

***Supporting Information***

**Enantioselective Organocatalytic Double Michael Addition Reactions**

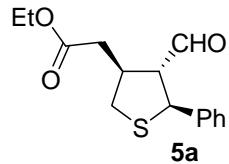
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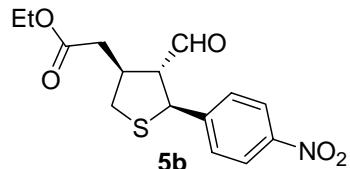
NM 87131-0001

**General Information:** Commercial reagents were used as received, unless otherwise stated. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence F<sub>254</sub> were used for thin-layer chromatography (TLC) analysis. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 500, and tetramethylsilane (TMS) was used as a reference. Data for <sup>1</sup>H are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Data for <sup>13</sup>C NMR are reported as ppm.

**General Procedure for double Michael addition of *trans* 4-Mercapto-but-2-enoic acid ethyl ester to unsaturated aldehydes (Table 2, entry 1, as an example):** To a solution of *trans*-cinnamaldehyde (25  $\mu$ L, 0.2 mmol) in the presence of catalyst (10 mol %) and PhCOOH (0.02 mmol) in toluene (0.5 mL) was 4-Mercapto-but-2-enoic acid ethyl ester (28  $\mu$ L, 0.2 mmol) and the resulting solution was stirred for 3 d at rt. The reaction mixture was directly purified by silica gel chromatography (EtOAc/Hexane = 10:1) and fractions were collected and concentrated *in vacuo* to give a colorless oil (42 mg, 76% yield), >99% ee (HPLC Daicel CHIRALCEL OD-H column, Hexane/*i*-PrOH = 80:20 at 0.5 mL/min,  $\lambda$  = 220 nm);  $t_{\text{minor}} = 16.36$  min,  $t_{\text{major}} = 17.02$  min;  $[\alpha]_D^{23}$ (major) = -41.7 (c = 1.0, CHCl<sub>3</sub>).

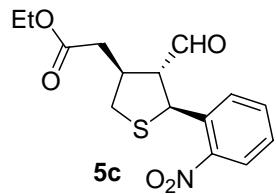


**(4-Formyl-5-phenyl-tetrahydro-thiophen-3-yl)-acetic acid ethyl ester (Table 2, entry 1):** Yield: 76%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.61 (s, 1H), 7.25-7.45 (m, 5H), 4.76 (d, 1H,  $J$  = 9.5 Hz), 4.14 (q, 1H,  $J$  = 6.5 Hz), 3.27 (m, 1H), 2.91-3.06 (m, 3H), 2.63 (dd, 1H,  $J_1$  = 4.5 Hz,  $J_2$  = 16.0 Hz), 2.49 (q, 1H,  $J$  = 8.0 Hz), 1.26 (t, 3H,  $J$  = 6.5 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  200.3, 199.9, 171.3, 139.5, 128.8, 128.6, 127.9, 127.8, 127.7, 67.6, 60.8, 52.3, 49.3, 42.3, 40.8, 37.4, 37.2, 37.0, 33.7, 29.6, 14.1;  $[\alpha]_D^{23} = -41.7$  (c = 1.0, CHCl<sub>3</sub>); HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min,  $\lambda$  = 220 nm);  $t_R$  = 16.36 (minor), 17.02 (major) min.

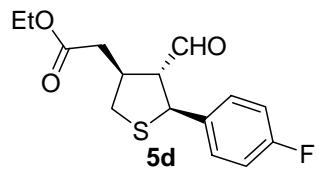


**[4-Formyl-5-(4-nitro-phenyl)-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 2):** Yield: 84%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.66 (d, 1H,  $J$  = 2.0 Hz), 8.17 (d, 2H,  $J$  = 8.5 Hz), 7.59 (d, 2H,  $J$  = 8.0 Hz), 4.87 (d, 1H,  $J$  = 9.5 Hz), 4.15 (q, 2H,  $J$  = 7.0 Hz), 3.31 (q, 1H,  $J$  = 5.0 Hz), 3.10 (m, 2H), 2.93 (td, 1H,  $J_1$  = 2.0 Hz,  $J_2$  = 9.5 Hz), 2.65 (dd, 1H,  $J_1$  = 5.5 Hz,  $J_2$  = 16.0 Hz), 2.56 (dd, 1H,  $J_1$  = 7.0 Hz,  $J_2$  = 16.0 Hz), 1.26 (t, 3H,  $J$  = 6.5 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  199.2, 171.1, 147.6, 147.4, 128.8, 124.0, 67.6, 61.0, 51.1, 42.8, 37.5, 37.1, 14.1;  $[\alpha]_D^{23} = +11.6$  (c = 2.0, CHCl<sub>3</sub>); HPLC (Daicel CHIRALPAK AS-H, Hexane/*i*-PrOH = 75:25, flow rate 0.5 mL/min,  $\lambda$  = 254 nm);  $t_R$  = 49.61 (major), 55.19

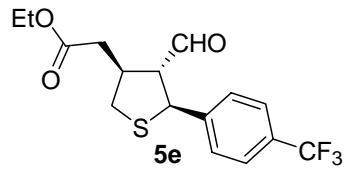
(minor) min.



**[4-Formyl-5-(2-nitro-phenyl)-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 3):** Yield: 84%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.67 (d, 1H,  $J = 3.5$  Hz), 7.94 (d, 1H,  $J = 8.0$  Hz), 7.79 (d, 1H,  $J = 8.0$  Hz), 7.63 (m, 1H), 7.42 (m, 1H), 5.39 (d, 1H,  $J = 9.0$  Hz), 4.14 (q, 2H,  $J = 7.0$  Hz), 3.33 (dd, 1H,  $J_1 = 6.0$  Hz,  $J_2 = 10.0$  Hz), 3.04-3.17 (m, 2H), 2.94 (td, 1H,  $J_1 = 3.5$  Hz,  $J_2 = 9.0$  Hz), 2.60 (dd, 1H,  $J_1 = 5.5$  Hz,  $J_2 = 16.0$  Hz), 2.50 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 16.0$  Hz), 1.26 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.7, 199.2, 171.9, 171.0, 149.4, 135.2, 133.3, 131.0, 130.6, 128.6, 128.5, 124.9, 124.4, 68.0, 64.0, 60.9, 60.8, 46.0, 45.6, 42.6, 40.0, 37.7, 37.0, 36.1, 33.7, 29.6, 14.1;  $[\alpha]_D^{23} = +14.5$  ( $c = 2.0$ ,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*-PrOH = 75:25, flow rate 0.5 mL/min,  $\lambda = 254$  nm);  $t_R = 26.26$  (major), 36.97 (minor) min.

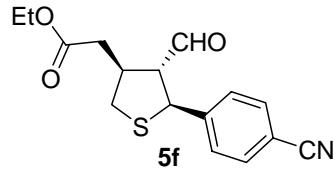


**[5-(4-Fluoro-phenyl)-4-formyl-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 4):** Yield: 81%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.60 (d, 1H,  $J = 3.0$  Hz), 7.37 (dd, 2H,  $J_1 = 5.0$  Hz,  $J_2 = 8.5$  Hz), 7.00 (t, 2H,  $J = 8.5$  Hz), 4.76 (d, 1H,  $J = 10.0$  Hz), 4.14 (q, 2H,  $J = 7.0$  Hz), 3.27 (dd, 1H,  $J_1 = 6.5$  Hz,  $J_2 = 10.0$  Hz), 2.98-3.10 (m, 2H), 2.87 (td, 1H,  $J_1 = 3.0$  Hz,  $J_2 = 10.0$  Hz), 2.63 (dd, 1H,  $J_1 = 5.5$  Hz,  $J_2 = 16.0$  Hz), 2.50 (dd, 1H,  $J_1 = 7.5$  Hz,  $J_2 = 16.0$  Hz), 1.26 (t, 3H,  $J = 6.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.1, 171.2, 163.2, 161.2, 135.1, 129.4, 129.4, 115.8, 115.6, 67.8, 60.9, 51.5, 42.3, 37.3, 37.2, 14.1;  $[\alpha]_D^{23} = -55.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALPAK AS-H, Hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min,  $\lambda = 220$  nm);  $t_R = 21.18$  (major), 23.58 (minor) min.

