (s, 3H), 2.63 (s, 3H), 1.98 (d, *J* = 14.0 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 171.7, 170.9, 144.1, 140.1, 136.8, 131.1, 130.6, 128.2, 127.3, 124.7, 124.4, 122.5, 121.9, 118.5, 116.7, 109.0, 107.6, 105.9, 66.9, 62.8, 47.4, 35.3, 29.8, 29.2, 25.9, 18.9, 13.4; IR (KBr) ν_{max}: 2965, 2933, 1733, 1698, 1685, 1609, 1558, 1541, 1507, 1490, 1471, 1457, 1435, 1364, 1341, 1258, 1122, 1089, 1057, 1023, 753, 702 cm^{-1}; HRMS (ESI): m/z = 486.2039 (calcd for $C_{28}H_{27}N_3O_5$+H^+ = 486.2023).

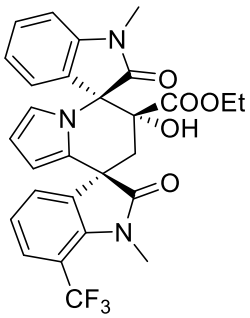
ethyl(3R,6'R,8'S)-7''-fluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodi spiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ia



4ia

White solid; mp 94–95 °C; 90% yield (44.0 mg), >20:1 *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) = 7.506, t (minor) = 9.978]; $[\alpha]_D^{25}$ = –260.8 (c 0.24, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.86 (m, 3H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.97 – 5.88 (m, 1H), 5.67 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.17 (s, 1H), 4.11 – 3.92 (m, 3H), 3.52 (d, *J* = 2.8 Hz, 3H), 3.21 (s, 3H), 2.00 (d, *J* = 14.0 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –137.5; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 171.6, 170.8, 148.1, 145.7, 144.0, 138.7, 130.7, 129.1, 127.3, 127.2, 124.2, 122.5, 122.4 (d, *J* = 6.7 Hz), 117.0, 115.2 (d, *J* = 18.9 Hz), 109.1, 107.7, 106.1, 76.2, 66.7, 62.9, 48.1, 34.9, 28.9, 25.9, 13.4; IR (KBr) ν_{max}: 2965, 2931, 1733, 1717, 1684, 1670, 1652, 1647, 1609, 1558, 1541, 1507, 1489, 1472, 1435, 1364, 1340, 1258, 1175, 1129, 1111, 1086, 1023, 753, 701, 668 cm^{-1}; HRMS (ESI): m/z = 490.1781 (calcd for $C_{27}H_{24}FN_3O_5$+H^+ = 490.1773).

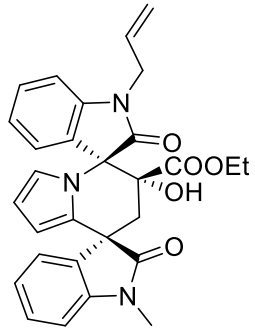
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7''-(trifluoromethyl)-6',7' -dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ja



4ja

White solid; mp 211–212 °C; 90% yield (48.5 mg), 91:9 *dr*, 95% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 26.934, t (minor) = 16.233]; $[\alpha]_D^{25}$ = –165.9 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.02 (t, *J* = 3.6 Hz, 1H), 5.96 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.62 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.23 (s, 1H), 4.14 – 3.92 (m, 3H), 3.52 (q, *J* = 2.4 Hz, 3H), 3.21 (s, 3H), 1.99 (d, *J* = 14.0 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –52.6; ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 171.5, 170.8, 144.0, 140.3, 138.4, 130.8, 130.5, 127.2, 127.1, 125.4, 125.3, 124.1, 122.6, 121.4, 117.1, 111.5, 109.1, 107.7, 106.2, 76.2, 66.7, 63.0, 46.4, 35.2, 29.0, 26.0, 13.4; IR (KBr) ν_{max}: 2973, 2921, 2849, 1733, 1699, 1652, 1647, 1541, 1507, 1489,1457, 1339, 1261, 1135, 1095, 1083, 1044, 752, 744, 711, 697 cm^{-1}; HRMS (ESI): m/z = 540.1754 (calcd for $C_{28}H_{24}F_3N_3O_5$+H^+ = 540.1741).

ethyl(3R,6'R,8'S)-1-allyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ac

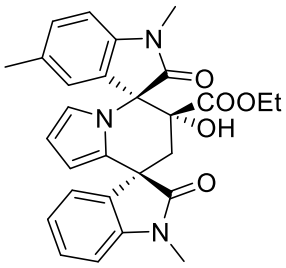


4ac

White solid; mp 124–125 °C; 88% yield (43.7 mg), >20:1 *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) = 10.282, t (minor) = 17.245]; $[\alpha]_D^{25}$ = –229.7 (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.73 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41 (td, *J* = 8.0, 1.2 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.13 (td, *J* = 7.6, 0.8 Hz, 1H), 7.00 (td, *J* = 7.6, 1.2 Hz, 1H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.01 (dd, *J* = 3.6, 3.2 Hz, 1H), 5.93 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.88 – 5.75 (m, 1H), 5.64 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.37 – 5.18 (m, 2H), 4.50 – 4.37 (m, 1H), 4.26 – 4.18 (m, 1H), 4.15 – 4.13 (m, 1H), 4.11 – 3.94 (m, 3H), 3.31 (s, 3H), 2.01 (d, *J* = 14.0 Hz, 1H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 171.6, 170.6, 143.3, 142.4, 136.0, 130.6, 130.5, 127.8, 127.4, 127.3, 126.6,

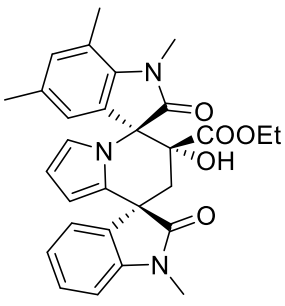
124.4, 122.5, 122.1, 118.0, 116.7, 109.2, 108.6, 107.1, 105.9, 76.3, 66.5, 62.9, 47.9, 42.2, 34.8, 26.3, 13.3; IR (KBr) ν_{max}: 2974, 2917, 2849, 1733, 1704, 1684, 1647, 1636, 1608, 1558, 1541, 1507, 1489, 1457, 1419, 1362, 1352, 1252, 1230, 1098, 1023, 762, 746, 707, 668 cm^{-1}; HRMS (ESI): m/z = 498.2022 (calcd for $C_{29}H_{27}N_3O_5+H^+$ = 498.2023).

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ad



4ad

White solid; mp 223–224 °C; 86% yield (41.2 mg), >20:1 *dr*, 96% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 90/10, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 87.491, t (minor) = 77.586]; $[\alpha]_D^{25}$ = –331.4 (c 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.94 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.63 (dd, *J* = 4.0, 1.6 Hz, 1H), 4.16 (s, 1H), 4.09 – 3.91 (m, 3H), 3.31 (s, 3H), 3.18 (s, 3H), 2.37 (s, 3H), 1.99 (d, *J* = 14.0 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 171.8, 170.9, 142.4, 141.6, 136.1, 132.1, 130.9, 127.9, 127.4, 126.7, 124.3, 122.1, 116.8, 108.9, 107.4, 107.1, 105.8, 99.5, 66.8, 62.8, 47.9, 34.7, 26.3, 26.0, 20.7, 13.4; IR (KBr) ν_{max}: 2972, 2926, 1734, 1717, 1699, 1684, 1652, 1647, 1605, 1558, 1541, 1521, 1506, 1498, 1489, 1472, 1457, 1362, 1340, 1252, 1138, 1096, 700 cm^{-1}; HRMS (ESI): m/z = 486.2019 (calcd for $C_{28}H_{27}N_3O_5+H^+$ = 486.2023).



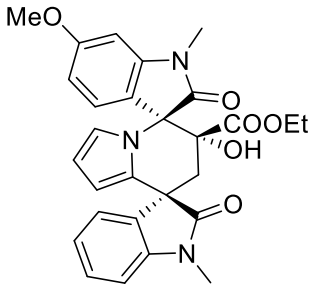
4ae

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ae

White solid; mp 133–134 °C; 88% yield (43.9 mg), >20:1 *dr*, 94% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 34.228, t (minor) = 22.621]; $[\alpha]_D^{25}$ = –138.0 (c 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.28 – 7.22

(m, 1H), 7.03 – 6.94 (m, 2H), 6.90 – 6.81 (m, 1H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.96 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.62 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.18 – 3.94 (m, 4H), 3.45 (s, 3H), 3.30 (s, 3H), 2.54 (s, 3H), 2.31 (s, 3H), 1.98 (d, *J* = 14.0 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 171.8, 171.8, 142.4, 139.3, 136.1, 134.8, 131.8, 127.9, 127.3, 126.7, 125.6, 125.0, 122.1, 118.8, 117.0, 108.8, 107.1, 105.7, 66.4, 62.7, 47.9, 34.6, 29.4, 29.2, 26.3, 20.4, 18.5, 13.4; IR (KBr) ν_{max}: 2974, 2922, 1733, 1716, 1706, 1684, 1652, 1647, 1607, 1558, 1541, 1521, 1507, 1488, 1473, 1457, 1436, 1339, 1258, 1145, 1105, 1094, 754, 745, 699 cm^{-1}; HRMS (ESI): m/z = 500.2191 (calcd for $C_{29}H_{29}N_3O_5$+H^+ = 500.2180).

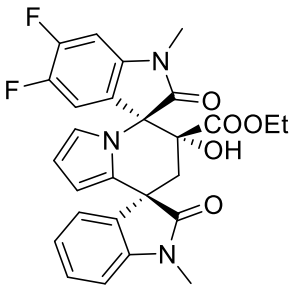
ethyl(3R,6'R,8'S)-6'-hydroxy-6-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ag



4ag

White solid; mp 125–126 °C; 64% yield (32.1 mg), >20:1 *dr*, 90% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 75/25, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 26.342, t (minor) = 22.684]; $[\alpha]_D^{25}$ = –273.0 (c 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.22 (m, 1H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.61 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.00 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.96 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.62 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.14 (s, 1H), 4.11 – 3.94 (m, 3H), 3.87 (s, 3H), 3.30 (s, 3H), 3.18 (s, 3H), 1.98 (d, *J* = 14.0 Hz, 1H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 171.9, 171.4, 161.8, 145.5, 142.4, 136.1, 128.2, 127.8, 127.3, 126.6, 122.1, 116.7, 116.1, 108.9, 107.1, 106.0, 105.9, 95.6, 76.4, 66.3, 62.8, 55.1, 47.9, 34.9, 26.6, 25.9, 13.4; IR (KBr) ν_{max}: 3289, 2962, 2922, 2850, 1733, 1700, 1652, 1647, 1624, 1558, 1541, 1506, 1489, 1457, 1431, 1372, 1258, 1207, 1138, 1128, 1090, 1056, 1046, 1022, 979, 963, 801, 790, 754, 709, 684, 661 cm^{-1}; HRMS (ESI): m/z = 502.1987 (calcd for $C_{28}H_{27}ClN_3O_6$+H^+ = 502.1973).

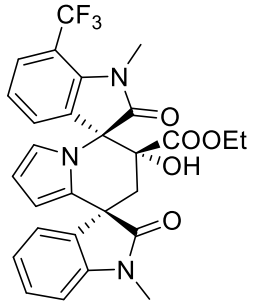
ethyl(3R,6'R,8'S)-5,6-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ah



4ah

White solid; mp 108–109 °C; 92% yield (46.6 mg), >20:1 *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) = 7.685, t (minor) = 13.880]; $[\alpha]_D^{25}$ = –218.9 (c 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 9.6, 7.6 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 2.8, 1.6 Hz, 1H), 6.73 (dd, *J* = 9.6, 6.0 Hz, 1H), 6.02 (t, *J* = 3.2 Hz, 1H), 5.90 (dd, *J* = 9.6, 6.0 Hz, 1H), 5.63 (dd, *J* = 3.6, 16 Hz, 1H), 4.21 – 3.99 (m, 3H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.30 (s, 3H), 3.18 (s, 3H), 1.99 (d, *J* = 14.0 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –131.9 (d, *J* = 19.6 Hz), –144.4 (d, *J* = 19.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 171.5, 170.6, 150.7, 147.3, 144.8, 142.4, 140.8, 135.8, 127.8, 127.5, 126.5, 122.2, 119.6, 117.5 (d, *J* = 20.6 Hz), 116.4, 109.6, 107.3, 106.3, 97.8 (d, *J* = 23.1 Hz), 76.3, 66.2, 63.1, 47.8, 35.1, 26.3, 26.2, 13.4; IR (KBr) ν_{max}: 2973, 2924, 1772, 1747, 1733, 1701, 1684, 1652, 1636, 1624, 1608, 1558, 1521, 1507, 1489, 1473, 1436, 1396, 1362, 1350, 1339, 1261, 1093, 1052, 1022, 702, 694 cm^{-1}; HRMS (ESI): m/z = 508.1689 (calcd for $C_{27}H_{23}F_2N_3O_5$+H^+ = 508.1679).

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ai

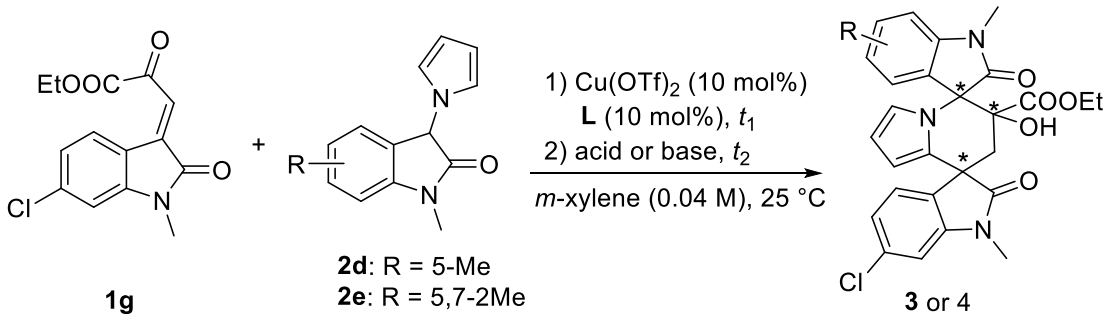


4ai

White solid; mp 242–243 °C; 87% yield (46.9 mg), >20:1 *dr*, 81% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 75/25, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 13.914, t (minor) = 12.219]; $[\alpha]_D^{25}$ = –20.0 (c 0.18, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.04 (t, *J* = 3.2 Hz, 1H), 5.92 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.66 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.14 (s, 1H), 4.10 – 3.98 (m, 2H), 3.93 (d, *J* = 14.0 Hz, 1H), 3.42 (q, *J* = 2.4 Hz, 3H), 3.31 (s, 3H), 2.01 (d, *J* = 14.0 Hz, 1H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –53.3; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 171.8, 171.5, 142.4, 142.1, 135.8, 130.9, 128.5, 128.1, 127.5,

126.9, 126.6, 122.2, 121.7, 116.6, 112.0, 109.5, 107.3, 106.2, 76.3, 65.1, 63.3, 47.8, 34.8, 28.8, 26.3, 13.2; IR (KBr) ν_{max}: 2973, 2935, 1747, 1733, 1716, 1706, 1699, 1684, 1652, 1647, 1558, 1541, 1521, 1507, 1489, 1473, 1457, 1338, 1256, 1116, 1094, 1051, 744, 685 cm^{-1}; HRMS (ESI): m/z = 540.1758 (calcd for $C_{28}H_{24}F_3N_3O_5+H^+$ = 540.1741).

2.4 Procedure for the preparation the stereoisomeric products



1g

2d: R = 5-Me
2e: R = 5,7-2Me

3 or 4

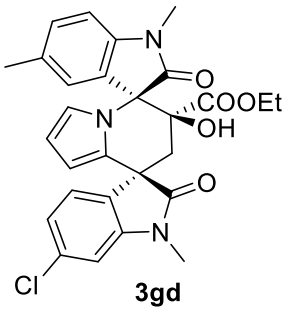
3gd: **L6** + QD, (2 + 8) h 85% yield, >20:1 *dr*, 93% *ee*	**3ge**: **L6** + QD, (2 + 8) h 82% yield, >20:1 *dr*, 96% *ee*
ent-**3gd**: **L2** + QD, (2 + 8) h 88% yield, >20:1 *dr*, 92% *ee*	*ent*-**3ge**: **L2** + QD, (2 + 8) h 91% yield, >20:1 *dr*, 95% *ee*
4gd: **L6** + *p*-TsOH, (2 + 8) h 75% yield, >20:1 *dr*, 95% *ee*	**4ge**: **L6** + *p*-TsOH, (2 + 8) h 88% yield, >20:1 *dr*, 94% *ee*
ent-**4gd**: **L2** + *p*-TsOH, (2 + 8) h 85% yield, >20:1 *dr*, 95% *ee*	*ent*-**4ge**: **L2** + *p*-TsOH, (2 + 8) h 84% yield, >20:1 *dr*, 92% *ee*

* QD = Quinidine: 20 mol%, *p*-TsOH: 20 mol%

Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** or **L2** (0.01 mmol, 10 mol%) were combined into a vessel, and *m*-xylene (2.50 mL) was added *via* syringe. After the reaction system was stirred at 25 °C for 0.5 h, the substrates **1g** (0.1 mmol) and **2d** or **2e** (0.22 mmol, 2.2 equiv) were added and the reaction mixture was stirred until the reaction was complete (detected by TLC). Then quinidine (0.02 mol, 20 mol%) or *p*-TsOH (0.02 mmol, 20 mol%) was introduced into the reaction mixture to promote the intramolecular aldol reaction at 25°C. After the reaction was detected complete (by TLC analysis), 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 **3** or **4** as white solids.

"Racemic" samples described in this part were obtained *via* mixing two isomer of corresponding chiral product **3** or **4**.

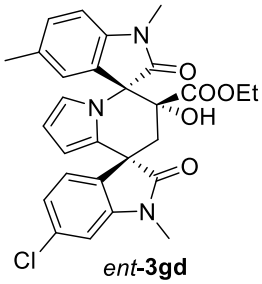
ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3gd



3gd

White solid; mp 155–156 °C; 85% yield (44.2 mg), >20:1 *dr*, 93% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 19.234, t (minor) = 9.665]; $[\alpha]_D^{25}$ = 201.3 (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.13 (t, *J* = 3.2 Hz, 1H), 5.63 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.87 (p, *J* = 7.2 Hz, 2H), 3.41 (s, 3H), 3.30 (s, 3H), 3.29 (d, *J* = 15.6 Hz, 1H), 2.54 (d, *J* = 15.6 Hz, 1H), 2.36 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 171.3, 168.3, 144.1, 140.2, 134.6, 131.6, 131.3, 130.2, 127.3, 124.6, 124.2, 123.6, 123.4, 120.4, 110.4, 109.2, 107.9, 106.7, 77.8, 67.6, 61.3, 47.6, 34.3, 26.6, 26.3, 20.9, 13.2; IR (KBr) ν_{max}: 2962, 2924, 2855, 1732, 1687, 1605, 1497, 1463, 1364, 1244, 1225, 1093, 1069, 1051, 1031, 943, 905, 798, 700 cm^{-1}; HRMS (ESI): m/z = 542.1452 (calcd for $C_{28}H_{26}ClN_3O_5$+Na^+ = 542.1453).

ethyl(3S,6'R,8'R)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate *ent*-3gd

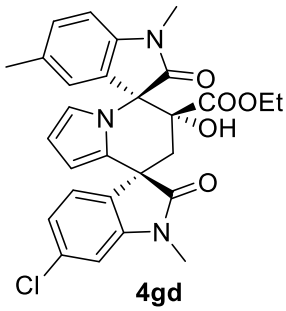


ent-**3gd**

White solid; mp 151–152 °C; 88% yield (45.7 mg), >20:1 *dr*, 92% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 9.332, t (minor) = 21.266]; $[\alpha]_D^{25}$ = −204.1 (c 0.10, $CHCl_3$); HRMS (ESI): m/z = 542.1460 (calcd for $C_{28}H_{26}ClN_3O_5$+Na^+ = 542.1453).

ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4gd

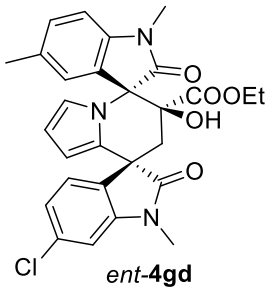
White solid; mp 255–256 °C; 75% yield (39.0 mg), >20:1 *dr*, 95% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t



4gd

(major) = 8.008, t (minor) = 12.580]; $[\alpha]_D^{25}$ = −201.4 (c 0.07, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.01 (t, *J* = 3.2 Hz, 1H), 5.94 (t, *J* = 2.4 Hz, 1H), 5.62 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.19 (s, 1H), 4.11 – 3.90 (m, 3H), 3.29 (s, 3H), 3.18 (s, 3H), 2.37 (s, 3H), 1.95 (d, *J* = 14.0 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 171.7, 170.8, 143.7, 141.6, 134.4, 133.1, 132.2, 131.0, 127.8, 127.8, 127.3, 124.1, 121.9, 117.0, 109.0, 107.8, 107.4, 105.9, 76.1, 66.8, 62.9, 47.6, 34.6, 26.4, 26.0, 20.7, 13.4; IR (KBr) ν_{max}: 2965, 2925, 1732, 1699, 1604, 1498, 1364, 1246, 1094, 1070, 1054, 794, 703 cm^{-1}; HRMS (ESI): m/z = 542.1456 (calcd for $C_{28}H_{26}ClN_3O_5+Na^+$ = 542.1453).

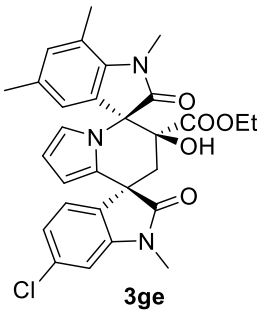
ethyl(3S,6'S,8'R)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydro dispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate *ent*-**4gd**



ent-**4gd**

White solid; mp 252–253 °C; 85% yield (44.2 mg), >20:1 *dr*, 95% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 11.774, t (minor) = 9.693]; $[\alpha]_D^{25}$ = 212.4 (c 0.14, $CHCl_3$); HRMS (ESI): m/z = 542.1459 (calcd for $C_{28}H_{26}ClN_3O_5+Na^+$ = 542.1453).

ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dih ydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ge

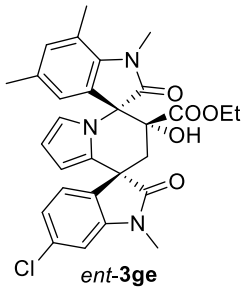


3ge

White solid; mp 235–236 °C; 82% yield (43.7 mg), >20:1 *dr*, 96% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 19.557, t (minor) = 11.141]; $[\alpha]_D^{25}$ = 52.3 (c 0.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.85 (s, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.26 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.85 (q, *J* = 7.2 Hz, 2H), 3.63 (s, 3H), 3.25 (d, *J* = 15.6 Hz, 1H), 3.24 (s, 3H), 2.54 (s, 3H), 2.43 (d, *J* = 15.6 Hz, 1H), 2.24 (s, 3H), 1.00 (t, *J* = 7.2 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 172.2, 168.4, 144.1, 137.7, 134.6, 134.0, 131.3, 131.3, 128.1, 124.7, 124.2, 123.3, 121.4, 120.5, 119.4, 110.3, 109.1, 106.6, 77.9, 67.3, 61.2, 47.5, 34.0, 29.7, 26.6, 20.5, 18.6, 13.2; IR (KBr) ν_{max}: 2926, 2872, 2361, 2341, 1724, 1707, 1603, 1489, 1459, 1433, 1366, 1351, 1289, 1247, 1141, 1105, 1078, 1043, 962, 813, 790, 748, 702 cm^{-1}; HRMS (ESI): m/z = 556.1609 (calcd for $C_{29}H_{28}ClN_3O_5+Na^+$ = 556.1610).

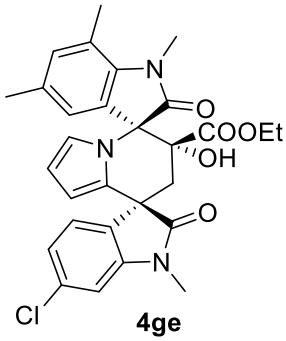
ethyl(3S,6'R,8'R)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate ***ent*-3ge**



ent-**3ge**

White solid; mp 230–231 °C; 91% yield (48.5 mg), >20:1 *dr*, 97% *ee* [Daicel Chiralcel AD-H, hexanes/*i*-PrOH = 70/30, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 11.035, t (minor) = 20.444]; $[\alpha]_D^{25}$ = −49.6 (c 0.12, $CHCl_3$); HRMS (ESI): m/z = 556.1614 (calcd for $C_{29}H_{28}ClN_3O_5+Na^+$ = 556.1610).

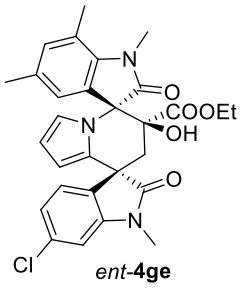
ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ge



4ge

White solid; mp 263–264 °C; 88% yield (46.9 mg), >20:1 *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) = 8.703, t (minor) = 13.148]; $[\alpha]_D^{25}$ = −130.5 (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.16 – 6.75 (m, 3H), 6.04 (d, *J* = 16.8 Hz, 2H), 5.67 (s, 1H), 4.29 – 3.95 (m, 4H), 3.50 (s, 3H), 3.34 (s, 3H), 2.59 (s, 3H), 2.36 (s, 3H), 1.99 (d, *J* = 14.0 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 171.7, 171.6, 143.7, 139.2, 134.9, 134.4, 133.0, 131.9, 127.9, 127.3, 125.5, 124.8, 121.9, 118.9, 117.1, 108.9, 107.7, 105.8, 76.1, 66.4, 62.8, 47.6, 34.5, 29.4, 26.4, 20.4, 18.5, 13.4; IR (KBr) ν_{max}: 2926, 2871, 1723, 1707, 1603, 1468, 1366, 1247, 105, 1078, 692, 702 cm^{-1}; HRMS (ESI): m/z = 556.1620 (calcd for $C_{29}H_{28}ClN_3O_5+Na^+$ = 556.1610).

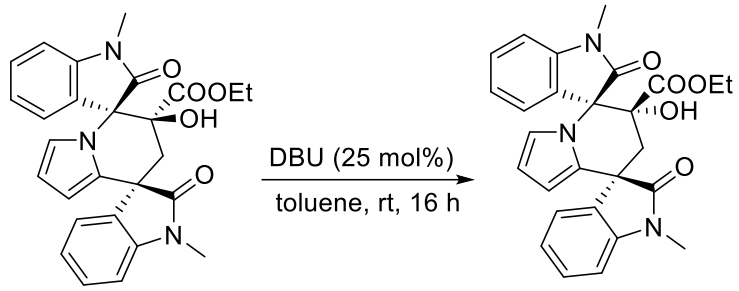
ethyl(3S,6'S,8'R)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate ***ent*-4ge**



ent-**4ge**

White solid; mp 260–261 °C; 84% yield (44.8 mg), >20:1 *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) = 12.008, t (minor) = 9.417]; $[\alpha]_D^{25}$ = 128.2 (c 0.11, $CHCl_3$); HRMS (ESI): m/z = 566.1618 (calcd for $C_{29}H_{28}ClN_3O_5$+Na^+ = 556.1610).

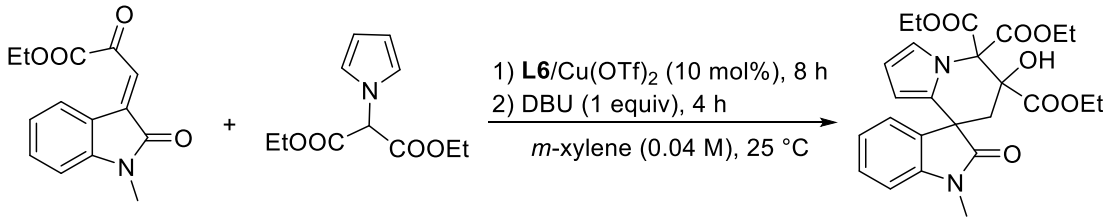
2.5 Procedure for the preparation of 4aa from 3aa



3aa, >20:1 *dr*, 95% *ee* **4aa**, 83% yield, 95% *ee*

The compound **3aa** (0.1 mmol) was introduced into a vessel, and toluene (1 mL) was added *via* syringe. Then DBU (0.025 mmol, 25 mol%) was added and the system was stirred at 25°C for 16 h. Followed evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with EtOAc/petroleum ether (1/1) as eluent to give **4aa** as a white solid.

2.6 Procedure for the preparation of the adduct 6

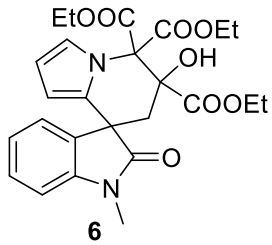


1a **5** (2.2 equiv) **6**, 87% yield
99:1 *dr*, 9% *ee*

Under N_2 atmosphere, $Cu(OTf)_2$ (0.01 mmol, 10 mol%) and **L6** (0.01 mmol, 10 mol%) were combined into a vessel, and *m*-xylene (2.50 mL) was added *via* syringe. After the catalyst system was stirred at 25°C for 0.5 h, the substrates **1a** (0.1 mmol) and **5** (0.22 mmol, 2.2 equiv) were added and the reaction mixture was stirred until the reaction was complete (detected by TLC). Then DBU (0.1 mmol, 1 equiv) was introduced to promote the intramolecular aldol reaction at 25°C. After the reaction

was detected complete (by TLC analysis), the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/petroleum ether (1/3) as eluent to give **6** as a white solid.

triethyl-6'-hydroxy-1-methyl-2-oxo-6',7'-dihydro-5'H-spiro[indoline-3,8'-indolizine]-5',5',6'-tricarboxylate 6



6

White solid; mp 123–124 °C; 87% yield (42.1 mg), >20:1 *dr*, 9% *ee* [Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 80/20, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 9.898, t (minor) = 16.001; $[\alpha]_D^{25}$ = –11.6 (c 0.37, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.15 (t, *J* = 3.2 Hz, 1H), 5.48 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.50 – 4.15 (m, 6H), 3.32 (d, *J* = 14.4 Hz, 1H), 3.23 (s, 3H), 2.29 (d, *J* = 14.8 Hz, 1H), 1.39 – 1.24 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 171.3, 166.0, 165.2, 142.5, 133.4, 128.6, 126.1, 123.9, 123.9, 123.6, 110.2, 108.1, 107.3, 99.5, 76.8, 74.1, 62.0, 61.7, 47.8, 35.2, 26.4, 13.6, 13.5, 13.4; IR (KBr) ν_{max}: 2986, 2901, 1734, 1668, 1609, 1541, 1507, 1472, 1379, 1259, 1150, 1097, 1039, 800, 757, 684, 613 cm^{-1}; HRMS (ESI): m/z = 498.1927 (calcd for $C_{25}H_{28}N_2O_8$+H^+ = 485.1918).

3. X-ray data

3.1 Crystal structure determination of chiral 3ae:

Crystal data and structure refinement for chiral **3ae**:

Empirical formula	$C_{29}H_{29}N_3O_5$
Formula weight	499.55
Temperature	210.01(10) K
Wavelength	1.54184 Å
Crystal system, space group	orthorhombic, P 2_1 2_1 2_1
	a = 9.6120(5) Å, alpha = 90 deg.

Unit cell dimensions	b = 9.9405(4) Å, beta = 90 deg.
	c = 52.933(3) Å, gamma = 90 deg.
Volume	5057.7(4) $Å^3$
Z, Calculated density	8, 1.312 Mg/m^3
Absorption coefficient	0.738 mm^{-1}
F(000)	2112
Crystal size	0.35 x 0.30 x 0.02 mm^3
Radiation	CuK\α (λ = 1.54184)
Theta range for data collection	4.526 to 67.077 deg.
Limiting indices	$-10 \leq h \leq 11$, $-11 \leq k \leq 8$, $-63 \leq l \leq 58$
Reflections collected / unique	18051/9040 [R(int) = 0.0644]
Completeness to theta = 67.077	99.9%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9040/0/679
Goodness-of-fit on F^2	0.977
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1025
Final R indexes [all data]	R_1 = 0.0814, wR_2 = 0.1169
Largest diff. peak/hole / $eÅ^{-3}$	0.203 and −0.222
Absolute structure parameter	0.0(2)

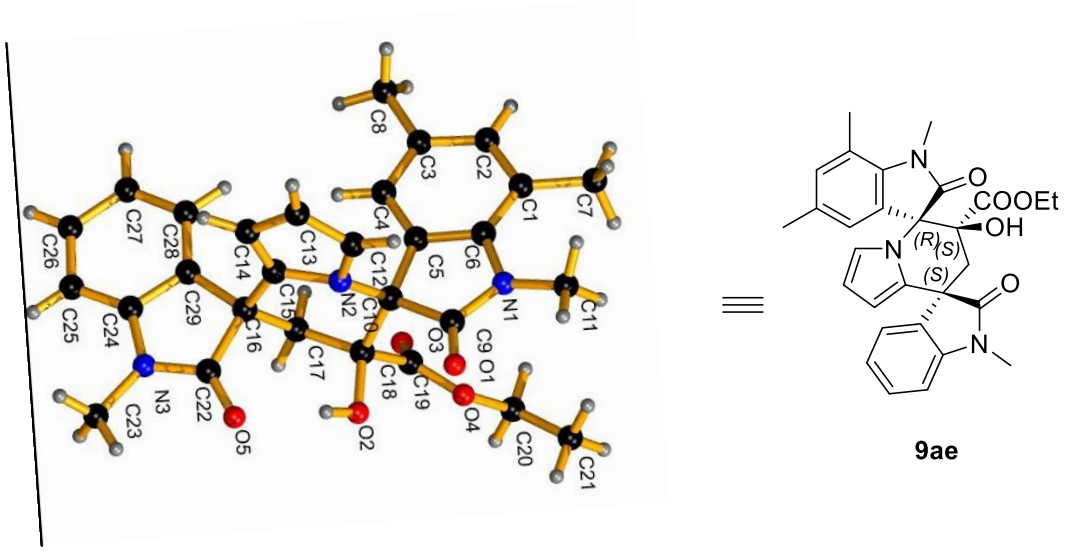


Figure S3. OPTEP drawing of chiral **3ae** (40% thermal ellipsoids)

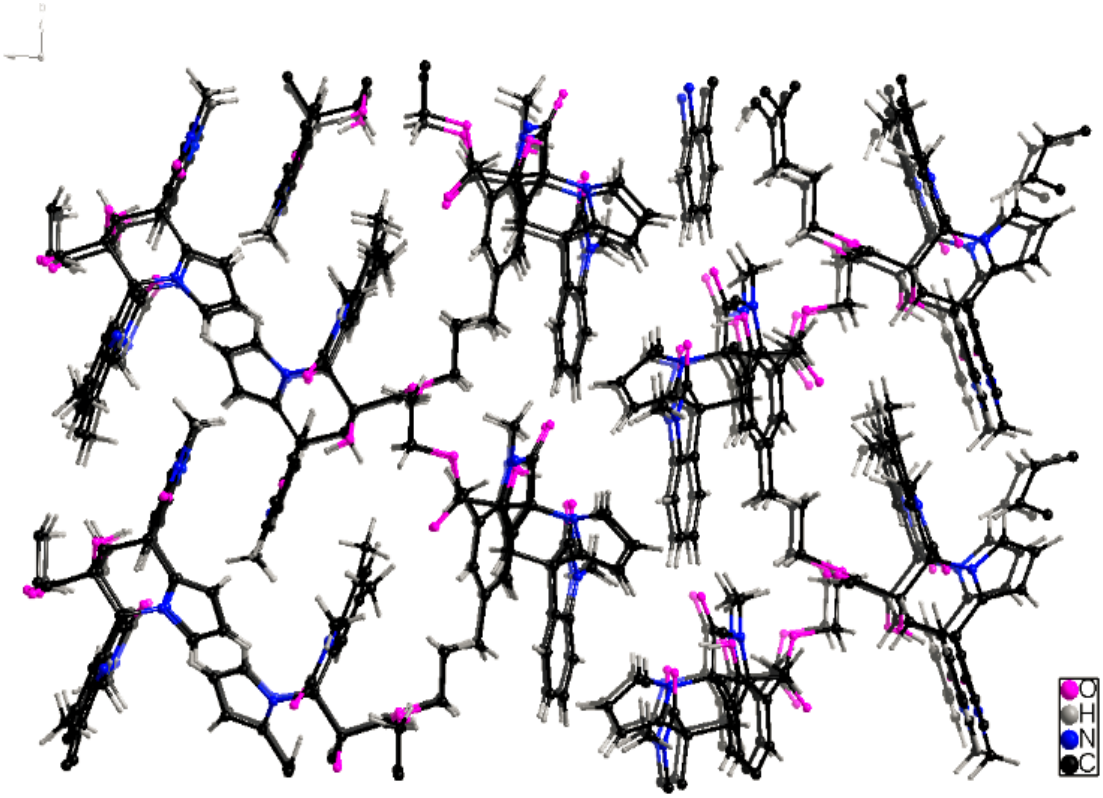


Figure S4. Packing of moleculars in a unit cell of chiral **3ae**

The crystal was prepared from the solution of chiral **3ae** in DCM and *n*-hexane. CCDC 1548552 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 racemic 3ae (7% *ee*):

Crystal data and structure refinement for racemic **3ae**:

Empirical formula	$C_{29}H_{29}N_3O_5$
Formula weight	499.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.851(5) Å, alpha = 90 deg. b = 10.081(6) Å, beta = 91.989(15) deg. c = 28.437(14) Å, gamma = 90 deg.
Volume	2536(2) $Å^3$
Z, Calculated density	4, 1.308 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	1056
Crystal size	0.22 x 0.10 x 0.06 mm^3
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	2.302 to 27.640 deg.
Limiting indices	$-10 \leq h \leq 11$, $-13 \leq k \leq 12$, $-33 \leq l \leq 36$
Reflections collected / unique	29701/ 11225 [R(int) = 0.0697]
Completeness to theta = 27.64	97.7 %
Data / restraints / parameters	11225/1/680
Goodness-of-fit on F^2	1.170
Final R indexes [I>=2σ (I)]	R_1 = 0.0579, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.1351, wR_2 = 0.1057
Largest diff. peak/hole / $eÅ^{-3}$	0.280 and −0.303
Absolute structure parameter	0.3(13)

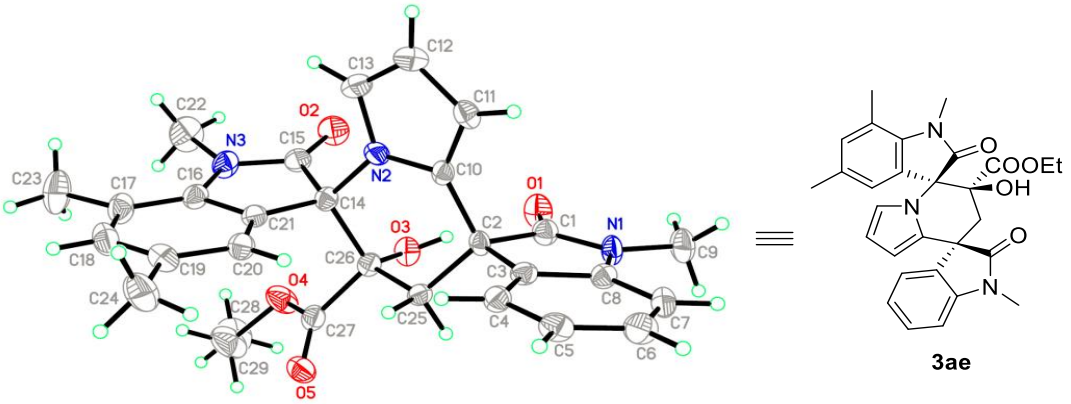


Figure S5. OPTEP drawing of racemic **3ae** (40% thermal ellipsoids)

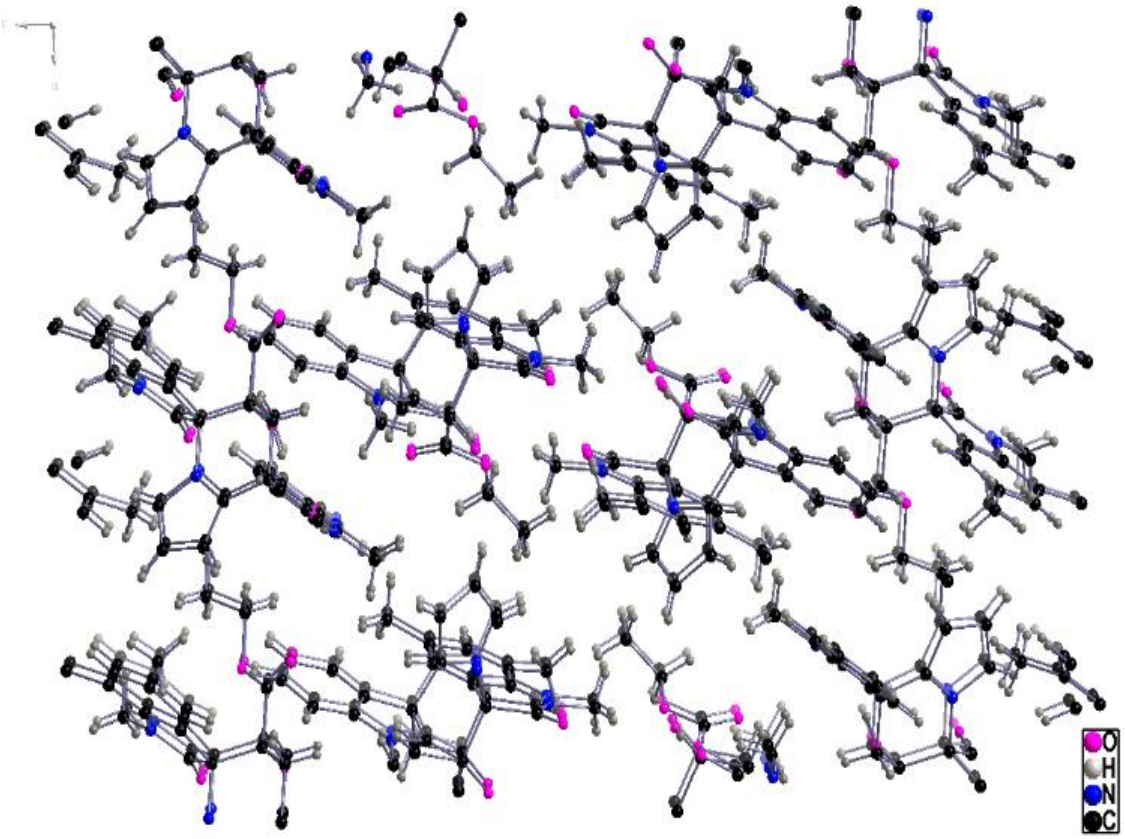


Figure S6. Packing of moleculars in a unit cell of racemic **3ae**

The crystal was prepared from the solution of racemic **3ae** in DCM and *n*-hexane. CCDC 1539269 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 racemic 4ia:

Crystal data and structure refinement for racemic **4ia:**

Empirical formula	$C_{28}H_{24}FN_3O_5$
Formula weight	572.4
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 12.2486(5) Å, alpha = 90 deg. b = 10.5812(5) Å, beta = 93.509(2) deg. c = 21.0573(11) Å, gamma = 90 deg.
Volume	2724.0(2) $Å^3$
Z, Calculated density	4, 1.396 Mg/m^3
Absorption coefficient	0.289 mm^{-1}
F(000)	1184
Crystal size	0.6 x 0.6 x 0.6 mm^3
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	2.73 to 27.53 deg.
Limiting indices	$-15 \leq h \leq 15$, $-13 \leq k \leq 13$, $-27 \leq l \leq 27$
Reflections collected / unique	65836/6251 [R(int) = 0.0495]
Completeness to theta = 27.53	99.6 %
Data / restraints / parameters	6251/0/354
Goodness-of-fit on F^2	1.140
Final R indexes [I>=2σ (I)]	R_1 = 0.0890, wR_2 = 0.2893
Final R indexes [all data]	R_1 = 0.1040, wR_2 = 0.3114
Largest diff. peak/hole / $eÅ^{-3}$	1.147 and −1.638

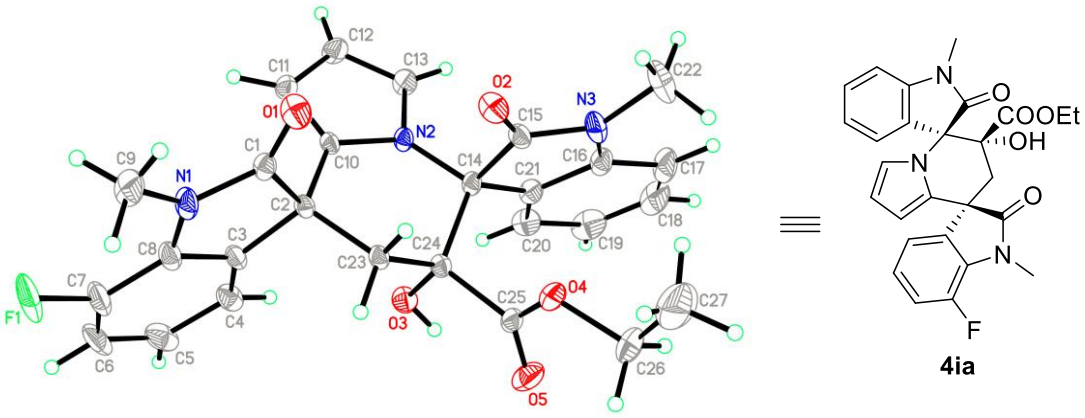


Figure S7. OPTEP drawing of racemic **4ia** (40% thermal ellipsoids)

