

Supporting Information for

Organocatalytic Synthesis of Spiro [pyrrolidin-3, 3'-Oxindoles] with High Enantiopurity and Structural Diversity

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- (4a) Ding, K.; Lu, Y.; Nikolovska-Coleska, Z.; Qiu, S.; Ding, Y.; Gao, W.; Stuckey, J.; Krajewski, K.; Roller, P. P.; Tomita, Y.; Parrish, D. A.; Deschamps, J. R.; Wang, S. *J. Am. Chem. Soc.* **2005**, *127*, 10130.
- (4b) Ding, K.; Lu, Y.; Nikolovska-Coleska, Z.; Wang, G.; Qiu, S.; Shangary, S.; Gao, W.; Qin, D.; Stuckey, J.; Krajewski, K.; Roller, P. P.; Wang, S. *J. Med. Chem.* **2006**, *49*, 3432.
- (4c) Shangary, S.; Qin, D.; McEachern, D.; Liu, M.; Miller, R. S.; Qiu, S.; Nikolovska-Coleska, Z.; Ding, K.; Wang, G.; Chen, J.; Bernard, D.; Zhang, J.; Lu, Y.; Gu, Q.; Shah, R. B.; Pienta, K. J.; Ling, X.; Kang, S.; Guo, M.; Sun, Y.; Yang, D.; Wang, S. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 3933.

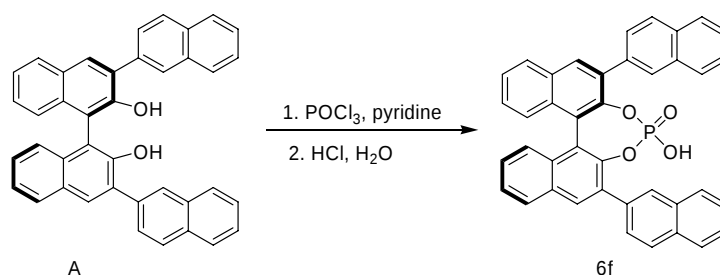
General data: NMR spectra were recorded on a Bruker-400 MHz spectrometer. HRMS spectra (Micromass GCT-MS) were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). Chiralpak AS, AD, OD, IA, and OJ columns were purchased from Daicel Chemical Industries, LTD. Dichloromethane was dried over CaH₂ and distilled prior to use. Hexane, petroleum ether and ethyl acetate for the column chromatography were distilled before use. The

relative and absolute configurations of **8d** were assigned by the X-ray analysis.

Materials: All starting materials were purchased from Acros, Alfa and Aldrich and used directly.

The arylidenoxindoles were prepared according to literature methods,¹ purified by chromatography, and recrystallization from ethanol. The absolute configuration of **1a** was assigned by the X-ray analysis.

Preparation of chiral phosphoric acid²



Catalyst **6f** had been reported by MacMillan, Reuping and list, respectively.^{2c-2e} Diol **A** was prepared from Suzuki coupling of (R)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl and naphthalen-2-ylboronic acid, then recrystallized from dichloromethane, the enantiomeric excess of diol **A** > 99%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm, t_R = 10.4 min(major), t_R = 13.4 min(minor). Diol **A** (1.0 mmol, 538 mg) was dissolved in pyridine (8.0 mL) under N₂ atmosphere in a flame-dried 50-ml round-bottom flask. To the resulting solution was added phosphorus oxychloride (3.0 equiv.) at room temperature and the reaction mixture was stirred at room temperature for 12 h. Then water (5 mL) was added and the resulting suspension was stirred at at room temperature for additional 6h. 200ml dichloromethane was used and pyridine was removed by reverse extractions with 6N HCl (3 X 50 mL). The organic phase was dried over anhydrous Na₂SO₄ and purified by column chromatography (eluent: 2% MeOH in CH₂Cl₂) to yield a white solid .The product was recrystallized from dichloromethane/hexane to give a white solid, and then purified again by column chromatography (eluent: 2% MeOH in CHCl₃) to give pure **6f** (468 mg, 78% yield) as a white solid (m.p.>250 °C), $[\alpha]_D^{25} = -265.0$ (c= 0.20 in CHCl₃); ¹H-NMR (DMSO, 400 MHz) δ (ppm): 4.25 (brs), 7.16 (d, J = 8.8 Hz, 2H), 7.30-7.35 (m, 2H), 7.47-7.52 (m, 6H), 7.91-7.96 (m, 6H), 8.03 (dd, J_1 = 1.6 Hz, J_2 = 8.8 Hz, 2H), 8.11 (d, J = 8.1 Hz, 2H), 8.27 (s, 2H), 8.33 (s, 2H); ¹³C NMR (DMSO, 100 MHz) δ (ppm): 122.4, 125.4, 126.0, 126.1, 126.2, 126.6, 127.2, 127.4, 128.1, 128.2, 128.6, 128.7, 130.6, 131.0, 131.5, 132.1, 132.8, 133.7, 134.9, 145.9; HRMS (FT-ICRMS) exact mass calcd for (C₄₀H₂₄O₄P1+Na₂)⁺ requires m/z 645.1208, found m/z 645.1201.

General Procedure for Directly Catalytic Asymmetric Synthesis of Spiro [pyrrolidin-3,3'-Oxindoles]

A mixture of an aldehyde (0.24 mmol), catalyst (0.02 mmol, 12mg), methyleneindolinones (0.24 mmol), and 3Å molecular sieves (300 mg) in CH₂Cl₂ (2.0 mL) was stirred at 25 °C. To the mixture was added the amino ester (0.2 mmol), the reaction mixture was stirred at 25 °C until the reaction was complete (the reaction time was 24-96 h, monitored by TLC). The resultant solution was purified through flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1-5:1) to yield pure products.

Diethyl-1-acetyl-5'-(4-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5a), 107 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1-5/1), 94% yield, white solid, m.p. 95-97°C; $[\alpha]_D^{25} = +158.1$ (c= 0.16 in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.71 (t, *J*= 7.1 Hz, 3H), 1.36 (t, *J*= 7.1 Hz, 3H), 2.54 (s 3H), 3.69-3.85(m, 3H), 4.39-4.43 (m, 2H), 4.48 (d, *J*= 11.0 Hz, 1H), 5.34 (d, *J*= 11.0 Hz, 1H), 6.75 (d, *J*= 7.2 Hz, 2H), 6.95 (m, 2H), 7.06-7.07 (m, 1H), 7.27-7.31 (m, 2H), 7.47-7.49 (m, 1H), 7.81 (d, *J*= 8.8 Hz, 2H), 7.98-8.01 (m, 1H), 8.07 (d, *J*= 8.8 Hz, 2H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 62.1, 62.2, 62.7, 63.6, 65.0, 77.9, 116.4, 123.3, 123.4, 125.0, 126.8, 128.2, 128.4, 128.6, 129.4, 131.6, 139.9, 147.5, 149.0, 168.6, 169.8, 170.2, 174.6; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 11.12 min(minor), *t_R* = 16.79 min(major); IR (KBr): γ 3363, 2980, 2924, 1756, 1610, 1518, 1455, 1342, 1273, 1135, 858, 752, 701, 588; HRMS (FT-ICRMS) exact mass calcd for (C₃₁H₂₉N₃O₈)⁺ requires *m/z* 571.1955, found *m/z* 571.1954.

Diethyl-1-acetyl-5'-(3-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5b), 110 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1-5/1), 96% yield, white solid, m.p. 108-109°C; $[\alpha]_D^{25} = +145.0$ (c= 0.10 in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.70 (t, *J*= 7.2 Hz, 3H), 1.39 (t, *J*= 7.2 Hz, 3H), 2.54 (s 3H), 3.50-3.84 (m, 3H), 4.43-4.46 (m, 2H), 4.52 (d, *J*= 11.0 Hz, 1H), 5.36 (d, *J*= 11.0 Hz, 1H), 6.78 (d, *J*= 7.2 Hz, 2H), 6.97 (t, *J*= 7.8 Hz, 2H), 7.05 (t, *J*=7.3 Hz, 1H), 7.27-7.30 (m, 2H), 7.37 (t, *J*= 7.8 Hz, 1H), 7.49 (d, *J*= 8.7 Hz, 1H), 7.91 (d, *J*= 7.8 Hz, 1H), 7.98-8.20 (m, 2H), 8.61 (t, *J*= 1.8 Hz, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.1, 14.0, 26.4, 62.0, 62.8, 63.4, 65.0, 77.9, 116.4, 122.7, 122.8, 123.3, 124.9, 126.8, 128.2, 128.4, 128.6, 129.1, 129.4, 131.6, 133.7, 139.9, 143.7, 148.4, 168.6, 169.8, 170.2, 174.6; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak

AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.98 min(major), t_R = 12.93 min(minor); IR (KBr): γ 3420, 3081, 2987, 2930, 1750, 1600, 1530, 1461, 1348, 1280, 764, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{29}N_3O_8)^+$ requires m/z 571.1955, found m/z 571.1953.

Diethyl-1-acetyl-5'-(2-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5c), 104 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1-5/1), 91% yield, white solid, m.p. 69-71°C; $[\alpha]_D^{25}$ = - 91.7 (c= 0.17 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.70 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H), 2.56 (s, 3H), 3.67-3.81 (m, 2H), 4.05 (brs, 1H), 4.36-4.41 (m, 2H), 4.82 (d, J = 11.3 Hz, 1H), 5.93 (d, J = 11.3 Hz, 1H), 6.70 (d, J = 7.4 Hz, 2H), 6.91 (t, J = 7.7 Hz, 2H), 7.00 (t, J = 7.4 Hz, 1H), 7.27-7.33 (m, 3H), 7.46-7.48 (m, 1H), 7.62 (m, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.97-7.99 (m, 1H), 8.48 (d, J = 8.1 Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 57.0, 60.0, 62.0, 62.4, 64.7, 116.2, 123.3, 124.3, 125.3, 126.5, 127.7, 128.2, 128.3, 128.5, 129.3, 129.7, 131.3, 133.4, 135.1, 139.8, 150.5, 168.2, 169.8, 170.1, 174.9; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.67 min(major), t_R = 7.22 min(minor); IR (KBr): γ 3363, 2987, 2924, 1750, 1600, 1530, 1461, 1373, 1273, 759, 710, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{29}N_3O_8)^+$ requires m/z 571.1955, found m/z 571.1951.

Diethyl-1-acetyl-5'-(4-cyanophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5d), 102 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1-5/1), 93% yield, white solid, m.p. 75-77°C; $[\alpha]_D^{25}$ = + 53.0 (c= 0.10 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.70 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H), 2.53 (s, 3H), 3.50-3.84 (m, 3H), 4.38-4.44 (m, 2H), 4.46 (d, J = 11.0 Hz, 1H), 5.30 (d, J = 11.0 Hz, 1H), 6.75 (d, J = 7.4 Hz, 2H), 6.96 (t, J = 7.7 Hz, 2H), 7.0 (d, J = 7.1 Hz, 1H), 7.25-7.31 (m, 2H), 7.47-7.51 (m, 3H), 7.75 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 7.4 Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.4, 61.9, 62.0, 62.7, 63.7, 65.0, 77.8, 111.4, 116.4, 118.8, 123.3, 124.9, 126.8, 128.1, 128.3, 128.6, 129.3, 131.7, 132.0, 139.8, 146.8, 168.6, 169.8, 170.1, 174.7; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.33 min(major), t_R = 10.78 min(minor); IR (KBr): γ 3370, 2980, 2937, 2227, 1750, 1600, 1467, 1373, 1280, 858, 759, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{32}H_{29}N_3O_6)^+$ requires m/z 551.2056, found m/z 551.2064.

Diethyl-1-acetyl-5'-(3-cyanophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5e), 100 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1-5/1), 91% yield, white solid, m.p. 48-50°C; $[\alpha]_D^{25} = +140.0$ ($c = 0.19$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.70 (t, $J = 7.1$ Hz, 3H), 1.39 (t, $J = 7.1$ Hz, 3H), 2.54 (s, 3H), 3.6-3.84 (m, 3H), 4.40-4.48 (m, 3H), 5.27 (d, $J = 11.0$ Hz, 1H), 6.74-6.76 (m, 2H), 6.95-6.99 (m, 2H), 7.05-7.06 (m, 1H), 7.25-7.33 (m, 3H), 7.45-7.47 (m, 2H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.98 (d, $J = 7.7$ Hz, 1H); 8.04 (t, $J = 1.6$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.4, 62.0, 62.8, 63.4, 65.0, 77.8, 112.3, 116.3, 118.9, 123.3, 124.9, 126.8, 128.1, 128.3, 128.5, 129.0, 129.3, 131.3, 131.4, 131.6, 132.1, 139.8, 142.9, 168.6, 169.8, 170.2, 174.7; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak Kromasil-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 10.62$ min(major), $t_R = 9.43$ min(minor); IR (KBr): γ 3439, 2924, 2227, 1750, 1719, 1631, 1455, 1084, 739, 701, 583; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{32}\text{H}_{29}\text{N}_3\text{O}_6)^+$ requires m/z 551.2056, found m/z 551.2050.

Diethyl-1-acetyl-5'-(4-bromophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5f), 116 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1-6/1), 96% yield, white solid, m.p. 65-66 °C; $[\alpha]_D^{25} = +40.0$ ($c = 0.10$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 2.54 (s, 3H), 3.50 (brs, 1H), 3.68-3.81 (m, 2H), 4.38-4.46 (m, 3H), 5.20 (d, $J = 11.0$ Hz, 1H), 6.74 (d, $J = 7.2$ Hz, 2H), 6.94 (t, $J = 7.8$ Hz, 2H), 7.01-7.03 (m, 1H), 7.24-7.28 (m, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.49-7.54 (m, 3H), 7.97 (d, $J = 9.2$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 61.7, 61.9, 62.7, 63.6, 65.1, 77.9, 116.3, 121.6, 123.5, 124.9, 127.1, 128.0, 128.1, 128.6, 129.2, 129.5, 131.4, 132.1 139.8, 168.8, 170.2, 175.0; Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 10.53$ min(major), $t_R = 7.80$ min(minor); IR (KBr): γ 3370, 3068, 2980, 2924, 1750, 1600, 1467, 1373, 1280, 815, 759, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{29}\text{BrN}_2\text{O}_6)^+$ requires m/z 604.1209, found m/z 604.1212.

Diethyl-1-acetyl-5'-(2-bromophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5g), 107 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 89% yield, white solid, m.p. 134-135°C; $[\alpha]_D^{25} = +20.0$ ($c = 0.10$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 1.37 (t, $J = 7.1$ Hz, 3H), 2.58 (s, 3H), 3.60 (brs, 1H), 3.68-3.82 (m, 2H), 4.36-4.42 (q, 2H), 4.78 (d, $J = 11.4$ Hz, 1H), 5.82 (d, $J = 11.4$ Hz, 1H), 6.83

(d, J = 7.7 Hz, 2H), 6.92 (t, J = 7.7 Hz, 2H), 6.90-7.05 (m, 2H), 7.25-7.28 (m, 2H), 7.33 (m, 1H), 7.44 (m, 1H), 7.60(m, 1H), 7.98(m, 1H), 8.23 (d, J = 6.3 Hz, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 60.1, 61.4, 61.9, 62.7, 64.9, 77.7, 116.2, 123.5, 125.1, 125.6, 127.0, 127.9, 128.1, 128.2, 128.6, 129.2, 129.4, 131.8, 132.7 138.9, 139.9, 168.6, 170.2, 170.3, 175.2; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 94/ 6, flow rate 1.0 mL/min, T = 30 $^\circ\text{C}$, 254 nm): t_R = 10.18 min(major), t_R = 9.18 min(minor); IR (KBr): γ 3351, 3062, 2980, 2943, 1750, 1724, 1600, 1461, 1367, 1280, 759, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{29}\text{BrN}_2\text{O}_6)^+$ requires m/z 604.1209, found m/z 604.1210.

Diethyl-1-acetyl-5'-(4-chlorophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5g), 109 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 97% yield, white solid, m.p.60-61 $^\circ\text{C}$; $[\alpha]_D^{25}$ = + 93.7 (c = 0.16 in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1Hz, 3H), 2.54 (s, 3H), 3.52 (brs, 1H), 3.68-3.83 (m, 2H), 4.37-4.46 (m, 3H), 5.15-5.25 (d, J = 11.3 Hz, 1H), 6.73 (d, J = 7.2 Hz, 2H), 6.94 (t, J = 7.7 Hz, 2H), 7.02 (m, 1H), 7.20 (d, J = 8.5 Hz, 1H), 7.24-7.28(m, 2H), 7.49 (m, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 7.6 Hz, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 61.8, 61.9, 62.8, 63.6, 65.2, 77.9, 116.3, 123.5, 124.9, 127.2, 128.0, 128.1, 128.5, 128.6, 129.1, 129.2, 132.1, 133.5, 139.3, 139.8, 168.8, 170.3, 175.0; Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 $^\circ\text{C}$, 254 nm): t_R = 9.87 min(major), t_R = 7.57 min(minor); IR (KBr): γ 3370, 2980, 2930, 1750, 1600, 1467, 1373, 1273, 1016, 840, 759, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{29}\text{ClN}_2\text{O}_6)^+$ requires m/z 560.1714, found m/z 560.1721.

Diethyl-1-acetyl-5'-(2,4-dinitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5i), 119 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1- 4/1), 97% yield, white solid, m.p. 86-88 $^\circ\text{C}$; $[\alpha]_D^{25}$ = - 28.8 (c = 0.17 in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1Hz, 3H), 2.53 (s, 3H), 3.67-3.85 (m, 2H), 4.36-4.42 (m, 2H), 4.65 (d, J = 11.2 Hz, 1H), 6.03 (d, J = 11.2 Hz, 1H), 6.63 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 2H), 6.93 (m, 2H), 7.05 (m, 1H), 7.3-7.33(m, 2H), 7.40-7.45(m, 1H), 7.99 -8.02 (m, 1H), 8.44-8.48 (m, 2H), 8.99 (d, J =8.5 Hz, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.4, 57.4, 61.5, 62.3, 62.8, 64.7, 77.5, 116.5 119.5, 123.0, 125.4, 126.1, 127.2, 128.3, 128.4, 128.8, 129.6, 130.2, 132.4, 139.9, 142.9, 168.1, 169.6, 170.0, 174.3; Enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min,

T = 30 °C, 254 nm): t_R = 10.79 min(major), t_R = 8.20 min(minor); IR (KBr): γ 3433, 3112, 2987, 2930, 1750, 1719, 1600, 1530, 1467, 1342, 1280, 858, 759, 727, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}N_4O_{10})^+$ requires m/z 616.1805, found m/z 616.1800.

Diethyl-1-acetyl-5'-(2,3-dichlorophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5j), 112 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 7/1), 94% yield, white solid, m.p. 50-52°C; $[a]_D^{25}$ = - 15.0 (c= 0.10 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.71 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H), 2.57 (s, 3H), 3.65-3.83 (m, 3H), 4.35-4.41 (m, 2H), 4.73 (d, J = 11.3 Hz, 1H), 5.90 (d, J = 11.3 Hz, 1H), 6.80 (d, J = 7.2 Hz, 2H), 6.94 (t, J = 7.7 Hz, 2H), 7.01 (m, 1H), 7.25-7.34 (m, 4H), 7.50-7.55 (m, 1H), 7.97-7.98 (m, 1H), 8.21 (dd, J_1 = 1.5 Hz, J_2 = 7.9 Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.2, 14.0, 26.5, 59.4, 60.3, 62.0, 62.8, 64.9, 77.7, 116.3, 123.5, 125.2, 126.9, 127.5, 127.9, 128.0, 128.3, 128.5, 129.3, 129.9, 131.5, 132.9, 139.9, 140.1, 168.6, 170.2, 175.1; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 94/ 6, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 11.34 min(major), t_R = 9.88 min(minor); IR (KBr): γ 3370, 3074, 2980, 2924, 1750, 1719, 1600, 1461, 1367, 1280, 759, 727, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}Cl_2N_2O_6)^+$ requires m/z 594.1324, found m/z 594.1331.

Diethyl-1-acetyl-5'-(3,4-dichlorophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5k), 111 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 7/1), 93% yield, white solid, m.p. 118-120°C; $[a]_D^{25}$ = + 134.5 (c= 0.24 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.70 (t, J = 7.1 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H), 2.54 (s, 3H), 3.50 (brs, 1H), 3.71-3.80 (m, 2H), 4.40-4.45 (m, 3H), 5.19 (d, J = 11.2 Hz, 1H), 6.74 (m, 2H), 6.96 (m, 2H), 7.03 (m, 1H), 7.23-7.34 (m, 4H), 8.46 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.97-7.99 (m, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 61.9, 62.0, 62.8, 63.2, 65.1, 77.9, 116.4, 123.3, 124.9, 126.9, 127.0, 128.1, 128.3, 128.6, 129.3, 129.7, 130.1, 131.5, 131.8, 132.4, 139.8, 141.5, 168.7, 169.9, 170.2, 174.8; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.88 min(major), t_R = 7.87 min(minor); IR (KBr): γ 3376, 2980, 1750, 1467, 1273, 1122, 1016, 752, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}Cl_2N_2O_6)^+$ requires m/z 594.1324, found m/z 594.1318.

Diethyl-1-acetyl-5'-(2-chloro-4-fluorophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5l), 111 mg (Flash column chromatography eluent, petroleum ether/ethyl

acetate = 12/1- 6/1), 96% yield, white solid, m.p. 58-60°C; $[\alpha]_D^{25} = + 48.0$ ($c = 0.20$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 2.56 (s, 3H), 3.58 (brs, 1H), 3.67-3.83 (m, 2H), 4.37-4.41 (m, 2H), 4.65 (d, $J = 11.3$ Hz, 1H), 5.79 (d, $J = 11.3$ Hz, 1H), 6.79 (d, $J = 7.4$ Hz, 2H), 6.90-7.02 (m, 5H), 7.26-7.29 (m, 1H), 7.53 (m, 1H), 7.98 (m, 1H), 8.36 (dd, $J_1 = 6.2$ Hz, $J_2 = 8.8$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 58.3, 60.7, 61.9, 62.8, 64.9, 77.6, 115.0 (d, $J = 20.8$ Hz), 116.3, 116.5 (d, $J = 24.5$ Hz), 123.5, 125.1, 127.0, 127.9, 128.2, 128.6, 129.2, 130.8, 114.9, 115.1, 116.3, 116.4, 116.6, 123.5, 125.1, 127.0, 127.9, 128.2, 128.6, 129.2, 130.8 (d, $J = 8.8$ Hz), 131.5, 133.7, 135.0 (d, $J = 10.1$ Hz), 139.9, 161.7 (d, $J = 248.6$ Hz), 168.6, 170.2, 170.4, 175.1; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 17.59$ min(major), $t_R = 11.76$ min(minor); IR (KBr): γ 3439, 2987, 2930, 1756, 1713, 1600, 1492, 1461, 1373, 1273, 1235, 903, 858, 759, 702, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{28}\text{ClFN}_2\text{O}_6)^+$ requires m/z 578.1620, found m/z 578.1625.