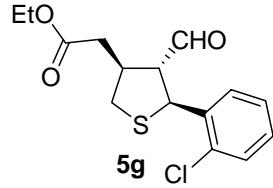


**[4-Formyl-5-(4-trifluoromethyl-phenyl)-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 5):** Yield: 69%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.63 (d, 1H,  $J = 3.0$  Hz), 7.58 (d, 2H,  $J = 7.5$  Hz), 7.53 (d, 2H,  $J = 8.0$  Hz), 4.82 (d, 1H,  $J = 9.5$  Hz), 4.14 (q, 2H,  $J = 7.0$  Hz), 3.29 (dd, 1H,  $J_1 = 6.0$  Hz,  $J_2 = 10.0$  Hz), 3.02-3.11 (m, 2H), 2.90 (td, 1H,  $J_1 = 2.5$  Hz,  $J_2 = 10.0$  Hz), 2.64 (dd, 1H,  $J_1 = 5.0$  Hz,  $J_2 = 16.0$  Hz), 2.54 (dd, 1H,  $J_1 = 8.5$  Hz,  $J_2 = 16.0$  Hz), 1.26 (t, 3H,  $J = 6.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.7, 171.2, 143.9, 130.2, 130.0, 128.2, 125.8, 67.6, 60.9, 51.5, 42.6, 37.4, 37.2, 14.1;  $[\alpha]_D^{23} = -29.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ );

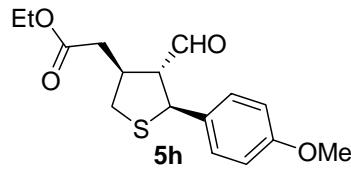
HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*-PrOH = 95:5, flow rate 0.5 mL/min,  $\lambda$  = 220 nm);  $t_R$  = 27.04 (major), 31.25 (minor) min.



**[5-(4-Cyano-phenyl)-4-formyl-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 6):** Yield: 65%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.62 (s, 1H), 7.59 (d, 2H,  $J$  = 8.0 Hz), 7.51 (d, 2H,  $J$  = 8.0 Hz), 4.80 (d, 1H,  $J$  = 9.5 Hz), 4.13 (q, 2H,  $J$  = 7.0 Hz), 3.27 (dd, 1H,  $J_1$  = 5.5 Hz,  $J_2$  = 9.0 Hz), 3.02 (m, 2H), 2.88 (t, 1H,  $J$  = 9.0 Hz), 2.62 (dd, 1H,  $J_1$  = 5.0 Hz,  $J_2$  = 16.0 Hz), 2.52 (dd, 1H,  $J_1$  = 7.0 Hz,  $J_2$  = 16.0 Hz), 1.24 (t, 3H,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.3, 171.1, 145.5, 132.5, 132.4, 128.7, 118.4, 111.7, 67.5, 60.9, 51.4, 42.7, 37.4, 37.1, 14.1;  $[\alpha]_D^{23} = +3.9$  ( $c$  = 1.0,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALCEL OJ-H, Hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min,  $\lambda$  = 220 nm);  $t_R$  = 83.45 (major) min.

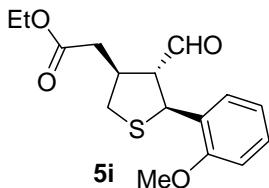


**[5-(2-Chloro-phenyl)-4-formyl-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 7):** Yield: 85%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.66 (d, 1H,  $J$  = 3.0 Hz), 7.72 (d, 1H,  $J$  = 8.0 Hz), 7.27-7.38 (m, 2H), 7.20 (t, 1H,  $J$  = 8.0 Hz), 5.32 (d, 1H,  $J$  = 9.0 Hz), 4.13 (q, 2H,  $J$  = 7.0 Hz), 3.29 (dd, 1H,  $J_1$  = 6.5 Hz,  $J_2$  = 10.0 Hz), 3.14 (m, 1H), 3.02 (m, 1H), 2.91 (m, 1H), 2.58 (dd, 1H,  $J_1$  = 5.5 Hz,  $J_2$  = 16.0 Hz), 2.47 (dd, 1H,  $J_1$  = 8.0 Hz,  $J_2$  = 16.0 Hz), 1.25 (t, 3H,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.6, 171.2, 137.3, 133.5, 129.7, 129.2, 128.9, 127.5, 67.2, 60.8, 47.8, 42.2, 37.3, 37.2, 14.1;  $[\alpha]_D^{23} = -50.7$  ( $c$  = 1.0,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALPAK AS-H, Hexane/*i*-PrOH = 85:15, flow rate 0.5 mL/min,  $\lambda$  = 220 nm);  $t_R$  = 26.48 (major), 36.13 (minor) min.

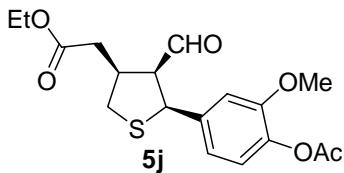


**[4-Formyl-5-(4-methoxy-phenyl)-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 8):** Yield: 87%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.58 (d, 1H,  $J$  = 3.0 Hz), 7.32 (d, 2H,  $J$  = 8.5 Hz), 6.84 (d, 2H,  $J$  = 8.5 Hz), 4.73 (d, 1H,  $J$  = 10.5 Hz), 4.13 (q, 2H,  $J$  = 7.0 Hz), 3.78 (s, 3H), 3.26 (dd, 1H,  $J_1$  = 6.5 Hz,  $J_2$  = 10.0 Hz), 2.97-3.09 (m, 2H), 2.89 (td, 1H,  $J_1$  = 2.5 Hz,  $J_2$  = 10.0 Hz), 2.62 (dd, 1H,  $J_1$  = 5.0 Hz,  $J_2$  = 16.0 Hz), 2.48 (dd, 1H,  $J_1$  = 8.0 Hz,  $J_2$  = 16.0 Hz), 1.26 (t, 3H,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.5, 164.3, 152.2, 124.0, 121.8, 107.1, 106.9, 60.6, 53.7, 48.2, 44.9, 35.0, 30.3, 30.0, 7.1;  $[\alpha]_D^{23} = -22.9$  ( $c$  = 2.0,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*-PrOH = 75:25, flow rate 0.5 mL/min,

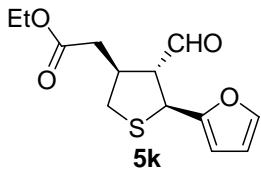
$\lambda = 220$  nm);  $t_R = 17.52$  (minor), 18.77 (major) min.



**[4-Formyl-5-(2-methoxy-phenyl)-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 9):** Yield: 96%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.60 (d, 1H,  $J = 3.5$  Hz), 7.64 (d, 1H,  $J = 7.5$  Hz), 7.24 (t, 1H,  $J = 8.0$  Hz), 6.96 (t, 1H,  $J = 7.5$  Hz), 6.84 (d, 1H,  $J = 8.5$  Hz), 5.21 (d, 1H,  $J = 9.0$  Hz), 4.12 (q, 2H,  $J = 7.0$  Hz), 3.80 (s, 3H), 3.24 (dd, 1H,  $J_1 = 6.5$  Hz,  $J_2 = 10.5$  Hz), 3.04-3.10 (m, 1H), 2.94 (t, 1H,  $J = 10.0$  Hz), 2.73 (td, 1H,  $J_1 = 3.0$  Hz,  $J_2 = 10.0$  Hz), 2.56 (dd, 1H,  $J_1 = 5.0$  Hz,  $J_2 = 16.0$  Hz), 2.41 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 16.0$  Hz), 1.24 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.3, 171.4, 156.5, 128.7, 127.9, 120.8, 110.5, 66.7, 60.7, 55.2, 45.5, 42.4, 37.2, 37.1, 14.1;  $[\alpha]_D^{23} = -39.3$  ( $c = 2.5$ ,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALPAK AS-H, Hexane/*i*-PrOH = 75:25, flow rate 0.5 mL/min,  $\lambda = 210$  nm);  $t_R = 23.34$  (major), 33.81 (minor) min.