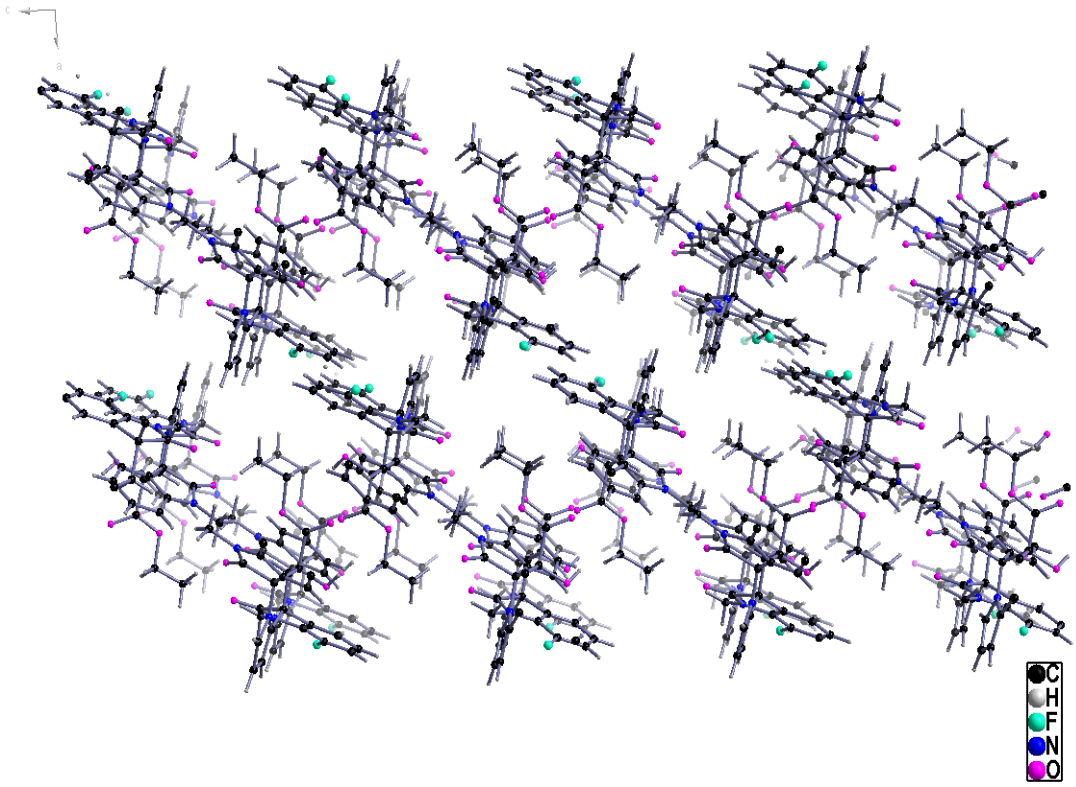
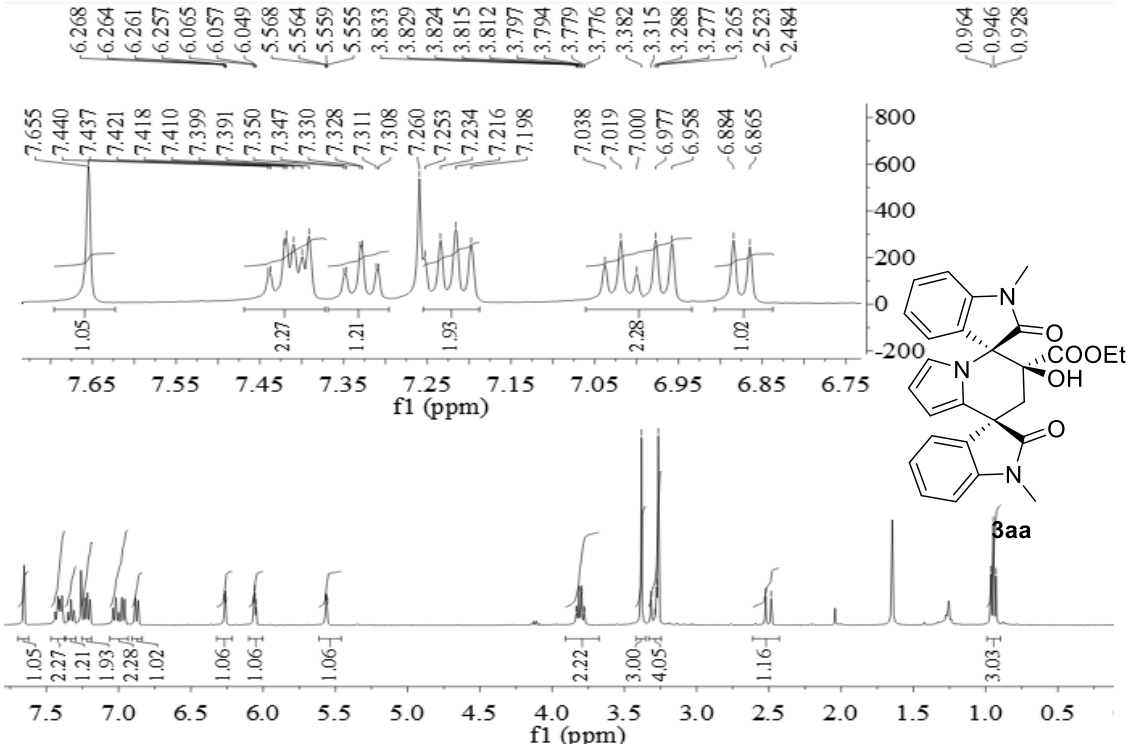


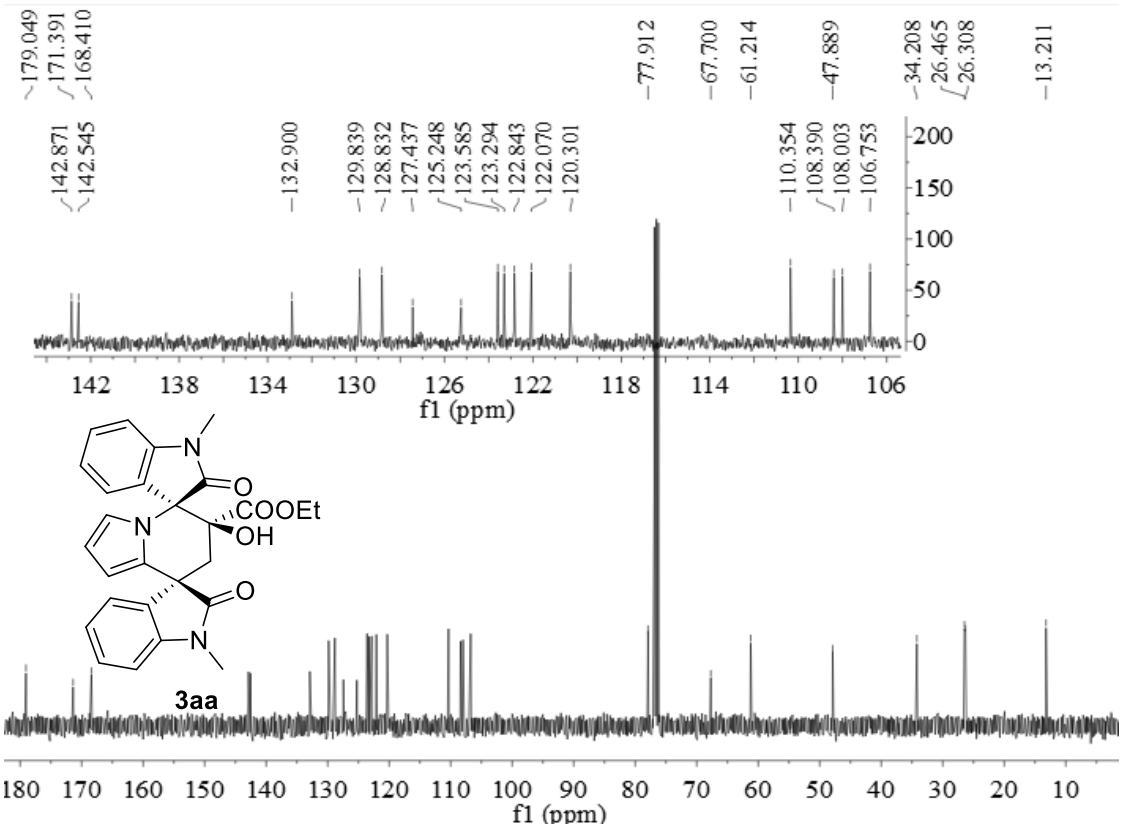
Figure S8. Packing of moleculars in a unit cell of racemic **4ia**

The crystal was prepared from the solution of racemic **4ia** in DCM and *n*-hexane. CCDC 1539270 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.

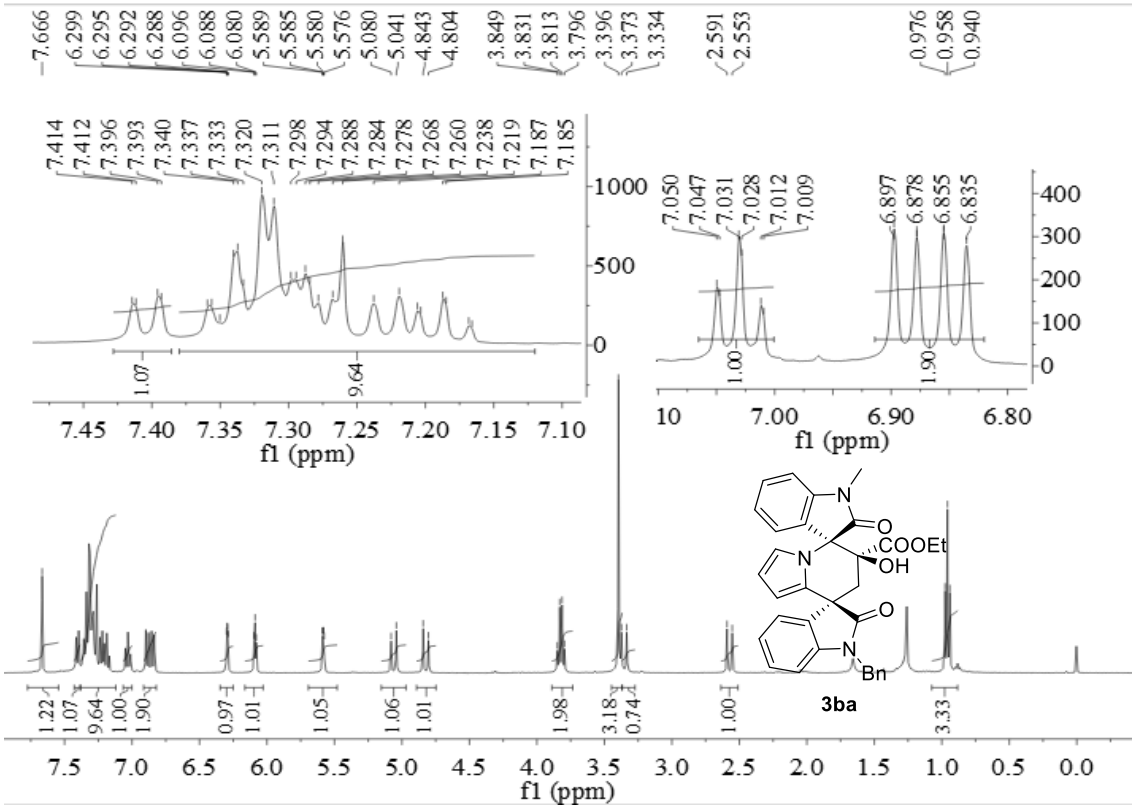
4. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

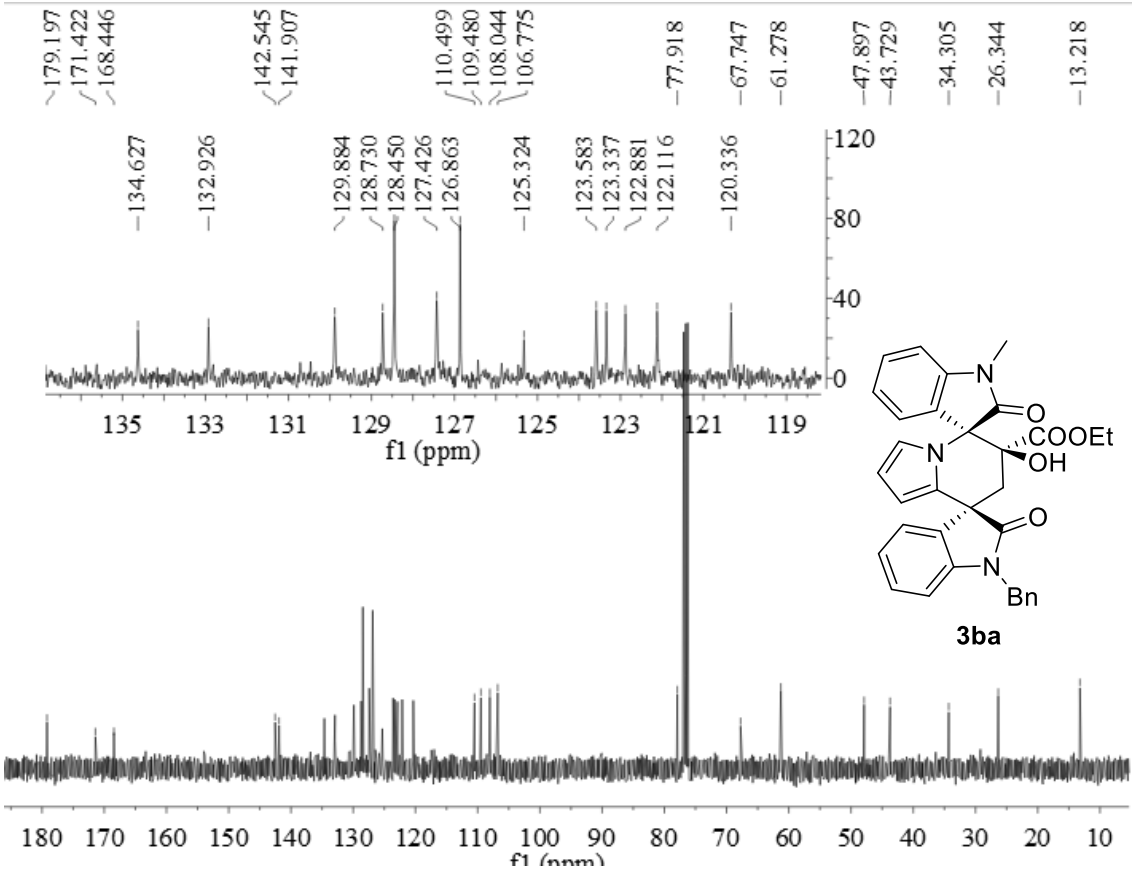
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3aa



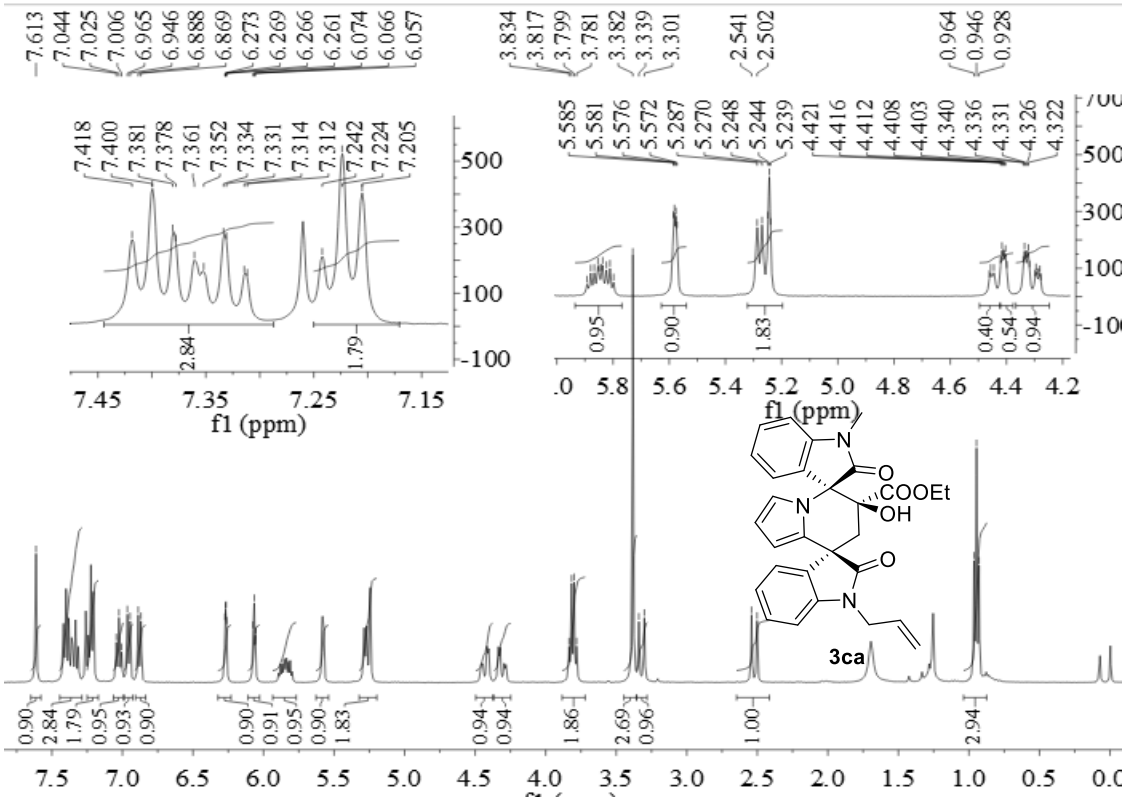


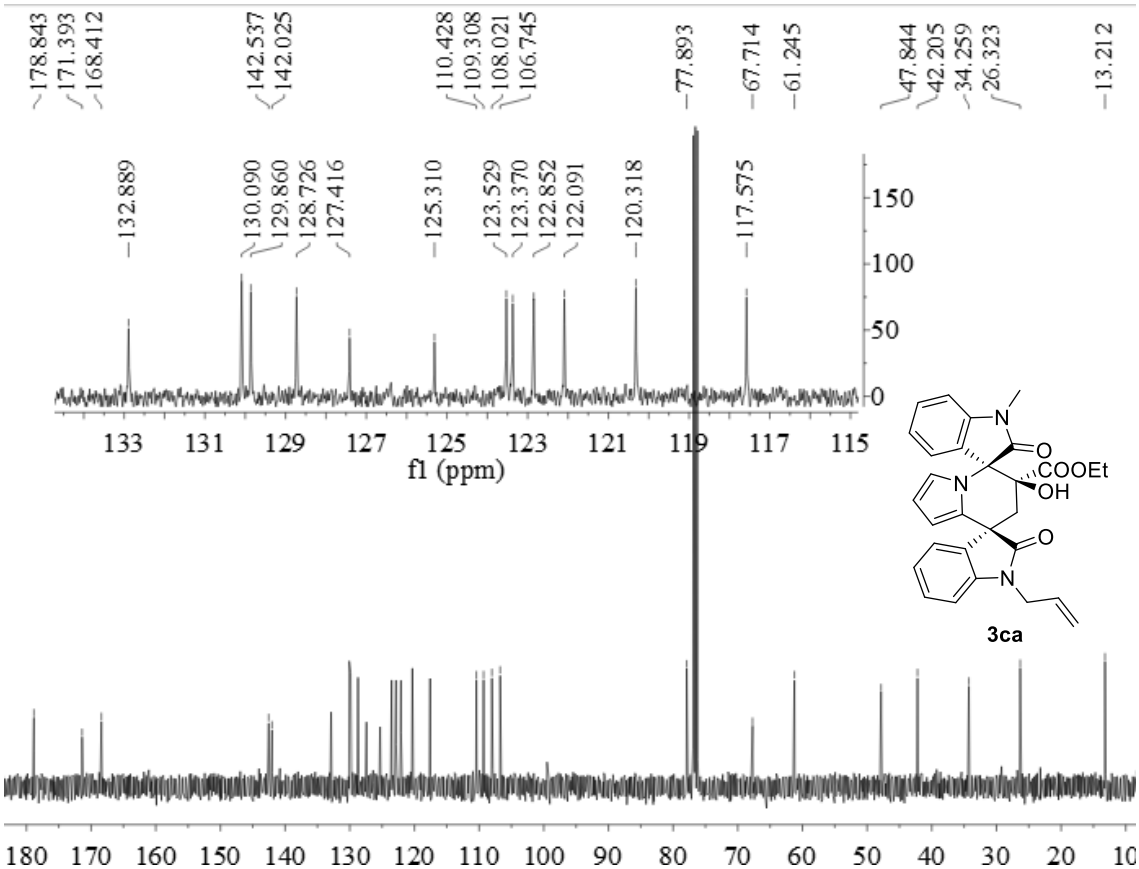
ethyl(3R,6'S,8'S)-1''-benzyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro [indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ba



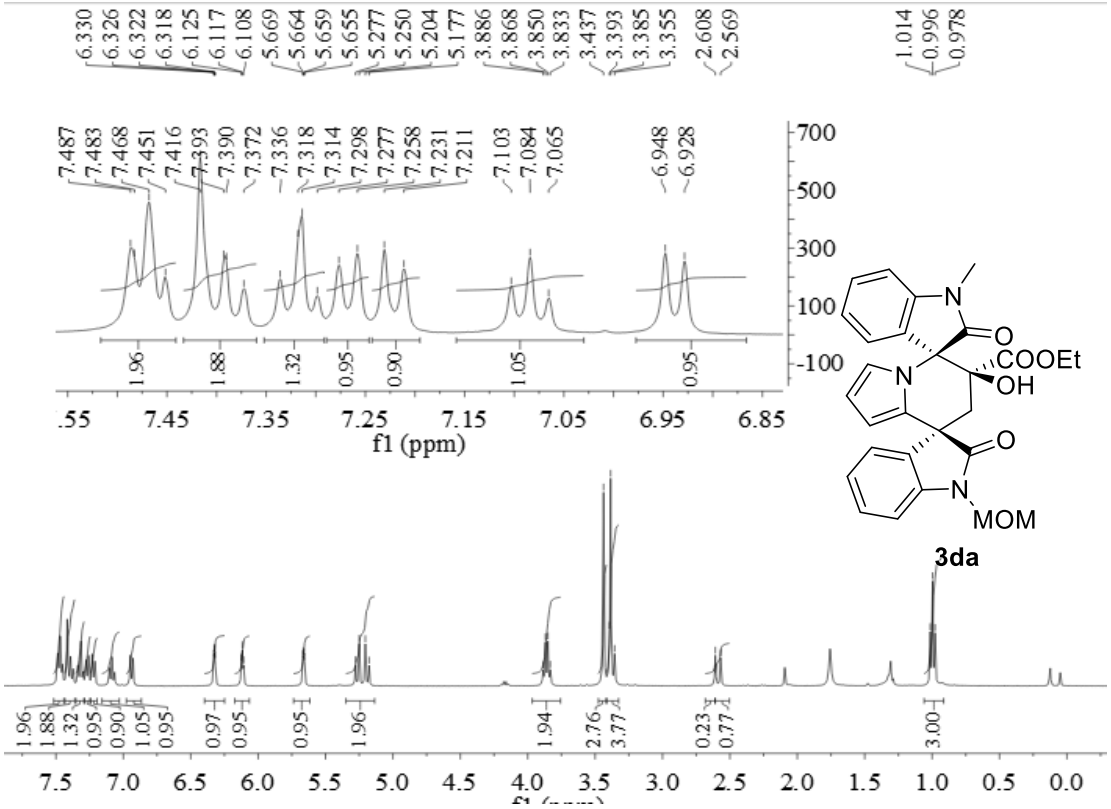


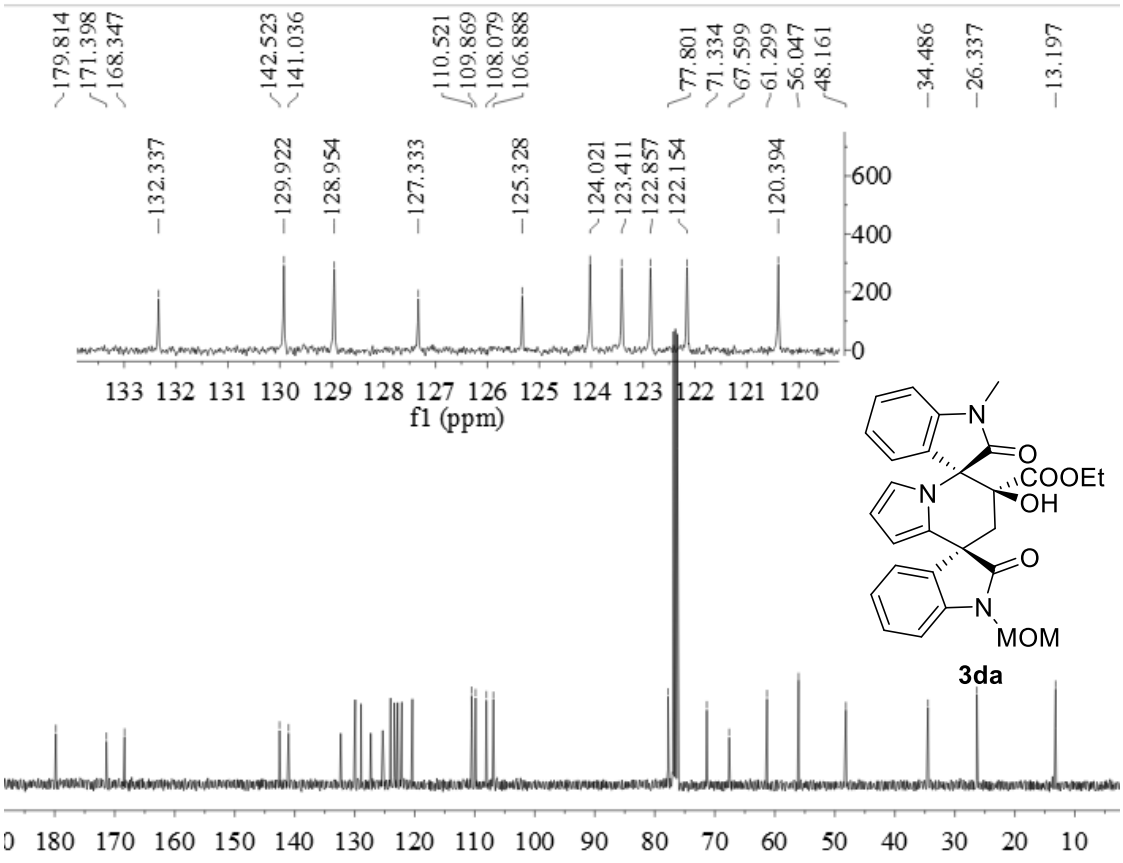
ethyl(3R,6'S,8'S)-1''-allyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ca



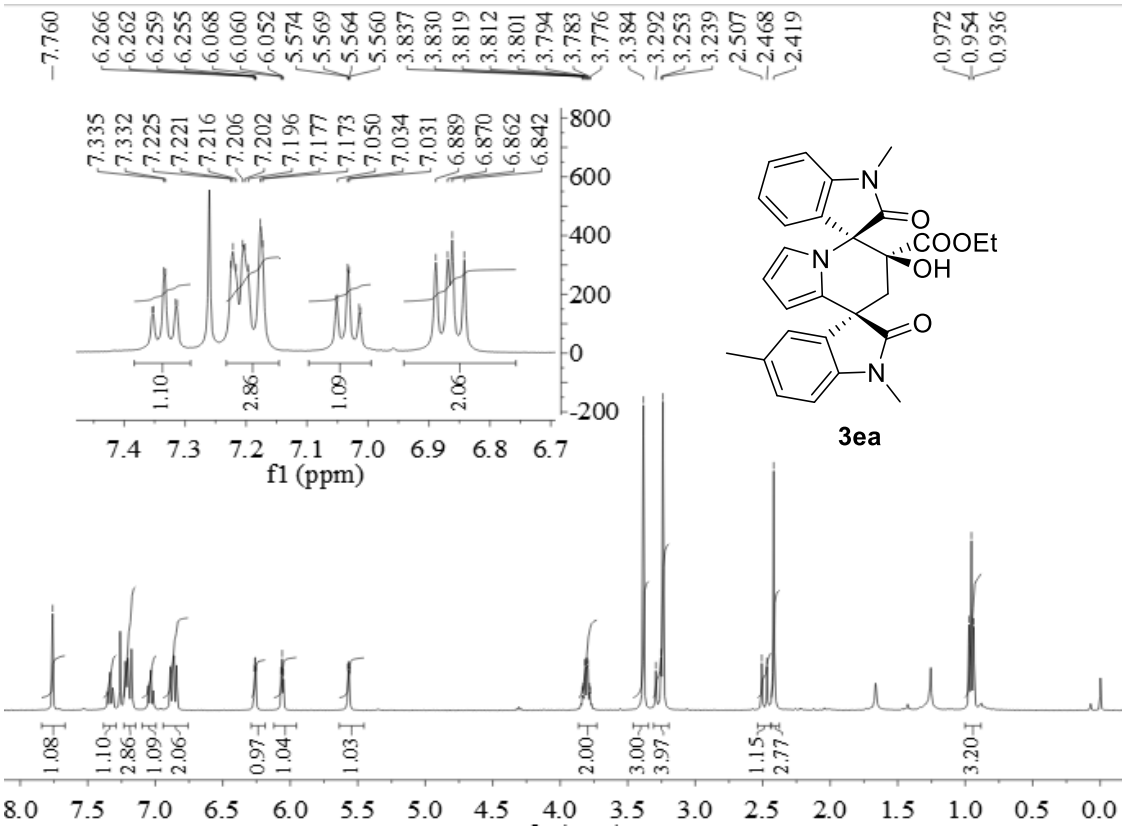


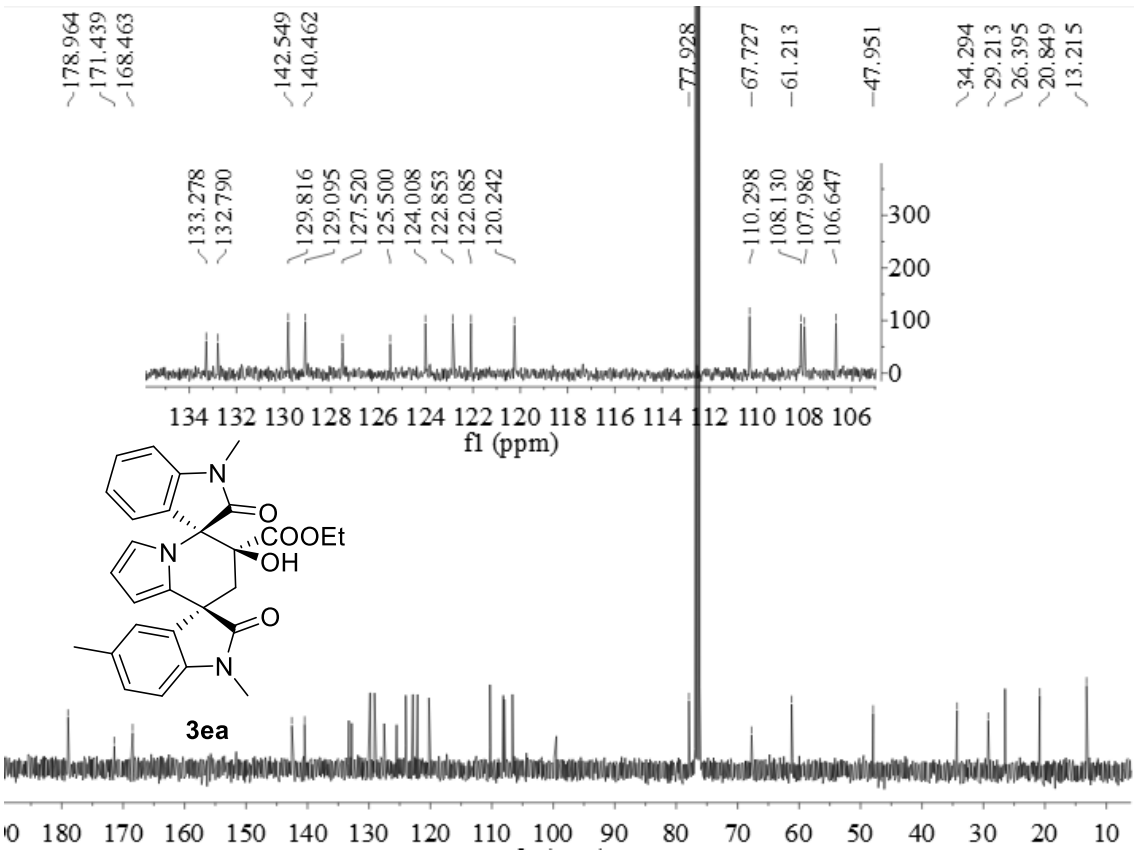
ethyl(3R,6'S,8'S)-6'-hydroxy-1''-(methoxymethyl)-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3da



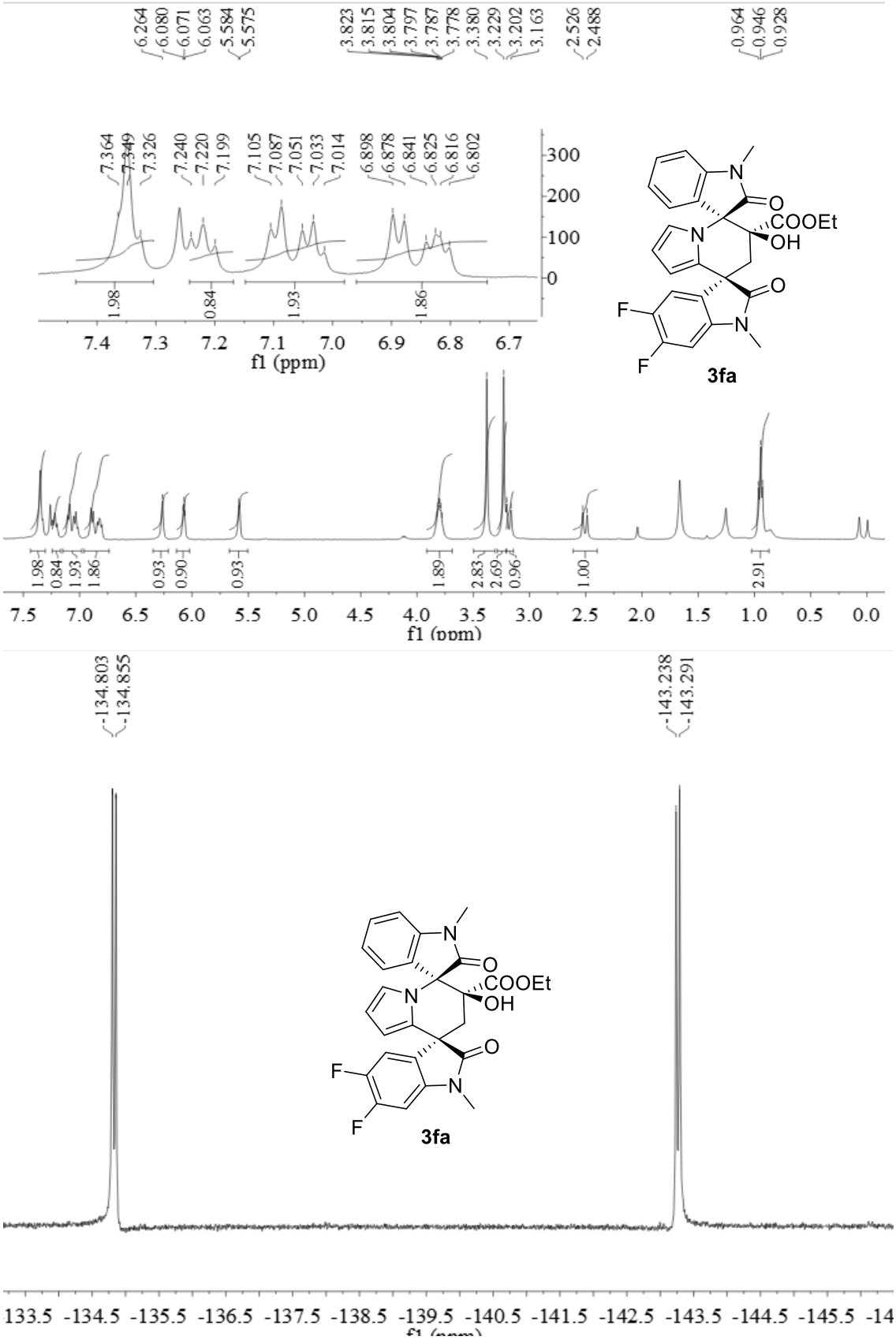


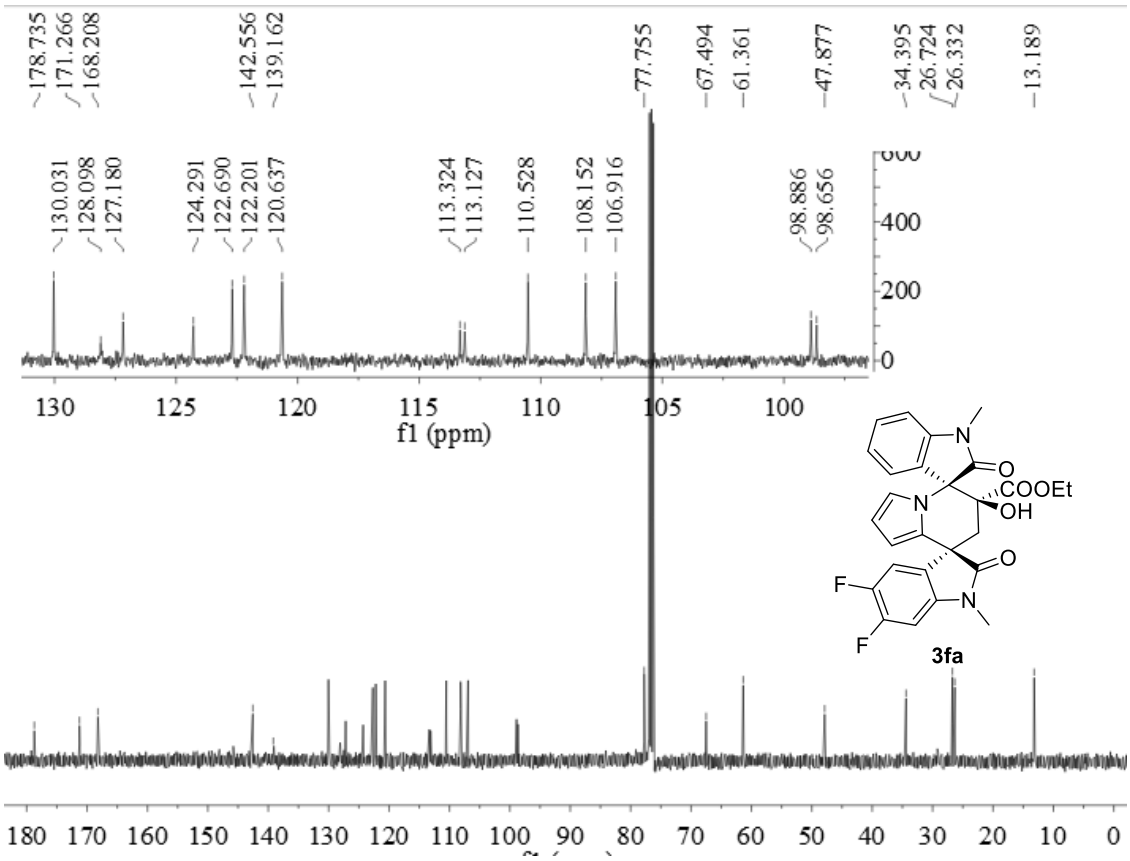
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ea



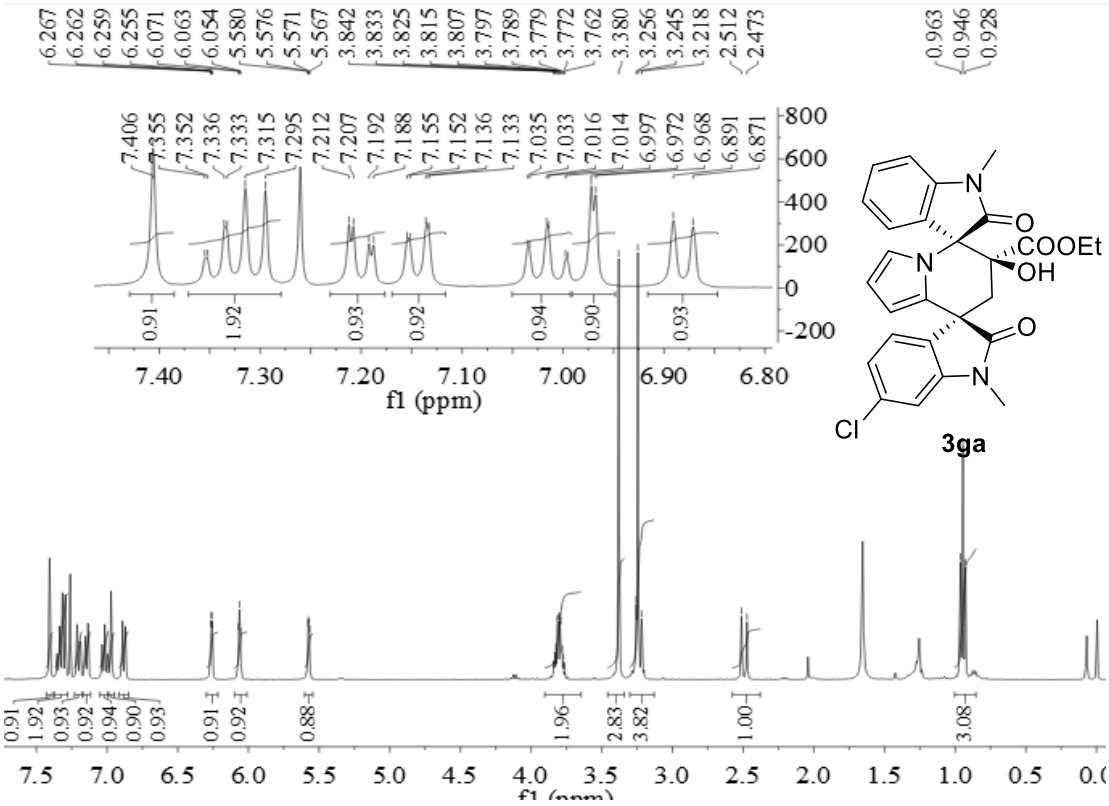


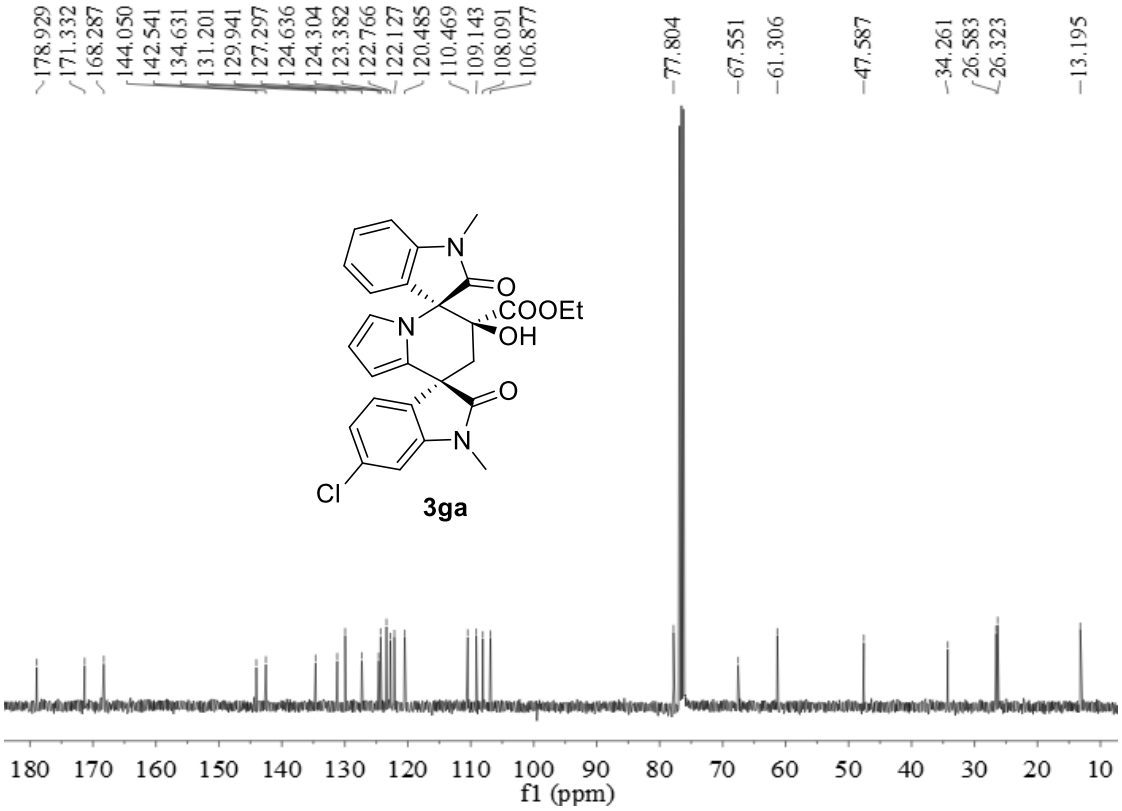
ethyl(3R,6'S,8'S)-5'',6''-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3fa



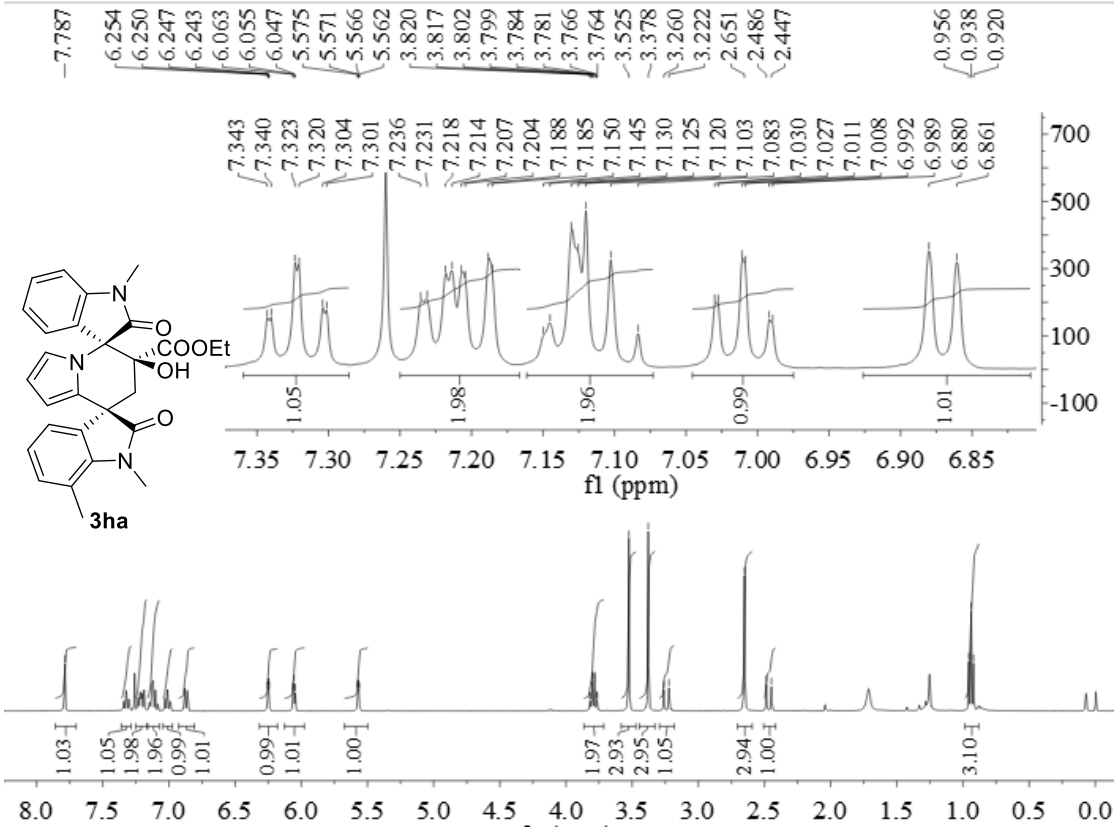


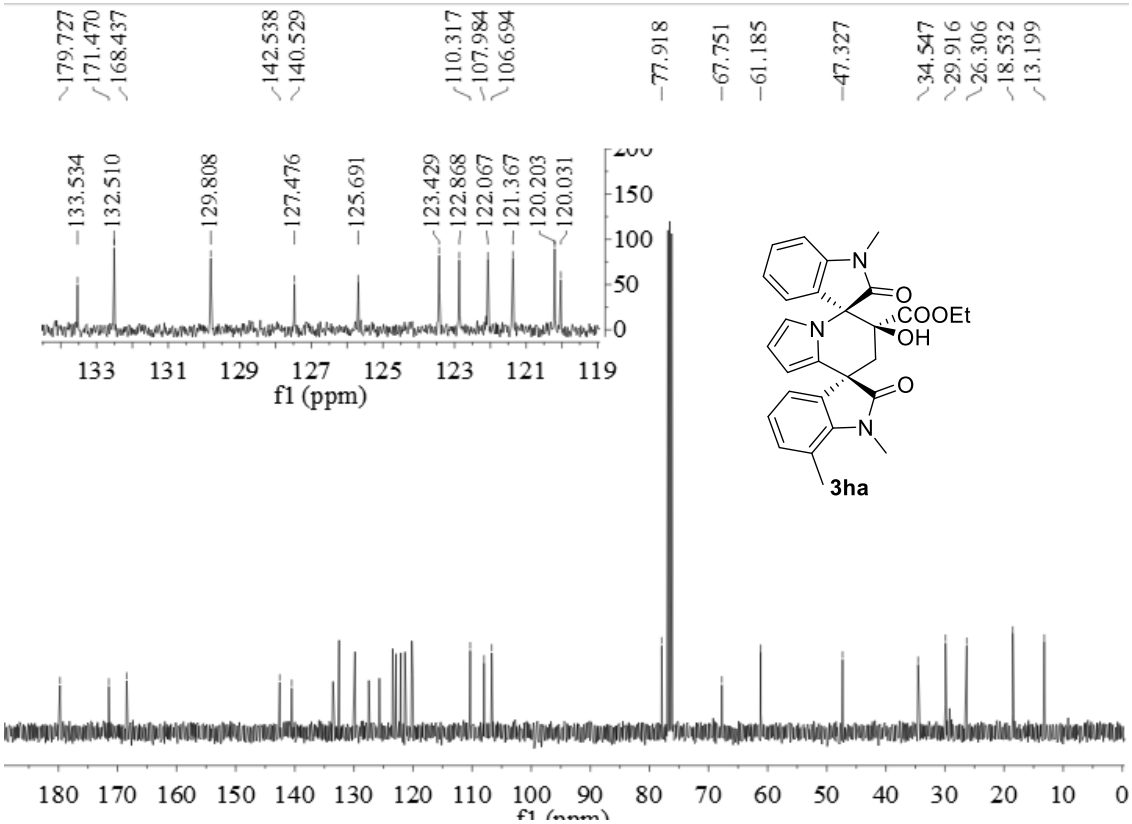
ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodi spiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ga