Diethyl-1-acetyl-5'-(4-chloro-3-fluorophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5m), 112 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 6/1), 97% yield, white solid, m.p. 73-75°C; $[\alpha]_D^{25} = + 126.0$ ($c = 0.20$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.70 (t, $J = 7.1$ Hz, 3H), 1.38 (t, $J = 7.1$ Hz, 3H), 2.54 (s, 3H), 3.58 (brs, 1H), 3.59-3.83 (m, 2H), 4.38-4.45 (m, 3H), 5.20 (dd, $J = 11.3$ Hz, 1H), 6.74 (d, $J = 7.3$ Hz, 2H), 6.96 (m, 2H), 7.04 (m, 1H), 7.19-7.45 (m, 4H), 7.45 (m, 1H), 7.65 (m, 1H), 7.98 (dd, $J_1 = 1.3$ Hz, $J_2 = 8.2$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 62.0, 62.1, 62.8, 63.3, 65.1, 77.8, 115.9 (d, $J = 21.9$ Hz), 116.4, 120.0 (d, $J = 17.8$ Hz), 123.4, 124.0, 124.9, 127.0, 128.1, 128.3, 128.6, 129.3, 130.2, 131.9, 139.9, 142.3 (d, $J = 6.4$ Hz), 158.0 (d, $J = 246.8$ Hz), 168.7, 170.0, 170.2, 174.8; Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 85/ 15, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 13.87$ min(major), $t_R = 10.44$ min(minor); IR (KBr): γ 3401, 2987, 2930, 1756, 1731, 1600, 1467, 1373, 1273, 865, 821, 764, 694, 608; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{28}\text{ClFN}_2\text{O}_6)^+$ requires m/z 578.1620, found m/z 578.1625.

Diethyl-1-acetyl-5'-(3-chloro-2-fluorophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5n), 108 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 93% yield, white solid, m.p. 74-76°C; $[\alpha]_D^{25} = + 52.0$ ($c = 0.10$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 2.57 (s, 3H),

3.57 (brs, 1H), 3.68-3.83 (m, 2H), 4.38-4.42 (m, 2H), 4.61 (d, $J = 11.2$ Hz, 1H), 5.69 (d, $J = 11.2$ Hz, 1H), 6.79 (d, $J = 7.5$ Hz, 2H), 6.94 (m, 2H), 7.02 (m, 1H), 7.12 (m, 1H), 7.23-7.28 (m, 2H), 7.50 (m, 1H), 7.97 (m, 1H), 8.25 (m, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.2, 14.0, 26.5, 55.3, 60.8, 62.0, 62.8, 65.1, 77.7, 116.3, 120.7 (d, $J = 18.6$ Hz), 123.5, 125.1, 126.9, 127.8, 128.0, 128.2, 128.4, 129.3, 129.5 (d, $J = 12.4$ Hz), 129.9, 131.5, 139.8, 156.5 (d, $J = 247.3$ Hz), 168.6, 170.2, 170.3, 175.1; Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 85/ 15, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 7.18$ min(major), $t_R = 8.58$ min(minor); IR (KBr): γ 3370, 2980, 2930, 1756, 1719, 1600, 1461, 1373, 1273, 1016, 759, 733, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{28}\text{ClFN}_2\text{O}_6)^+$ requires m/z 578.1620, found m/z 578.1611.

Diethyl-1-acetyl-2-oxo-4',5'-diphenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5o), 92 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 6/1), 87% yield, white solid, m.p. $64-66^\circ\text{C}$; $[\alpha]_D^{25} = +100.0$ ($c = 0.10$ in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 2.55 (s, 3H), 3.50 (brs, 1H), 3.72-3.80 (m, 2H), 4.39-4.42 (m, 2H), 4.53 (d, $J = 11.2$ Hz, 1H), 5.25 (d, $J = 11.2$ Hz, 1H), 6.75-6.77 (m, 2H), 6.90-6.99 (m, 3H), 7.18-7.27 (m, 5H), 7.54-7.56 (m, 1H), 7.65-7.67 (m, 2H), 7.97 (m, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 61.5, 61.7, 62.7, 64.1, 65.2, 78.0, 116.2, 123.7, 124.9, 127.3, 127.7, 127.8, 127.9, 128.0, 128.4, 128.5, 129.0, 132.4, 139.8, 140.4, 168.9, 170.2, 170.4, 175.2; Enantiomeric excess: 85%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 11.33$ min(major), $t_R = 15.05$ min(minor); IR (KBr): γ 3426, 3031, 2987, 2930, 1756, 1600, 1461, 1373, 1280, 759, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_6)^+$ requires m/z 526.2104, found m/z 526.2111.

Diethyl-1-acetyl-2-oxo-4'-phenyl-5'-p-tolylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5p), 103 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 95% yield, white solid, m.p. $65-67^\circ\text{C}$; $[\alpha]_D^{25} = +82.7$ ($c = 0.22$ in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 2.26 (s, 3H), 2.55 (s, 3H), 3.42 (brs, 1H), 3.69-3.82 (m, 2H), 4.37-4.43 (m, 2H), 4.51 (d, $J = 11.2$ Hz, 1H), 5.25 (d, $J = 11.2$ Hz, 1H), 6.74-6.77 (m, 2H), 6.92-6.94 (m, 2H), 6.90-7.02 (m, 1H), 7.06 (d, $J = 7.8$ Hz, 2H), 7.24-7.27 (m, 2H), 7.53-7.56 (m, 3H), 7.95-7.97 (m, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.2, 14.0, 21.2, 26.5, 61.4, 61.8, 62.7, 63.9, 65.3, 78.0, 116.2, 123.7, 124.9, 127.4, 127.8, 127.9, 128.5, 129.0, 129.1,

132.5, 137.2, 137.4, 139.8, 169.0, 170.3, 175.0, 175.3; Enantiomeric excess: 82%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.45 min(major), t_R = 12.39 min(minor); IR (KBr): γ 3370, 2980, 2924, 1750, 1724, 1600, 1461, 1367, 1273, 759, 710, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{32}H_{32}N_2O_6)^+$ requires m/z 540.2260, found m/z 540.2253.

Diethyl-1-acetyl-5'-(4-methoxyphenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5q), 96 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1- 5/1), 86% yield, white solid, m.p. 57-59°C; $[\alpha]_D^{25}$ = + 52.0 (c= 0.10 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.71 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1Hz, 3H), 2.55 (s, 3H), 3.40 (brs, 1H), 3.68-3.80 (m, 5H), 4.39-4.42 (m, 2H), 4.48 (d, J = 11.2 Hz, 1H), 5.19 (d, J = 11.2 Hz, 1H), 6.74-6.80 (m, 4H), 6.90-6.99 (m, 2H), 7.23-7.27 (m, 3H), 7.54-7.61 (m, 3H), 7.96 (d, J = 7.2 Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 55.2, 61.5, 61.7, 62.7, 63.7, 77.9, 113.3, 113.8, 116.2, 123.7, 124.9, 128.1, 128.5, 129.0, 129.9, 132.2, 132.5, 139.8, 159.2, 168.9, 170.3, 170.6, 175.3; Enantiomeric excess: 81%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 12.34 min(major), t_R = 8.89 min(minor); IR (KBr): γ 3363, 2980, 2937, 1750, 1724, 1600, 1518, 1467, 1373, 1280, 1242, 840, 759, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{32}H_{32}N_2O_7)^+$ requires m/z 556.2210, found m/z 556.2211.

Diethyl-1-acetyl-2-oxo-4'-phenyl-5'-propylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (5r), 70 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 71% yield, white solid, m.p. 114-115°C; $[\alpha]_D^{25}$ = + 20.0 (c= 0.10 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.71 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H), 1.28-1.36 (m, 4H), 1.43-1.50 (m, 1H), 1.58-1.66 (m, 1H), 1.83-1.91 (m, 1H), 2.55 (s, 3H), 3.10 (brs, 1H), 3.68-3.79 (m, 2H), 4.06-4.08 (m, 2H), 4.34-4.36 (m, 2H), 6.76-6.78 (m, 2H), 6.96-7.00 (m, 2H), 7.03-7.05 (m, 1H), 7.17-7.22 (m, 2H), 7.49-7.52 (m, 1H); 7.92-7.93 (m, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.2, 14.0, 14.3, 21.0, 26.5, 37.2, 59.9, 60.4, 61.6, 62.7, 116.0, 124.0, 124.9, 127.4, 127.8, 128.0, 128.4, 128.9, 133.7, 139.8, 168.8, 170.3, 170.8, 175.6; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 94/ 6, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 11.55 min(major), t_R = 5.66 min(minor); IR (KBr): γ 3351, 3056, 2955, 2937, 1756, 1731, 1600, 1467, 1373, 1273, 764, 694, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{28}H_{32}N_2O_6)^+$ requires m/z 492.2260, found m/z 492.2258.

Diethyl-1-acetyl-5'-butyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate

(5s), 60 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 59% yield, white solid, m.p. 75-77°C; $[\alpha]_D^{25} = +21.1$ ($c = 0.17$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 0.84 (t, $J = 6.9$ Hz, 3H), 1.28-1.36 (m, 6H), 1.40-1.51 (m, 1H), 1.60-1.72 (m, 1H), 1.85-1.95 (m, 1H), 2.56 (s, 3H), 3.10 (brs, 1H), 3.69-3.77 (m, 2H), 4.05-4.07 (m, 2H), 4.33-4.37 (m, 2H), 6.76-6.78 (m, 2H), 6.96-7.00 (m, 2H), 7.03-7.05 (m, 1H), 7.17-7.22 (m, 2H), 7.48-7.49 (m, 1H); 7.92-7.94 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 14.1, 22.8, 26.5, 29.9, 34.6, 59.9, 60.6, 61.6, 62.6, 65.0, 78.8, 116.0, 124.0, 124.9, 127.4, 127.8, 128.0, 128.4, 128.9, 133.7, 139.8, 168.8, 170.3, 170.7, 175.6; Enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 15.41$ min(major), $t_R = 6.99$ min(minor); IR (KBr): γ 3358, 2955, 2930, 1750, 1737, 1600, 1467, 1373, 1273, 759, 710, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_6)^+$ requires m/z 506.2417, found m/z 506.2412.

Diethyl-1-acetyl-5'-isobutyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate

(5t), 90 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 89% yield, white solid, m.p. 139-140°C; $[\alpha]_D^{25} = +29.0$ ($c = 0.20$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 0.91 (d, $J = 6.4$ Hz, 6H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.37-1.39 (m, 1H), 1.85-1.90 (m, 1H), 1.91-1.96 (m, 1H), 2.56 (s, 3H), 2.95 (brs, 1H), 3.71-3.76 (m, 2H), 4.03-4.06 (d, $J = 10.8$ Hz, 1H), 4.13-4.33 (m, 1H), 4.33-4.37 (m, 2H), 6.77 (d, $J = 7.2$ Hz, 2H), 6.96-7.00 (m, 2H), 7.03-7.05 (m, 1H), 7.18-7.22 (m, 2H), 7.50 (dd, $J_1 = 1.6$ Hz, $J_2 = 7.2$ Hz, 1H), 7.92-7.94 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 22.0, 23.6, 26.1, 26.5, 44.0, 58.2, 60.1, 61.6, 62.6, 78.9, 116.0, 124.0, 124.9, 127.4, 127.8, 128.0, 128.4, 128.8, 133.5, 139.9, 168.8, 170.3, 170.8, 175.6; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 6.89$ min(major), $t_R = 6.00$ min(minor); IR (KBr): γ 3353, 2962, 1755, 1727, 1704, 1466, 1375, 1313, 1273, 1216, 1171, 752, 689, 582; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_6)^+$ requires m/z 506.2417, found m/z 506.2424.

Diethyl-1-acetyl-5'-neopentyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate

(5u), 94 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 90% yield, white solid, m.p. 121-123°C; $[\alpha]_D^{25} = +35.0$ ($c = 0.10$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 0.97 (s, 9H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.42 (dd, $J_1 = 0.9$ Hz,

$J_2 = 14.3$ Hz 1H), 1.95 (dd, $J_1 = 9.0$ Hz, $J_2 = 14.3$ Hz 1H), 2.56 (s, 3H), 2.87 (brs, 1H), 3.71-3.75 (m, 2H), 4.03 (d, $J = 10.8$ Hz, 1H), 4.14-4.16 (m, 1H), 4.33-4.36 (m, 2H), 6.75-6.78 (m, 2H), 6.96-7.00 (m, 2H), 7.03-7.05 (m, 1H), 7.18-7.22 (m, 2H), 7.520-7.53 (m, 1H), 7.92-7.94 (m, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 30.1, 30.6, 48.5, 57.3, 60.4, 61.5, 62.6, 63.9, 79.4, 116.0, 124.0, 124.9, 127.5, 127.9, 128.0, 128.6, 128.8, 133.3, 139.9, 168.8, 170.3, 171.0, 175.8; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 5.61$ min(major), $t_R = 4.65$ min(minor); IR (KBr): γ 3358, 3062, 2955, 1756, 1731, 1600, 1467, 1373, 1280, 1210, 759, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_6)^+$ requires m/z 520.2573, found m/z 520.2570.

Methyl-1-acetyl-5'-(4-nitrophenyl)-2-oxo-2',4'-diphenylspiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (5v), 48 mg (0.1mmlo scale, Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 85% yield, white solid, m.p. 62-64°C; $[\alpha]_D^{25} = + 182.6$ ($c = 0.15$ in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 2.64 (s, 3H), 3.70 (brs, 1H), 3.81 (s, 3H), 4.24 (d, $J = 11.7$ Hz, 1H), 5.14 (d, $J = 11.6$ Hz, 1H), 6.68-6.70 (m, 2H), 6.84-6.86 (m, 2H), 6.91-6.93 (m, 2H), 6.99-7.07 (m, 5H), 7.25-7.26 (m, 2H), 7.89-7.93 (m, 3H), 8.17 (d, $J = 8.8$ Hz, 2H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 26.7, 29.7, 53.7, 64.4, 64.7, 68.7, 116.0, 124.0, 124.3, 126.0, 126.9, 127.2, 127.4, 128.1, 128.2, 128.4, 128.6, 128.9, 132.2, 139.7, 139.8, 147.4, 170.3, 174.7, 177.0; Enantiomeric excess: 82%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 11.29$ min(major), $t_R = 5.16$ min(minor); IR (KBr): γ 3426, 3062, 2930, 2855, 1744, 1719, 1600, 1524, 1467, 1342, 852, 809, 739, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{33}\text{H}_{27}\text{N}_3\text{O}_6)^+$ requires m/z 561.1900, found m/z 561.1903.

Methyl-1-acetyl-2'-(4-chlorophenyl)-5'-(4-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (5w), 48 mg (0.1mmlo scale, Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 80% yield, white solid, m.p. 88-90°C; $[\alpha]_D^{25} = + 190.0$ ($c = 0.20$ in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 2.63 (s, 3H), 3.73 (brs, 1H), 3.82 (s, 3H), 4.23 (d, $J = 11.6$ Hz, 1H), 5.12 (d, $J = 11.6$ Hz, 1H), 6.67-6.69 (m, 2H), 6.87-6.93 (m, 4H), 6.98-7.02 (m, 3H), 7.08-7.16 (m, 3H), 7.89-7.91 (m, 3H), 8.18 (dd, $J_1 = 1.6$ Hz, $J_2 = 7.2$ Hz, 2H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 26.7, 29.7, 53.9, 64.5, 64.7, 68.7, 116.2, 124.1, 124.6, 125.6, 126.9, 127.3, 128.1, 128.2, 128.3, 128.9, 129.8, 132.0, 133.3, 138.4, 139.7, 147.0, 147.9, 170.2, 174.3, 176.8; Enantiomeric excess: 85%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 12.83$ min(major), $t_R = 5.78$ min(minor); IR (KBr): γ 3401,

2930, 1744, 1703, 1600, 1530, 1461, 1373, 1280, 1167, 784, 759, 701; HRMS (FT-ICRMS) exact mass calcd for $(C_{33}H_{26}ClN_3O_6)^+$ requires m/z 595.1510, found m/z 595.1517.

Methyl-1-acetyl-2'-(4-fluorophenyl)-5'-(4-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (5x), 52 mg (0.1mmlo scale, Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 6/1), 90% yield, white solid, m.p. 137-139°C; $[a]_D^{25} = +174.0$ ($c=0.10$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.64 (s, 3H), 3.73 (brs, 1H), 3.82 (s, 3H), 4.22 (d, $J=11.7$ Hz, 1H), 5.12 (d, $J=11.7$ Hz, 1H), 6.67-6.73 (m, 4H), 6.85-6.93 (m, 4H), 6.97-6.99 (m, 1H), 7.03-7.11 (m, 1H), 7.24-7.25 (m, 2H), 7.89-7.91 (m, 3H), 8.18 (dd, $J_1=2.0$ Hz, $J_2=6.8$ Hz, 2H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 26.7, 29.7, 53.8, 64.6, 64.7, 68.9, 114.1 (d, $J=22.0$ Hz), 116.1, 124.1, 124.5, 125.7, 127.0, 128.1, 128.2, 128.3, 128.8, 128.9, 130.2 (d, $J=8.0$ Hz), 132.1, 135.5, 139.8, 147.1, 147.9, 161.9 (d, $J=245.3$ Hz), 170.3, 174.5, 177.0; Enantiomeric excess: 84%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T=30^\circ C$, 254 nm): $t_R=11.91$ min(major), $t_R=5.42$ min(minor); IR (KBr): γ 3408, 3068, 2955, 2924, 1750, 1719, 1600, 1524, 1474, 1348, 1084, 840, 815, 752, 701; HRMS (FT-ICRMS) exact mass calcd for $(C_{33}H_{26}FN_3O_6)^+$ requires m/z 579.1806, found m/z 579.1811.

Diethyl-1-acetyl-4'-(4-cyanophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7a), 113 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 95% yield, white solid, m.p. 175-177°C; $[a]_D^{25} = +193.0$ ($c=0.10$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.73 (t, $J=7.1$ Hz, 3H), 1.36 (t, $J=7.1$ Hz, 3H), 2.55 (s, 3H), 3.67-3.72 (m, 2H), 3.83-3.86 (m, 1H), 4.36-4.45 (m, 2H), 4.53 (d, $J=10.9$ Hz, 1H), 5.32 (d, $J=10.9$ Hz, 1H), 6.88-6.90 (m, 2H), 7.26-7.31 (m, 3H), 7.30-7.40 (m, 1H), 7.45-7.48 (m, 1H), 7.80 (d, $J=8.8$ Hz, 2H), 8.04-8.06 (m, 1H), 8.11 (d, $J=8.8$ Hz, 2H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.6, 61.6, 62.3, 63.0, 63.8, 64.7, 78.1, 112.6, 116.8, 117.9, 123.3, 123.7, 125.3, 126.0, 128.4, 129.5, 130.0, 132.0, 137.5, 139.9, 147.8, 148.0, 168.2, 169.6, 170.0, 174.2; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T=30^\circ C$, 254 nm): $t_R=21.03$ min(major), $t_R=18.14$ min(minor); IR (KBr): γ 3363, 2987, 924, 2227, 1750, 1724, 1600, 1518, 1461, 1342, 1267, 865, 764, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{32}H_{28}N_4O_8)^+$ requires m/z 596.1907, found m/z 596.1909.

Diethyl-1-acetyl-4'-(4-(methoxycarbonyl)phenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7b), 117 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1- 5/1), 93% yield, white solid, m.p. 177-179°C; $[a]_D^{25} = +185.9$ ($c=0.22$

in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.70-0.74 (m, 3H), 1.35-1.38 (m, 3H), 2.55 (s, 3H), 3.68-3.75 (m, 2H), 3.81-3.85 (m, 4H), 4.40-4.43 (m, 2H), 4.54 (d, *J* = 10.9 Hz, 1H), 5.42 (m, 1H), 6.86 (d, *J* = 8.3 Hz, 2H), 7.27-7.32 (m, 2H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 8.00-8.02 (m, 1H), 8.08 (d, *J* = 8.6 Hz, 2H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 52.1, 61.7, 62.1, 62.8, 63.6, 64.9, 78.0, 116.6, 123.3, 123.5, 123.9, 125.1, 126.3, 128.4, 128.7, 129.4, 129.7, 130.2, 137.0, 139.8, 147.6, 148.5, 166.3, 168.3, 169.6, 170.0, 174.4; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 19.39 min(major), t_R = 28.15 min(minor); IR (KBr): γ 3326, 3074, 2980, 2930, 1756, 1706, 1600, 1518, 1461, 1348, 1285, 865, 834, 764, 727, 588; HRMS (FT-ICRMS) exact mass calcd for (C₃₃H₃₁N₃O₁₀)⁺ requires *m/z* 629.2009, found *m/z* 629.2015.

Diethyl-1-acetyl-4'-(4-bromophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7c), 126 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 97% yield, white solid, m.p. 188-190°C; [α]_D²⁵ = + 193.8 (c= 0.21 in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.73 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2Hz, 3H), 2.55 (s, 3H), 3.67-3.73 (m, 2H), 3.80-3.85 (m, 1H), 4.36-4.45 (m, 3H), 5.29 (dd, *J*₁ = 3.4, *J*₂ = 10.5 Hz 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.25-7.36 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 8.05-8.09 (m, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.0, 14.0, 26.5, 61.3, 62.1, 62.7, 63.8, 64.7, 77.9, 116.6, 122.6, 123.2, 123.4, 125.0, 126.3, 128.3, 129.6, 130.2, 130.6, 130.8, 131.4, 139.9, 147.5, 148.6, 168.3, 169.6, 170.0, 174.3; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 18.23 min(major), t_R = 12.24 min(minor); IR (KBr): γ 3363, 3074, 2980, 1750, 1724, 1600, 1512, 1461, 1342, 1273, 858, 815, 764, 696, 588; HRMS (FT-ICRMS) exact mass calcd for (C₃₁H₂₈BrN₃O₈)⁺ requires *m/z* 649.1060, found *m/z* 649.1062.

Diethyl-1-acetyl-4'-(4-fluorophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7d), 107 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 91% yield, white solid, m.p. 90-92°C; [α]_D²⁵ = + 134 (c= 0.10 in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.72 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2Hz, 3H), 2.54 (s, 3H), 3.68-3.73 (m, 2H), 3.80-3.85 (m, 1H), 4.39-4.46 (m, 3H), 5.25 (d, *J*₁ = 11.0 Hz 1H), 6.68-6.73 (m, 4H), 7.26-7.34 (m, 2H), 7.46-7.50 (m, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 8.03-8.05 (m, 1H), 8.08-8.10 (m, 2H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 61.3, 62.1, 62.8, 64.0, 64.9, 77.8,

115.3(d, J = 21.2 Hz), 116.6, 123.3, 123.5, 125.1, 126.6, 127.5, 128.4, 129.6, 130.3 (d, J = 8.0 Hz), 139.9, 147.6, 148.7, 162.5 (d, J = 246.7 Hz), 168.5, 169.7, 170.1, 174.5; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.23 min(major), t_R = 11.18 min(minor); IR (KBr): γ 3376, 3074, 2987, 2937, 1750, 1719, 1600, 1518, 1461, 1348, 1273, 865, 840, 764, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}FN_3O_8)^+$ requires m/z 589.1860, found m/z 589.1865.