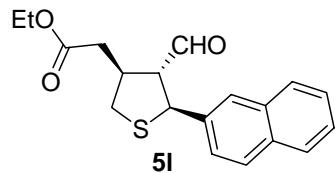


**[5-(4-Acetoxy-3-methoxy-phenyl)-4-formyl-tetrahydro-thiophen-3-yl]-acetic acid ethyl ester (Table 2, entry 10):** Yield: 89%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.61 (d, 1H,  $J = 2.5$  Hz), 7.02 (s, 1H), 6.94 (s, 2H), 4.74 (d, 1H,  $J = 10.0$  Hz), 4.11 (q, 2H,  $J = 7.0$  Hz), 3.81 (s, 3H), 3.23 (dd, 1H,  $J_1 = 6.0$  Hz,  $J_2 = 10.0$  Hz), 2.88-3.03 (m, 3H), 2.62 (dd, 1H,  $J_1 = 5.0$  Hz,  $J_2 = 16.0$  Hz), 2.47 (dd, 1H,  $J_1 = 7.5$  Hz,  $J_2 = 16.0$  Hz), 2.28 (s, 3H), 1.25 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.2, 171.2, 168.8, 151.1, 139.2, 138.3, 122.8, 119.8, 111.7, 67.4, 60.8, 55.8, 52.0, 42.3, 37.3, 37.1, 20.6, 14.1;  $[\alpha]_D^{23} = -13.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALCEL OJ-H, Hexane/*i*-PrOH = 70:30, flow rate 0.5 mL/min,  $\lambda = 220$  nm);  $t_R = 52.94$  (minor), 68.68 (major) min.

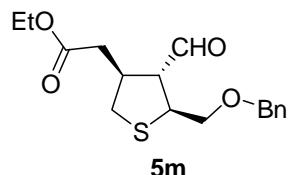


**(4-Formyl-5-furan-2-yl-tetrahydro-thiophen-3-yl)-acetic acid ethyl ester (Table 2, entry 11):** Yield: 88%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.68 (d, 1H,  $J = 2.0$  Hz), 7.37 (s, 1H), 6.28 (m, 2H), 4.83 (d, 1H,  $J = 7.5$  Hz), 4.15 (m, 2H), 3.20 (dd, 1H,  $J_1 = 6.0$  Hz,  $J_2 = 11.0$  Hz), 3.07-3.13 (m, 2H), 2.92-2.97 (m, 1H), 2.65 (m, 1H), 2.52 (dd, 1H,  $J_1 = 7.0$  Hz,  $J_2 = 16.0$  Hz), 1.27 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.5, 171.4, 152.7, 142.6, 110.4, 107.0, 63.9, 60.8, 43.8, 41.9, 37.3, 37.1, 14.1;  $[\alpha]_D^{23} = +44.2$  ( $c = 2.0$ ,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALCEL OJ-H, Hexane/*i*-PrOH = 85:15, flow rate 0.5 mL/min,  $\lambda = 220$  nm);  $t_R = 39.33$

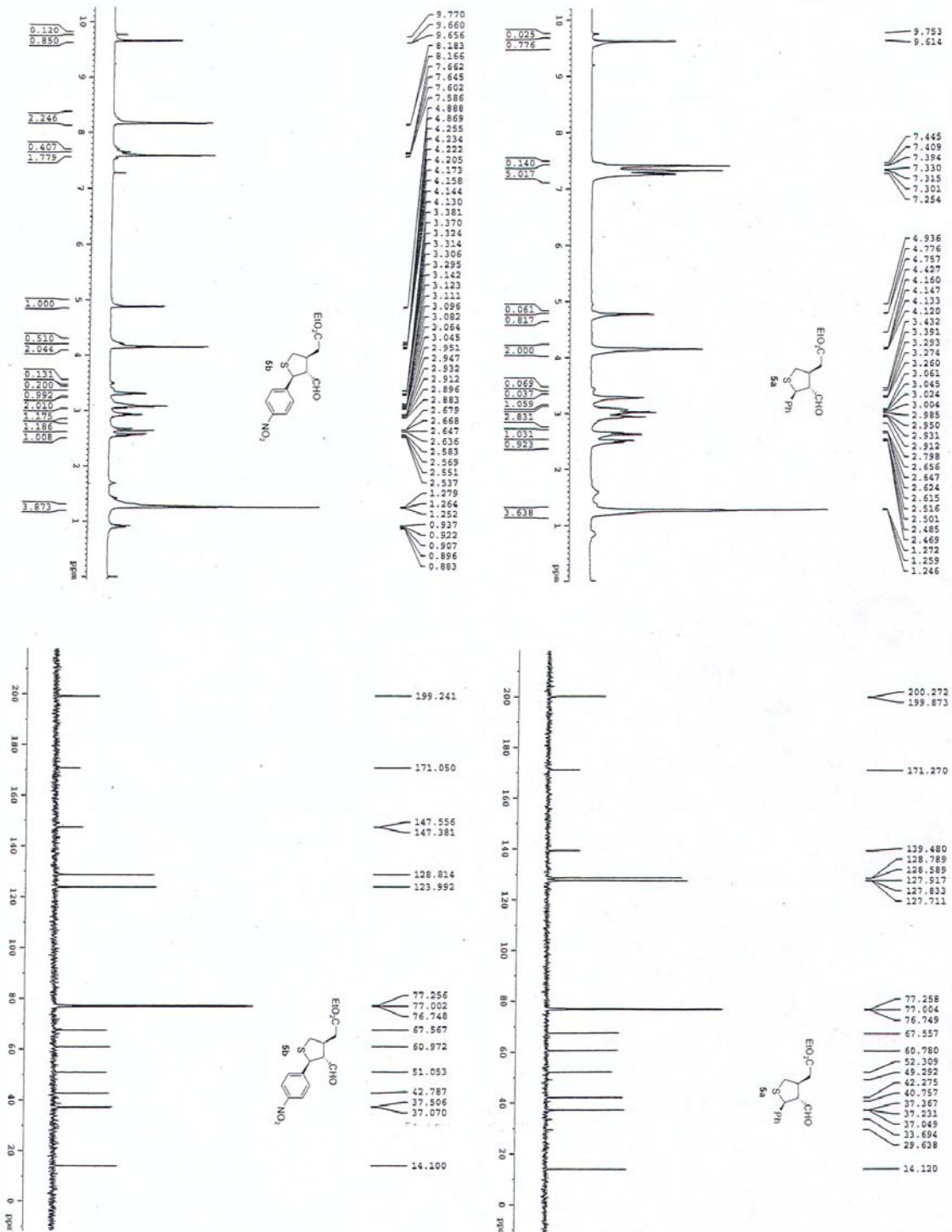
(minor), 43.94 (major) min.