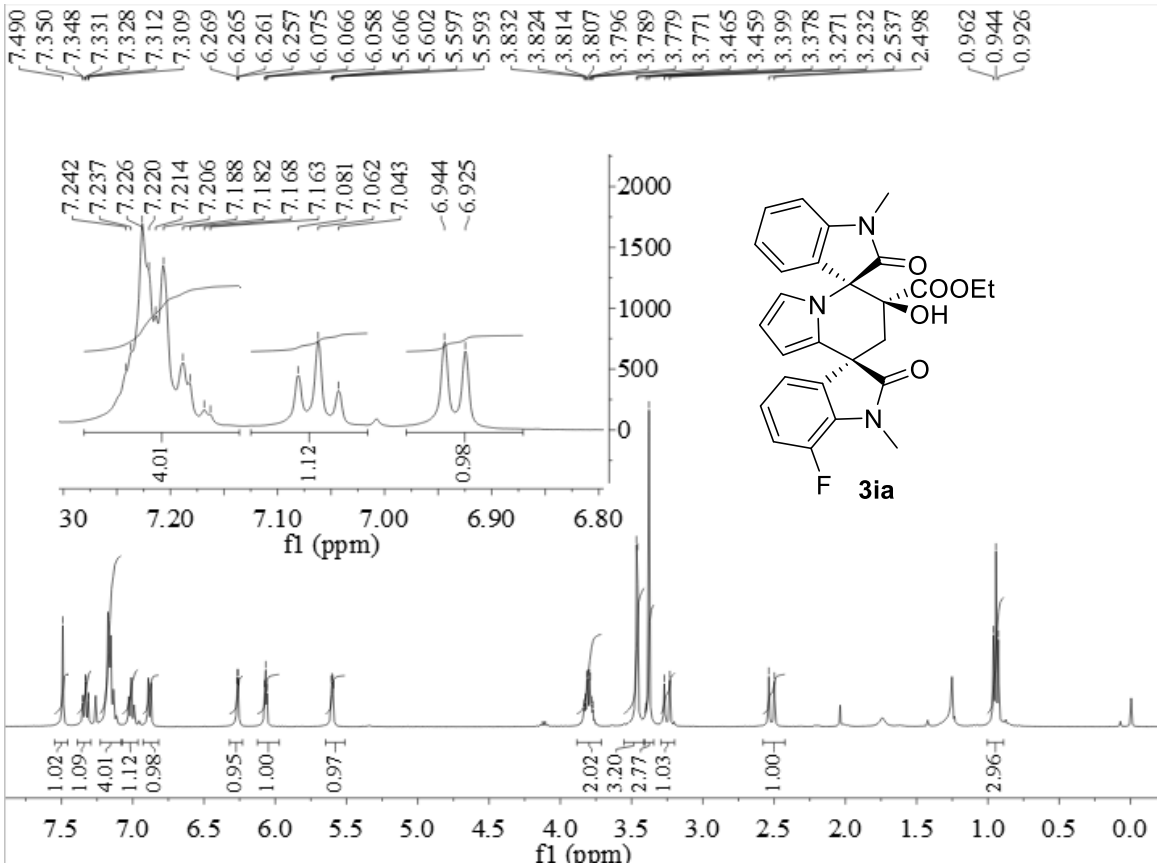


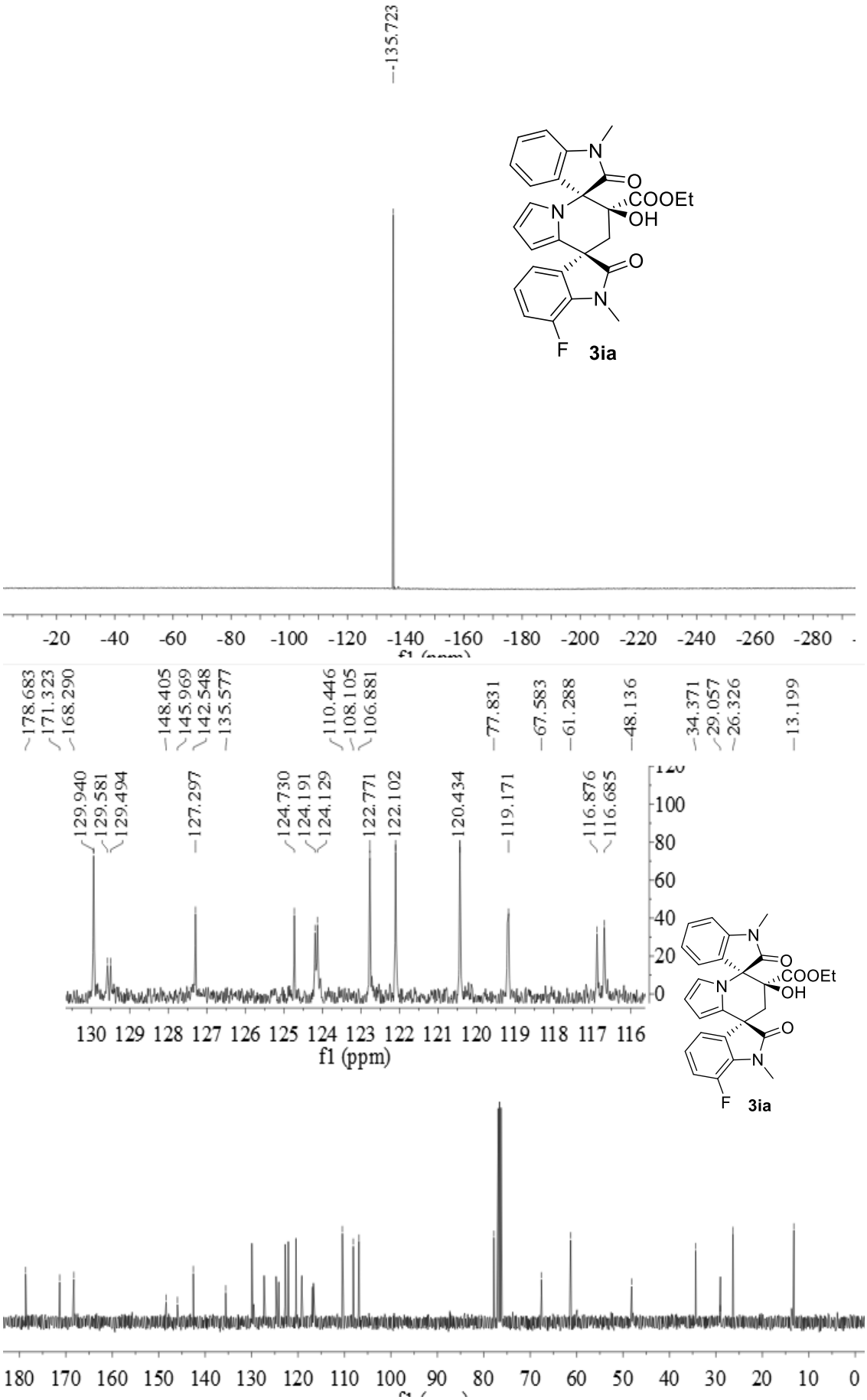
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',7''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ha



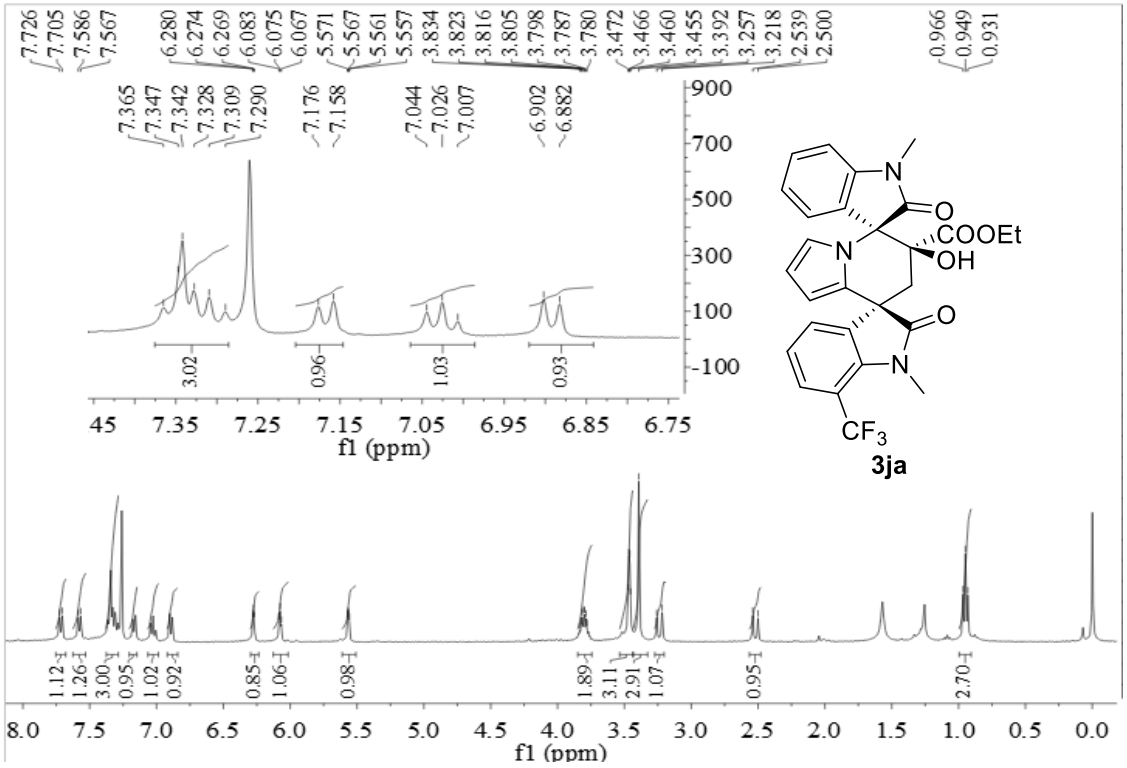


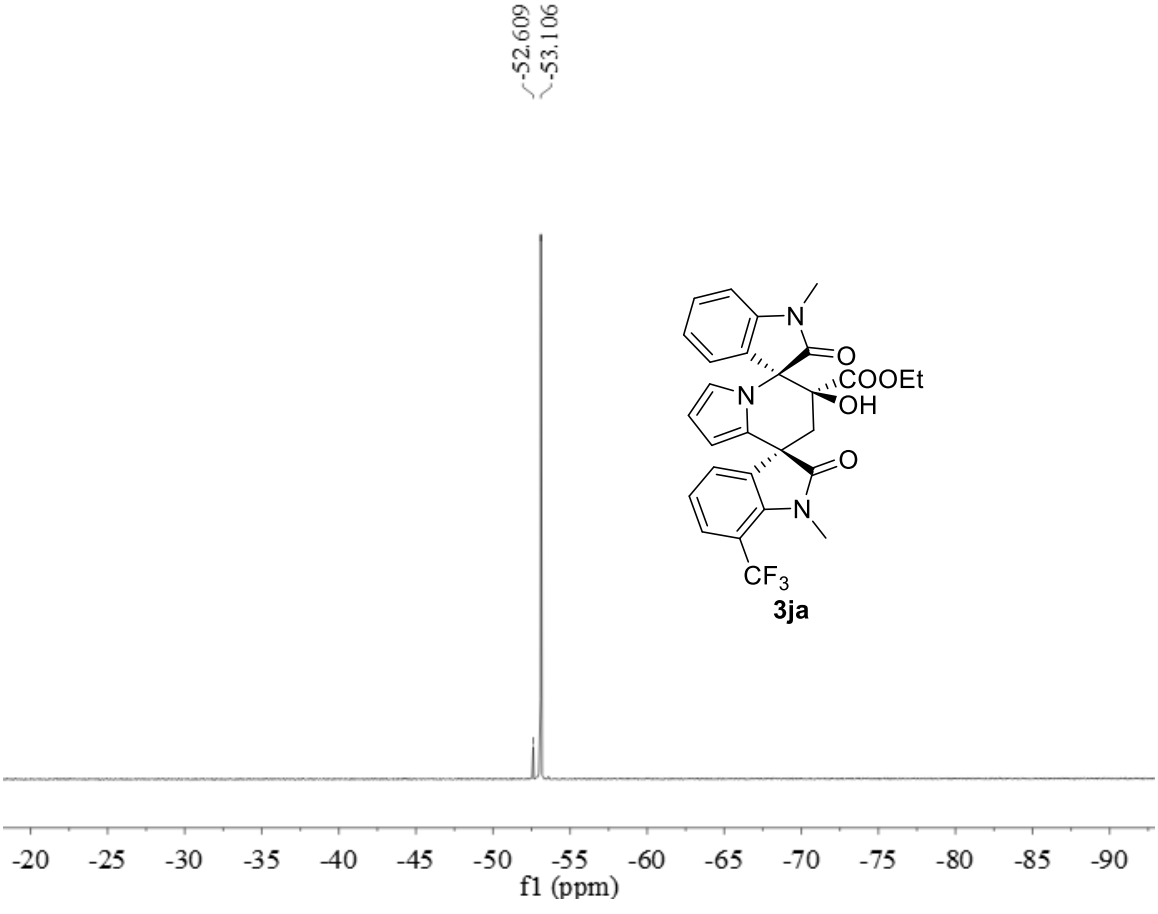
ethyl(3R,6'S,8'S)-7''-fluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodis piro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ia

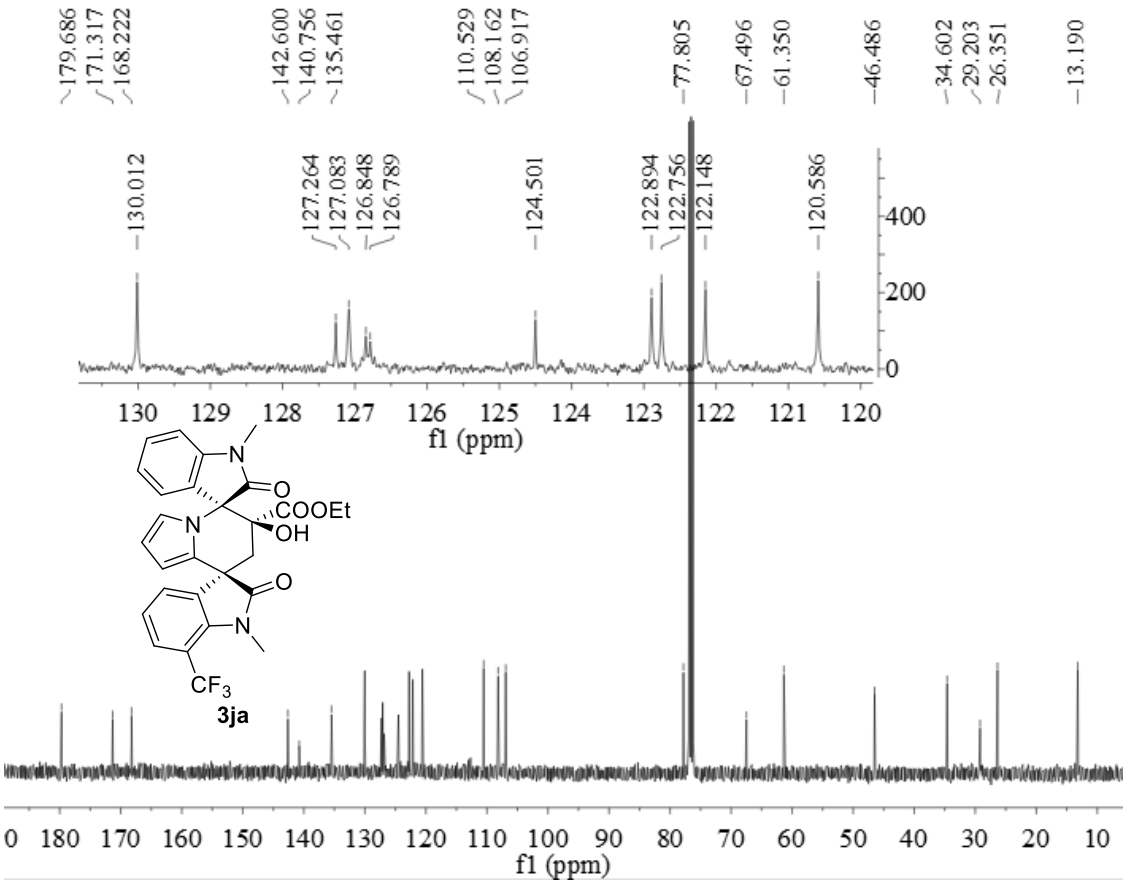



-135.723
COOEt
OH
F
3ia
-20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
178.683
171.323
168.290
148.405
145.969
142.548
135.577
110.446
108.105
106.881
77.831
67.583
61.288
48.136
34.371
29.057
26.326
13.199
129.940
129.581
129.494
127.297
124.730
124.191
124.129
122.771
122.102
120.434
119.171
116.876
116.685
130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

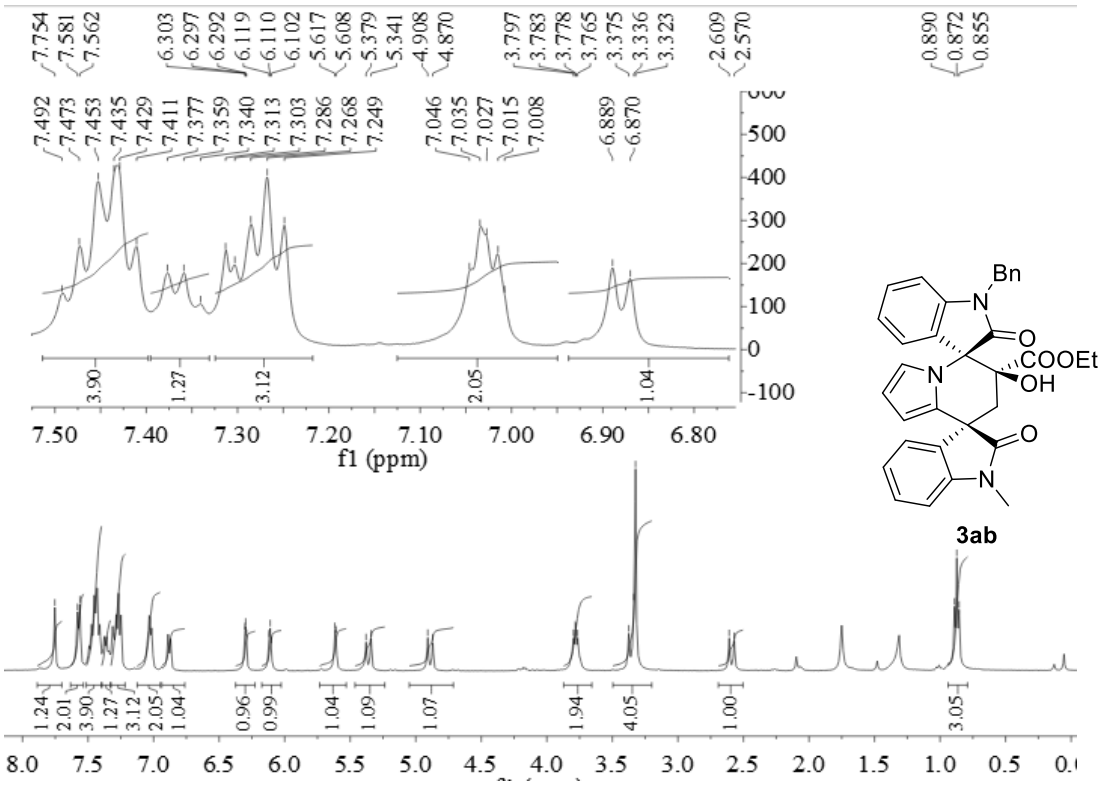
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7''-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ja

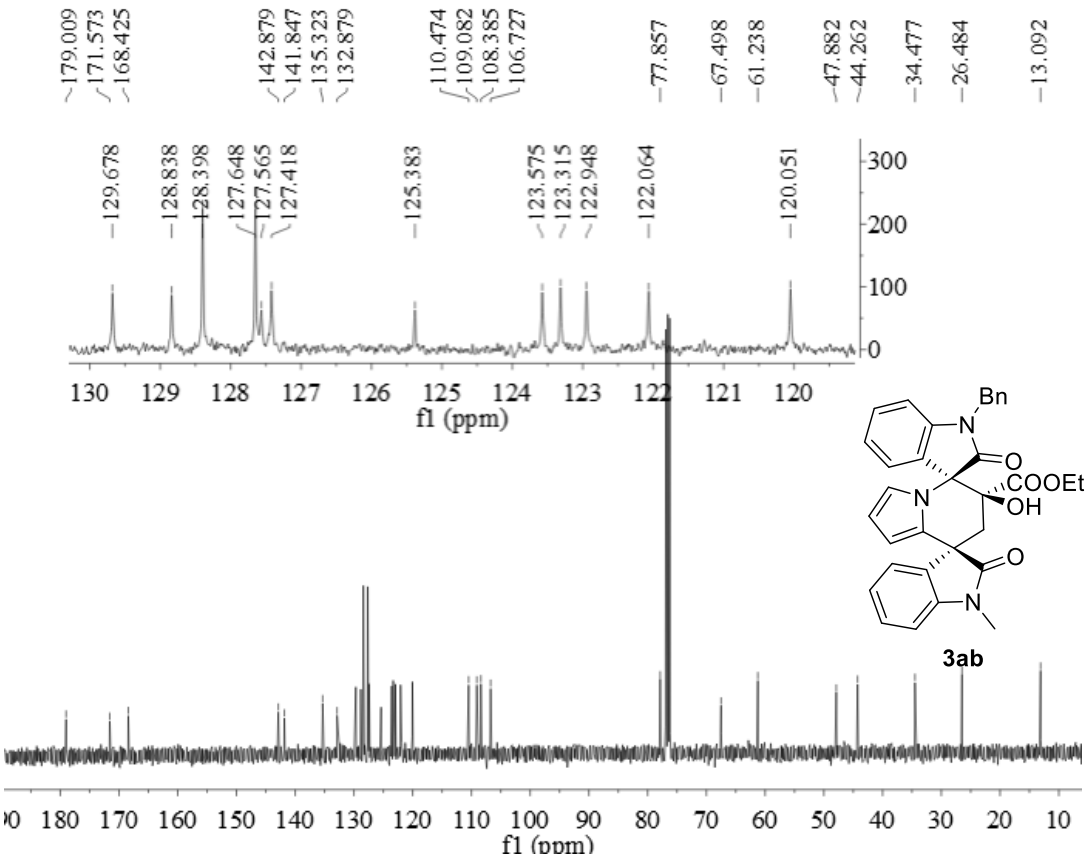




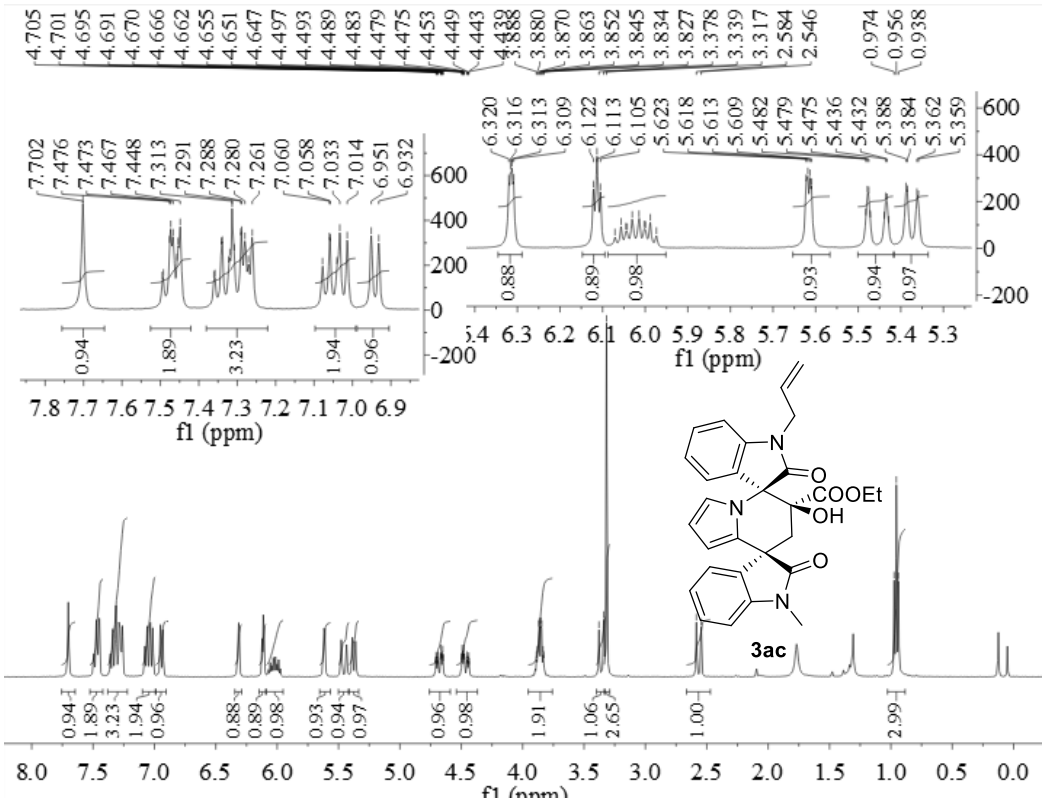


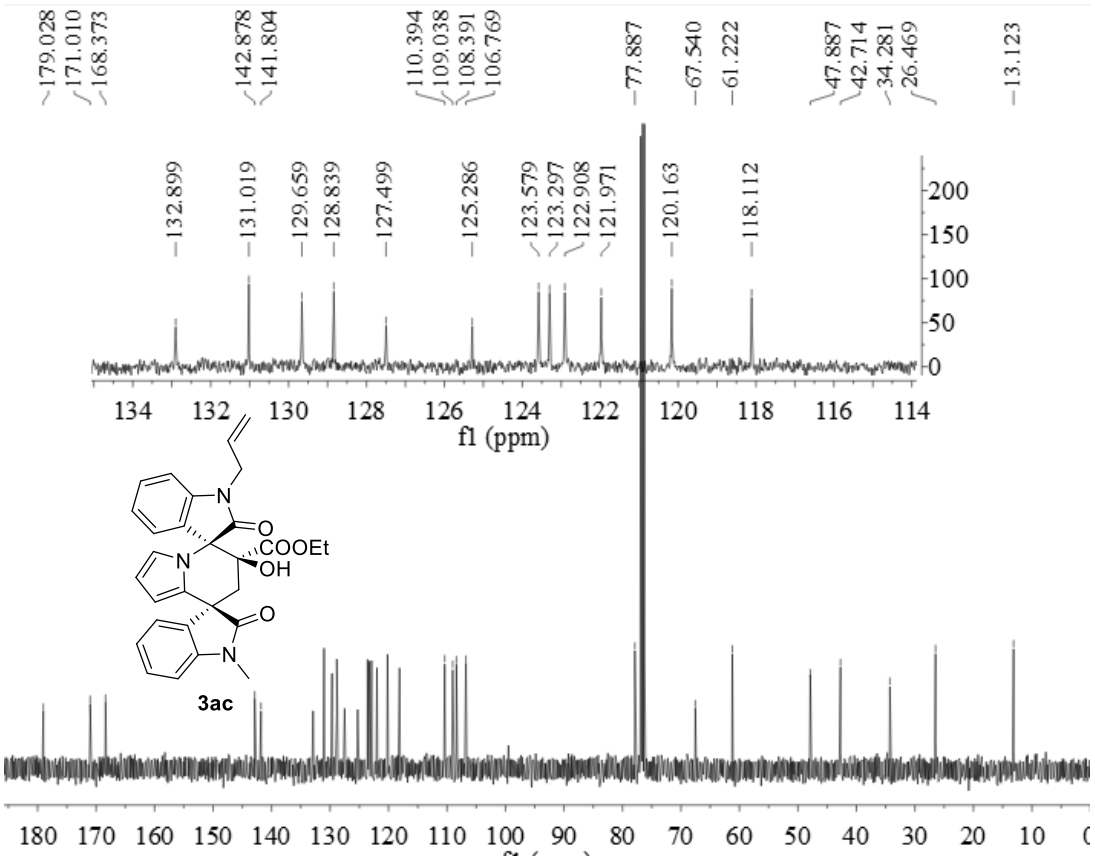
ethyl(3R,6'S,8'S)-1-benzyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro [indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ab



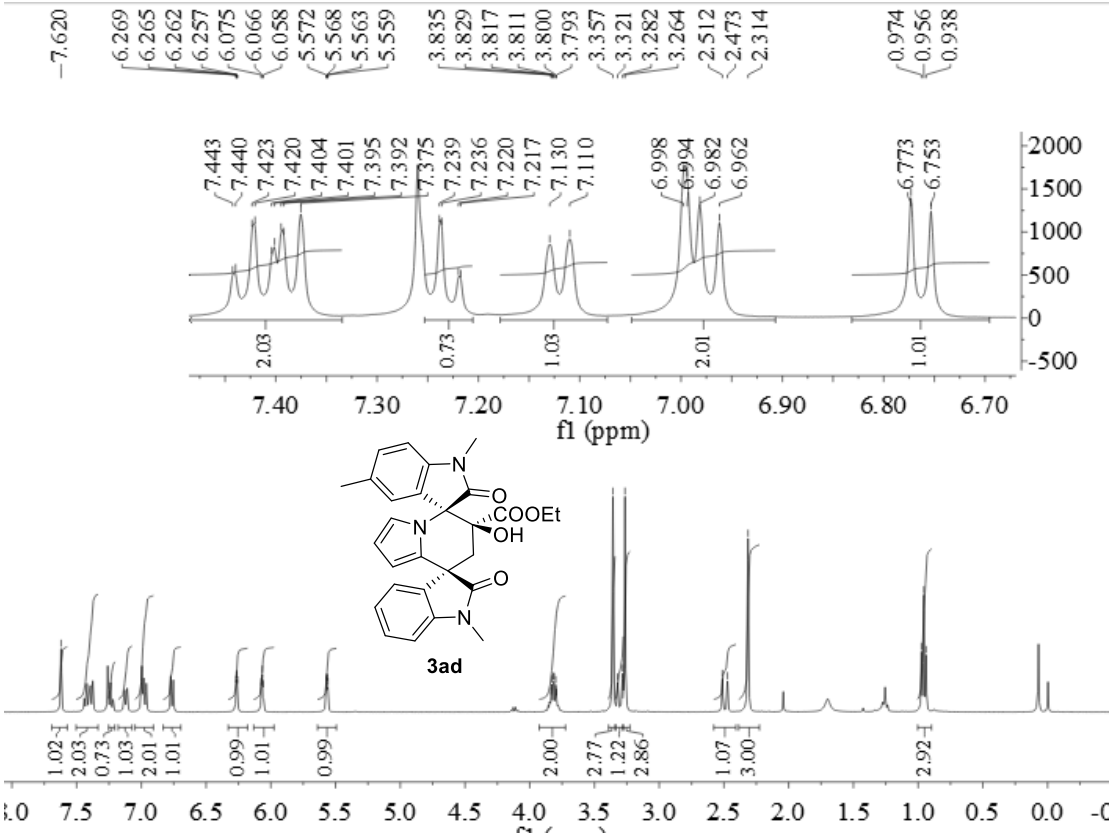


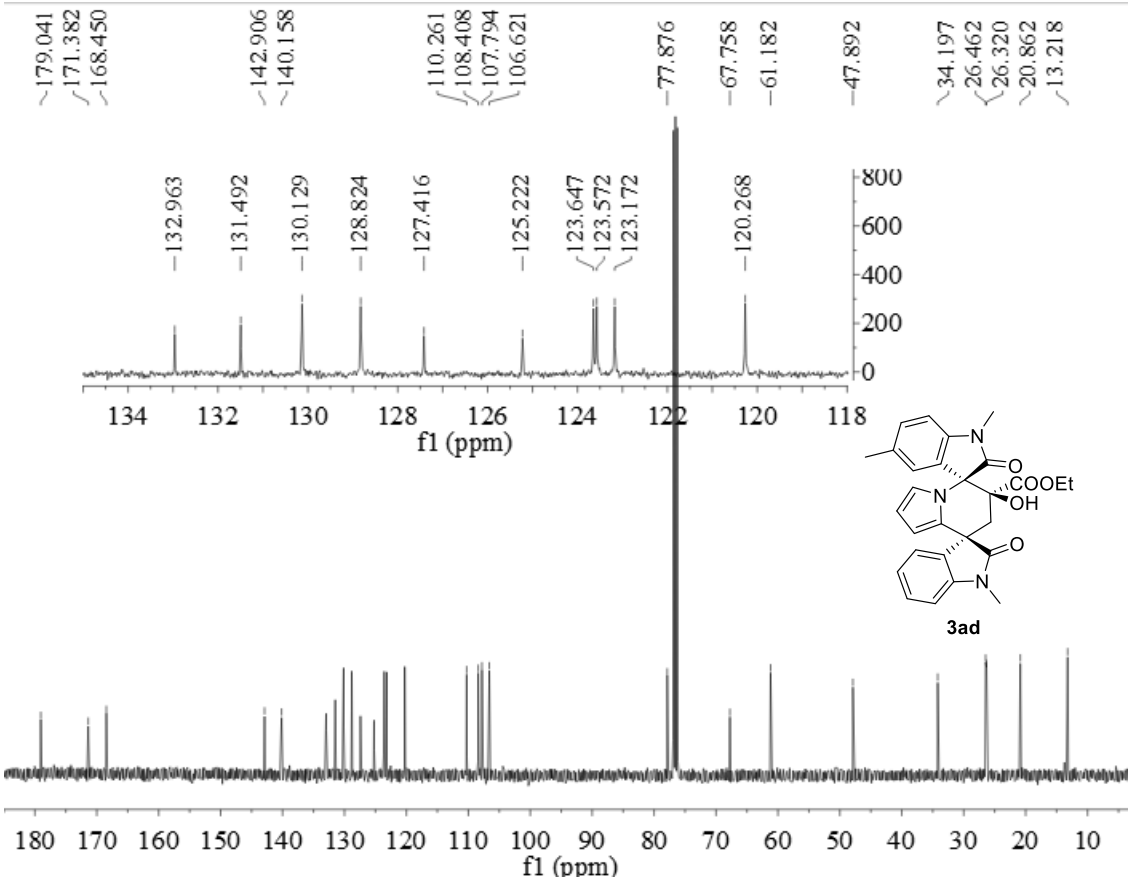
ethyl(3R,6'S,8'S)-1-allyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ac



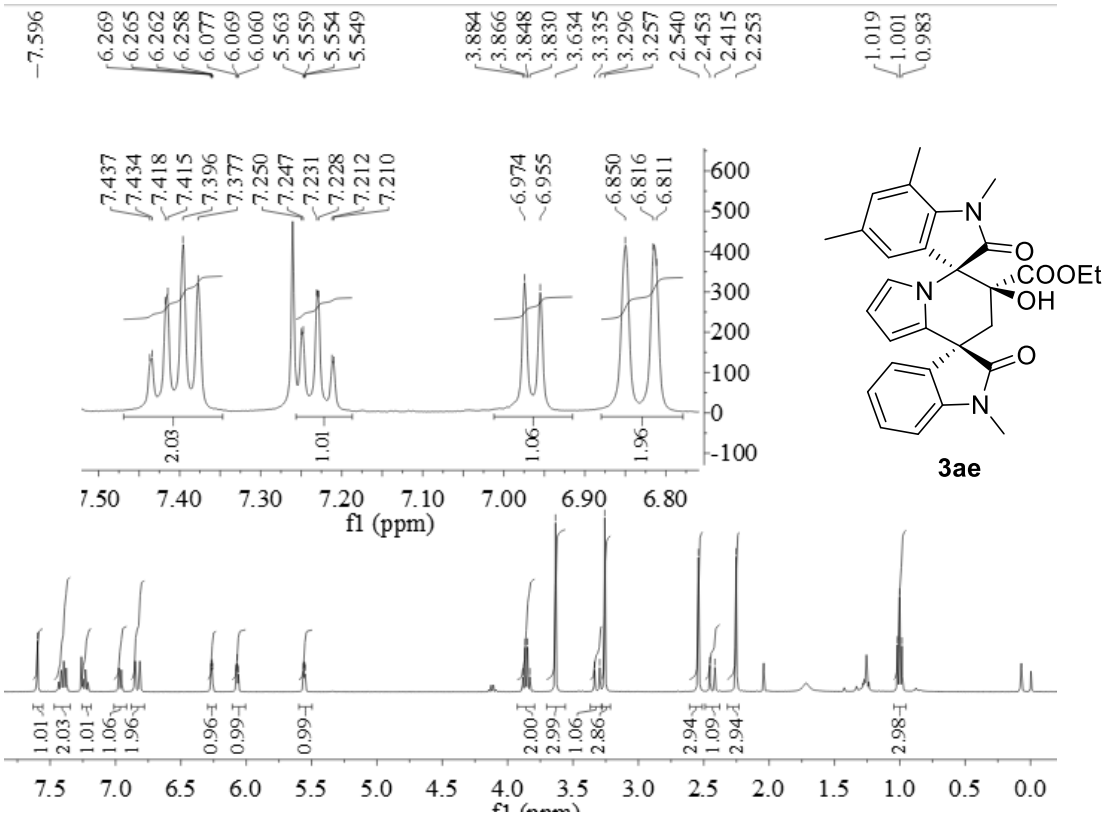


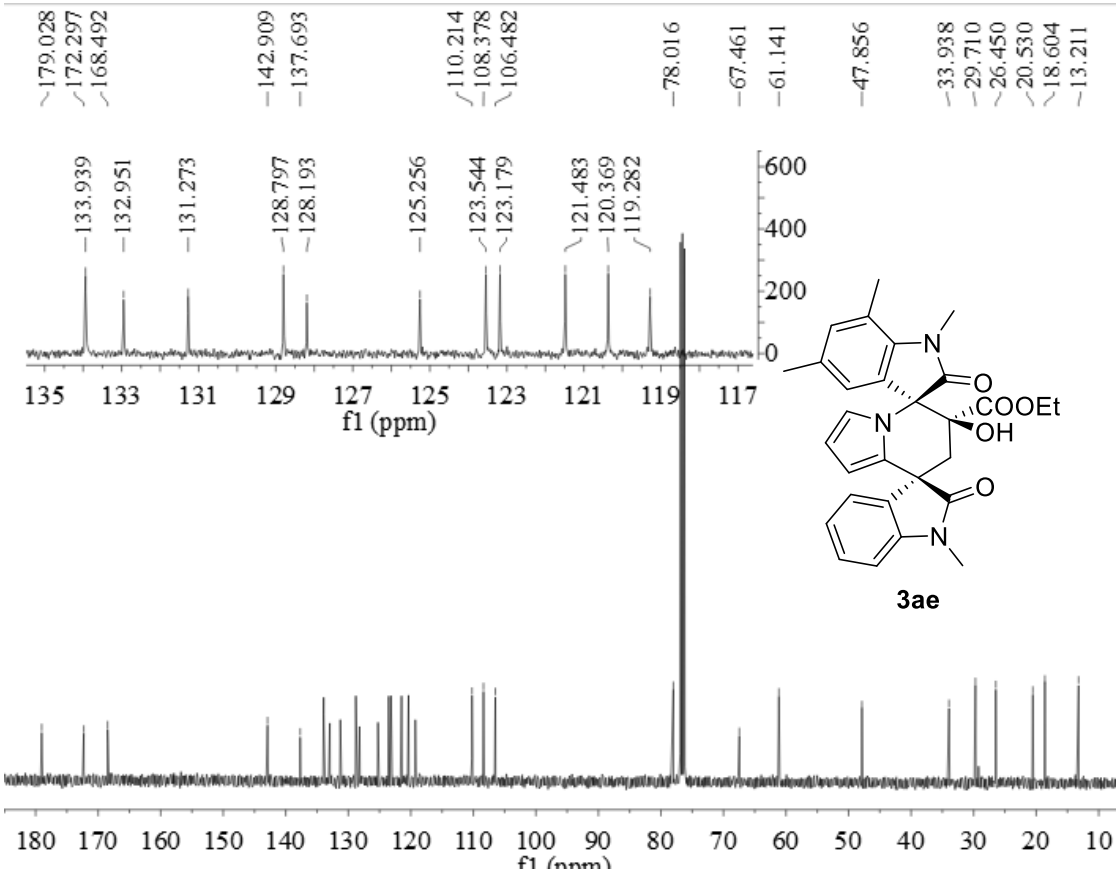
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ad



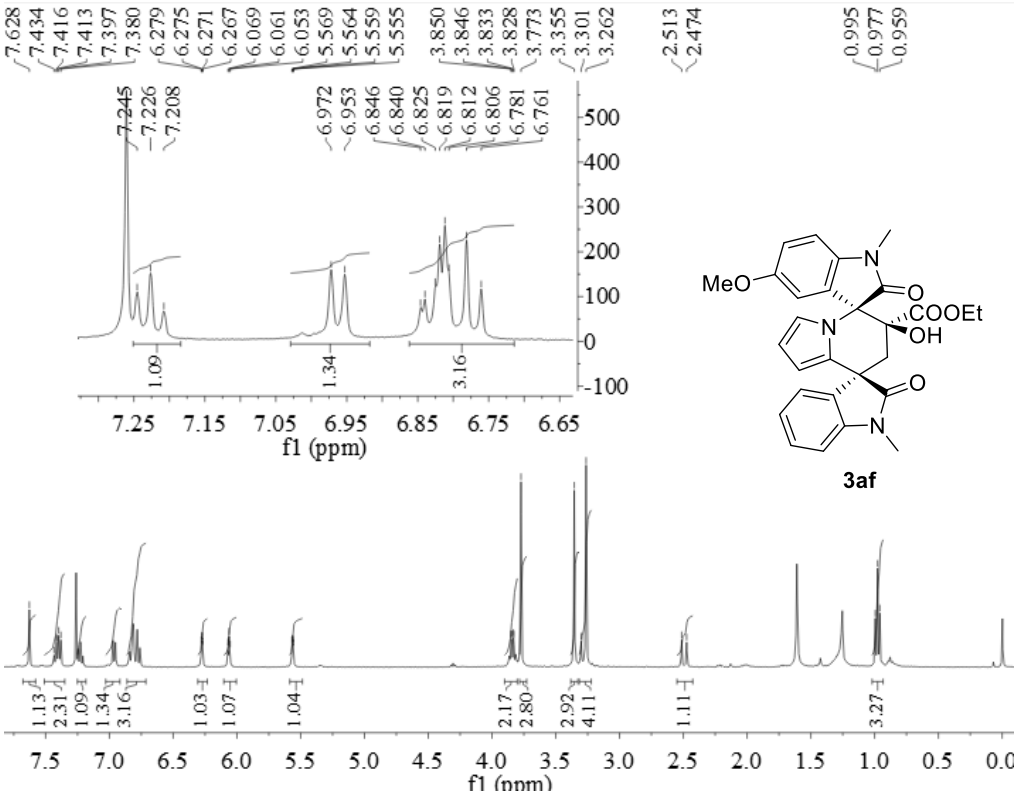


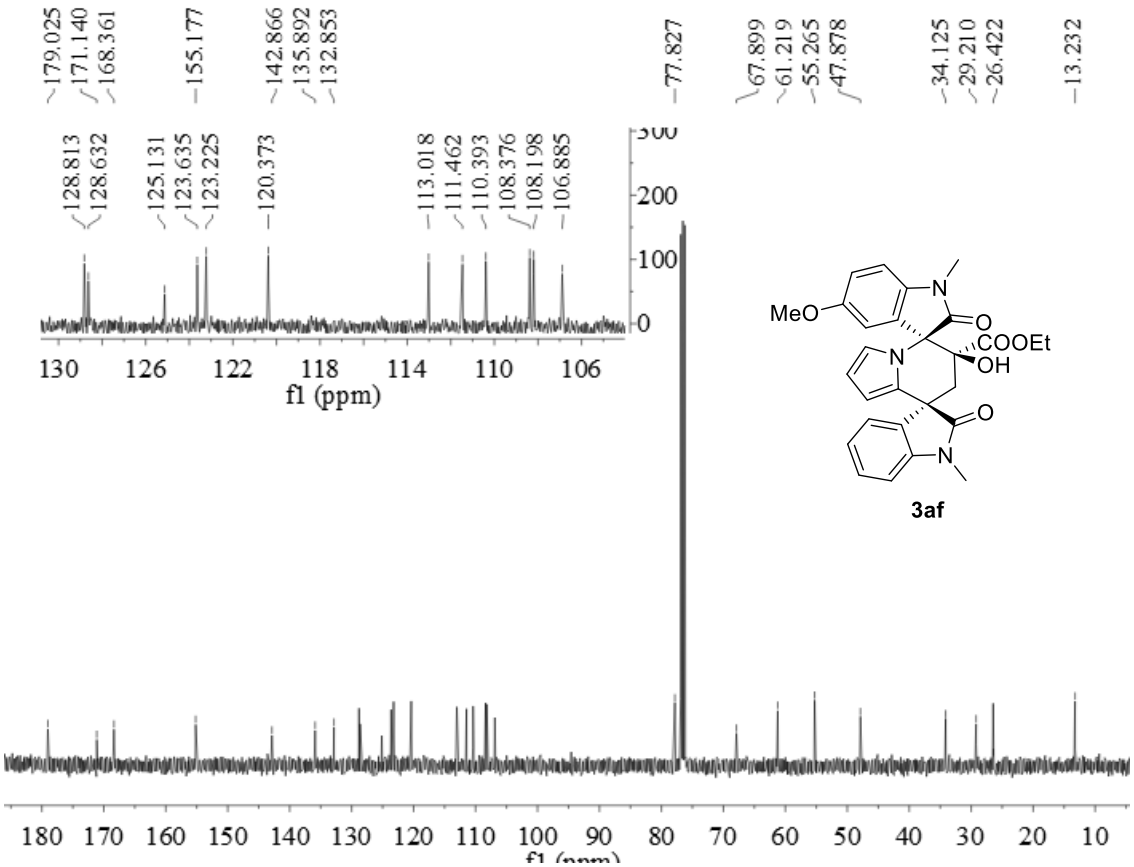
ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate3ae