Diethyl-1-acetyl-4'-(4-chlorophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7e), 114 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 94% yield, white solid, m.p. 172-174°C; $[\alpha]_D^{25}$ = + 178.5 (c = 0.20 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.72 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 2.55 (s, 3H), 3.67-3.72 (m, 2H), 3.80-3.83 (m, 1H), 4.38-4.45 (m, 3H), 5.30 (d, J_1 = 10.9 Hz 1H), 6.69 (d, J = 8.7 Hz, 2H), 6.95-6.97 (m, 2H), 7.26-7.34 (m, 2H), 7.46-7.50 (m, 1H), 7.79 (d, J = 8.8 Hz, 2H), 8.04-8.10 (m, 3H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.6, 61.3, 62.2, 62.8, 64.0, 64.8, 78.0, 116.7, 123.3, 123.6, 125.1, 126.5, 128.4, 128.5, 129.7, 130.0, 130.3, 134.5, 140.0, 147.6, 148.5, 168.4, 169.7, 170.1, 174.5; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 17.59 min(major), t_R = 11.76 min(minor); IR (KBr): γ 3376, 2980, 2937, 1750, 1724, 1600, 1505, 1461, 1366, 1273, 858, 759, 696, 583; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}ClN_3O_8)^+$ requires m/z 605.1565, found m/z 605.1560.

Diethyl-1-acetyl-4'-(4-methoxyphenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7f), 115 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 94% yield, white solid, m.p. 131-134°C; $[\alpha]_D^{25}$ = + 180.0 (c = 0.25 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.71 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 2.54 (s, 3H), 3.63 (s, 3H), 3.68-3.72 (m, 2H), 3.80-3.84 (m, 1H), 4.38-4.44 (m, 3H), 5.25 (dd, J_1 = 3.4, J_2 = 10.8 Hz 1H), 6.50 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 8.7 Hz, 2H), 7.26-7.32 (m, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.78 (d, J = 8.7 Hz, 2H), 8.02-8.8 (m, 3H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 55.0, 61.6, 62.0, 62.7, 63.9, 65.0, 77.8, 113.6, 116.5, 123.3, 123.4, 123.9, 124.9, 126.9, 128.4, 129.4, 129.7, 140.0, 147.4, 149.1, 159.4, 168.6, 169.8, 170.2, 174.7; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 18.94 min(major), t_R = 12.85 min(minor); IR (KBr): γ 3363, 3074, 2980, 2930, 1756, 1719, 1600, 1518, 1461, 1366, 1273, 858, 834, 758, 696, 588; HRMS (FT-ICRMS)

exact mass calcd for $(C_{32}H_{31}N_3O_9)^+$ requires m/z 601.2060, found m/z 601.2059.

Diethyl-1-acetyl-5'-(4-nitrophenyl)-2-oxo-4'-p-tolylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7g), 108 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 92% yield, white solid, m.p. 83-85°C; $[a]_D^{25} = +153.0$ ($c = 0.10$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.71 (t, $J = 7.2$ Hz, 3H), 1.36 (t, $J = 7.2$ Hz, 3H), 2.13 (s, 3H), 2.54 (s, 3H), 3.67-3.72 (m, 2H), 3.79-3.82 (m, 1H), 4.39-4.44 (m, 3H), 5.29 (d, $J_1 = 11.0$ Hz 1H), 6.62 (d, $J = 8.1$ Hz, 2H), 6.76 (d, $J = 8.1$ Hz, 2H), 7.26-7.31 (m, 2H), 7.46-7.48 (m, 1H), 7.79 (d, $J = 8.8$ Hz, 2H), 8.01-8.03 (m, 1H), 8.06-8.08 (m, 2H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.1, 21.0, 26.5, 61.8, 62.1, 62.7, 63.7, 65.0, 77.9, 116.5, 123.3, 123.4, 125.0, 126.9, 128.4, 128.5, 129.0, 129.4, 138.2, 140.0, 147.5, 149.1, 168.6, 169.8, 170.3, 174.7; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ C$, 254 nm): $t_R = 15.93$ min(major), $t_R = 9.83$ min(minor); IR (KBr): γ 3363, 2987, 2924, 1750, 1719, 1600, 1518, 1461, 1342, 1280, 858, 834, 759, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{32}H_{31}N_3O_8)^+$ requires m/z 585.2111, found m/z 585.2119.

Diethyl-1-acetyl-4'-(2-fluorophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7h), 114 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 97% yield, white solid, m.p. 80-82°C; $[a]_D^{25} = +27.0$ ($c = 0.20$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.73 (t, $J = 7.2$ Hz, 3H), 1.35 (t, $J = 7.2$ Hz, 3H), 2.58 (s, 3H), 3.74-3.89 (m, 3H), 4.38-4.44 (q, 2H), 4.92 (d, $J = 10.8$ Hz, 1H), 5.46 (d, $J = 10.8$ Hz, 2H), 6.74-6.79 (m, 2H), 6.81-6.85 (m, 1H), 7.03-7.05 (m, 1H), 7.16-7.20 (m, 1H), 7.26-7.35 (m, 2H), 7.82 (d, $J = 8.8$ Hz, 2H), 8.03 (d, $J = 8.0$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 2H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 13.9, 26.3, 54.1, 61.1, 62.7, 63.1, 63.9, 78.3, 115.5 (d, $J = 22.9$ Hz), 115.6, 119.5 (d, $J = 13.1$ Hz), 123.5, 123.6, 123.7, 124.7, 126.4, 128.4, 129.2, 129.4 (d, $J = 15.8$ Hz), 129.9 (d, $J = 8.6$ Hz), 140.0, 147.6, 148.7, 161.1 (d, $J = 246.2$ Hz), 168.7, 169.5, 170.4, 174.9; Enantiomeric excess: 81%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ C$, 254 nm): $t_R = 18.80$ min(major), $t_R = 12.58$ min(minor); IR (KBr): γ 3370, 2987, 1737, 1606, 1518, 1348, 1273, 1230, 1016, 852, 752, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}FN_3O_8)^+$ requires m/z 589.1860, found m/z 589.1852.

Diethyl-1-acetyl-4'-(2-chlorophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7i), 115 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 95% yield, white solid, m.p. 82-85°C; $[a]_D^{25} = +144.0$ ($c = 0.10$ in $CHCl_3$);

¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.79-0.83 (m, 3H), 1.34-1.37 (m, 3H), 2.56 (s, 3H), 3.65 (brs, 1H), 3.70-3.95 (m, 2H), 4.38-4.45 (m, 3H), 5.26 (d, *J* = 10.8 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.90-6.98 (m, 1H), 7.07-7.08 (m, 1H), 7.26-7.29 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 8.10-8.12 (m, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.2, 14.0, 26.4, 61.3, 62.3, 63.0, 63.4, 64.6, 77.8, 117.1, 123.7, 124.2, 124.9, 125.1, 126.4, 128.5, 128.8, 128.9, 129.6, 133.7, 134.4, 135.5, 140.6, 147.7, 148.1, 168.2, 169.5, 170.0, 174.2; Enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 18.25 min(major), t_R = 16.14 min(minor); IR (KBr): γ 3370, 2980, 2924, 1756, 1724, 1600, 1518, 1474, 1348, 1280, 852, 752, 689, 588; HRMS (FT-ICRMS) exact mass calcd for (C₃₁H₂₈ClN₃O₈)⁺ requires m/z 605.1565, found m/z 605.1562.

Diethyl-1-acetyl-4'-(3-chlorophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7j), 113 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 93% yield, white solid, m.p. 89-91°C; [α]_D²⁵ = + 148.0 (c= 0.10 in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.70-0.73 (m, 3H), 1.35-1.38 (m, 3H), 2.56 (s, 3H), 3.70-3.85 (m, 3H), 4.39-4.46 (m, 3H), 5.30 (d, *J* = 10.8 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 1.6 Hz, 1H), 6.89-6.93 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.26-7.34 (m, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.80-7.83 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 2H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.1, 14.0, 26.4, 61.5, 62.1, 62.8, 63.5, 64.9, 77.7, 116.6, 123.2, 123.6, 125.1, 126.4, 126.6, 128.4, 128.6, 128.8, 129.4, 129.7, 133.9, 134.1, 139.8, 147.6, 148.5, 168.4, 169.7, 170.1, 174.; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 20.74 min(major), t_R = 10.80 min(minor); IR (KBr): γ 3363, 2980, 2937, 1756, 1724, 1600, 1524, 1455, 1336, 1280, 858, 759, 696, 588; HRMS (FT-ICRMS) exact mass calcd for (C₃₁H₂₈ClN₃O₈)⁺ requires m/z 605.1565, found m/z 605.1558.

Diethyl-1-acetyl-4'-(3,4-dichlorophenyl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7k), 116 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 91% yield, white solid, m.p. 159-160°C; [α]_D²⁵ = + 175.8 (c= 0.17 in CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.70-0.74(m, 3H), 1.34-1.38 (m, 3H), 2.56 (s, 3H), 3.71-3.83 (m, 3H), 4.38-4.42 (m, 3H), 5.24 (d, *J* = 10.8 Hz, 1H), 6.56-6.60 (m, 1H), 6.86 (d, *J* = 1.6 Hz, 1H), 7.05(d, *J* = 8.4 Hz, 1H), 7.30-7.37 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 8.07-8.13 (m, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 13.1, 14.1, 26.6, 60.9, 62.2, 62.9, 63.9, 64.7, 77.9, 116.8, 123.3, 123.7, 125.2, 126.1, 127.7, 129.9, 130.2, 130.7, 132.2, 132.6, 132.8, 139.9,

147.8, 148.1, 168.3, 169.6, 170.1, 174.3; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 18.81 min(major), t_R = 10.94 min(minor); IR (KBr): γ 3426, 2987, 2924, 1750, 1719, 1606, 1518, 1467, 1342, 1016, 858, 759, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{27}Cl_2N_3O_8)^+$ requires m/z 639.1175, found m/z 605.1182.

Diethyl-1-acetyl-4'-(naphthalen-2-yl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7l), 112 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 90% yield, white solid, m.p. 99-101°C; $[\alpha]_D^{25} = +231.9$ ($c = 0.21$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.72 (t, $J = 7.2$ Hz, 3H), 1.38 (t, $J = 7.2$ Hz, 3H), 2.50 (s, 3H), 3.71-3.83 (m, 3H), 4.44 (m, 2H), 4.65 (d, $J = 11.2$ Hz, 1H), 5.46 (d, $J = 11.2$ Hz, 1H), 6.83 (dd, $J_1 = 1.6$, $J_2 = 8.4$ Hz 1H), 7.29-7.38 (m, 5H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.50-7.62 (m, 3H), 7.80 (dd, $J_1 = 2.0$, $J_2 = 6.8$ Hz 2H), 7.93 (d, $J = 9.2$ Hz, 1H), 8.04 (dd, $J_1 = 2.0$, $J_2 = 6.8$ Hz 2H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.1, 26.5, 62.1, 62.2, 62.8, 63.9, 65.1, 78.1, 116.6, 123.4, 123.5, 125.0, 125.6, 126.4, 126.5, 126.8, 127.5, 127.7, 127.9, 128.4, 128.7, 129.2, 129.5, 132.9, 140.0, 147.5, 148.9, 168.6, 169.8, 170.1, 174.7; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 25.38 min(major), t_R = 11.53 min(minor); IR (KBr): γ 3370, 2975, 2930, 1756, 1724, 1600, 1518, 1467, 1342, 1267, 858, 752, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{35}H_{31}N_3O_8)^+$ requires m/z 621.2111, found m/z 621.2110.

Diethyl-1-acetyl-4'-(naphthalen-1-yl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7m), 114 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 92% yield, white solid, m.p. 142-144°C; $[\alpha]_D^{25} = +233.9$ ($c = 0.23$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.69 (t, $J = 7.2$ Hz, 3H), 1.44 (t, $J = 7.2$ Hz, 3H), 2.06 (s, 3H), 3.79-3.84 (m, 3H), 4.51-4.53 (q, 2H), 5.49 (d, $J = 10.4$ Hz, 1H), 5.77 (d, $J = 10.4$ Hz, 1H), 6.94-7.00 (m, 2H), 7.25-7.28 (m, 3H), 7.35-7.41 (m, 2H), 7.50-7.56 (m, 2H), 7.66-7.68 (m, 1H), 7.80-7.82 (m, 2H), 7.87 (dd, $J_1 = 3.2$, $J_2 = 6.0$ Hz 2H), 7.97-8.02 (m, 3H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.1, 25.8, 54.3, 62.1, 62.8, 64.4, 64.5, 78.8, 116.3, 122.4, 123.4, 123.5, 124.1, 124.8, 125.7, 125.9, 126.5, 127.0, 127.4, 128.3, 128.8, 128.9, 129.3, 132.4, 133.7, 139.9, 147.5, 149.0, 168.8, 170.0, 170.1, 174.7; Enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 21.00 min(major), t_R = 12.26 min(minor); IR (KBr): γ 3383, 3062, 2980, 2937, 1750, 1724, 1600, 1524, 1467, 1348,

1273, 858, 777, 759, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{35}H_{31}N_3O_8)^+$ requires m/z 621.2111, found m/z 621.2119.

Diethyl-1-acetyl-4'-(furan-2-yl)-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7n), 83 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1- 5/1), 74% yield, white solid, m.p. 75-77°C; $[\alpha]_D^{25} = + 86.0$ ($c = 0.10$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.74 (t, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 2.64 (s, 3H), 3.66-3.86 (m, 3H), 4.34-4.41 (m, 2H), 5.56 (d, $J = 10.4$ Hz, 1H), 5.36 (d, $J = 10.4$ Hz, 1H), 5.77 (d, $J = 3.2$ Hz, 1H), 6.02 (dd, $J_1 = 2.0$, $J_2 = 3.2$ Hz 1H), 7.00-7.01 (m, 1H), 7.20-7.22 (m, 1H), 7.29-7.35 (m, 2H), 7.80 (d, $J = 8.8$ Hz, 2H), 8.11-8.15 (m, 3H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.6, 55.7, 62.2, 62.7, 63.1, 63.7, 78.3, 109.2, 110.3, 116.3, 123.0, 123.5, 123.6, 125.0, 126.7, 127.7, 128.3, 129.4, 139.9, 142.6, 147.3, 147.6, 148.8, 168.3, 169.4, 170.5, 174.8; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 16.33$ min(major), $t_R = 10.47$ min(minor); IR (KBr): γ 3363, 3119, 3081, 2980, 2937, 1750, 1600, 1518, 1461, 1342, 1273, 858, 752, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{29}H_{27}N_3O_9)^+$ requires m/z 561.1747, found m/z 561.1746.

Diethyl-1-acetyl-5'-(4-nitrophenyl)-2-oxo-4'-styrylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7o), 98 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 82% yield, white solid, m.p. 71-73°C; $[\alpha]_D^{25} = + 131.2$ ($c = 0.16$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.75 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 2.61 (s, 3H), 3.66-3.70 (m, 1H), 3.81-3.92 (m, 2H), 4.35-4.40 (m, 2H), 4.90-4.95 (m, 1H), 5.37 (dd, $J_1 = 9.6$, $J_2 = 15.6$ Hz 1H), 6.17 (d, $J = 15.6$ Hz, 1H), 6.94-6.96 (m, 2H), 7.16-7.18 (m, 3H), 7.21-7.25 (m, 1H), 7.30-7.44 (m, 3H), 7.90 (d, $J = 8.8$ Hz, 2H), 8.17 (d, $J = 8.8$ Hz, 2H), 8.28 (d, $J = 8.1$ Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.2, 14.1, 26.6, 56.5, 60.8, 62.4, 62.7, 65.4, 78.4, 116.7, 121.2, 122.9, 123.2, 123.5, 125.4, 126.4, 126.7, 127.5, 128.3, 128.6, 129.6, 135.7, 136.5, 140.2, 148.8, 168.4, 169.6, 170.5, 174.7; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 17.05$ min(major), $t_R = 10.91$ min(minor); IR (KBr): γ 3433, 2980, 2924, 1750, 1606, 1518, 1342, 1280, 1172, 1016, 852, 752, 689, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{33}H_{31}N_3O_8)^+$ requires m/z 597.2111, found m/z 597.2114

Diethyl-1-acetyl-4'-isobutyl-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7p), 104 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate =

15/1- 5/1), 94% yield, Colorless oil; $[\alpha]_{\text{D}}^{25} = + 81.6$ ($c = 0.18$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.46 (d, $J = 5.8$ Hz, 3H), 0.51 (d, $J = 5.8$ Hz, 3H), 0.76 (t, $J = 7.1$ Hz, 3H), 0.80-0.82 (m, 2H), 1.20 (d, $J = 6.1$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H), 2.68 (s, 3H), 3.30-3.40 (m, 1H), 3.50 (brs, 1H), 3.57-3.62 (m, 1H), 3.78-3.83 (m, 1H), 4.33-4.39 (m, 2H), 4.56 (d, $J = 10.8$ Hz, 1H), 7.24-7.27 (m, 2H), 7.39-7.42 (m, 1H), 8.00 (dd, $J_1 = 1.8$, $J_2 = 6.9$ Hz 2H), 8.24 (dd, $J_1 = 1.8$, $J_2 = 6.9$ Hz 2H), 8.32 (d, $J = 8.2$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 21.7, 23.0, 25.8, 26.7, 36.8, 53.4, 62.0, 62.6, 63.4, 67.5, 79.2, 116.5, 123.4, 123.7, 125.4, 127.0, 127.5, 129.3, 140.3, 147.8, 149.7, 168.6, 169.9, 170.6, 175.6; Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_{\text{R}} = 14.22$ min(major), $t_{\text{R}} = 8.64$ min(minor); IR (KBr): γ 3363, 3081, 2962, 1756, 1719, 1600, 1518, 1461, 1348, 1273, 858, 752, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_8)^+$ requires m/z 551.2268, found m/z 551.2274

Diethyl-1-acetyl-5'-(4-nitrophenyl)-2-oxo-4'-propylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7q), 101 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 94% yield, white solid, m.p. $49\text{-}51^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} = + 59.5$ ($c = 0.20$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.52 (t, $J = 7.2$ Hz, 3H), 0.77 (t, $J = 7.2$ Hz, 3H), 0.80-1.05 (m, 2H), 1.33-1.39 (m, 5H), 2.69 (s, 3H), 3.25-3.35 (m, 1H), 3.50-3.70 (m, 3H), 4.33-4.39 (m, 2H), 4.59 (d, $J = 10.4$ Hz, 1H), 7.25-7.27 (m, 1H), 7.30-7.42 (m, 2H), 8.01-8.03 (m, 2H), 8.23-8.25 (m, 2H), 8.33 (d, $J = 8.4$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 14.2, 20.6, 26.7, 29.6, 55.6, 62.1, 62.6, 67.2, 72.3, 79.3, 116.5, 123.1, 123.5, 123.7, 125.2, 127.5, 129.4, 140.4, 147.8, 149.8, 168.5, 169.9, 170.6, 175.8; Enantiomeric excess: 83%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_{\text{R}} = 16.40$ min(major), $t_{\text{R}} = 9.05$ min(minor); IR (KBr): γ 3363, 2962, 2930, 1750, 1600, 1518, 1461, 1342, 1273, 1210, 1016, 858, 752, 701, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{28}\text{H}_{31}\text{N}_3\text{O}_8)^+$ requires m/z 537.2111, found m/z 537.2108.

Diethyl-1-acetyl-5'-isobutyl-2-oxo-4'-p-tolylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7r), 92 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 88% yield, white solid, m.p. $145\text{-}147^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} = + 33.0$ ($c = 0.10$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.70 (t, $J = 7.1$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 6H), 1.32-1.35 (m, 4H), 1.75-1.90 (m, 2H), 2.15 (s, 3H), 2.56 (s, 3H), 2.85 (brs, 1H), 3.70-3.75 (m, 2H), 4.01 (d, $J = 10.6$ Hz, 1H), 4.10-4.15 (m, 1H), 4.32-4.36 (m, 2H), 6.65 (d, $J = 8.1$ Hz, 2H), 6.78 (d, $J = 8.1$ Hz, 2H), 7.18-7.23 (m, 2H), 7.50

(dd, $J_1 = 1.2$, $J_2 = 7.2$ Hz 1H), 7.95 (dd, $J_1 = 1.3$, $J_2 = 7.4$ Hz 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 21.0, 31.9, 23.7, 26.1, 26.6, 44.0, 58.3, 59.7, 61.5, 62.6, 79.0, 116.1, 124.0, 124.9, 127.6, 128.3, 128.8, 129.9, 130.4, 137.5, 139.9, 168.8, 170.4, 170.8, 175.7; Enantiomeric excess: 82%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 99/ 1, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 23.57$ min(major), $t_R = 20.32$ min(minor); IR (KBr): γ 3351, 3049, 2955, 1756, 1724, 1600, 1518, 1461, 1273, 1217, 846, 752, 696, 583; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_8)^+$ requires m/z 520.2573, found m/z 520.2560.

Diethyl-1-acetyl-4'-(4-chlorophenyl)-5'-isobutyl-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7s), 102 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 94% yield, white solid, m.p. $186\text{--}188^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} = +30.5$ ($c = 0.21$ in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 6H), 1.30-1.35 (m, 4H), 1.75-1.88 (m, 2H), 2.56 (s, 3H), 2.90 (brs, 1H), 3.70-3.76 (m, 2H), 4.01 (d, $J = 10.6$ Hz, 1H), 4.05-4.10 (m, 1H), 4.32-4.35 (m, 2H), 6.71 (d, $J = 8.5$ Hz, 2H), 6.96-6.98 (m, 2H), 7.19-7.26 (m, 2H), 7.50 (dd, $J_1 = 1.4$, $J_2 = 7.3$ Hz 1H), 7.98 (dd, $J_1 = 1.2$, $J_2 = 8.0$ Hz 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 22.0, 23.6, 26.1, 26.6, 44.0, 58.5, 59.3, 61.6, 62.7, 79.0, 116.3, 124.0, 125.0, 127.1, 128.3, 129.1, 129.7, 132.2, 133.8, 139.9, 168.6, 170.2, 170.7, 175.4; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 99/ 1, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 7.31$ min(major), $t_R = 6.33$ min(minor); IR (KBr): γ 3351, 3068, 2962, 1750, 1694, 1600, 1474, 1280, 1217, 846, 759, 696, 583; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_8)^+$ requires m/z 540.2027, found m/z 540.2024.