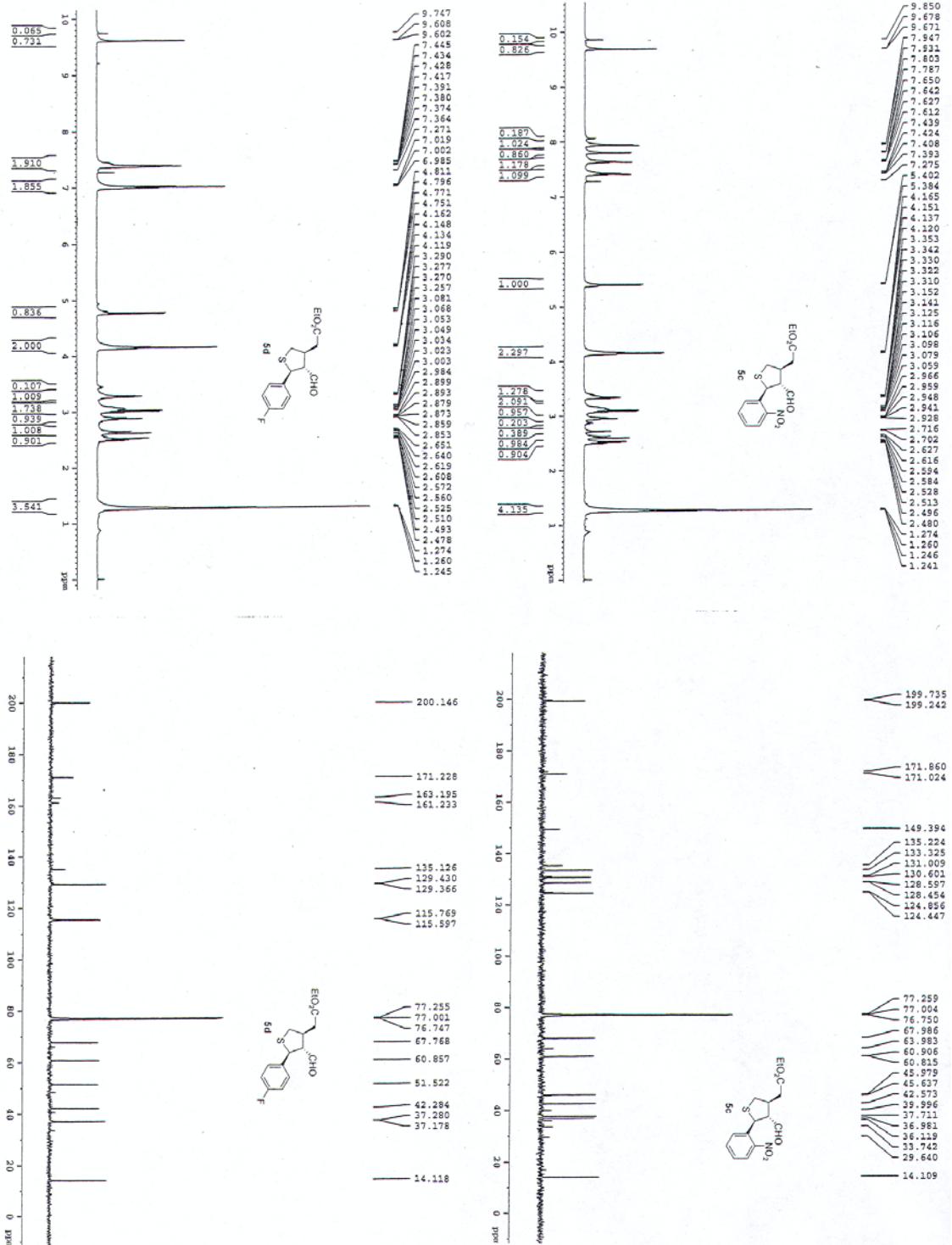


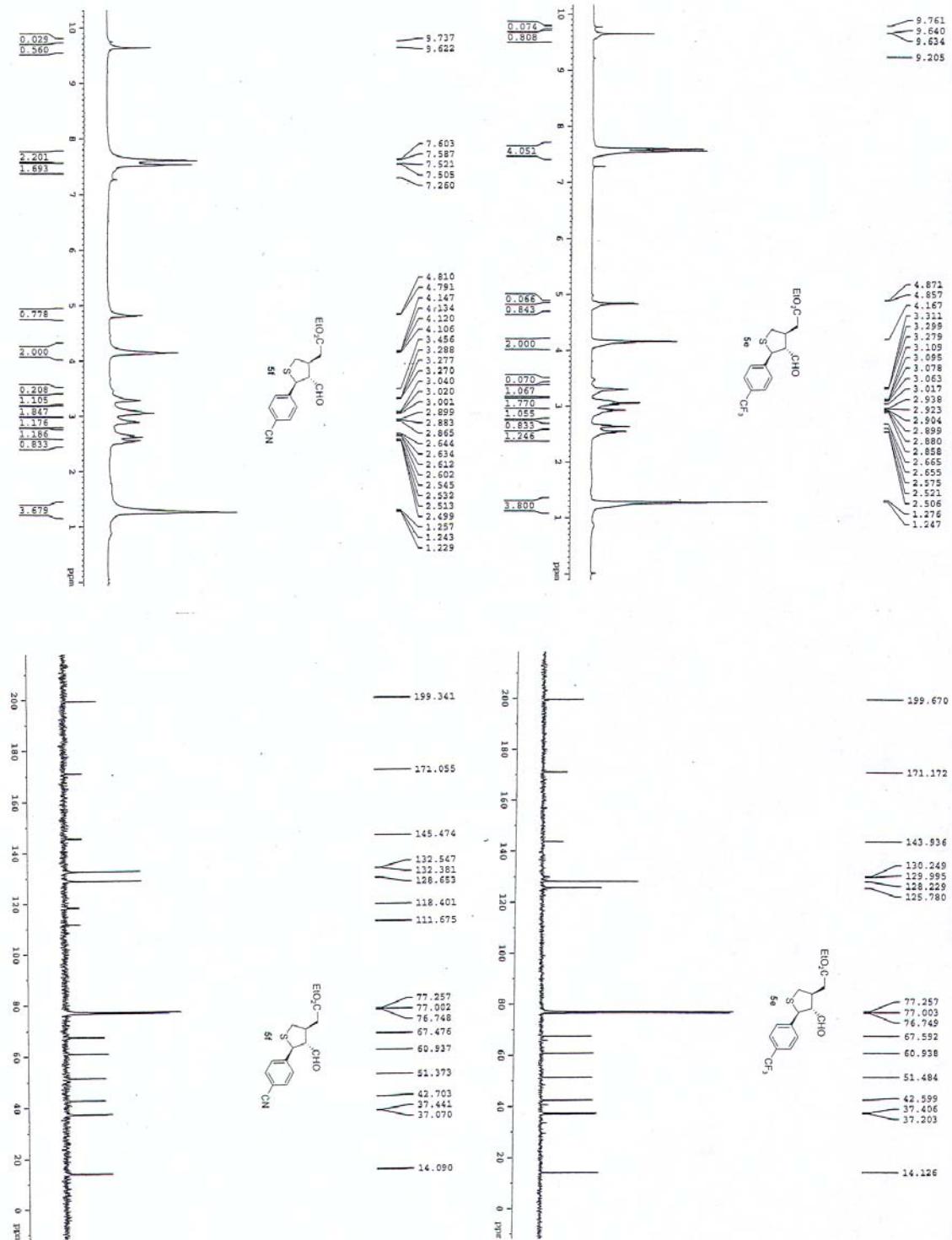
**4-Formyl-5-naphthalen-2-yl-tetrahydron-thiophen-3-yl)-acetic acid ethyl ester (Table 2, entry 12).** Yield: 55%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 9.63 (s, 1H), 7.46-7.83 (m, 7H), 4.93 (d, 1H,  $J = 9.5$  Hz), 4.15 (q, 2H,  $J = 7.0$  Hz), 3.29-3.33 (m, 1H), 3.02-3.10 (m, 3H), 2.63-2.68 (m, 1H), 2.49-2.53 (m, 1H), 1.26 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.3, 171.3, 136.7, 133.1, 133.0, 128.9, 127.8, 127.6, 126.7, 126.4, 126.2, 125.2, 67.3, 60.8, 52.6, 42.3, 37.4, 37.3, 14.1; HPLC (Chiralpak AS-H, Hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min,  $\lambda = 254$  nm):  $t_{\text{minor}} = 28.75$  min,  $t_{\text{major}} = 36.28$  min, ee = 96%, dr = 8:1.