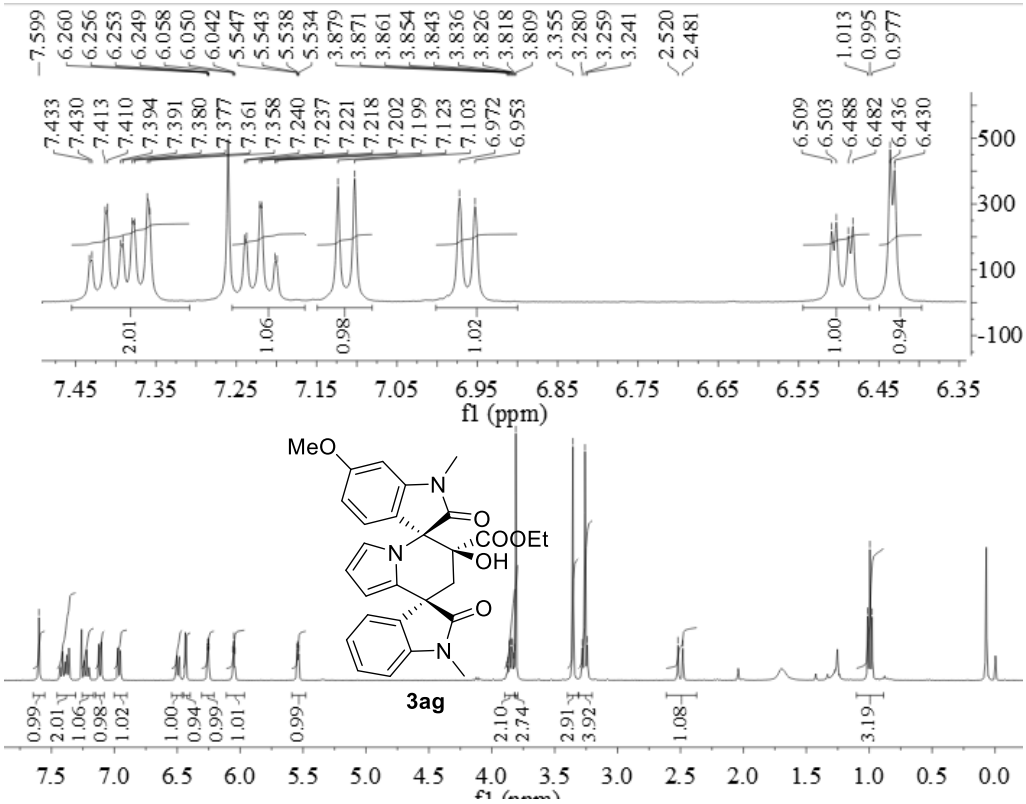


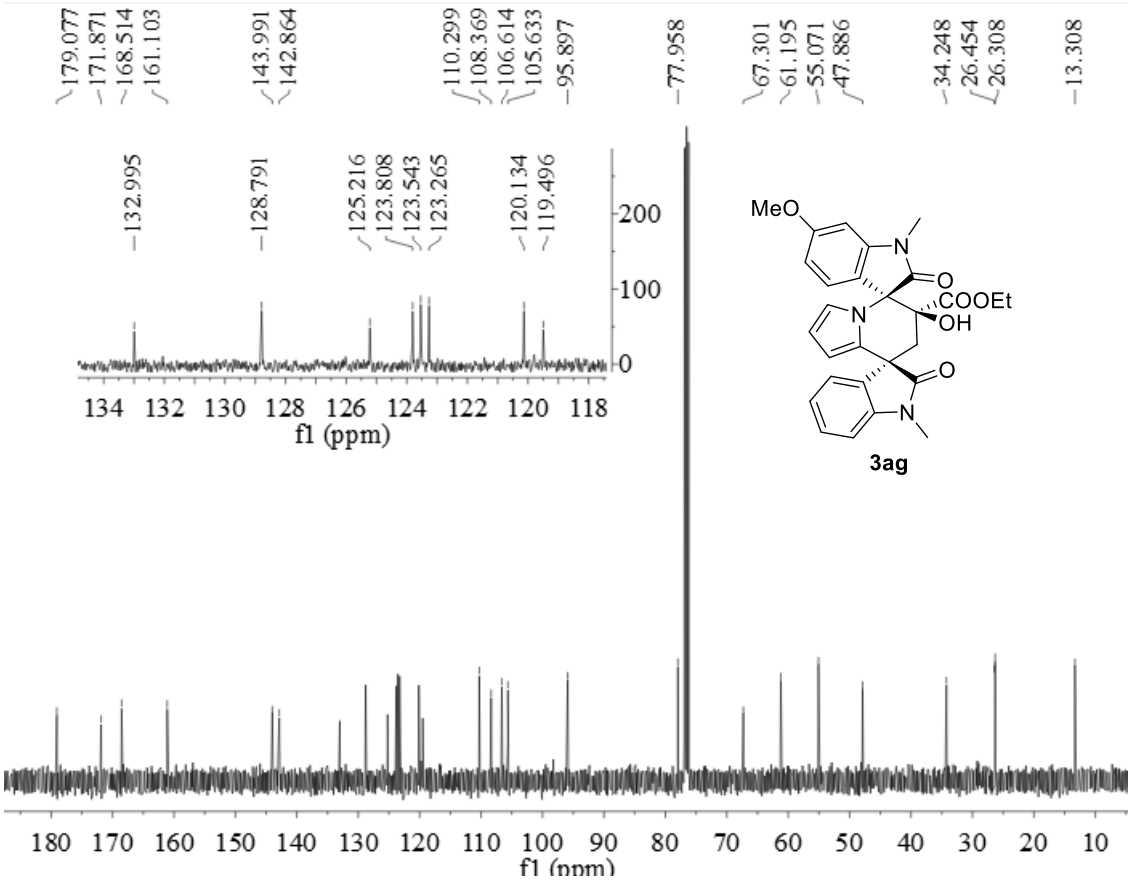
ethyl(3R,6'S,8'S)-6'-hydroxy-5-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3af



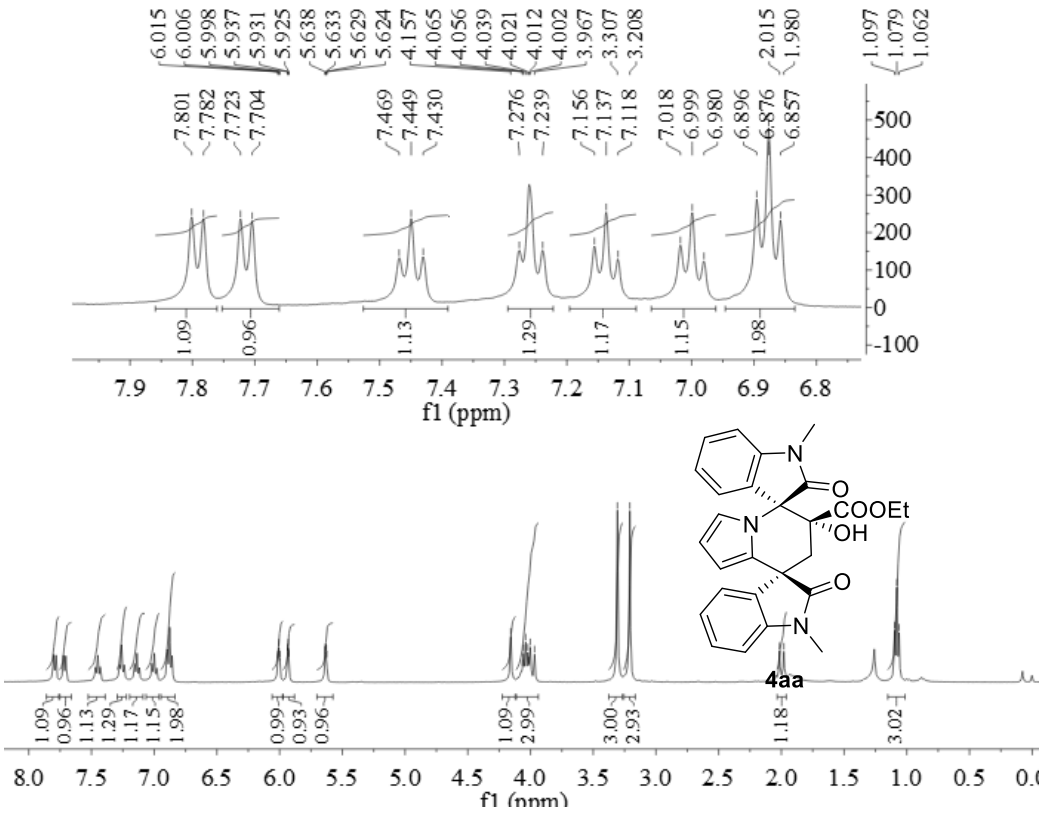


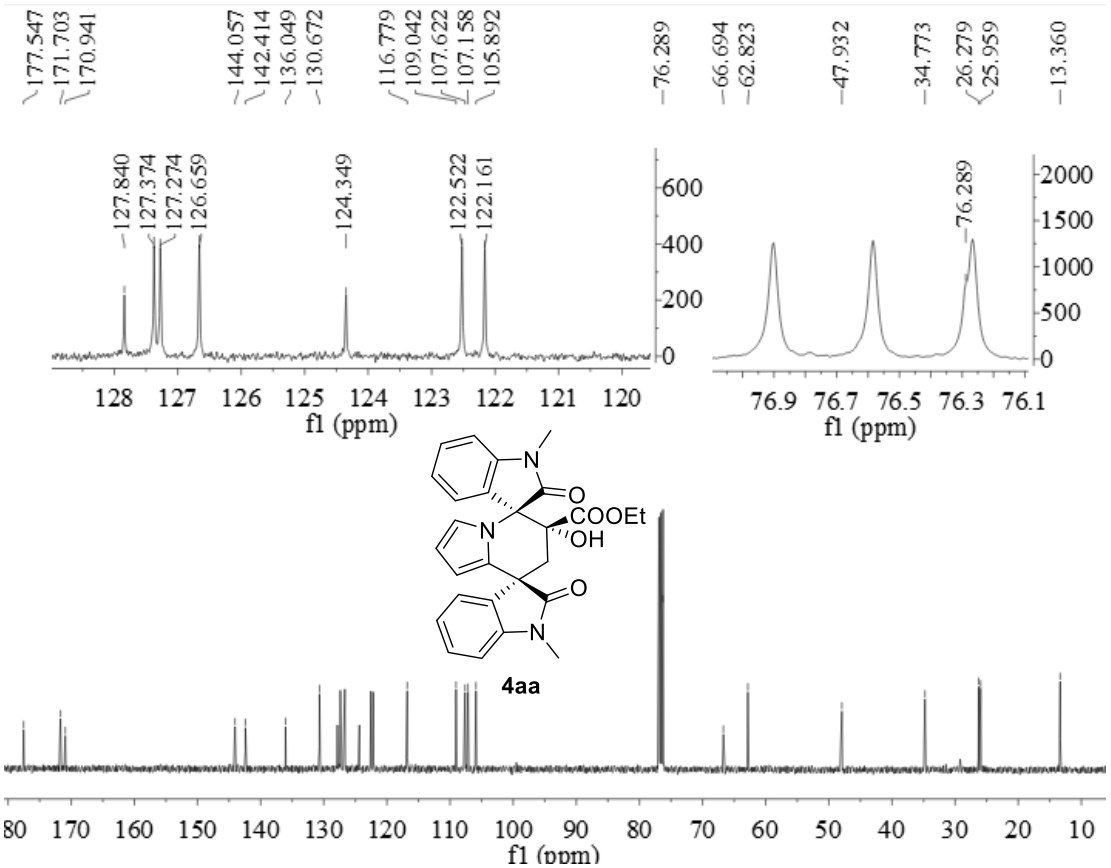
ethyl(3R,6'S,8'S)-6'-hydroxy-6-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ag



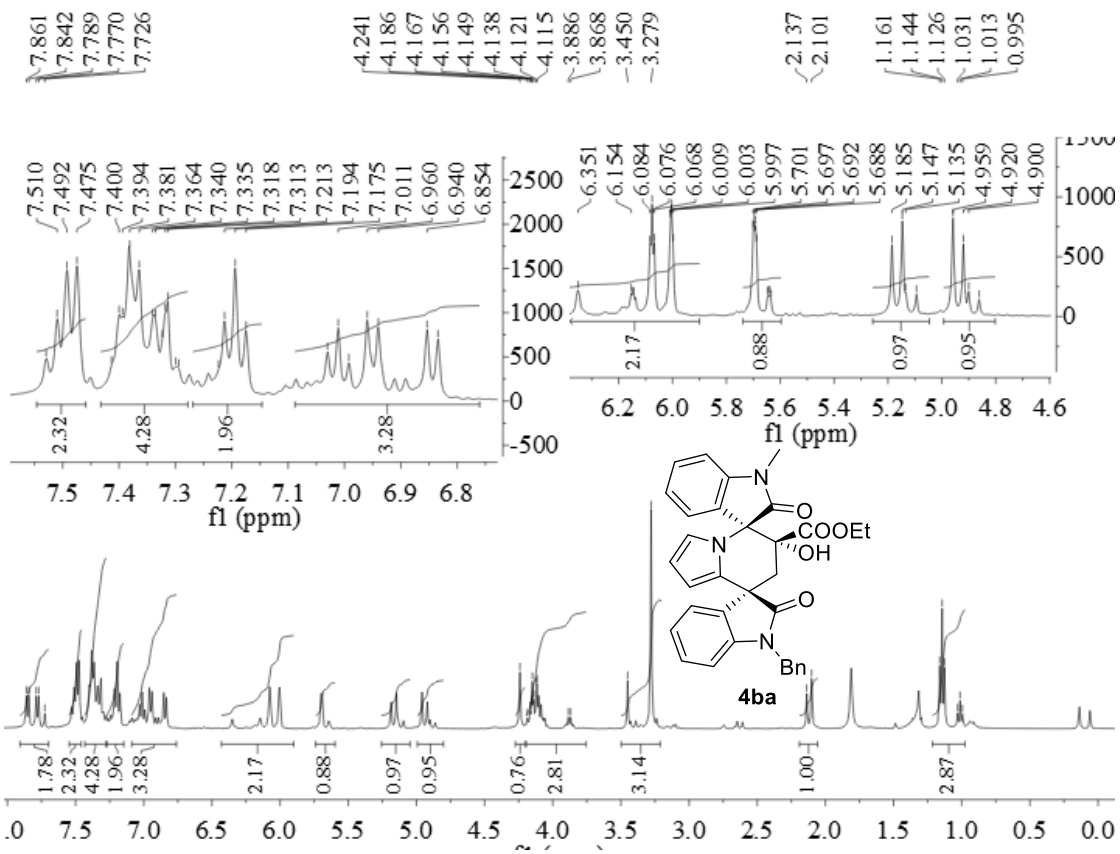


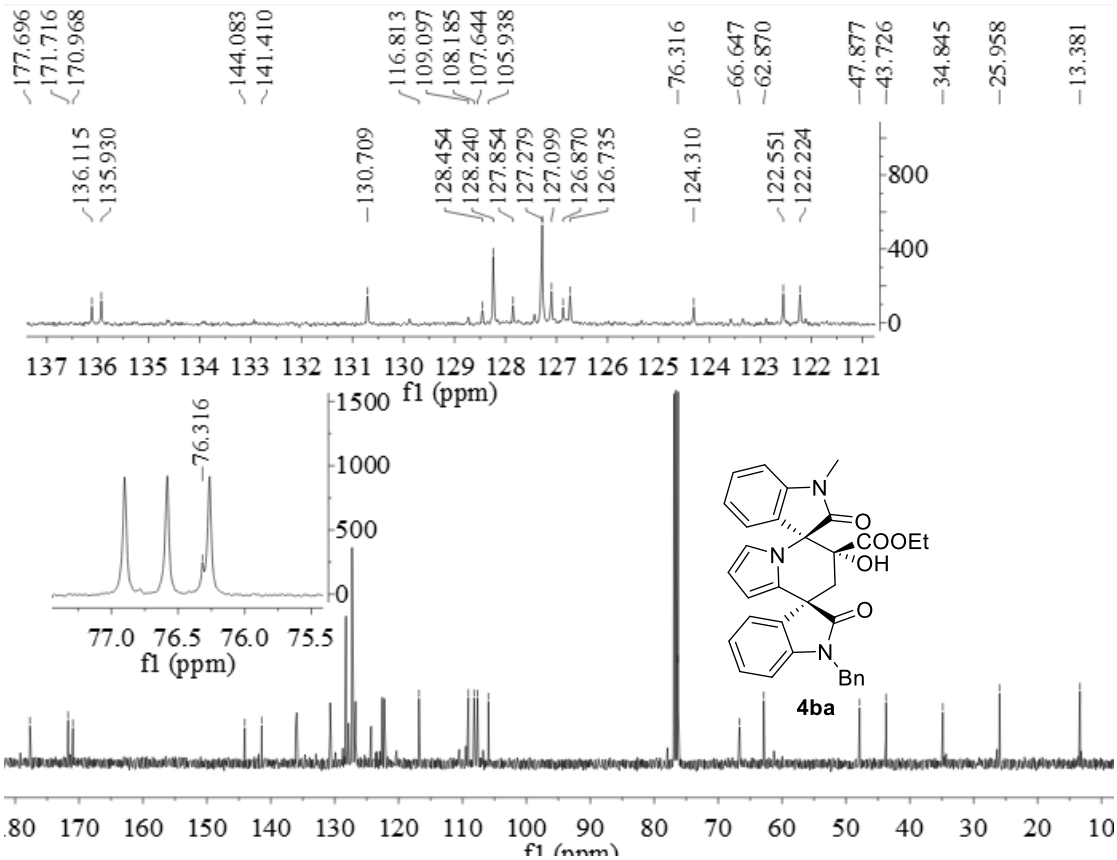
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4aa



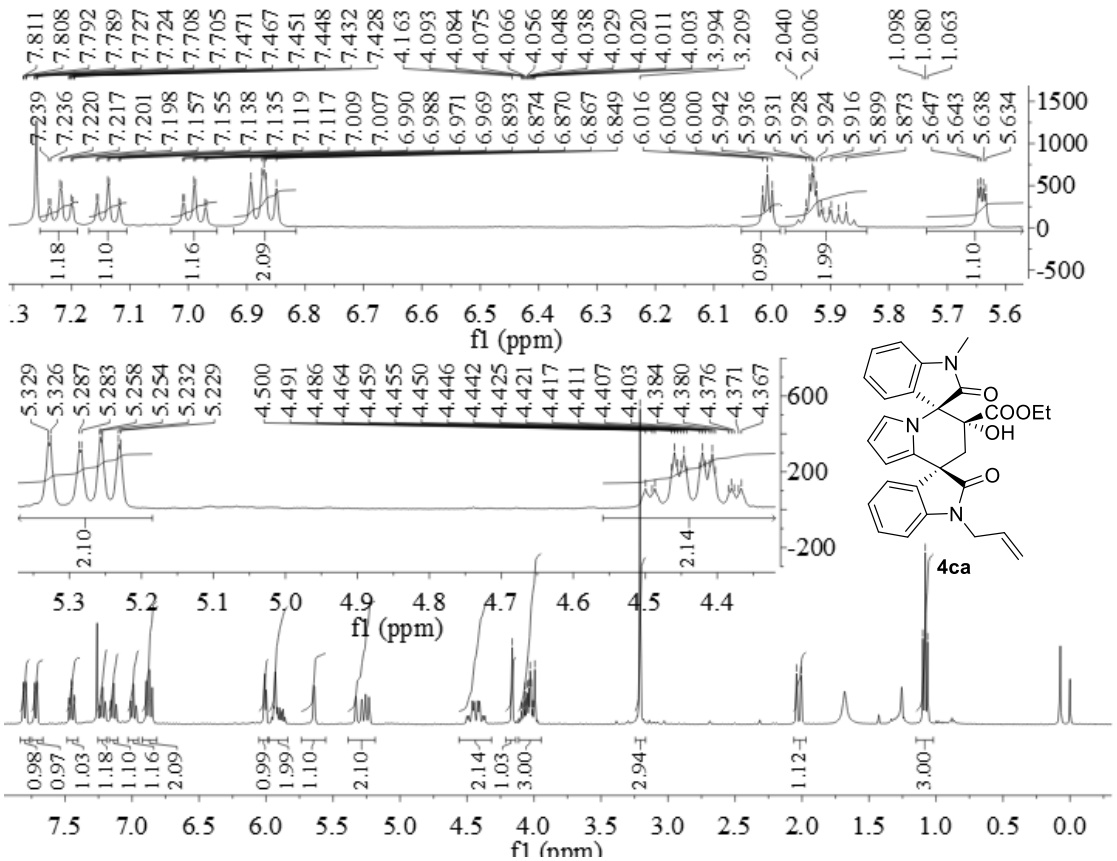


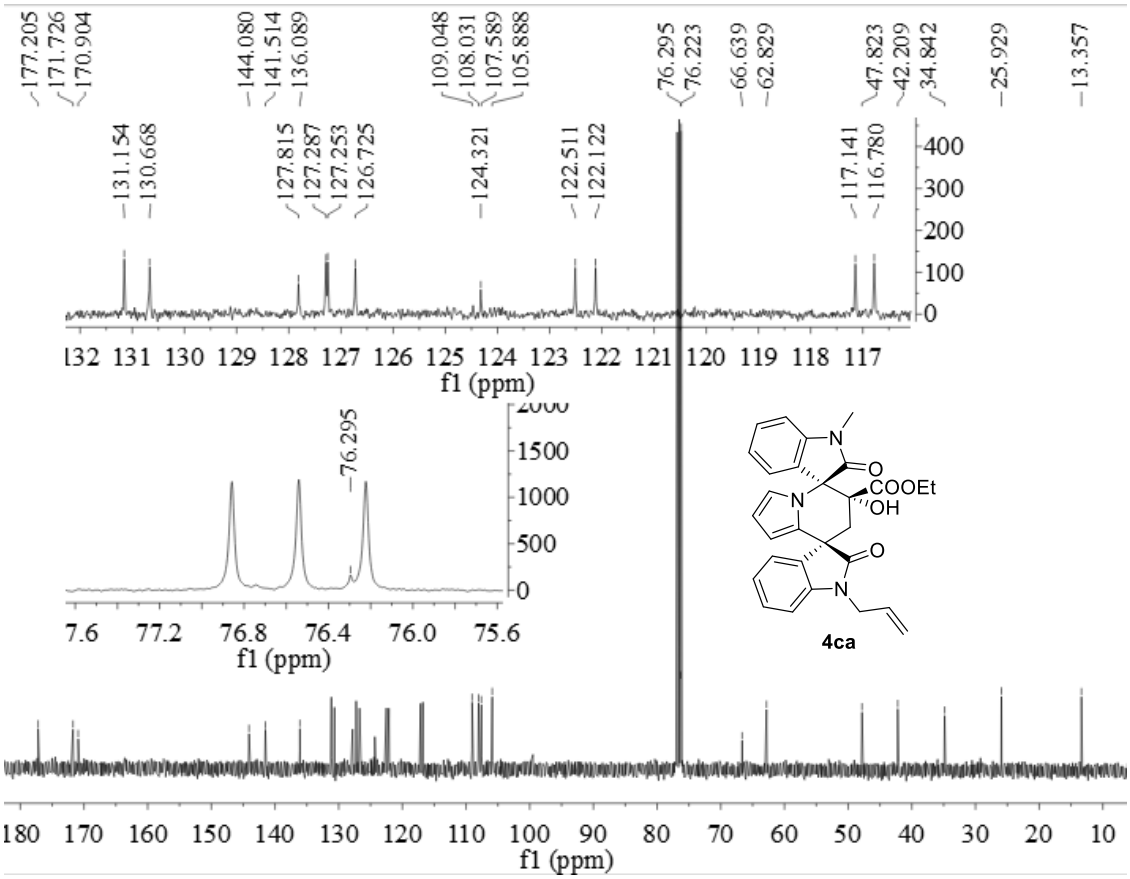
ethyl(3R,6'R,8'S)-1''-benzyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ba



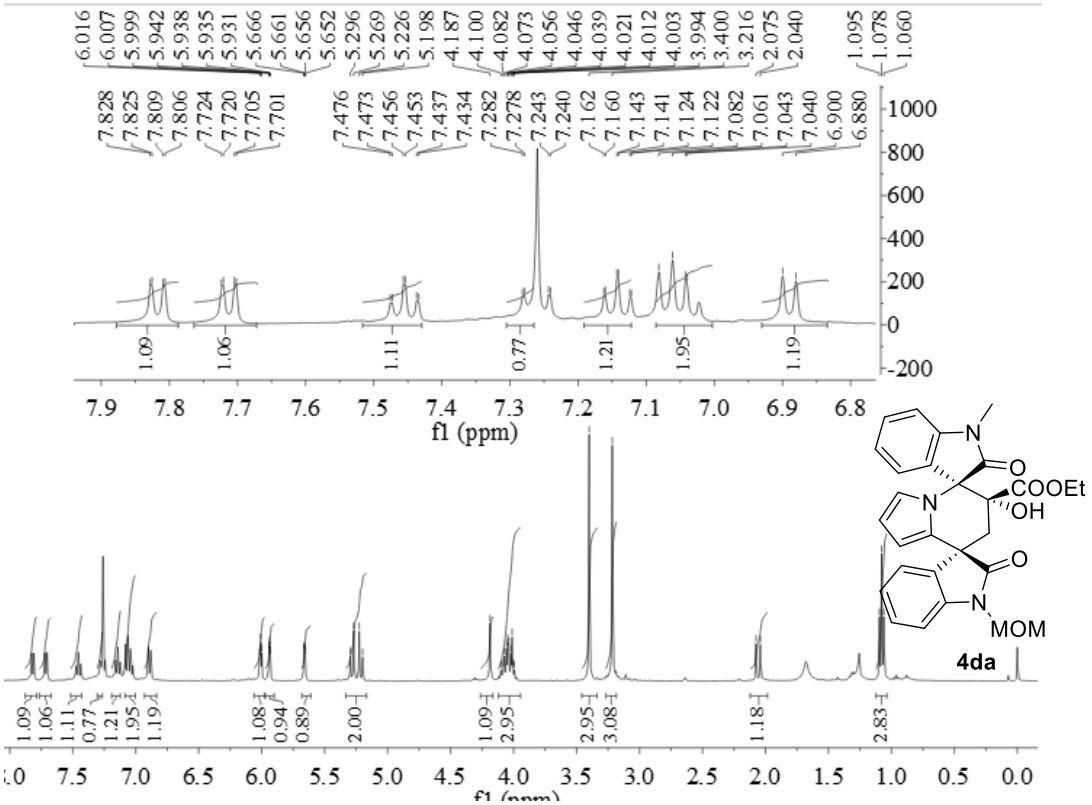


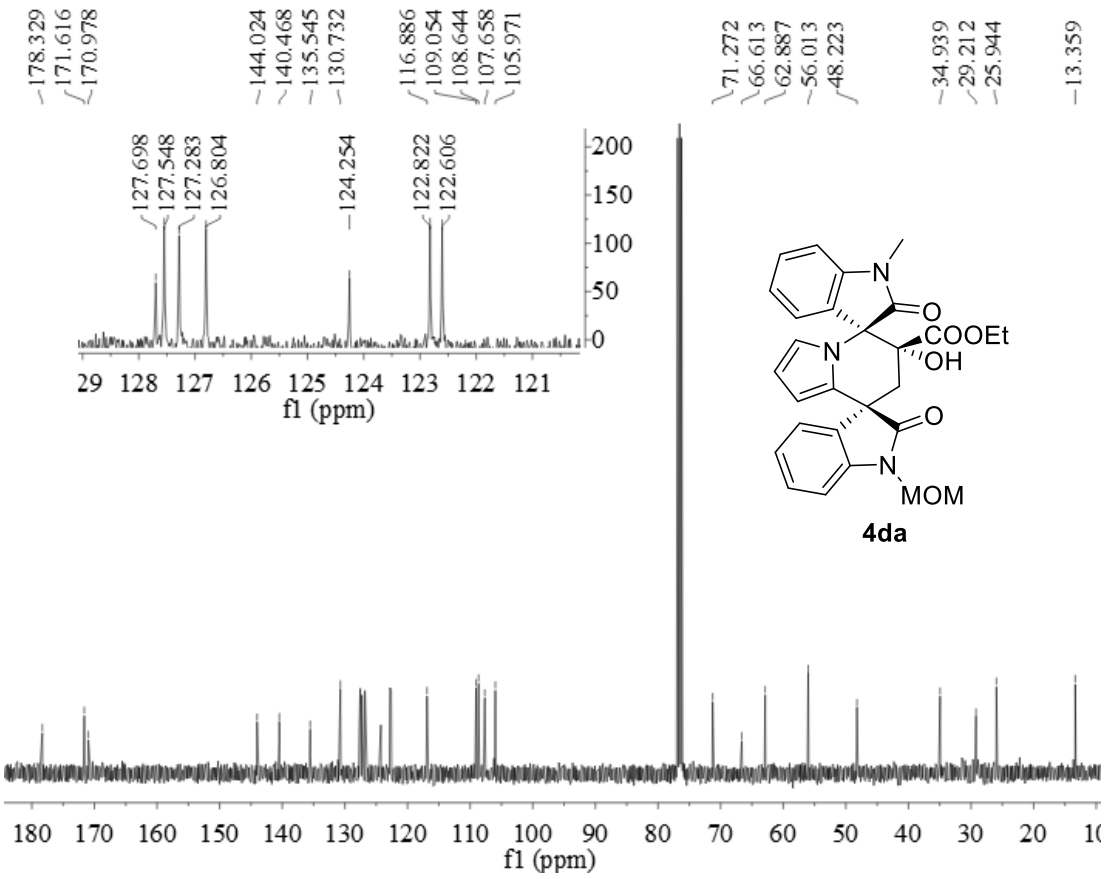
ethyl(3R,6'R,8'S)-1''-allyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ca



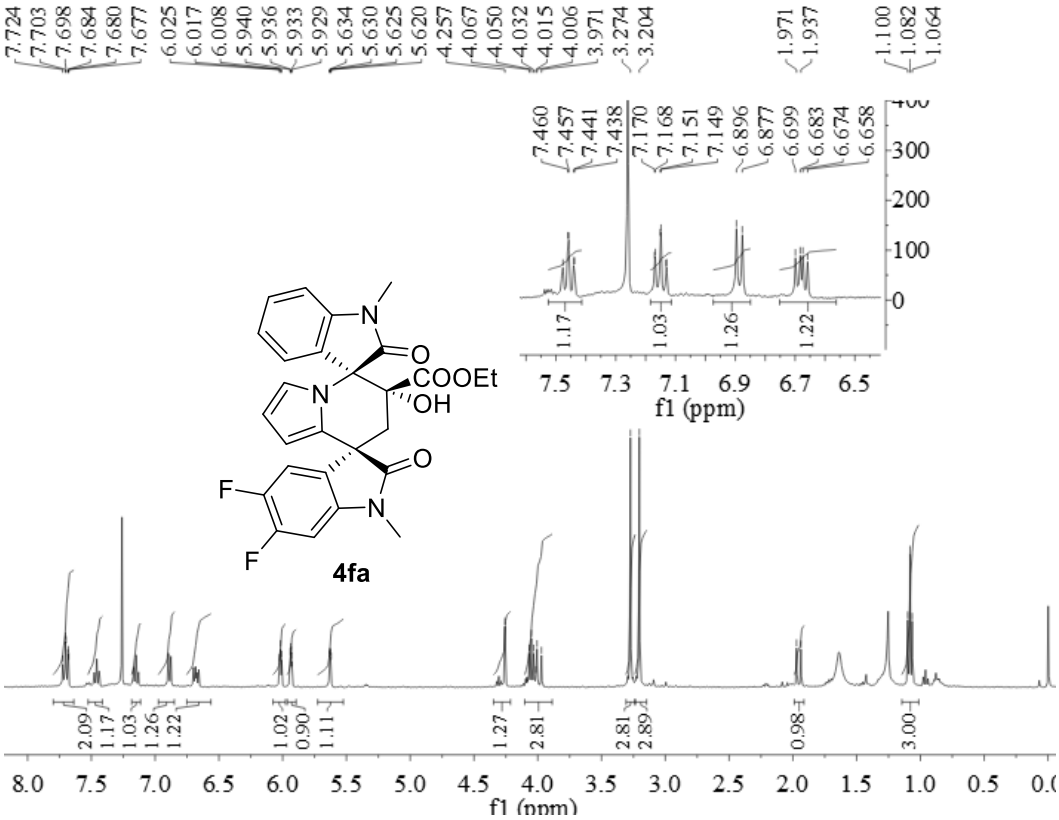


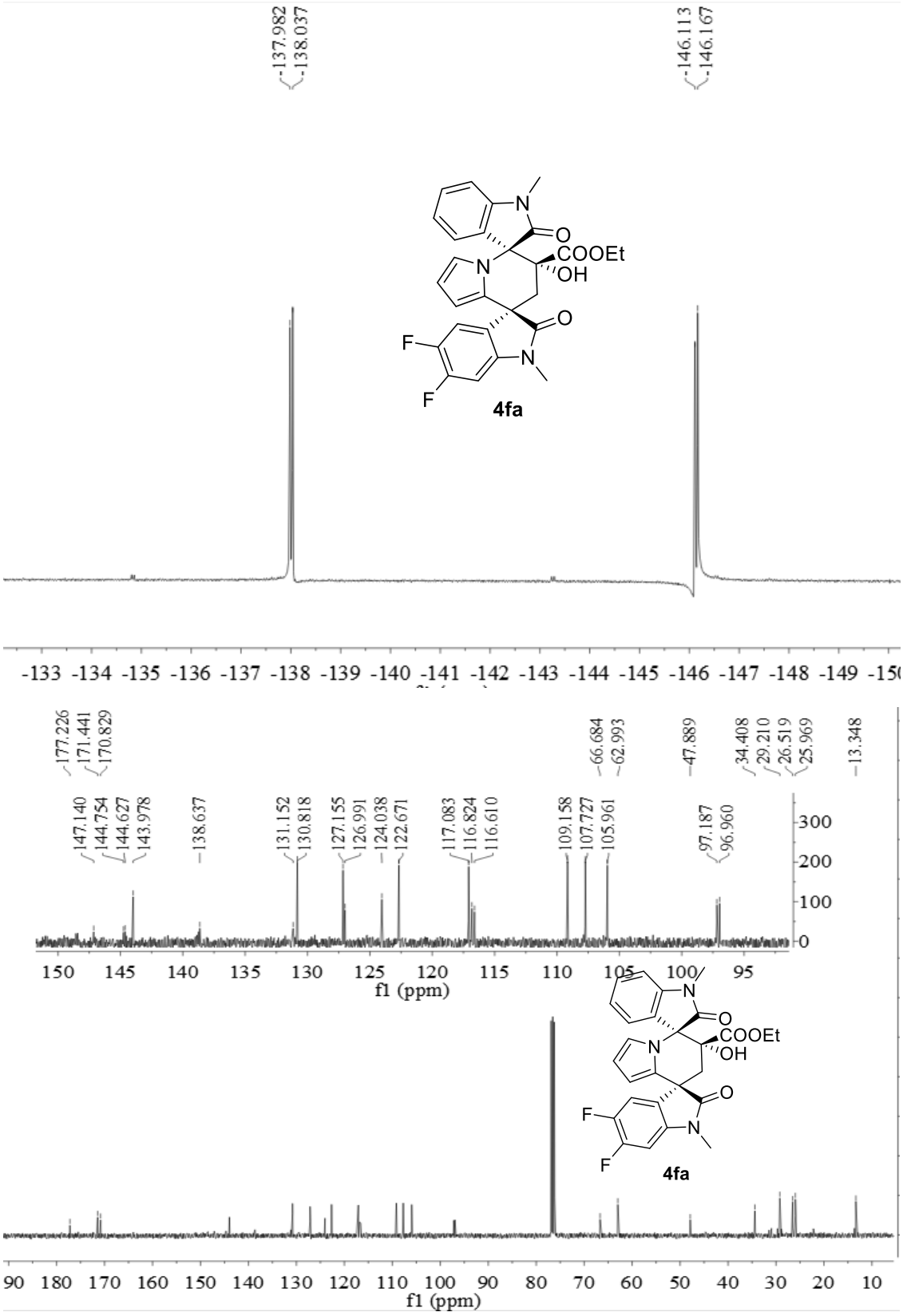
ethyl(3R,6'R,8'S)-6'-hydroxy-1''-(methoxymethyl)-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4da



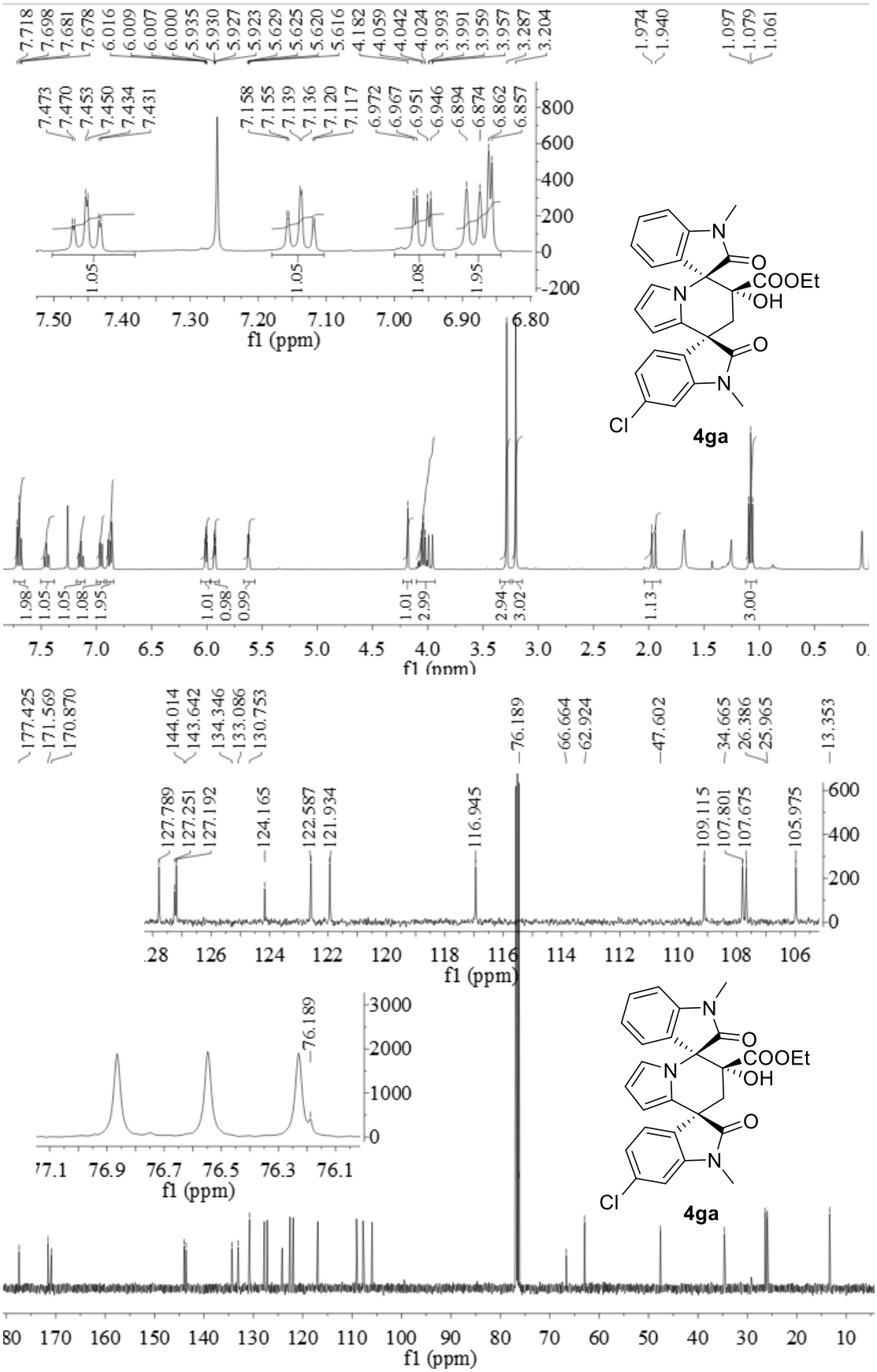


ethyl(3R,6'R,8'S)-5'',6''-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4fa