Diethyl-1-acetyl-4'-(4-fluorophenyl)-5'-isobutyl-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7t), 93 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 89% yield, white solid, m.p. $164\text{--}166^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} = +27.0$ ($c = 0.20$ in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 6H), 1.30-1.35 (m, 4H), 1.75-1.90 (m, 2H), 2.56 (s, 3H), 3.71-3.76 (m, 2H), 4.00-4.10 (m, 2H), 4.33-4.36 (m, 2H), 6.66-6.75 (m, 4H), 7.19-7.25 (m, 2H), 7.51 (dd, $J_1 = 1.6$, $J_2 = 7.2$ Hz 1H), 7.97 (dd, $J_1 = 0.8$, $J_2 = 8.0$ Hz 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 22.0, 23.6, 26.1, 26.5, 44.0, 58.6, 59.2, 61.6, 62.7, 78.9, 115.0 (d, $J = 21.0$ Hz), 116.2, 123.9, 125.0, 127.2, 129.0, 129.4, 130.0 (d, $J = 7.8$ Hz), 139.9, 162.5 (d, $J = 247.0$ Hz), 168.7, 170.2, 170.7, 175.5; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 7.17$ min(major), $t_R = 6.30$ min(minor); IR (KBr): γ 3433, 2955, 2930, 1756, 1724, 1600, 1512,

1455, 1280, 1210, 846, 752, 583; HRMS (FT-ICRMS) exact mass calcd for $(C_{29}H_{33}N_3O_8)^+$ requires m/z 524.2323, found m/z 524.2316.

Diethyl-1-acetyl-4'-(3-chlorophenyl)-5'-neopentyl-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (7u), 104 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 20/1- 5/1), 94% yield, white solid, m.p. 109-110°C; $[a]_D^{25} = + 32.0$ ($c = 0.10$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.71 (t, $J = 7.1$ Hz, 3H), 0.98 (s, 9H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.39 (dd, $J_1 = 0.7$, $J_2 = 14.2$ Hz 1H), 1.96 (dd, $J_1 = 9.0$, $J_2 = 14.3$ Hz 1H), 2.58 (s, 3H), 2.80 (s, 1H), 3.72-3.76 (m, 2H), 4.00 (d, $J = 10.7$ Hz, 1H), 4.07-4.09 (m, 1H), 4.32-4.36 (m, 2H), 6.62-6.63 (m, 1H), 6.80-6.81 (m, 1H), 6.89-6.93 (m, 1H), 7.02-7.03 (m, 1H), 7.21-7.26 (m, 2H), 7.51 (d, $J_1 = 1.8$, Hz 1H), 7.97 (dd, $J_1 = 1.5$, $J_2 = 8.0$ Hz 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.1, 14.0, 26.5, 30.0, 30.6, 48.4, 57.3, 59.8, 61.5, 62.6, 63.7, 79.3, 116.1, 123.9, 125.1, 126.5, 127.0, 128.1, 129.0, 129.2, 133.9, 135.5, 139.8, 168.6, 170.3, 170.9, 175.6; Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 5.75$ min(major), $t_R = 4.86$ min(minor); IR (KBr): γ 3389, 3074, 2962, 1756, 1719, 1600, 1461, 1367, 1273, 759, 708, 626, 588; HRMS (FT-ICRMS) exact mass calcd for $(C_{29}H_{33}N_3O_8)^+$ requires m/z 554.2184, found m/z 554.2186.

Diethyl-1-acetyl-5-fluoro-5'-isobutyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8a), 91 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 87% yield, white solid, m.p. 150-152°C; $[a]_D^{25} = + 24.0$ ($c = 0.20$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.80 (t, $J = 7.1$ Hz, 3H), 0.90-0.93 (m, 6H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.38-1.42 (m, 1H), 1.70-1.75 (m, 1H), 1.90-1.95 (m, 1H), 2.55 (s, 3H), 2.85 (brs, 1H), 3.79-3.85 (q, 2H), 4.02 (d, $J = 10.6$ Hz, 1H), 4.10-4.15 (m, 1H), 4.32-4.36 (m, 2H), 6.78-6.81 (m, 2H), 6.91-6.92 (m, 1H), 7.00-7.03 (m, 2H), 7.06-7.08 (m, 1H), 7.26-7.29 (m, 1H), 7.92 (dd, $J_1 = 4.7$ Hz, $J_2 = 8.9$ Hz 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.3, 14.0, 22.0, 23.6, 26.1, 26.4, 44.0, 58.0, 60.0, 61.7, 62.8, 78.8, 111.8 (d, $J = 25.0$ Hz), 115.2 (d, $J = 22.3$ Hz), 117.4 (d, $J = 7.8$ Hz), 128.0, 128.2, 128.3, 129.5 (d, $J = 8.3$ Hz), 133.2, 135.9, 160.1 (d, $J = 243.0$ Hz), 168.5, 170.0, 170.7, 175.3; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 6.51$ min(major), $t_R = 5.37$ min(minor); IR (KBr): γ 3345, 3062, 2955, 1750, 1706, 1600, 1474, 1373, 1291, 827, 771, 701, 583; HRMS (FT-ICRMS) exact mass calcd for $(C_{29}H_{33}FN_2O_6)^+$ requires m/z 524.2323, found m/z 524.2328.

Diethyl-1-acetyl-5-chloro-5'-isobutyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dica

rboxylate (8b), 102 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 94% yield, white solid, m.p. 163-165°C; $[\alpha]_{\text{D}}^{25} = + 87.0$ ($c = 0.20$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.80 (t, $J = 7.1$ Hz, 3H), 0.91-0.93 (m, 6H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.42-1.45 (m, 1H), 1.65-1.70 (m, 1H), 1.89-1.95 (m, 1H), 2.55 (s, 3H), 2.85 (brs, 1H), 3.81-3.86 (q, 2H), 4.00 (d, $J = 10.6$ Hz, 1H), 4.10-4.15 (m, 1H), 4.31-4.37 (m, 2H), 6.77-6.79 (m, 2H), 7.01-7.04 (m, 2H), 7.06-7.08 (m, 1H), 7.19 (dd, $J_1 = 2.2$ Hz, $J_2 = 8.7$ Hz 1H), 7.50 (d, $J = 2.2$ Hz, 1H), 7.88 (d, $J = 8.7$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.3, 14.0, 22.1, 23.6, 26.1, 26.4, 44.1, 58.1, 60.1, 61.8, 62.8, 64.7, 78.9, 117.2, 124.2, 128.1, 128.2, 128.3, 128.8, 129.5, 130.5, 133.2, 138.3, 168.4, 170.1, 170.5, 175.5; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_{\text{R}} = 6.12$ min(major), $t_{\text{R}} = 5.20$ min(minor); IR (KBr): γ 3345, 3062, 2955, 1750, 1706, 1600, 1467, 1373, 1298, 1273, 827, 752, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{33}\text{ClN}_2\text{O}_6)^+$ requires m/z 540.2027, found m/z 540.2034.

Diethyl-1-acetyl-5'-isobutyl-5-methyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8c), 99 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 18/1- 5/1), 95% yield, white solid, m.p. 122-124°C; $[\alpha]_{\text{D}}^{25} = + 60.5$ ($c = 0.18$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.80 (t, $J = 7.1$ Hz, 3H), 0.88-0.92 (m, 6H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.38-1.45 (m, 1H), 1.67-1.72 (m, 1H), 1.90-1.95 (m, 1H), 2.38 (s, 3H), 2.55 (s, 3H), 2.90 (brs, 1H), 3.73-3.77 (m, 2H), 4.01 (d, $J = 10.6$ Hz, 1H), 4.10-4.13 (m, 1H), 4.32-4.36 (m, 2H), 6.75-6.77 (m, 2H), 6.97-7.05 (m, 4H), 7.30 (d, $J = 1.1$ Hz, 1H), 7.80 (d, $J = 8.3$ Hz 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.1, 14.0, 14.1, 22.4, 22.1, 23.6, 26.1, 26.4, 44.1, 58.3, 60.1, 61.5, 62.6, 64.9, 79.0, 115.8, 124.4, 127.4, 127.8, 128.0, 128.4, 129.3, 133.7, 134.6, 137.6, 168.8, 170.2, 170.9, 175.8; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_{\text{R}} = 6.33$ min(major), $t_{\text{R}} = 5.36$ min(minor); IR (KBr): γ 3351, 3056, 2955, 1756, 1700, 1600, 1480, 1373, 1304, 1273, 827, 771, 689, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_6)^+$ requires m/z 520.2573, found m/z 520.2568.

Diethyl-1-acetyl-5-bromo-5'-isobutyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8d), 105 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 90% yield, white solid, m.p. 148-150°C; $[\alpha]_{\text{D}}^{25} = + 76.2$ ($c = 0.08$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.80 (t, $J = 7.1$ Hz, 3H), 0.90-0.93 (m, 6H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.40-1.45 (m, 1H), 1.70-1.75 (m, 1H), 1.90-1.95 (m, 1H), 2.55 (s, 3H), 2.90 (brs, 1H), 3.82-3.85 (m,

2H), 3.99 (d, J = 10.6 Hz, 1H), 4.10-4.15 (m, 1H), 4.31-4.36 (m, 2H), 6.77-6.79 (m, 2H), 7.01-7.04 (m, 2H), 7.06-7.08 (m, 1H), 7.34 (dd, J_1 = 2.1 Hz, J_2 = 8.7 Hz 1H), 7.63 (d, J = 2.1 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.3, 14.0, 22.1, 23.6, 26.1, 26.5, 44.1, 58.1, 60.1, 61.8, 62.8, 64.6, 78.9, 117.6, 118.0, 127.0, 128.1, 128.2, 128.3, 129.8, 131.8, 133.2, 168.5, 170.0, 170.7, 175.3; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, T = 30 $^{\circ}\text{C}$, 254 nm): t_R = 6.26 min(major), t_R = 5.27 min(minor); IR (KBr): γ 3351, 3056, 2962, 1756, 1706, 1600, 1467, 1373, 1298, 1273, 827, 721, 696, 588; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{33}\text{BrN}_2\text{O}_6)^+$ requires m/z 584.1522, found m/z 584.1520.

Diethyl-1-acetyl-6-chloro-5'-isobutyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8e), 102 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 94% yield, white solid, m.p. 123-125 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ = + 42.0 (c = 0.10 in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.80 (t, J = 7.1 Hz, 3H), 0.91 (d, J = 6.5 Hz, 6H), 1.33 (t, J = 7.1 Hz, 3H), 1.36-1.42 (m, 1H), 1.68-1.75 (m, 1H), 1.85-1.95 (m, 1H), 2.55 (s, 3H), 2.90 (brs, 1H), 3.78-3.81 (m, 2H), 4.02 (d, J = 10.6 Hz, 1H), 4.15-4.20 (m, 1H), 4.31-4.37 (m, 2H), 6.77-6.79 (m, 2H), 7.00-7.04 (m, 2H), 7.06-7.08 (m, 1H), 7.18 (dd, J_1 = 2.0 Hz, J_2 = 7.9 Hz 1H), 7.44 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 2.0 Hz, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.2, 13.7, 22.9, 23.5, 26.0, 26.3, 50.5, 58.1, 59.8, 61.6, 62.7, 64.4, 78.8, 116.6, 124.9, 126.0, 128.0, 128.1, 128.2, 133.2, 134.5, 140.5, 168.5, 170.0, 170.5, 175.2; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, T = 30 $^{\circ}\text{C}$, 254 nm): t_R = 6.14 min(major), t_R = 6.97 min(minor); IR (KBr): γ 3351, 3068, 2955, 1762, 1706, 1600, 1467, 1373, 1280, 1210, 746, 696, 613; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{29}\text{H}_{33}\text{ClN}_2\text{O}_6)^+$ requires m/z 540.2027, found m/z 540.2021.

Diethyl-1-acetyl-5'-isobutyl-6-methyl-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8f), 93 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 18/1- 5/1), 89% yield, white solid, m.p. 128-130 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ = + 40.0 (c = 0.10 in CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.73 (t, J = 7.1 Hz, 3H), 0.88-0.91 (m, 6H), 1.30-1.40 (m, 4H), 1.70-1.75 (m, 1H), 1.85-1.90 (m, 1H), 2.30 (s, 3H), 2.54 (s, 3H), 2.90 (brs, 1H), 3.69-3.77 (m, 2H), 4.03 (d, J = 10.7 Hz, 1H), 4.15-4.20 (m, 1H), 4.32-4.35 (m, 2H), 6.77-6.79 (m, 2H), 6.97-7.01 (m, 3H), 7.04-7.06 (m, 1H), 7.35 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 0.8 Hz 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 13.2, 14.0, 14.1, 21.9, 22.0, 23.6, 26.1, 26.5, 44.0, 58.3, 59.9, 61.5, 62.6, 64.7, 79.0, 116.7,

123.7, 124.3, 125.5, 127.8, 128.0, 128.5, 133.7, 139.0, 139.9, 168.8, 170.4, 170.8, 176.0; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.81 min(major), t_R = 6.39 min(minor); IR (KBr): γ 3358, 3062, 2955, 1756, 1700, 1618, 1492, 1379, 1285, 1217, 809, 701, 633; HRMS (FT-ICRMS) exact mass calcd for $(C_{30}H_{36}N_2O_6)^+$ requires m/z 520.2573, found m/z 520.2575.

Diethyl-1-acetyl-5-chloro-5'-(4-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8g), 110 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 91% yield, white solid, m.p. 78-80°C; $[\alpha]_D^{25} = + 176.0$ (c= 0.10 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.79 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1Hz, 3H), 2.54 (s, 3H), 3.67 (brs, 1H), 3.84-3.89 (m, 2H), 4.38-4.43(m, 2H), 4.46(d, J = 10.9 Hz, 1H), 5.35-5.42 (d, J = 10.9 Hz, 1H), 6.79 (d, J = 7.2 Hz, 2H), 7.00-7.04 (m, 2H), 7.07-7.09 (d, J = 7.2 Hz, 1H), 7.28-7.29 (m, 1H), 7.47 (d, J = 2.1 Hz, 1H), 7.82 (d, J = 8.7 Hz 2H), 7.95 (d, J = 8.7 Hz 1H), 8.06-8.09 (m, 2H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.2, 14.1, 26.4, 61.9, 62.3, 62.9, 63.3, 64.9, 77.8, 117.5, 123.4, 123.5, 128.3, 128.4, 128.5, 128.6, 128.8, 129.3, 130.5, 131.3, 138.3, 147.6, 148.5, 168.3, 169.6, 169.9, 174.2; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak 1-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 19.41 min(major), t_R = 6.20 min(minor); IR (KBr): γ 3376, 3068, 2987, 2930, 1762, 1724, 1606, 1518, 1474, 1348, 1304, 858, 821, 739, 701, 608; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{28}ClN_3O_8)^+$ requires m/z 605.1565, found m/z 605.1559.

Diethyl-1-acetyl-6-chloro-5'-(4-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8h), 104 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 15/1- 5/1), 86% yield white solid, m.p. 97-99°C; $[\alpha]_D^{25} = + 156.0$ (c= 0.10 in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.80 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.1Hz, 3H), 2.54 (s, 3H), 3.60 (brs, 1H), 3.75-3.90 (m, 2H), 4.38-4.42 (m, 2H), 4.46 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 6.76-6.78 (m, 2H), 7.00-7.04 (m, 2H), 7.08-7.10 (m, 1H), 7.25-7.27 (m, 1H), 7.39-7.41 (d, J = 8.0 Hz, 1H), 7.80 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz 2H), 8.08 (m, 3H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.2, 14.0, 26.4, 61.8, 62.3, 62.9, 63.5, 64.8, 77.9, 117.0, 123.5, 124.2, 125.0, 125.3, 128.4, 128.5, 128.7, 131.4, 135.2, 140.7, 147.6, 148.6, 168.4, 169.6, 170.0, 174.4; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 85/ 15, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 13.77 min(major), t_R = 8.94 min(minor); IR (KBr): γ 3433, 3074, 2975, 2924, 1756, 1731, 1600, 1518, 1342, 1291, 852, 746, 701, 613; HRMS (FT-ICRMS) exact

mass calcd for $(C_{31}H_{28}ClN_3O_8)^+$ requires m/z 605.1565, found m/z 605.1571.

Diethyl-1-acetyl-6-chloro-4'-(3-chlorophenyl)-5-fluoro-5'-isobutyl-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8i), 87 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 20/1- 5/1), 73% yield, white solid, m.p. 102-104°C; $[a]_D^{25} = +41.0$ ($c = 0.10$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.89 (t, $J = 7.1$ Hz, 3H), 0.93 (m, 6H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.42-1.47 (m, 1H), 1.60-1.70 (m, 1H), 1.92-1.97 (m, 1H), 2.57 (s, 3H), 2.80 (brs, 1H), 3.85-3.90 (q, 2H), 3.96 (d, $J = 10.4$ Hz, 1H), 4.03-4.05 (m, 1H), 4.31-4.36 (m, 2H), 6.65 (d, $J = 7.8$ Hz, 1H), 6.85 (s, 1H), 7.96-7.00 (m, 1H), 7.08-7.11 (m, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 8.12 (d, $J = 6.8$ Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.4, 13.9, 22.0, 23.5, 26.1, 26.3, 43.9, 57.9, 59.2, 61.9, 62.9, 64.3, 78.7, 112.6 (d, $J = 24.7$ Hz), 118.4, 121.2 (d, $J = 18.3$ Hz), 125.8, 127.4 (d, $J = 7.2$ Hz), 128.4, 128.8, 129.6, 134.3, 135.3, 136.1, 155.5 (d, $J = 246.0$ Hz), 168.0, 169.8, 170.4, 174.6. Enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 97/ 3, flow rate 1.0 mL/min, $T = 30^\circ C$, 254 nm): $t_R = 5.88$ min(major), $t_R = 4.47$ min(minor); IR (KBr): γ 3351, 3131, 2962, 1756, 1713, 1600, 1467, 1373, 1280, 1223, 883, 789, 689, 620; HRMS (FT-ICRMS) exact mass calcd for $(C_{29}H_{31}Cl_2FN_2O_6)^+$ requires m/z 592.1543, found m/z 605.1551.

Diethyl-1-acetyl-6-chloro-4'-(3-chlorophenyl)-5-fluoro-5'-neopentyl-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8j), 97 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 20/1- 5/1), 80% yield, white solid, m.p. 120-122°C; $[a]_D^{25} = +50.4$ ($c = 0.24$ in $CHCl_3$); 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.88 (t, $J = 7.2$ Hz, 3H), 0.98 (s, 9H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.31 (d, $J = 14.0$ Hz, 1H), 2.00 (dd, $J_1 = 8.94$, $J_2 = 14.0$ Hz, 1H), 2.57 (s, 3H), 2.58 (brs, 1H), 3.84-3.90 (q, 2H), 3.95 (d, $J = 10.7$ Hz, 1H), 4.01-4.05 (m, 1H), 4.31-4.36 (m, 2H), 6.64 (d, $J = 7.8$ Hz, 1H), 6.85-6.86 (m, 1H), 6.96-7.00 (m, 1H), 7.08-7.11 (m, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 8.13 (d, $J = 6.6$ Hz, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.4, 13.9, 26.3, 30.0, 30.6, 48.4, 56.8, 59.5, 61.8, 62.9, 63.4, 79.2, 112.6 (d, $J = 24.7$ Hz), 118.4, 121.1 (d, $J = 18.4$ Hz), 126.0, 127.5 (d, $J = 7.2$ Hz), 128.4, 129.0, 129.6, 134.3, 134.9, 136.1 (d, $J = 2.9$ Hz), 155.5 (d, $J = 246.0$ Hz), 168.0, 169.8, 170.6, 174.7; Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 98/ 2, flow rate 1.0 mL/min, $T = 30^\circ C$, 254 nm): $t_R = 5.25$ min(major), $t_R = 4.25$ min(minor); IR (KBr): γ 3389, 3131, 2962, 1756, 1731, 1600, 1467, 1367, 1298, 1223, 784, 708, 613; HRMS (FT-ICRMS) exact mass calcd for $(C_{31}H_{26}Cl_2FN_3O_8)^+$ requires m/z 606.1700, found m/z 606.1696.

Diethyl-1-acetyl-6-chloro-5-fluoro-5'-(4-nitrophenyl)-2-oxo-4'-phenylspiro[indoline-3,3'-pyrrol

idine]-2',2'-dicarboxylate (8k), 114 mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 18/1- 5/1), 91% yield, white solid, m.p. 135-137°C; $[\alpha]_D^{25} = +146.0$ ($c = 0.10$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.86 (t, $J = 7.2$ Hz, 3H), 1.35 (t, $J = 7.1$ Hz, 3H), 2.54 (s, 3H), 3.58 (brs, 1H), 3.83-3.96 (m, 2H), 4.37-4.43 (m, 2H), 4.47 (d, $J = 10.8$ Hz, 1H), 5.29 (d, $J = 10.8$ Hz, 1H), 6.80-6.82 (m, 2H), 7.03-7.07 (m, 2H), 7.10-7.12 (m, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.80-7.83 (m, 2H), 8.02-8.11 (m, 2H), 8.16 (d $J = 6.8$ Hz 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.3, 14.0, 26.3, 61.6, 62.4, 63.0, 63.2, 64.8, 77.9, 112.1 (d $J = 24.0$ Hz), 118.7, 121.6 (d $J = 18.0$ Hz), 123.6, 127.0 (d $J = 7.0$ Hz), 128.4, 128.5, 128.6, 128.8, 131.2, 136.2, 147.7, 148.1, 155.5 (d $J = 246.0$ Hz), 168.1, 169.5, 169.8, 174.0; Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 17.98$ min(major), $t_R = 5.89$ min(minor); IR (KBr): γ 3383, 3125, 2980, 1756, 1731, 1600, 1524, 1480, 1342, 1285, 1229, 858, 701, 613; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{27}\text{ClFN}_3\text{O}_8)^+$ requires m/z 623.1471, found m/z 623.1467.

Diethyl-1-acetyl-6-chloro-4'-(3-chlorophenyl)-5-fluoro-5'-(4-nitrophenyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2',2'-dicarboxylate (8l), 124mg (Flash column chromatography eluent, petroleum ether/ethyl acetate = 18/1- 5/1), 94% yield, white solid, m.p. 71-73°C; $[\alpha]_D^{25} = +144.6$ ($c = 0.15$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 0.87 (t, $J = 7.2$ Hz, 3H), 1.35 (t, $J = 7.1$ Hz, 3H), 2.57 (s, 3H), 3.57 (brs, 1H), 3.84-3.96 (m, 2H), 4.37-4.45 (m, 3H), 5.24 (d, $J = 10.8$ Hz, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 6.82-6.83 (m, 1H), 6.98-7.02 (m, 1H), 7.09-7.12 (m, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.82-7.84 (m, 2H), 8.11-8.13 (m, 2H), 8.19 (d $J = 6.8$ Hz 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 13.3, 14.0, 26.3, 61.0, 62.5, 63.1, 64.6, 77.9, 112.0 (d $J = 24.0$ Hz), 118.8, 121.9 (d $J = 19.0$ Hz), 123.7, 126.1, 126.5 (d $J = 7.0$ Hz), 128.5, 128.9, 129.0, 129.8, 133.4, 134.5, 136.1, 147.6, 147.8, 155.5 (d $J = 247.0$ Hz), 168.0, 169.4, 169.8, 173.8; Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 20.63$ min(major), $t_R = 5.56$ min(minor); IR (KBr): γ 3426, 3131, 3026, 2987, 2937, 1756, 1719, 1600, 1518, 1480, 1342, 1285, 1229, 852, 701, 608; HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{31}\text{H}_{26}\text{Cl}_2\text{FN}_3\text{O}_8)^+$ requires m/z 657.1081, found m/z 657.1081.