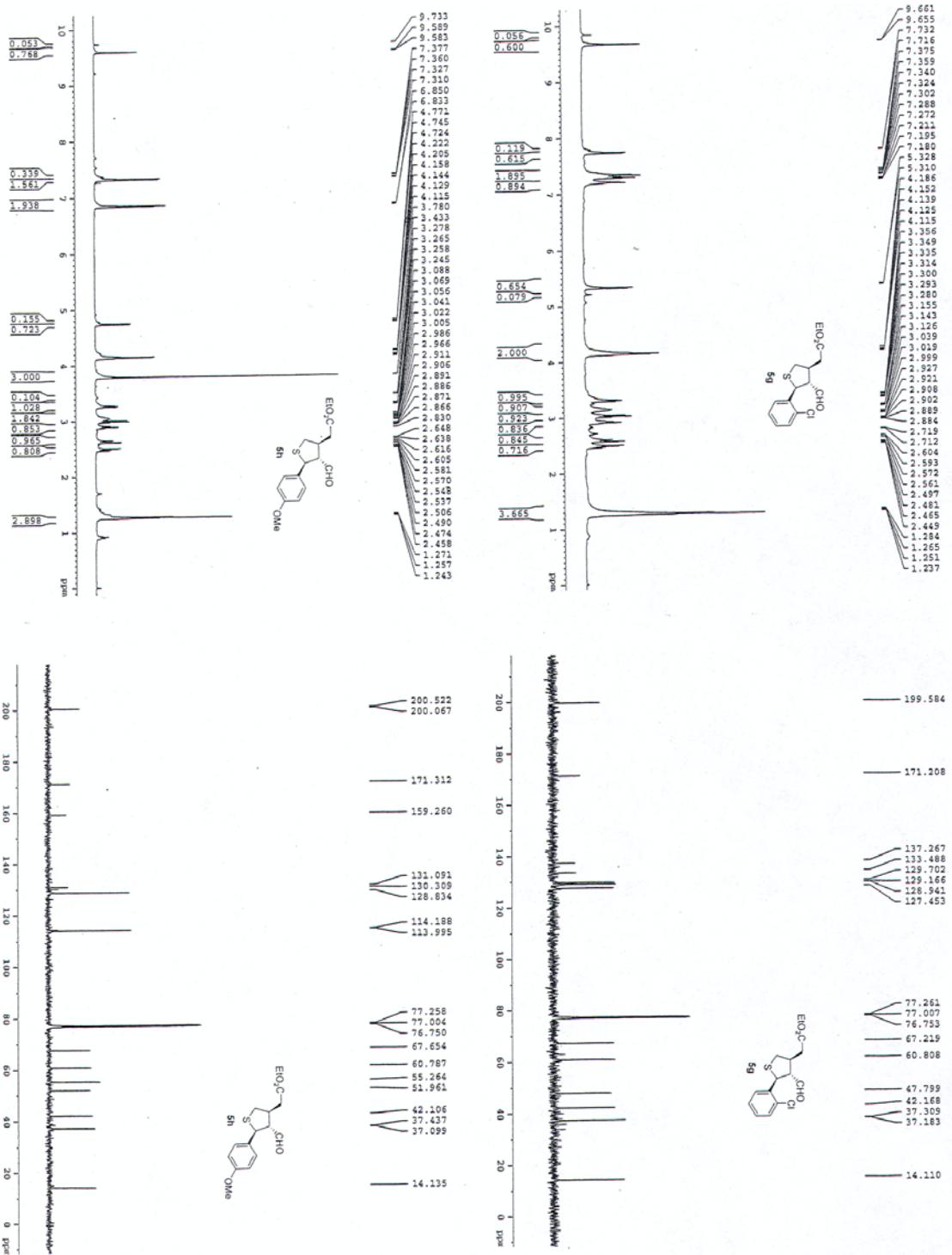


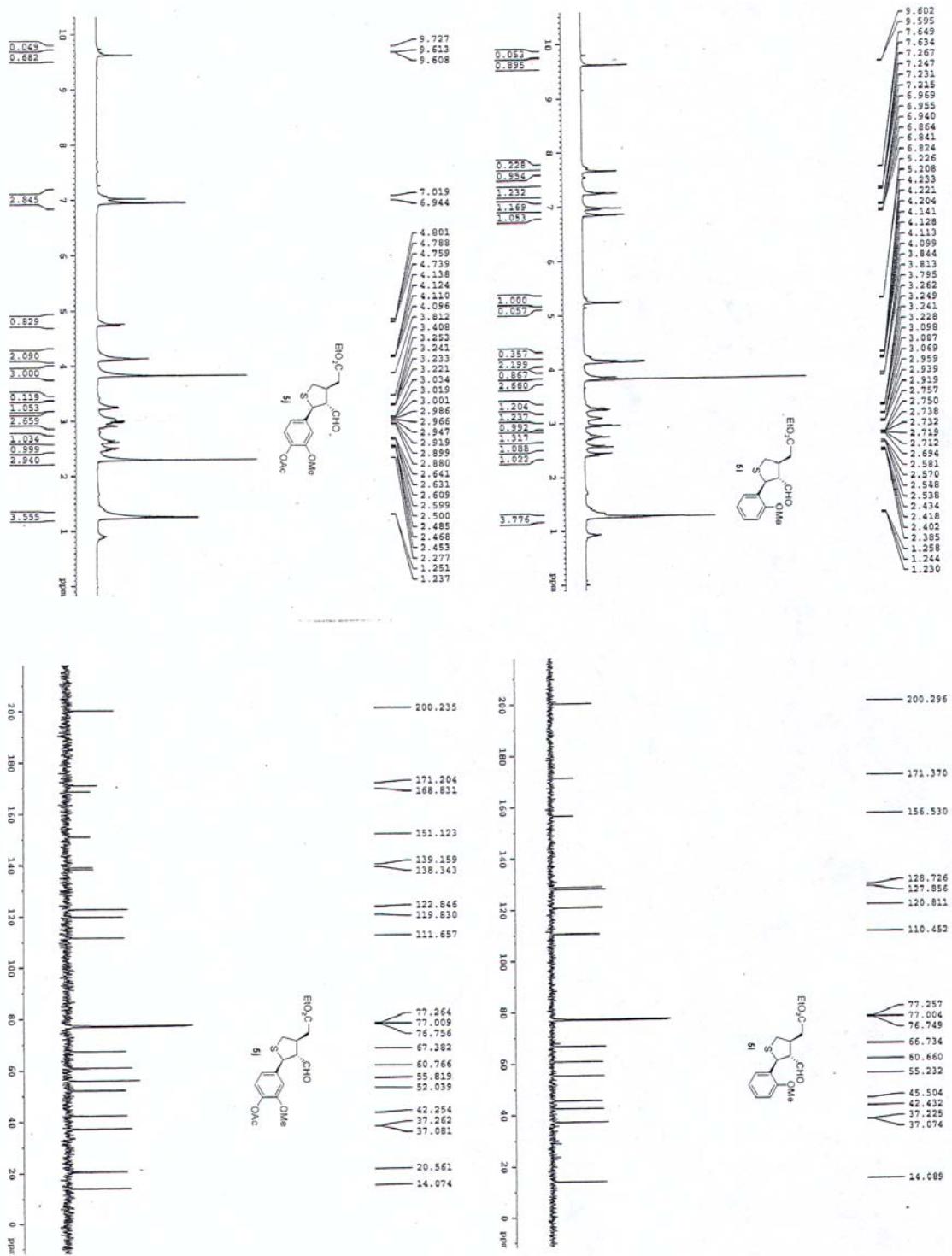
**(5-Benzylloxymethyl-4-formyl-tetrahydro-thiophen-3-yl)-acetic acid ethyl ester (Table 2, entry 13):** Yield: 62%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.66 (d, 1H,  $J = 2.5$  Hz), 7.26-7.36 (m, 5H), 4.53 (s, 2H), 4.12 (q, 2H,  $J = 7.0$  Hz), 3.87 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 14.0$  Hz), 3.60 (dd, 1H,  $J_1 = 5.0$  Hz,  $J_2 = 9.0$  Hz), 3.50 (t, 1H,  $J = 9.0$  Hz), 3.10 (dd, 1H,  $J_1 = 6.5$  Hz,  $J_2 = 10.5$  Hz), 2.99 (m, 1H), 2.73 (t, 1H,  $J = 10.0$  Hz), 2.54-2.58 (m, 2H), 2.38 (dd, 1H,  $J_1 = 8.5$  Hz,  $J_2 = 16.0$  Hz), 1.25 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.5, 190.5, 176.1, 171.4, 137.6, 130.8, 128.8, 128.4, 127.9, 127.7, 127.6, 73.2, 73.1, 68.1, 65.8, 63.6, 60.7, 47.1, 42.3, 37.2, 36.6, 34.6, 31.5, 30.3, 29.7, 29.0, 28.9, 25.2, 23.7, 22.9, 22.6, 18.7, 15.2, 14.1;  $[\alpha]_D^{23} = -7.3$  ( $c = 1.5$ ,  $\text{CHCl}_3$ ); HPLC (Daicel CHIRALPAK AS-H, Hexane/*i*-PrOH = 85:15, flow rate 0.5 mL/min,  $\lambda = 210$  nm);  $t_R = 25.91$  (minor), 32.39 (major) min.