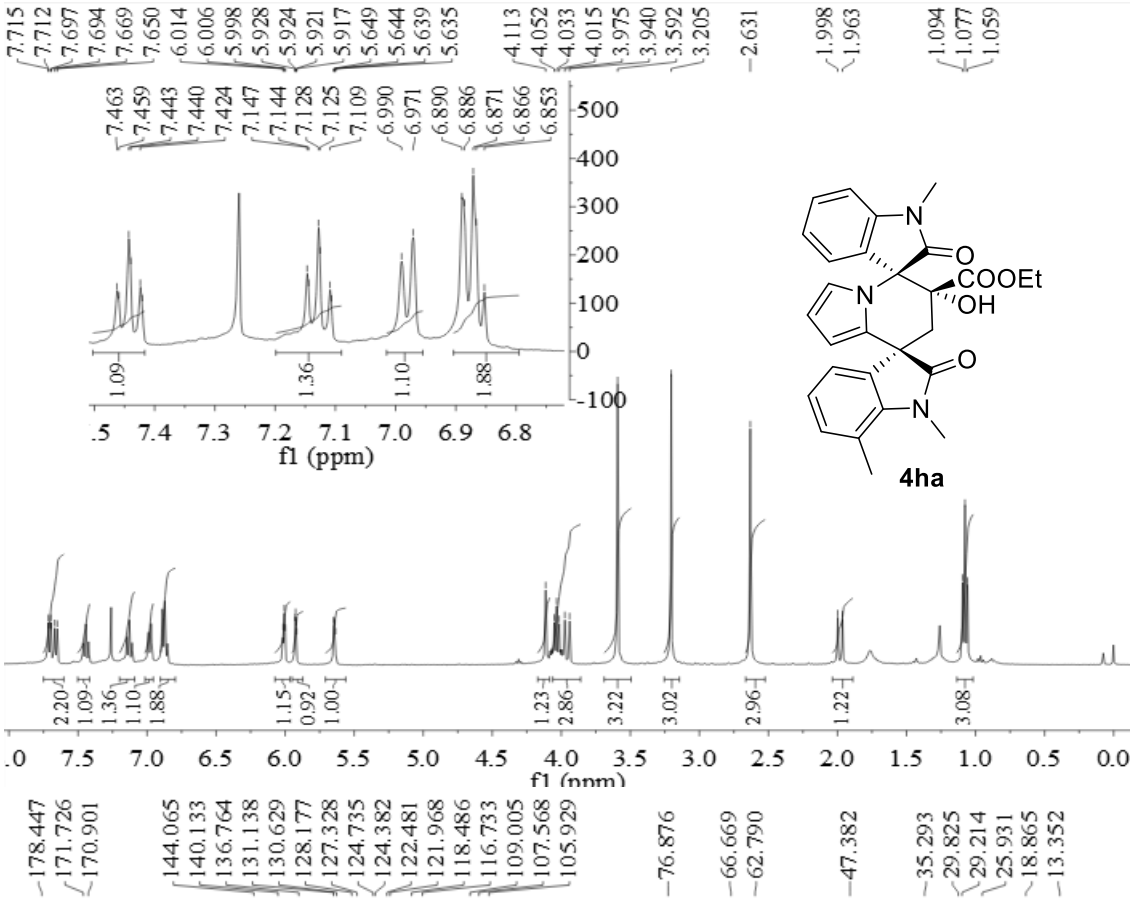


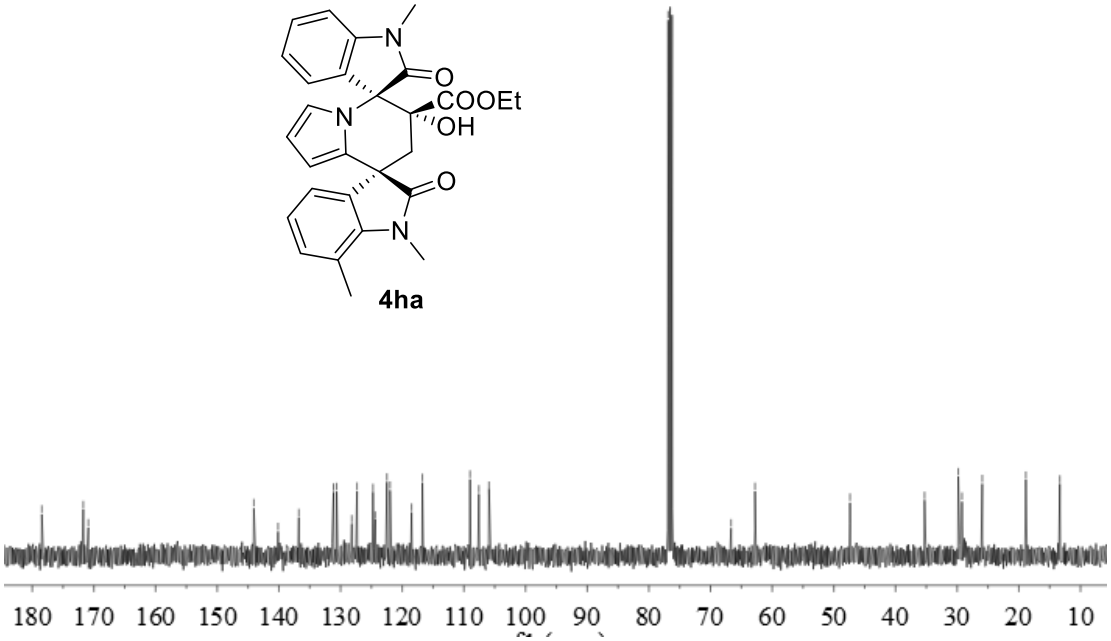


ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ga

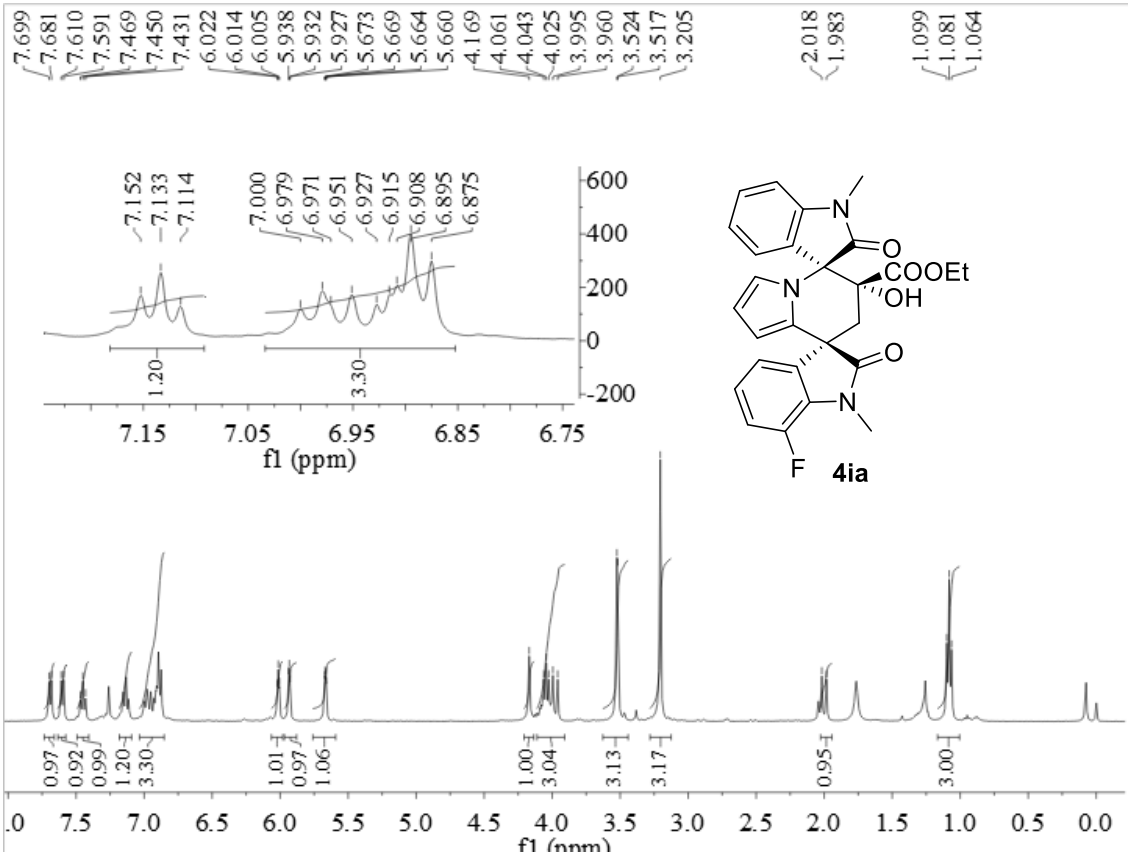


ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',7''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ha





ethyl(3R,6'R,8'S)-7''-fluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ia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7.681
7.610
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6.022
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6.005
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5.927
5.673
5.669
5.664
5.660
4.169
4.061
4.043
4.025
3.995
3.960
3.524
3.517
3.205
2.018
1.983
1.099
1.081
1.064
7.152
7.133
7.114
7.000
6.979
6.971
6.951
6.927
6.915
6.908
6.895
6.875
600
400
200
0
-200
1.20
3.30
7.15
7.05
6.95
6.85
6.75
f1 (ppm)
N
O
COOEt
OH
N
O
N
F
4ia
0.97
0.92
0.99
1.20
3.30
1.01
0.97
1.06
1.00
3.04
3.13
3.17
0.95
3.00
.0
7.5
7.0
6.5
6.0
5.5
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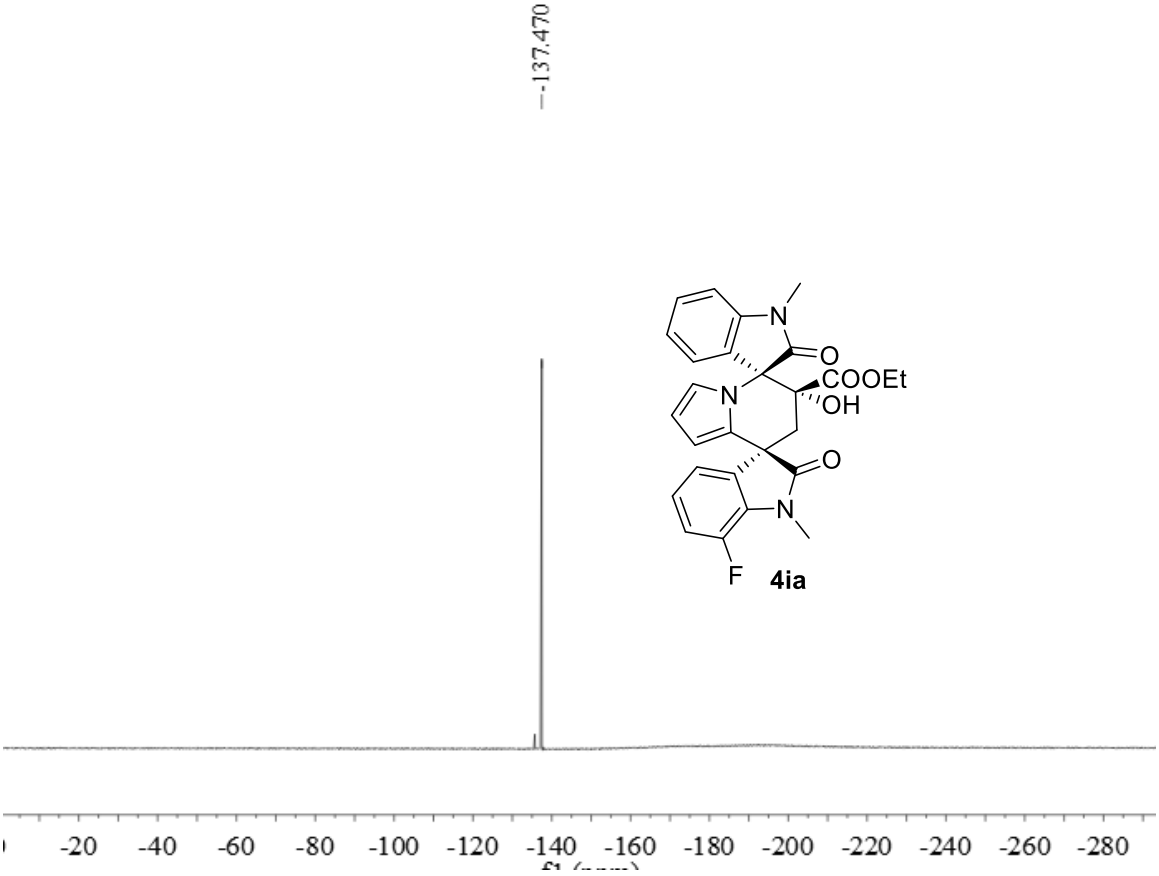
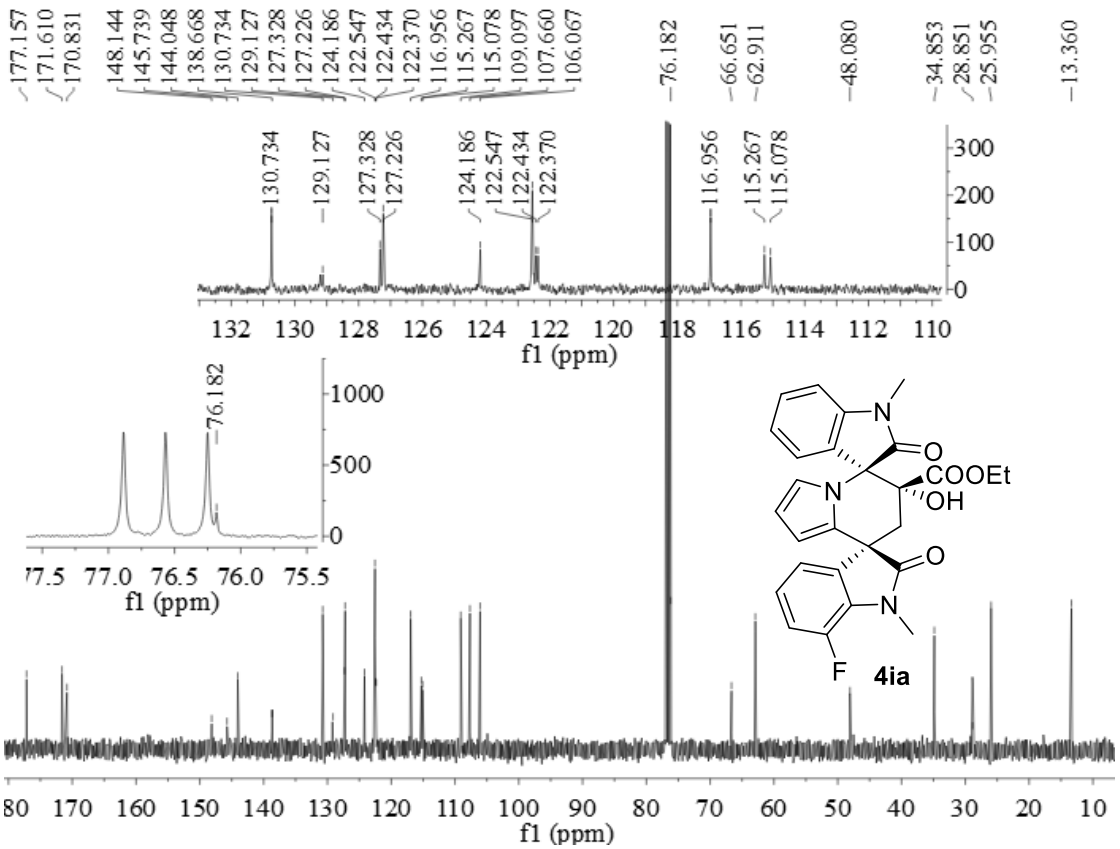
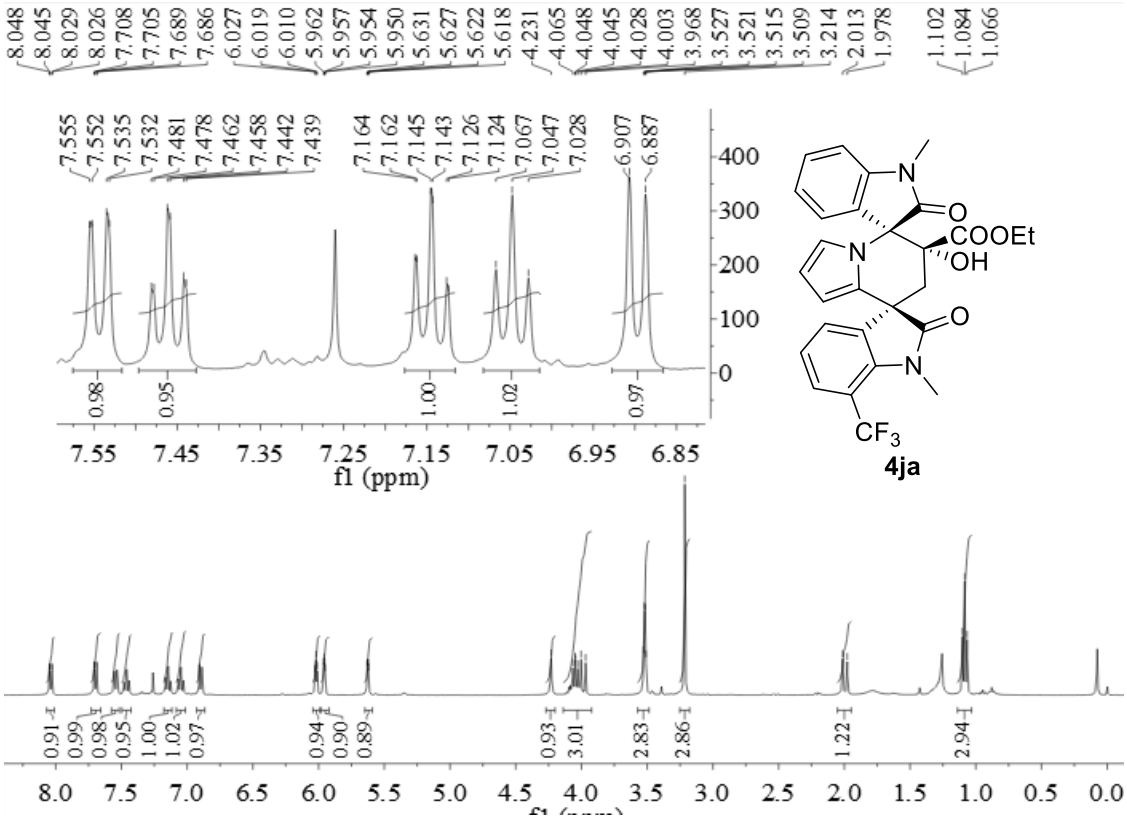
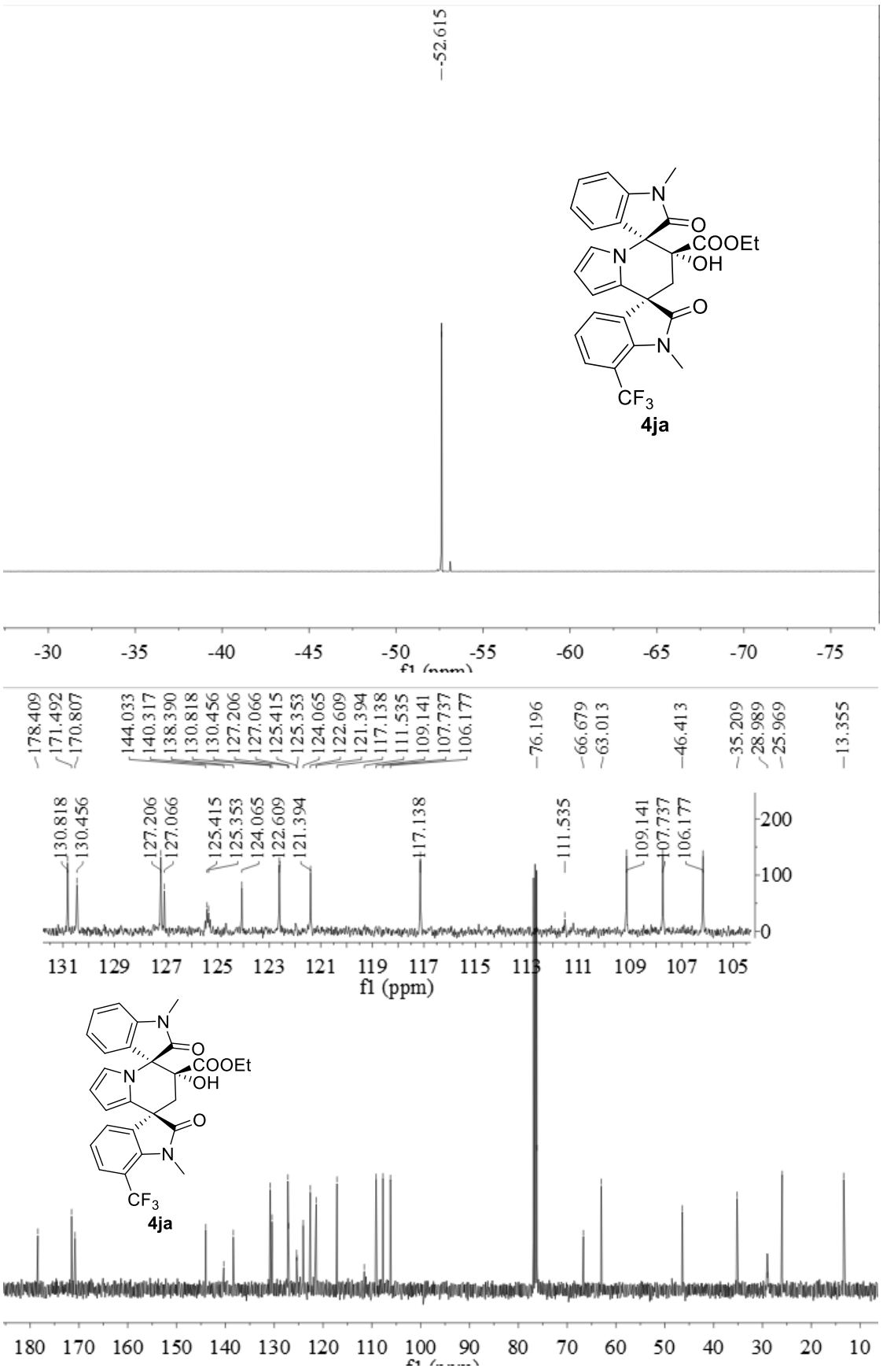
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-137.470
N
O
COOEt
OH
N
O
N
F
4ia
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280

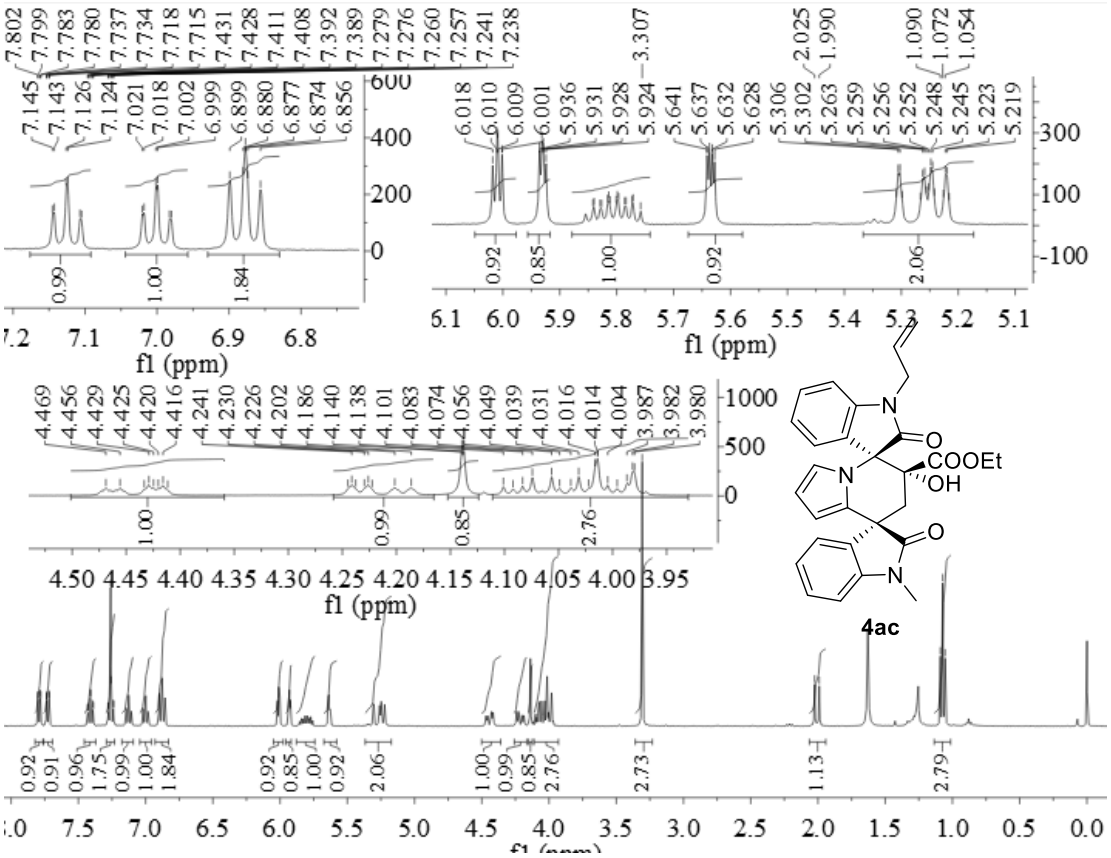


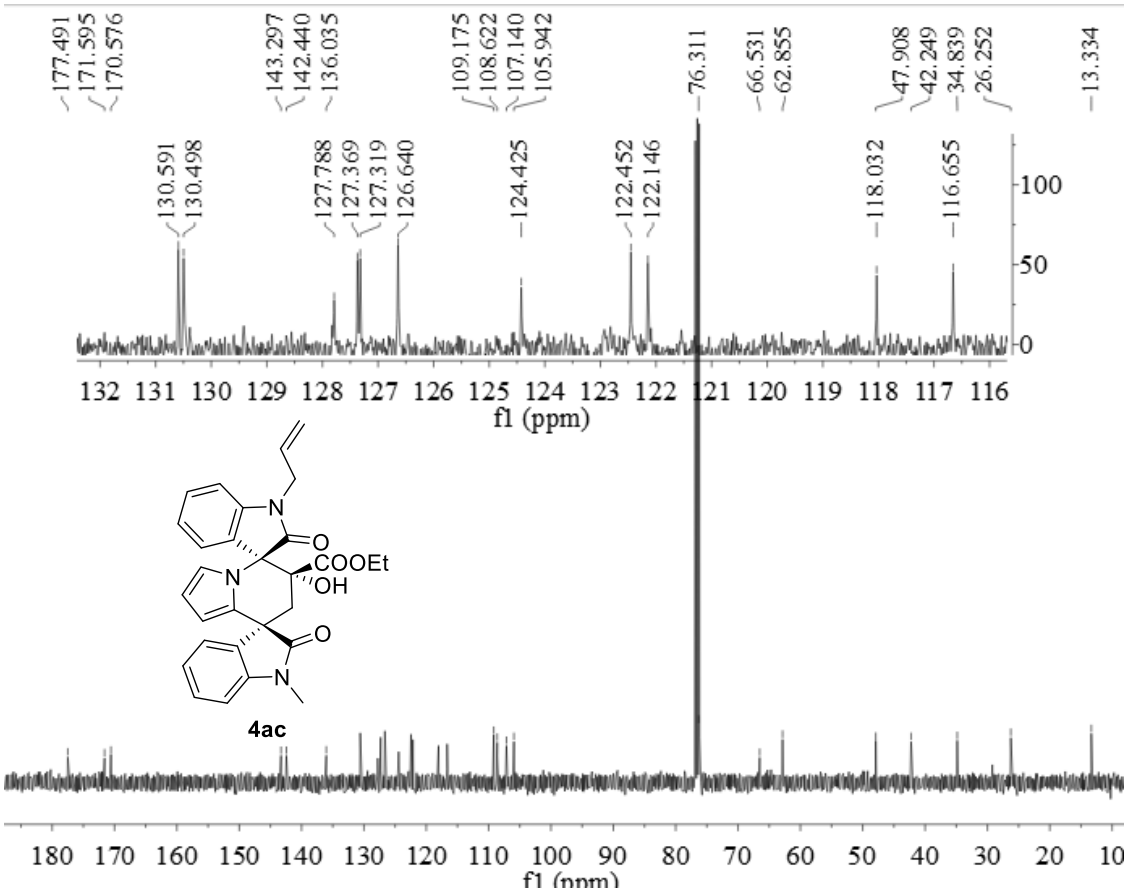
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7''-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ja





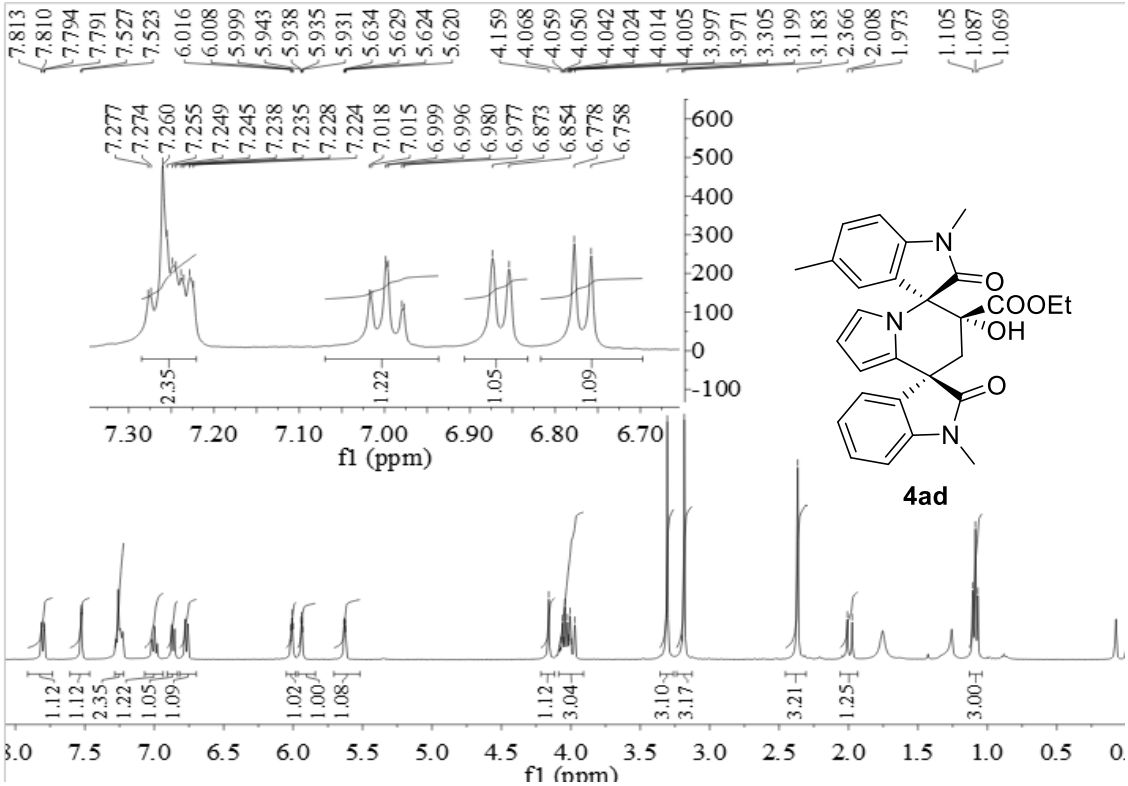
ethyl(3R,6'R,8'S)-1-allyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ac

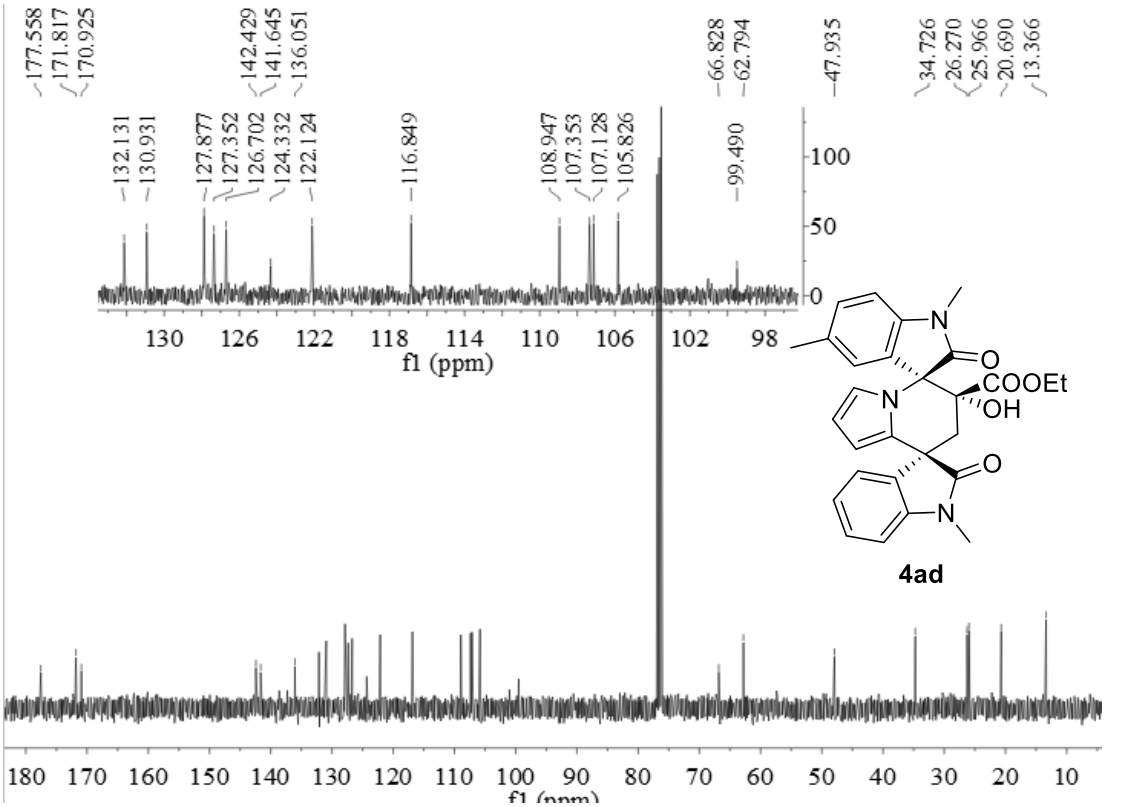




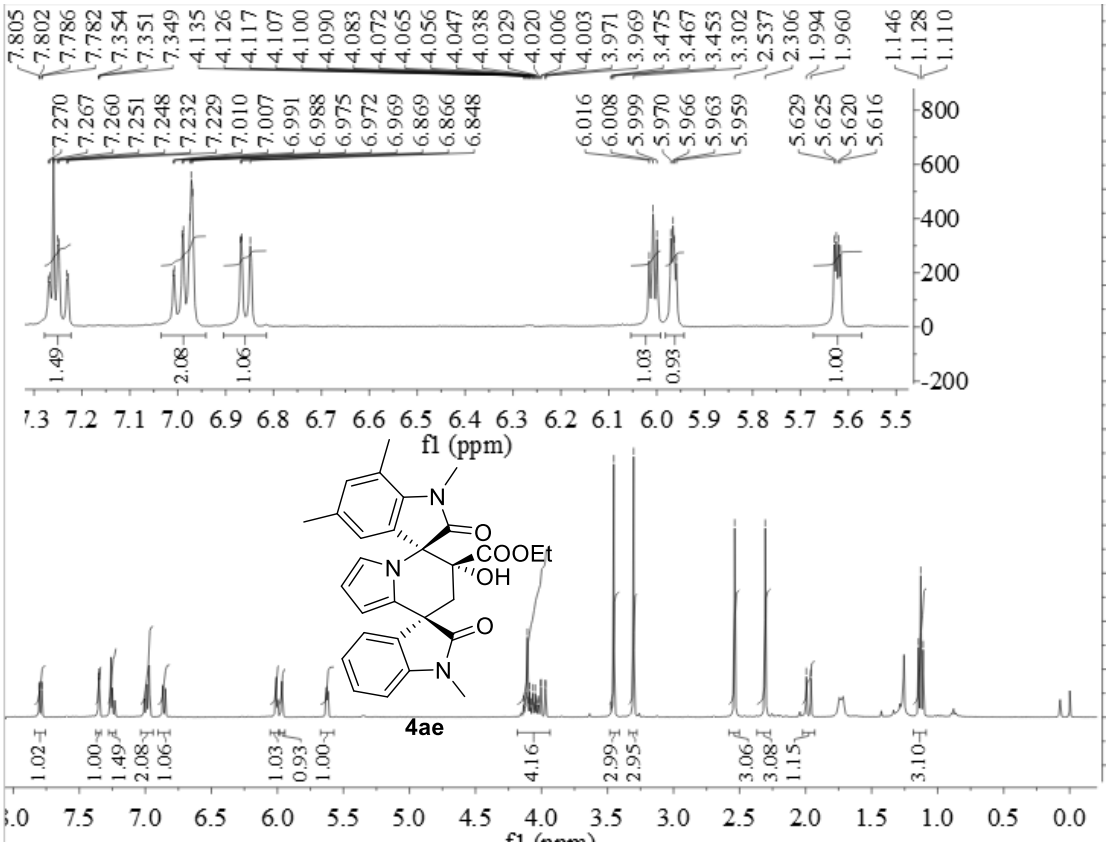
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[in

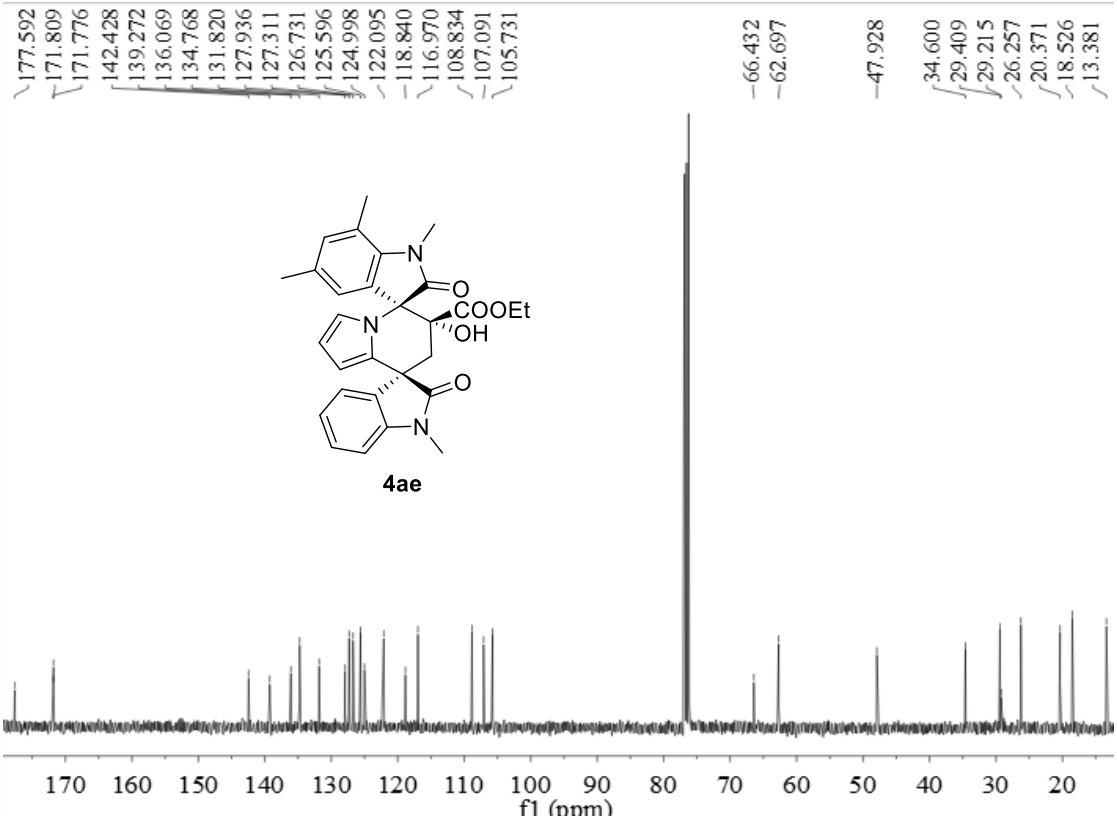
doline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ad



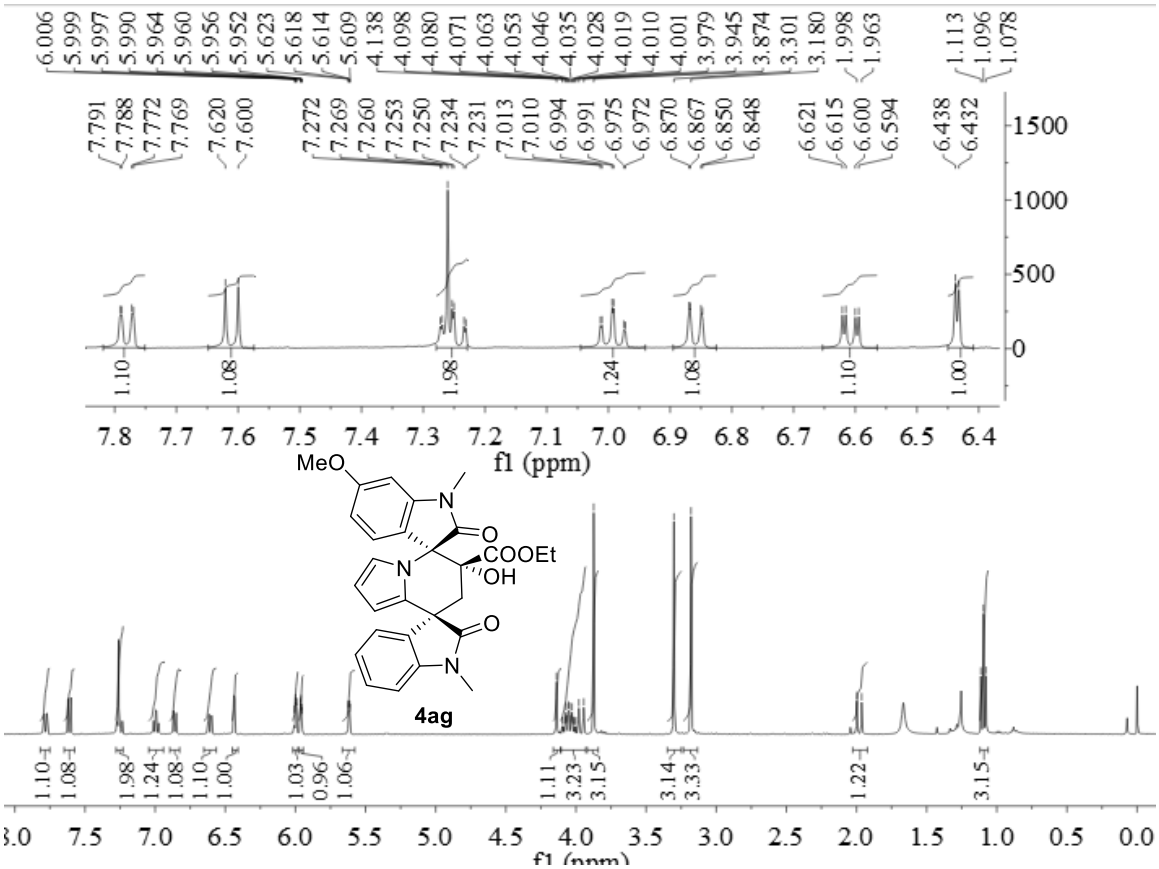


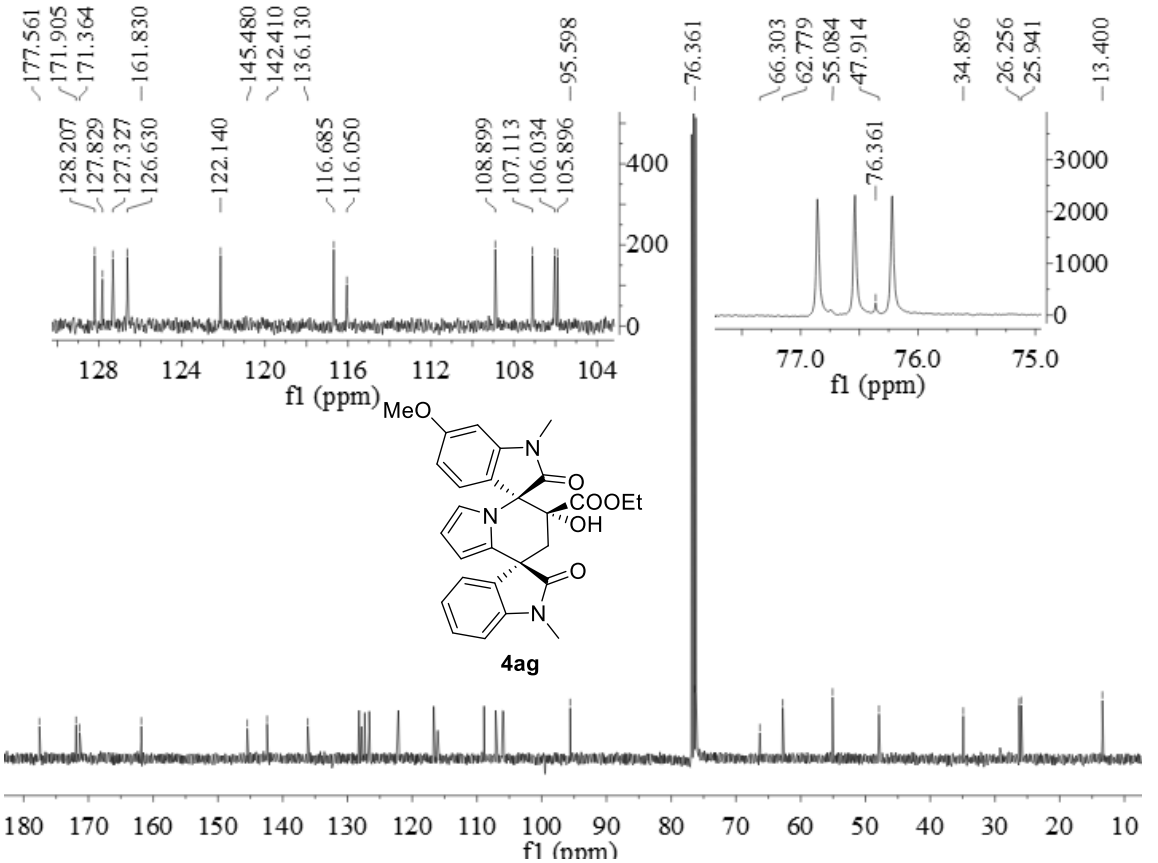
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispir o[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ae



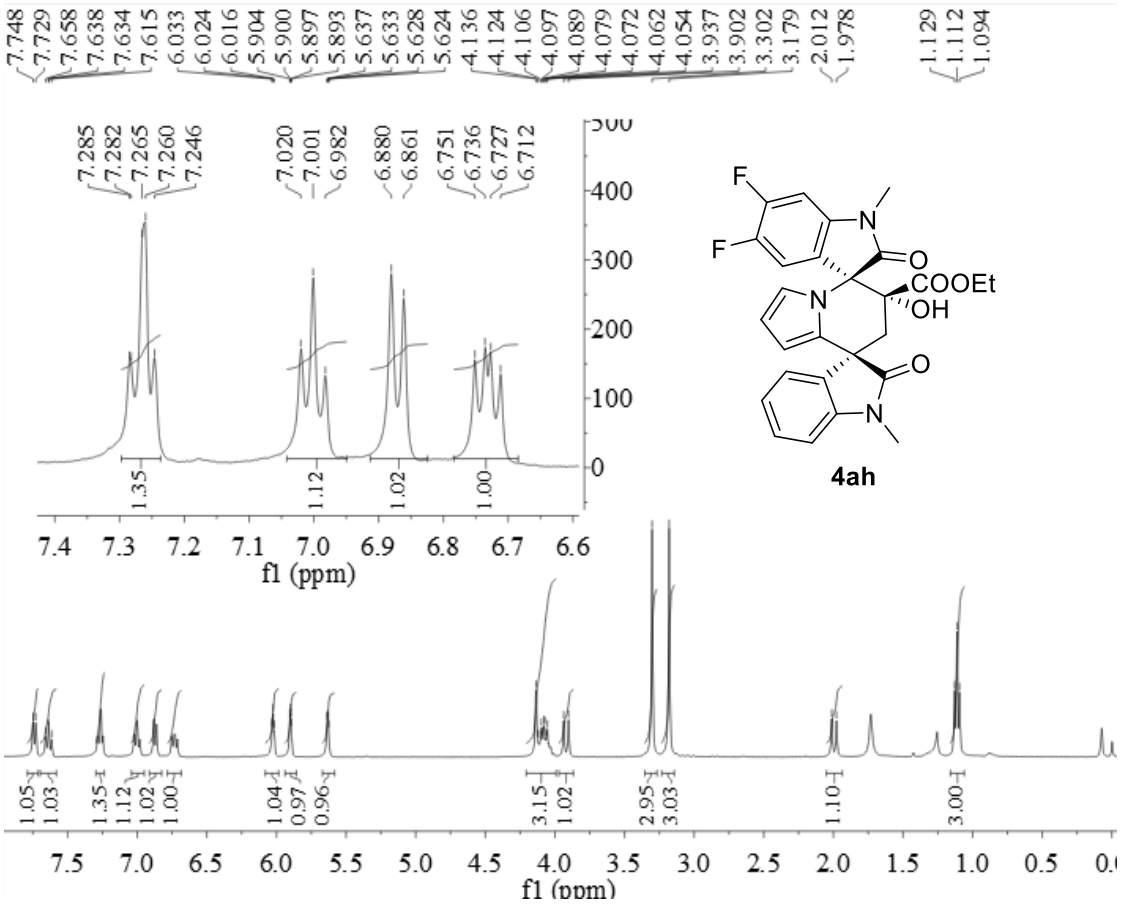


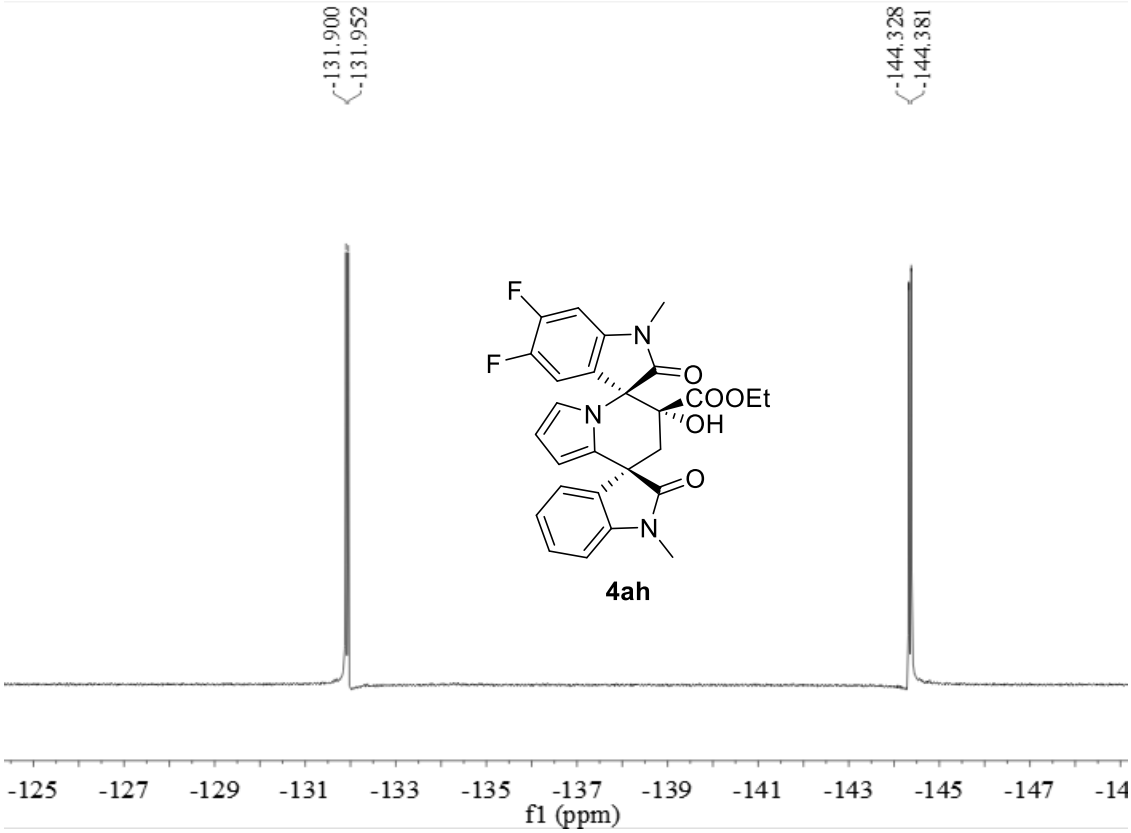
ethyl(3R,6'R,8'S)-6'-hydroxy-6-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ag