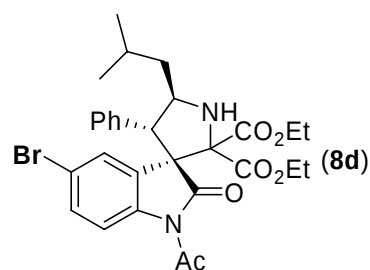
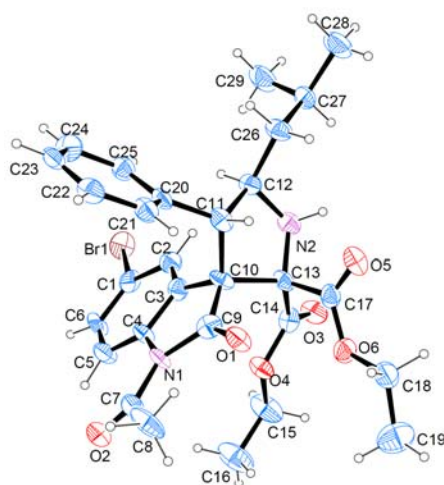
Reference:

- (1) (a) Milanesio, M.; Viterbo, D.; Albini, A.; Fasani, E.; Bianchi, R.; Barzaghi, M. *J. Org. Chem.* **2000**, 65, 3416. b) Ding, K.; Wang, G.; Deschamps, J. R.; Parrish, D. A.; Wang, S. *Tetrahedron*.

Lett. **2005**, 46, 5949.

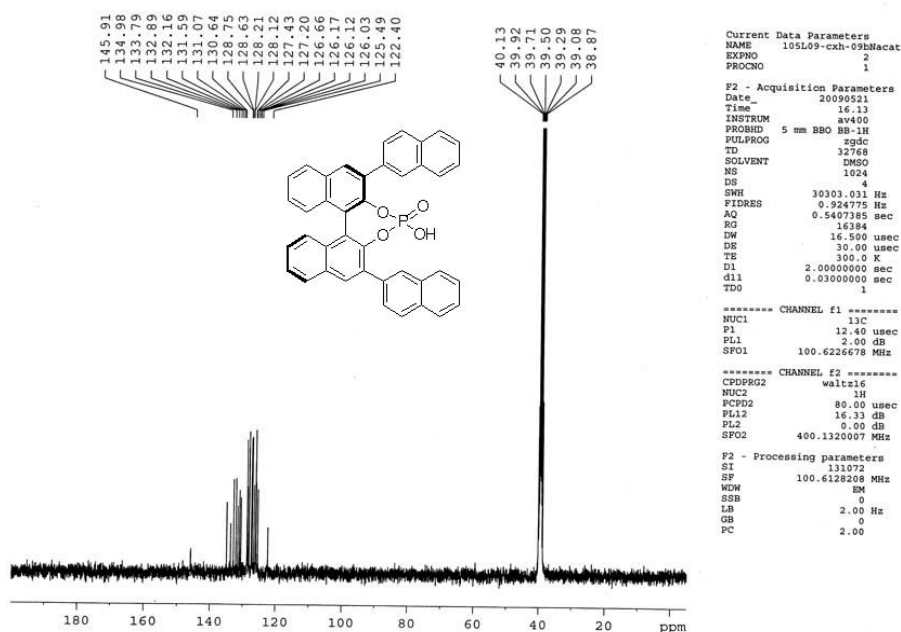
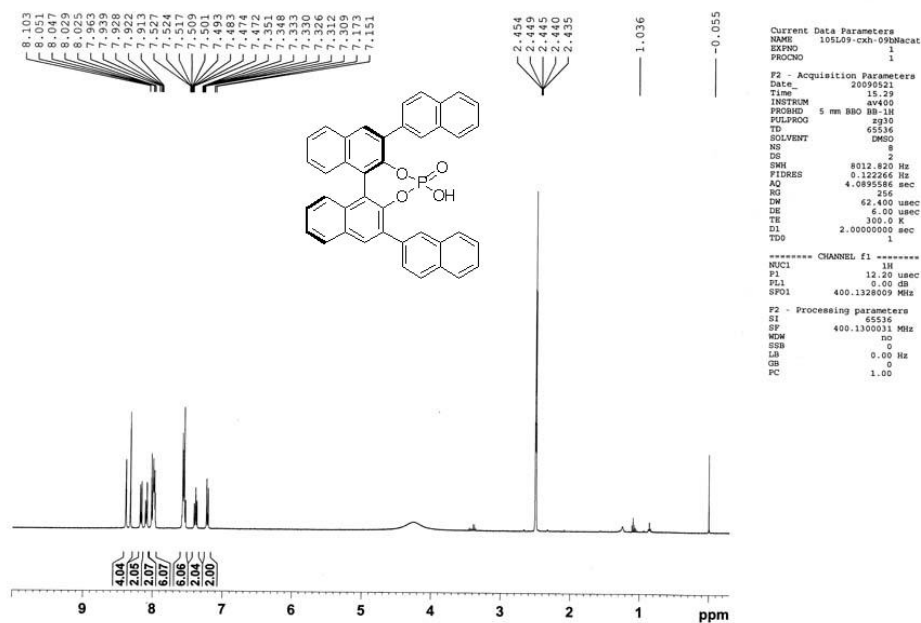
- (2) (a) Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. *J. Org. Chem.* **1998**, 63, 7536. (b) Wipf, P.; Jung, J. K. *J. Org. Chem.* **2000**, 65, 6319. (c) Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, 128, 84. (d) Reuping, M.; Sugiono, E.; Azap, C.; Theissmann, T.; Bolte, M. *Org. Lett.* **2005**, 7, 378. (e) Hoffman, S.; Seayad, A. M.; List, B. *Angew. Chem.Int. Ed.* **2005**, 44, 7424.

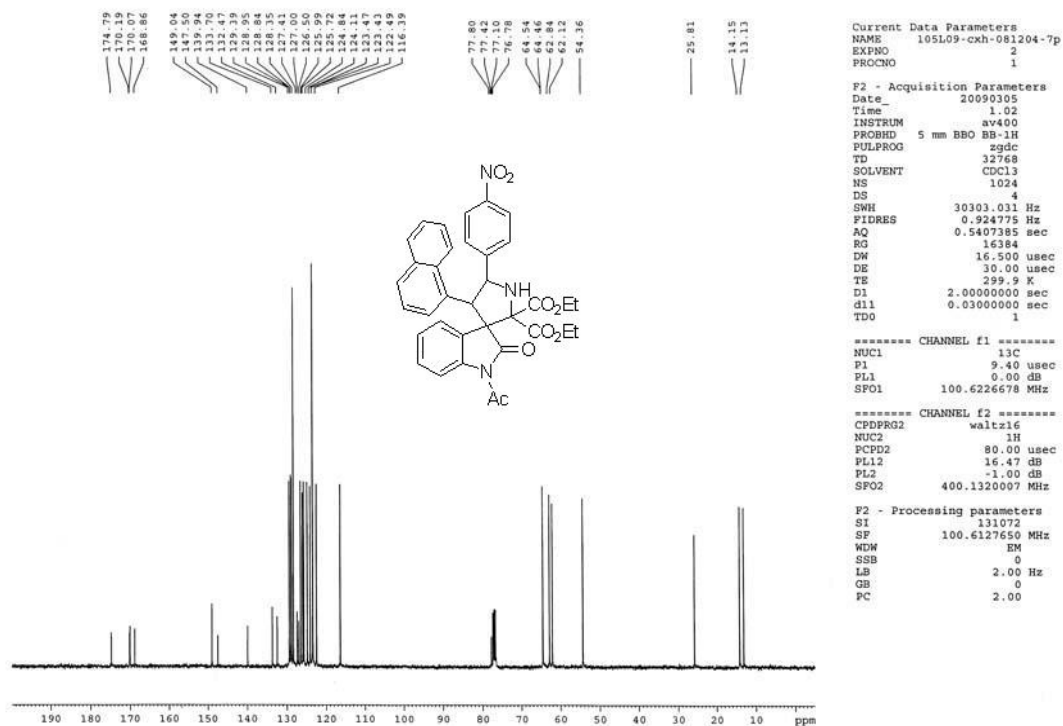
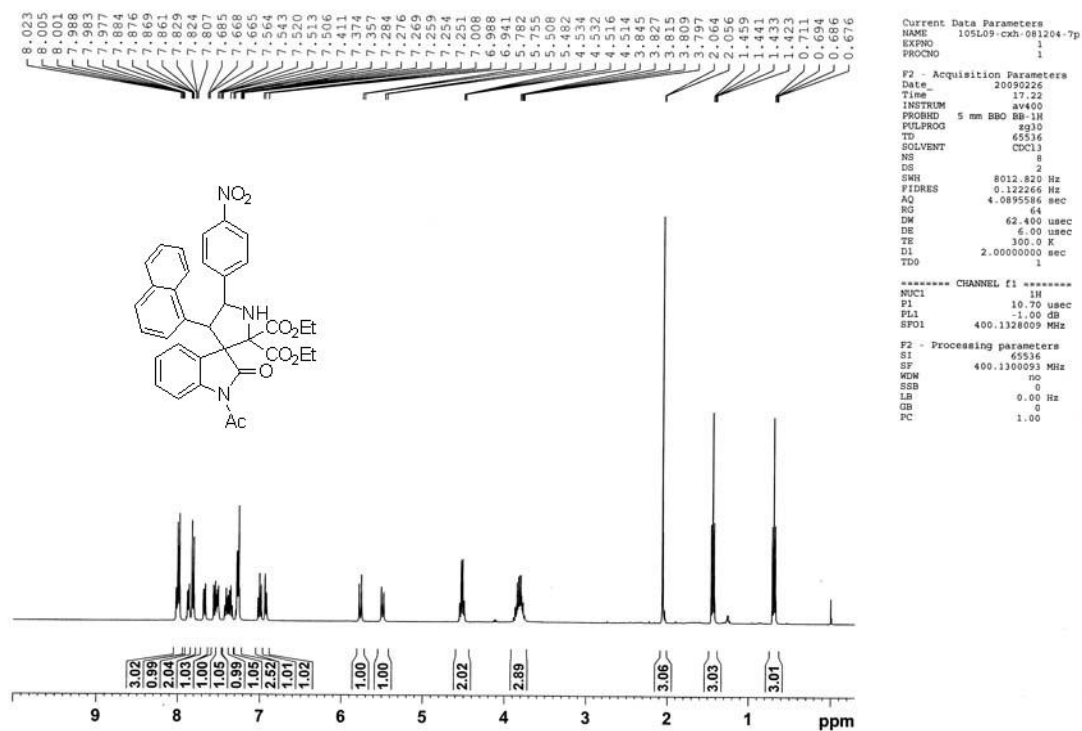
X-ray single crystal data for 8d

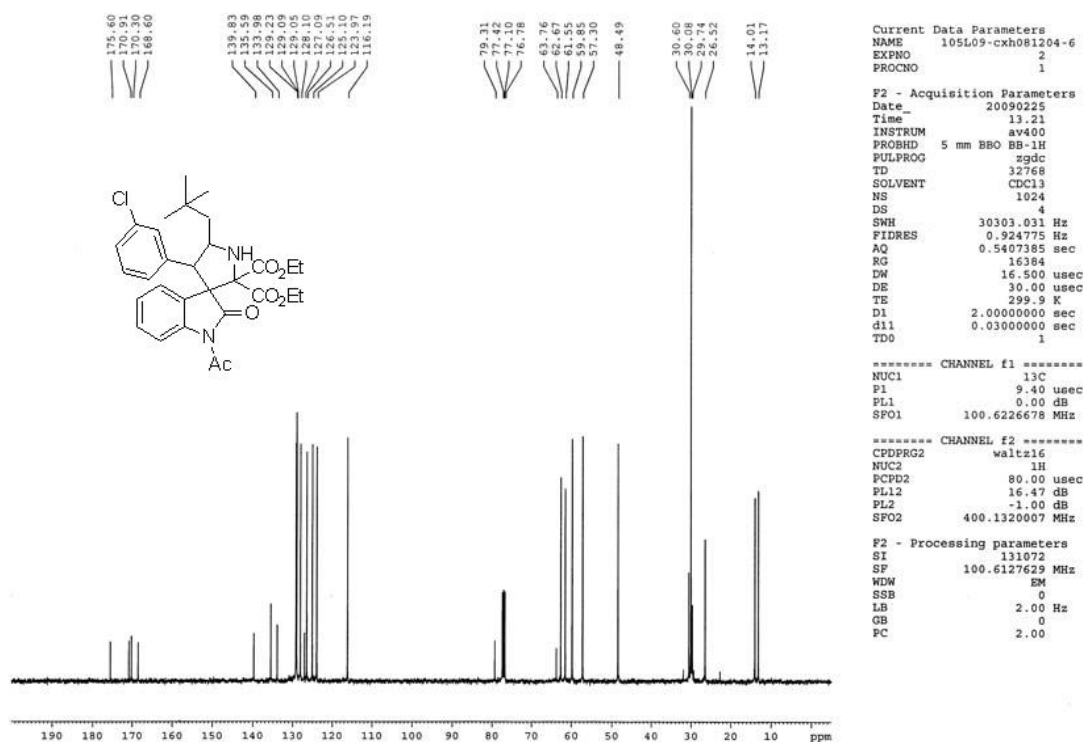
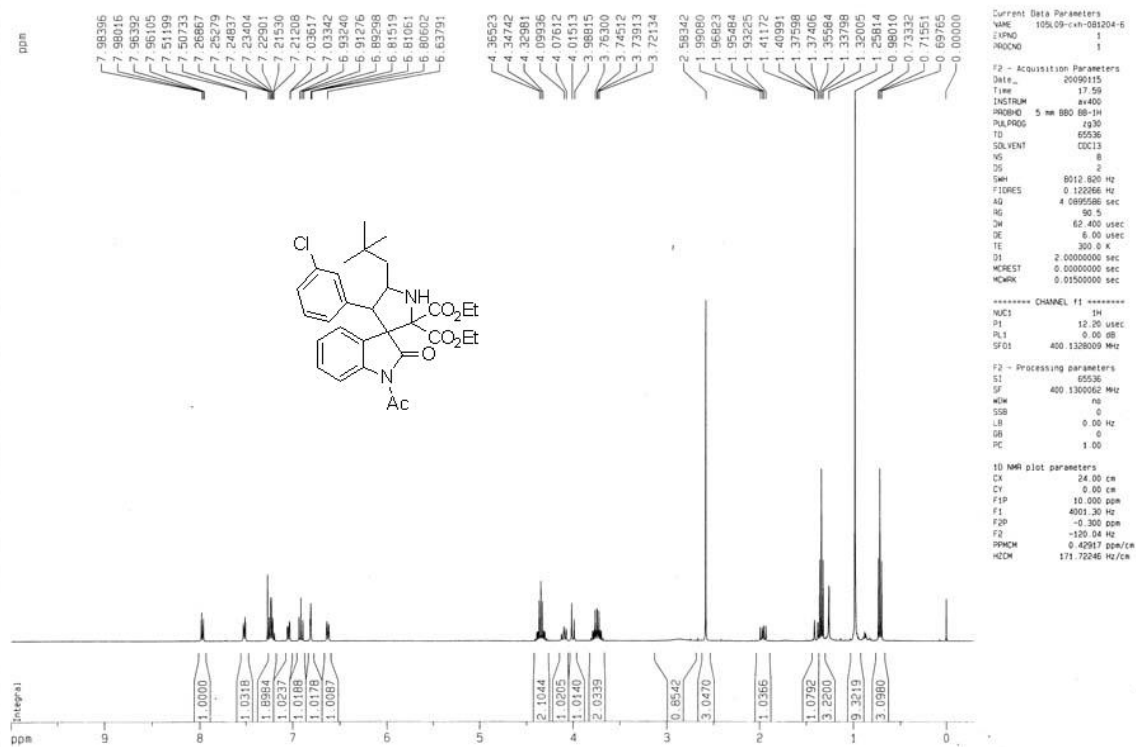


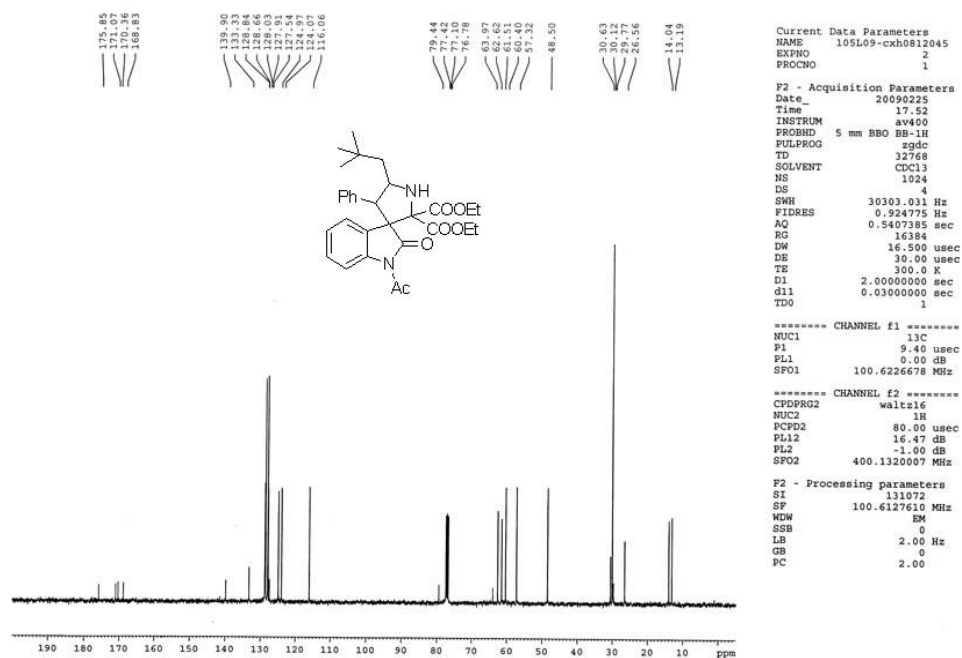
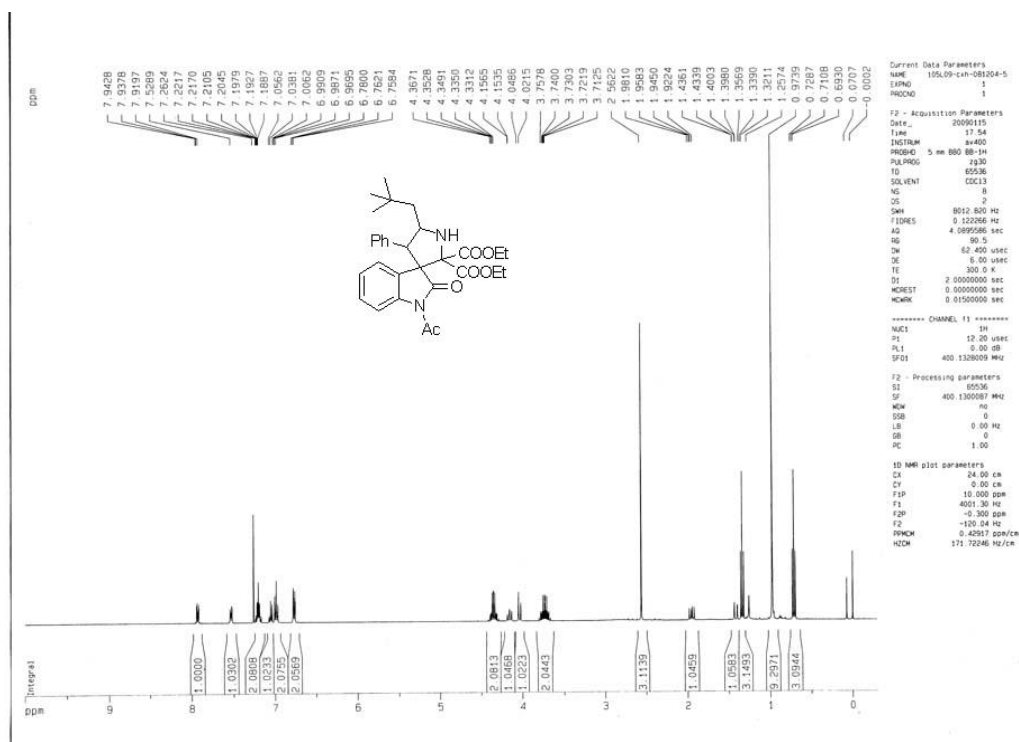
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b , Å	17.4596(5)
c , Å	36.6618(10)
α , °	90.00
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T, K	295(2)
ρ , g/cm ³	1.339

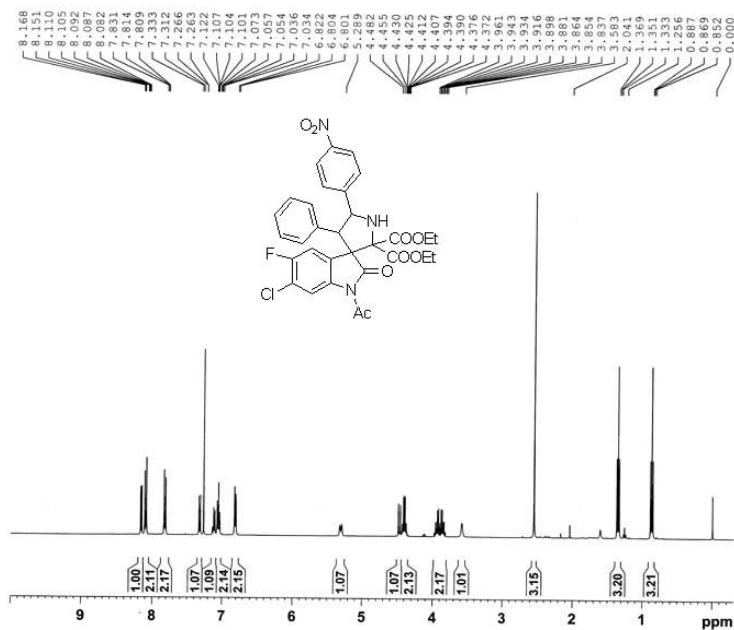
Selected NMR and HPLC Spectra









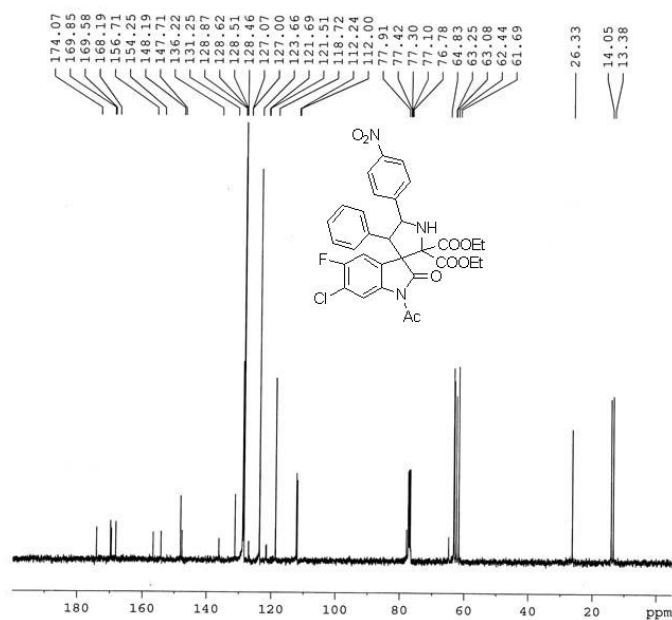


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PROCNO 1

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DE 6.00 usec
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TDO 1