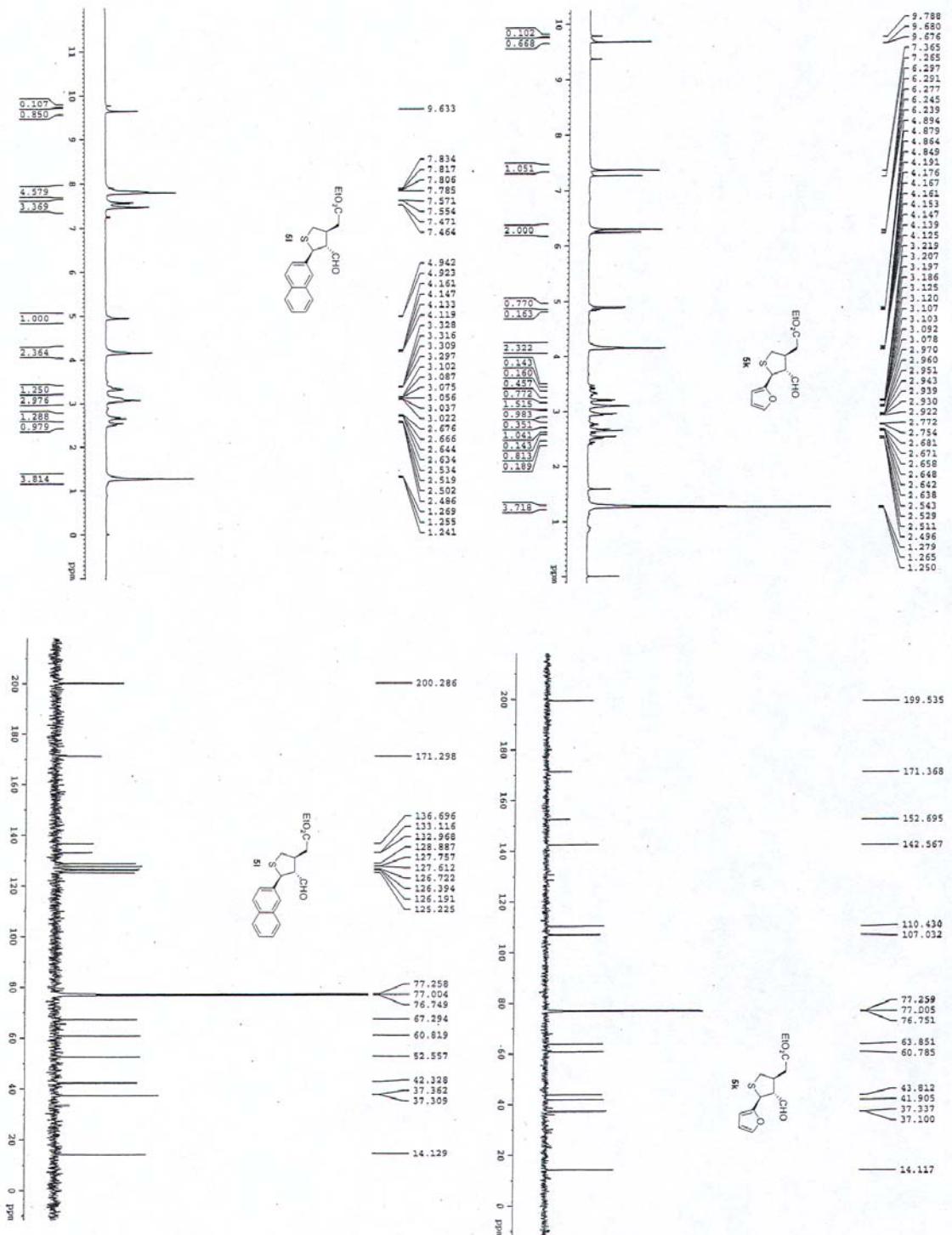


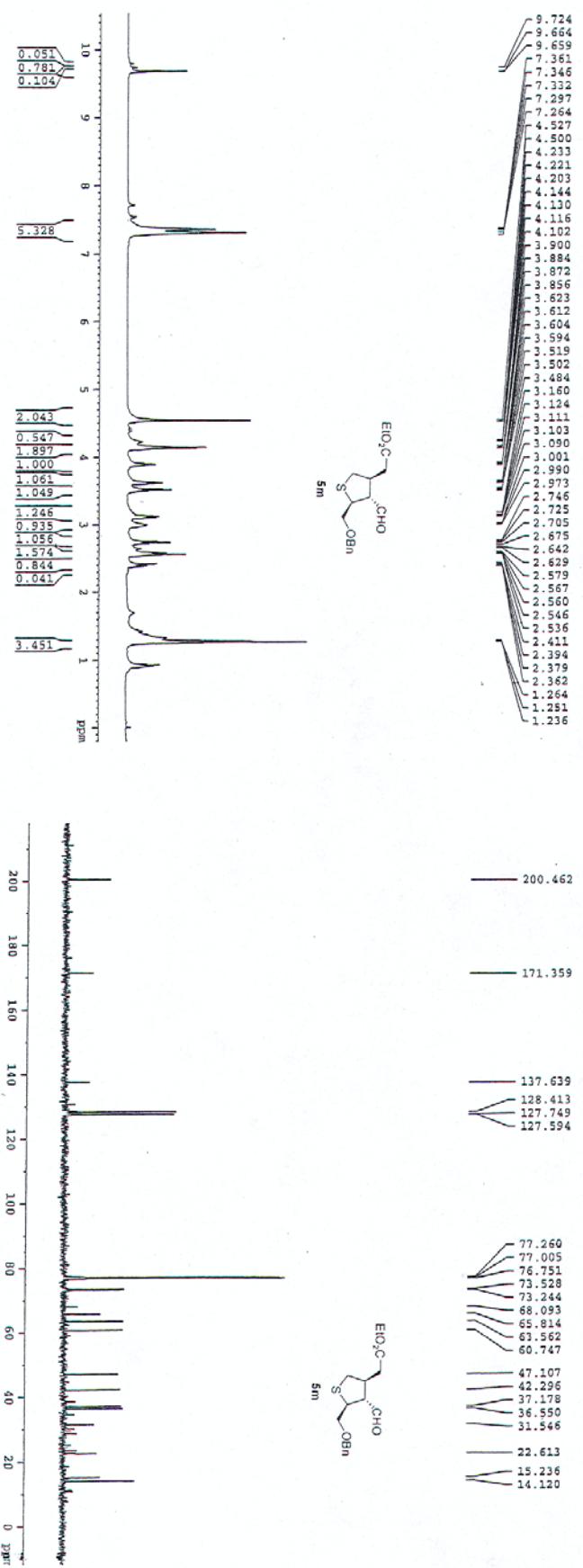






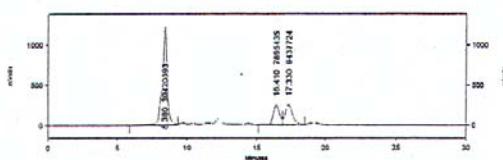
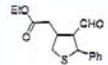