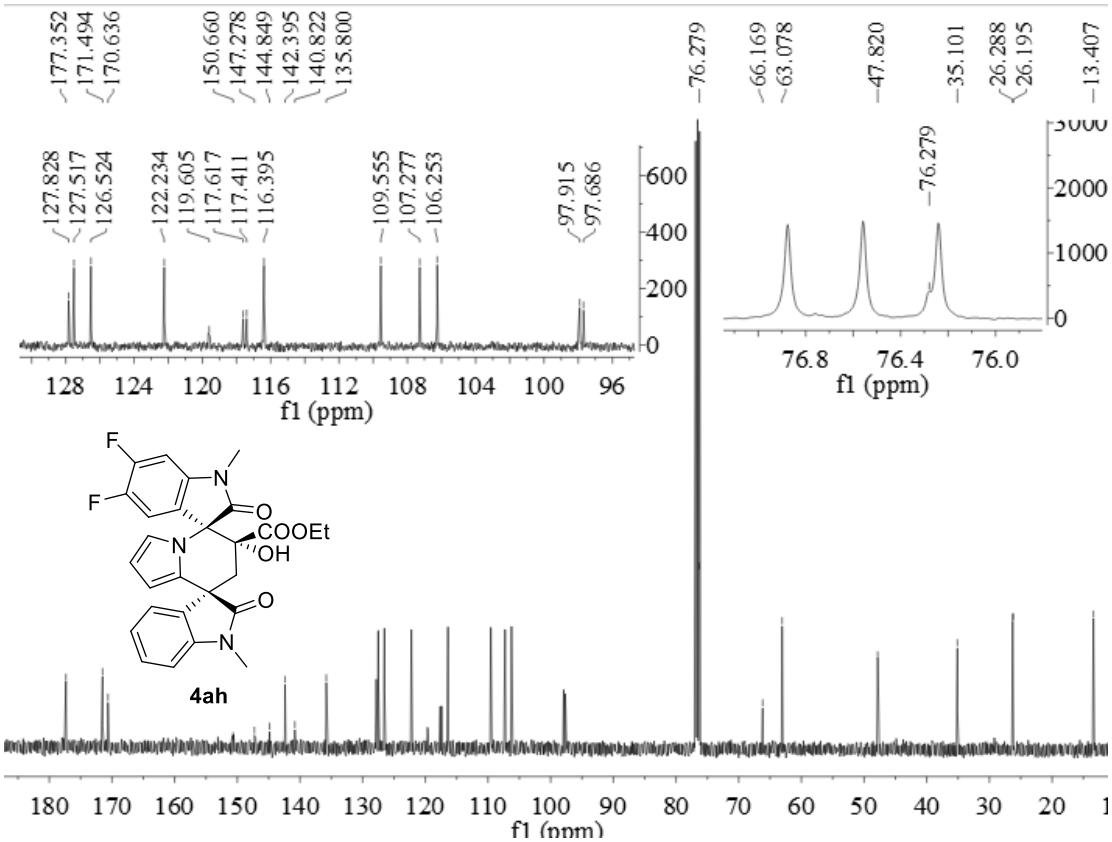




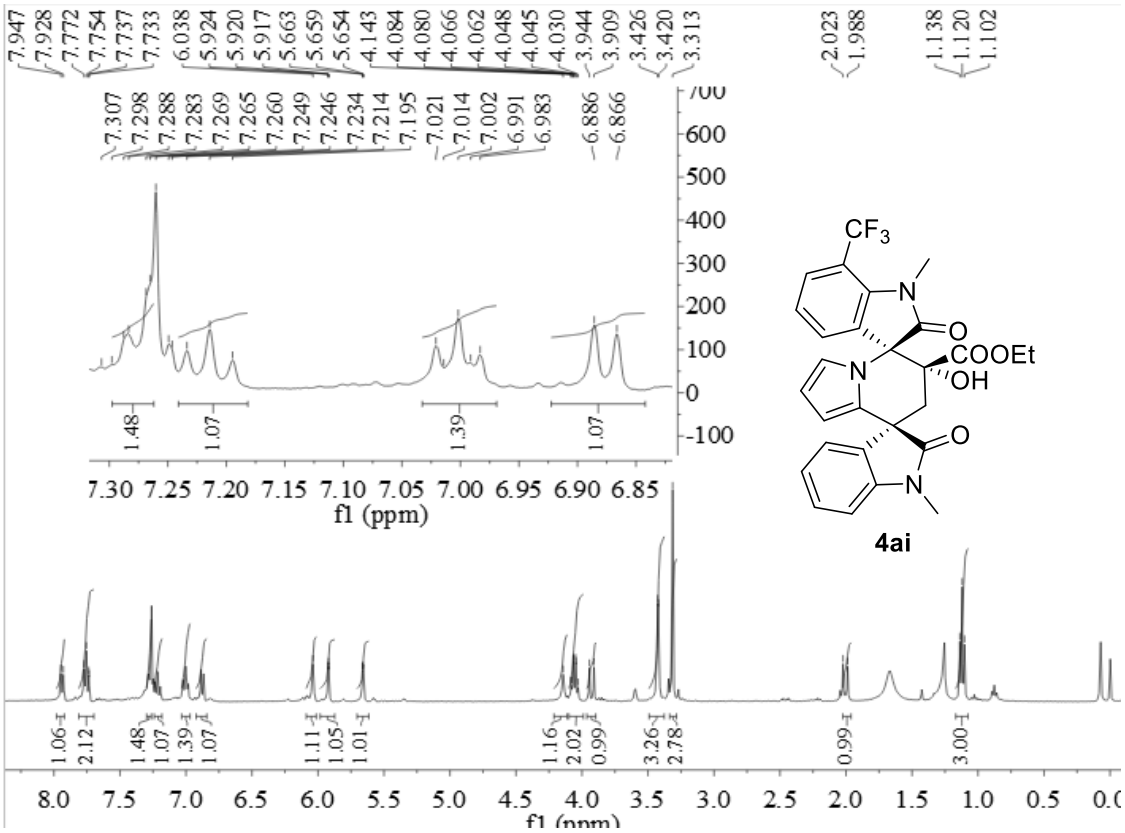
ethyl(3R,6'R,8'S)-5,6-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydro dispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ah

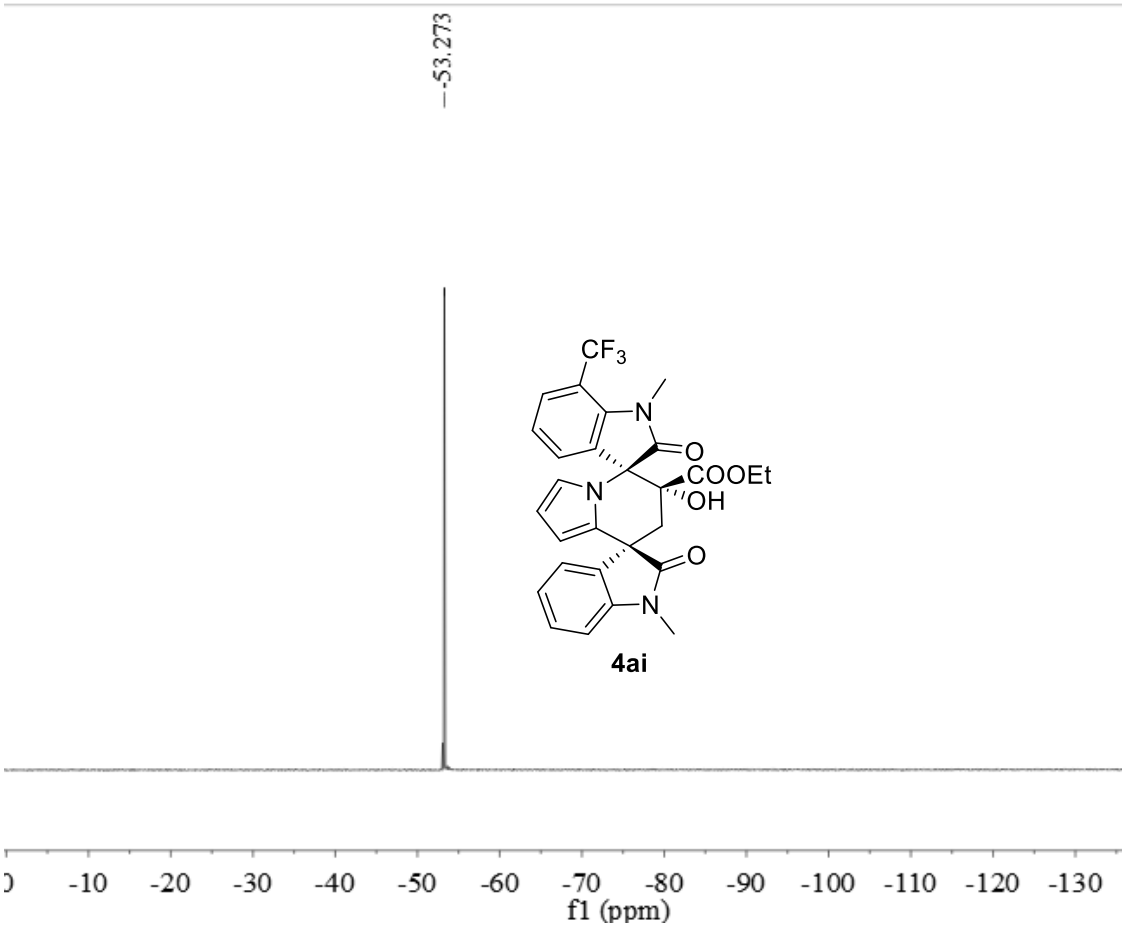

7.748
7.729
7.658
7.638
7.634
7.615
6.033
6.024
6.016
5.904
5.900
5.897
5.893
5.637
5.633
5.628
5.624
4.136
4.124
4.106
4.097
4.089
4.079
4.072
4.062
4.054
3.937
3.902
3.302
3.179
2.012
1.978
1.129
1.112
1.094
7.285
7.282
7.265
7.260
7.246
7.020
7.001
6.982
6.880
6.861
6.751
6.736
6.727
6.712
1.35
1.12
1.02
1.00
f1 (ppm)
1.05
1.03
1.35
1.12
1.02
1.00
1.04
0.97
0.96
3.15
1.02
2.95
3.03
1.10
3.00
f1 (ppm)
F
F
N
O
COOEt
OH
N
O
N
4ah

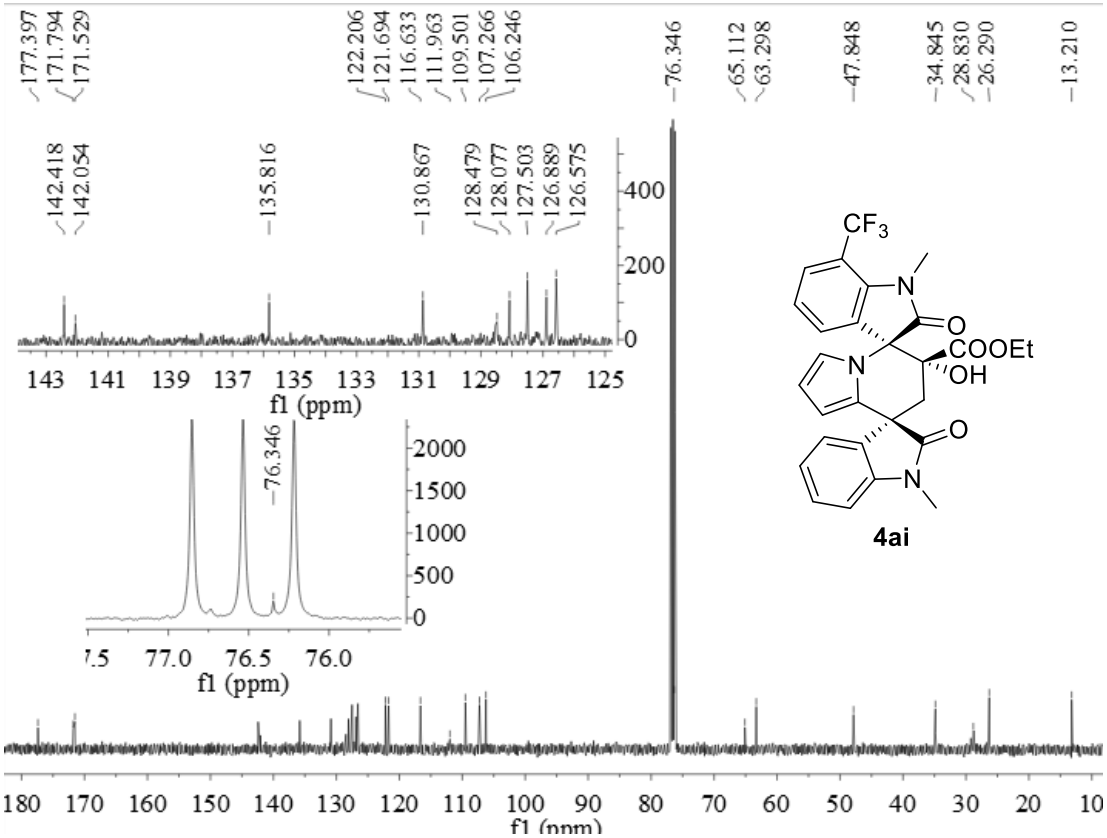

-131.900
-131.952
-144.328
-144.381
F
F
N
O
COOEt
OH
N
O
N
4ah
f1 (ppm)



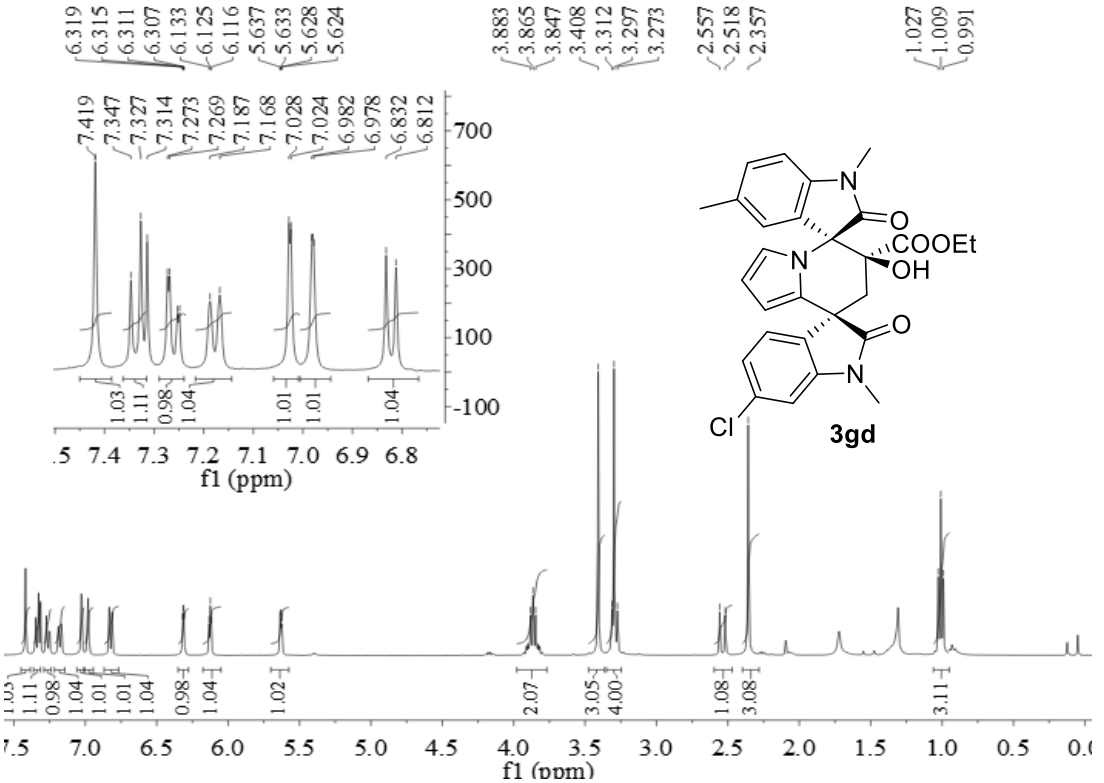
ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ai

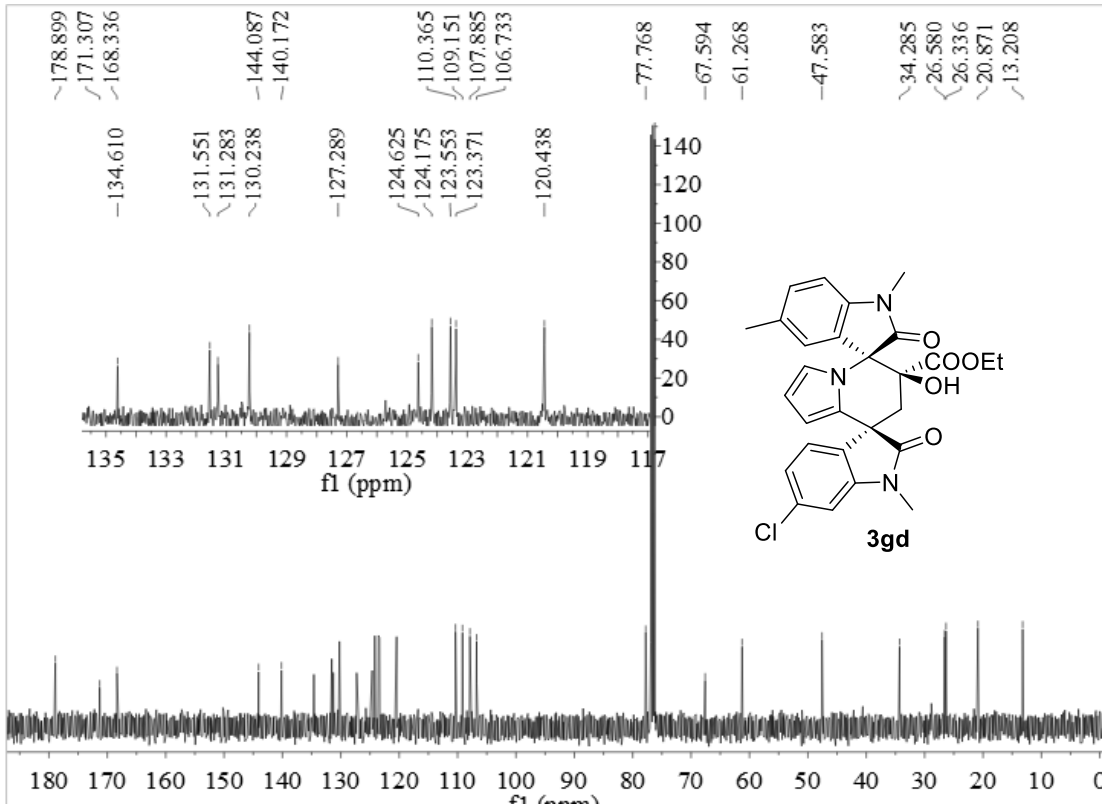



-53.273
CF3
N
O
COOEt
OH
N
O
N
4ai
f1 (ppm)

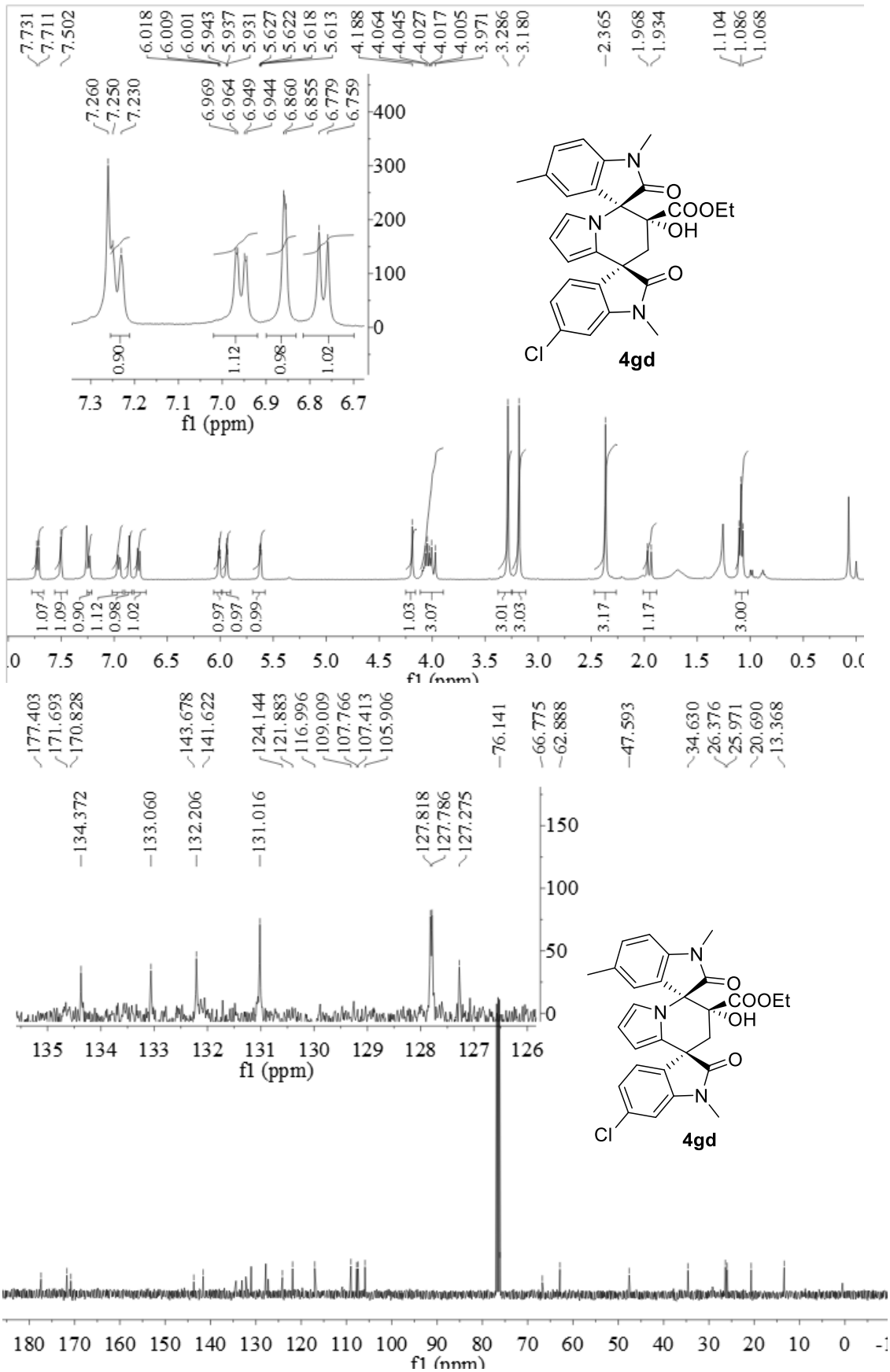

177.397
171.794
171.529
122.206
121.694
116.633
111.963
109.501
107.266
106.246
76.346
65.112
63.298
47.848
34.845
28.830
26.290
13.210
142.418
142.054
135.816
130.867
128.479
128.077
127.503
126.889
126.575
400
200
0
143 141 139 137 135 133 131 129 127 125
f1 (ppm)
76.346
2000
1500
1000
500
0
77.5 77.0 76.5 76.0
f1 (ppm)
CF3
N
O
COOEt
OH
N
O
N
4ai
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydro dispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3hd or *ent*-3gd

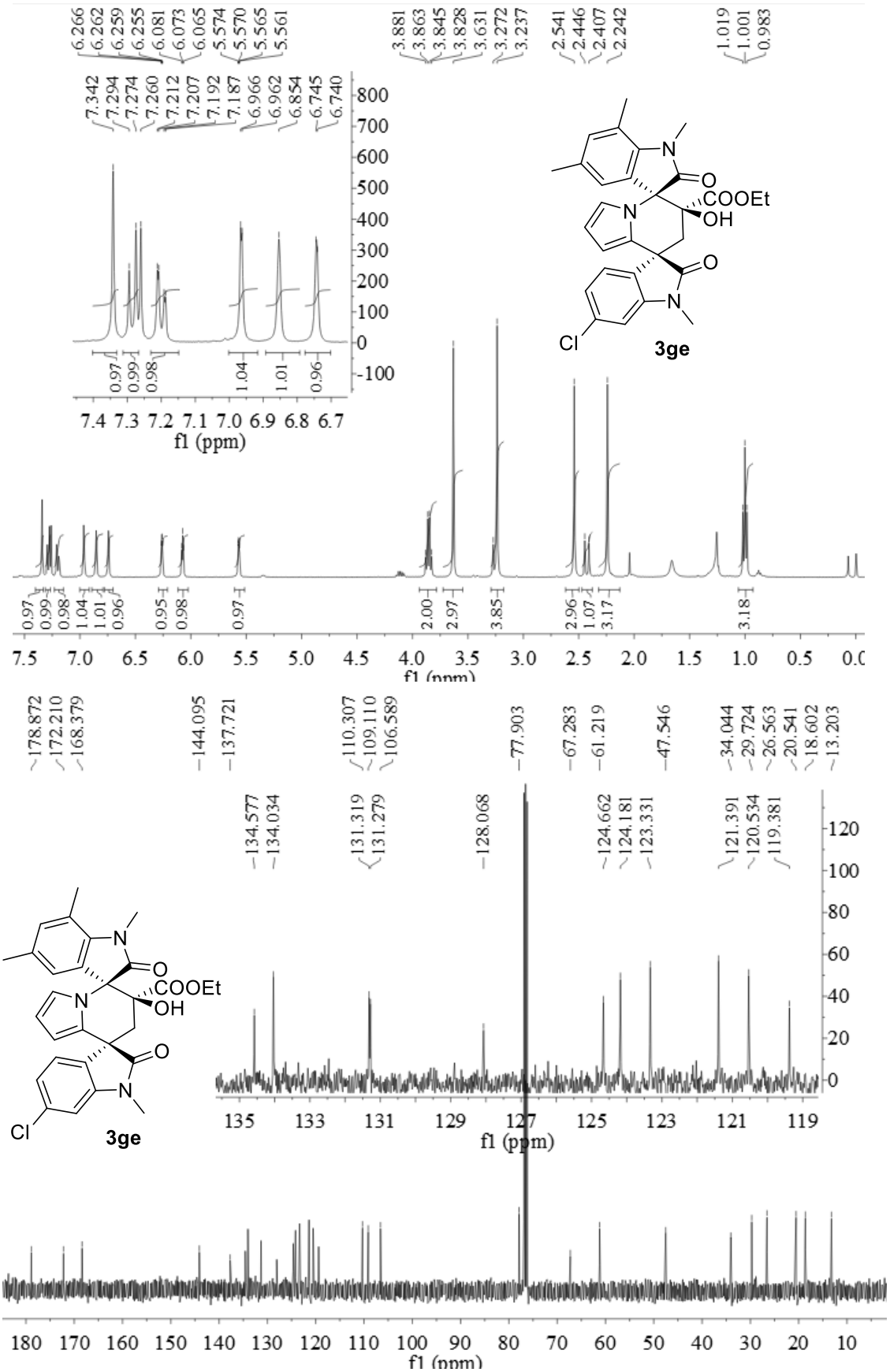




ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydr odispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4hd or *ent*-4gd

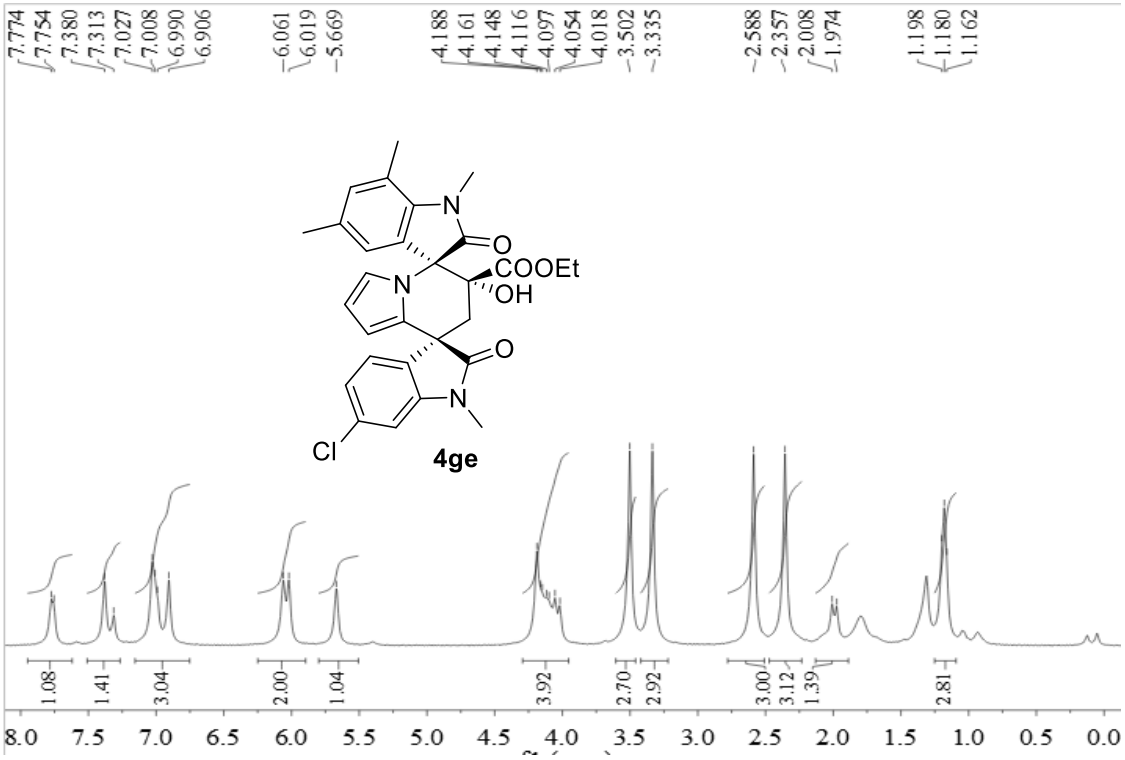


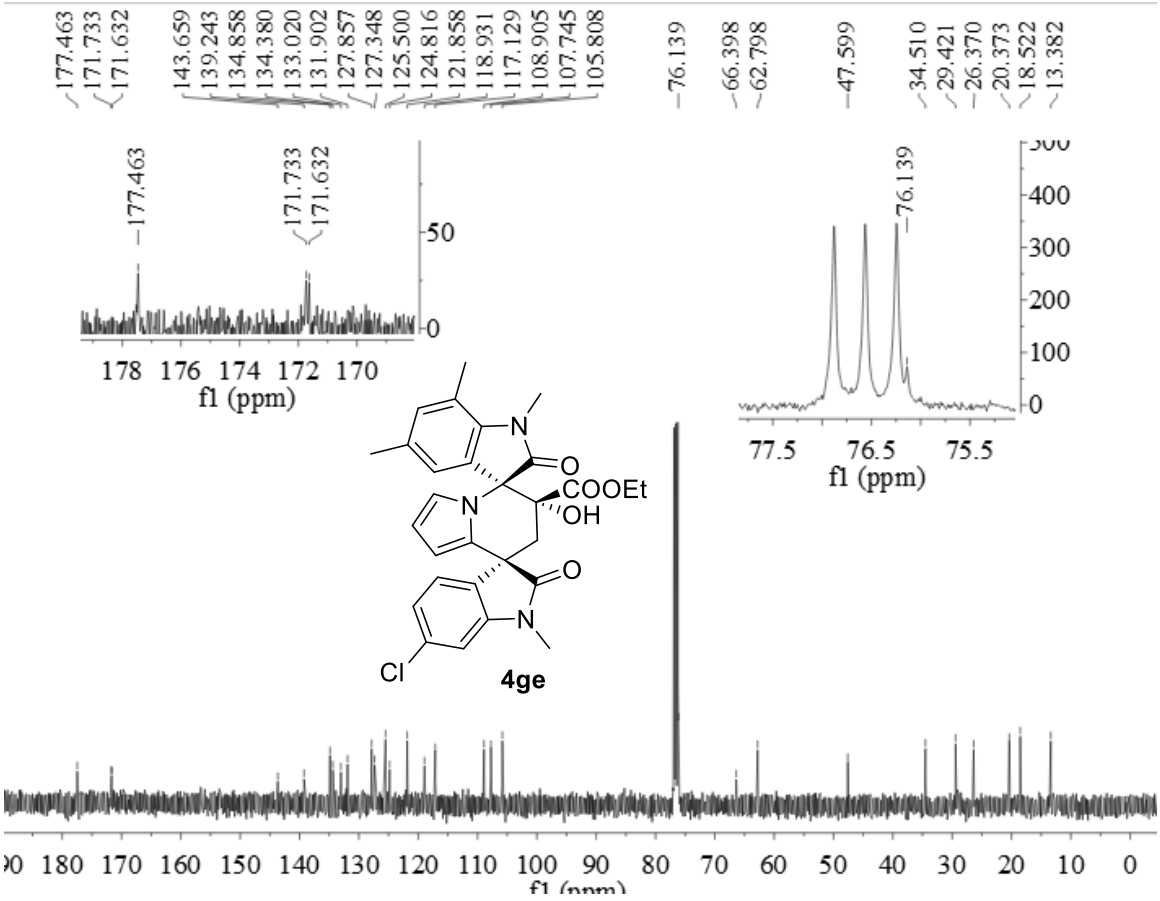
ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3he or *ent*-3ge



ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dih

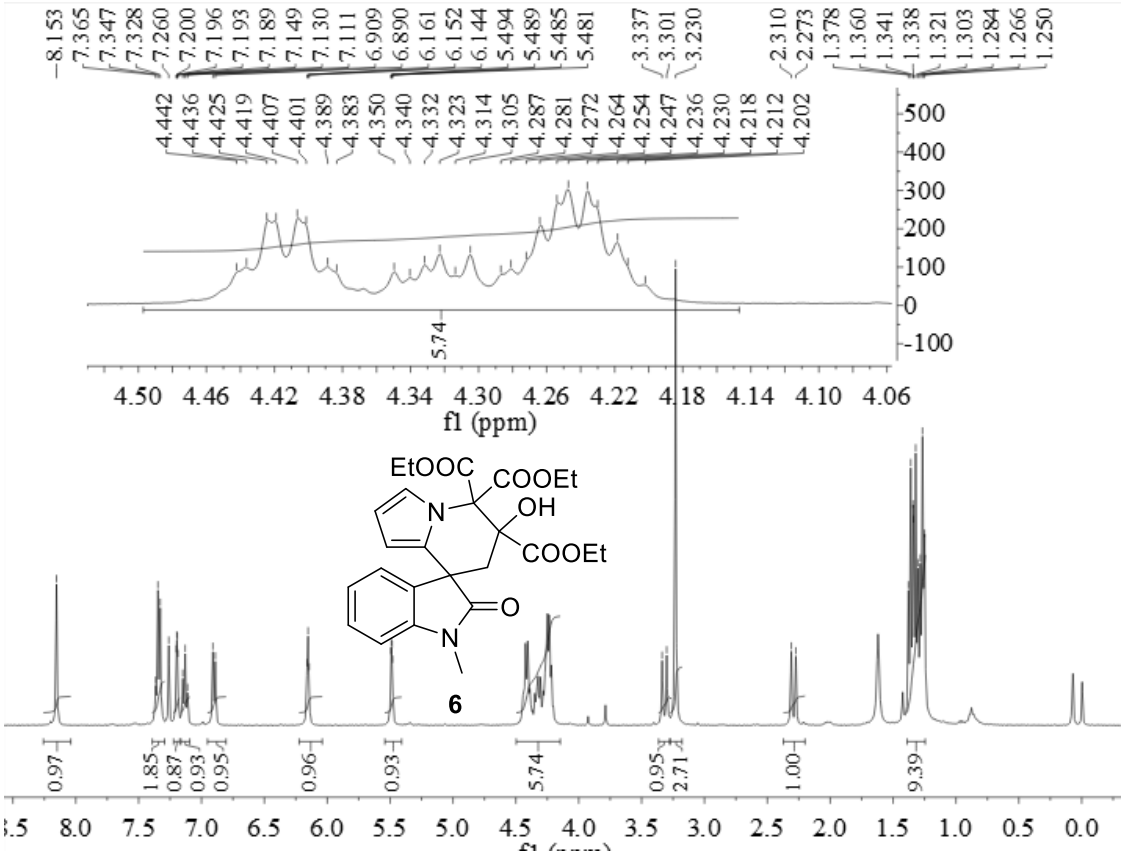
ydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4he or *ent*-4ge

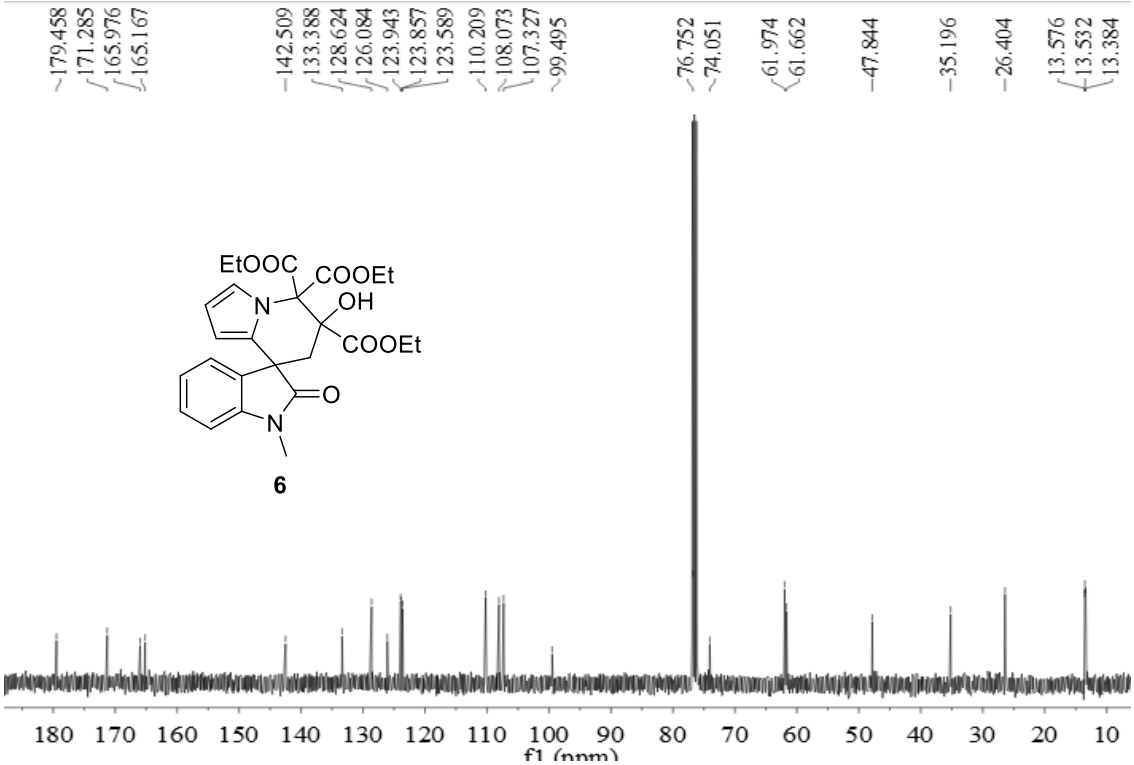




triethyl6'-hydroxy-1-methyl-2-oxo-6',7'-dihydro-5'H-spiro[indoline-3,8'-indolizin

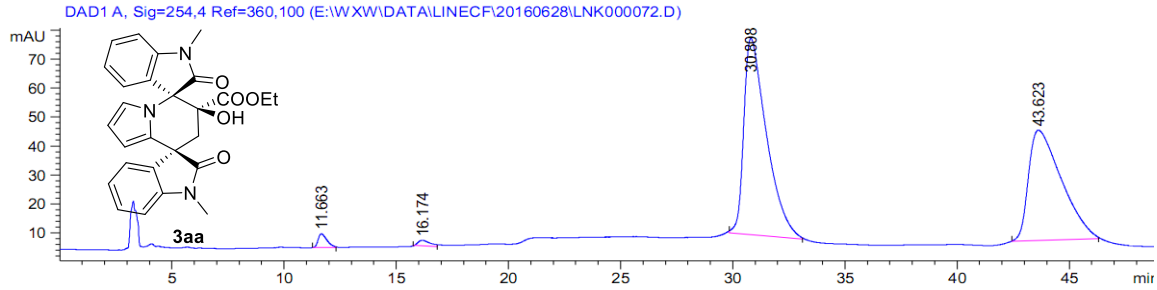
e]-5',5',6'-tricarboxylate 6



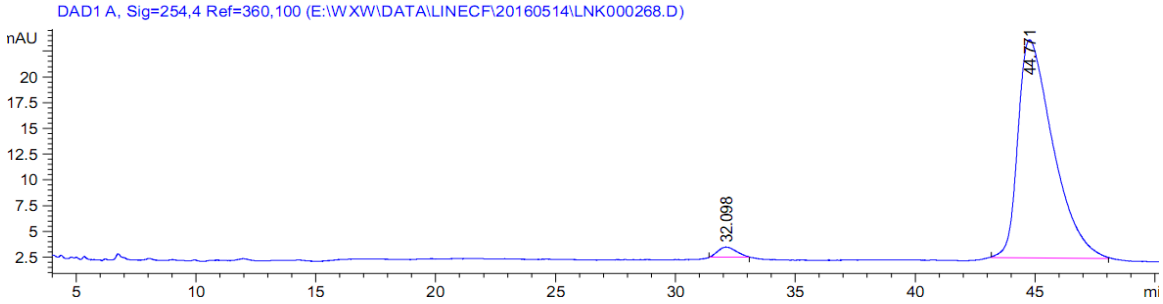


5. HPLC spectra

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3aa

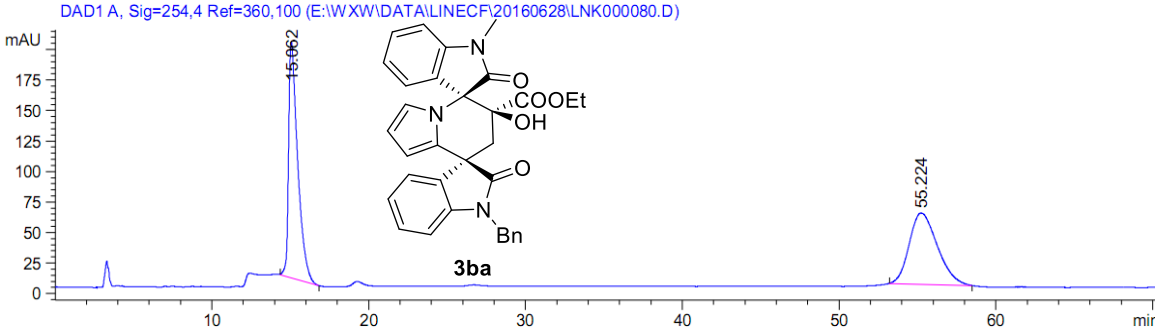


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.663	BB	0.4046	128.82217	4.74679	1.4542
2	16.174	MM R	0.6156	70.79432	1.91667	0.7991
3	30.808	BB	1.0100	4768.95068	67.68413	53.8332
4	43.623	BB	1.4102	3890.19458	38.06848	43.9135

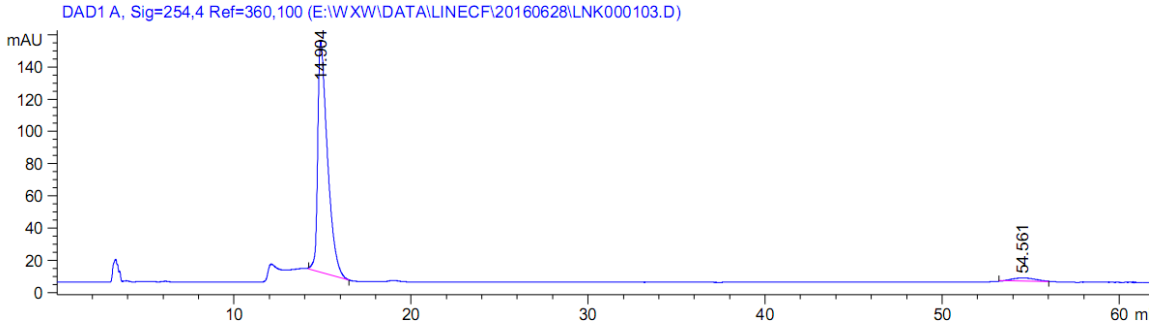


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.098	MM R	0.8896	52.65709	9.86549e-1	2.3816
2	44.771	MM R	1.6991	2158.37769	21.17238	97.6184

ethyl(3R,6'S,8'S)-1''-benzyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ba

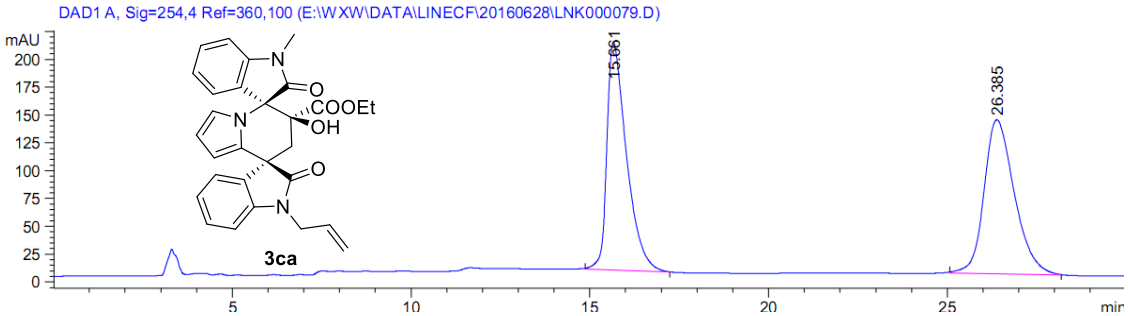


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.062	BB	0.5921	7796.20605	193.47450	51.6406
2	55.224	BB	1.7736	7300.84766	58.35640	48.3594