***** CHANNEL f1 *****
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F2 - Processing parameters
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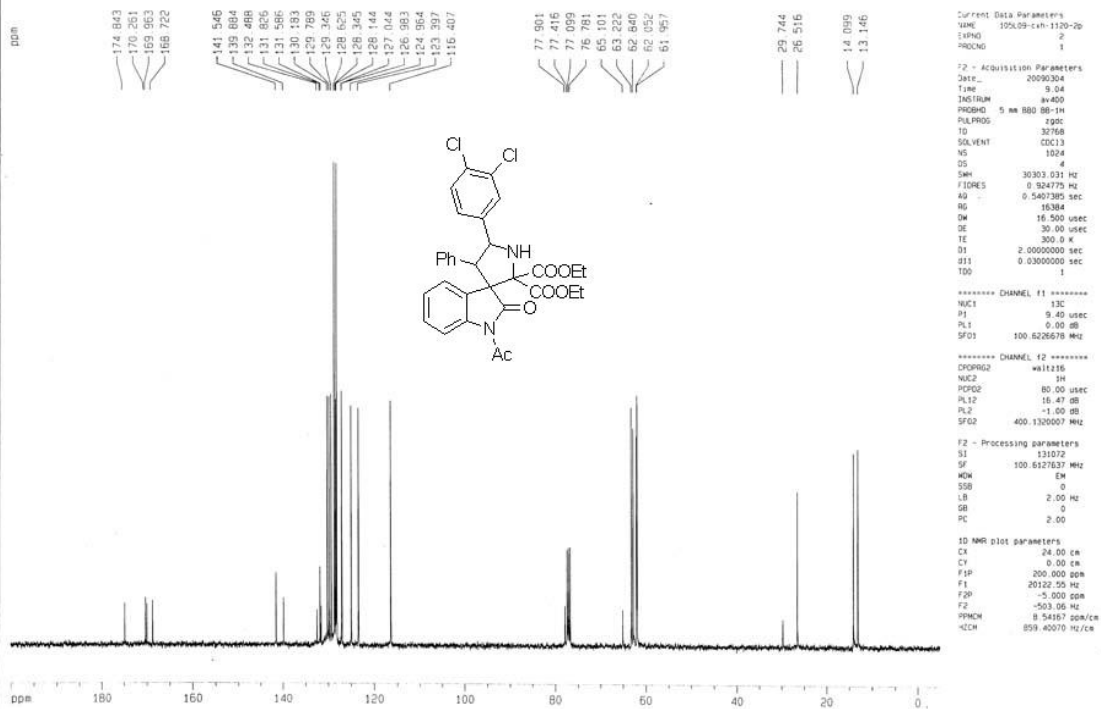
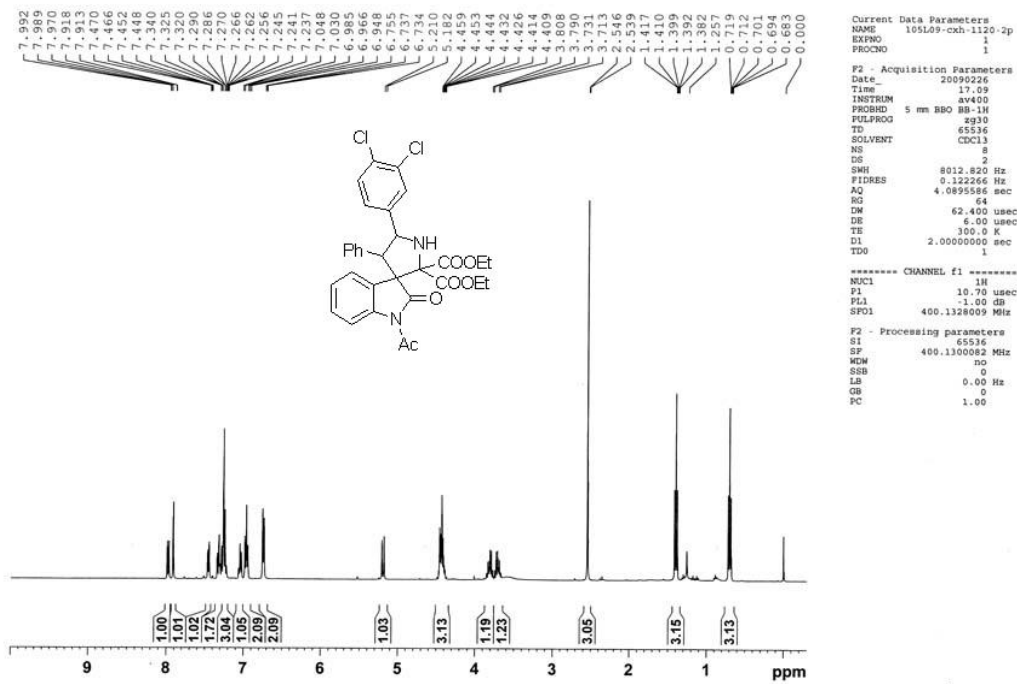
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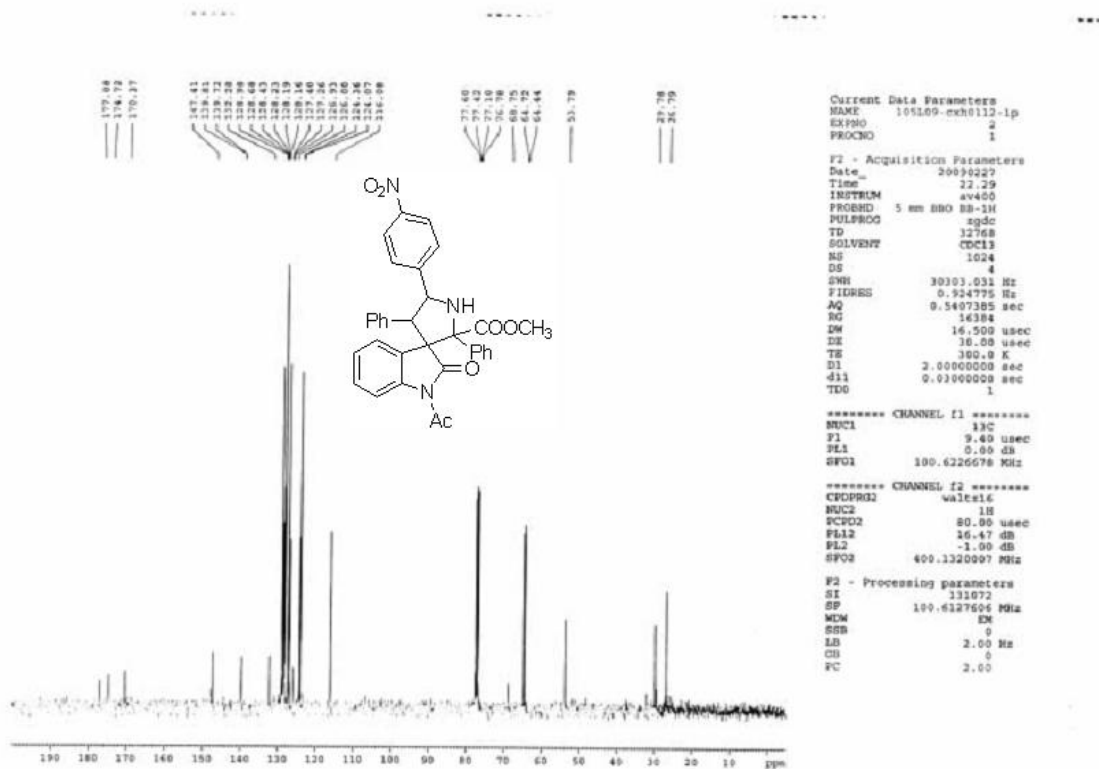
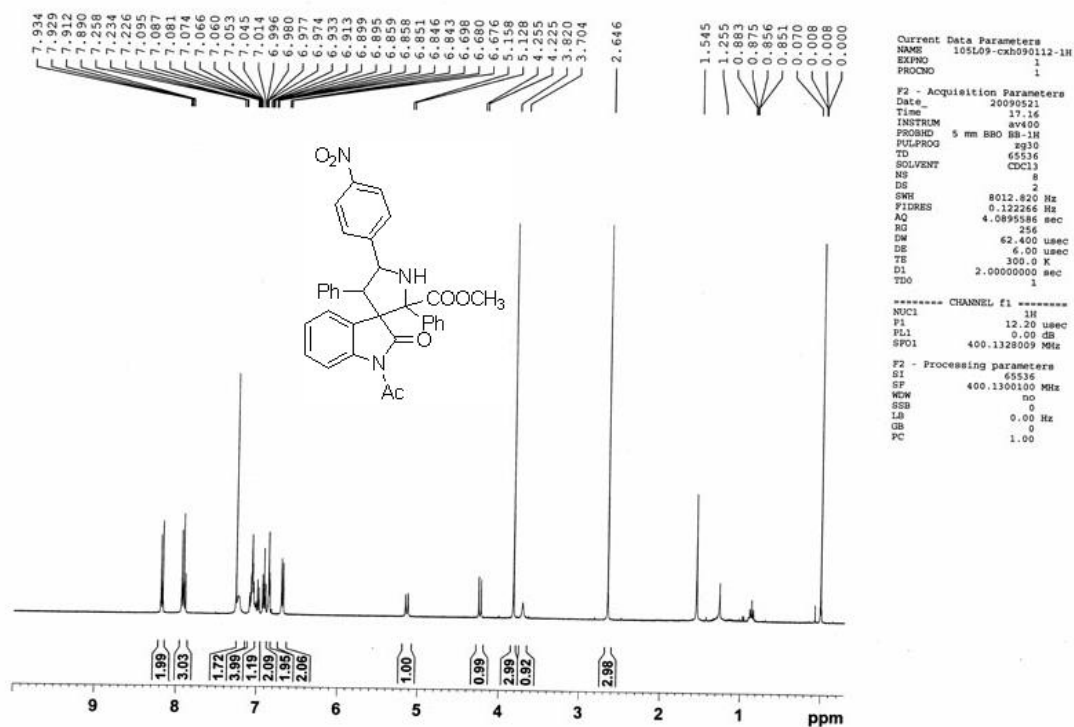
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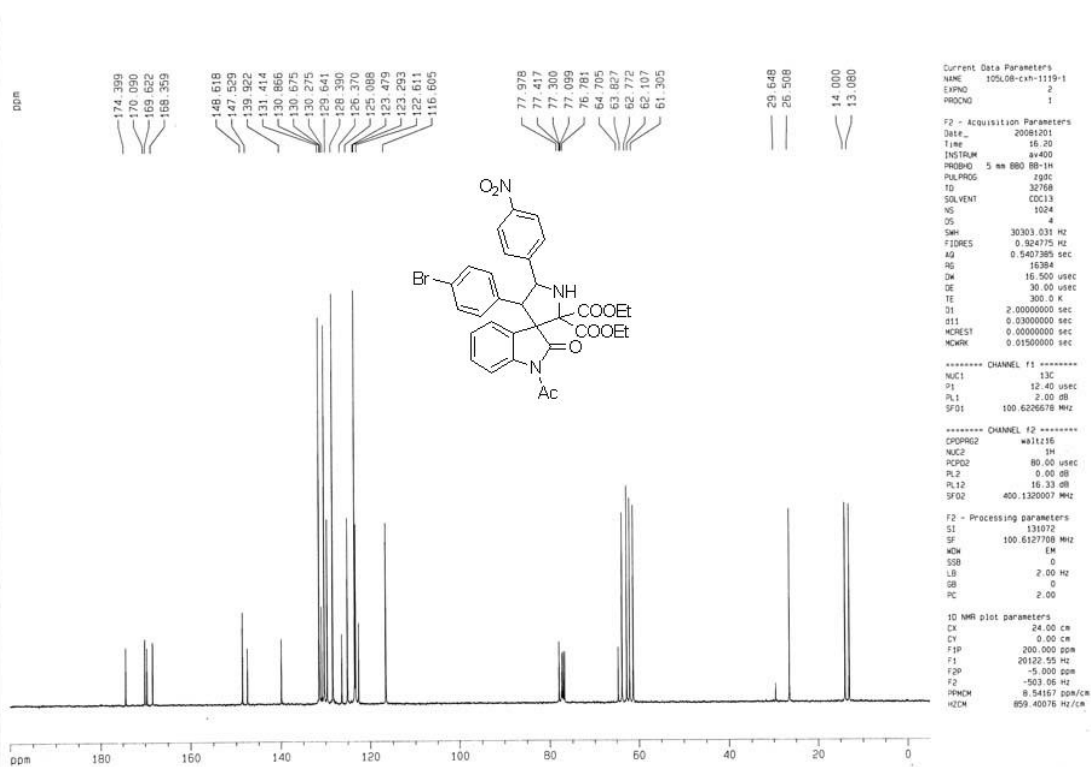
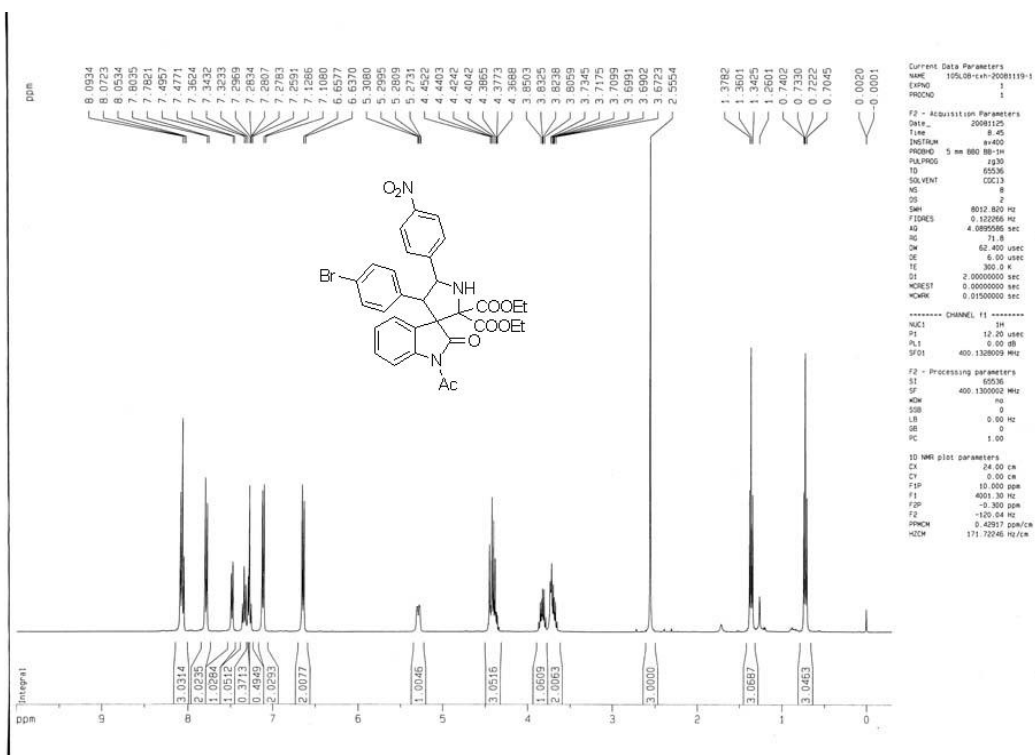
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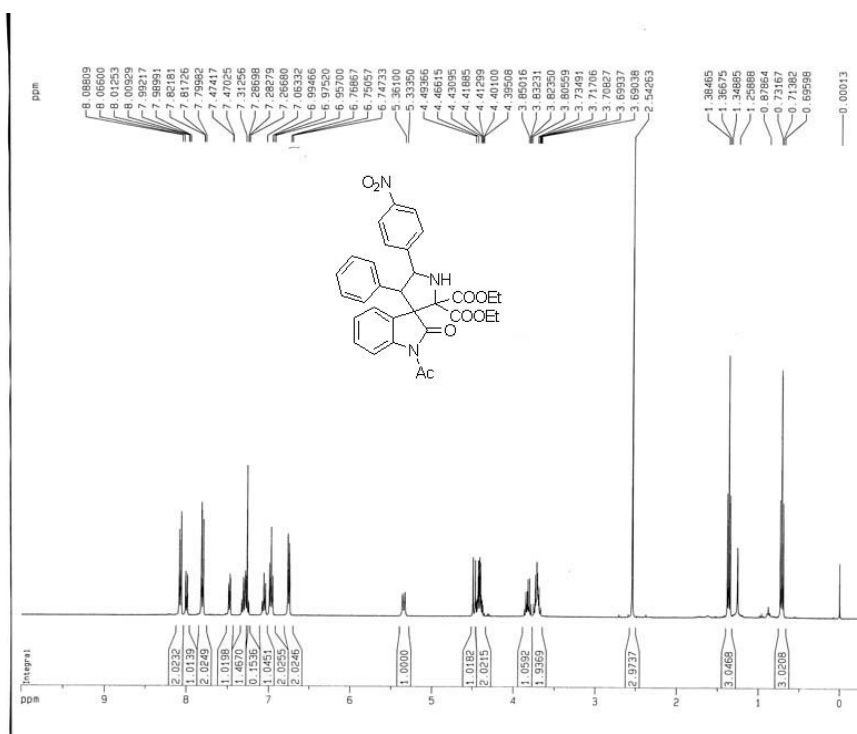
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F2 - Processing parameters
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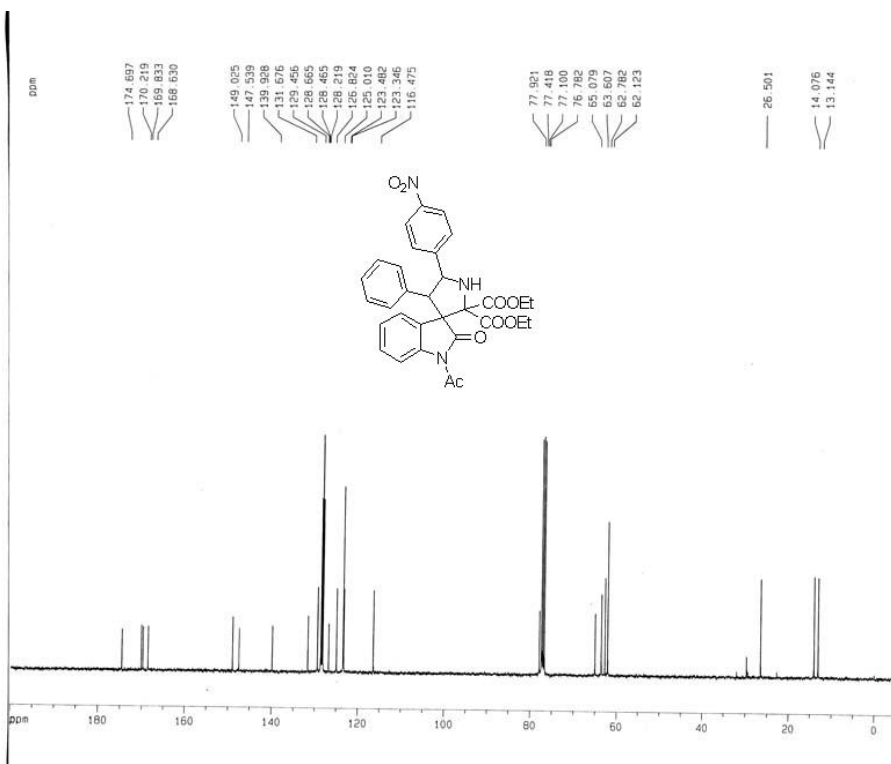
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1D NMR plot parameters
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Current Data Parameters
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EXPNO 2
PROCNO 1

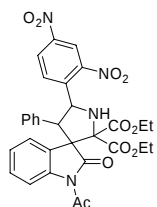
F2 - Acquisition Parameters
Date_ 20090105
Time 11.27
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl₃
NS 1024
DS 2
SWH 30303.031 Hz
FIDRES 0.924775 Hz
AQ 0.5407385 sec
RG 16384
DQ 16.500 usec
SE 30.00 usec
TE 300.0 K
D1 2.0000000 sec
MCHST 0.0300000 sec
MCHWK 0.0000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 12.40 usec
PL1 2.00 dB
SFO1 100.6260676 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
P2 80.00 usec
PL2 0.00 dB
PL12 16.35 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 131072
SF 100.6127644 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 24.00 cm
CY 0.00 cm
FIP 200.000 ppm
F1 201.20255 Hz
F2P -5.000 ppm
F2 -503.08 Hz
F1NCH 4.54167 ppm/cm
F2NCH 859.40070 Hz/cm



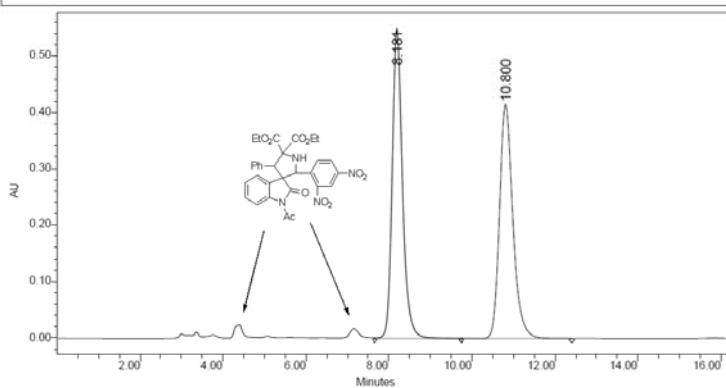
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	spiro-2,4-diNO ₂ -DL-IA30%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/20/2008 10:01:27 PM
Vial:	1	Acq. Method:	chenxh30
Injection #:	1	Date Processed:	10/21/2008 3:21:58 AM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.181	9471342	50.40	549163	56.93
2	10.800	9320092	49.60	415430	43.07

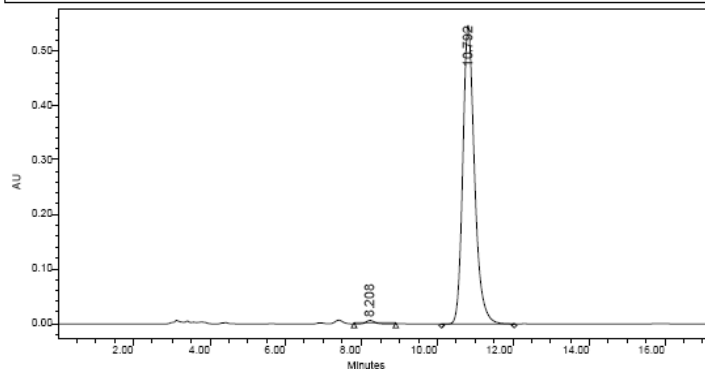
USTC

Project Name: chenxh
Reported by User: System

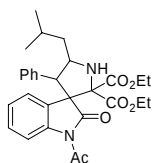
Breeze

SAMPLE INFORMATION

Sample Name:	spiro-20081015-5-2,4-2NO ₂ -IA30%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/21/2008 2:40:14 AM
Vial:	1	Acq. Method:	chenxh30
Injection #:	1	Date Processed:	10/21/2008 8:57:43 AM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.208	101167	0.85	6341	1.14
2	10.792	11813825	99.15	548368	98.86