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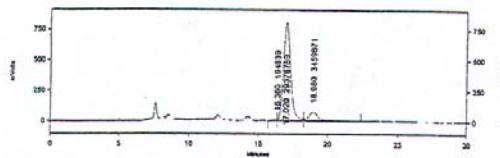
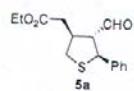
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SPO-10AVP Ch1-220nm Results				
Pk #	RT	Area	Area %	
2	16.410	7895435	16.534	
3	17.330	9437724	19.763	
<b>Totals</b>		<b>17333159</b>	<b>36.297</b>	

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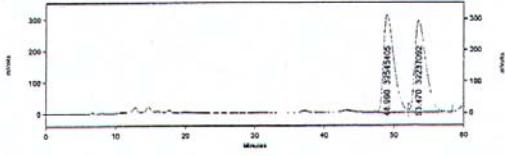
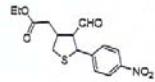
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Sample ID: hlq0e1



SPO-10AVP Ch1-220nm Results				
Pk #	RT	Area	Area %	
1	16.360	194839	0.590	
2	17.020	2937879	88.937	
3	17.980	3459671	10.473	
<b>Totals</b>		<b>33033299</b>	<b>100.000</b>	

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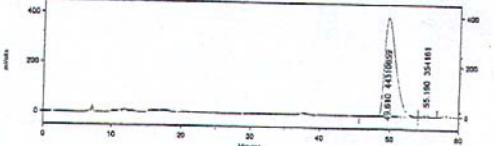
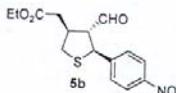
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SPO-10AVP Ch1-254nm Results				
Pk #	RT	Area	Area %	
1	48.990	32245405	50.238	
2	53.470	32237092	49.762	
<b>Totals</b>		<b>64762497</b>	<b>100.000</b>	

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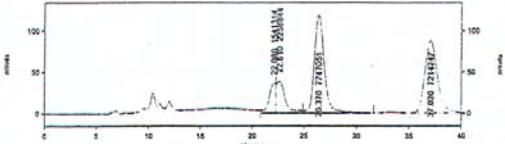
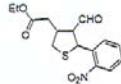
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SPO-10AVP Ch1-254nm Results				
Pk #	RT	Area	Area %	
1	49.610	44310659	99.207	
2	55.190	384161	0.793	
<b>Totals</b>		<b>44664820</b>	<b>100.000</b>	

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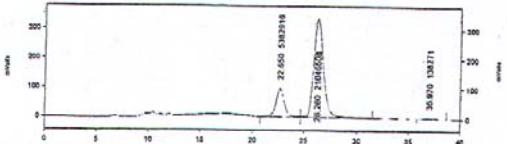
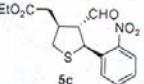
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SPO-10AVP Ch1-254nm Results				
Pk #	RT	Area	Area %	
1	22.080	1541314	8.215	
2	22.610	2258044	12.040	
3	26.370	7747051	41.292	
4	37.020	7214247	38.452	
<b>Totals</b>		<b>18761456</b>	<b>100.000</b>	

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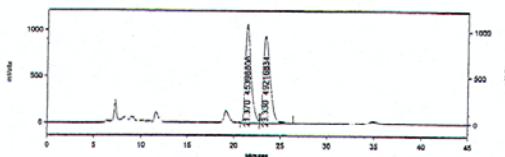
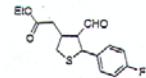
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SPO-10AVP Ch1-254nm Results				
Pk #	RT	Area	Area %	
1	22.460	5382916	20.281	
2	26.260	21046608	79.218	
3	36.970	136271	0.520	
<b>Totals</b>		<b>26567755</b>	<b>100.000</b>	

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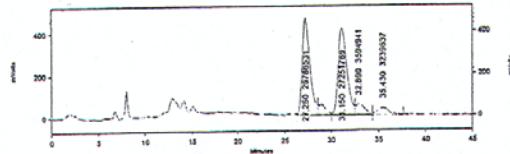
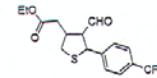
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Sample ID: hhr37e1



SPD-10Avp Chi=220nm Results		RT	Area	Area %
Pk #				
1		21.370	43398608	47.982
2		23.130	49216834	52.018
<b>TOTALS</b>			94615642	100.000

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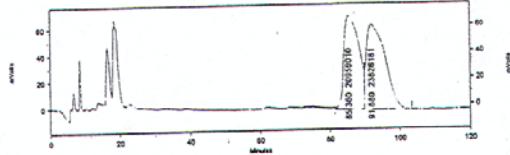
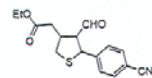
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Sample ID: hlr3%e



SPD-10AVP Ch1-220nm Results		RT	Area	Area %
Pk #				
1	21.250	26786531	44.004	
2	31.150	25715789	44.768	
3	32.890	3594941	5.905	
4	35.430	3239637	5.322	
<b>TOTALS</b>		60872898	100.000	

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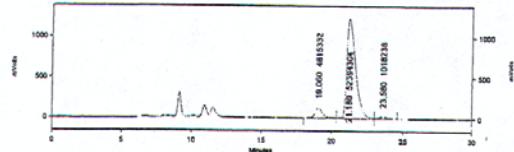
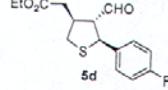
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Sample ID: hlez96



SRD-10AVP Ch1-220nm Results		RT	Area	Area %
Pk #				
1		85.360	20959010	46.789
2		91.880	23826181	53.201
<b>TOTALS</b>			44785191	100.000

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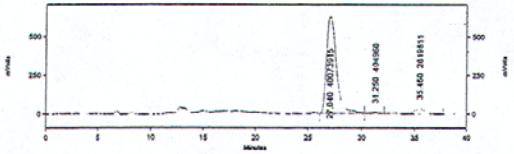
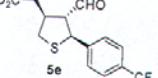
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Sample ID: h1r41a



SPD-10Avp Chi-220nm Results			
Pk #	RT	Area	Area %
1	19.060	4815332	8.270
2	21.180	52394304	85.981
3	22.580	1018239	1.749
<b>Totals</b>		<b>58227874</b>	<b>100.000</b>

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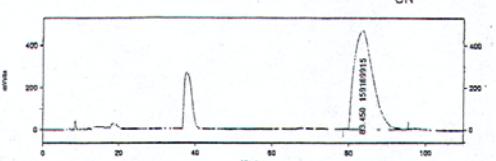
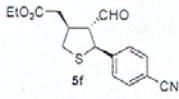
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SPD-10Avp Ch1-220nm Results			
Pk #	RT	Area	Area %
1	27.040	40073915	92.982
2	31.250	404980	0.940
3	35.460	2619811	6.079
Totals		42732666	100.000

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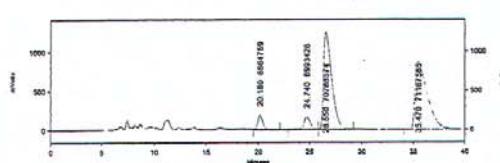
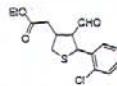
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SPD-10Avp		Ch1-220nm Results			
Pk #		RT		Area	Area %
1		83.450		1591169915	100.000
<b>Totals</b>					

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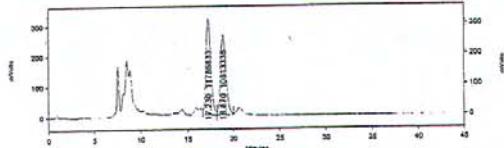
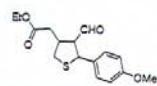
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AM  
Sample ID: hlr46e