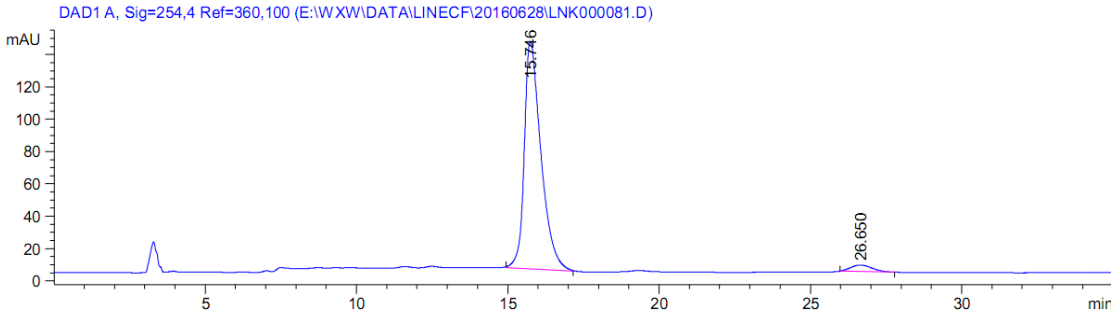


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.904	BB	0.5734	5507.76709	142.99634	96.6538
2	54.561	MM R	1.5471	190.68060	2.05412	3.3462

ethyl(3R,6'S,8'S)-1''-allyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ca

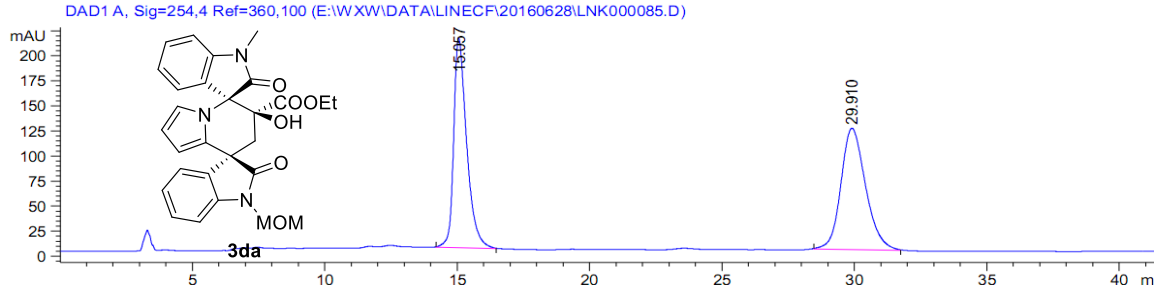


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.661	BB	0.5676	7823.24902	204.81892	48.9802
2	26.385	BB	0.8996	8149.00928	138.26909	51.0198

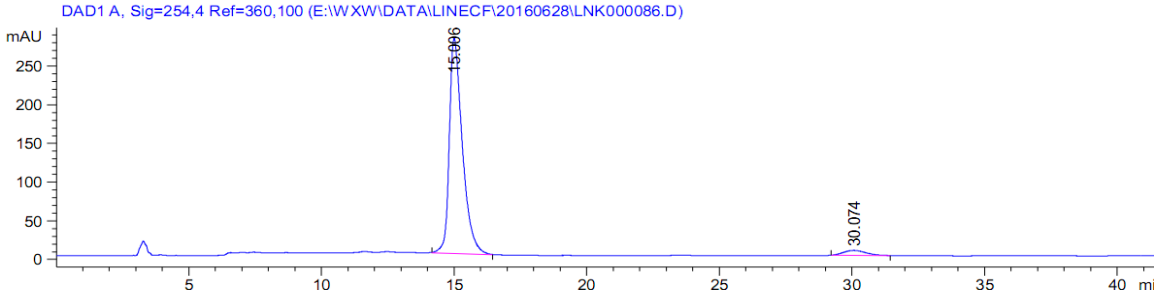


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.746	BB	0.5704	5381.90381	140.65460	96.4144
2	26.650	BB	0.6230	200.14813	4.04689	3.5856

ethyl(3R,6'S,8'S)-6'-hydroxy-1''-(methoxymethyl)-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3da

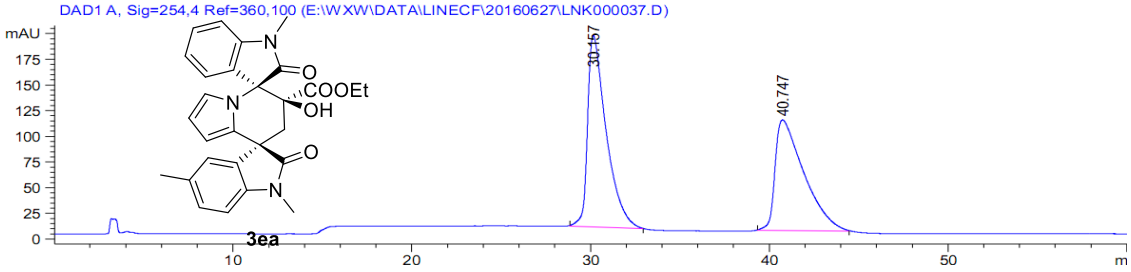


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.057	BB	0.5111	7130.04248	209.46086	47.6372
2	29.910	BB	0.9956	7837.35254	121.01861	52.3628

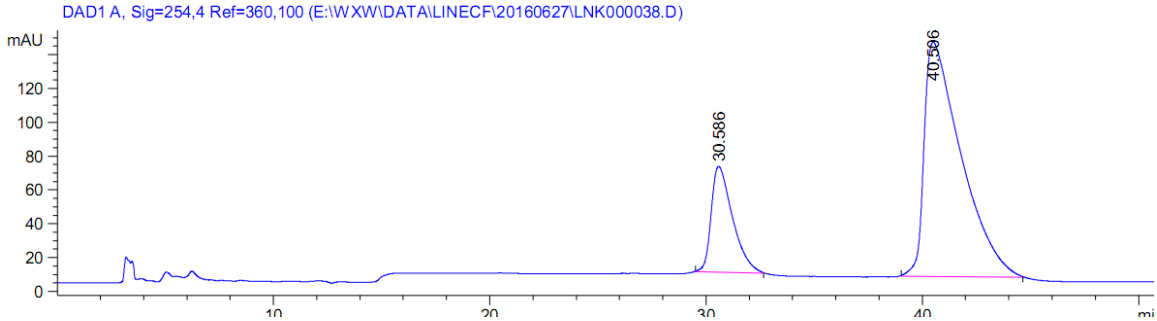


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.006	BB	0.5124	9496.37500	278.07816	96.1944
2	30.074	BB	0.7355	375.68774	6.45041	3.8056

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ea

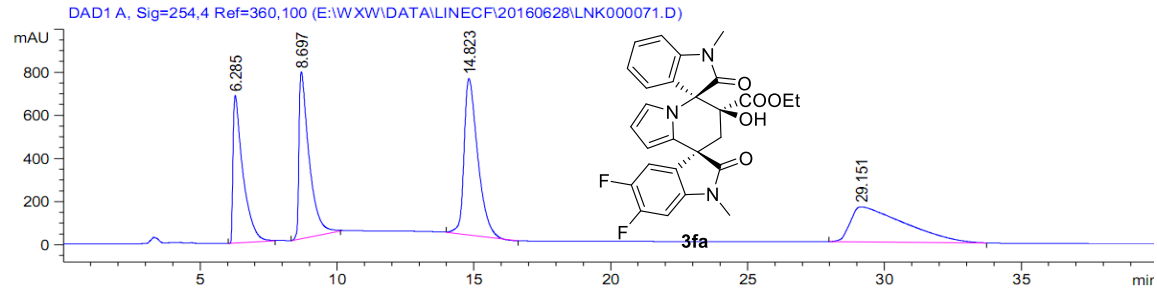


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.157	BB	1.0573	1.35181e4	186.56572	52.7769
2	40.747	BB	1.5274	1.20955e4	107.77081	47.2231

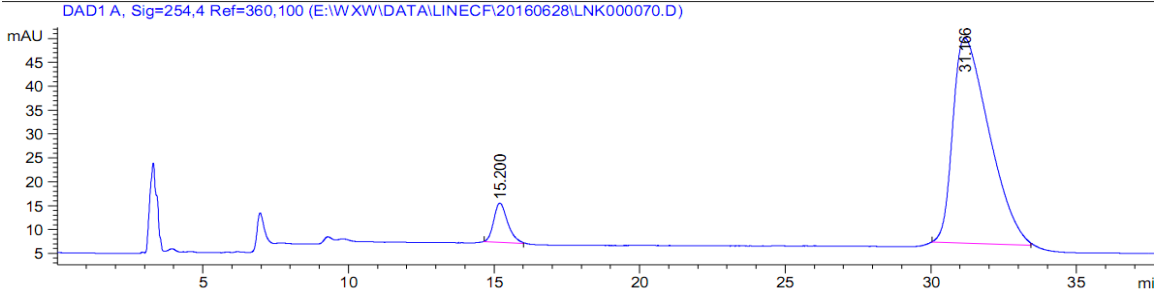


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.586	BB	0.9844	4293.83252	62.58365	20.6306
2	40.506	BB	1.6086	1.65191e4	138.59312	79.3694

ethyl(3R,6'S,8'S)-5'',6''-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3fa

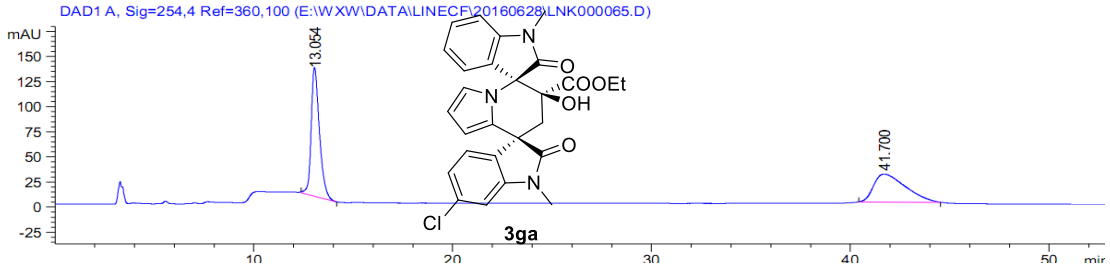


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.285	BB	0.3529	1.72849e4	683.76593	20.3019
2	8.697	BB	0.3700	2.00146e4	773.17438	23.5081
3	14.823	BB	0.5205	2.52780e4	725.42841	29.6901
4	29.151	BB	1.7649	2.25619e4	163.60869	26.4999

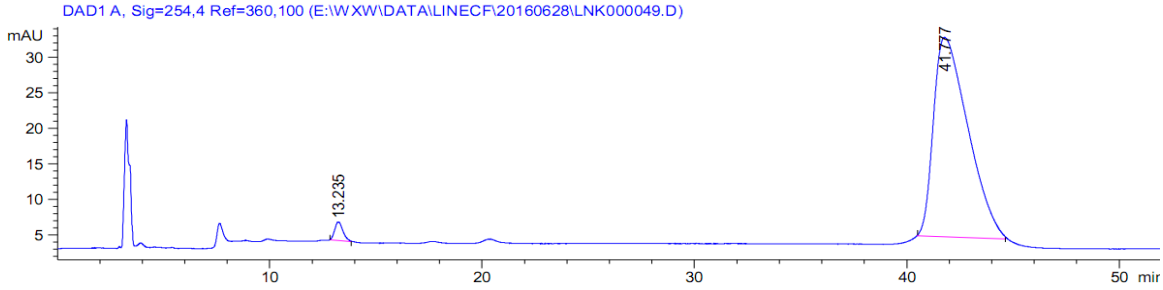


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.200	BB	0.5021	272.62802	8.23704	6.8450
2	31.166	BB	1.2090	3710.23828	42.98433	93.1550

ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodi spiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ga

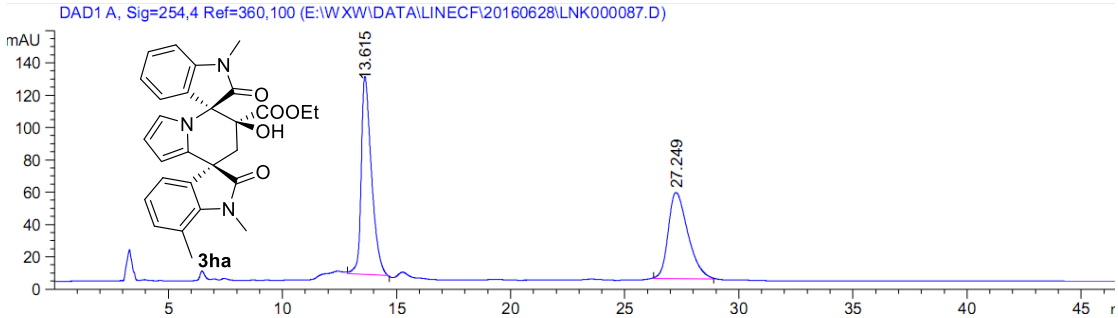


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.054	BB	0.4359	3714.87793	128.27119	54.2888
2	41.700	BB	1.4884	3127.93408	27.93376	45.7112

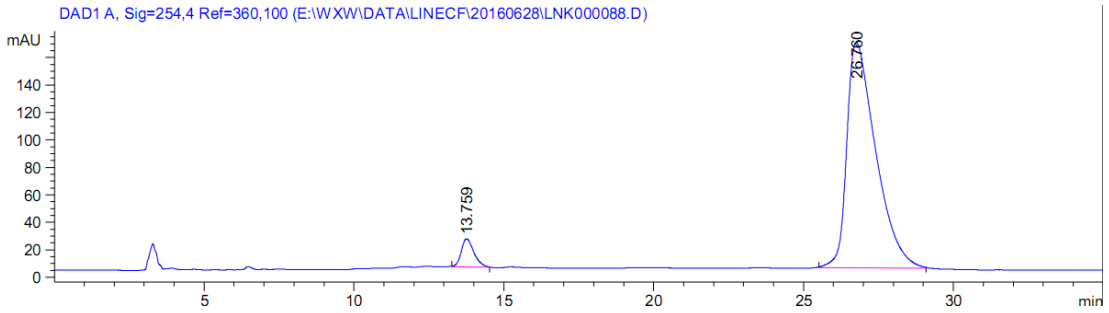


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.235	BB	0.3884	69.77161	2.62248	2.1591
2	41.777	BB	1.4784	3161.78003	28.06333	97.8409

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',7''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[i ndoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ha

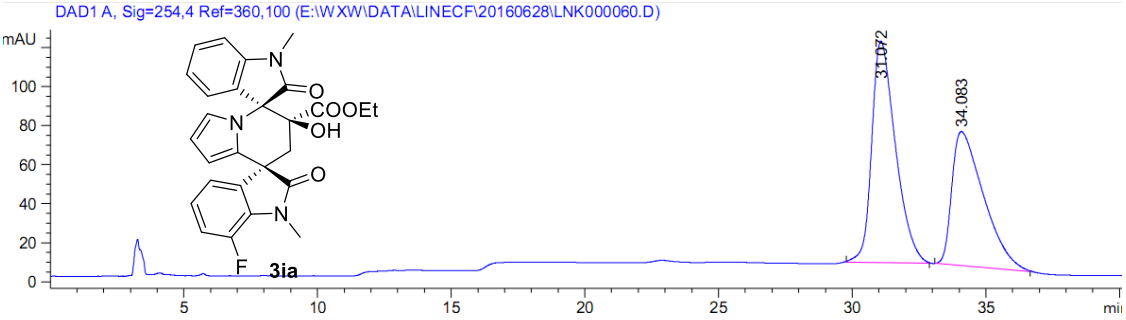


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.615	MM R	0.5202	3824.93701	122.54214	54.4986
2	27.249	BB	0.9030	3193.47754	53.30087	45.5014

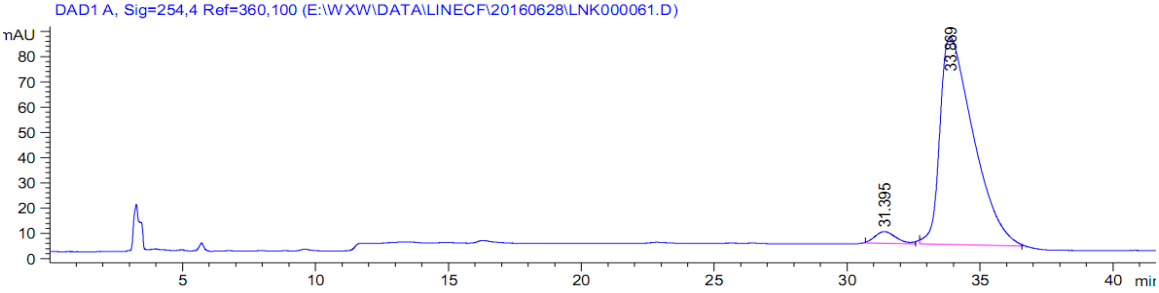


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.759	BB	0.4448	599.89398	20.53650	5.1681
2	26.760	BB	0.9736	1.10078e4	164.30705	94.8319

ethyl(3R,6'S,8'S)-7''-fluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ia

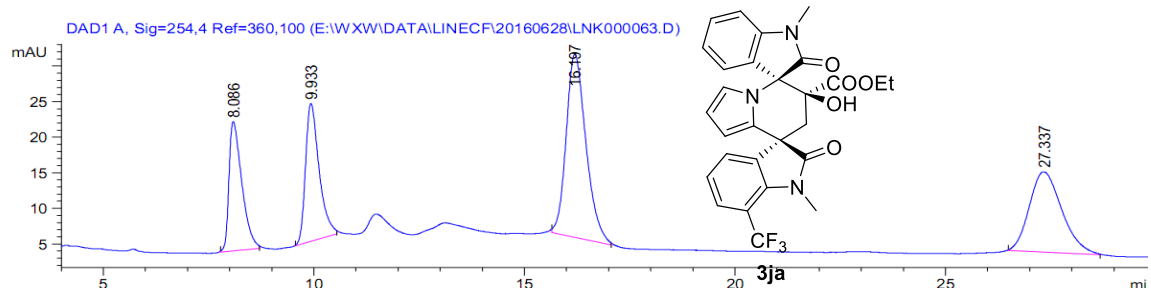


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.072	BB	0.9368	7035.45850	113.55798	55.3200
2	34.083	BB	1.1885	5682.30078	68.73003	44.6800

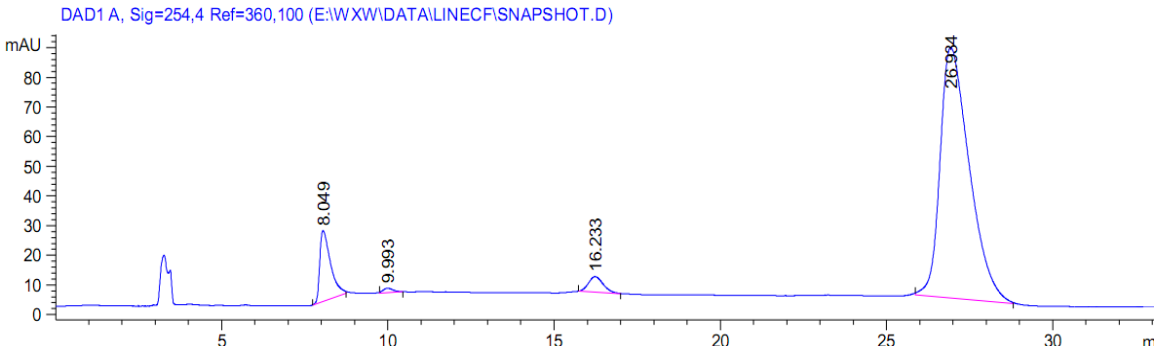


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.395	BB	0.6648	246.78447	4.53586	3.3276
2	33.869	BB	1.2550	7169.49561	82.08788	96.6724

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7''-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ja

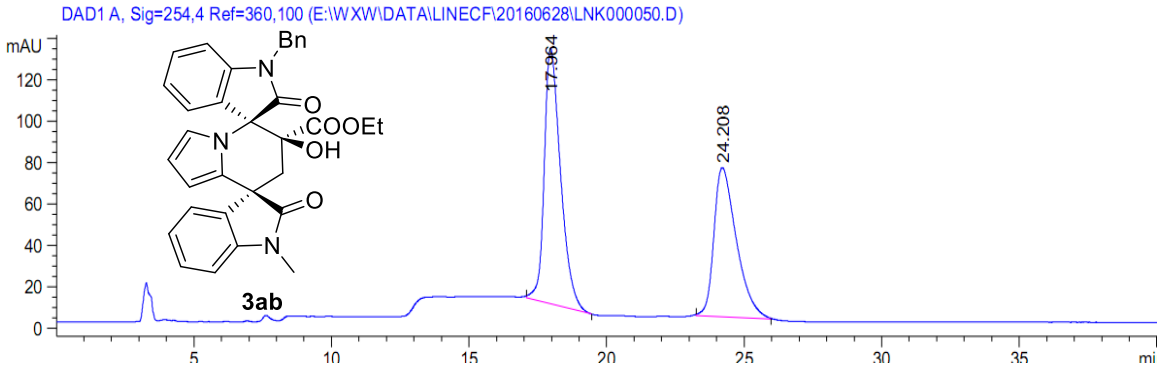


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.086	BB	0.3210	384.86307	18.18133	17.0006
2	9.933	BB	0.3397	434.51685	19.37179	19.1940
3	16.197	BB	0.4971	840.98096	25.74380	37.1488
4	27.337	BB	0.7784	603.45367	11.27564	26.6565

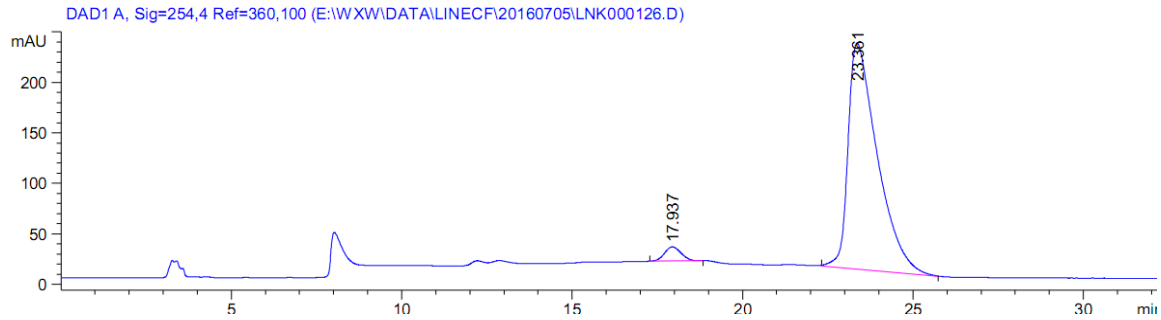


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.049	BB	0.3396	538.13025	23.81690	9.0984
2	9.993	MM R	0.4215	36.98940	1.46250	0.6254
3	16.233	BB	0.4542	162.34117	5.25765	2.7448
4	26.934	BB	0.9048	5177.11084	84.50356	87.5315

ethyl(3R,6'S,8'S)-1-benzyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ab

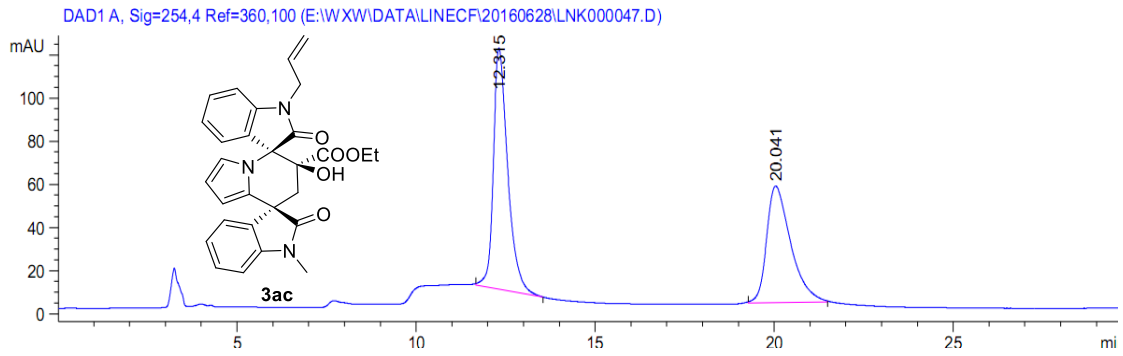


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.964	BB	0.6253	5087.22363	123.32282	55.3722
2	24.208	BB	0.8455	4100.10645	72.09806	44.6278

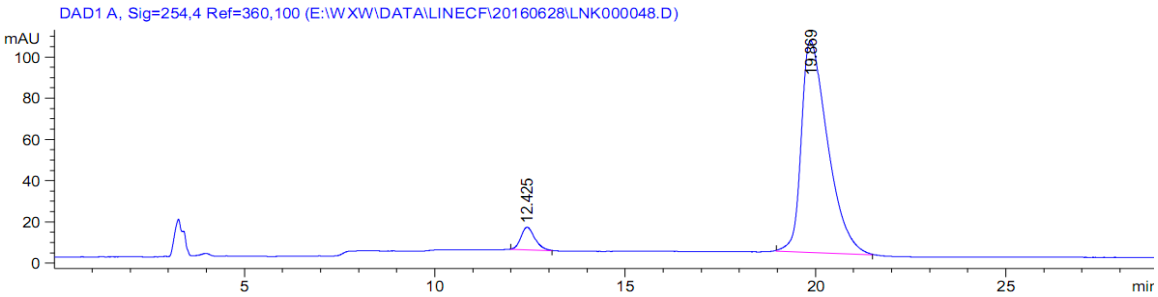


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.937	BB	0.5284	469.51559	13.95947	3.3987
2	23.361	BB	0.8883	1.33449e4	223.58569	96.6013

ethyl(3R,6'S,8'S)-1-allyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ac

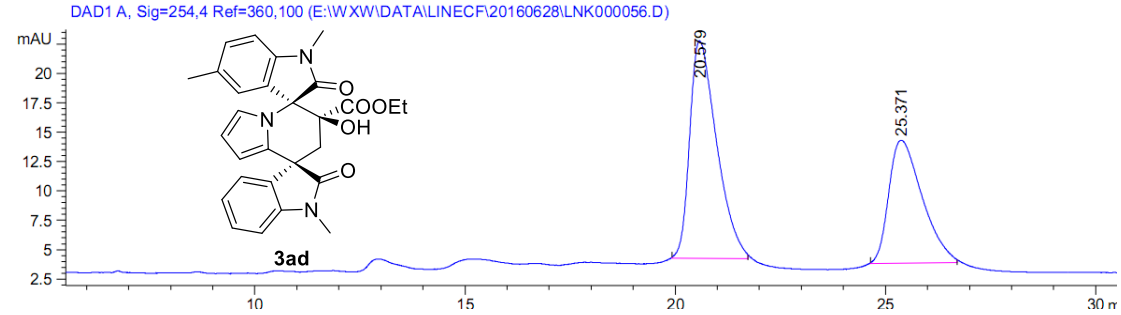


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.315	BB	0.4201	3123.50903	111.74386	55.3529
2	20.041	BB	0.6947	2519.38818	53.96105	44.6471

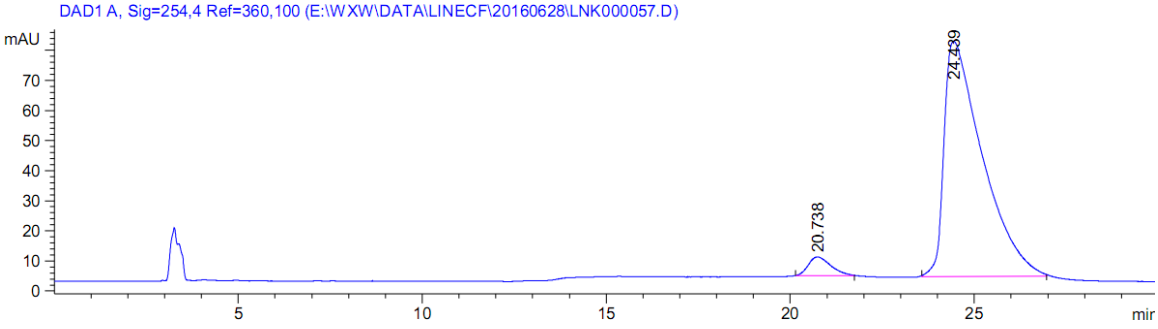


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.425	BB	0.3895	283.13516	11.02753	5.3877
2	19.869	BB	0.7256	4972.10449	102.92723	94.6123

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ad

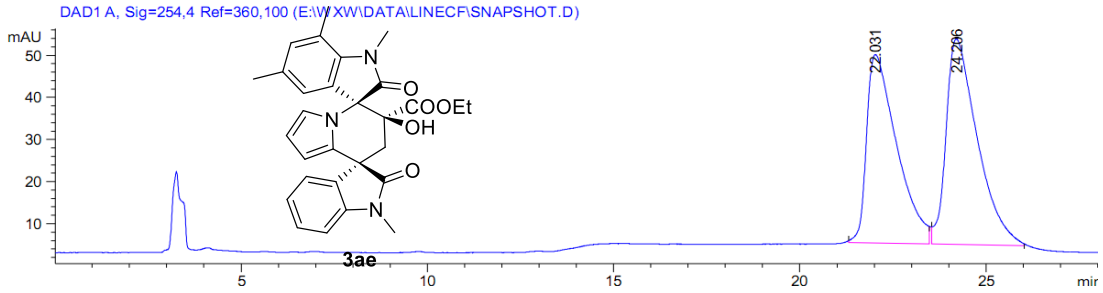


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.579	BB	0.6505	825.48279	18.50368	58.9018
2	25.371	BB	0.7650	575.97253	10.45091	41.0982

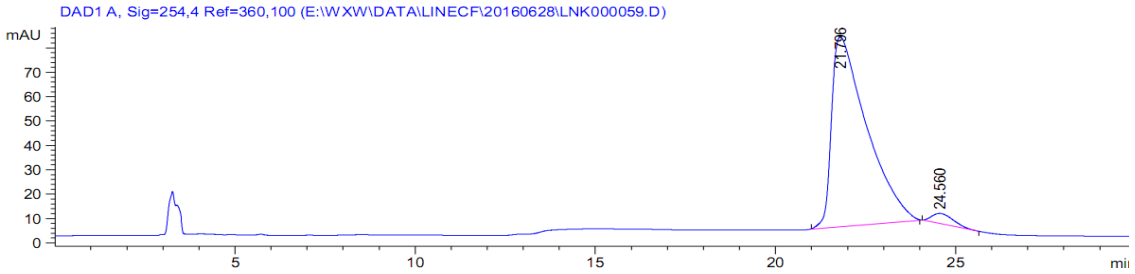


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.738	BB	0.6213	268.80820	6.25594	4.5201
2	24.439	BB	1.0228	5678.17480	78.23175	95.4799

ethyl(3R,6'S,8'S)-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ae

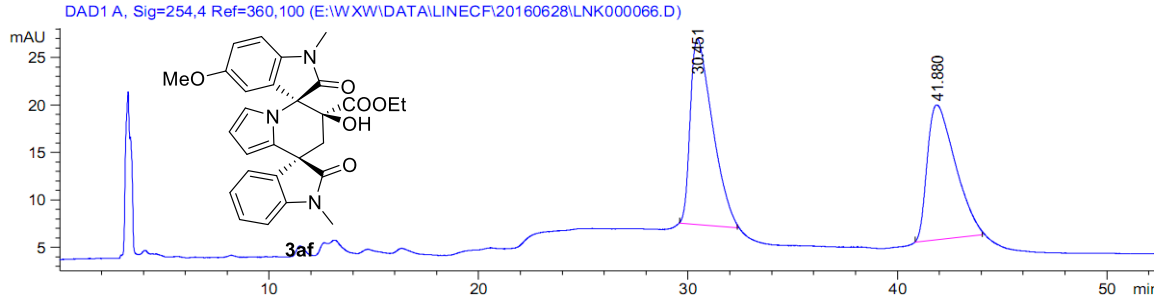


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.031	BB	0.8057	2512.06494	44.69767	46.8319
2	24.206	BB	0.8484	2851.93579	48.76033	53.1681

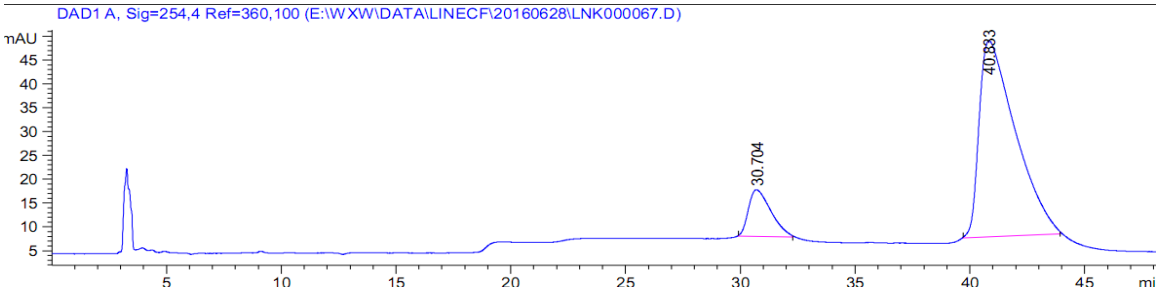


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.796	BB	0.9561	5292.00928	77.94000	96.8274
2	24.560	BB	0.5799	173.39516	4.14638	3.1726

ethyl(3R,6'S,8'S)-6'-hydroxy-5-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3af

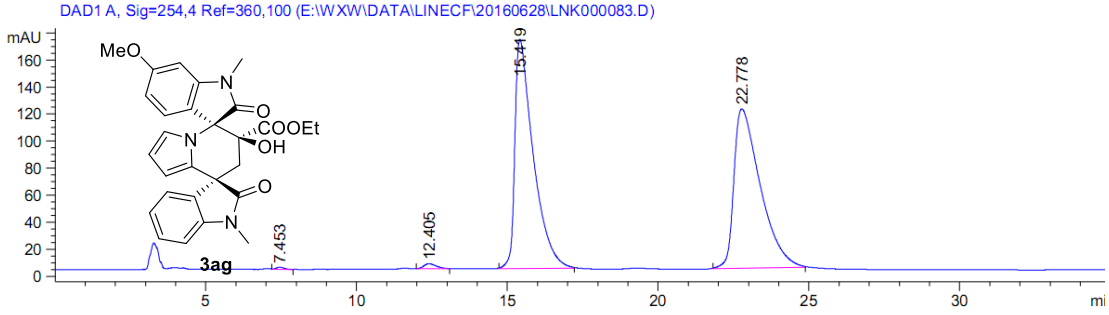


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.451	BB	1.0229	1446.77881	19.56049	52.3352
2	41.880	BB	1.2057	1317.66736	14.21112	47.6648

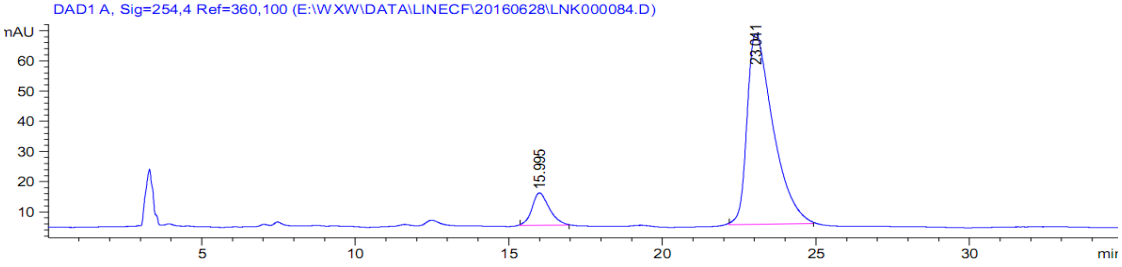


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.704	BB	0.8976	660.05243	9.77722	12.7573
2	40.833	BB	1.4866	4513.88232	41.18771	87.2427

ethyl(3R,6'S,8'S)-6'-hydroxy-6-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ag

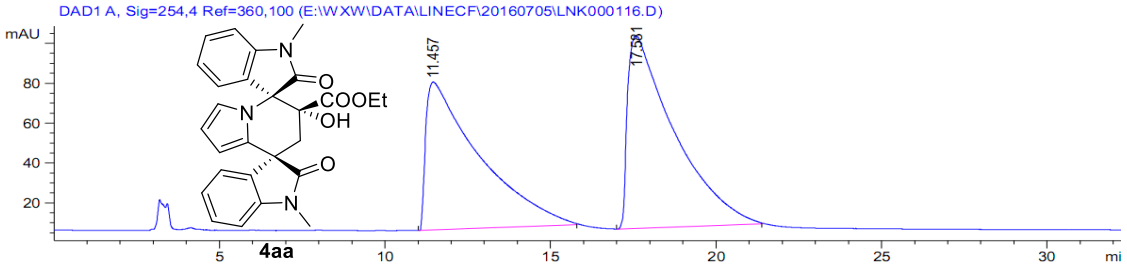


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.453	BB	0.2404	23.77424	1.50394	0.1646
2	12.405	BB	0.4354	107.48200	3.71706	0.7442
3	15.419	BB	0.6099	7156.93262	169.06561	49.5572
4	22.778	BB	0.8987	7153.58594	117.77079	49.5340

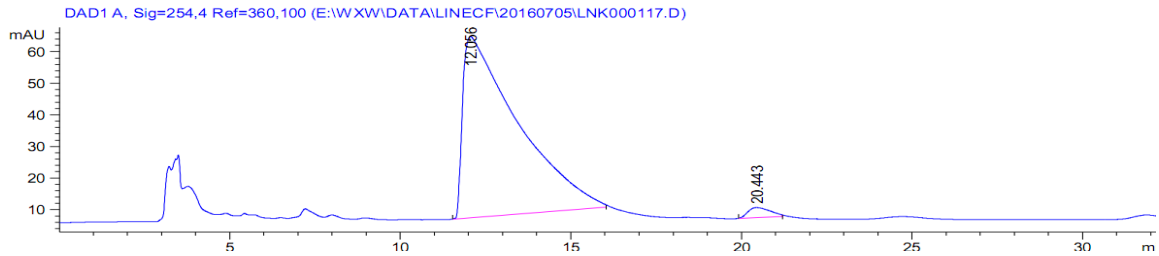


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.995	BB	0.5744	424.67615	10.76116	10.2712
2	23.041	BB	0.8766	3709.93652	63.04243	89.7288

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4aa

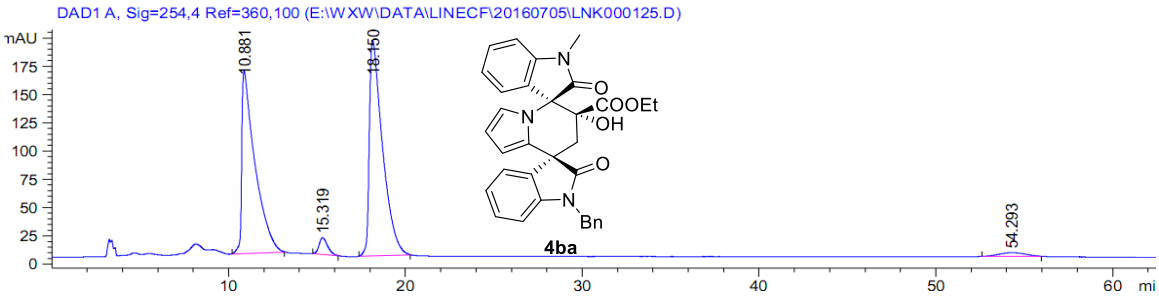


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.457	BB	1.4518	8312.74023	74.26776	46.7447
2	17.581	BB	1.3004	9470.53125	96.71484	53.2553

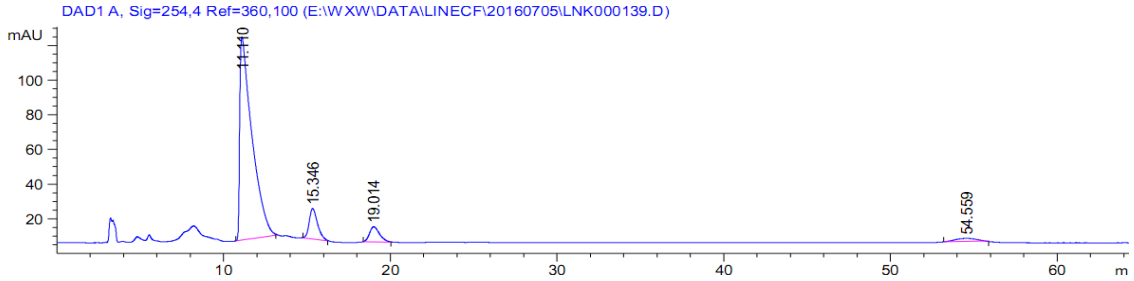


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.056	BB	1.4329	6419.70898	57.39798	97.8065
2	20.443	MM R	0.7557	143.97728	3.17527	2.1935

ethyl(3R,6'R,8'S)-1''-benzyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ba

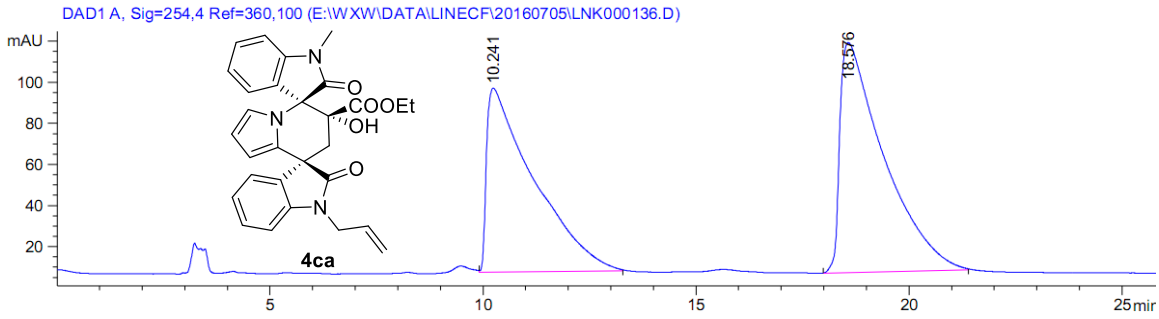


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.881	BB	0.6987	8437.78906	161.72289	44.0499
2	15.319	BB	0.5101	495.84161	14.75192	2.5886
3	18.150	BB	0.7437	9919.44922	191.05685	51.7850
4	54.293	MM R	1.6339	301.98962	3.08042	1.5766

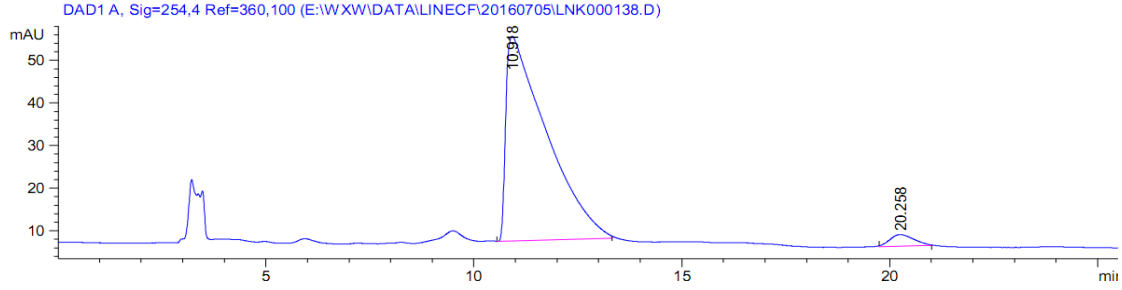


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.110	BB	0.7043	5978.67334	117.36501	84.1018
2	15.346	BB	0.5297	611.30591	17.58002	8.5992
3	19.014	BB	0.6056	367.10602	8.78307	5.1641
4	54.559	MM R	1.4402	151.76411	1.75624	2.1349

ethyl(3R,6'R,8'S)-1''-allyl-6'-hydroxy-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ca

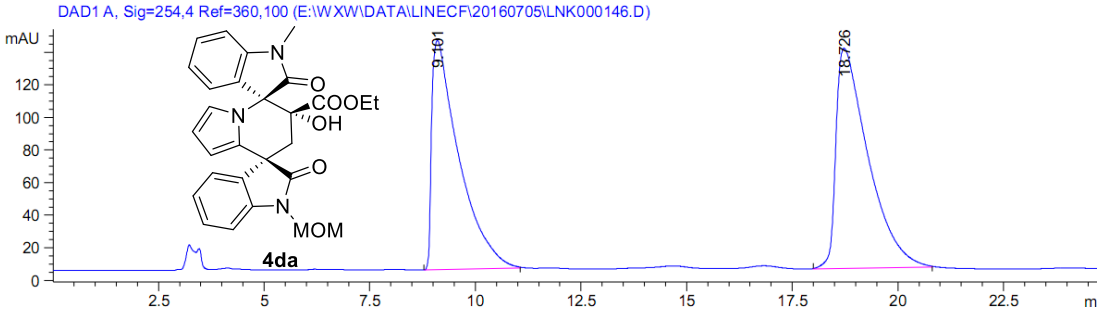


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.241	VB	0.9978	6889.79590	89.73499	46.1149
2	18.576	BB	0.9776	8050.71826	111.87263	53.8851

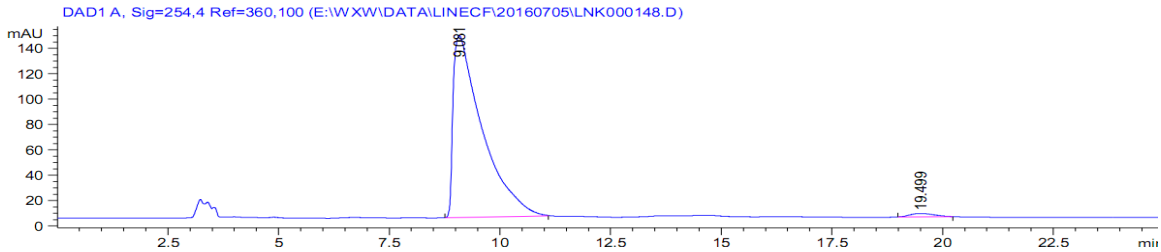


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.918	BB	0.8802	3261.38501	48.02853	96.7177
2	20.258	MM R	0.6745	110.68054	2.73470	3.2823

ethyl(3R,6'R,8'S)-6'-hydroxy-1''-(methoxymethyl)-1-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4da

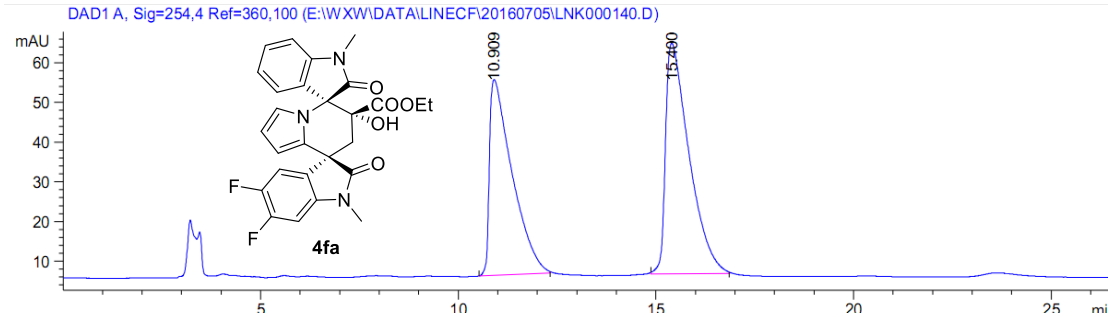


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.101	BB	0.6236	6287.42627	140.63007	46.7487
2	18.726	BB	0.7703	7161.99512	135.14900	53.2513