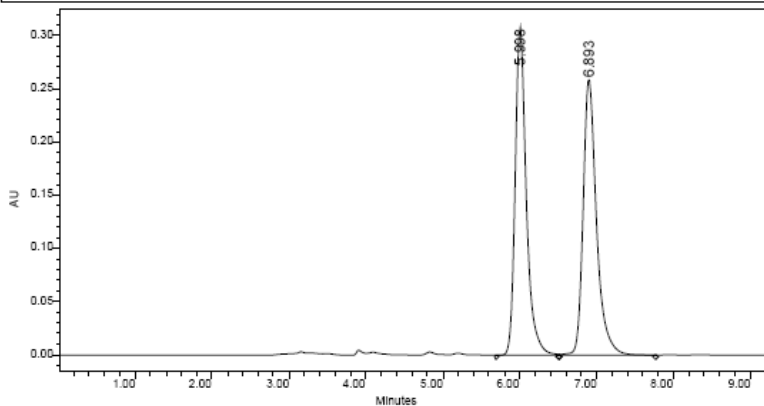
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	spiro-090224-phph-yiwu_DL-IA3%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2009 5:08:58 PM
Vial:	1	Acq. Method:	chenxh3
Injection #:	1	Date Processed:	2/26/2009 3:47:57 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.998	3107308	49.73	307989	54.27
2	6.893	3141480	50.27	259546	45.73

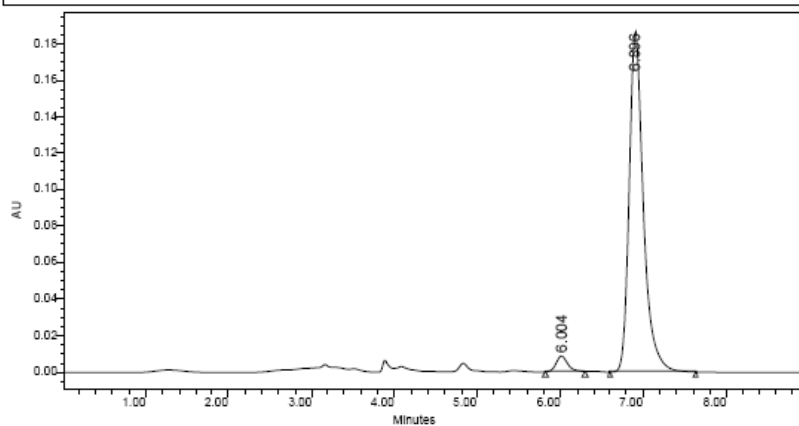
USTC

Project Name: chenxh
Reported by User: System

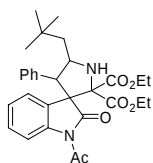
Breeze

SAMPLE INFORMATION

Sample Name:	spiro-090224-phph-yiwu-IA3%pro	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2009 5:18:45 PM
Vial:	1	Acq. Method:	chenxh3
Injection #:	2	Date Processed:	2/26/2009 3:49:32 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.004	82805	3.59	8824	4.41
2	6.896	2222486	96.41	186786	95.59

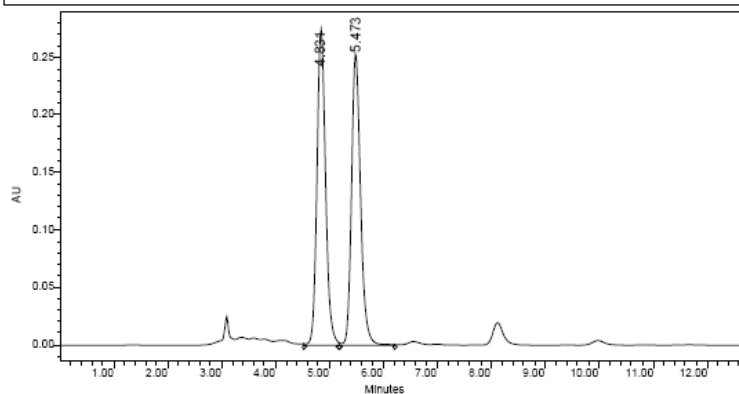


USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	spiro-t-Bu-yli'quan_DL-IA3%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/23/2008 10:58:34 AM
Vial:	1	Acq. Method:	chenxh3
Injection #:	1	Date Processed:	2/19/2009 11:42:01 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



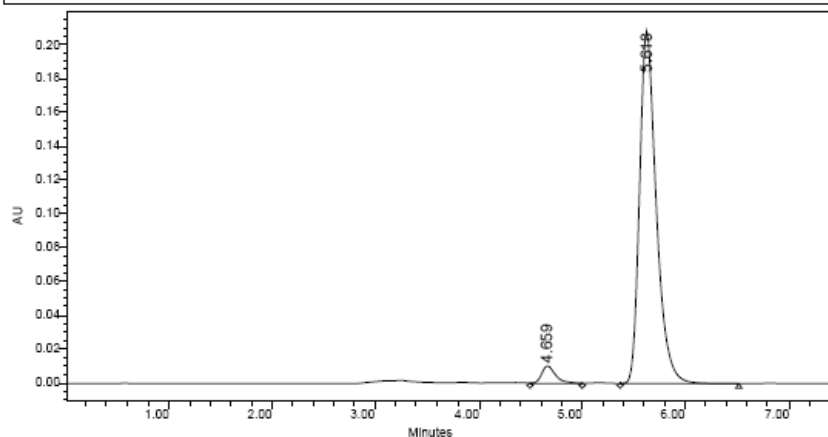
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.831	3058553	50.76	274860	51.98
2	5.473	2986377	49.24	254098	48.04

USTC

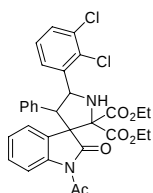
Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	spiro-1211-4-IA3%-2	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	12/17/2008 6:12:56 PM
Vial:	1	Acq. Method:	chenxh3
Injection #:	2	Date Processed:	2/19/2009 11:34:58 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.659	101200	4.14	10491	4.80
2	5.618	2344316	95.86	208173	95.20

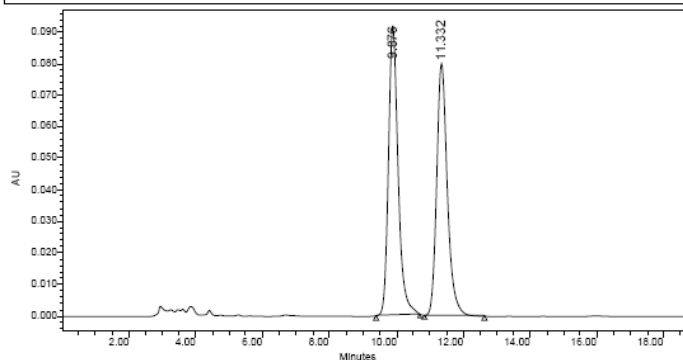


USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	spiro-090225-2,3-diCl-DL-IA6%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/26/2009 7:15:57 PM
Vial:	1	Acq. Method:	chenxh6%
Injection #:	1	Date Processed:	2/26/2009 3:23:42 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



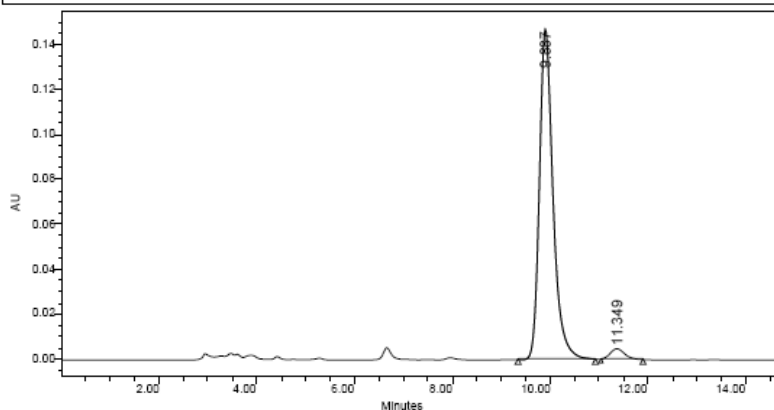
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.878	1837346	50.97	91755	53.46
2	11.332	1767743	49.03	79892	46.54

USTC

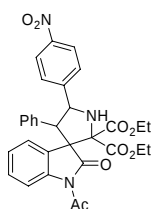
Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	spiro-090225-2,3-diCl-IA6%pro	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/26/2009 8:29:16 PM
Vial:	1	Acq. Method:	chenxh6%
Injection #:	5	Date Processed:	2/26/2009 3:20:11 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.887	2838216	96.79	146807	96.92
2	11.349	94148	3.21	4869	3.08



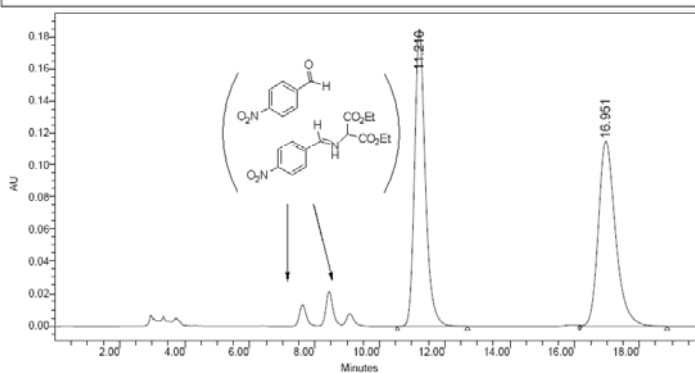
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-090224-4NO2_DL-IA30%N
Sample Type: Unknown
Vial: 1
Injection #: 4
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: System
Date Acquired: 2/24/2009 10:19:11 PM
Acq. Method: chenxh30
Date Processed: 2/26/2009 3:09:28 PM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.210	4273660	50.19	185805	61.58
2	16.951	4240565	49.81	115923	38.42

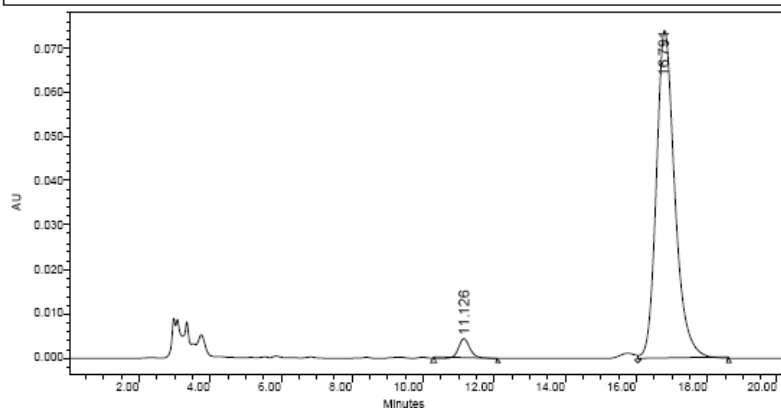
USTC

Project Name: chenxh
Reported by User: System

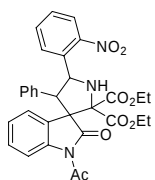
Breeze

SAMPLE INFORMATION

Sample Name: spiro-090225-4NO2-IA30%pro
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: System
Date Acquired: 2/25/2009 8:22:43 PM
Acq. Method: chenxh30
Date Processed: 2/26/2009 3:10:21 PM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.126	101209	3.62	4438	5.64
2	16.791	2681327	96.38	74270	94.36

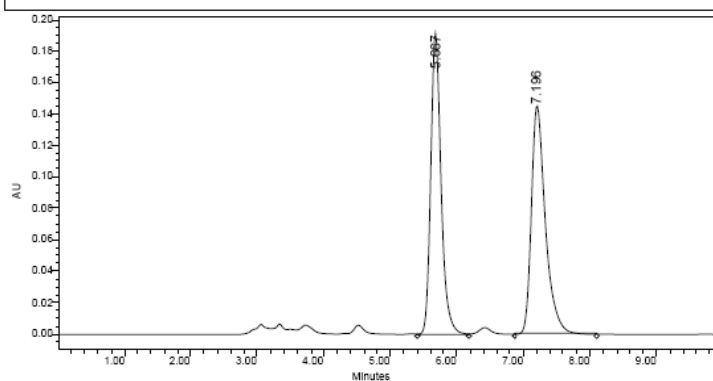


USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	spiro-090224-2NO2_DL-IA30%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2009 2:16:03 PM
Vial:	1	Acq. Method:	chenxh30
Injection #:	7	Date Processed:	2/26/2009 3:35:33 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



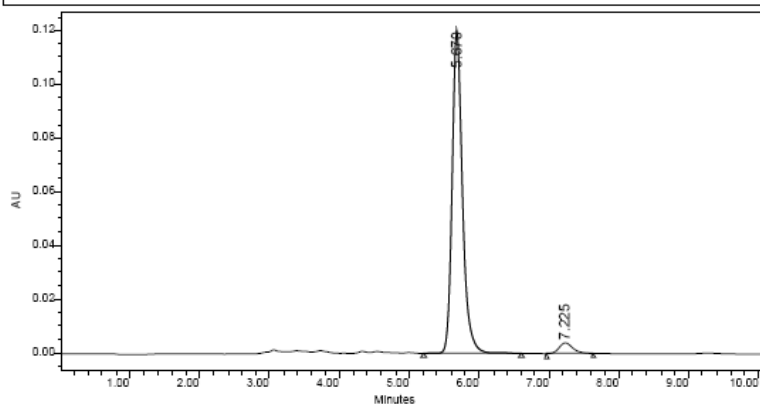
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.667	2069701	49.18	191244	56.81
2	7.196	2139033	50.82	145418	43.19

USTC

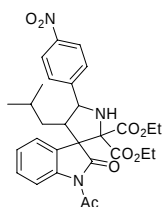
Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	spiro-090224-2NO2-IA30%proN	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2009 3:01:06 PM
Vial:	1	Acq. Method:	chenxh30
Injection #:	1	Date Processed:	2/26/2009 3:38:02 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.670	1236808	95.78	120130	98.79
2	7.225	54555	4.22	3989	3.21



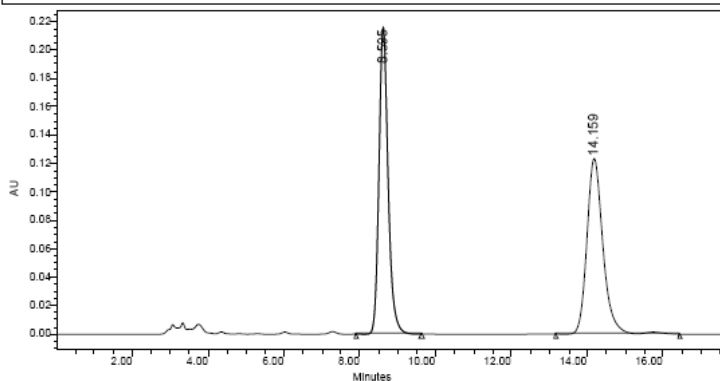
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-090225-yiwu4NO2-DL-IA30% Acquired By: System
Sample Type: Unknown Date Acquired: 2/25/2009 6:44:13 PM
Vial: 1 Acq. Method: chenxh30
Injection #: 2 Date Processed: 2/26/2009 3:42:00 PM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.595	3615933	49.72	215976	63.57
2	14.159	3660288	50.28	123767	36.43

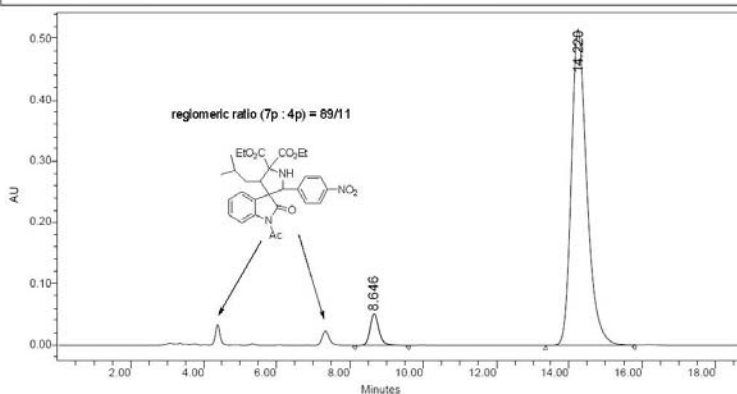
USTC

Project Name: chenxh
Reported by User: System

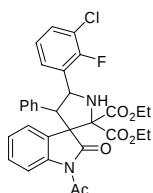
Breeze

SAMPLE INFORMATION

Sample Name: spiro-1119-6-4-NO2-IA30%pro-2 Acquired By: System
Sample Type: Unknown Date Acquired: 11/26/2008 12:12:10 AM
Vial: 1 Acq. Method: chenxh30
Injection #: 4 Date Processed: 2/20/2009 10:28:45 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.646	875129	5.42	51726	9.11
2	14.220	15263974	94.58	516167	90.89



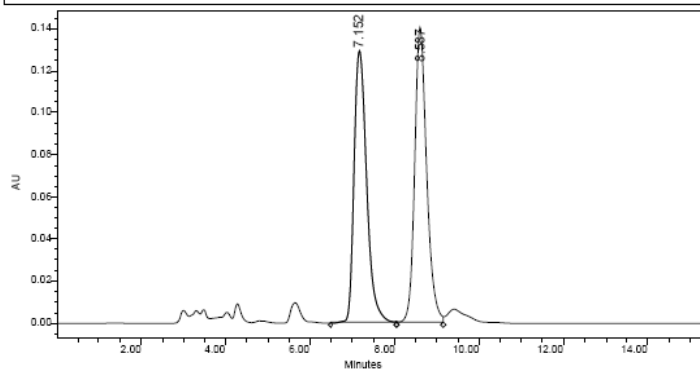
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	spiro-1026-2-3Cl2F_DL-AD15%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/29/2008 11:40:07 PM
Vial:	1	Acq. Method:	chenxh15%
Injection #:	2	Date Processed:	2/19/2009 10:21:42 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.152	2717223	49.27	129844	47.93
2	8.587	2797585	50.73	140846	52.07

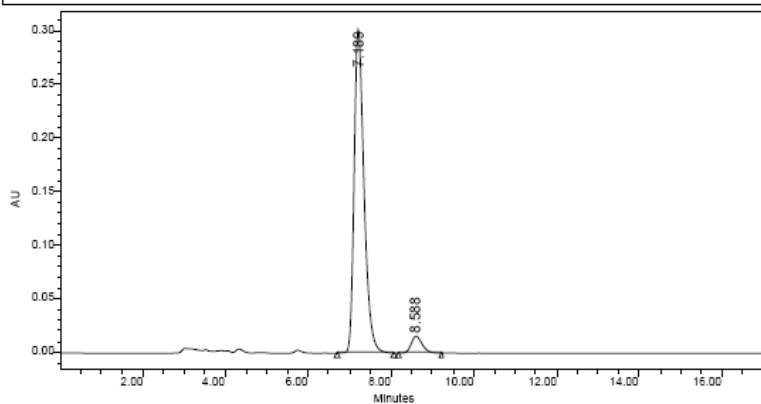
USTC

Project Name: chenxh
Reported by User: System

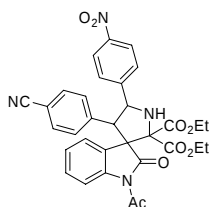
Breeze

SAMPLE INFORMATION

Sample Name:	spiro-102 4-2-3Cl-2F-1A15%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/31/2008 1:46:42 AM
Vial:	1	Acq. Method:	chenxh15%
Injection #:	2	Date Processed:	11/7/2008 9:38:58 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.189	5019512	94.51	302131	95.04
2	8.588	291663	5.49	15767	4.96



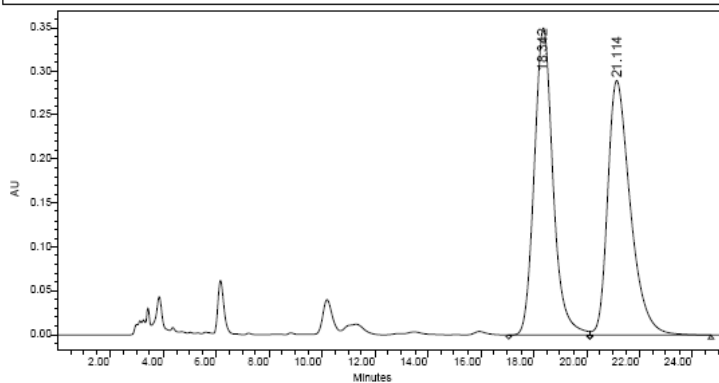
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1115-4-4-CN-4NO2-DL-AD3C Acquired By: System
Sample Type: Unknown Date Acquired: 11/19/2008 2:33:54 PM
Vial: 1 Acq. Method: chenxh30
Injection #: 1 Date Processed: 11/19/2008 3:32:11 PM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.342	17239786	50.06	350134	54.68
2	21.114	17200737	49.94	290200	45.32

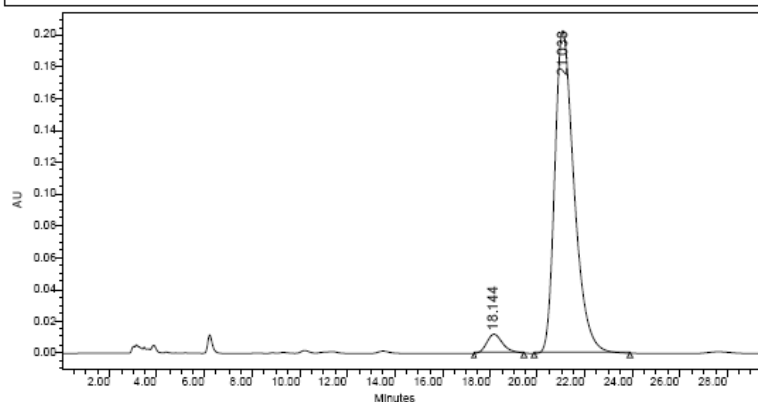
USTC

Project Name: chenxh
Reported by User: System

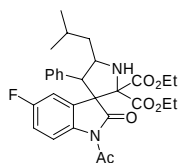
Breeze

SAMPLE INFORMATION

Sample Name: spiro-1115-4-4-CN-NO2-AD-30% Acquired By: System
Sample Type: Unknown Date Acquired: 11/19/2008 8:19:10 PM
Vial: 1 Acq. Method: chenxh30
Injection #: 1 Date Processed: 11/19/2008 8:50:25 PM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.144	568328	4.67	11997	5.57
2	21.038	11560736	95.33	203326	94.43