SPD-10AVP Ch1-220nm Results				
Pk #	RT	Area	Area %	
1	20.180	6664759	4.28%	
2	24.740	6993426	4.49%	
3	26.550	7079144	45.49%	
4	33.470	71167583	45.73%	
Totals		155614344	100.00%	

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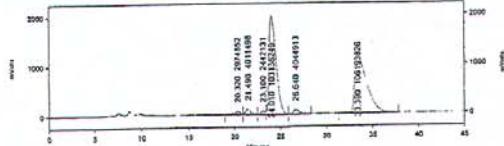
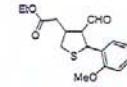
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SPD-10AVP Ch1-220nm Results				
Pk #	RT	Area	Area %	
1	17.230	11786633	52.15%	
2	18.670	10813338	47.84%	
Totals		22600171	100.00%	

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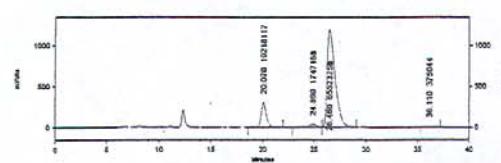
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AM  
Sample ID: hlr3e



SPD-10AVP Ch1-210nm Results				
Pk #	RT	Area	Area %	
1	20.270	2974652	1.33%	
2	21.490	4011498	1.80%	
3	23.100	2442131	1.09%	
4	24.010	103136249	46.29%	
5	26.640	6049493	1.81%	
6	33.390	106193026	47.63%	
Totals		222803469	100.00%	

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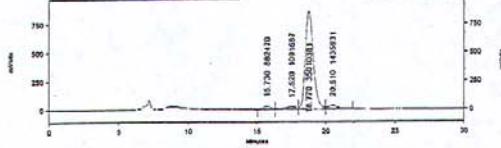
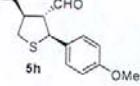
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AM  
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SPD-10AVP Ch1-220nm Results				
Pk #	RT	Area	Area %	
1	20.070	10218117	13.12%	
2	24.890	1747173	2.24%	
3	24.950	6552258	81.11%	
4	36.110	375044	0.48%	
Totals		77863607	100.00%	

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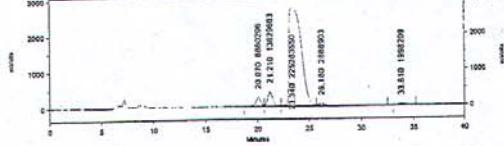
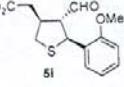
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Sample ID: hlr17e



SPD-10AVP Ch1-220nm Results				
Pk #	RT	Area	Area %	
1	15.730	882470	2.29%	
2	17.230	1091687	2.88%	
3	18.770	35010261	91.12%	
4	20.510	1433931	3.73%	
Totals		38420469	100.00%	

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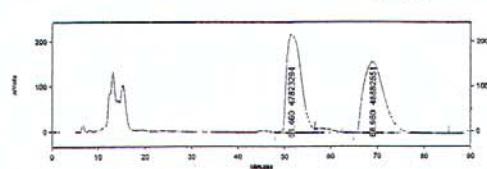
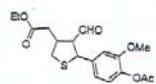
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SPD-10AVP Ch1-210nm Results				
Pk #	RT	Area	Area %	
1	20.070	8880296	3.51%	
2	21.210	13629663	5.1%	
3	23.340	22570070	89.15%	
4	26.180	2088903	1.14%	
5	33.810	1998209	0.791%	
Totals		252680621	100.00%	

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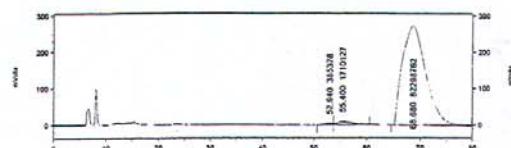
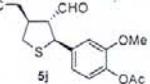
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Sample ID: hlr25e



SPO-10Avp Chl-220nm Results				
Pk #	RT	Area	Area %	
1	51.460	47823294	49.452	
2	68.980	48882551	50.548	
Totals		96705845	100.000	

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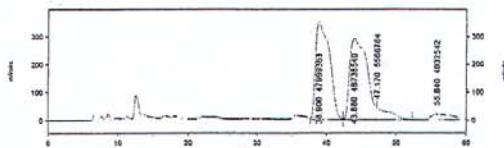
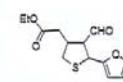
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Date Acquired: 12/3/2006 10:49:38 AM Date Printed: 12/11/2006 09:37:35 AM  
Sample ID: hlr30e



SPO-10Avp Chl-220nm Results				
Pk #	RT	Area	Area %	
1	52.940	385378	0.457	
2	55.400	1710127	2.026	
3	56.680	8129872	97.517	
Totals		84394267	100.000	

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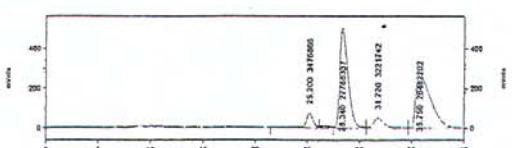
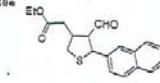
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Sample ID: hlr25e



SPO-10Avp Chl-220nm Results				
Pk #	RT	Area	Area %	
1	38.900	47999163	45.139	
2	43.880	46736540	45.034	
3	47.170	5566764	5.235	
4	55.840	4032342	1.792	
Totals		120545632	100.000	

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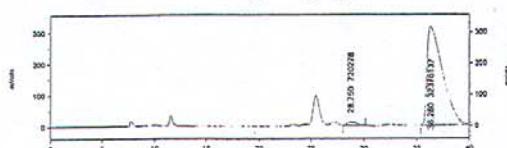
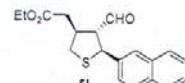
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Date Acquired: 12/10/2006 11:31:45 AM Date Printed: 12/11/2006 09:19:51 AM  
Sample ID: hlr49e



SPO-10Avp Chl-254nm Results				
Pk #	RT	Area	Area %	
1	25.200	2476066	5.703	
2	26.340	21768337	45.576	
3	31.720	3221742	5.284	
4	35.750	26442202	43.435	
Totals		60969147	100.000	

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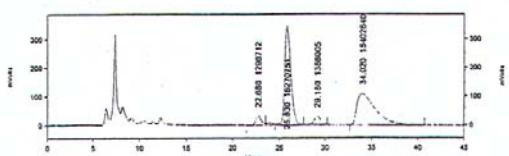
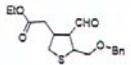
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Sample ID: hlr49



SPO-10Avp Chl-254nm Results				
Pk #	RT	Area	Area %	
1	26.750	710276	2.176	
2	36.280	32376137	97.624	
Totals		33096413	100.000	

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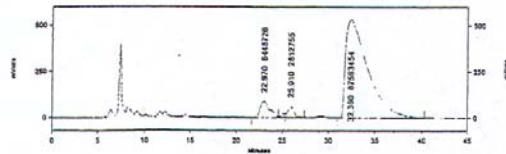
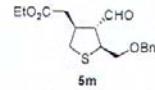
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Date Acquired: 12/3/2006 12:29:35 PM Date Printed: 12/11/2006 09:39:33  
AM  
Sample ID: hiz29e



SPD-10Avp Ch1-210nm Results			
Pk #	RT	Area	Area %
1	22.680	1296712	3.774
2	25.820	1702121	47.336
3	25.820	1388005	4.040
4	34.020	15402640	44.830
Totals		34358108	100.000

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Method Name: C:\ZZstart\Projects\WeiWang\hl00017.set  
Data File: C:\ZZstart\Projects\WeiWang\hlz29e1.dat  
Date Acquired: 12/3/2006 1:16:38 PM Date Printed: 12/11/2006 09:42:26 AM  
Sample ID: hiz29e



SPD-10Avp Ch1-210nm Results			
Pk #	RT	Area	Area %
1	22.670	6448726	6.656
2	25.910	2042755	2.904
3	32.390	87593454	90.438
Totals		960054935	100.000