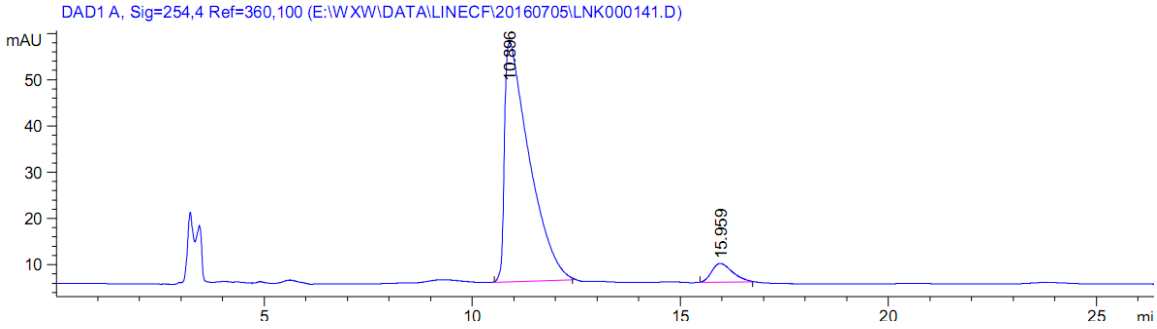


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.081	BB	0.6331	6564.95166	143.66658	98.4208
2	19.499	BB	0.4576	105.33597	2.78266	1.5792

ethyl(3R,6'R,8'S)-5'',6''-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4fa

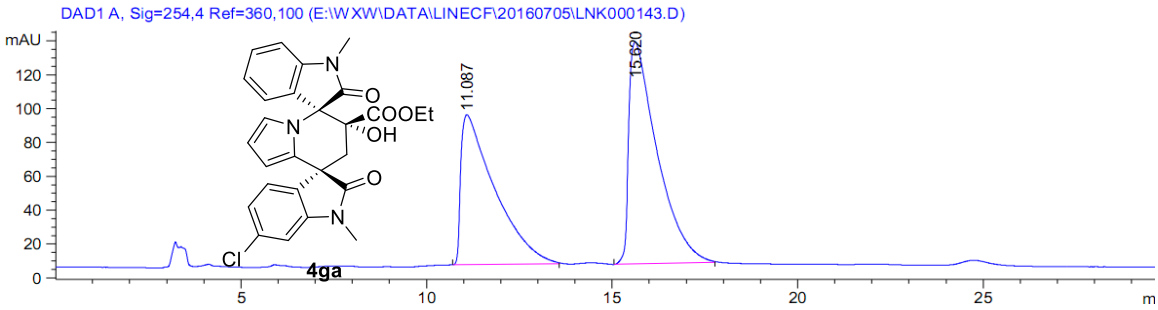


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.909	BB	0.5509	1967.33801	49.37359	44.9808
2	15.400	BB	0.6113	2406.38647	58.08821	55.0192

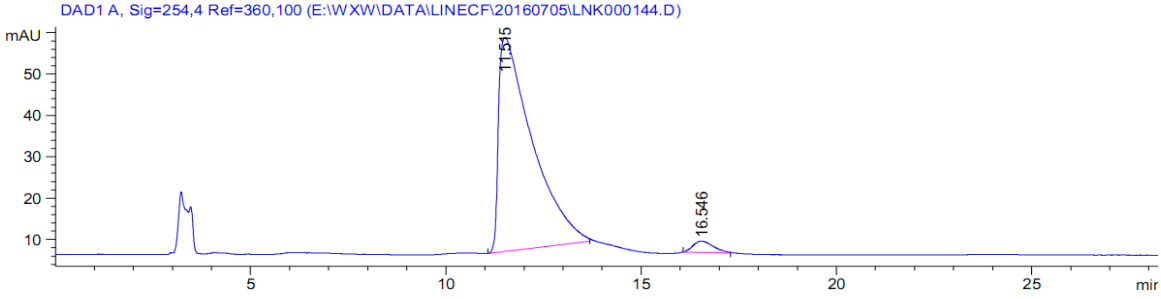


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.896	BB	0.5939	7543.13623	180.36272	93.2606
2	15.960	BB	0.5395	545.09442	14.73669	6.7394

ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodi spiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ga

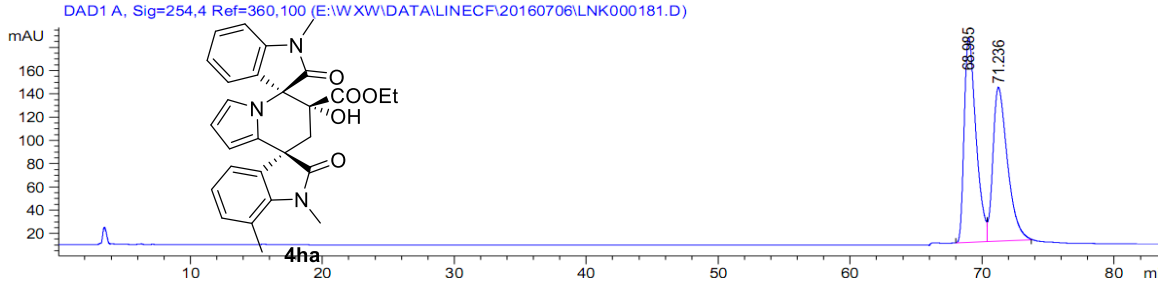


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.087	BB	0.8558	5606.50049	88.65630	44.6188
2	15.620	BB	0.7586	6958.84473	131.24751	55.3812

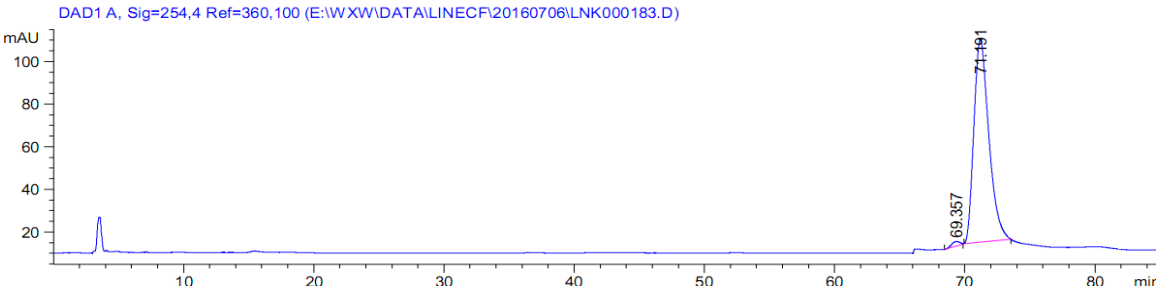


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.515	BB	0.8336	3088.57397	51.65327	96.8777
2	16.546	BB	0.4751	99.54147	2.75794	3.1223

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',7''-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ha

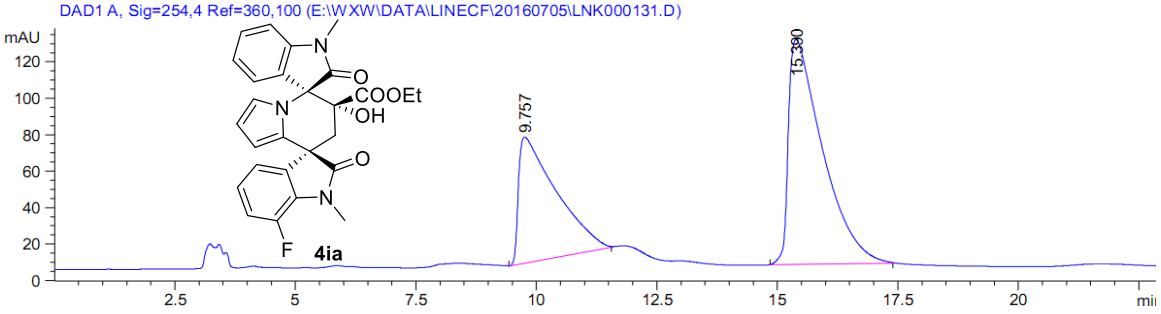


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.985	BV	0.9451	1.09506e4	176.18347	51.8638
2	71.236	VB	1.1540	1.01636e4	132.33456	48.1362

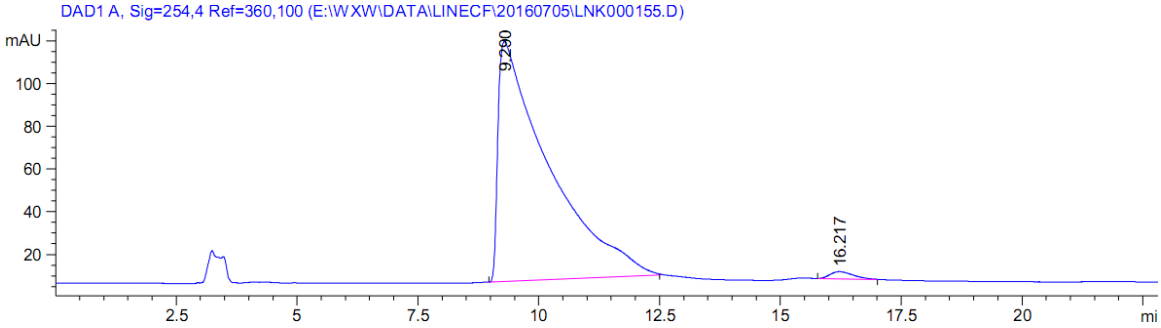


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.357	MM R	0.7311	93.25182	2.12577	1.2139
2	71.191	MM R	1.2816	7588.82520	94.99877	98.7861

ethyl(3R,6'R,8'S)-7''-fluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ia

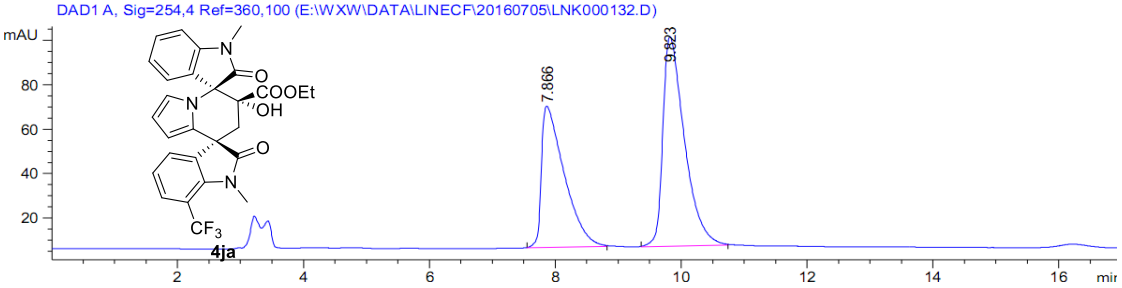


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.757	BB	0.7260	3734.20020	69.14733	37.9558
2	15.390	BB	0.7105	6104.09082	123.51839	62.0442

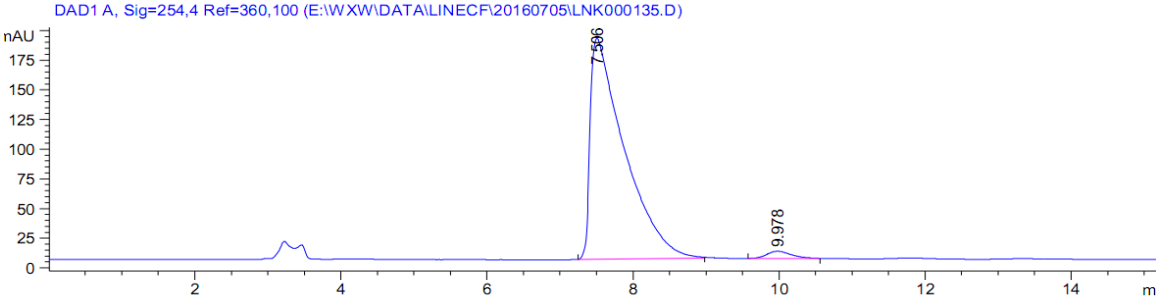


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.290	BB	0.9569	8208.55664	112.28548	98.6450
2	16.217	BB	0.4460	112.75404	3.35618	1.3550

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7''-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ja

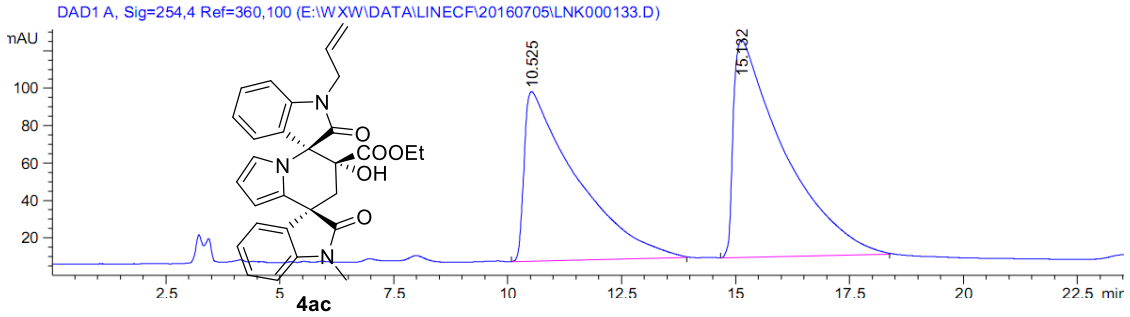


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.866	BB	0.3656	1600.62817	63.59448	41.6111
2	9.823	BB	0.3583	2246.00952	94.16921	58.3889

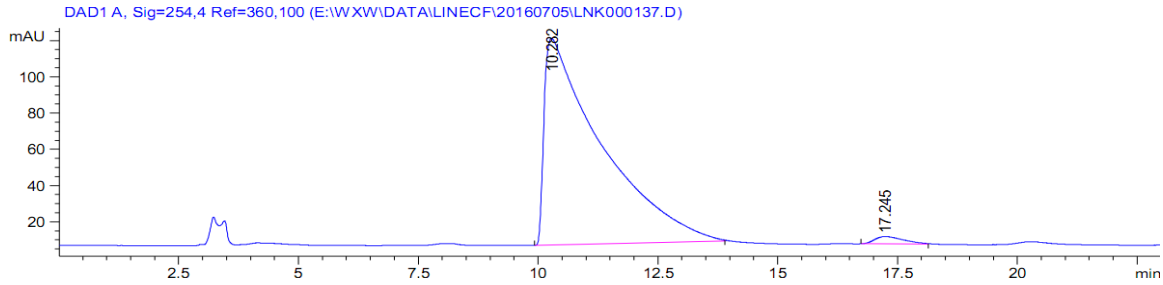


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.506	BB	0.4439	6036.15625	186.33029	97.7072
2	9.978	BB	0.3534	141.64317	6.04391	2.2928

ethyl(3R,6'R,8'S)-1-allyl-6'-hydroxy-1''-methyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ac

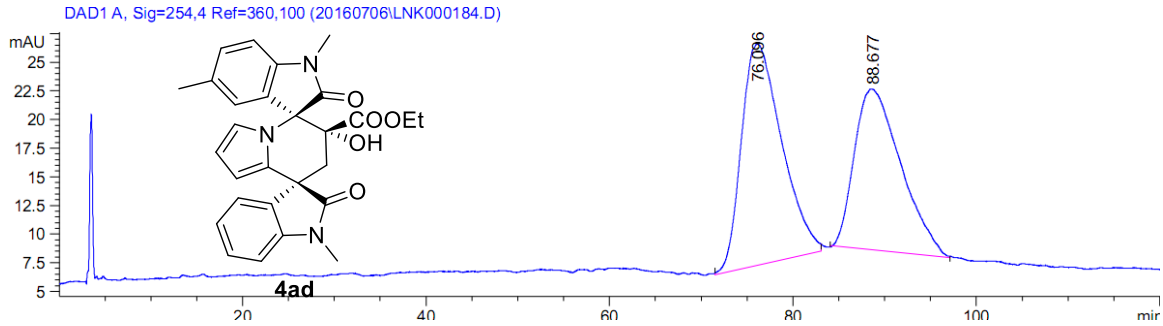


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.525	BB	1.0314	7244.99658	90.55166	44.6046
2	15.132	BB	1.0216	8997.70605	116.16976	55.3954

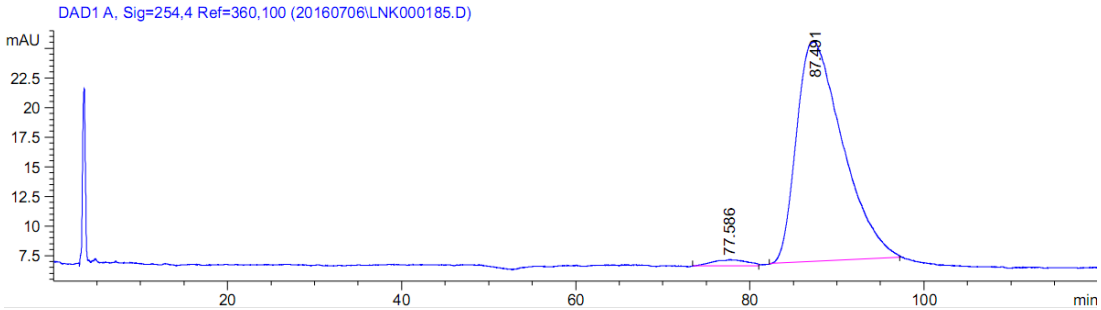


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.282	BB	1.0656	9474.59180	114.00687	98.2663
2	17.245	BB	0.5757	167.15695	4.01532	1.7337

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ad

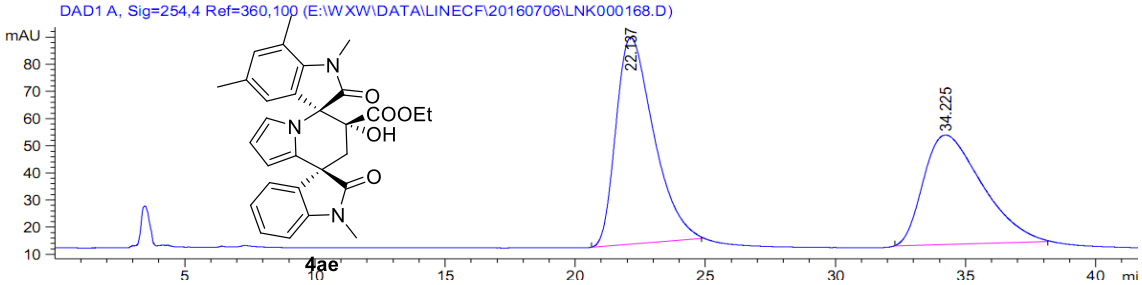


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	76.096	MM R	5.0735	5882.48438	19.32440	54.3647
2	88.677	MM R	5.8672	4937.91895	14.02693	45.6353

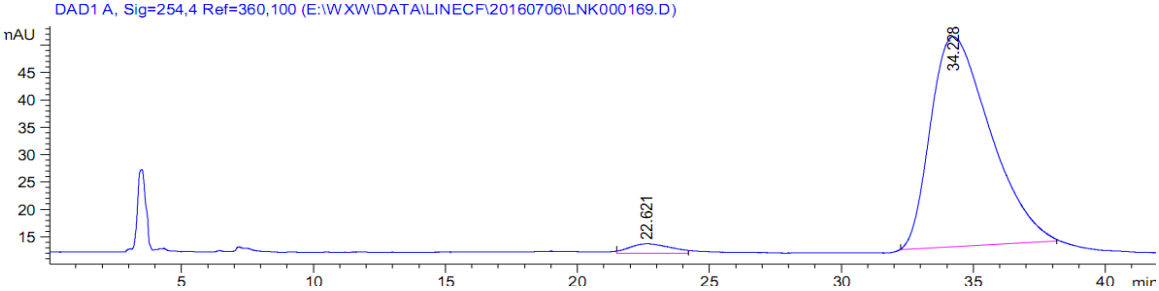


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.141	BV	0.1263	289.29608	30.59708	2.3957
2	3.499	VB	0.2960	1.17865e4	568.31531	97.6043

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ae

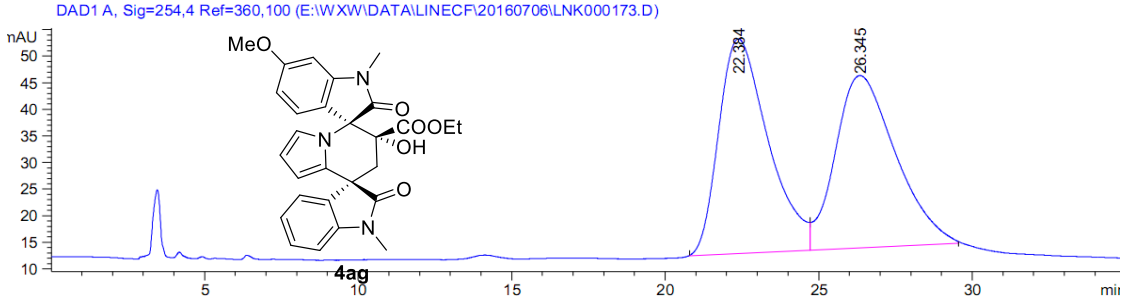


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.137	BB	1.4685	7678.86426	76.14636	54.9338
2	34.225	BB	1.8410	6299.53223	40.27135	45.0662

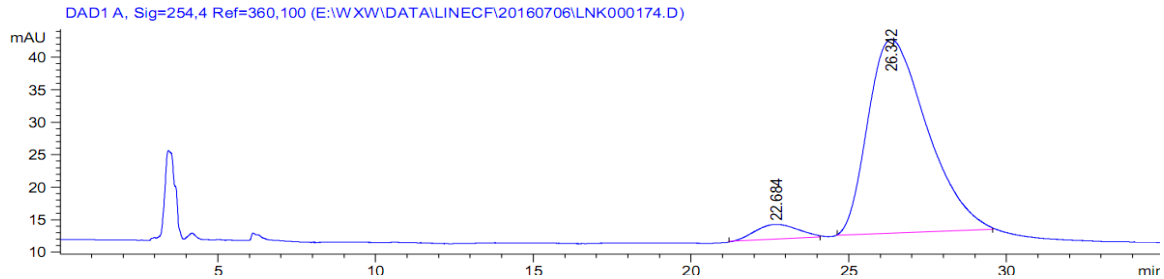


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.621	MM R	1.7992	184.08270	1.70525	2.9717
2	34.228	BB	1.8890	6010.52393	38.33954	97.0283

ethyl(3R,6'R,8'S)-6'-hydroxy-6-methoxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ag

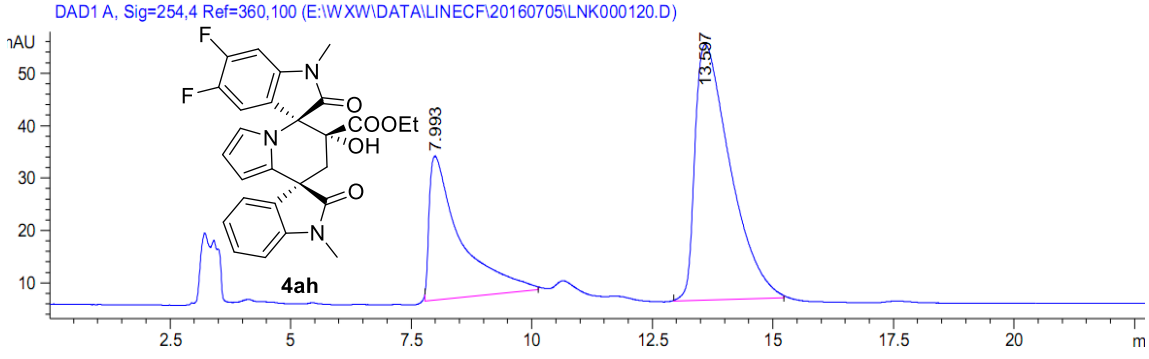


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.384	BV	1.4791	4504.37109	40.32702	50.4419
2	26.345	VB	1.6755	4425.44141	32.35941	49.5581

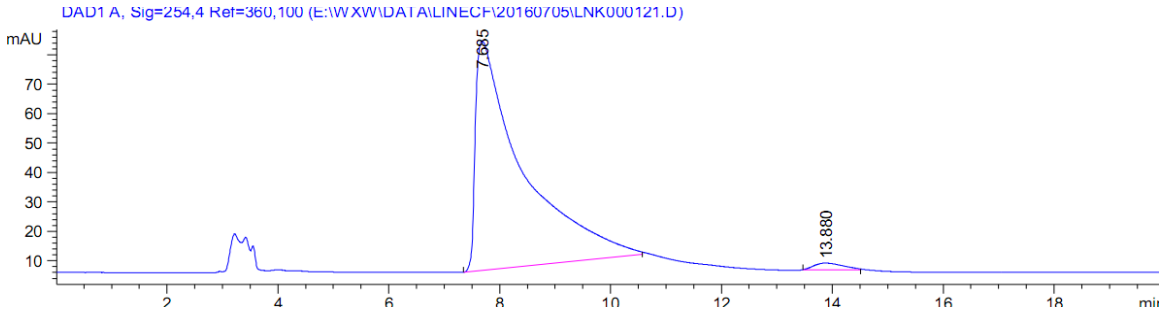


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.684	MM R	1.5510	211.77892	2.27578	5.1709
2	26.342	BB	1.6244	3883.82129	29.84232	94.8291

ethyl(3R,6'R,8'S)-5,6-difluoro-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ah

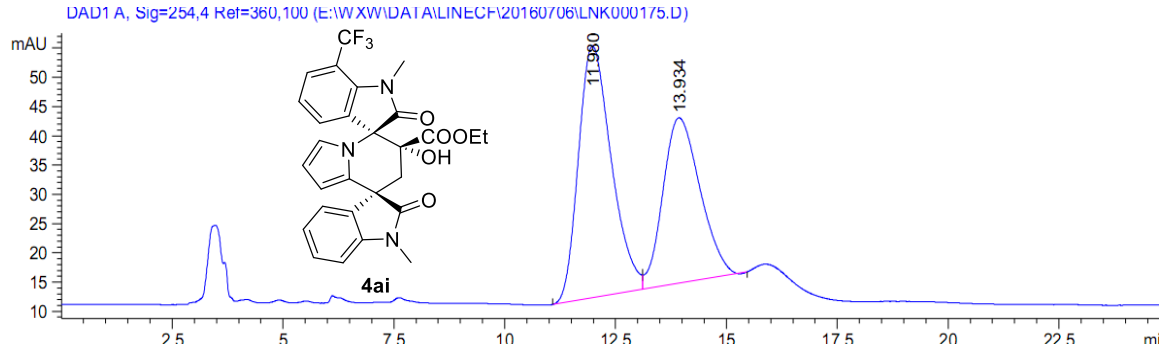


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.993	MM R	0.7539	1239.77649	27.40982	33.2603
2	13.597	BB	0.7531	2487.72021	48.77164	66.7397

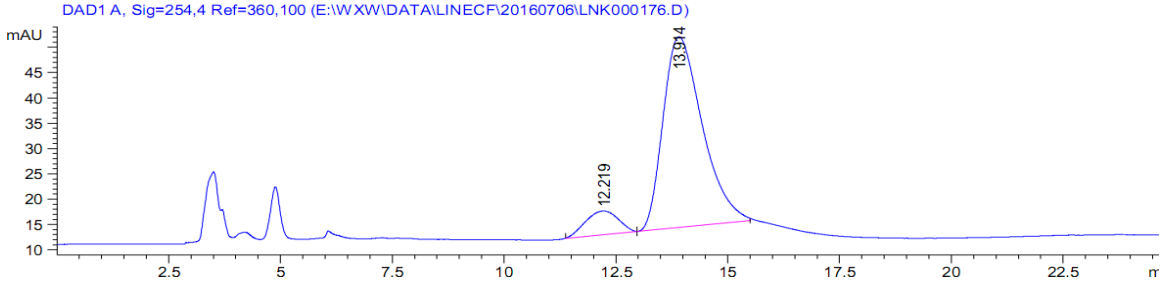


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.685	BB	0.7857	4626.48584	78.03500	98.1317
2	13.880	MM R	0.6234	88.08224	2.35478	1.8683

ethyl(3R,6'R,8'S)-6'-hydroxy-1,1''-dimethyl-2,2''-dioxo-7-(trifluoromethyl)-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ai

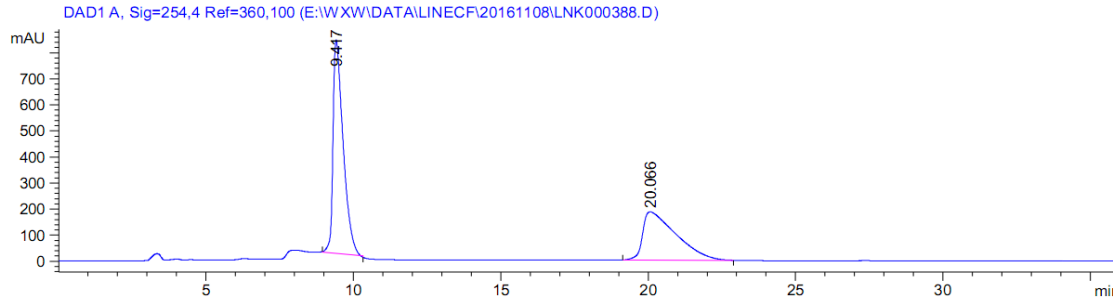


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.980	BV	0.7775	2219.39380	43.04605	57.4059
2	13.934	VB	0.8855	1646.74805	28.27464	42.5941

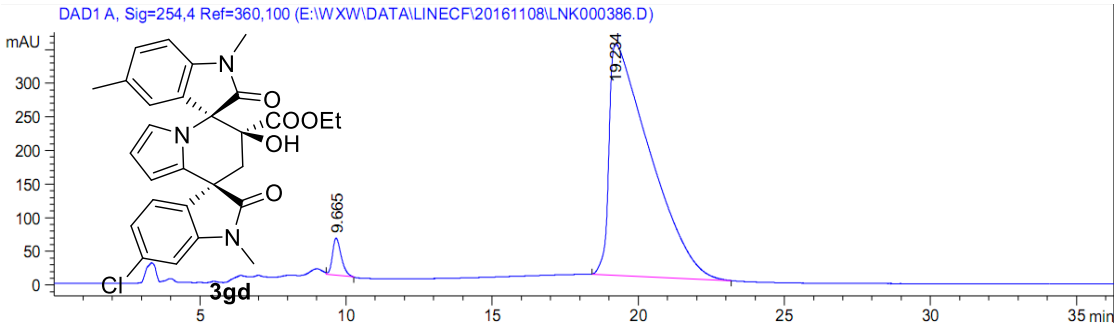


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.219	BV	0.6262	239.20749	4.69690	9.4421
2	13.914	VB	0.9271	2294.21289	37.63828	90.5579

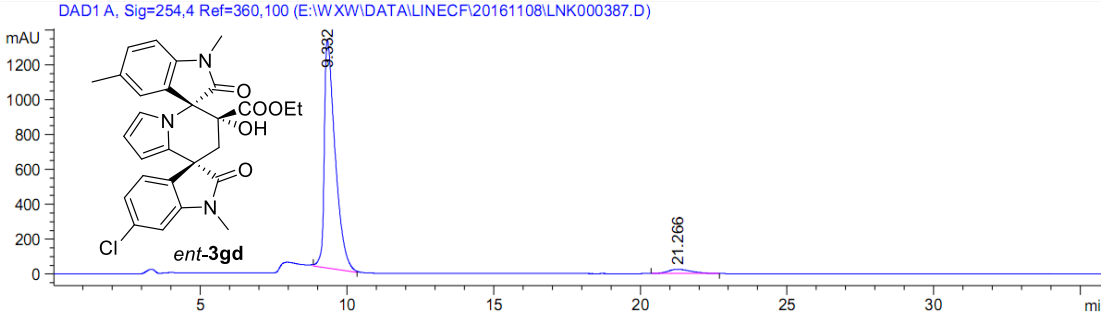
ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydro dispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3gd or *ent*-3gd



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.417	MM R	0.3974	1.94966e4	817.73187	57.1755
2	20.066	BB	1.1304	1.46030e4	185.49815	42.8245

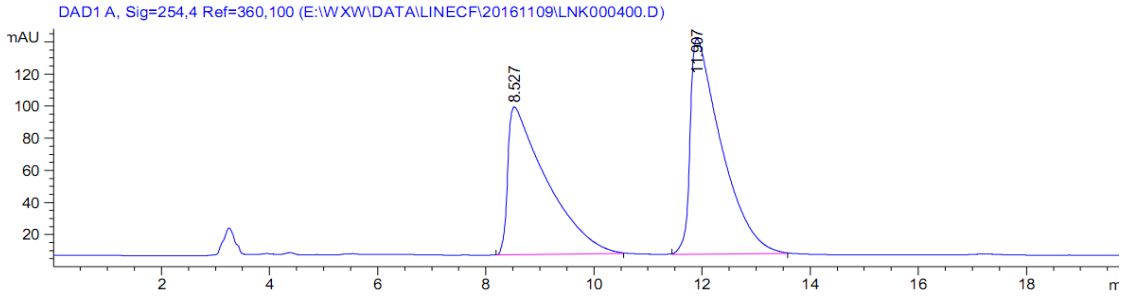


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.665	MM R	0.3454	1143.34631	55.16946	3.2750
2	19.234	BB	1.3381	3.37678e4	344.33698	96.7250

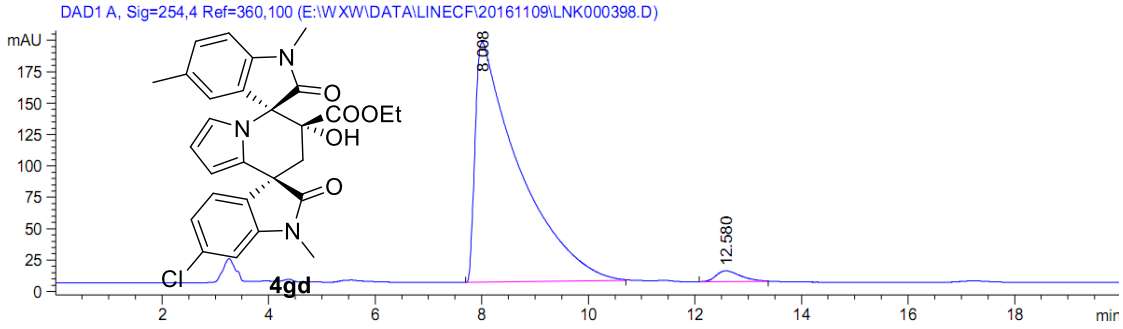


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.332	MM R	0.4295	3.36884e4	1307.19006	96.1607
2	21.266	BB	0.8165	1345.05652	24.27399	3.8393

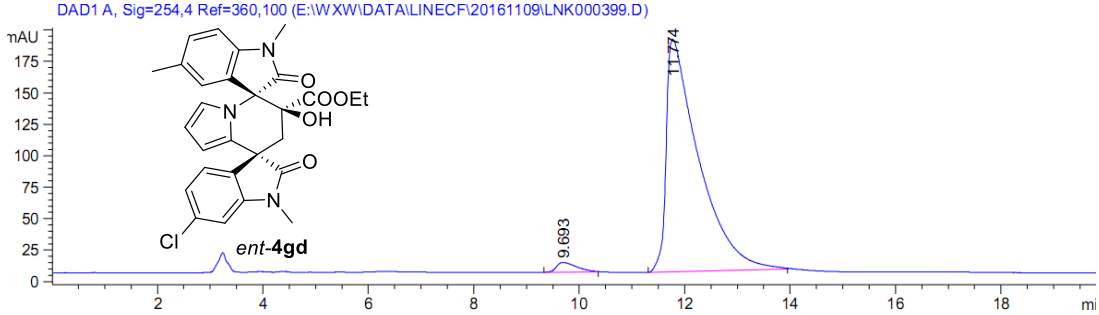
ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1'',5-trimethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4gd or *ent*-4gd



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.527	BB	0.6663	4593.53125	92.03374	46.0147
2	11.907	BB	0.5622	5389.20850	133.70930	53.9853

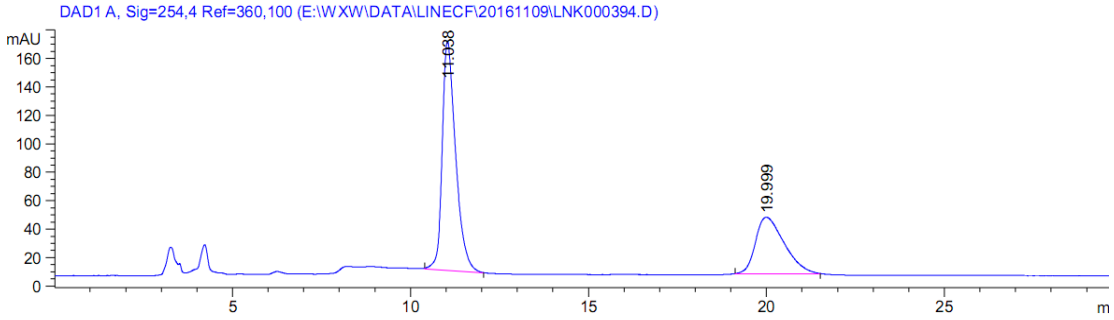


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.008	BB	0.7496	1.09556e4	190.89386	97.5400
2	12.580	BB	0.4541	276.30347	8.57111	2.4600

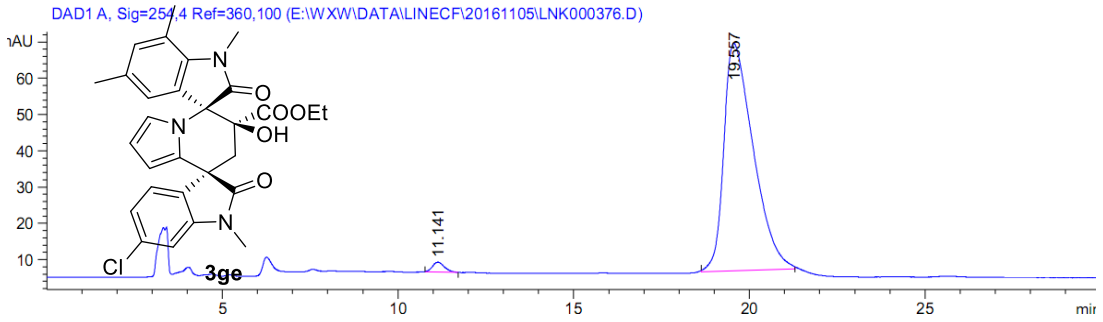


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.693	BB	0.3978	209.97121	7.80716	2.5726
2	11.774	BB	0.5959	7951.76904	184.84100	97.4274

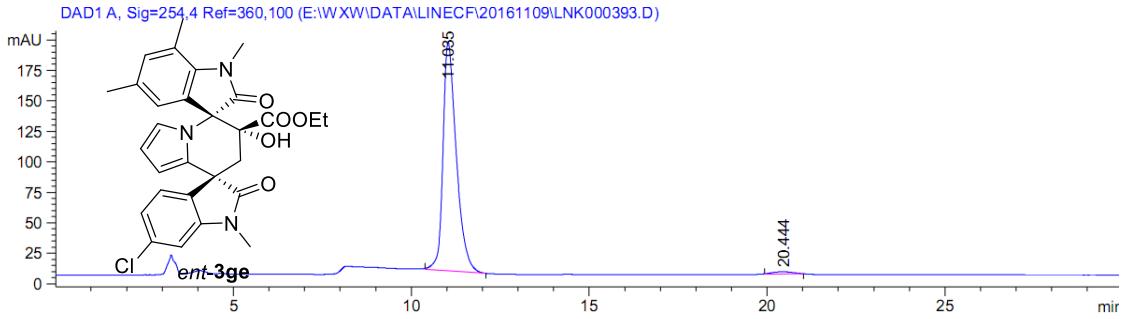
ethyl(3R,6'S,8'S)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 3ge or *ent*-3ge



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.038	BB	0.3951	4209.50977	160.97627	65.0590
2	19.999	BB	0.8256	2260.78271	39.98939	34.9410

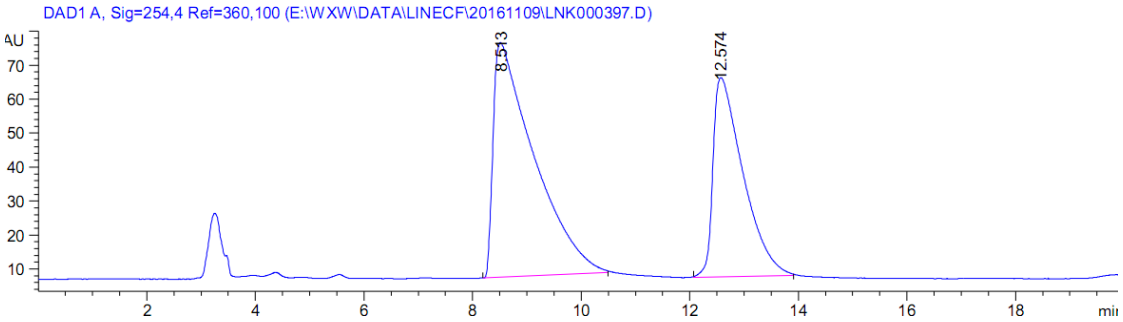


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.141	BB	0.3377	64.08397	2.71146	1.7205
2	19.557	BB	0.8569	3660.55347	62.72047	98.2795

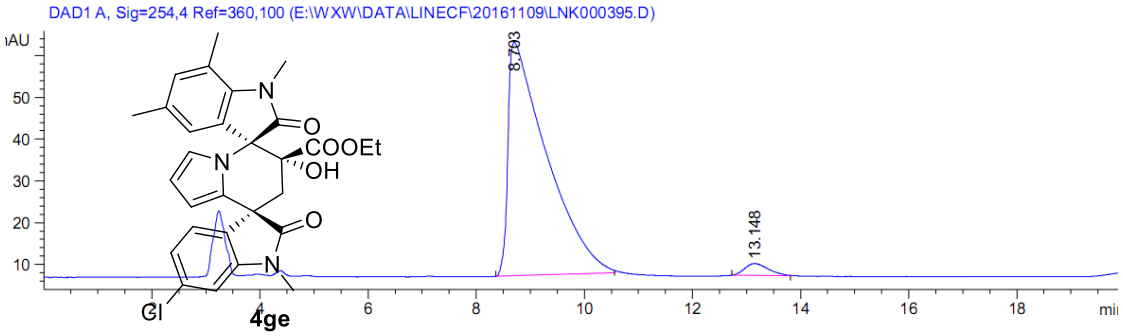


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.035	BB	0.3907	4861.48340	187.38495	98.7426
2	20.444	MM R	0.6215	61.90831	1.66023	1.2574

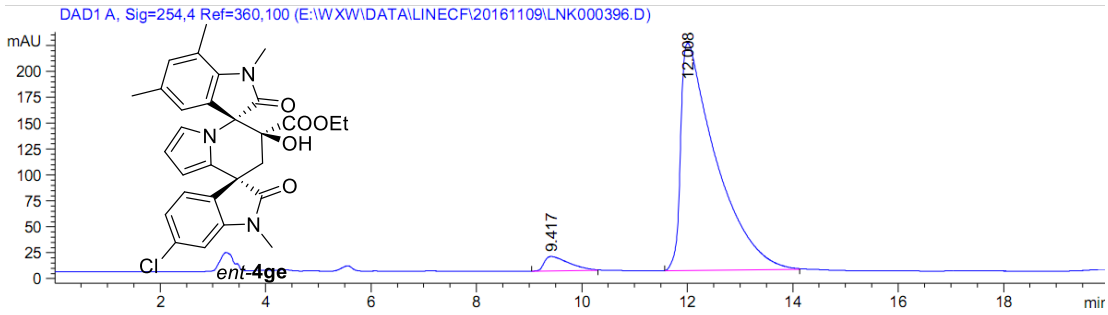
ethyl(3R,6'R,8'S)-6''-chloro-6'-hydroxy-1,1'',5,7-tetramethyl-2,2''-dioxo-6',7'-dihydrodispiro[indoline-3,5'-indolizine-8',3''-indoline]-6'-carboxylate 4ge or *ent*-4ge



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.513	BB	0.6899	3612.40137	69.09875	61.5568
2	12.574	BB	0.5586	2256.00635	58.67159	38.4432

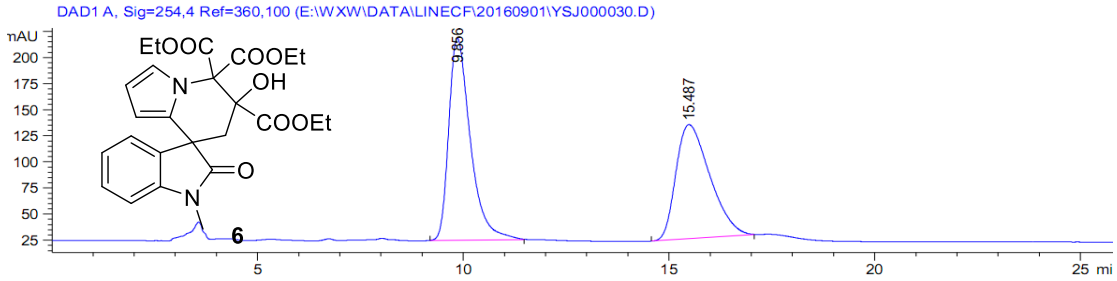


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.703	BB	0.6645	2780.66553	55.88404	96.9110
2	13.148	BB	0.4150	88.63148	2.88052	3.0890

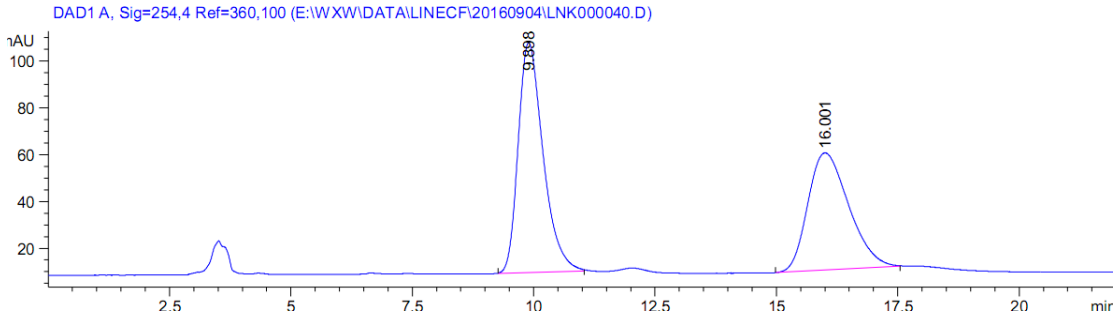


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.417	BB	0.4751	447.08209	13.83331	4.1924
2	12.008	BB	0.6377	1.02170e4	219.22348	95.8076

triethyl6'-hydroxy-1-methyl-2-oxo-6',7'-dihydro-5'H-spiro[indoline-3,8'-indolizine]-5',5',6'-tricarboxylate 6



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.856	BB	0.5530	7093.51123	193.80841	53.0481
2	15.487	BB	0.8779	6278.33545	109.34622	46.9519



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.898	BB	0.5453	3498.03198	98.27097	54.4371
2	16.001	BB	0.8961	2927.78809	50.07397	45.5629