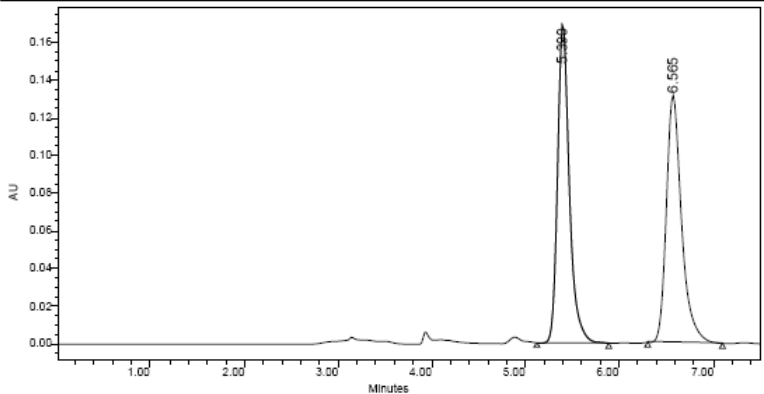


USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION				
Sample Name:	spiro-1225-1-5F-ph-yiw_DL-IA3%N	Acquired By:	System	
Sample Type:	Unknown	Date Acquired:	1/6/2009 11:02:19 AM	
Vial:	1	Acq. Method:	chenxh3	
Injection #:	8	Date Processed:	2/20/2009 11:31:49 AM	
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1	
Run Time:	70.00 Minutes	Sample Set Name:		



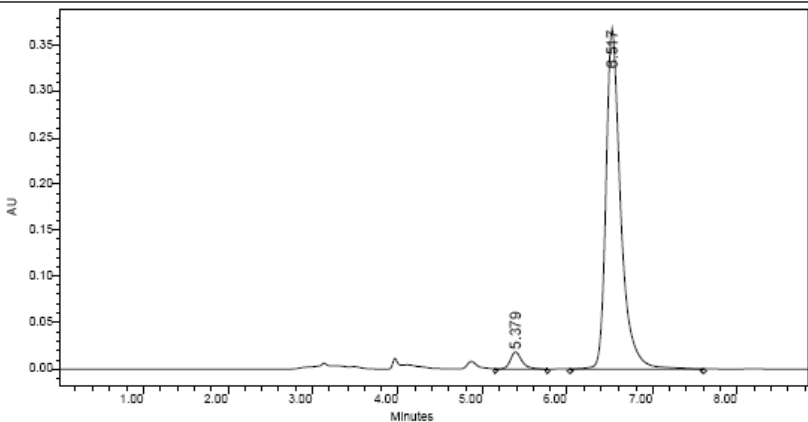
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.390	1479764	49.95	169523	56.33
2	6.565	1482574	50.05	131439	43.67

USTC

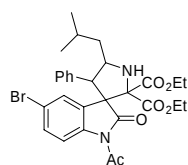
Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION				
Sample Name:	spiro-1225-1-5F-yiwu-IA3%pro	Acquired By:	System	
Sample Type:	Unknown	Date Acquired:	1/6/2009 10:22:09 PM	
Vial:	1	Acq. Method:	chenxh3	
Injection #:	2	Date Processed:	2/20/2009 11:32:38 AM	
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1	
Run Time:	70.00 Minutes	Sample Set Name:		



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.379	185364	3.97	18728	4.83
2	6.617	4478227	96.03	368790	95.17



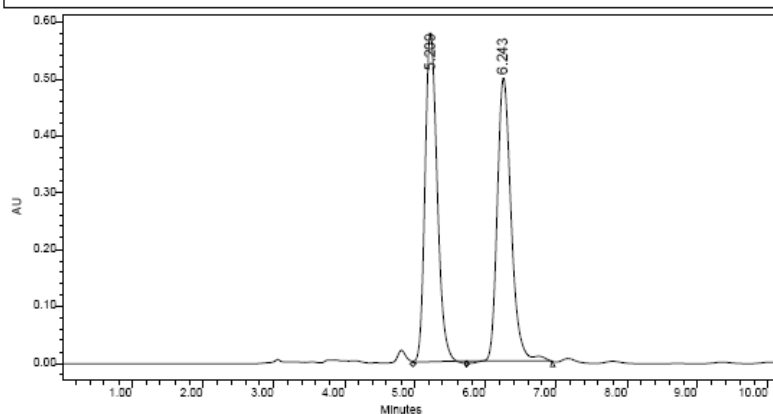
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-2-5Br-ph-yiwu_DL-IA3%
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: System
Date Acquired: 1/6/2009 9:39:11 AM
Acq. Method: chenxh3
Date Processed: 2/20/2009 11:35:49 AM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.209	8938721	50.16	580351	53.73
2	6.243	8891969	49.84	499963	46.27

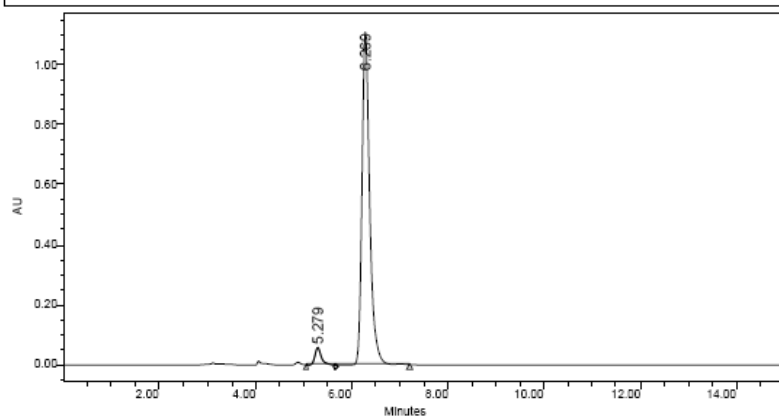
USTC

Project Name: chenxh
Reported by User: System

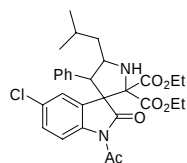
Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-2-5Br-yiwu-IA3%pro
Sample Type: Unknown
Vial: 1
Injection #: 3
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: System
Date Acquired: 1/6/2009 10:41:15 PM
Acq. Method: chenxh3
Date Processed: 2/20/2009 11:36:52 AM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.279	520659	4.03	57637	4.93
2	6.269	12400339	95.97	1111938	95.07



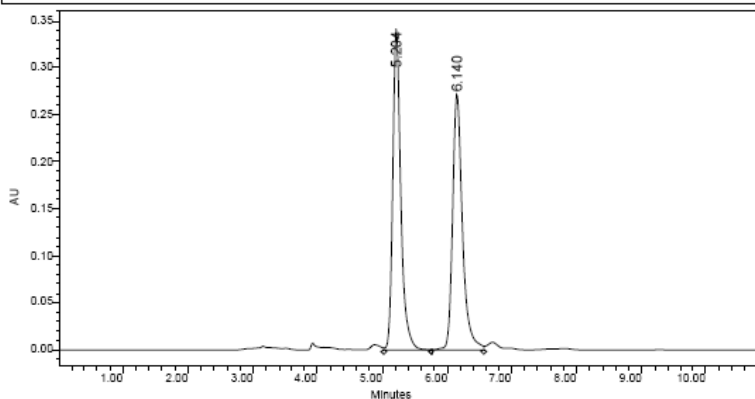
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-3-5Cl-ph-yiw-DL-IA3%h Acquired By: System
Sample Type: Unknown Date Acquired: 1/6/2009 10:45:57 AM
Vial: 1 Acq. Method: chenxh3
Injection #: 7 Date Processed: 2/26/2009 11:11:38 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.204	2968470	50.64	342694	55.62
2	6.140	2893974	49.36	273449	44.38

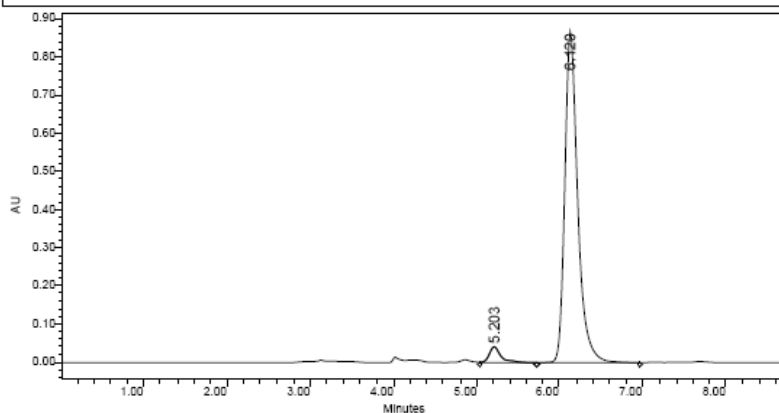
USTC

Project Name: chenxh
Reported by User: System

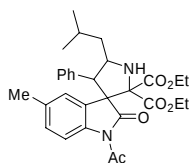
Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-3-5Cl-yiw-IA3%pro Acquired By: System
Sample Type: Unknown Date Acquired: 1/6/2009 10:07:50 PM
Vial: 1 Acq. Method: chenxh3
Injection #: 1 Date Processed: 2/26/2009 11:12:57 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.203	422111	4.30	42093	4.63
2	8.120	9392943	95.70	867864	95.37



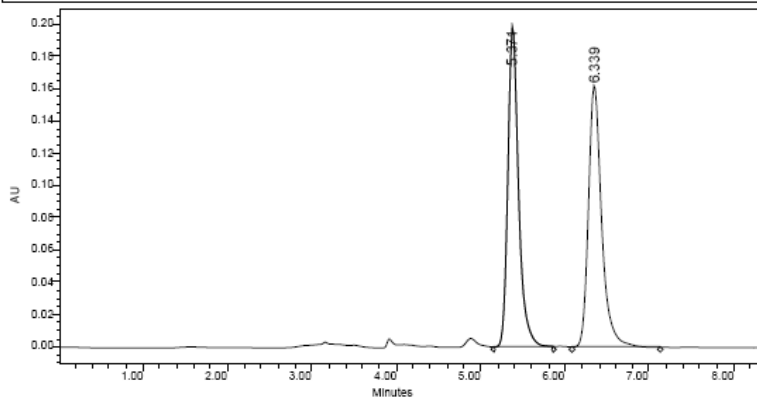
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-4-5CH-ph-yiw_DL-IA3% Acquired By: System
Sample Type: Unknown Date Acquired: 1/6/2009 11:50:18 AM
Vial: 1 Acq. Method: chenxh3
Injection #: 1 Date Processed: 2/26/2009 11:15:48 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.371	1778067	49.84	199167	55.00
2	6.339	1787373	50.16	162979	45.00

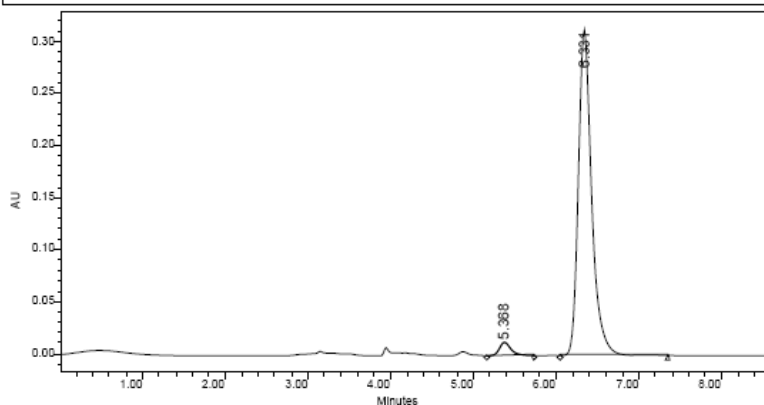
USTC

Project Name: chenxh
Reported by User: System

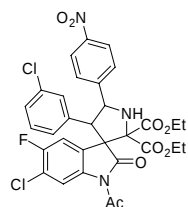
Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-4-5CH3-yiwu-IA3%pro Acquired By: System
Sample Type: Unknown Date Acquired: 1/6/2009 11:04:12 PM
Vial: 1 Acq. Method: chenxh3
Injection #: 4 Date Processed: 2/26/2009 11:16:35 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.368	128015	3.47	12851	3.95
2	6.331	3604814	96.53	312575	96.05



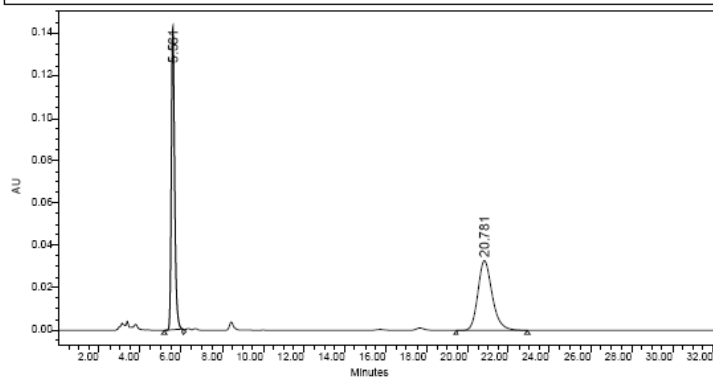
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	spiro-1205-5-4NO2-IA30%rac	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	12/10/2008 12:40:55 AM
Vial:	1	Acq. Method:	chenxh30
Injection #:	3	Date Processed:	2/26/2009 3:00:34 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.561	1609711	50.19	143196	81.31
2	20.781	1597834	49.81	32922	18.69

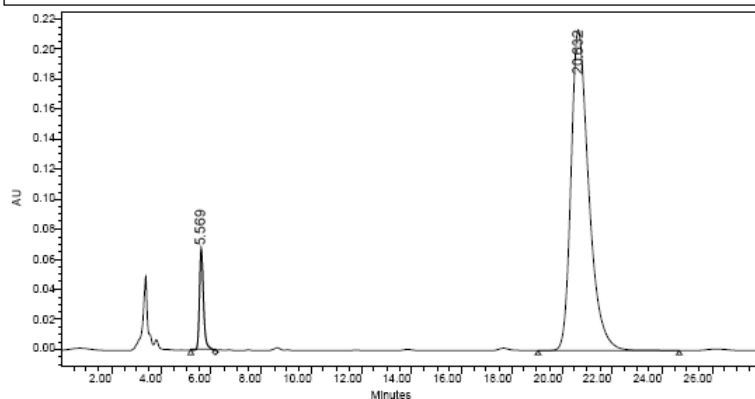
USTC

Project Name: chenxh
Reported by User: System

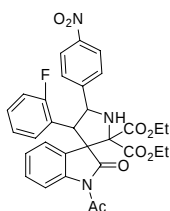
Breeze

SAMPLE INFORMATION

Sample Name:	spiro-1205-5-4NO2-IA30%pro	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	12/10/2008 1:49:58 AM
Vial:	1	Acq. Method:	chenxh30
Injection #:	5	Date Processed:	2/26/2009 3:07:32 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.589	755611	6.70	67387	23.97
2	20.832	10520448	93.30	213714	76.03



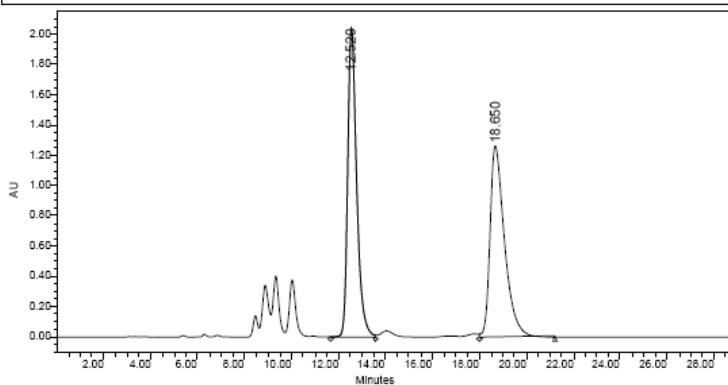
USTC

Project Name: chenxh
Reported by User: System

1/Breeze

SAMPLE INFORMATION

Sample Name:	spiro-1126-1-2F-4NO2_DL-IA30%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	12/1/2008 9:33:25 AM
Vial:	1	Acq. Method:	chenxh30
Injection #:	1	Date Processed:	2/20/2009 12:17:58 AM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.520	54262856	49.98	2044037	81.75
2	18.650	54308306	50.02	1266084	38.25

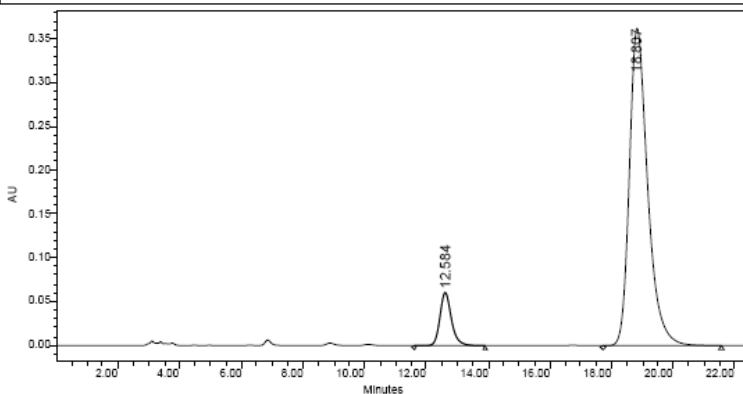
USTC

Project Name: chenxh
Reported by User: System

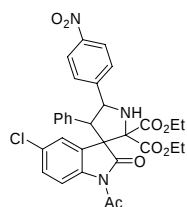
1/Breeze

SAMPLE INFORMATION

Sample Name:	spiro-1126-1-2F-4NO2-IA30%pro	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	12/2/2008 4:00:28 PM
Vial:	1	Acq. Method:	chenxh30
Injection #:	1	Date Processed:	2/20/2009 12:18:45 AM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.584	1574758	9.52	60760	14.35
2	18.807	14970543	90.48	362718	85.65



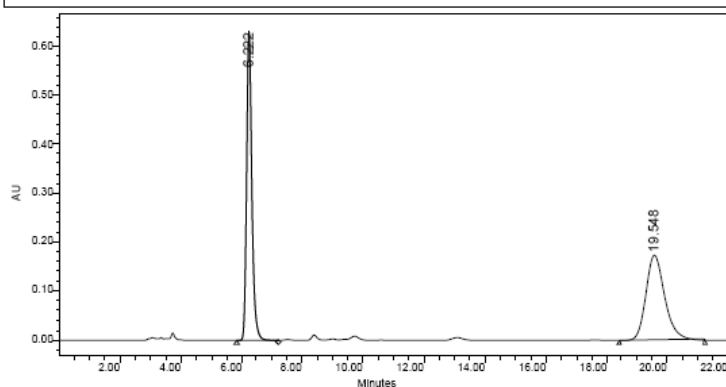
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-6-5Cl-ph-4NO-DL-IA30⁺ Acquired By: System
Sample Type: Unknown Date Acquired: 1/6/2009 12:10:18 PM
Vial: 1 Acq. Method: chenxh30
Injection #: 1 Date Processed: 2/26/2009 11:24:48 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.222	7593051	50.27	832876	78.43
2	19.548	7512786	49.73	174038	21.57

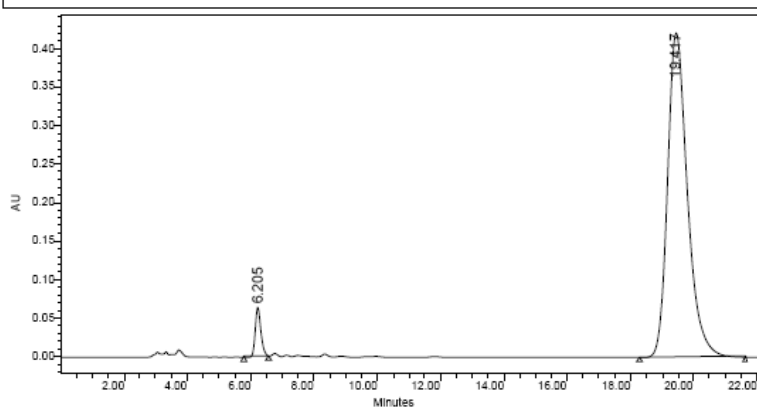
USTC

Project Name: chenxh
Reported by User: System

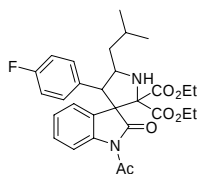
Breeze

SAMPLE INFORMATION

Sample Name: spiro-1225-6-5Cl-4NO2-IA30% Acquired By: System
Sample Type: Unknown Date Acquired: 1/7/2009 10:30:01 AM
Vial: 1 Acq. Method: chenxh30
Injection #: 1 Date Processed: 2/26/2009 11:26:25 AM
Injection Volume: 20.00 ul Channel Name: 2487Channel 1
Run Time: 70.00 Minutes Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.205	792955	4.14	64024	13.19
2	19.417	18359098	95.86	421369	86.81



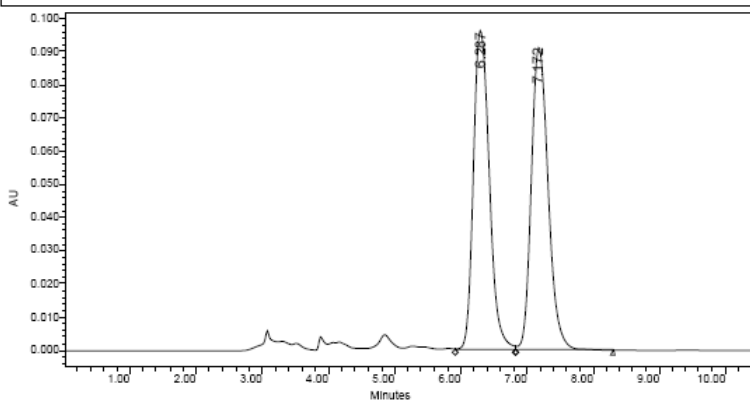
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1126-6-2F-yiwu_DL-IA3%
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: System
Date Acquired: 12/1/2008 2:58:31 PM
Acq. Method: chenxh3
Date Processed: 2/20/2009 11:16:46 AM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.287	1624814	49.96	98350	51.36
2	7.172	1627404	50.04	91258	48.64

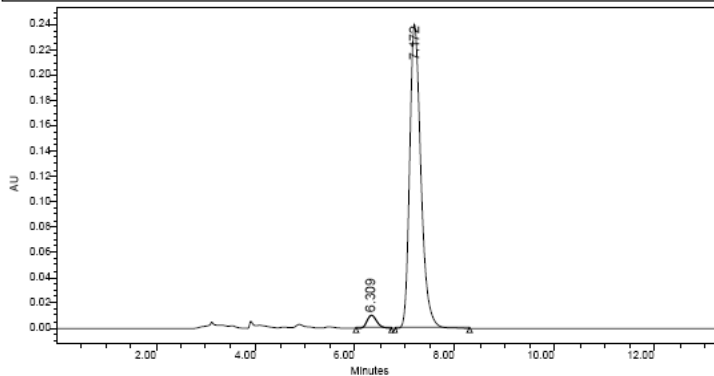
USTC

Project Name: chenxh
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: spiro-1126-6-IA30%pro
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: System
Date Acquired: 12/2/2008 7:16:44 PM
Acq. Method: chenxh3
Date Processed: 2/20/2009 11:18:04 AM
Channel Name: 2487Channel 1
Sample Set Name:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.309	139223	3.67	10252	4.08
2	7.172	3763356	96.43	240810	95.92